Supporting Information

An Atom-Economic Synthesis of Bicyclo[3.1.0]hexanes by Rhodium N-Heterocyclic Carbene-Catalyzed Diastereoselective Tandem Hetero-[5+2] Cycloaddition/Claisen Rearrangement Reaction of Vinylic Oxiranes with Alkynes

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Full list of authors for references from main paper with 16 or more authors

[19b] Bueno, A. B.; Collado, I.; de Dios, A.; Domínguez, C.; Martín, J. A.; Martín, L. M.; Martínez-Grau, M. A.; Montero, C.; Pedregal, C.; Catlow, J.; Coffey, D. S.; Clay, M. P.; Dantzig, A. H.; Lindstrom, T.; Monn, J. A.; Jiang, H.; Schoepp, D. D.; Stratford, R. E.; Tabas, L. B.; Tizzano, J. P.; Wright, R. A.; Herin, M. F. *J. Med. Chem.* **2005**, *48*, 5305.

[19c] McBriar, M. D.; Guzik, H.; Shapiro, S.; Paruchova, J.; Xu, R.; Palani, A.; Clader, J. W.; Cox, K.; Greenlee, W. J.; Hawes, B. E.; Kowalski, T. J.; O'Neill, K.; Spar, B. D.; Weig, B.; Weston, D. J.; Farley, C.; Cook, J. *J. Med. Chem.* **2006**, *49*, 2294.

Contents

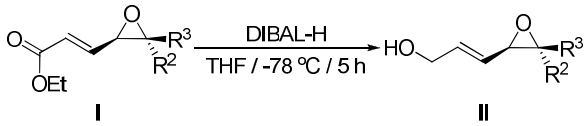
1. General

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under nitrogen. ^{1}H NMR, ^{13}C NMR spectra were measured at 400 MHz and 100 MHz in $CDCl_3$. Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm). Tetrahydrofuran, benzene and toluene were distilled from sodium and benzophenone prior to use. Dichloromethane and 1,2-dichloroethane (DCE) was distilled from CaH_2 prior to use.

The catalysts $[Rh(\eta^6\text{-}C_{10}H_8)(COD)]^+SbF_6^-$,[1] $[Rh(\eta^6\text{-}C_6H_6)(COD)]^+SbF_6^-$,[1] RhCl(IMes)(COD),[2] RhCl(IPr)(COD),[3] (*E*)-ethyl3-((2*R**,3*R**)3-phenyloxiran-2-yl)acrylate,[4] (*E*)-ethyl3-((2*R**,3*R**)-3-methyl oxiran-2-yl) acrylate[5] and (*E*)-ethyl 3-(3,3-dimethyloxiran-2-yl)acrylate[6] were synthesized following the literature procedures. All other chemicals and solvents were purchased from commercial company and used as received.

2. Experimental Procedures and Characterization Data

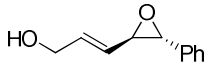
2.1 General Procedure for Synthesis of Racemic Vinylic Oxiranes Alcohols



I II

To a Schlenk flask charged with DIBAL-H (1.1 M in hexane, 2.5 equiv.) and THF at −78 °C was added a solution of the corresponding ester **I** (1.0 equiv) in dry THF (1.0 M-solution) dropwise. The mixture was stirred at −78 °C for 5 hours. Then the reaction was quenched with water (1 mL), aqueous potassium tartrate tetrahydrate and the resultant solution allowed to warm to room temperature until the solution is clear. Extraction with Et_2O, washed with brine, drying over $MgSO_4$, evaporation, and purification by flash column chromatography provided alcohol **II** as a clear, colorless oil.

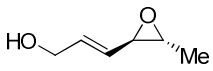
(*E*)-3-((2*R,3*R**)-3-phenyloxiran-2-yl)prop-2-en-1-ol.**



Colorless oil. R_f = 0.42 (hexanes/EtOAc = 2:1). 92% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.25 (m, 5H), 6.10 (dt, J = 15.6 and 5.2 Hz, 1H), 5.61 (dd, J = 15.6 and 7.6 Hz, 1H), 4.18 (broad s, 2H), 3.77 (s, 1H), 3.39 (d, J = 7.6 Hz, 1H), 2.41 (broad s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.8 (C), 134.8 (CH), 128.4 (CH), 128.2 (CH), 127.6 (CH), 125.4 (CH), 62.4 (CH_2), 62.1 (CH), 60.3 (CH). IR (neat): ν 3367, 3020, 2862, 2973, 1604, 1496, 1458, 1421, 1083, 966, 872, 751, 697 cm^{-1}. MS (EI): m/z (%) = 176 (M+, 0.11), 77 (100). HRMS calcd for $C_{11}H_{12}O_2$: 176.0837, found: 176.0836.

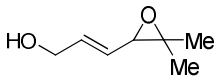
(*E*)-3-((2*R,3*R**)-3-methyloxiran-2-yl)prop-2-en-1-ol.**[5]



Colorless oil. R_f = 0.50 (CH_2Cl_2/Et_2O = 1:1). 90% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.07 (dt, *J* = 15.6 and 5.2 Hz, 1H), 5.47 (dd, *J* = 15.6 and 8.0 Hz, 1H), 4.17 (t, *J* = 5.2 Hz, 2H), 3.10 (d, *J* = 8.0 Hz, 1H), 2.95-2.91 (m, 1H), 1.76 (broad s, 1H), 1.35 (d, *J* = 5.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.3 (CH), 128.3 (CH), 62.4 (CH_2), 58.9 (CH), 56.4 (CH), 17.4 (CH_3). IR (neat): *v* 3365, 2973, 2926, 1677, 1377, 1089, 1008, 970, 852 cm^{-1}. MS (EI): m/z (%) = 115 ($(M+H)^+$, 9.91), 43 (100).

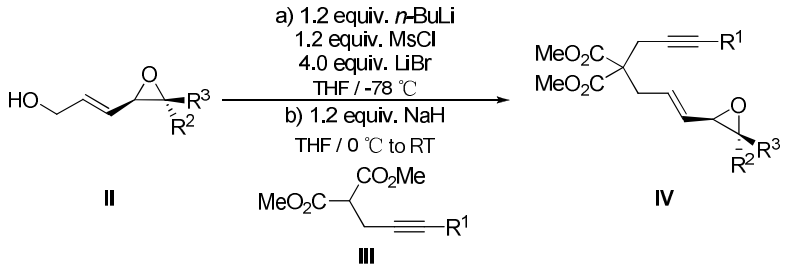
(*E*)-3-(3,3-dimethyloxiran-2-yl)prop-2-en-1-ol.



Colorless oil. R_f = 0.50 (CH_2Cl_2/Et_2O = 1:1). 95% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.07 (dt, *J* = 15.2 and 5.2 Hz, 1H), 5.63 (dd, *J* = 15.6 and 7.6 Hz, 1H), 4.20 (broad s, 2H), 3.24 (d, *J* = 7.6 Hz, 1H), 1.67 (broad s, 1H), 1.37 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.6 (CH), 125.8 (CH), 63.7 (CH), 62.3 (CH_2), 60.5 (C), 24.4 (CH_3), 18.7 (CH_3). IR (neat): *v* 3407, 2964, 2927, 2869, 1673, 1456, 1380, 1318, 1110, 1006, 967, 873, 824, 776, 672 cm^{-1}. MS (EI): m/z (%) = 128 (M^+, 10.64), 43 (100). HRMS calcd for $C_7H_{12}O_2$: 128.0837, found: 128.0838.

2.2 General Procedure for Synthesis of Racemic Geminal Diester-Tether Substrates

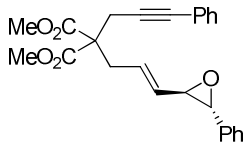


To a flame-dried 10 mL Schlenk flask containing alcohol **II** (1.0 equiv.) and THF at –78 °C was added *n*-BuLi (2.5 M in hexane, 1.2 equiv.). After the reaction mixture was stirred for 10 min, freshly distilled methane sulfonyl chloride (1.2 equiv.) was added slowly followed by the quick addition of anhydrous lithium bromide (4.0 equiv.) The mixture was stirred at –78 °C for 2.5 h to generate bromide *in situ*, which was directly submitted to the next reaction without work-up.

To a second flame-dried 100 mL schlenk flask charged with NaH (60 wt % in mineral oil, 1.2 equiv.) and THF was added **III** (1.0 equiv.) dropwise over 15 min at 0 °C. After the solution was stirred for 2 h, the resultant solution allowed to warm to room temperature. After 30 min at room temperature, the solution was cooled to −78 °C and the bromide solution prepared in the above was transferred via cannula into the second flask. The reaction mixture was stirred for 4 h at −78 °C, then allowed to warm to room temperature. Quenched by water, extraction with Et_2O, drying over $MgSO_4$, evaporation, and purification by flash column chromatography (hexanes/EtOAc = 10:1 to 5:1) provided geminal diester derivative **IV** as a clear colorless oil.

Physical data for vinylic oxiranes-alkyne substrates:

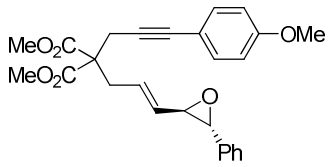
Substrate 1a



Colorless oil. R_f = 0.46 (hexanes/EtOAc = 5:1). 63% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.25 (m, 10H), 5.87-5.80 (m, 1H), 5.54 (dd, *J* = 15.2 and 7.6 Hz, 1H), 3.78 (s, 6H), 3.73 (broad s, 1H), 3.34 (d, *J* = 7.6 Hz, 1H), 3.03 (s, 2H), 2.92 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.10 (C), 170.08 (C), 136.9 (C), 132.1 (CH), 131.6(CH), 129.4 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 125.4 (CH), 123.0 (C), 83.9 (C), 83.8 (C), 62.3 (CH), 60.2 (CH), 57.2 (C), 52.8 (CH_3), 35.4 (CH_2), 23.8 (CH_2). IR (neat): *v* 2955, 1735, 1600, 1492, 1437, 1203, 1027, 971, 878, 755, 694 cm^{-1}. MS (EI): m/z (%) = 404 (M^+, 2.52), 115 (100). HRMS calcd for $C_{25}H_{24}O_5$: 404.1624, found: 404.1621.

Substrate 1b

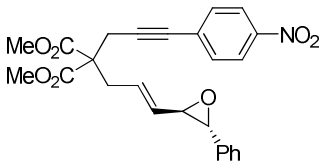


Colorless oil. R_f = 0.32 (hexanes/EtOAc = 5:1). 51% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.24 (m, 7H), 6.80 (d, *J* = 7.6 Hz, 2H), 5.88-5.80 (m, 1H), 5.53 (dd, *J* = 15.2 and 7.6 Hz, 1H), 3.79 (s, 3H), 3.76 (s, 6H), 3.73 (broad s, 1H), 3.33 (d, *J* = 7.6 Hz, 1H), 3.01 (s, 2H), 2.91 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2 (C), 170.1 (C), 159.4 (C), 136.9 (C), 133.0 (CH), 132.0 (CH), 129.5 (CH), 128.4 (CH), 128.2 (CH), 125.4(CH), 115.1 (C), 113.8 (CH), 83.6 (C), 82.3 (C), 62.3 (CH), 60.2 (CH), 57.2 (C), 55.2 (CH_3), 52.8 (CH_3), 35.4 (CH_2), 23.8 (CH_2). IR

(neat): *v* 2954, 2840, 1735, 1606, 1510, 1437, 1290, 1246, 1203, 1180, 1030, 833, 755, 699 cm^{-1}. MS (EI): m/z (%) = 434 (M^+, 2.51), 145 (100). HRMS calcd for $C_{26}H_{26}O_6$: 434.1729, found: 434.1730.

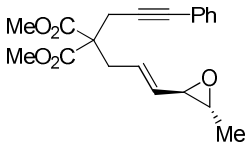
Substrate 1c



Yellow oil. R_f = 0.25 (hexanes/EtOAc = 5:1). 49% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.33-7.24 (m, 5H), 5.88-5.81 (m, 1H), 5.55 (dd, *J* = 14.8 and 7.2 Hz, 1H), 3.79 (s, 6H), 3.74 (broad s, 1H), 3.34 (d, *J* = 6.8 Hz, 1H), 3.09 (s, 2H), 2.92 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.72 (C), 169.70 (C), 146.8 (C), 136.7 (C), 132.3 (CH), 129.7 (C), 128.9 (CH), 128.3 (CH), 128.1 (CH), 125.3 (CH), 123.4 (CH), 90.0 (C), 82.1 (C), 62.0 (CH), 60.1 (CH), 56.9 (C), 52.8 (CH_3), 35.4 (CH_2), 23.8 (CH_2). IR (neat): *v* 2954, 2849, 1734, 1594, 1518, 1342, 1203, 1108, 853, 750, 698 cm^{-1}. MS (EI): m/z (%) = 449 (M^+, 0.94), 43 (100). HRMS calcd for $C_{25}H_{23}NO_7$: 449.1475, found: 449.1473.

Substrate 1d

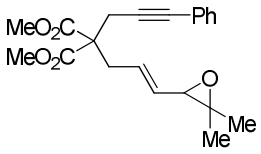


Colorless oil. R_f = 0.34 (hexanes/EtOAc = 5:1). 54% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (broad s, 2H), 7.28 (broad s, 3H), 5.80-5.72 (m, 1H), 5.38 (dd, *J* = 15.2 and 7.6 Hz, 1H), 3.76 (s, 6H), 3.04 (broad s, 1H), 3.02 (s, 2H), 2.89 (broad s, 1H), 2.87 (broad s, 2H), 1.31 (d, *J* = 3.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1 (C), 132.8 (CH), 131.6 (CH), 128.6 (CH), 128.2 (CH), 128.0 (CH), 123.0 (C), 84.0 (C), 83.7 (C), 58.9 (CH), 57.2 (C), 56.3 (CH), 52.7 (CH_3), 35.3 (CH_2), 23.7 (CH_2), 17.4 (CH_3). IR (neat): *v* 2977, 2957, 1735, 1598, 1491, 1437, 1203, 1067,

934, 758, 692 cm^{-1}. MS (EI): m/z (%) = 342 (M^+, 0.61), 115 (100). HRMS calcd for $C_{20}H_{22}O_5$: 342.1467, found: 342.1469.

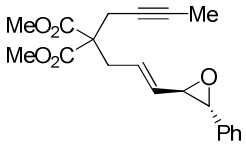
Substrate 1e



Colorless oil. R_f = 0.40 (hexanes/EtOAc = 5:1). 66% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (broad s, 2H), 7.28 (broad s, 3H), 5.79-5.71 (m, 1H), 5.55 (dd, *J* = 15.2 and 7.6 Hz, 1H), 3.76 (s, 6H), 3.17 (d, *J* = 7.2 Hz, 1H), 3.02 (s, 2H), 2.92 (d, *J* = 7.6 Hz, 2H), 1.33 (s, 3H), 1.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1 (2 C), 131.6 (CH), 130.8 (CH), 129.3 (CH), 128.2 (CH), 128.0 (CH), 123.0(C), 84.0 (C), 83.7 (C), 63.5 (CH), 60.1 (C), 57.2 (C), 52.7 (CH_3), 35.5 (CH_2), 24.5 (CH_3), 23.7 (CH_2), 18.7 (CH_3). IR (neat): *v* 2956, 1736, 1599, 1491, 1438, 1203, 1067, 972, 758, 692 cm^{-1}. MS (EI): m/z (%) = 356 (M^+, 0.09), 115 (100). HRMS calcd for $C_{21}H_{24}O_5$: 356.1624, found: 356.1625.

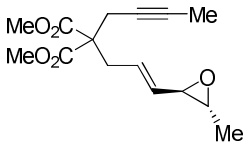
Substrate 1f



Colorless oil. R_f = 0.45 (hexanes/EtOAc = 5:1). 55% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.25 (m, 5H), 5.82-5.75 (m, 1H), 5.49 (dd, *J* = 15.6 and 8.0 Hz, 1H), 3.74 (s, 7H), 3.32 (d, *J* = 7.6 Hz, 1H), 2.84 (d, *J* = 8.0 Hz, 2H), 2.75 (s, 2H), 1.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.28 (C), 170.27 (C), 136.9 (C), 131.8 (CH), 129.6 (CH), 128.4 (CH), 128.2 (CH), 125.4 (CH), 79.2 (C), 73.0 (C), 62.3 (CH), 60.2 (CH), 57.1 (C), 52.7 (CH_3), 35.1 (CH_2), 23.2 (CH_2), 3.4 (CH_3). IR (neat): *v* 3010, 2954, 1735, 1605, 1437, 1289, 1202, 1057, 971, 755, 699 cm^{-1}. MS (EI): m/z (%) = 342 (M^+, 0.03), 53 (100). HRMS calcd for $C_{20}H_{22}O_5$: 342.1467, found: 342.1463.

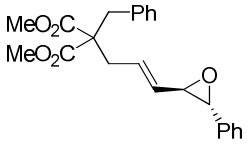
Substrate 1g



Colorless oil. R_f = 0.18 (hexanes/EtOAc = 10:1). 72% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.71 (dt, *J* = 15.6 and 7.6 Hz, 1H), 5.33 (ddt, *J* = 15.6, 7.6 and 1.2 Hz, 1H), 3.74 (s, 6H), 3.01 (dd, *J* = 8.0 and 2.4 Hz, 1H), 2.90-2.85 (m,1H), 2.79 (dd, *J* = 7.6 and 1.2 Hz, 2H), 2.74 (q, *J* = 2.4 Hz, 2H), 1.76 (t, *J* = 2.4 Hz, 3H), 1.32 (d, *J* = 5.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3 (2 C), 132.6 (CH), 128.8 (CH), 79.1 (C), 73.0 (C), 59.0 (CH), 57.2 (C), 56.3 (CH), 52.6 (CH_3), 35.1 (CH_2), 23.1 (CH_2), 17.5 (CH_3), 3.4 (CH_3). IR (neat): *v* 2989, 2956, 1735, 1437, 1328, 1239, 1202, 1057, 971 cm^{-1}. MS (ESI): m/z (%) = 281.2 [(M+H)]. HRMS (ESI) calcd for $C_{15}H_{21}O_5$ [(M+H)]: 281.13835, found: 281.13890.

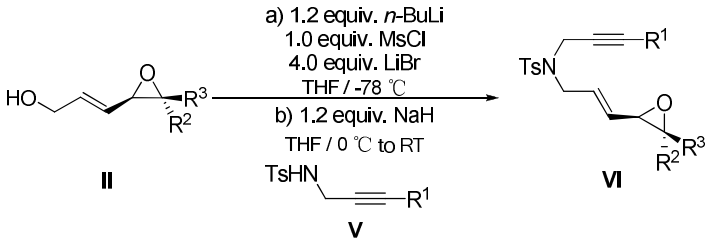
Substrate 1m



Colorless oil. R_f = 0.27 (hexanes/EtOAc = 10:1). 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.31 (m, 3H), 7.28-7.26 (m, 5H), 7.09-7.08 (m, 2H), 5.94-5.86 (m, 1H), 5.46 (dd, *J* = 15.2 and 7.6 Hz, 1H), 3.73 (s, 7H), 3.36 (d, *J* = 6.8 Hz, 1H), 3.26 (broad s, 2H), 2.60 (d, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.0 (C), 170.9 (C), 137.0 (C), 135.6 (C), 131.6 (CH), 130.2 (CH), 129.9 (CH), 128.5 (CH), 128.3 (CH), 128.2 (CH), 127.1 (CH), 125.4 (CH), 62.3 (CH), 60.1 (CH), 59.1(C), 52.4(CH_3), 38.5 (CH_2), 35.3 (CH_2). IR (neat): *v* 3003, 2952, 1732, 1604, 1435, 1236, 1200, 1086, 970, 744, 699 cm^{-1}. MS (ESI): m/z (%) = 403.2 [(M+Na)]. HRMS (ESI) calcd for $C_{23}H_{24}Na_1O_5$ [(M+Na)]: 403.15159, found: 403.15205.

2.3 General Procedure for Synthesis of Racemic Tosylamide-Tether Substrates

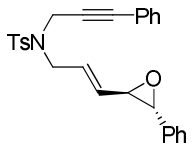


To a flame-dried 10 mL Schlenk flask containing alcohol **II** (1.0 equiv.) and THF at –78 °C was added *n*-BuLi (2.5 M in hexane, 1.2 equiv.). After the reaction mixture was stirred for 10 min, freshly distilled methane sulfonyl chloride (1.0 equiv.) was added slowly followed by the quick addition of anhydrous lithium bromide (4.0 equiv.) The mixture was stirred at –78 °C for 2.5 h to generate bromide *in situ*, which was directly submitted to the next reaction without work-up.

To a second flame-dried 100 mL schlenk flask charged with NaH (60 wt % in mineral oil, 1.2 equiv.) and THF was added **V** (1.0 equiv.) dropwise over 15 min at 0 °C. After the solution was stirred for 1 h, the resultant solution allowed to warm to room temperature. After 1 h at room temperature, the solution was cooled to −78 °C and the bromide solution prepared in the above was transferred via canula into the second flask. The reaction mixture was stirred for 4 h at −78 °C, then allowed to warm to room temperature and at RT for 12 h. Quenched by water, extraction with Et_2O, drying over $MgSO_4$, evaporation, and purification by flash column chromatography (hexanes/EtOAc = 10:1 to 5:1) provided the product **VI**.

Physical data for vinyl epoxide-alkyne substrates:

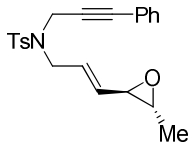
Substrate 1h



Colorless oil. R_f = 0.43 (hexanes/EtOAc = 5:1). 55% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 7.2 Hz, 2H), 7.37-7.22 (m, 10H), 7.07 (d, *J* = 7.6 Hz, 2H), 5.97-5.90 (m, 1H), 5.66 (dd, *J* = 15.6 and 7.6 Hz, 1H), 4.32 (s, 2H), 3.94 (d, *J* = 6.4 Hz, 2H), 3.74 (broad s, 1H), 3.37 (d, *J* = 7.6 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4 (C), 136.5 (C), 135.7 (C), 131.9 (CH), 131.3 (CH), 129.4 (CH), 129.1 (CH), 128.32 (CH), 128.28 (CH), 128.1 (CH), 128.0 (CH), 127.6 (CH), 125.3 (CH), 121.9 (C), 85.7 (C), 81.5 (C), 61.5 (CH), 60.0 (CH), 47.8 (CH_2), 36.9 (CH_2), 21.2 (CH_3). IR (neat): *v* 3034, 2922, 2243, 1598, 1492, 1347, 1160, 1092, 901, 756, 738, 695, 658 cm^{-1}. MS (EI): m/z (%) = 443 (M^+, 4.34), 115 (100). HRMS calcd for $C_{27}H_{25}NO_3S$: 443.1555, found: 443.1552.

Substrate 1i

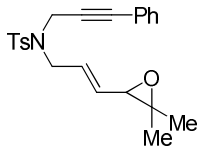


Colorless oil. R_f = 0.24 (hexanes/EtOAc = 5:1). 66% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.30-7.22 (m, 5H), 7.05 (d, *J* = 7.2 Hz, 2H), 5.91-5.84 (m, 1H), 5.49 (dd, *J* = 15.2 and 7.6 Hz, 1H), 4.30 (s, 2H), 3.90 (d, *J* = 6.0 Hz, 2H), 3.07 (d, *J* = 7.6 Hz, 1H), 2.89-2.87 (m, 1H), 2.33 (s, 3H), 1.33 (d, *J* = 4.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5 (C), 135.9 (C), 133.0 (CH), 131.4 (CH), 129.5 (CH), 128.7 (CH), 128.4 (CH), 128.1 (CH), 127.8 (CH), 122.1 (C), 85.8 (C), 81.6 (C), 58.4 (CH), 56.4 (CH), 47.9 (CH_2), 36.9 (CH_2), 21.3 (CH_3), 17.4

(CH_3). IR (neat): *v* 2971, 2924, 2242, 1598, 1491, 1347, 1160, 1092, 900, 756, 692, 658 cm^{-1}. MS (EI): m/z (%) = 381 (M^+, 0.03), 115 (100). HRMS calcd for $C_{22}H_{23}NO_3S$: 381.1399, found: 381.1395.

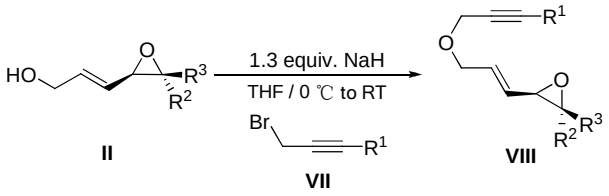
Substrate 1j



White solid. m.p. 77 - 79 ^oC. R_f = 0.30 (hexanes/EtOAc = 5:1). 43% yield.

^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.30-7.22 (m, 5H), 7.05 (d, *J* = 7.2 Hz, 2H), 5.90-5.82 (m, 1H), 5.65 (dd, *J* = 15.2 and 7.2 Hz, 1H), 4.30 (s, 2H), 3.93 (d, *J* = 6.0 Hz, 2H), 3.21 (d, *J* = 7.6 Hz, 1H), 2.34 (s, 3H), 1.35 (s, 3H), 1.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5 (C), 135.9 (C), 131.5 (CH), 131.1 (CH), 129.5 (CH), 128.4 (CH), 128.1 (CH), 127.8 (CH), 122.1 (C), 85.8 (C), 81.6 (C), 63.1 (CH), 60.3 (C), 48.1 (CH_2), 36.9 (CH_2), 24.5 (CH_3), 21.4 (CH_3), 18.8 (CH_3). IR (neat): *v* 2925, 2924, 2857, 1597, 1489, 1444, 1332, 1167, 1093, 900, 758, 660 cm^{-1}. MS (ESI): m/z (%) = 418.1 [(M+Na)]. HRMS (MALDI) calcd for $C_{23}H_{26}NO_3S$ [$(M+H)^+$]: 396.1632, found: 396.1628.

2.4 General Procedure for Synthesis of Racemic Ether-Tether Substrates

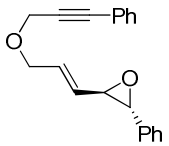


To a flame-dried 100 mL Schlenk flask a solution of NaH (60 wt % in mineral oil, 1.3 equiv.) in THF was added a solution of alcohol II (1.0 equiv.) in THF at 0 °C. After the solution was stirred for 30 min, the resultant solution was stirred at room temperature for 1 h. Then the solution was cooled to 0 °C, then propargyl bromide VII (1.3 equiv.) in THF was added and the mixture was stirred at room temperature overnight. Quenching with water, extraction with Et_2O, drying over $MgSO_4$, evaporation, and

purification by flash column chromatography (hexanes/EtOAc = 10:1) provided product VIII as a yellow oil.

Physical data for vinyl epoxide-alkyne substrates:

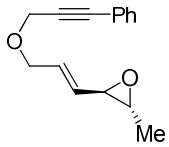
Substrate 1k



Yellow oil. R_f = 0.42 (hexanes/EtOAc = 10:1). 28% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (broad s, 2H), 7.35-7.25 (m, 8H), 6.09-6.02 (m, 1H), 5.68 (dd, *J* = 16.0 and 7.6 Hz, 1H), 4.38 (s, 2H), 4.16 (d, *J* = 5.6 Hz, 2H), 3.76 (broad s, 1H), 3.37 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.8 (C), 131.6 (CH), 131.2 (CH), 130.1 (CH), 128.4 (CH), 128.2 (CH), 128.1 (CH), 125.3 (CH), 122.4 (C), 86.4 (C), 84.7 (C), 69.0 (CH_2), 62.0 (CH), 60.1 (CH_2), 58.0 (CH). IR (neat): *v* = 2919, 2810, 2237, 1601, 1491, 1458, 1356, 1256, 1071, 965, 874, 754, 693 cm^{-1}; MS (EI, 70 ev) m/z (%): 290 (M^+, 1.10), 115 (100). HRMS calcd for $C_{20}H_{18}O_2$: 290.1307, found: 290.1306.

Substrate 1l

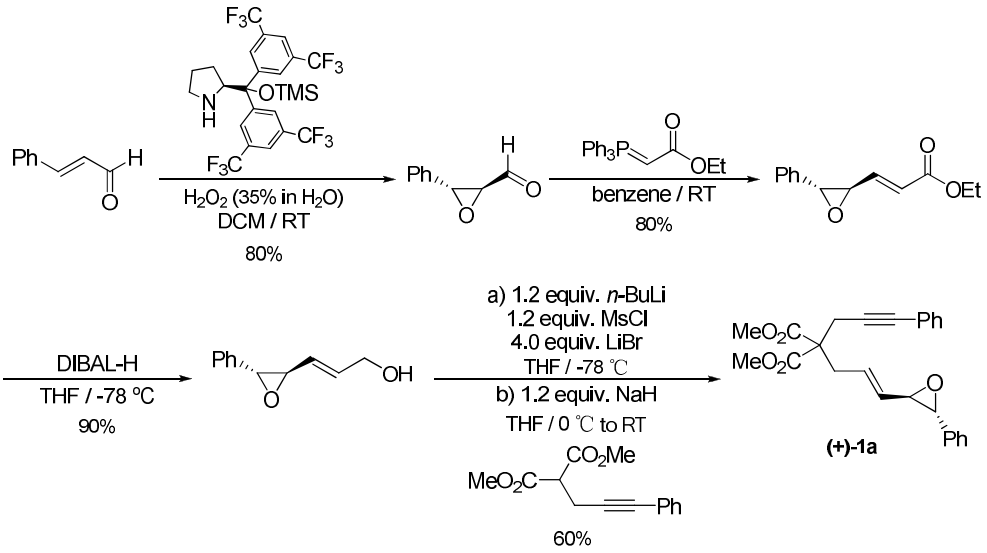


Yellow oil. R_f = 0.52 (hexanes/EtOAc = 5:1).72% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (broad s, 2H), 7.31 (broad s, 3H), 6.05-5.98 (m, 1H), 5.53 (dd, *J* = 15.6 and 8.0 Hz, 1H), 4.37 (s, 2H), 4.14 (d, *J* = 5.2 Hz, 2H), 3.09 (d, *J* = 8.0 Hz, 1H), 2.92-2.90 (m, 1H), 1.33 (d, *J* = 5.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.7 (CH), 131.1 (CH), 130.6 (CH), 128.4 (CH), 128.2 (CH), 122.5 (C), 86.3 (C), 84.8 (C), 69.2 (CH_2), 58.6 (CH), 58.0 (CH_2), 56.3 (CH), 17.4

(CH_3). IR (neat): *v* 2987, 2850, 2238, 1599, 1490, 1443, 1073, 965, 854, 757, 692 cm^{-1}. MS (EI): m/z (%) = 227 ($(M-H)^+$, 0.84), 43 (100). HRMS calcd for $C_{15}H_{16}O_2$: 228.1150, found: 228.1152.

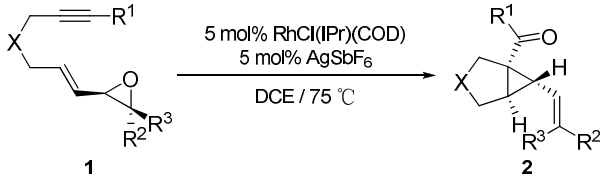
2.5 Synthesis of Optically Active Substrate (+)-1a



Cinnamic aldehyde was converted to (2*S*,3*R*)-3-Phenyl-oxirane-2-carbaldehyde following the asymmetric epoxidation procedure of Jørgensen et al.[7] (2*S*,3*R*)-3-Phenyl-oxirane-2-carbaldehyde was converted to crude (*E*)-ethyl 3-((2*R*,3*R*)-3-phenyloxiran-2-yl)acrylate following the general procedure for the preparation of alkene derivatives by a Wittig reaction.[8] Crude (*E*)-ethyl 3-((2*R*,3*R*)-3-phenyloxiran-2-yl)acrylate was reduced to crude (*E*)-3-((2*R*,3*R*)-3-phenyloxiran-2-yl) prop-2-en-1-ol following the general procedure for synthesis of racemic vinylic oxiranes alcohols. Crude (*E*)-3-((2*R*,3*R*)-3-phenyloxiran-2-yl)prop-2-en-1-ol was converted to (+)-1a (30% overall yield for 4 steps) following the general procedure for synthesis of racemic geminal diester-tether substrates.

(+)-1a: 90% ee. $[\alpha]^{20}_D$ = + 71.5° (*c* 1.0, $CHCl_3$). The ee was determined on a Daicel Chiralcel AD column with hexane/2-propanol = 80/20, flow = 0.8 mL/min. Retention times: 12.2 min, 15.6 min.

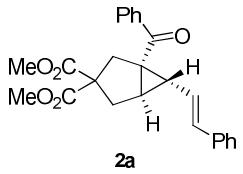
2.6 General Procedure for Rh(NHC)-Catalyzed Tandem Intramolecular Hetero-[5+2] Cycloaddition/Claisen Rearrangement Reaction of Vinylic Oxiranes-Alkyne Substrates 1.



1 2

A mixture of RhCl(IPr)(COD) (7.0 mg, 0.01 mmol, 5 mol %) and $AgSbF_6$ (3.4 mg, 0.01 mmol, 5 mol %) in DCE (1 mL) was stirred at room temperature under nitrogen for 30 min. A solution of vinylic oxiranes-alkyne substrates **1** (0.2 mmol) in DCE (1.5 mL) was added to this mixture at room temperature, and the resulting mixture was then stired at 75 ^{o}C until the reaction was complete (monitored by TLC). After evaporation, the residue was purified by column chromatography on silica gel (hexanes/EtOAc = 10:1 to 5:1) to afford the desired product.

(1*S,5*R**,6*R**)-dimethyl 1-benzoyl-6-styrylbicyclo[3.1.0]hexane-3,3-dicarboxylate (2a).**

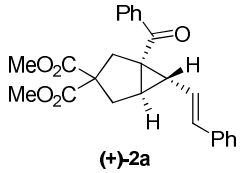


2a

Colorless oil. R_f = 0.38 (hexanes/EtOAc = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 7.2 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.20-7.19 (m, 4H), 7.14-7.11 (m, 1H), 6.55 (d, *J* = 15.6 Hz, 1H), 5.77 (dd, *J* = 15.6 and 9.6 Hz, 1H), 3.81 (s, 3H), 3.66 (s, 3H), 3.04 (d, *J* = 14.4 Hz, 1H), 2.80 (dd, *J* = 14.4 and 5.6 Hz, 1H), 2.70 (d, *J* = 14.4 Hz, 1H), 2.62 (d, *J* = 14.4 Hz, 1H), 2.48 (t, *J* = 5.2 Hz, 1H), 2.19 (dd, *J* = 8.8 and 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.3 (C), 172.7 (C), 171.5 (C), 138.2 (C), 136.9 (C), 132.5 (CH), 131.3 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 127.1 (CH), 125.9 (CH), 125.7 (CH), 61.5 (C), 53.09 (CH_3), 53.06 (CH_3), 46.6 (C), 40.3 (CH_2), 39.6 (CH), 35.8 (CH_2), 32.0 (CH). IR (neat): *v* 2953, 1731, 1667,

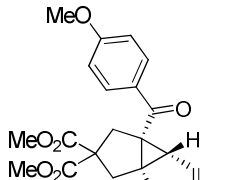
1598, 1435, 1251, 1200, 1067, 965, 749, 757, 693 cm^{-1}. MS (EI): m/z (%) = 404 (M^+, 2.97), 105 (100). HRMS calcd for $C_{25}H_{24}O_5$: 404.1624, found: 404.1624.



(+)-2a

(+)-2a: 94% ee. $[\alpha]^{20}_D$ = + 131.8° (*c* 1.0, $CHCl_3$). The ee was determined on a Daicel Chiralcel OD column with hexane/2-propanol = 90/10, flow = 0.8 mL/min. Retention times: 14.9 min, 17.9 min.

(1*S,5*R**,6*R**)-dimethyl1-(4-methoxybenzoyl)-6-styrylbicyclo[3.1.0]hexane-3,3-dicarboxylate (2b).**

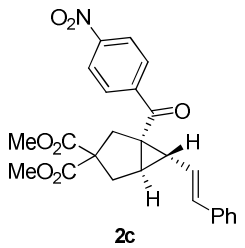


2b

White solid. m.p. 99-102 ^oC. R_f = 0.24 (hexanes/EtOAc = 5:1).

^1H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.18-7.12 (m, 5H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.52 (d, *J* = 15.6 Hz, 1H), 5.70 (dd, *J* = 15.6 and 9.6 Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.67 (s, 3H), 3.07 (d, *J* = 14.4 Hz, 1H), 2.81 (dd, *J* = 14.4 and 5.6 Hz, 1H), 2.70 (d, *J* = 14.4 Hz, 1H), 2.61 (d, *J* = 14.4 Hz, 1H), 2.42 (broad s, 1H), 2.13 (dd, *J* = 9.6 and 4.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2 (C), 172.7 (C), 171.4 (C), 163.2 (C), 136.9 (C), 131.01 (CH), 130.96 (CH), 130.7 (C), 128.3 (CH), 127.0 (CH), 126.1 (CH), 125.8 (CH), 113.7 (CH), 61.4 (C), 55.3 (CH_3), 53.0 (CH_3), 52.9 (CH_3), 46.1 (C), 40.5 (CH_2), 38.4 (CH), 35.7 (CH_2), 31.3 (CH). IR (neat): *v* 2952, 2926, 2854, 1727, 1640, 1601, 1438, 1251, 1171, 1074, 969, 752, 695 cm^{-1}. MS (EI): m/z (%) = 434 (M^+, 1.88), 135 (100). HRMS calcd for $C_{26}H_{26}O_6$: 434.1729, found: 434.1729.

(1*S,5*R**,6*R**)-dimethyl 1-(4-nitrobenzoyl)-6-styrylbicyclo[3.1.0]hexane-3,3-dicarboxylate (2c).**

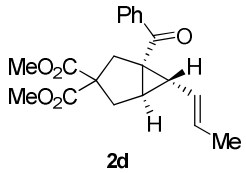


2c

Yellow oil. R_f = 0.23 (hexanes/EtOAc = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.21-7.14 (m, 5H), 6.58 (d, *J* = 15.6 Hz, 1H), 5.77 (dd, *J* = 15.6 and 9.6 Hz, 1H), 3.81 (s, 3H), 3.68 (s, 3H), 2.96 (d, *J* = 14.0 Hz, 1H), 2.81 (dd, *J* = 14.8 and 5.2 Hz, 1H), 2.67 (d, *J* = 15.6 Hz, 1H), 2.58 (d, *J* = 15.6 Hz, 1H), 2.55 (t, *J* = 5.2 Hz, 1H), 2.29 (dd, *J* = 9.2 and 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0 (C), 172.3 (C), 171.3 (C), 149.9 (C), 143.2 (C), 136.6 (C), 132.2 (CH), 129.3 (CH), 128.5 (CH), 127.4 (CH), 126.0 (CH), 124.7 (CH), 123.8 (CH), 61.7 (C), 53.20 (CH_3), 53.18 (CH_3), 46.9 (C), 41.2 (CH_2), 39.8 (CH), 35.8 (CH_2), 32.9 (CH). IR (neat): *v* 2955, 2854, 1732, 1675, 1603, 1525, 1347, 1254, 1203, 1068, 849, 750, 693 cm^{-1}. MS (EI): m/z (%) = 449 (M^+, 8.05), 104 (100). HRMS calcd for $C_{25}H_{23}NO_7$: 449.1475, found: 449.1477.

(1*S,5*R**,6*R**)-dimethyl1-benzoyl-6-((*E*)-prop-1-enyl)bicyclo[3.1.0]hexane-3,3-dicarboxylate (2d).**



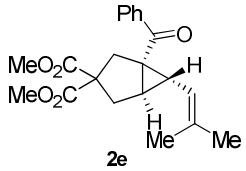
2d

Colorless oil. R_f = 0.34 (hexanes/EtOAc = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 2H), 5.66-5.58 (m, 1H), 5.01 (dd, *J* = 14.8 and 9.2 Hz, 1H), 3.77 (s, 3H), 3.65 (s, 3H), 2.95 (d, *J* = 14.0 Hz, 1H), 2.73 (dd, *J* = 14.4 and 4.8 Hz, 1H), 2.64 (d, *J* = 14.4 Hz, 1H), 2.55 (d, *J* = 14.0 Hz, 1H), 2.29 (broad s, 1H), 1.98-1.95 (m, 1H), 1.54 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.4 (C),

172.6 (C), 171.5 (C), 138.4 (C), 132.4 (CH), 128.6 (CH), 128.4 (CH), 127.4 (CH), 126.3 (CH), 61.6 (C), 53.0 (CH_3), 45.8 (C), 40.3 (CH), 39.2 (CH_2), 35.8 (CH_2), 30.9 (CH), 17.8 (CH_3). IR (neat): *v* 3029, 2955, 2852, 1733, 1669, 1598, 1436, 1252, 1202, 1067, 967, 722, 635 cm^{-1}. MS (EI): m/z (%) = 342 (M^+, 2.47), 105 (100). HRMS calcd for $C_{20}H_{22}O_5$: 342.1467, found: 342.1467.

(1*S,5*R**,6*R**)-dimethyl1-benzoyl-6-(2-methylprop-1-enyl)bicyclo[3.1.0]hexane-3,3-dicarboxylate (2e).**

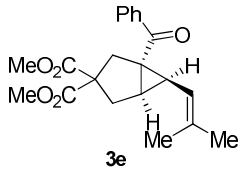


2e

Colorless oil. R_f = 0.29 (hexanes/EtOAc = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 2H), 4.71 (d, *J* = 8.8 Hz, 1H), 3.78 (s, 3H), 3.65 (s, 3H), 2.99 (d, *J* = 14.0 Hz, 1H), 2.73 (dd, *J* = 14.0 and 5.2 Hz, 1H), 2.64 (d, *J* = 14.0 Hz, 1H), 2.57 (d, *J* = 14.0 Hz, 1H), 2.28-2.25 (m, 1H), 2.12 (dd, *J* = 8.8 and 5.2 Hz, 1H), 1.73 (s, 3H), 1.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.7 (C), 172.8 (C), 171.6 (C), 138.6 (C), 134.5 (C), 132.3 (CH), 128.6 (CH), 128.3 (CH), 120.1 (CH), 61.6 (C), 53.0 (CH_3), 45.7 (C), 40.3 (CH_2), 35.9 (CH_2), 35.6 (CH), 31.7 (CH), 25.4 (CH_3), 18.4 (CH_3). IR (neat): *v* 2955, 2923, 1732, 1669, 1598, 1436, 1251, 1201, 1174, 1069, 950, 850, 722, 697 cm^{-1}. MS (EI): m/z (%) = 356 (M^+, 5.45), 105 (100). HRMS calcd for $C_{21}H_{24}O_5$: 356.1624, found: 356.1624.

(1*S,5*R**,6*S**)-dimethyl 1-benzoyl-6-(2-methylprop-1-enyl)bicyclo[3.1.0]hexane-3,3-dicarboxylate (3e).**

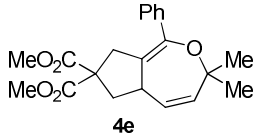


3e

Colorless oil. R_f = 0.29 (hexanes/EtOAc = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 7.2 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 2H), 5.10 (d, *J* = 7.2 Hz, 1H), 3.70 (s, 3H), 3.65 (s, 3H), 2.87 (d, *J* = 14.0 Hz, 1H), 2.73-2.69 (m, 1H), 2.61 (dd, *J* = 14.4 and 6.8 Hz, 1H), 2.48 (d, *J* = 14.4 Hz, 1H), 2.40-2.33 (m, 2H), 1.86 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.3 (C), 172.4 (C), 170.7 (C), 140.3 (C), 138.2 (C), 131.8 (CH), 128.3 (CH), 128.1 (CH), 115.7 (CH), 67.5 (C), 53.0 (CH_3), 52.7 (CH_3), 46.9 (C), 38.4 (CH), 35.7 (CH_2), 33.5 (CH), 32.1 (CH_2), 26.0 (CH_3), 19.0 (CH_3). IR (neat): *v* 2955, 2929, 1733, 1663, 1580, 1436, 1253, 1201, 1176, 1073, 903, 854, 723, 698 cm^{-1}. MS (EI): m/z (%) = 356 (M^+, 3.64), 41 (100). HRMS calcd for $C_{21}H_{24}O_5$: 356.1624, found: 356.1627.

Dimethyl 3,3-dimethyl-1-phenyl-5a,6-dihydro-3H-cyclopenta[c]oxepine-7,7(8H)-dicarboxylate (4e).



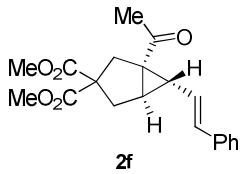
4e

Colorless oil. R_f = 0.57 (hexanes/EtOAc = 5:1).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 5.35 (d, *J* = 11.6 Hz, 1H), 5.27 (d, *J* = 12.0 Hz, 1H), 3.88-3.83 (m, 1H), 3.64 (s, 3H), 3.55 (s, 3H), 3.22 (d, *J* = 16.8 Hz, 1H), 3.05 (d, *J* = 16.8 Hz, 1H), 2.68-2.63 (m, 1H), 1.85 (t, *J* = 12.4 Hz, 1H), 1.32 (s, 3H), 1.01 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 171.2 (C), 170.9 (C), 144.8 (C), 138.8 (C), 135.3 (CH), 132.0 (C), 127.6 (CH), 126.7 (CH), 126.5 (CH), 126.3 (CH), 77.5 (C), 59.3 (C), 52.4 (CH_3), 40.5 (CH_2), 39.4 (CH), 38.6 (CH_2), 29.7 (CH_3), 26.5 (CH_3). IR (neat): *v* 3008, 2956, 2927, 1733, 1435, 1253,

1196, 1172, 1092, 938, 783, 699 cm^{-1}. MS (EI): m/z (%) = 356 (M^+, 7.30), 105 (100). HRMS calcd for $C_{21}H_{24}O_5$: 356.1624, found: 356.1627.

(1*S,5*R**,6*R**)-dimethyl 1-acetyl-6-styrylbicyclo[3.1.0]hexane-3,3-dicarboxylate (2f).**

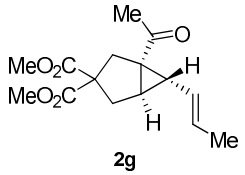


2f

Colorless oil. R_f = 0.18 (hexanes/EtOAc = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.24 (m, 4H), 7.17 (t, *J* = 6.8 Hz, 1H), 6.46 (d, *J* = 15.6 Hz, 1H), 6.03 (dd, *J* = 15.6 and 8.8 Hz, 1H), 3.80 (s, 3H), 3.73 (s, 3H), 2.93 (broad s, 2H), 2.64 (broad s, 2H), 2.30 (broad s, 1H), 2.25 (s, 3H), 1.92 (dd, *J* = 8.8 and 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.0 (C), 172.6 (C), 171.6 (C), 137.0 (C), 131.4 (CH), 128.4 (CH), 127.1 (CH), 125.9 (CH), 125.5 (CH), 60.5 (C), 53.2 (CH_3), 53.1 (CH_3), 47.7 (C), 39.6 (CH_2), 38.1 (CH), 35.7 (CH_2), 34.7 (CH), 29.8 (CH_3). IR (neat): *v* 2999, 2958, 1730, 1688, 1435, 1371, 1251, 1203, 1062, 964, 750, 693 cm^{-1}. MS (EI): m/z (%) = 342 (M^+, 0.79), 77 (100). HRMS calcd for $C_{20}H_{22}O_5$: 342.1467, found: 342.1469.

(*1S*,5R*,6R)-dimethyl 1-acetyl-6-((*E*)-prop-1-enyl)bicyclo[3.1.0]hexane-3,3-dicarboxylate(2g).**



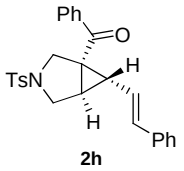
2g

Colorless oil. R_f = 0.18 (hexanes/EtOAc = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.55 (dq, *J* = 15.2 and 6.4 Hz, 1H), 5.24 (ddq, *J* = 15.2, 8.4 and 1.6 Hz, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 2.86 (s, 2H), 2.57 (d, *J* = 3.6 Hz, 2H), 2.22 (s, 3H), 2.13 (dt, *J* = 5.2 and 3.6 Hz,1H), 1.71 (dd, *J* = 8.4 and 5.2 Hz, 1H), 1.63 (dd, *J* = 6.4 and 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.2 (C), 172.6 (C), 171.7 (C), 127.6 (CH), 126.1 (CH), 60.7 (C), 53.1 (CH_3), 52.9 (CH_3), 47.1 (C), 39.1 (CH), 38.2 (CH_2), 35.8 (CH_2), 33.8 (CH), 29.7 (CH_3), 17.9 (CH_3). IR (neat): *v* 2888, 1732,

1689, 1435, 1367, 1160, 1079, 968 cm^{-1}. MS (ESI): m/z (%) = 281.1 [(M+H)]. HRMS (ESI) calcd for $C_{15}H_{21}O_5$ [(M+H)]: 281.13835, found: 281.13911.

Phenyl((1*R,5*R**,6*R**)-6-styryl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methanone (2h).**

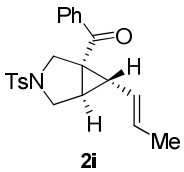


2h

White solid. m.p. 163-166 ^oC. R_f = 0.36 (hexanes/EtOAc = 5:1).

^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 6.8 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.19-7.13 (m, 5H), 6.58 (d, *J* = 16.0 Hz, 2H), 5.77 (dd, *J* = 16.0 and 9.2 Hz, 1H), 4.12 (d, *J* = 9.6 Hz, 1H), 3.75 (d, *J* = 9.6 Hz, 1H), 3.19-3.17 (m, 1H), 3.12 (d, *J* = 9.6 Hz, 1H), 2.58 (dd, *J* = 9.6 and 4.4 Hz, 1H), 2.48 (broad s, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.9 (C), 143.9 (C), 137.6 (C), 136.5 (C), 133.2 (CH), 132.5 (C), 132.4 (CH), 129.8 (CH), 128.7 (CH), 128.4 (CH), 128.3 (CH), 127.5 (CH), 127.3 (CH), 126.0 (CH), 123.8 (CH), 51.6 (CH_2), 49.1 (CH_2), 43.8 (C), 34.7 (CH), 29.3 (CH), 21.4 (CH_3). IR (neat): *v* 2923, 2850, 1669, 1598, 1343, 1166, 1097, 957, 749, 738, 696, 666 cm^{-1}. MS (EI): m/z (%) = 443 (M^+, 6.69), 105 (100). HRMS calcd for $C_{27}H_{25}NO_3S$: 443.1555, found: 443.1556.

Phenyl((1*R,5*R**,6*R**)-6-((*E*)-prop-1-enyl)-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methanone (2i).**



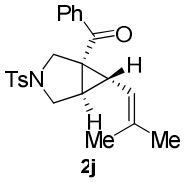
2i

White solid. m.p. 105-107 ^oC. R_f = 0.37 (hexanes/EtOAc = 5:1).

^1H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.2 Hz, 2H), 7.63-7.56 (m, 3H), 7.48-7.46 (m, 2H), 7.30 (d, *J* = 7.2 Hz, 2H), 5.70-5.64 (m, 1H), 5.04-4.99 (m, 1H), 4.04 (d, *J* = 9.2 Hz, 1H), 3.68 (d, *J* = 9.2 Hz, 1H), 3.14-3.12 (m, 1H), 3.05 (d, *J* = 8.8 Hz, 1H), 2.42 (s, 3H), 2.39-2.37 (m, 1H), 2.31 (broad s, 1H), 1.55 (d, *J* = 4.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0 (C), 143.9 (C), 137.9 (C), 133.1 (CH), 132.8 (C),

129.8 (CH), 128.70 (CH), 128.67 (CH), 128.4 (CH), 127.5 (CH), 124.7 (CH), 51.6 (CH_2), 49.2 (CH_2), 43.2 (C), 34.1 (CH), 28.4 (CH), 21.4 (CH_3), 17.9 (CH_3). IR (neat): *v* 2924, 2855, 1729, 1670, 1598, 1348, 1163, 1023, 963, 700, 666 cm^{-1}. MS (EI): m/z (%) = 381 (M^+, 0.47), 105 (100). HRMS calcd for $C_{22}H_{23}NO_3S$: 381.1399, found: 381.1400.

((1*R,5*R**,6*R**)-6-(2-methylprop-1-enyl)-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)(phenyl)methanone (2j).**

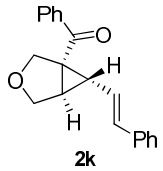


2j

White solid. m.p. 156-158 ^oC. R_f = 0.37 (hexanes/EtOAc = 5:1).

^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.6 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 6.8 Hz, 1H), 7.46 (t, *J* = 6.8 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 4.68 (d, *J* = 9.2 Hz, 1H), 4.06 (d, *J* = 9.2 Hz, 1H), 3.69 (d, *J* = 9.2 Hz, 1H), 3.16 (d, *J* = 9.2 Hz, 2H), 3.10 (d, *J* = 9.2 Hz, 1H), 2.42 (s, 4H), 2.26 (broad s, 1H), 1.71 (s, 3H), 1.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2 (C), 143.8 (C), 137.9 (C), 135.8 (C), 133.0 (CH), 132.8 (C), 129.8 (CH), 128.6 (CH), 128.4 (CH), 127.5 (CH), 118.3 (CH), 51.7 (CH_2), 49.3 (CH_2), 43.2 (C), 30.7 (CH), 29.3 (CH), 25.5 (CH_3), 21.4 (CH_3), 18.4 (CH_3). IR (neat): *v* 2974, 2925, 2850, 1659, 1598, 1348, 1162, 1096, 1022, 963, 702, 665 cm^{-1}. MS (EI): m/z (%) = 395 (M^+, 0.88), 105 (100). HRMS calcd for $C_{23}H_{25}NO_3S$: 395.1555, found: 395.1558.

Phenyl((1*R,5*R**,6*R**)-6-styryl-3-oxabicyclo[3.1.0]hexan-1-yl)methanone (2k).**

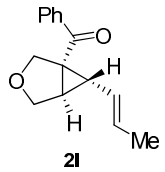


2k

Colorless oil. R_f = 0.33 (hexanes/EtOAc = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.25-7.15 (m, 5H), 6.61 (d, *J* = 16.0 Hz, 1H), 5.95 (dd, *J* = 15.2 and 9.6 Hz, 1H), 4.34 (d, *J* = 8.4 Hz, 1H), 4.03 (d, *J* = 8.4 Hz, 1H), 3.92 (d, *J* = 8.4 Hz, 1H), 3.84 (d, *J* = 8.4 Hz, 1H), 2.63 (broad s, 1H), 2.47-2.44 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.4 (C), 138.6 (C), 136.9 (C), 133.0 (CH), 131.6 (CH), 128.6 (CH), 128.4 (CH), 128.3 (CH), 127.2 (CH), 126.0 (CH), 124.8 (CH), 71.2 (CH_2), 69.3 (CH_2), 46.0 (C), 34.7 (CH), 31.9 (CH). IR (neat): *v* = 3027, 2925, 2859, 1665, 1598, 1448, 1240, 1071, 960, 750, 692 cm^{-1}; MS (EI, 70 ev) m/z (%): 290 (M^+, 2.82), 105 (100). HRMS calcd for $C_{20}H_{18}O_2$: 290.1307, found: 290.1307.

Phenyl((1*R,5*R**,6*R**)-6-((*E*)-prop-1-enyl)-3-oxabicyclo[3.1.0]hexan-1-yl)methanone (2l).**



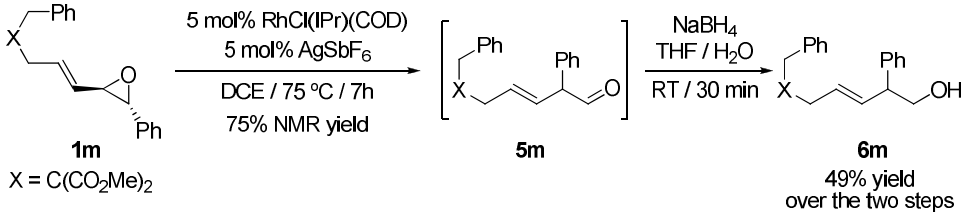
2l

Colorless oil. R_f = 0.35 (hexanes/EtOAc = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 2H), 5.73-5.64 (m, 1H), 5.18 (dd, *J* = 14.8 and 9.6 Hz, 1H), 4.26 (d, *J* = 8.4 Hz, 1H), 3.96 (d, *J* = 8.4 Hz, 1H), 3.86 (d, *J* = 8.0 Hz, 1H), 3.78 (d, *J* = 8.4 Hz, 1H), 2.45 (broad s, 1H), 2.26-2.22 (m, 1H), 1.58 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5 (C), 138.7 (C), 132.8 (CH), 128.6 (CH), 128.3 (CH), 127.7 (CH), 125.4 (CH), 71.1 (CH_2), 69.3 (CH_2), 45.3 (C), 34.1 (CH), 30.9 (CH), 17.9 (CH_3). IR

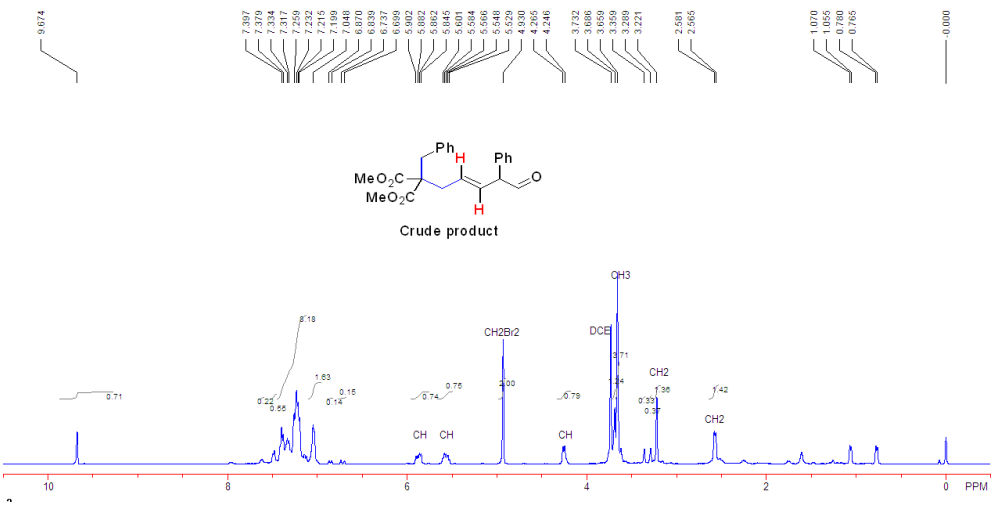
(neat): *v* 2964, 2857, 1668, 1598, 1448, 1287, 1240, 1055, 961, 802, 717, 638 cm^{-1}. MS (EI): m/z (%) = 227 ($(M-H)^+$, 0.22), 43 (100). HRMS calcd for $C_{15}H_{16}O_2$: 228.1150, found: 228.1150.

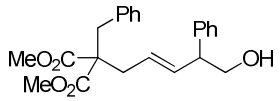
2.7 General Procedure for rearrangement of 1m.



A mixture of RhCl(IPr)(COD) (7.0 mg, 0.01 mmol, 5 mol %) and $AgSbF_6$ (3.4 mg, 0.01 mmol, 5 mol %) in DCE (1 mL) was stirred at room temperature under nitrogen for 30 min. A solution of **1m** (0.0761g, 0.2 mmol) in DCE (1.5 mL) was added to this mixture at room temperature, and the resulting mixture was then stired at 75 ^oC for 7 h. After evaporation, 0.6 mL THF-H_2O (3:0.1) and $NaBH_4$ (3.8 mg, 0.1 mmol) was added. The resulting mixture was stirred at room temperature under nitrogen for 30 min. After completion of the reaction, distilled water (2 mL) was added to the reaction mixture and this solution was then stirred for an additional 5 min. The mixture was extracted with CH_2Cl_2 (3×8 mL) and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (hexanes/EtOAc = 2:1) to afford the desired product.

Note: Aldehyde derivative **5m** is unstable and easy to undergo further isomerization. So **5m** is converterted in siu into the corresponding alcohols **6m** by reduction.



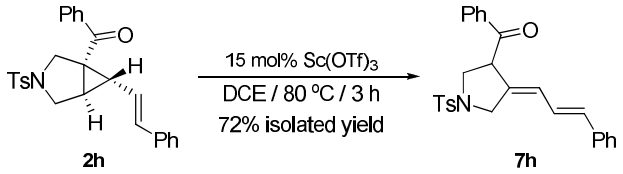


6m

Colorless oil. R_f = 0.44 (hexanes/EtOAc = 2:1).

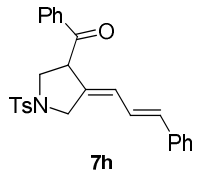
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.32 (m, 2H), 7.25-7.20 (m, 6H), 7.06-7.04 (m, 2H), 5.70-5.60 (m, 2H), 3.82-3.78 (m, 1H), 3.75-3.70 (m, 1H), 3.67 (s, 3H), 3.66 (s, 3H), 3.53-3.48 (m, 1H), 3.28-3.20 (m, 2H), 2.53 (d, *J* = 6.4 Hz, 2H), 1.73 (broad s, 1H),. ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4 (C), 171.1 (C), 140.8 (C), 135.6 (C), 134.9 (CH), 129.8 (CH), 128.7 (CH), 128.3 (CH), 127.7 (CH), 127.0 (CH), 126.9 (CH), 126.8 (CH), 66.1 (CH_2), 59.6 (C), 52.3 (CH_3), 52.2 (CH_3), 51.7 (CH), 38.5 (CH_2), 35.7 (CH_2). IR (neat): *v* 3542, 3029, 2951, 1729, 1495, 1436, 1277, 1199, 1047, 743, 700 cm^{-1}. MS (ESI): m/z (%) = 405.2 [(M+Na)]. HRMS (ESI) calcd for $C_{23}H_{26}Na_1O_5$ [(M+Na)]: 405.16725, found: 405.16840.

2.8 General Procedure for $Sc(OTf)_3$ Catalyzed Ring-Expansion Reaction of 2h.



2h **7h**

A mixture of $Sc(OTf)_3$ (4.8 mg, 0.01 mmol, 15 mol %) and 2g (31 mg, 0.07 mmol) was added DCE (1 mL) and then stirred at 80 ^{o}C for 3 hours. After evaporation, the residue was purified by column chromatography on silica gel (hexanes/EtOAc = 5:1) to afford the desired product.



7h

White solid. m.p. 192-194 ^{o}C. R_f = 0.44 (hexanes/EtOAc = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.78 (d, *J* = 7.2 Hz, 2H), 7.65 (t, *J* = 6.8 Hz, 1H), 7.53 (t, *J* = 6.8 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.33-7.24 (m, 5H), 6.61-6.54 (m, 1H), 6.34 (d, *J* = 15.2 Hz, 1H), 5.87 (d, *J* = 10.8 Hz, 1H), 4.69 (broad s, 1H), 4.38 (d, *J* = 14.4 Hz, 1H), 3.91 (d, *J* =

14.4 Hz, 1H), 3.82 (t, *J* = 8.0 Hz, 1H), 3.56 (t, *J* = 8.0 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.5 (C), 144.0 (C), 136.6 (C), 136.28 (C), 136.25 (C), 134.2 (CH), 133.8 (CH), 132.5 (C), 129.9 (CH), 129.0 (CH), 128.9 (CH), 128.7 (CH), 128.0 (CH), 127.9 (CH), 126.5 (CH), 125.1 (CH), 124.0 (CH), 50.6 (CH_2), 50.5 (CH_2), 49.8 (CH), 21.6 (CH_3). IR (neat): *v* 3068, 2976, 2873, 1683, 1596, 1447, 1333, 1159, 1071, 955, 819, 752, 700, 664 cm^{-1}. MS (EI): m/z (%) = 443 (M^+, 1.19), 91 (100). HRMS calcd for $C_{27}H_{25}NO_3S$: 443.1555, found: 443.1574.

3. Reference:

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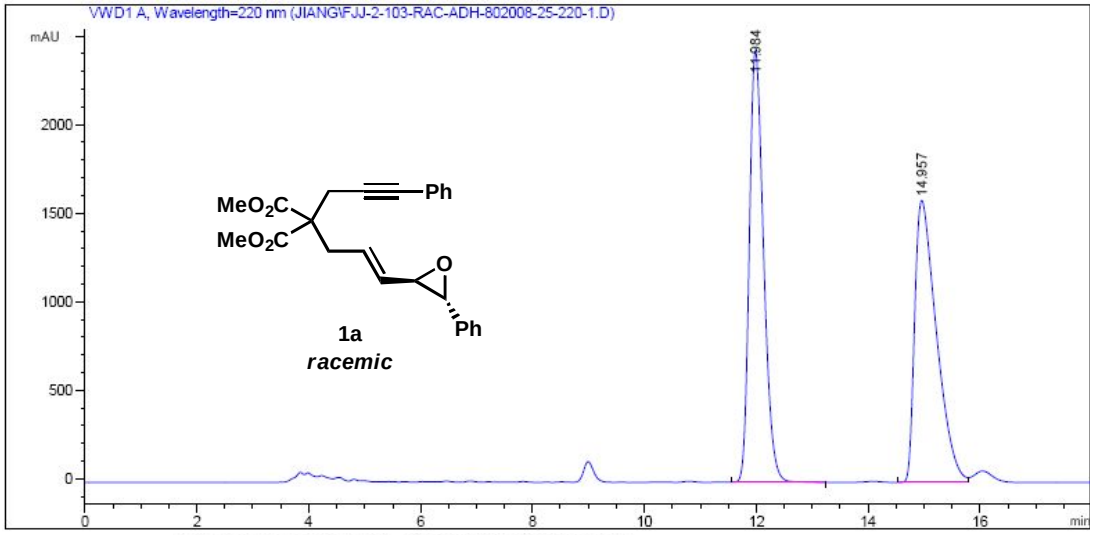
[7] Marigo, M.; Franzén, J.; Poulsen, T. B.; Zhuang, W.; Jørgensen, K. A. *J. Am. Chem. Soc.* **2005**, *127*, 6964.

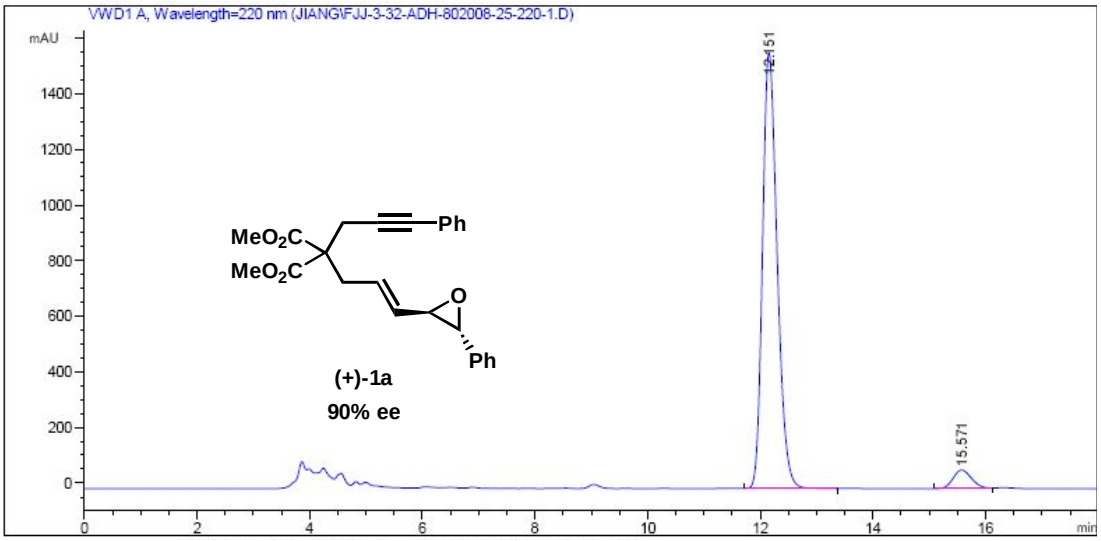
[8] Matsuo, J.-I.; Iida, D.; Yamanaka, H.; Mukaiyama, T. *Tetrahedron.* **2003**, *59*, 6739.

4. HPLC Diagrams for Enantiomeric Purity Determination



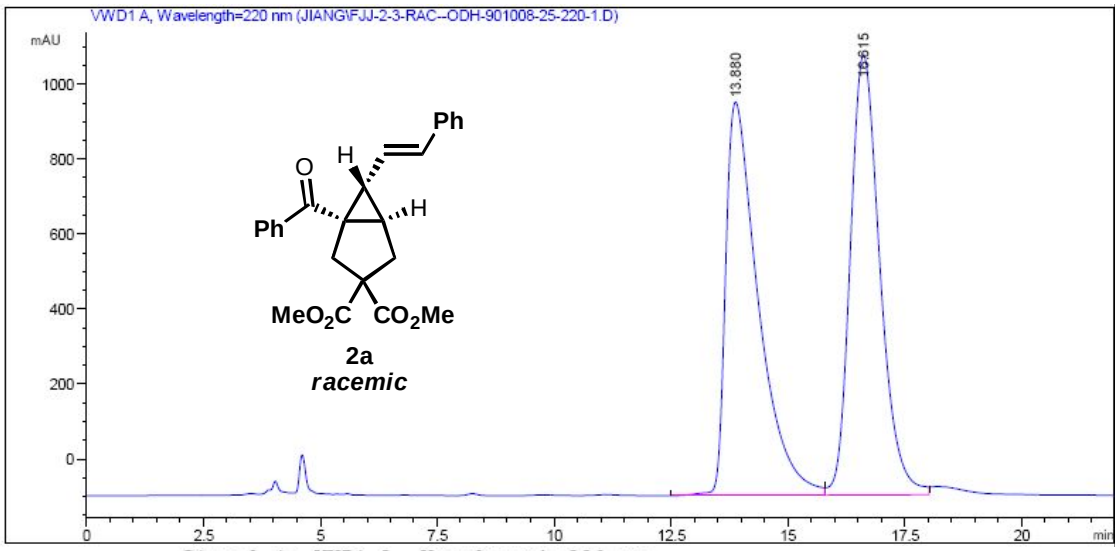
Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.984	VB	0.2739	4.31876e4	2435.54370	50.1201
2	14.957	VV	0.4080	4.29805e4	1592.89624	49.8799
Totals :				8.61681e4	4028.43994	



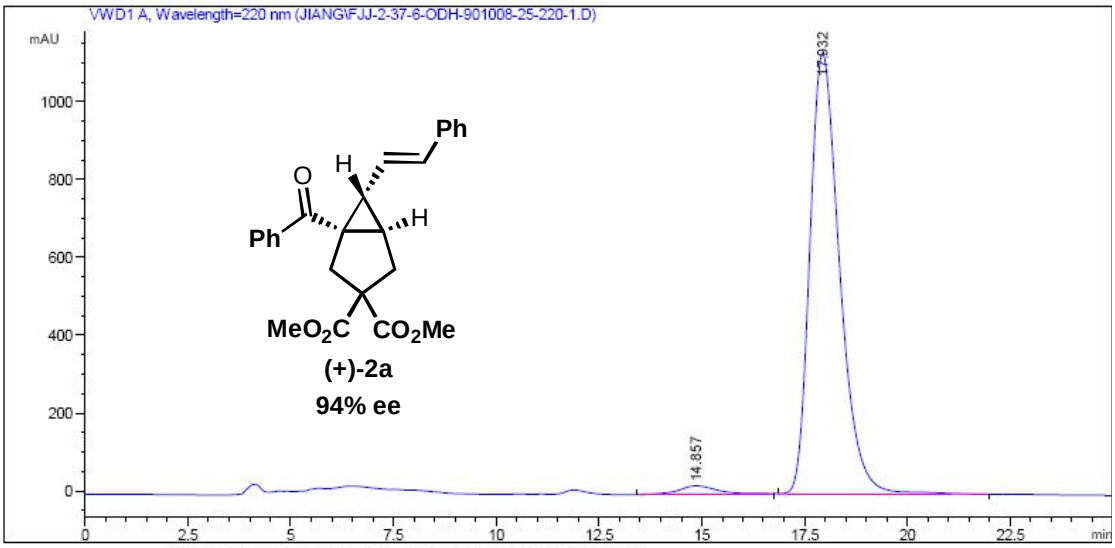
Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.151	VB	0.2790	2.83065e4	1568.49683	94.8008
2	15.571	BV	0.3605	1552.41406	67.02129	5.1992
Totals :				2.98589e4	1635.51811	



Signal 1: VWD1 A, Wavelength=220 nm

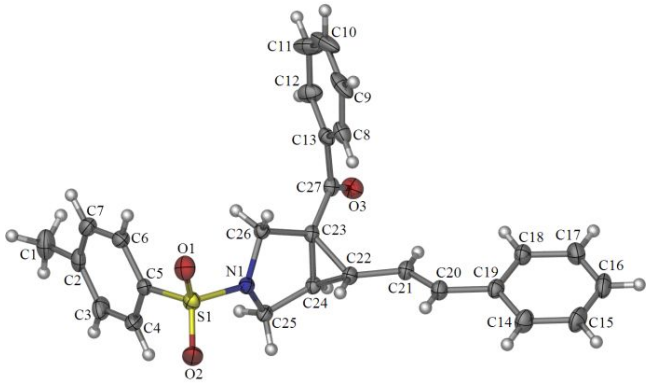
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.880	VV	0.7188	5.10697e4	1050.09229	49.5447
2	16.615	VV	0.6791	5.20083e4	1175.83289	50.4553
Totals :				1.03078e5	2225.92517	



Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.857	BB	1.0660	1667.10669	22.71294	2.8205
2	17.932	BB	0.7807	5.74401e4	1133.10596	97.1795
Totals :				5.91072e4	1155.81890	

5. Crystal Structure of Bicyclo [3.1.0]hexanes 2h



Bond precision:	C-C = 0.0035 A		Wavelength=0.71073
Cell:	a=12.7395(4)	b=5.5981(2)	c=32.0262(11)
	alpha=90	beta=96.383(1)	gamma=90
Temperature:	296 K		
	Calculated		Reported
Volume	2269.85(13)		2269.85(13)
Space group	P 21/c		P2(1)/c
Hall group	-P 2ybc		?
Moiety formula	C27 H25 N O3 S		?
Sum formula	C27 H25 N O3 S		C27 H25 N O3 S
Mr	443.55		443.54
Dx,g cm-3	1.298		1.298
Z	4		4
Mu (mm-1)	0.172		0.172
F000	936.0		936.0
F000'	936.89		
h,k,lmax	15,6,38		15,6,38
Nref	4002		3989
Tmin,Tmax	0.974,0.983		0.952,0.983
Tmin'	0.951		

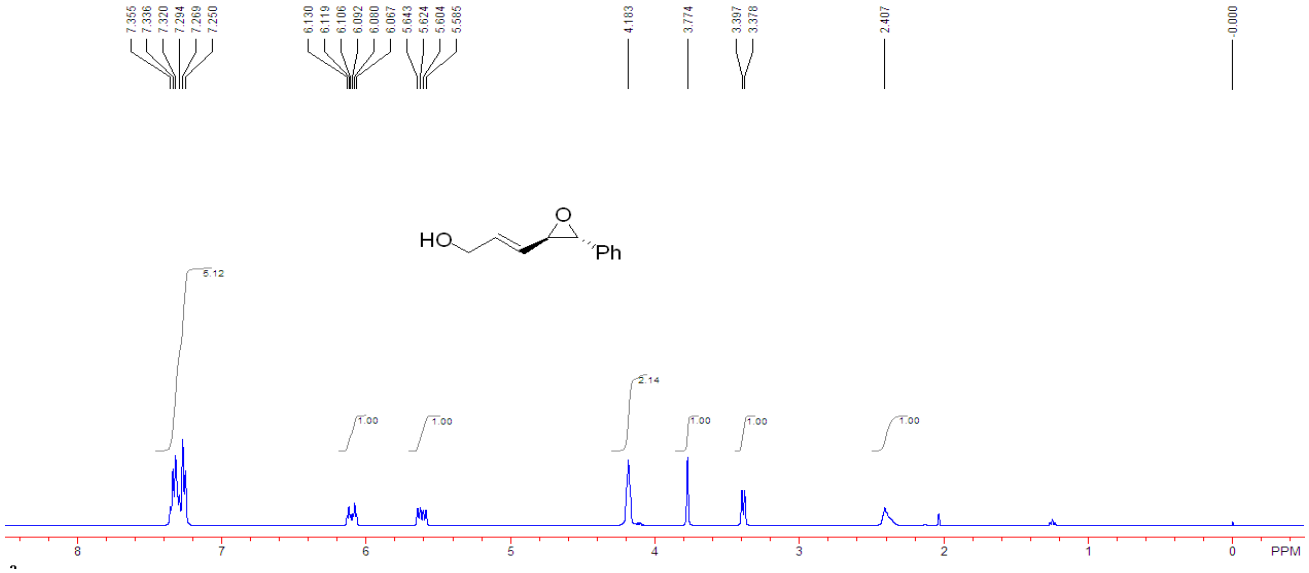
Correction method= MULTI-SCAN

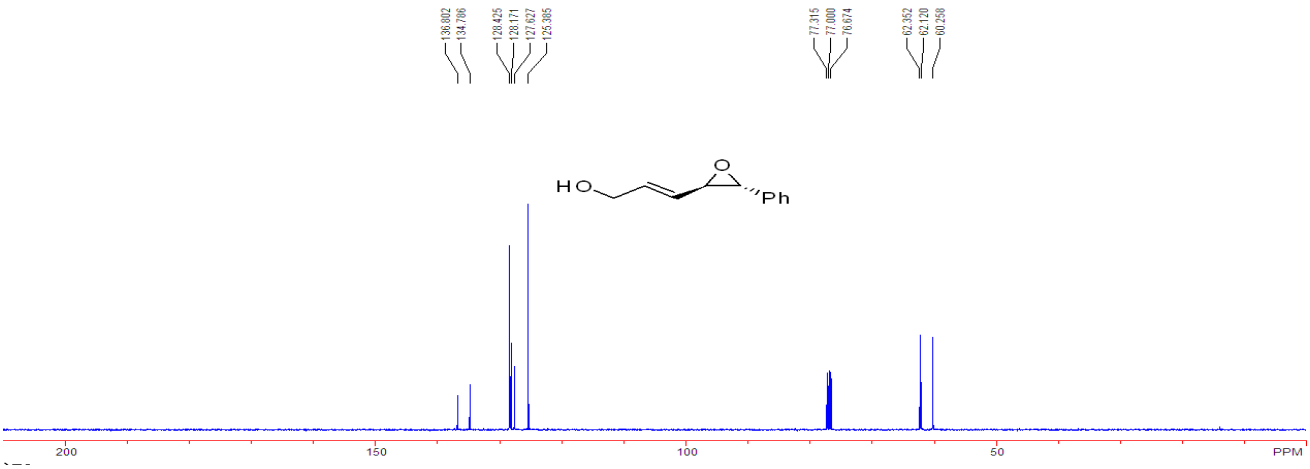
Data completeness= 0.997 Theta(max)= 25.010

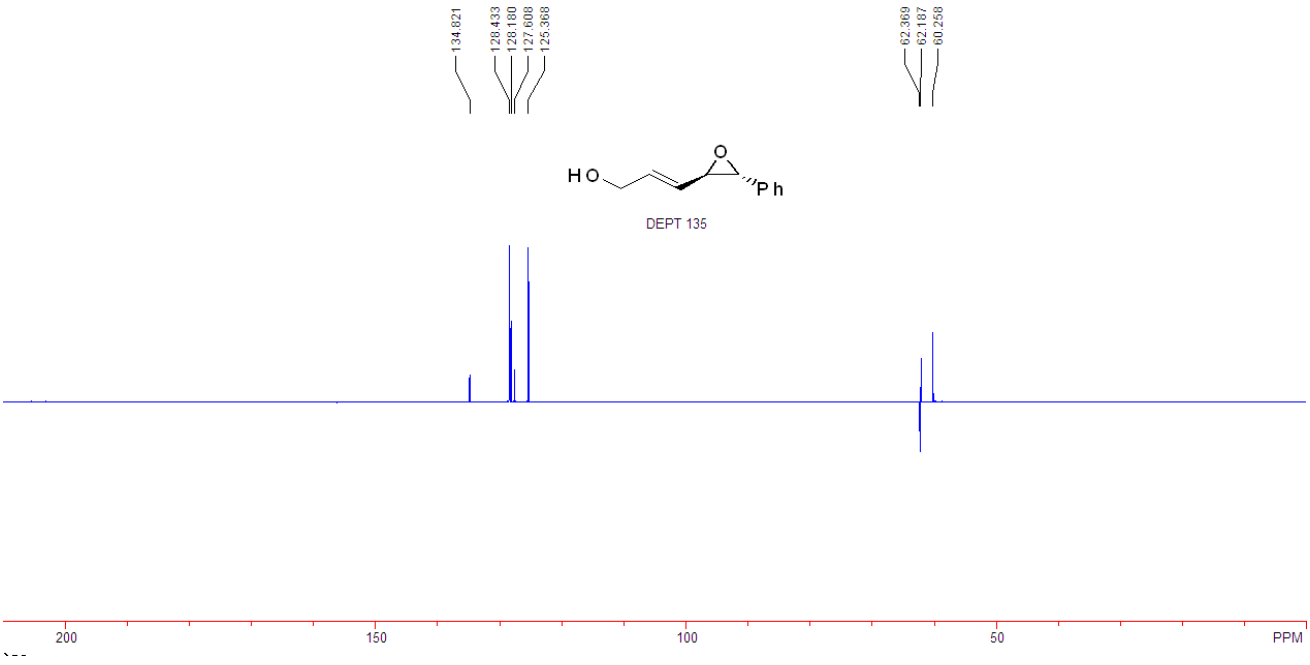
R(reflections)= 0.0416(3016) wR2(reflections)= 0.1097(3989)

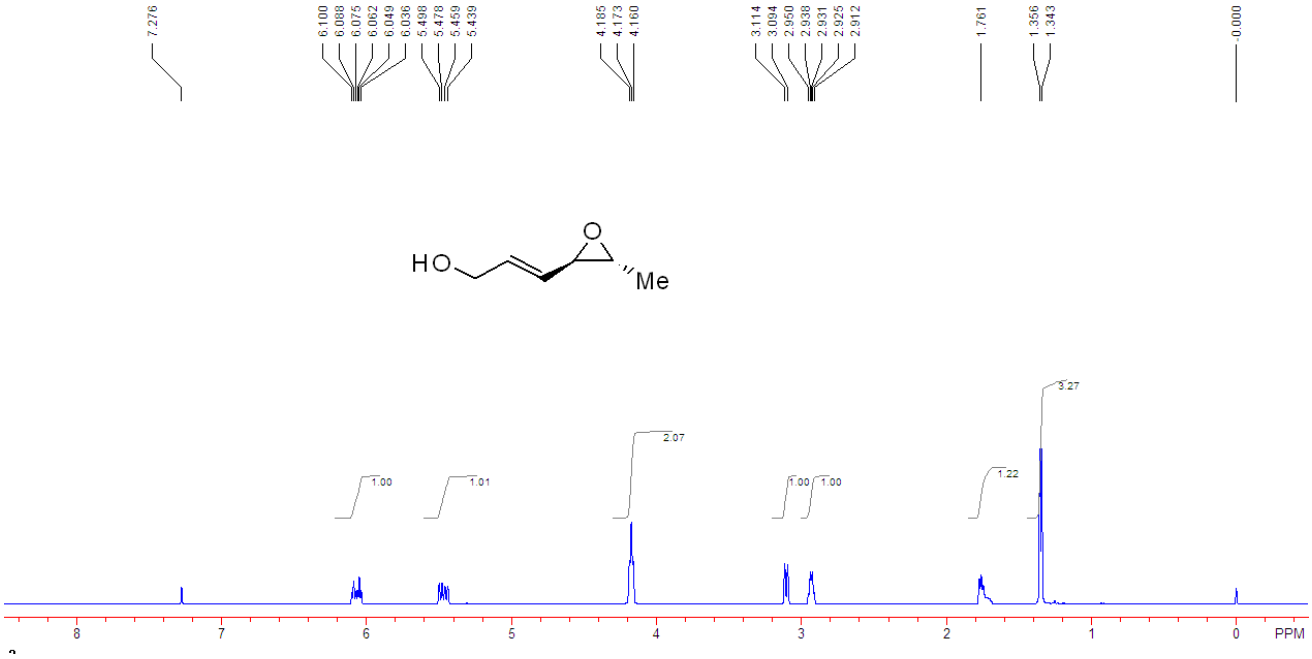
S = 1.027 Npar= 289

6. ^{1}H and ^{13}C NMR Spectra for New Compounds





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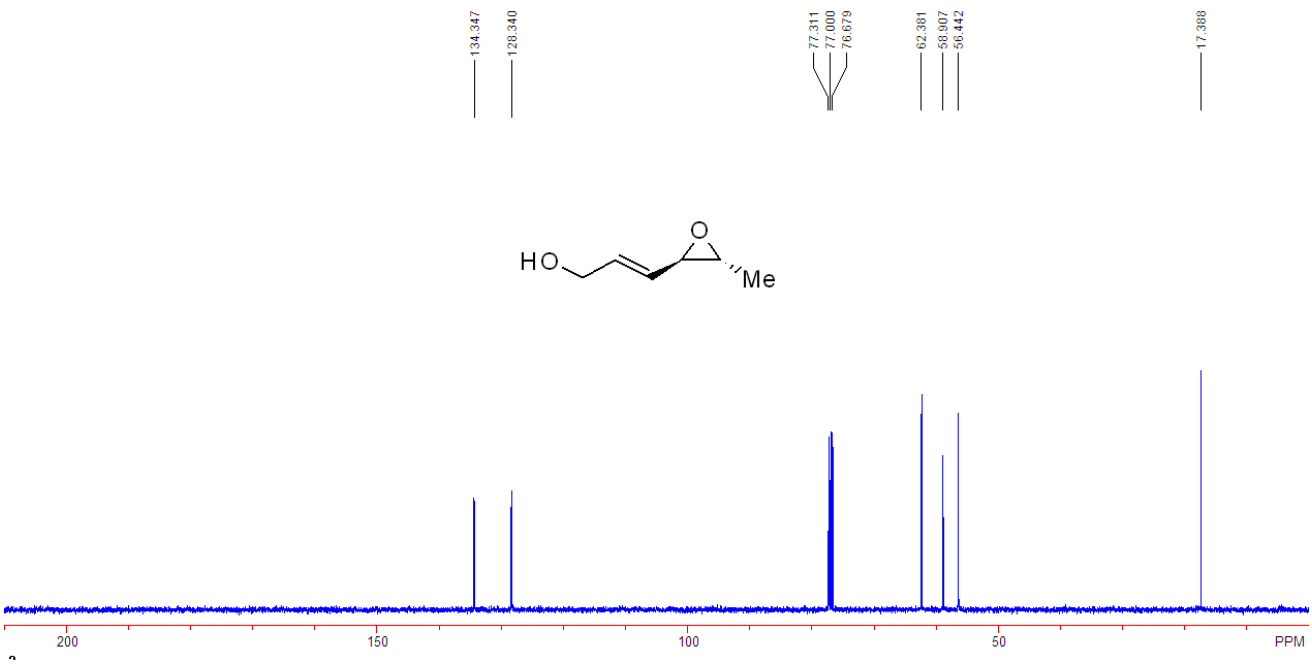
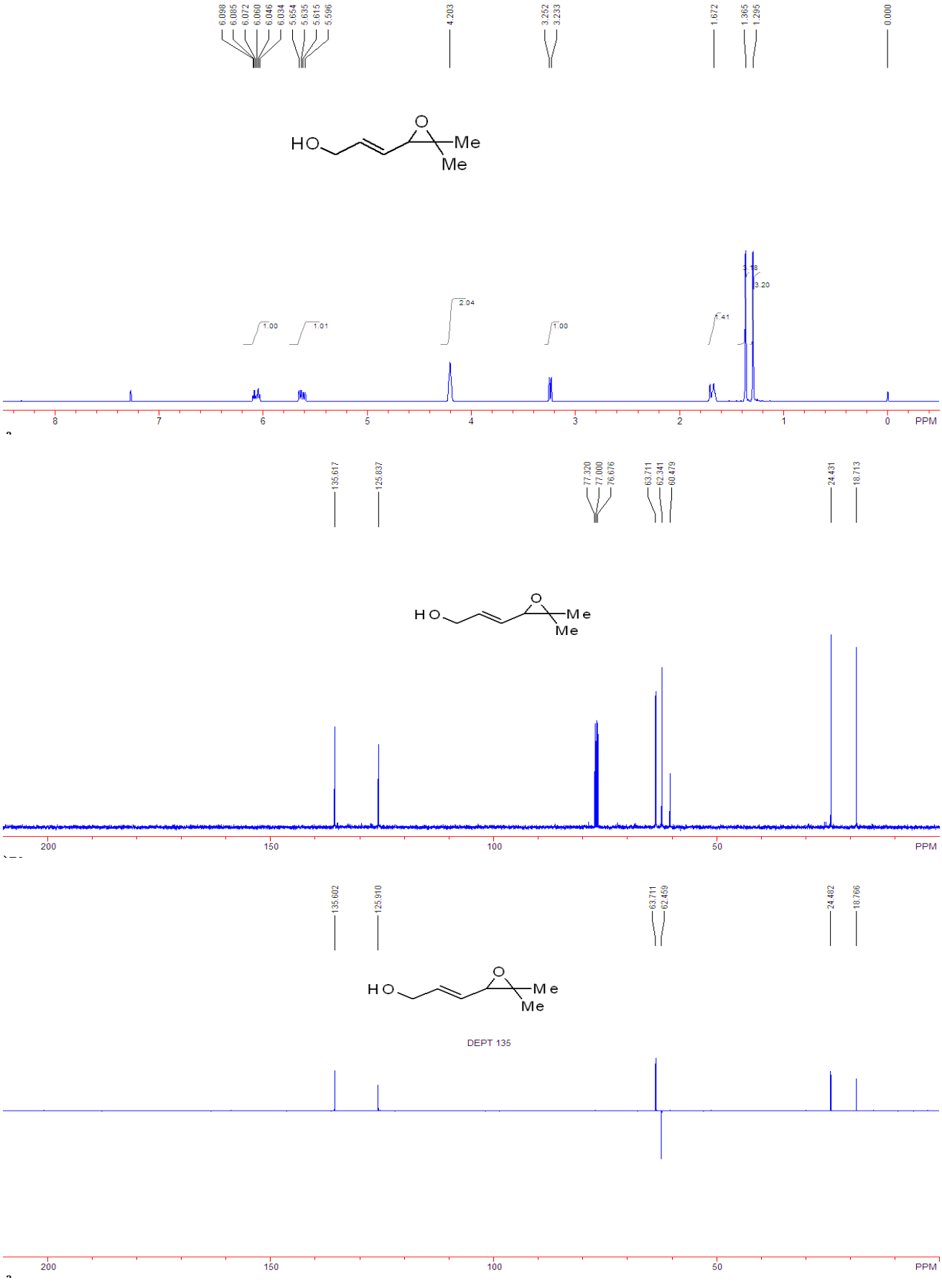
6.100
6.088
6.075
6.062
6.049
6.036
5.498
5.478
5.459
5.439
4.185
4.173
4.160
3.114
3.094
2.950
2.938
2.931
2.925
2.912
1.761
1.356
1.343
0.000
HO
Me
1.00
1.01
2.07
1.00
1.00
1.22
3.27
8
7
6
5
4
3
2
1
0
PPM


134.347
128.340
77.311
77.000
76.679
62.381
58.907
56.442
17.388
HO
Me
200
150
100
50
PPM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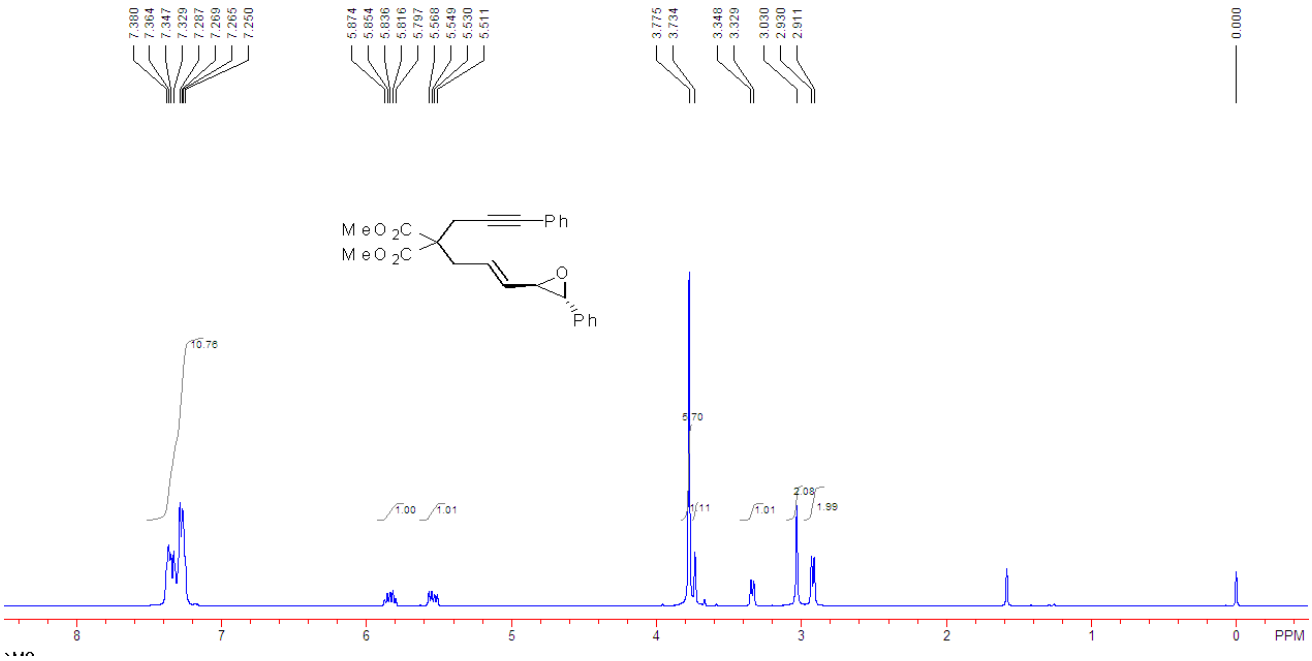
6.085
6.072
6.060
6.046
6.034
5.654
5.635
5.615
5.596
4.203
3.252
3.233
1.672
1.365
1.295
0.000
HO
O
Me
Me
1.00
1.01
2.04
1.00
1.41
3.18
3.20
8
7
6
5
4
3
2
1
0
PPM
135.617
125.837
77.320
77.000
76.676
63.711
62.341
60.479
24.431
18.713
HO
O
Me
Me
200
150
100
50
PPM
135.602
125.910
63.711
62.459
24.482
18.766
HO
O
Me
Me
DEPT 135
200
150
100
50
PPM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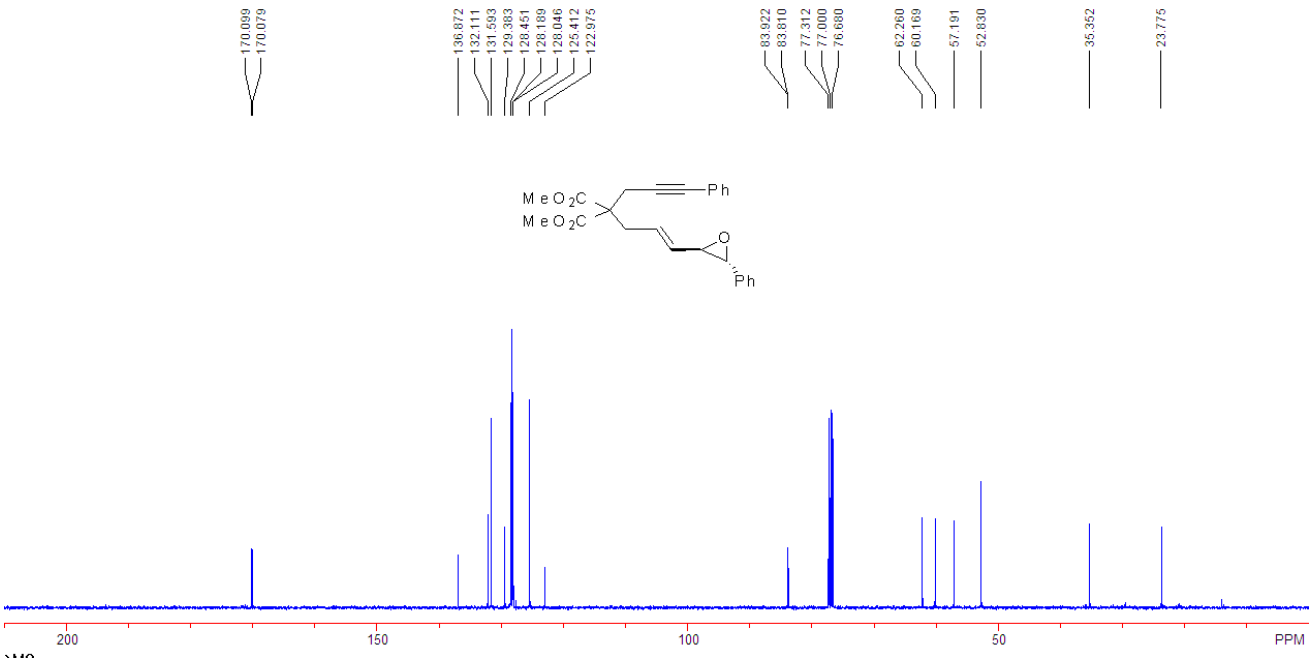
7.364
7.347
7.329
7.287
7.269
7.265
7.250
5.874
5.854
5.836
5.816
5.797
5.568
5.549
5.530
5.511
3.775
3.734
3.348
3.329
3.030
2.930
2.911
0.000
MeO2C
MeO2C
Ph
O
Ph
10.76
5.70
1.00
1.01
1.11
1.01
2.08
1.99
8
7
6
5
4
3
2
1
0
PPM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170.079
136.872
132.111
131.593
129.383
128.451
128.189
128.046
125.412
122.975
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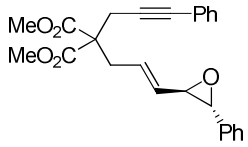
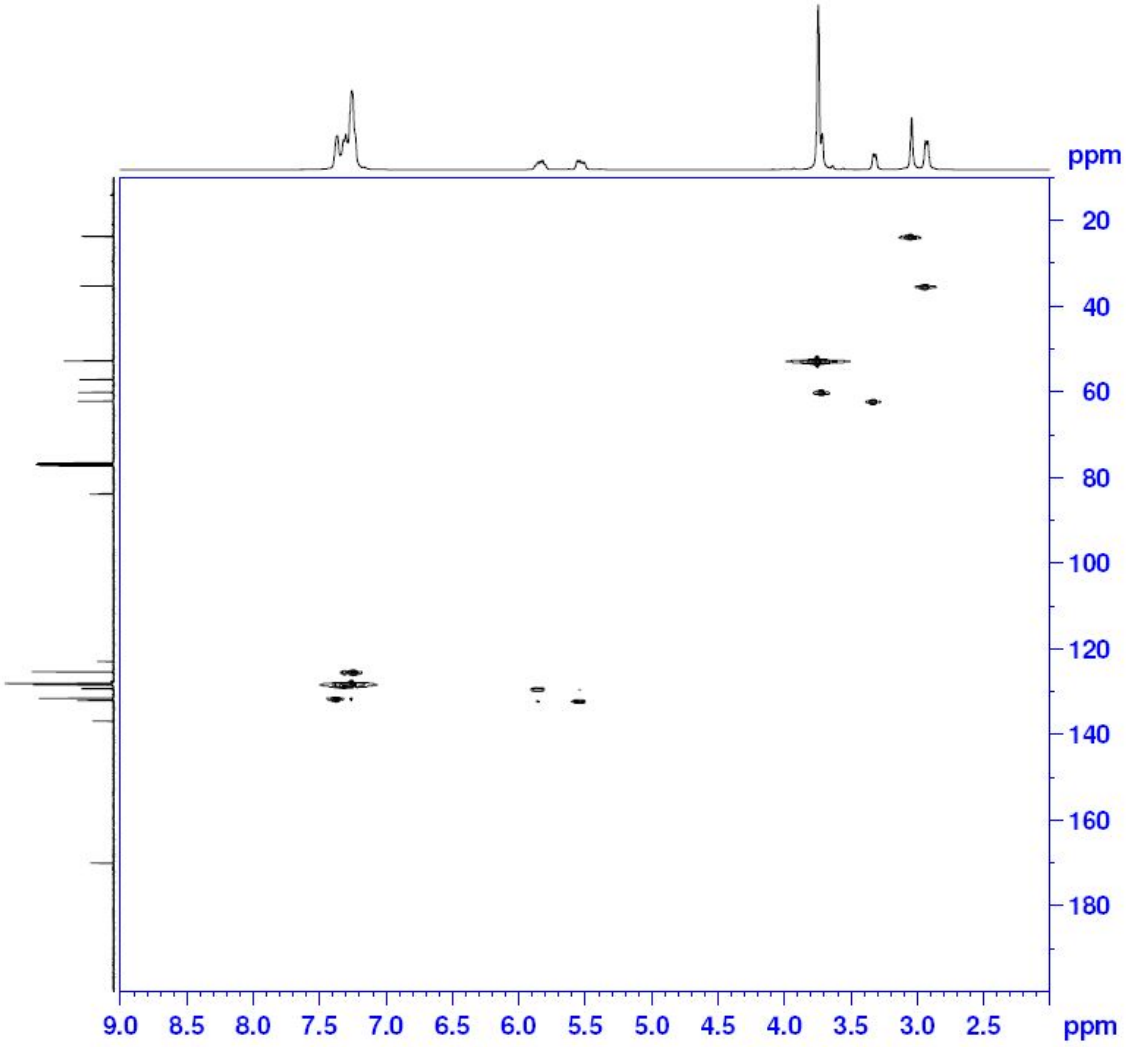
83.810
77.312
77.000
76.680
62.260
60.169
57.191
52.830
35.352
23.775
MeO2C
MeO2C
Ph
O
Ph
200
150
100
50
PPM


MeO2C
MeO2C
Ph
O
Ph

HSQC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80
100
120
140
160
180
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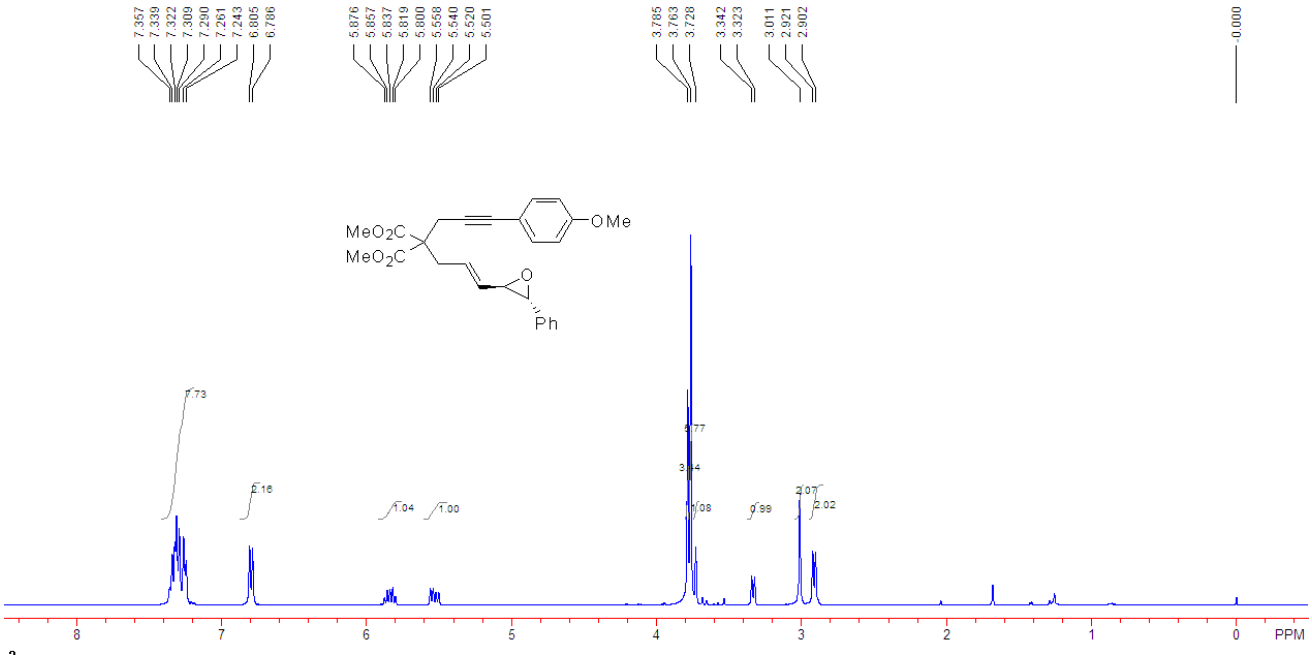
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm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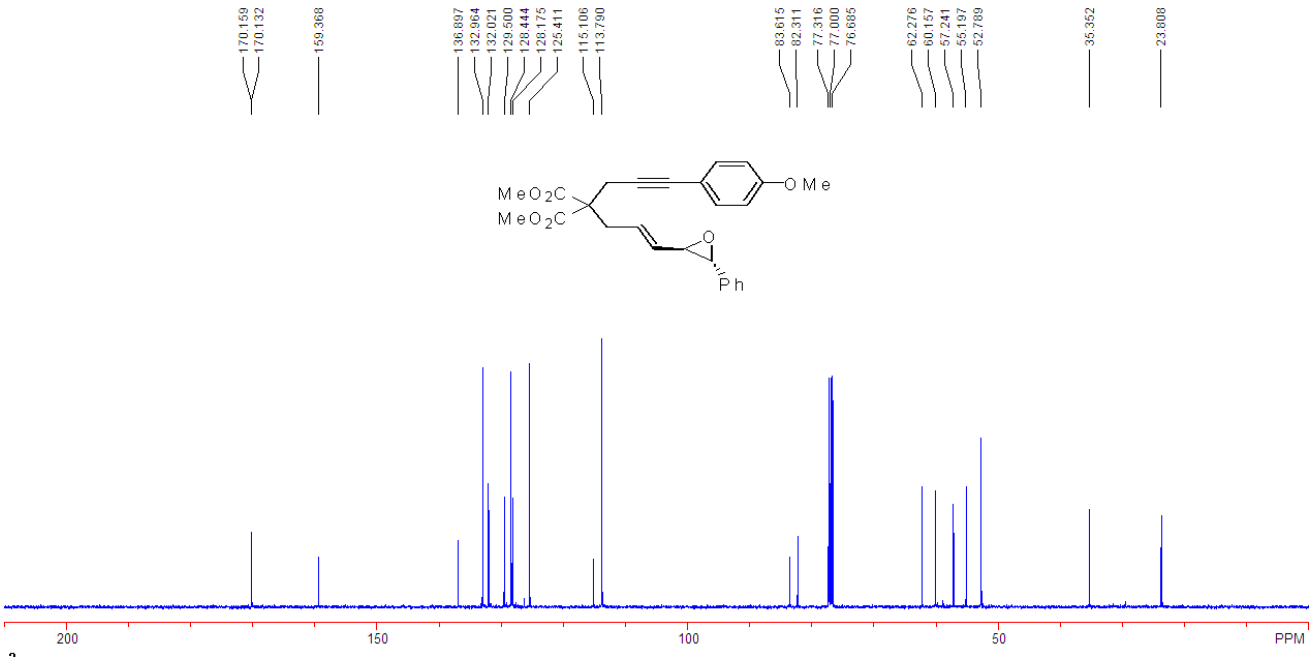
7.339
7.322
7.309
7.290
7.261
7.243
6.805
6.786
5.876
5.857
5.837
5.819
5.800
5.558
5.540
5.520
5.501
3.785
3.763
3.728
3.342
3.323
3.011
2.921
2.902
0.000
MeO2C
MeO2C
OMe
O
Ph
1.73
2.16
1.04
1.00
3.77
3.14
3.08
0.99
2.07
2.02
8
7
6
5
4
3
2
1
0
PPM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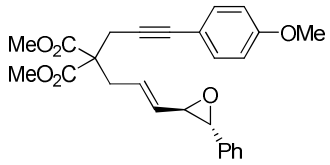
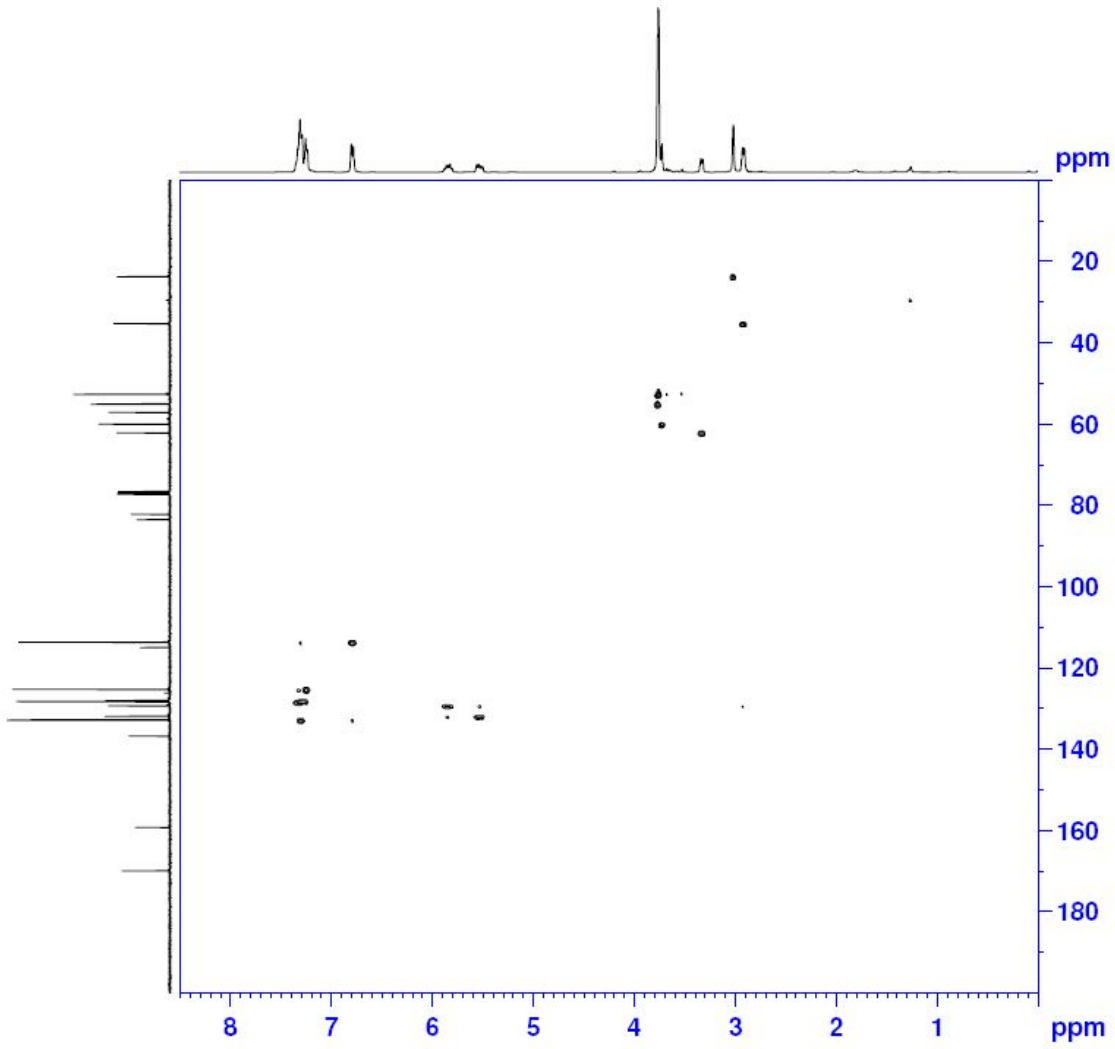
170.132
159.368
136.897
132.964
132.021
129.500
128.444
128.175
125.411
115.106
113.790
83.615
82.311
77.316
77.000
76.685
62.276
60.157
57.241
55.197
52.789
35.352
23.808
MeO2C
MeO2C
OMe
O
Ph
200
150
100
50
PPM


MeO2C
MeO2C
OMe
O
Ph

HSQC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80
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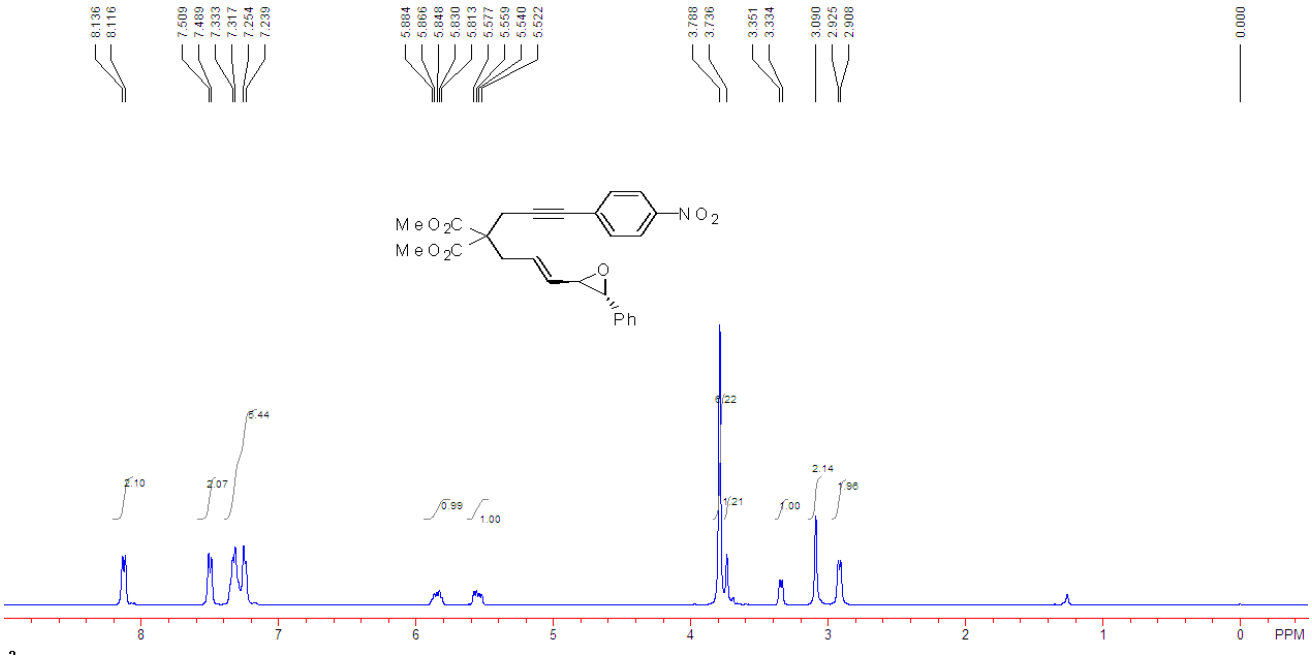
7
6
5
4
3
2
1
ppm


8.136
8.116
7.509
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7.333
7.317
7.254
7.239
5.884
5.866
5.848
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5.813
5.577
5.559
5.540
5.522
3.788
3.736
3.351
3.334
3.090
2.925
2.908
0.000
MeO2C
MeO2C
NO2
O
Ph
1.10
2.07
5.44
0.99
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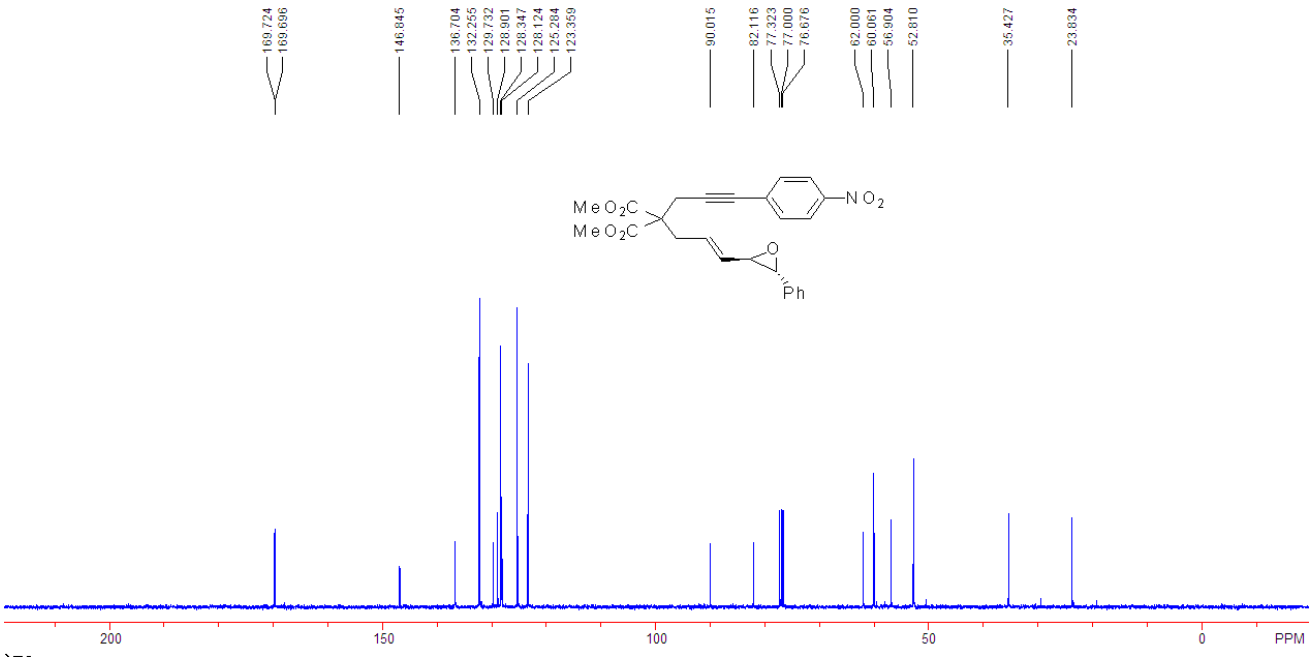
1.00
2.14
1.96
8
7
6
5
4
3
2
1
0
PPM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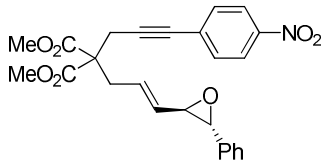
169.696
146.845
136.704
132.255
129.732
128.901
128.347
128.124
125.284
123.359
90.015
82.116
77.323
77.000
76.676
62.000
60.061
56.904
52.810
35.427
23.834
MeO2C
MeO2C
NO2
O
Ph
200
150
100
50
0
PPM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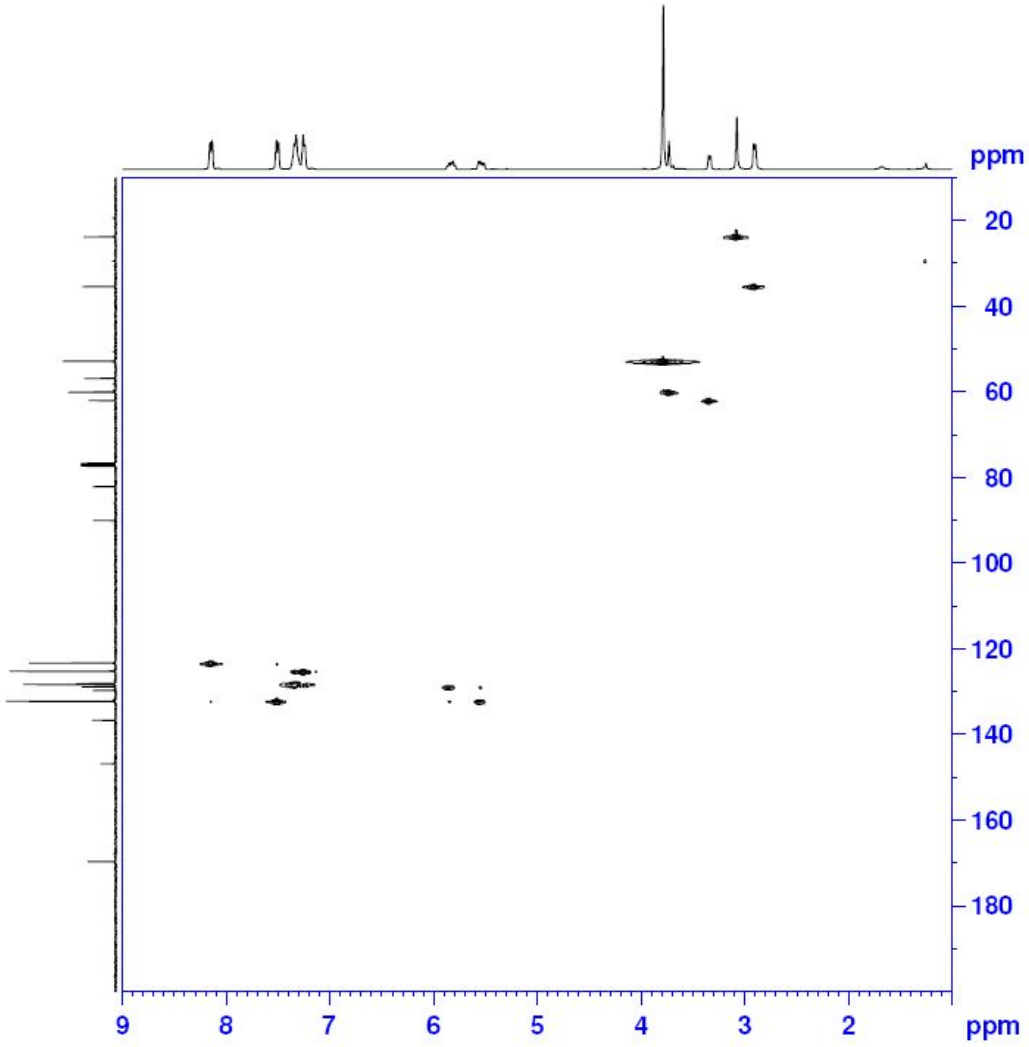
MeO2C
NO2
O
Ph

HSQC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60
80
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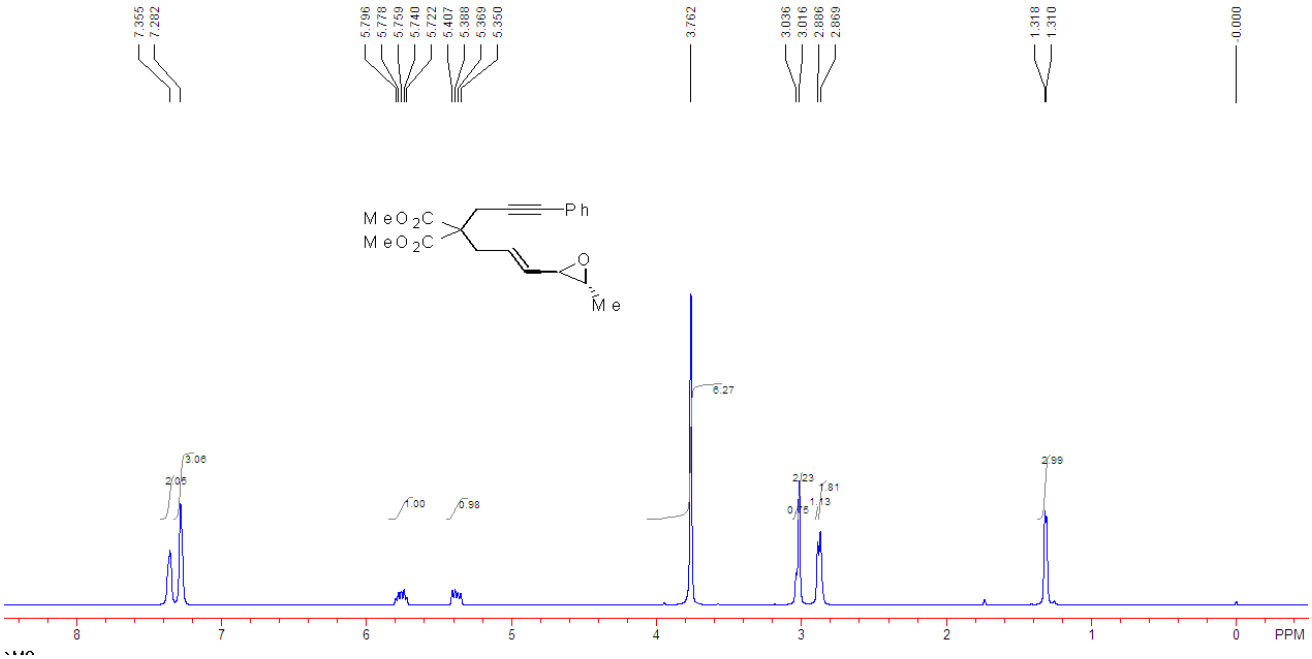
120
140
160
180
9
8
7
6
5
4
3
2
ppm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5.796
5.778
5.759
5.740
5.722
5.407
5.388
5.369
5.350
3.762
3.036
3.016
2.886
2.869
1.318
1.310
0.000
MeO2C
MeO2C
Ph
O
Me
6.27
3.06
2.05
1.00
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2.23
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1.13
0.75
2.99
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7
6
5
4
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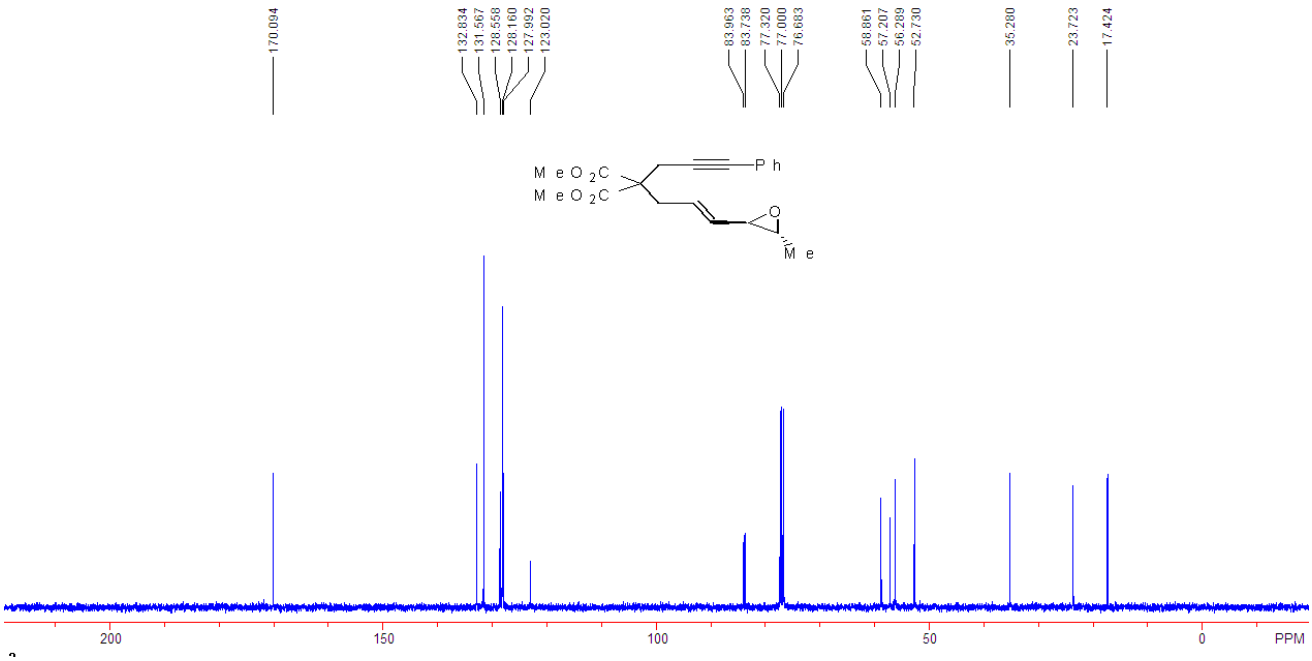
2
1
0
PPM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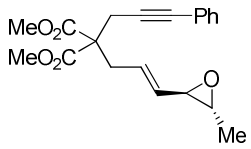
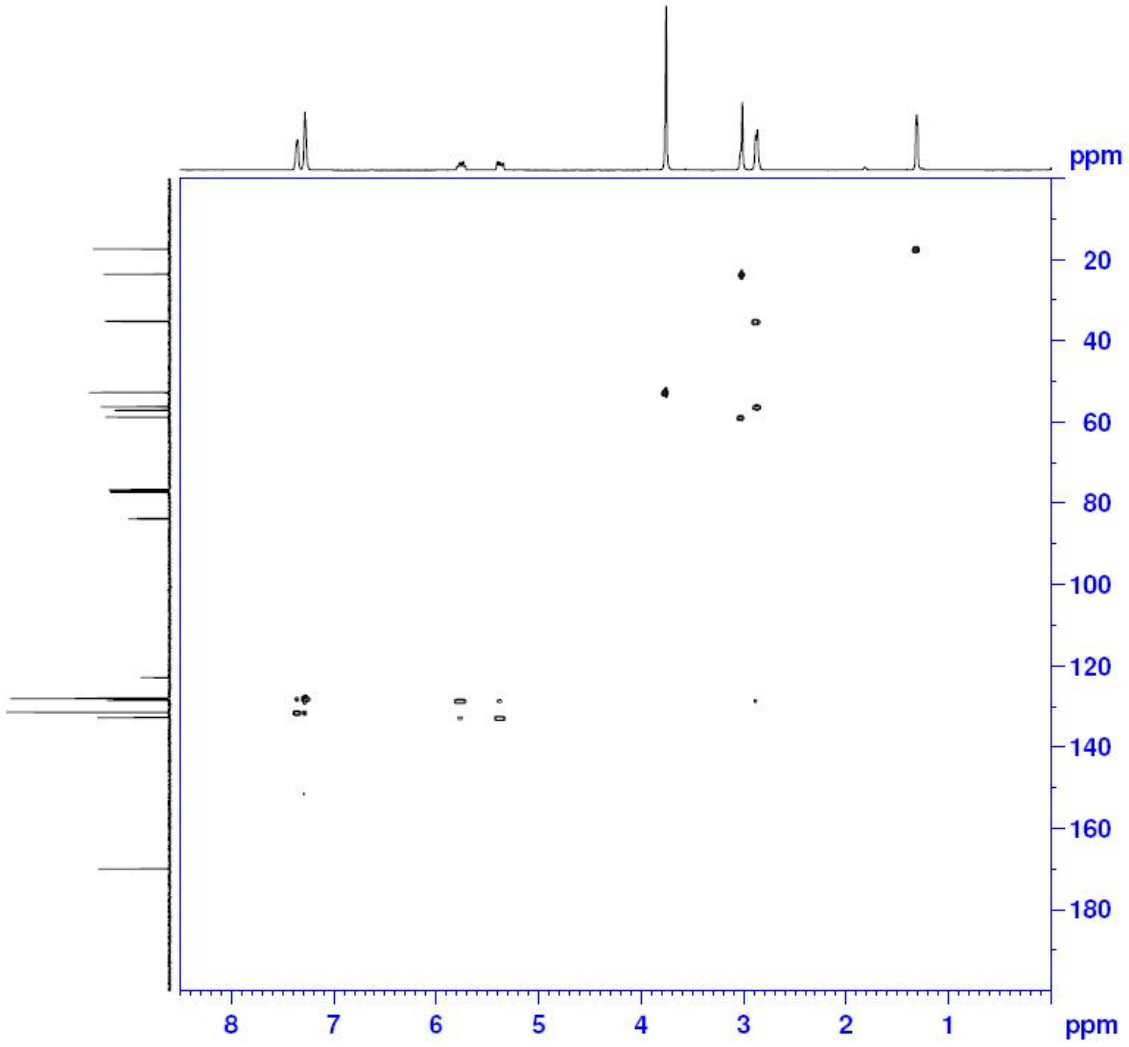
131.567
128.558
128.160
127.992
123.020
83.963
83.738
77.320
77.000
76.683
58.861
57.207
56.269
52.730
35.280
23.723
17.424
MeO2C
MeO2C
Ph
O
Me
200
150
100
50
0
PPM


MeO2C
MeO2C
Ph
O
Me

HSQC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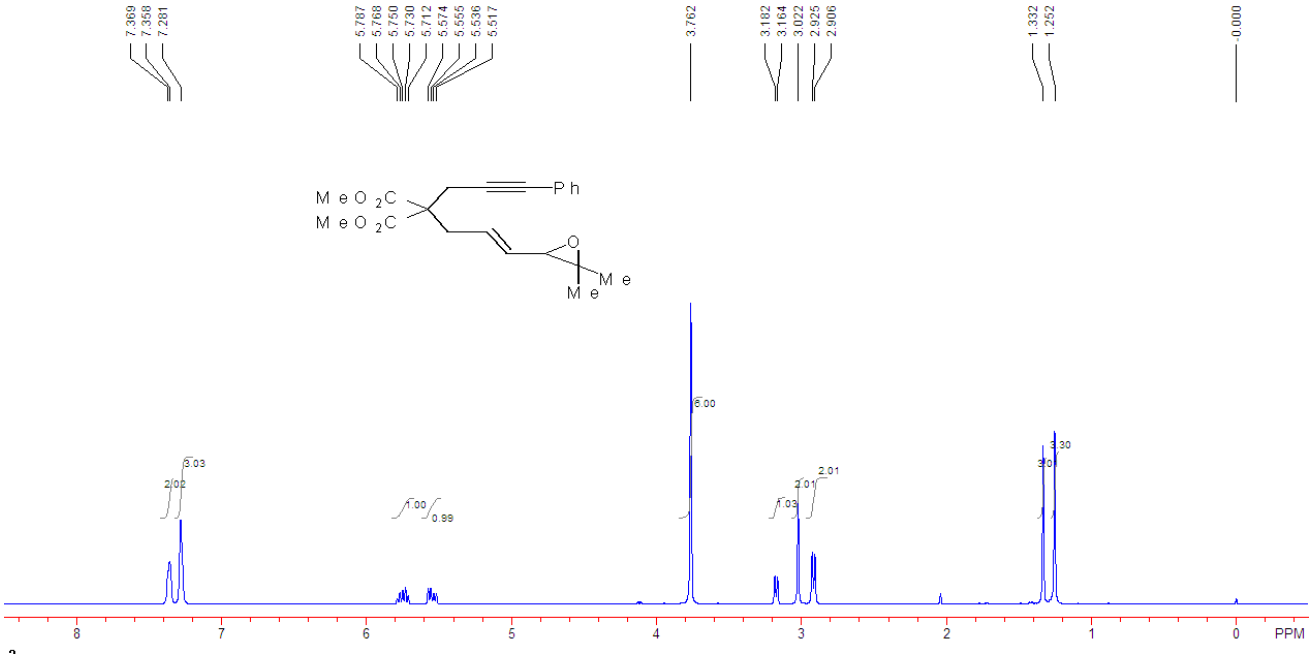
1
ppm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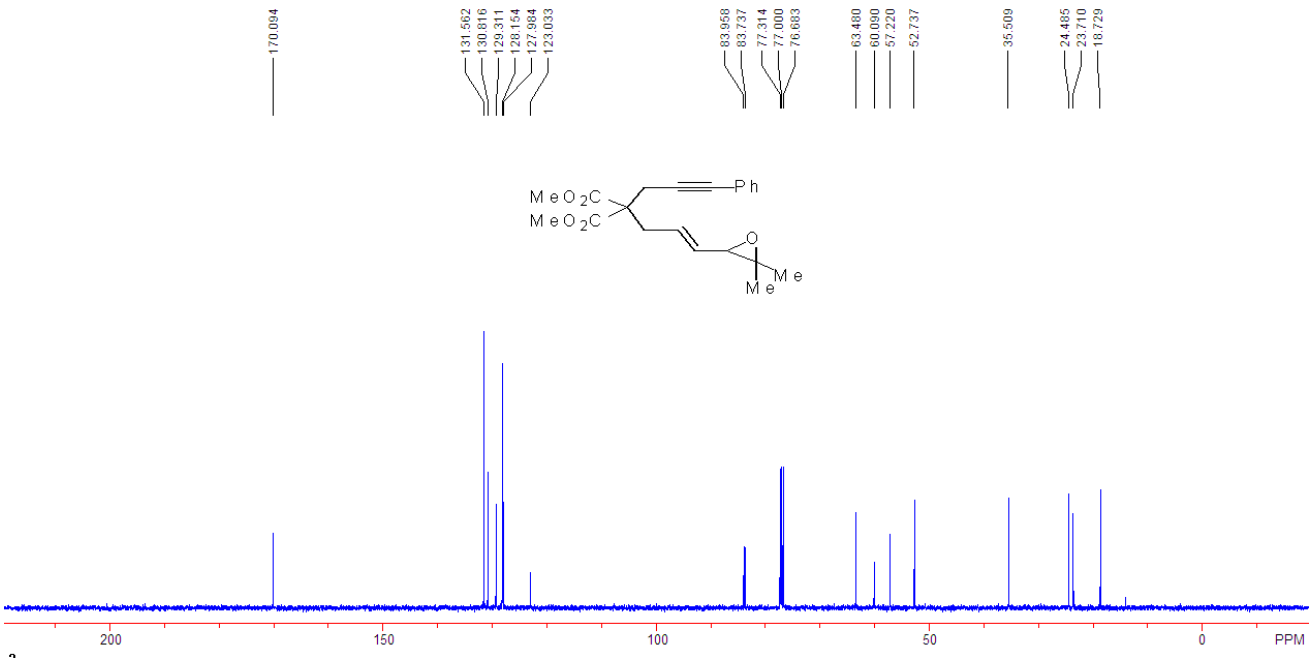
5.768
5.750
5.730
5.712
5.574
5.555
5.536
5.517
3.762
3.182
3.164
3.022
2.925
2.906
1.332
1.252
0.000
MeO2C
MeO2C
Ph
O
Me
Me
6.00
3.03
2.02
1.00
0.99
2.01
1.03
2.01
3.30
3.00
8
7
6
5
4
3
2
1
0
PPM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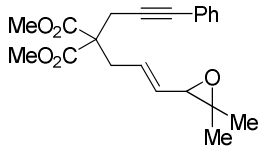
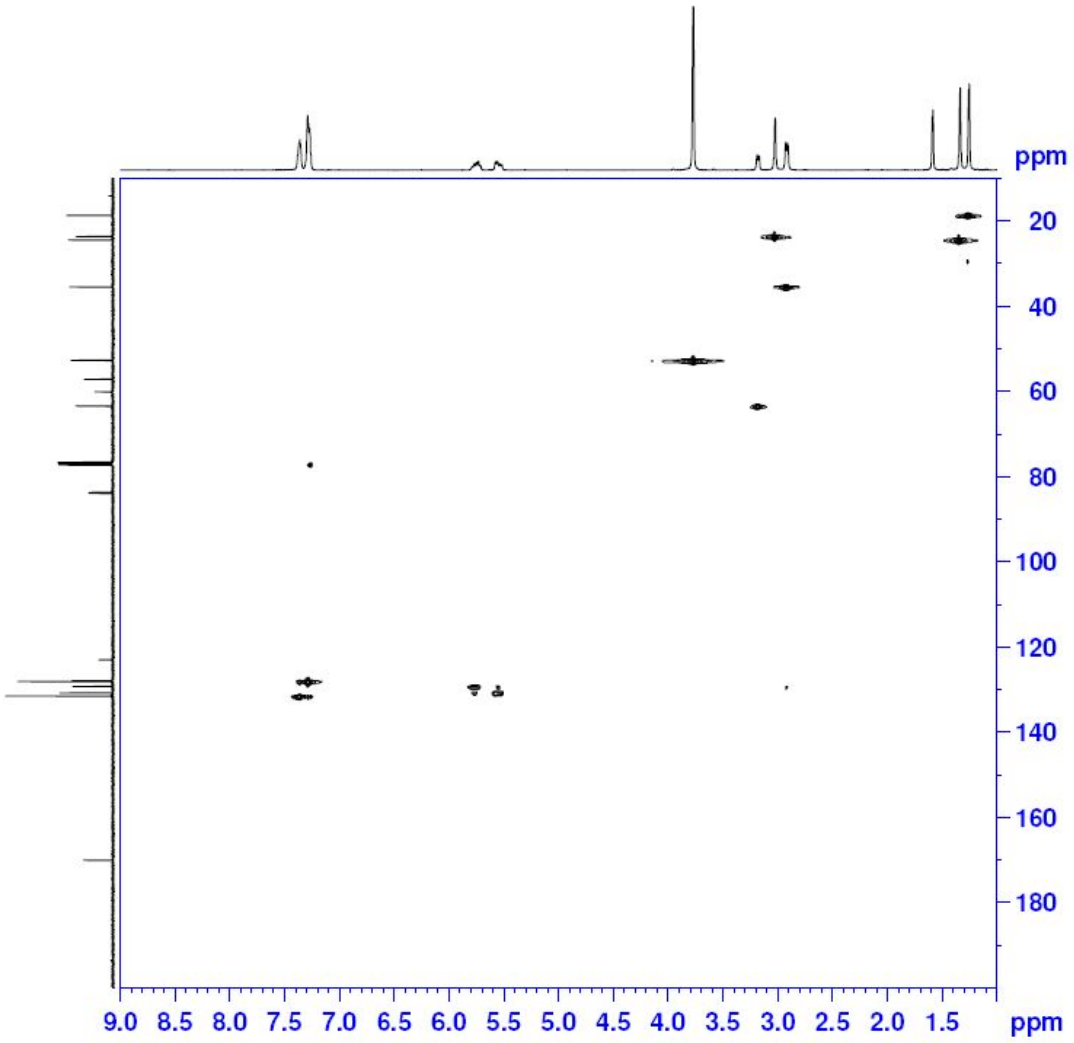
130.816
129.311
128.154
127.984
123.033
83.958
83.737
77.314
77.000
76.683
63.480
60.090
57.220
52.737
35.509
24.485
23.710
18.729
MeO2C
MeO2C
Ph
O
Me
Me
200
150
100
50
0
PPM


MeO2C
MeO2C
Ph
O
Me
Me

HSQC


ppm
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60
80
100
120
140
160
180
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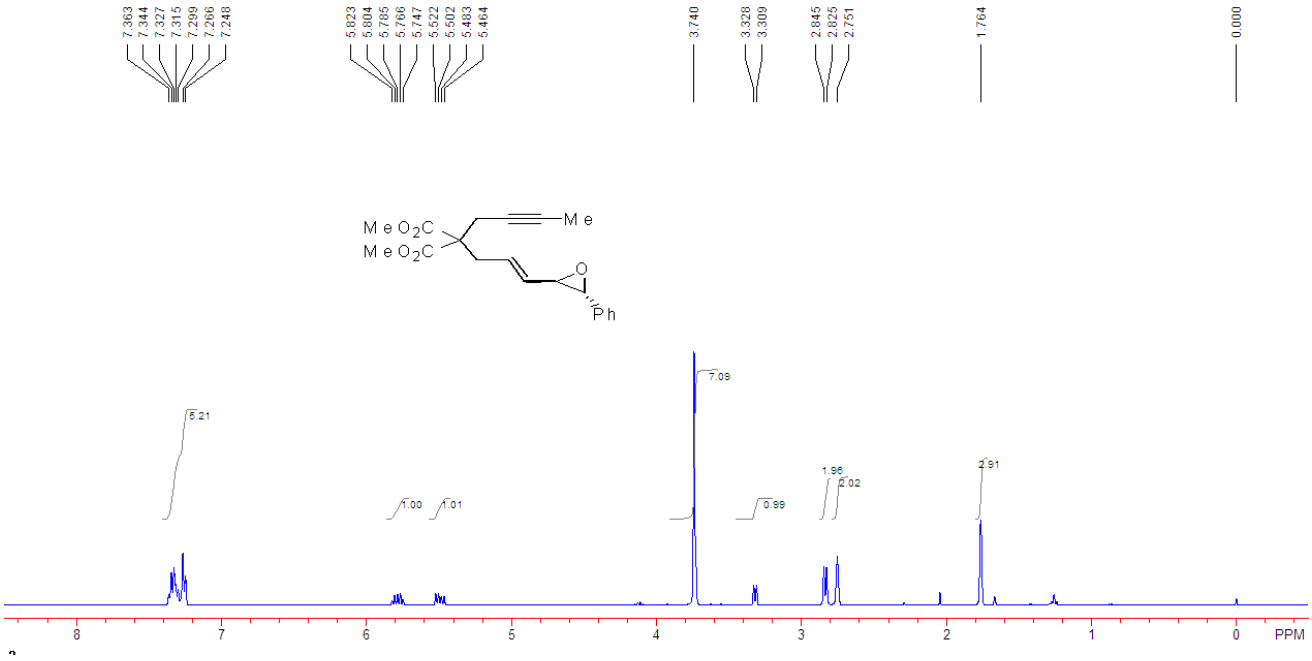
ppm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5.747
5.522
5.502
5.483
5.464
3.740
3.328
3.309
2.845
2.825
2.751
1.764
0.000
Me
MeO2C
MeO2C
O
Ph
6.21
1.00
1.01
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1.98
2.02
2.91
8
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5
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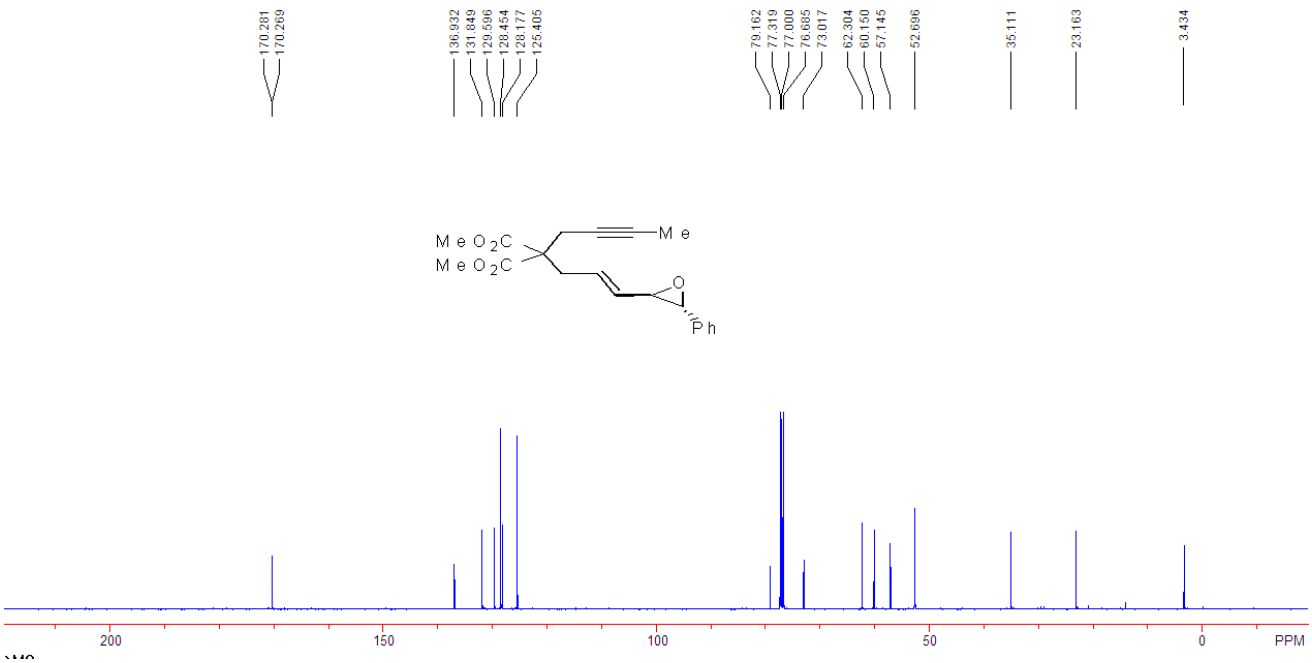
0
PPM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131.849
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128.454
128.177
125.405
79.162
77.319
77.000
76.685
73.017
62.304
60.150
57.145
52.696
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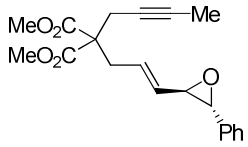
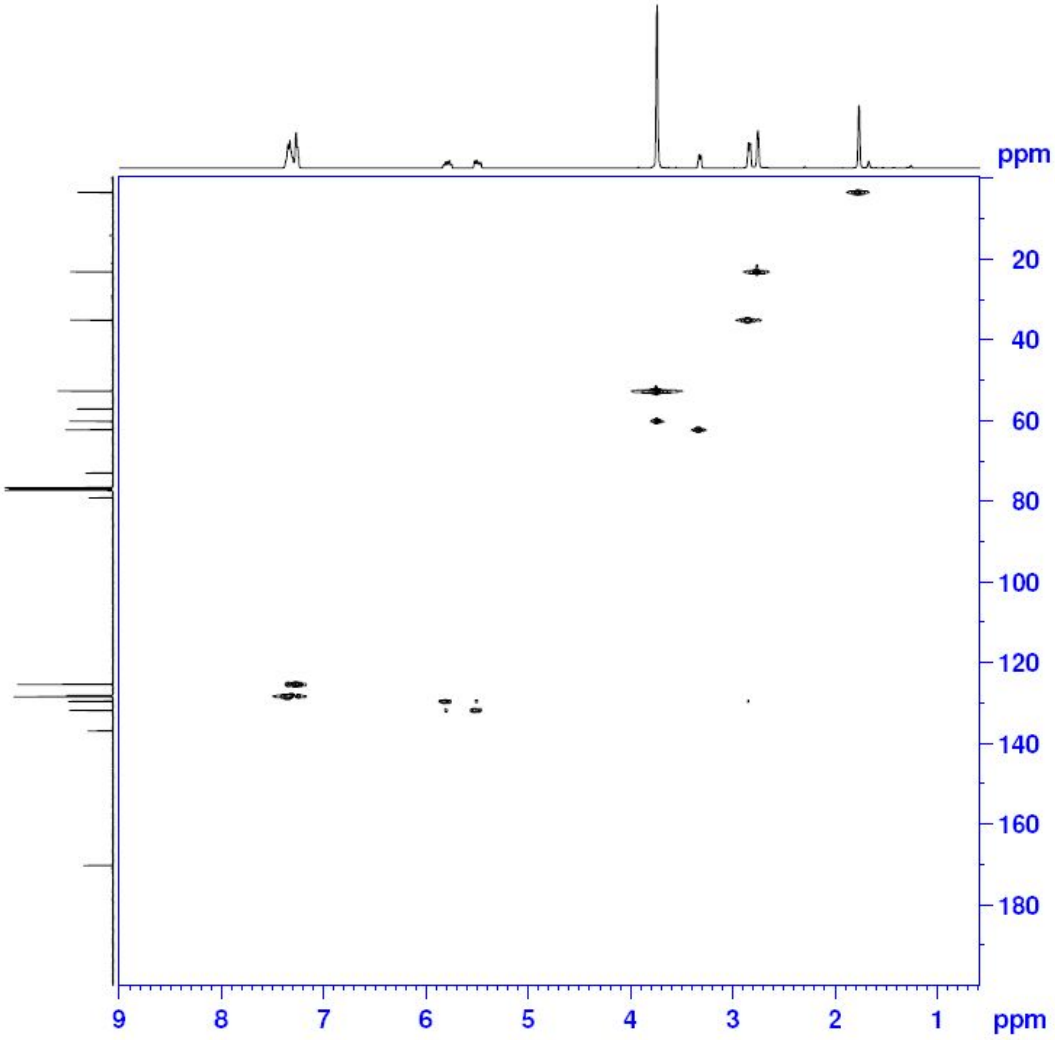
3.434
Me
MeO2C
MeO2C
O
Ph
200
150
100
50
0
PPM


MeO2C
MeO2C
Me
O
Ph

HSQC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9
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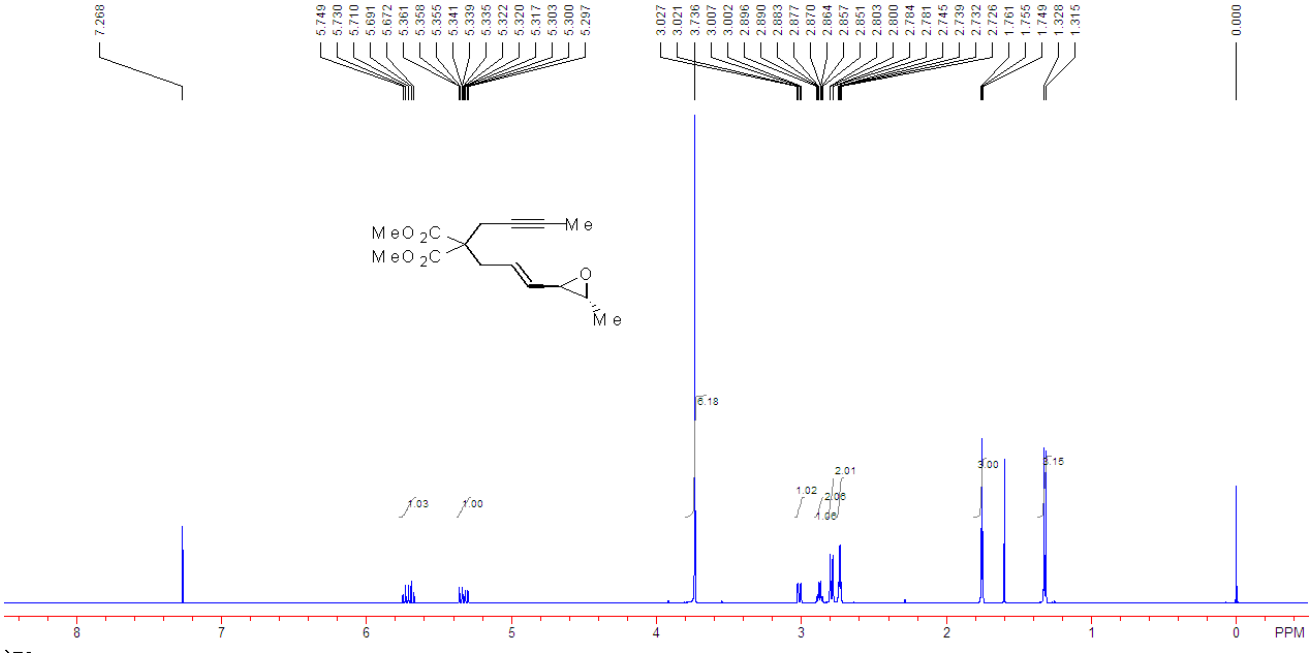
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5.358
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5.339
5.335
5.322
5.320
5.317
5.303
5.300
5.297
3.027
3.021
3.736
3.007
3.002
2.896
2.890
2.883
2.877
2.870
2.864
2.857
2.851
2.803
2.800
2.784
2.781
2.745
2.739
2.732
2.726
1.761
1.755
1.749
1.328
1.315
0.000
MeO2C
MeO2C
Me
O
Me
6.18
1.03
1.00
1.02
2.01
2.06
1.06
3.00
3.15
8
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6
5
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1
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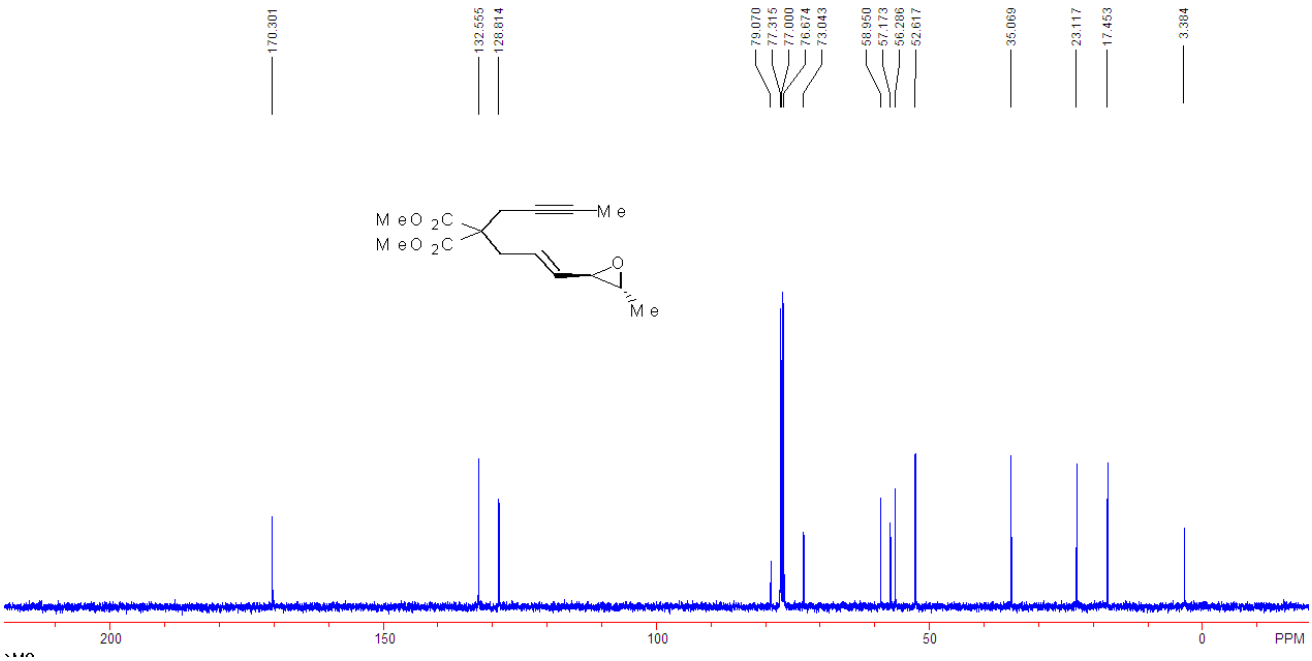
PPM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128.814
79.070
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76.674
73.043
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57.173
56.286
52.617
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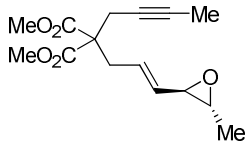
17.453
3.384
MeO2C
MeO2C
Me
O
Me
200
150
100
50
0
PPM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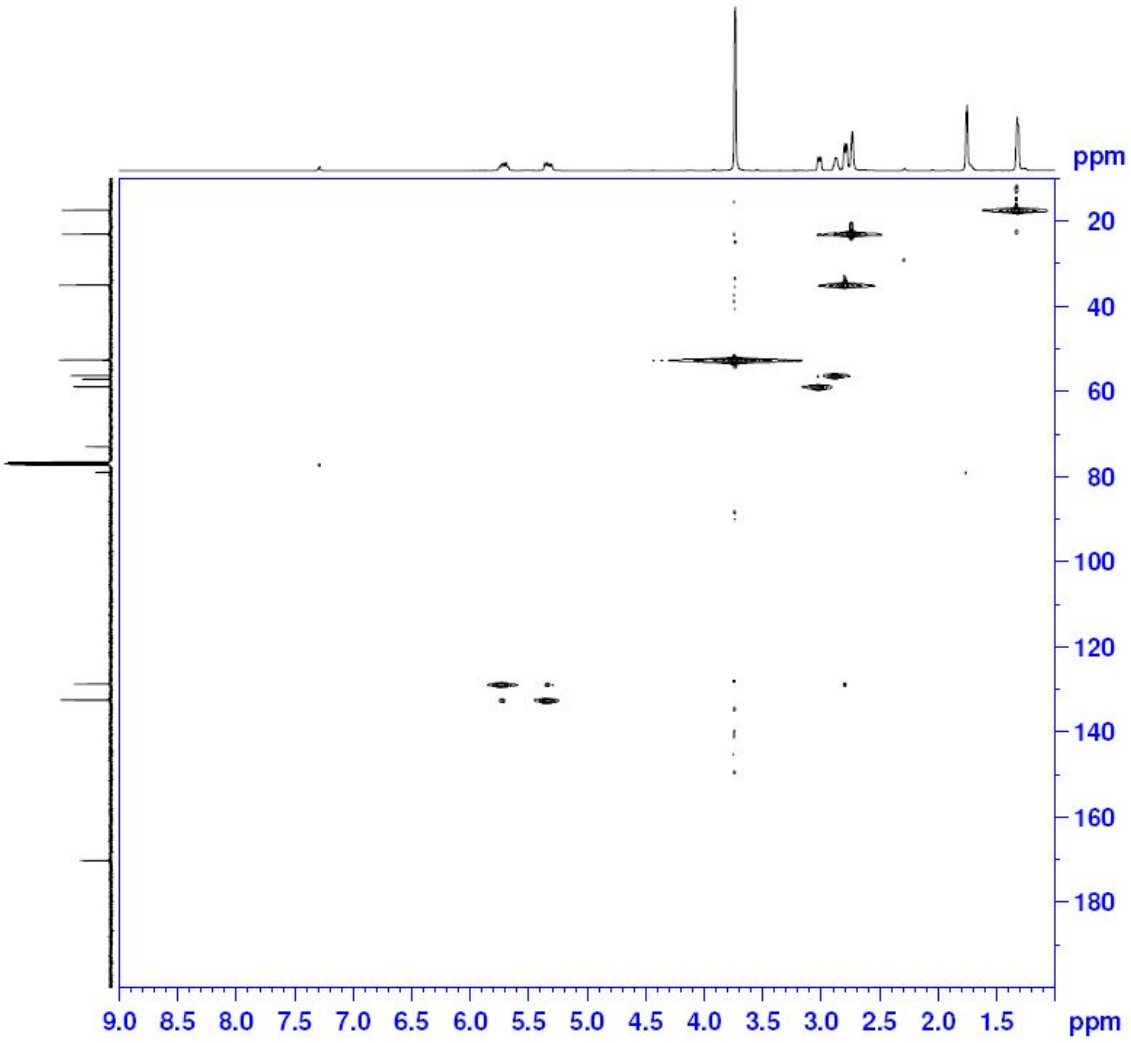
MeO2C
Me
O
Me

HSQC


ppm
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80
100
120
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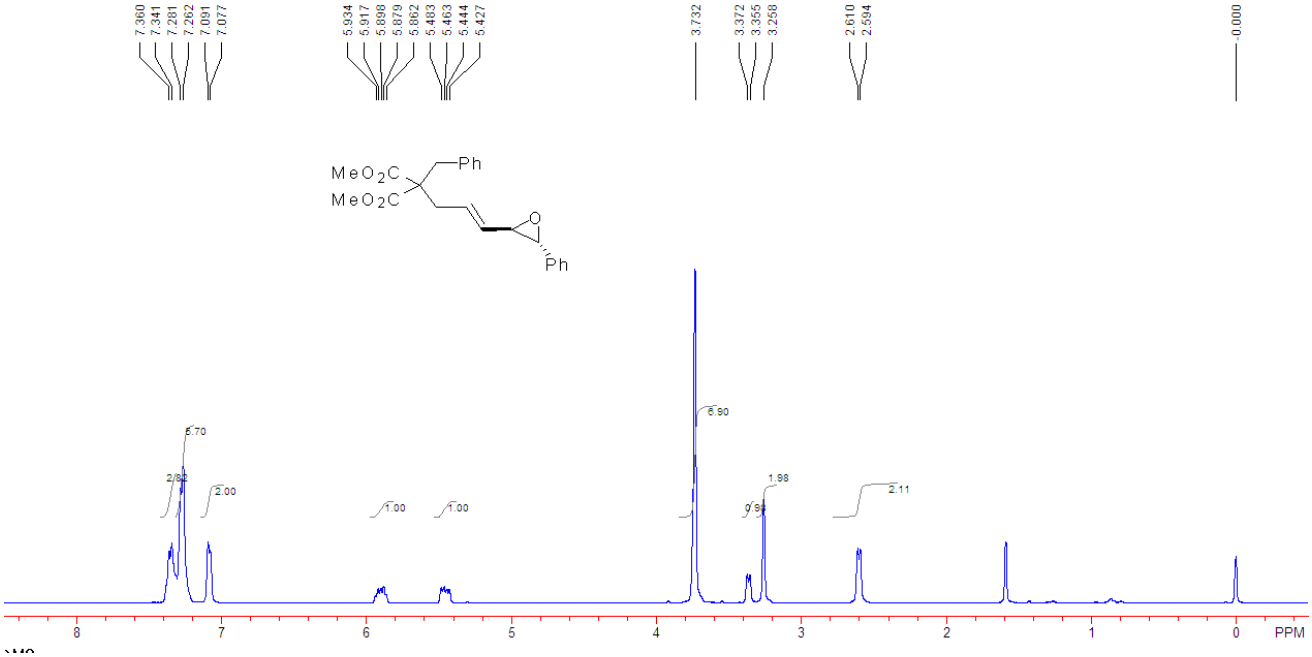
ppm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7.281
7.262
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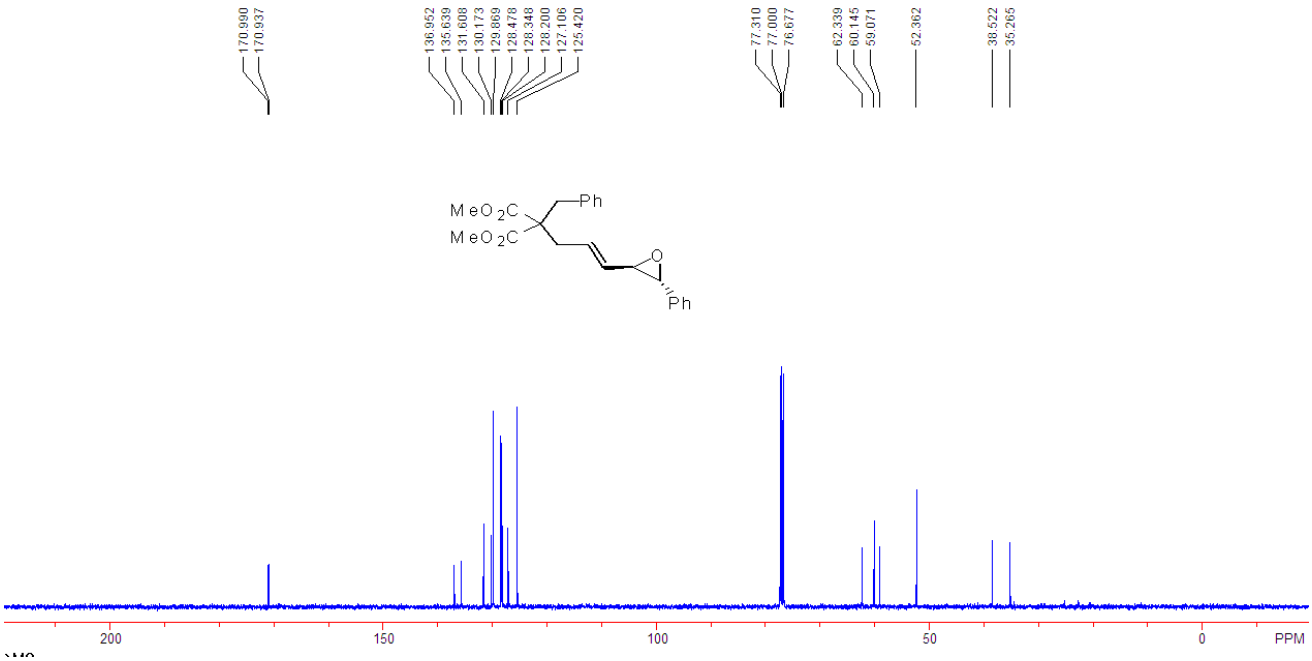
7.077
5.934
5.917
5.898
5.879
5.862
5.483
5.463
5.444
5.427
3.732
3.372
3.355
3.258
2.610
2.594
0.000
MeO2C
MeO2C
Ph
O
Ph
6.70
2.82
2.00
1.00
1.00
6.90
1.98
0.89
2.11
8
7
6
5
4
3
2
1
0
PPM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130.173
129.869
128.478
128.348
128.200
127.106
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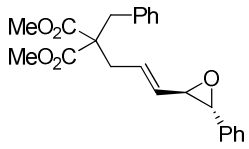
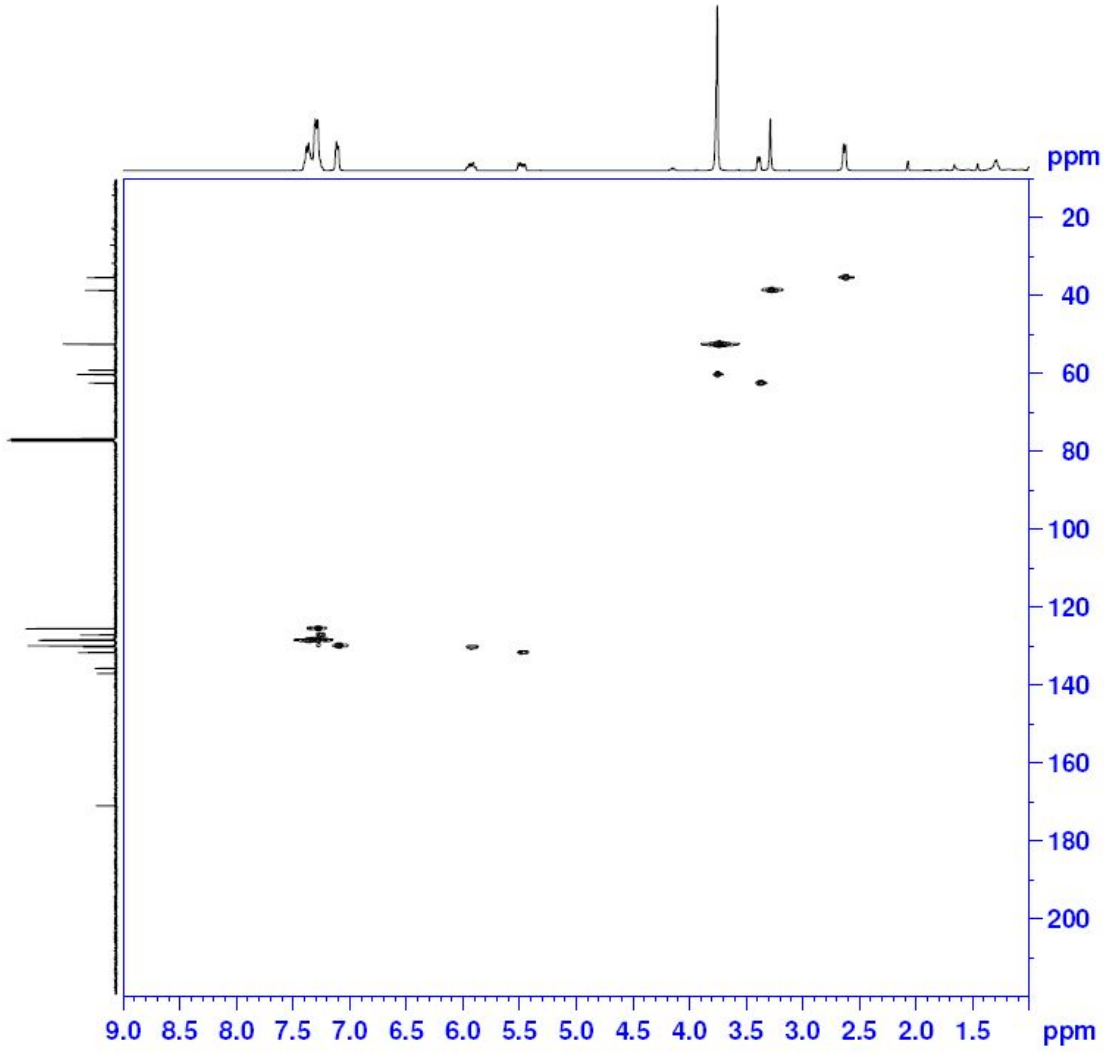
77.310
77.000
76.677
62.339
60.145
59.071
52.362
38.522
35.265
MeO2C
MeO2C
Ph
O
Ph
200
150
100
50
0
PPM


MeO2C
MeO2C
Ph
O
Ph

HSQC


ppm
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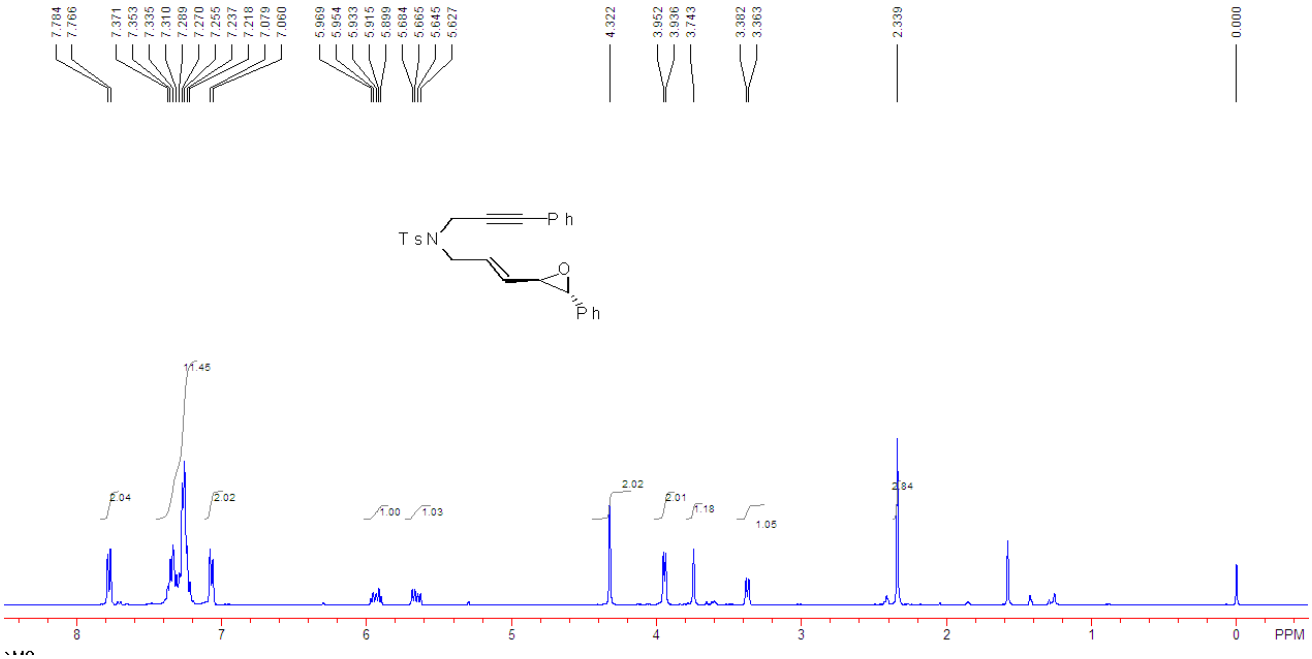
60
80
100
120
140
160
180
200
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
ppm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7.335
7.310
7.289
7.270
7.255
7.237
7.218
7.079
7.060
5.969
5.954
5.933
5.915
5.899
5.684
5.665
5.645
5.627
4.322
3.952
3.936
3.743
3.382
3.363
2.339
0.000
Ts
N
Ph
O
Ph
1.04
14.45
2.02
1.00
1.03
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1.18
1.05
2.84
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6
5
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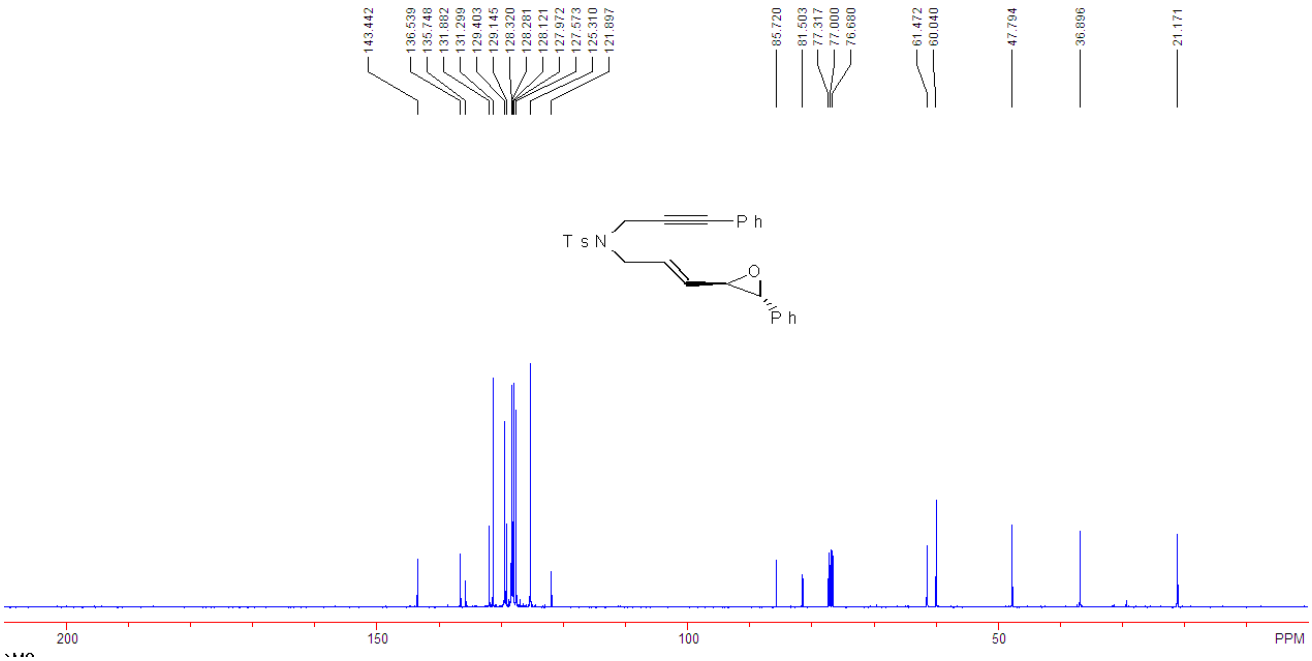
1
0
PPM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128.320
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121.897
85.720
81.503
77.317
77.000
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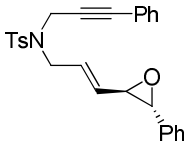
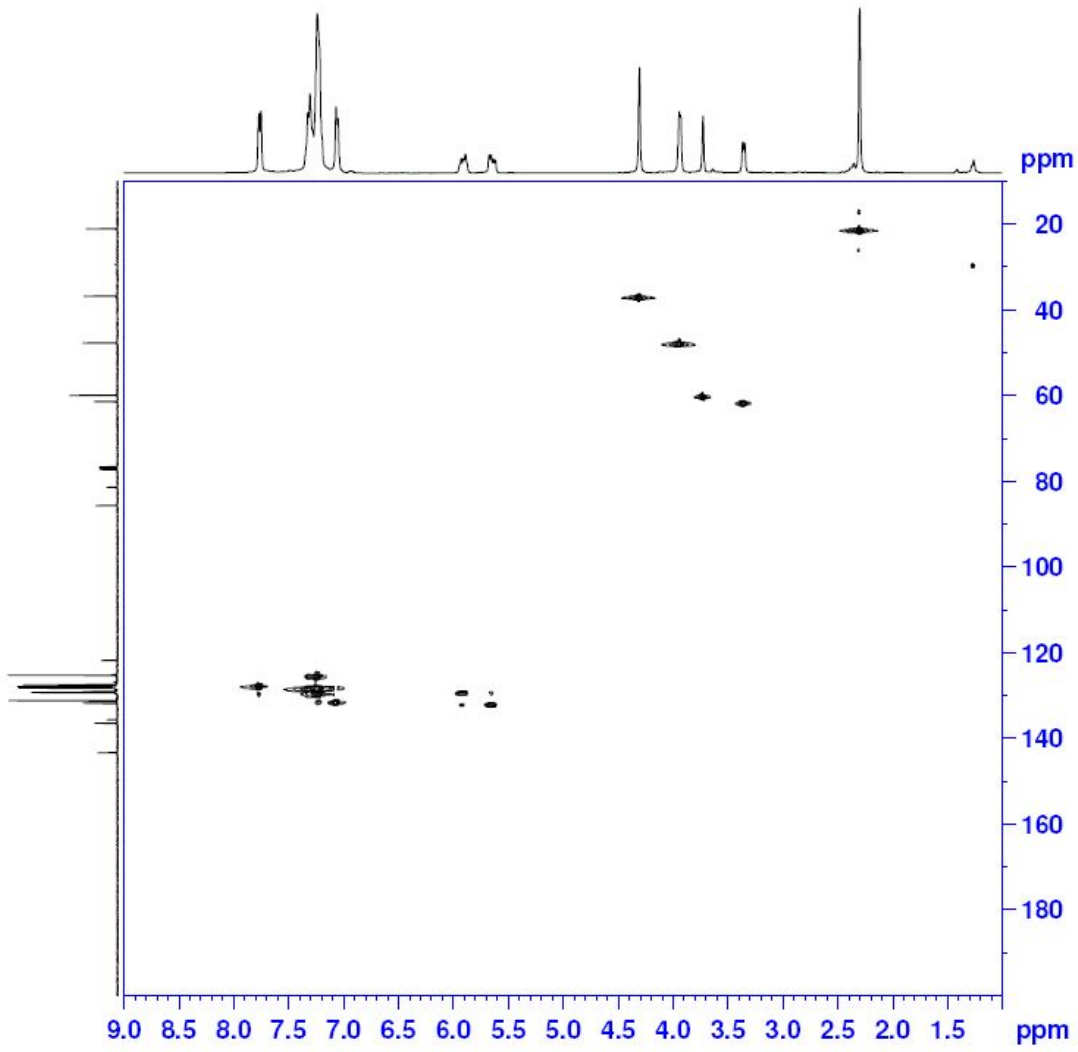
47.794
36.896
21.171
Ts
N
Ph
O
Ph
200
150
100
50
PPM


Ph
TsN
O
Ph

HSQC


ppm
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60
80
100
120
140
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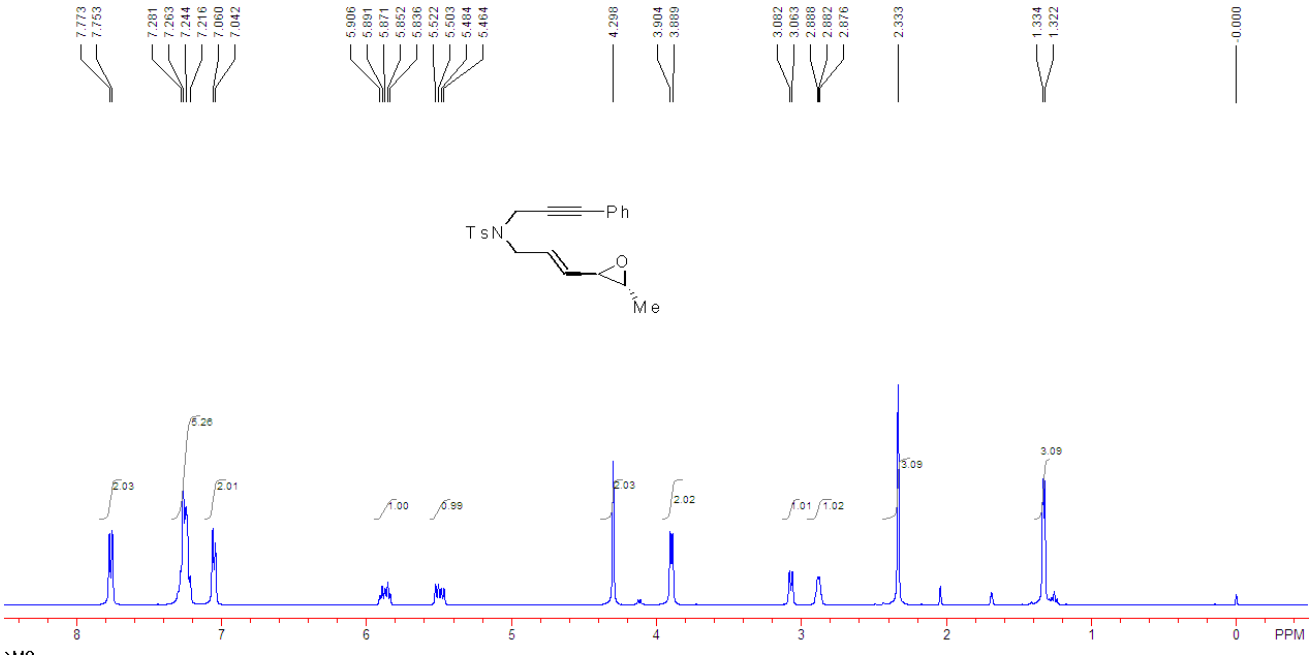
ppm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7.042
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5.871
5.852
5.836
5.522
5.503
5.484
5.464
4.298
3.904
3.889
3.082
3.063
2.888
2.882
2.876
2.333
1.334
1.322
0.000
Ph
TsN
O
Me
5.26
2.03
2.01
1.00
0.99
2.03
2.02
1.01
1.02
3.09
3.09
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6
5
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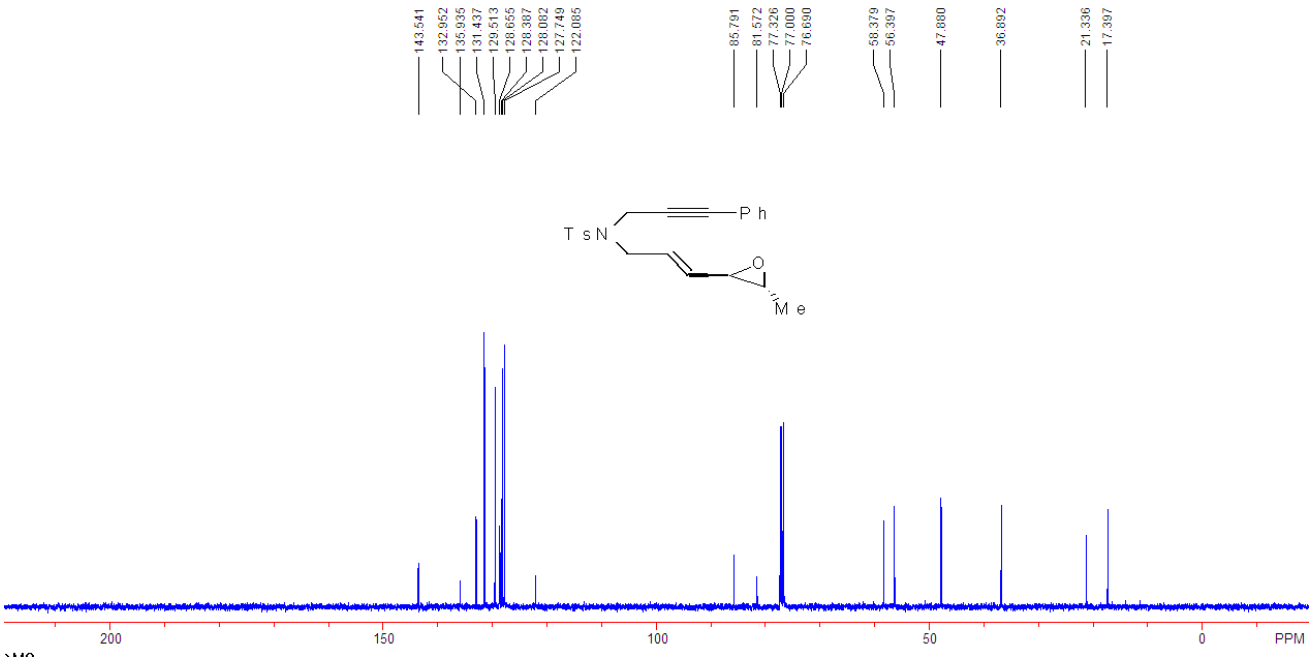
2
1
0
PPM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128.387
128.082
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122.085
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77.326
77.000
76.690
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36.892
21.336
17.397
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TsN
O
Me
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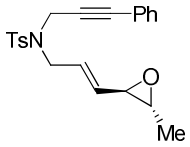
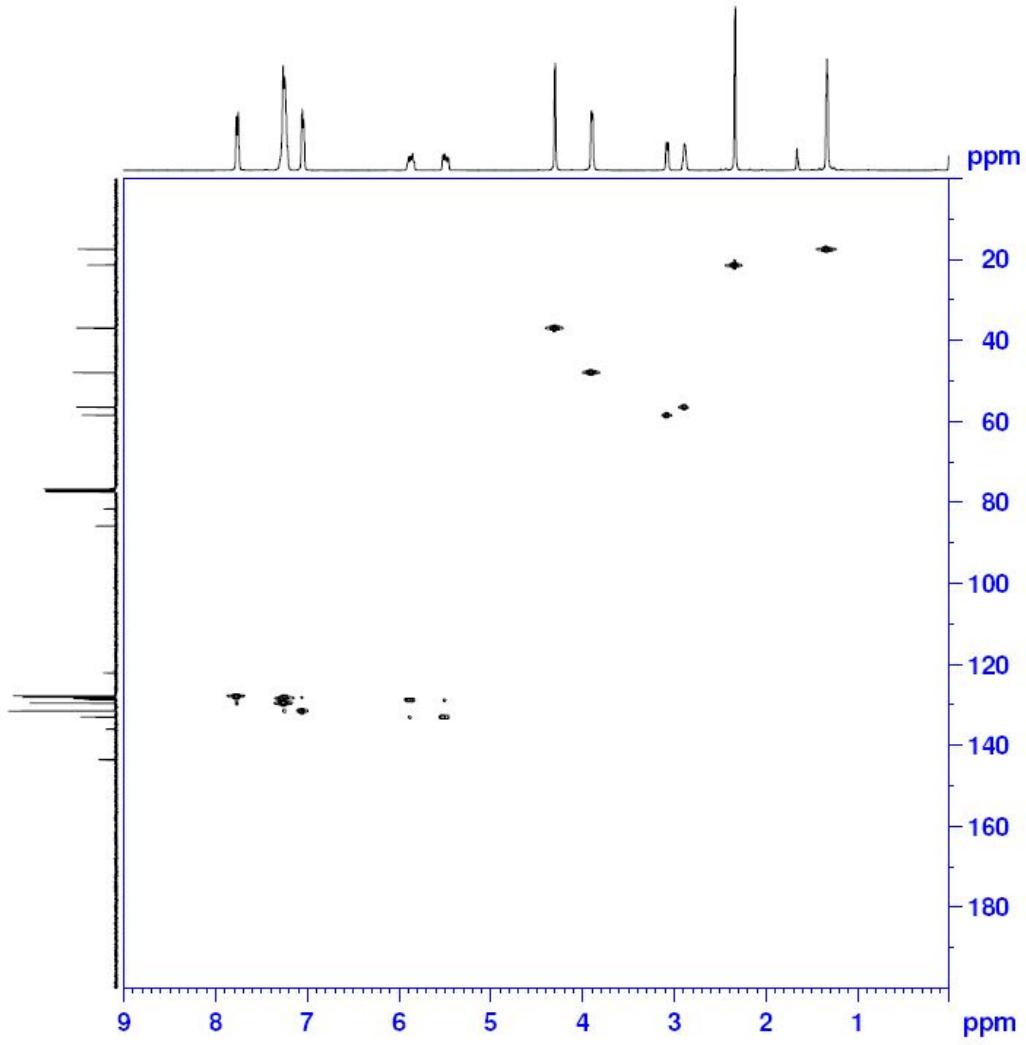
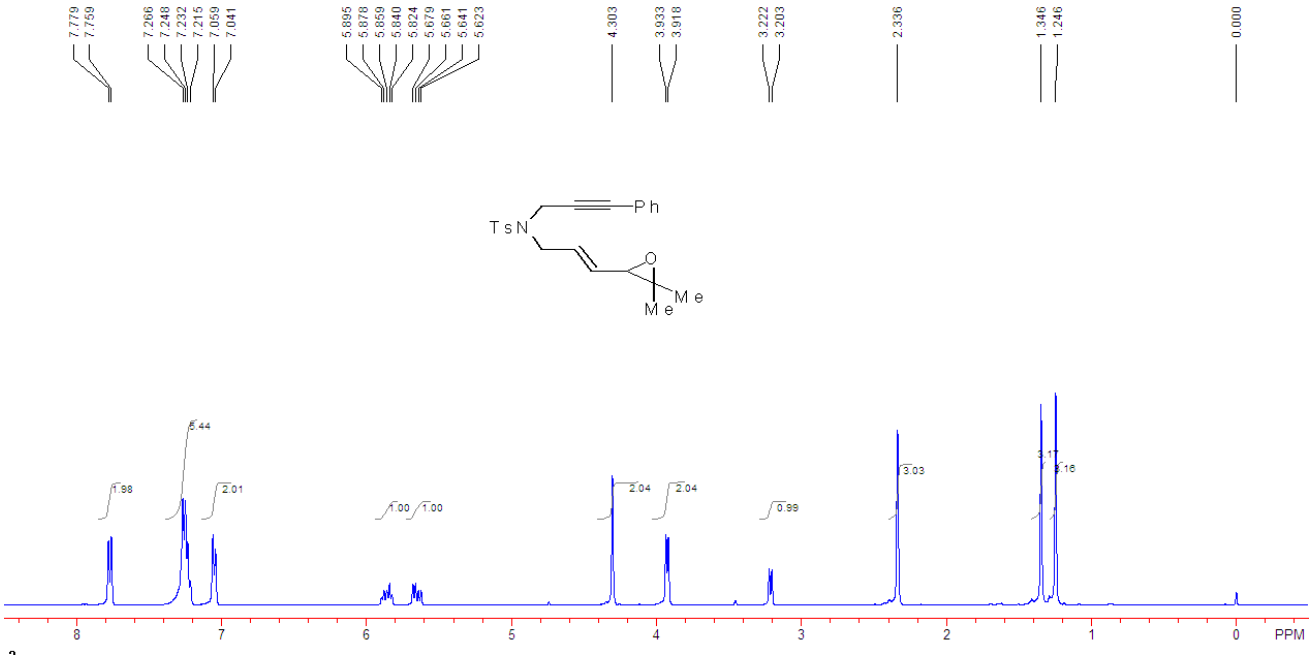
150
100
50
0
PPM



HSQC

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7.041
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5.679
5.661
5.641
5.623
4.303
3.933
3.918
3.222
3.203
2.336
1.346
1.246
0.000
Ph
TsN
O
Me
Me
5.44
1.98
2.01
1.00
1.00
2.04
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3.03
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3.16
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6
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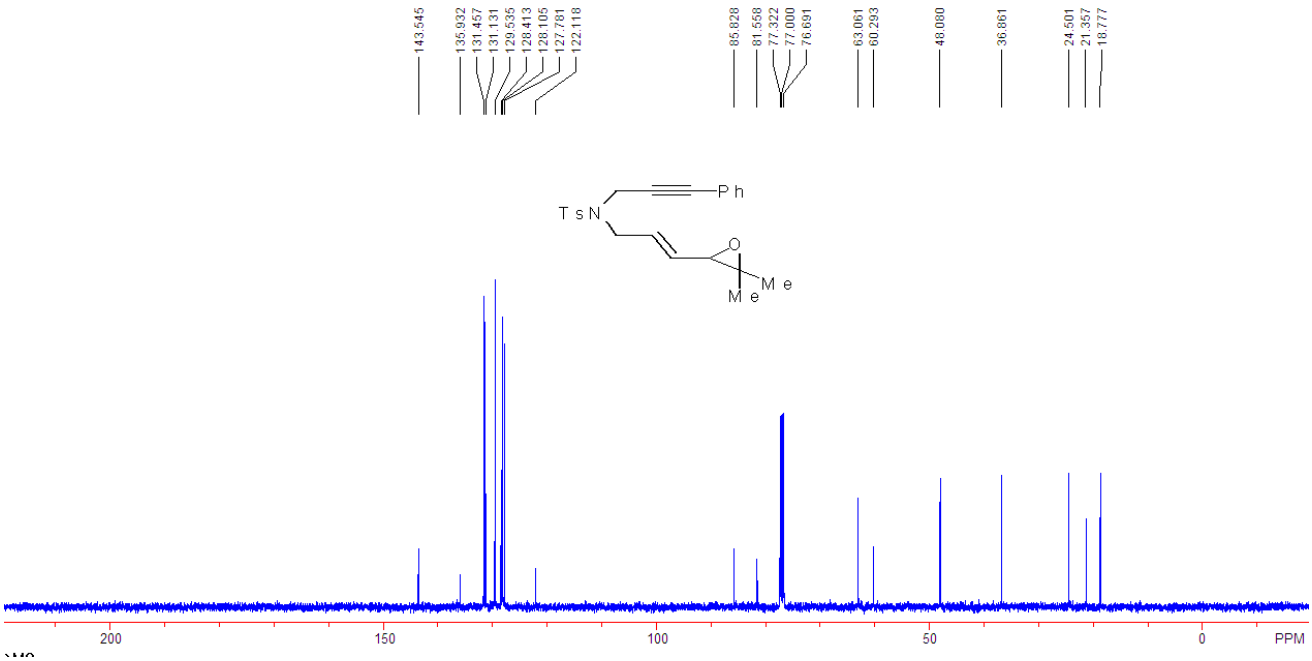
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127.781
122.118
85.828
81.558
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77.000
76.691
63.061
60.293
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21.357
18.777
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Me
Me
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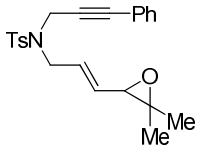
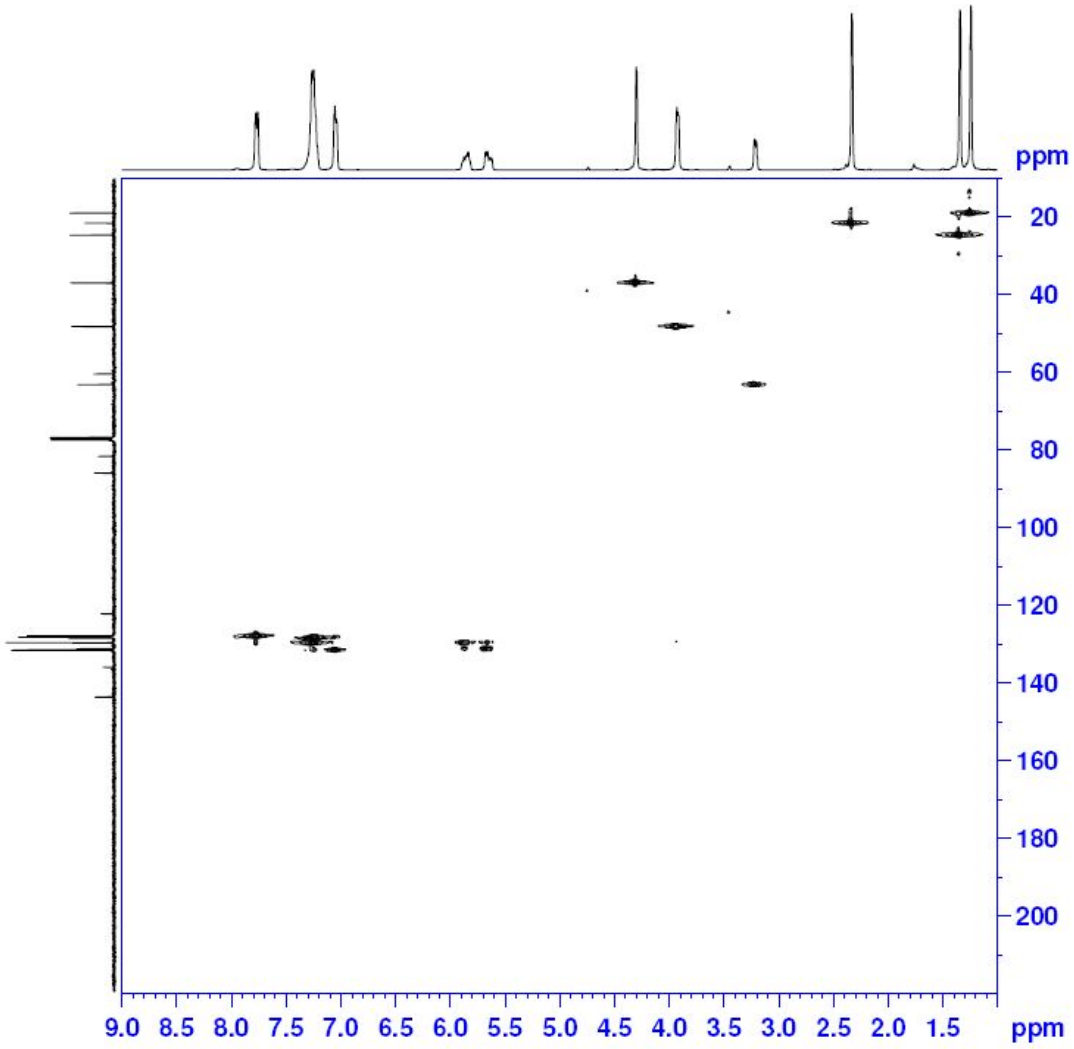
100
50
0
PPM


Ph
TsN
O
Me
Me

HSQC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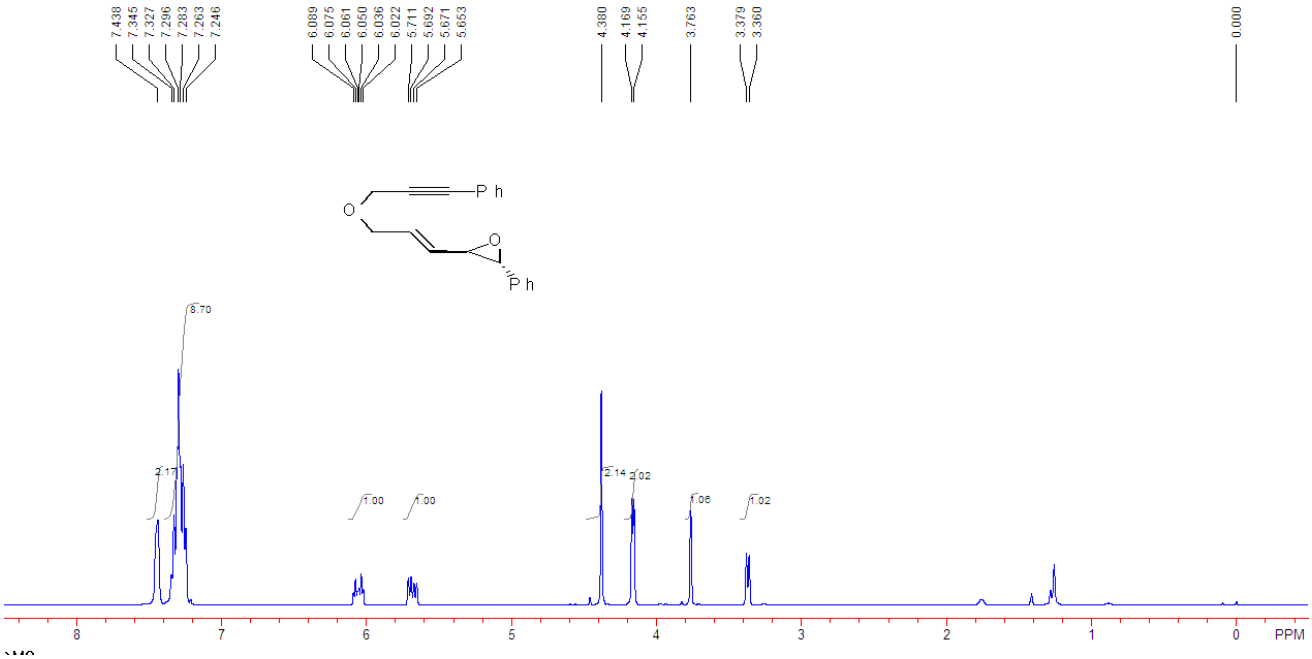
ppm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6.075
6.061
6.050
6.036
6.022
5.711
5.692
5.671
5.653
4.380
4.169
4.155
3.763
3.379
3.360
0.000
Ph
O
O
Ph
8.70
2.17
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1.00
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2.02
1.06
1.02
8
7
6
5
4
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2
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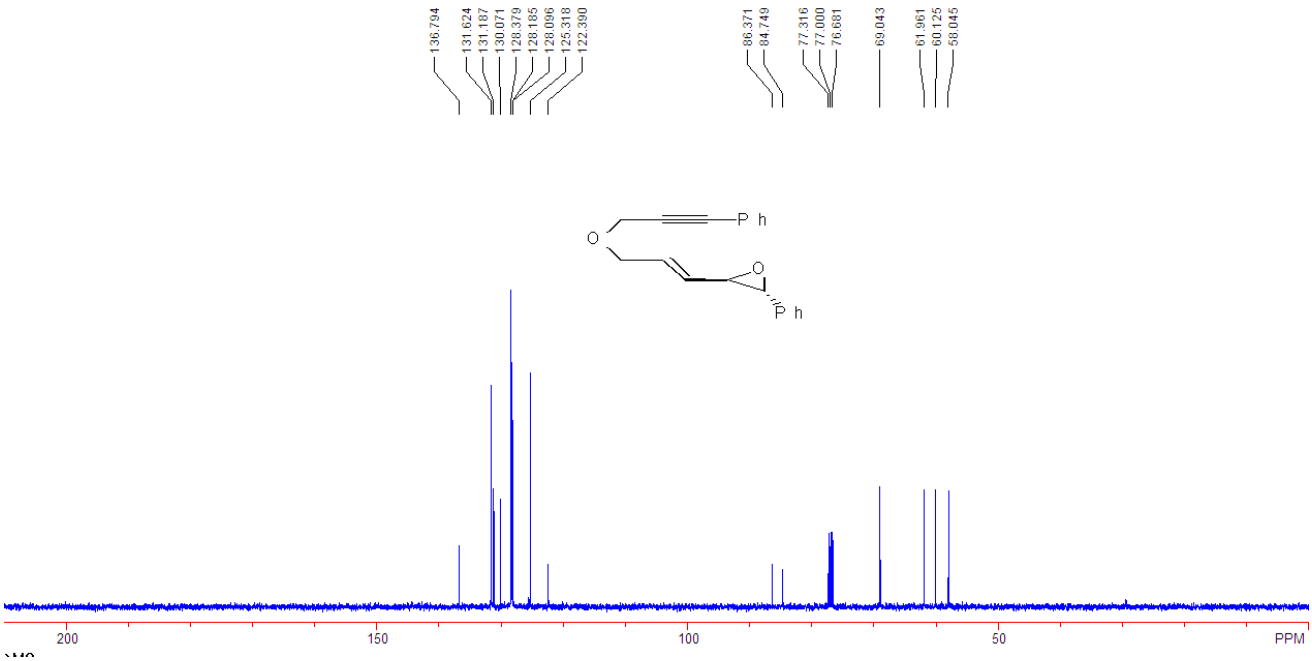
0
PPM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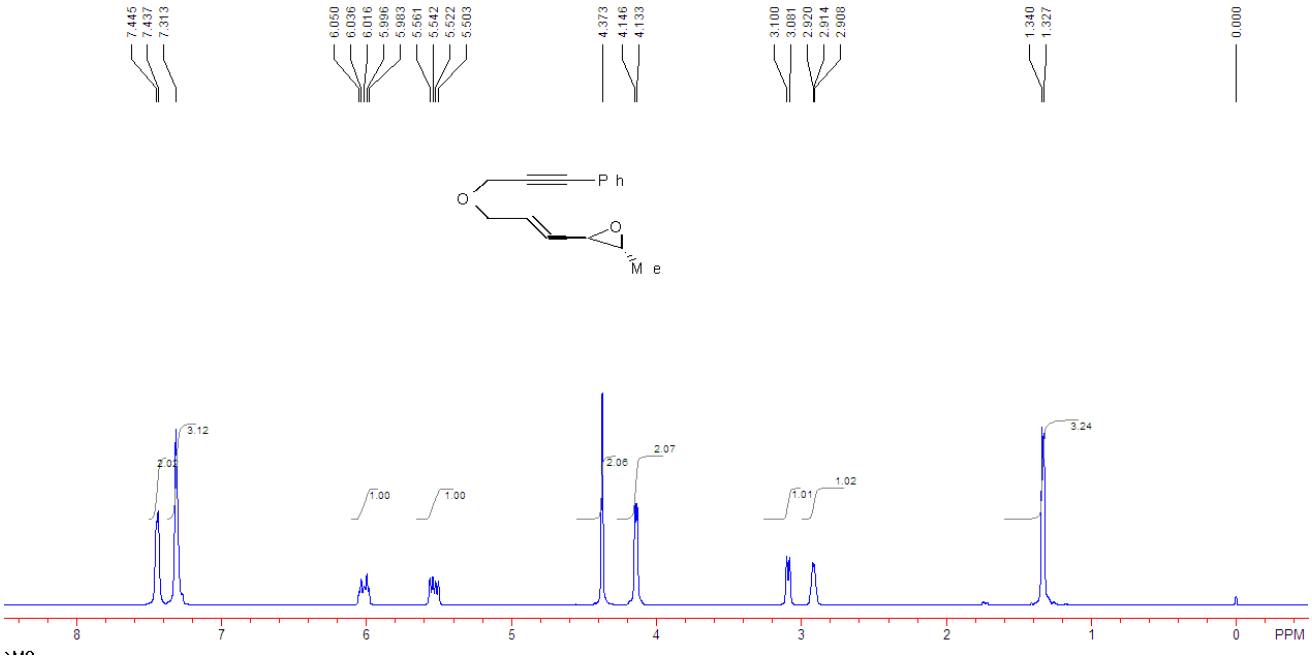
60.125
58.045
Ph
O
O
Ph
200
150
100
50
PPM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5.522
5.503
4.373
4.146
4.133
3.100
3.081
2.920
2.914
2.908
1.340
1.327
0.000
P h
O
O
M e
3.12
2.02
1.00
1.00
2.06
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1.01
1.02
3.24
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6
5
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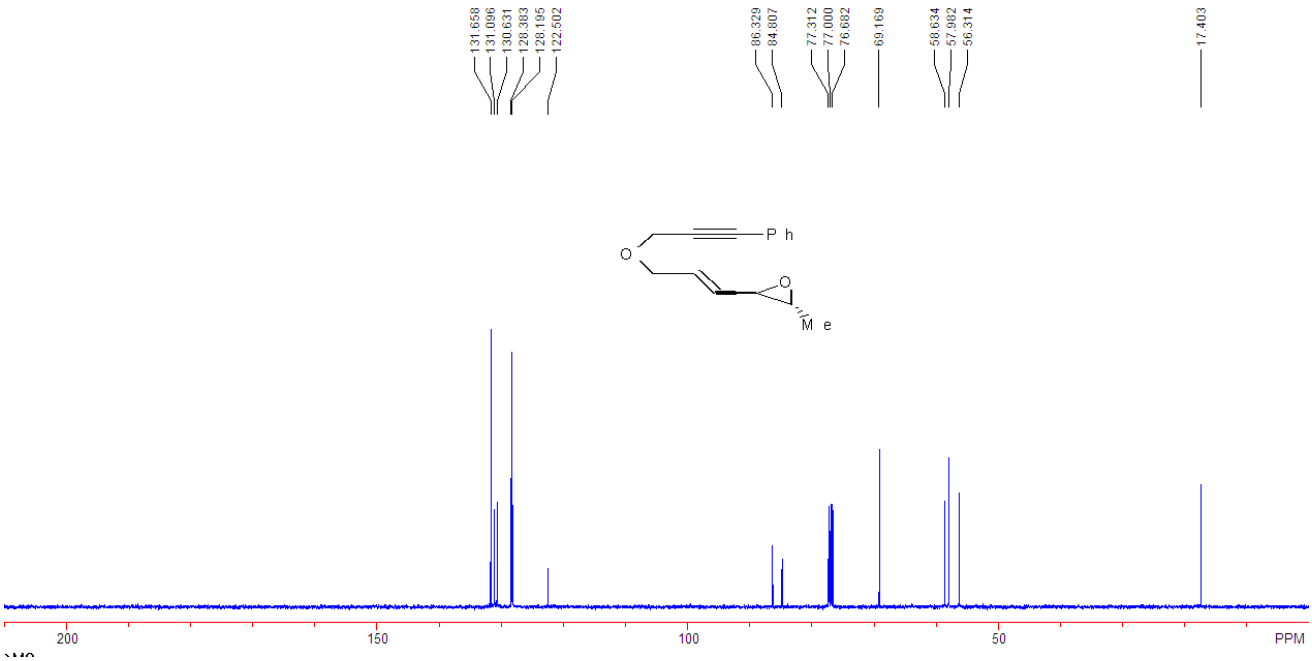
0
PPM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77.000
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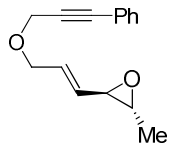
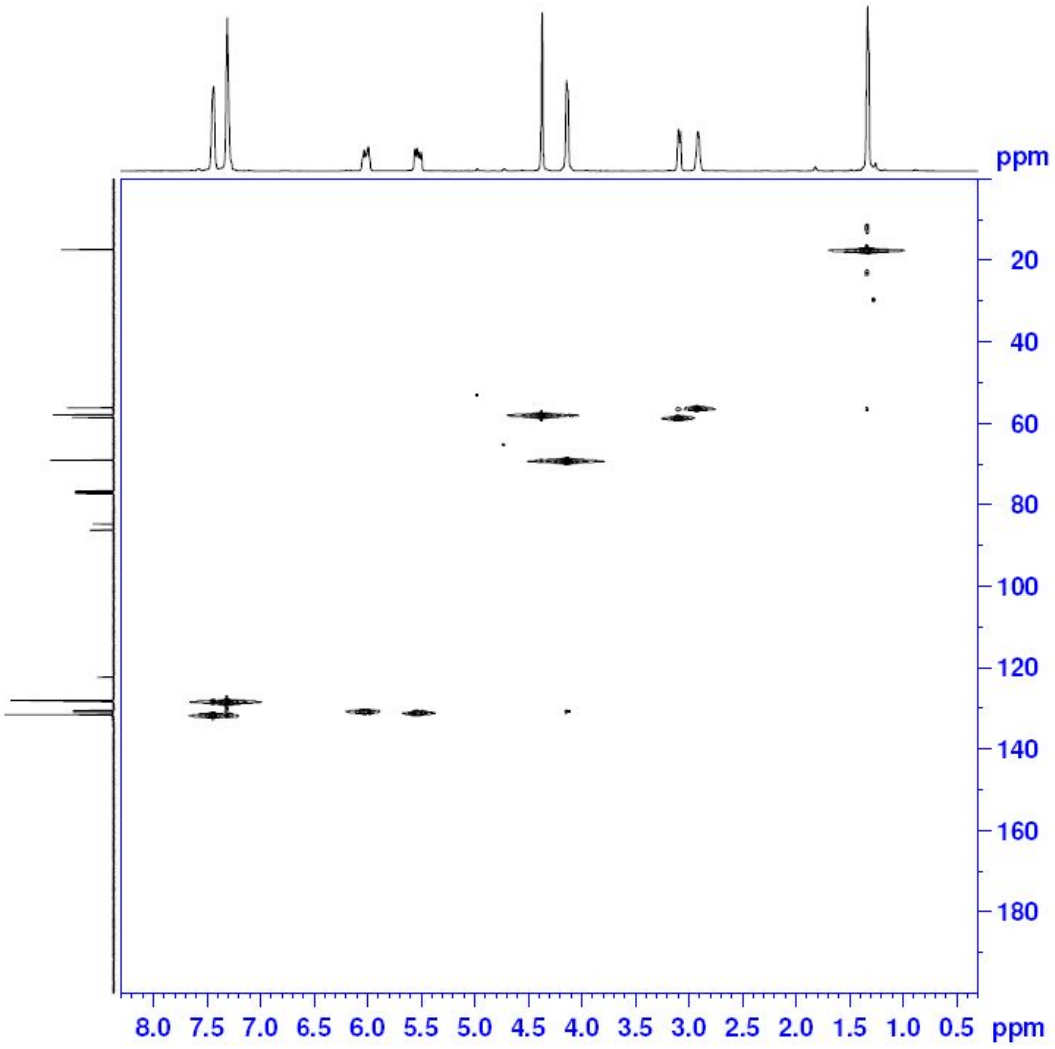
57.982
56.314
17.403
P h
O
O
M e
200
150
100
50
PPM


Ph
O
O
Me

HSQC


ppm
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80
100
120
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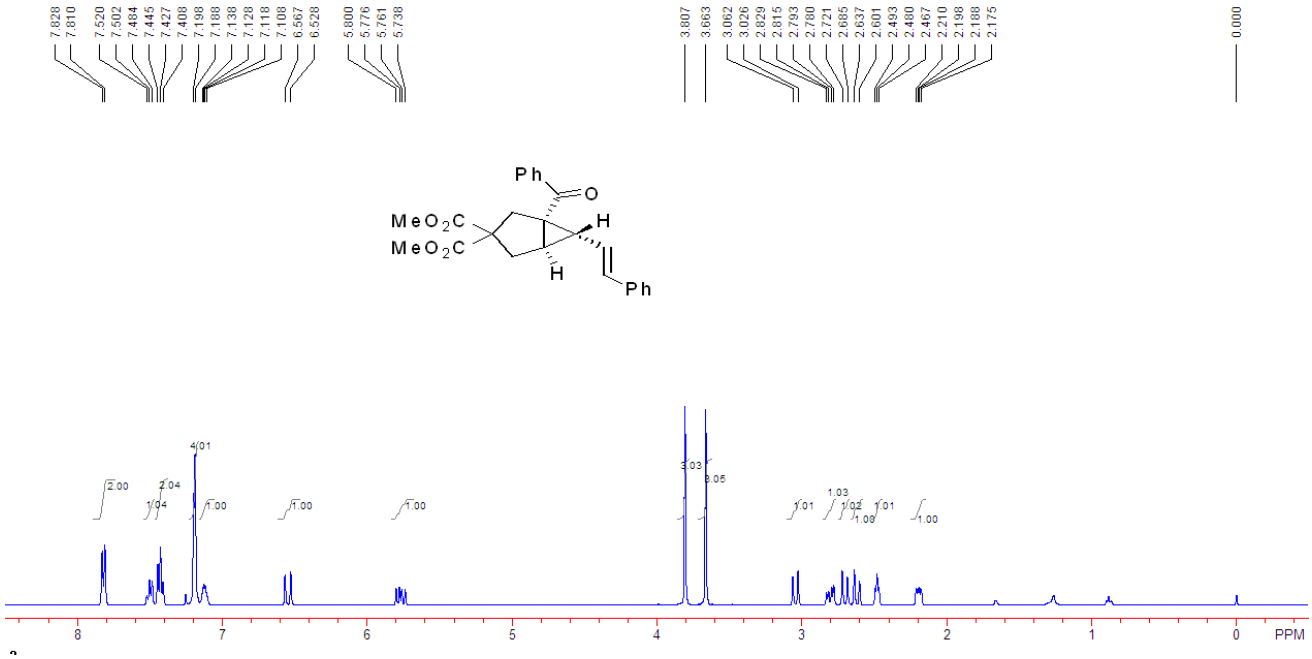
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7.108
6.567
6.528
5.800
5.776
5.761
5.738
3.807
3.663
3.062
3.026
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2.793
2.780
2.721
2.685
2.637
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2.493
2.480
2.467
2.210
2.198
2.188
2.175
0.000
Ph
O
MeO2C
MeO2C
H
H
Ph
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1.04
4.01
1.00
1.00
1.00
3.03
3.05
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1.00
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6
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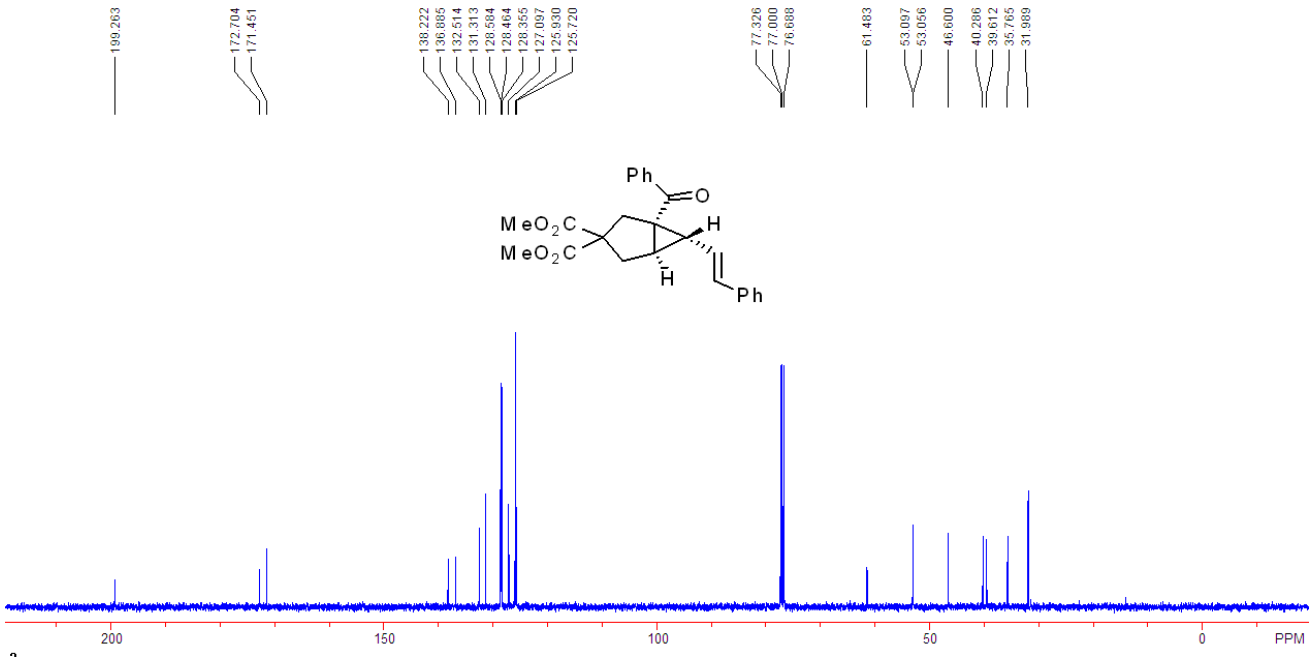
1
0
PPM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138.222
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132.514
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128.355
127.097
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125.720
77.326
77.000
76.688
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40.286
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Ph
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MeO2C
H
H
Ph
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100
50
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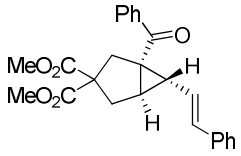
PPM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MeO2C
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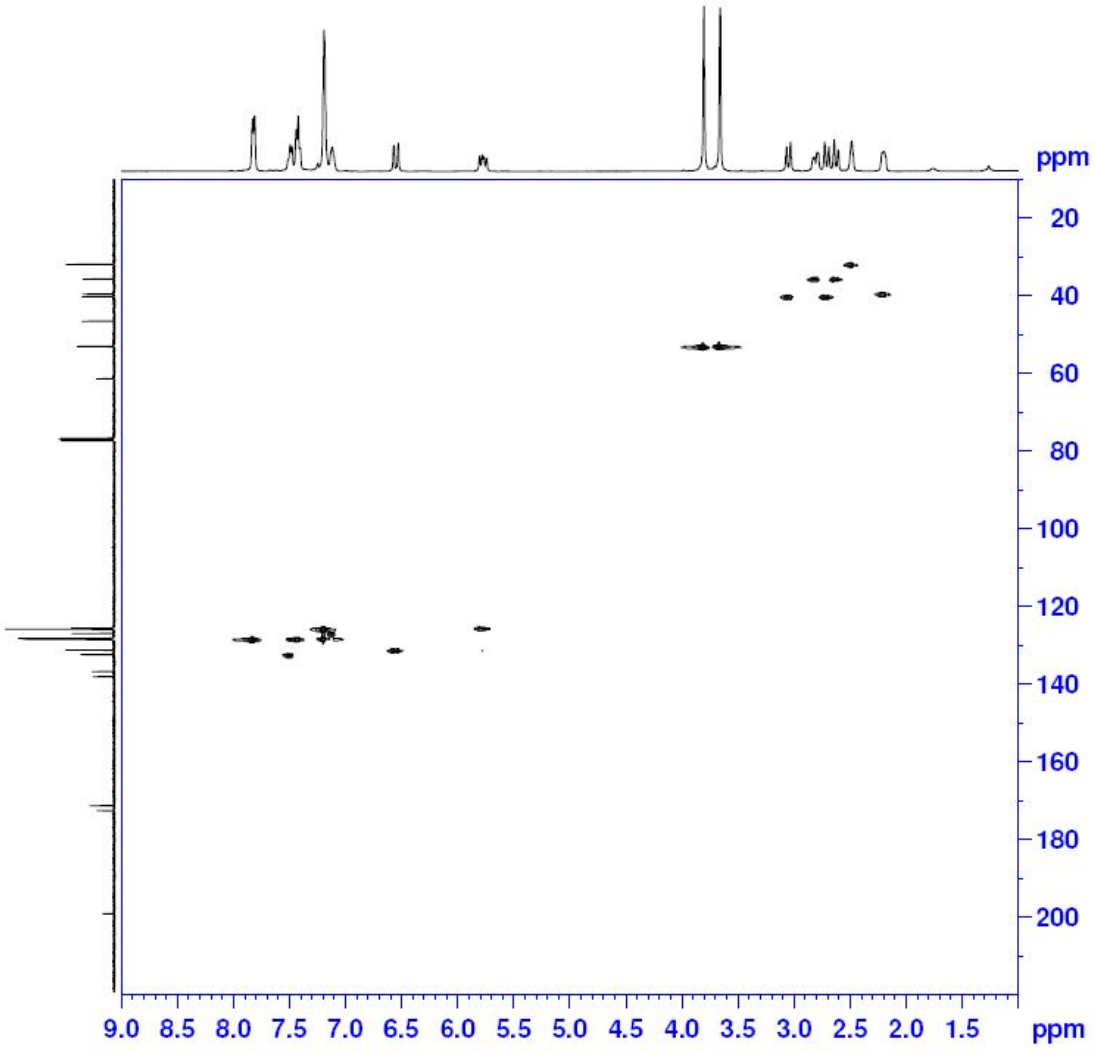
Ph

HSQC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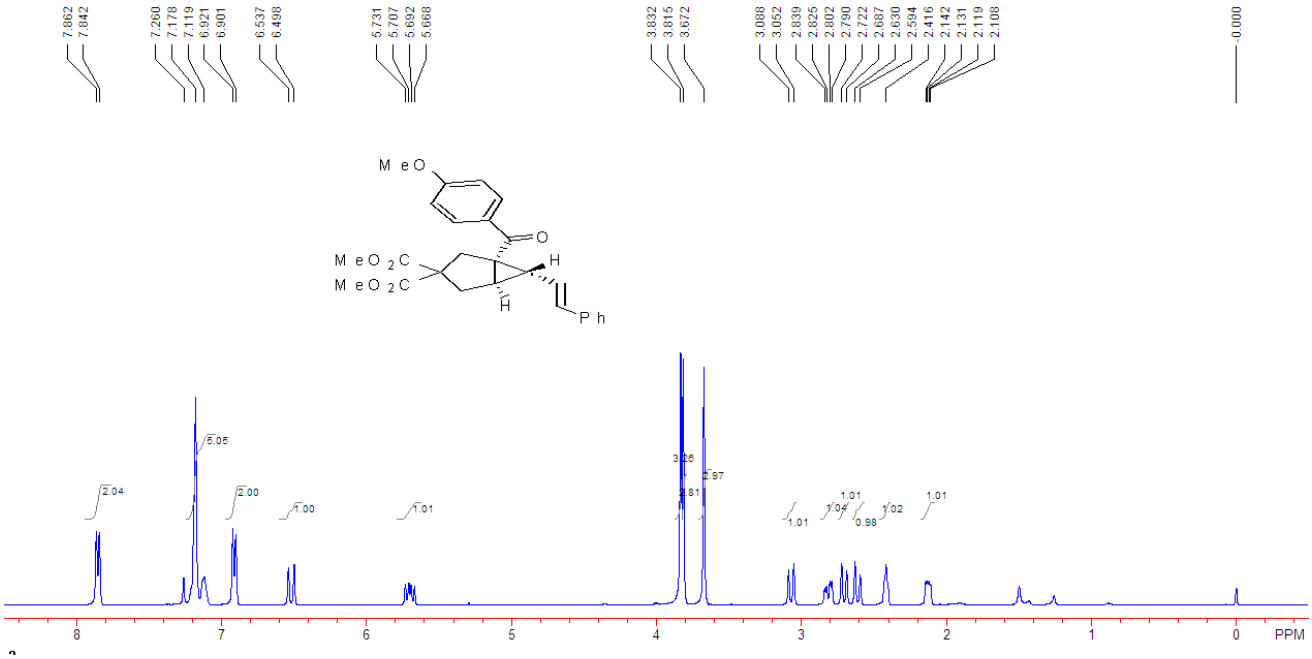
ppm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5.668
3.832
3.815
3.672
3.088
3.052
2.839
2.825
2.802
2.790
2.722
2.687
2.630
2.594
2.416
2.142
2.131
2.119
2.108
0.000
MeO
O
MeO2C
MeO2C
H
H
Ph
2.04
6.05
2.00
1.00
1.01
3.26
2.81
2.97
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1.04
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0.98
1.02
1.01
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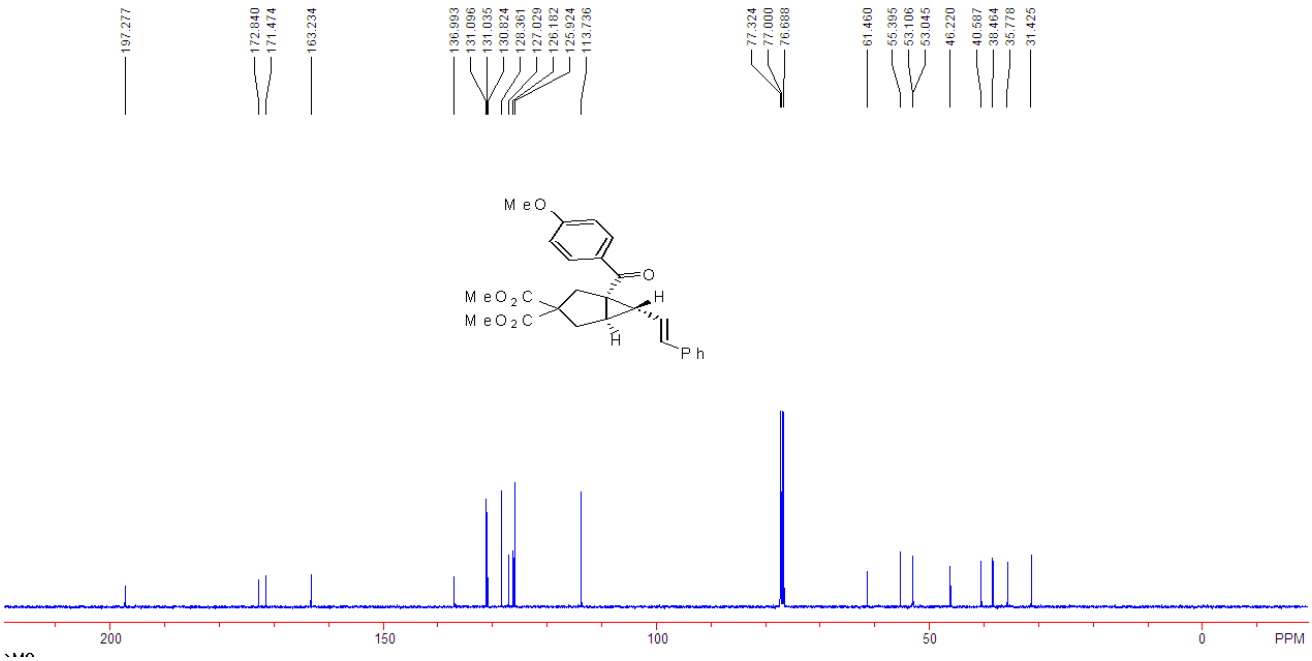
PPM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130.824
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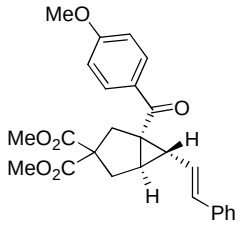
127.029
126.182
125.924
113.736
77.324
77.000
76.688
61.460
55.395
53.106
53.045
46.220
40.587
38.464
35.778
31.425
MeO
O
MeO2C
MeO2C
H
H
Ph
200
150
100
50
0
PPM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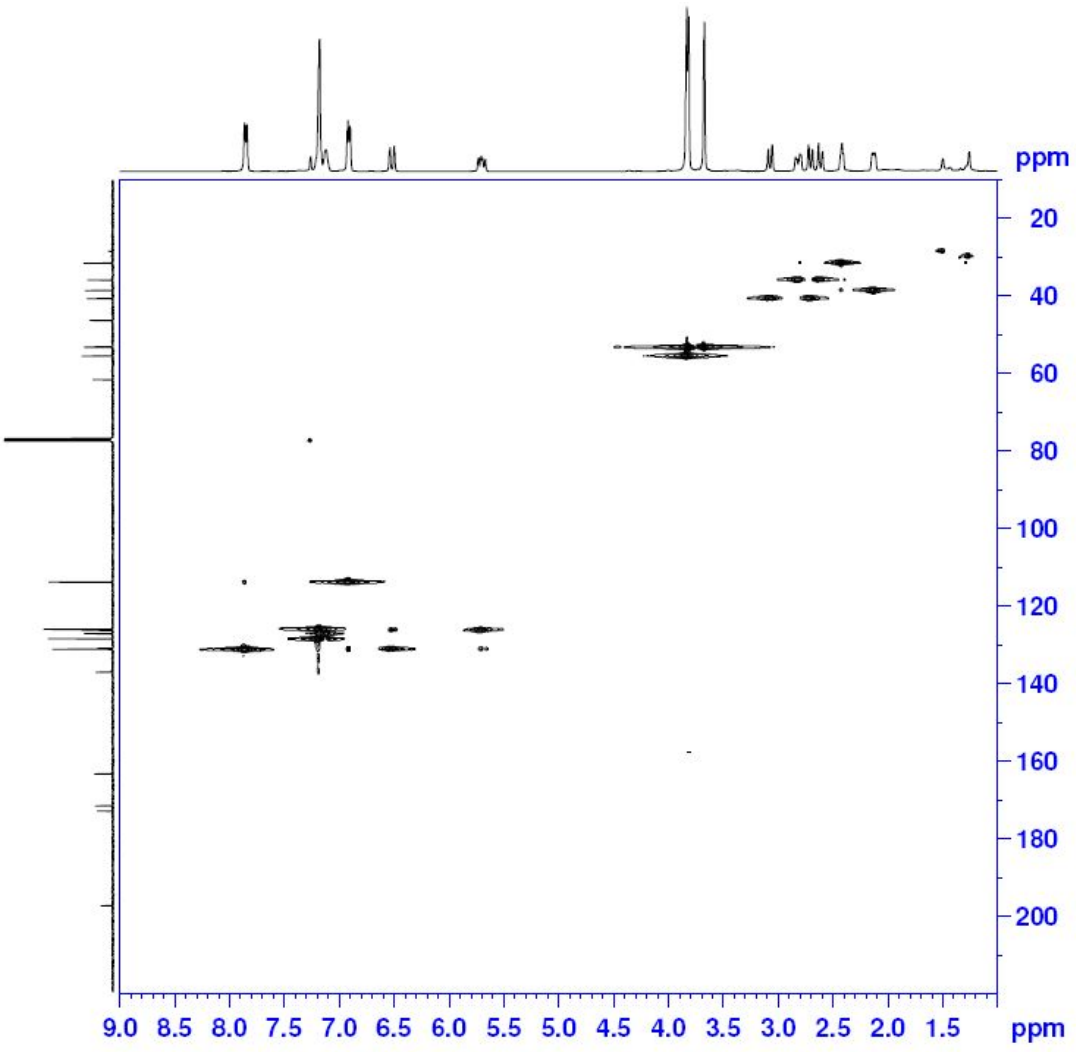
MeO2C
MeO2C
H
H
Ph

HSQC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80
100
120
140
160
180
200
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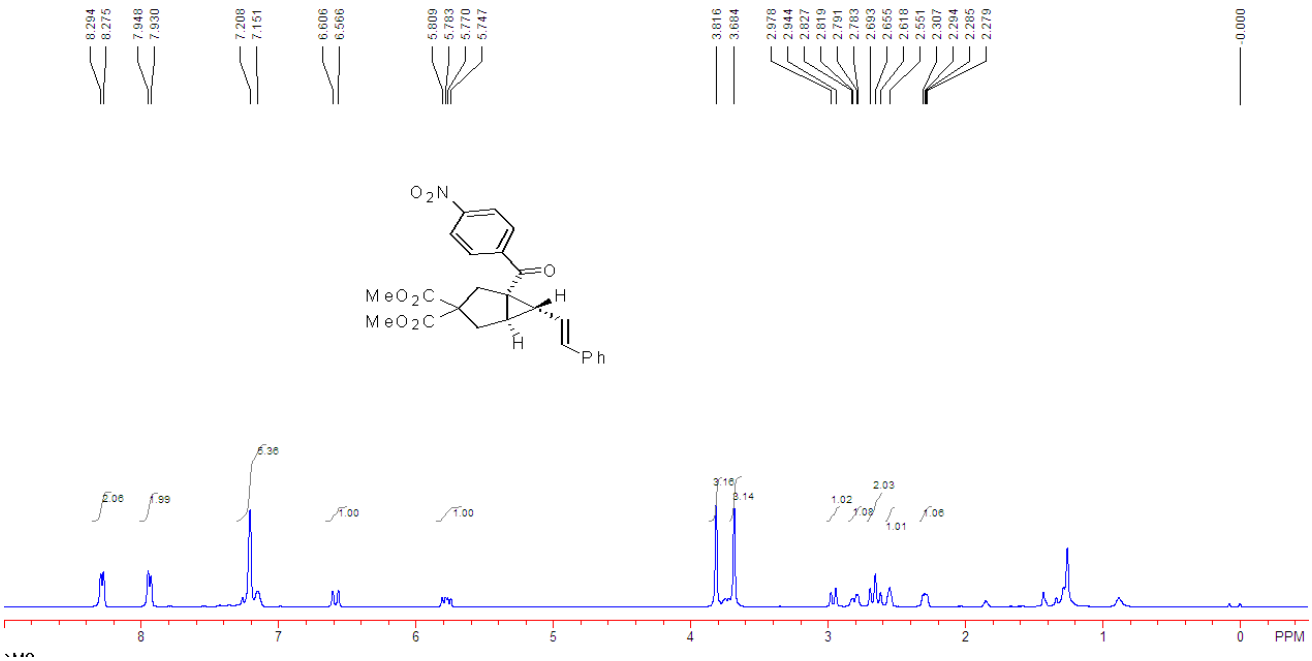
ppm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7.948
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5.783
5.770
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3.816
3.684
2.978
2.944
2.827
2.819
2.791
2.783
2.693
2.655
2.618
2.551
2.307
2.294
2.285
2.279
0.000
O2N
O
MeO2C
MeO2C
H
H
Ph
2.06
1.99
6.36
1.00
1.00
3.16
3.14
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2.03
1.01
1.06
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7
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5
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3
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1
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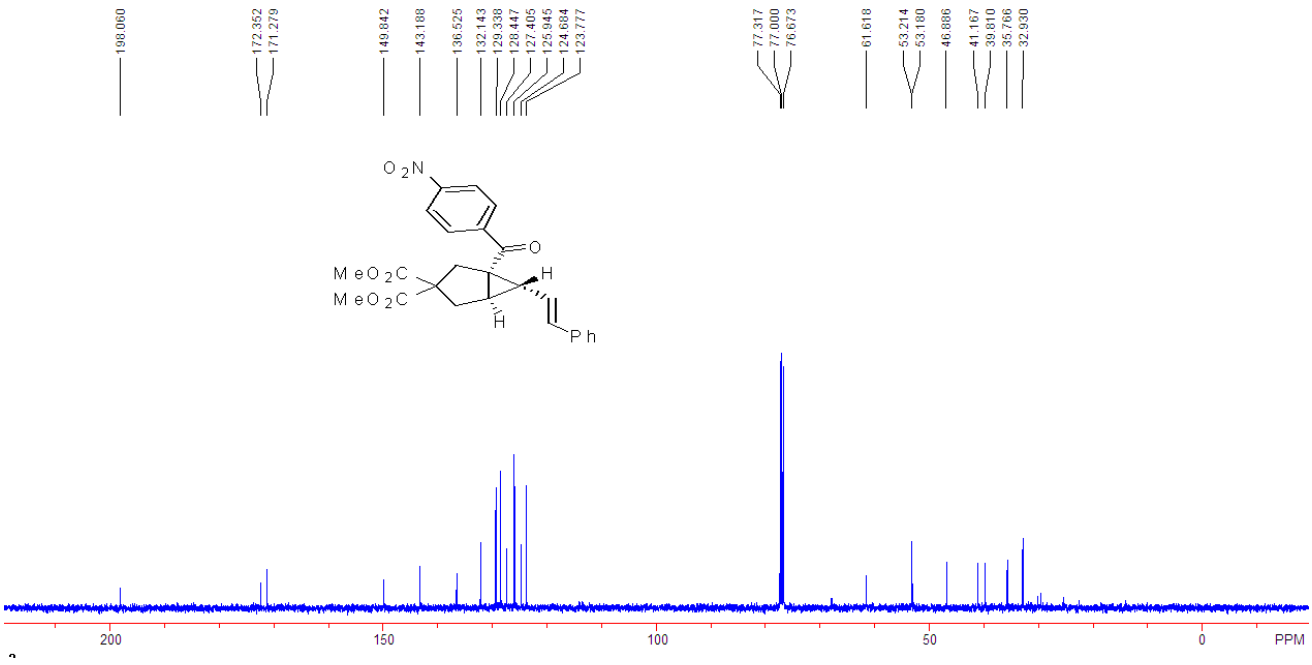
PPM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136.525
132.143
129.338
128.447
127.405
125.945
124.684
123.777
77.317
77.000
76.673
61.618
53.214
53.180
46.886
41.167
39.810
35.766
32.930
O2N
O
MeO2C
MeO2C
H
H
Ph
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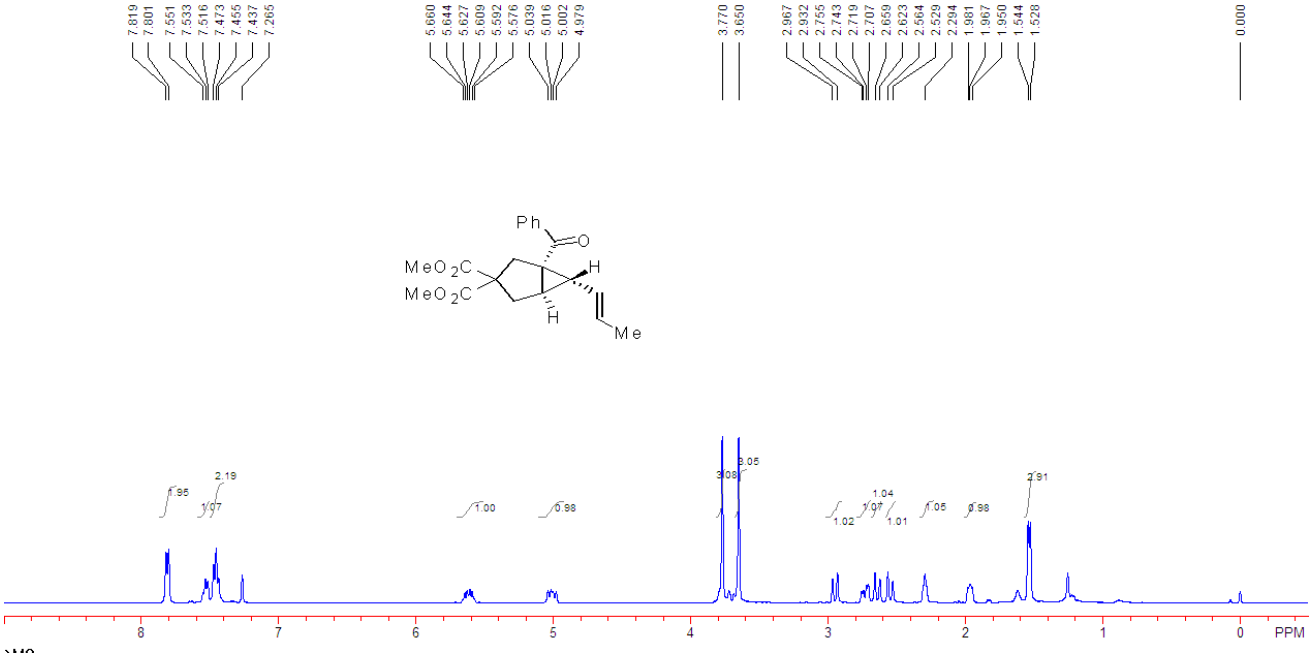
150
100
50
0
PPM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7.437
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5.644
5.627
5.609
5.592
5.576
5.039
5.016
5.002
4.979
3.770
3.650
2.967
2.932
2.755
2.743
2.719
2.707
2.659
2.623
2.564
2.529
2.294
1.981
1.967
1.950
1.544
1.528
0.000
Ph
O
MeO2C
MeO2C
H
H
Me
1.95
2.19
1.07
1.00
0.98
3.08
3.05
1.02
1.04
1.07
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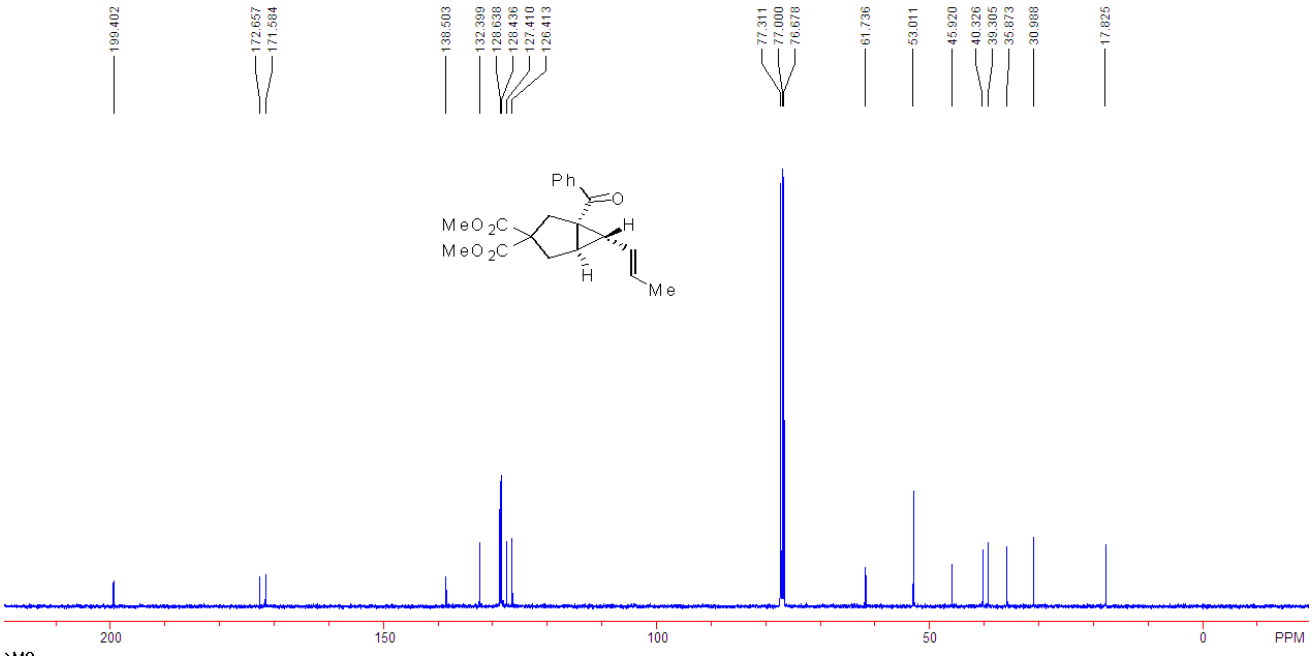
1.05
0.98
2.91
8
7
6
5
4
3
2
1
0
PPM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128.436
127.410
126.413
77.311
77.000
76.678
61.736
53.011
45.920
40.326
39.305
35.873
30.988
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Ph
O
MeO2C
MeO2C
H
H
Me
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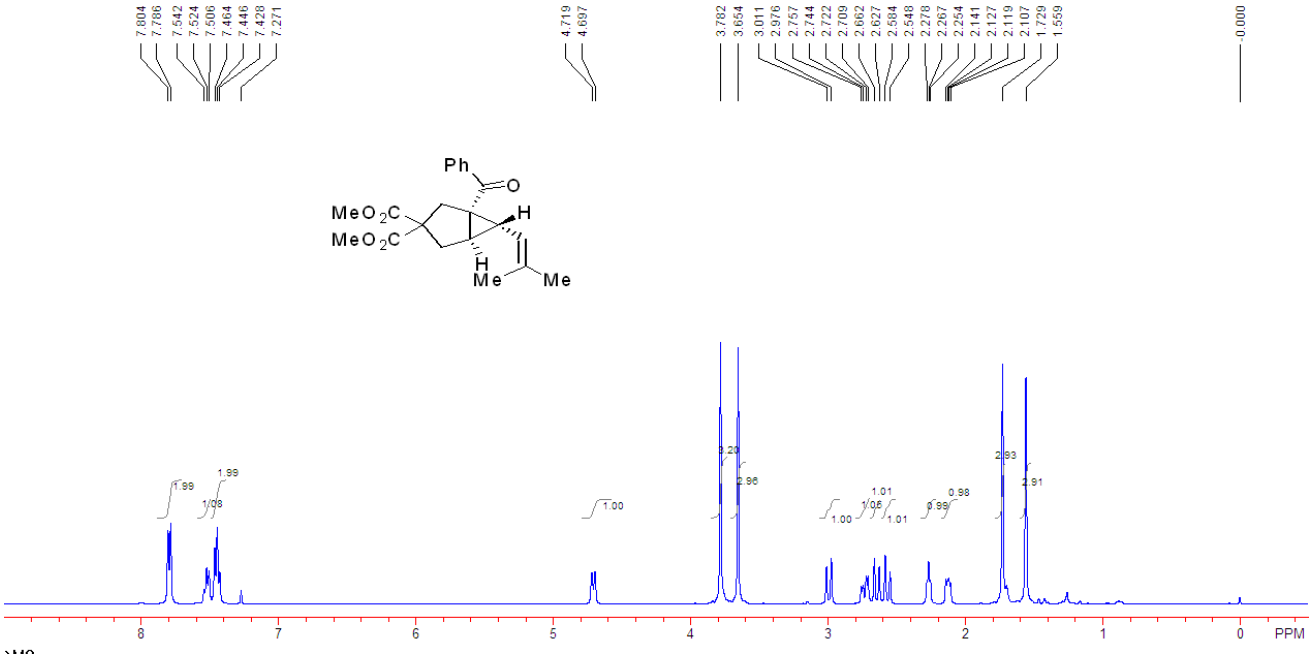
150
100
50
0
PPM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7.464
7.446
7.428
7.271
4.719
4.697
3.782
3.654
3.011
2.976
2.757
2.744
2.722
2.709
2.662
2.627
2.584
2.548
2.278
2.267
2.254
2.141
2.127
2.119
2.107
1.729
1.559
0.000
Ph
O
MeO2C
MeO2C
H
H
Me
Me
1.99
1.99
1.08
1.00
3.20
2.96
1.00
1.01
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0.98
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2.91
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6
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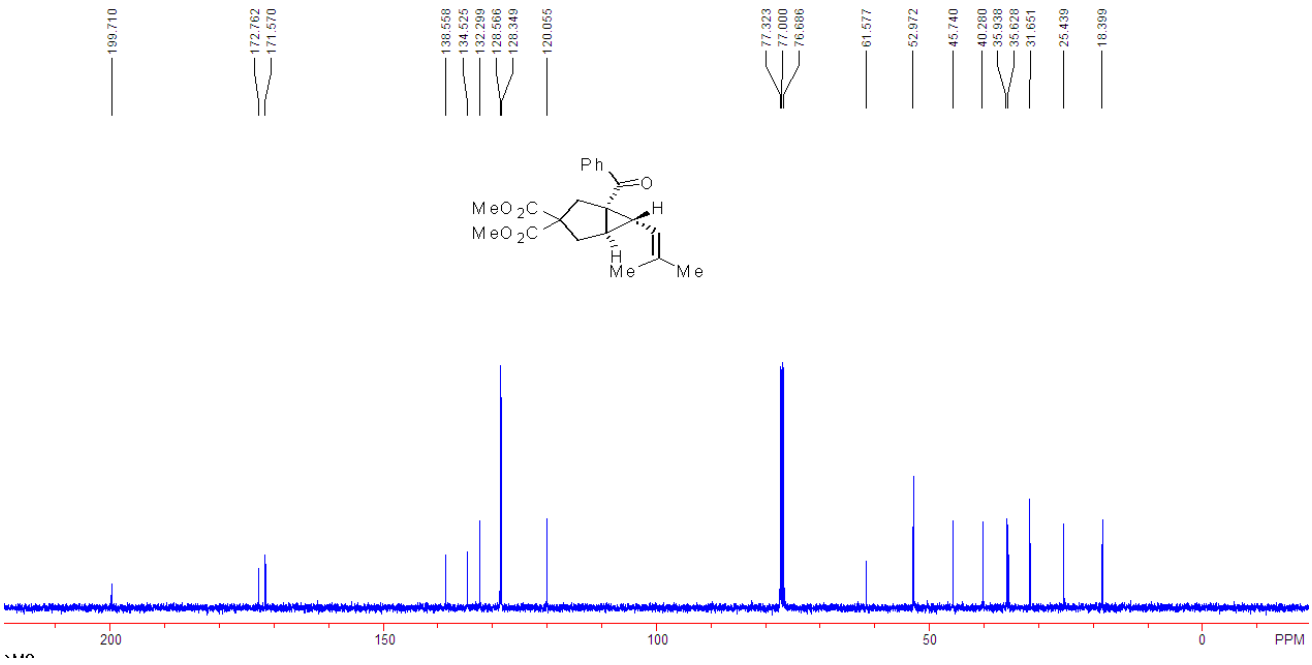
PPM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61.577
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45.740
40.280
35.938
35.628
31.651
25.439
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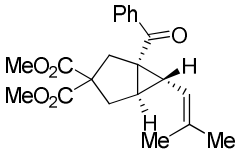
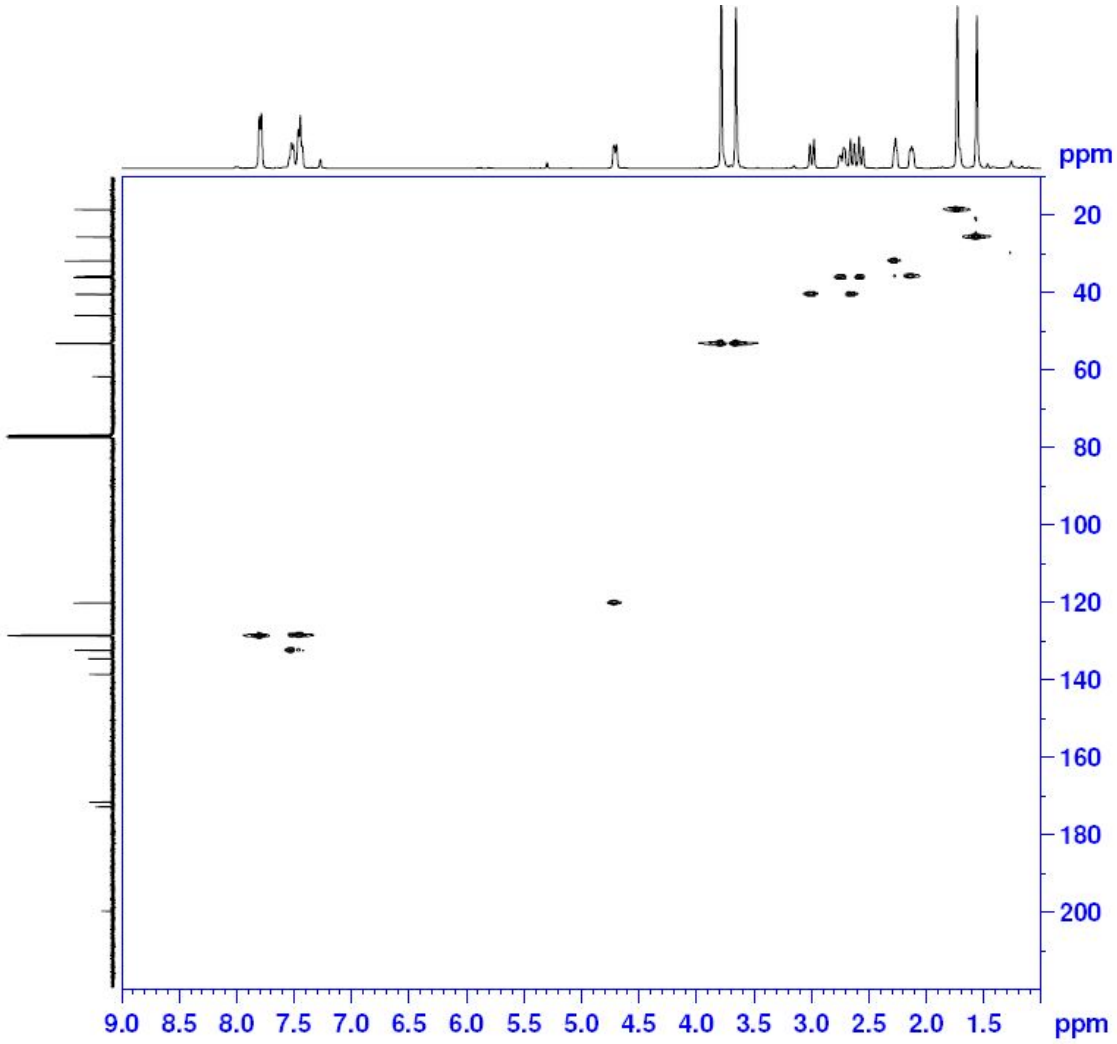
Ph
O
MeO2C
MeO2C
H
H
Me
Me
200
150
100
50
0
PPM


Ph
O
MeO2C
MeO2C
H
H
Me
Me

HSQC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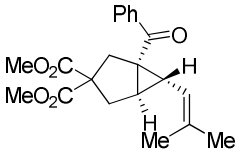
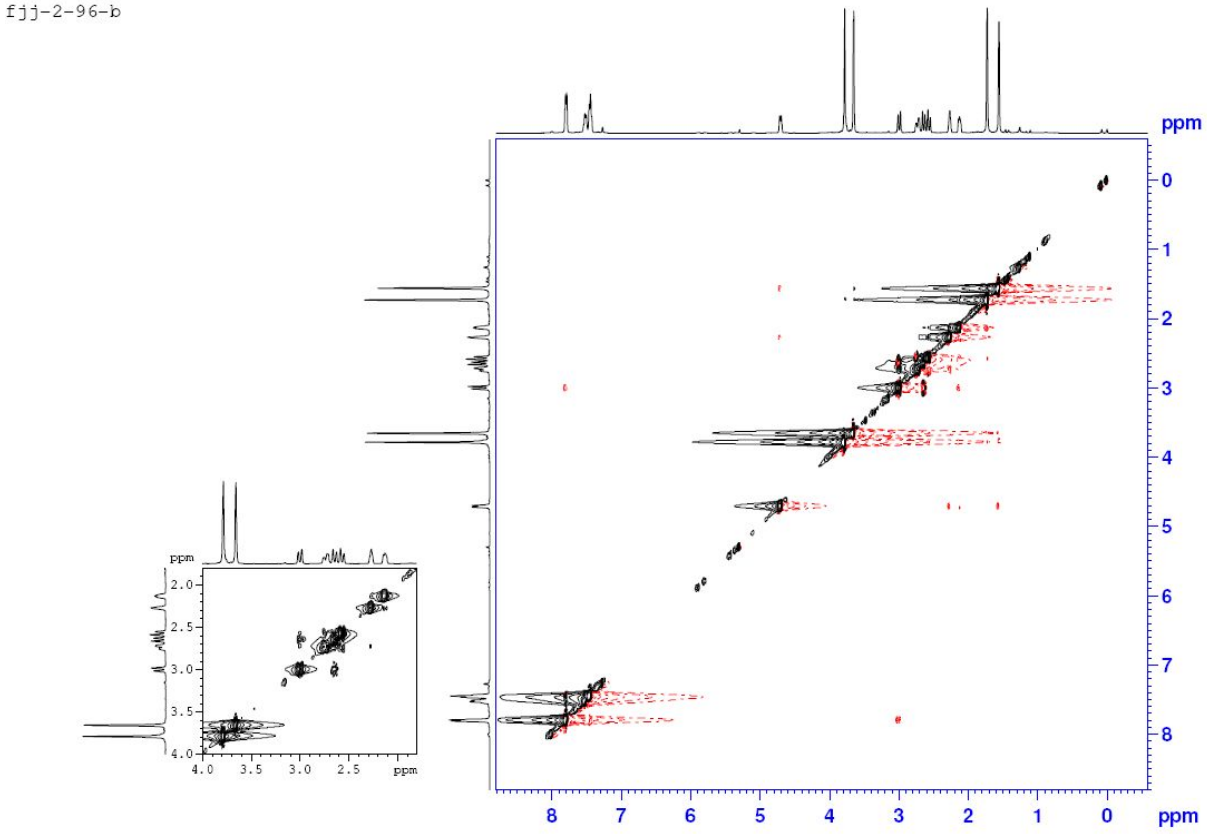
80
100
120
140
160
180
200
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
ppm


Ph
O
MeO2C
MeO2C
H
H
Me
Me

NOESY


fjj-2-96-b
ppm
0
1
2
3
4
5
6
7
8
8 7 6 5 4 3 2 1 0 ppm
ppm
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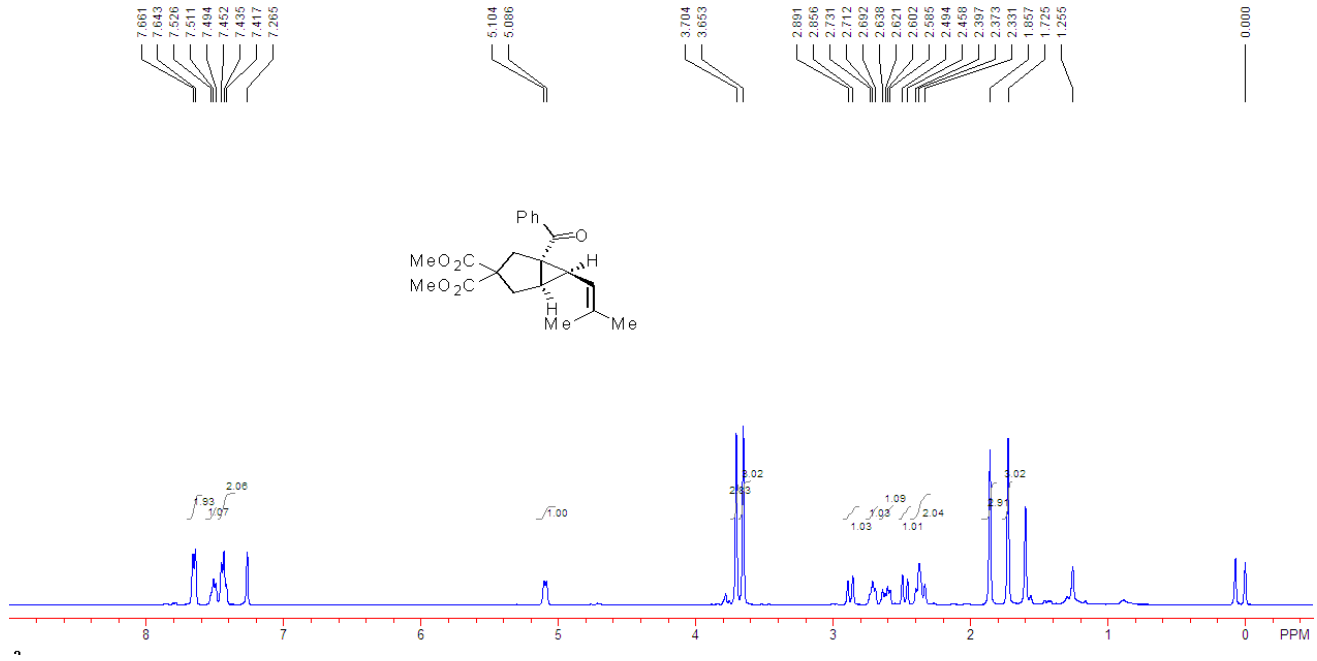
3.0
3.5
4.0
4.0 3.5 3.0 2.5 ppm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2.856
2.731
2.712
2.692
2.638
2.621
2.602
2.585
2.494
2.458
2.397
2.373
2.331
1.857
1.725
1.255
0.000
Ph
O
MeO2C
MeO2C
H
H
Me
Me
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1.93
1.97
1.00
3.02
2.83
1.09
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1.01
3.02
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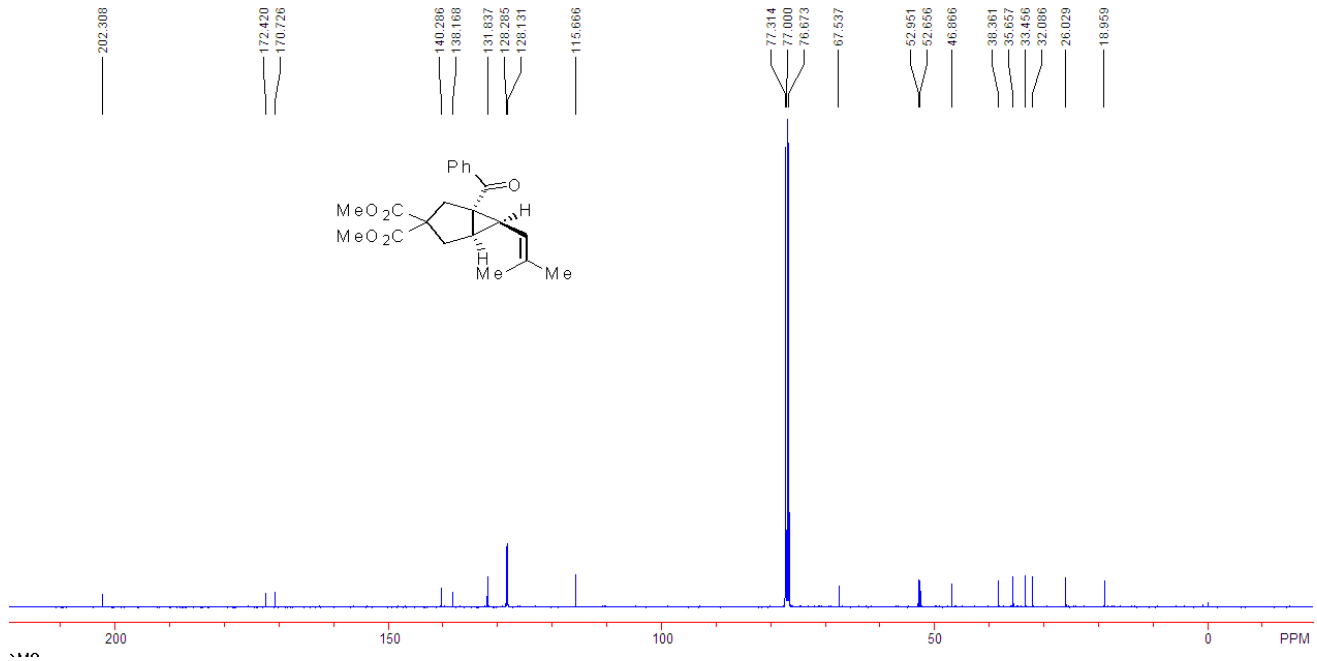
PPM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128.265
128.131
115.666
77.314
77.000
76.673
67.537
52.951
52.656
46.866
38.361
35.657
33.456
32.086
26.029
18.959
Ph
O
MeO2C
MeO2C
H
H
Me
Me
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150
100
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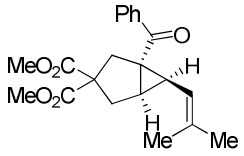
0
PPM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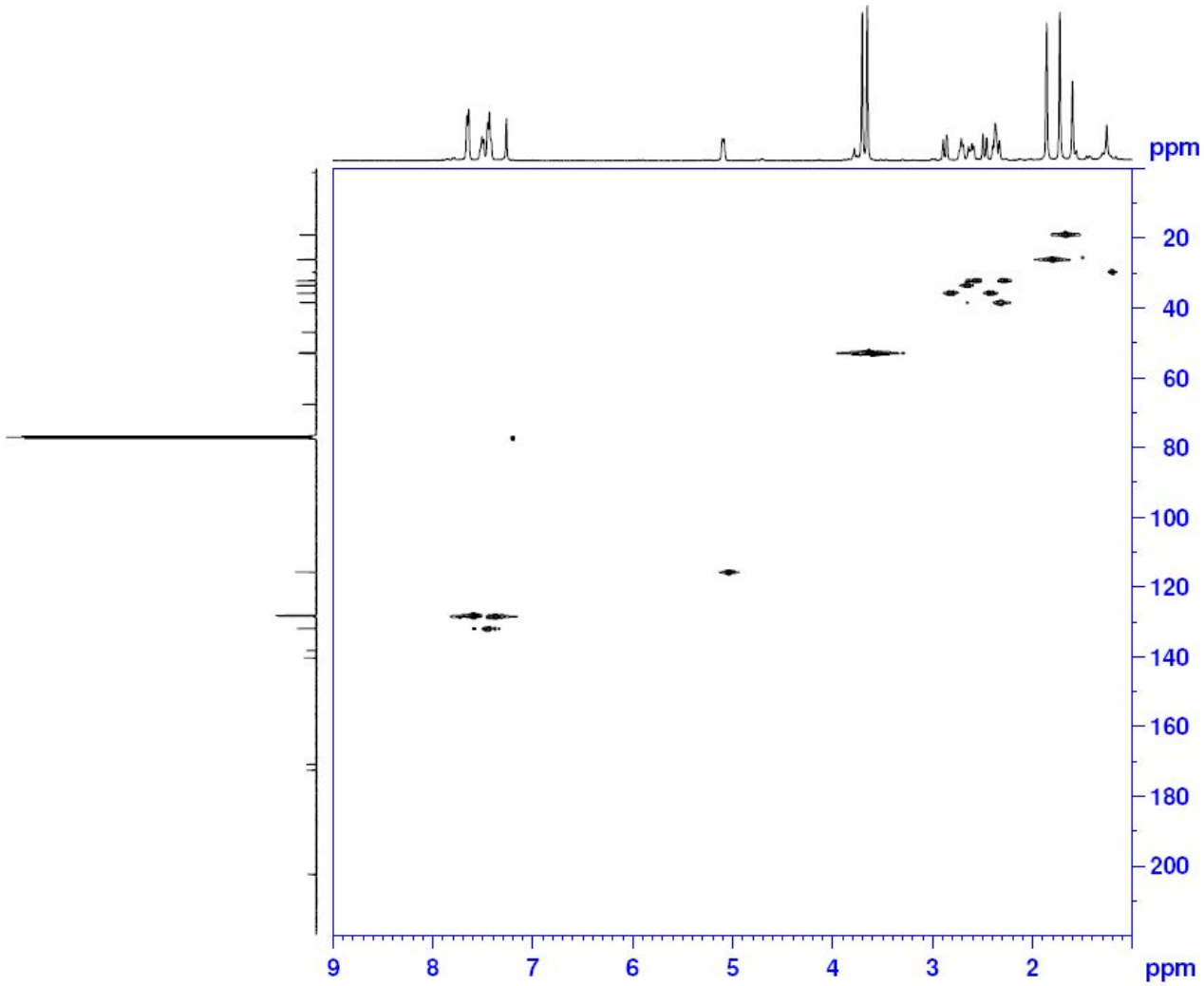
MeO2C
MeO2C
H
H
Me
Me

HSQC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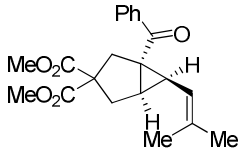
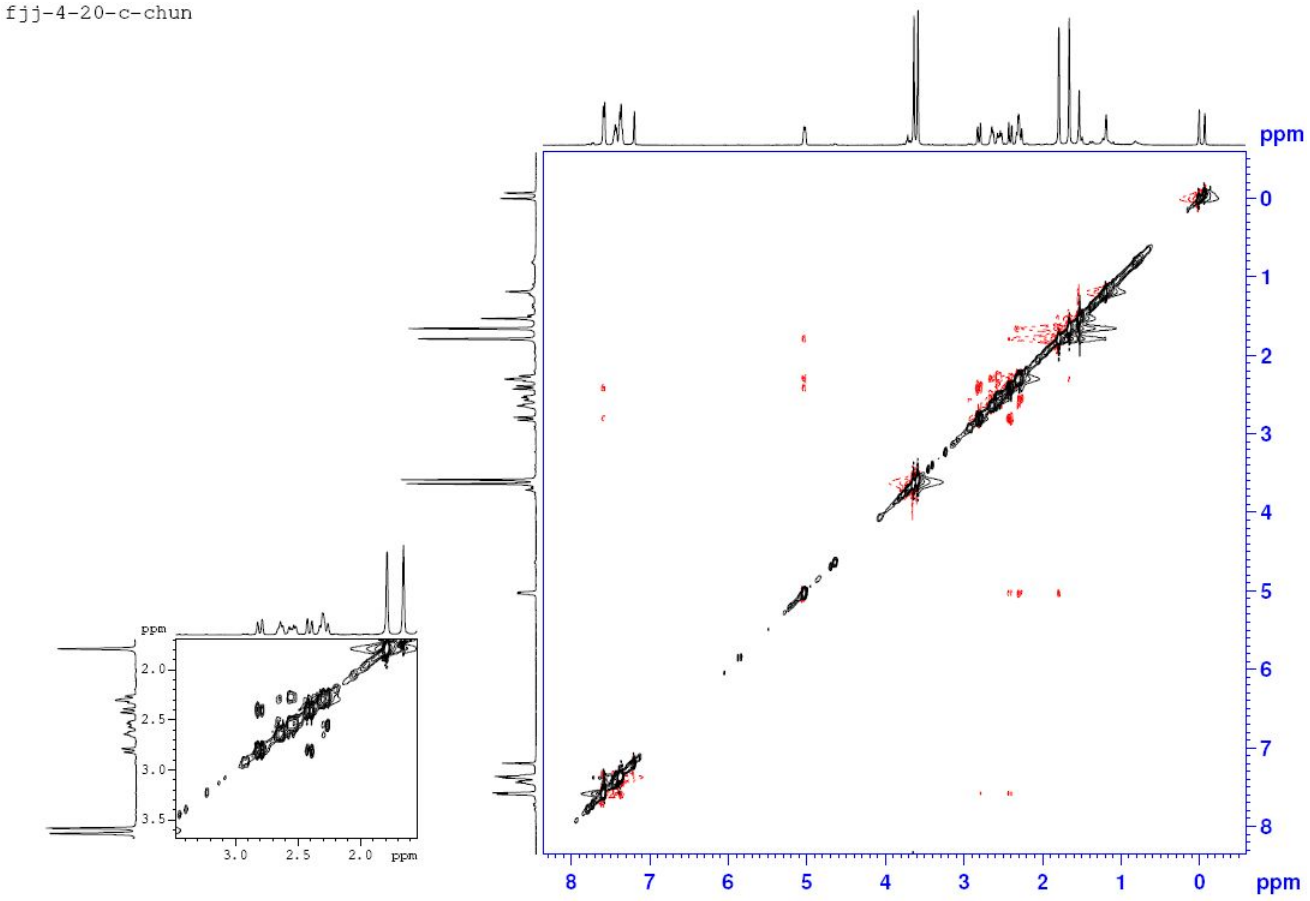
80
100
120
140
160
180
200
9
8
7
6
5
4
3
2
ppm


Ph
O
MeO2C
MeO2C
H
H
Me
Me

NOESY


fjj-4-20-c-chun
ppm
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2
3
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6
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8
8 7 6 5 4 3 2 1 0 ppm
ppm
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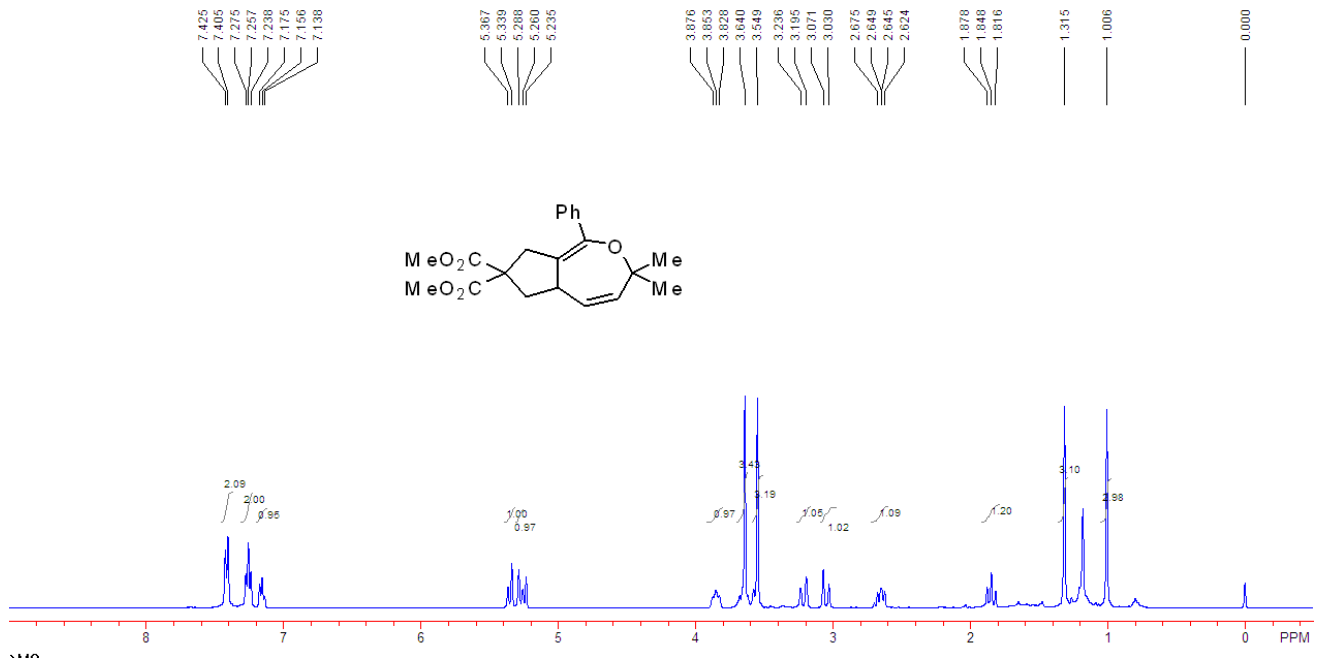
2.5
3.0
3.5
3.0 2.5 2.0 ppm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5.260
5.235
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3.853
3.828
3.640
3.549
3.236
3.195
3.071
3.030
2.675
2.649
2.645
2.624
1.878
1.848
1.816
1.315
1.006
0.000
Ph
MeO2C
MeO2C
O
Me
Me
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2.00
0.95
1.00
0.97
3.43
3.19
0.97
1.05
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1.20
3.10
2.98
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6
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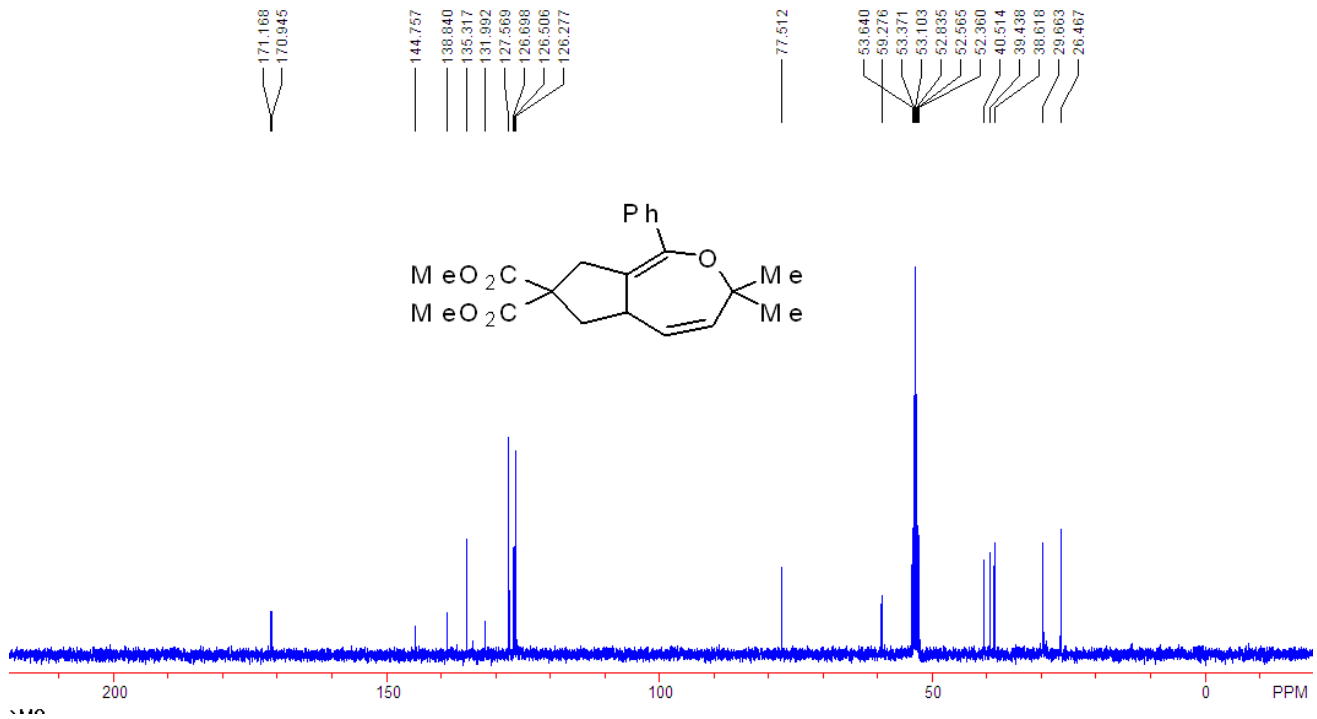
PPM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170.945
144.757
138.840
135.317
131.992
127.569
126.698
126.506
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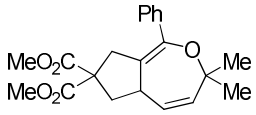
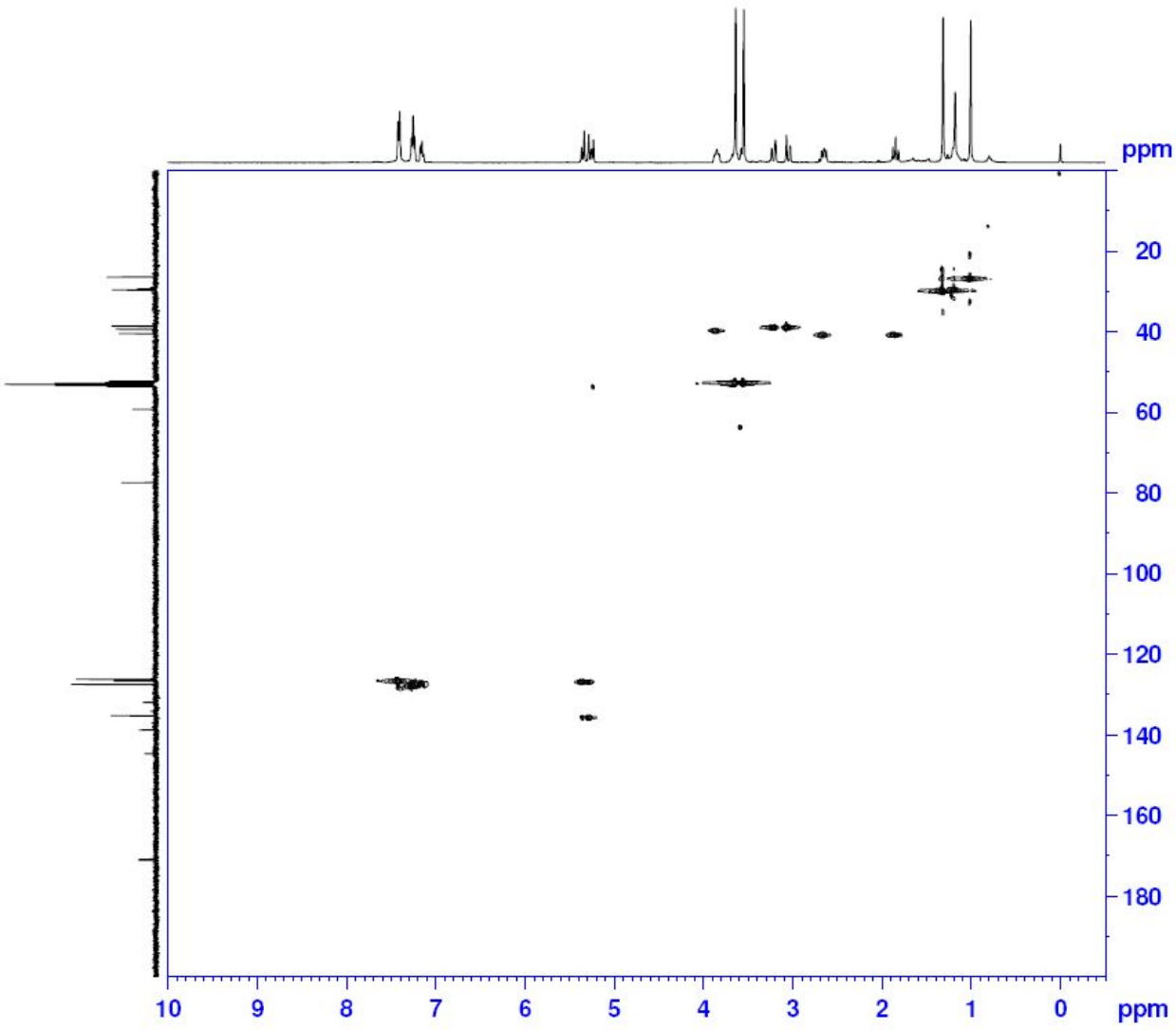
77.512
53.640
59.276
53.371
53.103
52.835
52.565
52.360
40.514
39.438
38.618
29.663
26.467
Ph
MeO2C
MeO2C
O
Me
Me
200
150
100
50
0
PPM


Ph
O
MeO2C
MeO2C
Me
Me

HSQC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10
9
8
7
6
5
4
3
2
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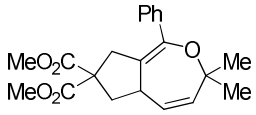
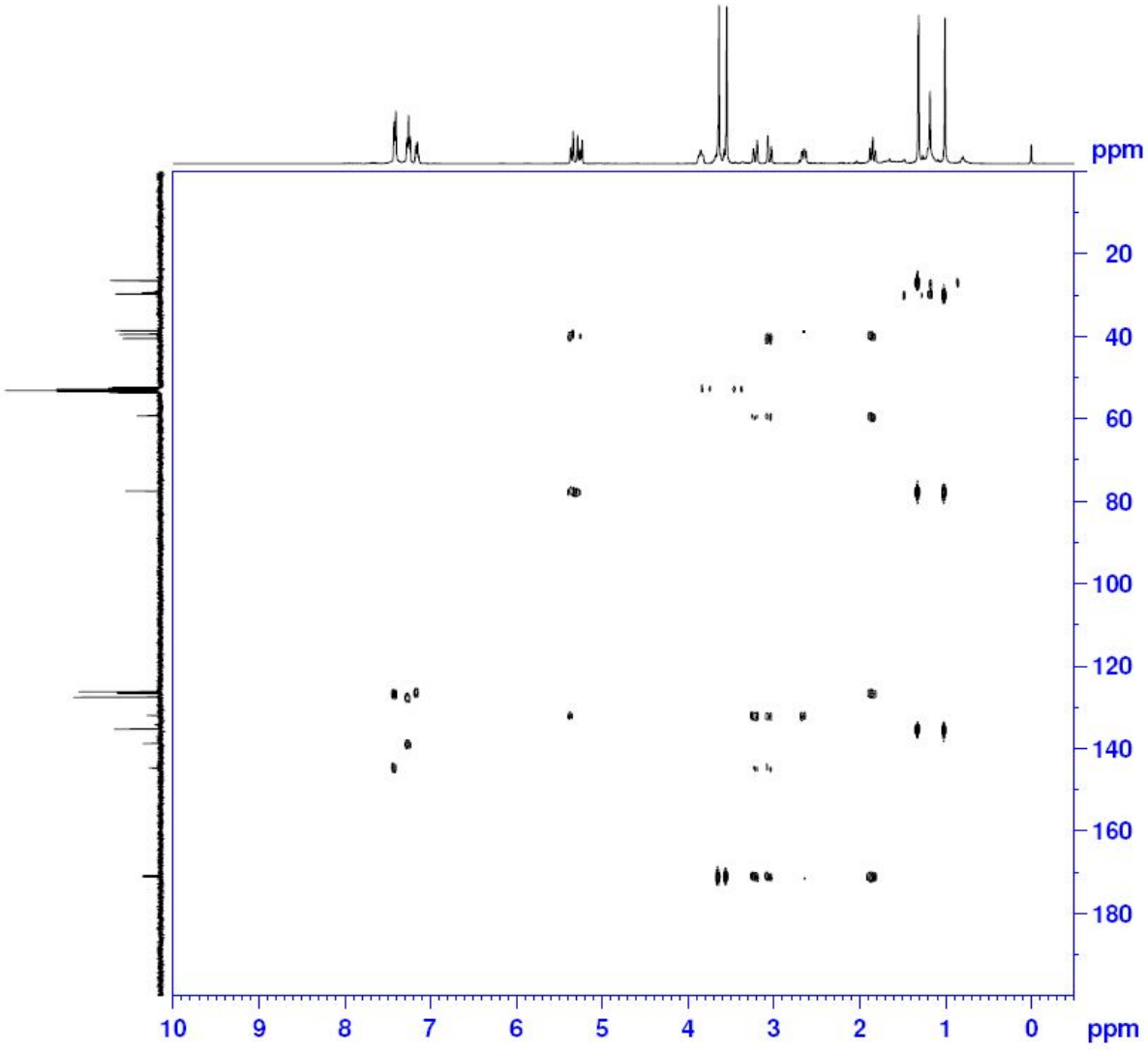
0
ppm


Ph
O
MeO2C
MeO2C
Me
Me

HMBC


ppm
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10
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0
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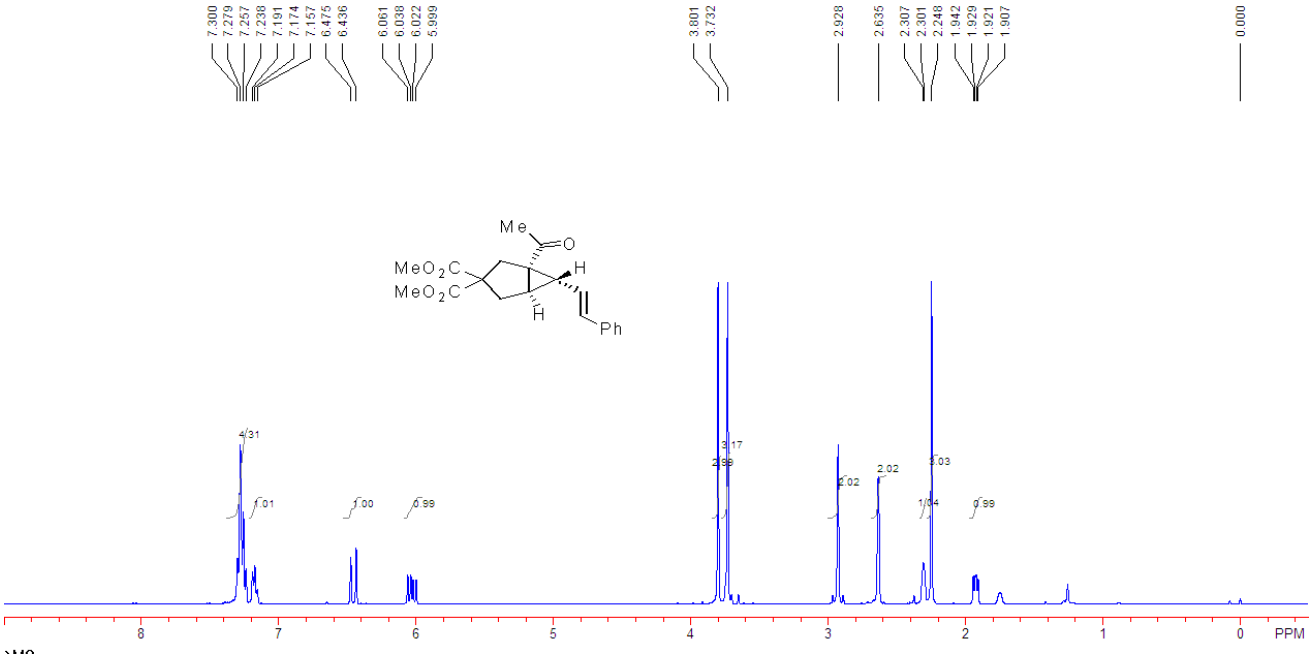
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7.257
7.238
7.191
7.174
7.157
6.475
6.436
6.061
6.038
6.022
5.999
3.801
3.732
2.928
2.635
2.307
2.301
2.248
1.942
1.929
1.921
1.907
0.000
Me
O
MeO2C
MeO2C
H
H
Ph
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1.00
0.99
3.17
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2.02
1.04
3.03
0.99
8
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6
5
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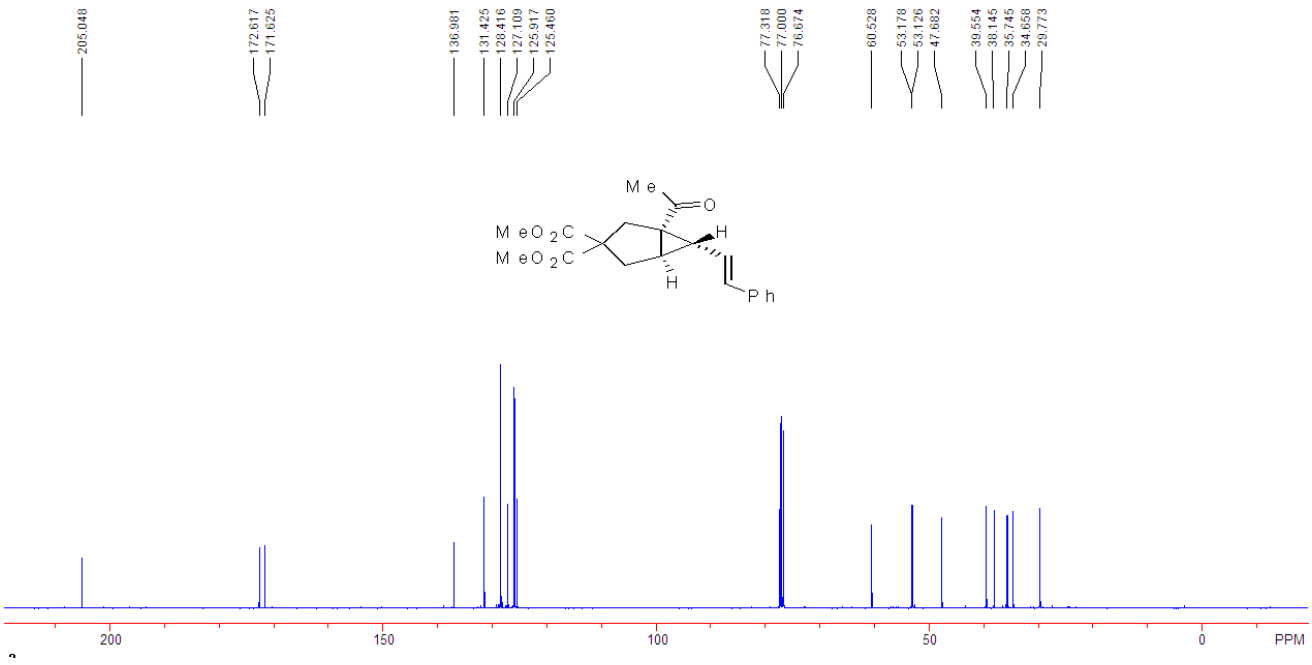
0
PPM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136.981
131.425
128.416
127.109
125.917
125.460
77.318
77.000
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60.528
53.178
53.126
47.682
39.554
38.145
35.745
34.658
29.773
Me
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MeO2C
MeO2C
H
H
Ph
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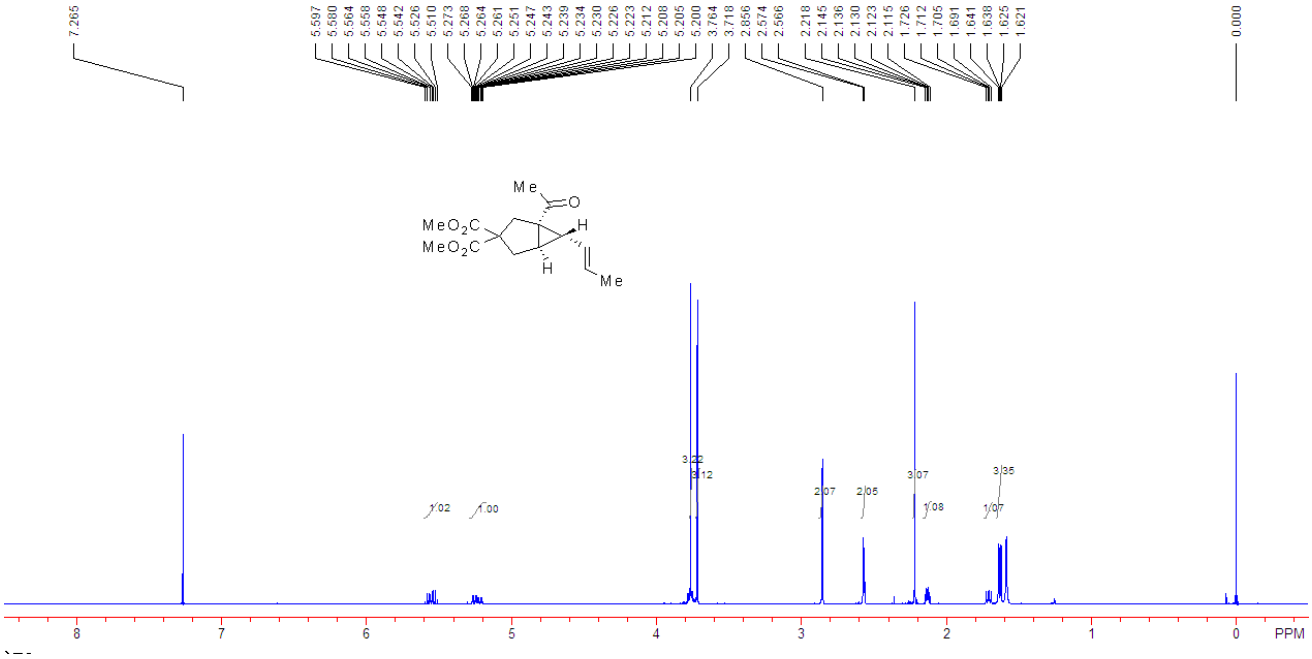
150
100
50
0
PPM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5.548
5.542
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5.273
5.268
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5.261
5.251
5.247
5.243
5.239
5.234
5.230
5.226
5.223
5.212
5.208
5.205
5.200
3.764
3.718
2.856
2.574
2.566
2.218
2.145
2.136
2.130
2.123
2.115
1.726
1.712
1.705
1.691
1.641
1.638
1.625
1.621
0.000
Me
O
MeO2C
MeO2C
H
H
Me
3.22
3.12
2.07
2.05
3.07
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1.07
1.02
1.00
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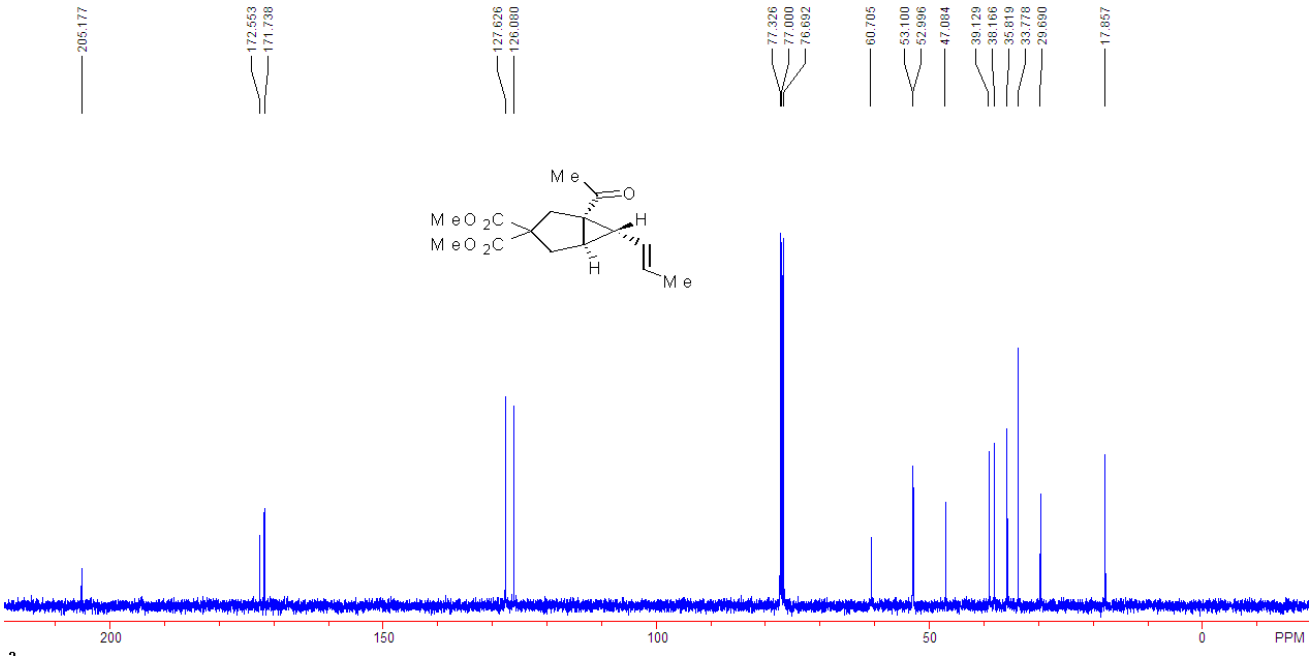
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126.080
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77.000
76.692
60.705
53.100
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38.166
35.619
33.778
29.690
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Me
O
MeO2C
MeO2C
H
H
Me
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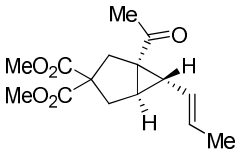
100
50
0
PPM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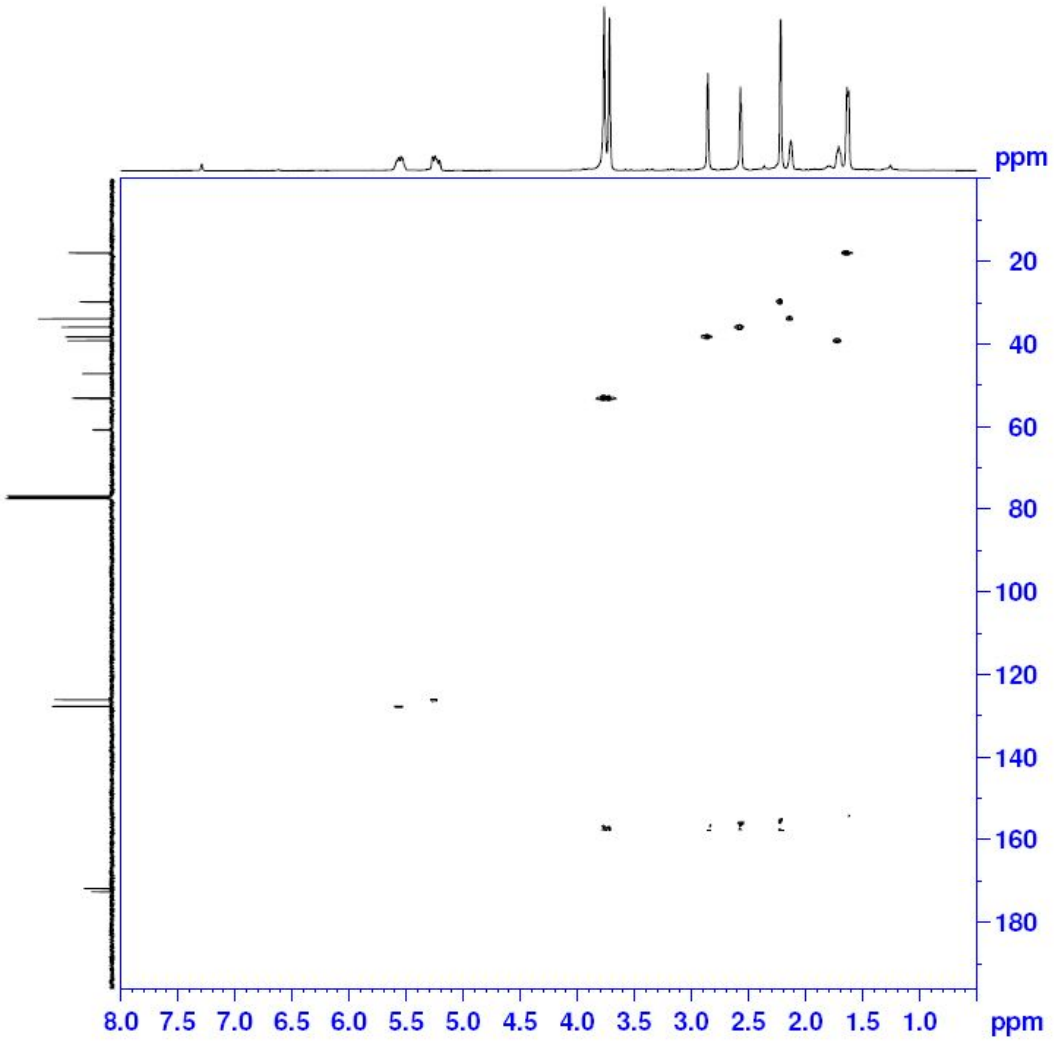
O
MeO2C
MeO2C
H
H
Me

HSQC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100
120
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160
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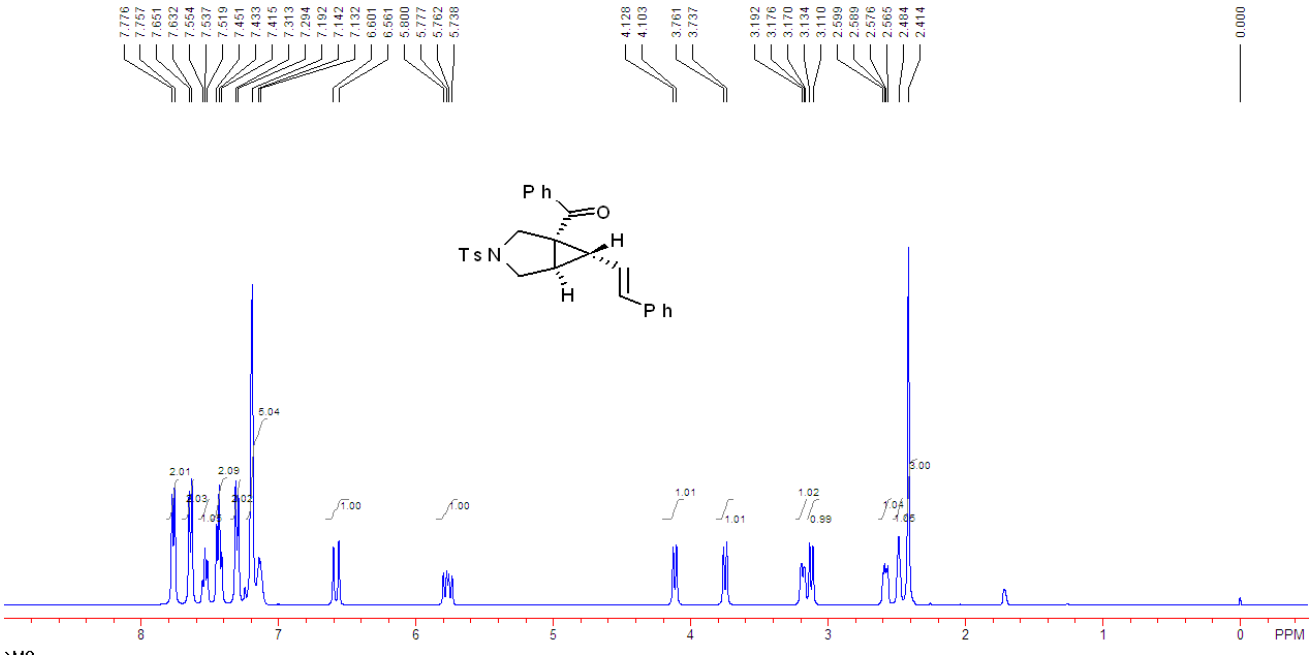
ppm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7.537
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7.451
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7.415
7.313
7.294
7.192
7.142
7.132
6.601
6.561
5.800
5.777
5.762
5.738
4.128
4.103
3.761
3.737
3.192
3.176
3.170
3.134
3.110
2.599
2.589
2.576
2.565
2.484
2.414
0.000
Ph
O
TsN
H
H
Ph
5.04
2.01
2.09
2.03
2.02
1.00
1.00
1.01
1.01
1.02
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1.04
1.05
5.00
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6
5
4
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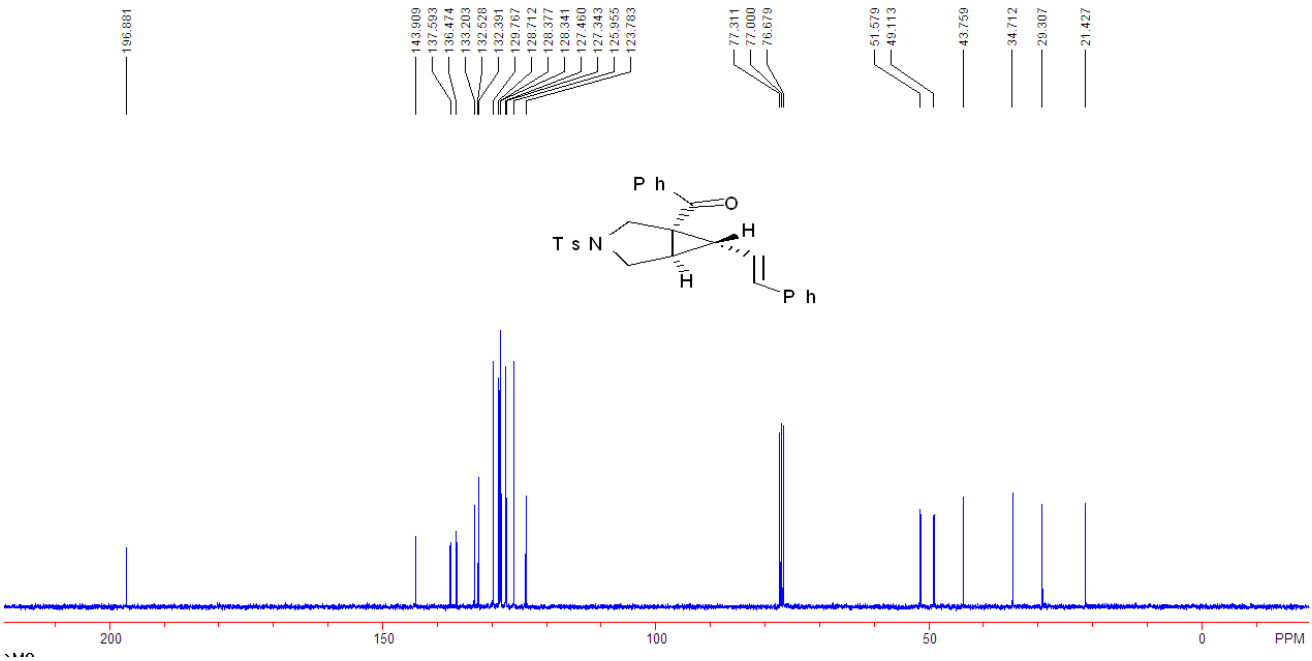
2
1
0
PPM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137.593
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133.203
132.528
132.391
129.767
128.712
128.377
128.341
127.460
127.343
125.955
123.783
77.311
77.000
76.679
51.579
49.113
43.759
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29.307
21.427
Ph
O
TsN
H
H
Ph
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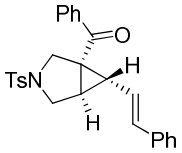
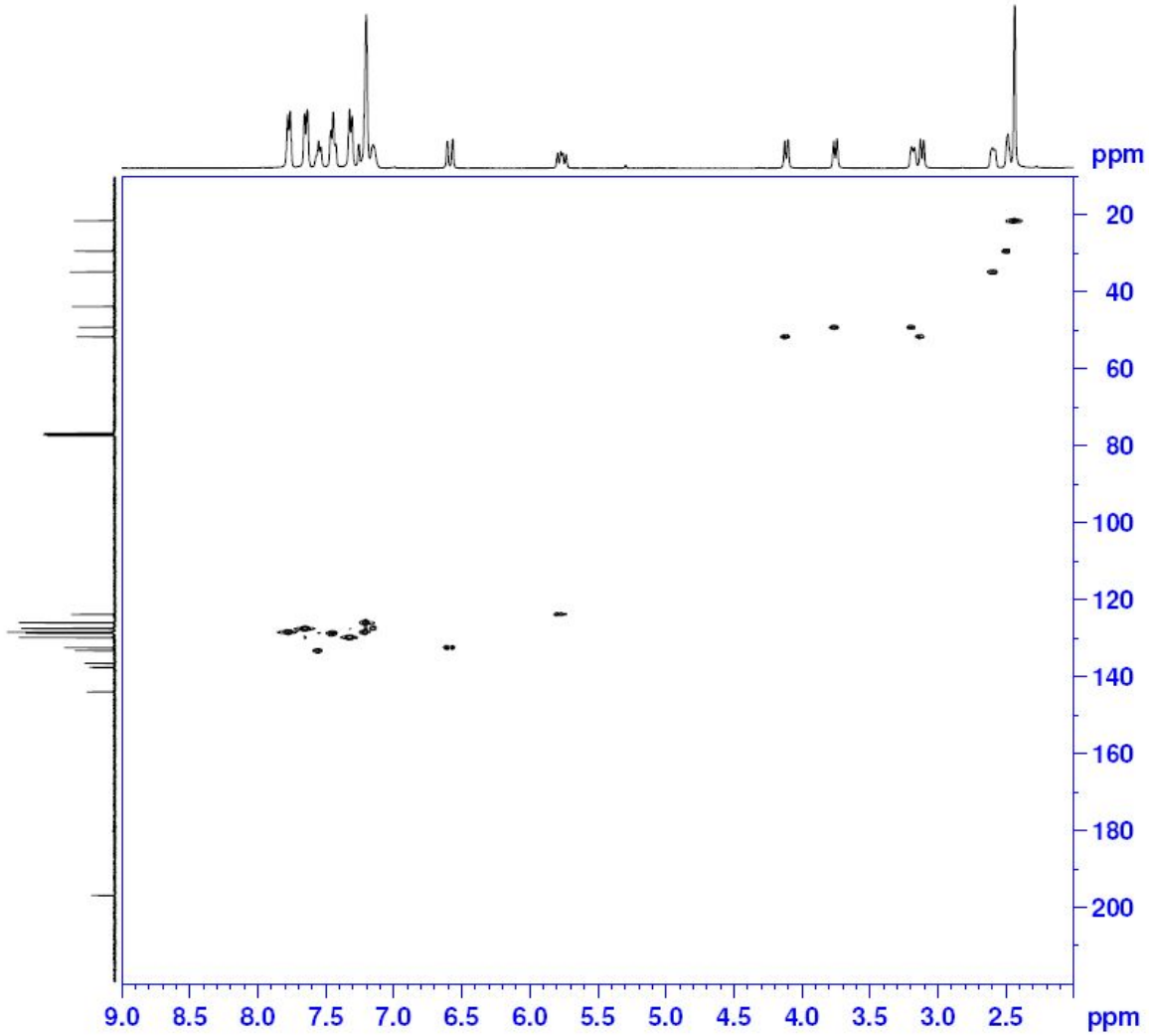
150
100
50
0
PPM


Ph
O
TsN
H
H
Ph

HSQC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80
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120
140
160
180
200
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8.5
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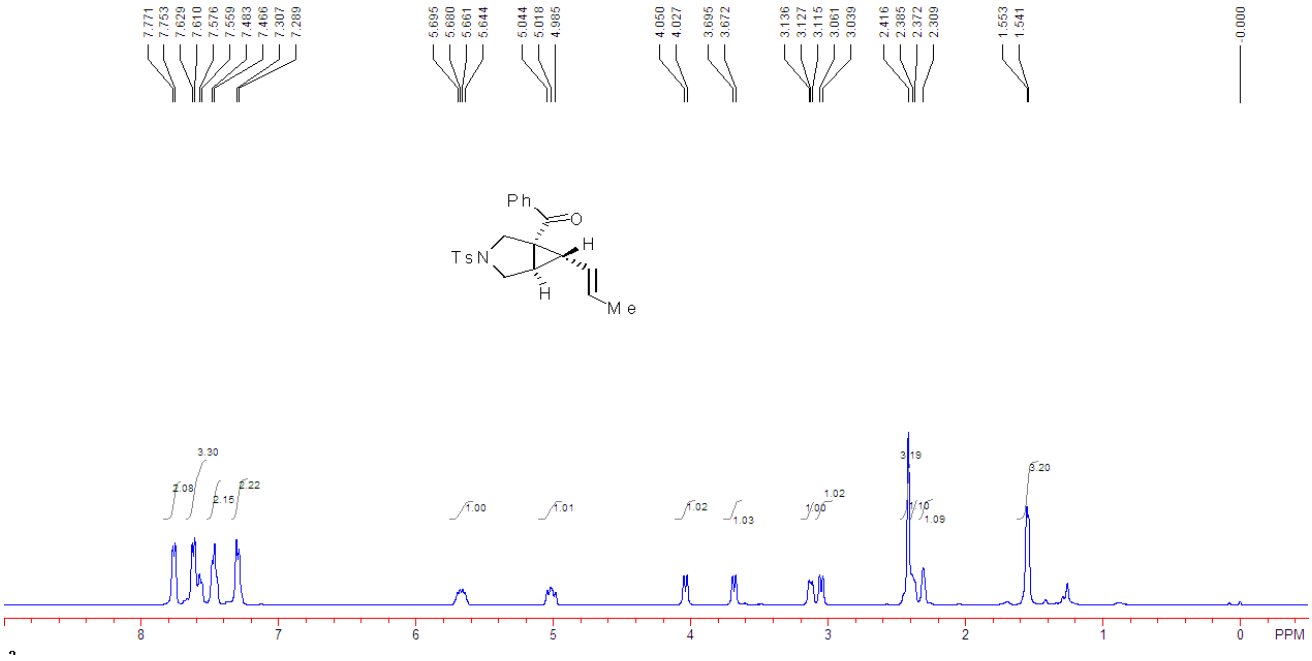
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm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7.753
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7.559
7.483
7.466
7.307
7.289
5.695
5.680
5.661
5.644
5.044
5.018
4.985
4.050
4.027
3.695
3.672
3.136
3.127
3.115
3.061
3.039
2.416
2.385
2.372
2.309
1.553
1.541
0.000
Ph
O
TsN
H
H
Me
3.30
2.08
2.15
2.22
1.00
1.01
1.02
1.03
1.06
1.02
3.19
3.10
1.09
6.20
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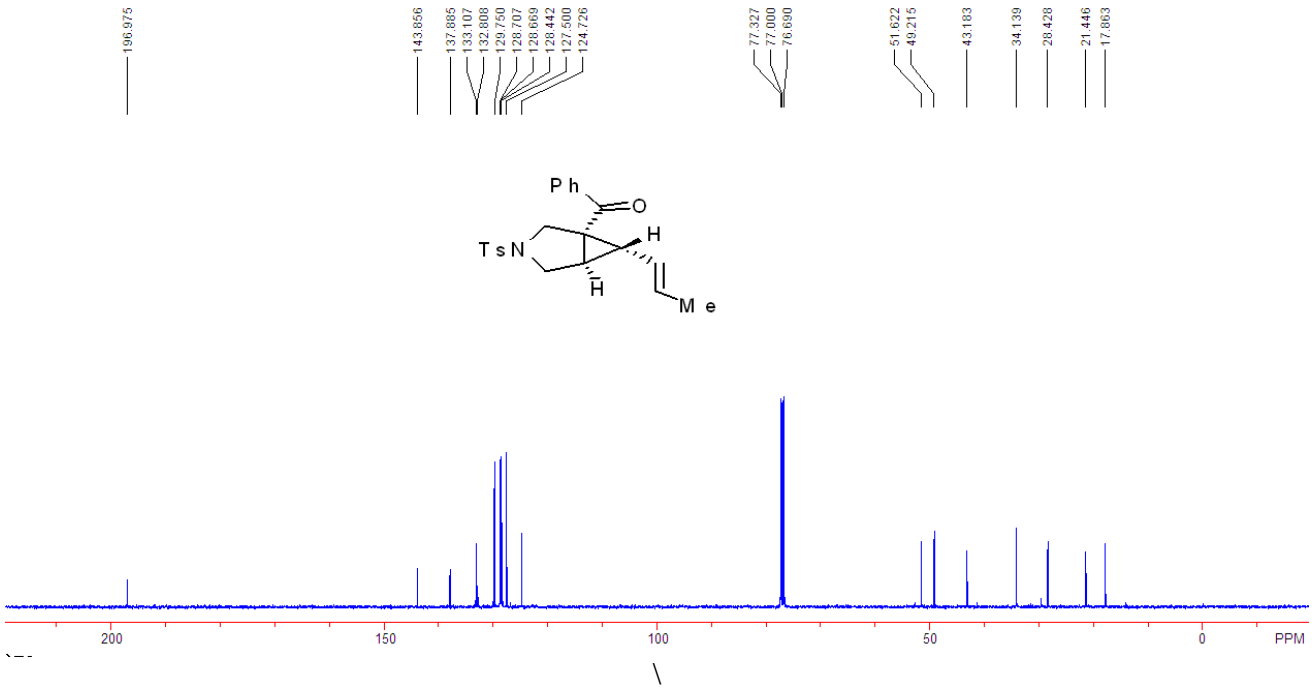
6
5
4
3
2
1
0
PPM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133.107
132.808
129.750
128.707
128.669
128.442
127.500
124.726
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77.000
76.690
51.622
49.215
43.183
34.139
28.428
21.446
17.863
Ph
O
TsN
H
H
Me
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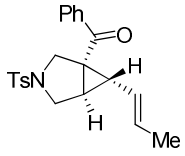
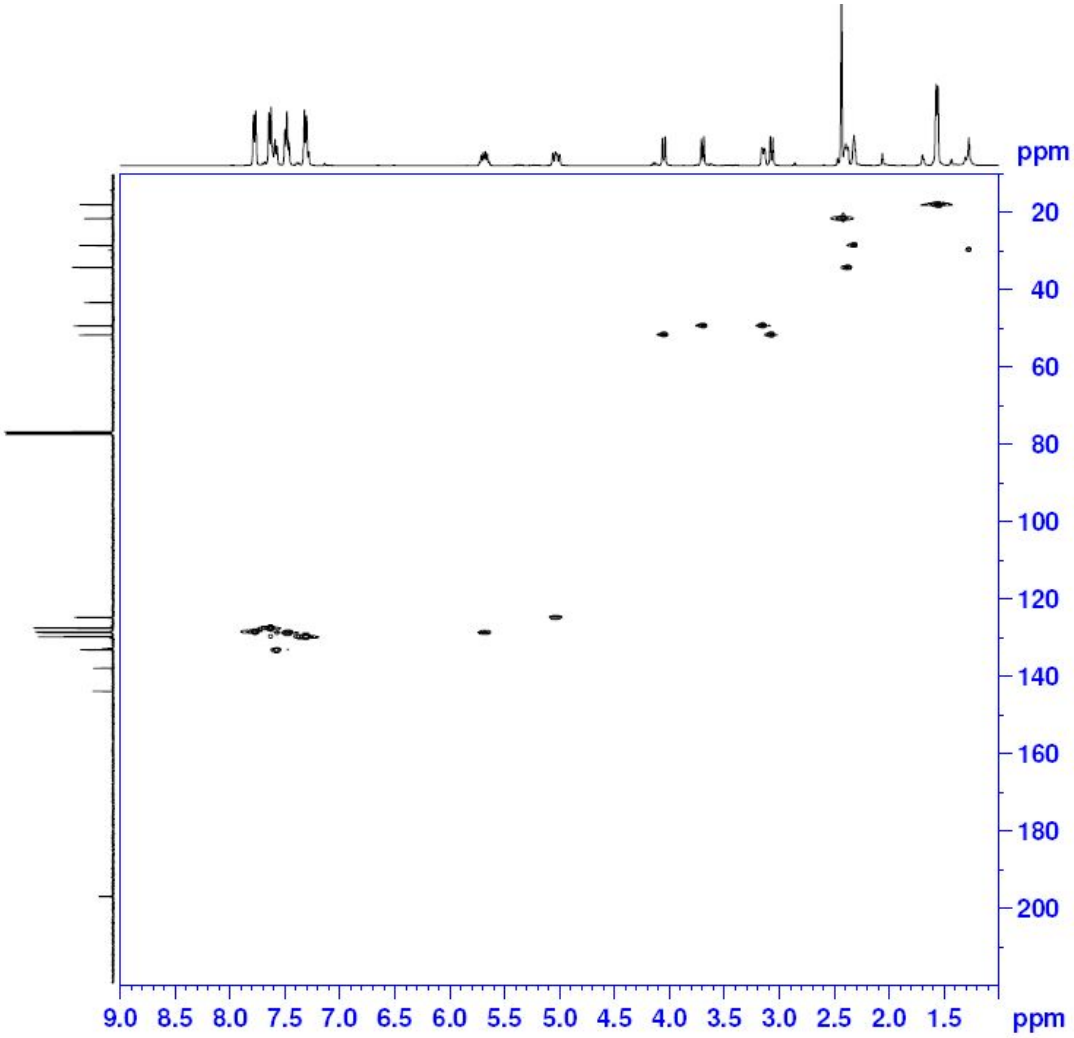
150
100
50
0
PPM


Ph
O
TsN
H
H
Me

HSQC


ppm
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60
80
100
120
140
160
180
200
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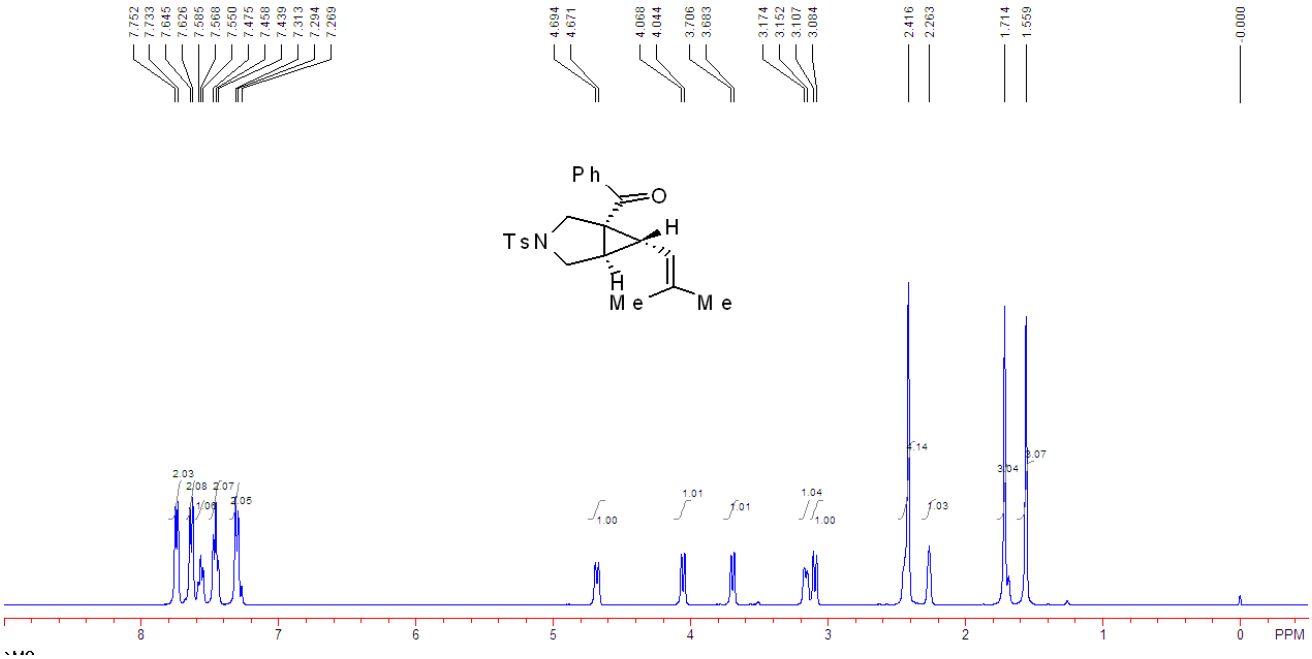
ppm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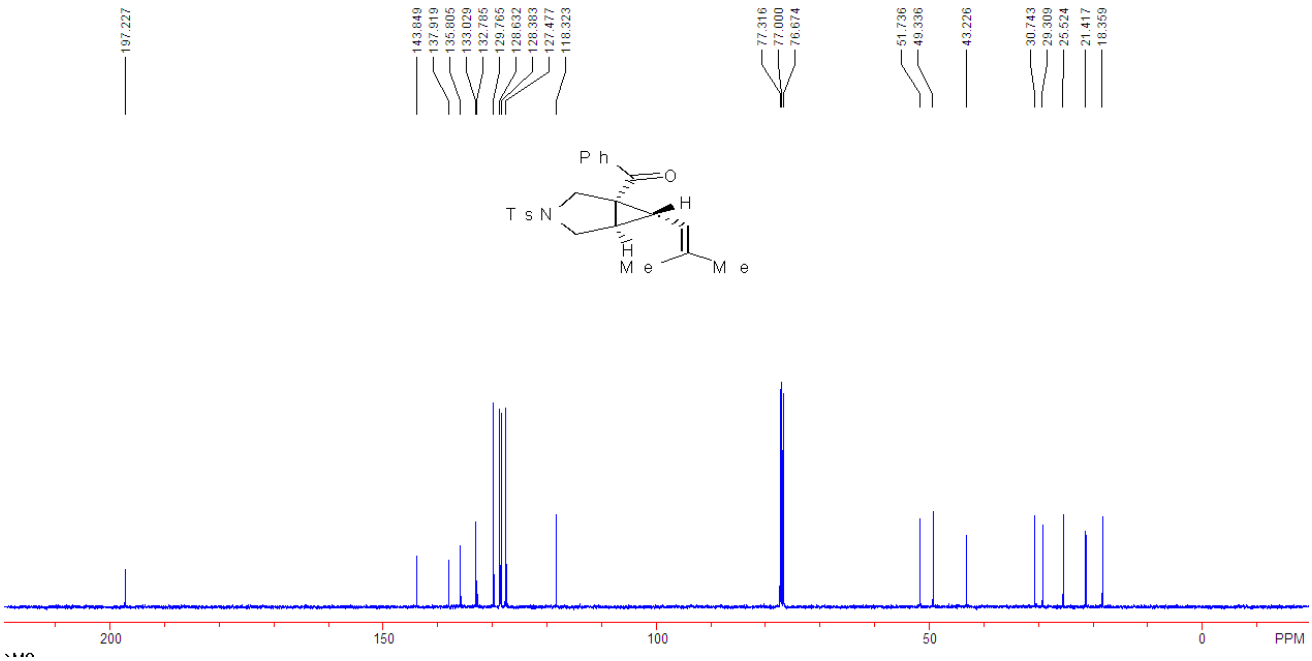
7.568
7.550
7.475
7.458
7.439
7.313
7.294
7.269
4.694
4.671
4.068
4.044
3.706
3.683
3.174
3.152
3.107
3.084
2.416
2.263
1.714
1.559
0.000
Ph
O
TsN
H
H
Me
Me
2.03
2.08
2.07
1.06
2.05
1.00
1.01
1.01
1.04
1.00
4.14
3.03
3.04
3.07
8
7
6
5
4
3
2
1
0
PPM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128.383
127.477
118.323
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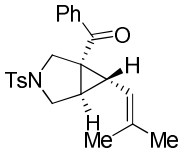
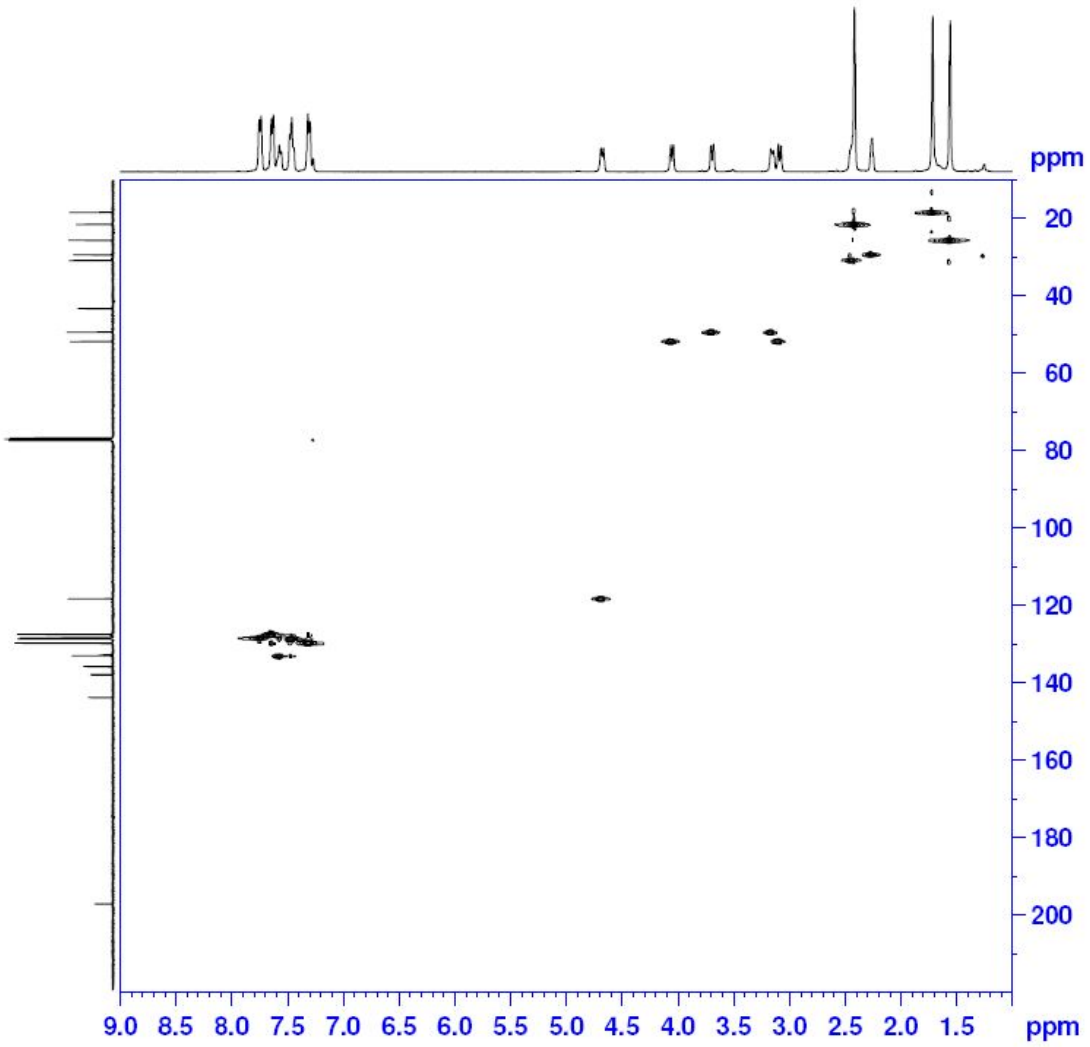
77.000
76.674
51.736
49.336
43.226
30.743
29.309
25.524
21.417
18.359
Ph
O
TsN
H
H
Me
Me
200
150
100
50
0
PPM


Ph
O
H
TsN
H
Me
Me

HSQC


ppm
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80
100
120
140
160
180
200
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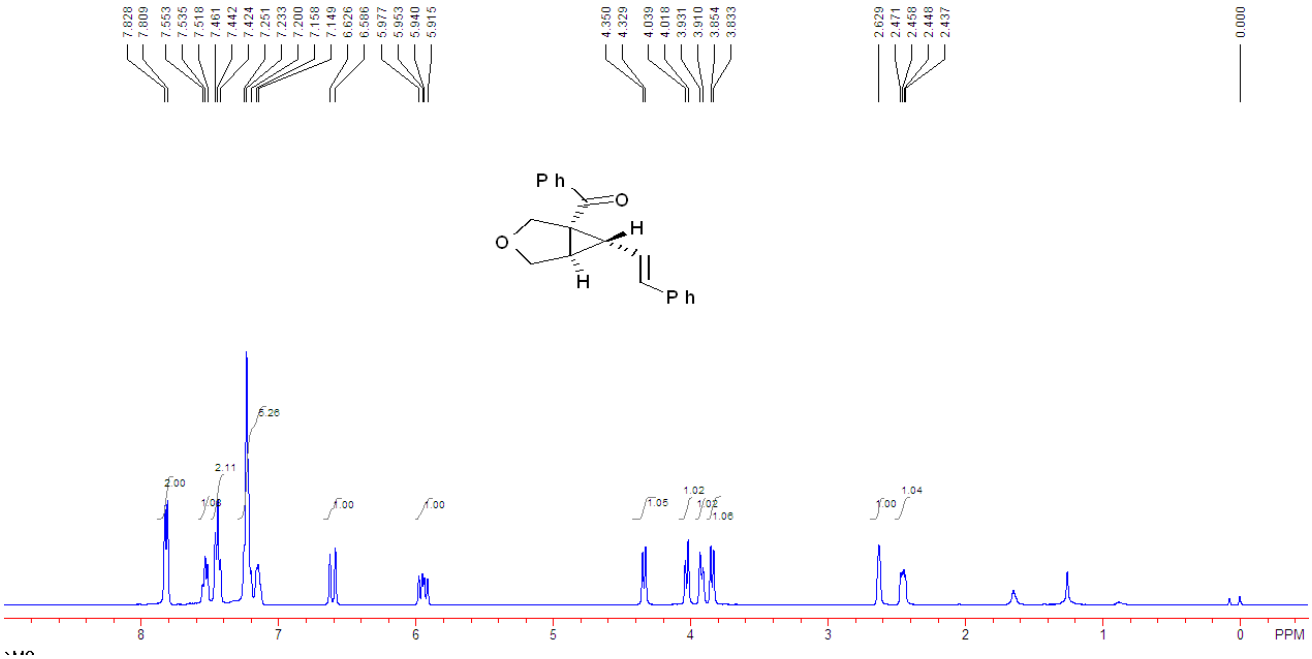
ppm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7.442
7.424
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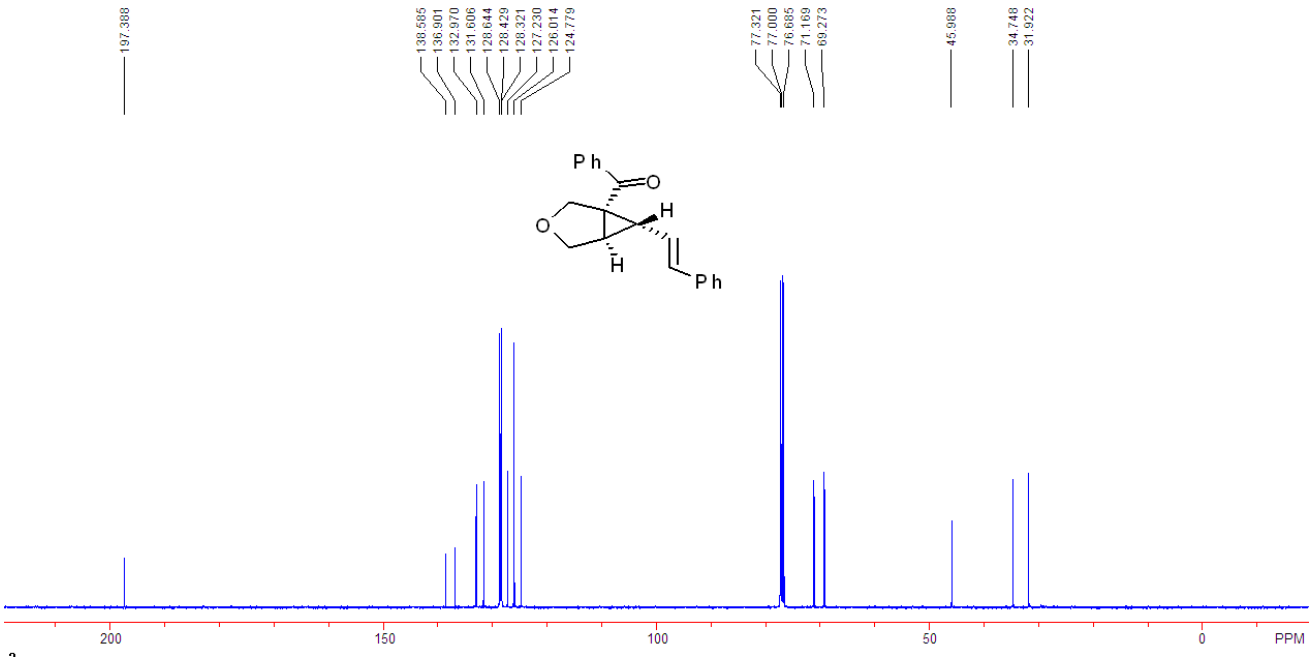
7.233
7.200
7.158
7.149
6.626
6.586
5.977
5.953
5.940
5.915
4.350
4.329
4.039
4.018
3.931
3.910
3.854
3.833
2.629
2.471
2.458
2.448
2.437
0.000
Ph
O
H
O
H
Ph
1.00
2.11
5.26
1.00
1.00
1.05
1.02
1.04
8
7
6
5
4
3
2
1
0
PPM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128.429
128.321
127.230
126.014
124.779
77.321
77.000
76.685
71.169
69.273
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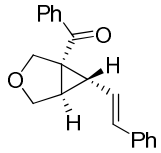
34.748
31.922
Ph
O
H
O
H
Ph
200
150
100
50
0
PPM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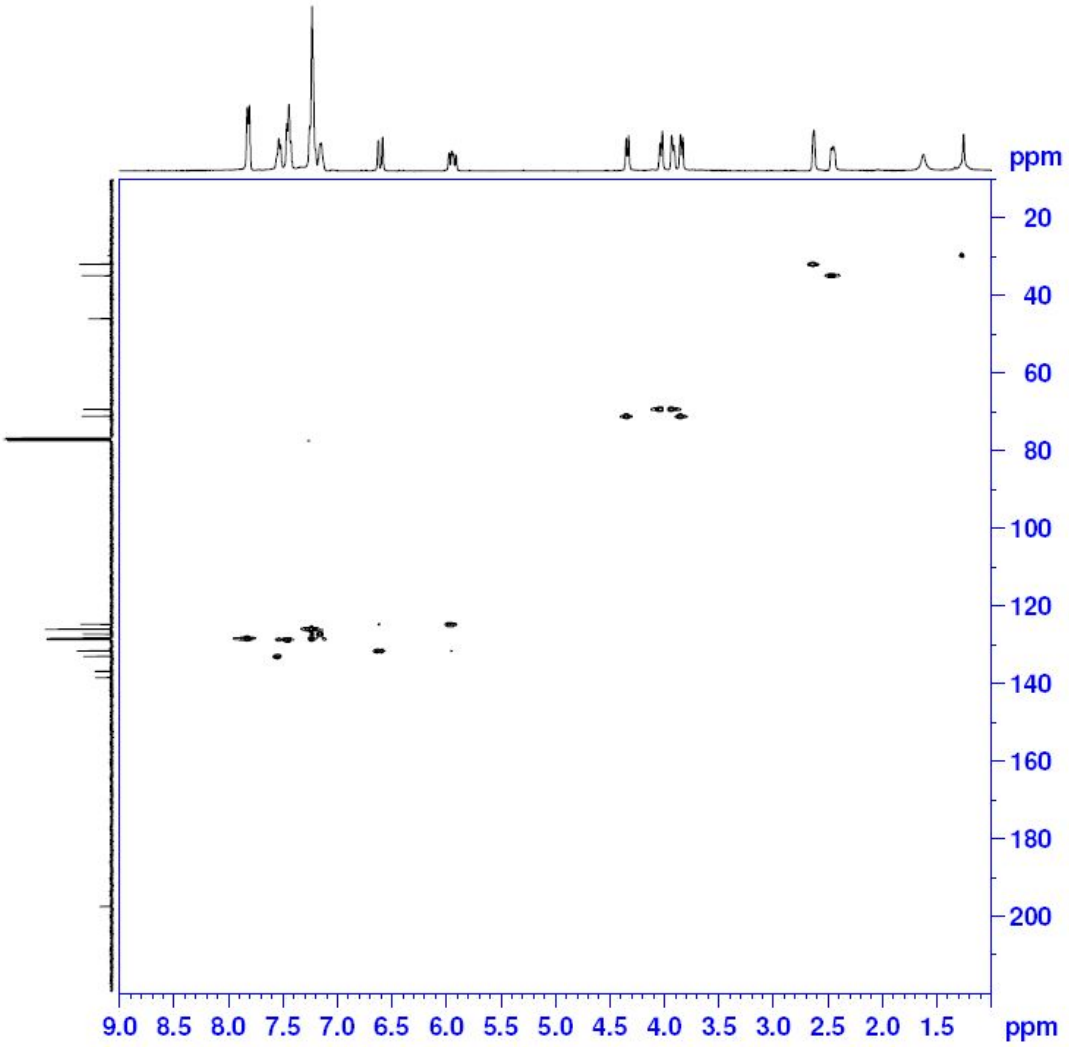
H
O
H
Ph

HSQC


ppm
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60
80
100
120
140
160
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200
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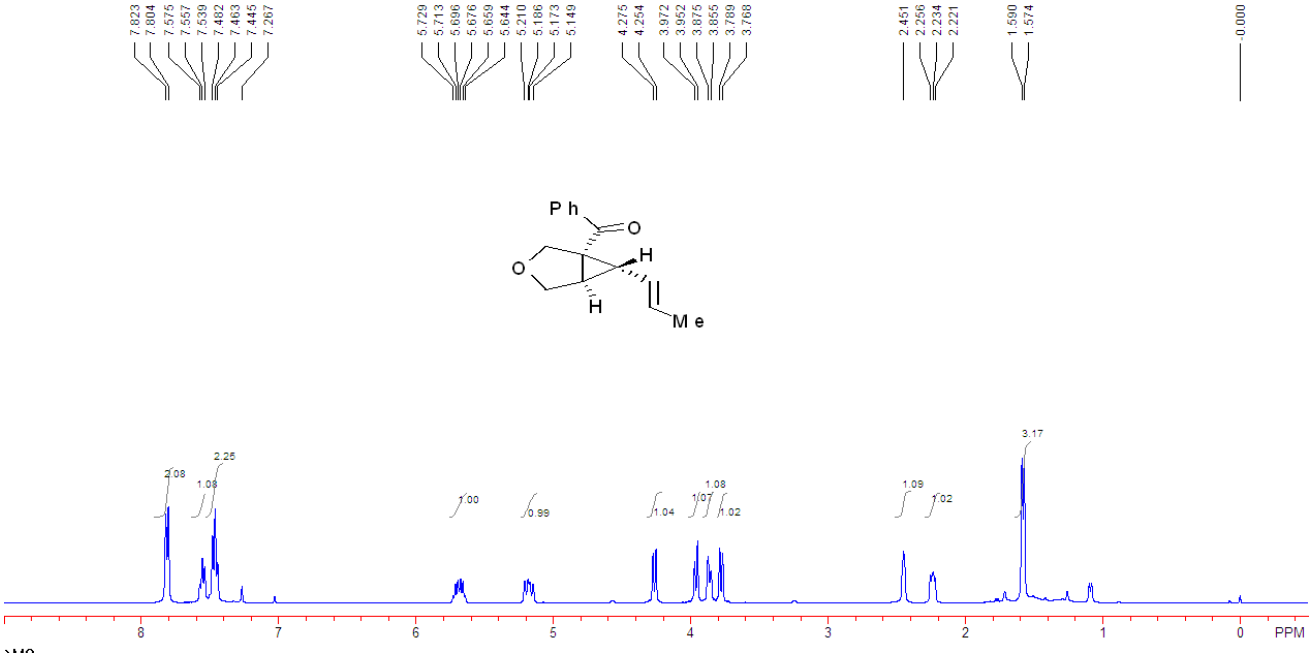
ppm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5.713
5.696
5.676
5.659
5.644
5.210
5.186
5.173
5.149
4.275
4.254
3.972
3.952
3.875
3.855
3.789
3.768
2.451
2.256
2.234
2.221
1.590
1.574
0.000
Ph
O
H
O
H
Me
2.08
2.25
1.08
1.00
0.99
1.04
1.08
1.07
1.02
1.09
1.02
3.17
8
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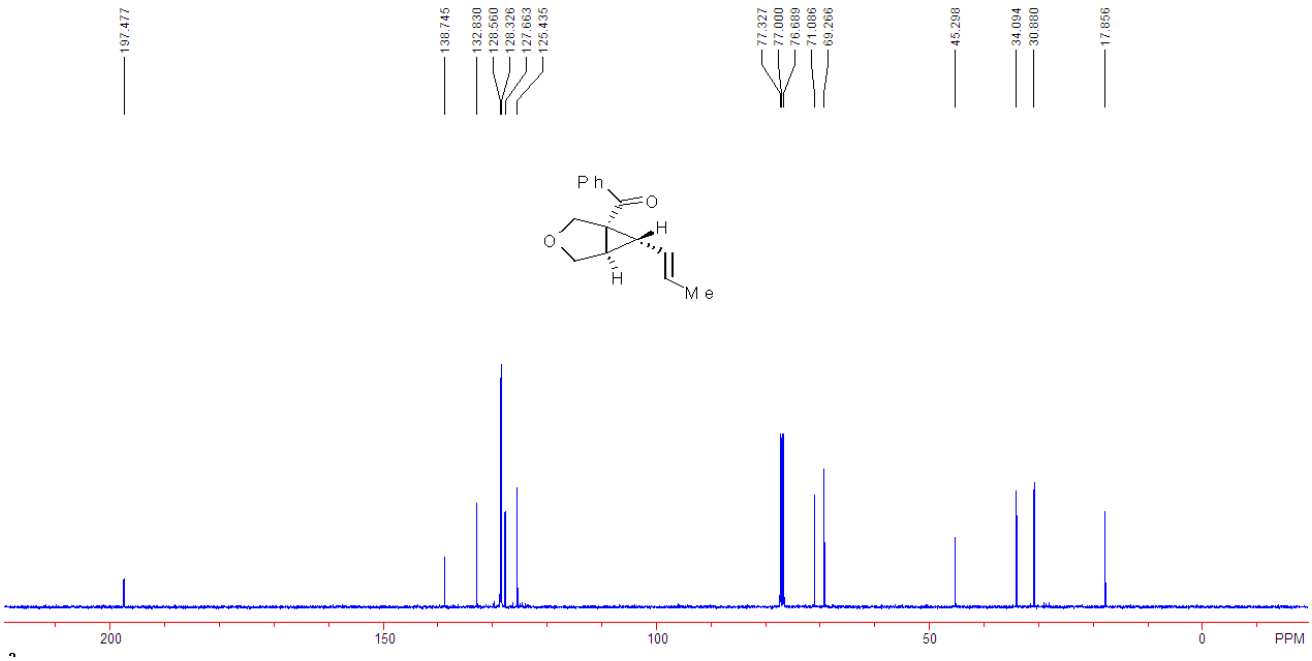
6
5
4
3
2
1
0
PPM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125.435
77.327
77.000
76.689
71.086
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45.298
34.094
30.880
17.856
Ph
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H
O
H
Me
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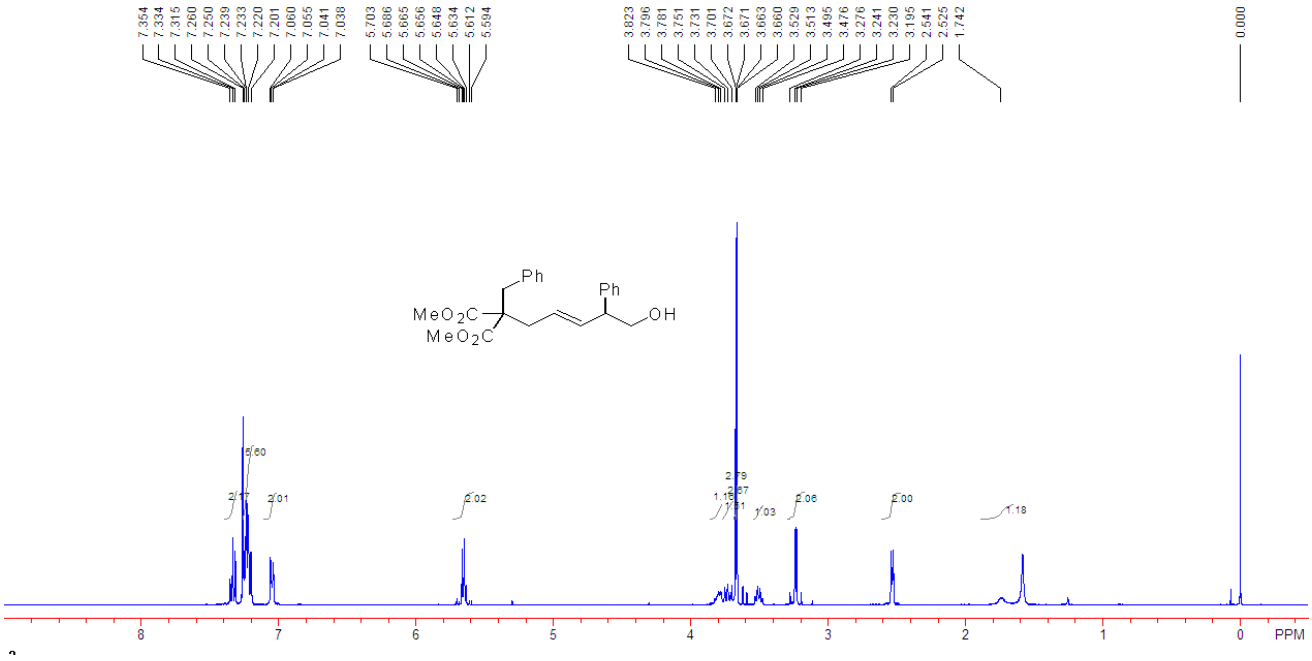
150
100
50
0
PPM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7.239
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7.220
7.201
7.060
7.055
7.041
7.038
5.703
5.686
5.665
5.656
5.648
5.634
5.612
5.594
3.823
3.796
3.781
3.751
3.731
3.701
3.672
3.671
3.663
3.660
3.529
3.513
3.495
3.476
3.276
3.241
3.230
3.195
2.541
2.525
1.742
0.000
Ph
Ph
MeO2C
MeO2C
OH
5.60
2.01
2.02
2.79
2.67
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2.06
2.00
1.18
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6
5
4
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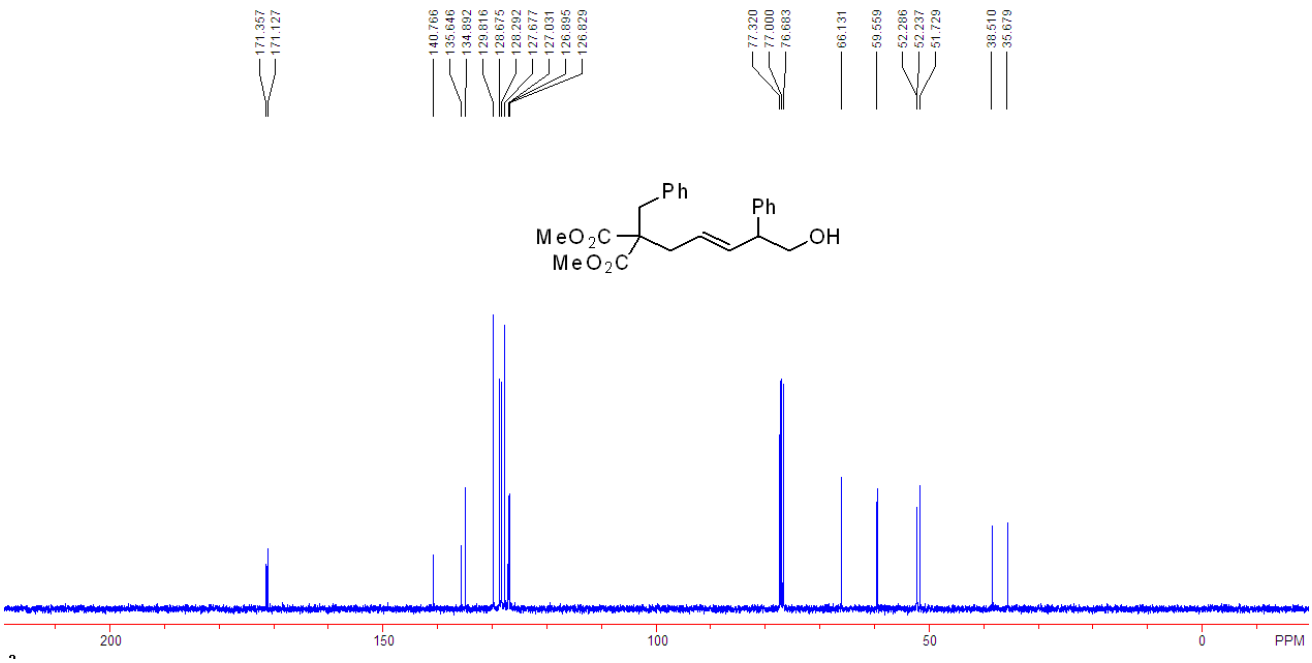
2
1
0
PPM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128.292
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127.031
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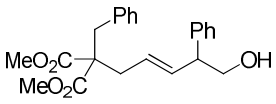
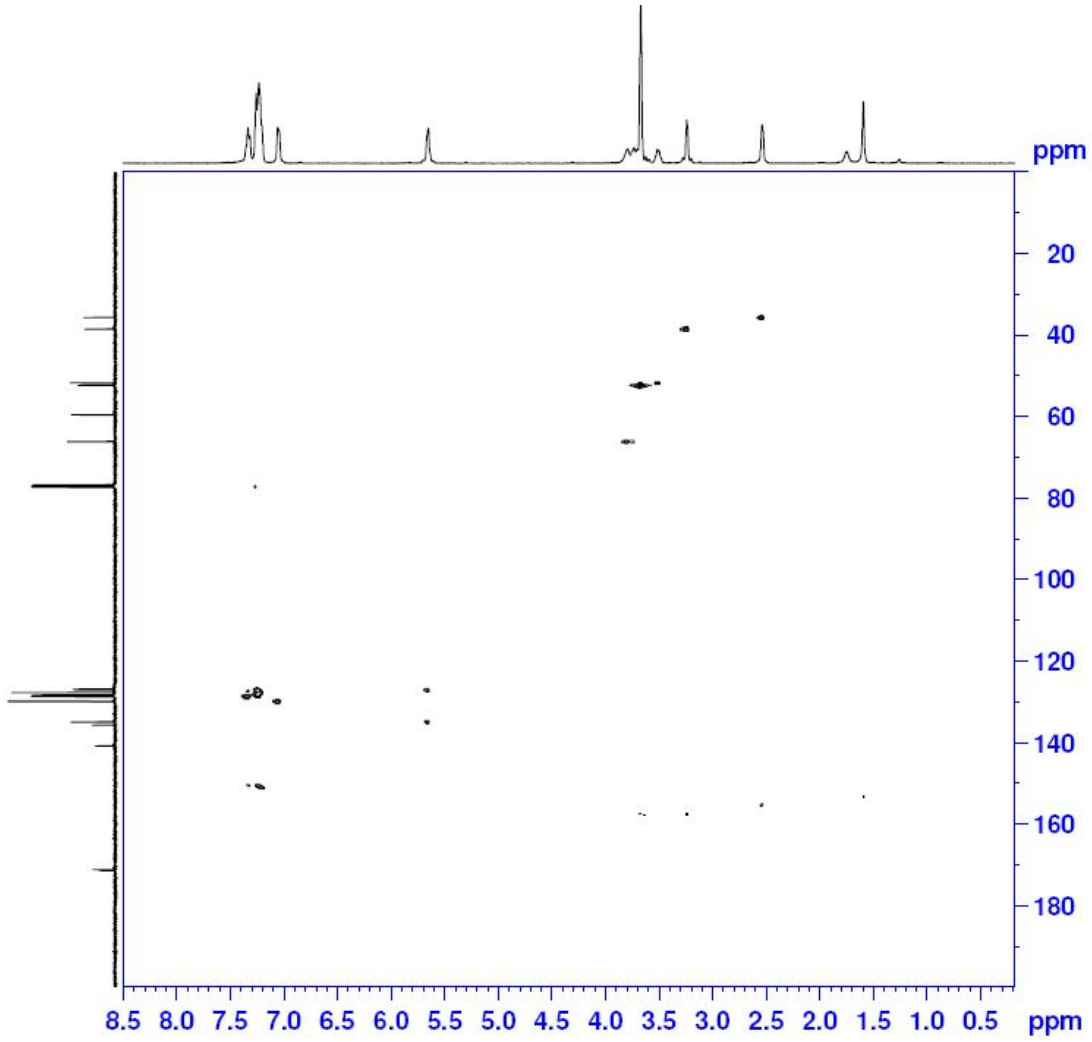
77.000
76.683
66.131
59.559
52.286
52.237
51.729
38.510
35.679
Ph
Ph
MeO2C
MeO2C
OH
200
150
100
50
0
PPM


Ph
Ph
MeO2C
MeO2C
OH

HSQC


ppm
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60
80
100
120
140
160
180
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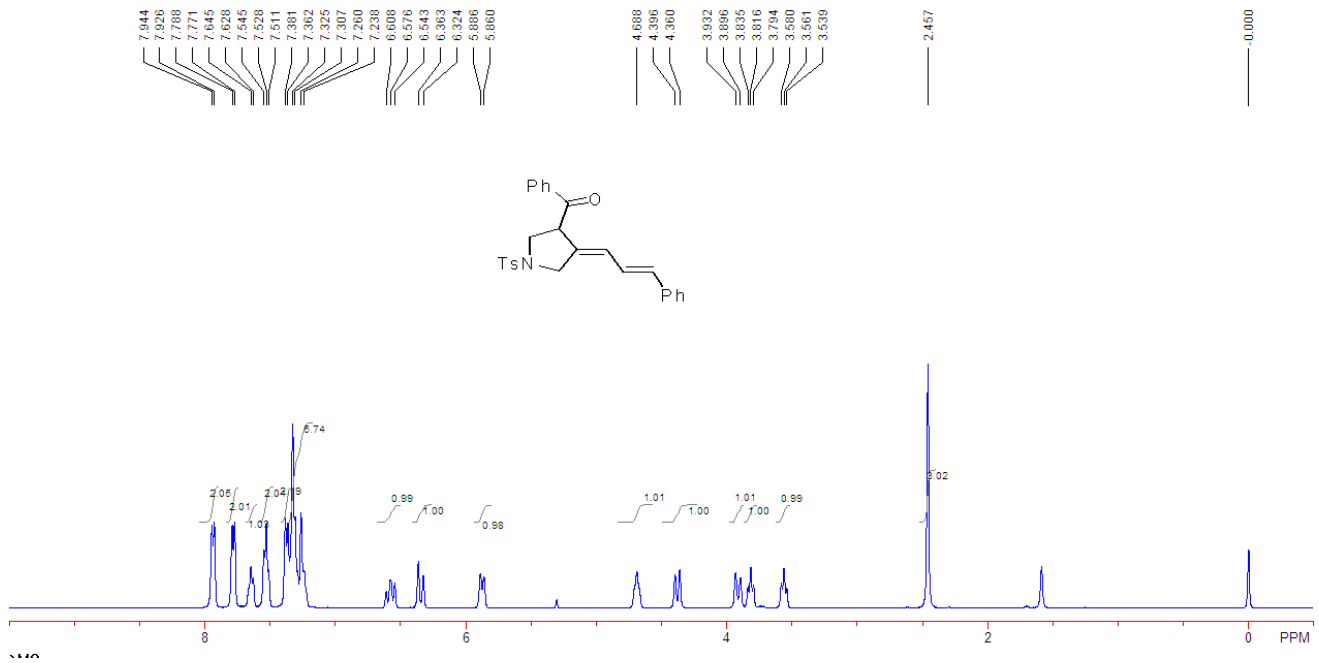
ppm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7.362
7.325
7.307
7.260
7.238
6.608
6.576
6.543
6.363
6.324
5.886
5.860
4.688
4.396
4.360
3.932
3.896
3.835
3.816
3.794
3.560
3.561
3.539
2.457
0.000
Ph
O
TsN
Ph
6.74
2.05
2.01
1.03
2.04
1.19
0.99
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1.00
1.01
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6.02
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6
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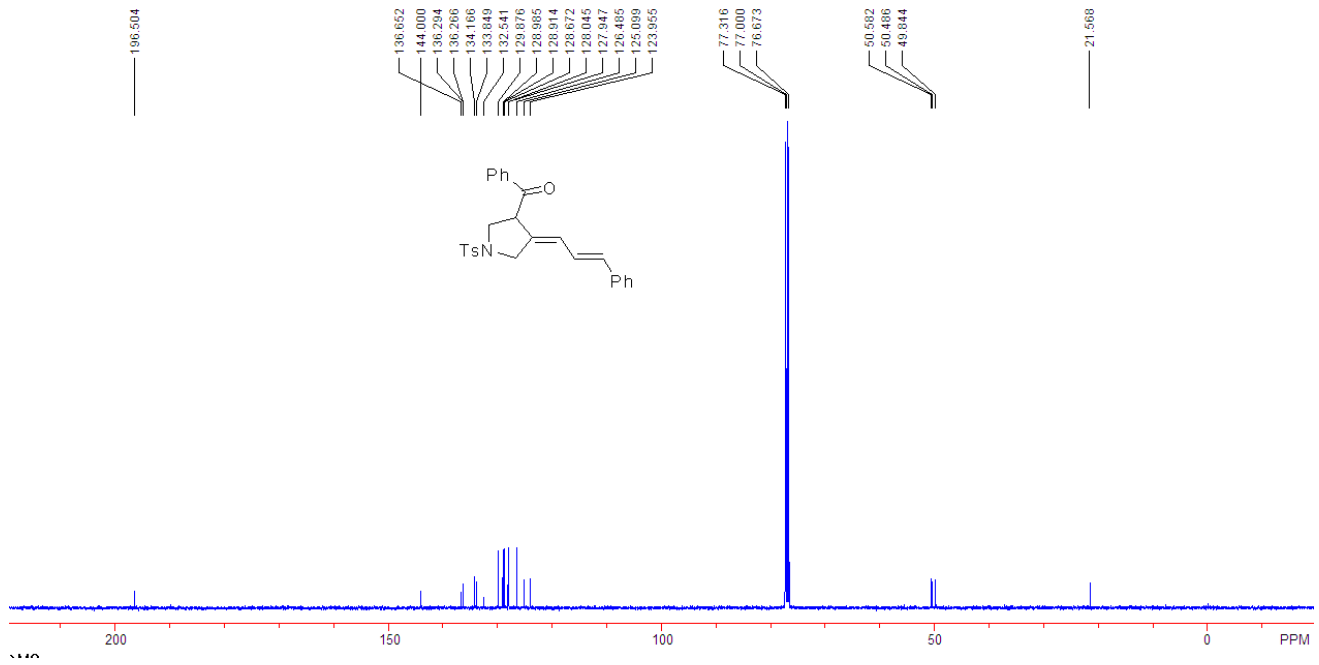
0
PPM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136.266
134.166
133.849
132.541
129.876
128.985
128.914
128.672
128.045
127.947
126.485
125.099
123.955
77.316
77.000
76.673
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50.486
49.844
21.568
Ph
O
TsN
Ph
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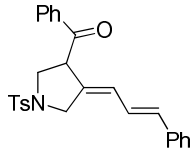
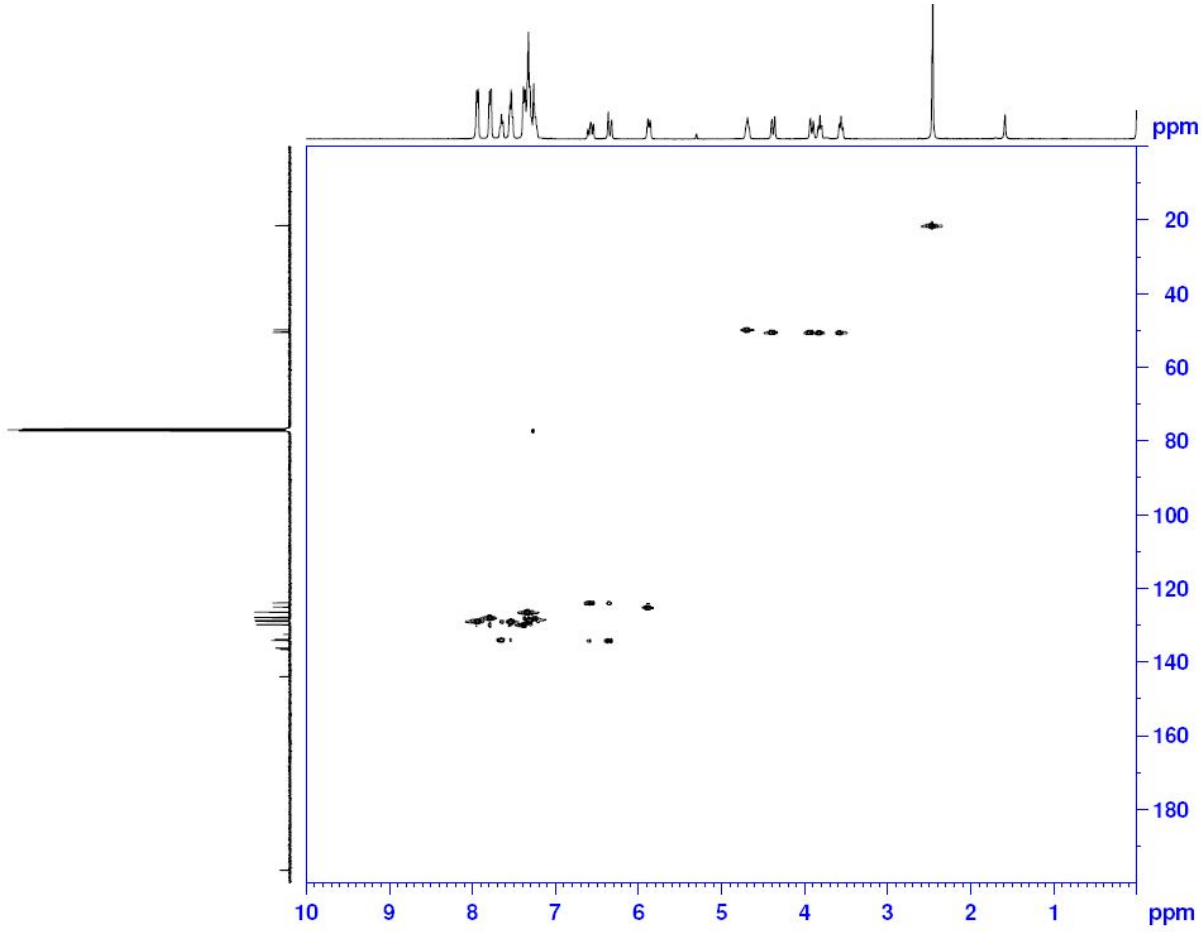
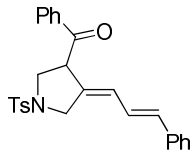
150
100
50
0
PPM

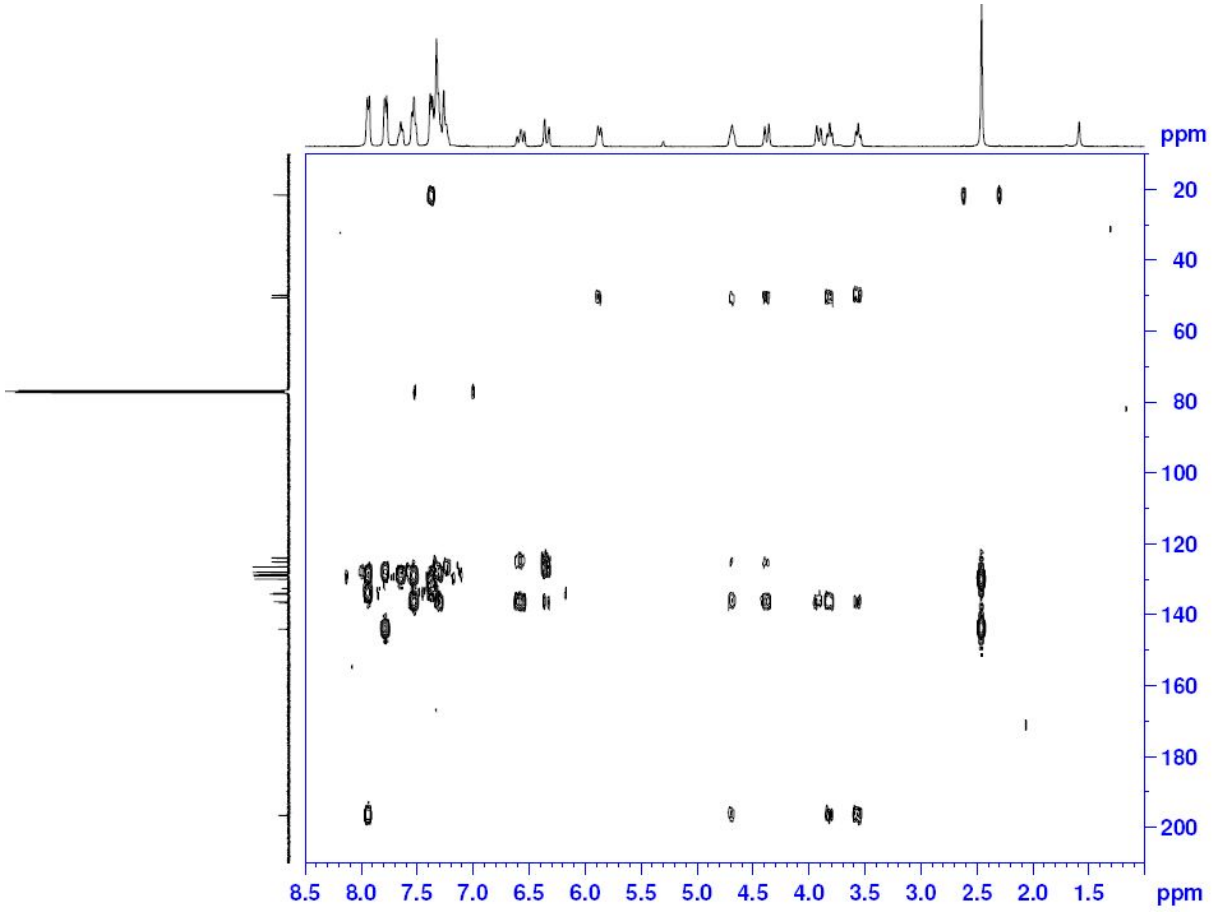


HSQC




Ph
O
TsN
Ph

HMBC


ppm
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100
120
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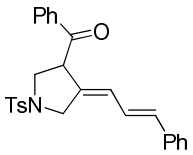
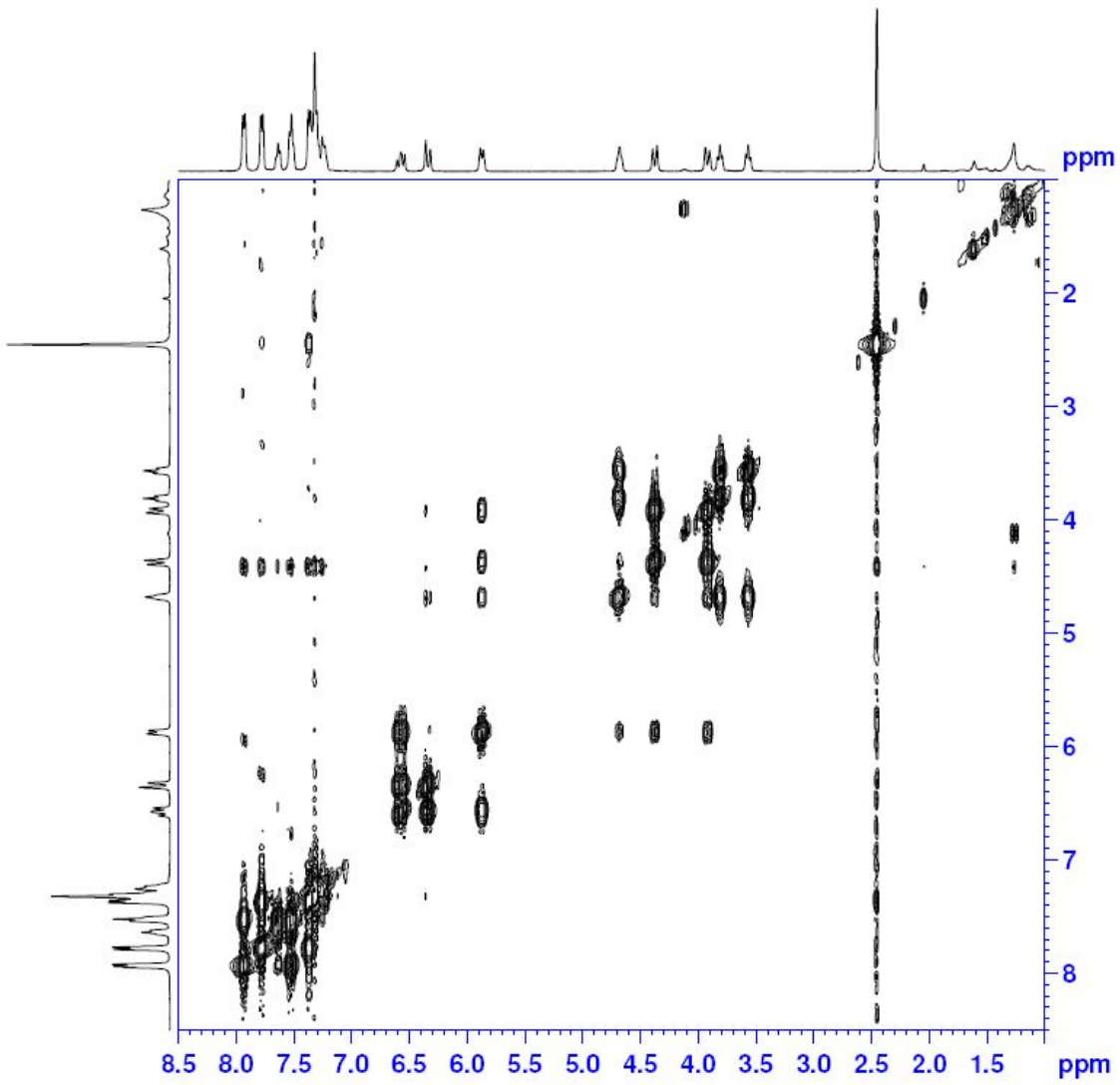
160
180
200
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


Ph
O
TsN
Ph

^{1}H-^{1}H COSY


ppm
2
3
4
5
6
7
8
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
ppm