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Supporting Information

Chemodivergence in Alkene/Allene Cycloetherification of Enallenols: Iron *versus* Noble Metal Catalysis

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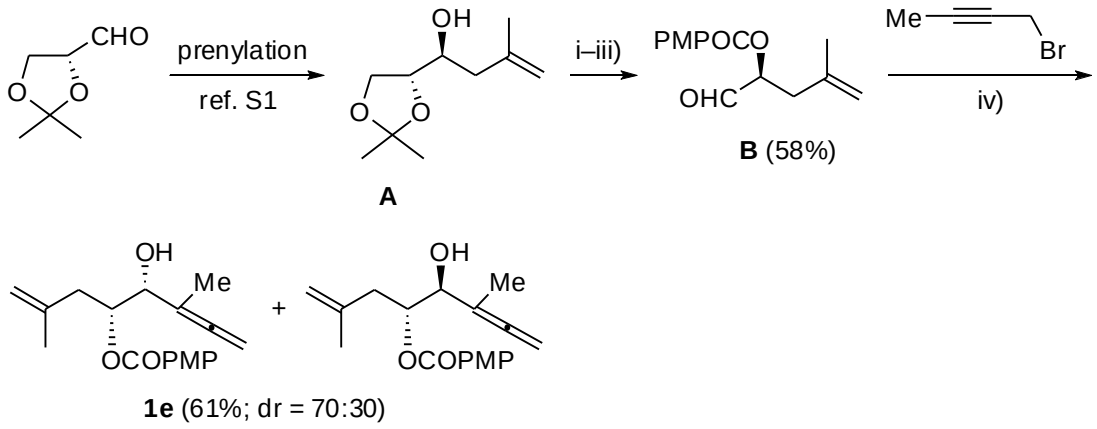
Enallenols *syn*-1e and ***anti*-1e were prepared from (*R*)-2,3-*O*-isopropylideneglyceraldehyde as shown in Scheme S1 via metal-mediated sequential prenylation[S1] and allenylation, followed by protecting groups manipulation.**



Scheme S1. Reagents and conditions: i) PMPCOCl, Et_3N, DMAP, CH_2Cl_2, reflux, 7 h. ii) 20 mol% $BiCl_3$, MeCN─H_2O, RT, 24 h. iii) $NaIO_4$, $NaHCO_3$ (aq. sat.), CH_2Cl_2, 5 h. iv) In, THF/NH_4Cl (aq. sat.), RT, 12 h. PMP = 4-$MeOC_6H_4$. DMPA = 4-Di(methylamino)pyridine.

Procedure for the preparation of aldehyde B. Triethylamine (3.0 mmol) and *p*-methoxybenzoyl chloride (1.2 mmol) were sequentially added dropwise via syringe to a solution of the alkenol **A** (1.0 mmol) and DMAP (cat) in dichloromethane (4 mL) at room temperature under argon. The resulting mixture was refluxed until disappearance of the starting material (TLC, 8 h). The crude mixture was diluted with CH_2Cl_2 (10 mL) and washed with saturated aqueous ammonium chloride (3 x 5 mL) and brine (3 x 5 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/hexanes (1:4) as eluent gave the corresponding ester (72%) as a colorless oil; $[\alpha]_D$ = +9.7 (*c* = 1.7 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.99 and 6.92 (d, *J* = 9.0 Hz, each 2H), 5.41 (m, 1H), 4.77 (t, *J* = 1.3 Hz, 2H), 4.26 (dd, *J* = 6.3, 5.1 Hz, 1H), 4.09 and 3.96 (dd, *J* = 8.3, 6.5 Hz, each 1H), 3.87 (s, 3H), 2.43 (d, *J* = 7.1 Hz, 2H), 1.37 and 1.36 (s, each 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 165.6, 163.4, 141.0, 131.7, 122.5, 113.8, 113.6, 109.6, 76.8, 71.7, 65.9, 55.4, 39.5, 26.4, 25.3, 22.5; IR ($CHCl_3$): ν = 1724 cm^{-1}; MS (EI): *m/z* (%): 320 (100) $[M]^+$.

The above acetonide derivative (2.43 mmol) was dissolved in acetonitrile (25 mL) and the solution was cooled to 0 °C. $BiCl_3$ (0.12 mmol) was added and the mixture was stirred at RT for 14 h (monitoring by TLC). The reaction mixture was poured into a satd aq solution of $NaHCO_3$. The aqueous layer was extracted with ethyl acetate (4 x 30 mL), and the combined organic extracts were dried ($MgSO_4$) and concentrated in vacuo to afford the corresponding diol. Further purification was not necessary. Saturated aqueous sodium hydrogen carbonate (243 μL) was added to a solution of the corresponding diol (2.43 mmol) in dichloromethane (15 mL), maintaining the temperature below 25 ^oC. Solid sodium periodate (4.86 mmol) was added over a 10 min period with vigorous stirring and the reaction was allowed to proceed for 2h, while the temperature was maintained below 25 ^oC. The solid was removed by filtration, the filtrate was dried ($MgSO_4$) and the solvent was removed under reduced pressure to give aldehyde **B** (58% overall yield from **A**). The crude product was used for next step without any further purification; $[\alpha]_D = -12.4$ (*c* = 0.8 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 9.67 (d, *J* = 1.0 Hz, 1H), 8.05 and 6.95 (d, *J* = 9.0 Hz, each 2H), 5.35 (ddd, *J* = 8.1, 5.1, 0.7 Hz, 1H), 4.88 (m, 2H), 3.88 (s, 3H), 2.63 (m, 2H), 1.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC): δ = 198.5, 165.8, 163.9, 149.9, 139.6, 132.0, 114.6, 113.8, 76.7, 55.5, 37.2, 22.5; IR ($CHCl_3$): ν = 1730, 1725, cm^{-1}; MS (EI): *m/z* (%): 249 (100) $[M + H]^+$, 240 (11) $[M]^+$.

Indium-promoted reaction between 3-substituted prop-2-ynyl bromides and aldehydes. General procedure for the synthesis of a**-allenic alcohols 1.** 1-Bromo-2-butyne or 1-bromo-3-phenyl-2-propyne (3.0 mmol) was added to a well stirred suspension of the appropriate aldehyde (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 5 mL). The organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/hexanes or dichloromethane/ethyl acetate mixtures gave analytically pure compounds. Spectroscopic and analytical data for pure forms of **1** follow.

a**-Allenic alcohol 1a.** Colorless solid; m. p. 100–102 ^oC; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 7.26 and 6.84 (d, *J* = 9.2 Hz, each 2H), 5.25 (br s, 1H), 5.21 (t, *J* = 1.5 Hz, 1H), 4.63 (m, 1H), 4.39 (m, 3H), 3.99 (m, 1H), 3.77 (s, 3H), 2.09 (br s, 1H), 1.92 (s, 3H), 1.65 (t, *J* = 2.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC): δ = 206.2, 165.8, 156.6, 138.3, 130.1, 120.8, 117.1, 114.0, 99.4, 76.6, 71.1, 58.5, 57.9, 55.4, 23.5, 14.8; IR ($CHCl_3$): ν = 3422, 2990, 1940, 1748 cm^{-1}; MS (ES): *m/z* (%): 299 (16) $[M]^+$, 298

(100) $[M - H]^+$; elemental analysis calcd (%) for $C_{18}H_{21}NO_3$ (299.4): C 72.22, H 7.07, N 4.68; found C 72.35, H 7.04, N 4.66.

a-**Allenic alcohol 1b.** Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.30 (m, 5H), 7.09 and 6.76 (d, *J* = 9.0 Hz, each 2H), 5.34 (d, *J* = 1.0 Hz, 1H), 5.28 (t, *J* = 1.5 Hz, 1H), 5.09 (t, *J* = 2.4 Hz, 2H), 5.01 (m, 1H), 4.51 (dd, *J* = 6.3, 5.6 Hz, 1H), 4.02 (dd, *J* = 5.6, 0.6 Hz, 1H), 3.77 (s, 3H), 2.30 (d, *J* = 6.6 Hz, 1H), 1.99 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 208.4, 165.8, 156.7, 138.5, 133.6, 129.8, 129.7, 127.3, 126.8, 121.4, 117.3, 113.9, 107.6, 80.7, 69.4, 59.2, 58.1, 55.5, 23.7; IR ($CHCl_3$): ν = 3424, 2988, 1938, 1748 cm^{-1}; MS (ES): *m/z* (%): 361 (11) $[M]^+$, 360 (100) $[M - H]^+$.

a-**Allenic alcohol 1c.** Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.45 and 6.85 (d, *J* = 9.0 Hz, each 2H), 4.79 (m, 1H), 4.72 (t, *J* = 3.1 Hz, 1H), 4.66 (dd, *J* = 3.2, 2.7 Hz, 1H), 4.56 (m, 1H), 3.78 (s, 3H), 2.13 and 1.83 (s, each 3H), 1.72 (t, *J* = 3.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 205.3, 162.0, 155.8, 138.2, 131.7, 130.7, 118.9, 114.2, 99.4, 78.0, 70.9, 63.2, 55.4, 21.4, 20.4, 15.7; IR ($CHCl_3$): ν = 3430, 2992, 1944, 1746 cm^{-1}; MS (ES): *m/z* (%): 299 (10) $[M]^+$, 298 (100) $[M - H]^+$.

a-**Allenic alcohol 1d.** Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.41 and 6.85 (d, *J* = 9.0 Hz, each 2H), 7.34 (m, 5H), 5.12 (m, 2H), 4.80 (m, 2H), 3.75 (s, 3H), 2.30 (d, *J* = 6.6 Hz, 1H), 2.09 and 1.85 (s, each 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 207.1, 162.3, 155.9, 138.5, 134.5, 131.6, 131.4, 130.3, 128.7, 126.6, 119.4, 113.9, 107.7, 82.0, 68.0, 62.0, 55.5, 21.5, 20.4; IR ($CHCl_3$): ν = 3428, 2991, 1939, 1746 cm^{-1}; MS (ES): *m/z* (%): 361 (7) $[M]^+$, 360 (100) $[M - H]^+$.

a-**Allenic alcohols 1e.** Diastereomeric mixture (syn:anti = 70:30); colorless oil; $[\alpha]_D$ = –5.4 (*c* = 0.5 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 8.11 (d, *J* = 9.0 Hz, 0.6H), 8.00 (d, *J* = 9.0 Hz, 1.4H), 6.92 (d, *J* = 9.0 Hz, 2H), 5.36 (m, 1H), 4.75 (m, 4H), 4.33 (q, *J* = 0.7 Hz, 2.2H), 4.08 (m, 0.3H), 3.90 (s, 0.9H), 3.86 (s, 2.1H), 2.50 (m, 2H), 1.80 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 205.9 (M), 205.3 (m), 166.1 (m), 165.9 (M), 164.6 (m), 163.4 (M), 141.6 (m), 141.2 (M), 131.7 (M + m), 122.5 (M + m), 114.1 (m), 113.6 (M + m), 113.4 (M), 99.8 (m), 99.0 (M), 77.7 (m), 77.1 (M), 73.1 (m), 72.5 (m), 73.9 (M), 73.8 (M), 55.4 (M + m), 39.4 (m), 37.7 (M), 22.5 (M + m), 15.2 (m), 15.0 (M),; IR ($CHCl_3$): ν = 3433, 2996, 1941, 1722, cm^{-1}; MS (ES): *m/z* (%): 301 (11) $[M]^+$, 300 (100) $[M - H]^+$.

General procedure for the Pt(II)-catalyzed cyclization of enallenols 1. Preparation of dihydrofurans 2. $[PtCl_2(CH_2{=}CH_2)]_2$ (0.05 mmol) and tris(2,6-dimethoxyphenyl)phosphine (0.10 mmol) were sequentially added to a stirred solution of the corresponding enallenol **1** (1.0 mmol) in dichloromethane (1.0 mL) under argon. The resulting mixture was stirred at room temperature until

disappearance of the starting material (TLC). The reaction was then quenched with brine (1.0 mL), the mixture was extracted with ethyl acetate (3 x 5 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 ethyl acetate/hexanes mixtures gave analytically pure dihydrofuran adducts **2**.

General procedure for the Ag(I)-promoted cyclization of enallenols 1. Preparation of dihydrofurans 2. Silver nitrate (0.20 mmol) was added to a stirred solution of the corresponding enallenol **1** (0.20 mmol) in acetone/water (1:1) (0.4 mL). The reaction was refluxed until disappearance of the starting material (TLC). The mixture was allowed to reach room temperature before brine (2 mL) was added, and then it was extracted with ethyl acetate (4 x 5 mL). The organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes mixtures gave analytically pure dihydrofuran adducts **2**.

General procedure for the Au(III)-catalyzed cyclization of enallenols 1. Preparation of dihydrofurans 2. $AuCl_3$ (0.05 mmol) was added to a stirred solution of the corresponding enallenol **1** (1.0 mmol) in dichloromethane (1.0 mL) under argon. The resulting mixture was stirred at room temperature until disappearance of the starting material (TLC). The reaction was then quenched with brine (1.0 mL), the mixture was extracted with ethyl acetate (3 x 5 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 ethyl acetate/hexanes mixtures gave analytically pure dihydrofuran adducts **2**.

Spectroscopic and analytical data for some representative forms of compounds **2** follow.

Dihydrofuran 2a. From 55 mg (0.18 mmol) of enallenol **1a**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **2a** (35 mg, 65%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.38 and 6.87 (d, J = 9.0 Hz, each 2H), 5.48 (m, 1H), 5.22 (d, J = 1.0 Hz, 1H), 5.15 (t, J = 1.3 Hz, 1H), 5.06 (m, 1H), 4.52 (m, 2H), 4.41 (dd, J = 6.1, 3.3 Hz, 1H), 4.01 (d, J = 6.1 Hz, 1H), 3.79 (s, 3H), 1.83 (br s, 1H), 1.68 (t, J = 1.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 165.7, 156.3, 136.4, 134.8, 131.1, 123.9, 119.3, 116.3, 114.3, 84.0, 75.0, 59.3, 57.7, 55.5, 23.1, 13.4; IR ($CHCl_3$): ν = 1746 cm^{-1}; HRMS (EI): calcd (%) for $C_{18}H_{21}NO_3[M]^+$: 299.1521; found: 299.1515.

Dihydrofuran 2b. From 33 mg (0.09 mmol) of enallenol **1b**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **2b** (28 mg, 84%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.22 (m, 5H), 7.17 and 6.75 (d, J = 9.0 Hz, each 2H), 6.09 (d, J =

1.9 Hz, 1H), 5.80 (m, 1H), 5.23 (m, 2H), 4.77 (m, 2H), 4.52 (dd, *J* = 6.0, 4.4 Hz, 1H), 3.93 (d, *J* = 6.0 Hz, 1H), 3.76 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 165.8, 156.2, 136.8, 134.9, 133.0, 130.5, 128.5, 128.0, 126.1, 124.6, 119.5, 116.3, 114.2, 81.4, 75.9, 58.4, 57.9, 55.5, 23.3, 13.4; IR ($CHCl_3$): ν = 1748 cm^{-1}; MS (EI): *m/z* (%): 362 (27) $[M + H]^+$, 361 (100) $[M]^+$.

Au(III)-catalyzed cyclization of enallenol 1e. Preparation of dihydrofurans 2ca and 2cb. From 43 mg (0.14 mmol) of a diastereomeric mixture (70:30) of enallenol **1e**, and after chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent, 19 mg (45%) of the less polar compound **2ca** and 8 mg (19%) of the more polar compound **2cb** were obtained.

Dihydrofuran 2ca. Colorless oil; $[\alpha]_D$ = –9.6 (*c* = 1.3 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 8.03 and 6.91 (d, *J* = 9.0 Hz, each 2H), 5.63 (m, 1H), 5.51 (dt, *J* = 10.3, 2.7 Hz, 1H), 4.91 (m, 1H), 4.76 (m, 2H), 4.64 (m, 2H), 3.86 (s, 3H), 2.59 (dd, *J* = 13.9, 10.1 Hz, 1H), 2.22 (d, *J* = 15.1 Hz, 1H), 1.83 (m, 3H), 1.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 165.9, 163.6, 145.3, 141.0, 131.8, 122.3, 119.4, 113.6, 111.2, 88.2, 72.5, 72.1, 55.5, 36.3, 22.5, 13.0; IR ($CHCl_3$): ν = 1724 cm^{-1}; HRMS (ES): calcd (%) for $C_{18}H_{22}O_4[M]^+$: 302.1518; found: 302.1513.

Dihydrofuran 2cb. Colorless oil; $[\alpha]_D$ = –5.0 (*c* = 1.0 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.97 and 6.91 (d, *J* = 9.0 Hz, each 2H), 5.44 (ddd, *J* = 8.8, 5.5, 1.5 Hz, 1H), 4.80 (m, 2H), 4.72 (br s, 1H), 4.65 (m, 2H), 3.86 (s, 3H), 2.56 (d, *J* = 8.1 Hz, 1H), 2.49 (d, *J* = 5.9 Hz, 1H), 1.82 (t, *J* = 1.1 Hz, 3H), 1.77 (d, *J* = 1.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 163.5, 159.9, 145.4, 131.7, 131.6, 127.7, 118.6, 113.7, 113.5, 87.8, 77.9, 76.3, 55.5, 33.4, 22.4, 12.6; IR ($CHCl_3$): ν = 1722 cm^{-1}; MS (EI): *m/z* (%): 302 (19) $[M]^+$, 135 (100).

Dihydrofuran 2d. From 35 mg (0.12 mmol) of enallenol **1c**, and after chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent gave compound **2d** (23 mg, 64%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.50 and 6.85 (d, *J* = 9.3 Hz, each 2H), 5.45 (t, *J* = 1.5 Hz, 1H), 5.18 (m, 1H), 4.84 (br s, 1H), 4.54 (m, 1H), 4.34 (m, 1H), 3.78 (s, 3H), 2.14 and 1.86 (s, each 3H), 1.73 (t, *J* = 1.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 169.0, 155.6, 135.5, 134.3, 132.1, 124.3, 122.9, 119.6, 114.1, 86.7, 74.6, 63.3, 55.5, 21.3, 20.3, 13.5; IR ($CHCl_3$): ν = 1745 cm^{-1}; HRMS (ES): calcd (%) for $C_{18}H_{21}NO_3[M]^+$: 299.1521; found: 299.1525.

Dihydrofuran 2e. From 30 mg (0.08 mmol) of enallenol **1d**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **2e** (20 mg, 68%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.35 (m, 3H), 7.22 (m, 2H), 7.04 and 6.74 (d, *J* = 9.0 Hz, each 2H),

5.91 (m, 1H), 5.77 (m, 1H), 4.85 (br s, 1H), 4.74 (dd, *J* = 3.4, 1.9 Hz, 1H), 4.67 (dd, *J* = 5.8, 1.7 Hz, 1H), 3.78 (s, 3H), 2.08 and 1.90 (s, each 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 169.0, 155.8, 139.2, 136.7, 132.9, 131.1, 128.7, 128.2, 126.4, 124.0, 119.3, 115.9, 113.8, 83.0, 76.6, 61.2, 55.4, 21.2, 20.2; IR ($CHCl_3$): ν = 1747 cm^{-1}; MS (ES): *m/z* (%): 362 (100) $[M + H]^+$, 361 (15) $[M]^+$.

General procedure for the [Bi(III), In(III), or Hf(IV)]-promoted cyclization of enallenols 1. Preparation of tetrahydrofurans 3. A suspension of the corresponding enallenol **1** (1.0 mmol) and the appropriate metallic chloride (1.5 mmol) in dichloromethane (5 mL) was heated at 70 ^{o}C in a sealed tube until complete disappearance (TLC) of the starting material. The reaction mixture was allowed to cool to room temperature and the solvent was removed under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes mixtures gave analytically pure tetrahydrofuran adducts **3**.

General procedure for the Fe(III)-catalyzed cyclization of enallenols 1. Preparation of tetrahydrofurans 3. $FeCl_3$ (0.10 mmol) was added to a stirred solution of the corresponding enallenol **1** (1.0 mmol) in 1,2-dichloroethane (1.0 mL). The resulting mixture was heated at 80 ^{o}C in a sealed tube until complete disappearance (TLC) of the starting material. The reaction mixture was allowed to cool to room temperature, and then was quenched with aqueous saturated NH_4Cl (1.0 mL). The mixture was extracted with ethyl acetate (3 x 5 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 ethyl acetate/hexanes mixtures gave analytically pure tetrahydrofuran adducts **3**.

Tetrahydrofuran 3a. From 122 mg (0.5 mmol) of enallenol **1a**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **3a** (101 mg, 83%) as a colorless solid. Mp: 107–108 ºC (hexanes/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.26 and 6.87 (d, *J* = 9.3 Hz, each 2H), 4.88 (m, 3H), 4.62 (t, *J* = 4.5 Hz, 1H), 3.79 (s, 3H), 3.55 (d, *J* = 4.4 Hz, 1H), 1.83 (td, *J* = 3.2, 0.7 Hz, 3H), 1.55 and 1.31 (s, each 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 204.3, 163.1, 156.2, 130.9, 117.8, 114.6, 100.3, 80.5, 76.7, 76.5, 63.2, 60.8, 55.5, 28.3, 25.4, 16.5; IR ($CHCl_3$): ν = 2995, 1945, 1750 cm^{-1}; MS (ES): *m/z* (%): 300 (100) $[M + H]^+$, 299 (18) $[M]^+$; elemental analysis calcd (%) for $C_{18}H_{21}NO_3$ (299.4): C 72.22, H 7.07, N 4.68; found C 72.34, H 7.04, N 4.71.

Tetrahydrofuran 3b. From 34 mg (0.09 mmol) of enallenol **1b**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **3b** (21 mg, 65%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.53 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.32 (m, 3H), 7.28 and 6.88 (d, *J* = 9.0 Hz, each 2H), 5.32 (m, 3H), 5.04 (d, *J* = 4.1 Hz, 1H), 3.79 (s, 3H), 3.63 (d, *J* = 4.1 Hz, 1H), 1.54 and

1.25 (s, each 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 207.4, 163.4, 156.2, 134.2, 129.0, 128.4, 127.3, 127.1, 117.8, 114.6, 106.8, 82.1, 80.8, 74.4, 63.6, 61.5, 55.5, 28.7, 25.7; IR ($CHCl_3$): ν = 3000, 1942, 1749 cm^{-1}; MS (ES): *m/z* (%): 362 (100) $[M + H]^+$, 361 (10) $[M]^+$.

Fe(III)-catalyzed cyclization of enallenol 1e. Preparation of tetrahydrofurans 3ca and 3cb. From 40 mg (0.13 mmol) of a diastereomeric mixture (70:30) of enallenol **1e**, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent, 13 mg (35%) of the less polar compound **3ca** and 6 mg (15%) of the more polar compound **3cb** were obtained.

Tetrahydrofuran 3ca. Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 8.00 and 6.95 (d, *J* = 9.0 Hz, each 2H), 5.65 (m, 1H), 4.66 (m, 3H), 3.88 (s, 3H), 2.26 (dd, *J* = 13.9, 5.9 Hz, 1H), 2.06 (dd, *J* = 13.9, 2.4 Hz, 1H), 1.74 (t, *J* = 2.9 Hz, 3H), 1.44 and 1.35 (s, each 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 207.0, 165.5, 163.4, 131.7, 122.6, 113.7, 96.1, 81.1, 80.2, 76.3, 75.8, 55.4, 45.4, 29.3, 28.7, 15.7; IR ($CHCl_3$): ν = 2994, 1947, 1724 cm^{-1}; HRMS (ES): calcd (%) for $C_{18}H_{22}O_4[M]^+$: 302.1518; found: 302.1522.

Tetrahydrofuran 3cb. Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 8.01 and 6.94 (d, *J* = 9.0 Hz, each 2H), 5.48 (dt, *J* = 6.6, 2.9 Hz, 1H), 4.78 (m, 2H), 4.58 (m, 1H), 3.88 (s, 3H), 2.24 (dd, *J* = 13.4, 6.5 Hz, 1H), 2.01 (dd, *J* = 13.9, 2.8 Hz, 1H), 1.79 (t, *J* = 3.1 Hz, 3H), 1.43 and 1.38 (s, each 3H); IR ($CHCl_3$): ν = 2996, 1950, 1722 cm^{-1}; MS (ES): *m/z* (%): 303 (100) $[M + H]^+$, 302 (12) $[M]^+$.

General procedure for the Fe(III)-catalyzed reaction of enallenols 1c and 1d. Preparation of morpholin-3-ones 4. $FeCl_3$ (0.10 mmol) was added to a stirred solution of the enallenol **1c** or **1d** (1.0 mmol) in 1,2-dichloroethane (1.0 mL). The resulting mixture was heated at 80 ^{o}C in a sealed tube until complete disappearance (TLC) of the starting material. The reaction mixture was allowed to cool to room temperature, and then was quenched with aqueous saturated NH_4Cl (1.0 mL). The mixture was extracted with ethyl acetate (3 x 5 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 ethyl acetate/hexanes mixtures gave analytically pure morpholin-3-one adducts **4**.

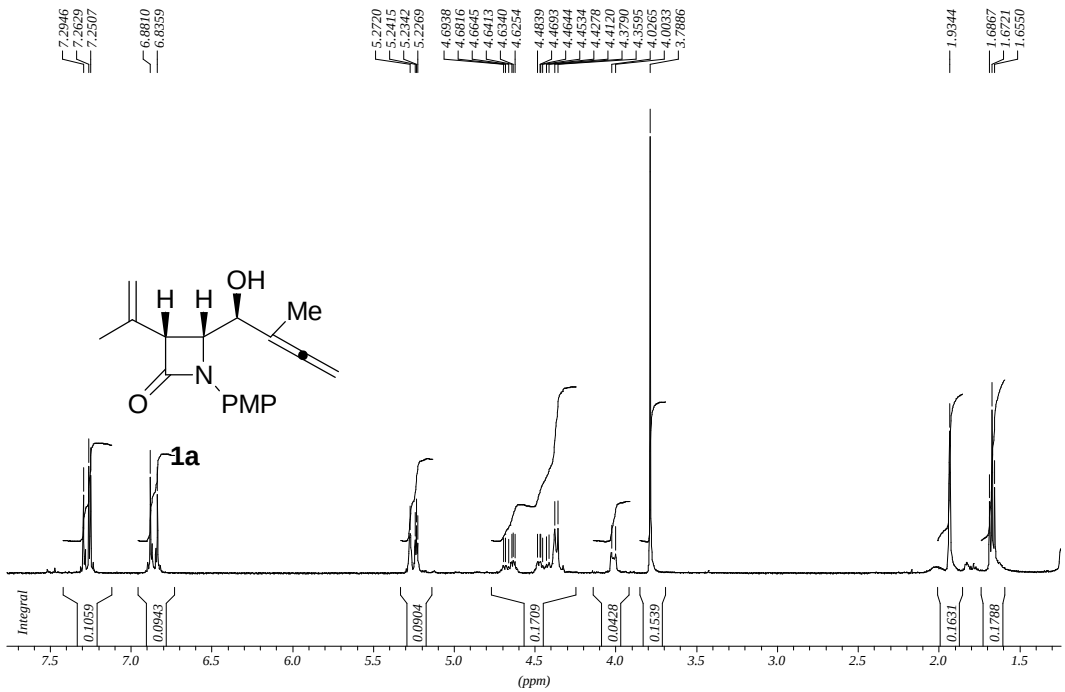
Morpholin-3-one 4a. From 40 mg (0.13 mmol) of enallenol **1c**, and after chromatography of the residue using hexanes/ethyl acetate (9:2) as eluent gave compound **4a** (34 mg, 85%) as a colorless solid. Mp: 118–120 ^{o}C (hexanes/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 6.81 and 6.55 (d, *J* = 9.0 Hz, each 2H), 4.90 (m, 2H), 4.71 (br s, 1H), 4.62 and 3.57 (d, *J* = 7.0 Hz, each 1H), 3.77 (s, 3H), 2.35 and 2.00 (s, each 3H), 1.77 (td, *J* = 2.9, 0.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 205.9, 169.1,

157.8, 147.8, 137.5, 121.6, 115.1, 98.1, 81.6, 77.4, 57.1, 55.7, 24.1, 20.5, 15.1; IR ($CHCl_3$): ν = 2994, 1959, 1664 cm^{-1}; MS (EI): *m/z* (%): 300 (8) $[M + H]^+$, 299 (42) $[M]^+$, 174 (100); elemental analysis calcd (%) for $C_{18}H_{21}NO_3$ (299.4): C 72.22, H 7.07, N 4.68; found C 72.10, H 7.03, N 4.64.

Morpholin-3-one 4b. From 33 mg (0.09 mmol) of enallenol **1d**, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent gave compound **4b** (25 mg, 78%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 7.35 (m, 5H), 7.36 and 6.77 (d, *J* = 9.0 Hz, each 2H), 5.32 (m, 3H), 4.73 (br s, 1H), 3.75 (s, 3H), 3.74 (m, 1H), 2.34 and 1.98 (s, each 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC): δ = 207.7, 166.8, 153.5, 131.6, 130.3, 128.7, 128.6, 128.3, 127.6, 126.9, 126.6, 115.2, 113.8, 81.5, 76.7, 55.7, 53.4, 24.2, 20.6; IR ($CHCl_3$): ν = 2999, 1956, 1662 cm^{-1}; MS (ES): *m/z* (%): 362 (100) $[M + H]^+$, 361 (20) $[M]^+$.

References

[S1] J.W. Faller, J. T. Nguyen, M. R. Mazzieri, *Appl. Organomet. Chem.* **1995**, *9*, 291.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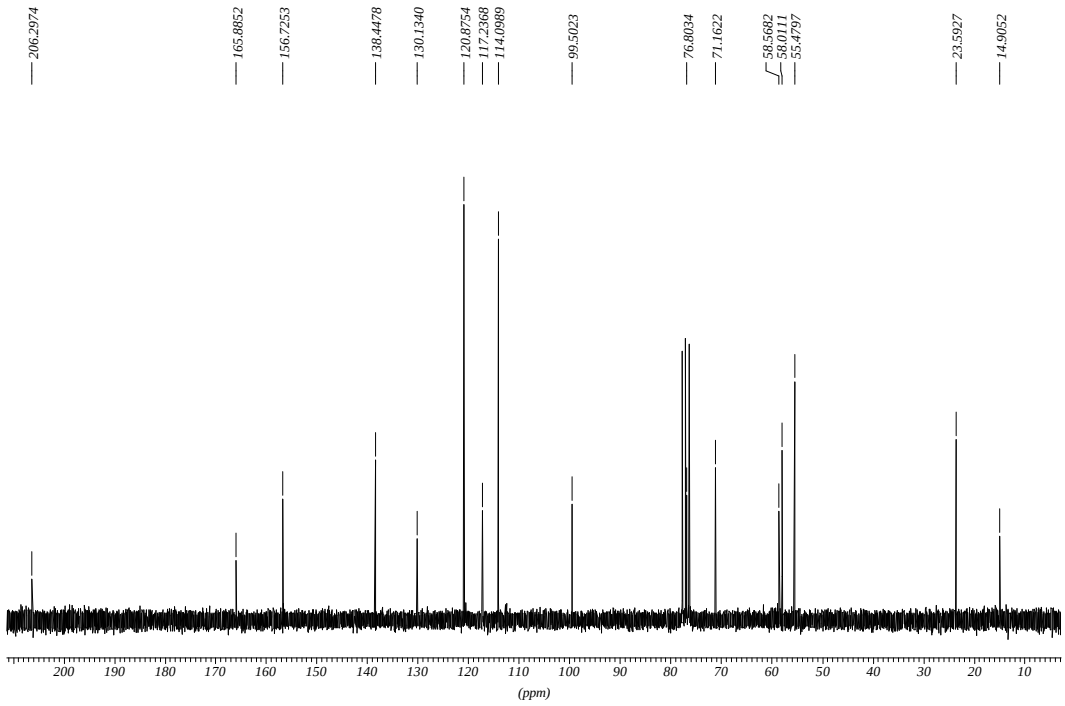
(ppm)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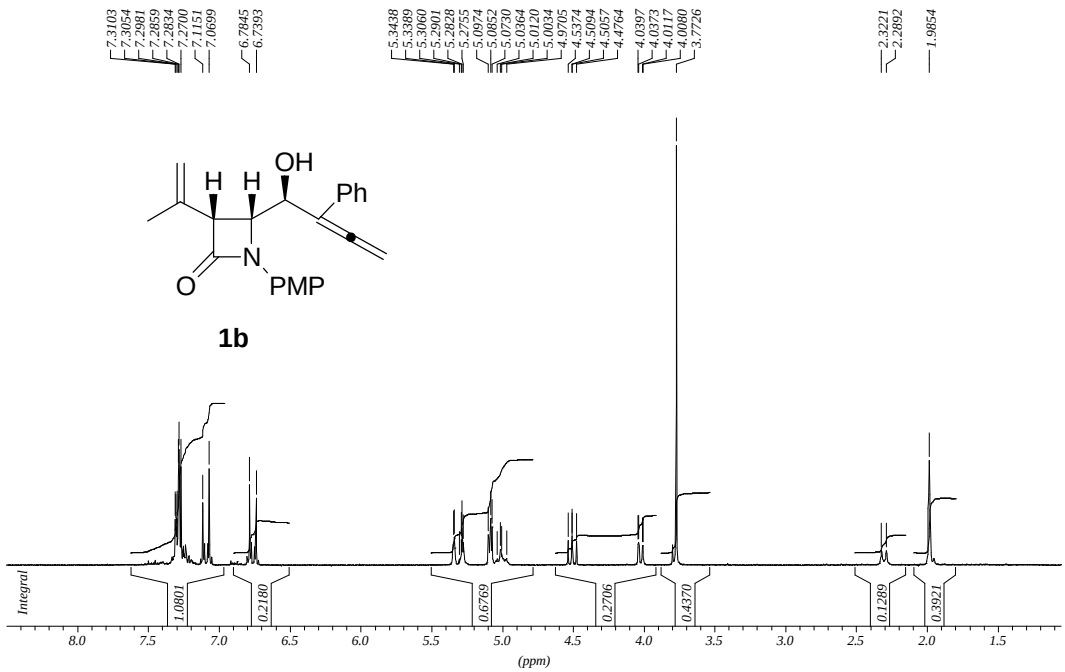

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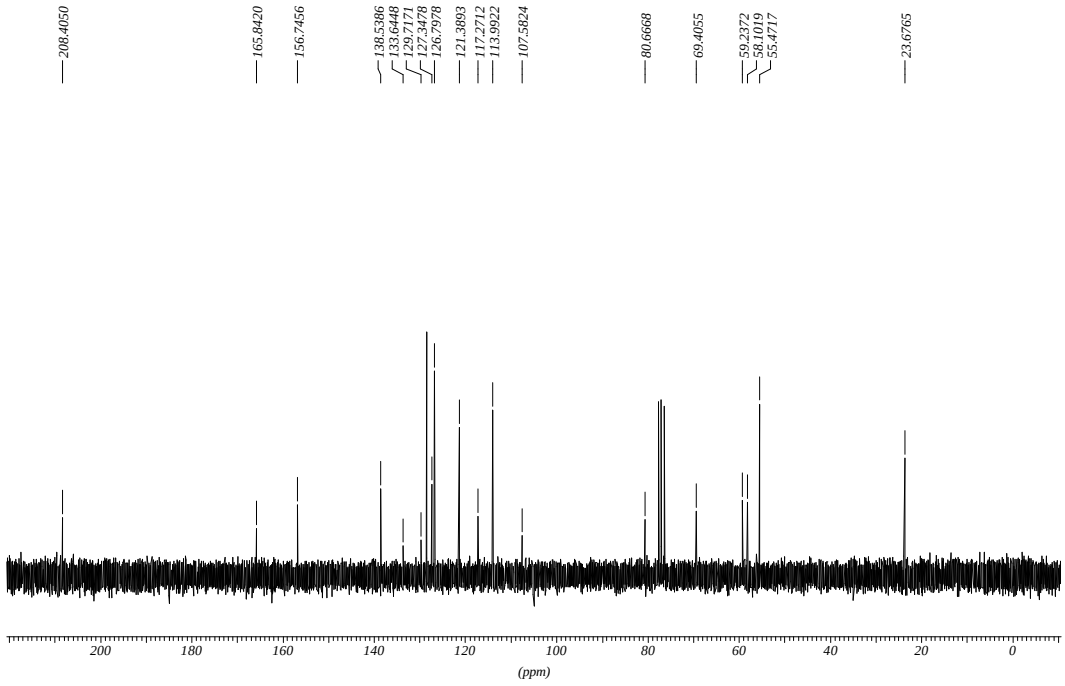

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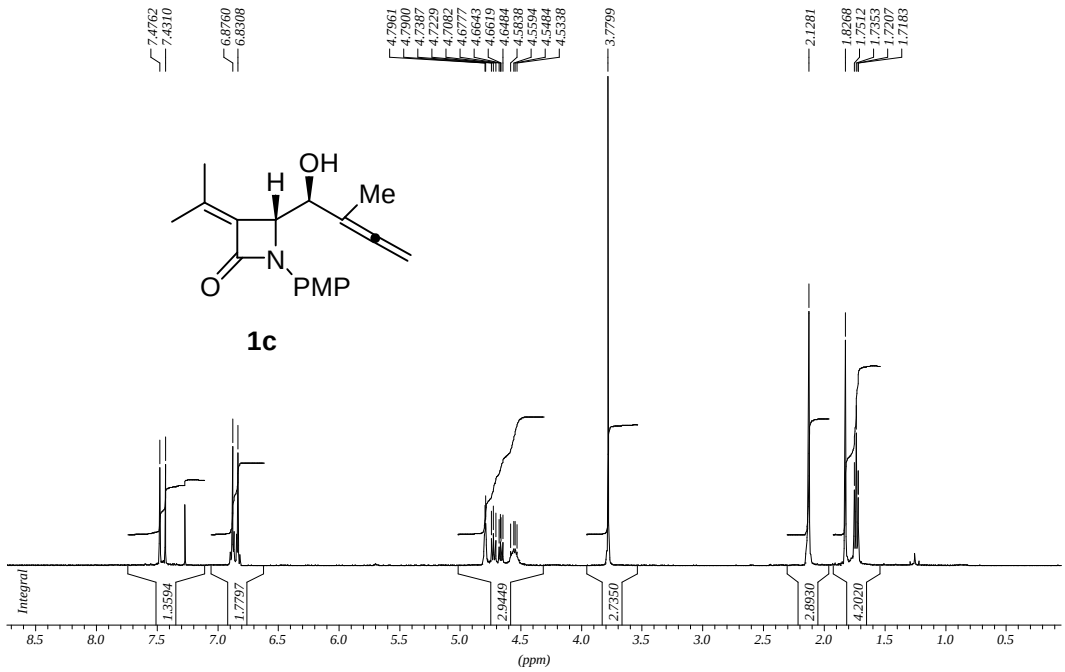

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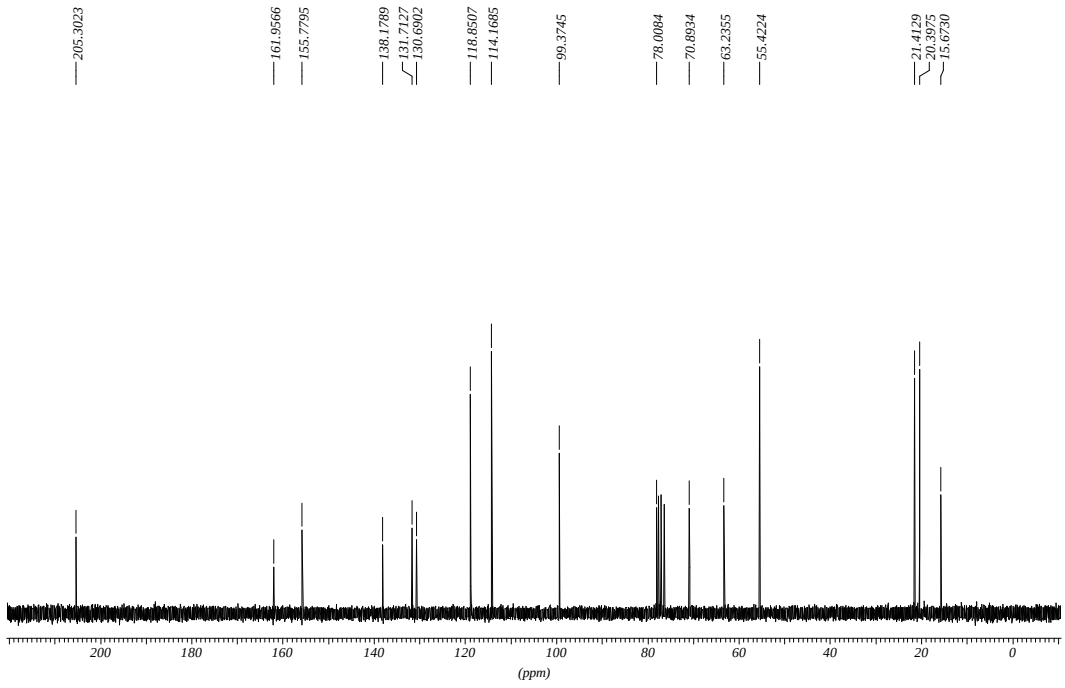

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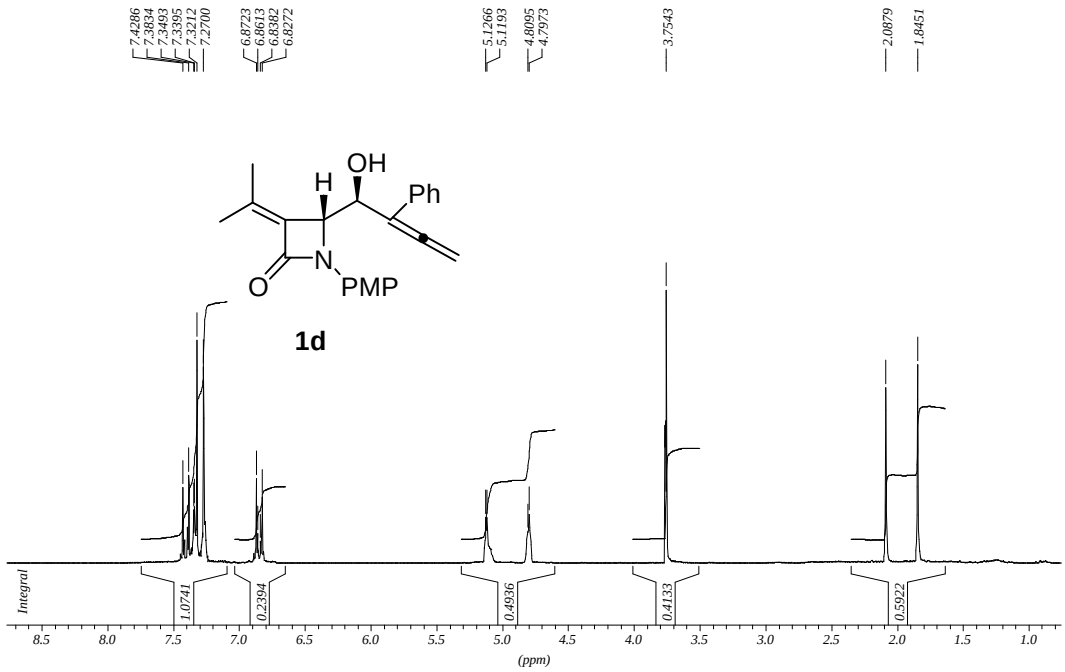

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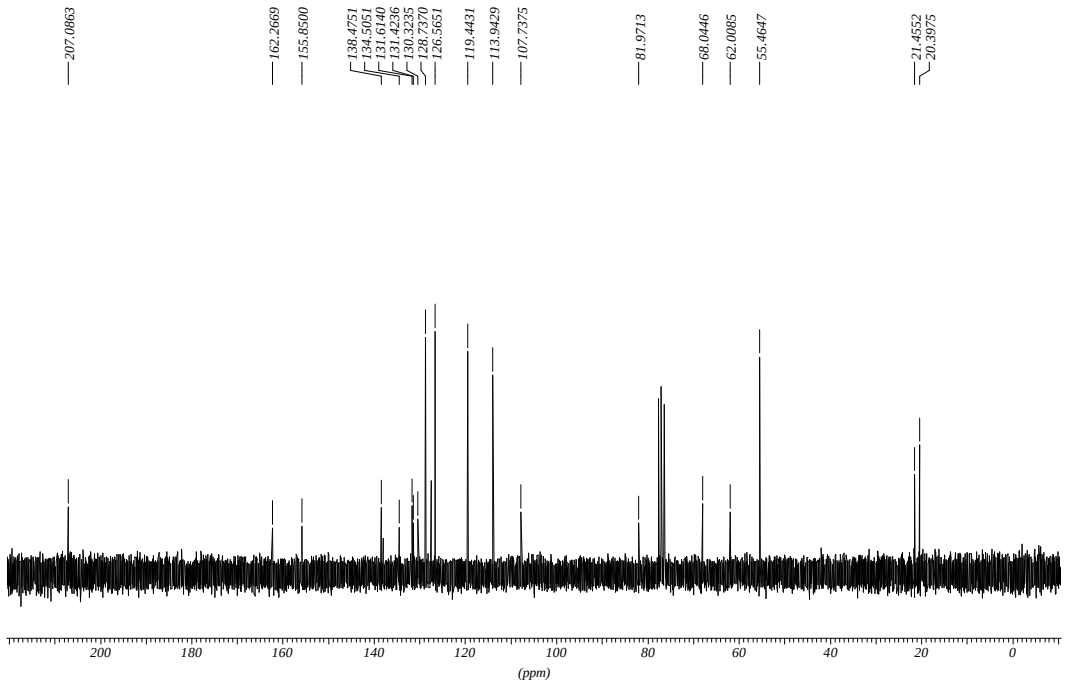

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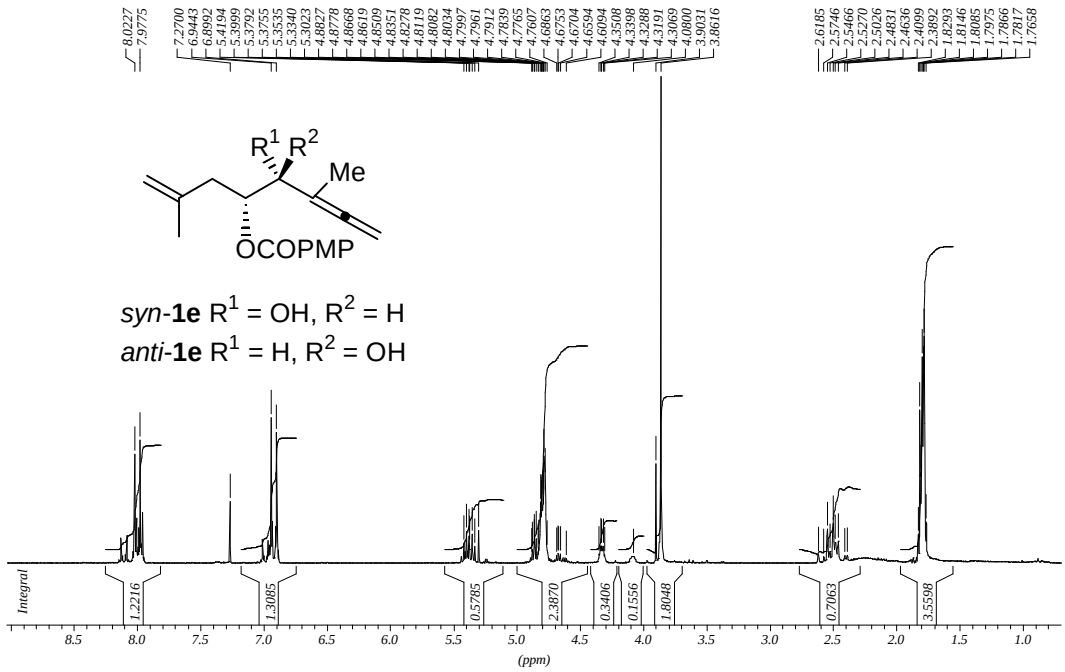

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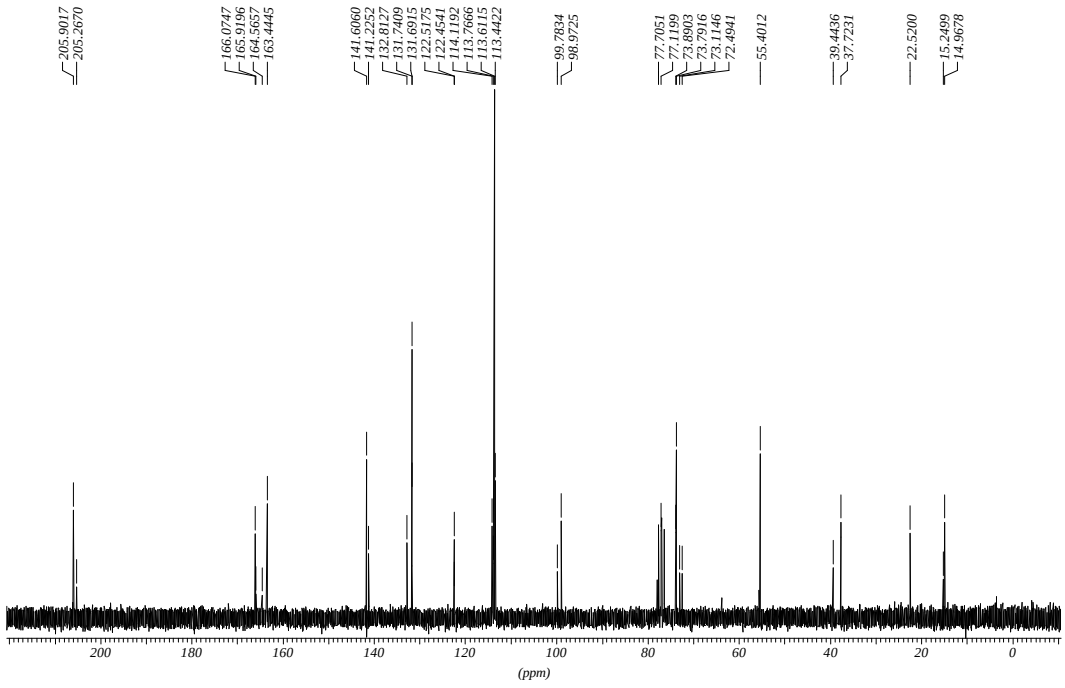

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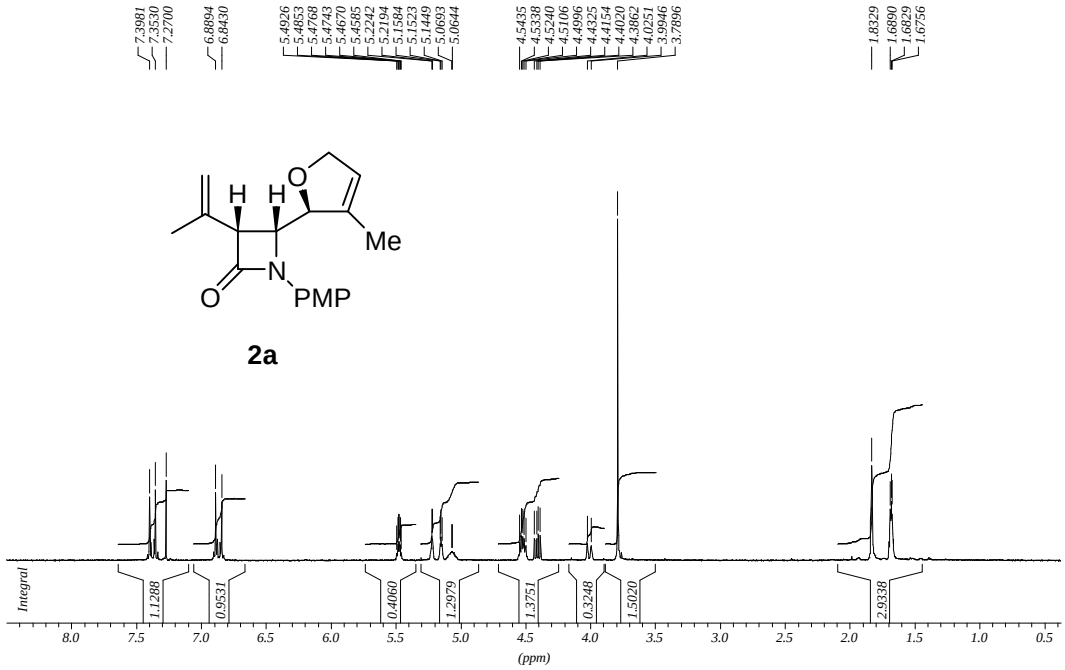

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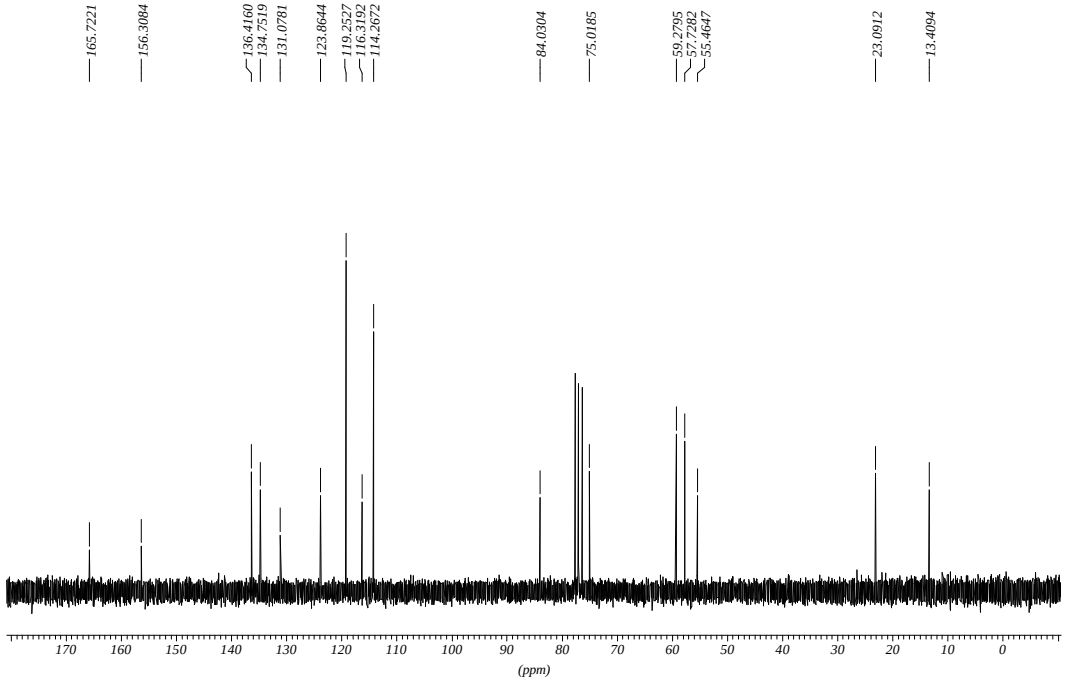

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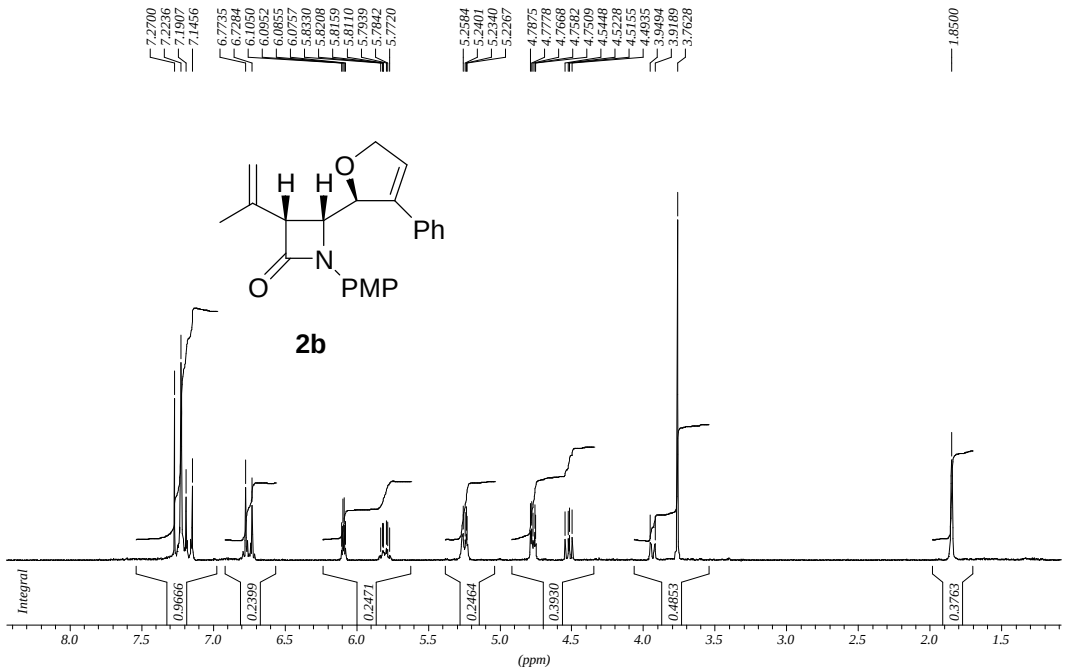

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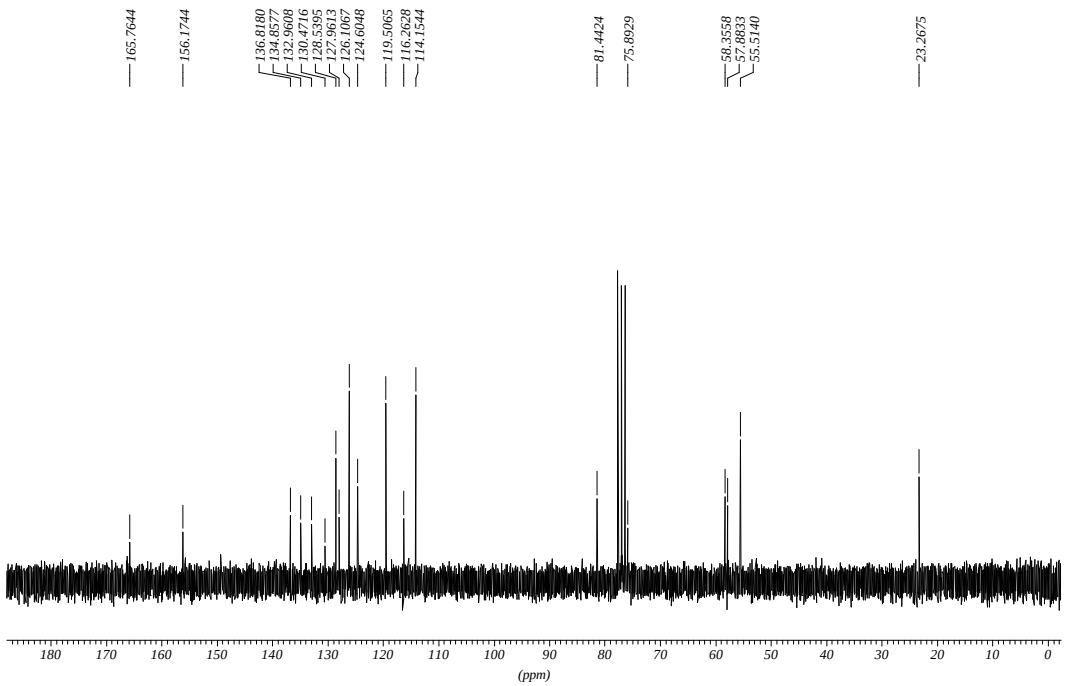

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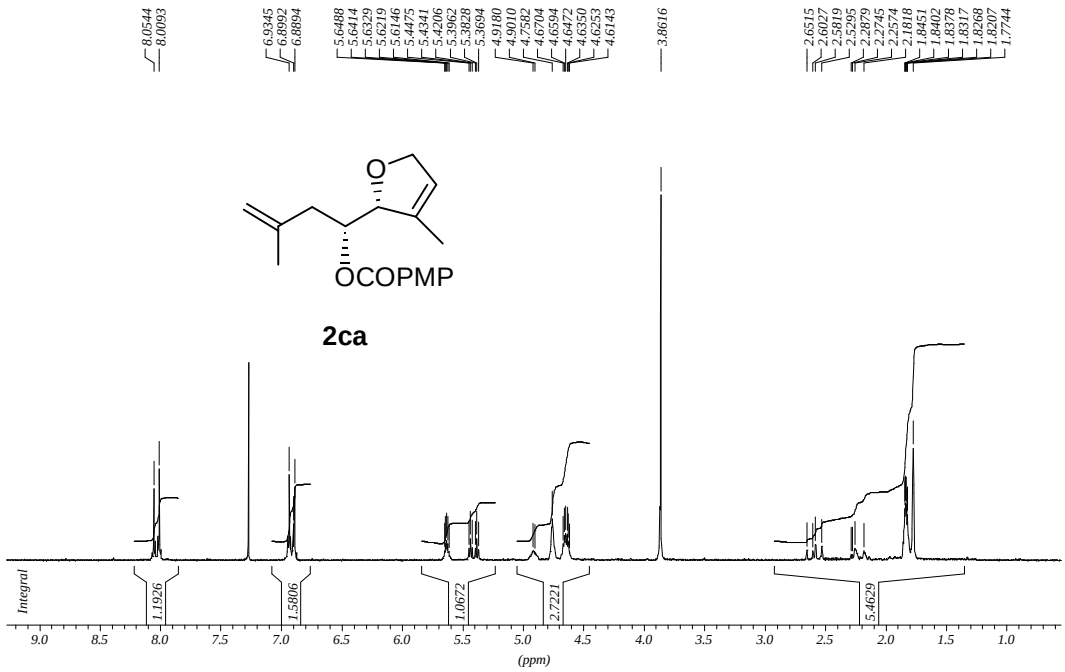

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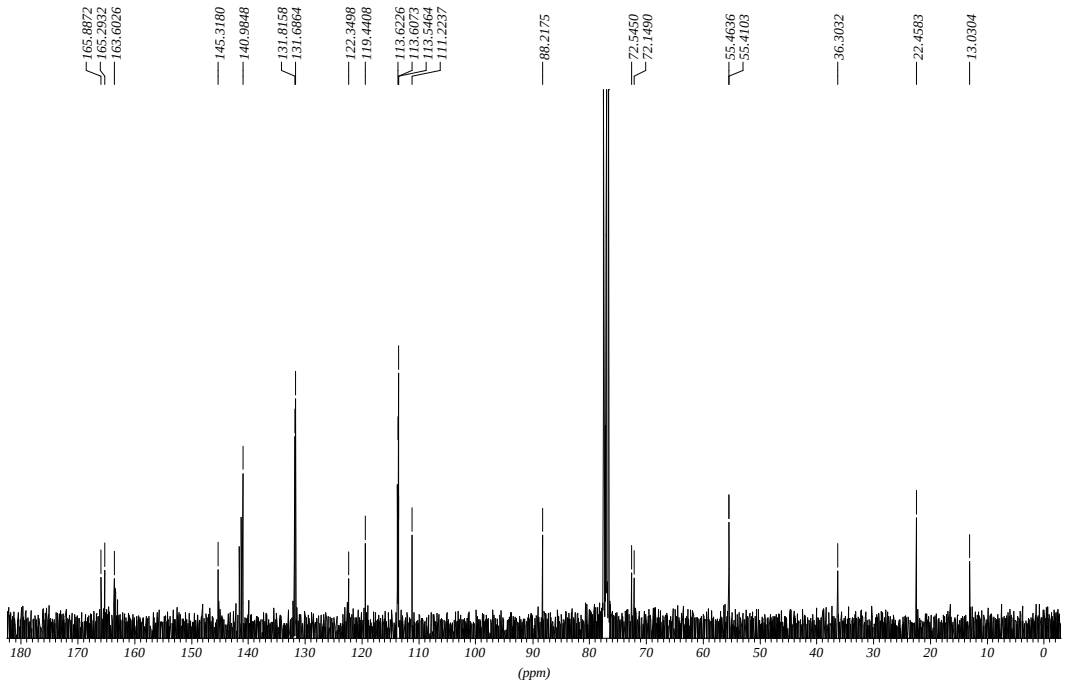

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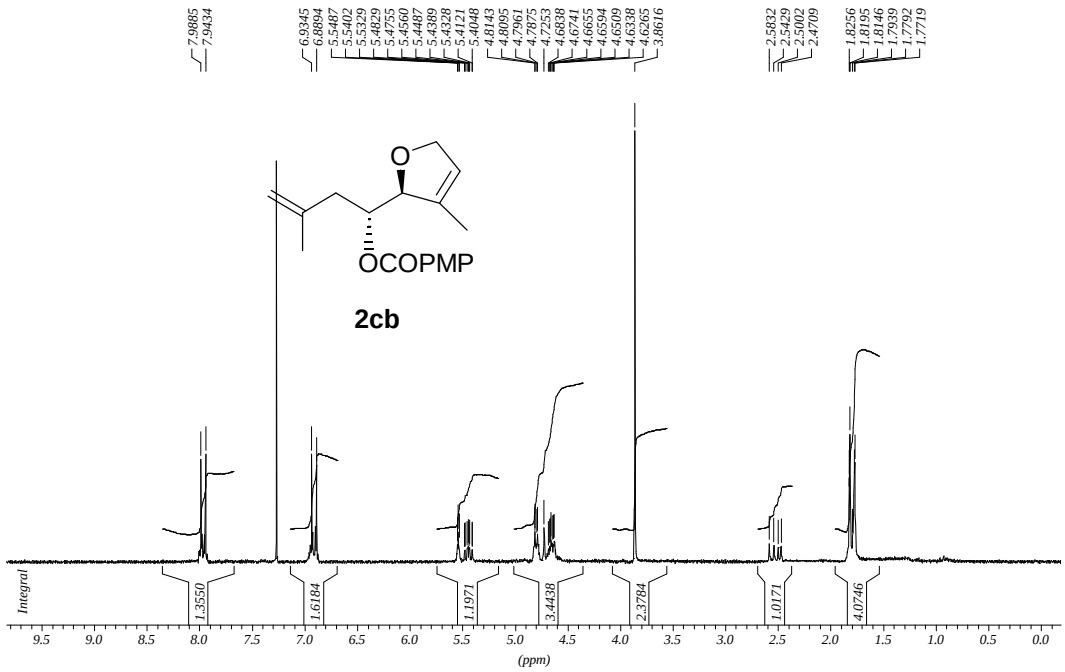

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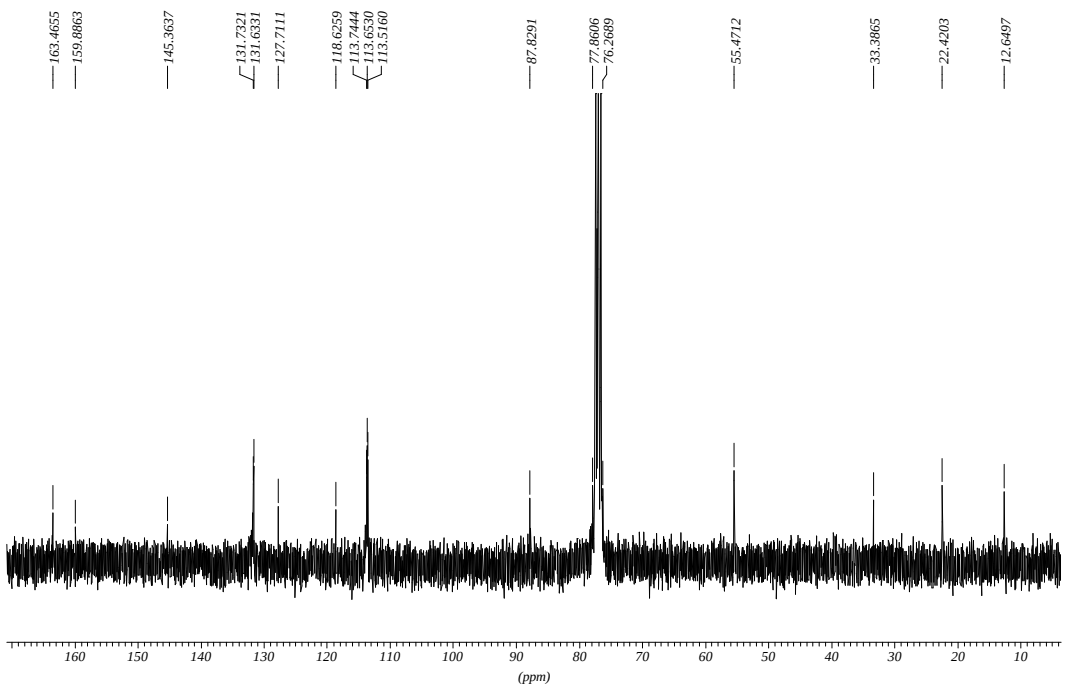

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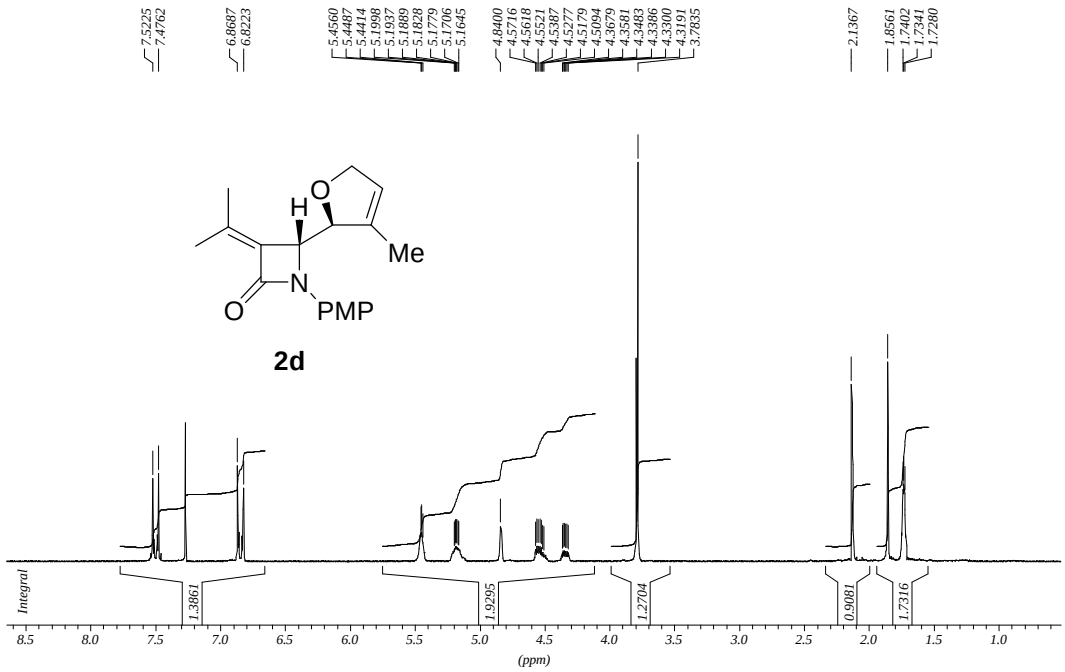

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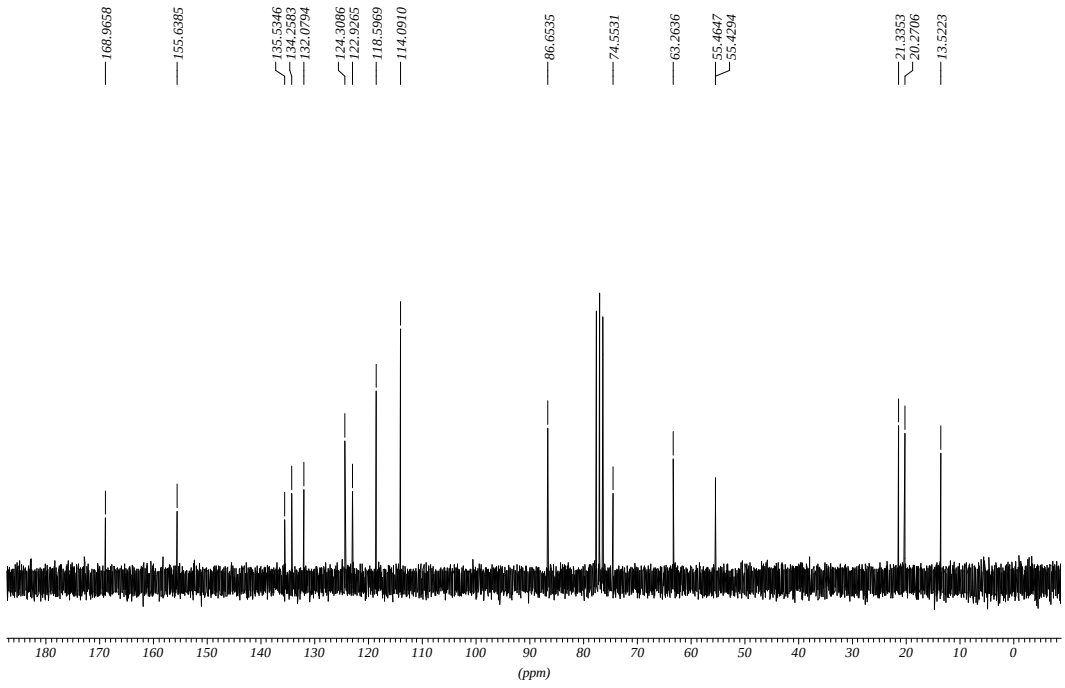

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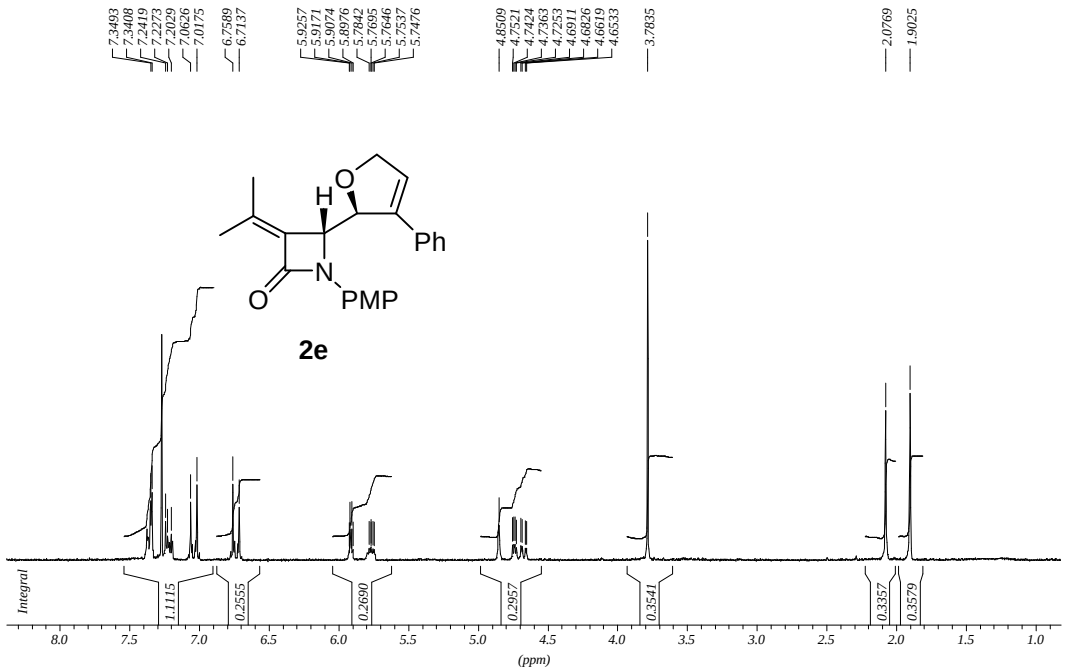

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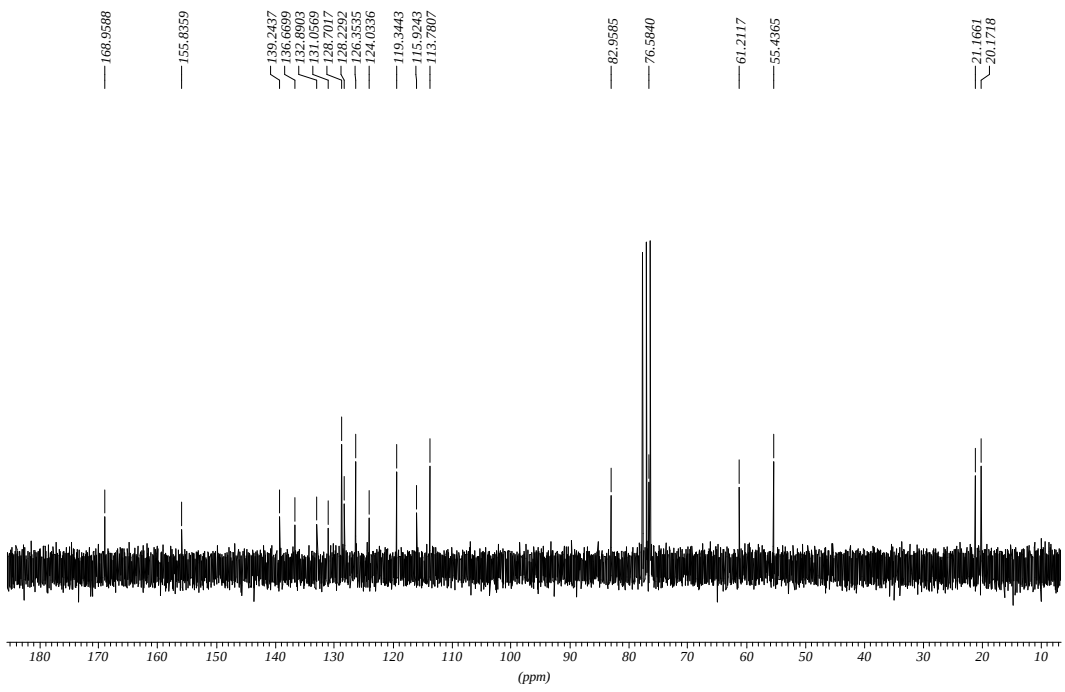

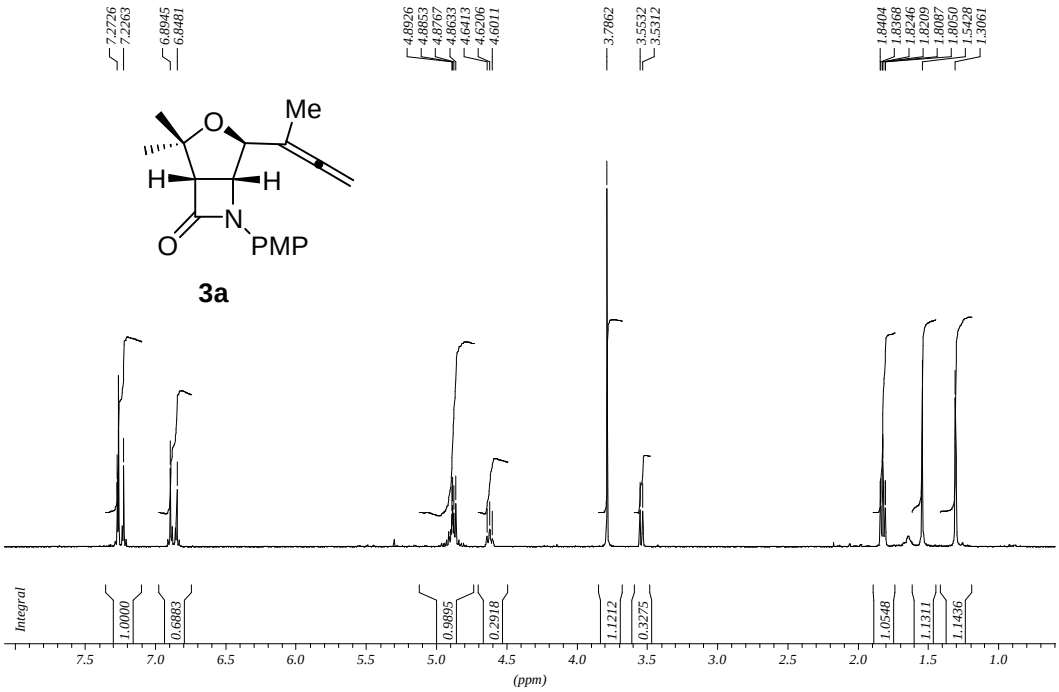
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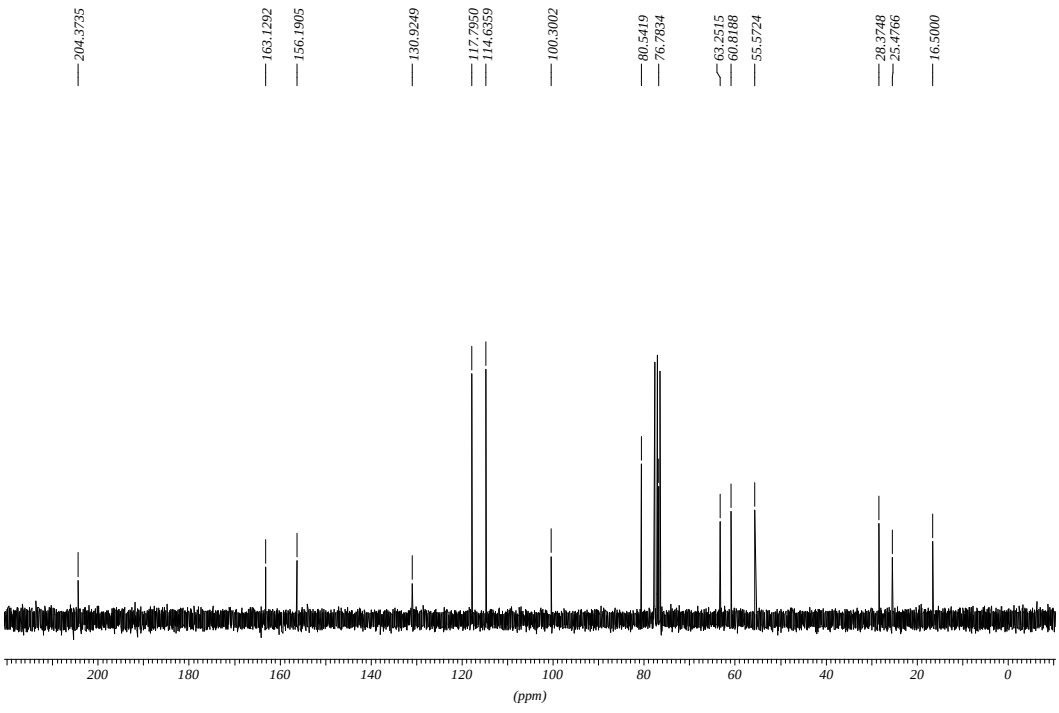
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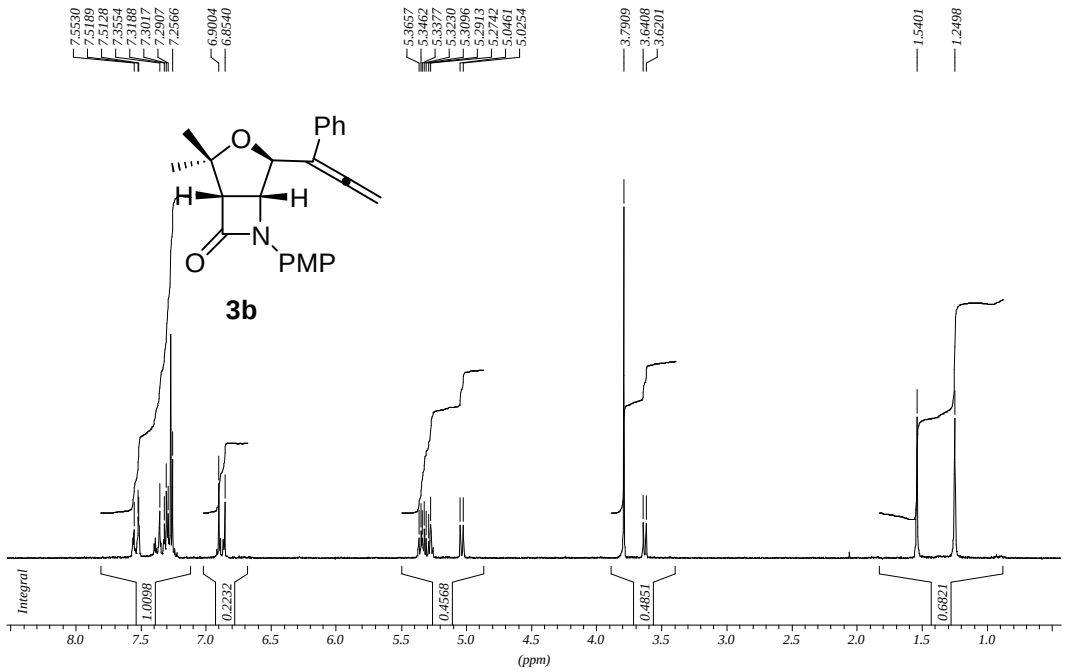

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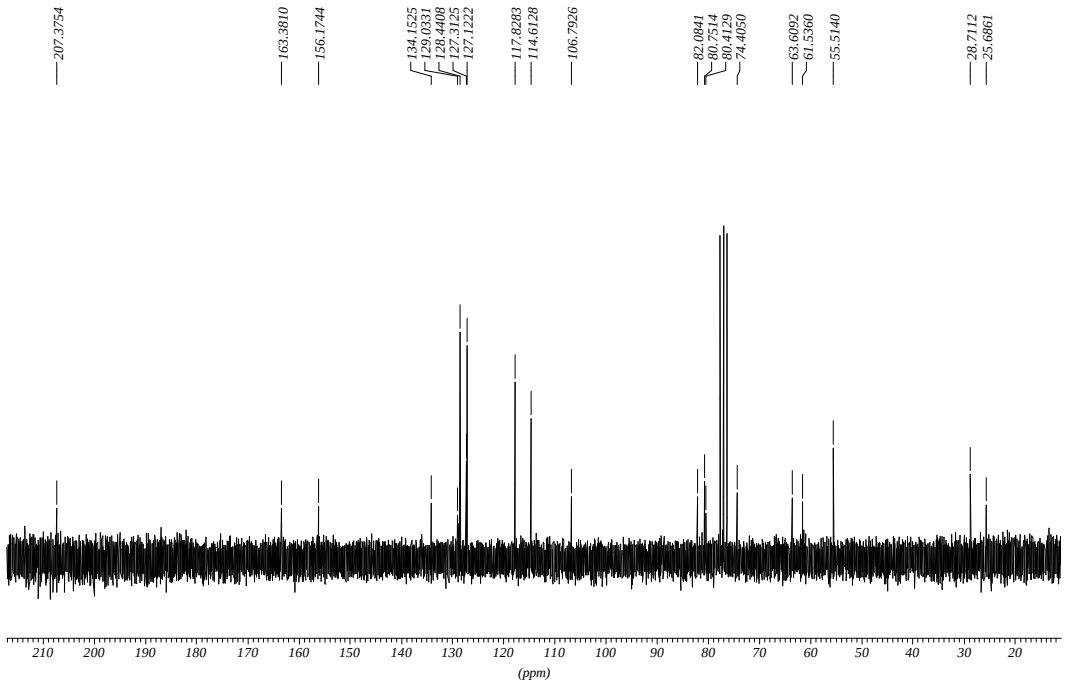

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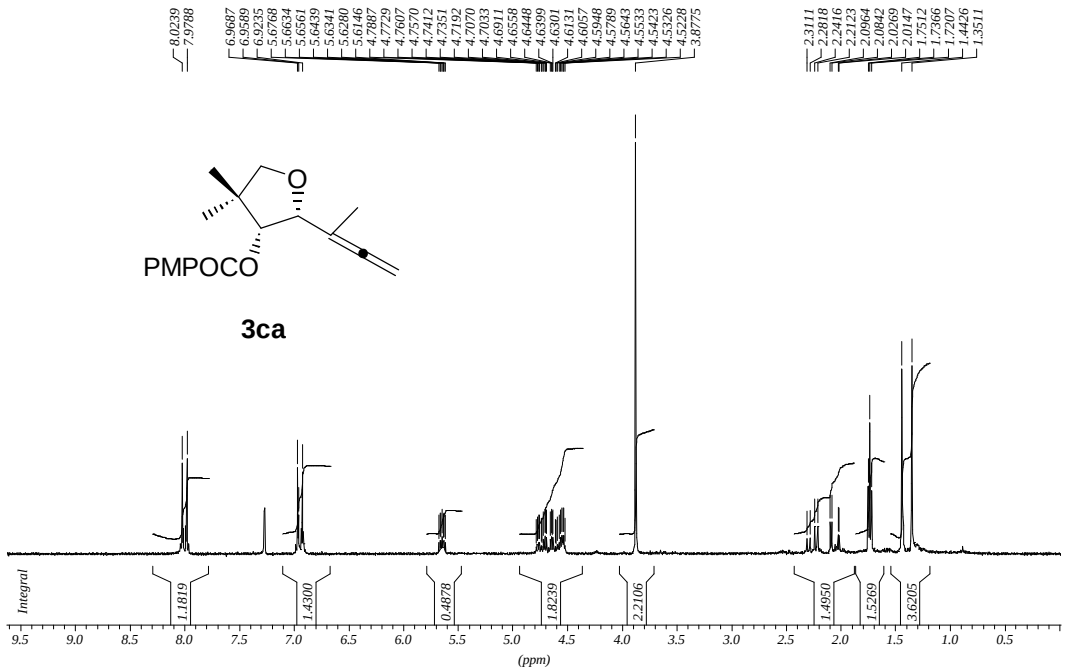

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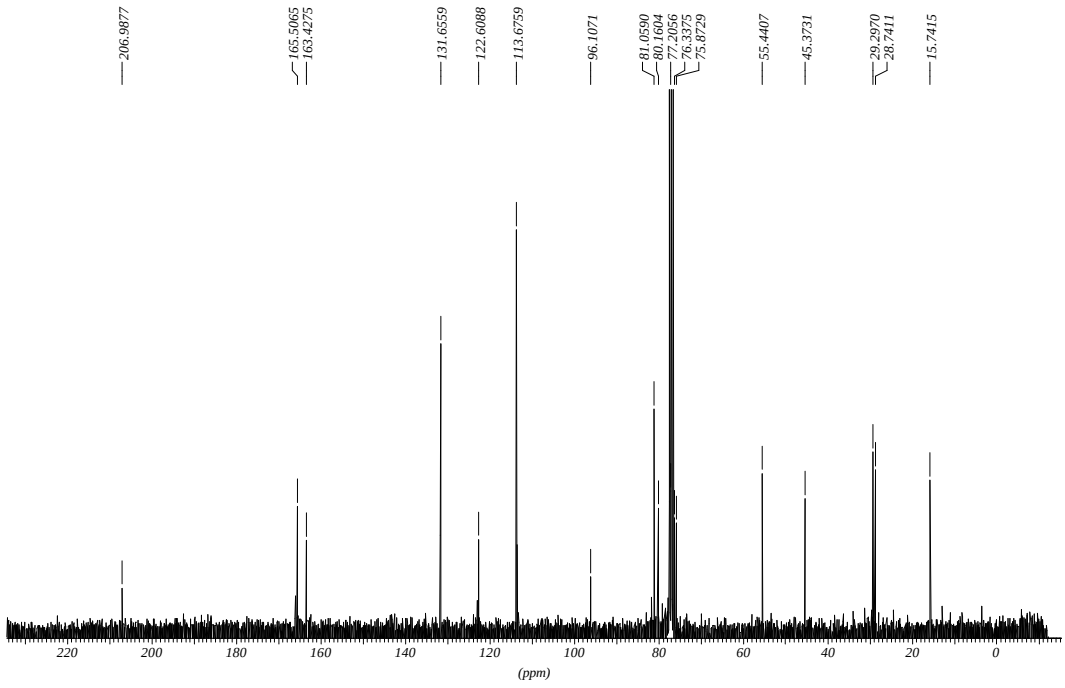

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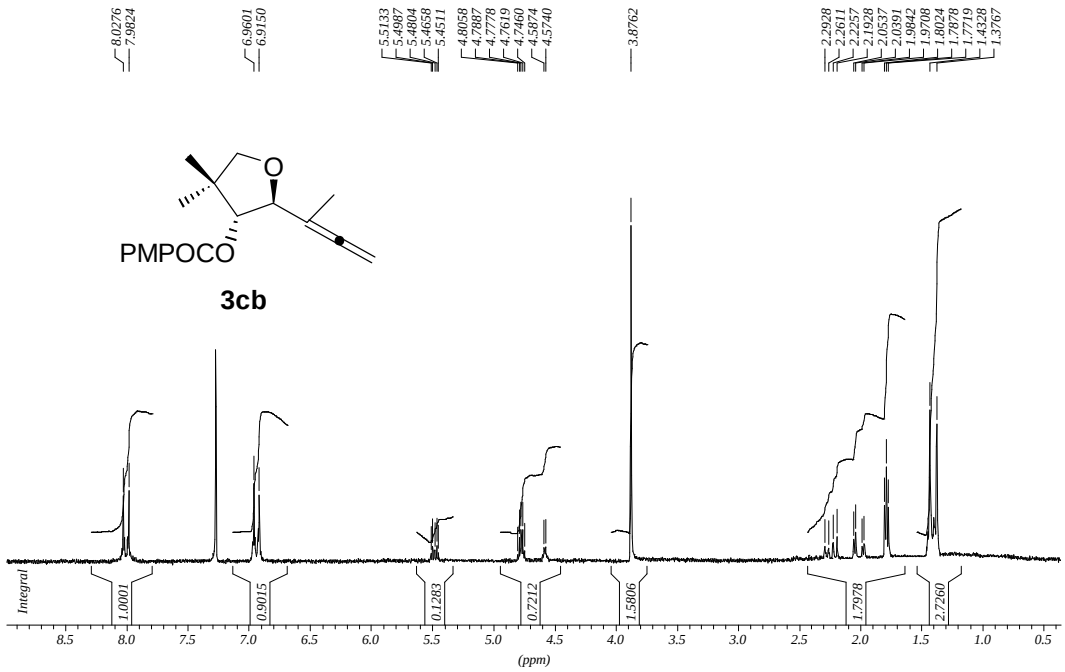
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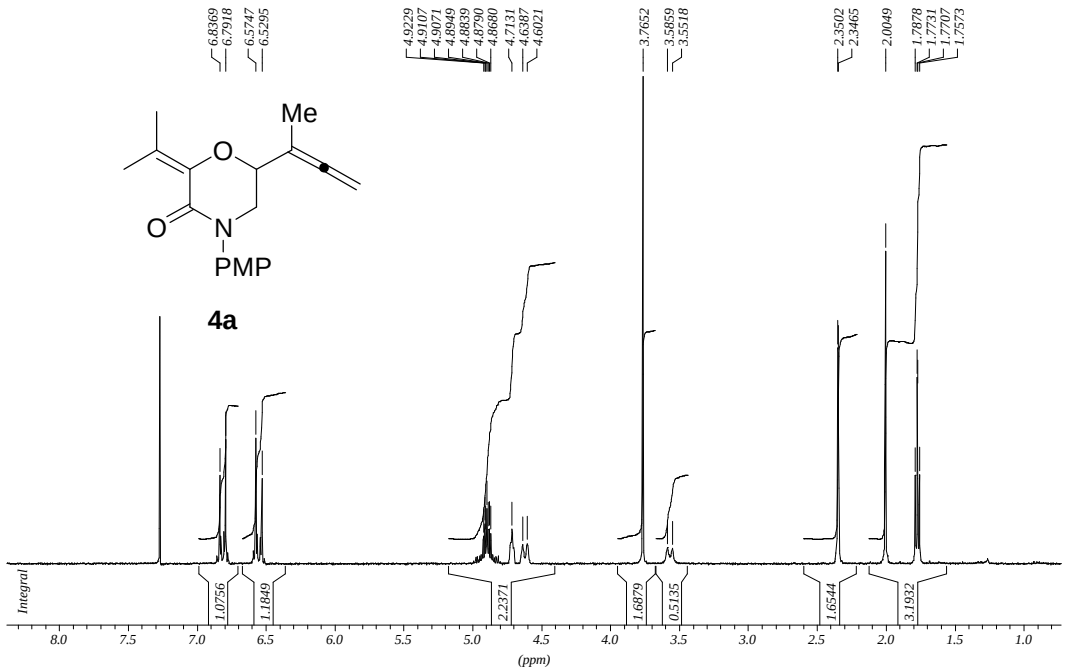

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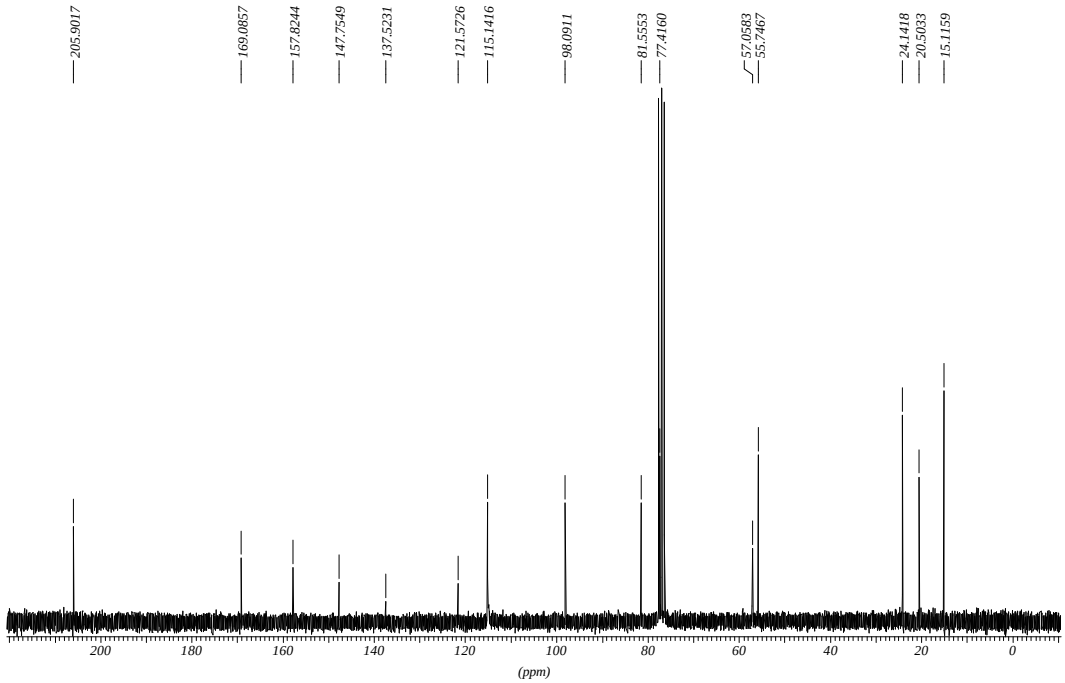

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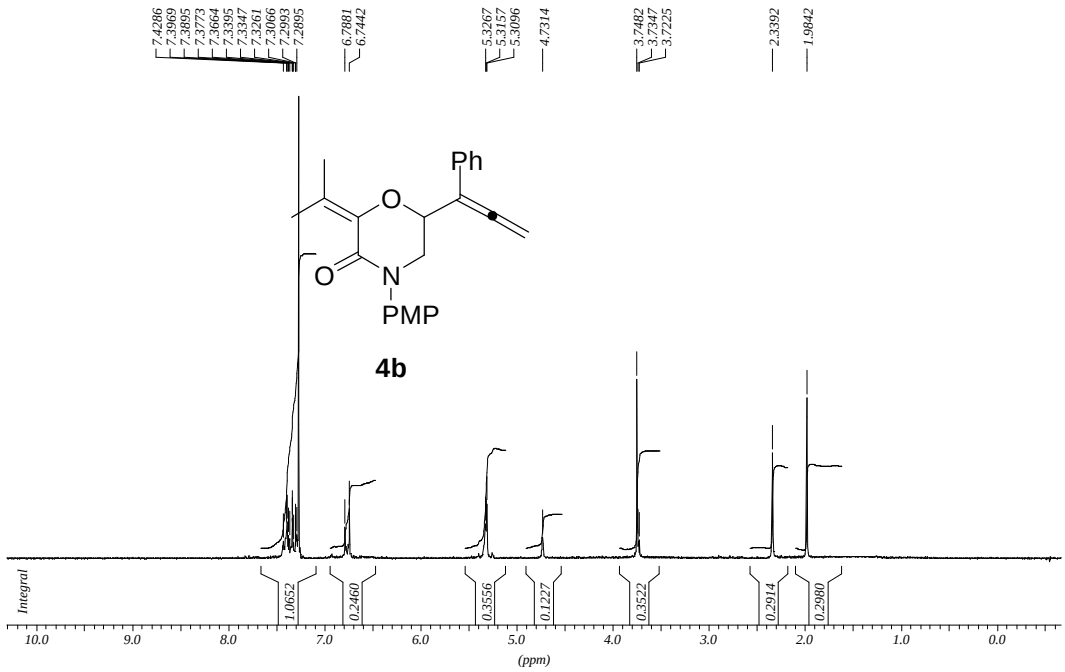
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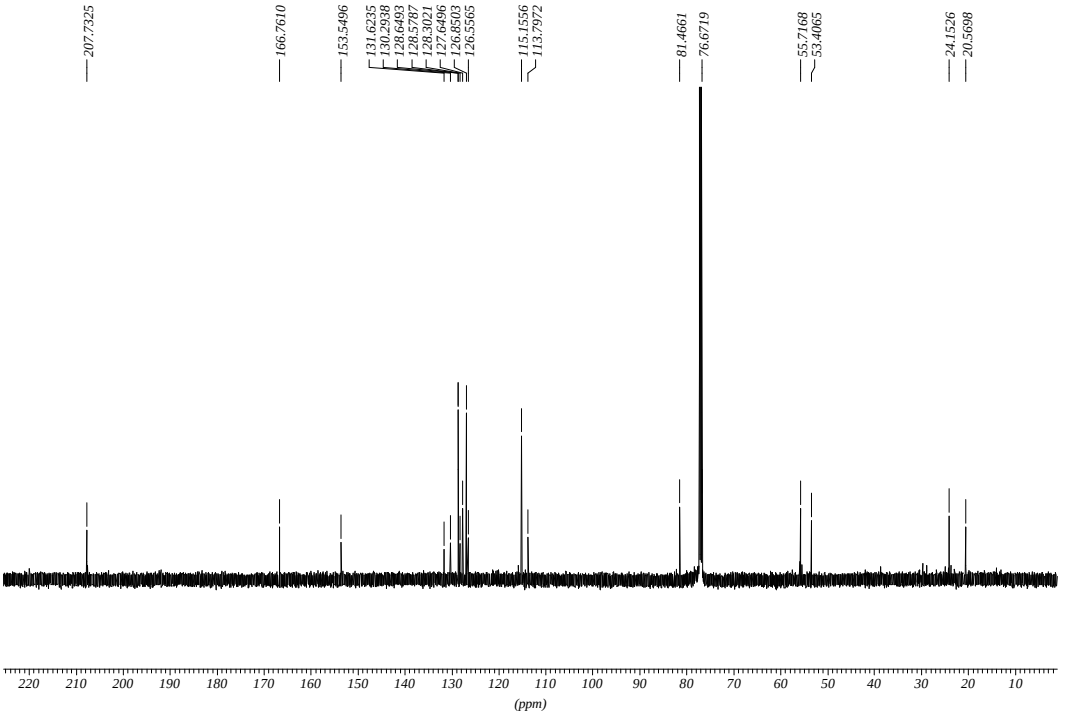
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