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Supporting Information for the Paper

Gold-Catalyzed Preparation of Anellated 2-Azetidinones via Divergent Heterocyclization of Enyne-Tethered Oxazolidines

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General methods: ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker Avance-300 or Varian VRX-300S. NMR spectra were recorded in $CDCl_3$ or $C_2D_2Cl_4$ solutions, except otherwise stated. Chemical shifts are given in ppm relative to TMS (^{1}H, 0.0 ppm), or $CDCl_3$ (^{13}C, 76.9 ppm), or $C_2D_2Cl_4$ (^{13}C, 73.8 ppm). Coupling constants "*J*" are expressed in Hertz (multiplicity: s = singulet, d = doublet, dd = double doublet, t = triplet, dt = double triplet, q = quadruplet, quint = quintuplet, sext = sextuplet, sept = septuplet, m =multiplet). Low and high resolution mass spectra were taken on a on an AGILENT 6520 Accurate-Mass QTOF LC/MS spectrometer using the electronic impact (EI) or electrospray modes (ES). IR spectra were recorded on a Bruker Tensor 27 spectrometer. Specific rotation $[\alpha]_D$ is given in 10^{-1} deg cm^2 g^{-1} at 20 °C, and the concentration (*c*) is expressed in g per 100 mL. Microwave irradiation was carried out in a Monowave 300 from Anton Paar GmbH. The reaction temperatures during microwave heating were measured with an internal infrared sensor.

General Procedure for the Synthesis of α-Allenic Alcohols 2a–2c. Indium-Promoted Reaction between (3-Bromoprop-1-yn-1-yl)benzene and Ketones 1. (3-Bromoprop-1-yn-1-yl)benzene (3.0 mmol) was added to a well stirred suspension of the corresponding ketone **1** (1.0 mmol) and indium powder (6.0 mmol) in THF/NH_4Cl (aq. sat.) (1:5, 5 mL) at 0 ºC. After disappearance of the starting material (TLC) the mixture was extracted with ethyl acetate (3 x 20 mL). The organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/hexanes mixtures gave analytically pure compounds **2**. Spectroscopic and analytical data for compounds **2** follows.

α-Allenic Alcohol (–)-2a. From 862 mg (2.21 mmol) of the oxo-β-lactam (–)-**1a**, and after flash chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent gave compound (–)-**2a** (780 mg, 70%) as a pale yellow oil; $[\alpha]_D$ = –12.0 (*c* 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 90 ºC): δ = 7.64 (d, 2H, *J* = 7.3 Hz), 7.34 (m, 5H), 6.91 (d, 2H, *J* = 9.1 Hz), 5.28 (m, 2H), 4.60 (m, 2H), 4.12

(m 2H), 3.82 (s, 3H), 1.51 (s, 3H), 1.41 (s, 12H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 90 ºC): δ = 207.9, 166.3, 156.9, 153.5, 133.2, 131.1, 128.5 (2C), 128.4 (2C), 125.5, 119.7 (2C), 114.7 (2C), 106.8, 95.3, 85.4, 81.5, 80.4, 65.7, 61.9, 61.6, 55.8, 28.4, 28.2 (3C), 26.2; IR (CH_2Cl_2): ν = 2976, 2932, 1941, 1737, 1683 cm^{-1}; HRMS (ES): calcd for $C_{29}H_{35}N_2O_6$ [*M*+H]$^+$: 507.2490; found: 507.2505.

α-Allenic Alcohol (–)-2b. From 1.62 g (4.33 mmol) of the oxo-β-lactam (–)-**1b**, and after flash chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound (–)-**2b** (1.35 g, 65%) as a colorless oil; $[\alpha]_D$ = –10.8 (*c* 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 95 ºC): δ = 7.63 (m, 2H), 7.34 (m, 6H), 7.10 (m, 2H), 5.16 (d, 1H, *J* = 12.3 Hz), 5.03 (d, 1H, *J* = 12.2 Hz), 4.90 (d, 1H, *J* = 15.1 Hz), 4.51 (m, 1H), 4.06 (d, 1H, *J* = 15.1 Hz), 3.97 (dd, 2H, *J* = 5.9, 9.6 Hz), 3.92 (d, 1H, *J* = 7.8 Hz), 3.78 (d, 1H, *J* = 9.6 Hz), 1.58 (s, 9H), 1.55 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 95 ºC): δ = 207.4, 168.8, 153.1, 135.3, 132.9, 128.9 (2C), 128.7 (2C), 128.6 (2C), 128.4 (2C), 127.7, 127.7, 106.3, 94.8, 85.2, 81.2, 80.3, 66.2, 63.5, 57.1, 45.1, 28.6 (3C), 27.2, 24.3; IR (CH_2Cl_2): ν = 2979, 2935, 1943, 1732, 1688 cm^{-1}; HRMS (ES): calcd for $C_{29}H_{35}N_2O_5$ [*M*+H]$^+$: 491.2540; found: 491.2545.

α-Allenic Alcohol (–)-2c. From 1.30 g (3.46 mmol) of the oxo-β-lactam (–)-**1c**, and after flash chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound (–)-**2c** (1.06 g, 63%) as a colorless oil; $[\alpha]_D$ = –15.3 (*c* 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 75 ºC): δ = 7.62 (m, 2H), 7.35 (m, 3H), 7.02 (d, 2H, *J* = 8.6 Hz), 6.83 (d, 2H, *J* = 8.8 Hz), 5.16 (d, 1H, *J* = 12.2 Hz), 5.05 (d, 1H, *J* = 12.2 Hz), 4.83 (d, 1H, *J* = 14.9 Hz), 4.47 (m, 1H), 3.99 (m, 2H), 3.90 (d, 1H, *J* = 7.8 Hz), 3.82 (s, 3H), 3.78 (d, 1H, *J* = 9.8 Hz), 1.58 (s, 9H), 1.55 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 75 ºC): δ = 207.4, 168.7, 159.4, 153.1, 132.9, 129.7 (2C), 128.9 (2C), 128.6 (2C), 127.7, 127.5, 114.4 (2C), 106.3, 94.8, 85.1, 81.2, 80.2, 66.2, 63.4, 57.1, 55.5, 44.5, 28.6 (3C), 27.3, 24.3; IR (CH_2Cl_2): ν = 2981, 2940, 1941, 1735, 1693 cm^{-1}; HRMS (ES): calcd for $C_{30}H_{36}N_2NaO_6$ [*M*+Na]$^+$: 543.2466; found: 543.2379.

General Procedure for the Synthesis of (*E*)-1,3-Enynes 3a–c. Tetrabutyl ammonium iodide (cat), 50% aqueous sodium hydroxide (5 mL) and acetyl chloride (0.22 mmol) were sequentially added at rt to a solution of the appropriate α-allenic alcohol **2** (0.20 mmol) in dichloromethane (4 mL). The reaction was stirred for 24 h before being partitioned between dichloromethane and water. The aqueous phase was extracted with dichloromethane (3 x 15 mL). The organic extract was washed with water and brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/hexanes mixtures gave analytically pure compounds. Spectroscopic and analytical data for compounds **3** follow.

(*E*)-1,3-Enyne (+)-3a. From 780 mg (1.55 mmol) of the α-allenic alcohol (–)-**2a**, and after flash chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent gave compound (+)-**3a** (750 mg, 99%) as a pale yellow oil; $[\alpha]_D$ = +38.0 (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 95 ºC): δ = 8.08 (m, 2H), 7.46 (m, 5H), 6.96 (d, 2H, *J* = 9.1 Hz), 5.29 (d, 1H, *J* = 3.4 Hz), 4.68 (m, 1H), 4.22 (dd, 1H, *J* = 3.3, 9.7 Hz), 4.04 (dd, 1H, *J* = 7.1, 9.6 Hz), 3.85 (s, 3H), 3.50 (s, 1H), 1.66 (s, 3H), 1.58 (s, 9H), 1.53 (s, 3H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 95 ºC): δ = 158.6, 156.9, 152.7, 143.0, 133.9, 130.9, 129.8, 129.3 (2C), 128.2 (2C), 119.4, 119.0 (2C), 115.0 (2C), 95.7, 85.3, 81.8, 80.6, 64.0, 60.3, 57.1, 55.8, 28.6 (3C), 26.4, 23.9; IR (CH_2Cl_2): ν = 2976, 2934, 2096, 1731, 1700 cm^{-1}; HRMS (ES): calcd for $C_{29}H_{33}N_2O_5$ $[M+H]^+$: 489.2384; found: 489.2386.

(*E*)-1,3-Enyne (+)-3b. From 1.30 g (2.65 mmol) of the α-allenic alcohol (–)-**2b**, and after flash chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent gave compound (+)-**3b** (1.0 g, 80%) as a colorless oil; $[\alpha]_D$ = +87.9 (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 80 ºC): δ = 8.05 (m, 2H), 7.37 (m, 8H), 4.90 (d, 1H, *J* = 15.1 Hz), 4.47 (m, 1H), 4.43 (d, 1H, *J* = 4.0 Hz), 4.33 (d, 1H, *J* = 15.1 Hz), 4.08 (dd, 1H, *J* = 1.9, 9.5 Hz), 3.99 (dd, 1H, *J* = 6.3, 9.5 Hz), 3.41 (s, 1H), 1.68 (s, 3H), 1.54 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 80 ºC): δ = 162.1, 152.7, 144.9, 135.8, 133.8, 129.7, 129.2 (2C), 129.0 (2C), 128.4 (2C), 128.2 (2C), 127.9, 122.7, 95.4, 84.7, 81.5,

80.5, 65.4, 61.1, 57.5, 45.7, 28.5 (3C), 26.8, 23.9; IR (CH_2Cl_2): ν = 2977, 2926, 2057, 1750, 1706 cm^{-1}; HRMS (ES): calcd for $C_{29}H_{33}N_2O_4$ $[M+H]^+$: 473.2435; found: 473.2450.

(*E*)-1,3-Enyne (+)-3c. From 990 mg (1.90 mmol) of the α-allenic alcohol (–)-**2c**, and after flash chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound (+)-**3c** (750 mg, 79%) as a colorless oil; $[\alpha]_D$ = +92.0 (*c* 0.1, $CHCl_3$); ^1H NMR (300 MHz, $C_2D_2Cl_4$, 75 ºC): δ = 8.05 (m, 2H), 7.45 (m, 3H), 7.22 (d, 2H, *J* = 8.5 Hz), 6.92 (d, 2H, *J* = 8.6 Hz), 4.84 (d, 1H, *J* = 15.1 Hz), 4.47 (m, 1H), 4.40 (d, 1H, *J* = 4.0 Hz), 4.26 (d, 1H, *J* = 15.0 Hz), 4.07 (dd, 1H, *J* = 2.2, 9.5 Hz), 3.99 (dd, 1H, *J* = 6.4, 9.5 Hz), 3.83 (s, 3H), 3.40 (s, 1H), 1.68 (s, 3H), 1.54 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 75 ºC): δ = 162.1, 159.5, 152.7, 144.9, 133.8, 129.7 (2C), 129.6, 129.2 (2C), 128.2 (2C), 127.9, 122.6, 114.6 (2C), 95.4, 84.7, 81.5, 80.5, 65.4, 61.0, 57.5, 55.5, 45.2, 28.5 (3C), 26.8, 23.9; IR (CH_2Cl_2): ν = 2975, 2931, 2097, 1741, 1698 cm^{-1}; HRMS (ES): calcd for $C_{30}H_{34}N_2NaO_5$ $[M+Na]^+$: 525.2360; found: 525.2331.

General Procedure for the Synthesis of Deuterated (*E*)-1,3-Enynes 4a–c. Deuterium oxide (500 mg, 25 mmol) was added at rt under argon atmosphere to a stirred suspension of K_2CO_3 (103 mg, 0.75 mmol) and the appropriate (*E*)-1,3-enyne **3** (0.5 mmol) in acetonitrile (0.1 mL). The reaction was stirred for 1 h before being partitioned between dichloromethane and water. The aqueous phase was extracted with dichloromethane (3 x 8 mL). The organic extract was washed with water and brine, dried ($MgSO_4$) and concentrated under reduced pressure to give analytically pure compounds. Spectroscopic and analytical data for compounds **4** follow.

Deuterated (*E*)-1,3-Enyne (+)-4a. From 200 mg (0.41 mmol) of the (*E*)-1,3-enyne (+)-**3a**, compound (+)-**4a** (190 mg, 95%) was obtained as a pale yellow oil; $[\alpha]_D$ = +51.0 (*c* 0.1, $CHCl_3$); ^1H NMR (300 MHz, $C_2D_2Cl_4$, 95 ºC): δ = 8.08 (m, 2H), 7.46 (m, 5H), 6.96 (d, 2H, *J* = 9.1 Hz), 5.29 (d, 1H, *J* = 3.5 Hz), 4.69 (m, 1H), 4.22 (dd, 1H, *J* = 3.3, 9.7 Hz), 4.05 (dd, 1H, *J* = 7.0, 9.6 Hz), 3.85 (s, 3H), 1.66 (s, 3H), 1.58 (s, 9H), 1.53 (s, 3H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 95 ºC): δ = 158.7, 156.9,

152.7, 143.0, 133.9, 130.9, 129.8, 129.3 (2C), 128.2 (2C), 123.9, 119.0 (2C), 115.0 (2C), 95.7, 88.9, 81.5, 80.6, 64.0, 60.3, 57.1, 55.8, 28.6 (3C), 26.4, 23.9; IR (CH_2Cl_2): ν = 2976, 2933, 2098, 1731, 1700 cm^{-1}; HRMS (ES): calcd for $C_{29}H_{32}DN_2O_5$ $[M+H]^+$: 490.2447; found: 490.2438.

Deuterated (*E*)-1,3-Enyne (+)-4b. From 143 mg (0.30 mmol) of the (*E*)-1,3-enyne (+)-**3b**, compound (+)-**4b** (135 mg, 94%) was obtained as a colorless oil; $[\alpha]_D$ = +180.8 (*c* 0.03, $CHCl_3$); ^1H NMR (300 MHz, $C_2D_2Cl_4$, 75 ºC): δ = 8.05 (m, 2H), 7.37 (m, 8H), 4.90 (d, 1H, *J* = 15.1 Hz), 4.47 (m, 1H), 4.42 (d, 1H, *J* = 4.0 Hz), 4.32 (d, 1H, *J* = 15.1 Hz), 4.02 (dd, 1H, *J* = 2.2, 9.6 Hz), 3.98 (dd, 1H, *J* = 6.4, 9.5 Hz), 1.67 (s, 3H), 1.54 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 75 ºC): δ = 162.1, 152.8, 144.8, 135.8, 133.8, 129.7, 129.2 (2C), 129.0 (2C), 128.4 (2C), 128.2 (2C), 127.9, 122.7, 95.4, 87.6, 81.1, 80.6, 65.3, 61.1, 57.5, 45.8, 28.5 (3C), 26.8, 23.9; IR (CH_2Cl_2): ν = 2978, 2935, 2060, 1740, 1697 cm^{-1}; HRMS (ES): calcd for $C_{29}H_{32}DN_2O_4$ $[M+H]^+$: 474.2498; found: 474.2500.

Deuterated (*E*)-1,3-Enyne (+)-4c. From 52 mg (0.10 mmol) of the (*E*)-1,3-enyne (+)-**3c**, compound (+)-**4c** (50 mg, 99%) was obtained as a colorless oil; $[\alpha]_D$ = +88.8 (*c* 0.1, $CHCl_3$); ^1H NMR (300 MHz, $C_2D_2Cl_4$, 60 ºC): δ = 8.04 (m, 2H), 7.45 (m, 3H), 7.21 (d, 2H, *J* = 8.5 Hz), 6.91 (d, 2H, *J* = 8.6 Hz), 4.84 (d, 1H, *J* = 15.1 Hz), 4.47 (m, 1H), 4.37 (d, 1H, *J* = 4.0 Hz), 4.24 (d, 1H, *J* = 15.1 Hz), 4.05 (dd, 1H, *J* = 2.1, 9.5 Hz), 3.98 (dd, 1H, *J* = 6.3, 9.5 Hz), 3.82 (s, 3H), 1.67 (s, 3H), 1.53 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 60 ºC): δ = 162.1, 159.4, 152.7, 144.8, 133.7, 129.7 (3C), 129.2 (2C), 128.2 (2C), 127.7, 122.6, 114.6 (2C), 95.4, 81.0, 80.5, 75.9, 65.4, 60.9, 57.4, 55.5, 45.2, 28.5 (3C), 26.8, 23.9; IR (CH_2Cl_2): ν = 2978, 2933, 2100, 1740, 1698 cm^{-1}; HRMS (ES): calcd for $C_{30}H_{33}DN_2NaO_5$ $[M+Na]^+$: 526.2423; found: 526.2421.

General Procedure for the Preparation of Bromo-Enynes 5a–c. To a solution of the appropriate (*E*)-1,3-enyne **3** (168 mg, 0.70 mmol) in acetone (4.8 mL) were added NBS (155 mg, 0.88 mmol) and silver acetate (35 mg, 0.21 mmol). The reaction mixture was stirred at room temperature in the

dark until disappearance (TLC) of the starting material. The solids were removed by filtration through a Celite pad (washing with ethyl acetate). The combined organic filtrate was washed with water and brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/hexanes mixtures gave analytically pure compounds. Spectroscopic and analytical data for compounds **5** follow.

Bromo-Enyne (+)-5a. From 335 mg (0.69 mmol) of the (*E*)-1,3-enyne (+)-**3a**, and after flash chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent gave compound (+)-**5a** (340 mg, 89%) as a colorless oil; $[\alpha]_D$ = +19.4 (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 80 ºC): δ = 8.00 (m, 2H), 7.46 (m, 5H), 6.95 (d, 2H, *J* = 9.1 Hz), 5.22 (d, 1H, *J* = 3.0 Hz), 4.63 (m, 1H), 4.18 (dd, 1H, *J* = 2.8, 9.7 Hz), 4.05 (dd, 1H, *J* = 7.0, 9.5 Hz), 3.84 (s, 3H), 1.70 (s, 3H), 1.59 (s, 9H), 1.52 (s, 3H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 80 ºC): δ = 158.6, 156.8, 152.8, 142.6, 134.0, 130.8, 129.9, 129.3 (2C), 128.2 (2C), 124.4, 119.0 (2C), 115.0 (2C), 95.6, 83.0, 80.8, 79.0, 63.8, 60.3, 56.9, 55.8, 28.6 (3C), 28.5, 26.1; IR (CH_2Cl_2): ν = 2977, 2934, 2178, 1734, 1701 cm^{-1}; HRMS (ES): calcd for $C_{29}H_{31}BrN_2NaO_5$ $[M+Na]^+$: 589.1309; found: 589.1308.

Bromo-Enyne (+)-5b. From 321 mg (0.67 mmol) of the (*E*)-1,3-enyne (+)-**3b**, and after flash chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound (+)-**5b** (320 mg, 87%) as a pale yellow oil; $[\alpha]_D$ = +35.0 (*c* 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 75 ºC): δ = 7.99 (m, 2H), 7.36 (m, 8H), 4.90 (d, 1H, *J* = 15.2 Hz), 4.42 (m, 1H), 4.39 (d, 1H, *J* = 4.1 Hz), 4.32 (d, 1H, *J* = 15.1 Hz), 4.02 (m, 2H), 1.70 (s, 3H), 1.55 (s, 3H), 1.49 (s, 9H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 75 ºC): δ = 162.0, 152.9, 144.8, 135.8, 133.9, 129.7, 129.2 (2C), 129.1 (2C), 128.5 (2C), 128.3 (2C), 128.0, 123.1, 95.3, 80.7, 78.6, 77.4, 65.3, 61.2, 57.6, 45.8, 28.5 (3C), 26.7, 23.6; IR (CH_2Cl_2): ν = 2978, 2927, 2107, 1743, 1701 cm^{-1}; HRMS (ES): calcd for $C_{29}H_{32}BrN_2O_4$ $[M+H]^+$: 551.1540; found: 551.1562.

Bromo-Enyne (+)-5c. From 199 mg (0.40 mmol) of the (*E*)-1,3-enyne (+)-**3c**, and after flash chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent gave compound (+)-**5c** (198 mg, 85%) as a colorless oil; $[\alpha]_D$ = +70.7 (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 75 ºC): δ = 7.98 (m, 2H), 7.44 (m, 3H), 7.21 (d, 2H, *J* = 8.6 Hz), 6.92 (d, 2H, *J* = 8.8 Hz), 4.84 (d, 1H, *J* = 15.1 Hz), 4.42 (m, 1H), 4.35 (d, 1H, *J* = 4.1 Hz), 4.25 (d, 1H, *J* = 15.1 Hz), 4.02 (m, 2H), 3.84 (s, 3H), 1.71 (s, 3H), 1.55 (s, 3H), 1.49 (s, 9H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 75 ºC): δ = 162.0, 159.5, 152.9, 144.9, 133.9, 129.7 (2C), 129.6, 129.2 (2C), 128.2 (2C), 127.9, 122.9, 114.6 (2C), 95.4, 80.6, 80.1, 78.7, 65.4, 61.0, 57.6, 55.5, 45.2, 28.5 (3C), 26.7, 23.6; IR (CH_2Cl_2): ν = 2975, 2932, 2111, 1739, 1700 cm^{-1}; HRMS (ES): calcd for $C_{30}H_{33}BrN_2NaO_5$ $[M+Na]^+$: 603.1465; found: 603.1446.

General Procedure for the Preparation of PMP-Functionalized (*E*)-1,3-Enynes 6a–c. $PdCl_2(PPh_3)_2$ (3.5 mg, 0.005 mmol), CuI (1.9 mg, 0.01 mmol), and triethylamine (30.3 mg, 0.3 mmol) were sequentially added under argon atmosphere to a solution of the appropriate enyne **3** (200 mg, 0.5 mmol) and 1-iodo-4-methoxybenzene (0.5 mmol) in acetonitrile (0.4 mL). The reaction mixture was stirred at rt until disappearance of the starting material (TLC). Then, the mixture was poured into water (3 mL) and extracted with ethyl acetate (3 x 10 mL). The organic layer was washed with water (2 x 5 mL) and brine (2 x 5 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/hexanes mixtures gave analytically pure compounds. Spectroscopic and analytical data for compounds **6** follow.

PMP-Functionalized (*E*)-1,3-Enyne (–)-6a. From 210 mg (0.43 mmol) of the (*E*)-1,3-enyne (+)-**3a**, and after flash chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent gave compound (–)-**6a** (146 mg, 57%) as a pale yellow oil; $[\alpha]_D$ = –20.5 (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 95 ºC): δ = 8.10 (m, 2H), 7.53 (m, 7H), 6.96 (dd, 4H, *J* = 2.9, 9.9 Hz), 5.17 (d, 1H, *J* = 3.8 Hz), 4.67 (m, 1H), 4.36 (dd, 1H, *J* = 2.2, 9.7 Hz), 4.08 (dd, 1H, *J* = 6.8, 9.6 Hz), 3.90 (s, 3H), 3.85 (s, 3H), 1.69 (s, 3H), 1.52 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 95 ºC): δ = 163.0, 160.8, 159.4, 156.7, 134.9, 133.7 (2C), 131.3, 129.6, 129.4 (2C), 128.3, 128.1 (2C), 125.1, 119.1

(2C), 114.9 (2C), 114.6, 114.5 (2C), 95.5, 87.0, 80.7, 77.3, 64.5, 61.3, 57.7, 55.8, 55.5, 28.5 (3C), 26.4, 23.5; IR (CH_2Cl_2): ν = 2977, 2935, 2198, 1732, 1699 cm^{-1}; HRMS (ES): calcd for $C_{36}H_{38}N_2NaO_6$ $[M+Na]^+$: 617.2622; found: 617.2613.

PMP-Functionalized (*E*)-1,3-Enyne (+)-6b. From 190 mg (0.40 mmol) of the (*E*)-1,3-enyne (+)-**3b**, and after flash chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent gave compound (+)-**6b** (113 mg, 49%) as a pale yellow oil; $[\alpha]_D$ = +58.3 (*c* 0.1, $CHCl_3$); ^1H NMR (300 MHz, $C_2D_2Cl_4$, 75 ºC): δ = 8.09 (m, 2H), 7.40 (m, 10H), 6.93 (d, 2H, *J* = 8.8 Hz), 4.98 (d, 1H, *J* = 15.4 Hz), 4.52 (m, 1H), 4.37 (d, 1H, *J* = 5.0 Hz), 4.31 (d, 1H, *J* = 15.4 Hz), 4.26 (m, 1H), 4.03 (dd, 1H, *J* = 6.2, 9.3 Hz), 3.87 (s, 3H), 1.68 (s, 3H), 1.56 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 75 ºC): δ = 162.7, 160.6, 153.0, 142.4, 136.1, 134.6, 133.5 (2C), 129.5, 129.3 (2C), 128.9 (2C), 128.3 (2C), 128.1 (2C), 127.8, 123.8, 114.5 (2C), 114.4, 97.5, 95.1, 86.6, 80.6, 65.8, 61.6, 58.3, 55.5, 45.8, 28.5 (3C), 27.0, 23.7; IR (CH_2Cl_2): ν = 2976, 2934, 2196, 1736, 1697 cm^{-1}; HRMS (ES): calcd for $C_{36}H_{38}N_2NaO_5$ $[M+Na]^+$: 601.2673; found: 601.2679.

PMP-Functionalized (*E*)-1,3-Enyne (+)-6c. From 139 mg (0.28 mmol) of the (*E*)-1,3-enyne (+)-**3c**, and after flash chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent gave compound (+)-**6c** (92 mg, 54%) as a pale yellow oil; $[\alpha]_D$ = +25.0 (*c* 0.1, $CHCl_3$); ^1H NMR (300 MHz, $C_2D_2Cl_4$, 75 ºC): δ = 8.07 (m, 2H), 7.47 (m, 5H), 7.23 (d, 2H, *J* = 8.5 Hz), 6.92 (m, 4H), 4.91 (d, 1H, *J* = 15.2 Hz), 4.52 (m, 1H), 4.34 (d, 1H, *J* = 4.9 Hz), 4.24 (m, 2H), 4.03 (dd, 1H, *J* = 6.3, 9.3 Hz), 3.87 (s, 3H), 3.83 (s, 3H), 1.70 (s, 3H), 1.56 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 75 ºC): δ = 162.6, 160.6, 159.4, 153.0, 142.5, 134.6, 133.5 (2C), 129.6 (2C), 129.5, 129.3 (2C), 128.2, 128.1 (2C), 123.7, 114.6 (2C), 114.5 (2C), 114.4, 97.4, 95.1, 86.6, 80.6, 65.9, 61.5, 58.3, 55.5, 55.4, 45.2, 28.5 (3C), 27.0, 23.7; IR (CH_2Cl_2): ν = 2976, 2935, 2197, 1738, 1696 cm^{-1}; HRMS (ES): calcd for $C_{37}H_{41}N_2O_6$ $[M+H]^+$: 609.2959; found: 609.2931.

General Procedure for the Preparation of Enediynes 7a–c. Hydroxylamine hydrochloride (a few crystals), $EtNH_2$ (70% aqueous solution, 0.21 mL), and CuCl (0.006 mmol, 0.0017 equiv) were sequentially added at rt to a solution of the appropriate bromo-enyne **5** (0.3 mmol) in methanol (1.5 mL). Next, ethynylbenzene (0.3 mmol) in CH_2Cl_2 (4.2 mL) was added to the above suspension cooled at 0ºC. More crystals of hydroxylamine hydrochloride were added throughout the reaction as necessary to prevent the solution from turning blue or green. The reaction mixture was stirred until disappearance of the starting material (TLC). Then, the mixture was poured into water (5 mL) and extracted with ethyl acetate (3 x 10 mL). The organic layer was washed with water (2 x 5 mL) and brine (2 x 5 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/hexanes mixtures gave analytically pure compounds. Spectroscopic and analytical data for compounds **7** follow.

Enediyne (–)-7a. From 137 mg (0.25 mmol) of the bromo-enyne (+)-**5a**, and after flash chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent gave compound (–)-**7a** (110 mg, 75%) as a pale yellow oil; $[\alpha]_D$ = –20.5 (*c* 0.02, $CHCl_3$); ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 90 ºC): δ = 8.04 (m, 2H), 7.50 (m, 10H), 6.97 (d, 2H, *J* = 9.1 Hz), 5.28 (d, 1H, *J* = 3.2 Hz), 4.68 (m, 1H), 4.23 (dd, 1H, *J* = 2.9, 9.7 Hz), 4.05 (dd, 1H, *J* = 7.1, 9.6 Hz), 3.85 (s, 3H), 1.74 (s, 3H), 1.58 (s, 9H), 1.54 (s, 3H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 90 ºC): δ = 158.6, 156.9, 155.0, 143.7, 134.0, 132.7 (2C), 130.9, 129.9, 129.7, 129.3 (2C), 128.5 (2C), 128.4, 128.3 (2C), 121.5, 119.1 (2C), 115.0 (2C), 95.7, 85.7, 82.1, 80.7, 79.6, 77.3, 64.0, 60.6, 57.0, 55.8, 28.6 (3C), 28.4, 26.2; IR (CH_2Cl_2): ν = 2976, 2934, 2231, 1733, 1700 cm^{-1}; HRMS (ES): calcd for $C_{37}H_{36}N_2NaO_5$ [*M*+Na]$^+$: 611.2516; found: 611.2534.

Enediyne (+)-7b. From 160 mg (0.29 mmol) of the bromo-enyne (+)-**5b**, and after flash chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound (+)-**7b** (142 mg, 85%) as a colorless oil; $[\alpha]_D$ = +68.8 (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 85 ºC): δ = 8.03 (m, 2H), 7.58 (m, 2H), 7.38 (m, 11H), 4.94 (d, 1H, *J* = 15.2 Hz), 4.51 (m, 1H), 4.44 (d, 1H, *J* = 4.0 Hz), 4.36 (d, 1H, *J* = 15.2 Hz), 4.07 (m, 2H), 1.74 (s, 3H), 1.57 (s, 3H), 1.50 (s, 9H); ^{13}C NMR

(75 MHz, $C_2D_2Cl_4$, 85 ºC): δ = 162.0, 152.9, 146.0, 135.8, 133.8, 132.7 (2C), 129.7 (2C), 129.2 (2C), 129.0 (2C), 128.5 (2C), 128.3 (2C), 128.2 (2C), 127.9, 122.7, 121.4, 95.4, 84.6, 81.1, 80.6, 79.4, 73.7, 65.5, 61.5, 57.6, 45.8, 28.5 (3C), 26.8, 23.7; IR (CH_2Cl_2): ν = 2979, 2933, 2211, 1743, 1701 cm^{-1}; HRMS (ES): calcd for $C_{37}H_{37}N_2O_4$ $[M+H]^+$: 573.2748; found: 573.2762.

Enediyne (+)-7c. From 99 mg (0.17 mmol) of the bromo-enyne (+)-**5c**, and after flash chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent gave compound (+)-**7c** (80 mg, 78%) as a colorless oil; $[\alpha]_D$ = +16.7 (*c* 0.05, $CHCl_3$); ^1H NMR (300 MHz, $C_2D_2Cl_4$, 75 ºC): δ = 8.02 (m, 2H), 7.58 (m, 2H), 7.41 (m, 6H), 7.23 (d, 2H, *J* = 8.6 Hz), 6.94 (d, 2H, *J* = 8.6 Hz), 4.88 (d, 1H, *J* = 15.1 Hz), 4.51 (m, 1H), 4.40 (d, 1H, *J* = 4.0 Hz), 4.28 (d, 1H, *J* = 15.1 Hz), 4.07 (m, 2H), 3.84 (s, 3H), 1.74 (s, 3H), 1.57 (s, 3H), 1.50 (s, 9H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 75 ºC): δ = 162.0, 159.5, 152.9, 146.0, 133.7, 132.7 (2C), 129.7, 129.7 (2C), 129.6 (2C), 129.2, 128.6 (2C), 128.3 (2C), 127.9, 122.6, 121.3, 114.7 (2C), 95.3, 84.5, 81.0, 80.6, 79.3, 73.9, 65.5, 61.3, 57.5, 55.5, 45.3, 28.5 (3C), 26.8, 23.7; IR (CH_2Cl_2): ν = 2975, 2931, 2211, 1740, 1702 cm^{-1}; HRMS (ES): calcd for $C_{38}H_{38}N_2NaO_5$ $[M+Na]^+$: 625.2673; found: 625.2660.

General Procedure for the Gold-Catalyzed Rearrangement Reaction of β-Lactam-Tethered Oxazolidine-Enynes 3–7. The appropriate enyne **3–7** (0.25 mmol) was added to a stirred solution of [AuClPPh$_3$] (0.023 mmol), AgOTf (0.023 mmol), 4-toluenesulfonic acid (0.093 mmol), and water (0.93 mmol) in 1,2-dichloroethane (0.93 mL). The resulting mixture was heated at 80 ºC under microwave irradiation until disappearance of the starting material (TLC). After filtration through a pad of Celite, the mixture was extracted with ethyl acetate (3 x 10 mL), and the combined extracts were washed twice with brine. The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with hexanes/ethyl acetate mixtures gave analytically pure adducts. Spectroscopic and analytical data for compounds **8–10** follow.

2-Azetidinone-Fused Furan (–)-8a. From 150 mg (0.31 mmol) of the (*E*)-1,3-enyne (+)-**3a**, and after flash chromatography of the residue using hexanes/ethyl acetate (12:1) as eluent gave compound (–)-**8a** (79 mg, 55%) as a pale yellow oil; $[\alpha]_D$ = –151.3 (*c* 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 7.24 (m, 5H), 7.13 (d, 2H, *J* = 9.1 Hz), 6.71 (d, 1H, *J* = 9.0 Hz), 6.23 (d, 2H, *J* = 9.5 Hz), 4.56 (s, 1H), 4.41 (m, 1H), 4.39 (s, 1H), 4.05 (d, 1H, *J* = 10.5 Hz), 3.96 (dd, 1H, *J* = 4.0, 10.5 Hz), 3.66 (s, 3H), 2.15 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 206.8, 162.6, 156.6, 155.6, 131.2, 129.3 (2C), 129.3 (2C), 129.2, 128.8, 118.5 (2C), 114.5 (2C), 97.3, 79.9, 74.5, 64.6, 56.8, 55.4, 51.1, 30.9, 28.5 (3C); IR (CH_2Cl_2): ν = 3391, 2975, 2926, 1753, 1707, 1512 cm^{-1}; HRMS (ES): calcd for $C_{26}H_{31}N_2O_6$ [*M*+H]$^+$: 467.2177; found: 467.2174.

2-Azetidinone-Fused Furan (–)-8b. From 149 mg (0.32 mmol) of the (*E*)-1,3-enyne (+)-**3b**, and after flash chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound (–)-**8b** (72 mg, 50%) as a colorless oil; $[\alpha]_D$ = –104.5 (*c* 0.02, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 7.38 (m, 5H), 7.14 (m, 3H), 6.43 (m, 2H), 4.63 (s, 1H), 4.58 (d, 1H, *J* = 15.5 Hz), 4.25 (dd, 1H, *J* = 2.8, 9.3 Hz), 4.12 (d, 1H, *J* = 10.4 Hz), 3.96 (dd, 1H, *J* = 3.5, 10.4 Hz), 3.96 (s, 1H), 3.75 (d, 1H, *J* = 15.5 Hz), 2.20 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 207.1, 165.8, 155.5, 134.2, 131.1, 129.5 (3C), 129.4 (2C), 128.7 (2C), 127.4, 127.3 (2C), 98.7, 79.7, 75.2, 63.8, 56.4, 50.5, 43.1, 31.0, 28.4 (3C); IR (CH_2Cl_2): ν = 3392, 2978, 1759, 1703 cm^{-1}; HRMS (ES): calcd for $C_{26}H_{31}N_2O_5$ [*M*+H]$^+$: 451.2227; found: 451.2243.

2-Azetidinone-Fused Furan (–)-8c. From 66 mg (0.13 mmol) of the (*E*)-1,3-enyne (+)-**3c**, and after flash chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound (–)-**8c** (33 mg, 52%) as a colorless oil; $[\alpha]_D$ = –94.3 (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 7.35 (m, 5H), 6.63 (d, 2H, *J* = 8.6 Hz), 6.38 (d, 2H, *J* = 8.5 Hz), 4.61 (s, 1H), 4.49 (d, 1H, *J* = 15.2 Hz), 4.23 (dd, 1H, *J* = 2.8, 8.9 Hz), 4.11 (d, 1H, *J* = 10.4 Hz), 3.96 (dd, 1H, *J* = 3.6, 10.4 Hz), 3.93 (s, 1H), 3.78 (s, 3H), 3.69 (d, 1H, *J* = 15.5 Hz), 2.19 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (75 MHz,

$CDCl_3$, 25 ºC): δ = 207.1, 165.6, 158.9, 155.5, 131.1, 129.5 (2C), 129.4 (2C), 128.7 (2C), 128.6, 126.2, 114.0 (2C), 98.5, 79.7, 75.2, 63.6, 56.3, 55.2, 50.6, 42.6, 31.0, 28.4 (3C); IR (CH_2Cl_2): ν = 3393, 2978, 2932, 1758, 1704, 1511 cm^{-1}; HRMS (ES): calcd for $C_{27}H_{33}N_2O_6$ $[M+H]^+$: 481.2333; found: 481.2335.

Reaction of Deuterated (*E*)-1,3-Enyne (+)-4a. From 150 mg (0.31 mmol) of deuterated (*E*)-1,3-enyne (+)-**4a**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent, 8 mg (6%) of less polar compound (–)-**8a-D** and 60 mg (44%) of more polar compound (+)-**9a-D** were obtained.

2-Azetidinone-Fused Furan (–)-8a-D. Pale yellow oil; $[\alpha]_D$ = –101.3 (*c* 0.01, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 7.53 (m, 2H), 7.34 (m, 3H), 7.23 (d, 2H, *J* = 9.1 Hz), 6.79 (d, 1H, *J* = 9.1 Hz), 6.32 (d, 2H, *J* = 9.4 Hz), 4.63 (s, 1H), 4.49 (m, 1H), 4.47 (s, 1H), 4.14 (m, 1H), 4.06 (dd, 1H, *J* = 4.0, 10.5 Hz), 3.74 (s, 3H), 2.22 (m, 2.1H), 1.53 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 206.9, 162.6, 156.6, 155.6, 134.1, 131.1, 129.3 (2C), 129.2 (2C), 128.8, 118.5 (2C), 114.5 (2C), 97.3, 79.9, 74.5, 64.5, 56.7, 55.4, 51.0, 29.7, 28.5 (3C); IR (CH_2Cl_2): ν = 3393, 2924, 2854, 1754, 1709, 1514 cm^{-1}; HRMS (ES): calcd for $C_{26}H_{30}DN_2O_6$ $[M+H]^+$: 468.2239; found: 468.2230.

2-Azetidinone-Fused Tetrahydropyridine (+)-9a. Pale yellow oil; $[\alpha]_D$ = +60.5 (*c* 0.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 8.07 (m, 2H), 7.56 (d, 2H, *J* = 8.8 Hz), 7.42 (m, 3H), 6.94 (d, 2H, *J* = 8.9 Hz), 5.22 (d, 1H, *J* = 9.2 Hz), 5.03 (s, 1H), 4.62 (m, 1H), 3.85 (m, 1H), 3.81 (s, 3H), 3.72 (m, 1H), 3.55 (s, 1H), 1.45 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 158.3, 156.7, 155.8, 142.7, 133.2, 130.5, 130.0, 129.0 (2C), 128.3 (2C), 123.3, 119.0 (2C), 114.7 (2C), 85.4, 81.3, 80.1, 61.5, 59.9, 55.5, 51.2, 23.3 (3C); IR (CH_2Cl_2): ν = 1729, 1707, 1511 cm^{-1}; HRMS (ES): calcd for $C_{26}H_{29}N_2O_5$ $[M+H]^+$: 449.2071; found: 449.2070.

2-Azetidinone-Fused Furan (–)-8b-D. From 150 mg (0.35 mmol) of deuterated (*E*)-1,3-enyne (+)-**4b**, and after flash chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave

compound (–)-**8b-D** (60 mg, 40%) as a colorless oil; $[\alpha]_D$ = –71.4 (*c* 0.02, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 7.38 (m, 5H), 7.14 (m, 3H), 6.43 (m, 2H), 4.63 (s, 1H), 4.58 (d, 1H, *J* = 15.5 Hz), 4.25 (dd, 1H, *J* = 3.2, 9.5 Hz), 4.13 (d, 1H, *J* = 10.4 Hz), 4.06 (dd, 1H, *J* = 3.7, 10.4 Hz), 3.96 (s, 1H), 3.75 (d, 1H, *J* = 15.5 Hz), 2.19 (m, 2.5H), 1.48 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 207.2, 165.8, 155.5, 134.2, 131.1, 129.5 (3C), 129.4 (2C), 128.7 (2C), 127.5, 127.3 (2C), 98.7, 79.8, 75.2, 63.9, 56.4, 50.6, 43.1, 31.1, 28.4 (3C); IR (CH_2Cl_2): ν = 3389, 2927, 1765, 1708 cm^{-1}; HRMS (ES): calcd for $C_{26}H_{29}DN_2NaO_5$ $[M+Na]^+$: 474.2110; found: 474.2109.

2-Azetidinone-Fused Furan (–)-8c-D. From 32 mg (0.06 mmol) of deuterated (*E*)-1,3-enyne (+)-**4c**, and after flash chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound (–)-**8c-D** (18 mg, 60%) as a colorless oil; $[\alpha]_D$ = –78.6 (*c* 0.01, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 7.35 (m, 5H), 6.63 (d, 2H, *J* = 8.6 Hz), 6.38 (d, 2H, *J* = 8.5 Hz), 4.62 (s, 1H), 4.49 (d, 1H, *J* = 15.3 Hz), 4.23 (dd, 1H, *J* = 2.8, 8.9 Hz), 4.11 (d, 1H, *J* = 10.4 Hz), 3.96 (dd, 1H, *J* = 3.6, 10.4 Hz), 3.93 (s, 1H), 3.78 (s, 3H), 3.69 (d, 1H, *J* = 15.5 Hz), 2.19 (m, 2.6H), 1.48 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 207.1, 165.6, 158.9, 155.5, 131.1, 129.5 (2C), 129.4 (2C), 128.7 (2C), 128.6, 126.2, 114.0 (2C), 98.5, 79.8, 75.2, 63.6, 56.3, 55.2, 50.6, 42.6, 31.1, 28.4 (3C); IR (CH_2Cl_2): ν = 3395, 2976, 2927, 1760, 1706, 1513 cm^{-1}; HRMS (ES): calcd for $C_{27}H_{31}DN_2NaO_6$ $[M+Na]^+$: 504.2215; found: 504.2226.

Reaction of Bromo-Enyne (+)-5a. From 113 mg (0.20 mmol) of bromo-enyne (+)-**5a**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent, 23 mg (22%) of the more polar compound (–)-**9a-Br** and 40 mg (42%) of the less polar compound (+)-**10a-Br** were obtained.

2-Azetidinone-Fused Tetrahydropyridine (–)-9a-Br. Pale brown solid; m.p. 142–143 ºC; $[\alpha]_D$ = –35.7 (*c* 0.02, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 8.01 (m, 2H), 7.59 (d, 2H, *J* = 8.6 Hz), 7.42 (m, 3H), 6.94 (d, 2H, *J* = 8.8 Hz), 5.23 (d, 1H, *J* = 8.6 Hz), 4.98 (d, 1H, *J* = 2.0 Hz), 4.55 (m, 1H), 3.81 (s, 3H), 3.78 (m, 2H), 1.48 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 158.0, 156.8,

155.9, 142.6, 133.3, 130.4, 130.0, 129.0 (2C), 128.3 (2C), 123.8, 119.0 (2C), 114.8 (2C), 80.1, 78.4, 61.3, 60.2, 58.9, 55.5, 51.1, 28.4 (3C); IR (CH_2Cl_2): ν = 2923, 2849, 1729, 1709, 1511 cm^{-1}; HRMS (ES): calcd for $C_{26}H_{27}BrN_2NaO_5$ [*M*+Na]$^+$: 549.0996; found: 549.1001.

2-Azetidinone-Fused Tetrahydropyridine (+)-10a-Br. Colorless oil; $[\alpha]_D$ = +66.2 (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 7.51 (m, 2H), 7.43 (m, 3H), 7.26 (m, 2H), 6.92 (d, 2H, *J* = 8.9 Hz), 6.08 (s, 1H), 5.28 (d, 1H, *J* = 6.7 Hz), 4.81 (m, 1H), 3.95 (m, 2H), 3.82 (s, 3H), 1.64 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 159.3, 156.8, 152.2, 135.6, 133.2, 132.0, 130.9, 130.1 (3C), 128.4 (2C), 118.1 (2C), 114.8 (2C), 104.8, 94.7, 64.8, 62.0, 58.0, 55.5, 24.6, 23.3; IR (CH_2Cl_2): ν = 1740, 1510 cm^{-1}.

Reaction of Bromo-Enyne (+)-5b. From 140 mg (0.25 mmol) of bromo-enyne (+)-**5b**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent, 34 mg (25%) of the more polar compound (–)-**9b-Br** and 43 mg (37%) of less polar compound (+)-**10b-Br** were obtained.

2-Azetidinone-Fused Tetrahydropyridine (–)-9b-Br. Colorless oil; $[\alpha]_D$ = –31.3 (*c* 0.02, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 7.49 (m, 2H), 7.35 (m, 8H), 5.59 (s, 1H), 5.14 (d, 1H, *J* = 8.5 Hz), 4.92 (d, 1H, *J* = 15.1 Hz), 4.39 (dd, 1H, *J* = 4.4, 12.8 Hz), 4.27 (m, 2H), 4.15 (m, 2H), 1.50 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 161.2, 157.1, 154.7, 136.6, 135.6, 132.7, 132.1, 129.9 (2C), 129.7, 128.8 (2C), 128.7 (2C), 128.3 (2C), 127.8, 98.4, 80.2, 74.9, 62.9, 53.5, 45.4, 28.4 (3C); IR (CH_2Cl_2): ν = 2981, 1736, 1709 cm^{-1}; HRMS (ES): calcd for $C_{26}H_{27}BrN_2NaO_4$ [*M*+Na]$^+$: 533.1046; found: 533.1061.

2-Azetidinone-Fused Tetrahydropyridine (+)-10b-Br. Colorless oil; $[\alpha]_D$ = +354.5 (*c* 0.02, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 7.53 (m, 2H), 7.35 (m, 8H), 5.86 (s, 1H), 5.13 (d, 1H, *J* = 15.6 Hz), 4.54 (d, 1H, *J* = 5.4 Hz), 4.50 (dd, 1H, *J* = 4.1, 5.4 Hz), 4.04 (m, 3H), 1.59 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 163.3, 151.7, 148.4, 135.8, 135.2, 134.4, 133.0,

130.3, 130.1, 129.2 (2C), 128.4 (2C), 128.3 (2C), 128.2, 102.4, 94.5, 64.6, 63.0, 58.0, 46.6, 24.3, 23.7; IR (CH_2Cl_2): ν = 2923, 1743 cm^{-1}.

2-Azetidinone-Fused Tetrahydropyridine (+)-10c-Br. From 68 mg (0.14 mmol) of bromo-enyne (+)-**5c**, and after flash chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent gave compound (+)-**10c-Br** (24 mg, 43%) as a colorless oil; $[\alpha]_D$ = +178.3 (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 7.53 (m, 2H), 7.42 (m, 3H), 7.19 (d, 2H, *J* = 8.6 Hz), 6.93 (d, 2H, *J* = 8.6 Hz), 5.85 (s, 1H), 5.05 (d, 1H, *J* = 15.2 Hz), 4.49 (m, 2H), 4.04 (d, 1H, *J* = 1.5 Hz), 4.03 (m, 1H), 3.98 (d, 1H, *J* = 15.2 Hz), 3.83 (s, 3H), 1.59 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 163.3, 159.5, 151.8, 148.5, 135.8, 135.1, 133.0, 130.3, 130.1, 129.7 (2C), 128.2 (2C), 126.6, 114.6 (2C), 102.3, 94.5, 64.7, 62.7, 58.0, 55.3, 46.1, 24.2, 23.7; IR (CH_2Cl_2): ν = 2986, 2934, 1736 cm^{-1}.

2-Azetidinone-Fused Tetrahydropyridine (+)-9a-PMP. From 69 mg (0.12 mmol) of PMP-functionalized (*E*)-1,3-enyne (–)-**6a**, and after flash chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound (+)-**9a-PMP** (43 mg, 65%) as a pale yellow oil; $[\alpha]_D$ = +8.6 (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 8.09 (m, 2H), 7.60 (d, 4H, *J* = 8.6 Hz), 7.43 (m, 3H), 6.93 (m, 4H), 5.41 (d, 1H, *J* = 9.0 Hz), 4.99 (d, 1H, *J* = 1.6 Hz), 4.64 (m, 1H), 3.85 (s, 3H), 3.81 (m, 2H), 3.80 (s, 3H), 1.41 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 160.7, 158.6, 156.6, 145.9, 139.6, 134.0, 133.7 (2C), 130.6, 129.8, 129.1 (2C), 128.2 (2C), 124.9, 118.9 (2C), 114.7 (2C), 114.3 (2C), 113.7, 86.3, 80.1, 77.2, 61.8, 60.7, 55.5, 55.4, 51.3, 28.3 (3C); IR (CH_2Cl_2): ν = 2932, 1726, 1709, 1511 cm^{-1}; HRMS (ES): calcd for $C_{33}H_{35}N_2O_6$ $[M+H]^+$: 555.2490; found: 555.2487.

2-Azetidinone-Fused Tetrahydropyridine (+)-9b-PMP. From 95 mg (0.16 mmol) of PMP-functionalized (*E*)-1,3-enyne (+)-**6b**, and after flash chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound (+)-**9b-PMP** (40 mg, 47%) as a colorless oil; $[\alpha]_D$ = +27.3 (*c* 0.04, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 8.05 (m, 2H), 7.31 (m, 10H),

6.80 (d, 2H, *J* = 8.9 Hz), 4.99 (d, 1H, *J* = 8.5 Hz), 4.81 (d, 1H, *J* = 15.0 Hz), 4.42 (m, 1H), 4.23 (m, 2H), 3.76 (m, 1H), 3.75 (s, 3H), 3.66 (m, 1H), 1.30 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 162.7, 160.5, 156.2, 140.6, 135.7, 133.8, 133.5 (2C), 129.7, 129.0 (2C), 128.9 (2C), 128.5 (2C), 128.4 (2C), 128.0, 124.6, 114.2 (2C), 113.8, 98.0, 85.2, 80.1, 63.9, 60.5, 55.3, 52.0, 46.1, 28.2 (3C); IR (CH_2Cl_2): ν = 2976, 2932, 1729, 1713 cm^{-1}; HRMS (ES): calcd for $C_{33}H_{34}N_2NaO_5$ [*M*+Na]$^+$: 561.2360; found: 561.2367.

2-Azetidinone-Fused Tetrahydropyridine (+)-9c-PMP. From 51 mg (0.09 mmol) of PMP-functionalized (*E*)-1,3-enyne (+)-**6c**, and after flash chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound (+)-**9c-PMP** (30 mg, 60%) as a colorless oil; $[\alpha]_D$ = +55.5 (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 8.12 (d, 2H, *J* = 6.6 Hz), 7.47 (m, 6H), 7.27 (m, 3H), 6.88 (d, 2H, *J* = 8.8 Hz), 5.06 (d, 1H, *J* = 7.9 Hz), 4.84 (d, 1H, *J* = 14.9 Hz), 4.49 (m, 1H), 4.29 (m, 1H), 4.24 (d, 1H, *J* = 14.9 Hz), 3.82 (s, 3H), 3.81 (m, 1H), 3.80 (s, 3H), 3.75 (m, 1H), 1.39 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 162.7, 160.5, 159.3, 156.2, 140.6, 133.8, 133.5 (2C), 129.9 (2C), 129.7, 129.0 (2C), 128.3 (2C), 127.8 (2C), 114.3 (2C), 114.2 (2C), 113.8, 98.0, 85.2, 80.1, 64.0, 60.2, 55.3, 55.2, 52.0, 45.6, 28.2 (3C); IR (CH_2Cl_2): ν = 2973, 2932, 1758, 1717, 1510 cm^{-1}; HRMS (ES): calcd for $C_{34}H_{37}N_2O_6$ [*M*+H]$^+$: 569.2646; found: 569.2626.

2-Azetidinone-Fused Tetrahydropyridine (+)-9a-Alkyn. From 100 mg (0.17 mmol) of enediyne (–)-**7a**, and after flash chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound (+)-**9a-Alkyn** (49 mg, 52%) as a pale yellow oil; $[\alpha]_D$ = +50.0 (*c* 0.01, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 8.04 (m, 2H), 7.59 (m, 4H), 7.41 (m, 6H), 6.95 (d, 2H, *J* = 8.9 Hz), 5.27 (d, 1H, *J* = 9.2 Hz), 5.04 (d, 1H, *J* = 1.9 Hz), 4.60 (m, 1H), 3.82 (m, 2H), 3.81 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 158.0, 156.8, 155.9, 143.4, 133.3, 132.7 (2C), 130.5, 130.0, 129.9, 129.0 (2C), 128.5 (2C), 128.3 (2C), 123.4, 121.0 (2C), 119.0, 114.7 (2C), 85.2, 81.7,

80.1, 78.7, 73.4, 61.4, 60.3, 55.5, 51.2, 28.3 (3C); IR (CH_2Cl_2): ν = 2931, 2208, 1731, 1709, 1510 cm^{-1}; HRMS (ES): calcd for $C_{34}H_{33}N_2O_5$ $[M+H]^+$: 549.2384; found: 549.2409.

2-Azetidinone-Fused Tetrahydropyridine (+)-9b-Alkyn. From 90 mg (0.14 mmol) of enediyne (+)-**7b**, and after flash chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound (+)-**9b-Alkyn** (43 mg, 58%) as a colorless oil; $[\alpha]_D$ = +15.0 (*c* 0.04, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 8.06 (m, 2H), 7.53 (m, 2H), 7.37 (m, 11H), 4.95 (d, 1H, *J* = 8.3 Hz), 4.88 (d, 1H, *J* = 15.1 Hz), 4.45 (m, 1H), 4.35 (d, 1H, *J* = 15.1 Hz), 4.31 (m, 1H), 3.76 (m, 2H), 1.39 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 162.2, 155.9 (2C), 144.6, 135.7, 133.1, 132.6 (2C), 129.9, 129.7, 129.0 (2C), 128.9 (2C), 128.5 (2C), 128.5 (2C), 128.3 (2C), 128.0, 121.0, 81.5, 81.4, 80.0, 77.7, 73.2, 63.7, 60.6, 51.7, 46.2, 28.2 (3C); IR (CH_2Cl_2): ν = 2922, 2851, 2210, 1740, 1720 cm^{-1}; HRMS (ES): calcd for $C_{34}H_{32}N_2NaO_4$ $[M+Na]^+$: 555.2254; found: 555.2273.

2-Azetidinone-Fused Tetrahydropyridine (+)-9c-Alkyn. From 70 mg (0.12 mmol) of enediyne (+)-**7c**, and after flash chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound (+)-**9c-Alkyn** (33 mg, 51%) as a colorless oil; $[\alpha]_D$ = +99.8 (*c* 0.01, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 8.06 (m, 2H), 7.53 (m, 4H), 7.36 (m, 6H), 6.89 (d, 2H, *J* = 8.6 Hz), 4.93 (d, 1H, *J* = 7.6 Hz), 4.84 (d, 1H, *J* = 14.9 Hz), 4.44 (m, 1H), 4.27 (m, 2H), 3.82 (m, 1H), 3.80 (s, 3H), 3.76 (m, 1H), 1.40 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 162.1, 159.3, 144.7, 134.2, 134.1, 132.6 (2C), 132.0, 129.9 (2C), 129.8, 129.3, 129.1, 128.9 (2C), 128.5 (2C), 128.4 (2C), 127.7, 121.0, 114.4 (2C), 84.7, 81.5, 80.1, 73.3, 63.9, 60.3, 55.3, 51.8, 45.7, 28.2 (3C); IR (CH_2Cl_2): ν = 2928, 2209, 17528, 1717, 1512 cm^{-1}; HRMS (ES): calcd for $C_{35}H_{35}N_2O_5$ $[M+H]^+$: 563.2540; found: 563.2516.

Procedure for the Preparation of Aldehyde (+)-11a. A solution of alcohol (+)-**9a** (150 mg, 0.33 mmol) in dichloromethane (0.31 mL) was added to a solution of DMP (103 mg, 0.24 mmol) in dichloromethane (1.3 mL) with stirring. After disappearance of the starting material (TLC), the

homogeneous reaction mixture was diluted with 2 mL of ethyl acetate and the resulting suspension was added to 0.63 mL of 1M sodium hydroxide. The organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with hexanes/ethyl acetate (1:1) gave 83 mg (54%) of analytically pure compound (+)-**11a**.

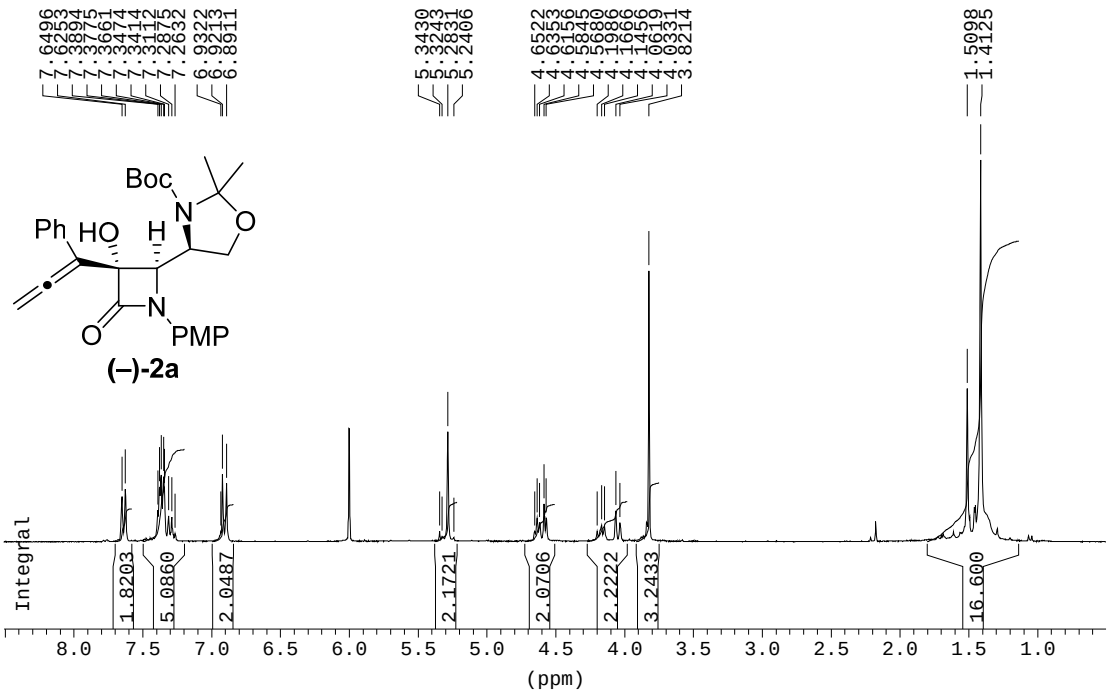
2-Azetidinone-Fused Tetrahydropyridine (+)-11a. Yellow oil; $[\alpha]_D$ = +70.5 (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 9.75 (s, 1H), 8.12 (m, 2H), 7.43 (m, 5H), 6.94 (d, 2H, *J* = 8.9 Hz), 5.25 (m, 3H), 3.82 (s, 3H), 3.61 (s, 1H), 1.41 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 198.9, 157.9, 157.1, 155.4, 141.2, 132.9, 130.3, 129.9, 129.0 (2C), 128.4 (2C), 128.3, 119.5 (2C), 114.9 (2C), 86.6, 80.9, 80.0, 58.8, 58.4, 55.5, 28.2 (3C); IR (CH_2Cl_2): ν = 1729, 1707, 1690, 1511 cm^{-1}; HRMS (ES): calcd for $C_{26}H_{27}N_2O_5$ [*M*+H]$^+$: 447.1914; found: 447.1879.

Procedure for the Preparation of Amino Alcohol (+)-11a-Br. CF_3COOH (23.8 mg, 0.21 mmol) was added dropwise to a stirred solution of the NBoc derivative (100 mg, 0.19 mmol) in dichloromethane (0.20 mL) at rt. The mixture was stirred at rt until disappearance of the starting material (TLC). Then, the mixture was poured into water (5 mL) and extracted with ethyl acetate (3 x 10 mL). The organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with hexanes/ethyl acetate (1:1) gave 67 mg (83%) of analytically pure compound (+)-**11a-Br**.

2-Azetidinone-Fused Tetrahydropyridine (+)-11a-Br. Yellow oil; $[\alpha]_D$ = +16.1 (*c* 0.02, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 7.77 (d, 2H, *J* = 9.1 Hz), 7.51 (m, 2H), 7.42 (m, 3H), 6.91 (d, 2H, *J* = 9.1 Hz), 5.63 (s, 1H), 4.61 (d, 1H, *J* = 4.8 Hz), 4.46 (dd, 1H, *J* = 3.5, 12.4 Hz), 4.21 (d, 1H, *J* = 12.4 Hz), 3.81 (s, 3H), 3.43 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 158.1, 157.5, 156.3, 135.7, 133.0, 132.7, 131.8 (2C), 130.1, 129.8, 128.3 (2C), 118.7 (2C), 114.5 (2C), 98.1, 78.3, 66.1, 55.5, 54.2; IR (CH_2Cl_2): ν = 2923, 2852, 1739, 1511 cm^{-1}; HRMS (ES): calcd for $C_{21}H_{19}BrN_2NaO_3$ [*M*+Na]$^+$: 449.0471; found: 449.0457.

Procedure for the Preparation of Ester (–)-11b-Alkyn. 4-Nitrobenzoyl chloride (10.4 mg, 0.056 mmol), DMAP (cat.), and triethylamine (11.4 mg, 0.11 mmol) were sequentially added dropwise to a stirred solution of the appropriate alcohol 2 (0.047 mmol) in dichloromethane (0.48 mL) at 0ºC, and the mixture was stirred at room temperature until disappearance of the starting material (TLC). Then, the mixture was poured into water (1 mL) and extracted with ethyl acetate (3 x 8 mL). The organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with hexanes/ethyl acetate (5:1) gave 46 mg (64%) of analytically pure compound (–)-**11b-Alkyn**.

2-Azetidinone-Fused Tetrahydropyridine (–)-11b-Alkyn. Yellow solid; m.p. 164–165 ºC; $[\alpha]_D$ = –12.0 (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 8.09 (m, 6H), 7.40 (m, 13H), 5.02 (d, 1H, *J* = 9.6 Hz), 4.87 (d, 1H, *J* = 15.2 Hz), 4.73 (m, 1H), 4.39 (m, 4H), 1.37 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 164.3, 161.5, 155.1, 150.5, 144.1, 135.1, 134.8, 132.8, 132.6 (2C), 130.8 (2C), 130.2, 130.0 (2C), 129.2 (2C), 128.9 (2C), 128.5 (2C), 128.5, 128.4 (2C), 123.6, 123.4 (2C), 120.7, 85.1, 81.6, 81.4, 80.2, 77.2, 73.0, 64.6, 59.9, 48.8, 46.2, 28.2 (3C); IR (CH_2Cl_2): ν = 2975, 2928, 2210, 1732 cm^{-1}; HRMS (ES): calcd for $C_{41}H_{36}N_3O_7$ $[M+H]^+$: 682.2548; found: 682.2513.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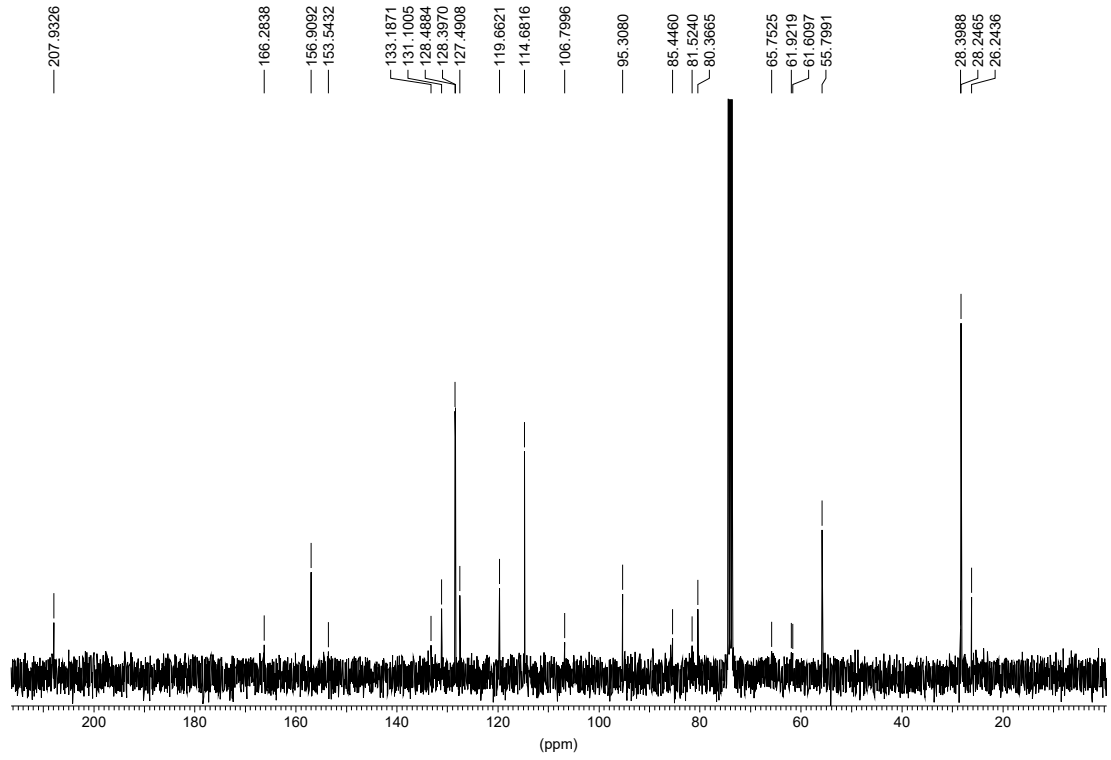
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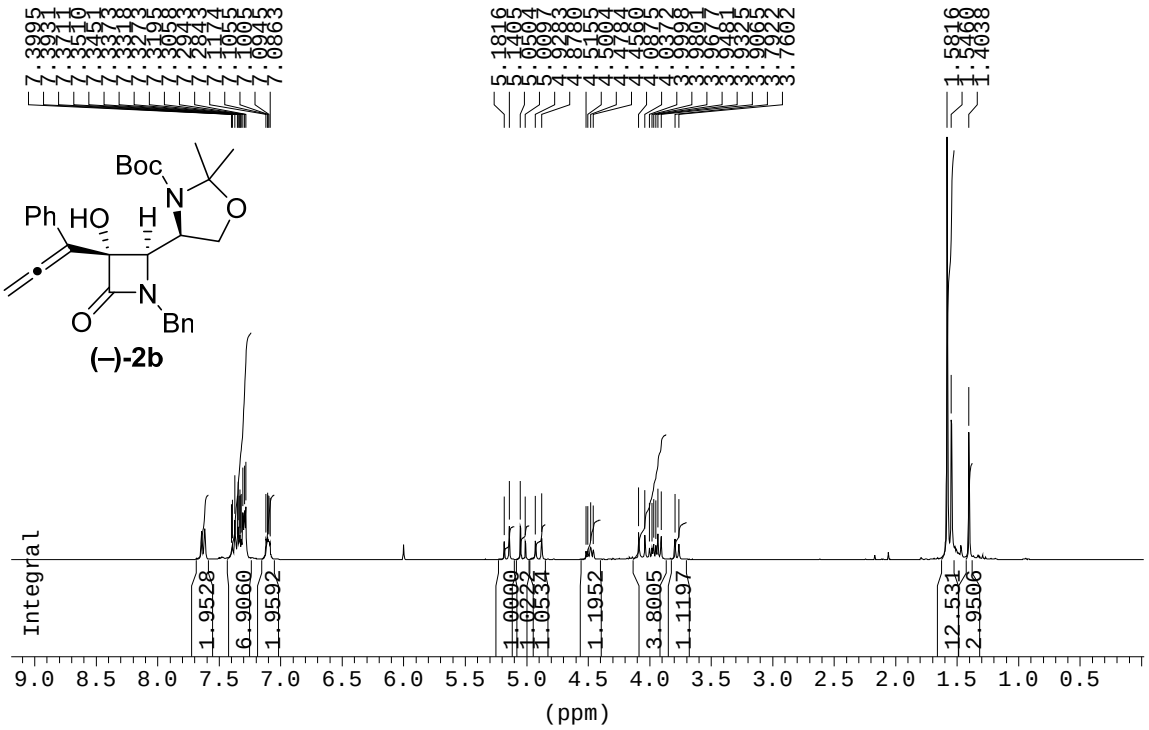
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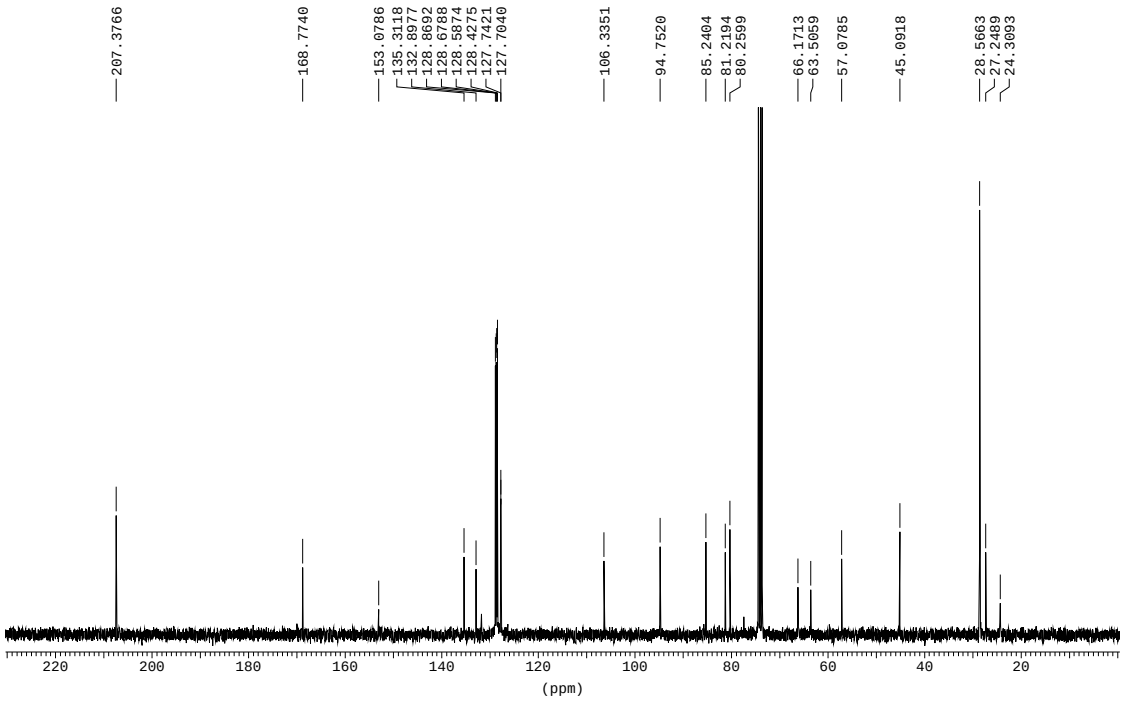
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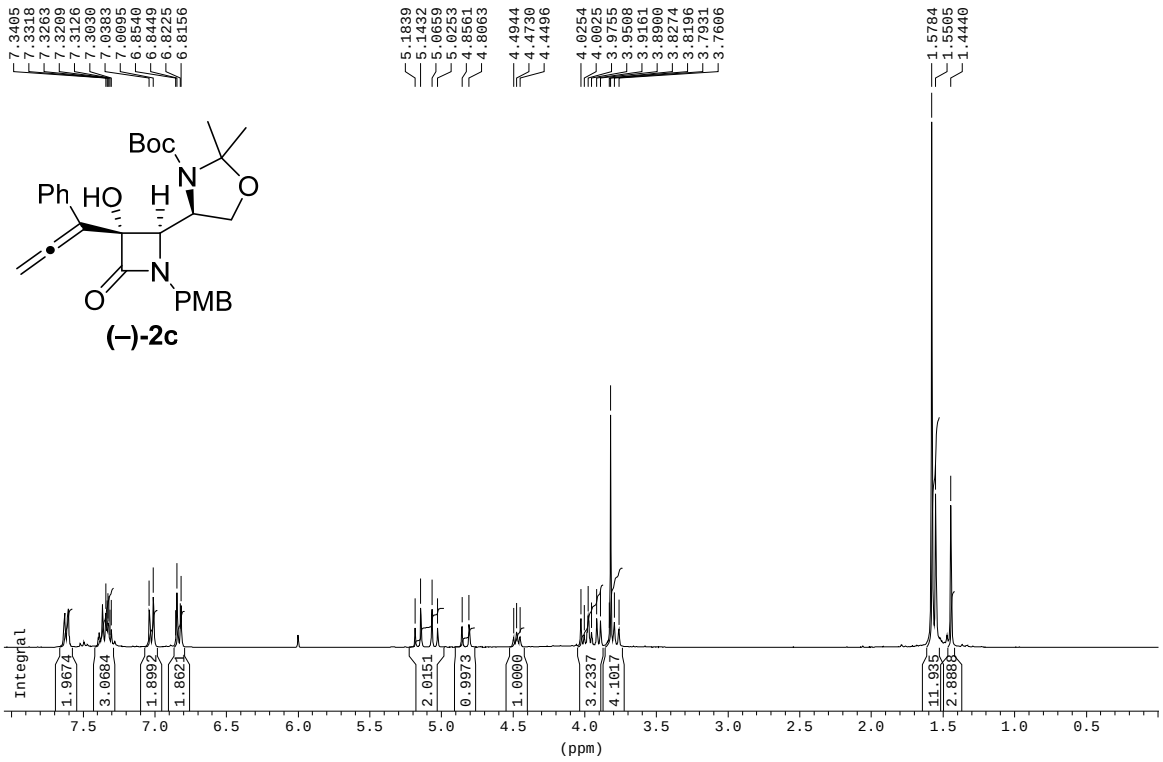
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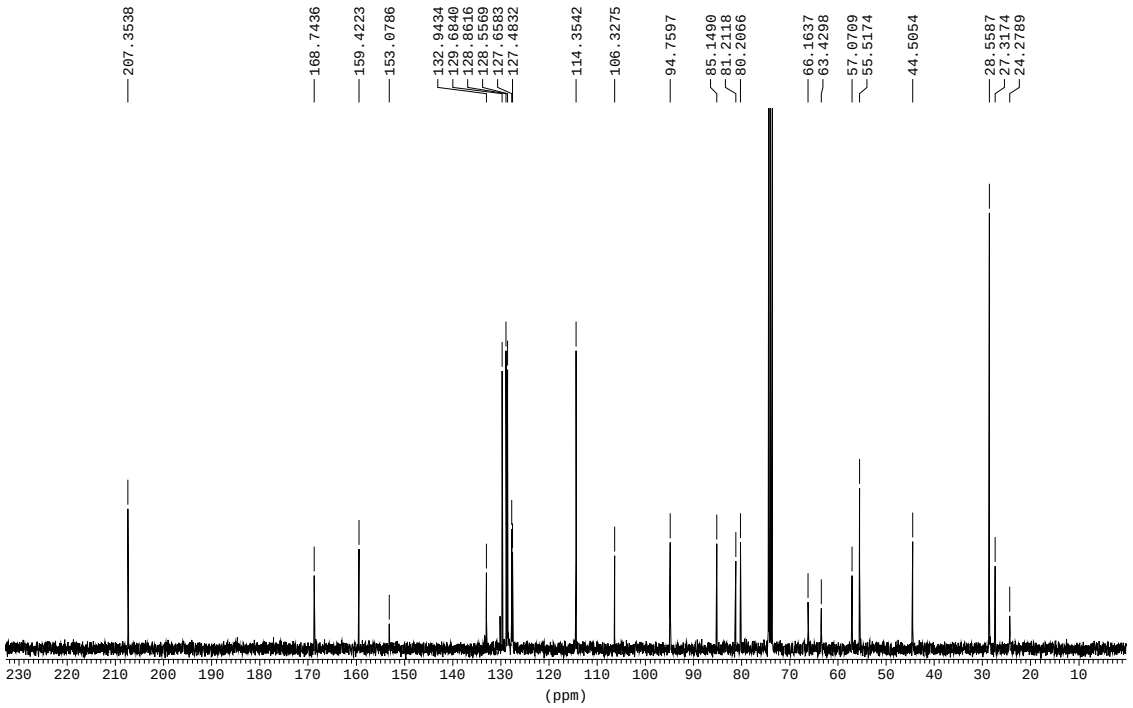
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106.3275
94.7597
85.1490
81.2118
80.2066
66.1637
63.4298
57.0709
55.5174
44.5054
28.5587
27.3174
24.2789
230
220
210
200
190
180
170
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150
140
130
120
110
100
90
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60
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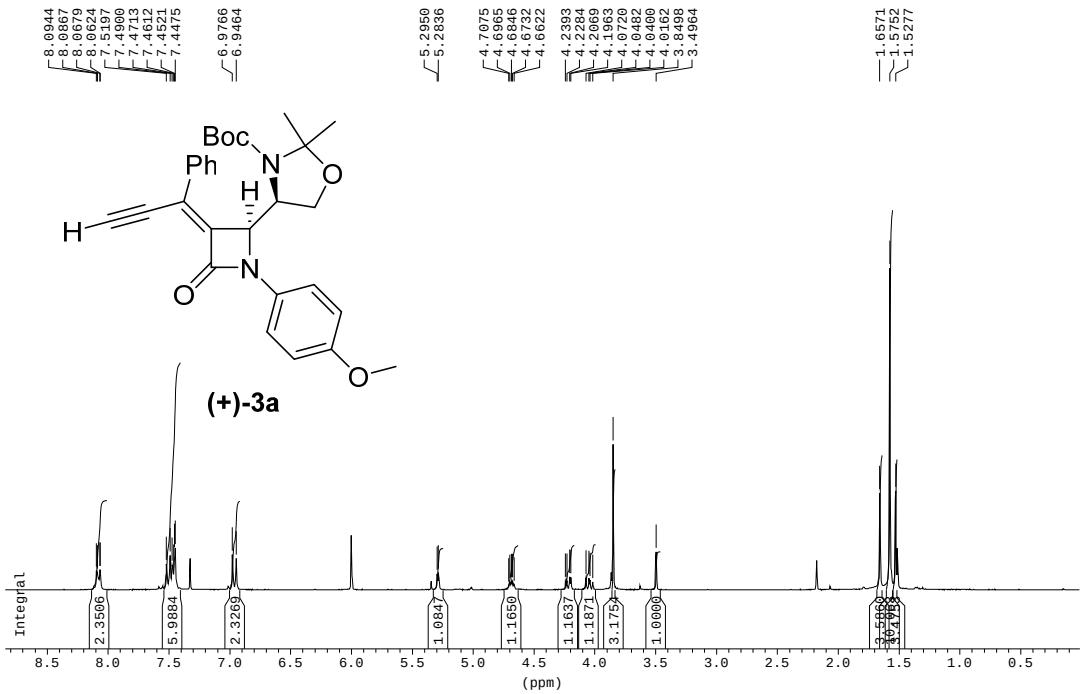
20
10
(ppm)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7.4713
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7.4521
7.4475
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6.9464
5.2950
5.2836
4.7075
4.6965
4.6846
4.6732
4.6622
4.2393
4.2284
4.2069
4.1963
4.0720
4.0482
4.0400
4.0162
3.8498
3.4964
1.6571
1.5752
1.5277
Boc
Ph
H
N
O
H
N
O
O
(+)-3a
Integral
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2.3269
1.0847
1.1650
1.1637
1.1871
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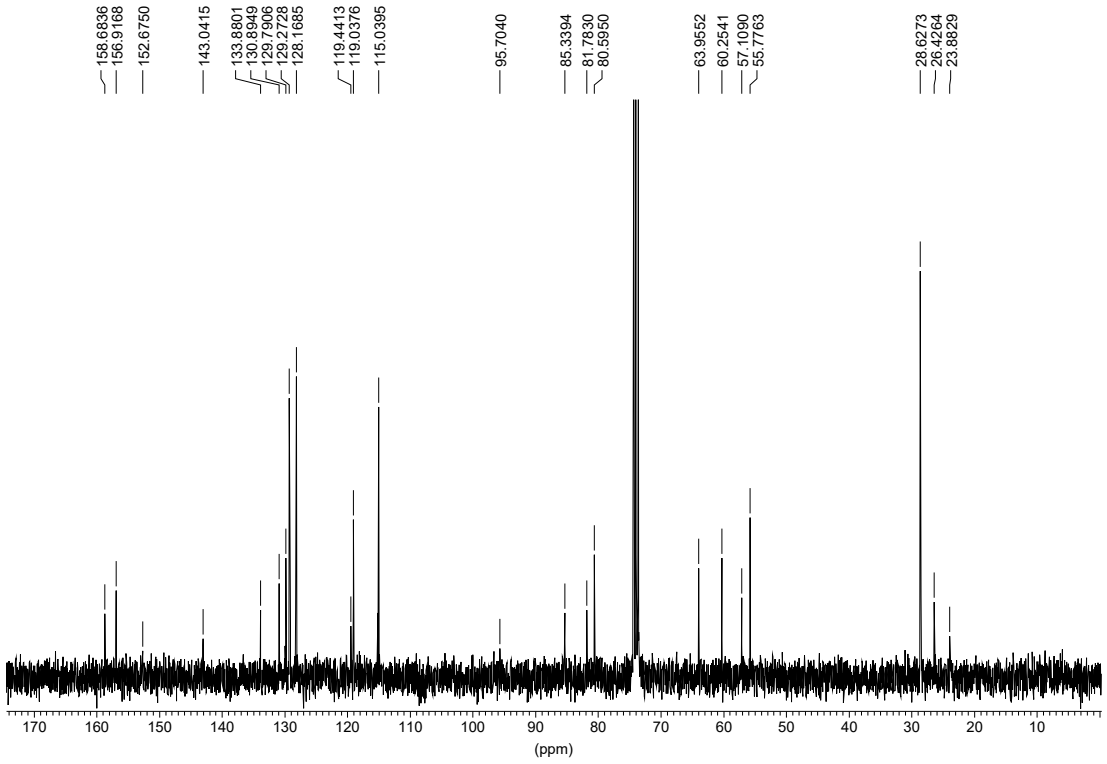
(ppm)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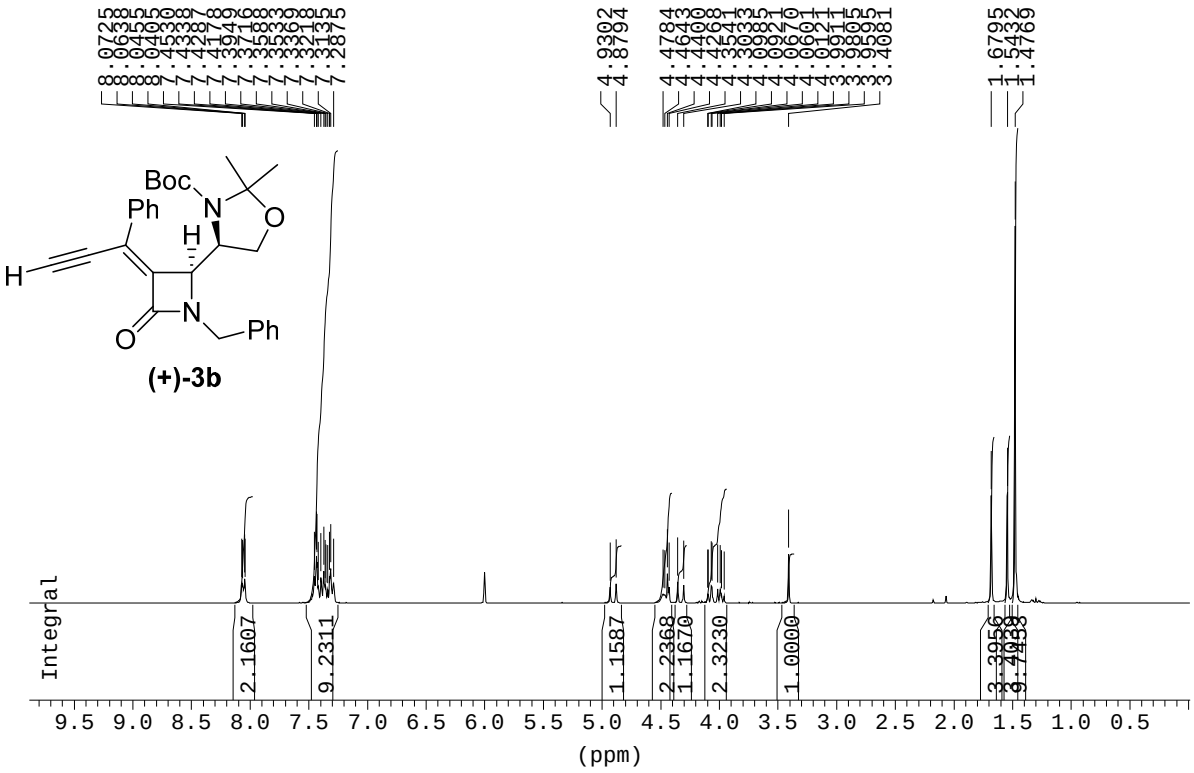
152.6750
143.0415
133.8801
130.8949
129.7906
129.2728
128.1685
119.4413
119.0376
115.0395
95.7040
85.3394
81.7830
80.5950
63.9552
60.2541
57.1090
55.7763
28.6273
26.4264
23.8829
(ppm)


Boc
Ph
N
O
H
H
N
O
Ph
(+)-3b
Integral
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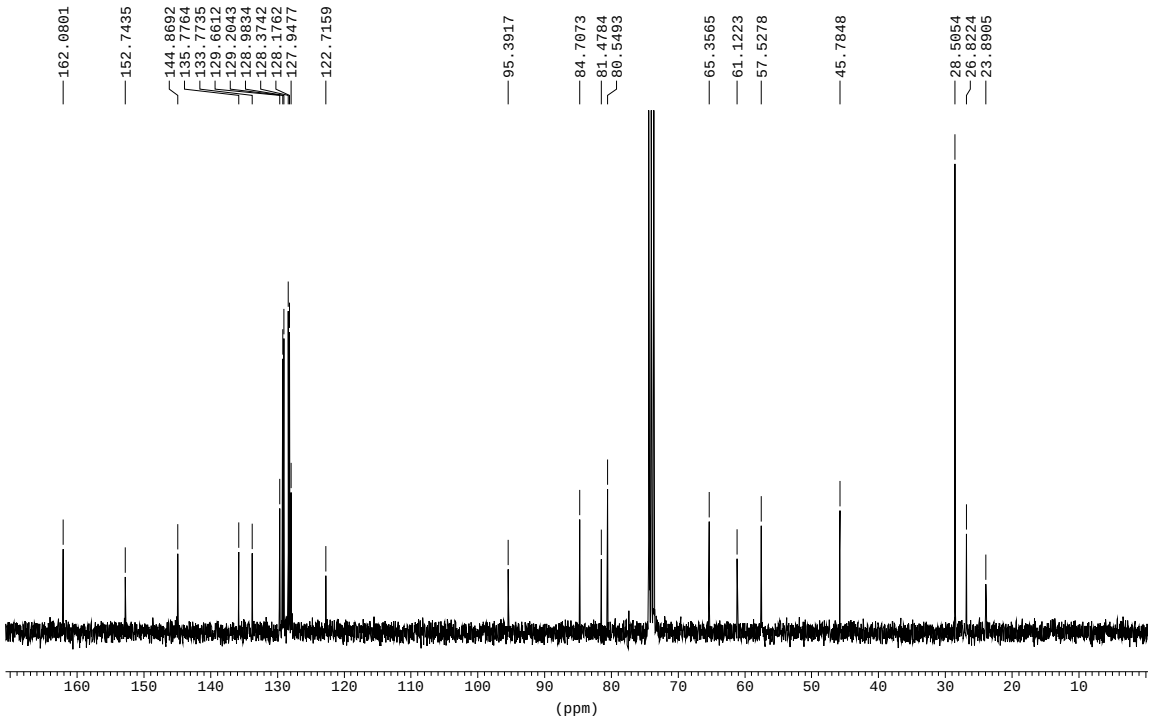
(ppm)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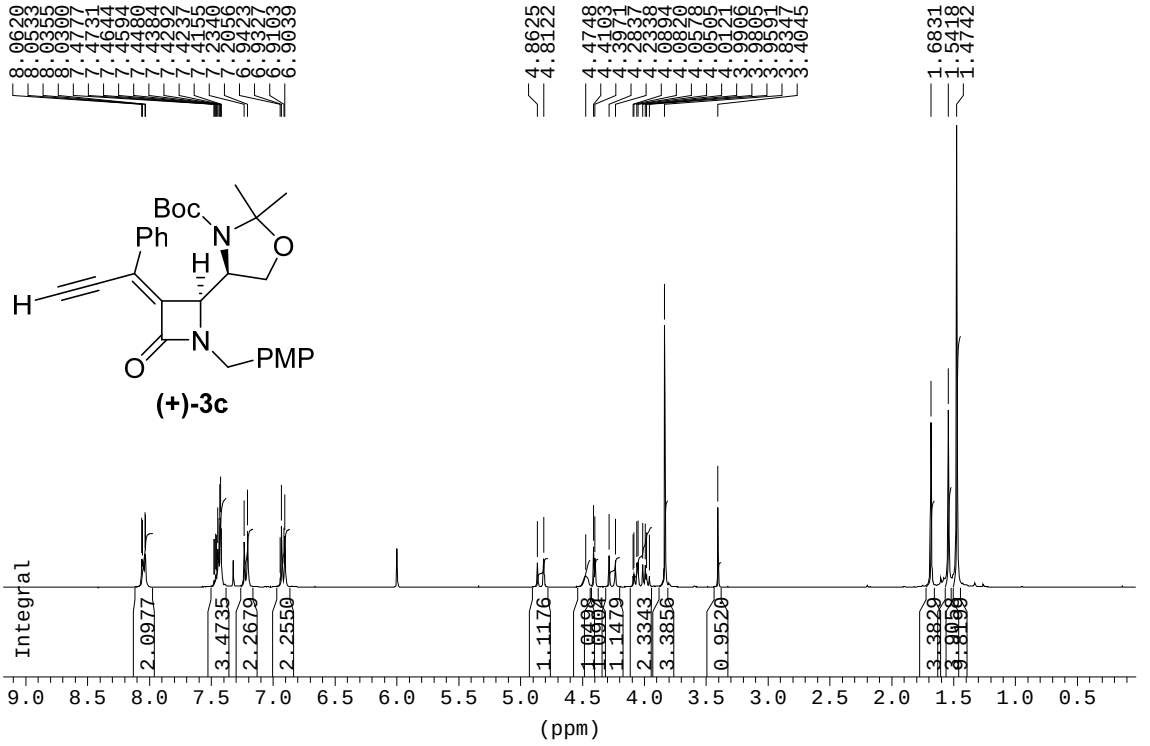
128.9934
128.3742
128.1762
127.9477
122.7159
95.3917
84.7073
81.4784
80.5493
65.3565
61.1223
57.5278
45.7848
28.5054
26.8224
23.8905
(ppm)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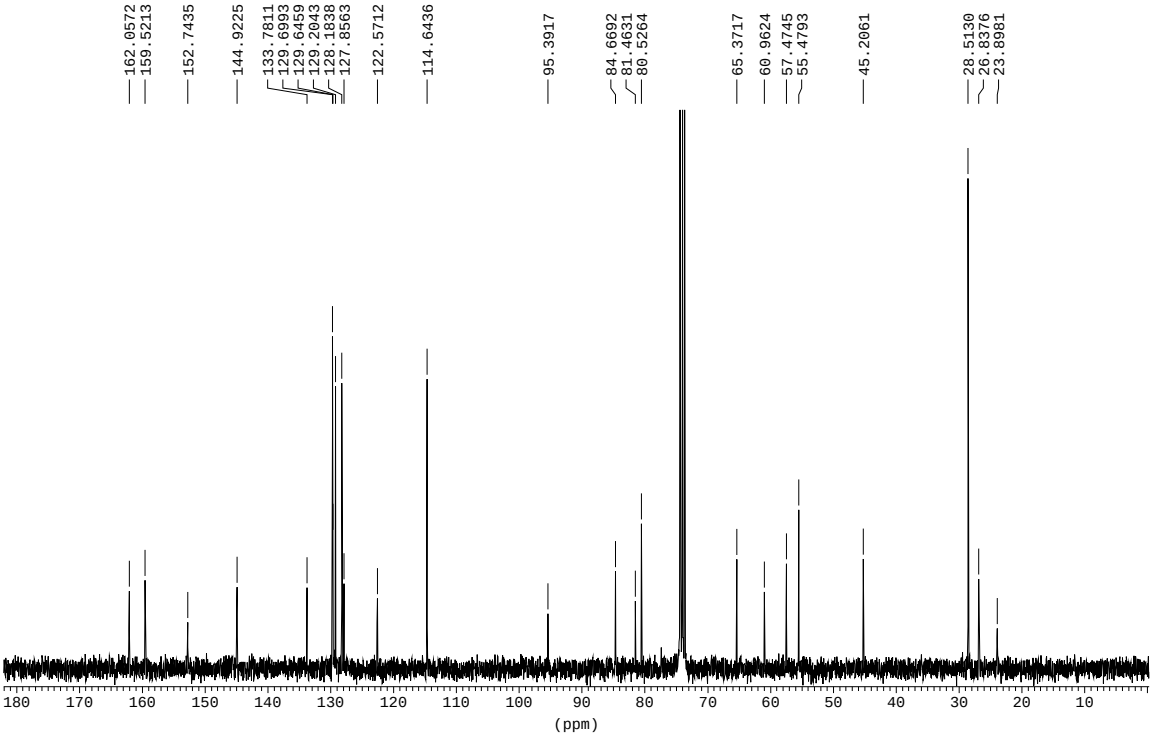
8.0533
8.0555
8.0399
7.4771
7.4731
7.4644
7.4594
7.4480
7.4384
7.4292
7.4237
7.4155
7.2340
7.2056
6.9423
6.9103
6.9039
4.8625
4.8122
4.4748
4.4103
4.3071
4.2837
4.2338
4.0894
4.0820
4.0578
4.0505
4.0121
3.9906
3.9805
3.9591
3.8347
3.4045
1.6831
1.5418
1.4742
Boc
Ph
N
O
H
H
N
PMP
O
(+)-3c
Integral
2.0977
3.4735
2.2679
2.2550
1.1176
1.0498
1.0902
1.1479
2.3343
3.3856
0.9520
3.3829
3.8053
3.8139
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)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128.1838
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122.5712
114.6436
95.3917
84.6692
81.4631
80.5264
65.3717
60.9624
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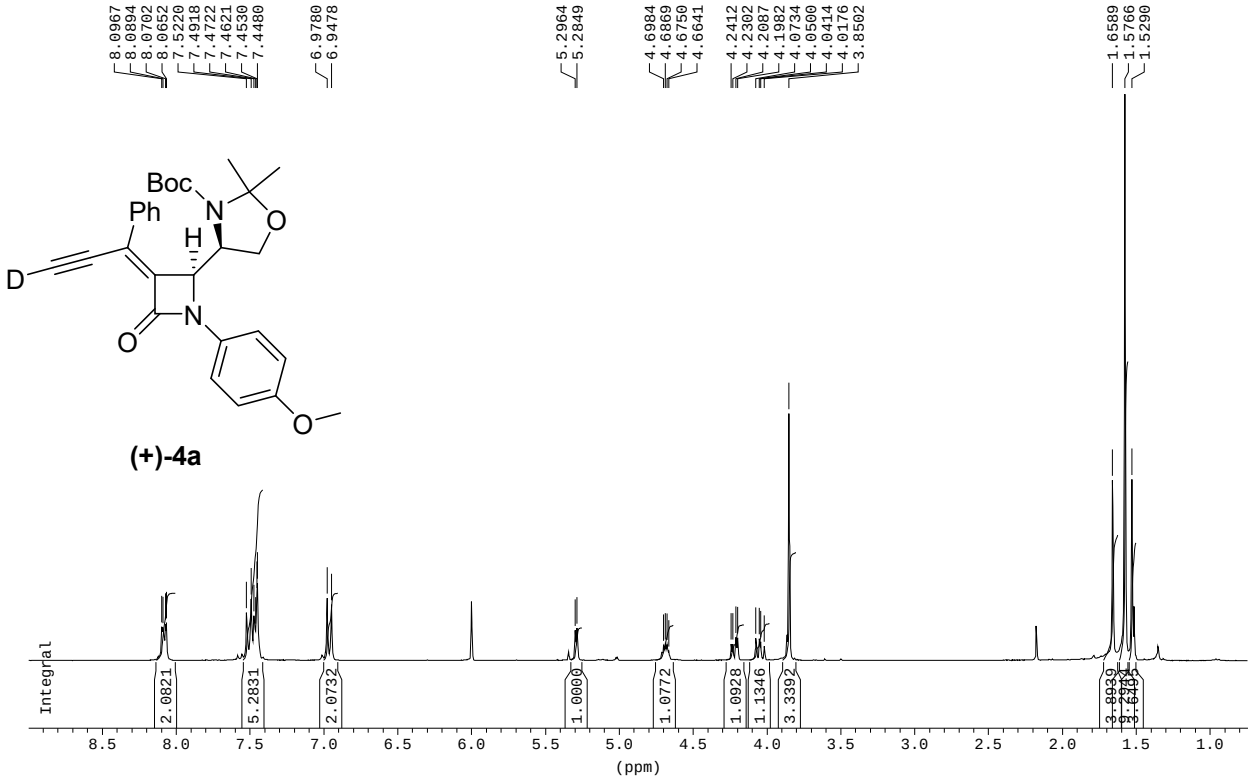
55.4793
45.2061
28.5130
26.8376
23.8981
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)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8.0702
8.0652
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7.4918
7.4722
7.4621
7.4530
7.4480
6.9780
6.9478
5.2964
5.2849
4.6984
4.6869
4.6750
4.6641
4.2412
4.2302
4.2087
4.1982
4.0734
4.0500
4.0414
4.0176
3.8502
1.6589
1.5766
1.5290
Boc
Ph
N
O
H
D
N
O
O
(+)-4a
Integral
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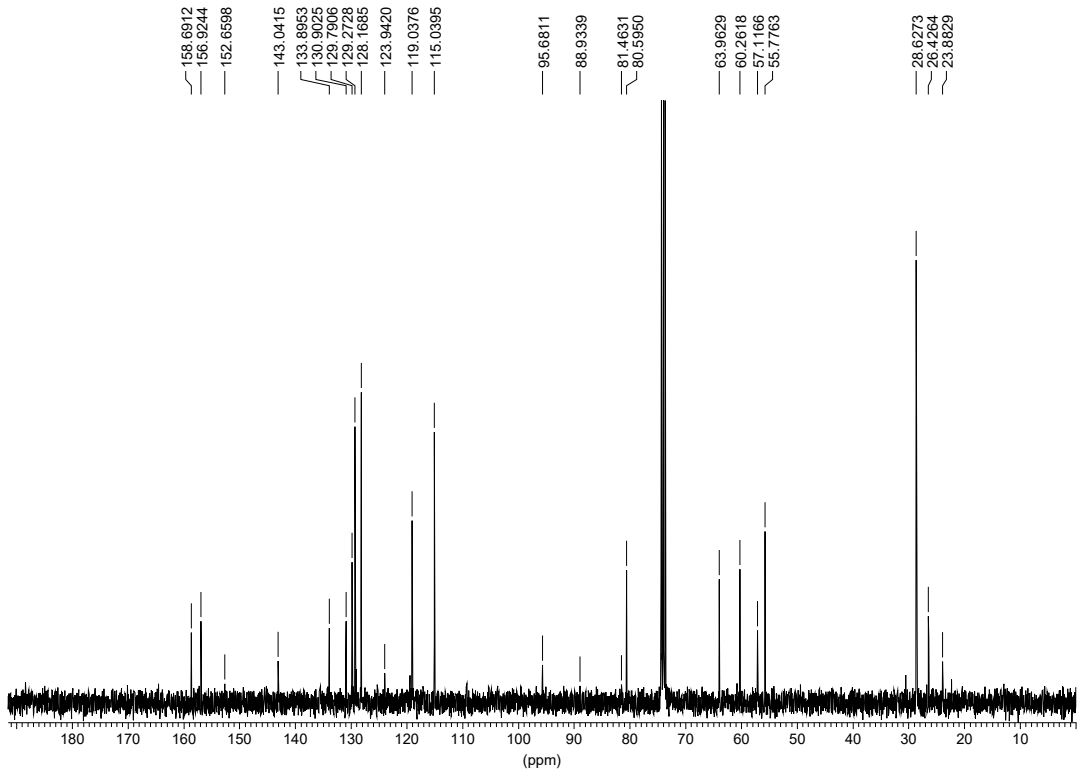
5.2831
2.0732
1.0000
1.0772
1.0928
1.1346
3.3392
(ppm)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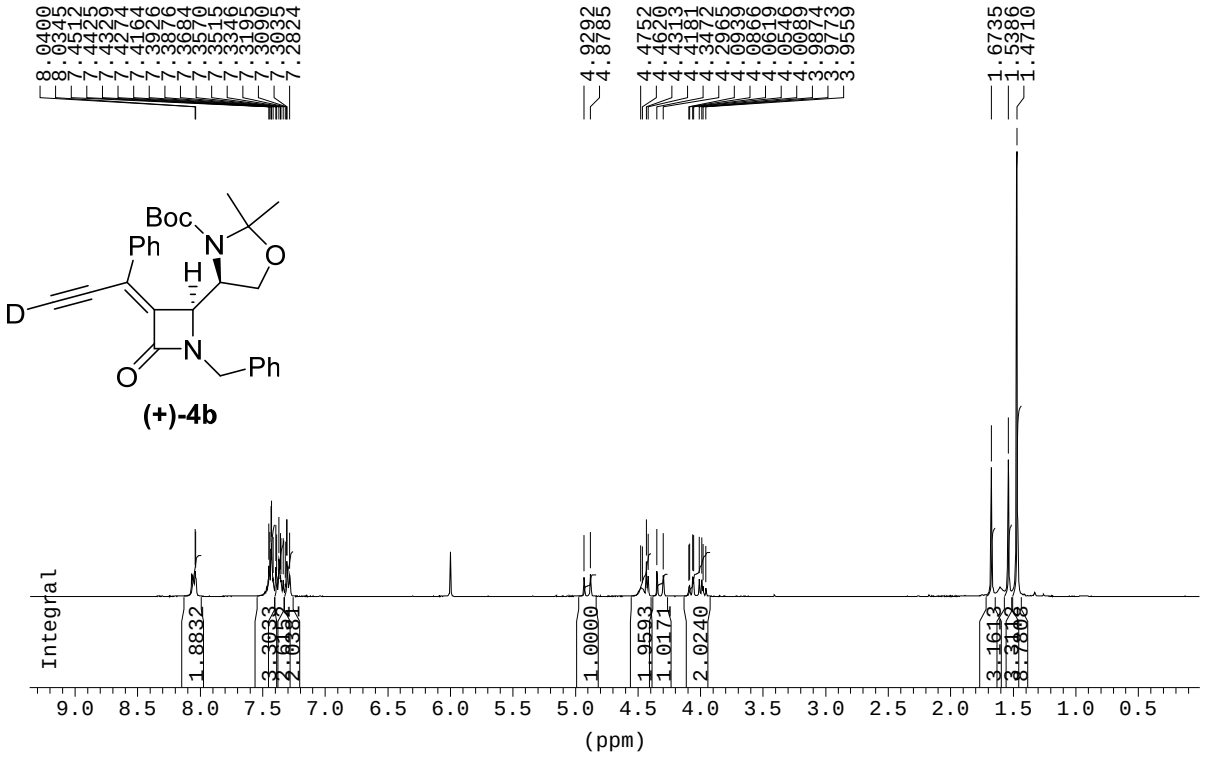
152.6598
143.0415
133.8953
130.9025
129.7906
129.2728
128.1685
123.9420
119.0376
115.0395
95.6811
88.9339
81.4631
80.5950
63.9629
60.2618
57.1166
55.7763
28.6273
26.4264
23.8829
(ppm)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7.4512
7.4425
7.4329
7.4274
7.4164
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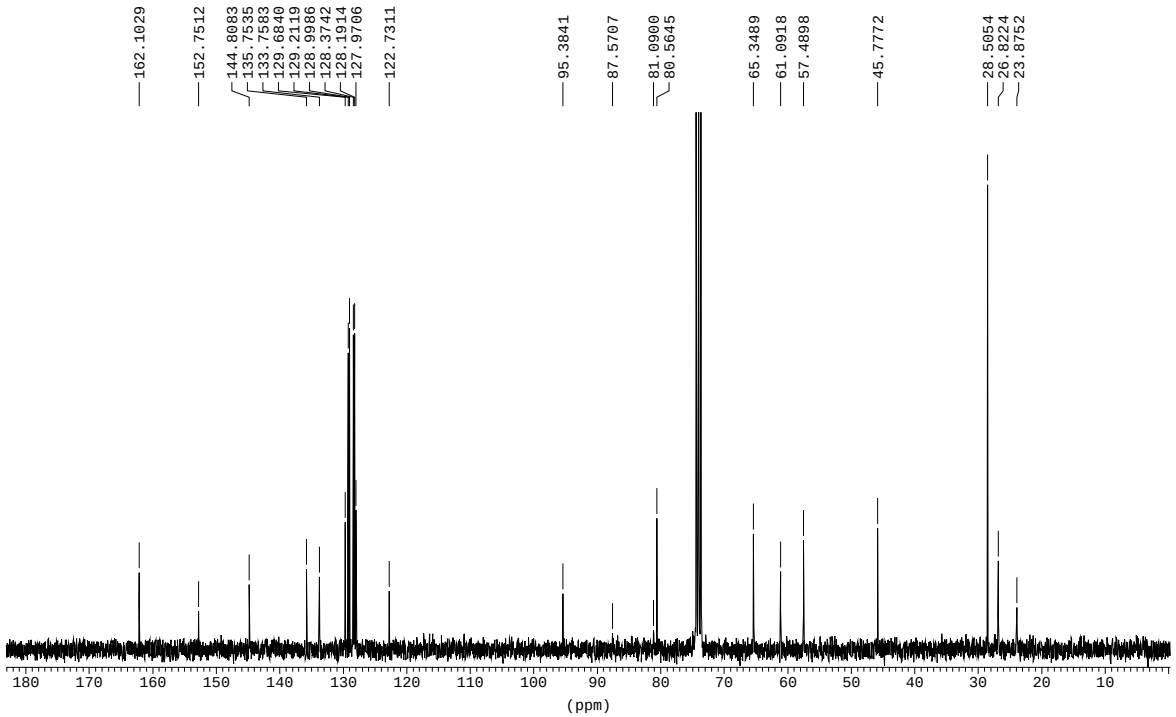
7.3876
7.3694
7.3515
7.3346
7.3195
7.3090
7.3035
7.2824
4.9292
4.8785
4.4752
4.4620
4.4313
4.4181
4.3472
4.2965
4.0939
4.0866
4.0619
4.0546
4.0099
3.9974
3.9773
3.9559
1.6735
1.5986
1.4710
Boc
N
O
Ph
H
D
N
O
Ph
(+)-4b
Integral
1.8832
3.3033
2.0431
1.0000
1.9593
1.0171
2.0240
3.1613
3.3108
8.1808
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)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152.7512
144.8083
135.7535
133.7583
129.6840
129.2119
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128.3742
128.1914
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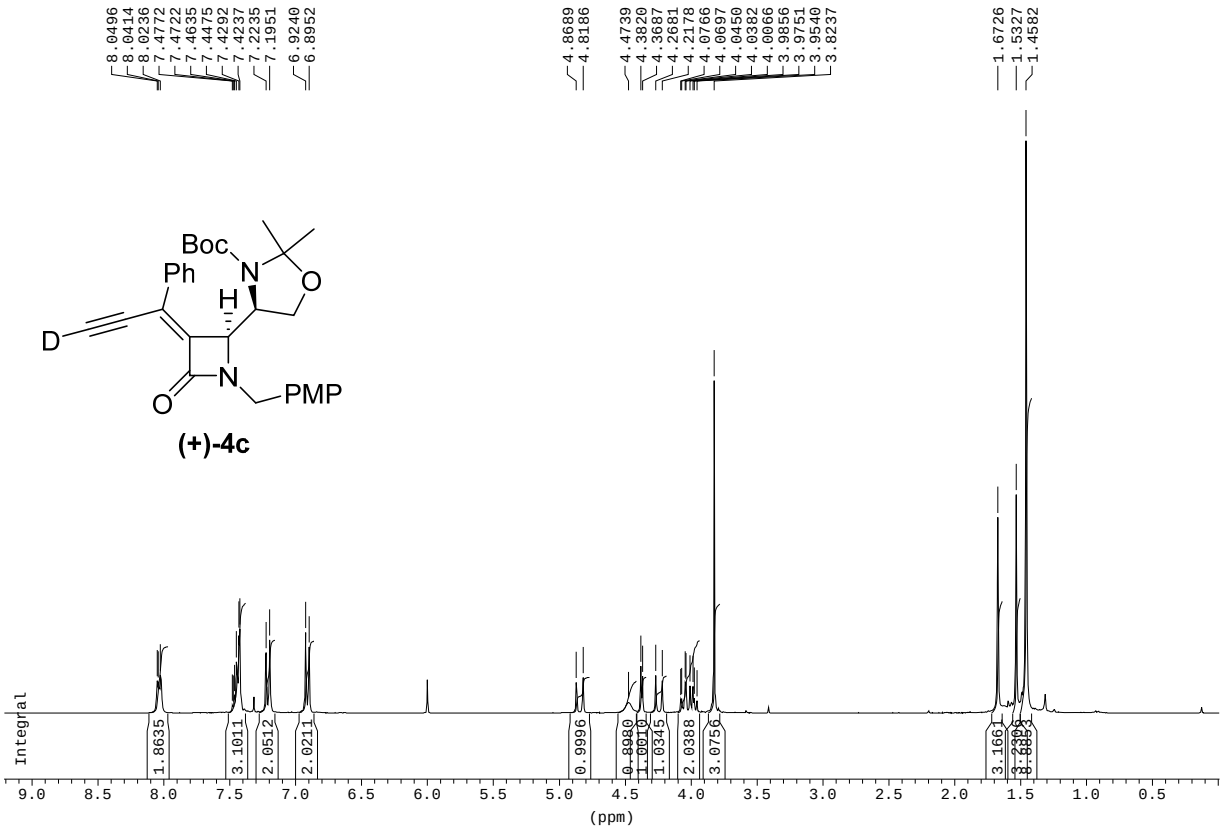
95.3841
87.5707
81.0900
80.5645
65.3489
61.0918
57.4898
45.7772
28.5054
26.8224
23.8752
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)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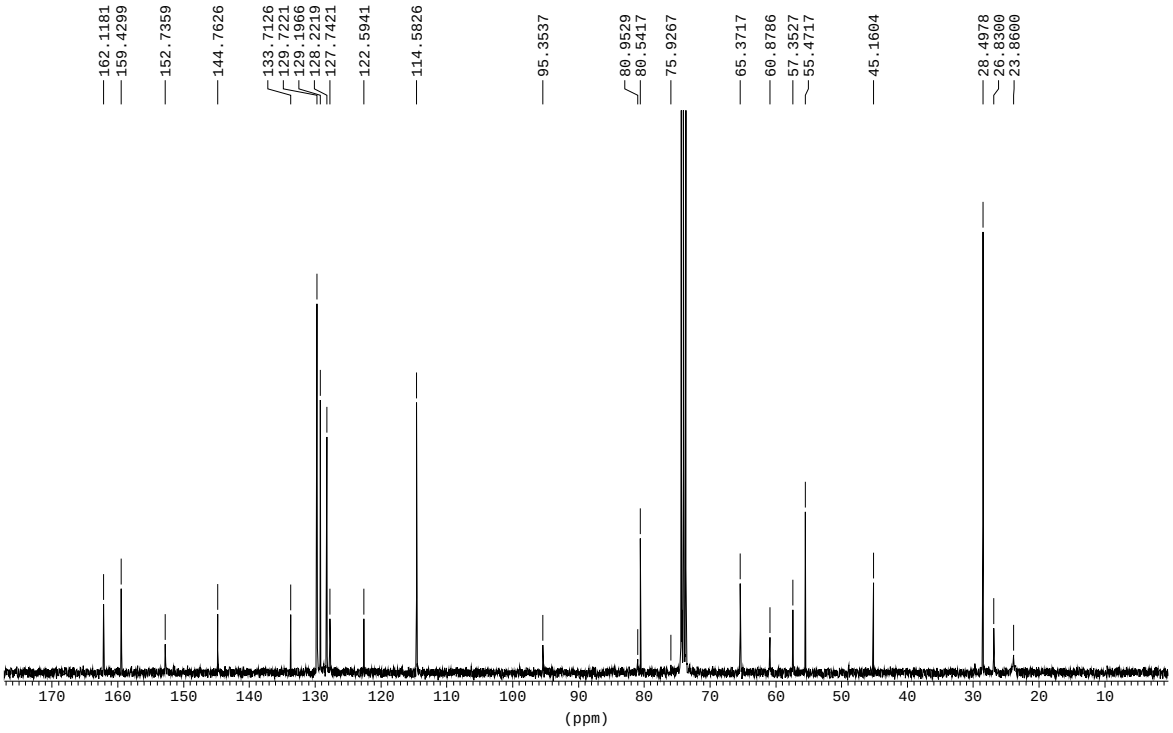
8.0414
8.0236
7.4772
7.4722
7.4635
7.4475
7.4292
7.4237
7.2235
7.1951
6.9240
6.8952
4.8689
4.8186
4.4739
4.3820
4.3687
4.2681
4.2178
4.0766
4.0697
4.0450
4.0382
4.0066
3.9856
3.9751
3.9540
3.8237
1.6726
1.5327
1.4582
Boc
Ph
N
O
H
D
N
PMP
O
(+)-4c
Integral
1.8635
3.1011
2.0512
2.0211
0.9996
0.8980
1.0010
1.0345
2.0388
3.0756
3.1661
3.2393
8.6803
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)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129.1966
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127.7421
122.5941
114.5826
95.3537
80.9529
80.5417
75.9267
65.3717
60.8786
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45.1604
28.4978
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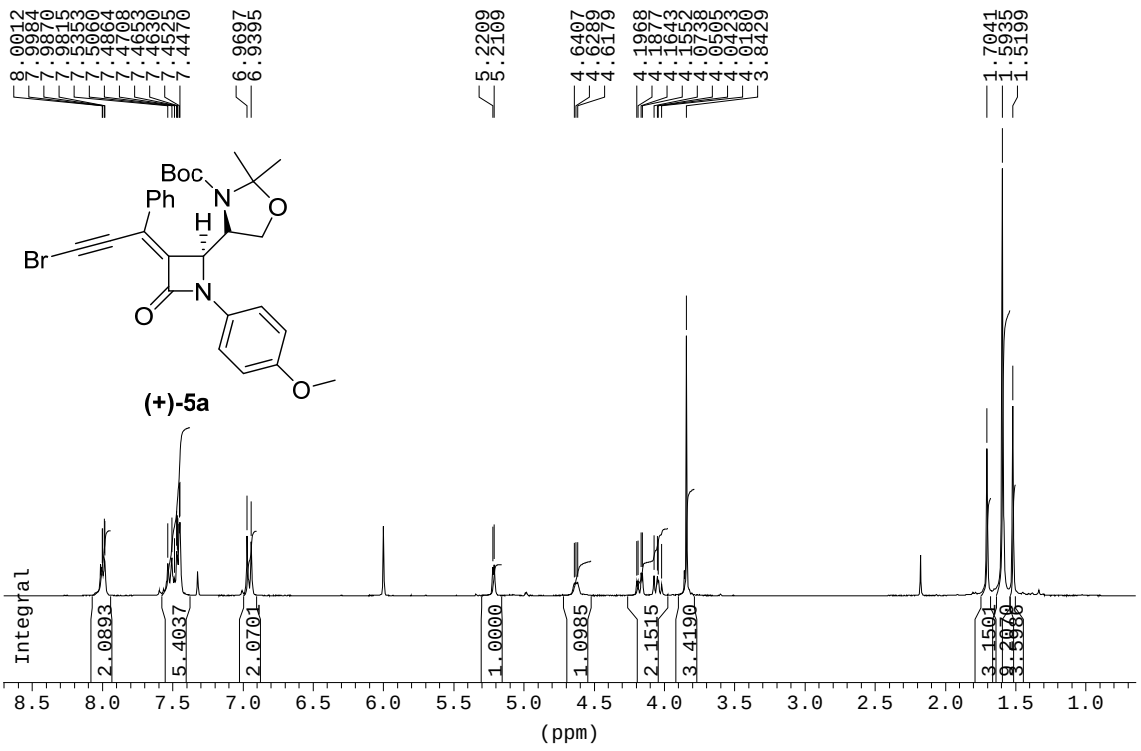
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)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7.9870
7.9815
7.5353
7.5060
7.4864
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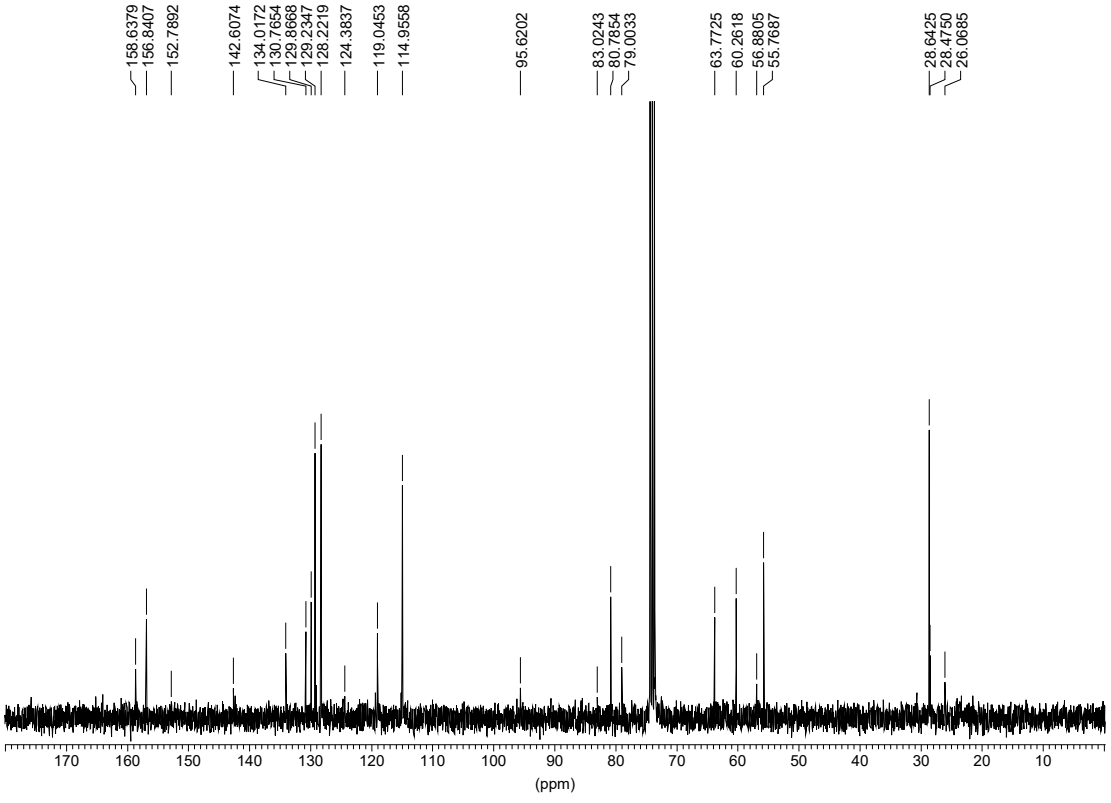
7.4653
7.4630
7.4525
7.4470
6.9697
6.9395
5.2209
5.2109
4.6407
4.6289
4.6179
4.1968
4.1877
4.1643
4.1552
4.0738
4.0505
4.0423
4.0180
3.8429
1.7041
1.5935
1.5199
Boc
Ph
N
O
H
Br
N
O
O
(+)-5a
Integral
2.0893
5.4037
2.0701
1.0000
1.0985
2.1515
3.4190
3.1591
9.2070
3.5930
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
(ppm)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128.2219
124.3837
119.0453
114.9558
95.6202
83.0243
80.7854
79.0033
63.7725
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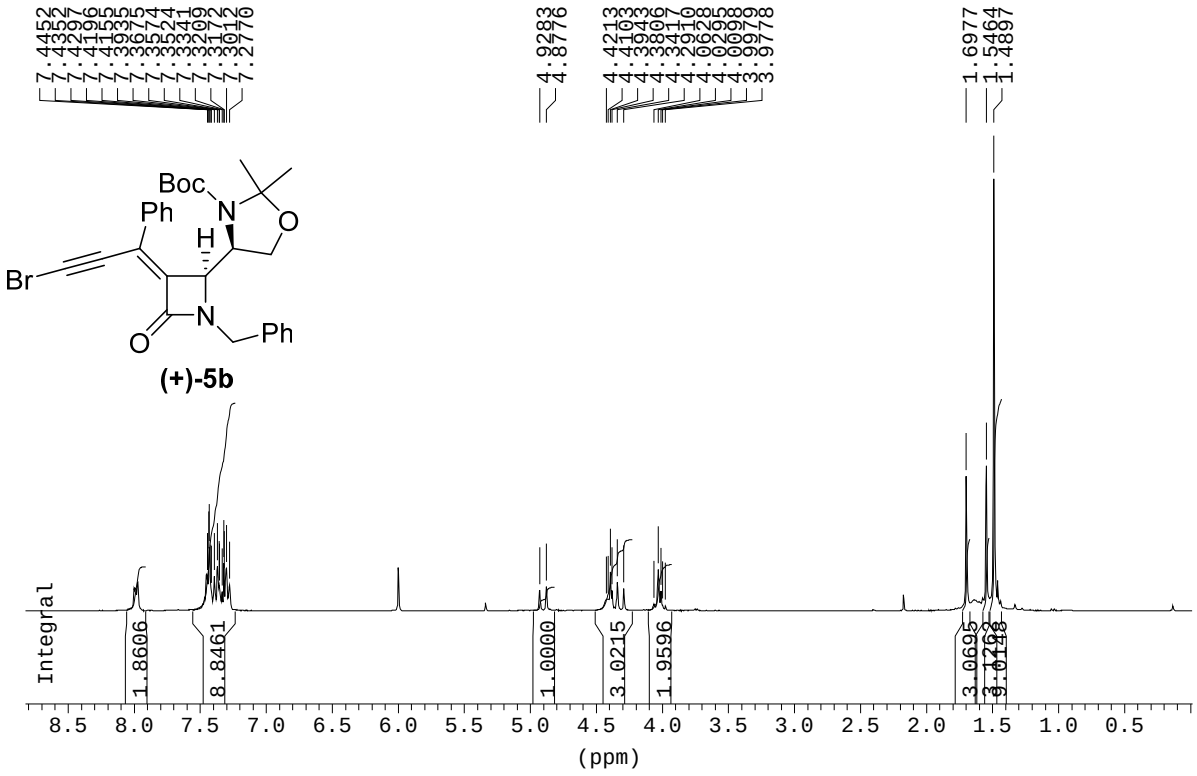
55.7687
28.6425
28.4750
26.0685
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)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7.3172
7.3012
7.2770
4.9283
4.8776
4.4213
4.4103
4.3843
4.3806
4.3417
4.2910
4.0628
4.0295
4.0098
3.9979
3.9778
1.6977
1.5464
1.4897
Boc
N
O
Ph
H
Br
N
O
Ph
(+)-5b
Integral
1.8606
8.8461
1.0000
3.0215
1.9596
3.0695
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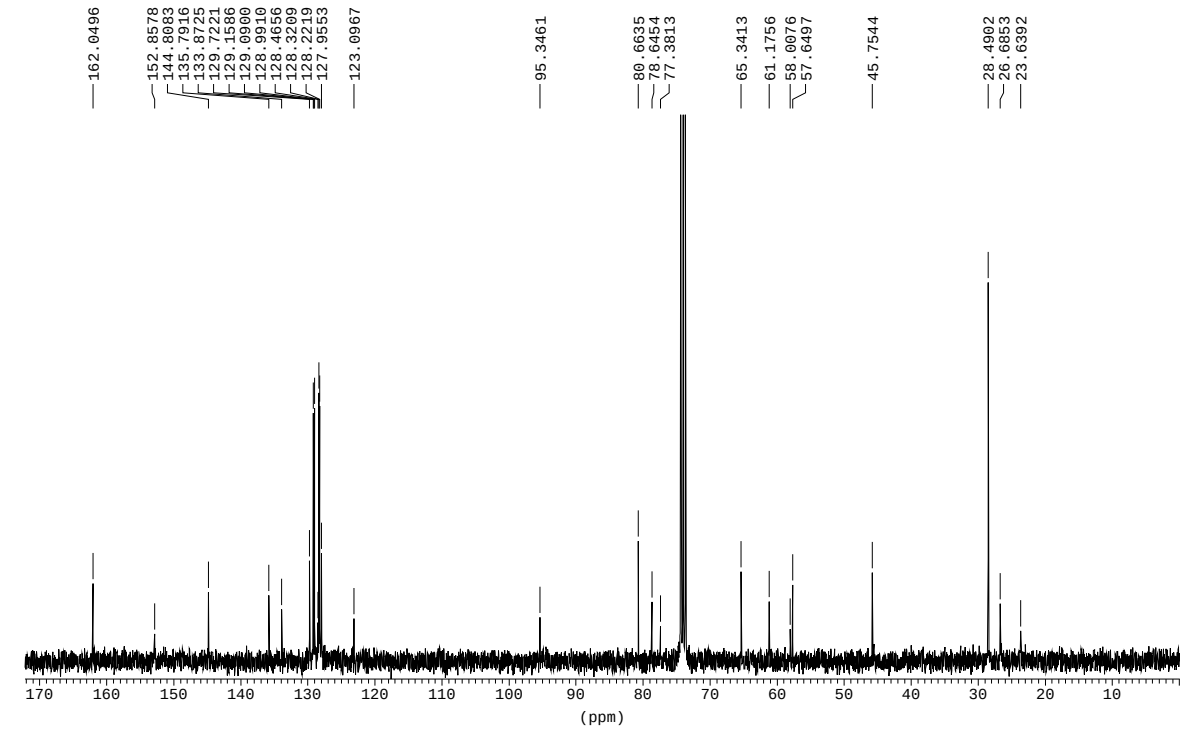
(ppm)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128.4656
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128.2219
127.9553
123.0967
95.3461
80.6635
78.6454
77.3813
65.3413
61.1756
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45.7544
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26.6853
23.6392
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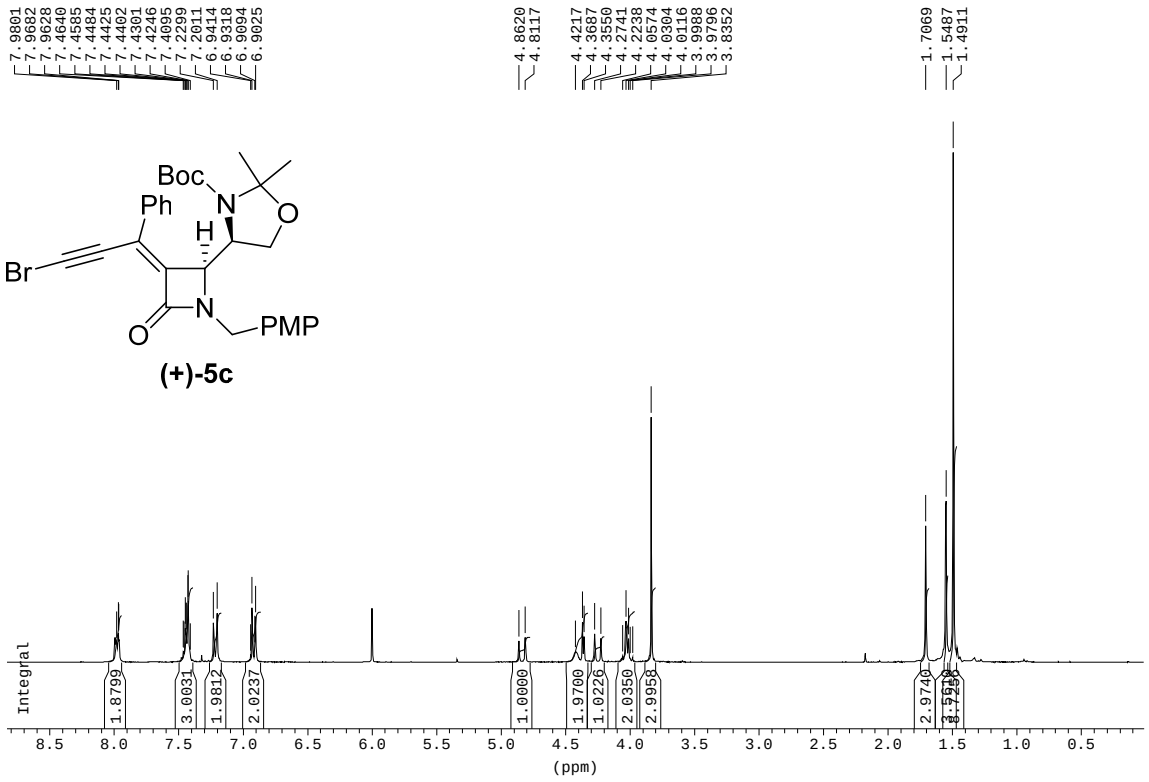
(ppm)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7.4484
7.4425
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7.4301
7.4246
7.4095
7.2299
7.2011
6.9414
6.9318
6.9094
6.9025
4.8620
4.8117
4.4217
4.3687
4.3550
4.2741
4.2238
4.0574
4.0304
4.0116
3.9988
3.9796
3.8352
1.7069
1.5487
1.4911
Boc
Ph
N
O
H
Br
N
PMP
O
(+)-5c
Integral
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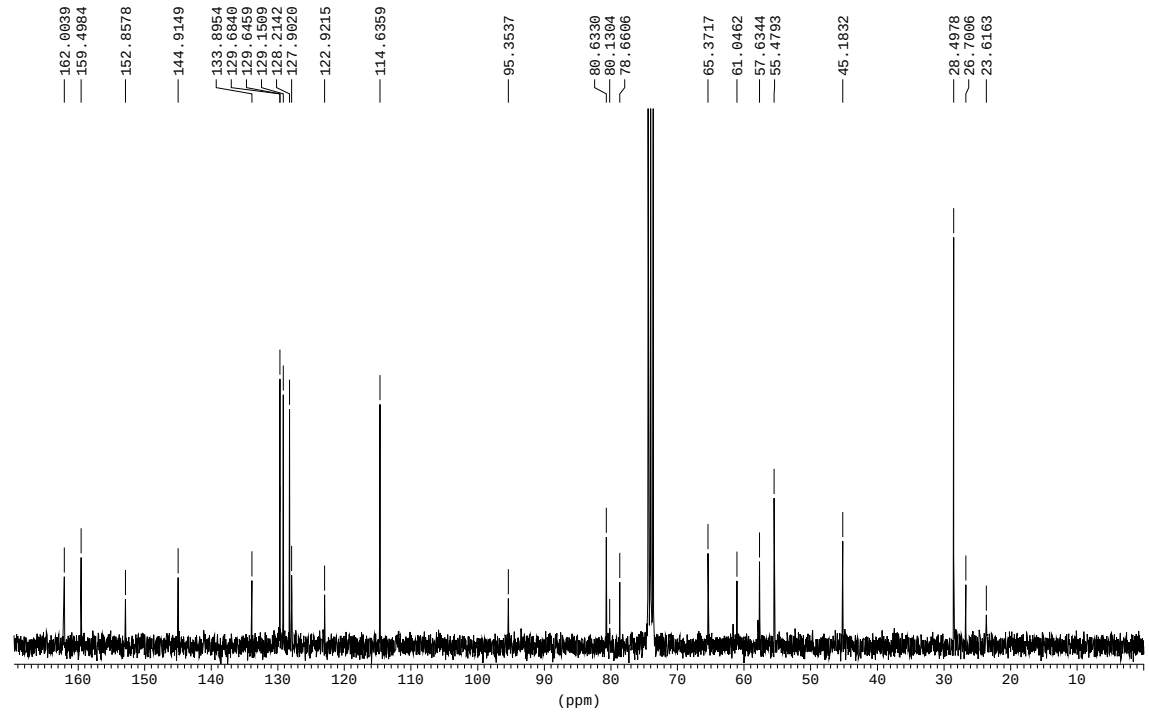
3.0031
1.9812
2.0237
1.0000
1.9700
1.0226
2.0350
2.9958
2.9740
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)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95.3537
80.6330
80.1304
78.6606
65.3717
61.0462
57.6344
55.4793
45.1832
28.4978
26.7006
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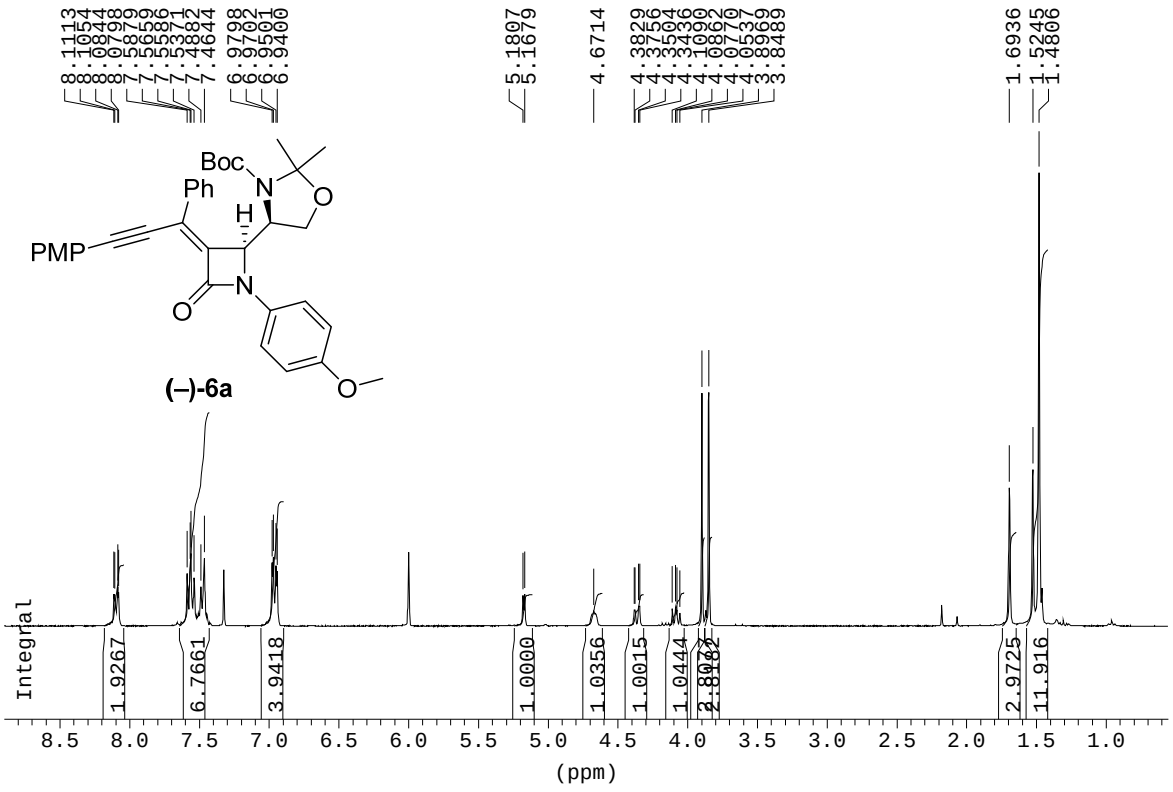
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)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7.5371
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7.4644
6.9798
6.9702
6.9501
6.9400
5.1807
5.1679
4.6714
4.3829
4.3756
4.3504
4.3436
4.1090
4.0862
4.0770
4.0537
4.0369
3.8489
1.6936
1.5245
1.4806
Boc
N
O
Ph
H
PMP
N
O
O
(–)-6a
Integral
1.9267
6.7661
3.9418
1.0000
1.0356
1.0015
1.0444
2.8807
2.8882
2.9725
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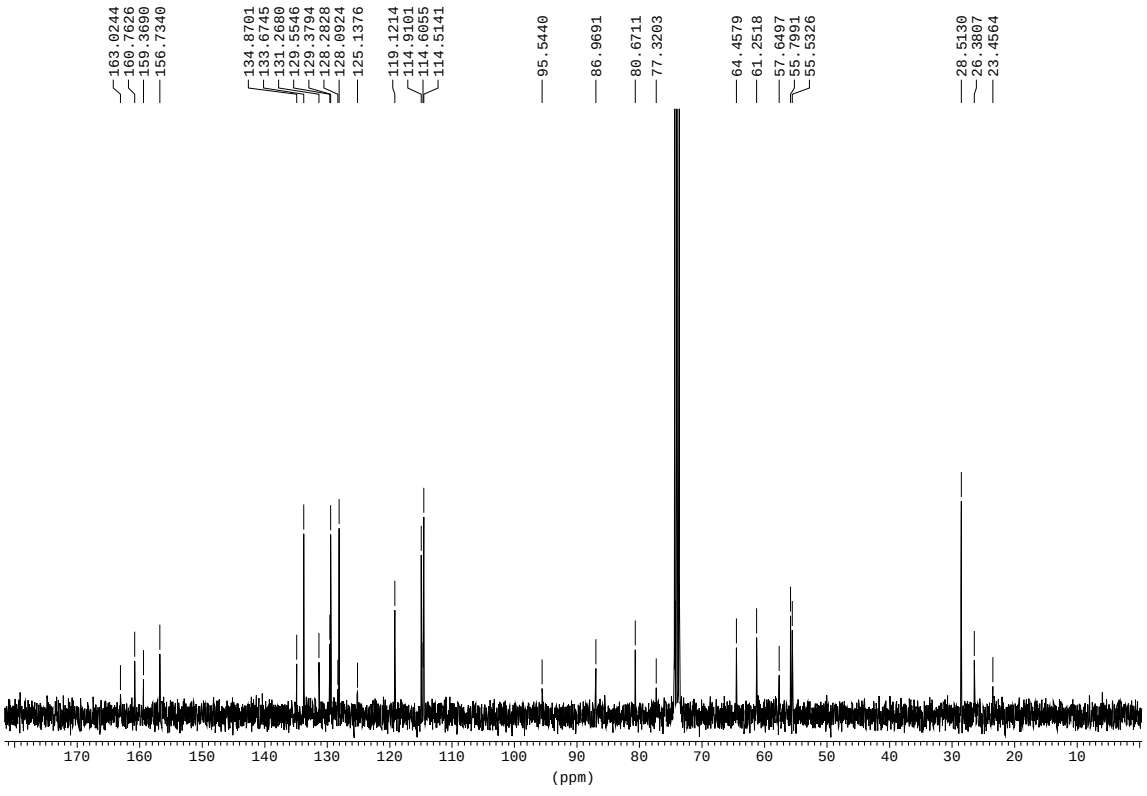
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
(ppm)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125.1376
119.1214
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114.6055
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95.5440
86.9691
80.6711
77.3203
64.4579
61.2518
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55.5326
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26.3807
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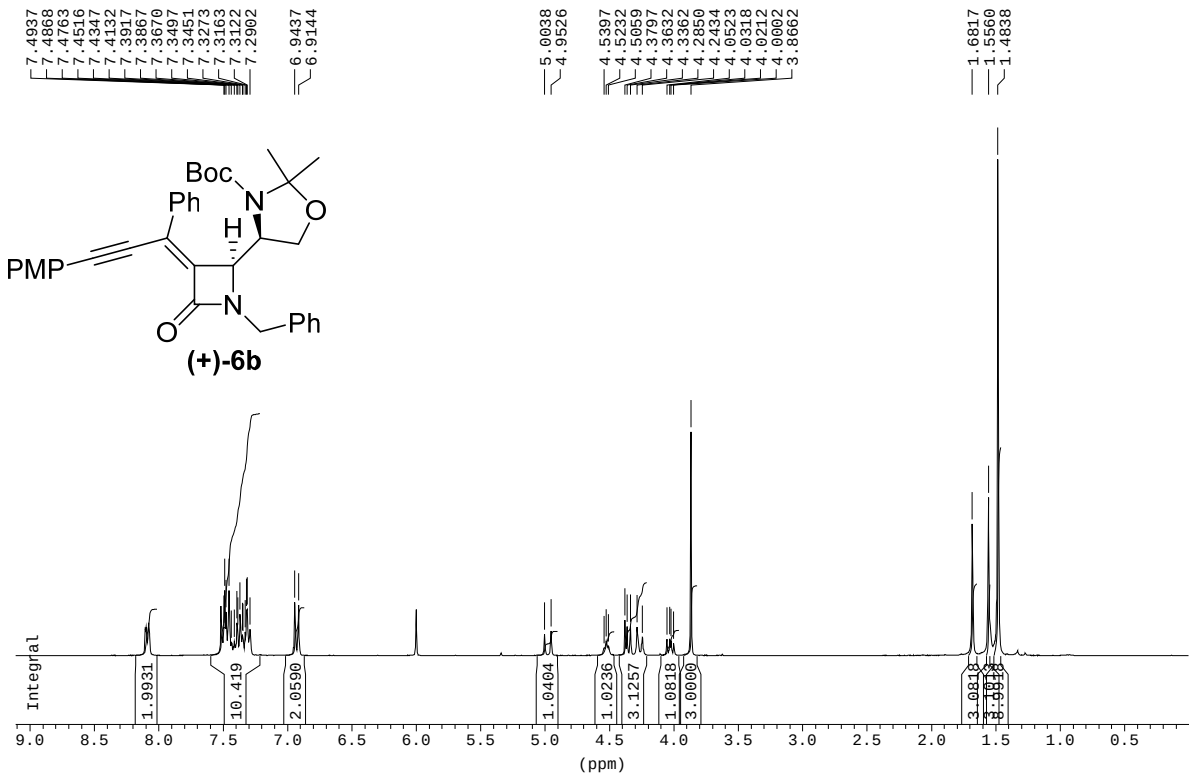
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)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7.3670
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7.3451
7.3273
7.3163
7.3122
7.2902
6.9437
6.9144
5.0038
4.9526
4.5397
4.5232
4.5059
4.3797
4.3632
4.3362
4.2850
4.2434
4.0523
4.0318
4.0212
4.0002
3.8662
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1.5560
1.4838
Boc
N
O
Ph
H
PMP
N
Ph
O
(+)-6b
Integral
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10.419
2.0590
1.0404
1.0236
3.1257
1.0818
3.0000
3.0818
3.1013
3.9938
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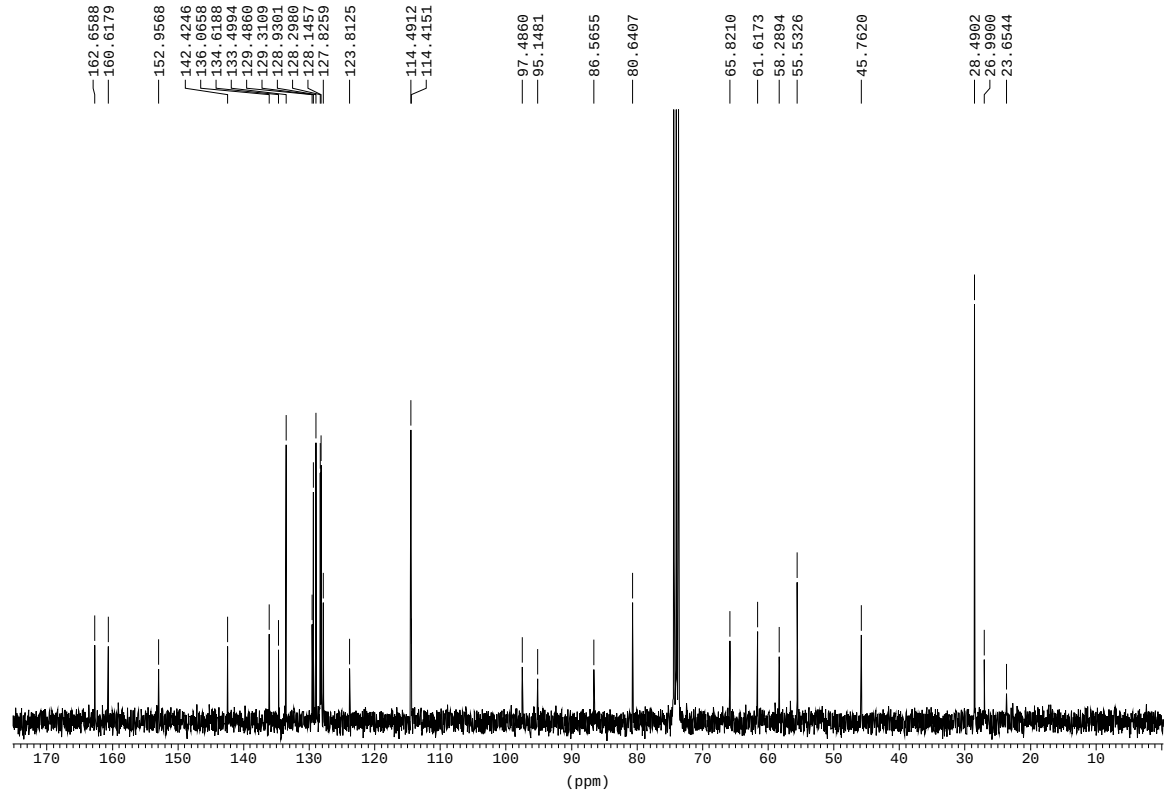
(ppm)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80.6407
65.8210
61.6173
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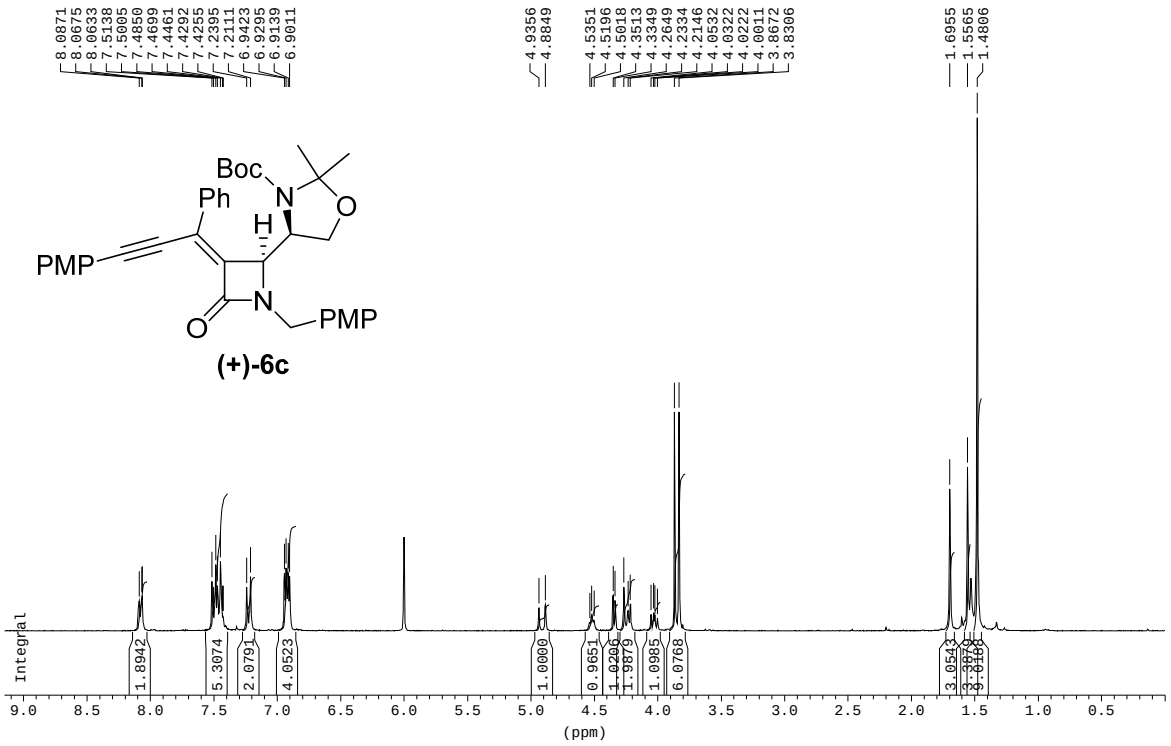
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7.2111
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6.9139
6.9011
4.9356
4.8849
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4.5018
4.3513
4.3349
4.2649
4.2334
4.2146
4.0532
4.0322
4.0222
4.0011
3.8672
3.8306
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1.5565
1.4806
Boc
Ph
N
O
H
PMP
N
PMP
O
(+)-6c
Integral
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5.3074
2.0791
4.0523
1.0000
0.9651
1.0206
1.9879
1.0985
6.0768
3.0543
3.3076
3.0181
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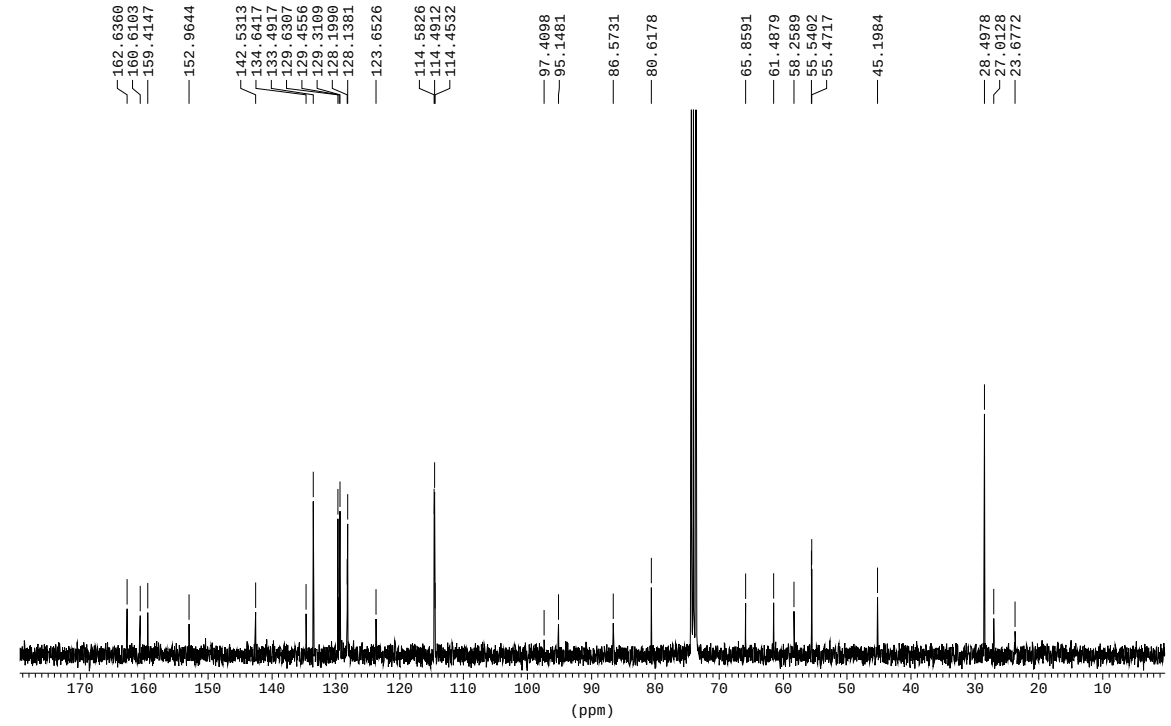
(ppm)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114.4912
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95.1481
86.5731
80.6178
65.8591
61.4879
58.2589
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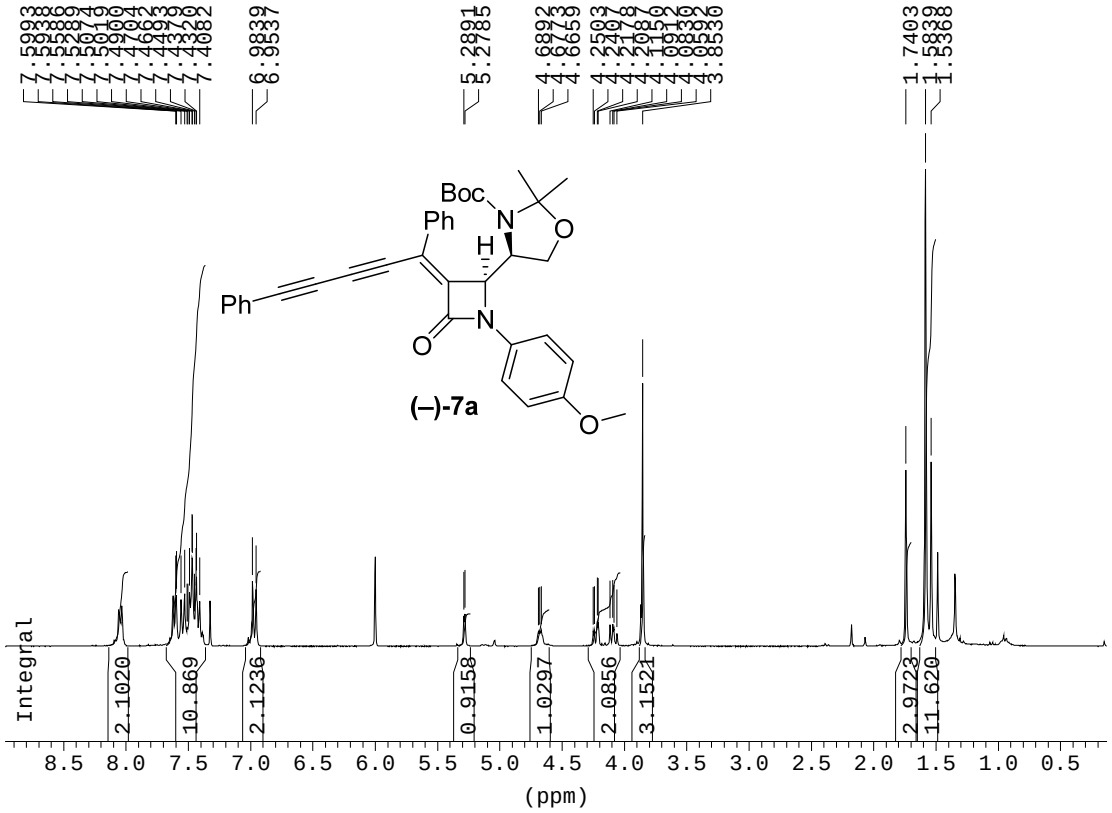
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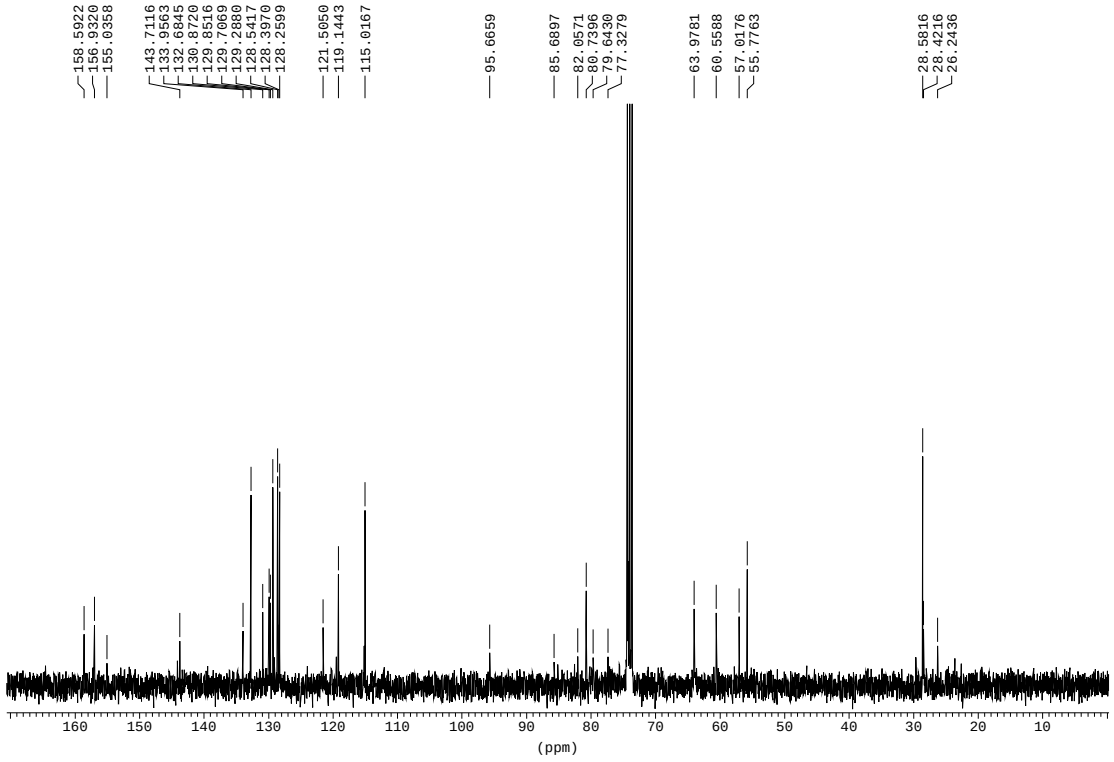
6.9839
6.9537
5.2891
5.2785
4.6892
4.6773
4.6659
4.2503
4.2407
4.2178
4.2087
4.1150
4.0912
4.0836
4.0592
3.8536
1.7403
1.5839
1.5368
Boc
N
O
Ph
H
Ph
N
O
O
(–)-7a
Integral
2.1020
10.869
2.1236
0.9158
1.0297
2.0856
3.1521
2.9723
11.620
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)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95.6659
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82.0571
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79.6430
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63.9781
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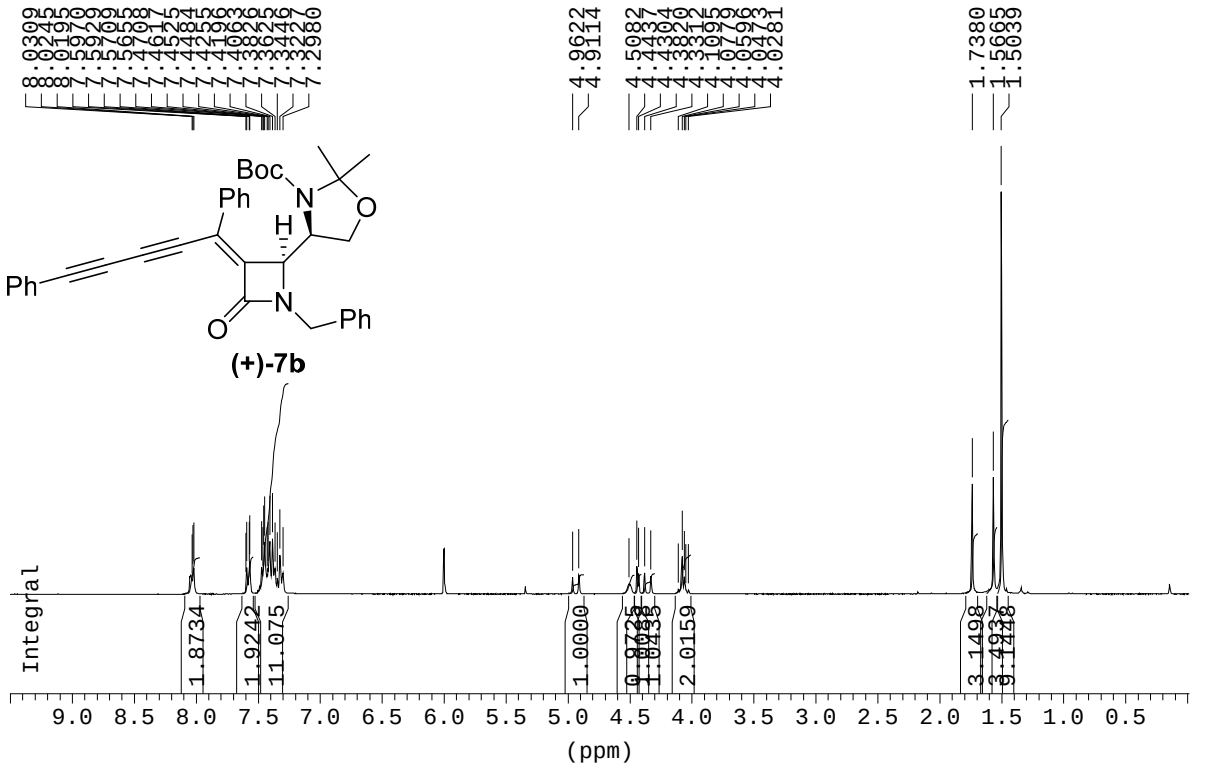
(ppm)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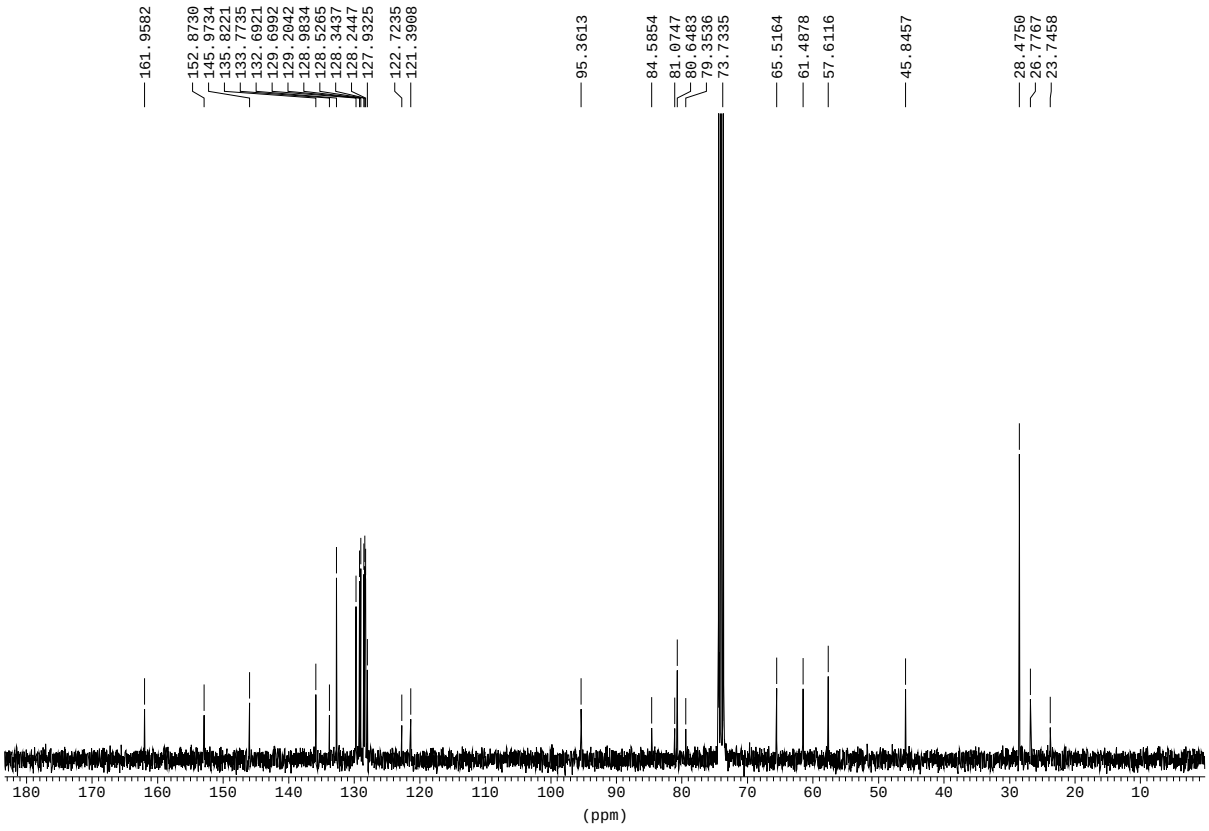
7.4484
7.4255
7.4136
7.4068
7.3826
7.3446
7.3227
7.2980
4.9622
4.9114
4.5082
4.4437
4.4304
4.3820
4.3412
4.3315
4.1079
4.0596
4.0473
4.0281
1.7380
1.5665
1.5039
Boc
N
O
Ph
H
Ph
N
Ph
O
(+)-7b
Integral
1.8734
1.9242
11.075
1.0000
2.0159
3.1498
9.1448
9.4937
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)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122.7235
121.3908
95.3613
84.5854
81.0747
80.6483
79.3536
73.7335
65.5164
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45.8457
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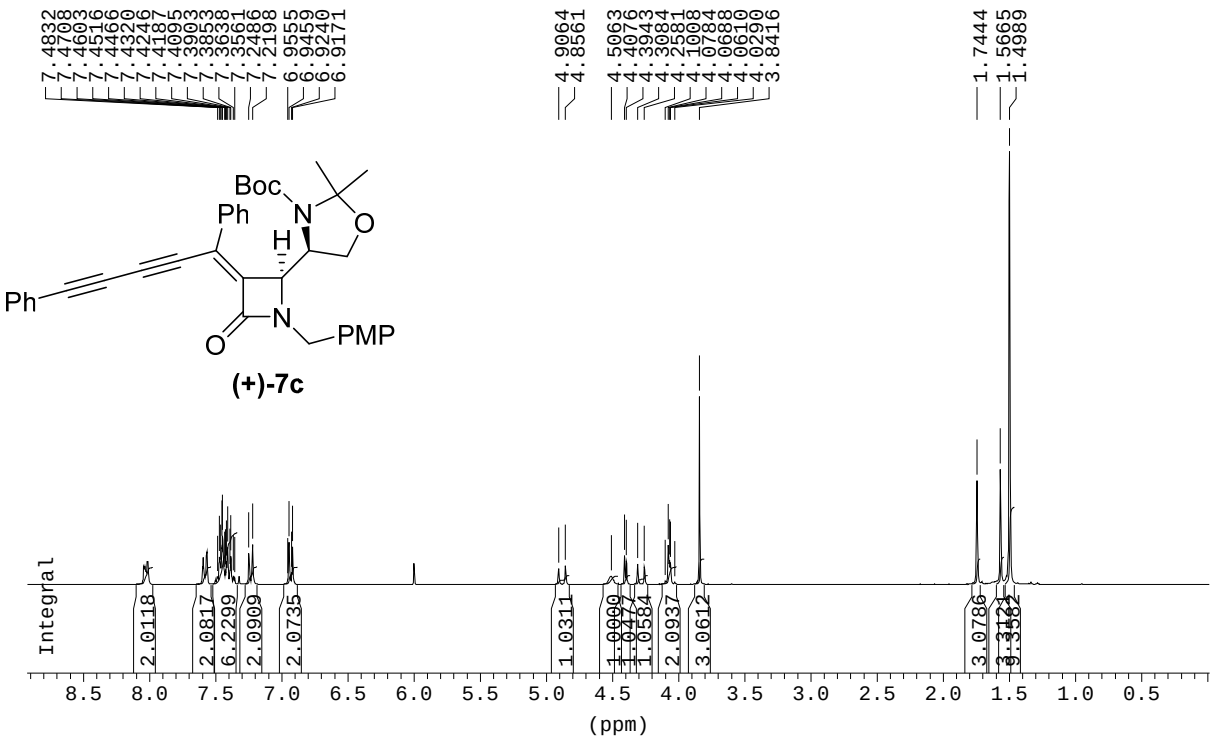
26.7767
23.7458
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)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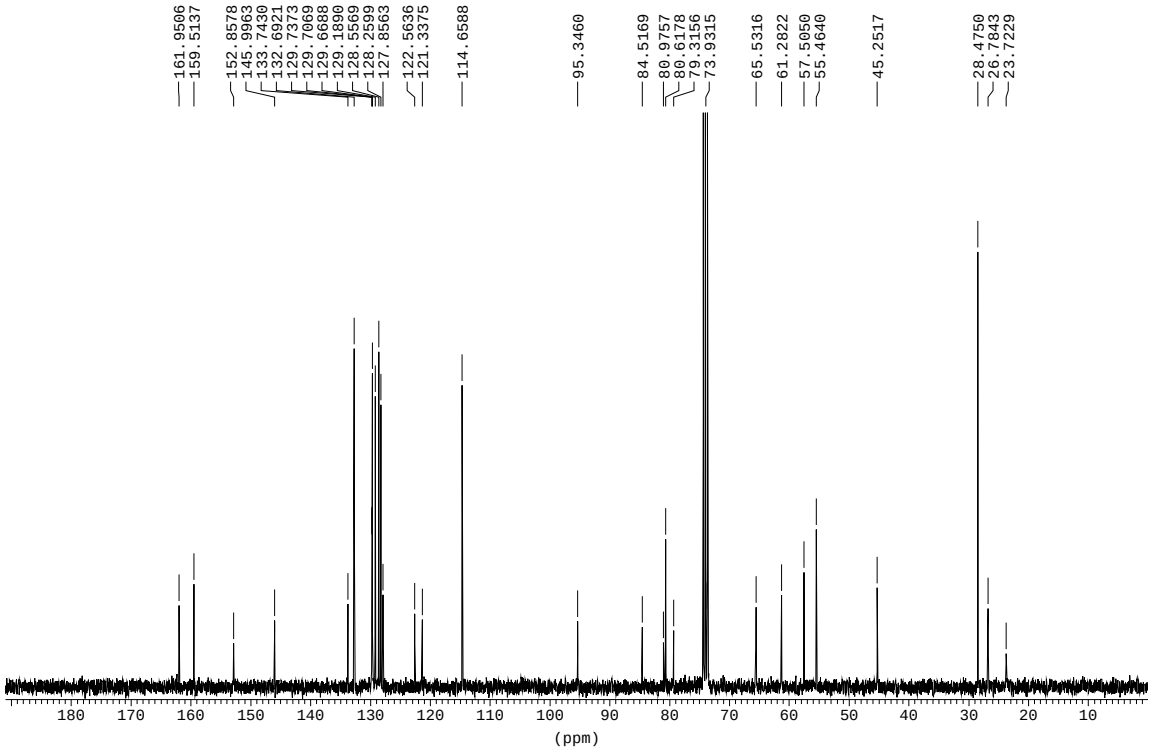
7.3561
7.2486
7.2198
6.9559
6.9459
6.9240
6.9171
4.9064
4.8561
4.5063
4.4076
4.3943
4.3084
4.2581
4.1008
4.0784
4.0688
4.0610
4.0290
3.8416
1.7444
1.5665
1.4989
Boc
N
O
Ph
H
Ph
N
PMP
O
(+)-7c
Integral
2.0118
2.0817
6.2299
2.0909
2.0735
1.0311
1.0000
1.0477
1.0584
2.0937
3.0612
3.0786
3.3121
9.3582
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)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80.9757
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79.3156
73.9315
65.5316
61.2822
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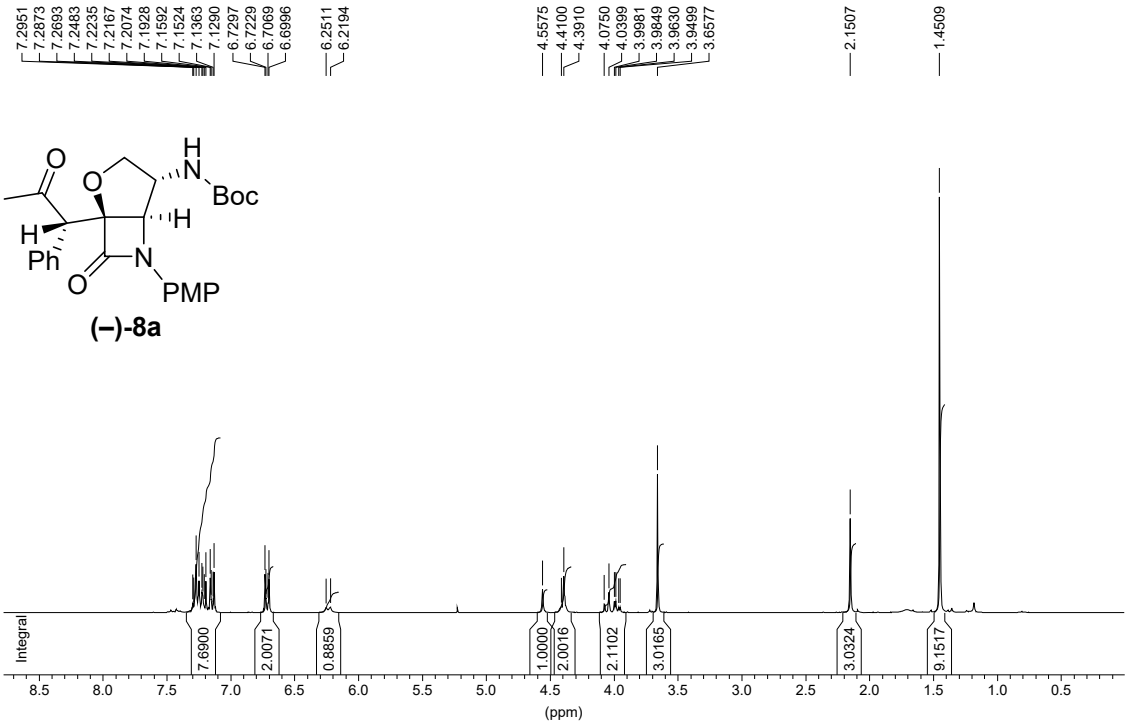
(ppm)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7.1592
7.1524
7.1363
7.1290
6.7297
6.7229
6.7069
6.6996
6.2511
6.2194
4.5575
4.4100
4.3910
4.0750
4.0399
3.9981
3.9849
3.9630
3.9499
3.6577
2.1507
1.4509
Integral
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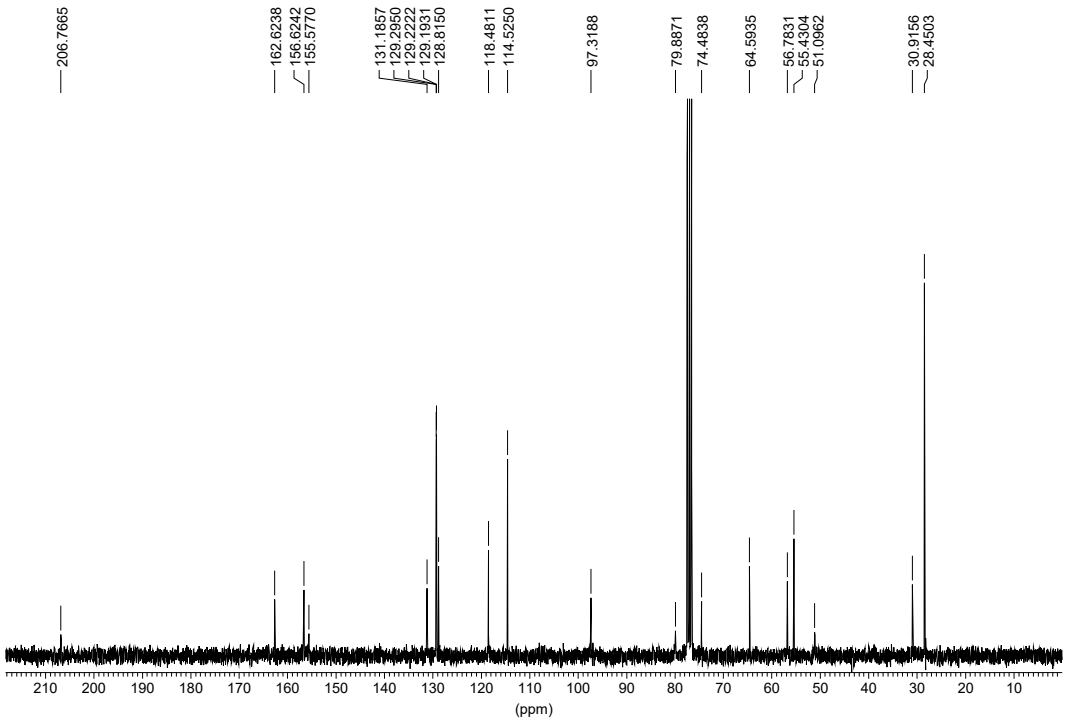
(ppm)

(–)-8a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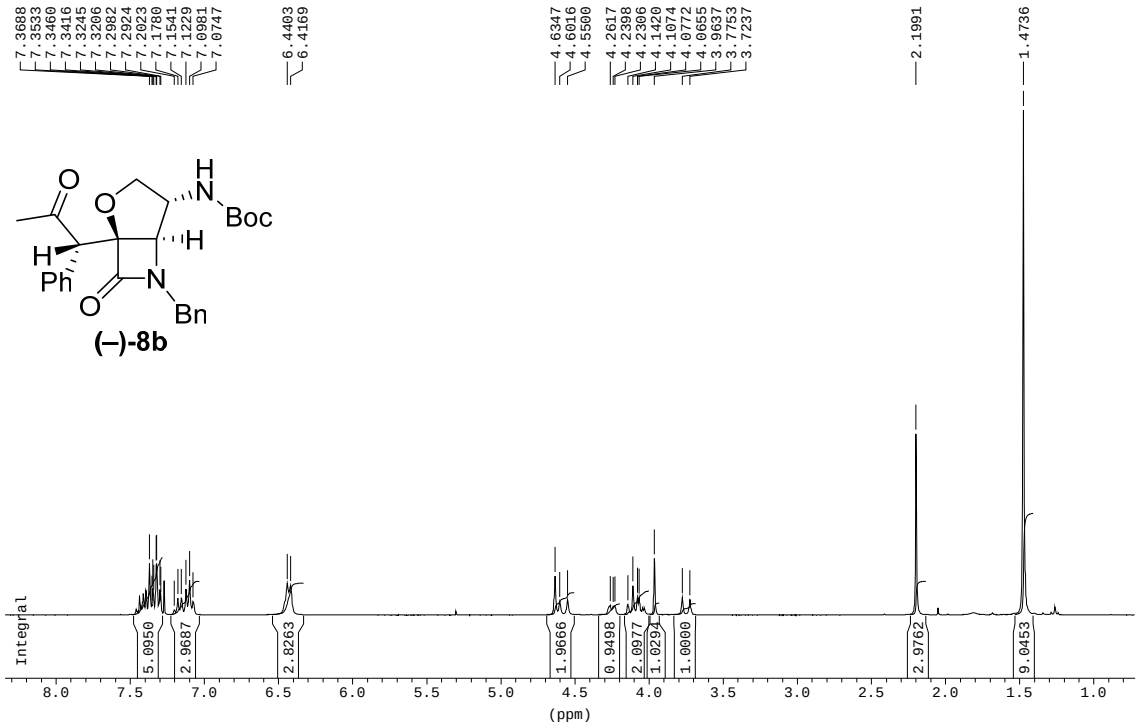

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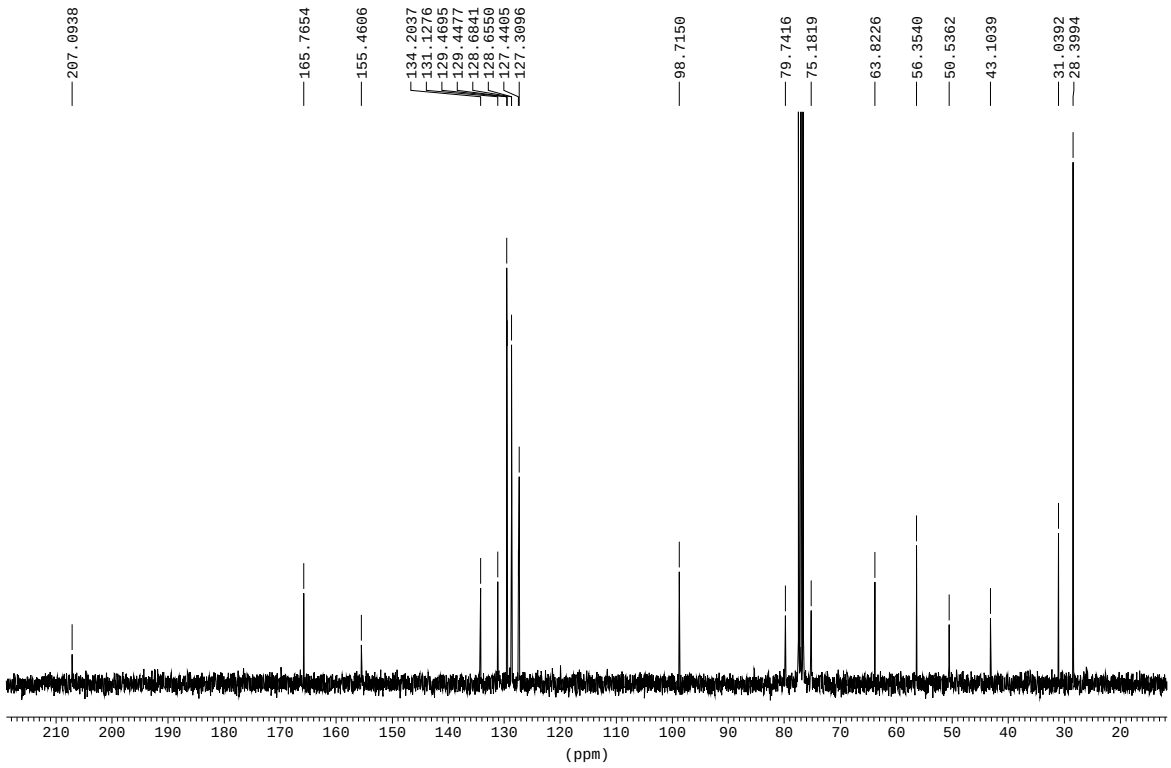

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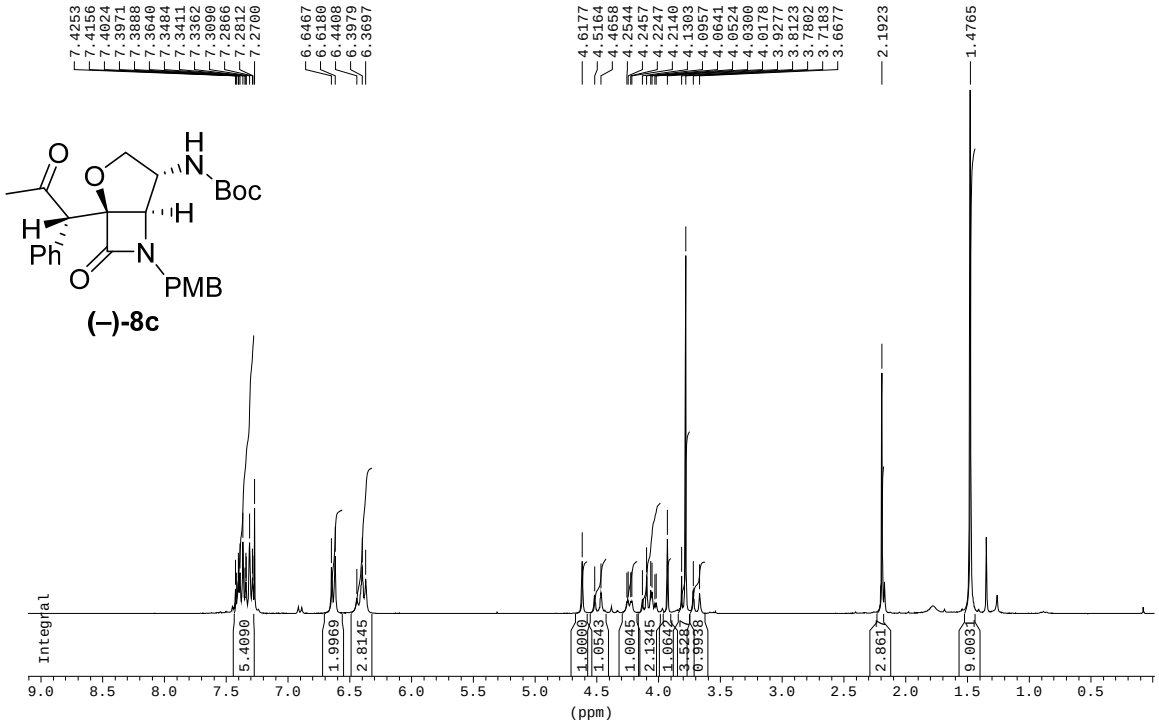

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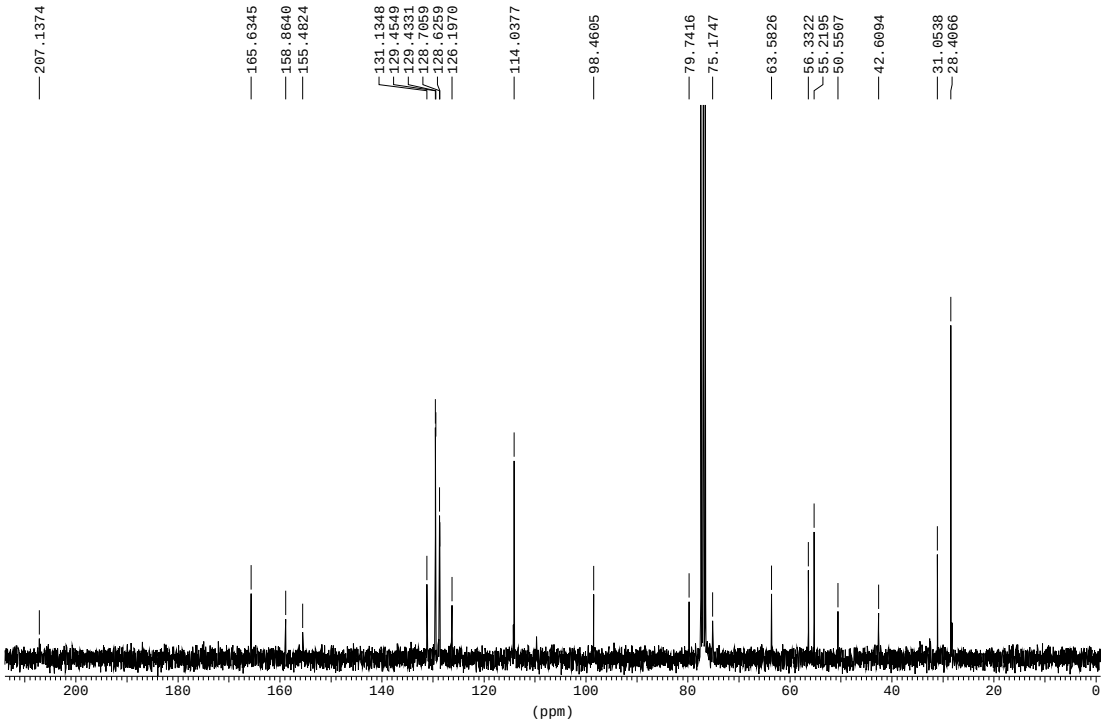

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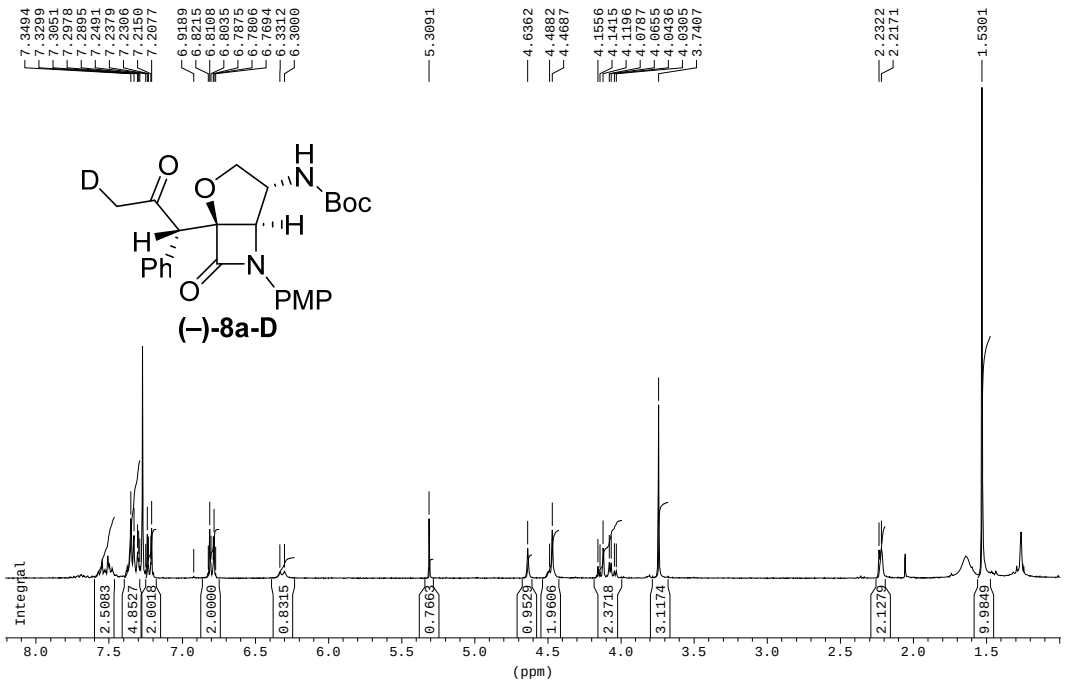

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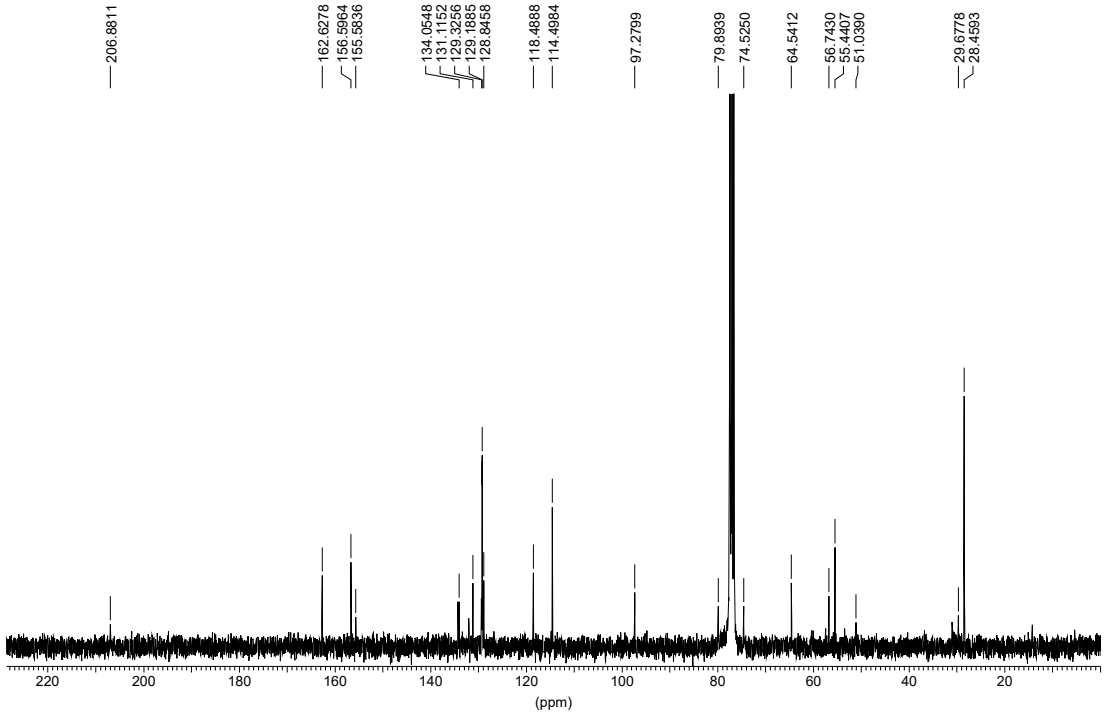

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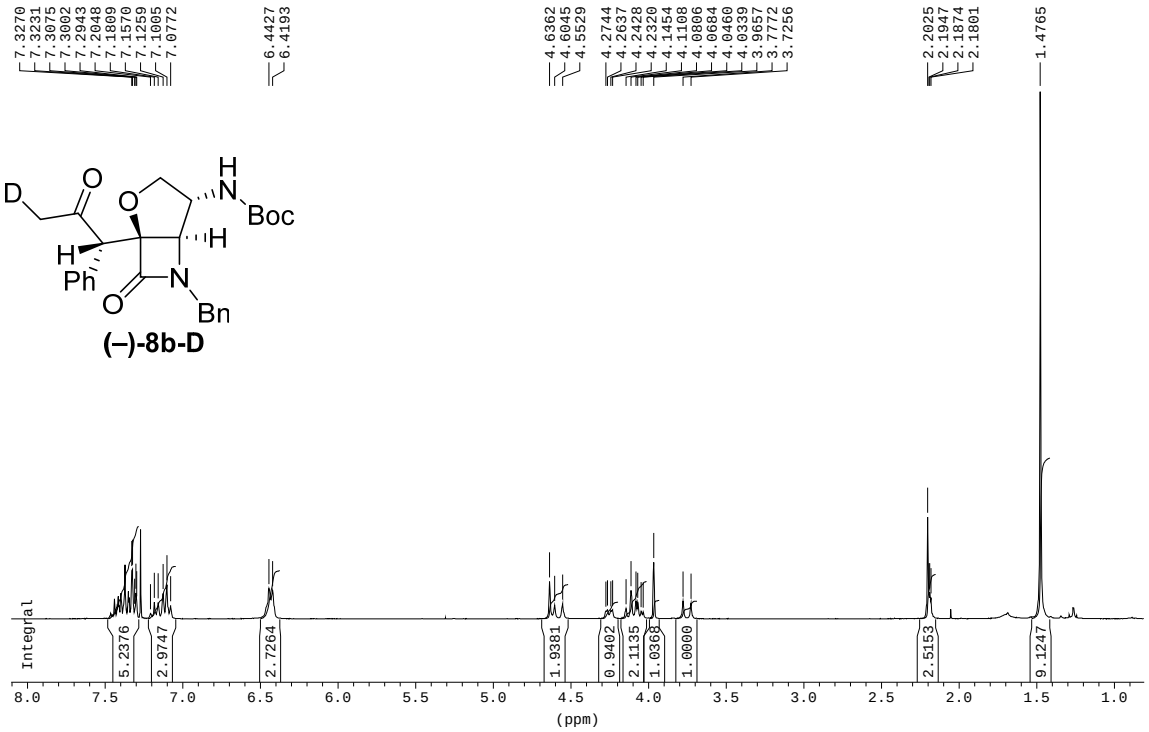

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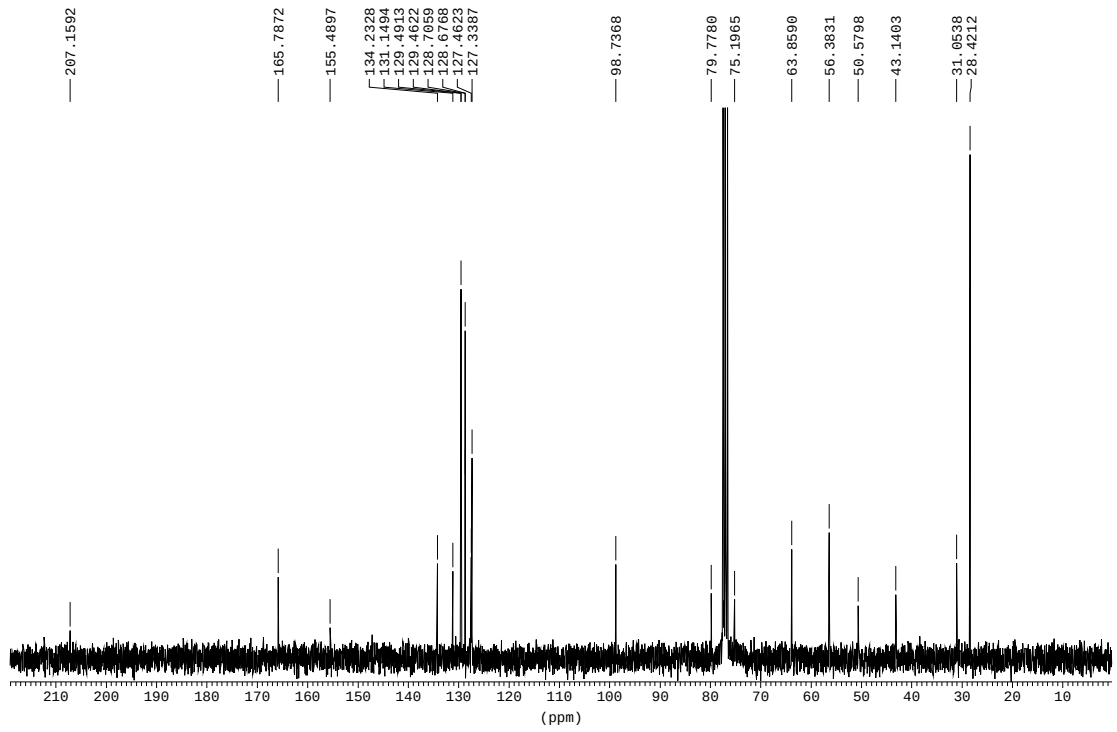

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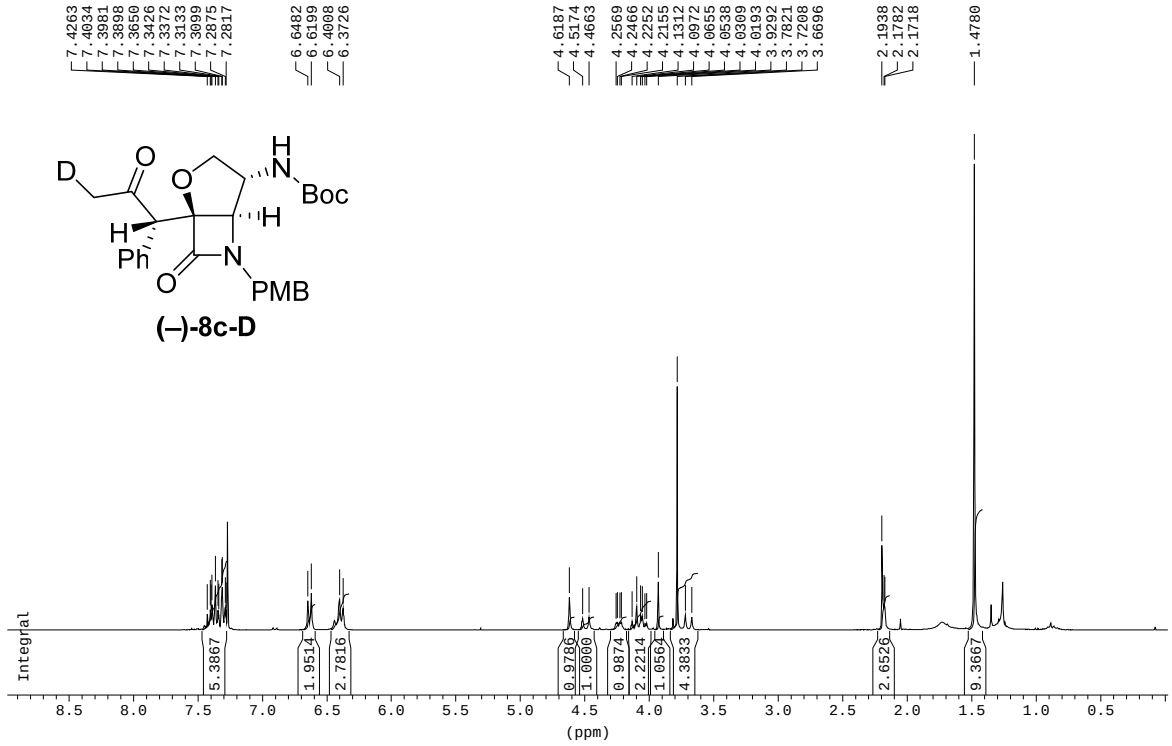

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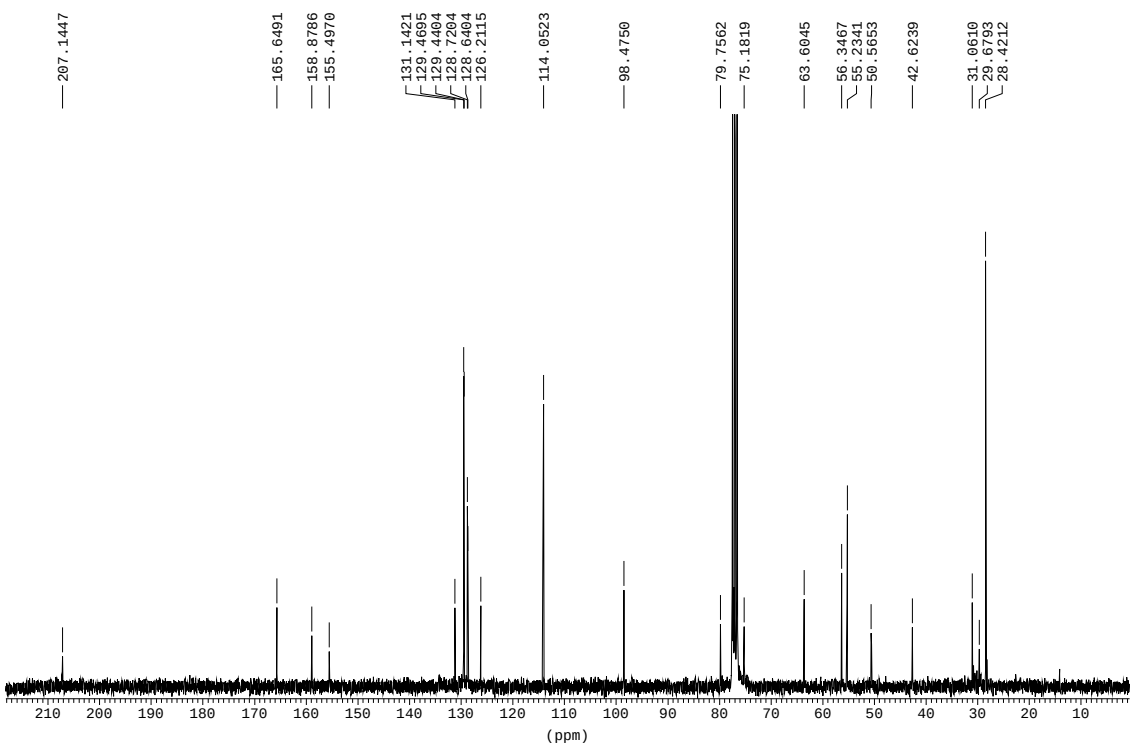

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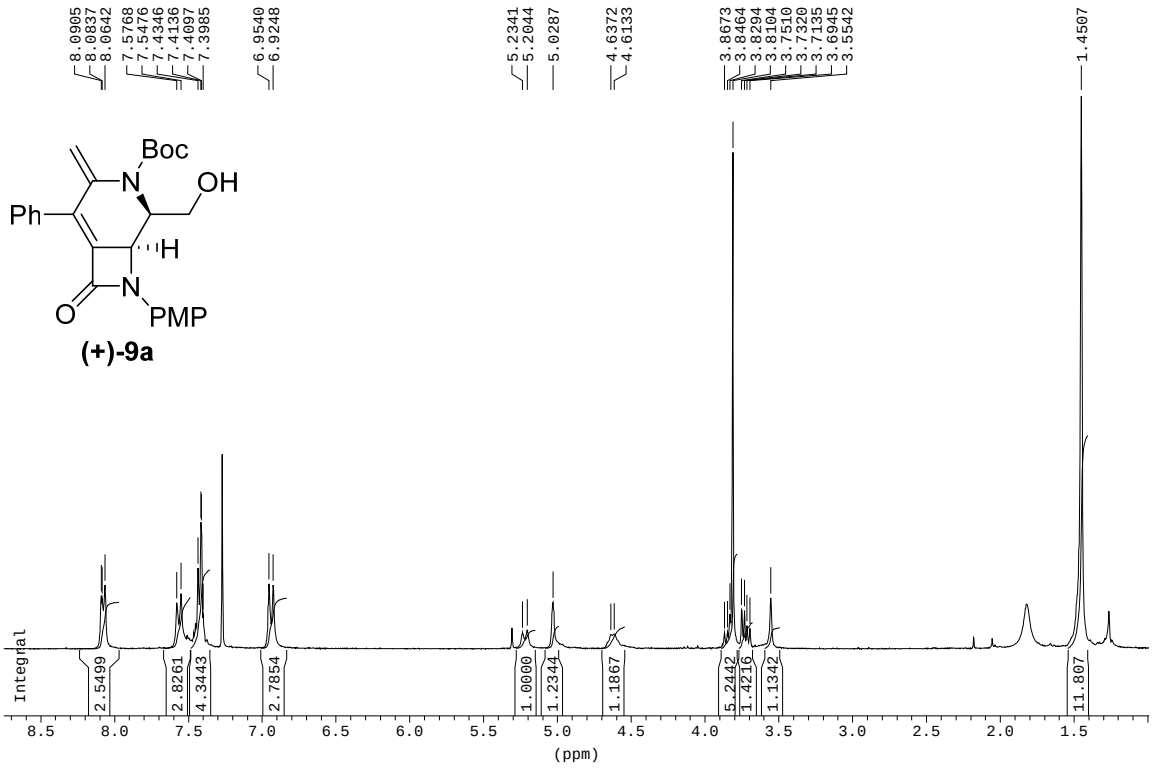

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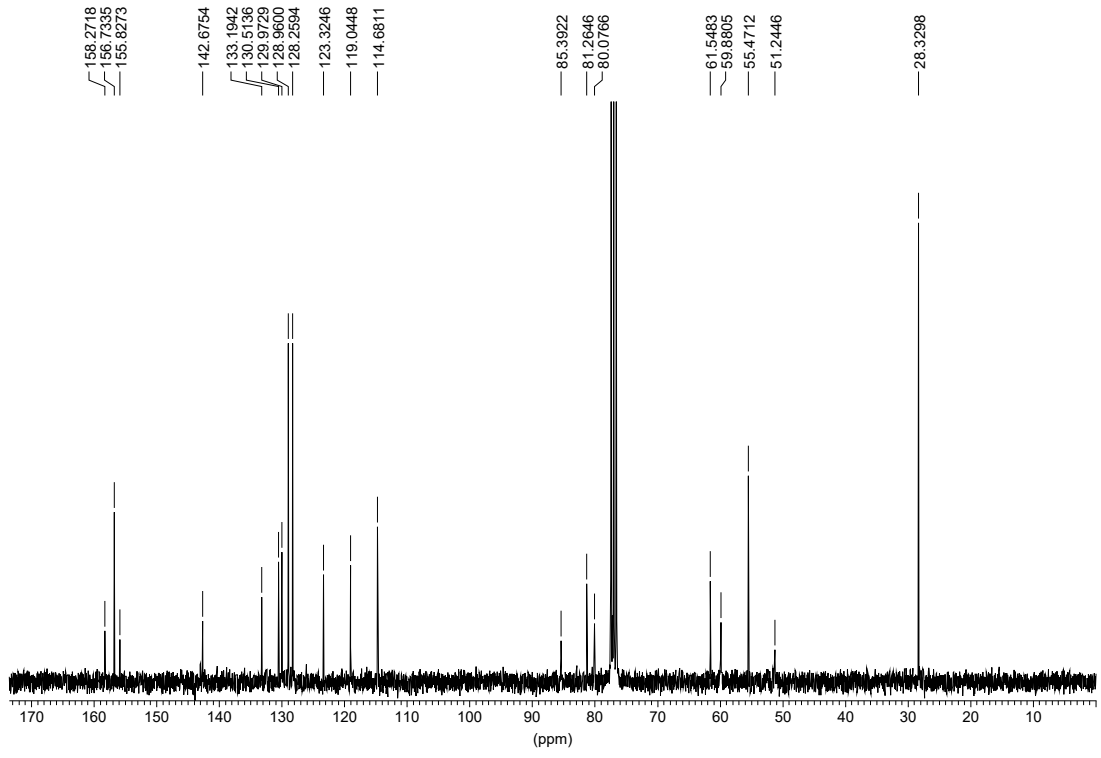

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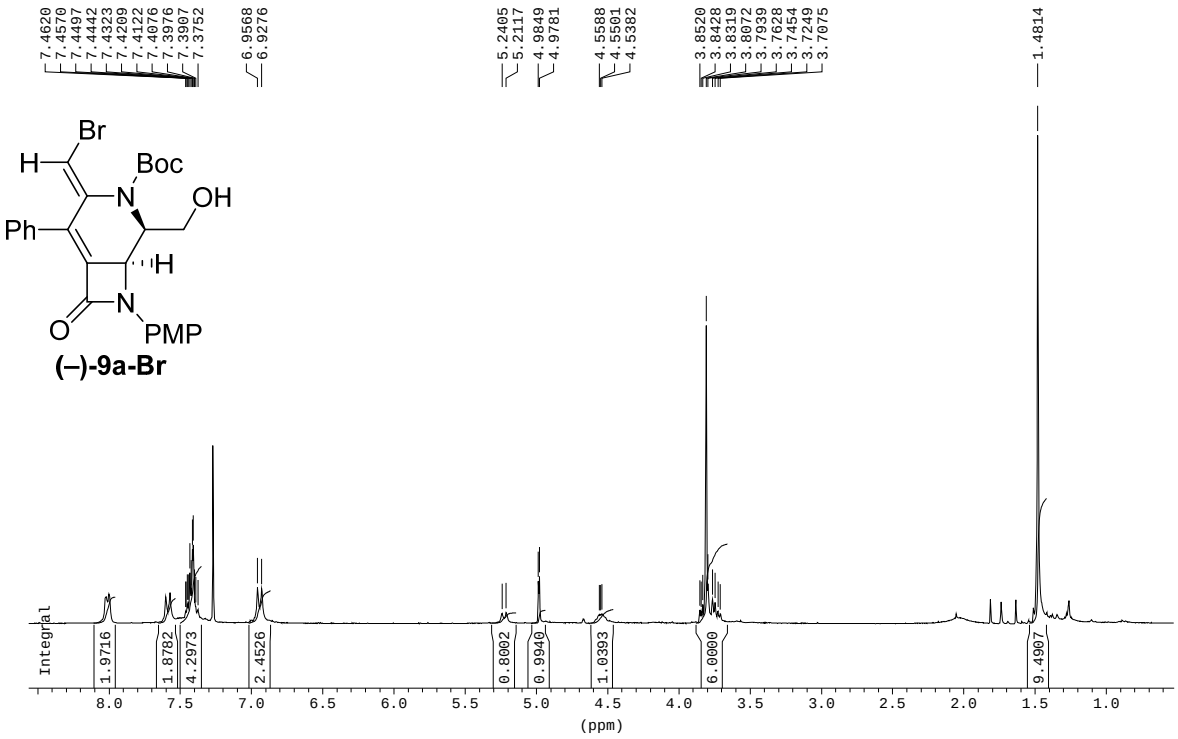
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3.8319
3.8072
3.7939
3.7628
3.7454
3.7249
3.7075
1.4814
Br
H
Boc
N
OH
Ph
H
N
O
PMP
(–)-9a-Br
Integral
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4.2973
2.4526
0.8002
0.9940
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6.0000
9.4907
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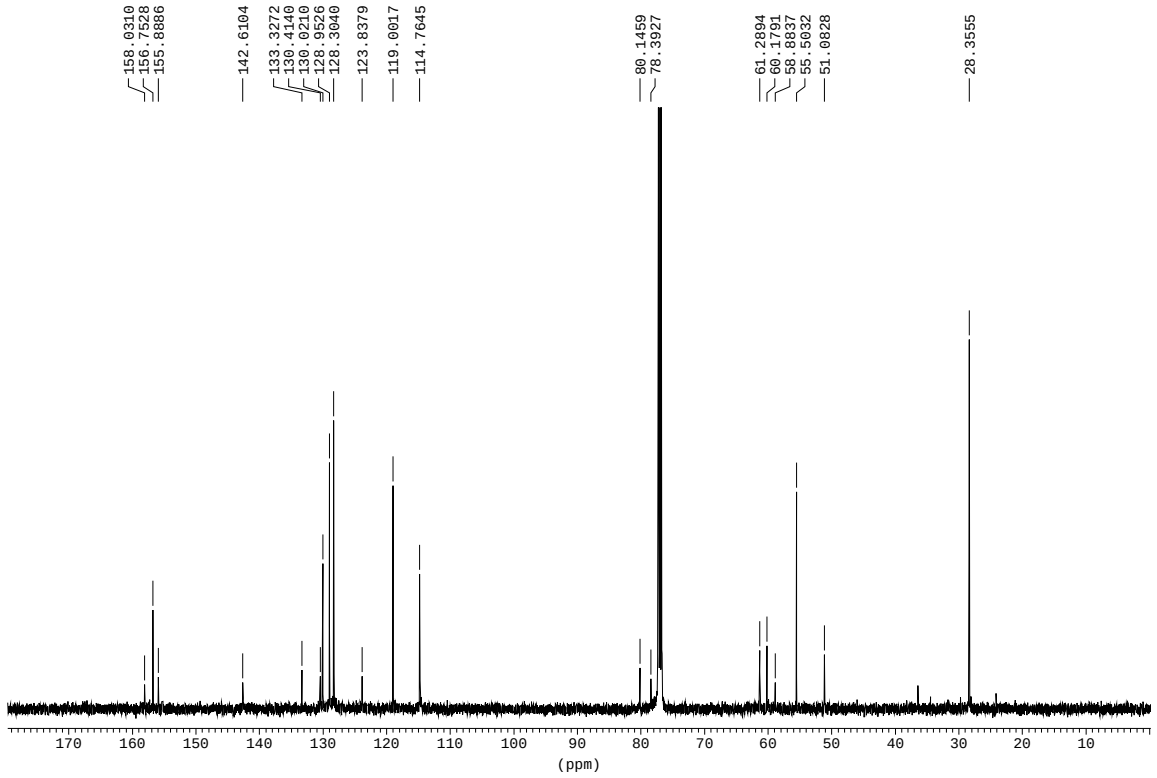
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119.0017
114.7645
80.1459
78.3927
61.2894
60.1791
58.8837
55.5032
51.0828
28.3555
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80
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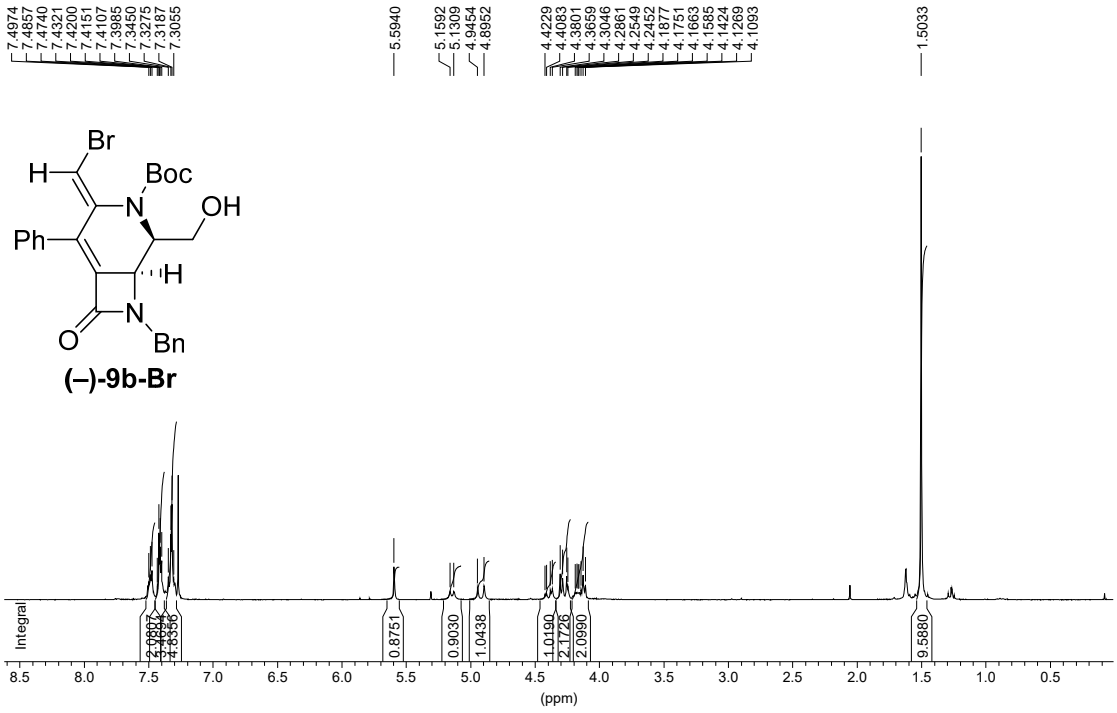
10
(ppm)

Q09TN620B



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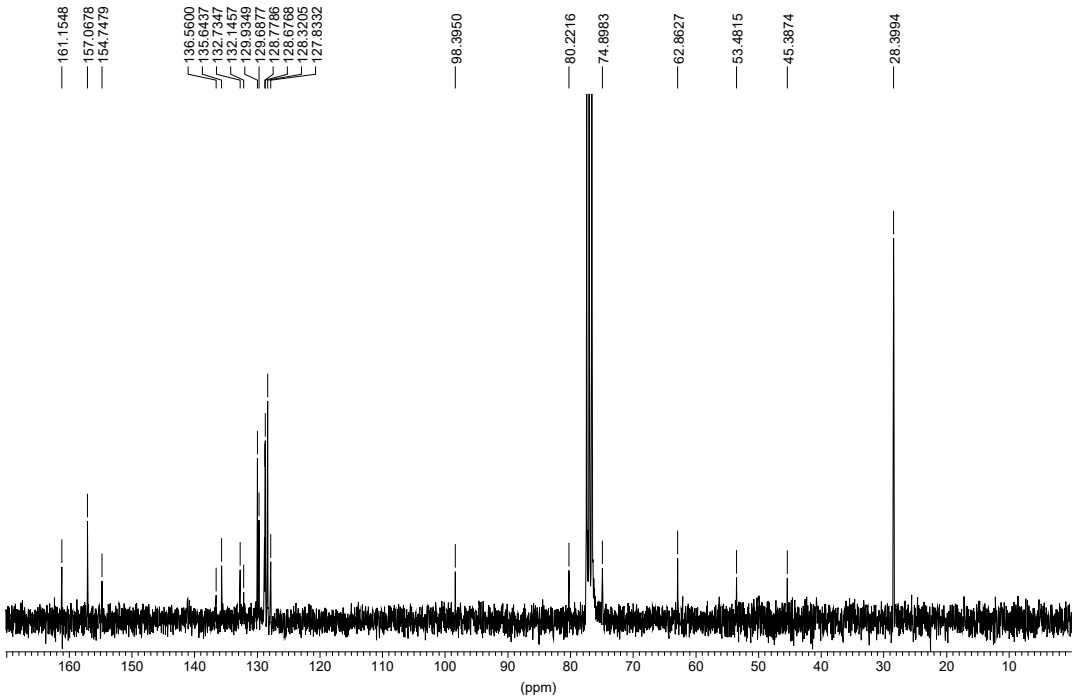

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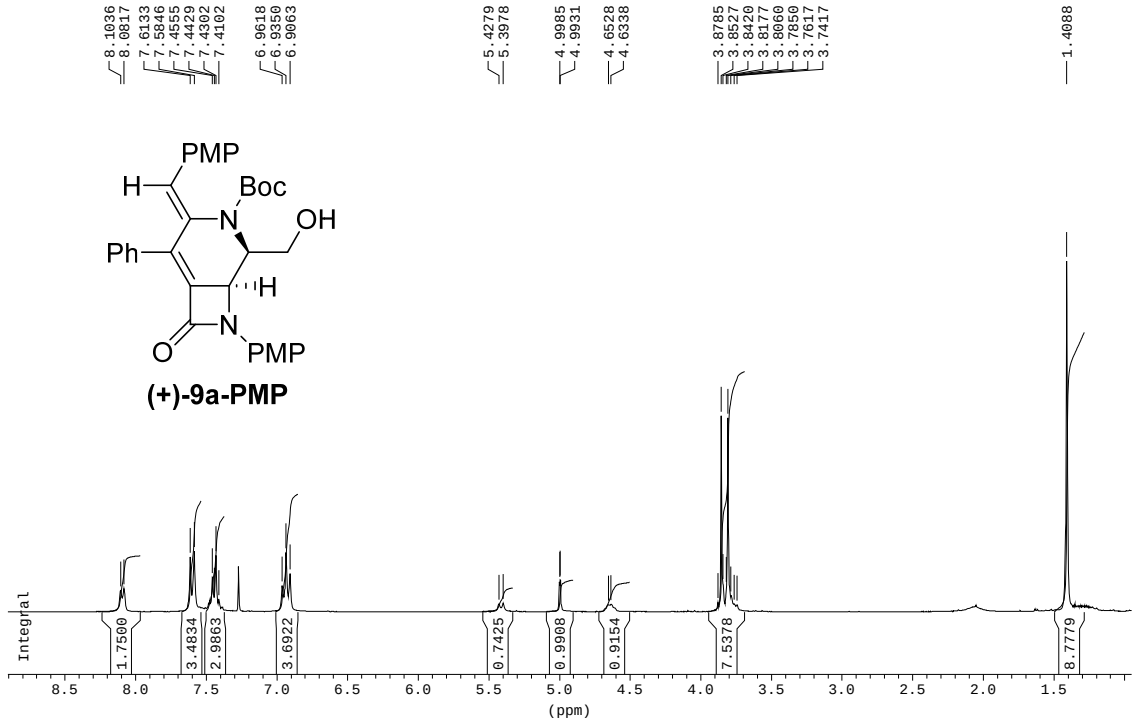

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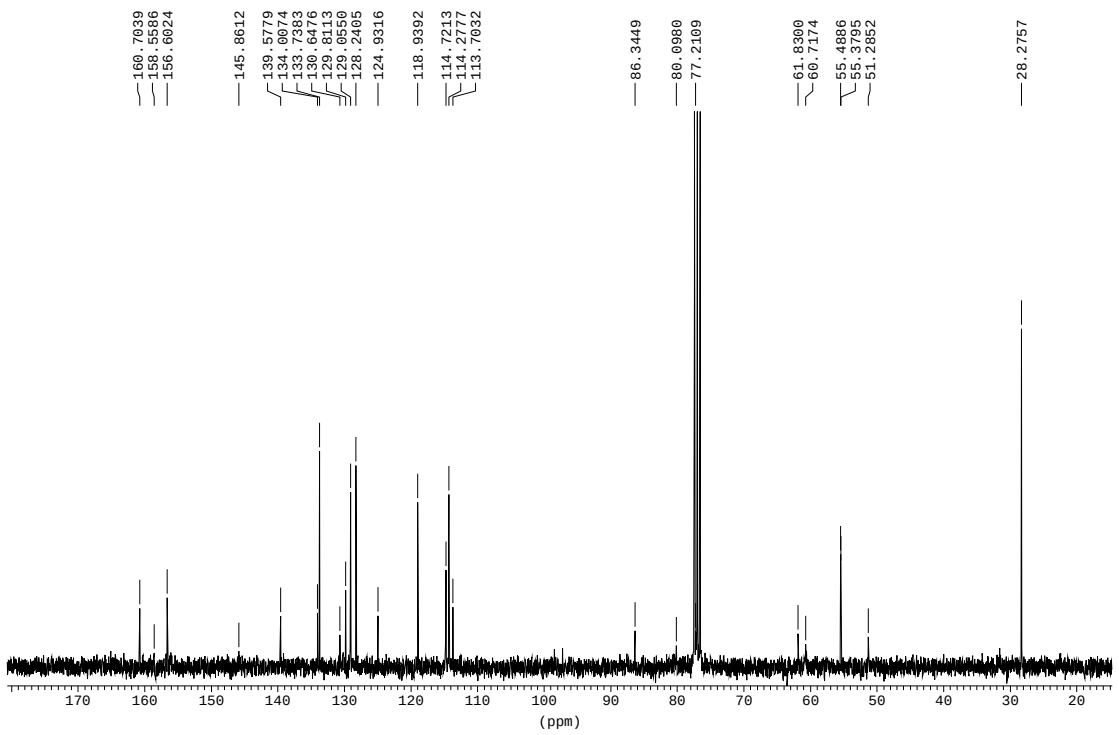

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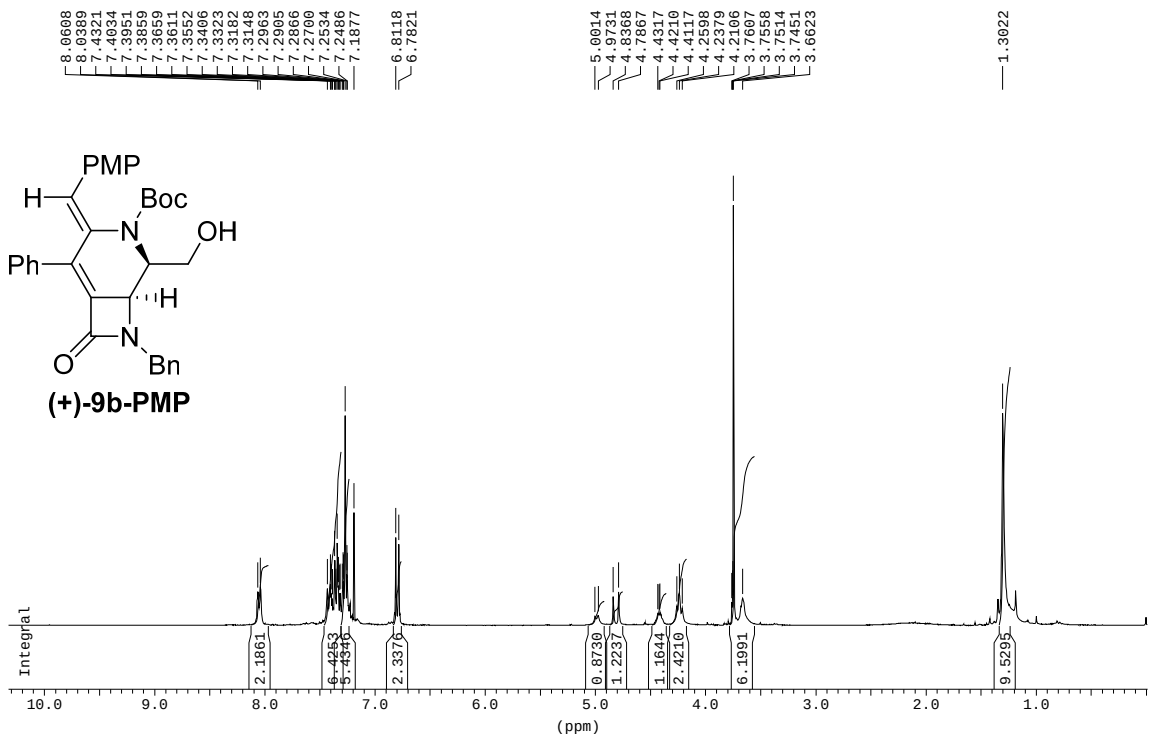

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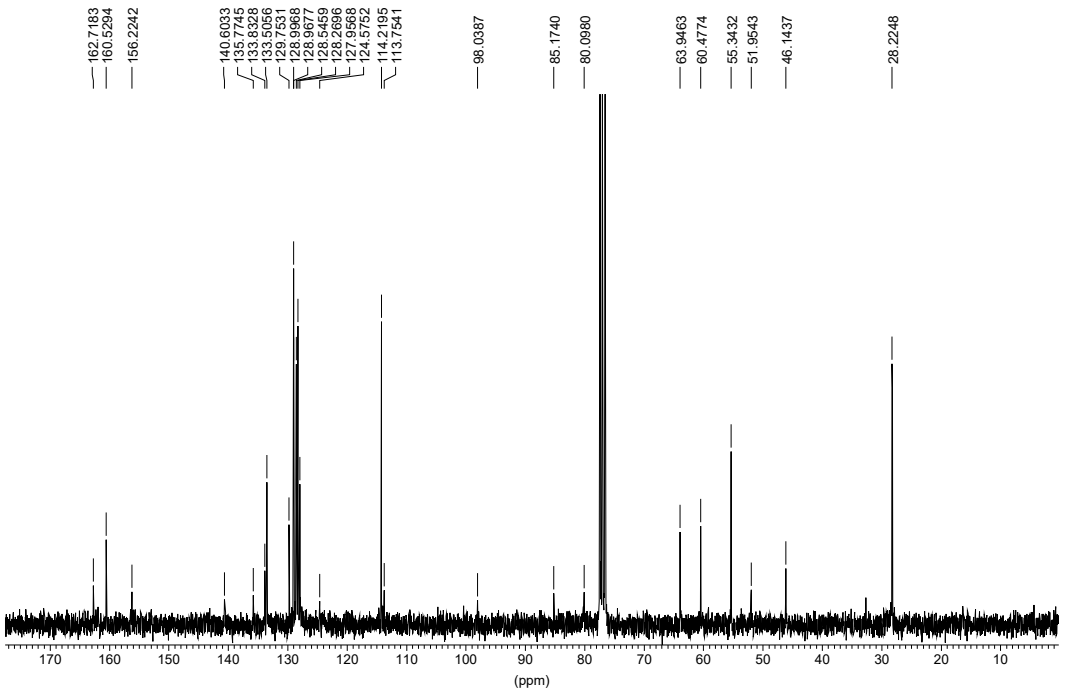

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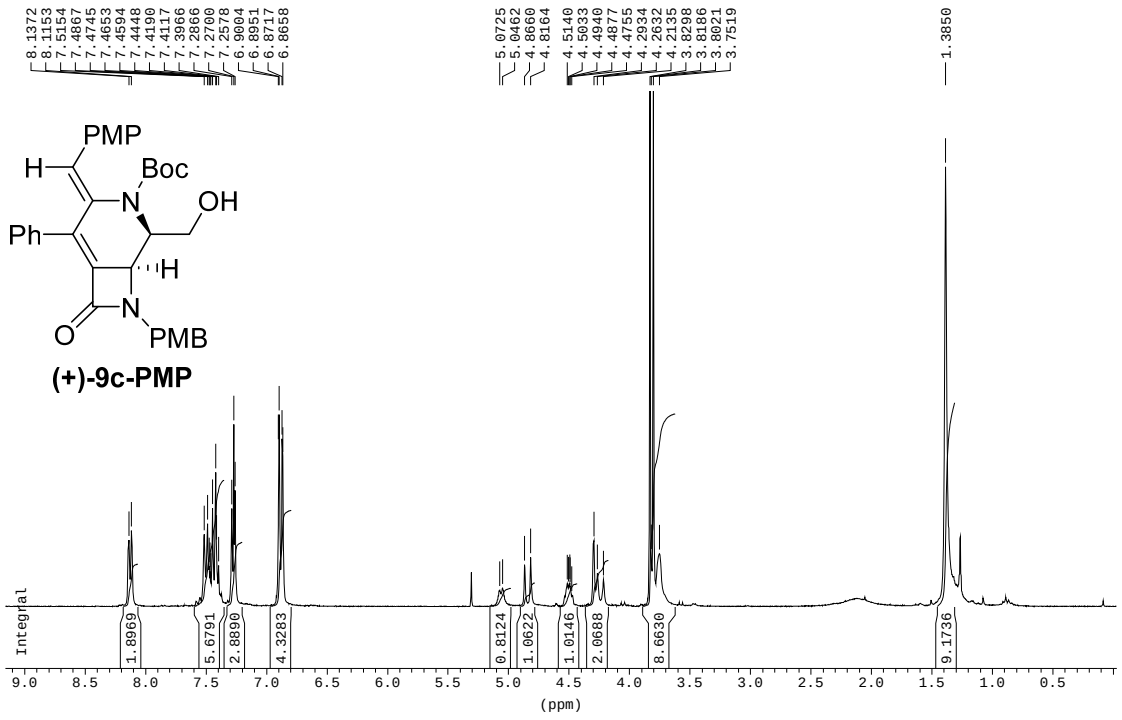

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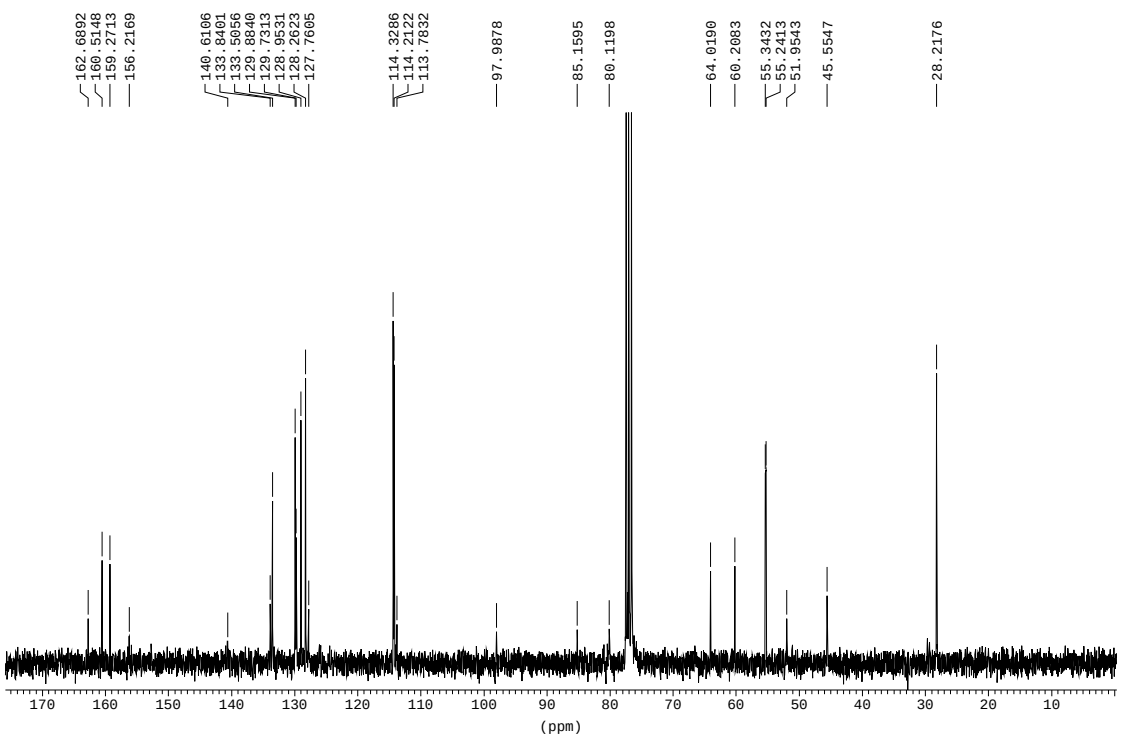

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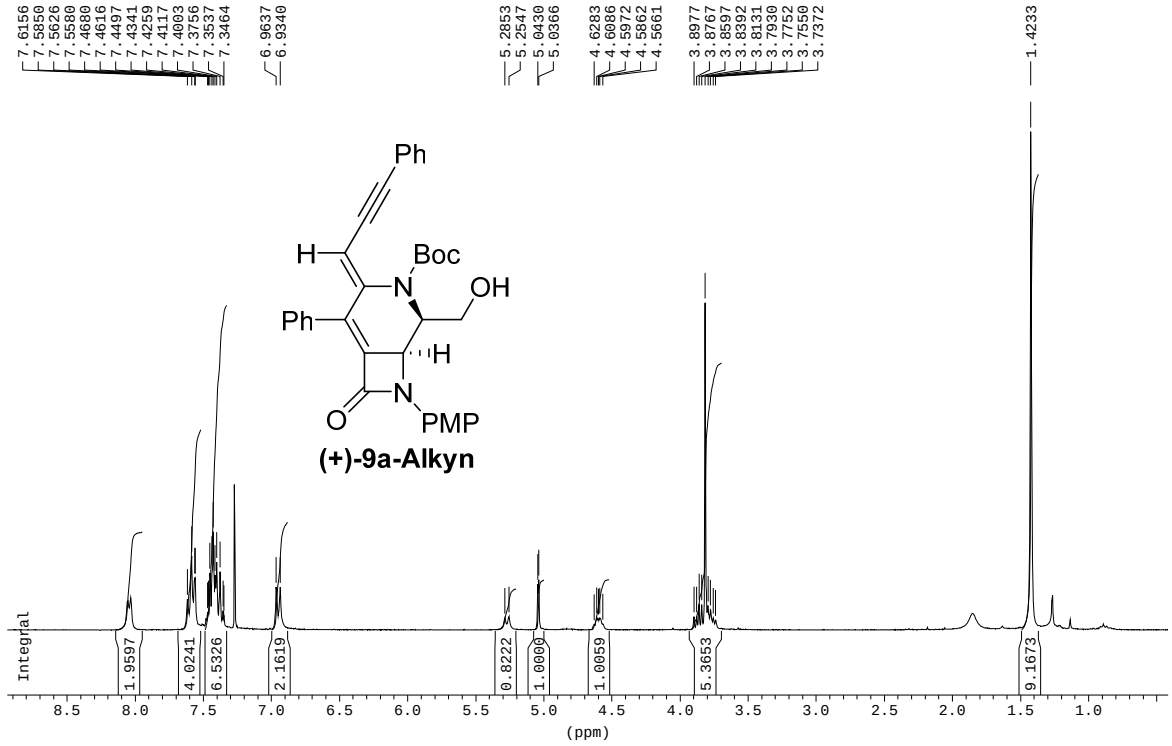

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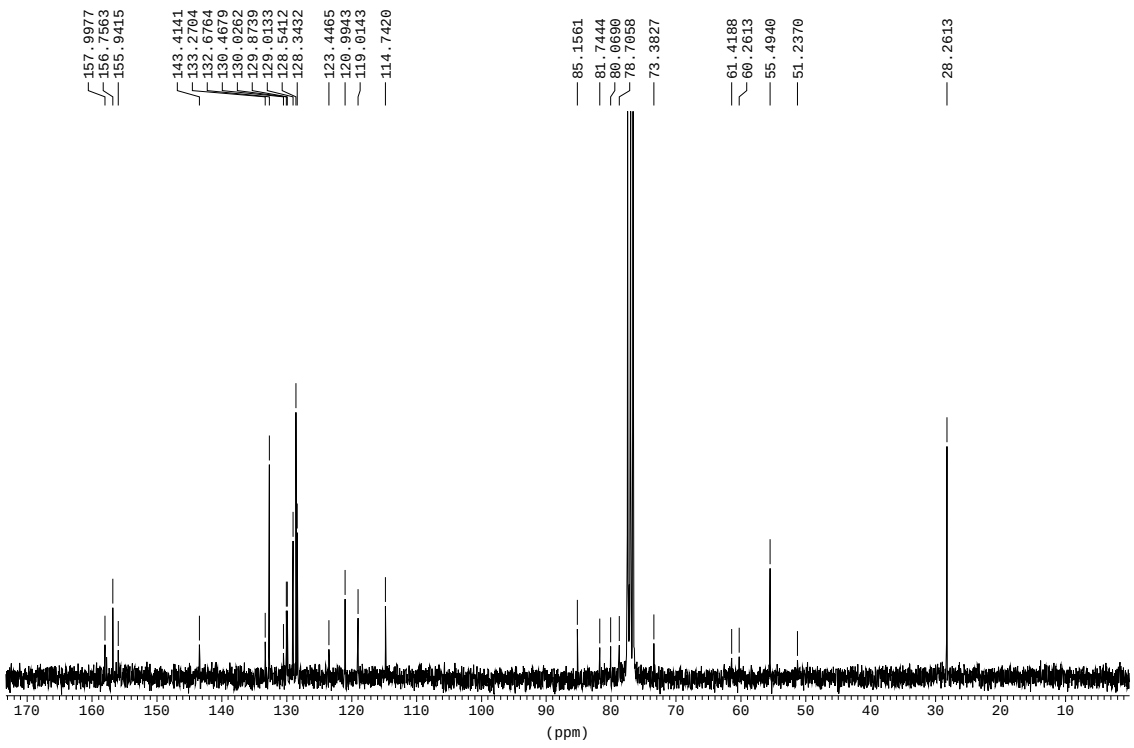

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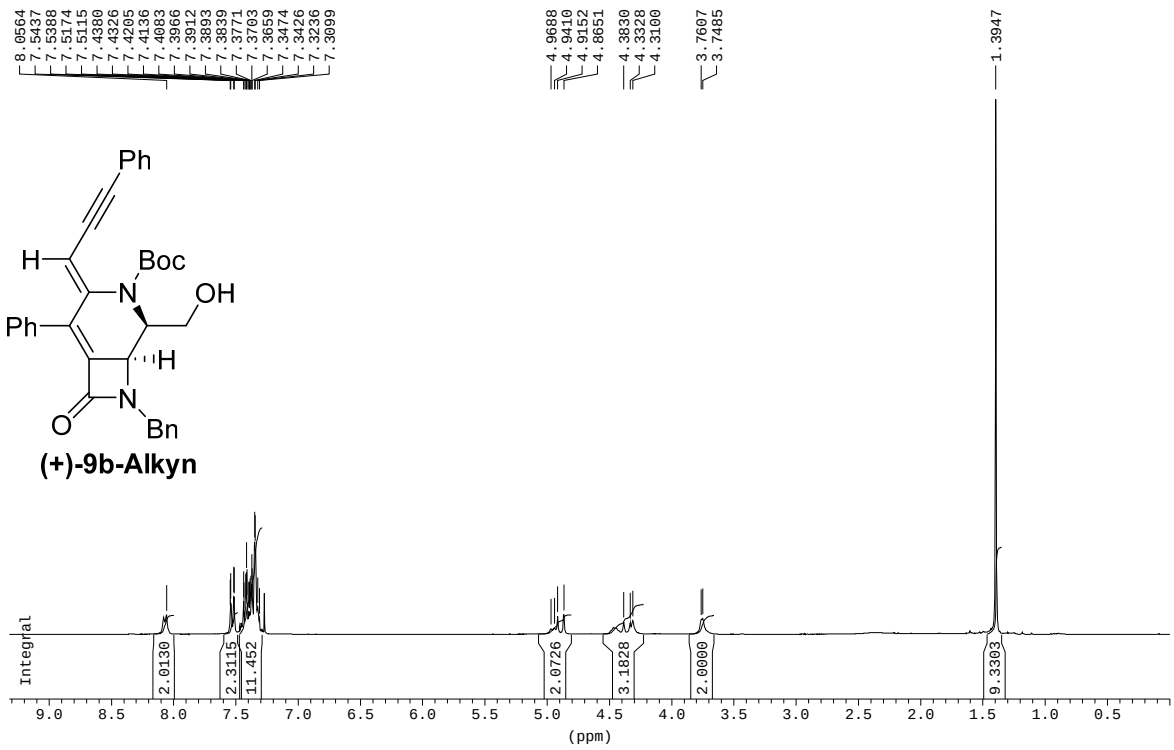

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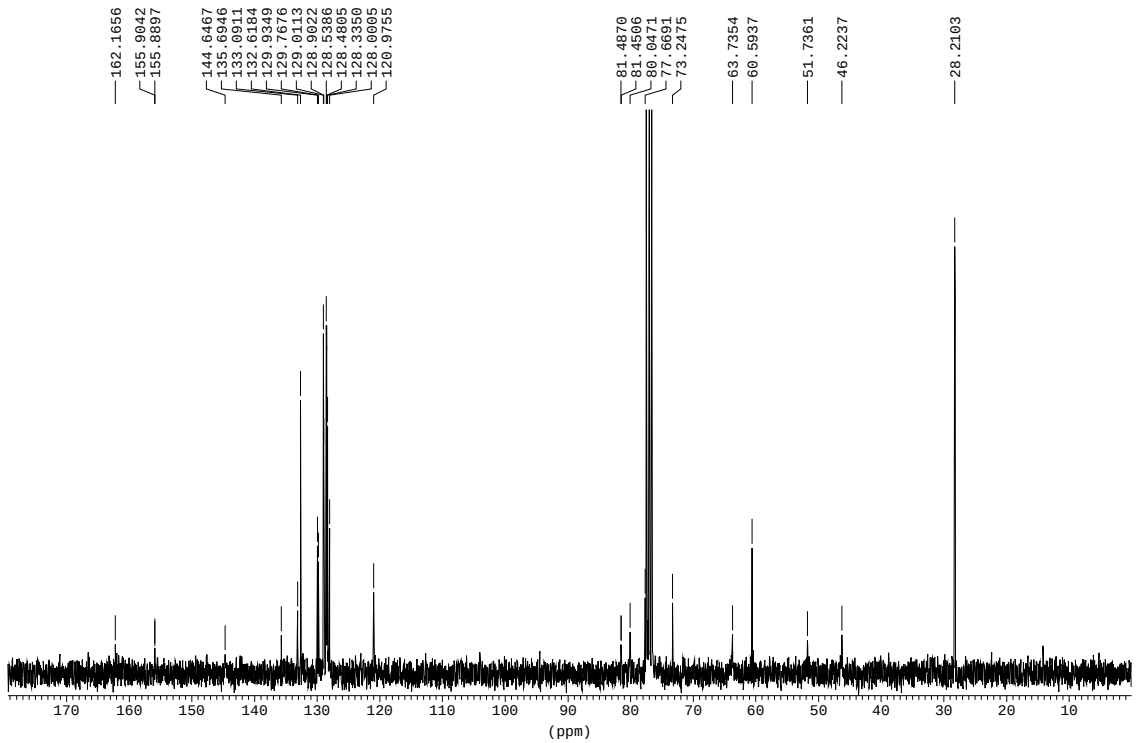

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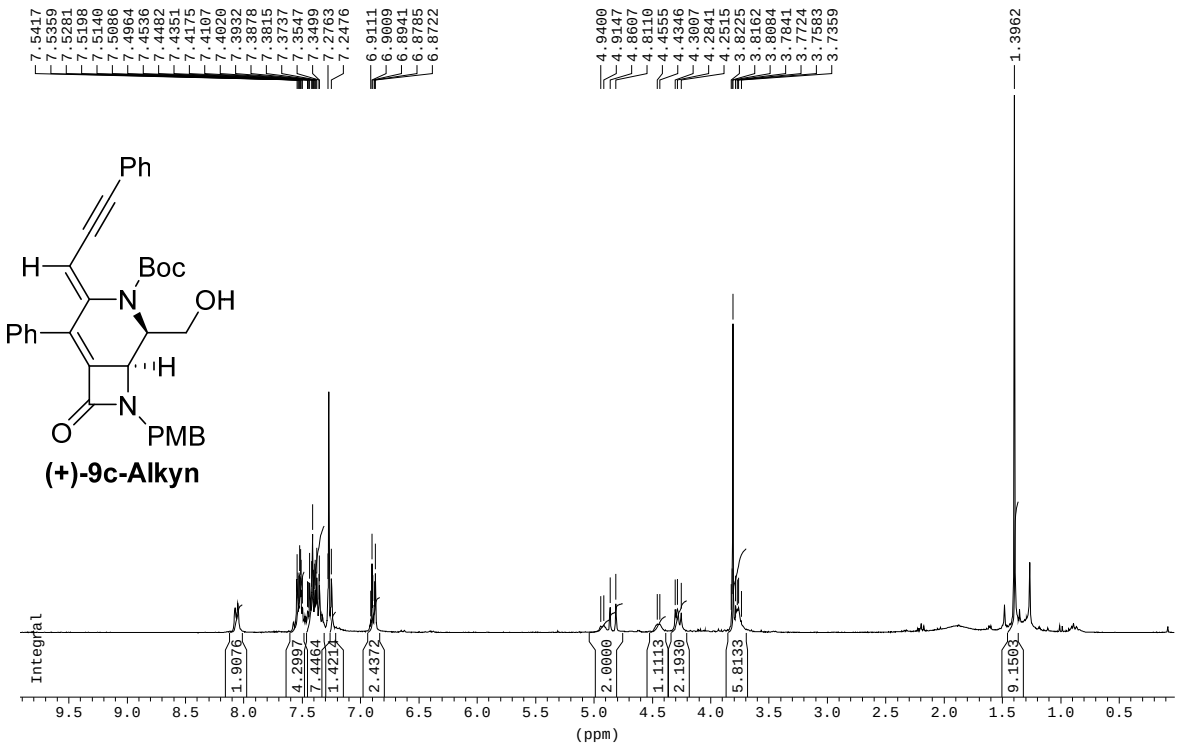

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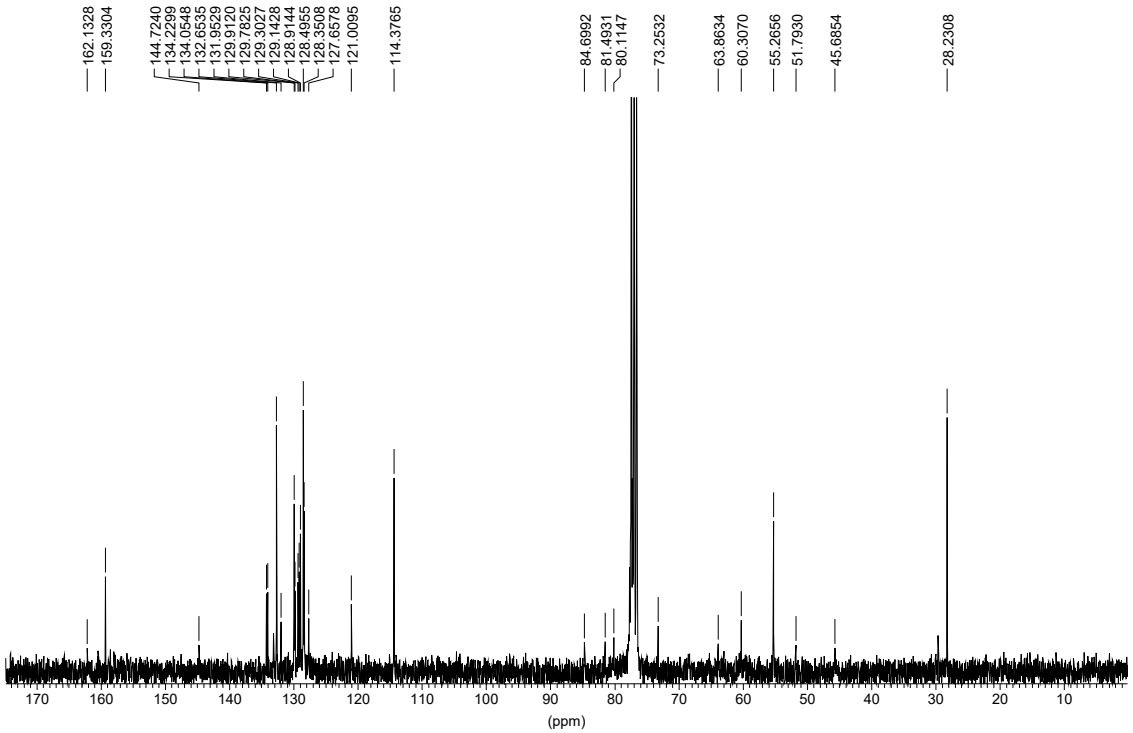

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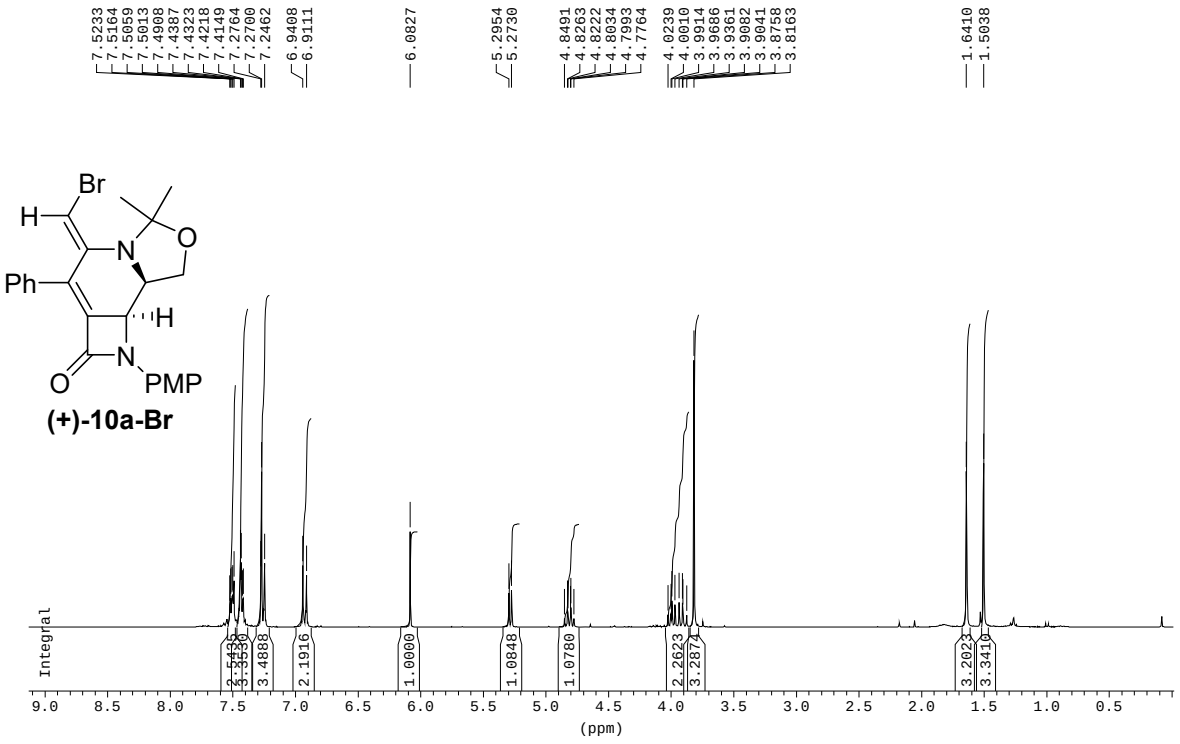

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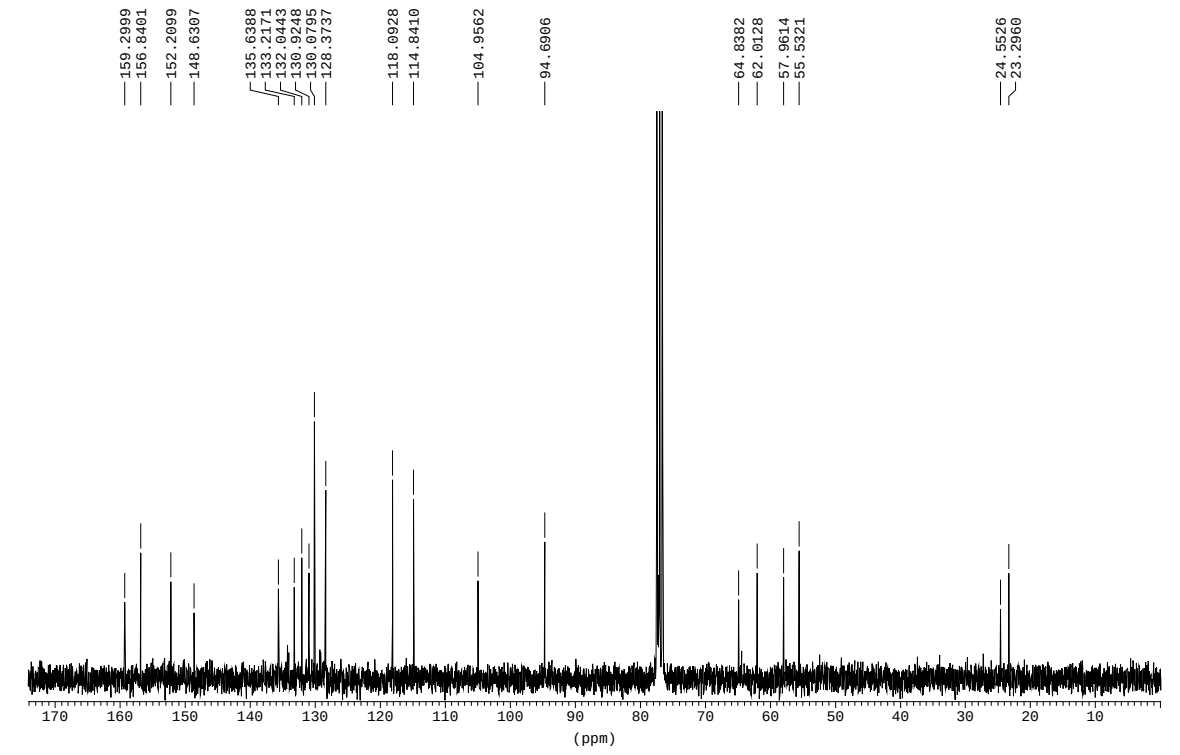

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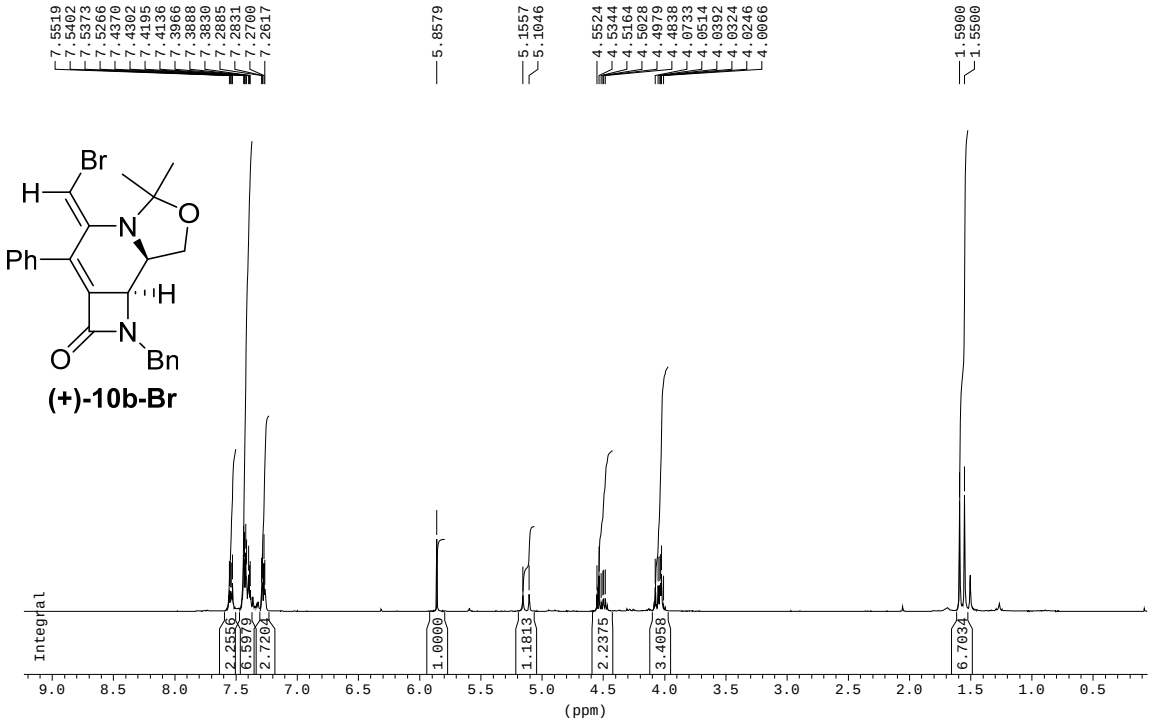

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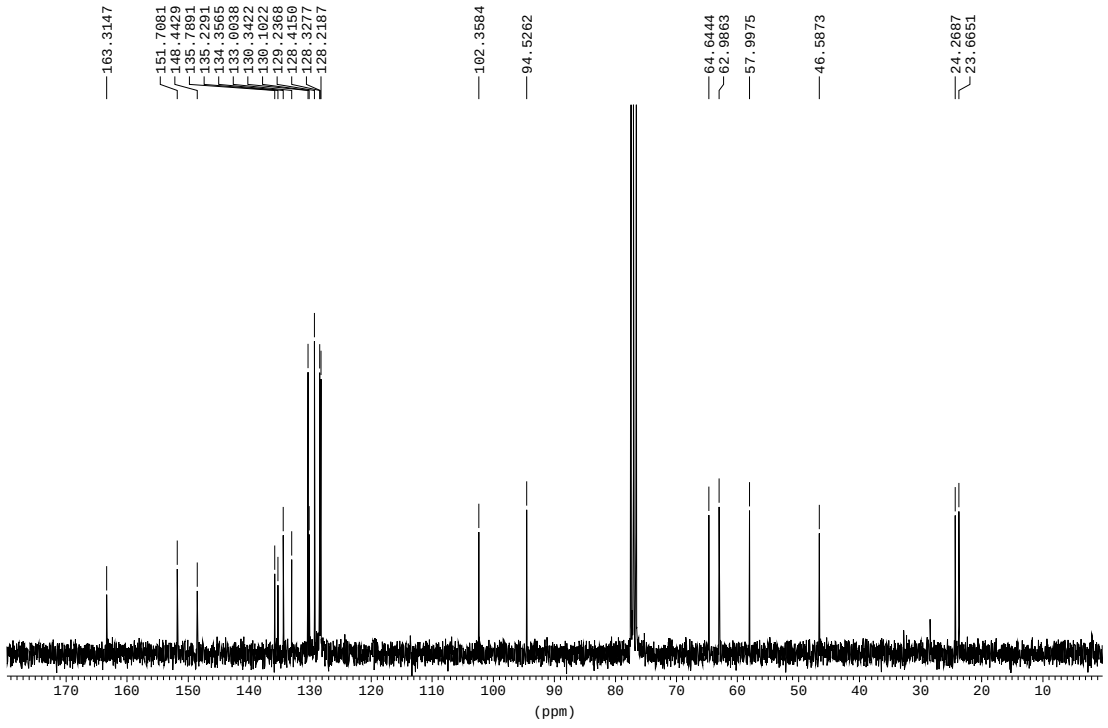

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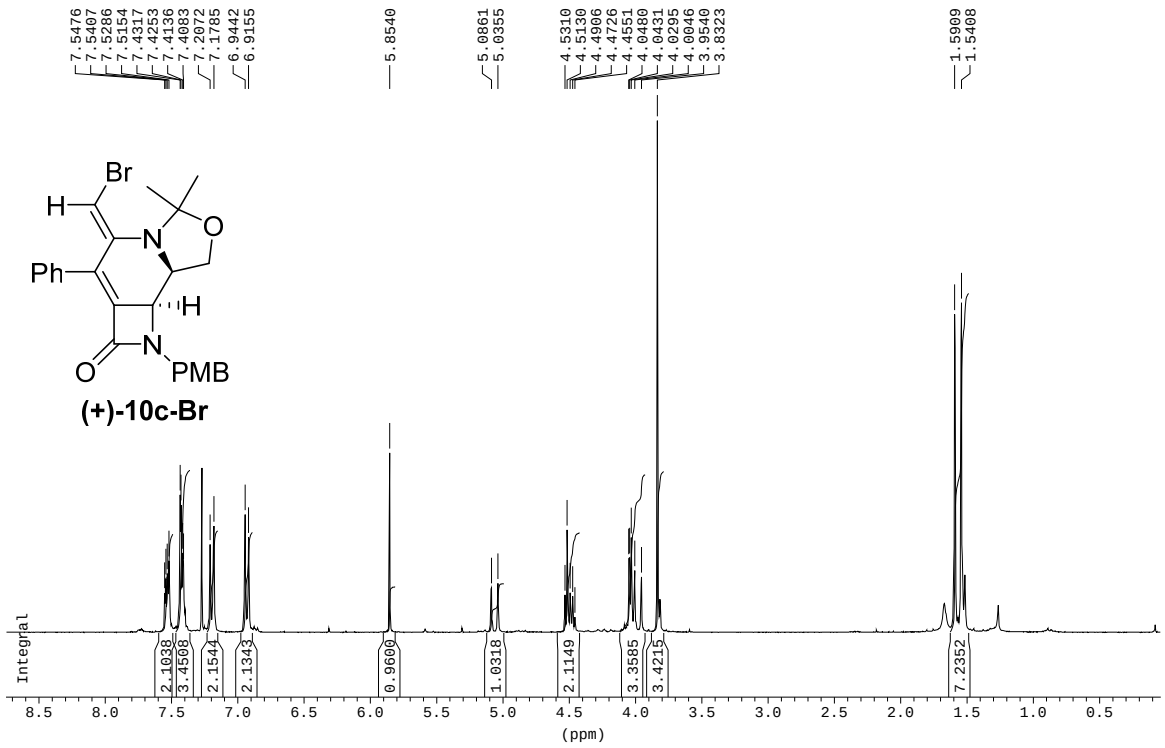

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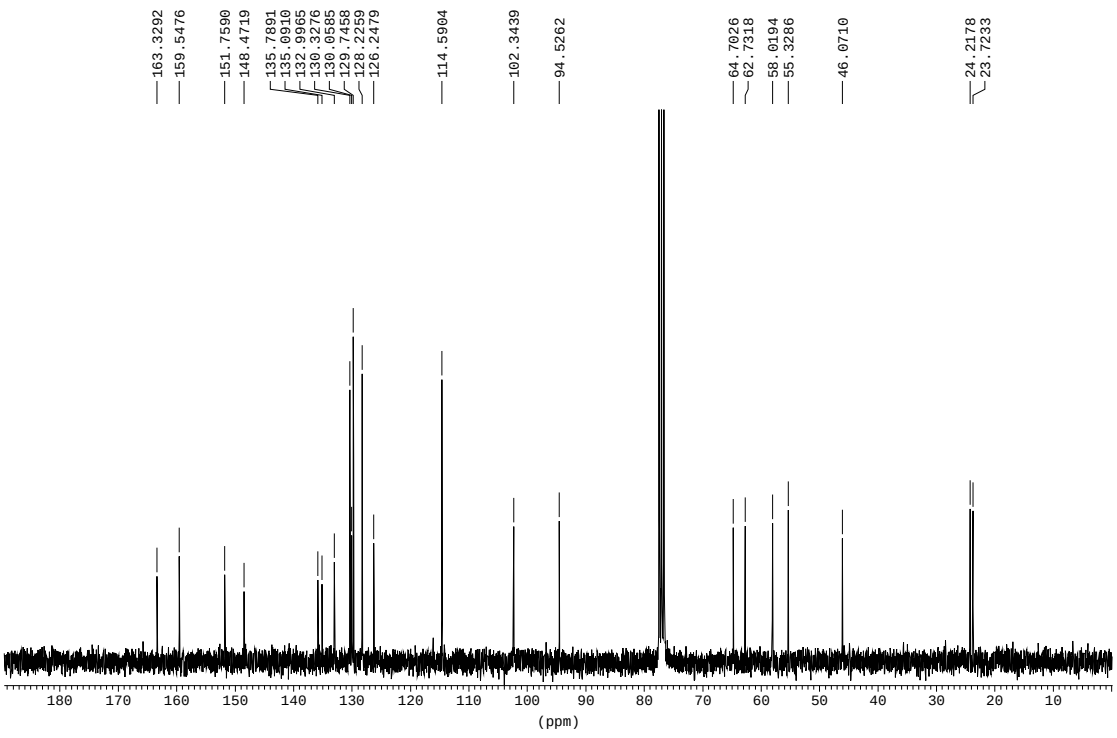

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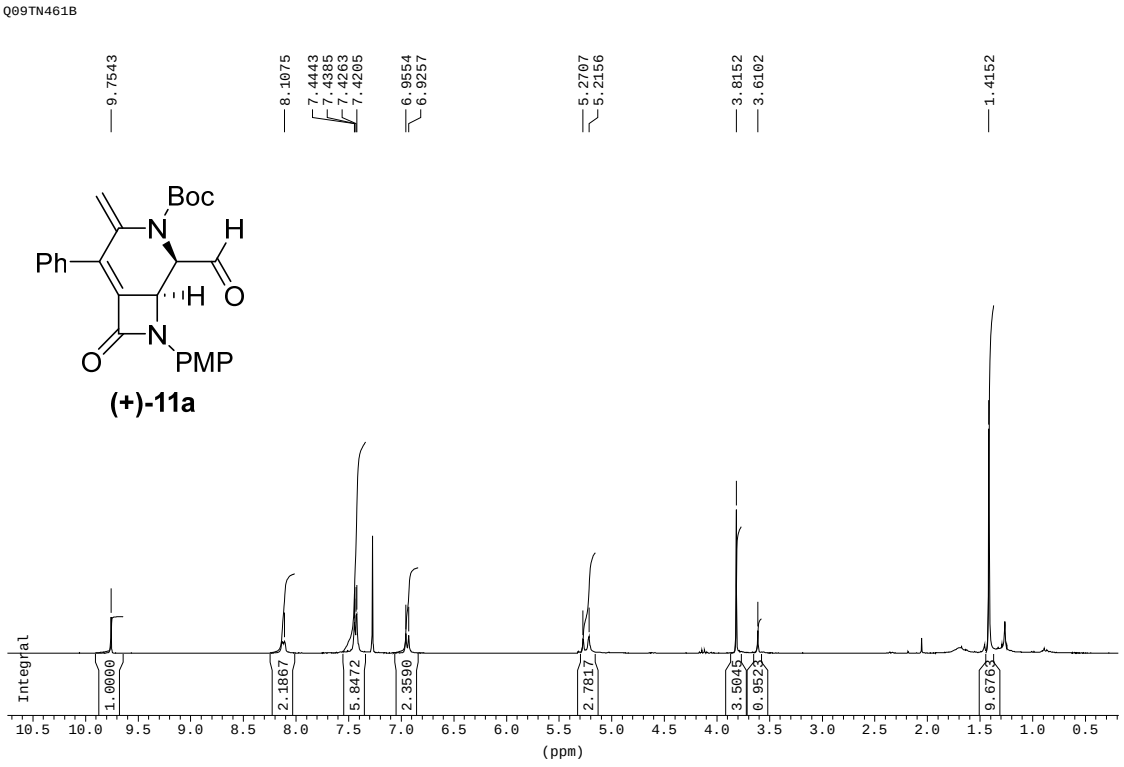

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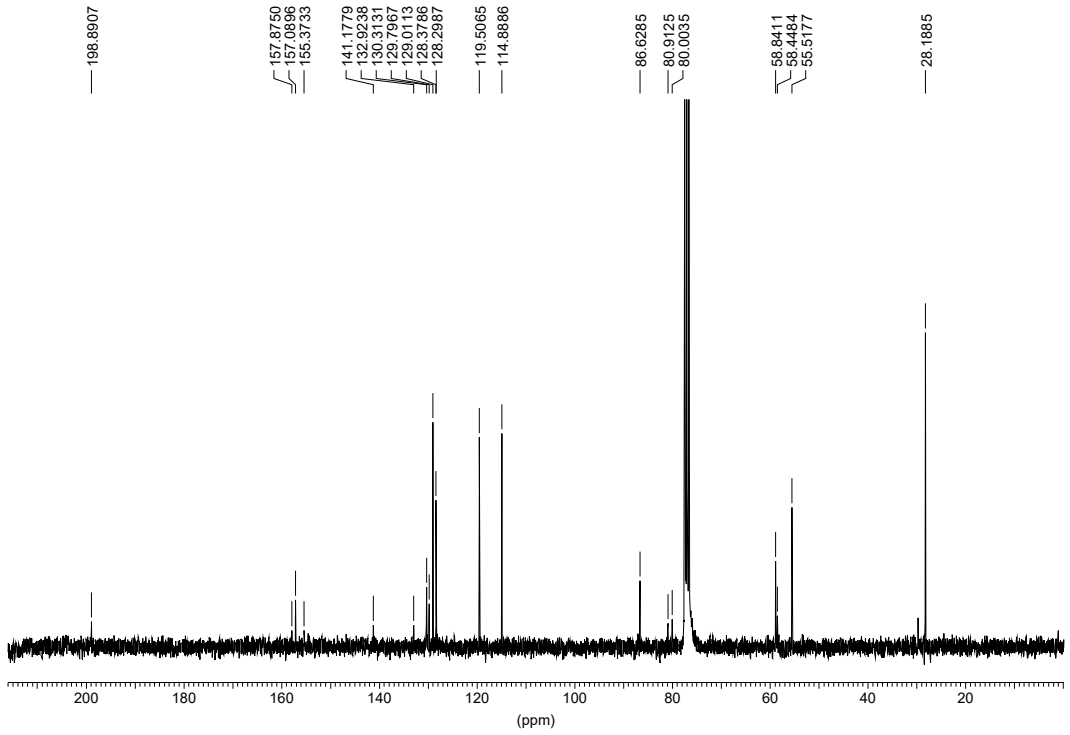

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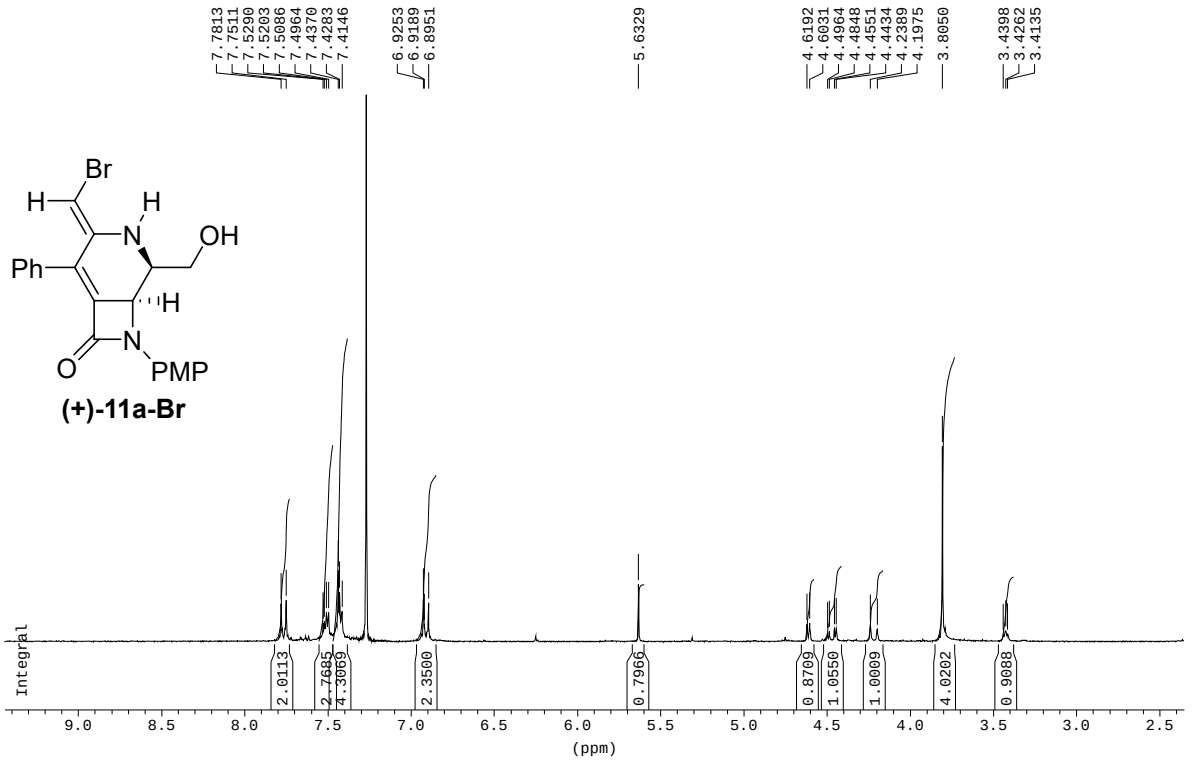
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3.4135
Br
H
N
H
OH
Ph
H
N
O
PMP
(+)-11a-Br
Integral
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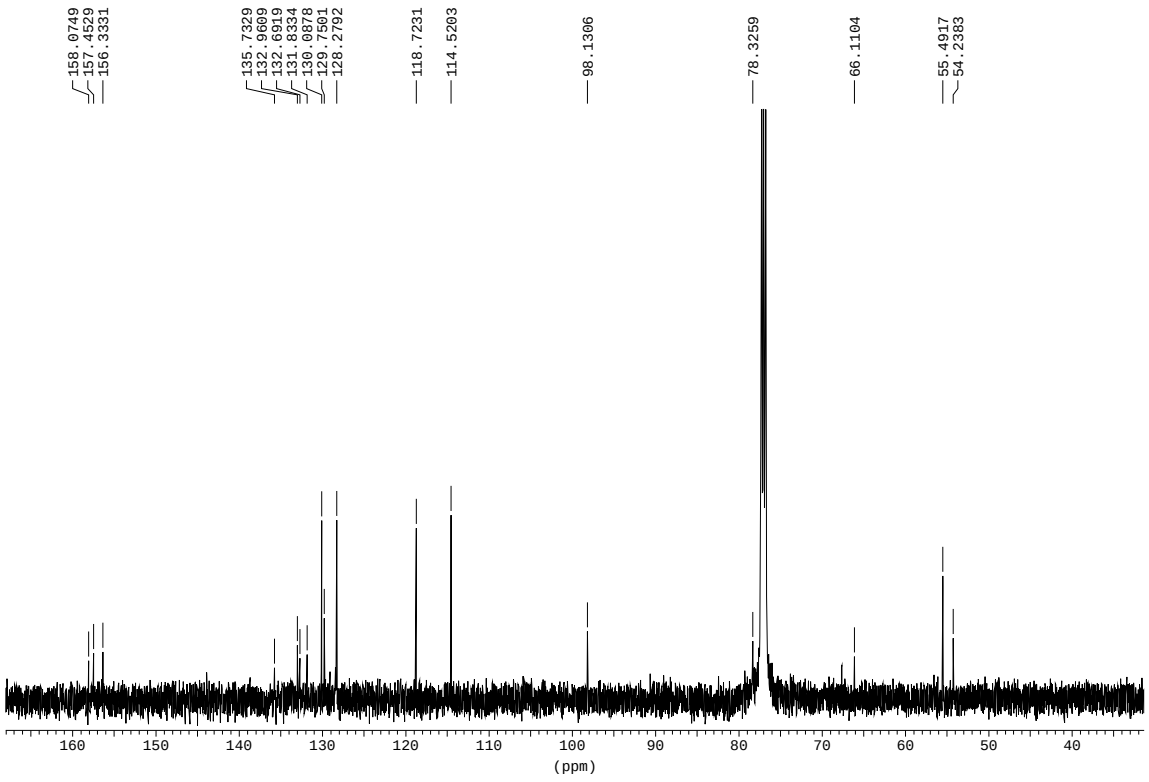
(ppm)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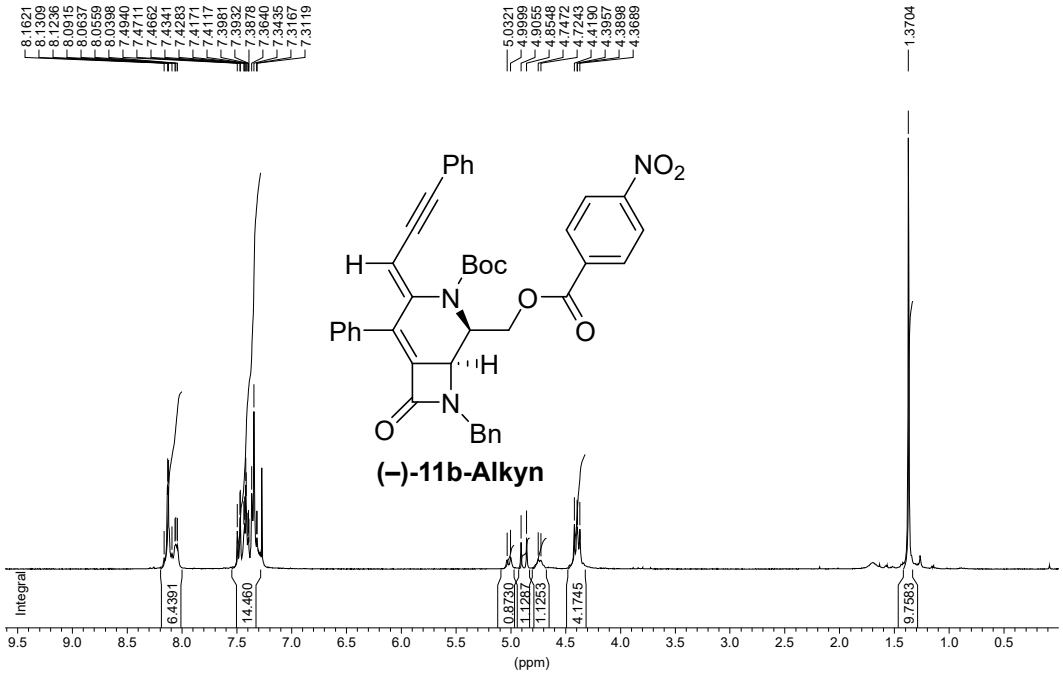

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