Electronic Supplementary Material (ESI) for RSC Advances.

Copper-Catalyzed Hydroboration of Propargyl-Functionalized Alkynes in Water

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SUPPORTING INFORMATION

CONTENTS

1. General Information.

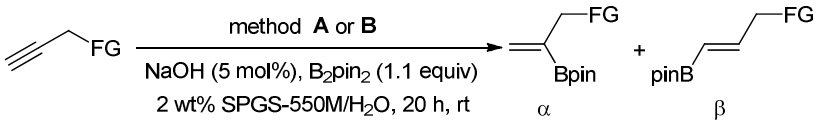
NMR spectra were recorded in $CDCl_3$ solution either on a Varian VNMRS 300 MHz or Varian VNMRJ 400 MHz spectrometers at room temperature. Chemical shifts (δ) are given in parts per million from the peak of tetramethylsilane (δ = 0.00 ppm) as internal standard in ^{1}H NMR or from the solvent peak of $CDCl_3$ (δ = 77.00 ppm) in ^{13}C-APT NMR. ESI-QTOF-MS measurements were performed in the positive ion mode (m/z 50-2000 range). IR spectra were obtained on a FTIR-ATR instrument. Flash chromatography was perforrmed using silica gel (230-400 mesh). Thin layer chromatography (TLC) was performed using supported silica gel GF254, 0.25 mm thickness. For visualization, TLC plates were either placed under UV light 254 nm or stained with iodine vapor.

Phosphines, phenanthroline and $Cu(OAc)_2.H_2O$ were purchased from commercial sources. Bis(pinacolato)diboron, SPGS-550M solution (2%, w/w, in H_2O), propargyl acetate, propargyl alcohol, homopropargyl alcohol, propargyl amine, *N*,*N*-dimethylpropargylamine and *N*-methyl-*N*-propargylbenzylamine were purchased from Aldrich and used as received.

Phenyl propargyl ether,[1] benzyl propargyl ether,[2] prop-2-yn-1-yl benzoate,[3] *tert*-butyl prop-2-yn-1-yl carbonate,[4] *tert*-butyldimethyl(prop-2-yn-1-yloxy)silane,[5] prop-2-yn-1-yl 4-methylbenzenesulfonate,[6] but-3-yn-1-yl *tert*-butyl carbonate,[4] *N*-Boc-propargylamine,[7] *N*,4-dimethyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide,[8] phenyl(prop-2-yn-1-yl)sulfane[1] were prepared according to reported procedures. Also [Cu(Cl)(IMes)],[9] [Cu(Cl)(IPr)][9] and $[Pd(Cl)_2(PPh_3)_2]$[10] were prepared according to procedures described in the literature.

[1] W. Zhang, Z. Li, M. Zhou, F. Wu, X. Hou, H. Luo, H. Liu, X. Han, G. Yan, Z. Ding and R. Li, *Bioorg. Med. Chem. Lett.*, 2014, **24**, 799.
[2] L. He, M. Schulz-Senft, B. Thiedemann, J. Linshoeft, P. J. Gates and A. Staubitz, *Eur. J. Org. Chem*., 2013, **78**, 6309.
[3] G. R. Pereira, G. C. Brandão, L. M. Arantes, H. A. Oliveira Jr., R. C. Paula, M. F. A. Nascimento, F. M. Santos, R. K. Rocha, J. C. D. Lopes and A. B. Oliveira, *Eur. J. Med. Chem.,* 2014, **73**, 295.
[4] T. D. Montgomery, A. E. Nibbs, Y. Zhu and V. H. Rawal, *Org. Lett*., 2014, **16**, 3480.
[5] J. Wang, H. Zhu, Y. Li, L. Wang, Y. Qiu, Z. Qiu, M. Zhong, X. Liu and Y. Liang, *Org. Lett.,* 2014, **16**, 2236.
[6] Q. Zhang, H. Ren and G. L. Baker, *Beilstein J. Org. Chem.,* 2014, **10***,* 1365.
[7] G. A. Molander and F. Cadoret, *Tetrahedron Lett.,* 2011, **52**, 2199.
[8] D. Campolo, T. Arif, C. Borie, D. Mouysset, N. Vanthuyne, J. Naubron, M. P. Bertrand and M. Nechab, *Angew. Chem. Int. Ed.,* 2014, **53**, 3227.
[9] C. A. Citadelle, E. L. Nouy, F. Bisaro, A. M. Z. Slawin and C. S. J. Cazin, *Dalton Trans.*, 2010, **39**, 4489.
[10] R. S. Barbiéri, *Quim. Nova*, 1991, **14**, 212.

2. General procedure for hydroboration of propargylic-substituted alkynes.

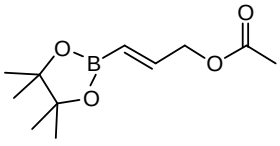


method **A**: $Cu(OAc)_2.H_2O$ (8 mol%), dppe (10 mol%)
method **B**: [Cu(Cl)(IMes)] (5 mol%)

Method A: A 5 mL vial with magnetic stir bar was charged with $Cu(OAc)_2.H_2O$ (8 mol%, 0.04 mmol, 8.0 mg), dppe (10 mol%, 0.05 mmol, 19.9 mg), B_2pin_2 (1.1 equiv., 0.55 mmol, 139.7 mg), alkyne (1.0 equiv., 0.50 mmol), SPGS-550M (2%, w/w, 0.50 mL) and NaOH 1 $molL^{-1}$ (25 µL). The resulting mixture was vigorously strirred at room temperature for 20 h. After this period, anhydrous Na_2SO_4 was added and the solid mixture was washed with ethyl acetate (2 x 1 mL). The organic layer was transferred to a round-bottom flask and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using hexane:EtOAc as an eluent to afford the desired alkenyl boronate.

Method B: A 5 mL vial with magnetic stir bar was charged with [Cu(Cl)(IMes)] (5 mol%, 0.025 mmol, 10.1 mg), B_2pin_2 (1.1 equiv., 0.55 mmol, 139.7 mg), alkyne (1.0 equiv., 0.50 mmol), SPGS-550M (2%, w/w, 0.50 mL) and NaOH 1 $molL^{-1}$ (25 µL). The resulting mixture was vigorously strirred at room temperature for 20 h. After this period, anhydrous Na_2SO_4 was added and the solid mixture was washed with ethyl acetate (2 x 1 mL). The organic layer was transferred to a round-bottom flask and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using hexane:EtOAc as an eluent to afford the desired alkenyl boronate.

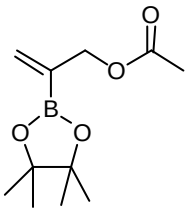
(*E*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl acetate (**β-1**)[11]



Pale yellow oil. Yield (method A): 88 mg, 78%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 6.61 (dt, *J* = 18.2, 4.5 Hz, 1H), 5.68 (dt, *J* = 18.2, 1.8 Hz, 1H), 4.66 (dd, *J* = 4.5, 1.8 Hz, 2H), 2.09 (s, 3H), 1.28 (s, 12H). ^{13}C-APT NMR (75 MHz, $CDCl_3$, ppm): 170.5, 145.9, 83.4, 65.4, 24.7, 20.8, C[B] was not detected.

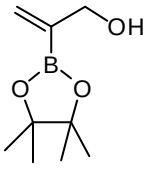
[11] K. Shirakawa, A. Arase and M. Hoshi, *Synthesis*, 2004, 1814.

2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl acetate (**α-1**)[12]



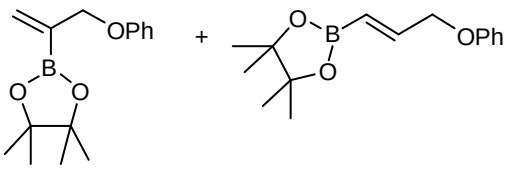
Pale yellow oil. Yield (method B): 84 mg, 75%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 5.95 - 5.93 (m, 1H), 5.84 (bs, 1H), 4.70 (t, *J* = 1.6 Hz, 2H), 2.09 (s, 3H), 1.27 (s, 12H). ^{13}C-APT NMR (100 MHz, $CDCl_3$, ppm): 170.6, 129.8, 83.7, 66.0, 24.7, 20.9, C[B] was not detected.

2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-1-ol (**α-2**)[13]



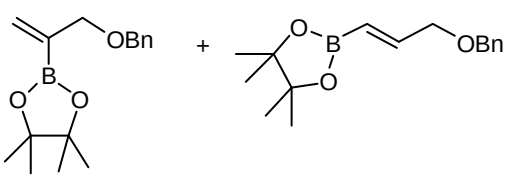
Pale yellow oil. Yield: α+β, method A: 18 mg, 20%; method B: 42 mg, 46%. Analytical data are given for pure **α-2**: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 5.95 - 5.89 (m, 1H), 5.85 (s, 1H), 4.26 (s, 2H), 1.30 (s, 12H). ^{13}C-APT NMR (75 MHz, $CDCl_3$, ppm): 128.9, 83.7, 65.9, 24.8, C[B] was not detected.

4,4,5,5-tetramethyl-2-(3-phenoxyprop-1-en-2-yl)-1,3,2-dioxaborolane and (*E*)-4,4,5,5-tetramethyl-2-(3-phenoxyprop-1-en-1-yl)-1,3,2-dioxaborolane (**3**)[13, 14]



Pale yellow oil. Yield: α+β, method A: 101 mg, 78%; method B: 110 mg, 85%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.29 - 7.23 (m, α + β), 6.96 - 6.87 (m, α + β), 6.76 (dt, *J* = 18.1, 4.4 Hz, β), 6.06 - 5.99 (2m, α), 5.83 (dt, *J* = 18.1, 1.8 Hz, β), 4.65 (t, *J* = 1.9 Hz, α), 4.61 (dd, *J* = 4.4, 1.8 Hz, β), 1.29 (s, α), 1.28 (s, β). ^{13}C-APT NMR (100 MHz, $CDCl_3$, ppm): 158.8, 158.5, 147.3, 129.8, 129.4, 129.3, 120.8, 120.5, 114.9, 114.6, 83.7, 83.3, 69.3, 69.2, 24.7, 24.8, C[B] was not detected.

2-(3-(benzyloxy)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and (*E*)-2-(3-(benzyloxy)prop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4**)[15]

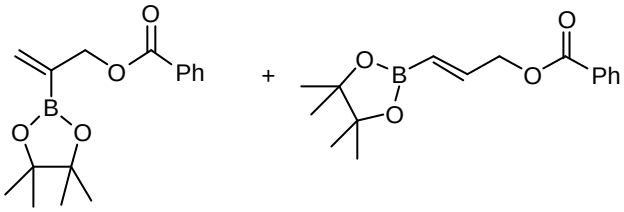


Pale yellow oil. Yield: α+β, method A: 120 mg, 88%; method B: 123 mg, 90%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.38 - 7.22 (m, α+β), 6.69 (dt, *J* = 18.1, 4.6 Hz, β), 6.02 - 5.94 (m, α), 5.77 (dt, *J* = 18.1, 1.8 Hz, β), 4.55 (s, α), 4.53 (s, β), 4.15 (t, *J* = 1.8 Hz, α), 4.11 (dd, *J* = 4.6, 1.8 Hz, β), 1.27 (s, β), 1.26 (s, α). ^{13}C-APT

[12] C. Morril, T. W. Funk and R. H. Grubbs, *Tetrahedron Lett.*, 2004, **45**, 7733.
[13] A. L. Moure, P. Mauleón, R. Gomez-Arrayás and J. C. Carretero, *Org. Lett.*, 2013, **15**, 2054.
[14] S. Hong, M. Liu, W. Zhang and W. Deng, *Tetrahedron Lett.*, 2016, **57**, 1.
[15] (a) H. Jang, A. R. Zhugralin, Y. Lee and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2011, **133**, 7859; (b) H. Yoshida, I. Kageyuki and K. Takaki, *Org. Lett.*, 2014, **16**, 3512.

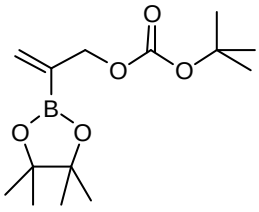
NMR (75 MHz, $CDCl_3$, ppm): 149.1, 138.7, 138.2, 129.4, 128.3, 128.2, 127.5, 127.4, 127.3, 83.4, 83.2, 72.2, 72.1, 71.8, 71.6, 24.7.

2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl benzoate and (*E*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl benzoate (**5**)[16]



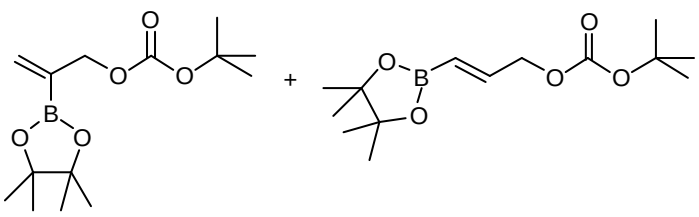
Pale yellow oil. Yield: α+β, method A: 115 mg, 80%; method B: 125 mg, 87%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 8.11 - 8.05 (m, α + β), 7.60 - 7.52 (m, α + β), 7.48 - 7.40 (m, α + β), 6.74 (dt, *J* = 18.1, 4.4 Hz, β), 6.02 - 5.98 (m, α), 5.97 - 5.92 (m, α), 5.80 (dt, *J* = 18.1, 1.7 Hz, β), 4.96 (t, *J* = 1.6 Hz, α), 4.92 (dd, *J* = 4.4, 1.7 Hz, β), 1.28 (s, α + β). ^{13}C-APT NMR (75 MHz, $CDCl_3$, ppm): 166.2, 166.0, 145.9, 133.3, 133.0, 132.8, 130.4, 129.9, 129.6, 129.5, 128.4, 128.3, 128.2, 83.7, 83.4, 66.4, 65.6, 24.7. IR (ν_{max}, cm^{-1}): 2982, 1714, 1345, 1315, 1275, 1105, 906, 706. HRMS (ESI): *m/z*, calcd for $C_{16}H_{21}BO_4$ $[M+H]^+$ 289.1614, found 289.1569.

tert-butyl (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl) carbonate (**α-6**)



Pale yellow oil. Yield (method B): 135 mg, 95%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 5.96 - 5.93 (m, 1H), 5.88 - 5.85 (m, 1H), 4.69 (t, *J* = 1.7 Hz, 2H), 1.49 (s, 9H), 1.26 (s, 12H). ^{13}C-APT NMR (75 MHz, $CDCl_3$, ppm): 153.4, 129.8, 83.6, 81.7, 68.1, 27.8, 24.8, C[B] was not detected. IR (ν_{max}, cm^{-1}): 2982, 1744, 1345, 1275, 1254, 1145, 865, 736. HRMS (ESI): *m/z*, calcd for $C_{14}H_{25}BO_5$ $[M+H]^+$ 285.1876, found 285.1831.

tert-butyl (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl) carbonate and (*E*)-*tert*-butyl (3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl) carbonate (**6**)[17]

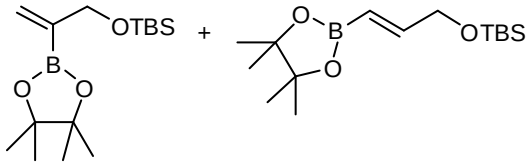


Pale yellow oil. Yield: α+β, method A: 72 mg, 51%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 6.61 (dt, *J* = 18.0, 4.7 Hz, β), 5.96 - 5.93 (m, α), 5.88 - 5.85 (m, α), 5.69 (dt, *J* = 18.0, 1.8 Hz, β), 4.69 (t, *J* = 1.7 Hz, α),

[16] C. Morril and R. H. Grubbs, *J. Org. Chem.*, 2003, **68**, 6031.
[17] J. Stambasky, A. V. Malkov and P. Kocovský, *Collect. Czech. Chem. Commun*., 2008, **73**, 705.

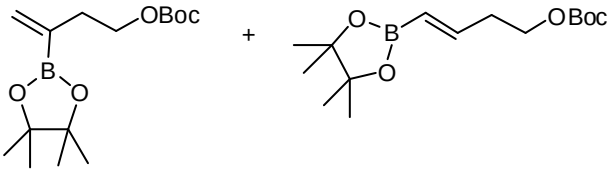
4.63 (dd, *J* = 4.7, 1.8 Hz, β), 1.49 (s, α), 1.48 (s, β), 1.26 (s, α). ^{13}C-APT NMR (100 MHz, $CDCl_3$, ppm): 153.4, 153.2, 145.7, 129.8, 83.6, 83.4, 82.1, 81.7, 68.1, 67.9, 27.8, 27.7, 24.8, C[B] was not detected.

tert-butyldimethyl((2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)oxy)silane and (*E*)-*tert*-butyldimethyl((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)oxy) silane (**7**)[15a,18]



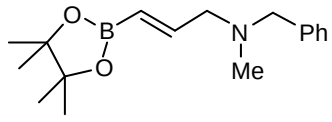
Pale yellow oil. Yield: α+β, method A: 116 mg, 78%; method B: 134 mg, 90%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 6.66 (dt, *J* = 17.9, 3.6 Hz, β), 5.98 - 5.92 (m, α), 5.88 - 5.84 (m, α), 5.74 (dt, *J* = 17.9, 2.2 Hz, β), 4.27 (t, *J* = 2.3 Hz, α), 4.23 (dd, *J* = 3.6, 2.2 Hz, β), 1.26 (s, β), 1.25 (s, α), 0.91 (s, α), 0.90 (s, β), 0.05 (s, α), 0.04 (s, β). ^{13}C-APT NMR (100 MHz, $CDCl_3$, ppm): 152.1, 127.1, 83.3, 83.0, 64.4 (2C), 26.0, 25.9, 24.74, 24.72, 18.4 (2C), -5.3, -5.4, C[B] was not detected.

tert-butyl (3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl) carbonate and (*E*)-*tert*-butyl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl) carbonate (**10**)



Pale yellow oil. Yield: α+β, method A: 51 mg, 34%; method B: 74 mg, 50%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 6.58 (dt, *J* = 18.0, 6.4 Hz, β), 5.87 (d, *J* = 3.2 Hz, α), 5.71 (bs, α), 5.54 (dt, *J* = 18.0, 1.5 Hz, β), 4.17 - 4.11 (m, α+β), 2.55 - 2.48 (m, α+β), 1.48 (s, β), 1.47 (s, α), 1.27 (s, α), 1.26 (s, β). ^{13}C-APT NMR (100 MHz, $CDCl_3$, ppm): 153.4, 148.6, 132.0, 83.5, 83.1, 81.9, 81.6, 66.4, 65.4, 34.9, 34.8, 27.8, 27.7, 24.7. IR (ν_{max}, cm^{-1}): 2982, 1744, 1634, 1354, 1275, 1245, 1135, 846. HRMS (ESI): *m/z*, calcd for $C_{15}H_{27}BO_5$ $[M+H]^+$ 299.2033, found 299.2078.

(*E*)-*N*-benzyl-*N*-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-1-amine (**13**)

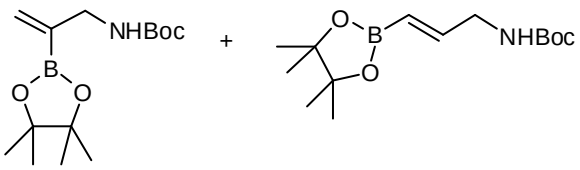


Pale yellow oil. Yield: method A: 83 mg, 58%; method B: 102 mg, 71%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.35 - 7.20 (m, 5H), 6.67 (dt, *J* = 18.0, 5.9 Hz, 1H), 5.65 (dt, *J* = 18.0, 1.6 Hz, 1H), 3.50 (s, 2H), 3.10 (dd, *J* = 5.9, 1.6 Hz, 2H), 2.19 (s, 3H), 1.27 (s, 12H). ^{13}C-APT NMR (75 MHz, $CDCl_3$, ppm): 150.9, 139.1, 129.0, 128.2, 126.9, 83.1, 61.9, 61.7, 42.4, 24.8, C[B] was not detected. IR (ν_{max}, cm^{-1}):

[18] R. W. Hoffmann and S. Dresely, *Synthesis*, 1988, 103.

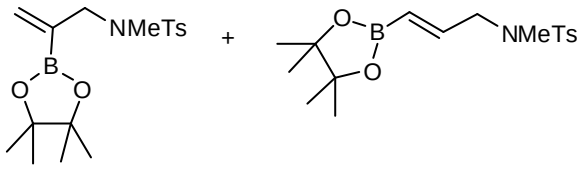
2972, 2782, 1644, 1354, 1315, 1145, 975, 736. HRMS (ESI): *m/z*, calcd for $C_{17}H_{26}BNO_2$ $[M+H]^+$ 288.2138, found 288.2100.

tert-butyl (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)carbamate and (*E*)-*tert*-butyl (3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)carbamate (**14**)[19]



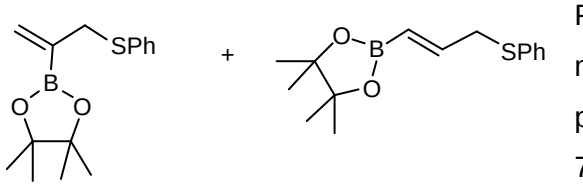
Pale yellow oil. Yield: α+β, method A: 61 mg, 43%; method B: 120 mg, 85%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 6.56 (dt, *J* = 18.1, 4.5 Hz, β), 5.86 - 5.82 (m, α), 5.75 - 5.70 (m, α), 5.55 (dt, *J* = 18.1, 1.8 Hz, β), 4.80 (s, NH, α), 4.68 (s, NH, β), 3.81 (d, *J* = 5.1 Hz, α), 3.16 (t, *J* = 6.4 Hz, β), 1.42 (s, α), 1.40 (s, β), 1.24 (s, α), 1.21 (s, β). ^{13}C-APT NMR (100 MHz, $CDCl_3$, ppm, α only): 155.8, 129.1, 83.6, 78.9, 44.3, 28.4, 24.7, C[B] was not detected.

N,4-dimethyl-*N*-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)benzenesulfonamide and (*E*)-*N*,4-dimethyl-*N*-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)benzenesulfonamide (**15**)



Pale yellow oil. Yield: α+β, method A: 119 mg, 68%; method B: 105 mg, 60%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.71-7.62 (m, α + β), 7.33-7.27 (m, α + β), 6.45 (dt, *J* = 17.8, 5.5 Hz, β), 6.01 - 5.97 (m, α), 5.94 - 5.90 (m, α), 5.60 (dt, *J* = 17.8, 1.6 Hz, β), 3.75 - 3.72 (m, α), 3.69 (dd, *J* = 5.5, 1.6 Hz, β), 2.67 (s, α + β), 2.43 (s, α + β), 1.26 and 1.25 (2s, α + β). ^{13}C-APT NMR (100 MHz, $CDCl_3$, ppm): 146.5, 143.3, 143.1, 134.9, 134.5, 130.9, 129.7, 129.6, 127.5, 127.4, 83.7, 83.4, 54.1, 53.2, 34.8, 34.7, 24.8, 24.7, 21.5, 21.4, C[B] was not detected. IR (ν_{max}, cm^{-1}): 2982, 1644, 1335, 1164, 1135, 915, 665, 546. HRMS (ESI): *m/z*, calcd for $C_{17}H_{26}BNO_4S$ $[M+H]^+$ 352.1757, found 352.1786.

4,4,5,5-tetramethyl-2-(3-(phenylthio)prop-1-en-2-yl)-1,3,2-dioxaborolane and (*E*)-4,4,5,5-tetramethyl-2-(3-(phenylthio)prop-1-en-1-yl)-1,3,2-dioxaborolane (**16**)[13, 18]



Pale yellow oil. Yield: α+β, method A: 108 mg, 78%; method B: 120 mg, 87%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.34 - 7.29 (m, α + β), 7.28 - 7.21 (m, α + β), 7.19 - 7.12 (m, α + β), 6.63 (dt, *J* = 17.7, 6.6 Hz, β),

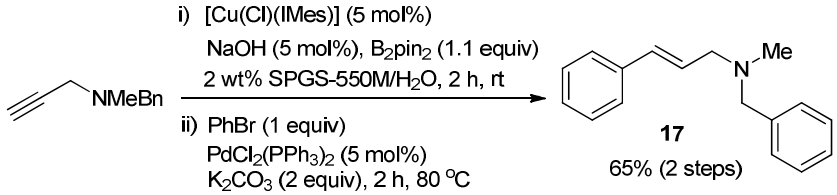
[19] (a) F. Berrée, P. G. Bleis and B. Carboni, *Tetrahedron Lett.*, 2002, **43**, 4935; (b) Y. Lee, H. Jang, A. and H. Hoveyda, *J. Am. Chem. Soc.*, 2009, **131**, 18234.

5.83 - 5.81 (m, α), 5.69 (s, α), 5.56 (dt, *J* = 17.7, 1.3 Hz, β), 3.67 (m, α), 3.62 (dd, *J* = 6.5, 1.3 Hz, β), 1.28 (s, α), 1.25 (s, β). ^{13}C-APT NMR (100 MHz, $CDCl_3$, ppm): 147.5, 136.6, 131,2, 129.3, 129.8, 128.8, 128.6, 126.0, 125.9, 83.8, 83.3, 38.5, 38.4, 24.7, C[B] was not detected.

3. Procedure for tandem hydroboration/Suzuki coupling

A 5 mL vial with magnetic stir bar was charged with [Cu(Cl)(IMes)] (5 mol%, 0.025 mmol, 10.1 mg), B_2pin_2 (1.1 equiv., 0.55 mmol, 139.7 mg), alkyne (1.0 equiv., 0.50 mmol), SPGS-550M (2%, w/w, 0.50 mL) and NaOH 1 molL^{-1} (25 µL). The resulting mixture was vigorously strirred at room temperature for 20 h or 2 h (according to the Scheme shown below). After this period, $[Pd(Cl)_2(PPh_3)_2]$ (5 mol%, 0.025 mmol, 17.5 mg), K_2CO_3 (2.0 equiv., 1.00 mmol, 138.2 mg) and bromobenzene (1.0 equiv., 0.50 mmol, 53 µL) were added. The resulting mixture was strirred at 80 ^{o}C for 2 h. Then, the reaction was allowed to reach room temperature and anhydrous Na_2SO_4 was added. The solid mixture was washed with ethyl acetate (2 x 1 mL) and the organic layer was transferred to a round-bottom flask. The solvent was removed under reduced pressure and the crude product was purified by column chromatography using hexane:EtOAc as an eluent to afford the desired product.

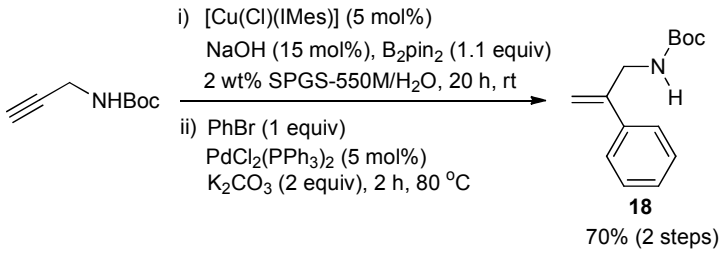
Synthesis of (*E*)-*N*-benzyl-*N*-methyl-3-phenylprop-2-en-1-amine (**17**)[20]



Yellow oil. Yield: 77 mg, 65% (2 steps). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.40 - 7.17 (m, 10H), 6.52 (d, *J* = 15.9 Hz, 1H), 6.30 (dt, *J* = 15.9, 6.6 Hz, 1H), 3.54 (s, 2H), 3.18 (dd, *J* = 6.6, 1.0 Hz, 2H), 2.23 (s, 3H). ^{13}C-APT NMR (100 MHz, $CDCl_3$, ppm): 138.9, 137.1, 132.6, 129.1, 128.6, 128.3, 127.6, 127.4, 127.0, 126.3, 61.9, 59.9, 42.2.

[20] J. Limberger, T. S. Claudino and A. L. Monteiro, *RSC Adv.*, 2014, **4**, 45558.

Synthesis of *tert*-butyl (2-phenylallyl)carbamate (**18**)[21]



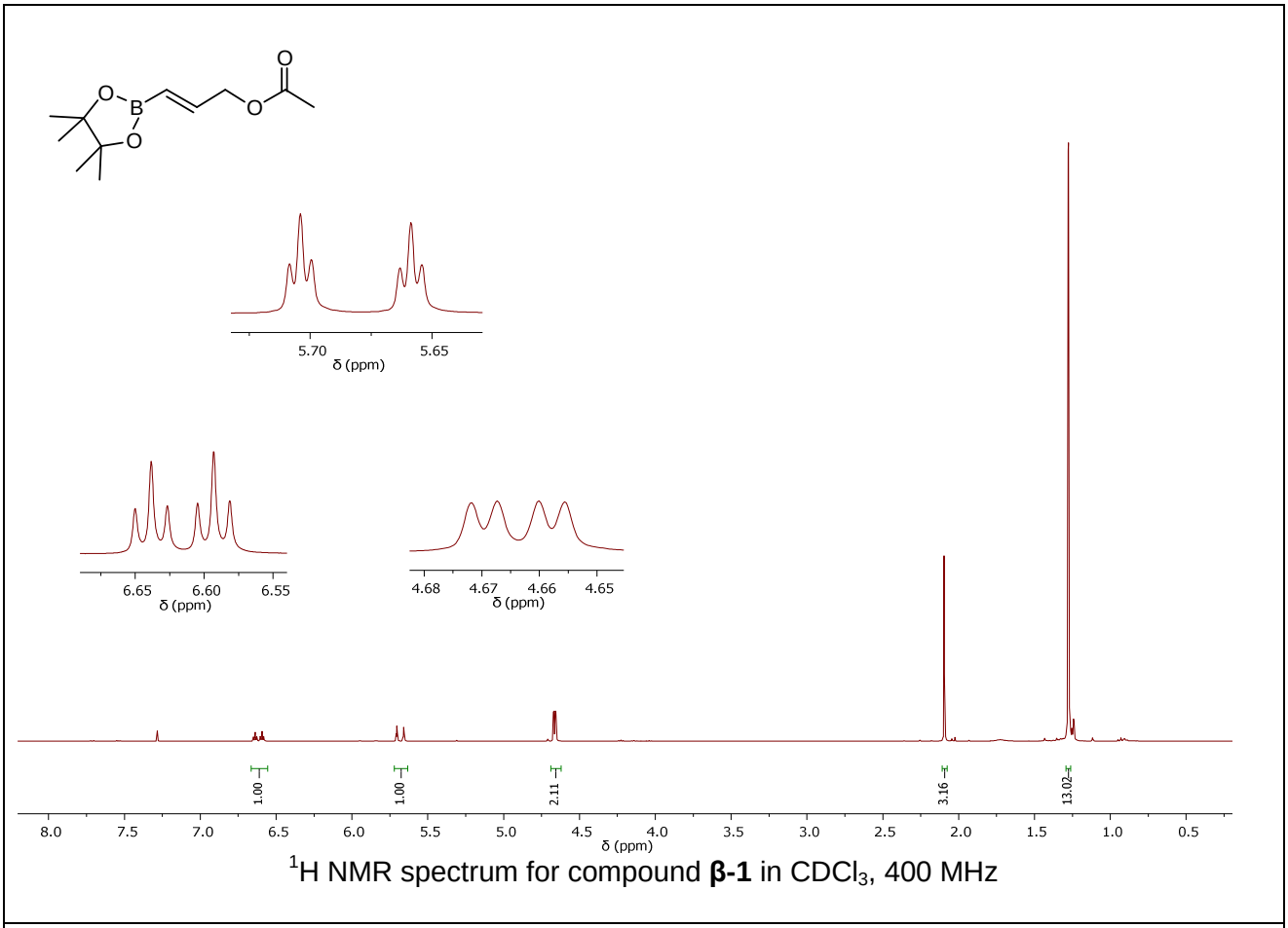
18

70% (2 steps)

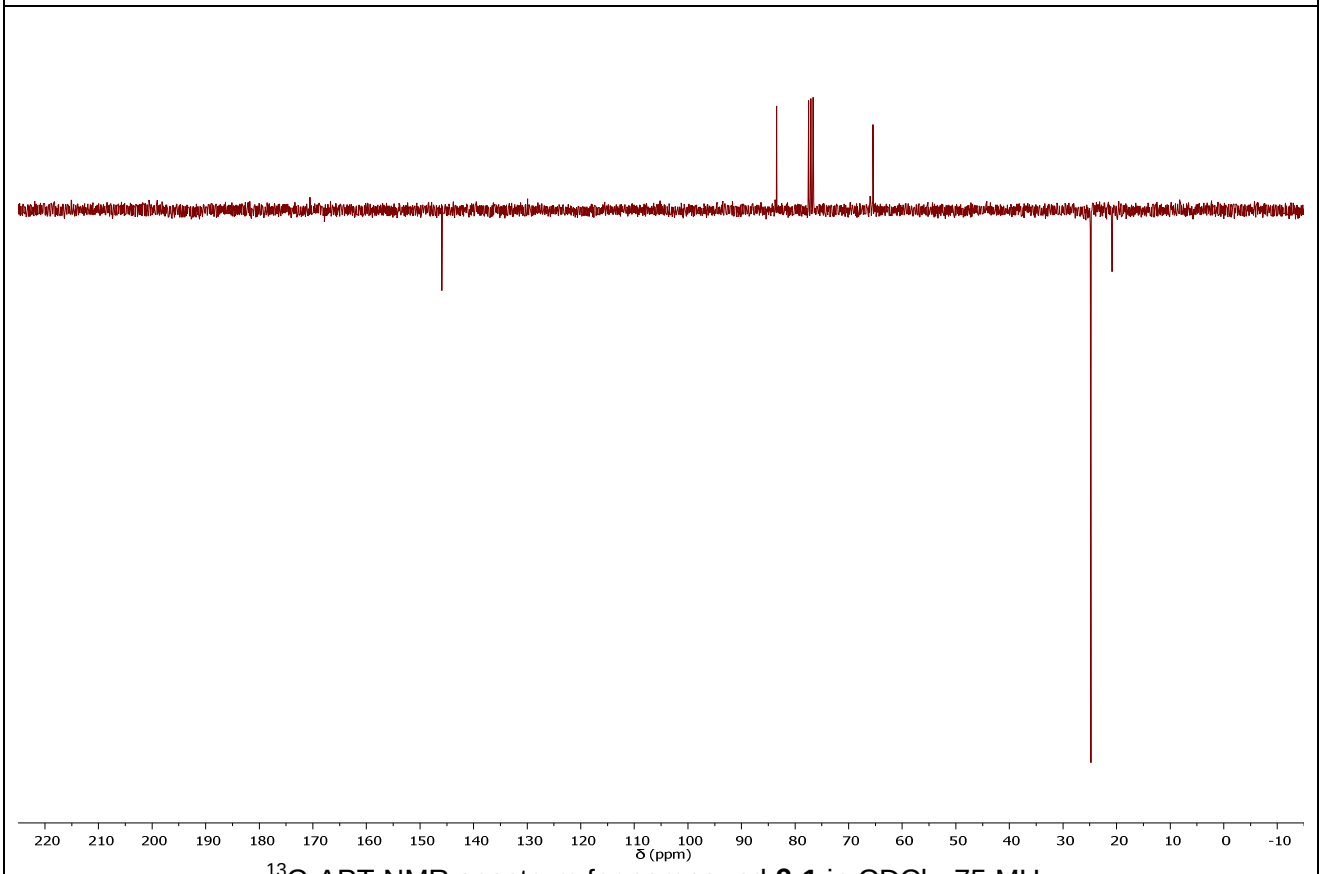
Pale yellow oil. Yield: 81,6 mg, 70% (2 steps). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.45 - 7.26 (m, 5H), 5.42 (s, 1H), 5.22 (s, 1H), 4.19 (d, *J* = 5.4 Hz, 2H), 1.43 (s, 9H). ^{13}C-APT NMR (75 MHz, $CDCl_3$, ppm): 155.7, 144.8, 138.6, 128.4, 127,9, 126.1, 113.2, 79.4, 44.4, 28.3.

[21] A. Garzan, A. Jaganathan, N. S. Marzijarani, R. Yousefi, D. C. Whitehead, J. E. Jackson and B. Borhan, *Chem. Eur. J.*, 2013, **19**, 9015.

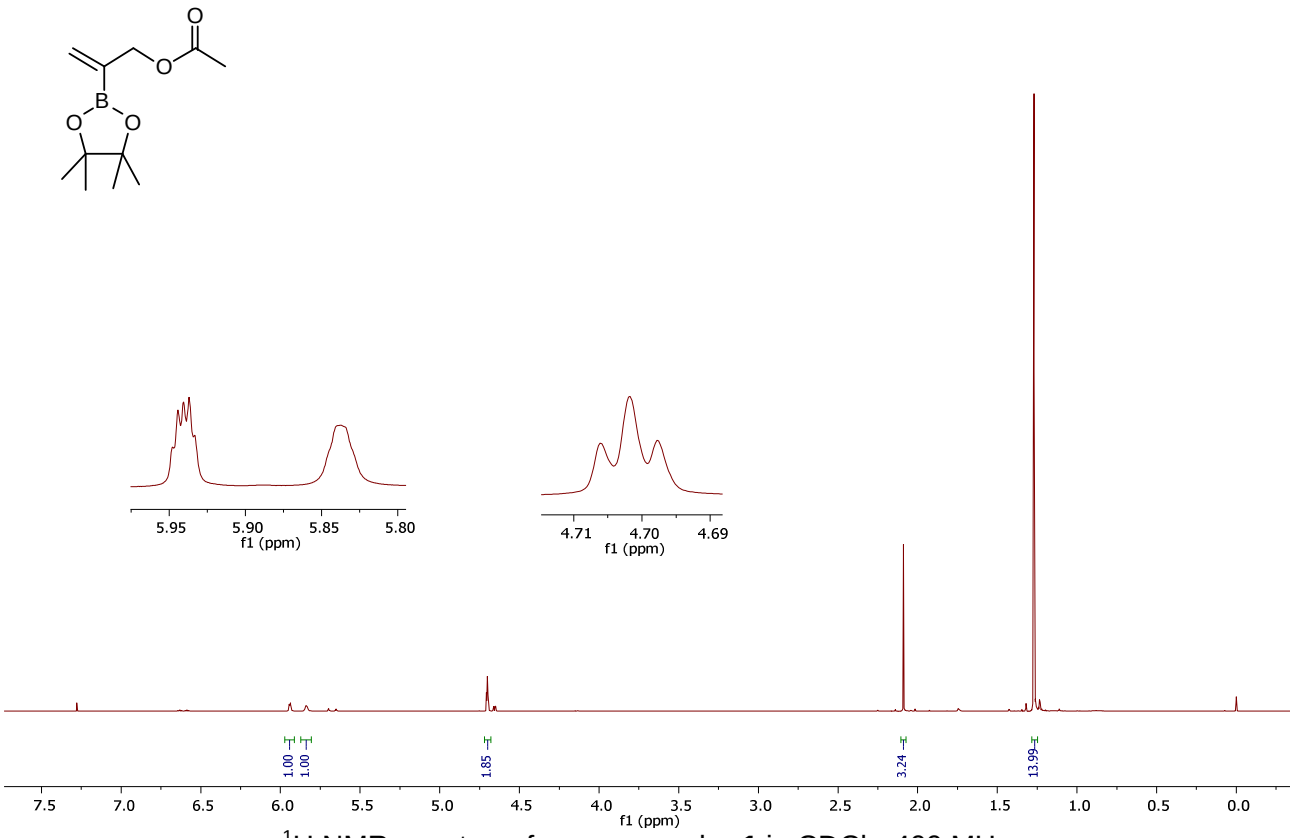
NMR Spectra



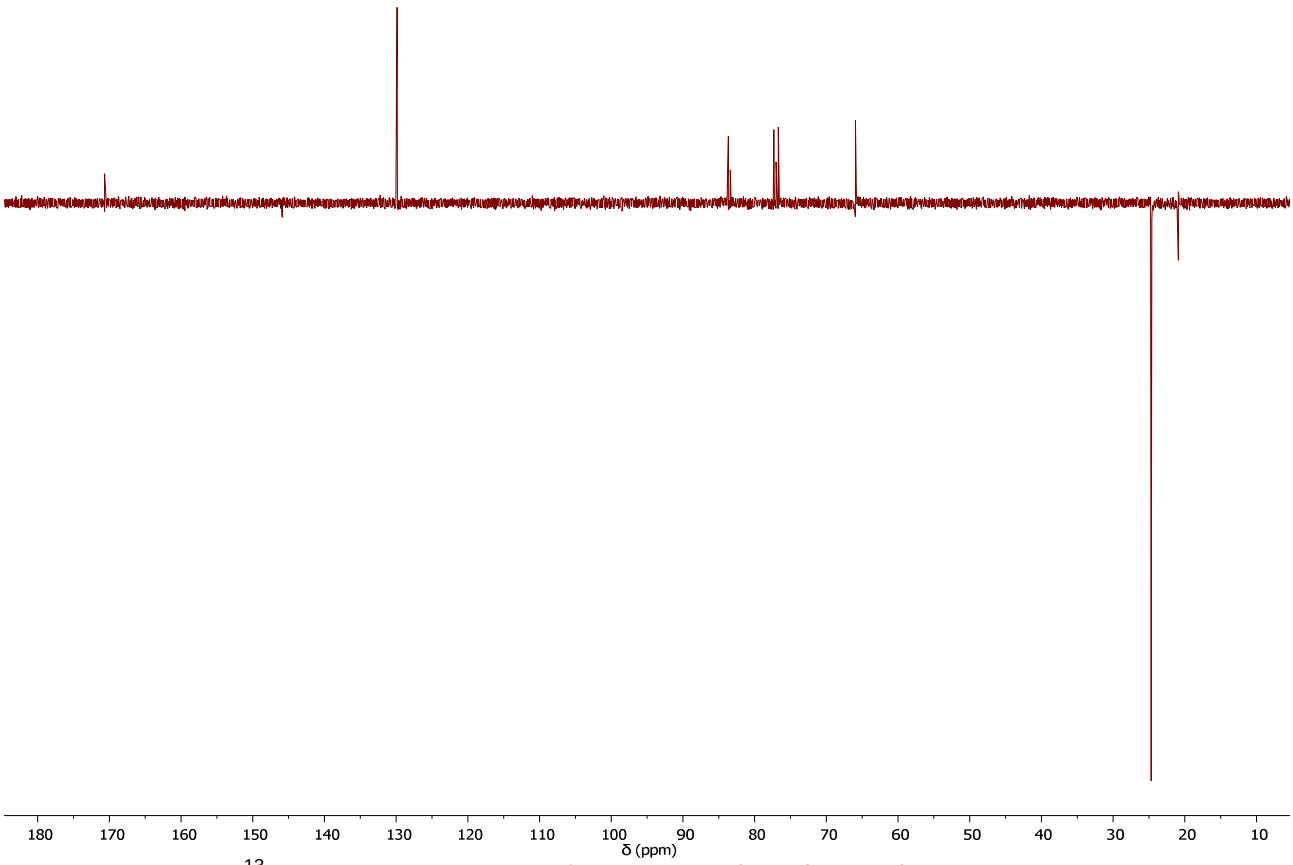
^{1}H NMR spectrum for compound **β-1** in $CDCl_3$, 400 MHz



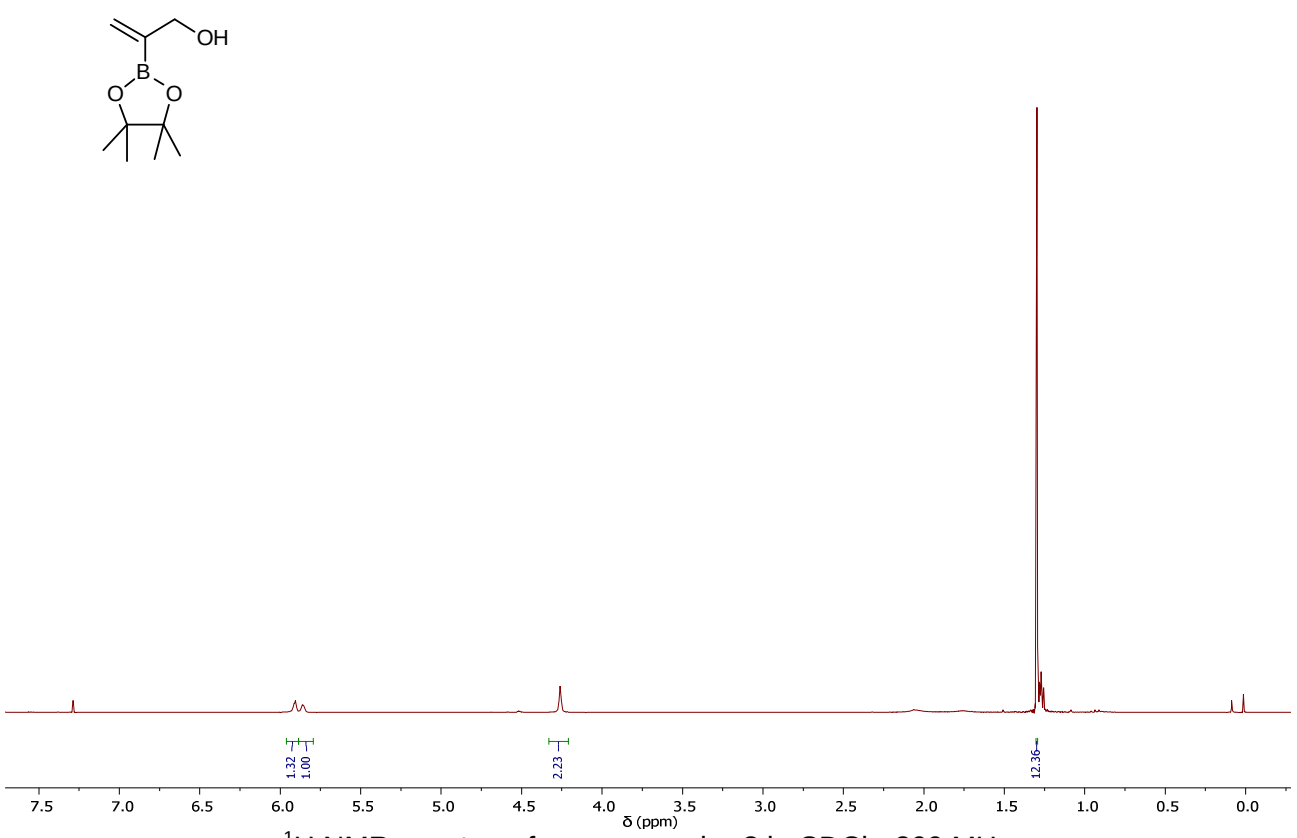
^{13}C-APT NMR spectrum for compound **β-1** in $CDCl_3$, 75 MHz



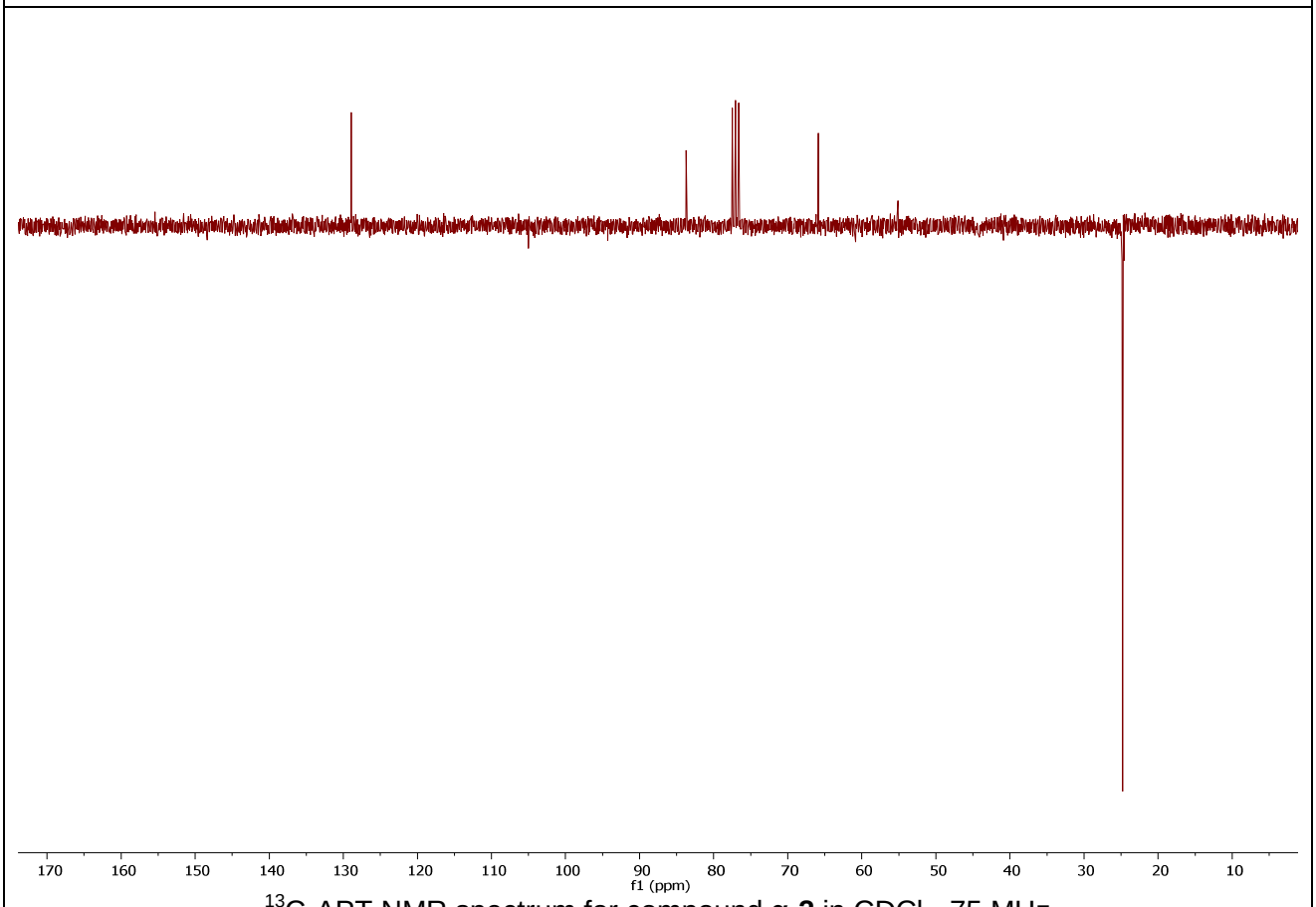
^{1}H NMR spectrum for compound **α-1** in $CDCl_3$, 400 MHz



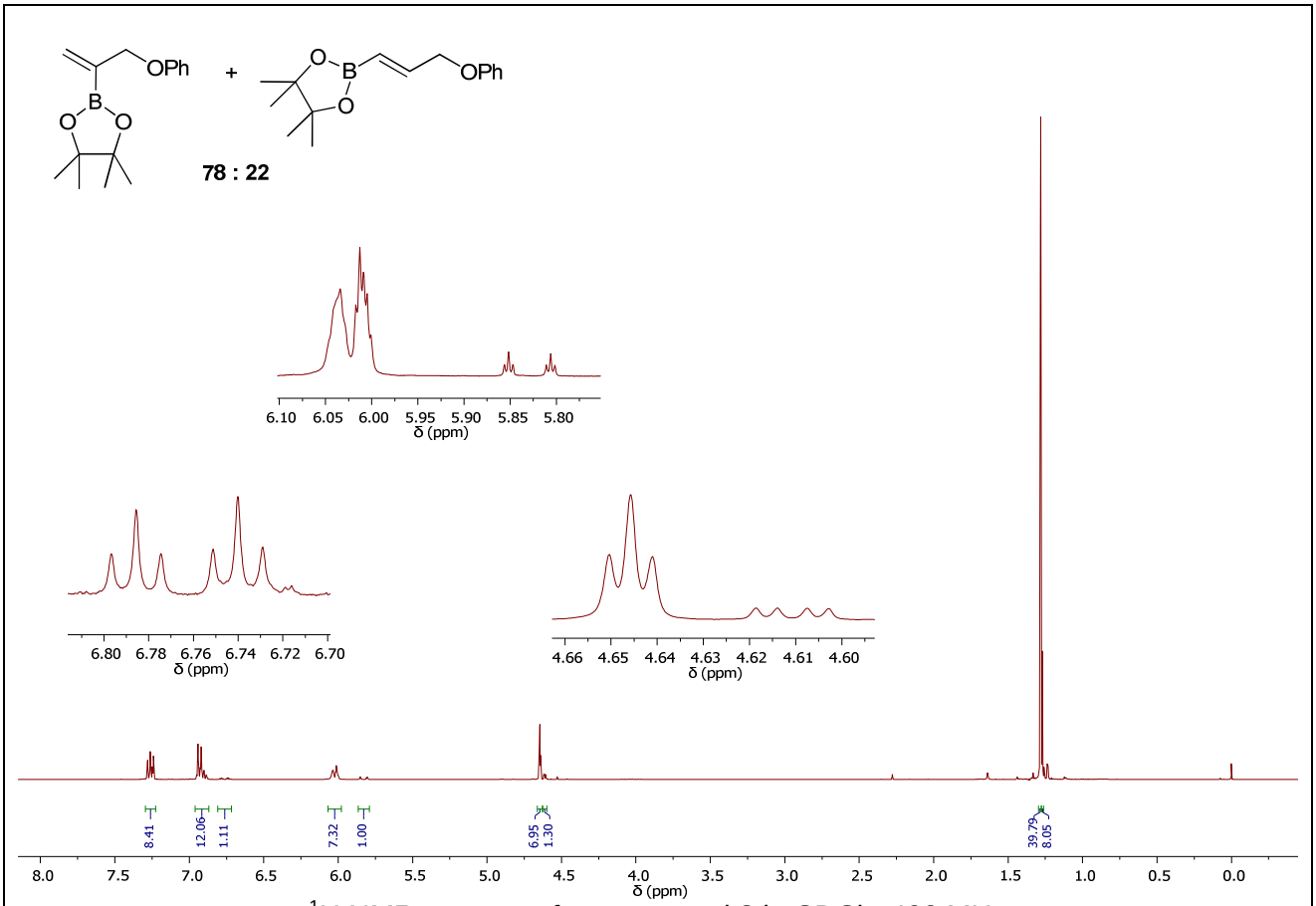
^{13}C-APT NMR spectrum for compound **α-1** in $CDCl_3$, 100 MHz



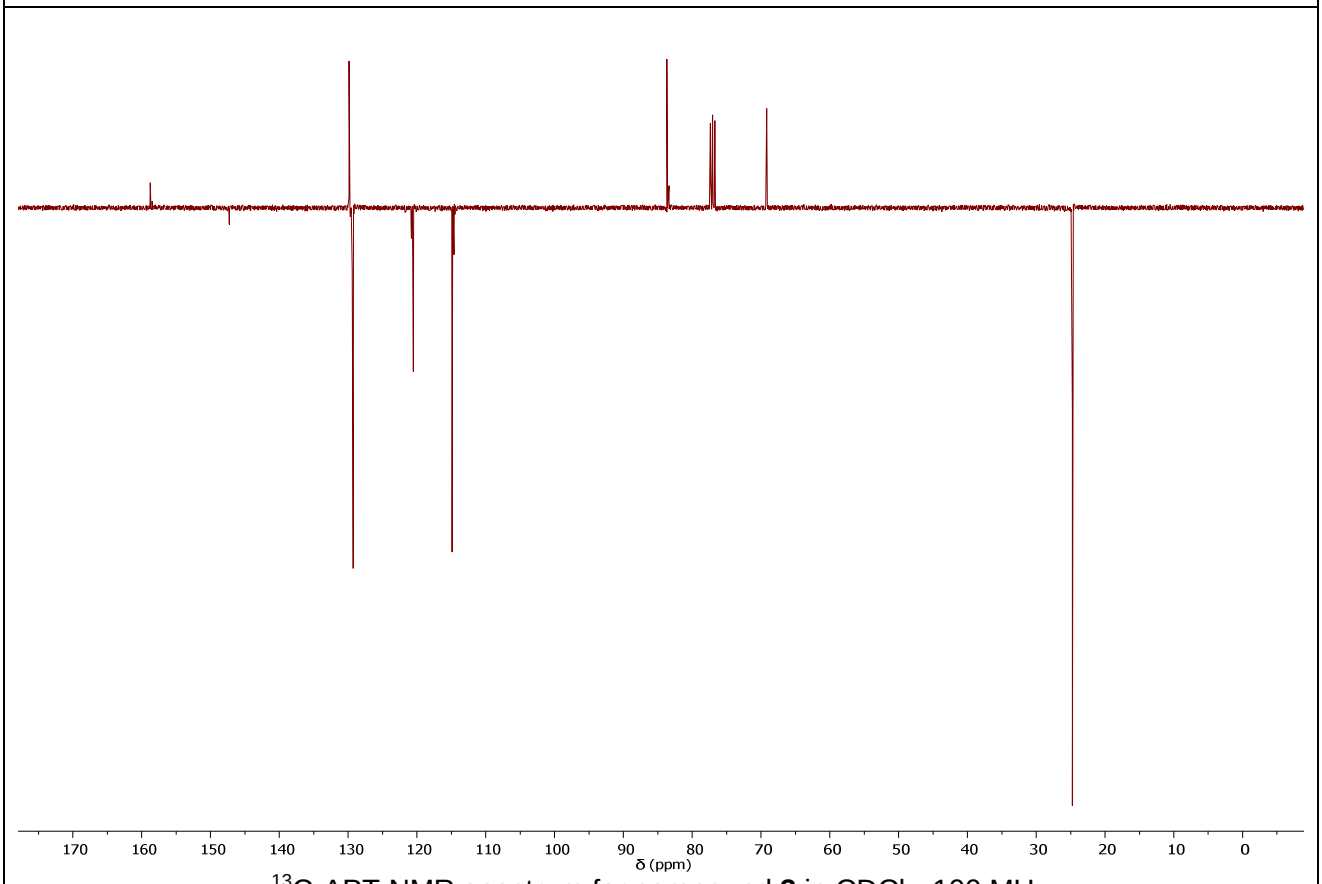
^{1}H NMR spectrum for compound **α-2** in $CDCl_3$, 300 MHz



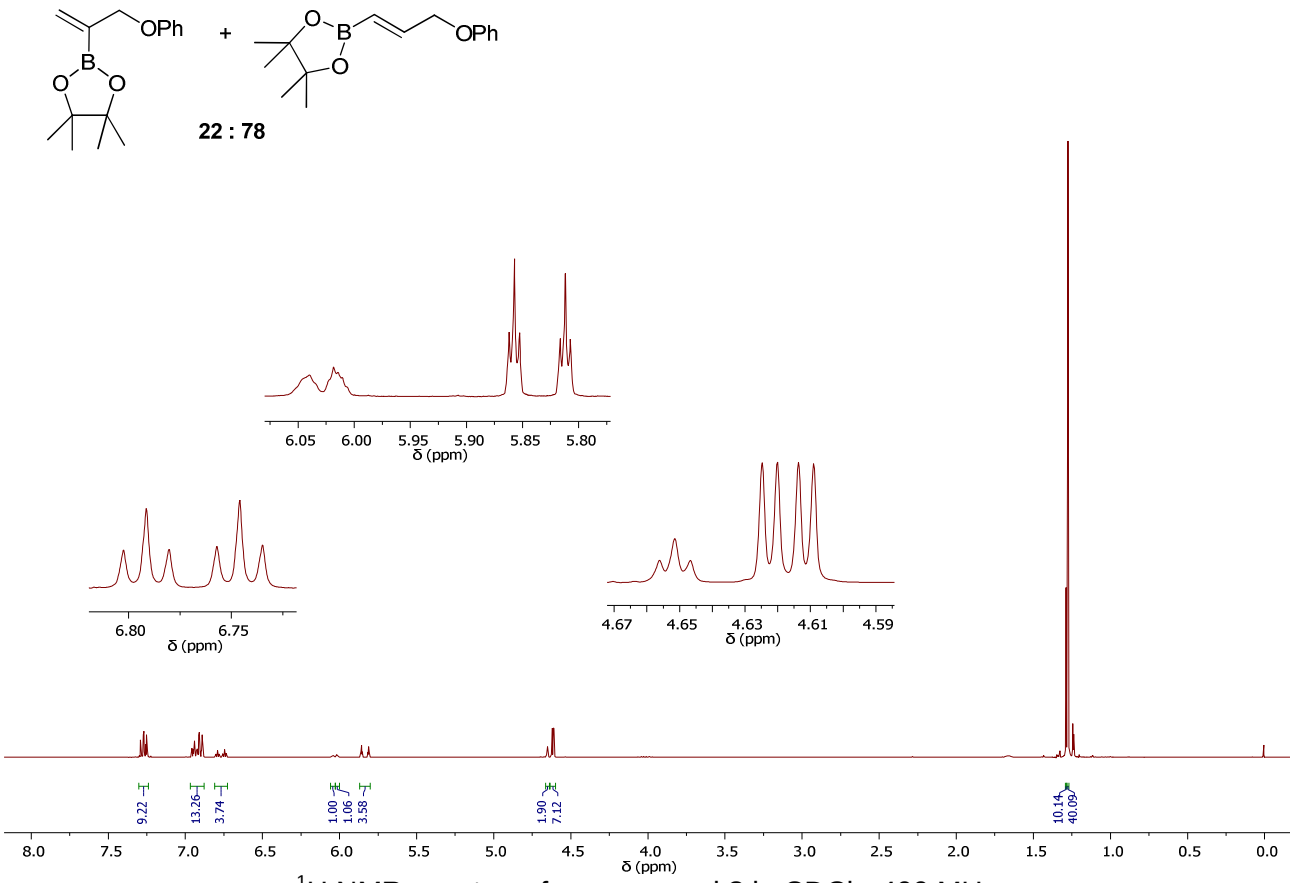
^{13}C-APT NMR spectrum for compound **α-2** in $CDCl_3$, 75 MHz



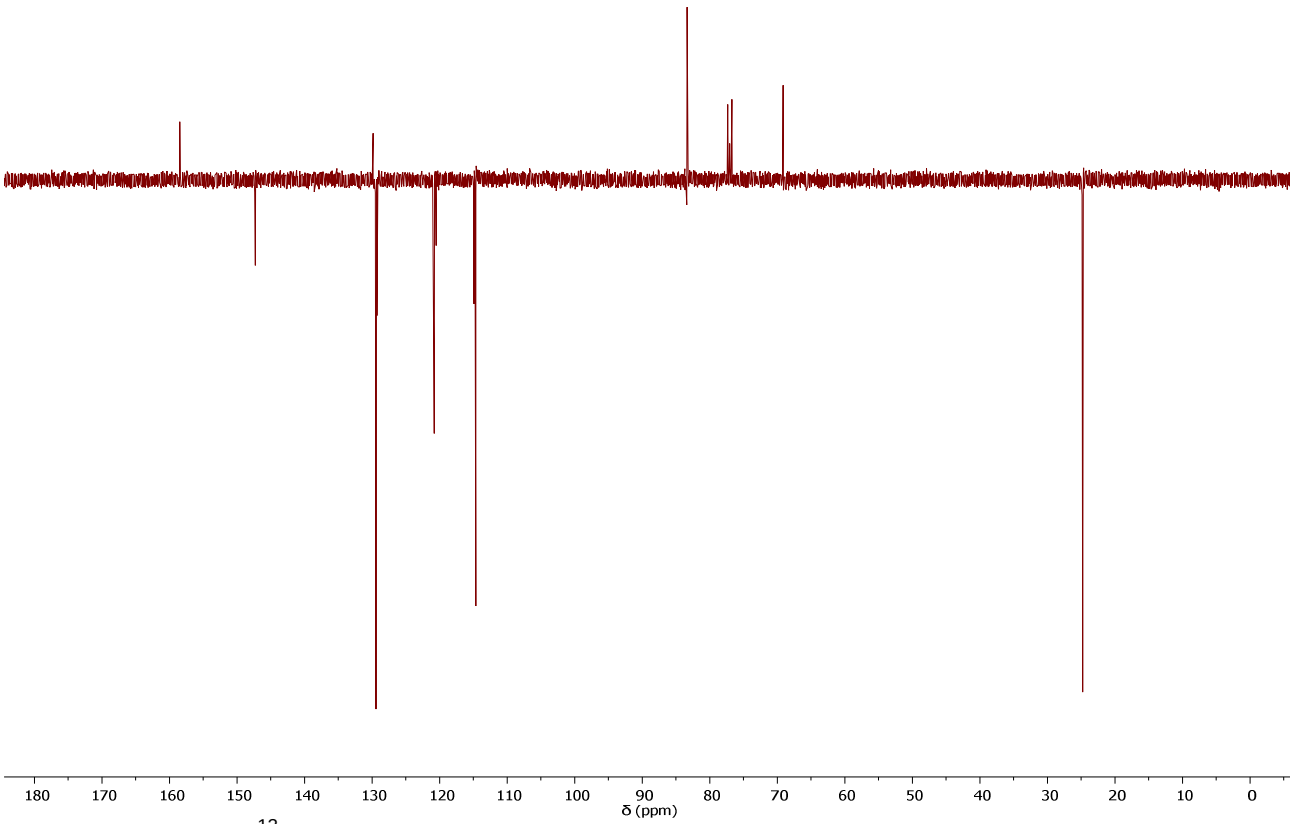
^{1}H NMR spectrum for compound **3** in $CDCl_3$, 400 MHz



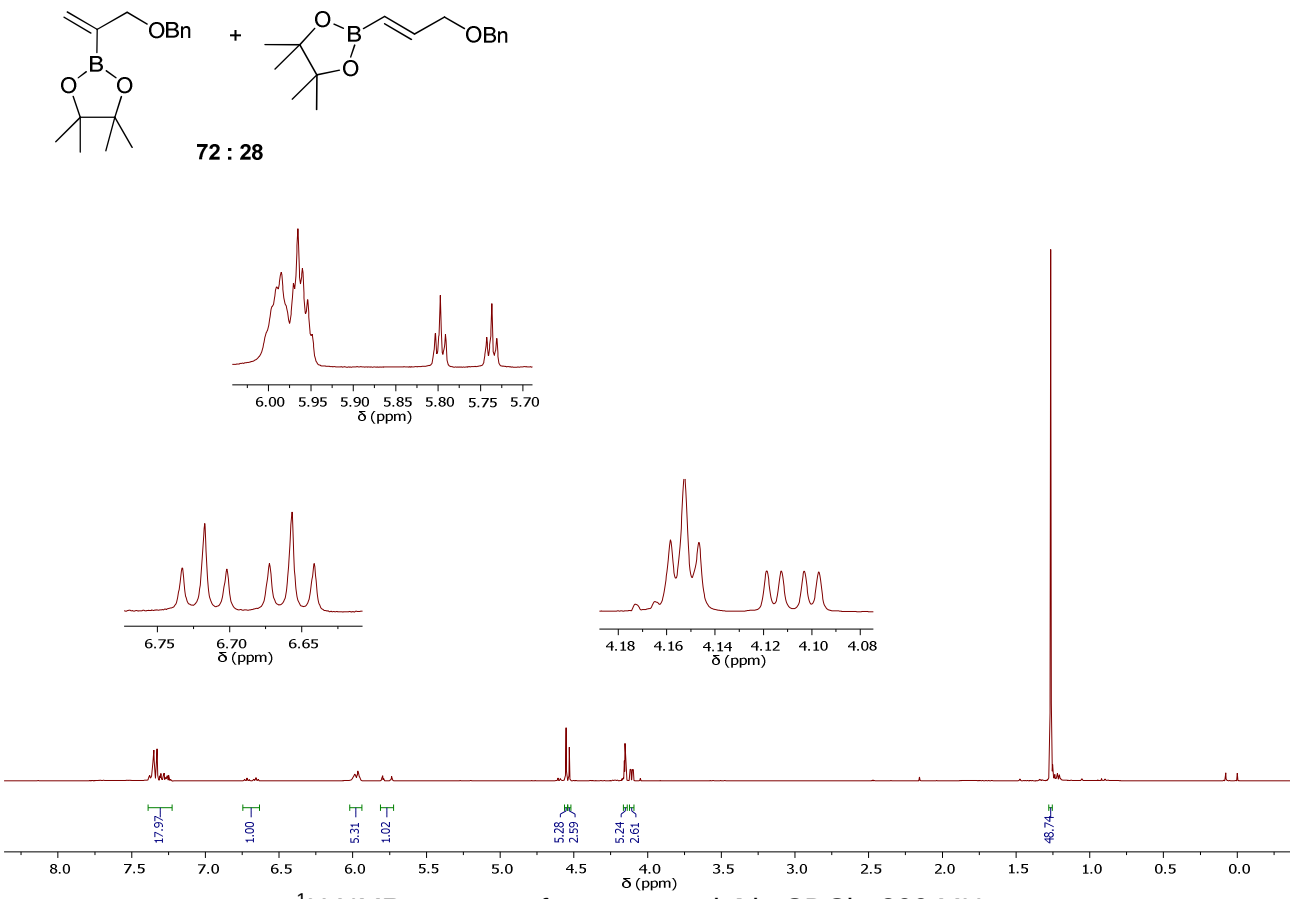
^{13}C-APT NMR spectrum for compound **3** in $CDCl_3$, 100 MHz



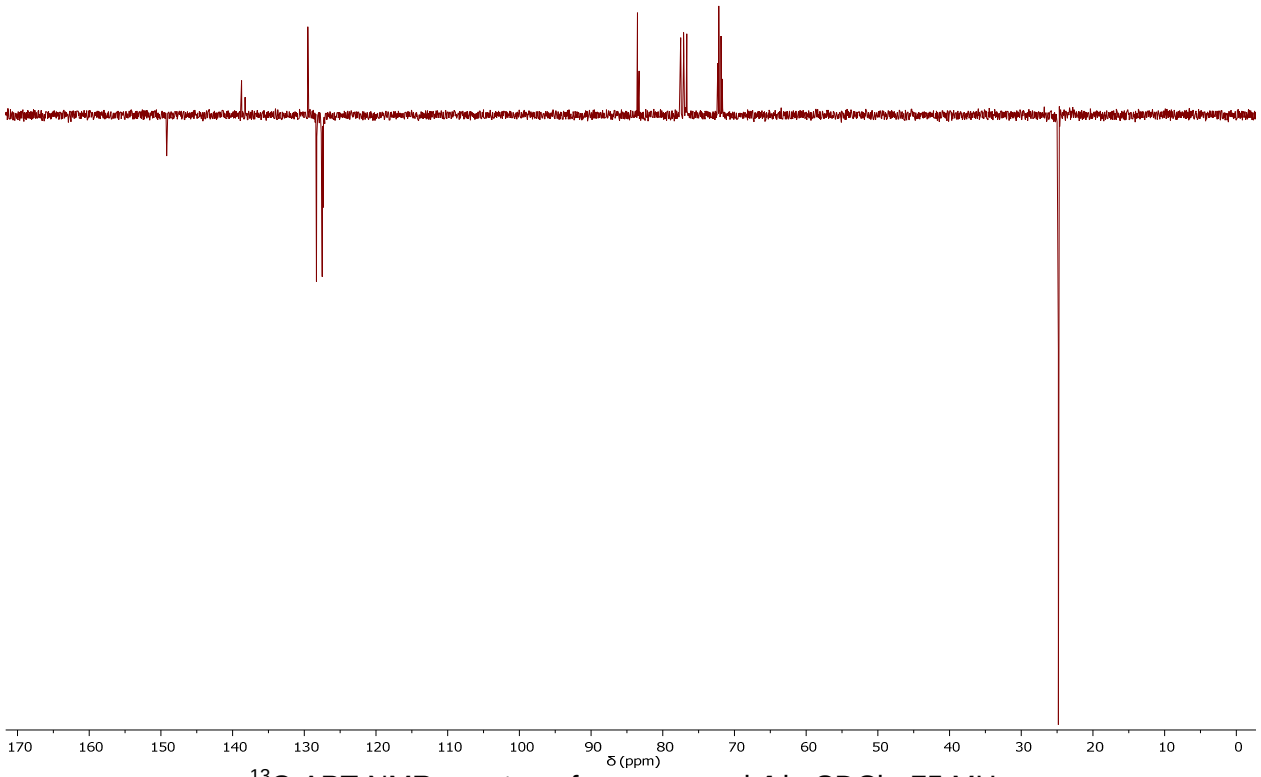
^{1}H NMR spectrum for compound **3** in $CDCl_3$, 400 MHz



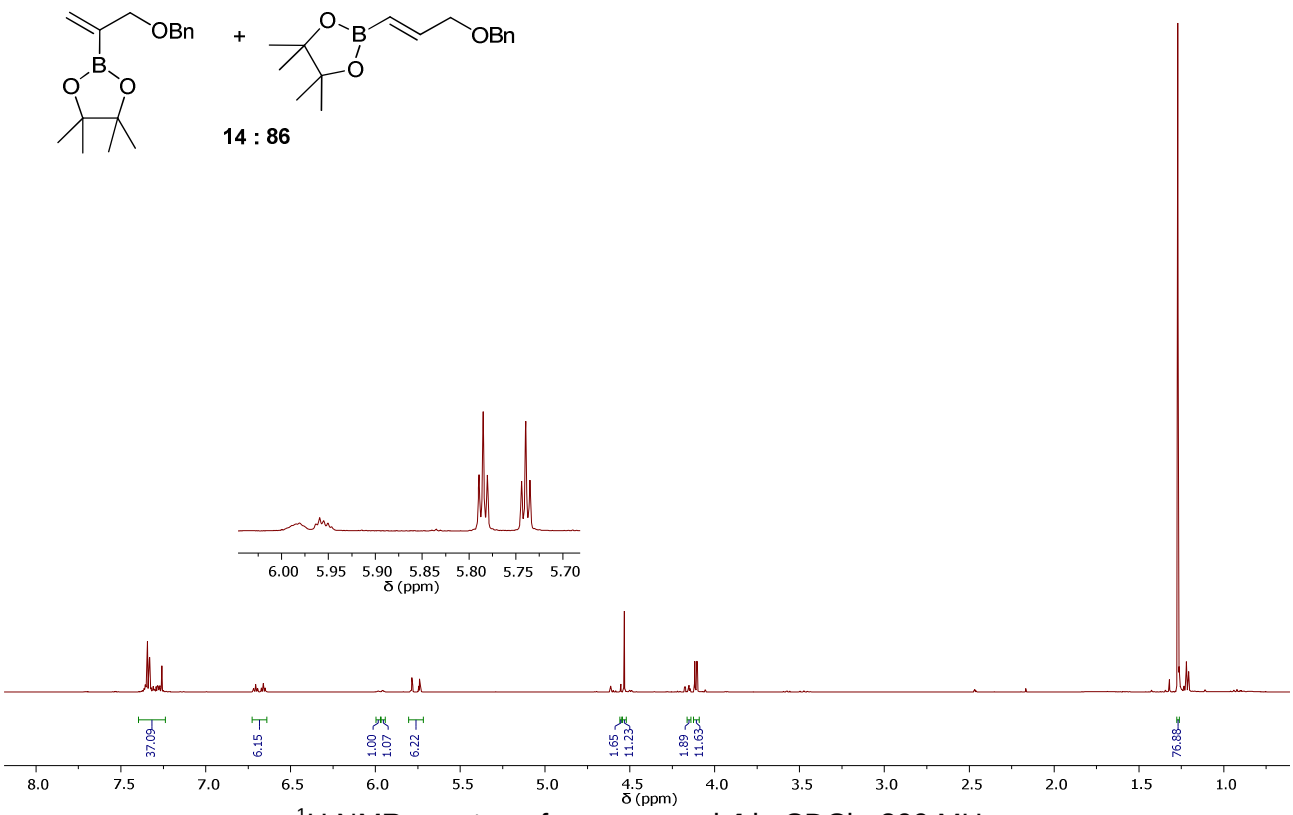
^{13}C-APT NMR spectrum for compound **3** in $CDCl_3$, 100 MHz



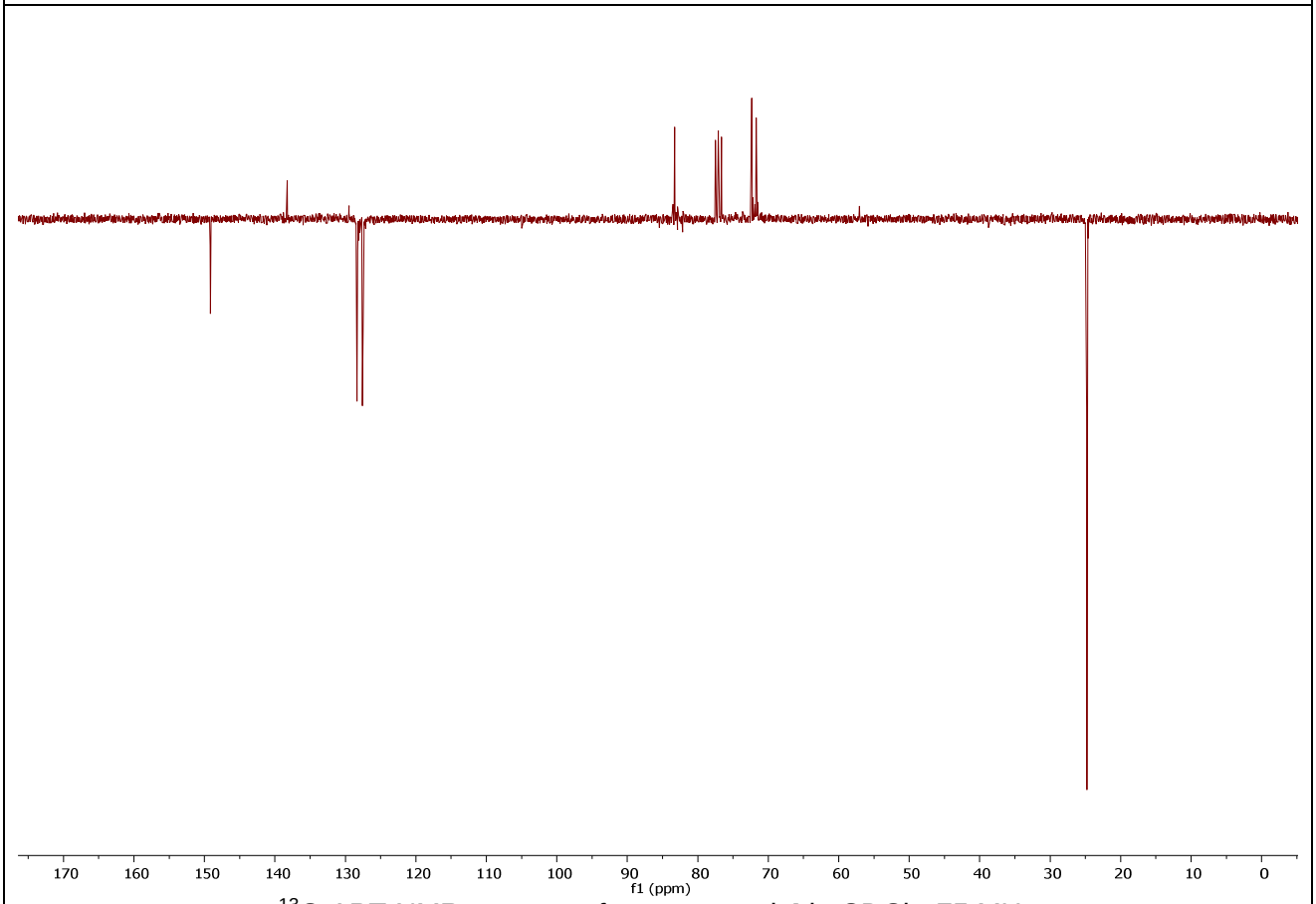
^{1}H NMR spectrum for compound **4** in $CDCl_3$, 300 MHz



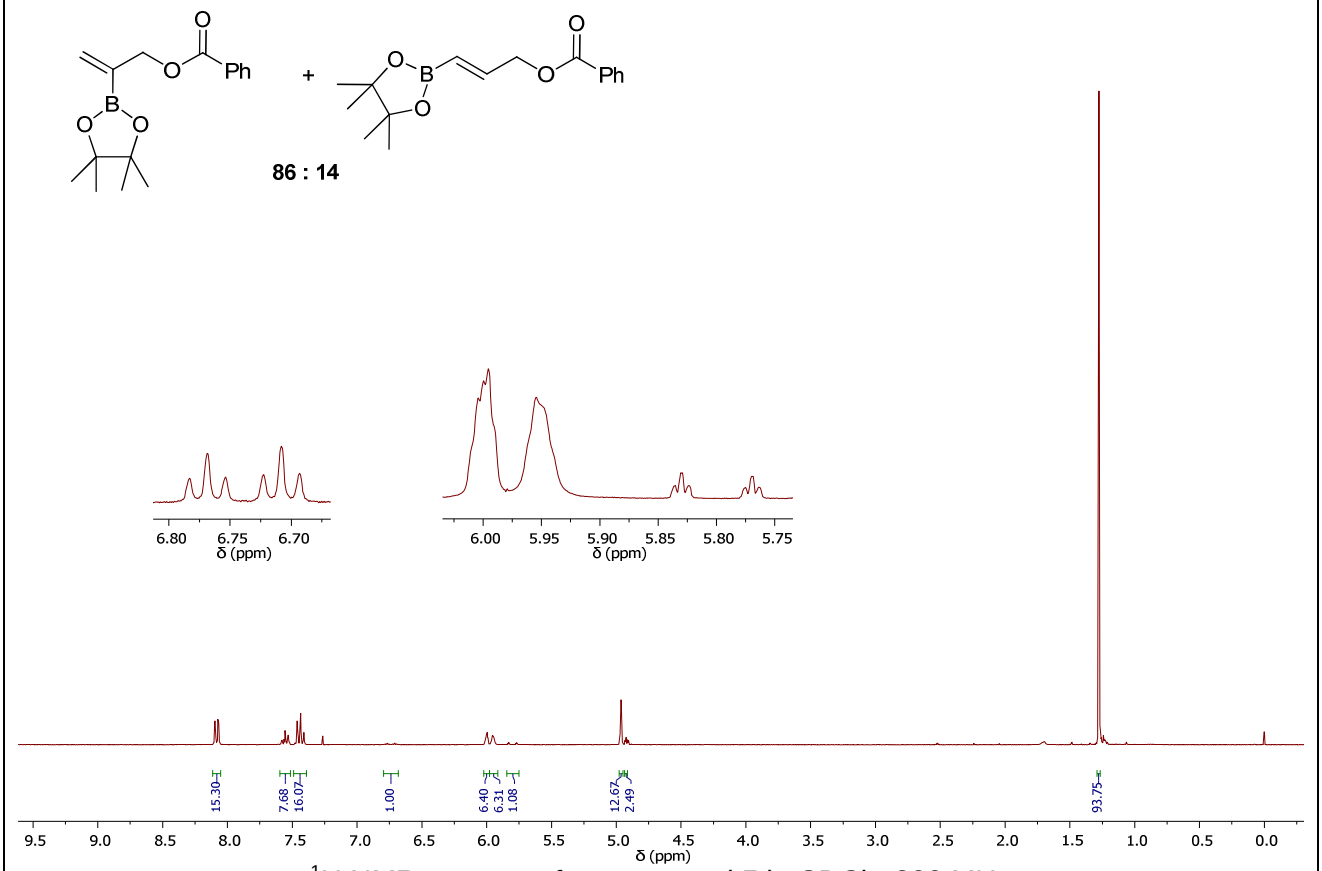
^{13}C-APT NMR spectrum for compound **4** in $CDCl_3$, 75 MHz



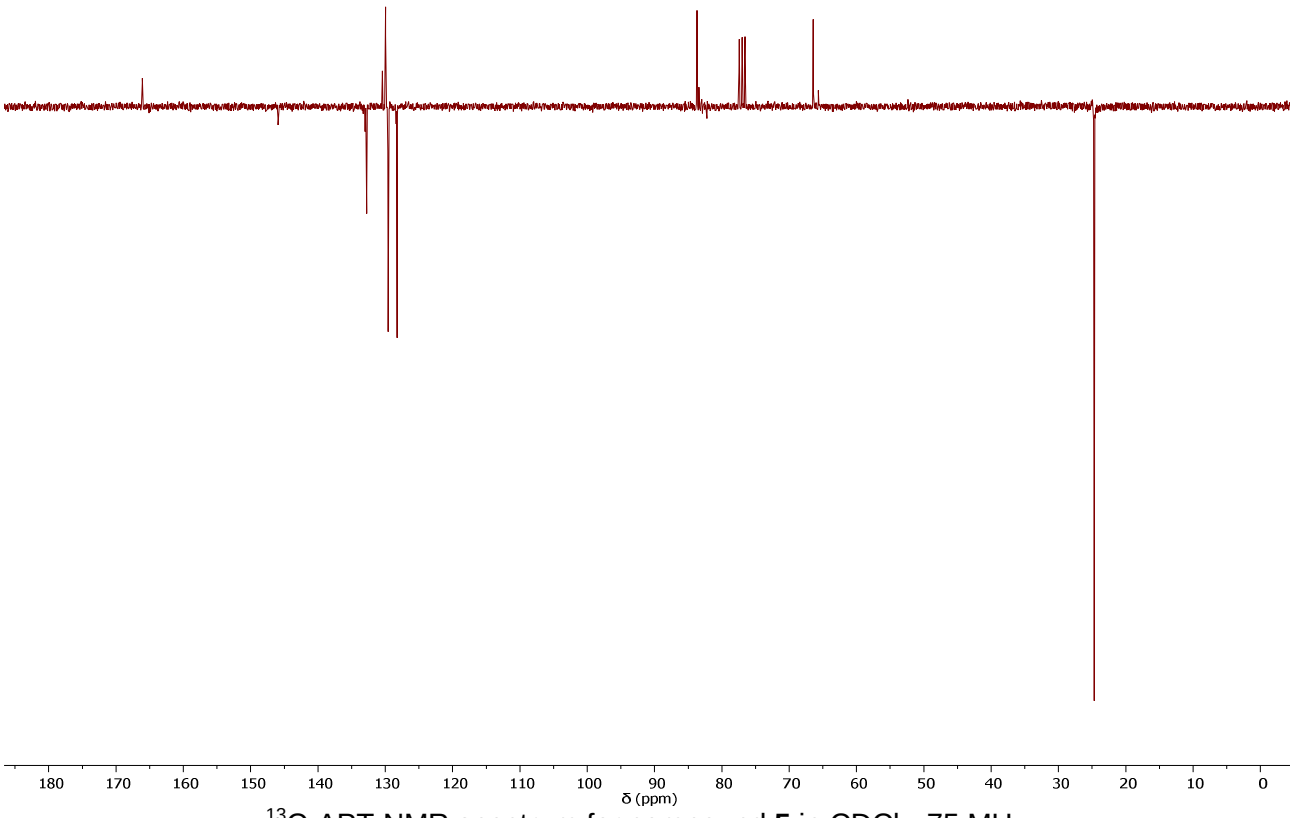
^{1}H NMR spectrum for compound **4** in $CDCl_3$, 300 MHz



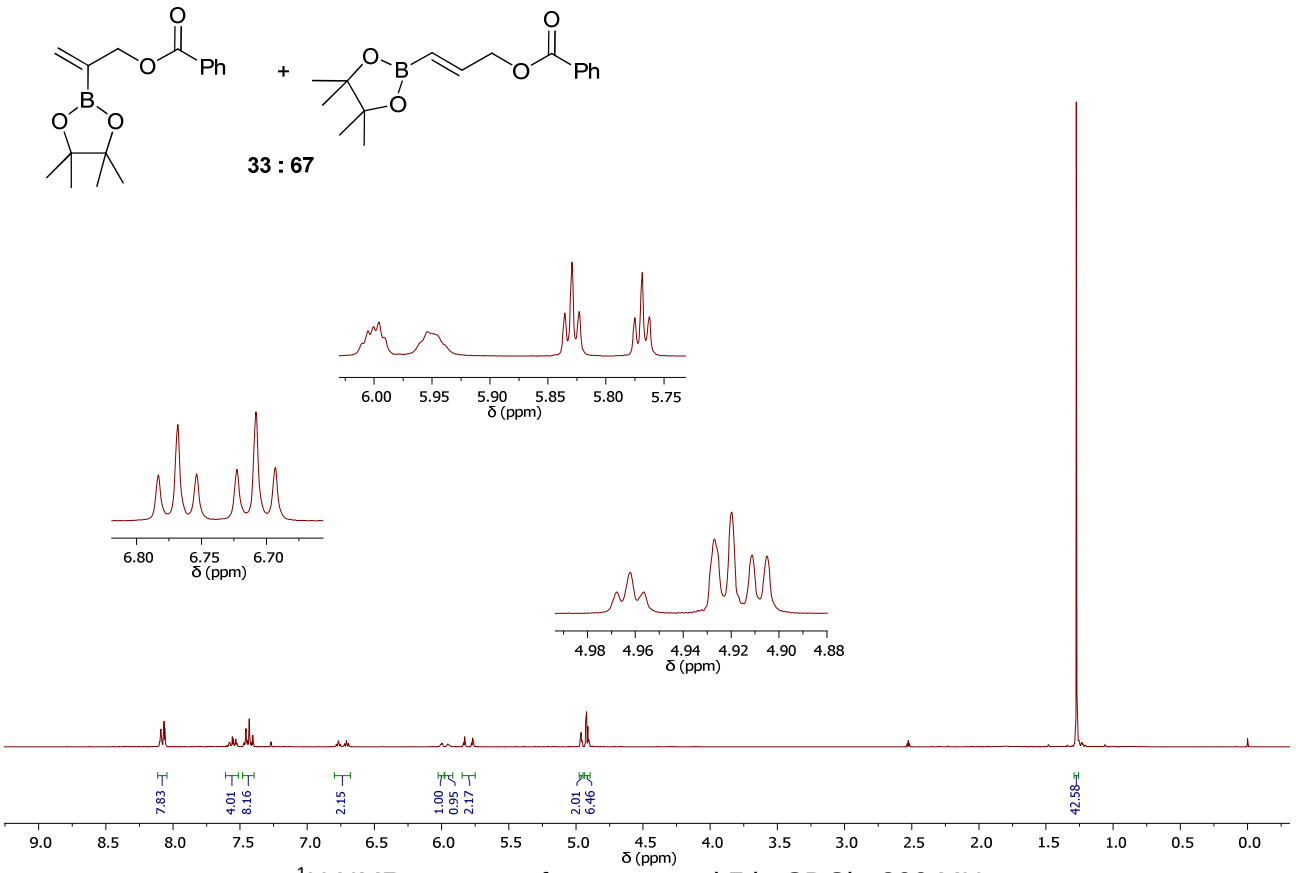
^{13}C-APT NMR spectrum for compound **4** in $CDCl_3$, 75 MHz



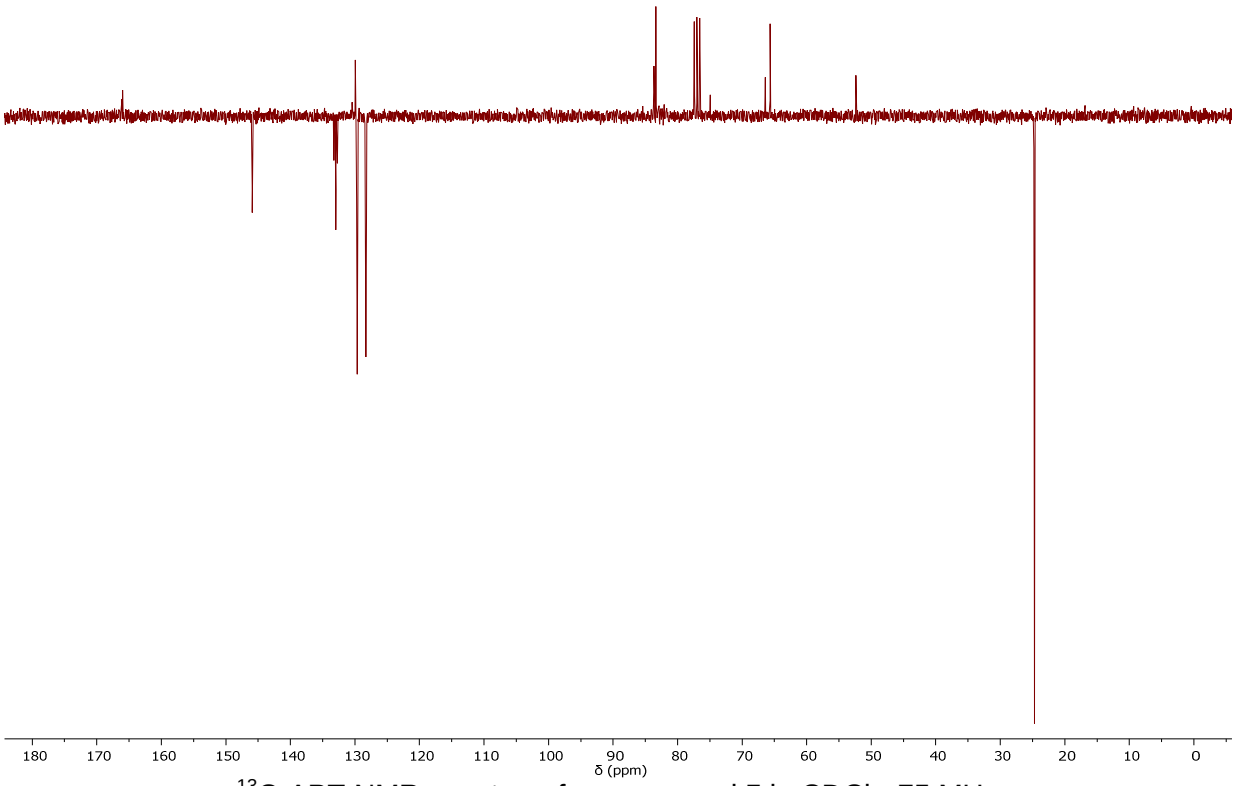
^{1}H NMR spectrum for compound **5** in $CDCl_3$, 300 MHz



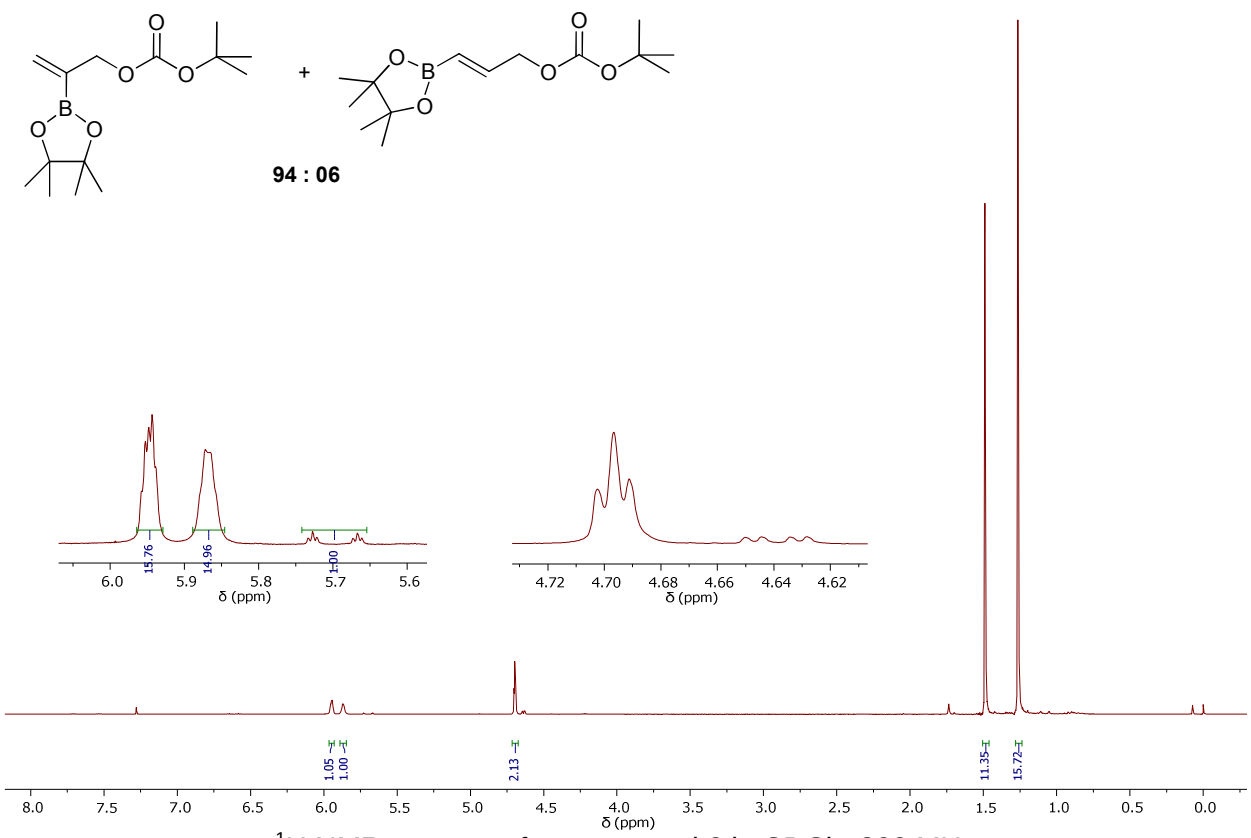
^{13}C-APT NMR spectrum for compound **5** in $CDCl_3$, 75 MHz



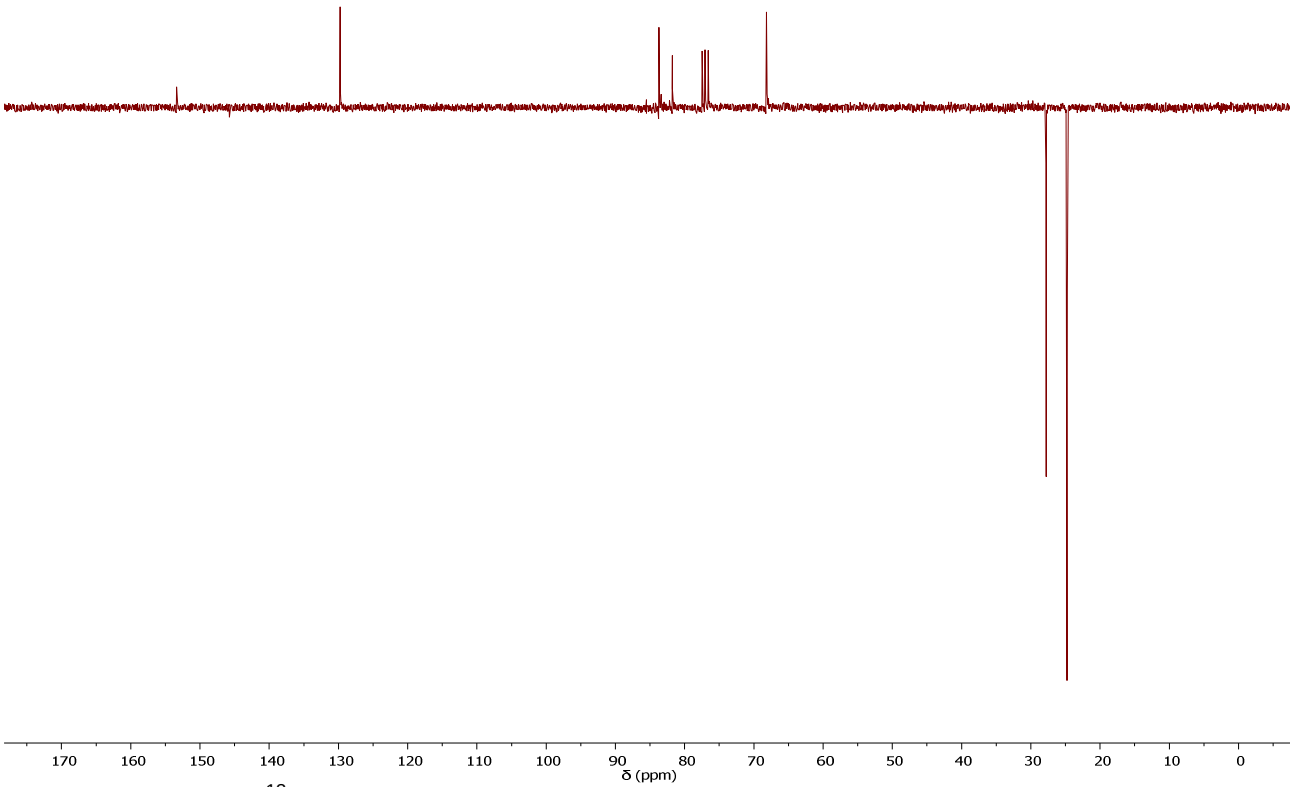
^{1}H NMR spectrum for compound **5** in $CDCl_3$, 300 MHz



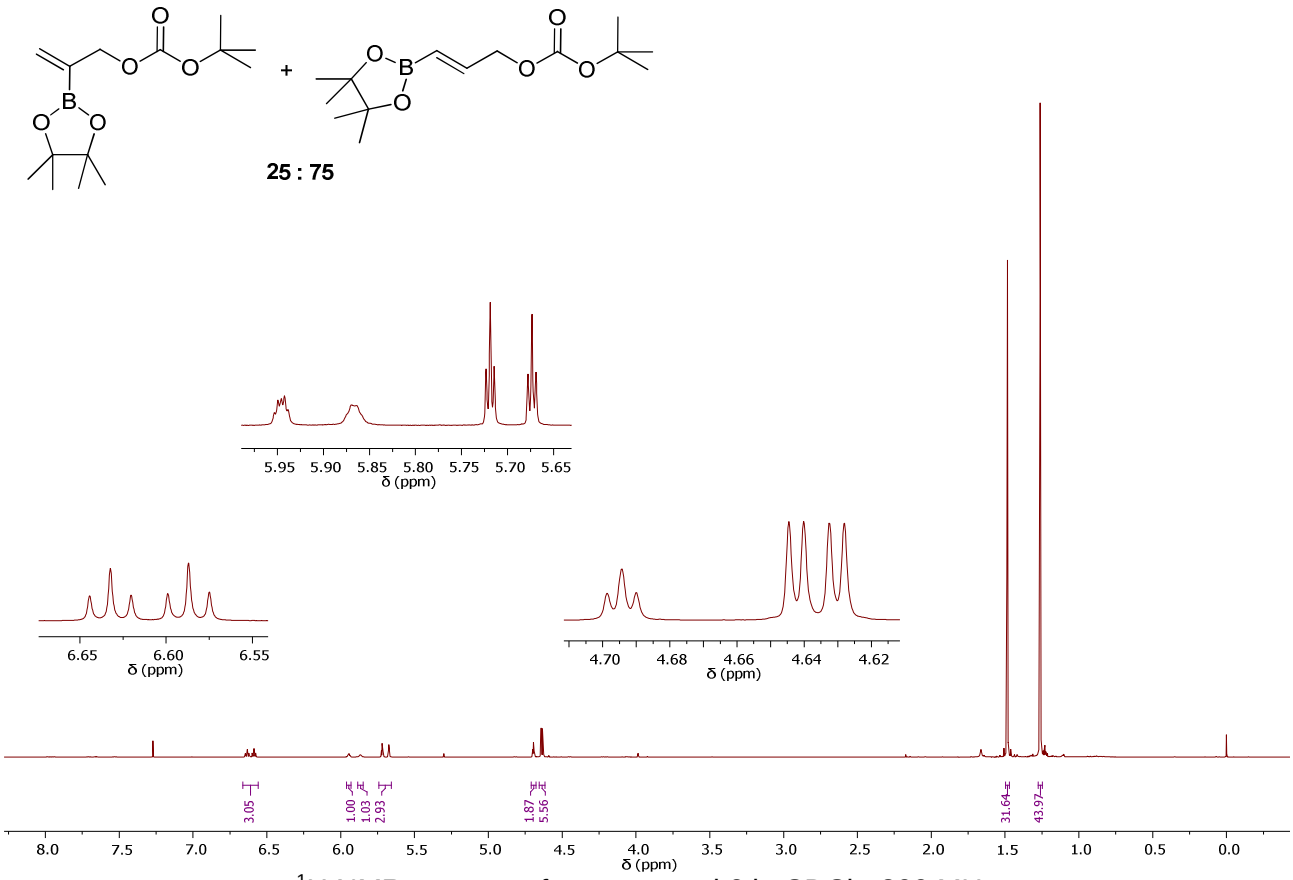
^{13}C-APT NMR spectrum for compound **5** in $CDCl_3$, 75 MHz



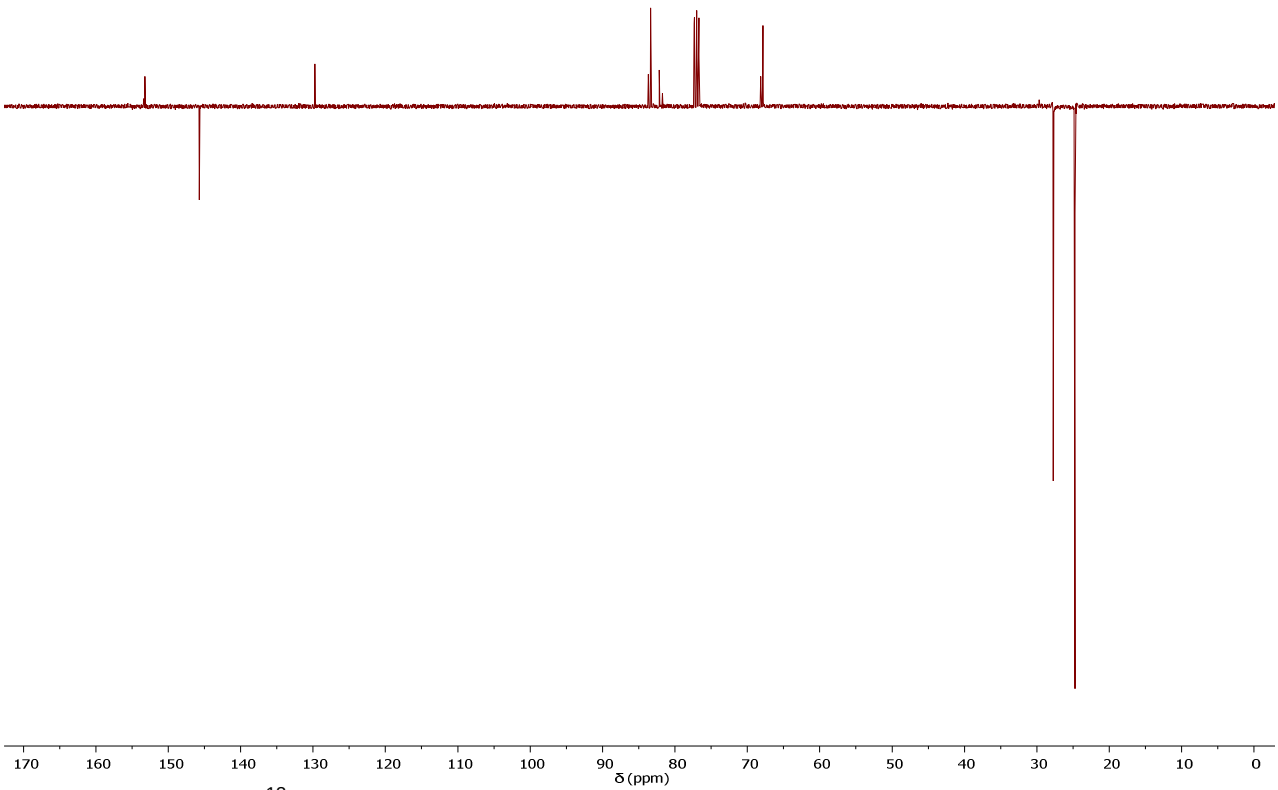
^{1}H NMR spectrum for compound **6** in $CDCl_3$, 300 MHz



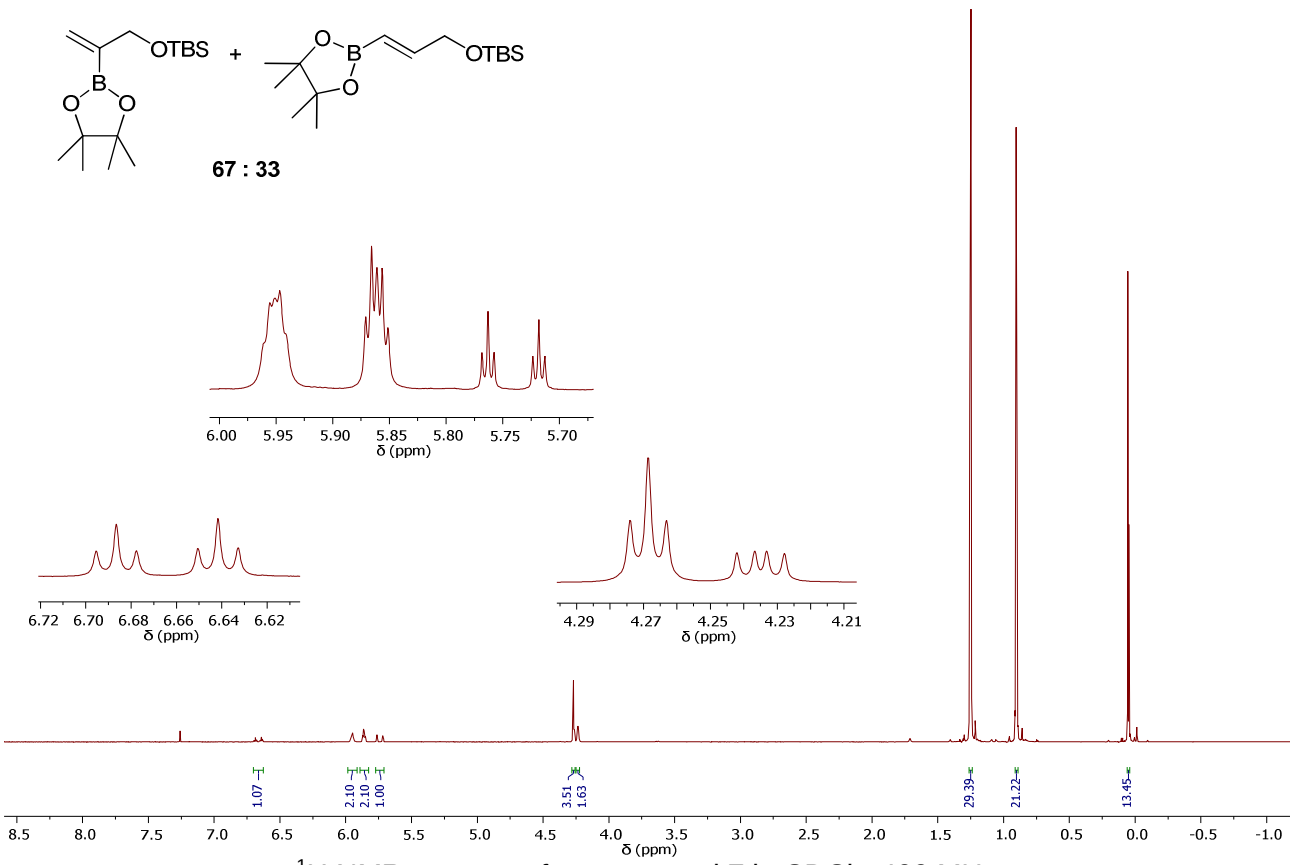
^{13}C-APT NMR spectrum for compound **6** in $CDCl_3$, 75 MHz



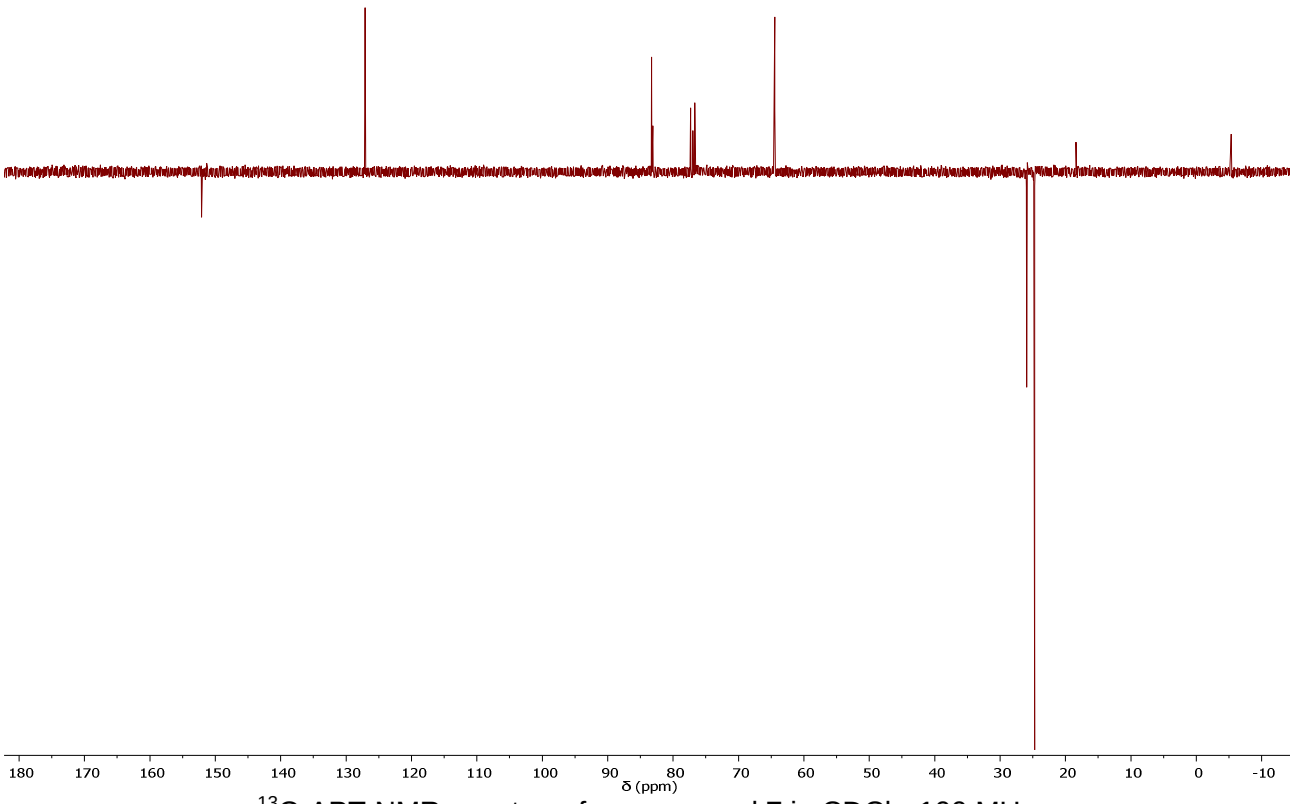
^{1}H NMR spectrum for compound **6** in $CDCl_3$, 300 MHz



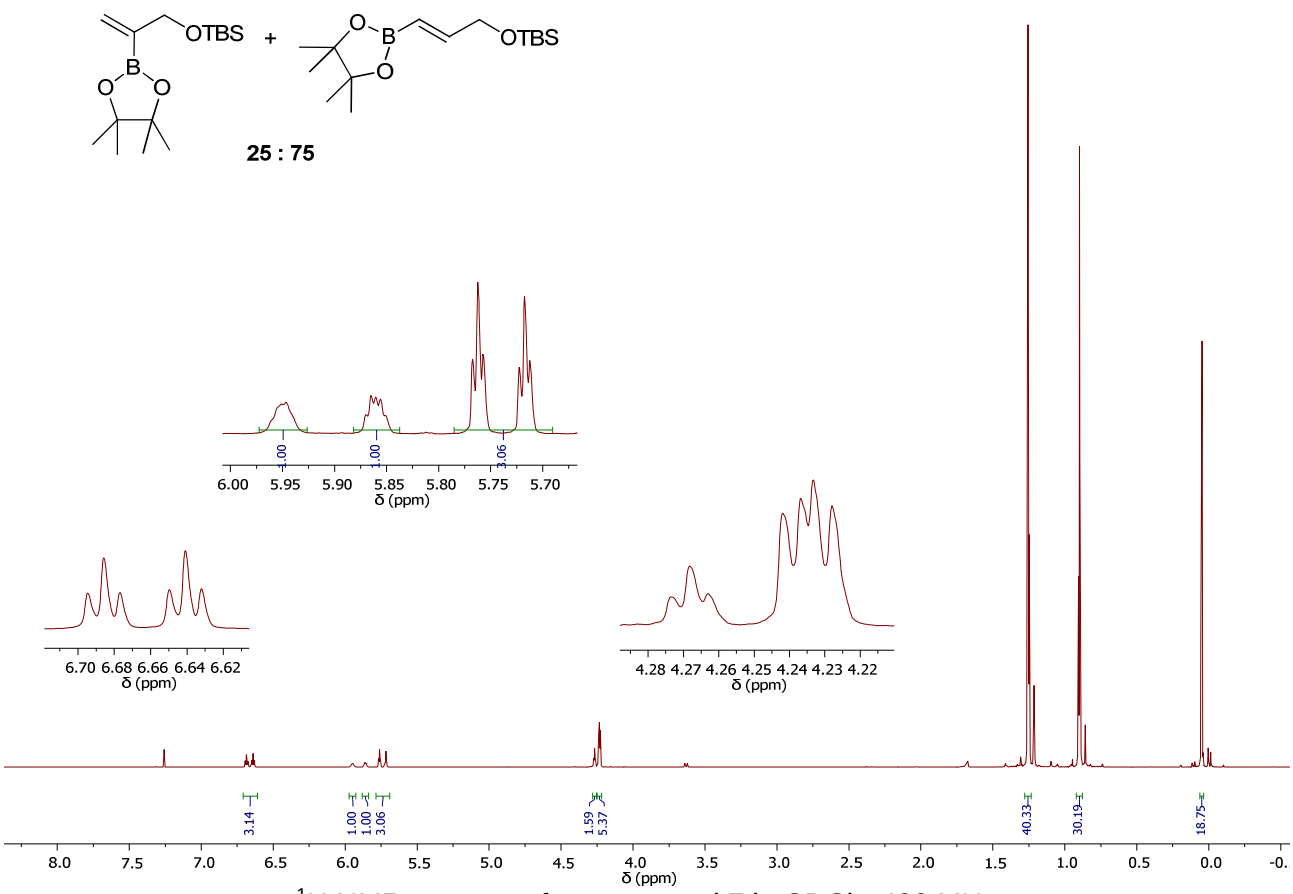
^{13}C-APT NMR spectrum for compound **6** in $CDCl_3$, 75 MHz



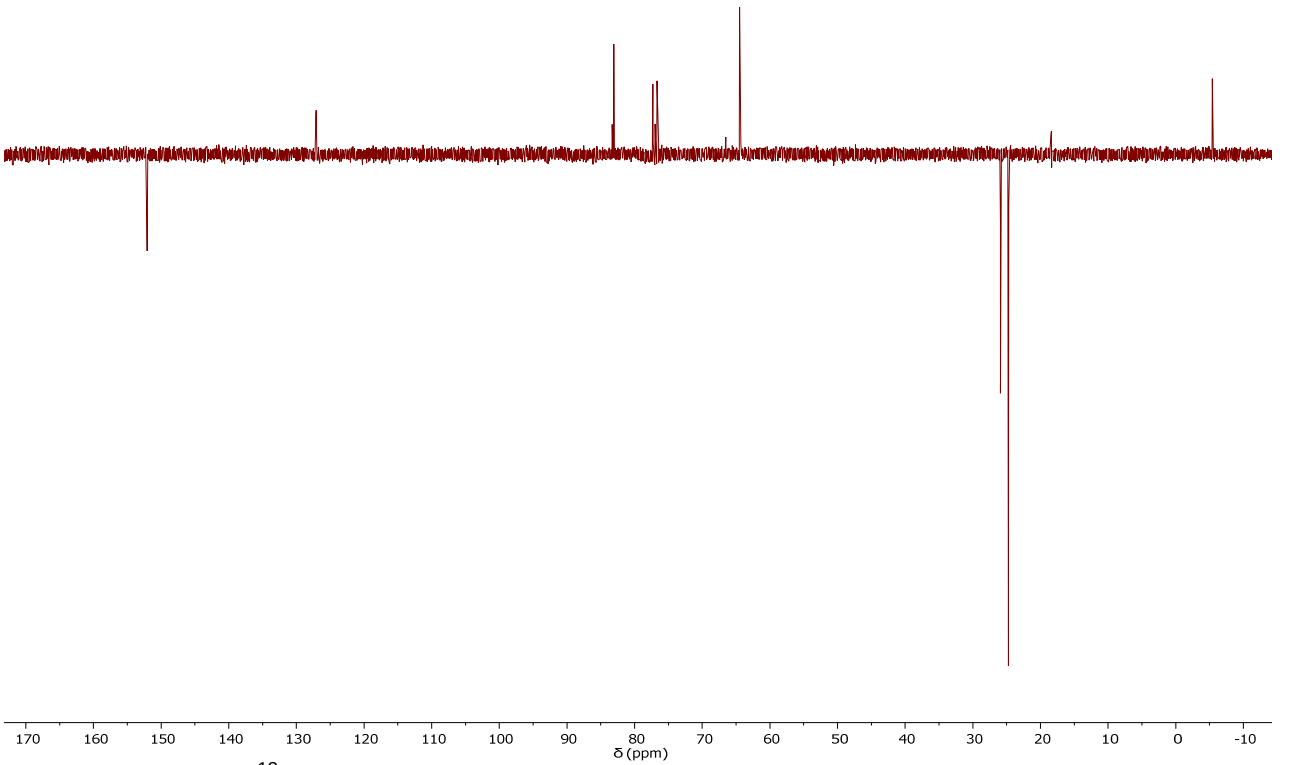
^{1}H NMR spectrum for compound **7** in $CDCl_3$, 400 MHz



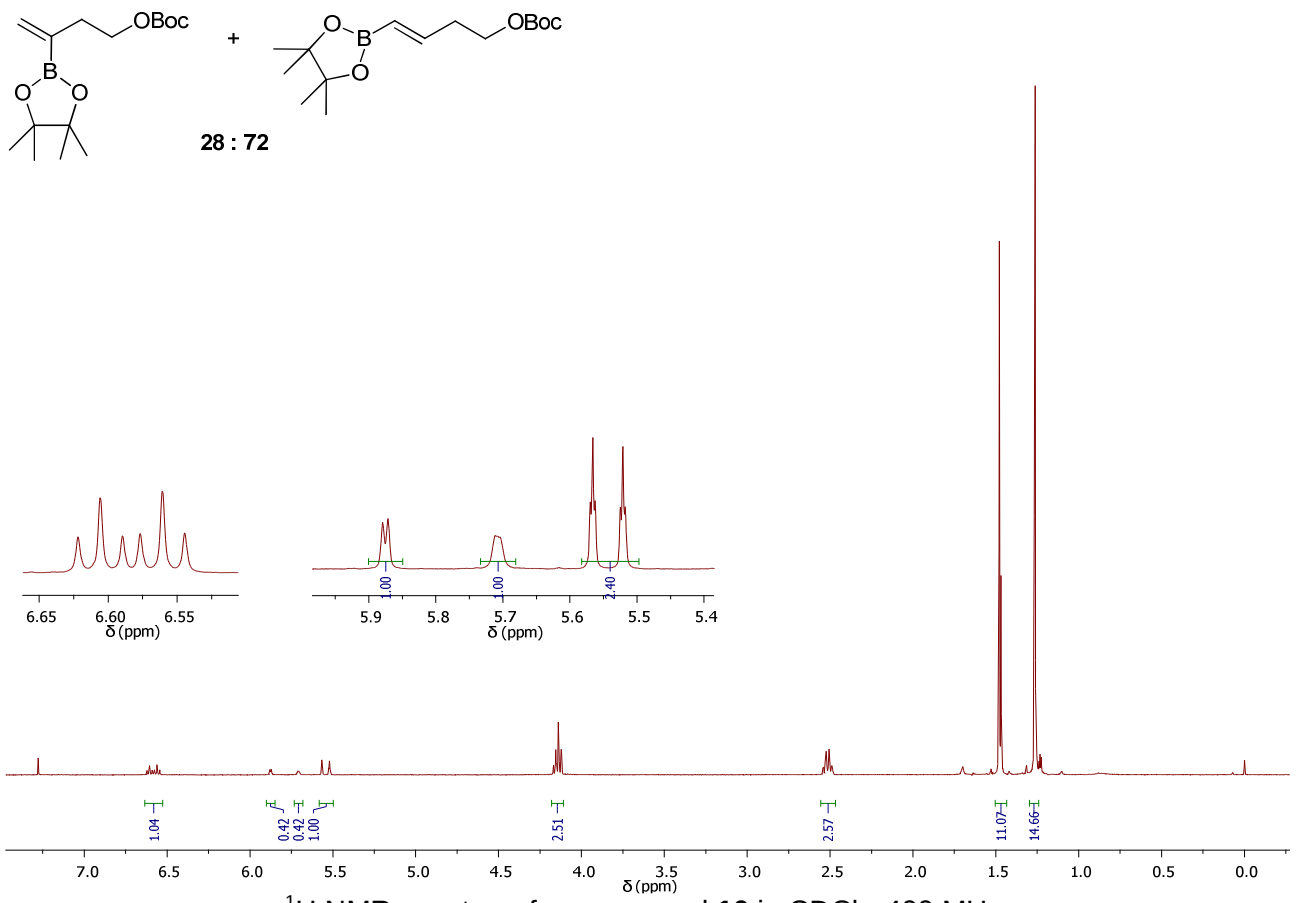
^{13}C-APT NMR spectrum for compound **7** in $CDCl_3$, 100 MHz



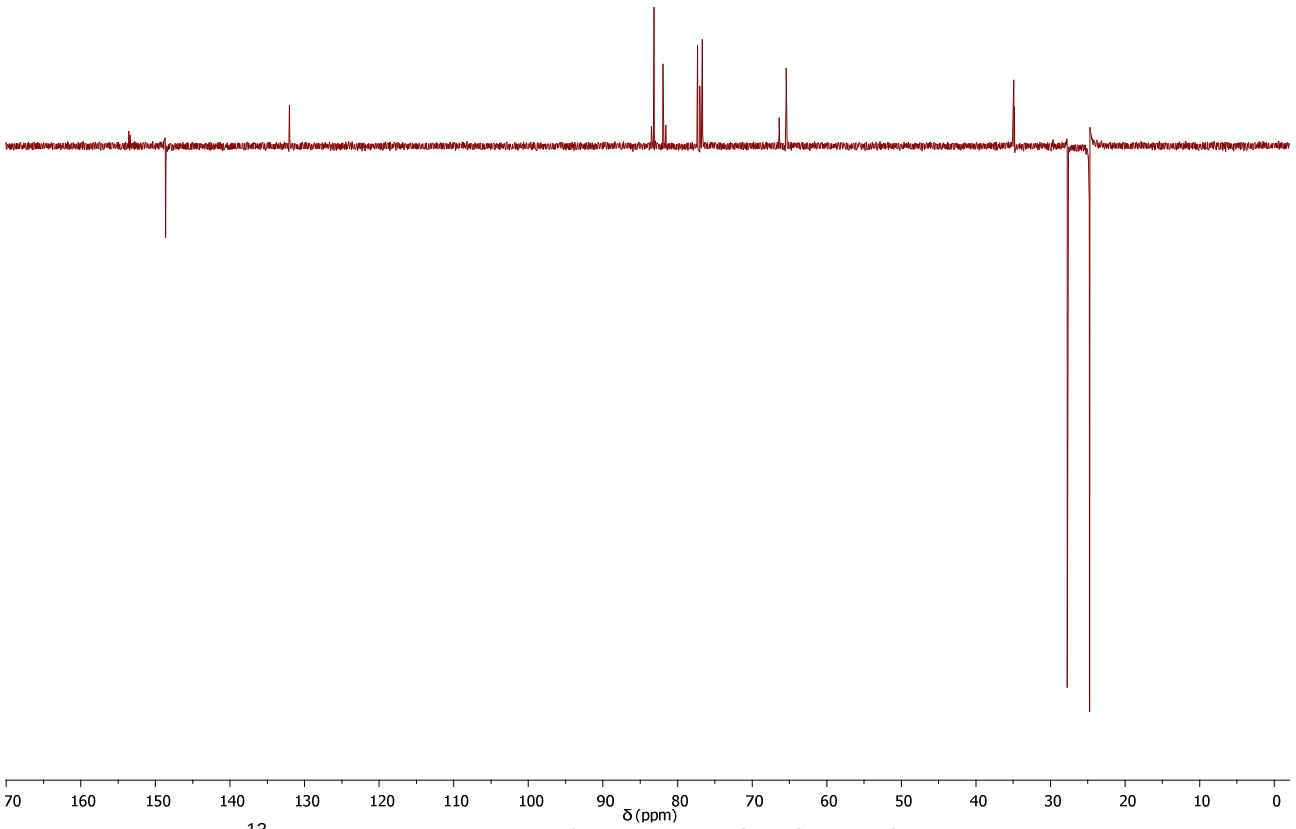
^{1}H NMR spectrum for compound **7** in $CDCl_3$, 400 MHz



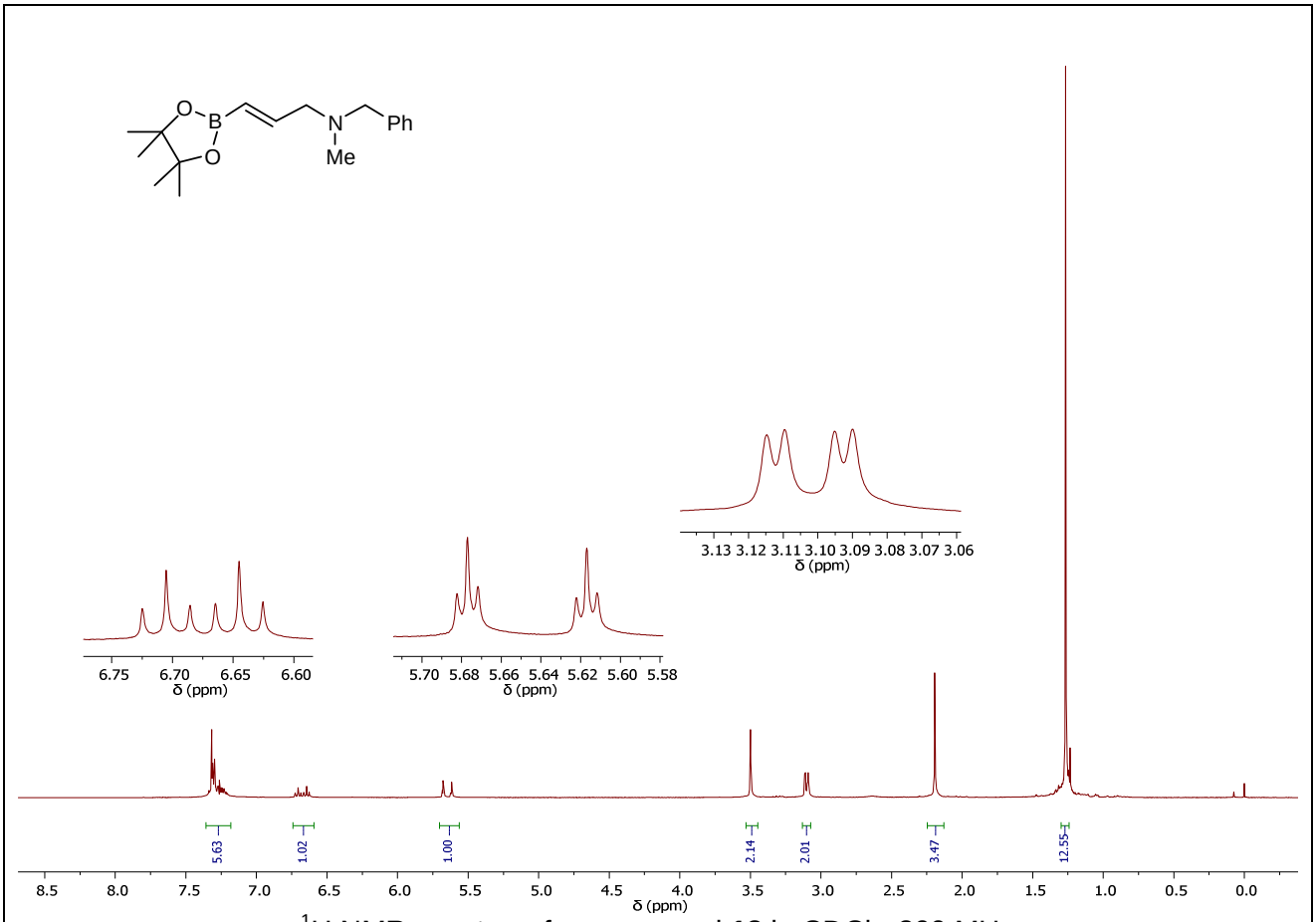
^{13}C-APT NMR spectrum for compound **7** in $CDCl_3$, 100 MHz



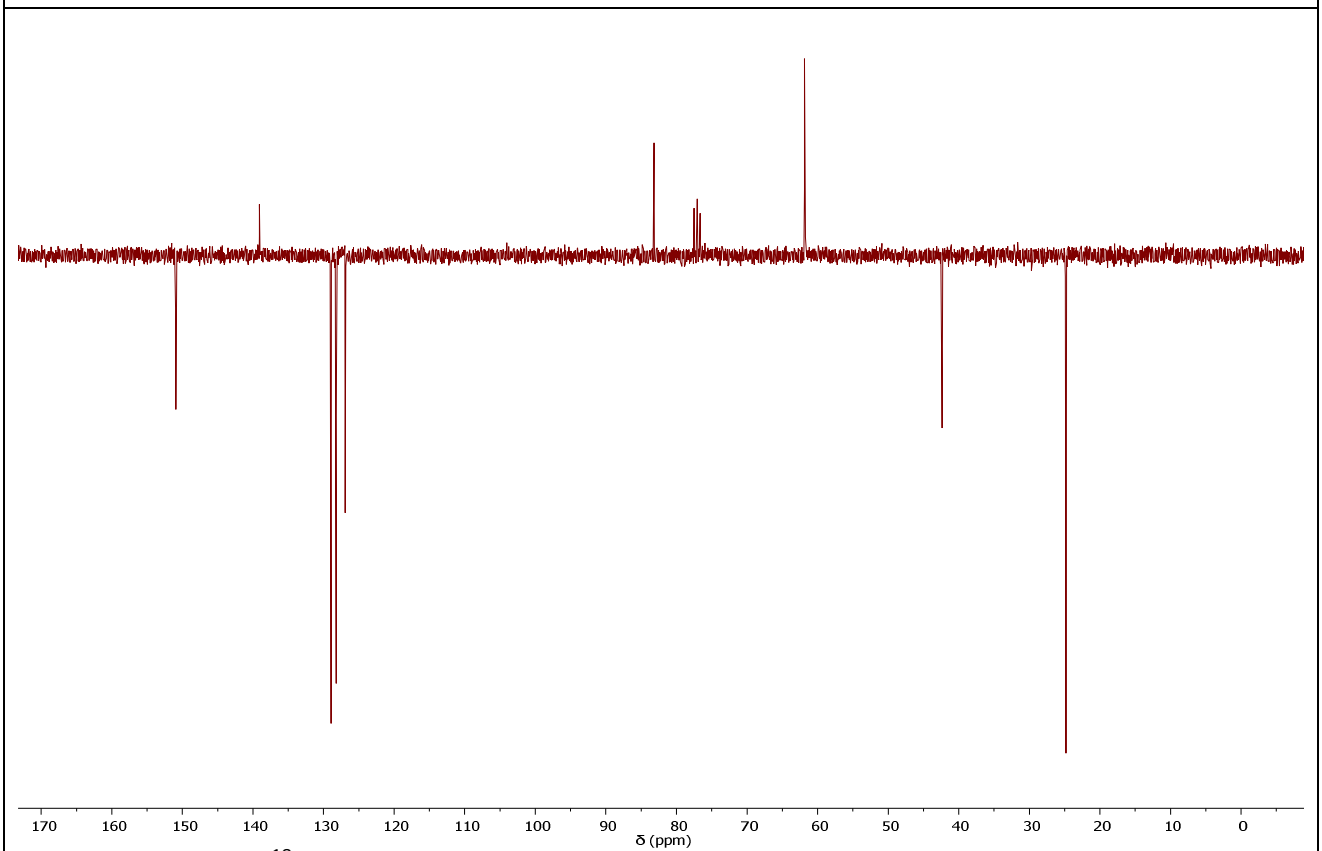
^{1}H NMR spectrum for compound **10** in $CDCl_3$, 400 MHz



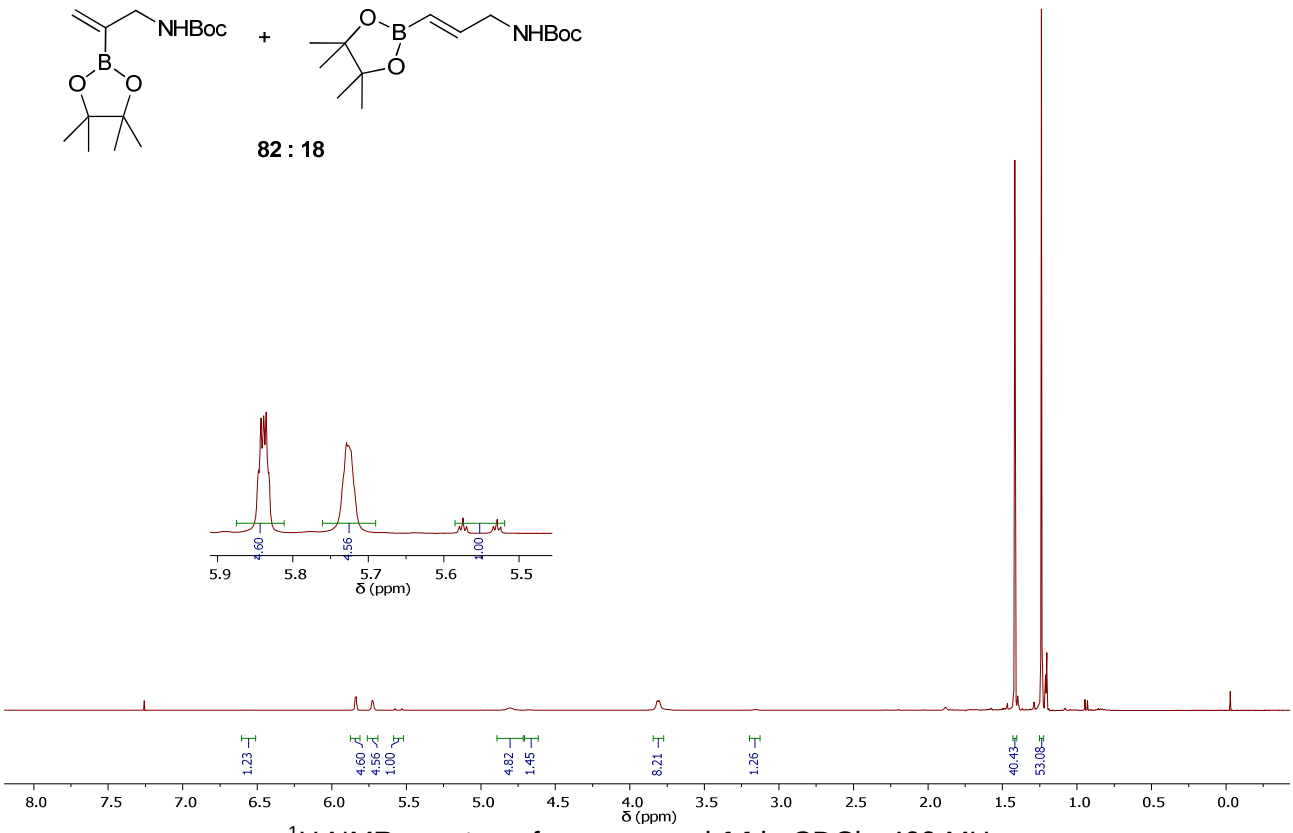
^{13}C-APT NMR spectrum for compound **10** in $CDCl_3$, 100 MHz



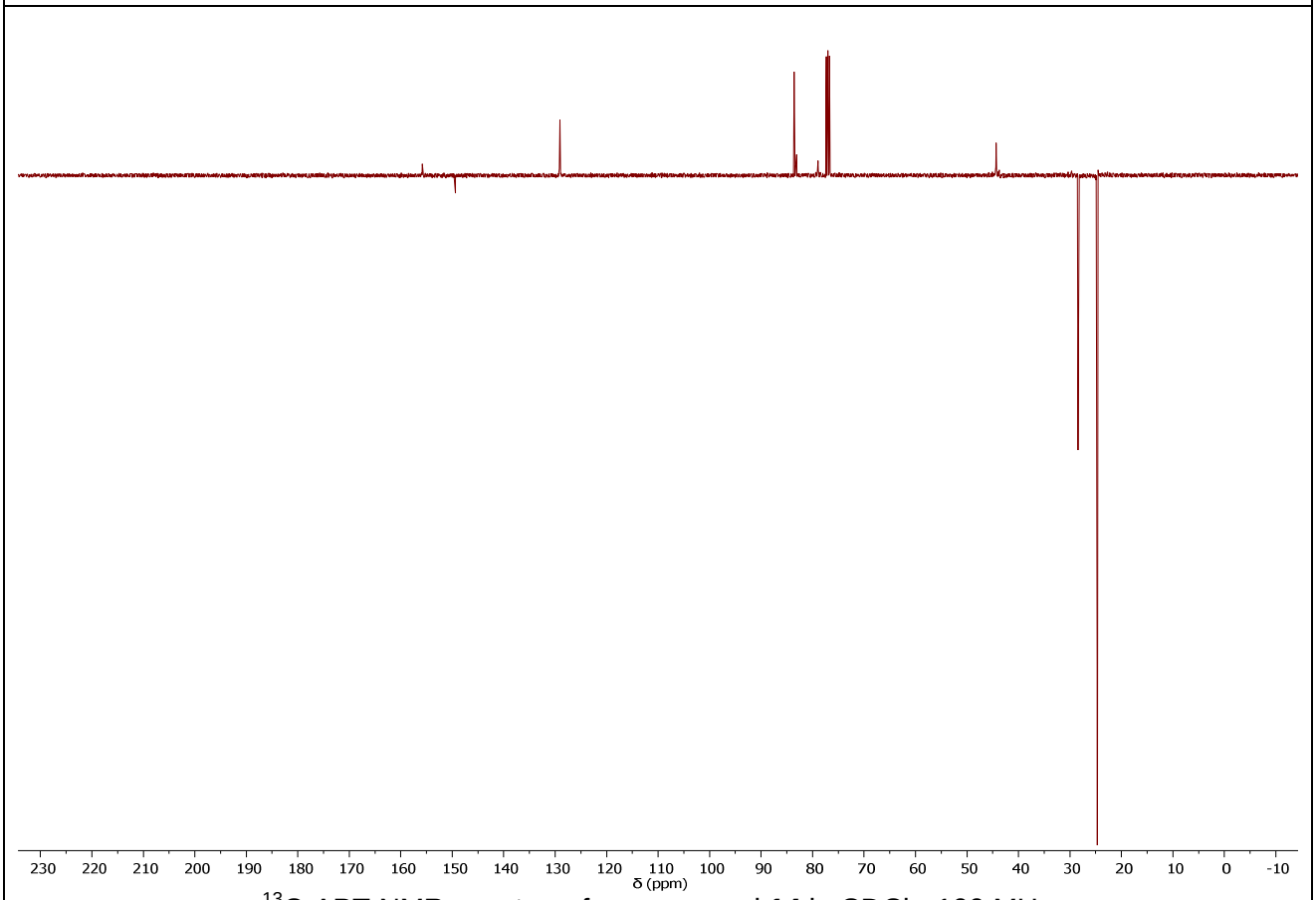
^{1}H NMR spectrum for compound **13** in $CDCl_3$, 300 MHz



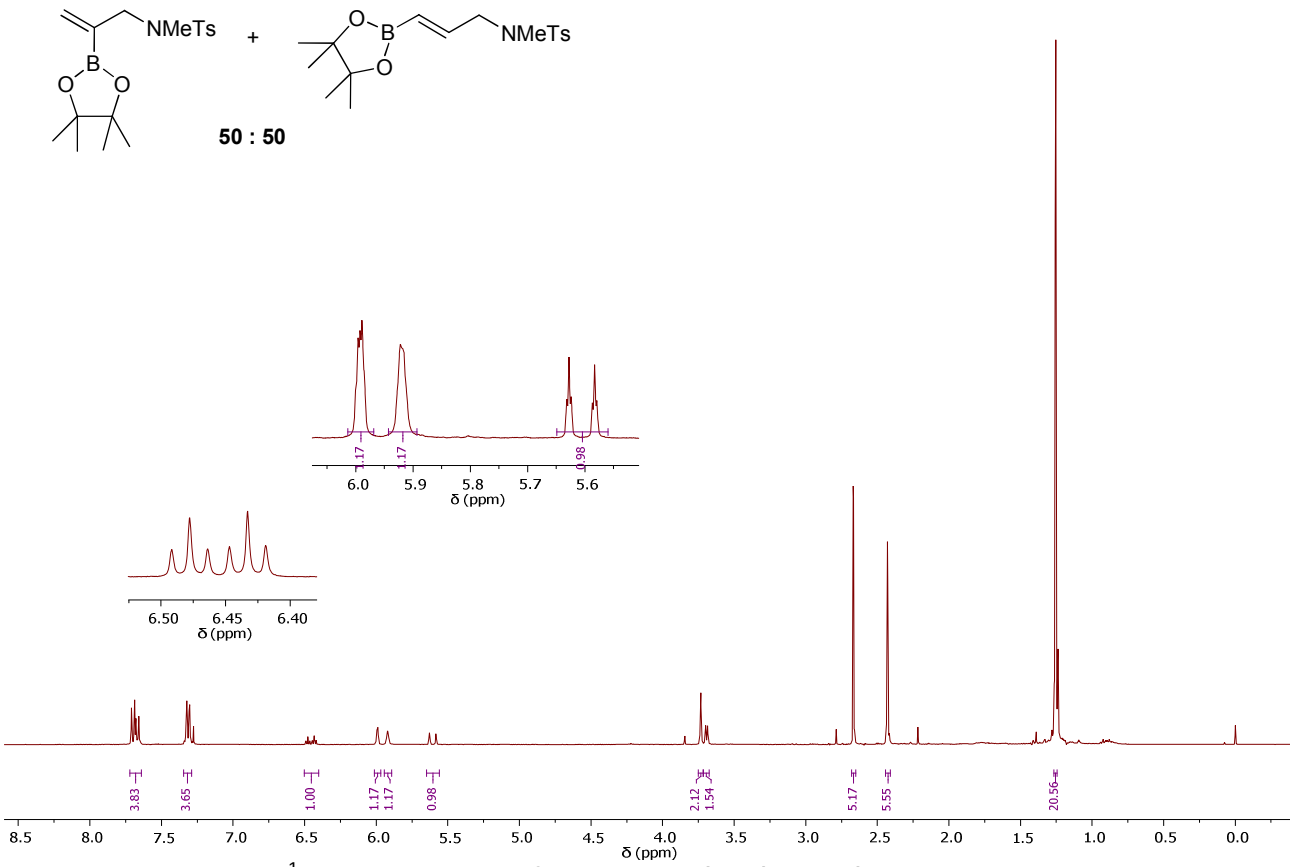
^{13}C-APT NMR spectrum for compound **13** in $CDCl_3$, 75 MHz



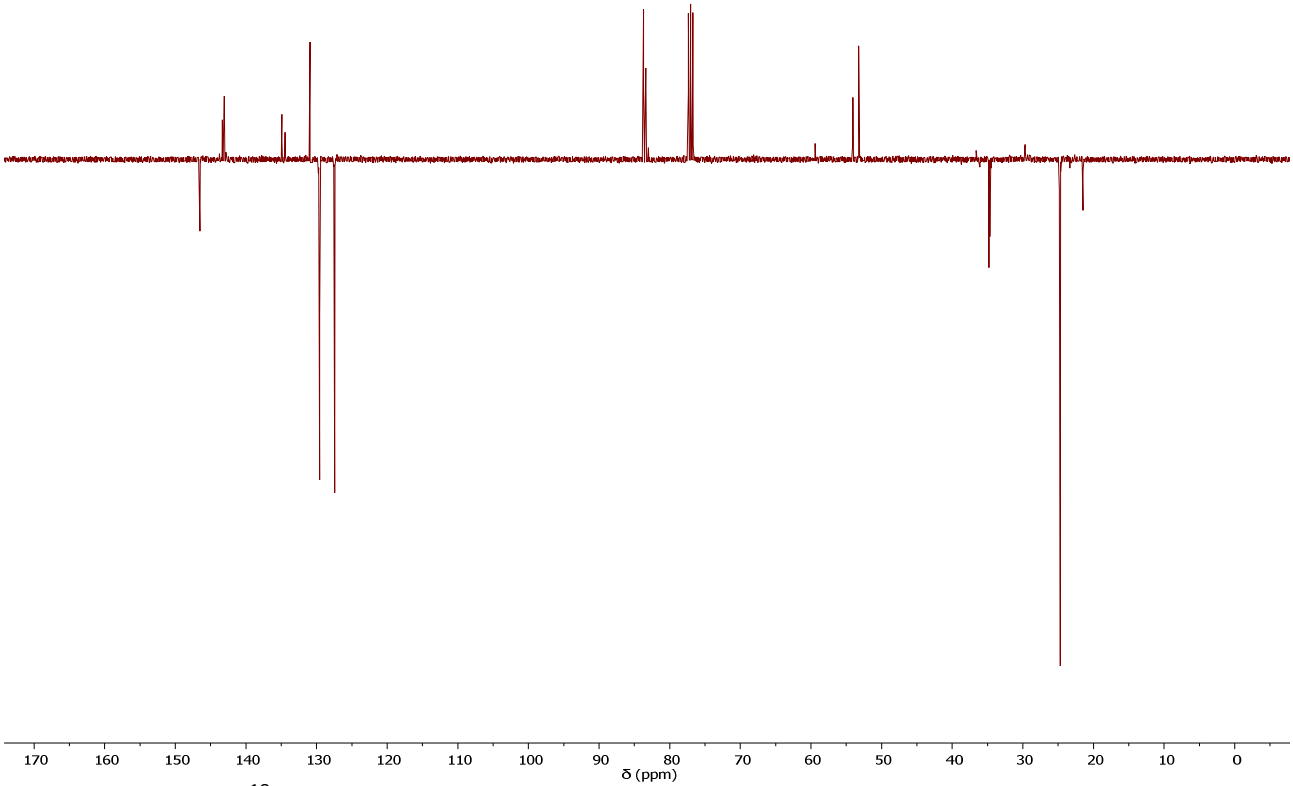
^{1}H NMR spectrum for compound **14** in $CDCl_3$, 400 MHz



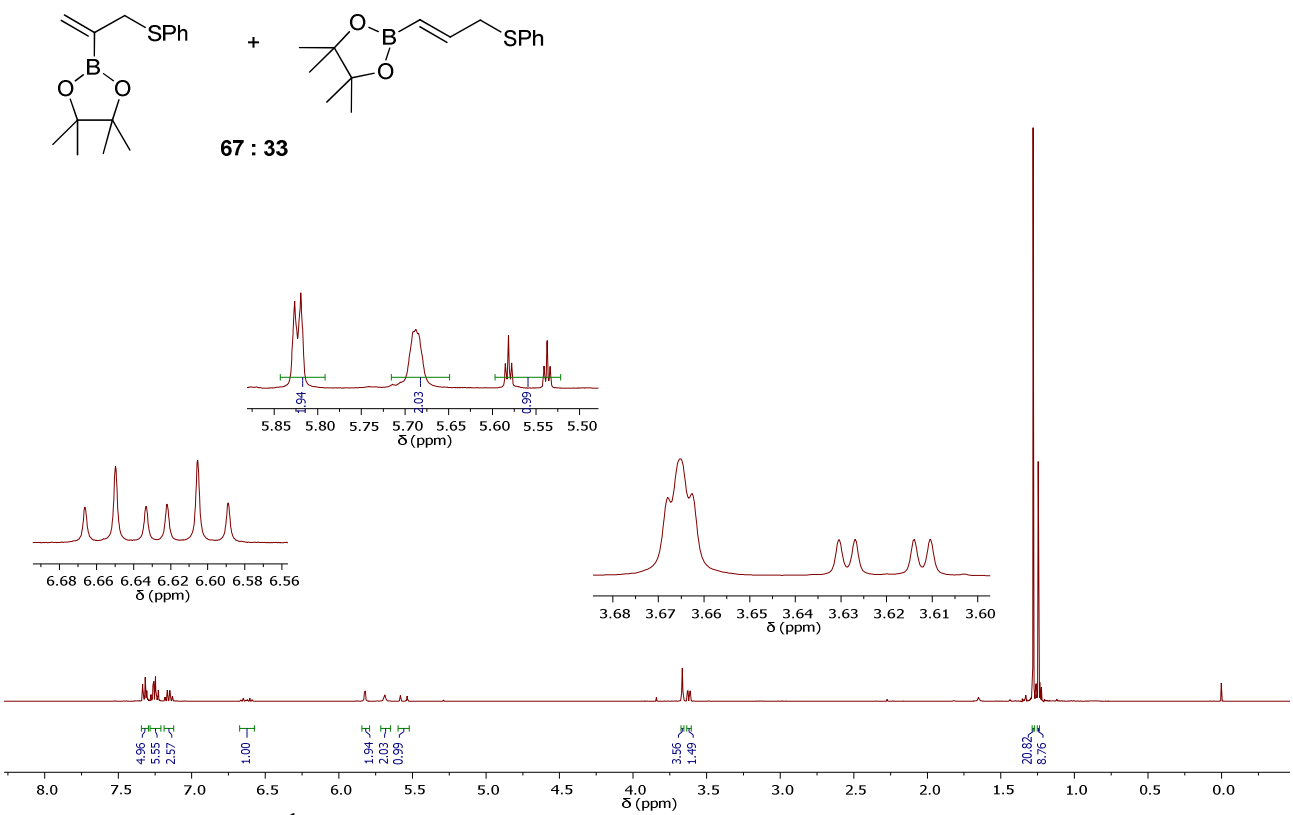
^{13}C-APT NMR spectrum for compound **14** in $CDCl_3$, 100 MHz



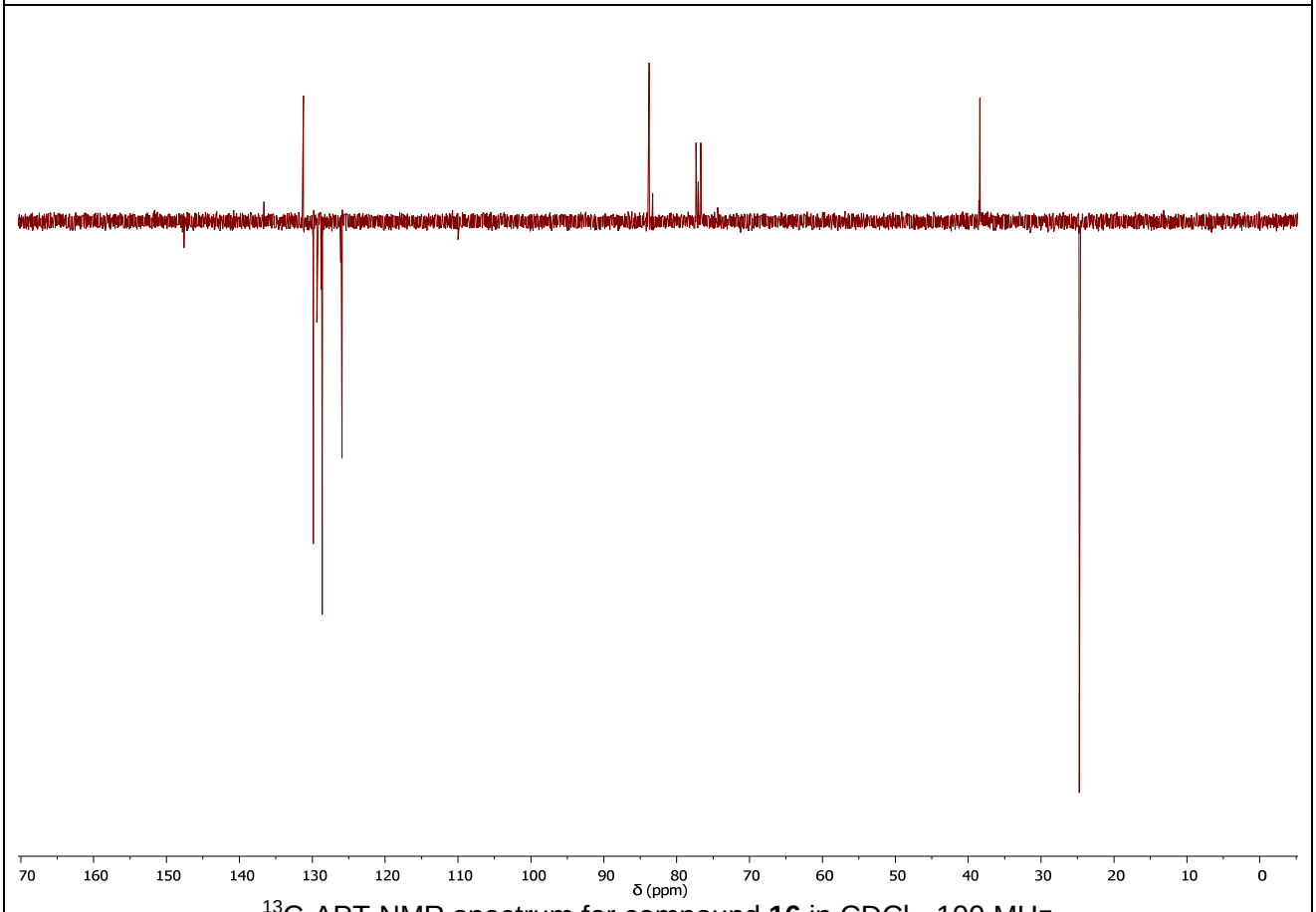
^{1}H NMR spectrum for compound **15** in $CDCl_3$, 400 MHz



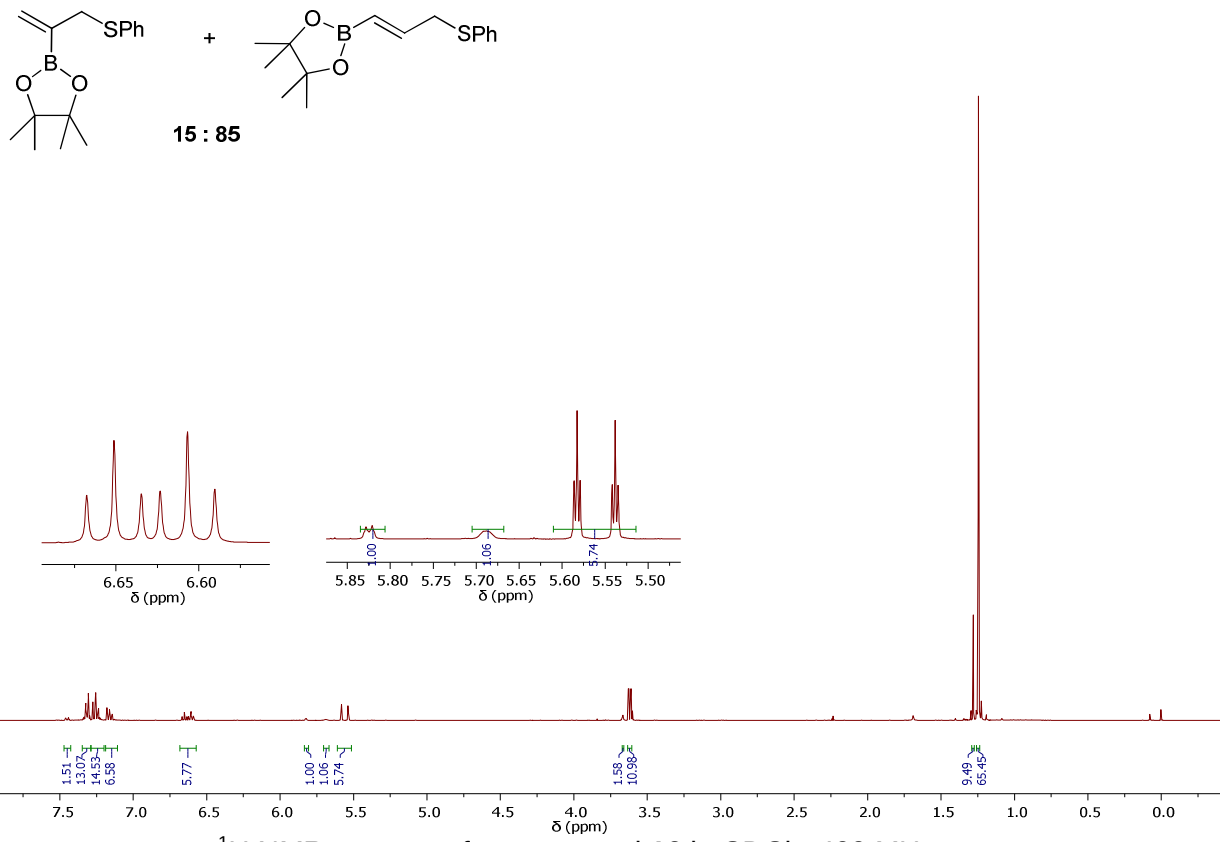
^{13}C-APT NMR spectrum for compound **15** in $CDCl_3$, 100 MHz



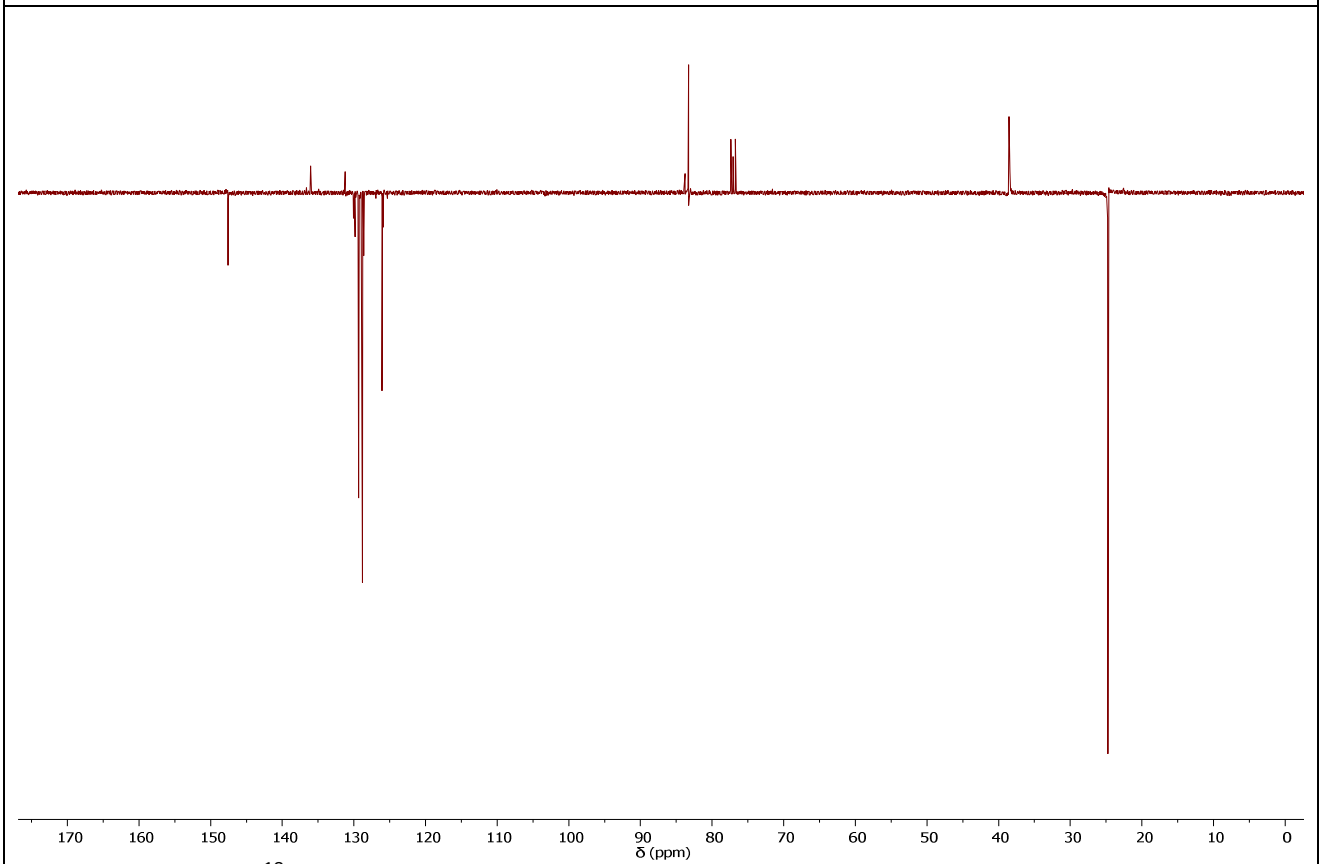
^{1}H NMR spectrum for compound **16** in $CDCl_3$, 400 MHz



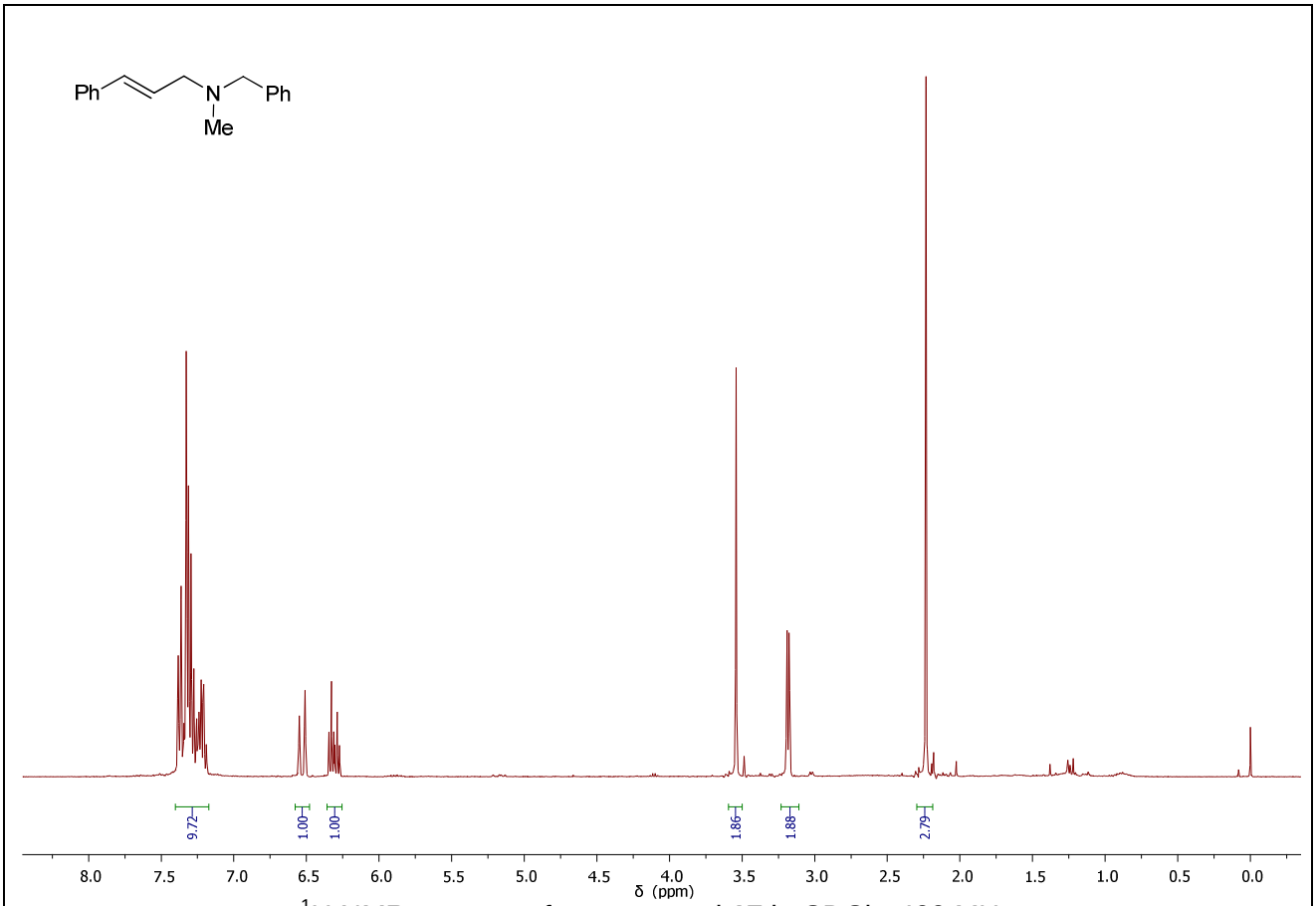
^{13}C-APT NMR spectrum for compound **16** in $CDCl_3$, 100 MHz



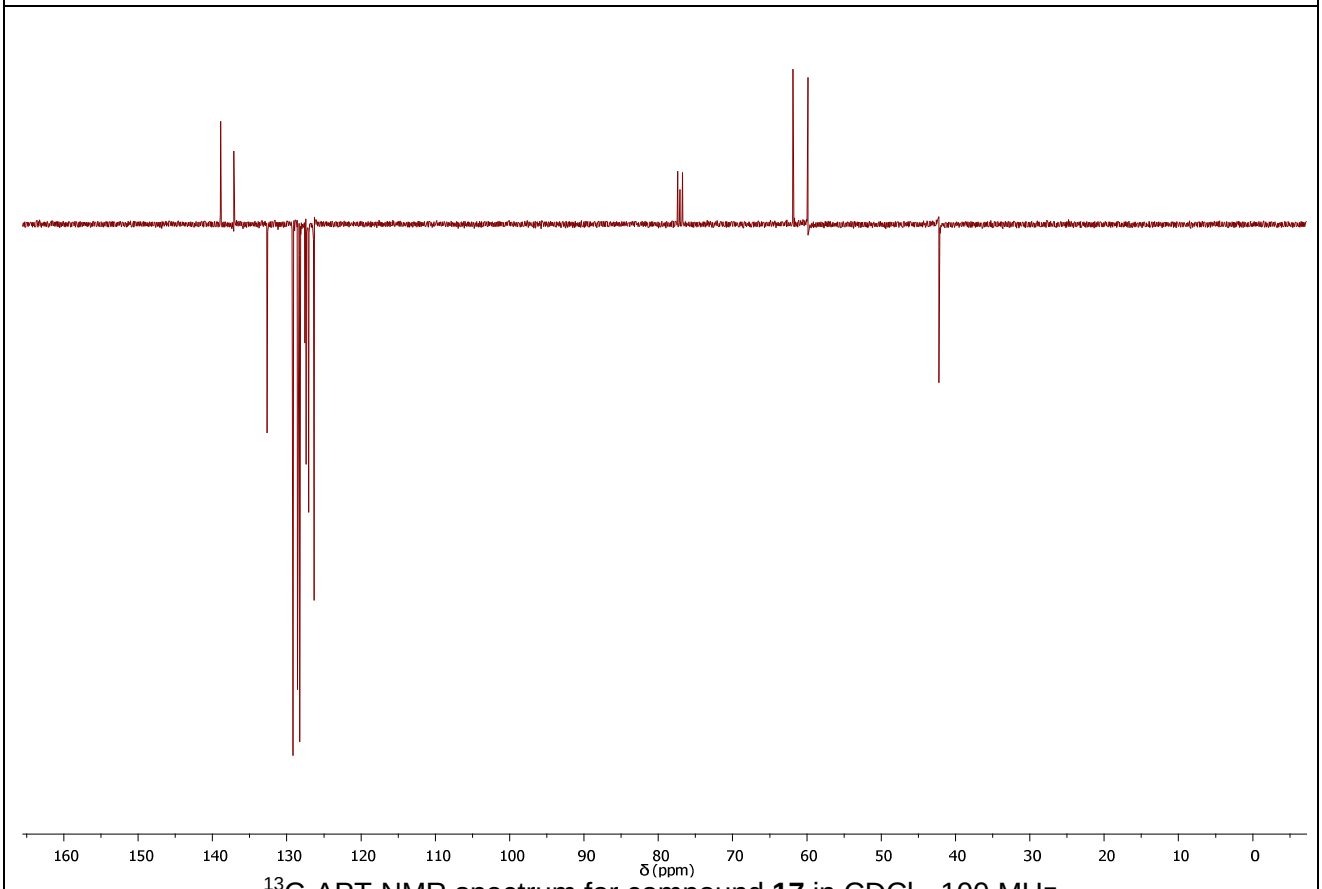
^{1}H NMR spectrum for compound **16** in $CDCl_3$, 400 MHz



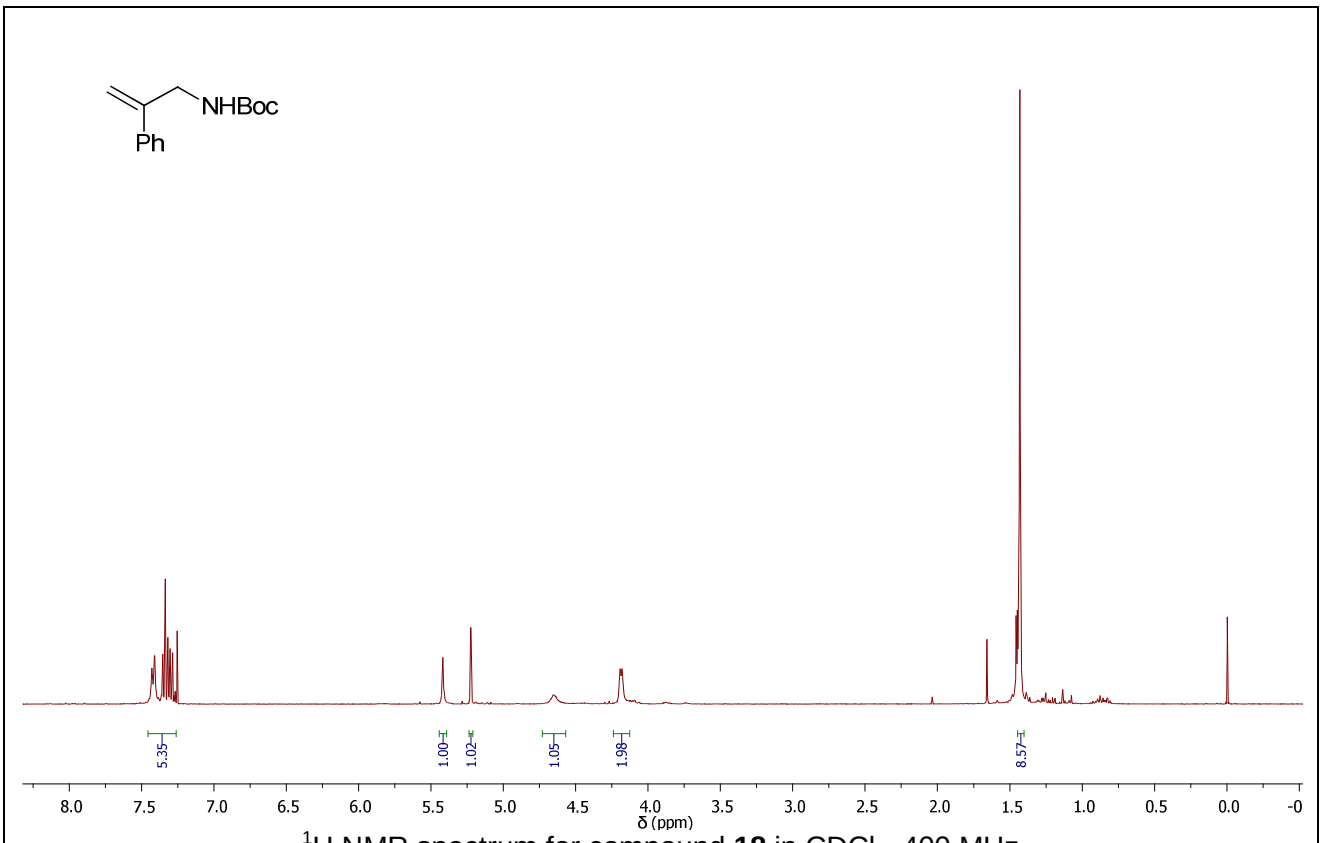
^{13}C-APT NMR spectrum for compound **16** in $CDCl_3$, 100 MHz



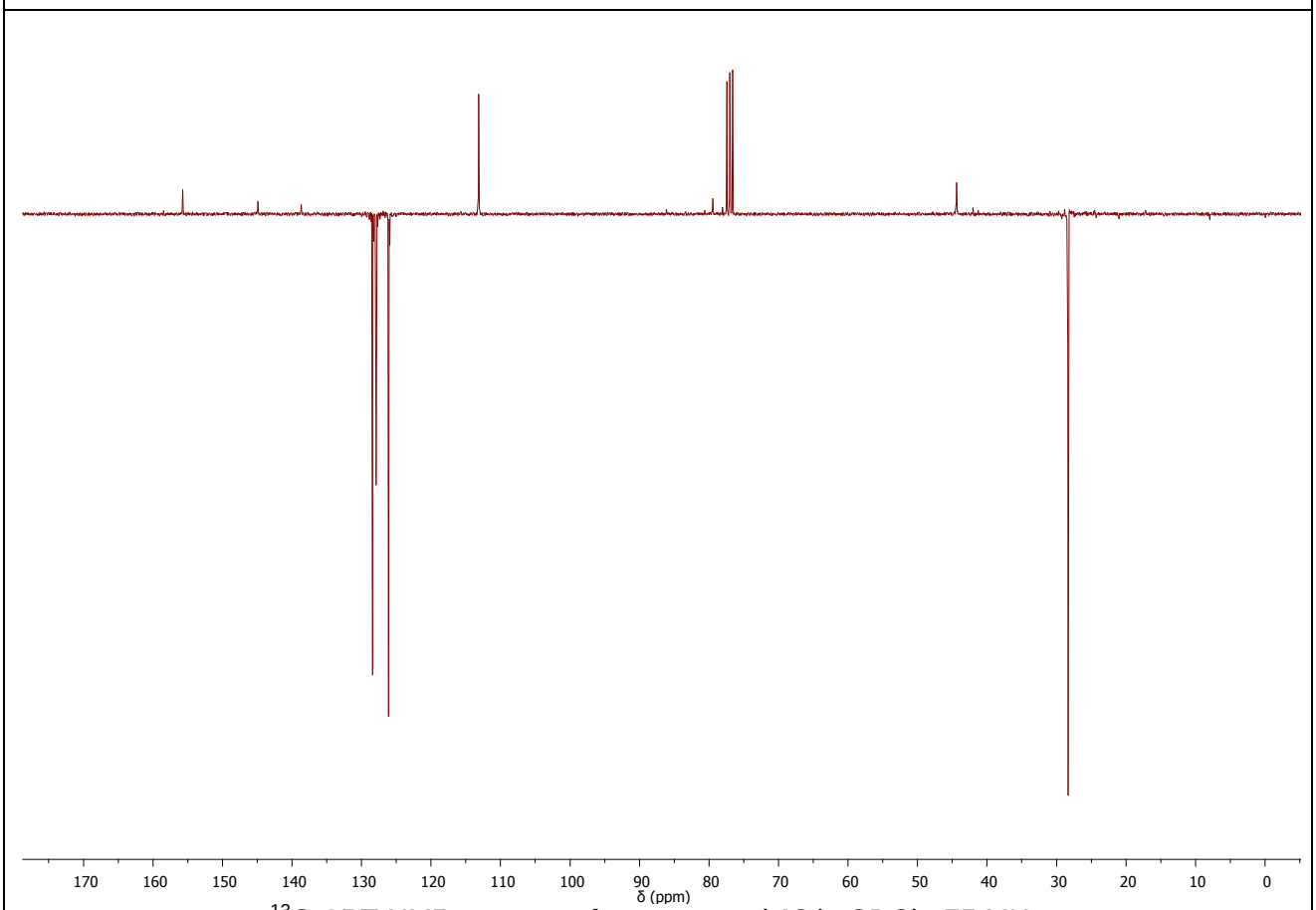
^{1}H NMR spectrum for compound **17** in $CDCl_3$, 400 MHz



^{13}C-APT NMR spectrum for compound **17** in $CDCl_3$, 100 MHz



^{1}H NMR spectrum for compound **18** in $CDCl_3$, 400 MHz



^{13}C-APT NMR spectrum for compound **18** in $CDCl_3$, 75 MHz