Supporting Information for the Paper

Stereoselective Synthesis of Strained Cage Compounds *via* Gold-Catalyzed Allene Functionalization

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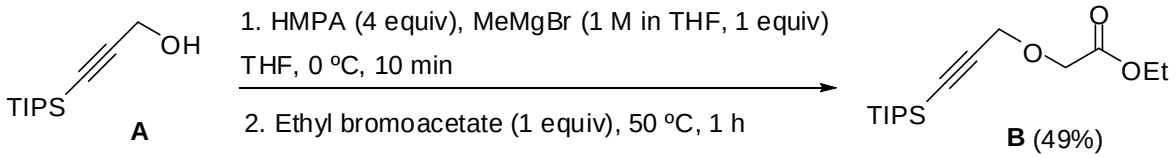
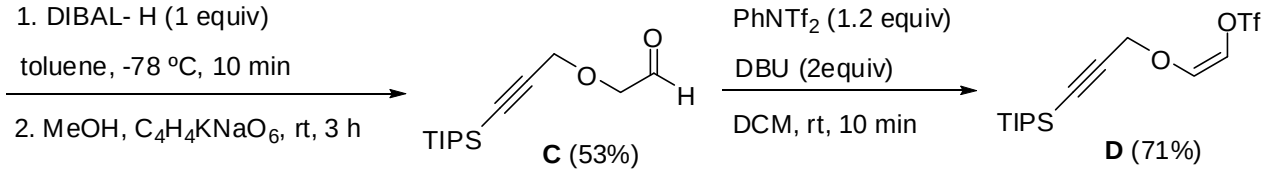
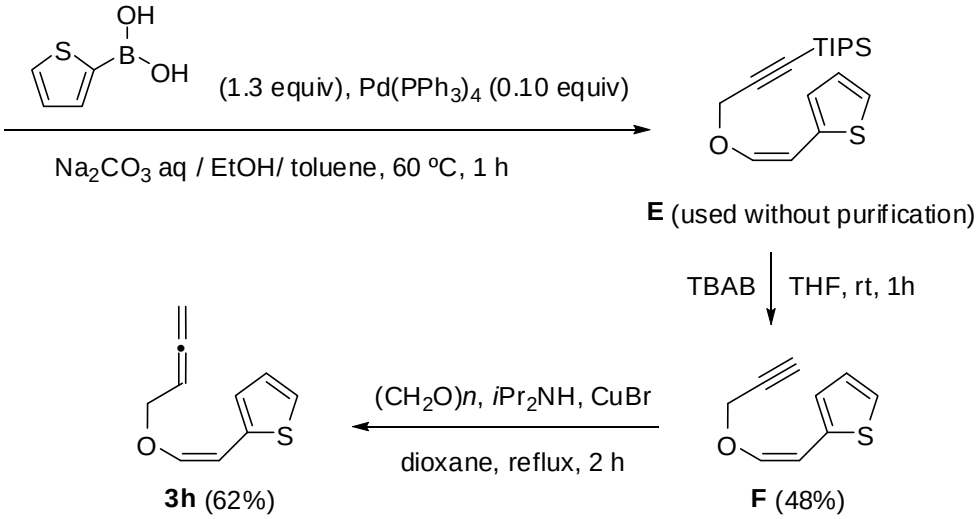
General Methods: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance AVIII-700 with cryoprobe or Varian VRX-300S. NMR spectra were recorded in $CDCl_3$ solutions, except otherwise stated. Chemical shifts are given in ppm relative to TMS (^{1}H, 0.0 ppm), or $CDCl_3$ (^{13}C, 76.9 ppm). Low and high resolution mass spectra were taken on an AGILENT 6520 Accurate-Mass QTOF LC/MS spectrometer using the electrospray mode (ES) unless otherwise stated. IR spectra were recorded on a Bruker Tensor 27 spectrometer. All commercially available compounds were used without further purification.



compound **A** was prepared in a three-step sequence from propargyl alcohol as reported in Le. C. M.; Menzies, P. J. C.; Petrone, D. A.; Lautens, M. *Angew. Chem. Int. Ed.* **2015**, *54*, 254



compound **D** was prepared according to a literature procedure: F.; Nakano, T.; Soeta, T.; Endo, K.; Ukaji, T. *J. Org. Chem.* **2015**, *80*, 5696



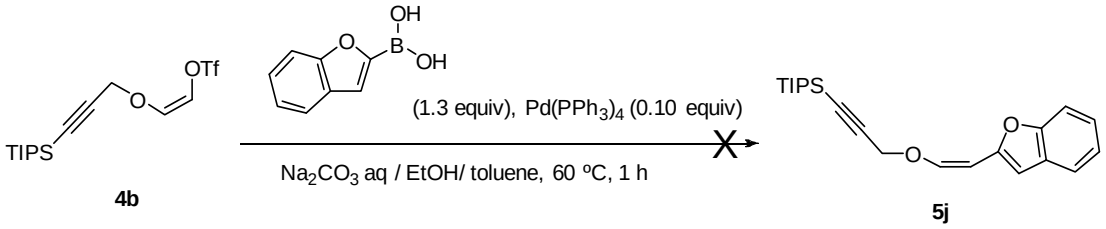
Scheme S1 Synthesis of (vinyloxy)buta-1,2-diene **3h**.

Preparation of (*Z*)-2-[2-(prop-2-ynyloxy)vinyl]thiophene F. To a solution of triflate **D** (354, 0.92 mmol) in toluene (15 mL) and EtOH (2.5 mL) was added 2 M aq solution of Na_2CO_3 (15 mL). After $Pd(PPh_3)_4$ (106 mg, 0.09 mmol, 10 mol %) and 2-thienylboronic acid (198 mg, 1.55 mmol) were added, the reaction mixture was stirred at 60 °C for 1 h under argon atmosphere. The reaction mixture was cooled to room temperature and insoluble substance was filtered off through a pad of Celite. The aqueous layer of the filtrate was separated and extracted with Et_2O. The combined organic extracts were washed with water and brine, dried over Na_2SO_4, and solvent was evaporated. The crude product, which contained (*Z*)-triisopropyl(3-(2-(thiophen-2-yl)vinyloxy)prop-1-ynyl)silane **E**, was used for next reaction without further purification.

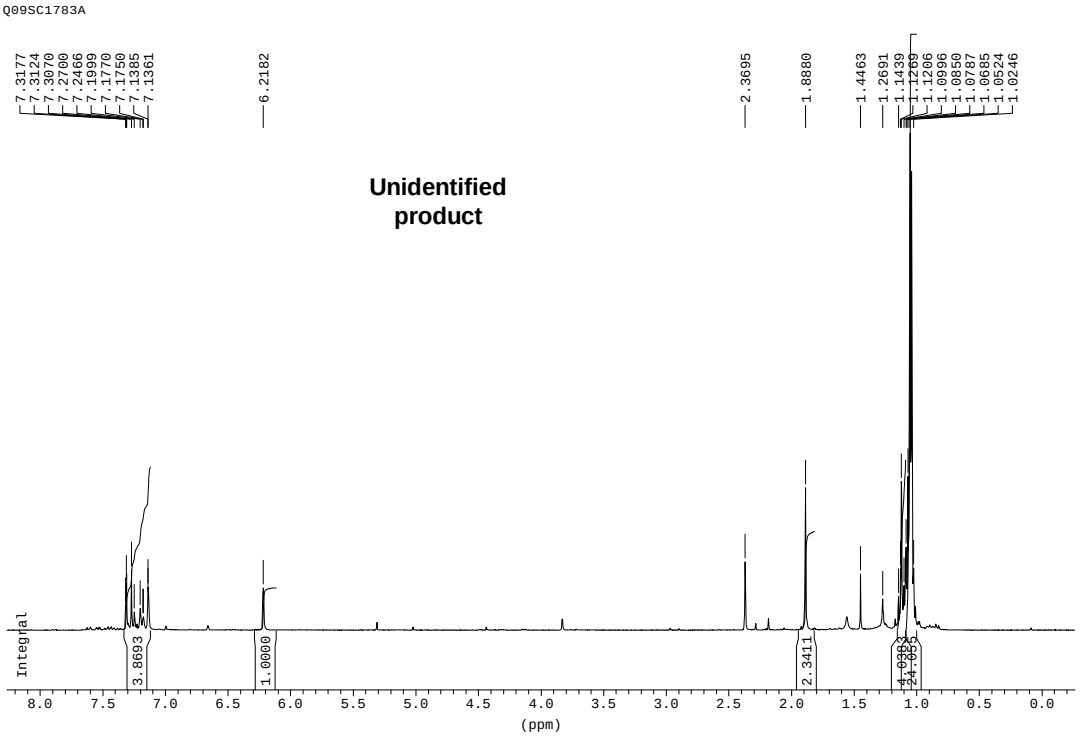
Tetra-*n*-butylammonium fluoride (1.0 equiv, THF solution 1M) was added to the crude residue containing 318 mg (0.99 mmol) of (*Z*)-triisopropyl(3-(2-(thiophen-2-yl)vinyloxy)prop-1-ynyl)silane **E** solved in THF (4 mL). After being stirred for 1 h at room temperature, the solution was diluted with ether. The organic layer was separated, washed with water, dried (Na_2SO_4), and concentrated under reduced pressure.Flash chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **F** (78 mg, 48%) as a colorless oil;^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.19 (d, 1H, *J* = 5.1 Hz, Ar), 7.04 (d, 1H, *J* = 3.5 Hz, Ar), 6.97 (dd, 1H, *J* = 5.1, 3.7 Hz, Ar), 6.32 (d, 1H, *J* = 6.4 Hz, =CH), 5.78 (d, 1H, *J* = 6.4 Hz, =CH), 4.60 (d, 2H, *J* = 2.5 Hz, OCH_2), 2.55 (t, 1H, *J* = 2.5 Hz, ≡CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 142.3 (=CH), 137.6, 126.3 (Ar, CH), 125.3 (Ar, CH), 124.5 (Ar, CH), 102.4 (=CH), 78.3, 75.8 (≡CH), 59.6 (OCH_2); IR ($CHCl_3$): ν = 2940, 1650, 1359, 695, 666 cm^{-1}; HRMS (ES): calcd for $C_9H_9OS[M]^+$: 165.0374; found: 165.0372.

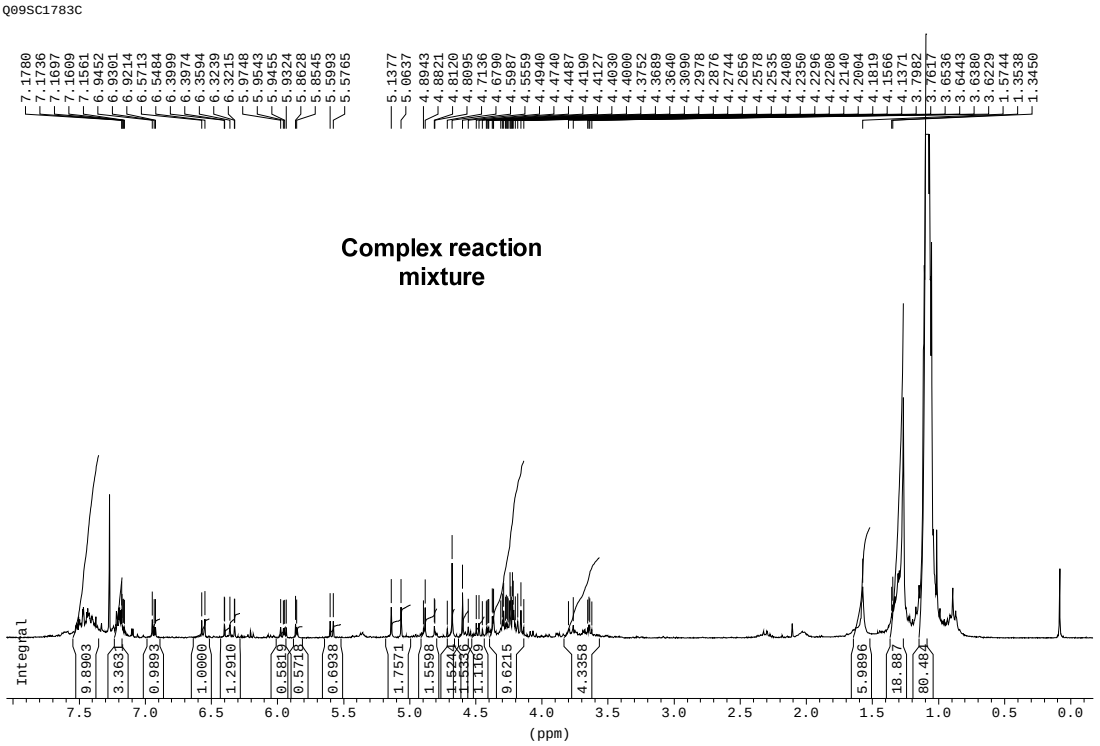
The reactions of two new (vinyloxy)buta-1,2-dienes **3** (**3g** and **3j**) were attempted. Unfortunately, the coupling step between enol triflate **D** and (5-methylfuran-2-yl)boronic acid or benzofuran-2-ylboronic acid were unproductive. The reaction of **D** with (5-methylfuran-2-yl)boronic acid was a

complete mess under different reaction conditions. Also, the coupling of **D** with benzofuran-2-ylboronic acid was not very competent. After column chromatography we can isolate two fractions: The more polar compound was a clean product with a structure different to the desired (Z)-(3-((2-(benzofuran-2-yl)vinyl)oxy)prop-1-yn-1-yl)triisopropylsilane, while the more polar fraction was a mixture of various products (for their recorded spectra, please see figures below). Consequently, it may be inferred that the synthesis of enol ether derivatives **3** is not trivial and our β-lactam based protocol is a more promising alternative.



4b **5j**





Cu-Catalyzed Reaction of β-Lactam-Tethered Alkynes and (*Z*)-2-[2-(Prop-2-ynyloxy)vinyl]thiophene F. General Procedure for the Preparation of β-Lactam-Tethered Allenes1a–p and (Vinyloxy)buta-1,2-diene 3h. A well stirred solution of$(CH_2O)_n$ (0.5 mmol), CuI (0.1 mmol), the appropriate alkyne (0.2 mmol), and *N*,*N*-diisopropylethylamine (Hüning's base) (0.36 mmol) in dioxane (1 mL) was refluxed under argon atmosphere. When the reaction was complete as monitored by TLC, it was cooled to RT. Water (5 mL) was added before being extracted with ethyl acetate(3 x 15 mL). The organic phase was washed with water (2 x 5 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with hexanes/ethyl acetate mixtures gave analytically pure compounds **1**. Spectroscopic and analytical data for allenes **1** follow.

β-Lactam-Tethered Allene 1a. From 91 mg (0.25 mmol) of the corresponding β-lactam-tethered alkyne, and after flash chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **1a** (58 mg, 61%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ= 7.82 (d,

1H, *J* = 8.0 Hz, ArH), 7.46 (d, 2H, *J* = 8.9 Hz, ArH), 7.45 (m, 1H, ArH), 7.38 (t, 1H, *J* = 7.4 Hz, ArH), 7.29 (m, 1H, ArH), 7.27 (s, 1H, ArH), 6.86 (d, 2H, *J* = 8.9 Hz, ArH), 5.62 (d, 1H, *J* = 4.7 Hz, H3), 5.20 (d, 1H, *J* = 4.5 Hz, H4), 5.04 (m, 1H, *J* = 7.0 Hz, =CH), 4.79 (m, 2H, $=CH_2$), 4.01 (m, 2H, OCH_2), 3.87 (s, 3H, NMe), 3.82 (s, 3H, OMe); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC): δ = 209.6, 164.1 (CO), 156.1, 137.0, 130.8, 129.1 (Ar, CH), 127.3, 121.8 (Ar, CH), 119.6 (Ar, CH), 118.9 (Ar, CH), 118.7 (Ar, 2CH), 114.1 (Ar, 2CH), 109.5 (Ar, CH), 106.4, 86.7 (=CH), 82.1 (CH, H3), 75.5 ($=CH_2$), 68.5 (OCH_2), 55.4 (CH, H4), 55.3 (OMe), 33.0 (NMe); IR ($CHCl_3$): ν = 2922, 1744 (CO), 1512, 1246, 832, 745 cm^{-1}; HRMS (ES): calcd for $C_{23}H_{23}N_2O_3[M+H]^+$: 375.1709; found: 375.1712.

β-Lactam-Tethered Allene 1b. From 370 mg (0.84 mmol) of the corresponding β-lactam-tethered alkyne, and after flash chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **1b** (273 mg, 71%) as a colorless oil; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 7.72 (d, 1H, *J* = 1.5 Hz, ArH), 7.57 (d, 2H, *J* = 9.1 Hz, ArH), 7.30 (dd, 1H, *J* =8.8, 1.7 Hz, ArH), 7.17 (t, 1H, *J* = 8.8 Hz, ArH), 6.96 (s, 1H, ArH), 6.87 (d, 2H, *J* = 9.1 Hz, ArH), 5.44 (m, 1H, =CH), 5.40 (d, 1H, *J* = 5.4 Hz, H3), 5.06 (d, 1H, *J* = 5.0 Hz, H4), 4.93 (m, 2H, $=CH_2$), 4.14 (m, 2H, OCH_2), 3.79 (s, 3H, NMe), 3.74 (s, 3H, OMe); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC): δ = 195.1, 164.3 (CO), 157.0, 142.3, 137.4, 130.6 (Ar, CH), 125.0 (Ar, CH), 121.9 (Ar, CH), 121.4, 121.1 (Ar, 2CH), 119.9, 114.2 (Ar, 2CH), 111.0 (Ar, CH), 106.8, 86.7 (=CH), 82.1 (CH, H3), 75.7 ($=CH_2$), 68.9 (OCH_2), 55.4 (CH, H4), 54.9 (OMe), 33.1 (NMe); IR ($CHCl_3$): ν = 2922, 1744 (CO), 1512, 1246, 1082, 797, 752 cm^{-1}; HRMS (ES): calcd for $C_{23}H_{22}BrN_2O_3$ $[M+H]^+$: 453.0814; found: 453.0813.

β-Lactam-Tethered Allene 1c. From 275 mg (0.63 mmol) of the corresponding β-lactam-tethered alkyne, and after flash chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **1c** (161 mg, 61%) as a colorless oil; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 8.06 (d, 1H, *J* = 7.9 Hz, ArH), 7.64 (d, 1H, *J* = 8.0 Hz, ArH), 7.41 (d, 2H, *J* = 8.9 Hz, ArH), 7.32 (t, 1H, *J* = 8.0 Hz, ArH), 7.13 (s, 1H, ArH), 6.85 (d, 2H, *J* = 8.9 Hz, ArH), 5.99 (d, 1H, *J* = 4.8 Hz, H3),

5.08 (d, 1H, *J* = 4.9 Hz, H4), 4.98 (m, 1H, *J* = 6.9 Hz, =CH), 4.63 (m, 2H, $=CH_2$), 4.01 (m, 2H, OCH_2), 3.79 (s, 3H, NMe), 3.78 (s, 3H, OMe); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC): δ = 209.4, 164.8 (CO), 156.2, 142.1, 139.8, 133.1 (Ar, CH), 130.8, 120.6 (Ar, CH), 119.4, 118.8 (Ar, 2CH), 118.3 (Ar, CH), 116.3 (Ar, CH), 114.4 (Ar, 2CH), 107.7, 87.0 (=CH), 83.5 (CH, H3), 75.6 ($=CH_2$), 69.1 (OCH_2), 57.2 (CH, H4), 55.5 (OMe), 33.5 (NMe); IR ($CHCl_3$): ν = 2924, 1738 (CO), 1513, 1252, 1031, 800, 741 cm^{-1}; HRMS (ES): calcd for $C_{23}H_{21}N_3O_5$ $[M+H]^+$: 420.1559; found: 420.1572.

β-Lactam-Tethered Allene 1d. From 110 mg (0.28 mmol) of the corresponding β-lactam-tethered alkyne, and after flash chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **1d** (62 mg, 55%, mixture of isomers = 75:25) as a colorless oil; ^1H NMR (300 MHz, C_6D_6, 25 ^oC): δ = 7.62 (d, 0.5H, *J* = 9.0 Hz, ArH), 7.60 (d, 1.5H, *J* = 9.0 Hz, ArH), 7.27 (d, 0.25H, *J* = 2.3 Hz, ArH), 7.23 (d, 0.75H, *J* = 2.3 Hz, ArH), 7.04 (dd, 1H, *J* = 8.9, 2.4 Hz, ArH), 6.81 (d, 0.25H, *J* = 8.9 Hz, ArH), 6.86 (d, 0.75H, *J* = 8.9 Hz, ArH), 6.67 (s, 0.25H, ArH), 6.59 (d, 0.5H, *J* = 9.0 Hz, ArH), 6.56 (d, 1.5H, *J* = 9.0 Hz, ArH), 6.30 (s, 0.75H, ArH), 5.25 (m, 1H, *J* = 6.8 Hz, =CH), 5.08 (d, 0.75H, *J* = 1.7 Hz, H3), 4.95 (d, 0.25H, *J* = 4.7 Hz, H3), 4.87 (d, 0.75H, *J* = 1.7 Hz, H4), 4.69 (d, 0.25H, *J* = 4.7 Hz, H4), 4.51 (m, 0.5H, $=CH_2$), 4.40 (m, 1.5H, $=CH_2$), 4.20 (m, 2H, OCH_2), 3.64 (s, 0.75H, OMe), 3.52 (s, 2.25H, OMe), 3.16 (s, 0.75H, OMe), 3.14 (s, 2.25H, OMe), 2.79 (s, 0.75H, NMe), 2.75 (s, 2.25H, NMe); ^{13}C NMR (75 MHz, C_6D_6, 25 ^oC): δ = 209.8, 164.1 (CO), 156.6, 155.3, 132.9, 132.1, 128.5 (Ar, CH), 127.7 (Ar, CH), 119.0 (Ar, 2CH), 114.6 (Ar, 2CH), 113.3 (Ar,CH), 110.9 (Ar, CH), 110.1, 100.6, 90.0 (=CH), 88.0 (CH, H3), 75.8 ($=CH_2$), 68.9 (OCH_2), 58.1 (CH, H4), 55.4 (OMe), 54.9 (OMe), 32.1 (NMe); IR ($CHCl_3$): ν = 2937, 1740 (CO), 1515, 1278, 1036, 812, 738 cm^{-1}; HRMS (ES): calcd for $C_{24}H_{24}NaN_2O_4[M+Na]^+$: 427.1634; found: 427.1620.

β-Lactam-Tethered Allene 1e. From 110 mg (0.29 mmol) of the corresponding β-lactam-tethered alkyne, and after flash chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **1e** (59 mg, 54%, mixture of isomers = 60:40) as a colorless oil; ^{1}H NMR (300 MHz, C_6D_6, 25 ^{o}C): δ = 7.62 (d, 1.2H, *J* = 9.0 Hz, ArH), 7.58 (d, 0.8H, *J* = 8.6, 3.5 Hz, ArH), 7.13 (t, 0.6H, *J* = 7.8 Hz, ArH), 6.99 (t, 0.4H, *J* = 7.6 Hz, ArH), 6.88 (d, 1.2H, *J* =7.1 Hz, ArH), 6.83 (d, 0.8H, *J* = 7.0 Hz, ArH), 6.60 (d, 1.2H, *J* = 8.9 Hz, ArH), 6.59 (d, 0.8H, *J* = 8.9 Hz, ArH), 6.55 (s, 0.6H, ArH), 6.24 (s, 0.4H, ArH), 5.25 (m, 0.4H, *J* = 6.8 Hz, =CH), 5.09 (d, 0.4H, *J* = 1.6 Hz, H3), 5.02 (d, 0.6H, *J* = 4.7 Hz, H3), 4.92 (m, 0.6H, *J* = 6.9 Hz, =CH), 4.84 (d, 0.4H, *J* = 1.8 Hz, H4), 4.67 (d, 0.4H, *J* = 4.7 Hz, H4), 4.44 (m, 1.2H, =CH_2), 4.20 (m, 2H, OCH_2), 3.79 (m, 0.6H, =CH_2), 3.16 (s, 1.8H, OMe), 3.13 (s, 1.2H, OMe), 3.02 (s, 1.8H, NMe), 2.97 (s, 1.2H, OMe), 2.27 (s, 3H, Me); ^{13}C NMR (75 MHz, C_6D_6, 25 ^{o}C): δ = 209.6, 164.2 (CO), 156.5, 131.9, 130.7, 128.3 (Ar, CH), 128.3, 124.8 (Ar, CH), 121.8, 120.3, 119.0 (Ar, 2CH), 116.9 (Ar, CH), 114.6 (Ar, 2CH), 106.7 (Ar, CH), 87.6 (=CH), 83.0 (CH, H3), 75.5 (=CH_2), 68.7 (OCH_2), 57.9 (CH, H4), 55.0 (OMe), 36.7 (NMe), 19.5 (Me); IR ($CHCl_3$): ν = 2939, 1742 (CO), 1507, 1260, 1042, 801, 742 cm^{-1}; HRMS (ES): calcd for $C_{24}H_{24}NaN_2O_3$[*M* +Na]$^{+}$: 411.1685; found: 411.1664.

β-Lactam-Tethered Allene 1f. From 130 mg (0.32 mmol) of the corresponding β-lactam-tethered alkyne, and after flash chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **1f** (62 mg, 55%, mixture of isomers = 55:45) as a colorless oil; ^{1}H NMR (300 MHz, C_6D_6, 25 ^{o}C): δ = 7.84 (dd, 0.45H, *J* = 8.2 Hz, ArH), 7.77 (dd, 0.55H, *J* = 8.6 Hz, ArH), 7.74 (d, 1.1H, *J* = 8.2 Hz, ArH), 7.71 (d, 0.9H, *J* = 8.9 Hz, ArH), 7.25 (dd, 0.45H, *J* = 8.2, 1.3 Hz, ArH), 7.09 (dd, 0.55H, *J* = 8.3, 1.3 Hz, ArH), 7.06 (s, 0.45H, ArH), 7.04 (s, 0.55H, ArH), 6.81 (s, 0.45H, ArH), 6.68 d, 1.1H, *J* = 9.3 Hz, ArH), 6.65 (d, 0.9H, *J* = 9.2 Hz, ArH), 6.46 (s, 0.55H, ArH), 5.38 (m, 0.45H, *J* = 6.9 Hz, =CH), 5.21 (d, 0.55H, *J* = 1.7 Hz, H3), 5.15 (d, 0.45H, *J* = 4.8 Hz, H3), 5.02 (m, 0.55H, *J* = 6.8 Hz, =CH), 4.98 (d, 0.55H, *J* = 1.7 Hz, H4), 4.82 (d, 0.45H, *J* = 4.7 Hz, H4), 4.56 (m, 2H, =CH_2), 4.32 (m, 1.1H, OCH_2), 3.90 (m, 0.9H, OCH_2), 3.27 (s, 1.35H, OMe), 3.25 (s,

1.65H, OMe), 3.03 (m, 1H, CH), 2.99 (s, 1.35H, NMe), 2.97 (s, 1.65H, NMe), 1.42 (dd, 2.7H, *J* = 6.9, 1.3 Hz, Me), 1.39 (dd, 3.3H, *J* = 6.9, 1.7 Hz, Me); ^{13}C NMR (75 MHz, C_6D_6, 25 ^{o}C): δ = 209.8 (0.55C), 209.7 (0.45C), 164.2 (0.55CO), 164.1 (0.45CO), 156.5 (0.55C), 156.4 (0.45C), 143.7 (0.55C), 143.1 (0.45C), 138.1 (0.55C), 137.8 (0.45C), 132.1 (0.55C), 132.0 (0.45C), 128.8 (Ar, 0.55CH), 126.9 (Ar, 0.45CH), 119.8 (Ar, 0.55CH), 119.4 (Ar, 0.45CH), 118.9 (Ar, 2CH), 114.6 (Ar, 2CH), 107.5 (Ar, 0.55CH), 107.1 (Ar, 0.45CH), 89.9 (0.55CH, H3), 88.0 (0.55=CH), 87.6 (0.45=CH), 83.1 (0.45CH, H3), 75.8 (0.55=CH_2), 75.5 (0.45=CH_2), 68.8 (0.55OCH_2), 68.6 (0.45OCH_2), 58.3 (0.55CH, H4), 55.4 (0.45CH, H4), 54.9 (0.55OMe), 54.8 (0.45OMe), 35.0 (NMe), 32.0 (CH), 24.8 (2Me); IR ($CHCl_3$): ν = 2935, 1740 (CO), 1512, 1258, 1043, 807, 736 cm^{-1}; HRMS (ES): calcd for $C_{26}H_{29}N_2O_3$[*M* +H]$^+$: 417.2178; found: 417.2163.

β-Lactam-Tethered Allene 1g. From 382 mg (1.23 mmol) of the corresponding β-lactam-tethered alkyne, and after flash chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **1g** (274 mg, 68%) as a colorless solid; mp 93–94 ºC;^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.33 (d, 2H, *J* = 9.1 Hz, ArH), 6.82 (d, 2H, *J* = 9.1 Hz, ArH), 6.33 (d, 1H, *J* = 3.2 Hz, ArH), 5.98 (dd, 1H, *J* = 3.1, 0.9 Hz, ArH), 5.15 (d, 1H, *J* = 4.5 Hz, H3), 5.08 (m, 1H, *J* = 7.0 Hz, =CH), 4.99 (d, 1H, *J* = 4.5 Hz, H4), 4.78 (m, 2H, =CH_2), 4.04 (m, 2H, OCH_2), 3.77 (s, 3H, OMe), 2.30 (d, 3H, *J* = 0.7 Hz, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 209.8, 163.5 (CO), 156.4, 152.9, 145.8, 130.7, 118.7 (Ar, 2CH), 114.3 (Ar, 2CH), 111.3 (Ar, CH), 106.9 (Ar, CH), 86.8 (=CH), 82.4 (CH, H3), 75.7 (=CH_2), 69.0 (OCH_2), 55.9 (CH, H4), 55.4 (OMe), 13.6 (Me); IR ($CHCl_3$): ν = 2919, 1755 (CO), 1512, 1247, 1022, 829, 752 cm^{-1}; HRMS (ES): calcd for $C_{19}H_{20}NO_4$[*M* +H]$^+$: 326.1392; found: 326.1389.

β-Lactam-Tethered Allene 1h. From 372 mg (1.2 mmol) of the corresponding β-lactam-tethered alkyne, and after flash chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **1h** (287 mg, 74%) as a colorless solid; mp 105–106 ºC; ^{1}H NMR (300 MHz,

$CDCl_3$, 25 °C): δ = 7.34 (m, 1H, ArH), 7.32 (d, 2H, *J* = 9.0 Hz, ArH), 7.19 (d, 1H, *J* = 2.9 Hz, ArH), 7.04 (dd, 1H, *J* = 5.1, 3.6 Hz, ArH), 6.80 (d, 2H, *J* = 9.1 Hz, ArH), 5.45 (d, 1H, *J* = 4.5 Hz, H3), 5.03 (d, 1H, *J* = 4.5 Hz, H4), 5.02 (m, 1H, *J* = 6.7 Hz, =CH), 4.76 (m, 2H, $=CH_2$), 3.97 (m, 2H, OCH_2), 3.75 (s, 3H, OMe); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 209.7, 163.4 (CO), 156.5, 136.8, 130.4, 127.7 (Ar, CH), 126.9 (Ar, CH), 126.7 (Ar, CH), 118.8 (Ar, 2CH), 114.3 (Ar, 2CH), 86.7 (=CH), 82.5 (CH, H3), 75.8 ($=CH_2$), 68.9 (OCH_2), 58.1 (CH, H4), 55.4 (OMe); IR ($CHCl_3$): ν = 2930, 1749 (CO), 1511, 1246, 1116, 830, 708 cm^{-1}; HRMS (ES): calcd for $C_{18}H_{18}NO_3S[M+H]^+$: 328.1007; found: 328.0996.

β-Lactam-Tethered Allene 1i. From 51 mg (0.11 mmol) of the corresponding β-lactam-tethered alkyne, and after flash chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **1i** (32 mg, 60%) as a colorless oil; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.70 (d, 1H, *J* = 8.3 Hz, ArH), 7.53 (t, 2H, *J* = 71 Hz, ArH), 7.40 (m, 3H, ArH), 7.27 (d, 2H, *J* = 8.9 Hz, ArH), 7.26 (m, 1H, ArH), 6.81 (m, 1H, ArH), 6.77 (d, 2H, *J* = 9.0 Hz, ArH), 5.46 (d, 1H, *J* = 4.7 Hz, H3), 5.16 (d, 1H, *J* = 4.7 Hz, H4), 5.11 (m, 1H, *J* = 6.7 Hz, =CH), 4.72 (m, 2H, $=CH_2$), 4.10 (m, 2H, OCH_2), 3.72 (s, 3H, OMe); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 209.8, 163.7 (CO), 156.4, 153.1, 150.6, 130.6, 130.3, 130.1, 129.0 (Ar, 2CH), 128.6 (Ar, 2CH), 128.2 (Ar, CH), 127.7 (Ar, CH), 126.4 (Ar, 2CH), 123.9 (Ar, 2CH), 118.6 (Ar, 2CH), 117.6, 114.3 (Ar, 2CH), 107.5, 86.7 (=CH), 82.1 (CH, H3), 75.8 ($=CH_2$), 68.9 (OCH_2), 55.4 (CH, H4), 54.9 (OMe); IR ($CHCl_3$): ν = 2926, 1754 (CO), 1512, 1248, 1118, 831, 695 cm^{-1}; HRMS (ES): calcd for $C_{30}H_{26}NO_4$ $[M+H]^+$: 464.1862; found: 464.1849.

β-Lactam-Tethered Allene 1j. From 169 mg (0.48 mmol) of the corresponding β-lactam-tethered alkyne, and after flash chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound **1j** (133 mg, 77%) as a colorless solid; mp 87–88 ºC; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.54 (d, 1H, *J* = 7.7 Hz, ArH), 7.51 (d, 1H, *J* = 8.5 Hz, ArH), 7.36 (d, 2H, *J* = 9.2 Hz,

ArH), 7.28 (m, 2H, ArH), 6.80 (m, 1H, ArH), 6.81 (d, 2H, *J* = 8.9 Hz, ArH), 5.35 (d, 1H, *J* = 4.7 Hz, H3), 5.13 (d, 1H, *J* = 4.7 Hz, H4), 5.04 (m, 1H, *J* = 6.7 Hz, =CH), 4.68 (m, 2H, $=CH_2$), 4.06 (m, 2H, OCH_2), 3.75 (s, 3H, OMe); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC): δ = 209.8, 163.3 (CO), 156.6, 155.1, 150.7, 130.4, 128.1, 124.5 (Ar, CH), 123.0 (Ar, CH), 121.2 (Ar, CH), 118.6 (Ar, 2CH), 114.4 (Ar, 2CH), 111.4 (Ar, CH), 107.0 (Ar, CH), 86.6 (=CH), 82.7 (CH, H3), 75.6 ($=CH_2$), 69.3 (OCH_2), 56.2 (CH, H4), 55.4 (OMe); IR ($CHCl_3$): ν = 2932, 1755 (CO), 1512, 1250, 1115, 830, 750 cm^{-1}; HRMS (ES): calcd for $C_{22}H_{20}NO_4$ $[M+H]^+$: 362.1392; found: 362.1392.

β-Lactam-Tethered Allene 1k. From 424 mg (1.1 mmol) of the corresponding β-lactam-tethered alkyne, and after flash chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound **1k** (304 mg, 69%) as a colorless oil; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 7.25 (d, 2H, *J* = 8.9 Hz, ArH), 6.77 (d, 2H, *J* = 9.0 Hz, ArH), 6.16 (d, 1H, *J* = 2.0 Hz, ArH), 6.07 (d, 1H, *J* = 2.0 Hz, ArH), 5.69 (d, 1H, *J* = 5.0 Hz, H3), 4.94 (d, 1H, *J* = 5.0 Hz, H4), 4.88 (m, 1H, *J* = 7.1 Hz, =CH), 4.71 (m, 2H, $=CH_2$), 4.02 (m, 1H, OC*H*H), 3.89 (s, 3H, OMe), 3.87 (m, 1H, OCH*H*), 3.80 (s, 3H, OMe), 3.73 (s, 3H, OMe), 3.62 (s, 3H, OMe); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC): δ = 209.6, 164.9 (CO), 162.1, 161.4, 159.8, 155.6, 131.8, 118.0 (Ar, 2CH), 114.1 (Ar, 2CH), 101.5, 91.6 (Ar, CH), 90.6 (Ar, CH), 87.1 (=CH), 81.7 (CH, H3), 75.3 ($=CH_2$), 69.2 (OCH_2), 56.2 (CH, H4), 55.9 (OMe), 55.4 (OMe), 55.2 (OMe), 54.0 (OMe); IR ($CHCl_3$): ν = 2939, 1749 (CO), 1513, 1122, 829, 750 cm^{-1}; HRMS (ES): calcd for $C_{23}H_{26}NO_6$[$M+H]^+$: 412.1760; found: 412.1763.

β-Lactam-Tethered Allene 1l. From 264 mg (0.79 mmol) of the corresponding β-lactam-tethered alkyne, and after flash chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **1l** (204 mg, 74%) as a colorless solid; mp 106–107 ºC; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 7.44 (m, 2H, ArH), 7.42 (d, 2H, *J* = 8.9 Hz, ArH), 7.32 (m, 3H, ArH), 6.87 (d, 2H, *J* = 16.1 Hz, =CH), 6.83 (d, 2H, *J* = 8.9 Hz, ArH), 6.36 (dd, 1H, *J* = 15.9, 8.8 Hz, =CH), 5.26 (m, 1H, *J* = 6.9 Hz, =CH), 4.95 (d, 1H, *J* = 4.7 Hz, H3), 4.78 (m, 2H, $=CH_2$), 4.77 (d, 1H, *J* = 4.4

Hz, H4), 4.20 (m, 2H, OCH_2), 3.77 (s, 3H, OMe); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC): δ = 209.8, 163.6 (CO), 156.3, 136.4, 135.9 (=CH), 131.2, 128.7 (Ar, 2CH), 128.4 (=CH), 126.8 (Ar, 2CH), 123.9 (Ar, CH), 118.7 (Ar, 2CH), 114.3 (Ar, 2CH), 86.9 (=CH), 82.4 (CH, H3), 75.9 (=CH_2), 69.0 (OCH_2), 61.1 (CH, H4), 55.4 (OMe); IR ($CHCl_3$): ν = 2912, 1742 (CO), 1511, 1244, 1118, 833, 753 cm^{-1}; HRMS (ES): calcd for $C_{22}H_{22}NO_3$ $[M+H]^+$: 348.1600; found: 348.1596.

β-Lactam-Tethered Allene 1m. From 250 mg (0.69 mmol) of the corresponding β-lactam-tethered alkyne, and after flash chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **1m** (200 mg, 77%) as a colorless solid; mp 98–99 ºC; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 7.42 (d, 2H, *J* = 9.1 Hz, ArH), 7.38 (d, 2H, *J* = 8.8 Hz, ArH), 6.87 (d, 2H, *J* = 8.9 Hz, ArH), 6.83 (d, 2H, *J* = 9.1 Hz, ArH), 6.80 (d, 1H, *J* = 16.3 Hz, =CH), 6.20 (dd, 1H, *J* = 15.9, 8.9 Hz, =CH), 5.26 (m, 1H, *J* = 6.7 Hz, =CH), 4.93 (d, 1H, *J* = 4.7 Hz, H3), 4.77 (d, 1H, *J* = 4.5 Hz, H4), 4.76 (m, 2H, =CH_2), 4.20 (m, 2H, OCH_2), 3.82 (s, 3H, OMe), 3.76 (s, 3H, OMe); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC): δ = 209.8, 163.7 (CO), 159.8, 156.3, 135.9 (=CH), 131.2, 128.7, 128.1 (Ar, 2CH), 121.4 (=CH), 118.7 (Ar, 2CH), 114.3 (Ar, 2CH), 114.0 (Ar, 2CH), 87.0 (=CH), 82.4 (CH, H3), 75.9 (=CH_2), 69.0 (OCH_2), 61.3 (CH, H4), 55.4 (OMe), 55.3 (OMe); IR ($CHCl_3$): ν = 2912, 1743 (CO), 1511, 1246, 1118, 832, 750 cm^{-1}; HRMS (ES): calcd for $C_{23}H_{24}NO_4$ $[M+H]^+$: 378.1705; found: 378.1711.

β-Lactam-Tethered Allene 1n. From 68 mg (0.16 mmol) of the corresponding β-lactam-tethered alkyne (mixture of isomers = 75:25), and after flash chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **1n**[(26 mg, 38%,mixture of isomers = 75:25) + (23 mg, 33%,isomerically pure)]. **β-Lactam-Tethered Allene 1n (d.r. = 75:25)**: Colorless oil; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 8.07 (dd, 0.75H, *J* = 7.9, 0.7 Hz, ArH), 8.06 (dd, 0.25H, *J* = 7.9, 0.8 Hz, ArH), 7.64 (dd, 0.75H, *J* = 8.2, 0.7 Hz, ArH), 7.63 (dd, 0.25H, *J* = 8.2, 0.7 Hz, ArH), 7.44 (m, 0.5H, ArH), 7.43 (d, 1.5H, *J* = 9.1 Hz, ArH), 7.32 (t, 0.75H, *J* = 8.0 Hz, ArH), 7.31 (t,

0.25H, *J* = 8.0 Hz, ArH), 7.15 (s, 0.75H, ArH), 7.11 (s, 0.25H, ArH), 6.86 (m, 0.5H, ArH), 6.85 (d, 1.5H, *J* = 9.0 Hz, ArH), 6.02 (dd, 0.25H, *J* = 5.1, 0.8 Hz, H3), 5.99 (dd, 0.75H, *J* = 4.8, 0.6 Hz, H3), 5.14 (d, 1H, *J* = 5.0 Hz, H4), 5.11 (m, 1H, =CH), 4.76 (m, 1.5H, $=CH_2$), 4.60 (m, 05H, $=CH_2$), 4.18 (m, 0.25H, OCH), 3.91 (m, 0.75H, OCH), 3.79 (s, 3H, NMe), 3.78 (s, 3H, OMe), 1.15 (d, 0.75H, *J* = 6.3 Hz, Me), 0.80 (d, 2.25H, *J* = 6.3 Hz, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 208.5, 165.0 (CO), 156.1, 139.8, 133.2, 130.9, 120.5 (Ar, CH), 118.8 (Ar, 2CH), 118.3 (Ar, CH), 116.2 (Ar, CH), 114.4 (Ar, 2CH), 107.9, 92.2 (=CH), 82.4 (CH, H3), 76.3 ($=CH_2$), 75.1 (OCH), 57.2 (CH, H4), 55.4 (OMe), 33.5 (NMe), 21.0 (Me); IR ($CHCl_3$): ν = 2916, 1740 (CO), 1514, 1240, 1112, 832, 752 cm^{-1}; HRMS (ES): calcd for $C_{24}H_{24}N_3O_5$[*M* +H]$^+$: 434.1716; found: 434.1711. **β-Lactam-Tethered Allene 1n (isomerically pure)**: Colorless solid; mp 110–111 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 8.06 (dd, 1H, *J* = 7.9, 0.6 Hz, ArH), 7.63 (d, 1H, *J* = 8.1, 0.7 Hz, ArH), 7.44 (d, 2H, *J* = 9.1 Hz, ArH), 7.31 (t, 1H, *J* = 8.0 Hz, ArH), 7.11 (s, 1H, ArH), 6.86 (d, 2H, *J* = 9.19 Hz, ArH), 6.03 (d, 1H, *J* = 4.7 Hz, H3), 5.08 (d, 1H, *J* = 5.1 Hz, H4), 4.64 (m, 1H, =CH), 4.58 (m, 2H, $=CH_2$), 4.18 (m, 1H, OCH), 3.79 (s, 3H, NMe), 3.78 (s, 3H, OMe), 1.16 (d, 3H, *J* = 6.3 Hz, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 208.0, 165.5 (CO), 156.1, 139.8, 133.0, 131.0, 120.5 (Ar, CH), 118.8 (Ar, 2CH), 118.2 (Ar, CH), 116.2 (Ar, CH), 114.4 (Ar, 2CH), 108.2, 92.3 (=CH), 82.5 (CH, H3), 76.2 ($=CH_2$), 75.1 (OCH), 57.2 (CH, H4), 55.5 (OMe), 33.5 (NMe), 20.7 (Me); IR ($CHCl_3$): ν = 2915, 1740 (CO), 1515, 1243, 1110, 832, 753 cm^{-1}; HRMS (ES): calcd for $C_{24}H_{24}N_3O_5$ [*M* +H]$^+$: 434.1716; found: 434.1711.

β-Lactam-Tethered Allene 1o. From 101 mg (0.31 mmol) of the corresponding β-lactam-tethered alkyne (mixture of isomers = 70:30), and after flash chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **1o** (58 mg, 55%, mixture of isomers = 70:30) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.33 (d, 1.4H, *J* = 8.9 Hz, ArH), 7.32 (d, 0.6H, *J* = 8.9 Hz, ArH), 6.82 (d, 2H, *J* = 9.0 Hz, ArH), 6.32 (d, 1H, *J* = 3.0 Hz, ArH), 5.97 (d, 1H, *J* = 1.8 Hz, ArH), 5.13 (m, 1H, H3), 5.11 (m, 0.7H, H4), 5.09 (m, 1H, =CH), 5.01 (d, 0.3H, *J* = 4.7

Hz, H4), 4.82 (m, 1.4H, =CH_2), 4.72 (m, 0.6H, =CH_2), 4.19 (m, 0.3H, OCH), 3.80 (m, 0.7H, OCH), 3.76 (s, 3H, OMe), 2.30 (s, 3H, Me), 1.26 (d, 0.9H, *J* = 6.3 Hz, Me), 1.08 (d, 2.1H, *J* = 6.3 Hz, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 208.9 (M), 208.4 (m), 163.8 (CO, m), 163.4 (CO, M), 156.3, 152.8 (M), 152.6 (m), 146.0 (M + m), 130.8 (M + m), 118.61 (Ar, 2C, M), 118.59 (Ar, 2C, m), 114.2 (Ar, 2CH), 111.3 (Ar, CH, M), 111.1 (Ar, CH, m), 106.8 (Ar, CH), 92.3 (=CH, m), 91.6 (=CH, M), 81.7 (H3, m), 80.6 (H3, M), 76.10 (=CH_2, m), 76.06 (=CH_2, M), 76.0 (OCH, m), 74.5 (OCH, M), 56.6 (H4, m), 55.9 (H4, M), 55.4 (OMe, M + m), 21.1 (Me, m), 20.8 (Me, M), 13.6 (Me, M + m); IR ($CHCl_3$): ν = 2915, 1756 (CO), 1510, 1244, 1025, 826, 752 cm^{-1}; HRMS (ES): calcd for $C_{20}H_{22}NO_4$[*M* +H]$^+$: 340.1549; found: 340.1542.

Bis(β-Lactam)-Tethered Bis(Allene) 1p. From 110 mg (0.21 mmol) of the corresponding bis(β-lactam)-tethered bis(alkyne)(mixture of isomers = 80:20), and after flash chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **1p** (62 mg, 53%, mixture of isomers = 80:20) as a colorless solid; mp 112–113ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.30 (d, 3.2H, *J* = 9.2 Hz, ArH), 7.20 (d, 0.8H, *J* = 9.2 Hz, ArH), 6.80 (d, 3.2H, *J* = 9.1 Hz, ArH), 6.71 (d, 0.8H, *J* = 9.0 Hz, ArH), 6.52 (s, 0.4H, ArH), 6.49 (s, 1.6H, ArH), 5.20 (d, 1.6H, *J* = 4.5 Hz, H3), 5.19 (d, 0.4H, *J* = 4.4 Hz, H3), 5.02 (m, 0.4H, =CH), 4.91 (d, 2H, *J* = 4.7 Hz, H4), 4.91 (m, 1.6H, *J* = 7.0 Hz, =CH), 4.79 (m, 0.8H, =CH_2), 4.74 (m, 3.2H, =CH_2), 4.03 (m, 0.8H, OCH_2), 3.89 (m, 3.2H, OCH_2), 3.75 (s, 4.8H, OMe), 3.74 (s, 1.2H, OMe); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 209.7 (2C, M + m), 163.3 (2CO, M + m), 156.5 (2C, M), 156.4 (2C, m), 148.6 (2C, M + m), 130.4 (2C, M + m), 118.5 (4C, Ar, CH, M), 118.4 (4C, Ar, CH, m), 114.3 (4C, Ar, CH, M + m), 112.0 (2C, Ar, CH, m), 111.7 (2C, Ar, CH, M), 86.7 (2C, =CH, m), 86.6 (2C, =CH, M), 82.3 (2C, CH3, M + m), 76.0 (2C, =CH_2, M), 75.9 (2C, =CH_2, m), 69.2 (2C, OCH_2, M), 69.0 (2C, OCH_2, m), 55.6 (2C, CH4, M + m), 55.4 (2C, OMe, m), 55.3 (2C, OMe, M); IR ($CHCl_3$): ν = 2925, 1750 (CO), 1511, 1253, 1020, 832, 751 cm^{-1}; HRMS (ES): calcd for $C_{32}H_{31}N_2O_7$[*M* +H]$^+$: 555.2131; found: 555.2136.

(Vinyloxy)buta-1,2-diene 3h. From 65 mg (0.40 mmol) of alkyne **F**, and after flash chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **3h** (44 mg, 62%) as a colorless oil; ^{1}H NMR (300 MHz, C_6D_6, 25 ^{o}C): δ = 7.01 (d, 1H, *J* = 3.5 Hz, Ar), 6.92 (d, 1H, *J* = 5.1 Hz, Ar), 6.82 (dd, 1H, *J* = 5.1, 3.4 Hz, Ar), 5.84 (d, 1H, *J* = 6.4 Hz, =CH), 5.58 (d, 1H, *J* = 6.5 Hz, =CH), 5.06 (qu, 1H, *J* = 6.7 Hz, =CH), 4.51 (dt, 2H, *J* = 6.6, 2.5 Hz, =CH_2), 3.99 (dt, 2H, *J* = 6.9, 2.5 Hz, OCH_2); ^{13}C NMR (75 MHz, C_6D_6, 25 ^{o}C): δ = 209.5, 143.6 (=CH), 138.8, 126.5 (Ar, CH), 125.2 (Ar, CH), 124.4 (Ar, CH), 101.7 (=CH), 87.7 (=CH), 76.3 (=CH_2), 70.4 (OCH_2); IR ($CHCl_3$): ν = 2940, 1650, 1359, 695, 666 cm^{-1}; HRMS (ES): calcd for $C_{10}H_{11}OS[M]^+$: 179.0531; found: 179.0520.

General Procedure for the Gold-Catalyzed Rearrangement Reaction of β-Lactam-Tethered Allenes 1. Preparation of Cage Adducts 2a–p. The appropriate allene **1** (0.10 mmol) was added to a stirred solution of [AuClIPr] (0.005 mmol) and $AgSbF_6$ (0.005 mmol) in 1,2-dichloroethane (1.3 mL)under argon. The resulting mixture was stirred under argon atmosphere at the appropriate temperature until disappearance of the starting material (TLC). After filtration through a pad of Celite, the mixture was extracted with ethyl acetate (3 x 3 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 cage adducts **2**.

Cage Adduct 2a. From 30 mg (0.08 mmol) of the β-lactam-tethered allene **1a**, and after flash chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent gave compound **2a** (15 mg, 83%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.67 (d, 1H, *J* = 7.9 Hz, ArH), 7.29 (d, 1H, *J* = 8.5 Hz, ArH), 7.22 (t, 1H, *J* = 6.9 Hz, ArH), 7.10 (td, 1H, *J* = 7.9, 1.2 Hz, ArH), 6.99 (s, 1H, ArH), 4.21 (d, 1H, *J* = 1.5 Hz, OCH), 4.12 (t, 1H, *J* = 3.9 Hz, OCH), 3.76 (s, 3H, NMe), 3.19 (s, 1H, CH), 1.77 (d, 1H, *J* = 10.6 Hz, C*H*H), 1.57 (d, 1H, *J* = 10.6 Hz, CH*H*), 1.51 (m,

1H, CH), 1.46 (m, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 136.7, 127.6, 126.6 (Ar, CH), 121.3 (Ar, CH), 118.7 (Ar, CH), 118.5 (Ar, CH), 112.5, 109.2 (Ar, CH), 73.7 (OCH), 51.4 (OCH), 40.0 (CH), 33.2 (CH_2), 32.7 (NMe), 16.0 (CH), 11.7 (CH); IR ($CHCl_3$): ν = 2936, 1685, 1475, 1062, 795, 741 cm^{-1}; HRMS (ES): calcd for $C_{15}H_{16}NO[M+H]^+$: 226.1232; found: 226.1226.

Cage Adduct 2b. From 99 mg (0.22 mmol) of the β-lactam-tethered allene **1b**, and after flash chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent gave compound **2b** (43 mg, 64%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.73 (d, 1H, *J* = 1.5 Hz, ArH), 7.28 (dd, 1H, *J* = 8.6, 1.7 Hz, ArH), 7.15 (d, 1H, *J* = 8.6 Hz, ArH), 6.99 (s, 1H, ArH), 4.18 (d, 1H, *J* = 1.9 Hz, OCH), 4.11 (t, 1H, *J* = 4.0 Hz, OCH), 3.73 (s, 3H, NMe), 3.10 (s, 1H, CH), 1.76 (d, 1H, *J* = 10.6 Hz, C*H*H), 1.53 (d, 1H, *J* = 10.8 Hz, C*H*H), 1.49 (m, 2H, 2CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 135.4, 129.2, 127.8 (Ar, CH), 124.1 (Ar, CH), 121.1 (Ar, CH), 112.3, 112.0, 110.7 (Ar, CH), 73.6 (OCH), 51.3 (OCH), 39.9 (CH), 33.2 (CH_2), 32.8 (NMe), 15.9 (CH), 11.7 (CH); IR ($CHCl_3$): ν = 2935, 1717, 1475, 1059, 792 cm^{-1}; HRMS (ES): calcd for $C_{15}H_{15}BrNO[M+H]^+$: 304.0337; found: 304.0336.

Cage Adduct 2c.From 35 mg (0.08 mmol) of the β-lactam-tethered allene **1c**, and after flash chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **2c** (19 mg, 85%) as a colorless solid; mp 107–108 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.86 (d, 1H, *J* = 7.9 Hz, ArH), 7.50 (d, 1H, *J* = 8.0 Hz, ArH), 7.25 (m, 2H, ArH), 4.18 (d, 1H, *J* = 1.6 Hz, OCH), 4.13 (t, 1H, *J* = 3.6 Hz, OCH), 3.84 (s, 3H, NMe), 3.44 (s, 1H, ArH), 1.83 (d, 1H, *J* = 10.2 Hz, C*H*H), 1.51 (dt, 1H, *J* = 10.5, 1.9 Hz, CH*H*), 1.47 (t, 2H, *J* = 3.9 Hz, 2CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 143.0, 139.4, 131.9 (Ar, CH), 119.9 (Ar, CH), 119.3, 117.2 (Ar, CH), 115.1 (Ar, CH), 112.2, 74.3 (OCH), 51.7 (OCH), 41.4 (CH), 33.2 (CH_2), 33.0 (NMe), 15.8 (CH), 11.7 (CH); IR ($CHCl_3$): ν = 2923, 1681, 1511, 1345, 750 cm^{-1}; HRMS (ES): calcd for $C_{15}H_{15}N_2O_3[M+H]^+$: 271.1083; found: 271.1060.

Cage Adduct 2d. From 38mg (0.09 mmol) of the β-lactam-tethered allene **1d**, and after flash chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent gave compound **2d** (18 mg, 74%) as a colorless solid; mp 100–101 ºC; ^{1}H NMR (300 MHz, C_6D_6, 25 ^{o}C): δ = 7.22 (d, 1H, *J* = 2.3 Hz, ArH), 7.12 (dd, 1H, *J* = 8.9, 2.4 Hz, ArH), 6.94 (d, 1H, *J* = 8.6 Hz, ArH), 6.87 (s, 1H, ArH), 4.12 (s, 1H, OCH), 3.90 (t, 1H, *J* = 3.9 Hz, OCH), 3.62 (s, 3H, NMe), 3.03 (s, 1H, CH), 2.97 (s, 3H, OMe), 1.39 (m, 2H, CH_2), 1.26 (t, 1H, *J* = 4.8 Hz, CH), 1.08 (t, 1H, *J* = 4.7 Hz, CH); ^{13}C NMR (75 MHz, C_6D_6, 25 ^{o}C): δ = 154.6, 132.7, 128.9, 112.5, 111.9 (Ar, CH), 110.3 (Ar, CH), 101.2 (Ar, CH), 74.0 (OCH), 55.6 (OMe), 51.6 (OCH), 40.5 (CH), 33.6 (CH_2), 32.1 (NMe), 17.1 (CH), 12.2 (CH); IR ($CHCl_3$): ν = 2935, 1654, 1461, 1060, 776, 720 cm^{-1}; HRMS (ES): calcd for $C_{16}H_{18}NO_2[M+H]^+$: 256.1338; found: 256.1326.

Cage Adduct 2e. From 33 mg (0.08 mmol) of the β-lactam-tethered allene **1e**, and after flash chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent gave compound **2e** (12 mg, 57%) as a colorless oil; ^{1}H NMR (300 MHz, acetone-d_6, 25 ^{o}C): δ = 7.39 (dd, 1H, *J* = 7.6, 0.9 Hz, ArH), 6.89 (s, 1H, ArH), 6.83 (m, 2H, ArH), 4.07 (d, 1H, *J* = 1.9 Hz, OCH), 4.02 (t, 1H, *J* = 4.0 Hz, OCH), 4.01 (s, 3H, NMe), 3.09 (s, 1H, CH), 2.71 (s, 3H, Me), 1.73 (d, 1H, *J* = 9.9 Hz, C*H*H), 1.40 (m, 1H, CH*H*), 1.38 (m, 1H, CH), 1.36 (m, 1H, CH); ^{13}C NMR (75 MHz, acetone-d_6, 25 ^{o}C): δ = 136.4, 130.0, 129.4 (Ar, CH), 124.5 (Ar, CH), 121.9, 119.5 (Ar, CH), 117.5 (Ar, CH), 113.1, 74.0 (OCH), 51.8 (OCH), 40.7 (CH), 36.7 (NMe), 33.8 (CH_2), 19.8 (Me), 16.5 (CH), 12.1 (CH); IR ($CHCl_3$): ν = 2940, 1683, 1475, 1054, 790, 732 cm^{-1}; HRMS (ES): calcd for $C_{16}H_{18}NO[M+H]^+$: 240.1388; found: 240.1387.

Cage Adduct 2f. From 38 mg (0.09 mmol) of the β-lactam-tethered allene **1f**, and after flash chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent gave compound **2f** (14 mg, 60%) as a colorless solid; mp 96–97 ºC; ^{1}H NMR (300 MHz, C_6D_6, 25 ^{o}C): δ = 7.62 (d, 1H, *J* = 8.3 Hz, ArH), 7.17 (m, 1H, ArH), 7.02 (d, 1H, *J* = 0.7 Hz, ArH), 6.84 (s, 1H, ArH), 4.11 (d, 1H, *J* =

1.2 Hz, OCH), 3.90 (t, 1H, *J* = 3.8 Hz, OCH), 3.06 (m, 1H, CH), 3.04 (s, 1H, CH), 3.02 (s, 3H, NMe), 1.40 (d, 6H, *J* = 7.0 Hz, 2Me), 1.36 (m, 2H, CH_2), 1.25 (t, 1H, *J* = 4.7 Hz, CH), 1.07 (t, 1H, *J* = 4.7 Hz, CH); ^{13}C NMR (75 MHz, C_6D_6, 25 ^{o}C): δ = 142.6, 137.7, 127.1, 126.5 (Ar, CH), 119.0 (Ar, CH), 118.3 (Ar, CH), 112.9, 106.7 (Ar, CH), 74.0 (OCH), 51.6 (OCH), 40.6 (CH), 35.1 (NMe), 33.6 (CH_2), 31.9 (CH), 25.0 ($2CH_3$), 17.0 (CH), 12.2 (CH); IR ($CHCl_3$): ν = 2935, 1676, 1475, 1078, 792, 737 cm^{-1}; HRMS (ES): calcd for $C_{18}H_{22}NO[M+H]^+$: 268.1701; found: 268.1709.

Cage Adduct 2g. From 50 mg (0.15 mmol) of the β-lactam-tethered allene **1g**, and after flash chromatography of the residue using hexanes/ethyl acetate (6:1) as eluent gave compound **2g** (17 mg, 65%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 5.98 (d, 1H, *J* = 2.9 Hz, ArH), 5.87 (dd, 1H, *J* = 2.9, 0.9 Hz, ArH), 4.25 (d, 1H, *J* = 2.0 Hz, OCH), 4.07 (t, 1H, *J* = 4.0 Hz, OCH), 2.89 (s, 1H, CH), 2.26 (s, 3H, Me), 1.64 (dd, 1H, *J* = 10.5, 0.9 Hz, C*H*H), 1.48 (d, 1H, *J* = 10.4 Hz, CH*H*), 1.46 (m, 1H, CH), 1.45 (m, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 152.2, 150.4, 106.6 (Ar, CH), 106.0 (Ar, CH), 72.7 (OCH), 51.2 (OCH), 42.8 (CH), 32.9 (CH_2), 14.4 (CH), 13.5 (Me), 11.3 (CH); IR ($CHCl_3$): ν = 2927, 1712, 1513, 1250, 927, 799, 755 cm^{-1}; HRMS (ES): calcd for $C_{11}H_{13}O_2$ $[M+H]^+$: 177.0916; found: 177.0904.

Cage Adduct 2h. From 50 mg (0.15 mmol) of the β-lactam-tethered allene **1h**, and after flash chromatography of the residue using hexanes/ethyl acetate (6:1) as eluent gave compound **2h** (18 mg, 68%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.17 (dd, 1H, *J* = 5.1, 1.3 Hz, ArH), 6.94 (dd, 1H, *J* = 5.0, 3.4 Hz, ArH), 6.90 (d, 1H, *J* = 3.4 Hz, ArH), 4.16 (m, 1H, OCH), 4.15 (t, 1H, *J* = 4.1 Hz, OCH), 3.21 (s, 1H, CH), 1.71 (d, 1H, *J* = 10.5 Hz, C*H*H), 1.55 (m, 1H, CH*H*), 1.51 (m, 1H, CH), 1.49 (m, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 142.9, 126.2 (Ar, CH), 124.3 (Ar, CH), 123.9 (Ar, CH), 74.8 (OCH), 51.6 (OCH), 44.7 (CH), 33.3 (CH_2), 17.9 (CH), 12.5 (CH); IR ($CHCl_3$): ν = 2920, 1717, 1510, 1200, 927, 796, 750 cm^{-1}; HRMS (ES): calcd for $C_{10}H_{11}OS[M+H]^+$: 179.0531; found: 179.0518.

Cage Adduct 2i. From 75 mg (0.16 mmol) of the β-lactam-tethered allene **1i**, and after flash chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent gave compound **2i** (23 mg, 45%) as a colorless solid; mp 103–104 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.73 (dd, 2H, *J* = 8.5, 1.3 Hz, ArH), 7.67 (dd, 2H, *J* = 8.5, 1.4 Hz, ArH), 7.42 (m, 4H, ArH), 7.29 (m, 2H, ArH), 6.87 (s, 1H, ArH), 4.28 (d, 1H, *J* = 1.9 Hz, OCH), 4.20 (t, 1H, *J* = 3.8 Hz, OCH), 3.13 (s, 1H, CH), 1.75 (d, 1H, *J* = 10.6 Hz, C*H*H), 1.56 (m, 1H, CH*H*), 1.53 (m, 1H, CH), 1.52 (m, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 152.1, 148.5, 131.5, 130.8, 128.6 (4C, Ar, CH), 127.1 (2C, Ar, CH), 126.0 (2C, Ar, CH), 123.7 (2C, Ar, CH), 122.1 108.4 (Ar, CH), 74.4 (OCH), 51.8 (OCH), 40.3 (CH), 33.5 (CH_2), 16.6 (CH), 11.8 (CH); IR ($CHCl_3$): ν = 2930, 1715, 1513, 1265, 996, 795 cm^{-1}; HRMS (ES): calcd for $C_{22}H_{19}O_2$ [*M* +H]$^{+}$: 315.1385; found: 315.1374.

Cage Adduct 2j. From 60 mg (0.17 mmol) of the β-lactam-tethered allene **1j**, and after flash chromatography of the residue using hexanes/ethyl acetate (6:1) as eluent gave compound **2j** (19 mg, 35%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.48 (dd, 1H, *J* = 6.7, 0.9 Hz, ArH), 7.41 (d, 1H, *J* = 7.9 Hz, ArH), 7.19 (m, 2H, ArH), 6.52 (s, 1H, ArH), 4.40 (d, 1H, *J* = 2.0 Hz, OCH), 4.16(t, 1H, *J* = 3.7 Hz, OCH), 3.08 (s, 1H, CH), 1.74 (d, 1H, *J* = 10.4 Hz, C*H*H), 1.63 (m, 1H, CH*H*), 1.53 (m, 2H, 2CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 157.2, 154.5, 128.8, 123.3 (Ar, CH), 122.4 (Ar, CH), 120.5 (Ar, CH), 110.7 (Ar, CH), 103.1 (Ar, CH), 72.6 (OCH), 51.4 (OCH), 43.2 (CH), 33.2 (CH_2), 14.6 (CH), 11.5 (CH); IR ($CHCl_3$): ν = 2934, 1723, 1483, 1060, 797 cm^{-1}; HRMS (ES): calcd for $C_{14}H_{13}O_2$ [*M* +H]$^{+}$: 213.0916; found: 213.0913.

Cage Adduct 2k. From 101 mg (0.24 mmol) of the β-lactam-tethered allene **1k**, and after flash chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent gave compound **2k** (20 mg, 32%) as a colorless solid; mp 96–97 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 6.12 (s, 2H, ArH), 4.30 (br s, 1H, OCH), 3.99 (t, 1H, *J* = 3.9 Hz, OCH), 3.79 (s, 9H, 3OMe), 3.01 (s, 1H, CH), 1.62 (d, 1H, *J* = 9.5 Hz, C*H*H), 1.34 (m, 1H, CH*H*), 1.32 (m, 2H, 2CH); ^{13}C NMR (75 MHz,

$CDCl_3$, 25 °C): δ = 160.0, 159.4, 123.3, 119.0, 91.5 (2C, Ar, CH), 74.6 (OCH), 55.9 (2OMe), 55.3 (OMe), 53.2 (OCH), 42.2 (CH), 31.2 (CH_2), 15.0 (CH), 11.9 (CH); IR ($CHCl_3$): ν = 2936, 1712, 1476, 1057, 795, 754 cm^{-1}; HRMS (ES): calcd for $C_{15}H_{19}O_4[M+H]^+$: 263.1283; found: 263.1288.

Cage Adduct 2l. From 63 mg (0.18 mmol) of the β-lactam-tethered allene **1l**, and after flash chromatography of the residue using hexanes/ethyl acetate (8:1) as eluent gave compound **2l** (13 mg, 37%) as a colorless oil; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.36 (d, 2H, *J* = 8.0 Hz, ArH), 7.30 (d, 2H, *J* = 7.1 Hz, ArH), 7.20 (t, 1H, *J* = 7.3 Hz, ArH), 6.47 (d, 1H, *J* = 16.1 Hz, =CH), 6.09 (d, 1H, *J* = 16.1, 8.5 Hz, =CH), 4.07 (m, 1H, OCH), 4.05 (t, 1H, *J* = 3.8 Hz, OCH), 2.48 (d, 1H, *J* = 8.5 Hz, CH), 1.59 (d, 1H, *J* = 10.6 Hz, C*H*H), 1.44 (m, 1H, CH*H*), 1.37 (m, 2H, 2CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 137.4, 130.7 (=CH), 128.8 (=CH), 128.4 (2C, Ar, CH), 127.0 (Ar, CH), 126.1 (Ar, 2CH), 73.9 (OCH), 51.2 (OCH), 47.5 (CH), 32.9 (CH_2), 15.6 (CH), 11.4 (CH); IR ($CHCl_3$): ν = 2934, 1710, 1475, 1060, 794 cm^{-1}; HRMS (ES): calcd for $C_{14}H_{15}O[M+H]^+$: 199 1123; found: 199.1119.

Cage Adduct 2m. From 81 mg (0.22 mmol) of the β-lactam-tethered allene **1m**, and after flash chromatography of the residue using hexanes/ethyl acetate (8:1) as eluent gave compound **2m** (16 mg, 32%) as a colorless oil; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.29 (d, 2H, *J* = 8.8 Hz, ArH), 6.84 (d, 2H, *J* = 8.8 Hz, ArH), 6.42 (d, 1H, *J* = 16.1 Hz, =CH), 5.94 (d, 1H, *J* = 15.9, 8.5 Hz, =CH), 4.05 (m, 1H, OCH), 4.04 (t, 1H, *J* = 4.1 Hz, OCH), 3.81 (s, 3H, OMe), 2.45 (d, 1H, *J* = 8.5 Hz, CH), 1.57 (d, 1H, *J* = 10.4 Hz, C*H*H), 1.41 (d, 1H, *J* = 10.6 Hz, CH*H*), 1.37 (t, 1H, *J* = 4.4 Hz, CH), 1.28 (t, 1H, *J* = 4.4 Hz, CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 158.8, 130.3, 130.0 (=CH), 127.2 (2C, Ar, CH), 126.5 (=CH), 113.9 (2C, Ar, CH), 74.0 (OCH), 55.3 (OMe), 51.2 (OCH), 47.4 (CH), 32.9 (CH_2), 15.6 (CH), 11.4 (CH); IR ($CHCl_3$): ν = 2934, 1711, 1479, 1062, 798, 750 cm^{-1}; HRMS (ES): calcd for $C_{15}H_{17}O_2[M+H]^+$: 229.1229; found: 229.1221.

Cage Adduct 2n. From 27 mg (0.06 mmol) of the β-lactam-tethered allene **1n**, and after flash chromatography of the residue using hexanes/ethyl acetate (8:1) as eluent gave compound **2n** (12 mg, 68%) as a colorless solid; mp 108–109 ºC; ^{1}H NMR (300 MHz, C_6D_6, 25 ^{o}C): δ = 7.72 (dd, 1H, *J* = 7.9, 0.9 Hz, ArH), 7.45 (dd, 1H, *J* = 8.2, 0.9 Hz, ArH), 7.12 (m, 2H, ArH), 4.00 (d, 1H, *J* = 1.6 Hz, OCH), 3.72 (s, 3H, NMe), 3.36 (s, 1H, CH), 1.73 (d, 1H, *J* = 10.7 Hz, C*H*H), 1.66 (s. 3H, Me), 1.55 (dt, 1H, *J* = 10.6, 2.0 Hz, CH*H*), 1.18 (m, 2H, 2CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 142.8, 139.5, 132.0 (Ar, CH), 120.0 (Ar, CH), 119.7, 117.2 (Ar, CH), 115.2 (Ar, CH), 112.2, 73.6 (OCH), 58.8, 43.3 (CH), 34.4 (CH_2), 33.3 (NMe), 21.4 (CH), 17.5 (CH), 14.3 (Me); IR ($CHCl_3$): ν = 2925, 1690, 1510, 1342, 751 cm^{-1}; HRMS (ES): calcd for $C_{16}H_{17}N_2O_3$ [*M* +H]$^{+}$: 285.1239; found: 285.1227.

Cage Adduct 2o. From 26 mg (0.08 mmol) of the β-lactam-tethered allene **1o**, and after flash chromatography of the residue using hexanes/ethyl acetate (6:1) as eluent gave compound **2o** (7 mg, 42%) as a colorless oil; ^{1}H NMR (300 MHz, C_6D_6, 25 ^{o}C): δ = 6.20 (d, 1H, *J* = 3.0 Hz, ArH), 5.97 (d, 1H, *J* = 2.9 Hz, ArH), 4.20 (d, 1H, *J* = 1.5 Hz, OCH), 2.92 (s, 1H, CH), 2.20 (d, 3H, *J* = 0.4 Hz Me), 1.66 (s, 3H, Me), 1.49 (dt, 1H, *J* = 10.5, 1.7 Hz, C*H*H), 1.33 (d, 1H, *J* = 10.3 Hz, CH*H*), 1.17 (d, 1H, *J* = 5.5 Hz, CH), 0.98 (t, 1H, *J* = 5.5 Hz, CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 152.2, 150.4, 106.7 (Ar, CH), 106.1 (Ar, CH), 74.6 (OCH), 58.6, 44.5 (CH), 34.4 (CH_2), 20.0 (Me), 17.1 (CH), 14.0 (CH), 13.5 (Me); IR ($CHCl_3$): ν = 2928, 1714, 1510, 1250, 921, 795, 757 cm^{-1}; HRMS (ES): calcd for $C_{12}H_{15}O_2$ [*M* +H]$^{+}$: 191.1072; found: 191.1063.

Bis(Cage)Adduct 2p. From 47 mg (0.09 mmol) of the bis(β-lactam)-tethered bis(allene) **1p**, and after flash chromatography of the residue using hexanes/ethyl acetate (8:1) as eluent gave compound **2p** (8 mg, 36%) as a colorless solid; mp 109–110 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 6.01 (s, 2H, ArH), 4.25 (s, 2H, 2OCH), 4.07 (t, 2H, *J* = 3.8 Hz, 2OCH), 2.89 (s, 2H, 2CH), 1.64 (d, 2H, *J* = 10.7 Hz, 2C*H*H), 1.48 (m, 2H, 2CH*H*), 1.45 (m, 2H, 2CH), 1.42 (m, 2H, 2CH); ^{13}C

NMR (175 MHz, $CDCl_3$, 25 ^oC): δ = 152.4 (2C), 106.7 (Ar, CH), 106.5 (Ar, CH), 72.7 (OCH), 72.6 (OCH), 51.3 (OCH), 51.2 (OCH), 42.8 (2C, CH), 33.0 (CH_2), 32.9 (CH_2), 14.6 (CH), 14.4 (CH), 11.4 (CH), 11.3 (CH); IR ($CHCl_3$): ν = 2930, 1708, 1515, 946, 790 cm^{-1}; HRMS (ES): calcd for $C_{16}H_{17}O_3[M+H]^+$: 257.1178; found: 257.1173.

Computational Details

All the calculations reported in this paper were obtained with the GAUSSIAN 09 suite of programs.[1] Electron correlation was partially taken into account using the hybrid functional usually denoted as B3LYP[2] in conjunction with the D3 dispersion correction suggested by Grimme et al.[3]using the standard double-ζ quality plus polarization def2-SVP basis set[4] for all atoms. Solvents effects were taken into account by means of the Polarizable Continuum Model (PCM)[5]using dichloroethane as solvent during the geometry optimizations. Reactants and products were characterized by frequency calculations,[6] and have positive definite Hessian matrices. Transition structures (TS's) show only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the Intrinsic Reaction Coordinate (IRC) method.[7] Single point calculations were performed to estimate the change in the Gibbs energies at the B3LYP-D3 level using the triple-ζ quality plus polarization def2-TZVP basis set for all atoms. This level is denoted PCM(dichloroethane)-B3LYP-D3/def2-TZVP//PCM(dichloroethane)-B3LYP-D3/def2-SVP.

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Cartesian coordinates (in Å) and total energies (in a. u., ZPVE included) of all the stationary points discussed in the text. All calculations have been performed at the PCM(dichloroethane)-B3LYP-D3/def2-SVP level.

1M: E=-536.864916

O	-1.859969000	-1.423086000	-0.337128000
C	1.249621000	-0.460619000	0.496608000
C	2.347785000	0.106670000	1.109666000
C	3.116464000	0.742013000	0.082678000
C	0.179904000	-1.237173000	1.090099000
C	-1.516314000	0.916650000	-1.030218000
C	-1.525575000	-0.548100000	-1.404726000
C	-2.377933000	1.909126000	1.236392000
C	-1.073713000	-1.617647000	0.740171000
H	4.047043000	1.294533000	0.197121000
H	2.564429000	0.074226000	2.175462000
H	-1.101954000	1.587177000	-1.794618000
H	0.446107000	-1.577935000	2.094851000
H	-1.623599000	-2.229056000	1.462127000
H	-1.698943000	2.015955000	2.090860000
H	-3.417631000	2.227037000	1.378677000
H	-0.554047000	-0.819568000	-1.842469000
O	1.321905000	-0.214525000	-0.845600000
C	2.445646000	0.515595000	-1.085268000
H	2.628391000	0.787739000	-2.121683000
C	-1.960011000	1.418118000	0.096163000
H	-2.300529000	-0.727017000	-2.167895000

3M: E=-977.058029

O	-4.150417000	-1.694068000	0.614656000
C	-3.249649000	1.303545000	-0.540645000
C	-2.513397000	2.196729000	-1.288188000
C	-1.843221000	3.060033000	-0.361825000
C	-4.107755000	0.219221000	-0.985923000
C	-1.913082000	-0.971093000	1.359585000
C	-3.375350000	-1.175566000	1.678070000
C	-1.069286000	-1.715147000	-1.032429000
C	-4.456498000	-0.996677000	-0.501956000
H	-1.175255000	3.887398000	-0.592802000
H	-2.455793000	2.218344000	-2.374367000
H	-1.329009000	-0.460512000	2.131965000
H	-4.518138000	0.399709000	-1.983681000
H	-5.113739000	-1.613527000	-1.121428000
H	-1.350201000	-1.079811000	-1.882173000
H	-0.785027000	-2.751688000	-1.251459000
H	-3.784636000	-0.215618000	2.031671000
O	-3.077880000	1.591936000	0.784967000
C	-2.221392000	2.644742000	0.883695000
H	-1.992801000	2.985436000	1.890209000
C	-1.349616000	-1.321725000	0.227331000
Au	0.775589000	-0.679153000	-0.213461000
C	2.597121000	0.221792000	0.075671000
C	4.805294000	0.559810000	0.322163000
C	4.194706000	1.778572000	0.349437000

H	5.853200000	0.286151000	0.408231000
H	4.605155000	2.777342000	0.469538000
N	3.808817000	-0.381666000	0.158341000
N	2.841181000	1.550808000	0.197125000
H	-3.469444000	-1.907735000	2.495678000
C	4.057850000	-1.815437000	0.042330000
H	3.127793000	-2.360574000	0.240906000
H	4.414808000	-2.057883000	-0.968963000
H	4.815925000	-2.112969000	0.778480000
C	1.843132000	2.616506000	0.173045000
H	1.991122000	3.247224000	-0.714869000
H	0.838305000	2.180195000	0.141691000
H	1.939491000	3.232818000	1.077353000

4M: E=-977.082055

O	-2.972178000	-1.117129000	1.447880000
C	-4.309663000	0.823162000	-0.383575000
C	-5.024765000	1.780141000	-1.070327000
C	-4.459702000	3.046047000	-0.717046000
C	-4.408136000	-0.616971000	-0.387586000
C	-0.975650000	-2.442925000	1.095640000
C	-1.951219000	-1.909145000	1.861609000
C	-1.073883000	-1.132755000	-1.101046000
C	-3.759119000	-1.500418000	0.393042000
H	-4.770535000	4.029737000	-1.062979000
H	-5.856779000	1.588331000	-1.744700000
H	-0.283263000	-3.110638000	1.614615000
H	-5.089444000	-1.036252000	-1.130502000
H	-3.847557000	-2.581998000	0.252234000
H	-1.711394000	-0.336203000	-0.713765000
H	-0.947651000	-1.180670000	-2.186332000
O	-3.337297000	1.436583000	0.360615000
C	-3.439022000	2.775001000	0.151358000
H	-2.725650000	3.399679000	0.683372000
C	-0.687565000	-2.208747000	-0.321783000
Au	0.983719000	-0.527355000	-0.339368000
C	2.687409000	0.509389000	0.111773000
C	4.746437000	1.406824000	0.028853000
C	4.169113000	1.804056000	1.198568000
H	5.724778000	1.624417000	-0.390569000
H	4.548878000	2.428561000	2.002417000
N	3.822918000	0.612514000	-0.622461000
N	2.905746000	1.247778000	1.228901000
H	-1.967201000	-2.076419000	2.943330000
H	-0.166583000	-3.032543000	-0.824232000
C	4.048411000	0.027367000	-1.940909000
H	5.035616000	-0.452827000	-1.963744000
H	3.275721000	-0.723694000	-2.140698000
H	4.004676000	0.809337000	-2.712580000
C	1.974198000	1.383538000	2.346138000
H	0.945540000	1.411447000	1.966312000
H	2.083623000	0.536724000	3.038780000
H	2.187471000	2.318988000	2.877804000

TS1: E=-977.051064

O	-3.228169000	-1.287040000	1.219232000
C	-4.613611000	0.517969000	-0.687135000
C	-5.391855000	1.349426000	-1.497042000
C	-5.668598000	2.509363000	-0.743867000

C	-4.077702000	-0.752317000	-0.946370000
C	-0.951849000	-2.060641000	1.379524000
C	-2.159834000	-1.806135000	1.916956000
C	-1.527045000	-0.808770000	-0.682576000
C	-3.227657000	-1.516877000	-0.139658000
H	-6.250545000	3.377497000	-1.044207000
H	-5.712158000	1.119552000	-2.511308000
H	-0.210322000	-2.549846000	2.015018000
H	-4.267264000	-1.142356000	-1.949175000
H	-3.090332000	-2.567902000	-0.426038000
H	-1.698996000	0.163813000	-0.210713000
H	-1.487805000	-0.761316000	-1.774747000
O	-4.409506000	1.145333000	0.519044000
C	-5.039439000	2.325838000	0.471222000
H	-4.966133000	2.949932000	1.359818000
C	-0.602451000	-1.720653000	-0.022649000
Au	1.201413000	-0.503189000	-0.065357000
C	2.955716000	0.583979000	-0.035223000
C	4.510603000	2.139365000	0.465186000
C	5.057381000	1.290492000	-0.448258000
H	4.922367000	3.014200000	0.960887000
H	6.041278000	1.277384000	-0.908963000
N	3.224689000	1.690053000	0.706301000
N	4.091180000	0.344594000	-0.741028000
H	-2.420302000	-1.999398000	2.959296000
H	-0.335417000	-2.602892000	-0.626596000
C	4.293602000	-0.742042000	-1.692502000
H	4.450061000	-0.334774000	-2.701676000
H	5.171650000	-1.334931000	-1.400119000
H	3.406632000	-1.385990000	-1.695122000
C	2.309185000	2.341829000	1.635816000
H	2.111032000	3.371971000	1.307065000
H	1.366763000	1.782804000	1.663375000
H	2.749525000	2.360391000	2.642721000

5M: E=-977.054545

O	-3.156526000	-1.118862000	1.246733000
C	-4.704680000	0.447081000	-0.671552000
C	-5.698307000	1.142176000	-1.403790000
C	-5.922101000	2.350022000	-0.744071000
C	-4.140770000	-0.786165000	-0.894434000
C	-0.923503000	-1.970441000	1.440775000
C	-2.116279000	-1.639932000	1.976852000
C	-1.662328000	-0.918369000	-0.691781000
C	-3.077858000	-1.428269000	-0.135245000
H	-6.616325000	3.143672000	-1.009385000
H	-6.180422000	0.770844000	-2.306338000
H	-0.197086000	-2.468773000	2.087592000
H	-4.468216000	-1.289870000	-1.807923000
H	-3.103043000	-2.522739000	-0.289096000
H	-1.663913000	0.154130000	-0.447601000
H	-1.603157000	-1.026236000	-1.783380000
O	-4.336411000	1.236398000	0.404177000
C	-5.054504000	2.347200000	0.346343000
H	-4.874409000	3.085796000	1.126846000
C	-0.568779000	-1.691144000	0.025236000
Au	1.231947000	-0.524031000	-0.038341000
C	2.982961000	0.592690000	-0.063491000
C	4.520451000	2.191296000	0.363867000
C	5.069120000	1.322380000	-0.529033000

H	4.924026000	3.088479000	0.825268000
H	6.047080000	1.310437000	-1.002432000
N	3.245342000	1.727898000	0.636722000
N	4.114154000	0.351821000	-0.777183000
H	-2.385337000	-1.786689000	3.025462000
H	-0.313711000	-2.627523000	-0.502900000
C	4.321183000	-0.762099000	-1.694693000
H	4.468658000	-0.386415000	-2.717595000
H	5.205867000	-1.339006000	-1.389843000
H	3.439252000	-1.412628000	-1.671188000
C	2.330846000	2.392144000	1.557500000
H	2.110293000	3.408681000	1.201201000
H	1.398979000	1.817449000	1.612887000
H	2.781937000	2.449090000	2.558414000

TS2: E=-977.036077

O	3.621177000	-1.890083000	0.152639000
C	3.372272000	1.083521000	0.171907000
C	3.238452000	2.430439000	-0.180262000
C	4.541357000	2.932482000	-0.371253000
C	2.406363000	0.100987000	0.421626000
C	1.720909000	-1.411800000	-1.145094000
C	3.053212000	-1.786356000	-1.039230000
C	1.442668000	-2.059421000	1.215177000
C	2.725567000	-1.237766000	1.093572000
H	4.834698000	3.942723000	-0.646704000
H	2.294150000	2.962142000	-0.280239000
H	1.381719000	-1.116216000	-2.141319000
H	1.391937000	0.493752000	0.525338000
H	3.288675000	-1.125502000	2.030582000
H	0.868933000	-1.737885000	2.096313000
H	1.740619000	-3.106220000	1.386831000
H	3.734795000	-1.956518000	-1.879833000
O	4.710126000	0.766868000	0.199597000
C	5.392734000	1.871806000	-0.125571000
H	6.477690000	1.786208000	-0.138391000
C	0.682718000	-1.861117000	-0.126583000
H	0.324103000	-2.840143000	-0.492326000
Au	-1.041377000	-0.622733000	-0.068953000
C	-2.730416000	0.593736000	0.002838000
C	-4.867335000	1.327767000	0.052893000
C	-4.057318000	2.417380000	0.156379000
H	-5.950587000	1.245005000	0.031960000
H	-4.293621000	3.473910000	0.248829000
N	-4.037225000	0.223853000	-0.039036000
N	-2.755774000	1.948323000	0.120620000
C	-1.579167000	2.799988000	0.248862000
H	-0.731214000	2.327366000	-0.261870000
H	-1.782135000	3.774860000	-0.213481000
H	-1.324610000	2.948071000	1.308774000
C	-4.530093000	-1.140435000	-0.184427000
H	-5.053553000	-1.253771000	-1.144972000
H	-3.680295000	-1.831916000	-0.151365000
H	-5.223483000	-1.376771000	0.635154000

6M: E=-977.078097

O	3.401371000	-2.069367000	-0.110153000
C	3.706472000	0.922189000	0.376505000

C	4.075171000	2.079713000	1.005696000
C	5.330805000	2.472089000	0.429075000
C	2.531028000	0.025430000	0.524988000
C	1.904178000	-0.487040000	-0.790833000
C	2.794874000	-1.573474000	-1.138243000
C	1.371833000	-2.022019000	1.075047000
C	2.777904000	-1.403211000	1.059729000
H	5.928066000	3.346476000	0.678939000
H	3.515899000	2.588362000	1.788068000
H	1.607729000	0.216973000	-1.569694000
H	1.779032000	0.529401000	1.146081000
H	3.432637000	-1.545243000	1.923912000
H	0.836520000	-1.639066000	1.955151000
H	1.419415000	-3.117371000	1.150983000
H	2.933691000	-2.071536000	-2.102049000
O	4.649952000	0.581164000	-0.549561000
C	5.628809000	1.526456000	-0.509021000
H	6.456603000	1.391188000	-1.200504000
C	0.777078000	-1.519004000	-0.263857000
H	0.611061000	-2.341367000	-0.981622000
Au	-1.078253000	-0.472576000	-0.152612000
C	-2.877918000	0.526728000	-0.001038000
C	-4.432048000	2.162751000	0.039320000
C	-5.066418000	0.986763000	0.300681000
H	-4.813086000	3.177900000	-0.029270000
H	-6.112241000	0.769959000	0.500220000
N	-3.094242000	1.860724000	-0.144069000
N	-4.098723000	-0.001769000	0.273864000
C	-2.073061000	2.866977000	-0.410706000
H	-1.904193000	3.483587000	0.484196000
H	-1.137880000	2.365882000	-0.685980000
H	-2.396207000	3.511731000	-1.239497000
C	-4.390171000	-1.416690000	0.473801000
H	-4.926271000	-1.821319000	-0.397149000
H	-3.449071000	-1.963083000	0.605175000
H	-5.010761000	-1.541941000	1.371652000

TS3: E=-977.073870

O	3.285196000	-2.069688000	-0.105068000
C	3.756841000	0.886657000	0.366517000
C	4.236239000	1.996428000	1.008744000
C	5.467711000	2.342130000	0.355712000
C	2.543580000	0.052701000	0.580512000
C	1.825067000	-0.359275000	-0.712260000
C	2.428095000	-1.622559000	-1.055754000
C	1.343947000	-1.978486000	1.146309000
C	2.769623000	-1.406709000	1.071624000
H	6.132342000	3.170366000	0.592724000
H	3.764635000	2.503627000	1.847947000
H	1.501618000	0.370606000	-1.453237000
H	1.872880000	0.585396000	1.267995000
H	3.443682000	-1.558618000	1.919688000
H	0.780181000	-1.530970000	1.975431000
H	1.354387000	-3.070799000	1.263167000
H	2.458386000	-2.108029000	-2.030301000
O	4.608886000	0.532713000	-0.637972000
C	5.640384000	1.419356000	-0.635726000
H	6.407610000	1.266106000	-1.390568000
C	0.864337000	-1.543009000	-0.245201000
H	0.371026000	-2.239416000	-0.937864000

Au	-1.075986000	-0.448535000	-0.165562000
C	-2.848002000	0.532309000	0.007740000
C	-4.403027000	2.157497000	0.093932000
C	-5.035920000	0.970036000	0.303442000
H	-4.786405000	3.173494000	0.063275000
H	-6.082353000	0.743015000	0.487404000
N	-3.062217000	1.869312000	-0.085780000
N	-4.066031000	-0.014276000	0.250824000
C	-2.045780000	2.892160000	-0.308806000
H	-1.083281000	2.407635000	-0.509009000
H	-2.327470000	3.511575000	-1.171458000
H	-1.952936000	3.529516000	0.582089000
C	-4.349928000	-1.440369000	0.376871000
H	-4.667909000	-1.854098000	-0.591243000
H	-3.447629000	-1.962664000	0.716048000
H	-5.149784000	-1.585094000	1.114376000

7M: E=-977.076434

O	3.524071000	-1.759896000	-0.574975000
C	3.161327000	0.874410000	0.699413000
C	3.529133000	1.751124000	1.685296000
C	4.482253000	2.649056000	1.096019000
C	2.230106000	-0.286433000	0.691152000
C	1.495788000	-0.488802000	-0.644884000
C	2.422584000	-1.503697000	-1.393470000
C	1.684284000	-2.650091000	0.533645000
C	2.886516000	-1.701386000	0.707581000
H	4.994390000	3.479856000	1.577212000
H	3.160949000	1.752595000	2.709228000
H	1.201558000	0.337853000	-1.310049000
H	1.556632000	-0.188063000	1.554118000
H	3.602697000	-1.907574000	1.508821000
H	0.950712000	-2.582494000	1.347998000
H	2.004811000	-3.694396000	0.405083000
H	2.623746000	-1.403035000	-2.459047000
O	3.819574000	1.181267000	-0.454651000
C	4.616194000	2.254501000	-0.204529000
H	5.207364000	2.619793000	-1.040612000
C	1.202666000	-2.061293000	-0.786910000
H	0.381313000	-2.477577000	-1.370289000
Au	-0.794264000	-0.131412000	-0.320209000
C	-2.713841000	0.306332000	0.099943000
C	-4.717714000	1.313291000	0.213909000
C	-4.786199000	0.171830000	0.955130000
H	-5.464231000	2.075897000	0.010706000
H	-5.603723000	-0.254402000	1.529756000
N	-3.436231000	1.379897000	-0.301819000
N	-3.546739000	-0.433867000	0.871832000
C	-2.972482000	2.453151000	-1.175942000
H	-1.892272000	2.350552000	-1.329906000
H	-3.486593000	2.396010000	-2.145815000
H	-3.182077000	3.424684000	-0.708272000
C	-3.174570000	-1.676592000	1.544124000
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2M: E=-536.906367

O	-1.238330000	-0.725857000	1.187360000
C	1.143306000	0.405616000	-0.212086000
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C	-0.298320000	0.724248000	-0.401851000
C	-1.112450000	-0.328266000	-1.156192000
C	-1.672617000	-1.216366000	-0.067840000
C	-2.593929000	0.956599000	0.316732000
C	-1.187966000	0.672534000	0.883323000
H	4.427227000	0.588886000	0.141889000
H	2.288467000	2.272448000	-0.331603000
H	-0.826587000	-0.703963000	-2.139318000
H	-0.367499000	1.721269000	-0.862432000
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H	-2.677492000	1.959214000	-0.128705000
H	-3.376935000	0.825844000	1.079321000
H	-1.797259000	-2.297325000	-0.130536000
O	1.499240000	-0.894035000	-0.000870000
C	2.848506000	-0.936523000	0.161892000
H	3.281469000	-1.918399000	0.337147000
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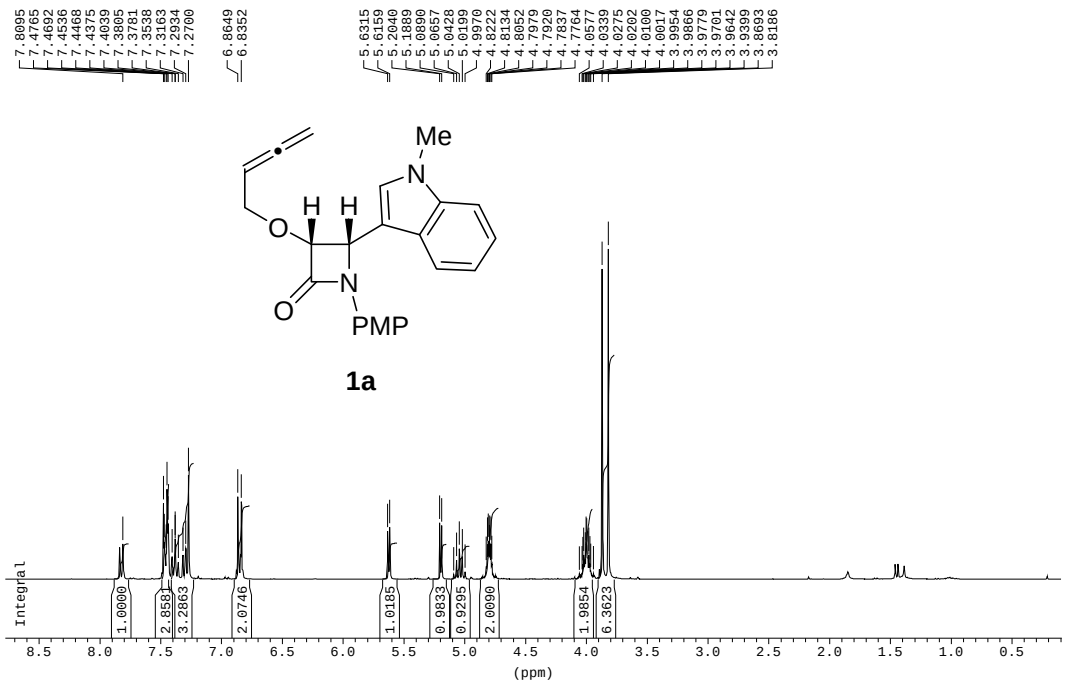

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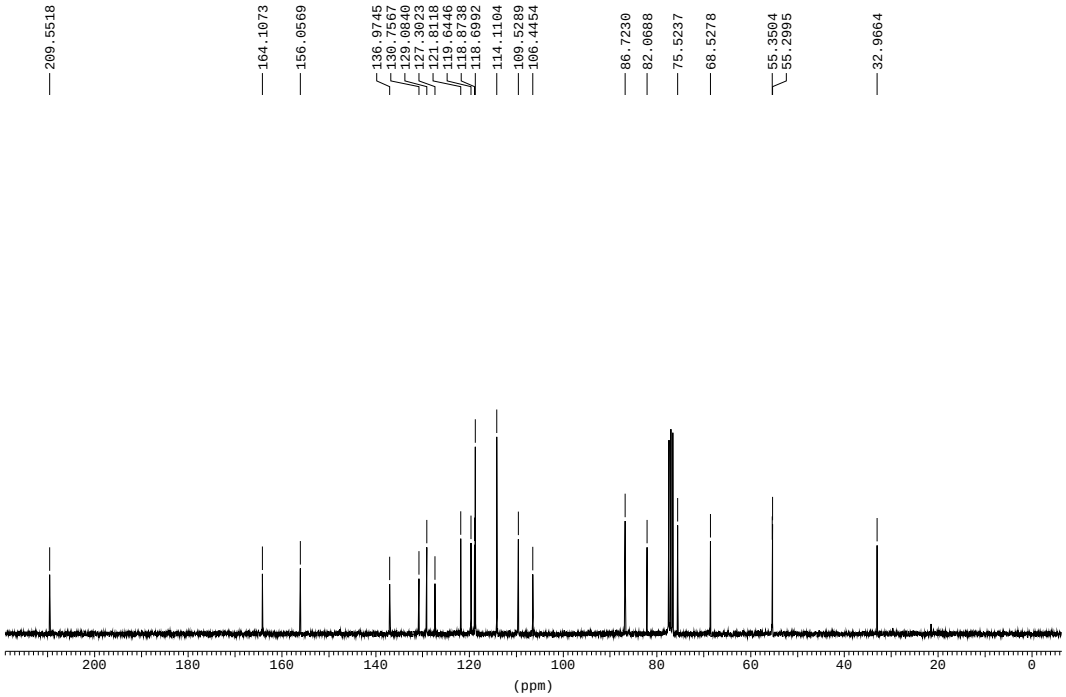

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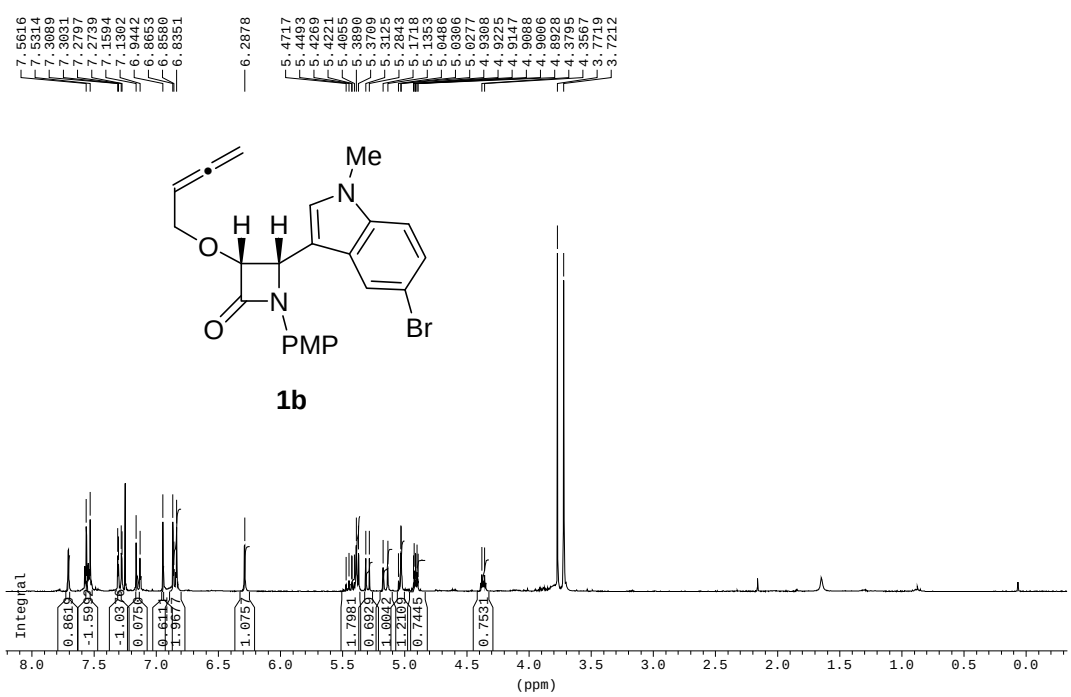

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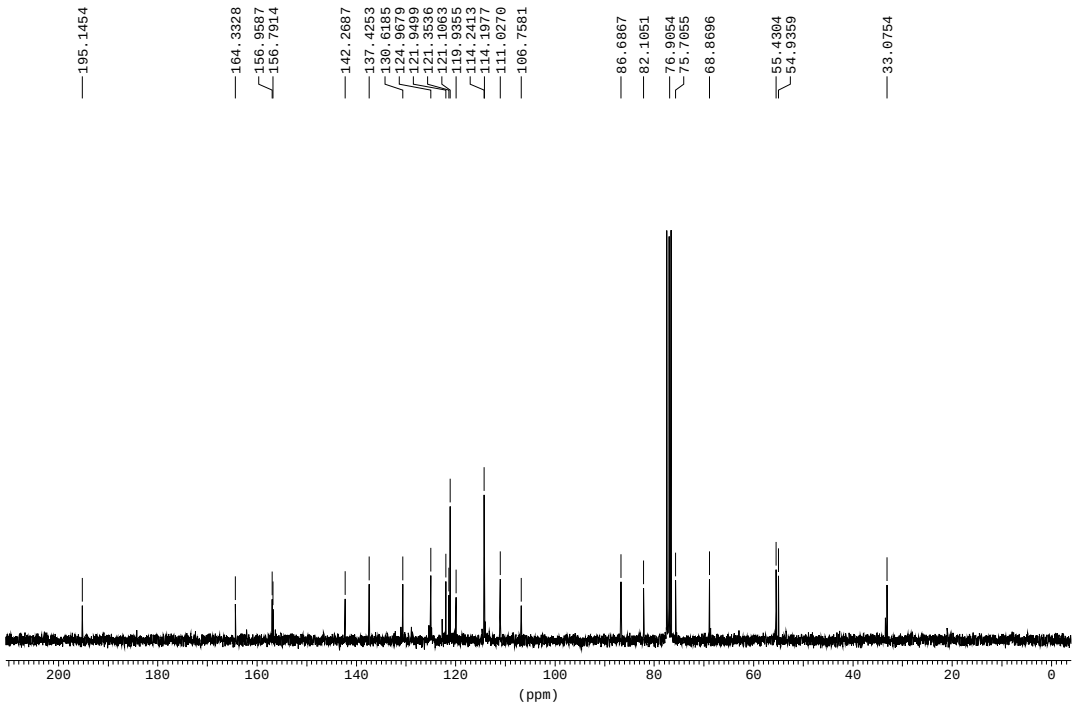

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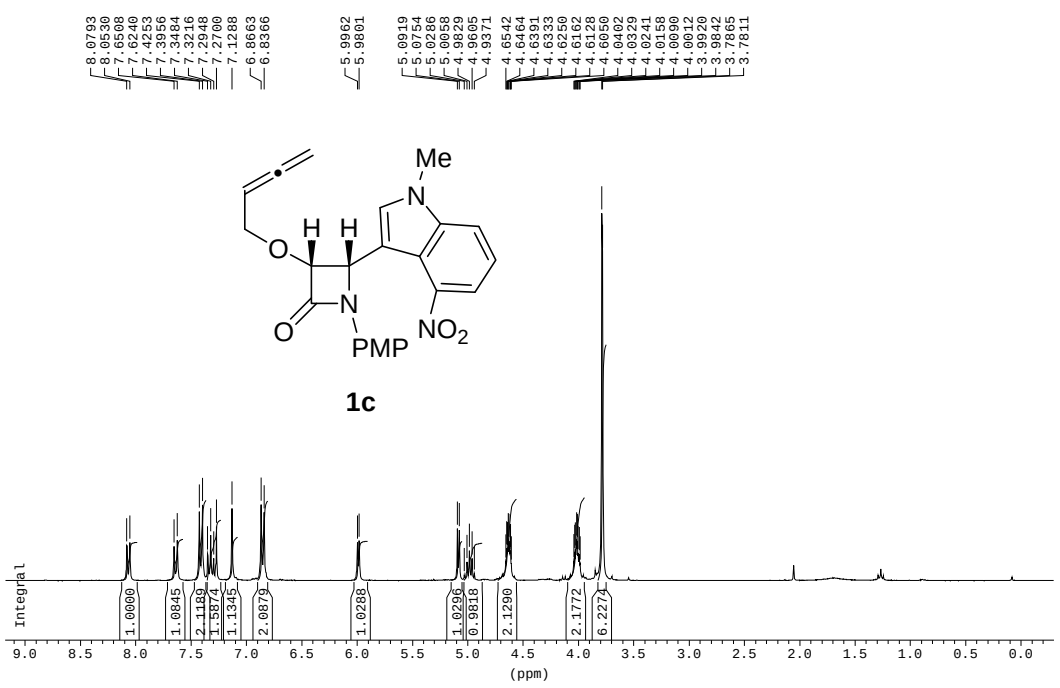

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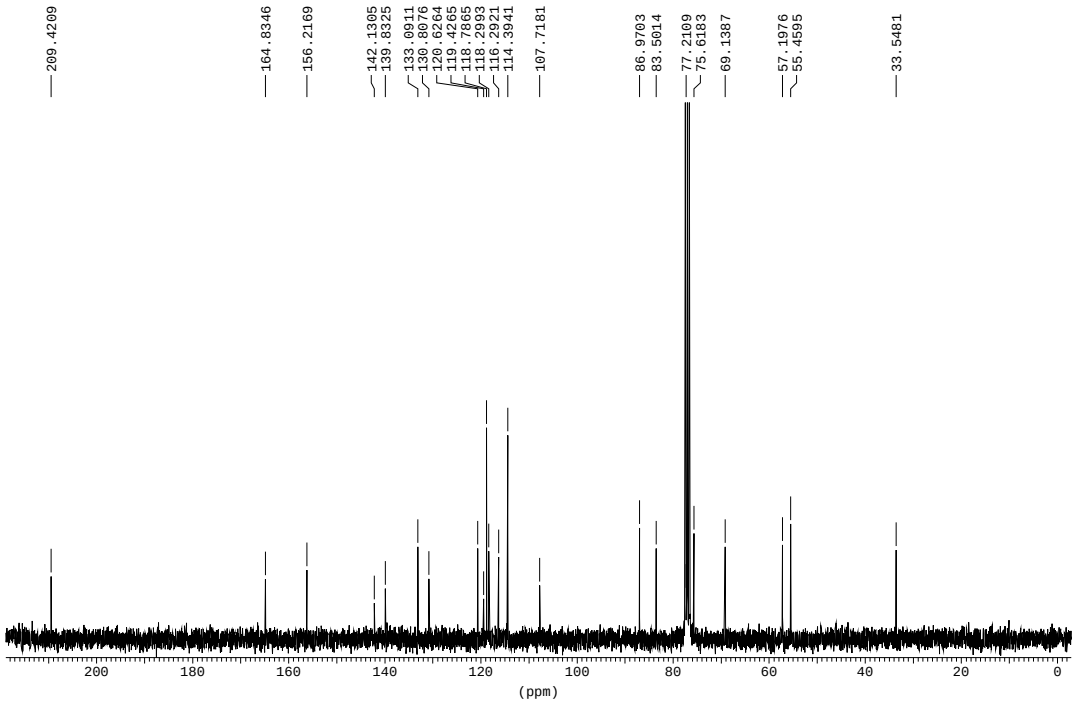

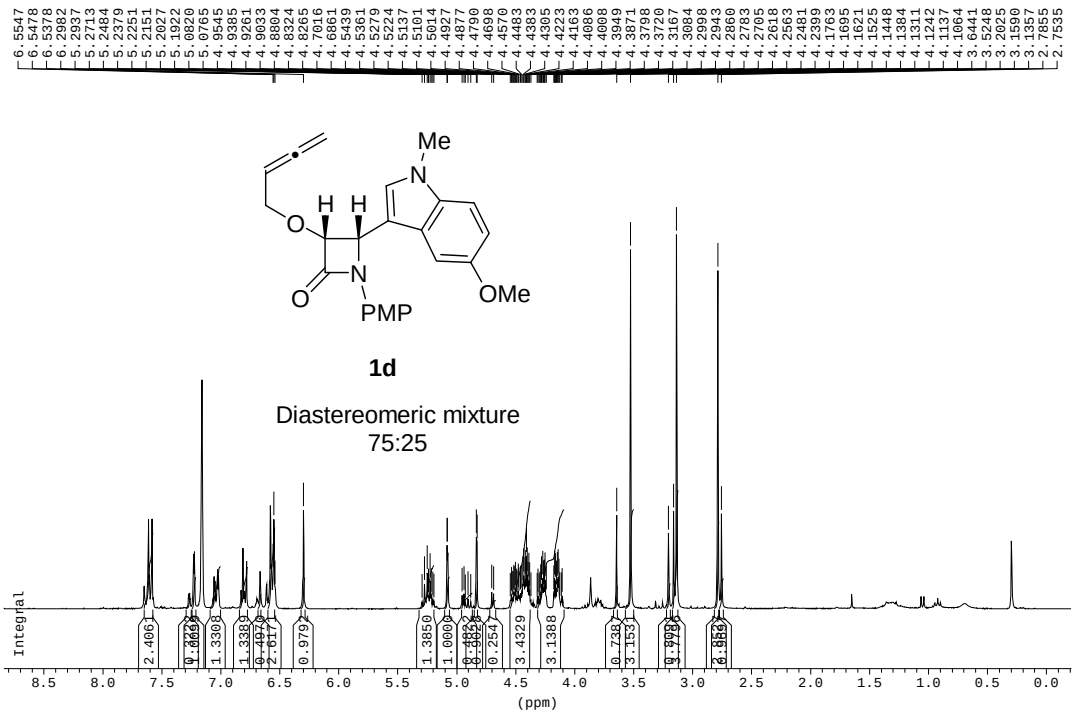
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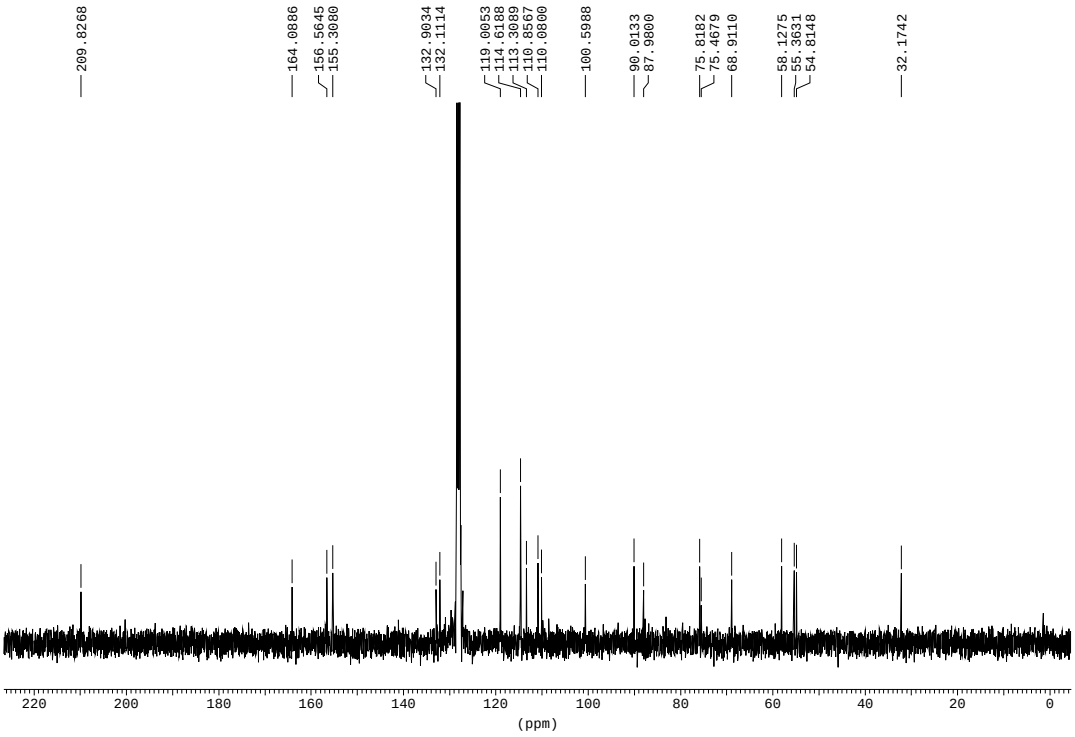
N
H H
O
N
O
PMP
OMe
1d
Diastereomeric mixture
75:25
Integral
(ppm)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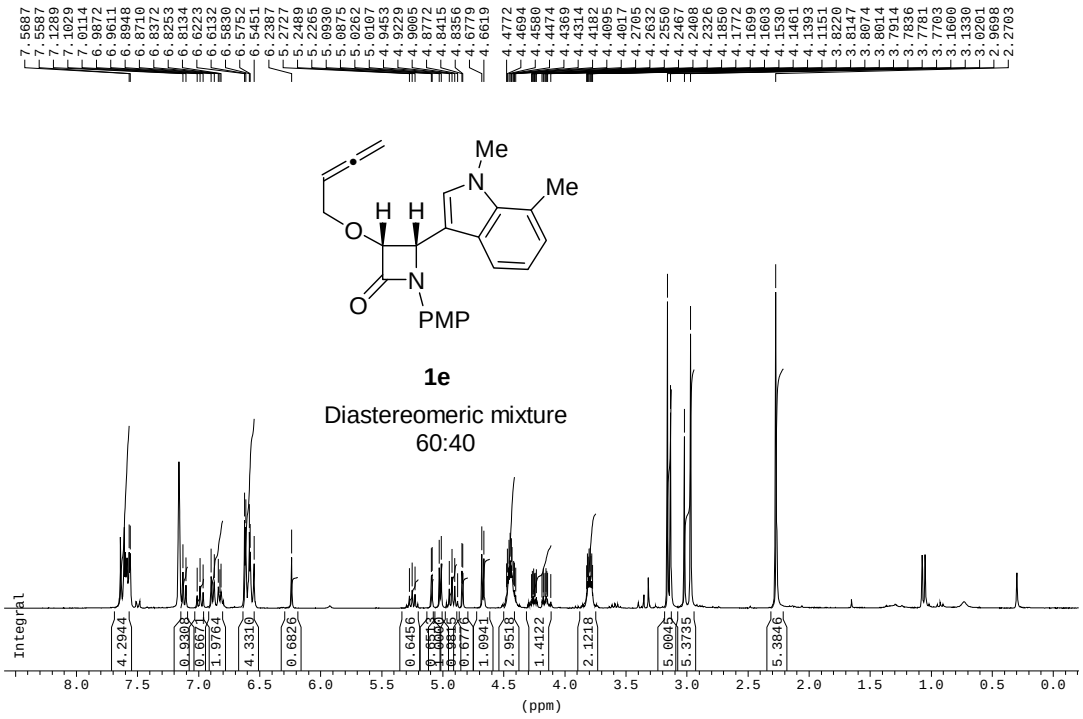
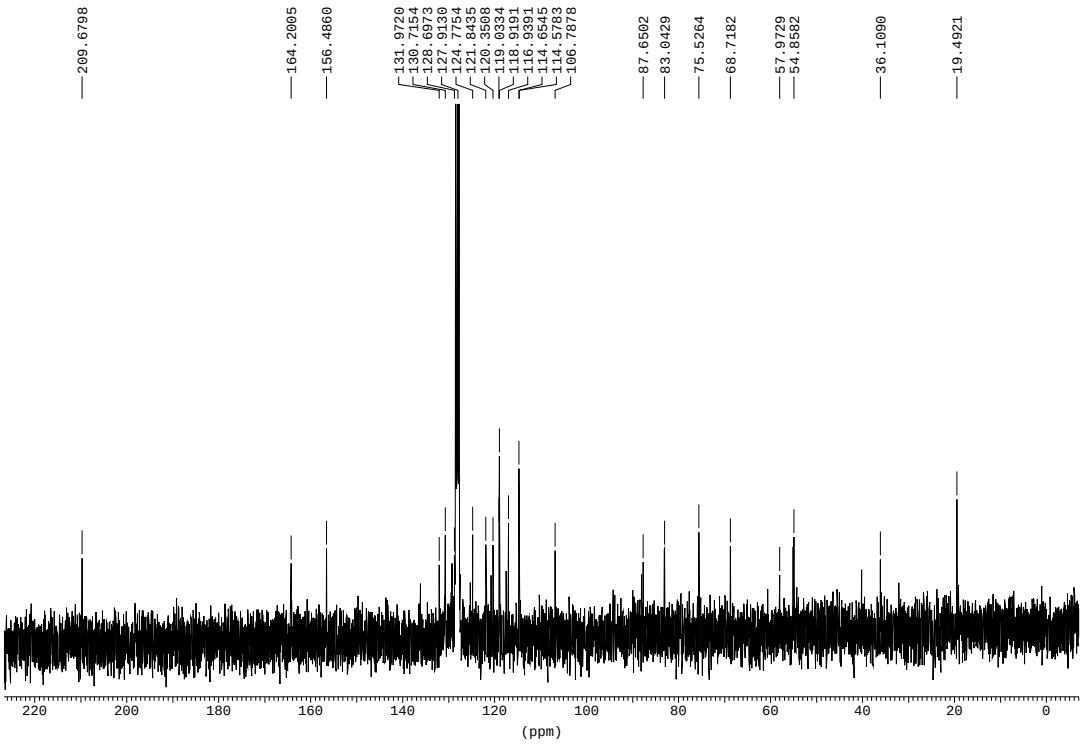
(ppm)


Me
N
Me
H H
O
N
O
PMP
1e
Diastereomeric mixture
60:40
Integral
(ppm)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127.9130
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118.9191
116.9391
114.6545
114.5783
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(ppm)

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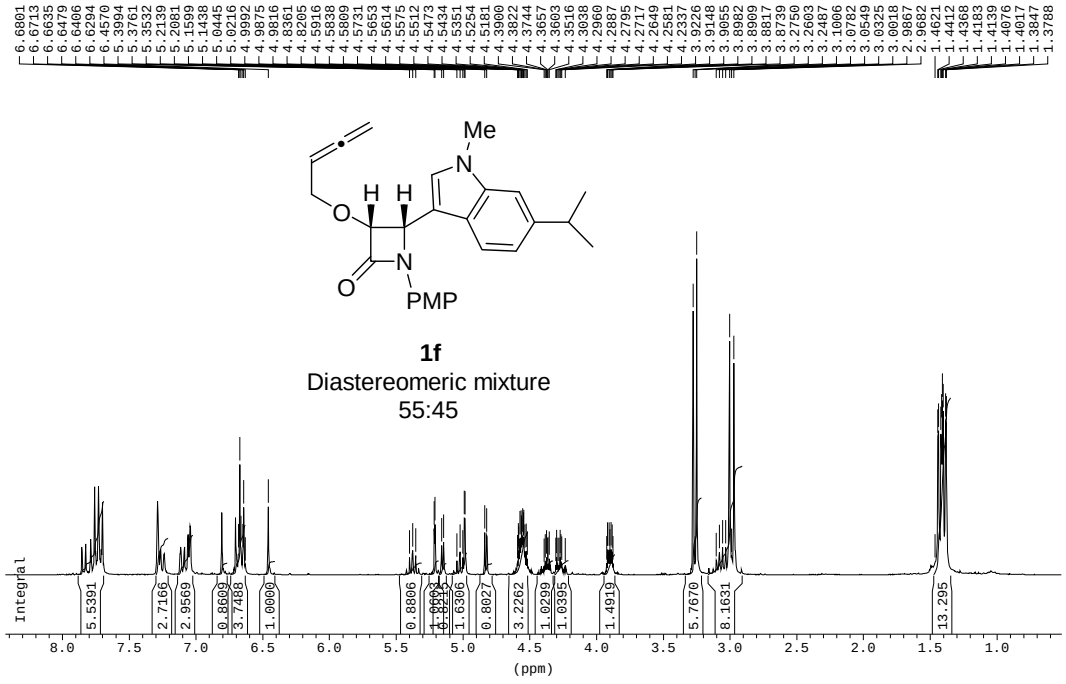

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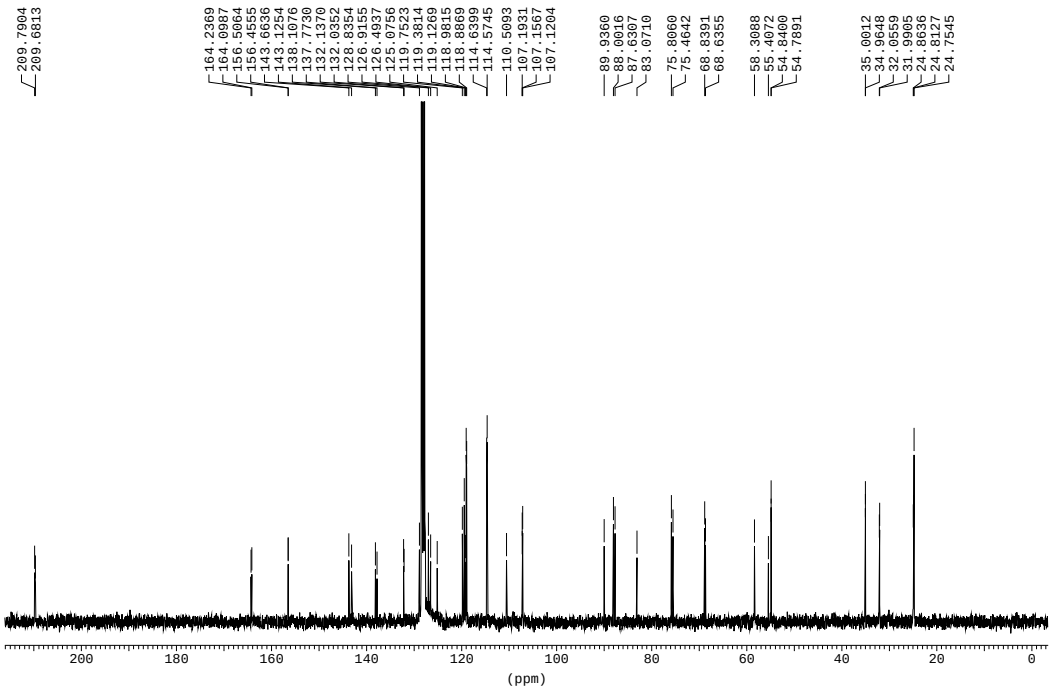

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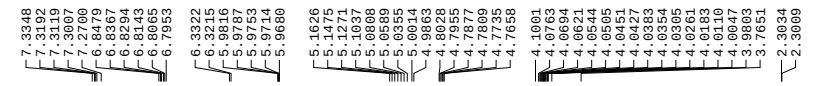

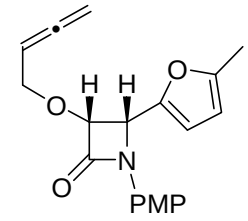

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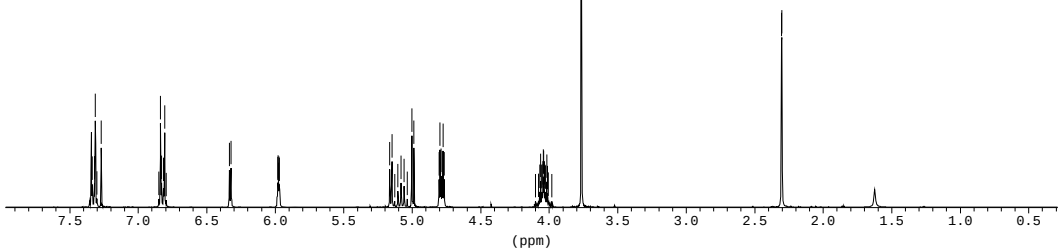

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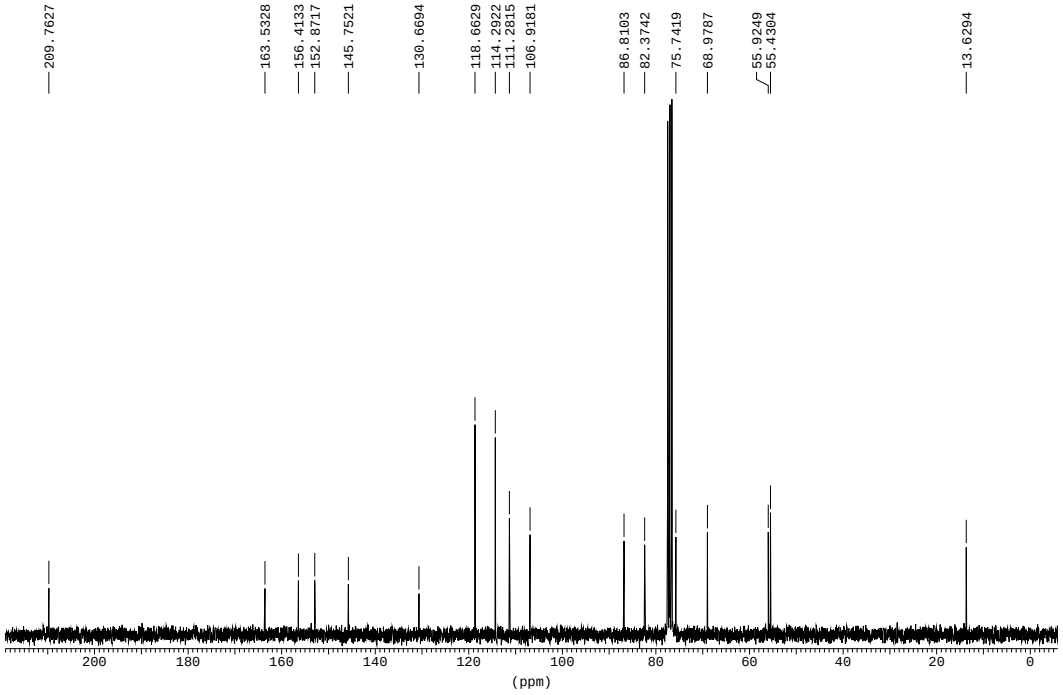

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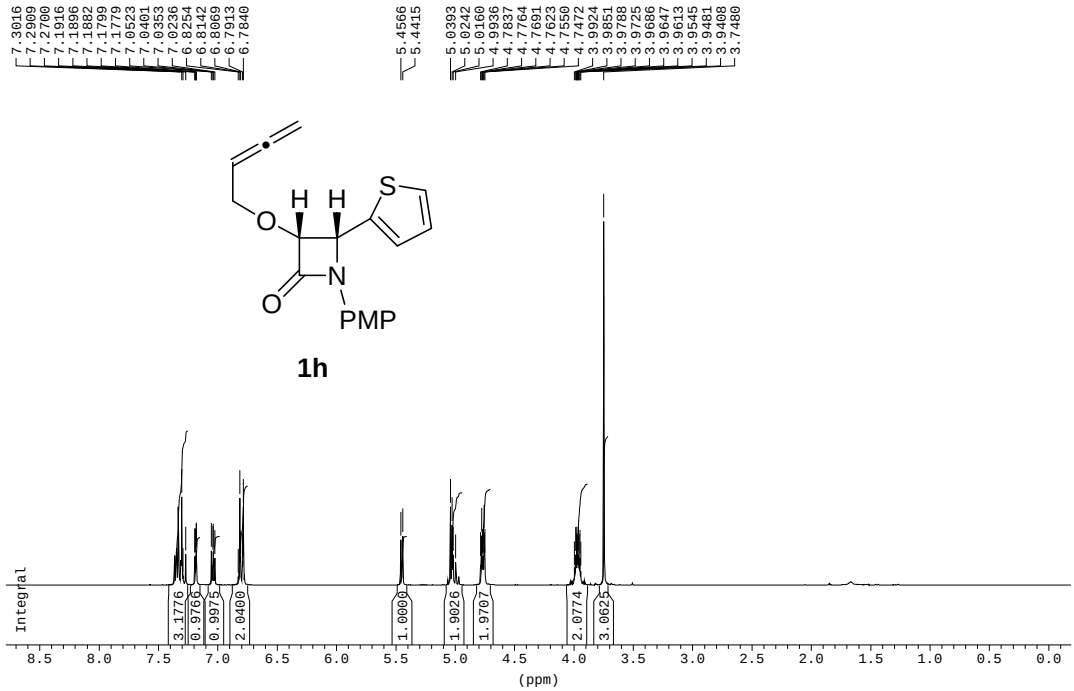

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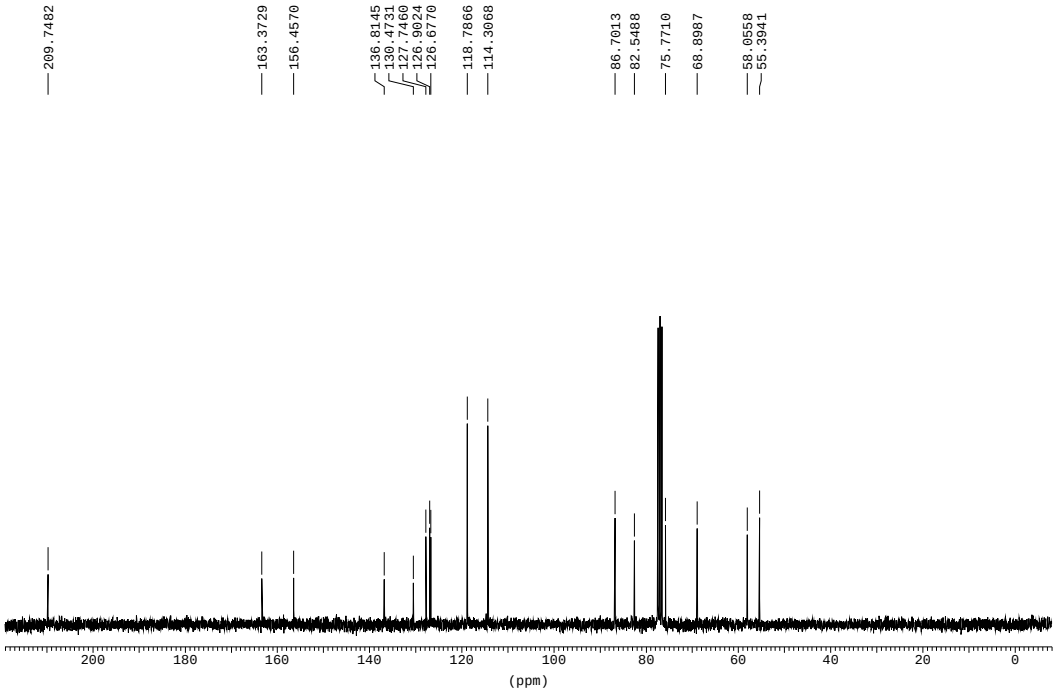

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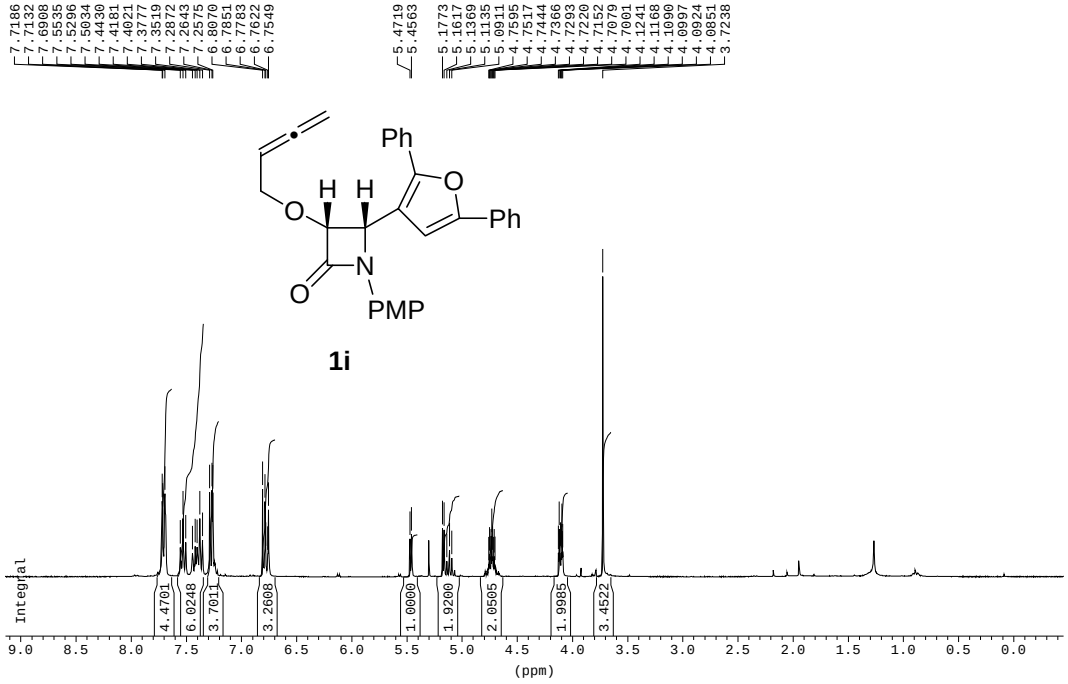

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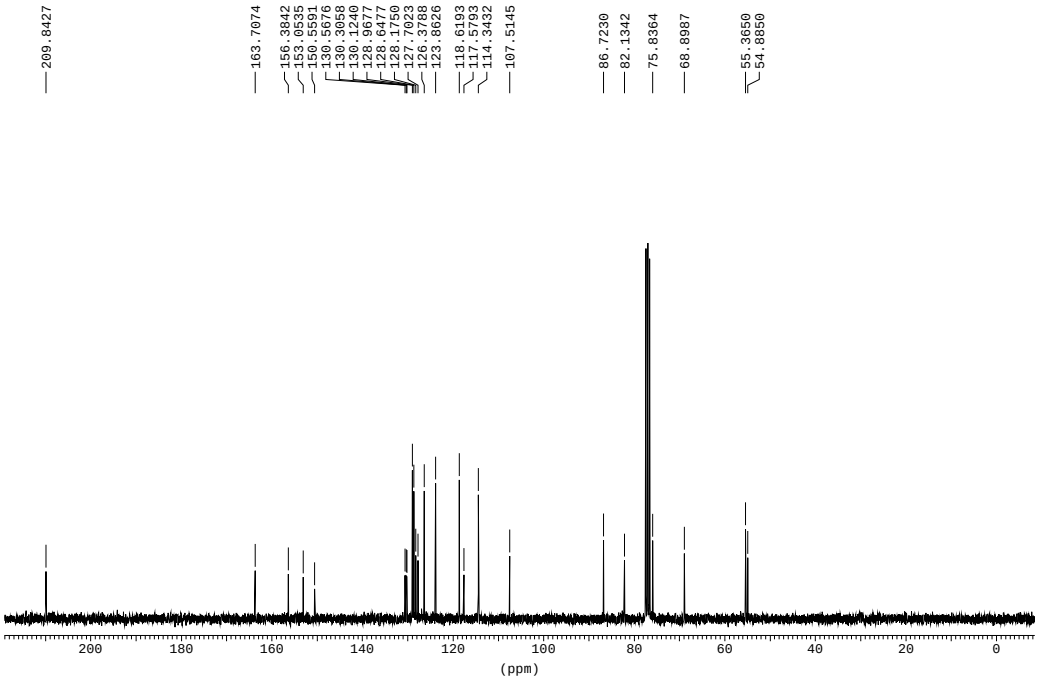

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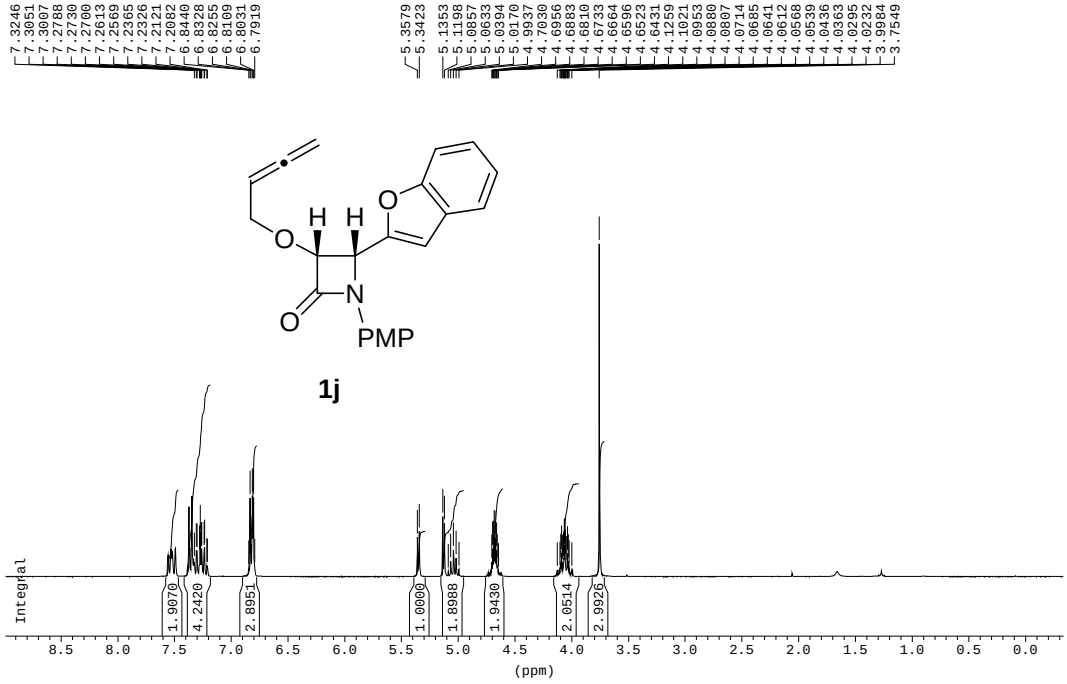

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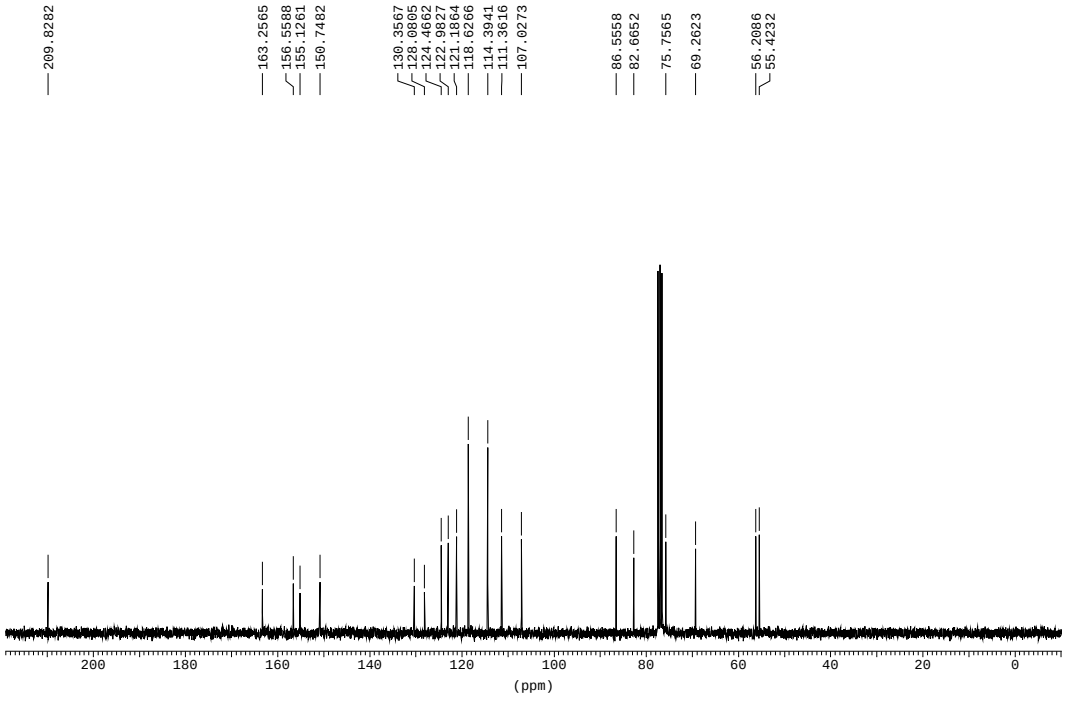

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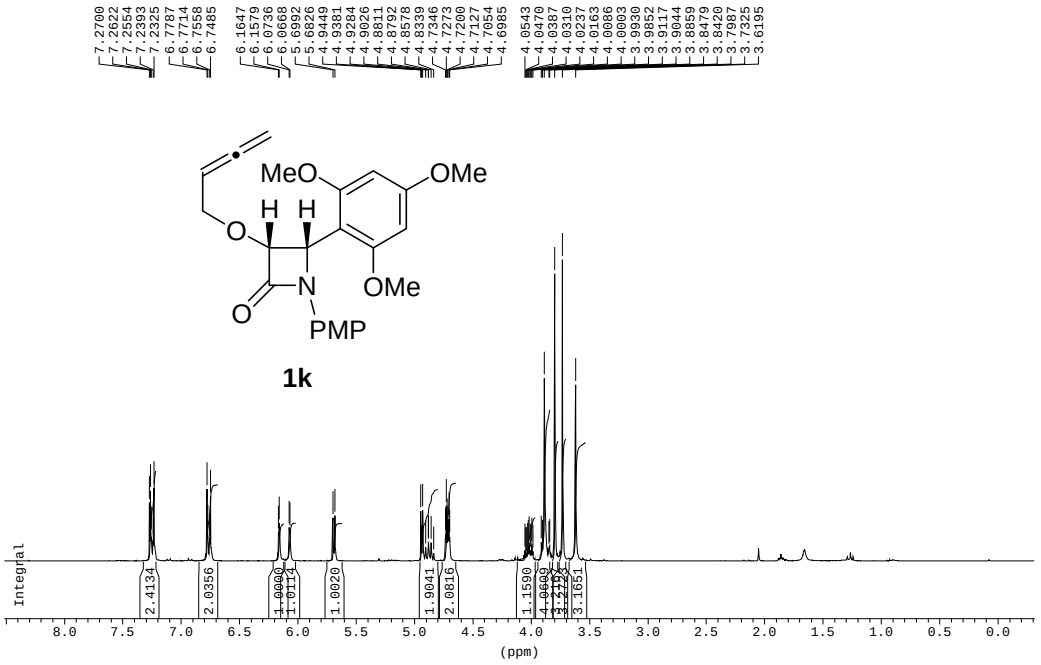

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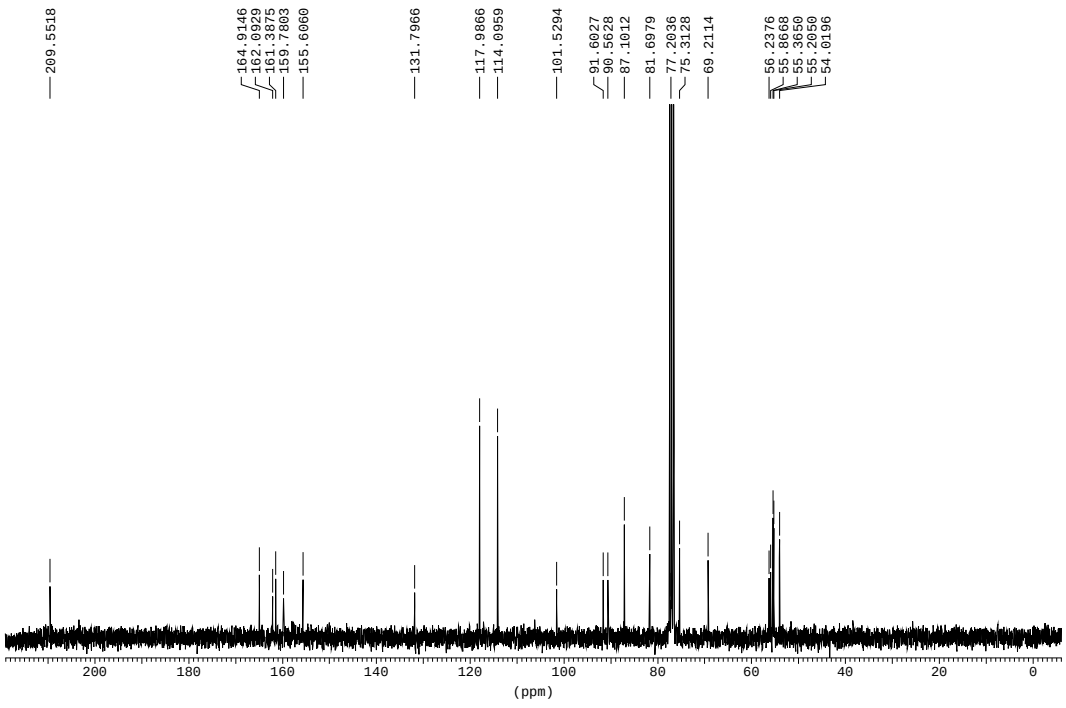

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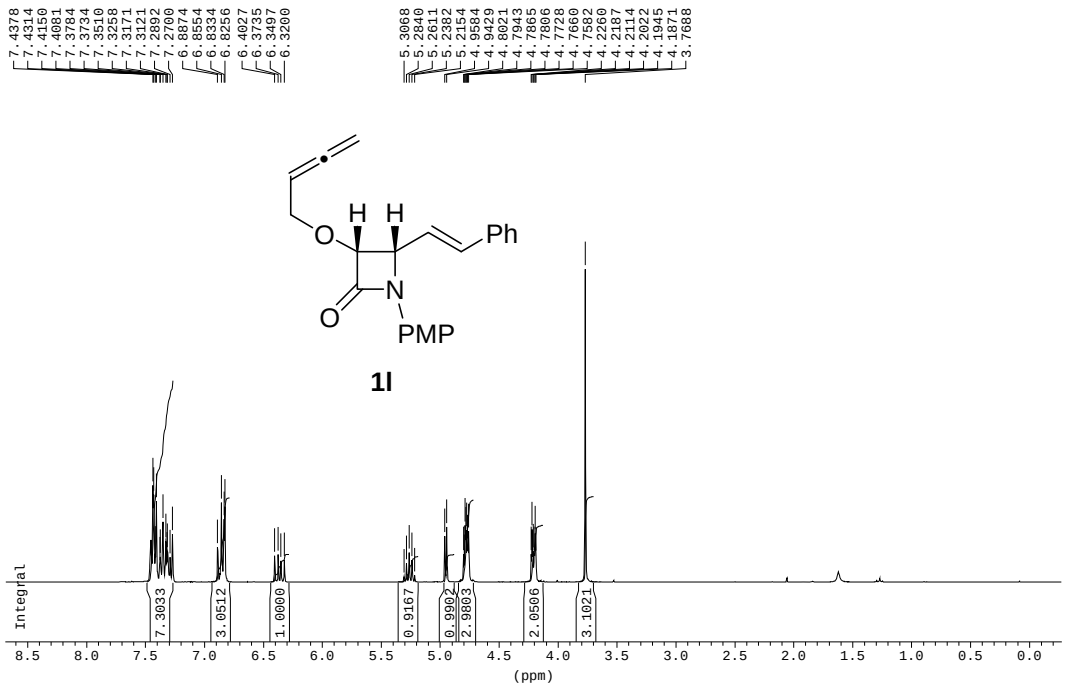

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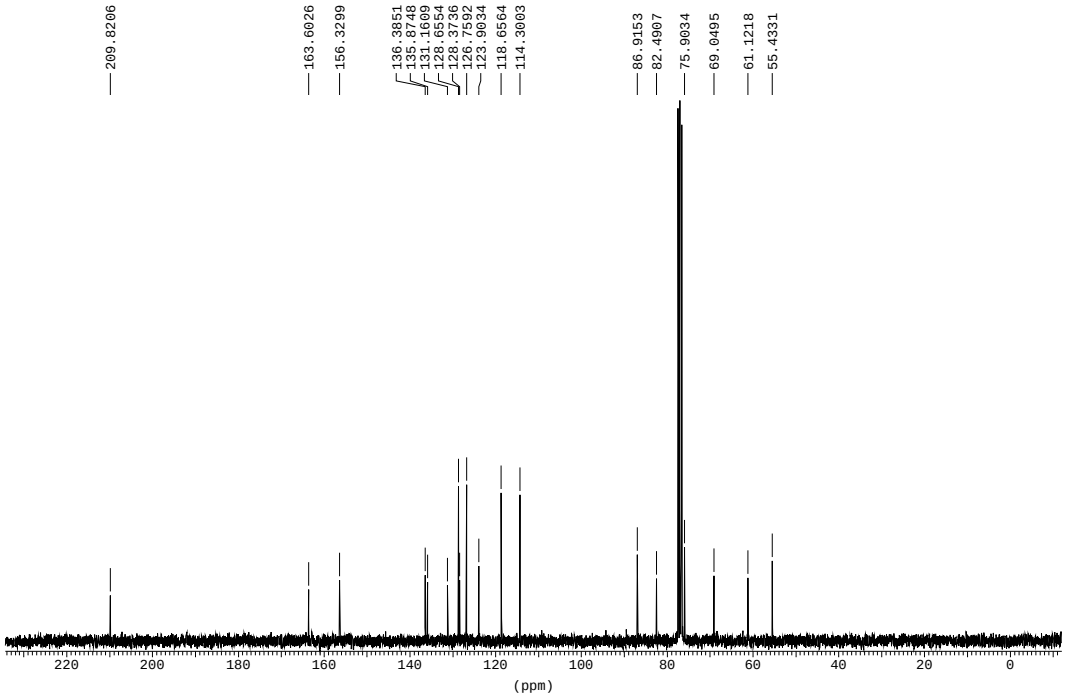

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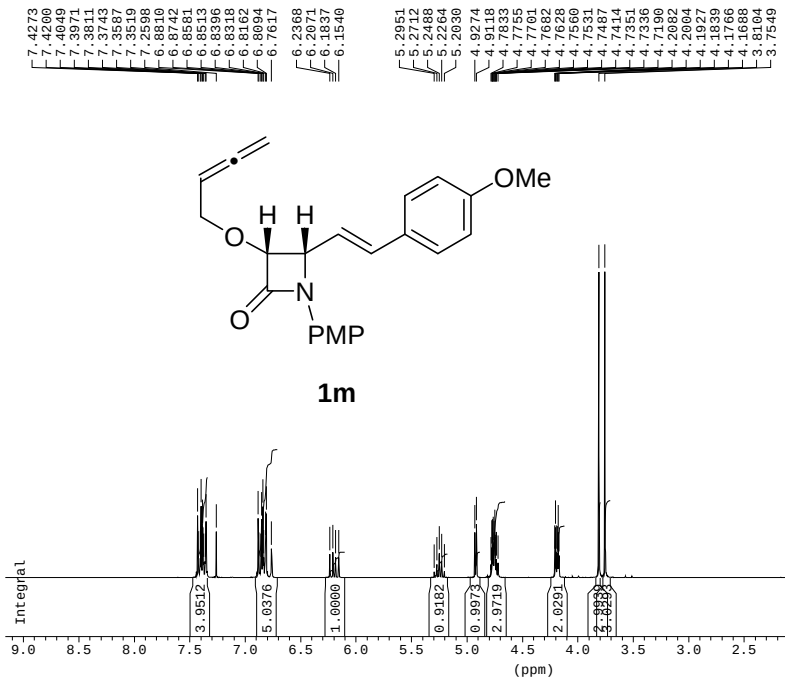

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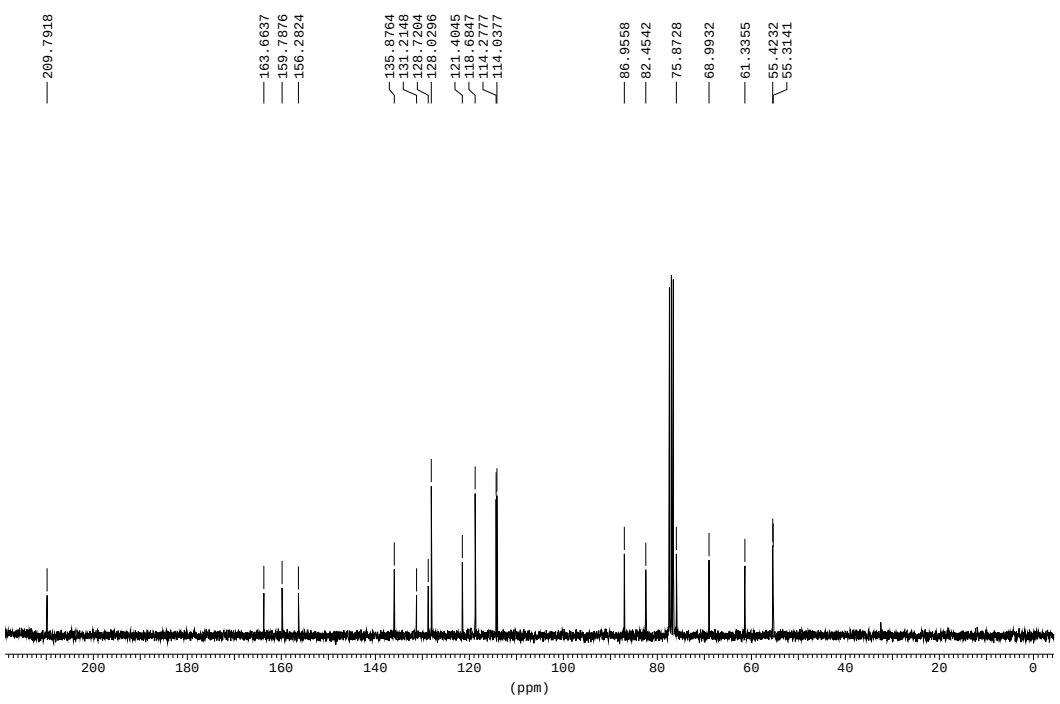

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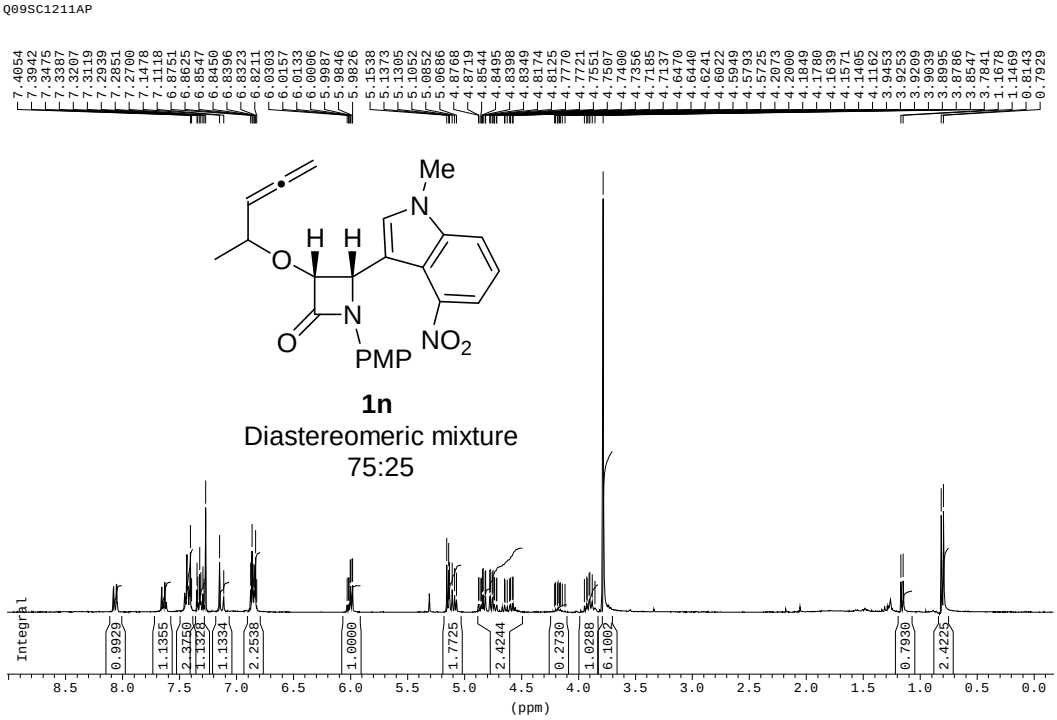

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Diastereomeric mixture
75:25

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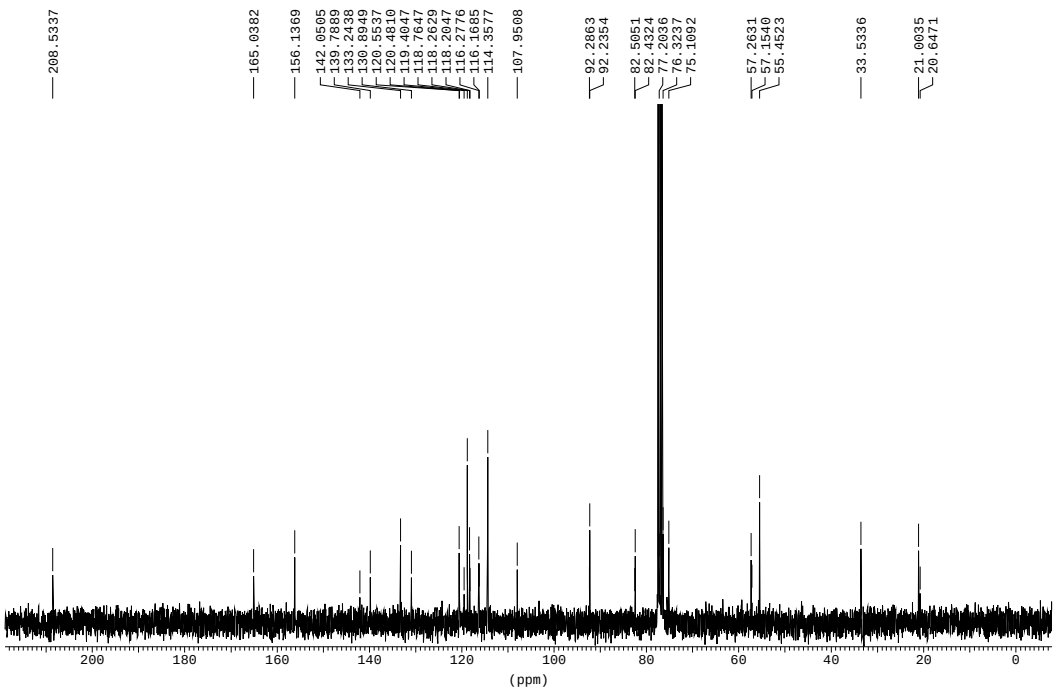

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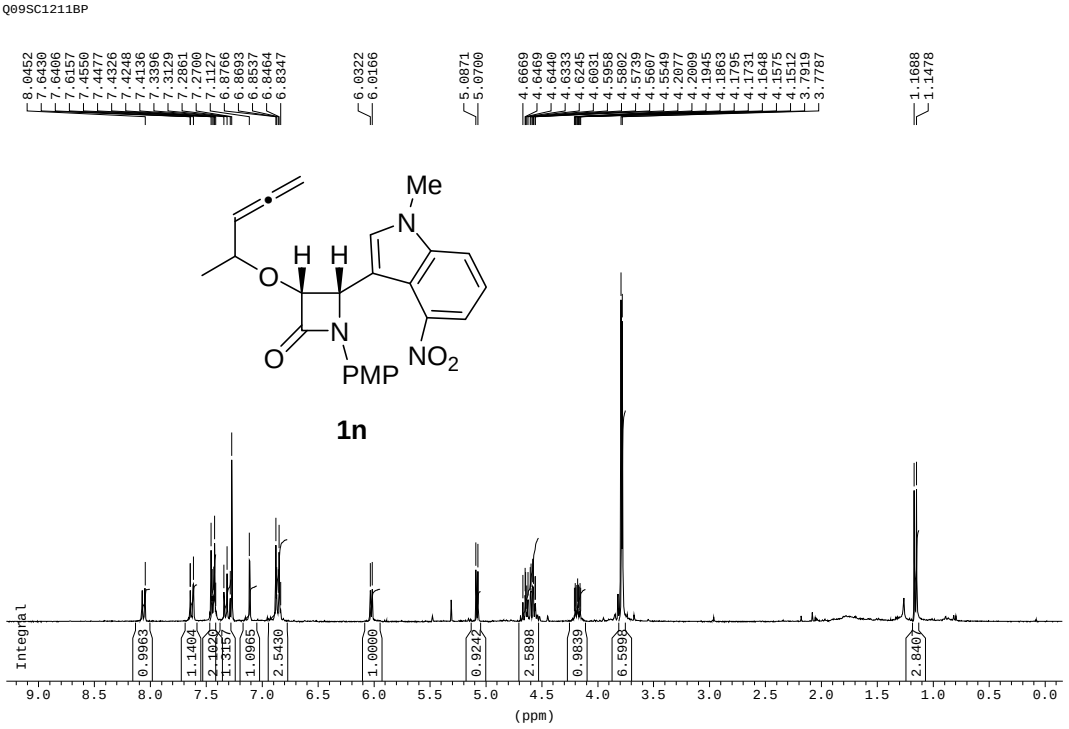

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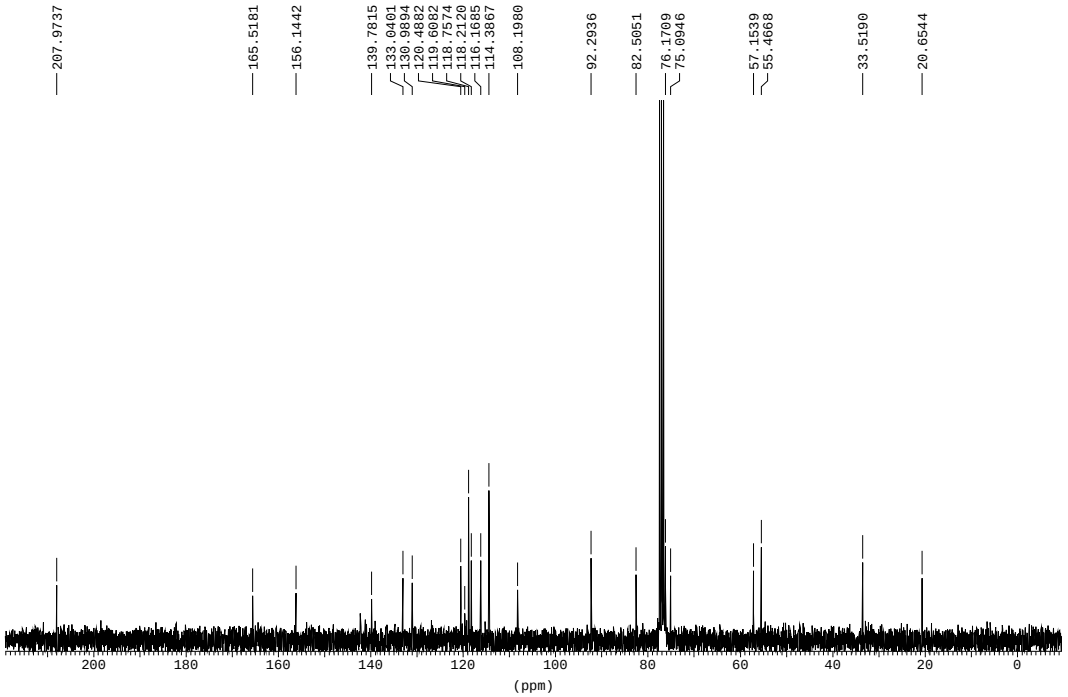

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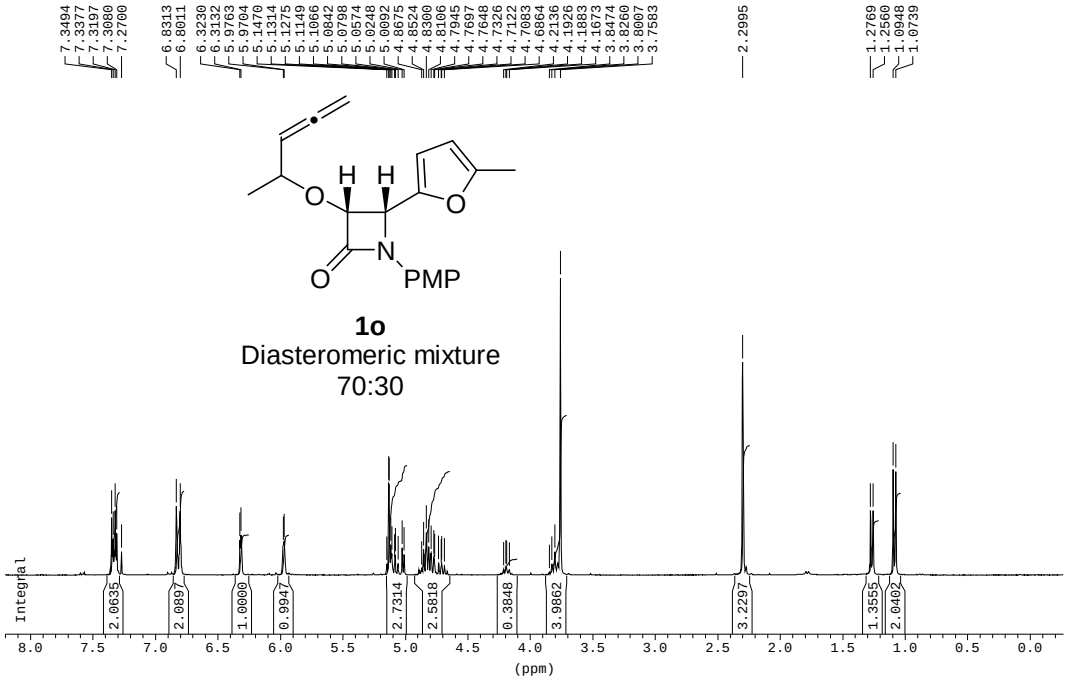

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Diasteromeric mixture
70:30

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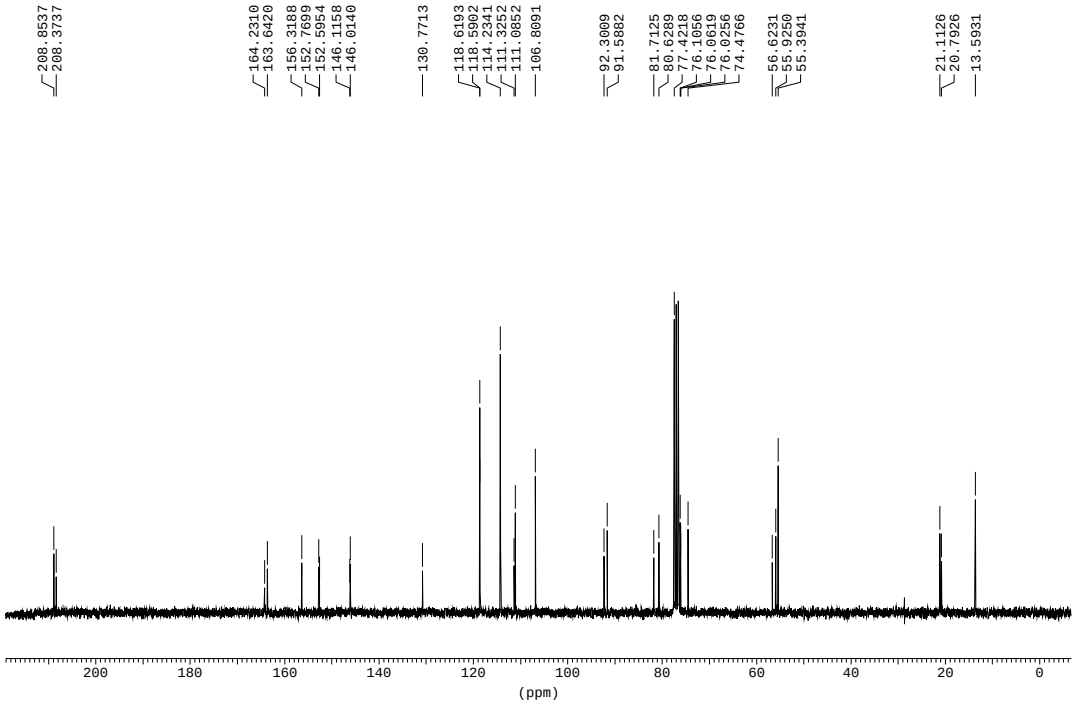

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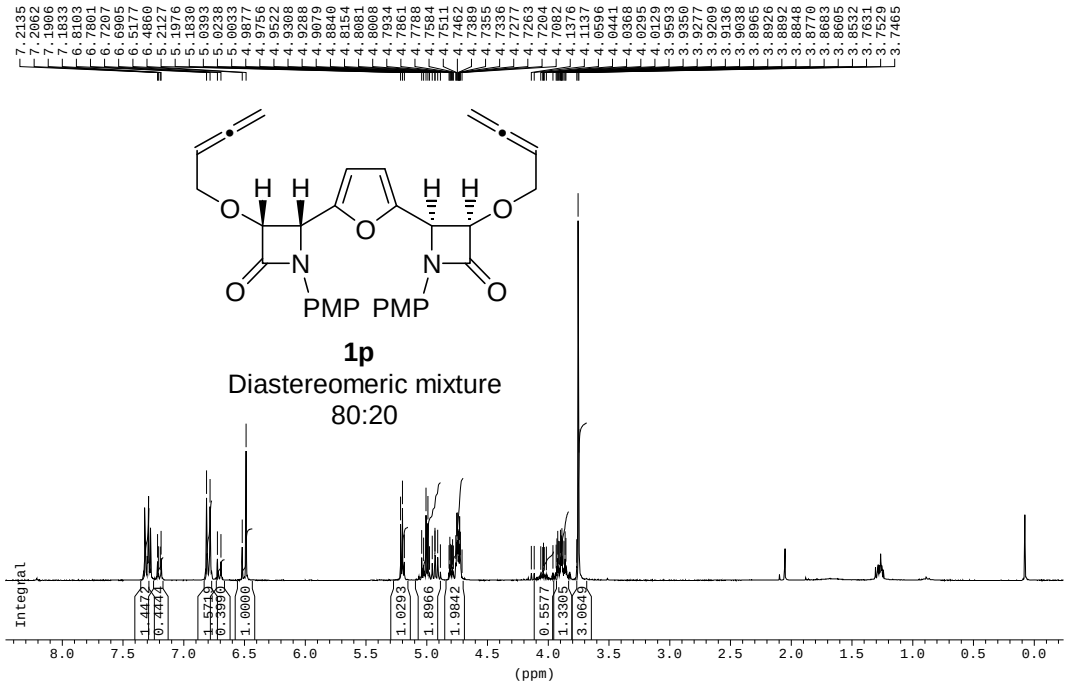

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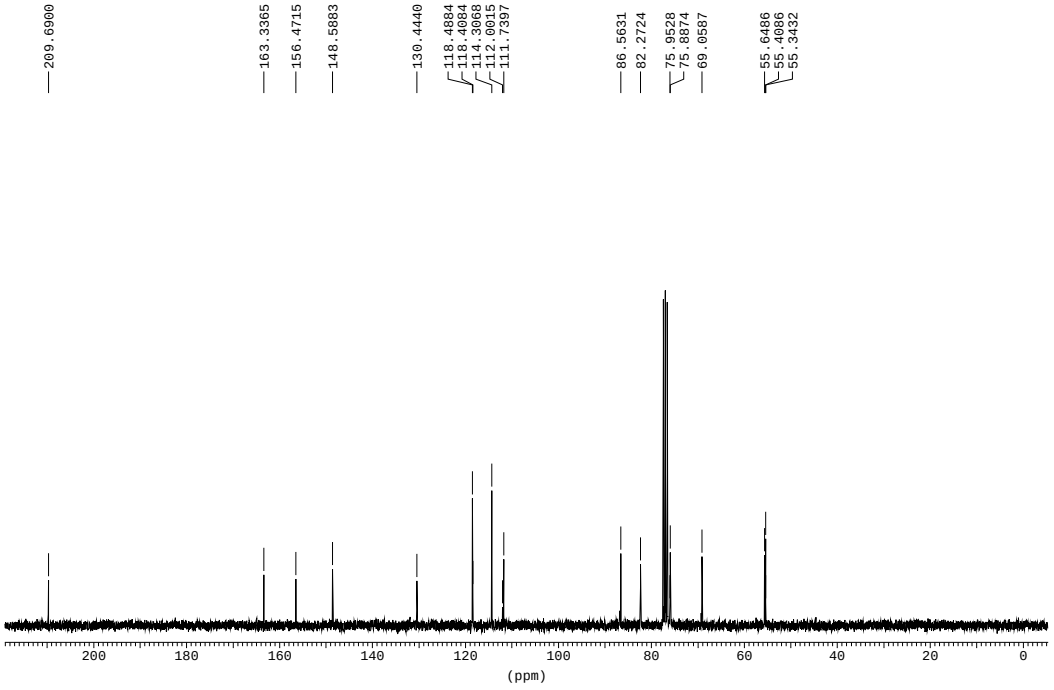

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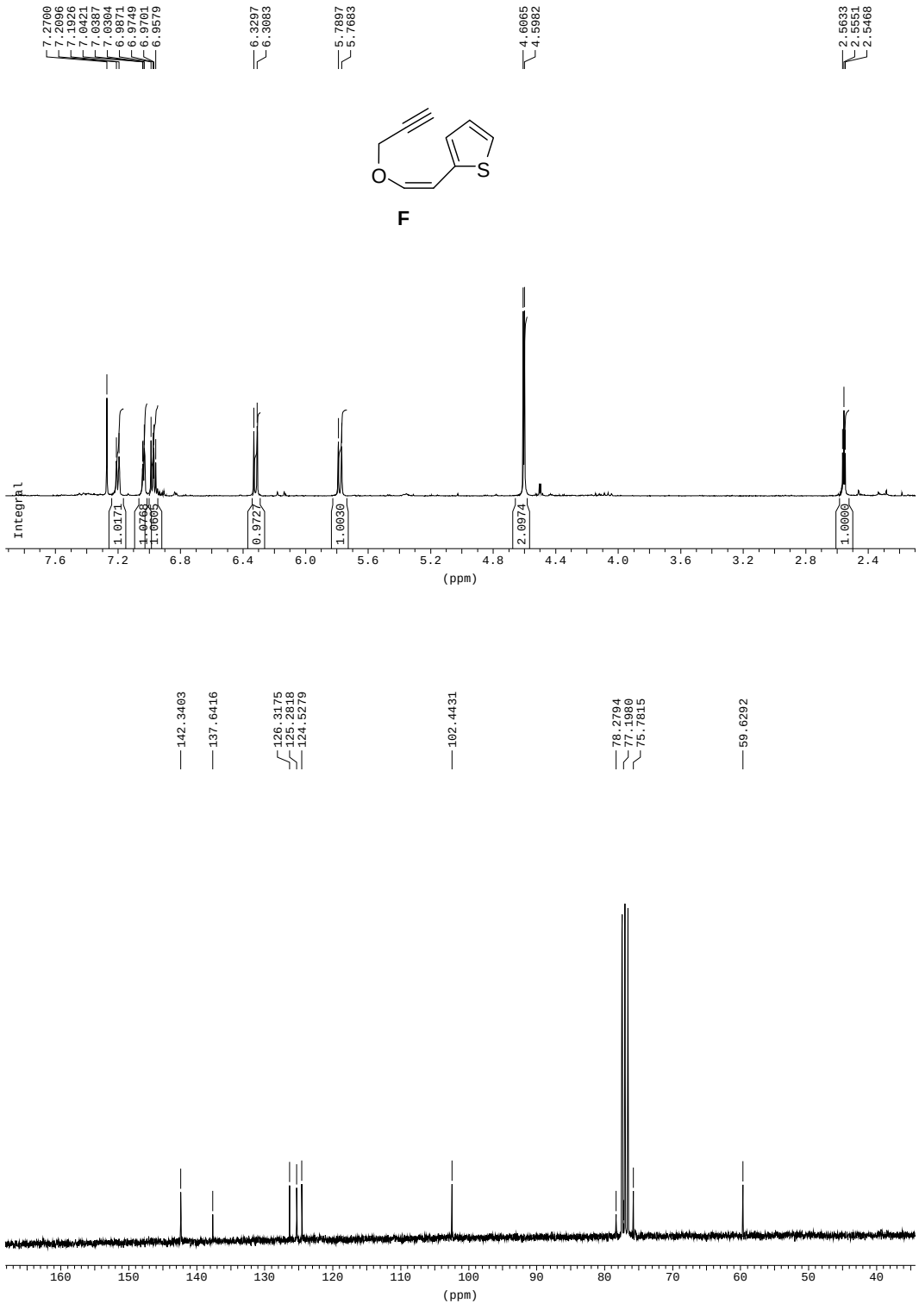

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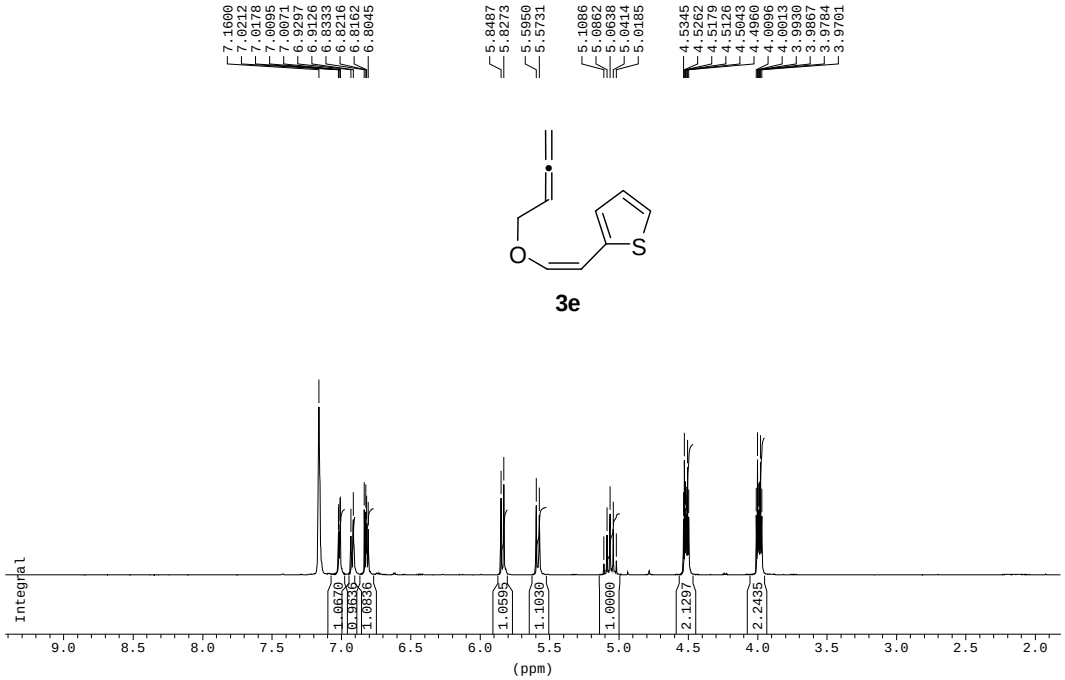

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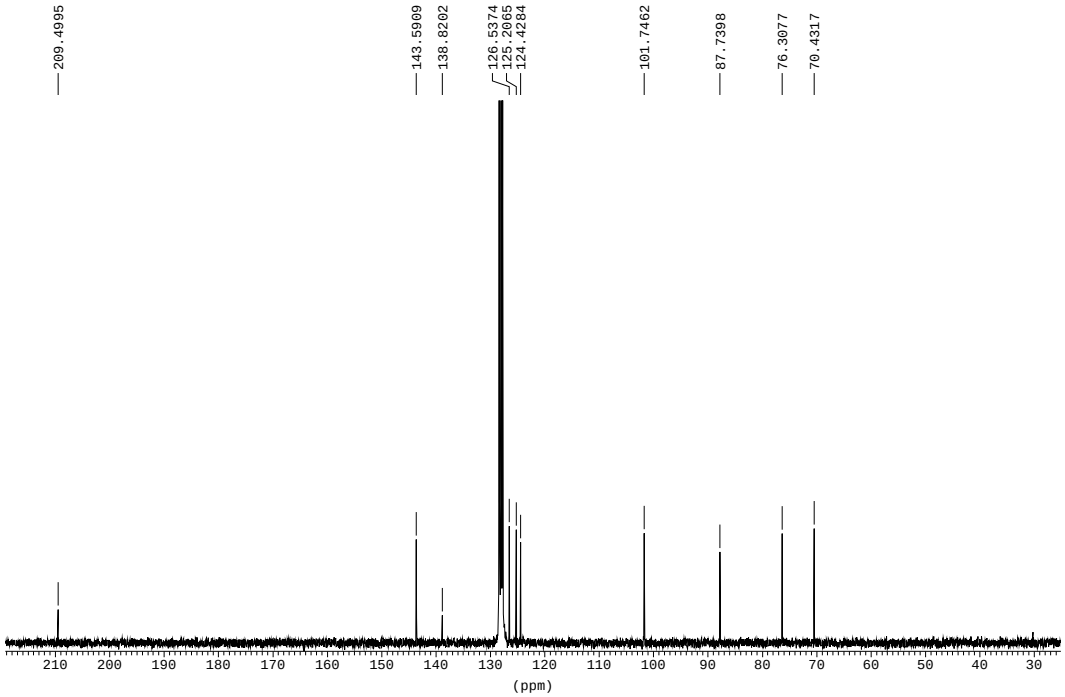

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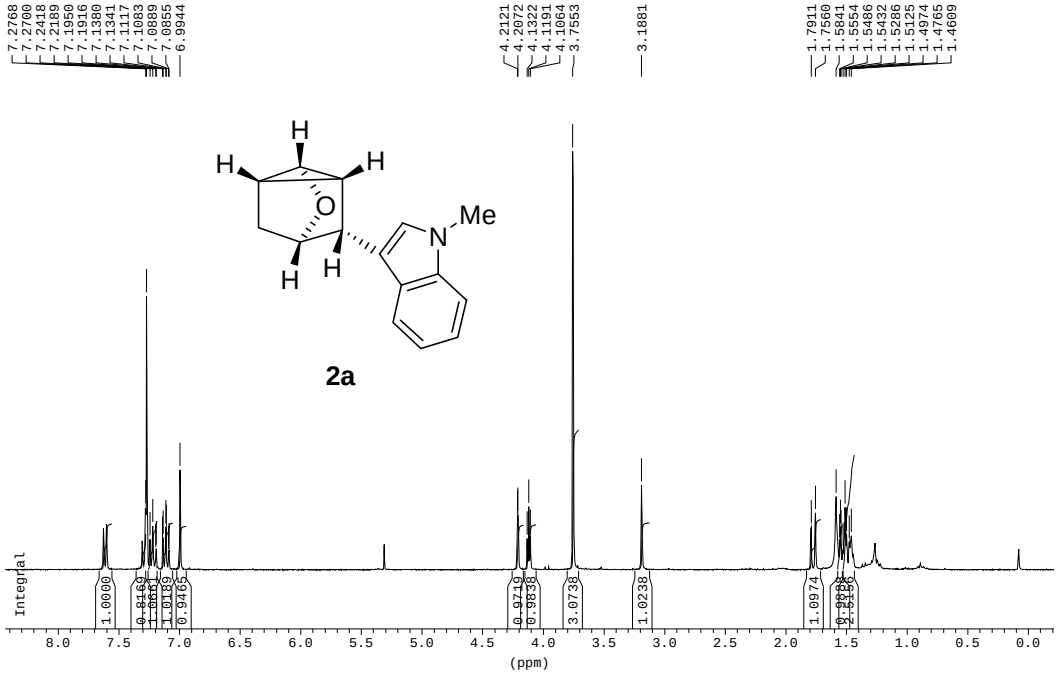

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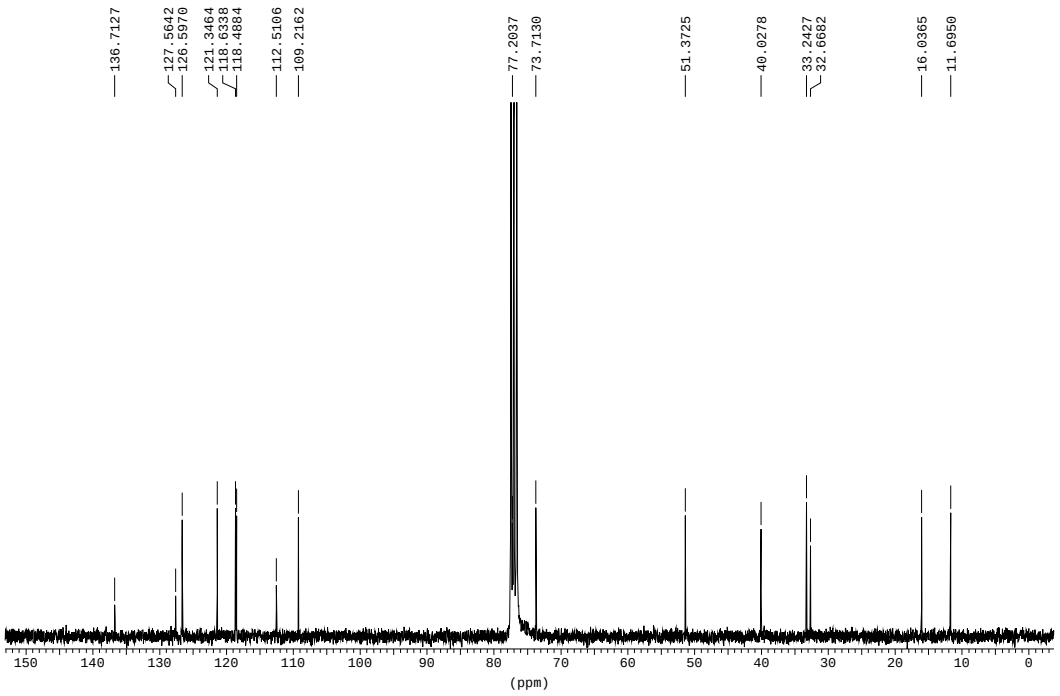

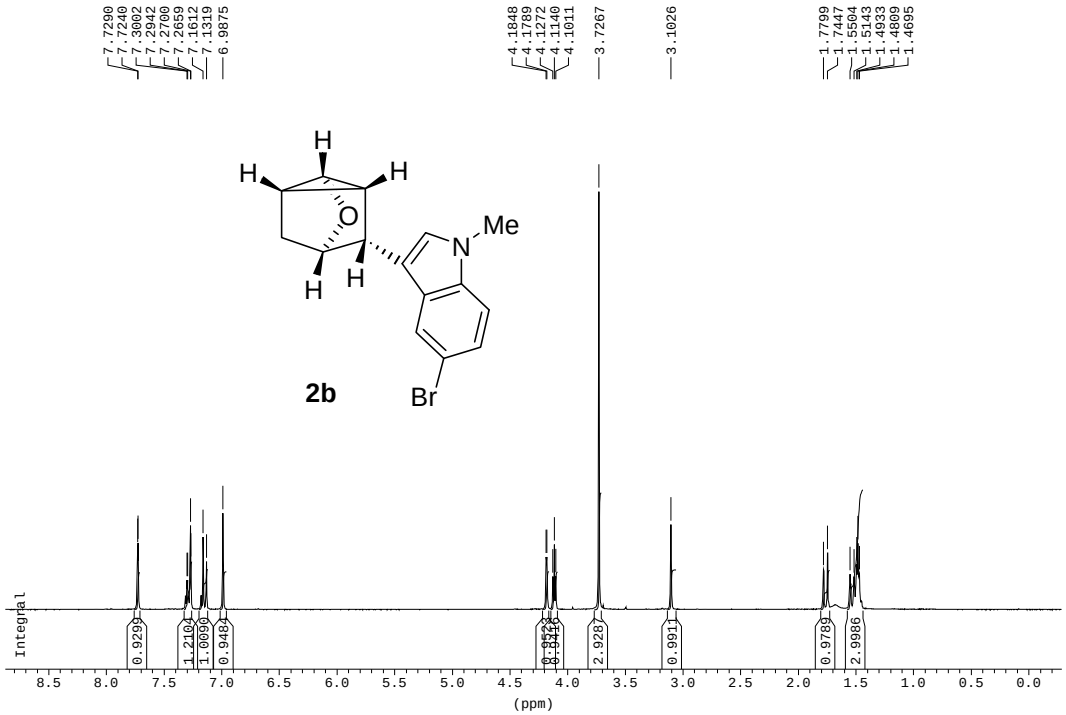
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3.1026
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1.5143
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1.4809
1.4695
H
H
H
O
Me
N
H
H
Br
2b
Integral
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1.009
0.948
2.928
0.991
0.978
2.998
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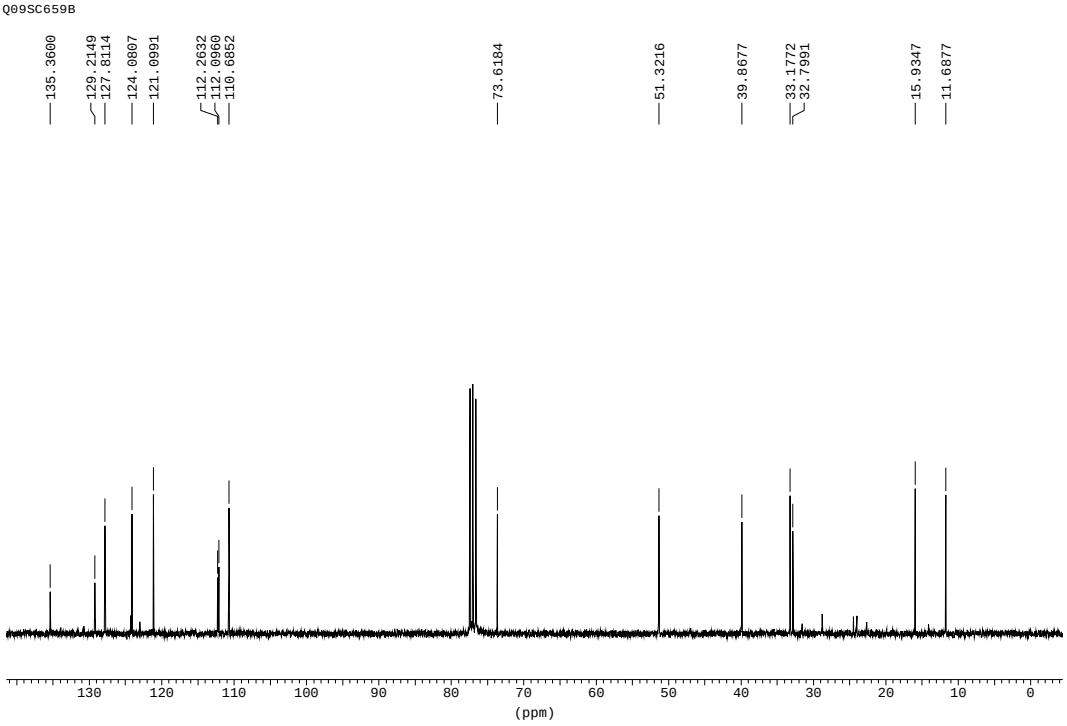
(ppm)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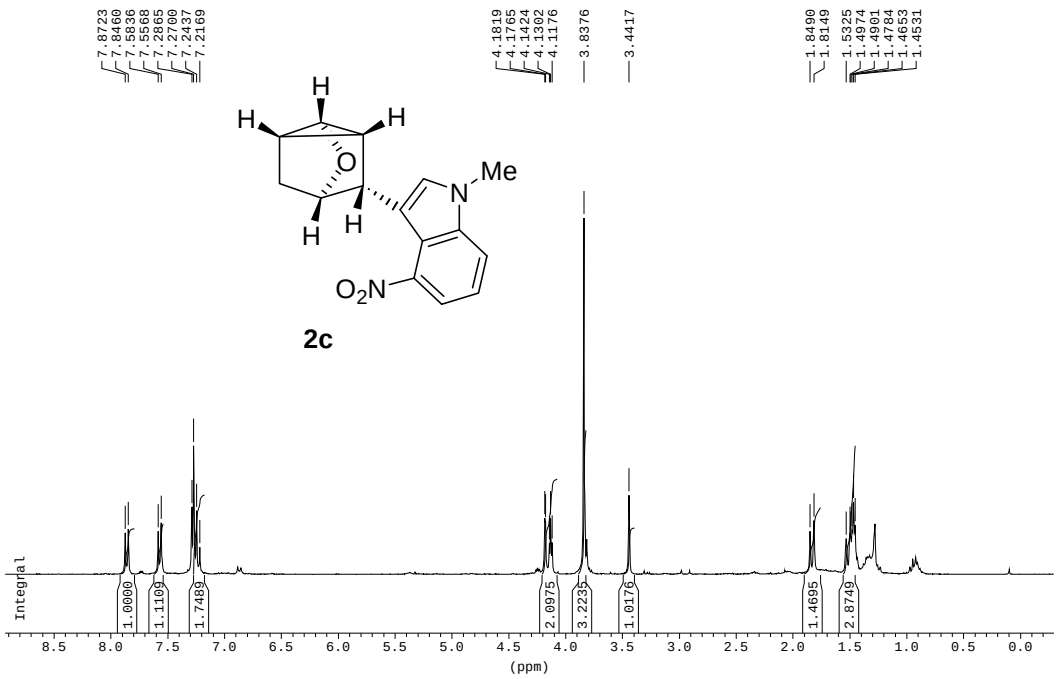

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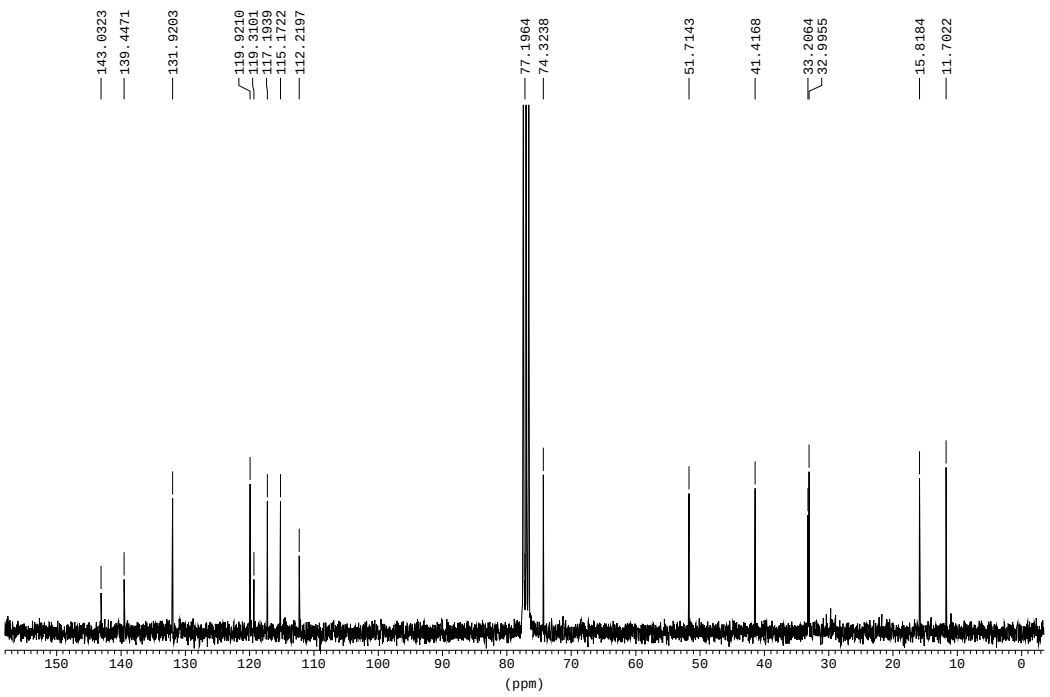

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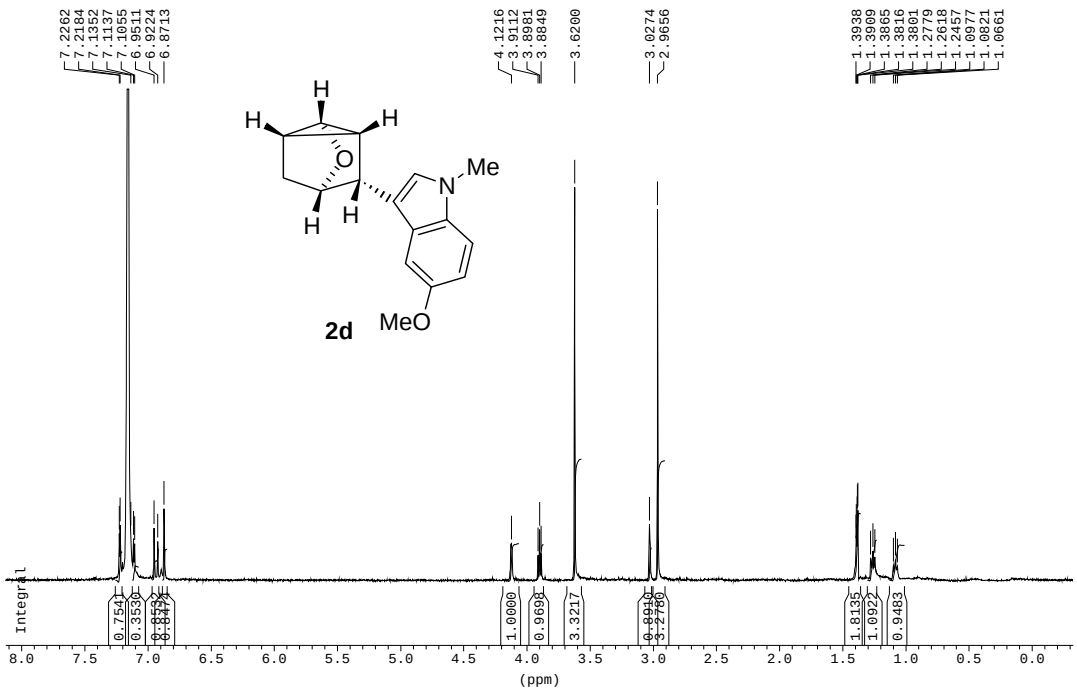

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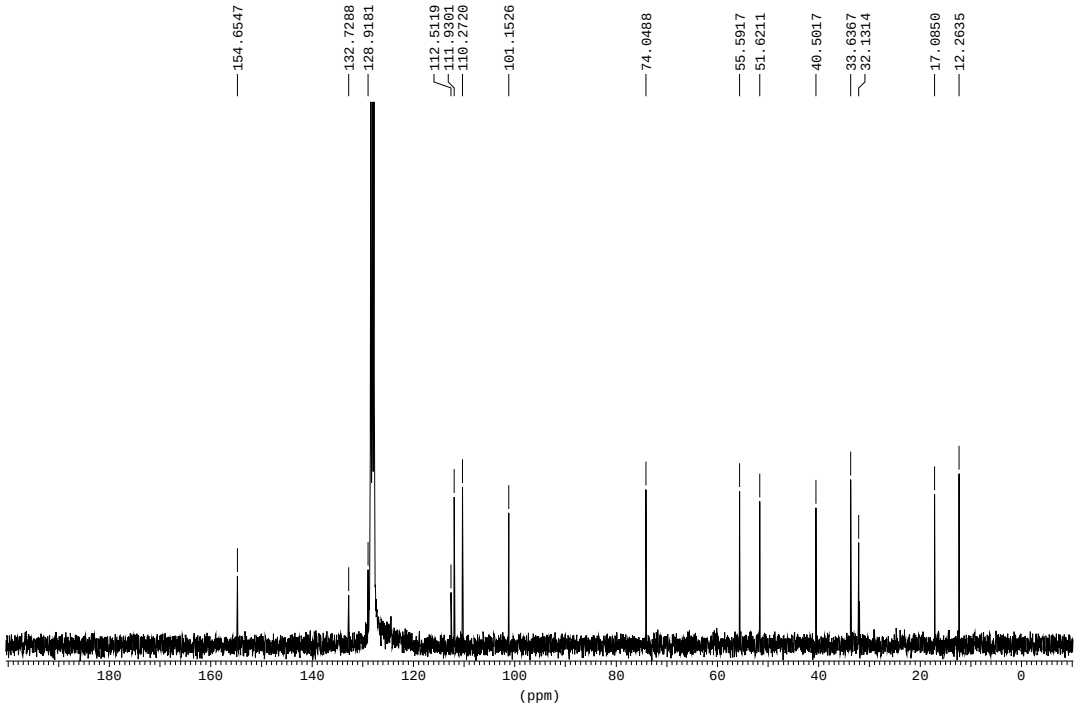

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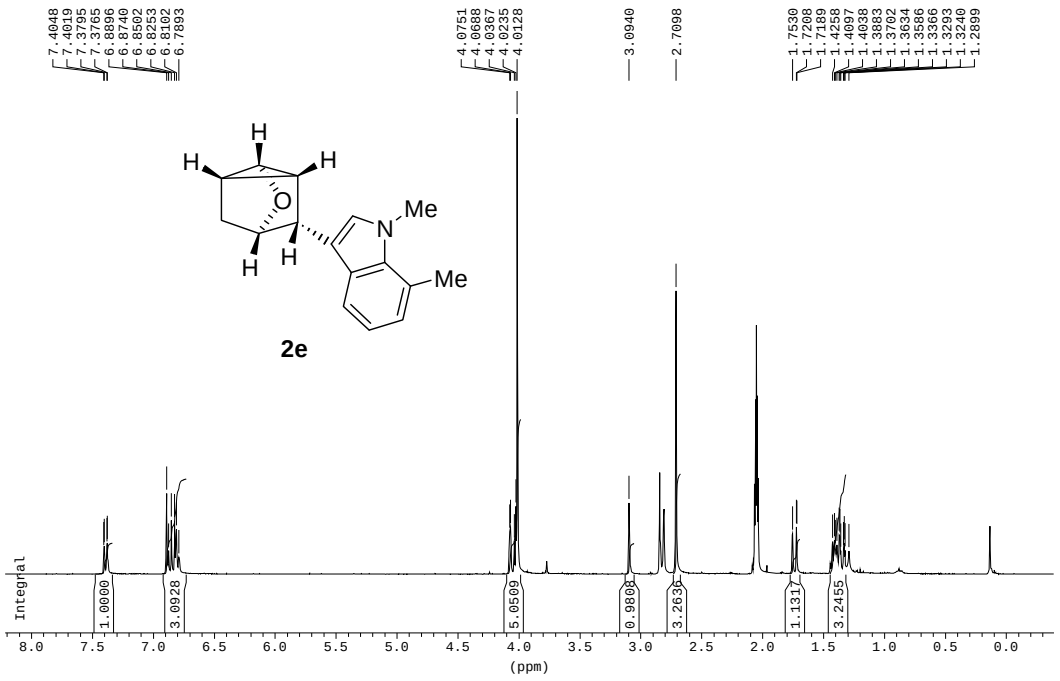

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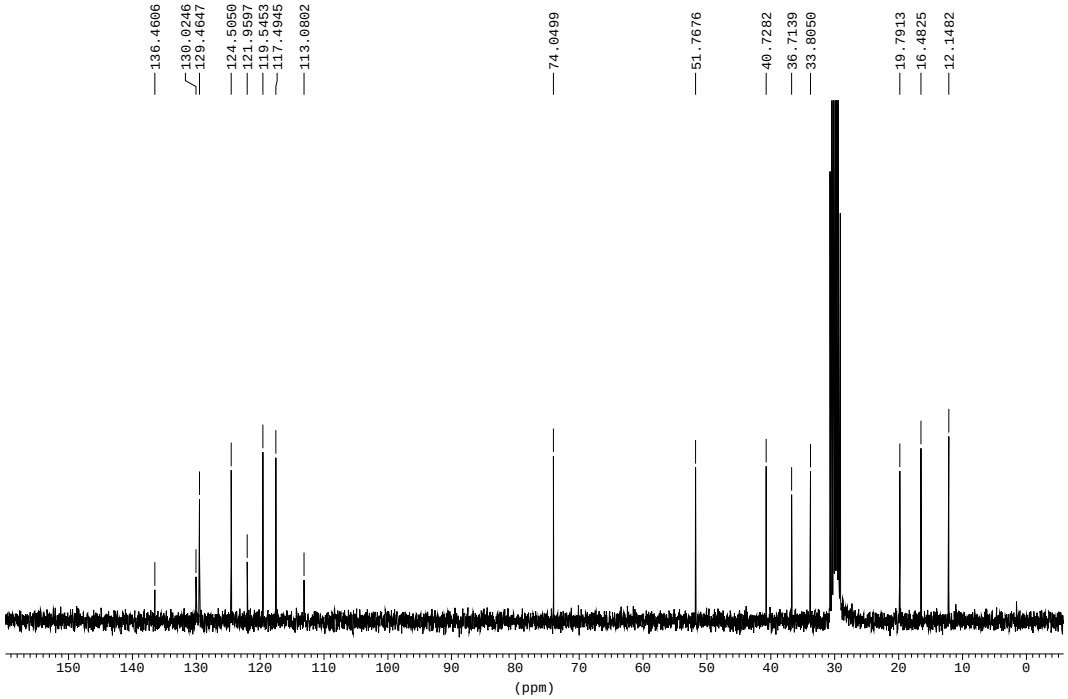

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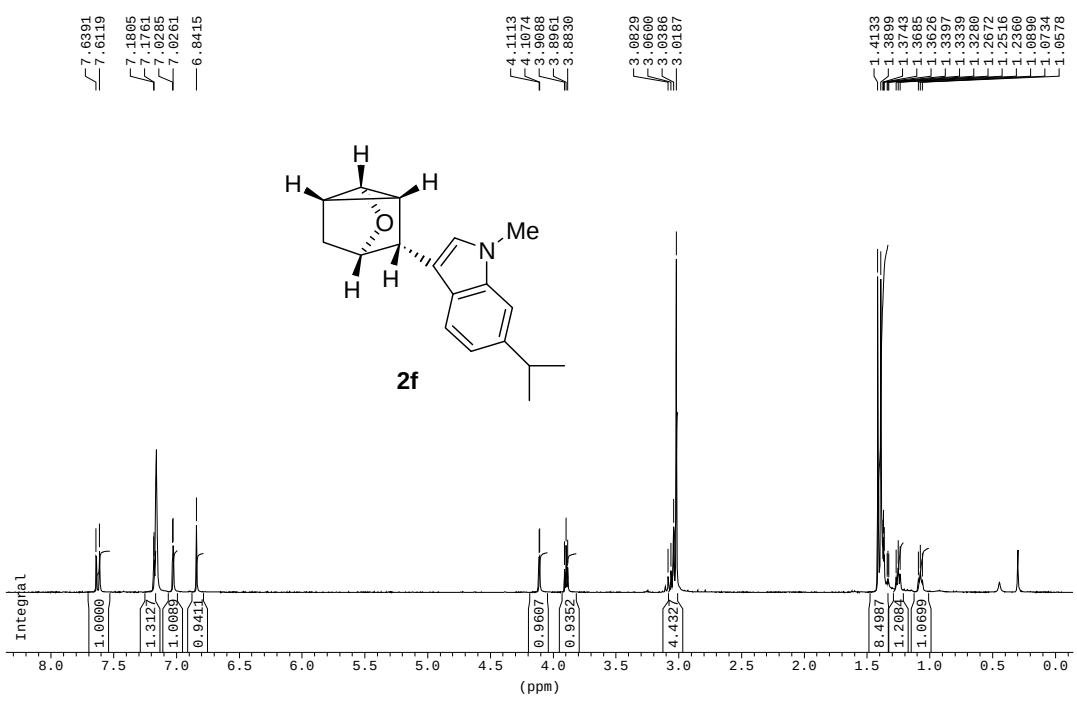

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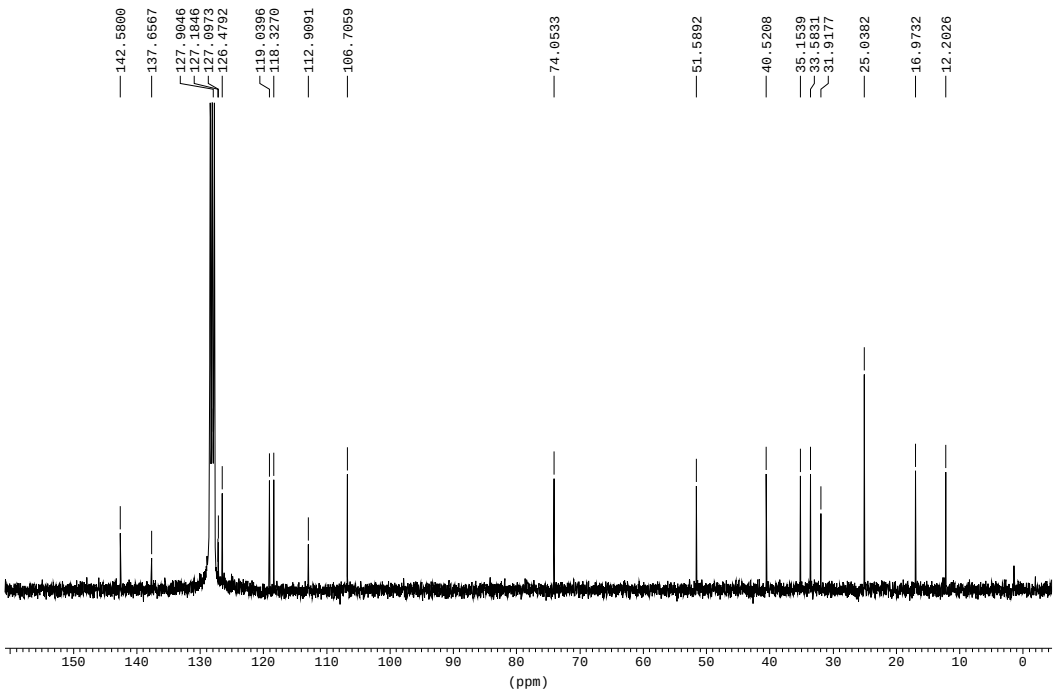

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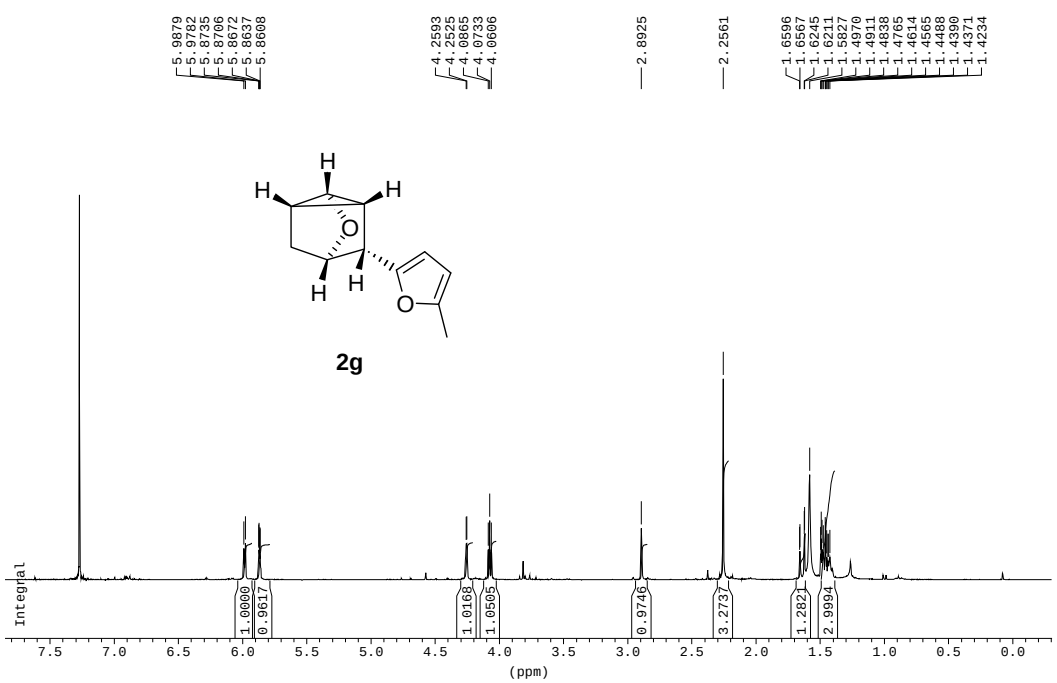

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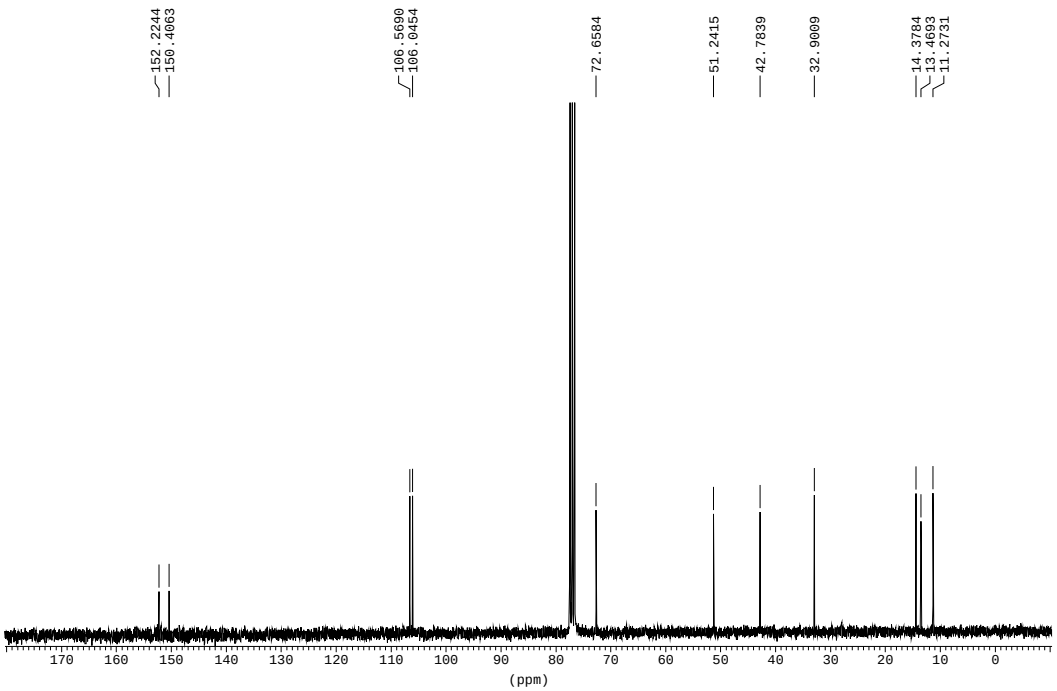

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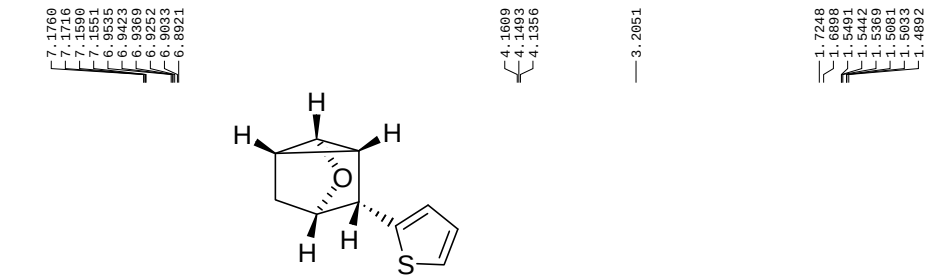

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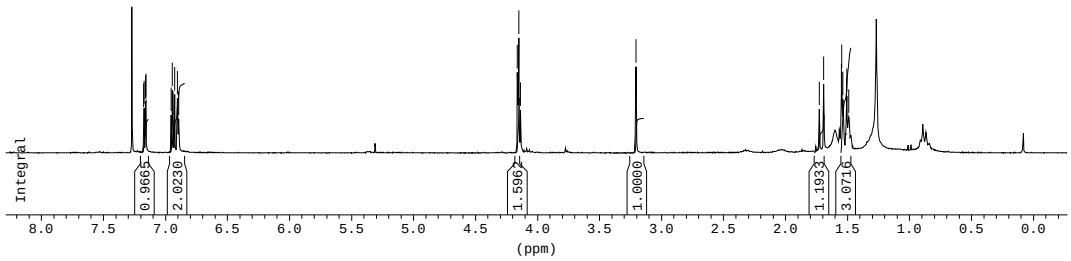

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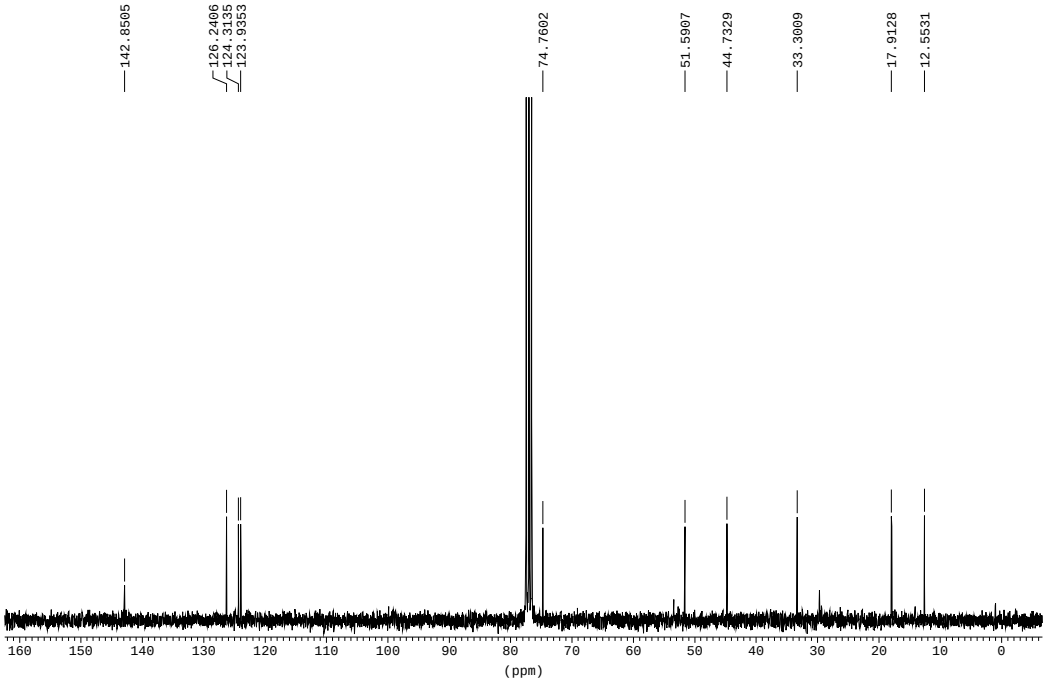

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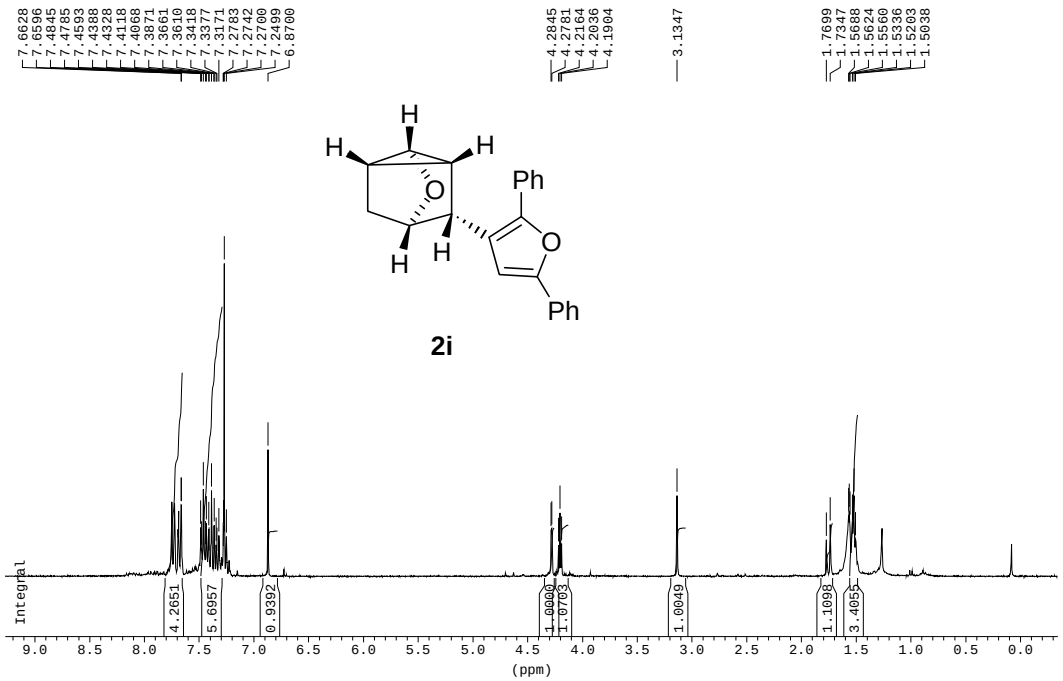

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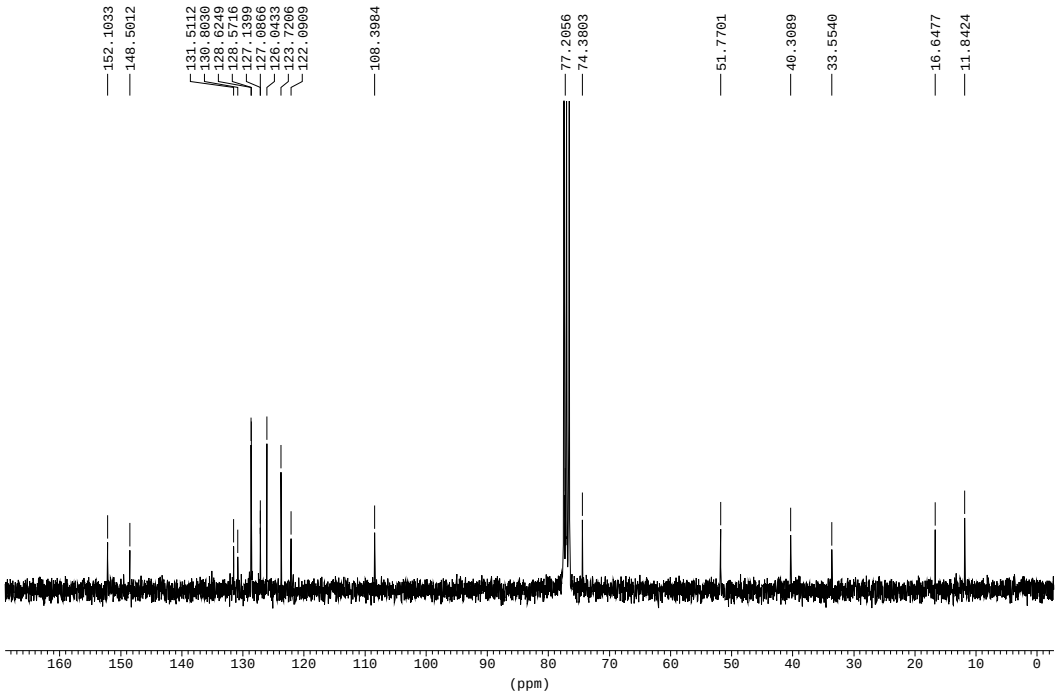

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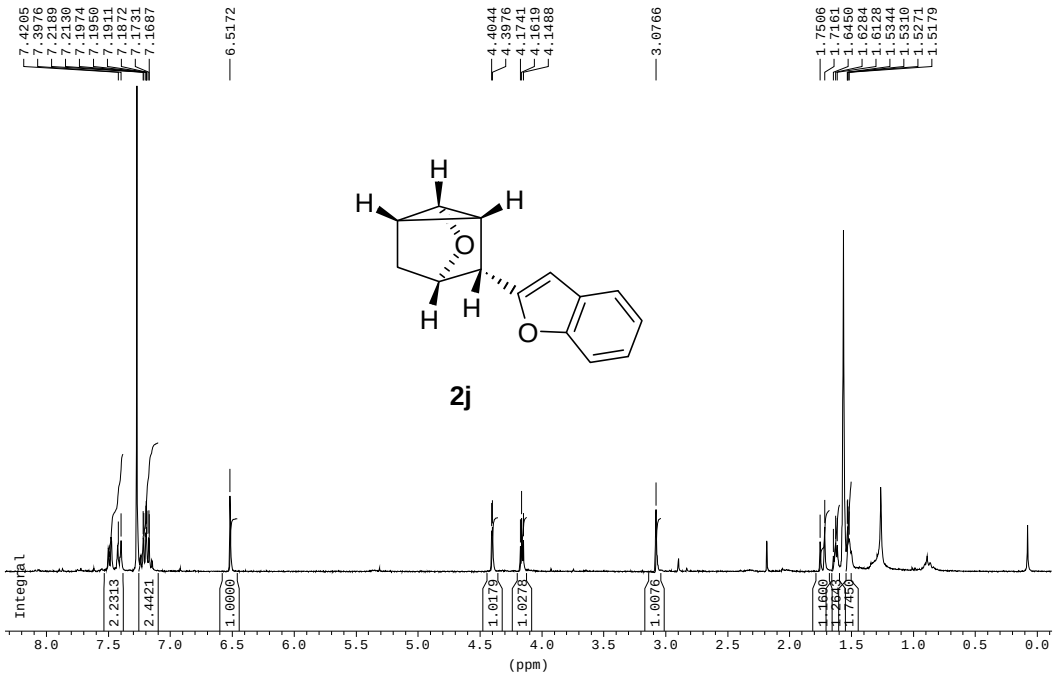

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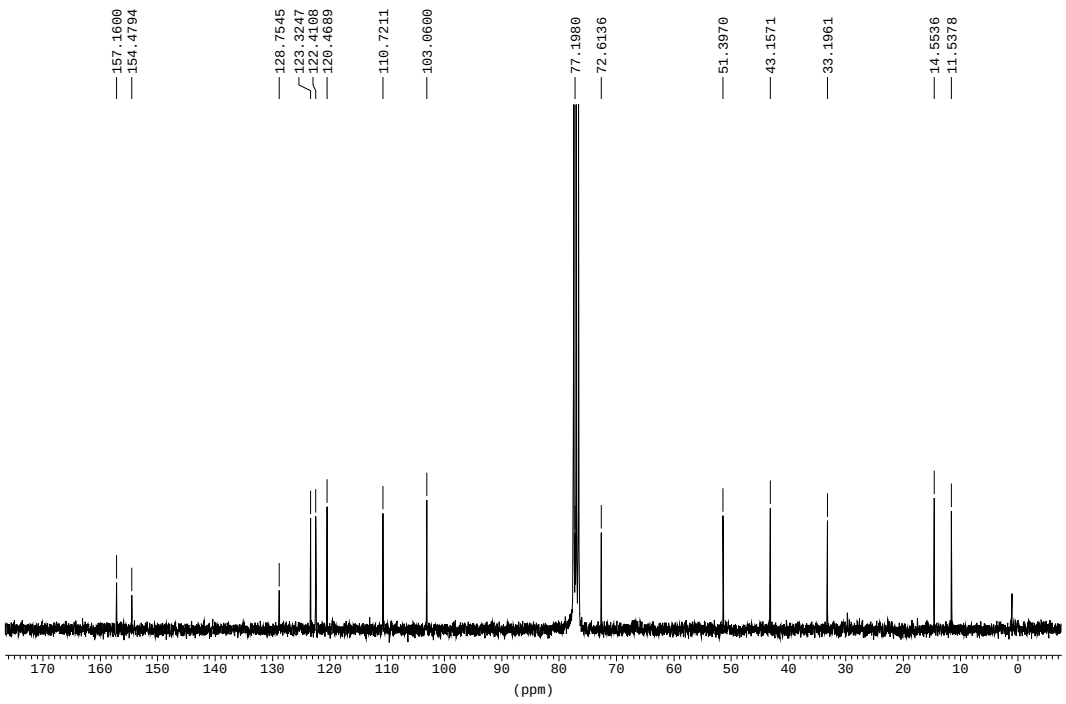

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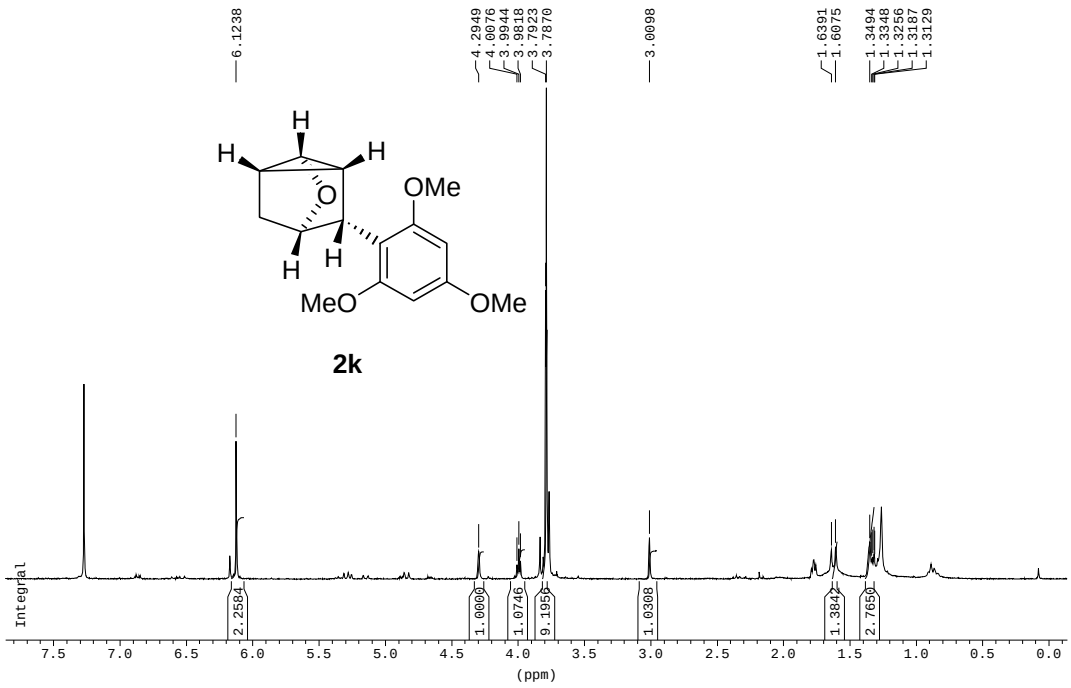

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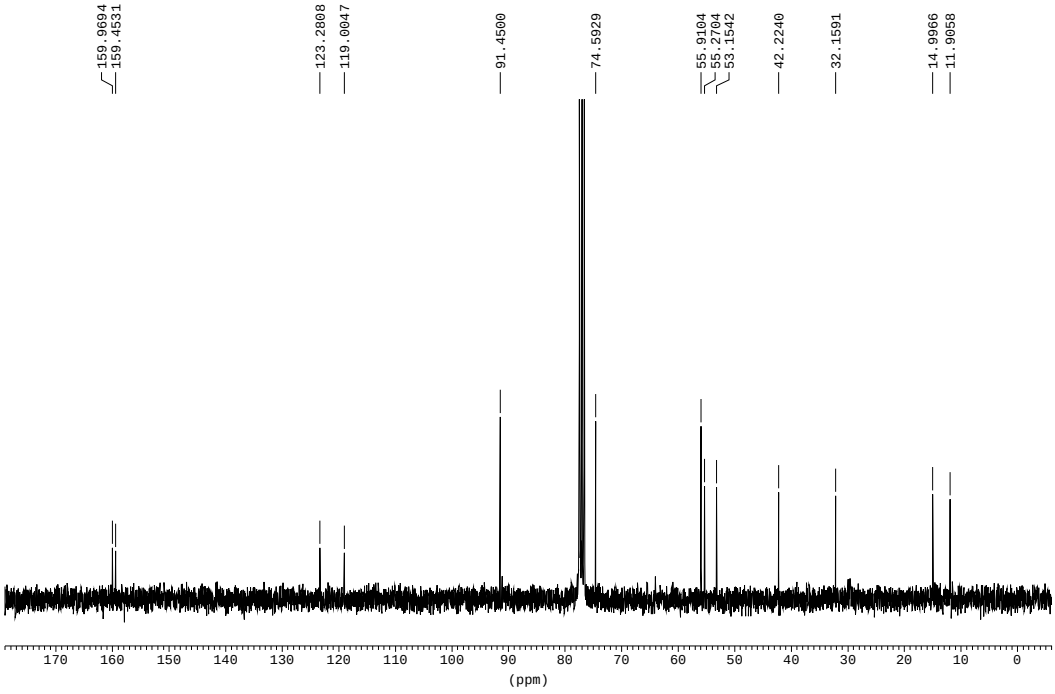

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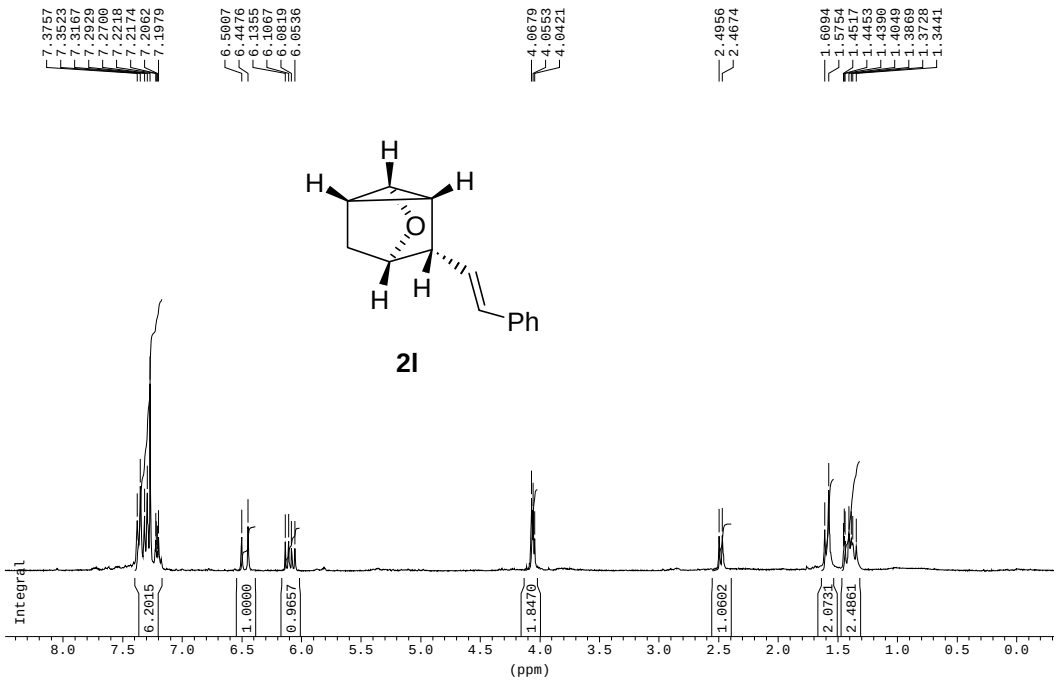

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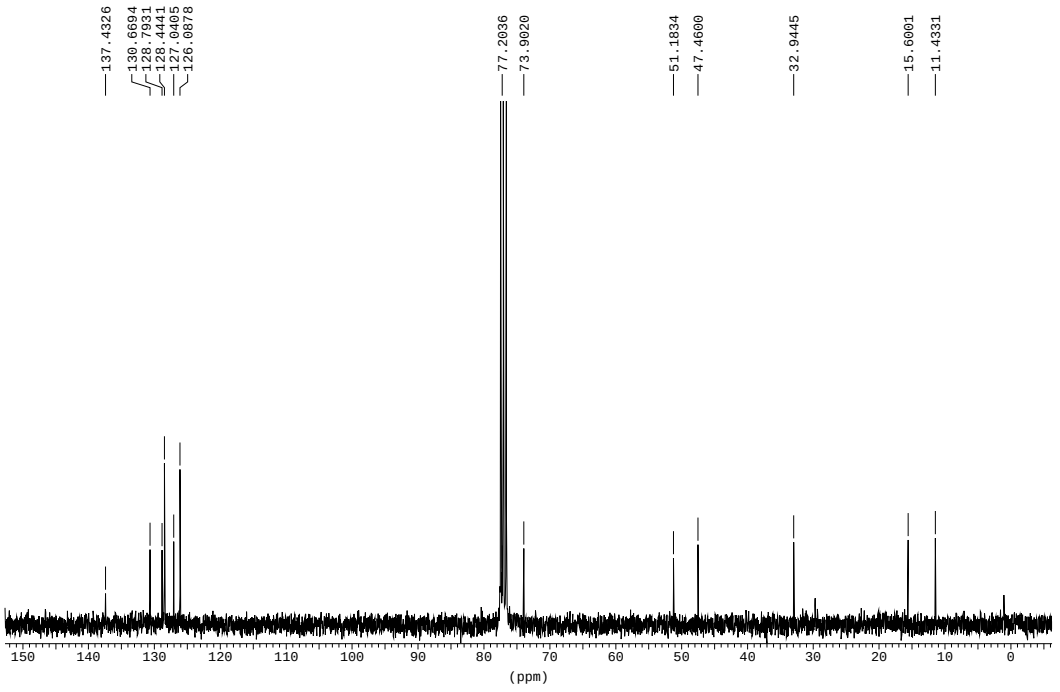

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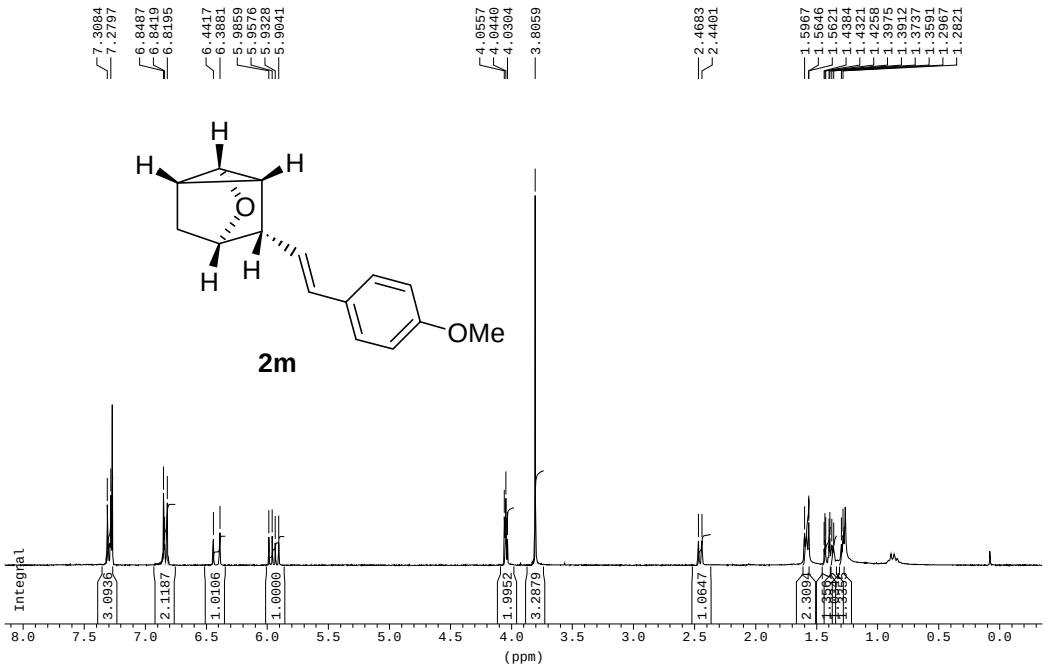

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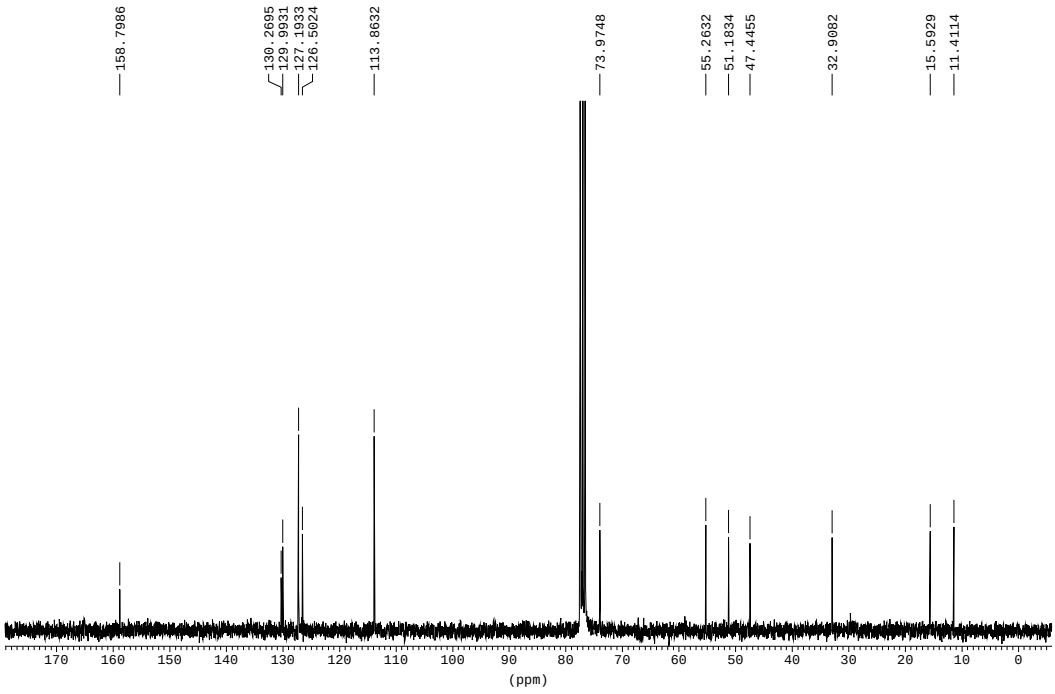

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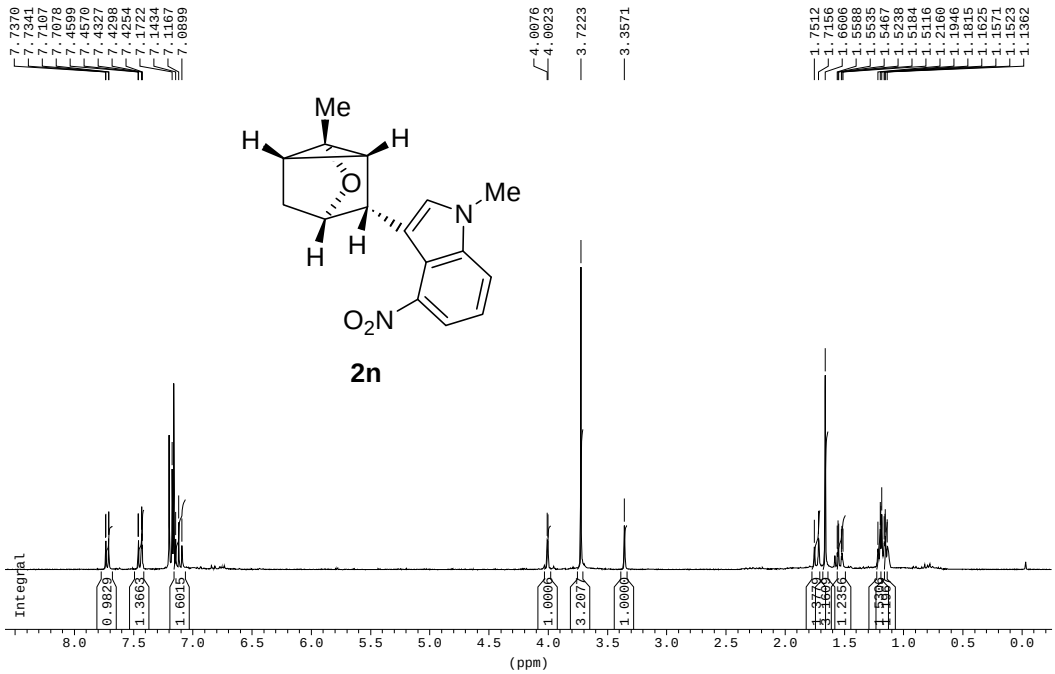

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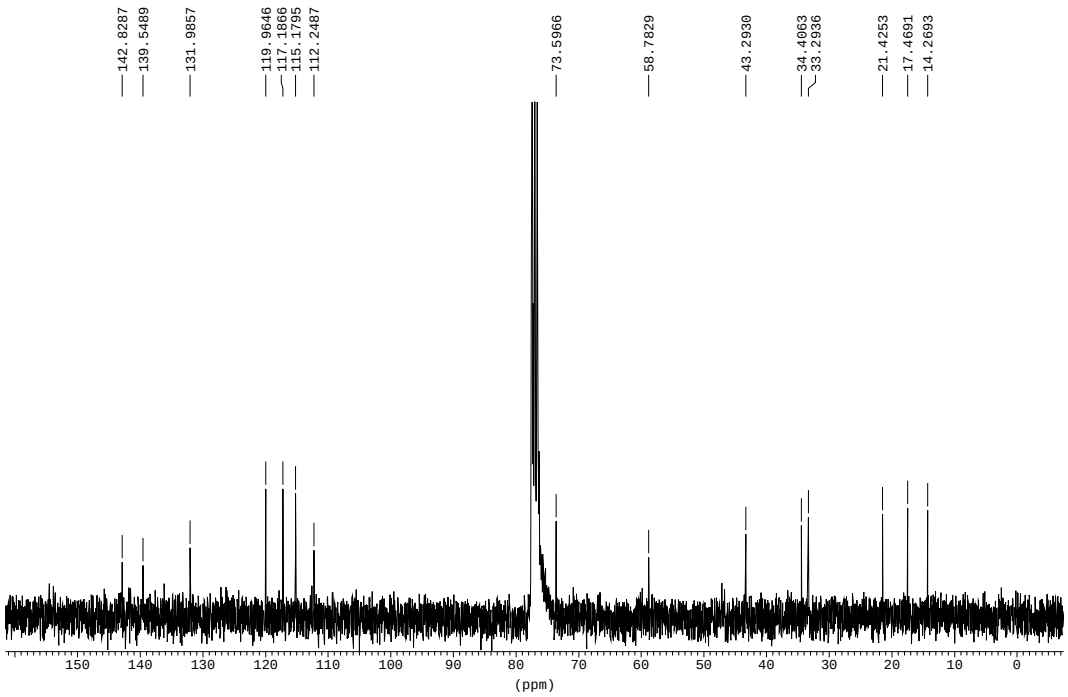
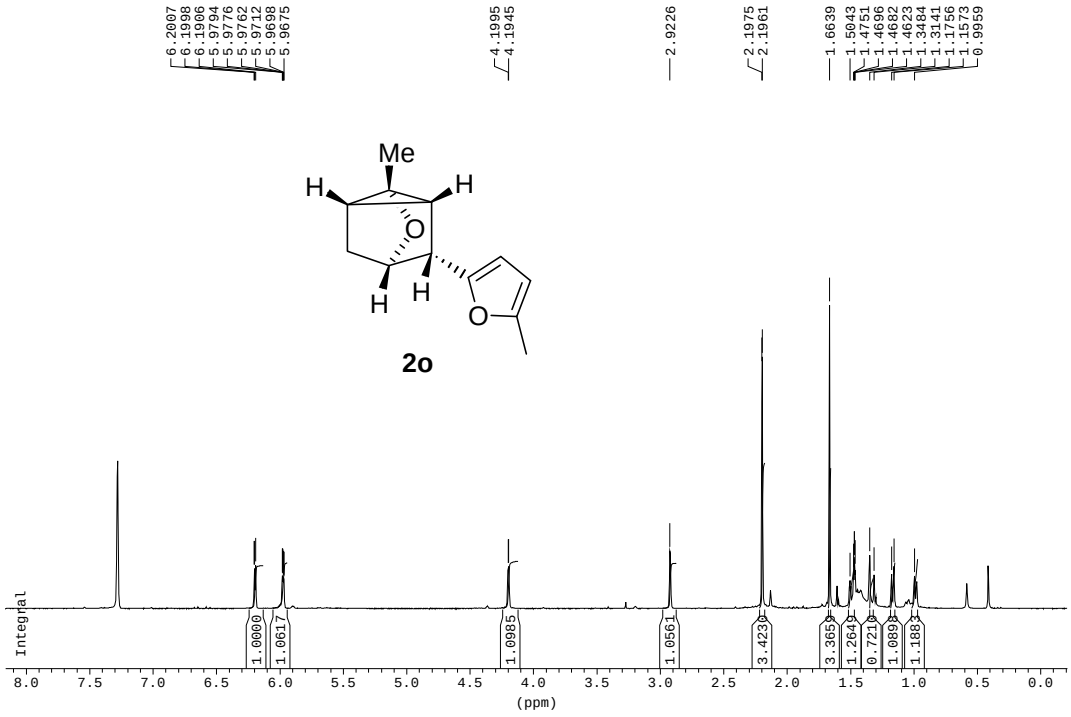
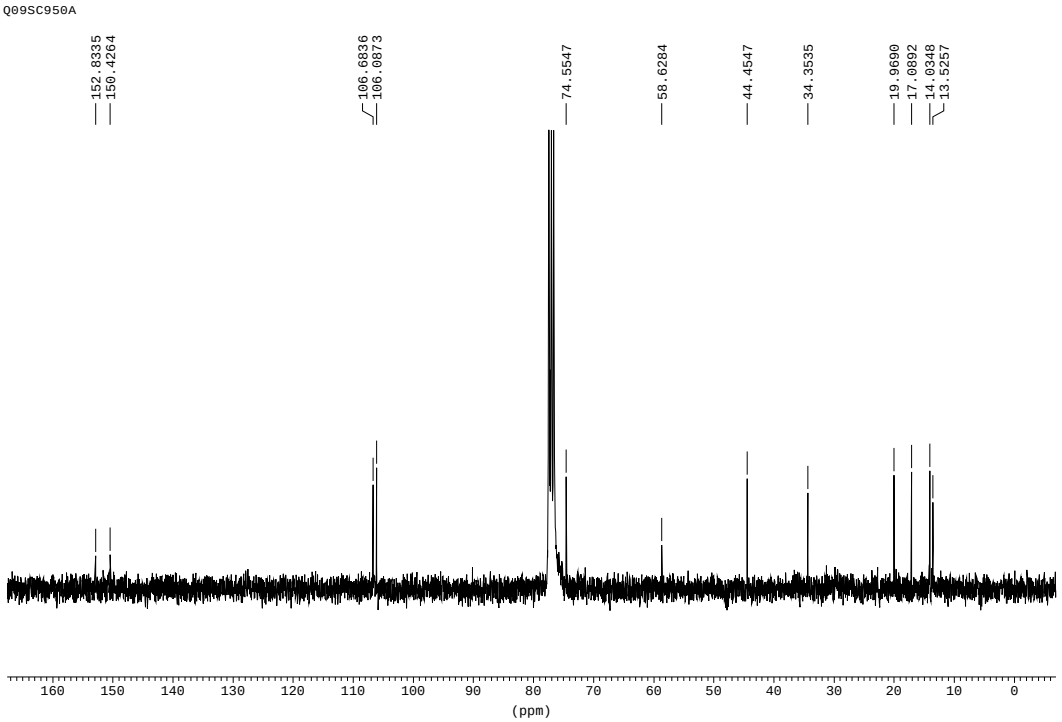



6.2007
6.1998
6.1906
5.9794
5.9776
5.9762
5.9712
5.9698
5.9675
4.1995
4.1945
2.9226
2.1975
2.1961
1.6639
1.5043
1.4751
1.4696
1.4682
1.4623
1.3484
1.3141
1.1756
1.1573
0.9959
Me
H
H
O
H
H
O
2o
Integral
1.0000
1.0617
1.0985
1.0561
3.4230
3.3655
1.2644
0.7210
1.0890
1.1883
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)


Q09SC950A
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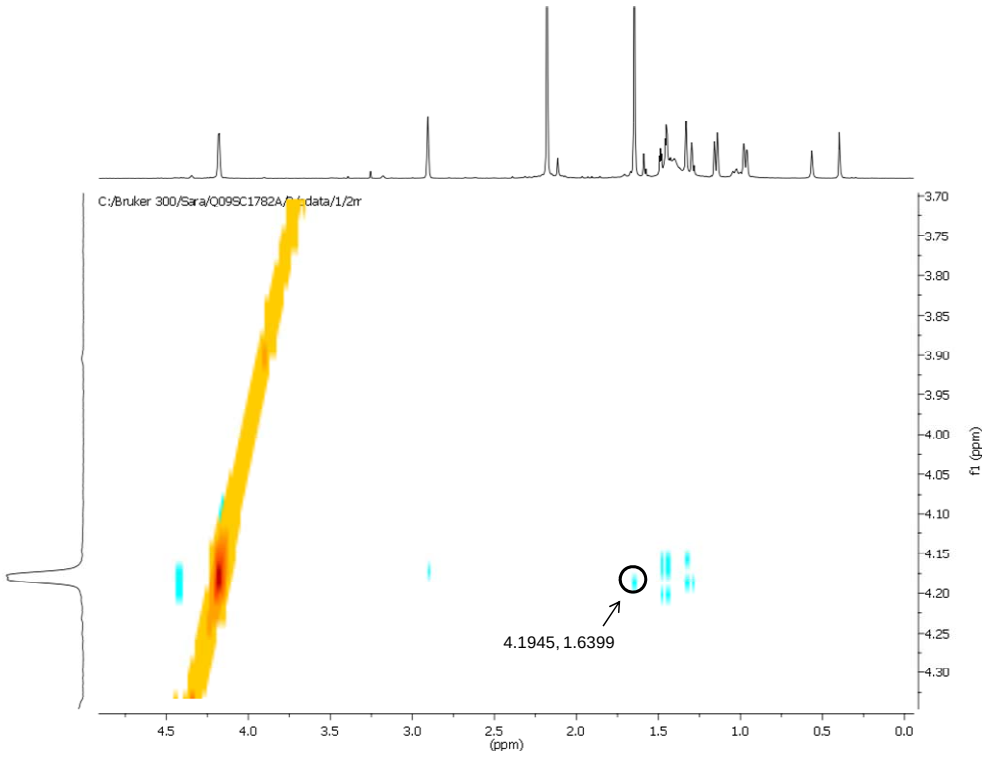
150.4264
106.6836
106.0873
74.5547
58.6284
44.4547
34.3535
19.9690
17.0892
14.0348
13.5257
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

NOESY (**2o**):



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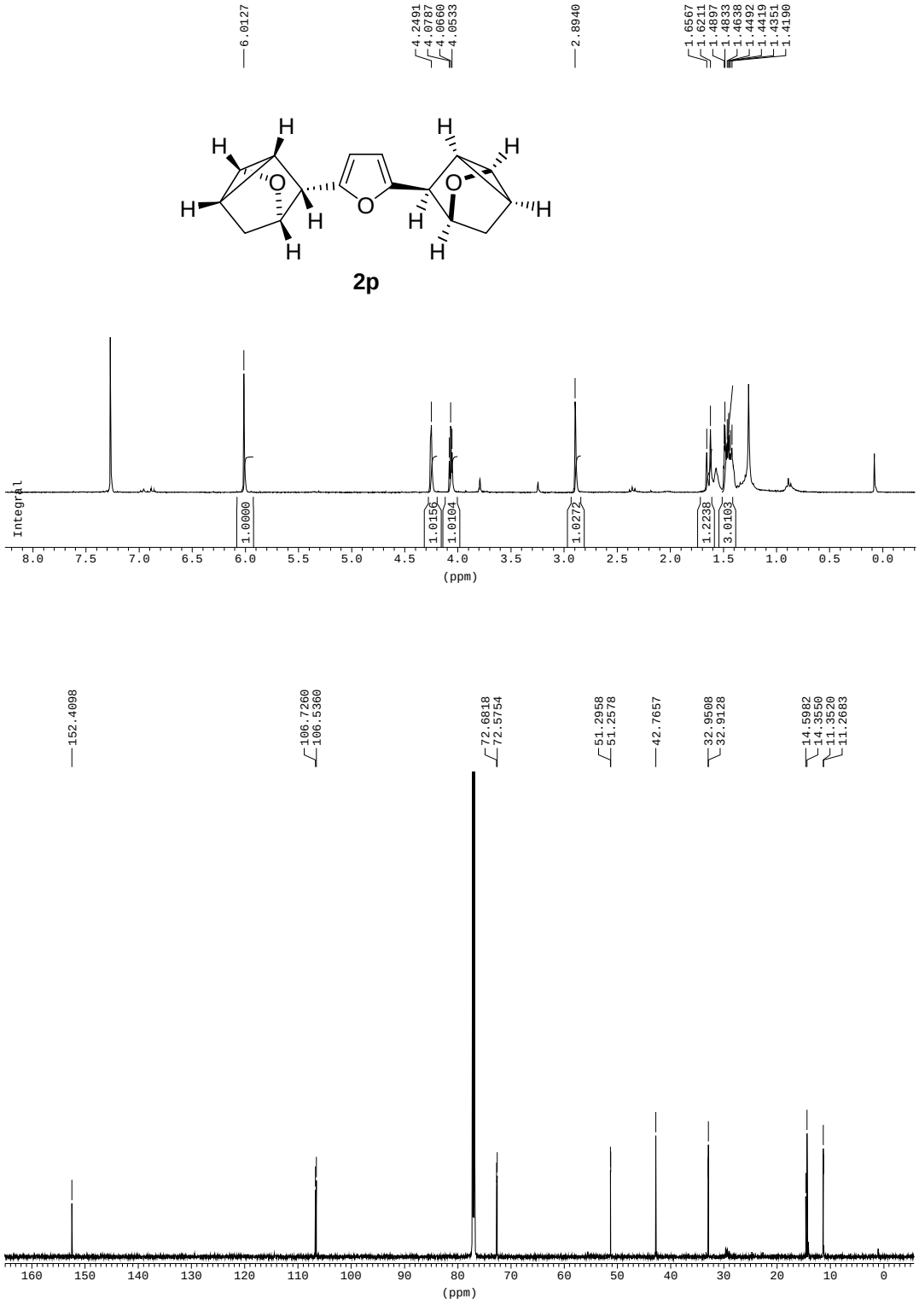
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4.0787
4.0660
4.0533
2.8940
1.6567
1.6211
1.4897
1.4833
1.4638
1.4492
1.4419
1.4351
1.4190
H
O
2p
Integral
1.0000
1.0156
1.0104
1.0272
1.2238
3.0103
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)
152.4098
106.7260
106.5360
72.6818
72.5754
51.2958
51.2578
42.7657
32.9508
32.9128
14.5982
14.3550
11.3520
11.2683
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)