

Iron-Catalyzed Hydroboration of Vinylcyclopropanes

Chenhui Chen, Xuzhong Shen, Jianhui Chen, Xin Hong, Zhan Lu*

Department of Chemistry, Zhejiang University, Hangzhou 310058, China

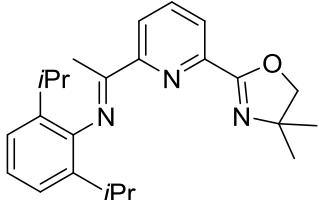
| | |
|---|-------------|
| I. General Information | S1 |
| II. Procedures for Preparation of Metal Complexes..... | S2 |
| III. Procedures for Synthesis of Vinylcyclopropanes | S4 |
| IV. Optimization for Hydroboration of Vinylcyclopropanes | S27 |
| V. Iron-Catalyzed Hydroboration of Vinylcyclopropanes..... | S28 |
| VI. Stereospecific Hydroboration of Vinylcyclopropanes..... | S51 |
| VII. Gram-Scale Reactions..... | S55 |
| VIII. Further Derivatizations..... | S57 |
| IX. References..... | S66 |
| X. NMR Spectra..... | S67 |
| XI. HPLC Spectra..... | S310 |

I. General Information

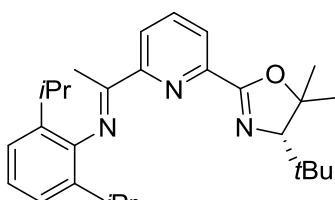
Ether, THF, and toluene were distilled from sodium benzophenone ketyl prior to use. HBpin (97%) was purchased from TCI and used as received. NaHB*Et*₃ (1.0 M in THF), FeCl₂ (99.7%), FeBr₂ (97%) were purchased from Aldrich and used as received. 1,2-Bis(diphenylphosphino)ethane (98%), Pd(OAc)₂ (98%) were purchased from energy and used as received. The other commercially available chemicals were used as received. NMR spectra were recorded on a Bruker-400 instrument. ¹H NMR chemical shifts were referenced to tetramethylsilane signal (0ppm), ¹³C NMR chemical shifts were referenced to the solvent resonance (77.00 ppm, CDCl₃). The following abbreviations (or combinations) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m= multiplet, br = broad, q = quadruplet. HPLC analyses were performed on a Shimadzu SPD-20A. High-resolution mass spectra (HRMS) were recorded on EI-TOF (electro-spray ionization-time of flight) or ESI-TOF (LCMS-IT-TOF). IR spectra were recorded

on a Perkin-Elmer Spectrum One FTIR spectrometer with diamond ATR accessory. The X-ray diffraction data was obtained on Gemini A Ultra.

II. Procedures for Preparation of Metal Complexes

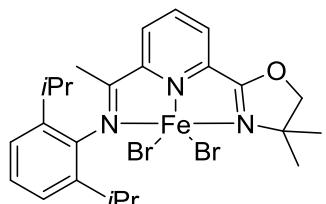


(*E*)-*N*-(2,6-diisopropylphenyl)-1-(6-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)pyridin-2-yl)ethan-1-imine (L1),¹ A 50 mL Schlenk flask was charged with 3.6047 g (10.0 mmol) of (*E*)-1-(6-bromopyridin-2-yl)-*N*-(2,6-diisopropylphenyl)ethan-1-imine, 1.1976 g (12.0 mmol) of 4,4-dimethyl-4,5-dihydrooxazole, 0.0595 g (0.25 mmol) of Pd(OAc)₂, 0.1159 g (0.28 mmol) of 1,2-bis(diphenylphosphino)ethane, 1.6815 g (20.0 mmol) of *t*BuOLi and 20 mL of 1,4-dioxane in the atmosphere of nitrogen, the mixture was placed in an oil bath and stirring at 110 °C for 74 h. Then the mixture was cooled to room temperature, filtered, and concentrated. The residue was purified by flash column chromatography using PE/EA (10/1) with 1 vol% of Et₃N as the eluent to give 2.7135 g (7.19 mmol, 72% yield) of the title compound as a yellow solid, mp: 193.3-195.2 °C (by flash column chromatography using PE/EA); IR (cm⁻¹): 2963, 1642, 1573, 1460, 1365. ¹H NMR (CDCl₃, 400 MHz): δ 8.50 (dd, J = 7.8, 1.0 Hz, 1H), 8.18 (dd, J = 7.6, 1.0 Hz, 1H), 7.88 (dd, J = 7.8, 7.6 Hz, 1H), 7.19-7.13 (m, 2H), 7.12-7.06 (m, 1H), 4.24 (s, 2H), 2.79-2.66 (m, 2H), 2.29 (s, 3H), 1.44 (s, 6H), 1.13 (d, J = 6.8 Hz, 12H); ¹³C NMR: (CDCl₃, 100 MHz): δ 166.7, 161.3, 156.1, 146.3, 146.2, 136.9, 135.6, 125.3, 123.6, 123.0, 122.9, 79.7, 67.9, 28.4, 28.2, 23.2, 22.8, 17.2; HRMS (EI) calculated for [C₂₄H₃₁N₃O]⁺ requires m/z 377.2467, found m/z 377.2466.

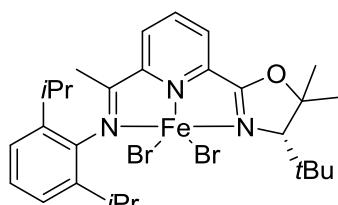


(*S,E*)-1-(6-(4-(tert-butyl)-5,5-dimethyl-4,5-dihydrooxazol-2-yl)pyridin-2-yl)-*N*-(2,6-diisopropylphenyl)ethan-1-imine (L2),¹ A 50 mL Schlenk flask was charged with 0.9338 g (2.5 mmol) of (*E*)-1-(6-bromopyridin-2-yl)-*N*-(2,6-diisopropylphenyl)ethan-1-imine, 0.4828 g (3.0 mmol) of (*S*)-4-(tert-butyl)-5,5-dimethyl-4,5-dihydrooxazole, 0.0179 g (0.0625 mmol) of Pd(OAc)₂, 0.0300 g (0.07 mmol) of 1,2-bis(diphenylphosphino)ethane, 0.4060 g (5.0 mmol) of *t*BuOLi and 10 mL of 1,4-dioxane in the atmosphere of nitrogen, the mixture was placed in an oil bath and stirring at 110 °C for 39 h. Then the mixture was cooled to room

temperature, filtered, and concentrated. The residue was purified by flash column chromatography using PE/EA (20/1 to 10/1) as the eluent to give 0.2289 g (0.53 mmol, 20% yield) of the title compound as a yellow solid, mp: 130.3-132.3 °C (by flash column chromatography using PE/EA). IR (cm^{-1}): 2961, 1641, 1572, 1461, 1367. ^1H NMR (CDCl_3 , 400 MHz): δ 8.48 (dd, $J = 8.0, 1.0$ Hz, 1H), 8.12 (dd, $J = 7.8, 1.0$ Hz, 1H), 7.86 (dd, $J = 8.0, 7.8$ Hz, 1H), 7.19-7.13 (m, 2H), 7.12-7.06 (m, 1H), 3.68 (s, 1H), 2.79-2.66 (m, 2H), 2.29 (s, 3H), 1.60 (s, 3H), 1.56 (s, 3H), 1.17-1.10 (m, 21H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 167.0, 161.2, 156.1, 146.9, 146.4, 136.7, 135.73, 135.68, 125.0, 123.5, 123.0, 122.7, 88.4, 83.2, 34.2, 30.8, 28.19, 28.15, 27.8, 23.3, 23.2, 22.8, 17.2; HRMS (EI) calculated for $[\text{C}_{28}\text{H}_{39}\text{N}_3\text{O}]^+$ requires m/z 433.3093, found m/z 433.3096.



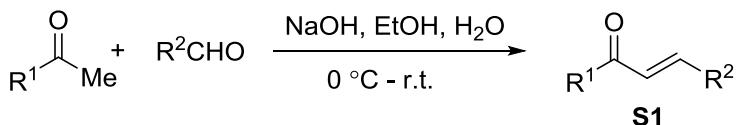
D₂OIP OIP FeBr₂ Prepared according to the previously reported procedure^{1b}, in a glove-box, a 50 mL Schlenk flask was charged with 1.0304 g (2.73 mmol) of **L1**, 25 mL of THF and 0.5749 g (2.68 mmol) of FeBr_2 under the atmosphere of nitrogen, then the mixture was stirred at room temperature for 3 h, then 25 mL of ether was injected to precipitate the complex. The resulting mixture was filtered under air. The cake was washed with ether and dried in vacuo to afford 1.3293 g (2.24 mmol, 84% yield) of blue powder; Anal. Calcd for $\text{C}_{24}\text{H}_{31}\text{Br}_2\text{FeN}_3\text{O}$: C, 48.60; H, 5.27; N, 7.08; Found: C, 48.16; H, 5.36; N, 6.89.



L2 FeBr₂ Prepared according to the previously reported procedure^{1b}, in a glove-box, a 50 mL Schlenk flask was charged with 0.4367 g (1.01 mmol) of **L2**, 10 mL of THF and 0.2112 g (0.98 mmol) of FeBr_2 under the atmosphere of nitrogen, then the mixture was stirred at room temperature for 3 h, then 10 mL of ether was injected to precipitate the complex. The resulting mixture was filtered under air. The cake was washed with ether and dried in vacuo to afford 0.4737 g (0.74 mmol, 74% yield) of blue powder; Anal. Calcd for $\text{C}_{28}\text{H}_{41}\text{Br}_2\text{FeN}_3\text{O}_2$ ($\text{M} + \text{H}_2\text{O}$): C, 50.40; H, 6.19; N, 6.30; Found: C, 50.36; H, 5.92; N, 6.19.

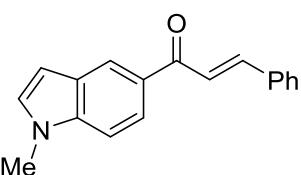
III. Procedures for Synthesis of Vinylcyclopropanes

1. General procedure for the synthesis of chalcones

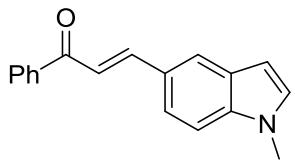


Method A: Prepared according to a previously reported procedure,^{2a} acetophenone (100 mmol) was dissolved in ethanol (150 mL) in a 500 mL round-bottom flask and cooled to 0 °C, a solution of sodium hydroxide (200 mmol) in water (60 mL) was added. Then the solution of alcohol (150 mL) containing benzaldehyde (100 mmol) was added drop wise with stirring over a period of 10 min. The reaction mixture was stirred at room temperature for about 4-12 h until the starting material disappeared (monitored by TLC with PE/EA (10/1)). The reaction mixture was concentrated by rotary evaporation and extracted with DCM (50 mL x 3). The combined organic layers were washed with saturated NaHCO₃ and then brine, dried over Na₂SO₄, concentrated by rotary evaporation and further purified by flash chromatography on silica gel or crystallized from ethanol.

The chalcones without additionally noted were prepared according to the method A, **S1am**^{2b}, **S1an**, **S1aq** and **S1ar**^{2c}, **S1at**^{2d} were prepared according to a previously reported procedure.

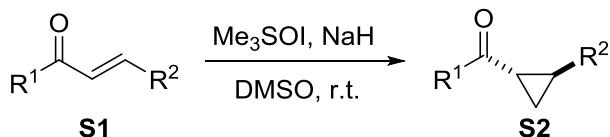


(E)-1-(1-methyl-1H-indol-5-yl)-3-phenylprop-2-en-1-one (S1p),
 using 8.74g (50.5 mmol) of
1-(1-methyl-1H-indol-5-yl)ethan-1-one and 5.10 ml (50 mmol) of
 benzaldehyde to give 10.74g (41.1 mmol, 81% yield) of **S1p**;
 yellow solid; mp: 105.7-106.9 °C (crystallized from ethanol); IR (cm⁻¹): 2922, 1653, 1596, 1338, 1156.. ¹H NMR (CDCl₃, 400 MHz): δ 8.40 (d, J = 1.6 Hz, 1H), 7.99 (dd, J = 8.8, 1.6 Hz, 1H), 7.83 (d, J = 15.8 Hz, 1H), 7.74-7.64 (m, 3H), 7.45-7.36 (m, 4H), 7.12 (d, J = 3.2 Hz, 1H), 6.63 (d, J = 3.0 Hz, 1H), 3.82 (s, 3H); ¹³C NMR: (CDCl₃, 100 MHz): δ 190.0, 143.1, 139.0, 135.2, 130.4, 130.1, 130.0, 128.8, 128.2, 127.9, 123.1, 122.5, 122.2, 109.3, 102.9, 32.9; HRMS (EI) calculated for [C₁₈H₁₅NO]⁺ requires m/z 261.1154, found m/z 261.1152.



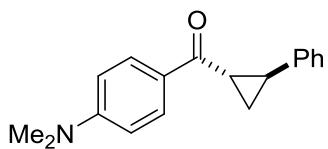
(E)-3-(1-methyl-1H-indol-6-yl)-1-phenylprop-2-en-1-one (S1al), using 6.01g (50.0 mmol) of **1-methyl-1H-indole-5-carbaldehyde** and 5.85 ml (50.0 mmol) of acetophenone to give 10.08g (38.6 mmol, 77% yield) of **S1al**; yellow solid; mp: 101.2-103.1 °C (crystallized from ethanol); IR (cm^{-1}): 2947, 1656, 1586, 1298, 1225. ^1H NMR (CDCl_3 , 400 MHz): δ 8.06-8.01 (m, 2H), 7.98 (d, J = 15.6 Hz, 1H), 7.89 (d, J = 1.6 Hz, 1H), 7.60-7.45 (m, 5H), 7.32 (d, J = 8.6 Hz, 1H), 7.06 (d, J = 3.2 Hz, 1H), 6.53 (dd, J = 3.2, 0.8 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 190.7, 147.1, 138.8, 138.1, 132.3, 130.1, 128.8, 128.5, 128.4, 126.4, 123.2, 121.5, 119.1, 109.8, 102.1, 33.0; HRMS (EI) calculated for $[\text{C}_{18}\text{H}_{15}\text{NO}]^+$ requires m/z 261.1154, found m/z 261.1157.

2. General procedure for the synthesis of cyclopropyl ketones



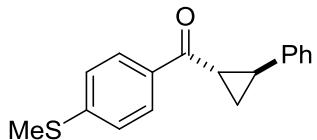
Method B: Prepared according to a previously reported procedure,^{3a} Me_3SOI (1.2 equiv.) and NaH (1.2 equiv., 60% dispersion in mineral oil) was mixed in a 250 mL three-necked flame-dried round-bottom flask under the atmosphere of nitrogen. 150 mL of DMSO were added dropwise and stirred at room temperature for 30 min. Then chalcone **S1** was added in portion and stirred at room temperature for about 4-12 h until the starting material disappeared (monitored by TLC with PE/EA (10/1)). The mixture was then treated with H_2O (150 mL) and extracted with DCM (50 mL x 3). The combined organic layers were washed with H_2O (50 mL x 2) and saturated NaHCO_3 (50 mL x 2) and then brine, dried over Na_2SO_4 , concentrated by rotary evaporation and further purified by flash chromatography on silica gel or crystallized from ethanol.

The cyclopropyl ketones without noted were prepared according to method B. **S2q**, **S2ae-ag** and **S2an** were prepared according to a previously reported procedure.^{3b}

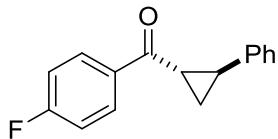


trans-(4-(dimethylamino)phenyl)(2-phenylcyclopropyl)methanone (S2f), using 9.33g (37.1 mmol) of **S1f** to give 9.54g (35.9 mmol, 97% yield) of **S2f**; yellow solid; mp: 98.0-99.2 °C

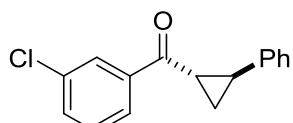
(crystallized from ethanol); IR (cm^{-1}): 2921, 1603, 1396, 1196. ^1H NMR (CDCl_3 , 400 MHz): δ 7.96-7.90 (m, 2H), 7.33-7.26 (m, 2H), 7.24-7.15 (m, 3H), 6.68-6.62 (m, 2H), 3.04 (s, 6H), 2.88-2.81 (m, 1H), 2.67-2.60 (m, 1H), 1.90-1.82 (m, 1H), 1.49-1.41 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 196.1, 153.3, 141.2, 130.3, 128.4, 126.23, 126.20, 125.6, 110.6, 40.0, 28.8, 28.4, 18.4; HRMS (EI) calculated for $[\text{C}_{18}\text{H}_{19}\text{NO}]^+$ requires m/z 265.1467, found m/z 265.1471.



***trans*-(4-(methylthio)phenyl)(2-phenylcyclopropyl)methanone (S2g)**, using 13.07g (51.4 mmol) of **S1g** to give 6.14g (22.9 mmol, 45% yield) of **S2g**; yellow oil; IR (cm^{-1}): 2922, 1656, 1589, 1406, 1228. ^1H NMR (CDCl_3 , 400 MHz): δ 7.92-7.87 (m, 2H), 7.33-7.27 (m, 2H), 7.27-7.20 (m, 3H), 7.19-7.14 (m, 2H), 2.87-2.81 (m, 1H), 2.71-2.64 (m, 1H), 2.49 (s, 3H), 1.93-1.87 (m, 1H), 1.56-1.49 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 197.3, 145.6, 140.5, 133.9, 128.49, 128.48, 126.5, 126.2, 125.0, 29.7, 29.0, 19.0, 14.7; HRMS (EI) calculated for $[\text{C}_{17}\text{H}_{16}\text{OS}]^+$ requires m/z 268.0922, found m/z 268.0919.

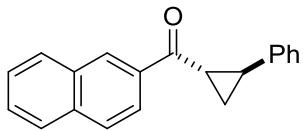


***trans*-(4-fluorophenyl)(2-phenylcyclopropyl)methanone (S2i)**, using 6.10g (26.9 mmol) of **S1i** to give 4.33g (18.0 mmol, 67% yield) of **S2i**; light yellow oil; IR (cm^{-1}): 3032, 1667, 1598, 1223. ^1H NMR (CDCl_3 , 400 MHz): δ 8.05-7.97 (m, 2H), 7.35-7.27 (m, 2H), 7.26-7.20 (m, 1H), 7.20-7.15 (m, 2H), 7.15-7.08 (m, 2H), 2.87-2.80 (m, 1H), 2.73-2.65 (m, 1H), 1.95-1.88 (m, 1H), 1.60-1.52 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 196.7, 165.5 (d, $J = 255.8$ Hz), 140.2, 133.9 (d, $J = 2.8$ Hz), 130.6 (d, $J = 9.6$ Hz), 128.4, 126.5, 126.0, 115.5 (d, $J = 22.0$ Hz), 29.8, 29.0, 19.1; ^{19}F NMR: (CDCl_3 , 376 MHz): δ -105.4; HRMS (EI) calculated for $[\text{C}_{16}\text{H}_{13}\text{FO}]^+$ requires m/z 240.0950, found m/z 240.0949.



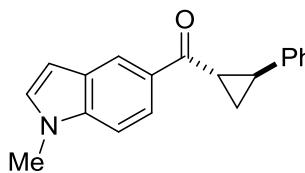
***trans*-(3-chlorophenyl)(-2-phenylcyclopropyl)methanone (S2l)**, using 8.38g (34.5 mmol) of **S1l** to give 3.89g (15.2 mmol, 44% yield) of **S2l**; light yellow oil; IR (cm^{-1}): 3065, 1670, 1572, 1456, 1218. ^1H NMR (CDCl_3 , 400 MHz): δ 7.95 (dd, $J = 1.8, 1.6$ Hz, 1H), 7.88-7.83 (m, 1H), 7.54-7.49 (m, 1H), 7.39 (dd, $J = 8.0, 7.8$ Hz, 1H), 7.35-7.28 (m, 2H), 7.26-7.20 (m, 1H), 7.20-7.14 (m, 2H), 2.86-2.79

(m, 1H), 2.76-2.68 (m, 1H), 1.95-1.88 (m, 1H), 1.62-1.55 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 197.3, 140.0, 139.1, 134.8, 132.8, 129.9, 128.6, 128.1, 126.7, 126.17, 126.15, 30.4, 29.4, 19.7; HRMS (EI) calculated for $[\text{C}_{16}\text{H}_{13}\text{ClO}]^+$ requires m/z 256.0655, found m/z 256.0657.



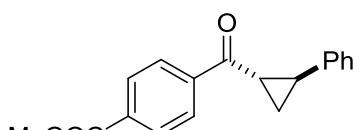
trans-naphthalen-2-yl(2-phenylcyclopropyl)methanone (S2n),

using 20.67g (80.0 mmol) of S1n to give 16.07g (59.0 mmol, 74% yield) of S2n; white solid; mp: 98.4-100.0 °C (crystallized from ethanol); IR (cm^{-1}): 3059, 1661, 1398, 1189, 1125. ^1H NMR (CDCl_3 , 400 MHz): δ 8.52 (s, 1H), 8.06 (dd, $J = 8.6, 1.6$ Hz, 1H), 7.95 (d, $J = 7.8$ Hz, 1H), 7.88 (dd, $J = 8.8, 8.6$ Hz, 2H), 7.63-7.50 (m, 2H), 7.38-7.30 (m, 2H), 7.27-7.20 (m, 3H), 3.10-3.03 (m, 1H), 2.82-2.74 (m, 1H), 2.01-1.94 (m, 1H), 1.66-1.60 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 198.4, 140.5, 135.5, 135.0, 132.5, 129.7, 129.5, 128.5, 128.4, 128.3, 127.7, 126.7, 126.6, 126.2, 123.9, 30.0, 29.3, 19.4; HRMS (EI) calculated for $[\text{C}_{20}\text{H}_{16}\text{O}]^+$ requires m/z 272.1201, found m/z 272.1209.



trans-(1-methyl-1*H*-indol-5-yl)(2-phenylcyclopropyl)methanone (S2p),

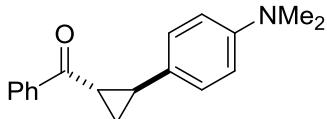
using 10.43g (39.9 mmol) of S1p to give 8.15g (29.6 mmol, 75% yield) of S2p; yellow solid; mp: 91.1-92.8 °C (crystallized from ethanol); IR (cm^{-1}): 2925, 1651, 1605, 1397, 1341, 1246, 1153. ^1H NMR (CDCl_3 , 400 MHz): δ 8.36 (d, $J = 1.4$ Hz, 1H), 7.93 (dd, $J = 8.8, 1.6$ Hz, 1H), 7.37-7.27 (m, 3H), 7.26-7.18 (m, 3H), 7.10 (d, $J = 3.0$ Hz, 1H), 6.59 (dd, $J = 3.2, 0.8$ Hz, 1H), 3.81 (s, 3H), 3.07-2.98 (m, 1H), 2.76-2.66 (m, 1H), 1.97-1.89 (m, 1H), 1.57-1.49 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 198.2, 140.9, 139.0, 130.3, 129.8, 128.4, 127.9, 126.3, 126.2, 122.8, 121.7, 109.0, 102.9, 32.9, 29.2, 29.0, 18.8; HRMS (EI) calculated for $[\text{C}_{19}\text{H}_{17}\text{NO}]^+$ requires m/z 275.1310, found m/z 275.1308.



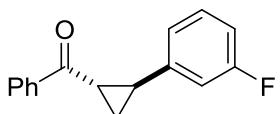
trans-methyl-4-(2-phenylcyclopropane-1-carbonyl)benzoate

(1h-S1), using 16.85g (63.3 mmol) to give 10.63g (37.9 mmol, 60% yield) of 1h-S1; white solid; mp: 98.5-100.2 °C (crystallized from ethanol); IR (cm^{-1}): 3032, 1718, 1660, 1281, 1110. ^1H NMR (CDCl_3 , 400 MHz): δ 8.11 (d, $J = 8.4$ Hz, 2H), 8.03 (d, $J = 8.2$ Hz, 2H), 7.36-7.28 (m, 2H), 7.27-7.21 (m, 1H), 7.21-7.14 (m, 2H), 3.94 (s, 3H), 2.94-2.85 (m, 1H), 2.77-2.69 (m, 1H), 1.99-1.91 (m, 1H),

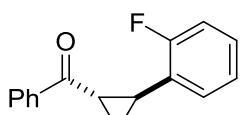
1.65-1.56 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 198.1, 166.2, 140.9, 140.1, 133.6, 129.8, 128.6, 128.0, 126.7, 126.2, 52.4, 30.5, 29.7, 19.6; HRMS (EI) calculated for $[\text{C}_{18}\text{H}_{16}\text{O}_3]^+$ requires m/z 280.1099, found m/z 280.1102.



trans-(2-(4-(dimethylamino)phenyl)cyclopropyl)(phenyl)methanone (S2ac), using 10.75g (42.8 mmol) of **S1ac** to give 13.83g (43.0 mmol, 99% yield) of **S2ac**; yellow solid; mp: 96.3-98.5 °C (crystallized from ethanol); IR (cm^{-1}): 2886, 2803, 1664, 1615, 1525, 1345, 1222. ^1H NMR (CDCl_3 , 400 MHz): δ 8.01-7.96 (m, 2H), 7.57-7.50 (m, 1H), 7.48-7.41 (m, 2H), 7.10-7.04 (m, 2H), 6.72-6.66 (m, 2H), 2.93 (s, 6H), 2.84-2.77 (m, 1H), 2.67-2.59 (m, 1H), 1.92-1.85 (m, 1H), 1.55-1.48 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 198.8, 149.6, 137.9, 132.7, 128.5, 128.1, 128.0, 127.1, 112.8, 40.7, 30.2, 29.3, 18.7; HRMS (EI) calculated for $[\text{C}_{18}\text{H}_{19}\text{NO}]^+$ requires m/z 265.1467, found m/z 265.1467.

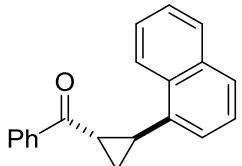


trans-(2-(3-fluorophenyl)cyclopropyl)(phenyl)methanone (S2af), using 4.91g (21.7 mmol) of **S1af** to give 3.30g (13.7 mmol, 63% yield) of **S2af**; colorless oil; IR (cm^{-1}): 3062, 1667, 1586, 1397, 1224. ^1H NMR (CDCl_3 , 400 MHz): δ 8.02-7.97 (m, 2H), 7.60-7.53 (m, 1H), 7.50-7.44 (m, 2H), 7.30-7.22 (m, 1H), 6.97 (d, $J = 7.6$ Hz, 1H), 6.95-6.88 (m, 1H), 6.88-6.82 (m, 1H), 2.93-2.87 (m, 1H), 2.72-2.66 (m, 1H), 1.96-1.89 (m, 1H), 1.56-1.50 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 197.9, 162.9 (d, $J = 245.6$ Hz), 143.1 (d, $J = 7.8$ Hz), 137.3, 132.8, 129.9 (d, $J = 8.8$ Hz), 128.4, 127.9, 121.9 (d, $J = 3.0$ Hz), 113.3 (d, $J = 21.2$ Hz), 112.7 (d, $J = 22.0$ Hz), 29.1 (d, $J = 1.4$ Hz), 29.0, 19.1; ^{19}F NMR: (CDCl_3 , 376 MHz): δ -112.8; HRMS (ESI) calculated for $[\text{C}_{16}\text{H}_{14}\text{FO}]^+ [\text{M} + \text{H}^+]$ requires m/z 241.1029, found m/z 241.1028.



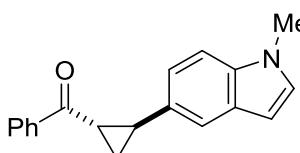
trans-(2-(2-fluorophenyl)cyclopropyl)(phenyl)methanone (S2ag), using 8.33g (36.8 mmol) of **S1ag** to give 6.29g (26.2 mmol, 71% yield) of **S2ag**; colorless oil; IR (cm^{-1}): 3063, 1668, 1495, 1451, 1398, 1223. ^1H NMR (CDCl_3 , 400 MHz): δ 8.03-7.97 (m, 2H), 7.57-7.51 (m, 1H), 7.48-7.41 (m, 2H), 7.22-7.14 (m, 1H),

7.12-7.04 (m, 2H), 7.04-6.98 (m, 1H), 2.97-2.90 (m, 1H), 2.86-2.78 (m, 1H), 1.92-1.85 (m, 1H), 1.60-1.53 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 198.5, 161.7 (d, $J = 246.4$ Hz), 137.6, 132.9, 128.5, 128.1, 128.0, 127.4 (d, $J = 14.2$ Hz), 127.2 (d, $J = 3.6$ Hz), 124.1 (d, $J = 3.6$ Hz), 115.4 (d, $J = 21.2$ Hz), 27.3, 23.6 (d, $J = 4.4$ Hz), 17.6; ^{19}F NMR: (CDCl_3 , 376 MHz): δ -118.2; HRMS (EI) calculated for $[\text{C}_{16}\text{H}_{13}\text{FO}]^+$ requires m/z 240.0950, found m/z 240.0952.



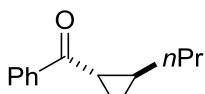
trans-(2-(naphthalen-1-yl)cyclopropyl)(phenyl)methanone (S2ah),

using 15.50g (60.0 mmol) of **S1ah** to give 8.61g (31.6 mmol, 53% yield) of **S2ah**; white solid; mp: 73.7-75.0 °C (crystallized from ethanol); IR (cm^{-1}): 3058, 1664, 1596, 1385, 1221. ^1H NMR (CDCl_3 , 400 MHz): δ 8.13 (d, $J = 8.2$ Hz, 1H), 8.08-8.02 (m, 2H), 7.86 (d, $J = 7.6$ Hz, 1H), 7.78 (d, $J = 8.4$ Hz, 1H), 7.60-7.54 (m, 1H), 7.52-7.40 (m, 5H), 7.36 (d, $J = 7.2$ Hz, 1H), 3.30-3.21 (m, 1H), 2.93-2.86 (m, 1H), 2.02-1.94 (m, 1H), 1.79-1.71 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 199.1, 137.7, 136.2, 133.5, 133.0, 128.6, 128.5, 128.2, 127.6, 126.3, 125.9, 125.3, 124.0, 123.8, 27.5, 27.3, 17.8; HRMS (EI) calculated for $[\text{C}_{20}\text{H}_{16}\text{O}]^+$ requires m/z 272.1201, found m/z 272.1200.



trans-(2-(1-methyl-1*H*-indol-5-yl)cyclopropyl)(phenyl)methanone (S2al),

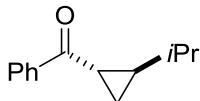
using 9.16g (35.1 mmol) of **S1al** to give 10.77g (35.0 mmol, 99% yield) of **S2al**; yellow solid; mp: 86.3-87.9 °C (crystallized from ethanol); IR (cm^{-1}): 2953, 1663, 1450, 1397, 1223. ^1H NMR (CDCl_3 , 400 MHz): δ 8.02-7.97 (m, 2H), 7.56-7.50 (m, 1H), 7.47-7.40 (m, 3H), 7.25 (d, $J = 8.4$ Hz, 1H), 7.07 (dd, $J = 8.4, 1.4$ Hz, 1H), 7.04 (d, $J = 3.2$ Hz, 1H), 6.43 (dd, $J = 3.2, 0.8$ Hz, 1H), 3.77 (s, 3H), 2.93-2.87 (m, 1H), 2.85-2.78 (m, 1H), 2.00-1.93 (m, 1H), 1.67-1.59 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 198.9, 137.9, 135.8, 132.7, 131.2, 129.4, 128.6, 128.5, 128.1, 120.6, 118.1, 109.2, 100.8, 32.9, 31.0, 29.8, 19.0; HRMS (EI) calculated for $[\text{C}_{19}\text{H}_{17}\text{NO}]^+$ requires m/z 275.1310, found m/z 275.1307.



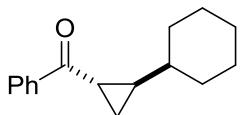
trans-phenyl(2-propylcyclopropyl)methanone (S2ao), using 6.50g (37.3 mmol) of **S1ao** to give 3.35g (17.8 mmol, 48% yield) of **S2ao**; colorless oil;

IR (cm^{-1}): 2959, 2926, 1667, 1450, 1220. ^1H NMR (CDCl_3 , 300 MHz): δ 8.04-7.97 (m, 2H),

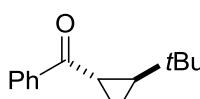
7.60-7.52 (m, 1H), 7.51-7.42 (m, 2H), 2.48-2.40 (m, 1H), 1.66-1.54 (m, 1H), 1.54-1.37 (m, 5H), 0.97-0.88 (m, 4H); ^{13}C NMR: (CDCl_3 , 75 MHz): δ 200.2, 138.1, 132.6, 128.4, 127.9, 35.6, 27.1, 25.2, 22.4, 19.0, 13.9; HRMS (EI) calculated for $[\text{C}_{13}\text{H}_{16}\text{O}]^+$ requires m/z 188.1201, found m/z 188.1204.



***trans*-(2-isopropylcyclopropyl)(phenyl)methanone (S2aq)**, using 5.89g (33.8 mmol) of **S1aq** to give 4.76g (25.3 mmol, 75% yield) of **S2aq**; colorless oil; IR (cm^{-1}): 2958, 1668, 1357, 1222. ^1H NMR (CDCl_3 , 300 MHz): δ 8.05-7.98 (m, 2H), 7.60-7.53 (m, 1H), 7.52-7.43 (m, 2H), 2.53-2.45 (m, 1H), 1.51-1.40 (m, 2H), 1.27-1.15 (m, 1H), 1.04 (d, $J = 4.0$ Hz, 3H), 1.02 (d, $J = 4.0$ Hz, 3H), 1.09-0.93 (m, 1H); ^{13}C NMR: (CDCl_3 , 75 MHz): δ 200.2, 138.1, 132.6, 128.5, 127.9, 35.2, 32.7, 24.3, 22.0, 21.8, 18.0; HRMS (EI) calculated for $[\text{C}_{13}\text{H}_{16}\text{O}]^+$ requires m/z 188.1201, found m/z 188.1202.

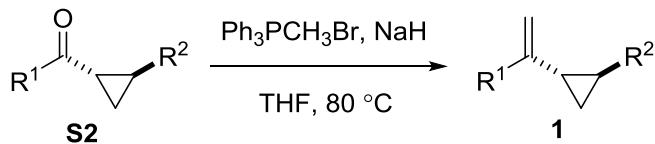


***trans*-(2-cyclohexylcyclopropyl)(phenyl)methanone (S2ar)**, using 4.53g (21.1 mmol) of **S1ar** to give 4.11g (18.0 mmol, 85% yield) of **S2ar**; colorless oil; IR (cm^{-1}): 2923, 2850, 1666, 1448, 1218. ^1H NMR (CDCl_3 , 400 MHz): δ 8.04-7.97 (m, 2H), 7.58-7.51 (m, 1H), 7.51-7.42 (m, 2H), 2.51-2.45 (m, 1H), 1.84-4.67 (m, 4H), 1.67-1.59 (m, 1H), 1.50-1.41 (m, 2H), 1.27-1.05 (m, 5H), 0.97-0.92 (m, 1H), 0.90-0.79 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 200.1, 138.1, 132.5, 128.4, 127.9, 42.2, 33.9, 32.8, 32.5, 26.3, 26.1, 26.0, 23.9, 17.5; HRMS (EI) calculated for $[\text{C}_{16}\text{H}_{20}\text{O}]^+$ requires m/z 228.1514, found m/z 228.1516.



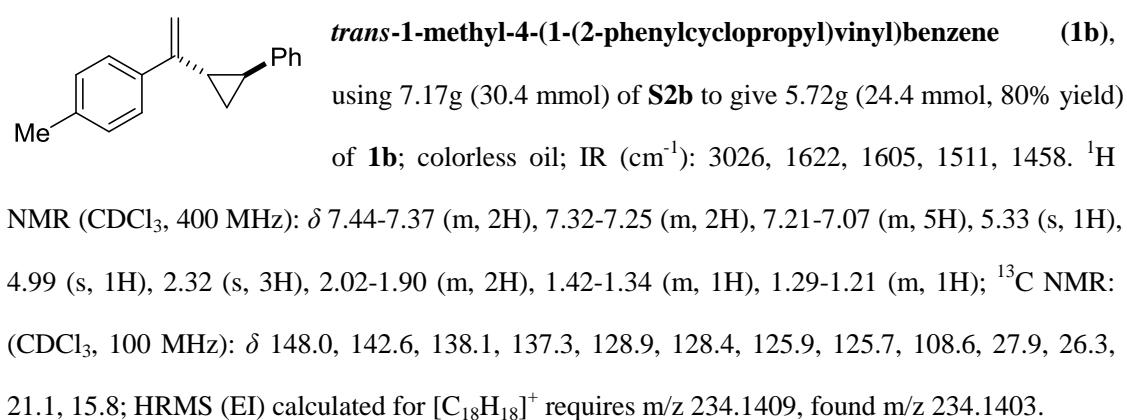
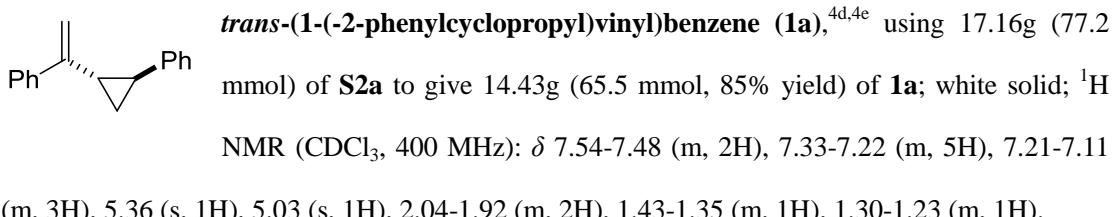
***trans*-(2-(tert-butyl)cyclopropyl)(phenyl)methanone (S2as)**, using 1.82g (9.67 mmol) of **S1i** to give 1.30g (6.41 mmol, 66% yield) of **S2as**; colorless oil; IR (cm^{-1}): 2957, 1667, 1332, 1221. ^1H NMR (CDCl_3 , 400 MHz): δ 8.04-7.96 (m, 2H), 7.59-7.52 (m, 1H), 7.51-7.43 (m, 2H), 2.60-2.53 (m, 1H), 1.62-1.53 (m, 1H), 1.43-1.36 (m, 1H), 1.07-1.01 (m, 1H), 0.93 (s, 9H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 200.4, 138.1, 132.5, 128.4, 127.9, 38.7, 30.0, 28.3, 21.3, 14.8; HRMS (EI) calculated for $[\text{C}_{14}\text{H}_{18}\text{O}]^+$ requires m/z 202.1358, found m/z 202.1358.

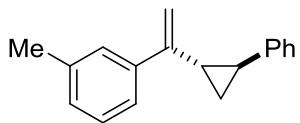
3. General procedure for the synthesis of vinylcyclopropanes

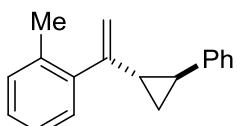


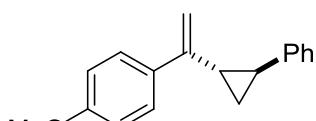
Method C: prepared by Wittig olefination of the corresponding ketones **S2** according to previously reported procedures,^{4a} a 250 mL of three-necked flame-dried round-bottom flask was cooled at room temperature under the atmosphere of nitrogen, charged with Methyltriphenylphosphonium bromide (1.2 equiv.), NaH (1.3 equiv., 60% dispersion in mineral oil), THF (150 mL). The mixture was refluxed in 80 °C for 1 h and then cooled to 0 °C, a solution of cyclopropyl ketone in THF (20 mL) was added dropwise and continued to reflux for about 4-12 h. The reaction was quenched by 1.0 mL saturated NH₄Cl until the starting material disappeared (monitored by TLC with PE). The reaction mixture was concentrated by rotary evaporation and then filtrated on silica gel. The combined filtrates were concentrated by rotary evaporation and further purified by flash chromatography on silica gel.

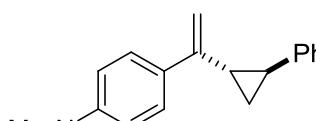
The vinylcyclopropanes without noted were prepared according to method C except. **1h** and **1ap**,^{4b} **1r-t**^{4c} were prepared of the corresponding ketones according to a previously reported procedure.



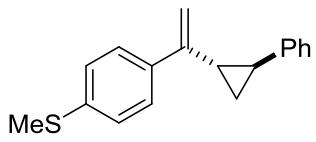

***trans*-1-methyl-3-(1-(2-phenylcyclopropyl)vinyl)benzene (1c),** using 9.99g (42.3 mmol) of **S2c** to give 6.16g (26.3 mmol, 62% yield) of **1c**; colorless oil; IR (cm^{-1}): 3028, 1603, 1496, 1458, 1078. ^1H NMR (CDCl_3 , 400 MHz): δ 7.34-7.25 (m, 4H), 7.20-7.11 (m, 4H), 7.06 (d, $J = 7.6$ Hz, 1H), 5.34 (s, 1H), 5.01 (s, 1H), 2.31 (s, 3H), 2.03-1.96 (m, 1H), 1.96-1.89 (m, 1H), 1.40-1.33 (m, 1H), 1.30-1.24 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 148.4, 142.5, 141.0, 137.6, 128.4, 128.3, 128.1, 126.9, 125.70, 125.66, 123.2, 109.1, 28.0, 26.3, 21.4, 15.8; HRMS (EI) calculated for $[\text{C}_{18}\text{H}_{18}]^+$ requires m/z 234.1409, found m/z 234.1405.


***trans*-1-methyl-2-(1-(2-phenylcyclopropyl)vinyl)benzene (1d),** using 16.32g (69.1 mmol) of **S2d** to give 15.60g (66.7 mmol, 96% yield) of **1d**; colorless oil; IR (cm^{-1}): 3023, 1603, 1492, 1456, 1077. ^1H NMR (CDCl_3 , 400 MHz): δ 7.28-7.21 (m, 2H), 7.19-7.11 (m, 4H), 7.10-7.03 (m, 3H), 5.18 (s, 1H), 4.84 (s, 1H), 2.30 (s, 3H), 1.91-1.85 (m, 2H), 1.22-1.15 (m, 1H), 1.14-1.06 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 149.9, 142.5, 141.1, 135.5, 129.9, 128.9, 128.3, 127.1, 125.8, 125.6, 125.3, 111.5, 29.7, 25.2, 20.0, 16.0; HRMS (EI) calculated for $[\text{C}_{18}\text{H}_{18}]^+$ requires m/z 234.1409, found m/z 234.1412.


***trans*-1-methoxy-4-(1-(2-phenylcyclopropyl)vinyl)benzene (1e),** using 20.49g (81.2 mmol) of **S2e** to give 17.40g (69.6 mmol, 86% yield) of **1e**; white solid; mp: 58.0–59.9 °C (crystallized from ethanol); IR (cm^{-1}): 2927, 1607, 1511, 1247, 1180. ^1H NMR (CDCl_3 , 400 MHz): δ 7.48-7.42 (m, 2H), 7.34-7.26 (m, 2H), 7.22-7.16 (m, 1H), 7.16-7.12 (m, 2H), 6.86-6.80 (m, 2H), 5.29 (s, 1H), 4.96 (s, 1H), 3.79 (s, 3H), 2.01-1.89 (m, 2H), 1.44-1.36 (m, 1H), 1.30-1.21 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 159.2, 147.5, 142.6, 133.5, 128.4, 127.1, 125.7, 113.6, 107.7, 55.2, 28.0, 26.3, 15.7; HRMS (EI) calculated for $[\text{C}_{18}\text{H}_{18}\text{O}]^+$ requires m/z 250.1358, found m/z 250.1353.

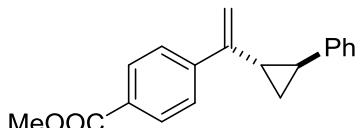

***trans*-N,N-dimethyl-4-(1-(2-phenylcyclopropyl)vinyl)aniline (1f),** using 9.54g (36.0 mmol) of **S2f** to give 4.07g (15.5 mmol, 43% yield) of **1f**; yellow solid; mp: 82.8-84.4 °C (crystallized from ethanol); IR (cm^{-1}): 2891, 1608, 1521, 1353, 1226. ^1H NMR (CDCl_3 , 400 MHz): δ 7.46-7.40 (m,

2H), 7.33-7.26 (m, 2H), 7.21-7.12 (m, 3H), 6.69-6.63 (m, 2H), 5.26 (s, 1H), 4.88 (s, 1H), 2.93 (s, 6H), 1.99-1.90 (m, 2H), 1.44-1.36 (m, 1H), 1.27-1.19 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 150.1, 147.5, 142.9, 129.0, 128.4, 126.7, 125.6, 125.5, 112.1, 105.8, 40.4, 28.0, 26.2, 15.6; HRMS (EI) calculated for $[\text{C}_{19}\text{H}_{21}\text{N}]^+$ requires m/z 263.1674, found m/z 263.1677.

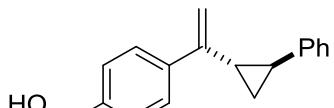


trans-methyl(4-(1-(2-phenylcyclopropyl)vinyl)phenyl)sulfane (1g), using 6.14g (22.9 mmol) of **S2g** to give 5.17g (19.4 mmol, 85% yield) of **1g**; yellow oil; IR (cm^{-1}): 3025, 1603, 1494, 1434, 1110.

^1H NMR (CDCl_3 , 400 MHz): δ 7.46-7.39 (m, 2H), 7.33-7.25 (m, 2H), 7.22-7.10 (m, 5H), 5.35 (s, 1H), 5.01 (s, 1H), 2.44 (s, 3H), 2.00-1.86 (m, 2H), 1.44-1.35 (m, 1H), 1.29-1.21 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 147.2, 142.3, 137.7, 137.5, 128.3, 126.3, 126.1, 125.6, 125.5, 108.7, 27.7, 26.2, 15.6, 15.5; HRMS (EI) calculated for $[\text{C}_{18}\text{H}_{18}\text{S}]^+$ requires m/z 266.1129, found m/z 266.1126.

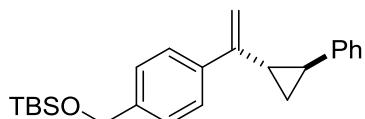


trans-methyl-4-(1-(2-phenylcyclopropyl)vinyl)benzoate (1h-S2), using 10.03g (35.8 mmol) of **1h-S1** to give 7.60g (27.3 mmol, 76% yield) of **1h-S2**; white solid; mp: 63.9-66.2 °C (crystallized from ethanol); IR (cm^{-1}): 2950, 1721, 1606, 1457, 1279. ^1H NMR (CDCl_3 , 400 MHz): δ 7.99-7.94 (m, 2H), 7.58-7.53 (m, 2H), 7.33-7.26 (m, 2H), 7.22-7.16 (m, 1H), 7.16-7.11 (m, 2H), 5.46 (s, 1H), 5.14 (s, 1H), 3.89 (s, 3H), 2.04-1.96 (m, 1H), 1.96-1.90 (m, 1H), 1.43-1.36 (m, 1H), 1.34-1.27 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 166.9, 147.5, 145.4, 142.1, 129.6, 129.1, 128.5, 126.0, 125.9, 125.7, 111.4, 52.0, 27.6, 26.3, 15.8; HRMS (EI) calculated for $[\text{C}_{19}\text{H}_{18}\text{O}_2]^+$ requires m/z 278.1307, found m/z 278.1302.

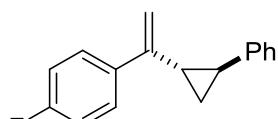


trans-(4-(1-(2-phenylcyclopropyl)vinyl)phenyl)methanol (1h-S3), a 100 mL of three-necked flame-dried round-bottom flask was cooled at 0 °C under the atmosphere of nitrogen, charged with LiAlH_4 (0.3978 g, 10.5 mmol, 1.0 equiv.) and 30 mL ether. A solution of **1h-S2** (2.8046 g, 10.1 mmol, 1.0 equiv.) in 10 mL ether was added dropwise at 0 °C. Then the reaction was stirred at room temperature for 7 h until the starting material disappeared (monitored by TLC).

with PE/EA (10/1)). The reaction was quenched by 20 mL saturated NH₄Cl and extracted with EA (20 mL x 3) . The combined organic layers were washed with brine (30 mL), dried over Na₂SO₄, filtered, and concentrated under reduced pressure to give 2.5034 g (10.0 mmol, 99% yield) of the title compound as colorless oil; IR (cm⁻¹): 3335, 2923, 1604, 1498, 1214. ¹H NMR (CDCl₃, 400 MHz): δ 7.54-7.49 (m, 2H), 7.33-7.23 (m, 3H), 7.11-7.06 (m, 2H), 7.88-7.83 (m, 2H), 5.35 (s, 1H), 5.02 (s, 1H), 3.80 (s, 3H), 1.99-1.92 (m, 1H), 1.91-1.84 (m, 1H), 1.39-1.32 (m, 1H), 1.24-1.17 (m, 1H); ¹³C NMR: (CDCl₃, 100 MHz): δ 157.8, 148.4, 141.1, 134.5, 128.2, 127.5, 126.8, 126.1, 113.9, 109.1, 55.3, 27.4, 25.7, 15.4; HRMS (EI) calculated for [C₁₈H₁₈O]⁺ requires m/z 250.1358, found m/z 250.1358.

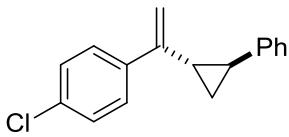


trans-tert-butyldimethyl((4-(1-(2-phenylcyclopropyl)vinyl)b enzyloxy)silane (1h), prepared according to a previously reported procedure,^{4b} to a solution of **1h-S3** (0.2534 g, 10.0 mmol, 1.0 equiv.), DMAP (0.0184 g, 0.15 mmol, 0.015 equiv.), and Et₃N (1.7 mL, 1.2 equiv.) in 10 mL DCM was added *tert*-butylchlorodimethylsilane (1.7556 g, 11.6 mmol, 1.16 equiv.). The reaction mixture was stirred at room temperature for 11 h. The reaction mixture was diluted with DCM (50 mL) and washed with water (30 mL) and then brine (30 mL). The organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using PE/EA (50/1) to give 3.2224 g (8.84 mmol, 88% yield) of the title compound as a colorless oil; IR (cm⁻¹): 2954, 2856, 1500, 1466, 1255. ¹H NMR (CDCl₃, 400 MHz): δ 7.50-7.44 (m, 2H), 7.33-7.22 (m, 4H), 7.22-7.16 (m, 1H), 7.16-7.12 (m, 2H), 5.35 (s, 1H), 5.02 (s, 1H), 4.72 (s, 2H), 2.02-1.95 (m, 2H), 1.42-1.35 (m, 1H), 1.30-1.22 (m, 1H), 0.93 (s, 9H), 0.09 (s, 6H); ¹³C NMR: (CDCl₃, 100 MHz): δ 148.1, 142.6, 140.8, 139.7, 128.4, 125.9, 125.73, 125.70, 109.0, 64.7, 27.9, 26.3, 26.0, 18.4, 15.9, -5.3; HRMS (EI) calculated for [C₂₄H₃₂OSi]⁺ requires m/z 364.2222, found m/z 364.2223.

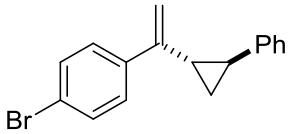


trans-1-fluoro-4-(1-(2-phenylcyclopropyl)vinyl)benzene (1i), using 4.33g (18.0 mmol) of **S2i** to give 3.02g (12.7 mmol, 70% yield) of **1i**; colorless oil; IR (cm⁻¹): 3028, 1603, 1507, 1230, 1160. ¹H NMR (CDCl₃, 400 MHz): δ 7.50-7.42 (m, 2H), 7.33-7.26 (m, 2H), 7.22-7.16 (m, 1H), 7.16-7.10 (m, 2H),

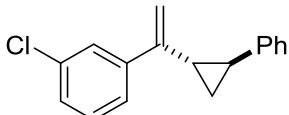
7.01-6.92 (m, 2H), 5.30 (s, 1H), 5.02 (s, 1H), 2.01-1.94 (m, 1H), 1.93-1.86 (m, 1H), 1.42-1.35 (m, 1H), 1.30-1.23 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 162.4 (d, $J = 246.6$ Hz), 147.2, 142.3, 137.0 (d, $J = 2.8$ Hz), 128.5, 127.7 (d, $J = 8.2$ Hz), 125.8, 125.6, 115.0 (d, $J = 21.2$ Hz), 109.2, 27.9, 26.3, 15.7; ^{19}F NMR (CDCl_3 , 376 MHz): δ -114.8; HRMS (EI) calculated for $[\text{C}_{17}\text{H}_{15}\text{F}]^+$ requires m/z 238.1158, found m/z 238.1157.



trans-1-chloro-4-(1-(2-phenylcyclopropyl)vinyl)benzene (1j), using 10.29g (40.1 mmol) of **S2j** to give 6.32g (24.9 mmol, 62% yield) of **1j**; colorless oil; IR (cm^{-1}): 3028, 1602, 1492, 1096. ^1H NMR (CDCl_3 , 400 MHz): δ 7.46-7.40 (m, 2H), 7.35-7.23 (m, 4H), 7.23-7.17 (m, 1H), 7.17-7.11 (m, 2H), 5.35 (s, 1H), 5.06 (s, 1H), 2.02-1.94 (m, 1H), 1.94-1.86 (m, 1H), 1.44-1.35 (m, 1H), 1.33-1.23 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 147.2, 142.3, 139.4, 133.4, 128.5, 128.4, 127.4, 125.9, 125.7, 109.9, 27.8, 26.3, 15.8; HRMS (EI) calculated for $[\text{C}_{17}\text{H}_{15}\text{Cl}]^+$ requires m/z 254.0862, found m/z 254.0862.

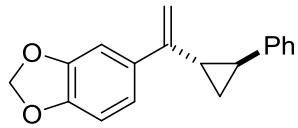


trans-1-bromo-4-(1-(2-phenylcyclopropyl)vinyl)benzene (1k), using 12.83g (42.6 mmol) of **S2k** to give 10.99g (36.8 mmol, 86% yield) of **1k**; white solid; mp: 32.2-33.4 °C (crystallized from ethanol); IR (cm^{-1}): 3027, 2923, 1622, 1488, 1390. ^1H NMR (CDCl_3 , 400 MHz): δ 7.45-7.34 (m, 4H), 7.33-7.26 (m, 2H), 7.23-7.16 (m, 1H), 7.13 (d, $J = 7.6$ Hz, 2H), 5.36 (s, 1H), 5.06 (s, 1H), 2.00-1.93 (m, 1H), 1.93-1.86 (m, 1H), 1.42-1.34 (m, 1H), 1.32-1.23 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 147.2, 142.2, 139.9, 131.3, 128.5, 127.7, 125.8, 125.7, 121.6, 110.0, 27.7, 26.3, 15.7; HRMS (EI) calculated for $[\text{C}_{17}\text{H}_{15}\text{Br}]^+$ requires m/z 298.0357, found m/z 298.0350.

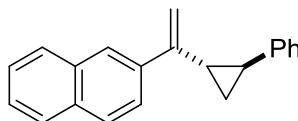


trans-1-chloro-3-(1-(2-phenylcyclopropyl)vinyl)benzene (1l), using 3.71g (14.5 mmol) of **S2l** to give 3.00g (11.8 mmol, 82% yield) of **1l**; colorless oil; IR (cm^{-1}): 3027, 1595, 1563, 1475, 1256. ^1H NMR (CDCl_3 , 400 MHz): δ 7.50 (s, 1H), 7.39-7.34 (m, 1H), 7.33-7.26 (m, 2H), 7.25-7.18 (m, 3H), 7.18-7.12 (m, 2H), 5.36 (s, 1H), 5.08 (s, 1H), 2.04-1.97 (m, 1H), 1.93-1.85 (m, 1H), 1.40-1.33 (m, 1H), 1.33-1.27 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 147.2, 143.0, 142.1, 134.2, 129.5, 128.5,

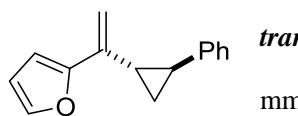
127.6, 126.3, 125.9, 125.8, 124.3, 110.7, 27.7, 26.2, 15.9; HRMS (EI) calculated for $[C_{17}H_{15}Cl]^+$ requires m/z 254.0862, found m/z 254.0863.



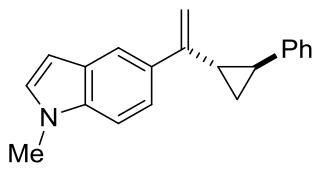
trans-5-(1-(2-phenylcyclopropyl)vinyl)benzo[d][1,3]dioxole (1m), using 13.40g (50.3 mmol) of **S2m** to give 10.66g (40.4 mmol, 80% yield) of **1m**; yellow oil; IR (cm^{-1}): 3026, 2889, 1603, 1488, 1439, 1227. ^1H NMR (CDCl_3 , 400 MHz): δ 7.32-7.25 (m, 2H), 7.21-7.15 (m, 1H), 7.15-7.11 (m, 2H), 7.03-6.97 (m, 2H), 6.75-6.70 (m, 1H), 5.93-5.90 (m, 2H), 5.25 (s, 1H), 4.95 (s, 1H), 2.01-1.93 (m, 1H), 1.92-1.85 (m, 1H), 1.41-1.34 (m, 1H), 1.27-1.22 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 147.6, 147.5, 147.0, 142.4, 135.3, 128.4, 125.7, 125.6, 119.6, 108.3, 107.9, 106.5, 100.9, 28.0, 26.3, 15.7; HRMS (EI) calculated for $[C_{18}H_{16}O_2]^+$ requires m/z 264.1150, found m/z 264.1149.



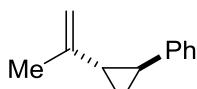
trans-2-(1-(2-phenylcyclopropyl)vinyl)naphthalene (1n), using 13.67g (50.2 mmol) of **S2n** to give 10.63g (39.3 mmol, 78% yield) of **1n**; white solid; mp: 40.2-41.2 °C (crystallized from ethanol); IR (cm^{-1}): 3057, 1602, 1499, 1276. ^1H NMR (CDCl_3 , 400 MHz): δ 7.94 (s, 1H), 7.80-7.64 (m, 4H), 7.44-7.37 (m, 2H), 7.35-7.28 (m, 2H), 7.24-7.15 (m, 3H), 5.51 (s, 1H), 5.15 (s, 1H), 2.04 (dd, $J = 7.2, 7.4$ Hz, 2H), 1.47-1.40 (m, 1H), 1.38-1.31 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 148.0, 142.4, 138.1, 133.3, 132.8, 128.4, 128.3, 127.7, 127.4, 126.0, 125.8, 125.7, 125.0, 124.3, 110.0, 28.1, 26.3, 15.6; HRMS (EI) calculated for $[C_{21}H_{18}]^+$ requires m/z 270.1409, found m/z 270.1414.



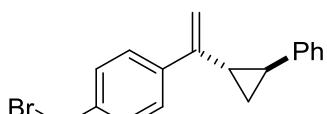
trans-2-(1-(2-phenylcyclopropyl)vinyl)furan (1o), using 1.78g (8.40 mmol) of **S2o** to give 1.73g (8.23 mmol, 97% yield) of **1o**; yellow solid; mp: 36.5-38.5 °C (crystallized from ethanol); IR (cm^{-1}): 3027, 2924, 1606, 1494, 1160. ^1H NMR (CDCl_3 , 400 MHz): δ 7.37-7.34 (m, 1H), 7.33-7.25 (m, 2H), 7.22-7.17 (m, 1H), 7.16-7.10 (m, 2H), 6.35-6.28 (m, 2H), 5.52 (s, 1H), 4.95 (s, 1H), 2.00-1.86 (m, 2H), 1.40-1.31 (m, 1H), 1.24-1.18 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 154.8, 142.4, 142.0, 137.8, 128.4, 125.74, 125.71, 111.1, 106.9, 106.8, 25.4, 25.2, 14.7; HRMS (EI) calculated for $[C_{15}H_{14}O]^+$ requires m/z 210.1045, found m/z 210.1042.



trans-1-methyl-5-(1-(2-phenylcyclopropyl)vinyl)-1H-indole (1p), using 8.01g (29.1 mmol) of **S2p** to give 7.04g (25.8 mmol, 88% yield) of **1p**; white solid; mp: 69.4-70.6 °C (crystallized from ethanol); IR (cm⁻¹): 2924, 1612, 1493, 1336, 1247. ¹H NMR (CDCl₃, 400 MHz): δ 7.78 (s, 1H), 7.42 (dd, J = 8.6, 1.6 Hz, 1H), 7.34-7.27 (m, 2H), 7.26-7.22 (m, 1H), 7.22-7.15 (m, 3H), 7.01 (d, J = 3.0 Hz, 1H), 6.43 (d, J = 2.8 Hz, 1H), 5.34 (s, 1H), 5.00 (s, 1H), 3.76 (s, 3H), 2.09-2.02 (m, 2H), 1.46-1.38 (m, 1H), 1.33-1.27 (m, 1H); ¹³C NMR: (CDCl₃, 100 MHz): δ 149.1, 142.8, 136.3, 132.6, 129.2, 128.4, 128.3, 125.8, 125.6, 120.3, 118.5, 108.8, 107.5, 101.3, 32.7, 28.5, 26.3, 16.0; HRMS (EI) calculated for [C₂₀H₁₉N]⁺ requires m/z 273.1517, found m/z 273.1513.

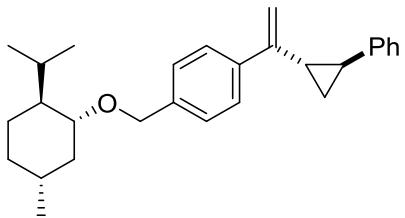


trans-(2-(prop-1-en-2-yl)cyclopropyl)benzene (1q), using 4.20g (26.2 mmol) of **S2q** to give 1.84g (11.7 mmol, 44% yield) of **1q**; colorless oil; IR (cm⁻¹): 2957, 2926, 1645, 1497, 1457. ¹H NMR (CDCl₃, 400 MHz): δ 7.29-7.21 (m, 2H), 7.17-7.11 (m, 1H), 7.11-7.05 (m, 2H), 4.77-4.71 (m, 2H), 2.00-1.94 (m, 1H), 1.73 (s, 3H), 1.69-1.61 (m, 1H), 1.25-1.18 (m, 1H), 1.12-1.05 (m, 1H); ¹³C NMR: (CDCl₃, 100 MHz): δ 145.3, 142.9, 128.3, 125.8, 125.5, 108.6, 30.0, 24.0, 20.7, 15.2; HRMS (EI) calculated for [C₁₂H₁₄]⁺ requires m/z 158.1096, found m/z 158.1098.



trans-1-(bromomethyl)-4-(1-(2-phenylcyclopropyl)vinyl)benzen e (1r-S1), a 100 mL of three-necked round-bottom flask was charged with **1h-S3** (2.9103 g, 11.6 mmol, 1.0 equiv.), CBr₄ (5.03 g, 15.2 mmol, 1.25 equiv.) and 20 mL ether. A solution of triphenylphosphine (3.99 g, 15.2 mmol, 1.25 equiv.) in 20 mL ether was added dropwise and stirred at room temperature for 5 h. The reaction mixture was filtrated on silica gel and washed with ether. The combined filtrates were concentrated by rotary evaporation and purified by flash column chromatography on silica gel using PE/EA (20/1) to give 3.1310 g (10.0 mmol, 86% yield) of the title compound as a colorless oil; IR (cm⁻¹): 3057, 1603, 1498, 1406, 1227. ¹H NMR (CDCl₃, 400 MHz): δ 7.51-7.45 (m, 2H), 7.34-7.25 (m, 4H), 7.22-7.16 (m, 1H), 7.16-7.10 (m, 2H), 5.38 (s, 1H), 5.06 (s, 1H), 4.46 (s, 2H), 2.01-1.98 (m, 2H), 1.43-1.35 (m, 1H), 1.31-1.23 (m, 1H); ¹³C NMR: (CDCl₃, 100 MHz): δ 147.5, 142.3, 141.1, 137.0, 129.0, 128.4, 126.4, 125.8, 125.6, 110.0, 33.3, 27.8, 26.4, 15.7; HRMS (EI)

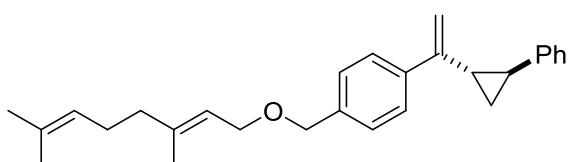
calculated for $[C_{18}H_{17}Br]^+$ requires m/z 312.0514, found m/z 312.0517.



trans-1-(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)methyl-4-(1-(2-phenylcyclopropyl)vinyl)benzene (1r),

prepared according to a previously reported procedure,^{4e} a 100 mL of three-necked flame-dried round-bottom flask

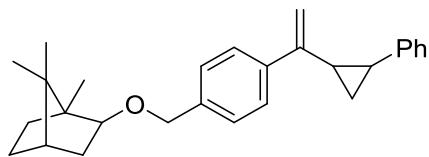
was cooled at room temperature under the atmosphere of nitrogen, charged with **1r-S1** (0.8687 g, 2.8 mmol, 1.0 equiv.), menthol (0.7556 g, 4.8 mmol, 1.7 equiv.) and 25 mL THF. A solution of NaH (0.2527 g, 6.3 mmol, 2.3 equiv., 60% dispersion in mineral oil) in 25 mL THF was added dropwise at room temperature. Then the reaction was stirred reflux for 11 h until the starting material disappeared (monitored by TLC with PE/EA (100/1)). The reaction was quenched by 20 mL saturated NH₄Cl and extracted with EA (20 mL x 3). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using PE/EA (100/1) to give 1.0271 g (2.64 mmol, 1:1 *dr*, 95% yield) of the title compound as a yellow oil; IR (cm^{-1}): 2953, 2921, 2867, 1623, 1457, 1368. ¹H NMR (CDCl₃, 400 MHz): δ 7.50-7.44 (m, 2H), 7.32-7.25 (m, 4H), 7.21-7.17 (m, 1H), 7.16-7.11 (m, 2H), 5.35 (d, *J* = 1.6 Hz, 1H), 5.02 (s, 1H), 4.63 (d, *J* = 11.6 Hz, 1H), 4.37 (d, *J* = 11.6 Hz, 1H), 3.15 (td, *J* = 10.4, 3.4 Hz, 1H), 2.35-2.23 (m, 1H), 2.21-2.13 (m, 1H), 2.02-1.91 (m, 2H), 1.70-1.67 (m, 2H), 1.42-1.32 (m, 2H), 1.30-1.22 (m, 2H), 0.99-0.82 (m, 9H), 0.71 (d, *J* = 6.8 Hz, 3H); HRMS (EI) calculated for [C₂₈H₃₆O]⁺ requires m/z 388.2766, found m/z 388.2767.



trans-(E)-1-(((3,7-dimethylocta-2,6-dien-1-yl)oxy)methyl)-4-(1-(2-phenylcyclopropyl)vinyl)benzene (1s), prepared according to a previously reported procedure,^{4e} a 100 mL of three-necked flame-dried round-bottom flask was

cooled at room temperature under the atmosphere of nitrogen, charged with **1r-S1** (3.1310 g, 10.0 mmol, 1.0 equiv.), geraniol (1.8 mL, 1.0 equiv) and 50 mL THF. A solution of NaH (0.69 g, 17.3 mmol, 1.7 equiv., 60% dispersion in mineral oil) in 20 mL THF was added dropwise at room temperature. Then the reaction was stirred at room temperature for 9 h until the starting material

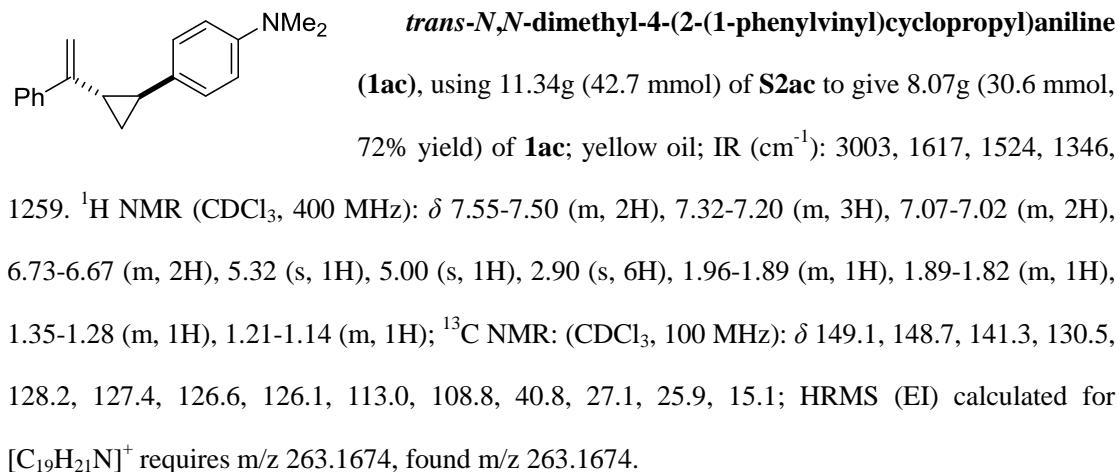
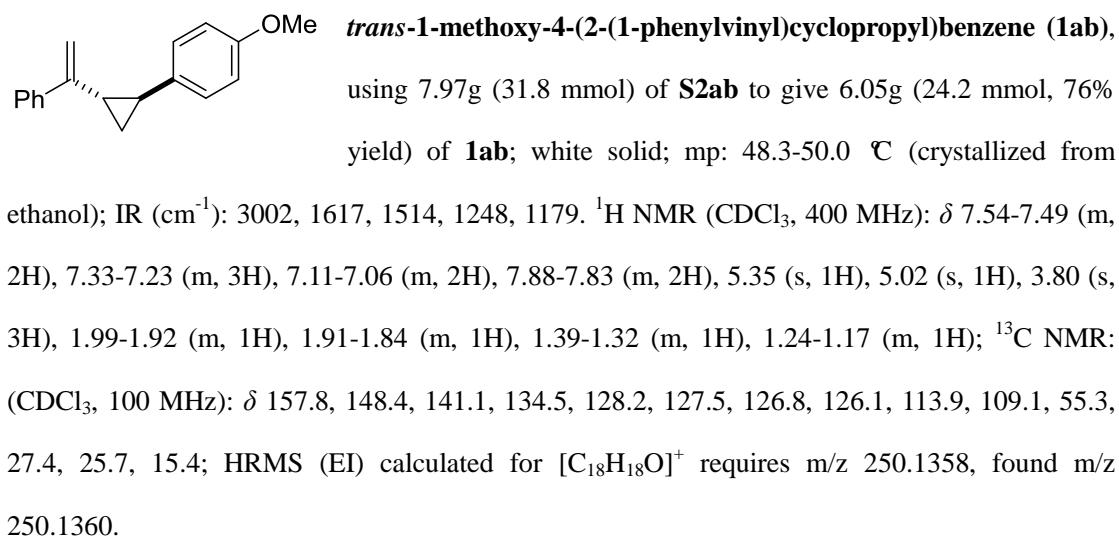
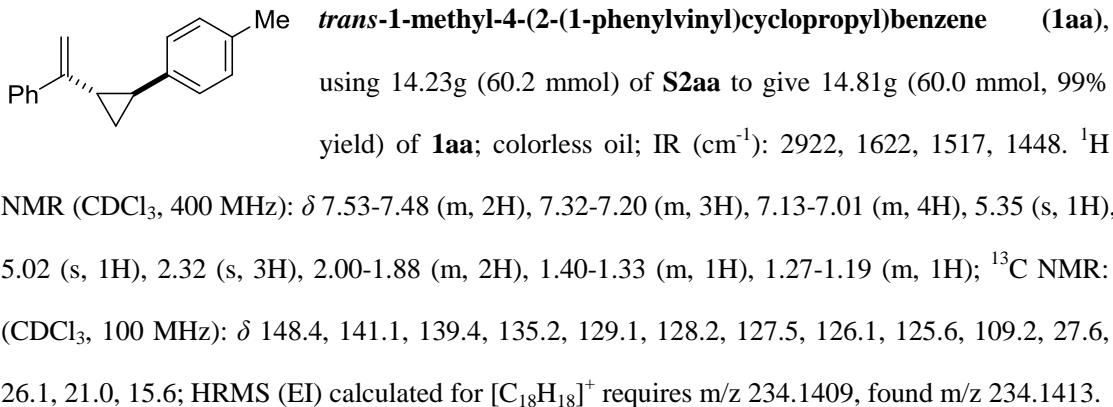
disappeared (monitored by TLC with PE/EA (100/1)). The reaction was quenched by 20 mL saturated NH₄Cl and extracted with EA (20 mL x 3). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using PE/EA (100/1) to give 3.3851 g (8.76 mmol, 88% yield) of the title compound as a yellow oil; IR (cm⁻¹): 2916, 2854, 1775, 1672, 1442, 1104. ¹H NMR (CDCl₃, 400 MHz): δ 7.51-7.45 (m, 2H), 7.34-7.26 (m, 4H), 7.22-7.16 (m, 1H), 7.16-7.12 (m, 2H), 5.42-5.34 (m, 2H), 5.13-5.05 (m, 1H), 5.03 (s, 1H), 4.48 (s, 2H), 4.01 (d, J = 6.8 Hz, 2H), 2.15-2.07 (m, 2H), 2.07-2.01 (m, 2H), 2.01-1.91 (m, 2H), 1.67 (s, 3H), 1.64 (s, 3H), 1.60 (s, 3H), 1.42-1.35 (m, 1H), 1.31-1.24 (m, 1H); ¹³C NMR: (CDCl₃, 100 MHz): δ 148.0, 142.5, 140.4, 140.3, 138.0, 131.6, 128.4, 127.7, 126.1, 125.7, 124.0, 120.8, 109.3, 71.6, 66.6, 39.6, 27.9, 26.4, 26.3, 25.7, 17.7, 16.5, 15.8; HRMS (EI) calculated for [C₂₈H₃₄O]⁺ requires m/z 386.2610, found m/z 386.2608.

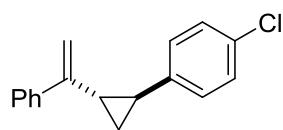


trans-1,7,7-trimethyl-2-((4-(1-(2-phenylcyclopropyl)vinyl)benzyl)oxy)bicyclo[2.2.1]heptane (1t), prepared according to a previously reported procedure,^{4e} a 100 mL

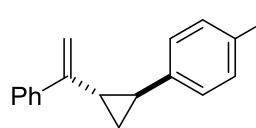
of three-necked flame-dried round-bottom flask was cooled at room temperature under the atmosphere of nitrogen, charged with **1r-S1** (1.2621 g, 4.0 mmol, 1.0 equiv.), borneol (0.7942 g, 5.1 mmol, 1.2 equiv) and 25 mL THF. A solution of NaH (0.2488 g, 6.2 mmol, 1.5 equiv., 60% dispersion in mineral oil) in 25 mL THF was added dropwise at room temperature. Then the reaction was stirred reflux for 18 h until the starting material disappeared (monitored by TLC with PE/EA (100/1)). The reaction was quenched by 20 mL saturated NH₄Cl and extracted with EA (20 mL x 3). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using PE/EA (100/1) to give 1.3885 g (3.59 mmol, 89% yield) of the title compound as a yellow oil; IR (cm⁻¹): 2948, 2873, 1622, 1455, 1358, 1119. ¹H NMR (CDCl₃, 400 MHz): δ 7.51-7.45 (m, 2H), 7.34-7.25 (m, 4H), 7.22-7.16 (m, 1H), 7.16-7.12 (m, 2H), 5.36 (s, 1H), 5.02 (s, 1H), 4.54 (d, J = 12.2 Hz, 1H), 4.42 (d, J = 12.2 Hz, 1H), 3.72-7.65 (m, 1H), 2.17-2.03 (m, 2H), 2.03-1.92 (m, 2H), 1.76-1.66 (m, 1H), 1.66-1.61 (m, 1H), 1.43-1.36 (m, 1H), 1.30-1.18 (m, 3H), 1.08 (dd, J = 13.0, 3.4 Hz, 1H), 0.89 (s, 3H), 0.84 (s, 3H), 0.82 (s, 3H); ¹³C

NMR: (CDCl_3 , 100 MHz): δ 148.1, 142.6, 139.9, 138.9, 128.4, 127.1, 125.9, 125.7, 109.1, 84.3, 71.3, 49.3, 47.8, 45.0, 36.1, 28.2, 27.9, 26.8, 26.3, 19.8, 18.9, 15.8, 14.0; HRMS (EI) calculated for $[\text{C}_{28}\text{H}_{34}\text{O}]^+$ requires m/z 386.2610, found m/z 386.2608.

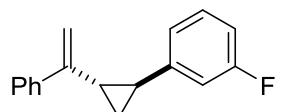




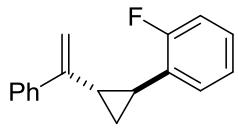
trans-1-chloro-4-(2-(1-phenylvinyl)cyclopropyl)benzene (1ad), using 8.71g (33.9 mmol) of **S2ad** to give 6.90g (27.1 mmol, 80% yield) of **1ad**; white solid; mp: 44.0-44.9 °C (crystallized from ethanol); IR (cm⁻¹): 3027, 1623, 1494, 1092. ¹H NMR (CDCl₃, 400 MHz): δ 7.51-7.46 (m, 2H), 7.36-7.23 (m, 5H), 7.10-7.04 (m, 2H), 5.37 (s, 1H), 5.03 (s, 1H), 1.99-1.88 (m, 2H), 1.45-1.38 (m, 1H), 1.28-1.21 (m, 1H); ¹³C NMR: (CDCl₃, 100 MHz): δ 147.9, 141.1, 140.8, 131.3, 128.5, 128.3, 127.7, 127.0, 126.0, 109.6, 28.1, 25.8, 15.9; HRMS (EI) calculated for [C₁₇H₁₅Cl]⁺ requires m/z 254.0862, found m/z 254.0859.



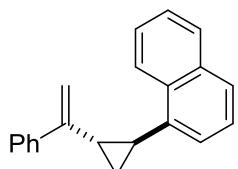
trans-1-fluoro-4-(2-(1-phenylvinyl)cyclopropyl)benzene (1ae), using 12.75g (53.1 mmol) of **S2ae** to give 9.95g (41.7 mmol, 78% yield) of **1ae**; colorless oil; IR (cm⁻¹): 3055, 1623, 1511, 1228, 1159. ¹H NMR (CDCl₃, 400 MHz): δ 7.52-7.47 (m, 2H), 7.33-7.22 (m, 3H), 7.12-7.05 (m, 2H), 7.01-7.94 (m, 2H), 5.36 (s, 1H), 5.02 (s, 1H), 2.01-1.93 (m, 1H), 1.93-1.85 (m, 1H), 1.41-1.34 (m, 1H), 1.25-1.17 (m, 1H); ¹³C NMR: (CDCl₃, 100 MHz): δ 161.2 (d, J = 243.2 Hz), 148.0, 140.9, 138.0 (d, J = 2.8 Hz), 128.2, 127.6, 127.1 (d, J = 7.4 Hz), 126.0, 115.2 (d, J = 21.2 Hz), 109.4, 27.7, 25.6, 15.7; ¹⁹F NMR (CDCl₃, 376 MHz): δ -117.2; HRMS (ESI) calculated for [C₁₇H₁₆F]⁺ [M + H⁺] requires m/z 239.1236, found m/z 239.1232.



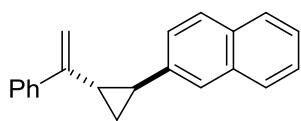
trans-1-fluoro-3-(2-(1-phenylvinyl)cyclopropyl)benzene (1af), using 3.07g (12.8 mmol) of **S2af** to give 2.18g (9.15 mmol, 71% yield) of **1af**; colorless oil; IR (cm⁻¹): 3081, 1616, 1586, 1492, 1251, 1144. ¹H NMR (CDCl₃, 400 MHz): δ 7.52-7.46 (m, 2H), 7.34-7.20 (m, 4H), 6.93 (d, J = 7.8 Hz, 1H), 6.91-6.84 (m, 1H), 6.84-6.78 (m, 1H), 5.37 (s, 1H), 5.03 (s, 1H), 2.01-1.91 (m, 2H), 1.46-1.39 (m, 1H), 1.29-1.22 (m, 1H); ¹³C NMR: (CDCl₃, 100 MHz): δ 163.1 (d, J = 245.2 Hz), 147.8, 145.4 (d, J = 7.4 Hz), 140.7, 129.8 (d, J = 8.8 Hz), 128.3, 127.6, 126.0, 121.5 (d, J = 3.0 Hz), 112.6 (d, J = 18.2 Hz), 112.3 (d, J = 19.0 Hz), 109.6, 28.2, 26.0 (d, J = 1.6 Hz), 16.0; ¹⁹F NMR (CDCl₃, 376 MHz): δ -113.2; HRMS (ESI) calculated for [C₁₇H₁₆F]⁺ [M + H⁺] requires m/z 239.1236, found m/z 239.1232.



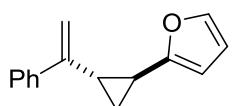
***trans*-1-fluoro-2-(2-(1-phenylvinyl)cyclopropyl)benzene (1ag)**, using 7.63g (31.7 mmol) of **S2ag** to give 4.56g (19.2 mmol, 60% yield) of **1ag**; colorless oil; IR (cm^{-1}): 3083, 1623, 1495, 1239, 1100. ^1H NMR (CDCl_3 , 400 MHz): δ 7.55-7.49 (m, 2H), 7.35-7.20 (m, 3H), 7.18-7.11 (m, 1H), 7.09-6.95 (m, 3H), 5.37 (s, 1H), 5.09 (s, 1H), 2.31-2.24 (m, 1H), 2.03-1.95 (m, 1H), 1.40-1.27 (m, 2H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 161.7 (d, $J = 245.2$ Hz), 148.0, 141.0, 129.3 (d, $J = 13.4$ Hz), 128.2, 127.5, 126.9 (d, $J = 8.2$ Hz), 126.1, 125.9 (d, $J = 3.6$ Hz), 124.0 (d, $J = 3.6$ Hz), 115.1 (d, $J = 21.8$ Hz), 109.9, 26.6, 19.1 (d, $J = 5.2$ Hz), 14.9; ^{19}F NMR (CDCl_3 , 376 MHz): δ -119.5; HRMS (ESI) calculated for $[\text{C}_{17}\text{H}_{16}\text{F}]^+ [\text{M} + \text{H}^+]$ requires m/z 239.1236, found m/z 239.1232.



***trans*-1-(2-(1-phenylvinyl)cyclopropyl)naphthalene (1ah)**, using 8.61g (31.6 mmol) of **S2ah** to give 5.79g (21.4 mmol, 68% yield) of **1ah**; white solid; mp: 36.8-39.1 °C (crystallized from ethanol); IR (cm^{-1}): 3049, 1621, 1494, 1388, 1256. ^1H NMR (CDCl_3 , 400 MHz): δ 8.29-8.22 (m, 1H), 7.85-7.79 (m, 1H), 7.69 (d, $J = 8.2$ Hz, 1H), 7.57-7.52 (m, 2H), 7.48-7.42 (m, 2H), 7.37 (dd, $J = 7.2, 8.0$ Hz, 1H), 7.31-7.21 (m, 4H), 5.38 (s, 1H), 5.16 (s, 1H), 2.62-2.56 (m, 1H), 2.08-2.01 (m, 1H), 1.41-1.34 (m, 2H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 149.1, 141.5, 138.1, 133.6, 133.2, 128.5, 128.2, 127.6, 126.8, 126.3, 125.9, 125.7, 125.5, 124.4, 123.2, 109.4, 25.3, 23.1, 15.4; HRMS (EI) calculated for $[\text{C}_{21}\text{H}_{18}]^+$ requires m/z 270.1409, found m/z 270.1407.

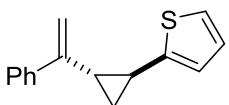


***trans*-2-(2-(1-phenylvinyl)cyclopropyl)naphthalene (1ai)**, using 8.20g (30.1 mmol) of **S2ai** to give 7.20g (26.6 mmol, 88% yield) of **1ai**; white solid; mp: 73.1-74.4 °C (crystallized from ethanol); IR (cm^{-1}): 3054, 1626, 1509, 1263. ^1H NMR (CDCl_3 , 400 MHz): δ 7.83-7.74 (m, 3H), 7.60 (s, 1H), 7.55-7.50 (m, 2H), 7.48-7.38 (m, 2H), 7.32-7.21 (m, 4H), 5.40 (s, 1H), 5.08 (s, 1H), 2.19-2.11 (m, 1H), 2.11-2.03 (m, 1H), 1.53-1.45 (m, 1H), 1.43-1.36 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 148.2, 141.0, 140.1, 133.6, 132.0, 128.3, 128.1, 127.62, 127.58, 127.3, 126.09, 126.06, 125.1, 124.5, 123.8, 109.4, 28.1, 26.8, 15.8; HRMS (EI) calculated for $[\text{C}_{21}\text{H}_{18}]^+$ requires m/z 270.1409, found m/z 270.1411.

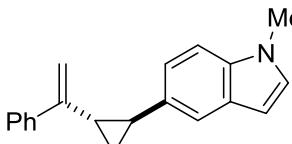


***trans*-2-(2-(1-phenylvinyl)cyclopropyl)furan (1aj)**, using 13.31g (62.7

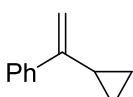
mmol) of **S2aj** to give 11.29g (53.7 mmol, 86% yield) of **1aj**; yellow oil; IR (cm^{-1}): 2925, 1598, 1498, 1446, 1075. ^1H NMR (CDCl_3 , 400 MHz): δ 7.60-7.53 (m, 2H), 7.36-7.24 (m, 4H), 6.30 (dd, J = 3.2, 1.8 Hz, 1H), 6.05 (d, J = 3.0 Hz, 1H), 5.36 (s, 1H), 5.01 (s, 1H), 2.10-1.98 (m, 2H), 1.36-1.25 (m, 2H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 155.8, 147.4, 140.7, 140.6, 128.2, 127.6, 126.0, 110.3, 109.7, 103.9, 25.1, 19.2, 13.4; HRMS (EI) calculated for $[\text{C}_{15}\text{H}_{14}\text{O}]^+$ requires m/z 210.1045, found m/z 210.1044.



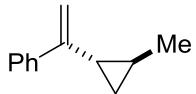
trans-2-(2-(1-phenylvinyl)cyclopropyl)thiophene (1ak), using 8.63g (37.8 mmol) of **S2ak** to give 7.87g (34.8 mmol, 92% yield) of **1ak**; yellow oil; IR (cm^{-1}): 3078, 1623, 1494, 1443, 1259. ^1H NMR (CDCl_3 , 400 MHz): δ 7.59-7.53 (m, 2H), 7.36-7.24 (m, 3H), 7.07 (dd, J = 5.2, 1.0 Hz, 1H), 6.92 (dd, J = 5.2, 3.4 Hz, 1H), 6.84 (d, J = 3.4 Hz, 1H), 5.37 (s, 1H), 5.01 (s, 1H), 2.22-2.14 (m, 1H), 2.03-1.96 (m, 1H), 1.46-1.40 (m, 1H), 1.31-1.24 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 147.6, 146.9, 140.7, 128.2, 127.6, 126.9, 126.0, 122.7, 122.2, 109.6, 28.5, 21.7, 16.7; HRMS (EI) calculated for $[\text{C}_{15}\text{H}_{14}\text{S}]^+$ requires m/z 226.0816, found m/z 226.0820.



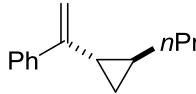
trans-1-methyl-5-(2-(1-phenylvinyl)cyclopropyl)-1H-indole (1al), using 9.63g (35.0 mmol) of **S2al** to give 5.59g (20.4 mmol, 58% yield) of **1al**; yellow oil; IR (cm^{-1}): 2954, 1592, 1511, 1247. ^1H NMR (CDCl_3 , 400 MHz): δ 7.58-7.51 (m, 2H), 7.41 (d, J = 1.6 Hz, 1H), 7.33-7.19 (m, 4H), 7.04 (dd, J = 8.6, 1.8 Hz, 1H), 7.01 (d, J = 3.0 Hz, 1H), 6.41 (dd, J = 3.0, 0.4 Hz, 1H), 5.35 (s, 1H), 5.04 (s, 1H), 3.75 (s, 3H), 2.14-2.6 (m, 1H), 2.00-1.93 (m, 1H), 1.43-1.36 (m, 1H), 1.33-1.25 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 148.8, 141.3, 135.5, 133.2, 129.1, 128.7, 128.2, 127.4, 126.1, 120.3, 117.4, 109.1, 108.8, 100.5, 32.8, 27.6, 26.9, 15.5; HRMS (EI) calculated for $[\text{C}_{20}\text{H}_{19}\text{N}]^+$ requires m/z 273.1517, found m/z 273.1516.



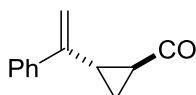
(1-Cyclopropylvinyl)benzene (1am),^{4f} using 4.83g (33.0 mmol) of **S2am** to give 4.14g (28.7 mmol, 87% yield) of **1am**; colorless oil. ^1H NMR (CDCl_3 , 400 MHz): δ 7.62-7.56 (m, 2H), 7.36-7.30 (m, 2H), 7.30-7.24 (m, 1H), 5.27 (d, J = 0.8 Hz, 1H), 4.93 (t, J = 1.0 Hz, 1H), 1.69-1.60 (m, 1H), 0.86-0.80 (m, 2H), 0.62-0.56 (m, 2H).



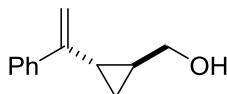
trans-(1-(2-methylcyclopropyl)vinyl)benzene (1an), using 8.83g (55.1 mmol) of **S2an** to give 6.42g (40.6 mmol, 74% yield) of **1an**; colorless oil. IR (cm^{-1}): 2955, 2925, 1622, 1459, 1400. ^1H NMR (CDCl_3 , 400 MHz): δ 7.57-7.52 (m, 2H), 7.36-7.30 (m, 2H), 7.29-7.22 (m, 1H), 5.23 (s, 1H), 4.87 (s, 1H), 1.36-1.28 (m, 1H), 1.21 (d, $J = 5.6$ Hz, 3H), 0.94-0.80 (m, 2H), 0.60-0.53 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 149.4, 141.8, 128.1, 127.3, 126.0, 108.4, 24.4, 19.0, 16.0, 14.4; HRMS (EI) calculated for $[\text{C}_{12}\text{H}_{14}]^+$ requires m/z 158.1096, found m/z 158.1094.



trans-(1-(2-propylcyclopropyl)vinyl)benzene (1ao), using 3.35g (17.8 mmol) of **S2ao** to give 1.78g (9.54 mmol, 54% yield) of **1ao**; colorless oil. IR (cm^{-1}): 2998, 2958, 1623, 1494, 1449, 1235. ^1H NMR (CDCl_3 , 400 MHz): δ 7.56-7.52 (m, 2H), 7.36-7.31 (m, 2H), 7.31-7.23 (m, 1H), 5.21 (d, $J = 1.0$ Hz, 1H), 4.87 (t, $J = 1.0$ Hz, 1H), 1.57-1.41 (m, 3H), 1.41-1.34 (m, 1H), 1.31-1.20 (m, 1H), 0.97-0.89 (m, 4H), 0.81-0.75 (m, 1H), 0.64-0.57 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 149.6, 141.9, 128.1, 127.3, 126.1, 108.6, 36.4, 23.2, 22.5, 21.3, 14.0, 13.8; HRMS (EI) calculated for $[\text{C}_{14}\text{H}_{18}]^+$ requires m/z 186.1409, found m/z 186.1406.



trans-tert-Butyl-2-(1-phenylvinyl)cyclopropanecarboxylate (1ap-S1), using 15.89g (65.0 mmol) to give 10.51g (43.0 mmol, 66% yield) of **1ap-S1**; colorless oil. IR (cm^{-1}): 2977, 2868, 1720, 1626, 1399, 1367, 1343, 1152. ^1H NMR (CDCl_3 , 400 MHz): δ 7.55-7.49 (m, 2H), 7.38-7.26 (m, 3H), 5.37 (s, 1H), 5.00 (s, 1H), 2.28-2.17 (m, 1H), 1.72-1.64 (m, 1H), 1.48 (s, 9H), 1.45-1.37 (m, 1H), 1.18-1.10 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 172.7, 146.3, 140.3, 128.3, 127.7, 126.0, 110.7, 80.5, 28.2, 25.8, 23.4, 14.8; HRMS (EI) calculated for $[\text{C}_{16}\text{H}_{20}\text{O}_2]^+$ requires m/z 244.1463, found m/z 244.1466.

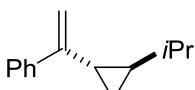


trans-(2-(1-phenylvinyl)cyclopropyl)methanol (1ap-S2), a 100 mL of three-necked flame-dried round-bottom flask was cooled at 0 °C under the atmosphere of nitrogen, charged with LiAlH₄ (1.04 g, 27.4 mmol, 1.0 equiv.) and 50 mL ether. A solution of **1ap-S1** (5.9822 g, 24.5 mmol, 1.0 equiv.) in 20 mL ether was added dropwise at 0 °C.

Then the reaction was stirred at room temperature for 12 h until the starting material disappeared (monitored by TLC with PE/EA (10/1)). The reaction was quenched by 20 mL saturated NH₄Cl and extracted with EA (30 mL x 3). The combined organic layers were washed with brine (30 mL), dried over Na₂SO₄, filtered, and concentrated under reduced pressure to give 3.6665 g (21.0 mmol, 86% yield) of the title compound as colorless oil. IR (cm⁻¹): 3333, 2915, 1623, 1493, 1443, 1239. ¹H NMR (CDCl₃, 400 MHz): δ 7.58-7.53 (m, 2H), 7.36-7.30 (m, 2H), 7.30-7.23 (m, 1H), 5.28 (s, 1H), 4.94 (s, 1H), 3.67-3.57 (m, 2H), 1.75 (br, 1H), 1.62-1.55 (m, 1H), 1.36-1.26 (m, 1H), 0.91-0.84 (m, 1H), 0.81-0.74 (m, 1H); ¹³C NMR: (CDCl₃, 100 MHz): δ 148.0, 141.4, 128.2, 127.5, 126.0, 109.7, 66.5, 23.1, 21.5, 11.4; HRMS (EI) calculated for [C₁₂H₁₄O]⁺ requires m/z 174.1045, found m/z 174.1046.

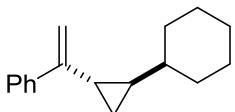


trans-tert-butyldimethyl((2-(1-phenylvinyl)cyclopropyl)methoxy)silane (1ap), prepared according to a previously reported procedure,^{4b} to a solution of **1ap-S2** (1.73 g, 9.9 mmol, 1.0 equiv.), DMAP (0.0192 g, 0.16 mmol, 0.016 equiv.), and Et₃N (1.7 mL, 1.2 equiv.) in 10 mL DCM was added *tert*-butylchlorodimethylsilane (1.6872 g, 11.2 mmol, 1.12 equiv.). The reaction mixture was stirred at room temperature for 23 h. The reaction mixture was diluted with DCM (50 mL) and washed with water (30 mL) and brine (30 mL). The organic layer were dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using PE/EA (50/1) to give 2.6711 g (9.26 mmol, 93% yield) of the title compound as a colorless oil; IR (cm⁻¹): 2955, 2888, 1624, 1495, 1255. ¹H NMR (CDCl₃, 400 MHz): δ 7.76-7.71 (m, 2H), 7.42-7.36 (m, 2H), 7.36-7.31 (m, 1H), 5.35 (s, 1H), 4.99 (s, 1H), 3.89 (dd, J = 10.8, 5.4 Hz, 1H), 3.59 (dd, J = 10.8, 7.2 Hz, 1H), 1.68-1.60 (m, 1H), 1.31-1.22 (m, 1H), 0.99 (s, 9H), 0.98-0.93 (m, 1H), 0.82-0.75 (m, 1H), 0.15 (s, 6H); ¹³C NMR: (CDCl₃, 100 MHz): δ 148.5, 141.6, 128.1, 127.4, 126.2, 109.2, 66.4, 26.0, 24.0, 21.5, 18.4, 9.9, -5.23, -5.25; HRMS (EI) calculated for [C₁₈H₂₈OSi]⁺ requires m/z 288.1909, found m/z 288.1912.

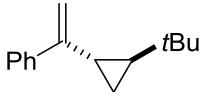


trans-(1-(2-isopropylcyclopropyl)vinyl)benzene (1aq), using 4.76g (25.3 mmol) of **S2aq** to give 3.60g (19.3 mmol, 76% yield) of **1aq**; colorless oil. IR (cm⁻¹): 2957, 2870, 1668, 1532, 1494, 1282. ¹H NMR (CDCl₃, 400 MHz): δ 7.56-7.51 (m, 2H),

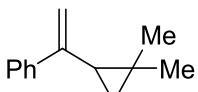
7.35-7.29 (m, 2H), 7.29-7.23 (m, 1H), 5.18 (d, $J = 1.0$ Hz, 1H), 4.88 (t, $J = 1.2$ Hz, 1H), 1.48-1.41 (m, 1H), 1.19-1.09 (m, 1H), 1.04 (d, $J = 6.4$ Hz, 3H), 0.99 (d, $J = 6.4$ Hz, 3H), 0.87-0.77 (m, 1H), 0.73-0.63 (m, 2H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 149.8, 142.1, 128.1, 127.3, 126.2, 108.8, 32.9, 29.2, 22.3, 21.7, 13.3; HRMS (EI) calculated for $[\text{C}_{14}\text{H}_{18}]^+$ requires m/z 186.1409, found m/z 186.1407.



trans-(1-(2-cyclohexylcyclopropyl)vinyl)benzene (1ar), using 4.11g (18.0 mmol) of **S2ar** to give 3.10g (13.7 mmol, 76% yield) of **1ar**; colorless oil. IR (cm^{-1}): 2922, 2850, 1670, 1622, 1541, 1447, 1029. ^1H NMR (CDCl_3 , 400 MHz): δ 7.56-7.50 (m, 2H), 7.36-7.29 (m, 2H), 7.29-7.22 (m, 1H), 5.17 (s, 1H), 4.87 (s, 1H), 1.90-1.58 (m, 5H), 1.48-1.41 (m, 1H), 1.27-1.01 (m, 5H), 0.87-0.72 (m, 2H), 0.71-0.62 (m, 2H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 150.0, 142.2, 128.0, 127.3, 126.3, 108.8, 42.6, 33.2, 32.5, 27.9, 26.6, 26.3, 21.9, 13.0; HRMS (EI) calculated for $[\text{C}_{17}\text{H}_{22}]^+$ requires m/z 226.1722, found m/z 226.1725.



trans-(1-(2-(tert-Butyl)cyclopropyl)vinyl)benzene (1as), using 1.30g (6.43 mmol) of **S2as** to give 1.09g (5.44 mmol, 85% yield) of **1as**; colorless oil. IR (cm^{-1}): 2957, 2867, 1670, 1622, 1470, 1396, 1364, 1267. ^1H NMR (CDCl_3 , 400 MHz): δ 7.56-7.51 (m, 2H), 7.35-7.29 (m, 2H), 7.29-7.22 (m, 1H), 5.19 (s, 1H), 4.90 (s, 1H), 1.60-1.52 (m, 1H), 0.98-0.93 (m, 1H), 0.90 (s, 9H), 0.79-0.72 (m, 1H), 0.62-0.55 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 150.1, 142.2, 128.1, 127.3, 126.3, 108.9, 32.8, 29.8, 28.5, 19.1, 10.3; HRMS (EI) calculated for $[\text{C}_{15}\text{H}_{20}]^+$ requires m/z 200.1565, found m/z 200.1563.

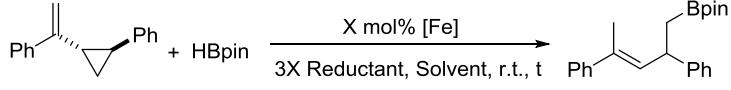


(1-(2,2-Dimethylcyclopropyl)vinyl)benzene (1at), using 2.91g (16.7 mmol) of **S2at** to give 2.45g (14.2 mmol, 85% yield) of **1at**; colorless oil. IR (cm^{-1}): 2942, 2867, 1622, 1493, 1448, 1381, 1253. ^1H NMR (CDCl_3 , 400 MHz): δ 7.52-7.46 (m, 2H), 7.37-7.30 (m, 2H), 7.29-7.22 (m, 1H), 5.49 (s, 1H), 4.90 (s, 1H), 1.52 (t, $J = 6.8$ Hz, 1H), 1.29 (s, 3H), 0.92 (s, 3H), 0.72-0.63 (m, 2H); ^{13}C NMR: (CDCl_3 , 100 MHz): δ 146.3, 141.7, 128.2, 127.3, 125.9, 111.1, 30.4, 26.9, 19.1, 18.9, 17.5; HRMS (EI) calculated for $[\text{C}_{13}\text{H}_{16}]^+$ requires m/z 172.1252, found m/z 172.1256.

IV. Optimization for Hydroboration of Vinylcyclopropanes

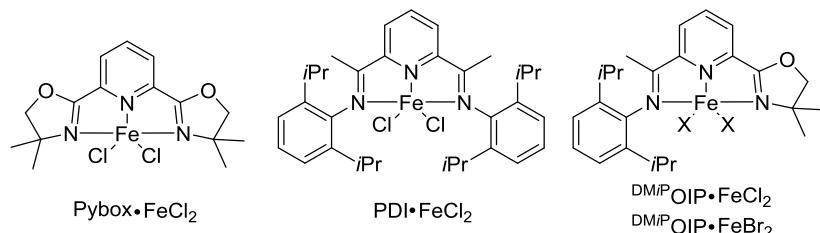
A variety of precatalysts, solvents and reductants, the ratio of **1**/HBpin, the loading of precatalysts, and time of reaction have been investigated for the Hydroboration of Vinylcyclopropanes.

Table S1. Optimization for Hydroboration of Vinylcyclopropanes.^[a]

| Entry | Reductant | Solvent (mL) | [Fe] (mol%) | X mol% [Fe] 3X Reductant, Solvent, r.t., t |  | | |
|-------------------|------------------------------------|-------------------------|---|---|--|--------------------------|--------------------|
| | | | | | t | Yield (%) ^[a] | E/Z ^[a] |
| 1 | NaBH ₃ Et | Toluene (1) | Pybox FeCl ₂ (5) | 3 | < 2 | - | - |
| 2 | NaBH ₃ Et | Toluene (1) | PDI FeCl ₂ (5) | 3 | < 2 | - | - |
| 3 | NaBH ₃ Et | Toluene (1) | ^{DMiP} OIP FeCl ₂ (5) | 3 | 90 | 12/1 | |
| 4 | NaBH ₃ Et | Toluene (1) | ^{DMiP} OIP FeBr ₂ (5) | 3 | 93 | 15/1 | |
| 5 ^[b] | NaBH ₃ Et | Toluene (1) | ^{DMiP} OIP FeBr ₂ (5) | 3 | 54 | 12/1 | |
| 6 ^[c] | NaBH ₃ Et | Toluene (1) | ^{DMiP} OIP FeBr ₂ (5) | 3 | 56 | 13/1 | |
| 7 ^[d] | NaBH ₃ Et | Toluene (1) | ^{DMiP} OIP FeBr ₂ (5) | 3 | 49 | 10/1 | |
| 8 ^[e] | NaBH ₃ Et | Toluene (1) | ^{DMiP} OIP FeBr ₂ (5) | 3 | 69 | 11/1 | |
| 9 | NaBH ₃ sBu ₃ | Toluene (1) | ^{DMiP} OIP FeBr ₂ (5) | 3 | 82 | 11/1 | |
| 10 | LiBH ₃ Et | Toluene (1) | ^{DMiP} OIP FeBr ₂ (5) | 3 | 21 | - | - |
| 11 | ZnEt ₂ | Toluene (1) | ^{DMiP} OIP FeBr ₂ (5) | 3 | 0 | - | - |
| 12 | AlMe ₃ | Toluene (1) | ^{DMiP} OIP FeBr ₂ (5) | 3 | 0 | - | - |
| 14 | MeMgBr | Toluene (1) | ^{DMiP} OIP FeBr ₂ (5) | 3 | 0 | - | - |
| 15 | tBuOLi | Toluene (1) | ^{DMiP} OIP FeBr ₂ (5) | 3 | 0 | - | - |
| 16 | tBuONa | Toluene (1) | ^{DMiP} OIP FeBr ₂ (5) | 3 | <2 | - | - |
| 17 | tBuOK | Toluene (1) | ^{DMiP} OIP FeBr ₂ (5) | 3 | 0 | - | - |
| 18 | NaOH | Toluene (1) | ^{DMiP} OIP FeBr ₂ (5) | 3 | 0 | - | - |
| 14 | NaBH ₃ Et | Toluene (1) | ^{DMiP} OIP FeBr ₂ (2.5) | 3 | 85 | 12/1 | |
| 14 ^[f] | NaBH ₃ Et | Toluene (1) | ^{DMiP} OIP FeBr ₂ (1.0) | 3 | 24 | - | - |
| 15 | NaBH ₃ Et | Toluene (0.5) | ^{DMiP} OIP FeBr ₂ (2.5) | 3 | 79 | 11/1 | |
| 16 | NaBH ₃ Et | Et ₂ O (0.5) | ^{DMiP} OIP FeBr ₂ (2.5) | 3 | 77 | 11/1 | |

| | | | | | | |
|-----------|---------------------------|--------------------|---|------------|---------------|-------------|
| 17 | NaBHEt ₃ | THF (0.5) | ^{DM<i>iP</i>} OIP FeBr ₂ (2.5) | 3 | 57 | 8/1 |
| 18 | NaBHEt ₃ | neat | ^{DM<i>iP</i>} OIP FeBr ₂ (2.5) | 3 | 53 | 10/1 |
| 19 | NaBHEt ₃ | dioxane (0.5) | ^{DM<i>iP</i>} OIP FeBr ₂ (2.5) | 3 | 82 | 11/1 |
| 20 | NaBHEt ₃ | DCM (0.5) | ^{DM<i>iP</i>} OIP FeBr ₂ (2.5) | 3 | 0 | - |
| 21 | NaBHEt ₃ | Toluene (1) | ^{DM<i>iP</i>} OIP FeBr ₂ (5) | 0.17 | 85(79) | 13/1 |
| 22 | NaBHEt ₃ | Toluene (1) | ^{DM<i>iP</i>} OIP FeBr ₂ (5) | 0.33 | 80(75) | 12/1 |
| 23 | NaBHEt₃ | Toluene (1) | ^{DM<i>iP</i>}OIP FeBr₂ (5) | 0.5 | 97(87) | 12/1 |
| 24 | NaBHEt ₃ | Toluene (1) | ^{DM<i>iP</i>} OIP FeBr ₂ (5) | 1.0 | 93(86) | 13/1 |
| 25 | NaBHEt ₃ | Toluene (1) | ^{DM<i>iP</i>} OIP FeBr ₂ (5) | 2.0 | 90(86) | 10/1 |
| 26 | NaBHEt ₃ | Toluene (1) | FeBr ₂ (5) | 3.0 | 0 | - |
| 27 | - | Toluene (1) | ^{DM<i>iP</i>} OIP FeBr ₂ (5) | 3.0 | 0 | - |
| 28 | NaBHEt ₃ | Toluene (1) | - | 3.0 | 0 | - |

[a] Using HBpin (0.5 mmol), **1a** (1.0 mmol), [Fe] (5 mol%), NaBHEt₃(15 mol%), and toluene (1 mL). Yields and ratio of *E/Z* were determined by ¹H NMR analysis, and isolated yield in the parenthesis. [b] **1**/HBpin = 1/2. [c] **1**/HBpin = 1/1. [d] **1**/HBpin = 1.2/1. [e] **1**/HBpin = 1.5/1. [f] 6 mol% NaBHEt₃.



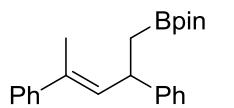
V. Iron-Catalyzed Hydroboration of Vinylcyclopropanes

General Procedure A for Hydroboration of Vinylcyclopropanes: to a 25 mL flame-dried Schlenk flask cooled under nitrogen, ^{DM*iP*}OIP FeBr₂ complex (0.025 mmol, 5 mol%) and vinylcyclopropane (1.0 mmol, 2.0 equiv.) were added. The mixture was vacuumed and flushed with nitrogen for three times, and then, 1.0 mL of toluene (0.5 M) and HBpin (75 µL, 97%, 0.5 mmol, 1.0 equiv.) were added in sequence. The mixture was injected with NaBHEt₃ (1.0 M in THF, 75 µL, 0.075 mmol) by dropwise. The reaction was run at ambient temperature for 0.5 h. Then the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored

by ^1H NMR analysis. The resulting mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give the corresponding product.

General Procedure B for Hydroboration of Vinylcyclopropanes: to a 25 mL flame-dried Schlenk flask cooled under nitrogen, $^{\text{DMiP}}$ OIP FeBr₂ complex (0.05 mmol, 10 mol%) and vinylcyclopropane (1.0 mmol, 2.0 equiv.) were added. The mixture was vacuumed and flushed with nitrogen for three times, and then, 1.0 mL of toluene (0.5 M) and HBpin (75 μL , 97%, 0.5 mmol, 1.0 equiv.) were added in sequence. The mixture was injected with NaBHEt₃ (1.0 M in THF, 75 μL , 0.075 mmol) by dropwise. The reaction was run at ambient temperature for 3 h. Then the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The resulting mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give the corresponding product.

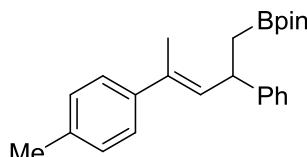
General Procedure C for Hydroboration of Vinylcyclopropanes: to a 25 mL flame-dried Schlenk flask cooled under nitrogen, $^{\text{DMiP}}$ OIP FeBr₂ complex (0.05 mmol, 10 mol%) and vinylcyclopropane (1.0 mmol, 2.0 equiv.) were added. The mixture was vacuumed and flushed with nitrogen for three times, and then, 1.0 mL of toluene (0.5 M) and HBpin (75 μL , 97%, 0.5 mmol, 1.0 equiv.) were added in sequence. The mixture was injected with NaBHEt₃ (1.0 M in THF, 150 μL , 0.150 mmol) by dropwise. The reaction was run at ambient temperature for 10 h. Then the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The resulting mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give the corresponding product.



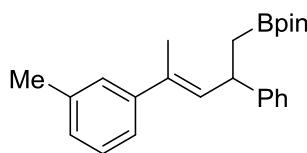
(*E*)-2-(2,4-diphenylpent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborola

ne (2a) Prepared according to the general procedure A, using 0.2198 g (1.0 mmol) of **1a**, 75 μL (97%, 0.5 mmol) of HBpin, 0.0149 g (0.025 mmol) of $^{\text{DMiP}}$ OIP FeBr₂, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by

ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.1510 g (0.435 mmol, 12/1 *E/Z*, 87% yield) of the title compound as a colorless oil. IR (cm^{-1}): 2978, 2927, 1600, 1493, 1448, 1366, 1144. ^1H NMR (CDCl_3 , 400 MHz): δ 7.40-7.33 (m, 2H), 7.33-7.23 (m, 6H), 7.22-7.11 (m, 2H), 5.89 (dd, J = 9.8, 0.8 Hz, 1H), 4.04-3.95 (m, 1H), 2.13 (s, 3H), 1.41-1.28 (m, 2H), 1.14 (s, 12H); ^{13}C NMR: (CDCl_3 , 100 MHz) : δ 146.8, 144.0, 133.8, 133.3, 128.3, 128.0, 127.1, 126.5, 125.84, 125.81, 83.1, 40.3, 24.8, 24.7, 16.3. HRMS (EI) calculated for $[\text{C}_{23}\text{H}_{29}\text{BO}_2]^+$ requires m/z 348.2261, found m/z 348.2260.

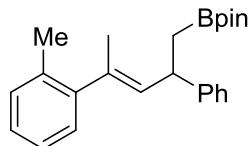


(*E*)-4,4,5,5-tetramethyl-2-(2-phenyl-4-(*p*-tolyl)pent-3-en-1-yl)-1,3,2-dioxaborolane (2b) Prepared according to the general procedure A, using 0.2339 g (1.0 mmol) of **1b**, 75 μL (97%, 0.5 mmol) of HBpin, 0.0149 g (0.025 mmol) of $^{\text{DMiP}}$ OIP FeBr_2 , 75 μL (1.0 M in THF, 0.075 mmol) of NaBH Et_3 , and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.1485 g (0.410 mmol, 11/1 *E/Z*, 82% yield) of the title compound as a colorless oil. IR (cm^{-1}): 3025, 2978, 1602, 1366, 1327, 1145. ^1H NMR (CDCl_3 , 400 MHz): δ 7.31-7.23 (m, 6H), 7.17-7.13 (m, 1H), 7.10-7.05 (m, 2H), 5.86 (dd, J = 9.8, 1.2 Hz, 1H), 4.04-3.94 (m, 1H), 2.31 (s, 3H), 2.10 (d, J = 1.2 Hz, 3H), 1.38-1.30 (m, 2H), 1.14 (s, 12H); ^{13}C NMR: (CDCl_3 , 100 MHz) : δ 146.9, 141.1, 136.1, 133.1, 133.0, 128.7, 128.3, 127.1, 125.74, 125.69, 83.1, 40.2, 24.8, 24.7, 21.0, 16.3. HRMS (EI) calculated for $[\text{C}_{24}\text{H}_{31}\text{BO}_2]^+$ requires m/z 362.2417, found m/z 362.2415.

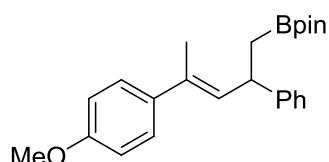


(*E*)-4,4,5,5-tetramethyl-2-(2-phenyl-4-(*m*-tolyl)pent-3-en-1-yl)-1,3,2-dioxaborolane (2c) Prepared according to the general procedure A, using 0.2368 g (1.0 mmol) of **1c**, 75 μL (97%, 0.5 mmol) of HBpin, 0.0152 g (0.026 mmol) of $^{\text{DMiP}}$ OIP FeBr_2 , 75 μL (1.0 M in THF, 0.075 mmol) of NaBH Et_3 , and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of

ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.1539 g (0.425 mmol, 15/1 *E/Z*, 85% yield) of the title compound as a colorless oil. IR (cm^{-1}): 3026, 2978, 1602, 1364, 1325, 1144. ^1H NMR (CDCl_3 , 400 MHz): δ 7.31-7.21 (m, 4H), 7.19-7.10 (m, 4H), 7.01-6.97 (m, 1H), 5.88 (dd, J = 9.8, 1.2 Hz, 1H), 4.04-3.65 (m, 1H), 2.31 (s, 3H), 2.11 (d, J = 1.6 Hz, 3H), 1.41-1.30 (m, 2H), 1.13 (s, 12H); ^{13}C NMR: (CDCl_3 , 100 MHz) : δ 146.7, 143.9, 137.4, 133.6, 133.3, 128.2, 127.9, 127.3, 127.0, 126.6, 125.7, 122.9, 83.0, 40.2, 24.7, 24.6, 21.4, 16.3. HRMS (EI) calculated for $[\text{C}_{24}\text{H}_{31}\text{BO}_2]^+$ requires m/z 362.2417, found m/z 362.2419.

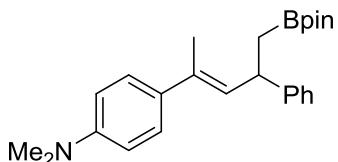


(*E*)-4,4,5,5-tetramethyl-2-(2-phenyl-4-(*o*-tolyl)pent-3-en-1-yl)-1,3,2-dioxaborolane (2d) Prepared according to the general procedure C, using 0.2344 g (1.0 mmol) of **1d**, 75 μL (97%, 0.5 mmol) of HBpin, 0.0303 g (0.051 mmol) of $^{\text{DMiP}}$ OIP FeBr_2 , 150 μL (1.0 M in THF, 0.150 mmol) of NaBHET_3 , and 1.0 mL (0.5 M) of toluene. After 10 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.0879 g (0.245 mmol, > 99/1 *E/Z*, 49% yield) of the title compound as a colorless oil. IR (cm^{-1}): 3023, 2978, 1600, 1367, 1325, 1144. ^1H NMR (CDCl_3 , 400 MHz): δ 7.34-7.23 (m, 4H), 7.19-7.14 (m, 1H), 7.14-7.08 (m, 3H), 7.06-7.00 (m, 1H), 5.46 (dd, J = 9.6, 1.2 Hz, 1H), 4.05-3.89 (m, 1H), 2.20 (s, 3H), 1.99 (d, J = 1.4 Hz, 3H), 1.32 (d, J = 7.6 Hz, 2H), 1.17 (s, 12H); ^{13}C NMR: (CDCl_3 , 100 MHz) : δ 147.0, 145.4, 135.3, 134.9, 134.4, 130.0, 128.2, 127.1, 126.4, 125.7, 125.4, 83.1, 39.9, 24.79, 24.77, 19.8, 18.3. HRMS (EI) calculated for $[\text{C}_{24}\text{H}_{31}\text{BO}_2]^+$ requires m/z 362.2417, found m/z 362.2418.

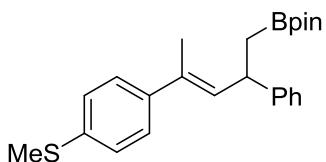


(*E*)-2-(4-(4-methoxyphenyl)-2-phenylpent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e) Prepared according to the

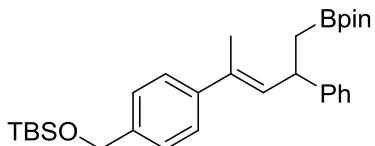
general procedure A, using 0.2499 g (1.0 mmol) of **1e**, 75 μ L (97%, 0.5 mmol) of HBpin, 0.0151 g (0.025 mmol) of ^{D_MiP}OIP FeBr₂, 75 μ L (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EA (100/1, 150 mL to 20/1, 250 mL) as the eluent to give 0.1657 g (0.440 mmol, 12/1 E/Z, 88% yield) of the title compound as a colorless oil. IR (cm^{-1}): 2978, 2930, 1729, 1607, 1511, 1365. ¹H NMR (CDCl₃, 400 MHz): δ 7.32-7.22 (m, 6H), 7.17-7.09 (m, 1H), 6.85-6.79 (m, 2H), 5.82 (dd, J = 9.8, 1.2 Hz, 1H), 4.02-3.94 (m, 1H), 3.78 (s, 3H), 2.10 (d, J = 1.2 Hz, 3H), 1.40-1.27 (m, 2H), 1.14 (s, 12H); ¹³C NMR: (CDCl₃, 100 MHz) : δ 158.4, 146.9, 136.5, 132.6, 132.3, 128.3, 127.1, 126.8, 125.7, 113.4, 83.1, 55.2, 40.2, 24.8, 24.7, 16.3. HRMS (EI) calculated for [C₂₄H₃₁BO₃]⁺ requires m/z 378.2366, found m/z 378.2369.



(E)-N,N-dimethyl-4-(4-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-en-2-yl)aniline (2f) Prepared according to the general procedure A, using 0.2634 g (1.0 mmol) of **1f**, 75 μ L (97%, 0.5 mmol) of HBpin, 0.0149 g (0.025 mmol) of ^{D_MiP}OIP FeBr₂, 75 μ L (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EA (100/1, 150 mL to 20/1, 250 mL) as the eluent to give 0.1490 g (0.380 mmol, 7/1 E/Z, 76% yield) of the title compound as a colorless oil. IR (cm^{-1}): 2977, 2926, 1610, 1521, 1361, 1326, 1143. ¹H NMR (CDCl₃, 400 MHz): δ 7.32-7.20 (m, 6H), 7.16-7.09 (m, 1H), 6.69-6.60 (m, 2H), 5.80 (dd, J = 9.8, 1.2 Hz, 1H), 4.05-3.93 (m, 1H), 2.89 (s, 6H), 2.09 (d, J = 1.2 Hz, 3H), 1.36-1.27 (m, 2H), 1.13 (s, 12H); ¹³C NMR: (CDCl₃, 100 MHz) : δ 149.4, 147.2, 132.7, 132.1, 130.7, 128.1, 127.0, 126.4, 125.6, 112.2, 82.9, 40.5, 40.1, 24.7, 24.6, 16.1. HRMS (EI) calculated for [C₂₅H₃₄BNO₂]⁺ requires m/z 391.2683, found m/z 391.2688.



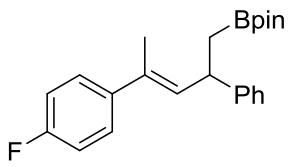
(E)-4,4,5,5-tetramethyl-2-(4-(methylthio)phenyl)-2-phenylpent-3-en-1-yl)-1,3,2-dioxaborolane (2g) Prepared according to the general procedure B, using 0.2690 g (1.0 mmol) of **1g**, 75 μ L (97%, 0.5 mmol) of HBpin, 0.0149 g (0.025 mmol) of ^{DMiP}OIP FeBr₂, 75 μ L (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of toluene. After 3 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EA (100/1, 150 mL to 20/1, 250 mL) as the eluent to give 0.1255 g (0.320 mmol, 16/1 E/Z, 64% yield) of the title compound as a colorless oil. IR (cm^{-1}): 3025, 2922, 1643, 1492, 1364, 1325, 1143. ¹H NMR (CDCl_3 , 400 MHz): δ 7.34-7.25 (m, 6H), 7.20-7.13 (m, 3H), 5.89 (dd, J = 9.8, 1.2 Hz, 1H), 4.05-3.93 (m, 1H), 2.44 (s, 3H), 2.10 (dd, J = 1.2 Hz, 3H), 1.40-1.30 (m, 2H), 1.13 (s, 12H); ¹³C NMR: (CDCl_3 , 100 MHz) : δ 146.6, 140.8, 136.3, 133.4, 132.5, 128.3, 127.0, 126.5, 126.2, 125.8, 83.0, 40.2, 24.7, 24.6, 16.1, 16.0. HRMS (EI) calculated for [C₂₄H₃₁BO₂S]⁺ requires m/z 394.2138, found m/z 394.2134.



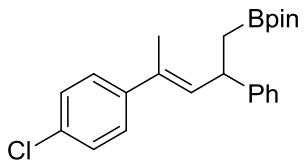
(E)-tert-butyldimethyl((4-(4-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-en-2-yl)benzyl)oxy)silane (2h)

(2h) Prepared according to the general procedure B, using 0.3665 g (1.0 mmol) of **1h**, 75 μ L (97%, 0.5 mmol) of HBpin, 0.0147 g (0.025 mmol) of ^{DMiP}OIP FeBr₂, 75 μ L (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of toluene. After 3 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EA (100/1, 150 mL to 20/1, 250 mL) as the eluent to give 0.2154 g (0.435 mmol, 12/1 E/Z, 87% yield) of the title compound as a colorless oil. IR (cm^{-1}): 3026, 2887, 1511, 1364, 1325, 1254, 1144. ¹H NMR (CDCl_3 , 400 MHz): δ 7.42-7.38 (m, 2H), 7.36-7.27 (m, 6H), 7.23-7.18 (m, 1H), 5.95 (dd, J = 9.8, 1.2 Hz, 1H), 4.77 (s, 2H), 4.10-4.01 (m, 1H), 2.18 (d, J = 1.2 Hz, 3H), 1.45-1.34 (m, 2H), 1.20 (s, 12H), 1.00 (s, 9H), 0.15 (s, 6H); ¹³C NMR: (CDCl_3 , 100 MHz) : δ 146.8, 142.6, 139.7, 133.4, 133.1, 128.3, 127.1, 125.90, 125.86, 125.7, 83.1, 64.8, 40.3, 25.9, 24.8, 24.7, 18.4, 16.3, -5.2. HRMS (EI) calculated for [C₃₀H₄₅BO₃Si]⁺ requires m/z 492.3231, found

m/z 492.3234.

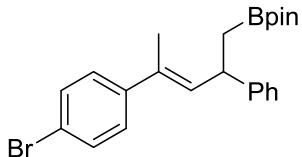


(E)-2-(4-(4-fluorophenyl)-2-phenylpent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2i) Prepared according to the general procedure A, using 0.2391 g (1.0 mmol) of **1i**, 75 μ L (97%, 0.5 mmol) of HBpin, 0.0151 g (0.026 mmol) of ^{D*M*P}OIP FeBr₂, 75 μ L (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.1655 g (0.450 mmol, 13/1 *E/Z*, 90% yield) of the title compound as a colorless oil. IR (cm⁻¹): 3027, 2929, 1601, 1508, 1365, 1226, 1143. ¹H NMR (CDCl₃, 400 MHz): δ 7.24-7.14 (m, 6H), 7.08-7.02 (m, 1H), 6.88-6.82 (m, 2H), 5.75 (dd, J = 9.8, 1.2 Hz, 1H), 3.94-3.84 (m, 1H), 2.01 (d, J = 1.2 Hz, 3H), 1.32-1.20 (m, 2H), 1.04 (s, 12H); ¹³C NMR (CDCl₃, 100 MHz) : δ 161.8 (d, J = 241.4 Hz), 146.6, 139.9 (d, J = 2.7 Hz), 133.7, 132.3, 128.3, 127.3 (d, J = 8.2 Hz), 127.0, 125.9, 114.8 (d, J = 20.9 Hz), 83.1, 40.3, 24.75, 24.67, 16.4; ¹⁹F NMR (CDCl₃, 376 MHz): δ -116.6. HRMS (EI) calculated for [C₂₃H₂₈BFO₂]⁺ requires m/z 366.2166, found m/z 366.2162.

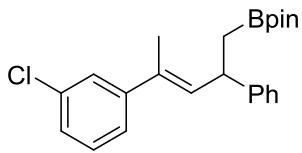


(E)-2-(4-(4-chlorophenyl)-2-phenylpent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2j) Prepared according to the general procedure A, using 0.2554 g (1.0 mmol) of **1j**, 75 μ L (97%, 0.5 mmol) of HBpin, 0.0150 g (0.026 mmol) of ^{D*M*P}OIP FeBr₂, 75 μ L (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.1776 g (0.465 mmol, 16/1 *E/Z*, 93% yield) of the title compound as a colorless oil. IR (cm⁻¹): 2978, 2928, 1599, 1490, 1364, 1325, 1143. ¹H NMR (CDCl₃, 400 MHz): δ 7.32-7.25 (m, 6H), 7.25-7.19 (m, 2H), 7.18-7.11 (m, 1H), 5.88 (dd, J = 9.8, 1.2 Hz, 1H), 4.04-3.93 (m, 1H), 2.10 (d, J = 1.2 Hz, 3H), 1.40-1.29 (m, 2H), 1.13

(s, 12H); ^{13}C NMR: (CDCl_3 , 100 MHz) : δ 146.4, 142.2, 134.3, 132.2, 132.1, 128.3, 128.1, 127.03, 126.99, 125.9, 83.1, 40.3, 24.7, 24.6, 16.1. HRMS (EI) calculated for $[\text{C}_{23}\text{H}_{28}\text{BClO}_2]^+$ requires m/z 382.1871, found m/z 382.1871.

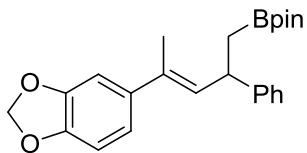


(*E*)-2-(4-(4-bromophenyl)-2-phenylpent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k) Prepared according to the general procedure C, using 0.2988 g (1.0 mmol) of **1k**, 75 μL (97%, 0.5 mmol) of HBpin, 0.0299 g (0.050 mmol) of $^{\text{DMiP}}$ OIP FeBr_2 , 150 μL (1.0 M in THF, 0.150 mmol) of NaBHEt_3 , and 1.0 mL (0.5 M) of toluene. After 10 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.1227 g (0.285 mmol, 11/1 *E/Z*, 57% yield) of the title compound as a colorless oil. IR (cm^{-1}): 3026, 2977, 1487, 1364, 1325, 1143. ^1H NMR (CDCl_3 , 400 MHz): δ 7.41-7.35 (m, 2H), 7.30-7.28 (m, 4H), 7.24-7.20 (m, 2H), 7.19-7.10 (m, 1H), 5.89 (dd, J = 9.8, 1.2 Hz, 1H), 4.04-3.90 (m, 1H), 2.10 (d, J = 1.2 Hz, 3H), 1.40-1.29 (m, 2H), 1.13 (s, 12H); ^{13}C NMR: (CDCl_3 , 100 MHz) : δ 146.4, 142.7, 134.4, 132.2, 131.1, 128.4, 127.4, 127.0, 125.9, 120.3, 83.1, 40.3, 24.74, 24.66, 16.1. HRMS (EI) calculated for $[\text{C}_{23}\text{H}_{28}\text{BBrO}_2]^+$ requires m/z 426.1366, found m/z 426.1372.

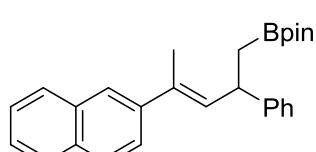


(*E*)-2-(4-(3-chlorophenyl)-2-phenylpent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2l) Prepared according to the general procedure A, using 0.2555 g (1.0 mmol) of **1l**, 75 μL (97%, 0.5 mmol) of HBpin, 0.0147 g (0.025 mmol) of $^{\text{DMiP}}$ OIP FeBr_2 , 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt_3 , and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.1536 g (0.405 mmol, > 99/1 *E/Z*, 81% yield) of the title compound as a colorless oil. IR (cm^{-1}): 3026, 2977, 1593, 1364, 1325, 1143. ^1H NMR (CDCl_3 , 400 MHz): δ 7.36-7.32 (m,

1H), 7.30-7.23 (m, 4H), 7.23-7.20 (m, 1H), 7.19-7.11 (m, 3H), 5.91 (dd, J = 9.8, 1.2 Hz, 1H), 4.05-3.91 (m, 1H), 2.10 (d, J = 1.2 Hz, 3H), 1.38-1.29 (m, 2H), 1.14 (s, 12H); ^{13}C NMR: (CDCl_3 , 100 MHz) : δ 146.3, 145.7, 134.9, 134.0, 132.1, 129.2, 128.3, 127.0, 126.5, 126.0, 125.9, 123.9, 83.1, 40.3, 24.7, 24.6, 16.1. HRMS (EI) calculated for $[\text{C}_{23}\text{H}_{28}\text{BClO}_2]^+$ requires m/z 382.1871, found m/z 382.1863.

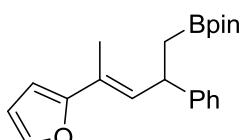


(E)-2-(4-(benzo[d][1,3]dioxol-5-yl)-2-phenylpent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2m) Prepared according to the general procedure C, using 0.2642 g (1.0 mmol) of **1m**, 75 μL (97%, 0.5 mmol) of HBpin, 0.0304 g (0.051 mmol) of $^{\text{DMiP}}$ OIP FeBr_2 , 150 μL (1.0 M in THF, 0.150 mmol) of NaBHET_3 , and 1.0 mL (0.5 M) of toluene. After 10 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EA (100/1, 150 mL to 20/1, 250 mL) as the eluent to give 0.1513 g (0.385 mmol, 11/1 *E/Z*, 77% yield) of the title compound as a colorless oil. IR (cm^{-1}): 3025, 2978, 1603, 1486, 1363, 1323, 1143. ^1H NMR (CDCl_3 , 400 MHz): δ 7.31-7.21 (m, 4H), 7.18-7.10 (m, 1H), 6.89-6.86 (m, 1H), 6.85-6.80 (m, 1H), 6.74-6.69 (m, 1H), 5.88 (s, 2H), 5.80 (dd, J = 9.8, 1.2 Hz, 1H), 4.05-3.90 (m, 1H), 2.08 (d, J = 1.2 Hz, 3H), 1.39-1.29 (m, 2H), 1.13 (s, 12H); ^{13}C NMR: (CDCl_3 , 100 MHz) : δ 147.4, 146.7, 146.2, 138.3, 132.83, 132.76, 128.3, 127.0, 125.7, 119.1, 107.7, 106.4, 100.8, 83.0, 40.2, 24.7, 24.6, 16.5. HRMS (EI) calculated for $[\text{C}_{24}\text{H}_{29}\text{BO}_4]^+$ requires m/z 392.2159, found m/z 392.2160.

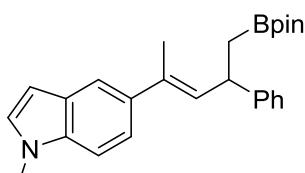


(E)-4,4,5,5-tetramethyl-2-(4-(naphthalen-2-yl)-2-phenylpent-3-en-1-yl)-1,3,2-dioxaborolane (2n) Prepared according to the general procedure A, using 0.2707 g (1.0 mmol) of **1n**, 75 μL (97%, 0.5 mmol) of HBpin, 0.0149 g (0.025 mmol) of $^{\text{DMiP}}$ OIP FeBr_2 , 75 μL (1.0 M in THF, 0.075 mmol) of NaBHET_3 , and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EA (100/1, 150 mL to

20/1, 250 mL) as the eluent to give 0.1752 g (0.440 mmol, 23/1 *E/Z*, 88% yield) of the title compound as a white solid. mp: 69.4-71.2 °C (by flash column chromatography using PE/EA). IR (cm⁻¹): 3025, 2979, 1598, 1365, 1326, 1144. ¹H NMR (CDCl₃, 400 MHz): δ 7.80-7.71 (m, 4H), 7.56 (dd, J = 8.8, 1.8 Hz, 1H), 7.45-7.36 (m, 2H), 7.36-7.31 (m, 2H), 7.31-7.25 (m, 2H), 7.19-7.13 (m, 1H), 6.07 (dd, J = 9.8, 1.2 Hz, 1H), 4.11-4.01 (m, 1H), 2.23 (d, 3H), 1.45-1.33 (m, 2H), 1.14 (s, 12H); ¹³C NMR: (CDCl₃, 100 MHz) : δ 146.7, 141.0, 134.4, 133.4, 133.2, 132.4, 128.4, 127.9, 127.45, 127.41, 127.1, 125.91, 125.85, 125.4, 124.5, 124.2, 83.1, 40.4, 24.8, 24.7, 16.3. HRMS (EI) calculated for [C₂₇H₃₁BO₂]⁺ requires m/z 398.2417, found m/z 398.2422.

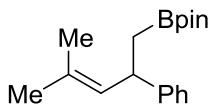


(*E*)-2-(4-furan-2-yl)-2-phenylpent-3-en-1-yl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2o) Prepared according to the general procedure A, using 0.2093 g (1.0 mmol) of **1o**, 75 μL (97%, 0.5 mmol) of HBpin, 0.0148 g (0.025 mmol) of ^{DMiP}OIP FeBr₂, 75 μL (1.0 M in THF, 0.75 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EA (100/1, 150 mL to 20/1, 250 mL) as the eluent to give 0.1103 g (0.325 mmol, 20/1 *E/Z*, 65% yield) of the title compound as a colorless oil. IR (cm⁻¹): 3027, 2978, 1799, 1366, 1327, 1144. ¹H NMR (CDCl₃, 400 MHz): δ 7.32-7.23 (m, 5H), 7.16-7.11 (m, 1H), 6.32 (dd, J = 3.4, 1.8 Hz, 1H), 6.22-6.16 (m, 2H), 4.02-3.92 (m, 1H), 2.01 (d, J = 1.6 Hz, 3H), 1.41-1.29 (m, 2H), 1.111 (s, 6H), 1.107 (s, 6H); ¹³C NMR: (CDCl₃, 100 MHz) : δ 156.1, 146.5, 141.2, 130.8, 128.3, 127.1, 125.9, 123.1, 110.9, 104.9, 83.1, 39.6, 24.7, 24.6, 13.7. HRMS (EI) calculated for [C₂₁H₂₇BO₃]⁺ requires m/z 338.2053, found m/z 338.2052.

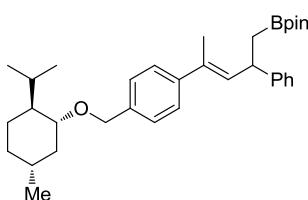


(*E*)-1-methyl-5-(4-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-en-2-yl)-1H-indole (2p) Prepared according to the general procedure A, using 0.2734 g (1.0 mmol) of **1p**, 75 μL (97%, 0.5 mmol) of HBpin, 0.0151 g (0.026 mmol) of ^{DMiP}OIP FeBr₂, 75 μL (1.0 M in THF, 0.75 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by

ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EA (50/1, 150 mL to 10/1, 250 mL) as the eluent to give 0.1759 g (0.440 mmol, 15/1 *E/Z*, 88% yield) of the title compound as a colorless oil. IR (cm^{-1}): 2977, 2925, 1602, 1489, 1365, 1329, 1246, 1144. ^1H NMR (CDCl_3 , 400 MHz): δ 7.60 (d, J = 1.6 Hz, 1H), 7.35-7.30 (m, 2H), 7.29-7.23 (m, 3H), 7.19-7.10 (m, 2H), 6.93 (d, J = 2.8 Hz, 1H), 6.41 (d, J = 2.8 Hz, 1H), 5.89 (dd, J = 9.8, 1.0 Hz, 1H), 4.08-3.98 (m, 1H), 3.66 (s, 3H), 2.19 (d, 3H), 1.41-1.32 (m, 2H), 1.13 (s, 12H); ^{13}C NMR: (CDCl_3 , 100 MHz) : δ 147.2, 135.8, 135.6, 134.2, 132.1, 128.9, 128.3, 128.2, 127.1, 125.6, 120.2, 117.9, 108.6, 101.0, 83.0, 40.3, 32.7, 24.8, 24.7, 24.6, 16.9. HRMS (EI) calculated for $[\text{C}_{20}\text{H}_{20}\text{N}]^+$ ($[\text{M}-\text{Bpin}]^+$) requires m/z 274.1596, found m/z 274.1597.

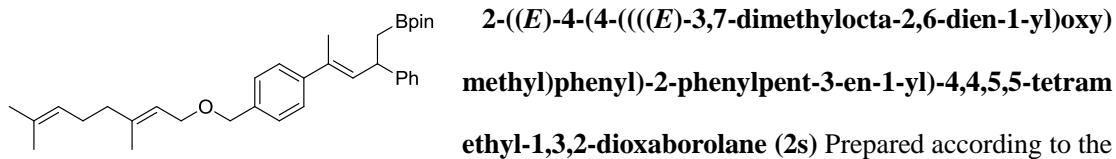


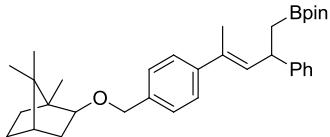
4,4,5,5-Tetramethyl-2-(4-methyl-2-phenylpent-3-en-1-yl)-1,3,2-dioxaborolane (2q) Prepared according to the general procedure B, using 0.1601 g (1.0 mmol) of **1q**, 75 μL (97%, 0.5 mmol) of HBpin, 0.0297 g (0.025 mmol) of $^{\text{DMiP}}$ OIP FeBr_2 , 75 μL (1.0 M in THF, 0.75 mmol) of NaBHET_3 , and 1.0 mL (0.5 M) of toluene. After 3 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.0758 g (0.265 mmol, 53% yield) of the title compound as a colorless oil. IR (cm^{-1}): 3026, 2977, 1601, 1366, 1324, 1145. ^1H NMR (CDCl_3 , 400 MHz): δ 7.26-7.21 (m, 4H), 7.15-7.10 (m, 1H), 5.31-5.23 (m, 1H), 3.86-3.72 (m, 1H), 1.71 (s, 3H), 1.66 (s, 3H), 1.21-1.17 (m, 2H), 1.14 (s, 12H); ^{13}C NMR: (CDCl_3 , 100 MHz) : δ 147.5, 130.4, 129.9, 128.2, 126.9, 125.6, 83.0, 39.7, 25.8, 24.7, 24.6, 18.2. HRMS (EI) calculated for $[\text{C}_{18}\text{H}_{27}\text{BO}_2]^+$ requires m/z 286.2104, found m/z 286.2107.



2-((E)-4-(((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)phenyl)-2-phenylpent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2r) Prepared according to the general procedure C, using 0.2002 g (0.51 mmol) of **1r**, 37.5 μL (97%, 0.5 mmol) of HBpin, 0.0152 g (0.051 mmol) of $^{\text{DMiP}}$ OIP FeBr_2 , 75 μL (1.0 M in THF, 0.75 mmol) of NaBHET_3 , and 0.5 mL (0.5 M) of toluene. After 10 h, the resulting solution was added 10 mL of ether and

filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EA (100/1, 150 mL to 20/1, 250 mL) as the eluent to give 0.1123 g (0.218 mmol, > 20/1 *E/Z*, 87% yield) of the title compound as a colorless oil. IR (cm^{-1}): 2954, 2923, 1491, 1365, 1327, 1144. ^1H NMR (CDCl_3 , 400 MHz): δ 7.35-7.29 (m, 2H), 7.29-7.22 (m, 6H), 7.17-7.11 (m, 1H), 5.88 (dd, J = 9.8, 1.0 Hz, 1H), 4.61 (d, J = 11.4 Hz, 1H), 4.36 (d, J = 11.4 Hz, 1H), 4.03-3.94 (m, 1H), 3.15 (td, J = 10.6, 3.8 Hz, 1H), 2.36-2.22 (m, 1H), 2.21-2.14 (m, 1H), 2.12 (s, 3H), 1.69-1.66 (m, 2H), 1.37-1.25 (m, 4H), 1.14 (s, 12H), 0.95-0.85 (m, 9H), 0.70 (d, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) : δ 146.8, 143.1, 137.4, 133.5, 133.2, 128.3, 127.65, 127.61, 127.1, 125.8, 83.1, 78.6, 70.1, 48.3, 40.30, 40.26, 34.6, 31.5, 25.5, 24.8, 24.7, 23.2, 22.4, 21.0, 16.3, 16.1. HRMS (EI) calculated for $[\text{C}_{34}\text{H}_{49}\text{BO}_3]^+$ requires m/z 516.3775, found m/z 516.3770.



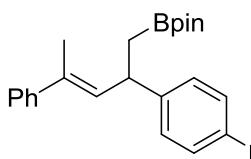


4,4,5,5-tetramethyl-2-(*E*)-2-phenyl-4-(4-((2*S*)-1,7,7-trimethyl

bicyclo[2.2.1]heptan-2-yl)oxy)methyl)phenyl)pent-3-en-1-yl)-1,

3,2-dioxaborolane (2t) Prepared according to the general procedure C, using 0.1967 g (0.51 mmol) of **1t**, 37.5 μ L (97%, 0.5 mmol) of HBpin, 0.0149 g (0.050 mmol) of ^{D*M*P}OIP FeBr₂, 75 μ L (1.0 M in THF, 0.75 mmol) of NaBHEt₃, and 0.5 mL (0.5 M) of toluene. After 10 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EA (100/1, 150 mL to 20/1, 250 mL) as the eluent to give 0.1106 g (0.215 mmol, > 20/1 *E/Z*, 86% yield) of the title compound as a colorless oil. IR (cm^{-1}): 2978, 2948, 1452, 1364, 1326, 1143. ¹H NMR (CDCl_3 , 400 MHz): δ

7.35-7.27 (m, 5H), 7.27-7.24 (m, 2H), 7.24-7.22 (m, 1H), 7.17-7.11 (m, 1H), 5.89 (d, *J* = 9.8 Hz, 1H), 4.54 (d, *J* = 12.4 Hz, 1H), 4.41 (d, *J* = 12.4 Hz, 1H), 4.03-3.94 (m, 1H), 3.70-3.64 (m, 1H), 2.15-2.03 (m, 5H), 1.76-1.65 (m, 1H), 1.65-1.60 (m, 1H), 1.38-1.29 (m, 2H), 1.27-1.21 (m, 2H), 1.14 (s, 12H), 1.08 (dd, *J* = 13.2, 3.2 Hz, 1H), 0.89 (s, 3H), 0.84 (s, 3H), 0.81 (s, 3H); ¹³C NMR (CDCl_3 , 100 MHz) : δ 146.8, 142.9, 137.8, 133.5, 133.1, 128.3, 127.1, 127.0, 125.8, 125.7, 84.2, 83.1, 71.3, 49.3, 47.8, 45.0, 40.3, 36.1, 28.2, 26.8, 24.8, 24.7, 19.8, 18.9, 16.3, 14.03. HRMS (EI) calculated for [C₃₄H₄₇BO₃]⁺ requires m/z 514.3618, found m/z 514.3615.

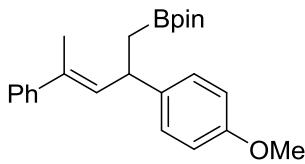


(*E*)-4,4,5,5-tetramethyl-2-(4-phenyl-2-(p-tolyl)pent-3-en-1-yl)-1,3-

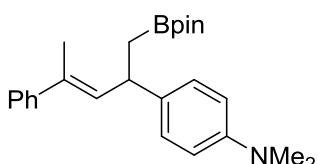
2-dioxaborolane (2aa) Prepared according to the general procedure

A, using 0.2541 g (1.0 mmol) of **1aa**, 75 μ L (97%, 0.5 mmol) of HBpin, 0.0148 g (0.025 mmol) of ^{D*M*P}OIP FeBr₂, 75 μ L (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.1358 g (0.375 mmol, 18/1 *E/Z*, 75% yield) of the title compound as a colorless oil. IR (cm^{-1}): 2978, 2926, 1598, 1364, 1326, 1144.

¹H NMR (CDCl₃, 400 MHz): δ 7.36-7.34 (m, 2H), 7.29-7.23 (m, 2H), 7.21-7.16 (m, 3H), 7.10-7.04 (m, 2H), 5.88 (d, J = 10.0 Hz, 1H), 4.03-3.91 (m, 1H), 2.29 (s, 3H), 2.12 (s, 3H), 1.36-1.27 (m, 2H), 1.15 (s, 12H); ¹³C NMR: (CDCl₃, 100 MHz) : δ 144.0, 143.8, 135.2, 133.9, 133.1, 129.0, 128.0, 126.9, 126.5, 125.8, 83.1, 39.8, 24.8, 24.7, 20.9, 16.2. HRMS (EI) calculated for [C₂₄H₃₁BO₂]⁺ requires m/z 362.2417, found m/z 362.2415.

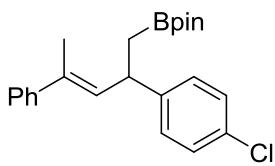


(E)-2-(2-(4-methoxyphenyl)-4-phenylpent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2ab) Prepared according to the general procedure A, using 0.2509 g (1.0 mmol) of **1ab**, 75 μ L (97%, 0.5 mmol) of HBpin, 0.0149 g (0.025 mmol) of ^{DMiP}OIP FeBr₂, 75 μ L (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EA (100/1, 150 mL to 20/1, 250 mL) as the eluent to give 0.1802 g (0.475 mmol, 10/1 E/Z, 95% yield) of the title compound as a colorless oil. IR (cm⁻¹): 2978, 2930, 1609, 1510, 1364, 1325, 1247, 1144. ¹H NMR (CDCl₃, 400 MHz): δ 7.38-7.33 (m, 2H), 7.30-7.15 (m, 5H), 6.85-6.78 (m, 2H), 5.86 (dd, J = 9.8, 1.2 Hz, 1H), 4.01-3.91 (m, 1H), 3.75 (s, 3H), 2.12 (d, J = 1.2 Hz, 3H), 1.38-1.25 (m, 2H), 1.14 (s, 12H); ¹³C NMR: (CDCl₃, 100 MHz) : δ 157.7, 144.0, 138.9, 134.1, 132.9, 128.0, 127.9, 126.5, 125.8, 113.7, 113.6, 83.0, 55.2, 39.4, 24.8, 24.7, 16.2. HRMS (EI) calculated for [C₂₄H₃₁BO₃]⁺ requires m/z 378.2366, found m/z 378.2362.

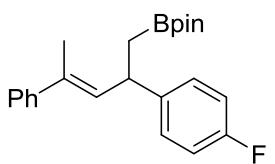


(E)-N,N-dimethyl-4-(4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-en-2-yl)aniline (2ac) Prepared according to the general procedure B, using 0.2610 g (1.0 mmol) of **1ac**, 75 μ L (97%, 0.5 mmol) of HBpin, 0.0147 g (0.025 mmol) of ^{DMiP}OIP FeBr₂, 75 μ L (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of toluene. After 3 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EA (100/1, 150 mL to

20/1, 250 mL) as the eluent to give 0.1825 g (0.465 mmol, 12/1 *E/Z*, 93% yield) of the title compound as a colorless oil. IR (cm^{-1}): 2973, 2927, 1612, 1521, 1364, 1332, 1142. ^1H NMR (CDCl_3 , 400 MHz): δ 7.38-7.34 (m, 2H), 7.29-7.23 (m, 2H), 7.20-7.14 (m, 3H), 6.71-6.65 (m, 2H), 5.86 (dd, $J = 10.0, 1.2$ Hz, 1H), 3.96-3.88 (m, 1H), 2.89 (s, 6H), 2.12 (d, $J = 1.0$ Hz, 3H), 1.38-1.25 (m, 2H), 1.15 (s, 12H); ^{13}C NMR: (CDCl_3 , 100 MHz) : δ 149.0, 144.2, 135.1, 134.4, 132.5, 128.0, 127.6, 126.4, 125.8, 113.0, 83.0, 40.9, 39.2, 24.8, 24.7, 16.2. HRMS (EI) calculated for $[\text{C}_{25}\text{H}_{34}\text{BNO}_2]^+$ requires m/z 391.2683, found m/z 391.2687.

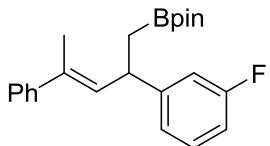


(*E*)-2-(2-(4-chlorophenyl)-4-phenylpent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2ad) Prepared according to the general procedure A, using 0.2557 g (1.0 mmol) of **1ad**, 75 μL (97%, 0.5 mmol) of HBpin, 0.0150 g (0.026 mmol) of $^{\text{DMiP}}$ OIP FeBr_2 , 75 μL (1.0 M in THF, 0.075 mmol) of NaBHET_3 , and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.1676 g (0.440 mmol, 16/1 *E/Z*, 88% yield) of the title compound as a colorless oil. IR (cm^{-1}): 2956, 2925, 1491, 1367, 1326, 1144. ^1H NMR (CDCl_3 , 400 MHz): δ 7.37-7.33 (m, 2H), 7.31-7.26 (m, 2H), 7.24-7.21 (m, 4H), 7.21-7.17 (m, 1H), 5.83 (dd, $J = 9.6, 1.2$ Hz, 1H), 4.01-3.91 (m, 1H), 2.11 (d, $J = 1.2$ Hz, 3H), 1.33-1.28 (m, 2H), 1.15 (s, 12H); ^{13}C NMR: (CDCl_3 , 100 MHz) : δ 145.3, 143.7, 133.9, 133.2, 131.4, 128.5, 128.4, 128.1, 126.7, 125.8, 83.2, 39.7, 24.8, 24.7, 16.3. HRMS (ESI) calculated for $[\text{C}_{23}\text{H}_{28}\text{BClO}_2\text{Na}]^+ [\text{M} + \text{Na}^+]$ requires m/z 405.1767, found m/z 405.1768.

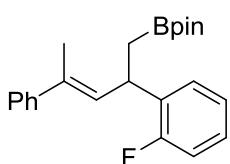


(*E*)-2-(2-(4-fluorophenyl)-4-phenylpent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2ae) Prepared according to the general procedure B, using 0.2395 g (1.0 mmol) of **1ae**, 75 μL (97%, 0.5 mmol) of HBpin, 0.0300 g (0.051 mmol) of $^{\text{DMiP}}$ OIP FeBr_2 , 150 μL (1.0 M in THF, 0.150 mmol) of NaBHET_3 , and 1.0 mL (0.5 M) of toluene. After 3 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates

were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.1699 g (0.460 mmol, 14/1 *E/Z*, 92% yield) of the title compound as a colorless oil. IR (cm^{-1}): 2978, 2931, 1601, 1508, 1365, 1326, 1224, 1144. ^1H NMR (CDCl_3 , 400 MHz): δ 7.41-7.33 (m, 2H), 7.30-7.16 (m, 5H), 6.99-6.91 (m, 2H), 5.85 (dd, $J = 9.8, 1.2$ Hz, 1H), 4.01-3.94 (m, 1H), 2.11 (d, $J = 1.2$ Hz, 3H), 1.36-1.28 (m, 2H), 1.14 (s, 12H); ^{13}C NMR (CDCl_3 , 100 MHz) : δ 161.2 (d, $J = 243.4$ Hz), 143.7, 142.4 (d, $J = 2.8$ Hz), 133.6, 133.4, 128.4 (d, $J = 8.4$ Hz), 128.1, 126.6, 125.8, 114.9 (d, $J = 20.9$ Hz), 83.1, 39.5, 24.72, 24.66, 16.2; ^{19}F NMR (CDCl_3 , 100 MHz) : δ -117.6. HRMS (ESI) calculated for $[\text{C}_{23}\text{H}_{29}\text{BFO}_2]^+$ [M + H $^+$] requires m/z 367.2245, found m/z 367.2234.

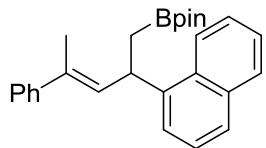


(*E*)-2-(2-(3-fluorophenyl)-4-phenylpent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2af) Prepared according to the general procedure B, using 0.2419 g (1.0 mmol) of **1af**, 75 μL (97%, 0.5 mmol) of HBpin, 0.0300 g (0.051 mmol) of $^{\text{DMiP}}$ OIP FeBr_2 , 150 μL (1.0 M in THF, 0.150 mmol) of NaBH Et_3 , and 1.0 mL (0.5 M) of toluene. After 3 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.1179 g (0.320 mmol, > 20/1 *E/Z*, 64% yield) of the title compound as a colorless oil. IR (cm^{-1}): 2979, 2928, 1589, 1366, 1328, 1143. ^1H NMR (CDCl_3 , 400 MHz): δ 7.39-7.33 (m, 2H), 7.31-7.25 (m, 2H), 7.25-7.16 (m, 2H), 7.10-7.04 (m, 1H), 7.03-6.97 (m, 1H), 6.87-6.80 (m, 1H), 5.84 (dd, $J = 9.6, 0.8$ Hz, 1H), 4.04-3.94 (m, 1H), 2.12 (d, $J = 1.2$ Hz, 3H), 1.49-1.28 (m, 2H), 1.15 (s, 12H); ^{13}C NMR (CDCl_3 , 100 MHz) : δ 162.9 (d, $J = 244.9$ Hz), 149.4 (d, $J = 6.6$ Hz), 143.7, 134.0, 133.0, 129.6 (d, $J = 8.7$ Hz), 128.1, 126.7, 125.8, 122.7 (d, $J = 2.2$ Hz), 114.0 (d, $J = 21.2$ Hz), 112.6 (d, $J = 21.2$ Hz), 83.2, 40.0, 24.72, 24.66, 16.3; ^{19}F NMR (CDCl_3 , 100 MHz) : δ -113.6. HRMS (EI) calculated for $[\text{C}_{23}\text{H}_{28}\text{BFO}_2]^+$ requires m/z 366.2166, found m/z 366.2166.



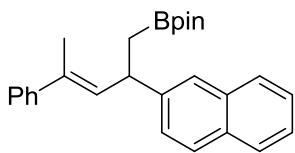
(*E*)-2-(2-(2-fluorophenyl)-4-phenylpent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2ag)

1,3,2-dioxaborolane (2ag) Prepared according to the general procedure B, using 0.2390 g (1.0 mmol) of **1ag**, 75 μ L (97%, 0.5 mmol) of HBpin, 0.0302 g (0.051 mmol) of ^{DMiP}OIP FeBr₂, 150 μ L (1.0 M in THF, 0.150 mmol) of NaBH₃Et₃, and 1.0 mL (0.5 M) of toluene. After 3 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.1535 g (0.420 mmol, 9/1 E/Z, 84% yield) of the title compound as a colorless oil. IR (cm^{-1}): 2979, 1489, 1367, 1327, 1144. ¹H NMR (CDCl₃, 400 MHz): δ 7.38-7.33 (m, 2H), 7.33-7.29 (m, 1H), 7.29-7.23 (m, 2H), 7.21-7.15 (m, 1H), 7.15-7.08 (m, 1H), 7.08-7.02 (m, 1H), 7.00-6.94 (m, 1H), 5.88 (d, J = 9.8 Hz, 1H), 4.34-4.24 (m, 1H), 2.12 (s, 3H), 1.37 (d, J = 7.8 Hz, 2H), 1.13 (d, J = 2.4 Hz, 12H); ¹³C NMR (CDCl₃, 100 MHz) : δ 160.5 (d, J = 245.5 Hz), 143.9, 134.1, 133.4 (d, J = 133.4 Hz), 132.4, 128.4 (d, J = 5.1 Hz), 128.04, 127.97, 127.8, 127.2 (d, J = 8.8 Hz), 126.6, 125.8, 124.0 (d, J = 3.7 Hz), 115.3 (d, J = 22.7 Hz), 83.1, 33.9, 24.72, 24.65, 24.5, 16.2; ¹⁹F NMR (CDCl₃, 100 MHz) : δ -117.4. HRMS (EI) calculated for [C₂₃H₂₈BFO₂]⁺ requires m/z 366.2166, found m/z 366.2162.



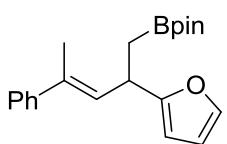
(E)-4,4,5,5-tetramethyl-2-(2-(naphthalen-1-yl)-4-phenylpent-3-en-1-yl)-1,3,2-dioxaborolane (2ah) Prepared according to the general procedure A, using 0.1371 g (0.51 mmol) of **1ah**, 75 μ L (97%, 0.5 mmol) of HBpin, 0.0152 g (0.026 mmol) of ^{DMiP}OIP FeBr₂, 75 μ L (1.0 M in THF, 0.75 mmol) of NaBH₃Et₃, and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.1196 g (0.300 mmol, 9/1 E/Z, 60% yield) of the title compound as a colorless oil. IR (cm^{-1}): 2978, 2936, 1598, 1363, 1326, 1143. ¹H NMR (CDCl₃, 400 MHz): δ 8.28 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.54-7.48 (m, 2H), 7.47-7.39 (m, 2H), 7.39-7.34 (m, 2H), 7.29-7.23 (m, 2H), 7.22-7.16 (m, 1H), 6.07 (d, J = 9.4 Hz, 1H), 4.82-4.73 (m, 1H), 2.16 (s, 3H), 1.60-1.50 (m, 1H), 1.49-1.39 (m, 1H), 1.11 (s, 6H), 1.08 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) : δ 143.9, 143.3, 134.0, 133.9, 133.7, 131.4, 128.8, 128.1, 126.6, 126.4, 125.8,

125.62, 125.59, 125.2, 123.8, 123.6, 83.1, 35.6, 24.7, 24.6, 16.5. HRMS (EI) calculated for $[C_{27}H_{31}BO_2]^+$ requires m/z 398.2417, found m/z 398.2412.



(E)-4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)-4-phenylpent-3-en-1-yl)-1,3,2-dioxaborolane (2ai)

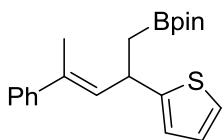
(E)-4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)-4-phenylpent-3-en-1-yl)-1,3,2-dioxaborolane (2ai) Prepared according to the general procedure A, using 0.2731 g (1.0 mmol) of **1ai**, 75 μ L (97%, 0.5 mmol) of HBpin, 0.0151 g (0.026 mmol) of ^{DMiP}OIP FeBr₂, 75 μ L (1.0 M in THF, 0.75 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EA (100/1, 150 mL to 20/1, 250 mL) as the eluent to give 0.1681 g (0.420 mmol, 20/1 E/Z, 84% yield) of the title compound as a colorless oil. IR (cm^{-1}): 2978, 2931, 1599, 1362, 1325, 1142. ¹H NMR (CDCl_3 , 400 MHz): δ 7.80-7.70 (m, 4H), 7.42-7.34 (m, 5H), 7.31-7.24 (m, 2H), 7.21-7.15 (m, 1H), 5.98 (dd, J = 9.8, 1.0 Hz, 1H), 4.21-4.12 (m, 1H), 2.16 (d, J = 1.0 Hz, 3H), 1.51-1.39 (m, 2H), 1.12 (s, 12H); ¹³C NMR (CDCl_3 , 100 MHz) : δ 144.3, 143.9, 133.7, 133.6, 132.1, 128.1, 127.9, 127.6, 127.5, 126.6, 126.2, 125.9, 125.7, 125.1, 124.8, 83.1, 40.4, 24.8, 24.7, 16.4. HRMS (EI) calculated for $[C_{27}H_{31}BO_2]^+$ requires m/z 398.2417, found m/z 398.2415.



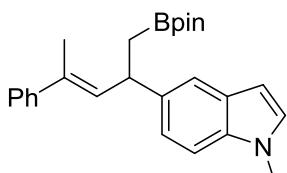
(E)-2-(2-(furan-2-yl)-4-phenylpent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2aj) Prepared according to the general procedure A, using

0.2139 g (1.0 mmol) of **1aj**, 75 μ L (97%, 0.5 mmol) of HBpin, 0.0148 g (0.025 mmol) of ^{DMiP}OIP FeBr₂, 75 μ L (1.0 M in THF, 0.75 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography

using PE/EA (100/1, 150 mL to 20/1, 250 mL) as the eluent to give 0.0811 g (0.240 mmol, > 20/1 *E/Z*, 48% yield) of the title compound as a colorless oil. IR (cm^{-1}): 2979, 2931, 1595, 1367, 1328, 1145. ^1H NMR (CDCl_3 , 400 MHz): δ 7.41-7.36 (m, 2H), 7.32-7.27 (m, 3H), 7.24-7.18 (m, 1H), 6.27-6.23 (m, 1H), 6.03-5.99 (m, 1H), 5.76 (dd, $J = 9.8, 1.2$ Hz, 1H), 4.10-4.01 (m, 1H), 2.15 (d, $J = 1.2$ Hz, 3H), 1.45-1.37 (m, 1H), 1.27-1.23 (m, 1H), 1.20 (s, 6H), 1.19 (s, 6H); ^{13}C NMR (CDCl_3 , 100 MHz) : δ 159.2, 143.7, 140.9, 134.7, 130.6, 128.1, 126.7, 125.9, 109.9, 103.8, 83.2, 34.3, 24.8, 24.7, 16.2. HRMS (EI) calculated for $[\text{C}_{21}\text{H}_{27}\text{BO}_3]^+$ requires m/z 338.2053, found m/z 338.2056.

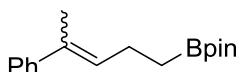


(*E*)-4,4,5,5-tetramethyl-2-(4-phenyl-2-thiophen-2-yl)pent-3-en-1-yl-1,3,2-dioxaborolane (2ak) Prepared according to the general procedure A, using 0.2247 g (1.0 mmol) of **1ak**, 75 μL (97%, 0.5 mmol) of HBpin, 0.0149 g (0.025 mmol) of $^{\text{DMiP}}$ OIP FeBr_2 , 75 μL (1.0 M in THF, 0.75 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EA (100/1, 150 mL to 20/1, 250 mL) as the eluent to give 0.0961 g (0.270 mmol, > 20/1 *E/Z*, 54% yield) of the title compound as a colorless oil. IR (cm^{-1}): 2979, 2938, 1605, 1366, 1327, 1144. ^1H NMR (CDCl_3 , 400 MHz): δ 7.41-7.36 (m, 2H), 7.31-7.26 (m, 2H), 7.24-7.18 (m, 1H), 7.11-7.08 (m, 1H), 6.92-6.88 (m, 1H), 6.86-6.83 (m, 1H), 5.83 (dd, $J = 9.8, 1.0$ Hz, 1H), 4.30-4.21 (m, 1H), 2.15 (d, $J = 1.2$ Hz, 3H), 1.53-1.45 (m, 1H), 1.39-1.31 (m, 1H), 1.17 (s, 12H); ^{13}C NMR (CDCl_3 , 100 MHz) : δ 151.1, 143.7, 133.9, 133.0, 128.1, 126.7, 126.5, 125.9, 122.9, 122.5, 83.2, 35.8, 24.8, 24.7, 16.2. HRMS (EI) calculated for $[\text{C}_{21}\text{H}_{27}\text{BO}_2\text{S}]^+$ requires m/z 354.1825, found m/z 354.1827.



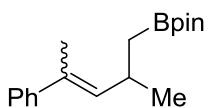
(*E*)-1-methyl-5-(4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborola-2-yl)pent-3-en-2-yl)-1*H*-indole (2al) Prepared according to the general procedure B, using 0.2728 g (1.0 mmol) of **1al**, 75 μL (97%, 0.5 mmol) of HBpin, 0.0151 g (0.026 mmol) of $^{\text{DMiP}}$ OIP FeBr_2 , 75 μL (1.0 M in THF, 0.75 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of toluene. After 3 h, the resulting solution was added 10 mL of

ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EA (50/1, 150 mL to 10/1, 250 mL) as the eluent to give 0.2035 g (0.495 mmol, 11/1 *E/Z*, 99% yield) of the title compound as a colorless oil. IR (cm^{-1}): 2978, 2927, 1491, 1363, 1326, 1144. ^1H NMR (CDCl_3 , 400 MHz): δ 7.53 (s, 1H), 7.39-7.34 (m, 2H), 7.30-7.23 (m, 2H), 7.22-7.14 (m, 3H), 6.98 (d, J = 3.2 Hz, 1H), 6.42-6.38 (m, 1H), 6.00-5.94 (m, 1H), 4.15-4.05 (m, 1H), 3.73 (s, 3H), 2.15 (s, 3H), 1.46-1.35 (m, 2H), 1.14 (s, 12H); ^{13}C NMR (CDCl_3 , 100 MHz) : δ 144.2, 137.9, 135.4, 134.8, 132.6, 128.7, 128.5, 128.0, 126.3, 125.9, 121.3, 118.5, 109.0, 100.7, 83.0, 40.2, 32.8, 24.8, 24.7, 16.3. HRMS (EI) calculated for $[\text{C}_{26}\text{H}_{32}\text{BNO}_2]^+$ requires m/z 401.2526, found m/z 401.2531.



(*E*)-4,4,5,5-tetramethyl-2-(4-phenylpent-3-en-1-yl)-1,3,2-dioxaborolan e (2am)

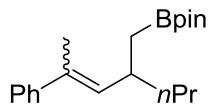
Prepared according to the general procedure B, using 0.0746 g (0.5 mmol) of **1am**, 75 μL (97%, 0.5 mmol) of HBpin, 0.0147 g (0.025 mmol) of $^{\text{DMiP}}$ OIP FeBr_2 , 75 μL (1.0 M in THF, 0.75 mmol) of NaBHET_3 , and 1.0 mL (0.5 M) of toluene. After 3 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.0882 g (0.325 mmol, 3/1 *E/Z*, 65% yield) of the title compound as a colorless oil. IR (cm^{-1}): 2978, 2935, 1600, 1374, 1326, 1145. ^1H NMR (CDCl_3 , 400 MHz): δ 7.40-7.36 (m, 2.08H), 7.32-7.24 (m, 2.98H), 7.22-7.16 (m, 1.59H), 5.78 (t, J = 7.4 Hz, 1H), 5.46 (t, J = 7.4 Hz, 0.29H), 2.32 (q, J = 7.6 Hz, 2H), 2.09 (q, J = 7.6 Hz, 0.44H), 2.03 (s, 3H), 2.01 (s, 0.62H), 1.24 (s, 12H), 1.22 (s, 3.55H), 0.95 (t, J = 7.4 Hz, 2H), 0.82 (t, J = 7.4 Hz, 0.48H); HRMS (EI) calculated for $[\text{C}_{17}\text{H}_{25}\text{BO}_2]^+$ requires m/z 272.1948, found m/z 272.1949.



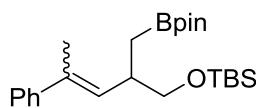
(*E*)-4,4,5,5-tetramethyl-2-(2-methyl-4-phenylpent-3-en-1-yl)-1,3,2-dioxaborolan (2an)

Prepared according to the general procedure A, using 0.0824 g (0.52 mmol) of **1an**, 75 μL (97%, 0.5 mmol) of HBpin, 0.0151 g (0.026 mmol) of $^{\text{DMiP}}$ OIP FeBr_2 , 75 μL (1.0 M in THF, 0.75 mmol) of NaBHET_3 , and 1.0 mL (0.5 M) of toluene. After 0.5 h, the

resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.1209 g (0.420 mmol, 3.7/1 *E/Z*, 84% yield) of the title compound as a colorless oil. IR (cm^{-1}): 2977, 2926, 1599, 1366, 1324, 1144. ^1H NMR (CDCl_3 , 400 MHz): δ 7.40-7.34 (m, 2.06H), 7.32-7.25 (m, 2.60H), 7.24-7.16 (m, 1.96H), 5.60 (d, J = 9.4 Hz, 1H), 5.31 (d, J = 10.2 Hz, 0.27H), 2.91-2.77 (m, 1H), 2.57-2.46 (m, 0.29H), 2.06 (s, 3H), 1.98 (s, 0.82H), 1.22 (s, 16.02H), 1.07 (d, J = 6.6 Hz, 3H), 0.97 (d, J = 6.6 Hz, 0.95H), 0.92 (d, J = 7.2 Hz, 2H), 0.81 (d, J = 7.2 Hz, 0.56H). HRMS (EI) calculated for $[\text{C}_{18}\text{H}_{27}\text{BO}_2]^+$ requires m/z 286.2104, found m/z 286.2105.

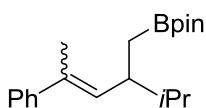


(*E*)-4,4,5,5-tetramethyl-2-(4-phenyl-2-propylpent-3-en-1-yl)-1,3,2-dioxaborolane (2ao) Prepared according to the general procedure A, using 0.0933 g (0.50 mmol) of **1ao**, 75 μL (97%, 0.5 mmol) of HBpin, 0.0150 g (0.026 mmol) of $^{\text{DMiP}}$ OIP FeBr_2 , 75 μL (1.0 M in THF, 0.75 mmol) of NaBHET_3 , and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.1386 g (0.440 mmol, 5.1/1 *E/Z*, 88% yield) of the title compound as a colorless oil. IR (cm^{-1}): 2977, 2927, 1599, 1370, 1321, 1145. ^1H NMR (CDCl_3 , 400 MHz): δ 7.39-7.34 (m, 2H), 7.31-7.24 (m, 2.69H), 7.22-7.15 (m, 1.27H), 5.51 (s, J = 10.2 Hz, 1H), 5.25 (s, J = 10.2 Hz, 0.20H), 2.77-2.65 (m, 1H), 2.46-2.35 (m, 0.22H), 2.06 (s, 3H), 1.99 (s, 0.62H), 1.45-1.25 (m, 5.03H), 1.23 (s, 2.37H), 1.20 (s, 12H), 1.01-0.94 (m, 1.03H), 0.91-0.82 (m, 4.15H), 0.74-0.67 (m, 0.87H). HRMS (EI) calculated for $[\text{C}_{20}\text{H}_{31}\text{BO}_2]^+$ requires m/z 314.2417, found m/z 314.2415.

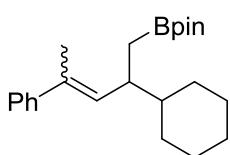


(*E*)-tert-butyldimethyl((4-phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pent-3-en-1-yl)oxy)silane (2ap) Prepared according to the general procedure A, using 0.1459 g (0.51 mmol) of **1ap**, 75 μL (97%, 0.5 mmol) of HBpin, 0.0151 g (0.026 mmol) of $^{\text{DMiP}}$ OIP FeBr_2 , 75 μL (1.0 M in THF, 0.75 mmol) of

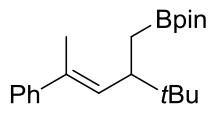
NaBHEt₃, and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EA (100/1, 150 mL to 20/1, 250 mL) as the eluent to give 0.1938 g (0.465 mmol, 4.7/1 *E/Z*, 93% yield) of the title compound as a colorless oil. IR (cm⁻¹): 2954, 2857, 1491, 1368, 1322, 1254, 1145, 1067. ¹H NMR (CDCl₃, 400 MHz): δ 77.40-7.33 (m, 2.11H), 7.32-7.25 (m, 2.99H), 7.23-7.16 (m, 1.32H), 5.52 (d, J = 10.0 Hz, 1H), 5.25 (d, J = 10.0 Hz, 0.21H), 3.51 (d, J = 6.8 Hz, 2H), 3.43 (d, J = 6.8 Hz, 0.41H), 2.94-2.83 (m, 1H), 2.67-2.56 (m, 0.21H), 2.08 (s, 3H), 2.01 (s, 0.65H), 1.20 (s, 14. 1H), 1.13-1.02 (m, 1H), 0.88 (s, 9H), 0.85 (s, 2.03H), 0.82-0.73 (m, 1H), 0.03 (s, 3H), 0.02 (s, 3H), -0.03 (s, 0.60H), -0.04 (s, 0.60H). HRMS (ESI) calculated for [c]⁺ [M + H⁺] requires m/z 417.2996, found m/z 417.2988.



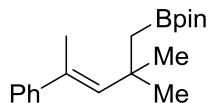
(*E*)-2-(2-isopropyl-4-phenylpent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2aq**)** Prepared according to the general procedure A, using 0.0934 g (0.50 mmol) of **1aq**, 75 μ L (97%, 0.5 mmol) of HBpin, 0.0149 g (0.025 mmol) of ^{D*MiP*}OIP FeBr₂, 75 μ L (1.0 M in THF, 0.75 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.1515 g (0.480 mmol, 6.5/1 *E/Z*, 88% yield) of the title compound as a colorless oil. IR (cm⁻¹): 2974, 2928, 1599, 1365, 1319, 1145. ¹H NMR (CDCl₃, 400 MHz): δ 7.39-7.34 (m, 2.01H), 7.31-7.25 (m, 2.61H), 7.22-7.16 (m, 1.14H), 5.57 (dd, J = 10.6, 1.2 Hz, 1H), 5.32 (dd, J = 10.6, 1.2 Hz, 0.15H), 2.58-2.47 (m, 1H), 2.31-2.20 (m, 0.18H), 2.06 (s, 3H), 2.01 (s, 0.50H), 1.65-1.54 (m, 1H), 1.50-1.42 (m, 0.23H), 1.23 (s, 2.08H), 1.18 (s, 12H), 1.07-1.00 (m, 1H), 0.92 (d, J = 6.6 Hz, 3H), 0.87 (d, J = 6.6 Hz, 3H), 0.85-0.79 (m, 1H), 0.74 (d, J = 2.8 Hz, 0.43H), 0.72 (d, J = 2.8 Hz, 0.43H). HRMS (EI) calculated for [C₂₀H₃₁BO₂]⁺ requires m/z 314.2417, found m/z 314.2415.



ioxaborolane (2ar) Prepared according to the general procedure A, using 0.1145 g (0.51 mmol) of **1ar**, 75 μ L (97%, 0.5 mmol) of HBpin, 0.0147 g (0.025 mmol) of ^{DMiP}OIP FeBr₂, 75 μ L (1.0 M in THF, 0.75 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.1782 g (0.495 mmol, 6.4/1 E/Z, 99% yield) of the title compound as a colorless oil. IR (cm^{-1}): 2925, 2852, 1449, 1367, 1323, 1146. ¹H NMR (CDCl_3 , 400 MHz): δ 7.39-7.35 (m, 2.04H), 7.31-7.25 (m, 2.60H), 7.22-7.16 (m, 1.12H), 5.57 (dd, J = 10.6, 1.2 Hz, 1H), 5.31 (dd, J = 10.6, 1.2 Hz, 0.15H), 2.57-2.47 (m, 1H), 2.31-2.19 (m, 0.16H), 2.04 (d, J = 1.2 Hz, 3H), 2.00 (d, J = 1.2 Hz, 0.51H), 1.82-1.50 (m, 6.24H), 1.23 (s, 2.15H), 1.18 (s, 12H), 1.15-0.76 (m, 8.45H). HRMS (EI) calculated for $[\text{C}_{23}\text{H}_{35}\text{BO}_2]^+$ requires m/z 354.2730, found m/z 354.2730.



(E)-2-(2-(tert-butyl)-4-phenylpent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-di-oxaborolane (2as) Prepared according to the general procedure A, using 0.1000 g (0.50 mmol) of **1as**, 75 μ L (97%, 0.5 mmol) of HBpin, 0.0148 g (0.025 mmol) of ^{DMiP}OIP FeBr₂, 75 μ L (1.0 M in THF, 0.75 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.1478 g (0.450 mmol, 10.6/1 E/Z, 90% yield) of the title compound as a colorless oil. IR (cm^{-1}): 2970, 1599, 1364, 1327, 1145. ¹H NMR (CDCl_3 , 400 MHz): δ 7.40-7.34 (m, 2H), 7.31-7.25 (m, 2H), 7.22-7.16 (m, 1H), 5.60 (dd, J = 11.0, 1.2 Hz, 1H), 2.52 (td, J = 11.6, 3.4 Hz, 1H), 2.07 (d, J = 1.2 Hz, 3H), 1.16 (s, 6H), 1.15 (s, 6H), 1.10-1.03 (m, 1H), 0.90 (s, 9H), 0.84-0.75 (m, 1H); ¹³C NMR (CDCl_3 , 100 MHz) : δ 144.6, 134.2, 132.6, 128.0, 126.3, 125.9, 82.9, 44.4, 34.8, 27.2, 25.0, 24.7, 16.7. HRMS (EI) calculated for $[\text{C}_{21}\text{H}_{33}\text{BO}_2]^+$ requires m/z 328.2574, found m/z 328.2570.

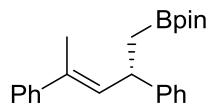


(E)-2-(2,2-dimethyl-4-phenylpent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2at)

Prepared according to the general procedure A, using 0.0886 g (0.51 mmol) of **1at**, 75 μ L (97%, 0.5 mmol) of HBpin, 0.0152 g (0.026 mmol) of ^{DMP}OIP FeBr₂, 75 μ L (1.0 M in THF, 0.75 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.0961 g (0.320 mmol, > 30/1 E/Z, 64% yield) of the title compound as a colorless oil. IR (cm^{-1}): 2977, 1598, 1354, 1321, 1142. ¹H NMR (CDCl_3 , 400 MHz): δ 7.37-7.32 (m, 2H), 7.30-7.24 (m, 2H), 7.21-7.15 (m, 1H), 5.79 (s, 1H), 2.14 (s, 3H), 1.29 (s, 6H), 1.21 (s, 12H), 1.14 (s, 2H); ¹³C NMR (CDCl_3 , 100 MHz): δ 146.4, 140.0, 133.6, 127.9, 126.1, 126.0, 82.8, 34.4, 31.3, 24.9, 17.2. HRMS (EI) calculated for [C₁₉H₂₉BO₂]⁺ requires m/z 300.2261, found m/z 300.2259.

VI. Stereospecific Hydroboration of Vinylcyclopropanes

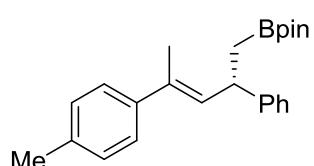
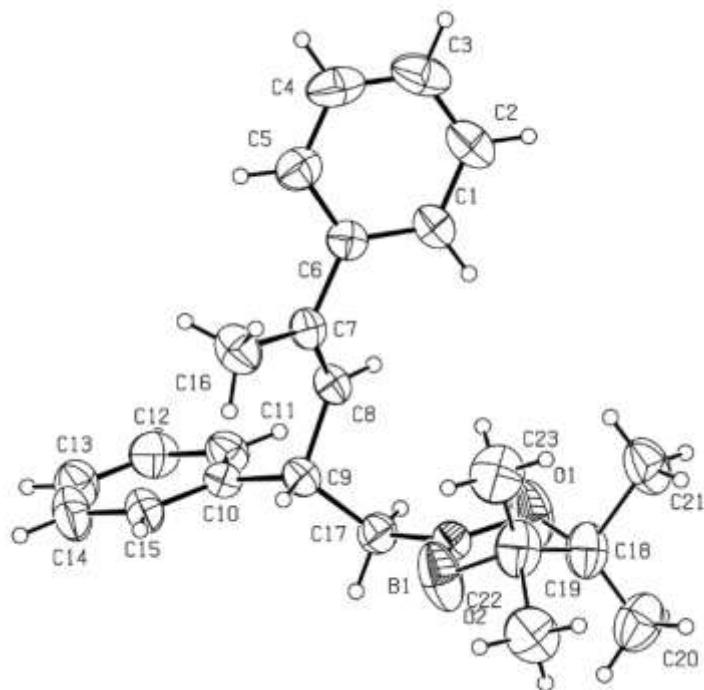
General Procedure D for Stereospecific Hydroboration of Vinylcyclopropanes: to a 25 mL flame-dried Schlenk flask cooled under nitrogen, **L2** FeBr₂ complex (0.0125 mmol, 5 mol%) and vinylcyclopropane (1.0 mmol, 4.0 equiv.) were added. The mixture was vacuumed and flushed with nitrogen for three times, and then, 0.5 mL of toluene (0.5 M) and HBpin (37.5 μ L, 97%, 0.25 mmol, 1.0 equiv.) were added in sequence. The mixture was injected with NaBHEt₃ (1.0 M in THF, 37.5 μ L, 0.0375 mmol) by dropwise. The reaction was run at ambient temperature for 0.5 h. Then the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The resulting mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give the corresponding product.



(S,E)-2-(2,4-diphenylpent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S-2a) Prepared according to the general procedure D, using 0.2234 g (1.0 mmol) of **1a**, 37.5 μ L (97%, 0.25 mmol) of HBpin, 0.0085 g (0.0131 mmol) of **L2** FeBr₂, 37.5 μ L (1.0 M in THF, 0.0375 mmol) of NaBHEt₃, and 0.5 mL (0.5 M) of

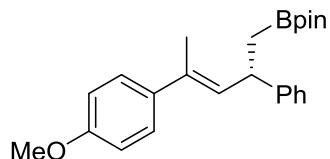
toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.0502 g (0.144 mmol, 10/1 *E/Z*, 58% yield) of the title compound as a white solid, Optical Rotation: $[\alpha]_{20}^D = +6.3$ (c 1.03, CHCl_3), 83.3% *ee* determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 98/2, 1.0 mL/min, n = 254 nm, tr 4.2 (minor), 5.2 (major). The analysis data are same as **2a**. 98.8 % *ee* of **S-2a** was afforded by crystallized from ethanol at 0 °C, mp: 78.3-79.2 °C (crystallized from ethanol). Optical Rotation: $[\alpha]_{20}^D = +12.1$ (c 1.05, CHCl_3). 98.8% *ee* determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 98/2, 1.0 mL/min, n = 254 nm, tr 4.2 (minor), 5.2 (major).

X-ray diffraction of **S-2a**;CCDC 1528870

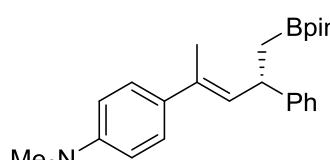


(*S,E*)-4,4,5,5-tetramethyl-2-(2-phenyl-4-(*p*-tolyl)pent-3-en-1-yl)-1,3,2-dioxaborolane (S-2b**)** Prepared according to the general procedure D, using 0.2343 g (1.0 mmol) of **1b**, 37.5 μL (97%, 0.25 mmol) of HBpin, 0.0080 g (0.0124 mmol) of **L2** FeBr_2 , 37.5 μL (1.0 M in THF, 0.0375 mmol) of NaBHET_3 , and 0.5 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by

ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.0876 g (0.242 mmol, 13/1 *E/Z*, 97% yield) of the title compound as a colorless oil; Optical Rotation: $[\alpha]_{20}^D = -0.4$ (c 1.08, CHCl_3), 86.3% *ee* determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 98/2, 1.0 mL/min, n = 254 nm, tr 4.4 (minor), 6.1 (major). The analysis data are same as **2b**.

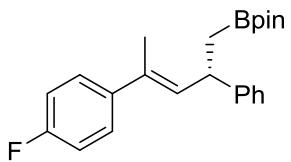


(*S,E*)-2-(4-(4-methoxyphenyl)-2-phenylpent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*S*-2e**)** Prepared according to the general procedure D, using 0.2510 g (1.0 mmol) of **1e**, 37.5 μL (97%, 0.25 mmol) of HBpin, 0.0082 g (0.0126 mmol) of **L2** FeBr_2 , 37.5 μL (1.0 M in THF, 0.0375 mmol) of NaBHEt₃, and 0.5 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EA (100/1, 150 mL to 20/1, 250 mL) as the eluent to give 0.0895 g (0.237 mmol, 12/1 *E/Z*, 95% yield) of the title compound as a colorless oil; Optical Rotation: $[\alpha]_{20}^D = -5.6$ (c 1.08, CHCl_3), 86.7% *ee* determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 98/2, 1.0 mL/min, n = 254 nm, tr 5.8 (minor), 7.9 (major). The analysis data are same as **2e**.

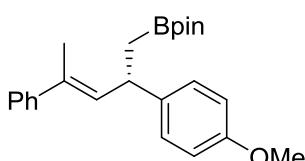


(*S,E*)-*N,N*-dimethyl-4-(4-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-en-2-yl)aniline (*S*-2f**)** Prepared according to the general procedure D, using 0.2658 g (1.0 mmol) of **1f**, 37.5 μL (97%, 0.25 mmol) of HBpin, 0.0082 g (0.0126 mmol) of **L2** FeBr_2 , 37.5 μL (1.0 M in THF, 0.0375 mmol) of NaBHEt₃, and 0.5 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EA (100/1, 150 mL to 20/1, 250 mL) as the eluent to give 0.0907 g (0.232 mmol, 12/1 *E/Z*, 93% yield) of the title compound as light yellow oil; Optical

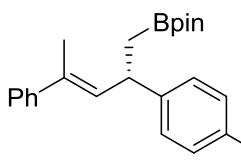
Rotation: $[\alpha]_{20}^D = -26.6$ (c 1.04, CHCl₃), 83.8% *ee* determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 98/2, 1.0 mL/min, n = 254 nm, tr 6.0 (minor), 9.6 (major). The analysis data are same as **2f**.



(*S,E*)-2-(4-(4-fluorophenyl)-2-phenylpent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*S*-2i**)** Prepared according to the general Procedure D, using 0.2376 g (1.0 mmol) of **1i**, 37.5 μ L (97%, 0.25 mmol) of HBpin, 0.0086 g (0.0133 mmol) of **L2** FeBr₂, 37.5 μ L (1.0 M in THF, 0.0375 mmol) of NaBHEt₃, and 0.5 mL (0.5 M) of toluene. After 3.0 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.0824 g (0.225 mmol, >20/1 *E/Z*, 90% yield) of the title compound as a colorless oil; Optical Rotation: $[\alpha]_{20}^D = +6.1$ (c 1.03, CHCl₃), 80.1% *ee* determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 98/2, 1.0 mL/min, n = 254 nm, tr 4.4 (minor), 5.4 (major). The analysis data are same as **2i**.

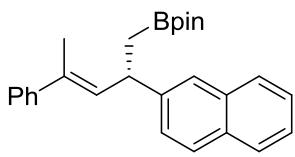


(*S,E*)-2-(2-(4-methoxyphenyl)-4-phenylpent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*S*-2ab**)** Prepared according to the general Procedure D, using 0.2366 g (1.0 mmol) of **1ab**, 37.5 μ L (97%, 0.25 mmol) of HBpin, 0.0086 g (0.0133 mmol) of **L2** FeBr₂, 37.5 μ L (1.0 M in THF, 0.0375 mmol) of NaBHEt₃, and 0.5 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EA (100/1, 150 mL to 20/1, 250 mL) as the eluent to give 0.0903 g (0.239 mmol, >20/1 *E/Z*, 95% yield) of the title compound as a colorless oil; Optical Rotation: $[\alpha]_{20}^D = +3.3$ (c 1.02, CHCl₃), 77.3% *ee* determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 98/2, 1.0 mL/min, n = 254 nm, tr 5.5 (minor), 9.5 (major). The analysis data are same as **2ab**.



(*S,E*)-2-(2-(4-chlorophenyl)-4-phenylpent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S-2ad**)**

Prepared according to the general procedure D, using 0.2526 g (1.0 mmol) of **1ad**, 37.5 μ L (97%, 0.25 mmol) of HBpin, 0.0085 g (0.0131 mmol) of **L2** FeBr₂, 37.5 μ L (1.0 M in THF, 0.0375 mmol) of NaBHEt₃, and 0.5 mL (0.5 M) of toluene. After 3.0 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.0582 g (0.152 mmol, >20/1 *E/Z*, 61% yield) of the title compound as a colorless oil; Optical Rotation: $[\alpha]_{20}^D = -1.0$ (c 1.06, CHCl₃), 87.1% *ee* determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 98/2, 1.0 mL/min, n = 254 nm, tr 4.5 (minor), 6.3 (major). The analysis data are same as **2ad**.



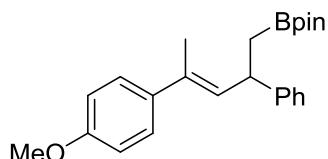
(*S,E*)-4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)-4-phenylpent-3-en-1-yl)-1,3,2-dioxaborolane (S-2ai**)**

Prepared according to the general procedure D, using 0.2721 g (1.0 mmol) of **1ai**, 37.5 μ L (97%, 0.25 mmol) of HBpin, 0.0083 g (0.0129 mmol) of **L2** FeBr₂, 37.5 μ L (1.0 M in THF, 0.0375 mmol) of NaBHEt₃, and 0.5 mL (0.5 M) of toluene. After 3.0 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EA (100/1, 150 mL to 20/1, 250 mL) as the eluent to give 0.0390 g (0.098 mmol, >20/1 *E/Z*, 39% yield) of the title compound as a colorless oil; Optical Rotation: $[\alpha]_{20}^D = -16.1$ (c 1.43, CHCl₃), 90.1% *ee* determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 99/1, 1.0 mL/min, n = 254 nm, tr 7.2 (minor), 11.4 (major). The analysis data are same as **2ai**.

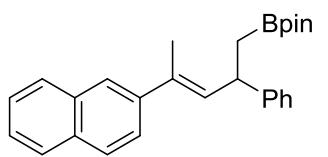
VII. Gram-Scale Reactions

General Procedure E: to a 50 mL flame-dried Schlenk flask cooled under nitrogen, ^{DMiP}OIP FeBr₂ complex (0.25 mmol, 5 mol%) and vinylcyclopropane (10.0 mmol, 2.0 equiv.) were added. The mixture was vacuumed and flushed with nitrogen for three times, and then, 10.0

mL toluene (0.5 M) and HBpin (750 μ L, 97%, 5.0 mmol, 1.0 equiv.) were added in sequence. The mixture was injected with NaBHEt₃ (1.0 M in THF, 750 μ L, 0.75 mmol) by dropwise. Then the reaction was run at ambient temperature. After 3 h, the resulting solution was added 20 mL of ether and filtered through a pad of silica gel, washed by ether (20 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The resulting solution was purified by flash column chromatography using PE/EA (100/1 to 20/1) as the eluent to give the corresponding product.

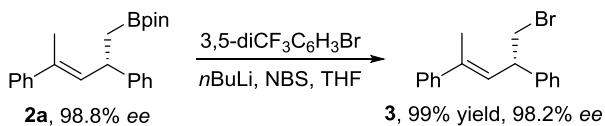


(E)-2-(4-(4-methoxyphenyl)-2-phenylpent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e) Prepared according to the general procedure E, using 2.5029 g (10.0 mmol) of **1e**, 750 μ L (97%, 5.0 mmol) of HBpin, 0.1483 g (0.25 mmol) of ^{DMiP}OIP FeBr₂, 750 μ L (1.0 M in THF, 0.75 mmol) of NaBHEt₃, and 10.0 mL (0.5 M) of toluene. After 3.0 h, the resulting solution was added 20 mL of ether and filtered through a pad of silica gel, washed by ether (20 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EA (100/1 to 20/1) as the eluent to give 1.7160 g (4.54 mmol, 11/1 *E/Z*, 91% yield) of the title compound as a colorless oil.

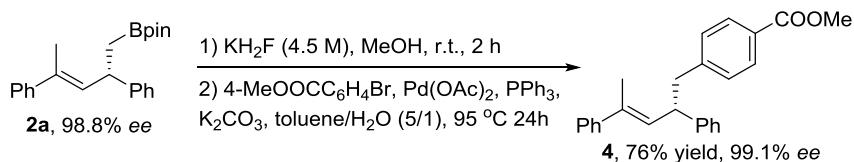


(E)-4,4,5,5-tetramethyl-2-(4-(naphthalen-2-yl)-2-phenylpent-3-en-1-yl)-1,3,2-dioxaborolane (2n) Prepared according to the general procedure E, using 2.7124 g (10.0 mmol) of **1n**, 750 μ L (97%, 0.5 mmol) of HBpin, 0.1483 g (0.25 mmol) of ^{DMiP}OIP FeBr₂, 750 μ L (1.0 M in THF, 0.75 mmol) of NaBHEt₃, and 10.0 mL (0.5 M) of toluene. After 3.0 h, the resulting solution was added 20 mL of ether and filtered through a pad of silica gel, washed by ether (20 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ¹H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EA (100/1 to 20/1) as the eluent to give 1.6948 g (4.25 mmol, > 20/1 *E/Z*, 85% yield) of the title compound as a white solid.

VIII. Further Derivatizations

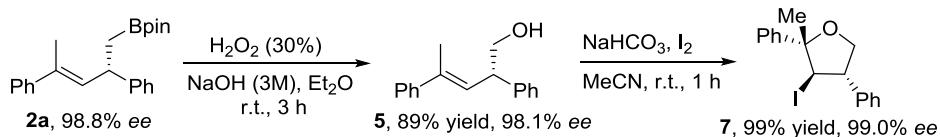


(S,E)-(5-bromopent-2-ene-2,4-diyl)dibenzene (3): Prepared according to a previously reported procedure,⁵ a 10 mL flame-dried Schlenk flask cooled under nitrogen was charged with 3,5-bis(trifluoromethyl)-1-bromobenzene (0.1766 g, 2.0 equiv.) and THF (1 mL), then cooled to -78 °C. A solution of *n*BuLi (240 μL, 2.5 M in hexanes, 2.0 equiv.) was added dropwise. After stirred at -78 °C for 1 h, a solution of **2a** (0.1032 g, 0.3 mmol) in THF (1 mL) was then added dropwise. The reaction mixture was allowed to stir at -78 °C for 30 min and at r.t. for 30 min. Then a solution of NBS (0.1087 g, 2.0 equiv.) in THF (1 mL) was added dropwise and stir at r.t. for 1 h. The reaction was quenched with saturated aqueous Na₂S₂O₃ (2 mL), extracted with ethyl acetate (15 mL x 3). The organic layers were combined, washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The crude product was purified by column chromatography using PE/EA (50/1) as the eluent to give 0.1007 g (0.297 mmol, 99% yield) of the title compound as a brown oil. Optical Rotation: [α]₂₀^D = +5.4 (c 1.34, CHCl₃), 98.2% ee determined by HPLC, HPLC conditions: Chiralcel AD-H x 2, *n*-hexane/*i*-PrOH = 99.1/0.1, 0.5 mL/min, n = 220 nm, tr 30.0 (minor), 33.2 (major). IR (cm⁻¹): 3027, 2956, 1599, 1493, 1449, 1279. ¹H NMR (CDCl₃, 400 MHz): δ 7.42-7.37 (m, 2H), 7.37-7.22 (m, 8H), 5.95 (dd, J = 9.4, 1.6 Hz, 1H), 4.13-4.04 (m, 1H), 3.71-7.59 (m, 2H), 2.07 (d, J = 1.2 Hz, 3H); ¹³C NMR: (CDCl₃, 100 MHz) : δ 143.2, 142.2, 137.8, 128.7, 128.5, 128.2, 127.6, 127.14, 127.06, 125.9, 47.2, 37.8, 16.6. HRMS (EI) calculated for [C₁₇H₁₇Br]⁺ requires m/z 300.0514, found m/z 300.0508.



Methyl (S,E)-4-(2,4-diphenylpent-3-en-1-yl)benzoate (4): Prepared according to a previously reported procedure,⁶ to a solution of **2a** (0.1056 g, 0.3 mmol, 1.0 equiv.) in 1.5 mL of MeOH (0.20 M), KH₂F (0.3 mL, 4.5 M in water) was added dropwise. Then the mixture was stirred at ambient

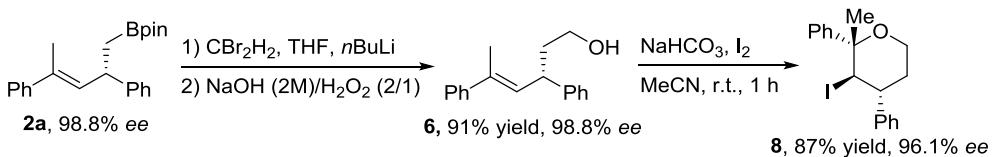
for 2 h. Then the mixture was concentrated in vacuo and the solid residue was triturated with dry acetone (5 mL). The liquid phase was carefully decanted, and the residual inorganic salts were washed with additional acetone (3×2 mL). The combined solution was concentrated in vacuo to give a white solid. The solid was washed with ether (3×5 mL) to remove pinacol and dried under vacuum, affording potassium alkyltrifluoroborate 0.0860 g (0.262 mmol, 86% yield). To a 25 mL dried seal tube cooled under nitrogen was charged with potassium alkyltrifluoroborate (0.0667 g, 0.2 mmol) obtained above, methyl 4-bromobenzoate (0.0450 g, 0.2 mmol, 1.0 equiv.), K_2CO_3 (0.0846 g, 0.6 mmol, 3.0 equiv.), $PPPh_3$ (0.0121 g, 0.04 mmol, 20 mol%), $Pd(OAc)_2$ (0.0046 g, 0.02 mmol, 10 mol%), toluene (2.0 mL) and H_2O (0.4 mL). The mixture was added and stirred at 95 °C for 24 h, then cooled to room temperature and extracted with Et_2O (15 mL x 3). The organic layers were combined, washed with brine, dried over Na_2SO_4 , concentrated and purified by column chromatography using PE/EA (100/1 to 20/1) as the eluent to give 0.0635 g (0.178 mmol, 76% total yield via two steps) of the title compound as a colorless oil. Optical Rotation: $[\alpha]_{20}^D = +47.5$ (c 0.90, $CHCl_3$), 99.1% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, n = 254 nm, tr 13.8 (major), 24.0 (minor). IR (cm^{-1}): 2950, 1720, 1680, 1438, 1280. 1H NMR ($CDCl_3$, 400 MHz): δ 7.90 (d, $J = 8.4$ Hz, 2H), 7.32-7.15 (m, 12H), 5.94 (dd, $J = 9.6, 1.2$ Hz, 1H), 3.97-3.89 (m, 1H), 3.89 (s, 3H), 3.16 (dd, $J = 13.2, 6.2$ Hz, 1H), 3.04 (dd, $J = 13.2, 9.0$ Hz, 1H), 1.80 (d, $J = 1.2$ Hz, 3H); ^{13}C NMR: ($CDCl_3$, 100 MHz) : δ 167.2, 145.7, 144.3, 143.7, 135.8, 130.6, 129.4, 129.3, 128.6, 128.1, 127.9, 127.4, 126.8, 126.3, 125.8, 52.0, 46.8, 43.8, 16.2. HRMS (EI) calculated for $[C_{25}H_{24}O_2]^+$ requires m/z 356.1776, found m/z 356.1174.



(S,E)-2,4-diphenylpent-3-en-1-ol (5): Prepared according to a previously reported procedure,⁸ to a solution of **2a** (0.1759 g, 0.5 mmol, 1.0 equiv.) in 4 mL of Et_2O (0.125 M), hydrogen peroxide (3.0 mL, 30% aqueous solution) and $NaOH$ aqueous solution (4.0 mL, 3.0 M) were added in sequence. The mixture was stirred at r.t. for 3 h and then extracted with Et_2O (5 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo.

The residue was purified by column chromatography using PE/EA (5/1) as the eluent to give 0.1138 g (0.451 mmol, 89% yield) of the title compound as a white solid. mp: 56.0–56.9 °C (by column chromatography using PE/EA). Optical Rotation: $[\alpha]_{20}^D = -67.5$ (c 1.01, CHCl₃), 98.1% *ee* determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, n = 254 nm, tr 6.9 (major), 7.7 (minor). IR (cm⁻¹): 3373, 3027, 2924, 1599, 1493, 1448, 1381. ¹H NMR (CDCl₃, 400 MHz): δ 7.42–7.37 (m, 2H), 7.37–7.28 (m, 6H), 7.27–7.20 (m, 2H), 5.97 (dd, J = 9.2, 1.0 Hz, 1H), 3.98–3.78 (m, 3H), 2.10 (d, J = 1.0 Hz, 3H), 1.48 (t, J = 6.6 Hz, 1H); ¹³C NMR: (CDCl₃, 100 MHz) : δ 143.3, 141.6, 138.1, 128.8, 128.2, 127.9, 127.5, 127.1, 126.8, 125.8, 67.3, 47.9, 16.5. HRMS (EI) calculated for [C₁₇H₁₈O]⁺ requires m/z 238.1358, found m/z 238.1360.

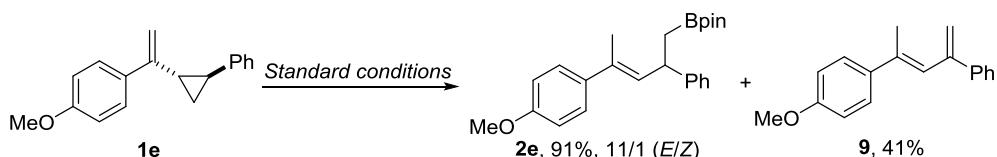
(2*S*,3*R*,4*S*)-3-iodo-2-methyl-2,4-diphenyltetrahydrofuran (7): Prepared according to a previously reported procedure,⁷ under the atmosphere of nitrogen, to a solution of **5** (0.0493 g, 0.2 mmol, 1.0 equiv.) in 20 mL of MeCN, NaHCO₃ (0.0548 g, 0.60 mmol, 3.0 equiv.) and I₂ (0.1052 g, 0.4 mmol, 2.0 equiv.) were added in sequence. The mixture was stirred at r.t. for 1 h. Then the mixture was quenched with saturated aqueous Na₂S₂O₃, extracted with ethyl acetate (15 mL x 3). The organic layers were combined, washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The crude product was purified by column chromatography using PE/EA (100/1 to 50/1) as the eluent to give 0.0778 g (0.198 mmol, 99% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]_{20}^D = -24.3$ (c 1.09, CHCl₃), 99.0% *ee* determined by HPLC, HPLC conditions: Chiralcel AD-H x 2, *n*-hexane/*i*-PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 18.1 (major), 20.4 (minor). IR (cm⁻¹): 3030, 2927, 1671, 1602, 1495, 1447, 1375, 1214. ¹H NMR (CDCl₃, 400 MHz): δ 7.66–7.61 (m, 2H), 7.41–7.25 (m, 6H), 7.25–7.20 (m, 2H), 4.32 (dd, J = 8.6, 8.4 Hz, 1H), 4.24 (d, J = 10.8 Hz, 1H), 3.94 (dd, J = 9.6, 8.6 Hz, 1H), 3.84–3.75 (m, 1H), 1.88 (s, 3H); ¹³C NMR: (CDCl₃, 100 MHz) : δ 145.4, 137.7, 128.8, 128.5, 127.62, 127.58, 127.4, 124.8, 85.2, 72.8, 56.8, 42.9, 29.4. HRMS (EI) calculated for [C₁₆H₁₄IO]⁺ ([M-Me]⁺) requires m/z 349.0089, found m/z 349.0092.



(S,E)-3,5-diphenylhex-4-en-1-ol (6): Prepared according to a previously reported procedure,⁵ a 10 mL flame-dried Schlenk flask cooled under nitrogen was charged with **2a** (0.1036 g, 0.3 mmol), dibromomethane (52.6 uL, 2.5 equiv) and THF (2 mL), then cooled to -78 °C. A solution of *n*BuLi (264 uL, 2.5 M in hexanes, 2.2 equiv) was added dropwise. The resulting mixture was stirred at -78 °C for 10 min and warm to room temperature. After stirred at r.t. for 2 h, the reaction mixture was cooled to 0 °C, a premixed solution of NaOH (2 M, aq.)/30% H₂O₂ (2:1, 3 mL) was added dropwise and stirred at r.t. for 3 h. The reaction was quenched with 10 mL water, extracted with ethyl acetate (15 mL x 3). The organic layers were combined, washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The crude product was purified by column chromatography using PE/EA (10/1) as the eluent to give 0.0684 g (0.271 mmol, 91% yield) of the title compound as a colorless oil. Optical Rotation: [α]₂₀^D = -30.3 (c 0.90, CHCl₃), 98.8% ee determined by HPLC, HPLC conditions: Chiralcel AD-H x 2, *n*-hexane/*i*-PrOH = 98/2, 1.0 mL/min, n = 254 nm, tr 52.0 (major), 54.0 (minor). IR (cm⁻¹): 3362, 3026, 1599, 1493, 1449, 1381. ¹H NMR (CDCl₃, 400 MHz): δ 7.40-7.34 (m, 2H), 7.34-7.25 (m, 6H), 7.24-7.16 (m, 2H), 5.92 (dd, J = 9.6, 1.0 Hz, 1H), 3.92-3.85 (m, 1H), 3.70-3.61 (m, 2H), 2.10 (d, J = 1.0 Hz, 3H), 2.07-1.95 (m, 2H), 1.31 (br, 1H); ¹³C NMR: (CDCl₃, 100 MHz) : δ 144.8, 143.6, 135.3, 131.5, 128.6, 128.1, 127.4, 126.8, 126.2, 125.8, 61.0, 41.3, 39.9, 16.3. HRMS (EI) calculated for [C₁₈H₂₀O]⁺ requires m/z 252.1514, found m/z 252.1518.

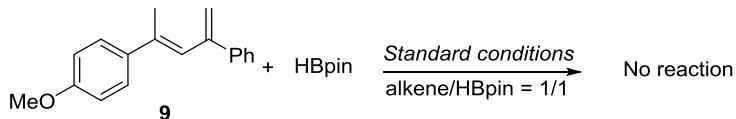
(2*S*,3*R*,4*R*)-3-iodo-2-methyl-2,4-diphenyltetrahydro-2*H*-pyran (8): Prepared according to a previously reported procedure,⁷ under the atmosphere of nitrogen, to a solution of **6** (0.0382 g, 0.15 mmol, 1.0 equiv.) in 15 mL of MeCN, NaHCO₃ (0.0399 g, 0.45 mmol, 3.0 equiv.) and I₂ (0.0791 g, 0.30 mmol, 2.0 equiv.) were added in sequence. The mixture was stirred at r.t. for 1 h. Then the mixture was quenched with saturated aqueous Na₂S₂O₃, extracted with ethyl acetate (15 mL x 3). The organic layers were combined, washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The crude product was purified by column chromatography using PE/EA (100/1 to 50/1) as the eluent to give 0.0499 g (0.132 mmol, 87% yield) of the title compound as a

white solid, mp: >130 °C (decomposed, by column chromatography using PE/EA). Optical Rotation: $[\alpha]_{20}^D = +80.5$ (c 1.40, CHCl₃), 96.1% *ee* determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 98/2, 1.0 mL/min, n = 220 nm, tr 5.4 (minor), 6.1 (major). IR (cm⁻¹): 2922, 1726, 1492, 1451, 1375, 1146. ¹H NMR (CDCl₃, 400 MHz): δ 7.70-7.65 (m, 2H), 7.40-7.25 (m, 6H), 7.23-7.17 (m, 2H), 4.37 (d, J = 12.4 Hz, 1H), 4.10 (td, J = 12.4, 2.6 Hz, 1H), 4.04-3.97 (m, 1H), 3.40 (td, J = 12.4, 4.0 Hz, 1H), 2.21-2.10 (m, 1H), 2.09 (d, 3H), 1.96-7.88 (m, 1H); ¹³C NMR: (CDCl₃, 100 MHz) : δ 145.4, 145.3, 128.6, 127.9, 127.8, 127.2, 127.1, 126.2, 78.9, 61.5, 48.9, 48.6, 37.0, 17.0. HRMS (EI) calculated for [C₁₈H₁₉IO]⁺ requires m/z 378.0481, found m/z 378.0473.

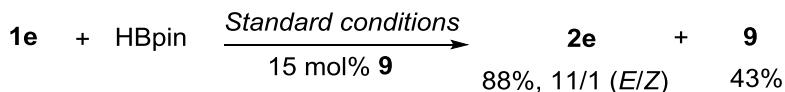


Prepared according to the general procedure A, using 0.2499 g (1.0 mmol) of **1e**, 75 μL (97%, 0.5 mmol) of HBpin, 0.0151 g (0.025 mmol) of ^{DMP}OIP FeBr₂, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated, yield and stereoselectivity were monitored by ¹H NMR analysis (using 10 uL trimethylphenylsilane as internal standard).

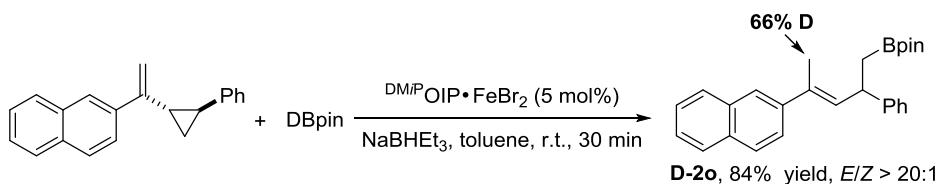
(E)-1-methoxy-4-(4-phenylpenta-2,4-dien-2-yl)benzene (9), 41%
 NMR yield; white solid; mp: 124.6-126.5 °C (crystallized from ethanol). IR (cm⁻¹): 2954, 2835, 1598, 1512, 1447, 1257, 1186. ¹H NMR (CDCl₃, 400 MHz): δ 7.49-7.41 (m, 4H), 7.32 (t, J = 7.6 Hz, 2H), 7.24-7.14 (m, 2H), 6.89 (d, J = 8.2 Hz, 2H), 6.68-6.55 (m, 2H), 3.83 (s, 3H), 2.25 (s, 3H); ¹³C NMR: (CDCl₃, 100 MHz): δ 159.0, 137.9, 136.3, 135.5, 132.0, 128.6, 127.2, 126.7, 126.2, 126.0, 125.8, 113.7, 55.3, 16.2; HRMS (EI) calculated for [C₁₈H₁₈O]⁺ requires m/z 250.1358, found m/z 250.1357.



Prepared according to the general procedure A, using 0.1266 g (0.5 mmol) of **9**, 75 μ L (97%, 0.5 mmol) of HBpin, 0.0151 g (0.025 mmol) of ^{DMiP}OIP FeBr₂, 75 μ L (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated, yield and stereoselectivity were monitored by ¹H NMR analysis (using 10 uL trimethylphenylsilane as internal standard).

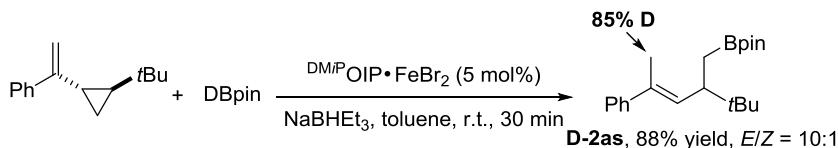


Prepared according to the general procedure A, using 0.2503 g (1.0 mmol) of **1e**, 0.0187 g (0.075 mmol) of **9**, 75 μ L (97%, 0.5 mmol) of HBpin, 0.0151 g (0.025 mmol) of ^{DMiP}OIP FeBr₂, 75 μ L (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated, yield and stereoselectivity were monitored by ¹H NMR analysis (using 10 uL trimethylphenylsilane as internal standard).



(E)-4,4,5,5-tetramethyl-2-(4-(naphthalen-2-yl)-2-phenylpent-3-en-1-yl-5-d)-1,3,2-dioxaborola ne (D-2o): to a 25 mL flame-dried Schlenk flask cooled under nitrogen, 0.0148 g of ^{DMiP}OIP FeBr₂ complex (0.025 mmol, 5 mol%) and 0.2717 g of **1n** (1.0 mmol, 2.0 equiv.) were added. The mixture was vacuumed and flushed with nitrogen for three times, and then, 1.0 mL of toluene (0.5 M) and DBpin (75 μ L, 96%, 0.5 mmol, 1.0 equiv.) were added in sequence. The mixture was injected with NaBHEt₃ (1.0 M in THF, 75 μ L, 0.075 mmol) by dropwise. Then the reaction was run at ambient temperature. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates

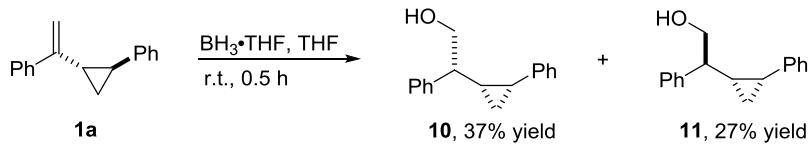
were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EA (100/1, 150 mL to 20/1, 250 mL) as the eluent to give 0.1682 g (0.421 mmol, > 20/1 *E/Z*, 84% yield) of the title compound as a white solid. mp: 70.5-72.5 °C (by flash column chromatography using PE/EA). IR (cm^{-1}): 2978, 1598, 1365, 1327, 1144. ^1H NMR (CDCl_3 , 400 MHz): δ 7.81-7.71 (m, 4H), 7.57 (dd, J = 8.6, 1.8 Hz, 1H), 7.46-7.37 (m, 2H), 7.36-7.31 (m, 2H), 7.31-7.25 (m, 2H), 7.19-7.13 (m, 1H), 6.09-6.04 (m, 1H), 4.10-4.02 (m, 1H), 2.25-2.20 (m, 2.34H), 1.45-1.34 (m, 2H), 1.15 (s, 12H); ^{13}C NMR: (CDCl_3 , 100 MHz) : δ 146.7, 141.1, 134.4, 133.4, 133.2, 133.1, 132.4, 128.4, 128.0, 127.5, 127.4, 127.1, 125.9, 125.9, 125.4, 124.6, 124.2, 83.1, 40.4, 24.8, 24.7, 16.4-15.8 (m); ^2D NMR: (CDCl_3 , 77 MHz) : δ 2.34. HRMS (EI) calculated for $[\text{C}_{27}\text{H}_{30}\text{DBO}_2]^+$ requires m/z 399.2480, found m/z 399.2479.



(*E*)-2-(2-(tert-butyl)-4-phenylpent-3-en-1-yl-5-*d*)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

(D-2as): to a 25 mL flame-dried Schlenk flask cooled under nitrogen, 0.0150 g of $^{\text{DMiP}}$ OIP FeBr₂ complex (0.025 mmol, 5 mol%) and 0.1020 g of **1as** (1.0 mmol, 2.0 equiv.) were added. The mixture was vacuumed and flushed with nitrogen for three times, and then, 1.0 mL of toluene (0.5 M) and DBpin (75 μL , 96%, 0.5 mmol, 1.0 equiv.) were added in sequence. The mixture was injected with NaBHET₃ (1.0 M in THF, 75 μL , 0.075 mmol) by dropwise. Then the reaction was run at ambient temperature. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE (150 mL) to PE/EA (50/1, 250 mL) as the eluent to give 0.1451 g (0.441 mmol, 10/1 *E/Z*, 88% yield) of the title compound as a colorless oil. IR (cm^{-1}): 2965, 1491, 1365, 1328, 1145. ^1H NMR (CDCl_3 , 400 MHz): δ 7.40-7.34 (m, 2H), 7.31-7.24 (m, 2H), 7.22-7.16 (m, 1H), 5.60 (d, J = 10.8 Hz, 1H), 2.52 (td, J = 11.6, 3.6 Hz, 1H), 2.08-2.03 (m, 2.15H), 1.16 (s, 6H), 1.15 (s, 6H), 1.10-1.03 (m, 1H), 0.89 (s, 9H), 0.86-0.73 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz) : δ 144.6, 134.1, 132.6, 128.0, 126.3, 125.9, 82.9, 44.4, 34.8.

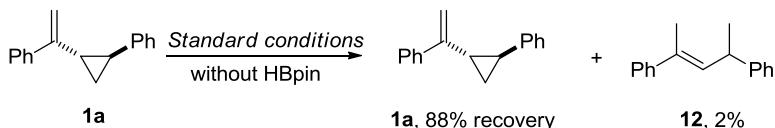
27.2, 25.0, 24.7, 16.7-16.2 (m); 2 D NMR: (CDCl_3 , 77 MHz) : δ 2.10. HRMS (EI) calculated for $[\text{C}_{21}\text{H}_{32}\text{DBO}_2]^+$ requires m/z 329.2636, found m/z 329.2635.



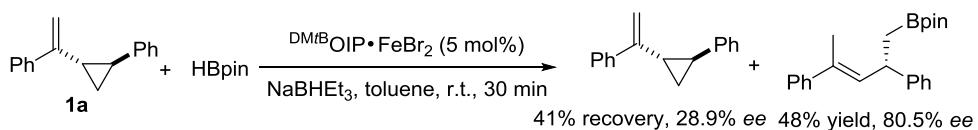
cis/trans-2-phenyl-2-(2-phenylcyclopropyl)ethan-1-ol (10/11): A 25 mL flame-dried Schlenk flask cooled under nitrogen charged with 0.1154 g of **1a** (0.5 mmol) and 1.0 mL of THF (0.5 M). The mixture was injected with $\text{BH}_3 \cdot \text{THF}$ (1.0 M in THF, 500 μL , 0.5 mmol) by dropwise and stirred at ambient temperature. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE/EA (10/1) as the eluent to give 0.0465 g (0.195 mmol, 37% yield) of **10** as a colorless oil and 0.0331 g (0.139 mmol, 27% yield) of **11** as a colorless oil.

cis-2-phenyl-2-(2-phenylcyclopropyl)ethan-1-ol (10): ^1H NMR (CDCl_3 , 400 MHz): δ 7.39-7.32 (m, 2H), 7.31-7.24 (m, 5H), 7.19-7.13 (m, 1H), 7.11-7.06 (m, 2H), 3.98-3.83 (m, 2H), 2.35-2.27 (m, 1H), 1.94-1.87 (m, 1H), 1.47 (tr, 1H), 1.35-1.24 (m, 1H), 0.96-0.89 (m, 1H), 0.85-0.78 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz) : δ 142.8, 141.6, 128.6, 128.4, 128.0, 126.9, 125.7, 125.6, 67.3, 53.2, 25.8, 23.8, 14.1. HRMS (EI) calculated for $[\text{C}_{17}\text{H}_{18}\text{O}]^+$ requires m/z 238.1358, found m/z 238.1359.

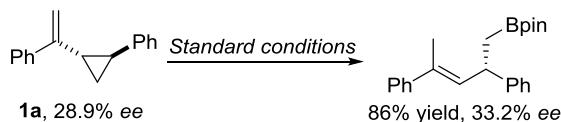
trans-2-phenyl-2-(2-phenylcyclopropyl)ethan-1-ol (11): ^1H NMR (CDCl_3 , 400 MHz): δ 7.34-7.28 (m, 2H), 7.27-7.22 (m, 3H), 7.22-7.16 (m, 2H), 7.14-7.07 (m, 1H), 6.99-6.93 (m, 2H), 4.00-3.85 (m, 2H), 2.38-2.29 (m, 1H), 1.75-1.67 (m, 1H), 1.48 (tr, 1H), 1.43-1.33 (m, 1H), 1.14-1.07 (m, 1H), 1.03-0.95 (m, 1H); ^{13}C NMR: (CDCl_3 , 100 MHz) : δ 142.7, 141.6, 128.6, 128.2, 128.0, 126.8, 126.0, 125.4, 67.2, 53.0, 24.7, 21.7, 15.7. HRMS (EI) calculated for $[\text{C}_{17}\text{H}_{18}\text{O}]^+$ requires m/z 238.1358, found m/z 238.1361.



Prepared according to the general procedure A, using 0.2499 g (1.0 mmol) of **1a**, 0.0147 g (0.025 mmol) of ^{DMiP}OIP FeBr₂, 75 μ L (1.0 M in THF, 0.075 mmol) of NaBHEt₃, and 1.0 mL (0.5 M) of toluene. After 3 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated. The yield and stereoselectivity were monitored by ¹H NMR analysis (using 10 μ L trimethylphenylsilane as internal standard).



Prepared according to the general procedure A, using 0.8787 g (4.0 mmol) of **1a**, 300 μ L (97%, 2.0 mmol) of HBpin, 0.0649 g (0.10 mmol) of ^{DMiB}OIP FeBr₂, 300 μ L (1.0 M in THF, 0.3 mmol) of NaBHEt₃, and 4.0 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (20 mL x 3). The combined filtrates were concentrated, yield and stereoselectivity were monitored by ¹H NMR analysis (using 40 μ L trimethylphenylsilane as internal standard).

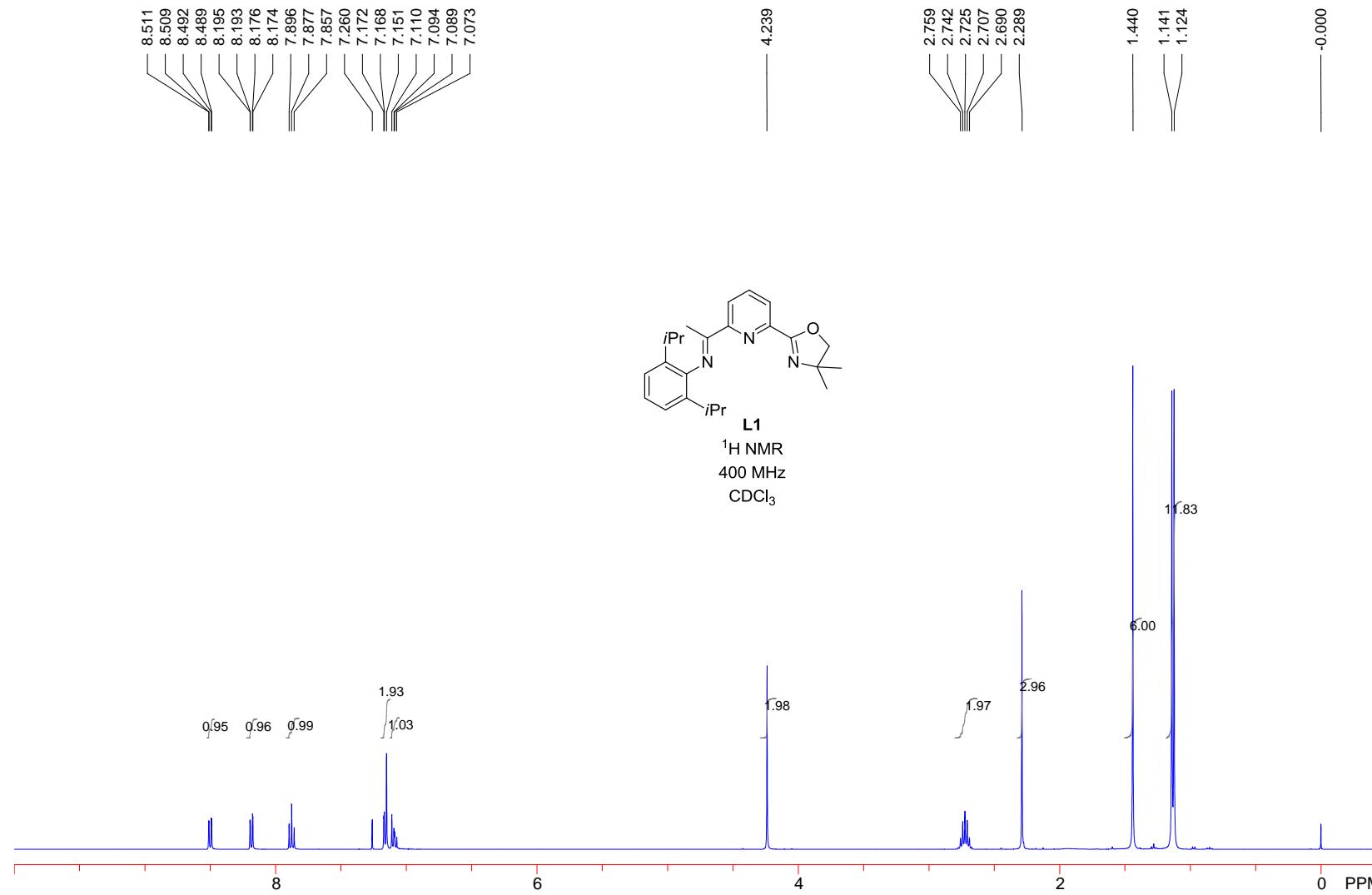


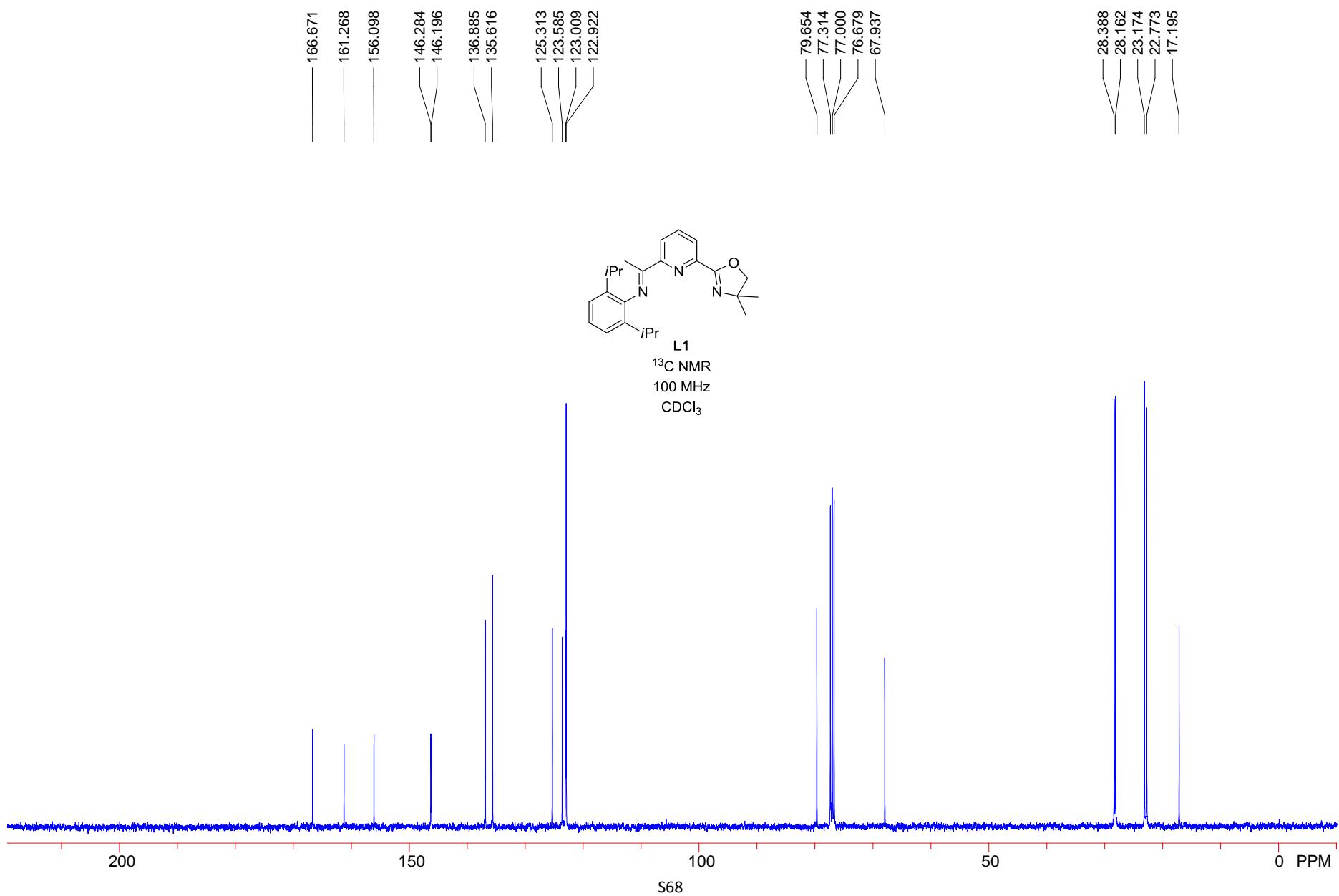
Prepared according to the general procedure A, using 0.1382 g (0.6 mmol) of **1a**, 45 μ L (97%, 0.3 mmol) of HBpin, 0.0091 g (0.015 mmol) of ^{DMiP}OIP FeBr₂, 45 μ L (1.0 M in THF, 0.045 mmol) of NaBHEt₃, and 0.6 mL (0.5 M) of toluene. After 0.5 h, the resulting solution was added 10 mL of ether and filtered through a pad of silica gel, washed by ether (10 mL x 3). The combined filtrates were concentrated, yield and stereoselectivity were monitored by ¹H NMR analysis (using 10 μ L trimethylphenylsilane as internal standard).

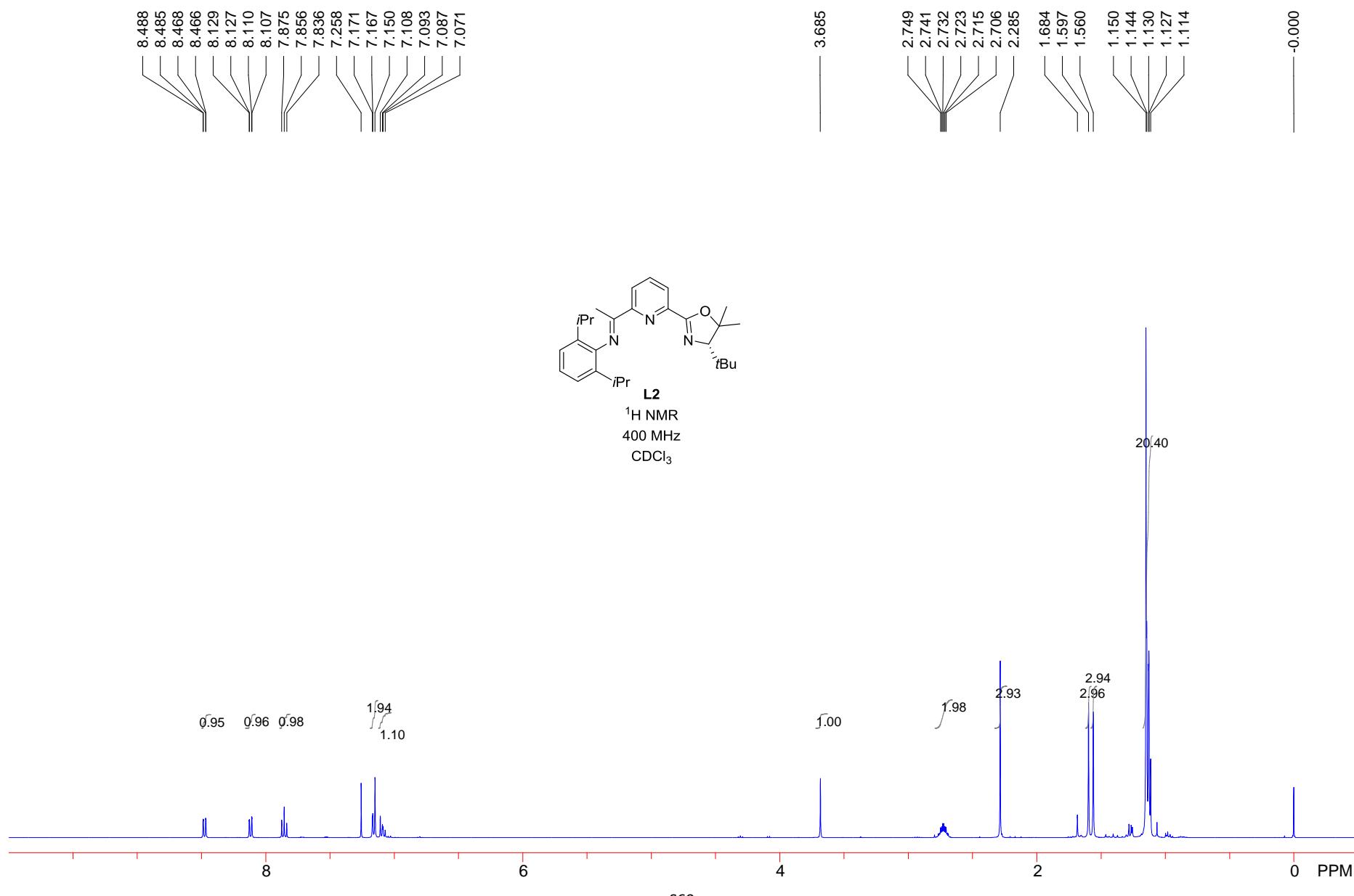
IX. References

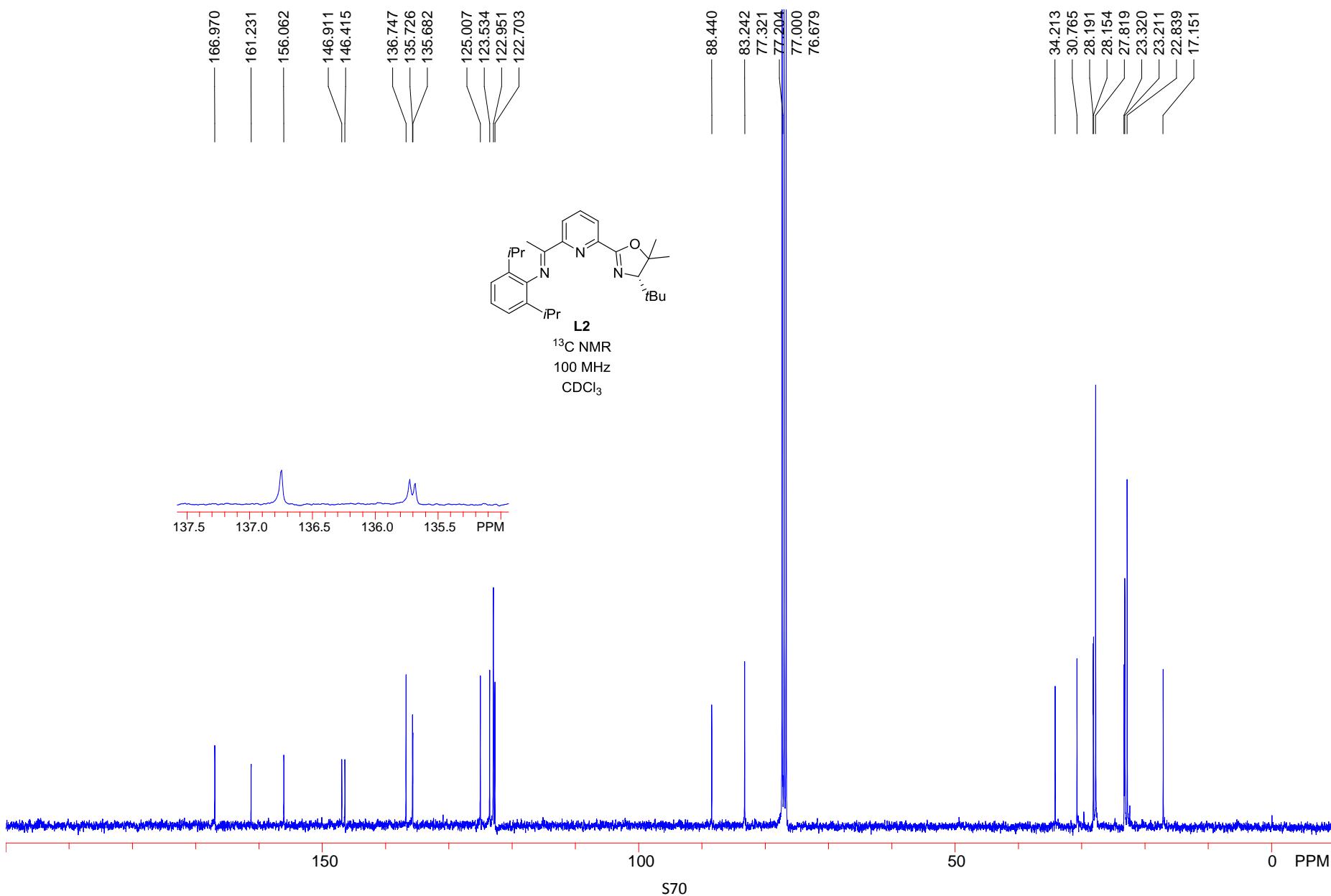
- (1) (a) J.-H. Chen, T. Xi, Z. Lu, *Org. Lett.* **2014**, 16, 6452-6455. (b) J.-H. Chen, T. Xi, X. Ren, B. Cheng, J. Guo, Z. Lu, *Org. Chem. Front.* **2014**, 1, 1306-1309. (c) T. Xi, Y.-C. Mei, Z. Lu, *Org. Lett.* **2015**, 17, 5939-5941.
- (2) (a) R.-Y. Jin, X.-H. Sun, Y.-F. Liu, W. Long, B. Chen, S.-Q. Shen, H.-X. Ma, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2016**, 152, 226. (b) M. Breugst, E. Detmar, D. von der Heiden, *ACS Catal.* **2016**, 6, 3203. (c) K. Kumar, S. S. More, S. Goyal, M. Gangar, G. L. Khatik, R. K. Rawal, V. A. Nair, *Tetrahedron Letters* **2016**, 57, 2315. (d) M. R. Harris, M. O. Konev, E. R. Jarvo, *J. Am. Chem. Soc.* **2014**, 136, 7825.
- (3) (a) J. A. Ciaccio, C. E. Aman, *Synthetic Communications* **2006**, 36, 1333. (b) J. Xu, N. B. Samsuri, H. A. Duong, *Chem. Commun.* **2016**, 52, 3372.
- (4) (a) M. Yilmaz, *Tetrahedron* **2011**, 67, 8255. (b) T. Ikawa, K. Hattori, H. Sajiki, K. Hirota, *Tetrahedron* **2004**, 60, 6901. (c) G. Urgoitia, R. SanMartin, M. T. Herrero, E. Dominguez, *Adv. Synth. Catal.* **2016**, 358, 3307. (d) Y. Arai, R. Tomita, G. Ando, T. Koike, M. Akita, *Chem. Eur. J.* **2016**, 22, 1262. (e) K. Miyazawa, T. Koike, M. Akita, *Chem. Eur. J.* **2015**, 21, 11677. (f) C. Chatalova-Sazepin, Q. Wang, G. M. Sammis, J. Zhu, *Angew. Chem. Int. Ed.* **2015**, 54, 5443.
- (5) Y. Xi, J. F. Hartwig, *J. Am. Chem. Soc.* **2016**, 138, 6703.
- (6) H. Zhang, Z. Lu, *ACS Catal.* **2016**, 6, 6596.
- (7) J. L. Nallasivam, R. A. Fernandes, *J. Am. Chem. Soc.* **2016**, 138, 13238.
- (8) C. Mazet, D. Geirard, *Chem. Commun.* **2011**, 47, 298.

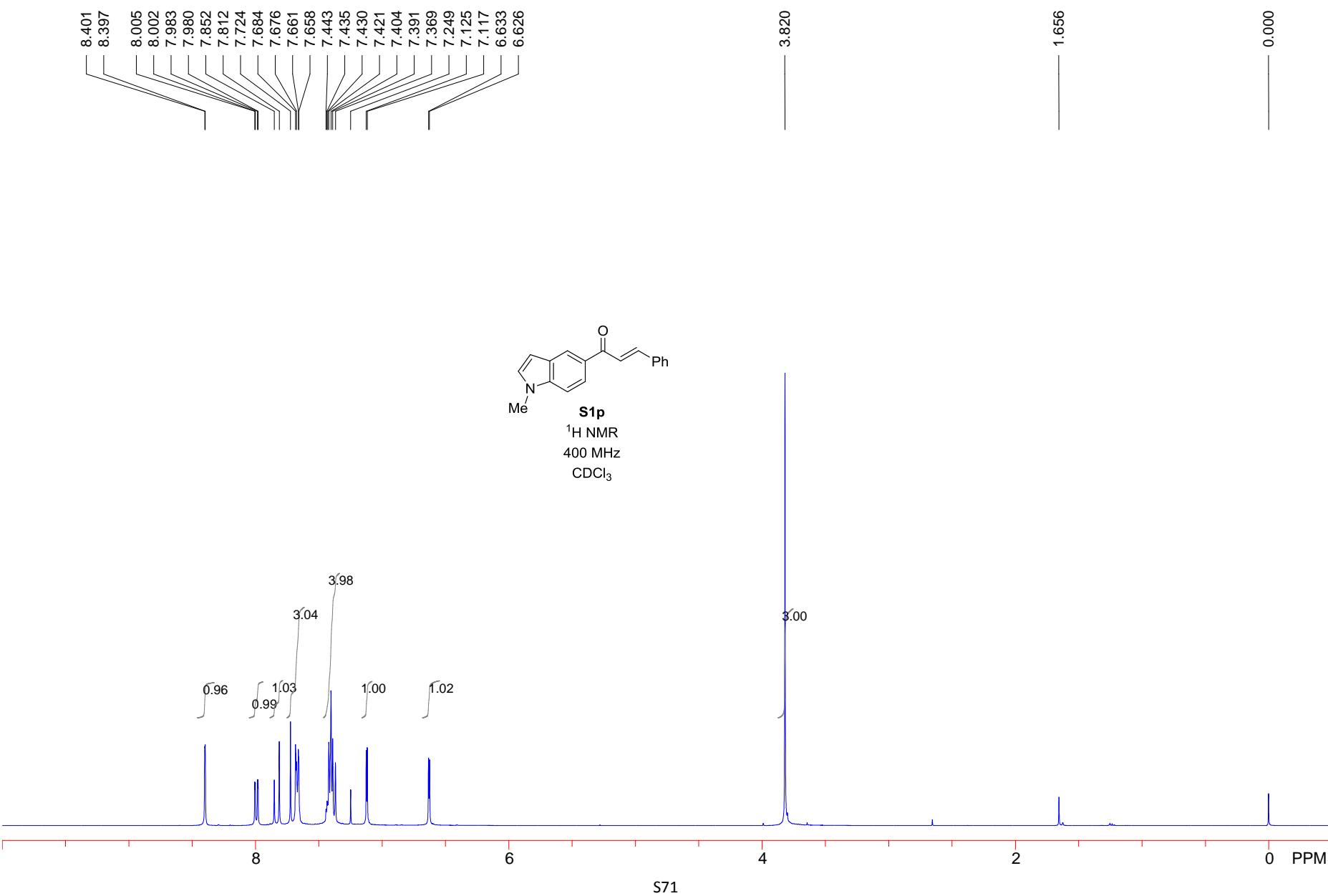
X. NMR Spectra

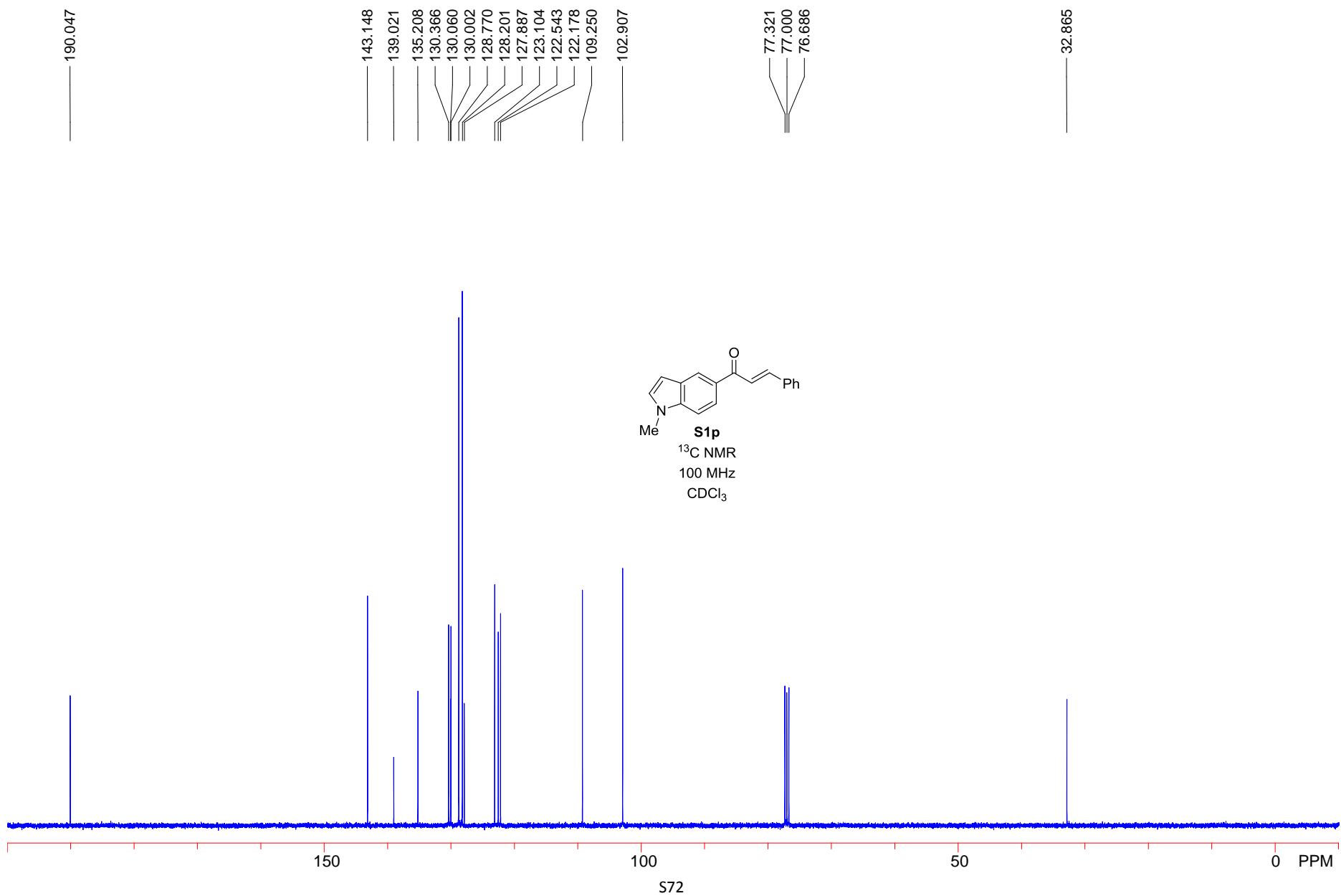


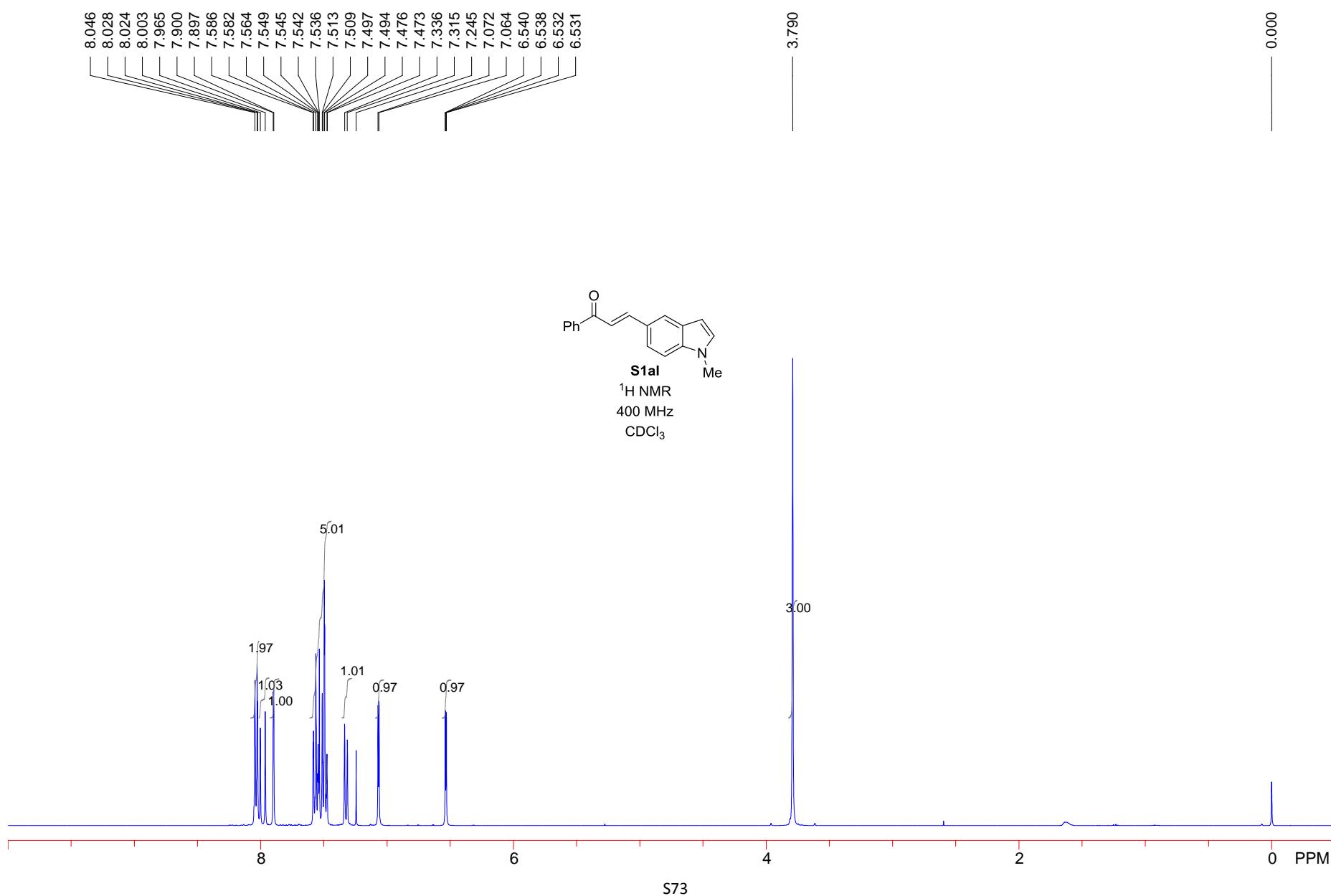


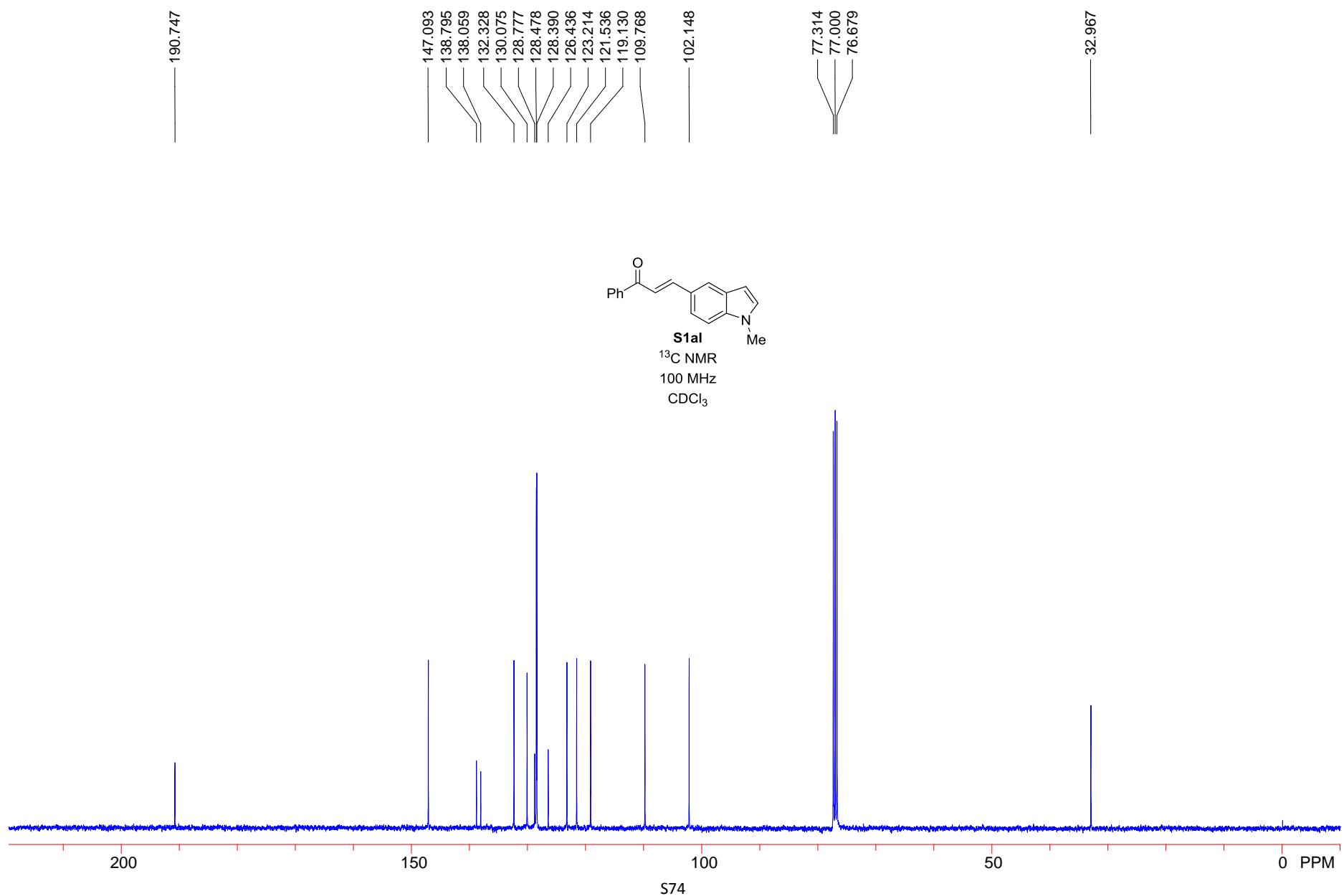


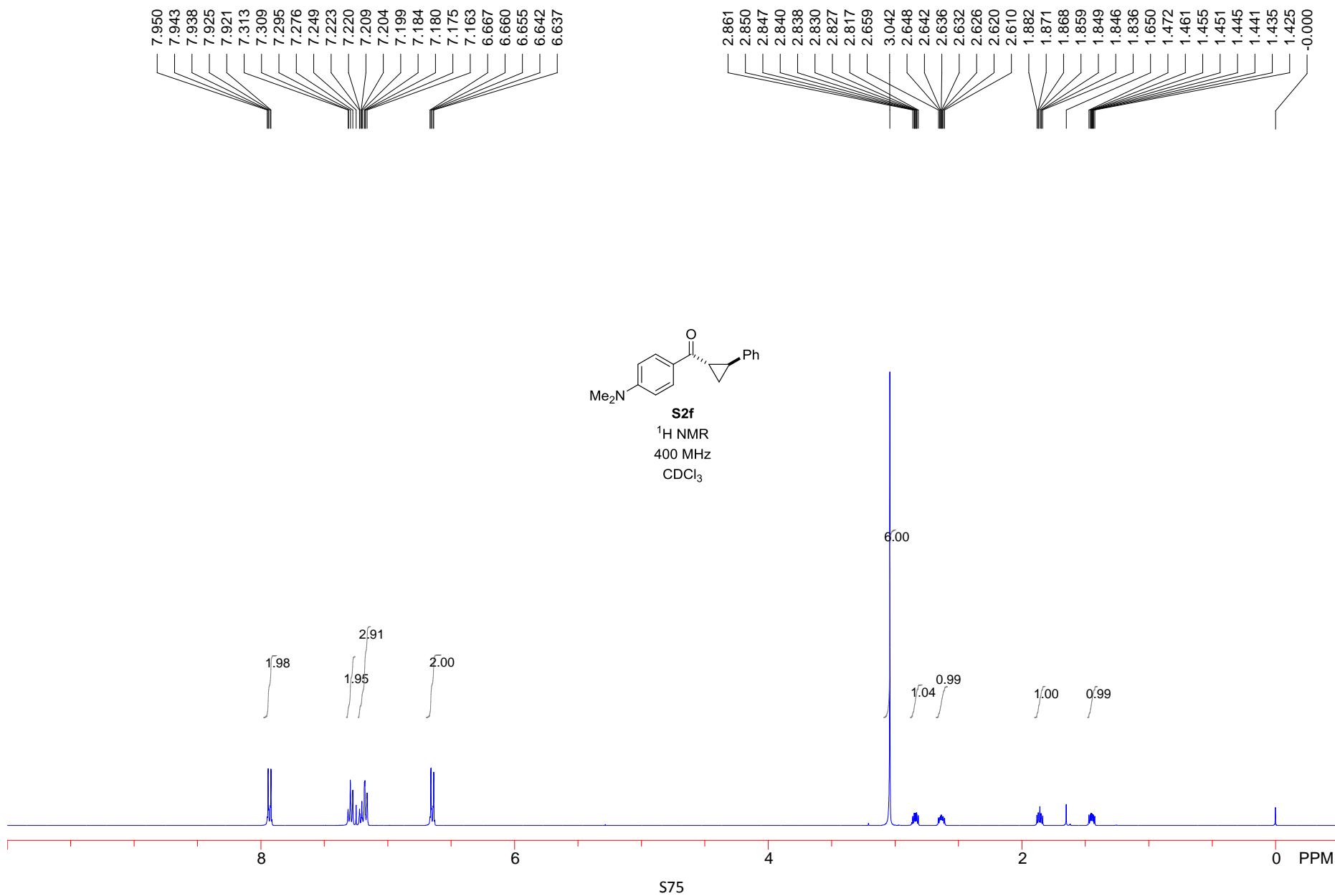


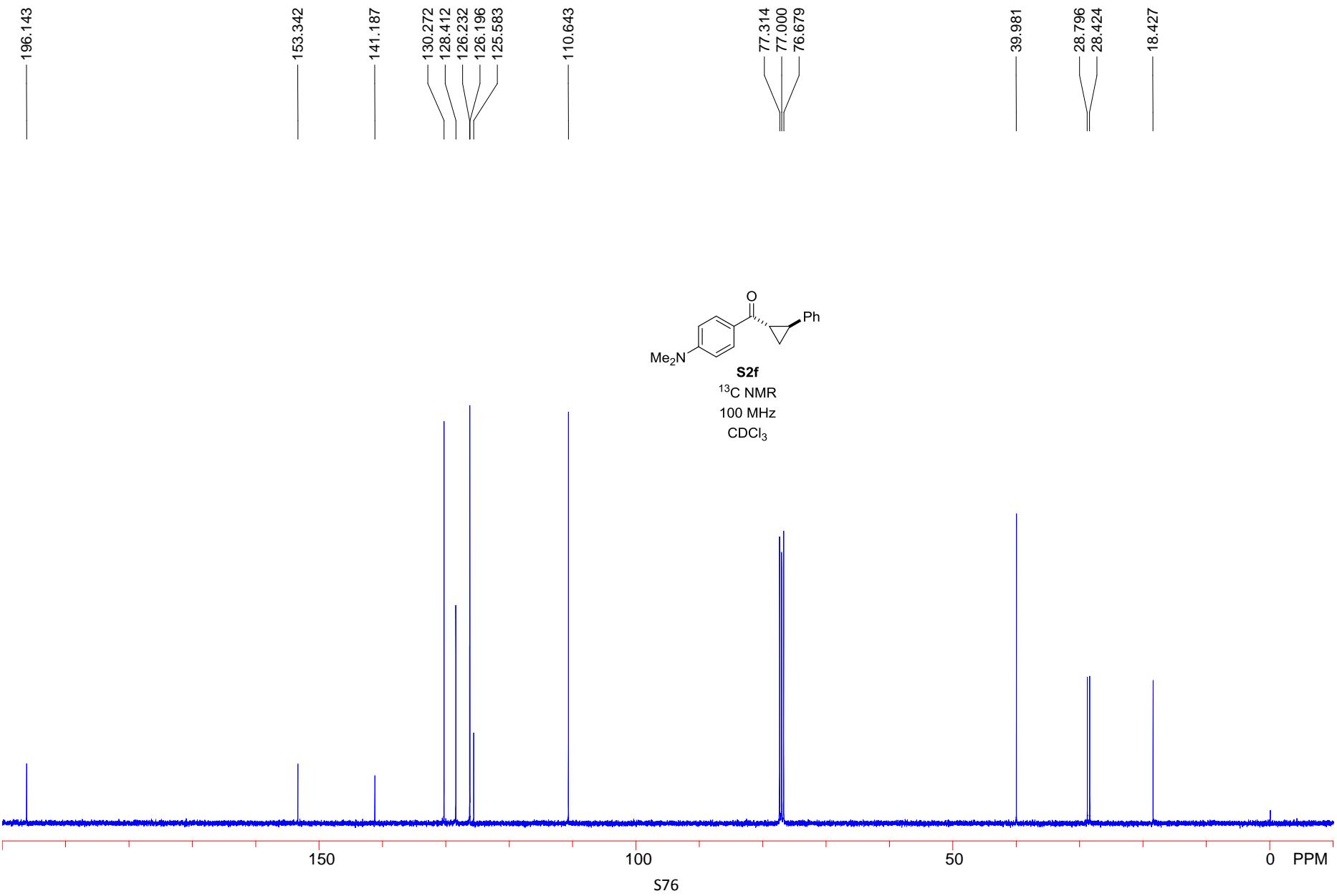


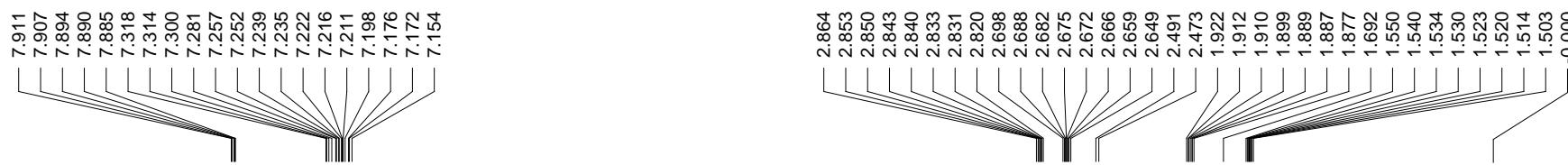
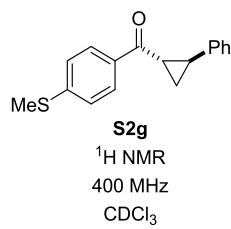
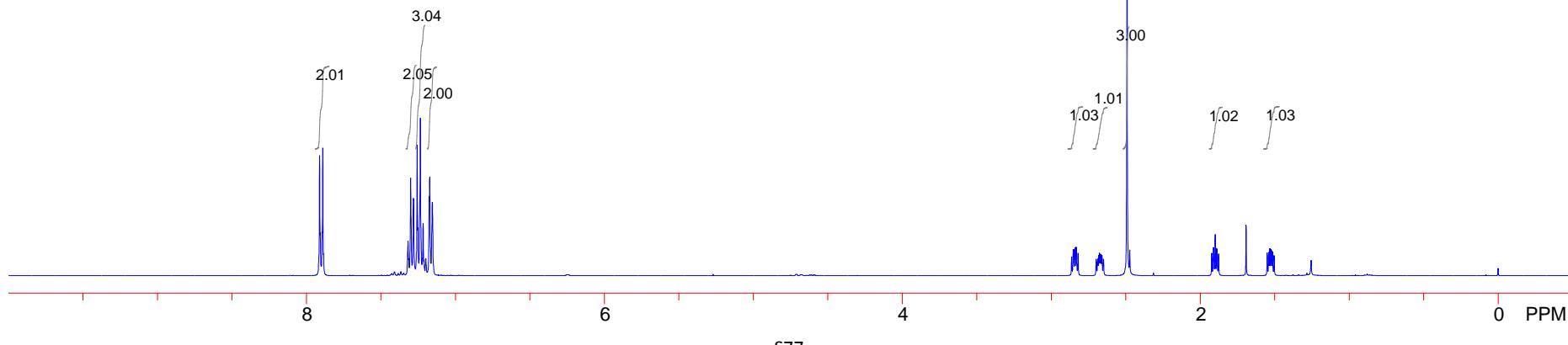


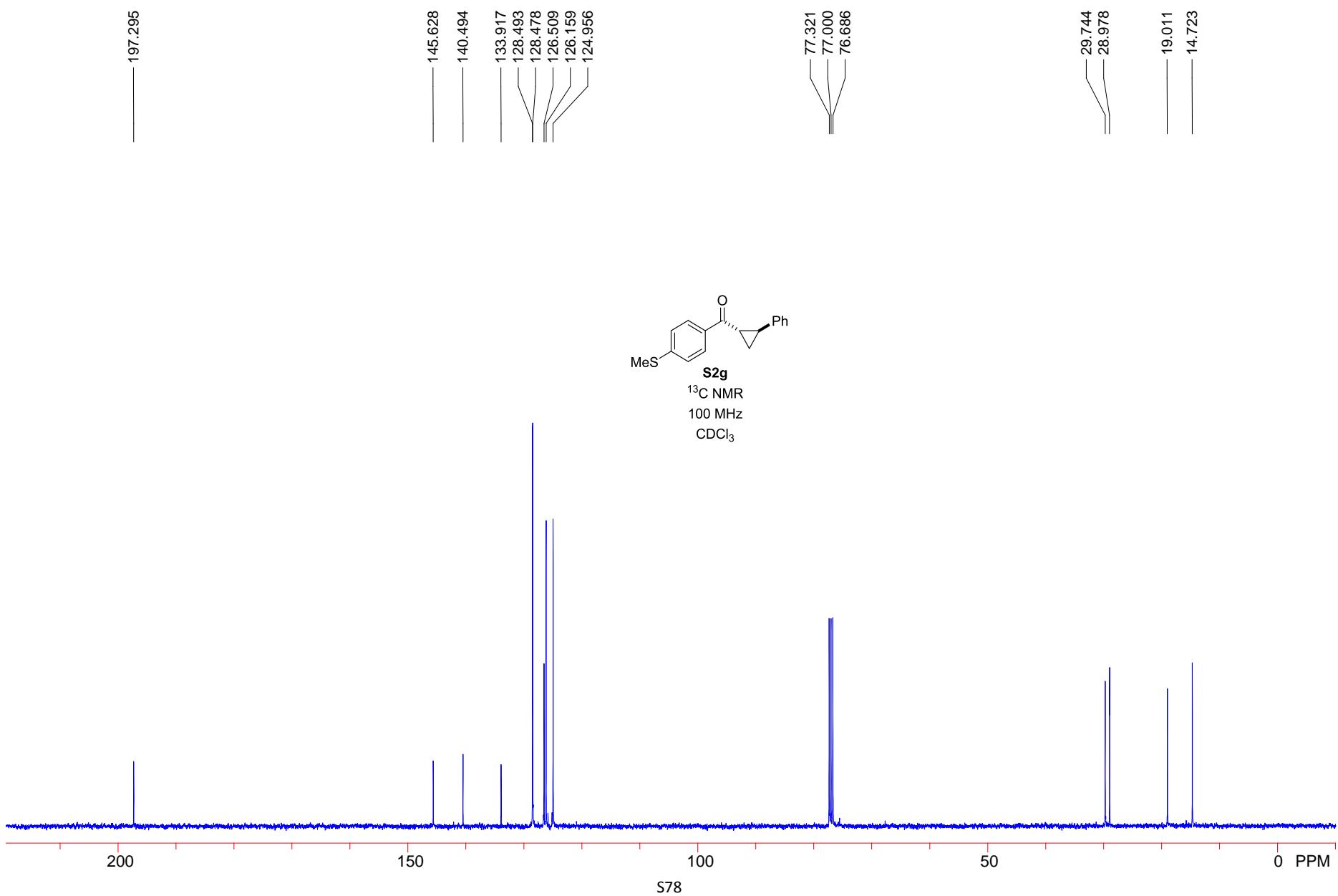


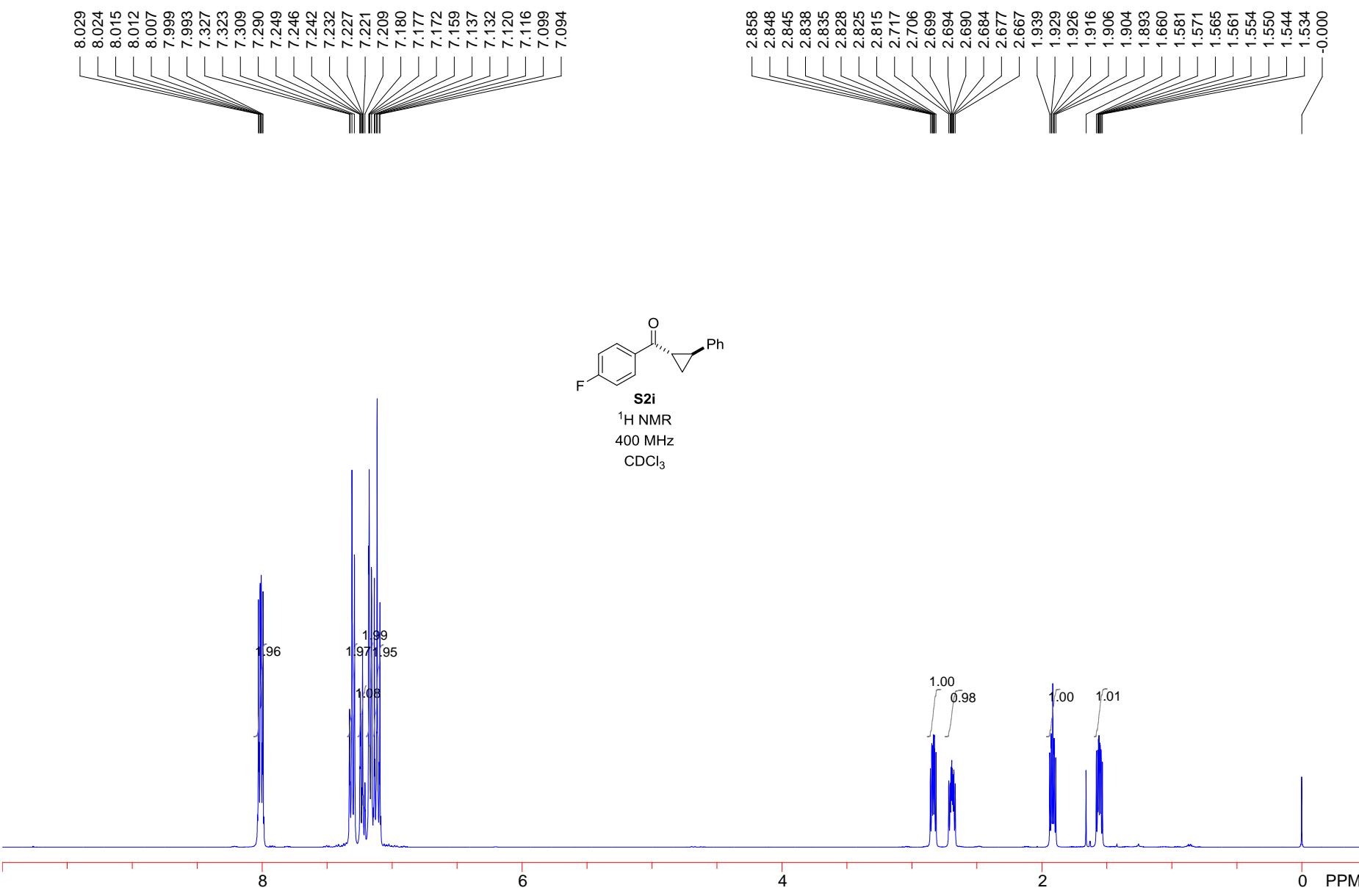


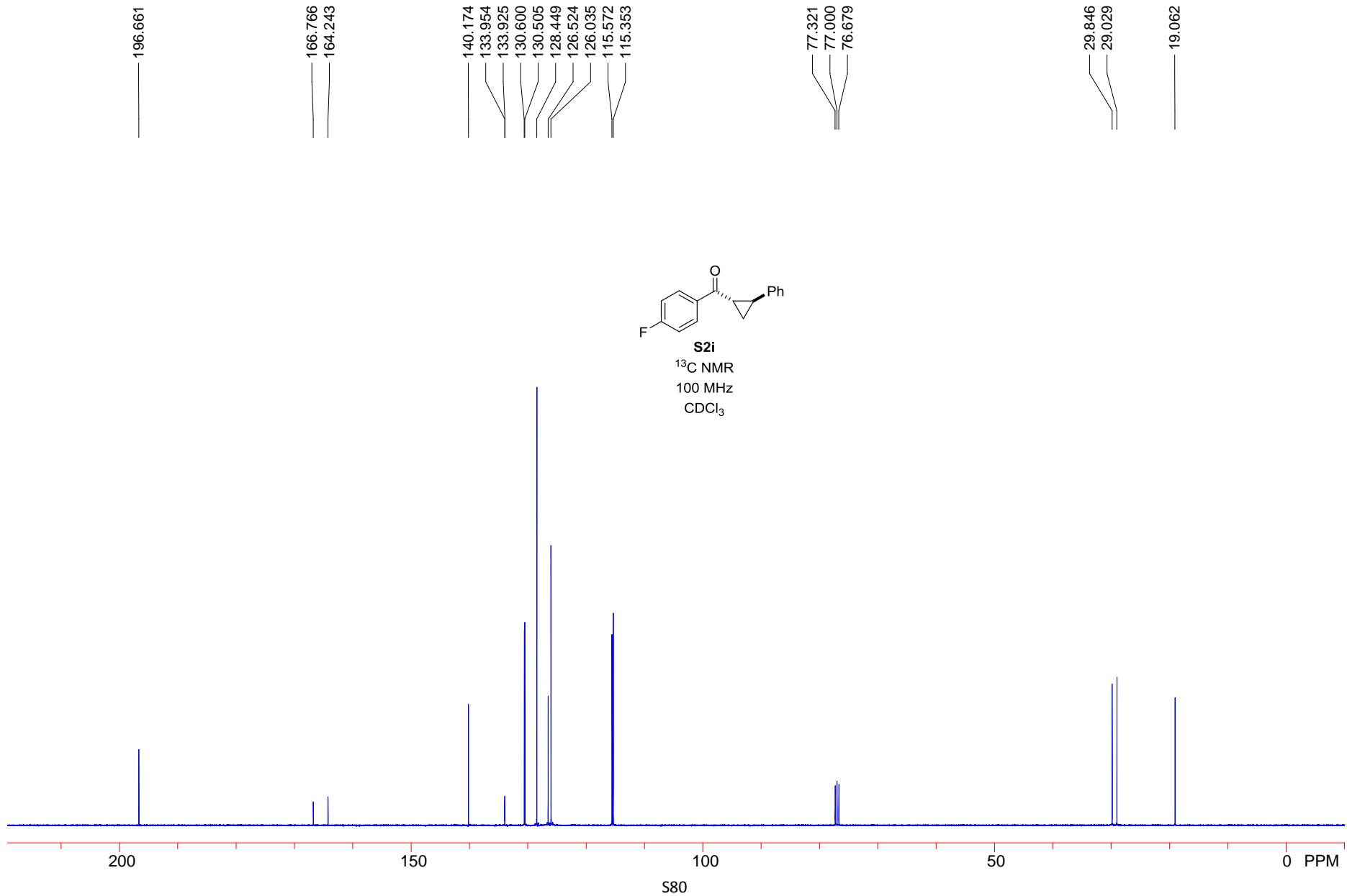




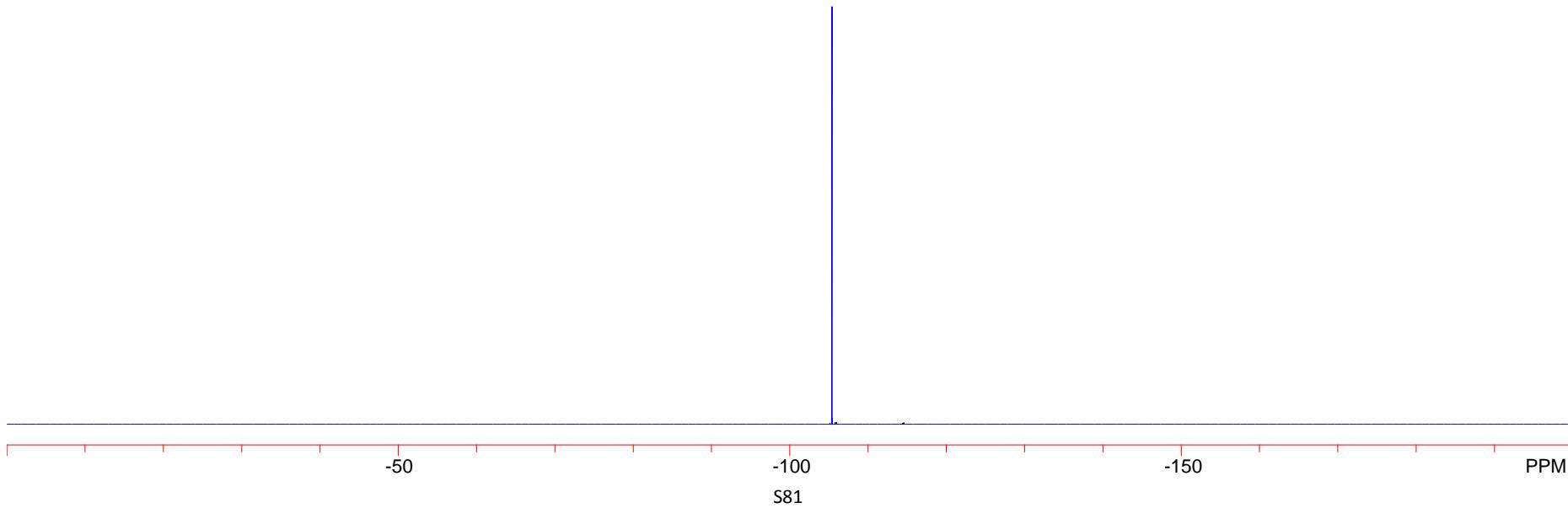
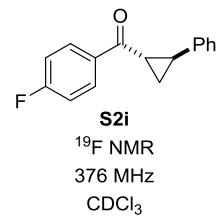


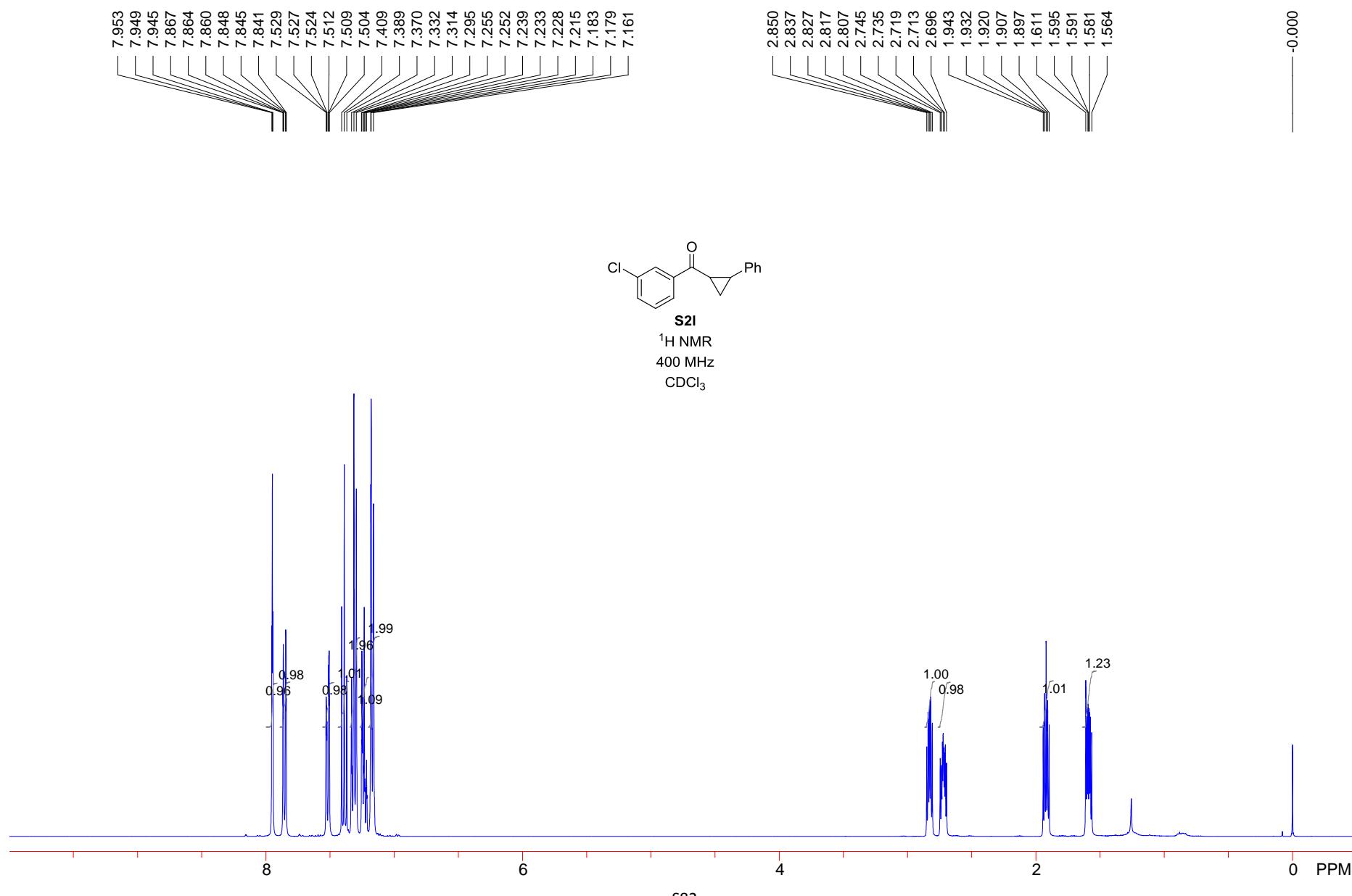


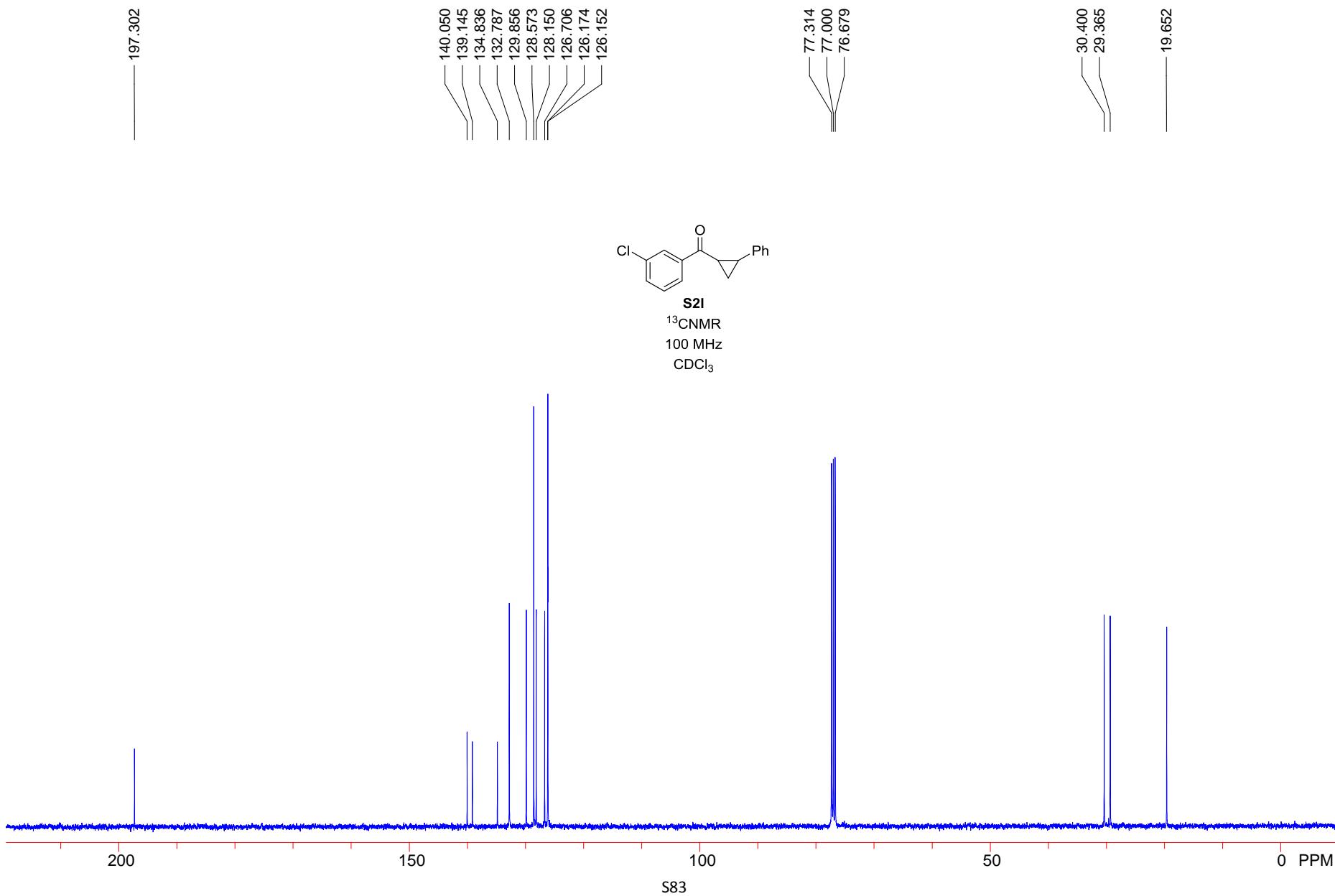


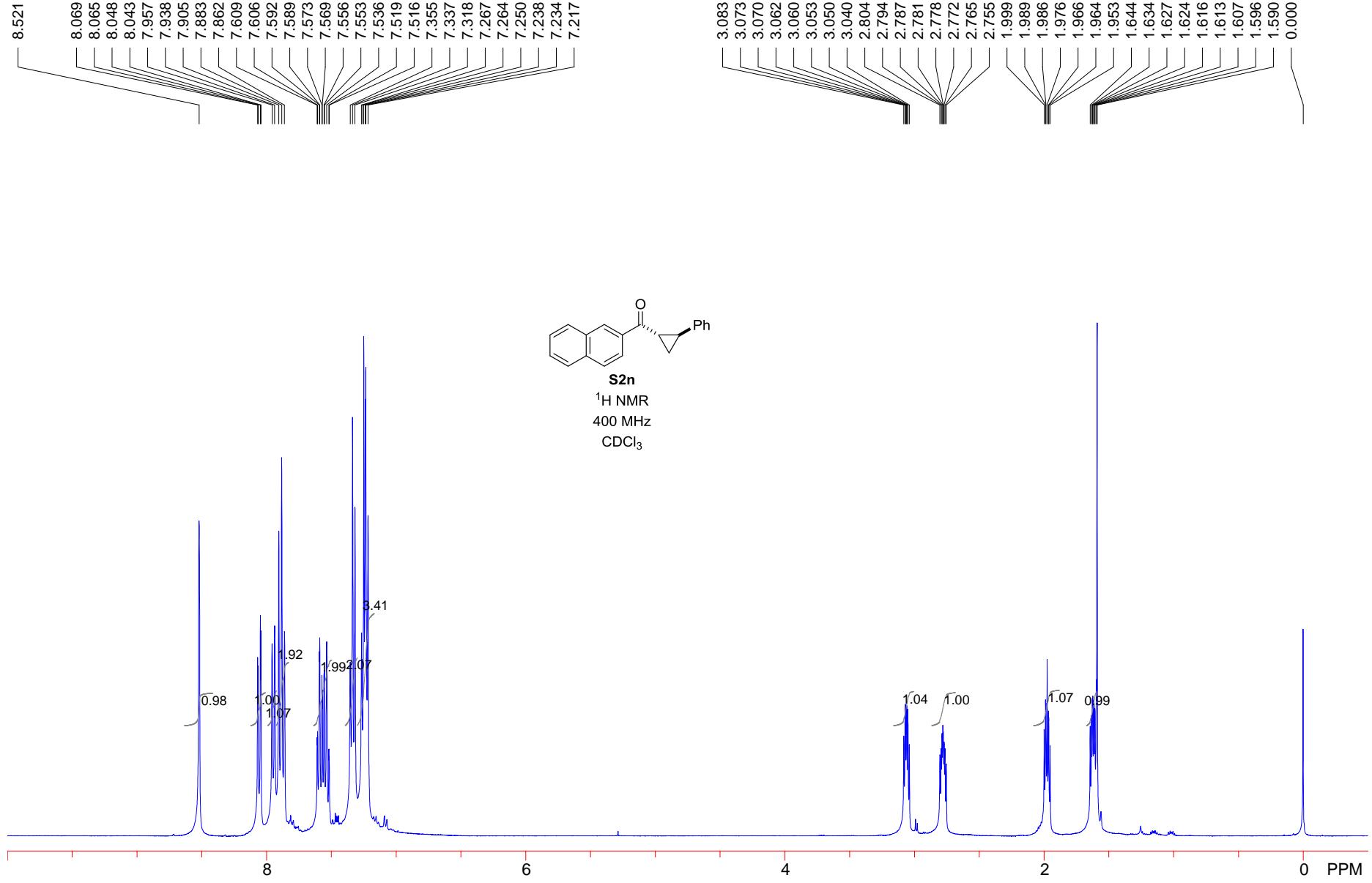


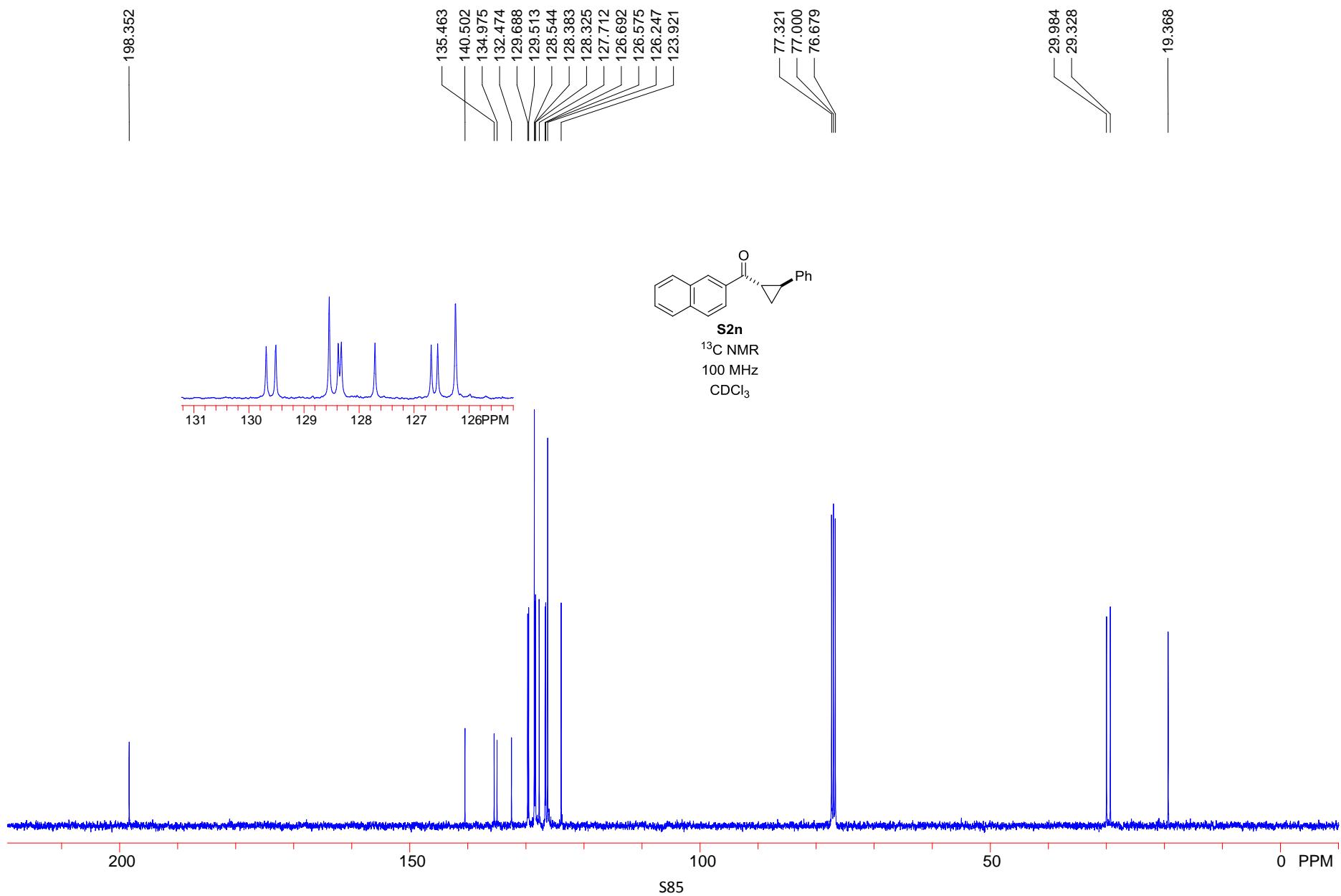
—105.395

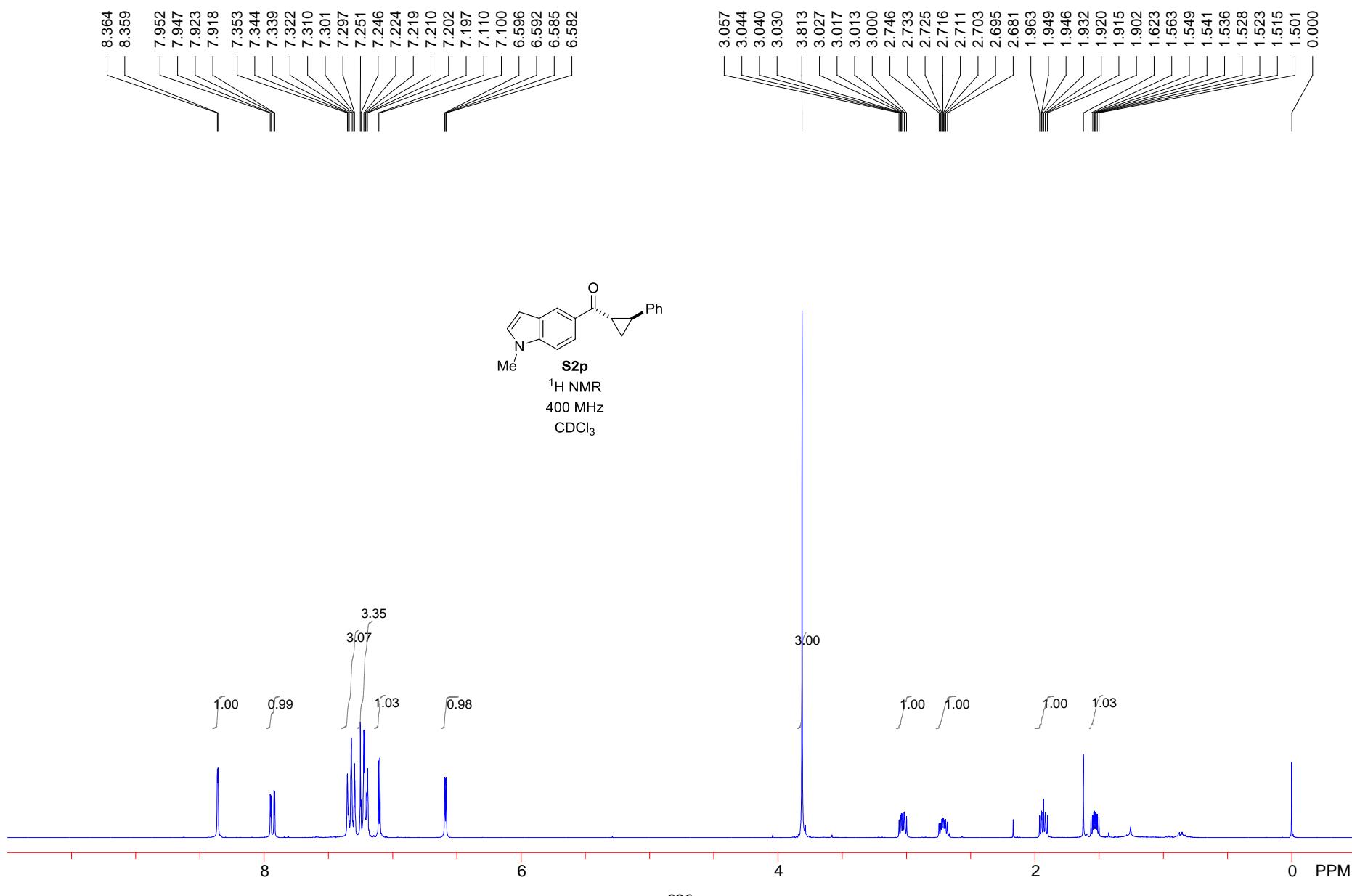


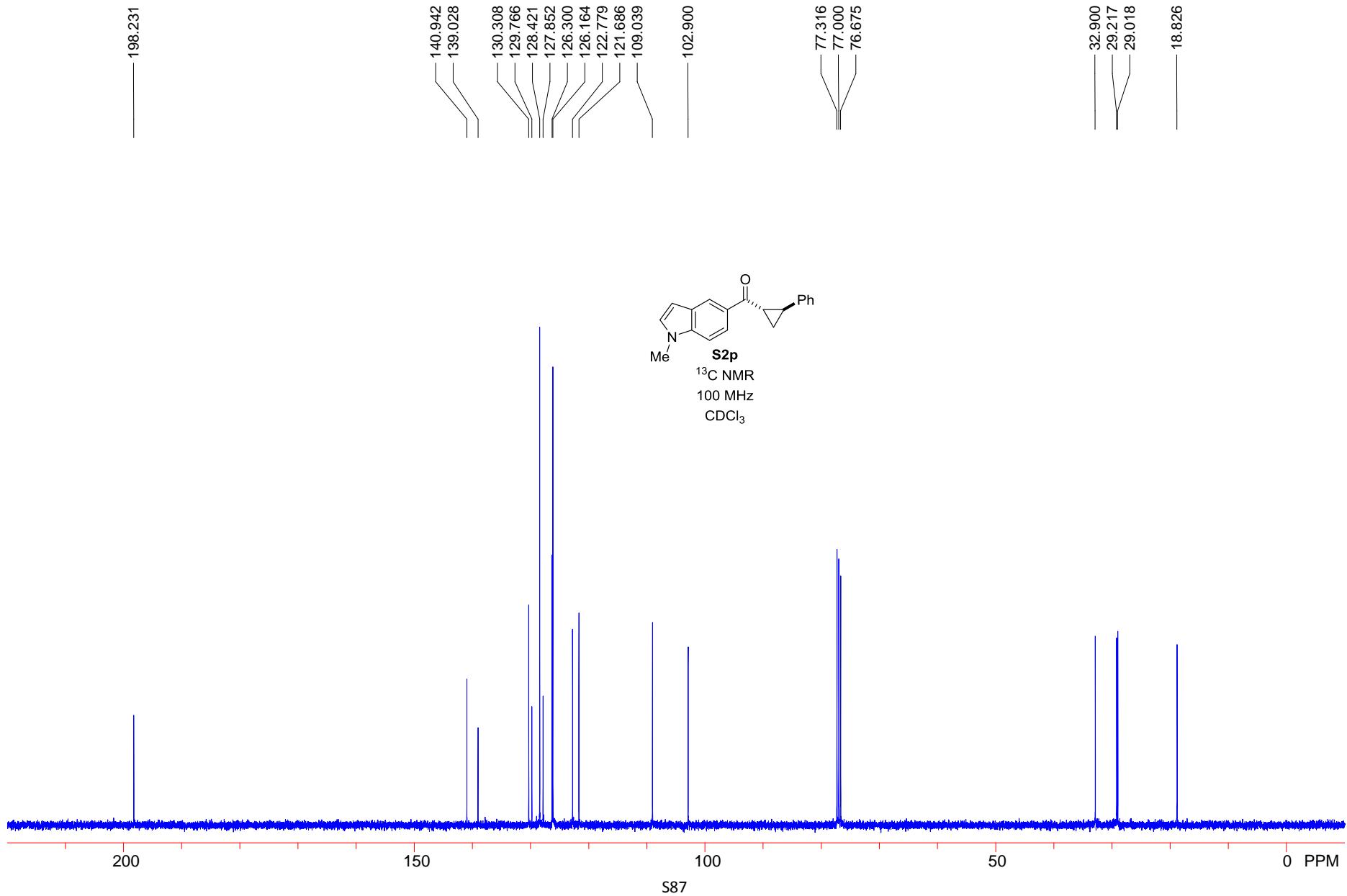


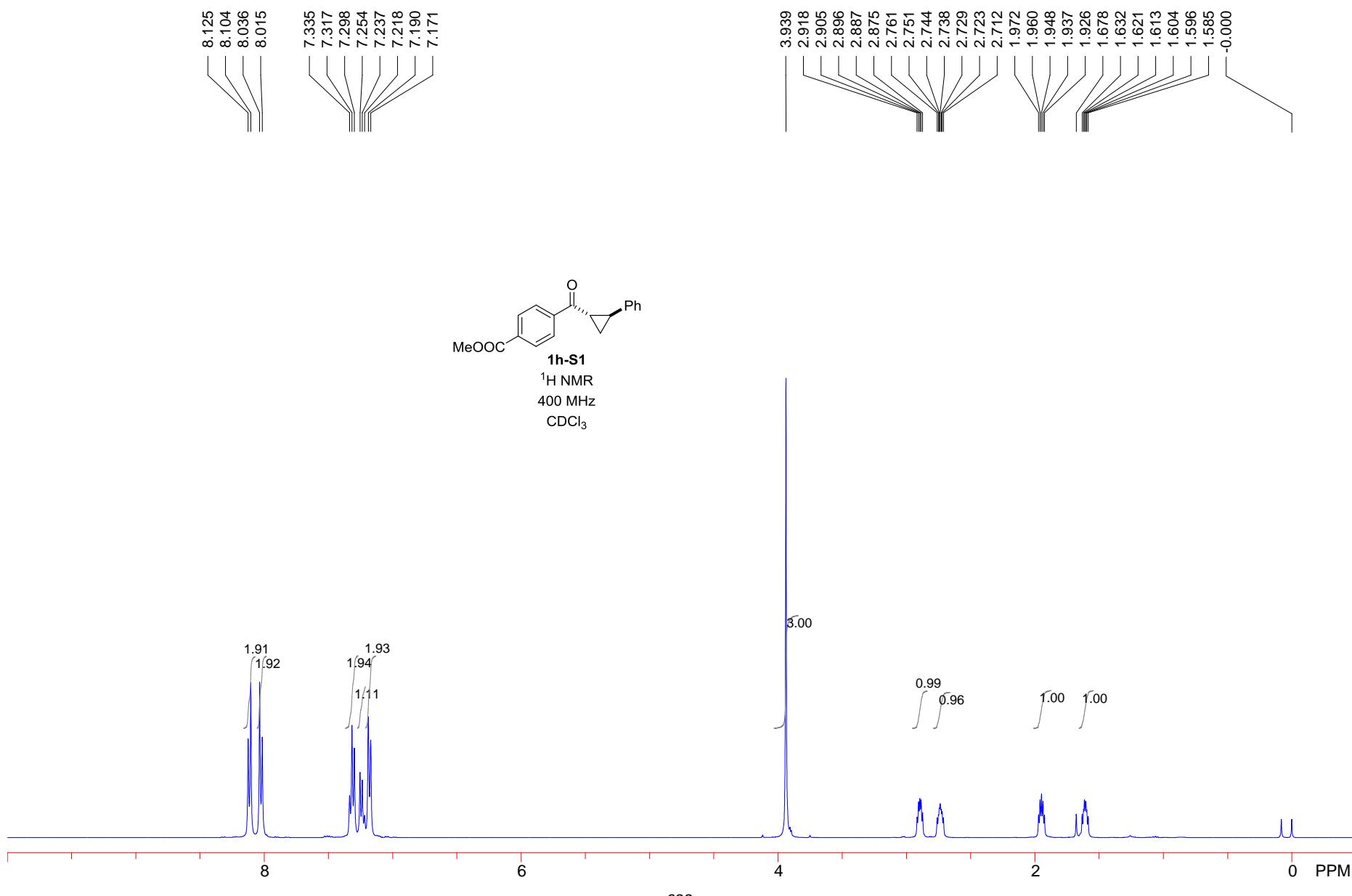


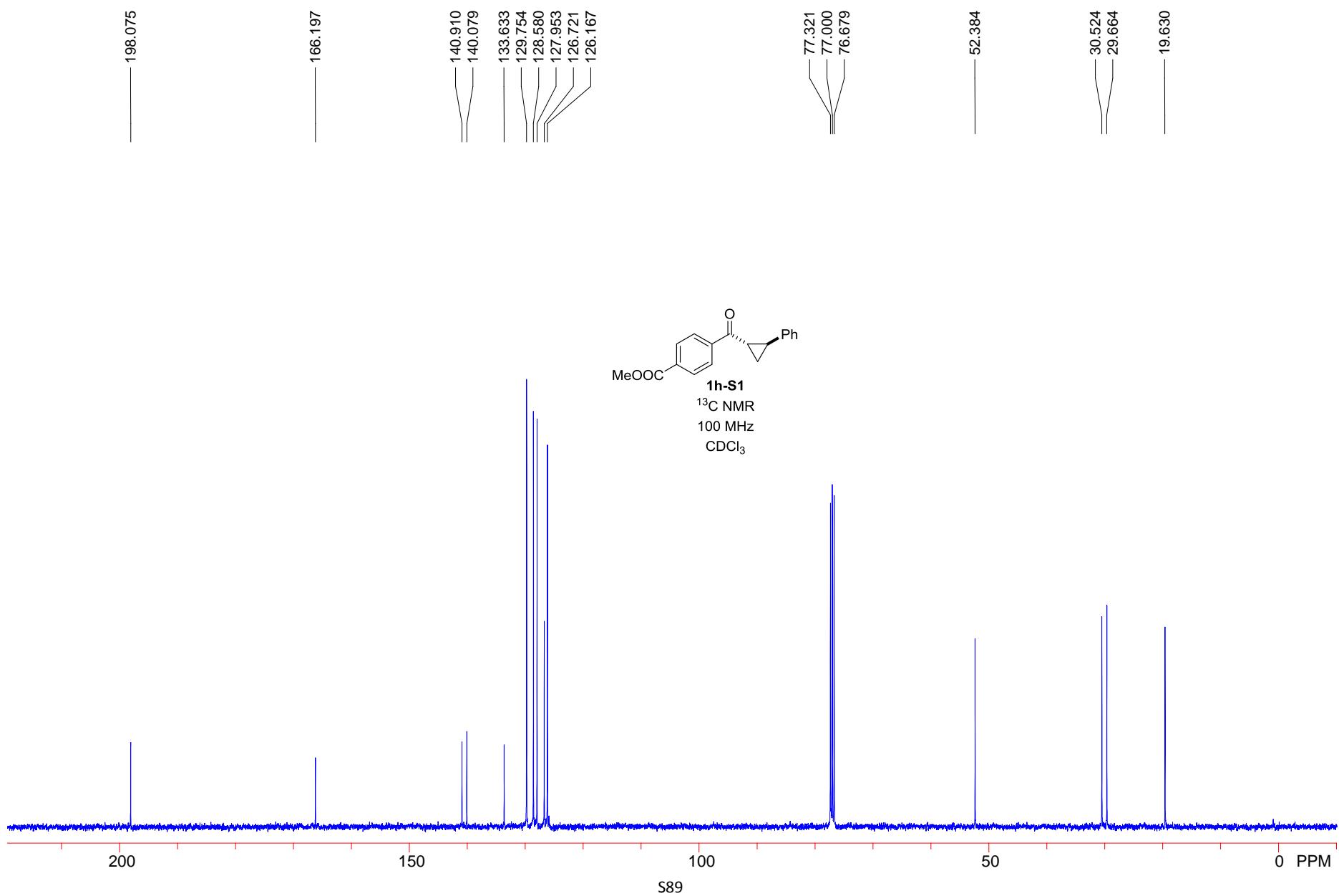


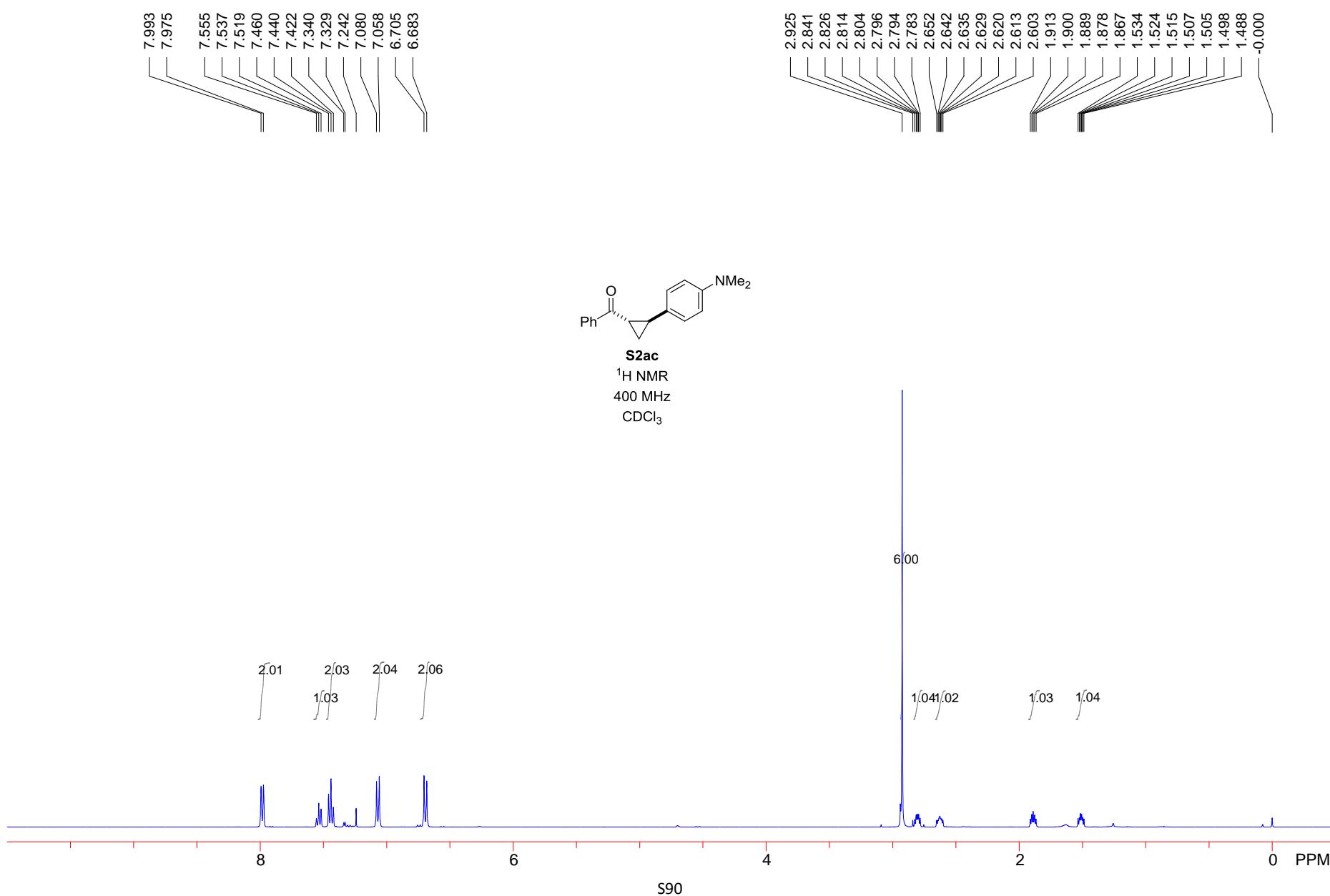


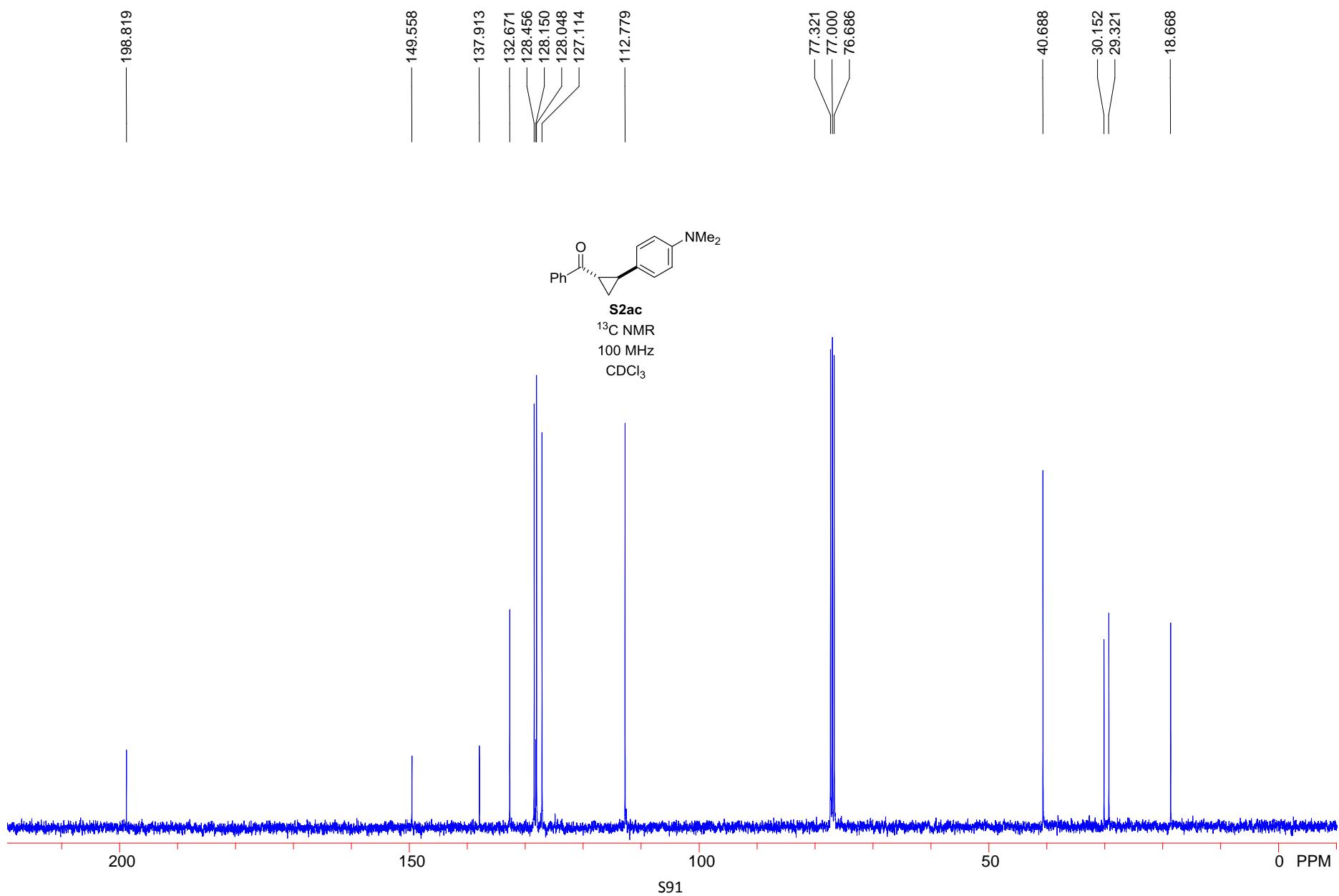


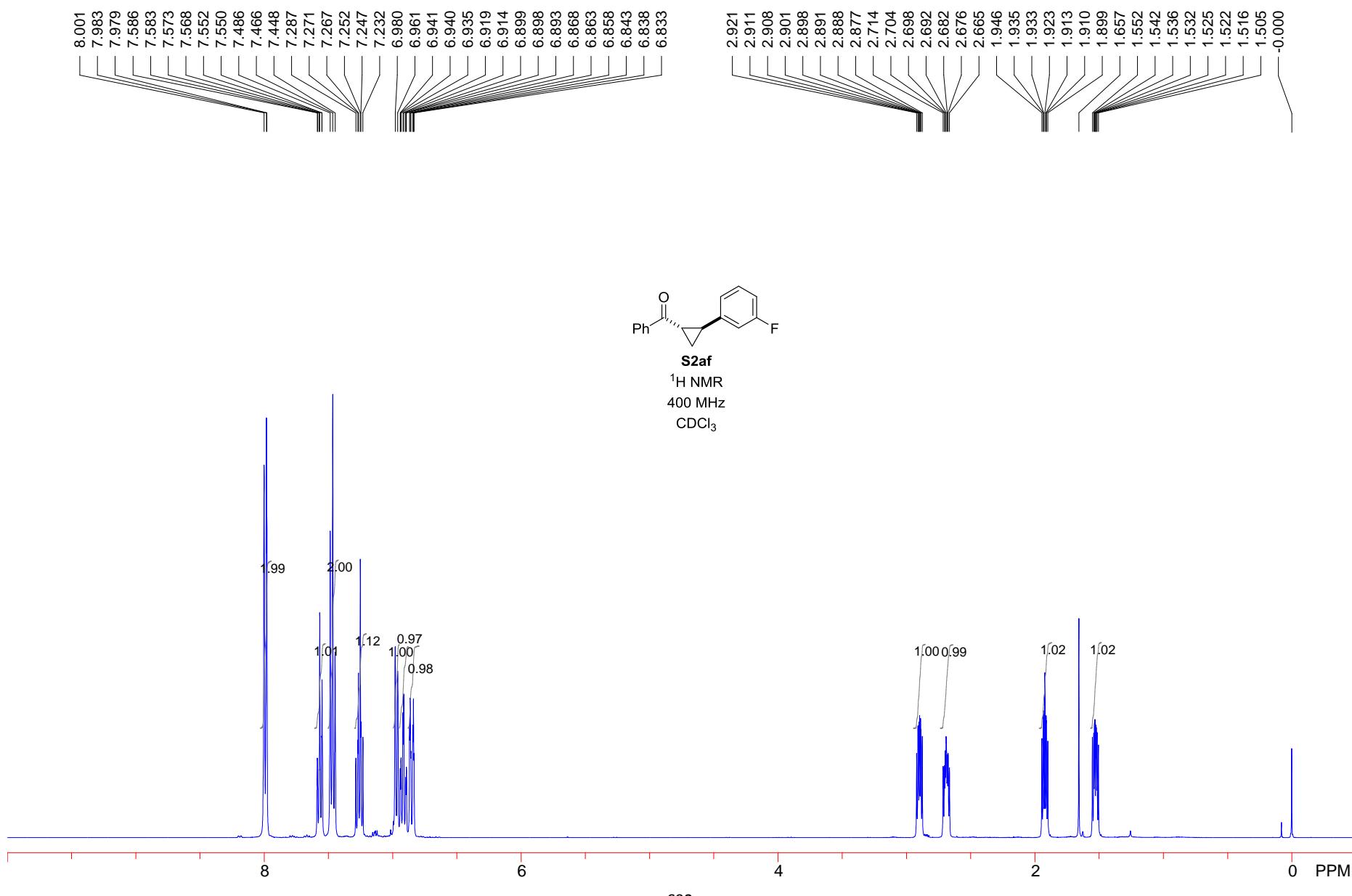


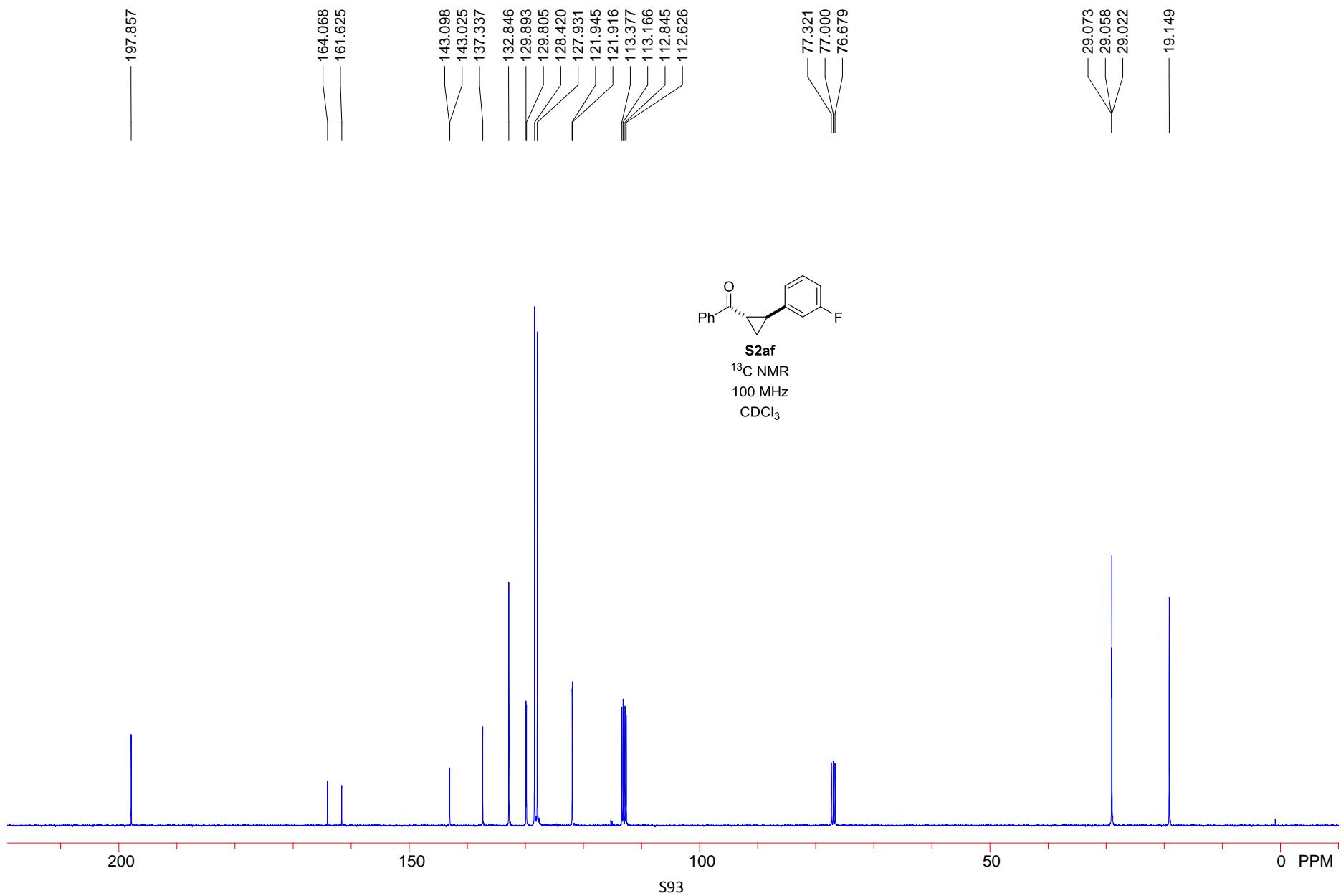




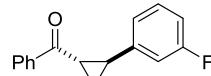








-112.835

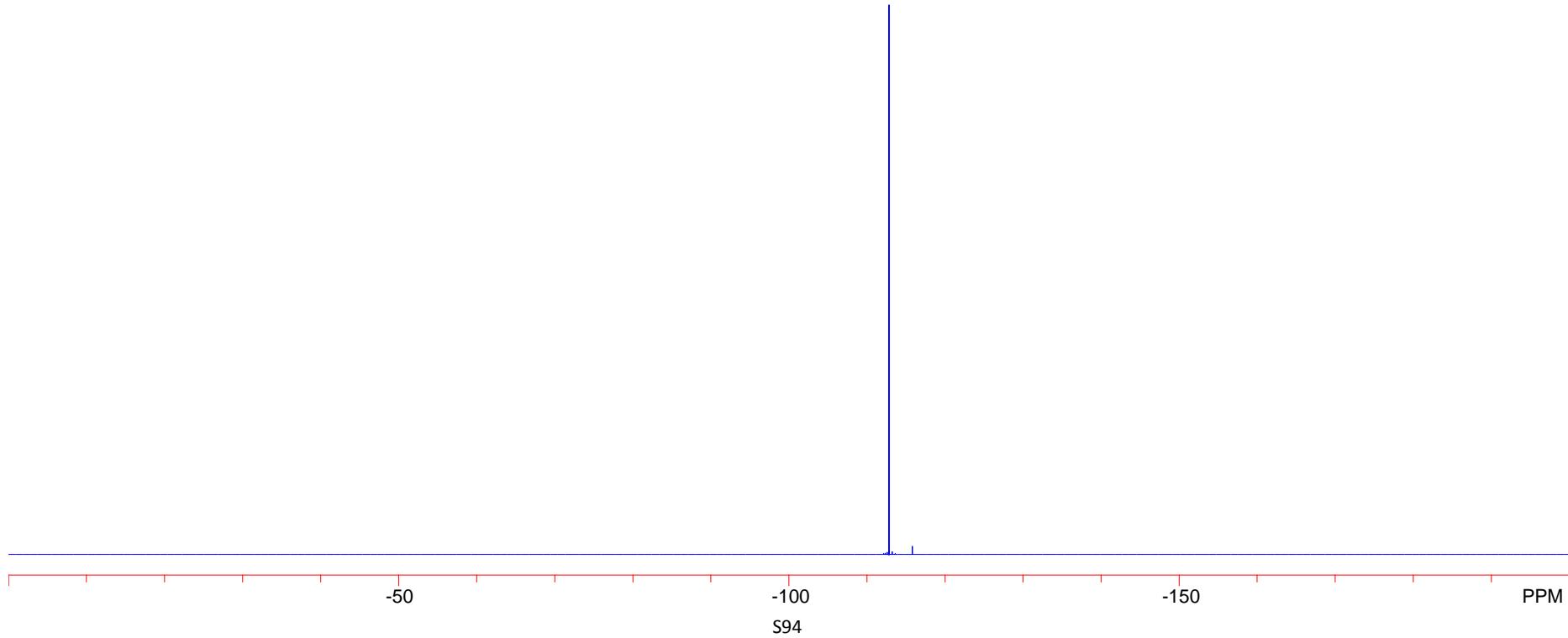


S2af

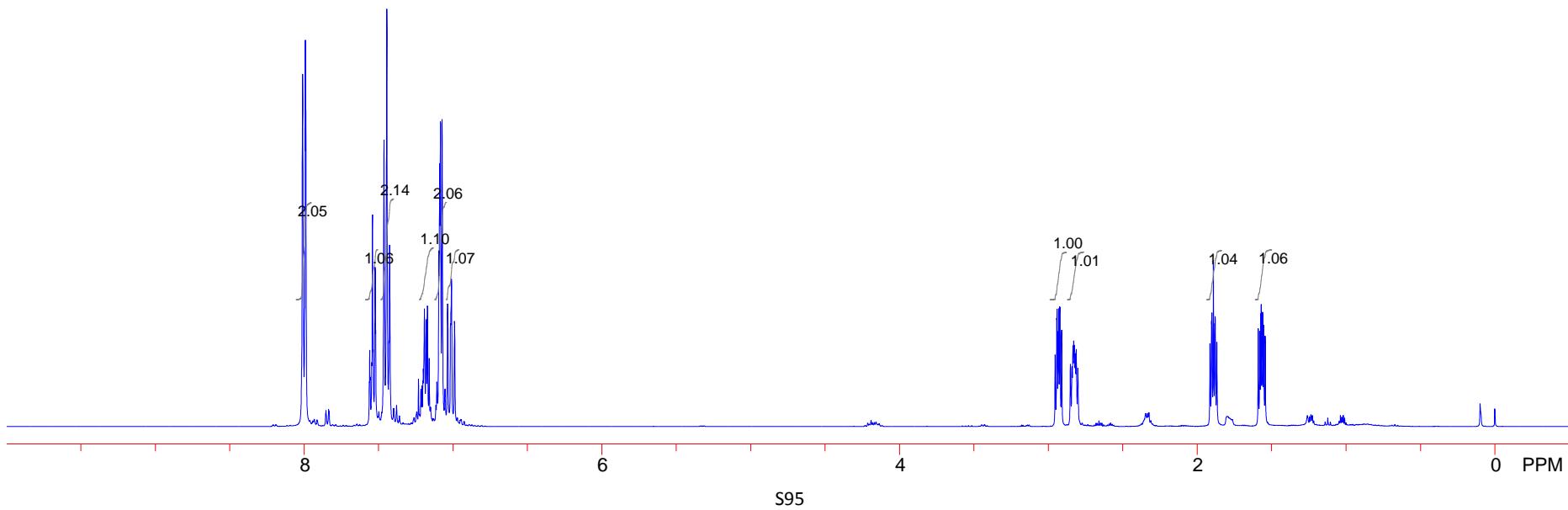
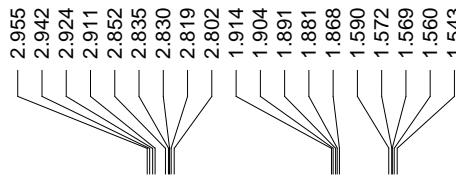
^{19}F NMR

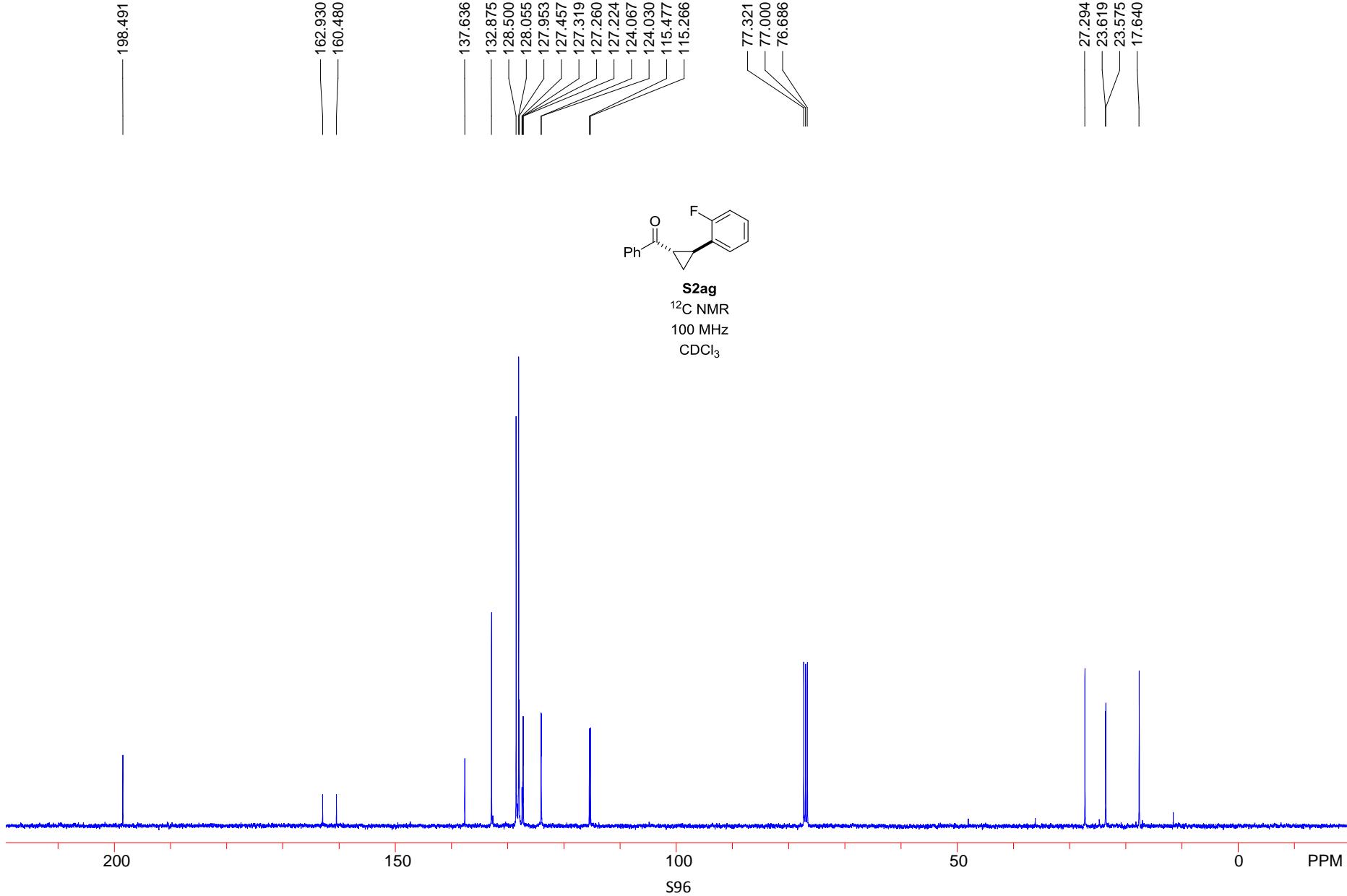
376 MHz

CDCl_3

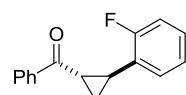


0.000





-118.249

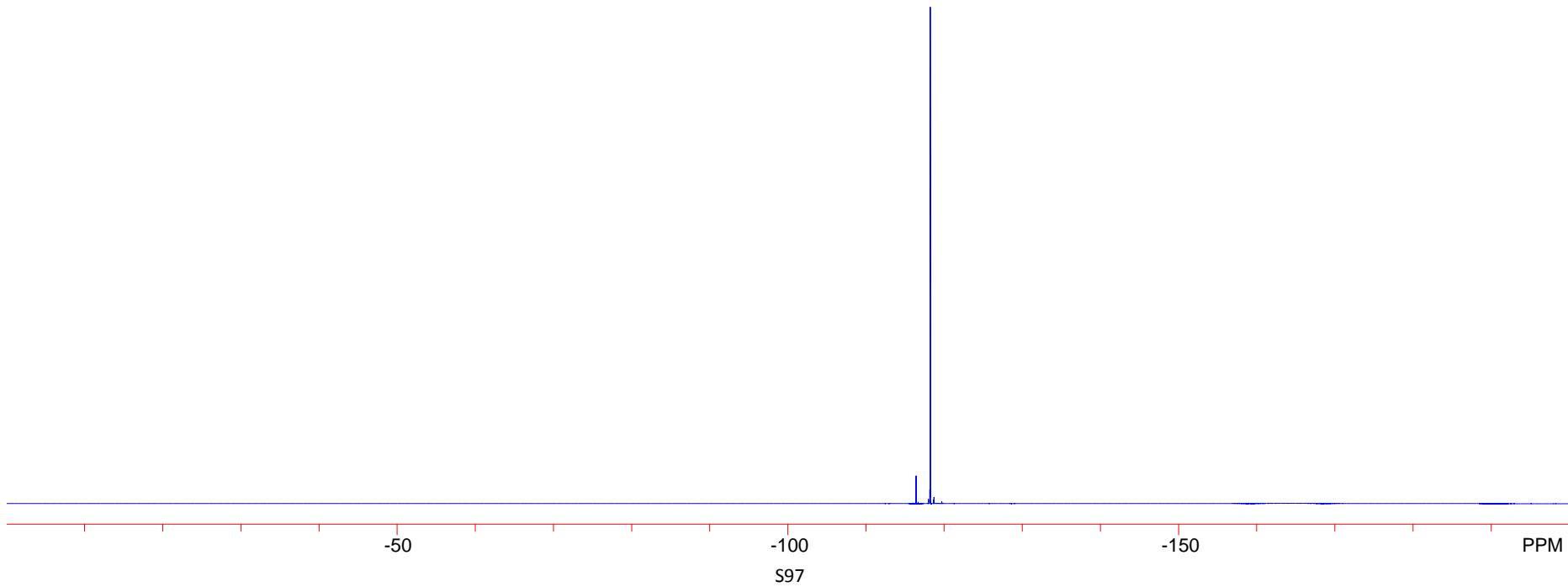


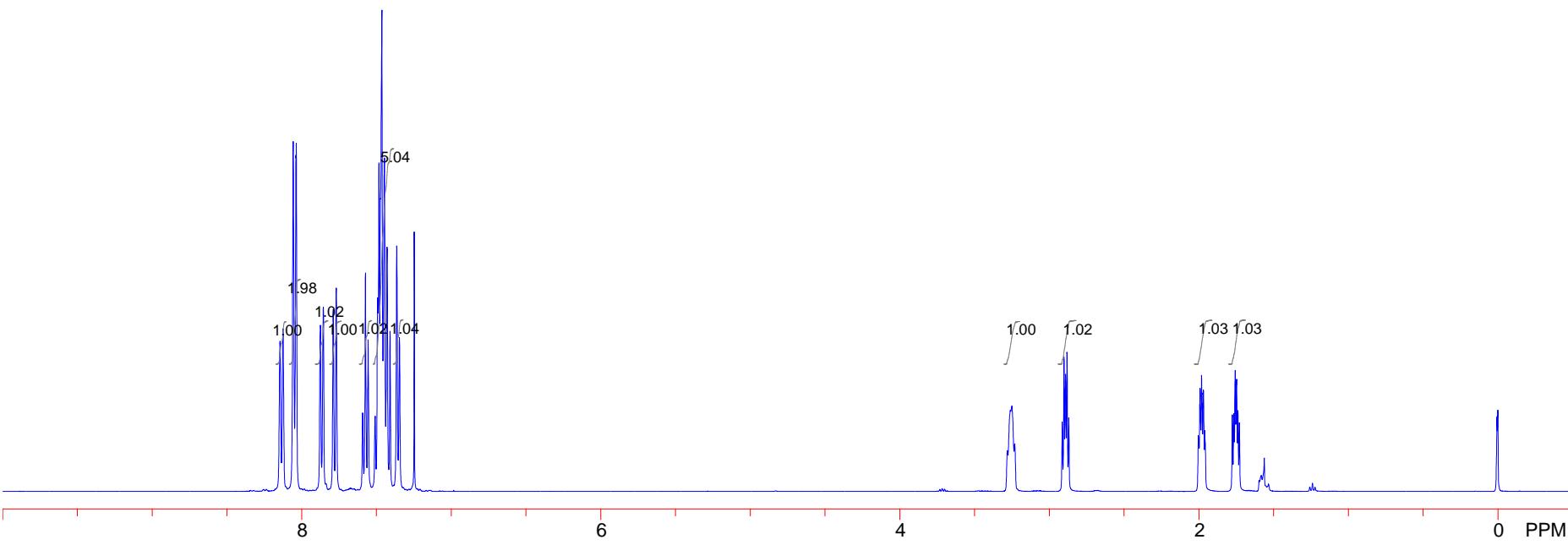
S2ag

¹⁹F NMR

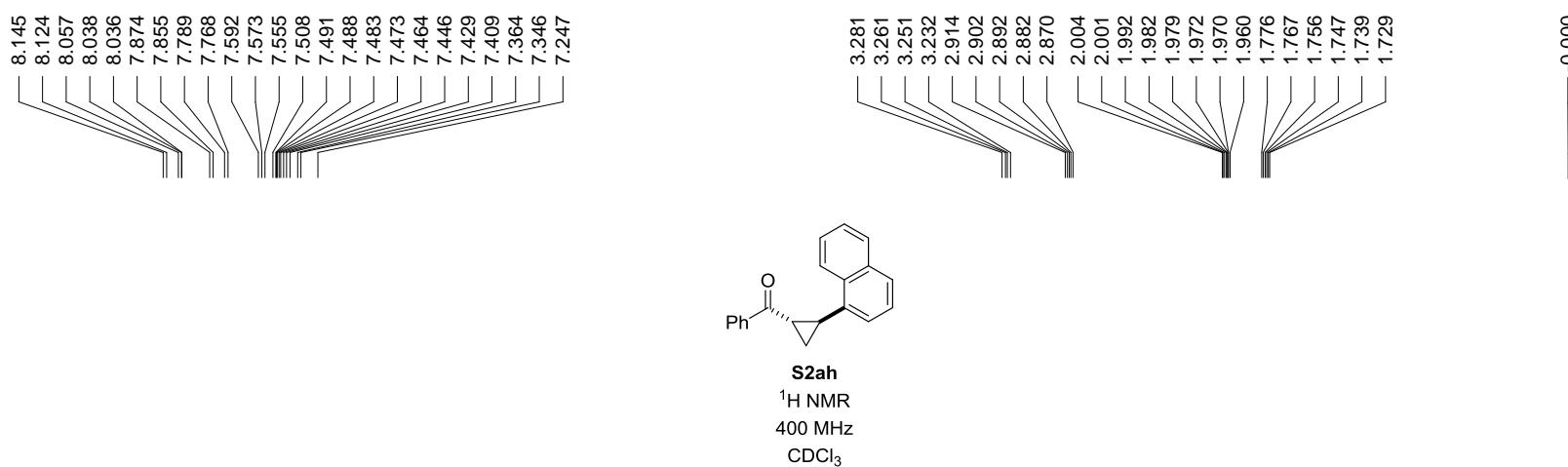
376 MHz

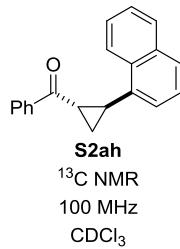
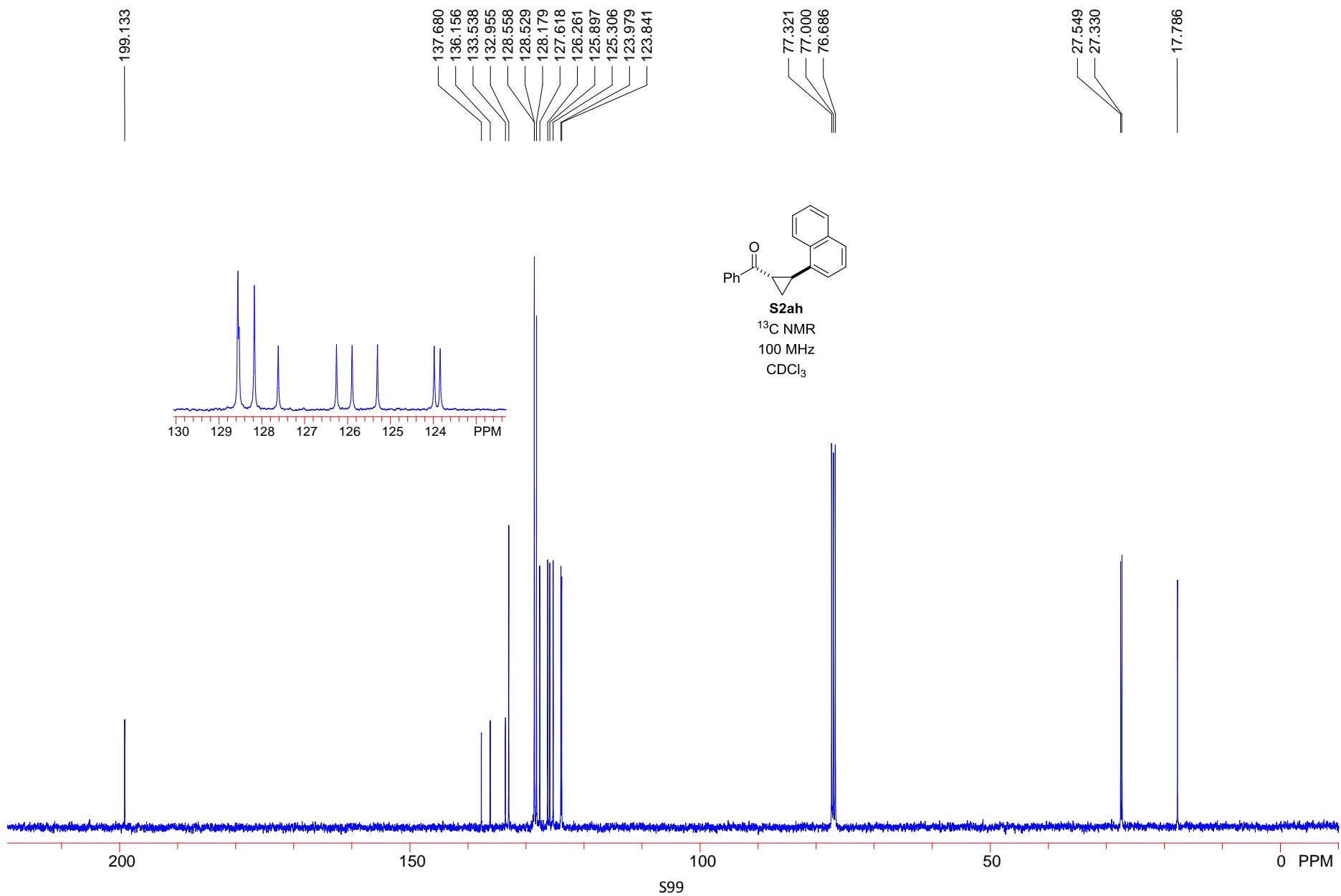
CDCl₃

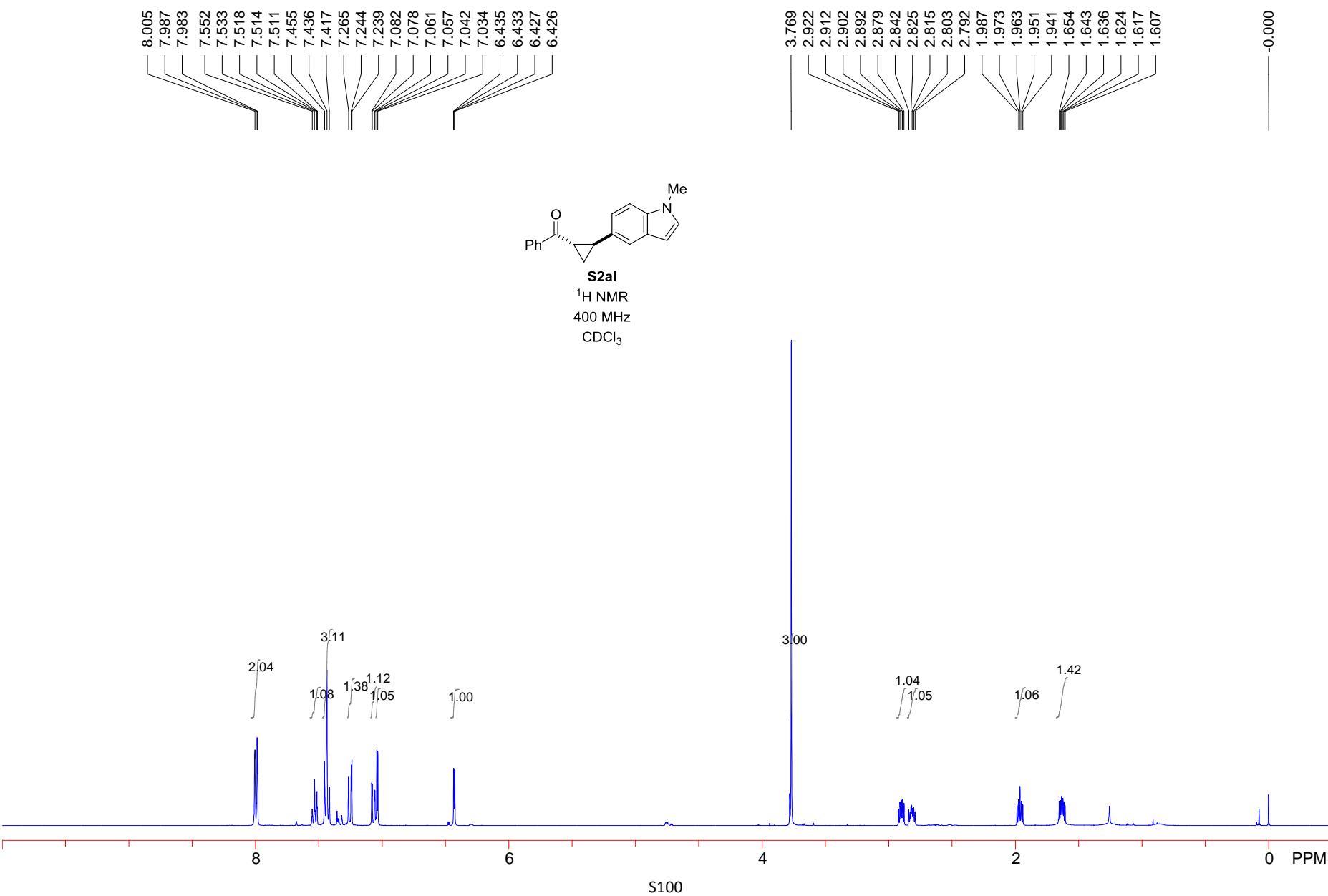


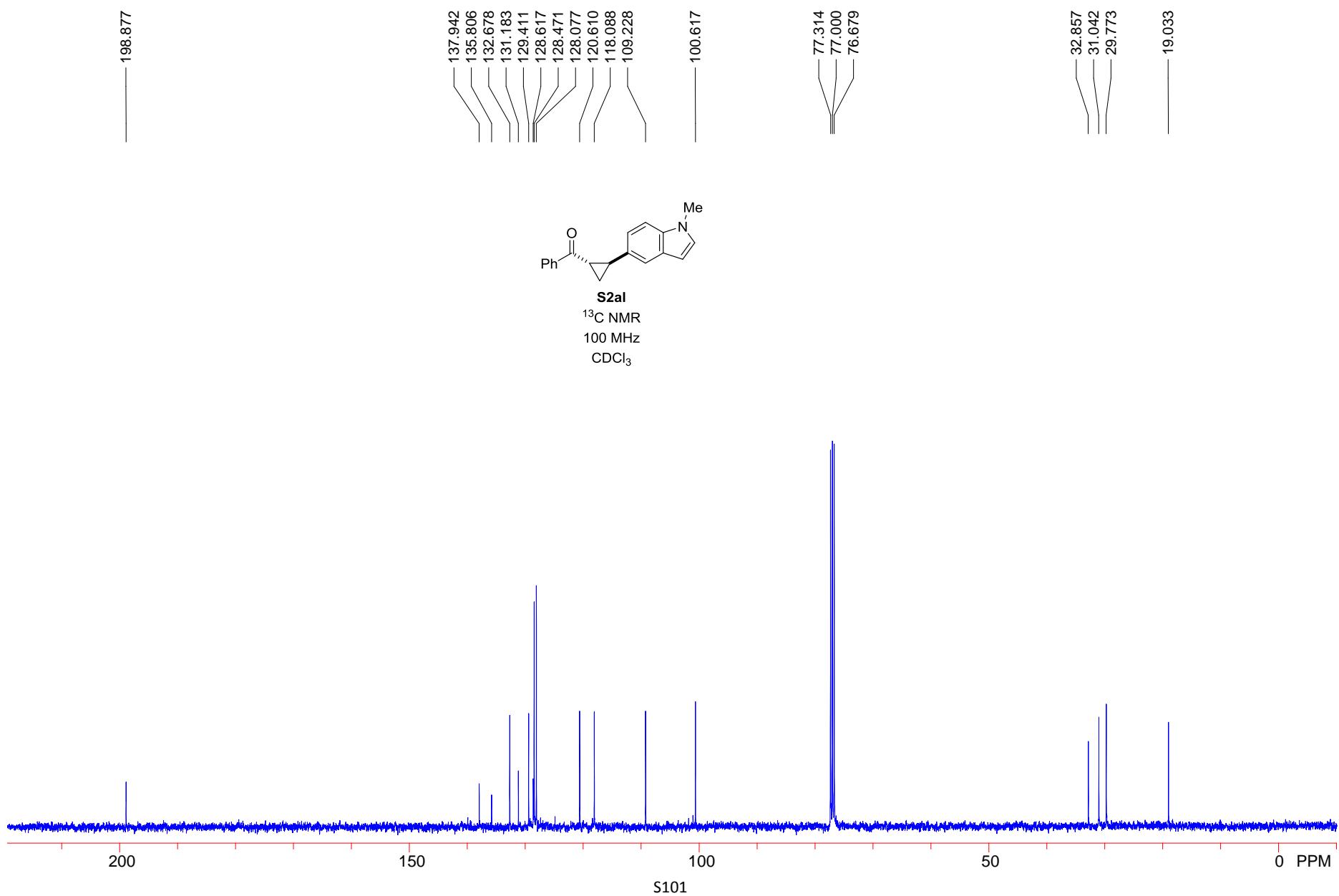


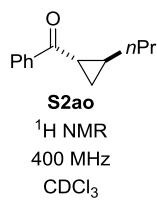
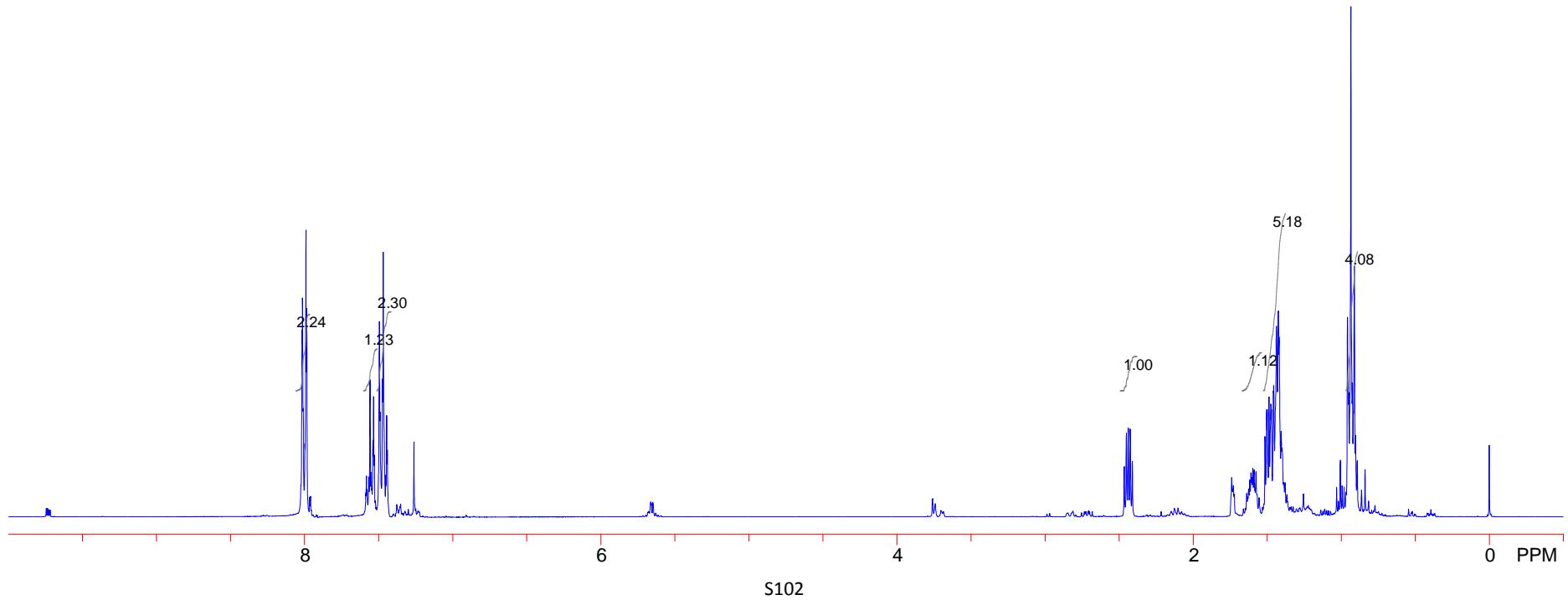
S98

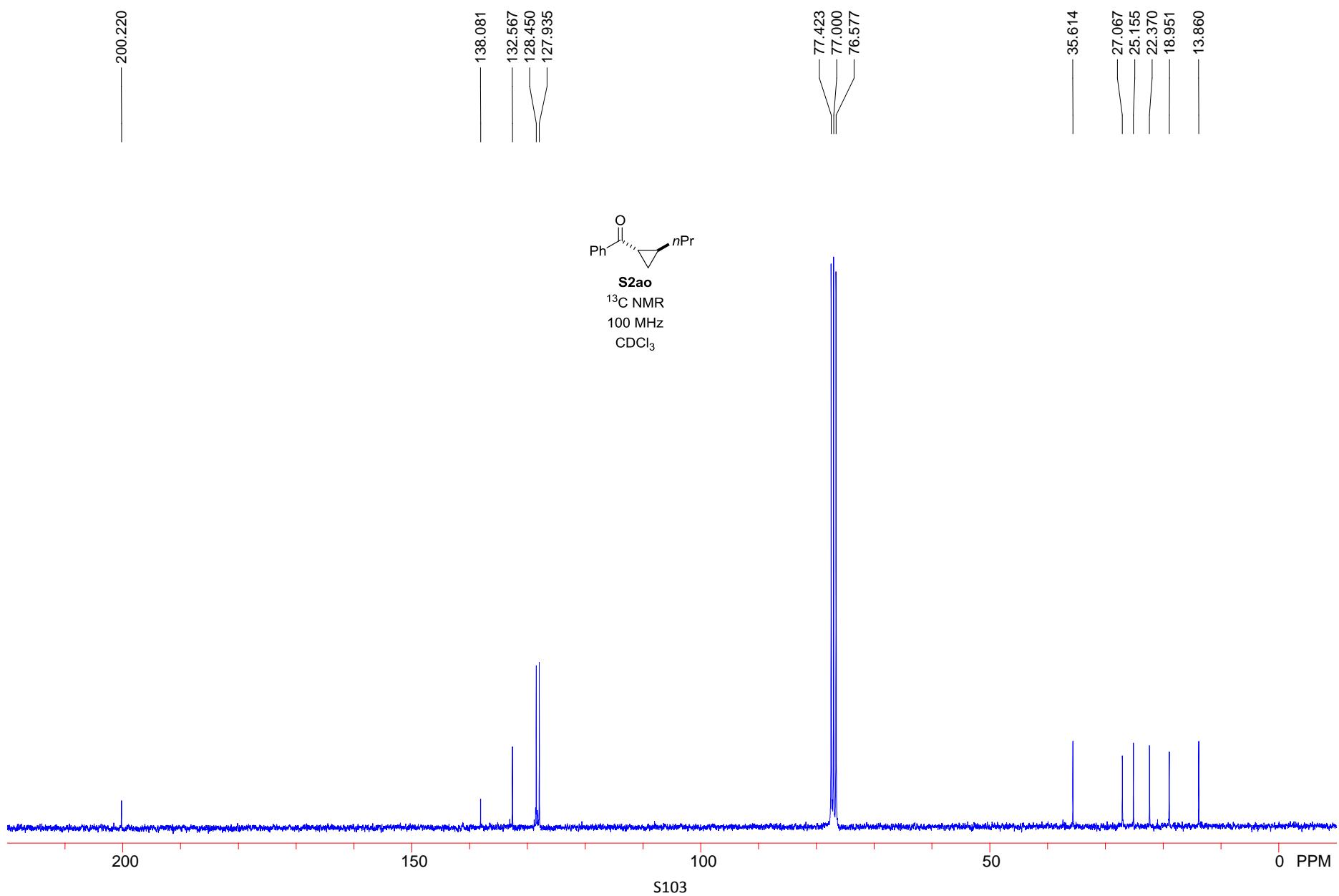


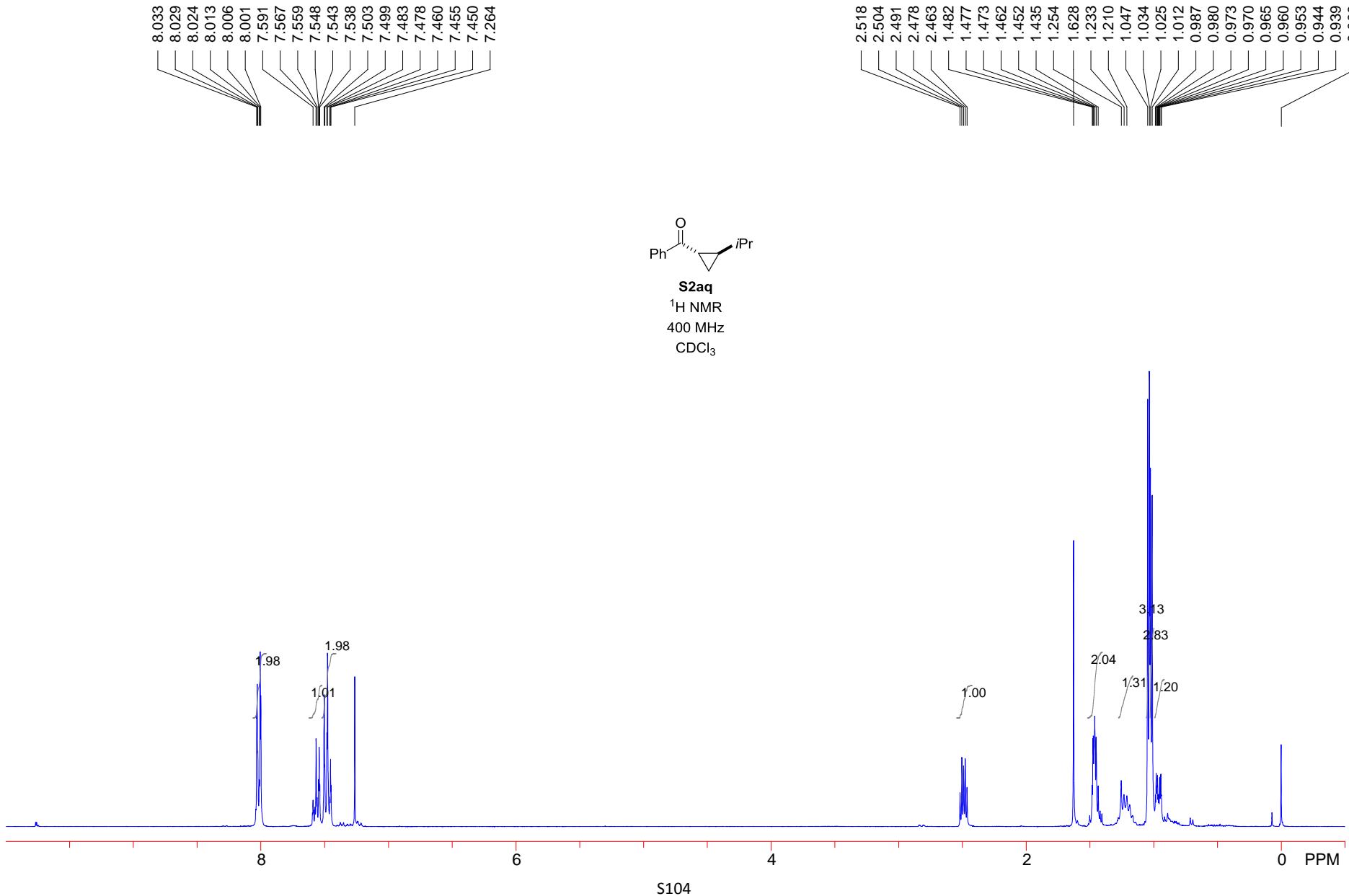




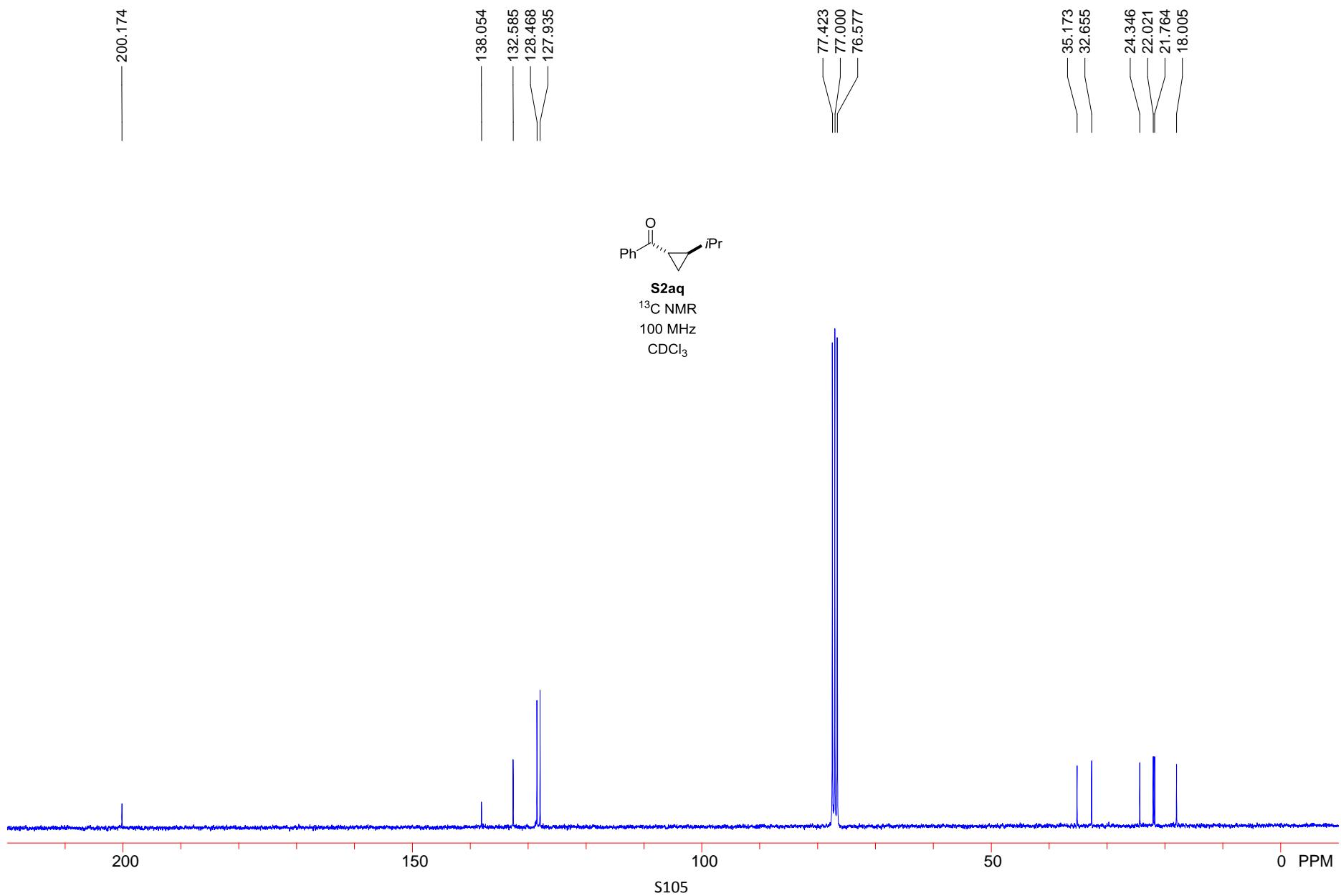


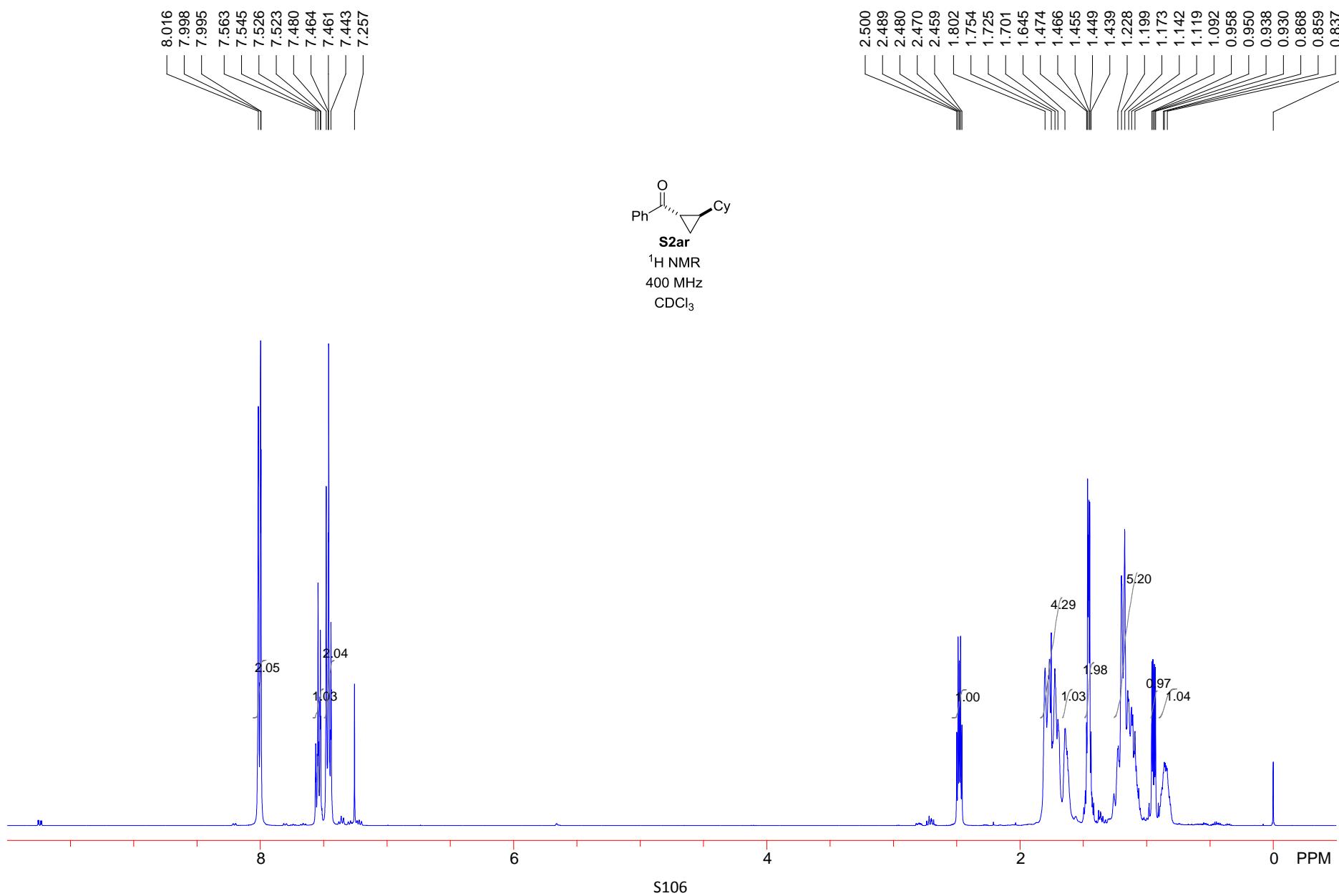


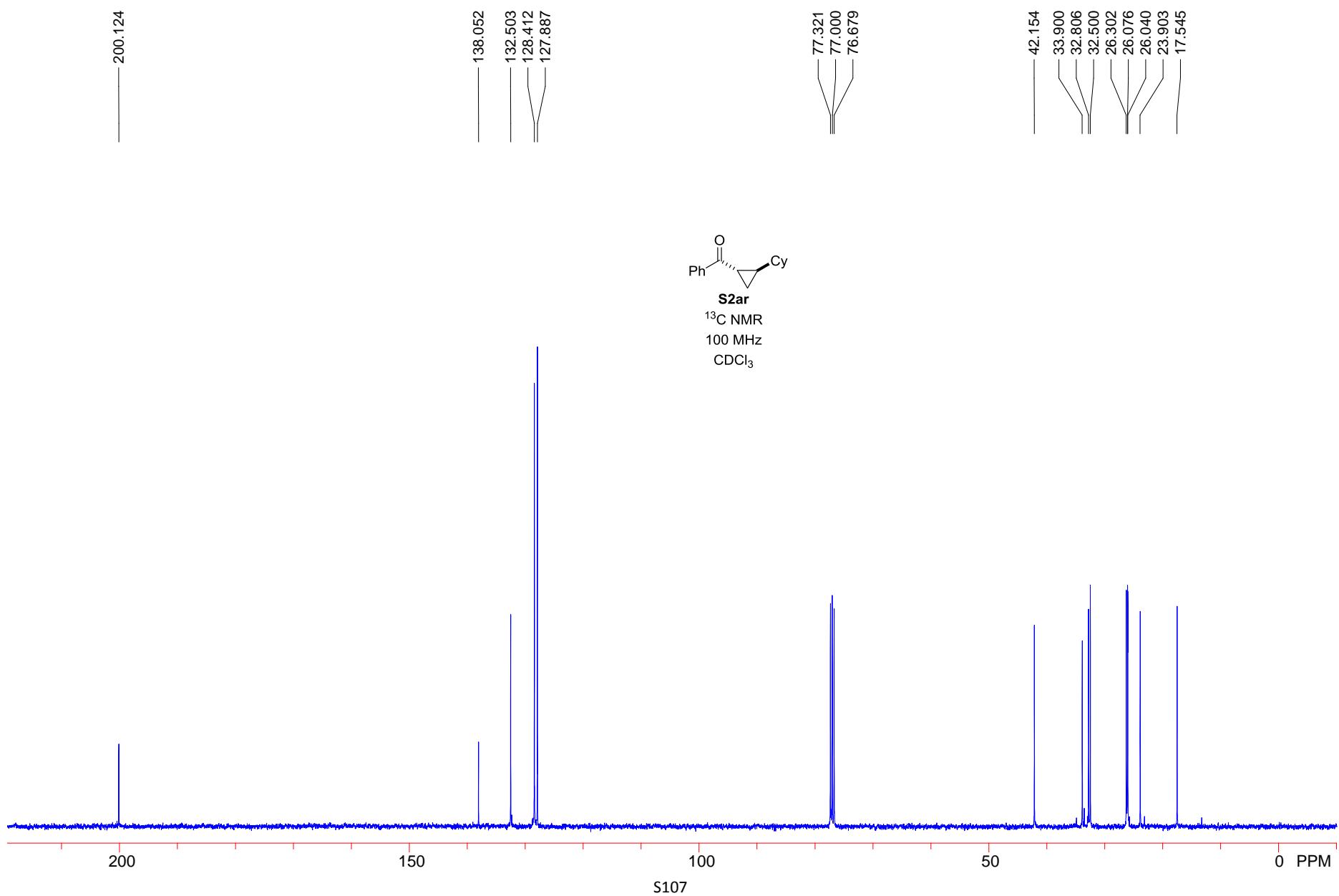


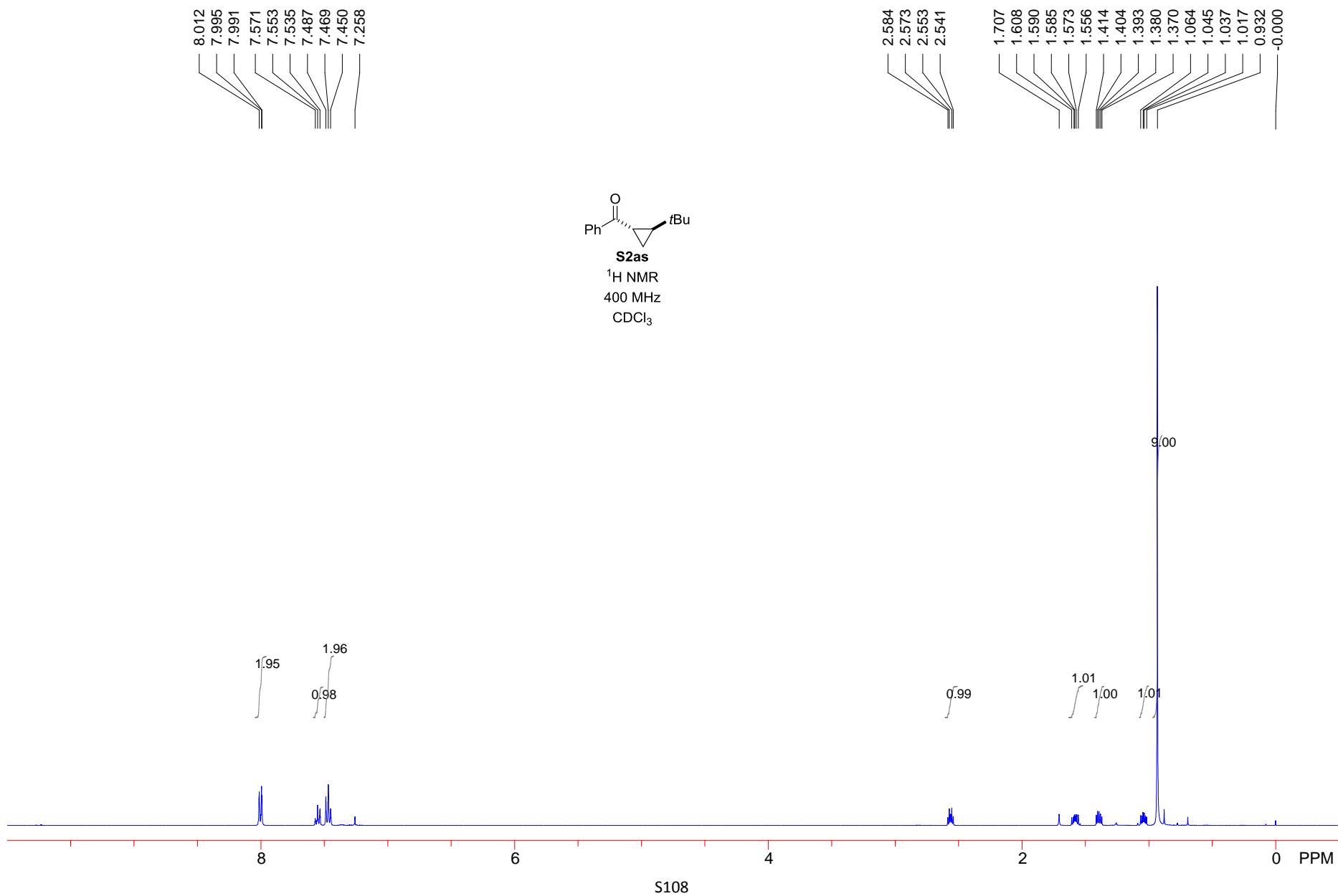


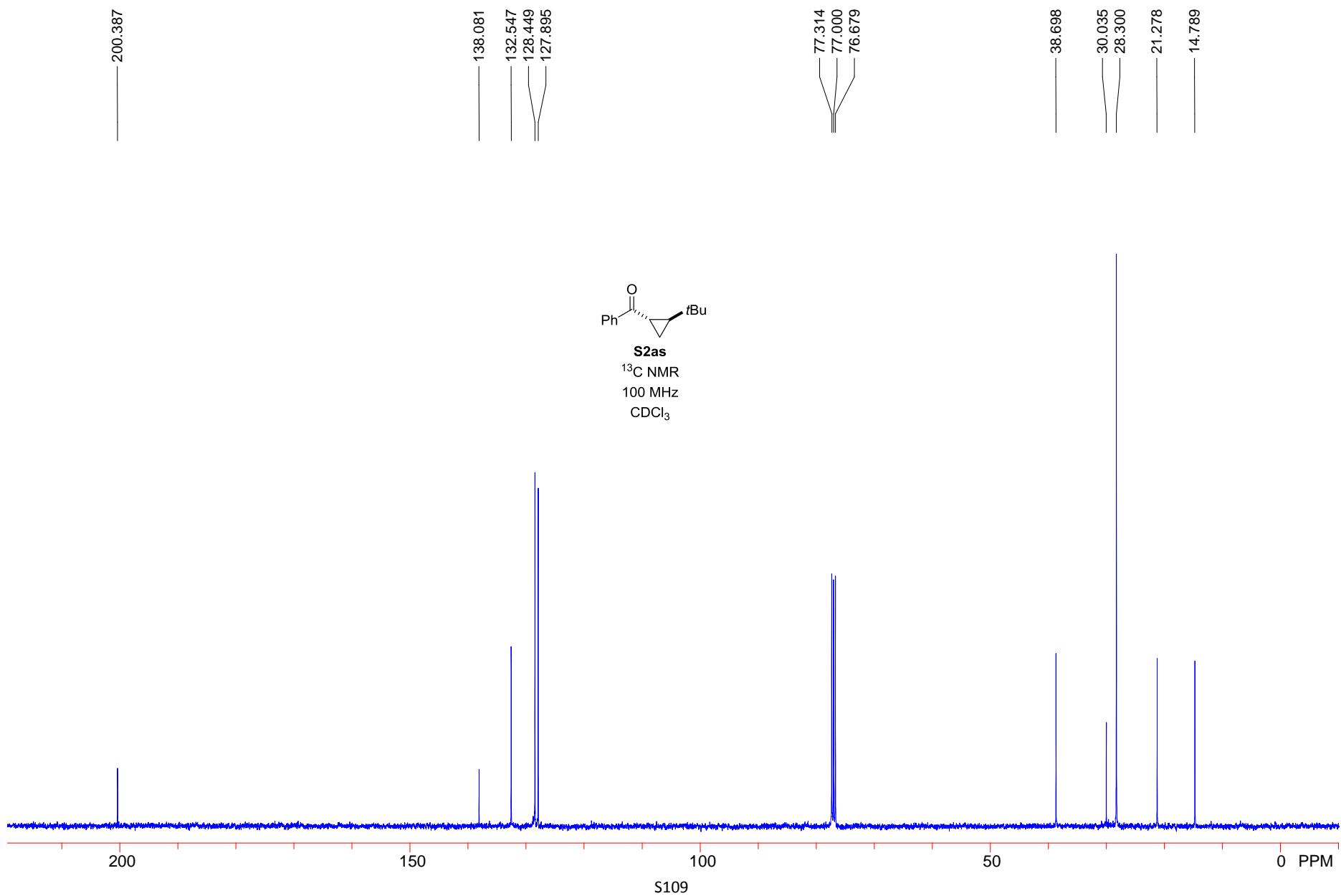
S104

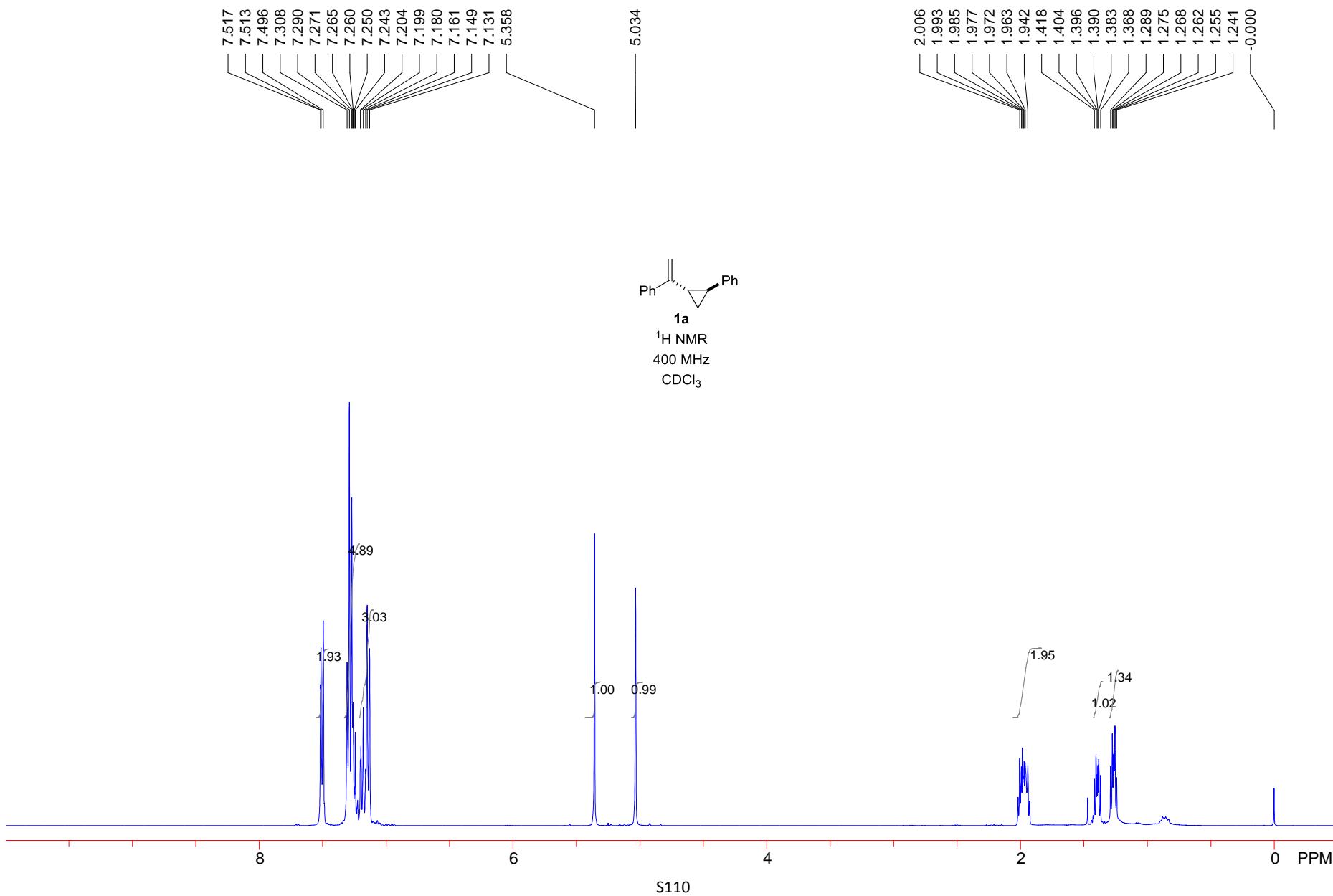


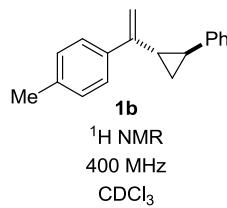
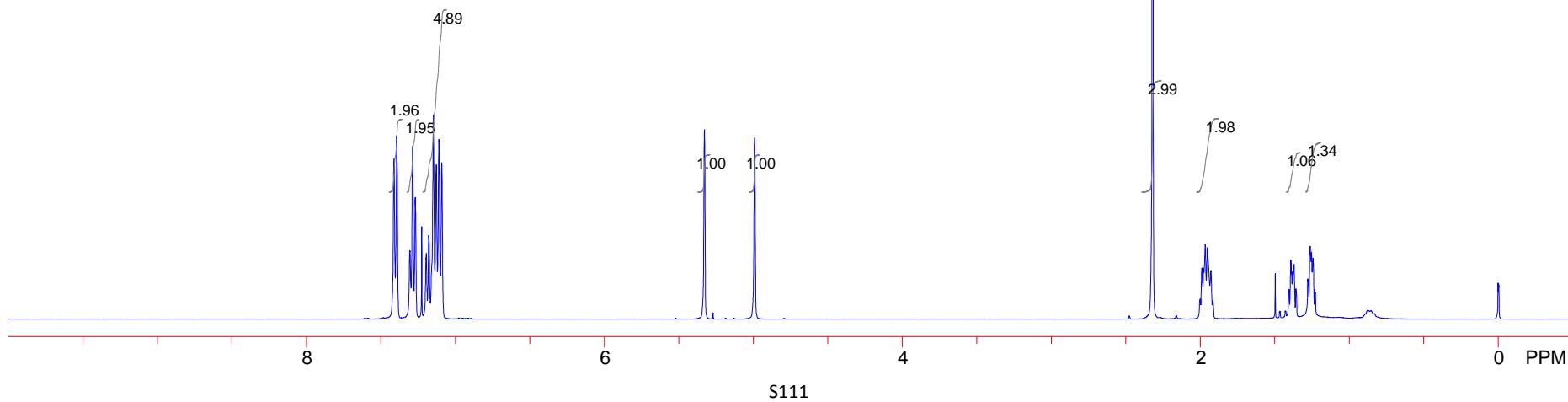


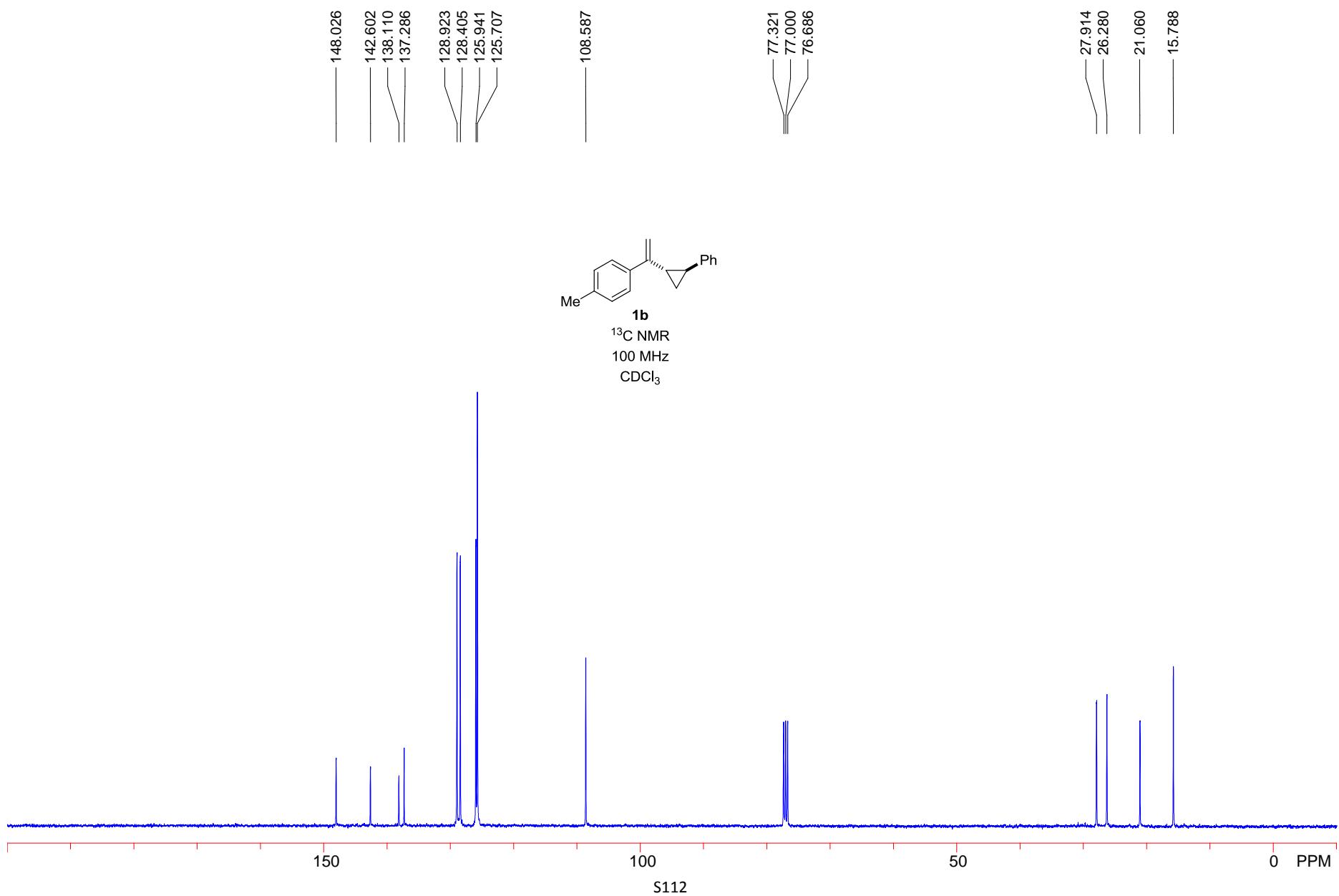


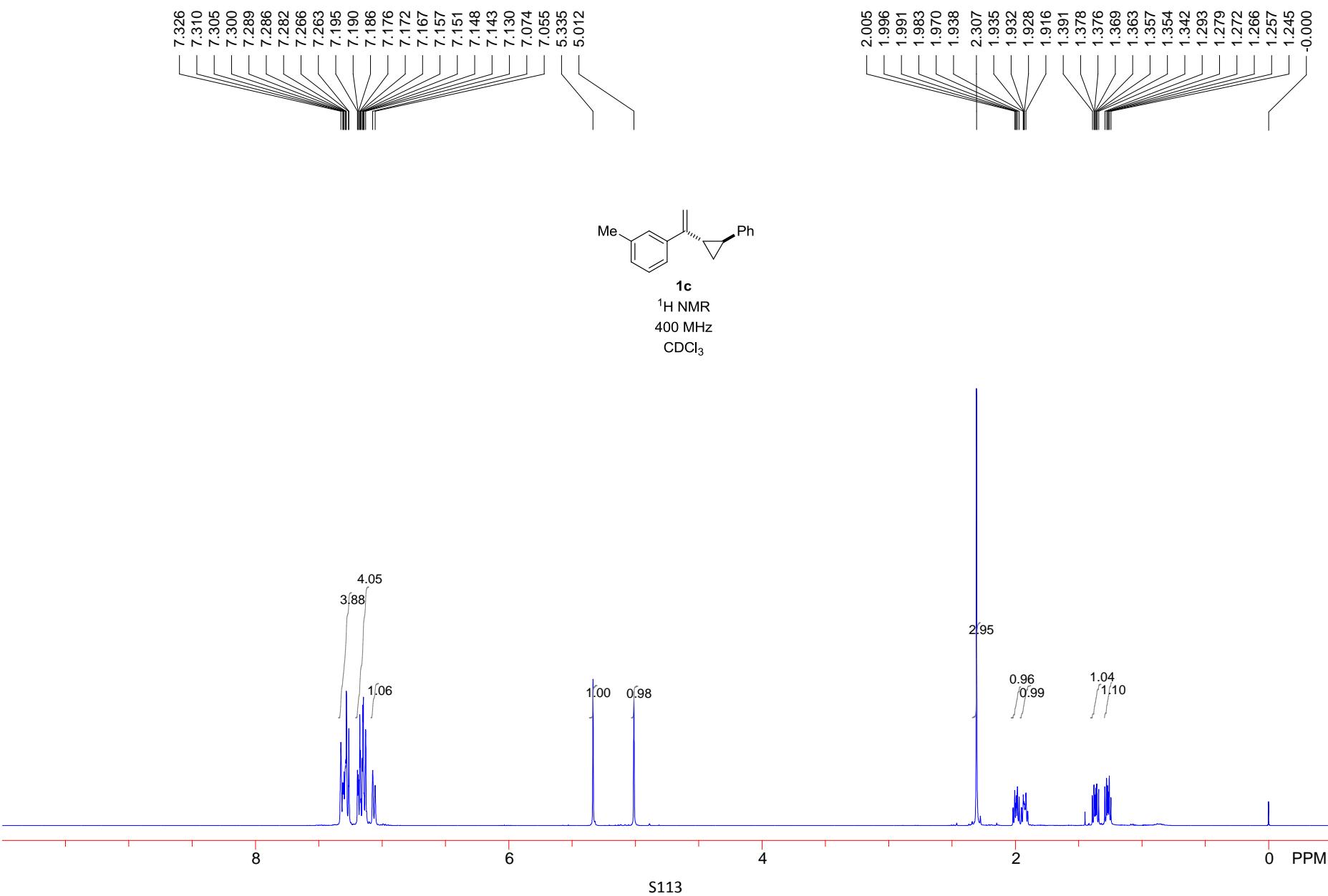


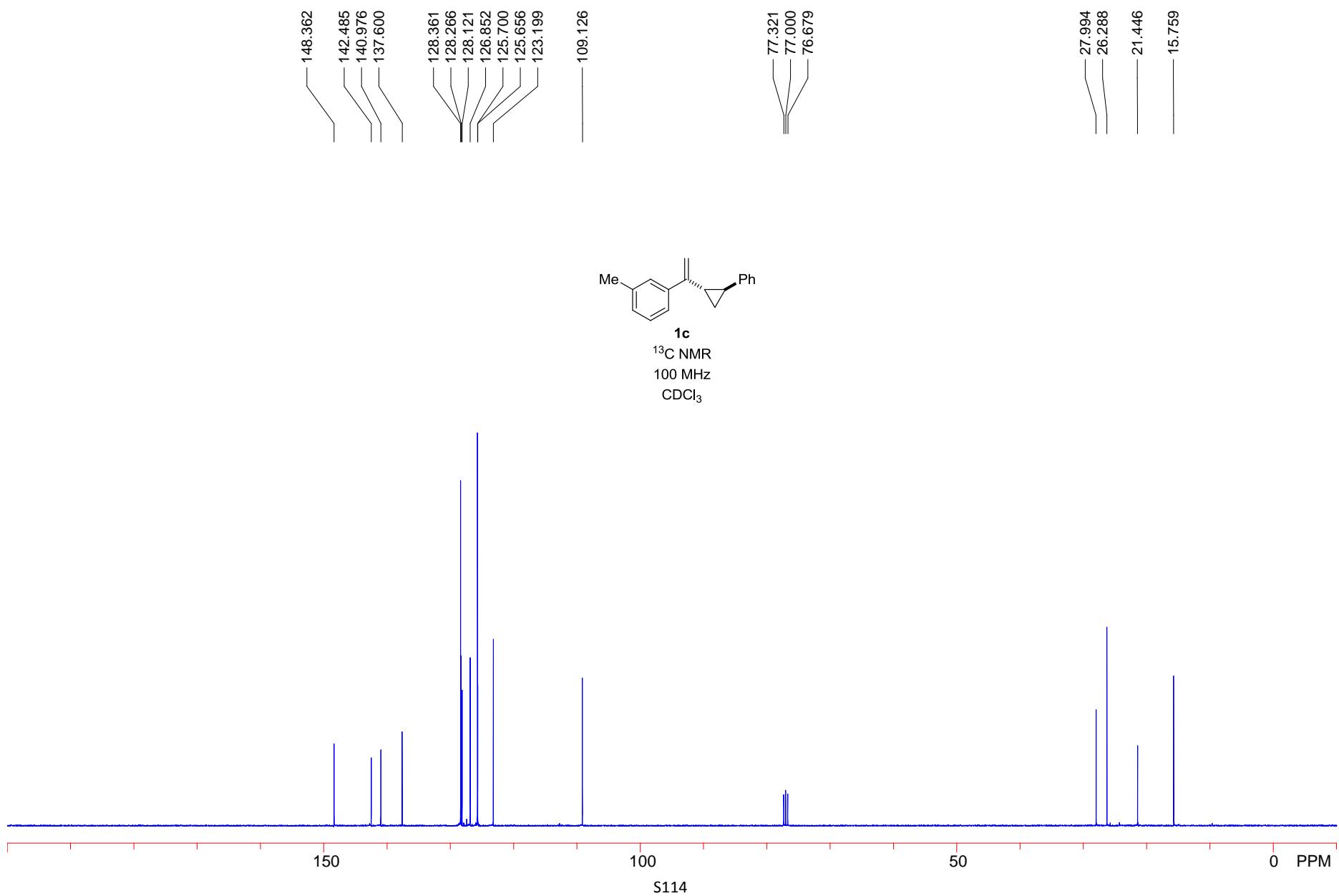


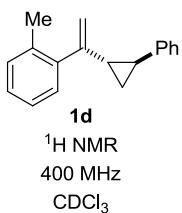
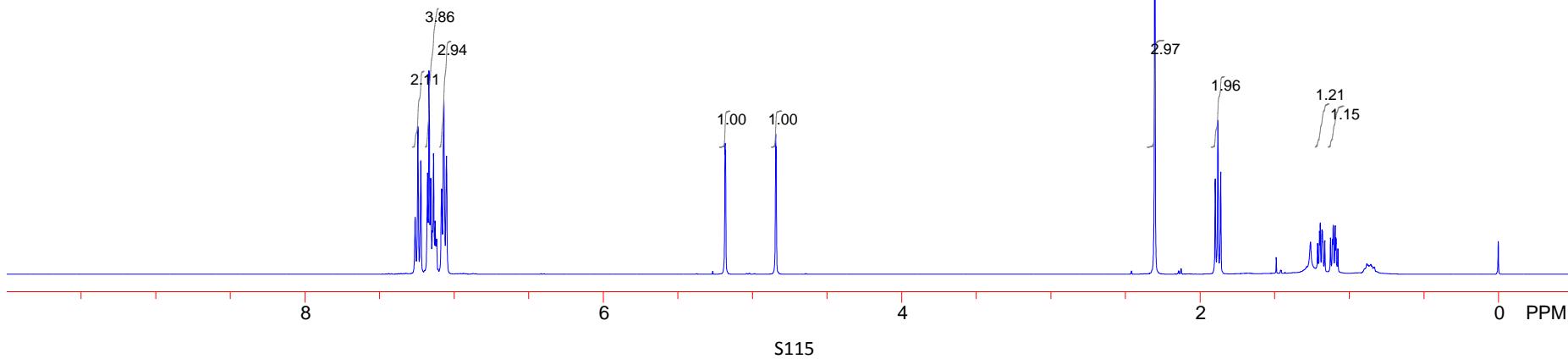


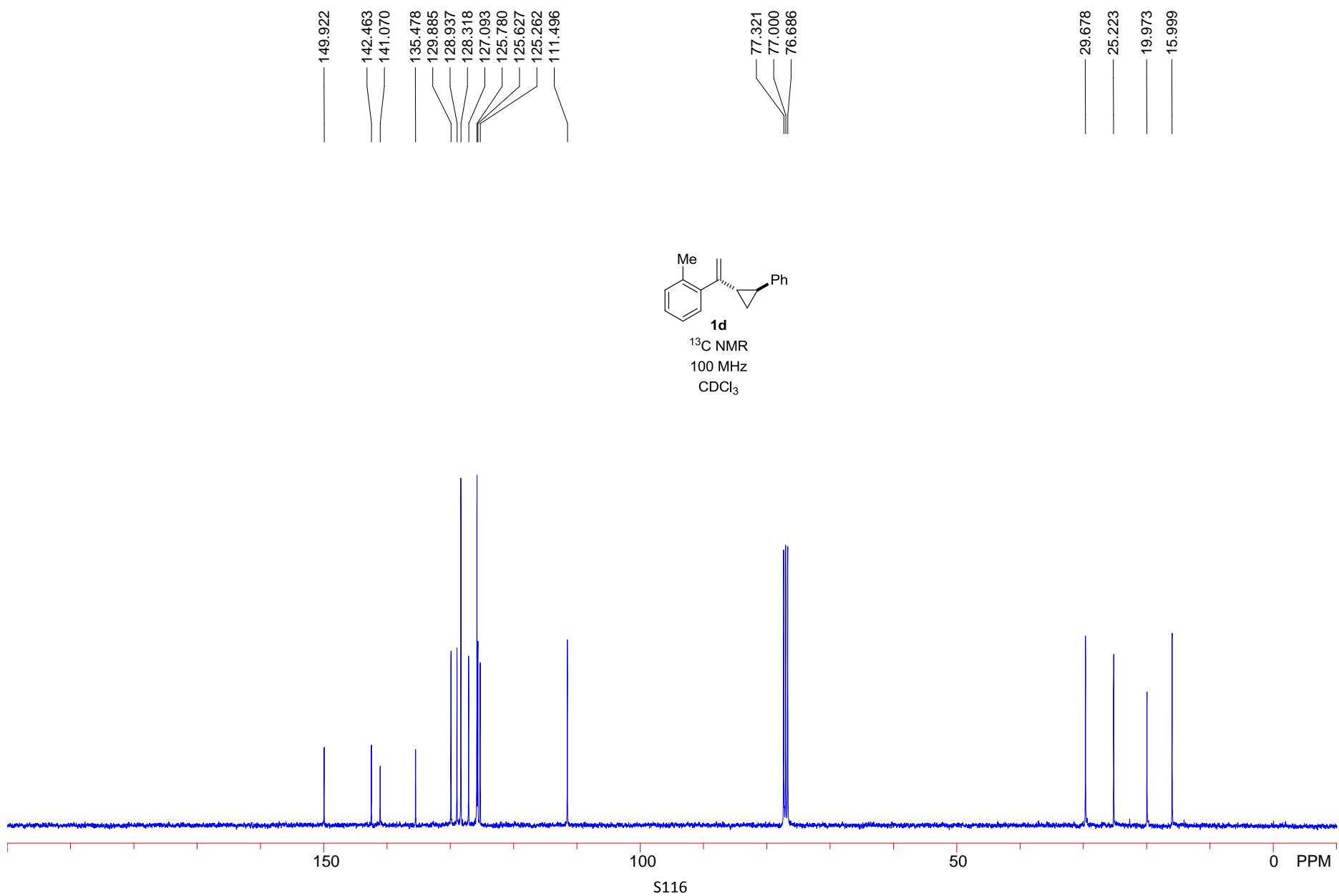


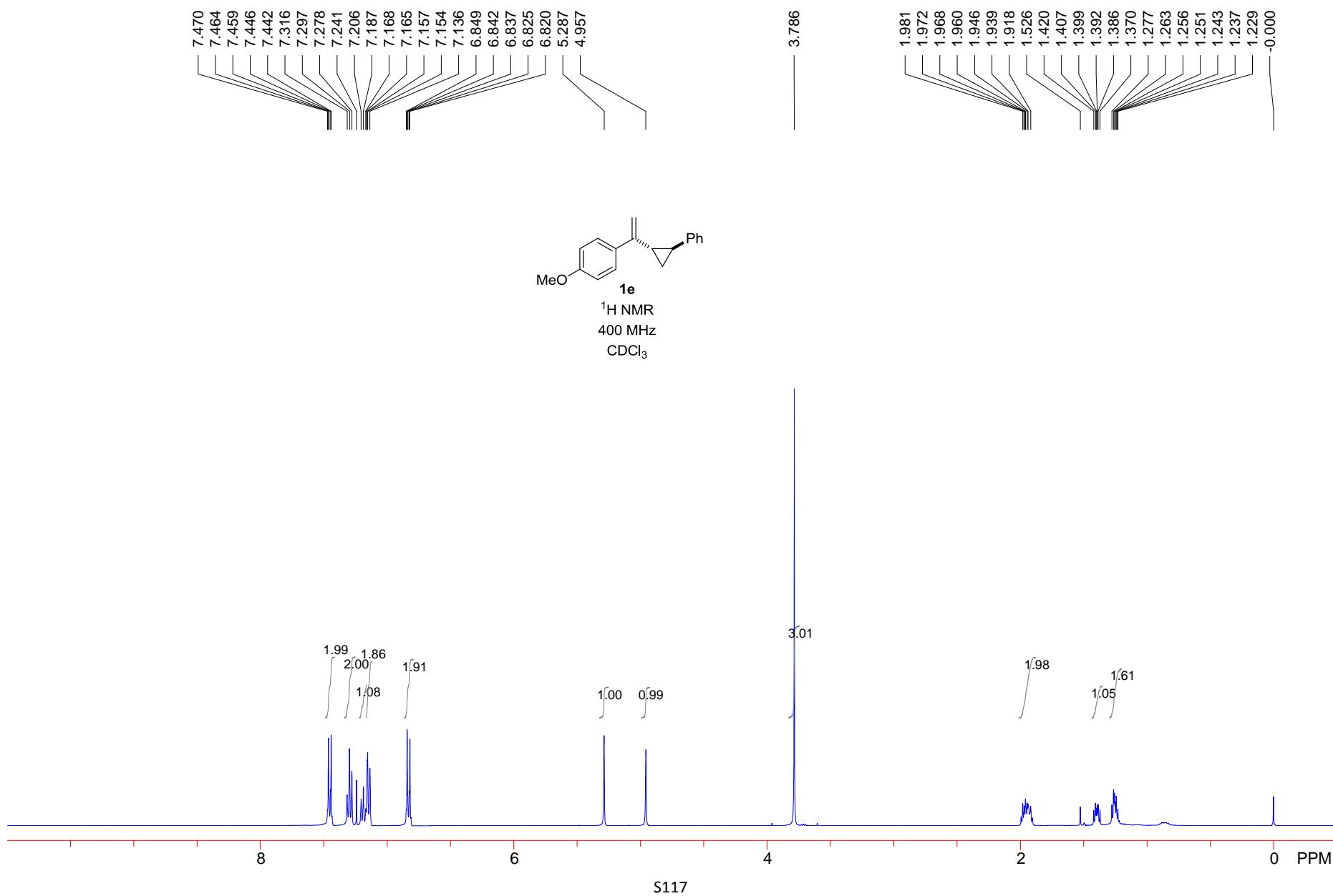


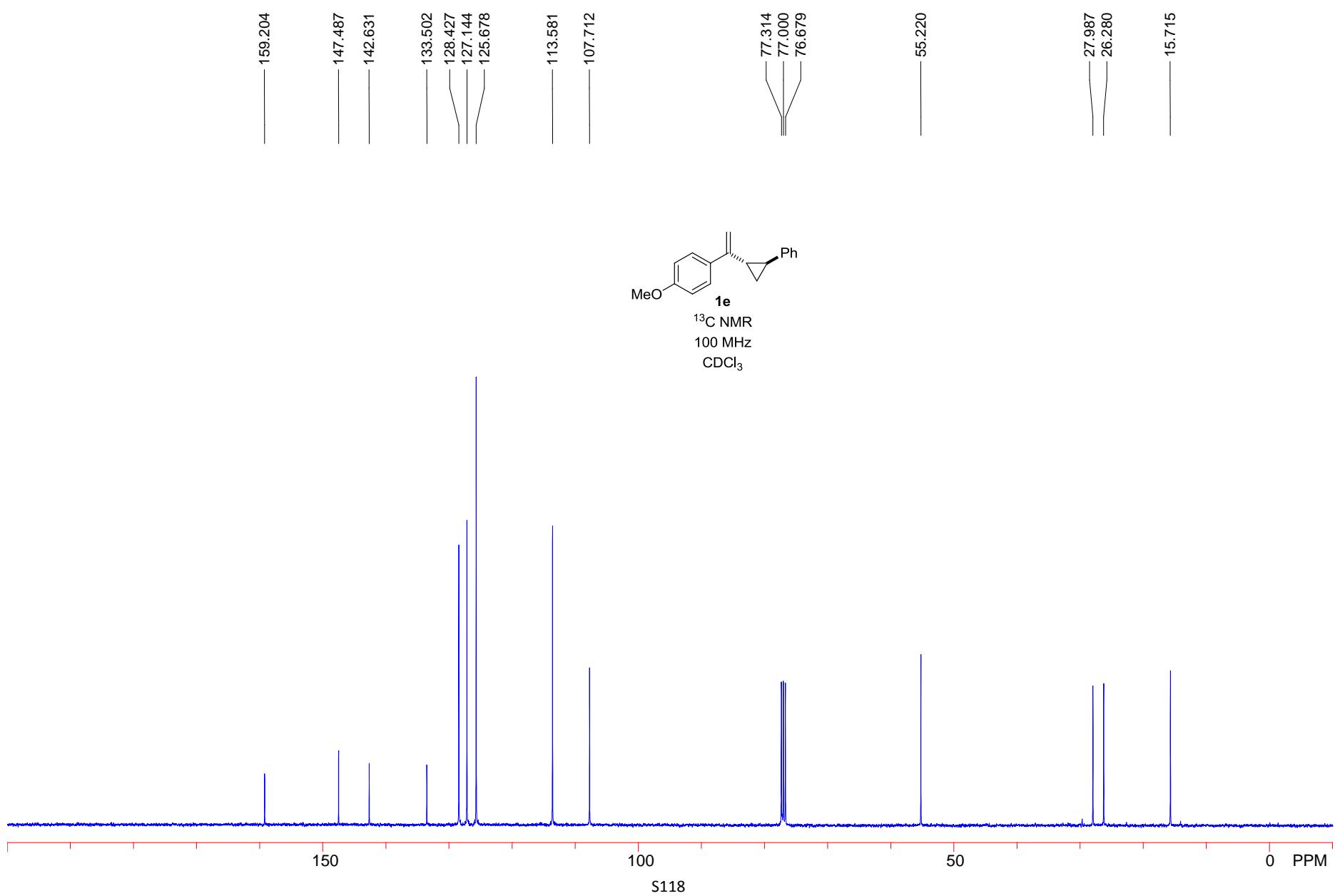


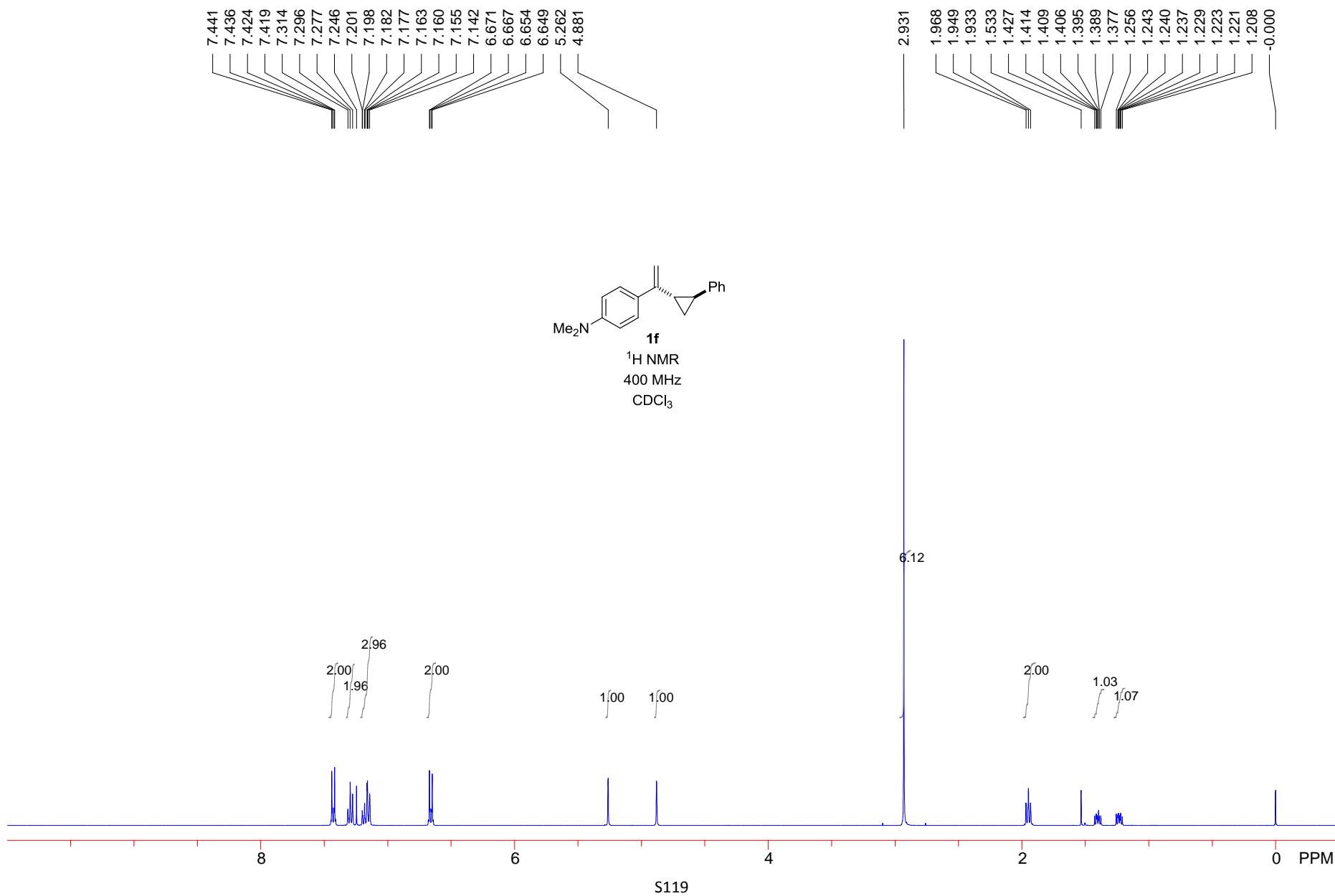


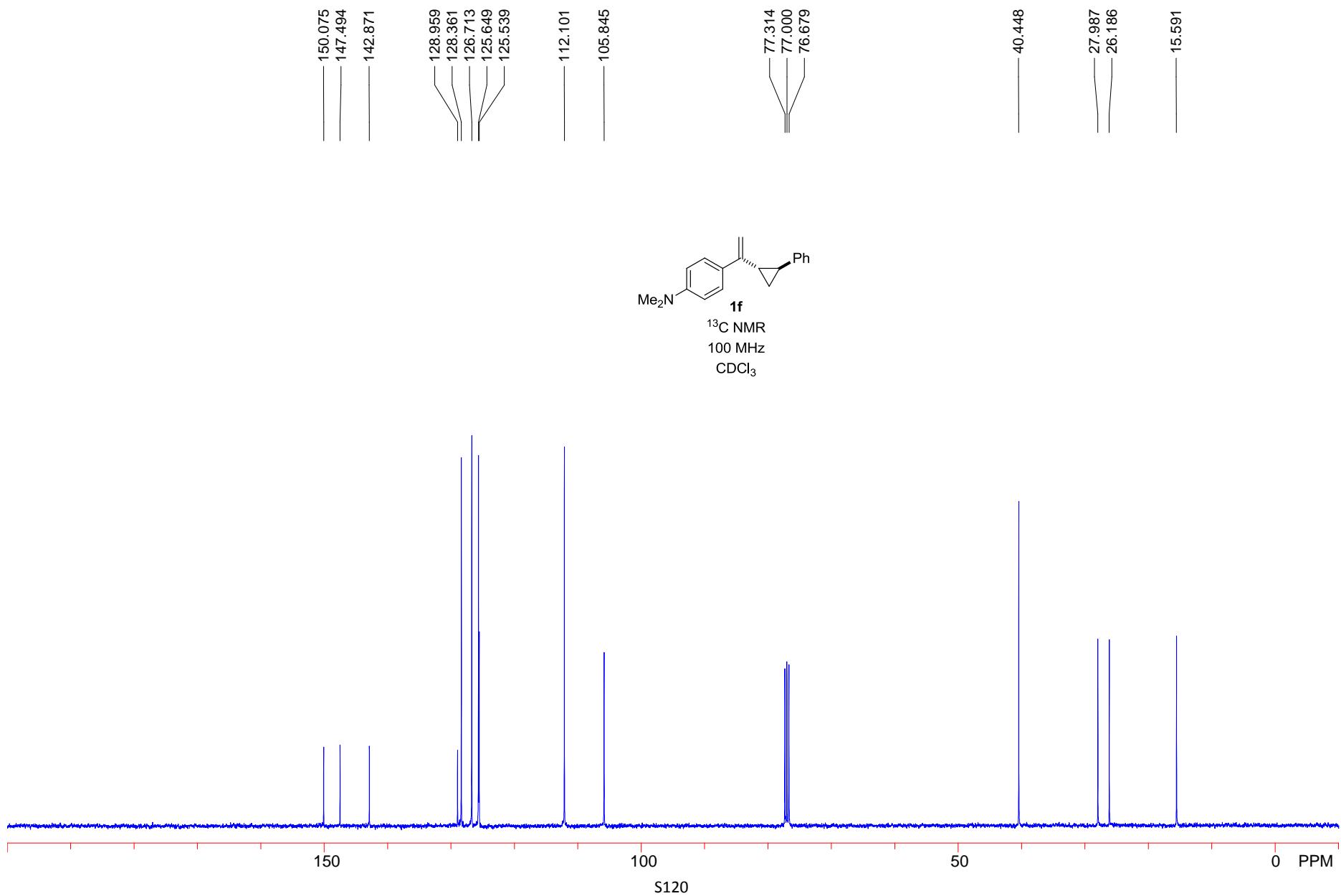


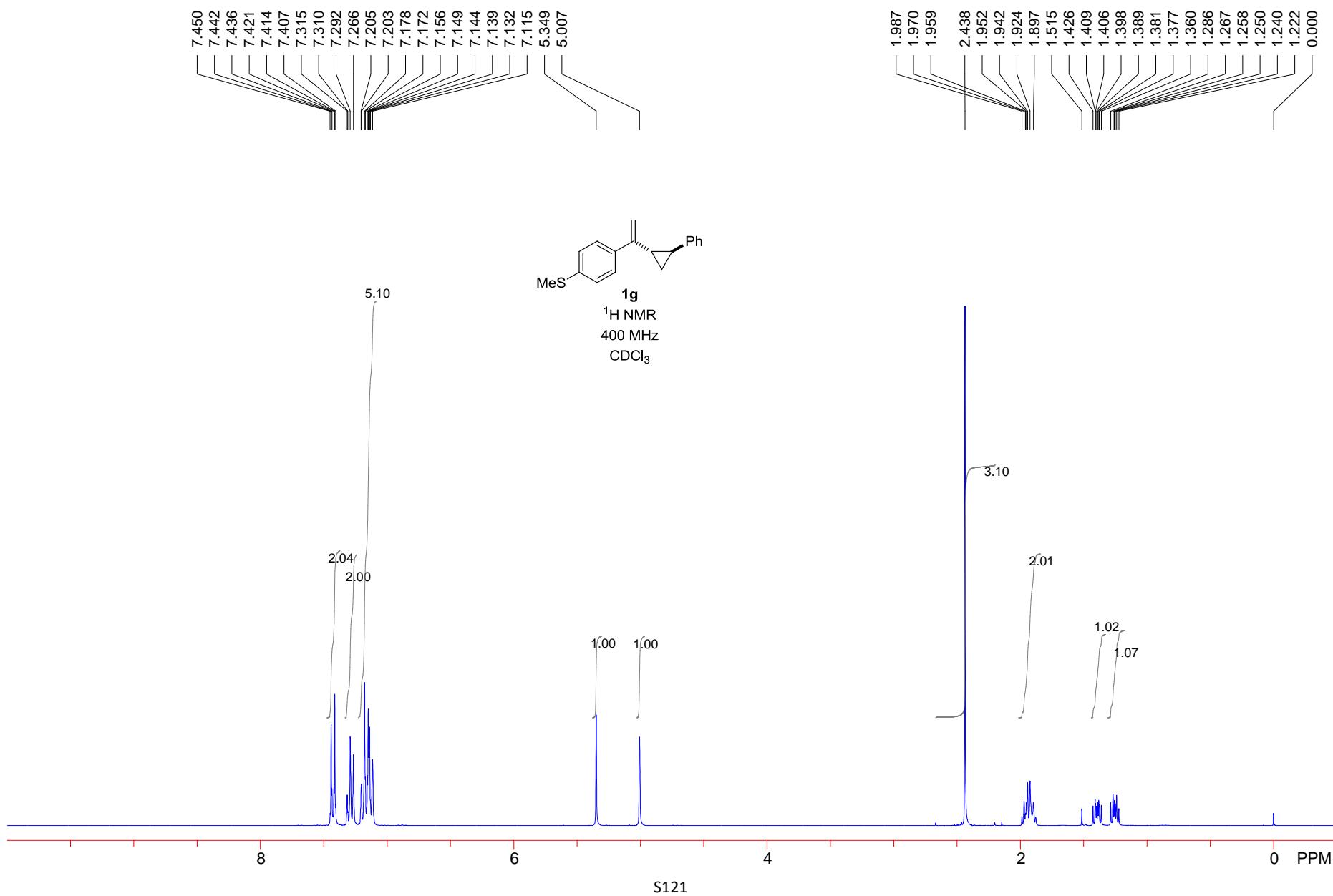


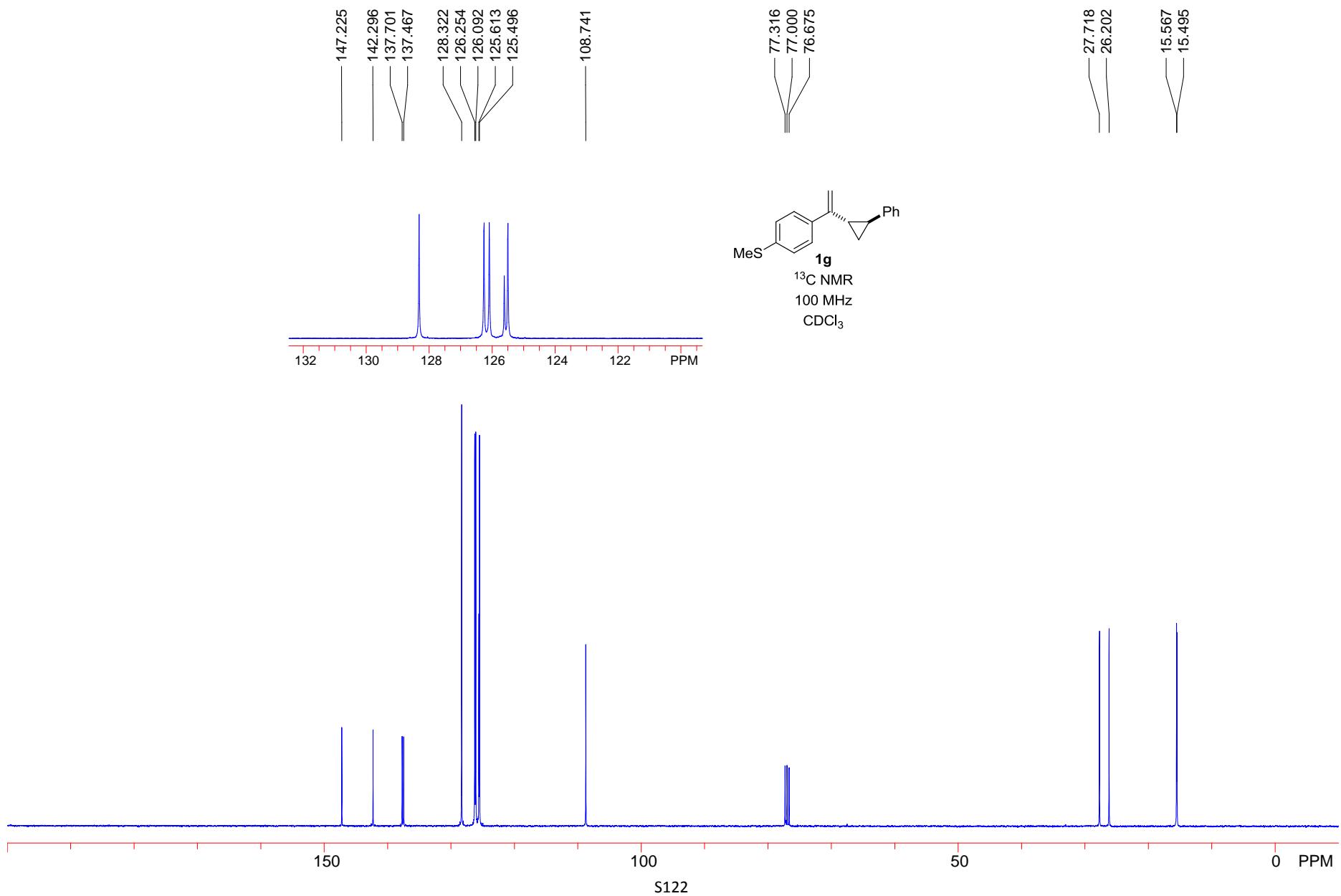


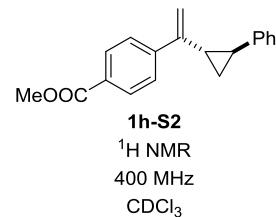
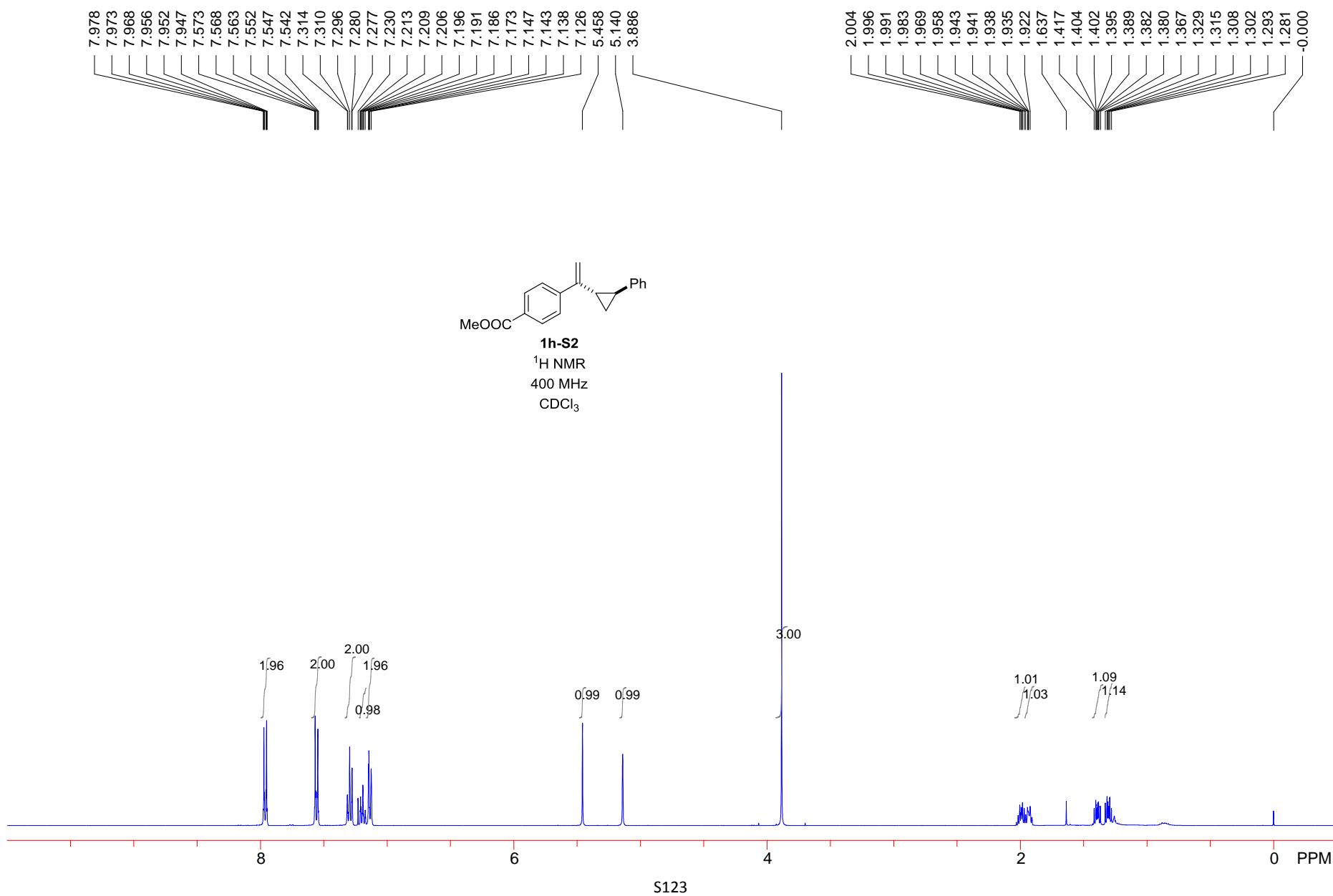


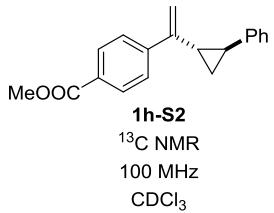
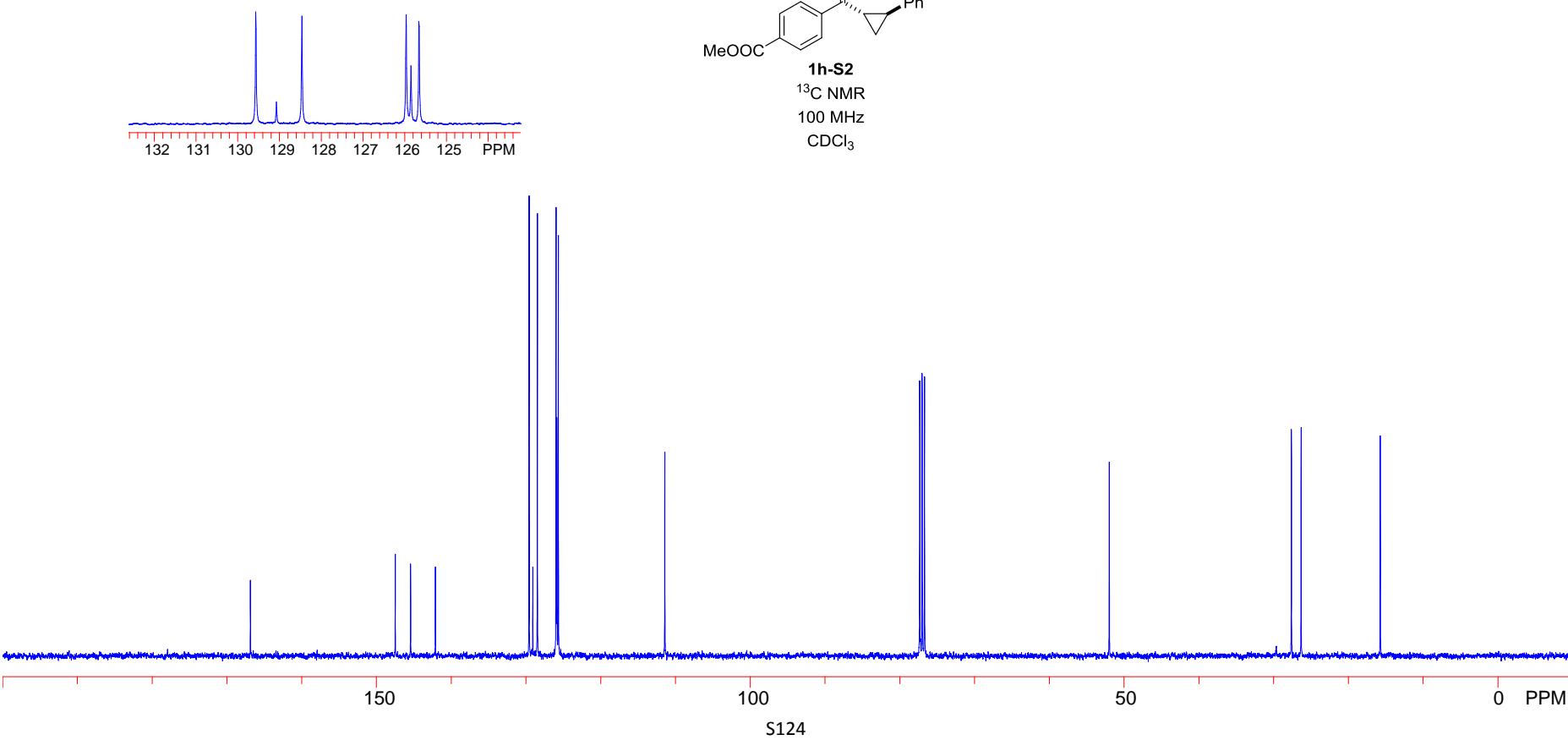












166.853

147.472
145.423
142.113

129.572
129.076
128.463
125.970
125.853
125.663

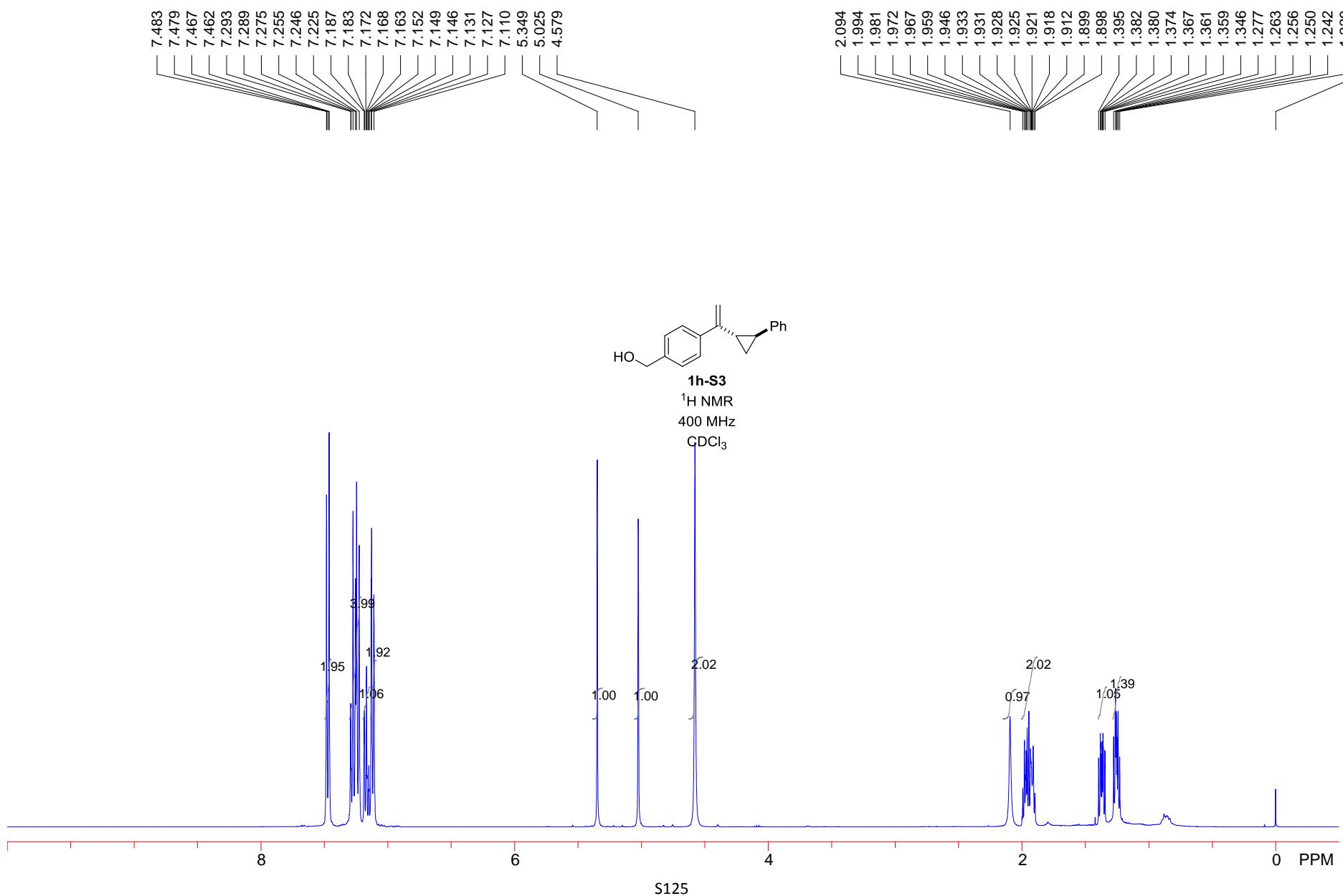
111.423

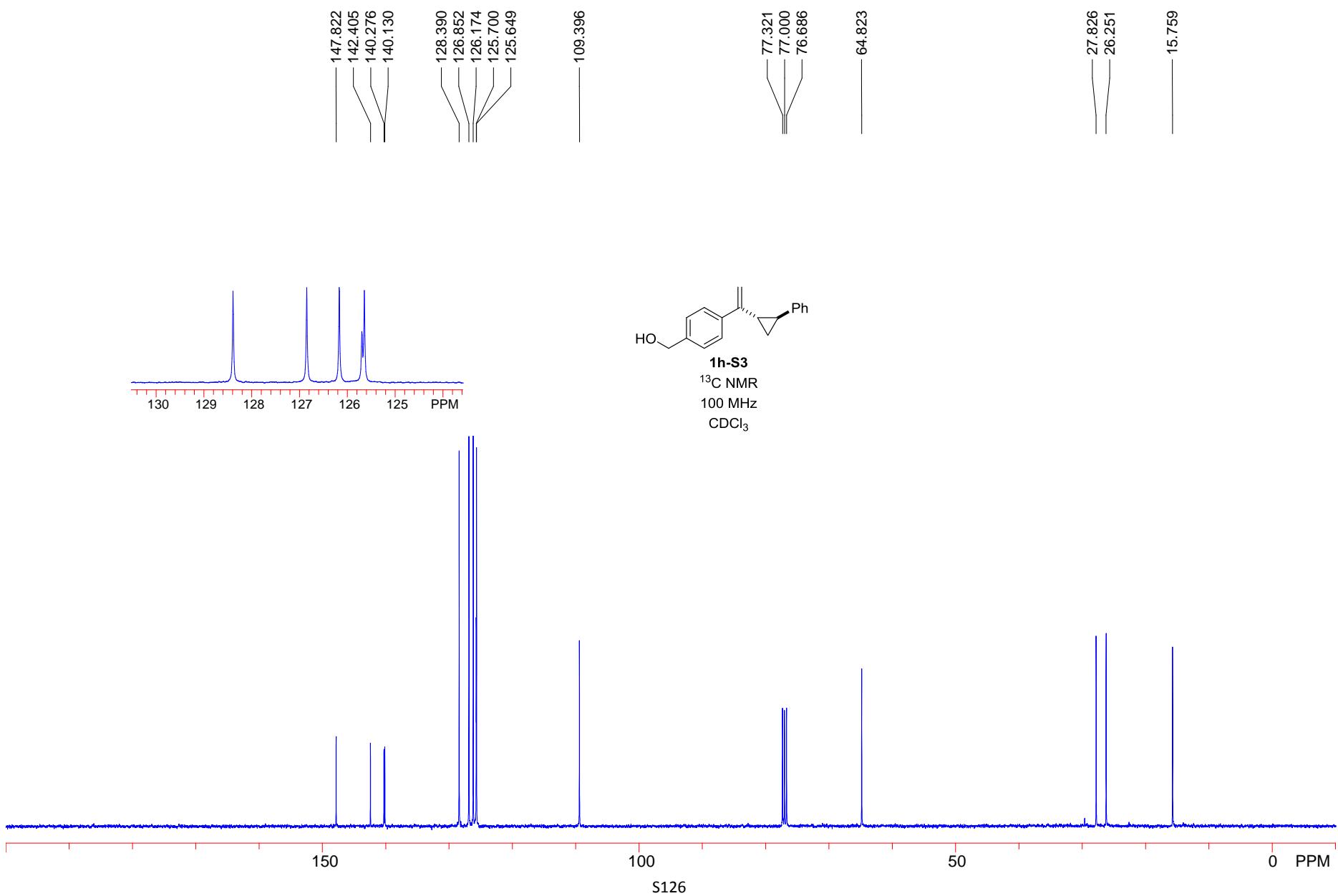
77.314
77.000
76.679

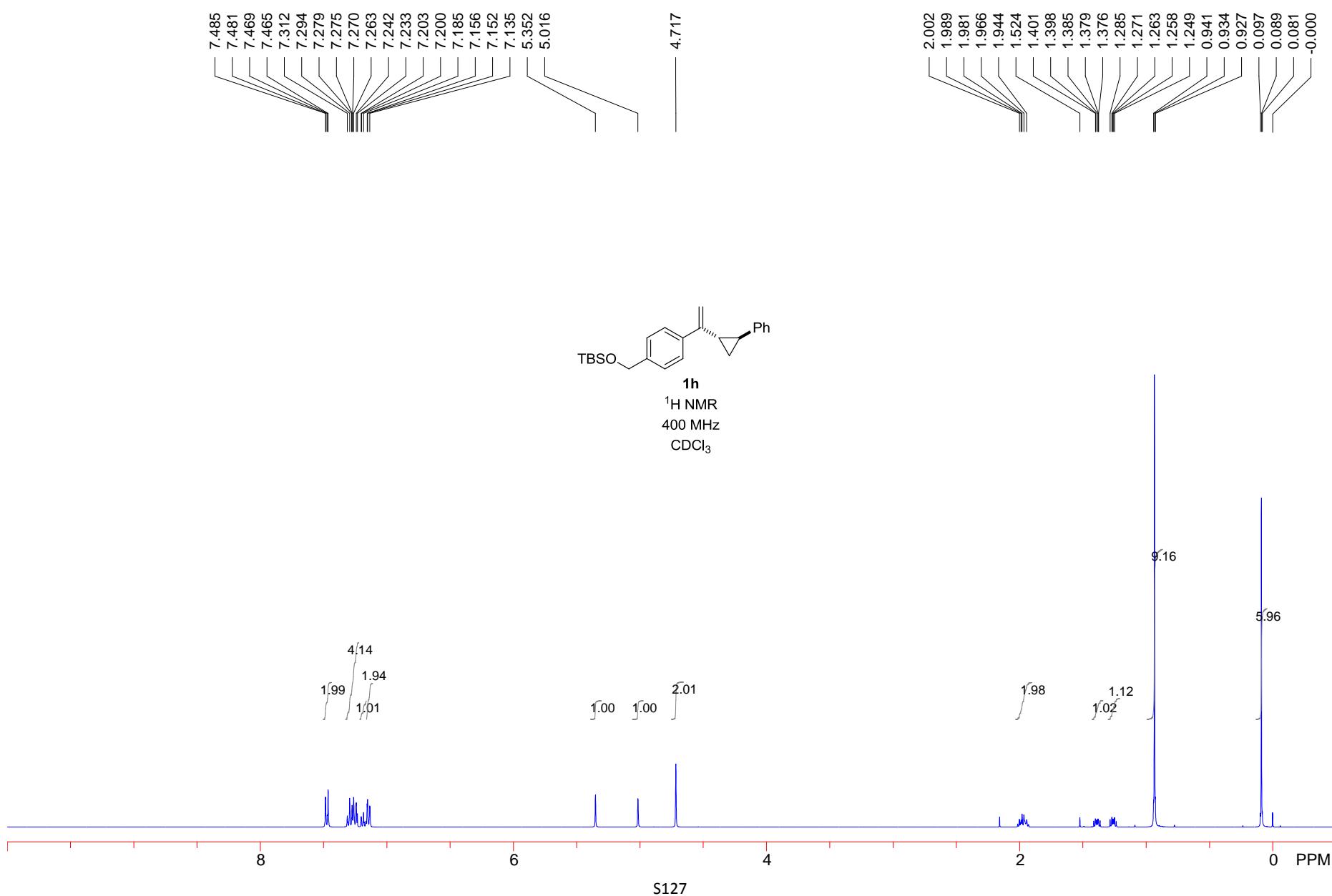
51.983

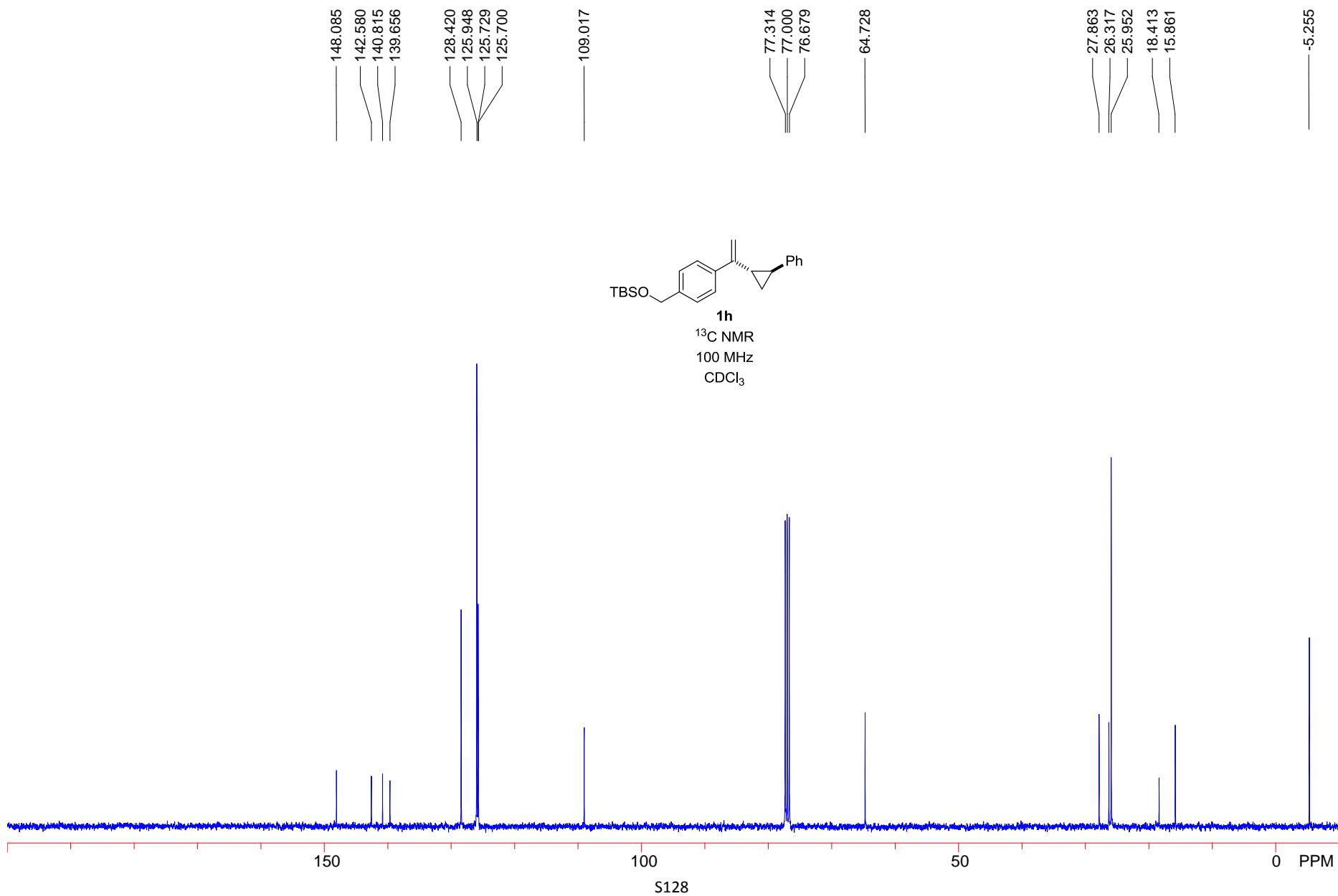
27.644
26.346

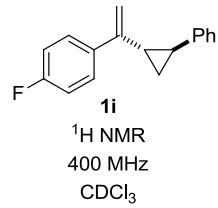
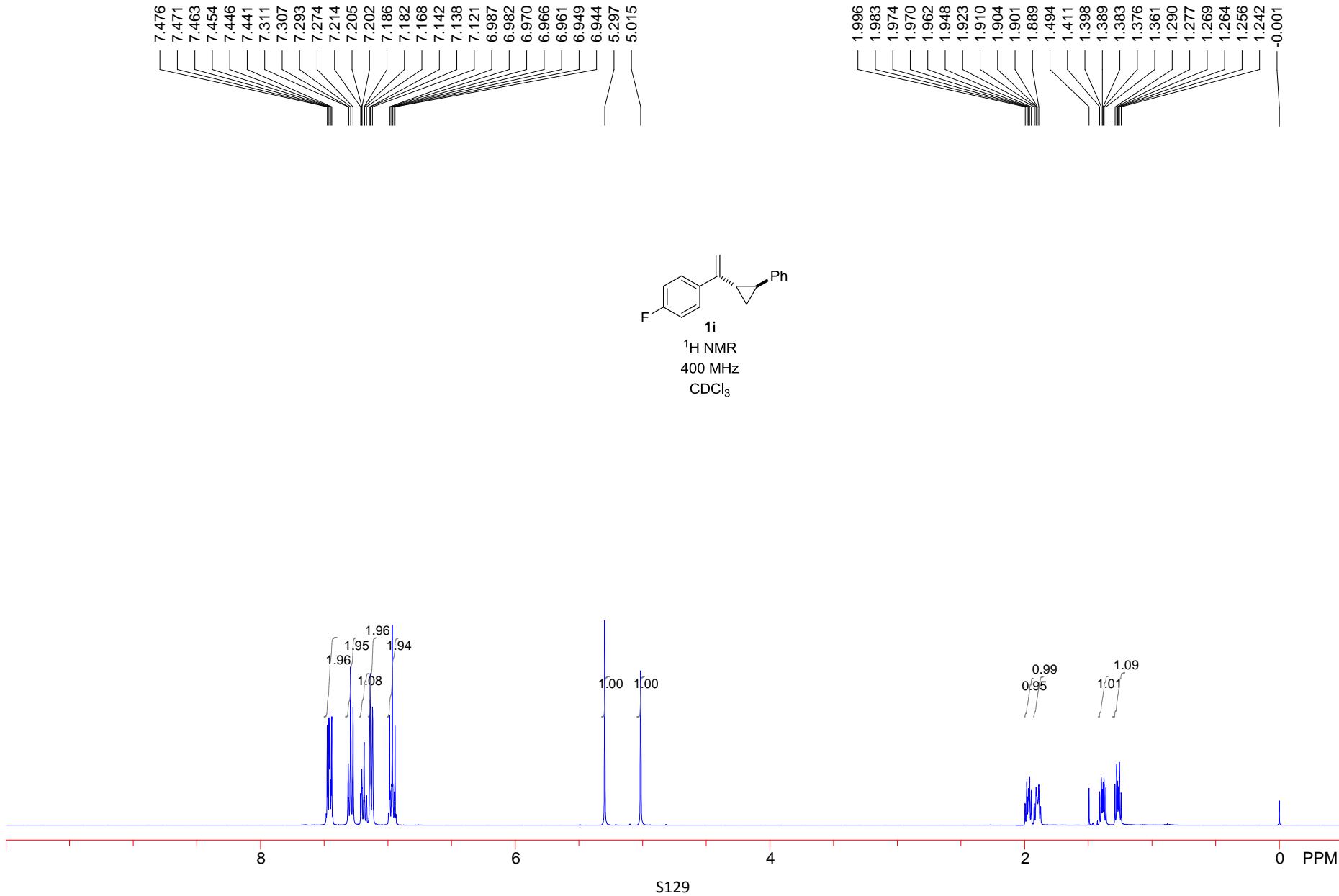
15.766

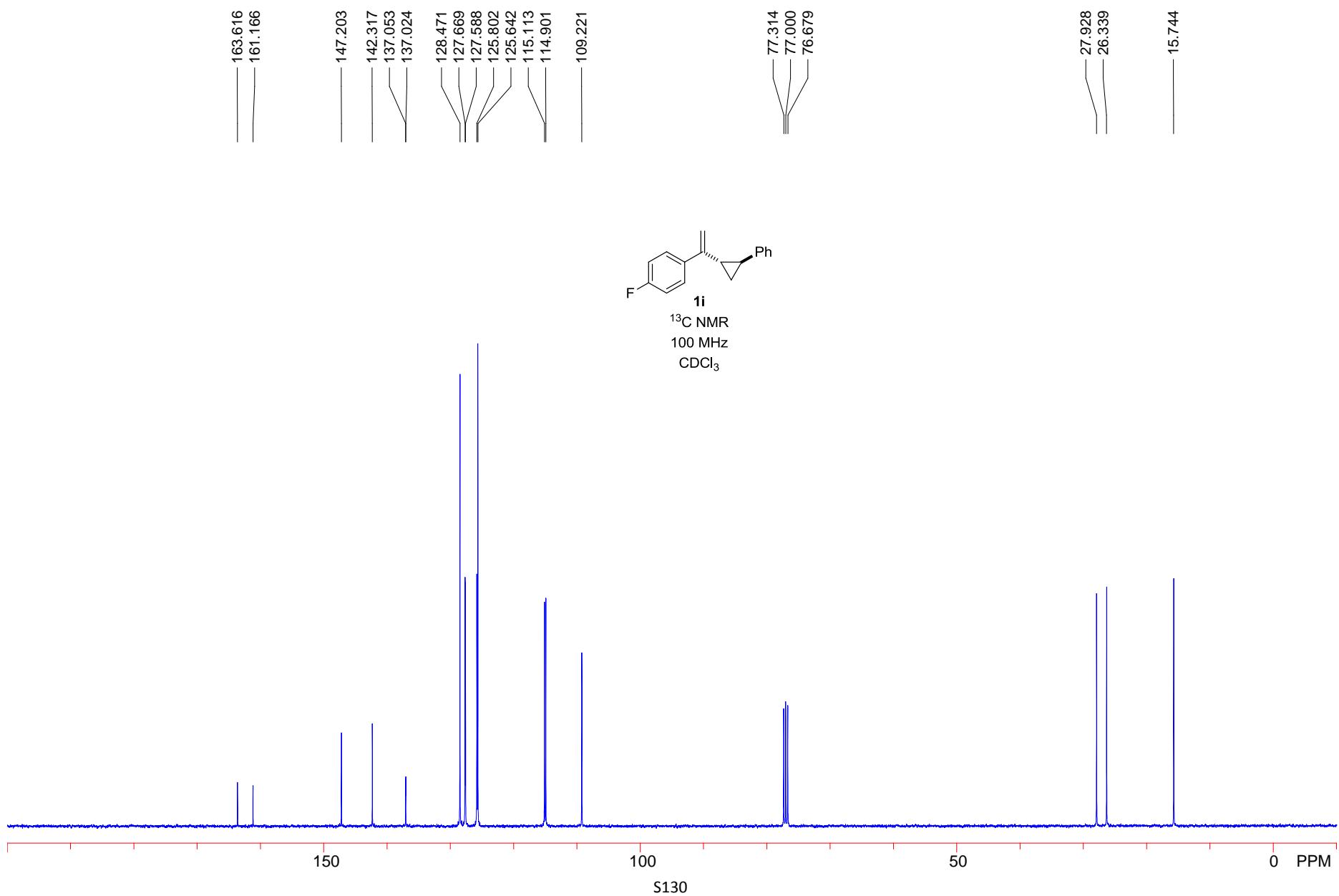


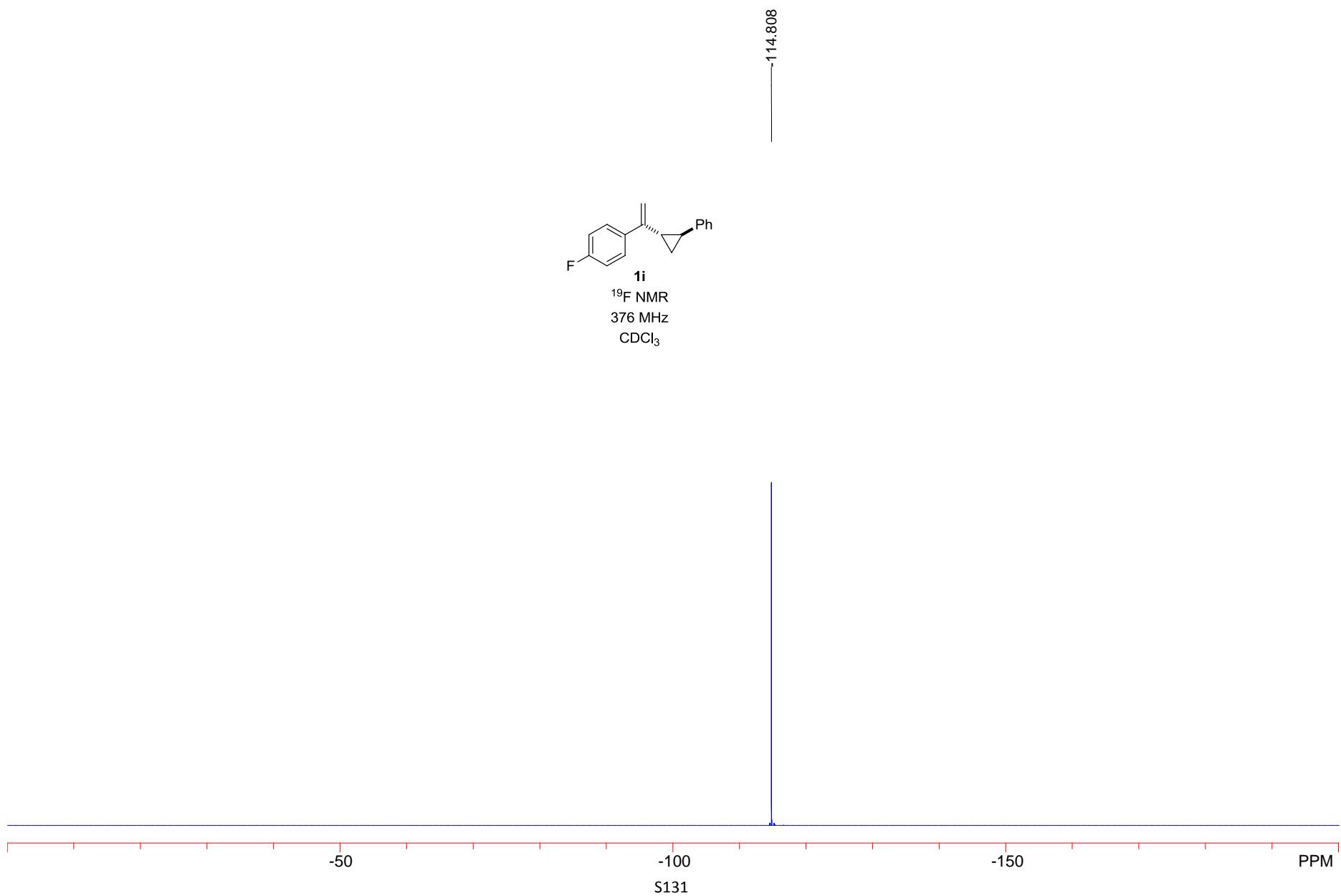


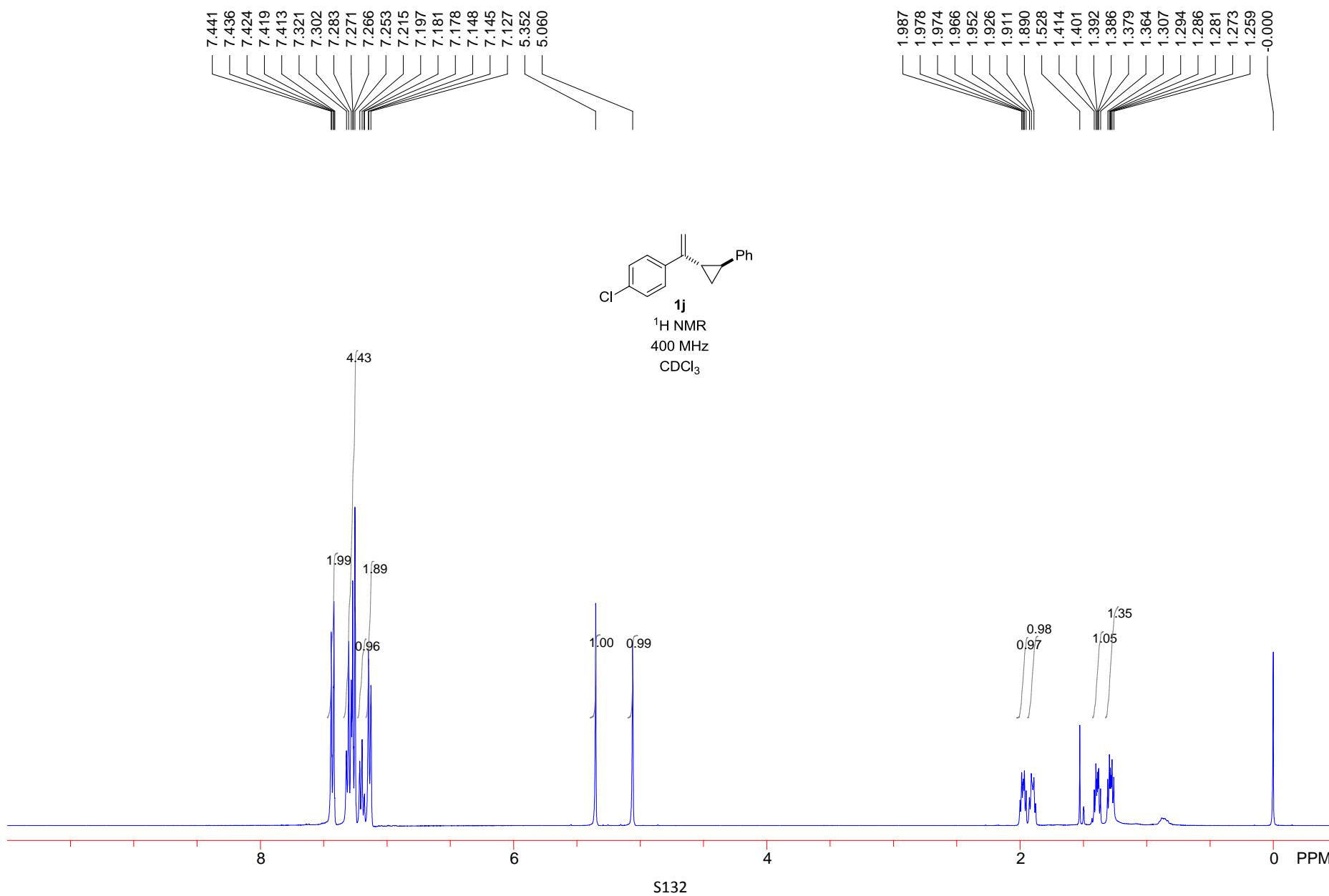


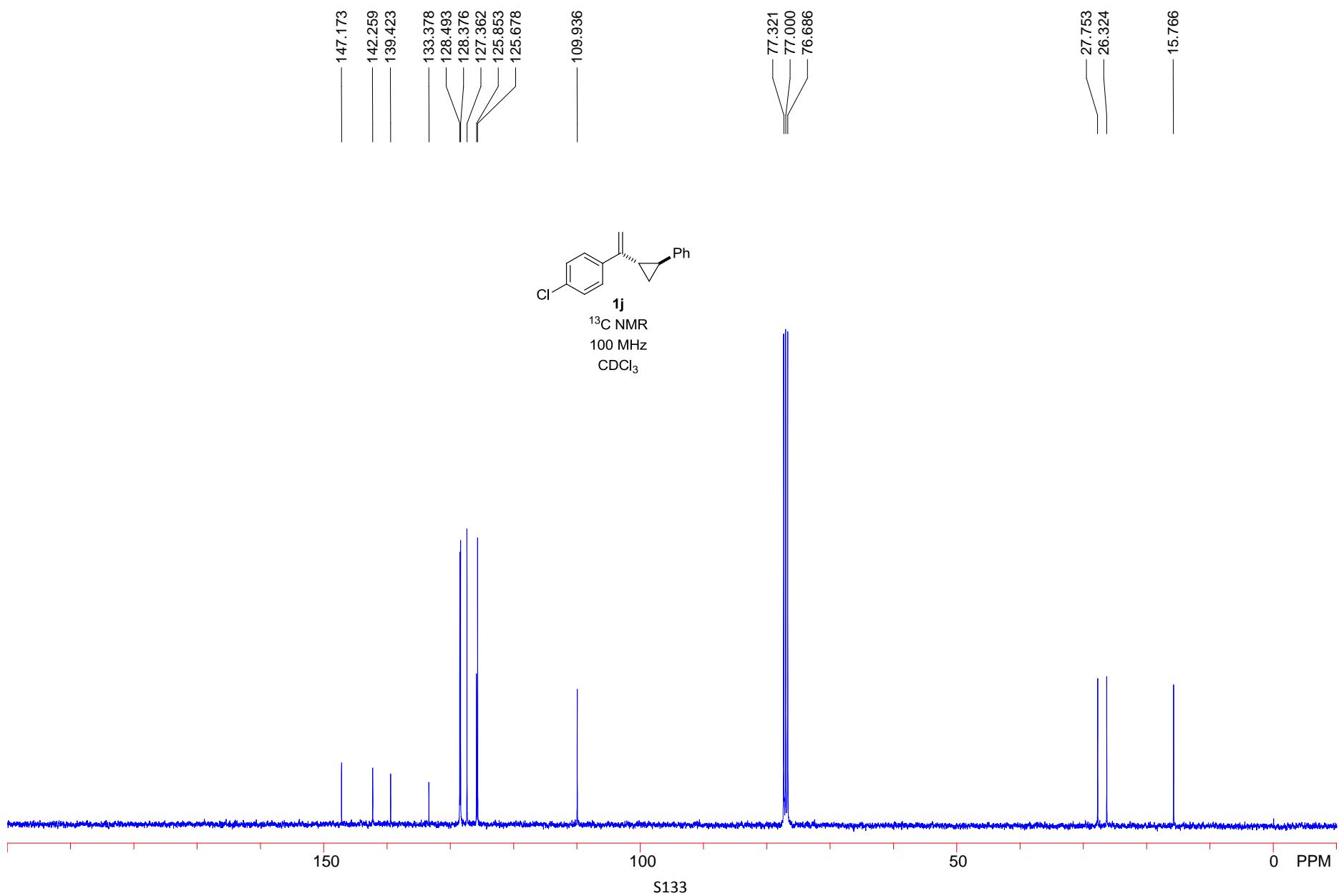


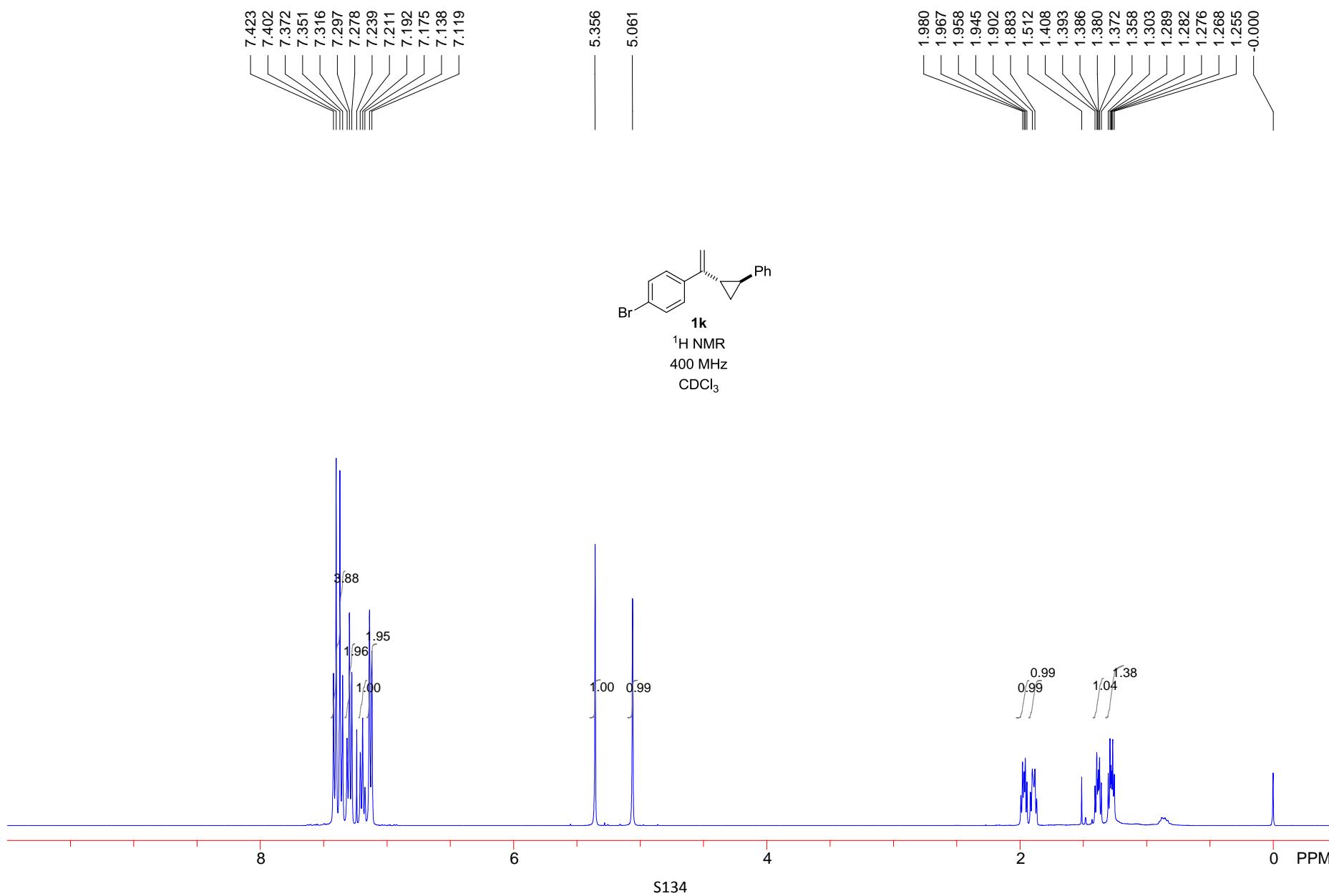


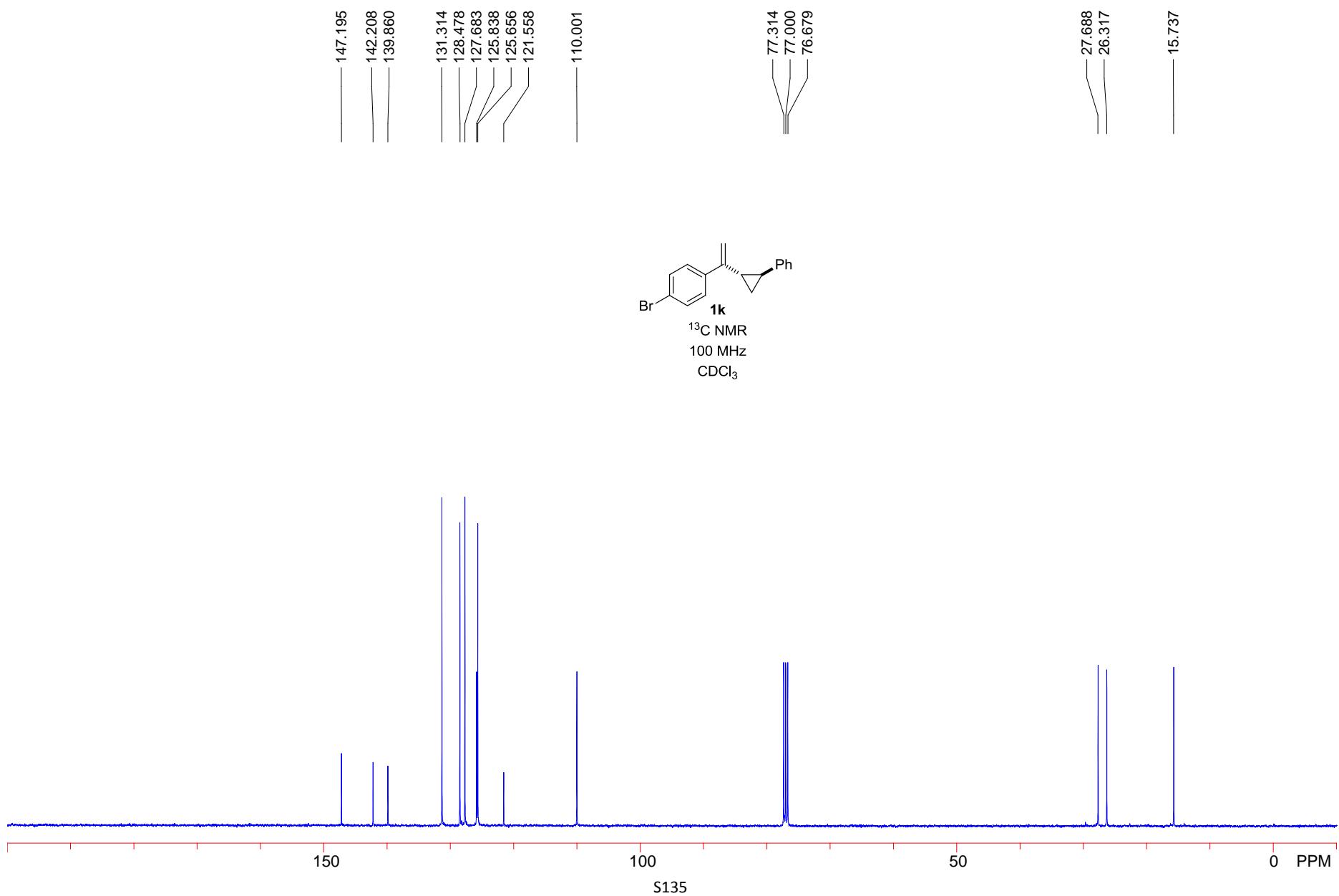


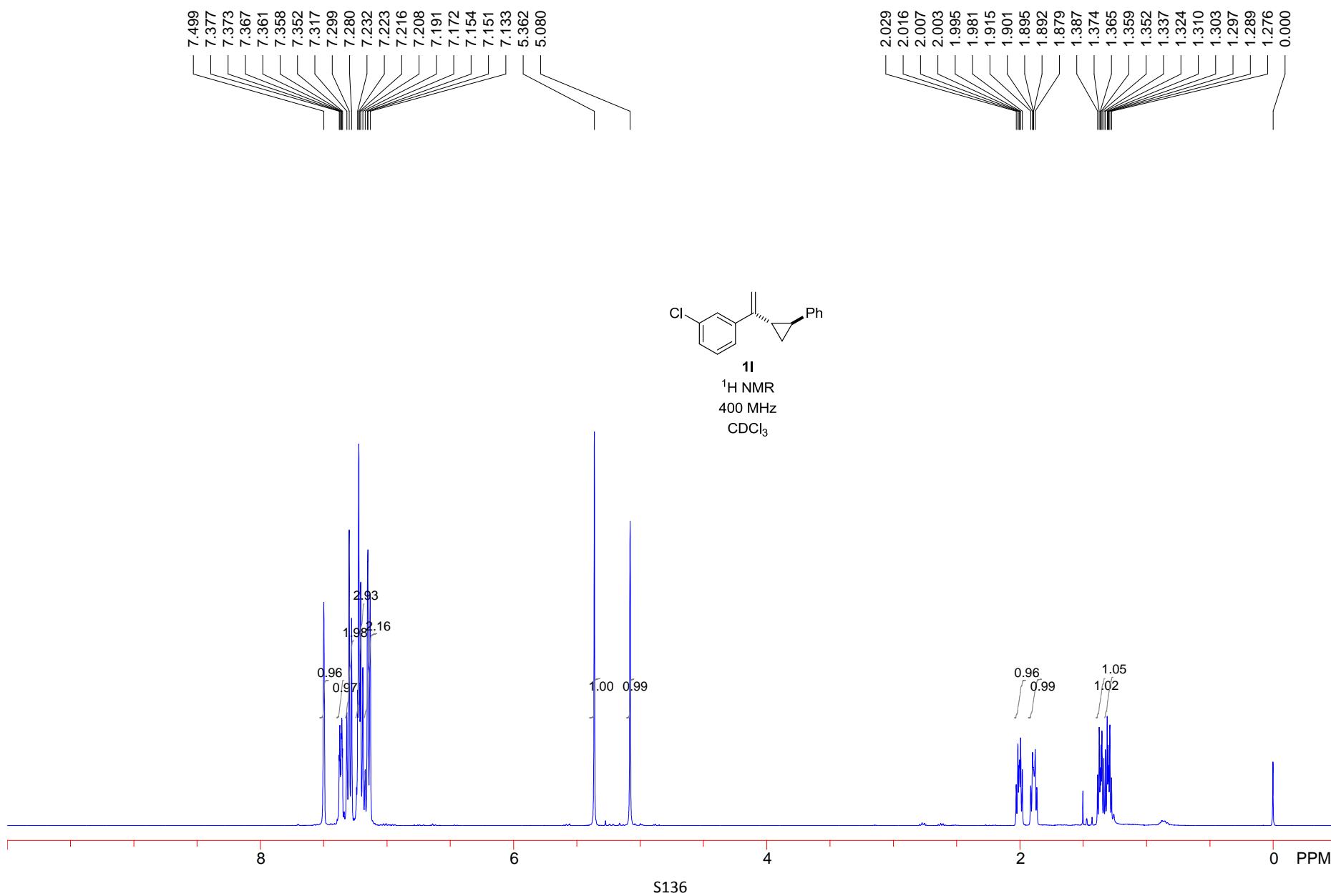


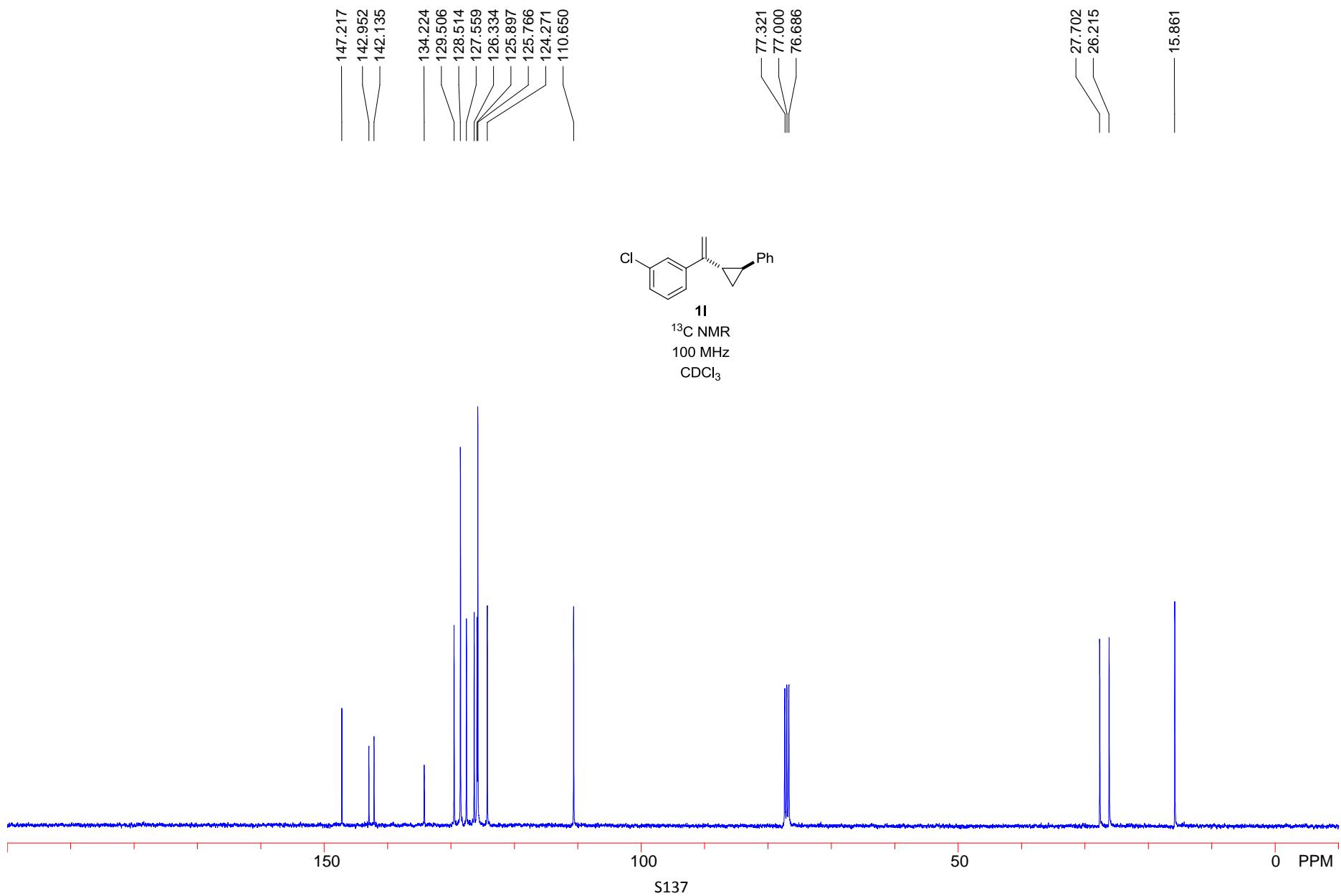


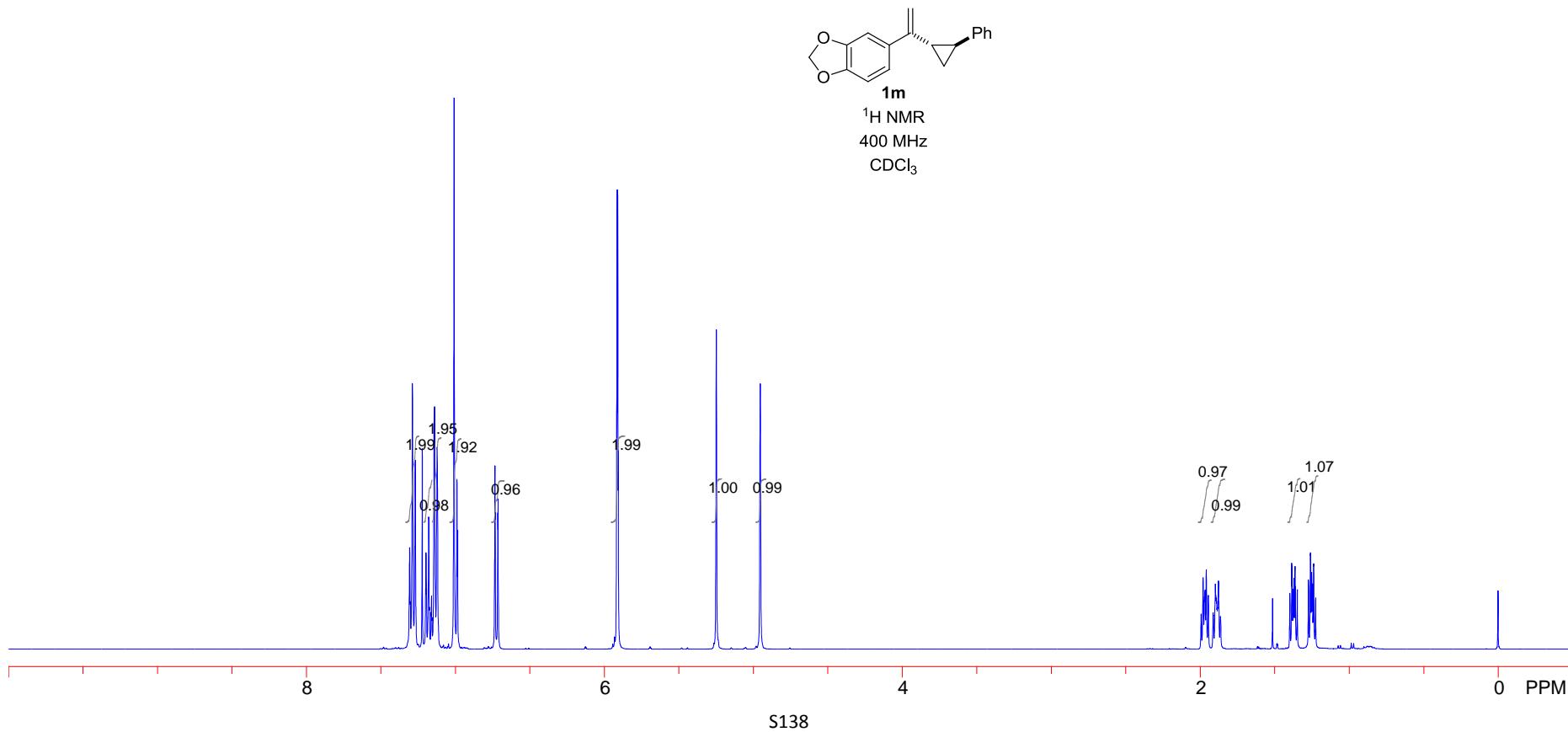


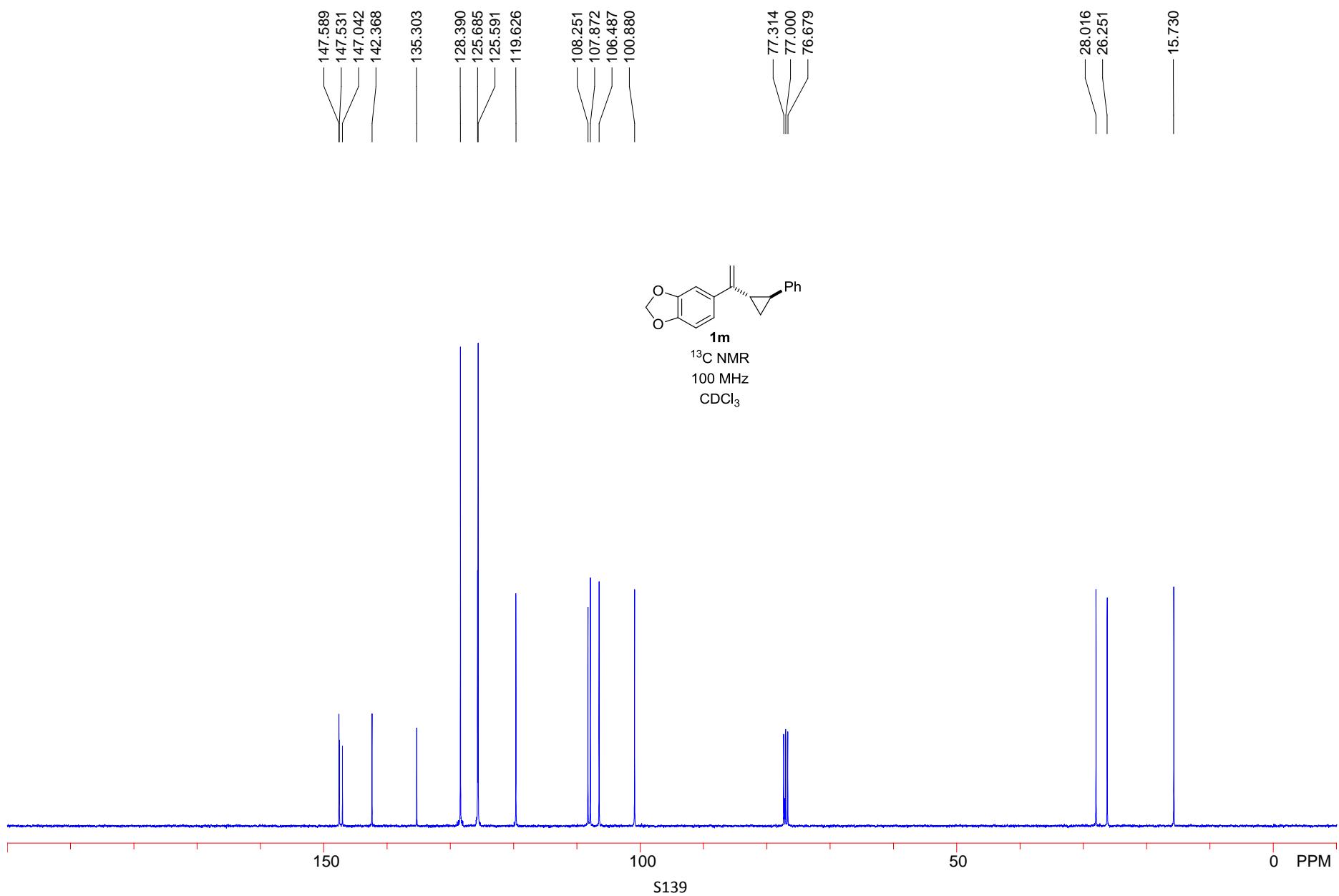


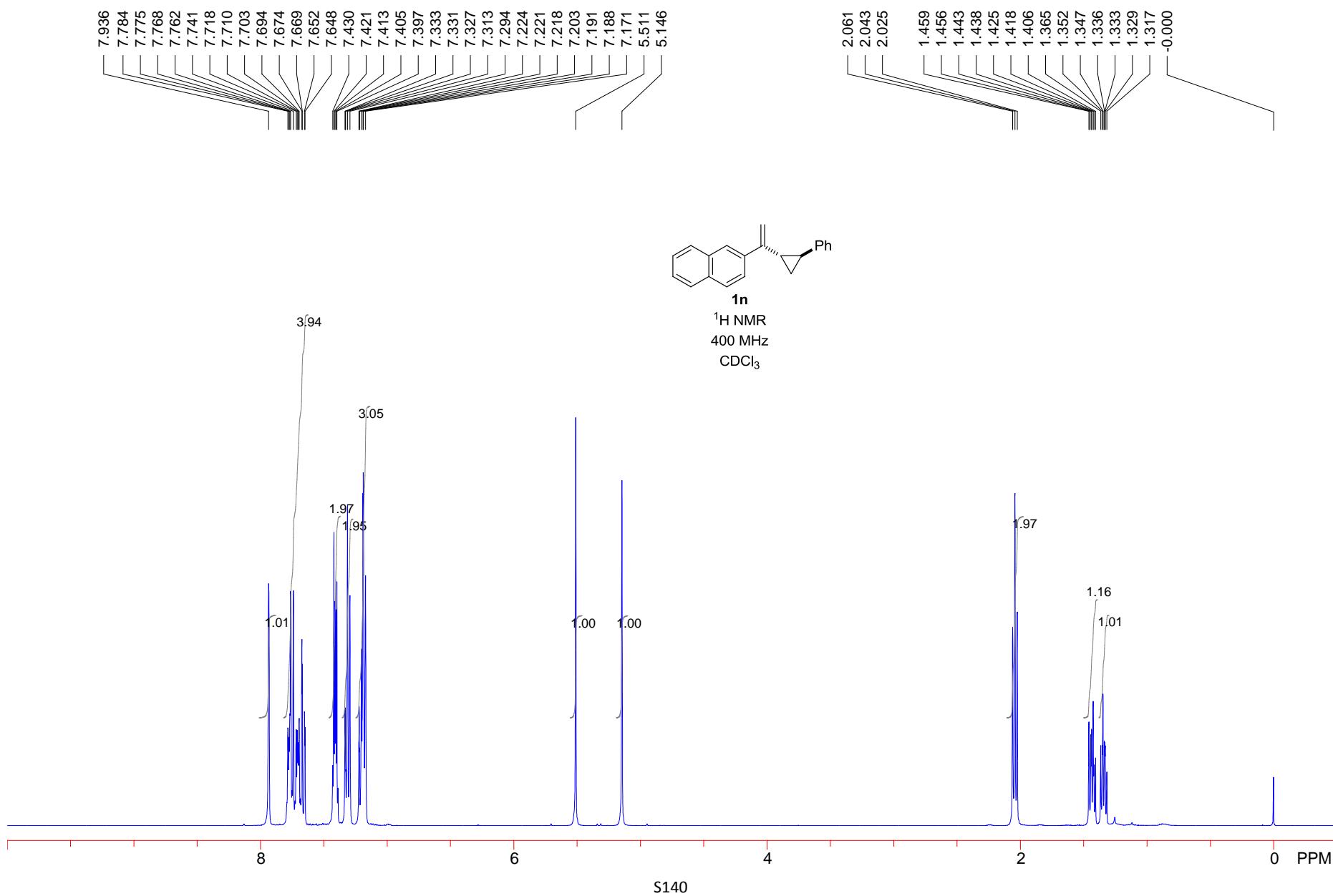


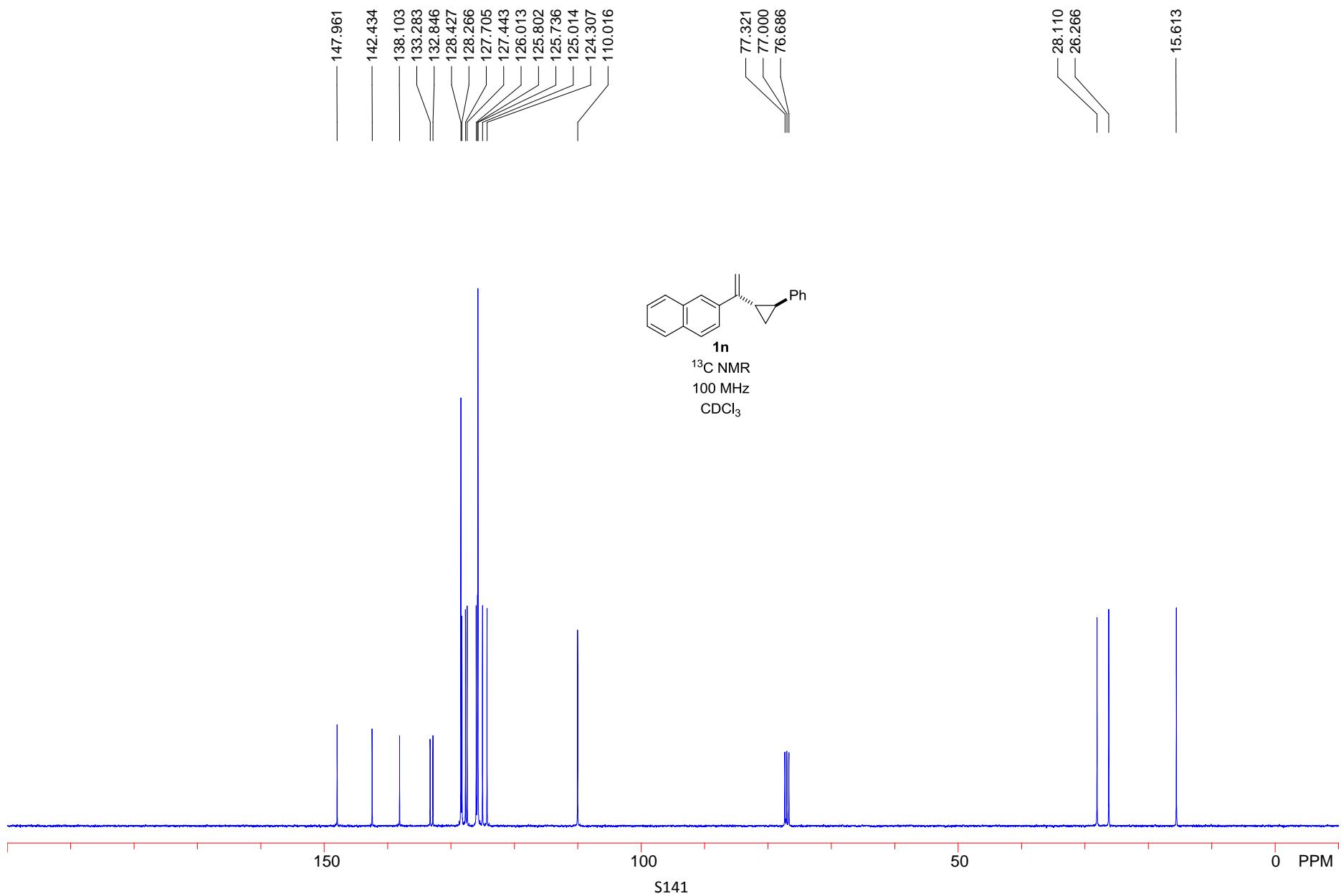


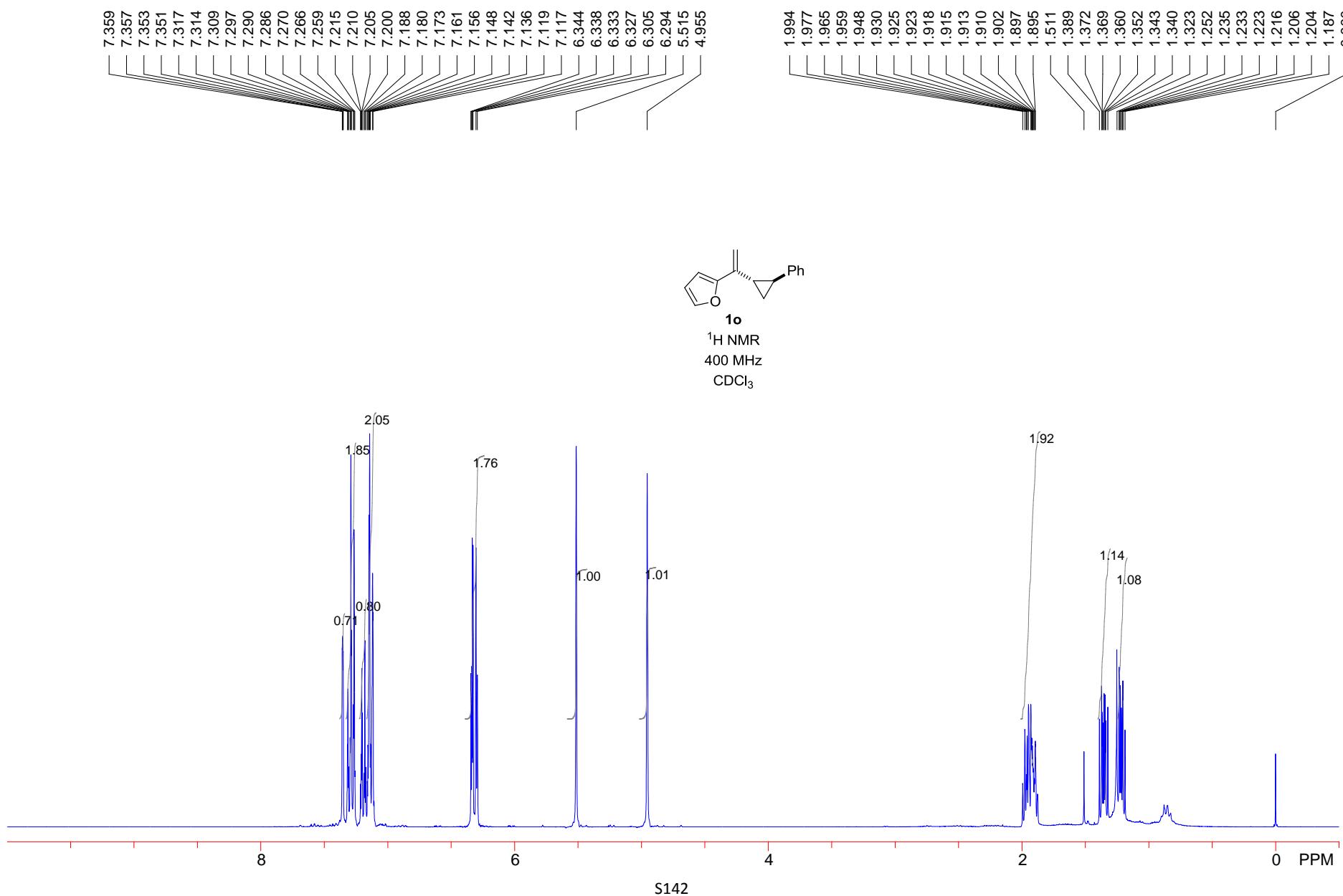


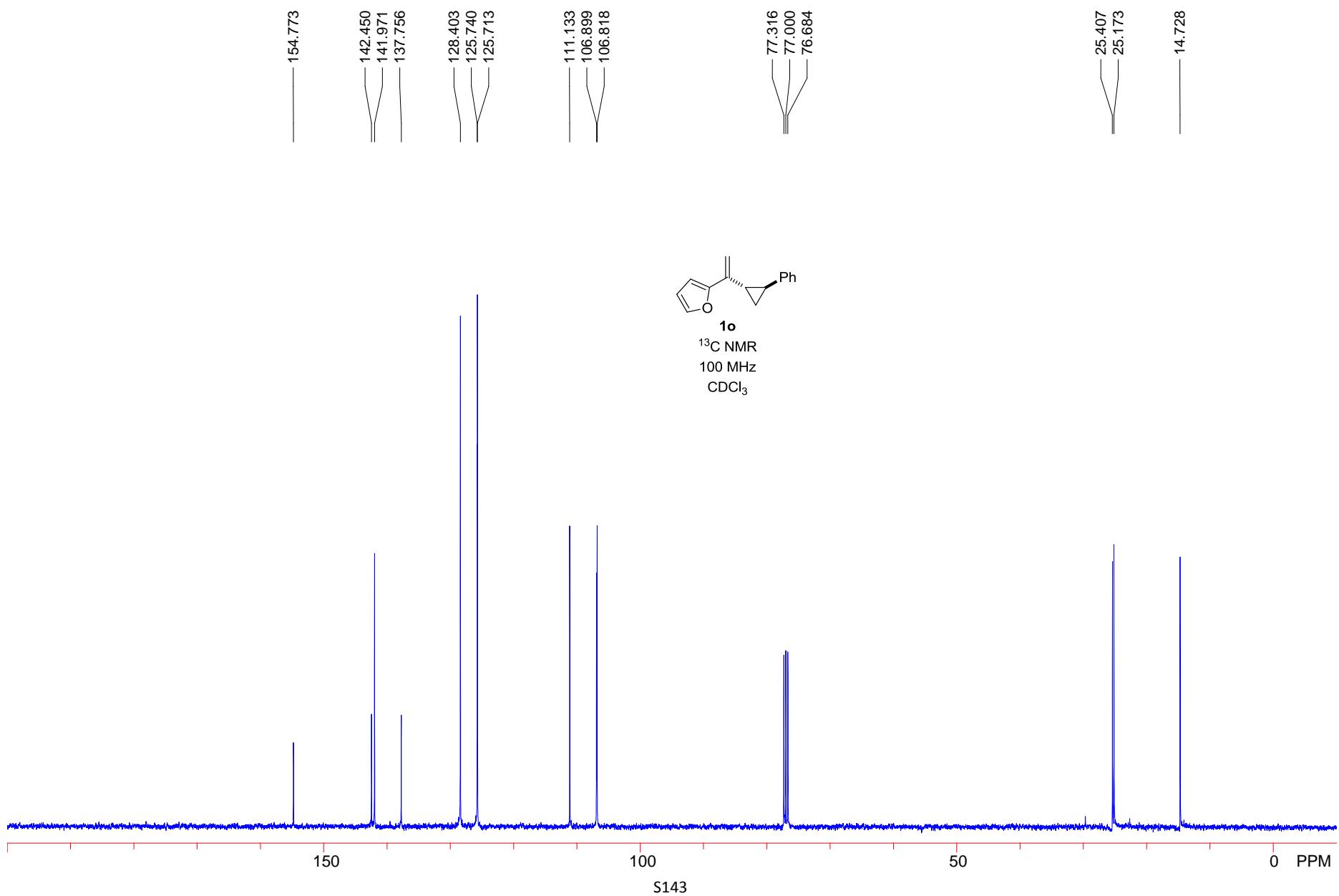


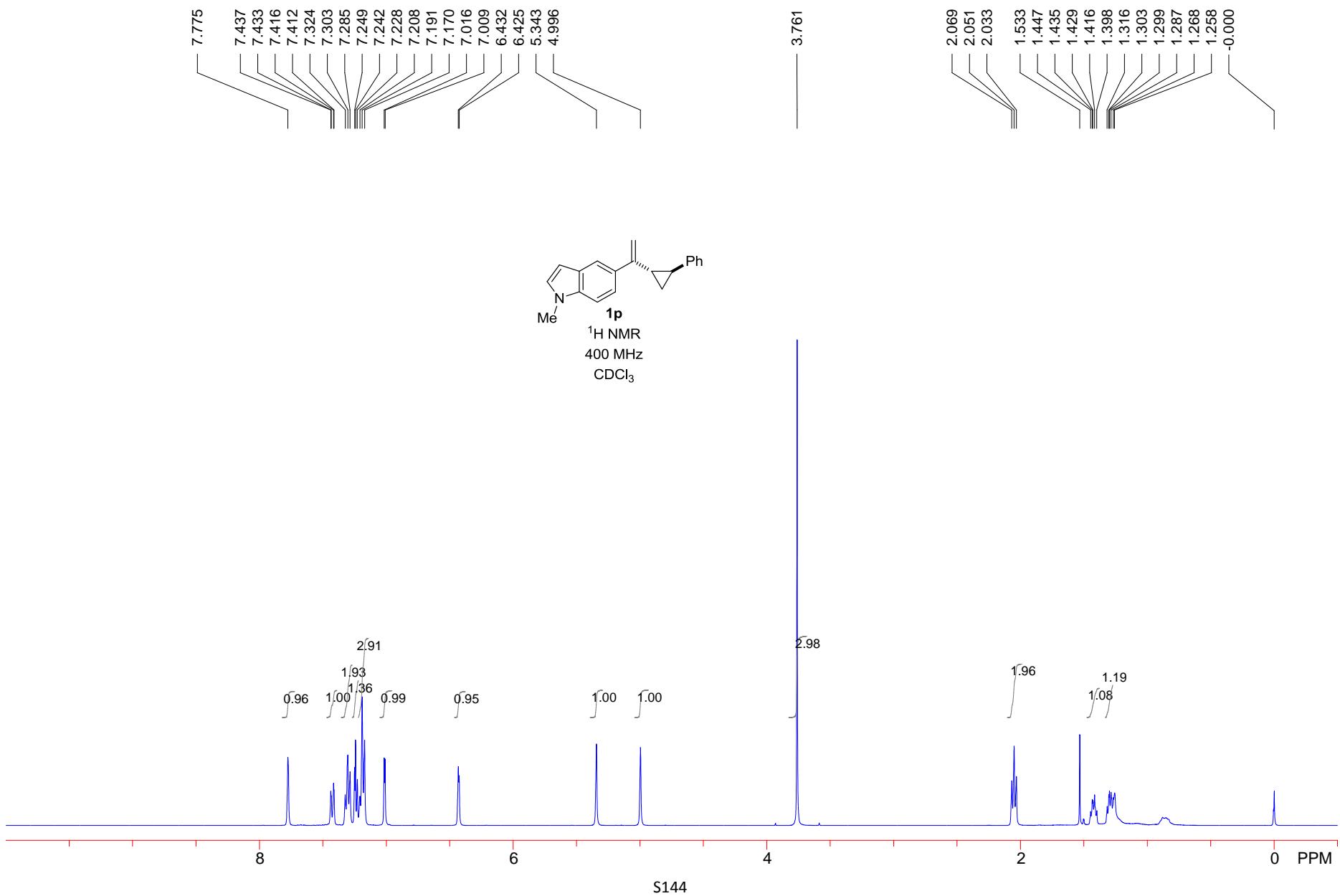
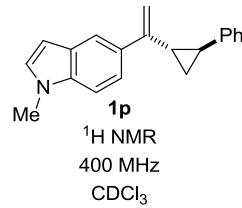


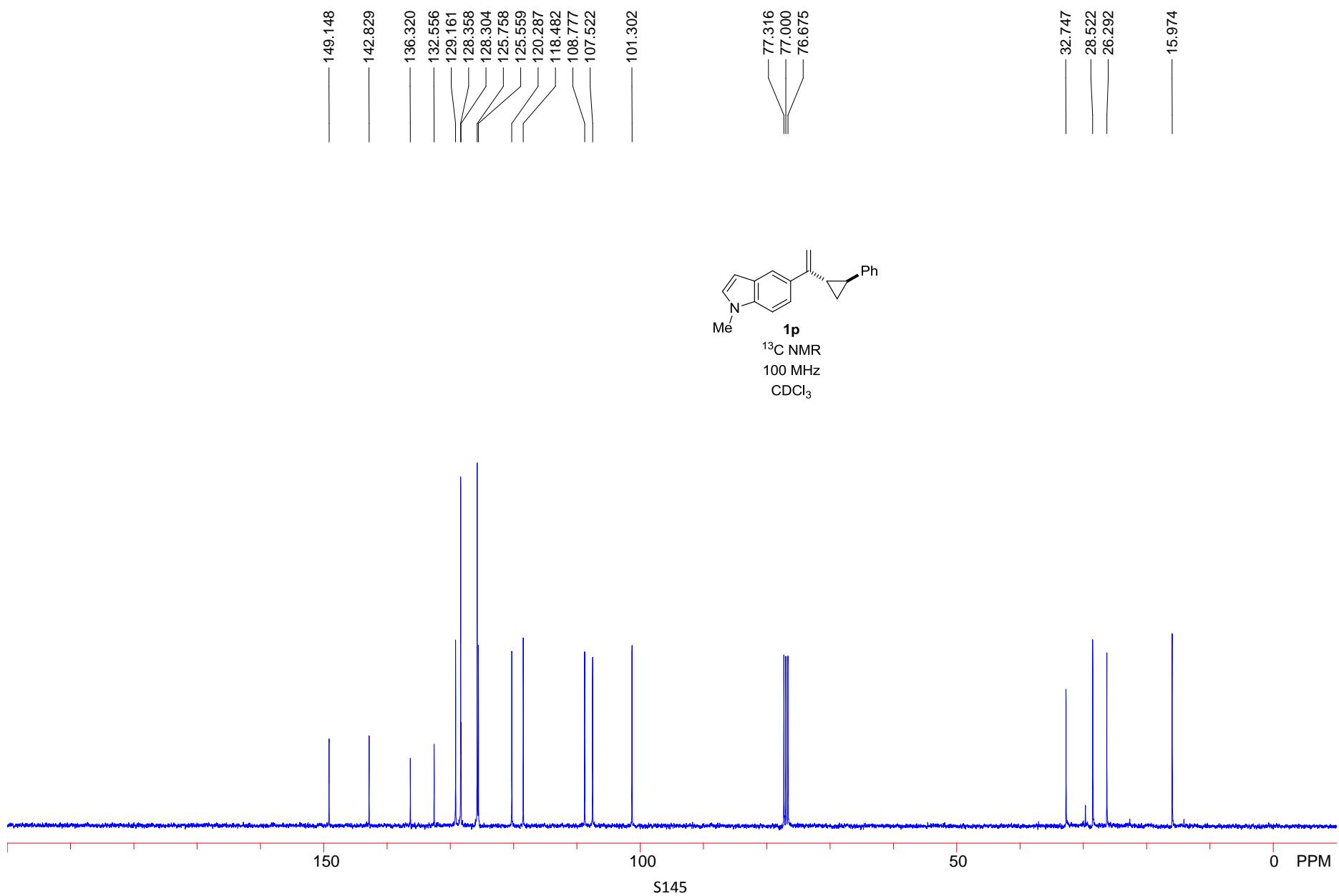


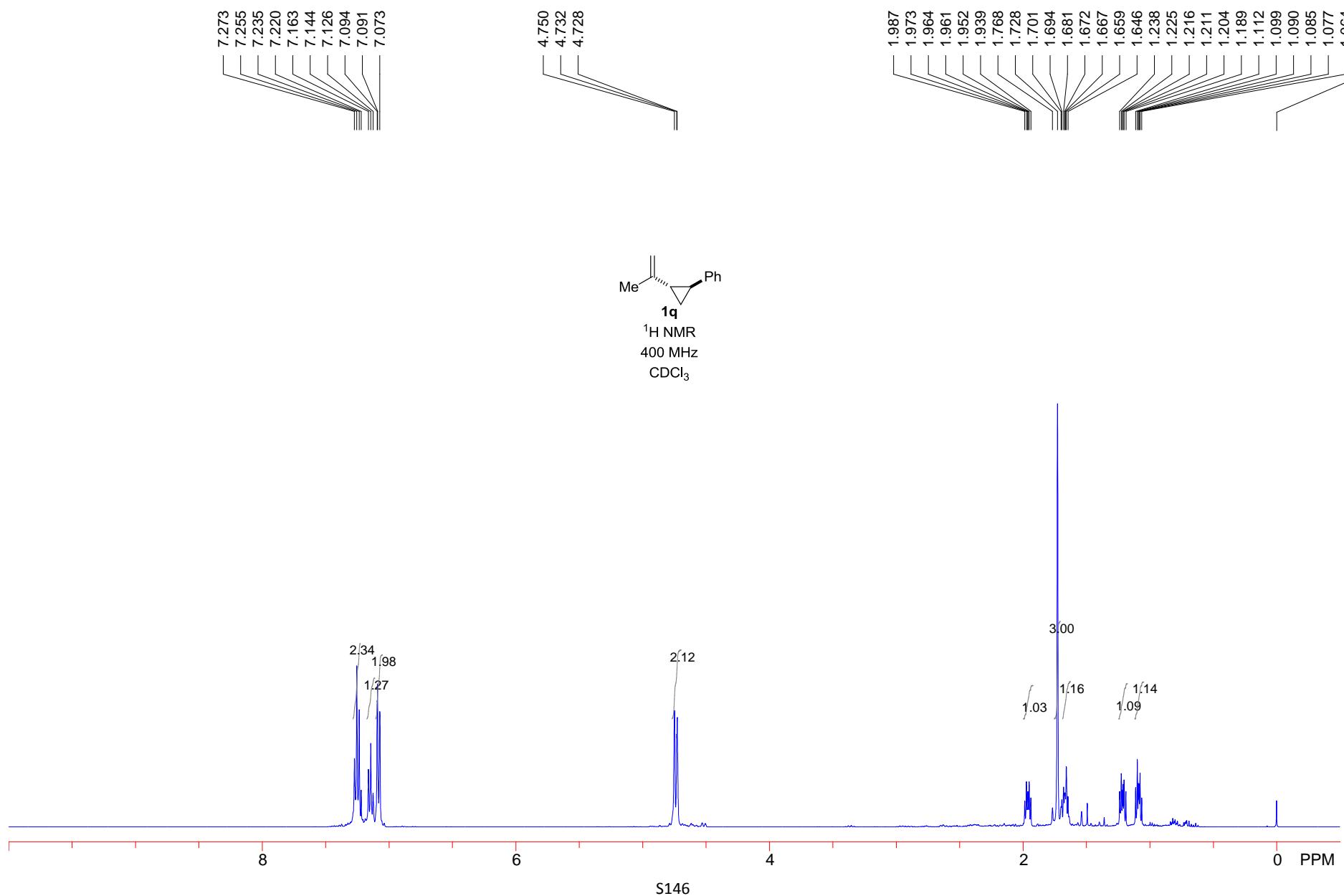


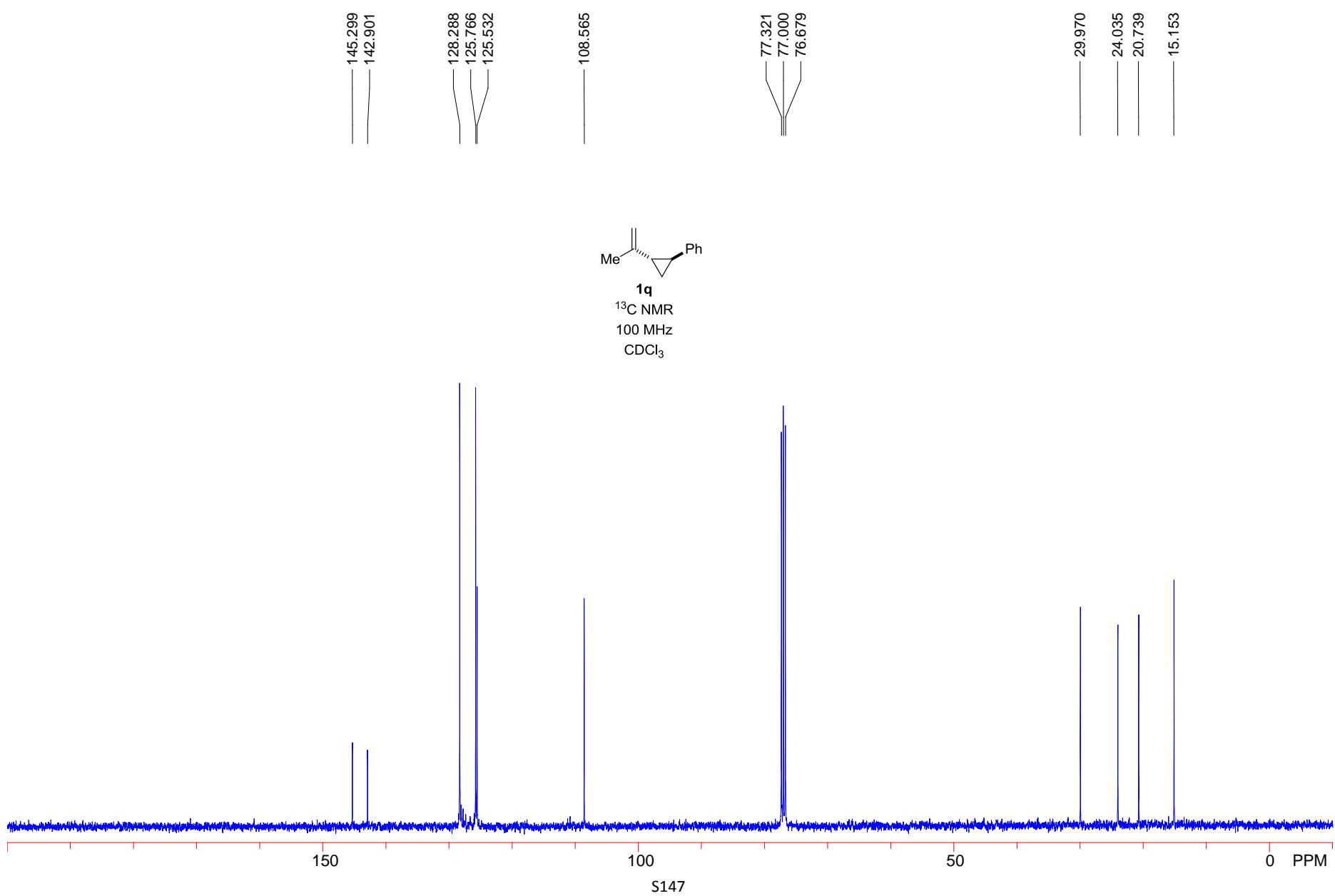


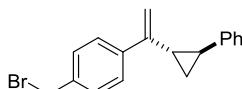
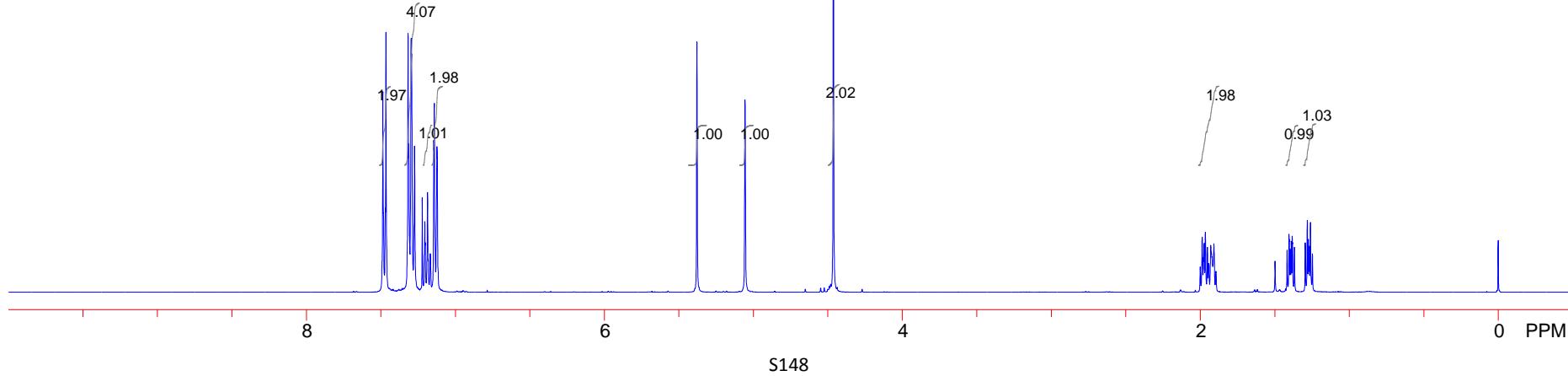




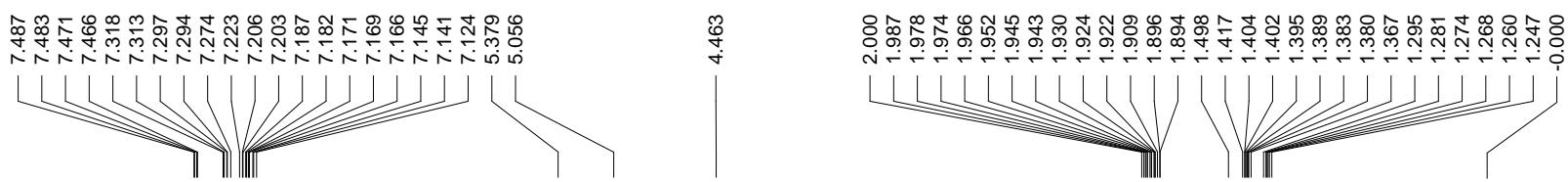




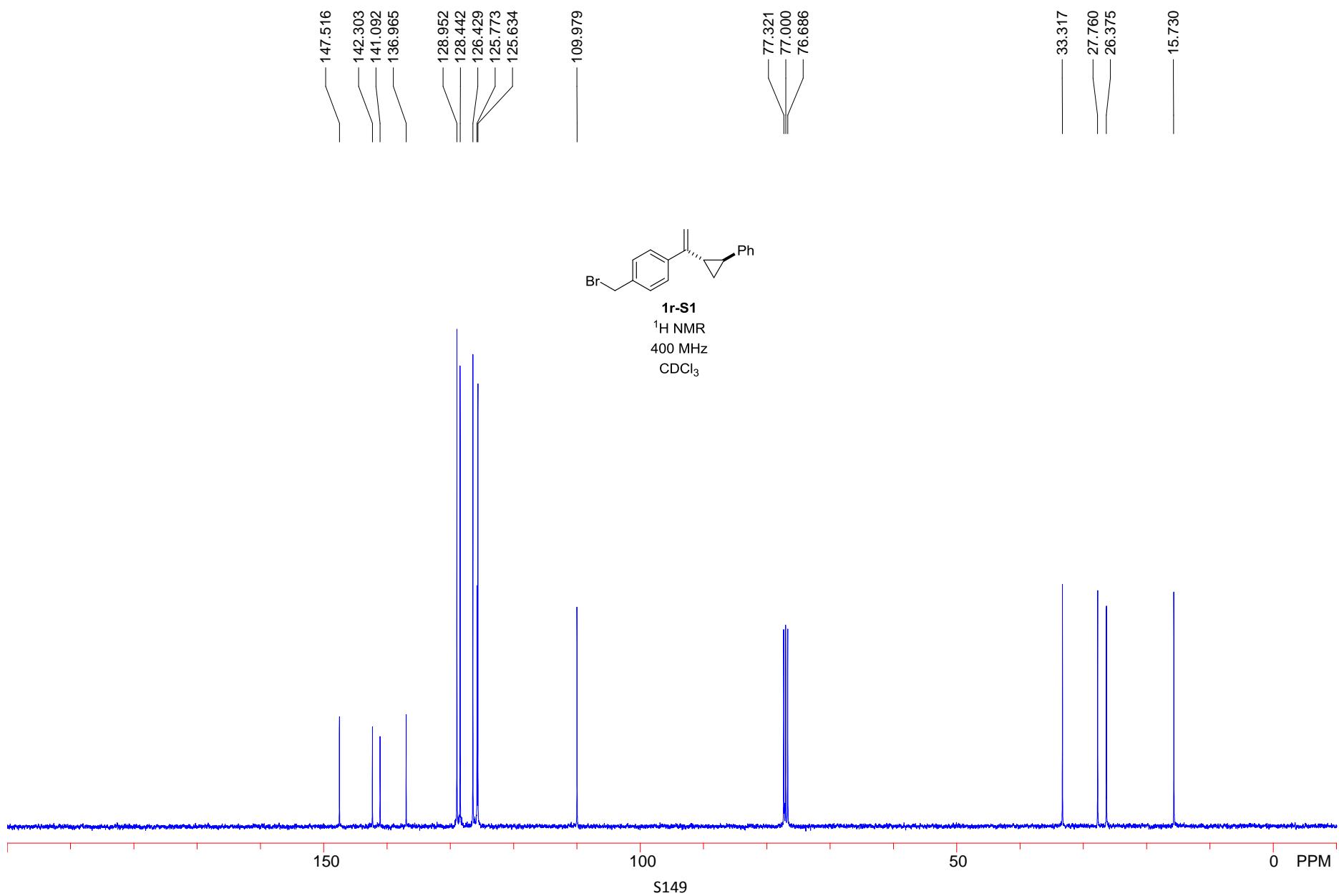


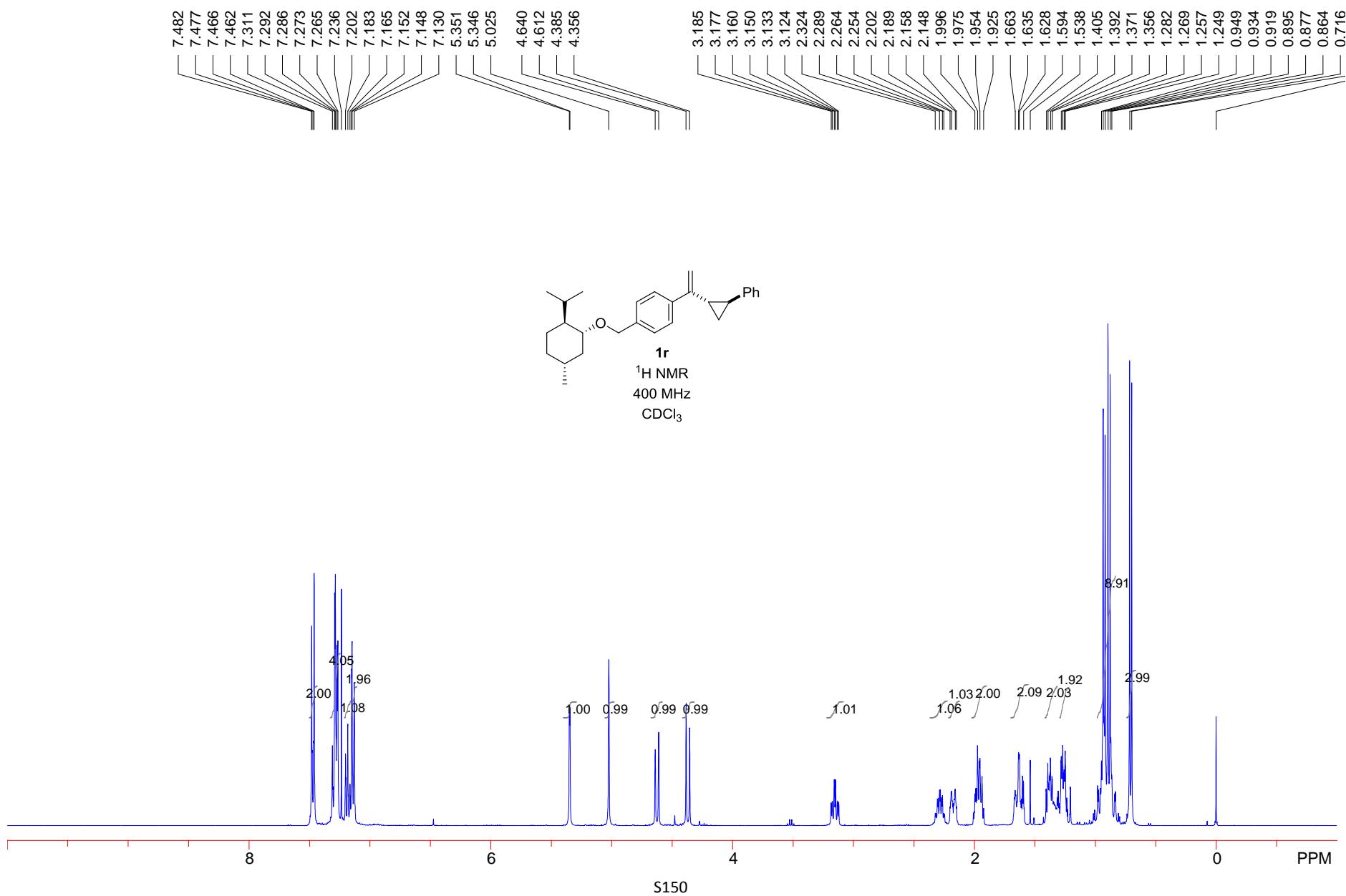


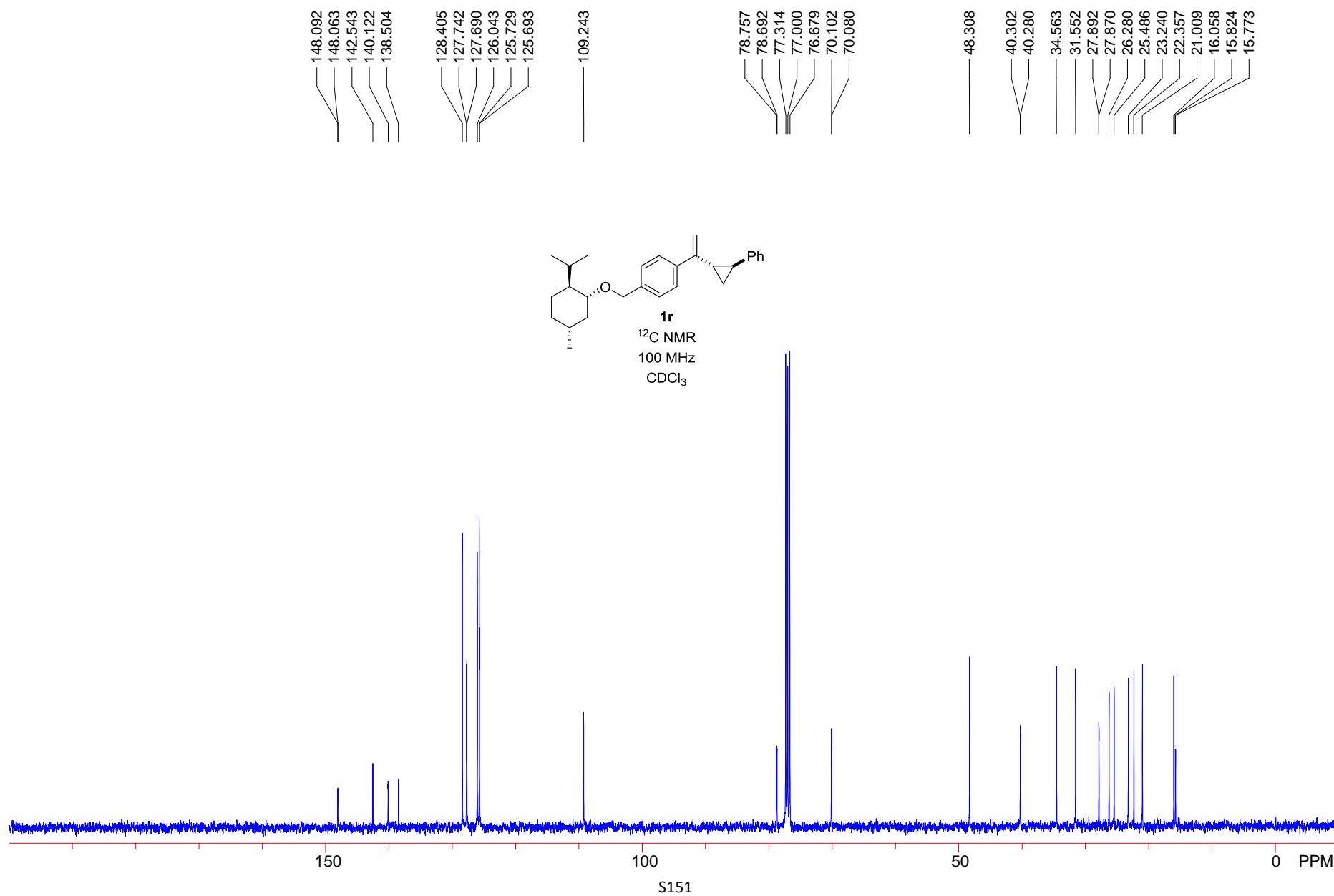
1r-S1
 ^1H NMR
400 MHz
 CDCl_3

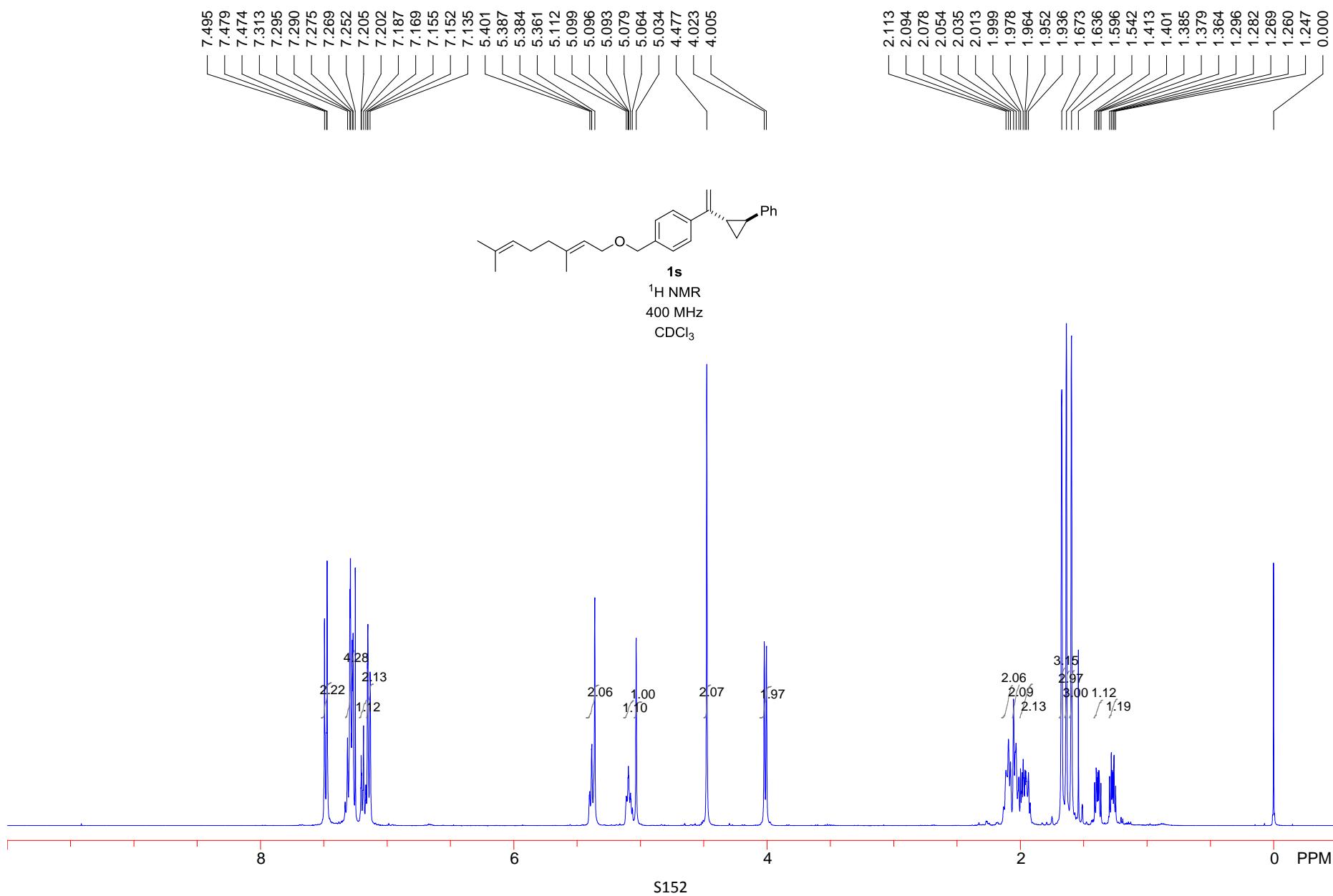


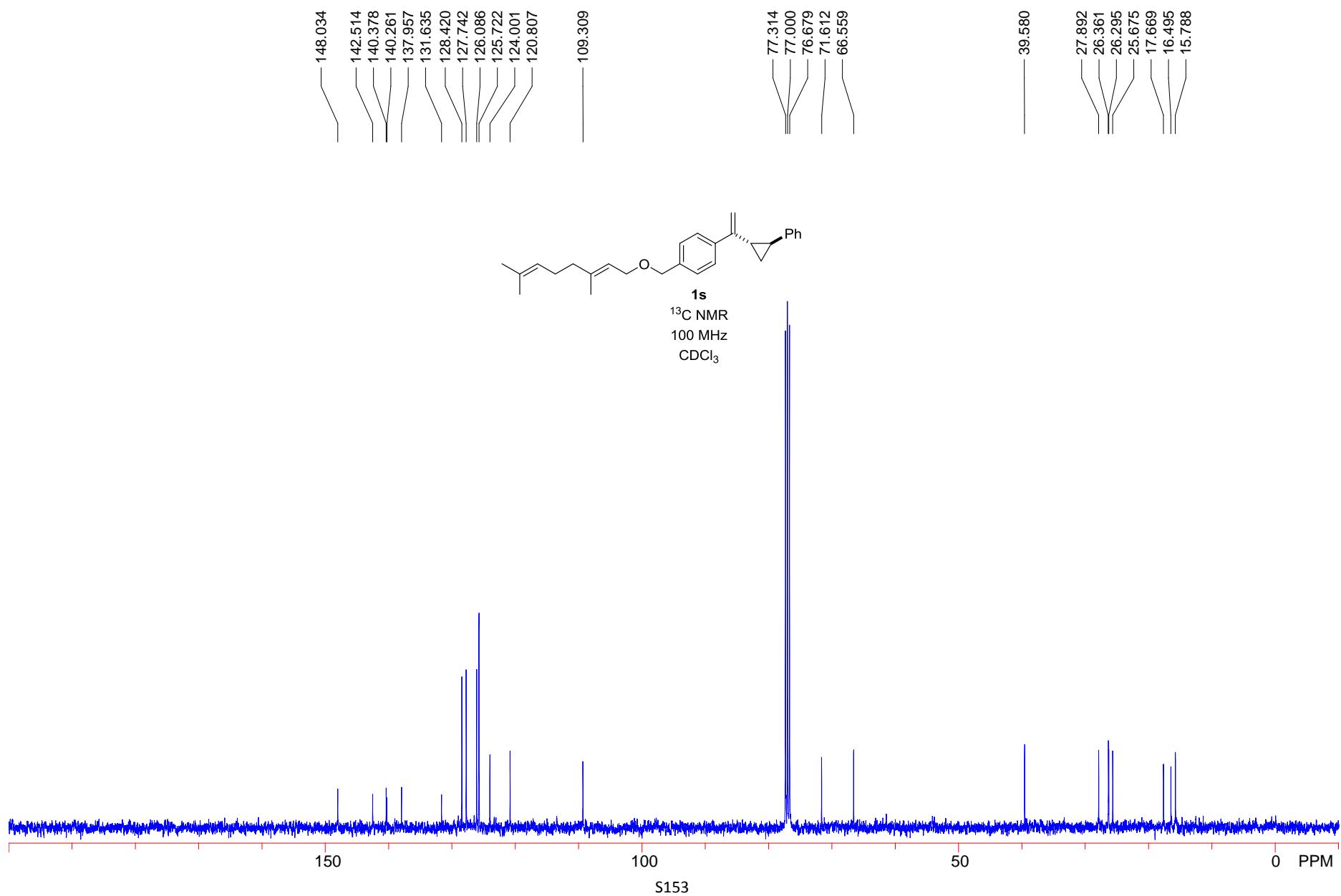
4.463

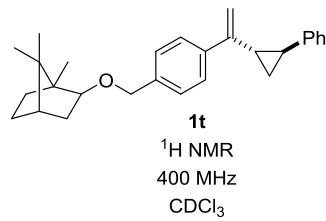
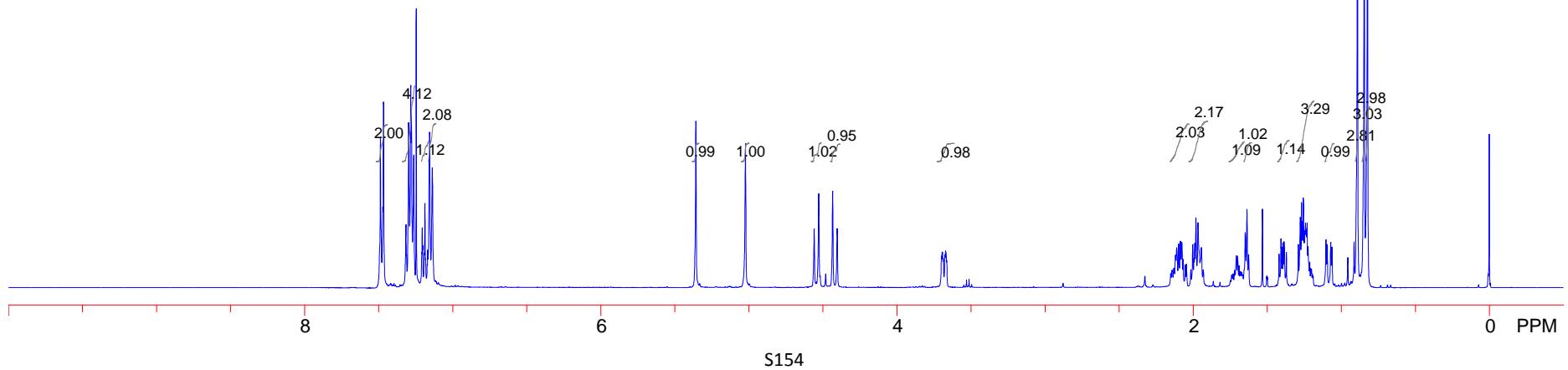








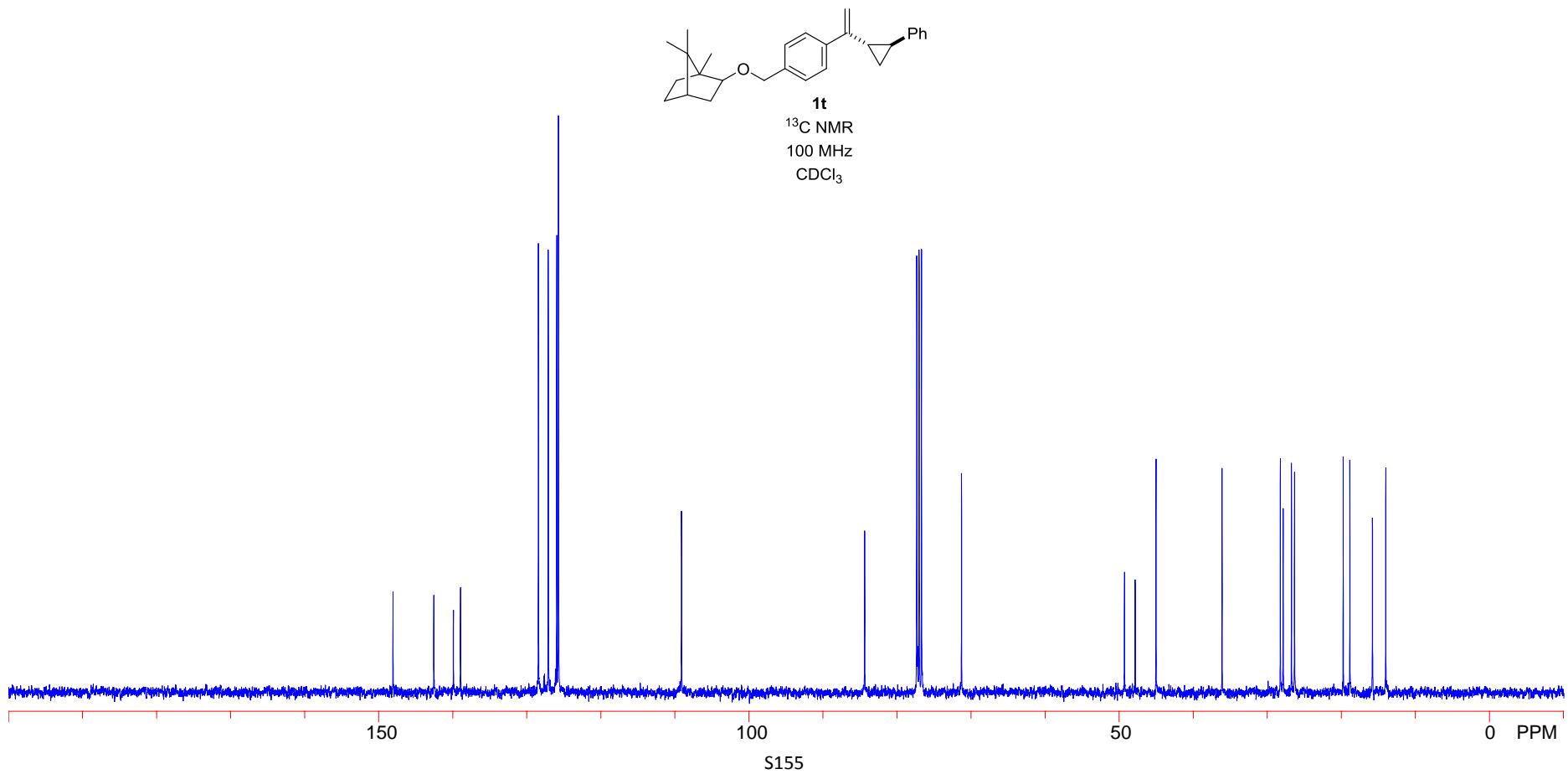


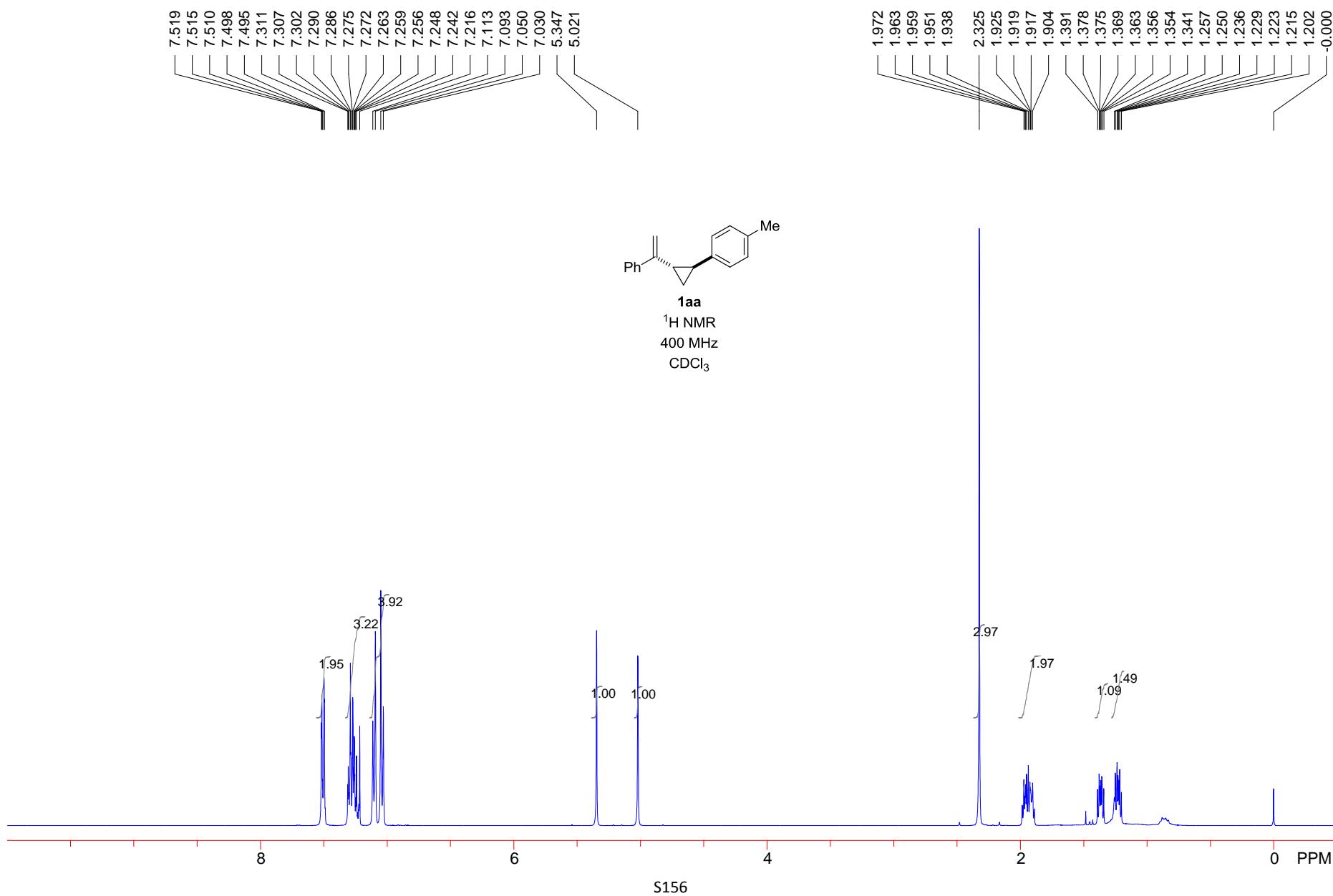


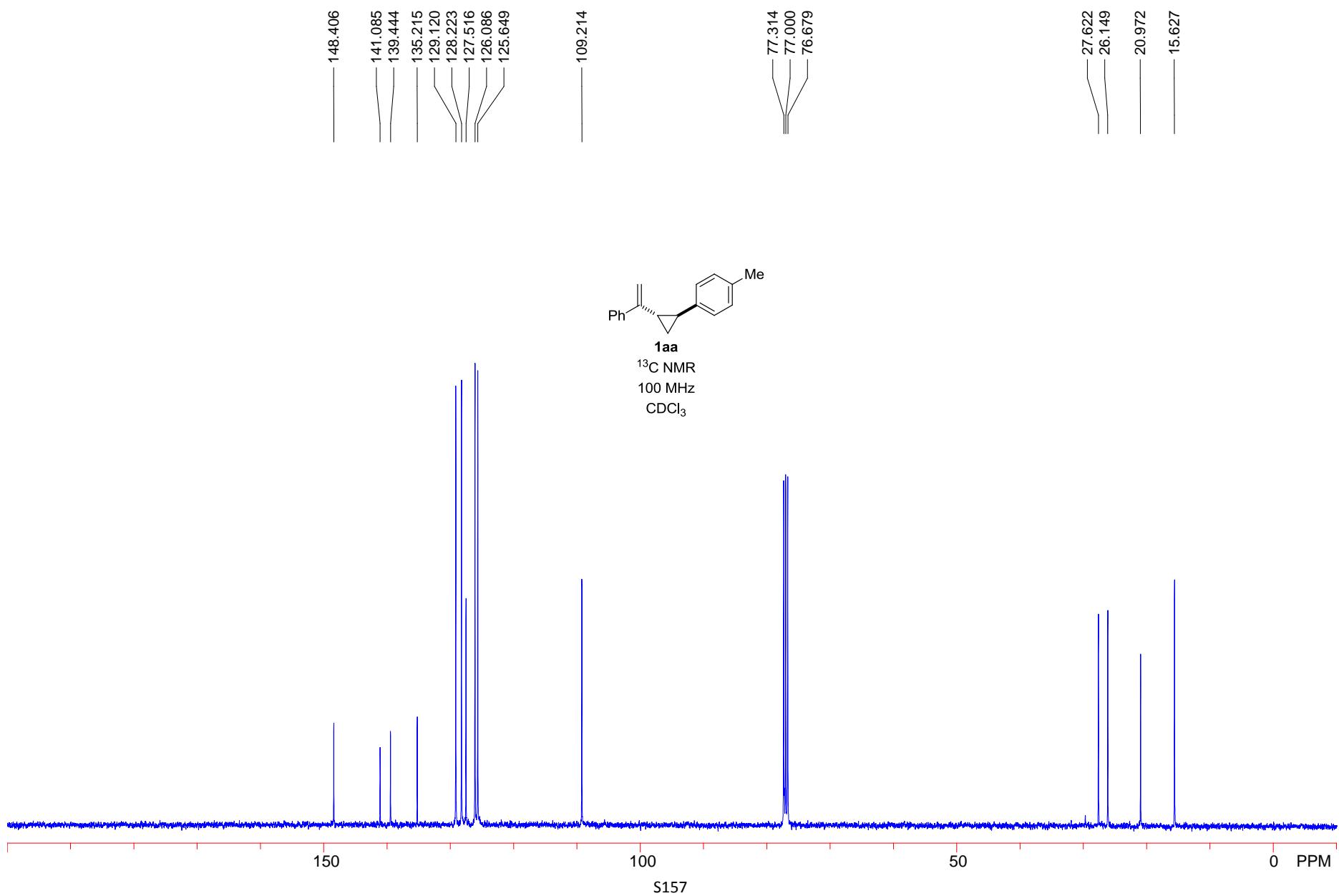
7.488
 7.472
 7.468
 7.316
 7.298
 7.284
 7.279
 7.264
 7.246
 7.206
 7.188
 7.160
 7.156
 7.138

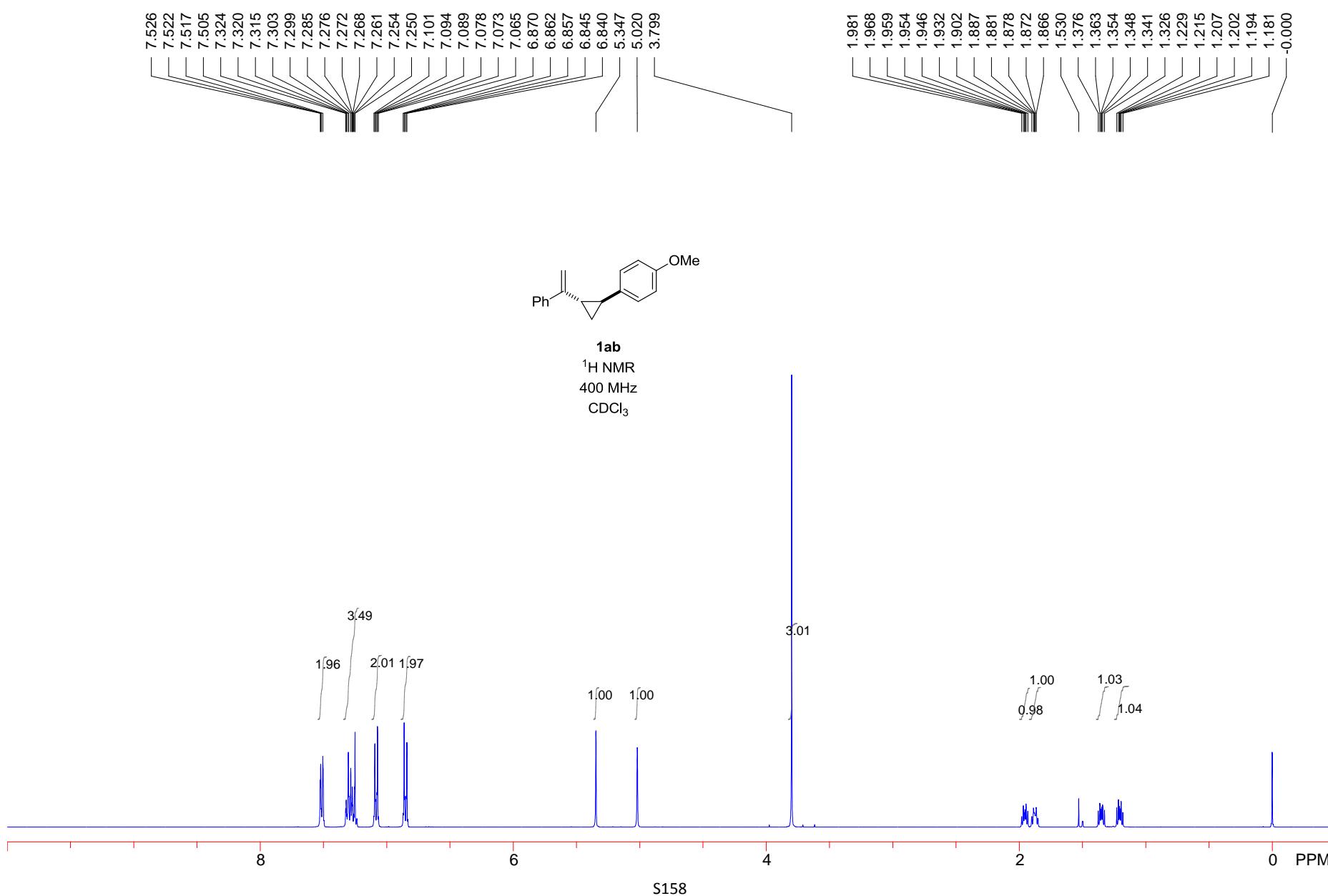
4.560
 5.359
 4.529
 4.435
 4.024
 4.405
 3.701
 3.688
 3.677
 3.665

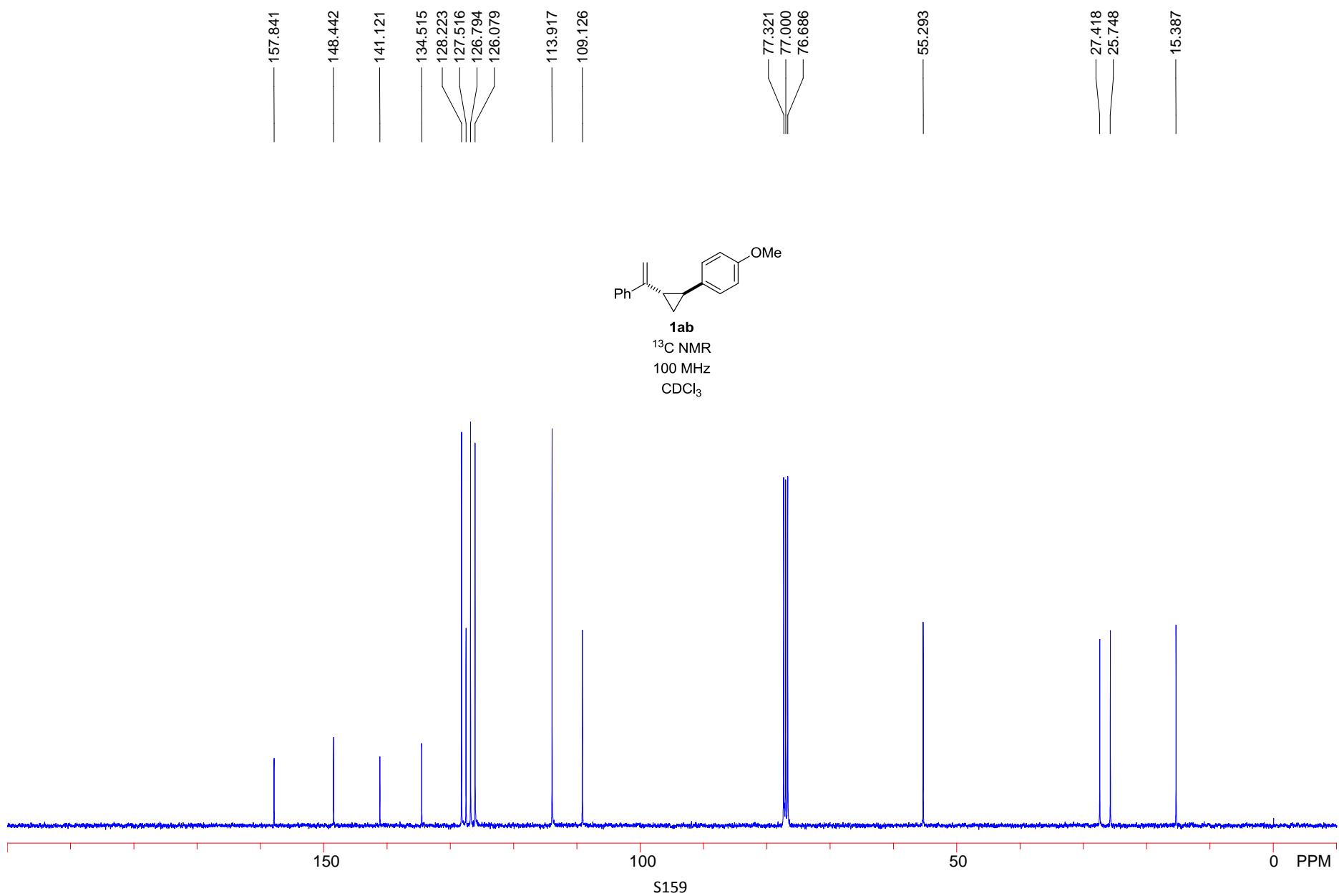
2.152
 2.112
 2.077
 2.053
 2.016
 1.982
 1.967
 1.945
 1.741
 1.709
 1.679
 1.648
 1.637
 1.626
 1.532
 1.420
 1.407
 1.370
 1.277
 1.256
 1.230
 1.103
 1.095
 1.071
 1.062
 0.891
 0.845
 0.823

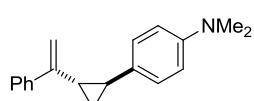
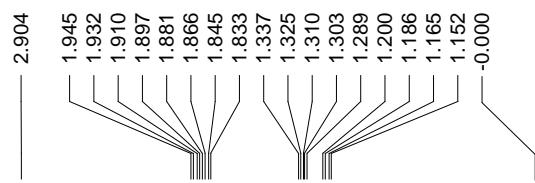
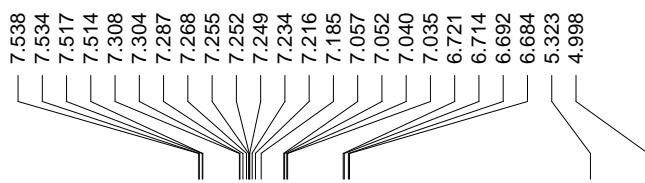




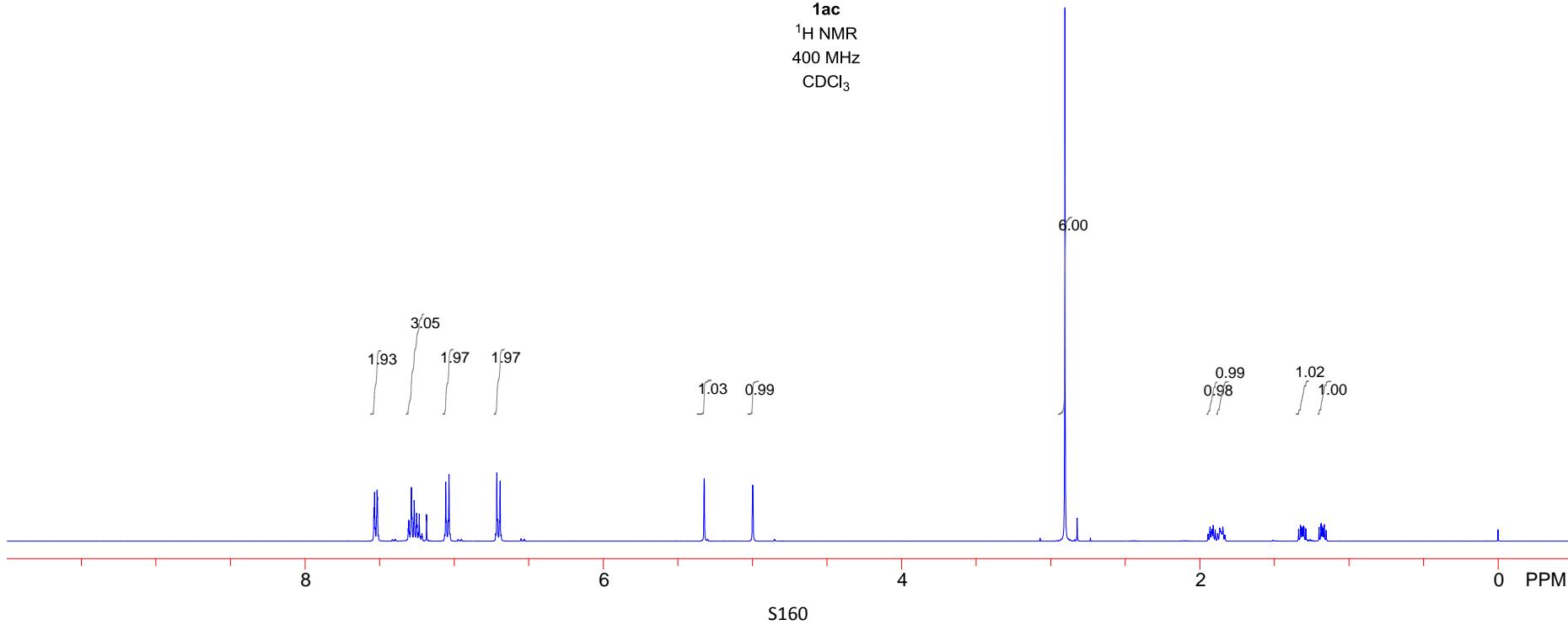


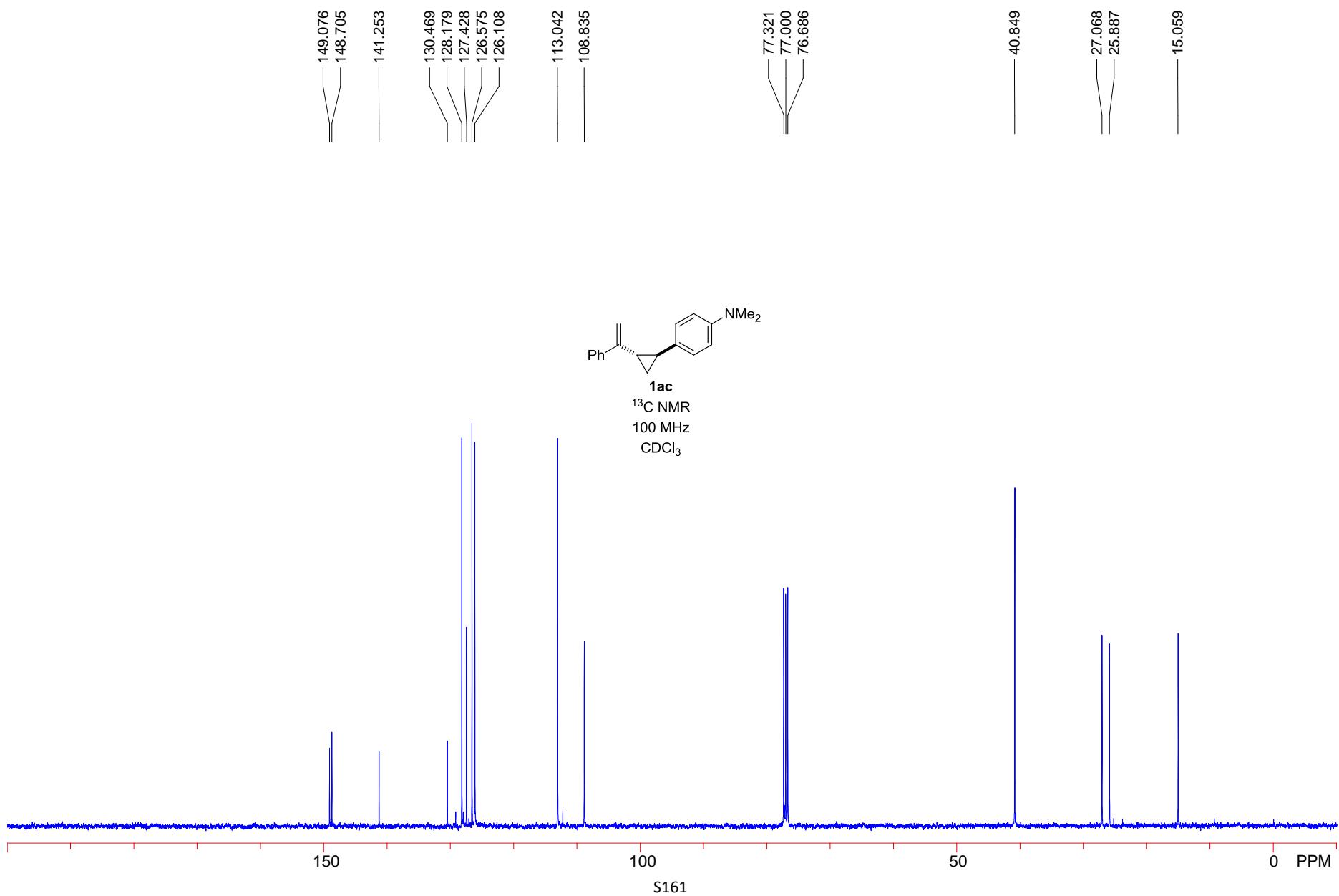


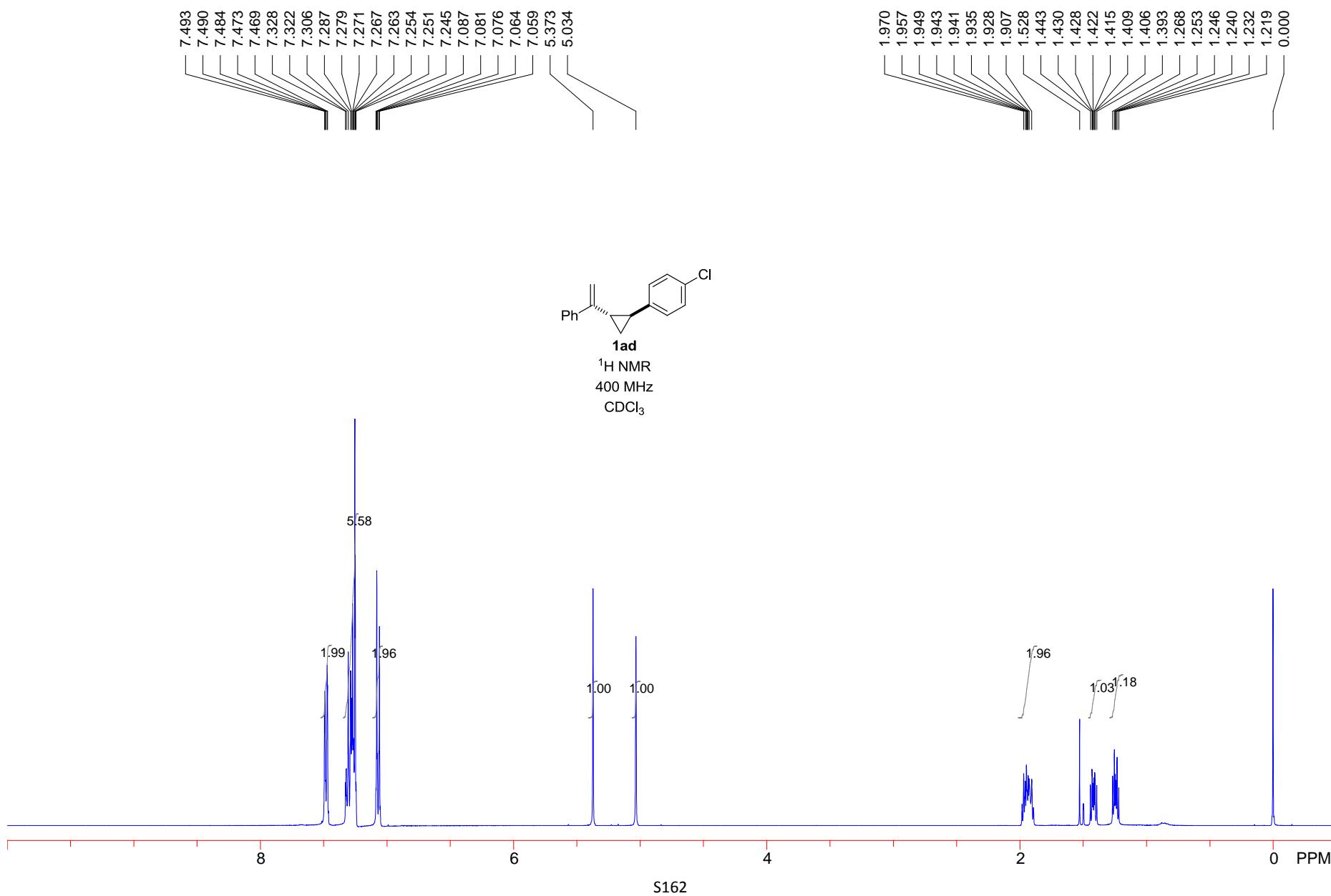


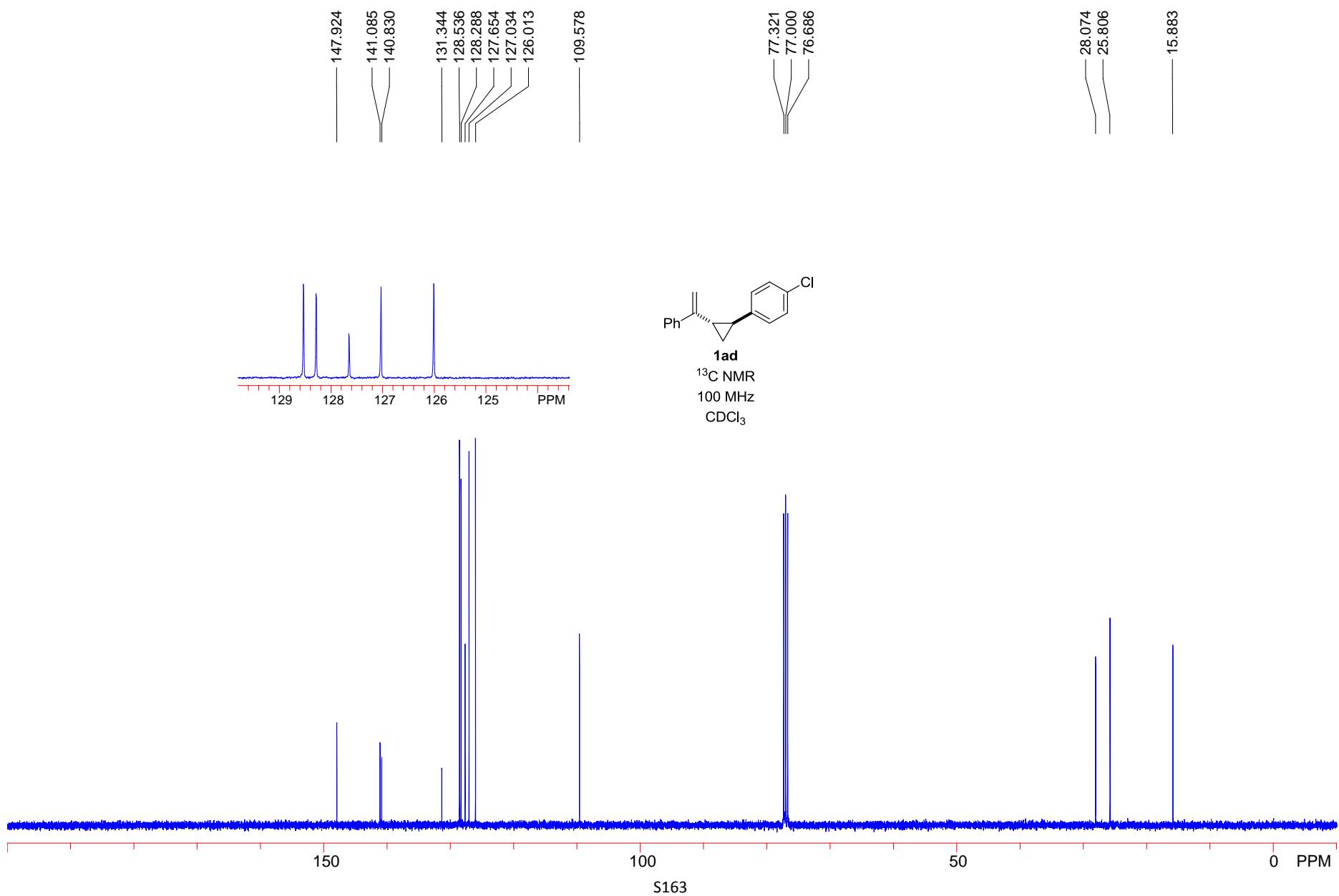


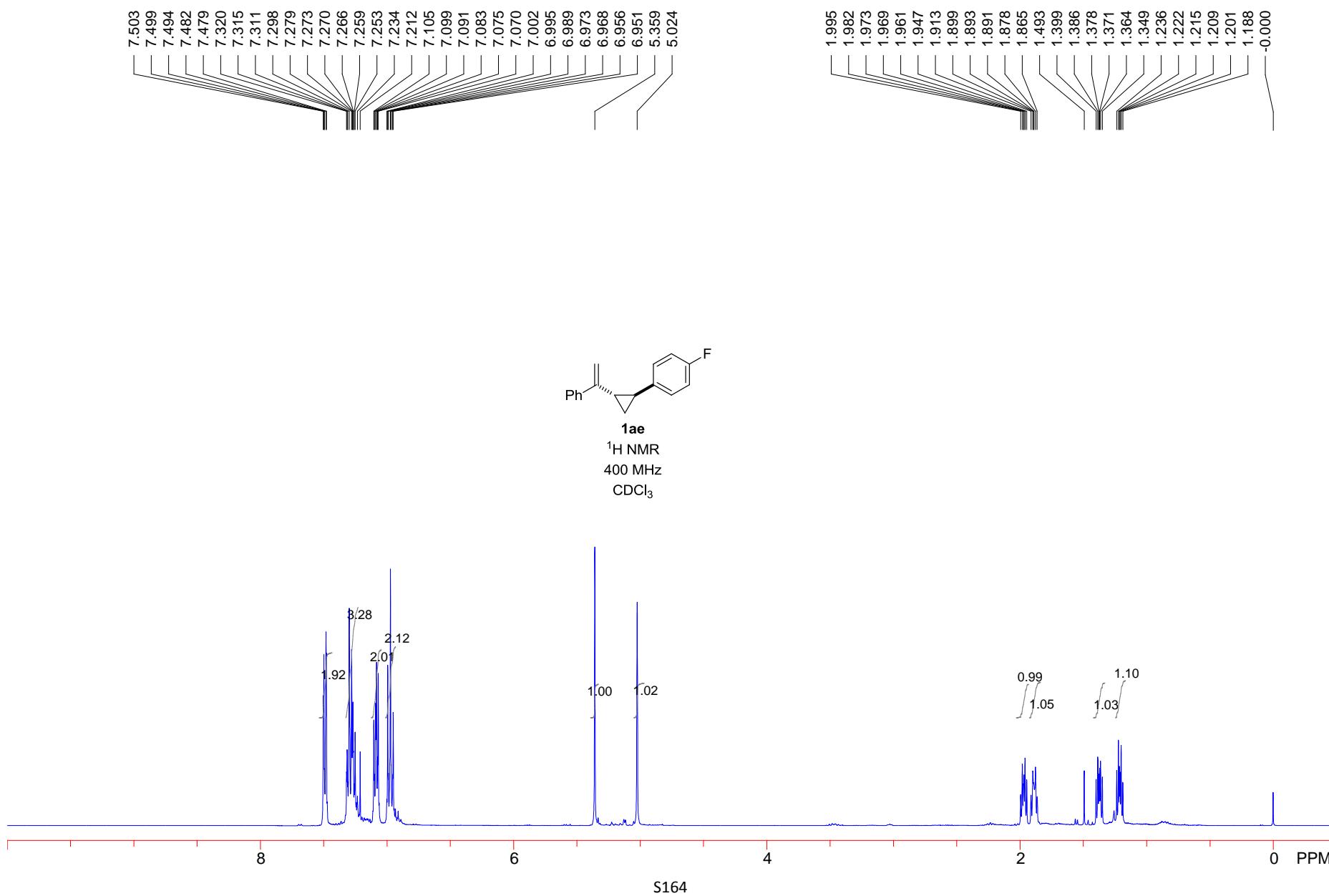
1ac
¹H NMR
400 MHz
CDCl₃

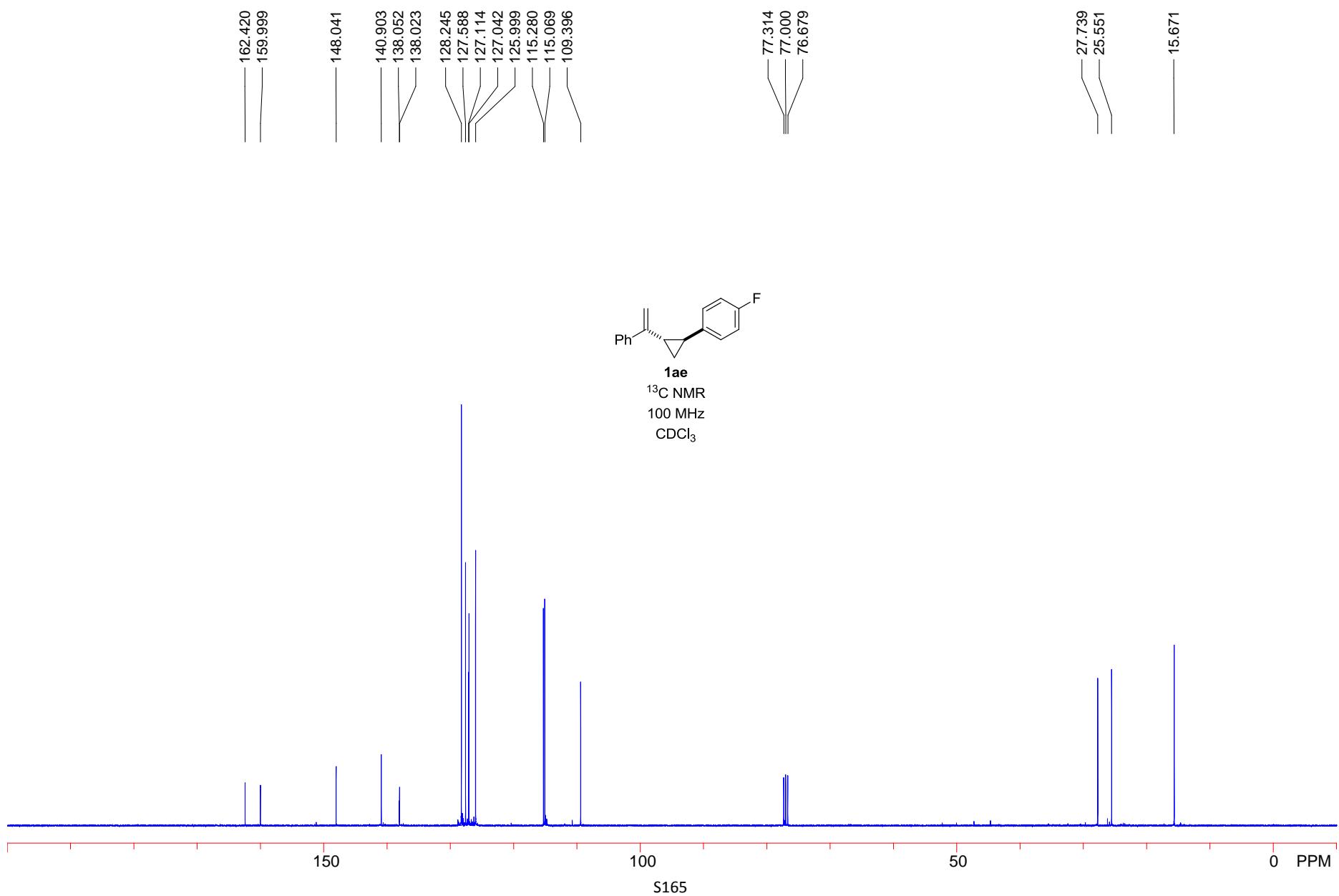




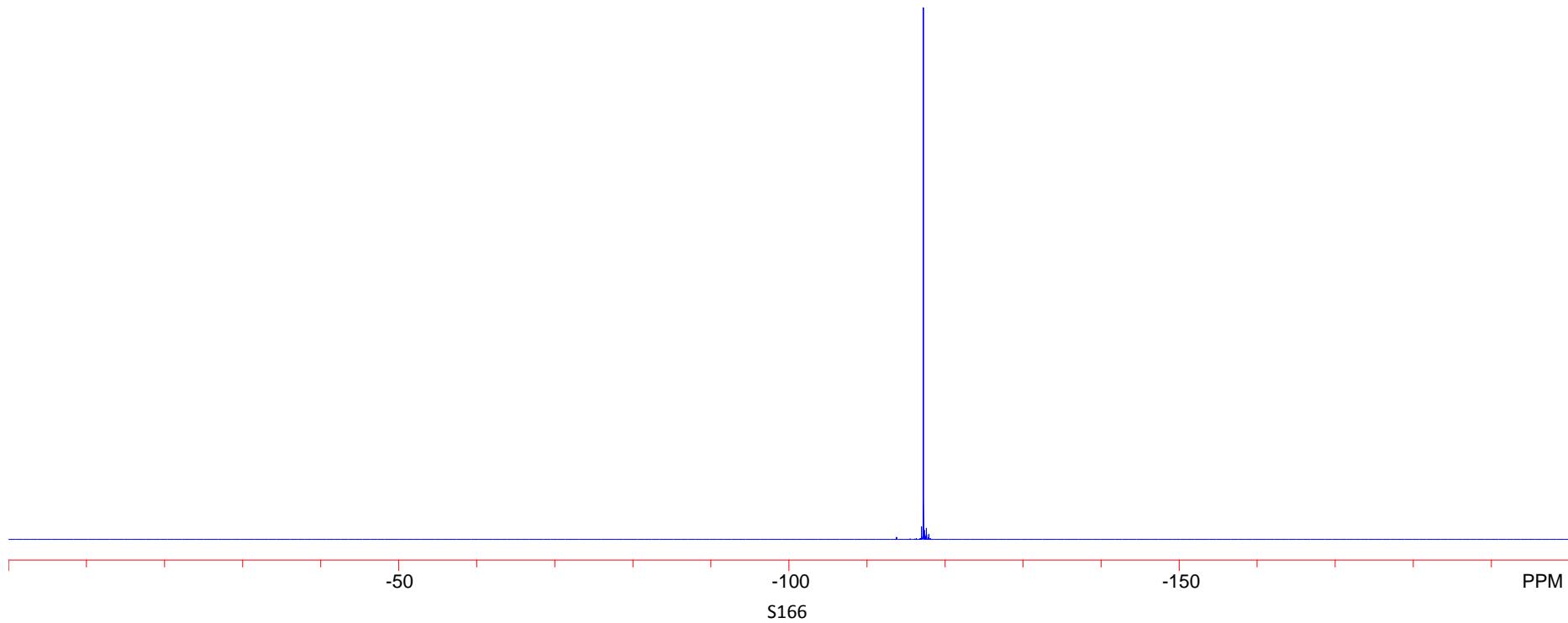
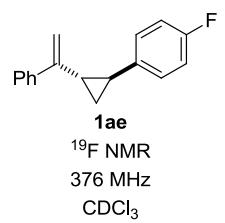


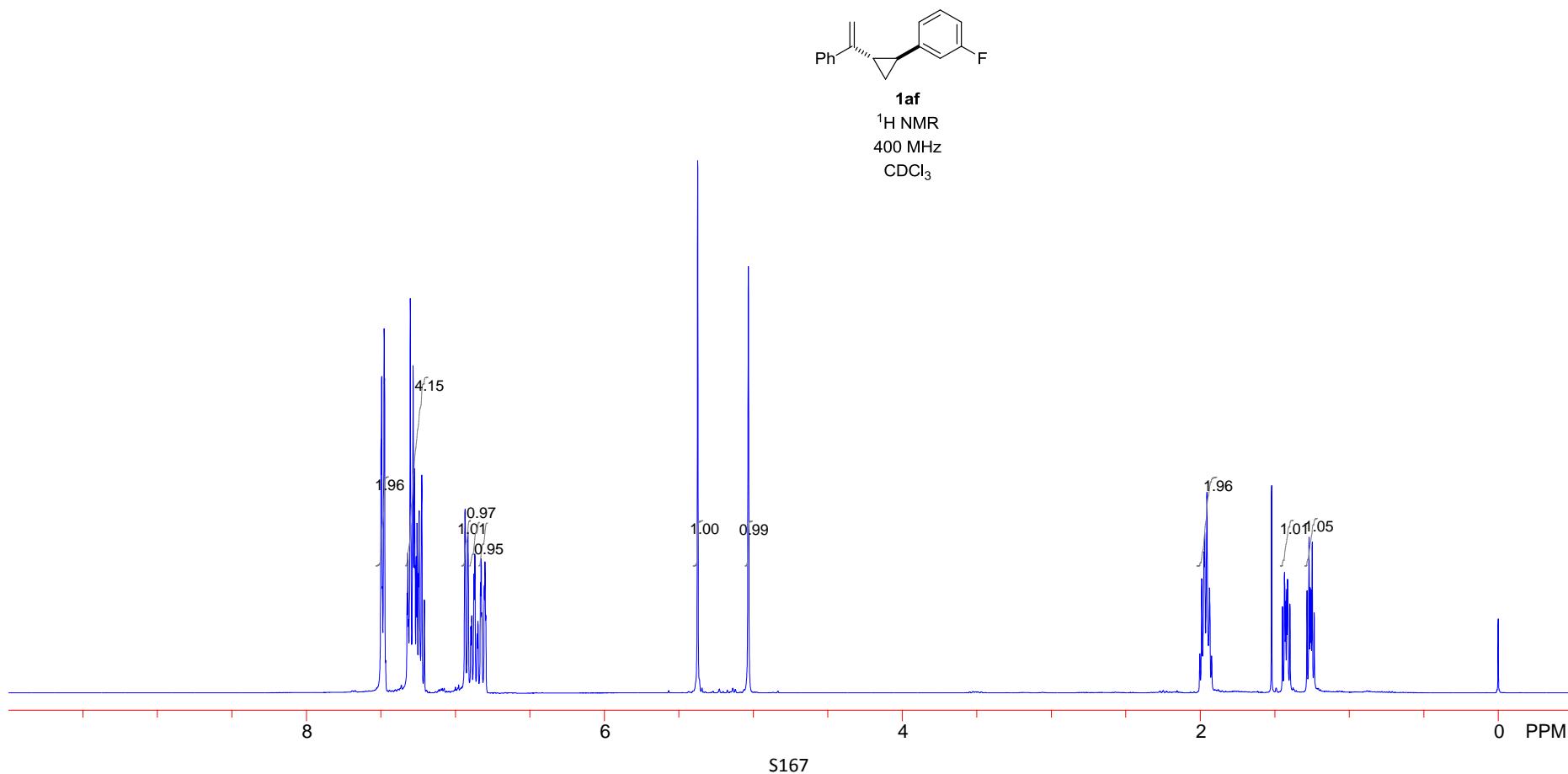


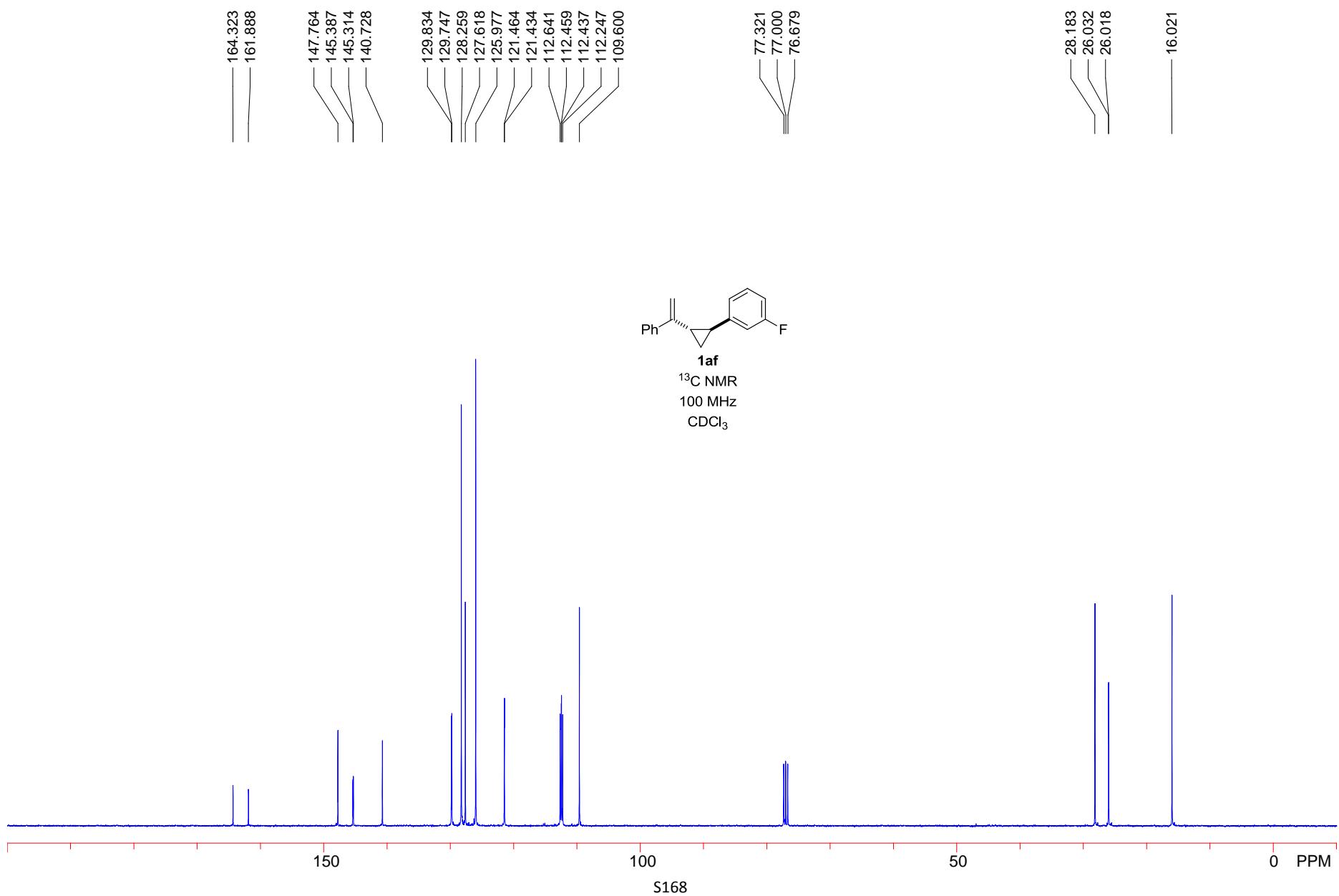




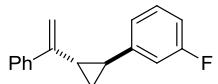
-117.242



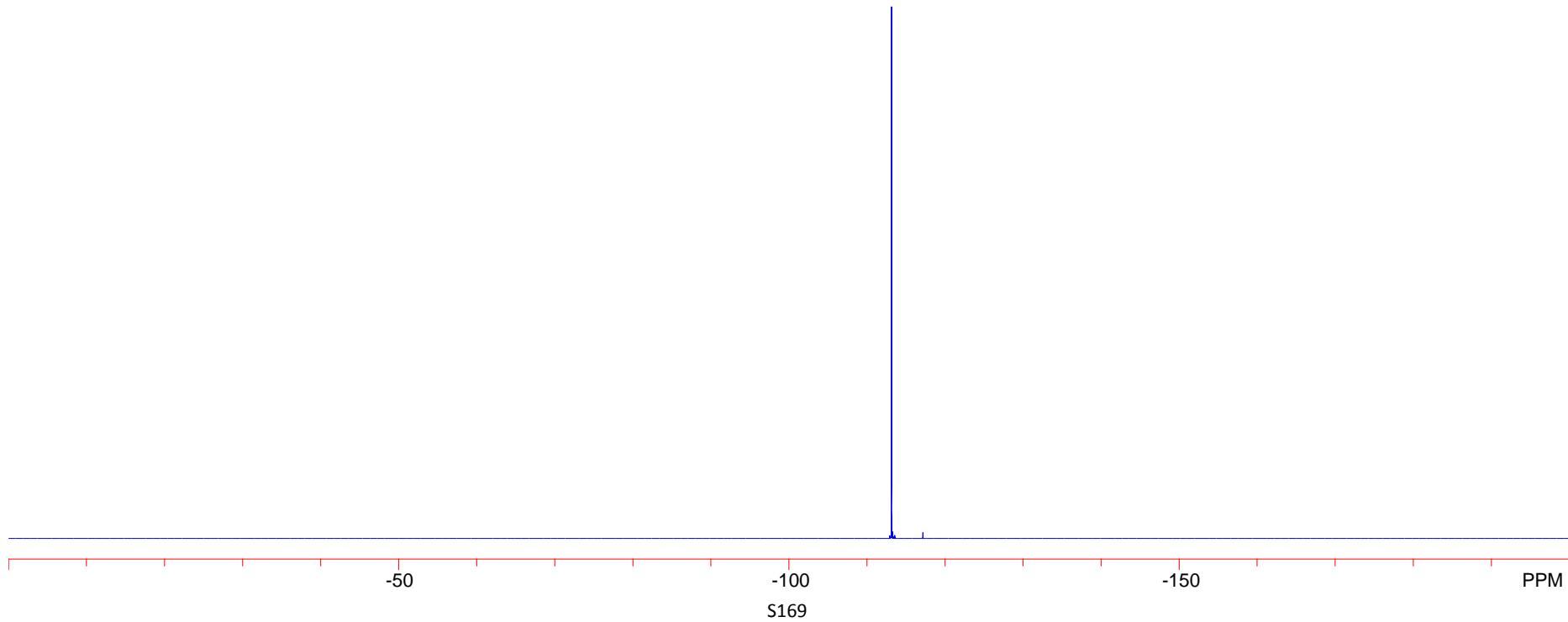




113.157



^{19}F NMR
376 MHz
 CDCl_3



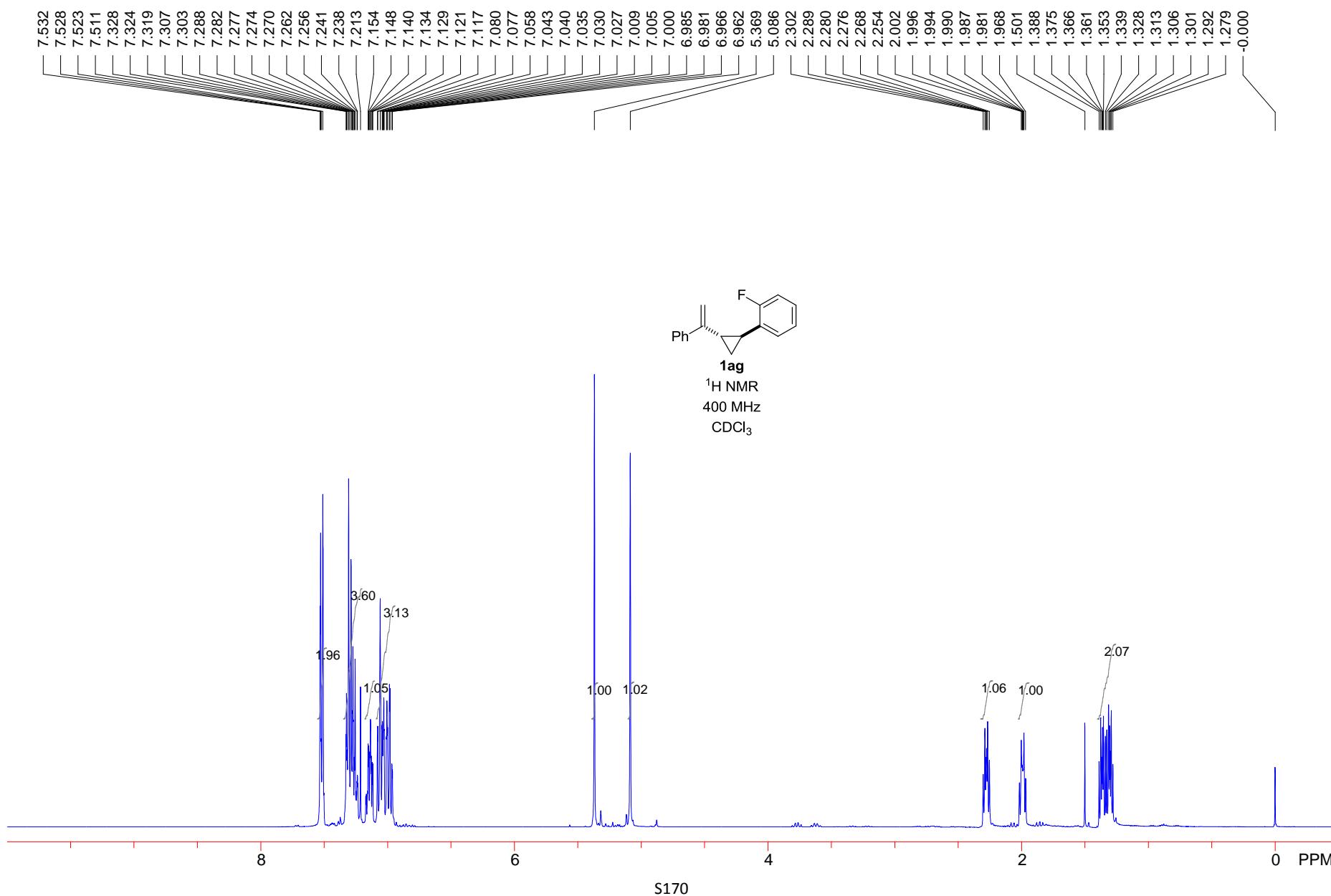
-50

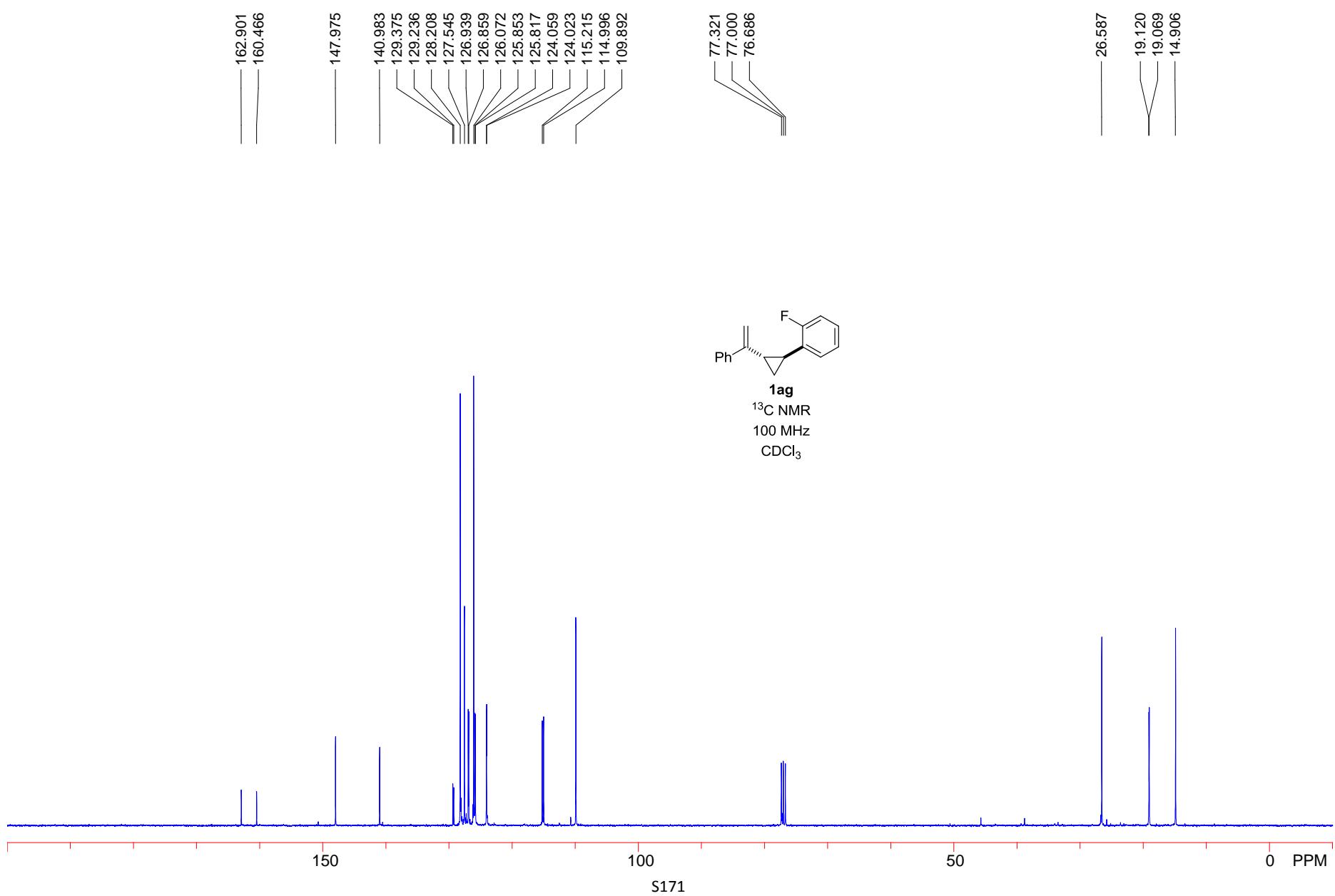
-100

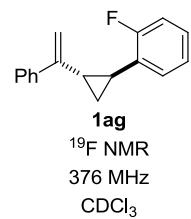
-150

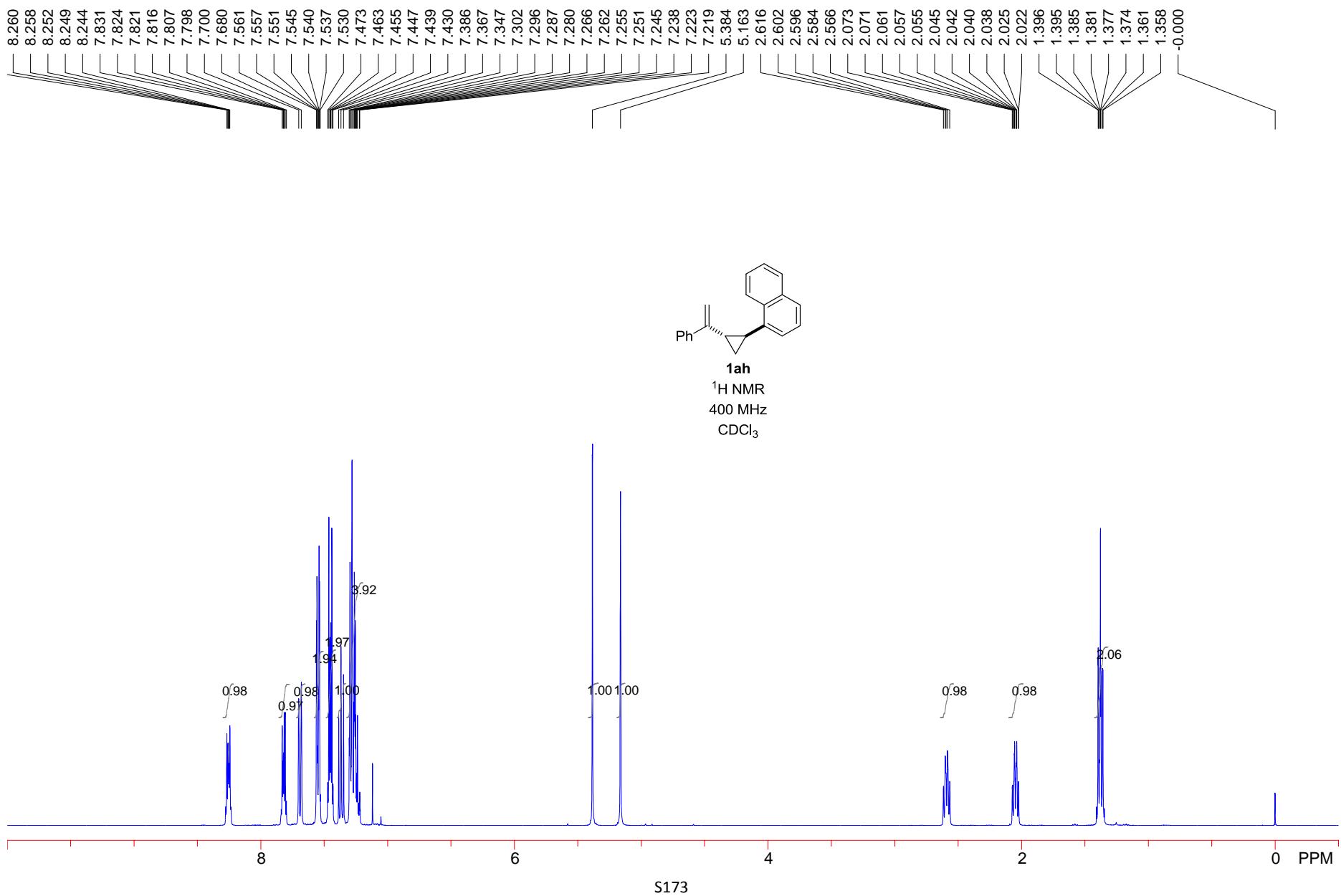
PPM

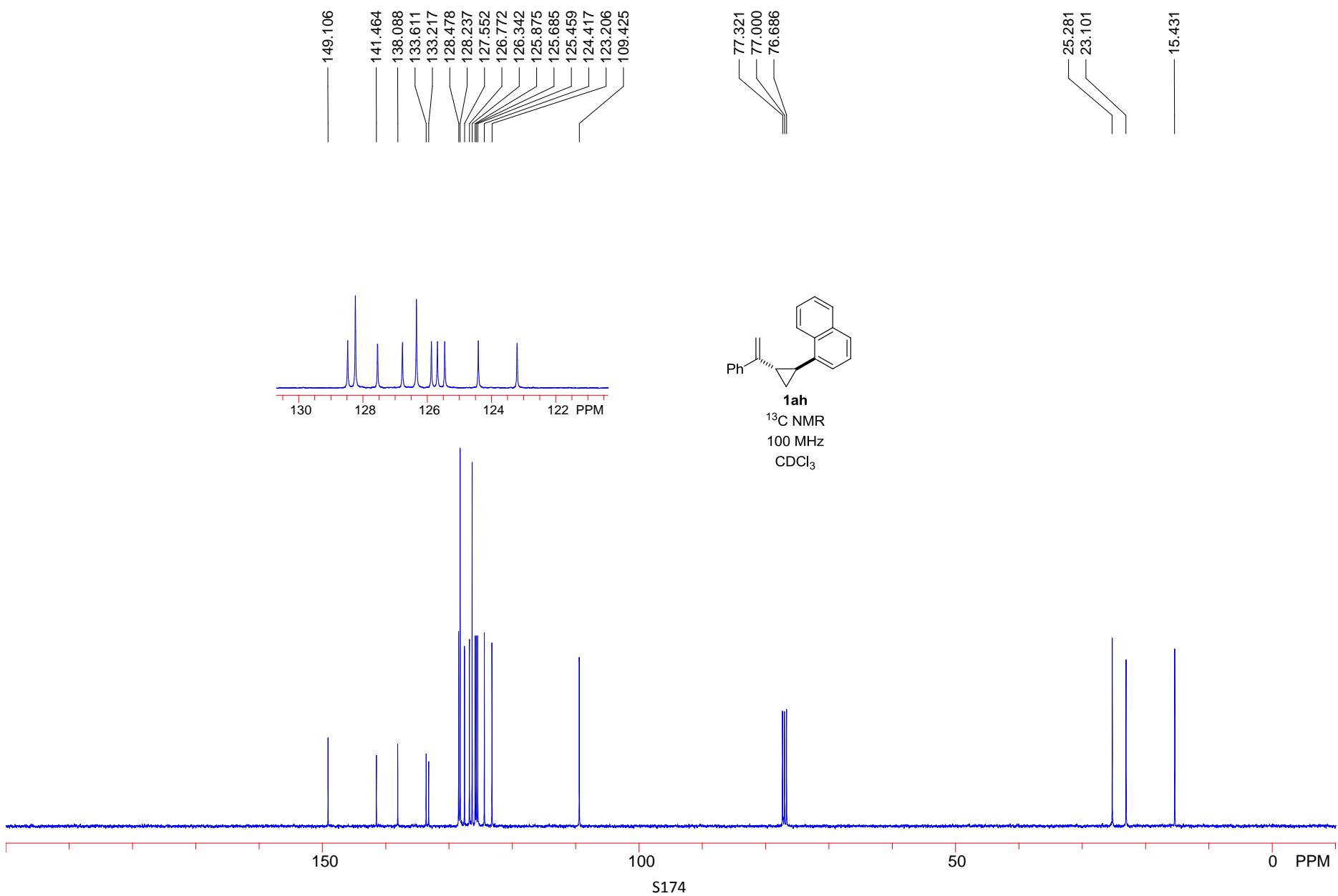
S169

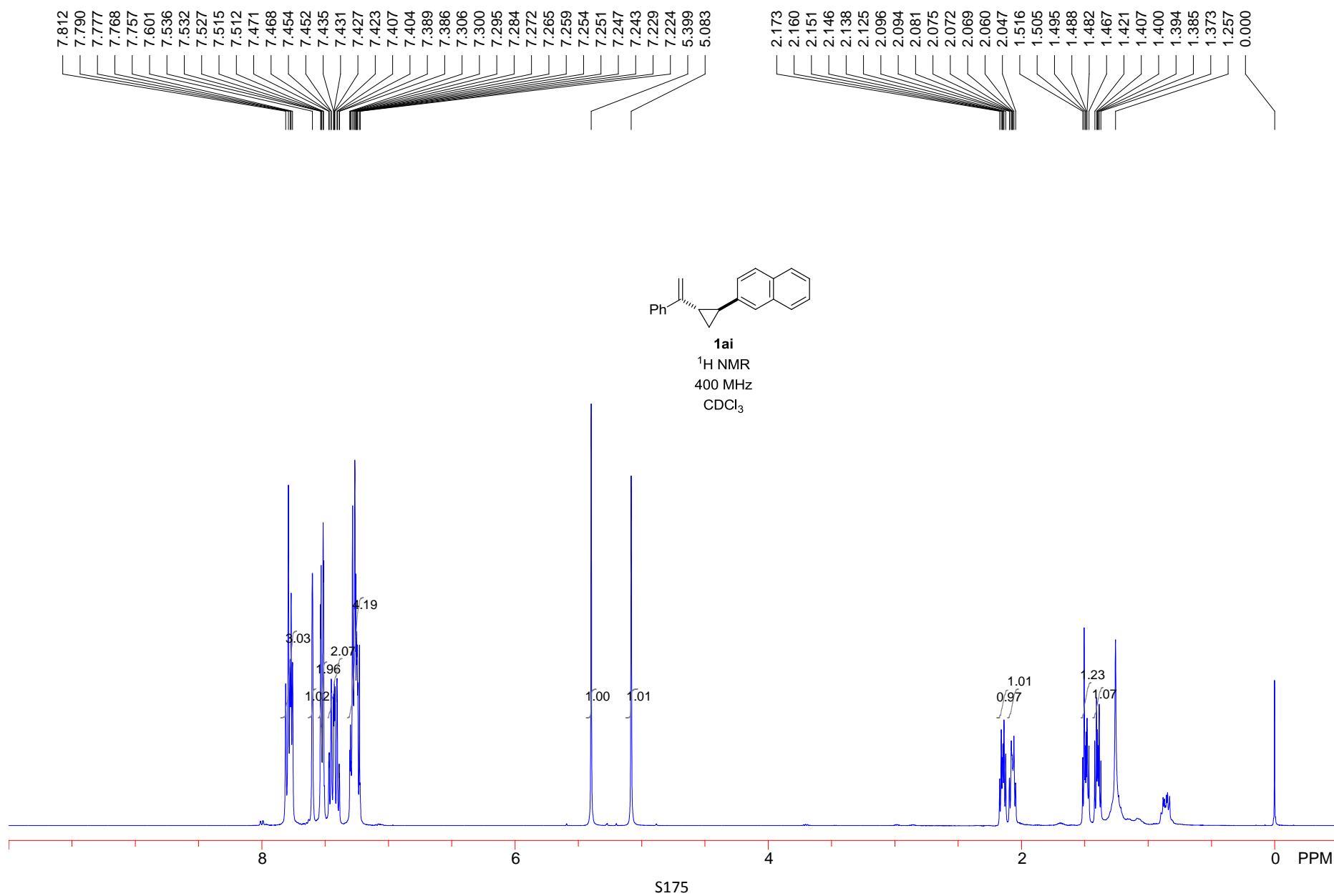


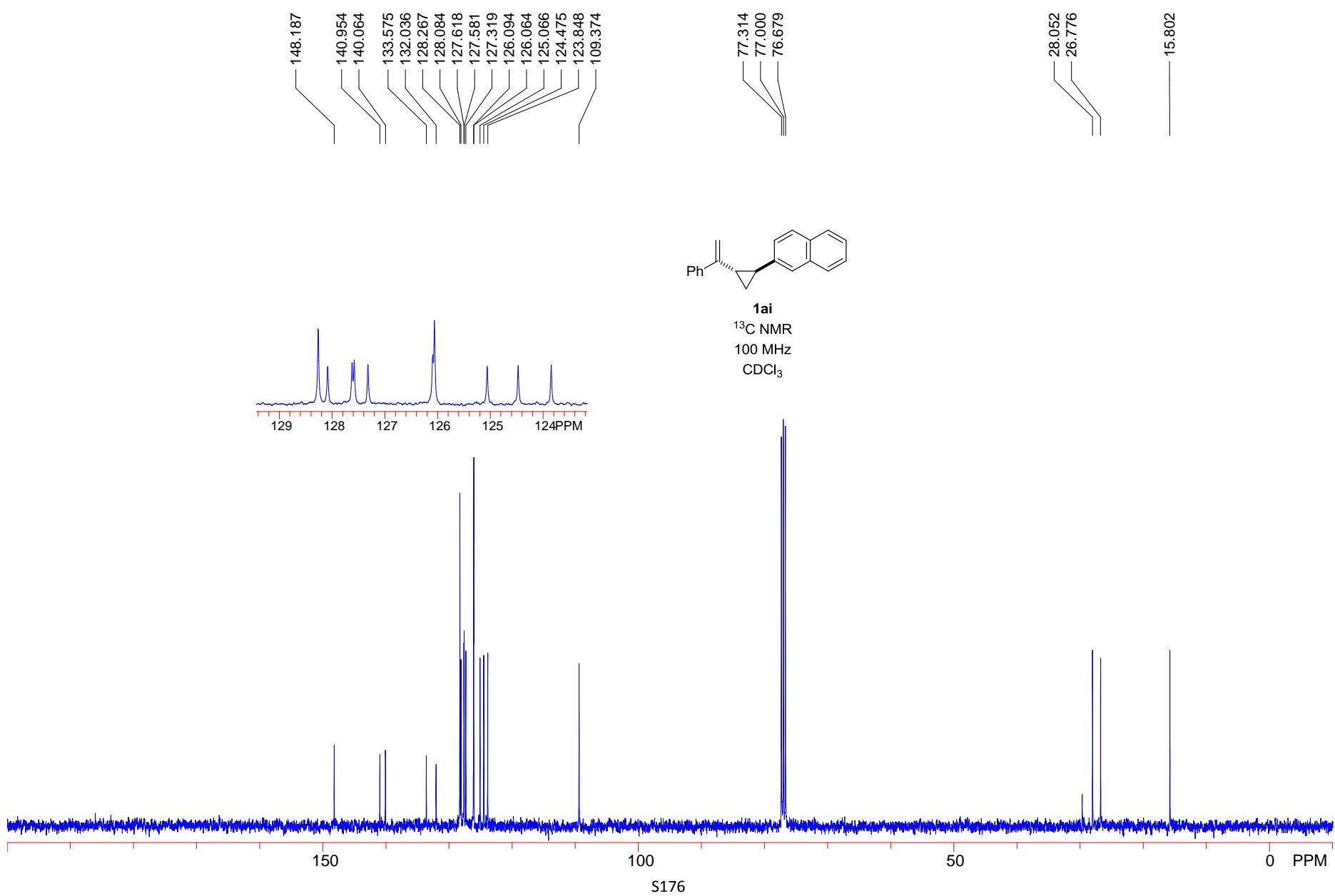


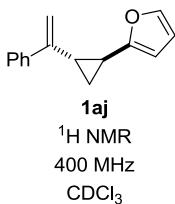
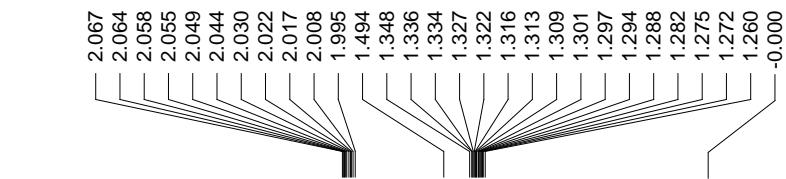
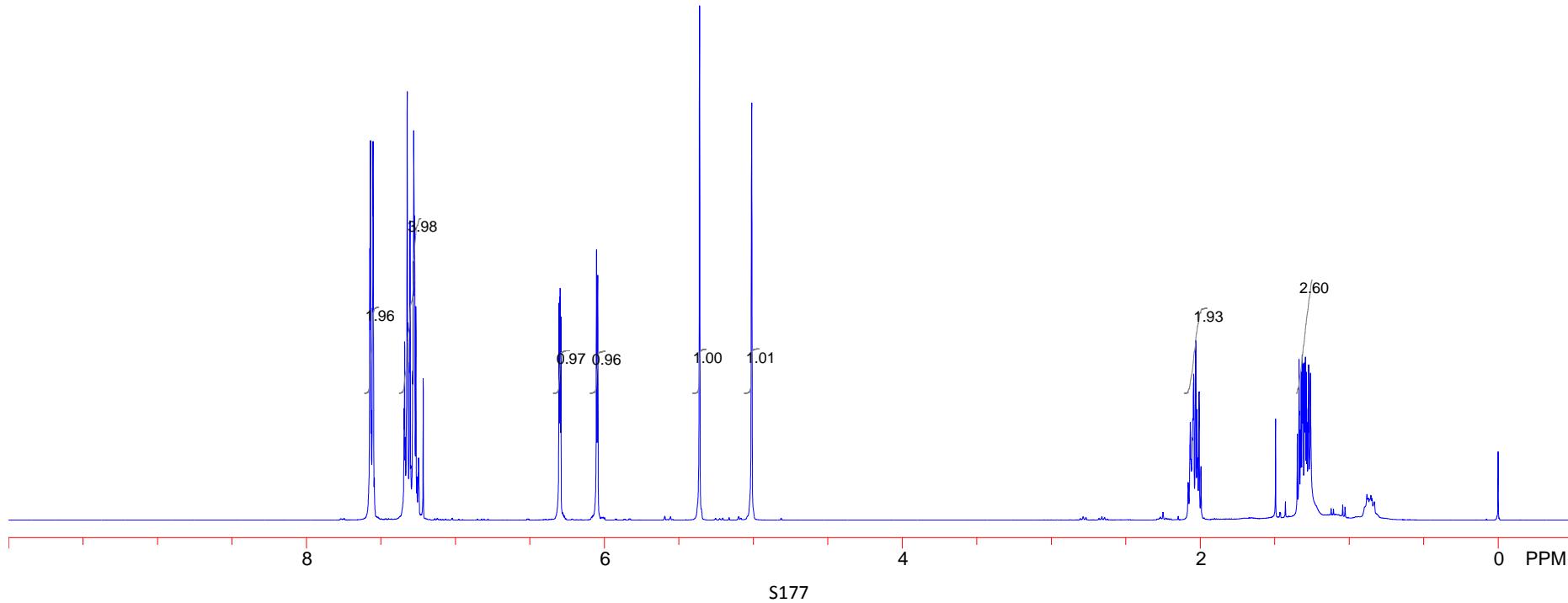


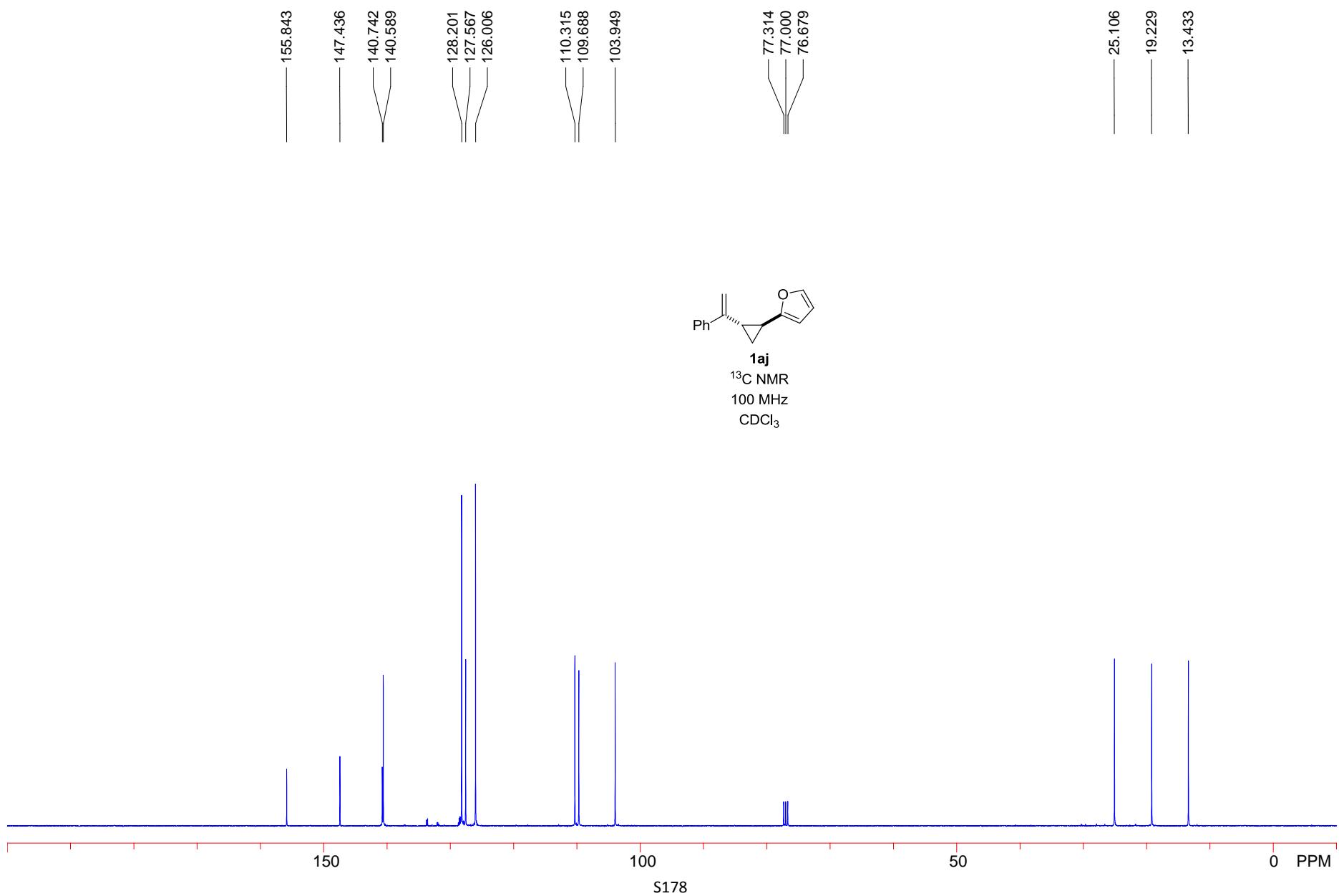


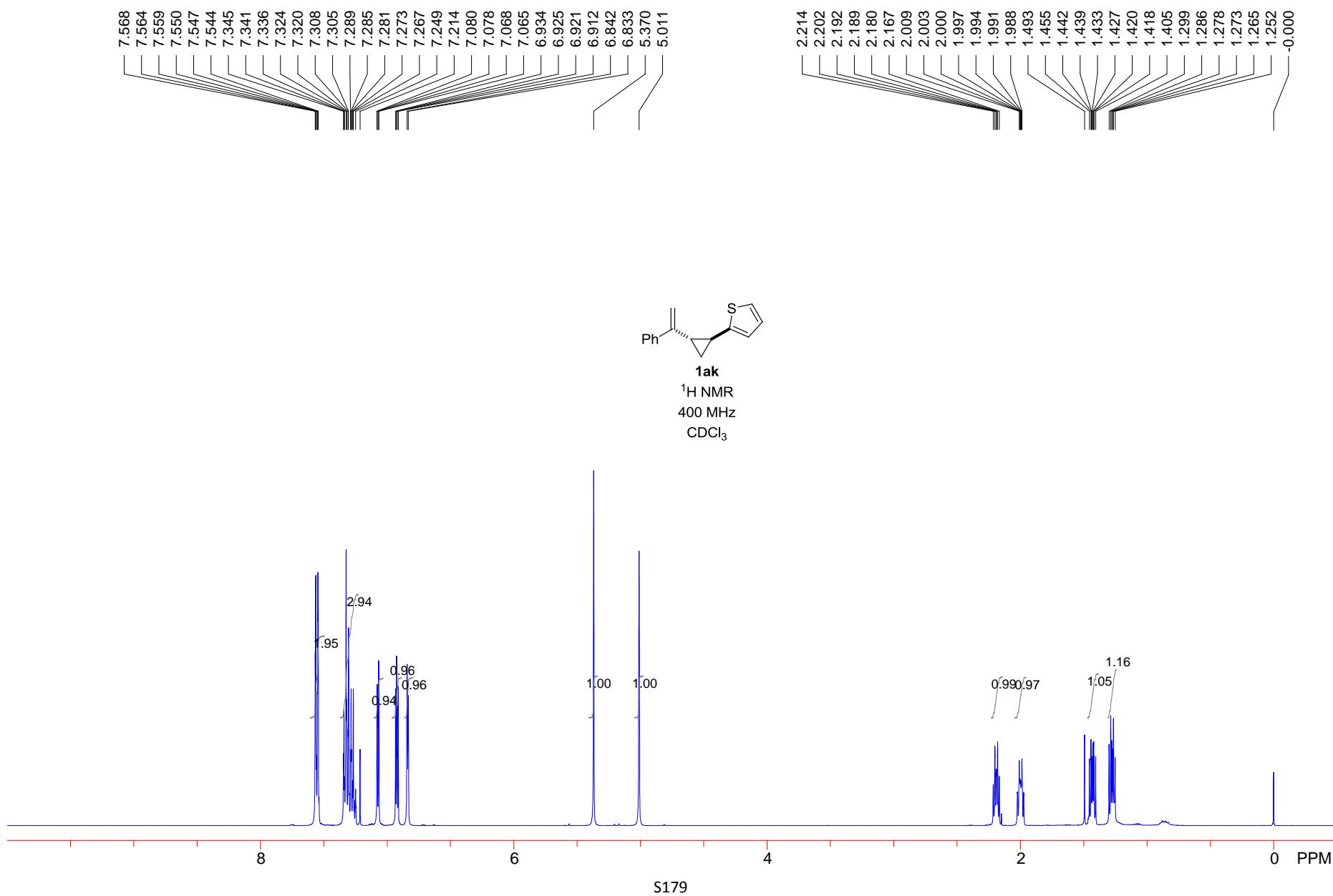


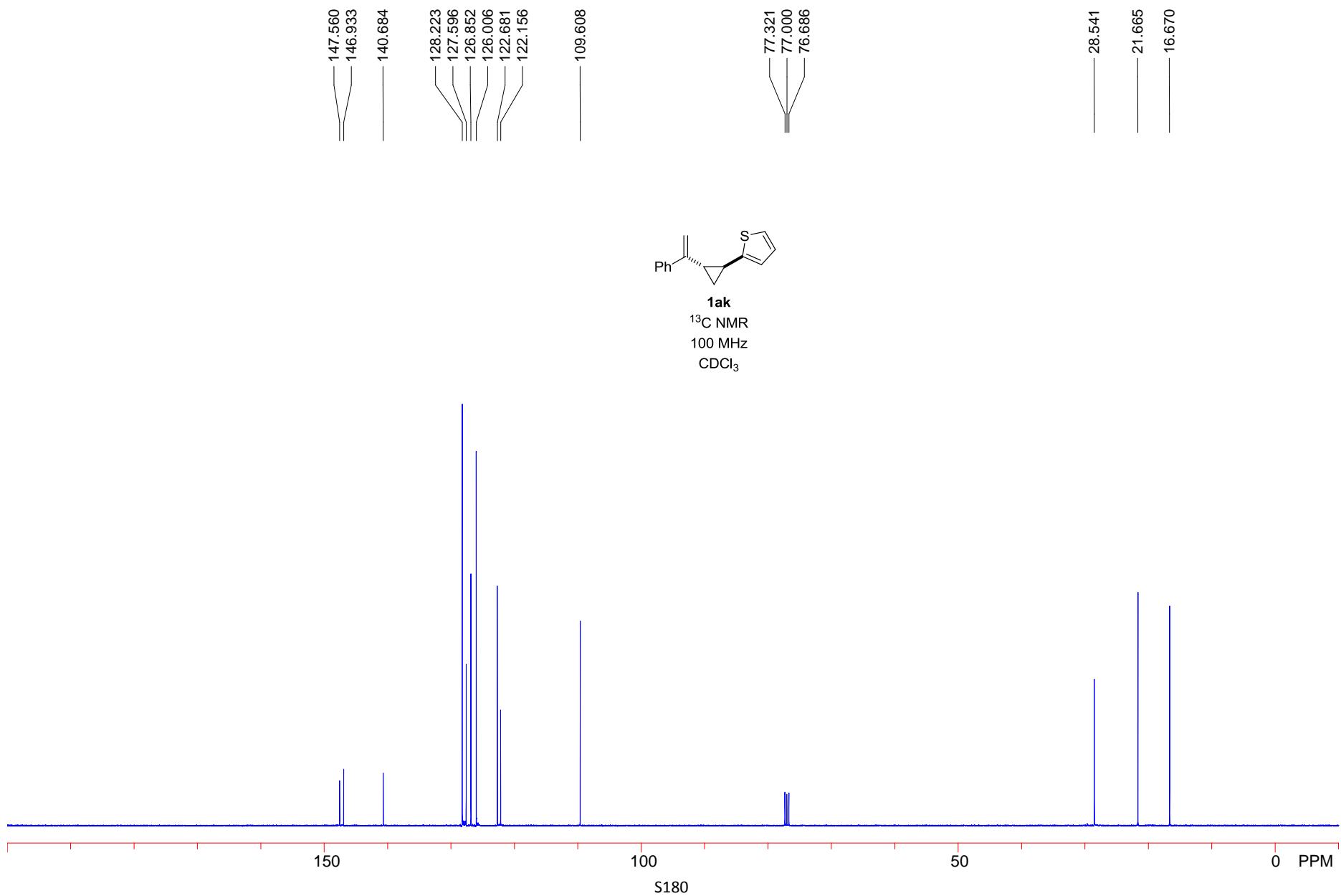


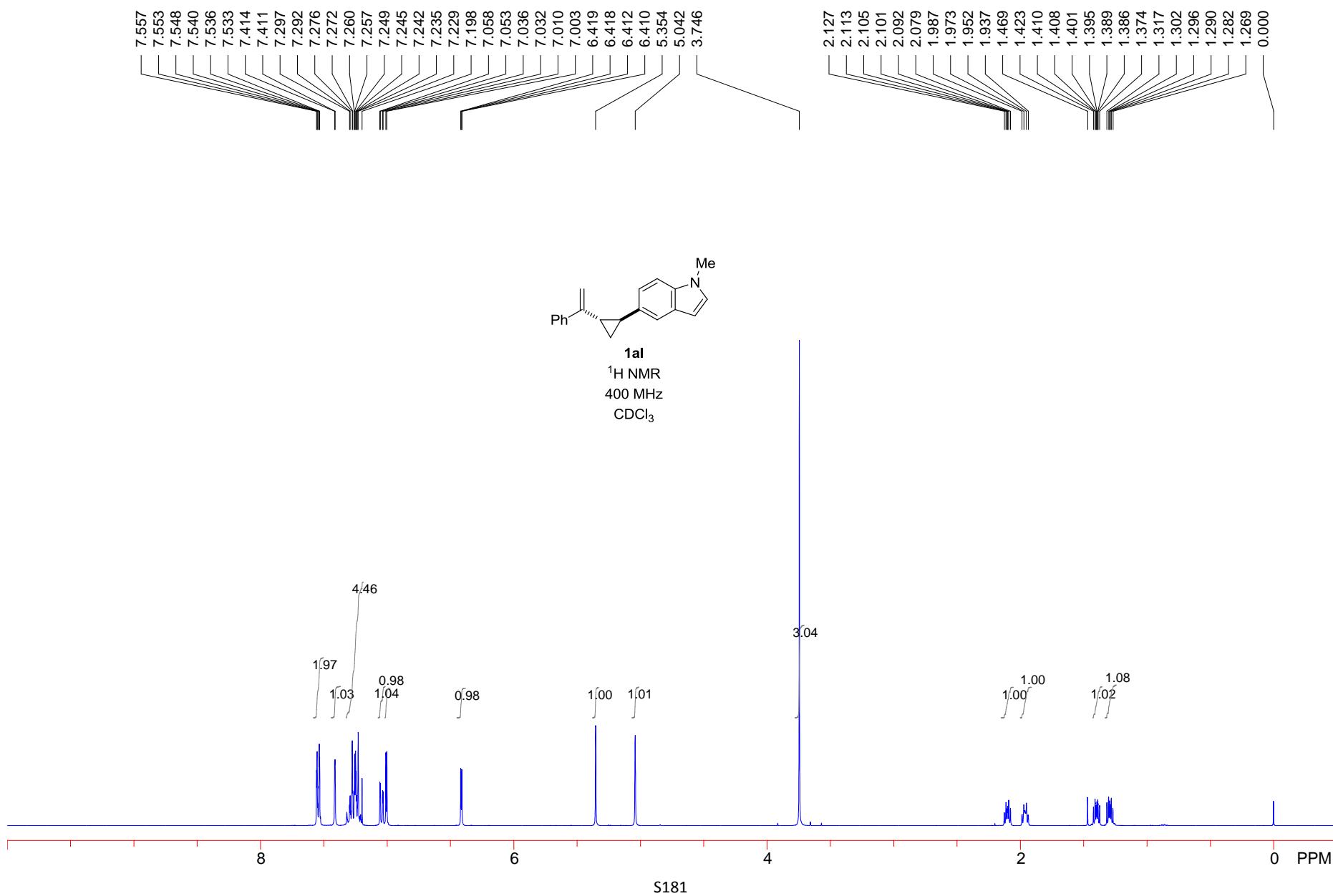


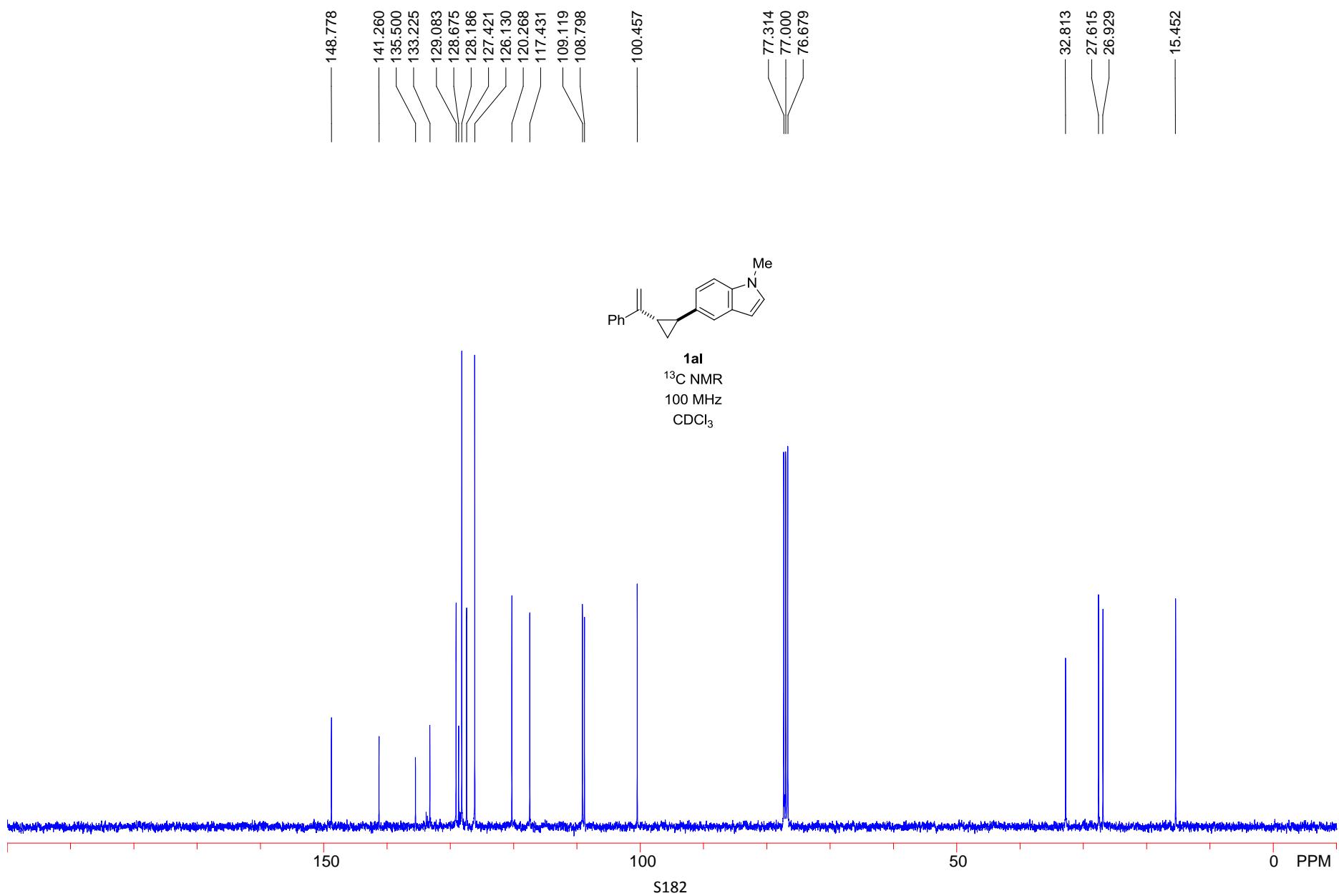


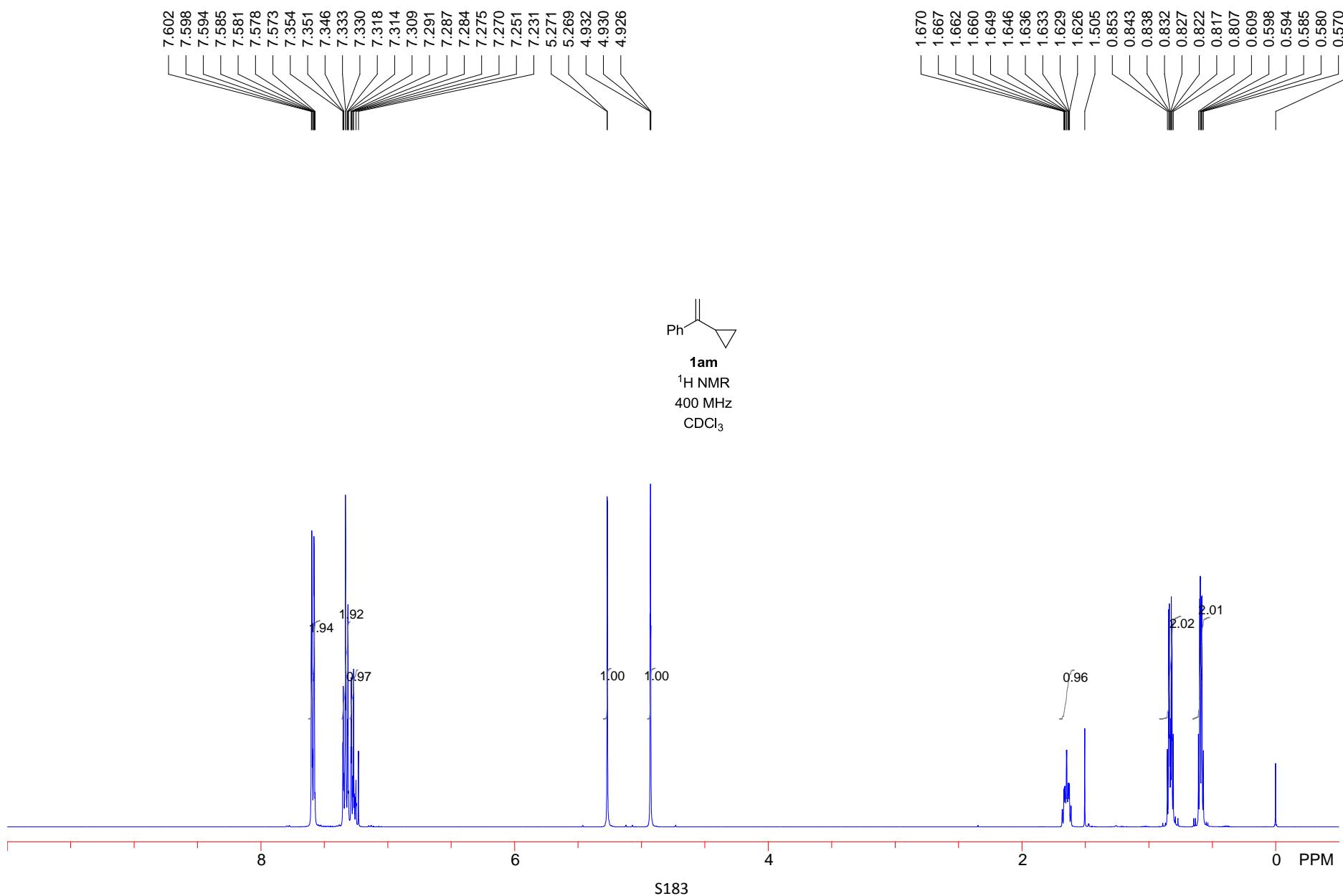


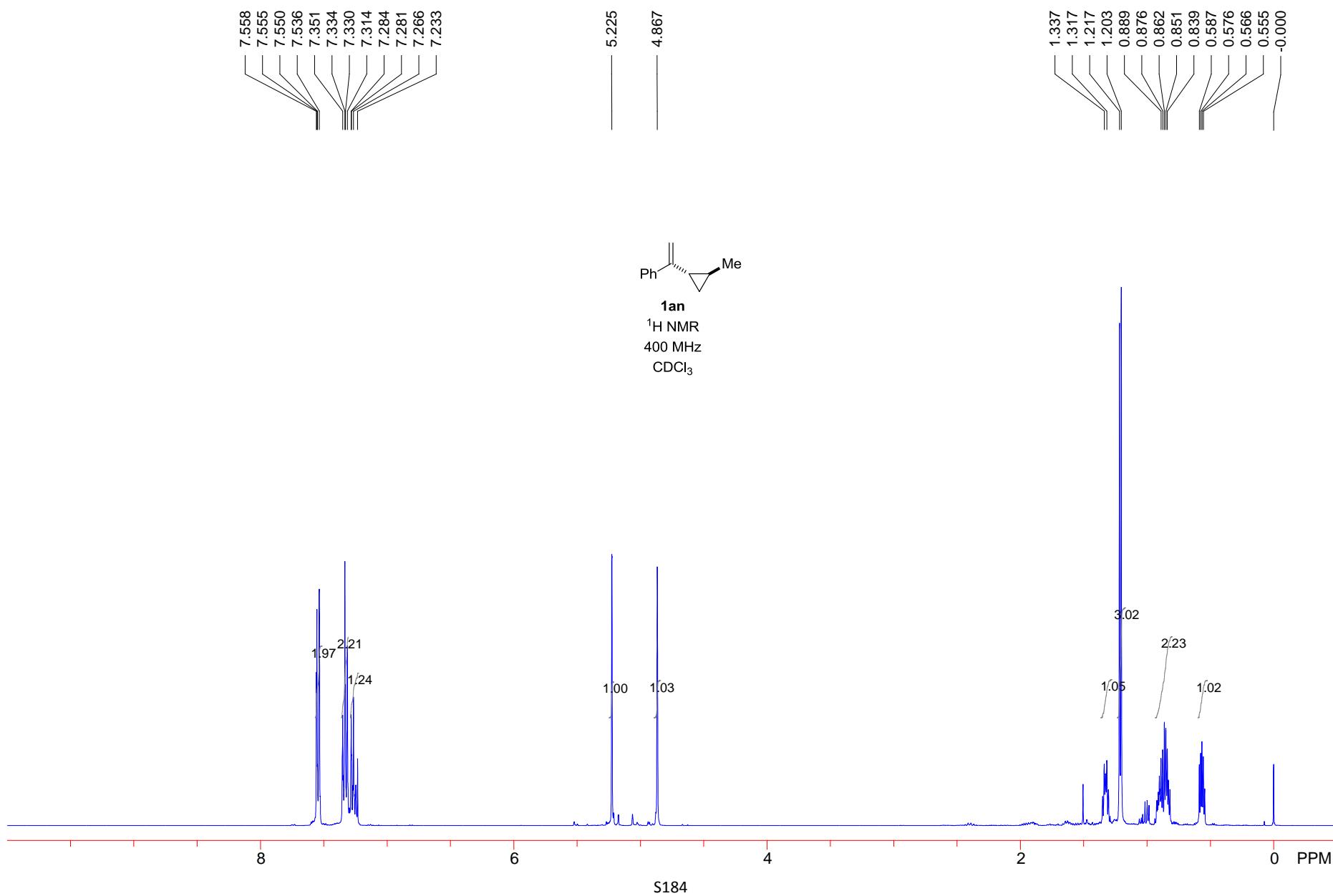




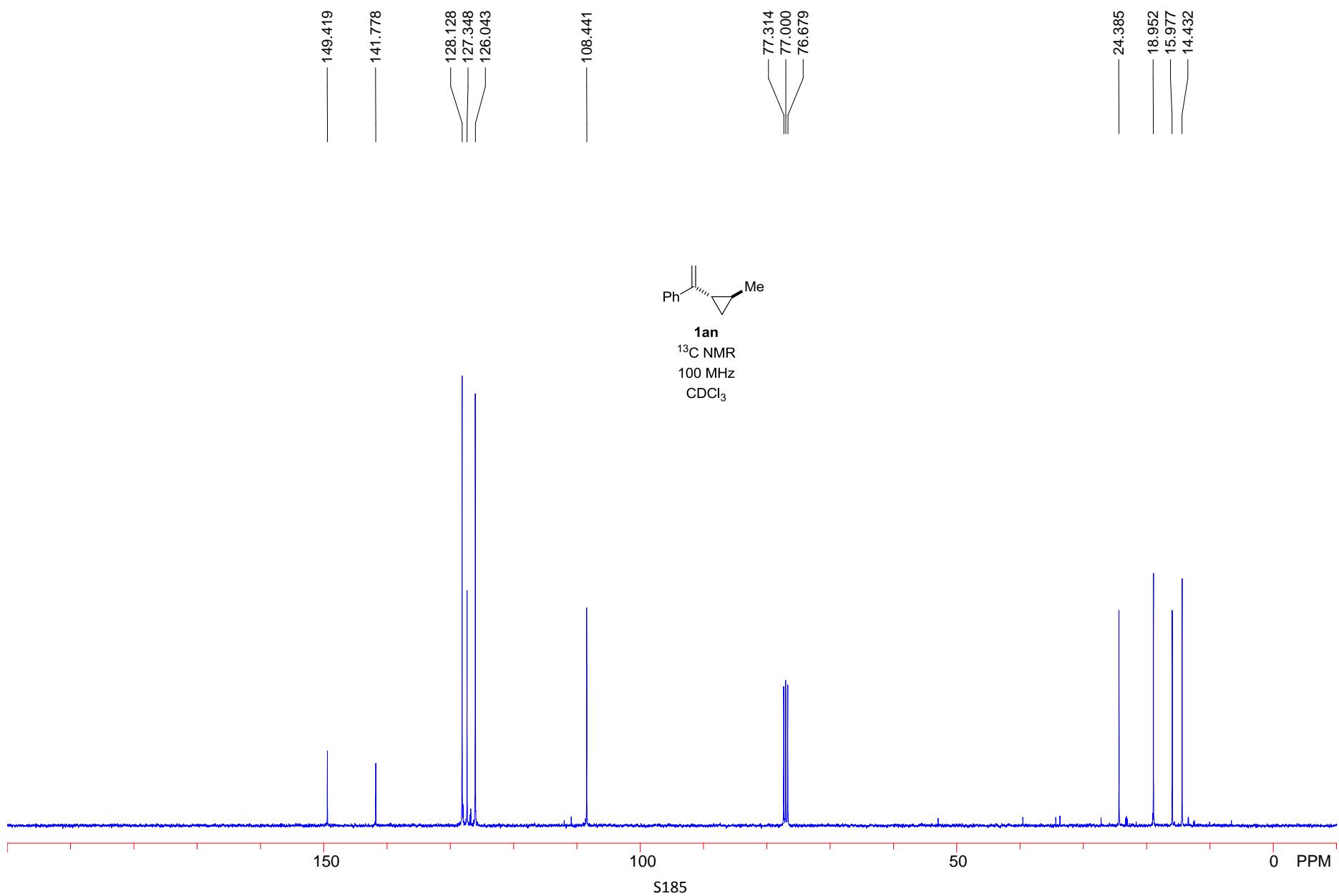


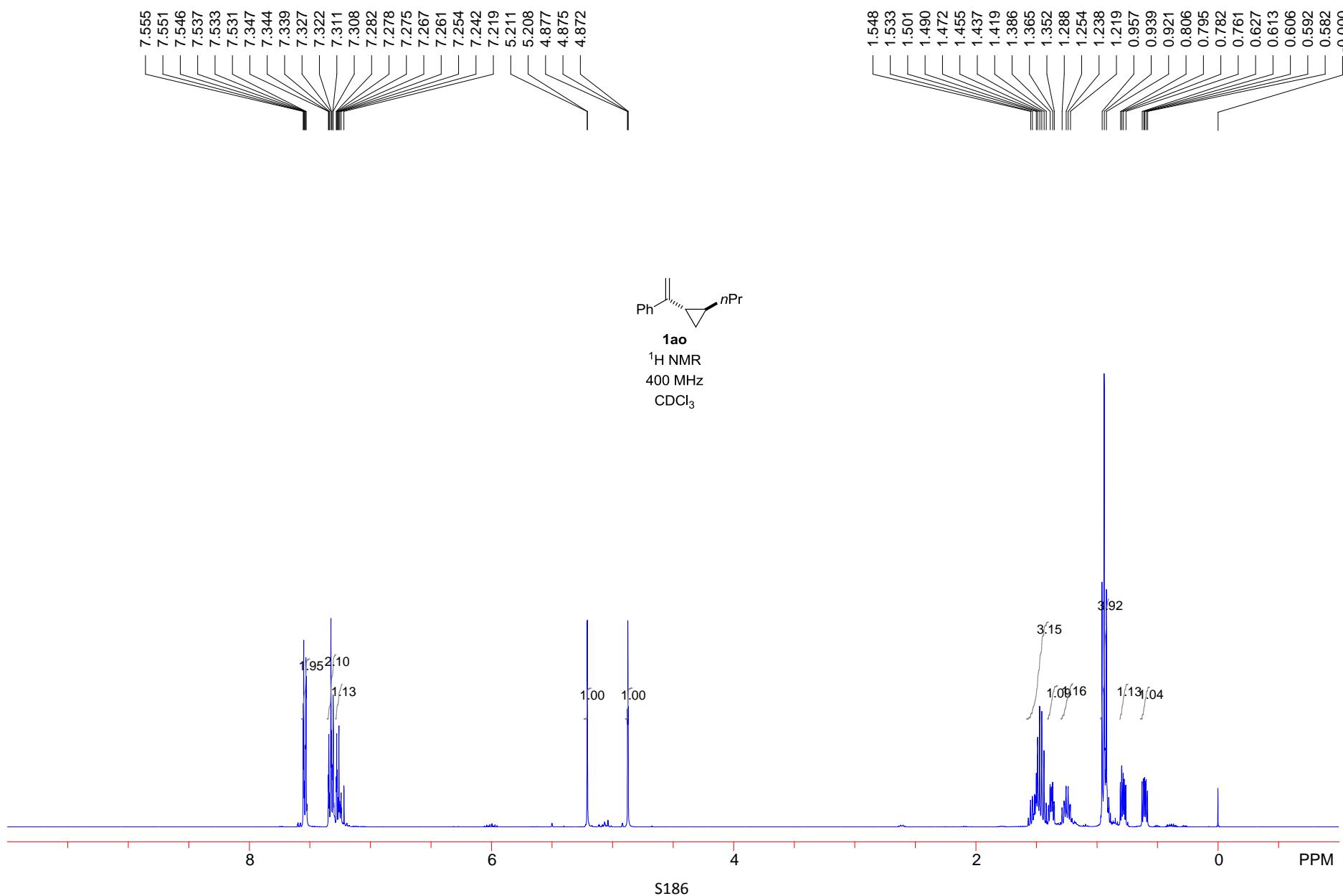


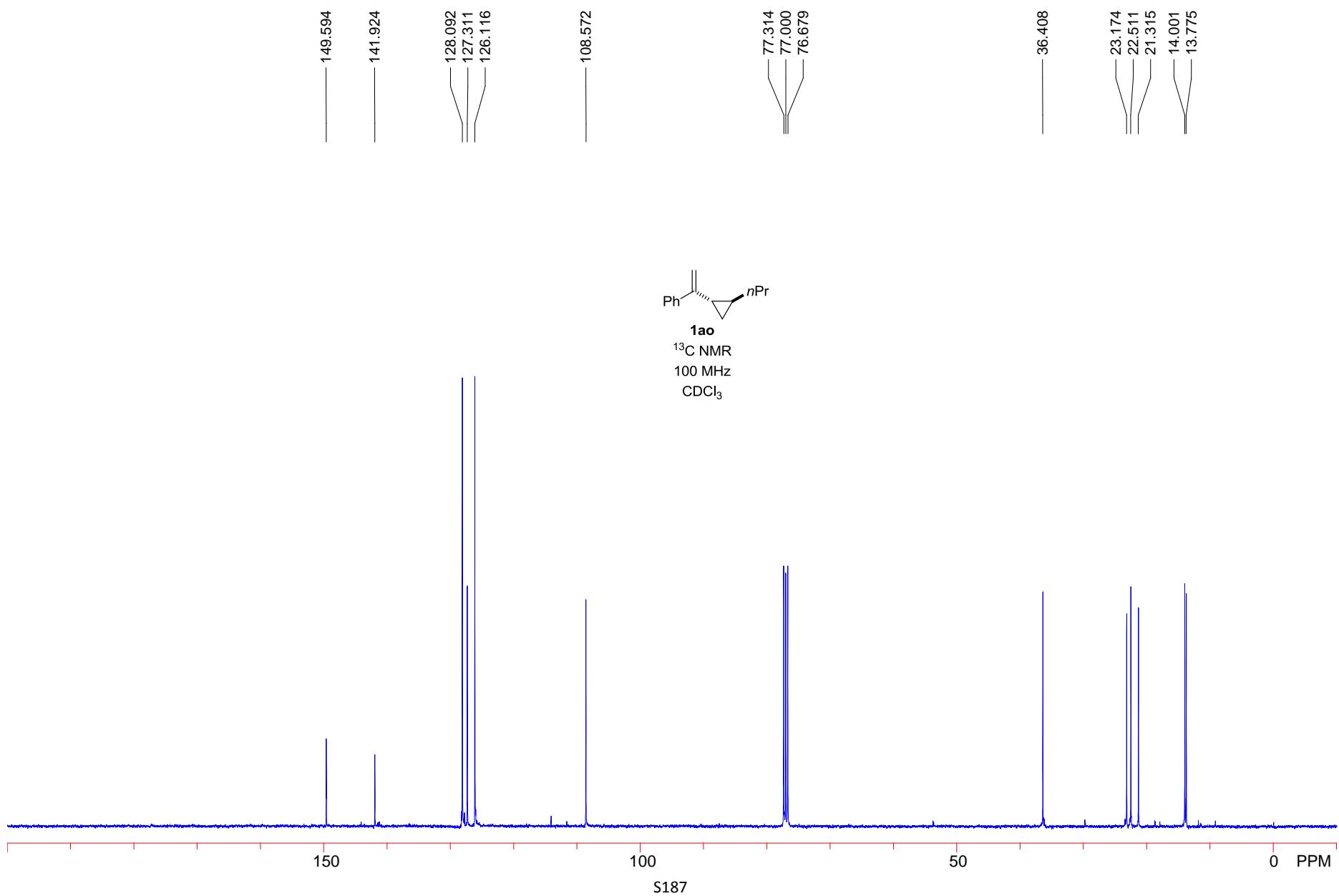


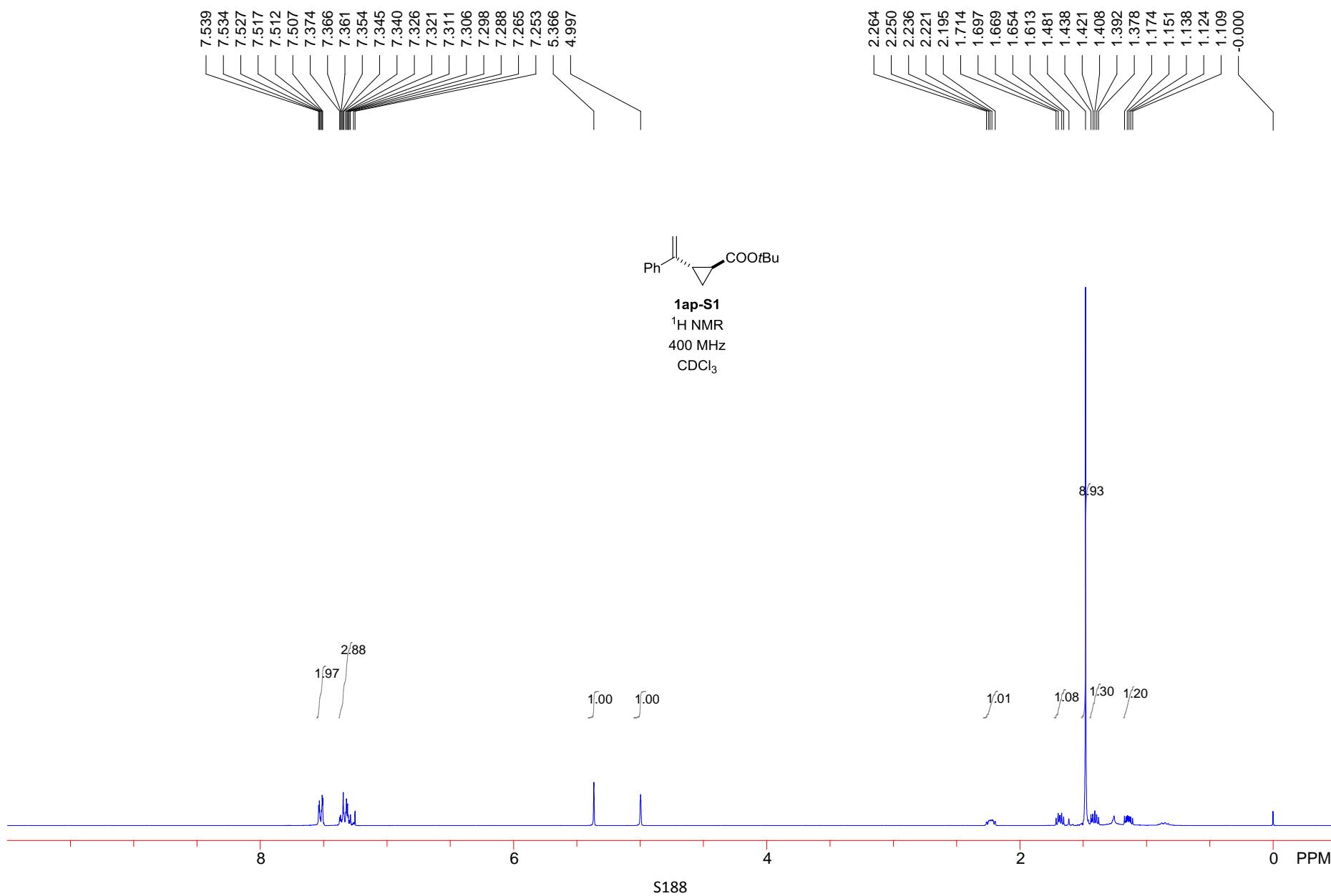


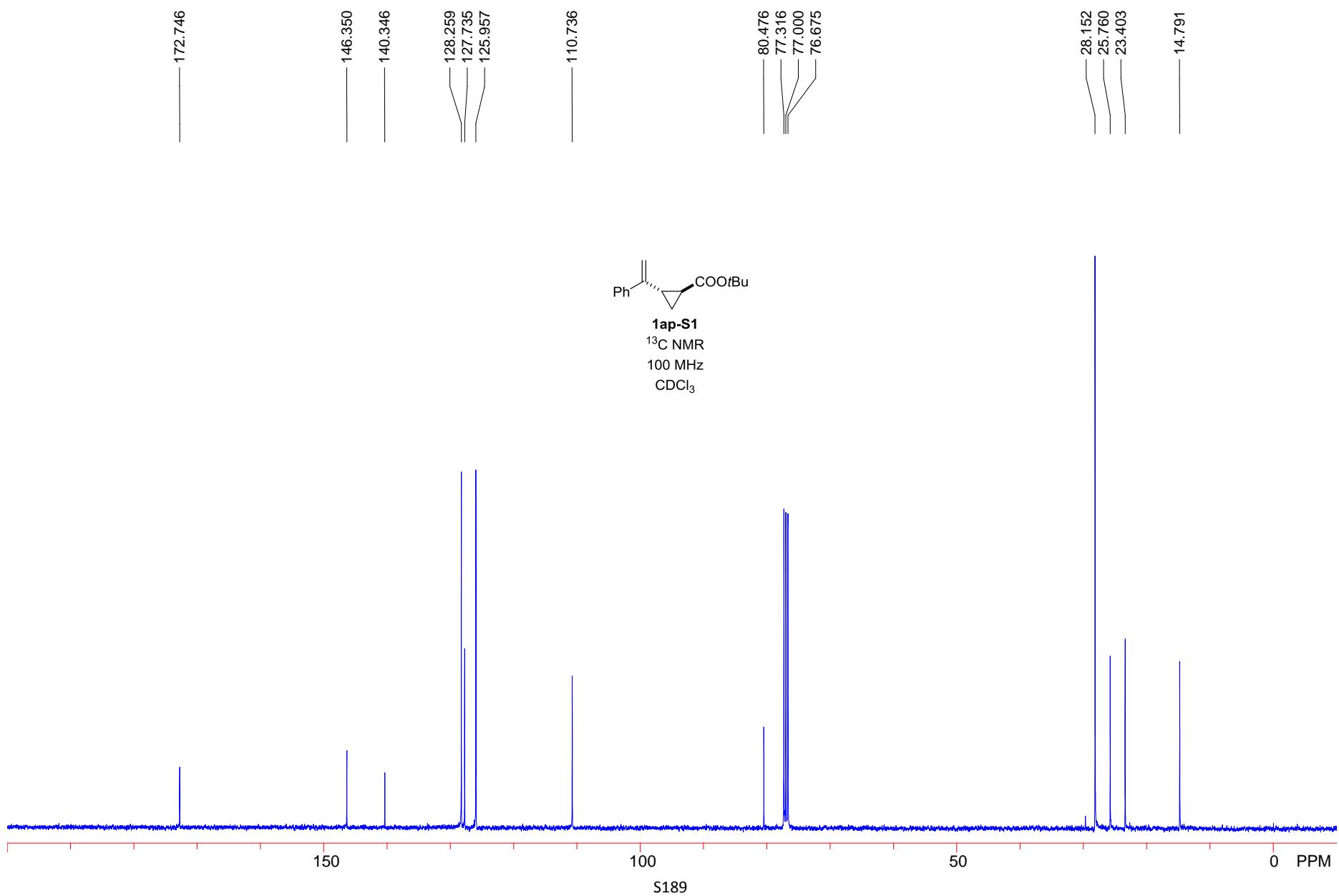
S184

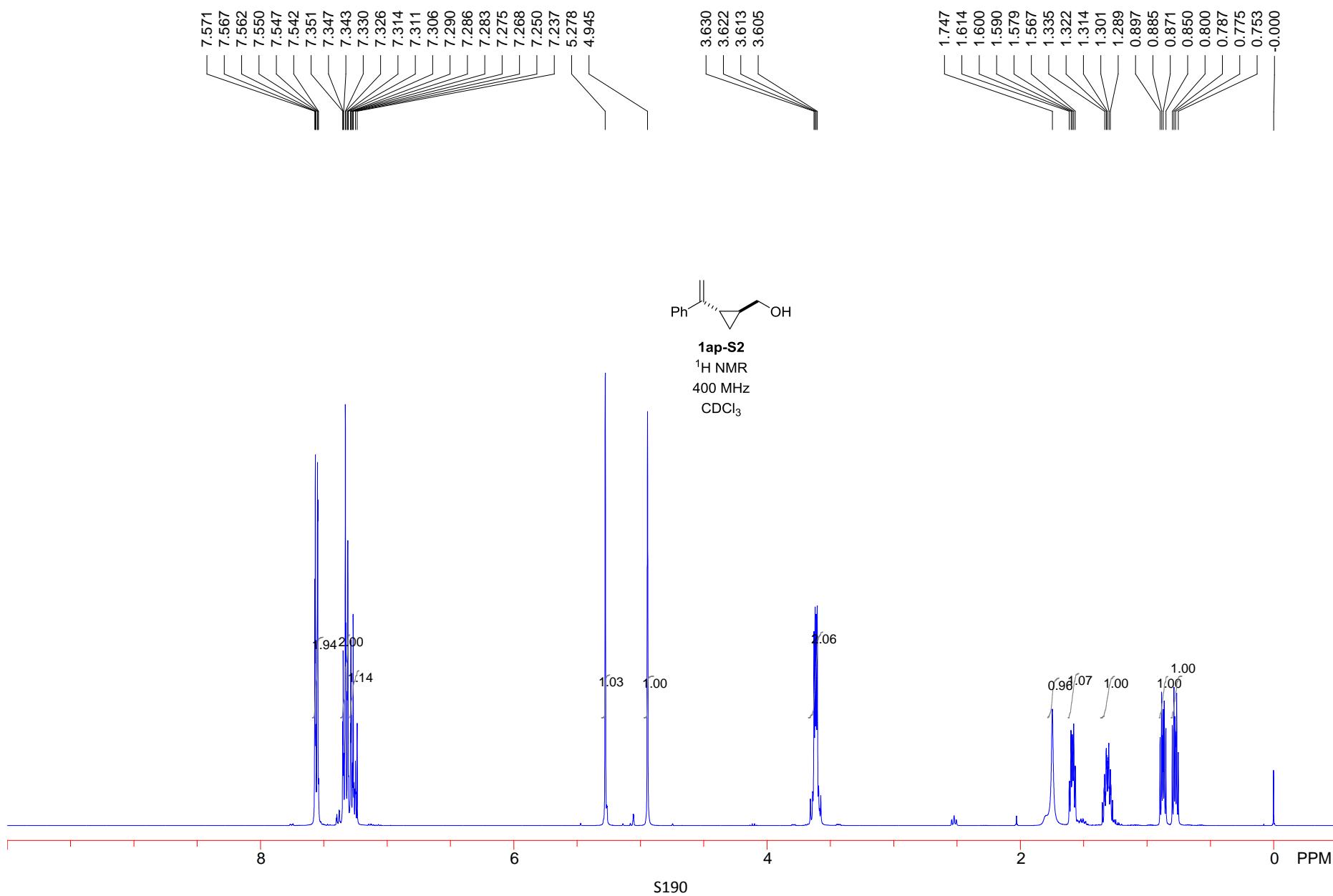


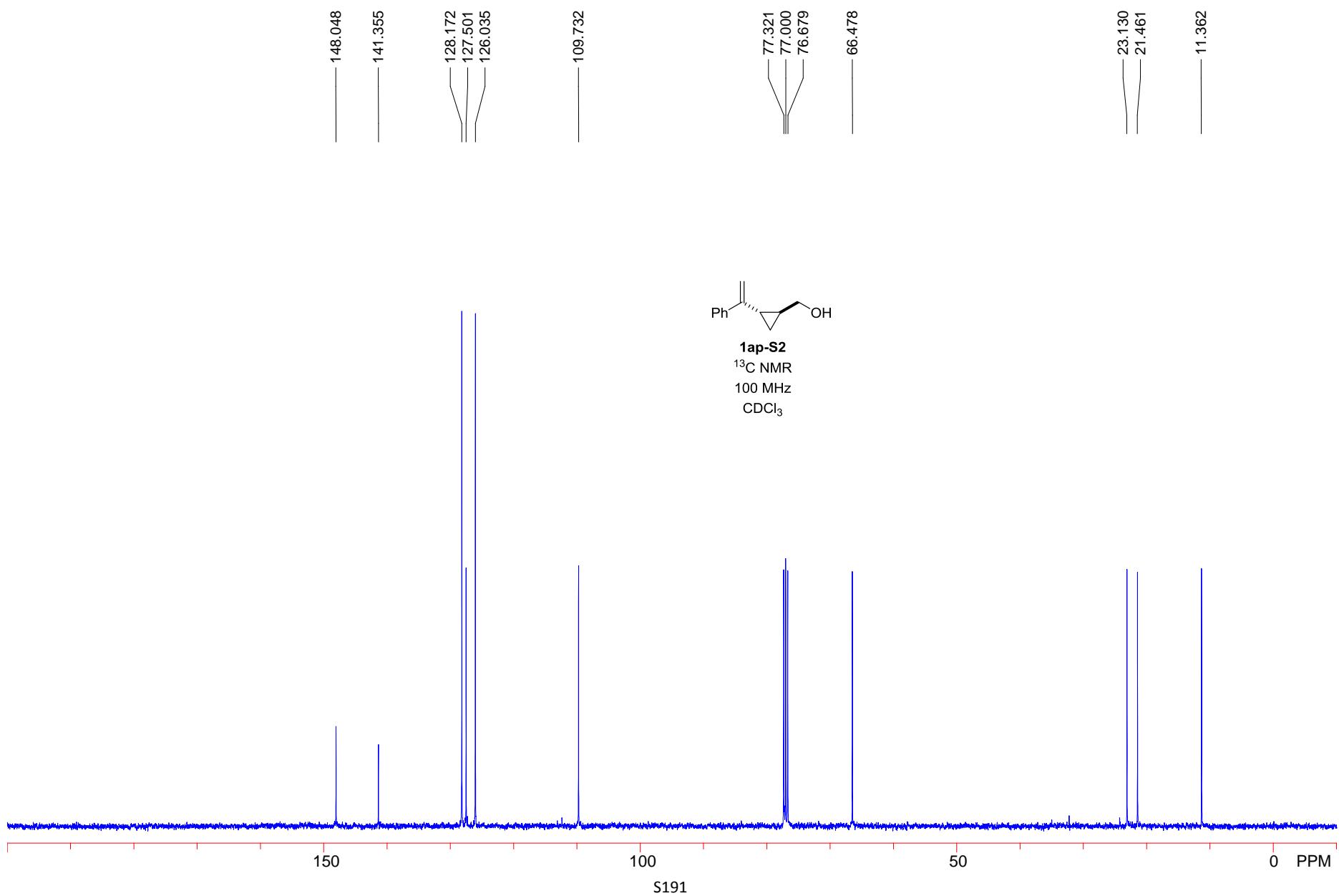


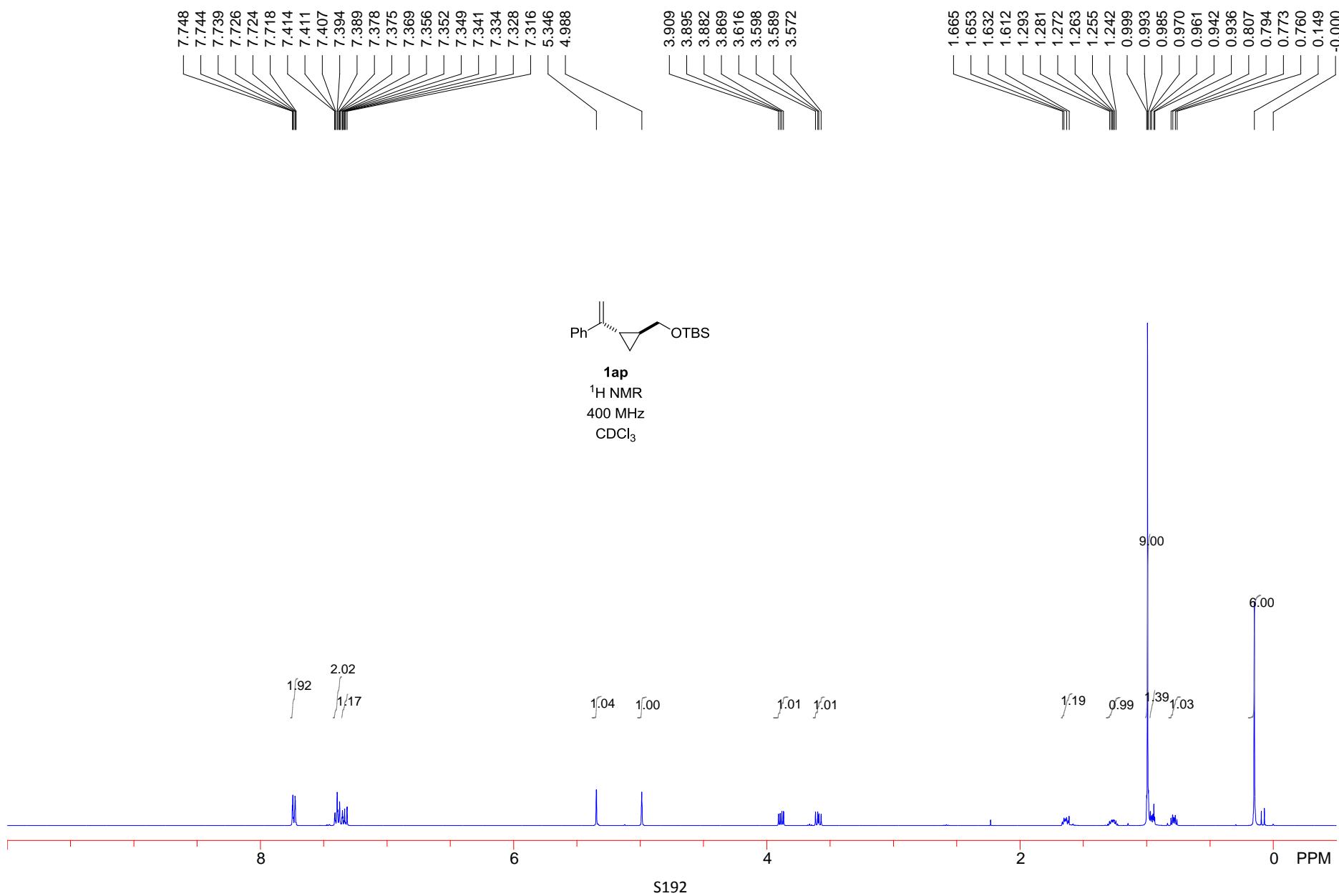


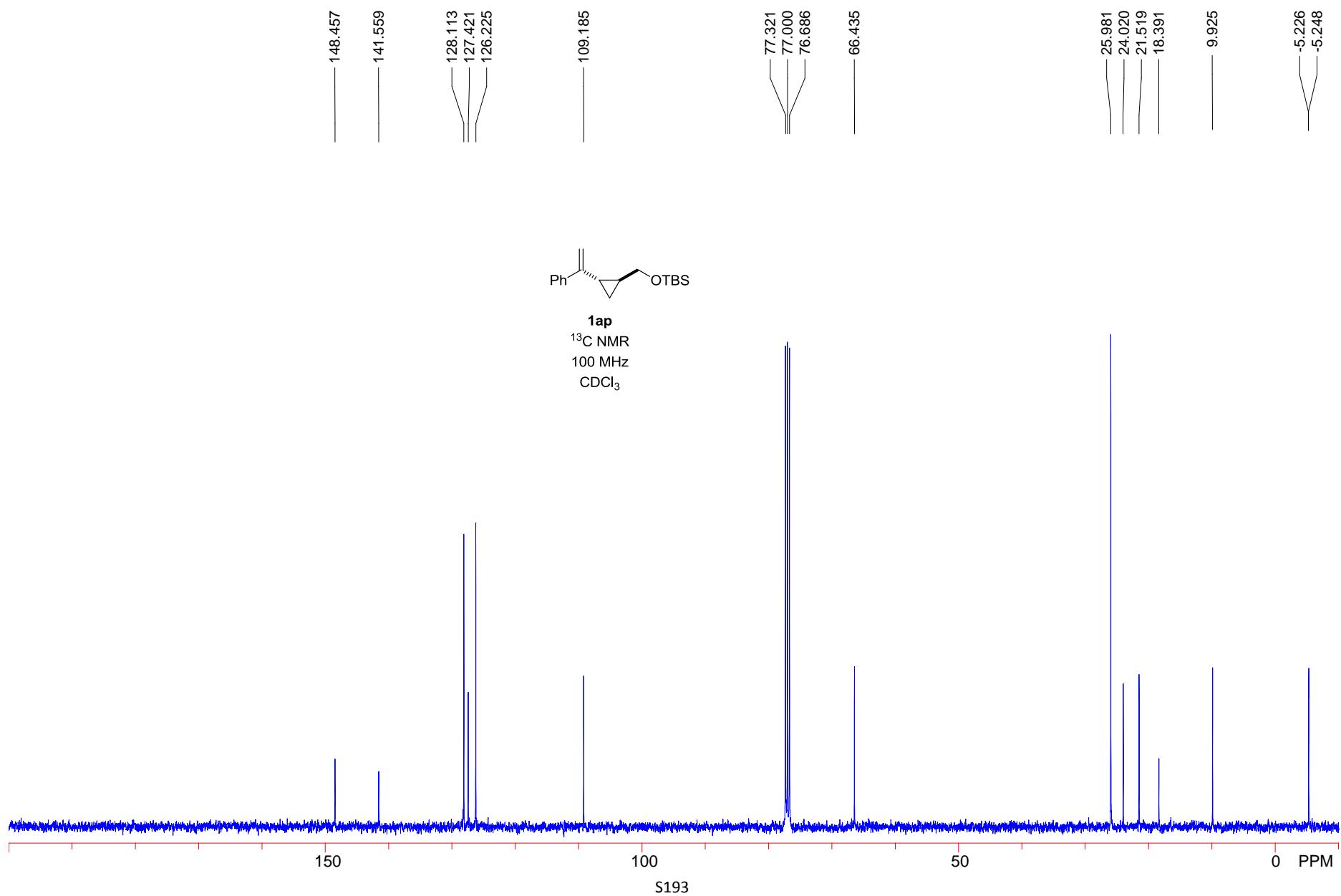


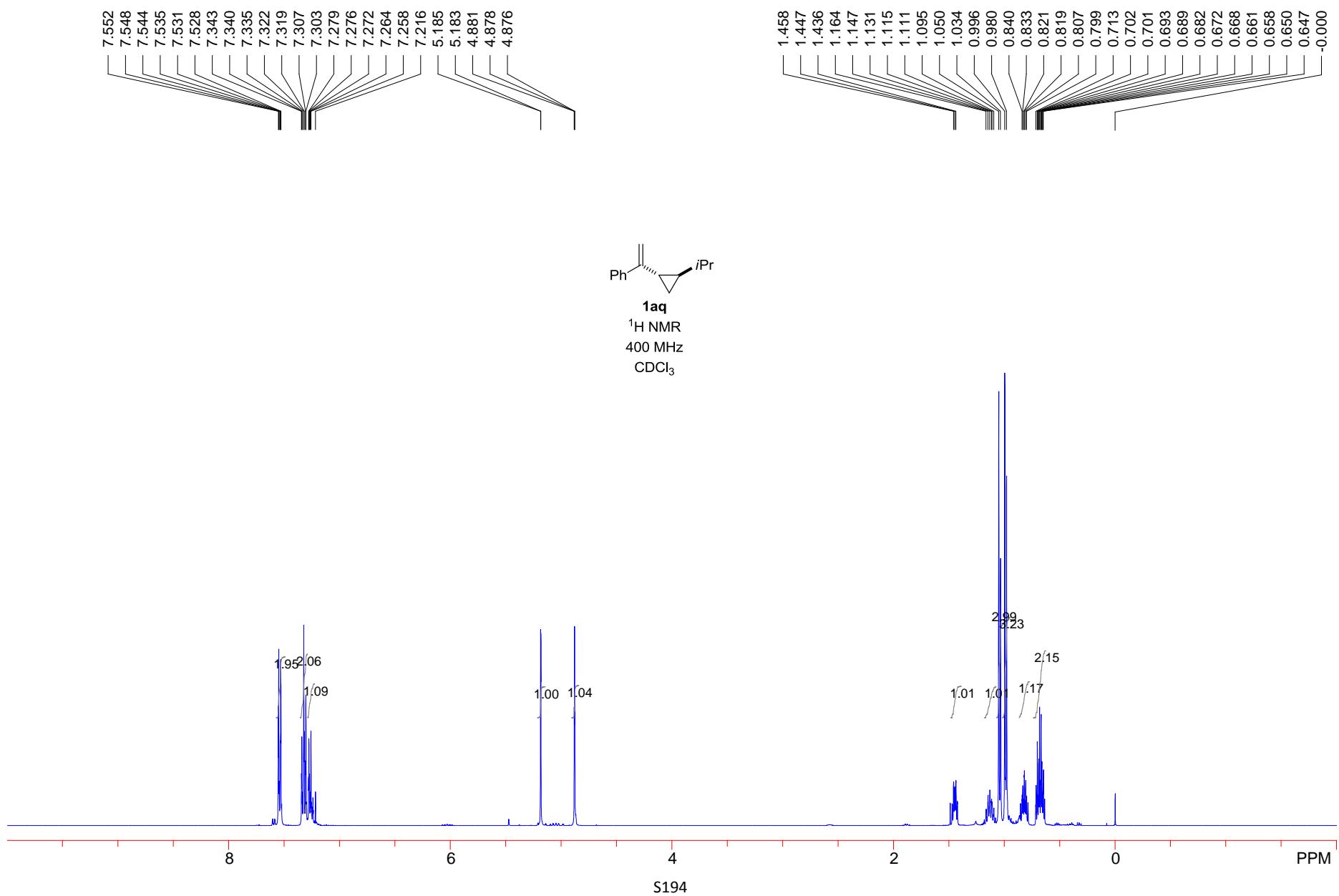


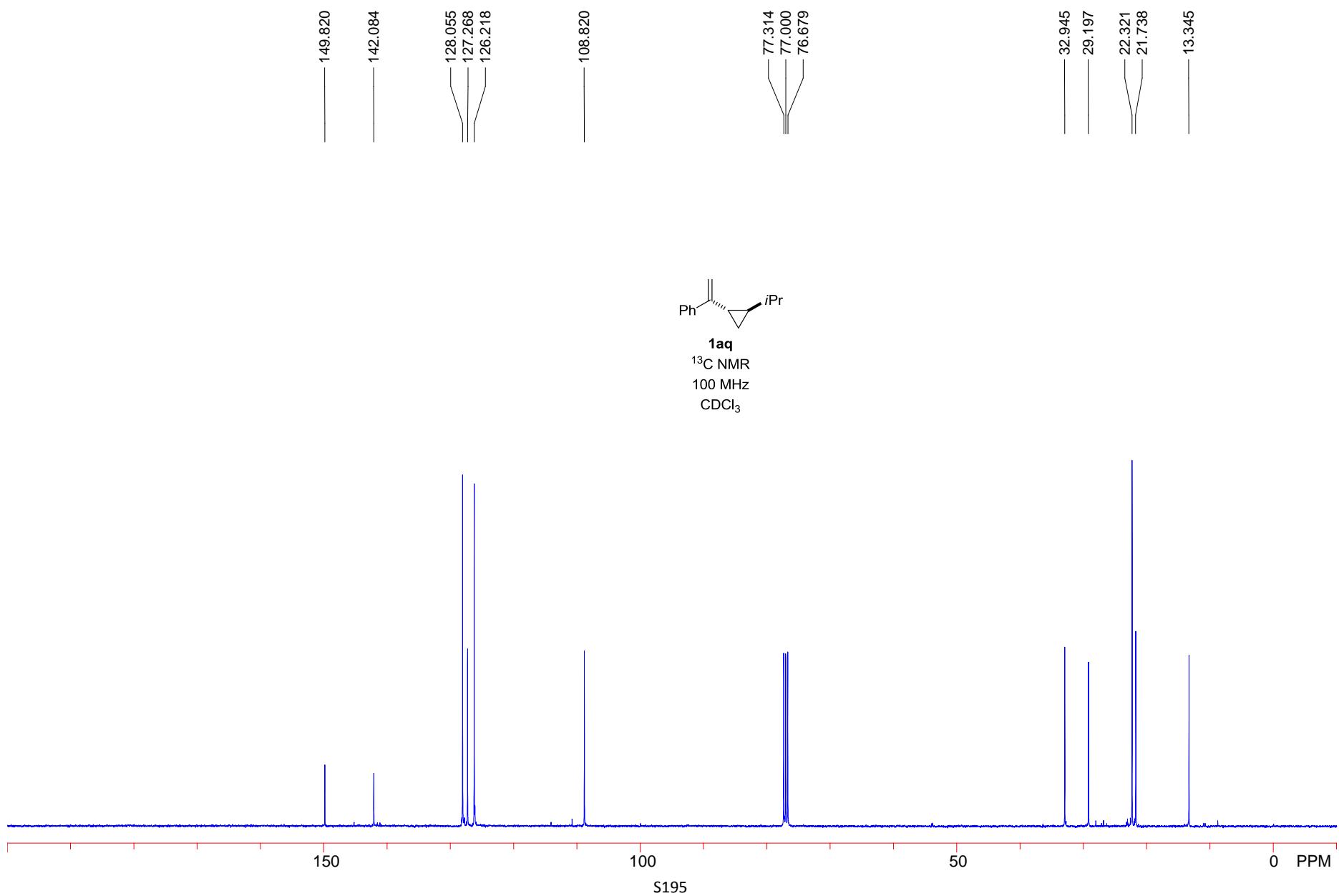


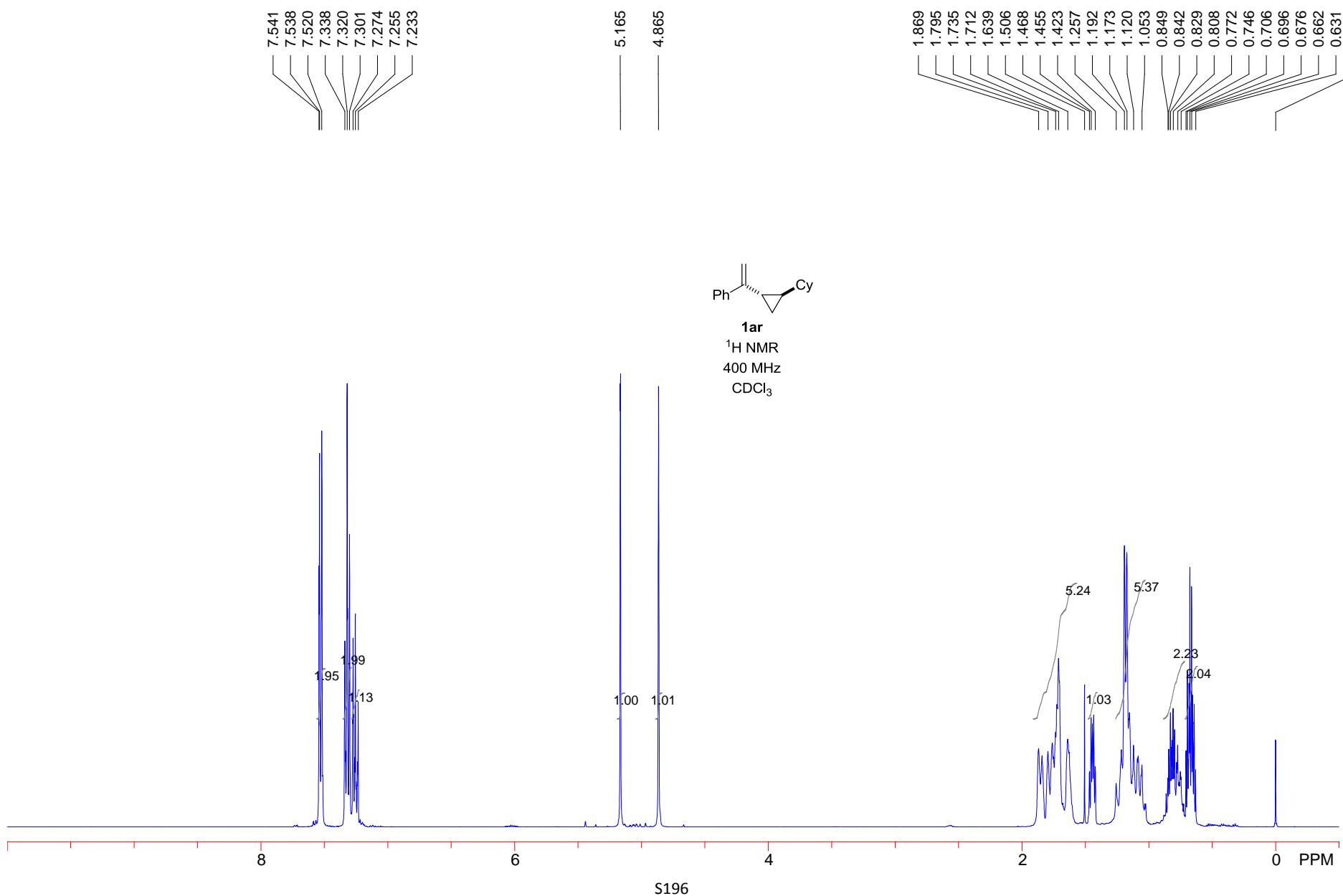


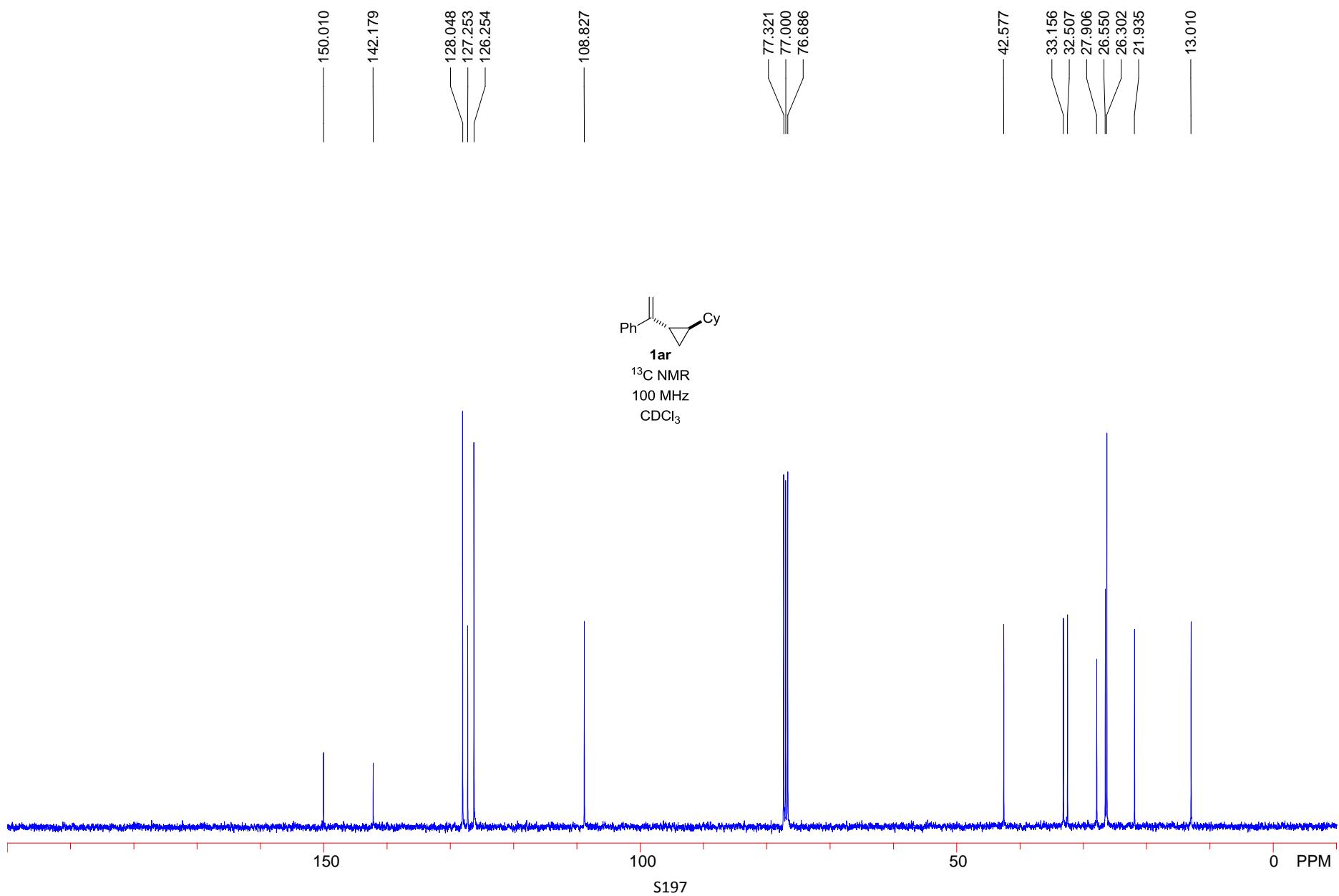


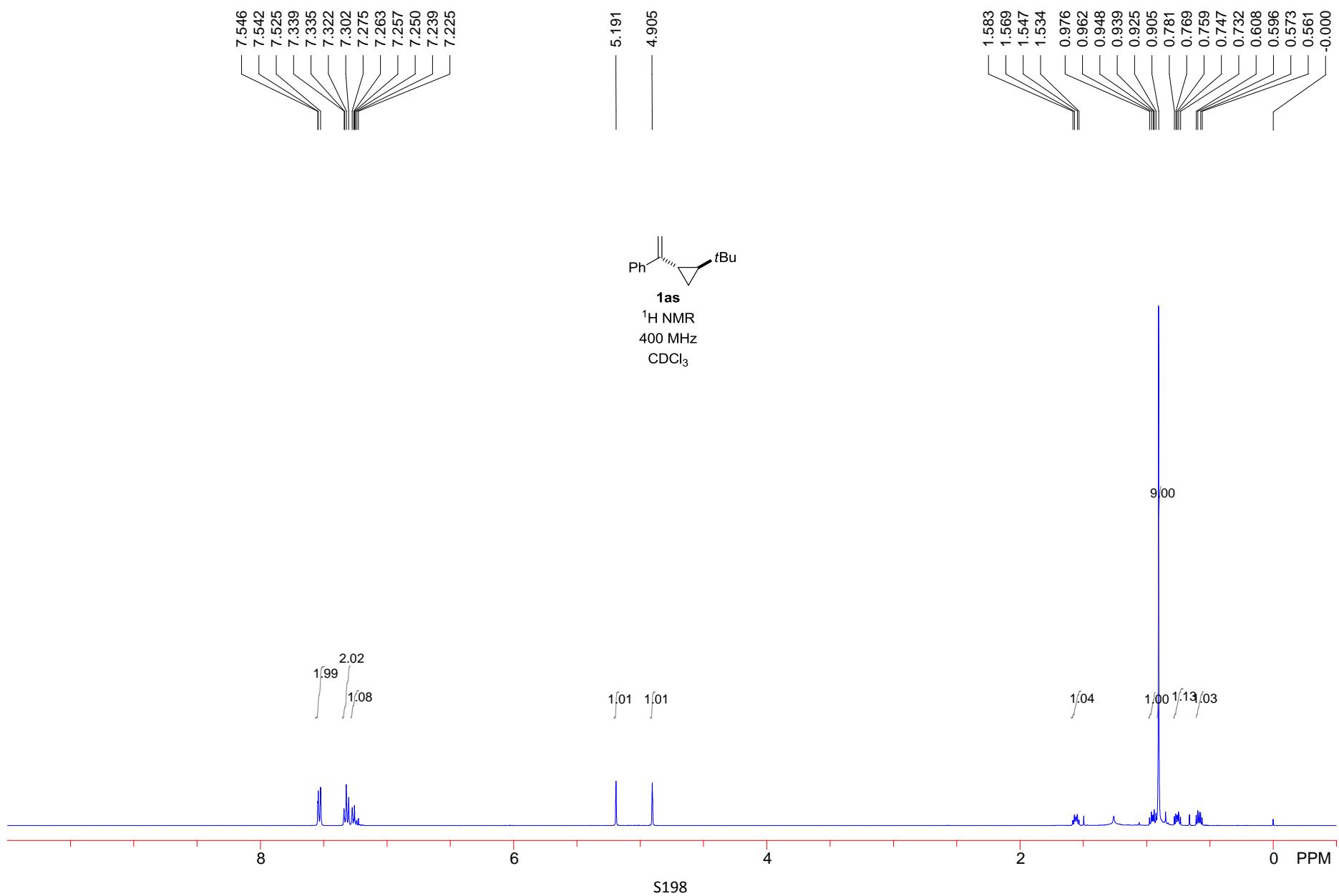


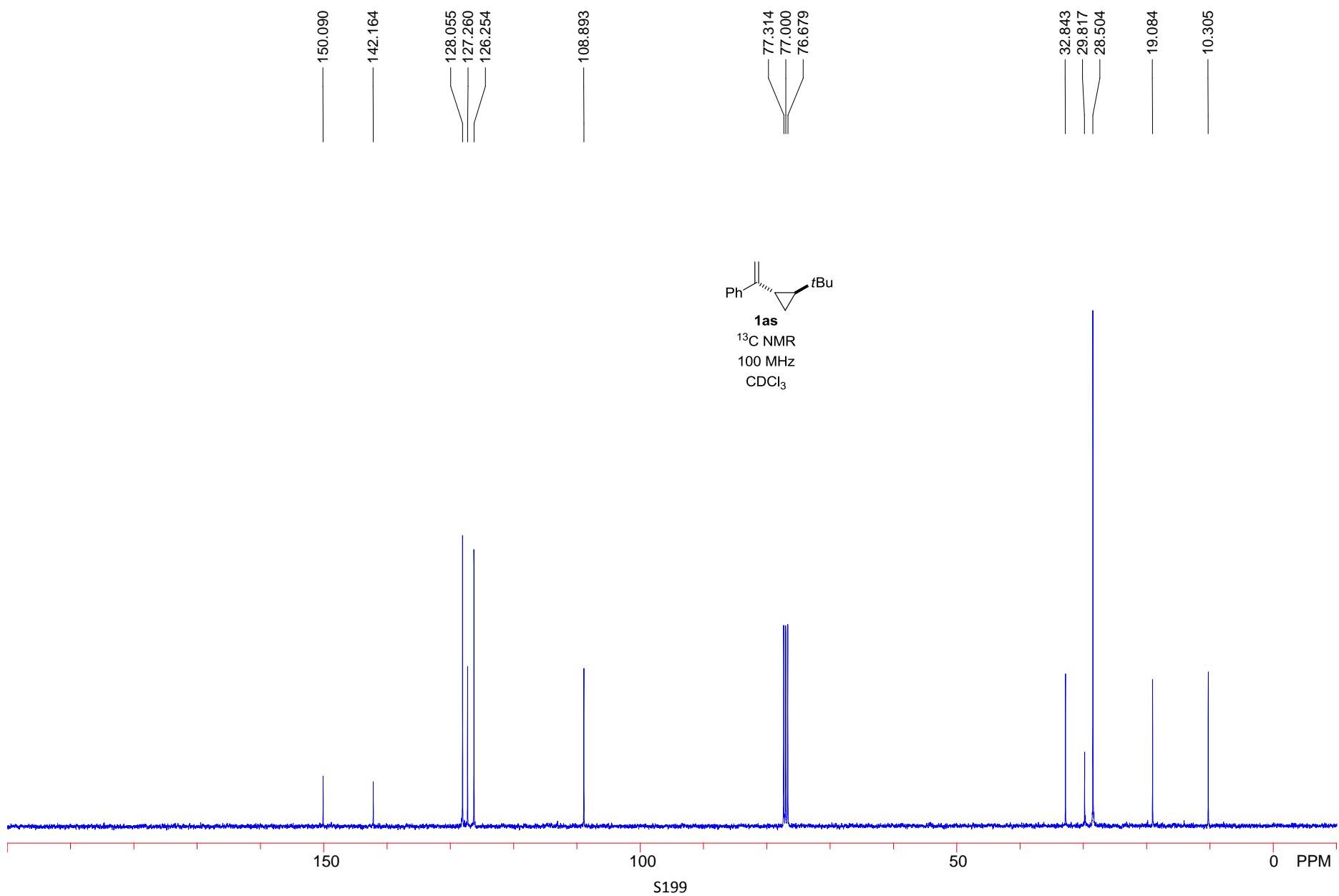


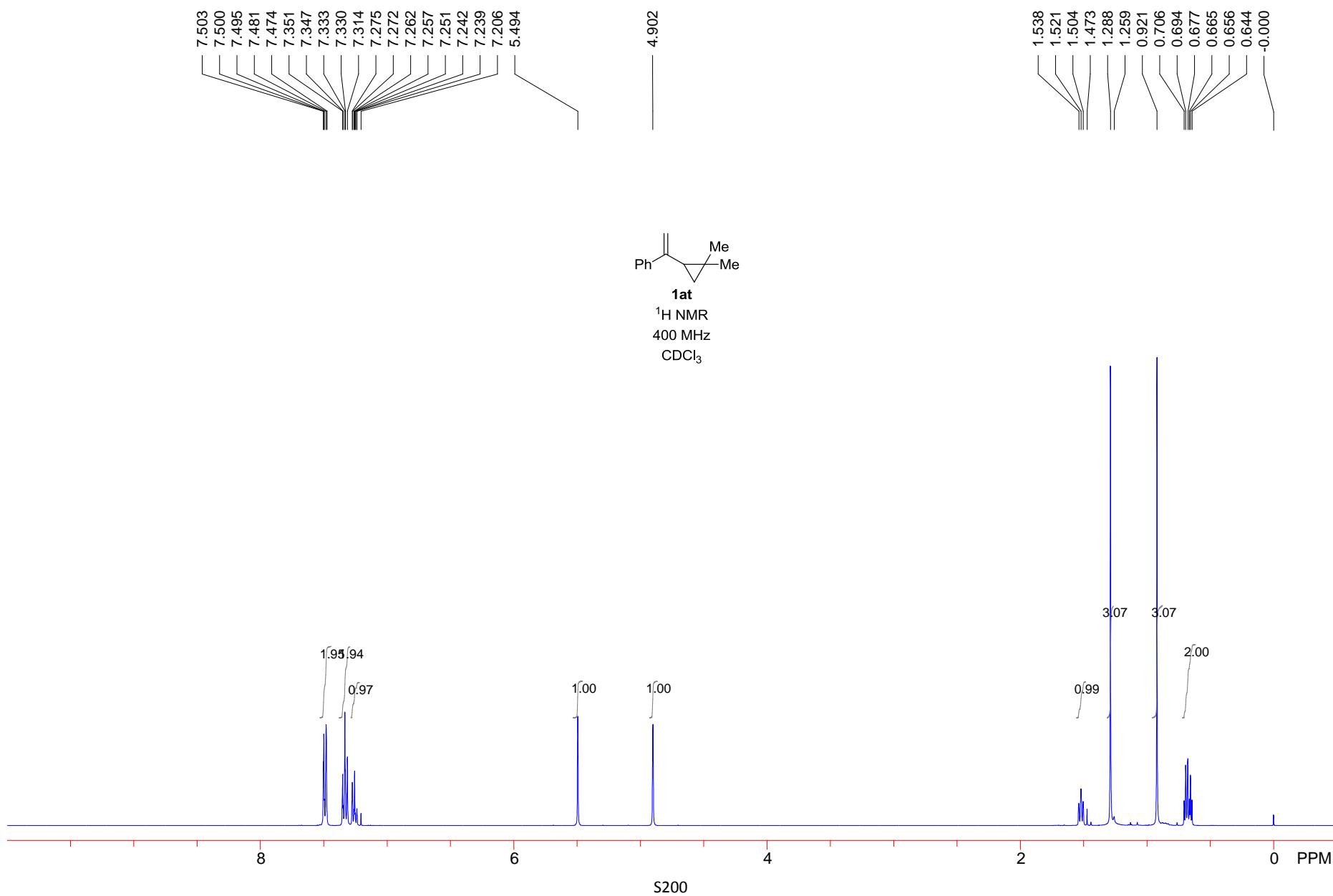


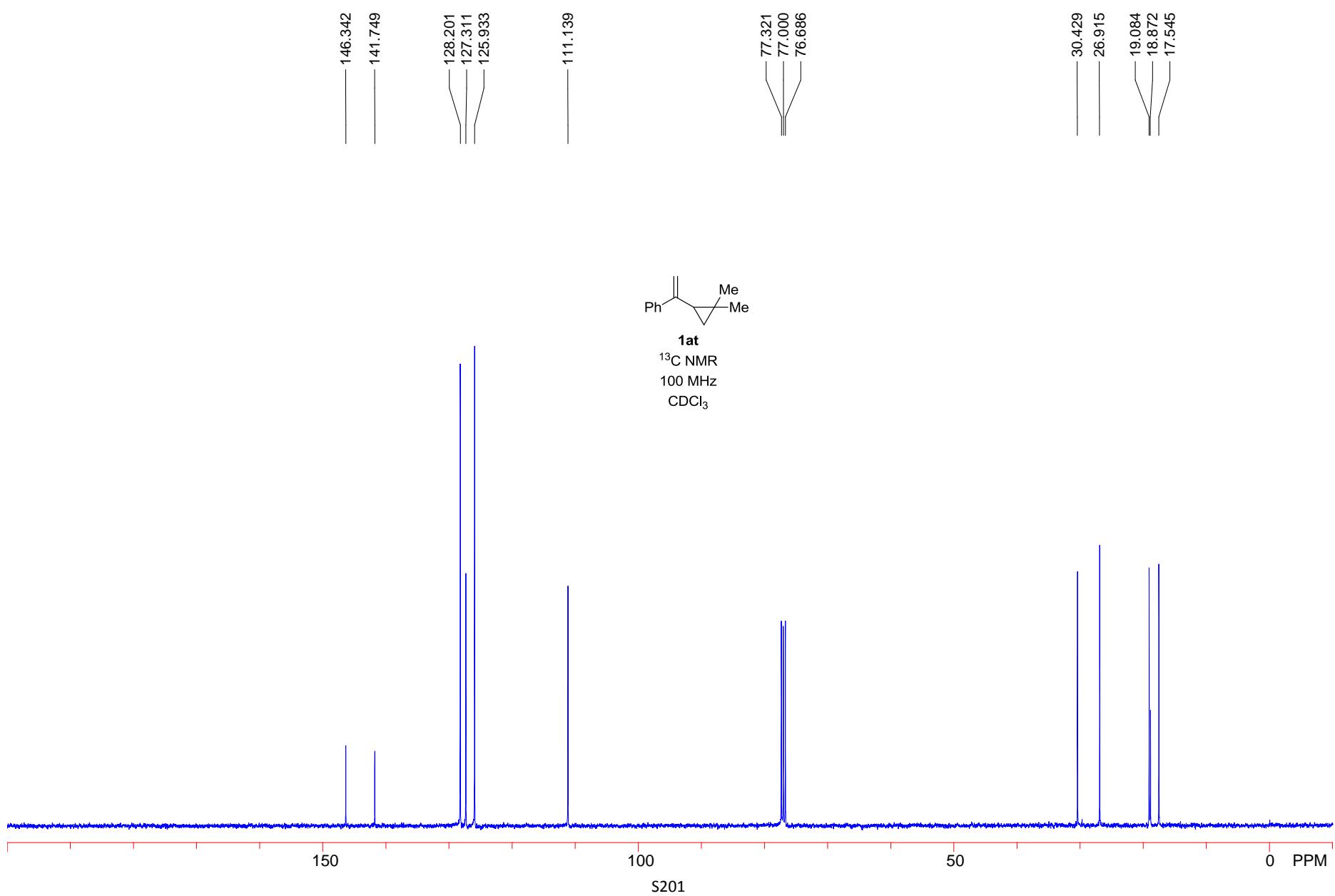


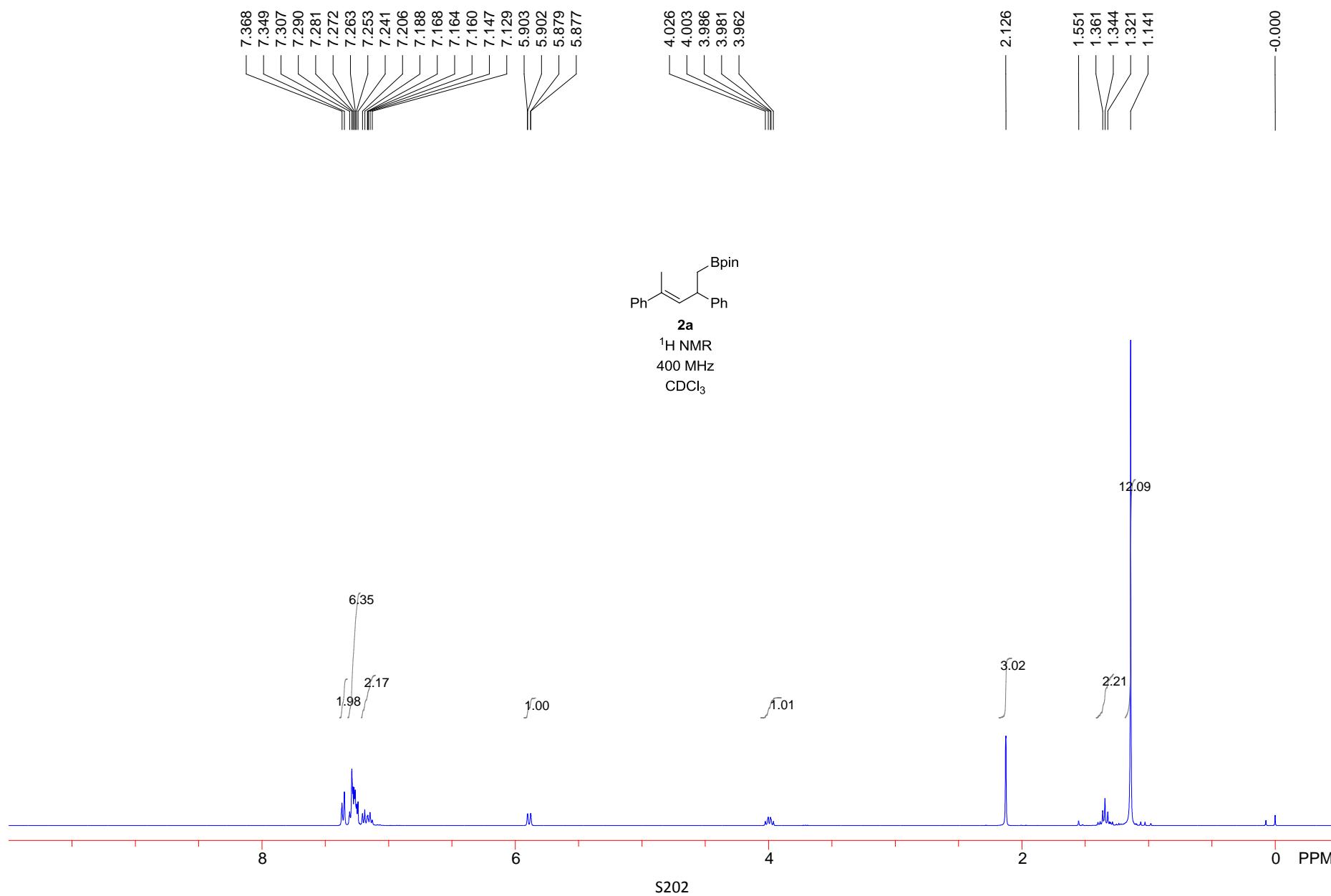


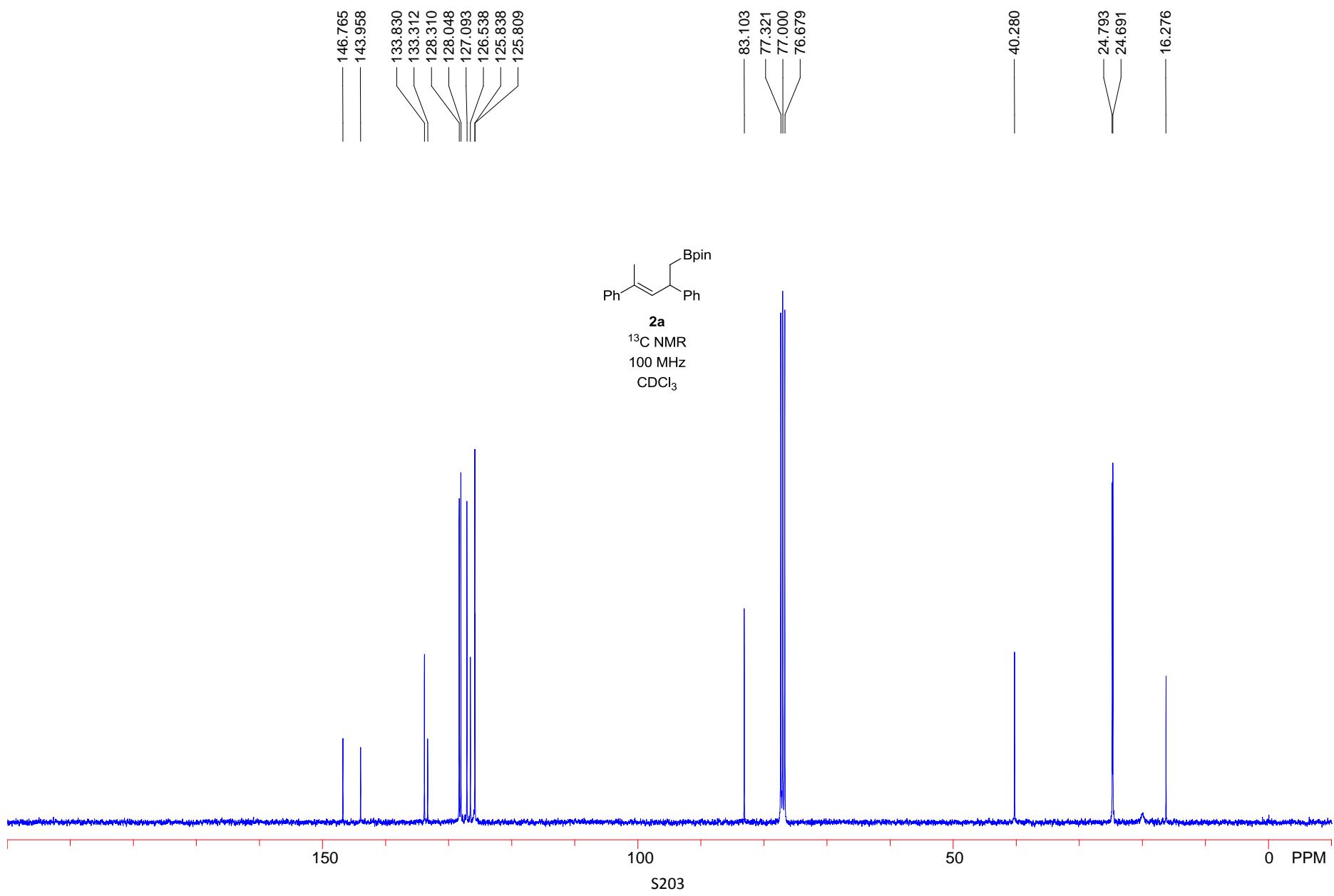


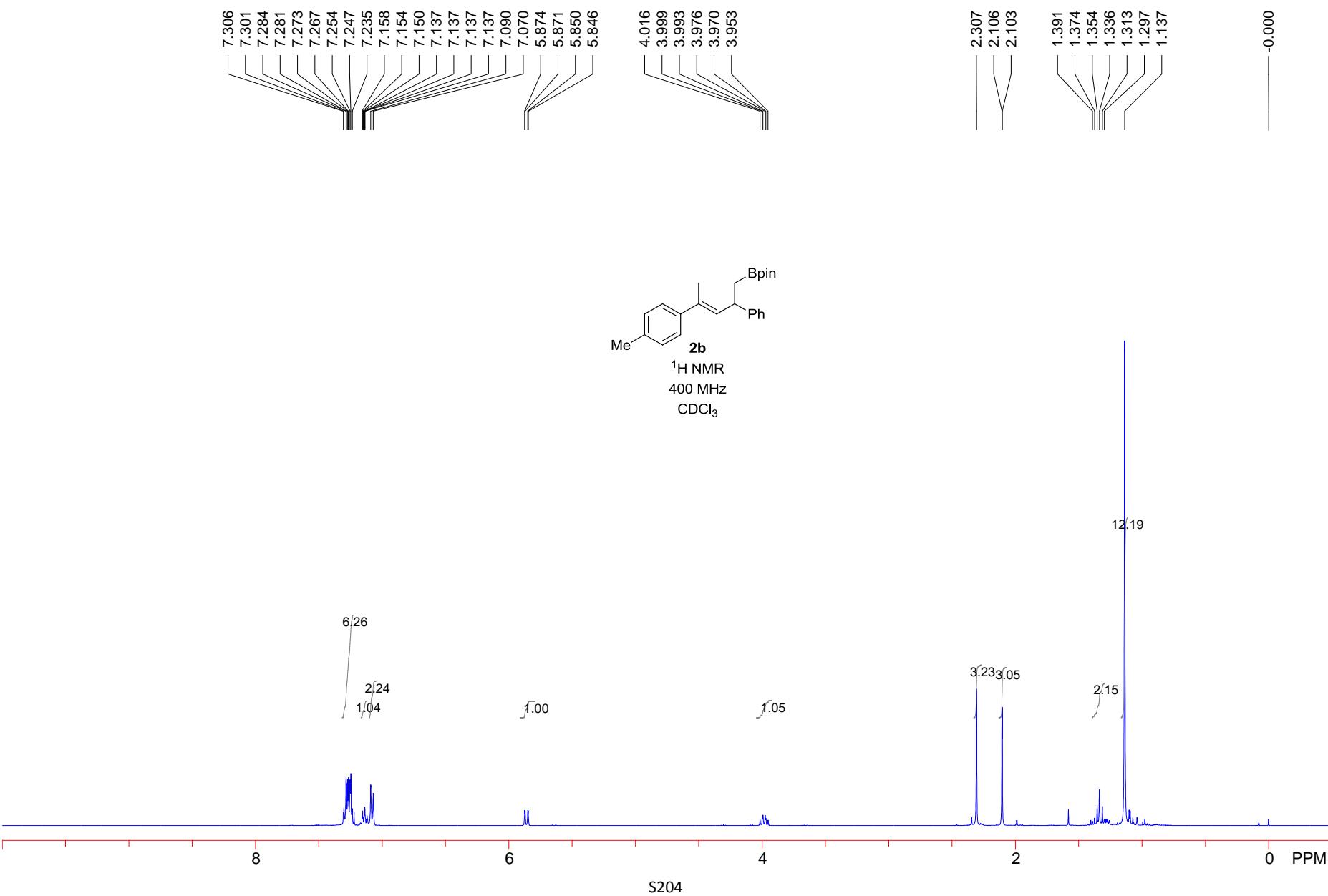


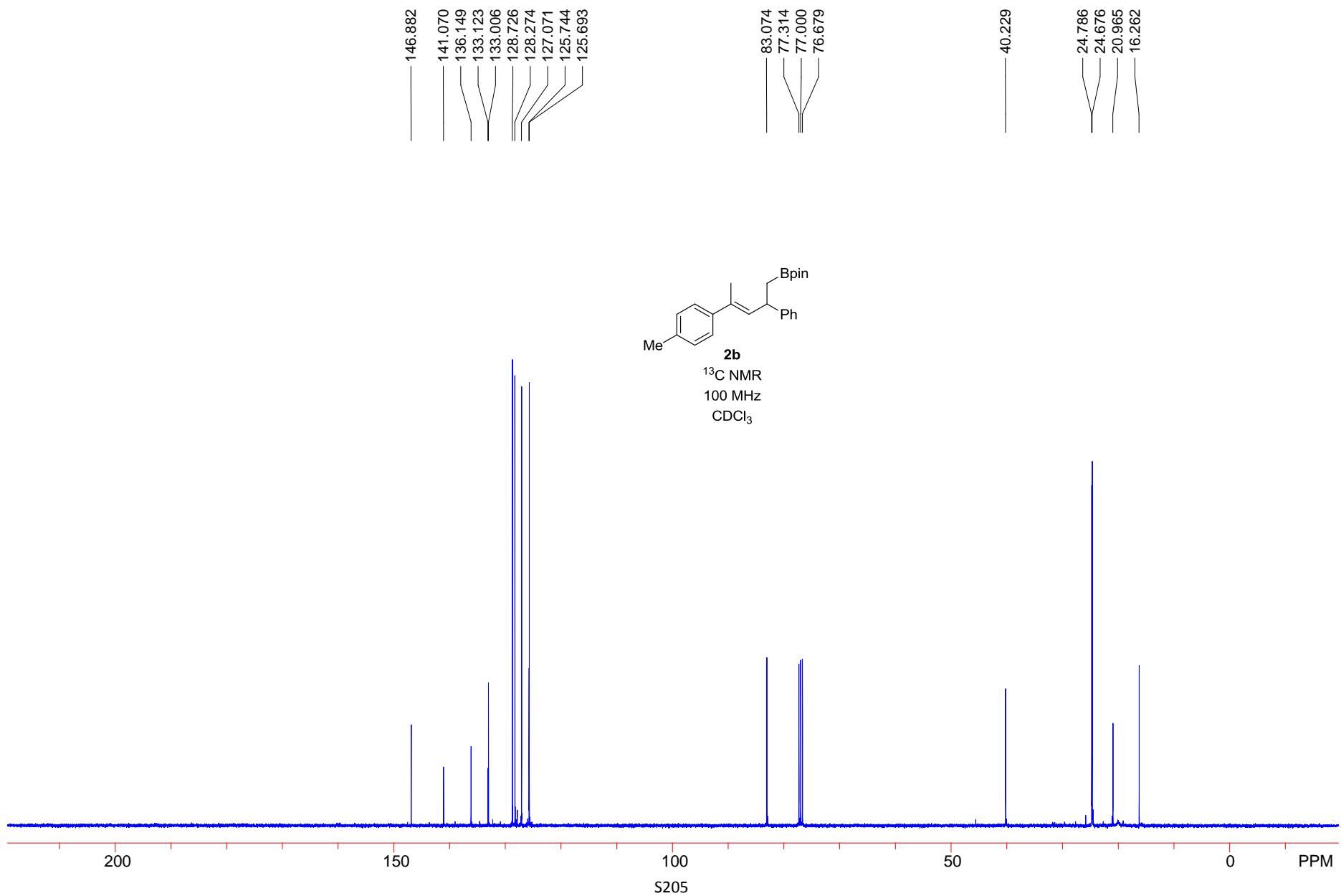


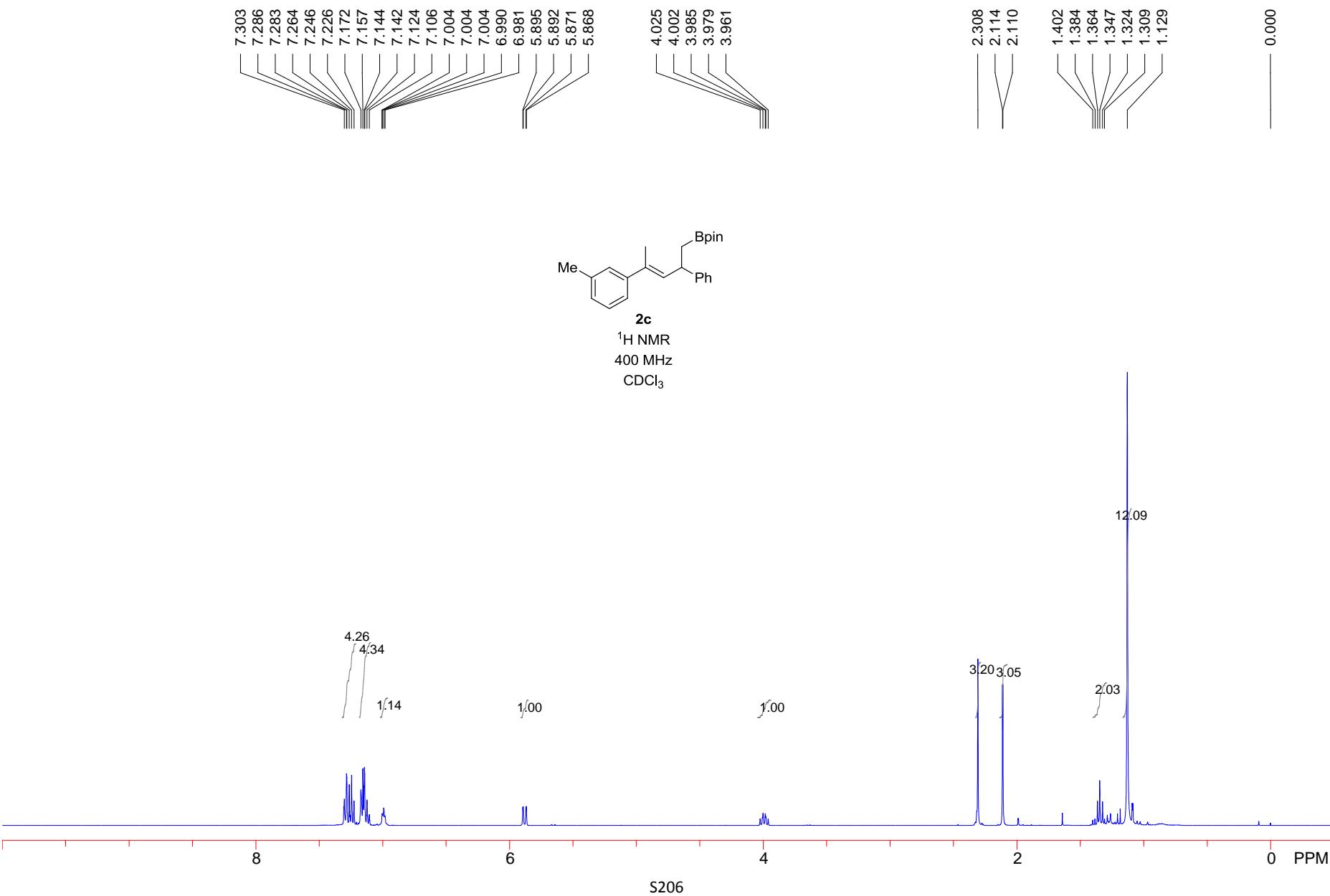


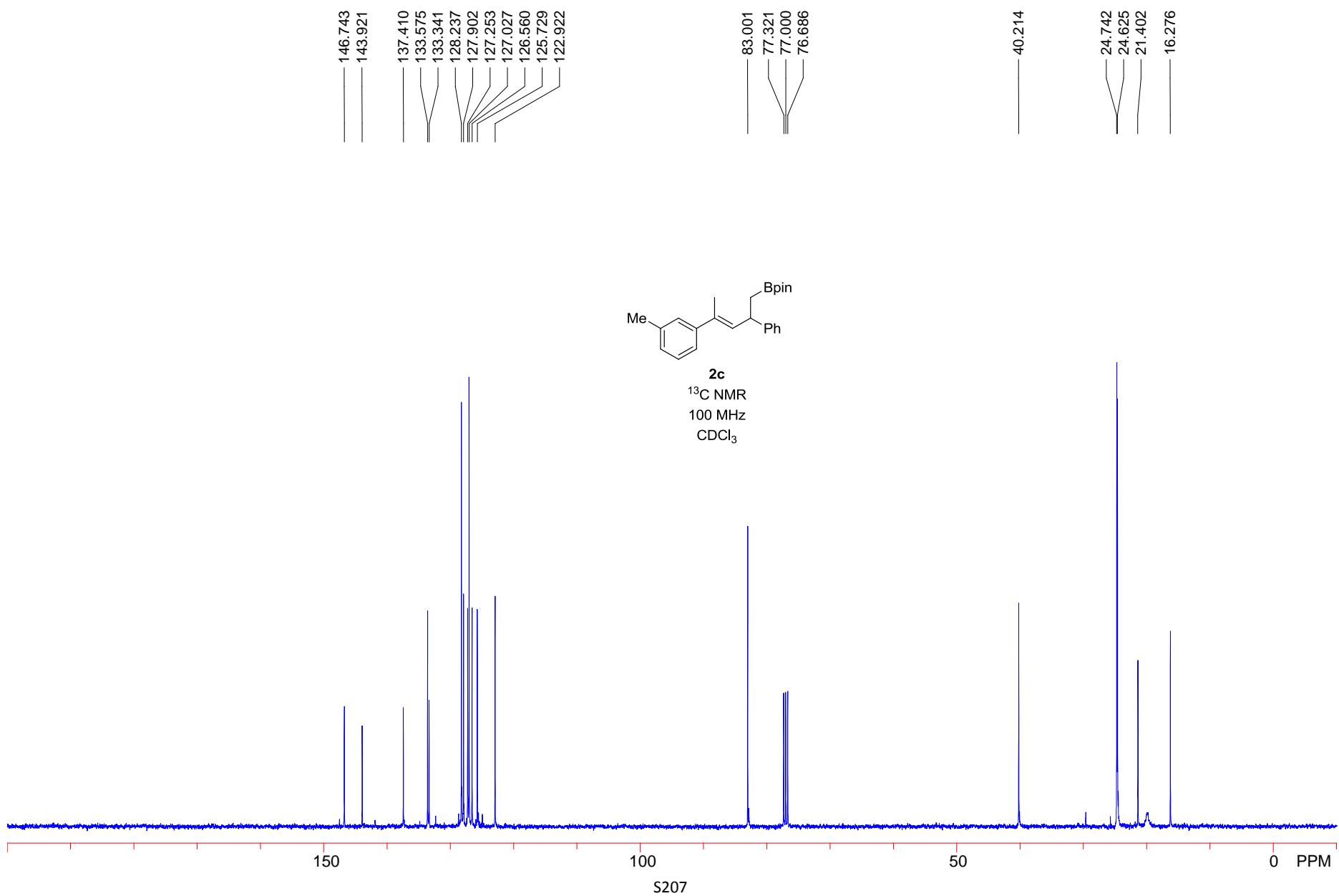


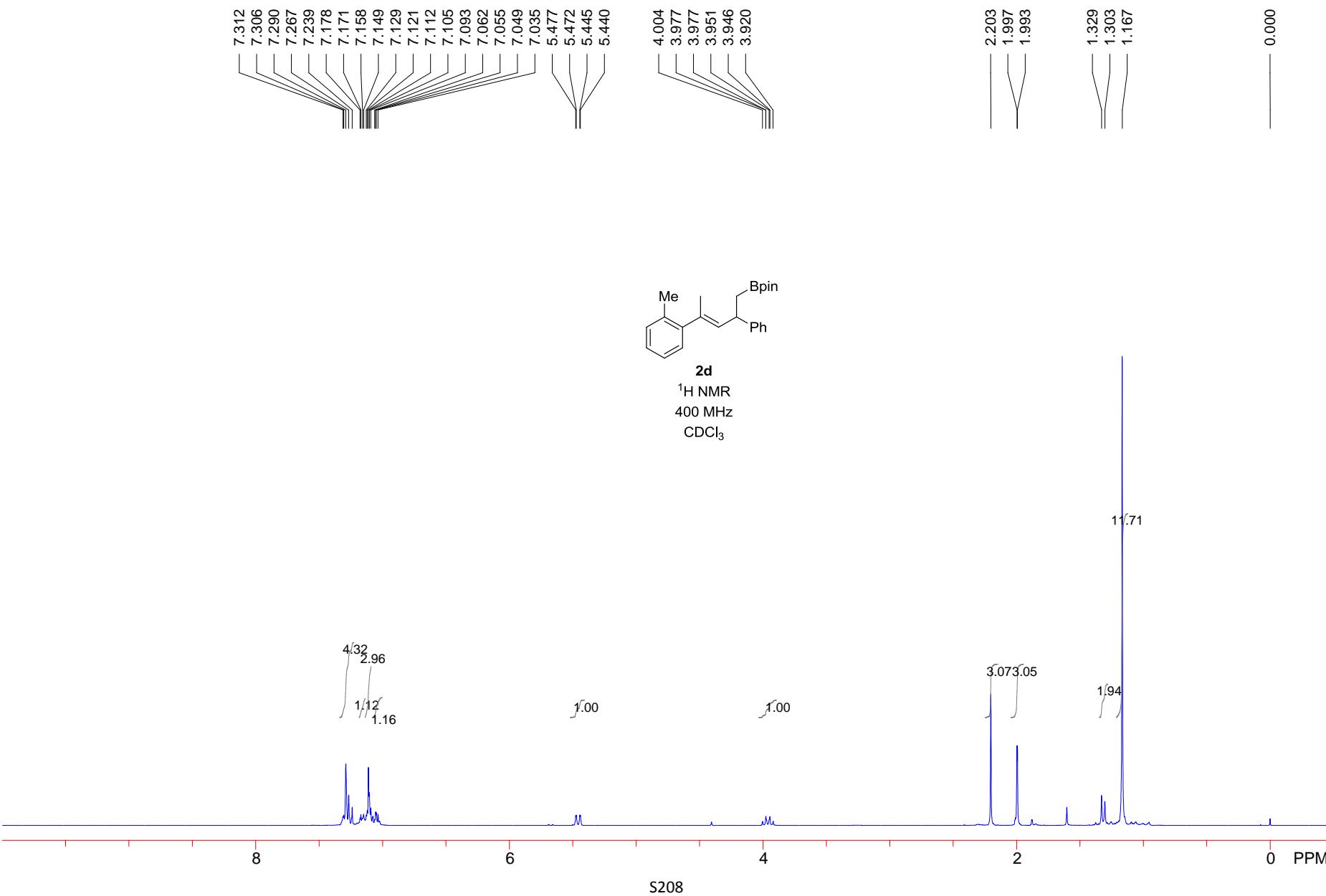




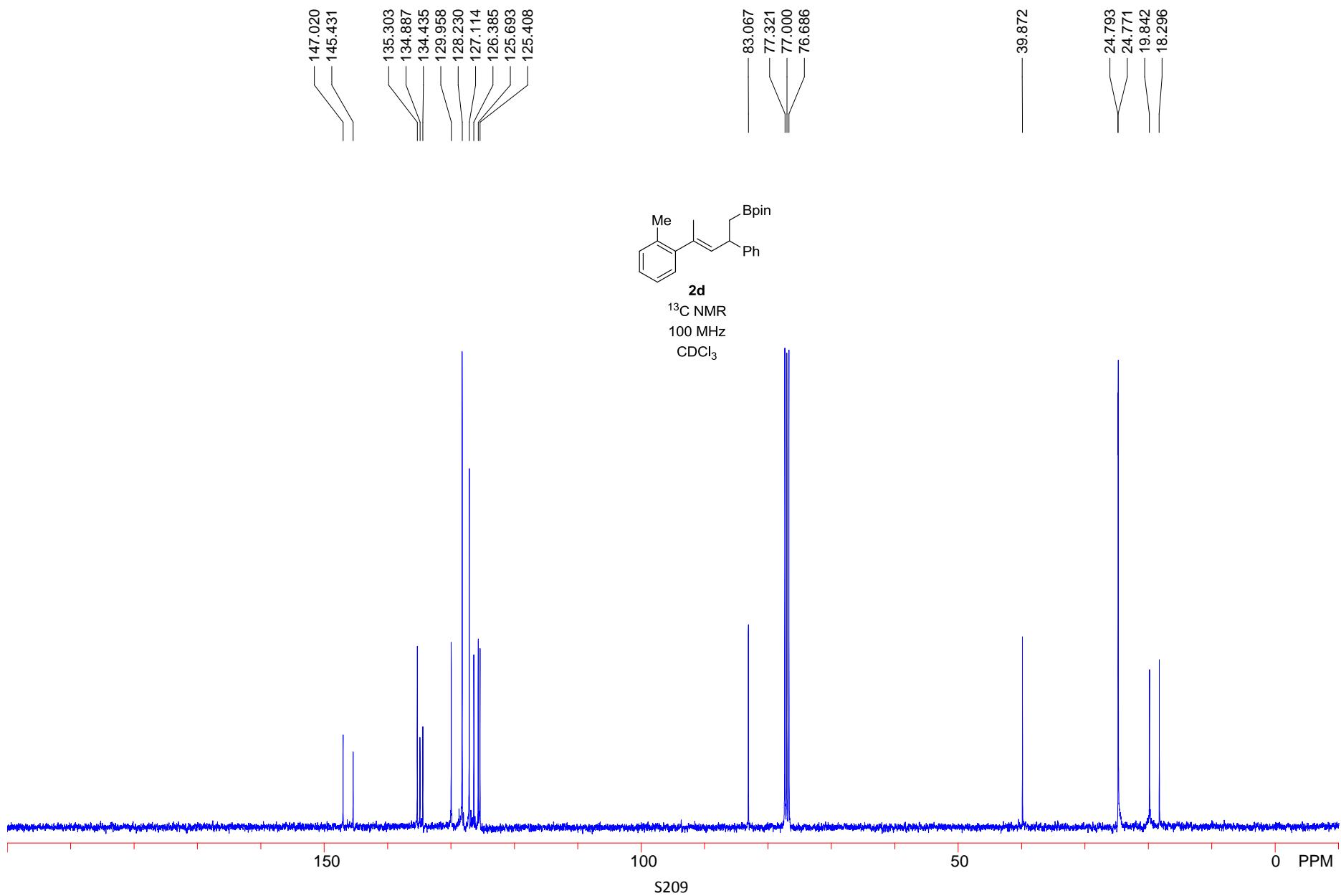


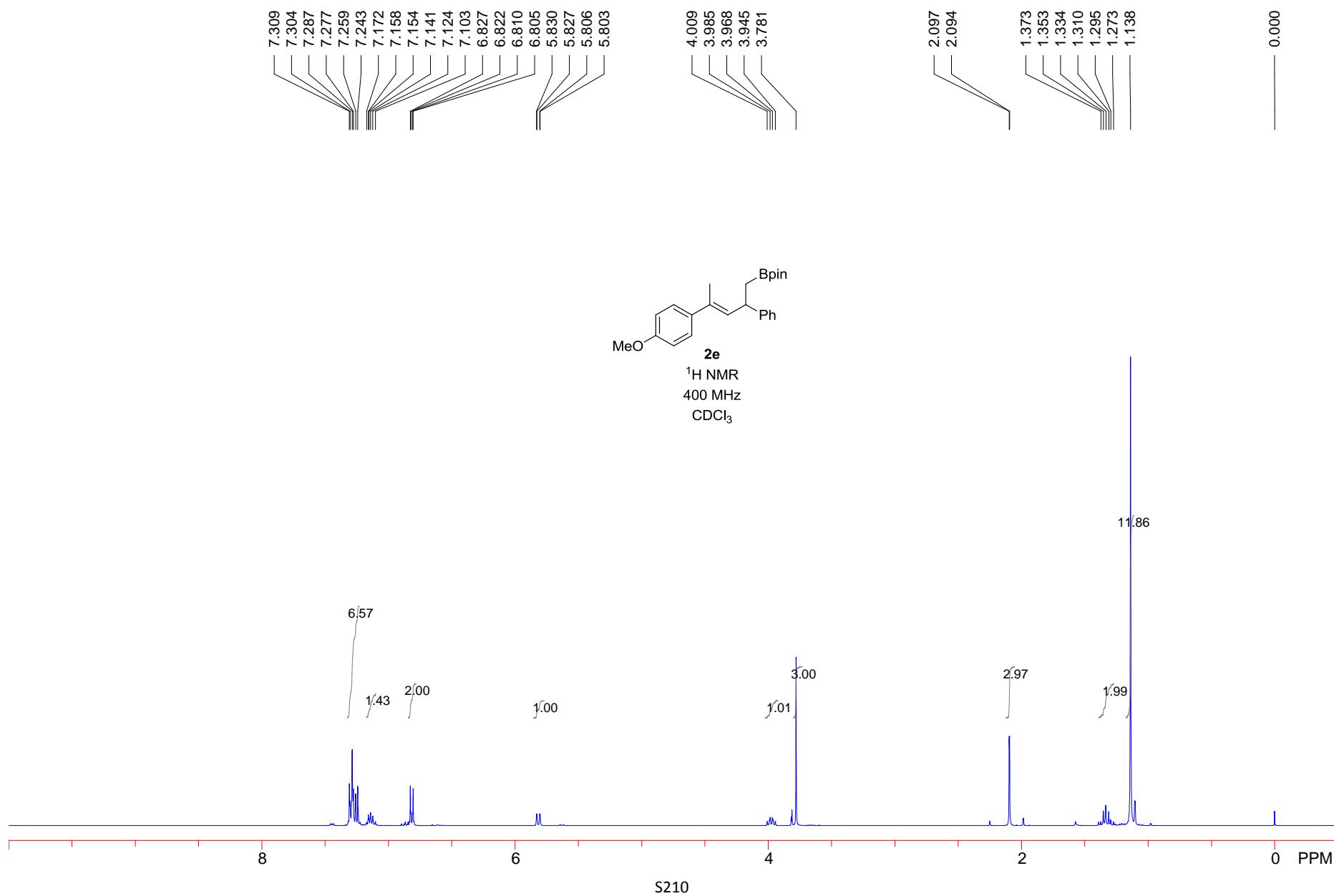


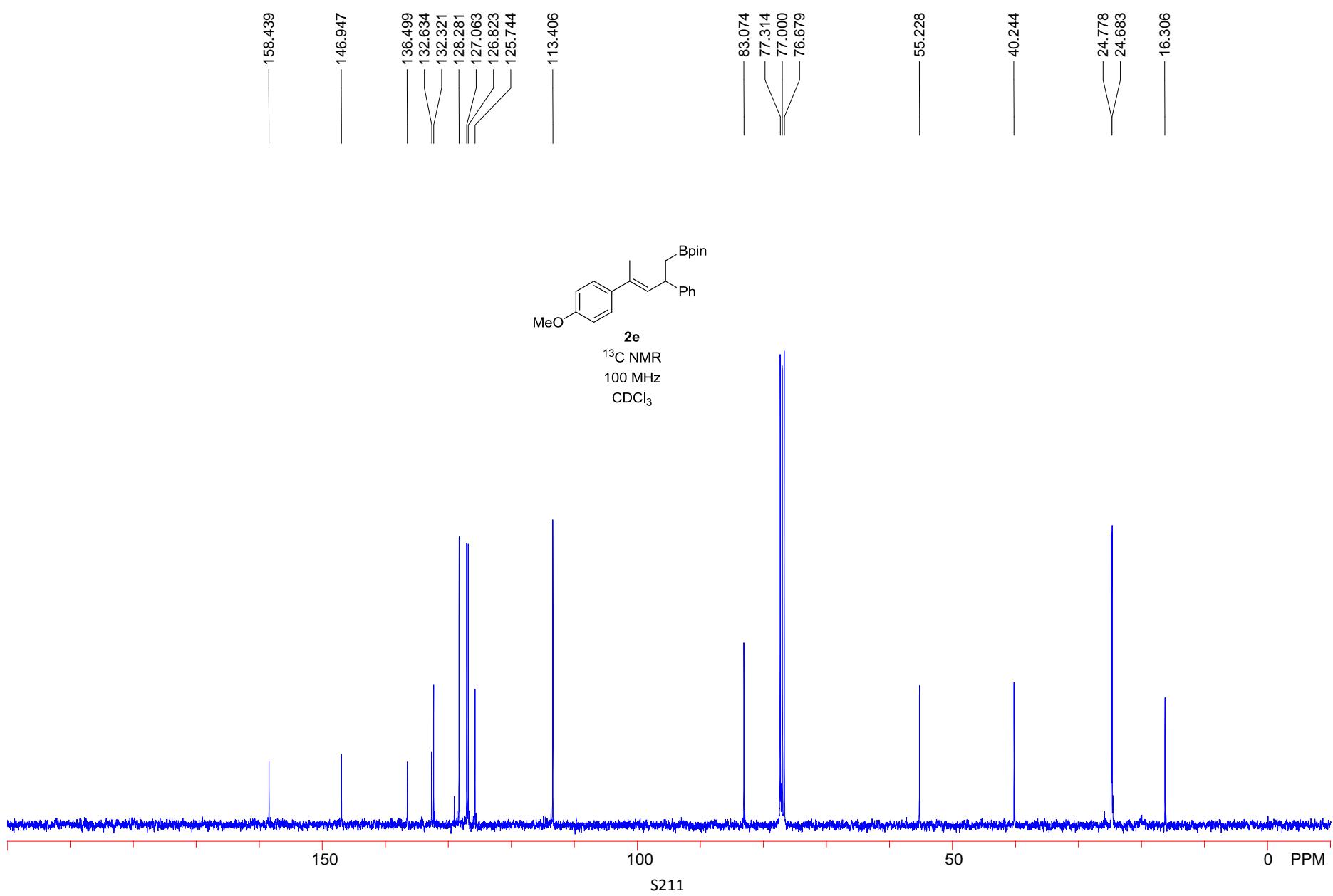


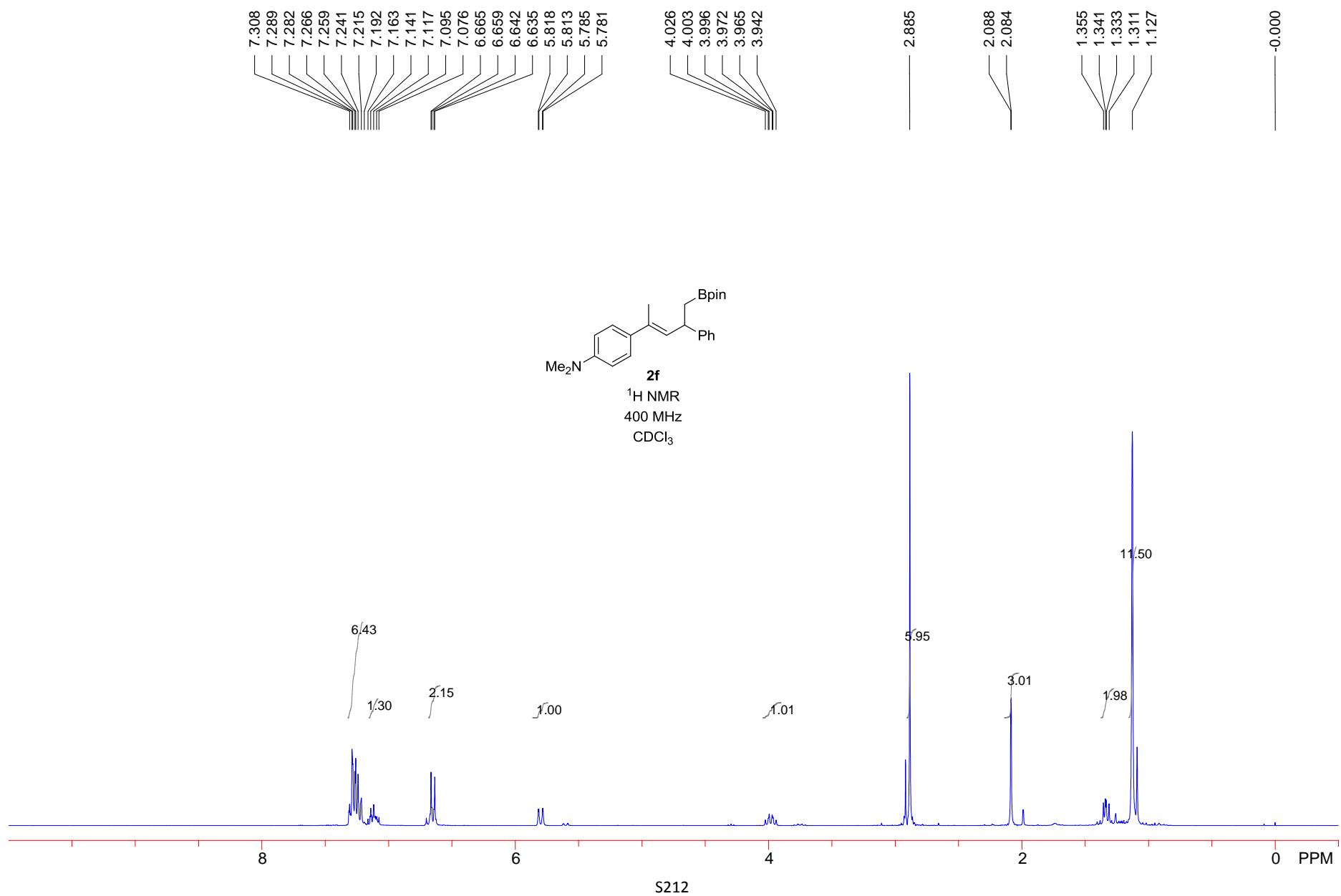


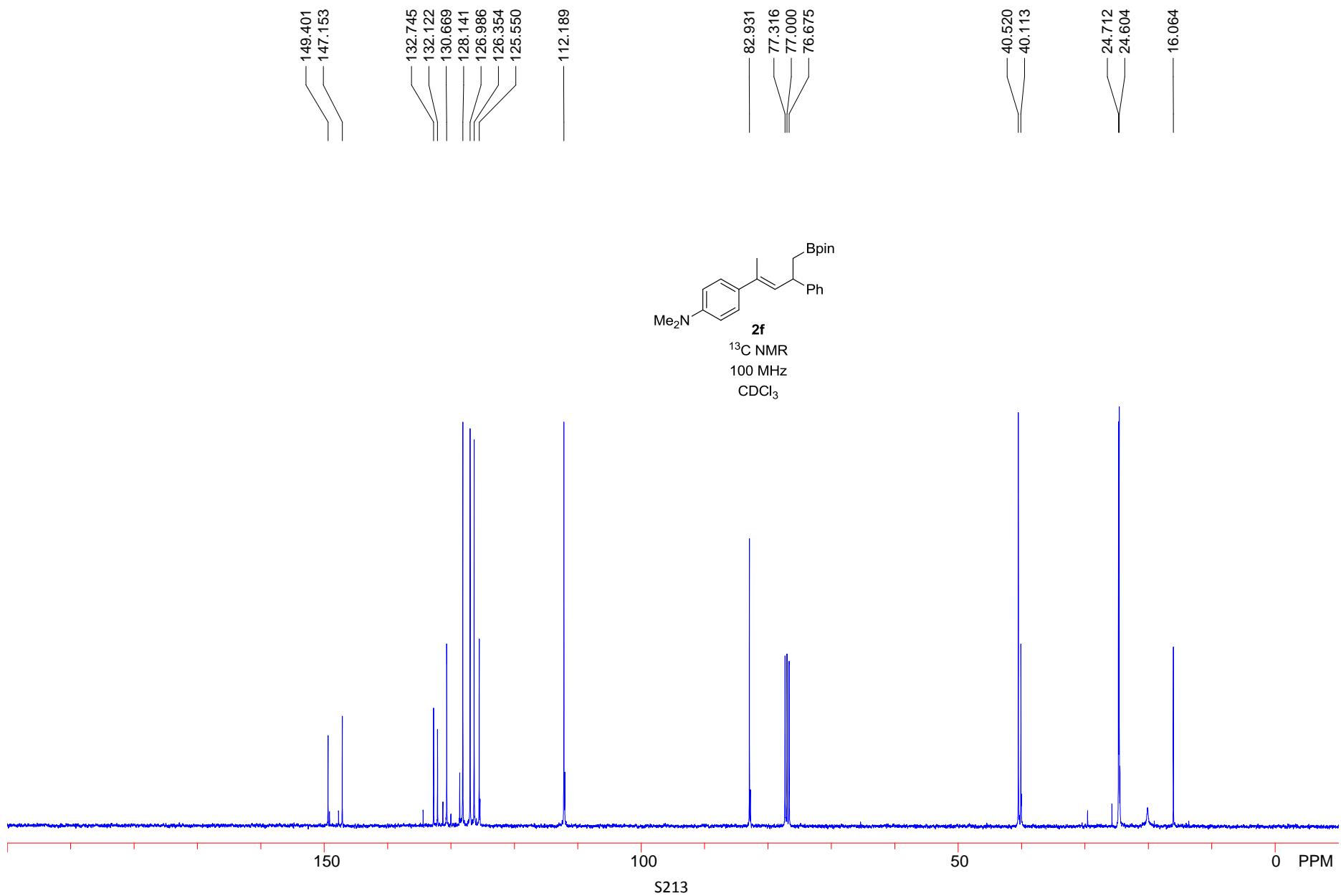
S208

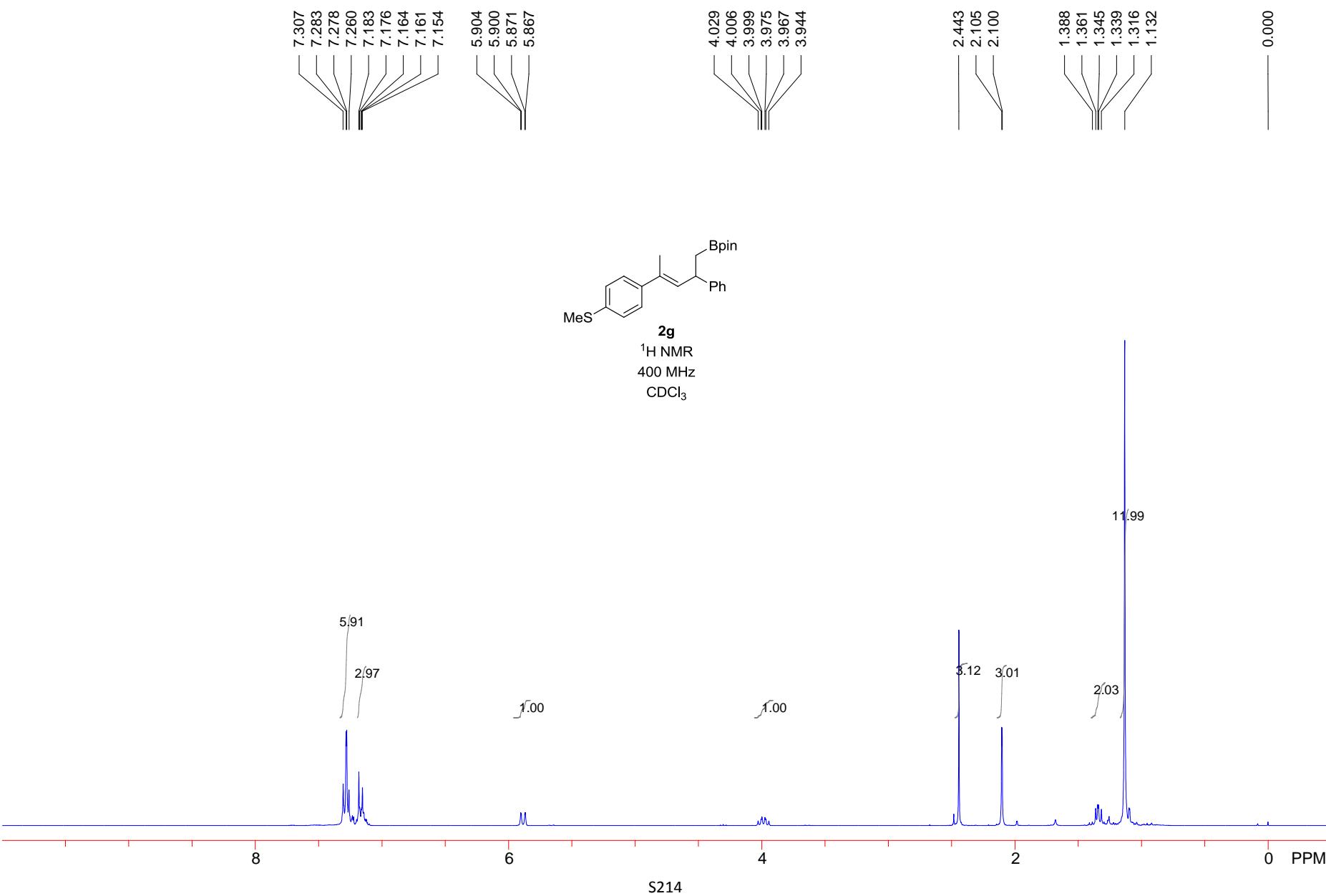




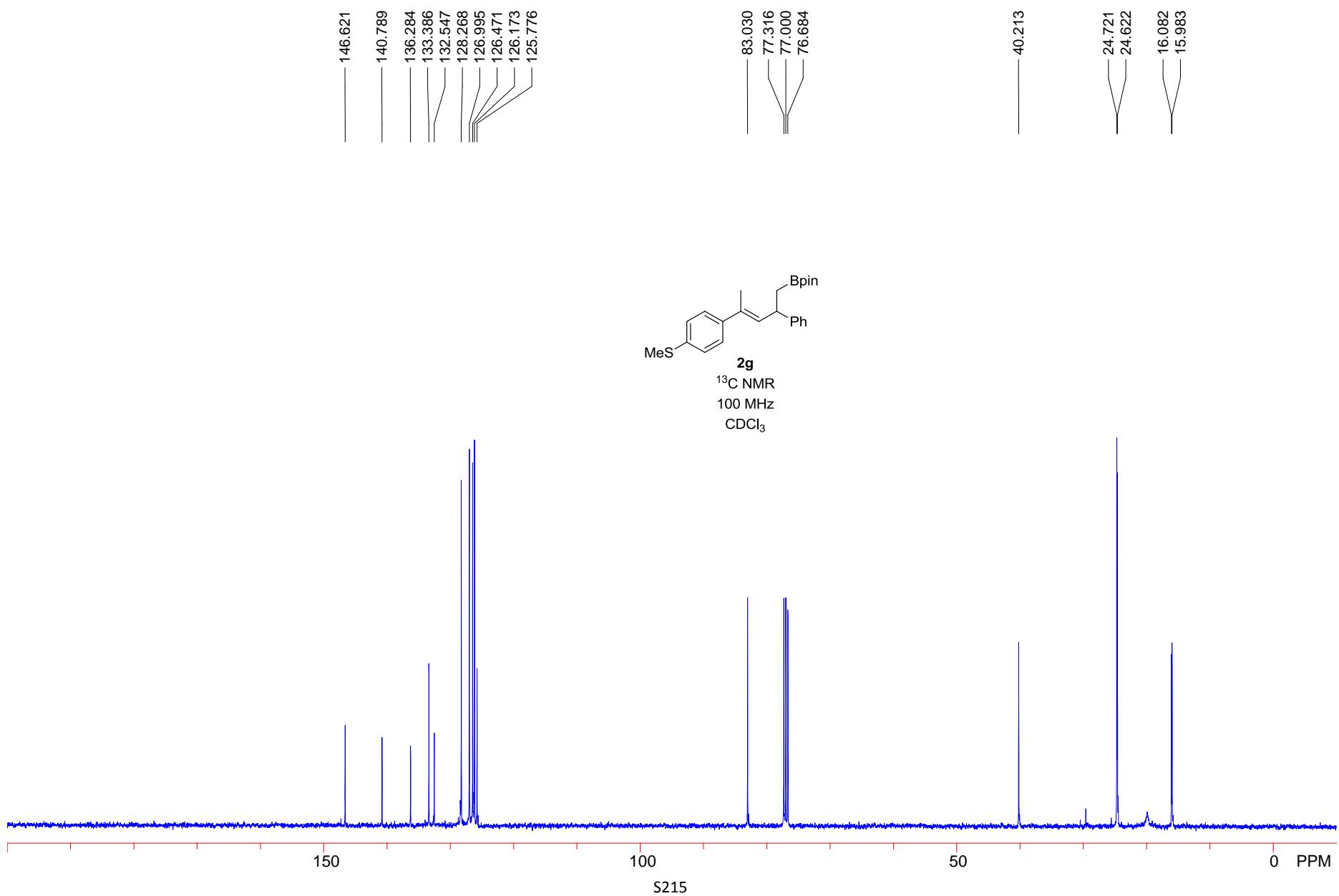


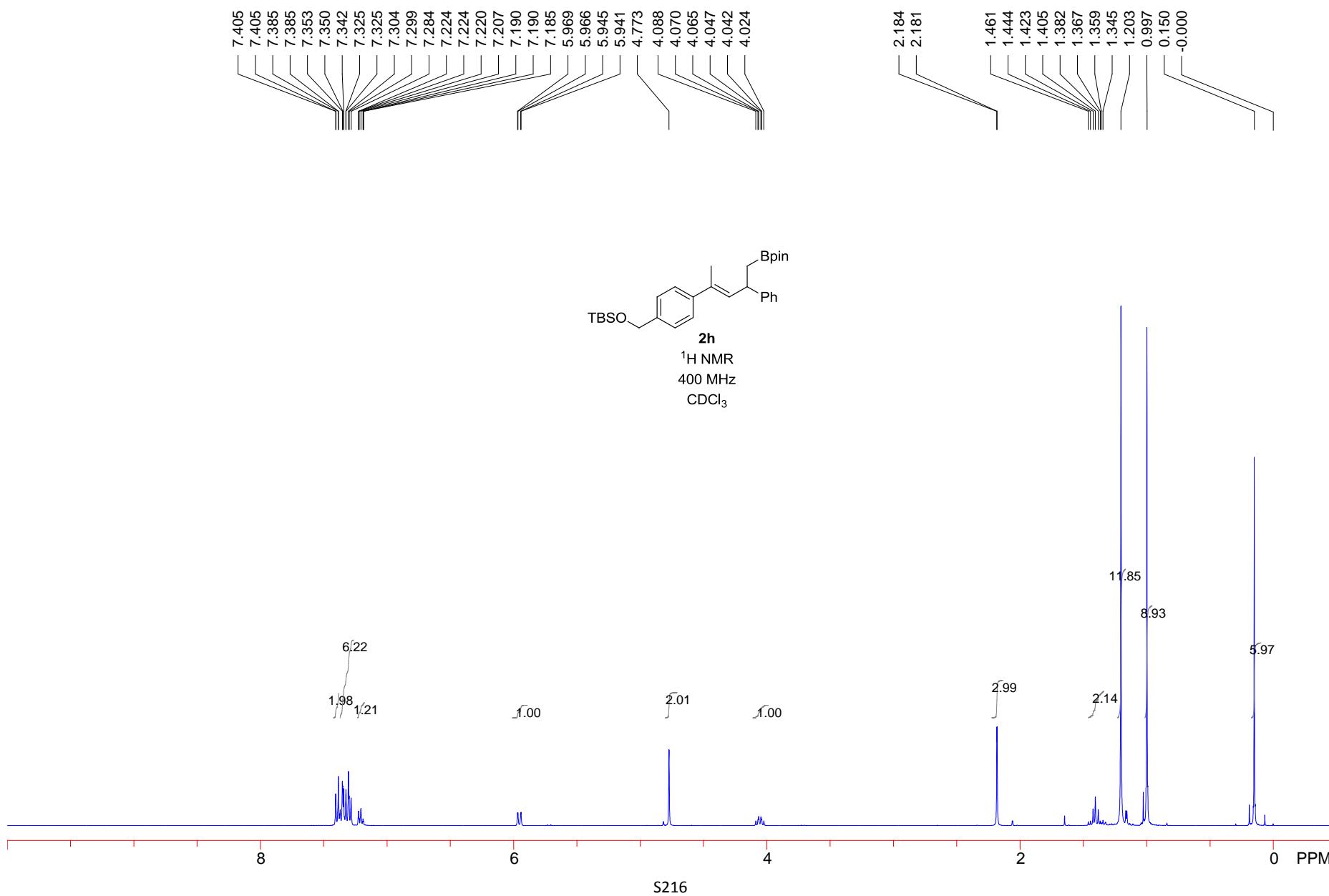


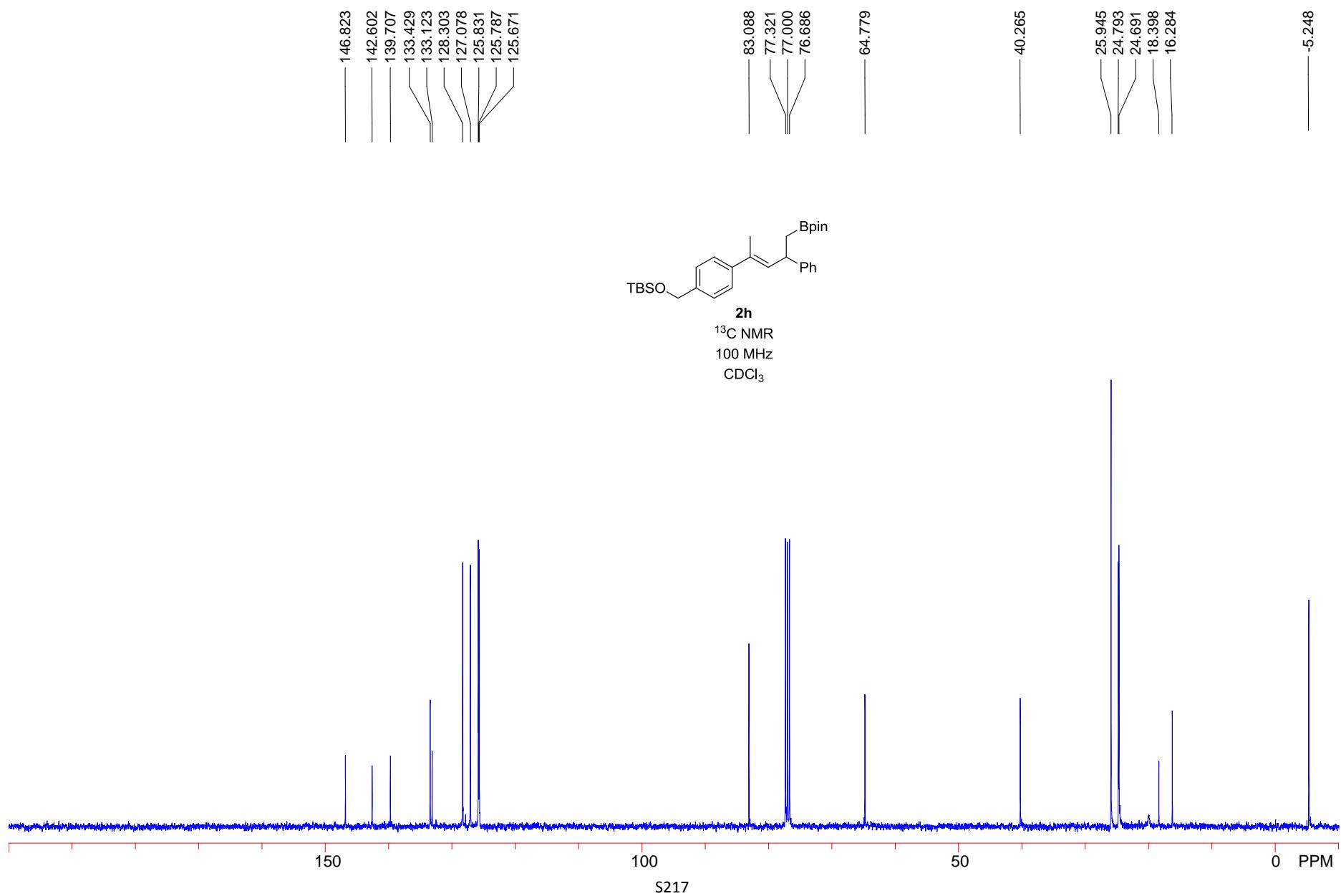


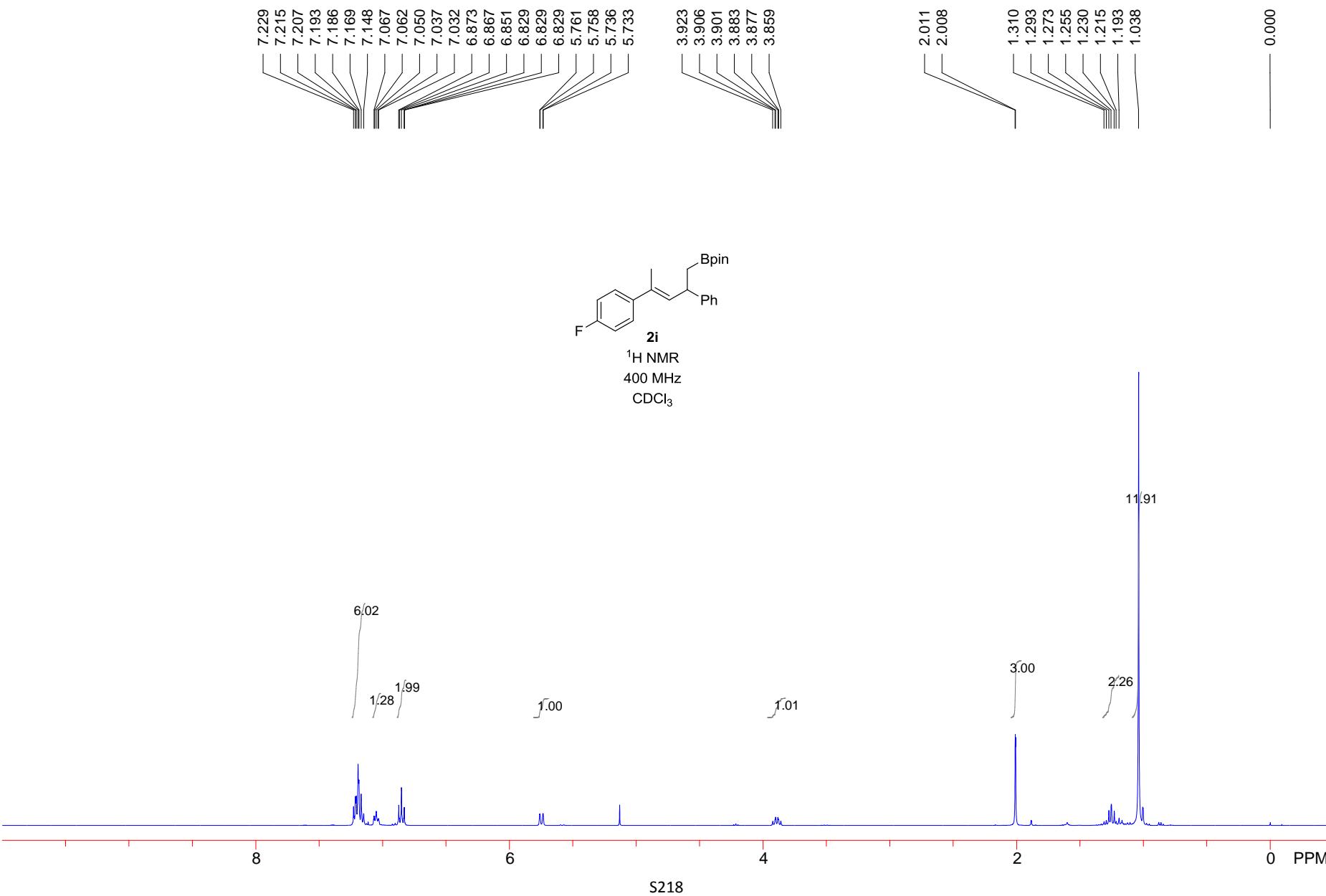


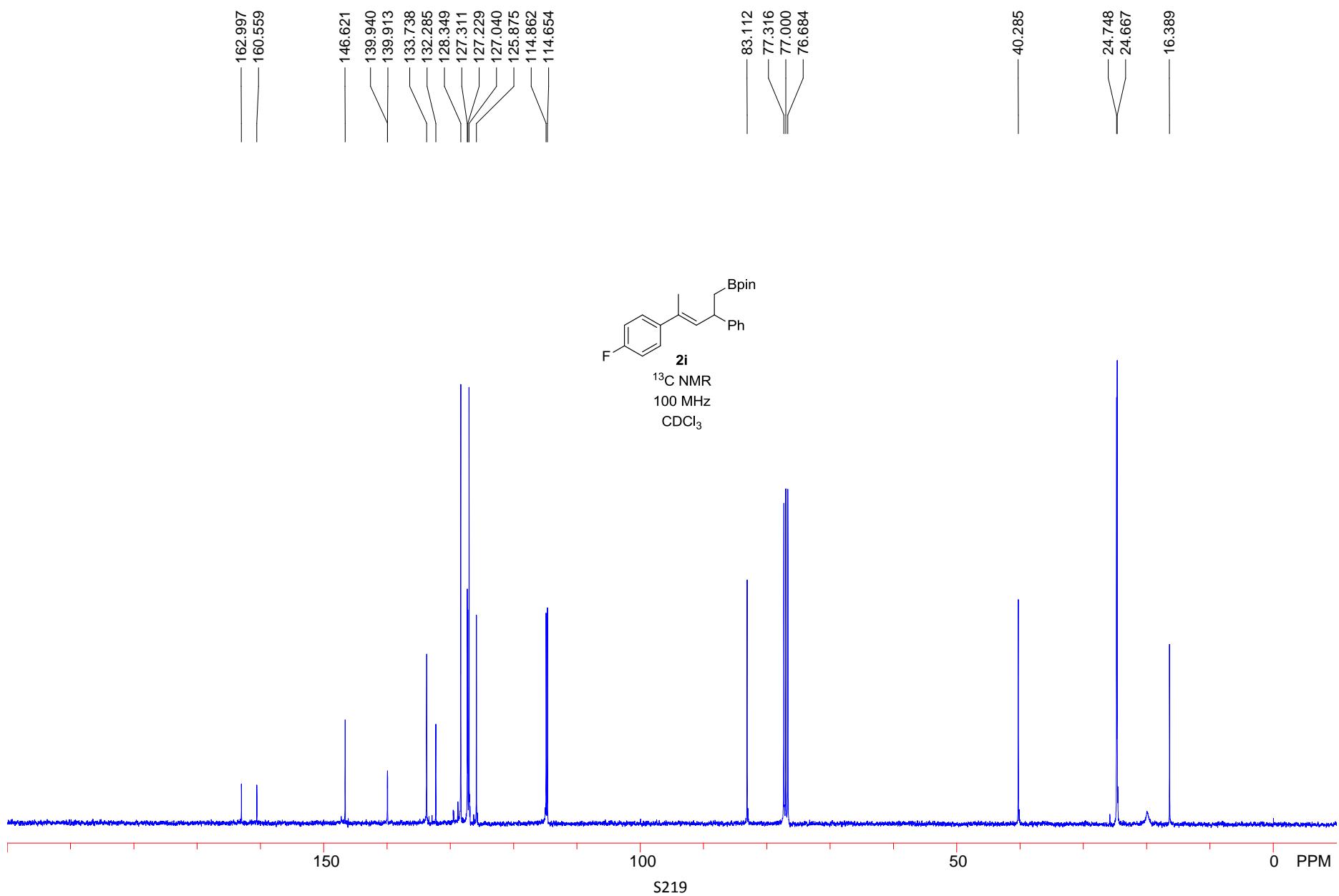
S214

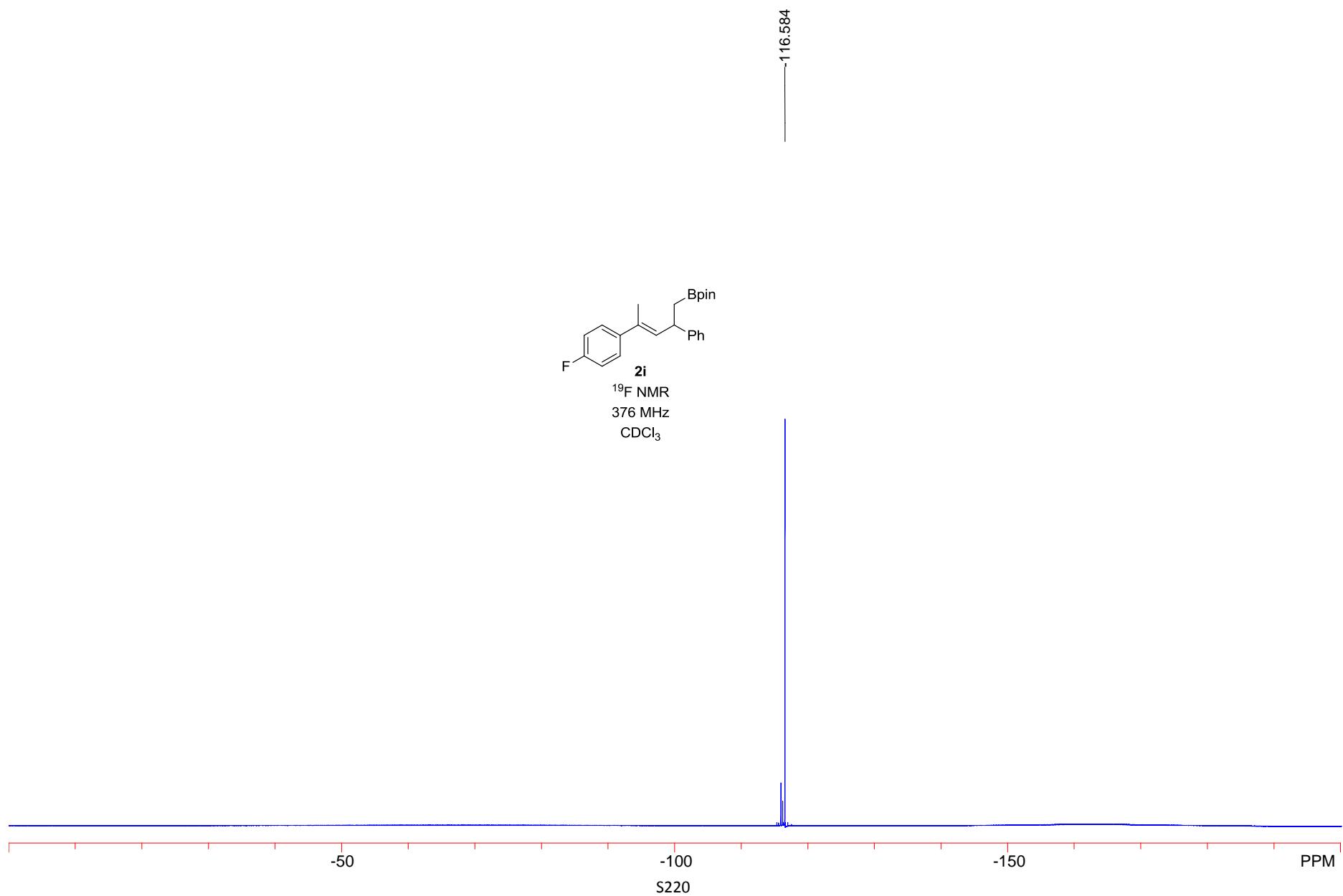


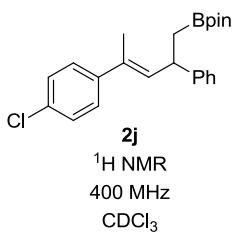
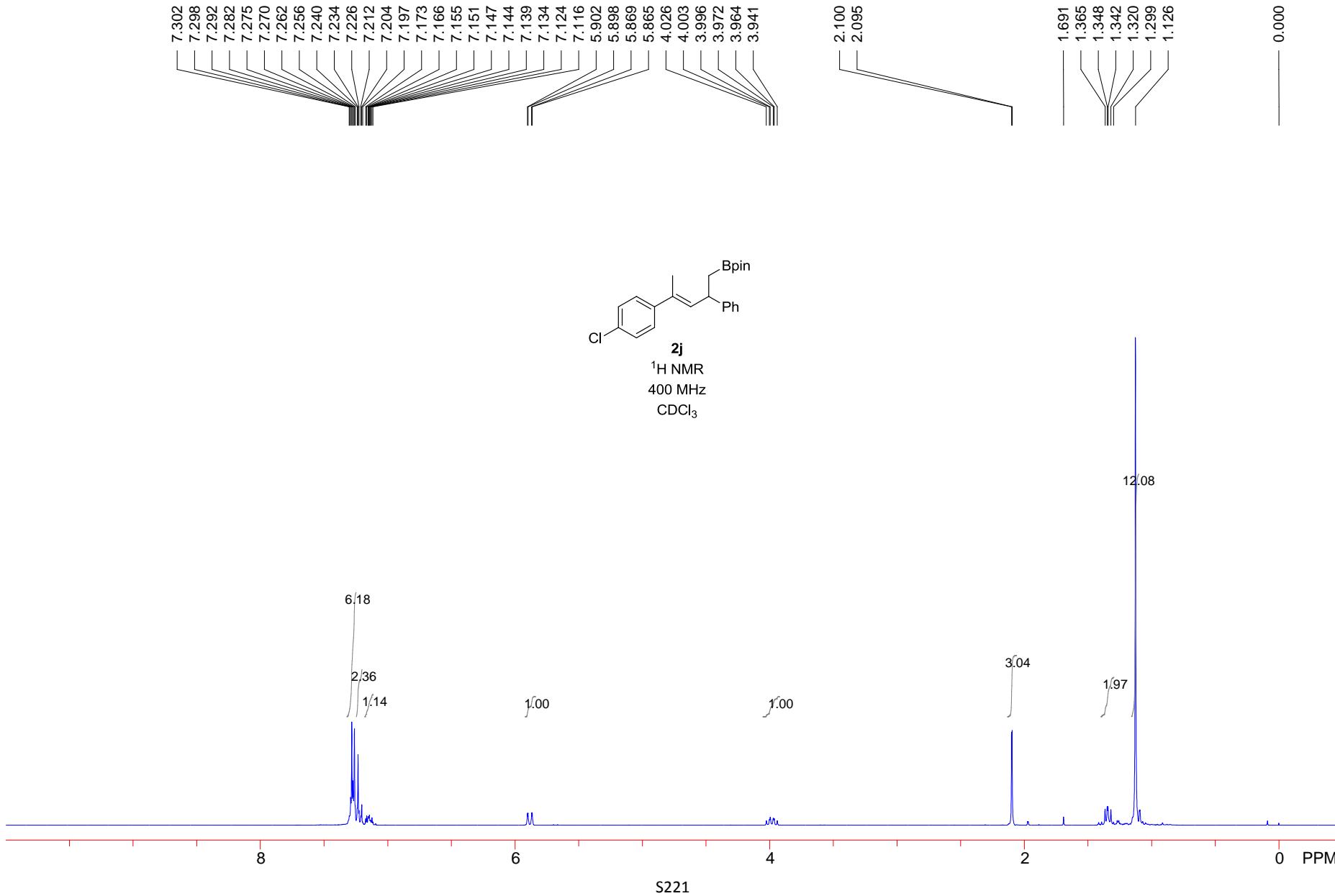


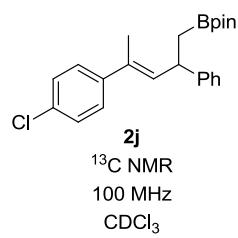
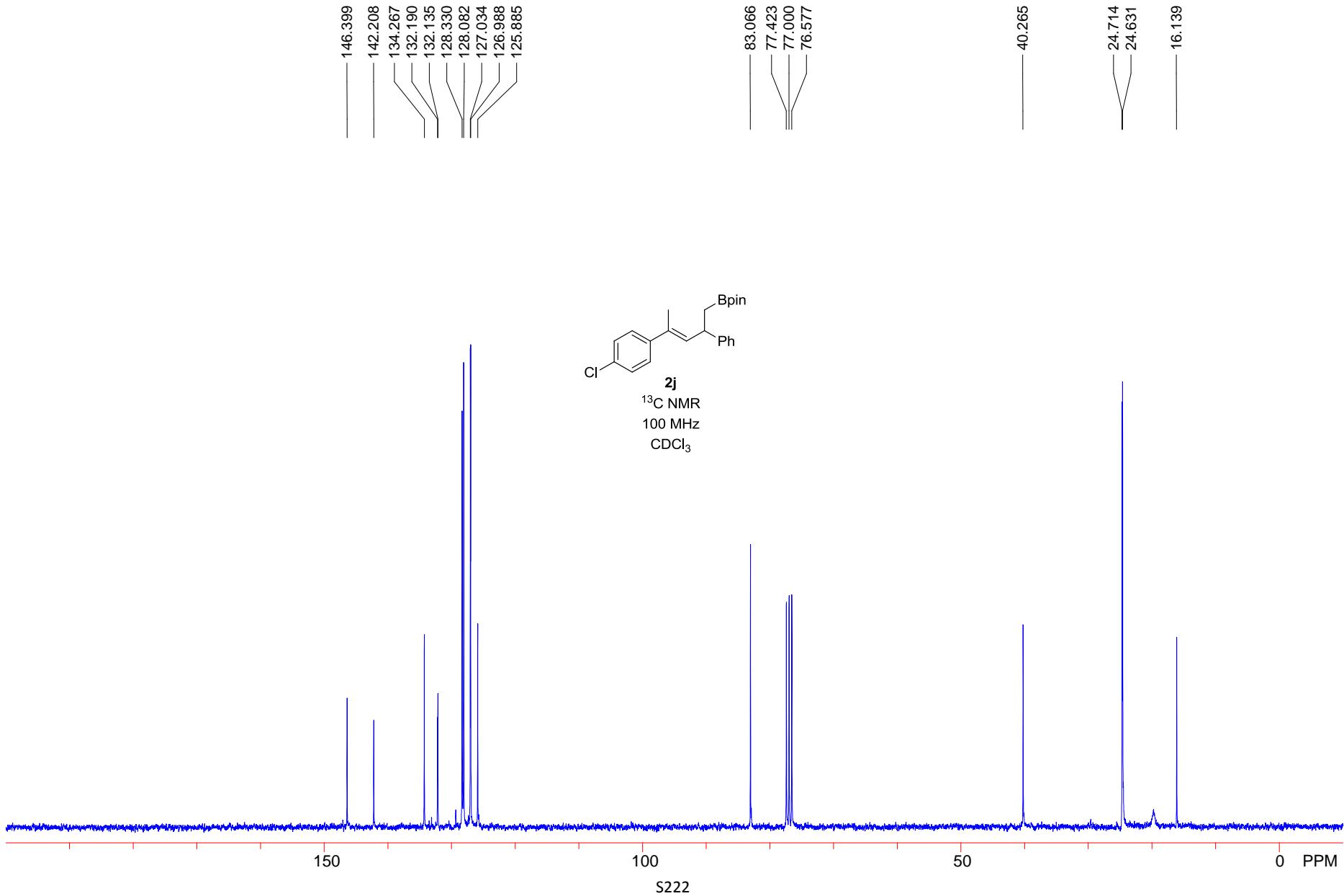


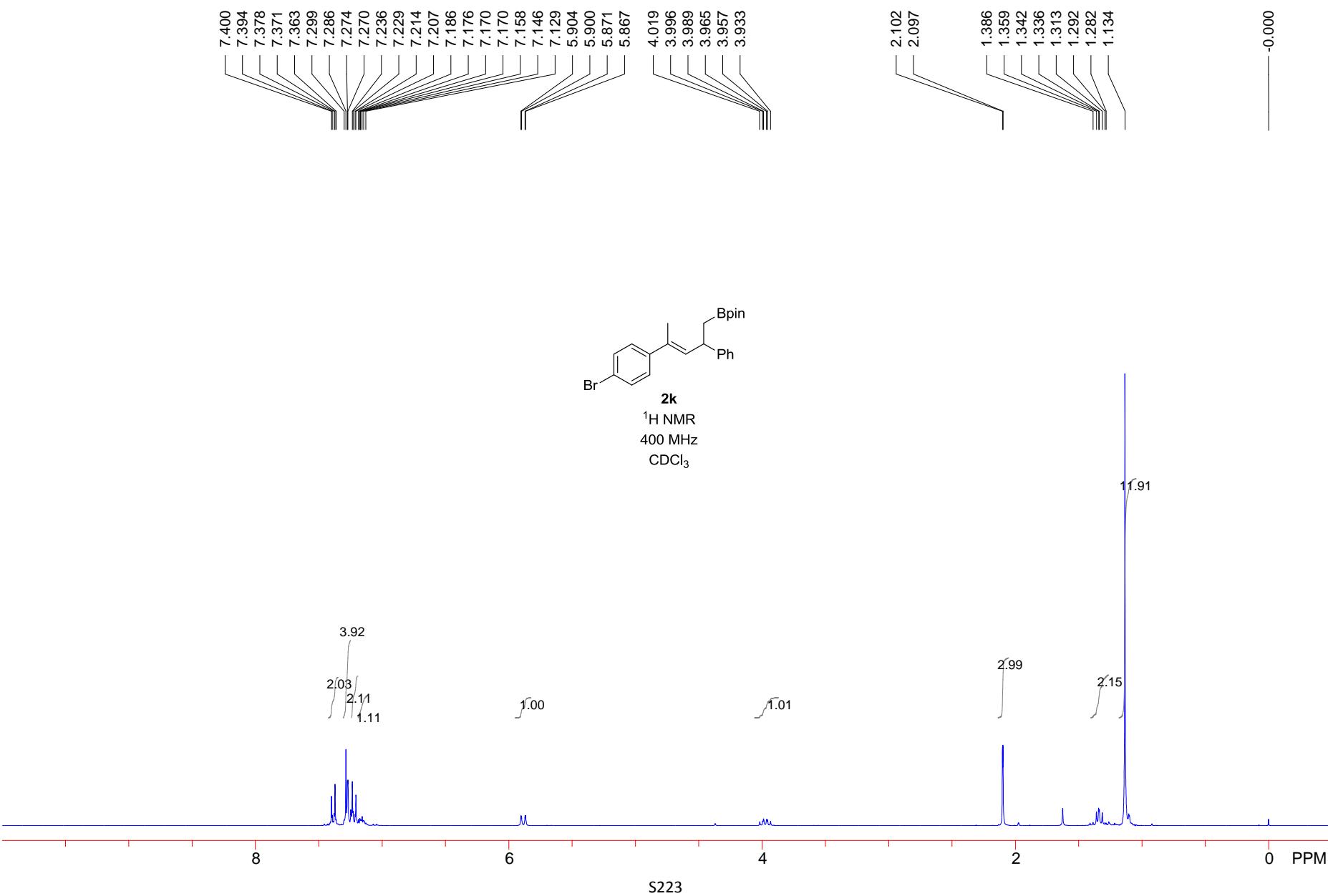


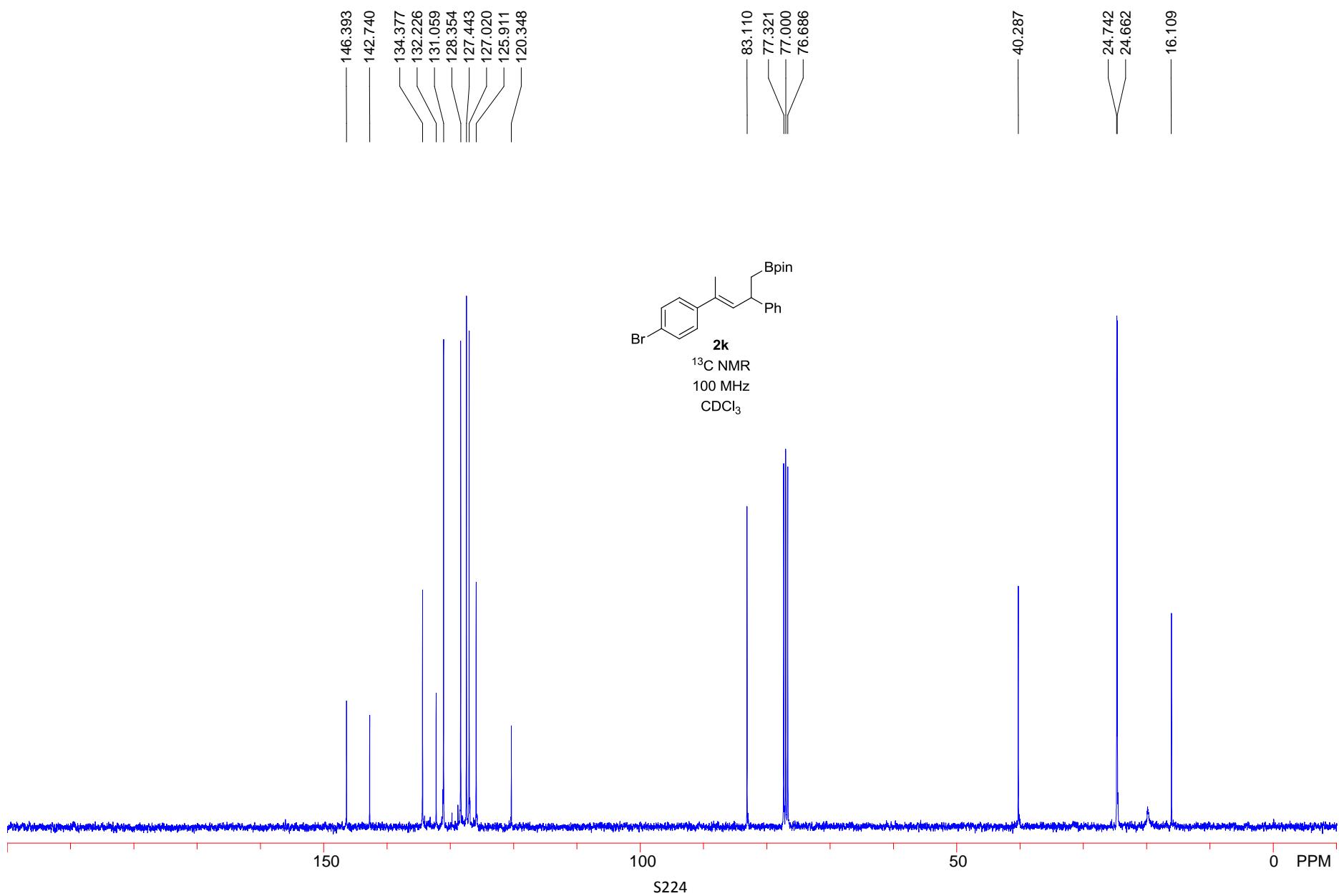


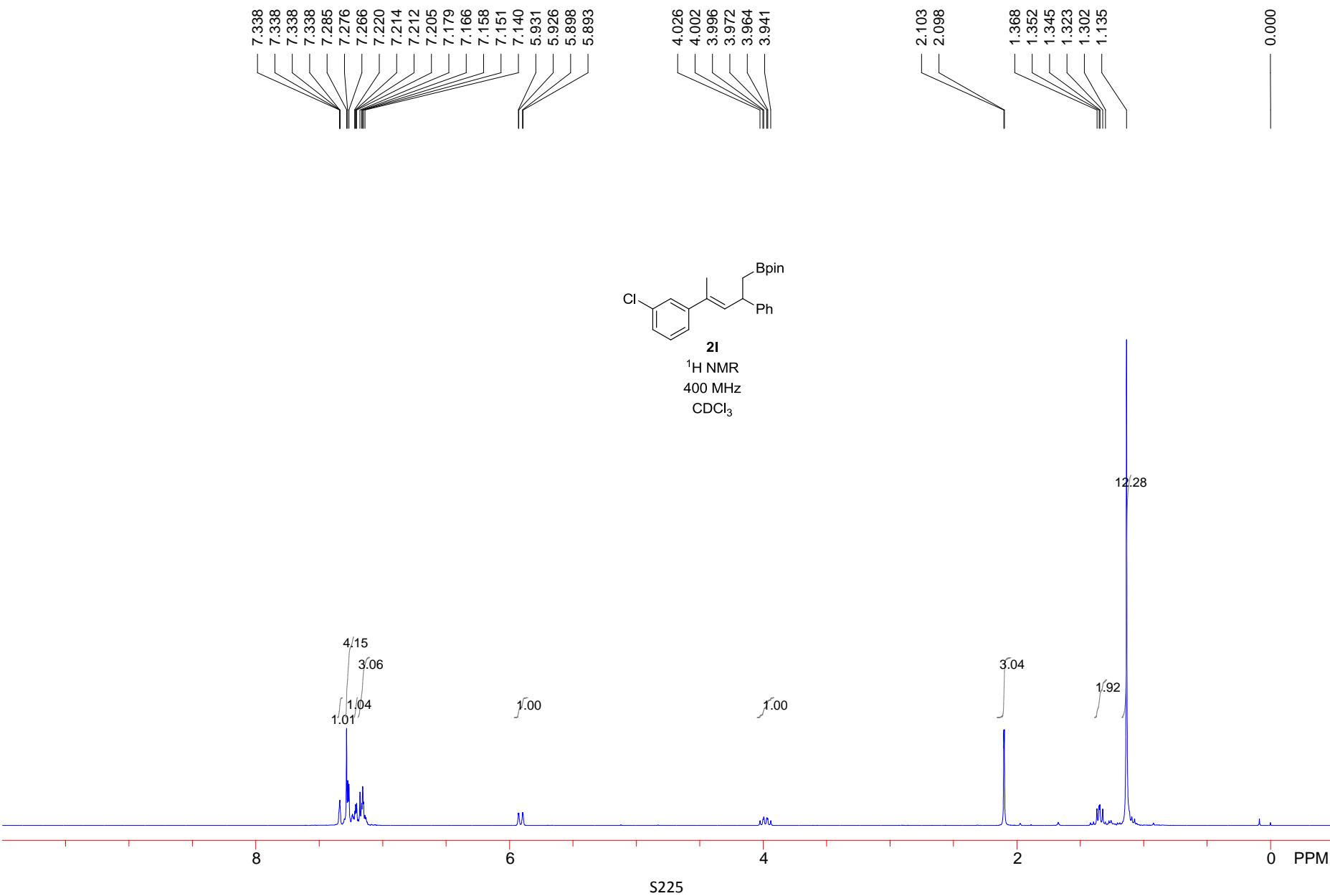


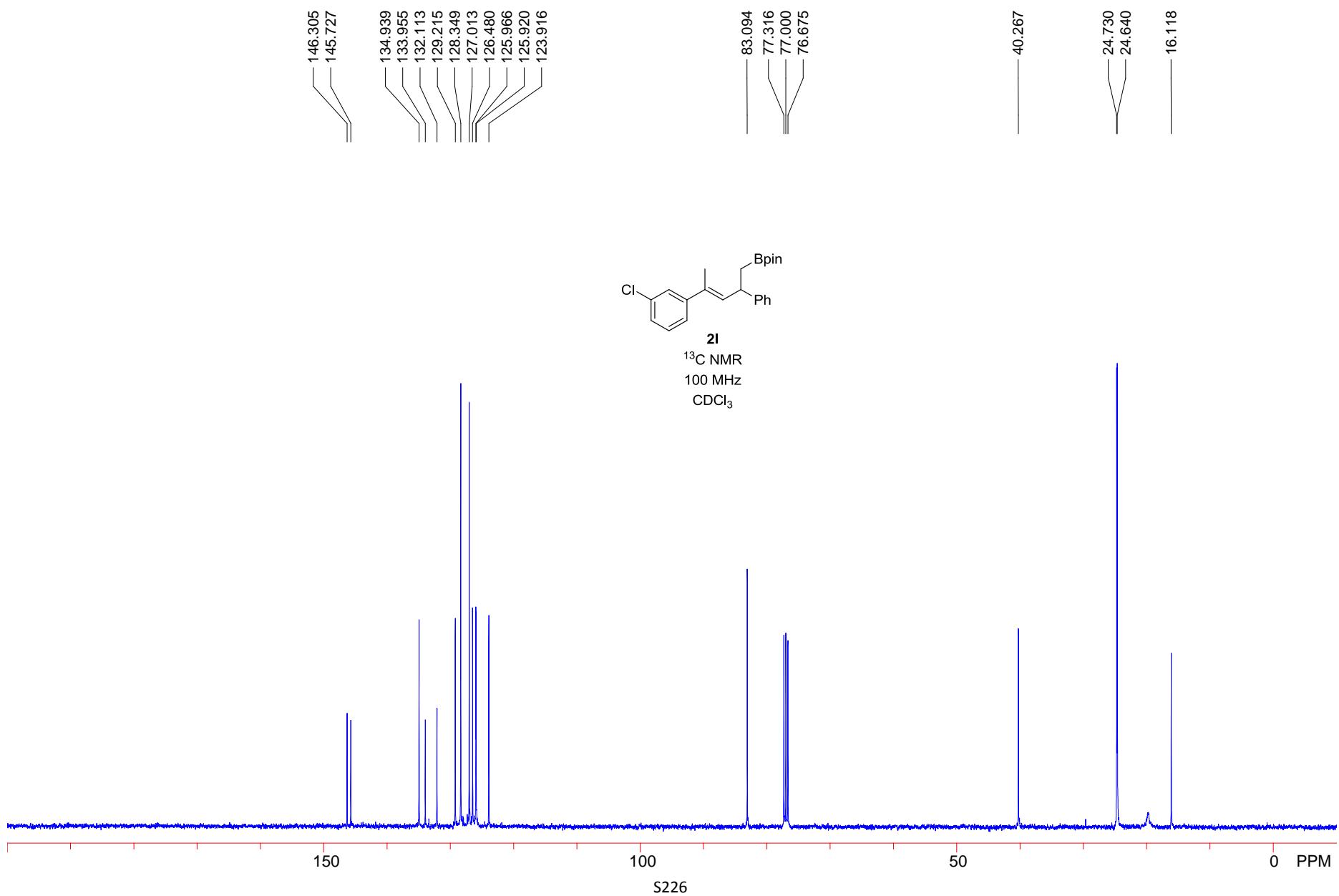


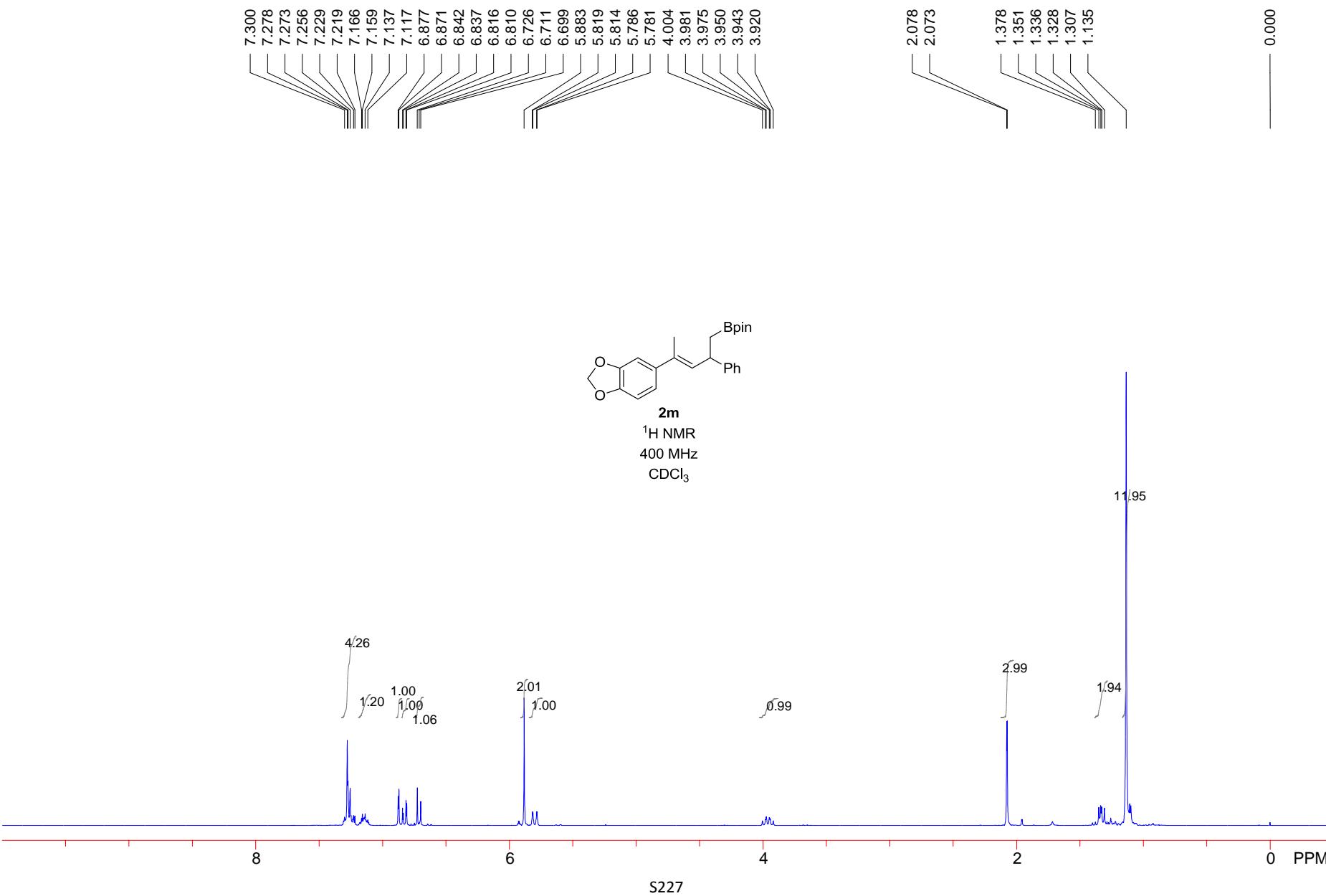


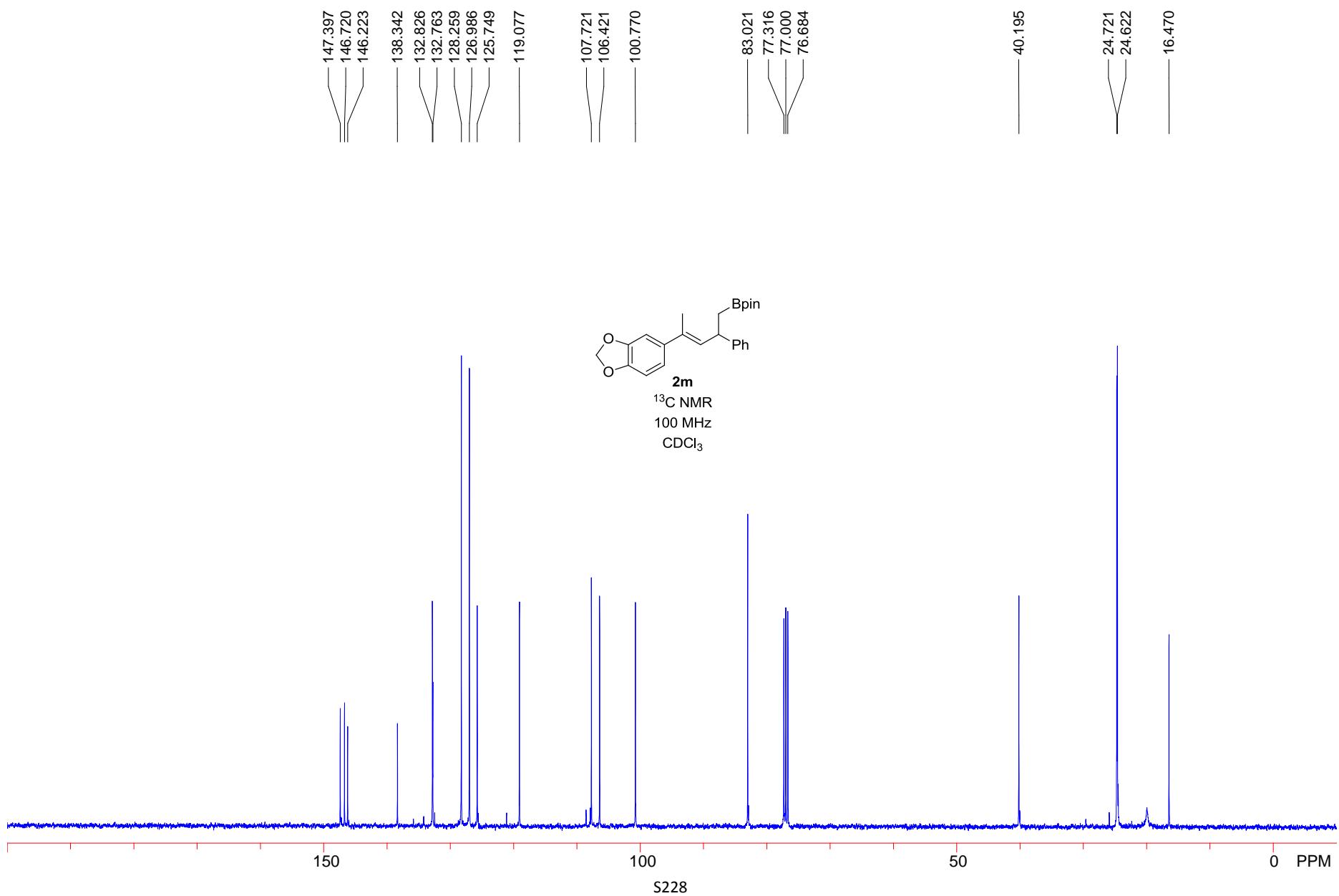




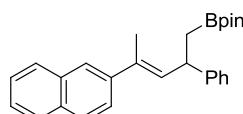
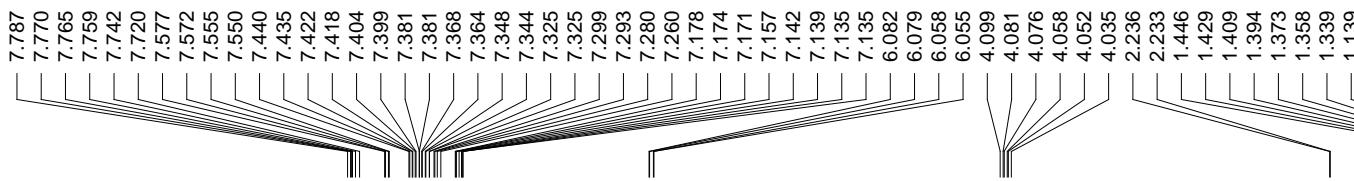




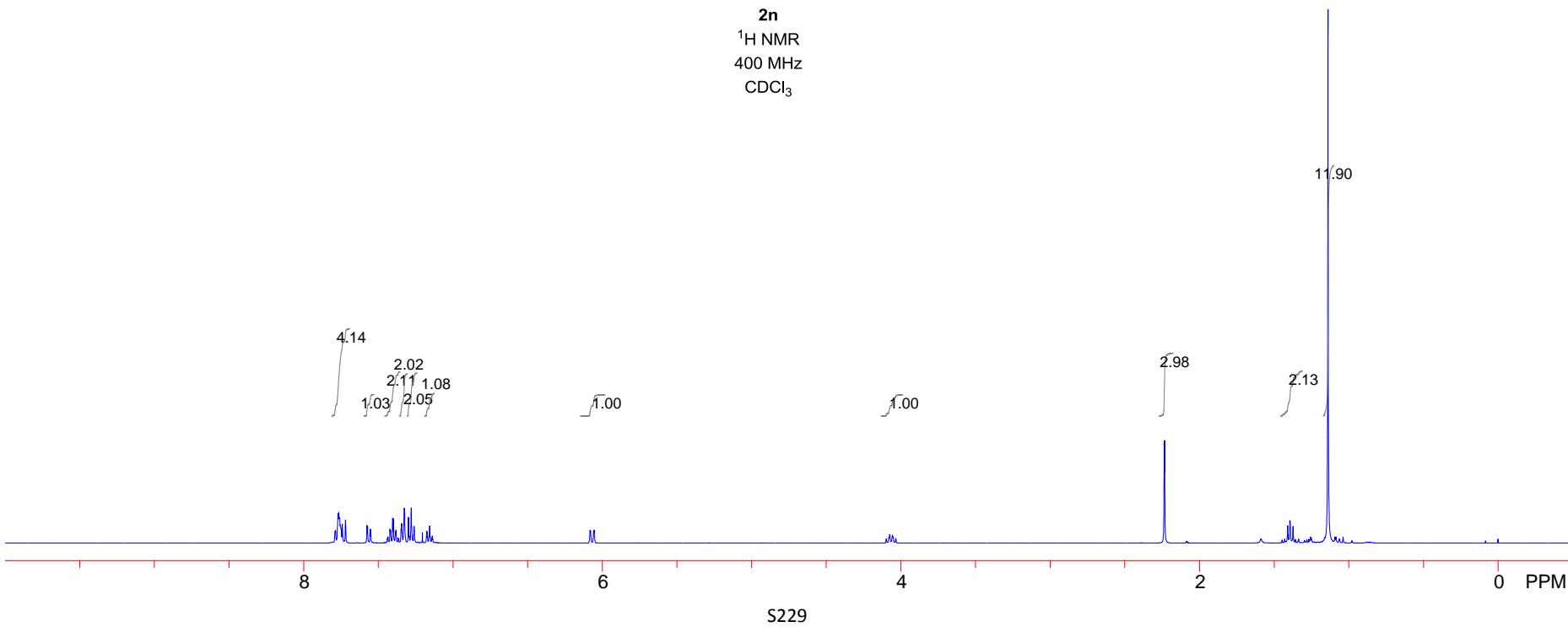




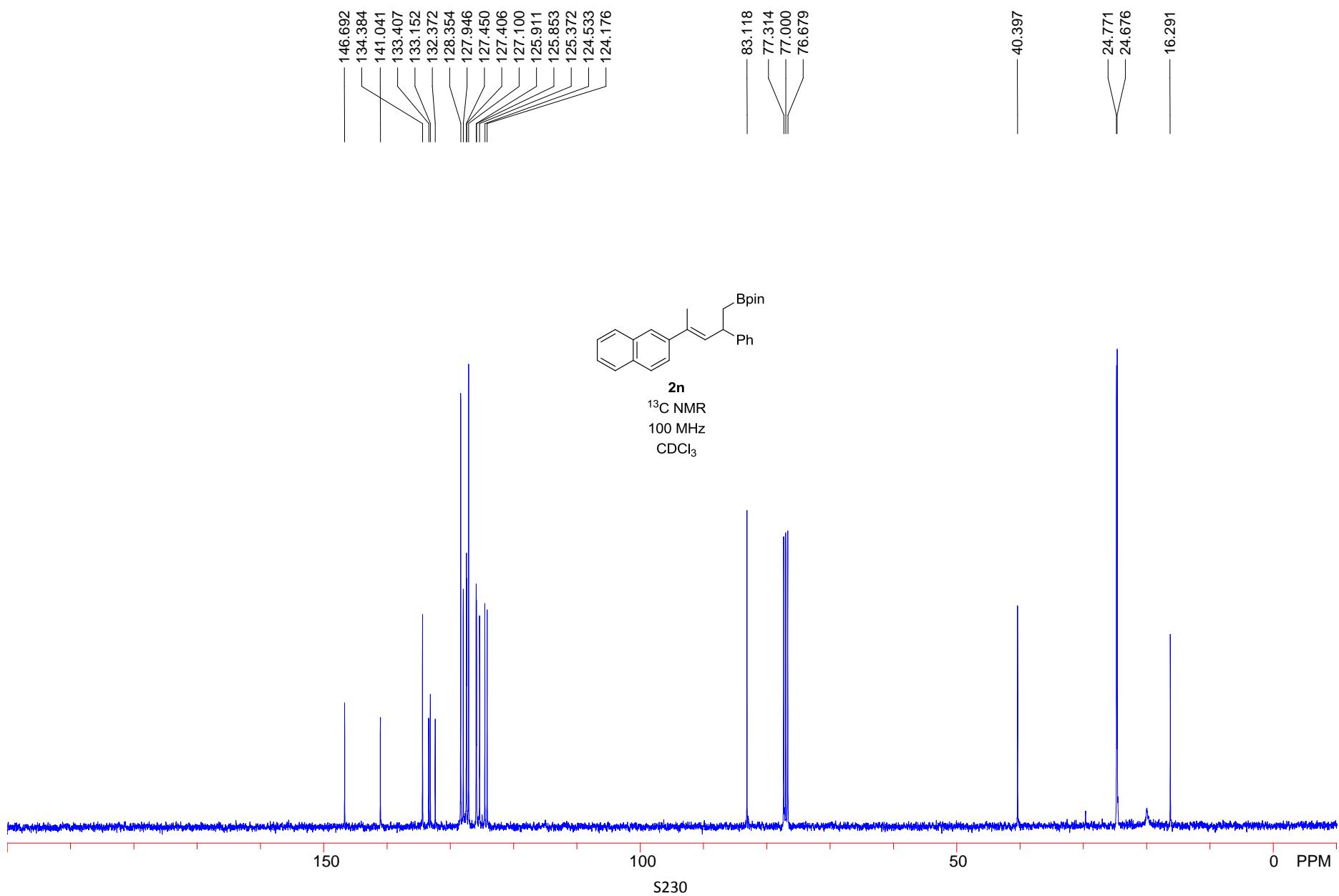
-0.000

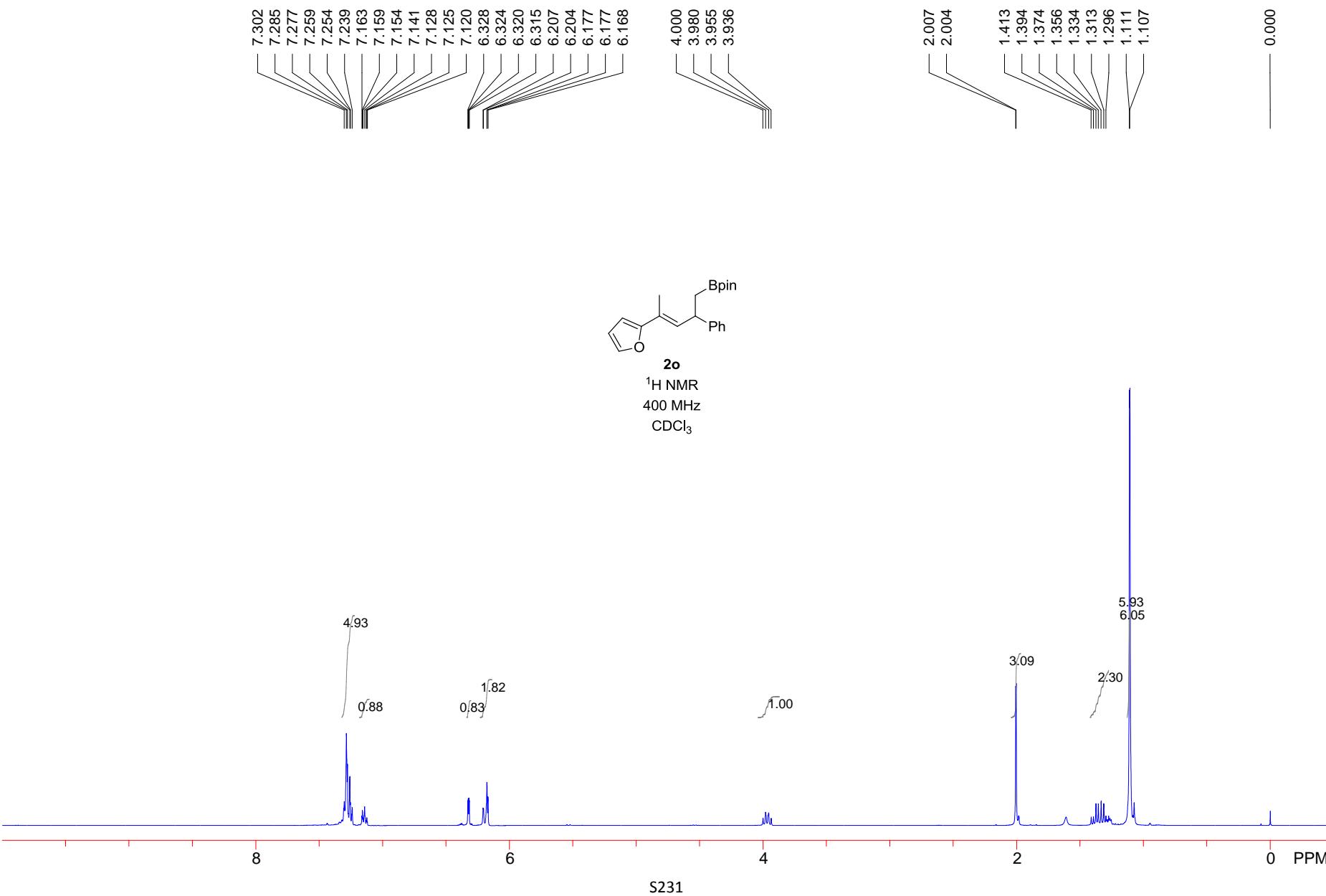


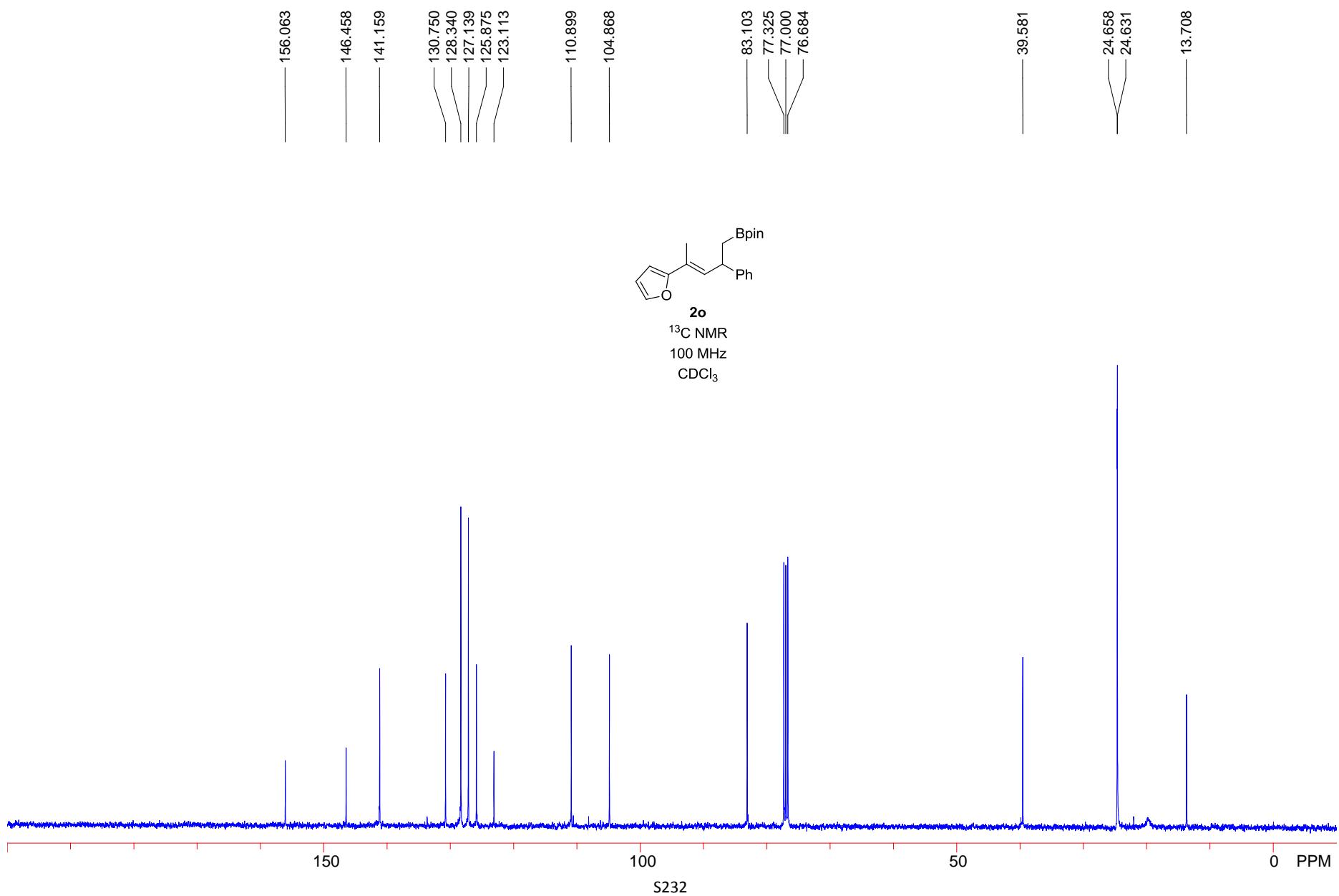
2n
¹H NMR
400 MHz
CDCl₃

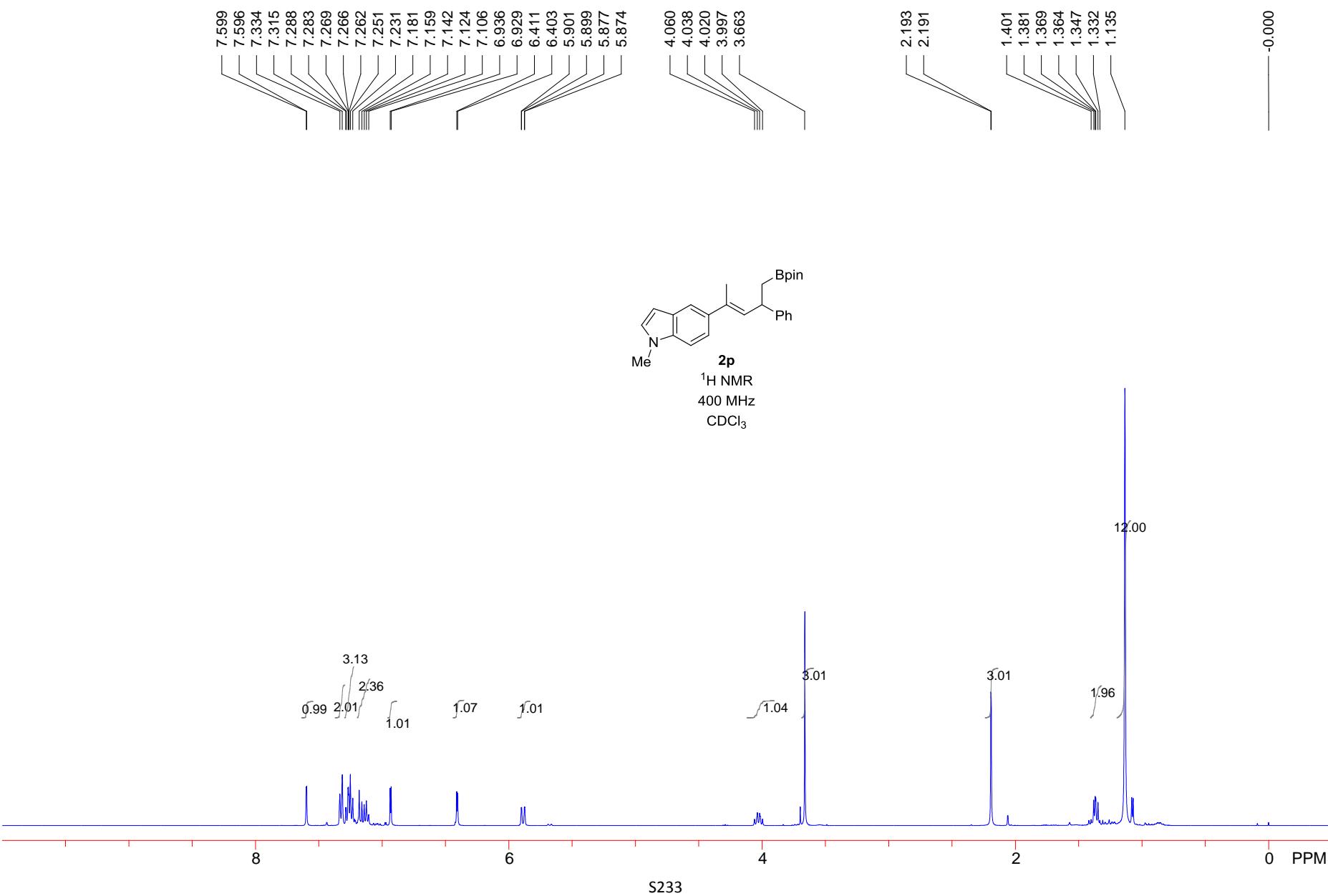


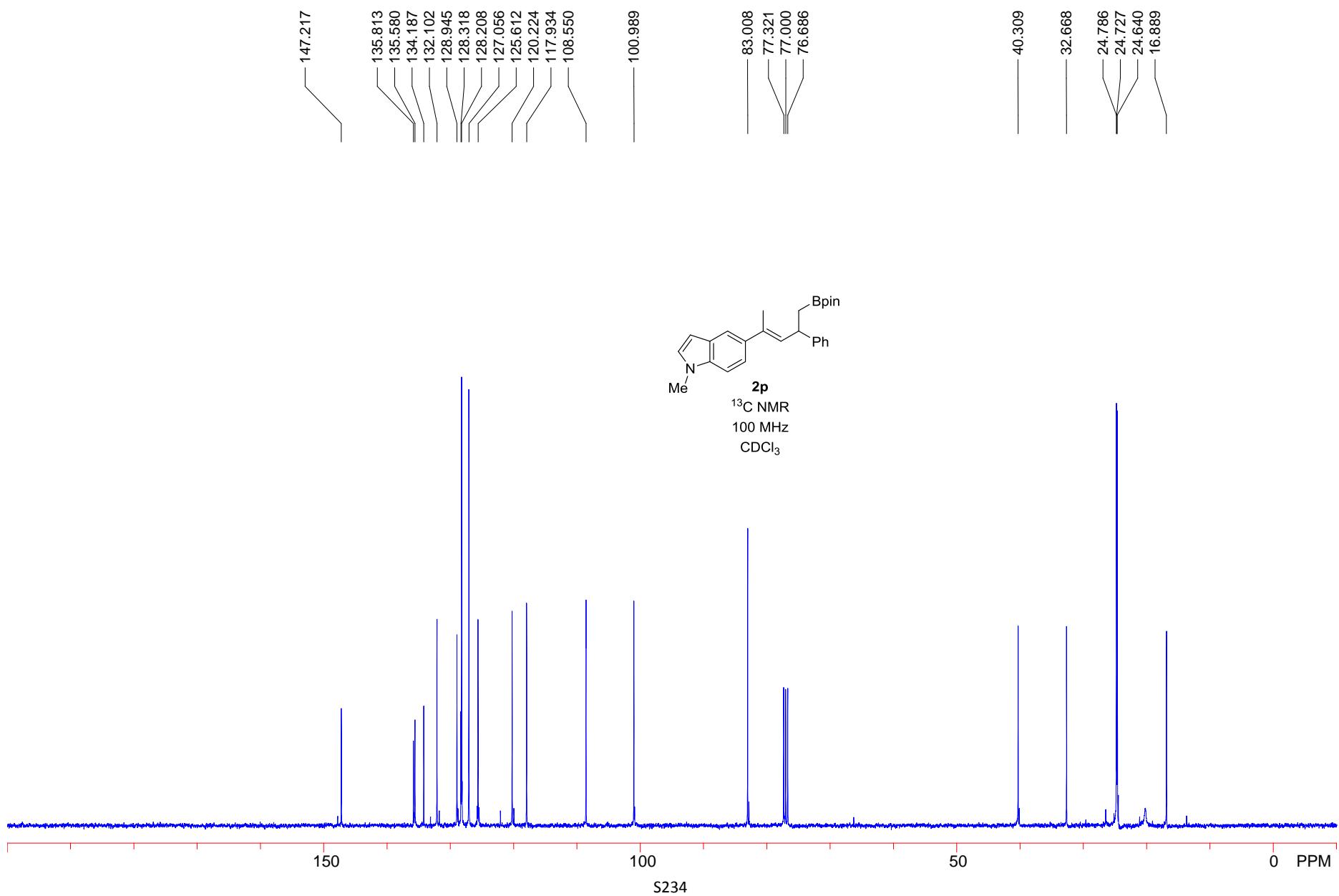
S229

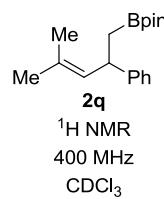
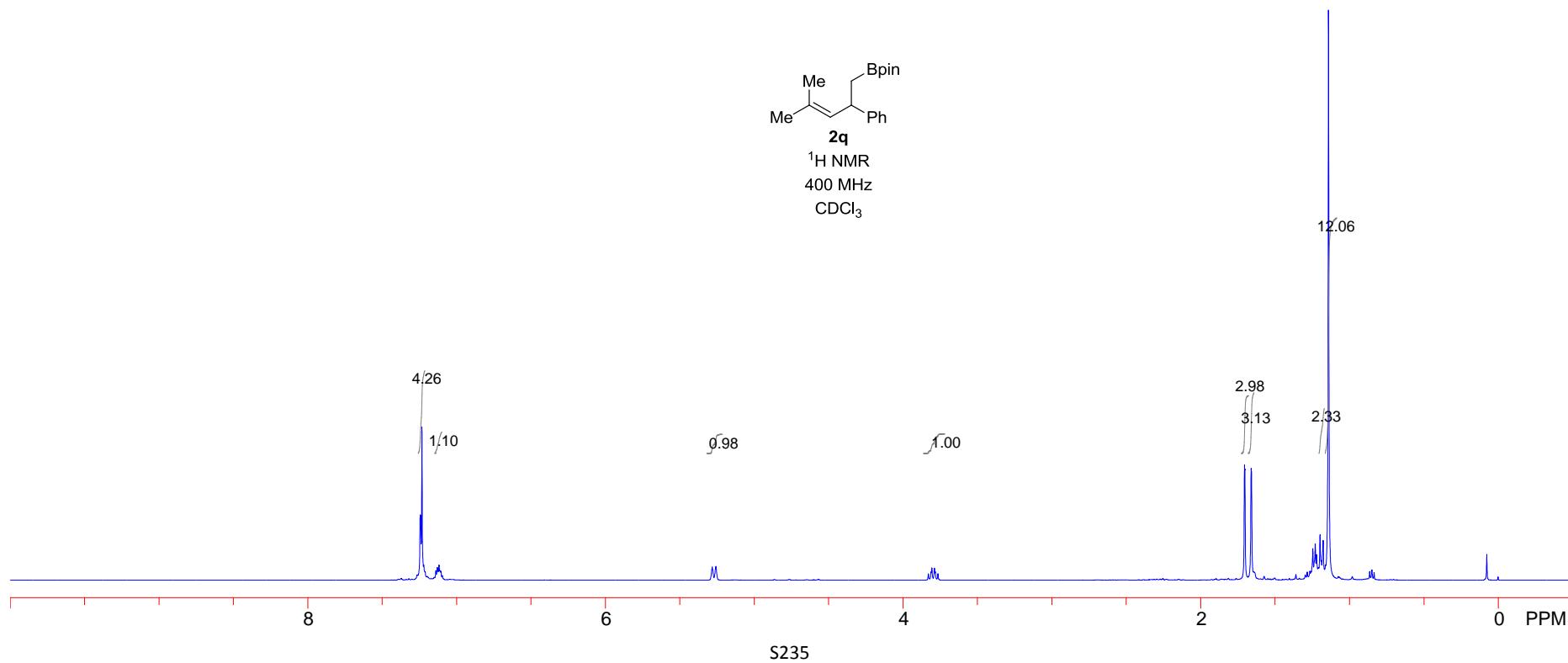








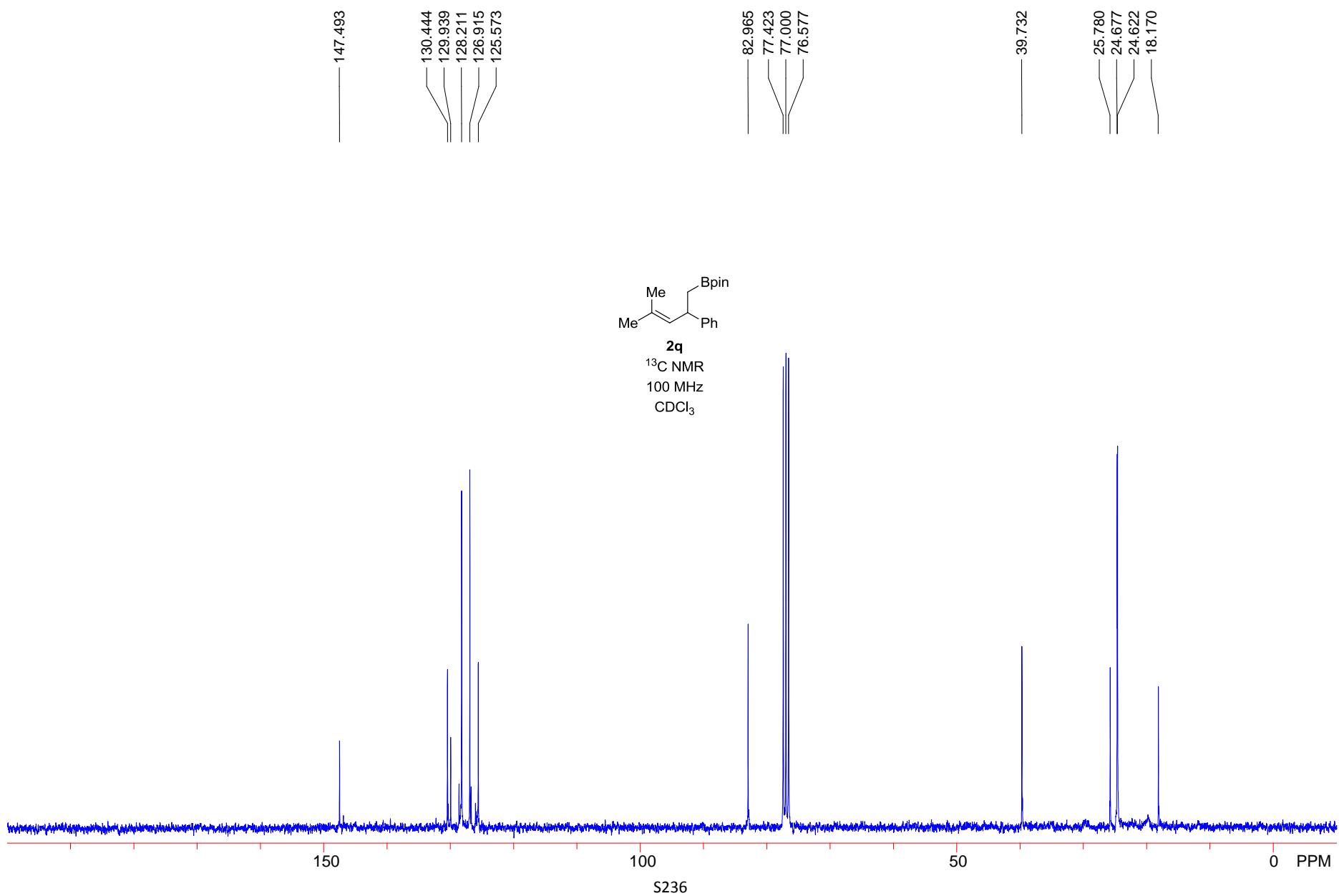


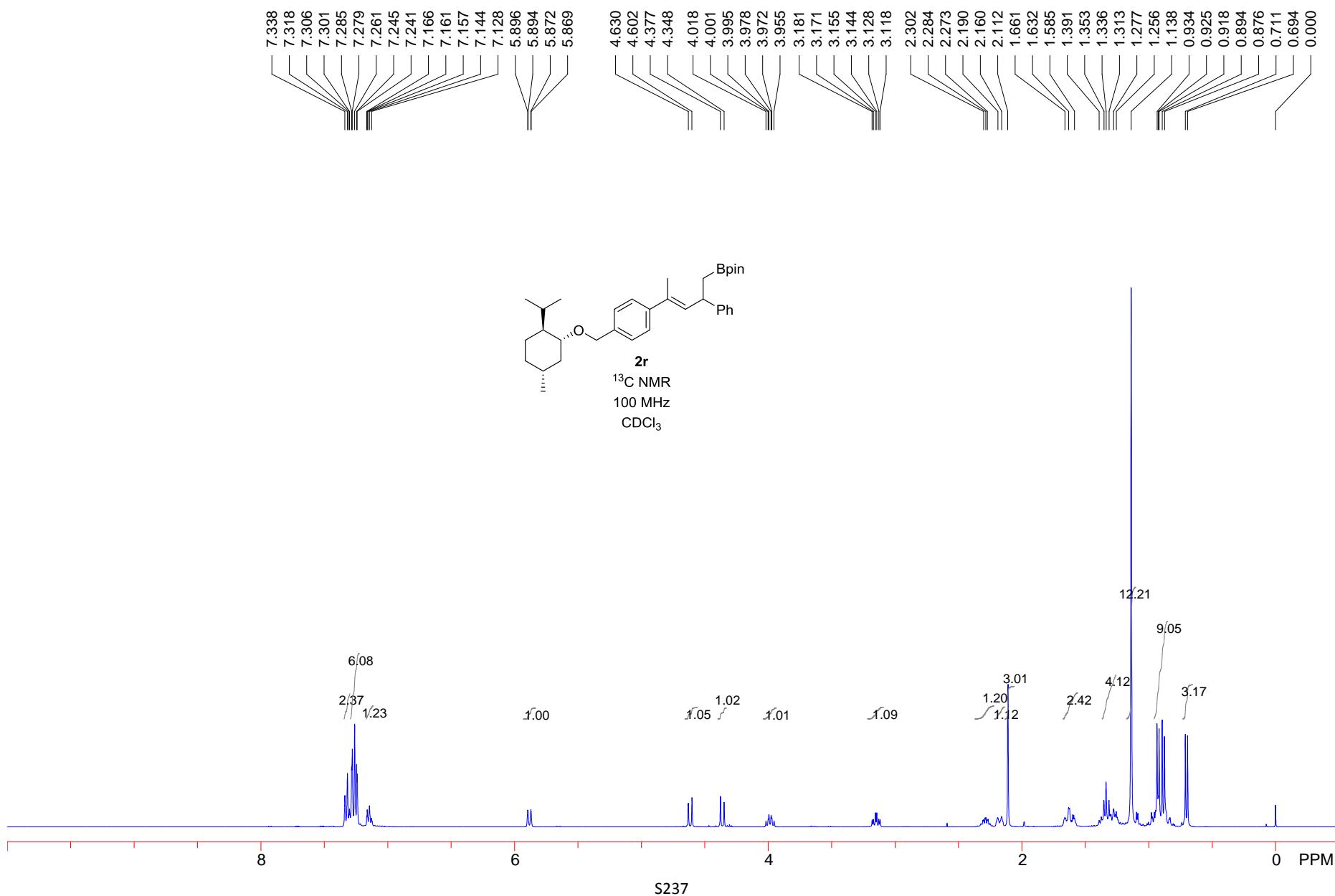


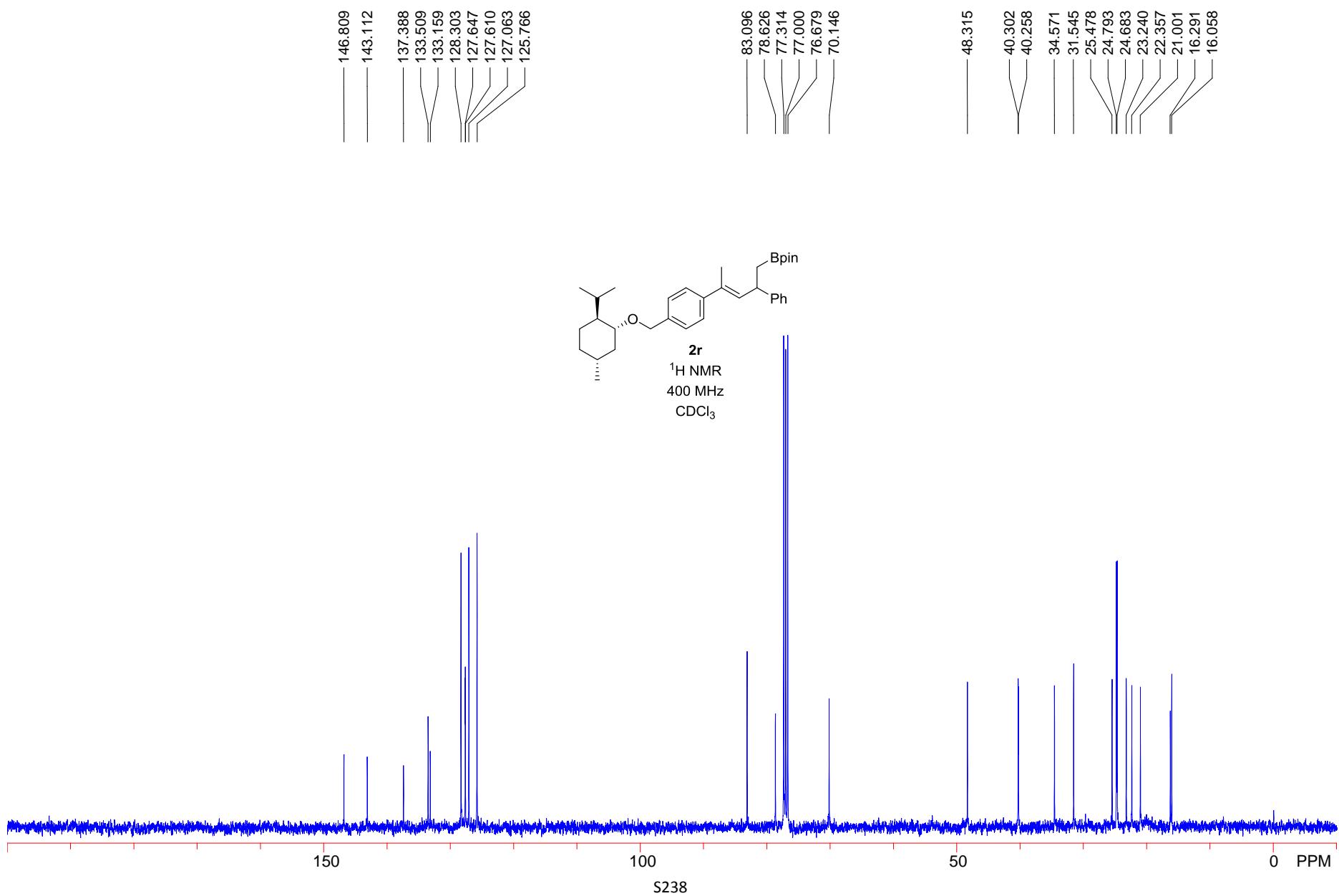
7.245
7.242
7.233
7.139
7.130
7.127
7.118
7.111
7.105

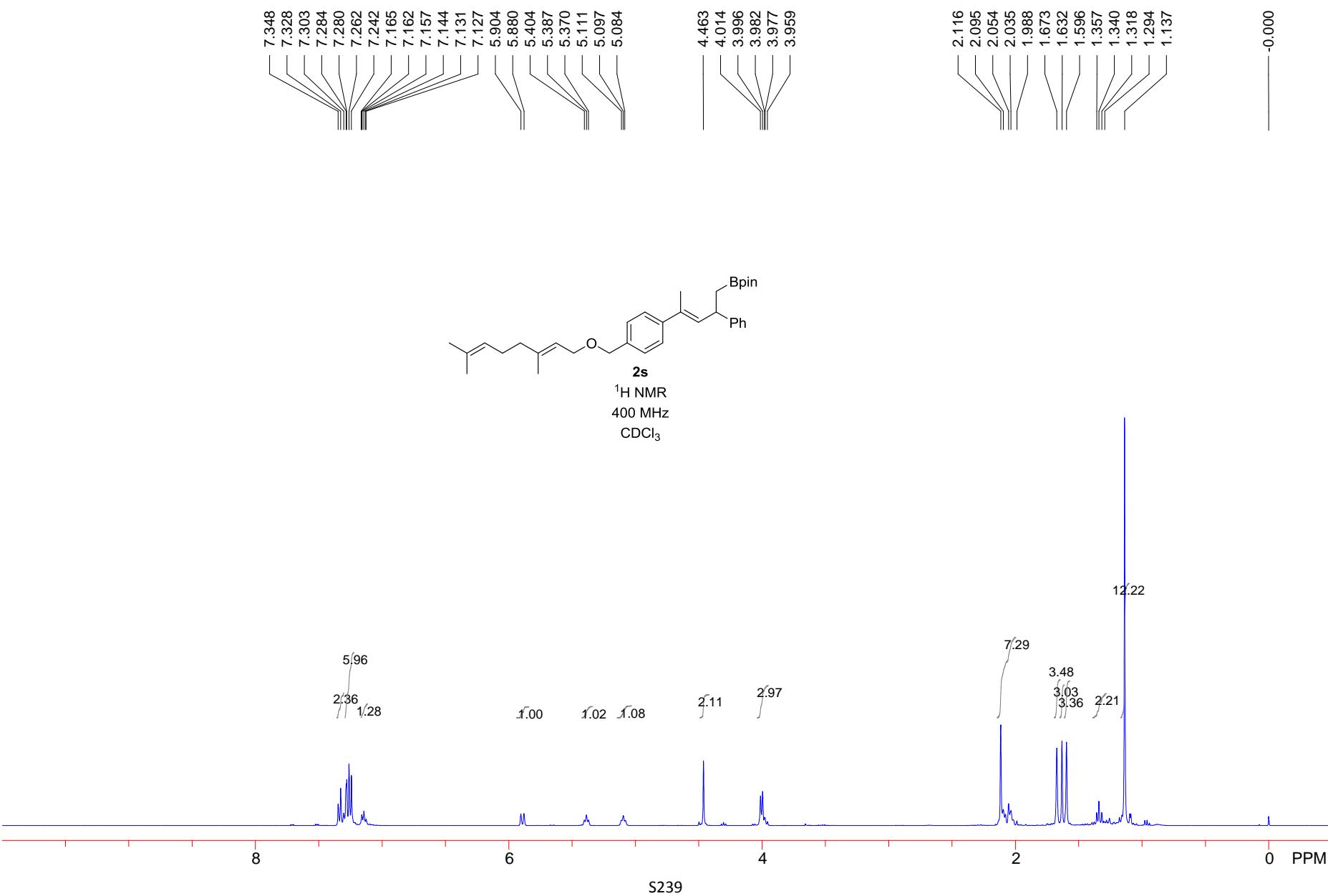
5.286
5.283
5.280
5.261
5.258
5.255

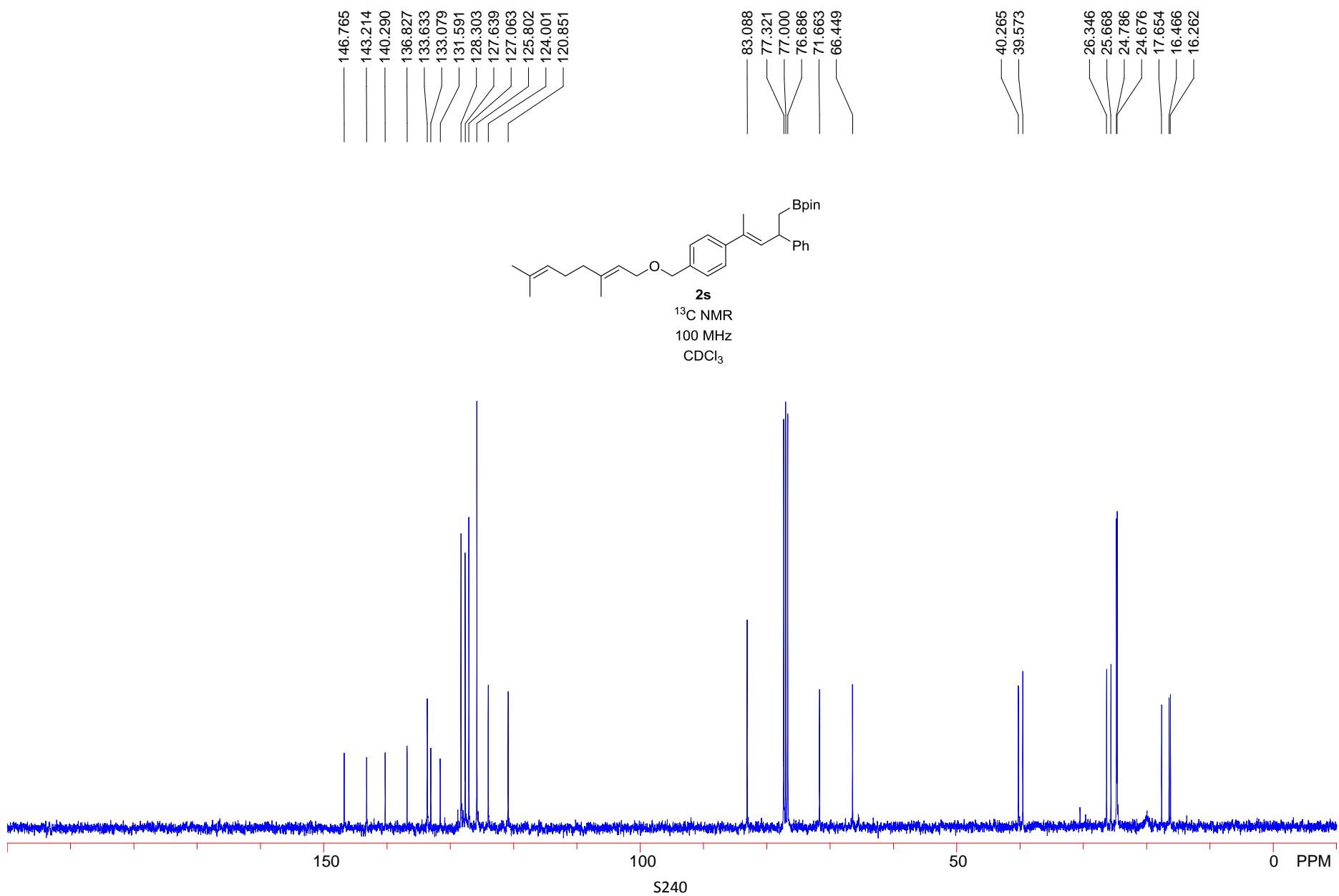
3.830
3.813
3.807
3.790
3.784
3.766

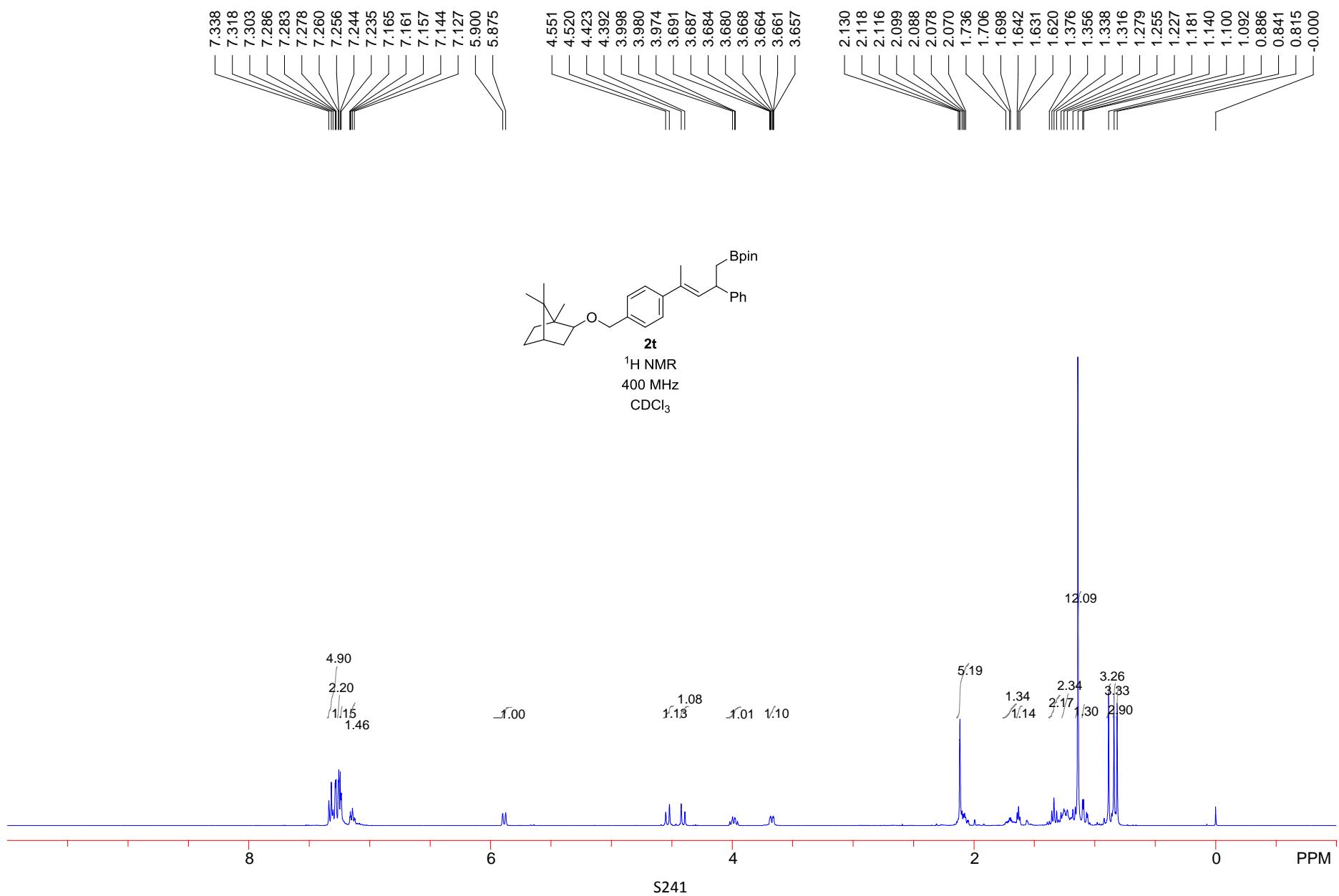


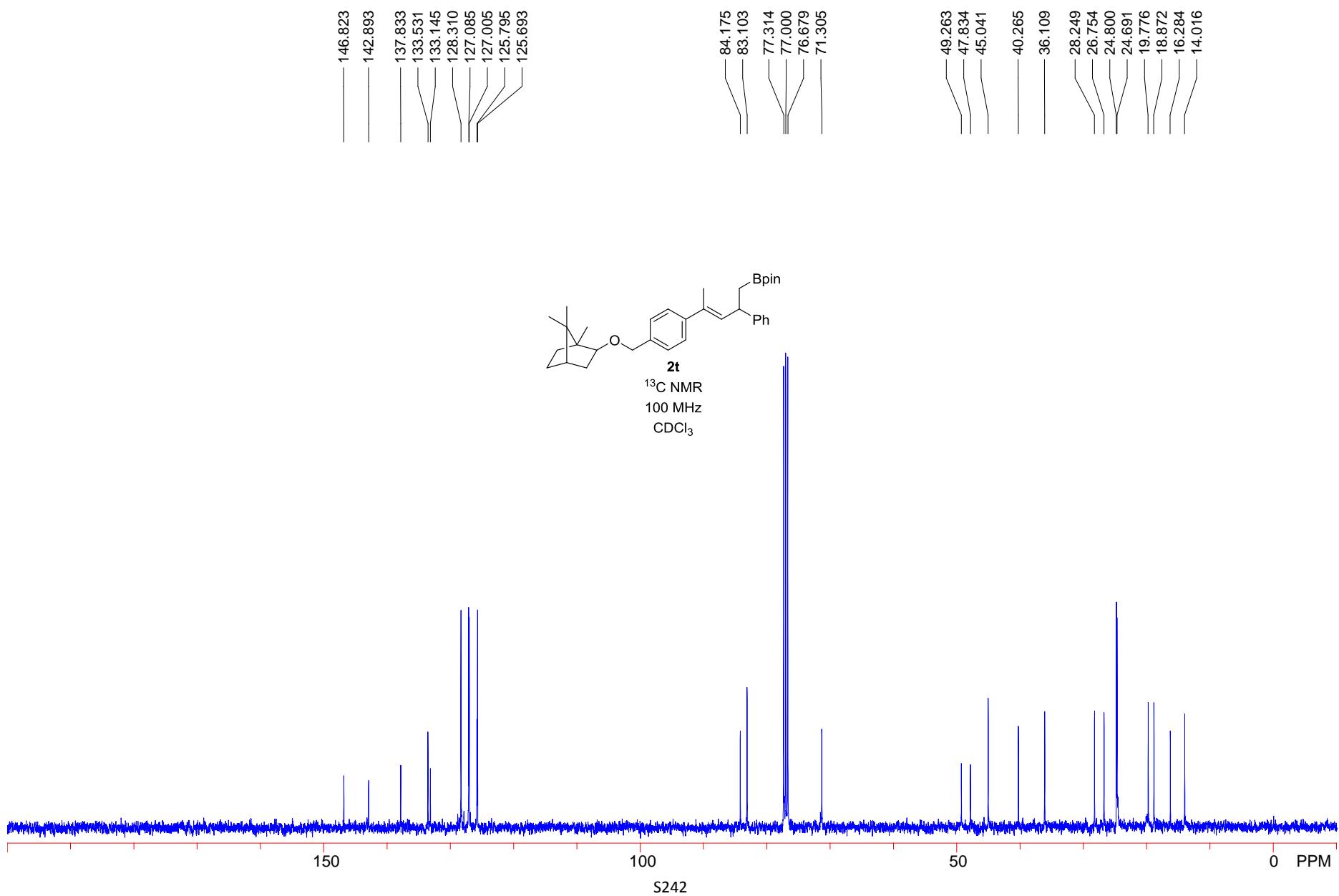


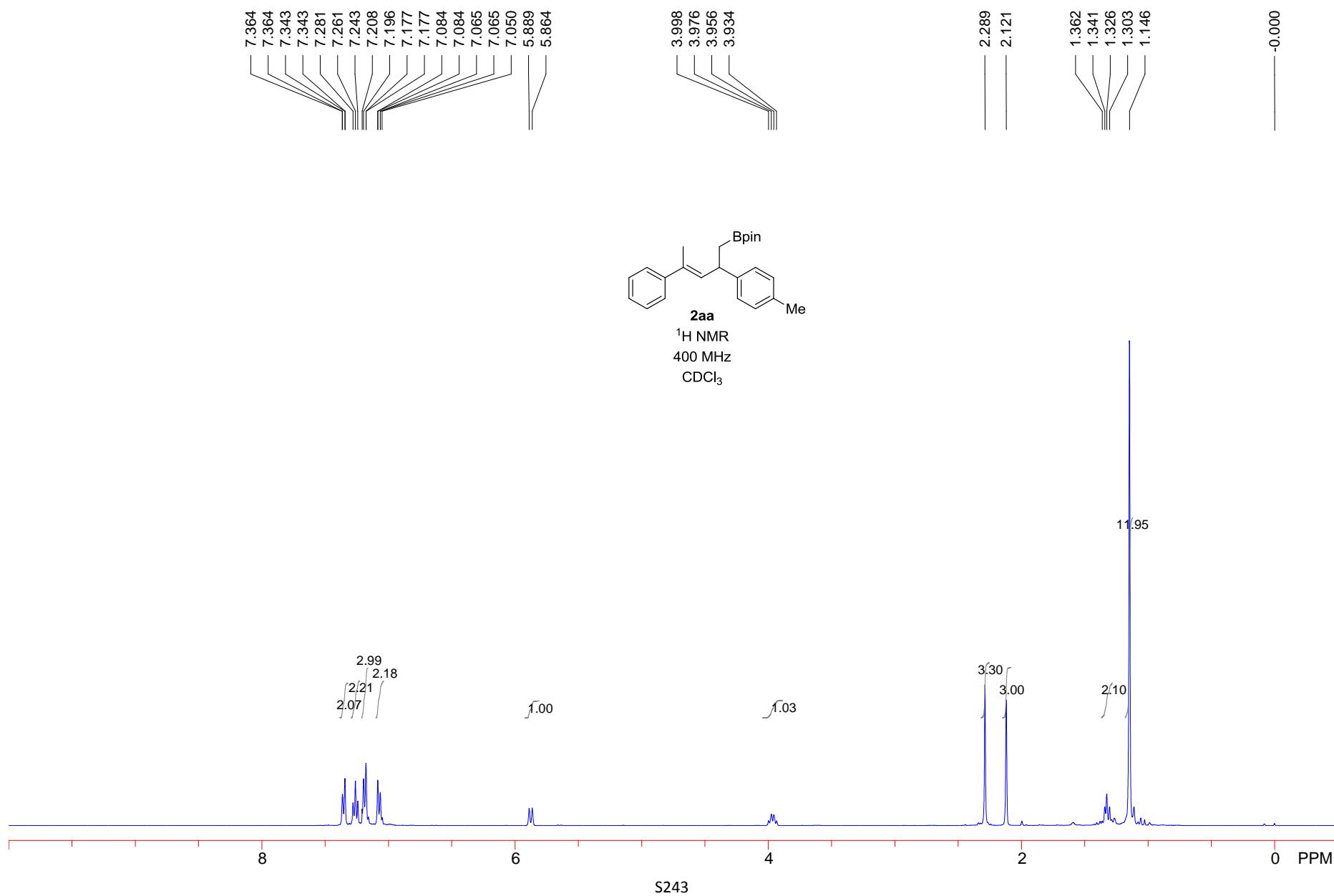


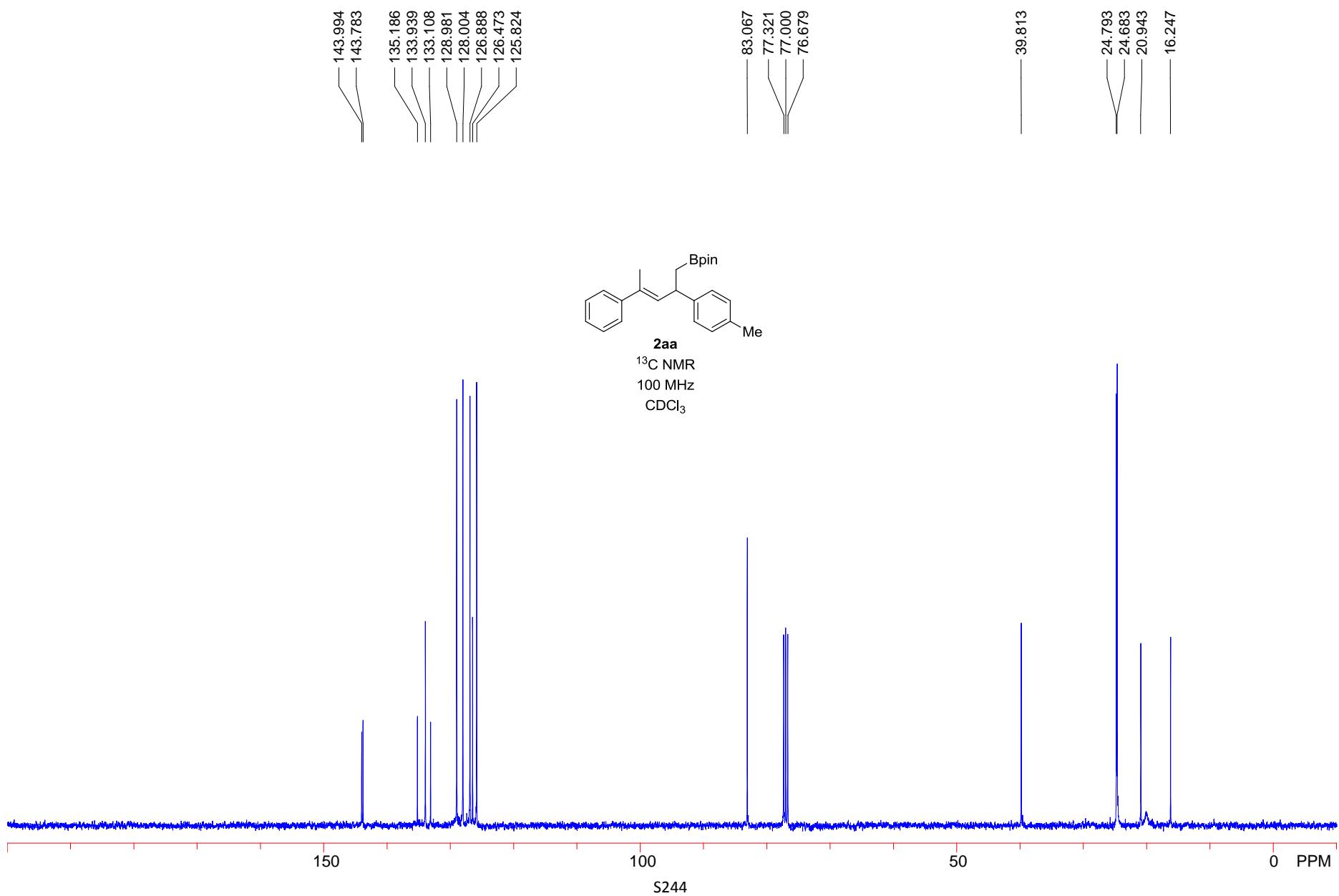


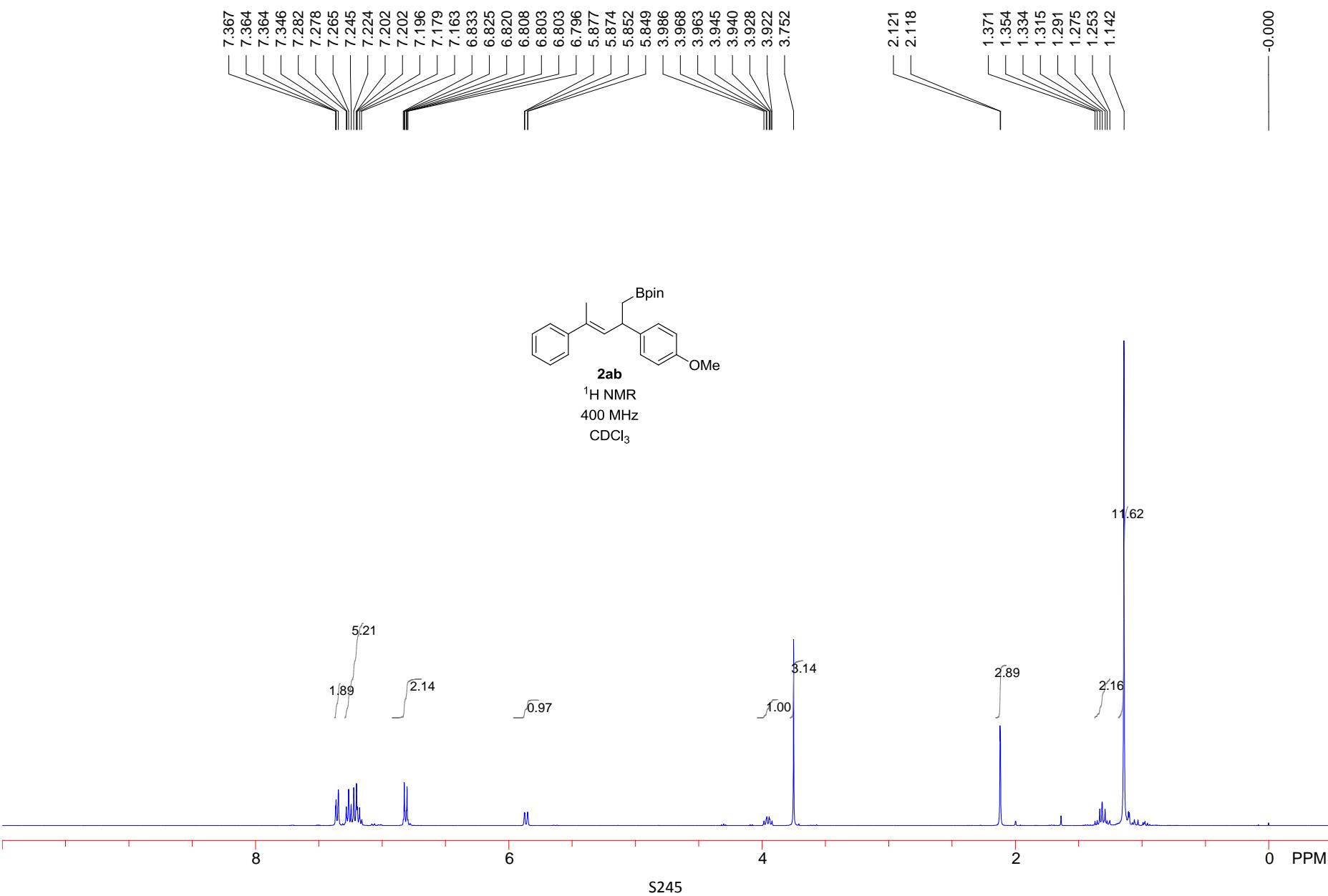


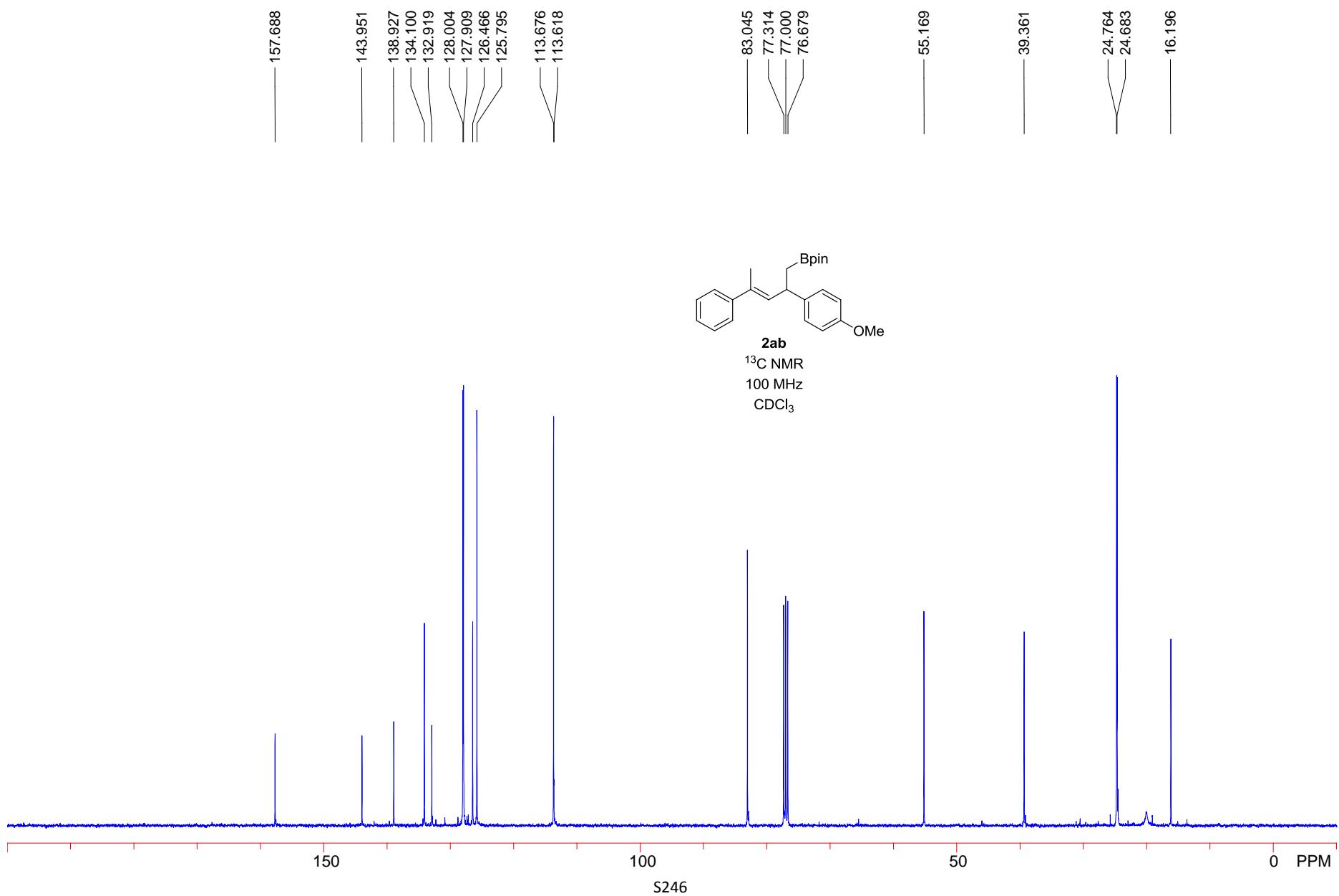


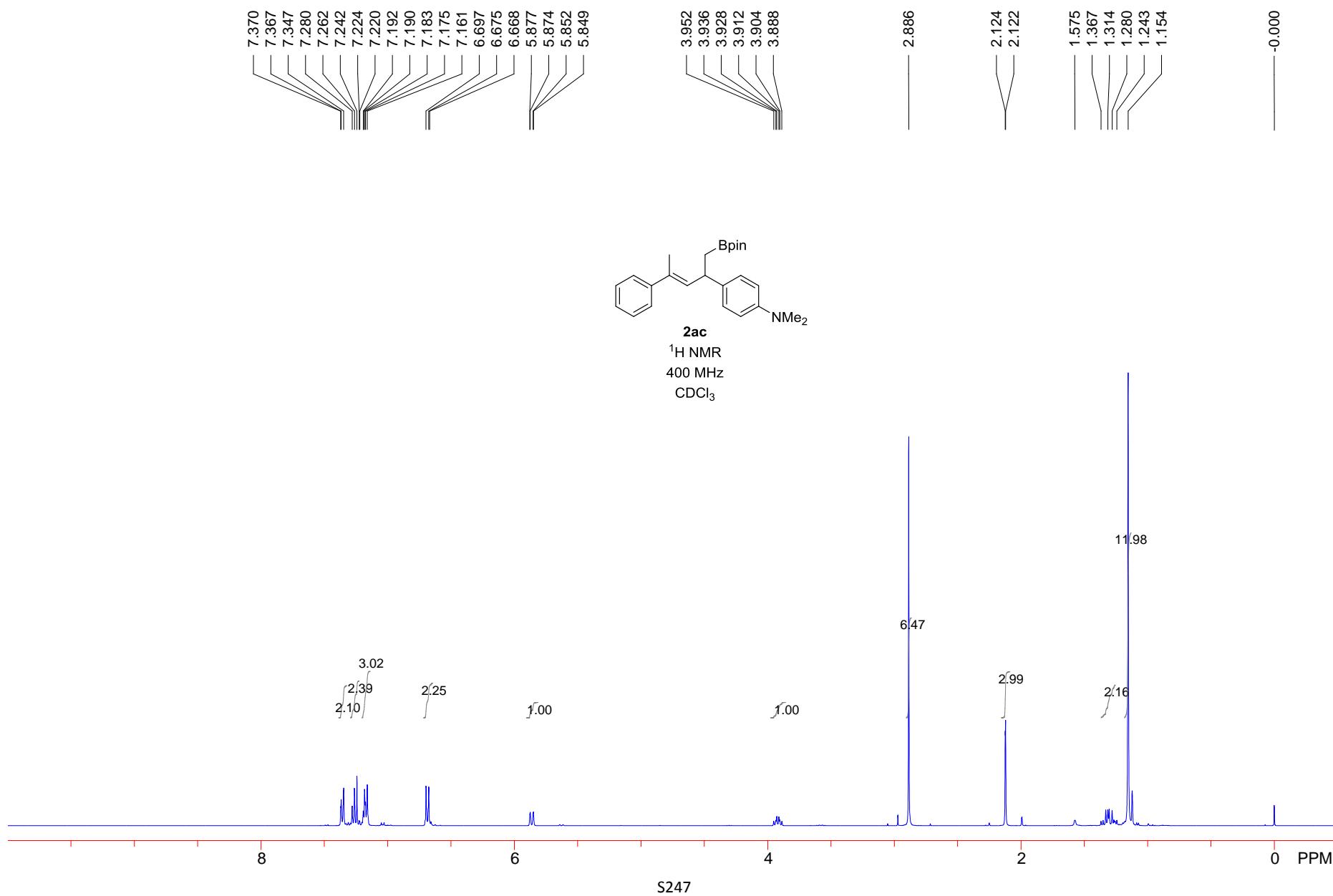


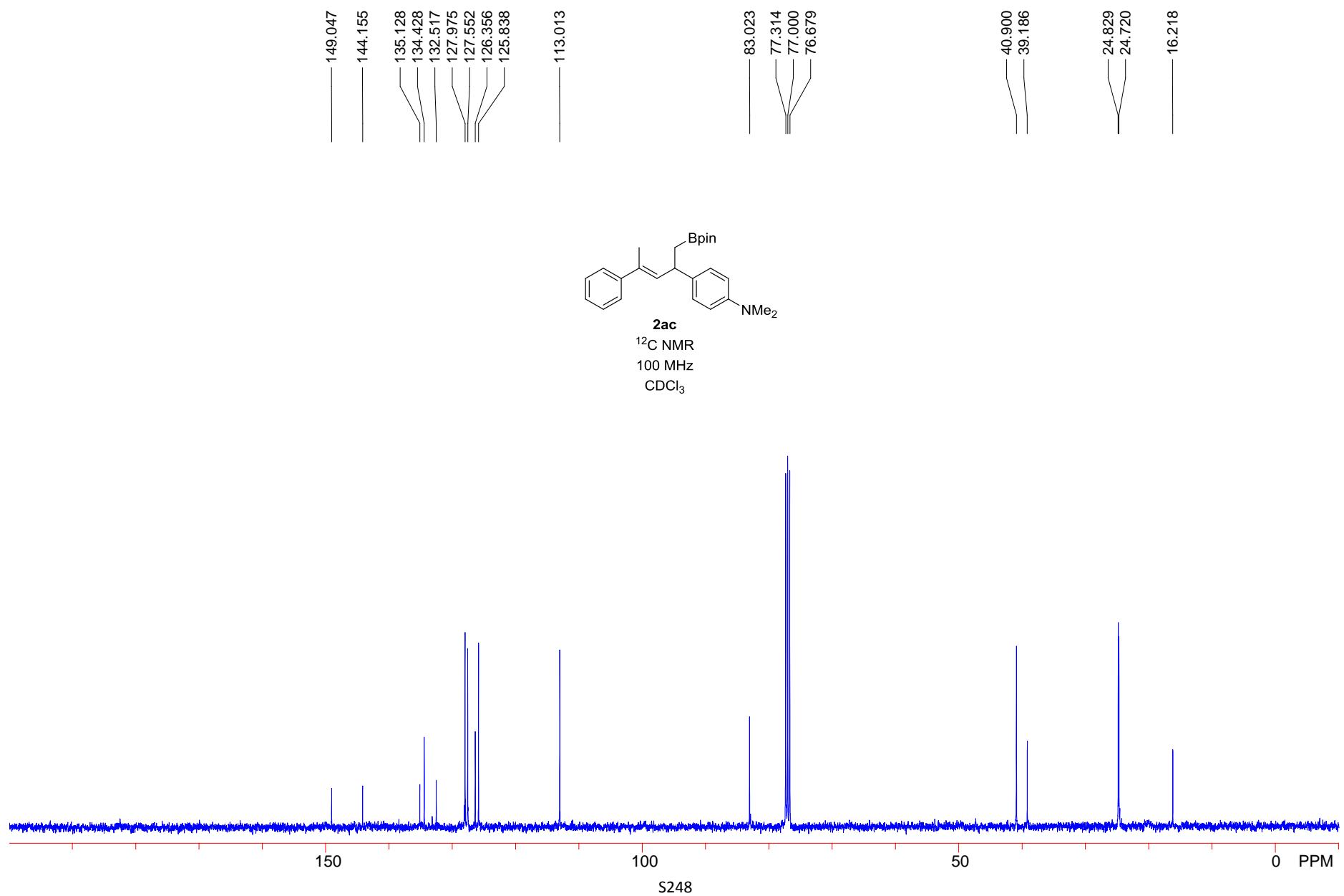


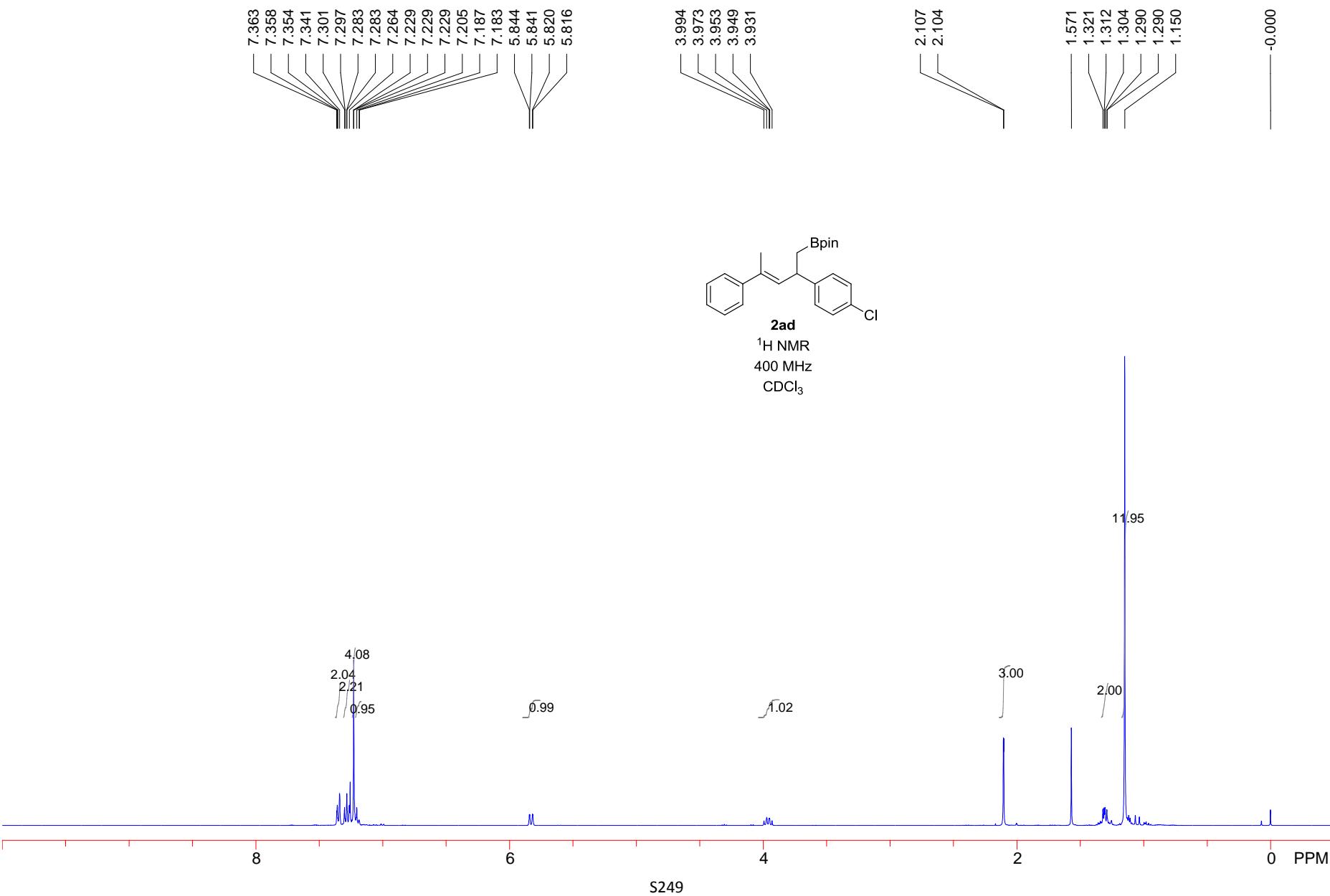


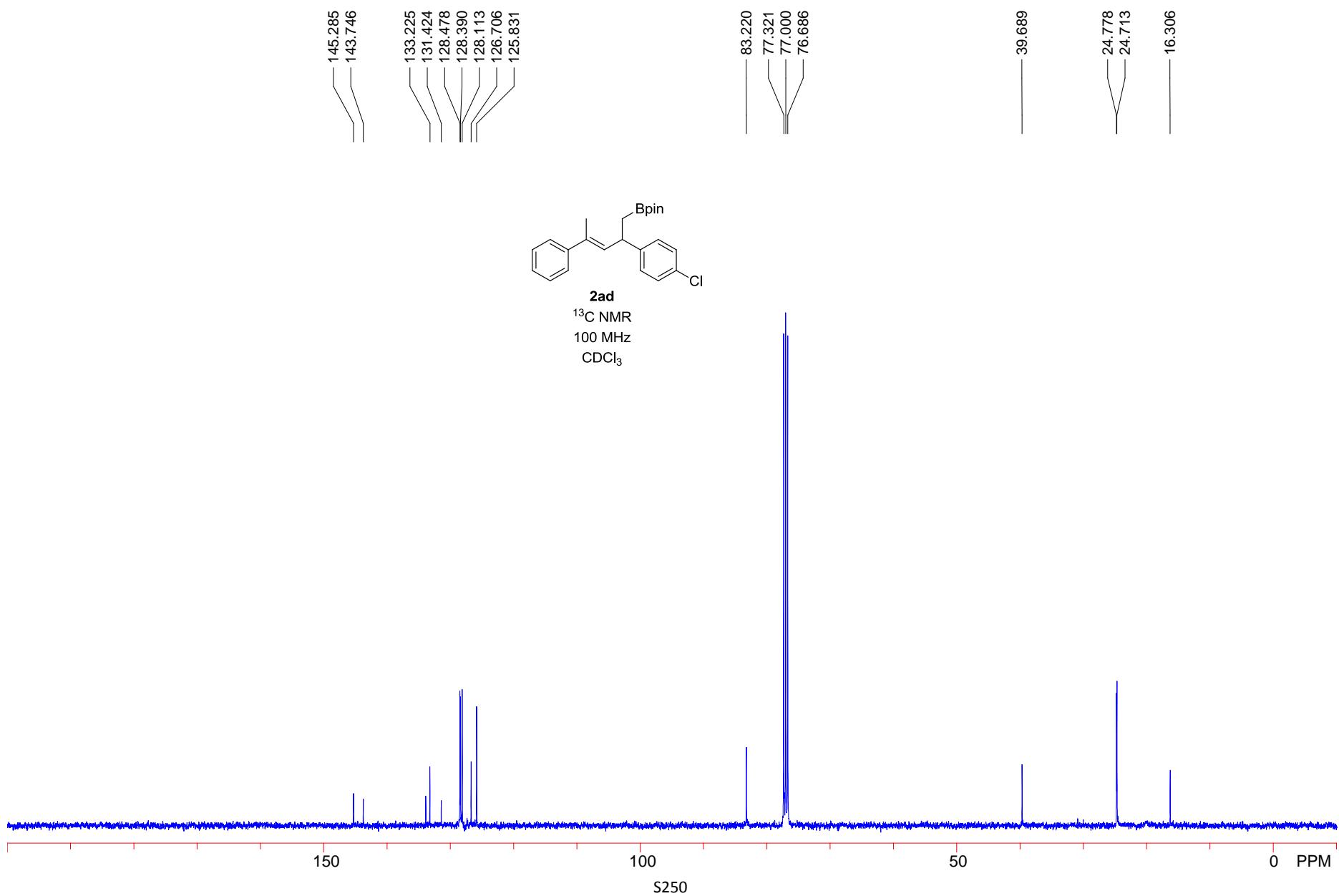


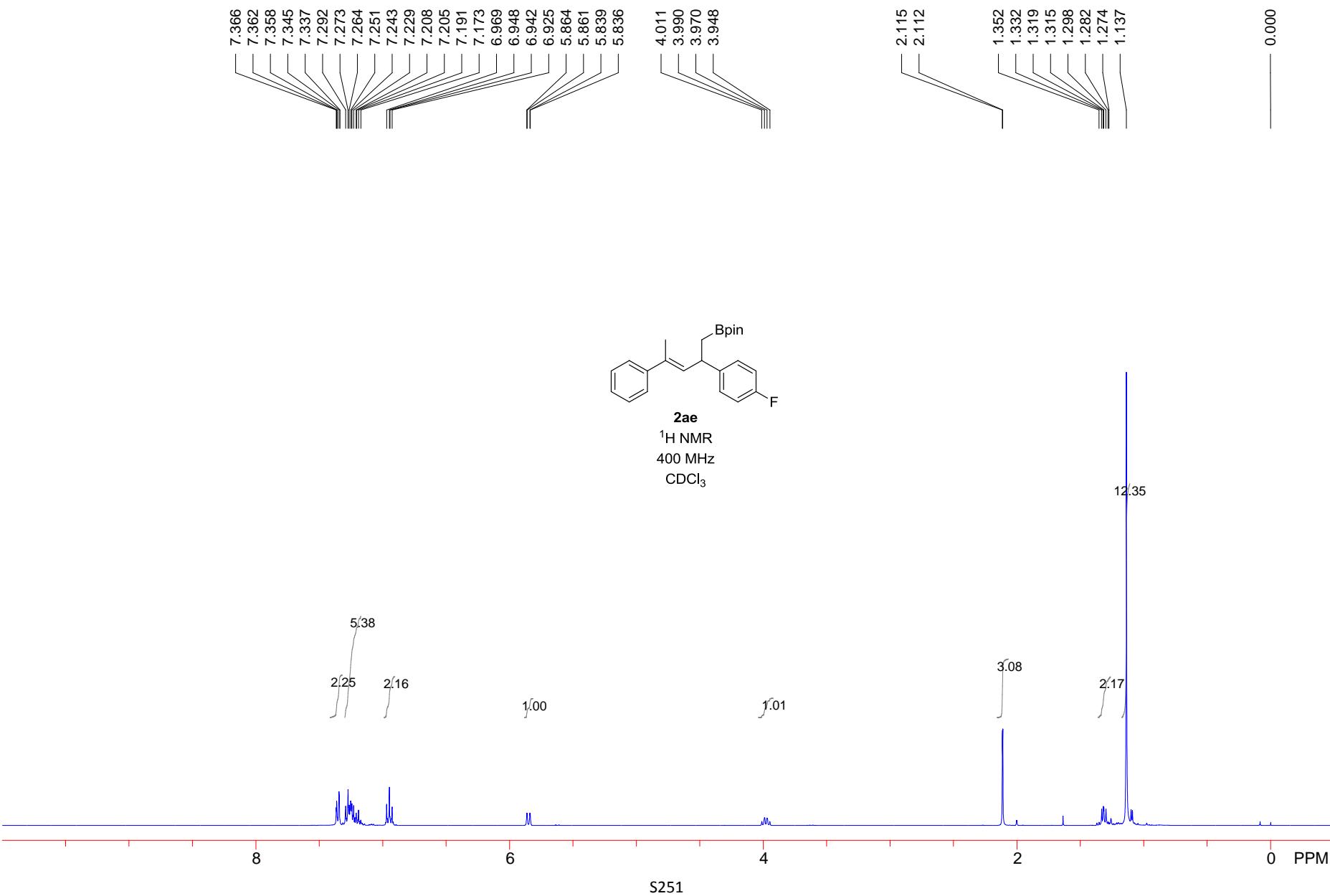


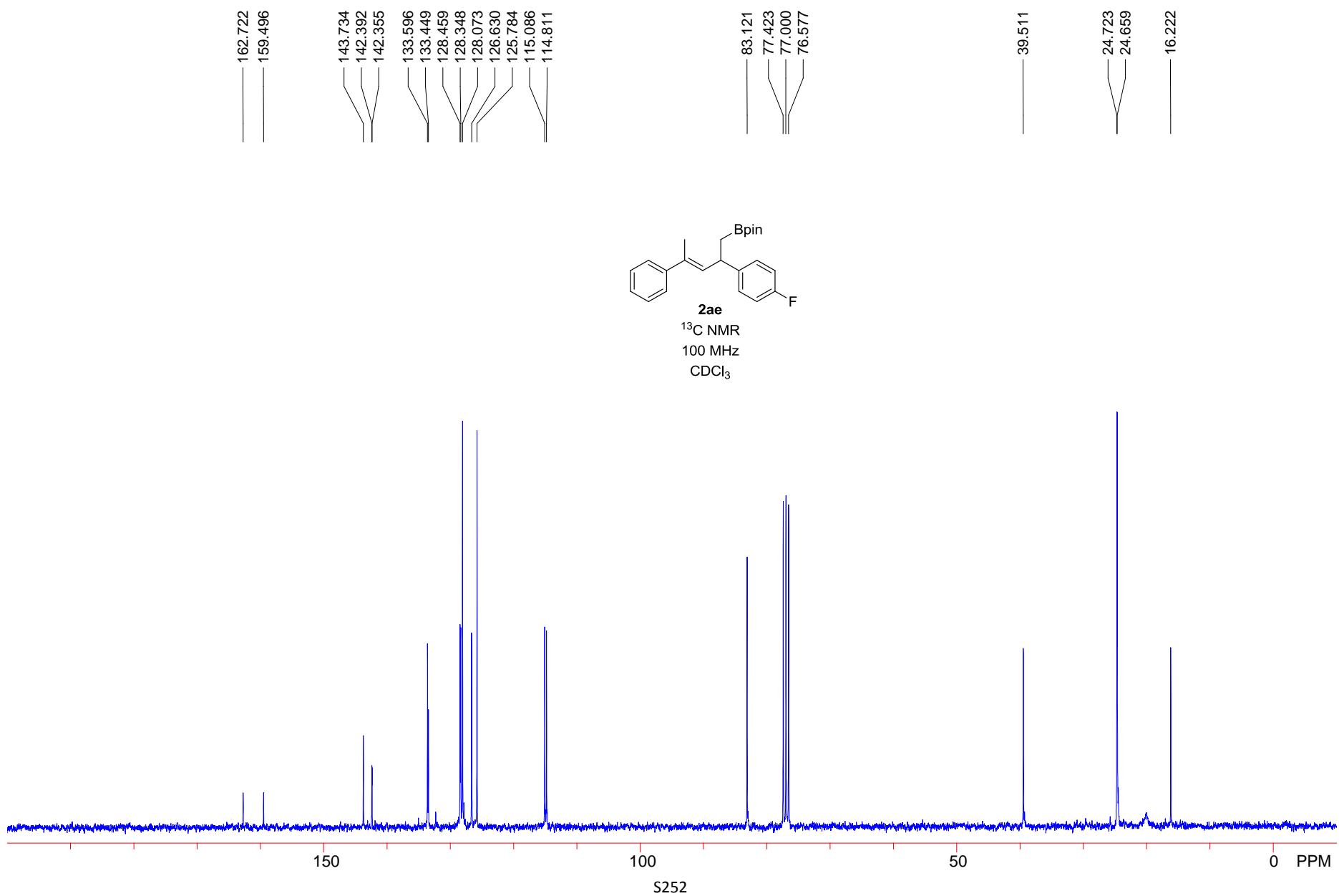


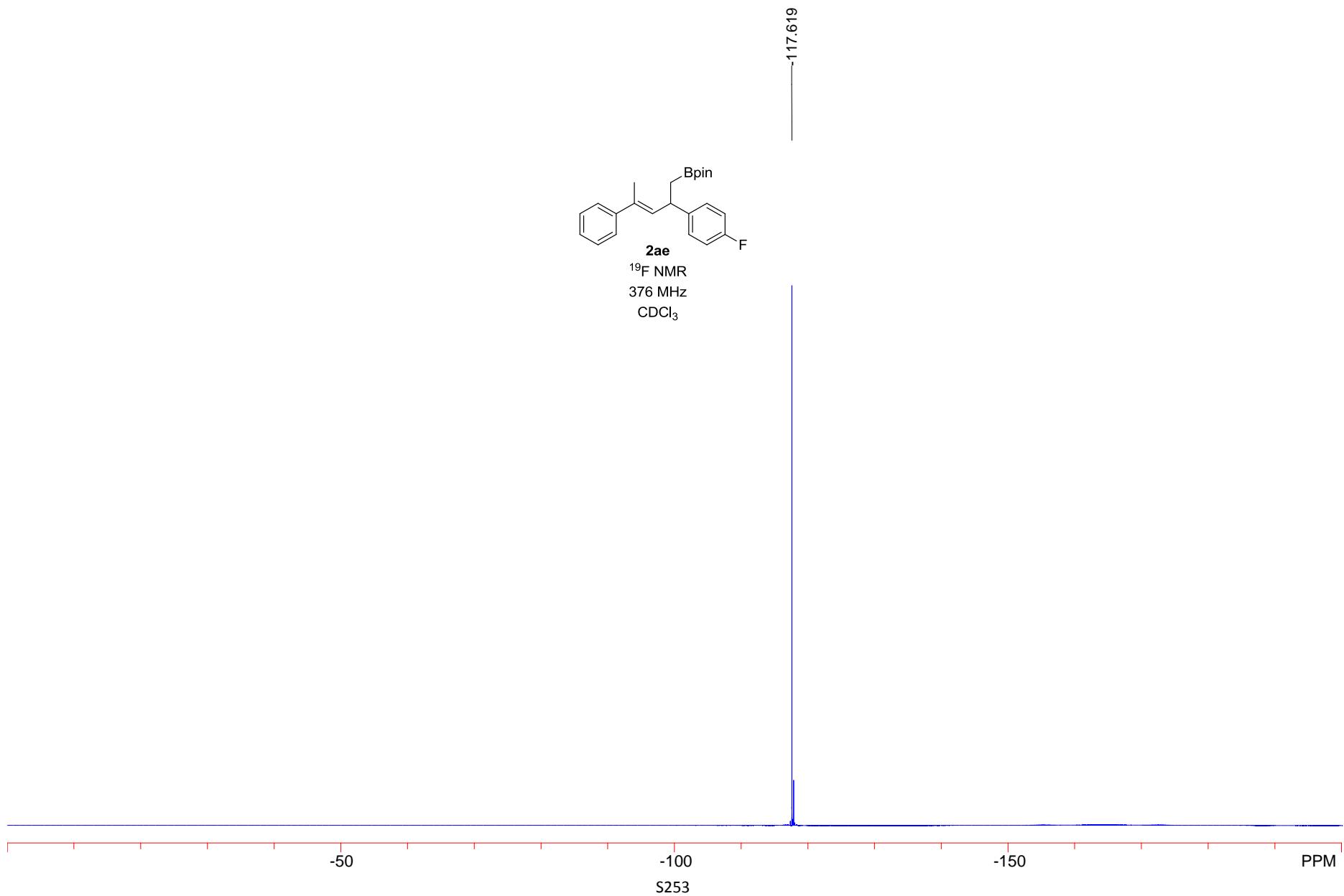




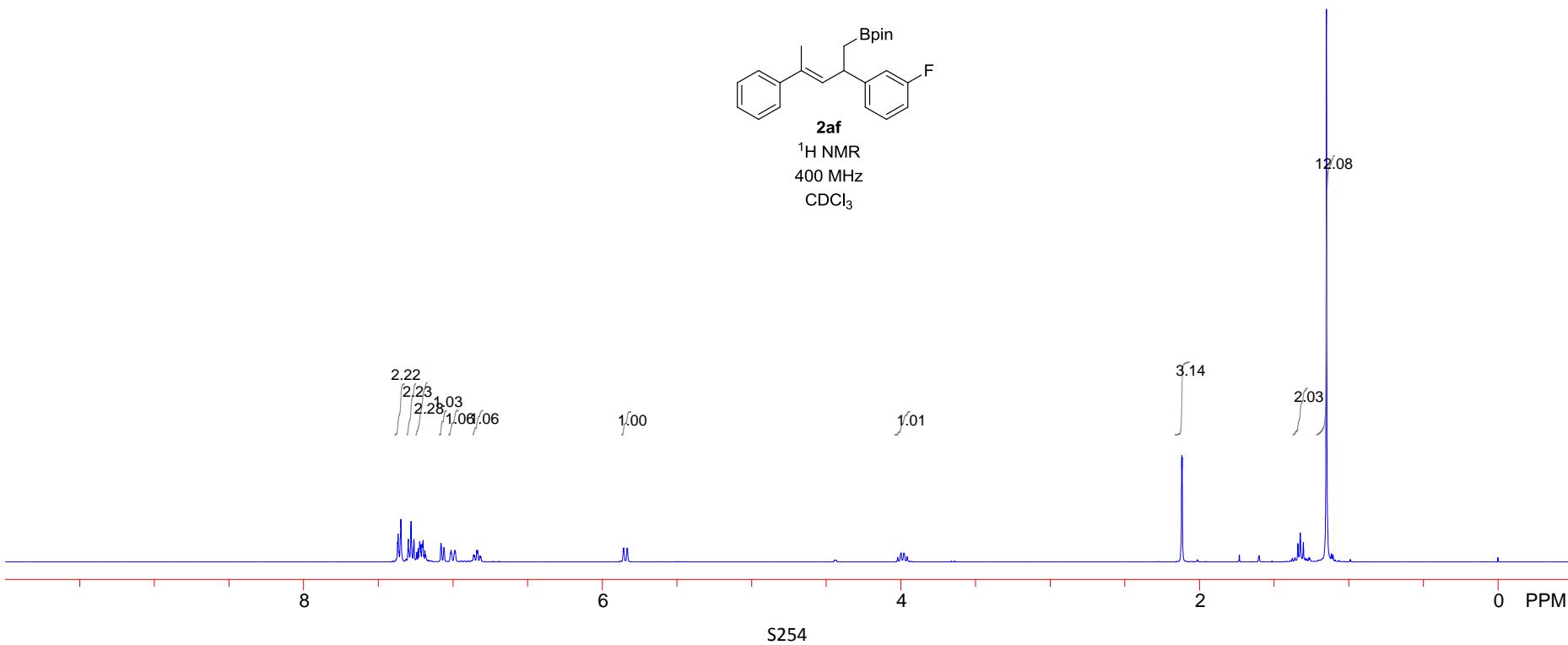
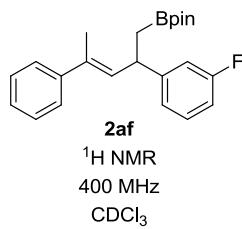
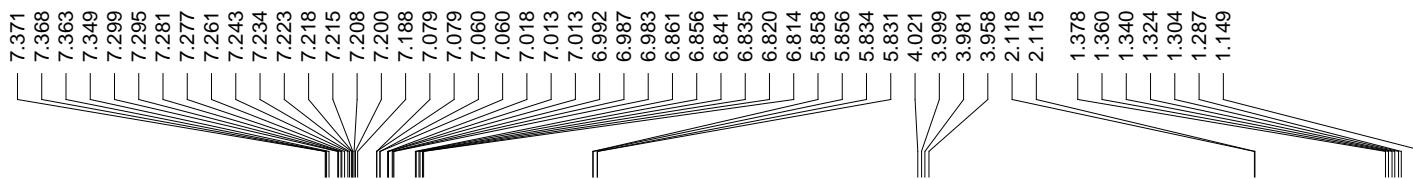


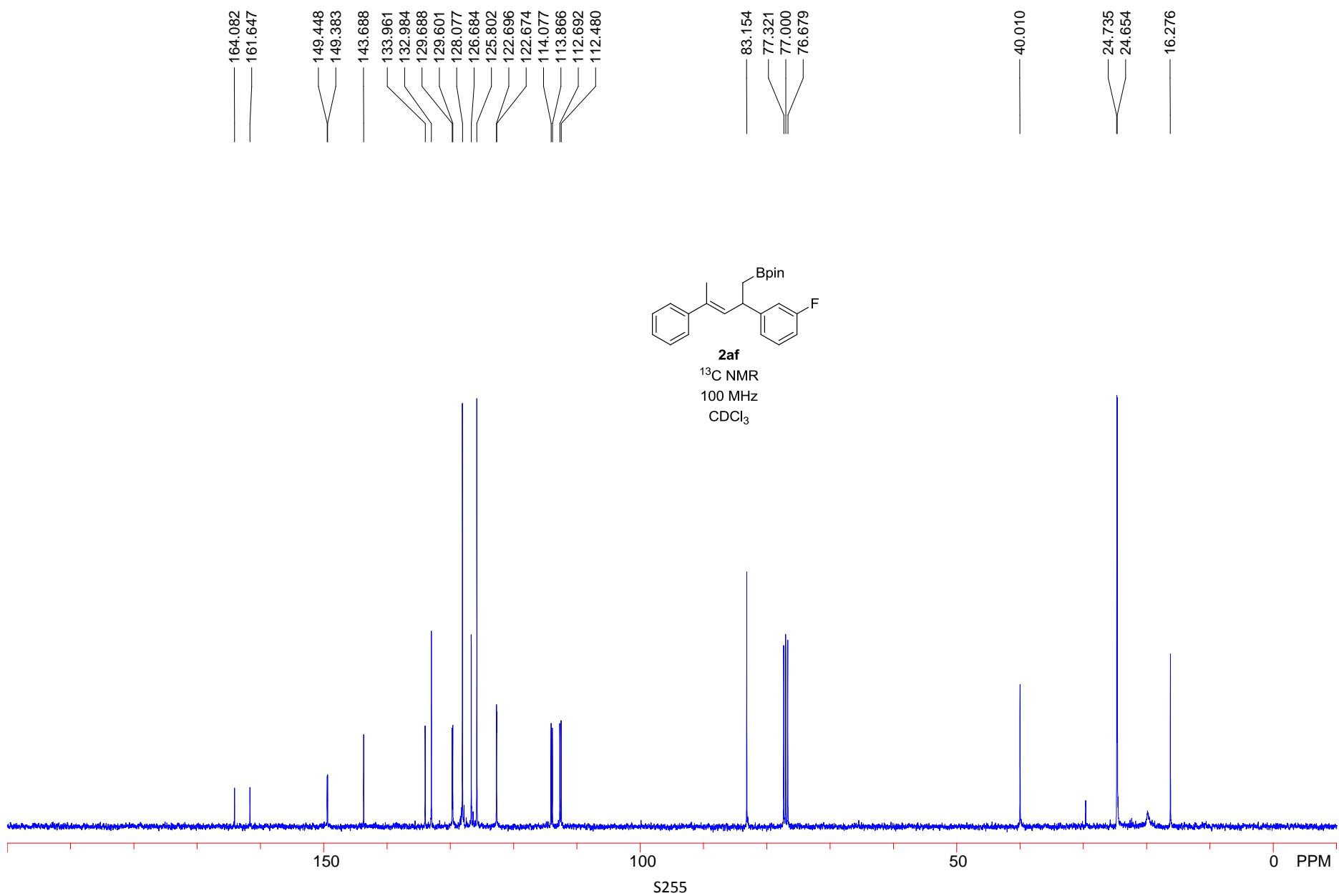


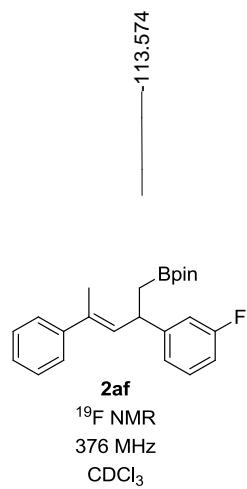
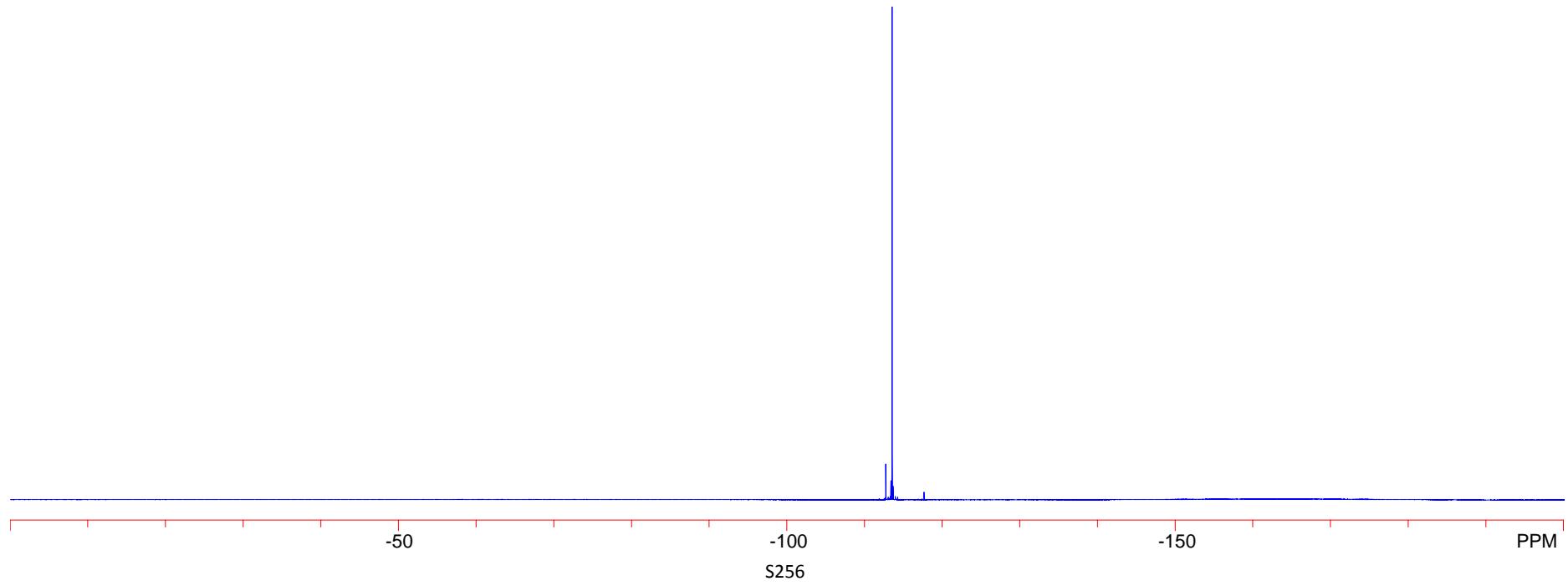


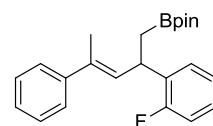
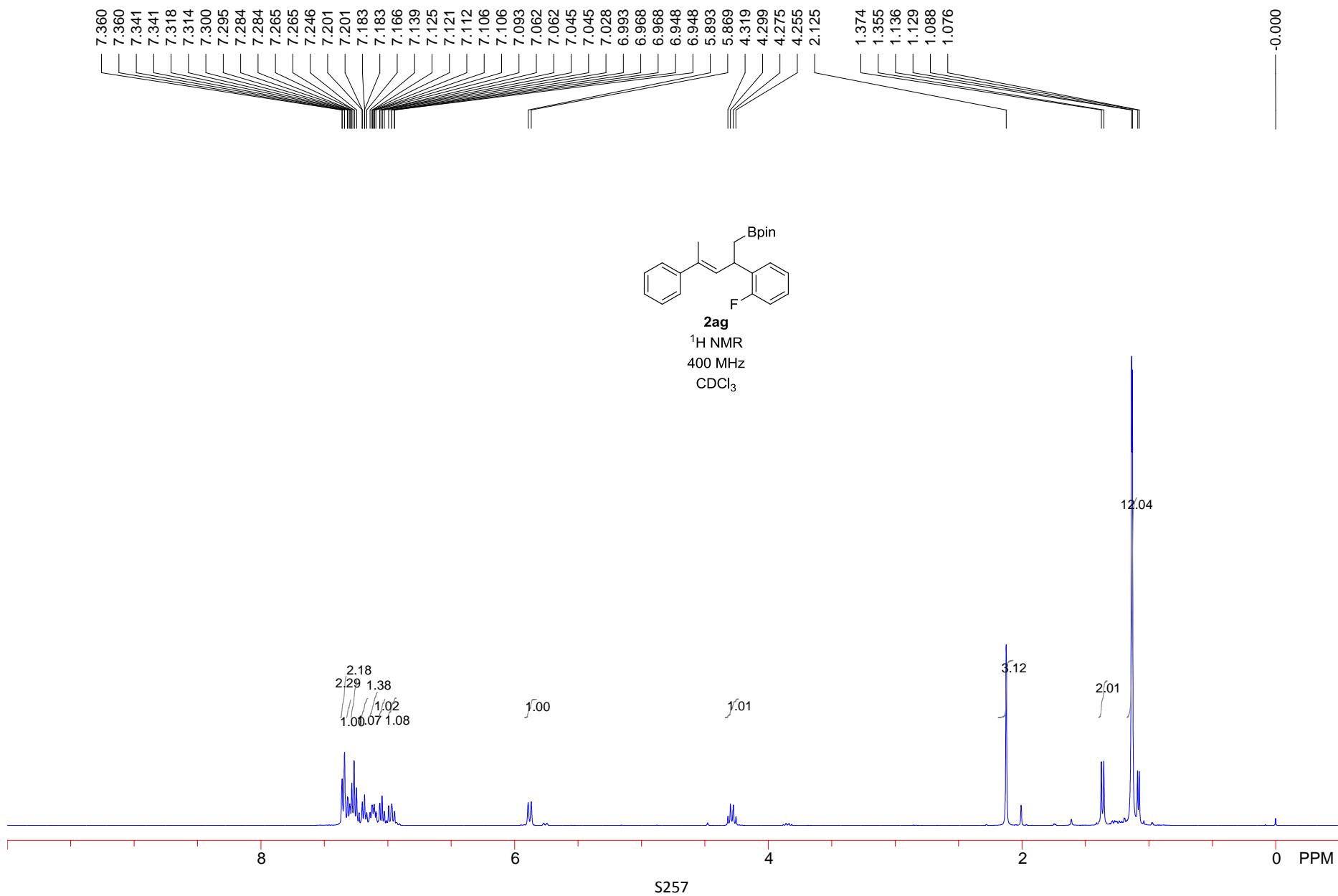


-0.000



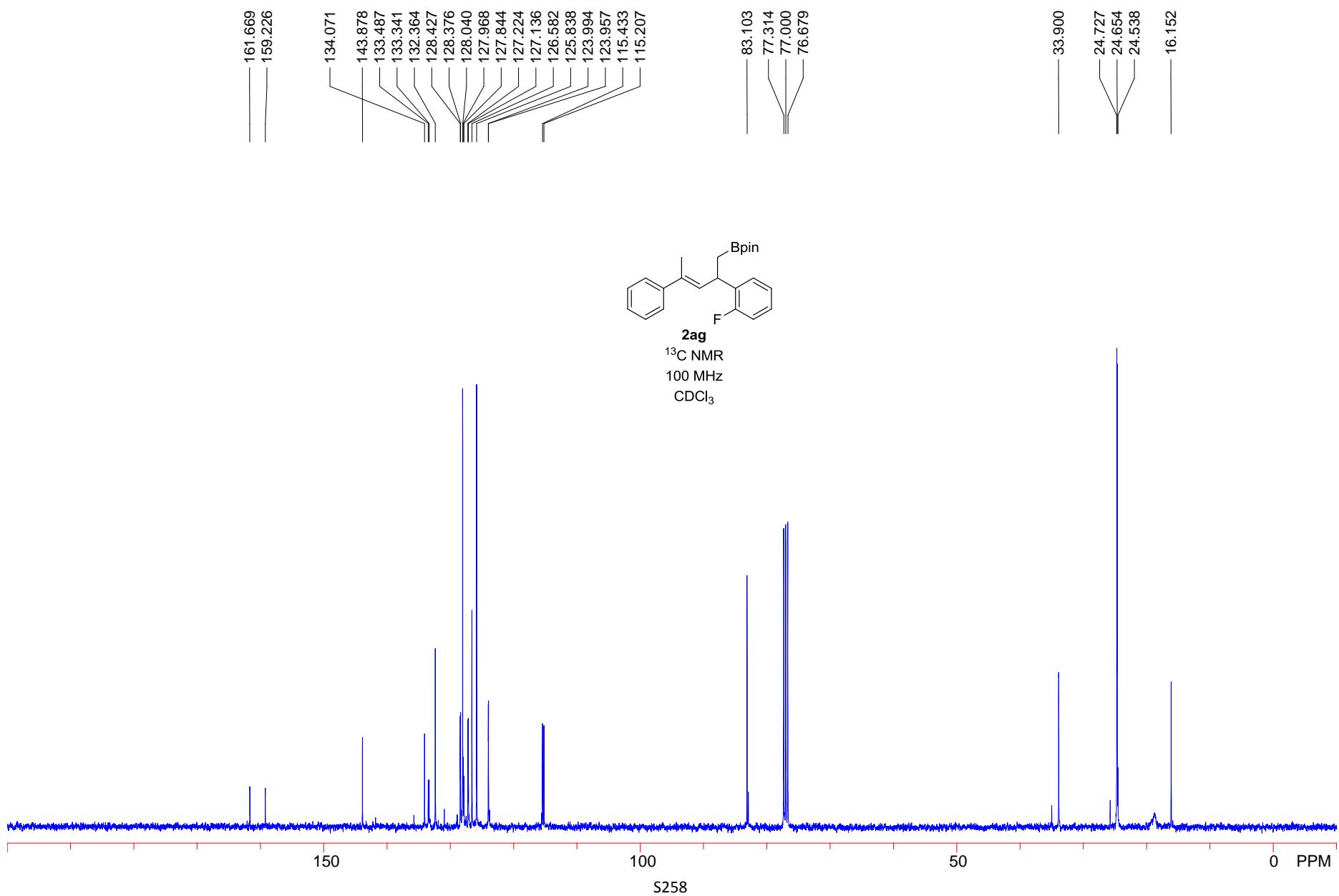


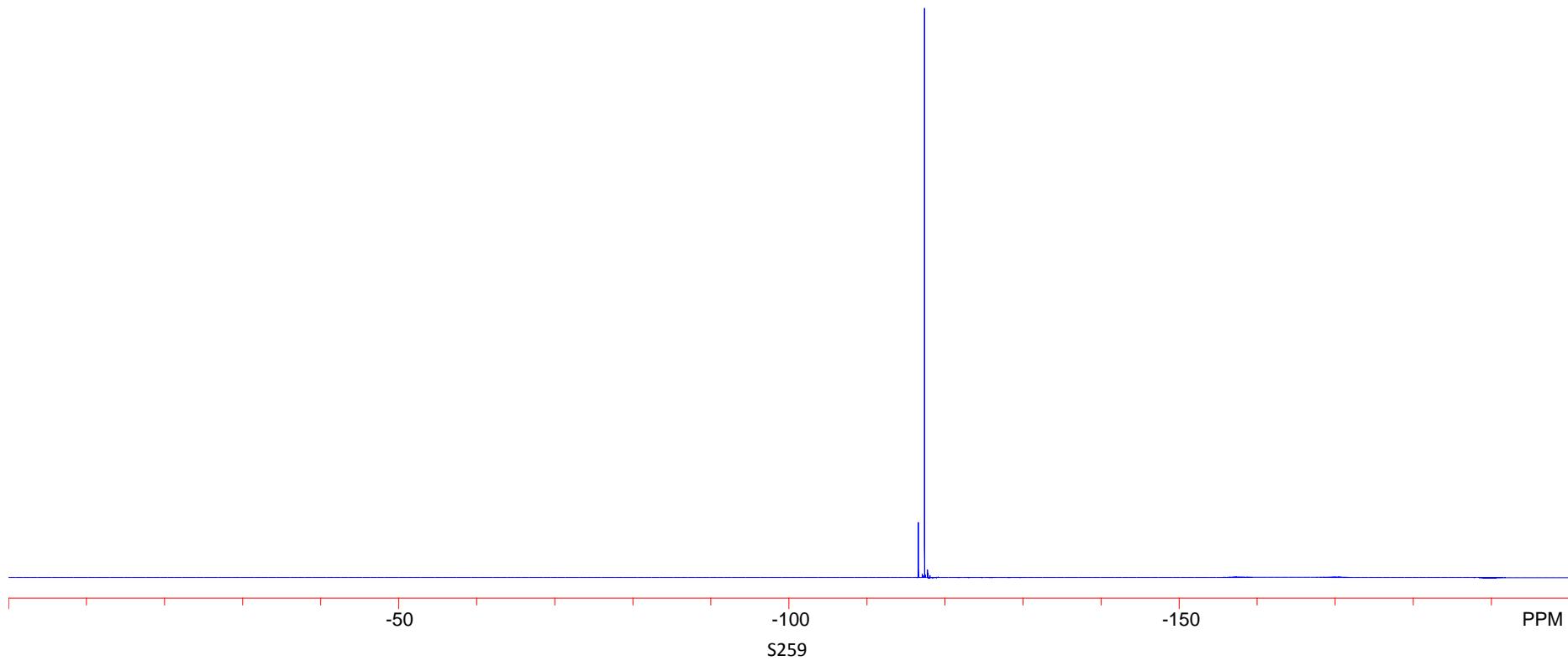
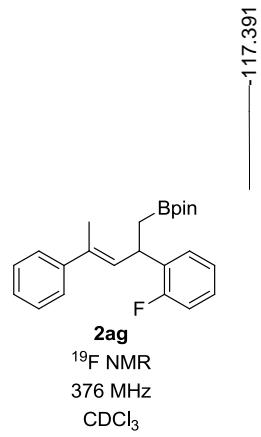


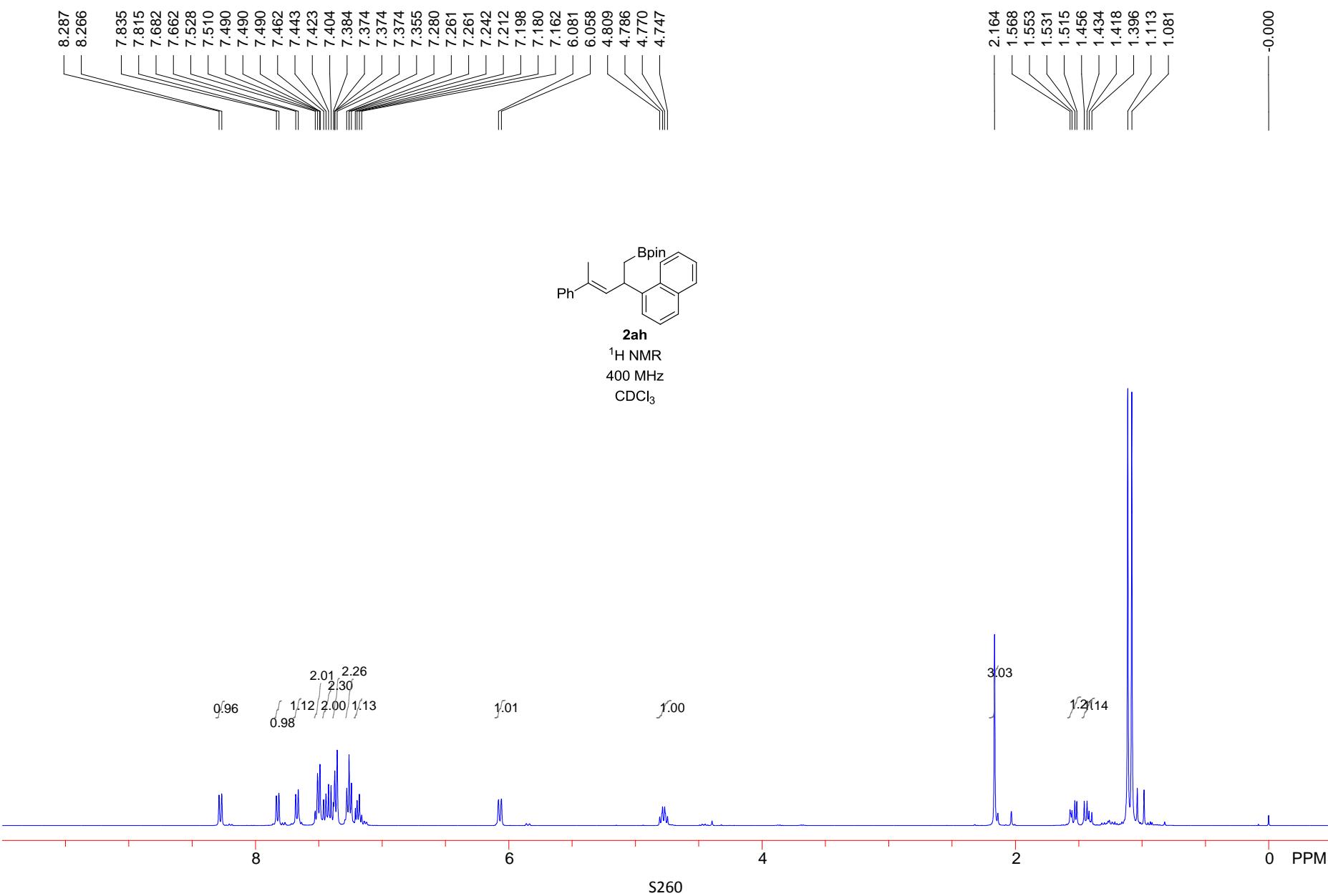


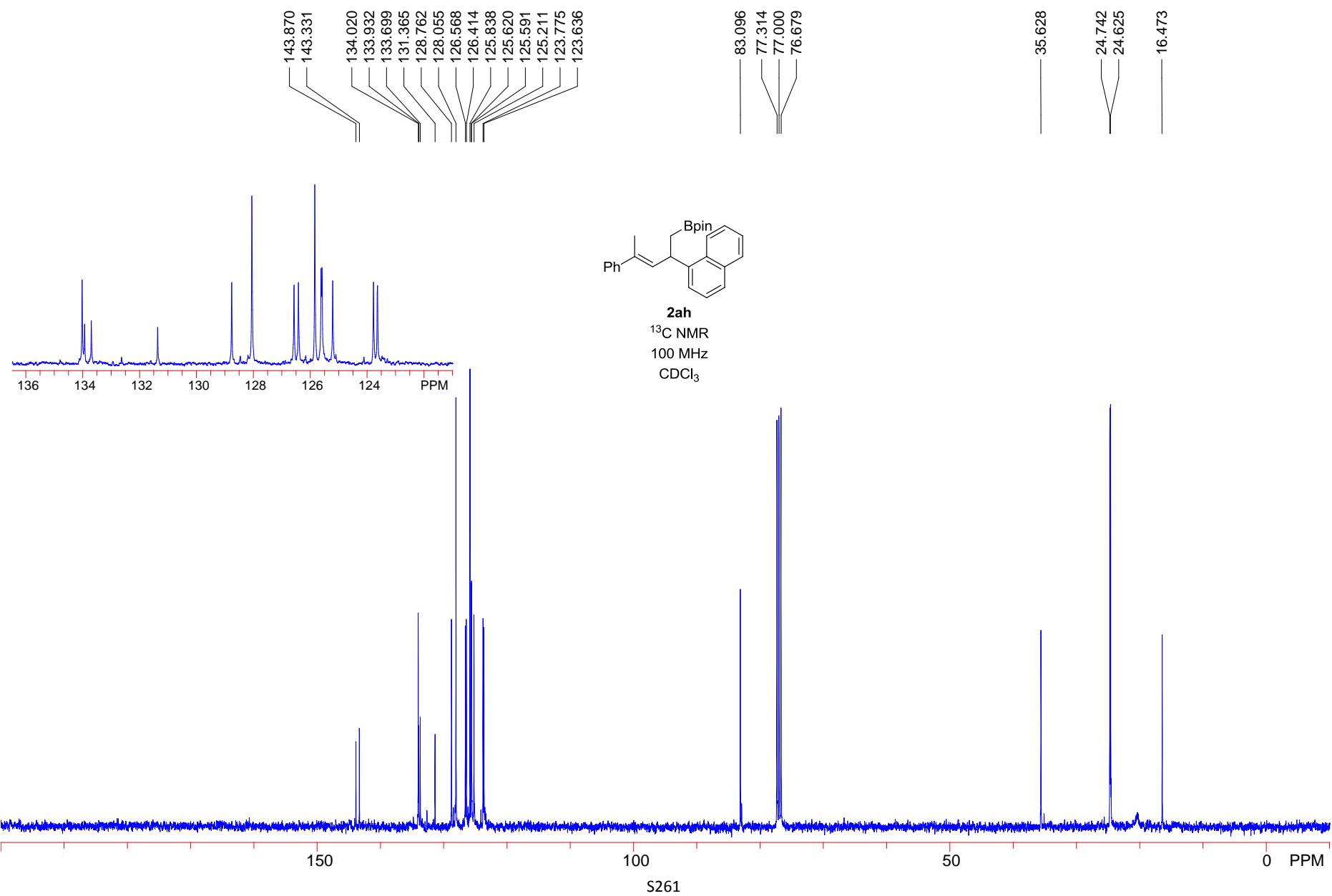
2ag
¹H NMR
400 MHz
CDCl₃

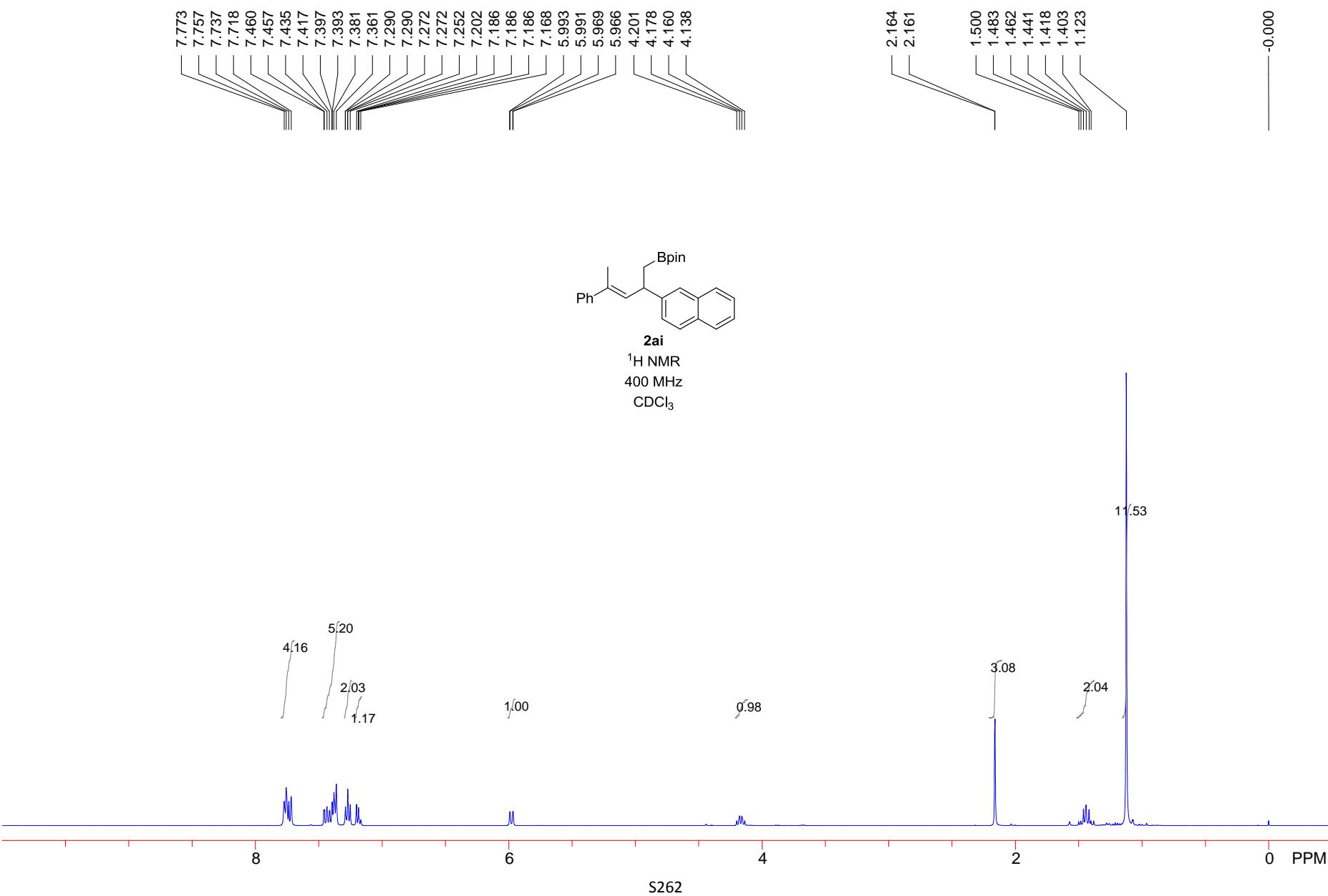
¹H NMR
400 MHz
CDCl₃

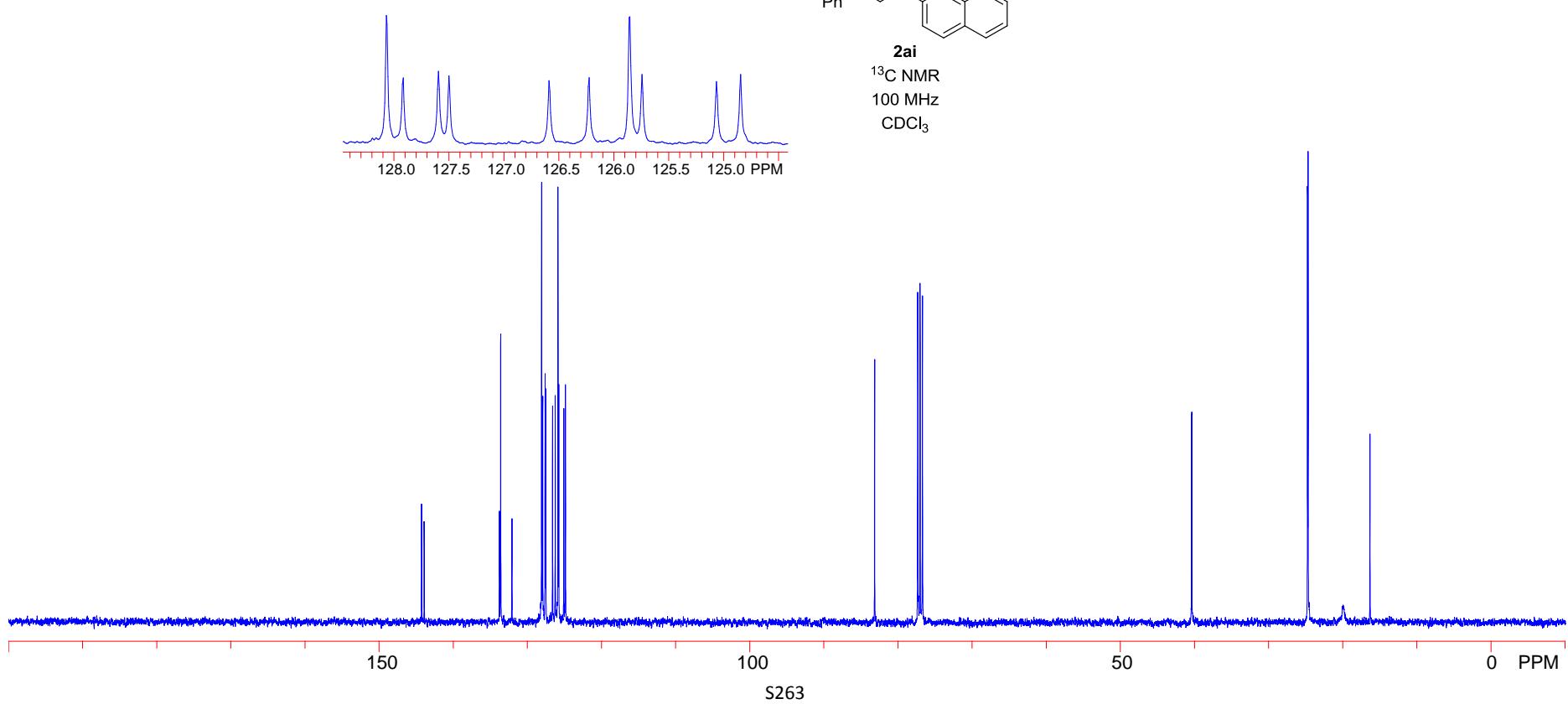


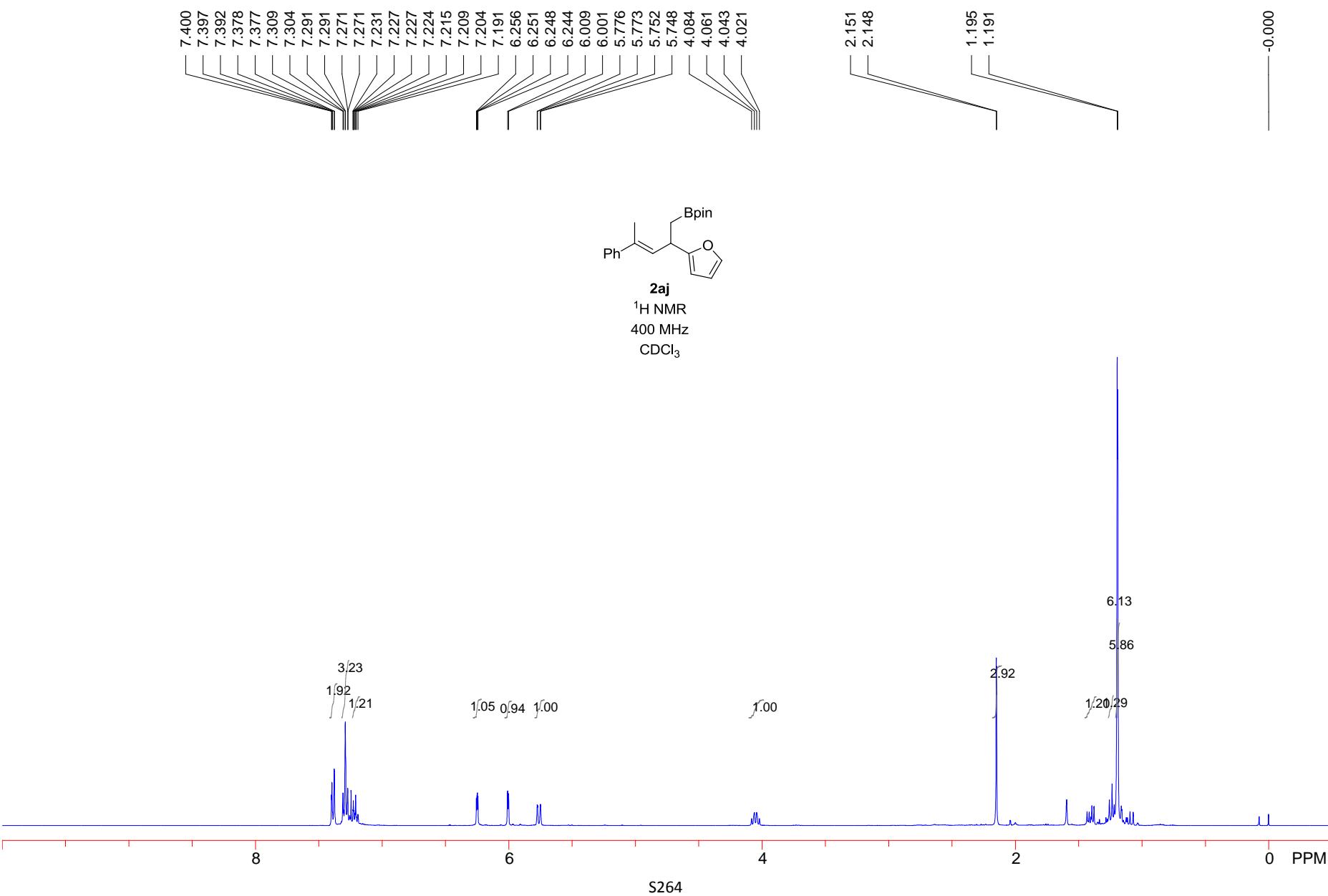


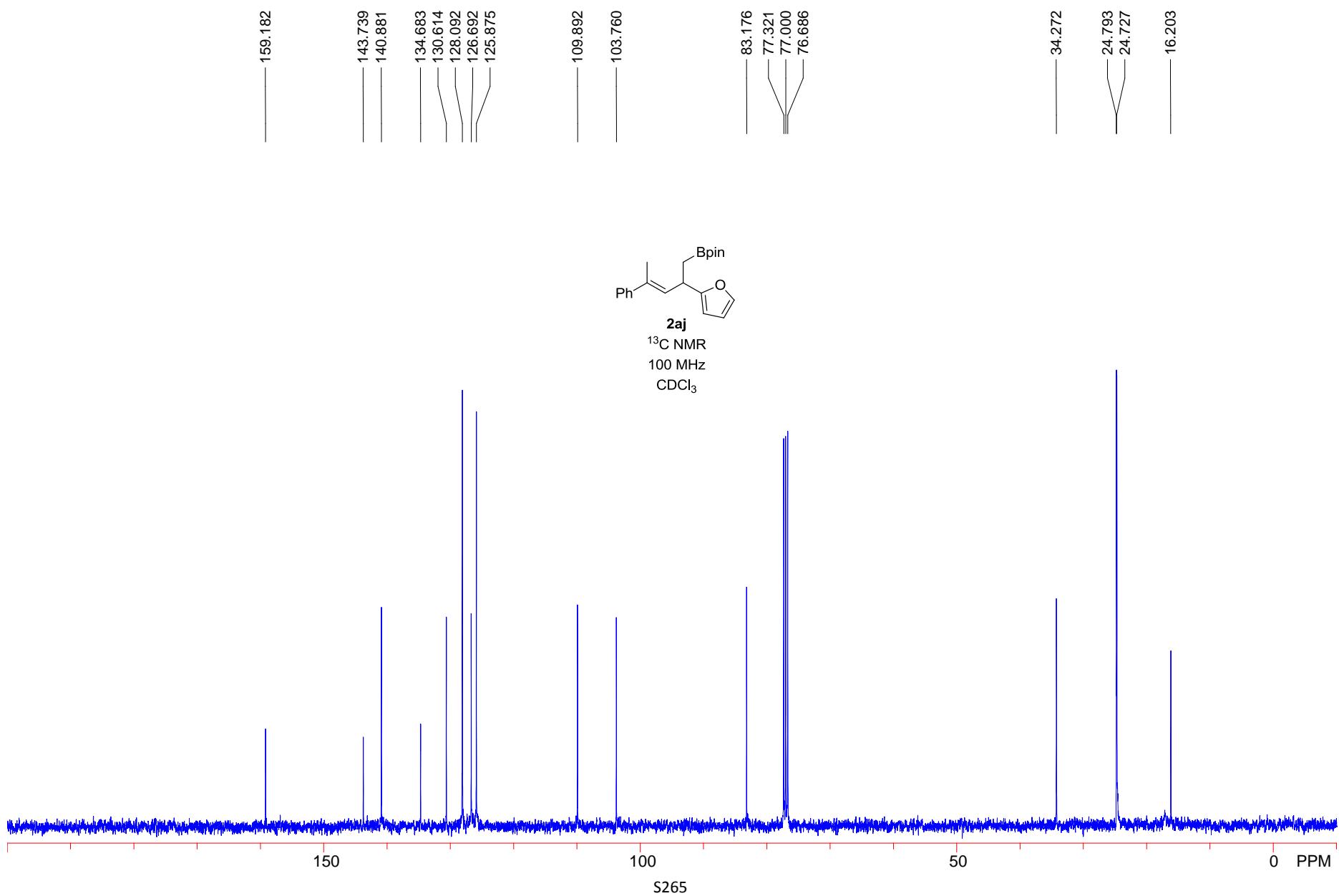


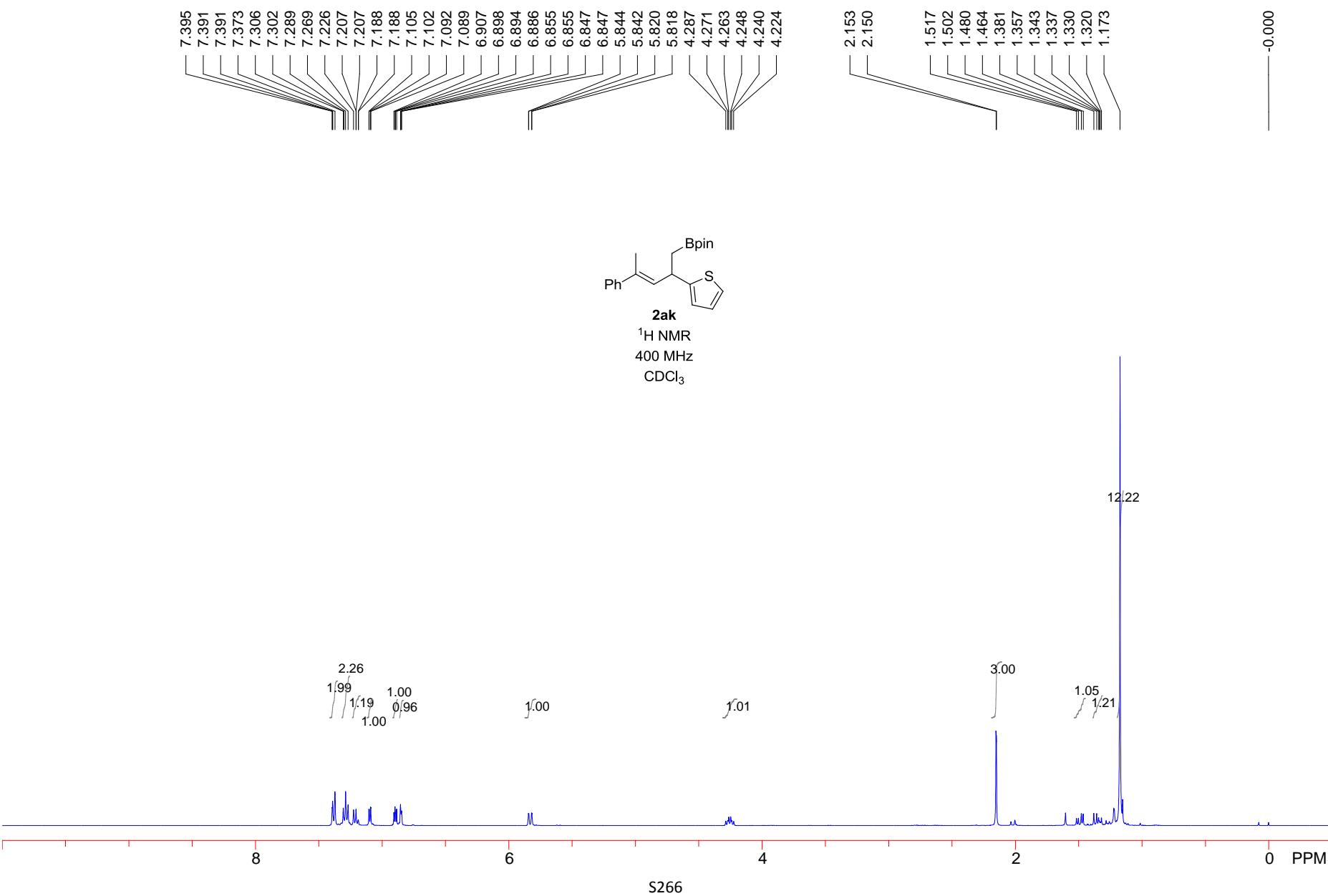


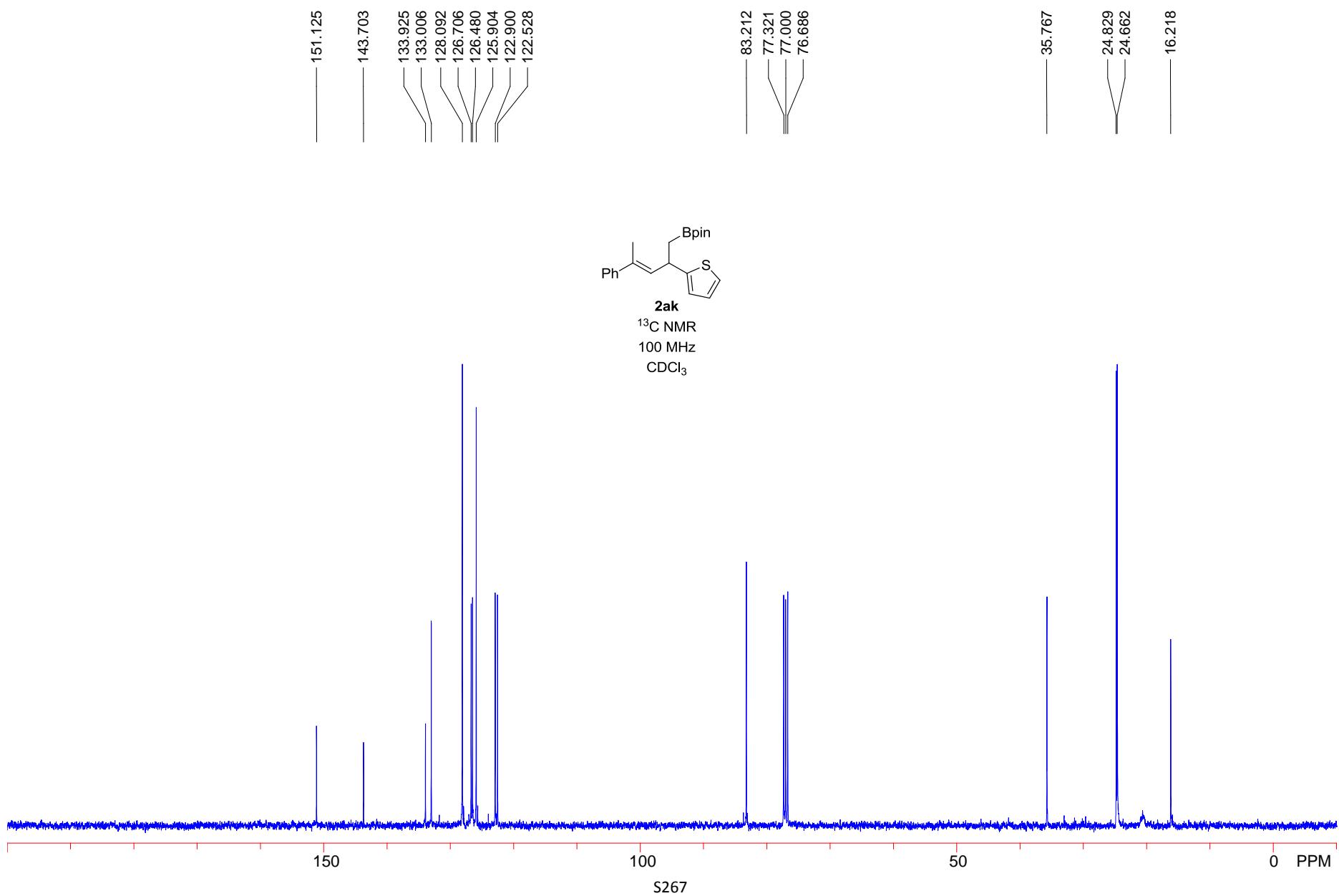


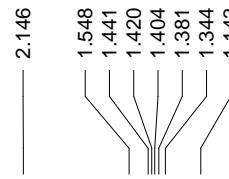
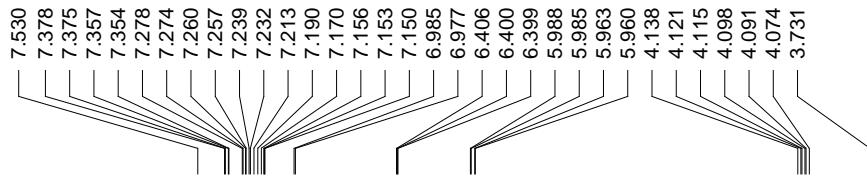




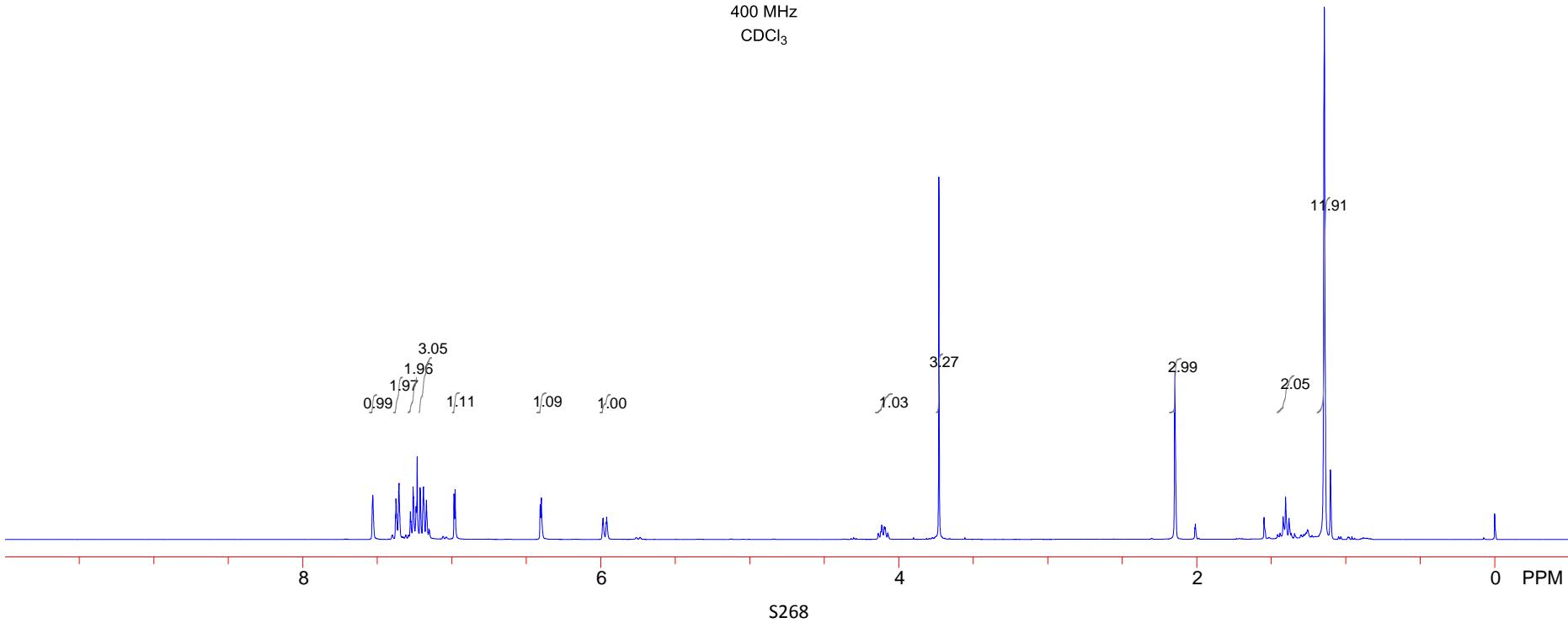
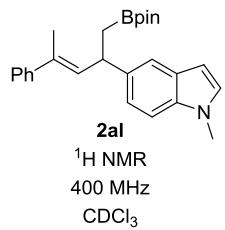


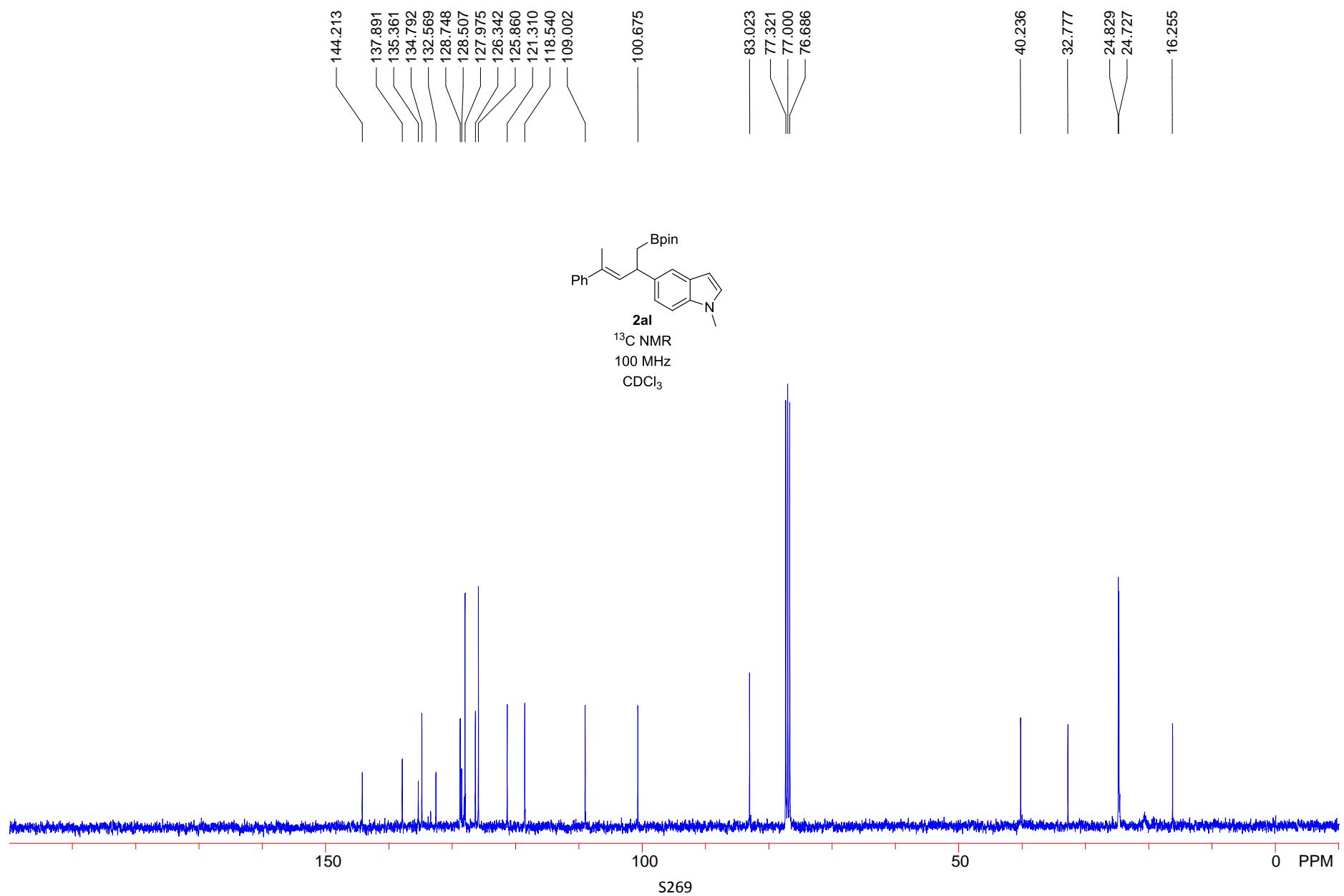


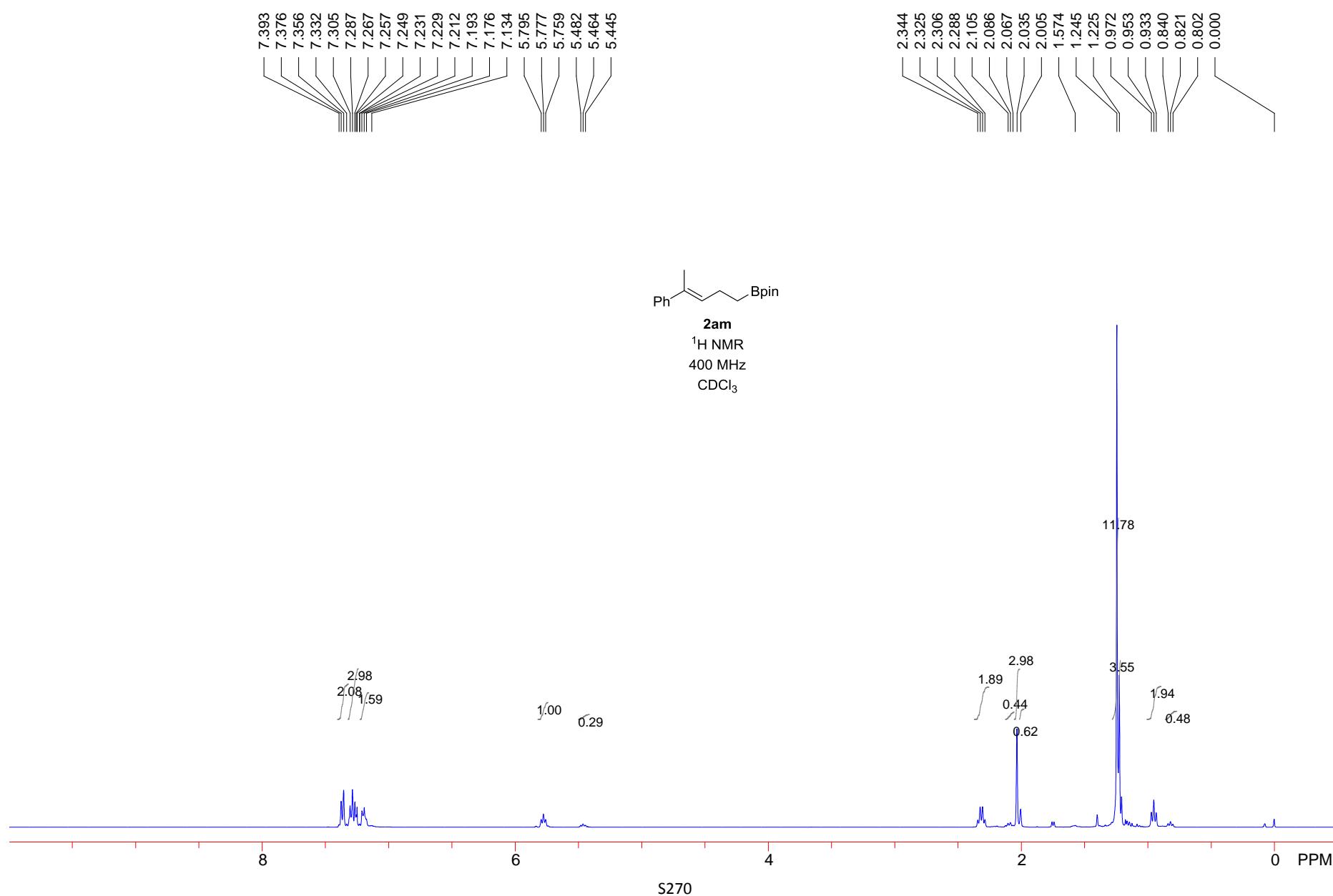


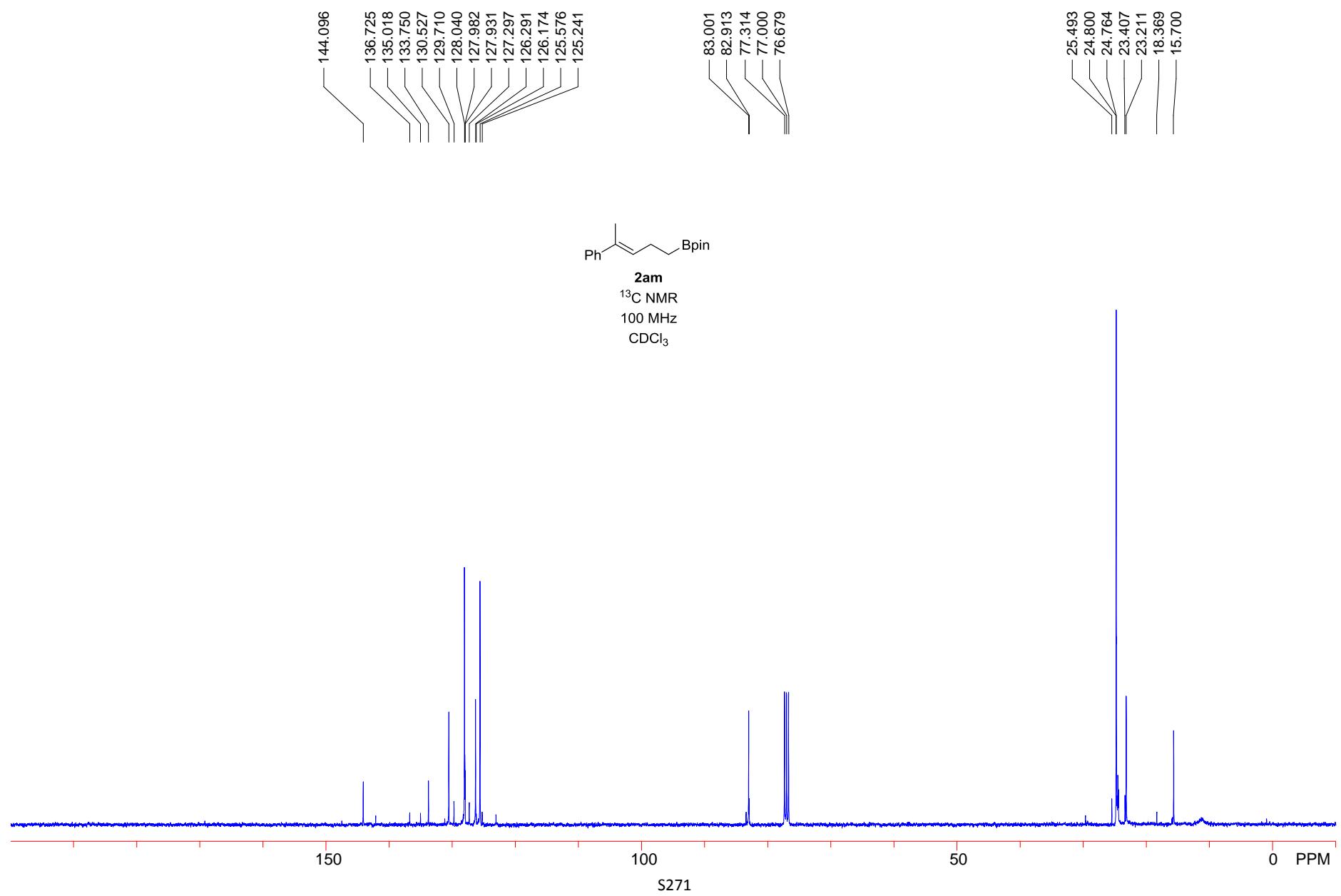


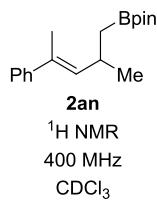
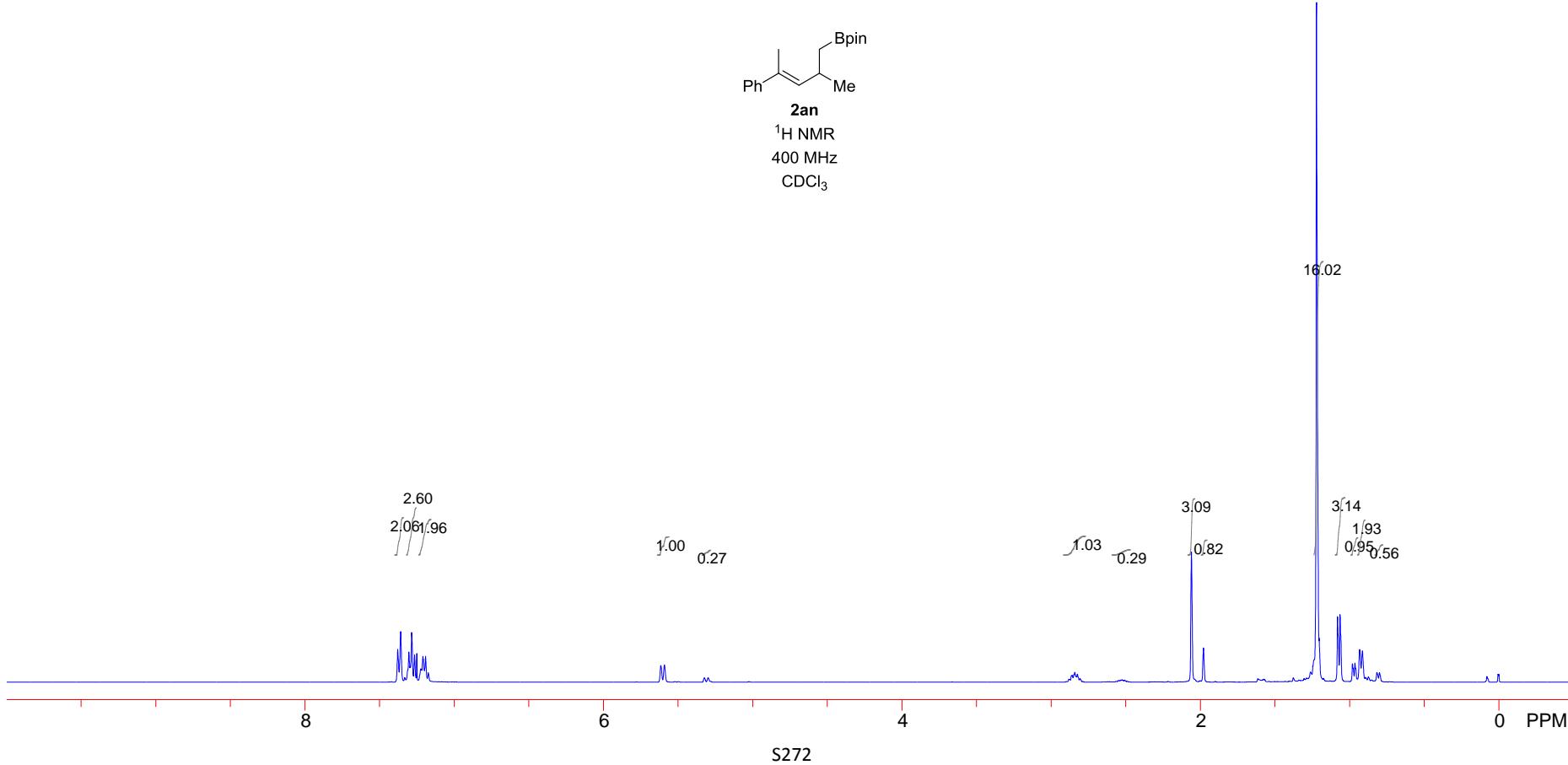
-0.000





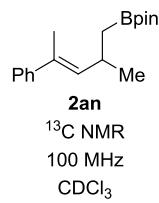
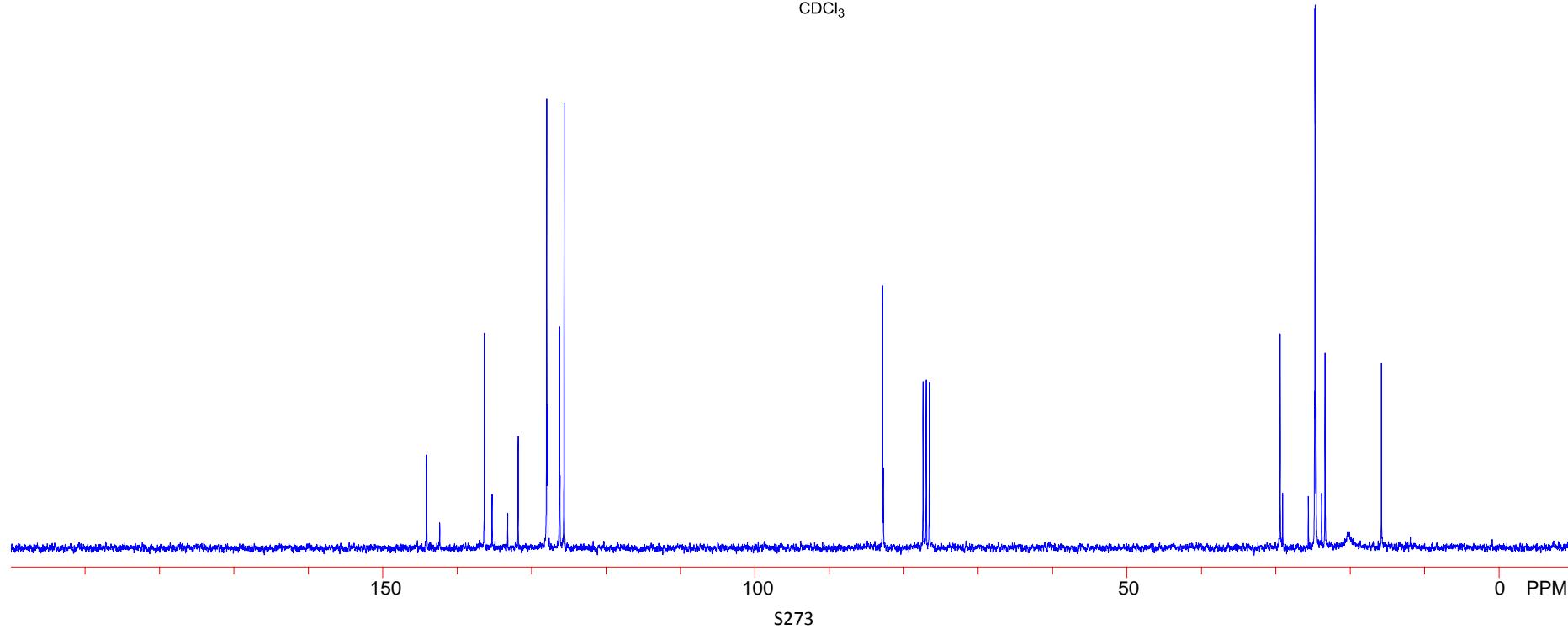


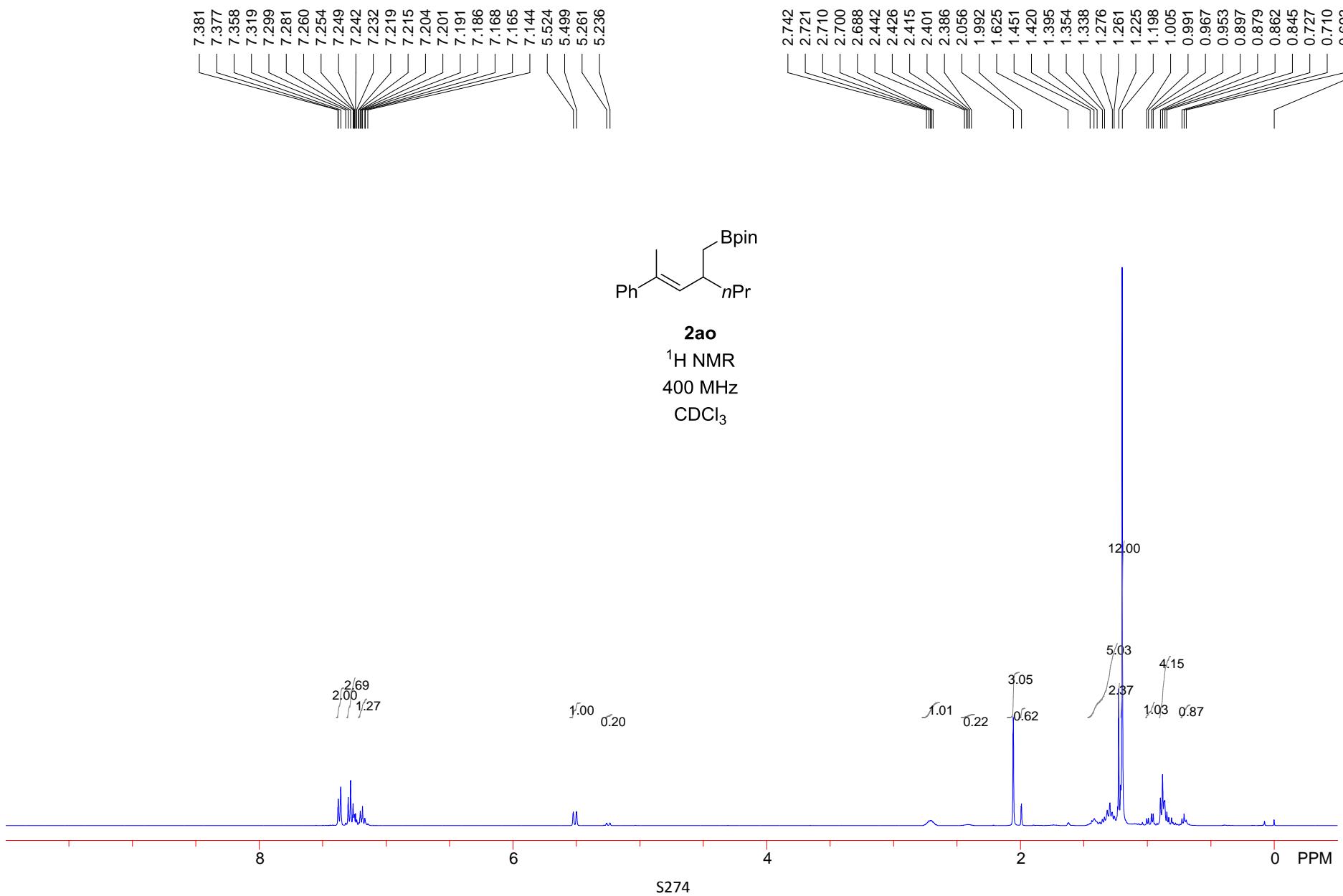


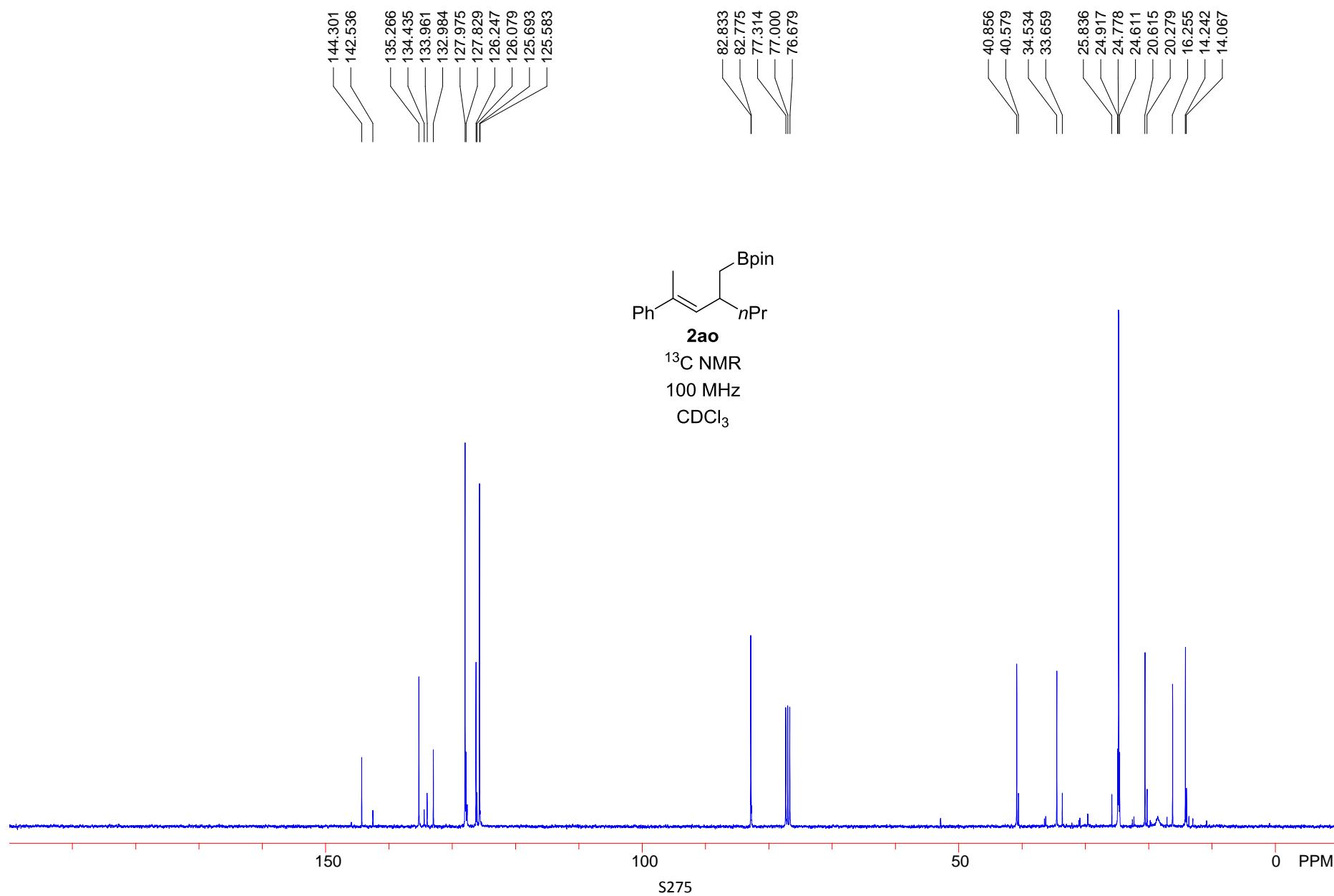


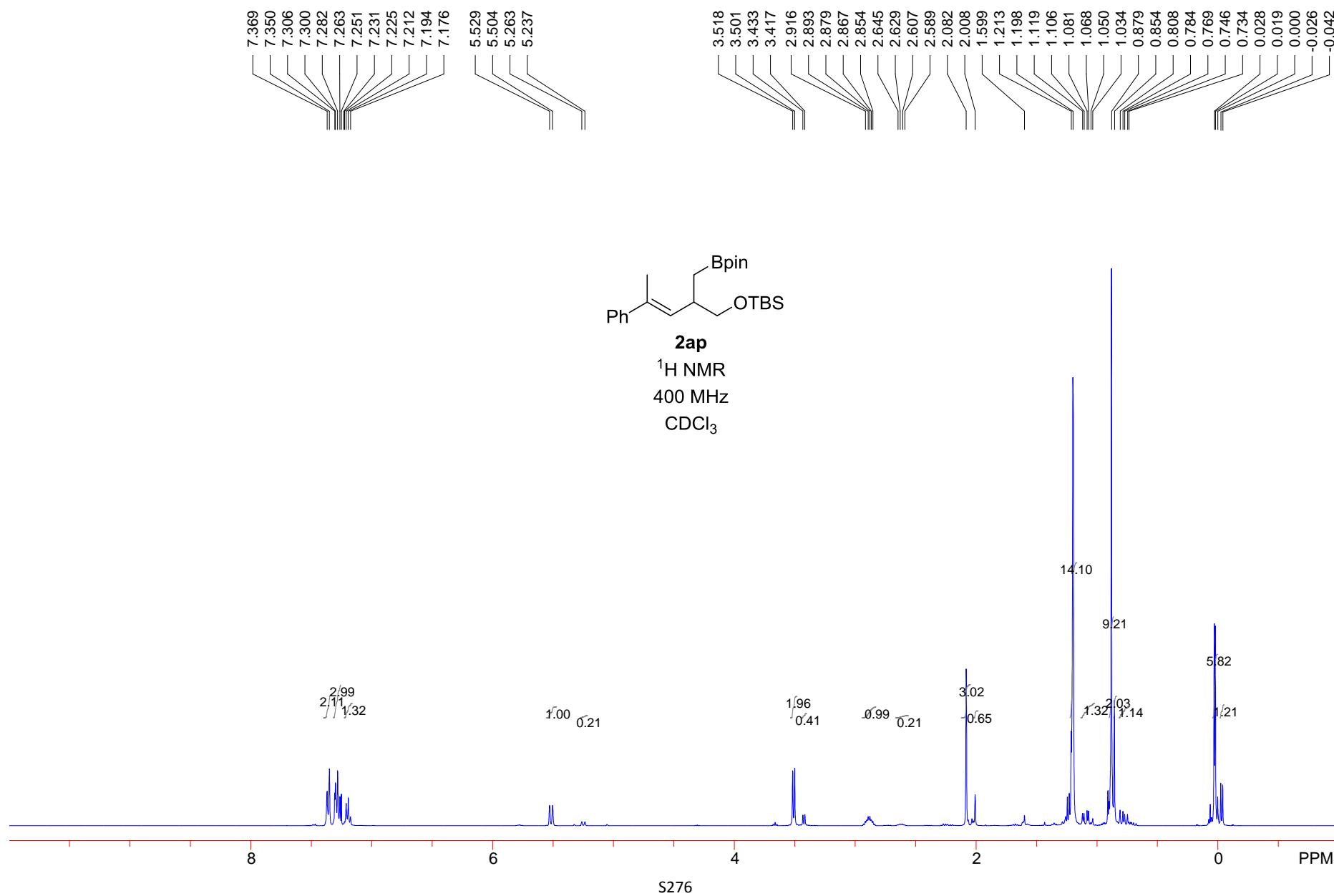
7.378
7.359
7.332
7.304
7.295
7.285
7.266
7.251
7.223
7.219
7.210
7.207
7.192
7.174
5.616
5.592
5.324
5.299

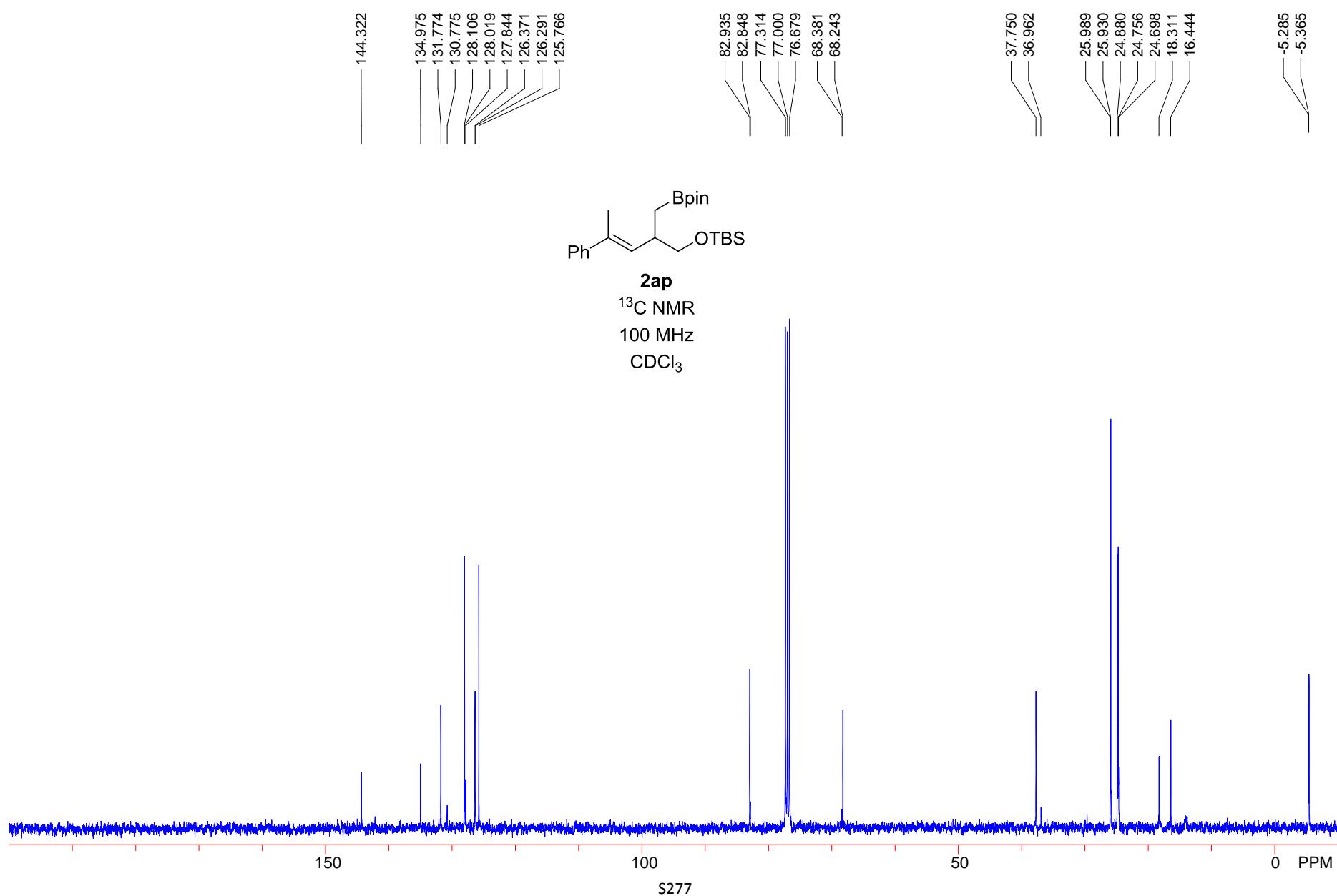
2.881
2.877
2.864
2.859
2.847
2.842
2.824
2.807
2.790
2.567
2.561
2.550
2.543
2.534
2.526
2.517
2.509
2.492
2.059
1.979
1.616
1.222
1.080
0.981
0.964
0.932
0.914
0.817
0.799
-0.000

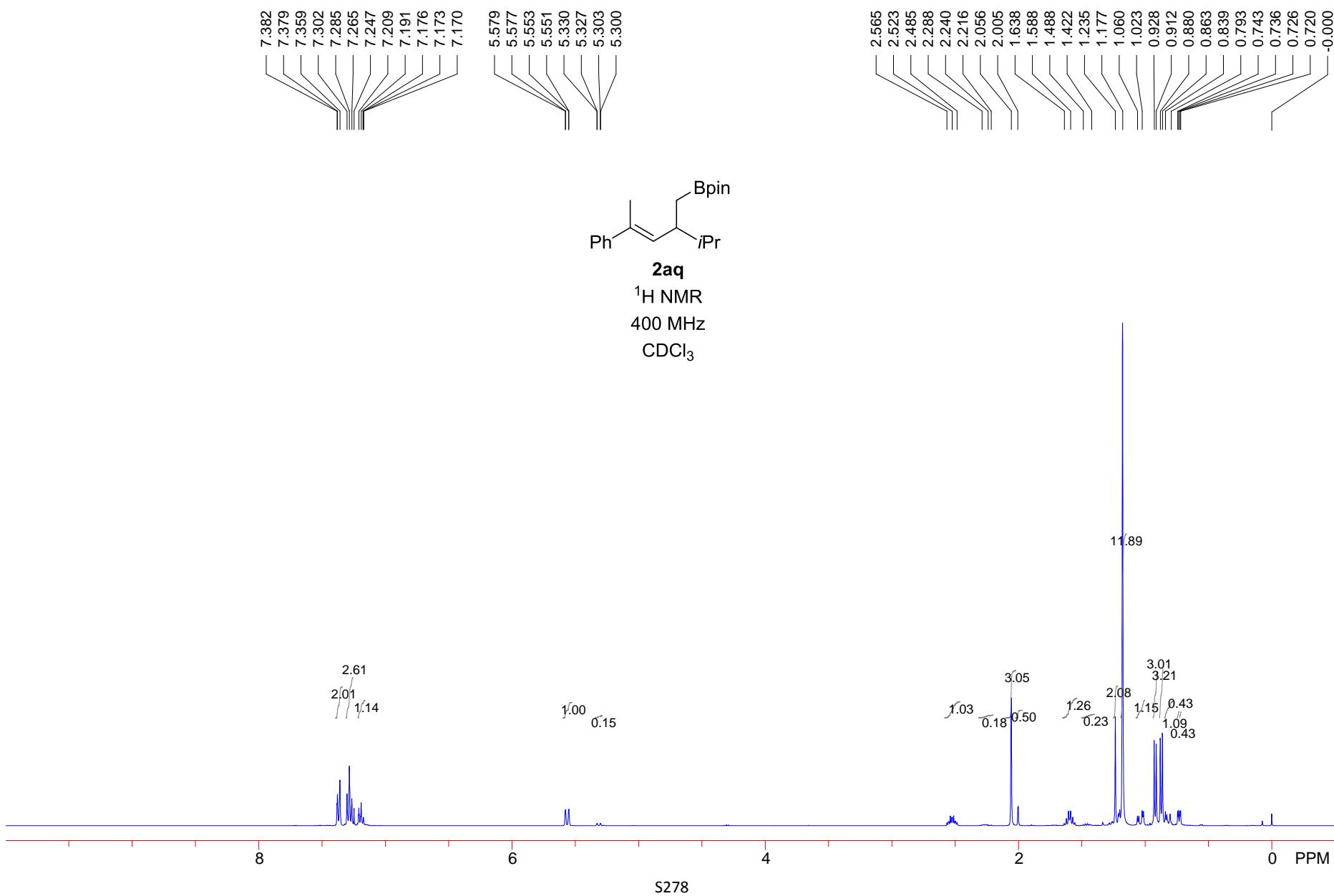


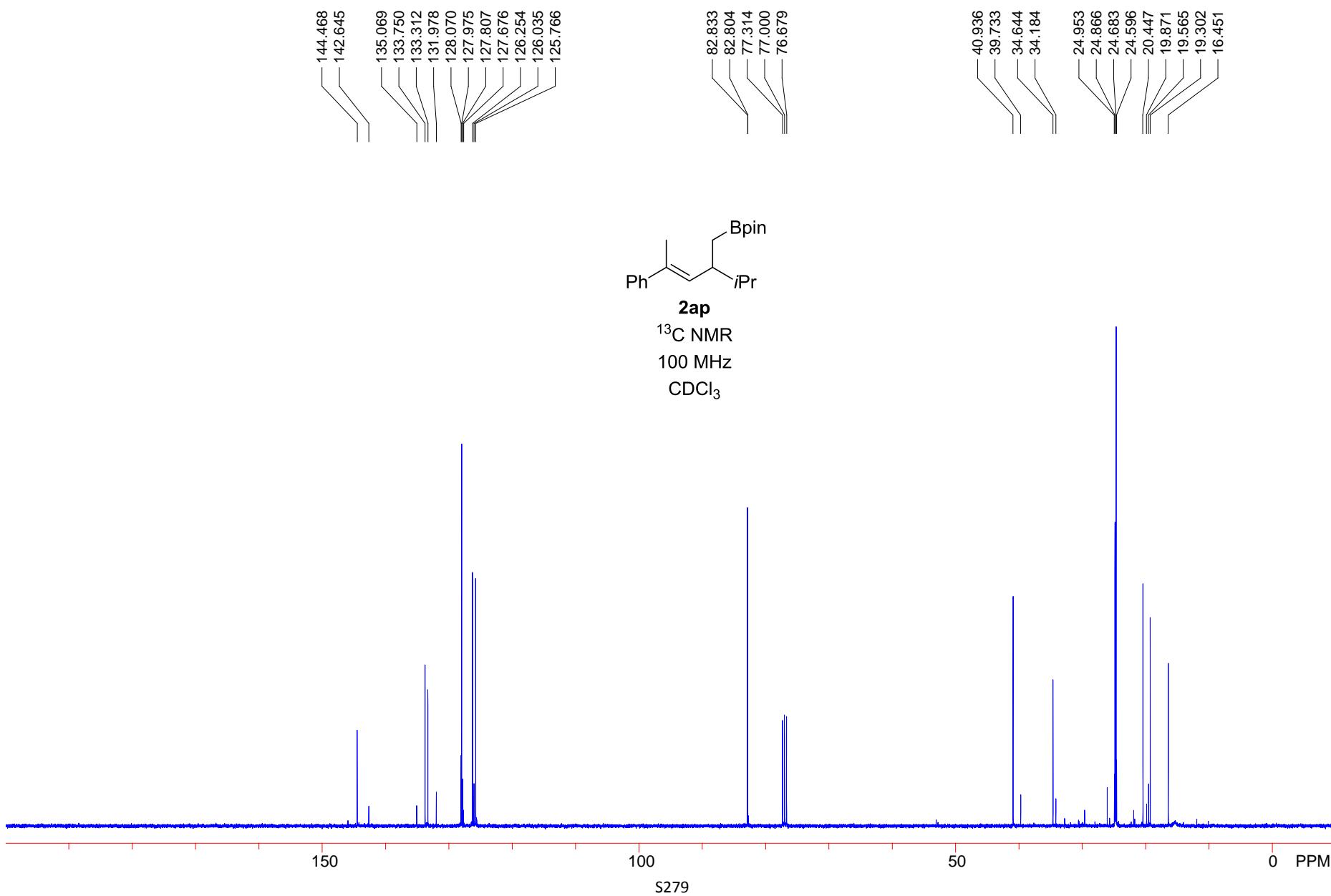


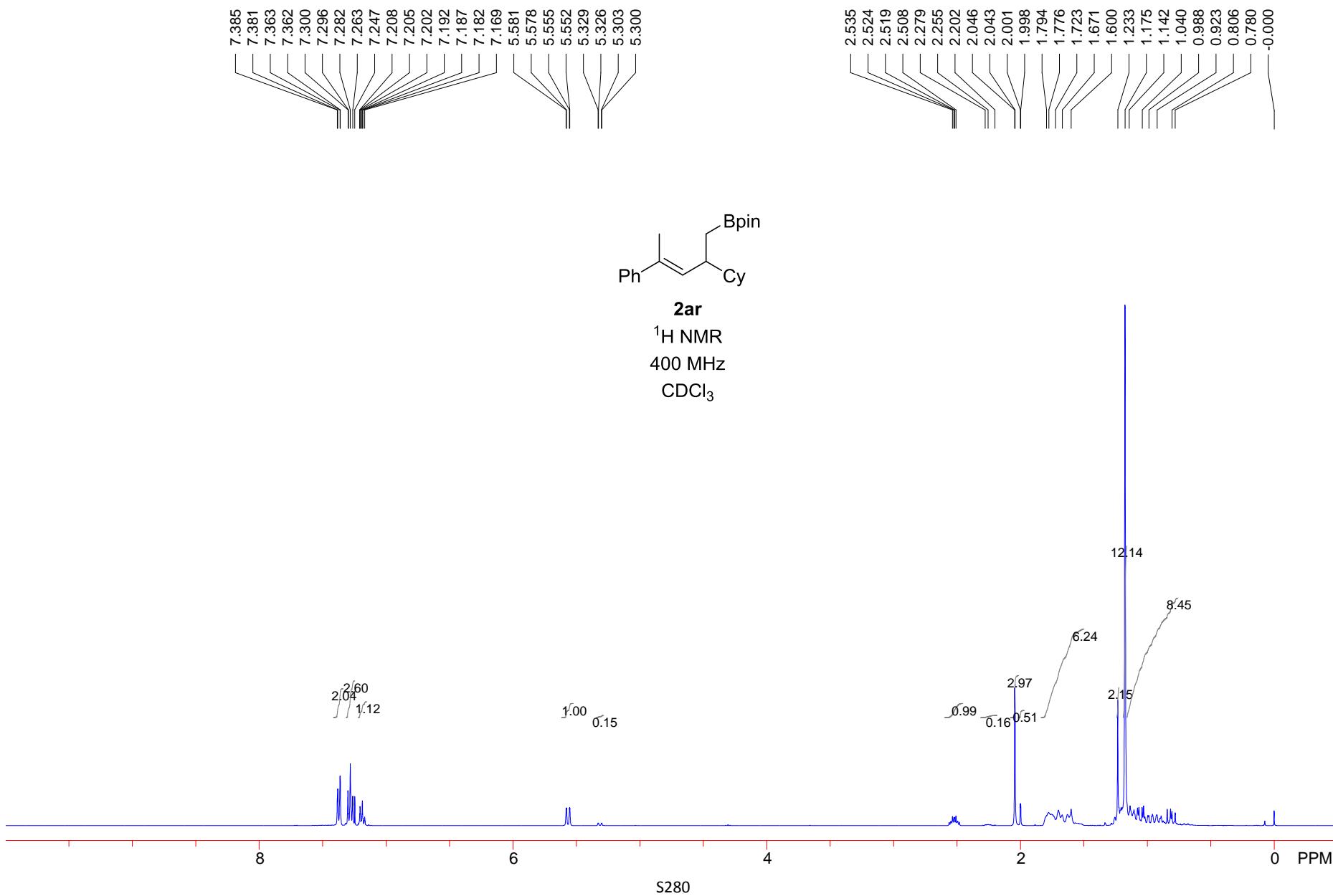


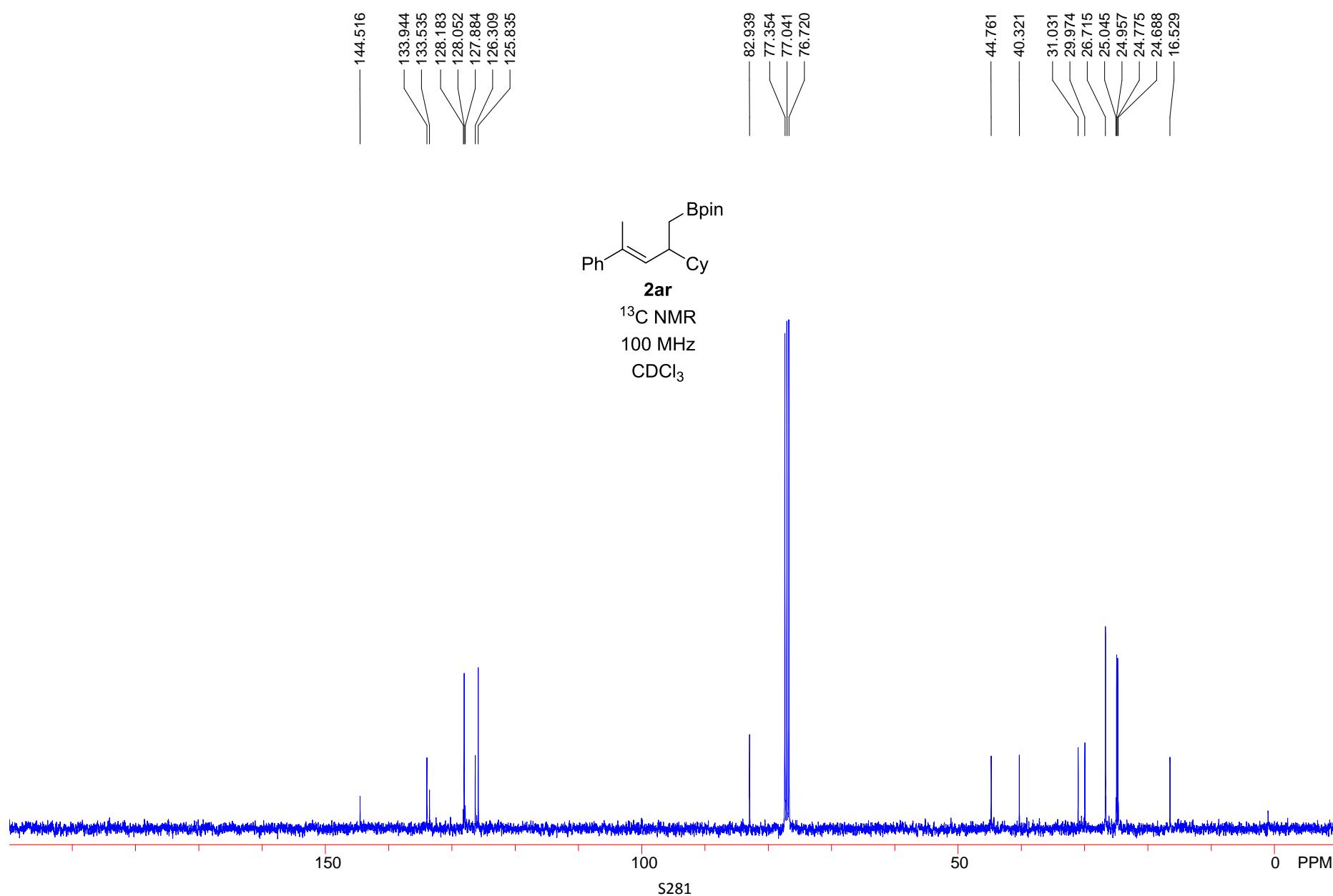


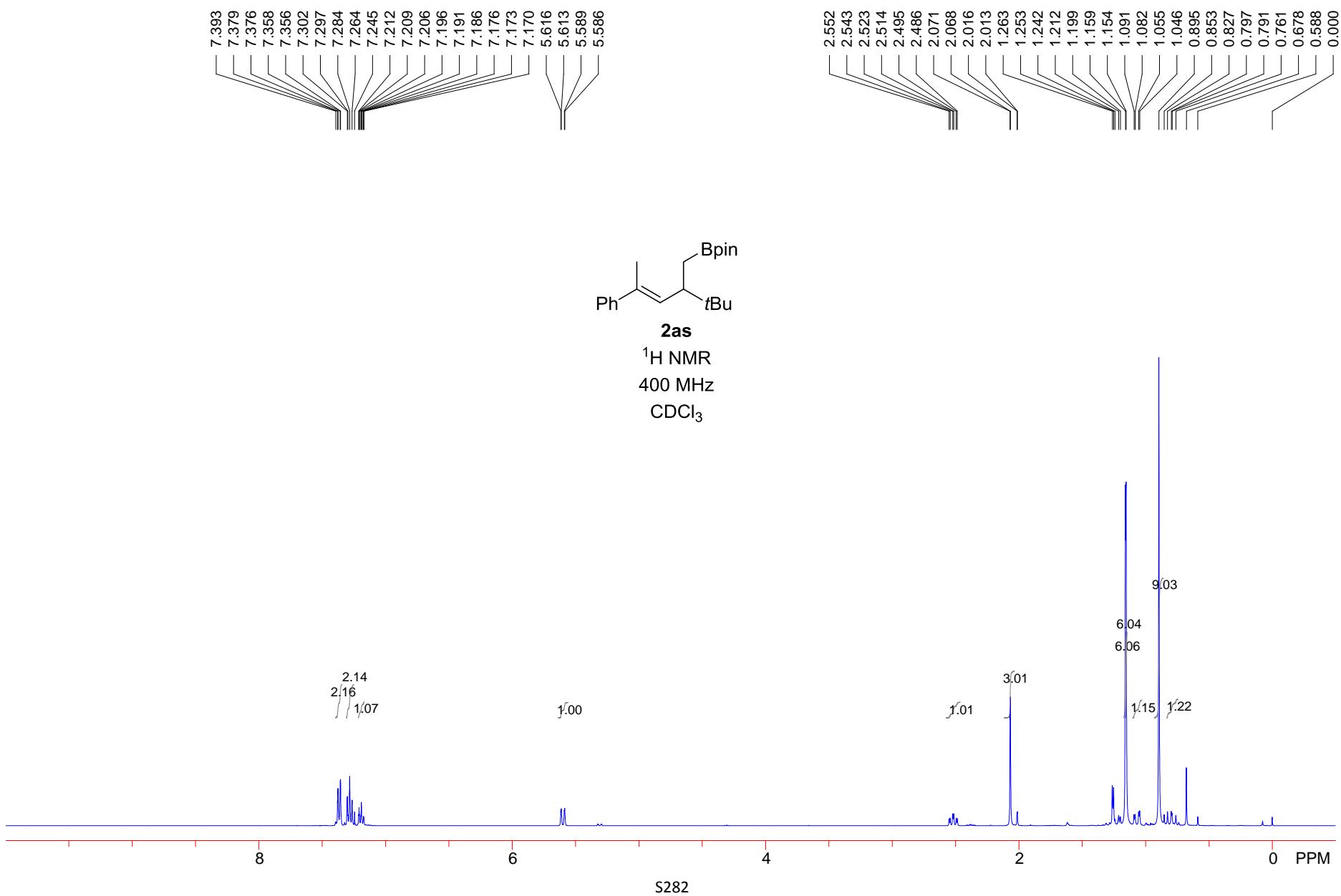


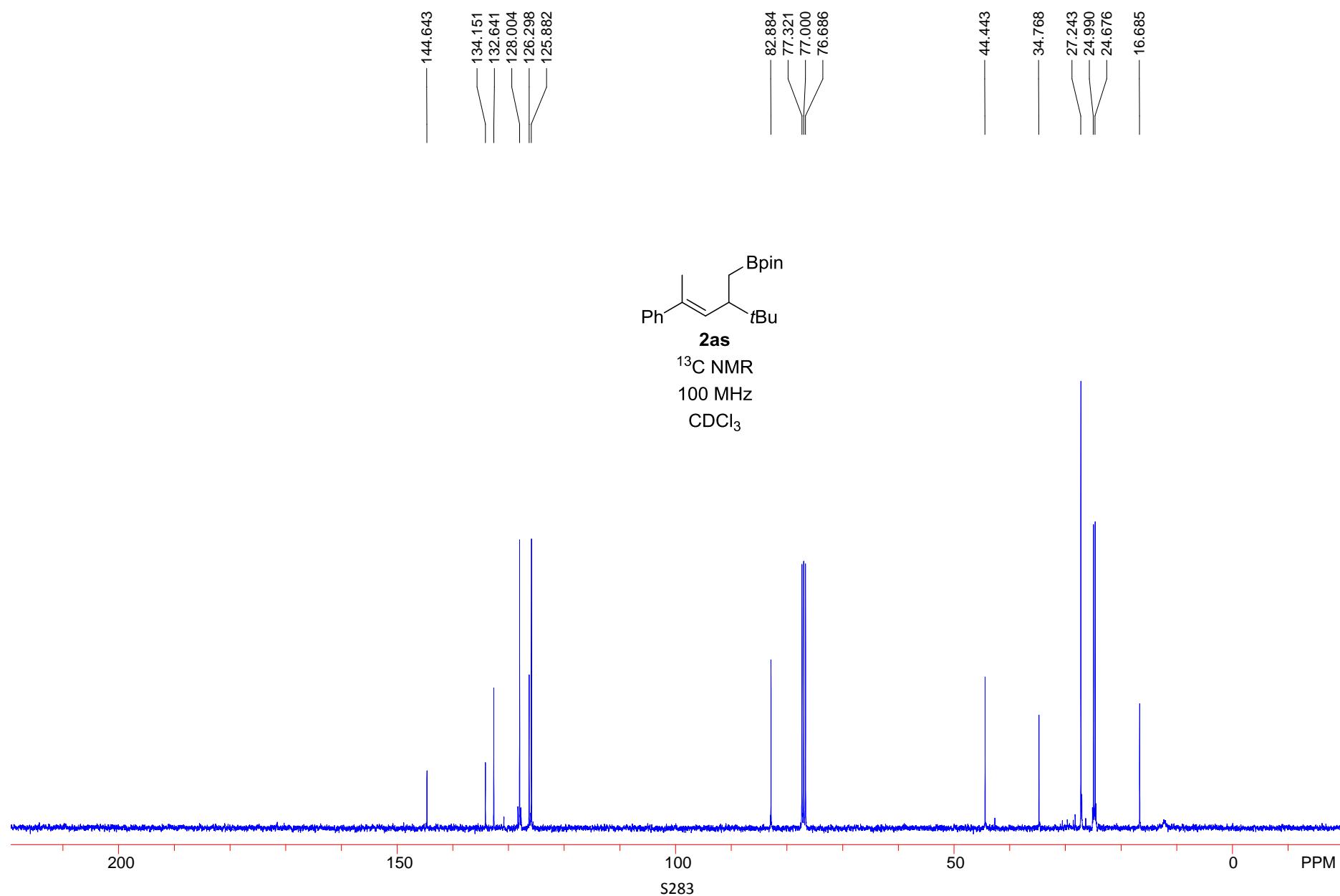


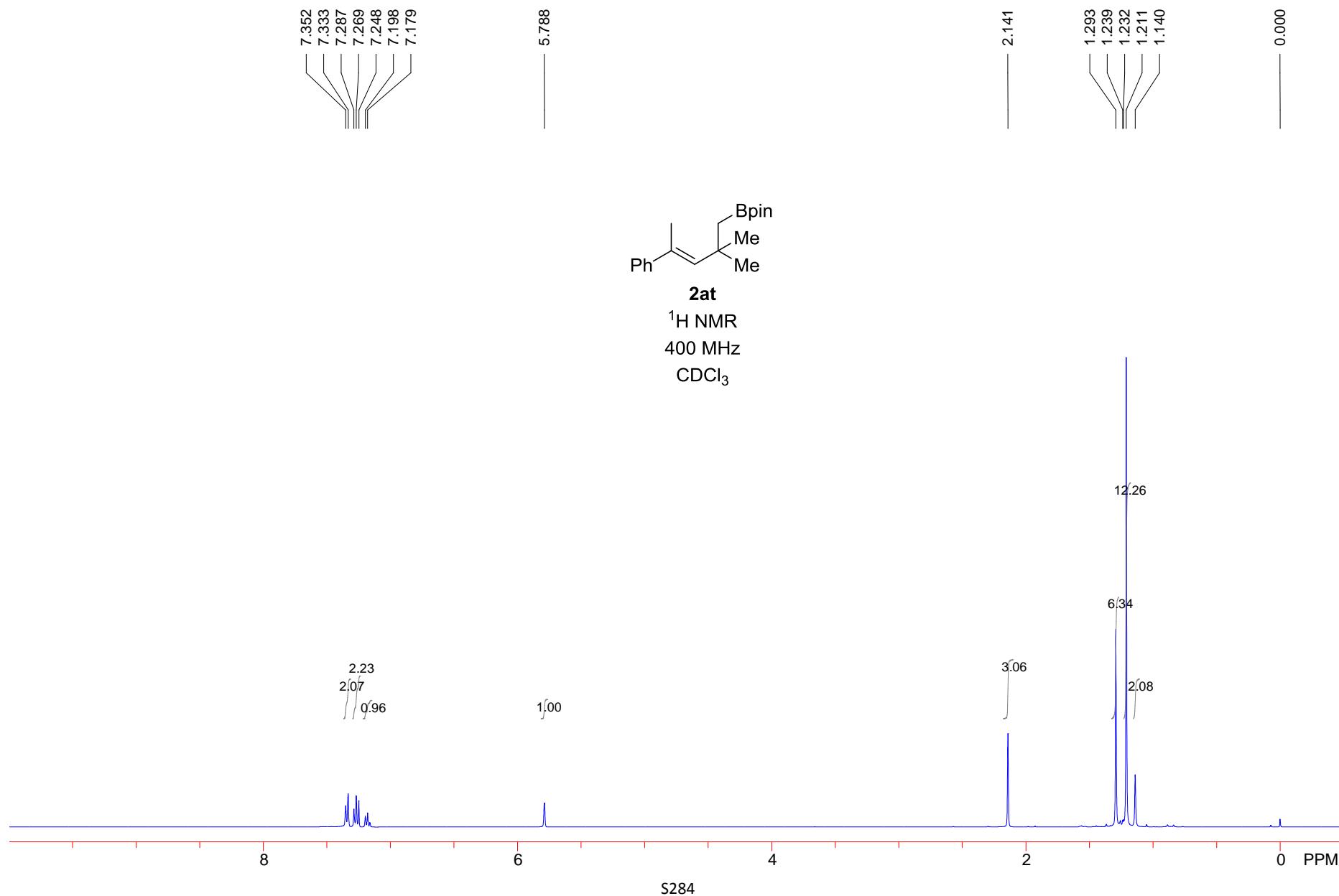


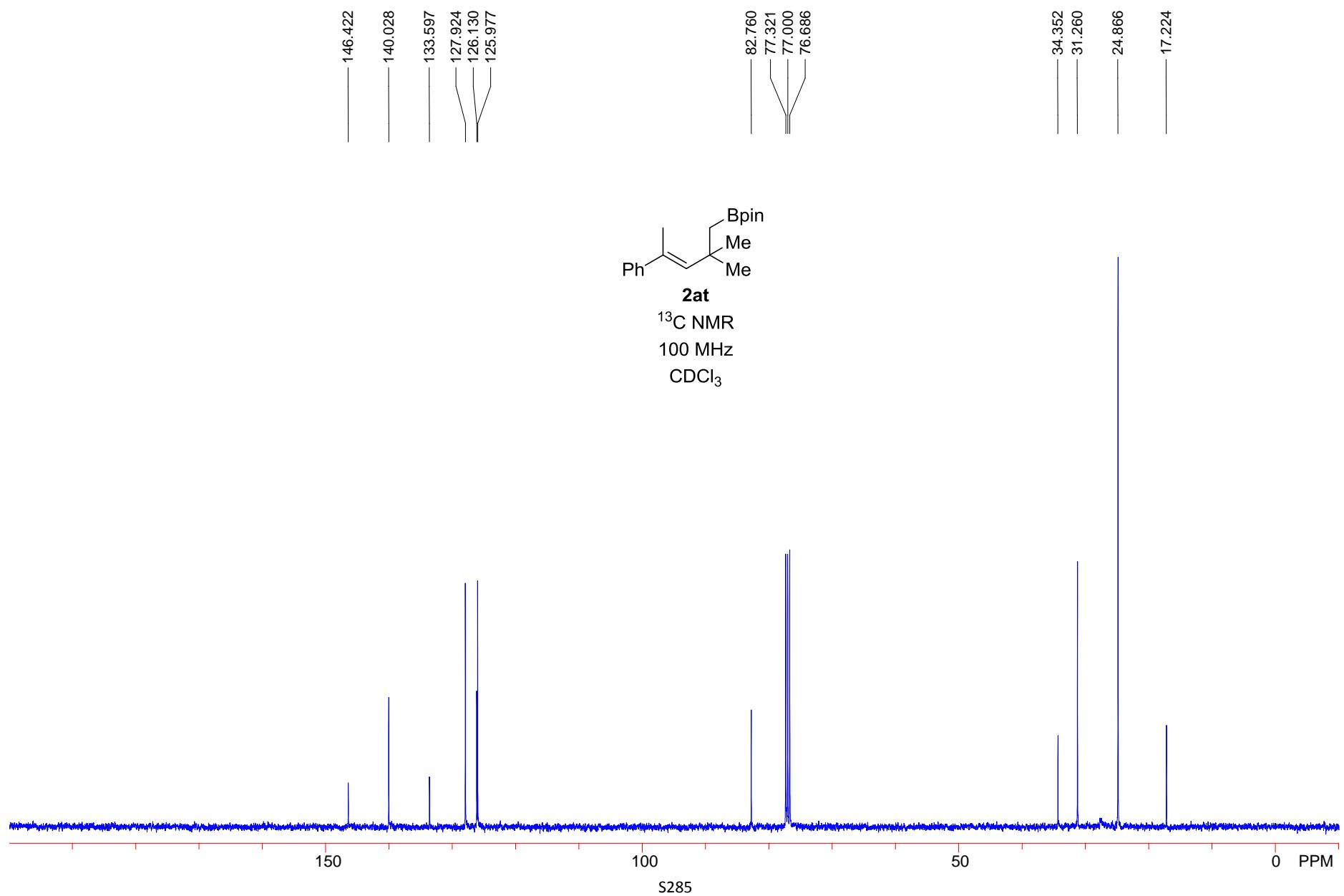


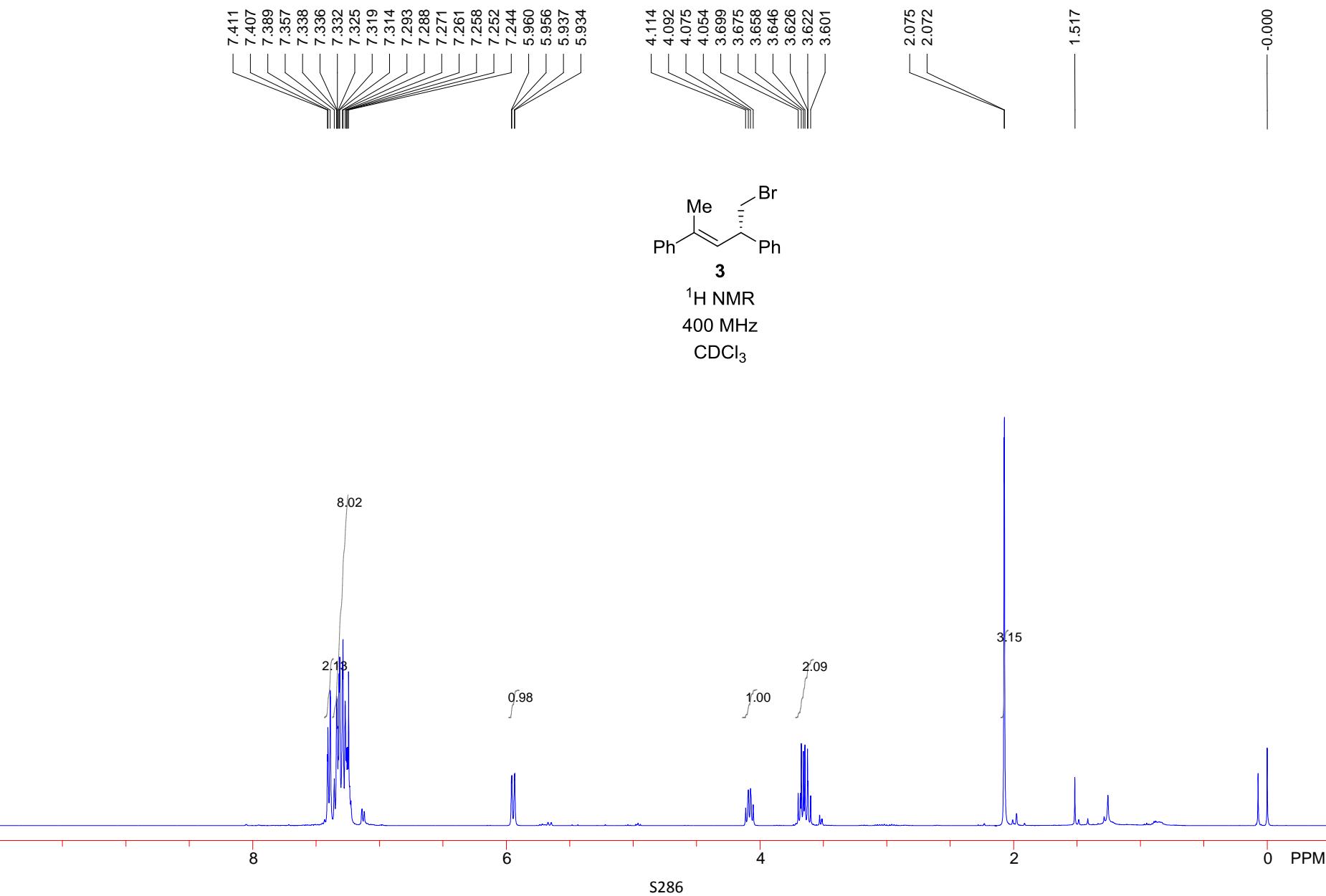


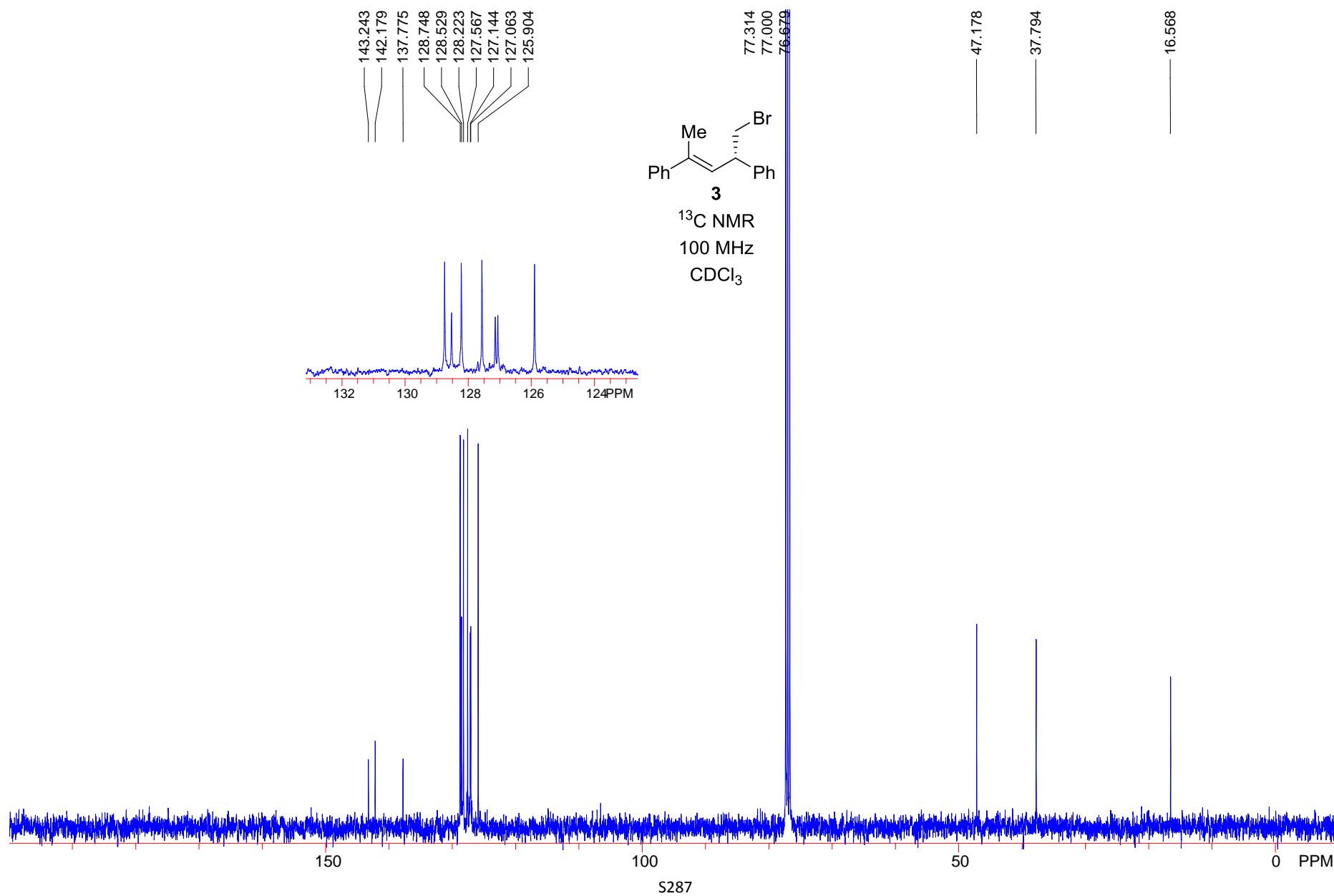




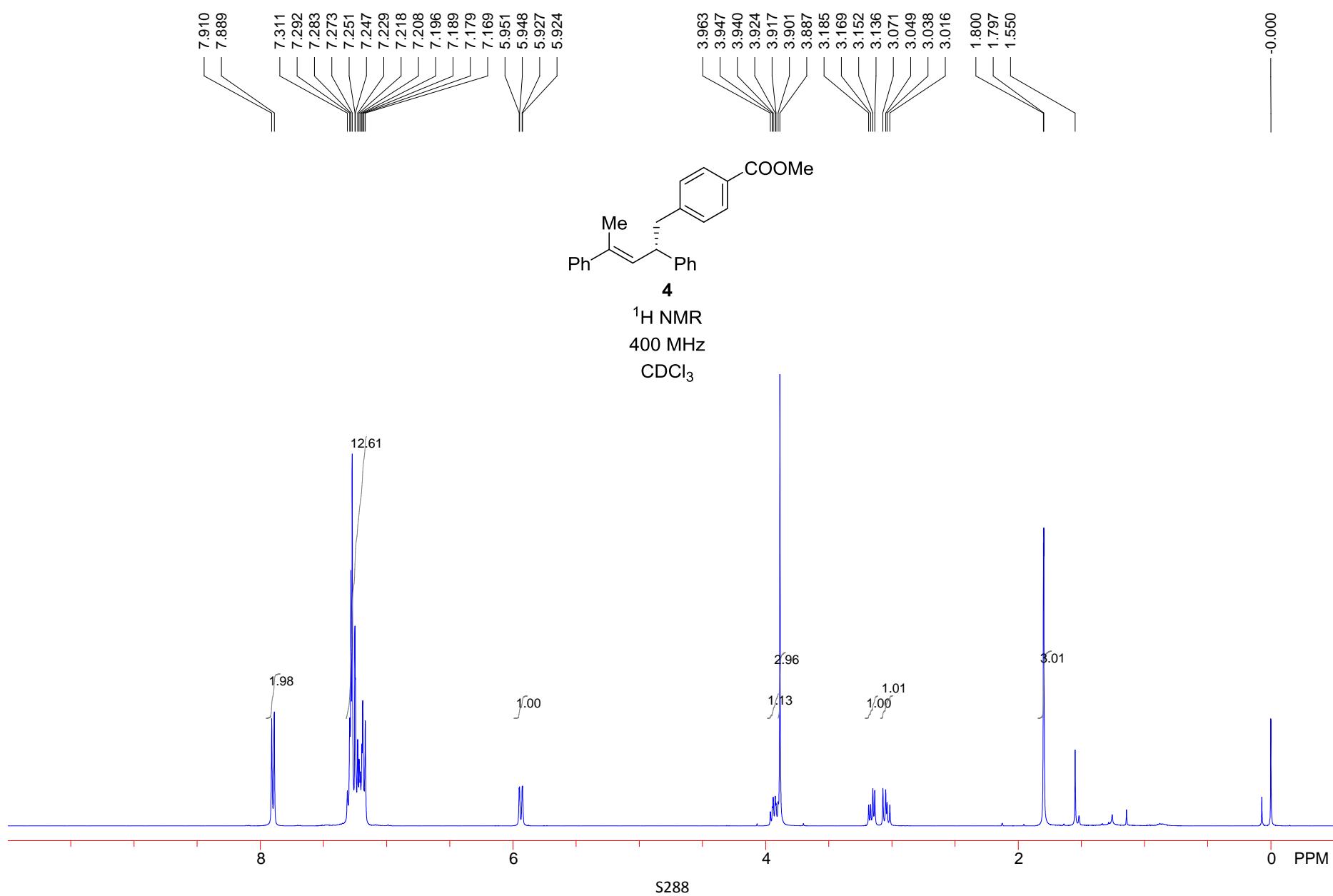


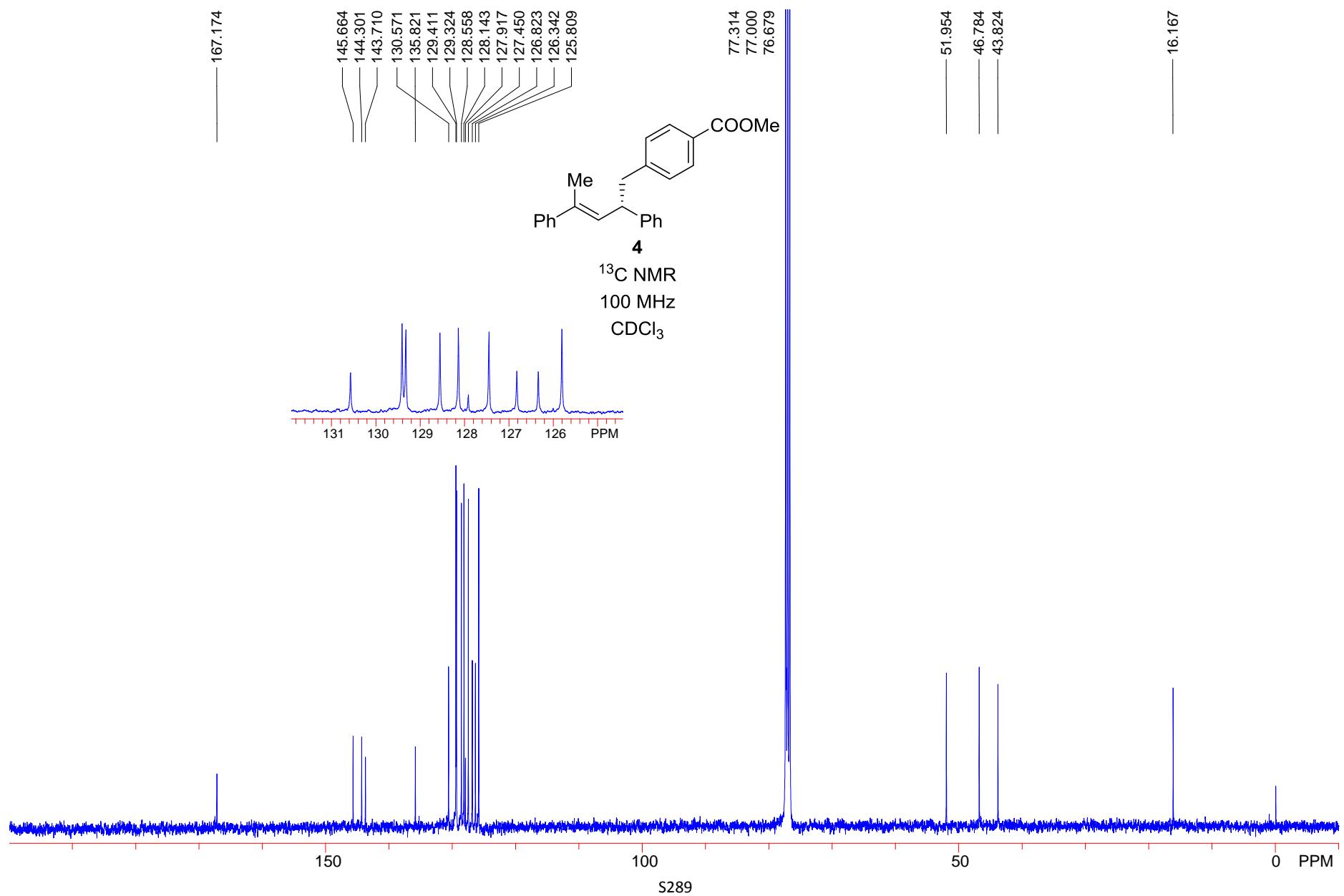




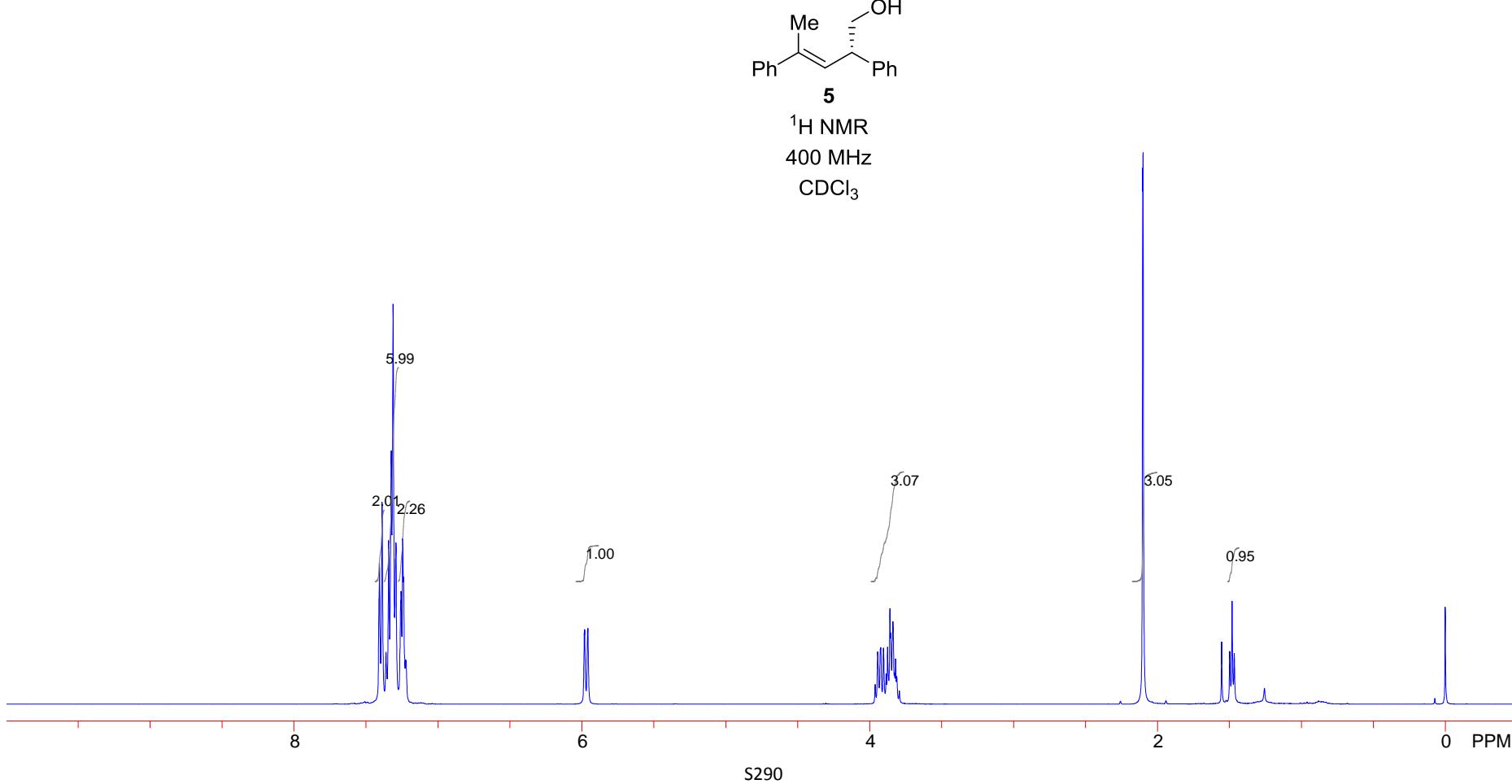


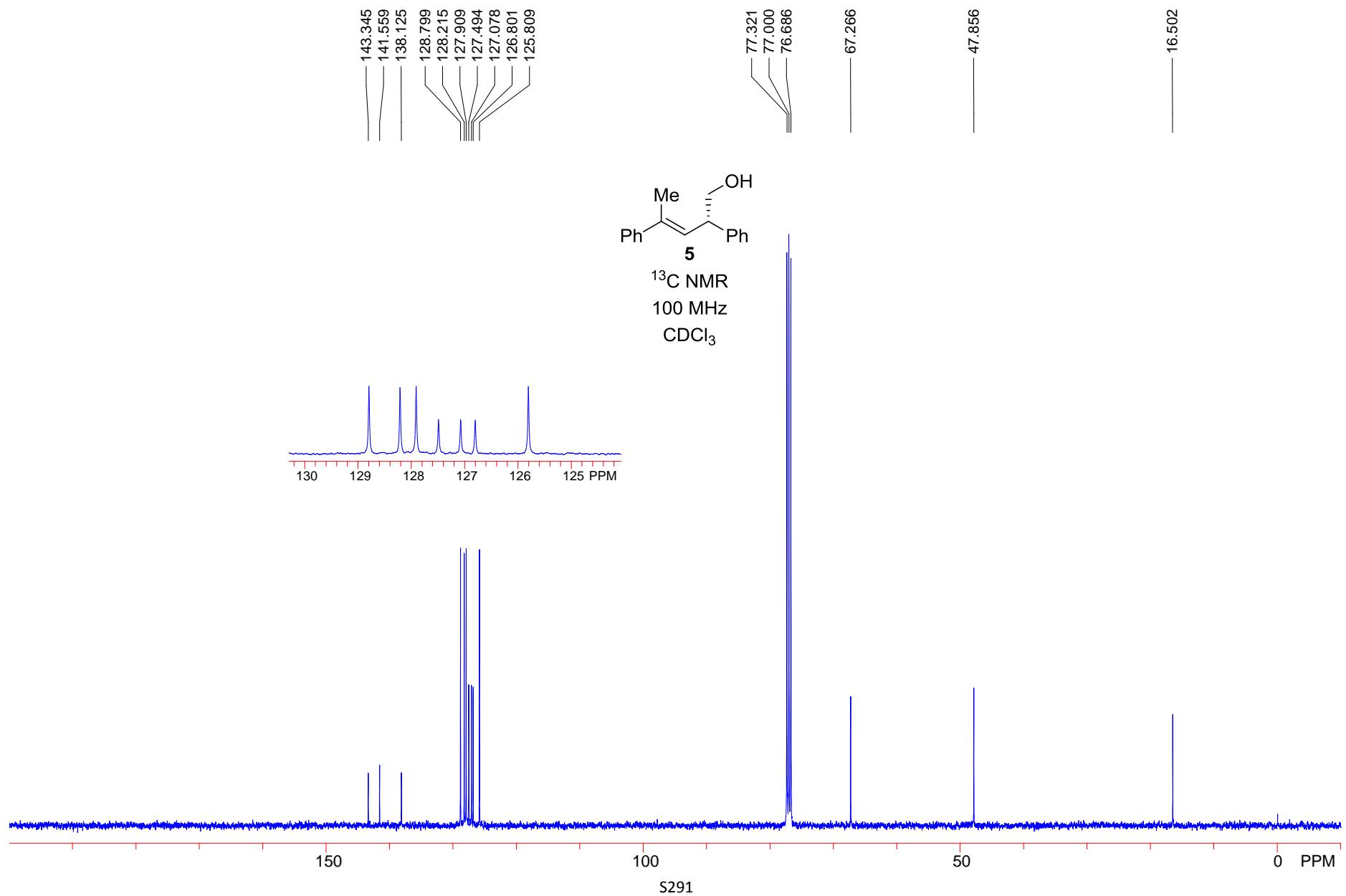
-0.000

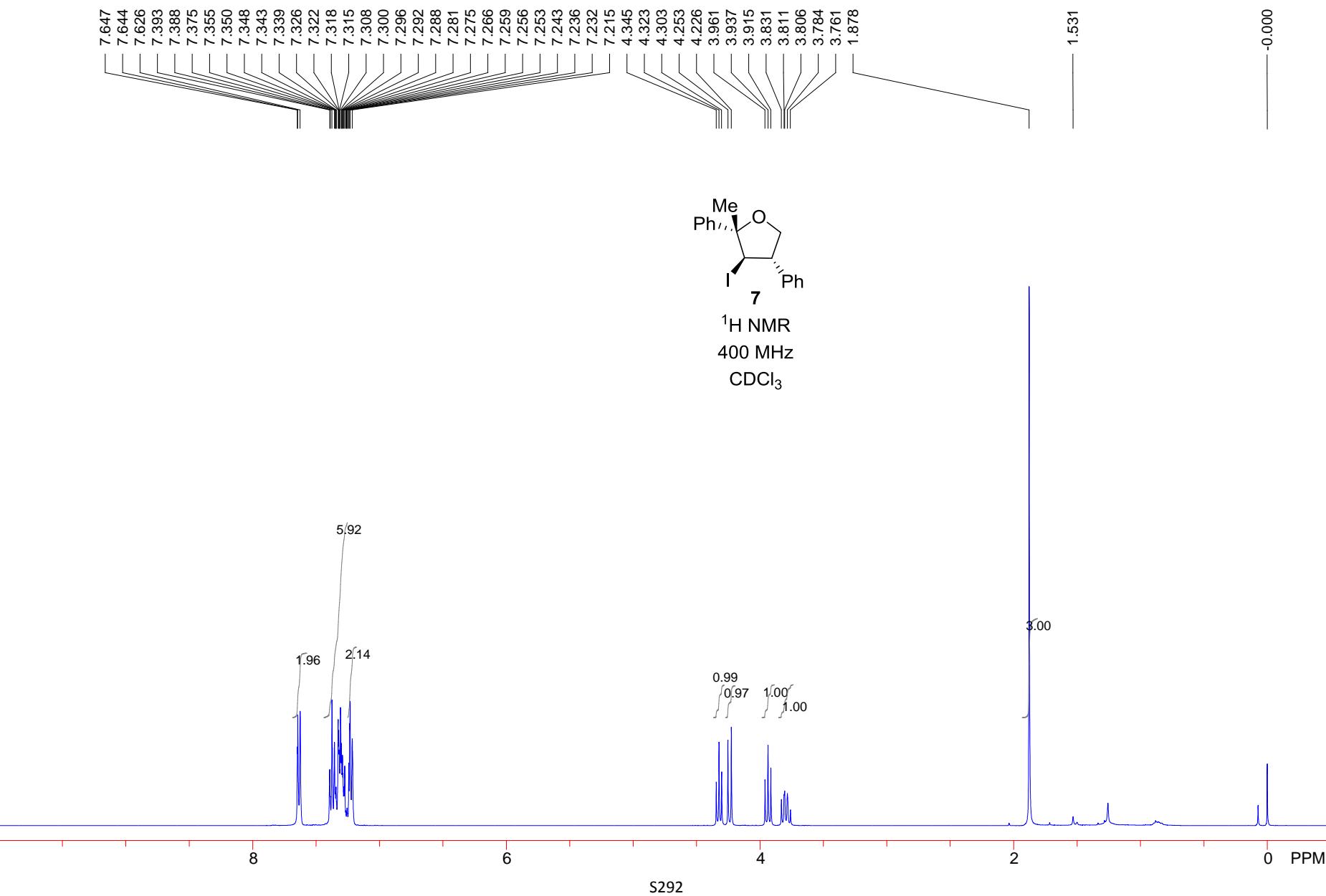


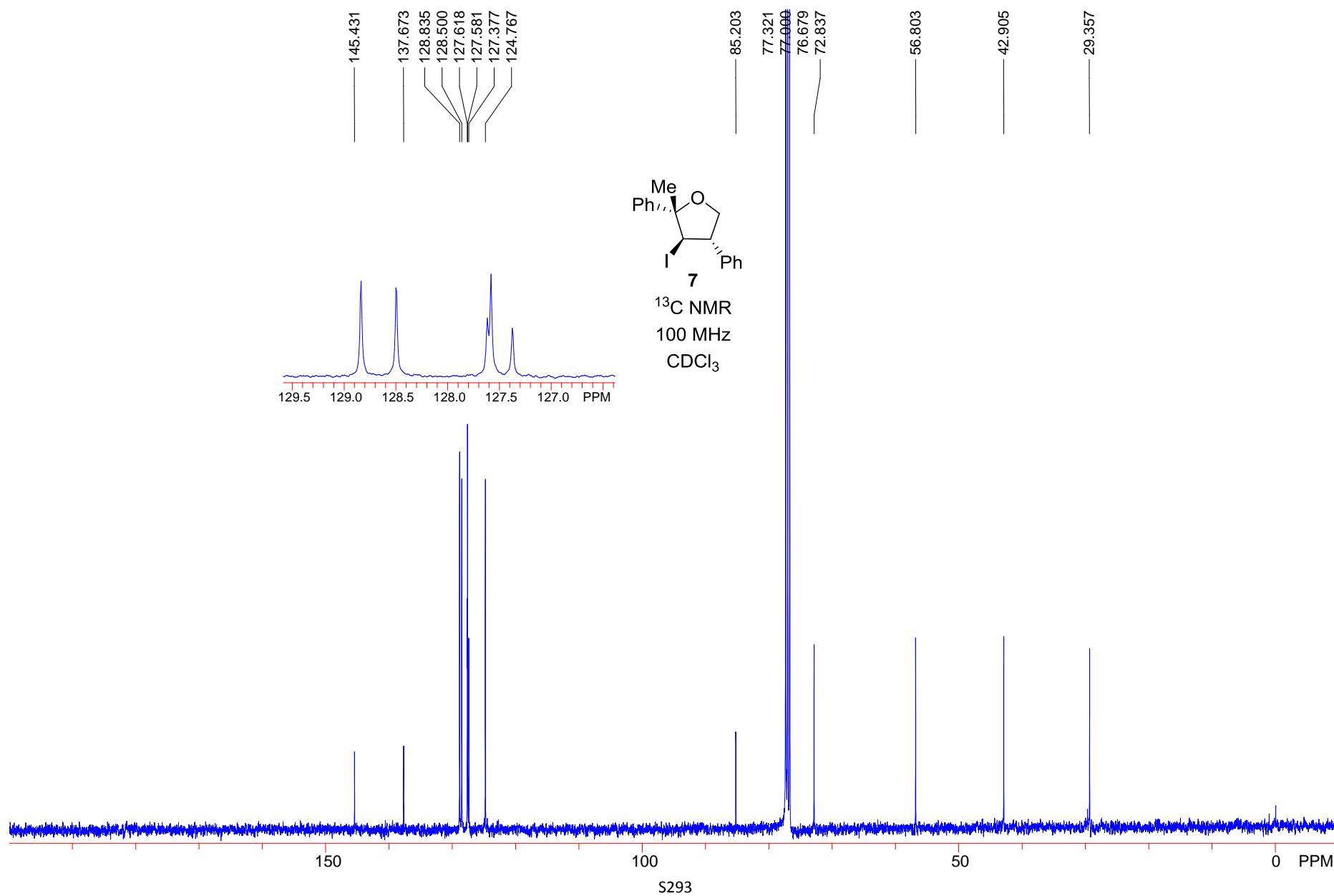


-0.000

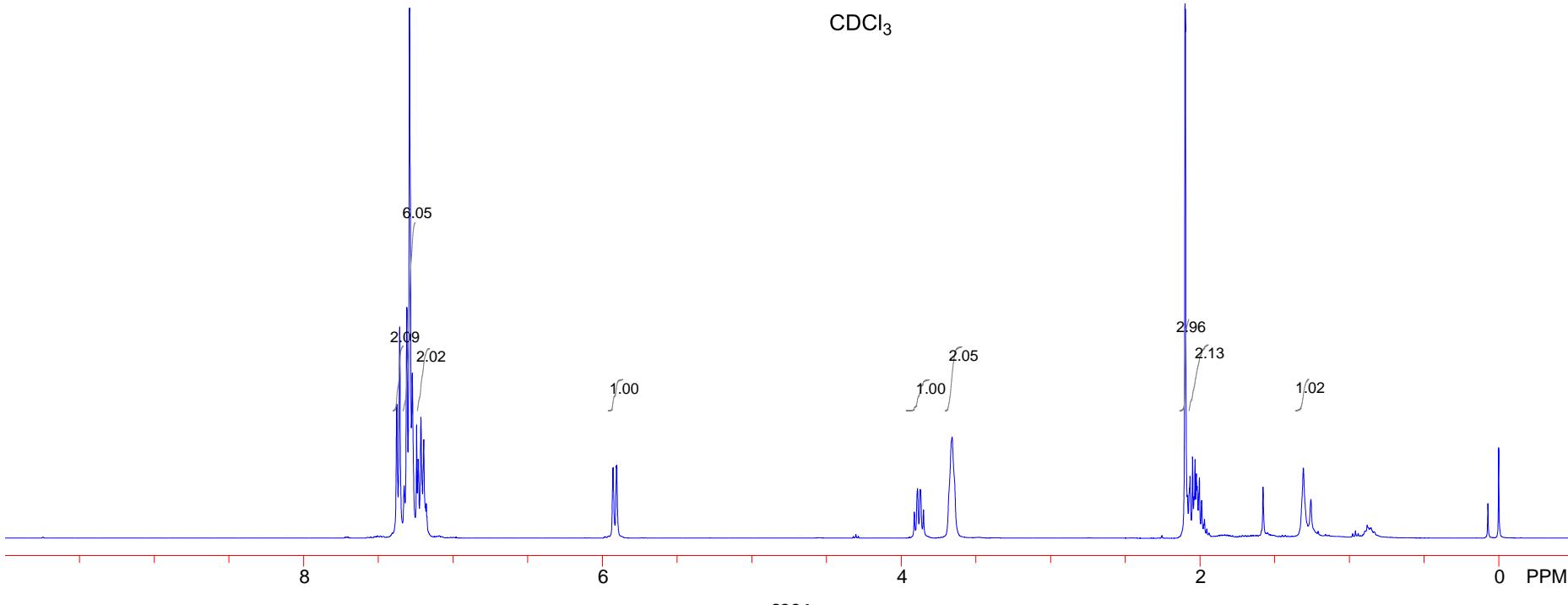
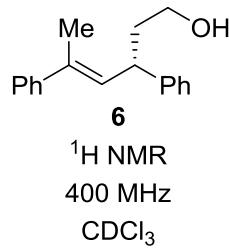
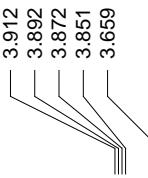
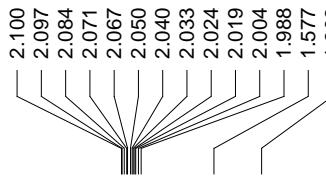


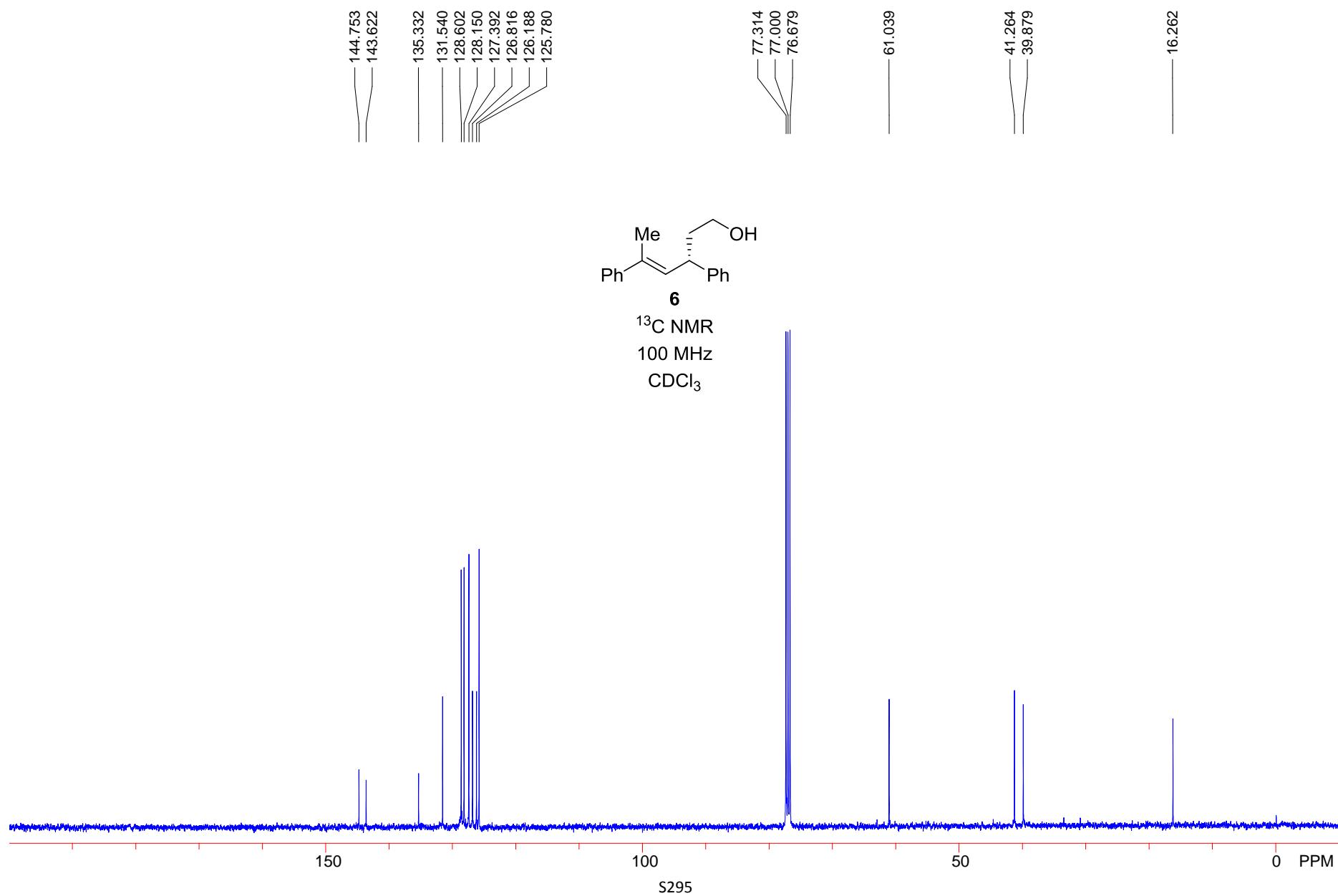




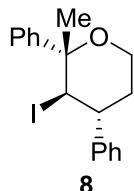
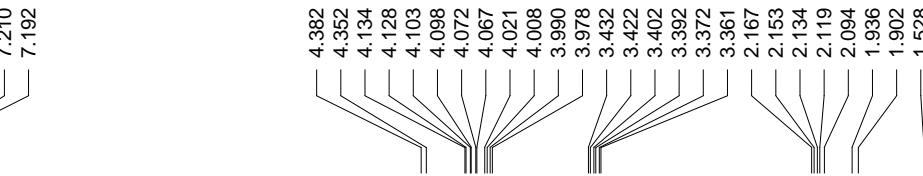


-0.000

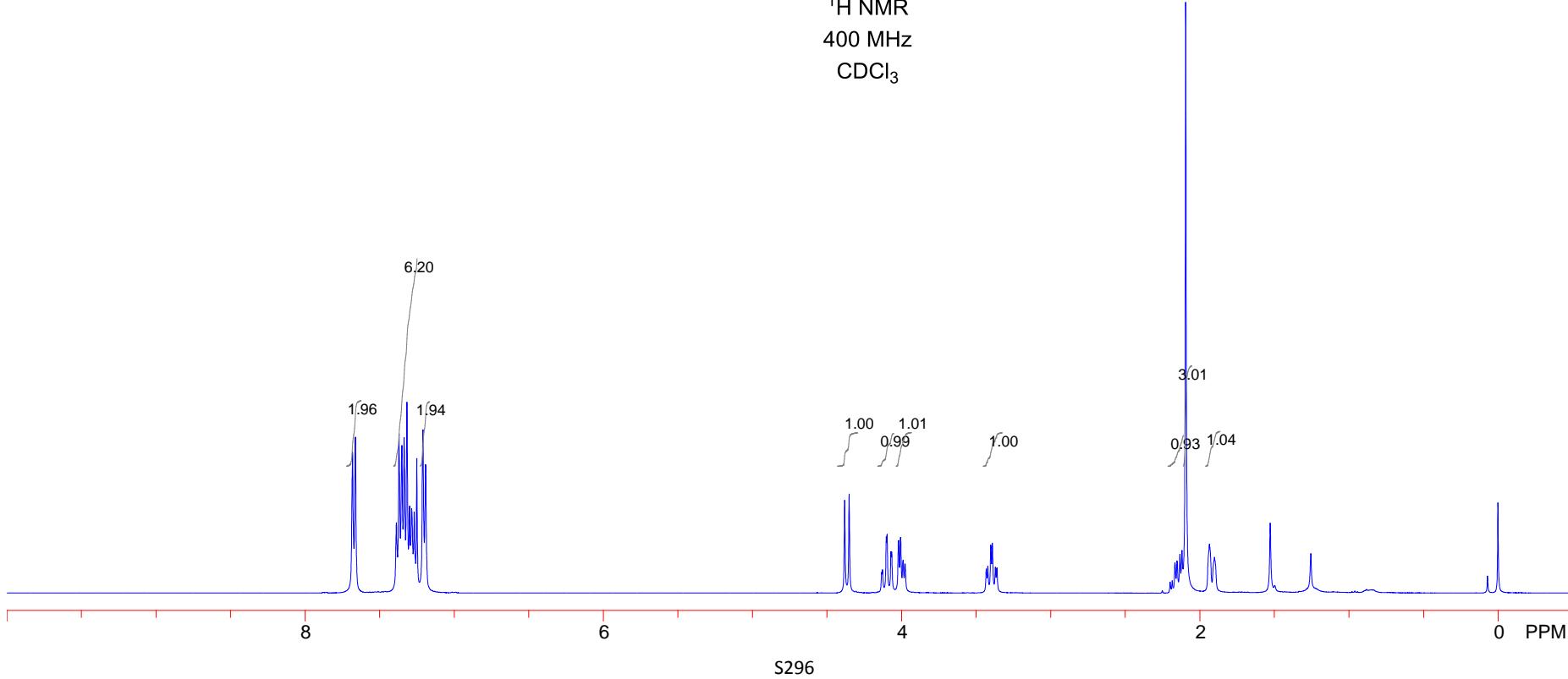


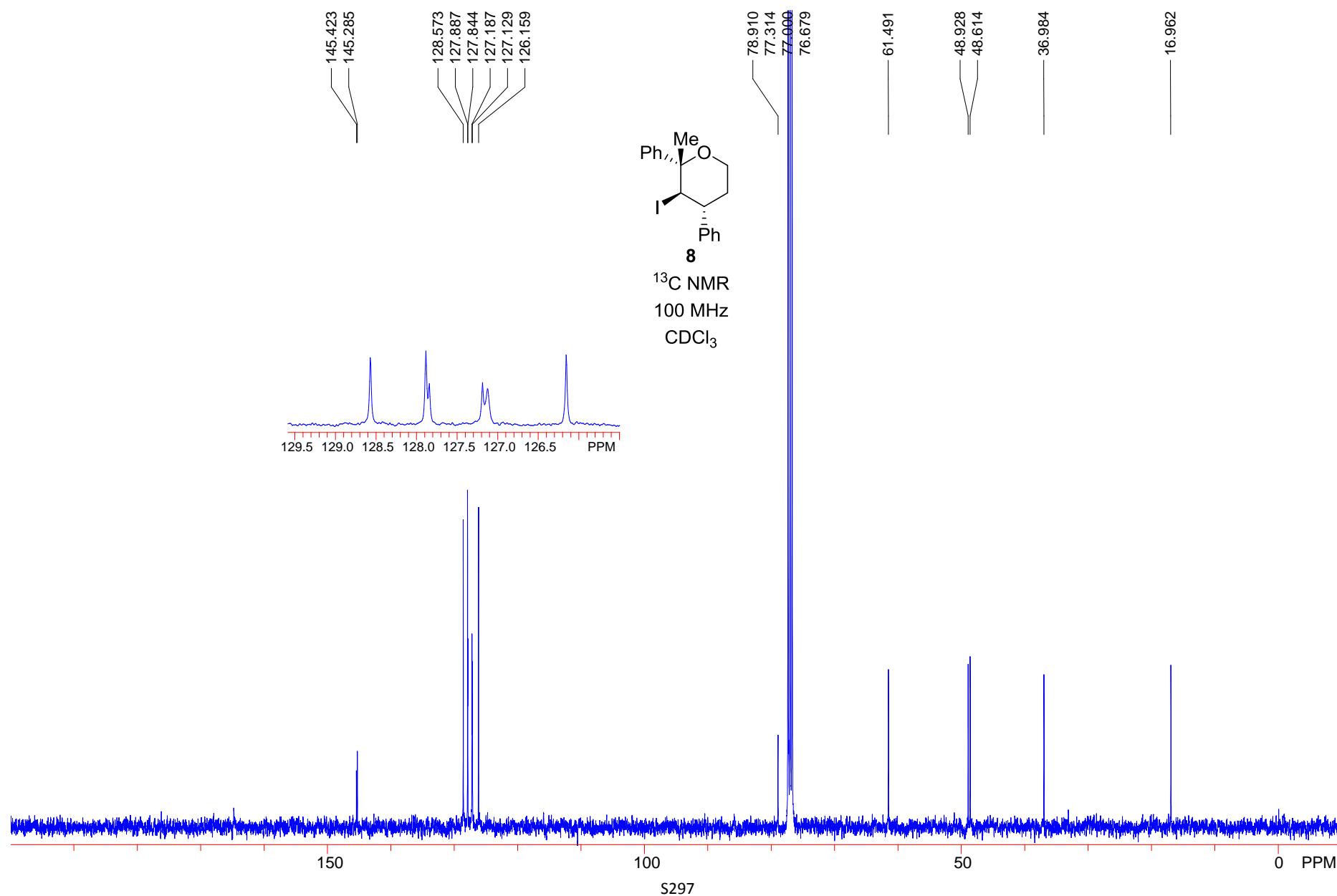


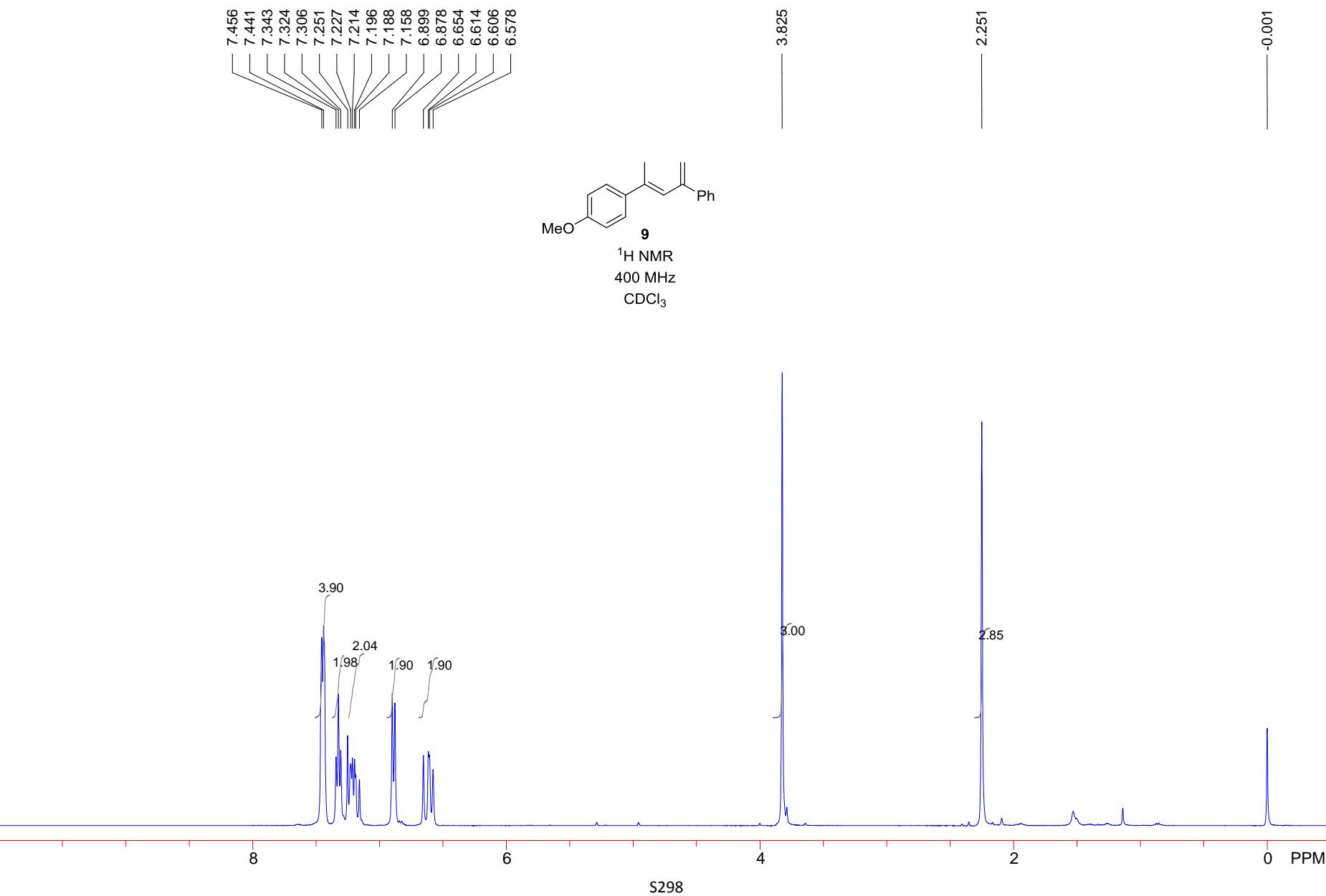
-0.000

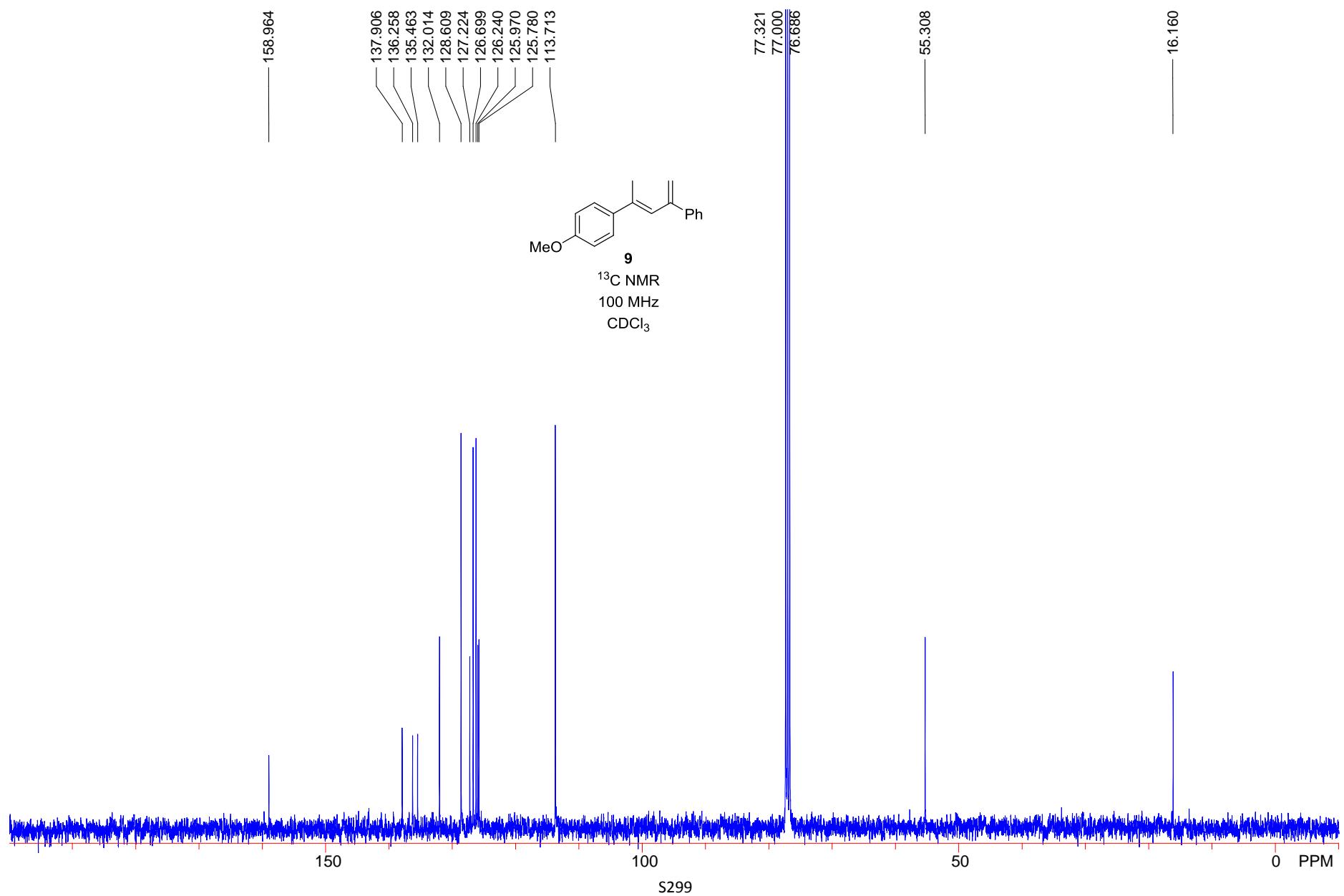


8
 ^1H NMR
400 MHz
 CDCl_3

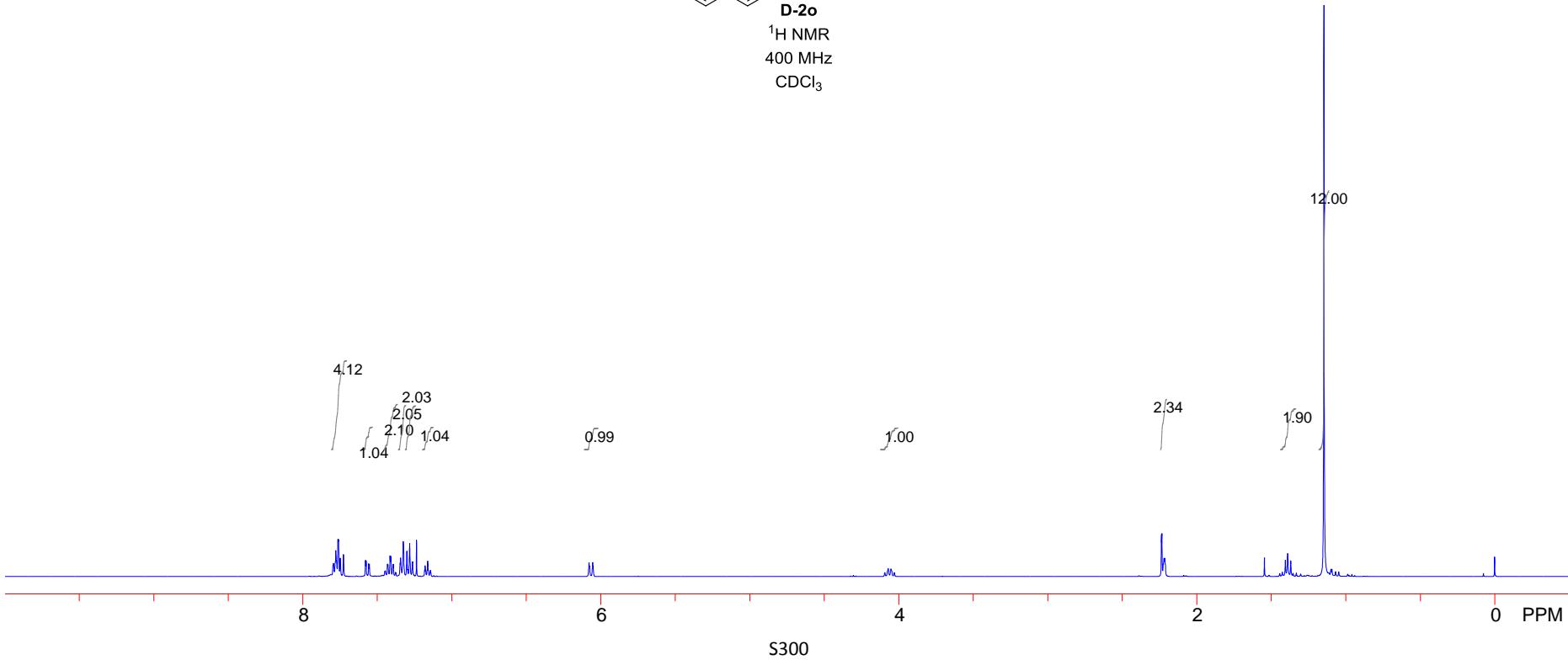
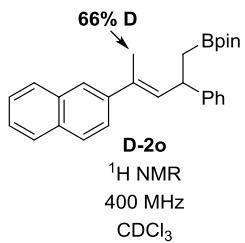
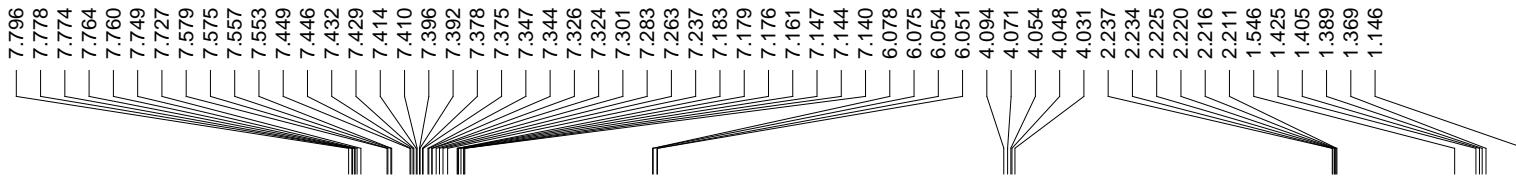


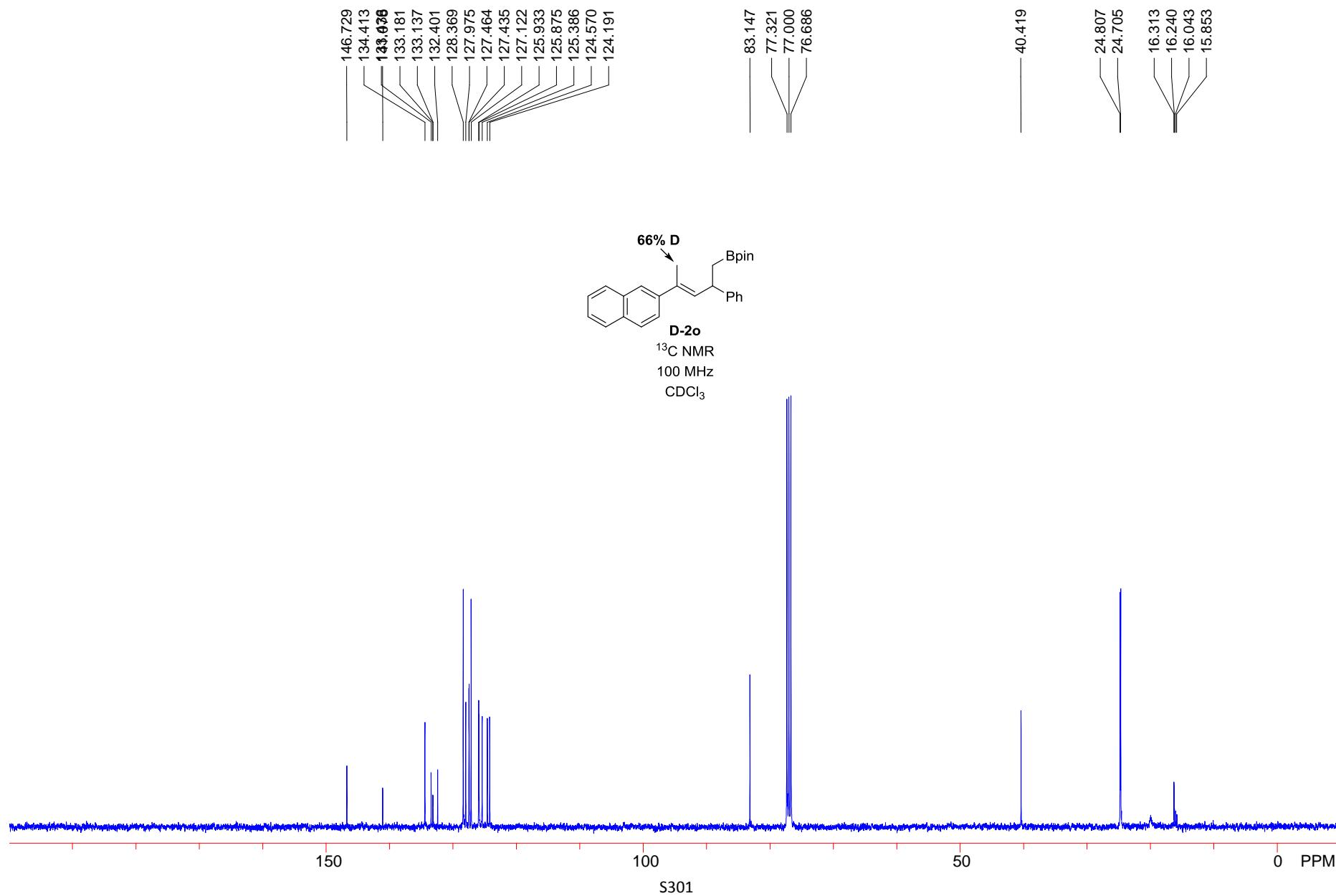


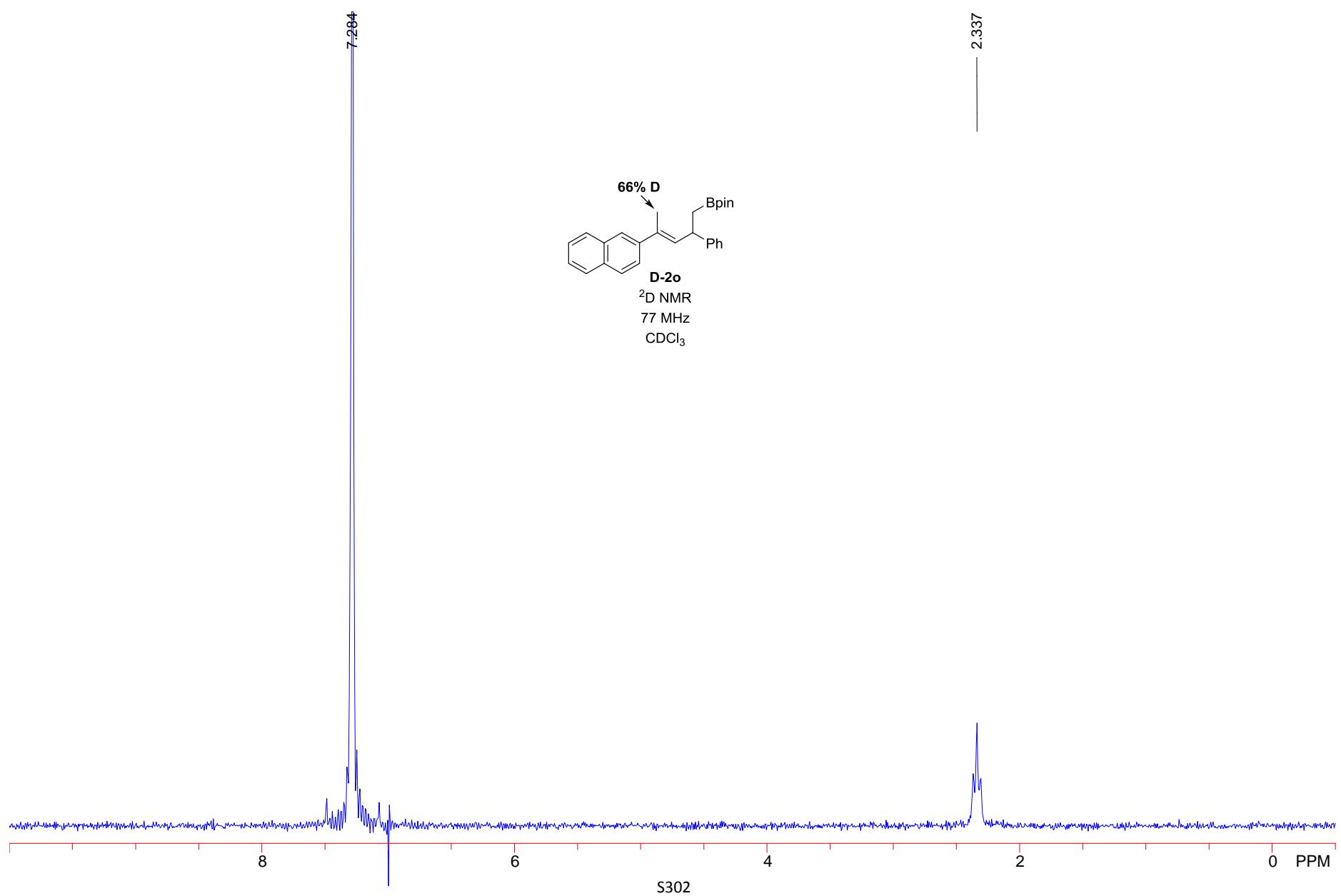


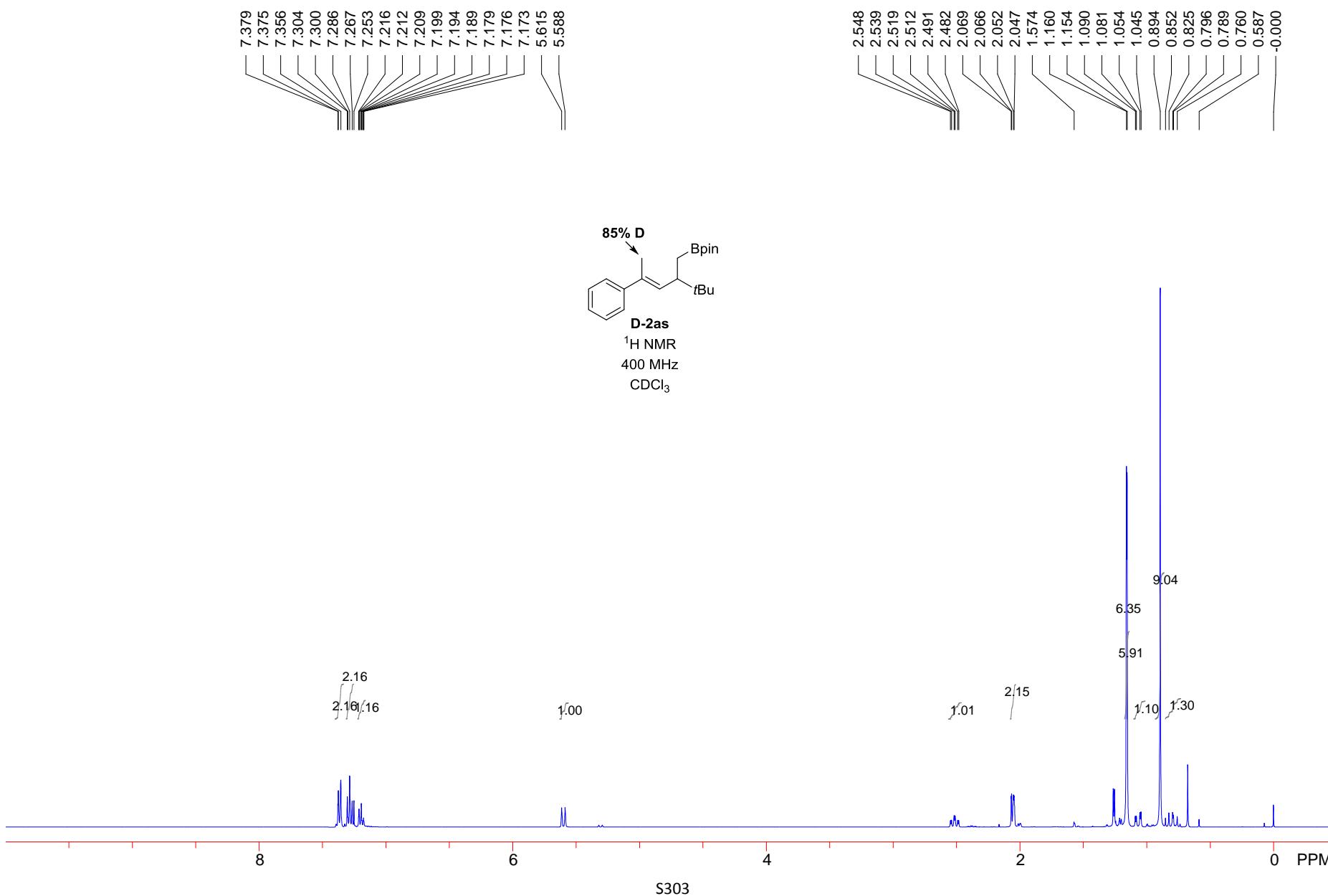


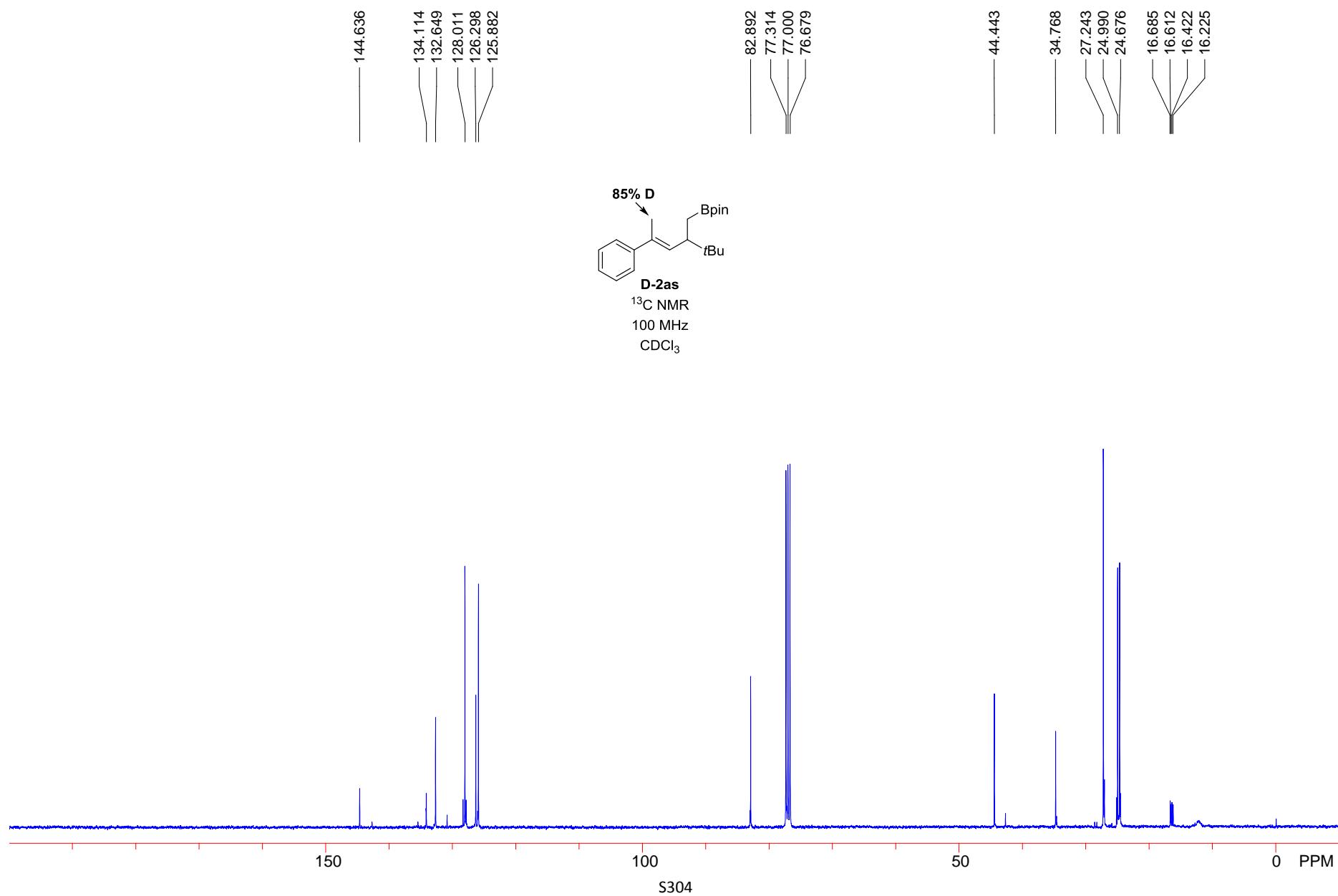
0.000

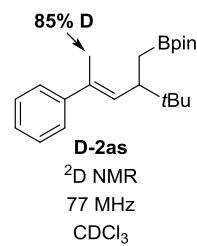
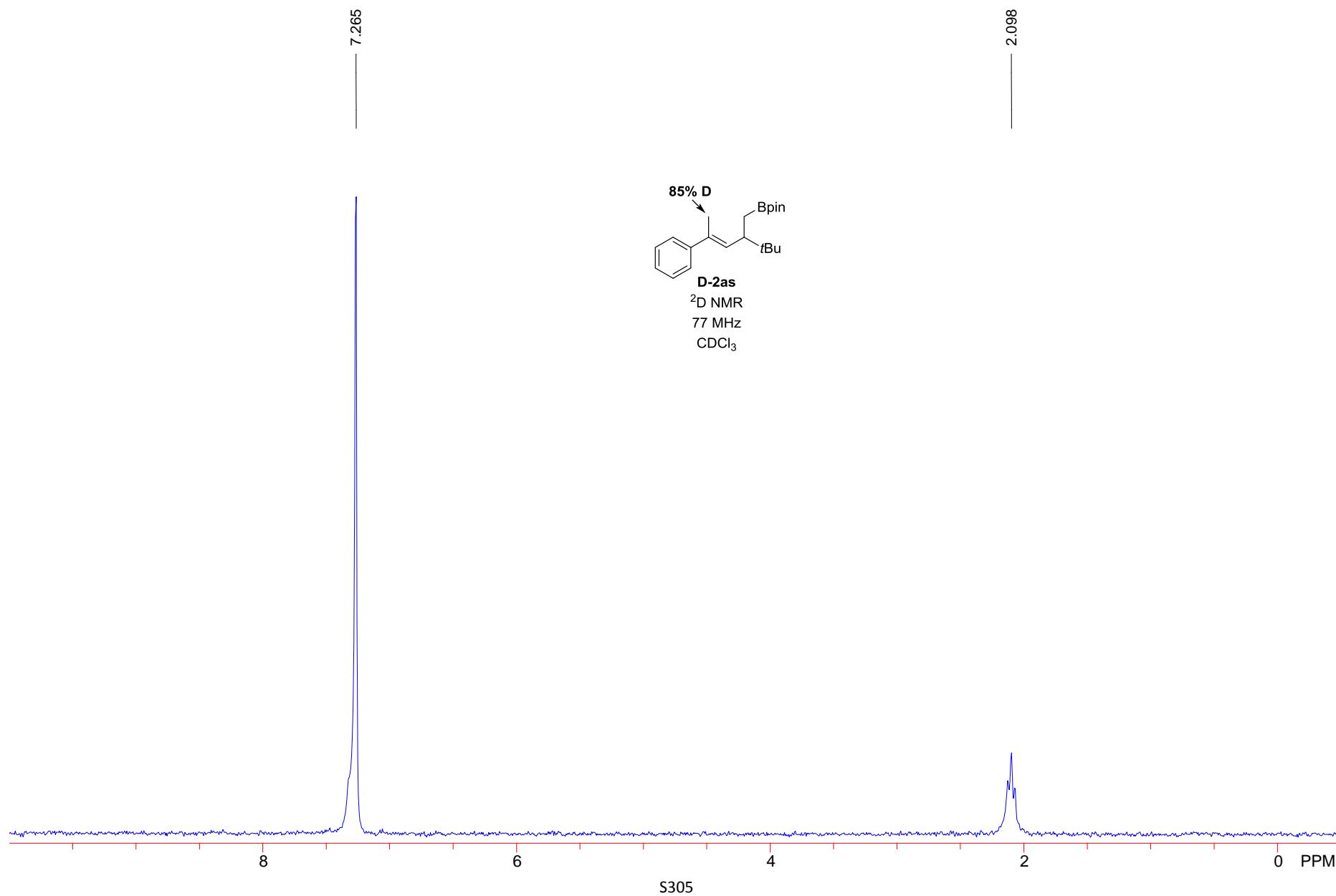


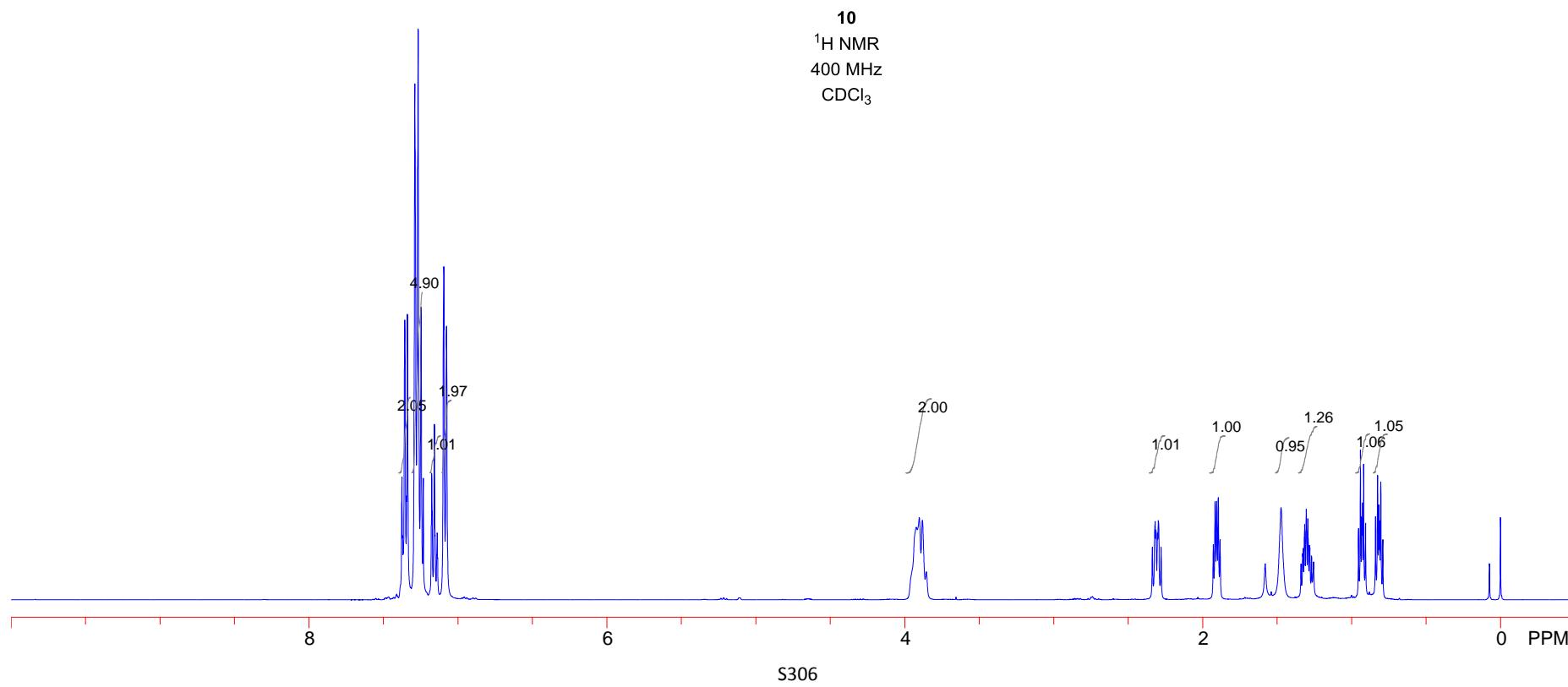




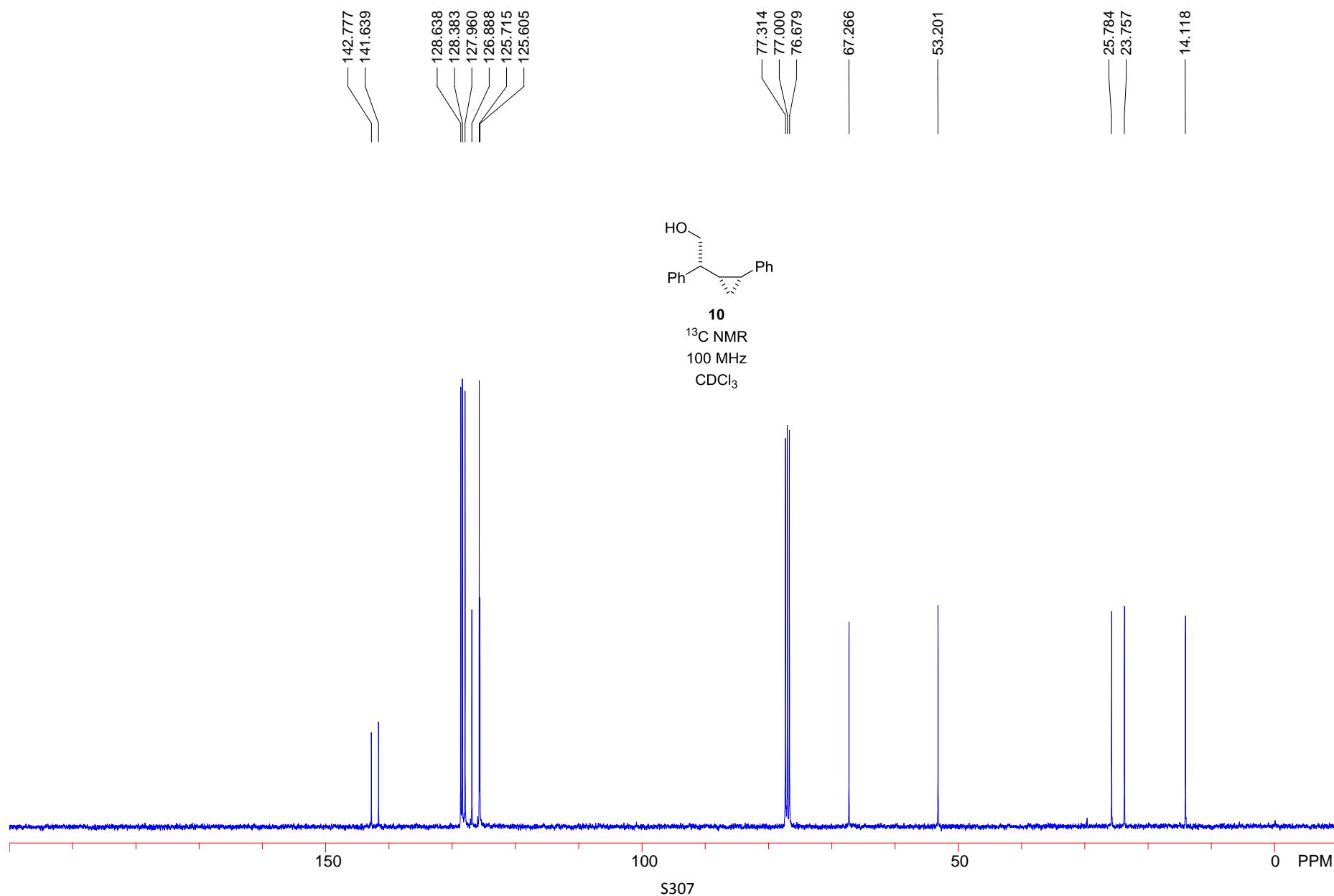


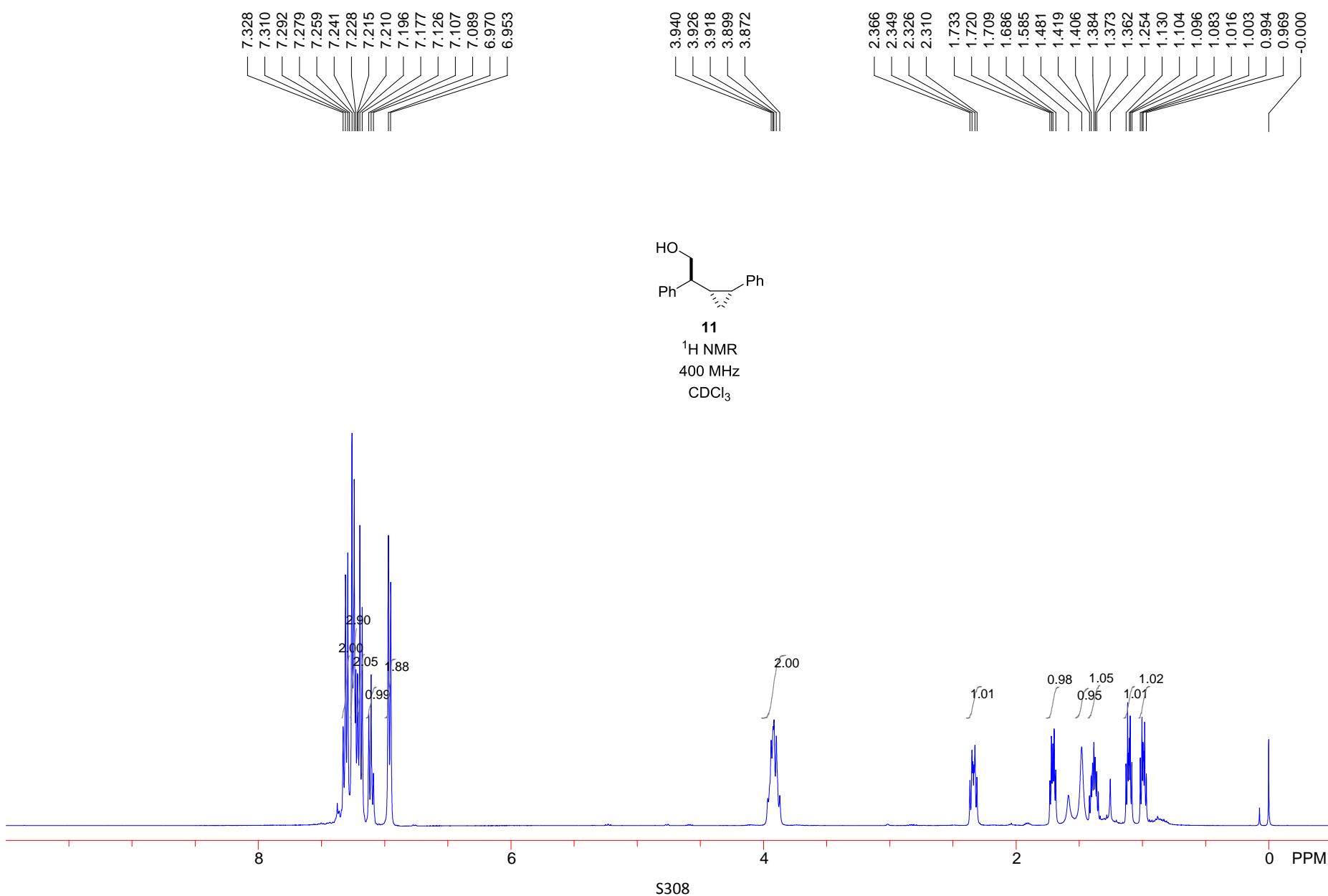




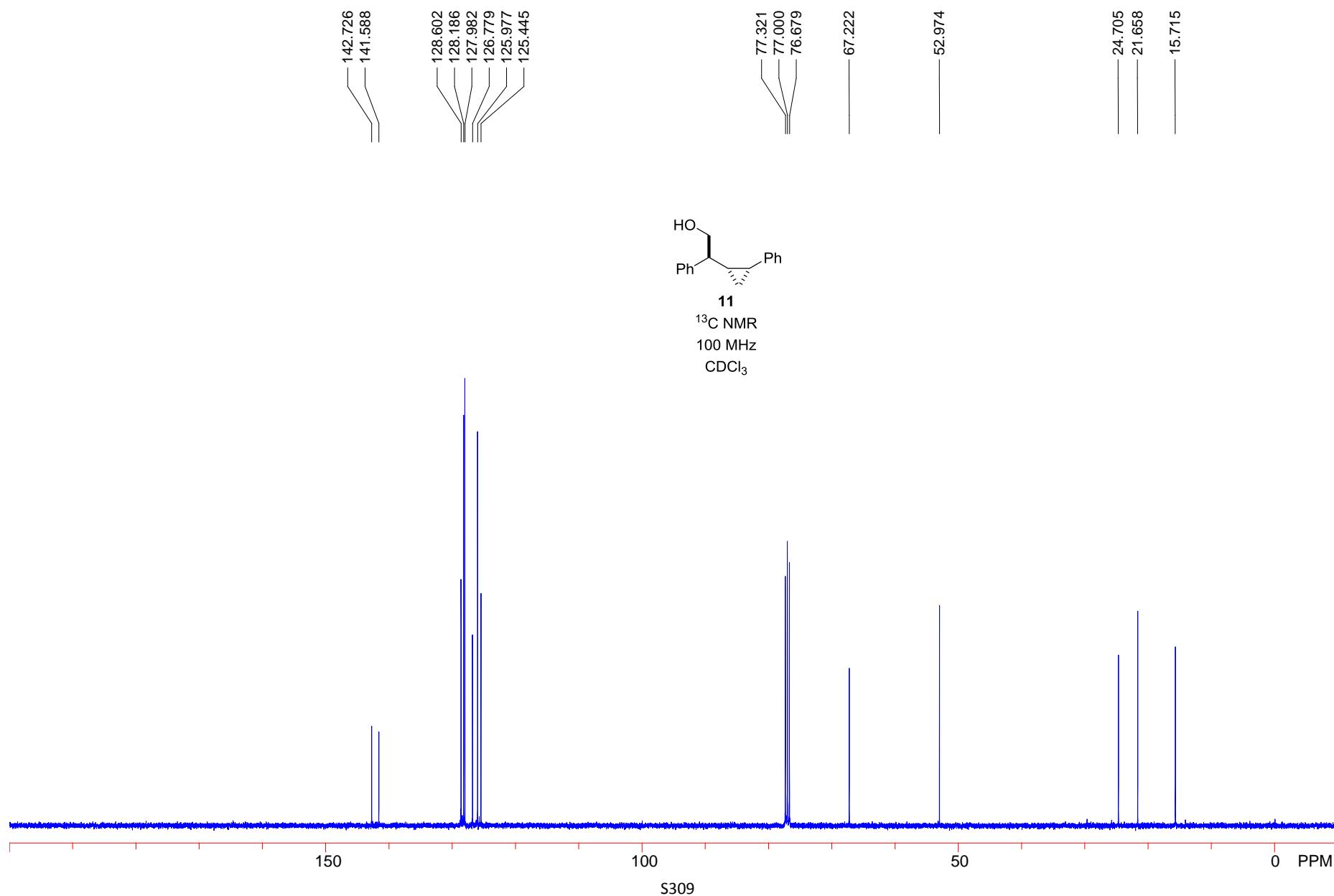


S306





S308



XI HPLC spectra

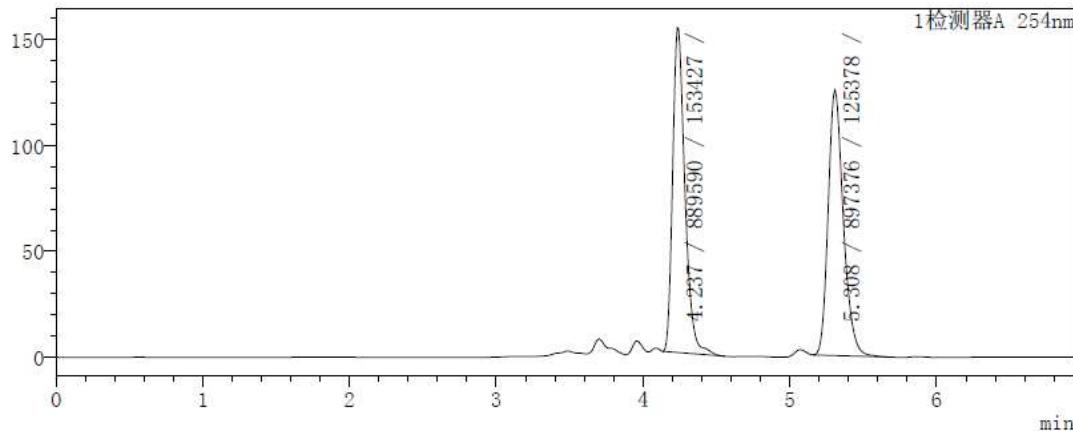
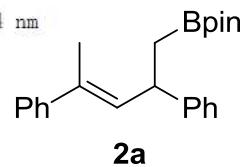
Translation of Chinese characters in HPLC spectra to English

| Chinese characters | English |
|--------------------|----------------------------|
| 处理日期/时间 | Processing Date/Time |
| 重复进样计数 | Number of Repeat Injection |
| 描述 | HPLC Condition |
| 色谱图 | HPLC Spectra |
| 检测器 | Detector |
| 峰表 | Area Percent Report |
| 峰号 | Peak |
| 保留时间 | Remaining Time |
| 面积 | Area |
| 高度 | Height |
| 标记 | Note |
| 总计 | Total |

处理日期/时间
重复进样计数
描述

: 2015-11-18 12:03:12
: 1
: AD-H, n-hex : iPrOH= 98/2, 1.0 ml/min, 254 nm

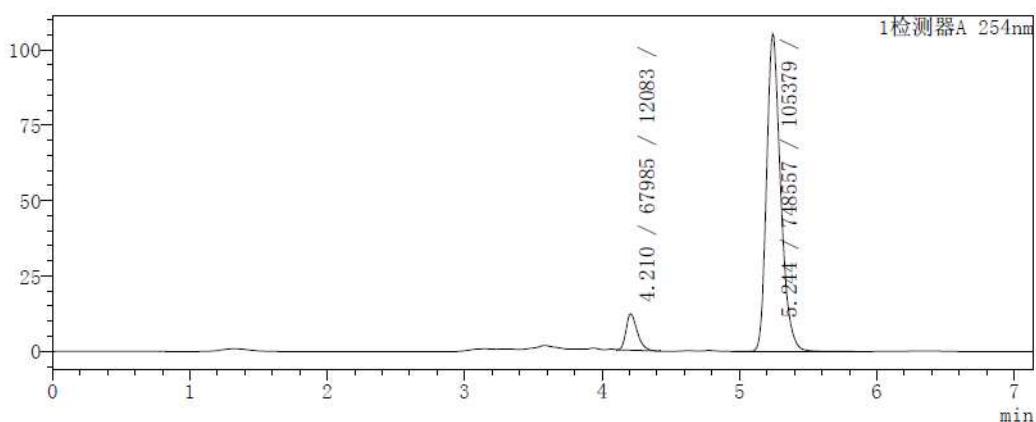
色谱图
CCH2068-R



峰表

| 检测器A 254nm | | | | | |
|------------|-------|---------|--------|----|---------|
| 峰号 | 保留时间 | 面积 | 高度 | 标记 | 面积% |
| 1 | 4.237 | 889590 | 153427 | | 49.782 |
| 2 | 5.308 | 897376 | 125378 | | 50.218 |
| 总计 | | 1786965 | 278804 | | 100.000 |

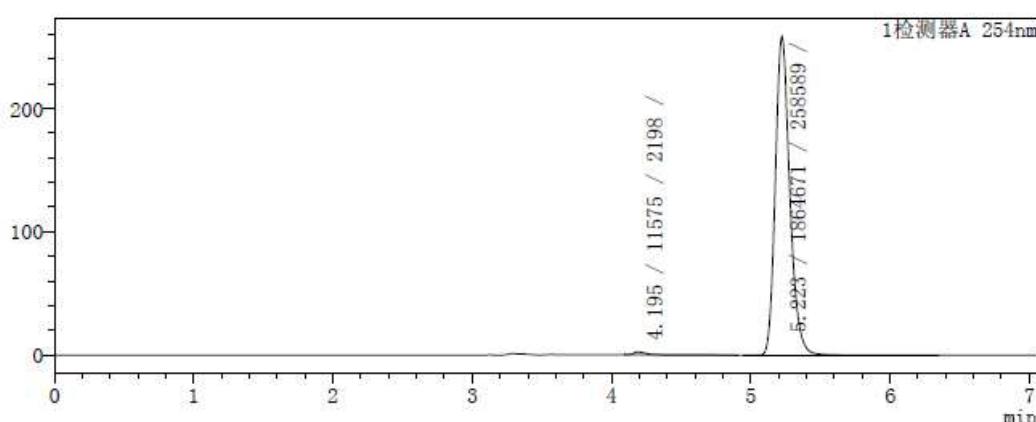
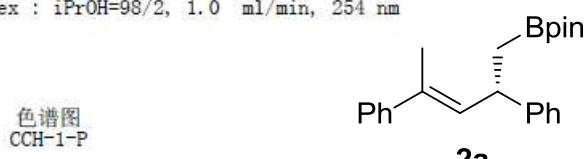
处理日期/时间 : 2016-12-29 15:32:38
 重复进样计数 : 1
 描述 : AD-H, n-hexane:iPrOH=98/2, 1.0 ml/min, 254nm



峰表
检测器A 254nm

| 峰号 | 保留时间 | 面积 | 高度 | 标记 | 面积% |
|----|-------|--------|--------|----|---------|
| 1 | 4.210 | 67985 | 12083 | | 8.326 |
| 2 | 5.244 | 748557 | 105379 | M | 91.674 |
| 总计 | | 816541 | 117461 | | 100.000 |

分析日期/时间 : 2016-1-14 13:07:24
 处理日期/时间 : 2016-1-14 13:14:30
 重复进样计数 : 1
 描述 : AD-H, n-hex : iPrOH=98/2, 1.0 ml/min, 254 nm



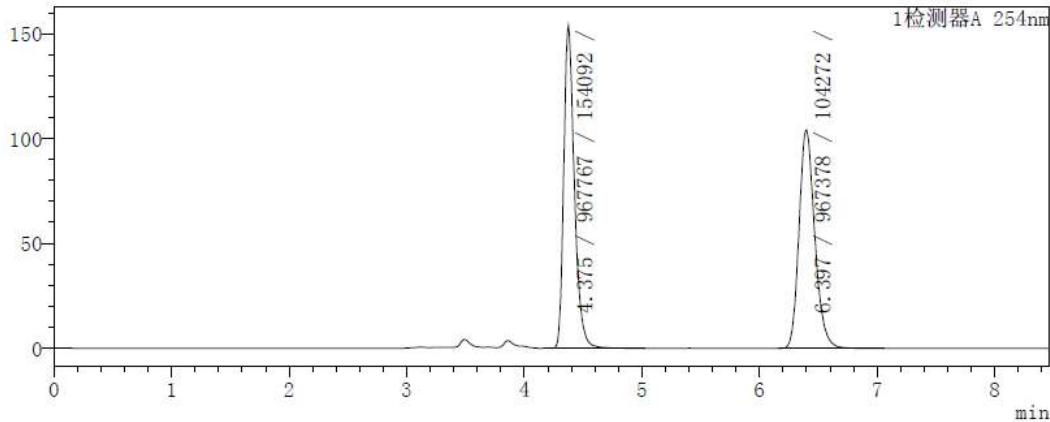
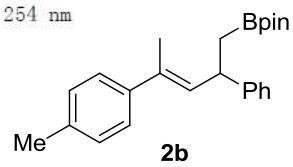
峰表
检测器A 254nm

| 峰号 | 保留时间 | 面积 | 高度 | 标记 | 面积% |
|----|-------|---------|--------|----|---------|
| 1 | 4.195 | 11575 | 2198 | S | 0.617 |
| 2 | 5.223 | 1864671 | 258589 | S | 99.383 |
| 总计 | | 1876247 | 260787 | | 100.000 |

处理日期/时间
重复进样计数
描述

: 2016-3-16 17:13:47
: 1
: AD-H, n-hex : iPrOH=98/2, 1.0 ml/min, 254 nm

色谱图
CCH3045A-P



检测器A 254nm

峰表

| 峰号 | 保留时间 | 面积 | 高度 | 标记 | 面积% |
|----|-------|---------|--------|----|---------|
| 1 | 4.375 | 967767 | 154092 | V | 50.010 |
| 2 | 6.397 | 967378 | 104272 | | 49.990 |
| 总计 | | 1935146 | 258364 | | 100.000 |

处理日期/时间

: 2016-12-29 15:52:07

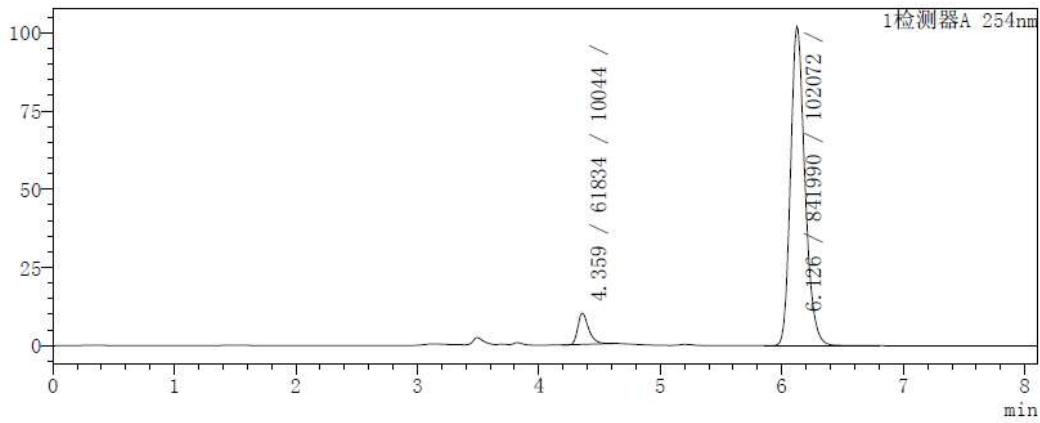
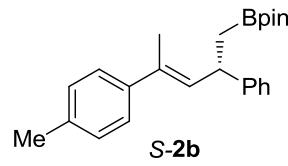
重复进样计数

: 1

描述

: AD-H, n-hexane:iPrOH=98/2, 1.0 ml/min, 254 nm

色谱图
CCH5092B-P



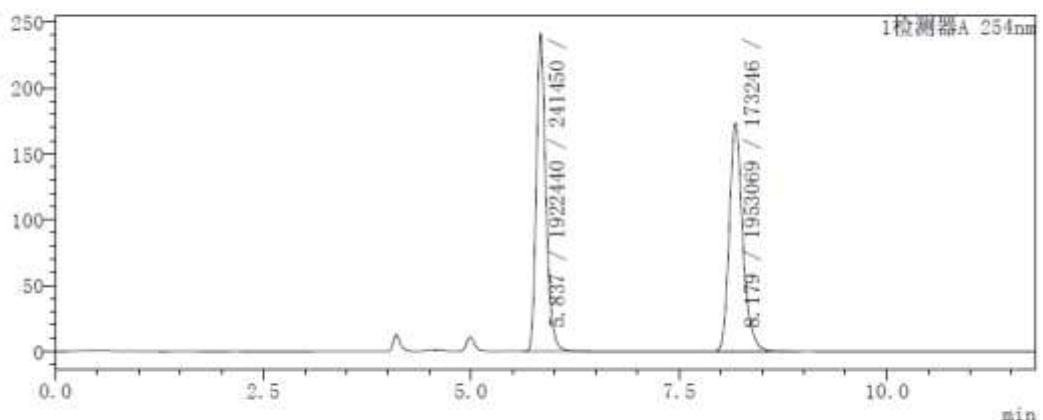
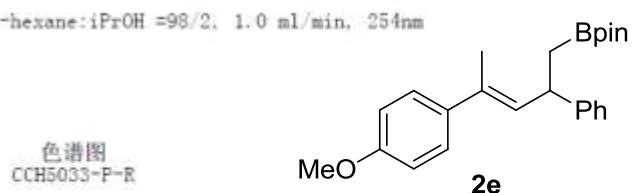
检测器A 254nm

峰表

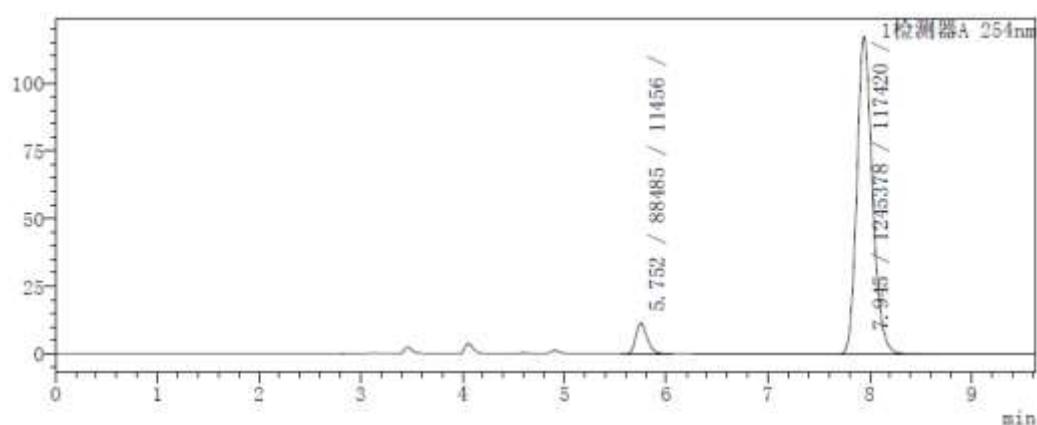
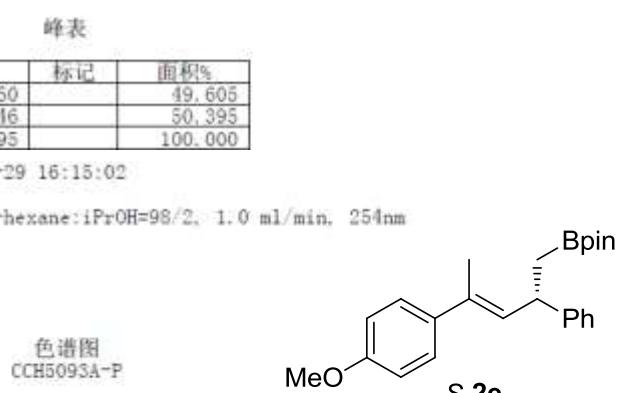
| 峰号 | 保留时间 | 面积 | 高度 | 标记 | 面积% |
|----|-------|--------|--------|----|---------|
| 1 | 4.359 | 61834 | 10044 | M | 6.841 |
| 2 | 6.126 | 841990 | 102072 | | 93.159 |
| 总计 | | 903824 | 112116 | | 100.000 |

处理日期/时间
重复进样计数
描述

: 2017-1-18 18:37:28
: 1
: AD-H, n-hexane:iPrOH =98/2, 1.0 ml/min., 254nm



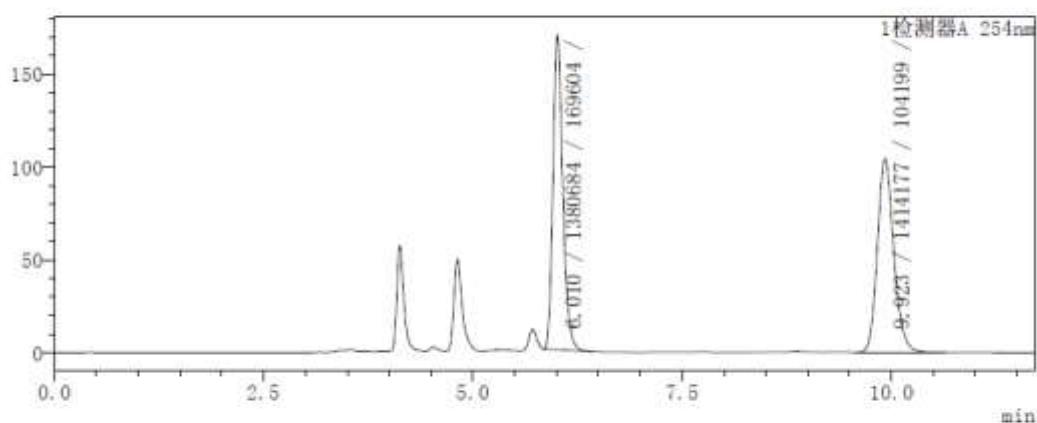
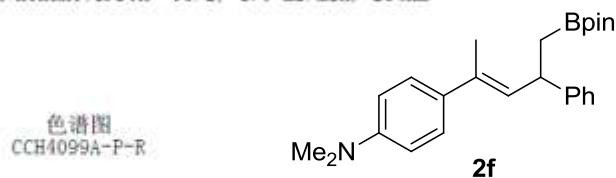
检测器A 254nm
峰号
1
2
总计
保留时间
: 2016-12-29 16:15:02
重复进样计数
: 1
描述
: AD-H, n-hexane:iPrOH=98/2, 1.0 ml/min., 254nm



检测器A 254nm
峰号
1
2
总计
保留时间
: 2016-12-29 16:15:02
重复进样计数
: 1
描述
: AD-H, n-hexane:iPrOH=98/2, 1.0 ml/min., 254nm

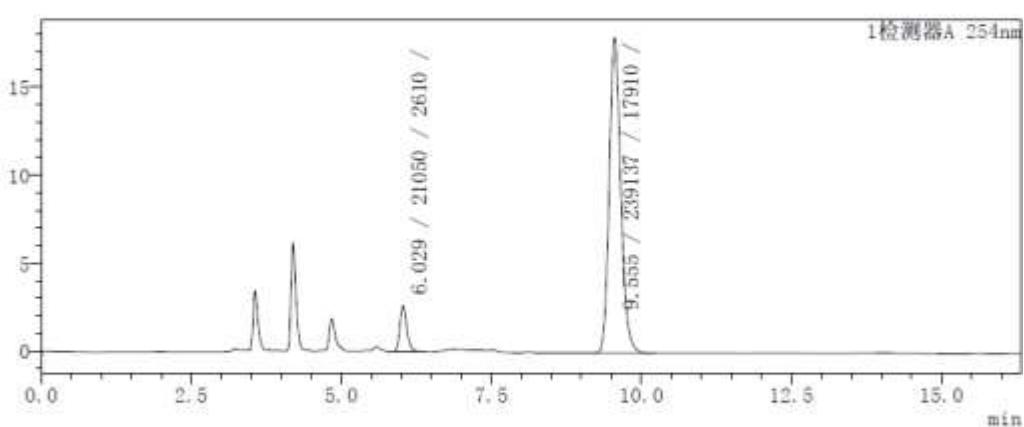
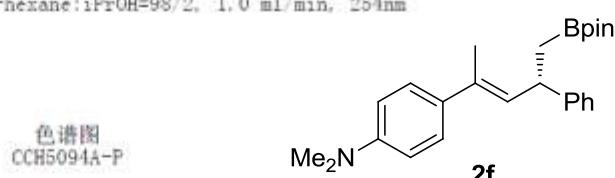
处理日期/时间
重复进样计数
描述

: 2017-1-18 18:05:24
: 1
: AD-H, n-hexane:iPrOH =98/2, 1.0 ml/min, 254nm



检测器A 254nm
处理日期/时间
重复进样计数
描述

: 2016-12-29 17:13:51
: 1
: AD-H, n-hexane:iPrOH=98/2, 1.0 ml/min, 254nm

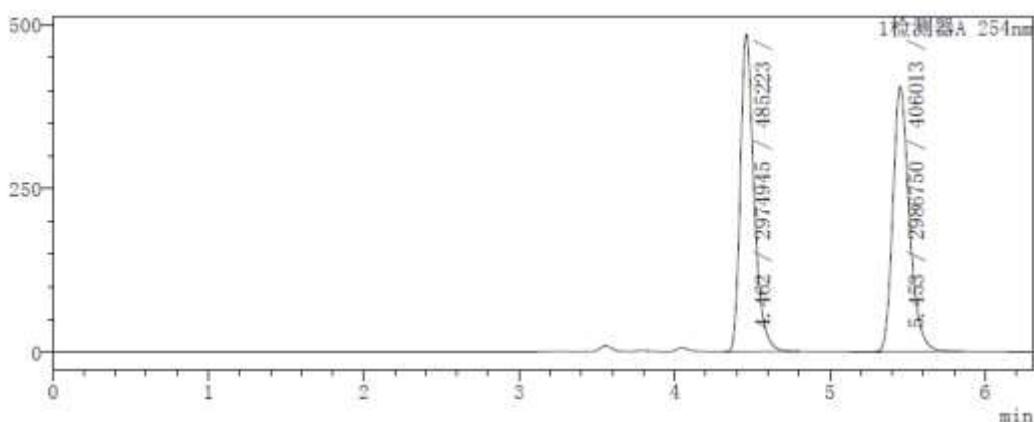
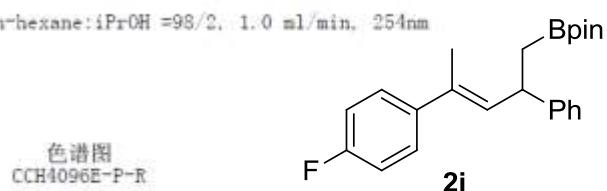


检测器A 254nm
处理日期/时间
重复进样计数
描述

: 2016-12-29 17:13:51
: 1
: AD-H, n-hexane:iPrOH=98/2, 1.0 ml/min, 254nm

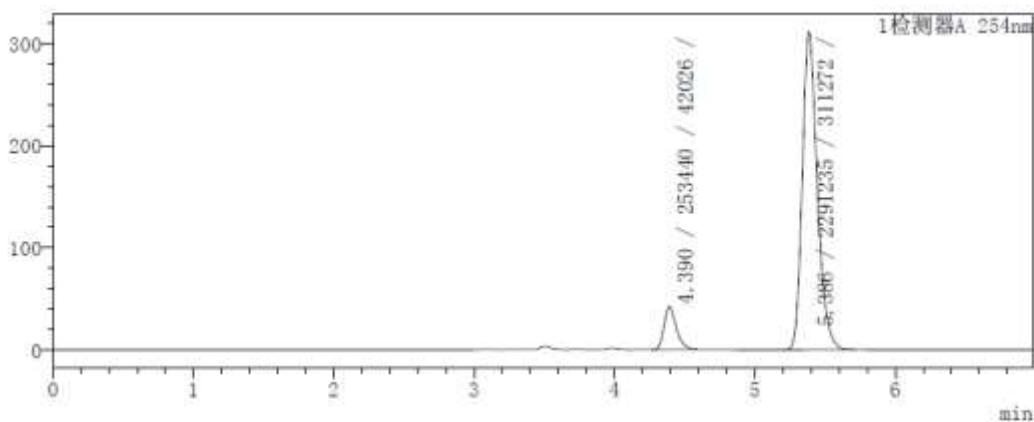
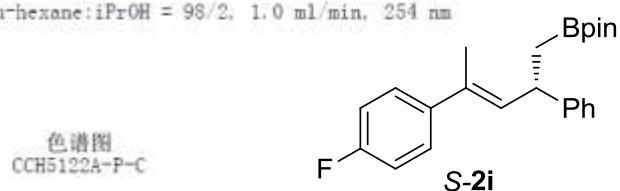
处理日期/时间
重复进样计数
描述

: 2017-1-18 18:24:23
: 1
: AD-H, n-hexane:iPrOH = 98/2, 1.0 ml/min, 254nm



检测器A 254nm
峰号 保留时间 面积 高度 标记 面积%
1 4.462 2974945 485223 M 49.901
2 5.453 2986750 406013 M 50.099
总计 5961695 891236 100.000

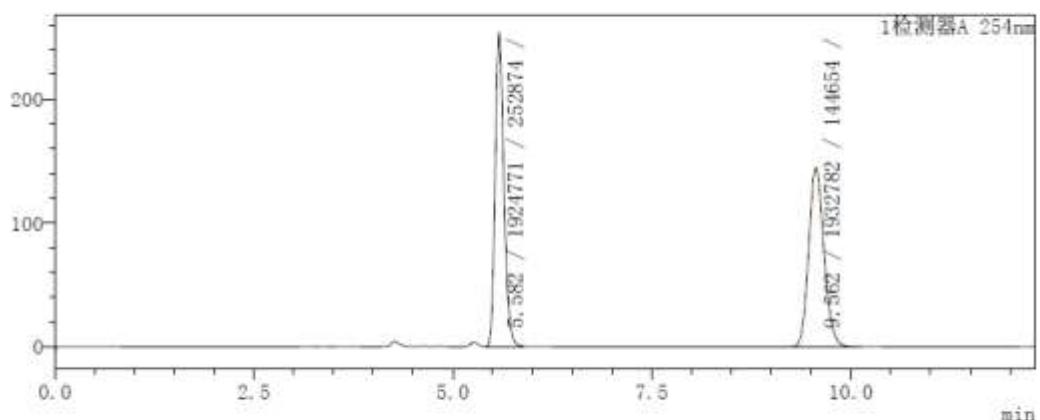
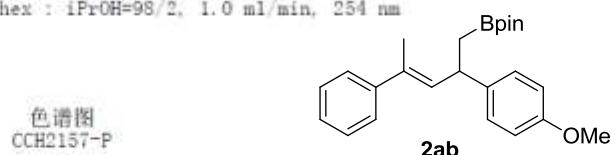
处理日期/时间 : 2017-1-15 00:24:45
重复进样计数 : 1
描述 : AD-H, n-hexane:iPrOH = 98/2, 1.0 ml/min, 254 nm



检测器A 254nm
峰号 保留时间 面积 高度 标记 面积%
1 4.390 253440 42026 M 9.960
2 5.386 2291235 311272 M 90.040
总计 2544675 353298 100.000

处理日期/时间
重复进样计数
描述

: 2016-1-7 18:50:32
: 1
: AD-H, n-hexane:iPrOH=98/2, 1.0 ml/min, 254 nm



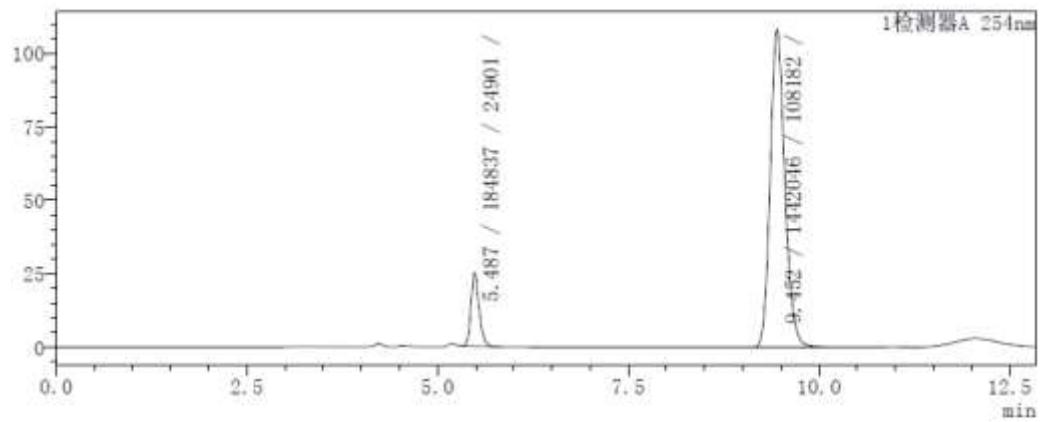
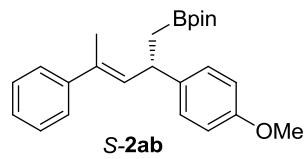
检测器A 254nm

| 峰号 | 保留时间 | 面积 | 高度 | 标记 | 面积% |
|----|-------|---------|--------|----|---------|
| 1 | 5.582 | 1924771 | 252874 | M | 49.896 |
| 2 | 9.562 | 1932782 | 144654 | | 50.104 |
| 总计 | | 3857553 | 397527 | | 100.000 |

处理日期/时间
重复进样计数
描述

: 2017-1-14 23:28:00
: 1
: AD-H, n-hexane:iPrOH = 98/2, 1.0 ml/min, 254 nm

色谱图
CCH5117B-P-C



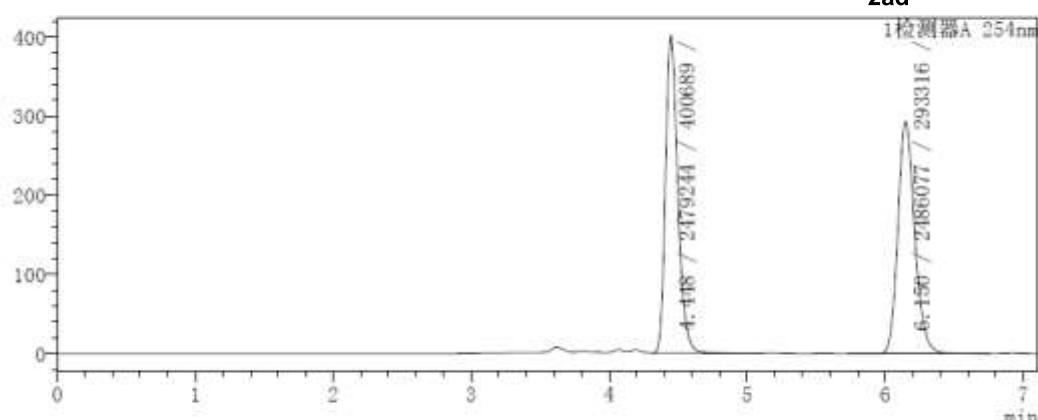
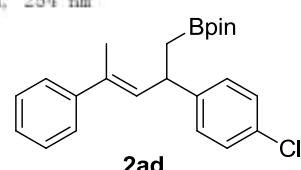
检测器A 254nm

| 峰号 | 保留时间 | 面积 | 高度 | 标记 | 面积% |
|----|-------|---------|--------|----|---------|
| 1 | 5.487 | 184837 | 24901 | | 11.361 |
| 2 | 9.452 | 1442046 | 108182 | | 88.639 |
| 总计 | | 1626883 | 133083 | | 100.000 |

处理日期/时间
重复进样计数
描述

: 2016-1-7 19:13:28
: 1
: AD-H, n-hex : iPrOH=98/2, 1.0 ml/min, 254 nm

色谱图
CCH2155-P



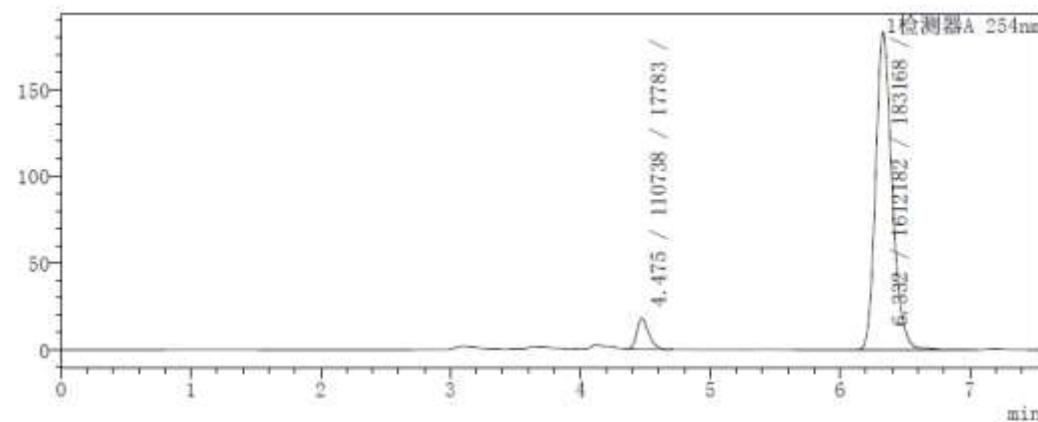
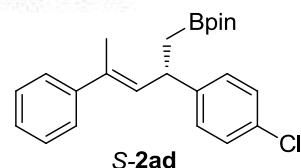
检测器A 254nm
峰表

| 峰号 | 保留时间 | 面积 | 高度 | 标记 | 面积% |
|----|-------|---------|--------|----|---------|
| 1 | 4.418 | 2479244 | 400699 | | 49.931 |
| 2 | 6.150 | 2486077 | 293316 | | 50.069 |
| 总计 | | 4965321 | 694006 | | 100.000 |

处理日期/时间
重复进样计数
描述

: 2017-1-15 00:16:03
: 1
: AD-H, n-hexane:iPrOH = 98/2, 1.0 ml/min, 254 nm

色谱图
CCH5121B-P-C



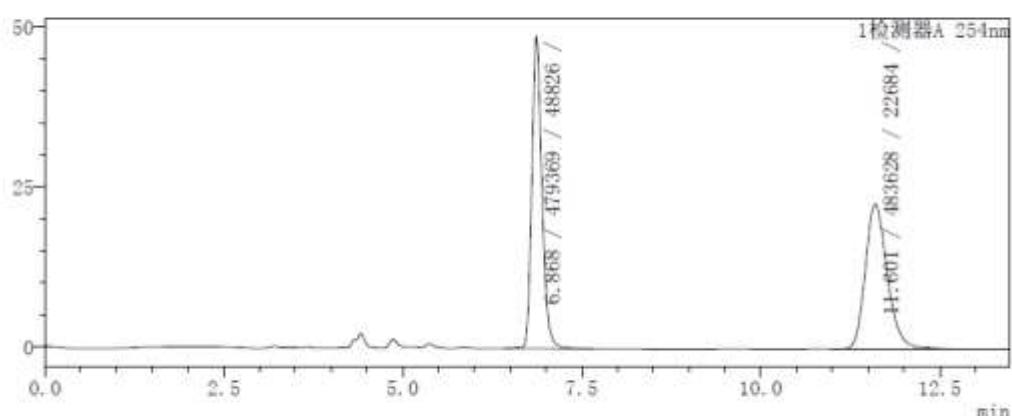
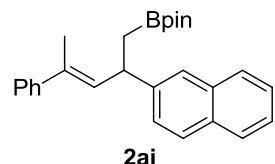
检测器A 254nm
峰表

| 峰号 | 保留时间 | 面积 | 高度 | 标记 | 面积% |
|----|-------|---------|--------|----|---------|
| 1 | 4.475 | 110738 | 17783 | | 6.427 |
| 2 | 6.332 | 1612182 | 183168 | SV | 93.573 |
| 总计 | | 1722920 | 200951 | | 100.000 |

处理日期/时间
重复进样计数
描述

: 2017-1-18 20:07:43
: 1
: AD-H, n-hexane:iPrOH = 99/1, 1.0 ml/min, 254nm

色谱图
CCH4186A-P-R



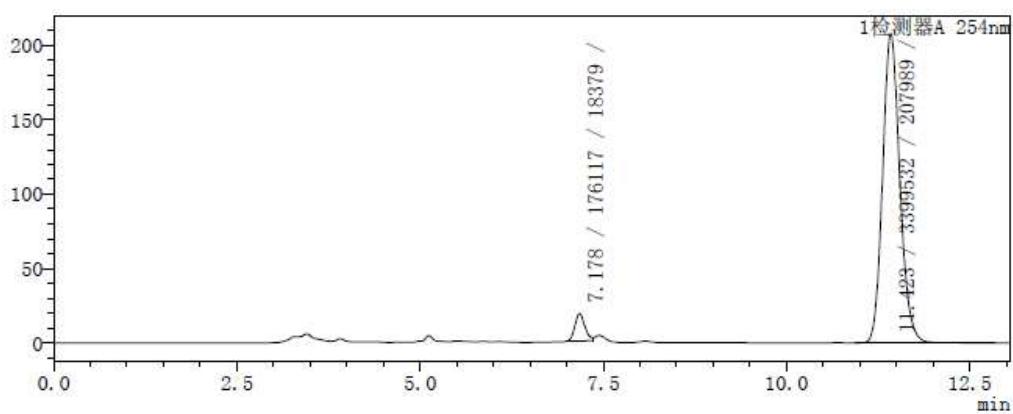
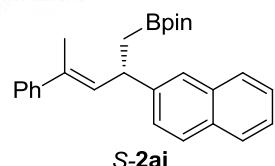
峰表
检测器A 254nm

| 峰号 | 保留时间 | 面积 | 高度 | 标记 | 面积% |
|----|--------|--------|-------|----|---------|
| 1 | 6.868 | 479369 | 48826 | | 49.779 |
| 2 | 11.601 | 483628 | 22684 | | 50.221 |
| 总计 | | 962997 | 71510 | | 100.000 |

分析日期/时间
处理日期/时间
重复进样计数
描述

: 2017-1-16 23:00:18
: 2017-1-16 23:13:22
: 1
: AD, n-hexane:iPrOH = 99/1, 1.0 ml/min, 254 nm

色谱图
CCH5129B-P-C



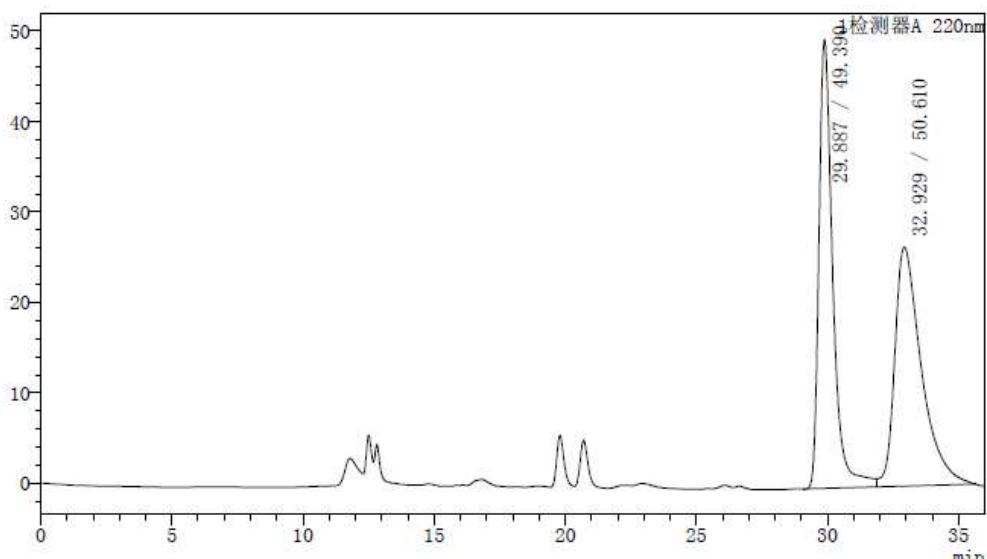
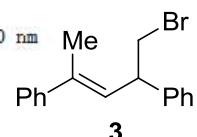
峰表
检测器A 254nm

| 峰号 | 保留时间 | 面积 | 高度 | 标记 | 面积% |
|----|--------|---------|--------|----|---------|
| 1 | 7.178 | 176117 | 18379 | M | 4.925 |
| 2 | 11.423 | 3399532 | 207989 | | 95.075 |
| 总计 | | 3575649 | 226368 | | 100.000 |

处理日期/时间
描述

: 2017/3/9 17:41:12
: 2*AD-H, n-Hex:iPrOH =99.9/0.1, 0.5 mL/min, 220 nm

色谱图



峰表

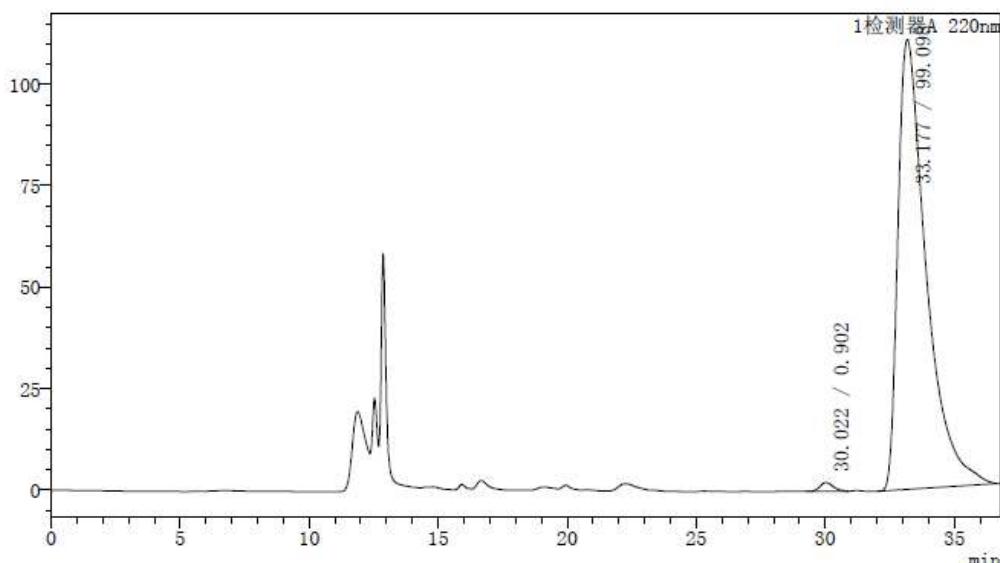
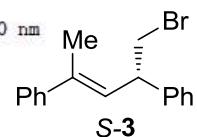
检测器A 220nm

| 峰号 | 保留时间 | 面积 | 高度 | 标记 | 面积% |
|----|--------|---------|-------|-----|---------|
| 1 | 29.887 | 1820269 | 49645 | | 49.390 |
| 2 | 32.929 | 1865203 | 26433 | V M | 50.610 |
| 总计 | | 3685472 | 76078 | | 100.000 |

处理日期/时间
描述

: 2017/3/9 18:31:08
: 2*AD-H, n-Hex:iPrOH =99.9/0.1, 0.5 mL/min, 220 nm

色谱图



峰表

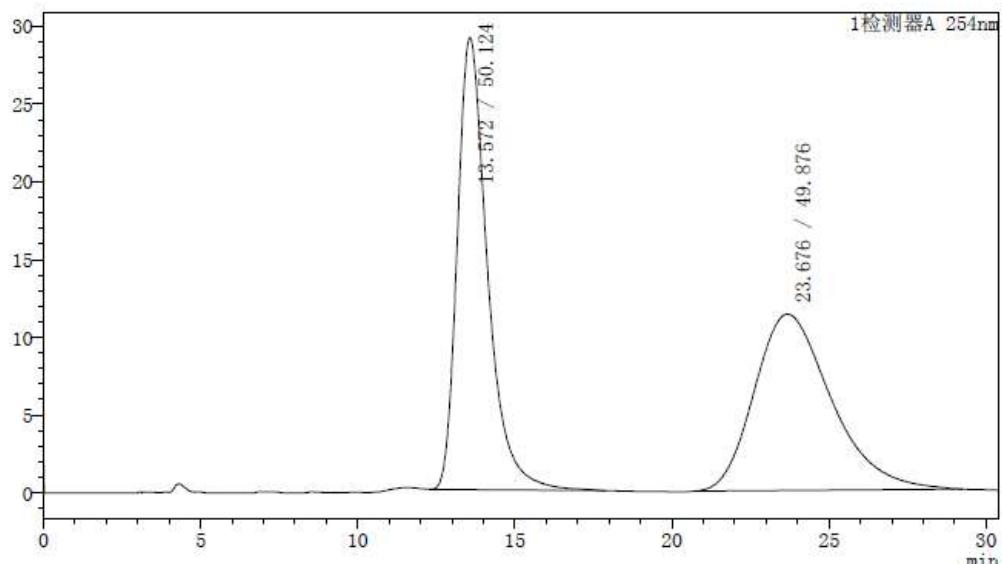
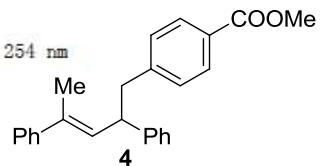
检测器A 220nm

| 峰号 | 保留时间 | 面积 | 高度 | 标记 | 面积% |
|----|--------|---------|--------|----|---------|
| 1 | 30.022 | 76828 | 2174 | | 0.902 |
| 2 | 33.177 | 8440906 | 110846 | M | 99.098 |
| 总计 | | 8517733 | 113020 | | 100.000 |

处理日期/时间
描述

: 2017/3/22 22:34:42
: OJ-H, n-Hex:iPrOH =90/10, 1.0 mL/min, 254 nm

色谱图



峰表

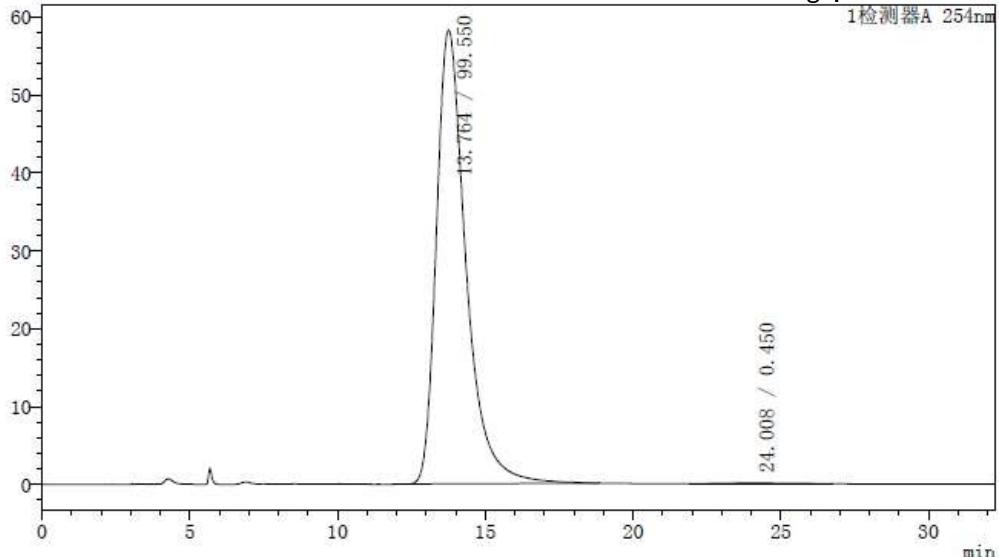
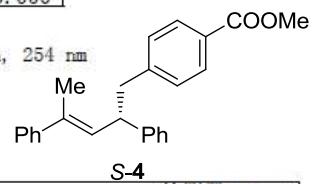
检测器A 254nm

| 峰号 | 保留时间 | 面积 | 高度 | 标记 | 面积% |
|----|--------|---------|-------|----|---------|
| 1 | 13.572 | 1941007 | 29071 | | 50.124 |
| 2 | 23.676 | 1931387 | 11344 | | 49.876 |
| 总计 | | 3872394 | 40415 | | 100.000 |

处理日期/时间
描述

: 2017/3/22 23:08:57
: OJ-H, n-Hex:iPrOH =90/10, 1.0 mL/min, 254 nm

色谱图



峰表

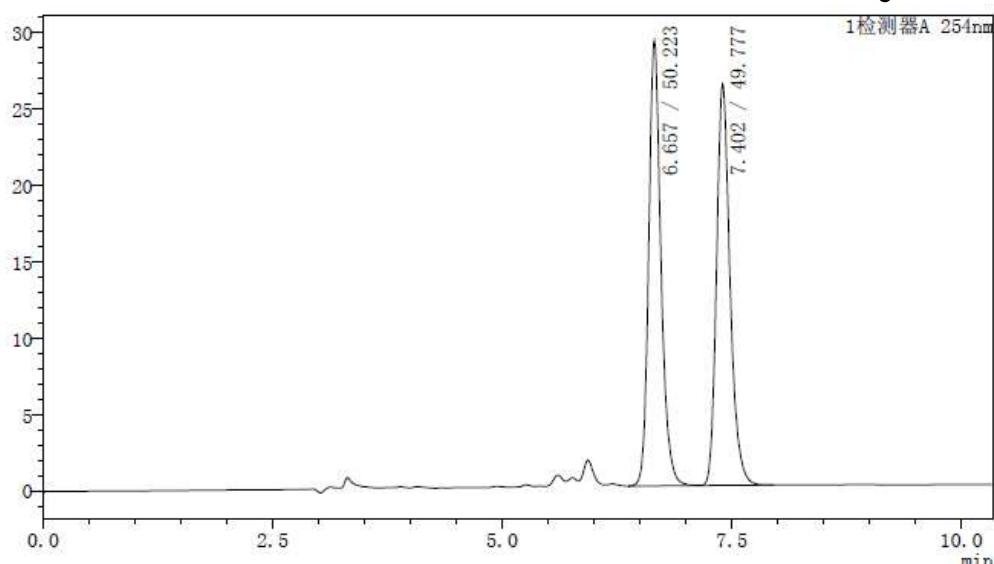
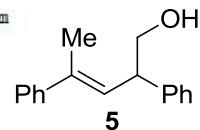
检测器A 254nm

| 峰号 | 保留时间 | 面积 | 高度 | 标记 | 面积% |
|----|--------|---------|-------|----|---------|
| 1 | 13.764 | 4059953 | 58301 | | 99.550 |
| 2 | 24.008 | 18334 | 126 | M | 0.450 |
| 总计 | | 4078287 | 58428 | | 100.000 |

处理日期/时间
描述

: 2017/2/16 16:16:45
: AD-H, n-Hex:iPrOH =90/10, 1.0 mL/min, 254 nm

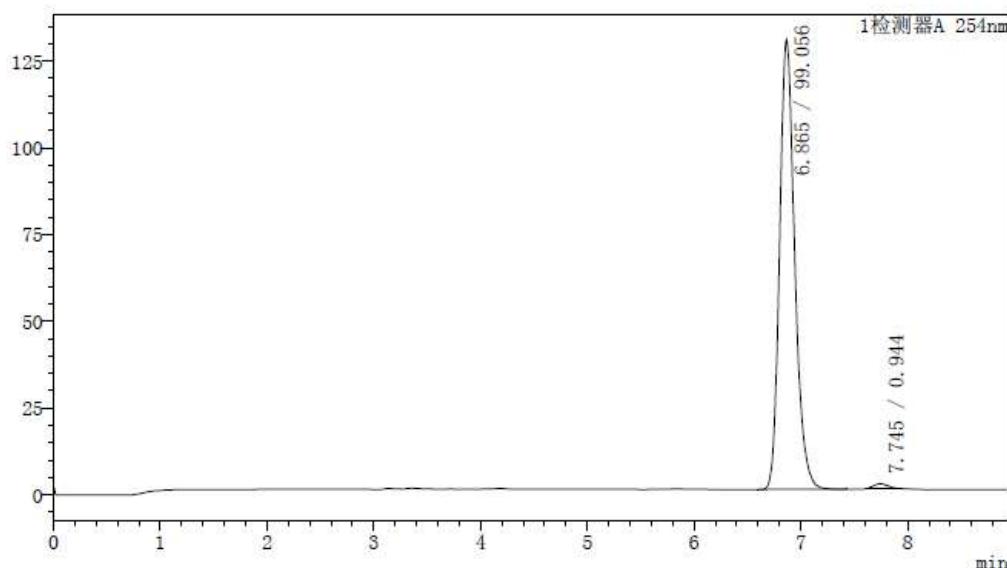
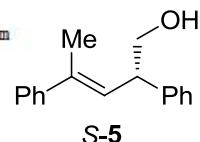
色谱图



处理日期/时间
描述

: 2017/3/14 22:43:45
: AD-H, n-Hex:iPrOH =90/10, 1.0 mL/min, 254 nm

色谱图

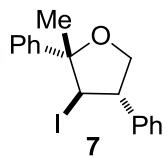


检测器A 254nm

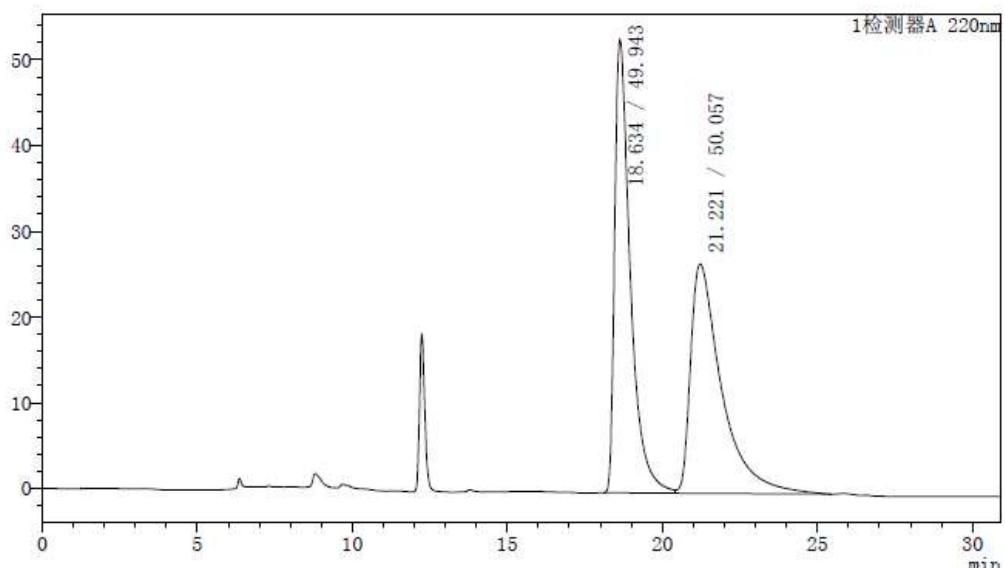
| 峰号 | 保留时间 | 面积 | 高度 | 标记 | 面积% |
|----|-------|---------|--------|----|---------|
| 1 | 6.865 | 1274787 | 129554 | M | 99.056 |
| 2 | 7.745 | 12145 | 1349 | M | 0.944 |
| 总计 | | 1286932 | 130903 | | 100.000 |

处理日期/时间
描述

: 2017/3/14 20:57:22
: 2*AD-H, n-Hex:iPrOH =99.9/0.1, 1.0 mL/min, 220 nm



色谱图

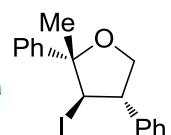


峰表
检测器A 220nm

| 峰号 | 保留时间 | 面积 | 高度 | 标记 | 面积% |
|----|--------|---------|-------|----|---------|
| 1 | 18.634 | 1855174 | 52867 | | 49.943 |
| 2 | 21.221 | 1859420 | 26738 | V | 50.057 |
| 总计 | | 3714594 | 79605 | | 100.000 |

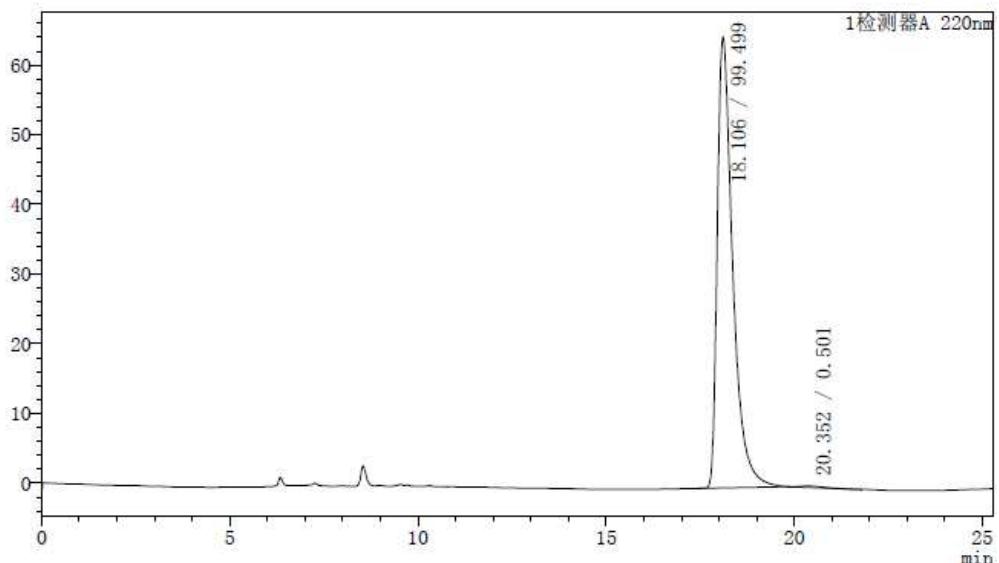
处理日期/时间
描述

: 2017/3/14 19:31:32
: 2*AD-H, n-Hex:iPrOH =99.9/0.1, 1.0 mL/min, 220 nm



色谱图

(2S,3R,4S)-7



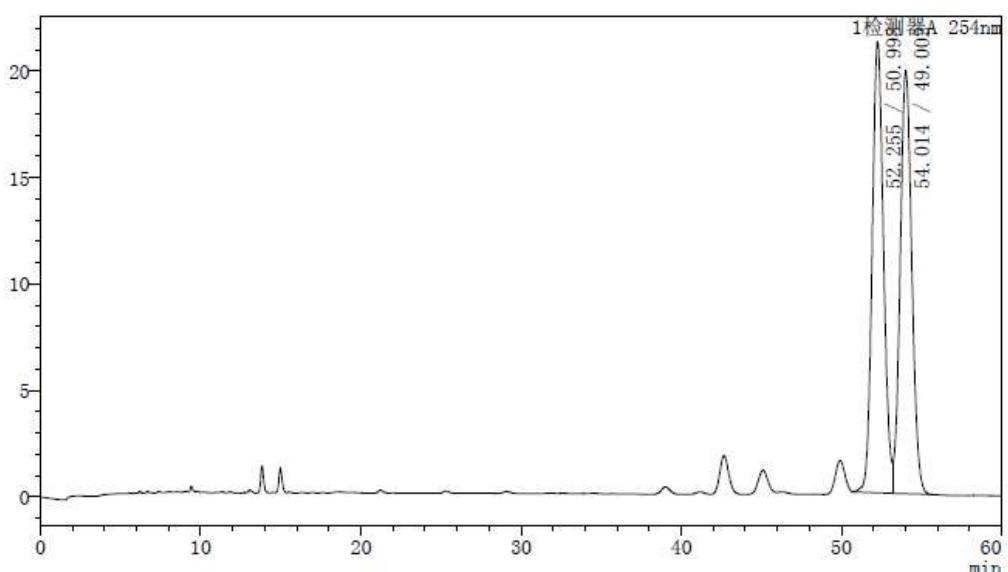
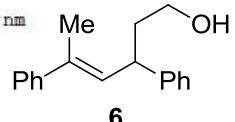
峰表
检测器A 220nm

| 峰号 | 保留时间 | 面积 | 高度 | 标记 | 面积% |
|----|--------|---------|-------|----|---------|
| 1 | 18.106 | 1848395 | 64760 | M | 99.499 |
| 2 | 20.352 | 9302 | 231 | M | 0.501 |
| 总计 | | 1857697 | 64991 | | 100.000 |

处理日期/时间
描述

: 2017/3/9 12:35:51
: 2*AD-H, n-Hex:iPrOH =98/2, 1.0 mL/min, 254 nm

色谱图



峰表

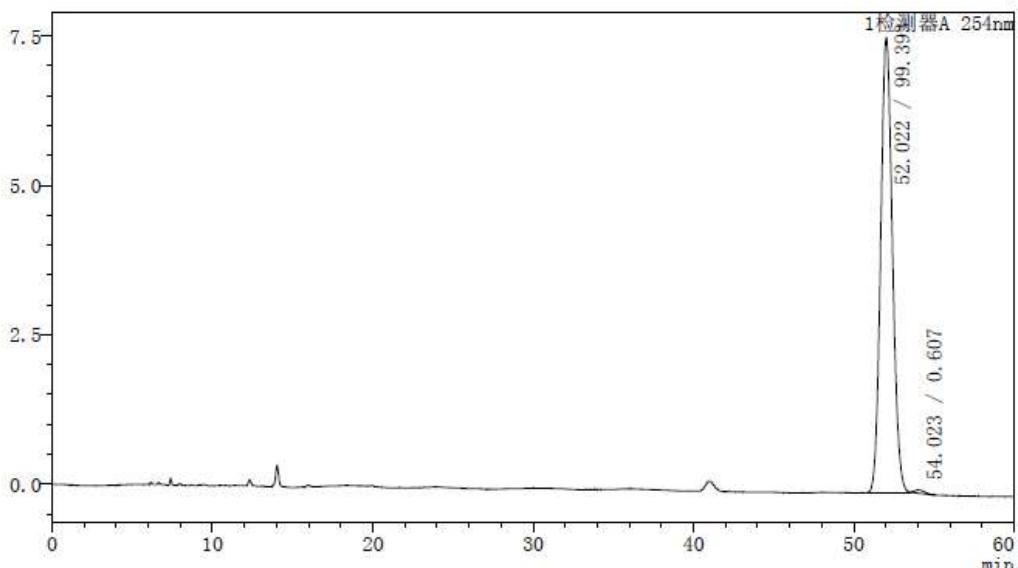
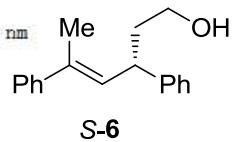
检测器A 254nm

| 峰号 | 保留时间 | 面积 | 高度 | 标记 | 面积% |
|----|--------|---------|-------|----|---------|
| 1 | 52.255 | 1039811 | 21193 | | 50.998 |
| 2 | 54.014 | 999122 | 19878 | V | 49.002 |
| 总计 | | 2038932 | 41070 | | 100.000 |

处理日期/时间
描述

: 2017/3/9 13:47:09
: 2*AD-H, n-Hex:iPrOH =98/2, 1.0 mL/min, 254 nm

色谱图



峰表

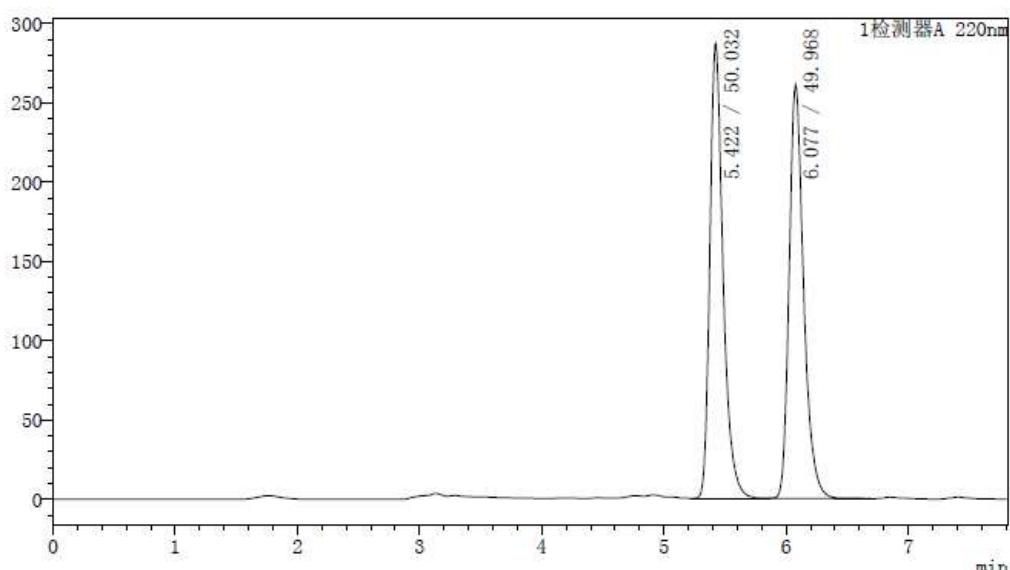
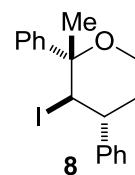
检测器A 254nm

| 峰号 | 保留时间 | 面积 | 高度 | 标记 | 面积% |
|----|--------|--------|------|----|---------|
| 1 | 52.022 | 386146 | 7604 | | 99.393 |
| 2 | 54.023 | 2358 | 56 | M | 0.607 |
| 总计 | | 388504 | 7661 | | 100.000 |

处理日期/时间
描述

: 2017/3/21 21:40:35
: AD-H, n-Hex:iPrOH =98/2, 1.0 mL/min, 220 nm

色谱图



峰表

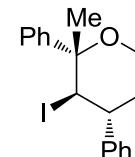
检测器A 220nm

| 峰号 | 保留时间 | 面积 | 高度 | 标记 | 面积% |
|----|-------|---------|--------|----|---------|
| 1 | 5.422 | 2156861 | 286984 | | 50.032 |
| 2 | 6.077 | 2154122 | 260943 | SV | 49.968 |
| 总计 | | 4310983 | 547927 | | 100.000 |

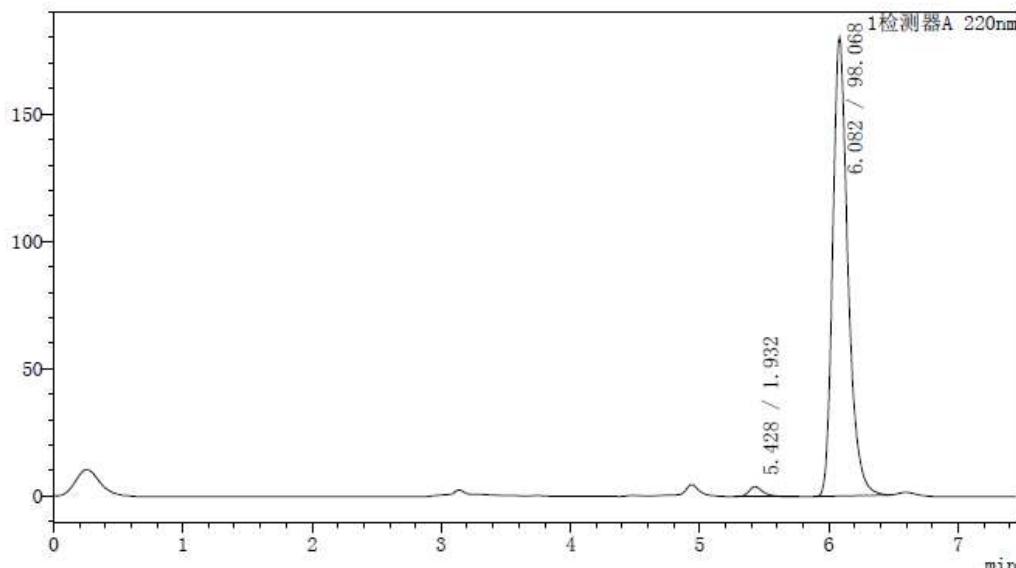
处理日期/时间
描述

: 2017/3/21 21:50:29
: AD-H, n-Hex:iPrOH =98/2, 1.0 mL/min, 220 nm

色谱图



(2S,3R,4R)-8



峰表

检测器A 220nm

| 峰号 | 保留时间 | 面积 | 高度 | 标记 | 面积% |
|----|-------|---------|--------|----|---------|
| 1 | 5.428 | 29046 | 3864 | M | 1.932 |
| 2 | 6.082 | 1474546 | 180051 | | 98.068 |
| 总计 | | 1503592 | 183915 | | 100.000 |