Supplementary Information

Borylstannylation of alkynes with inverse regioselectivity: Copper-catalyzed three-component coupling using a masked diboron

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Contents

General remarks.

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on a Varian System 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{119}Sn, 186 MHz) spectrometer using residual chloroform (^{1}H, δ = 7.26) or $CDCl_3$ (^{13}C, δ = 77.0) as an internal standard, and tetramethyltin (^{119}Sn, δ = 0.00) as an external standard. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet), coupling constants (Hz), integration. High-resolution mass spectra were obtained with a Thermo Fisher Scientific LTQ Orbitrap XL spectrometer. Melting points were measured with Yanaco Micro Melting Point apparatus and uncorrected. Preparative recycling gel permeation chromatography was performed with GL Science PU 614 equipped with Shodex GPC H-2001L and -2002L columns (toluene as an eluent). Column chromatography was carried out using Merk Kieselgel 60. Unless otherwise noted, commercially available reagents were used without purification. Toluene was distilled from sodium/benzophenone ketyl. DMF and DMSO were distilled from CaH_2.

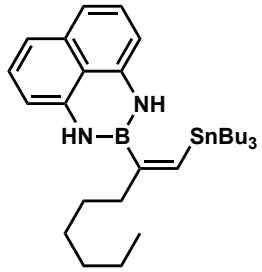
Materials.

(SIPr)CuCl,[1] (SIMes)CuCl,[1] (*t*Bu-SIPr)CuCl,[2] (IPr*)CuCl,[2] undeca-1,2-diene (**3a**),[3] and propa-1,2-dien-1-ylbenzene (**3b**)[4] were prepared according to literature procedures.

Cu-catalyzed borylstannylation of alkynes: a general procedure.

A Schlenk tube equipped with a magnetic stirring bar was charged with (SIPr)CuCl (6.0 μmol) were added an alkyne (0.30 mmol), a masked diboron (0.36 mmol), tributyltin methoxide (0.60 mmol) and THF (1.0 mL), and the resulting mixture was stirred at room temperature for 1 h. The mixture was diluted with diethyl ether and filtered through a Celite plug. The organic solution was washed with brine, dried over $MgSO_4$, and evaporated. The residual tin alkoxide was removed by passing through column chromatography (10% w/w anhydrous K_2CO_3–silica gel; diethyl ether as an eluent), and evaporation of the solvent followed by gel permeation chromatography (toluene as an eluent) gave the corresponding product. Stereochemistry of the product was determined by NOE experiment and by H–Sn coupling constants.[5]

(*E*)-2-(1-(tributylstannyl)oct-1-en-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diaza borinine (2a)



Isolated in 86% as a colorless liquid

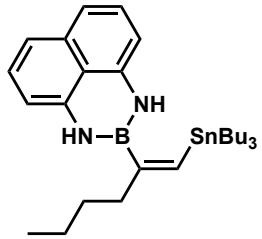
^{1}H NMR (C_6D_6) δ 0.83 (t, J = 7.4 Hz, 9H), 0.89 (t, J = 7.1 Hz, 3H), 0.93-1.08 (m, 6H), 1.22-1.38 (m, 12H), 1.46-1.64 (m, 8H), 2.3 (t, J = 7.8 Hz, 2H), 5.39 (s, 2H), 6.05-6.12 (m, 2H), 6.58 (s, $J_{H\text{-}Sn}$ = 81.9 Hz, 1H), 7.00-7.06 (m, 4H)

^{13}C NMR (C_6D_6) δ 11.0 ($J_{C\text{-}Sn}$ = 329.0 Hz), 13.9, 14.3, 23.1, 27.8 ($J_{C\text{-}Sn}$ = 56.1 Hz), 29.6, 29.7, 30.0, 32.1, 42.7 ($J_{C\text{-}Sn}$ = 71.9 Hz), 106.3, 118.5, 120.5, 137.0, 137.5, 141.1

^{119}Sn NMR (C_6D_6) δ -62.3

HRMS Calcd for $C_{30}H_{50}N_2BSn$: $[M+H]^+$, 569.30835. Found: m/z 569.30682

(*E*)-2-(1-(tributylstannyl)hex-1-en-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diaz aborinine (2b)



Isolated in 78% as a colorless liquid

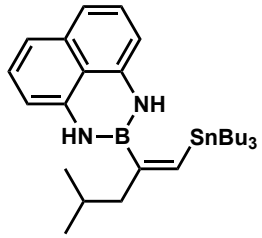
^{1}H NMR (C_6D_6) δ 0.81 (t, J = 7.4 Hz, 9H). 0.91 (t, J = 7.2 Hz, 3H), 0.93-1.07 (m, 6H), 1.21-1.39 (m, 8H), 1.40-1.64 (m, 8H), 2.29 (t, J = 7.4 Hz, 2H), 5.37 (s, 2H), 6.02-6.13 (m, 2H), 6.57 (s, $J_{H\text{-}Sn}$ = 82.3 Hz, 1H), 6.99-7.07 (m, 4H)

^{13}C NMR (C_6D_6) δ 11.0 ($J_{C\text{-}Sn}$ = 329.1 Hz), 13.9, 14.2, 23.0, 27.8 ($J_{C\text{-}Sn}$ = 56.4 Hz), 29.7 ($J_{C\text{-}Sn}$ = 20.2 Hz), 32.2, 42.4 ($J_{C\text{-}Sn}$ = 71.7 Hz), 106.3, 118.5, 120.5, 137.0, 137.5, 141.1

^{119}Sn NMR (C_6D_6) δ -62.4

HRMS Calcd for $C_{28}H_{46}N_2BSn$: $[M+H]^+$, 541.27705. Found: m/z 541.27698

(*E*)-2-(4-methyl-1-(tributylstannyl)pent-1-en-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2c)



Isolated in 81% as a colorless liquid

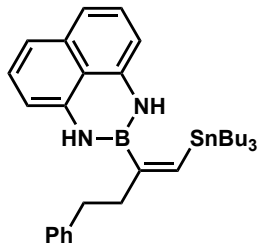
^{1}H NMR (C_6D_6) δ 0.83 (t, J = 7.4 Hz, 9H), 0.92 (d, J = 6.6 Hz, 6H), 0.94-1.08 (m, 6H), 1.27 (tq, J = 7.4 Hz, 7.4 Hz, 6H), 1.47-1.65 (m, 6H), 1.72 (sep, J = 6.7 Hz, 1H), 2.19 (d, J = 7.2 Hz, 2H), 5.39 (s, 2H), 6.05-6.11 (m, 2H), 6.52 (s, $J_{H\text{-}Sn}$ = 82.3 Hz, 1H), 7.00-7.07 (m, 4H)

^{13}C NMR (C_6D_6) δ 11.0 ($J_{C\text{-}Sn}$ = 328.8 Hz), 13.9, 22.8, 27.8 ($J_{C\text{-}Sn}$ = 55.5 Hz), 28.3, 29.8 ($J_{C\text{-}Sn}$ = 20.5 Hz), 52.7 ($J_{C\text{-}Sn}$ = 70.6 Hz), 106.4, 118.5, 120.5, 137.0, 139.4, 141.0

^{119}Sn NMR (C_6D_6) δ -62.6

HRMS Calcd for $C_{28}H_{46}N_2BSn$: $[M+H]^+$, 541.27705. Found: m/z 541.27722

(*E*)-2-(4-phenyl-1-(tributylstannyl)but-1-en-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2d)



Isolated in 74% as a colorless liquid

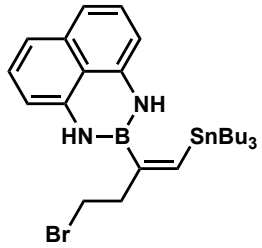
^{1}H NMR (C_6D_6) δ 0.95 (t, J = 7.4 Hz, 9H), 1.02-1.16 (m, 6H), 1.38 (tq, J = 7.4 Hz, 7.4 Hz, 6H), 1.56-1.73 (m, 6H), 2.65 (t, J = 7.6 Hz, 2H), 2.84 (d, J = 7.6 Hz, 2H), 5.23 (s, 2H), 6.13-6.23 (m, 2H), 6.69 (s, $J_{H\text{-}Sn}$ = 79.0 Hz, 1H), 7.12-7.32 (m, 9H)

^{13}C NMR (C_6D_6) δ 10.9 ($J_{C\text{-}Sn}$ = 329.8 Hz), 13.9, 27.8 ($J_{C\text{-}Sn}$ = 57.2 Hz), 29.7 ($J_{C\text{-}Sn}$ = 20.5 Hz), 36.9, 43.2, ($J_{C\text{-}Sn}$ = 71.6 Hz), 106.3, 118.4, 120.4, 126.3, 128.6, 129.1, 137.0, 139.0, 141.1, 142.2

^{119}Sn NMR (C_6D_6) δ -61.6

HRMS Calcd for $C_{32}H_{46}N_2BSn$: $[M+H]^+$, 589.27705. Found: m/z 589.27698

(*E*)-2-(4-bromo-1-(tributylstannyl)but-1-en-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2e)



Isolated in 87% as a colorless liquid

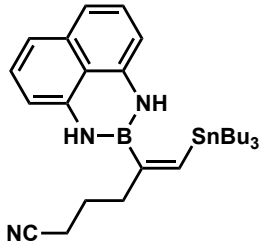
^{1}H NMR (C_6D_6) δ 0.82 (t, J = 7.3 Hz, 9H), 0.89-1.05 (m, 6H), 1.25 (tq, J = 7.4 Hz, 7.4 Hz, 6H), 1.44-1.61 (m, 6H), 2.54 (t, J = 7.0 Hz, 2H), 3.13 (t, J = 7.0 Hz, 2H), 5.32 (s, 2H), 6.03-6.13 (m, 2H), 6.48 (s, $J_{H\text{-}Sn}$ = 75.9 Hz, 1H), 6.98-7.09 (m, 4H)

^{13}C NMR (C_6D_6) δ 10.9 ($J_{C\text{-}Sn}$ = 329.9 Hz), 13.9, 27.8 ($J_{C\text{-}Sn}$ = 56.8 Hz), 29.7 ($J_{C\text{-}Sn}$ = 20.3 Hz), 32.9, 44.9 ($J_{C\text{-}Sn}$ = 72.3 Hz), 106.5, 118.6, 120.5, 137.0, 140.8, 141.9

^{119}Sn NMR (C_6D_6) δ -60.7

HRMS Calcd for $C_{26}H_{41}N_2BBrSn$: $[M+H]^+$, 591.15627. Found: m/z 591.15601

(*E*)-5-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)-6-(tributylstannyl)hex-5-enenitrile (2f)



Isolated in 79% as a colorless liquid

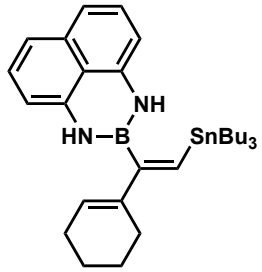
^{1}H NMR (C_6D_6) δ 0.84 (t, J = 7.4 Hz, 9H), 0.92-1.11 (m, 6H), 1.16-1.36 (m, 8H), 1.43-1.67 (m, 8H), 2.08 (t, J = 7.5 Hz, 2H), 5.43 (s, 2H), 6.13-6.23 (m, 2H), 6.49 (s, $J_{H\text{-}Sn}$ = 78.0 Hz, 1H), 7.01-7.10 (m, 4H)

^{13}C NMR (C_6D_6) δ 10.9 ($J_{C\text{-}Sn}$ = 330.4 Hz), 13.9, 16.4, 24.8, 27.8 ($J_{C\text{-}Sn}$ = 57.2 Hz), 29.7 ($J_{C\text{-}Sn}$ = 20.1 Hz), 41.1 ($J_{C\text{-}Sn}$ = 71.1 Hz), 106.4, 118.6, 119.7, 120.5, 127.9, 137.0, 140.1, 140.9

^{119}Sn NMR (C_6D_6) δ -50.9

HRMS Calcd for $C_{28}H_{43}N_3BSn$: $[M+H]^+$, 552.25665. Found: m/z 552.25800

(*E*)-2-(1-(cyclohex-1-en-1-yl)-2-(tributylstannyl)vinyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2g)



Isolated in 81% as a colorless liquid

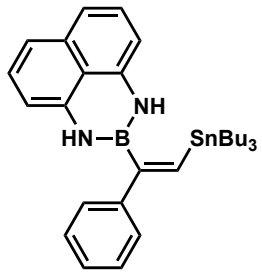
^{1}H NMR (C_6D_6) δ 0.83 (t, J = 7.3 Hz, 9H), 0.93-1.08 (m, 6H), 1.26 (tq, J = 7.4 Hz, 7.4 Hz, 6H), 1.47-1.61 (m, 8H), 1.62-1.71 (m, 2H), 2.02-2.09 (m, 2H), 2.28-2.35 (m, 2H), 5.30 (s, 2H), 5.90-6.03 (m, 3H), 6.76 (s, $J_{H\text{-}Sn}$ = 73.7 Hz, 1H), 6.98-7.09 (m, 4H)

^{13}C NMR (C_6D_6) δ 10.7 (J = 330.5 Hz), 13.9, 23.0, 23.4, 25.2, 26.6, 27.8, (58 Hz), 29.7 (19.8 Hz), 106.2, 118.3, 120.4, 129.7, 132.5, 137.0, 140.4, 141.2

^{119}Sn NMR (C_6D_6) δ -56.7

HRMS Calcd for $C_{30}H_{46}N_2BSn$: $[M+H]^+$, 565.27705. Found: m/z 565.27716

(*E*)-2-(1-phenyl-2-(tributylstannyl)vinyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2h)



Isolated in 73% as a colorless liquid

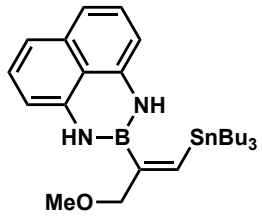
^{1}H NMR (C_6D_6) δ 0.84 (t, J = 7.3 Hz, 9H), 0.96-1.10 (m, 6H), 1.27 (tq, J = 7.4 Hz, 7.4 Hz, 6H), 1.48-1.63 (m, 6H), 5.35 (s, 2H), 5.90-6.00 (m, 2H), 6.99-7.07 (m, 4H), 7.10-7.14 (m, 1H), 7.22 (t, J = 7.7 Hz, 2H), 7.34 (s, $J_{H\text{-}Sn}$ = 71.2 Hz, 1H), 7.50 (d, J = 7.3 Hz, 2H)

^{13}C NMR (C_6D_6) δ 10.9 ($J_{C\text{-}Sn}$ = 331.8 Hz), 13.8, 27.8 ($J_{C\text{-}Sn}$ = 58.1 Hz), 29.7 ($J_{C\text{-}Sn}$ = 19.4 Hz), 106.4, 118.5, 120.5, 127.1, 127.6, 128.9, 137.0, 140.6, 141.0, 143.8

^{119}Sn NMR (C_6D_6) -57.1

HRMS Calcd for $C_{30}H_{42}N_2BSn$: $[M+H]^+$, 561.24575. Found: m/z 561.24573

(*E*)-2-(3-methoxy-1-(tributylstannyl)prop-1-en-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2i)



Isolated in 66% as a colorless liquid

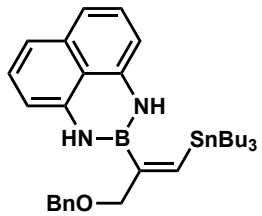
^{1}H NMR (C_6D_6) δ 0.82 (t, J = 7.4 Hz, 9H), 0.93-1.08 (m, 6H), 1.26 (tq, J = 7.4 Hz, 7.4 Hz, 6H), 1.46-1.64 (m, 6H), 3.15 (s, 3H), 3.98 (d, J = 1.3 Hz, 2H), 5.80 (s, 2H), 6.11-6.16 (m, 2H), 6.78 (s, $J_{H\text{-}Sn}$ = 76.8 Hz, 1H), 7.00-7.07 (m, 4H)

^{13}C NMR (C_6D_6) δ 11.1 ($J_{C\text{-}Sn}$ = 331.0 Hz), 13.8, 27.7 ($J_{C\text{-}Sn}$ = 56.3 Hz), 29.6 ($J_{C\text{-}Sn}$ = 20.7 Hz), 57.6, 81.5 ($J_{C\text{-}Sn}$ = 76.2 Hz), 106.3, 118.4, 120.7, 127.9, 137.1, 141.2, 142.3

^{119}Sn NMR (C_6D_6) -60.7

HRMS Calcd for $C_{26}H_{42}ON_2BSn$: $[M+H]^+$, 529.24067. Found: m/z 529.24152

(*E*)-2-(3-(benzyloxy)-1-(tributylstannyl)prop-1-en-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2j)



Isolated in 66% as a colorless liquid

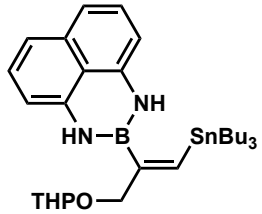
^{1}H NMR (C_6D_6) δ 0.82 (t, J = 7.3 Hz, 9H), 0.92-1.09 (m, 6H), 1.26 (tq, J = 7.4 Hz, 7.4 Hz, 6H), 1.46-1.62 (m, 6H), 4.11 (s, 2H), 4.39 (s, 2H), 5.83 (s, 2H), 6.13 (t, J = 4.0 Hz, 2H), 6.80 (s, $J_{H\text{-}Sn}$ = 75.7 Hz, 1H), 7.03 (d, J = 4.0 Hz, 4H), 7.09 (t, J = 7.3 Hz, 1H), 7.16 (t, J = 7.3 Hz, 2H), 7.32 (d, J = 7.4 Hz, 2H)

^{13}C NMR (C_6D_6) δ 11.1 ($J_{C\text{-}Sn}$ = 331.6 Hz), 13.8, 27.7 ($J_{C\text{-}Sn}$ = 56.6 Hz), 29.6 ($J_{C\text{-}Sn}$ = 20.1 Hz), 72.3, 79.1 ($J_{C\text{-}Sn}$ = 77.2 Hz), 106.3, 118.4, 120.7, 127.9, 128.1, 128.7, 137.1, 138.9, 141.2, 142.6

^{119}Sn NMR (C_6D_6) δ -60.8

HRMS Calcd for $C_{32}H_{46}ON_2BSn$: $[M]^+$, 605.27197. Found: m/z 605.27332

(*E*)-2-(3-((tetrahydro-2*H*-pyran-2-yl)oxy)-1-(tributylstannyl)prop-1-en-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2k)



Isolated in 66% as a colorless liquid

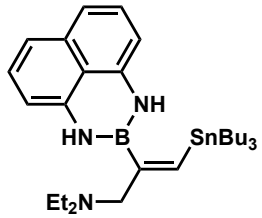
^{1}H NMR (C_6D_6) δ 0.83 (t, *J* = 7.4 Hz, 9H), 0.93-1.08 (m, 6H), 1.17-1.37 (m, 9H), 1.46-1.64 (m, 8H), 1.66-1.78 (m, 1H), 3.33-3.44 (m, 1H), 3.85 (dd, *J* = 11.7 Hz, 8.2 Hz, 1H), 4.17 (dd, *J* = 11.7 Hz, 1.2 Hz, 1H), 4.58 (dd, *J* = 11.7 Hz, 1.2 Hz, 1H), 4.68 (t, *J* = 3.5 Hz, 1H), 5.92 (s, 2H), 6.17-6.23 (m, 2H), 6.88 (s, $J_{H\text{-}Sn}$ = 76.2 Hz, 1H), 7.03-7.10 (m, 4H)

^{13}C NMR (C_6D_6) δ 11.1 ($J_{C\text{-}Sn}$ = 331 Hz), 13.8, 19.8, 25.8, 27.7, 29.6 ($J_{C\text{-}Sn}$ = 20.3 Hz), 31.0, 62.1, 75.7 ($J_{C\text{-}Sn}$ = 79.0 Hz), 98.2, 106.2, 118.4, 120.7, 127.9, 137.1, 141.3, 142.0

^{119}Sn NMR (C_6D_6) δ -60.9

HRMS Calcd for $C_{30}H_{48}O_2N_2BSn$: $[M+H]^+$, 599.28253. Found: m/z 599.28351

(*E*)-*N*,*N*-diethyl-2-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)-3-(tributylstannyl)prop-2-en-1-amine (2l)



Isolated in 69% as a colorless liquid

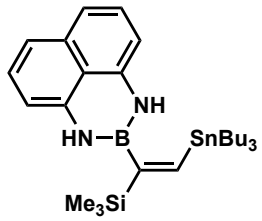
^{1}H NMR (C_6D_6) δ 0.85 (t, *J* = 7.4 Hz, 9H), 0.96 (t, *J* = 7.2 Hz, 6H), 0.99-1.12 (m, 6H), 1.29 (tq, *J* = 7.4 Hz, 7.4 Hz, 6H), 1.50-1.67 (m, 6H), 2.4 (q, *J* = 7.2 Hz, 4H), 3.18 (s, 2H), 6.24-6.36 (m, 2H), 6.63 (s, $J_{H\text{-}Sn}$ = 77.2 Hz, 1H), 68.0 (s, 2H), 7.03-7.10 (m, 4H)

^{13}C NMR (C_6D_6) δ 11.4 ($J_{C\text{-}Sn}$ = 329.0), 12.3, 13.9, 27.7 ($J_{C\text{-}Sn}$ = 53.9), 29.7 ($J_{C\text{-}Sn}$ = 20.9), 46.6, 67.1 ($J_{C\text{-}Sn}$ = 78.1), 106.1, 118.1, 121.1, 128.0, 137.3, 141.7, 143.6 ($J_{C\text{-}Sn}$ = 372.4)

^{119}Sn NMR (C_6D_6) δ -60.2

HRMS Calcd for $C_{29}H_{49}N_3BSn$: $[M+H]^+$, 570.30360. Found: m/z 570.30371

(*E*)-2-(2-(tributylstannyl)-1-(trimethylsilyl)vinyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2m)



Isolated in 75% as a colorless liquid

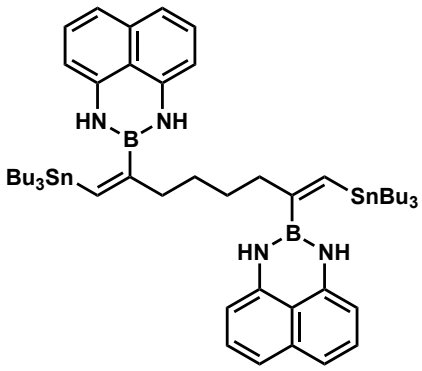
^{1}H NMR (C_6D_6) δ 0.18 (s, 9H), 0.81 (t, J = 7.3 Hz, 9H), 0.92-1.08 (m, 6H), 1.24 (tq, J = 7.4 Hz, 7.4 Hz, 6H), 1.46-1.62 (m, 6H), 5.31 (s, 2H), 6.03-6.10 (m, 2H), 6.99-7.07 (m, 4H), 7.73 (s, $J_{H\text{-}Sn}$ = 113.7 Hz, 1H)

^{13}C NMR (C_6D_6) δ -0.69 ($J_{C\text{-}Sn}$ = 51.0 Hz), 11.0 ($J_{C\text{-}Sn}$ = 318.5 Hz), 13.9, 27.8 ($J_{C\text{-}Sn}$ = 55.5 Hz), 29.7 ($J_{C\text{-}Sn}$ = 19.9 Hz), 106.3, 118.4, 120.2, 127.8, 137.0, 141.1, 158.4 ($J_{C\text{-}Sn}$ = 359.9 Hz)

^{119}Sn NMR (C_6D_6) δ -68.1

HRMS Calcd for $C_{27}H_{46}N_2BSiSn$: $[M+H]^+$, 557.25398. Found: m/z 557.25494

2,2'-((1*E*,7*E*)-1,8-bis(tributylstannyl)octa-1,7-diene-2,7-diyl)bis(2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine) (2n)



Isolated in 58% as a colorless solid: mp 55-56 °C

^{1}H NMR (C_6D_6) δ 0.83 (t, J = 7.3 Hz, 18H), 0.91-1.08 (m, 12H), 1.26 (tq, J = 7.4 Hz, 7.4 Hz, 12H), 1.46-1.73 (m, 16H), 2.36 (s, 4H), 5.40 (s, 4H), 6.04-6.11 (m, 4H), 6.62 (s, $J_{H\text{-}Sn}$ = 80.9 Hz, 2H), 6.69-7.11 (m, 8H)

^{13}C NMR (C_6D_6) δ 11.0 ($J_{C\text{-}Sn}$ = 329.1 Hz), 13.9, 27.8 ($J_{C\text{-}Sn}$ = 56.2 Hz), 29.7 ($J_{C\text{-}Sn}$ = 20.0 Hz), 30.0, 42.7 ($J_{C\text{-}Sn}$ = 71.9 Hz), 106.4, 118.5, 120.4, 127.8, 137.0, 138.0, 141.0

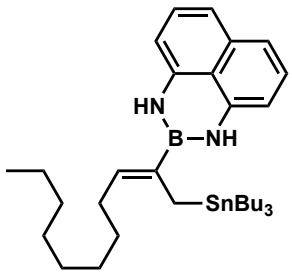
^{119}Sn NMR (C_6D_6) δ -62.4

HRMS Calcd for $C_{52}H_{81}N_4B_2Sn_2$: $[M+H]^+$, 1023.46858. Found: m/z 1023.46893

Cu-catalyzed borylstannylation of allenes.

A THF solution (1 mL) of an allene (0.30 mmol), a masked diboron (0.36 mmol), tributyltin methoxide (0.36 mmol) and (IMes)CuCl (6.0 μmol) was stirred at room temperature for 1 h. Then the mixture was diluted with diethyl ether and filtered through a Celite plug. The organic solution was washed with brine, dried over $MgSO_4$, and evaporated. The residual tin alkoxide was removed by passing through column chromatography (10% w/w anhydrous K_2CO_3–silica gel; diethyl ether as an eluent), and evaporation of the solvent followed by gel permeation chromatography (toluene as an eluent) gave the corresponding product. Stereochemistry of the product was determined by NOE experiment.

(*Z*)-2-(1-(tributylstannyl)undec-2-en-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (4a)



Isolated in 72% as a colorless liquid

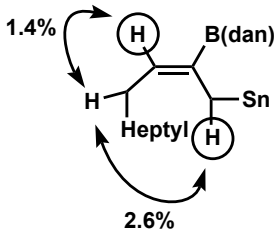
^{1}H NMR (C_6D_6) δ 0.84-0.97 (m, 18H), 1.24-1.48 (m, 16H), 1.47-1.63 (m, 8H), 1.90 (s, $J_{H\text{-}Sn}$ = 60.4 Hz, 2H), 2.22 (q, J = 7.2 Hz, 2H), 5.52 (s, 2H), 5.66 (t, J = 6.6 Hz, 1H), 6.06-6.11 (m, 2H), 7.02-7.10 (m, 4H)

^{13}C NMR (C_6D_6) δ 10.1 ($J_{C\text{-}Sn}$ = 302.8 Hz), 12.3, 13.9, 14.4, 23.1, 27.9 ($J_{C\text{-}Sn}$ = 54.7 Hz), 29.4, 29.7 ($J_{C\text{-}Sn}$ = 19.7 Hz), 29.8, 29.9, 30.1, 30.2, 32.3, 106.1, 118.1, 120.4, 133.5 ($J_{C\text{-}Sn}$ = 42.9 Hz), 137.0, 141.5

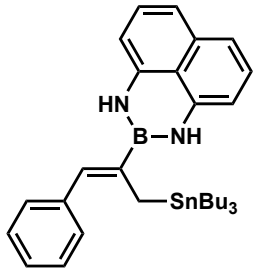
^{119}Sn NMR (C_6D_6) δ -14.2

HRMS Calcd for $C_{33}H_{56}N_2BSn$: $[M+H]^+$, 611.35530. Found: m/z 611.35645

The stereochemistry of **4a** was determined by NOE experiment as shown below.



(*Z*)-2-(1-phenyl-3-(tributylstannyl)prop-1-en-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (4b)



Isolated in 65% as a colorless liquid

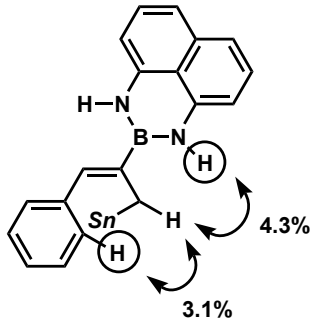
^{1}H NMR (C_6D_6) δ 0.79-1.02 (m, 15H), 1.25 (tq, J = 7.3 Hz, 7.3 Hz, 6H), 1.37-1.57 (m, 6H), 2.25 (s, $J_{H\text{-}Sn}$ = 62.1 Hz, 2H), 5.55 (s, 2H), 6.04-6.19 (m, 2H), 6.57 (s, $J_{H\text{-}Sn}$ = 21.3 Hz, 1H), 7.04-7.13 (m, 5H), 7.29 (dd, *J* = 7.7 Hz, 7.7 Hz, 2H), 7.43 (d, *J* = 7.7 Hz, 2H)

^{13}C NMR (C_6D_6) δ 10.33 ($J_{C\text{-}Sn}$ = 305.4 Hz), 13.9, 14.3, 27.8 $J_{C\text{-}Sn}$ = 56.3 Hz), 29.5 ($J_{C\text{-}Sn}$ = 20.2 Hz), 106.3, 118.3, 120.5, 126.7, 127.9, 128.6, 129.3, 130.5, 137.1, 139.3, 141.4

^{119}Sn NMR (C_6D_6) δ -14.9

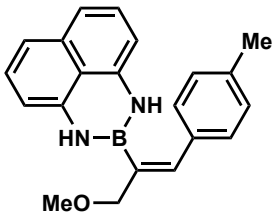
HRMS Calcd for $C_{31}H_{44}N_2BSn$: $[M+H]^+$, 575.26140. Found: m/z 575.26251

The stereochemistry of **4b** was determined by NOE experiment as shown below.



Synthesis of (*E*)-2-(3-methoxy-1-(*p*-tolyl)prop-1-en-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (5)

A DMF solution (1 mL) of **2i** (0.10 mmol), 4-iodotoluene (0.12 mmol), LiCl (0.10 mmol), $Pd_2(dba)_3$ (1.0 μmol) and dicyclohexyl(2',4',6'-triisopropyl-[1,1'-biphenyl]-2-yl)phosphine (Xphos, 3.0 μmol) was stirred at 100 ºC for 1 h. After the mixture was diluted with diethyl ether and filtered through a Celite plug, the organic solution was washed with brine, dried over $MgSO_4$, and evaporated. The residual tin halide was removed by passing through column chromatography (10% w/w anhydrous K_2CO_3–silica gel; diethyl ether as an eluent). Evaporation of the solvent followed by gel permeation chromatography (toluene as an eluent) gave **5**.



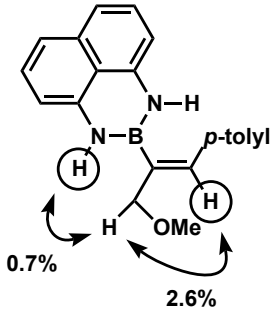
Isolated in 82% as a colorless solid: mp 103-105 ºC

^{1}H NMR (C_6D_6) δ 2.02 (s, 3H), 3.14 (s, 3H), 3.93 (d, *J* = 1.3 Hz, 2H), 5.62 (s, 2H), 5.85 (dd, *J* = 7.1 Hz, 1.2 Hz, 2H), 6.80 (d, *J* = 7.9 Hz, 2H), 6.96 (s, 2H), 6.97 (dd, *J* = 8.2 Hz, 7.1 Hz, 2H), 7.02 (dd, *J* = 8.1 Hz, 1.2 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H)

^{13}C NMR (C_6D_6) δ 21.1, 57.6, 78.9, 106.3, 118.1, 120.5, 127.8, 128.8, 129.4, 135.3, 137.0, 137.6, 140.8, 141.3

HRMS Calcd for $C_{21}H_{22}ON_2B$: $[M+H]^+$, 329.18197. Found: m/z 329.18195

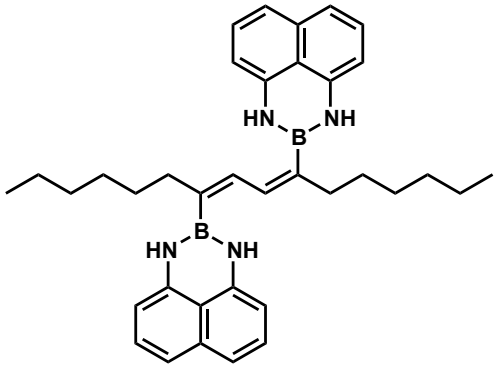
The stereochemistry of **5** was determined by NOE experiment as shown below.



Copper-mediated oxidative homocoupling of 2

A DMF solution (2 mL) of **2** (0.10 mmol) and CuCl (0.25 mmol) was stirred at room temperature for 3 h. After the mixture was diluted with CH_2Cl_2 and filtered through a Celite plug, the organic solution was washed with brine, dried over $MgSO_4$, and evaporated. The residual tin halide was removed by passing through column chromatography (10% w/w anhydrous K_2CO_3–silica gel; CH_2Cl_2 as an eluent). Evaporation of the solvent followed by gel permeation chromatography (toluene as an eluent) gave the corresponding product. Stereochemistry of the product was determined by NOE experiment.

2,2'-((7*E*,9*E*)-hexadeca-7,9-diene-7,10-diyl)bis(2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine) (6)



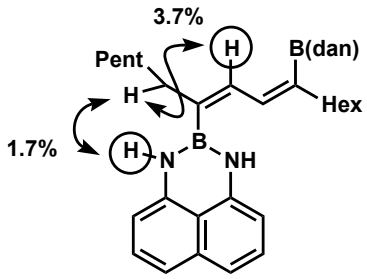
Isolated in 97% as a colorless liquid

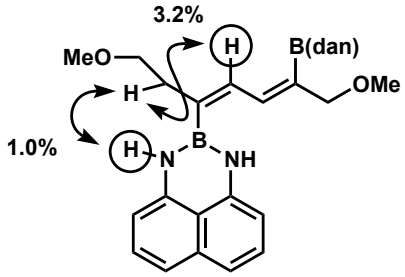
^{1}H NMR (C_6D_6) δ 0.84 (t, *J* = 7.1 Hz, 6H), 1.11-1.31 (m, 12H), 1.35-1.49 (m, 4H), 2.14 (t, *J* = 7.6 Hz, 4H), 5.43 (s, 4H), 5.99 (dd, *J* = 6.8 Hz, 1.5 Hz, 4H), 6.93 (s, 2H), 7.00-7.10 (m, 8H)

^{13}C NMR (C_6D_6) δ 14.3, 23.0, 29.7, 30.4, 32.0, 38.3, 106.3, 118.4, 120.4, 127.9, 137.0, 137.2, 141.2

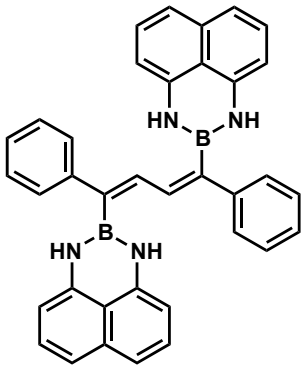
HRMS Calcd for $C_{36}H_{45}N_4B_2$: $[M+H]^+$, 555.38248. Found: m/z 555.38239

The stereochemistry of **6** was determined by NOE experiment as shown below.





(1*E*,3*E*)-1,4-bis(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)-1,4-diphenylbuta-1,3-diene (7)



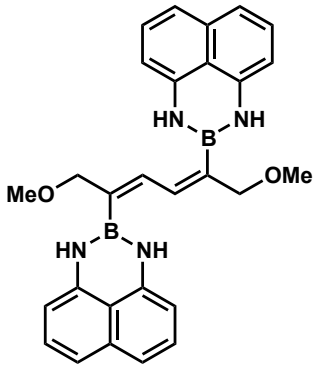
Isolated in 90% as a colorless solid

^{1}H NMR ($CDCl_3$) δ 5.86 (s, 4H), 6.35 (dd, *J* = 7.2 Hz, 0.9 Hz, 4H), 7.09 (dd, *J* = 8.2 Hz, 0.9 Hz, 2H), 7.15 (dd, *J* = 8.2 Hz, 7.2 Hz, 4H), 7.24 (t, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 4H), 7.34 (s, 2H), 7.46 (d, *J* = 8.2 Hz, 4H)

^{13}C NMR ($CDCl_3$) δ 106.1, 118.0, 119.9, 127.2, 127.5, 127.6, 128.8, 136.3, 136.6, 140.8, 141.6

HRMS Calcd for $C_{36}H_{28}N_4B_2$: $[M]^+$, 538.24946. Found: m/z 538.24957

2,2'-((2*E*,4*E*)-1,6-dimethoxyhexa-2,4-diene-2,5-diyl)bis(2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine) (8)



Isolated in 90% as a colorless solid

^{1}H NMR ($CDCl_3$) δ 3.37 (s, 6H), 4.09 (s, 4H), 5.98 (s, 4H), 6.34 (d, *J* = 7.0 Hz, 4H), 6.94 (s, 2H), 7.04 (d, *J* = 8.4 Hz, 4H), 7.12 (dd, *J* = 8.4 Hz, 7.3 Hz, 4H)

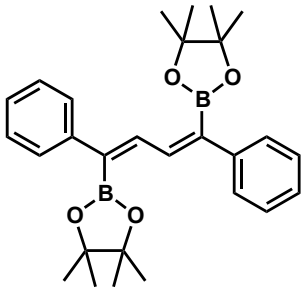
^{13}C NMR ($CDCl_3$) δ 58.2, 78.3, 106.0, 117.8, 118.0, 127.6, 136.3, 139.2, 140.8

HRMS Calcd for $C_{28}H_{28}O_2N_4B_2$: $[M]^+$, 474.23929. Found: m/z 474.23889

The stereochemistry of **8** was determined by NOE experiment as shown below.

Synthesis of (1*E*,3*E*)-1,4-diphenyl-1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,3-diene

A THF solution (2 mL) of **7** (0.20 mmol), 6M H_2SO_4aq (1.60 mmol) and pinacol (1.2 mmol) was stirred at 50 °C for 48 h. Then the mixture was diluted with ethyl acetate and filtered through a Celite plug. The organic solution was washed with brine and dried over $MgSO_4$. Evaporation of the solvent followed by gel permeation chromatography (toluene as an eluent) gave the corresponding product. Stereochemistry of the product was determined by NOE experiment.



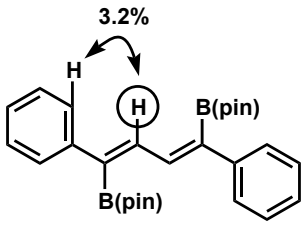
Isolated in 52% as a colorless solid: 215-216 °C

^{1}H NMR (C_6D_6) δ 1.04 (s, 24H), 7.10 (t, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 4H), 7.83 (d, *J* = 7.9 Hz, 4H), 8.41(s, 2H)

^{13}C NMR (C_6D_6) δ 24.8, 83.6, 127.1, 128.5, 144.2, 144.9

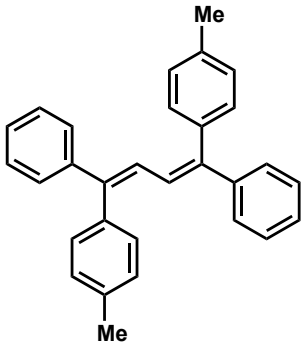
HRMS Calcd for $C_{28}H_{37}O_4B_2$: $[M]^+$, 459.28769. Found: m/z 459.28769

The stereochemistry of the product was determined by NOE experiment as shown below.



Synthesis of (1*Z*,3*Z*)-1,4-diphenyl-1,4-di-*p*-tolylbuta-1,3-diene (9)

A DMSO Solution (1 mL) of (1*E*,3*E*)-1,4-diphenyl-1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,3-diene (0.0436 mmol), 4-iodotoluene (0.113 mmol), K_3PO_4 (0.523 mmol) and PdCl(dppf)•CH_2Cl_2 (2.2 μmol) was stirred at 45 °C for 24 h. The mixture was diluted with diethyl ether and filtered through a Celite plug. Then the organic solution was washed with brine and dried over $MgSO_4$. Evaporation of the solvent followed by gel permeation chromatography (toluene as an eluent) gave **9**.



Isolated in 65% as a olorless solid

^1H NMR ($CDCl_3$) δ 2.42 (s, 6H), 6.78 (s, 2H), 7.14-7.25 (m, 18H)

^{13}C NMR ($CDCl_3$) δ 21.3, 126.1, 127.2, 127.8, 128.0, 128.9, 130.6, 136.9, 137.1, 142.8, 143.8

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(2) H. Yoshida, Y. Takemoto and K. Takaki, *Asian J. Org. Chem*., 2014, **3**, 1204.

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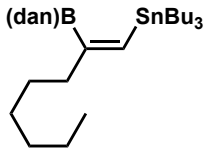
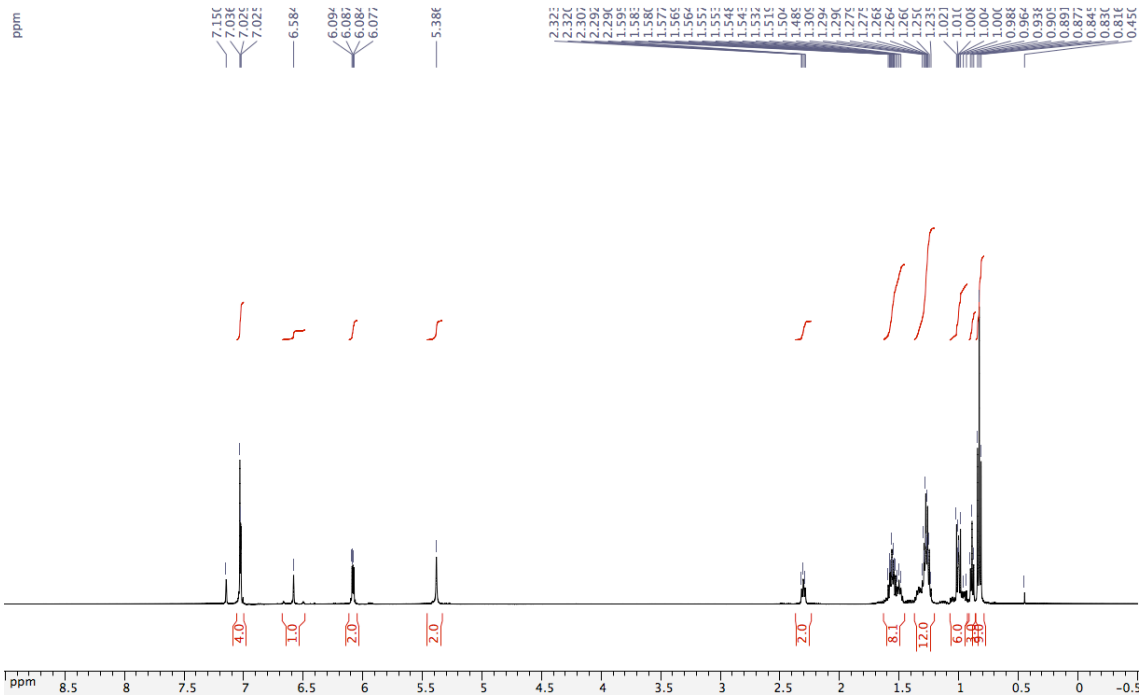
(5) H. Yoshida, Y. Takemoto and K. Takaki, *Chem.–Eur. J*., 2012, **18**, 14841.

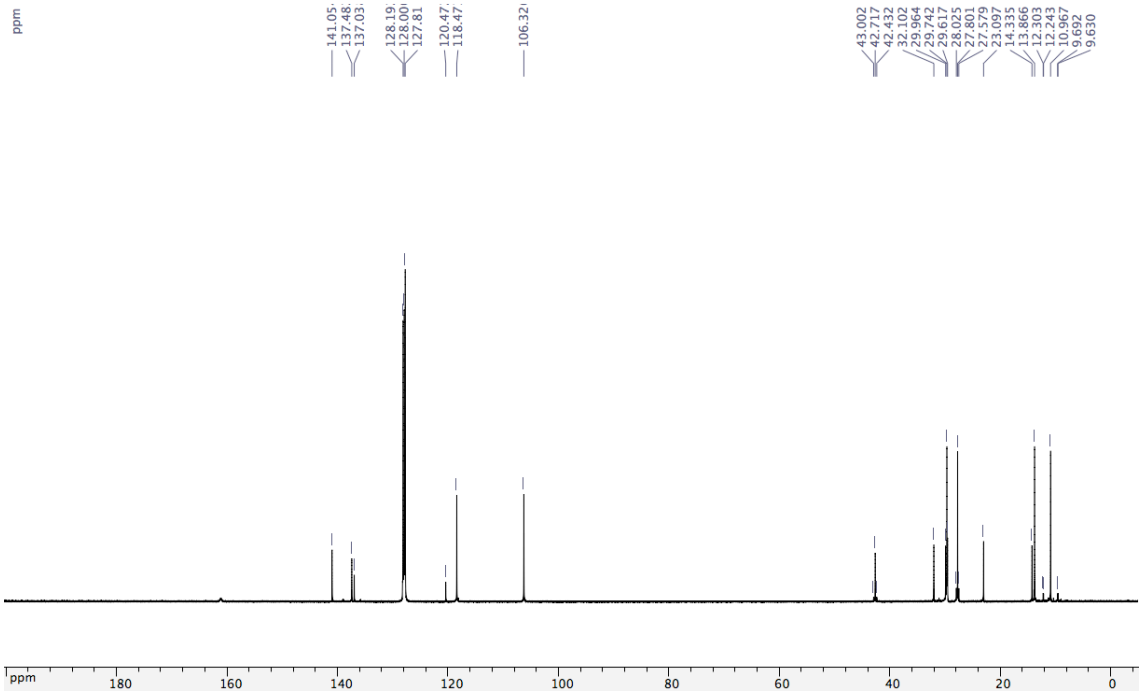


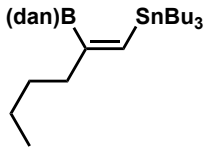
(**2a**)

^{1}H NMR



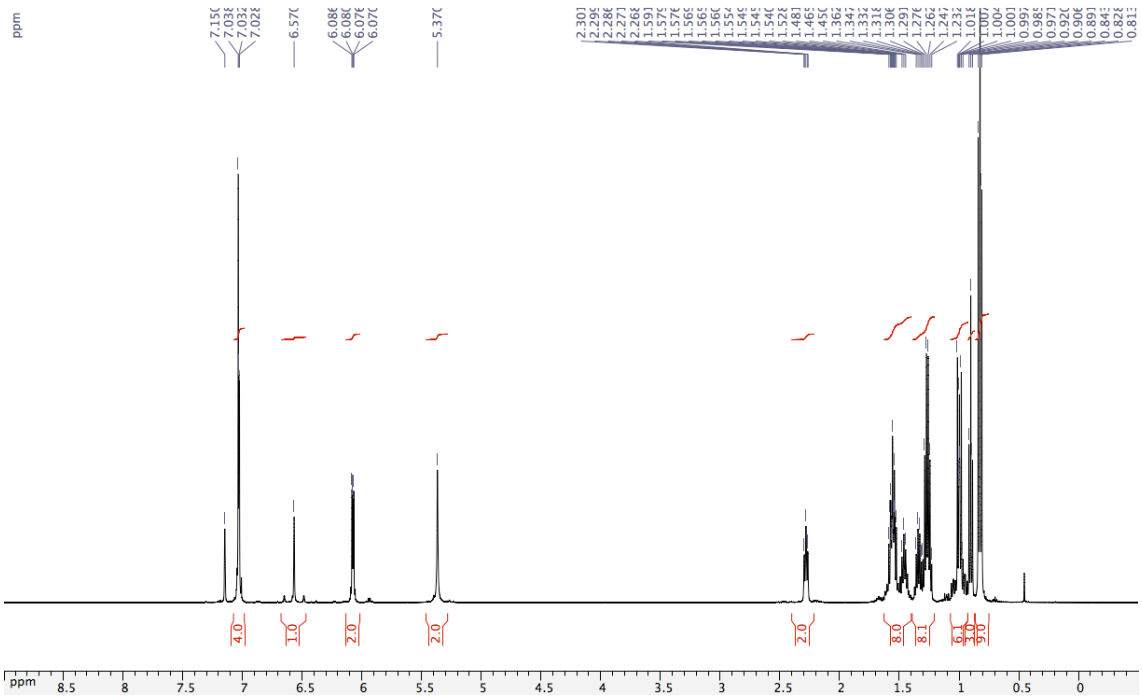
^{13}C NMR



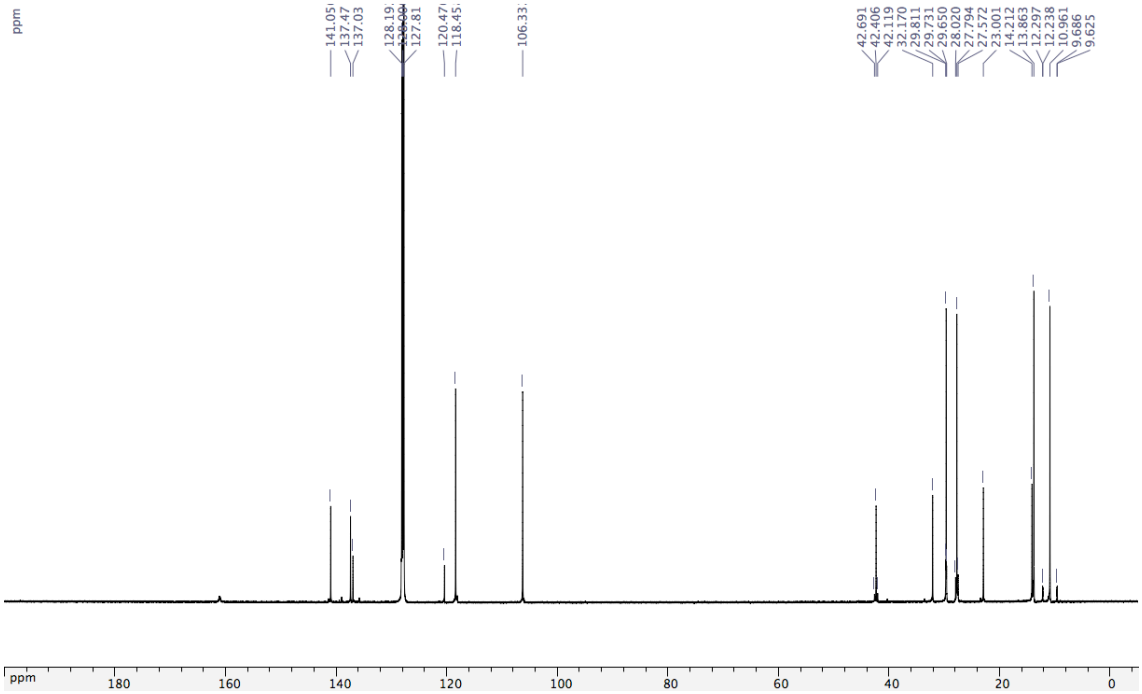


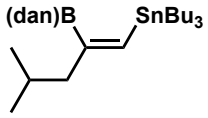
(**2b**)

^{1}H NMR



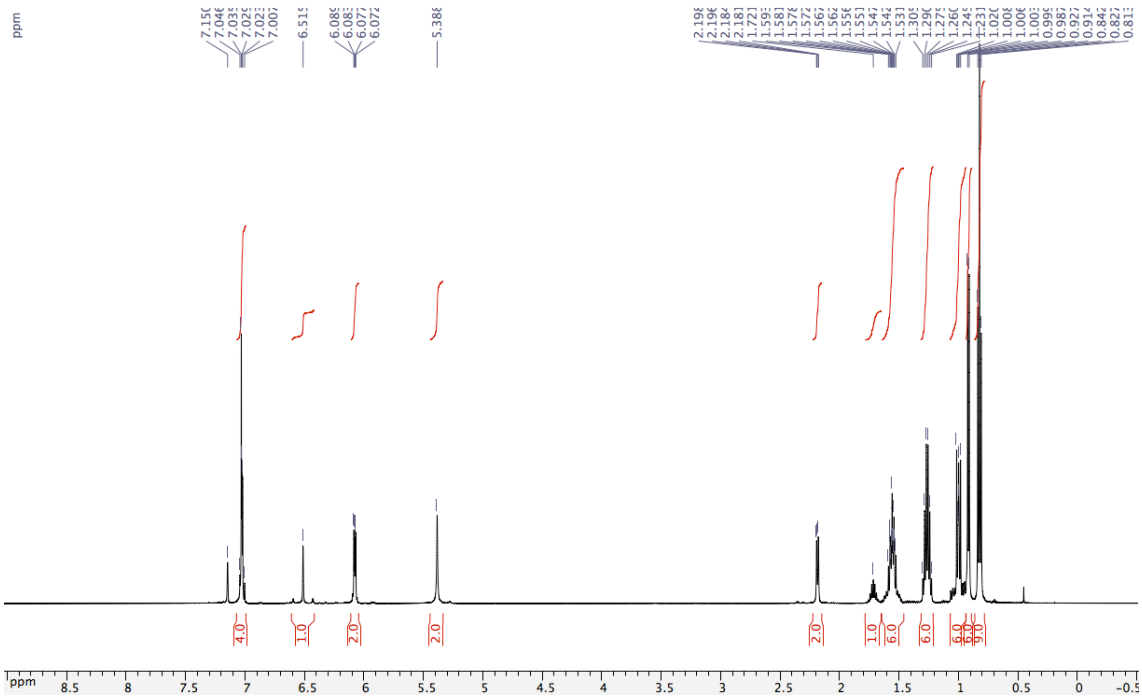
^{13}C NMR



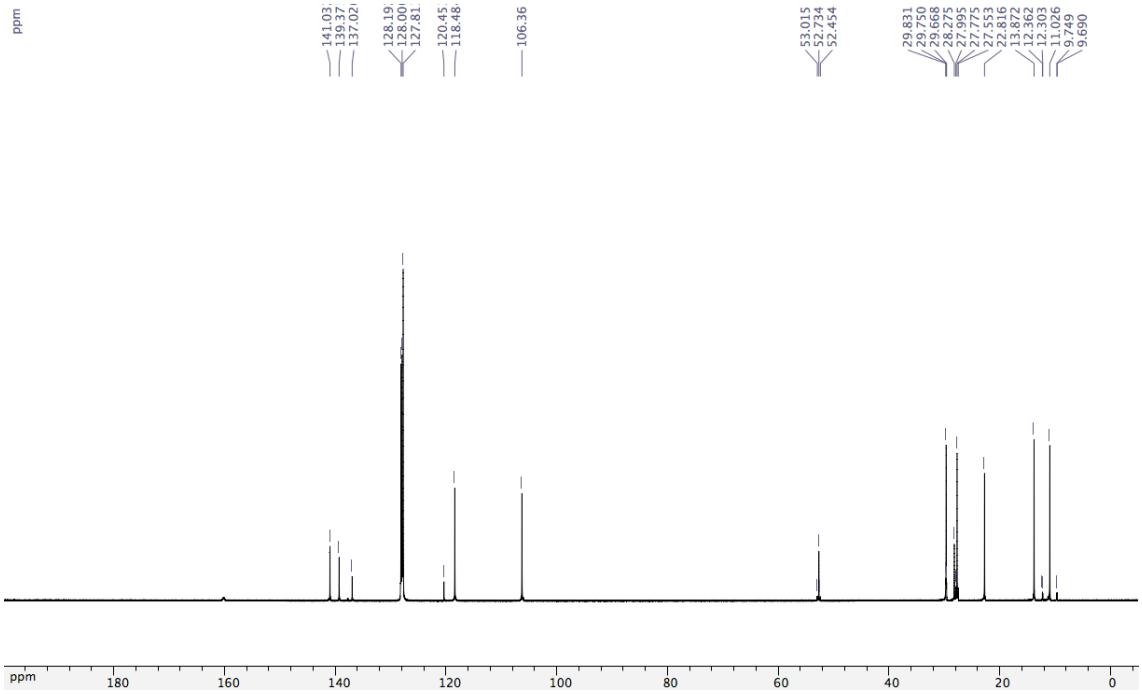


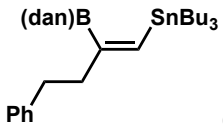
(**2c**)

^{1}H NMR



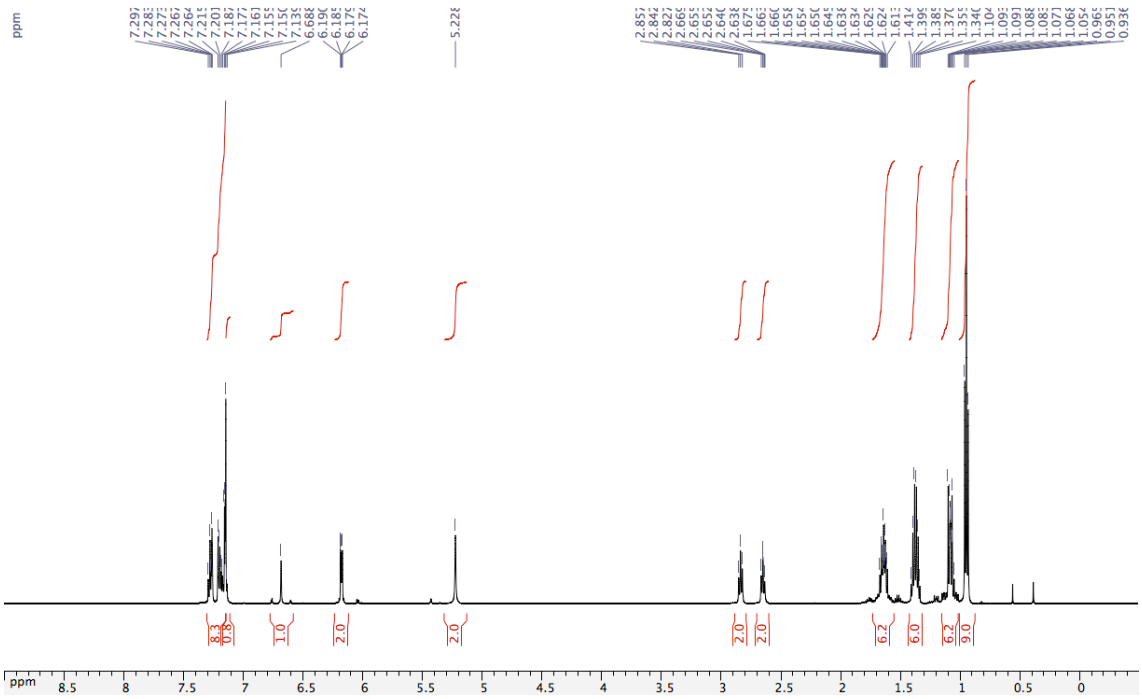
^{13}C NMR



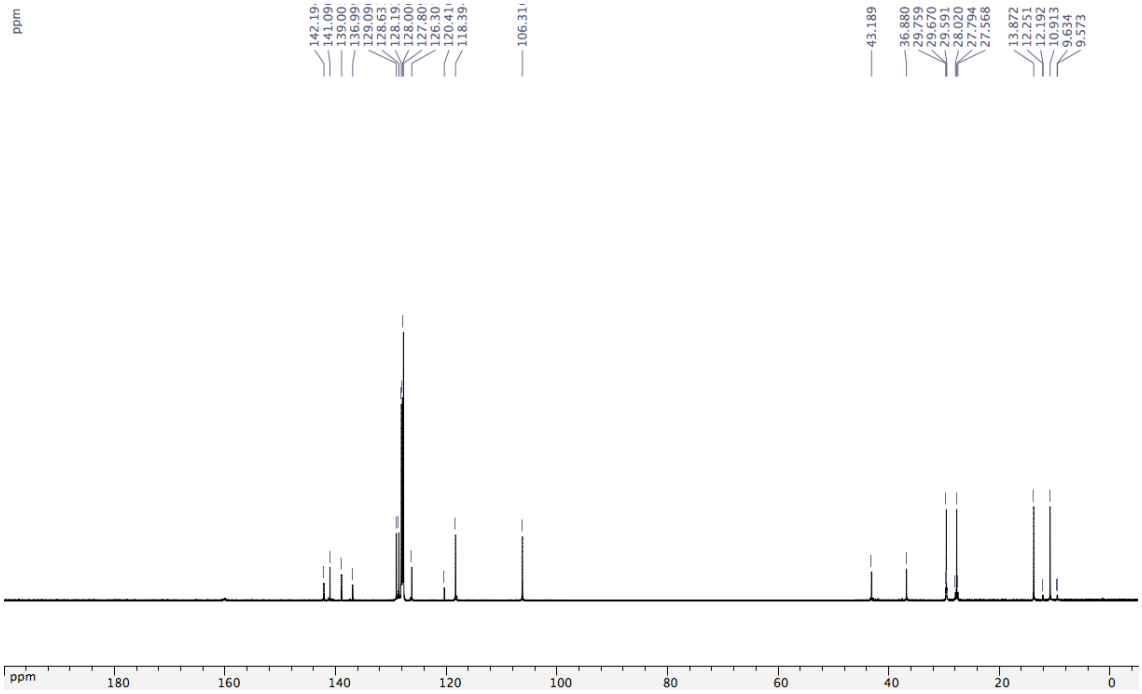


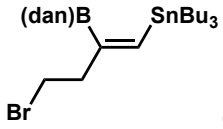
(**2d**)

^{1}H NMR



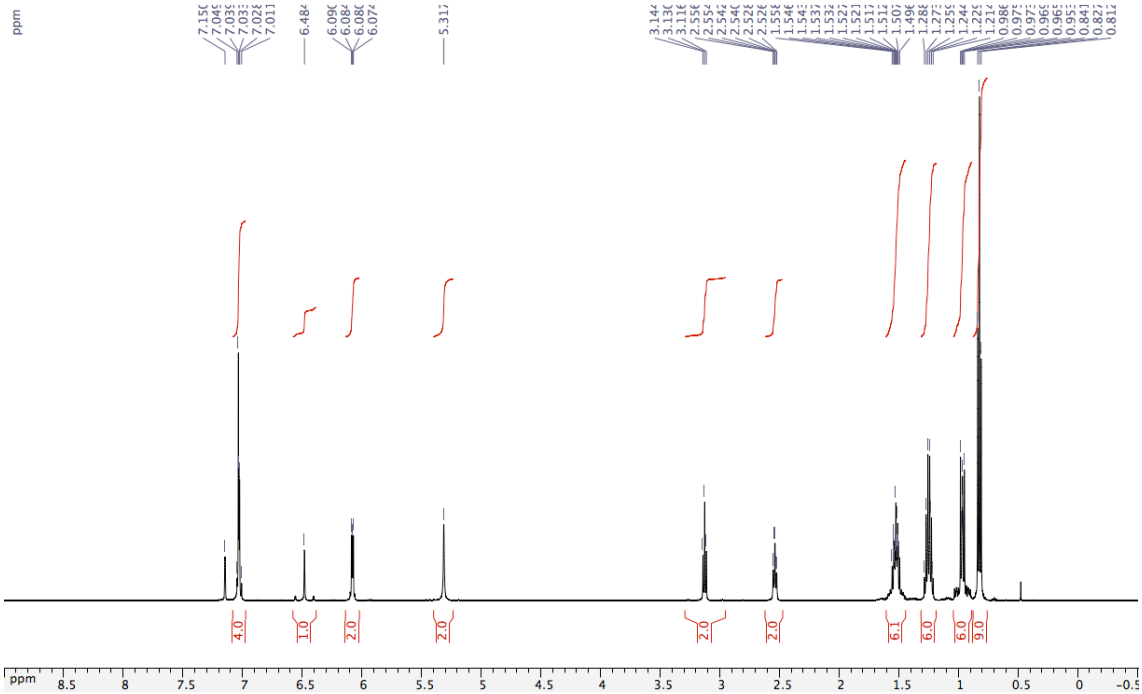
^{13}C NMR



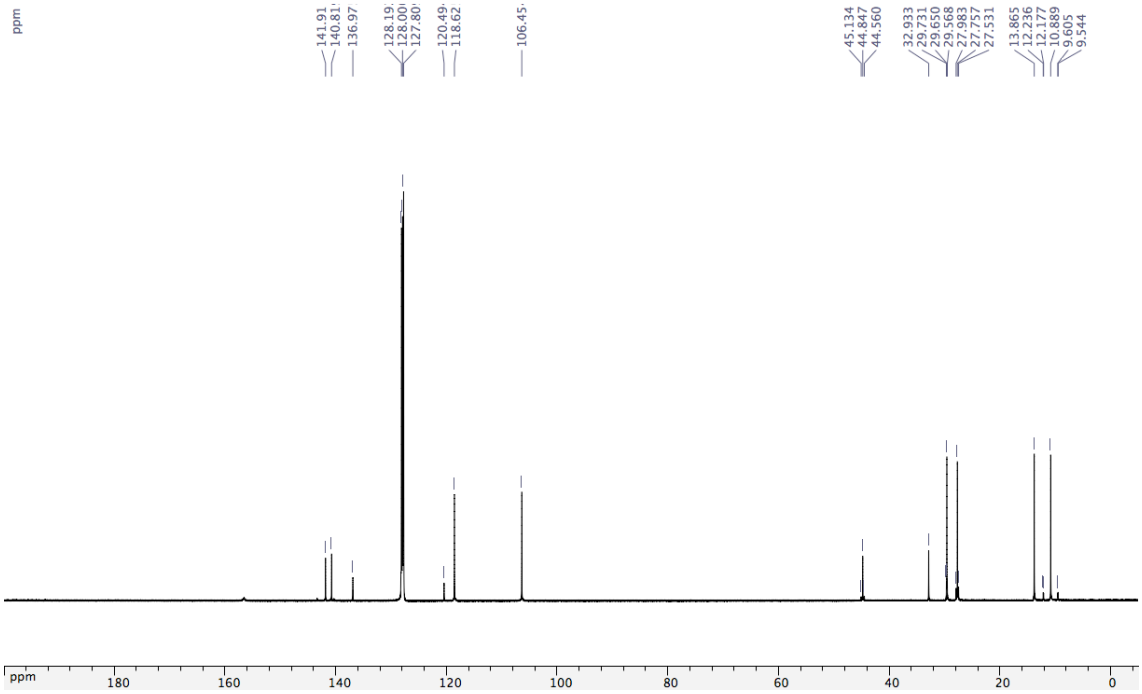


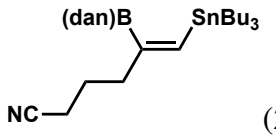
(**2e**)

^{1}H NMR



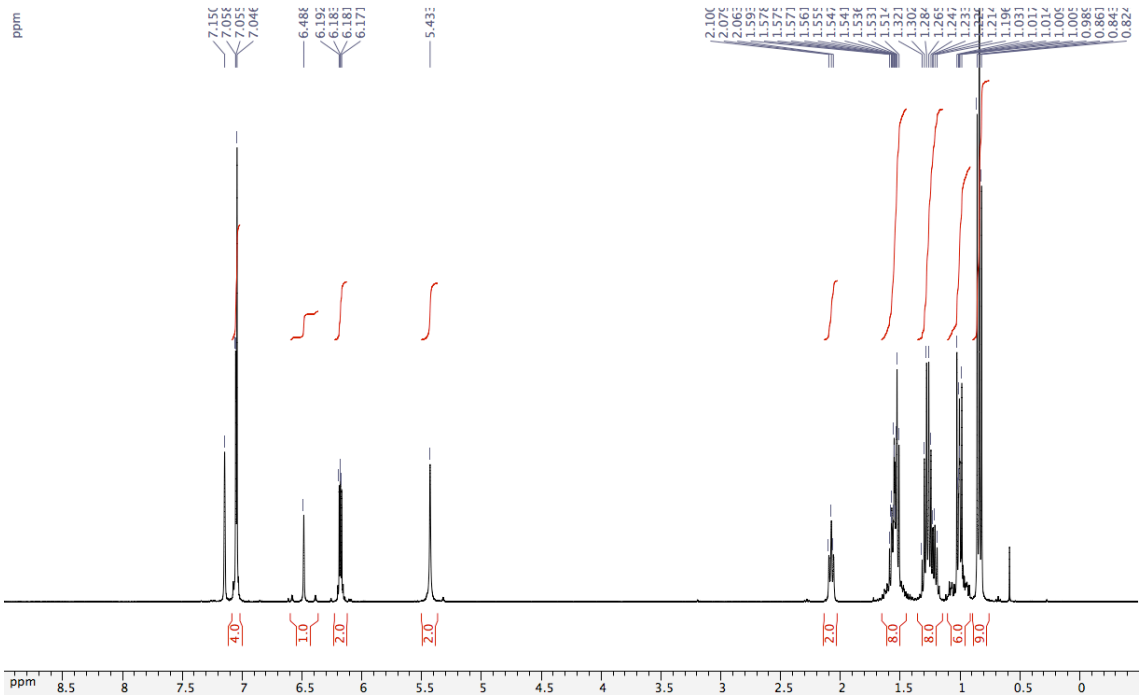
^{13}C NMR





(**2f**)

^{1}H NMR



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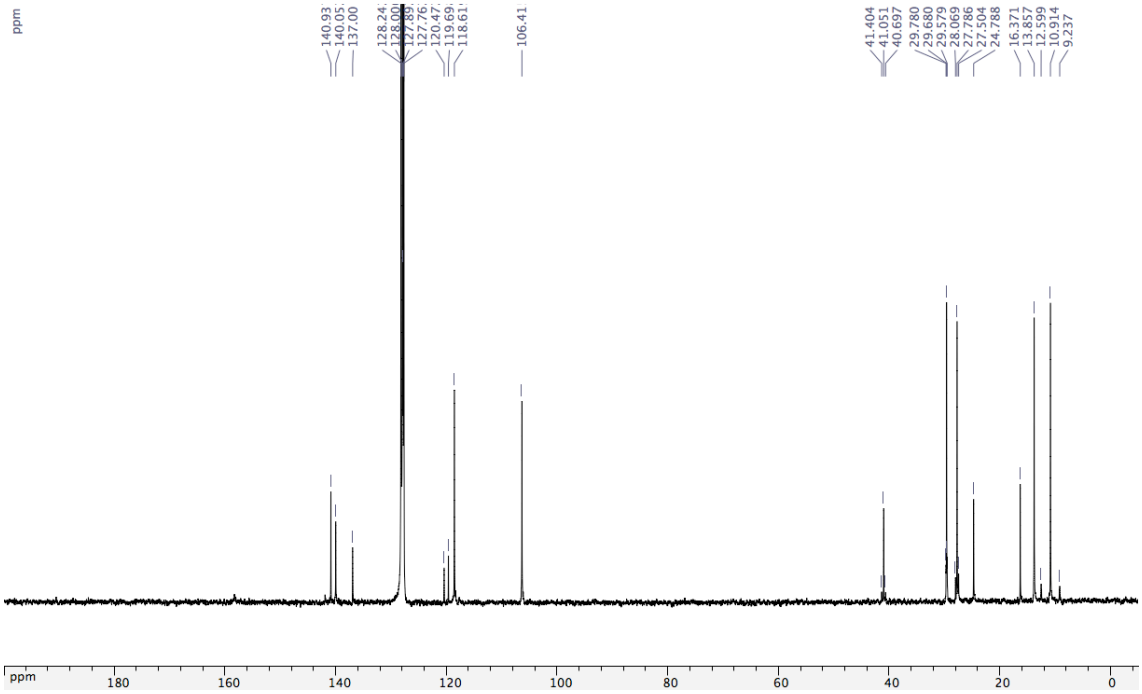
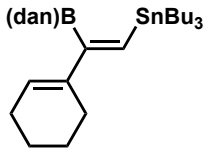
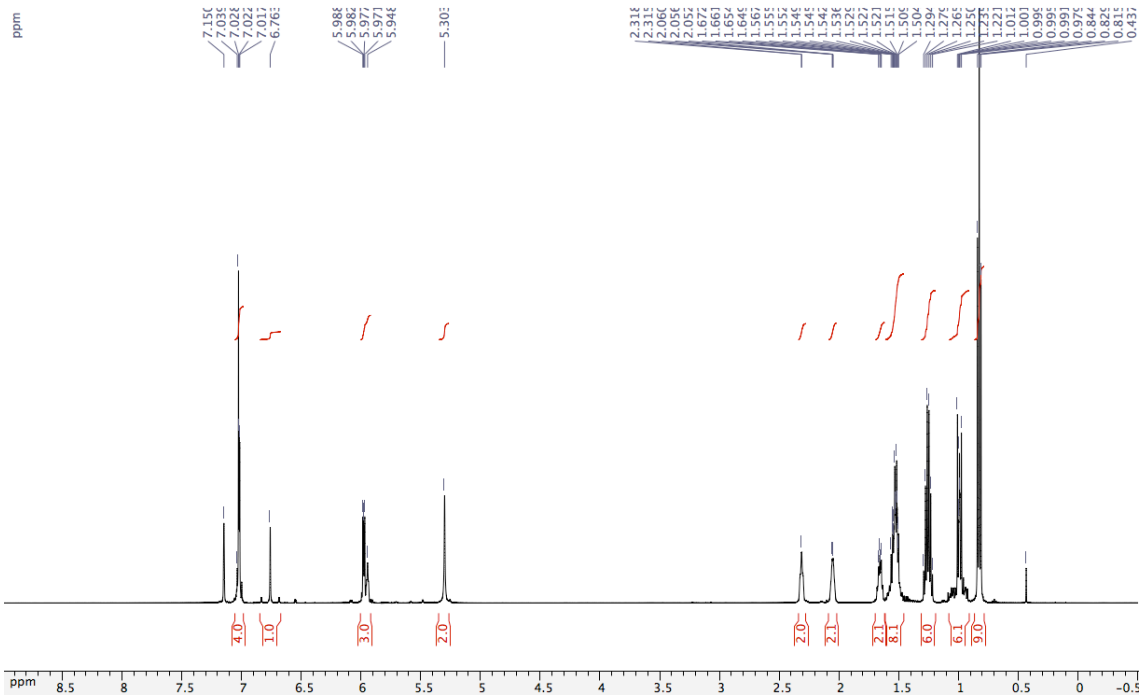


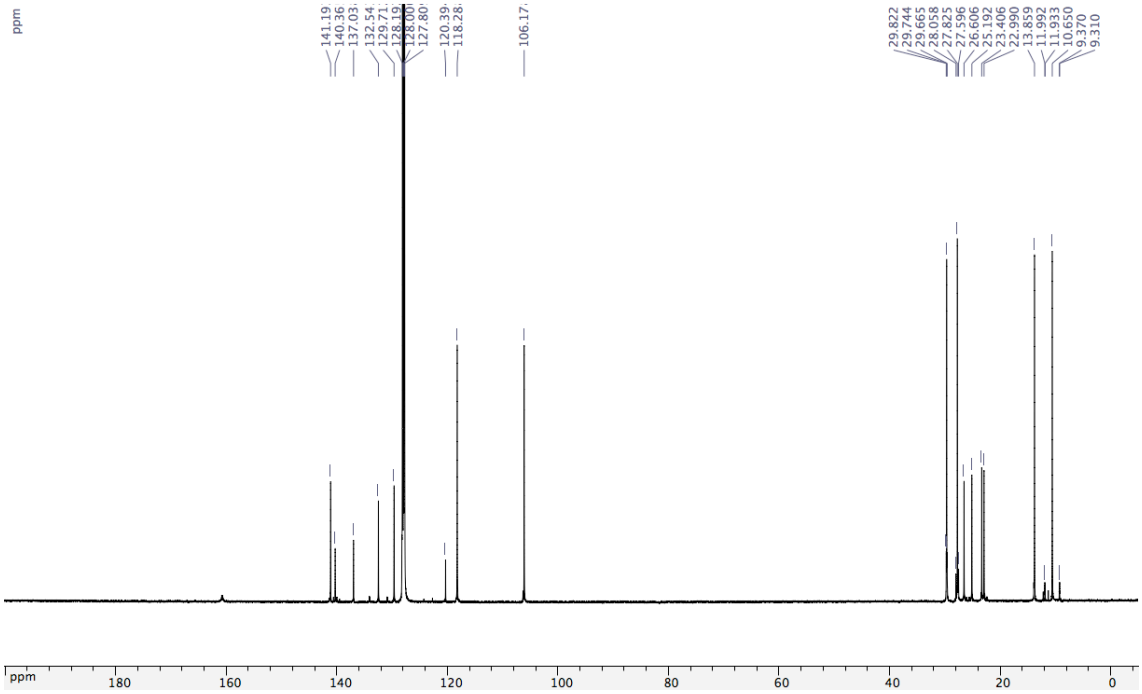


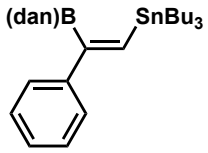
(**2g**)

^{1}H NMR



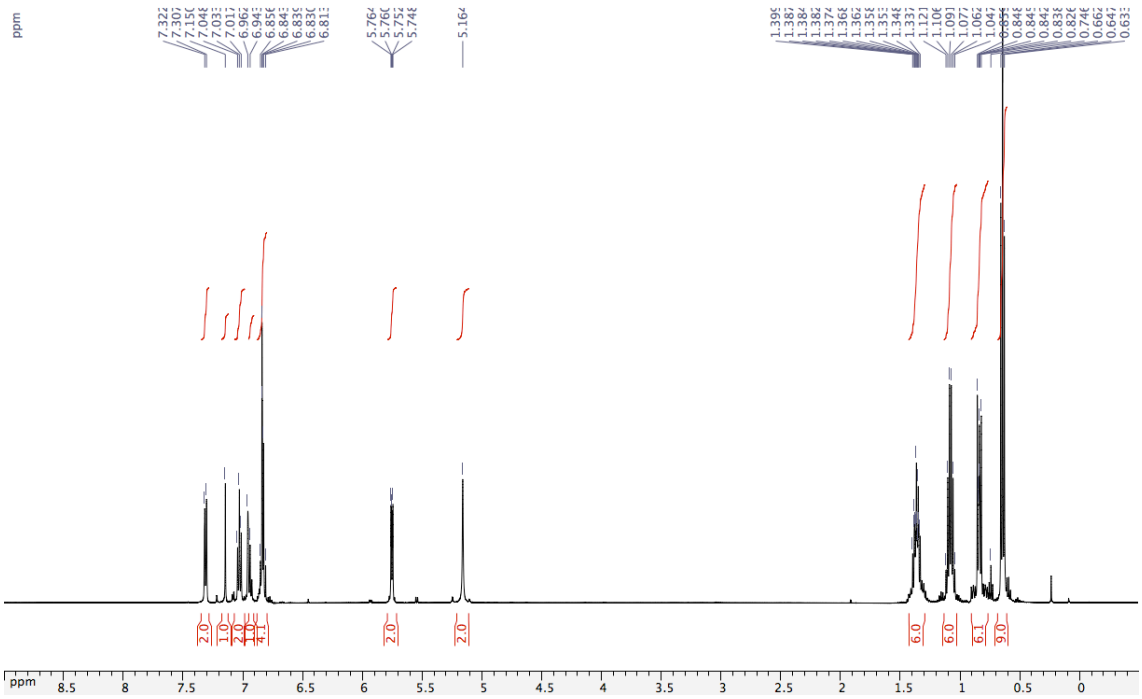
^{13}C NMR





(**2h**)

^{1}H NMR



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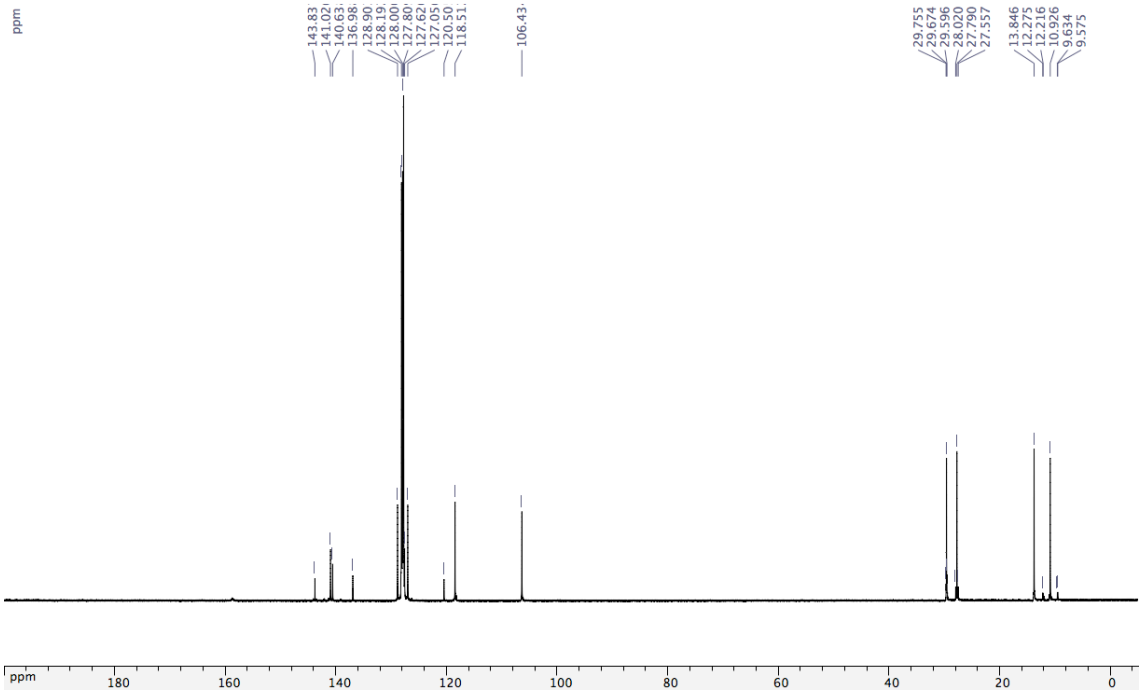
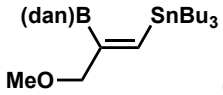
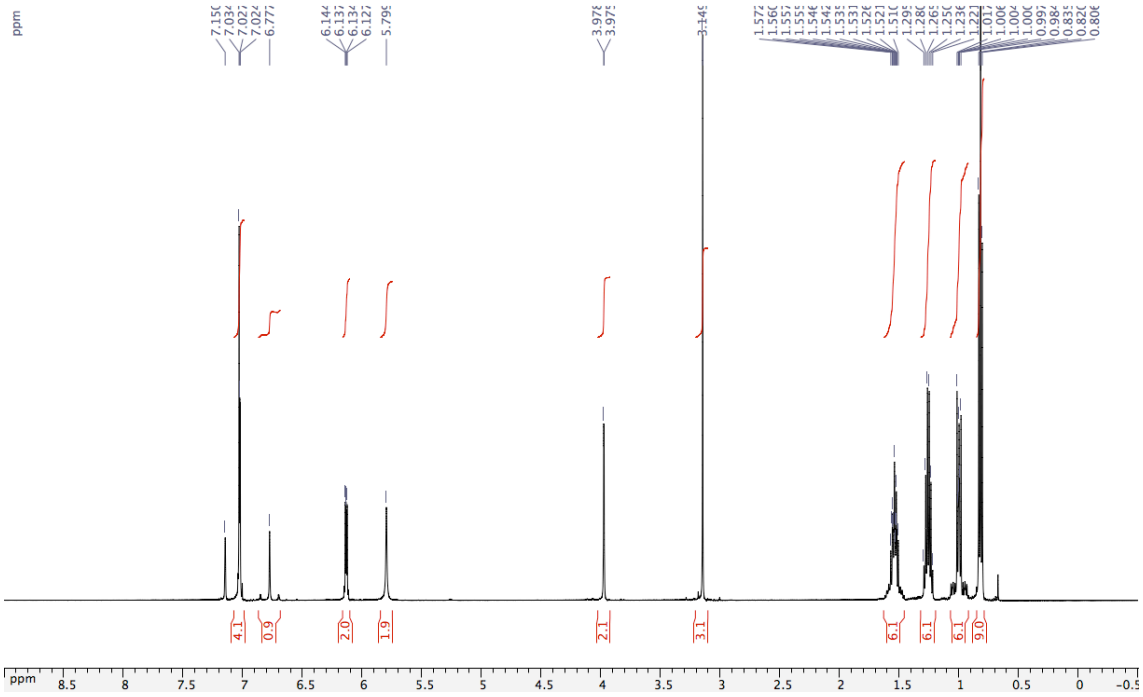


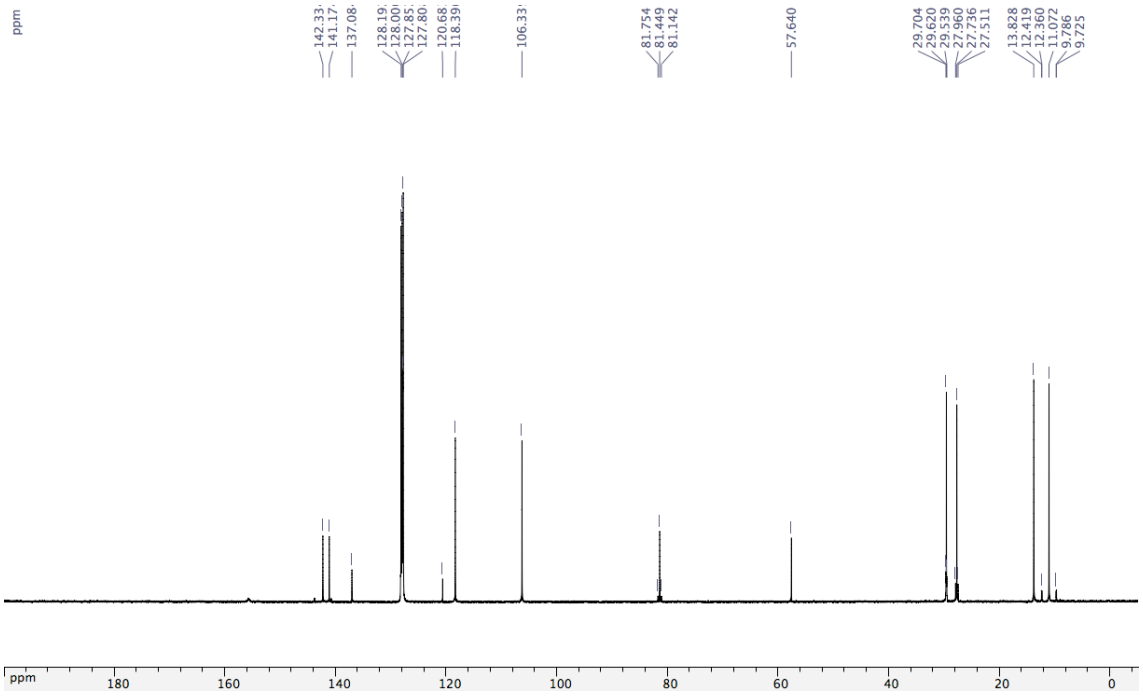


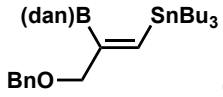
(**2i**)

^{1}H NMR



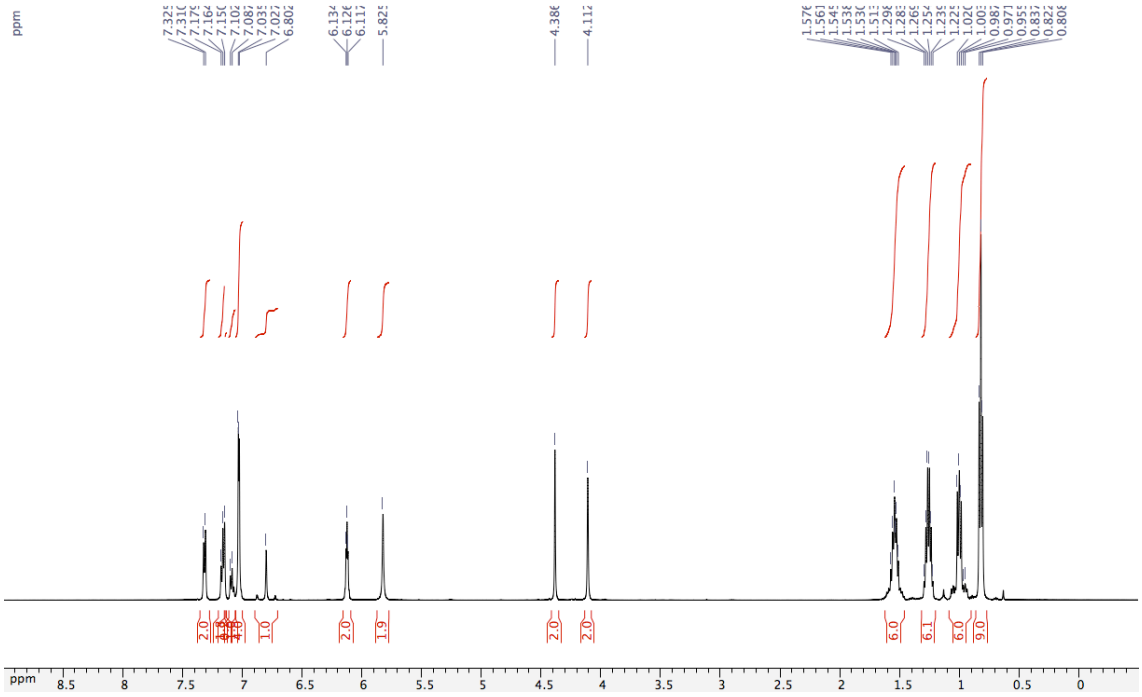
^{13}C NMR



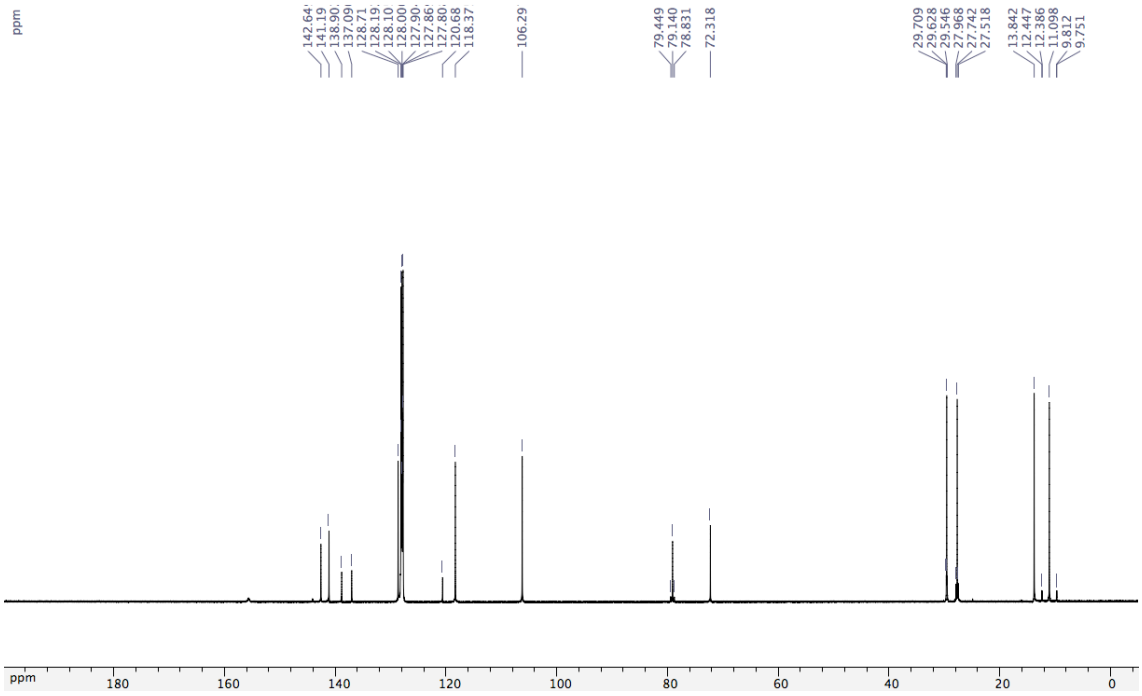


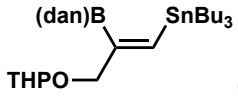
(**2j**)

^{1}H NMR



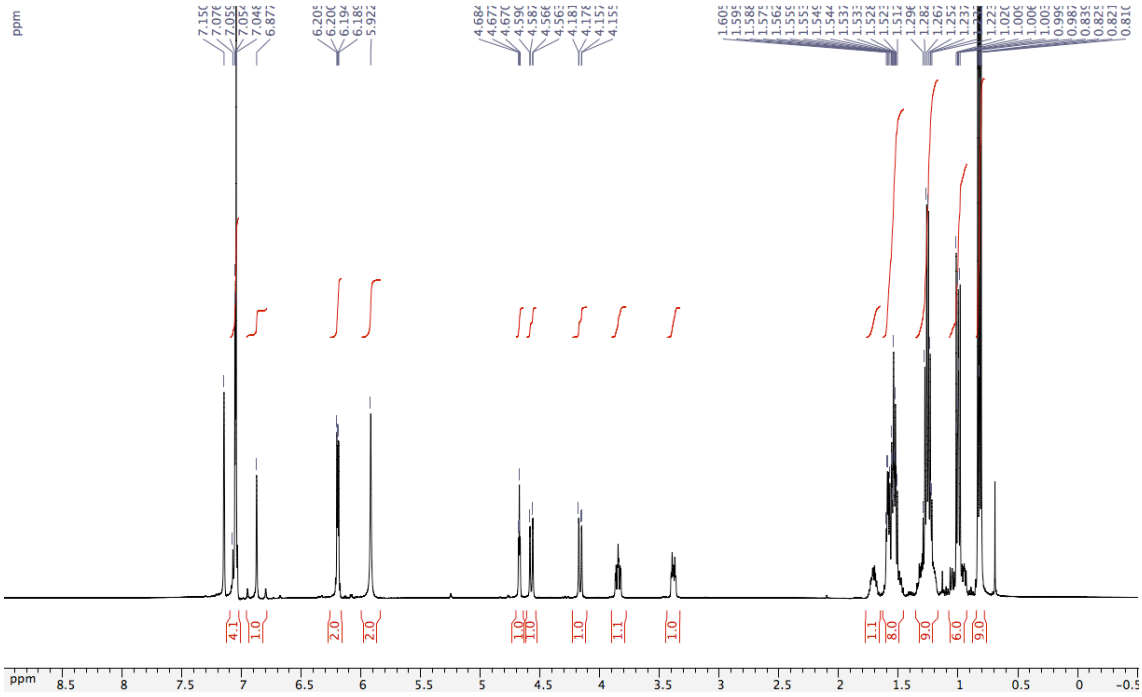
^{13}C NMR



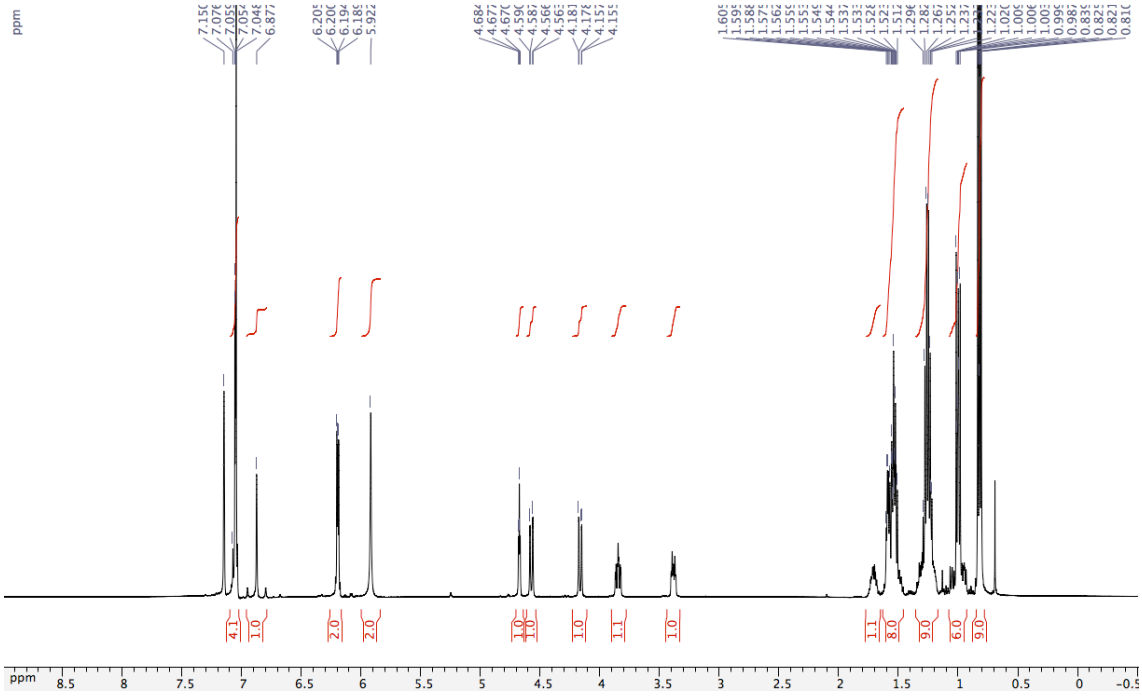


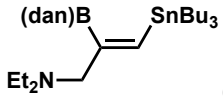
(**2k**)

^{1}H NMR



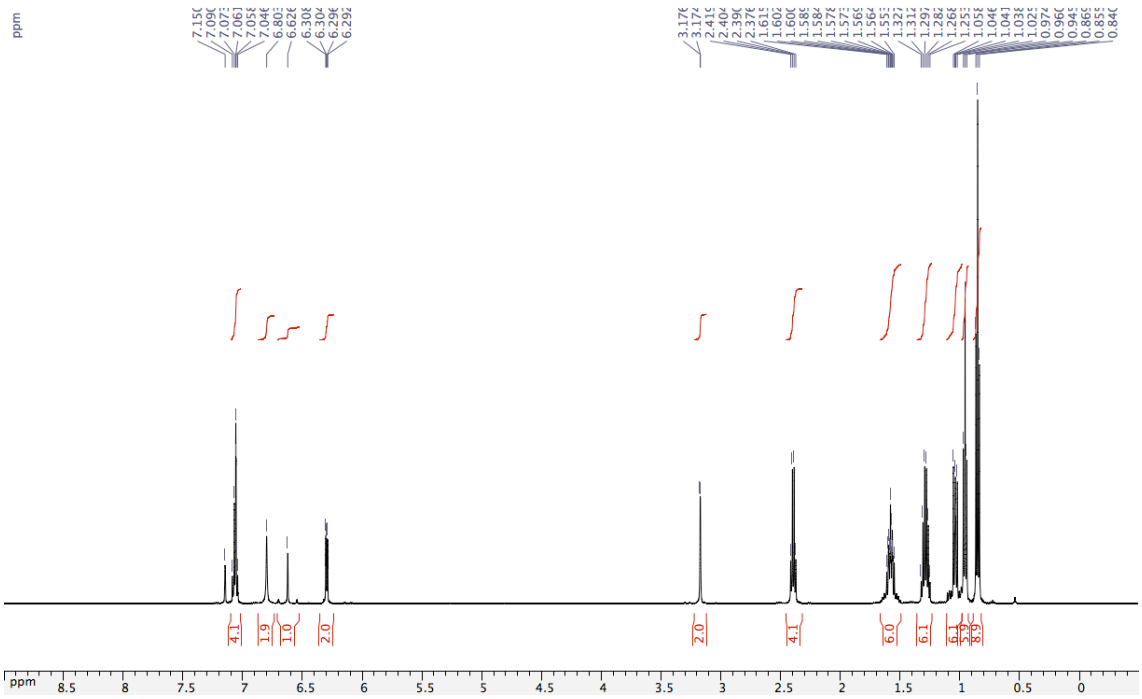
^{13}C NMR



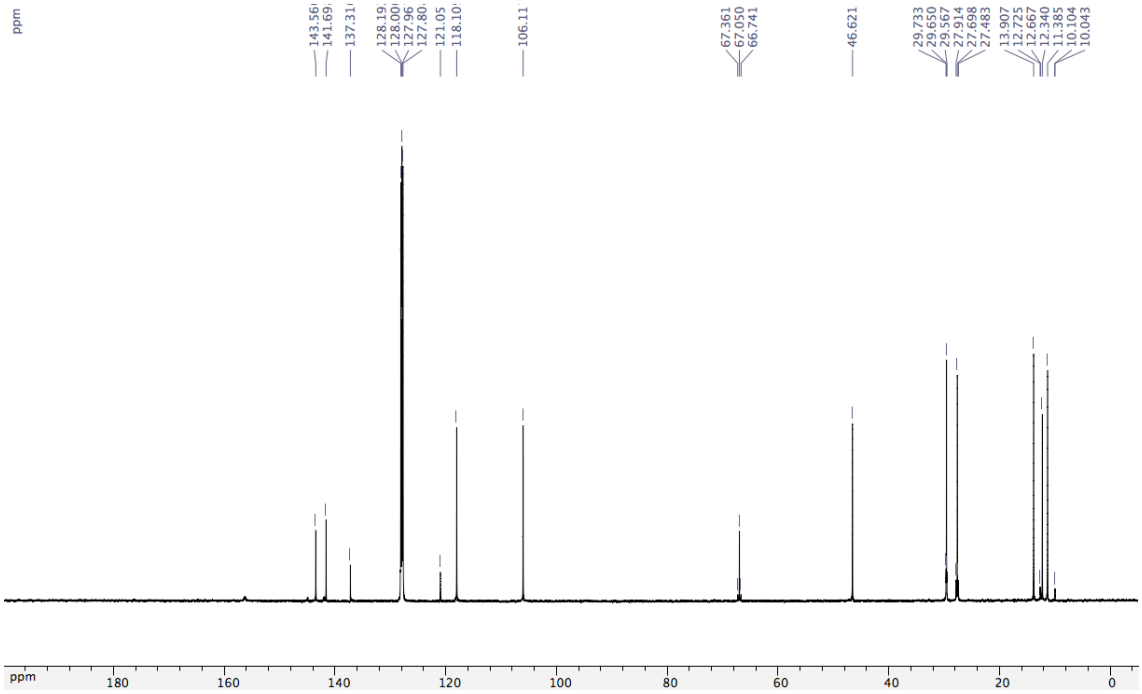


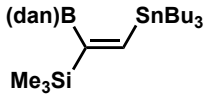
(**2l**)

^{1}H NMR



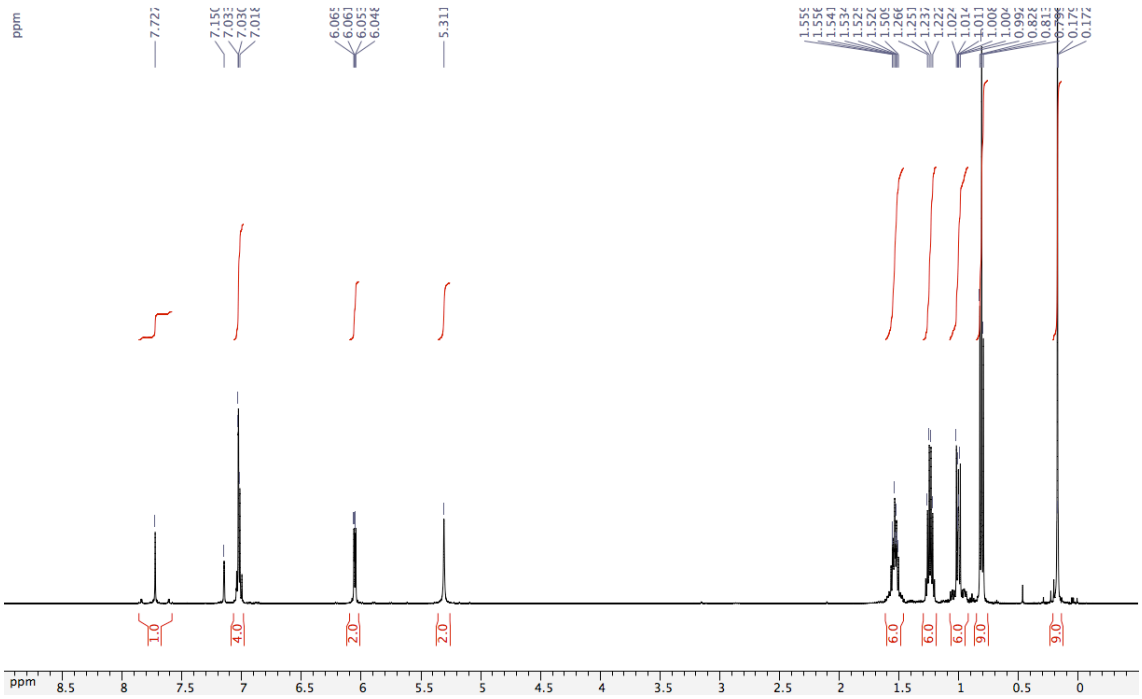
^{13}C NMR



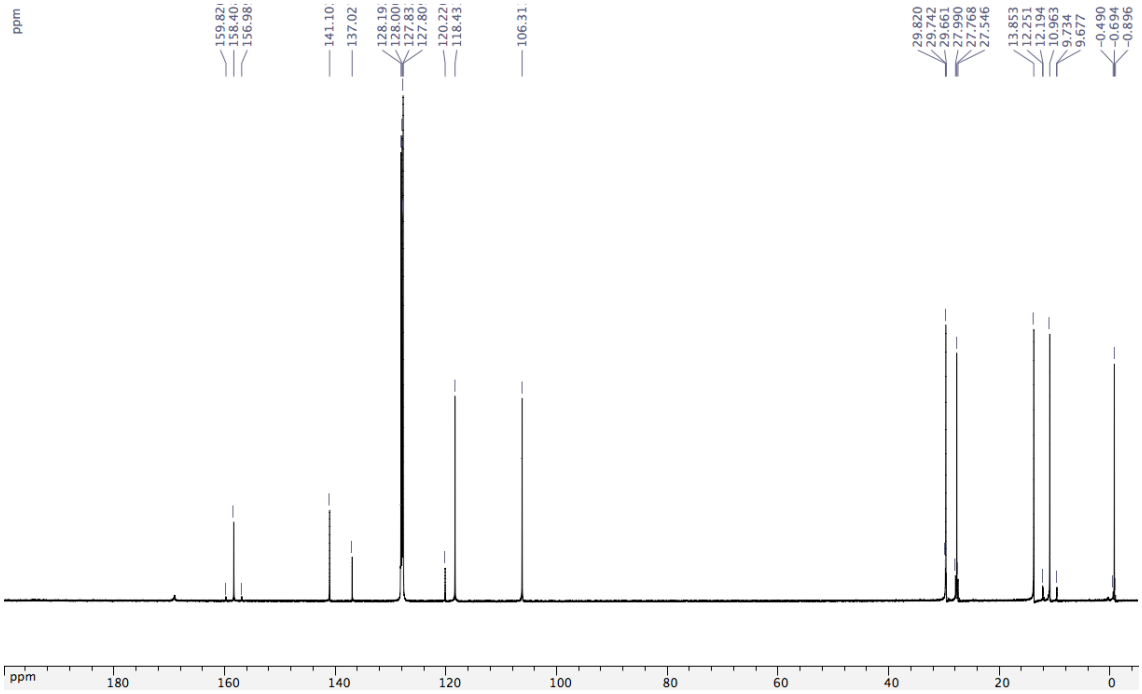


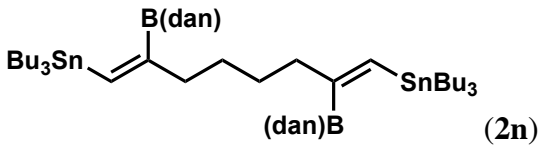
(**2m**)

^{1}H NMR



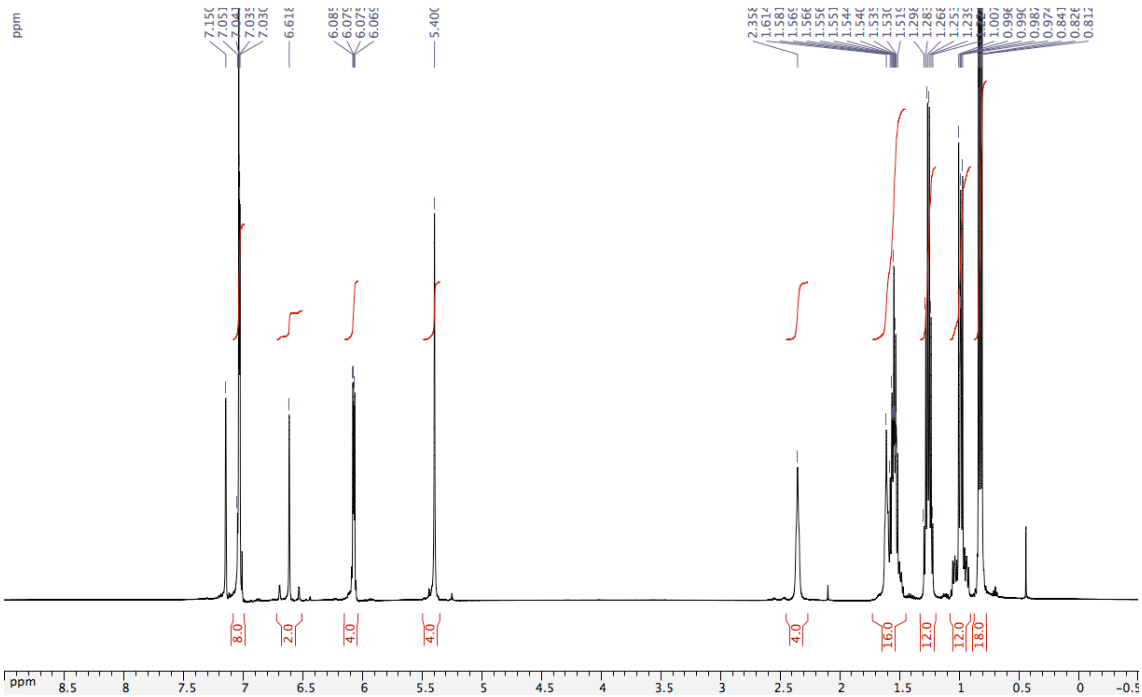
^{13}C NMR



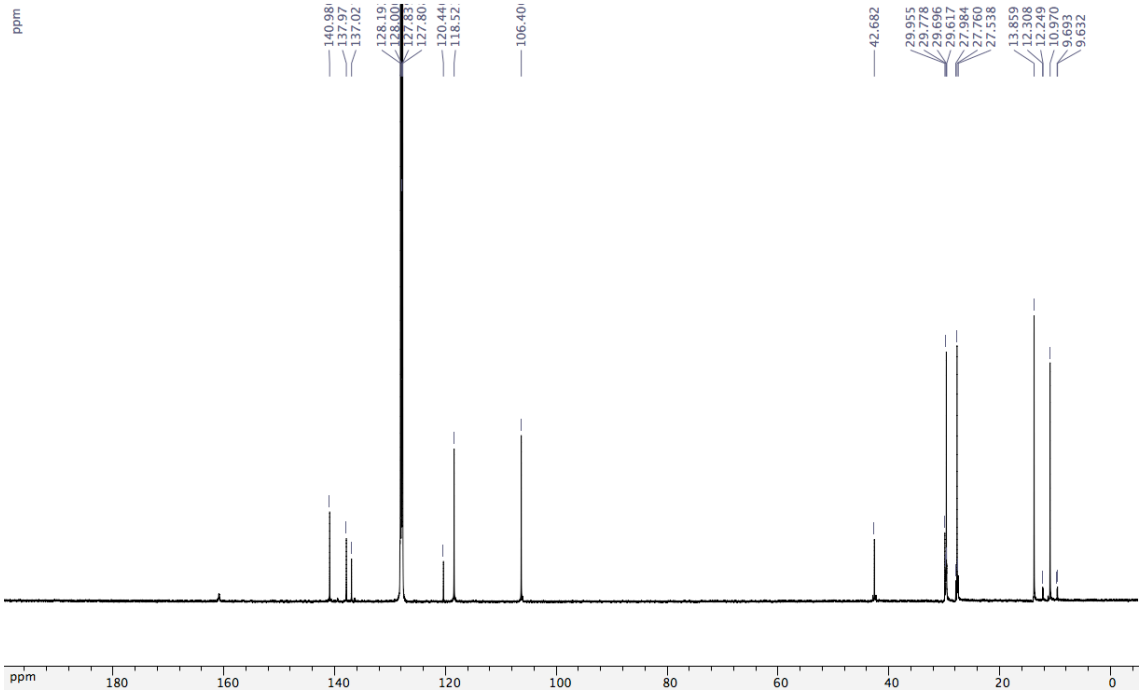


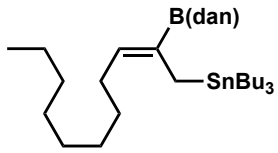
(**2n**)

^{1}H NMR



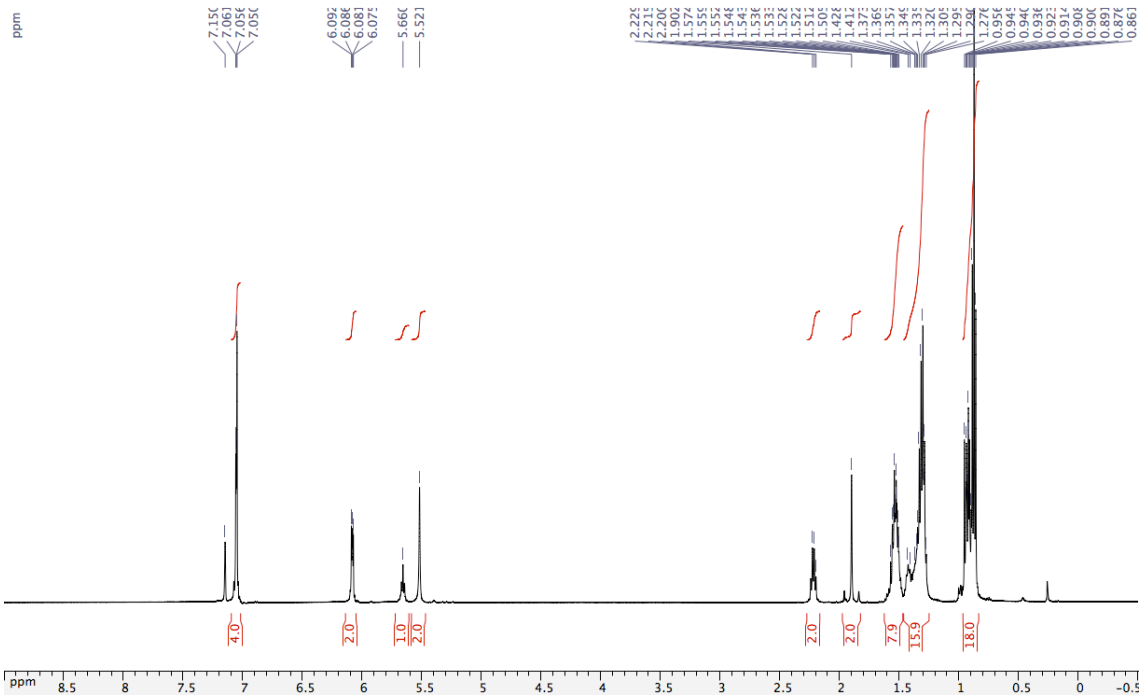
^{13}C NMR



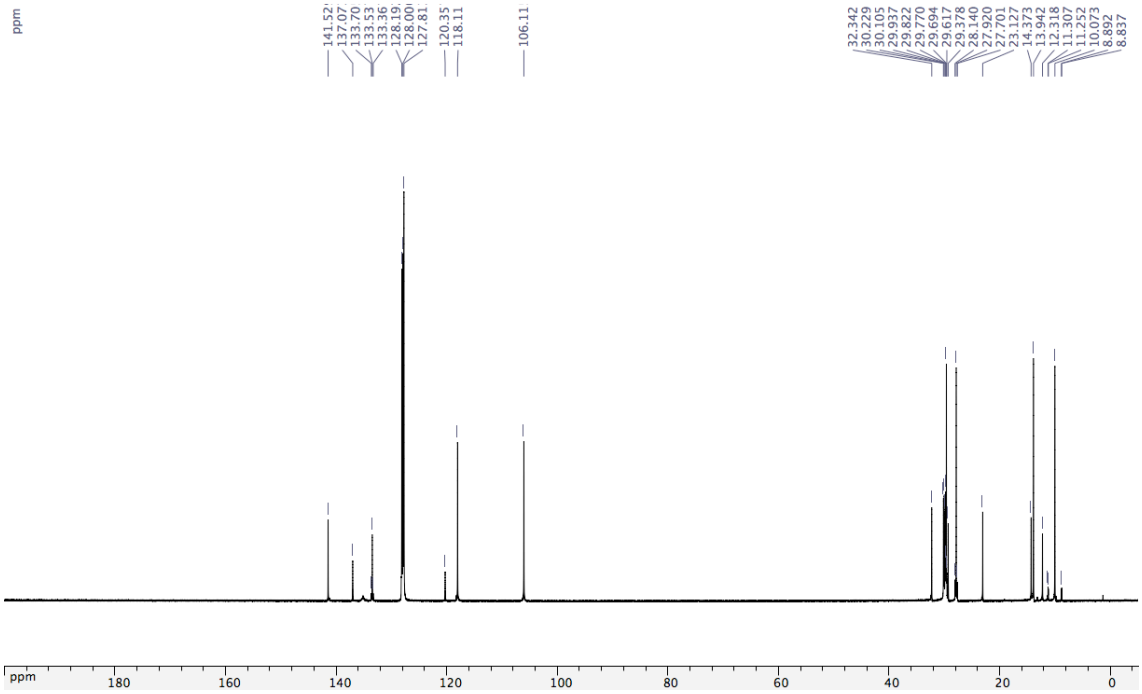


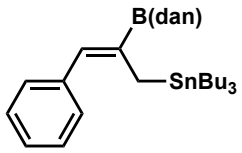
(**4a**)

^{1}H NMR



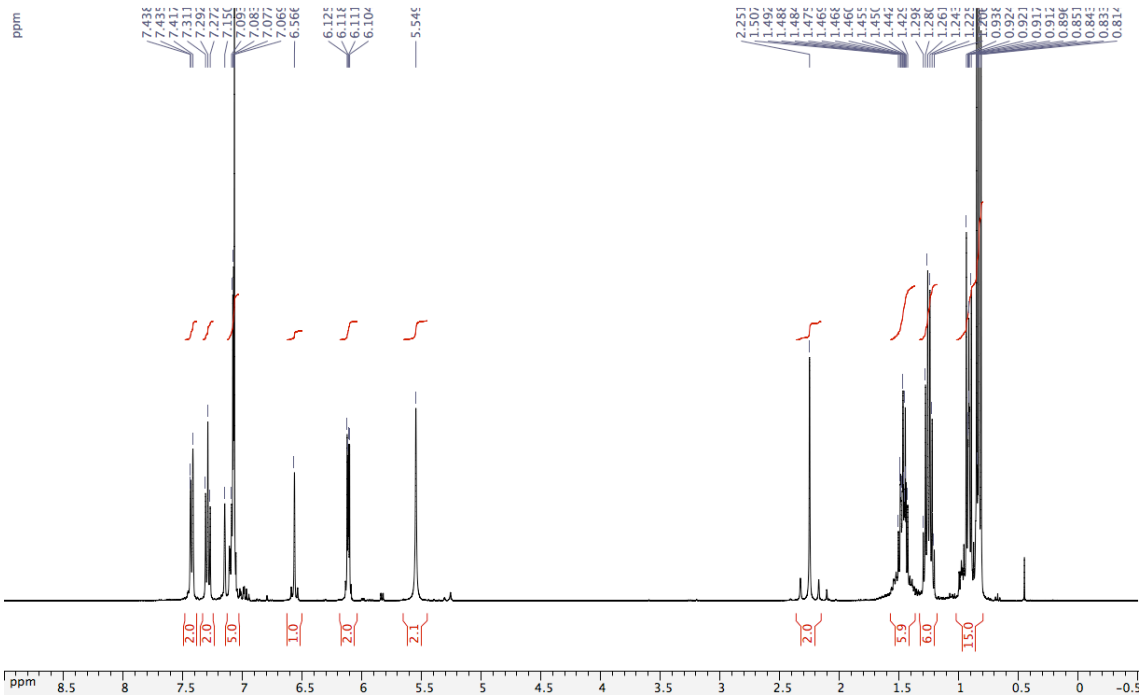
^{13}C NMR



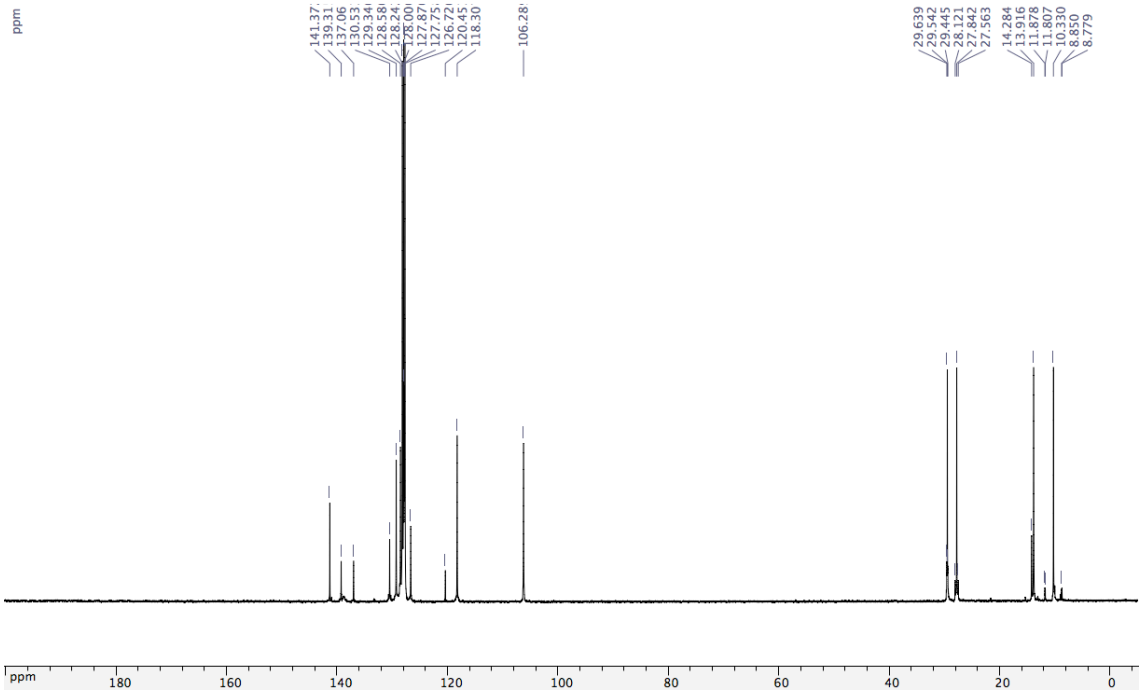


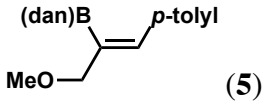
(**4b**)

^{1}H NMR



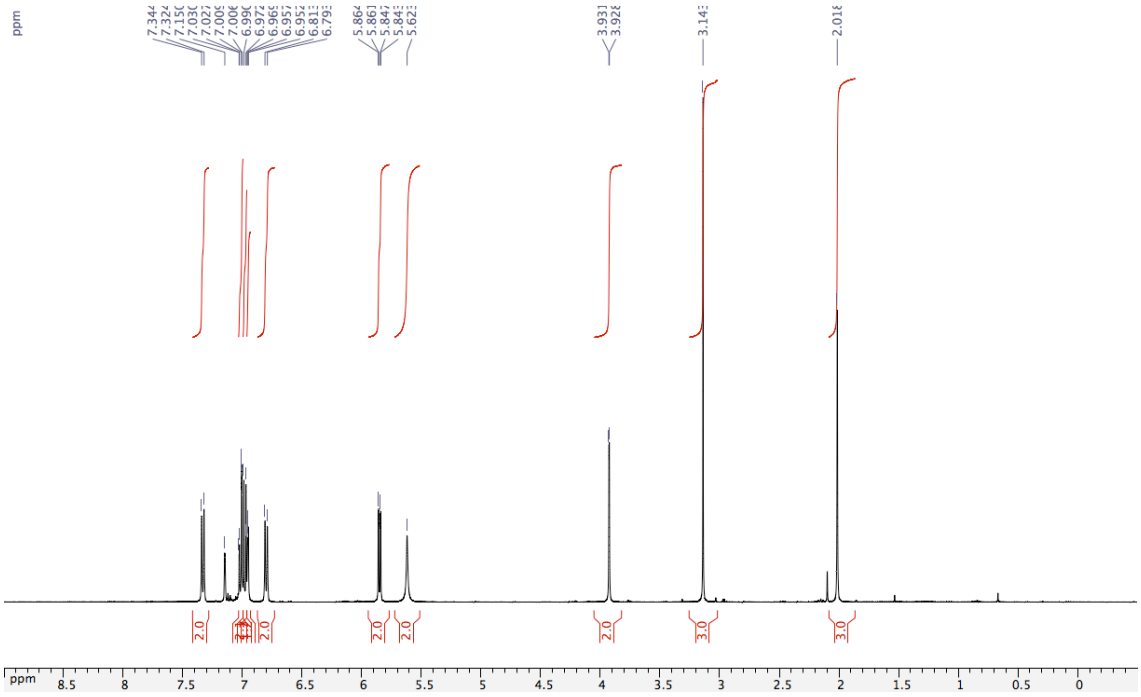
^{13}C NMR



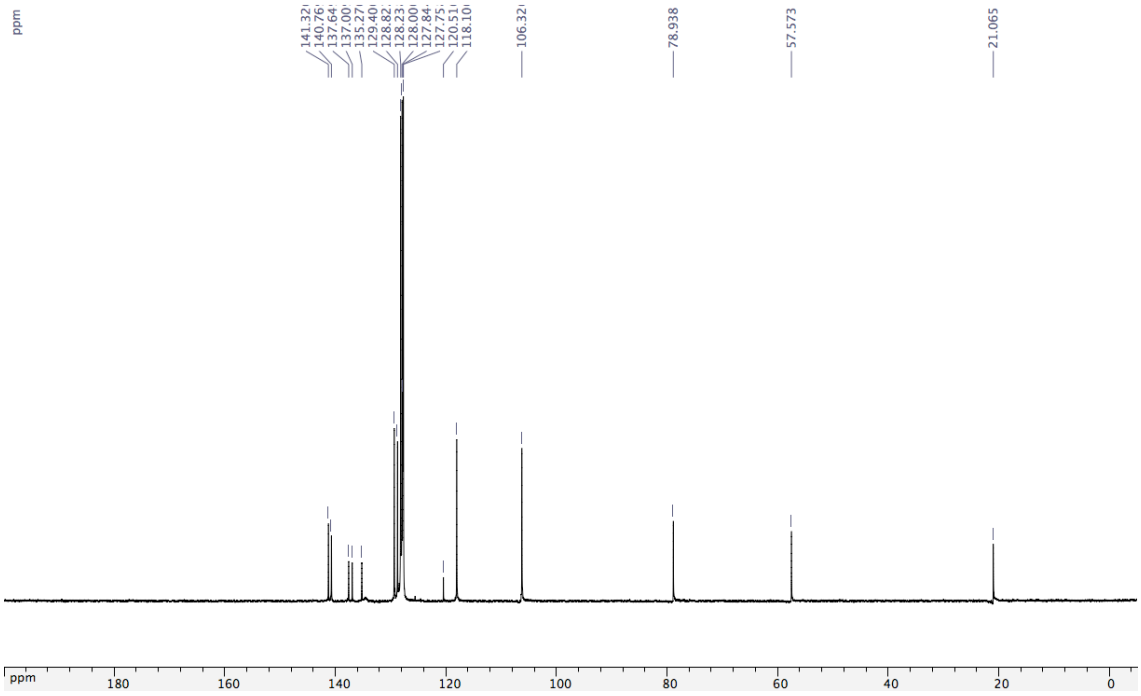


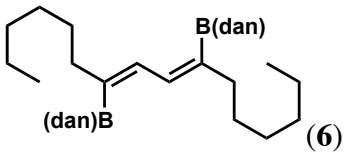
(**5**)

^{1}H NMR



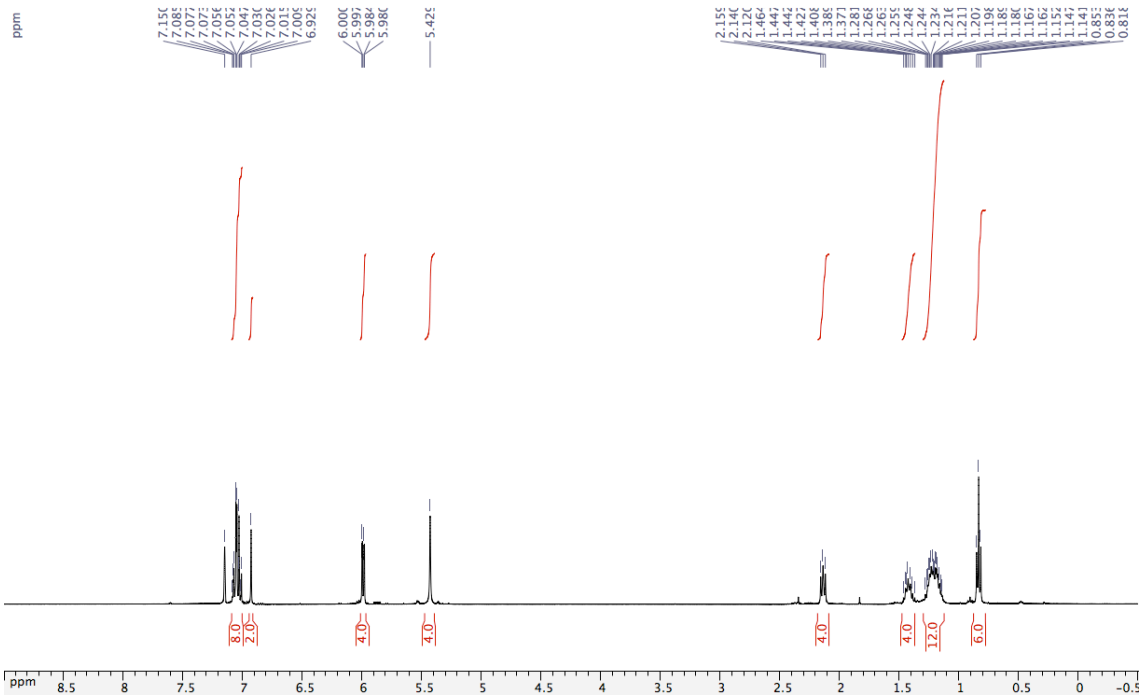
^{13}C NMR



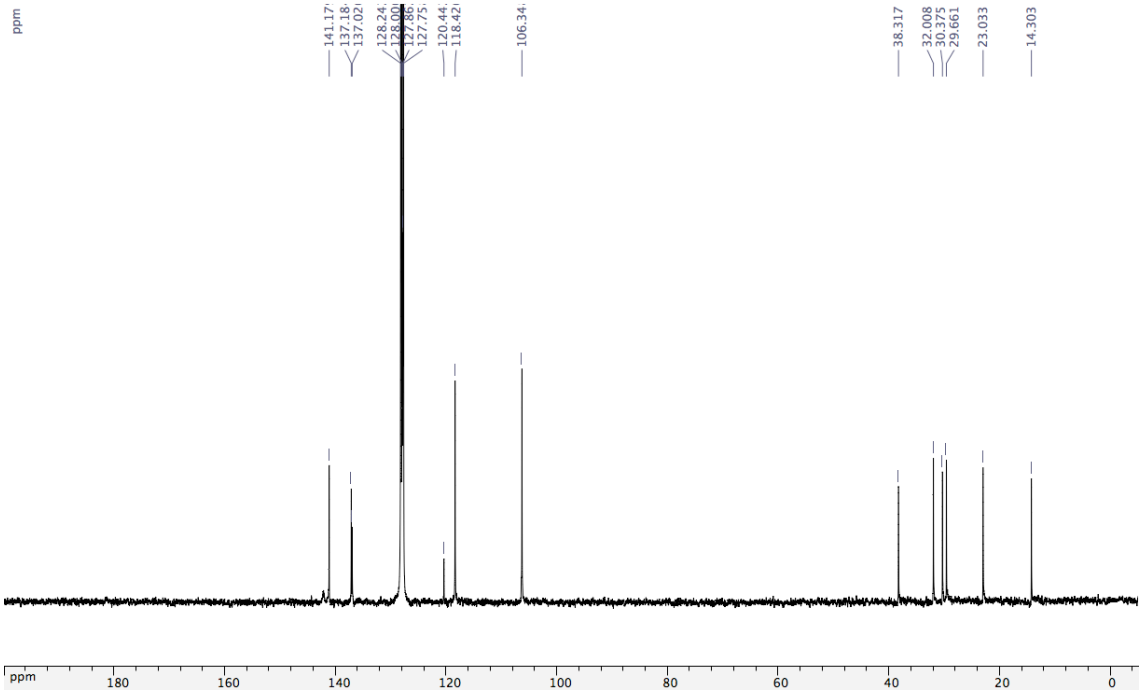


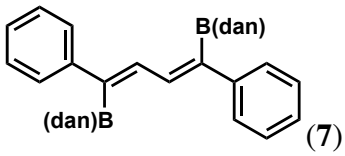
(**6**)

^{1}H NMR



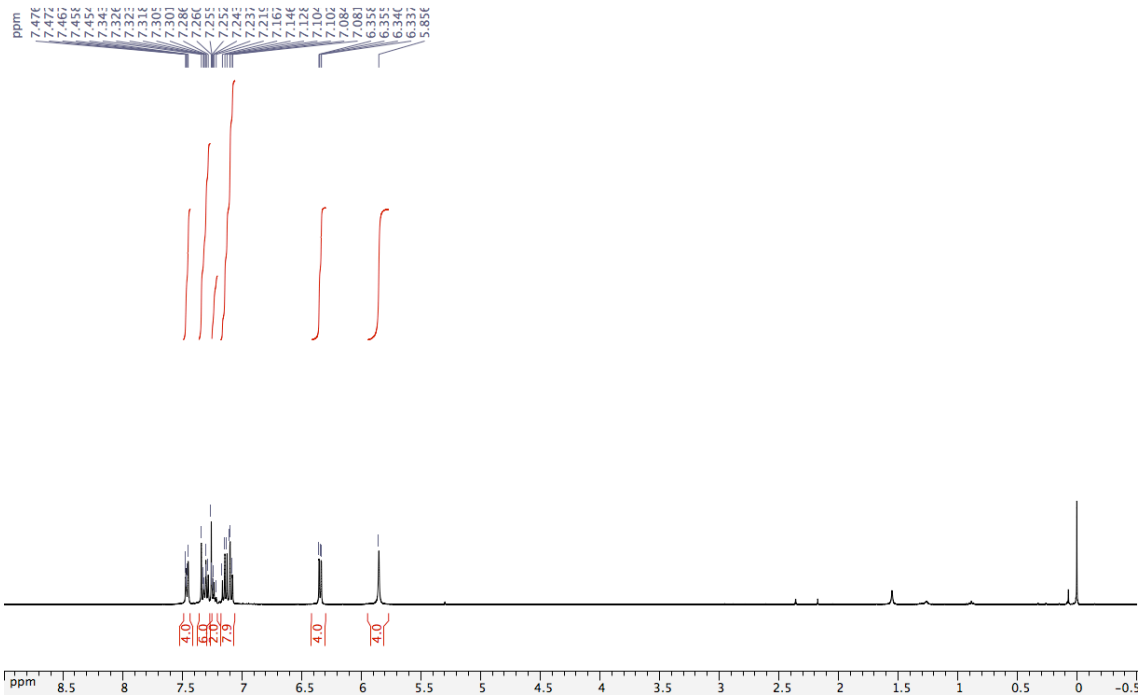
^{13}C NMR



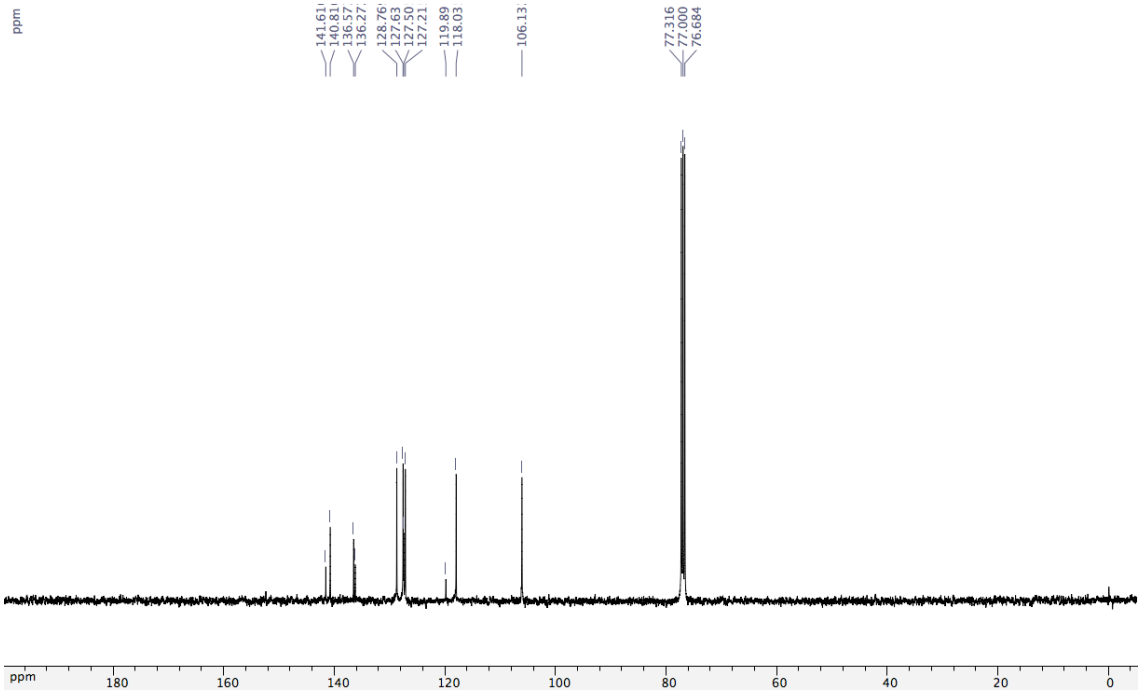


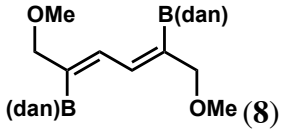
(**7**)

^{1}H NMR



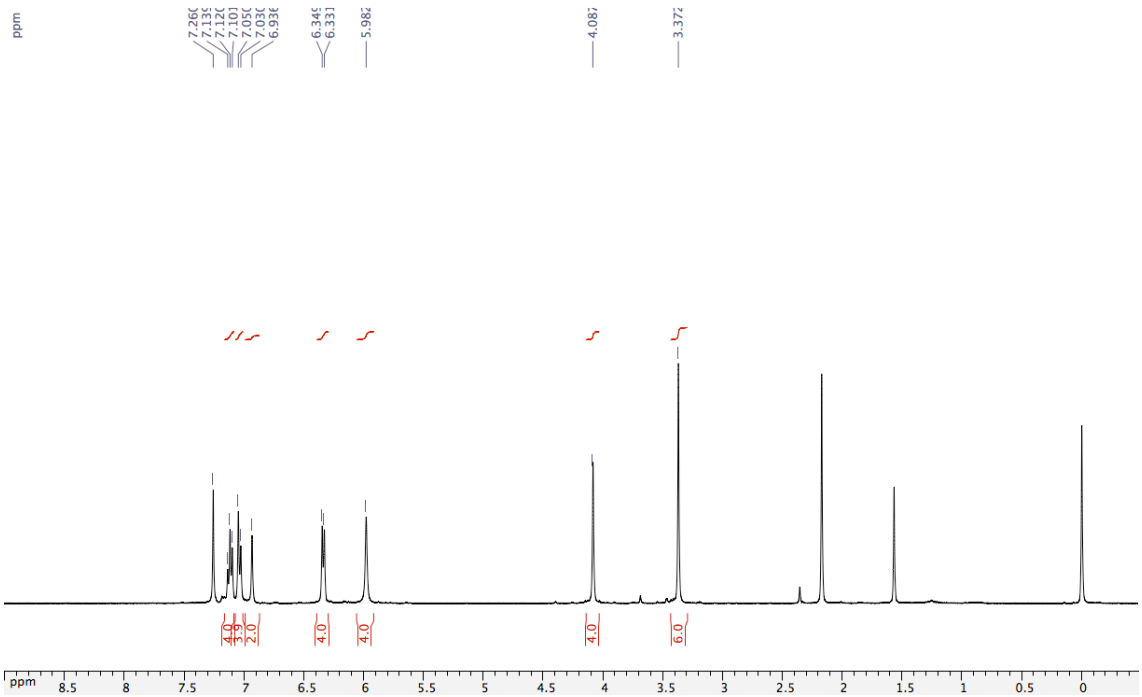
^{13}C NMR



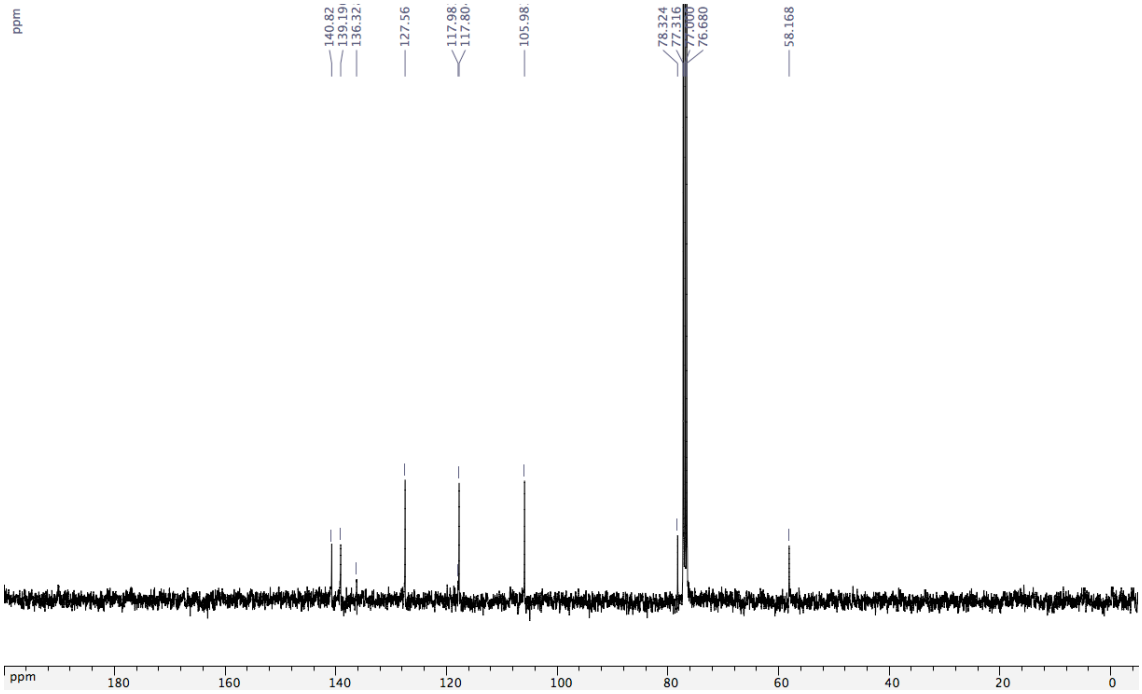


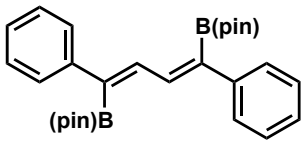
(**8**)

^{1}H NMR

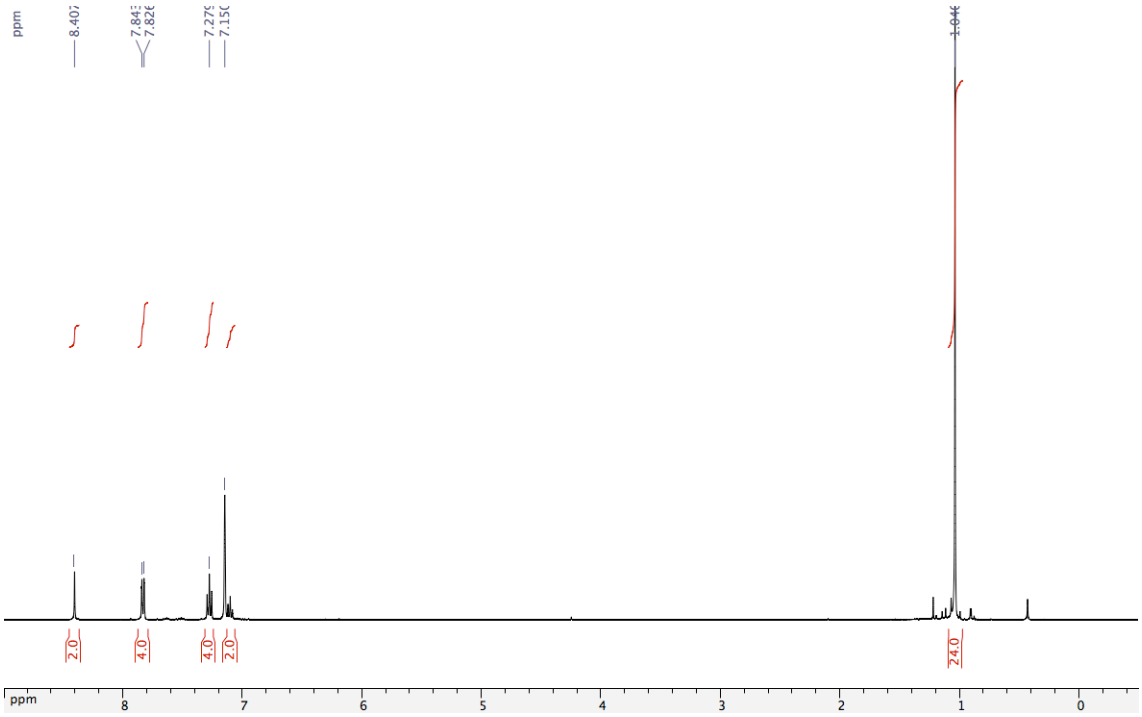


^{13}C NMR





^{1}H NMR



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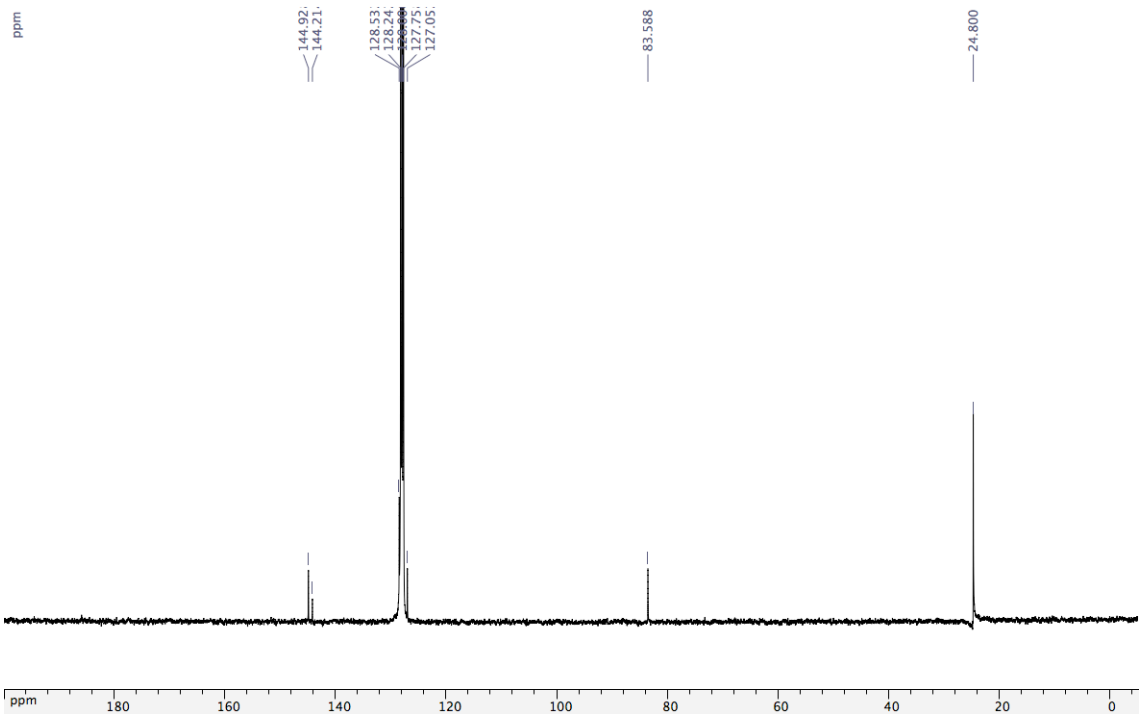
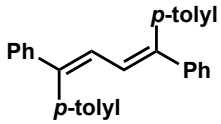
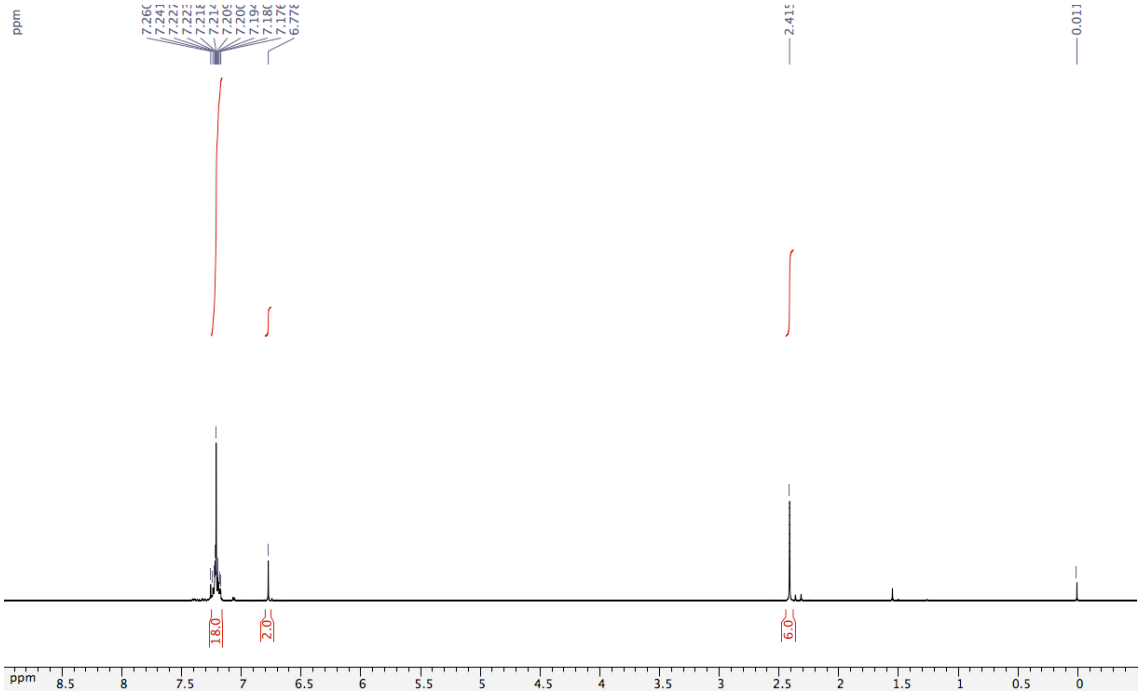




(**9**)

^{1}H NMR



^{13}C NMR