Supporting Information

Lewis and Brønsted Acid-Induced (3+2)-Annulation of Donor-Acceptor Cyclopropanes to Alkynes: Indene Assembly

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Table of Content

General Information

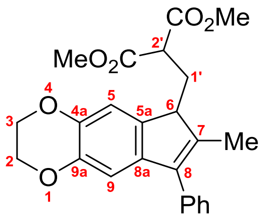
NMR spectra were acquired on Bruker Avance 600 spectrometer at room temperature; the chemical shifts δ were measured in ppm with respect to solvents ($CDCl_3$: $\delta_H = 7.26$, $\delta_C = 77.0$; DMSO-d_6: $\delta_H = 2.50$, $\delta_C = 39.5$). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, double doublet. Coupling constants (J) are in Hertz. The structures of all compounds were elucidated with the aid of 1D NMR (^1H, ^{13}C) and 2D NMR (^1H-^1H COSY, ^1H-^{13}C HSQC and HMBC, ^1H-^1H NOESY) spectroscopy. Infrared spectra were recorded on Thermo Nicolet IR200 FT-IR and Agilent FTIR Cary 630 spectrometers with ATR (Attenuated Total Reflectance) module. MALDI-TOF (Matrix Assisted Laser Desorption Ionization / Time of Flight) mass spectra were recorded on Bruker Daltonics Ultrafex II spectrometer in positive mode; anthracene or 1,8,9-trihydroxyanthracene were used as a matrix. High resolution and accurate mass measurements were carried out using a Bruker micro TOF-Q™ ESI-TOF (Electro Spray Ionization / Time of Flight) and Thermo Scientific™ LTQ Orbitrap mass spectrometers. Elemental analyses were performed with Fisons EA-1108 CHNS elemental analyser instrument. Absorption spectra were measured on a Shimadzu UV-2450 UV-Vis spectrophotometer with 1 nm resolution and corrected for the blank. Steady state emission and excitation spectra were taken on a PTI luminescence spectrometer with a 1 nm resolution. Analytical thin layer chromatography (TLC) was carried out with silica gel plates (silica gel 60, F_{254}, supported on aluminium); the revelation was done by UV lamp (365 nm) and chemical staining (iodine vapour and potassium permanganate solution in water). Column chromatography was performed on silica gel 60 (230-400 mesh, Merck). Lewis acids ($SnCl_4$, $BF_3{\cdot}OEt_2$), TfOH and alkynes (phenylacetylene, hexyne-1, octyne-4, 1-phenylpropyne, 1-phenylbutyne, tolan) were commercially available. All the reactions were carried out using freshly distilled and dry solvents. Parent arylidenemalonates and 2-aryl-1,1-cyclopropane diesters **1** were prepared by published procedures.[S1,S2] 4,4′-Dimethoxytolan was prepared from 4-iodoanisole and 2-methyl-3-butyn-2-ol *via* double Sonogashira coupling according to known procedures.[S3,S4]

All the calculations have been performed within density functional theory (DFT),[S5] using the hybrid functional B3LYP.[S6] The standard SVP basis set,[S7] as implemented in the ORCA 3.0 suite of programs,[S8] has been used in all cases together with the RIJCOSX approximation.[S9] Frequency analysis was carried out to check whether optimized structures were local minima or transition states. No imaginary frequencies were found for local minima, and only one imaginary frequency was found for each transition state. The geometries of *ortho*-σ-complex **P1** and *ipso*-σ-complex **P2**, as well as initial vinyl cation **C1**, were proved by performing the intrinsic reaction coordinate (IRC) calculations[S10] from corresponding TS points using GAMESS-US suite of programs[S11] at the same level of theory.

General procedure for the (3+2)-annulation of cyclopropanes 1 to alkynes 2

To solution of cyclopropane **1** (0.30 mmol) in dry $MeNO_2$ (10 mL) alkyne **2** (1.2 mmol) and LA (120 mol%) or TfOH (10 mol%, as a 10 vol% solution in $MeNO_2$) were added sequentially under argon atmosphere in the presence of 4 Å molecular sieves. The resulting mixture was stirred under conditions specified, poured into aqueous $NaHCO_3$ solution (10 mL) and extracted with CH_2Cl_2 (3×5 mL). The combined organic layers were washed with water (2×5 mL) and dried with Na_2SO_4. Solvent was evaporated under reduced pressure. Indene **3** was purified by column chromatography on silica gel (eluent petroleum ether – ethyl acetate).

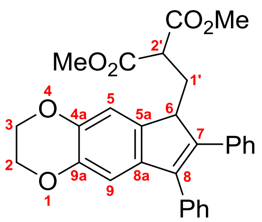
Dimethyl 2-[(7-methyl-8-phenyl-3,6-dihydro-2*H*-indeno[5,6-*b*][1,4]dioxin-6-yl)methyl]-malonate (3a)



TfOH, 10 h (25 °C); yield 87 mg (71%); yellow oil; R_f 0.65 (petroleum ether – ethyl acetate, 2:1).

^{1}H NMR ($CDCl_3$, 600 MHz) δ = 2.01 (s, 3H, CH_3), 2.45 (ddd, ^2J = 14.3, ^3J = 6.2, ^3J = 5.2 Hz, 1H, C(1′)H_2), 2.73 (ddd, ^2J = 14.3, ^3J = 7.8, ^3J = 4.8 Hz, 1H, C(1′)H_2), 3.17 (dd, ^3J = 7.8, ^3J = 6.2 Hz, 1H, C(2′)H), 3.40 (ddd, ^3J = 5.2, ^3J = 4.8, ^4J = 0.7 Hz, 1H, C(6)H), 3.60 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 4.22–4.24 (m, 4H, OCH_2CH_2O), 6.71 (s, 1H, C(9)H), 6.94 (d, ^4J = 0.7 Hz, 1H, C(5)H), 7.33–7.45 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 13.1 (CH_3), 29.2 (C(1′)H_2), 47.7 (CH), 49.9 (CH), 52.4 (OCH_3), 52.5 (OCH_3), 64.4 (2×OCH_2), 108.5 (CH), 112.9 (CH), 127.1 (CH), 128.4 (2×CH), 129.0 (2×CH), 135.1 (C), 137.4 (C), 139.0 (C), 139.6 (C), 141.0 (2×C), 142.7 (C), 169.9 (2×$\underline{C}O_2$Me); IR (Nujol) 1748, 1731, 1585, 1477, 1435, 1355, 1333, 1275, 1260, 1156, 1065, 881, 731, 703 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{25}O_6$ $[M+H]^+$: 409.1946, found: 409.1948.

Dimethyl 2-[(7,8-diphenyl-3,6-dihydro-2*H*-indeno[5,6-b][1,4]dioxin-6-yl)methyl]malonate (3b)

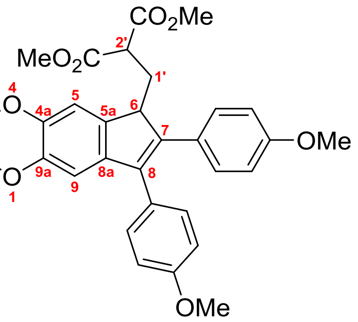


TfOH, 24 h (25 °C); yield 58 mg (41%); white foam; R_f 0.60 (petroleum ether – ethyl acetate, 2:1).

^{1}H NMR ($CDCl_3$, 600 MHz) δ = 2.19 (ddd, ^2J = 14.2, ^3J = 7.3, ^3J = 5.2 Hz, 1H, C(1′)H_2), 2.64 (ddd, ^2J = 14.2, ^3J = 9.2, ^3J = 4.4 Hz, 1H, C(1′)H_2), 3.29 (dd, ^3J = 9.2, ^3J = 5.2 Hz, 1H, C(2′)H), 3.51 (s, 3H, OCH_3), 3.62 (s, 3H, OCH_3), 4.10 (ddd, ^3J = 7.3, ^3J = 4.4, ^4J = 0.7 Hz, 1H, C(6)H), 4.23–4.28 (m, 4H, OCH_2CH_2O), 6.74 (s, 1H, C(9)H), 7.05 (d, ^4J = 0.7 Hz, 1H, C(5)H), 7.13–7.41 (m, 10H, Ph); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 30.1 (C(1′)H_2), 47.8 (CH), 48.2 (CH), 52.3 (OCH_3), 52.4 (OCH_3), 64.3 (OCH_2), 64.4 (OCH_2), 109.5

(CH), 113.2 (CH), 126.8 (CH), 127.4 (CH), 128.2 (2×CH), 128.6 (2×CH), 129.1 (2×CH), 129.3 (2×CH), 135.0 (C), 135.5 (C), 137.9 (C), 139.8 (C), 139.9 (C), 141.8 (C), 143.0 (C), 143.3 (C), 169.4 (<u>C</u>O_2Me), 169.7 (<u>C</u>O_2Me); IR (Nujol) 1755, 1740, 1600, 1590, 1470, 1385, 1365, 1340, 1290, 1235, 1165, 1080, 940, 915, 885, 780, 720, 670 cm^{-1}; MALDI-TOF MS: m/z = 470 $[M]^+$ (470 calcd for $C_{29}H_{26}O_6$). Anal. calcd for $C_{29}H_{26}O_6$: C, 74.03; H, 5.57; Found: C, 74.05; H, 5.53.

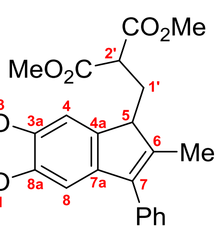
Dimethyl 2-{[7,8-bis(4-methoxyphenyl)-3,6-dihydro-2*H*-indeno[5,6-b][1,4]dioxin-6-yl]methyl}malonate (3c)



TfOH, 10 h (25 °C); yield 129 mg (81%, estimated purity 90%); yellow oil; R_f 0.64 (petroleum ether – ethyl acetate, 2:1)

^{1}H NMR ($CDCl_3$, 600 MHz) δ = 2.13 (ddd, ^2J = 14.0, ^3J = 7.3, ^3J = 5.0 Hz, 1H, C(1′)H_2), 2.62 (ddd, ^2J = 14.0, ^3J = 9.4, ^3J = 4.3 Hz, 1H, C(1′)H_2), 3.30 (dd, ^3J = 9.4, ^3J = 5.0 Hz, 1H, C(2′)H), 3.52 (s, 3H, OCH_3), 3.62 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 4.01 (dd, ^3J = 7.3, ^3J = 4.3 Hz, 1H, C(6)H), 4.23–4.27 (m, 4H, OCH_2CH_2O), 6.72 (s, 1H, C(4)H), 6.78 (d, ^3J = 8.8 Hz, 2H, Ar), 6.92 (d, ^3J = 8.7 Hz, 2H, Ar), 7.02 (s, 1H, C(9)H), 7.09 (d, ^3J = 8.8 Hz, 2H, Ar), 7.22 (d, ^3J = 8.7 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz) δ= 30.3 (C(1′)H_2), 47.7 (CH), 48.2 (CH), 52.3 (OCH_3), 52.4 3 (OCH_3), 55.1 (OCH_3), 55.2 (OCH_3), 64.3 (OCH_2), 64.4 (OCH_2), 109.2 (CH), 113.2 (CH), 113.7 (2×CH), 114.1 (2×CH), 127.7 (C), 127.9 (C), 130.3 (2×CH), 130.5 (2×CH), 137.7 (C), 138.1 (C), 140.2 (C), 141.5 (C), 142.5 (C), 142.9 (C), 158.4 (C), 158.8 (C), 169.5 (<u>C</u>O_2Me), 169.8 (<u>C</u>O_2Me); IR (Nujol) 1749, 1733, 1684, 1605, 1581, 1513, 1506, 1476, 1437, 1245, 1175, 1065, 1027, 834 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{30}NaO_8$ $[M+Na]^+$: 553.1834, found: 553.1833.

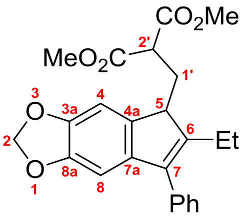
Dimethyl 2-[(6-methyl-7-phenyl-5*H*-indeno[5,6-d][1,3]dioxol-5-yl)methyl]malonate (3d)



Conditions 1: TfOH, 6 h (25 °C); yield 100 mg (85%); conditions 2: $BF_3·Et_2O$, 3 h (25 °C); yield 85 mg (72%); yellow oil; R_f 0.69 (petroleum ether – ethyl acetate, 2:1).

^{1}H NMR ($CDCl_3$, 600 MHz) δ = 2.00 (s, 3H, CH_3), 2.52 (ddd, ^2J = 14.4, ^3J = 6.2, ^3J = 5.3 Hz, 1H, C(1′)H_2), 2.75 (ddd, ^2J = 14.4, ^3J = 7.5, ^3J = 4.8 Hz, 1H, C(1′)H_2), 3.06 (dd, ^3J = 7.5, ^3J = 6.2 Hz, 1H, C(2′)H), 3.40 (dd, ^3J = 5.3, ^3J = 4.8 Hz, 1H, C(5)H), 3.57 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 5.92 (d, ^2J = 7.7 Hz, 1H, C(2)H_2), 5.93 (d, ^2J = 7.7 Hz, 1H, C(2)H_2), 6.69 (s, 1H, C(8)H), 6.93 (s, 1H, C(4)H), 7.34–7.37 (m, 3H, Ph), 7.44–7.47 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 13.1 (CH_3), 28.9 (C(1′)H_2), 47.4 (CH), 50.6 (CH), 52.4 (OCH_3), 52.5 (OCH_3), 100.9 ($C(2)H_2$), 101.0 (CH, Ar), 105.1 (CH, Ar), 127.2 (CH, Ph), 128.4 (2×CH, Ph), 129.0 (2×CH, Ph), 135.1 (C), 137.9 (C), 139.4 (C), 140.0 (C), 140.8 (C), 145.3 (C), 146.9 (C), 169.8 (2×$\underline{C}O_2Me$); IR (Nujol) 1748, 1733, 1474, 1436, 1282, 1260, 1237, 1145, 1033, 932, 702 cm^{-1}. HRMS (ESI) calcd for $C_{23}H_{22}NaO_6$ $[M+Na]^+$: 417.1294, found: 417.1309.

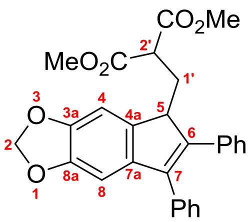
Dimethyl 2-[(6-ethyl-7-phenyl-5*H*-indeno[5,6-d][1,3]dioxol-5-yl)methyl]malonate (3e)



TfOH, 8 h (25 °C); yield 104 mg (85%); yellow oil; R_f 0.66 (petroleum ether – ethyl acetate, 2:1).

^{1}H NMR ($CDCl_3$, 600 MHz) δ = 1.10 (t, ^3J = 7.6 Hz, 3H, $CH_2C\underline{H}_3$), 2.23–2.25 (m, 1H, $C\underline{H}_2CH_3$), 2.43 (ddd, ^2J = 14.3, ^3J = 5.9, ^3J = 5.5 Hz, 1H, $C(1')H_2$), 2.53–2.55 (m, 1H, $C\underline{H}_2CH_3$), 2.76 (ddd, ^2J = 14.3, ^3J = 8.2, ^3J = 4.5 Hz, 1H, $C(1')H_2$), 3.10 (dd, ^3J = 8.2, ^3J = 5.5 Hz, 1H, C(2′)H), 3.57 (s, 3H, OCH_3), 3.58 (dd, ^3J = 5.9, ^3J = 4.5 Hz, 1H, C(5)H), 3.66 (s, 3H, OCH_3), 5.92 (dd, ^2J = 8.8, ^5J = 1.5 Hz, 1H, $C(2)H_2$), 5.93 (dd, ^2J = 8.8, ^5J = 1.5 Hz, 1H, $C(2)H_2$), 6.65 (br. s, 1H, C(8)H), 6.95 (br. s, 1H, C(4)H), 7.32–7.37 (m, 3H, Ph), 7.44–7.47 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 14.9 ($CH_2C\underline{H}_3$), 19.9 ($C\underline{H}_2CH_3$), 28.9 ($C(1')H_2$), 46.7 (CH), 47.6 (CH), 52.4 (OCH_3), 52.6 (OCH_3), 100.9 ($C(2)H_2$), 101.2 (CH, Ar), 105.3 (CH, Ar), 127.3 (CH, Ph), 128.4 (2×CH, Ph), 129.0 (2×CH, Ph), 135.2 (C), 137.9 (C), 139.0 (C), 140.1 (C), 145.4 (C), 146.9 (C), 147.0 (C), 169.8 ($\underline{C}O_2Me$), 169.9 ($\underline{C}O_2Me$); IR (Nujol) 1750, 1733, 1470, 1436, 1364, 1265, 1145, 1036, 938, 862, 807, 702 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{25}O_6$ $[M+H]^+$: 409.1646, found: 409.1639.

Dimethyl 2-[(6,7-diphenyl-5*H*-indeno[5,6-d][1,3]dioxol-5-yl)methyl]malonate (3f)

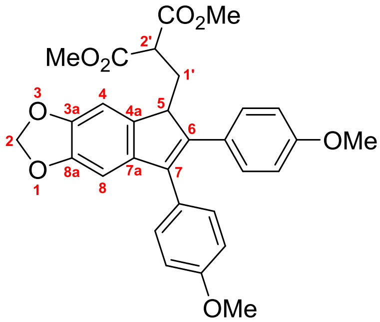


TfOH, 24 h (25 °C); yield 47 mg (34%, estimated purity 90%); yellow oil; R_f 0.57 (petroleum ether – ethyl acetate, 2:1).

^{1}H NMR ($CDCl_3$, 600 MHz) δ = 2.29 (ddd, ^2J = 14.3, ^3J = 6.6, ^3J = 5.2 Hz, 1H, $C(1')H_2$), 2.69 (ddd, ^2J = 14.3, ^3J = 8.8, ^3J = 4.5 Hz, 1H, $C(1')H_2$), 3.16 (dd, ^3J = 8.8, ^3J = 5.2 Hz, 1H, C(2′)H), 3.49 (s, 3H, OCH_3), 3.58 (s, 3H, OCH_3), 4.11 (ddd, ^3J = 6.6, ^3J = 4.5, ^4J = 0.6 Hz, 1H, C(5)H), 5.95 (dd, ^2J = 8.4, ^5J = 1.5 Hz, 1H, $C(2)H_2$), 5.98 (d, ^2J = 8.4, ^5J = 1.5 Hz, 1H, $C(2)H_2$), 6.71 (br. s, 1H, C(8)H), 7.05 (br. s, 1H, C(4)H), 7.13–7.24 (m, 5H, Ph), 7.30–7.41 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 29.7 ($C(1')H_2$), 47.8 (CH), 48.0 (CH), 52.4 (OCH_3), 52.4 (OCH_3), 101.1 ($C(2)H_2$), 101.7 (CH), 105.3 (CH), 126.8 (CH), 127.5 (C), 128.2 (2×CH), 128.7 (2×CH), 129.1 (2×CH), 129.3 (2×CH), 134.8 (C), 135.4 (C), 138.6

(C), 140.2 (C), 140.3 (C), 143.1 (C), 146.1 (C), 147.2 (C), 169.4 ($\underline{C}O_2Me$), 169.7 ($\underline{C}O_2Me$); HRMS (ESI) calcd for $C_{28}H_{24}NaO_6$ $[M+Na]^+$: 479.1465, found: 479.1467.

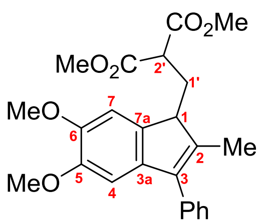
Dimethyl 2-{[6,7-bis(4-methoxyphenyl)-5*H*-indeno[5,6-*d*][1,3]dioxol-5-yl]methyl}malonate (3g)



TfOH, 8 h (25 °C); yield 138 mg (89%); yellow oil; R_f 0.55 (petroleum ether – ethyl acetate, 2:1).

^{1}H NMR ($CDCl_3$, 600 MHz) δ = 2.23 (ddd, ^2J = 14.3, ^3J = 6.7, ^3J = 5.1 Hz, 1H, C(1′)H$_2$), 2.66 (ddd, ^2J = 14.3, ^3J = 9.0, ^3J = 4.3 Hz, 1H, C(1′)H$_2$), 3.16 (dd, ^3J = 9.0, ^3J = 5.1 Hz, 1H, C(2′)H), 3.51 (s, 3H, OCH_3), 3.57 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 4.02 (dd, ^3J = 6.7, ^3J = 4.3 Hz, 1H, C(5)H), 5.92 (dd, ^2J = 8.5, ^5J = 1.5 Hz, 1H, C(2)H$_2$), 5.96 (dd, ^2J = 8.5, ^5J = 1.5 Hz, 1H, C(2)H$_2$), 6.69 (br. s, 1H, C(8)H), Ar), 6.77 (d, ^3J = 8.7 Hz, 2H, Ar), 6.83 (d, ^3J = 8.7 Hz, 2H, Ar), 7.01 (br. s, 1H, C(4)H, Ar), 7.07 (d, ^3J = 8.7 Hz, 2H, Ar), 7.22 (d, ^3J = 8.7 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 30.0 (C(1′)H$_2$), 47.8 (CH), 47.9 (CH), 52.3 (OCH_3), 52.4 (OCH_3), 55.1 (OCH_3), 55.2 (OCH_3), 101.0 (C(2)H$_2$), 101.5 (CH), 105.3 (CH), 113.7 (2×CH), 114.2 (2×CH), 127.6 (C), 127.8 (C), 130.2 (2×CH), 130.5 (2×CH), 138.3 (C), 138.5 (C), 140.6 (C), 142.4 (C), 145.8 (C), 147.1 (C), 158.4 (C), 158.8 (C), 169.4 ($\underline{C}O_2Me$), 169.8 ($\underline{C}O_2Me$); HRMS (ESI) calcd for $C_{30}H_{28}NaO_8$ $[M+Na]^+$: 539.1676, found: 539.1682.

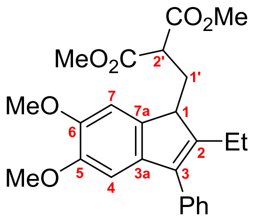
Dimethyl 2-[(5,6-dimethoxy-2-methyl-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3h)



Conditions 1: TfOH, 8 h (25 °C); yield 91 mg (74%); conditions 2: $SnCl_4$, 40 min (25 °C); yield 76 mg (62%); yellow oil; R_f 0.67 (petroleum ether – ethyl acetate, 2:1).

^{1}H NMR ($CDCl_3$, 600 MHz) δ = 2.01 (s, 3H, CH_3), 2.55 (ddd, ^2J = 14.4, ^3J = 5.4, ^3J = 5.4 Hz, 1H, C(1′)H$_2$), 2.79 (ddd, ^2J = 14.4, ^3J = 7.8, ^3J = 4.8 Hz, 1H, C(1′)H$_2$), 2.99 (dd, ^3J = 7.8, ^3J = 5.4 Hz, 1H, C(2′)H), 3.43 (ddd, ^3J = 5.4, ^3J = 4.8, ^4J = 0.6 Hz, 1H, C(1)H), 3.48 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3), 6.74 (s, 1H, C(4)H), 7.01 (d, ^4J = 0.6 Hz, 1H, C(7)H), 7.35–7.38 (m, 3H, Ph), 7.46–7.48 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 13.0 (CH_3), 28.9 (C(1′)H$_2$), 47.3 (CH), 50.3 (CH), 52.3 (OCH_3), 52.5 (OCH_3), 56.2 (OCH_3), 56.4 (OCH_3), 103.6 (CH), 108.2 (CH), 127.2 (CH), 128.5 (2×CH), 129.0 (2×CH), 135.3 (C), 136.3 (C), 138.7 (C), 139.5 (C), 140.6 (C), 146.9 (C), 148.6 (C), 169.9 ($\underline{C}O_2Me$), 170.0 ($\underline{C}O_2Me$); IR (Nujol) 1747, 1732, 1684, 1604, 1506, 1437, 1279, 1265, 1214, 1078, 1017, 705 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{26}NaO_6$ $[M+Na]^+$: 433.1622, found: 433.1611.

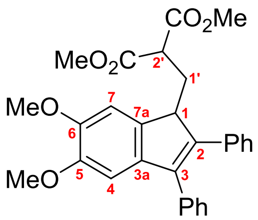
Dimethyl 2-[(2-ethyl-5,6-dimethoxy-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3i)



TfOH, 17 h (25 °C); yield 76 mg (60%); yellow oil; R_f 0.60 (petroleum ether – ethyl acetate, 2:1).

^{1}H NMR ($CDCl_3$, 600 MHz) δ = 1.10 (t, ^3J = 7.6 Hz, 3H, $CH_2C\underline{H}_3$), 2.25–2.27 (m, 1H, $C\underline{H}_2CH_3$), 2.46 (ddd, ^2J = 14.3, ^3J = 5.6, ^3J = 5.0 Hz, 1H, C(1′)H$_2$), 2.54–2.56 (m, 1H, $C\underline{H}_2CH_3$), 2.81 (ddd, ^2J = 14.3, ^3J = 8.5, ^3J = 4.6 Hz, 1H, C(1′)H$_2$), 3.03 (dd, ^3J = 8.5, ^3J = 5.0 Hz, 1H, C(2′)H), 3.48 (s, 3H, OCH_3), 3.62 (dd, ^3J = 5.6, ^3J = 4.6 Hz, 1H, C(1)H), 3.65 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 6.70 (s, 1H, C(4)H), 7.03 (s, 1H, C(7)H), 7.35–7.37 (m, 3H, Ph), 7.45–7.47 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 14.9 ($CH_2C\underline{H}_3$), 19.9 ($C\underline{H}_2CH_3$), 28.9 (C(1′)H$_2$), 46.9 (CH), 47.4 (CH), 52.3 (OCH_3), 52.5 (OCH_3), 56.2 (OCH_3), 56.4 (OCH_3), 103.7 (CH), 108.5 (CH), 127.2 (CH), 128.5 (2×CH), 129.0 (2×CH), 135.4 (C), 136.4 (C), 138.9 (C), 139.2 (C), 146.7 (C), 147.0 (C), 148.7 (C), 169.9 (2×$\underline{C}O_2$Me); IR (Nujol) 1747, 1732, 1605, 1493, 1437, 1271, 1212, 1146, 1117, 1026, 857, 732, 705 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{29}O_6$ $[M+H]^+$: 425.1959, found: 425.1942.

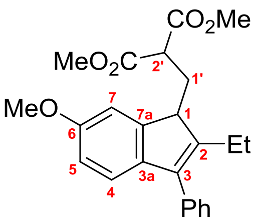
Dimethyl 2-[(5,6-dimethoxy-2,3-diphenyl-1*H*-inden-1-yl)methyl]malonate (3j)



TfOH, 24 h (25 °C); yield 53 mg (38%, estimated purity 90%); yellow oil; R_f 0.57 (petroleum ether – ethyl acetate, 2:1).

^{1}H NMR ($CDCl_3$, 600 MHz) δ = 2.32 (ddd, ^2J = 14.3, ^3J = 6.2, ^3J = 4.9 Hz, 1H, C(1′)H$_2$), 2.72 (ddd, ^2J = 14.3, ^3J = 8.9, ^3J = 4.6 Hz, 1H, C(1′)H$_2$), 3.09 (dd, ^3J = 8.9, ^3J = 4.9 Hz, 1H, C(2′)H), 3.49 (s, 3H, OCH_3), 3.50 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 4.14 (dd, ^3J = 6.2, ^3J = 4.6 Hz, 1H, C(1)H), 6.74 (s, 1H, C(4)H), 7.12 (s, 1H, C(7)H), 7.13–7.41 (m, 10H, Ph); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 29.6 (C(1′)H$_2$), 47.7 (CH), 48.3 (CH), 52.3 (OCH_3), 52.4 (OCH_3), 56.2 (OCH_3), 56.4 (OCH_3), 104.1 (CH), 108.2 (CH), 126.8 (CH), 127.4 (CH), 128.2 (2×CH), 128.7 (2×CH), 129.1 (2×CH), 129.3 (2×CH), 135.0 (C), 135.6 (C), 137.0 (C), 138.8 (C), 140.4 (C), 143.0 (C), 147.7 (C), 148.9 (C), 169.5 ($\underline{C}O_2$Me), 169.8 ($\underline{C}O_2$Me); IR (Nujol) 1760, 1735, 1610, 1585, 1500, 1470, 1385, 1370, 1310, 1290, 1270, 1255, 1230, 1210, 1160, 1135, 1040, 1025, 895, 860, 760, 720 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{29}O_6$ $[M+H]^+$: 473.1959, found: 473.1961.

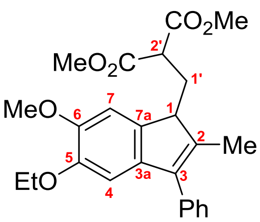
Dimethyl 2-[(2-ethyl-6-methoxy-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3k)



BF_3·Et_2O, 1.5 h (25 °C); yield 48 mg (41%, estimated purity 90%); yellow oil; R_f 0.51 (petroleum ether – ethyl acetate, 2:1).

^{1}H NMR ($CDCl_3$, 600 MHz) δ = 1.11 (t, ^3J = 7.6 Hz, 3H, $CH_2C\underline{H}_3$), 2.25–2.27 (m, 1H, $C\underline{H}_2CH_3$), 2.43 (ddd, ^2J = 14.3, ^3J = 6.0, ^3J = 5.2 Hz, 1H, C(1′)H_2), 2.55–2.58 (m, 1H, $C\underline{H}_2CH_3$), 2.80 (ddd, ^2J = 14.3, ^3J = 8.5, ^3J = 4.5 Hz, 1H, C(1′)H_2), 3.15 (dd, ^3J = 8.5, ^3J = 5.2 Hz, 1H, C(2′)H), 3.52 (s, 3H, OCH_3), 3.66 (dd, ^3J = 6.0, ^3J = 4.5 Hz, 1H, C(1)H), 3.66 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 6.77 (dd, ^3J = 8.3, ^4J = 2.4 Hz, 1H, C(5)H), 7.04 (d, ^4J = 2.4 Hz, 1H, C(7)H), 7.05 (d, ^3J = 8.3 Hz, 1H, C(4)H), 7.35–7.37 (m, 3H, Ph), 7.44–7.46 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 14.7 ($CH_2\underline{C}H_3$), 19.8 ($\underline{C}H_2CH_3$), 28.9 (C(1′)H_2), 46.9 (CH(1)), 47.7 (C(2′)H), 52.3 ($CO_2\underline{C}H_3$), 52.5 ($CO_2\underline{C}H_3$), 55.6 (C(6)O$\underline{C}H_3$), 110.6 (C(7)H), 112.3 (C(5)H), 120.1 (C(4)H), 127.1 (*para*-CH), 128.4 (2×CH), 129.0 (2×CH), 135.4 (C, Ph), 138.9 (C(3)), 139.1 (C(3a)), 145.8 (C(2)), 146.0 (C(7a)), 157.7 (C(6)), 169.9 (2×$\underline{C}O_2$Me); IR (Nujol) 1751, 1733, 1606, 1581, 1478, 1435, 1253, 1242, 1145, 1033, 703 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{27}O_5$ $[M+H]^+$: 395.1853, found: 395.1848.

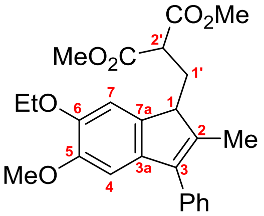
Dimethyl 2-[(5-ethoxy-6-methoxy-2-methyl-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3l)



BF_3·Et_2O, 3 h (25 °C); yield 28 mg (20%); yellow oil; R_f 0.61 (petroleum ether – ethyl acetate, 2:1).

^{1}H NMR ($CDCl_3$, 600 MHz) δ = 1.41 (t, ^3J = 7.1 Hz, 3H, CH_3), 2.01 (s, 3H, CH_3), 2.54 (ddd, ^2J = 14.4, ^3J = 5.5, ^3J = 5.3 Hz, 1H, C(1′)H_2), 2.79 (ddd, ^2J = 14.4, ^3J = 7.9, ^3J = 4.8 Hz, 1H, C(1′)H_2), 3.01 (dd, ^3J = 7.9, ^3J = 5.5 Hz, 1H, C(2′)H), 3.44 (dd, ^3J = 5.3, ^3J = 4.8 Hz, 1H, C(1)H), 3.49 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 4.03 (q, ^3J = 7.1 Hz, 2H, OCH_2), 6.75 (s, 1H, C(4)H), 7.01 (s, 1H, C(7)H), 7.36–7.40 (m, 3H, Ph), 7.46–7.49 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 13.06 (CH_3), 14.85 ($\underline{C}H_3CH_2O$), 28.92 (C(1′)H_2), 47.31 (C(2′)H), 50.24 (C(1)H), 52.39 ($CO_2\underline{C}H_3$), 52.57 ($CO_2\underline{C}H_3$), 56.49 ($\underline{C}H_3OC(5)$), 64.72 ($CH_3\underline{C}H_2O$), 105.30 (C(4)H), 108.52 (C(7)H), 127.13 (*para*-CH), 128.46 (2×*ortho*-CH), 128.99 (2×*meta*-CH), 135.33 (C,Ph), 136.47 (C(7a)), 138.74 (C(3a)), 139.50 (C(3)), 140.50 (C(2)), 147.26 (C(6)), 147.81 (C(5)), 169.99 (2×$\underline{C}O_2$Me); IR (film) 1750, 1740, 1605, 1500, 1450, 1360, 1295, 1275, 1215, 1175, 1125, 1085, 1055, 1045 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{28}NaO_6$ $[M+Na]^+$: 447.1778, found: 447.1772.

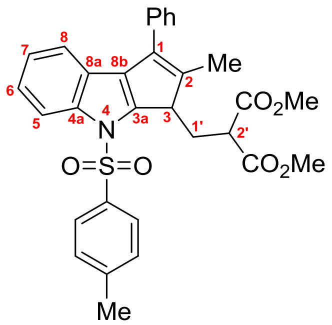
Dimethyl 2-[(6-ethoxy-5-methoxy-2-methyl-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3m)



Yield 83 mg (60%); yellow oil; R_f 0.68 (petroleum ether – ethyl acetate, 2:1).

^{1}H NMR ($CDCl_3$, 600 MHz) δ = 1.49 (t, ^3J = 7.1 Hz, 3H, CH_3), 2.01 (s, 3H, CH_3), 2.54 (ddd, ^2J = 14.3, ^3J = 5.5, ^3J = 5.4 Hz, 1H, C(1′)H_2), 2.78 (ddd, ^2J = 14.3, ^3J = 7.8, ^3J = 4.8 Hz, 1H, C(1′)H_2), 3.02 (dd, ^3J = 7.8, ^3J = 5.5 Hz, 1H, C(2′)H), 3.43 (dd, ^3J = 5.4, ^3J = 4.8 Hz, 1H, C(1)H), 3.49 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 4.13 (dq, ^2J = 9.5, ^3J = 7.1 Hz, 1H, OCH_2), 4.16 (dq, ^2J = 9.5, ^3J = 7.1 Hz, 1H, OCH_2), 6.75 (s, 1H, C(4)H), 7.02 (s, 1H, C(7)H), 7.36–7.40 (m, 3H, Ph), 7.47–7.49 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 13.06 ($^1J_{CH}$ = 127 Hz, CH_3), 14.93 ($^1J_{CH}$ = 127 Hz, $\underline{C}H_3CH_2O$), 28.94 ($^1J_{CH}$ = 133 Hz, C(1′)H_2), 47.30 ($^1J_{CH}$ = 132 Hz, C(2′)H), 50.20 ($^1J_{CH}$ = 128 Hz, C(1)H), 52.40 ($^1J_{CH}$ = 147 Hz, $CO_2\underline{C}H_3$), 52.56 ($^1J_{CH}$ = 148 Hz, $CO_2\underline{C}H_3$), 56.26 ($^1J_{CH}$ = 144 Hz, $\underline{C}H_3$OC(5)), 64.94 ($^1J_{CH}$ = 144 Hz, $CH_3\underline{C}H_2O$), 103.83 ($^1J_{CH}$ = 158 Hz, C(4)H), 109.91 ($^1J_{CH}$ = 156 Hz, C(7)H), 127.15 ($^1J_{CH}$ = 161 Hz, *para*-CH), 128.48 ($^1J_{CH}$ = 161 Hz, 2×*ortho*-CH), 128.99 ($^1J_{CH}$ = 160 Hz, 2×*meta*-CH), 135.34 (C, Ph), 136.35 (C(7a)), 138.83 (C(3a)), 139.52 (C(3)), 140.61 (C(2)), 146.09 (C(6)), 148.96 (C(5)), 169.97 ($\underline{C}O_2CH_3$), 170.01 ($\underline{C}O_2CH_3$); IR (film) 1755, 1740, 1660, 1609, 1585, 1500, 1448, 1365, 1295, 1275, 1215, 1192, 1163, 1123, 1088, 1058, 1048 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{28}NaO_6$ $[M+Na]^+$: 447.1778, found: 447.1777.

Dimethyl 2-[(2-methyl-3-phenyl-8-tosyl-3,4-dihydrocyclopenta[b]indol-1-yl)methyl]malonate (3n)

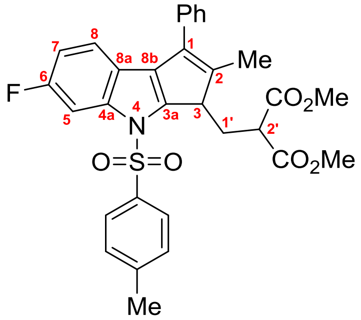


TfOH, 5 h (50 °C); yield 83 mg (51%, estimated purity 90%); yellow oil; R_f 0.53 (petroleum ether – ethyl acetate, 2:1).

^{1}H NMR ($CDCl_3$, 600 MHz) δ = 2.12 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.82 (ddd, ^2J = 13.7, ^3J = 6.3, ^3J = 4.0 Hz, 1H, C(1′)H_2), 2.86 (dd, ^3J = 6.3, ^3J = 6.0 Hz, 1H, C(2′)H), 3.35 (ddd, ^2J = 13.7, ^3J = 6.0, ^3J = 4.8 Hz, 1H, C(1′)H_2), 3.43 (s, 3H, OCH_3), 3.57 (s, 3H, OCH_3), 3.90 (dd, ^3J = 4.8, ^3J = 4.0 Hz, 1H, C(1)H), 7.13 (dd, ^3J = 8.0, 7.7 Hz, 1H, Ar), 7.15 (d, ^3J = 8.4 Hz, 2H, Ar), 7.24 (ddd, ^3J = 8.4, 7.3, ^4J = 1.2 Hz, 1H, Ar), 7.31 (br. d, ^3J = 7.8 Hz, 1H, Ar), 7.35-7.38 (m, 1H, Ar), 7.45–7.48 (m, 4H, Ar), 7.66 (d, ^3J = 8.4 Hz, 2H, Ar), 8.06 (d, ^3J = 8.4 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 13.3 (CH_3), 21.5 (CH_3, Ts), 28.5 (C(1′)H_2), 46.8 (CH), 49.1 (CH), 52.3 (OCH_3), 52.5 (OCH_3), 115.2 (CH), 120.0 (CH), 123.6 (CH), 123.8 (CH), 124.9 (C), 126.6 (2×CH), 127.4 (CH), 128.3 (2×CH), 128.9 (2×CH), 129.6 (C), 129.7 (2×CH), 132.4 (C), 134.9 (C), 135.4 (C), 139.3 (C), 140.7 (C), 144.3 (C), 144.8 (C), 169.1 ($\underline{C}O_2$Me), 169.8

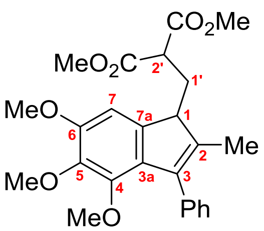
($\underline{C}O_2$Me); IR (Nujol) 1748, 1733, 1598, 1370, 1173, 1089, 813, 730, 703, 667 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{30}NO_6S$ [M+H]$^+$: 544.1788, found: 544.1785.

Dimethyl 2-[(6-fluoro-2-methyl-1-phenyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indol-3-yl)methyl]malonate (3o)



BF_3·Et_2O, 3 h (25 °C); yield 76 mg (60%); yellow oil; R_f 0.55 (petroleum ether – ethyl acetate, 2:1).
^{1}H NMR ($CDCl_3$, 600 MHz) δ = 2.11 (s, 3H, CH_3C(2)), 2.32 (s, 3H, CH_3, Ts), 2.82 (ddd, ^2J = 13.8, ^3J = 6.2, ^3J = 4.1 Hz, 1H, C(1′)H_2), 2.85 (dd, ^3J = 6.2, ^3J = 5.9 Hz, 1H, C(2′)H), 3.34 (ddd, ^2J = 13.8, ^3J = 5.9, ^3J = 5.0 Hz, 1H, C(1′)H_2), 3.46 (s, 3H, OCH_3), 3.58 (s, 3H, OCH_3), 3.88 (dd, ^3J = 5.0, ^3J = 4.1 Hz, 1H, C(3)H), 6.89 (ddd, $^3J_{HF}$ = 8.9, $^3J_{HH}$ = 8.7, $^4J_{HH}$ = 2.3 Hz, 1H, C(7)H), 7.19 (d, ^3J = 8.3 Hz, 2H, Ts), 7.23 (dd, $^3J_{HH}$ = 8.7, $^4J_{HF}$ = 5.4 Hz, 1H, C(8)H), 7.34–7.38 (m, 2H, Ph), 7.44-7.47 (m, 3H, Ph), 7.67 (d, ^3J = 8.3 Hz, 2H, Ts), 7.82 (dd, $^3J_{HF}$ = 9.9, $^4J_{HH}$ = 2.3 Hz, 1H, (C(5)H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 13.2 ($\underline{C}H_3$C(2)), 21.5 (CH_3, Ts), 28.4 (C(1′)H_2), 46.9 (C(2′)H), 49.1 (C(3)H), 52.3 (OCH_3), 52.5 (OCH_3), 102.8 ($^2J_{CF}$ = 28 Hz, C(5)H), 111.8 ($^2J_{CF}$ = 23 Hz, C(7)H), 120.5 ($^3J_{CF}$ = 9 Hz, C(8)H), 121.3 (C), 126.7 (2×CH, Ts), 127.5 (CH, *para*-Ph), 128.4 (2×CH), 128.8 (2×CH), 129.8 (2×CH, Ts), 132.0 (C), 134.5 (CSO_2), 134.8 (C), 135.2 (C(1)), 139.6 (C(2)), 140.9 ($^3J_{CF}$ = 11 Hz, C(4a)), 144.3 ($^4J_{CF}$ = 4 Hz, C(8a)), 145.1 ($\underline{C}CH_3$, Ts), 160.2 ($^1J_{CF}$ = 242 Hz, C(6)F), 169.0 ($\underline{C}O_2$Me), 169.8 ($\underline{C}O_2$Me); IR (film) 1755, 1740, 1660, 1618, 1605, 1590, 1553, 1496, 1460, 1445, 1386, 1355, 1303, 1278, 1250, 1230, 1198, 1189, 1165, 1128, 1103 1053, 1029, 1005 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{29}FNO_6S$ [M+H]$^+$: 562.1694, found: 562.1691.

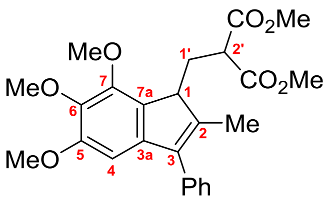
Dimethyl 2-[(4,5,6-trimethoxy-2-methyl-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3p)



BF_3·Et_2O, 3 h (25 °C); yield 69 mg (52%); yellow oil; R_f 0.63 (petroleum ether – ethyl acetate, 2:1).
^{1}H NMR ($CDCl_3$, 600 MHz) δ = 2.06 (s, 3H, CH_3), 2.61 (ddd, ^2J = 14.3, ^3J = 5.4, ^3J = 4.8 Hz, 1H, C(1′)H_2), 2.81 (ddd, ^2J = 14.3, ^3J = 7.9, ^3J = 4.5 Hz, 1H, C(1′)H_2), 3.05 (dd, ^3J = 7.9, ^3J = 5.4 Hz, 1H, C(2′)H), 3.32 (s, 3H, OCH_3), 3.50 (s, 3H, OCH_3), 3.55 (dd, ^3J = 4.8, ^3J = 4.5 Hz, 1H, C(1)H), 3.69 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 6.85 (s, 1H, C(7)H), 7.32–7.34 (m, 3H, Ph), 7.38–7.41 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 12.6 (CH_3), 29.0 (C(1′)H_2), 47.2 (C(2′)H), 50.6 (C(1)H), 52.3 ($CO_2\underline{C}H_3$), 52.6 ($CO_2\underline{C}H_3$), 56.4 (OCH_3), 61.0 (2×OCH_3), 104.6 (C(7)H), 126.7

(*para*-CH, Ph), 127.4 (2×*meta*-CH, Ph), 129.3 (2×*ortho*-CH, Ph), 131.5 (C(3a)), 136.8 (C, Ph), 138.7 (C(3)), 140.3 (C(7a)), 140.5 (C(2)), 142.0 (C(5)), 147.6 (C(4)), 151.4 (C(6)), 169.9 (<u>C</u>O$_2$Me), 170.0 (<u>C</u>O$_2$Me); HRMS (ESI) calcd for $C_{25}H_{28}NaO_7$ $[M+Na]^+$: 463.1727, found: 463.1720.

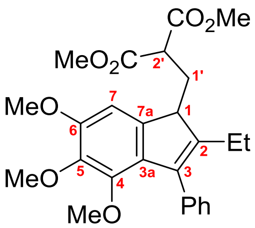
Dimethyl 2-[(5,6,7-trimethoxy-2-methyl-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3q)



Yield 28 mg (21%); yellow oil; R_f 0.69 (petroleum ether – ethyl acetate, 2:1).

^{1}H NMR ($CDCl_3$, 600 MHz) δ = 2.00 (s, 3H, CH$_3$), 2.52 (ddd, ^2J = 14.2, ^3J = 6.5, ^3J = 5.1 Hz, 1H, C(1′)H$_2$), 2.97 (ddd, ^2J = 14.2, ^3J = 7.3, ^3J = 4.4 Hz, 1H, C(1′)H$_2$), 3.15 (dd, ^3J = 7.3, ^3J = 6.5 Hz, 1H, C(2′)H), 3.54 (s, 3H, OCH$_3$), 3.63 (s, 3H, OCH$_3$), 3.64 (dd, ^3J = 5.1 Hz, ^3J = 4.4 Hz, 1H, C(1)H), 3.80 (s, 3H, OCH$_3$), 3.88 (s, 3H, OCH$_3$), 4.03 (s, 3H, OCH$_3$), 6.51 (s, 1H, C(4)H), 7.36–7.39 (m, 3H, Ph), 7.47–7.50 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 13.1 (CH$_3$), 27.6 (C(1′)H$_2$), 47.6 (C(2′)H), 49.2 (C(1)H), 52.3 (CO$_2$<u>C</u>H$_3$), 52.5 (CO$_2$<u>C</u>H$_3$), 56.3 (OCH$_3$), 60.4 (OCH$_3$), 61.1 (OCH$_3$), 99.4 (C(4)H, Ar), 127.2 (*para*-CH, Ph), 127.7 (C(7a)), 128.5 (2×*meta*-CH, Ph), 129.0 (2×*ortho*-CH, Ph), 135.1 (C, Ph), 139.3 (C(3)), 139.4 (C(6)), 141.8 (C(3a)), 142.6 (C(2)), 149.8 (C-OMe), 153.7 (C-OMe), 169.9 (<u>C</u>O$_2$Me), 170.0 (<u>C</u>O$_2$Me); IR (film) 1750, 1735, 1600, 1470, 1360, 1270, 1125, 1050, 740 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{28}NaO_7$ $[M+Na]^+$: 463.1727, found: 463.1722.

Dimethyl 2-[(2-ethyl-4,5,6-trimethoxy-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3r)

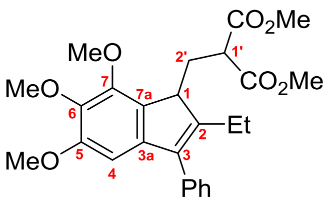


TfOH, 5 h (25 °C); yield 79 mg (58%); yellow oil; R_f 0.57 (petroleum ether – ethyl acetate, 2:1).

^{1}H NMR ($CDCl_3$, 600 MHz) δ = 1.04 (t, ^3J = 7.5 Hz, 3H, CH$_2$C<u>H</u>$_3$), 2.12–2.14 (m, 1H, C<u>H</u>$_2$CH$_3$), 2.37–2.39 (m, 1H, C<u>H</u>$_2$CH$_3$), 2.49 (ddd, ^2J = 14.3, ^3J = 5.4, ^3J = 4.8 Hz, 1H, C(1′)H$_2$), 2.78 (ddd, ^2J = 14.3, ^3J = 8.6, ^3J = 4.5 Hz, 1H, C(1′)H$_2$), 3.05 (dd, ^3J = 8.6, ^3J = 4.8 Hz, 1H, C(2′)H), 3.28 (s, 3H, OCH$_3$), 3.58 (s, 3H, OCH$_3$), 3.61 (dd, ^3J = 5.4, ^3J = 4.5 Hz, 1H, C(1)H), 3.69 (s, 3H, OCH$_3$), 3.83 (s, 3H, OCH$_3$), 3.90 (s, 3H, OCH$_3$), 6.83 (s, 1H, C(7)H), 7.32–7.34 (m, 3H, Ph), 7.38–7.41 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 14.8 (CH$_2$C<u>H</u>$_3$), 19.6 (C<u>H</u>$_2$CH$_3$), 28.9 (C(1′)H$_2$), 47.27 (C(2′)H), 47.28 (C(1)H), 52.3 (OCH$_3$), 52.6 (OCH$_3$), 56.4 (OCH$_3$), 61.0 (2×OCH$_3$), 104.7 (CH, Ar), 126.7 (*para*-CH, Ph), 127.4 (2×*meta*-CH, Ph), 129.3 (2×*ortho*-CH, Ph), 131.4 (C(3a)), 136.8 (C(Ph)), 138.7 (C(3)), 140.5 (C(7a)), 142.0 (C(5)), 146.3 (C(2)), 147.6 (C(4)), 151.4 (C(6)), 169.9

($\underline{C}O_2Me$), 170.0 ($\underline{C}O_2Me$); IR (Nujol) 1748, 1733, 1473, 1436, 1281, 1260, 1237, 1145, 1124, 1034, 702 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{31}O_7$ $[M+H]^+$: 455.2064, found: 455.2059.

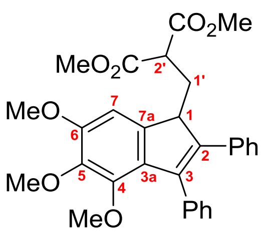
Dimethyl 2-[(2-ethyl-5,6,7-trimethoxy-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3s)



Yield 29 mg (21%, estimated purity 90%); yellow oil; R_f 0.65 (petroleum ether – ethyl acetate, 2:1).

^{1}H NMR ($CDCl_3$, 600 MHz) δ = 1.11 (t, ^3J = 7.6 Hz, 3H, $CH_2C\underline{H}_3$), 2.21–2.27 (m, 1H, $C\underline{H}_2CH_3$), 2.41 (ddd, ^2J = 14.3, ^3J = 5.7, ^3J = 5.6 Hz, 1H, C(1′)H_2), 2.48–2.54 (m, 1H, $C\underline{H}_2CH_3$), 2.97 (ddd, ^2J = 14.3, ^3J = 7.9, ^3J = 4.3 Hz, 1H, C(1′)H_2), 3.17 (dd, ^3J = 7.9, ^3J = 5.7 Hz, 1H, C(2′)H), 3.51 (s, 3H, OCH_3), 3.62 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 3.83 (dd, ^3J = 5.6, ^3J = 4.3 Hz, 1H, C(1)H), 3.87 (s, 3H, OCH_3), 4.03 (s, 3H, OCH_3), 6.46 (s, 1H, C(4)H), 7.32–7.34 (m, 2H, Ph), 7.36–7.39 (m, 1H, Ph), 7.45–7.48 (m, 1H, Ph); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 14.8 ($CH_2C\underline{H}_3$), 19.9 ($C\underline{H}_2CH_3$), 27.8 (C(1′)H_2), 45.8 (C(1)H), 47.7 (C(2′)H), 52.2 (OCH_3), 52.4 (OCH_3), 56.3 (OCH_3), 60.4 (OCH_3), 61.0 (OCH_3), 99.6 (C(4)H), Ar), 127.2 (*para*-CH, Ph), 127.7 (C(7a)), 128.5 (2×*meta*-CH, Ph), 129.0 (2×*ortho*-CH, Ph), 135.2 (C, Ph), 138.9 (C(3)), 139.5 (C(6)), 141.9 (C(3a)), 148.7 (C(2)), 149.9 (C-OMe), 153.8 (C-OMe), 169.9 ($\underline{C}O_2Me$), 170.0 ($\underline{C}O_2Me$);HRMS (ESI) calcd for $C_{26}H_{31}O_7$ $[M+H]^+$: 455.2064, found: 455.2055.

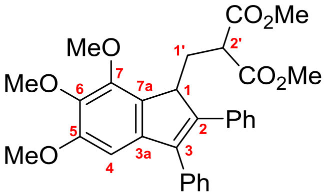
Dimethyl 2-[(4,5,6-trimethoxy-2,3-diphenyl-1*H*-inden-1-yl)methyl]malonate (3t)



TfOH, 24 h (25 °C); yield 42 mg (28%); yellow oil; R_f 0.63 (petroleum ether – ethyl acetate, 2:1).

^{1}H NMR ($CDCl_3$, 600 MHz) δ = 2.34 (ddd, ^2J = 14.3, ^3J = 6.0, ^3J = 5.1 Hz, 1H, C(1′)H_2), 2.68 (ddd, ^2J = 14.3, ^3J = 8.9, ^3J = 4.6 Hz, 1H, C(1′)H_2), 3.11 (dd, ^3J = 8.9, ^3J = 5.1 Hz, 1H, C(2′)H), 3.29 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3), 3.50 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 4.13 (ddd, ^3J = 6.0, ^3J = 4.6, ^4J = 0.6 Hz, 1H, C(1)H), 6.92 (d, ^4J = 0.6 Hz, 1H, C(7)H), 7.06–7.07 (m, 2H, Ph), 7.12–7.14 (m, 1H, Ph), 7.17–7.19 (m, 2H, Ph), 7.33–7.40 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 29.8 (C(1′)), 47.5 (CH), 48.7 (CH), 52.3 (OCH_3), 52.4 (OCH_3), 59.4 (OCH_3), 61.0 (OCH_3), 61.1 (OCH_3), 104.6 (C(7)H), 126.6 (CH), 126.8 (CH), 127.7 (2×CH), 128.1 (2×CH), 129.2 (2×CH), 129.7 (2×CH), 131.4 (C), 135.0 (C), 137.0 (C), 140.1 (C), 140.9 (C), 142.3 (C), 142.6 (C), 148.5 (C), 152.2 (C), 169.4 ($\underline{C}O_2Me$), 169.9 ($\underline{C}O_2Me$); IR (Nujol) 1747, 1733, 1684, 1601, 1577, 1466, 1446, 1436, 1259, 1243, 1121, 1026, 701 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{31}O_7$ $[M+H]^+$: 503.2064, found: 503.2072.

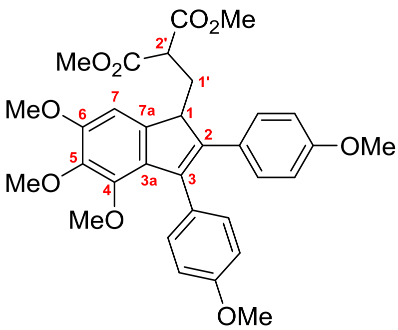
Dimethyl 2-[(5,6,7-trimethoxy-2,3-diphenyl-1*H*-inden-1-yl)methyl]malonate (3u)



Yield 24 mg (16%); yellow oil; R_f 0.71 (petroleum ether – ethyl acetate, 2:1).

^{1}H NMR ($CDCl_3$, 600 MHz) δ = 2.27 (ddd, ^2J = 14.2, ^3J = 6.3, ^3J = 5.3 Hz, 1H, C(1′)H), 2.88 (ddd, ^2J = 14.2, ^3J = 9.0, ^3J = 4.0 Hz, 1H, C(1′)H), 3.24 (dd, ^3J = 9.0, ^3J = 5.3 Hz, 1H, C(2′)H), 3.47 (s, 3H, CO_2CH_3), 3.50 (s, 3H, CO_2CH_3), 3.79 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 4.07 (s, 3H, OCH_3), 4.38 (dd, ^3J = 6.3, ^3J = 4.0 Hz, 1H, C(1)H), 6.50 (s, 1H, C(4)H), 7.15 (d, ^3J = 6.9 Hz, 2H, Ph), 7.16-7.19 (m, 1H, Ph), 7.22 (dd, ^3J = 7.6, ^3J = 6.9 Hz, 2H, Ph), 7.30 (d, ^3J = 6.9 Hz, 2H, Ph), 7.35–7.37 (m, 1H, Ph), 7.41 (dd, ^3J = 7.6, ^3J = 6.9 Hz, 2H, Ph); ^{13}C NMR ($CDCl_3$, 150 MHz): 28.6 (C(1′)), 47.0 (CH), 47.9 (CH), 52.2 ($CO_2\underline{C}H_3$), 52.3 ($CO_2\underline{C}H_3$), 56.3 (OCH_3), 60.5 (OCH_3), 61.1 (OCH_3), 100.1 (C(4)H), 127.0 (CH, Ph), 127.4 (CH, Ph), 128.2 (2×CH), 128.3 (C(7a)), 128.8 (2×CH), 129.2 (2×CH), 129.3 (2×CH), 134.7 (C, Ph), 135.4 (C, Ph), 140.1 (C(3)), 140.2 ($\underline{C}$OMe), 142.0 (C(3a)), 144.6 (C(2)), 149.9 ($\underline{C}$OMe), 154.0 ($\underline{C}$OMe), 169.6($\underline{C}O_2$Me), 169.8($\underline{C}O_2$Me); IR (film) 1730, 1600, 1465, 1360, 1195, 1105, 1025, 830, 700 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{30}NaO_7$ $[M+Na]^+$: 525.1884, found: 525.1877.

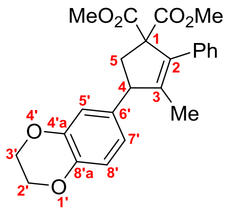
Dimethyl 2-{[4,5,6-trimethoxy-2,3-bis(4-methoxyphenyl)-1*H*-inden-1-yl]methyl}malonate (3v)



TfOH, 15 h (25 °C); yield 125 mg (74%, estimated purity 90%); yellow oil; R_f 0.50 (petroleum ether – ethyl acetate, 2:1).

^{1}H NMR ($CDCl_3$, 600 MHz, 333K) δ = 2.32 (ddd, ^2J = 14.2, ^3J = 6.0, ^3J = 5.0 Hz, 1H, C(1′)H_2), 2.66 (ddd, ^2J = 14.2, ^3J = 9.0, ^3J = 4.5 Hz, 1H, C(1′)H_2), 3.11 (dd, ^3J = 9.0, ^3J = 5.0 Hz, 1H, C(2′)H), 3.30 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3), 3.51 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 4.05 (dd, ^3J = 6.0, ^3J = 4.5 Hz, 1H, C(1)H), 6.74 (d, ^3J = 8.7 Hz, 2H, Ar), 6.87 (d, ^3J = 7.7 Hz, 2H, Ar), 6.89 (s, 1H, C(7)H), 6.99 (d, ^3J = 8.7 Hz, 2H, Ar), 7.27 (d, ^3J = 7.7 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 29.9 (C(1′)), 47.5 (CH), 48.5 (CH), 52.3 (OCH_3), 52.4 (OCH_3), 55.09 (OCH_3), 55.14 (OCH_3), 56.4 (OCH_3), 61.0 (OCH_3), 61.2 (OCH_3), 104.6 (C(7)H), 113.2 (2×CH), 113.6 (2×CH), 127.6 (C), 129.4 (C), 130.3 (2×CH), 130.9 (2×CH), 131.7 (C), 138.4 (C), 140.7 (C), 142.2 (2×C), 148.3 (C), 151.8 (C), 158.2 (C), 158.4 (C), 169.5 ($\underline{C}O_2$Me), 169.9 ($\underline{C}O_2$Me); IR (film) 1735, 1610, 1450, 1390, 1250, 1065, 740 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{34}NaO_9$ $[M+Na]^+$: 585.2095, found: 585.2095.

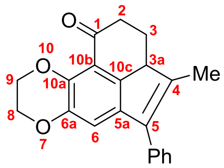
Dimethyl 4-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-3-methyl-2-phenylcyclopent-2-ene-1,1-dicarboxylate (4)



Cyclopentene **4** was obtained together with indene **3a** when reaction was carried out under non-optimized conditions: $SnCl_4$, 6 h (–40 °C, $EtNO_2$); yield 33 mg (27%); yellow oil; R_f 0.43 (petroleum ether – ethyl acetate, 2:1).

^{1}H NMR ($CDCl_3$, 600 MHz) δ = 1.43 (d, ^4J = 1.2 Hz, 3H, CH_3), 2.56 (dd, ^2J = 13.7, ^3J = 7.5 Hz, 1H, C(5)H_2), 3.07 (dd, ^2J = 13.7, ^3J = 8.3 Hz, 1H, C(5)H_2), 3.58 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 3.85 (m, 1H, C(4)H), 4.25–4.27 (m, 4H, OCH_2CH_2O), 6.73 (dd, ^3J = 8.3, ^4J = 2.0 Hz, 1H, C(7′)H), 6.77 (d, ^4J = 2.0 Hz, 1H, C(5′)H), 6.84 (d, ^3J = 8.3 Hz, 1H, C(8′)H), 7.24-7.33 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 14.3 (CH_3), 43.2 (C(5)H_2), 52.2 (OCH_3), 52.4 (OCH_3), 53.6 (C(4)H), 64.3 (OCH_2), 64.4 (OCH_2), 69.4 (C), 116.7 (CH), 117.3 (CH), 121.0 (CH), 127.1 (CH), 127.7 (2×CH), 129.8 (2×CH), 136.1 (C), 136.5 (C), 136.8 (C), 142.3 (C), 143.6 (C), 145.4 (C), 171.8 ($\underline{C}O_2$Me), 172.1 ($\underline{C}O_2$Me); MALDI-TOF MS: *m/z* = 409 $[M+1]^+$ (409 calcd for $C_{24}H_{25}O_6$). Anal. calcd for $C_{24}H_{24}O_6$: C, 70.43; H, 5.77; Found: C, 70.57; H, 5.92.

4-Methyl-5-phenyl-3,3a,8,9-tetrahydroacenaphtho[4,5-*b*][1,4]dioxin-1(2*H*)-one (5)



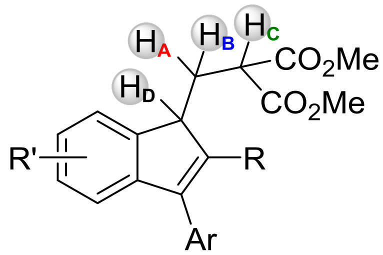
To solution of indene **3a** (150 mg, 0.37 mmol) in MeOH (0.4 mL) the solution of KOH (84 mg, 1.5 mmol) in H_2O (0.75 mL) was added and the resulting mixture was stirred overnight. Then, the reaction mixture was concentrated under reduced pressure and the residue was diluted with H_2O (10 mL). The resulting solution was once washed with Et_2O (10 mL) and acidified with 1 M HCl up to pH 1. The mixture was extracted with Et_2O (3×10 mL), the combined organic layers were dried with Na_2SO_4 and concentrated. The resulting yellowish oil (85 mg, 0.22 mmol) was dissolved in solution of P_2O_5 (450 mg, 3.1 mmol) in TfOH (3.2 mL). The reaction mixture was stirred at room temperature for 3 h and then poured into ice/water (10 mL). Product **5** was extracted with Et_2O (3×10 mL), the combined organic layers were dried with Na_2SO_4 and concentrated under reduce pressure. Product **5** was purified by column chromatography on silica gel; yield 21 mg (30%); yellowish oil; R_f 0.31 (eluent ethyl acetate).

^{1}H NMR ($CDCl_3$, 600 MHz) δ = 1.57 (dddd, ^2J = 12.2, ^3J = 13.2, ^3J = 13.1, ^3J = 4.5 Hz, 1H, C(3)H_2), 2.13 (d, ^4J = 0.6 Hz, 3H, CH_3), 2.50 (ddd, ^2J = 12.2, ^3J = 5.1, ^3J = 4.9, ^3J = 2.0 Hz, 1H, C(3)H_2), 2.76 (ddd, ^2J = 18.1, ^3J = 13.1, ^3J = 5.1 Hz, 1H, C(2)H_2), 2.88 (ddd, ^2J = 18.1, ^3J = 4.5, ^3J = 2.0 Hz, 1H, C(2)H_2), 3.36 (ddq, ^3J = 13.2, ^3J = 4.9, ^4J = 0.6 Hz, 1H, CH), 4.26–4.29 (m, 2H, CH_2O), 4.30–4.32 (m, 1H, CH_2O), 4.45–4.48 (m, 1H, CH_2O), 6.99 (s, 1H, C(6)H), 7.35–7.38 (m, 1H, Ph), 7.40–7.41 (m, 2H, Ph), 7.46–7.48 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 13.0 ($^1J_{CH}$ = 127 Hz, CH_3), 25.9 ($^1J_{CH}$ = 131 Hz, CH_2), 40.8 ($^1J_{CH}$ = 130 Hz, CH_2), 50.3 ($^1J_{CH}$ = 127 Hz, CH), 63.9 ($^1J_{CH}$ = 148 Hz, CH_2O), 64.8 ($^1J_{CH}$ = 149 Hz, CH_2O), 113.7 (CH), 118.3 (C), 127.3 (CH), 128.5 (2×CH), 128.8 (2×CH), 134.7 (C), 136.1 (C), 137.8 (C), 140.2 (C), 142.9 (C), 143.3 (C), 146.4 (C), 196.5 (C=O); IR (film) 1410, 1395, 1375, 1250, 1050, 920, 750 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{18}NaO_3$ [M+Na]$^+$: 341.1148, found: 341.1146.

Structural assignments of indenes 3

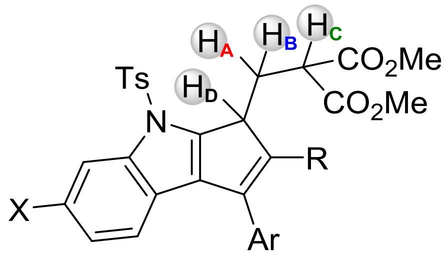
To elucidate the structure of indenes **3**, the careful analysis of ^{1}H and ^{13}C NMR 1D and 2D spectra and their comparison with the described spectral data of related systems was carried out. Herein we present a summary of the structural characterization of **3**.

The ^{1}H and ^{13}C NMR spectra of **3** were assigned using HSQC, HMBC and NOESY 2D NMR spectroscopy. The NMR data of **3** revealed the formation of indene core, containing CH–CH_2–CH system. In ^{1}H NMR spectra, this four-spin system is characterized by the following patterns (Figure S1).



3a-m,p-v

ppm		Hz	
δ_A	2.13-2.61	J_{AB}	14.0-14.4
δ_B	2.62-2.97	J_{AC}	5.4-7.3
δ_C	2.99-3.30	J_{AD}	4.8-5.6
δ_D	3.40-3.83 (R = Alk)	J_{BC}	7.3-9.4
	4.01-4.38 (R = Ar)	J_{BD}	4.0-4.8



3n,o

ppm		Hz	
δ_A	~2.8	J_{AB}	~13.8
δ_B	~3.4	J_{AC}	~6.3
δ_C	~2.9	J_{AD}	~4.1
δ_D	~3.9	J_{BC}	~6.0
		J_{BD}	~5.0

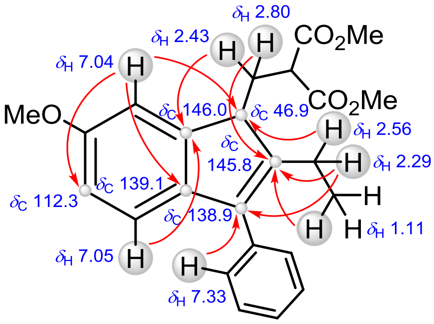
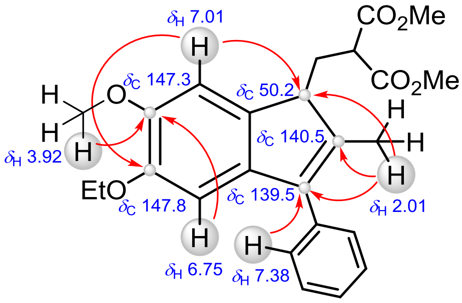
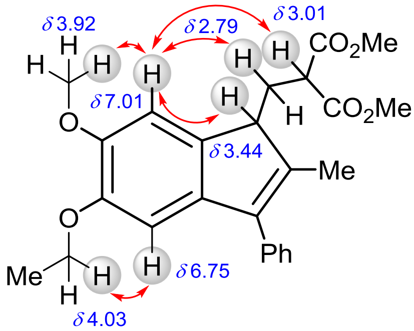
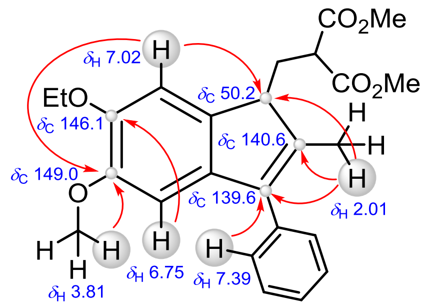
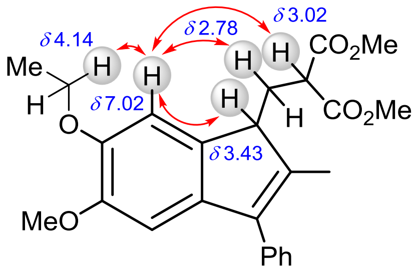
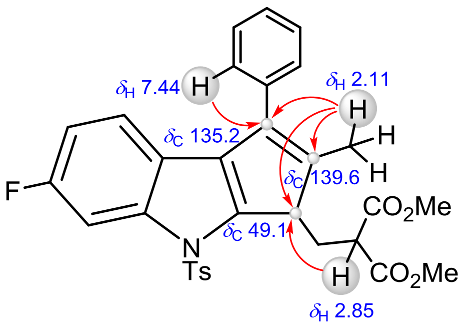
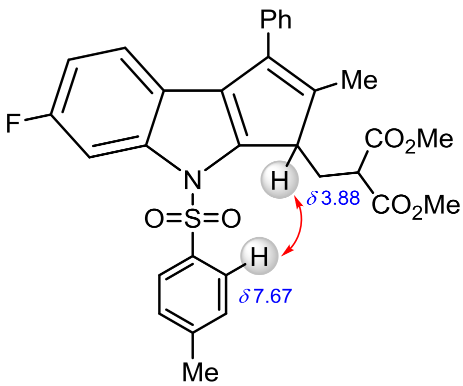
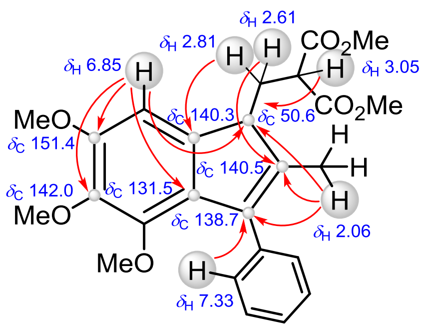
Figure S1

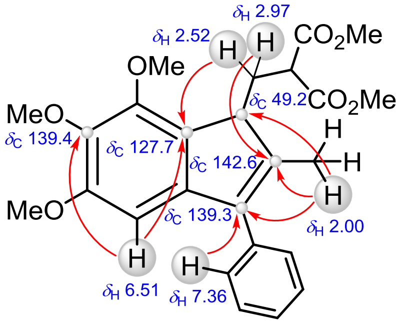
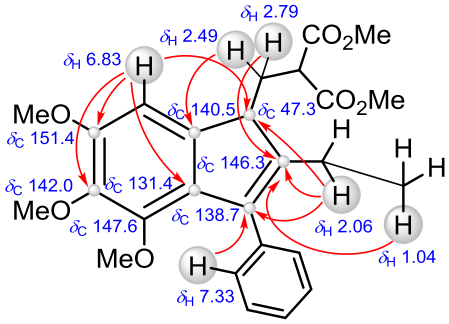
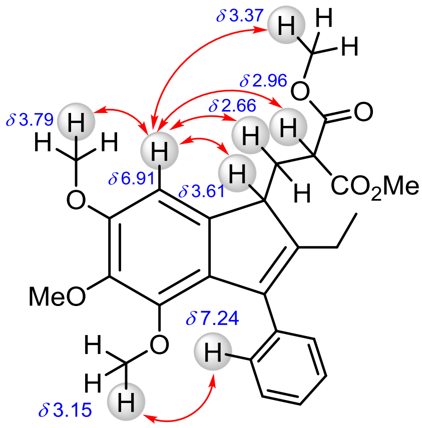
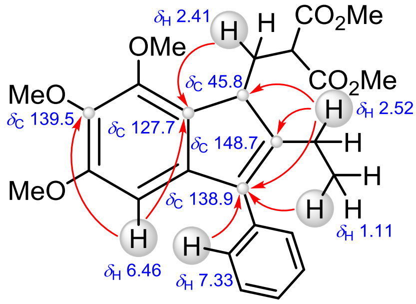
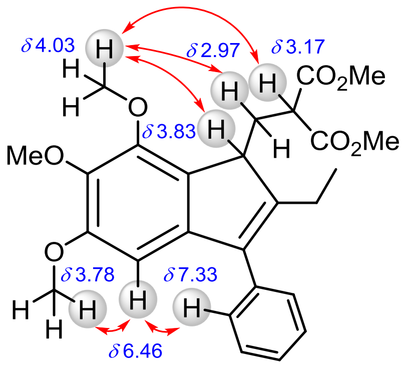
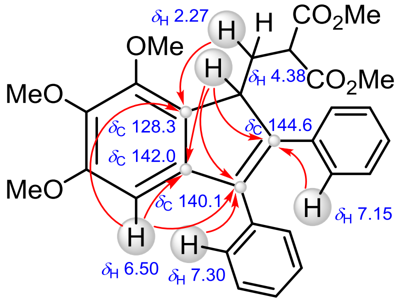
To determine what regioisomers were formed *via* annulation the comprehensive assignments of ^{1}H and ^{13}C were made for indenes **3k-m,o-s,u** by means of HSQC, HMBC, and NOESY analysis (Table S1). This allowed us to elucidate a set of spectral criteria which provided correct assignment of **3** to definite regioisomer.

Analysis of chemical shifts for H(4) and H(7) protons of the indene core and their comparison with the literature data support assignments deduced from 2D NMR. Thus, for 5,6-dialkoxy substituted indenes **3a-j,l,m**, H(4) shifts were found to be 0.2–0.3 ppm upfield than H(7) shifts (Table S2). This difference is caused by shielding effect of aromatic substituent at C(3) position of indene due to “ring current” of aryl which is arranged orthogonally to the plane of the indene system.

According to the literature data,[S11-S17] the same pattern of chemical shifts of the identical protons is observed for the related 3-aryl-5,6-dialkoxyindenes (Table S3).

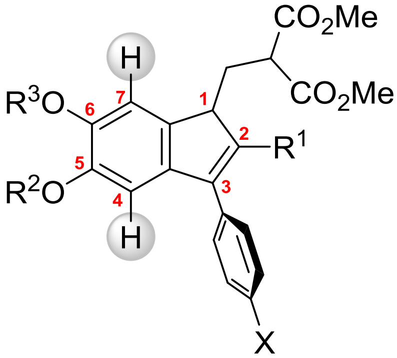
Table S1. Representative responses in 2D spectra of indenes **3**

Indene	HMBC	NOESY
3k		-
3l		
3m		
3o		
3p		-

3q		-
3r[Sa]		
3s		
3u		-

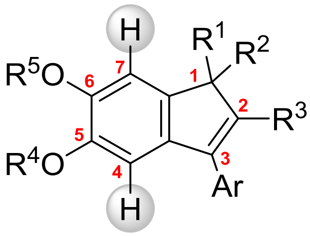
[Sa] Different solvents were used to record 2D spectra for **3r**: $CDCl_3$ (HMBC), DMSO-d_6 (NOESY).

Table S2. Chemical shifts of H(4) and H(7) for 3-aryl-5,6-dialkoxyindenes **3a-j,l,m**



Indene **3**	R^1	X	R^2	R^3	δ_H (ppm)	
					H(4)	H(7)
a	Me	H	$-CH_2CH_2-$		6.71	6.94
b	Ph	H	$-CH_2CH_2-$		6.74	7.05
c	$4-MeOC_6H_4$	MeO	$-CH_2CH_2-$		6.72	7.02
d	Me	H	$-CH_2-$		6.69	6.93
e	Et	H	$-CH_2-$		6.65	6.95
f	Ph	H	$-CH_2-$		6.71	7.05
g	$4-MeOC_6H_4$	MeO	$-CH_2-$		6.69	7.01
h	Me	H	Me	Me	6.74	7.01
i	Et	H	Me	Me	6.70	7.03
j	Ph	H	Me	Me	6.74	7.12
l	Me	H	Et	Me	6.75	7.01
m	Me	H	Me	Et	6.75	7.02

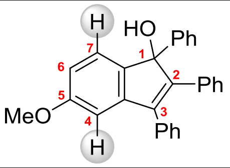
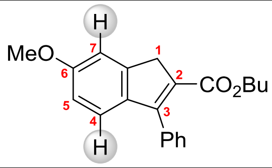
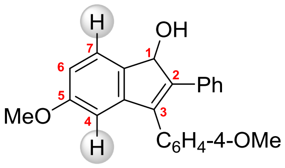
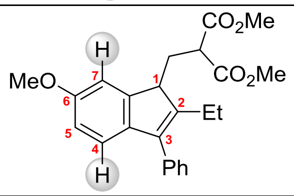
Table S3. Chemical shifts of H(4) and H(7) for related 3-aryl-5,6-dialkoxyindenes



R^1	R^2	R^3	Ar	R^4	R^5	δ_H (ppm)		[Ref]
						H(4)	H(7)	
H	Ph	H	Ph	Me	H	6.89	7.04	[S11]
H	Ph	Ph	Ph	H	Me	6.51	6.77	[S12]
H	H	Me	Ph	$-CH_2-$		6.60	6.78	[S13]
H	H	Me	Ph	Me	Me	6.78	7.02	[S13]
H	Cl	Me	Ph	$-CH_2-$		6.62	7.02	[S13]
H	Cl	Me	Ph	Me	Me	6.70	7.14	[S13]
H	OH	Ph	Ph	$-CH_2-$		6.64	>7.19	[S14]
Me	OH	Ph	Ph	Me	Me	6.75	7.12	[S15]
H	OH	CO_2Me	$4-MeOC_6H_4$	$-CH_2-$		6.70	7.14	[S16]
H	2-oxooxazolidin-1-yl	OMe	Ph	Me	Me	6.76	6.95	[S17]

The above spectral data allow for clear-cut differentiation between regioisomeric indenes with other sets of substituents in benzene moiety of the indene system. Thus, according to HMBC data, indene **3k** was assigned to 6-methoxy- rather than 5-methoxy-isomer. Additional evidence is provided by comparison of chemical shifts of H(4) and H(7) in 3-aryl-5-methoxy- and 3-aryl-6-methoxy-indenes (Table S4). In 5-methoxyisomers, both 3-aryl and 5-methoxy groups have shielding effect on H(4), whereas H(7) is not induced by these substituents. As a result, shifts of these two protons are quite different.[S8,S12] Oppositely, in 3-aryl-6-methoxyindenes, H(4) is shielded by aryl group while H(7) is shielded by methoxy group that provides similar values of chemical shifts for these protons.[S8]

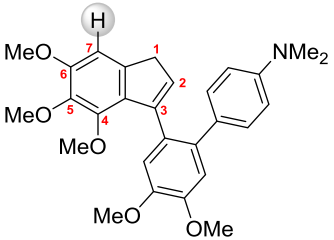
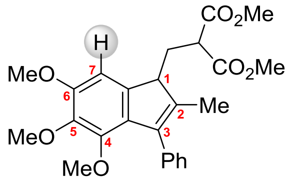
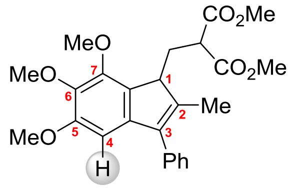
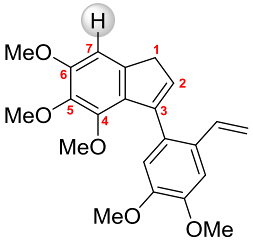
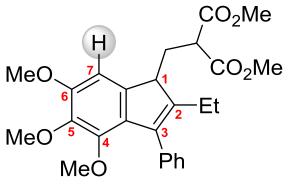
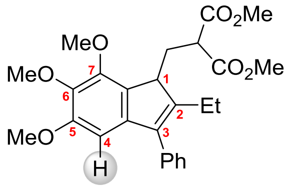
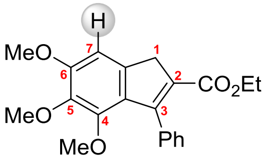
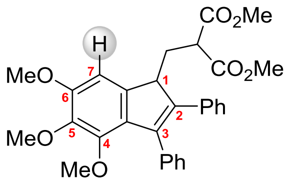
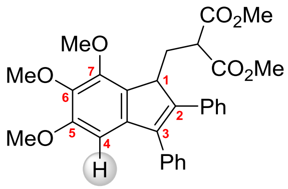
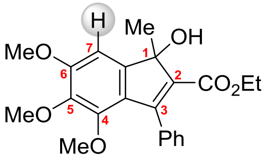
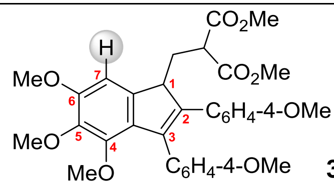
Table S4. Chemical shifts of H(4) and H(7) for 3-aryl-5-methoxy- and 3-aryl-6-methoxyindenes

5-MeO-Indenes	δ_H (ppm)		[Ref]	6-MeO-Indenes	δ_H (ppm)		[Ref]/ label
	H(4)	H(7)			H(4)	H(7)	
	6.76	> 7	[S14]		7.14	7.10	[S14]
	6.74	8.4	[S18]		7.05	7.04	**3k**

Similar analysis can be applied to make structural assignments for trimethoxy-substituted indenes. In 3-aryl-4,5,6-trimethoxyindenes, H(7) is shielded by two methoxy groups at C(4) and C(6) positions of indene core. This shielding effect provides H(7) chemical shifts at *ca.* 6.9 ppm, according to the literature, and *ca.* 6.8-6.9 ppm for synthesized indenes **3p,r,t,v** (Table S5).

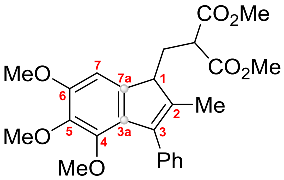
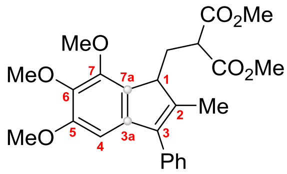
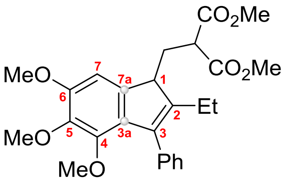
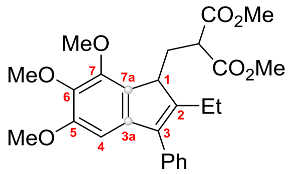
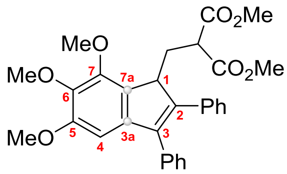
In 5,6,7-trimethoxy-substituted isomers, H(4) atom is shielded not only two methoxy groups at C(5) and C(7) but also aryl substituent at C(3). This additional shielding effect leads to upfield shift of H(4) resonance which are observed at *ca.* 6.5 ppm for indenes **3q,s,u** (Table S5).

Table S5. Chemical shifts of H(4) and H(7) for 3-aryl-4,5,6- and 3-aryl-5,6,7-trimethoxyindenes

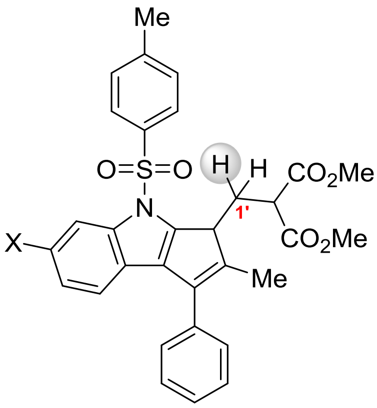
3-Aryl-4,5,6-trimethoxyindenes [Ref]	$\delta_{H(7)}$ (ppm)	3-Aryl-4,5,6-trimethoxyindenes **3**	$\delta_{H(7)}$ (ppm)	3-Aryl-5,6,7-trimethoxyindenes **3**	$\delta_{H(4)}$ (ppm)
 [S19]	6.88	 **3p**	6.85	 **3q**	6.51
 [S19]	6.91	 **3r**	6.83	 **3s**	6.46
 [S20]	6.89	 **3t**	6.92	 **3u**	6.50
 [S20]	6.94	 **3v**	6.89	-	-

Analogous regularities are observed for chemical shifts of C(3a) and C(7a) in ^{13}C NMR spectra of 4,5,6- and 5,6,7-trimethoxyindenes (Table S6). In 4,5,6-trimethoxyindenes **3p,r,t,v**, C(3a) is induced by shielding effect of two methoxy groups at C(4) and C(6) that leads to upfield shift of C(3a) resonance in comparison with C(7a) resonance. Directly opposed regularity is observed for 3-aryl-5,6,7-trimethoxyindenes **3q,s,u** wherein C(7a) resonance is upfield shifted due to shielding effect of two methoxy groups at C(7) and C(5).

Table S6. Chemical shifts of C(3a) and C(7a) for 4,5,6- and 5,6,7-trimethoxyindenes

4,5,6-Trimethoxyindenes **3**	δ_C (ppm)		5,6,7-Trimethoxyindenes **3**	δ_C (ppm)	
	C(3a)	C(7a)		C(3a)	C(7a)
 **3p**	131.5	140.3	 **3q**	141.8	127.7
 **3r**	131.4	140.5	 **3s**	141.9	127.7
-	-	-	 **3u**	142.0	128.3

Strong downfield shift (*ca*. 0.5 ppm) of one of H(1′) resonances is observed in ^{1}H NMR spectra of cyclopentaindoles **3n,o**. This is apparently caused by deshielding effect of SO_2 moiety of the tosyl group that together with HMBC and NOESY data supports formation of isomers **3n,o** with unidirectional tosyl and methylmalonate fragments.

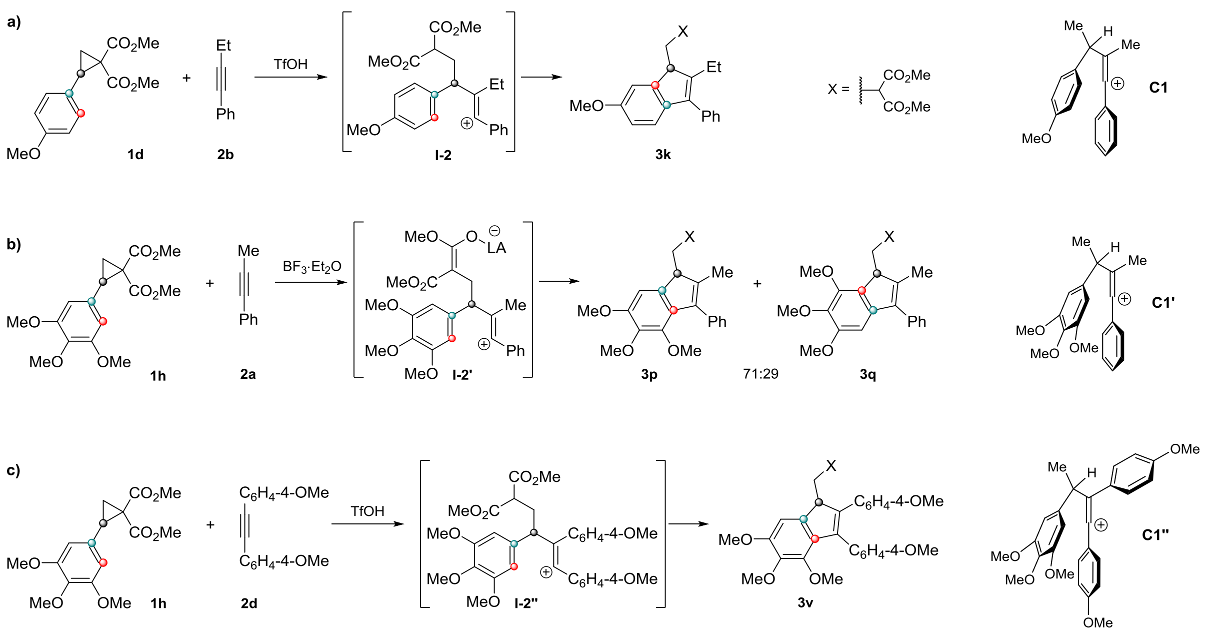


DFT calculations

In order to provide a better understanding of regioselectivity of D-A cyclopropane annulation to alkynes, we carried out DFT calculations of energy barriers for three model processes, the prototypes of which were: **a**) the reaction of dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (**1d**) with 1-phenylbutyne (**2b**) which affords the rearranged product **3k** exclusively; **b**) the reaction of dimethyl 2-(3,4,5-trimethoxyphenyl)cyclopropane-1,1-dicarboxylate (**1h**) with 1-phenylpropyne (**2a**), producing both "normal" and rearranged isomers **3p** and **3q**; **c**) the reaction of **1h** with 4,4′-dimethoxytolan (**2d**) which leads to the "normal" product **3v** exclusively (Table S7). Vinyl cations **C1**, **C1′** and **C1″,** which were chosen as starting points of the calculations, are simplified models of intermediates **I-2**, **I-2′** and **I-2″** due to the absence of the malonyl fragment in their structure (the fragment does not participate in this annulation).

Table S7

Experiment | **Calculations: Starting points**



a) C1 as a starting point

We started our calculations with the geometry optimization of **C1** in a conformation appropriate for the intramolecular electrophilic attack of the vinyl cation moiety on the *ortho*- and *ipso*-atoms of the proximal aryl group (Figure S1). σ-Complex **P1** formed *via* an *ortho*-attack was found to be 1.2 kcal/mol more stable than the isomeric σ-complex **P2** which is formed *via* an *ipso*-attack. This minor difference in stability between **P1** and **P2** can be ascribed to the stabilization of **P2** by a *para*-methoxy group despite the obvious concurrent destabilization due to the presence of a highly strained *spiro*-cyclobutene fragment. However, the energy barrier of **P2** formation *via* **TS2** was found to be 7.5 kcal/mol lower than that for **P1** formation *via* **TS1**. The reversed transformation of **P2** to vinyl cation **C1** *via* **TS2** has a calculated activation barrier of 4.9 kcal/mol while the formation of allyl cation **P3** *via* **TS3** has an analogous barrier of 4.1 kcal/mol. Moreover, the latter route is thermodynamically preferable as well: allyl cation **P3** was found to be the most stable intermediate (-30.6 kcal/mol) within both calculated pathways. The intramolecular *ortho*-attack of the allyl cation in **P3** produces a new *ortho*-*σ*-complex **P4** which is 17.7 kcal/mol more stable than *ipso*-*σ*-complex **P2** and 16.5 kcal/mol more stable than *ortho*-*σ*-complex **P1**.

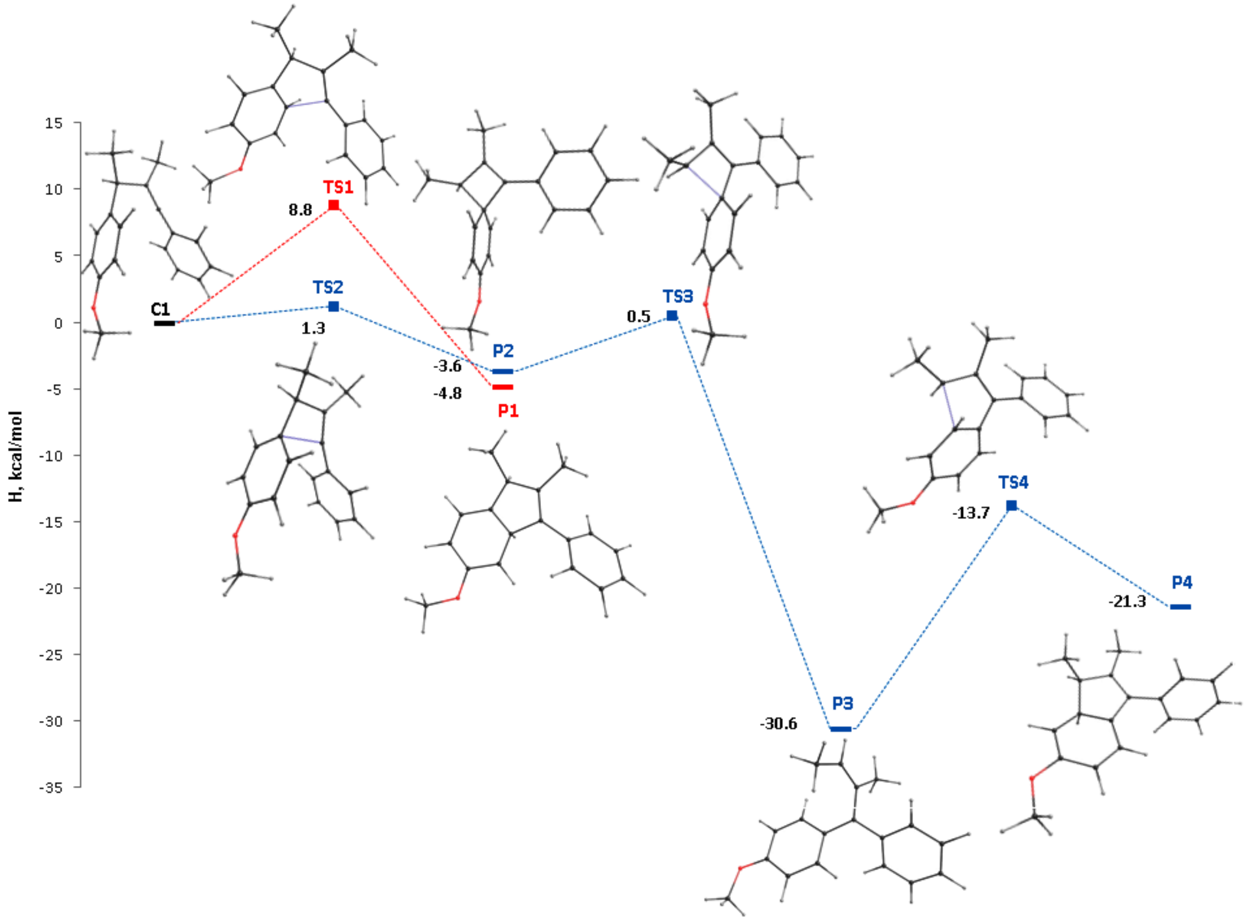


Figure S1. DFT-computed pathways for *ortho* (red) and *ipso* (blue) attacks within vinyl cation **C1**

b) C1′ as a starting point

In contrast to **C1**, vinyl cation **C1′** contains two additional MeO groups at the C(3) and C(5) positions of an aromatic substituent acting as a nucleophile. These groups influence the energy barriers and reaction thermodynamics for *ortho*-attacks significantly due to their activation and stabilization of intermediates **P1′** and **P4′** produced in the reaction (Figure S2). For instance, *σ*-complex **P1′**, the formation of which was found to be a virtually barrier-less process, is 27.2 kcal/mol more stable than the initial vinyl cation **C1′**. Oppositely, these two MeO groups have no significant effect on the *ipso*-attack. The calculated energy barrier for the *ipso*-attack (**TS2′**) is 0.4 kcal/mol. This suggests that both *ortho*- and *ipso*-attacks are possible though the *ortho*-path is thermodynamically more preferable. If formed, *ipso*-σ-complex **P2′** can undergo a reverse transformation *via* **TS2′** to **C1′** or be further transformed *via* **TS3′** to allyl cation **P3′** which is 30.7 kcal/mol more stable than the initial vinyl cation **C1′**. The activation energy of the subsequent *ortho*-attack *via* **TS4′** is 5.9 kcal/mol lower than the analogous barrier for **TS4** that is also provided by the activating effect of MeO groups. An *ortho*-attack in **P3′** leads to a new *σ*-complex **P4′** which is 15.7 kcal/mol more stable than the *ortho*-*σ*-complex **P1′**.

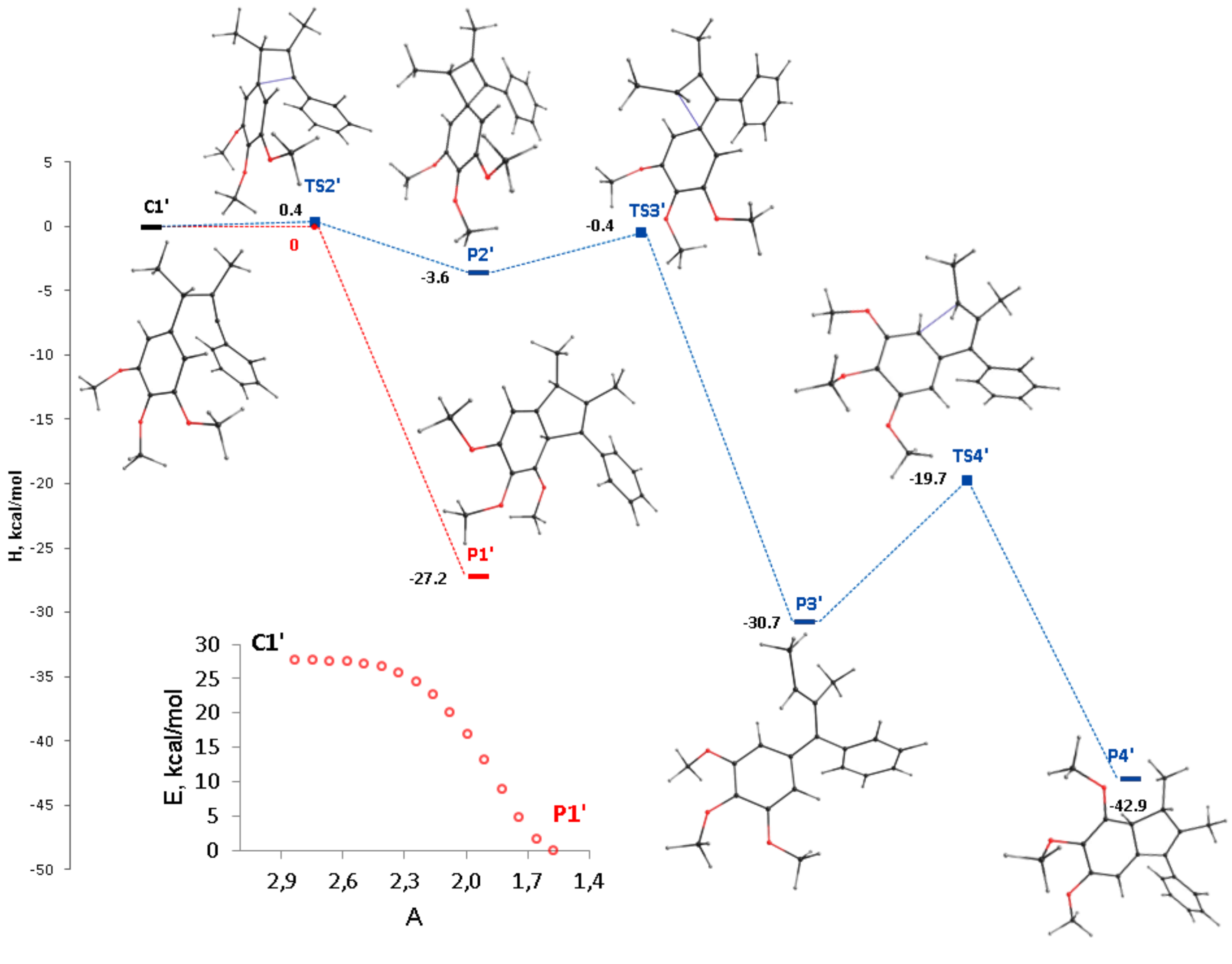


Figure S2. DFT-computed pathways for *ortho* (red) and *ipso* (blue) attacks within vinyl cation **C1′**. Relaxed surface scan along C-C bond forming *via ortho* path

c) C1″ as a starting point

In contrast to **C1′**, vinyl cation **C1″** contains two additional MeO groups at the *para*-positions of two aromatic substituents at the double bond. One of these groups provides additional stabilization of the vinyl cationic center in **C1″** that ensures a more positive value of ΔH_r. For example, *ortho*-σ-complex **P1″** is 16.5 kcal/mol more stable than **C1″**, while for **P1′** formation, this gain in energy is 27.2 kcal/mol. Meanwhile, for the *ipso*-attack, this effect becomes more significant. Namely, while the transformation of **C1′** to *ipso*-σ-complex **P2′** is exothermic (ΔH_r = -3.6 kcal/mol), the analogous cyclization of **C1″** to **P2″** is an endothermic process (ΔH_r = +3.0 kcal/mol). Moreover, the stabilization of the cationic center in **C1″** results in the activation barriers of **P1″** and **P2″** formation becoming 0.7 and 4.1 kcal/mol higher than those for **P1′** and **P2′**, respectively. In contrast to **C1′**, the energy barrier of *ipso*-attack for **C1″** becomes tangibly higher (by 3.8 kcal/mol) than that of *ortho*-attack. Analogously to **P2** and **P2′**, *ipso*-σ-complex **P2″**, if formed, can undergo reverse transformation *via* **TS2″** to initial cation **C1″** or be transformed *via* **TS3″** to thermodynamically more preferable allyl cation **P3″**. However, in contrast to the previous two cases, the activation barrier of **P2″**-*via*-**TS3″**-to-**P3″** transformation is higher than the barrier of **P2″**-*via*-**TS2″**-to-**C1″** transformation. Therefore, the increase in activation barrier of the *ipso*-attack while the decrease in the barrier of the reverse transformation reduces possibility of reaction *via ipso*-path**.**

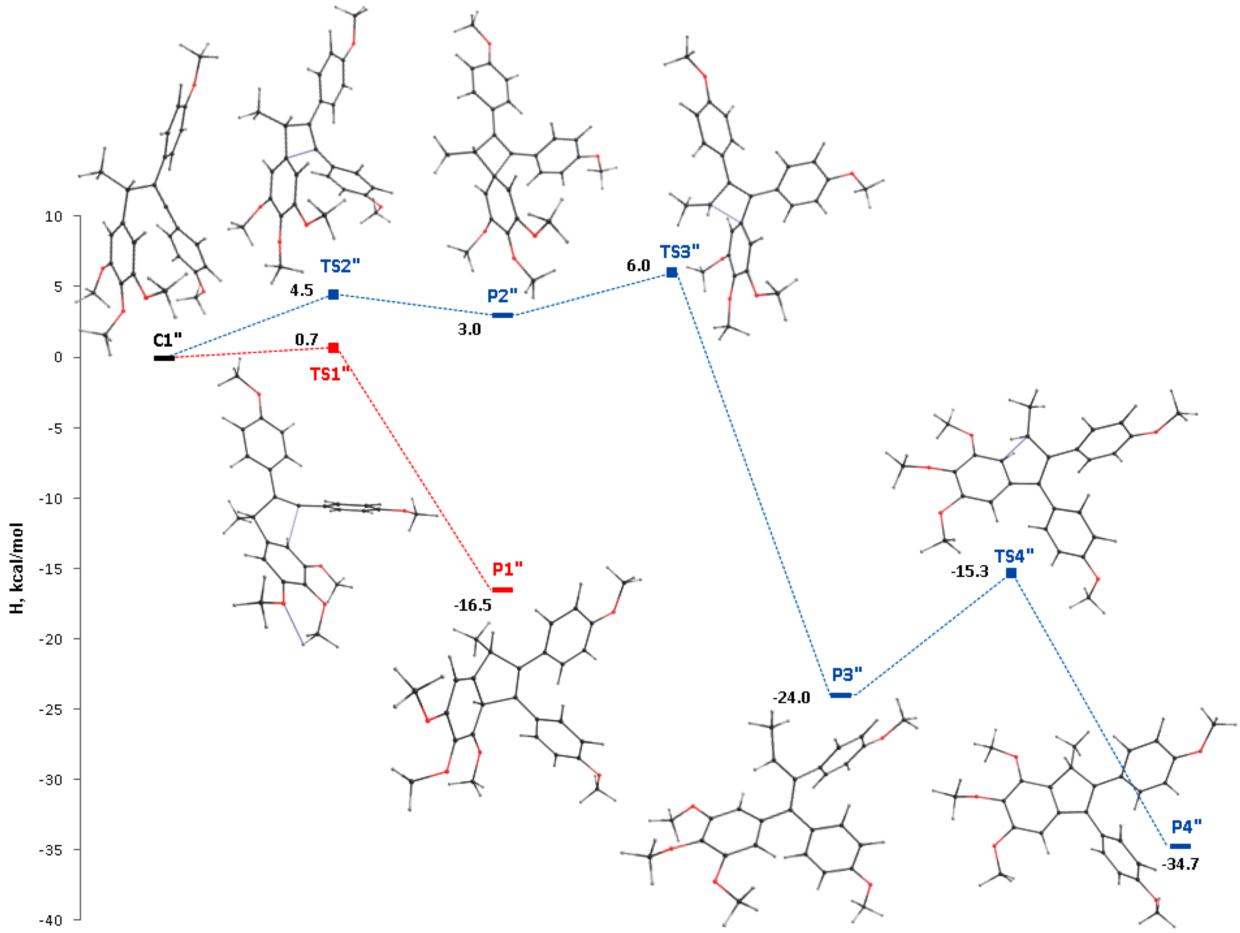


Figure S3. DFT-computed pathways for *ortho* (red) and *ipso* (blue) attacks within vinyl cation **C1″**

Therefore, the obtained results were found to strongly correlate with the experimental data. Regiochemistry of the annulation is determined by the relative activating energies of *ortho*- and *ipso*-attacks (kinetically controlled process). Thus, the model reaction **a**), wherein the activating barrier of *ipso*-attack is 7.5 kcal/mol lower than that of *ortho*-attack, leads to rearranged product **3k** exclusively. The model reaction **b**), wherein analogous barriers have close values, yields the mixture of "normal" and rearranged products **3p** and **3q**. Finally, the reaction **c**), wherein the barrier of the *ortho*-attack is 3.8 kcal/mol lower than that for the *ipso*-attack, affords "normal" product **3v** only.

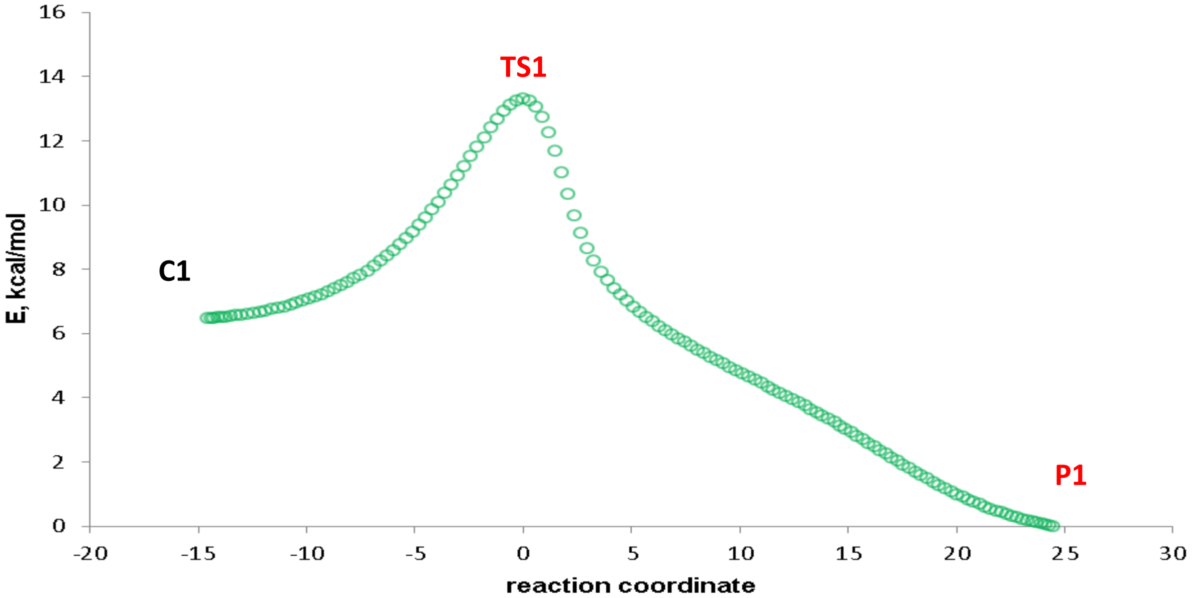


Figure S4. IRC scan for **C1**-to-**P1** transformation

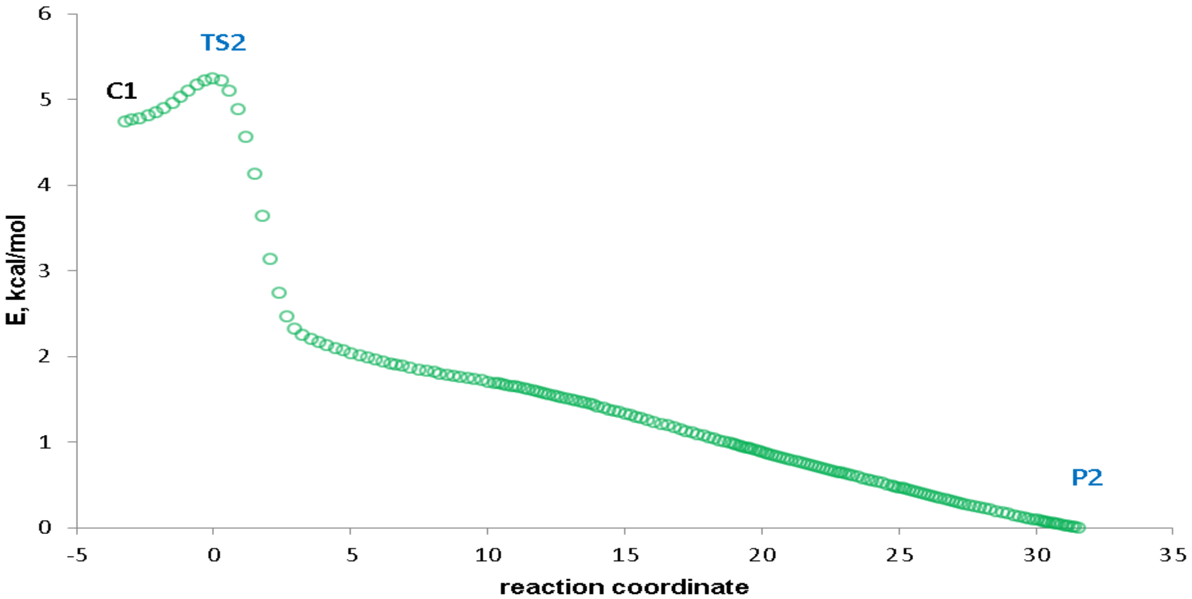
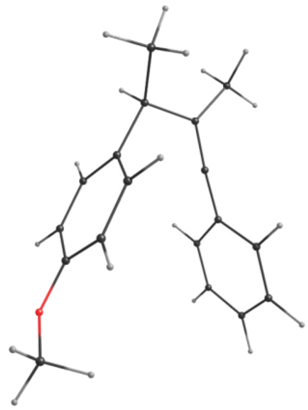


Figure S5. IRC scan for for **C1**-to-**P2** transformation

Cartesian coordinates and energies (in hartrees) of all stationary points

a) C1 as a starting point

C1



E = -771.2293 E_h

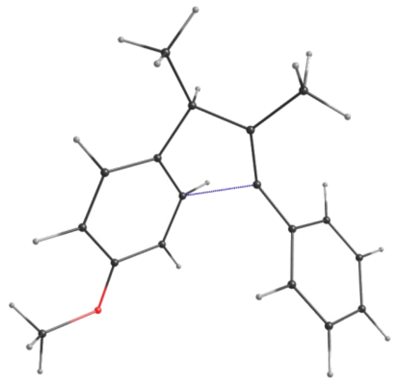
E_{ZPE} = 0.3184 E_h

H^{298} = -770.8933 E_h

C	2.244164000	-0.617121000	-1.036401000
C	0.877567000	-0.741494000	-0.725358000
C	0.104292000	0.438309000	-0.671891000
C	0.674185000	1.684584000	-0.886525000
C	2.048779000	1.795063000	-1.194021000
C	2.832245000	0.626656000	-1.263360000
C	0.237571000	-2.108062000	-0.456945000
C	0.507510000	-2.450709000	1.006050000
H	2.869093000	-1.509535000	-1.121995000
H	0.077986000	2.598582000	-0.852803000
H	3.889062000	0.677629000	-1.523746000
C	1.109968000	-1.515006000	1.691999000
O	2.509843000	3.034105000	-1.415489000
C	3.858024000	3.225555000	-1.821933000
H	4.563557000	2.916783000	-1.031758000
H	4.081087000	2.670850000	-2.748964000
H	3.973697000	4.300015000	-2.010072000
C	0.638370000	-3.216367000	-1.437104000
H	1.709751000	-3.462945000	-1.377104000

H	0.067831000	-4.138985000	-1.254988000
H	0.420718000	-2.885697000	-2.464837000
H	-0.967354000	0.371220000	-0.460137000
H	-0.859382000	-1.985136000	-0.523408000
C	0.083539000	-3.768364000	1.616273000
H	-0.989458000	-3.939137000	1.431261000
H	0.642943000	-4.581358000	1.127517000
H	0.276927000	-3.815106000	2.696706000
C	1.709641000	-0.619912000	2.555722000
C	0.948533000	0.442316000	3.144253000
C	3.094430000	-0.760234000	2.893893000
C	1.550741000	1.313434000	4.037719000
C	3.669354000	0.101214000	3.813818000
C	2.903345000	1.136893000	4.378514000
H	-0.101762000	0.557982000	2.869584000
H	3.675173000	-1.562888000	2.435242000
H	0.975435000	2.127371000	4.483705000
H	4.715229000	-0.022381000	4.103003000
H	3.369620000	1.819334000	5.094603000

TS1



Imaginary frequency 210*i* cm^{-1}

E = -771.2158 E_h

E_{ZPE} = 0.3182 E_h

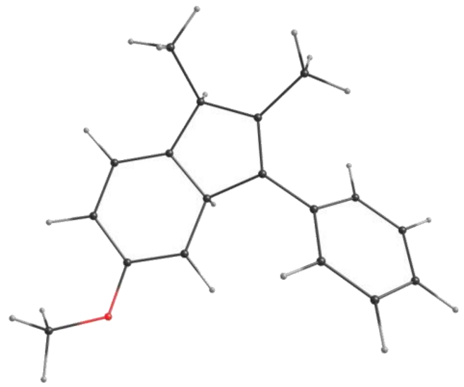
H^{298} = -770.8802 E_h

C	-0.588245000	-0.150329000	-2.956476000
C	-1.078457000	-0.674195000	-1.763800000

C	-1.255187000	0.208463000	-0.657384000
C	-0.900181000	1.571344000	-0.759339000
C	-0.377479000	2.079109000	-1.955095000
C	-0.254946000	1.205506000	-3.062187000
C	-1.198047000	-2.159758000	-1.446487000
C	-0.280722000	-2.308448000	-0.240870000
H	-0.424892000	-0.795115000	-3.821444000
H	-1.069925000	2.261906000	0.069702000
H	0.138624000	1.576060000	-4.009502000
C	0.057018000	-1.195140000	0.396263000
O	-0.047476000	3.378655000	-1.977586000
C	0.368100000	3.994519000	-3.190953000
H	1.296662000	3.542264000	-3.578749000
H	-0.420755000	3.935787000	-3.960213000
H	0.558883000	5.046818000	-2.947363000
C	-0.895210000	-3.116213000	-2.598289000
H	0.143839000	-3.026799000	-2.952784000
H	-1.065956000	-4.158944000	-2.292495000
H	-1.565867000	-2.913390000	-3.446383000
H	-1.930453000	-0.078515000	0.154668000
H	-2.231950000	-2.367353000	-1.102588000
C	0.246146000	-3.650938000	0.208622000
H	-0.597111000	-4.334906000	0.400280000
H	0.862826000	-4.100769000	-0.585633000
H	0.853106000	-3.578358000	1.120530000
C	0.625640000	-0.570699000	1.533082000
C	0.041321000	-0.807515000	2.808460000
C	1.771050000	0.262519000	1.435666000
C	0.618974000	-0.263534000	3.949940000
C	2.319180000	0.826023000	2.580637000
C	1.749261000	0.558916000	3.836344000
H	-0.849500000	-1.435296000	2.882813000
H	2.207670000	0.463833000	0.455384000
H	0.184550000	-0.472886000	4.930176000
H	3.198564000	1.469324000	2.505753000

H	2.191003000	1.000734000	4.733059000

P1



E = -771.2385 E_h

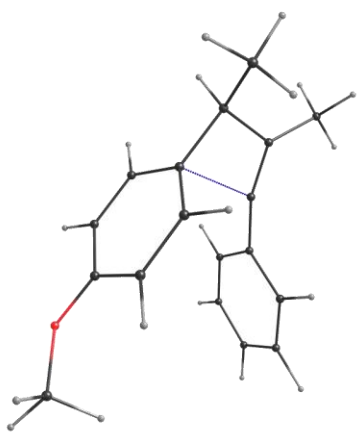
E_{ZPE} = 0.3182 E_h

H^{298} = -770.9020 E_h

C	-1.062573000	-0.053568000	-3.097790000
C	-0.902700000	-0.683632000	-1.878830000
C	-0.443020000	0.083910000	-0.717202000
C	0.017797000	1.456390000	-0.925961000
C	-0.152061000	2.064040000	-2.168450000
C	-0.695856000	1.297132000	-3.236611000
C	-1.008271000	-2.129752000	-1.492087000
C	-0.270640000	-2.186275000	-0.154442000
H	-1.425245000	-0.595728000	-3.973228000
H	0.394657000	2.047897000	-0.089207000
H	-0.825684000	1.764302000	-4.215002000
C	0.054443000	-0.945761000	0.298063000
O	0.230841000	3.340413000	-2.271063000
C	0.116229000	4.047251000	-3.503649000
H	0.727442000	3.578400000	-4.292212000
H	-0.934559000	4.111899000	-3.832589000
H	0.495374000	5.056775000	-3.305883000
C	-0.556518000	-3.113385000	-2.586410000
H	0.502279000	-2.965458000	-2.849179000
H	-0.690131000	-4.148852000	-2.241435000
H	-1.163057000	-2.991690000	-3.495844000
H	-1.457921000	0.386471000	-0.293357000

H	-2.081670000	-2.347618000	-1.291970000
C	0.012362000	-3.494267000	0.518294000
H	-0.920767000	-4.006160000	0.813262000
H	0.545609000	-4.177730000	-0.163229000
H	0.625818000	-3.363850000	1.418917000
C	0.617591000	-0.545366000	1.604246000
C	0.047848000	-1.028198000	2.799391000
C	1.703221000	0.350034000	1.690445000
C	0.548671000	-0.628124000	4.039847000
C	2.201722000	0.750099000	2.931665000
C	1.622858000	0.265009000	4.109193000
H	-0.806118000	-1.708555000	2.752815000
H	2.181858000	0.722234000	0.780799000
H	0.090260000	-1.012142000	4.954310000
H	3.048884000	1.438529000	2.981906000
H	2.011084000	0.588007000	5.078243000

TS2



Imaginary frequency 176*i* cm^{-1}

E = -771.2281 E_h

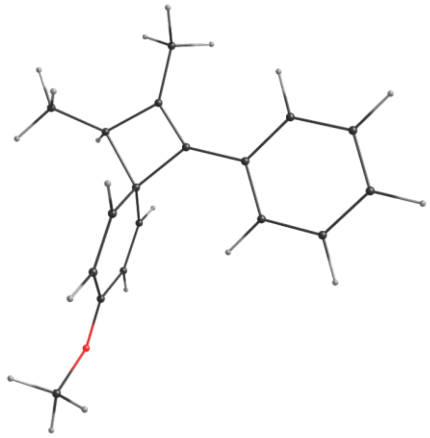
E_{ZPE} = 0.3181 E_h

H^{298} = -770.8923 E_h

C	0.182960000	-1.151689000	-1.315371000
C	-0.805797000	-1.849442000	-0.566355000
C	-1.654516000	-1.073379000	0.282029000
C	-1.431567000	0.269487000	0.479177000

C	-0.372235000	0.926445000	-0.204826000
C	0.424922000	0.199754000	-1.122060000
C	-1.063535000	-3.359980000	-0.754304000
C	-0.088003000	-3.870927000	0.288466000
H	0.796365000	-1.698087000	-2.034844000
H	-2.058832000	0.866215000	1.144063000
H	1.214941000	0.691971000	-1.689144000
C	0.480226000	-2.795065000	0.807136000
O	-0.221976000	2.214029000	0.074455000
C	0.806567000	2.989543000	-0.537910000
H	1.801175000	2.575890000	-0.302692000
H	0.666592000	3.041415000	-1.629782000
H	0.719295000	3.994964000	-0.110304000
C	-0.880106000	-3.905782000	-2.171345000
H	0.164036000	-3.835769000	-2.513266000
H	-1.180030000	-4.963359000	-2.223893000
H	-1.510369000	-3.343801000	-2.877148000
H	-2.475458000	-1.567850000	0.808336000
H	-2.090792000	-3.585228000	-0.415592000
C	0.149943000	-5.303385000	0.667591000
H	-0.793911000	-5.765043000	1.003461000
H	0.500971000	-5.874449000	-0.207906000
H	0.893446000	-5.403065000	1.470097000
C	1.305096000	-2.006196000	1.636808000
C	0.801277000	-1.487485000	2.860575000
C	2.630478000	-1.680167000	1.237229000
C	1.604496000	-0.680639000	3.659126000
C	3.424880000	-0.878063000	2.047563000
C	2.910738000	-0.374017000	3.252123000
H	-0.214707000	-1.741493000	3.169288000
H	3.017665000	-2.076171000	0.296170000
H	1.216992000	-0.284463000	4.600097000
H	4.444530000	-0.632491000	1.742071000
H	3.537670000	0.261836000	3.882808000

P2



E = -771.2365 E_h

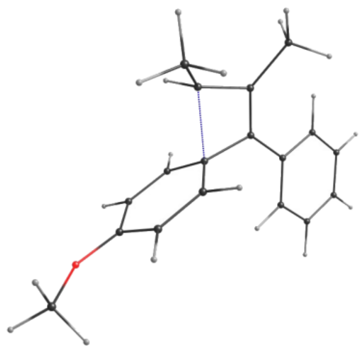
E_{ZPE} = 0.3192 E_h

H^{298} = -770.9001 E_h

C	0.482924000	-0.743049000	-0.982154000
C	-0.250533000	-1.612736000	-0.051061000
C	-1.344047000	-0.938426000	0.671387000
C	-1.689850000	0.359235000	0.451740000
C	-0.947145000	1.139373000	-0.492492000
C	0.152581000	0.562914000	-1.208672000
C	-0.783292000	-3.033257000	-0.726644000
C	0.143452000	-3.728811000	0.237882000
H	1.332408000	-1.177569000	-1.515534000
H	-2.512545000	0.846284000	0.978398000
H	0.728297000	1.163096000	-1.913826000
C	0.616838000	-2.592136000	0.801376000
O	-1.341262000	2.373642000	-0.627204000
C	-0.724427000	3.307455000	-1.531950000
H	0.335341000	3.448400000	-1.272106000
H	-0.832243000	2.957305000	-2.569645000
H	-1.269813000	4.247272000	-1.394939000
C	-0.591129000	-3.235990000	-2.222603000
H	0.465665000	-3.180849000	-2.522972000
H	-0.957470000	-4.240726000	-2.489972000
H	-1.171511000	-2.512504000	-2.814260000
H	-1.902959000	-1.535115000	1.398645000

H	-1.850811000	-3.152567000	-0.469255000
C	0.359878000	-5.192431000	0.409057000
H	-0.539403000	-5.758529000	0.117779000
H	1.184991000	-5.552973000	-0.230368000
H	0.609671000	-5.456306000	1.446995000
C	1.574174000	-2.223067000	1.844194000
C	1.724037000	-0.882176000	2.250643000
C	2.375837000	-3.203715000	2.467249000
C	2.633833000	-0.532572000	3.251262000
C	3.277485000	-2.852601000	3.471445000
C	3.410127000	-1.516828000	3.869397000
H	1.118204000	-0.100708000	1.785573000
H	2.300857000	-4.245945000	2.153244000
H	2.734971000	0.511538000	3.558001000
H	3.884194000	-3.627091000	3.945826000
H	4.116107000	-1.243770000	4.657489000

TS3



Imaginary frequency 259*i* cm^{-1}

E = -771.2302 E_h

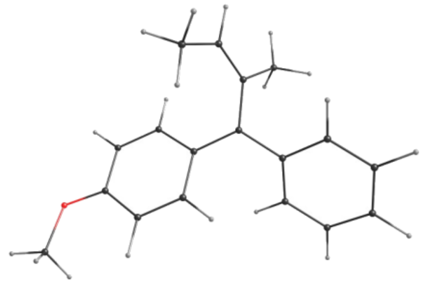
E_{ZPE} = 0.3183 E_h

H^{298} = -770.8935 E_h

C	0.535134000	-0.594072000	-0.832580000
C	-0.029193000	-1.283777000	0.293544000
C	-1.089403000	-0.599742000	1.003803000
C	-1.609815000	0.579709000	0.545902000
C	-1.062072000	1.205322000	-0.618975000

C	0.023546000	0.601843000	-1.301431000
C	-0.685628000	-2.885319000	-0.734196000
C	0.334549000	-3.496212000	0.148284000
H	1.389036000	-1.049712000	-1.340441000
H	-2.432323000	1.086140000	1.054532000
H	0.469467000	1.076156000	-2.174985000
C	0.704895000	-2.444120000	0.925530000
O	-1.632015000	2.337825000	-0.974074000
C	-1.242301000	3.032306000	-2.165371000
H	-0.193376000	3.360036000	-2.102322000
H	-1.390512000	2.390175000	-3.047737000
H	-1.897511000	3.907515000	-2.229874000
C	-0.665828000	-3.019742000	-2.223262000
H	0.347546000	-3.082524000	-2.643874000
H	-1.199088000	-3.957398000	-2.473697000
H	-1.226980000	-2.212510000	-2.715911000
H	-1.496965000	-1.066551000	1.904456000
H	-1.695896000	-2.781092000	-0.319761000
C	0.797633000	-4.914576000	0.031205000
H	0.216036000	-5.581927000	0.690026000
H	0.660271000	-5.288489000	-0.995533000
H	1.858979000	-5.019985000	0.301056000
C	1.621566000	-2.304190000	2.057857000
C	2.094480000	-1.030480000	2.439977000
C	2.040628000	-3.429151000	2.803316000
C	2.958780000	-0.885313000	3.526110000
C	2.914337000	-3.280896000	3.879464000
C	3.376709000	-2.010537000	4.243896000
H	1.796613000	-0.146635000	1.870135000
H	1.655970000	-4.419667000	2.555811000
H	3.317629000	0.106263000	3.812597000
H	3.230696000	-4.158696000	4.447689000
H	4.057839000	-1.895905000	5.090760000

P3



E = -771.2818 E_h

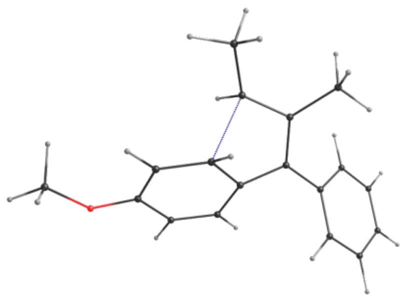
E_{ZPE} = 0.3198 E_h

H^{298} = -770.9430 E_h

C	0.911525000	-0.492658000	-1.341004000
C	0.662528000	-0.727802000	0.045571000
C	0.285718000	0.402538000	0.841684000
C	0.147028000	1.653851000	0.288410000
C	0.402498000	1.861657000	-1.093793000
C	0.798337000	0.767139000	-1.900861000
C	-0.455046000	-3.236385000	-1.086599000
C	0.581377000	-3.232509000	-0.191966000
H	1.264290000	-1.314888000	-1.964660000
H	-0.177534000	2.509152000	0.883844000
H	1.044382000	0.912323000	-2.952570000
C	0.790349000	-2.035533000	0.618798000
O	0.249193000	3.100992000	-1.531624000
C	0.444645000	3.432368000	-2.908509000
H	1.493272000	3.271292000	-3.206354000
H	-0.224629000	2.842655000	-3.553584000
H	0.196168000	4.496155000	-3.000016000
C	-0.911928000	-4.399149000	-1.894788000
H	-0.159671000	-5.191826000	-2.000502000
H	-1.807647000	-4.843891000	-1.419659000
H	-1.240973000	-4.070128000	-2.894016000
H	0.043722000	0.255562000	1.895045000
H	-1.074536000	-2.336804000	-1.157529000
C	1.437777000	-4.465739000	0.032164000
H	0.872696000	-5.291019000	0.493651000

H	1.821509000	-4.838877000	-0.930789000
H	2.301819000	-4.250933000	0.673002000
C	1.140494000	-2.196241000	2.031456000
C	2.070715000	-1.333172000	2.664101000
C	0.567094000	-3.246808000	2.790794000
C	2.427943000	-1.531670000	3.996437000
C	0.905937000	-3.421987000	4.127794000
C	1.847732000	-2.574140000	4.728826000
H	2.552948000	-0.541714000	2.087843000
H	-0.172350000	-3.903959000	2.328683000
H	3.167748000	-0.878050000	4.464427000
H	0.439420000	-4.220637000	4.708676000
H	2.136904000	-2.734967000	5.770527000

TS4



Imaginary frequency 330*i* cm^{-1}

E = -771.2530 E_h

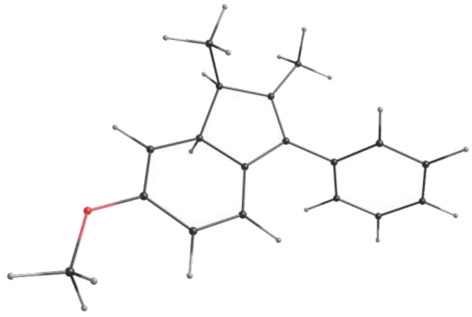
E_{ZPE} = 0.3188 E_h

H^{298} = -770.9162 E_h

C	0.269095000	-0.662414000	-0.965758000
C	0.456426000	-0.773427000	0.470916000
C	-0.065050000	0.246991000	1.306002000
C	-0.847722000	1.240720000	0.760395000
C	-1.112393000	1.315265000	-0.650226000
C	-0.533326000	0.387967000	-1.507654000
C	-0.318390000	-2.582129000	-1.041987000
C	0.649798000	-3.027467000	-0.058383000
H	1.107371000	-0.967284000	-1.599303000

H	-1.324004000	1.993713000	1.393208000
H	-0.608523000	0.495168000	-2.589993000
C	0.936521000	-2.055007000	0.911428000
O	-1.876675000	2.341885000	-1.016081000
C	-2.229779000	2.525140000	-2.384278000
H	-1.337448000	2.733815000	-2.997068000
H	-2.755148000	1.638845000	-2.778491000
H	-2.900167000	3.392188000	-2.414572000
C	-0.419345000	-3.192617000	-2.408044000
H	0.559735000	-3.368062000	-2.877346000
H	-0.932043000	-4.168682000	-2.331829000
H	-1.032805000	-2.569658000	-3.074540000
H	0.069541000	0.187167000	2.387990000
H	-1.281186000	-2.273444000	-0.623931000
C	1.337231000	-4.351987000	-0.202657000
H	0.616366000	-5.185976000	-0.232994000
H	1.889941000	-4.383626000	-1.158334000
H	2.056187000	-4.532329000	0.605594000
C	1.631131000	-2.271503000	2.191170000
C	2.592045000	-1.343462000	2.647804000
C	1.346387000	-3.401870000	2.986710000
C	3.257385000	-1.548872000	3.857658000
C	2.005182000	-3.597408000	4.200253000
C	2.965076000	-2.675268000	4.634808000
H	2.840155000	-0.472998000	2.034542000
H	0.584395000	-4.116093000	2.664889000
H	4.008165000	-0.829876000	4.194363000
H	1.765223000	-4.468168000	4.814884000
H	3.484075000	-2.835170000	5.582784000

P4



E = -771.2666 E_h

E_{ZPE} = 0.3201 E_h

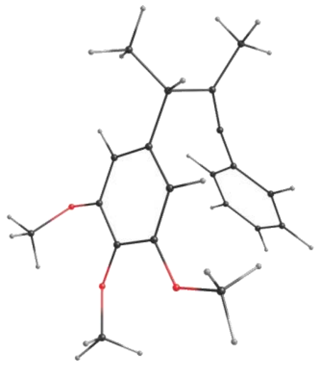
H^{298} = -770.9283 E_h

C	0.050385000	-0.853526000	-0.933793000
C	0.434419000	-0.784056000	0.497412000
C	0.171446000	0.385306000	1.239010000
C	-0.622764000	1.362522000	0.671847000
C	-1.175510000	1.269969000	-0.662325000
C	-0.884406000	0.178854000	-1.440700000
C	-0.172606000	-2.388318000	-1.167056000
C	0.633916000	-2.994560000	-0.040952000
H	1.001316000	-0.642251000	-1.481023000
H	-0.896442000	2.253320000	1.245448000
H	-1.235976000	0.098777000	-2.470055000
C	0.934540000	-2.052521000	0.937867000
O	-1.934547000	2.316514000	-1.006576000
C	-2.479648000	2.391325000	-2.318363000
H	-1.677555000	2.410322000	-3.076066000
H	-3.158890000	1.545159000	-2.518248000
H	-3.045745000	3.329400000	-2.363327000
C	0.105434000	-2.898258000	-2.580334000
H	1.168799000	-2.796555000	-2.849906000
H	-0.180233000	-3.954912000	-2.689610000
H	-0.485003000	-2.330470000	-3.314031000
H	0.510325000	0.478872000	2.272241000
H	-1.234782000	-2.576610000	-0.920356000
C	1.047333000	-4.420748000	-0.065309000
H	0.169319000	-5.082836000	-0.164798000

H	1.667611000	-4.611399000	-0.958889000
H	1.620053000	-4.711490000	0.822816000
C	1.624433000	-2.286872000	2.227831000
C	2.714270000	-1.477416000	2.603987000
C	1.214568000	-3.320657000	3.091499000
C	3.387508000	-1.709585000	3.806121000
C	1.888060000	-3.548277000	4.293326000
C	2.977825000	-2.747085000	4.649947000
H	3.057309000	-0.680407000	1.937713000
H	0.353082000	-3.940389000	2.830414000
H	4.240266000	-1.084278000	4.081359000
H	1.557453000	-4.350282000	4.957763000
H	3.507867000	-2.932516000	5.587043000

b) C1′ as a starting point

C1′



E = -999.9730 E_h

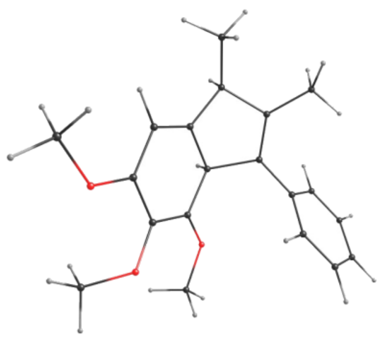
E_{ZPE} = 0.3822 E_h

H^{298} = -999.5692 E_h

C	-0.911334000	-1.425922000	-2.670027000
C	0.347146000	-0.928283000	-2.269526000
C	1.504273000	-1.581739000	-2.713649000
C	1.426650000	-2.709718000	-3.536107000
C	0.161570000	-3.244830000	-3.904919000
C	-1.016923000	-2.585528000	-3.443652000
C	0.424493000	0.315458000	-1.367310000
C	0.283731000	-0.189668000	0.063340000
H	-1.816061000	-0.908758000	-2.349816000
C	0.154362000	-1.487342000	0.167789000
O	0.199988000	-4.377268000	-4.623327000
C	-0.858964000	-4.862889000	-5.451989000
H	-1.643845000	-5.342977000	-4.852828000
H	-1.302404000	-4.057423000	-6.055335000
H	-0.388869000	-5.603712000	-6.112908000
H	2.502907000	-1.225014000	-2.460082000
C	0.300621000	0.735261000	1.257113000
H	1.290588000	1.208630000	1.352177000
H	-0.437822000	1.538631000	1.103523000
H	0.068554000	0.211131000	2.193856000
C	-0.076985000	-2.817937000	0.453831000
C	1.011382000	-3.738518000	0.577002000

C	-1.418239000	-3.289334000	0.631173000
C	0.758757000	-5.068356000	0.873429000
C	-1.648978000	-4.619447000	0.938842000
C	-0.564108000	-5.505997000	1.055159000
H	2.031457000	-3.377767000	0.429722000
H	-2.244614000	-2.582043000	0.537633000
H	1.585288000	-5.774720000	0.972173000
H	-2.667043000	-4.983062000	1.095464000
H	-0.754780000	-6.554679000	1.298812000
O	-2.194573000	-3.165540000	-3.782286000
C	-3.420215000	-2.546044000	-3.443373000
H	-3.557948000	-2.487941000	-2.348421000
H	-3.496292000	-1.532293000	-3.872292000
H	-4.211480000	-3.175325000	-3.869671000
O	2.590590000	-3.277754000	-3.918854000
C	2.819068000	-3.599847000	-5.294021000
H	2.285507000	-2.901470000	-5.958477000
H	3.900283000	-3.492993000	-5.460839000
H	2.507567000	-4.628376000	-5.523813000
H	-0.459806000	0.946061000	-1.570720000
C	1.677749000	1.181487000	-1.554958000
H	1.792141000	1.451870000	-2.615699000
H	1.606524000	2.114630000	-0.977529000
H	2.591296000	0.657047000	-1.236082000

P1′



E = -1000.0207 E_h

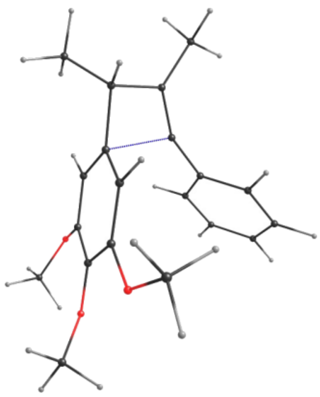
E_{ZPE} = 0.3851 E_h

H^{298} = -999.6125 E_h

C	-0.603013000	0.079947000	-3.158026000
C	-0.799769000	-0.458132000	-1.927736000
C	-0.498949000	0.292069000	-0.675539000
C	0.052988000	1.672942000	-0.856957000
C	0.309504000	2.186638000	-2.131570000
C	-0.046264000	1.400170000	-3.270668000
C	-1.002237000	-1.909113000	-1.577172000
C	0.039559000	-2.018694000	-0.457581000
H	-0.762828000	-0.516819000	-4.055857000
C	0.363784000	-0.800711000	0.040458000
O	0.955036000	3.368622000	-2.272656000
C	0.333280000	4.468735000	-2.948586000
H	0.521946000	4.424168000	-4.030624000
H	-0.753554000	4.494278000	-2.759549000
H	0.793462000	5.378413000	-2.539343000
H	-1.429635000	0.430729000	-0.086425000
C	0.547535000	-3.353113000	-0.007892000
H	-0.284561000	-4.001645000	0.317085000
H	1.051012000	-3.880028000	-0.837943000
H	1.256673000	-3.266941000	0.825824000
C	1.346555000	-0.499325000	1.105337000
C	0.954073000	0.051443000	2.340740000
C	2.707198000	-0.794701000	0.898200000
C	1.895458000	0.277543000	3.346201000
C	3.649270000	-0.559100000	1.902079000
C	3.244476000	-0.026312000	3.129742000
H	-0.096106000	0.294841000	2.521789000
H	3.026734000	-1.213325000	-0.059573000
H	1.572714000	0.693434000	4.303963000
H	4.700409000	-0.800308000	1.723624000
H	3.978888000	0.154777000	3.918135000
O	0.227938000	1.957472000	-4.428924000
C	-0.025841000	1.307962000	-5.685366000
H	0.602938000	0.411339000	-5.786283000

H	-1.089728000	1.044996000	-5.783678000
H	0.250667000	2.039338000	-6.453054000
O	0.207276000	2.296354000	0.284079000
C	0.551649000	3.685549000	0.456515000
H	-0.168821000	4.325310000	-0.070562000
H	0.478897000	3.855909000	1.536925000
H	1.568579000	3.880219000	0.097487000
H	-0.737097000	-2.553971000	-2.432920000
C	-2.440569000	-2.248970000	-1.127048000
H	-3.152363000	-2.124385000	-1.957235000
H	-2.497340000	-3.292423000	-0.782521000
H	-2.766307000	-1.607173000	-0.294044000

TS2′



Imaginary frequency 190*i* cm^{-1}

E = -999.9726 E_h

E_{ZPE} = 0.3817 E_h

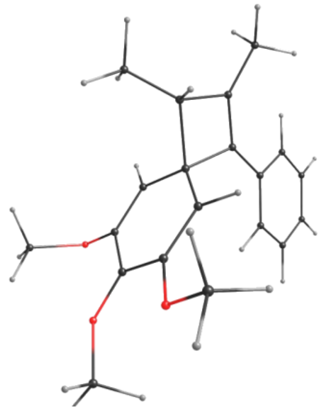
H^{298} = -999.5701 E_h

C	0.007153000	-0.589530000	-2.641023000
C	-0.924277000	-0.768411000	-1.578546000
C	-1.389321000	0.381694000	-0.889296000
C	-0.865249000	1.653269000	-1.134196000
C	0.069274000	1.824384000	-2.192928000
C	0.516351000	0.667019000	-2.927933000
C	-1.553205000	-2.156000000	-1.311393000
C	-0.697370000	-2.517800000	-0.116603000
H	0.341340000	-1.461389000	-3.202153000

C	0.102382000	-1.475389000	0.053639000
O	0.533527000	3.054312000	-2.408996000
C	0.899754000	3.560231000	-3.705831000
H	1.951787000	3.342175000	-3.927691000
H	0.259919000	3.131349000	-4.488613000
H	0.741658000	4.645701000	-3.649765000
H	-2.158636000	0.306486000	-0.119781000
C	-0.722494000	-3.799313000	0.659733000
H	-1.732023000	-3.987860000	1.059951000
H	-0.470491000	-4.642240000	-0.006040000
H	-0.012311000	-3.789558000	1.497590000
C	1.203444000	-0.806341000	0.648570000
C	1.010926000	0.207872000	1.622510000
C	2.524368000	-1.185170000	0.292071000
C	2.107812000	0.794184000	2.244022000
C	3.614103000	-0.594084000	0.924064000
C	3.406791000	0.392052000	1.899148000
H	-0.001670000	0.523783000	1.881874000
H	2.674742000	-1.960638000	-0.462609000
H	1.954024000	1.565676000	3.002063000
H	4.627616000	-0.905498000	0.660438000
H	4.263267000	0.854951000	2.395329000
O	1.456840000	0.914721000	-3.860096000
C	2.048030000	-0.156227000	-4.579428000
H	2.548154000	-0.864447000	-3.896568000
H	1.303229000	-0.695601000	-5.188828000
H	2.795561000	0.297552000	-5.242247000
O	-1.283552000	2.623778000	-0.298454000
C	-1.417271000	3.997606000	-0.672761000
H	-1.869704000	4.099905000	-1.671543000
H	-2.091454000	4.439051000	0.072487000
H	-0.450396000	4.517951000	-0.648051000
H	-1.293953000	-2.824617000	-2.151710000
C	-3.066761000	-2.186853000	-1.095038000
H	-3.591063000	-1.803350000	-1.984698000

H	-3.412416000	-3.216570000	-0.915802000
H	-3.376943000	-1.581084000	-0.230723000

P2′



E = -999.9809 E_h

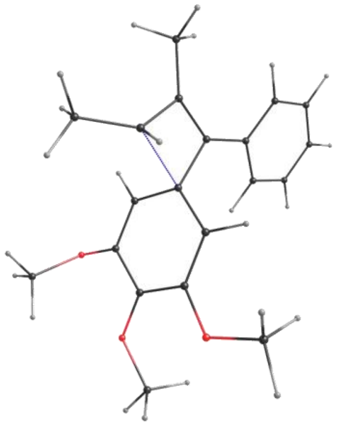
E_{ZPE} = 0.3833 E_h

H^{298} = -999.5749 E_h

C	-0.405504000	0.754468000	-1.273308000
C	-0.702251000	-0.316266000	-0.305781000
C	-1.454078000	0.115713000	0.876997000
C	-1.834594000	1.411146000	1.091843000
C	-1.493905000	2.424769000	0.113066000
C	-0.856582000	2.041447000	-1.132714000
C	-1.371362000	-1.611950000	-1.099774000
C	-0.162349000	-2.392976000	-0.645294000
H	0.143437000	0.467304000	-2.171874000
C	0.422824000	-1.359464000	0.004409000
O	-1.818621000	3.634458000	0.454442000
C	-1.518566000	4.879720000	-0.225821000
H	-0.450635000	4.935208000	-0.466559000
H	-2.118627000	4.962180000	-1.138912000
H	-1.799497000	5.654429000	0.496365000
H	-1.697010000	-0.616916000	1.649380000
C	0.163505000	-3.822581000	-0.908675000
H	-0.279969000	-4.484010000	-0.143553000
H	-0.245186000	-4.143865000	-1.880284000

H	1.247968000	-4.005869000	-0.915243000
C	1.615766000	-1.158873000	0.830438000
C	2.055496000	0.134022000	1.177009000
C	2.331601000	-2.266837000	1.335554000
C	3.177487000	0.316763000	1.988261000
C	3.451804000	-2.080933000	2.145166000
C	3.879279000	-0.790030000	2.475087000
H	1.514085000	1.007542000	0.805691000
H	1.994454000	-3.280031000	1.112109000
H	3.507295000	1.325591000	2.249324000
H	3.990419000	-2.949220000	2.531900000
H	4.755575000	-0.646325000	3.111837000
O	-0.765622000	3.019009000	-2.056994000
C	-0.395153000	2.681043000	-3.391900000
H	0.666988000	2.392693000	-3.455768000
H	-1.025145000	1.860477000	-3.774480000
H	-0.565010000	3.582176000	-3.993699000
O	-2.422644000	1.772392000	2.248792000
C	-3.782280000	2.222824000	2.226523000
H	-4.446384000	1.429011000	1.845258000
H	-4.044355000	2.449081000	3.267445000
H	-3.902191000	3.131503000	1.618584000
H	-1.353508000	-1.394571000	-2.182034000
C	-2.770733000	-2.066610000	-0.710045000
H	-3.525195000	-1.303341000	-0.955973000
H	-3.022557000	-2.970902000	-1.287905000
H	-2.854635000	-2.320953000	0.356778000

TS3′



Imaginary frequency 269*i* cm^{-1}

E = -999.9752 E_h

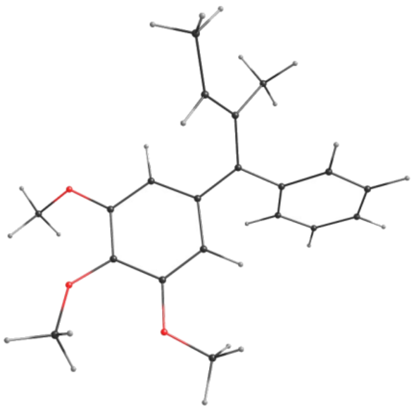
E_{ZPE} = 0.3821 E_h

H^{298} = -999.5698 E_h

C	-0.186340000	0.878588000	-1.052134000
C	-0.534490000	-0.152958000	-0.102016000
C	-1.505300000	0.185087000	0.904138000
C	-2.118736000	1.424918000	0.957758000
C	-1.716627000	2.445280000	0.040292000
C	-0.804332000	2.112048000	-1.037250000
C	-1.512960000	-1.701551000	-0.864678000
C	-0.371869000	-2.384928000	-0.206984000
H	0.565759000	0.648887000	-1.807861000
C	0.392961000	-1.321917000	0.160211000
O	-2.240817000	3.631044000	0.252203000
C	-1.789801000	4.894491000	-0.277998000
H	-0.703627000	4.997115000	-0.152595000
H	-2.063383000	4.993046000	-1.334887000
H	-2.311496000	5.645445000	0.325679000
H	-1.767372000	-0.545043000	1.672351000
C	-0.267780000	-3.861290000	0.010565000
H	0.452267000	-4.103099000	0.803978000
H	-1.245205000	-4.280325000	0.302174000
H	0.045789000	-4.391690000	-0.905909000
C	1.733943000	-1.191779000	0.734398000

C	2.139694000	0.013812000	1.345141000
C	2.663367000	-2.254016000	0.664252000
C	3.428138000	0.154254000	1.863958000
C	3.944162000	-2.114808000	1.196447000
C	4.331915000	-0.910461000	1.795732000
H	1.433584000	0.843775000	1.432417000
H	2.393346000	-3.183781000	0.162016000
H	3.727754000	1.092361000	2.337260000
H	4.649492000	-2.947283000	1.133637000
H	5.336756000	-0.802562000	2.210887000
O	-0.620928000	3.087104000	-1.942696000
C	0.316560000	2.909333000	-2.997930000
H	1.334166000	2.760512000	-2.599506000
H	0.036745000	2.054201000	-3.635799000
H	0.285618000	3.829885000	-3.593262000
O	-2.977811000	1.693617000	1.963331000
C	-4.331833000	2.032560000	1.648240000
H	-4.821245000	1.209616000	1.099801000
H	-4.839678000	2.176716000	2.609611000
H	-4.395598000	2.959372000	1.059993000
H	-1.327306000	-1.362597000	-1.891131000
C	-2.948890000	-2.049424000	-0.618526000
H	-3.626126000	-1.242335000	-0.934053000
H	-3.187937000	-2.920303000	-1.258767000
H	-3.160693000	-2.328477000	0.423182000

P3′



E = -1000.0254 E_h

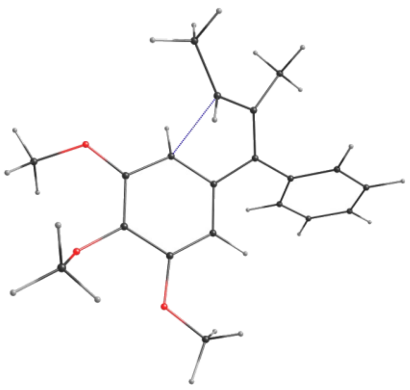
E_{ZPE} = 0.3833 E_h

H^{298} = -999.6181 E_h

C	0.526259000	1.162606000	-0.973877000
C	-0.243960000	0.313041000	-0.123380000
C	-1.465304000	0.814293000	0.402413000
C	-1.956884000	2.063685000	0.039819000
C	-1.273182000	2.823999000	-0.957364000
C	0.023168000	2.385055000	-1.398467000
C	-1.964316000	-2.053156000	-0.324876000
C	-0.784447000	-2.089162000	0.374812000
H	1.480338000	0.806048000	-1.354565000
C	0.188218000	-1.028798000	0.150507000
O	-1.888329000	3.922330000	-1.380677000
C	-1.712606000	4.513047000	-2.680230000
H	-2.586727000	5.161570000	-2.819215000
H	-0.789606000	5.102163000	-2.729753000
H	-1.701049000	3.734803000	-3.457000000
H	-2.037575000	0.246803000	1.135530000
C	-0.456751000	-3.236537000	1.314394000
H	-1.292238000	-3.412238000	2.008951000
H	-0.282578000	-4.180045000	0.772302000
H	0.435684000	-3.028074000	1.916845000
C	1.618506000	-1.352931000	0.208233000
C	2.520046000	-0.499904000	0.887920000
C	2.117621000	-2.544385000	-0.370728000
C	3.864866000	-0.847277000	1.011463000
C	3.469598000	-2.863187000	-0.282311000
C	4.342314000	-2.024774000	0.425253000
H	2.145181000	0.410043000	1.360983000
H	1.440632000	-3.206081000	-0.915254000
H	4.543063000	-0.200089000	1.572137000
H	3.848249000	-3.773002000	-0.753986000
H	5.395562000	-2.299051000	0.526716000
O	0.664531000	3.222436000	-2.239356000

C	1.984252000	2.919905000	-2.671458000
H	2.672756000	2.836219000	-1.813804000
H	2.014891000	1.987416000	-3.260598000
H	2.297392000	3.756365000	-3.308214000
O	-3.126305000	2.444689000	0.583739000
C	-3.357839000	3.792523000	1.009734000
H	-3.707107000	4.422723000	0.181079000
H	-4.136643000	3.733572000	1.781699000
H	-2.447291000	4.232117000	1.447704000
H	-2.109250000	-1.240329000	-1.042856000
C	-3.066360000	-3.047098000	-0.258520000
H	-3.325853000	-3.406098000	-1.269388000
H	-2.852997000	-3.911165000	0.382309000
H	-3.980285000	-2.550482000	0.119734000

TS4′



Imaginary frequency 270*i* cm^{-1}

E = -1000.0074 E_h

E_{ZPE} = 0.3831 E_h

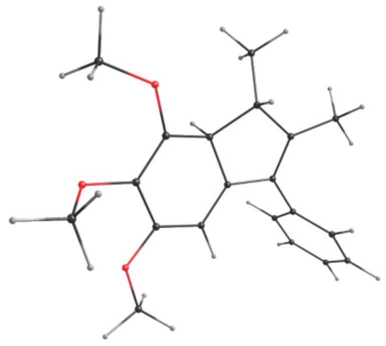
H^{298} = -999.6006 E_h

C	0.932671000	0.985047000	-1.254996000
C	0.113527000	0.239953000	-0.391699000
C	-1.247373000	0.648234000	-0.168953000
C	-1.818344000	1.719582000	-0.921130000
C	-1.026404000	2.377115000	-1.868636000
C	0.371654000	2.039356000	-1.985194000
C	-1.789617000	-1.499942000	-0.476316000

C	-0.646736000	-1.891588000	0.290701000
H	1.957409000	0.664215000	-1.432746000
C	0.470608000	-1.050878000	0.163055000
O	-1.523267000	3.382307000	-2.623639000
C	-1.841618000	3.060931000	-3.984558000
H	-2.219137000	3.983542000	-4.443429000
H	-0.950818000	2.717210000	-4.532839000
H	-2.625189000	2.284703000	-4.030422000
H	-1.730131000	0.445896000	0.786888000
C	-0.742152000	-3.055113000	1.240914000
H	-1.513516000	-2.849931000	2.002961000
H	-1.041502000	-3.983541000	0.727672000
H	0.203756000	-3.230278000	1.767510000
C	1.848145000	-1.401341000	0.539463000
C	2.668938000	-0.470887000	1.213979000
C	2.377980000	-2.675181000	0.237454000
C	3.965193000	-0.815055000	1.596617000
C	3.681737000	-3.007552000	0.602837000
C	4.474203000	-2.083419000	1.293478000
H	2.273996000	0.515518000	1.467741000
H	1.769211000	-3.398131000	-0.310137000
H	4.580604000	-0.092289000	2.137480000
H	4.083747000	-3.990344000	0.345842000
H	5.488532000	-2.353077000	1.597162000
O	1.034237000	2.773198000	-2.877287000
C	2.420971000	2.550625000	-3.117134000
H	3.010862000	2.700693000	-2.198952000
H	2.596802000	1.536790000	-3.514344000
H	2.720311000	3.290316000	-3.868404000
O	-3.091106000	2.006276000	-0.611109000
C	-3.668164000	3.304127000	-0.819761000
H	-3.969887000	3.449824000	-1.866050000
H	-4.554786000	3.334990000	-0.174470000
H	-2.964537000	4.096985000	-0.529620000
H	-1.607256000	-1.220229000	-1.516085000

C	-3.187768000	-1.925271000	-0.184390000
H	-3.381996000	-2.885593000	-0.699475000
H	-3.392405000	-2.069517000	0.885541000
H	-3.905126000	-1.202309000	-0.600258000

P4′



E = -1000.0452 E_h

E_{ZPE} = 0.3856 E_h

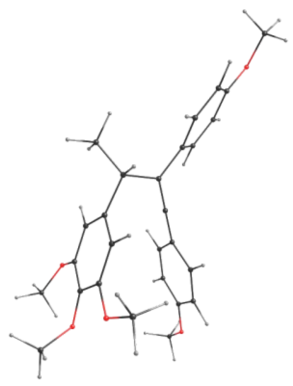
H^{298} = -999.6376 E_h

C	1.060731000	1.176091000	-1.125841000
C	0.259920000	0.362539000	-0.357175000
C	-1.186804000	0.667369000	-0.157317000
C	-1.806641000	1.578357000	-1.171474000
C	-0.995253000	2.368573000	-1.969237000
C	0.439438000	2.187141000	-1.907709000
C	-1.833184000	-0.702874000	0.184954000
C	-0.622548000	-1.538187000	0.568186000
H	2.127279000	0.972417000	-1.219791000
C	0.561514000	-0.902146000	0.271504000
O	-1.505962000	3.339327000	-2.771120000
C	-1.524983000	3.087826000	-4.179892000
H	-1.901481000	4.003416000	-4.653814000
H	-0.518847000	2.866378000	-4.565905000
H	-2.200522000	2.248950000	-4.420600000
H	-1.224496000	1.268481000	0.778363000
C	-0.775327000	-2.891503000	1.170348000
H	-1.346657000	-2.838987000	2.112985000
H	-1.355826000	-3.547902000	0.497758000

H	0.192598000	-3.364672000	1.377001000
C	1.940998000	-1.414669000	0.483734000
C	2.784782000	-0.772790000	1.409203000
C	2.419695000	-2.543193000	-0.205958000
C	4.067323000	-1.265881000	1.659976000
C	3.708367000	-3.027204000	0.038160000
C	4.529404000	-2.396045000	0.977734000
H	2.423739000	0.104007000	1.953742000
H	1.779074000	-3.045535000	-0.935718000
H	4.705829000	-0.770674000	2.395648000
H	4.069966000	-3.904978000	-0.503035000
H	5.527778000	-2.788870000	1.184820000
O	1.110449000	3.002411000	-2.692133000
C	2.542669000	2.985165000	-2.759317000
H	2.980206000	3.143309000	-1.762567000
H	2.899671000	2.035639000	-3.186894000
H	2.818178000	3.813239000	-3.421503000
O	-3.122061000	1.582082000	-1.095148000
C	-3.996117000	2.527571000	-1.739805000
H	-3.997593000	2.370459000	-2.827110000
H	-4.990220000	2.311326000	-1.330951000
H	-3.696164000	3.556195000	-1.505154000
H	-2.254742000	-1.123726000	-0.747304000
C	-2.944047000	-0.643926000	1.238417000
H	-3.752860000	0.013978000	0.893687000
H	-3.376272000	-1.637738000	1.425380000
H	-2.561359000	-0.250836000	2.195032000

c) C1″ as a starting point

C1″



E = -1420.2355 E_h

E_{ZPE} = 0.5007 E_h

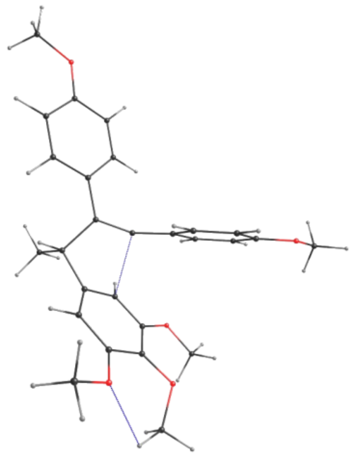
H^{298} = -1419.7069 E_h

C	-1.017582000	-0.278852000	-1.989392000
C	-1.111252000	-0.679834000	-0.646260000
C	-0.801909000	0.231067000	0.362045000
C	-0.346782000	1.530090000	0.067672000
C	-0.221315000	1.933875000	-1.277105000
C	-0.570919000	1.011480000	-2.303510000
C	-1.383864000	-2.141723000	-0.291777000
C	-0.023372000	-2.830344000	-0.034380000
H	-1.268240000	-0.983600000	-2.782067000
C	1.048628000	-2.087299000	-0.171001000
O	0.332547000	3.139887000	-1.589149000
C	-0.495283000	4.120167000	-2.213769000
H	-0.865341000	3.775620000	-3.190184000
H	-1.353924000	4.380264000	-1.569755000
H	0.131678000	5.011340000	-2.352382000
H	-0.872906000	-0.033722000	1.418172000
C	2.148364000	-1.307722000	-0.382515000
C	2.781497000	-0.606548000	0.700555000
C	2.628790000	-1.066700000	-1.721262000
C	3.798529000	0.290360000	0.470695000
C	3.633203000	-0.163104000	-1.952585000
C	4.224826000	0.541644000	-0.865168000

H	2.424846000	-0.785656000	1.717266000
H	2.158051000	-1.600623000	-2.548384000
H	4.255875000	0.816318000	1.308119000
H	3.995840000	0.057611000	-2.958022000
O	-0.383854000	1.465688000	-3.564692000
C	-0.573455000	0.595703000	-4.662811000
H	0.107384000	-0.272742000	-4.612142000
H	-1.612702000	0.227580000	-4.725541000
H	-0.343865000	1.182647000	-5.561943000
O	0.018545000	2.252809000	1.150418000
C	0.123942000	3.670632000	1.149776000
H	-0.797446000	4.143657000	0.770705000
H	0.259488000	3.956294000	2.201811000
H	0.978130000	4.021112000	0.555122000
C	0.105976000	-4.262575000	0.346631000
C	-0.685575000	-5.258125000	-0.251611000
C	1.052067000	-4.654104000	1.320056000
C	-0.540856000	-6.601870000	0.100024000
C	1.202875000	-5.984001000	1.679009000
C	0.411575000	-6.978565000	1.068588000
H	-1.424364000	-4.991309000	-1.011199000
H	1.657336000	-3.894281000	1.819217000
H	-1.171994000	-7.347498000	-0.383665000
H	1.922513000	-6.291358000	2.440466000
O	0.637461000	-8.236091000	1.479179000
C	-0.081413000	-9.321594000	0.919248000
H	-1.162625000	-9.243002000	1.128467000
H	0.080852000	-9.392385000	-0.170527000
H	0.311147000	-10.225850000	1.400341000
O	5.155593000	1.415604000	-1.191967000
C	5.823398000	2.213353000	-0.208892000
H	5.101609000	2.829862000	0.349485000
H	6.397907000	1.577452000	0.482597000
H	6.507284000	2.861679000	-0.768989000
H	-1.801021000	-2.640171000	-1.184772000

C	-2.363714000	-2.338313000	0.871647000
H	-3.304766000	-1.812986000	0.645575000
H	-2.590416000	-3.401517000	1.033903000
H	-1.965550000	-1.933527000	1.813918000

TS1′′



Imaginary frequency 114*i* cm^{-1}

E = -1420.2354 E_h

E_{ZPE} = 0.5008 E_h

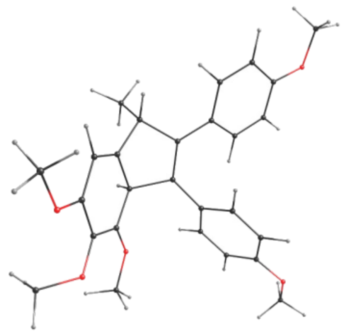
H^{298} = -1419.7058 E_h

C	-1.574115000	-0.253158000	-2.122675000
C	-1.409142000	-0.677879000	-0.807196000
C	-0.795922000	0.174175000	0.129588000
C	-0.302960000	1.451811000	-0.245614000
C	-0.452036000	1.884057000	-1.571812000
C	-1.109682000	1.020889000	-2.502328000
C	-1.627721000	-2.118345000	-0.364296000
C	-0.224333000	-2.582021000	0.039353000
H	-2.009713000	-0.925160000	-2.861234000
C	0.718522000	-1.647182000	0.062609000
O	0.110532000	3.050012000	-1.989037000
C	-0.751594000	4.104815000	-2.421054000
H	-1.329663000	3.816318000	-3.310066000
H	-1.443292000	4.403192000	-1.613723000
H	-0.098030000	4.951293000	-2.670147000
H	-0.807805000	-0.045464000	1.197531000

C	1.977681000	-1.066823000	-0.031911000
C	2.592961000	-0.393522000	1.066253000
C	2.668751000	-1.076326000	-1.288351000
C	3.825677000	0.217308000	0.931860000
C	3.892074000	-0.462733000	-1.427024000
C	4.490115000	0.195760000	-0.320707000
H	2.073570000	-0.358687000	2.026044000
H	2.206474000	-1.580684000	-2.138880000
H	4.273584000	0.717107000	1.790514000
H	4.428932000	-0.460123000	-2.377472000
O	-1.177264000	1.495980000	-3.753057000
C	-1.638917000	0.681575000	-4.821219000
H	-1.023063000	-0.227479000	-4.920616000
H	-2.695907000	0.394713000	-4.690073000
H	-1.535833000	1.289808000	-5.728730000
O	0.340124000	2.092343000	0.746973000
C	0.739354000	3.462293000	0.699079000
H	-0.123108000	4.121171000	0.514118000
H	1.149296000	3.678390000	1.695133000
H	1.503646000	3.639391000	-0.068320000
C	0.099612000	-3.993504000	0.363545000
C	-0.556490000	-5.057129000	-0.281919000
C	1.092897000	-4.310195000	1.318065000
C	-0.231968000	-6.386995000	-0.004093000
C	1.421396000	-5.624744000	1.605220000
C	0.766771000	-6.683972000	0.943134000
H	-1.329268000	-4.855518000	-1.027741000
H	1.598742000	-3.506973000	1.857216000
H	-0.761672000	-7.181477000	-0.529139000
H	2.179530000	-5.873857000	2.350386000
O	1.159811000	-7.920999000	1.289236000
C	0.559564000	-9.057170000	0.690412000
H	-0.524119000	-9.097448000	0.897269000
H	0.727331000	-9.074855000	-0.400734000
H	1.043480000	-9.931630000	1.142084000

O	5.665020000	0.766433000	-0.554265000
C	6.363422000	1.470586000	0.469698000
H	5.754816000	2.296690000	0.871323000
H	6.654424000	0.789664000	1.285039000
H	7.262404000	1.879418000	-0.006243000
H	-1.931384000	-2.712930000	-1.242550000
C	-2.691327000	-2.292315000	0.729401000
H	-3.659157000	-1.908679000	0.370009000
H	-2.818113000	-3.350936000	0.999644000
H	-2.425469000	-1.742079000	1.644775000

P1′′



E = -1420.2660 E_h

E_{ZPE} = 0.5030 E_h

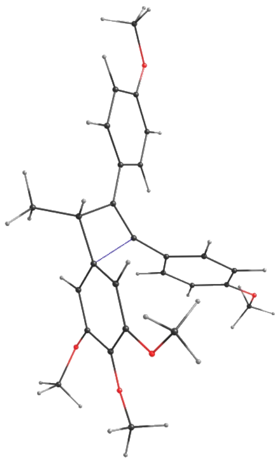
H^{298} = -1419.7334 E_h

C	-2.054583000	-0.182528000	-2.158021000
C	-1.653593000	-0.642195000	-0.942022000
C	-0.694488000	0.105984000	-0.089553000
C	-0.247676000	1.432799000	-0.615690000
C	-0.669520000	1.893633000	-1.862096000
C	-1.544726000	1.066766000	-2.638349000
C	-1.782139000	-2.044539000	-0.407874000
C	-0.312594000	-2.262057000	-0.014178000
H	-2.673757000	-0.804993000	-2.804760000
C	0.348258000	-1.067038000	0.069958000
O	-0.181867000	3.046037000	-2.391908000
C	-1.082081000	4.139522000	-2.603450000
H	-1.855459000	3.890601000	-3.343582000

H	-1.562253000	4.447686000	-1.657921000
H	-0.469969000	4.966444000	-2.986223000
H	-1.128334000	0.314871000	0.909153000
C	1.800946000	-0.844699000	0.164534000
C	2.412444000	-0.098112000	1.188043000
C	2.635517000	-1.419163000	-0.823618000
C	3.800884000	0.055871000	1.247220000
C	4.011158000	-1.265098000	-0.783125000
C	4.612929000	-0.530072000	0.258825000
H	1.799214000	0.358585000	1.968080000
H	2.183880000	-1.999879000	-1.631130000
H	4.241524000	0.625038000	2.066235000
H	4.656653000	-1.708339000	-1.543778000
O	-1.804087000	1.526672000	-3.843567000
C	-2.582554000	0.789355000	-4.796019000
H	-2.091217000	-0.166101000	-5.033127000
H	-3.602453000	0.613443000	-4.421592000
H	-2.618567000	1.417829000	-5.692787000
O	0.524386000	2.058730000	0.241751000
C	1.055746000	3.389057000	0.096814000
H	0.237985000	4.124105000	0.095411000
H	1.682713000	3.537375000	0.983775000
H	1.651329000	3.478611000	-0.817817000
C	0.222618000	-3.609674000	0.248736000
C	-0.329719000	-4.749073000	-0.368191000
C	1.292840000	-3.821975000	1.153931000
C	0.170096000	-6.033798000	-0.136203000
C	1.787852000	-5.090550000	1.405642000
C	1.242430000	-6.216664000	0.754577000
H	-1.166073000	-4.644001000	-1.063353000
H	1.732117000	-2.974865000	1.679941000
H	-0.282590000	-6.880615000	-0.651530000
H	2.607115000	-5.250958000	2.109619000
O	1.806425000	-7.401118000	1.056171000
C	1.324259000	-8.594005000	0.465114000

H	0.259162000	-8.761027000	0.702205000
H	1.460035000	-8.587746000	-0.630878000
H	1.918389000	-9.410097000	0.894433000
O	5.954697000	-0.448645000	0.219200000
C	6.655996000	0.232535000	1.240931000
H	6.381367000	1.301723000	1.277634000
H	6.474239000	-0.224556000	2.229547000
H	7.721999000	0.142848000	0.993578000
H	-2.083799000	-2.724348000	-1.220809000
C	-2.786882000	-2.190218000	0.750521000
H	-3.802910000	-1.921015000	0.420293000
H	-2.803862000	-3.229898000	1.109364000
H	-2.517997000	-1.550259000	1.605199000

TS2′′



Imaginary frequency 236*i* cm^{-1}

E = -1420.2280 E_h

E_{ZPE} = 0.5000 E_h

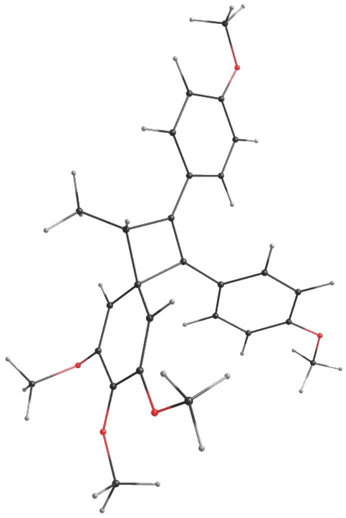
H^{298} = -1419.6998 E_h

C	-0.679499000	-0.001887000	-2.002260000
C	-1.039161000	-0.630340000	-0.766273000
C	-1.241196000	0.211019000	0.368423000
C	-0.918982000	1.562135000	0.344051000
C	-0.458085000	2.153224000	-0.869218000
C	-0.357191000	1.342284000	-2.056574000

C	-1.539268000	-2.101344000	-0.748778000
C	-0.254888000	-2.668602000	-0.167445000
H	-0.598553000	-0.620235000	-2.896086000
C	0.515560000	-1.574555000	-0.093613000
O	-0.110304000	3.430250000	-0.787623000
C	-0.060258000	4.370148000	-1.872261000
H	0.854658000	4.241252000	-2.463002000
H	-0.938703000	4.267511000	-2.523163000
H	-0.063360000	5.354688000	-1.387092000
H	-1.614035000	-0.195390000	1.308825000
C	1.803233000	-1.004719000	0.117366000
C	2.200211000	-0.474044000	1.369713000
C	2.758635000	-1.010861000	-0.938475000
C	3.498399000	-0.029118000	1.586042000
C	4.049077000	-0.562246000	-0.734284000
C	4.442145000	-0.078107000	0.536237000
H	1.476743000	-0.431022000	2.187250000
H	2.469692000	-1.412951000	-1.912125000
H	3.776922000	0.359972000	2.565256000
H	4.794740000	-0.584106000	-1.531752000
O	0.082458000	1.981178000	-3.161939000
C	0.250353000	1.259302000	-4.373207000
H	0.982724000	0.442309000	-4.255340000
H	-0.706392000	0.840084000	-4.729573000
H	0.627054000	1.980064000	-5.109650000
O	-1.018072000	2.241611000	1.505912000
C	-1.598993000	3.546328000	1.580001000
H	-2.397485000	3.677371000	0.832585000
H	-2.037285000	3.627138000	2.584632000
H	-0.838484000	4.327916000	1.445923000
C	0.088050000	-4.053287000	0.177684000
C	-0.580552000	-5.139350000	-0.415719000
C	1.121948000	-4.338343000	1.100640000
C	-0.231274000	-6.460377000	-0.122703000
C	1.470795000	-5.642062000	1.407930000

C	0.804078000	-6.723676000	0.793761000
H	-1.383621000	-4.958199000	-1.134592000
H	1.647828000	-3.518156000	1.591734000
H	-0.769770000	-7.272983000	-0.609724000
H	2.261661000	-5.868525000	2.125944000
O	1.228196000	-7.947734000	1.152666000
C	0.627956000	-9.105882000	0.598715000
H	-0.448105000	-9.157988000	0.839645000
H	0.762305000	-9.146997000	-0.496430000
H	1.138377000	-9.962690000	1.055318000
O	5.715367000	0.308164000	0.648613000
C	6.225745000	0.772685000	1.892755000
H	5.668045000	1.652663000	2.252580000
H	6.194473000	-0.023595000	2.655175000
H	7.267914000	1.059158000	1.706164000
H	-1.649105000	-2.430499000	-1.796318000
C	-2.849617000	-2.372091000	-0.011220000
H	-3.664373000	-1.770690000	-0.443965000
H	-3.128009000	-3.432622000	-0.100430000
H	-2.781451000	-2.140608000	1.062346000

P2′′



E = -1420.2318 E_h

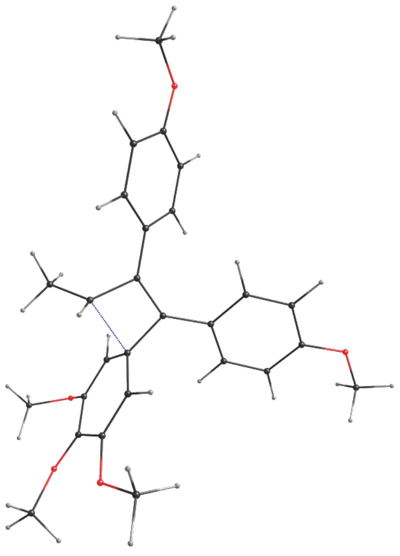
E_{ZPE} = 0.5015 E_h

H^{298} = -1419.7021 E_h

C	-0.032932000	0.048304000	-1.837464000
C	-0.729181000	-0.594871000	-0.716452000
C	-1.590902000	0.293295000	0.066073000
C	-1.635025000	1.645617000	-0.132271000
C	-0.792227000	2.246547000	-1.145261000
C	-0.003077000	1.407559000	-2.023599000
C	-1.289328000	-2.079747000	-0.992017000
C	-0.253717000	-2.611488000	-0.015880000
H	0.551936000	-0.601293000	-2.489574000
C	0.314227000	-1.399349000	0.214561000
O	-0.834133000	3.547218000	-1.160810000
C	-0.079396000	4.468484000	-1.978307000
H	0.996170000	4.305717000	-1.842341000
H	-0.354346000	4.352173000	-3.033595000
H	-0.371853000	5.457508000	-1.607146000
H	-2.193536000	-0.120299000	0.876331000
C	1.510608000	-0.872323000	0.864599000
C	1.489492000	0.252045000	1.709567000
C	2.756722000	-1.509615000	0.645300000
C	2.645166000	0.710254000	2.346412000
C	3.909184000	-1.067745000	1.273470000
C	3.866254000	0.040268000	2.146174000
H	0.547817000	0.772674000	1.902093000
H	2.807305000	-2.372308000	-0.023429000
H	2.581251000	1.575524000	3.006501000
H	4.867865000	-1.564560000	1.110480000
O	0.700316000	2.059824000	-2.973107000
C	1.521079000	1.311857000	-3.863874000
H	2.273107000	0.724147000	-3.310953000
H	0.912945000	0.638632000	-4.491665000
H	2.028468000	2.043999000	-4.503773000
O	-2.370103000	2.442483000	0.675494000
C	-3.502172000	3.112448000	0.106341000
H	-4.204142000	2.383972000	-0.334759000

H	-3.996320000	3.637071000	0.933922000
H	-3.201361000	3.845459000	-0.657658000
C	-0.025852000	-3.962727000	0.482339000
C	-0.663938000	-5.071478000	-0.106776000
C	0.823881000	-4.211394000	1.589829000
C	-0.470848000	-6.371879000	0.367081000
C	1.027717000	-5.494523000	2.065999000
C	0.383953000	-6.595944000	1.461336000
H	-1.321709000	-4.926804000	-0.967057000
H	1.321712000	-3.379537000	2.089640000
H	-0.987629000	-7.198329000	-0.120229000
H	1.678375000	-5.686910000	2.921346000
O	0.649561000	-7.797896000	2.003997000
C	0.049220000	-8.969199000	1.480529000
H	-1.048047000	-8.951644000	1.603742000
H	0.297380000	-9.108980000	0.414081000
H	0.461109000	-9.806971000	2.056490000
O	5.028522000	0.378210000	2.731355000
C	5.084059000	1.515656000	3.572558000
H	4.802722000	2.432064000	3.024162000
H	4.429907000	1.399883000	4.453694000
H	6.123605000	1.602413000	3.912255000
H	-1.047213000	-2.345979000	-2.036010000
C	-2.772909000	-2.324865000	-0.736432000
H	-3.396302000	-1.652095000	-1.345497000
H	-3.037586000	-3.355896000	-1.013783000
H	-3.042864000	-2.193633000	0.321698000

TS3′′



Imaginary frequency 265*i* cm^{-1}

E = -1420.2252 E_h

E_{ZPE} = 0.4998 E_h

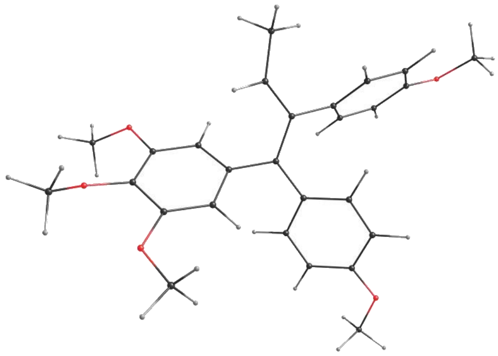
H^{298} = -1419.6973 E_h

C	0.452253000	0.492490000	-1.357369000
C	-0.186712000	-0.170072000	-0.243985000
C	-1.270265000	0.530340000	0.388902000
C	-1.792155000	1.705969000	-0.127299000
C	-1.223644000	2.269208000	-1.316757000
C	-0.049544000	1.654474000	-1.901827000
C	-1.123369000	-1.806247000	-0.771280000
C	-0.136217000	-2.362660000	0.195197000
H	1.351172000	0.034065000	-1.769141000
C	0.591103000	-1.245740000	0.486914000
O	-1.812374000	3.359766000	-1.762960000
C	-1.658718000	3.948445000	-3.069893000
H	-0.685865000	4.443778000	-3.163526000
H	-1.769375000	3.184358000	-3.850977000
H	-2.469539000	4.683354000	-3.142542000
H	-1.732033000	0.119266000	1.288725000
C	1.845283000	-0.988358000	1.188628000
C	2.188521000	0.312354000	1.606025000
C	2.805599000	-2.014202000	1.379363000

C	3.435665000	0.601169000	2.162846000
C	4.047677000	-1.738662000	1.924250000
C	4.385398000	-0.423981000	2.316436000
H	1.461261000	1.122849000	1.505954000
H	2.579004000	-3.032003000	1.056034000
H	3.657216000	1.619227000	2.483066000
H	4.795716000	-2.523483000	2.055448000
O	0.514637000	2.328490000	-2.923833000
C	1.812325000	1.956248000	-3.376464000
H	2.541967000	1.998405000	-2.549817000
H	1.814144000	0.946056000	-3.819352000
H	2.087619000	2.685529000	-4.147554000
O	-2.773129000	2.331478000	0.558422000
C	-4.033866000	2.627873000	-0.052107000
H	-4.415321000	1.758166000	-0.614400000
H	-4.721966000	2.850506000	0.773342000
H	-3.972524000	3.500099000	-0.716900000
C	-0.121130000	-3.757046000	0.652599000
C	-0.323000000	-4.805947000	-0.263466000
C	0.091785000	-4.098775000	2.008317000
C	-0.276219000	-6.144207000	0.130467000
C	0.130988000	-5.423454000	2.414831000
C	-0.034454000	-6.465674000	1.477764000
H	-0.491718000	-4.578708000	-1.320472000
H	0.224574000	-3.307443000	2.749925000
H	-0.419812000	-6.926237000	-0.615063000
H	0.297655000	-5.692674000	3.459890000
O	0.054915000	-7.716362000	1.961361000
C	-0.053824000	-8.827005000	1.088261000
H	-1.044740000	-8.869009000	0.602862000
H	0.727796000	-8.806865000	0.308827000
H	0.080713000	-9.719971000	1.711651000
O	5.621360000	-0.252004000	2.815691000
C	6.038880000	1.031803000	3.248029000
H	6.066675000	1.749186000	2.409433000

H	5.382579000	1.424565000	4.042888000
H	7.052287000	0.908508000	3.650673000
H	-0.795439000	-1.750573000	-1.817046000
C	-2.601550000	-2.008327000	-0.622200000
H	-3.176091000	-1.267564000	-1.196917000
H	-2.850298000	-2.998452000	-1.046631000
H	-2.928884000	-2.005296000	0.426491000

P3′′



E = -1420.2756 E_h

E_{ZPE} = 0.5009 E_h

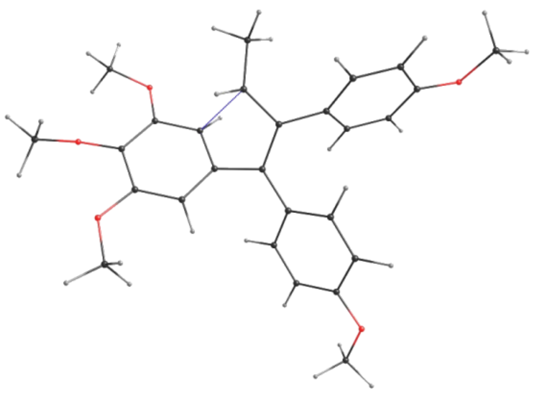
H^{298} = -1419.7451 E_h

C	0.130867000	1.163590000	-0.722750000
C	-0.566871000	0.286202000	0.149273000
C	-1.819782000	0.688472000	0.659147000
C	-2.399891000	1.906301000	0.285245000
C	-1.758382000	2.719995000	-0.686789000
C	-0.458340000	2.352050000	-1.150574000
C	-2.011069000	-2.124511000	-0.313868000
C	-0.829859000	-2.206194000	0.396120000
H	1.103149000	0.865657000	-1.108757000
C	0.015834000	-1.020568000	0.462086000
O	-2.397578000	3.829864000	-1.084825000
C	-2.429799000	4.249056000	-2.455712000
H	-1.534209000	4.824828000	-2.720920000
H	-2.522591000	3.380853000	-3.126977000
H	-3.323436000	4.880145000	-2.551910000

H	-2.360121000	0.076709000	1.382004000
C	1.413835000	-1.061104000	0.829715000
C	2.000003000	0.065859000	1.475373000
C	2.263972000	-2.184524000	0.590787000
C	3.330544000	0.086992000	1.861014000
C	3.595792000	-2.162776000	0.944595000
C	4.152629000	-1.030188000	1.593195000
H	1.371415000	0.922423000	1.722052000
H	1.867783000	-3.062478000	0.083498000
H	3.722959000	0.956178000	2.388477000
H	4.252723000	-3.008405000	0.732210000
O	0.115523000	3.219521000	-2.013421000
C	1.423351000	2.968175000	-2.501422000
H	2.156769000	2.924415000	-1.677735000
H	1.469373000	2.029744000	-3.080911000
H	1.673477000	3.808187000	-3.161483000
O	-3.599639000	2.190938000	0.826285000
C	-3.995466000	3.525468000	1.156086000
H	-4.449985000	4.034981000	0.295498000
H	-4.737350000	3.427730000	1.960530000
H	-3.141355000	4.118046000	1.518936000
C	-0.441284000	-3.500152000	1.039482000
C	-0.360230000	-4.670183000	0.265938000
C	-0.163711000	-3.606824000	2.417709000
C	-0.010907000	-5.903040000	0.823099000
C	0.174404000	-4.827652000	2.988877000
C	0.262039000	-5.992497000	2.198858000
H	-0.561695000	-4.620343000	-0.807624000
H	-0.223103000	-2.720528000	3.054634000
H	0.049098000	-6.781363000	0.179967000
H	0.388833000	-4.914509000	4.055990000
O	0.613228000	-7.124319000	2.837870000
C	0.811091000	-8.319723000	2.101134000
H	-0.121468000	-8.662788000	1.619400000
H	1.589870000	-8.195266000	1.328403000

H	1.140886000	-9.076522000	2.824056000
O	5.439698000	-1.110287000	1.915298000
C	6.108763000	-0.015270000	2.535595000
H	6.120264000	0.865776000	1.873267000
H	5.639615000	0.247768000	3.497281000
H	7.136396000	-0.353212000	2.714395000
H	-2.177100000	-1.230519000	-0.919837000
C	-3.114608000	-3.117083000	-0.346420000
H	-4.058807000	-2.594114000	-0.104258000
H	-3.258048000	-3.516019000	-1.367361000
H	-2.974523000	-3.956819000	0.344670000

TS4′′



Imaginary frequency 286*i* cm^{-1}

E = -1420.2600 E_h

E_{ZPE} = 0.5008 E_h

H^{298} = -1419.7313 E_h

C	0.682323000	1.249610000	-0.864413000
C	0.010739000	0.244905000	-0.150975000
C	-1.417580000	0.302016000	-0.034405000
C	-2.170933000	1.333238000	-0.678630000
C	-1.496678000	2.310969000	-1.422534000
C	-0.056545000	2.262187000	-1.487892000
C	-1.405789000	-1.759577000	-0.781263000
C	-0.304374000	-2.076073000	0.095156000
H	1.760663000	1.186026000	-1.000172000
C	0.601116000	-1.008531000	0.289420000

O	-2.181509000	3.349928000	-1.946775000
C	-2.064752000	3.699999000	-3.331388000
H	-1.233164000	4.397075000	-3.497799000
H	-1.925123000	2.803962000	-3.957386000
H	-3.011331000	4.187601000	-3.604311000
H	-1.913913000	-0.150672000	0.823681000
C	1.954205000	-1.090529000	0.832606000
C	2.515759000	-0.000243000	1.535079000
C	2.761011000	-2.247502000	0.669237000
C	3.810129000	-0.042435000	2.046883000
C	4.049816000	-2.299878000	1.166089000
C	4.596561000	-1.197089000	1.861646000
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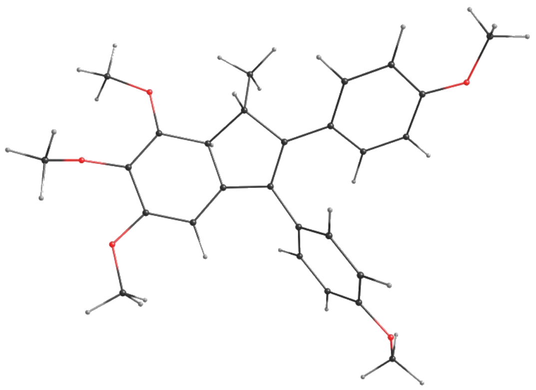
P4′′



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E_{ZPE} = 0.5039 E_h

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H	-2.934073000	-1.599078000	1.501467000

Fluorescence properties

For all spectroscopic measurements a 1 cm four-sided Carl Zeiss quartz cuvette was used.

Absorption and fluorescence spectra were measured for solutions of indenes **3b-d,f,g** in dichloromethane (DCM).

Quantum yields (eq. s1) were determined using solution of quinine bisulfate in 0.5 M H_2SO_4 (Φ_q = 0.546[S21]) with A_q < 0.30 at the λ_{ex} as a standard:

$$\Phi_i = \frac{I_i}{I_q} \cdot \frac{A_q}{A_i} \cdot \left(\frac{n_i}{n_q}\right)^2 \cdot \Phi_q \qquad (s1)$$

In eq. s1, the subscripts i and q denote sample (indene) and standard (quinine bisulfate), Φ – quantum yield, I – integrated emission intensity, A – optical density at λ_{ex}, and n – refractive index (n_{water} = 1.333, n_{DCM} = 1.4242).

The main photophysical characteristics of indenes **3b-d,f,g** are summarized in Table S8.

Table S8

indene	absorption		emission		Stokes shifts (cm^{-1})
	λ_{max} (nm)	$\varepsilon\times10^3$ M^{-1}cm^{-1}	λ_{max} (nm)	Φ_i	
3b	325	11.3	427	0.29	7350
3c	330	8.5	431	0.34	7101
3d	293	2.1	-	-	-
3f	330	9.8	437	0.28	7420
3g	332	17.6	428	0.33	6756

Cell assays

The cytotoxicity of tested compounds was assessed using the MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) assay[S22] with some modifications. 4000 cells per well were plated out in 100 mL of DMEM media containing 10% FBS in 96-well plate and incubated at 37 °C in 5% CO_2 incubator for 24 h. Then 10 mL of water-DMSO solution of tested compound was added to the cells (DMSO concentration in the media was kept below 1%) in such way that effective concentrations of studied compounds were in a range of 50 nM to 100 mM (eight dilutions). Doxorubicin (3 nM to 6 mM) was used as a control. After incubation for 72 h 10 mL MTT solution in PBS (5 mg/ml) was added, cells were incubated for 2 h. Medium was removed and 100 mL of DMSO was added. Samples were incubated for 15 min with shaking to completely solubilize formazan. Cell survival was measured spectrophotometrically at 565 nm.

Obtained results are summarized in Table S9.

Table S9

Cell lines	IC_{50} (mM)			
	3a	**3c**	**3g**	**3p**
MCF7	n/o	n/o	n/o	0.25
HEK293	0.37	0.32	n/o	0.26
A549	0.30	0.33	0.24	n/o

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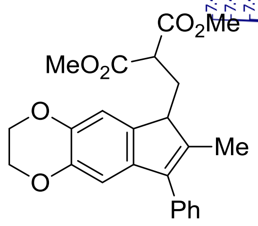
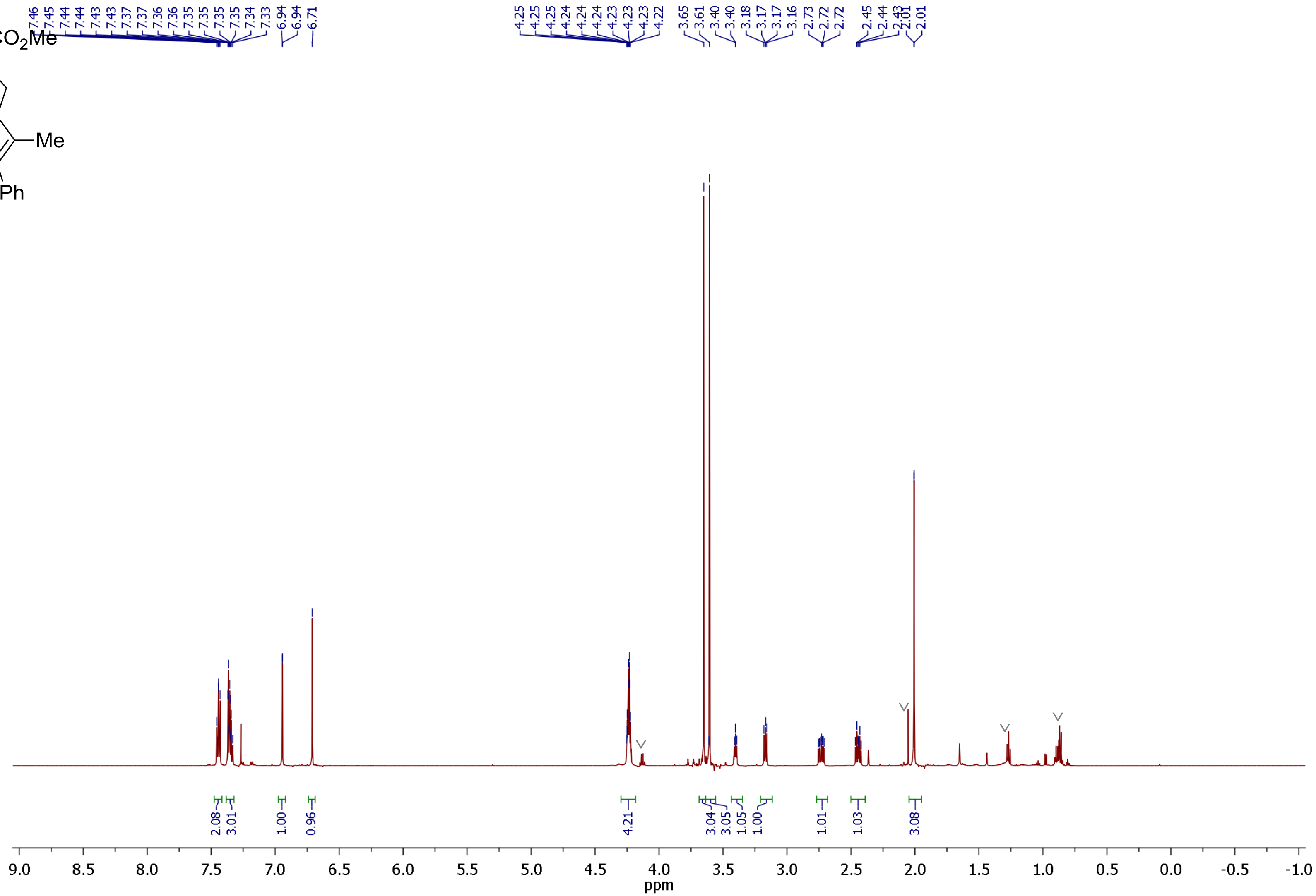
Dimethyl 2-[(7-methyl-8-phenyl-3,6-dihydro-2*H*-indeno[5,6-*b*][1,4]dioxin-6-yl)methyl]malonate (3a)

^{1}H NMR ($CDCl_3$, 600 MHz)

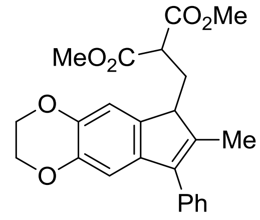


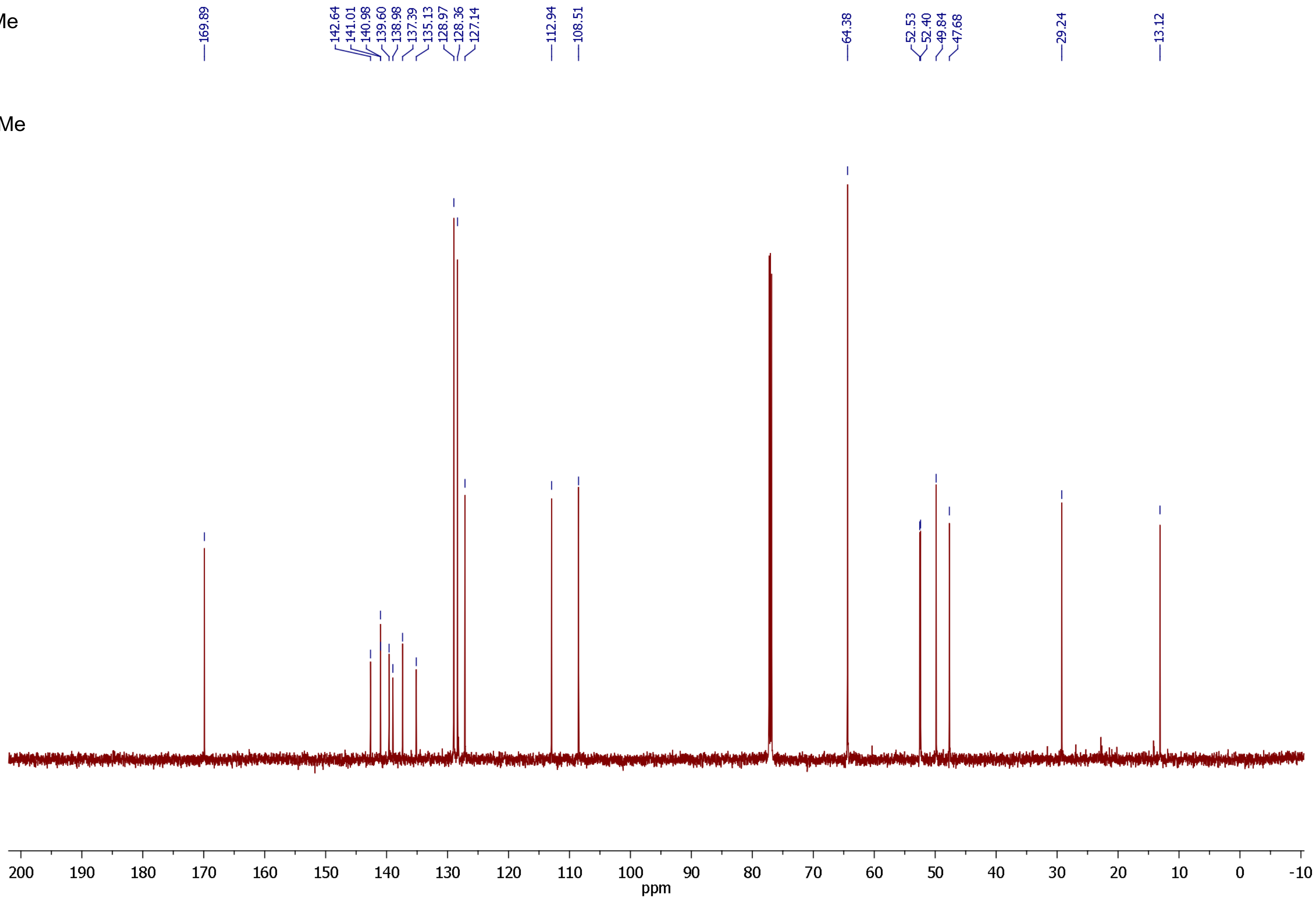
∨ Solvent



Dimethyl 2-[(7-methyl-8-phenyl-3,6-dihydro-2*H*-indeno[5,6-*b*][1,4]dioxin-6-yl)methyl]malonate (3a)

^{13}C NMR ($CDCl_3$, 150 MHz)





Dimethyl 2-[(7,8-diphenyl-3,6-dihydro-2H-indeno[5,6-b][1,4]dioxin-6-yl)methyl]malonate (3b)

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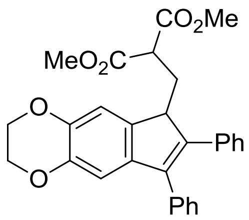
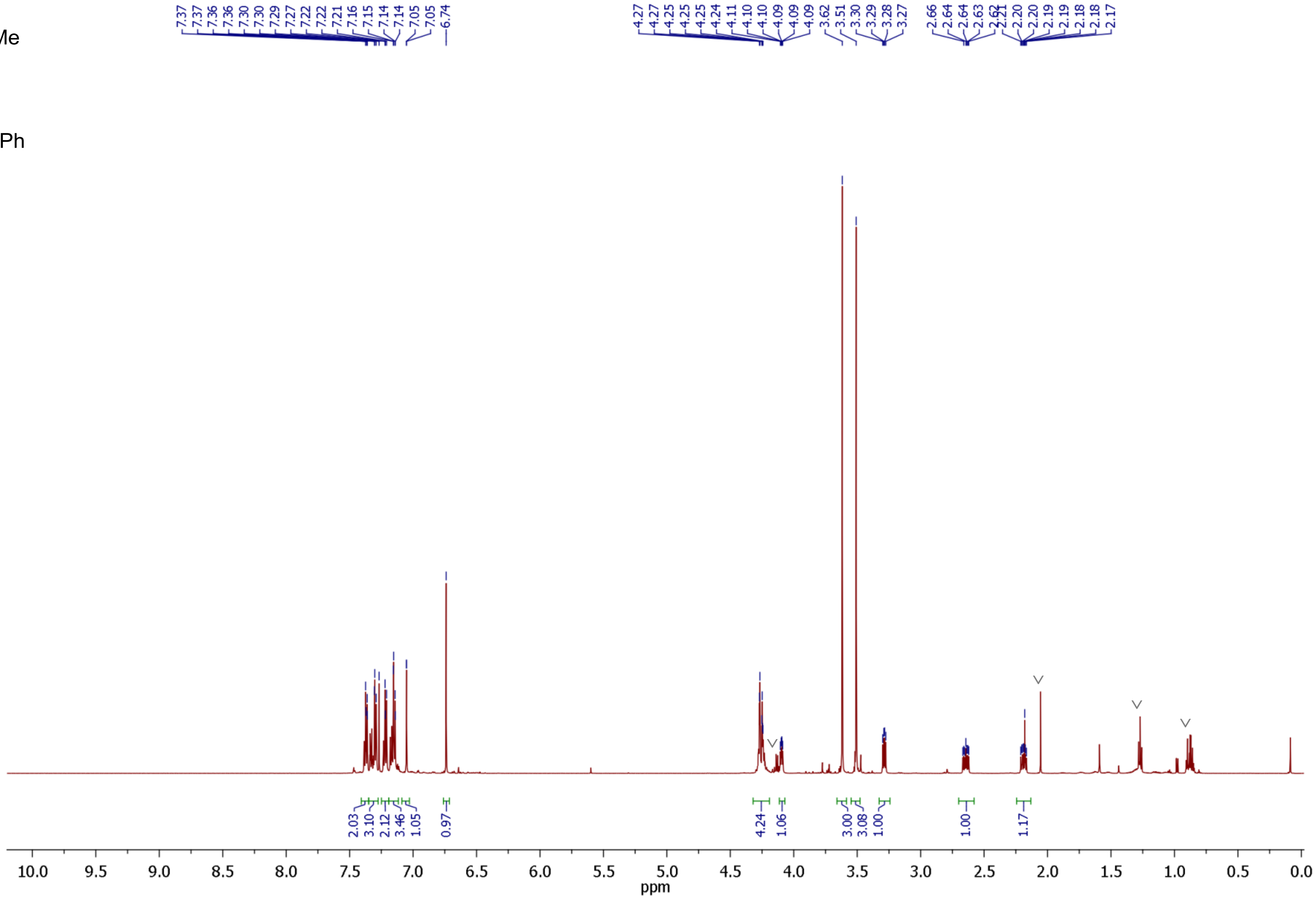
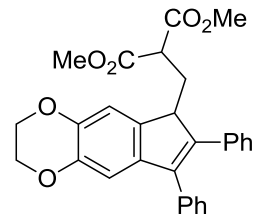
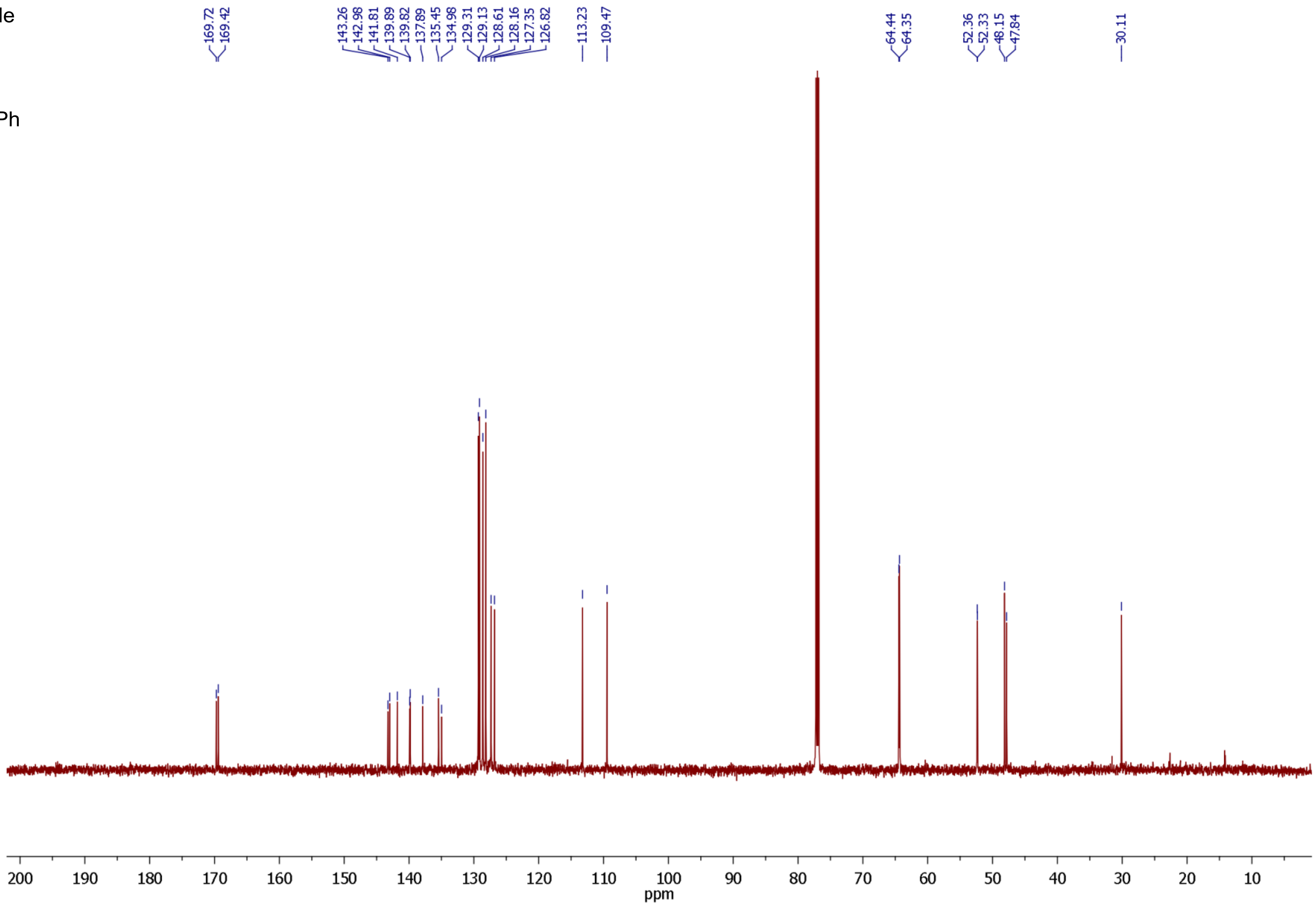




Dimethyl 2-[(7,8-diphenyl-3,6-dihydro-2H-indeno[5,6-b][1,4]dioxin-6-yl)methyl]malonate (3b)

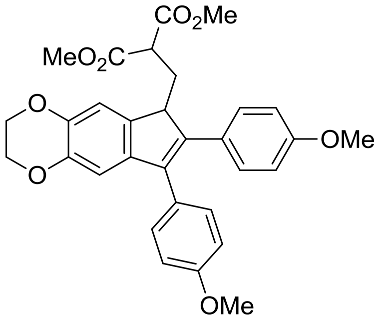
^{13}C NMR ($CDCl_3$, 150 MHz)

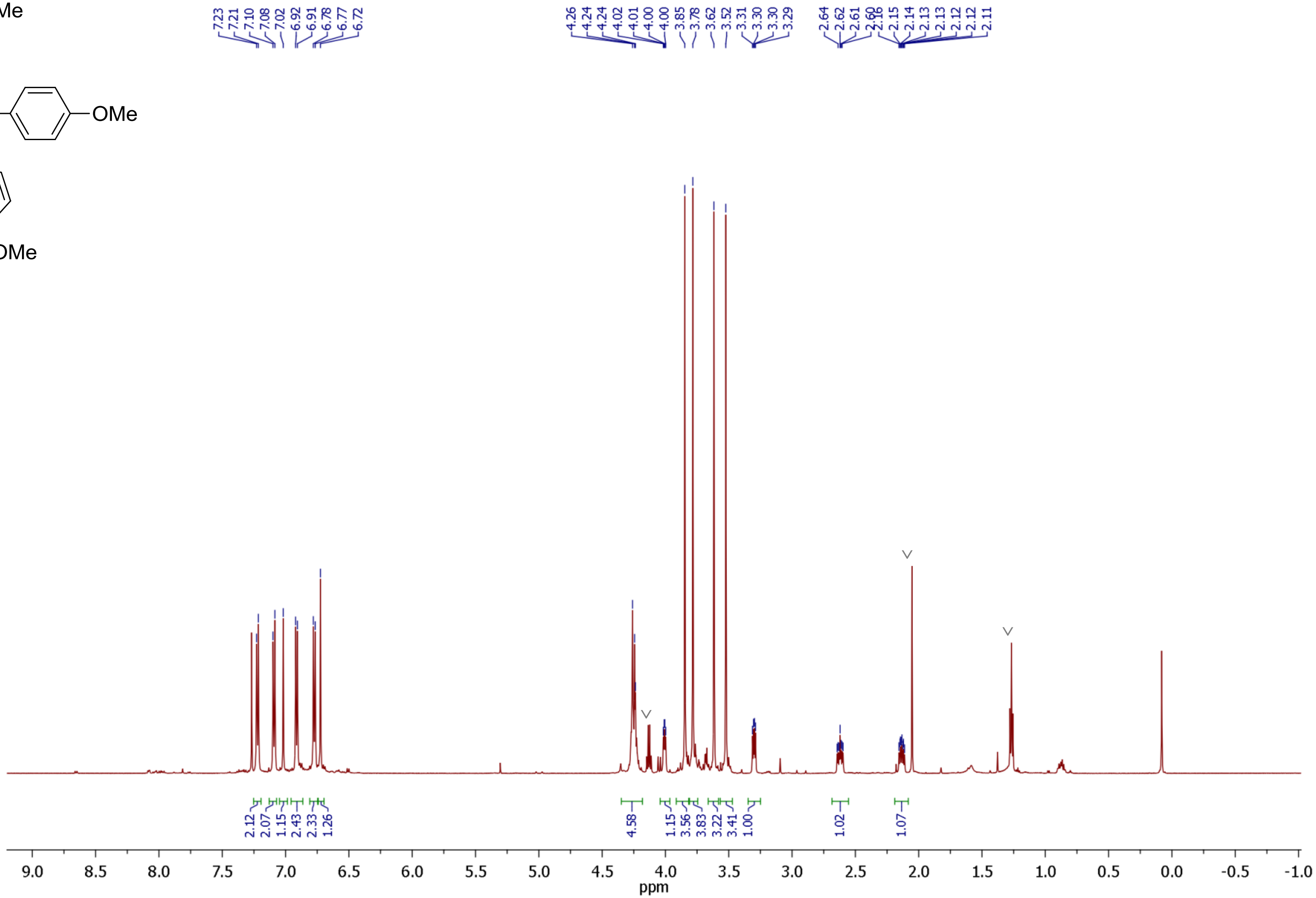




Dimethyl 2-{[7,8-bis(4-methoxyphenyl)-3,6-dihydro-2*H*-indeno[5,6-*b*][1,4]dioxin-6-yl]methyl}malonate (3c)

^{1}H NMR ($CDCl_3$, 600 MHz)





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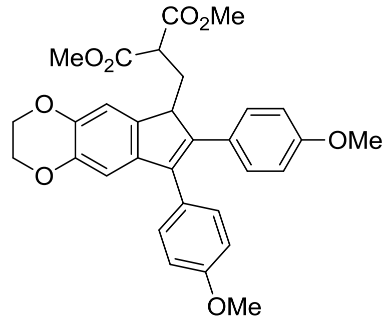
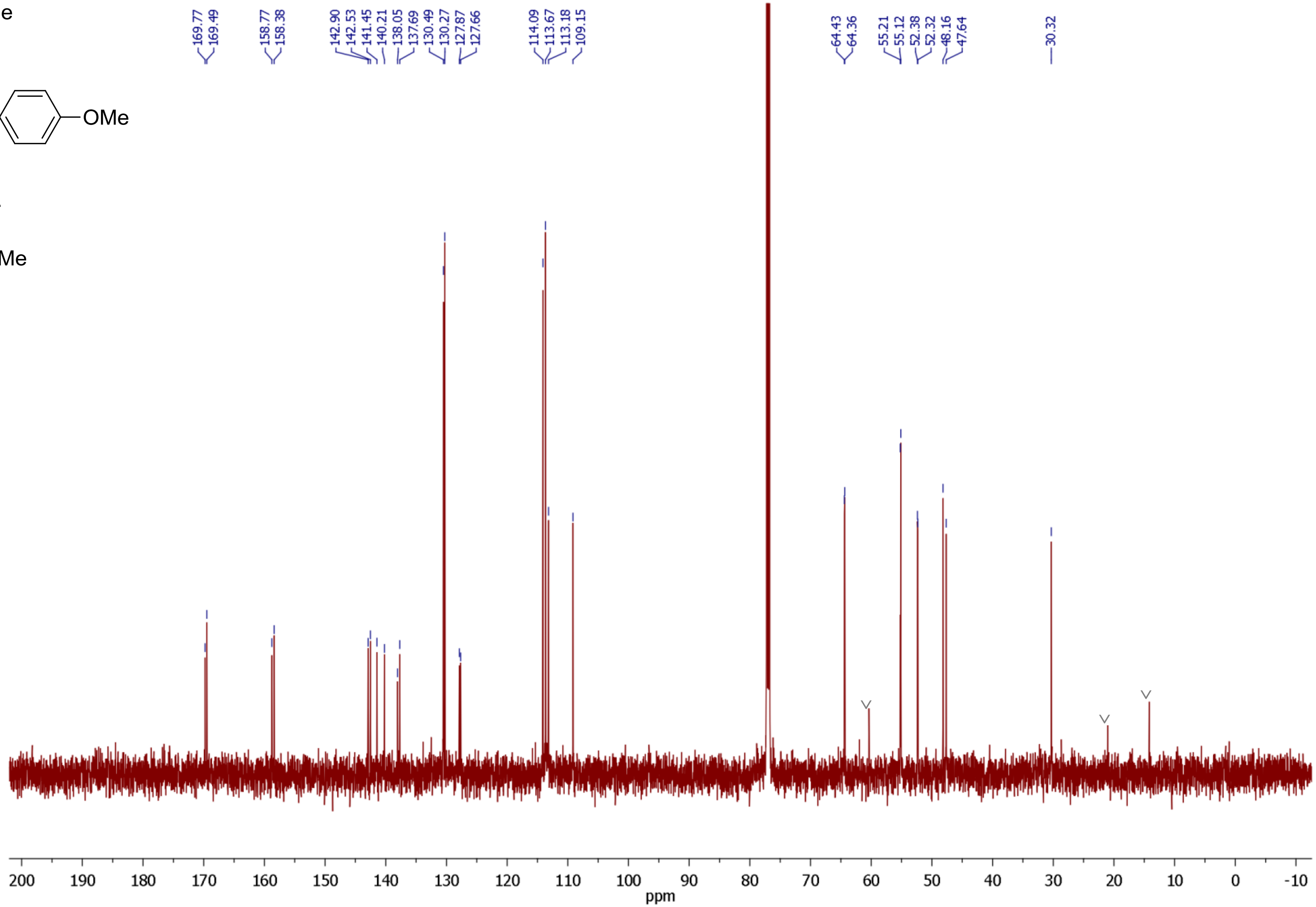
^{13}C NMR ($CDCl_3$, 150 MHz)





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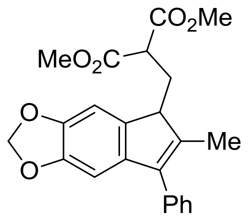
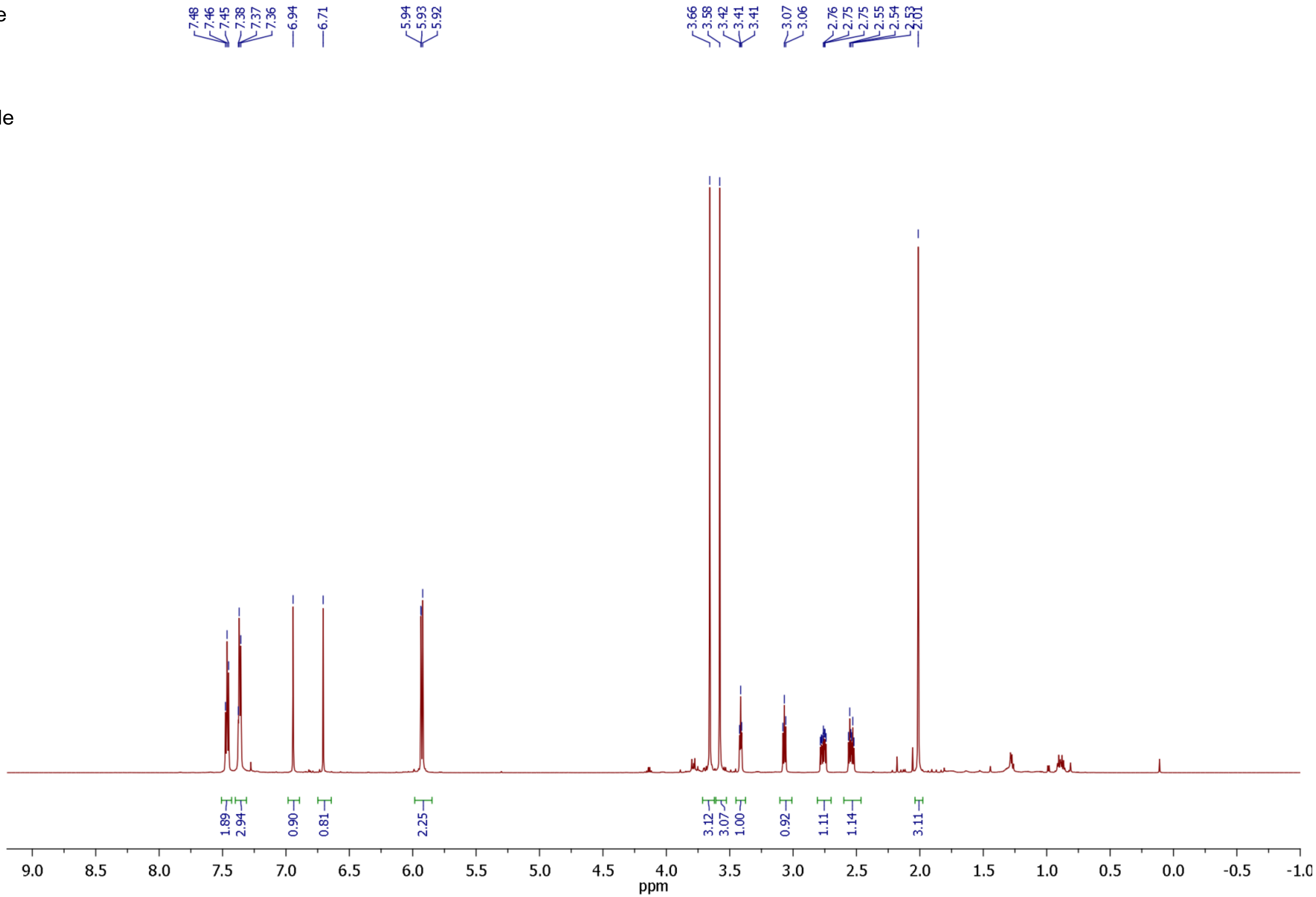
^{1}H NMR ($CDCl_3$, 600 MHz)





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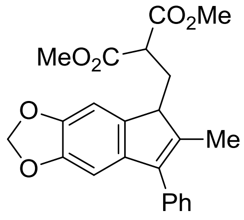
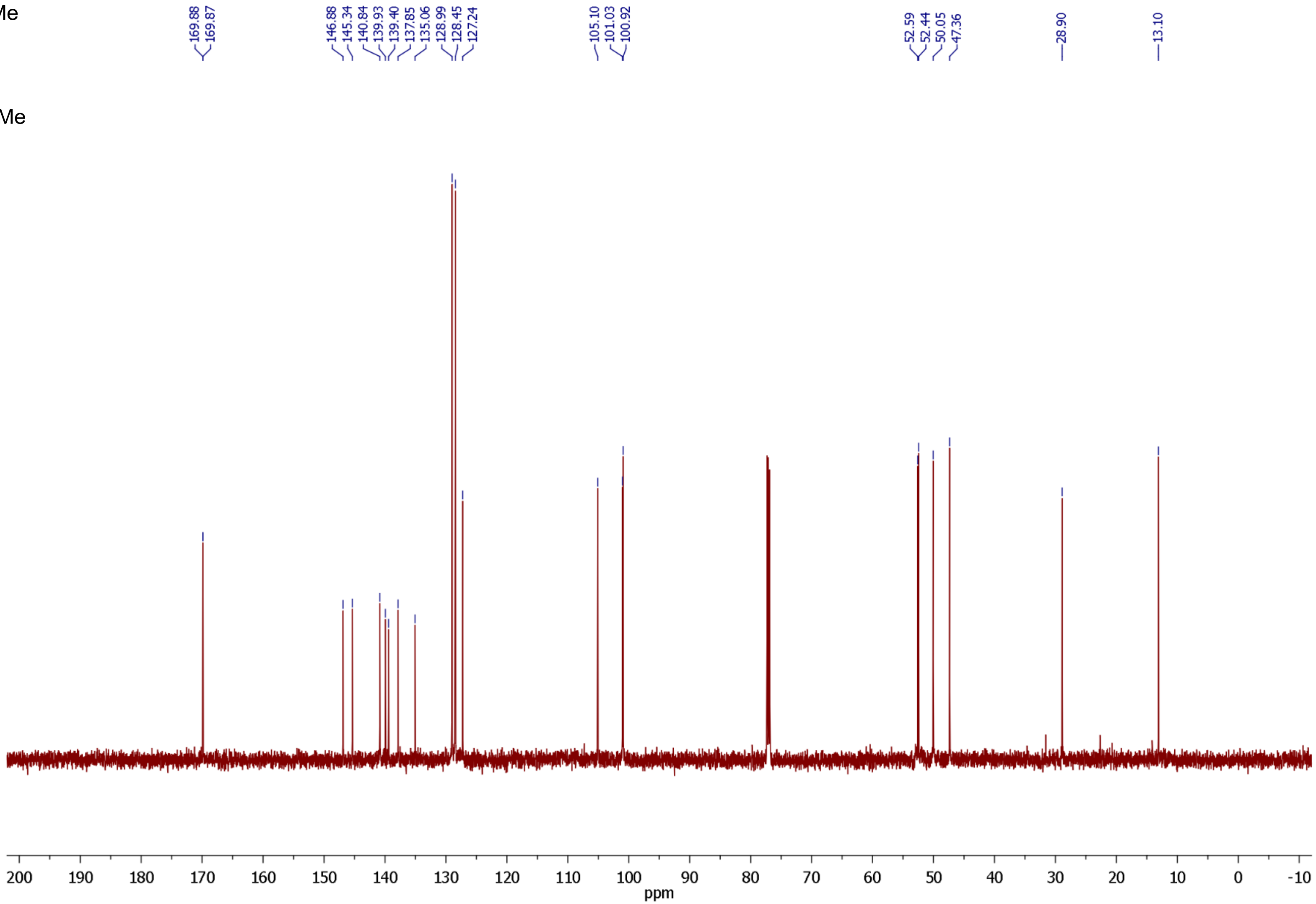
^{13}C NMR ($CDCl_3$, 150 MHz)





Dimethyl 2-[(6-ethyl-7-phenyl-5*H*-indeno[5,6-d][1,3]dioxol-5-yl)methyl]malonate (3e)

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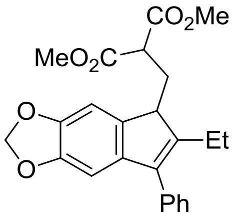

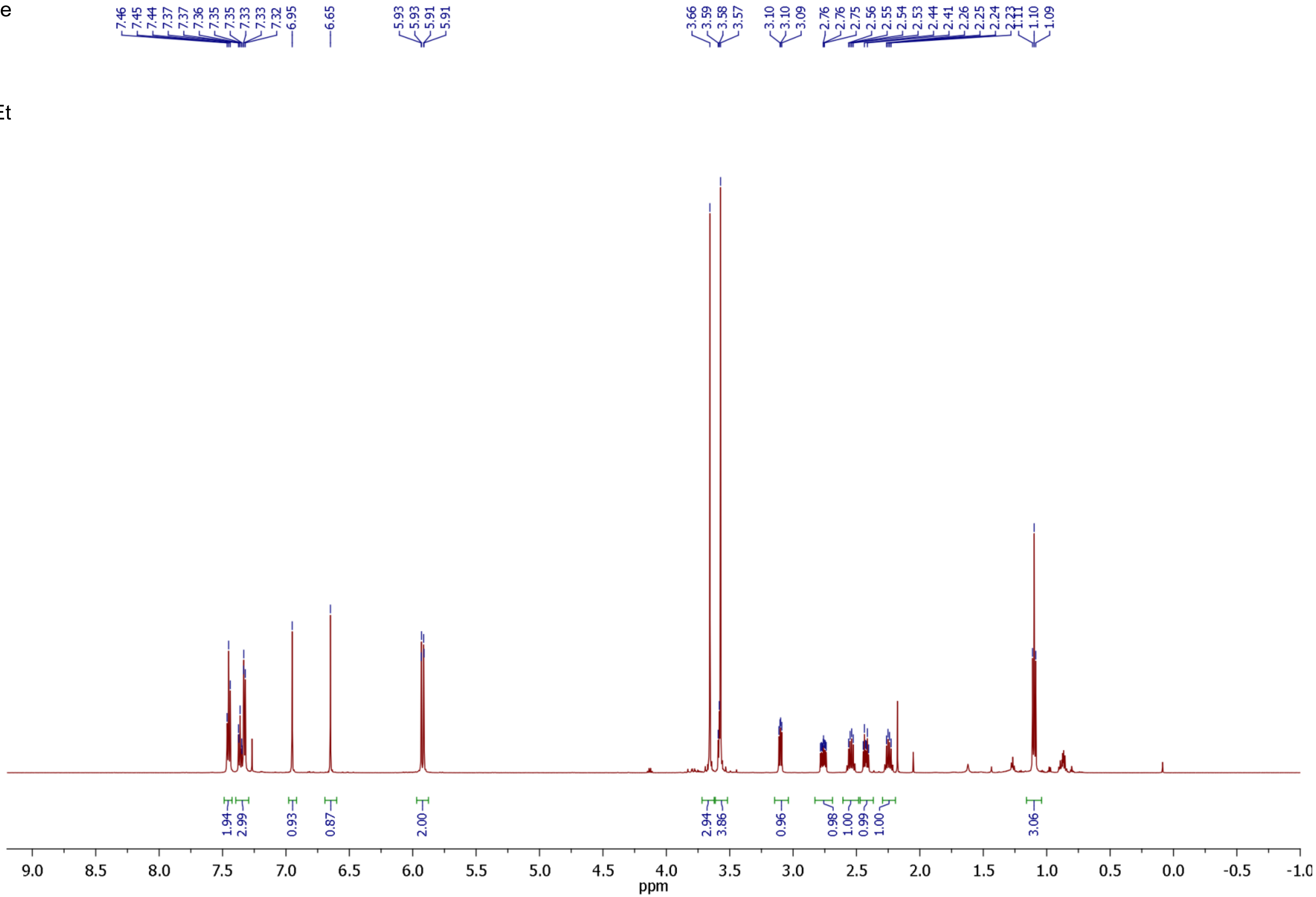

Dimethyl 2-[(6-ethyl-7-phenyl-5*H*-indeno[5,6-d][1,3]dioxol-5-yl)methyl]malonate (3e)

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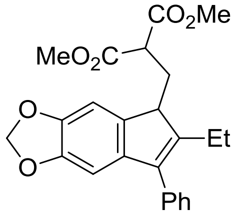
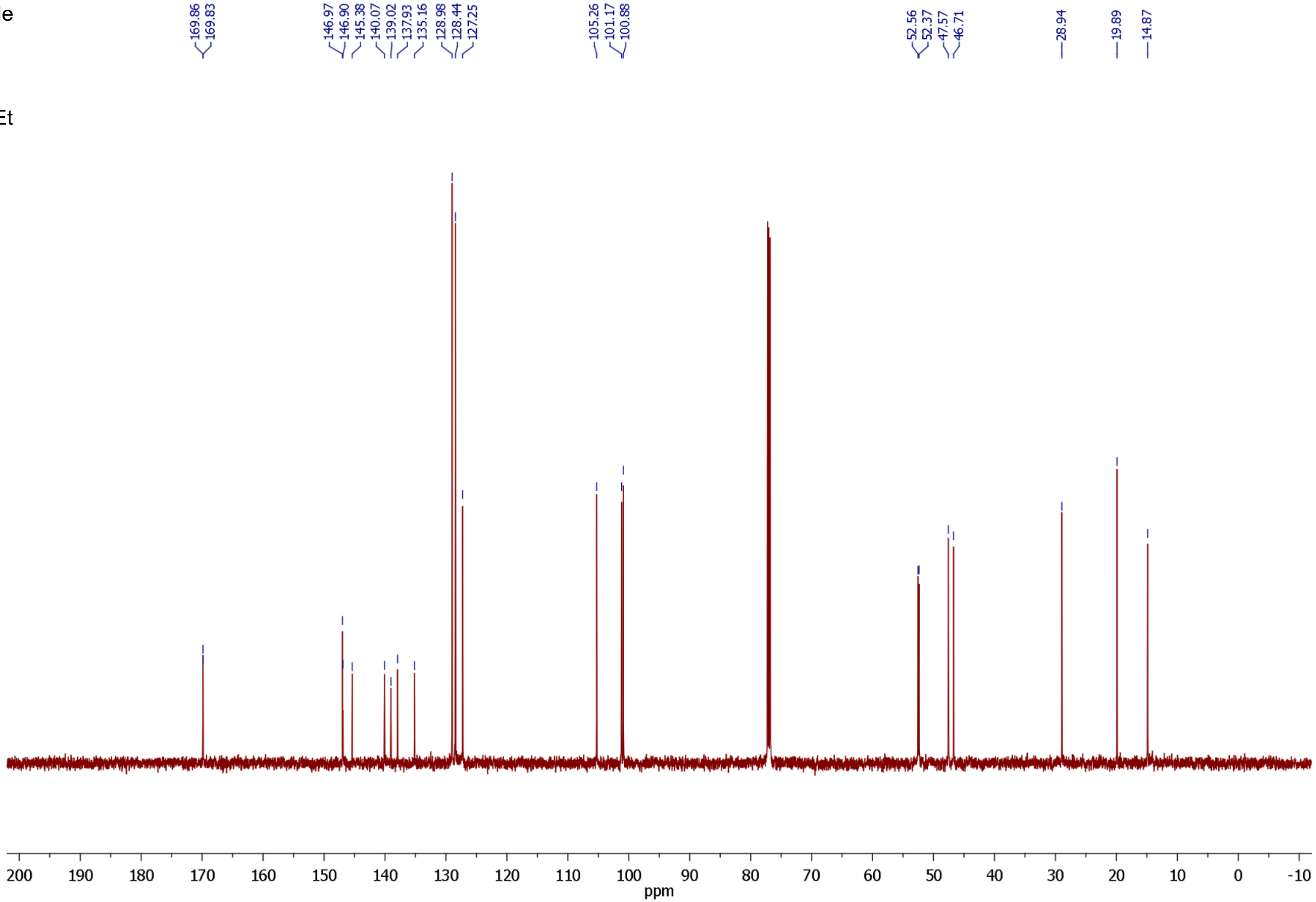
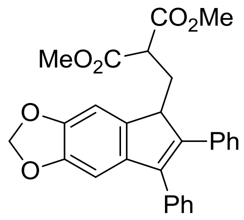
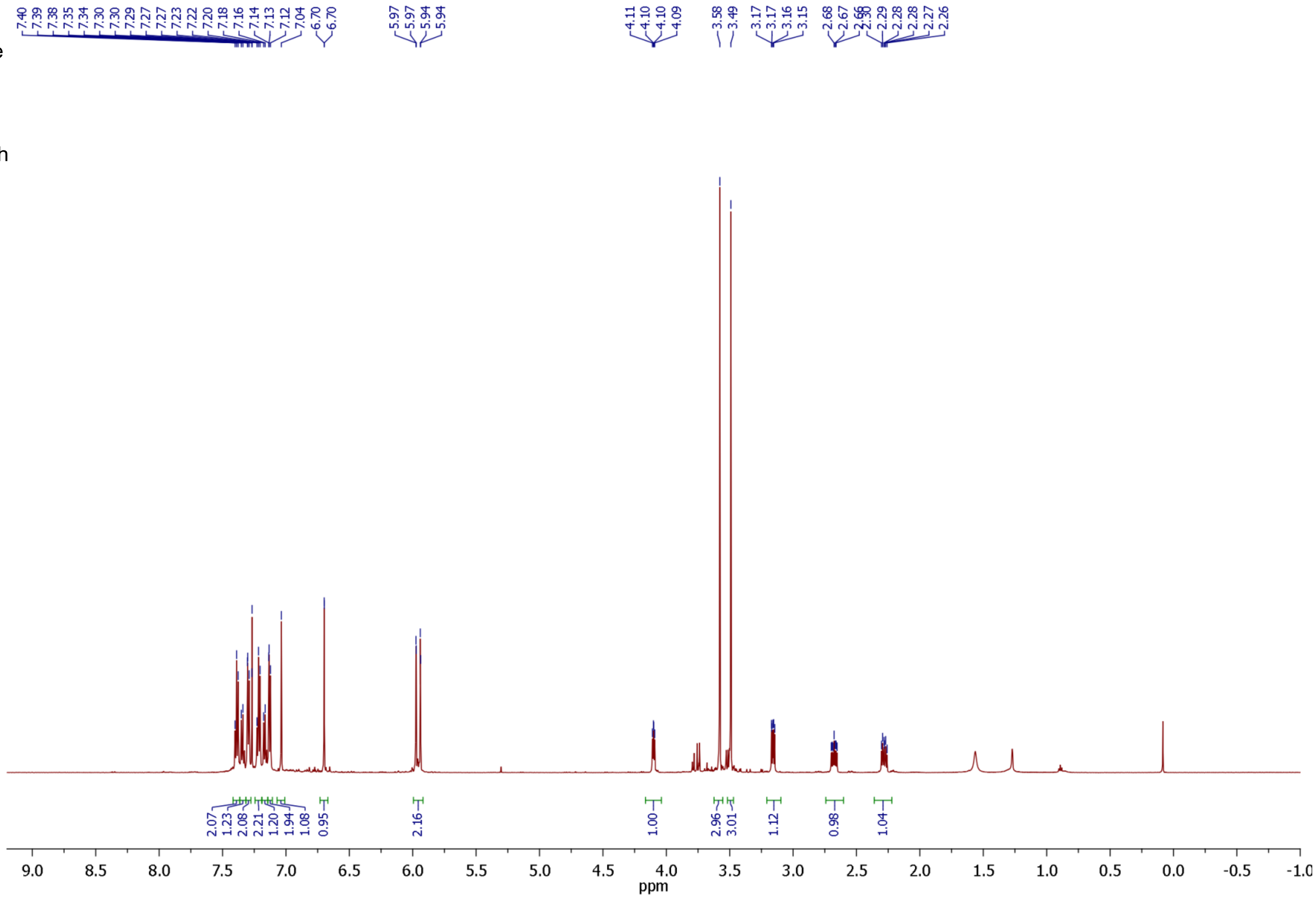




Dimethyl 2-[(6,7-diphenyl-5H-indeno[5,6-d][1,3]dioxol-5-yl)methyl]malonate (3f)

^{1}H NMR ($CDCl_3$, 600 MHz)





Dimethyl 2-[(6,7-diphenyl-5H-indeno[5,6-d][1,3]dioxol-5-yl)methyl]malonate (3f)

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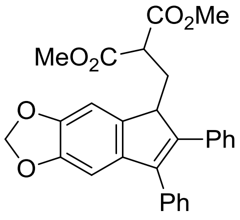
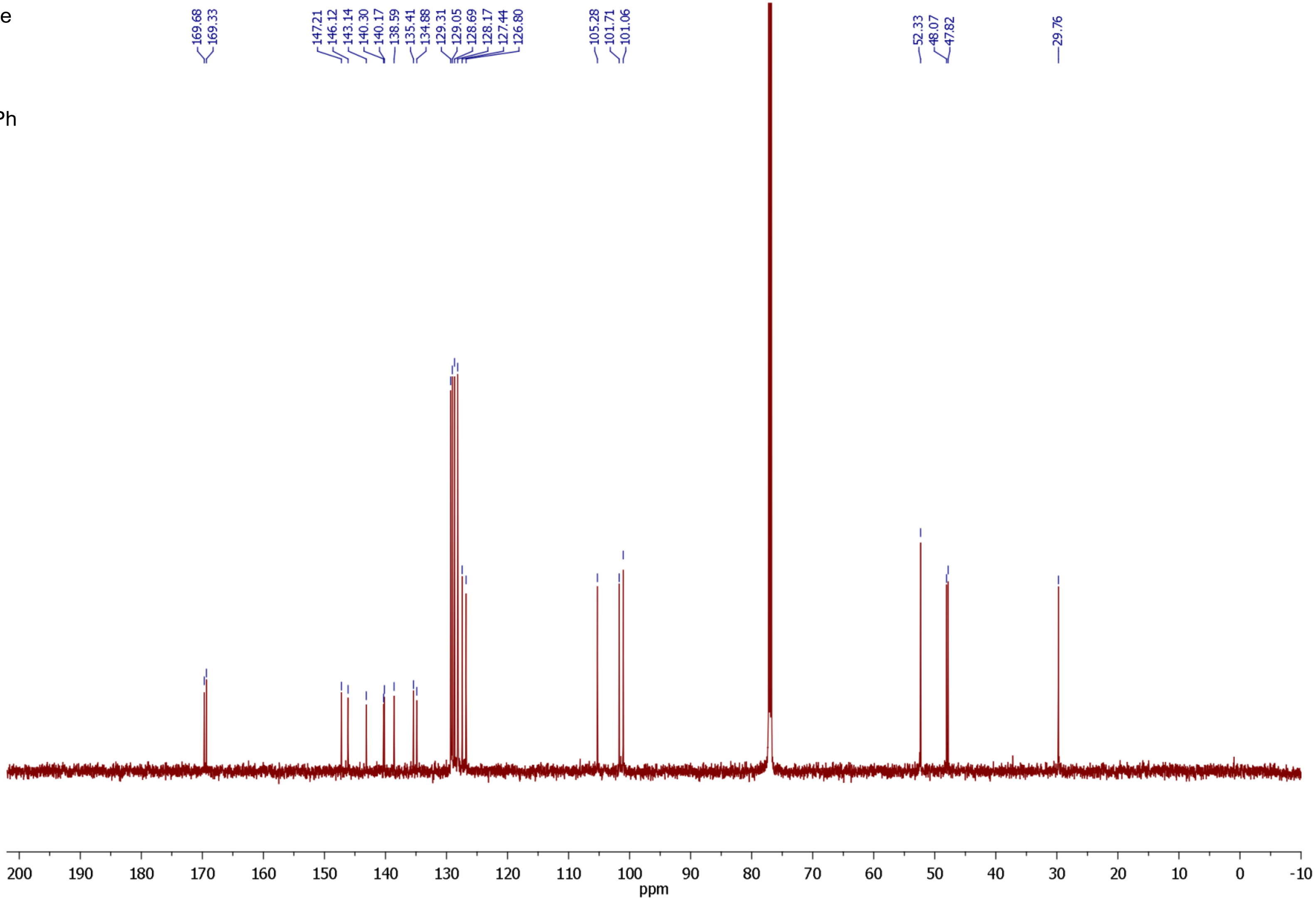
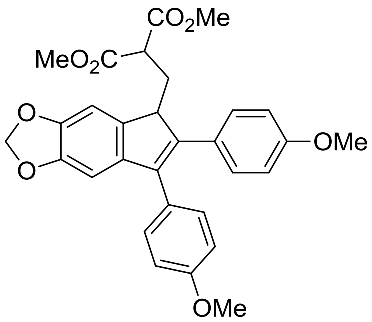
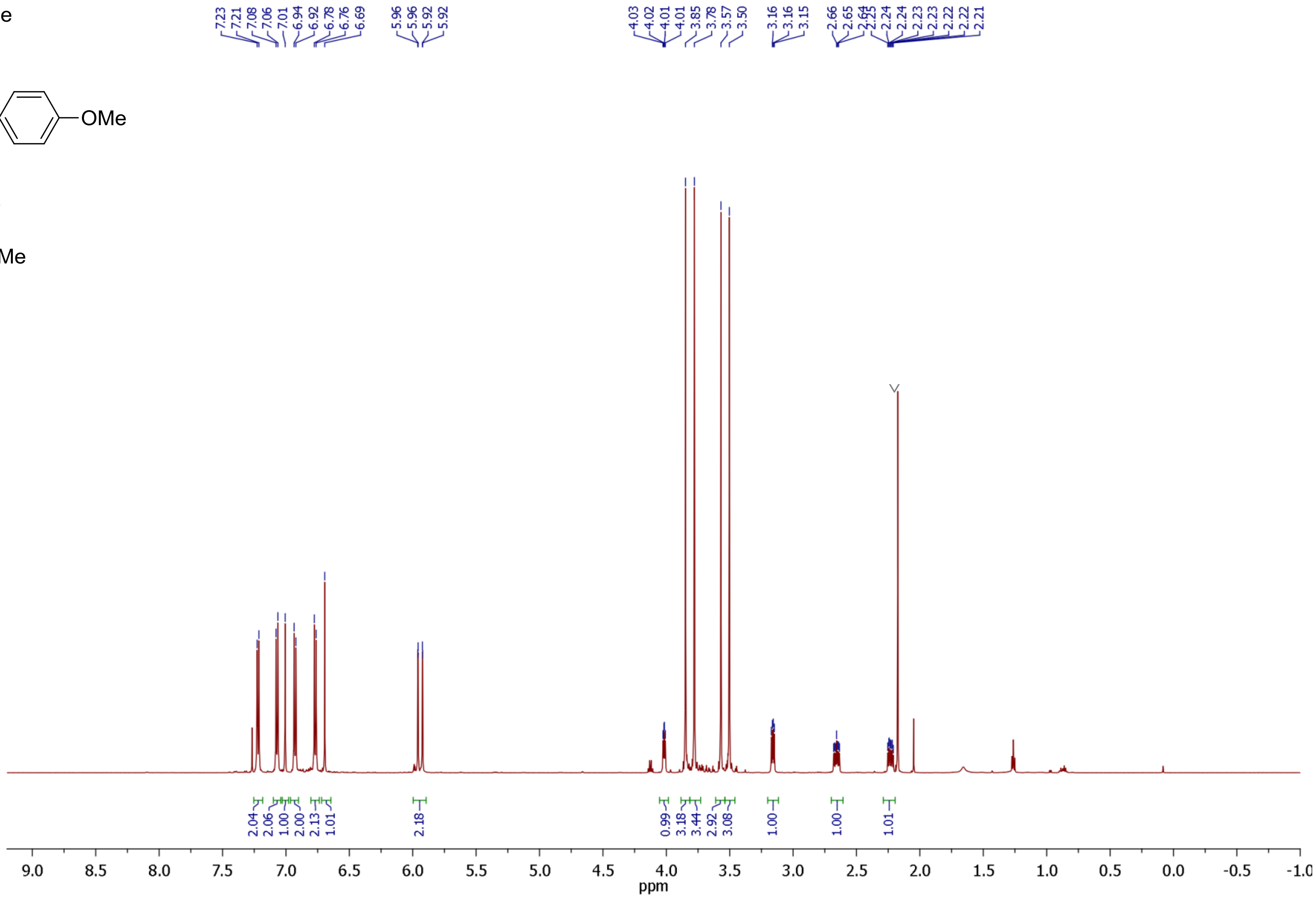




Dimethyl 2-{[6,7-bis(4-methoxyphenyl)-5*H*-indeno[5,6-*d*][1,3]dioxol-5-yl]methyl}malonate (3g)

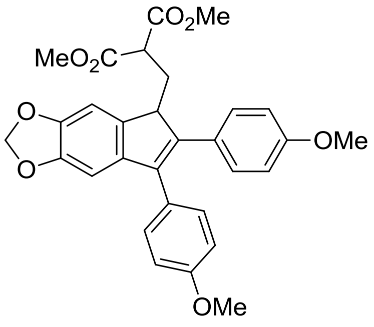
^{1}H NMR ($CDCl_3$, 600 MHz)

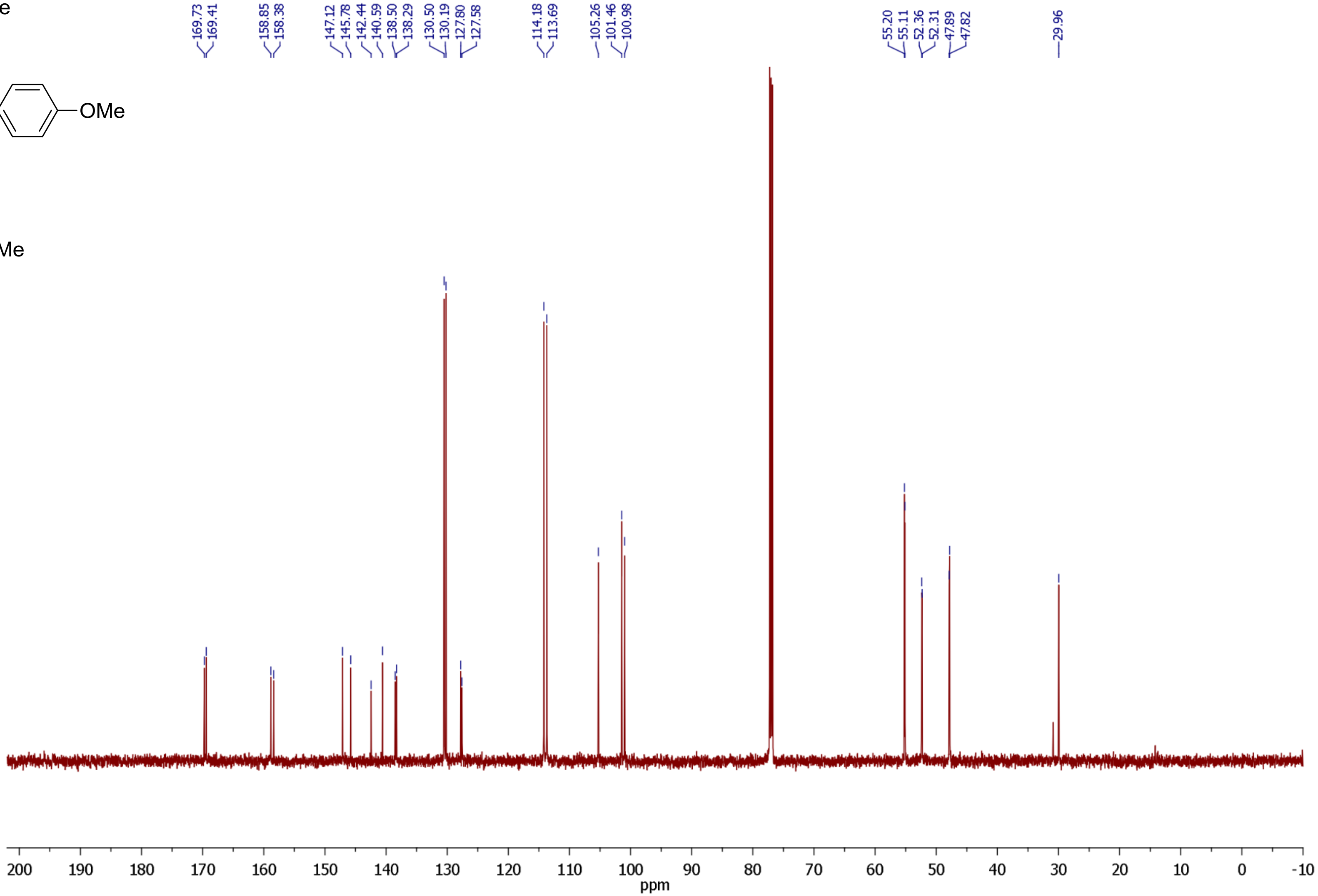




Dimethyl 2-{[6,7-bis(4-methoxyphenyl)-5*H*-indeno[5,6-*d*][1,3]dioxol-5-yl]methyl}malonate (3g)

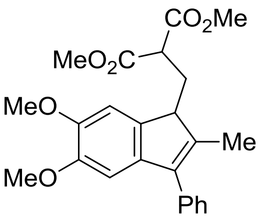
^{13}C NMR ($CDCl_3$, 150 MHz)

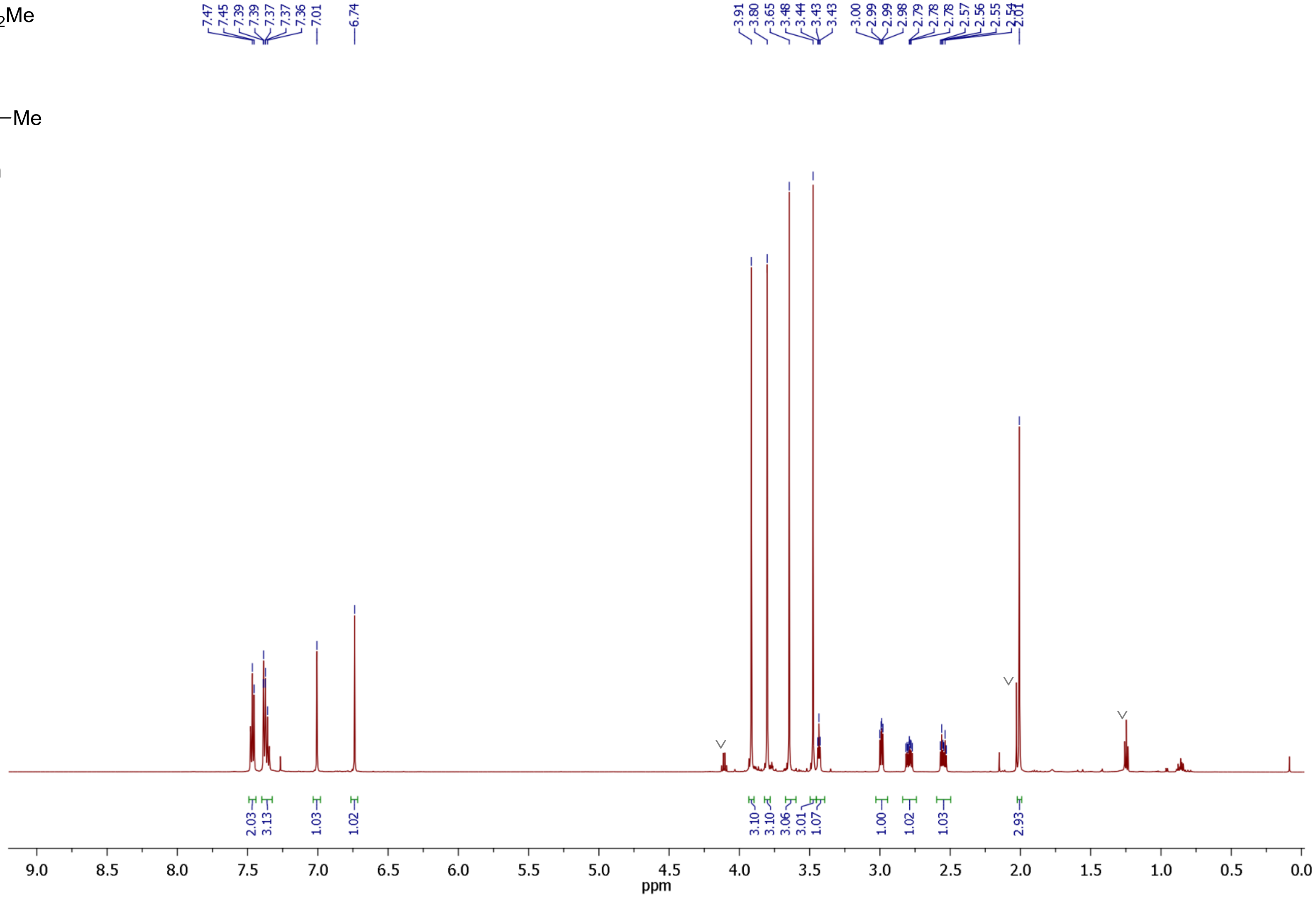




Dimethyl 2-[(5,6-dimethoxy-2-methyl-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3h)

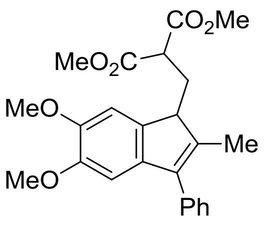
^{1}H NMR ($CDCl_3$, 600 MHz)

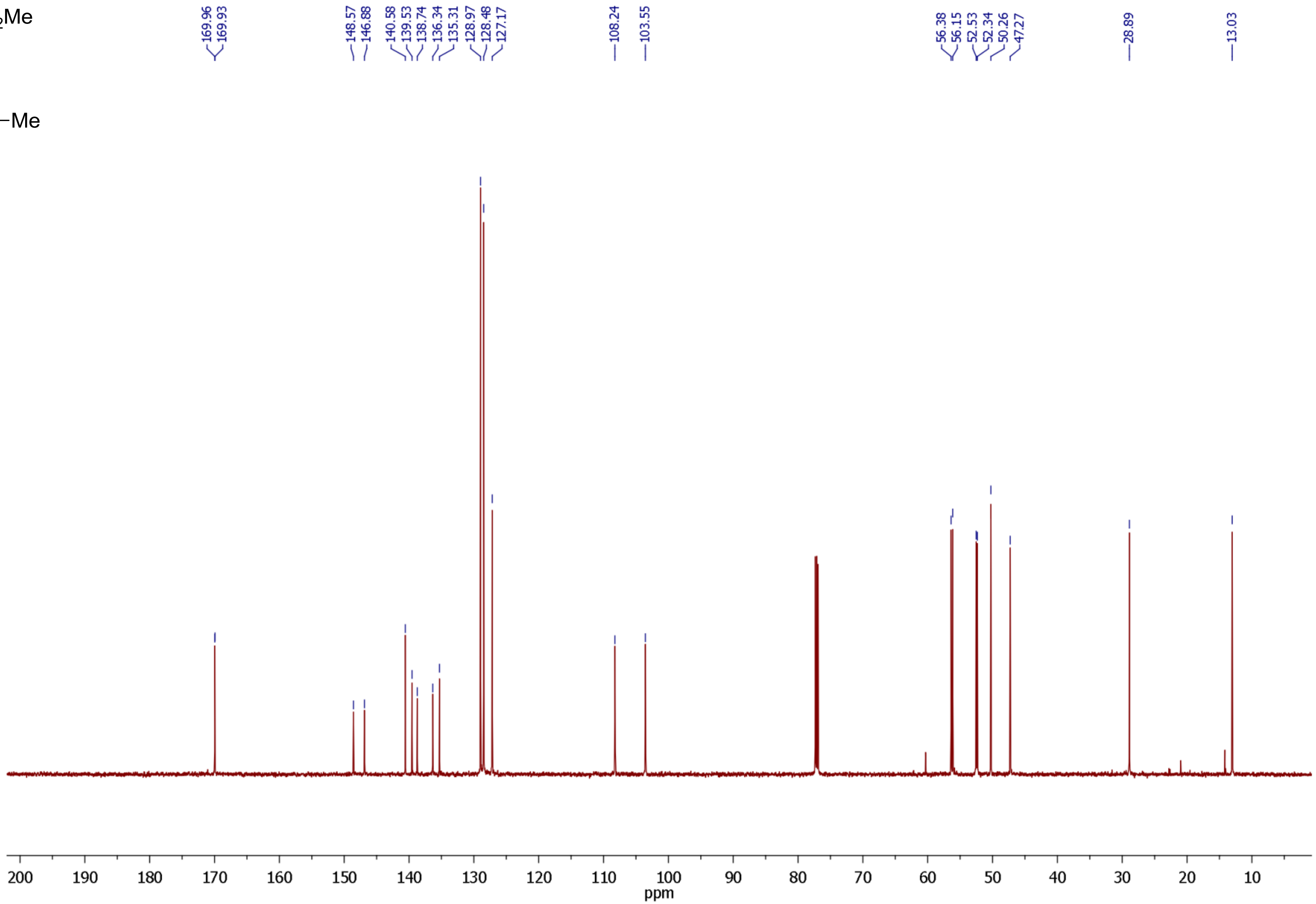




Dimethyl 2-[(5,6-dimethoxy-2-methyl-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3h)

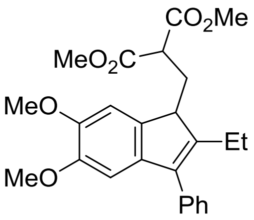
^{13}C NMR ($CDCl_3$, 150 MHz)

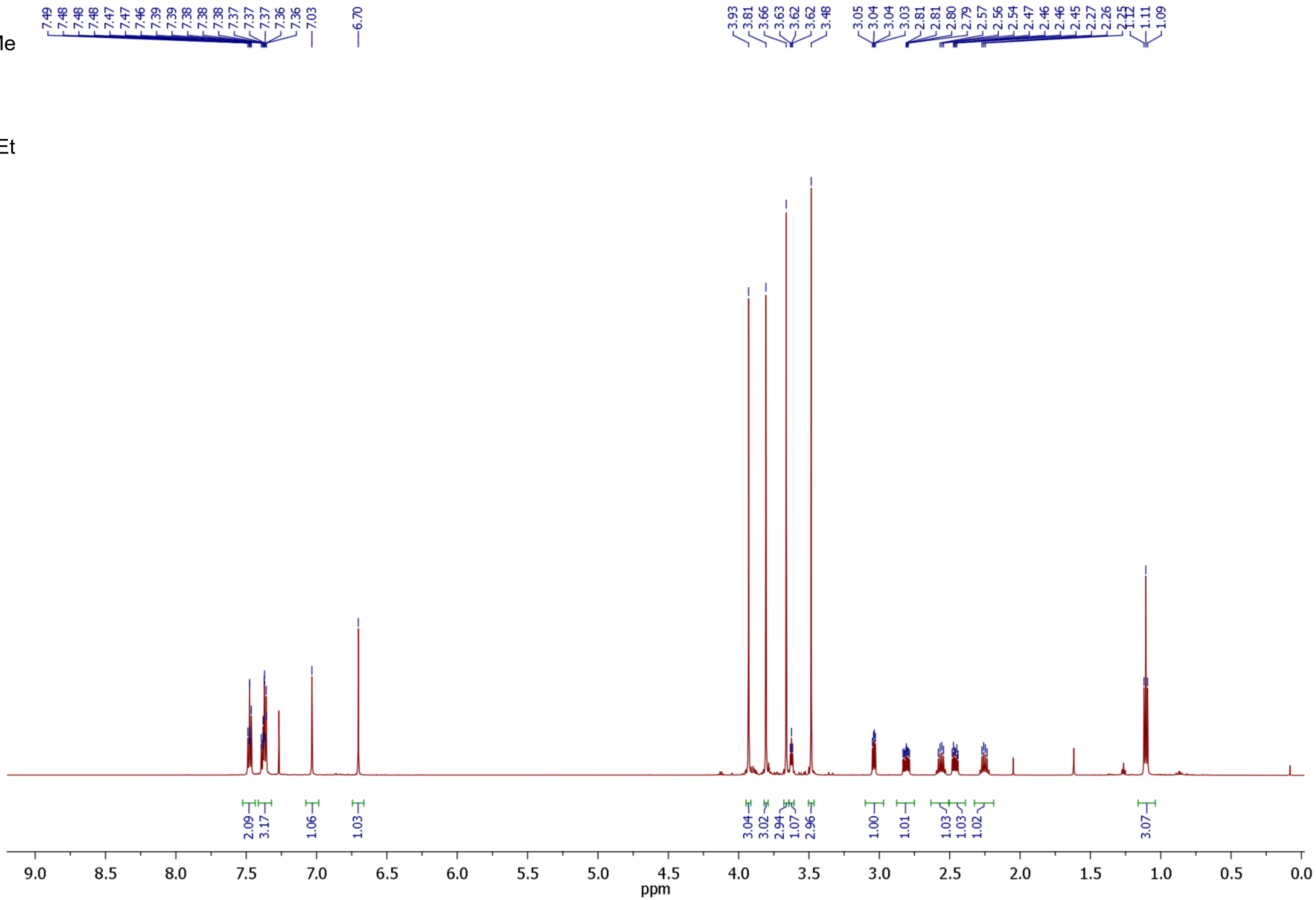




Dimethyl 2-[(2-ethyl-5,6-dimethoxy-3-phenyl-1H-inden-1-yl)methyl]malonate (3i)

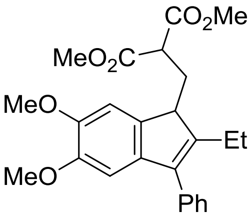
^{1}H NMR ($CDCl_3$, 600 MHz)

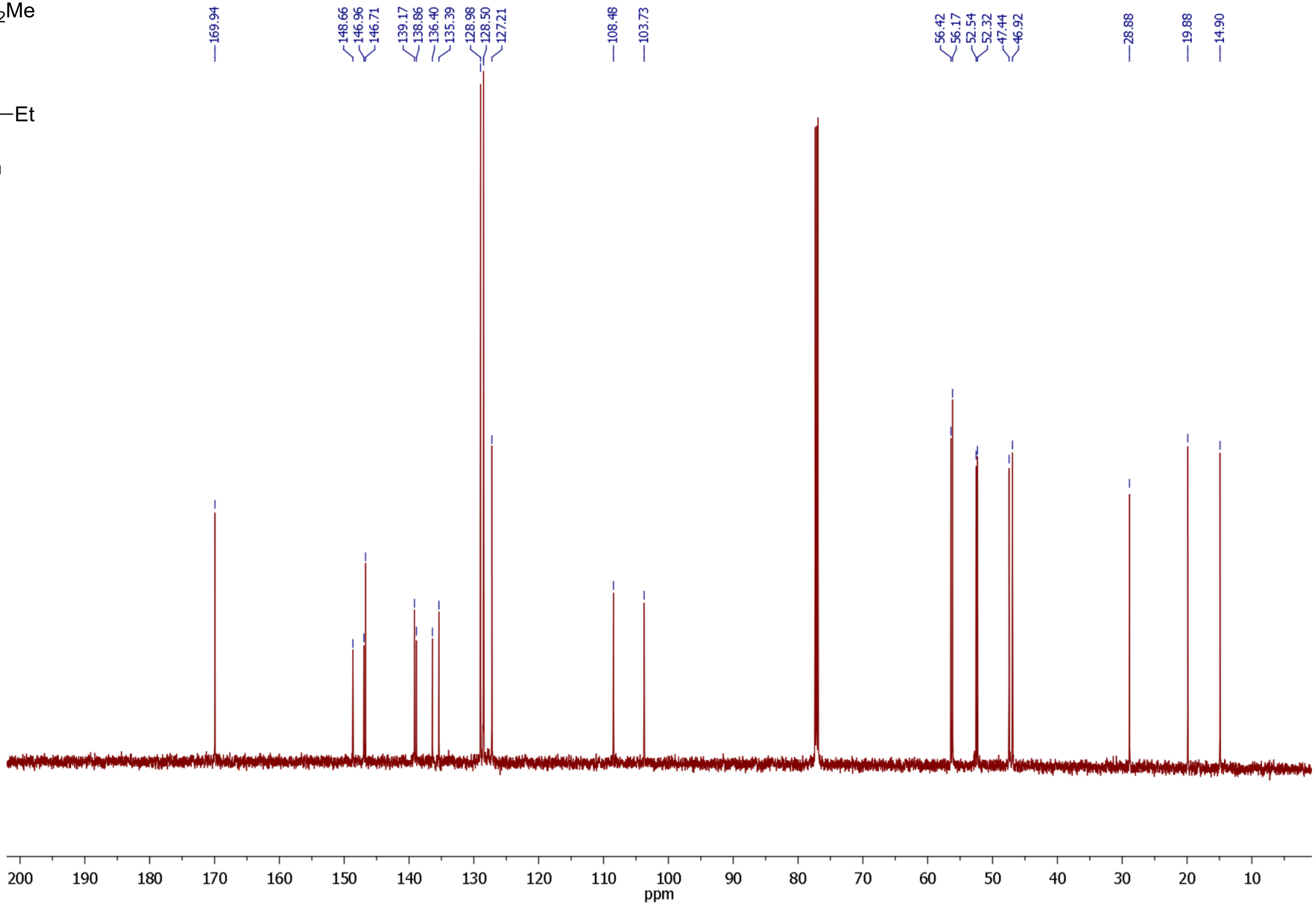




Dimethyl 2-[(2-ethyl-5,6-dimethoxy-3-phenyl-1H-inden-1-yl)methyl]malonate (3i)

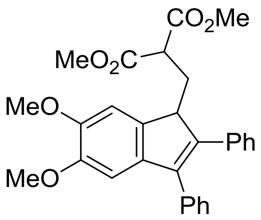
^{13}C NMR ($CDCl_3$, 150 MHz)

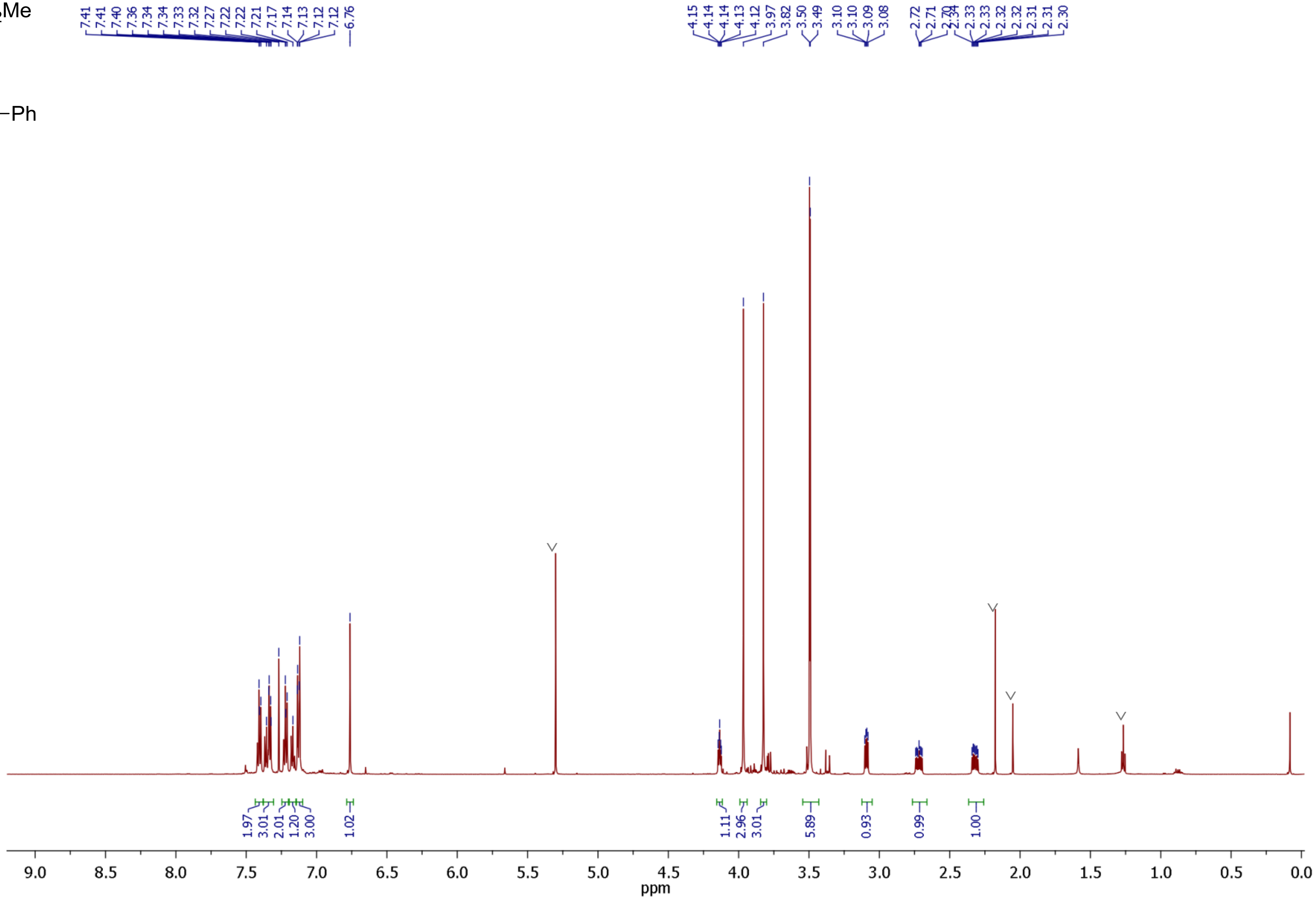




Dimethyl 2-[(5,6-dimethoxy-2,3-diphenyl-1*H*-inden-1-yl)methyl]malonate (3j)

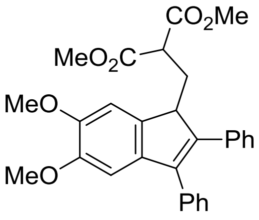
^{1}H NMR (CDCl$_3$, 600 MHz)

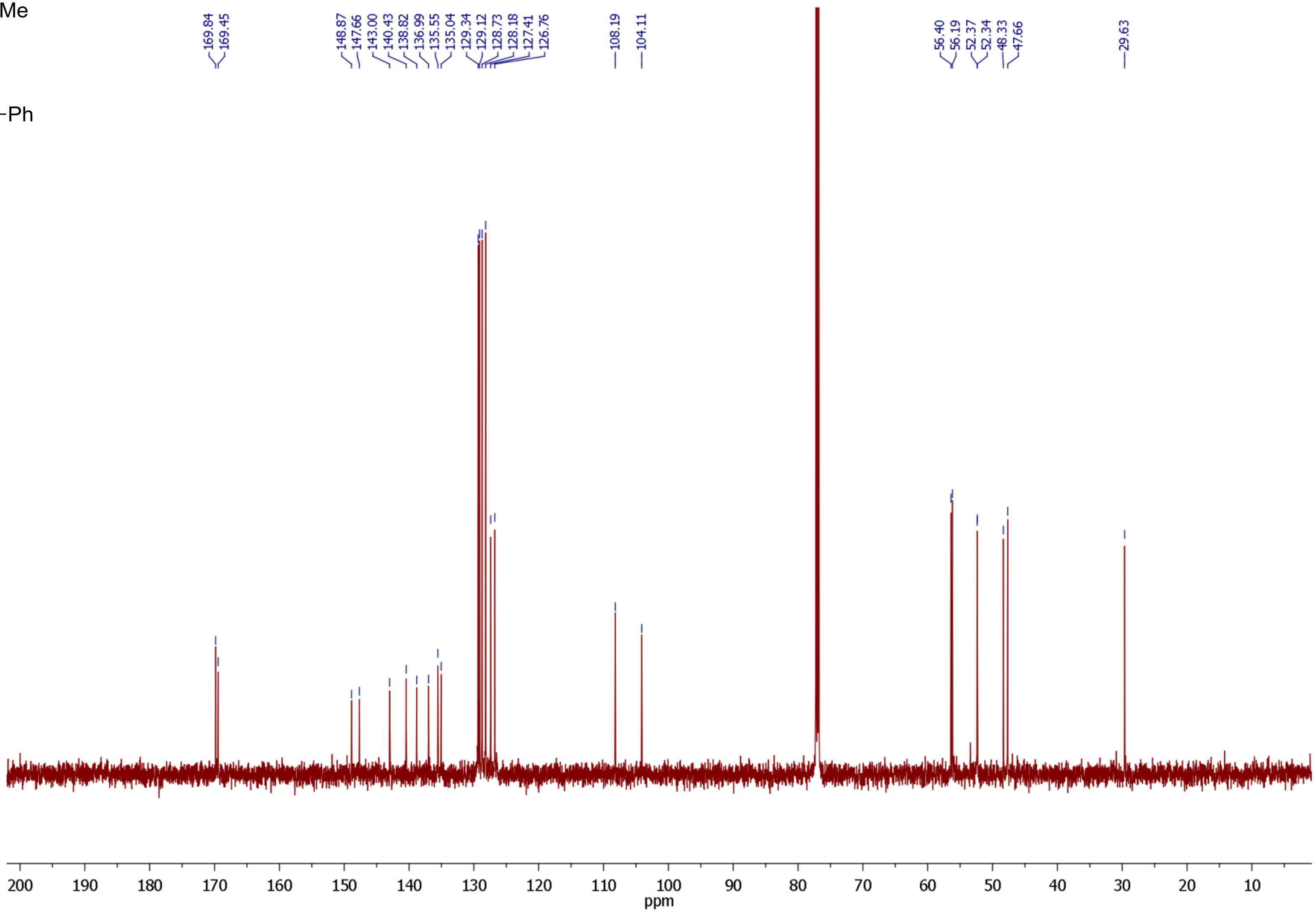




Dimethyl 2-[(5,6-dimethoxy-2,3-diphenyl-1*H*-inden-1-yl)methyl]malonate (3j)

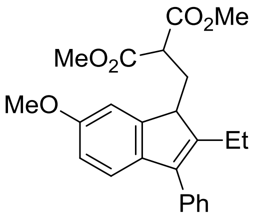
^{13}C NMR ($CDCl_3$, 150 MHz)

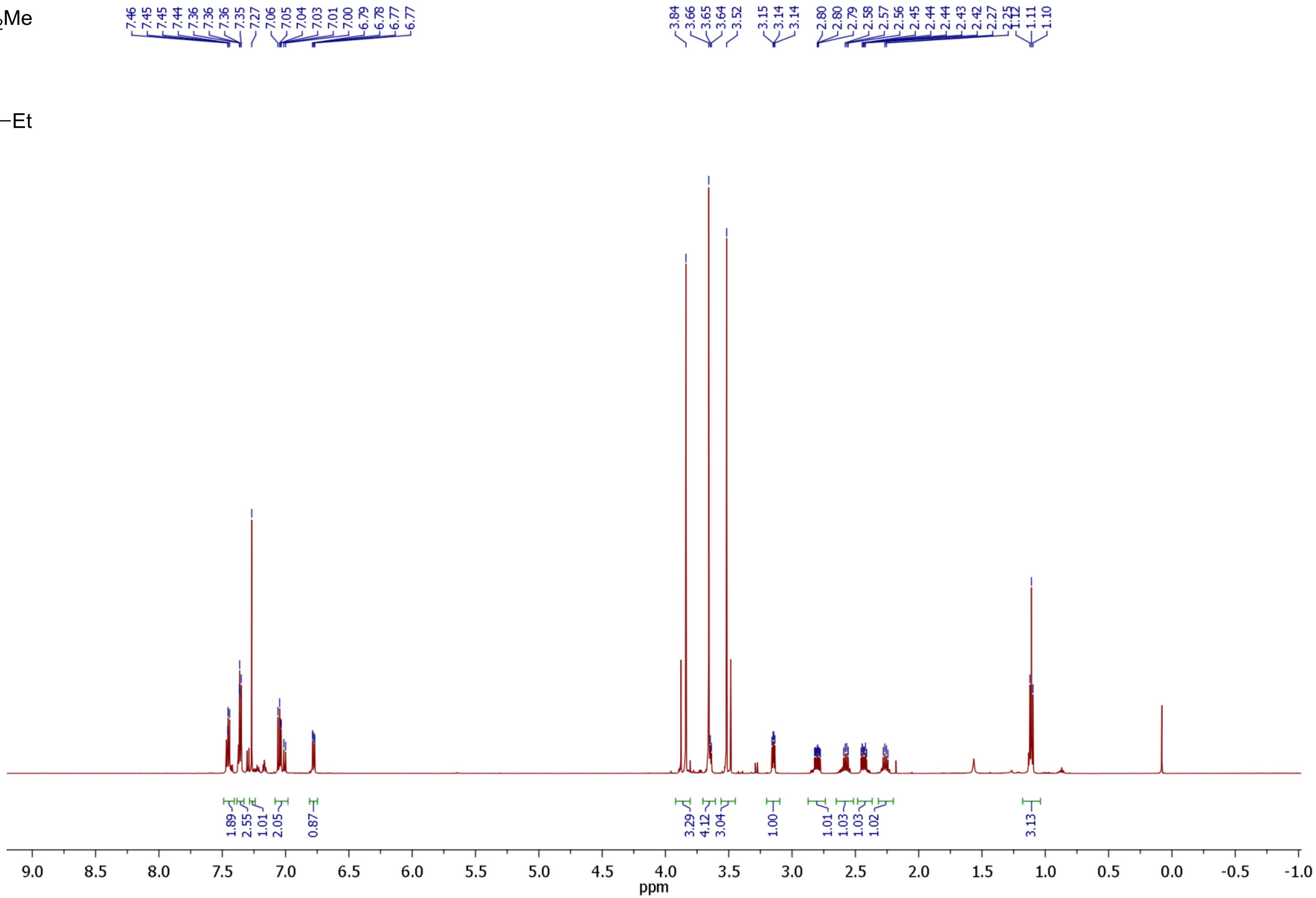




Dimethyl 2-[(2-ethyl-6-methoxy-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3k)

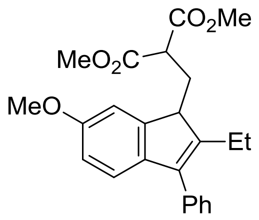
^{1}H NMR ($CDCl_3$, 600 MHz)

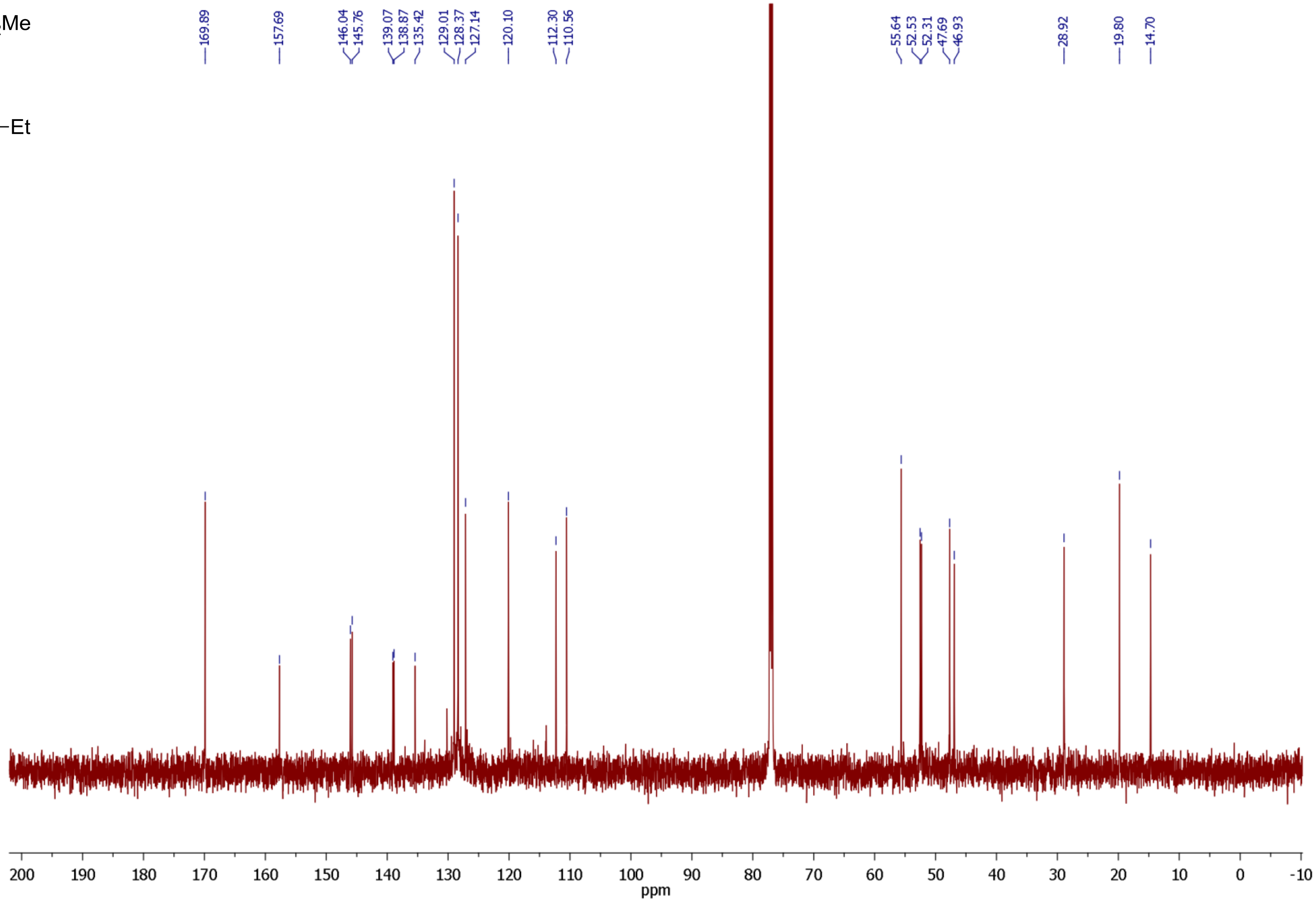




Dimethyl 2-[(2-ethyl-6-methoxy-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3k)

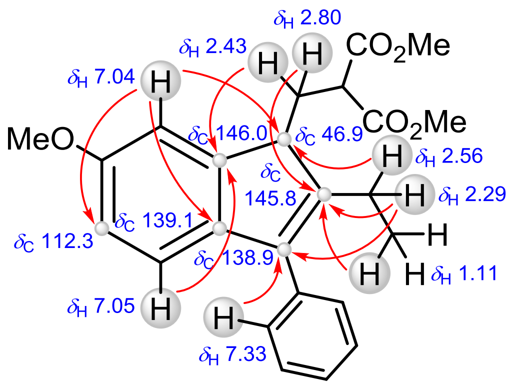
^{13}C NMR ($CDCl_3$, 150 MHz)

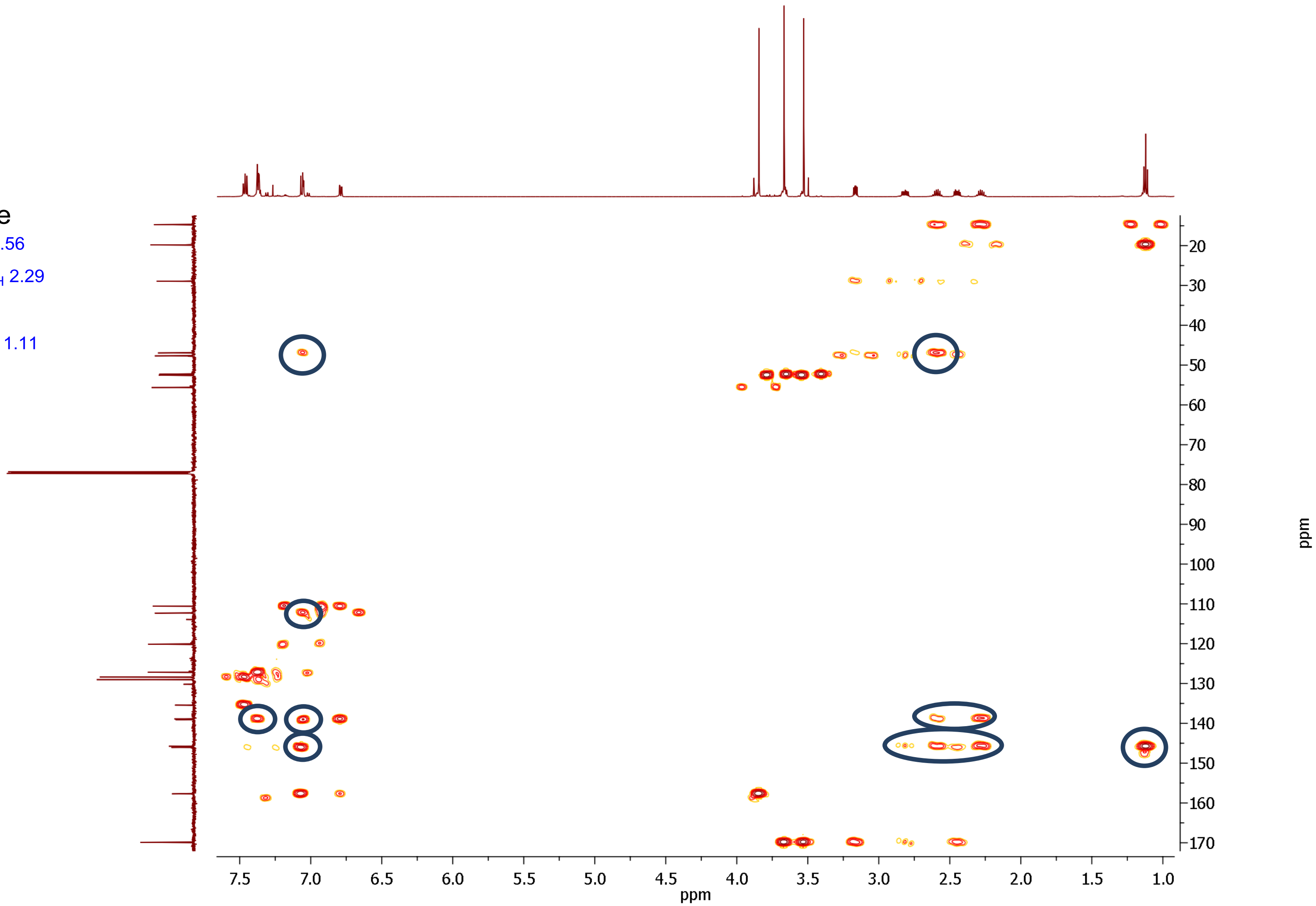




Dimethyl 2-[(2-ethyl-6-methoxy-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3k)

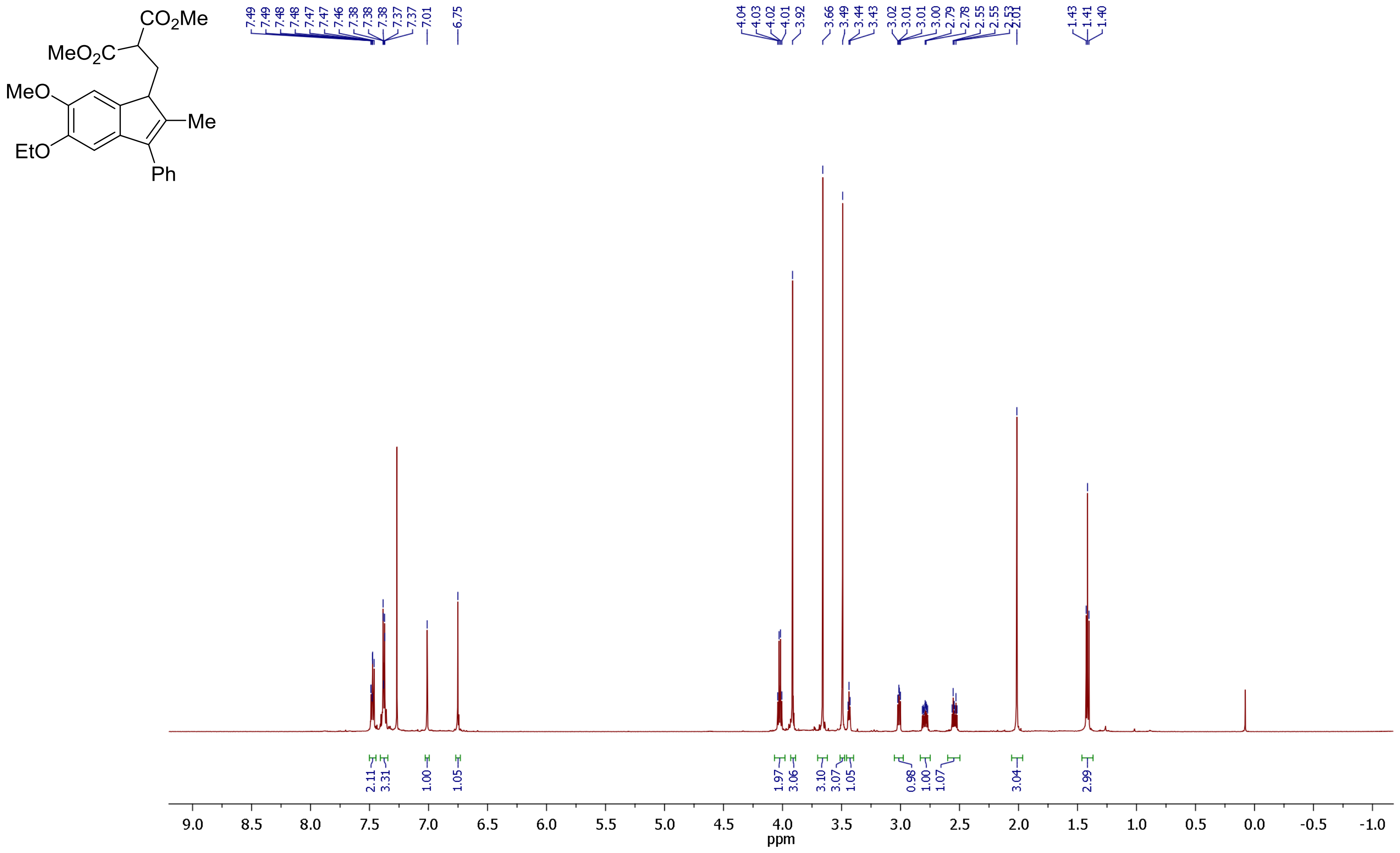
^{1}H-^{13}C HMBC ($CDCl_3$)





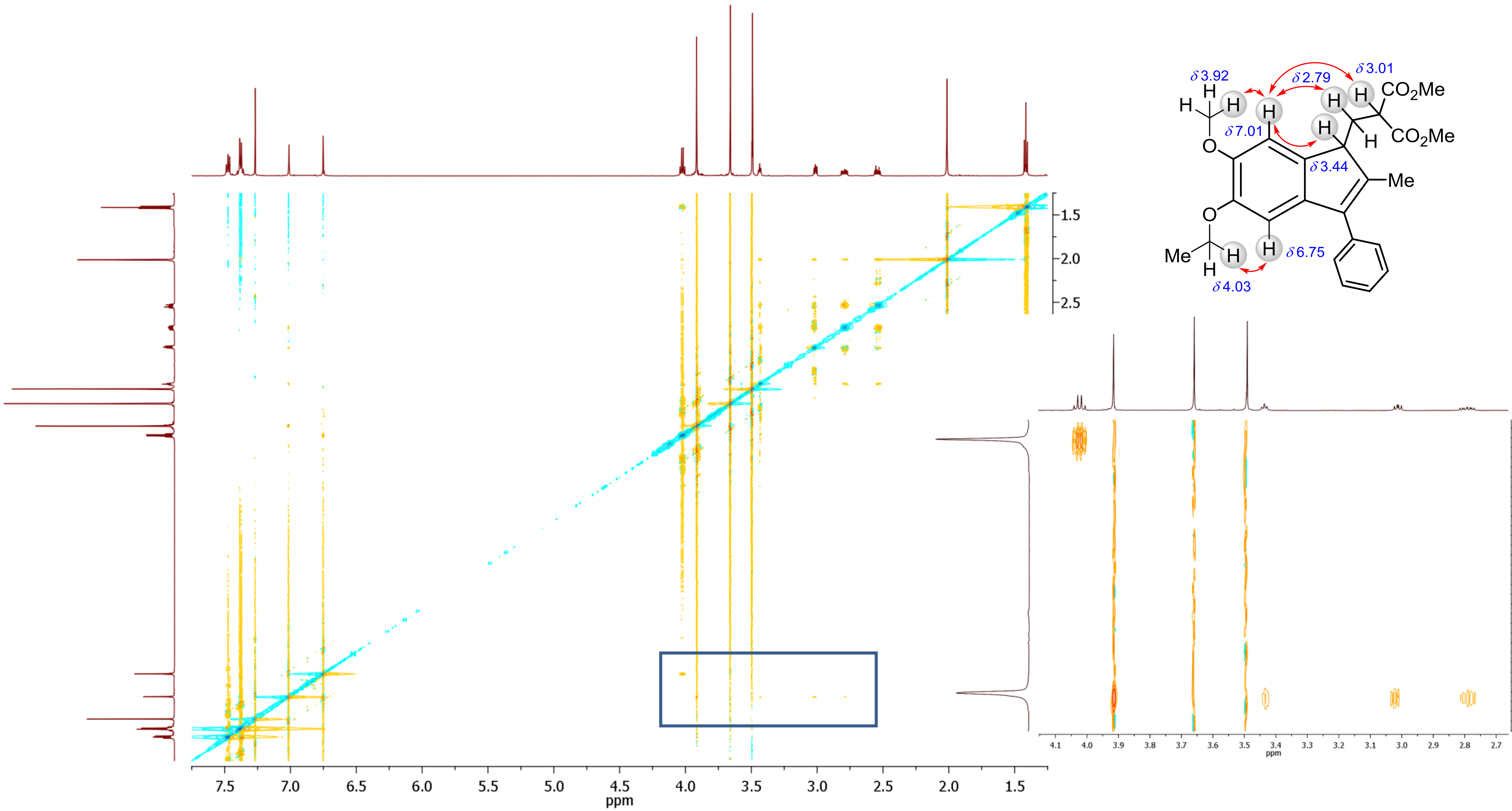
Dimethyl 2-[(5-ethoxy-6-methoxy-2-methyl-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3l)

^{1}H NMR ($CDCl_3$, 600 MHz)



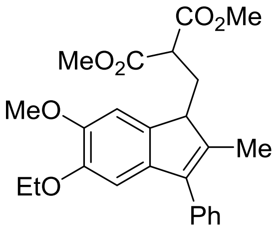
Dimethyl 2-[(5-ethoxy-6-methoxy-2-methyl-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3l)

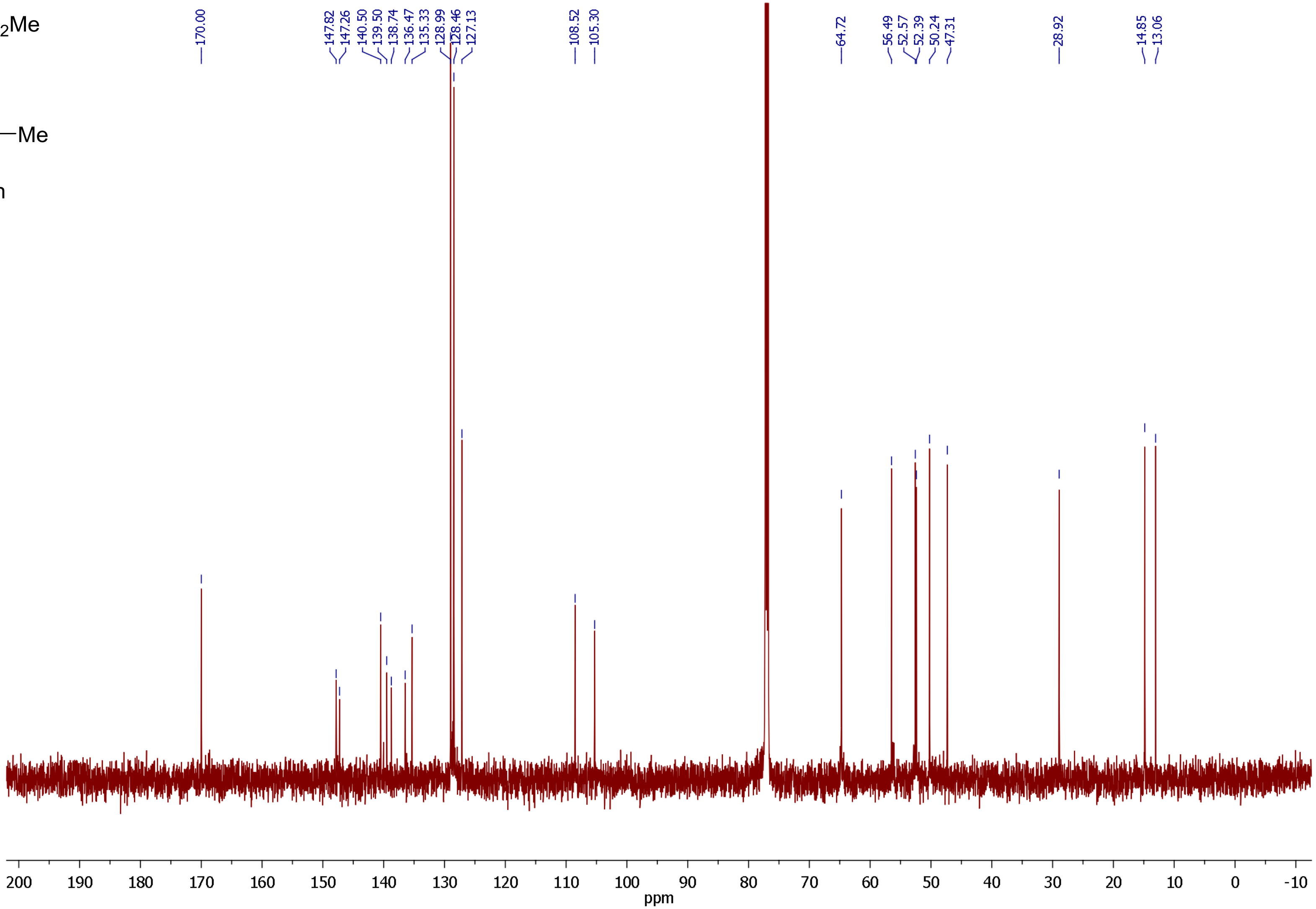
^{1}H-^{1}H NOESY ($CDCl_3$)



Dimethyl 2-[(5-ethoxy-6-methoxy-2-methyl-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3l)

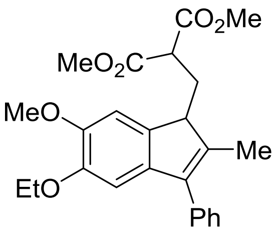
^{13}C NMR ($CDCl_3$, 150 MHz)

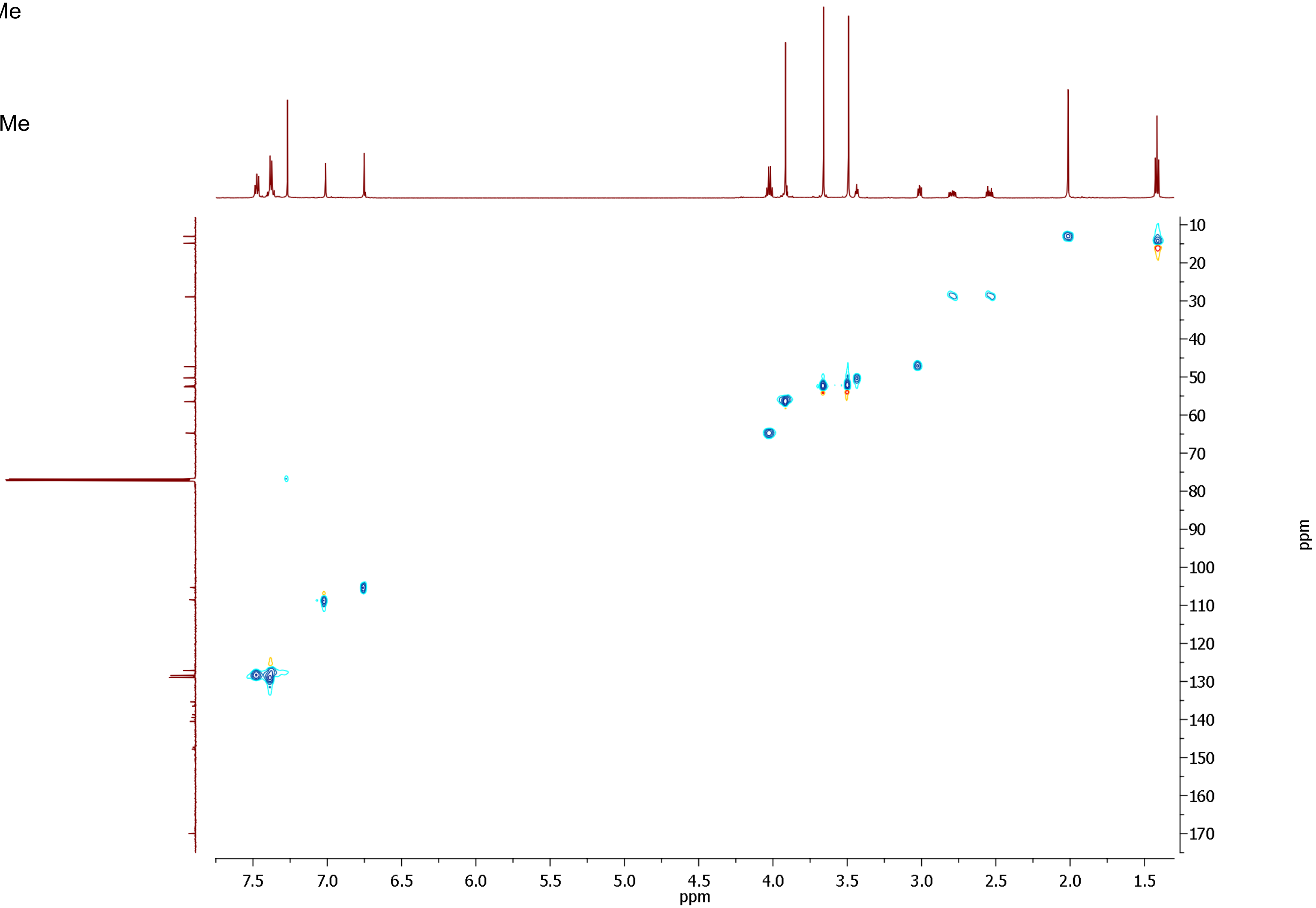




Dimethyl 2-[(5-ethoxy-6-methoxy-2-methyl-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3l)

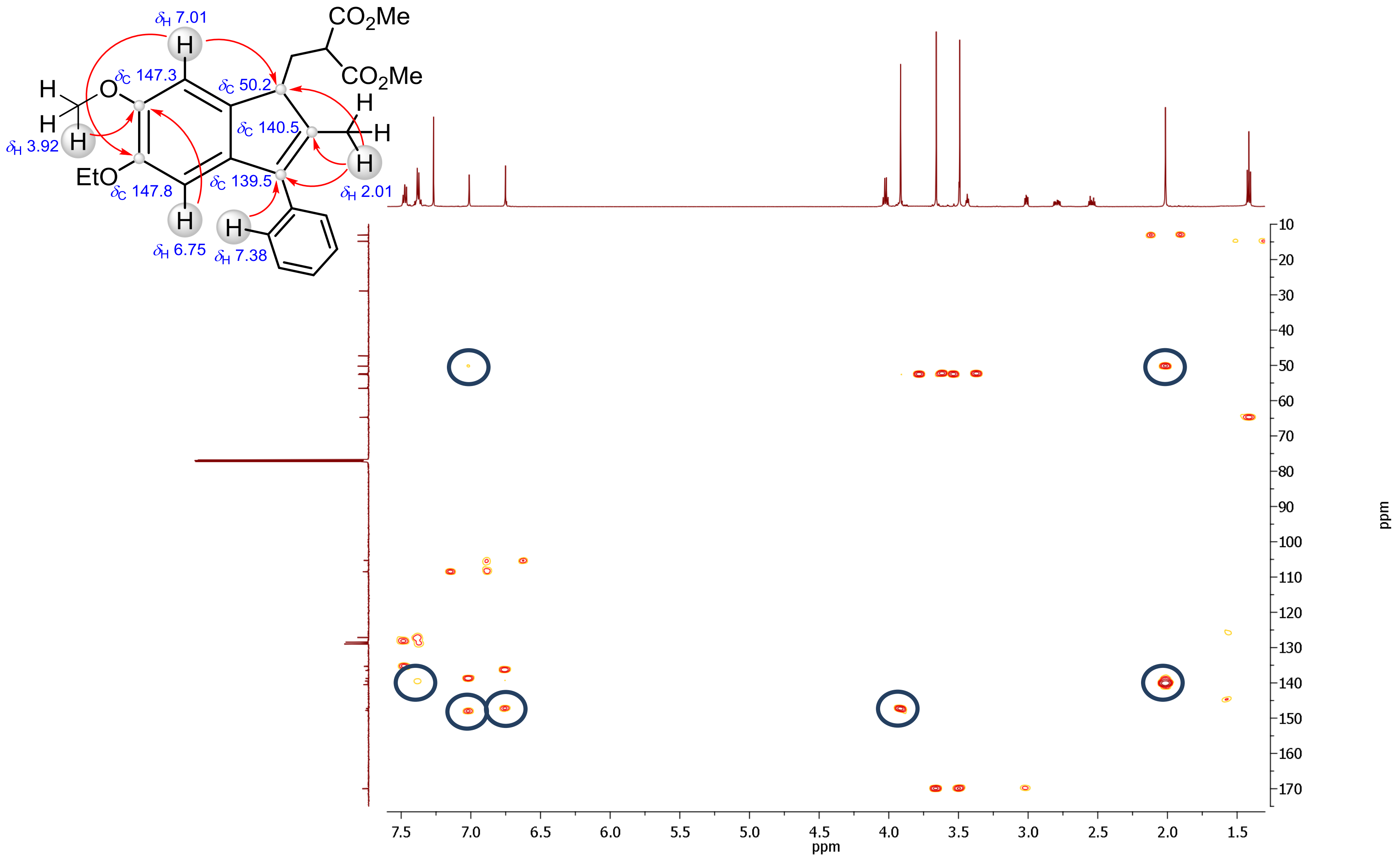
^{1}H-^{13}C HSQC ($CDCl_3$)





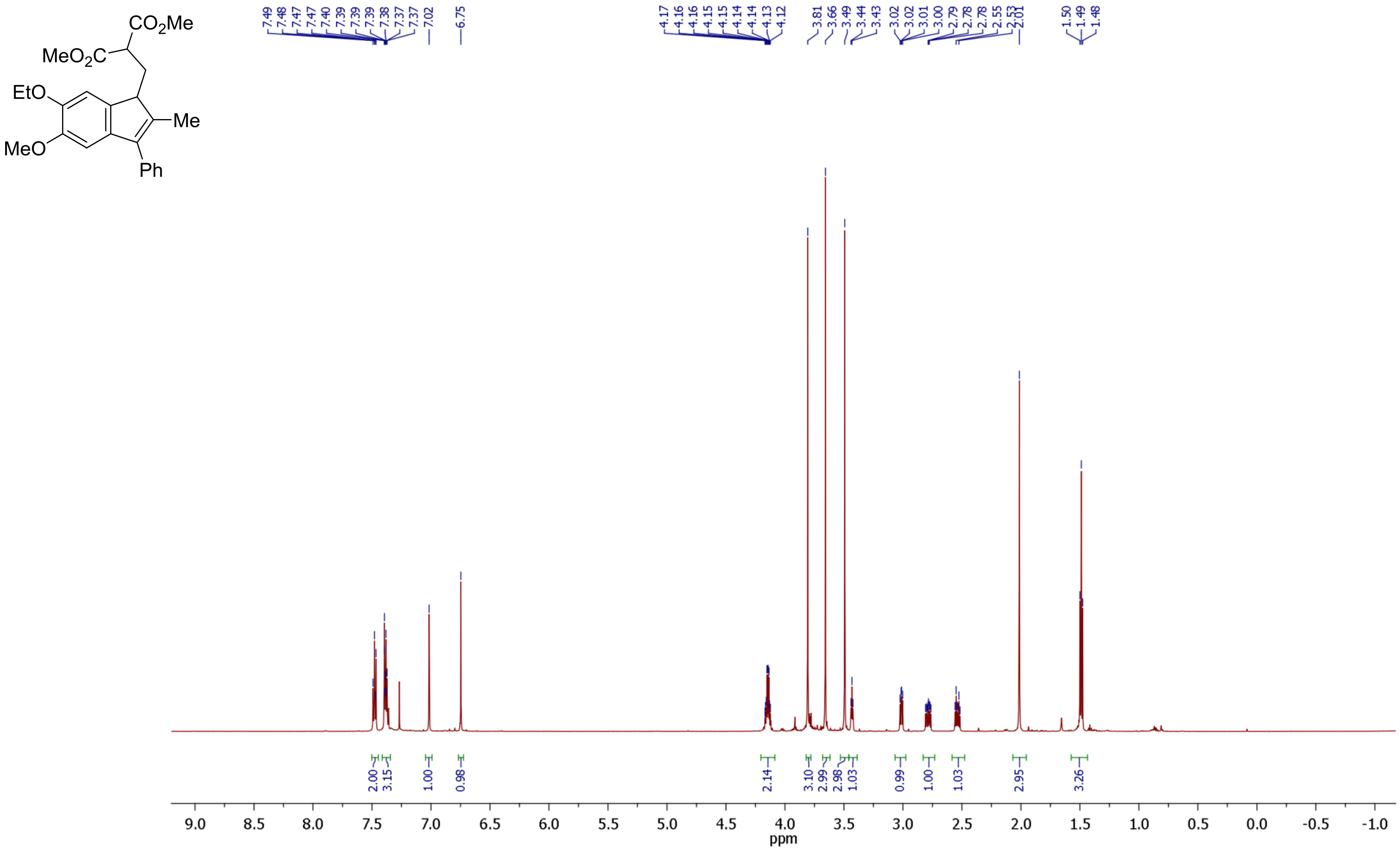
Dimethyl 2-[(5-ethoxy-6-methoxy-2-methyl-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3l)

^{1}H-^{13}C HMBC ($CDCl_3$)



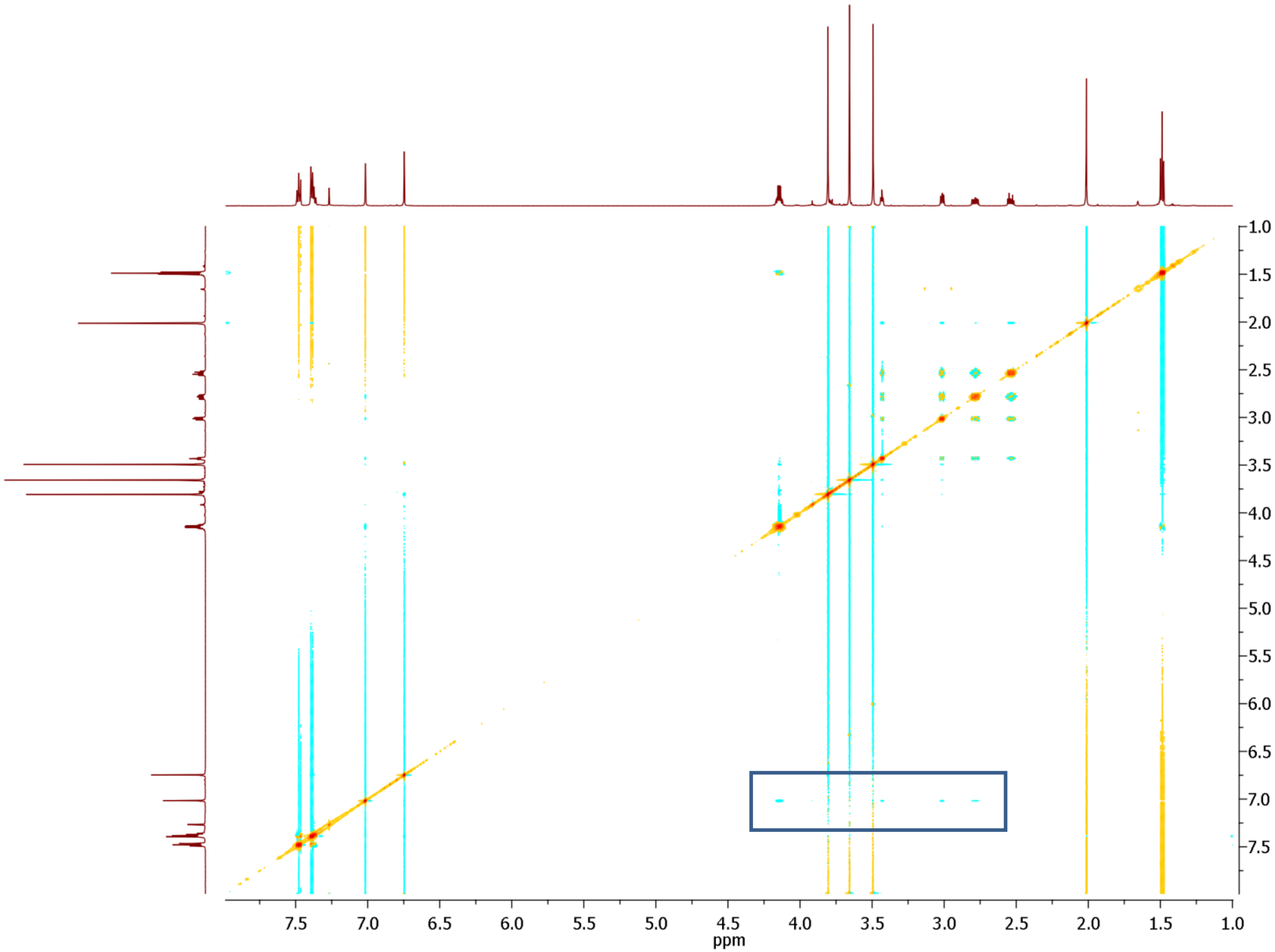
Dimethyl 2-[(6-ethoxy-5-methoxy-2-methyl-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3m)

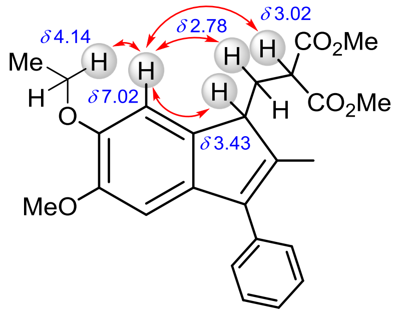
^{1}H NMR ($CDCl_3$, 600 MHz)

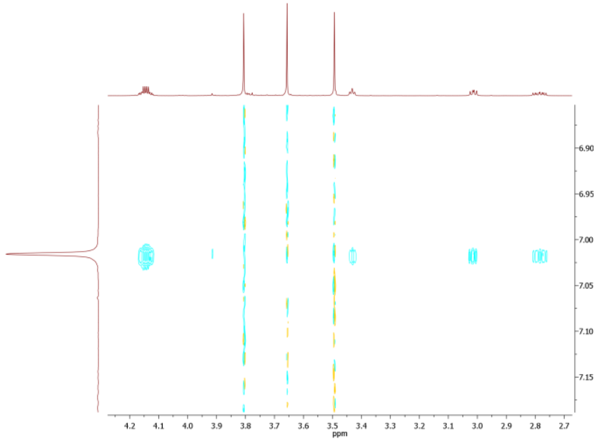


Dimethyl 2-[(6-ethoxy-5-methoxy-2-methyl-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3m)

^{1}H-^{1}H NOESY ($CDCl_3$)

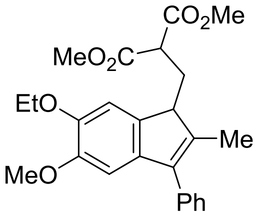


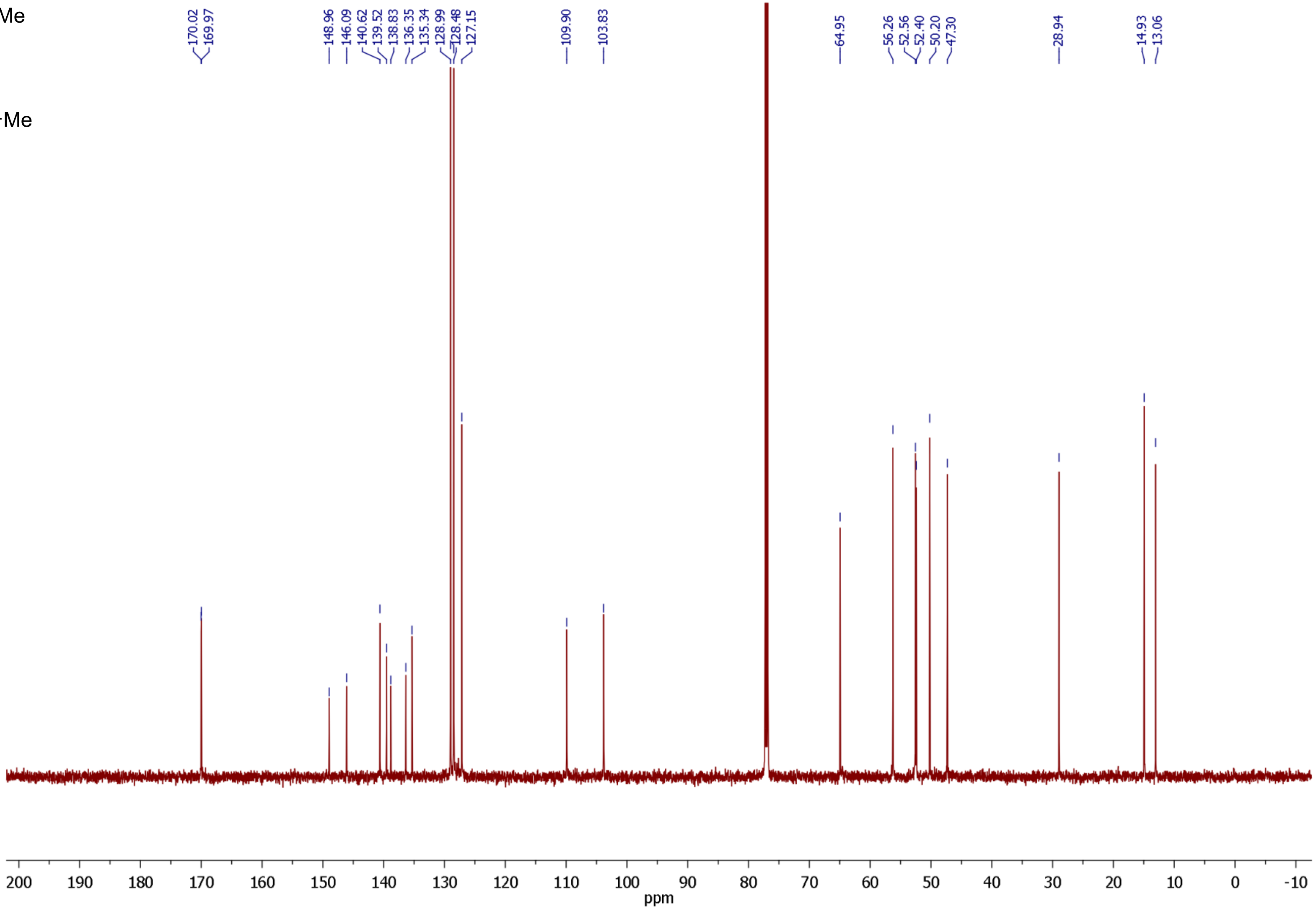




Dimethyl 2-[(6-ethoxy-5-methoxy-2-methyl-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3m)

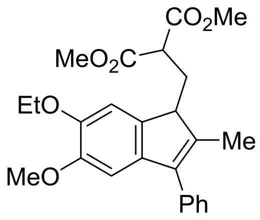
^{13}C NMR ($CDCl_3$, 150 MHz)

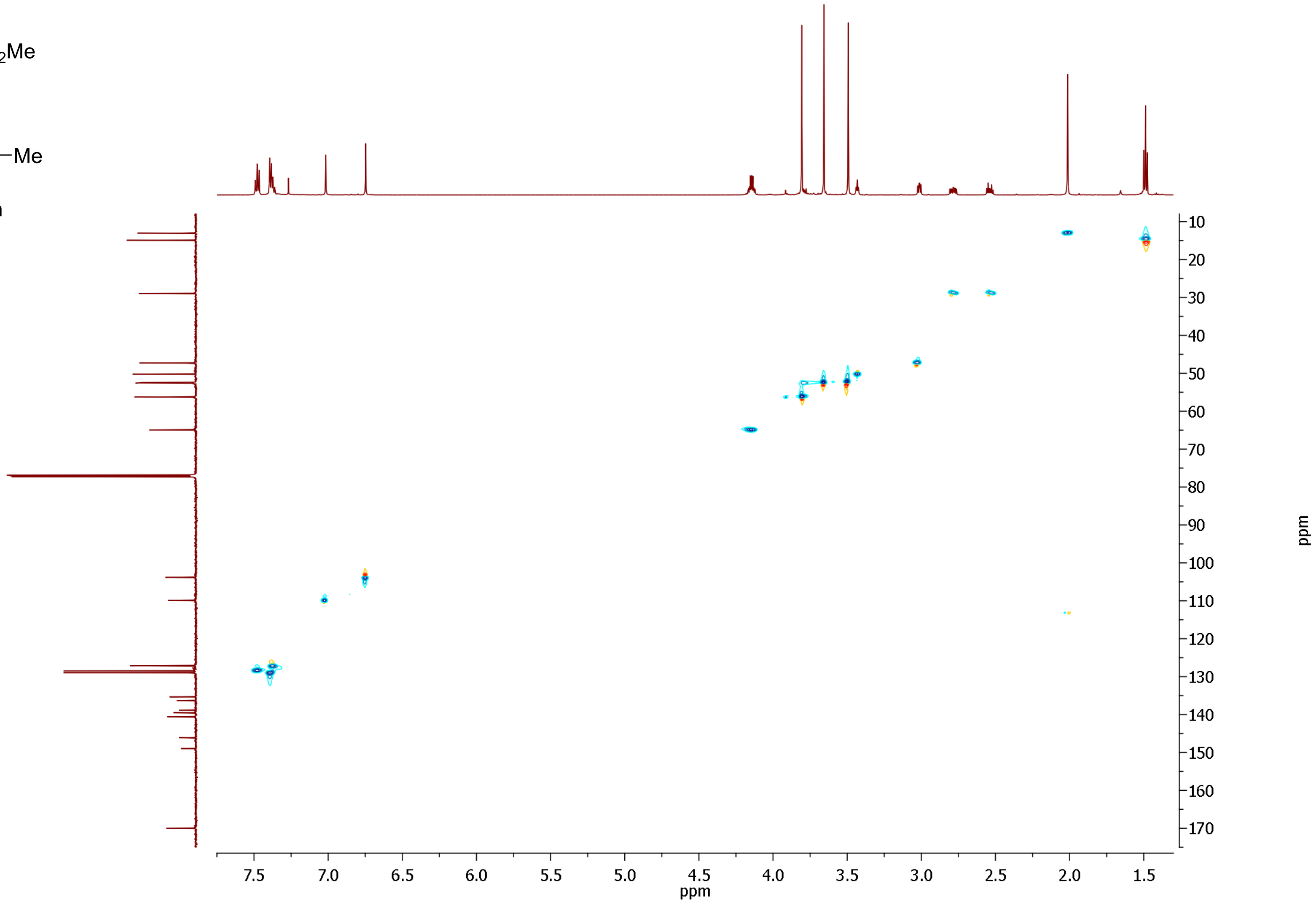




Dimethyl 2-[(6-ethoxy-5-methoxy-2-methyl-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3m)

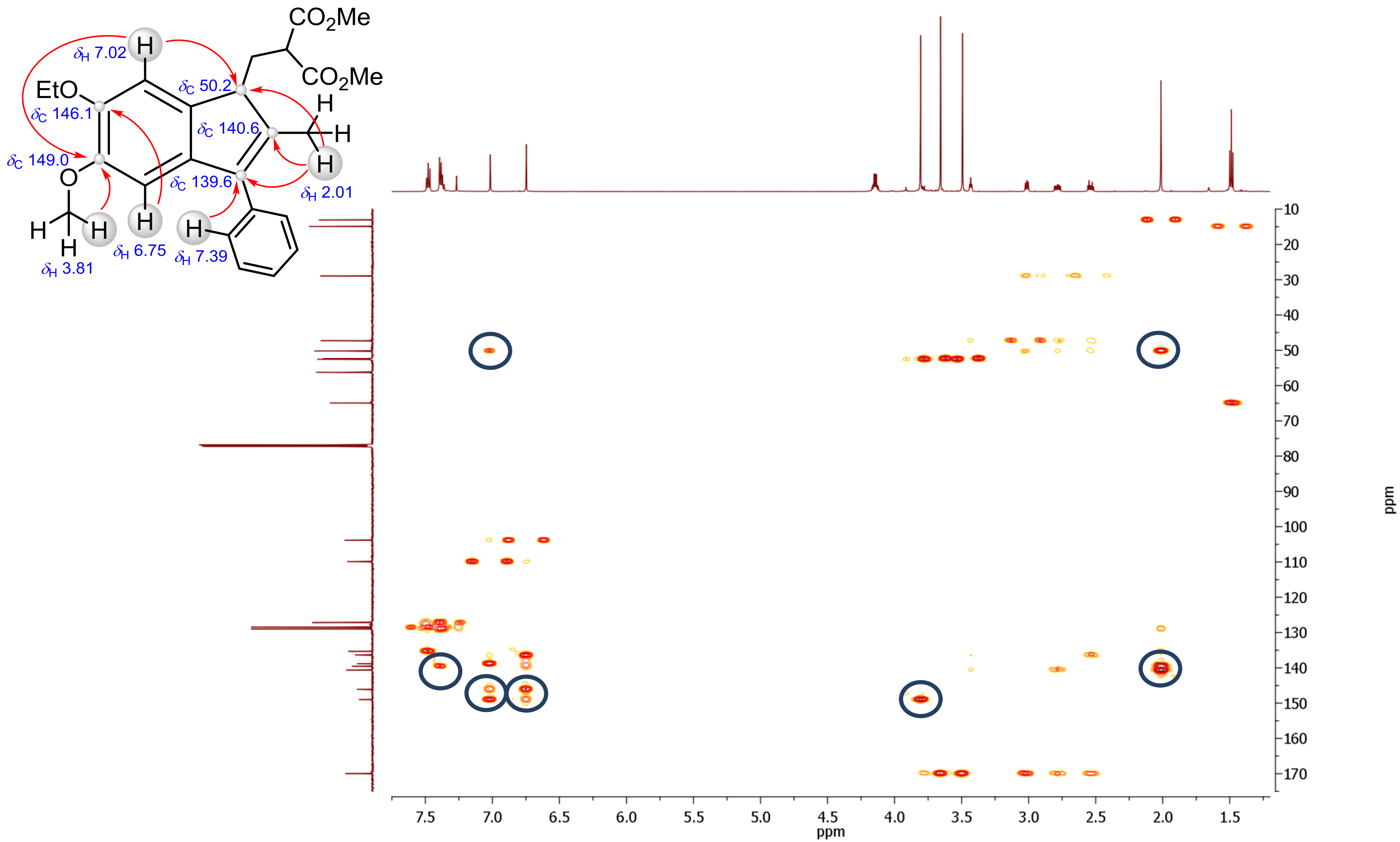
^{1}H-^{13}C HSQC ($CDCl_3$)





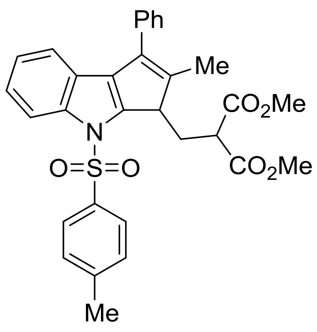
Dimethyl 2-[(6-ethoxy-5-methoxy-2-methyl-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3m)

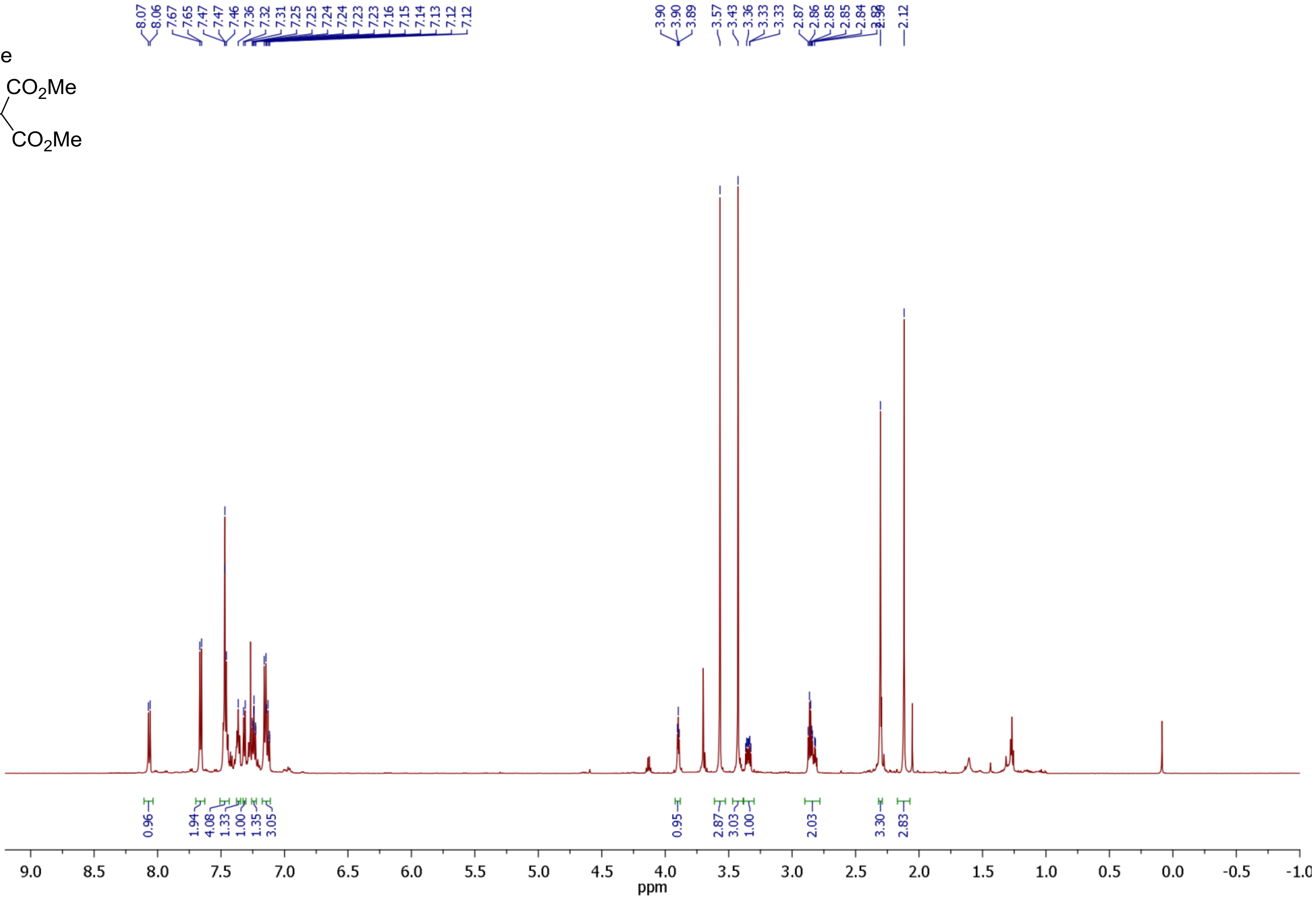
^{1}H-^{13}C HMBC ($CDCl_3$)



Dimethyl 2-[(2-methyl-3-phenyl-8-tosyl-3,4-dihydrocyclopenta[*b*]indol-1-yl)methyl]malonate (3n)

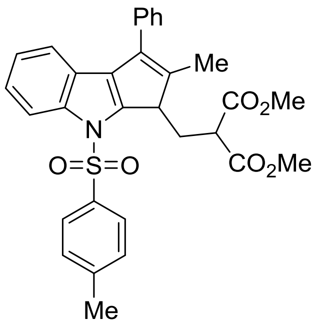
^{1}H NMR ($CDCl_3$, 600 MHz)

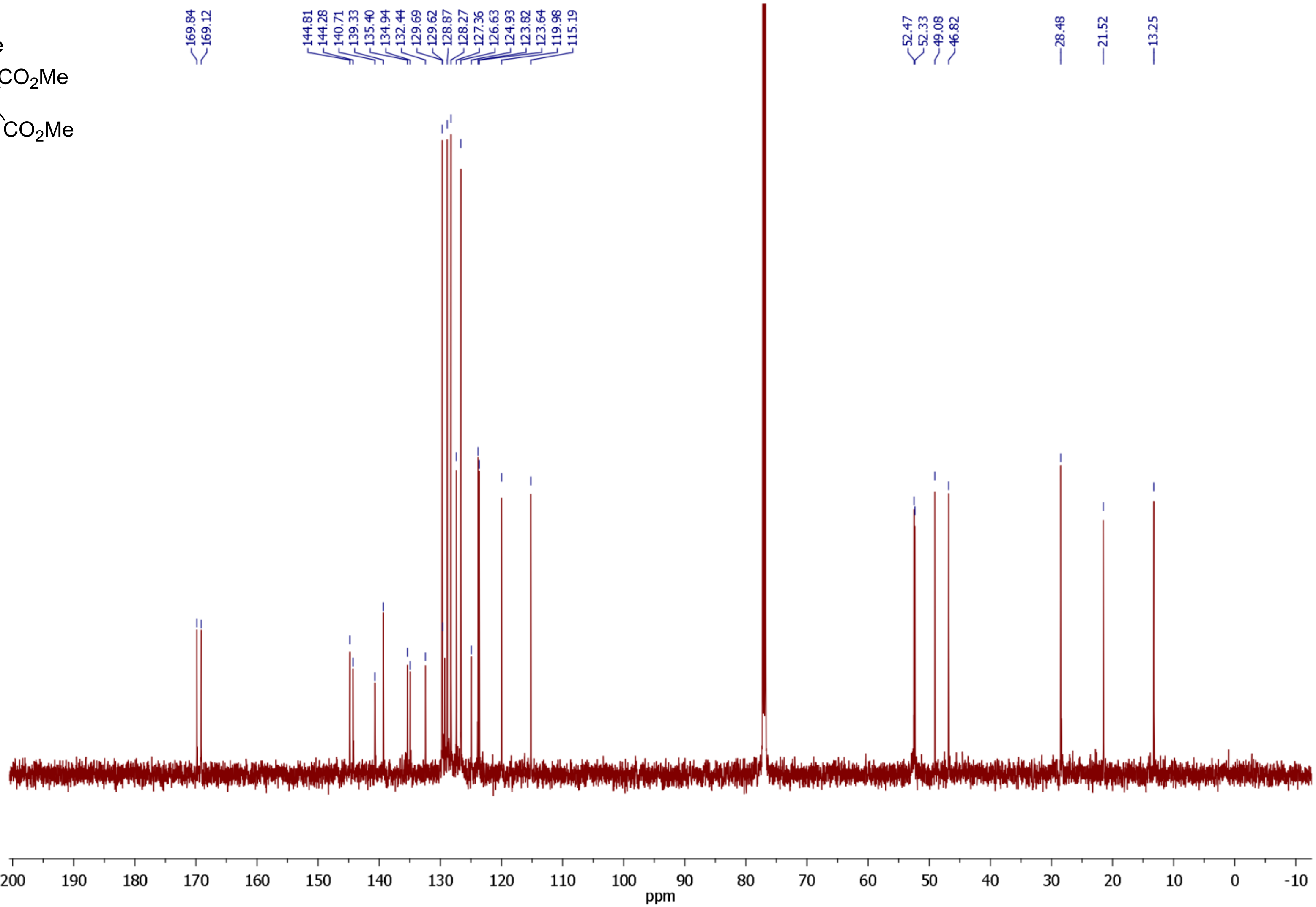




Dimethyl 2-[(2-methyl-3-phenyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indol-1-yl)methyl]malonate (3n)

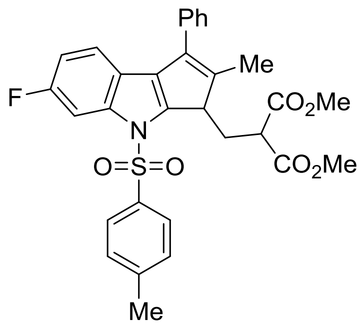
^{13}C NMR ($CDCl_3$, 150 MHz)

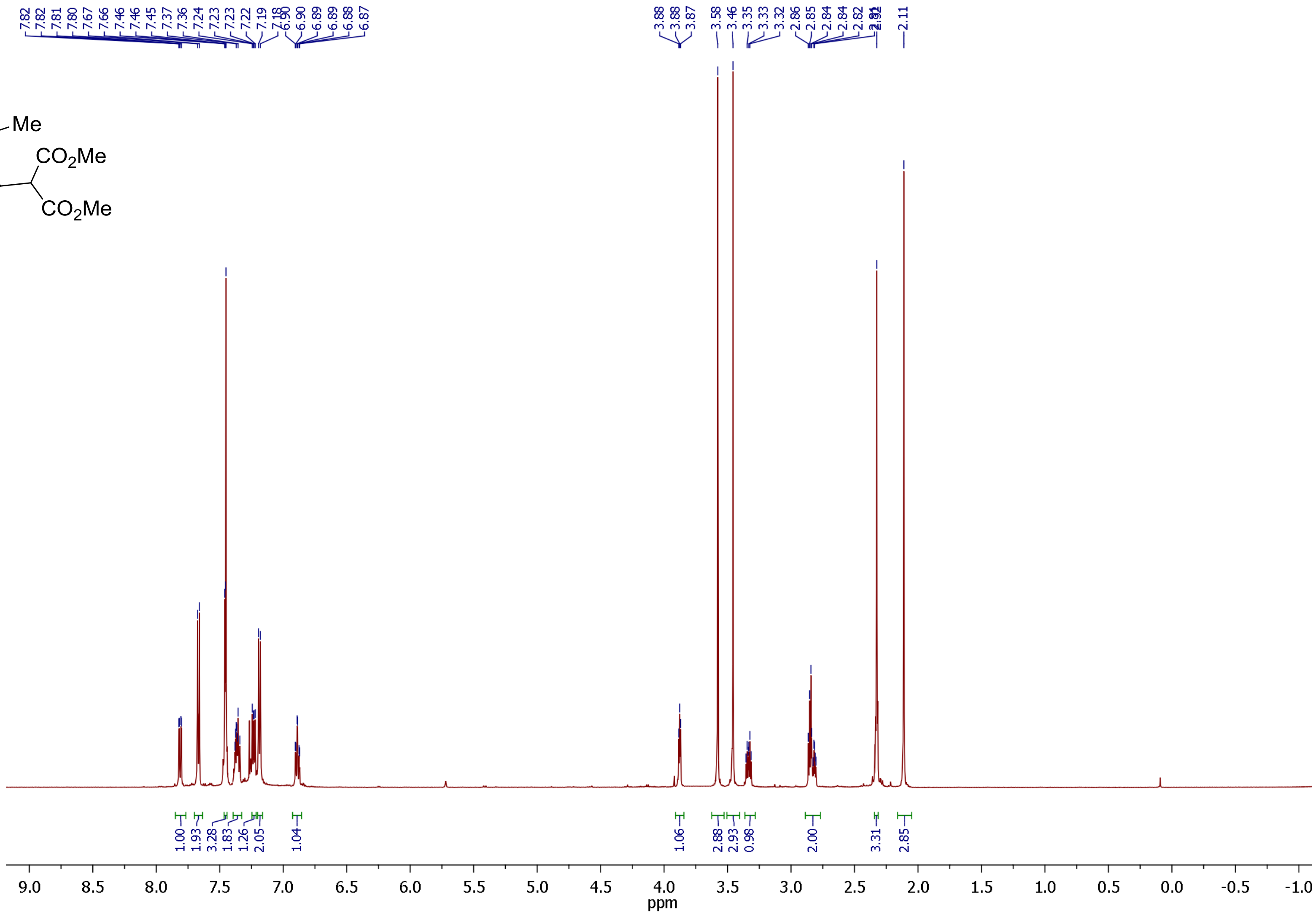




Dimethyl 2-[(6-fluoro-2-methyl-1-phenyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indol-3-yl)methyl]malonate (3o)

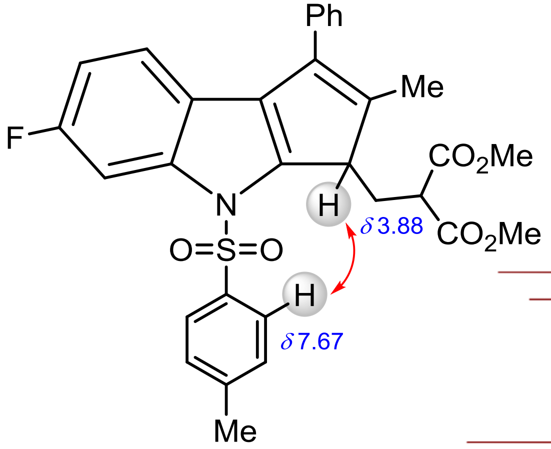
^{1}H NMR ($CDCl_3$, 600 MHz)

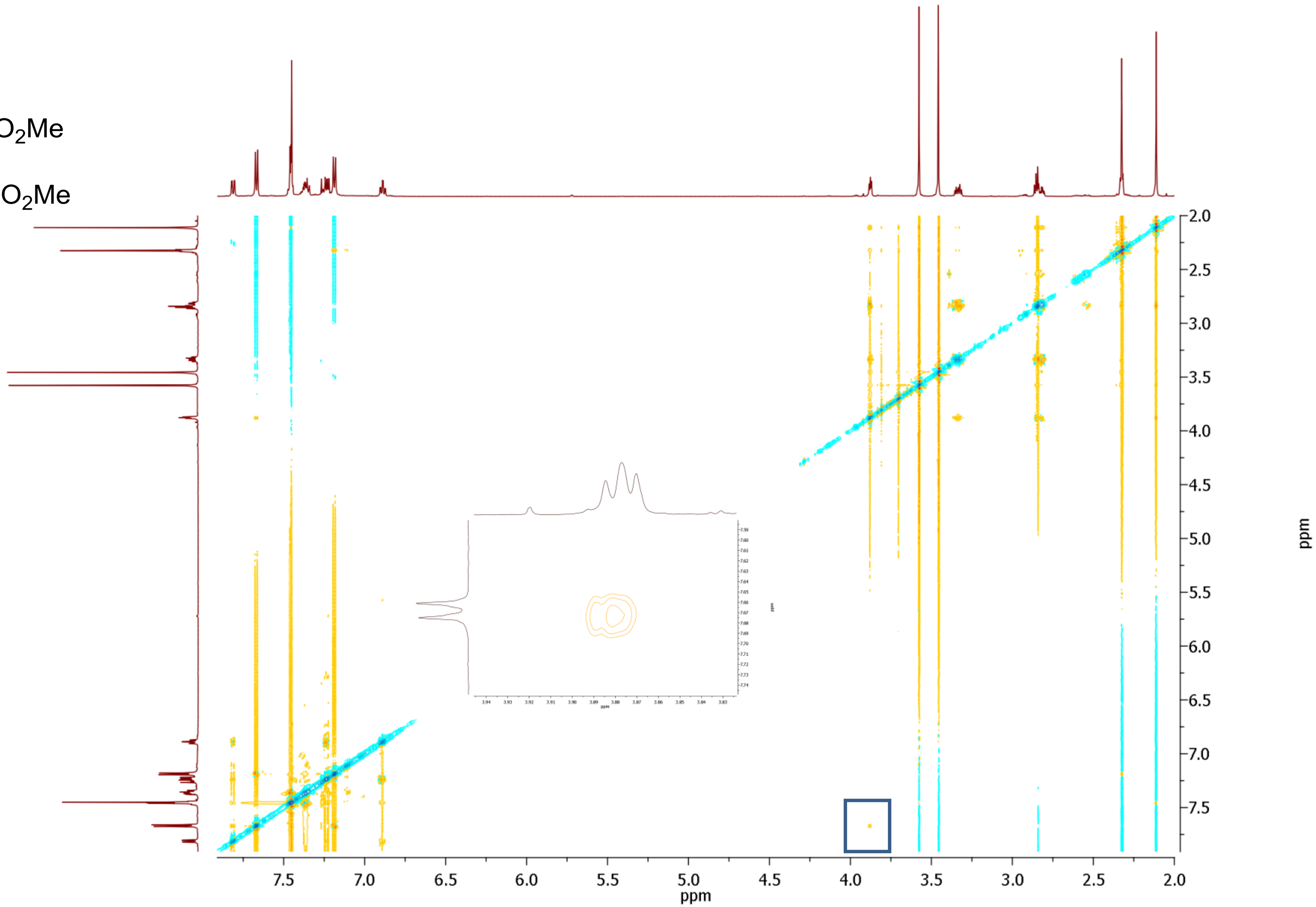




Dimethyl 2-[(6-fluoro-2-methyl-1-phenyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indol-3-yl)methyl]malonate (3o)

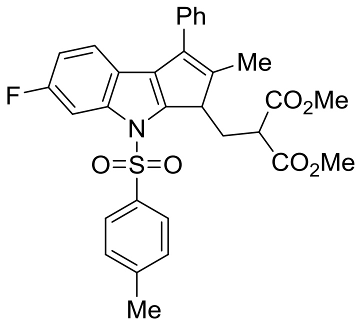
^{1}H-^{1}H NOESY ($CDCl_3$)

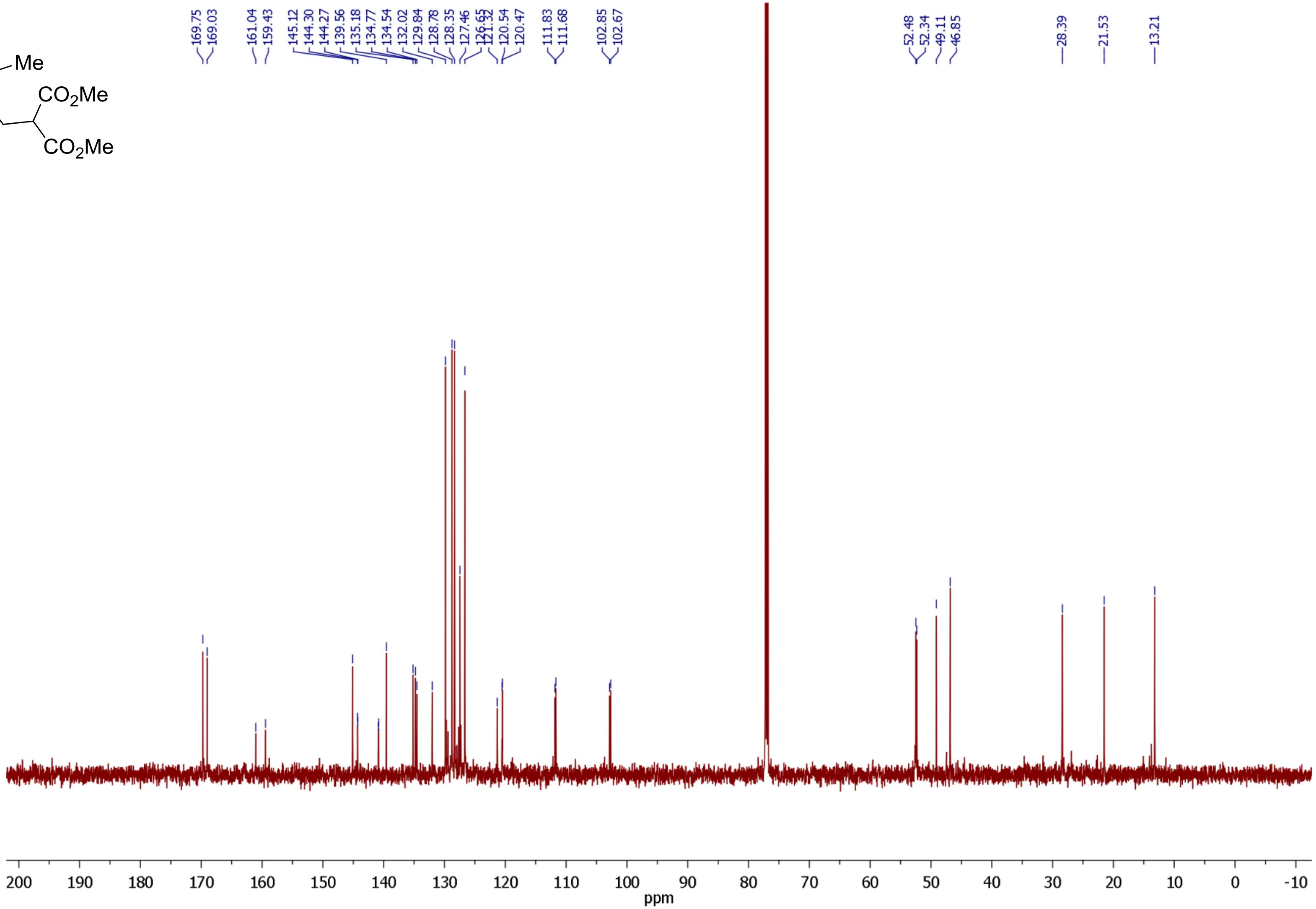




Dimethyl 2-[(6-fluoro-2-methyl-1-phenyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indol-3-yl)methyl]malonate (3o)

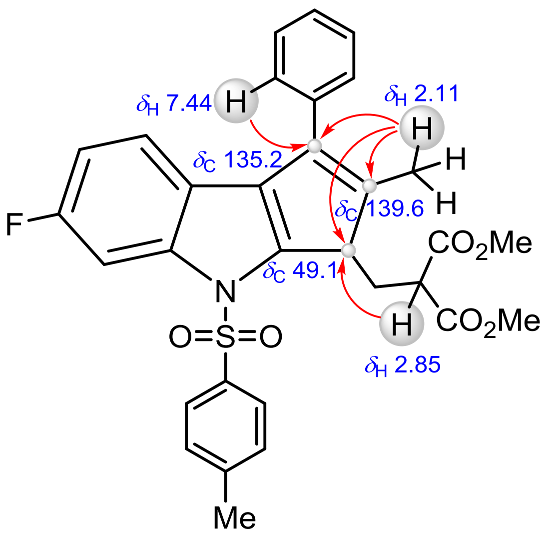
^{13}C NMR ($CDCl_3$, 150 MHz)

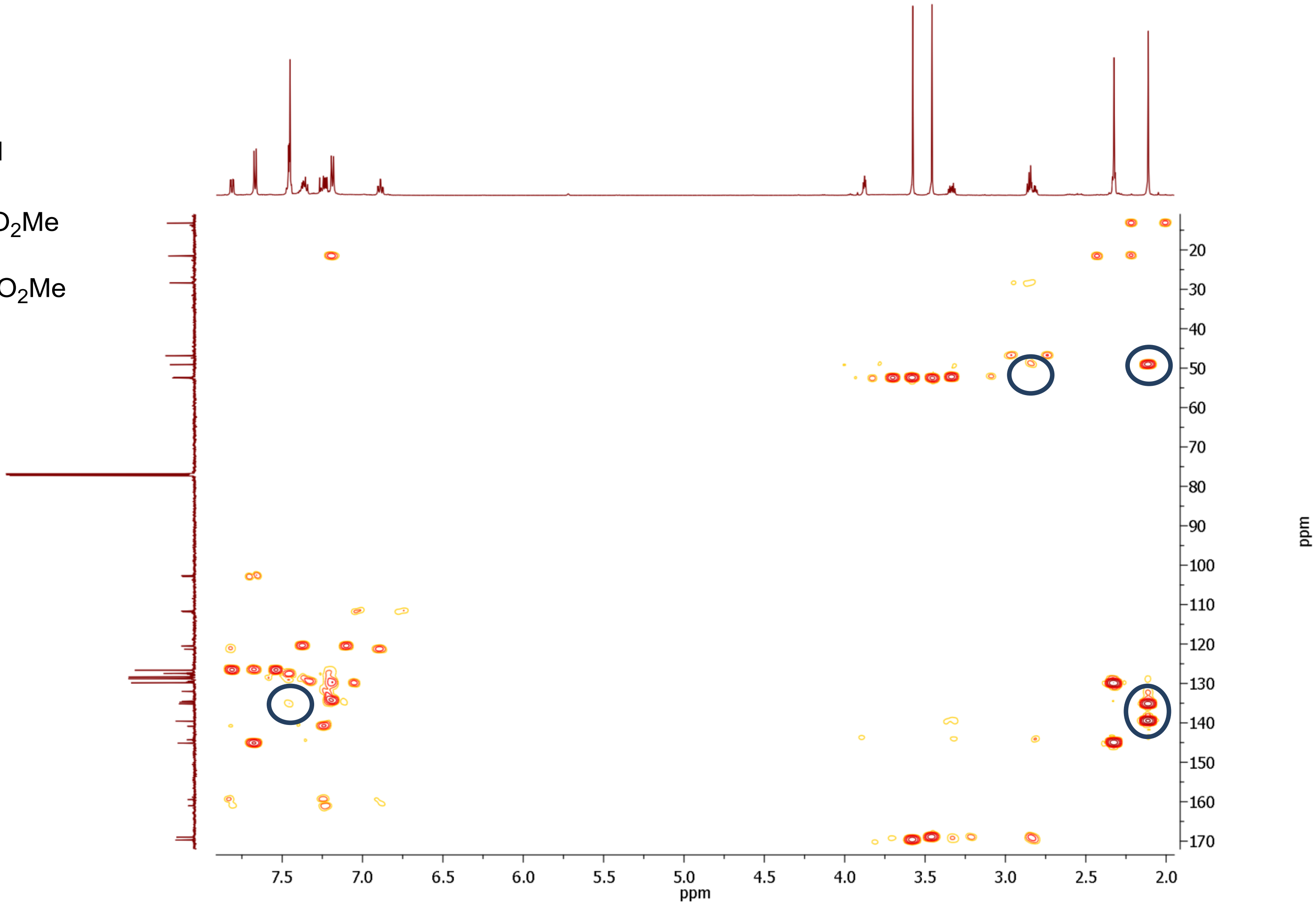




Dimethyl 2-[(6-fluoro-2-methyl-1-phenyl-4-tosyl-3,4-dihydrocyclopenta[*b*]indol-3-yl)methyl]malonate (3o)

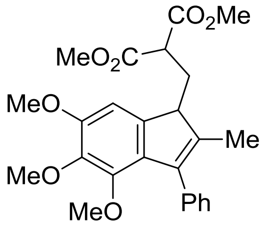
^{1}H-^{13}C HMBC ($CDCl_3$)

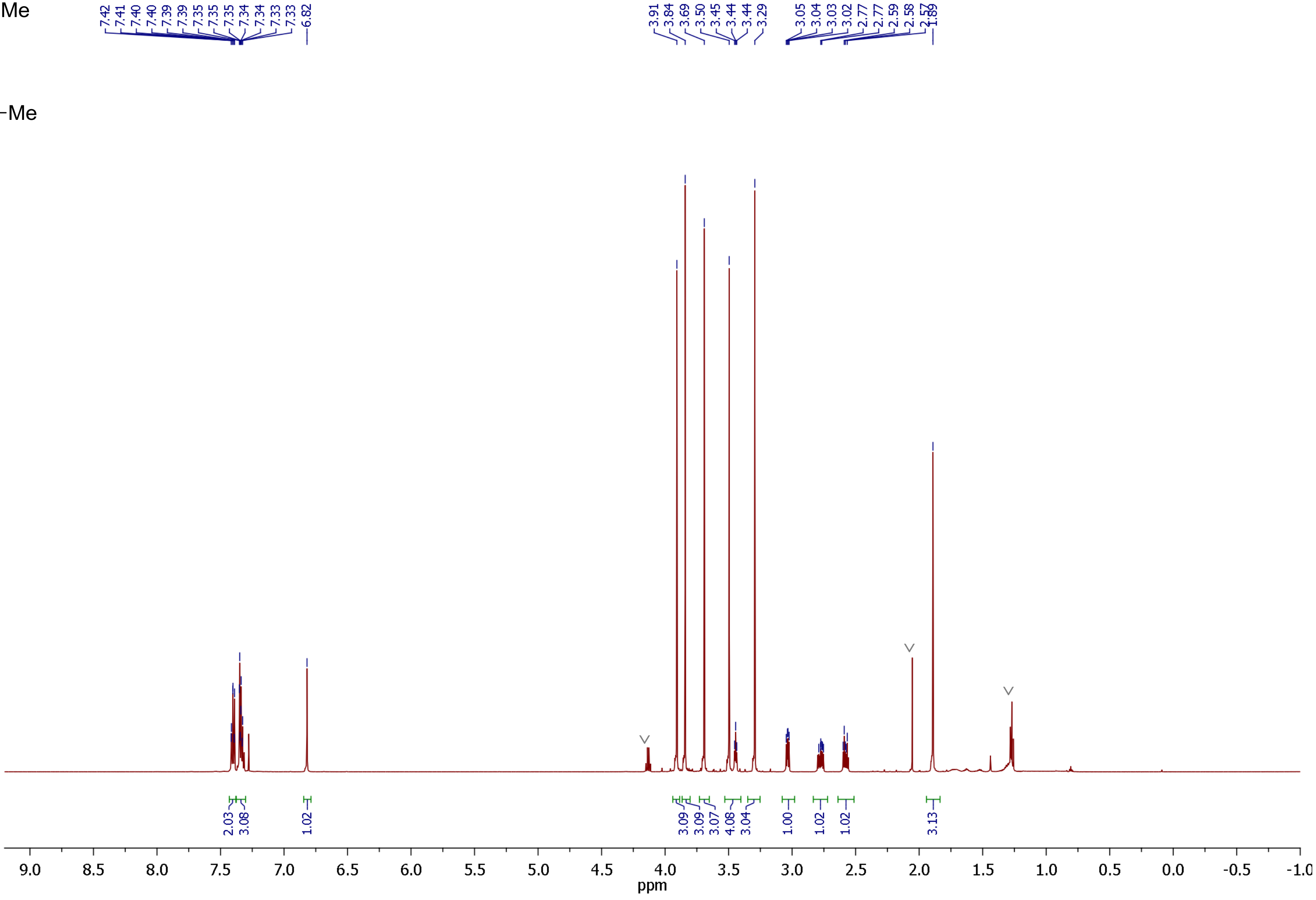




Dimethyl 2-[(4,5,6-trimethoxy-2-methyl-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3p)

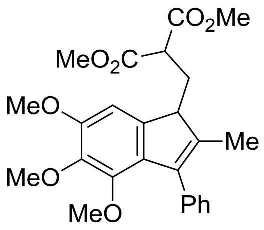
^{1}H NMR ($CDCl_3$, 600 MHz)

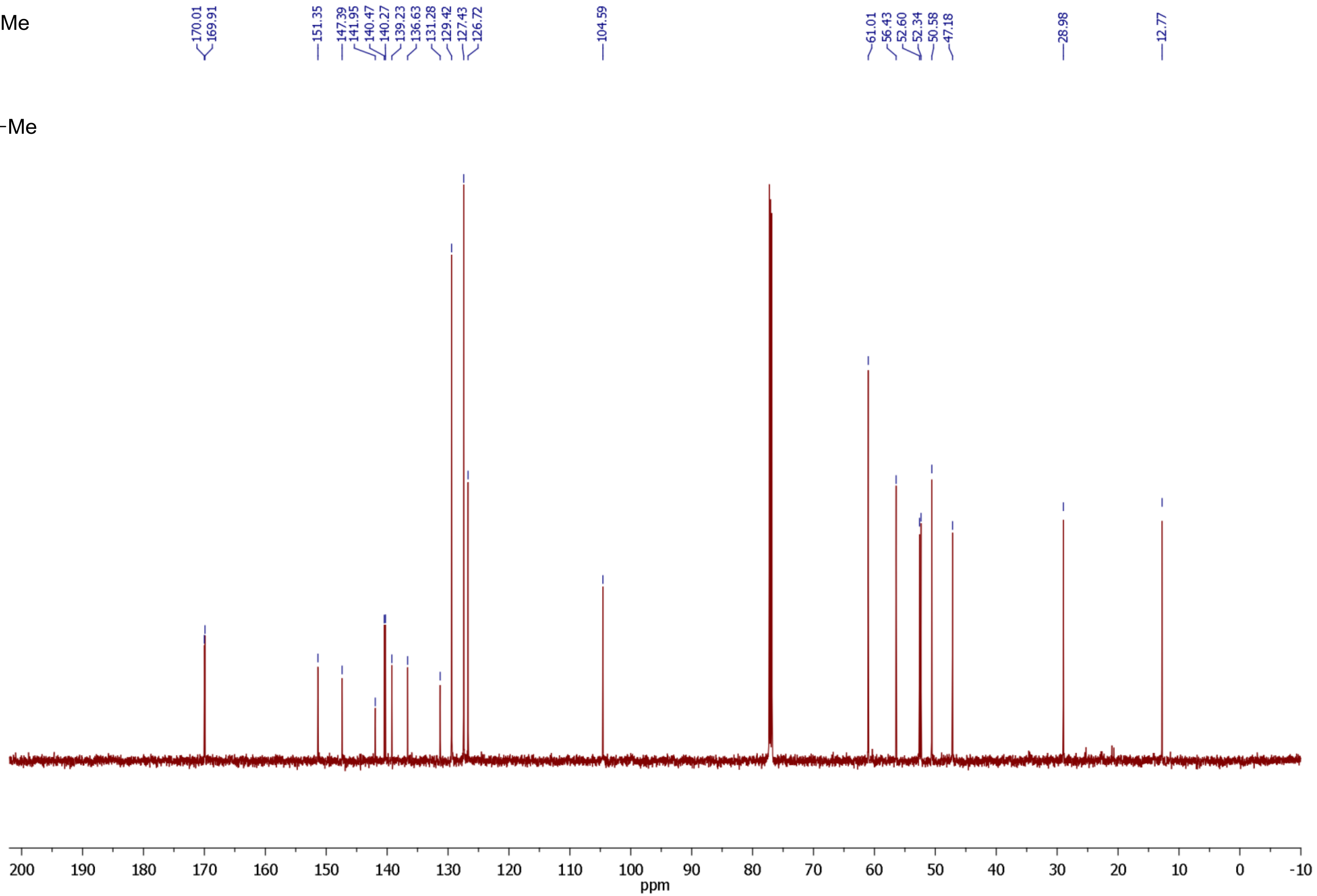




Dimethyl 2-[(4,5,6-trimethoxy-2-methyl-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3p)

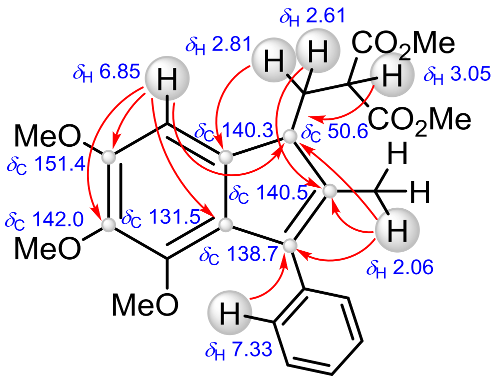
^{13}C NMR ($CDCl_3$, 150 MHz)

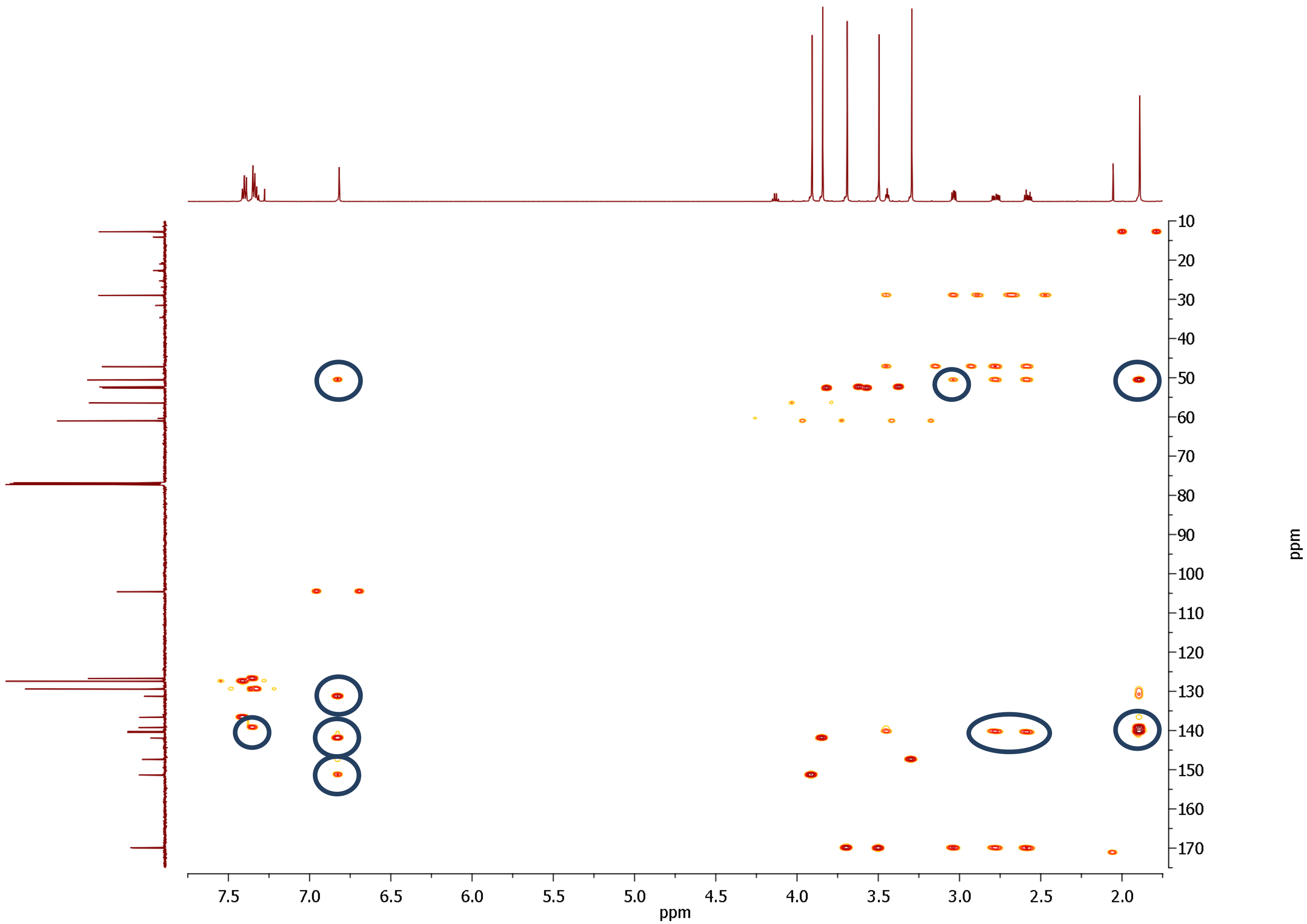




Dimethyl 2-[(4,5,6-trimethoxy-2-methyl-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3p)

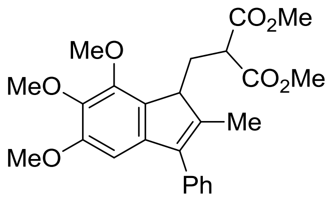
^{1}H-^{13}C HMBC ($CDCl_3$)

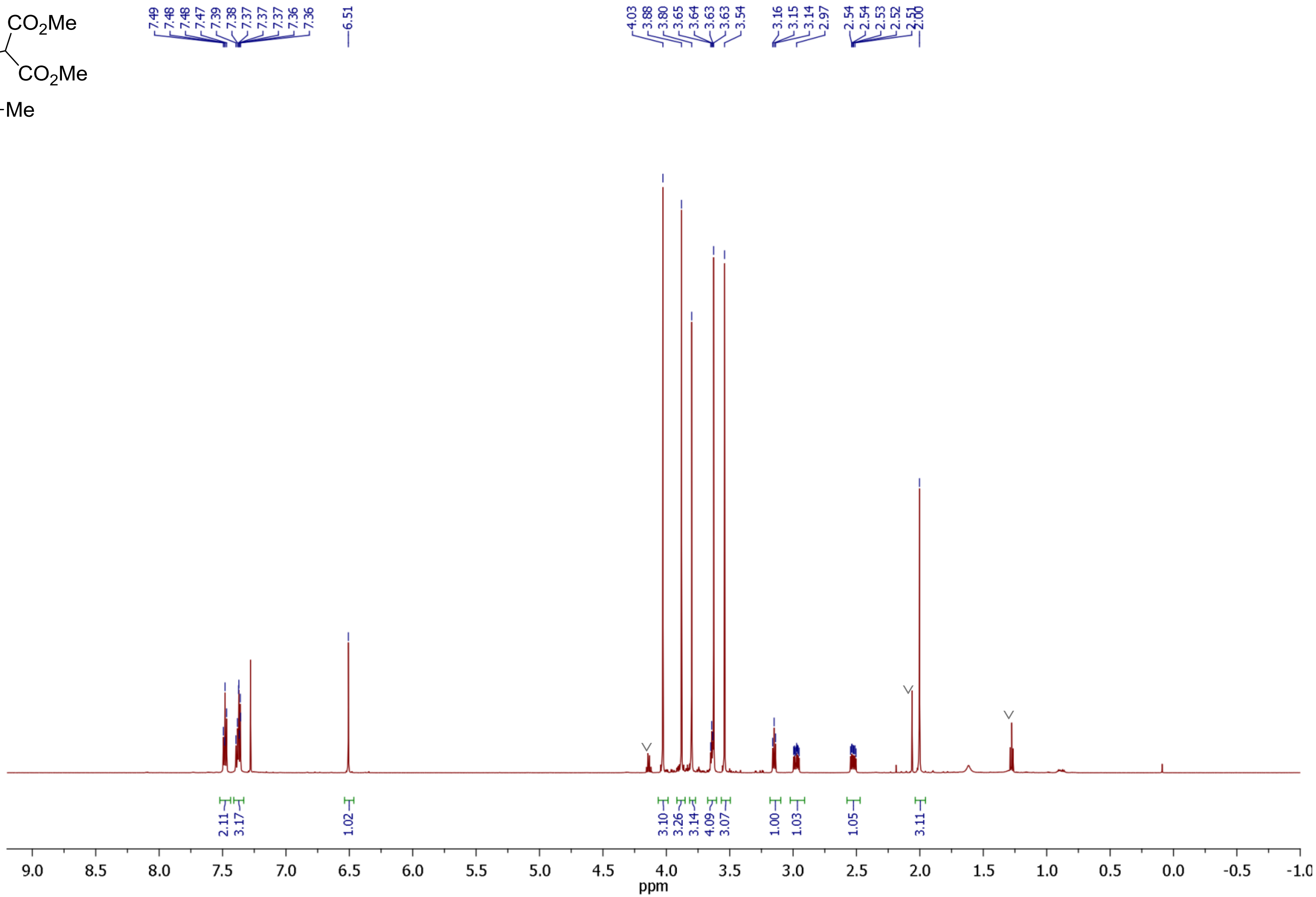




Dimethyl 2-[(5,6,7-trimethoxy-2-methyl-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3q)

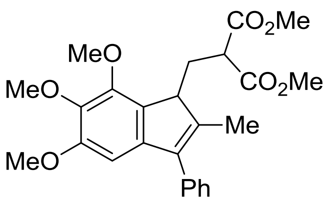
^{1}H NMR ($CDCl_3$, 600 MHz)

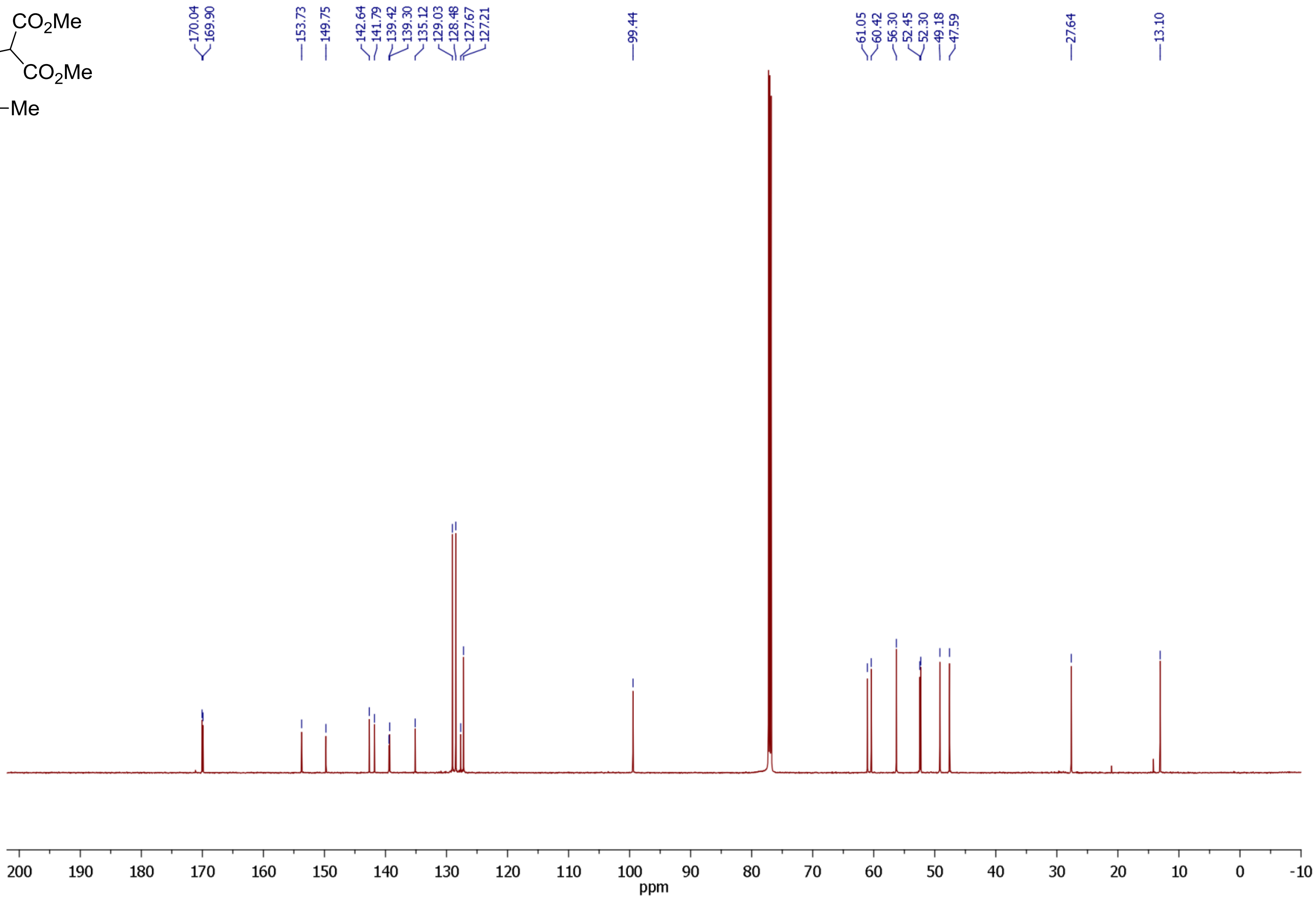




Dimethyl 2-[(5,6,7-trimethoxy-2-methyl-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3q)

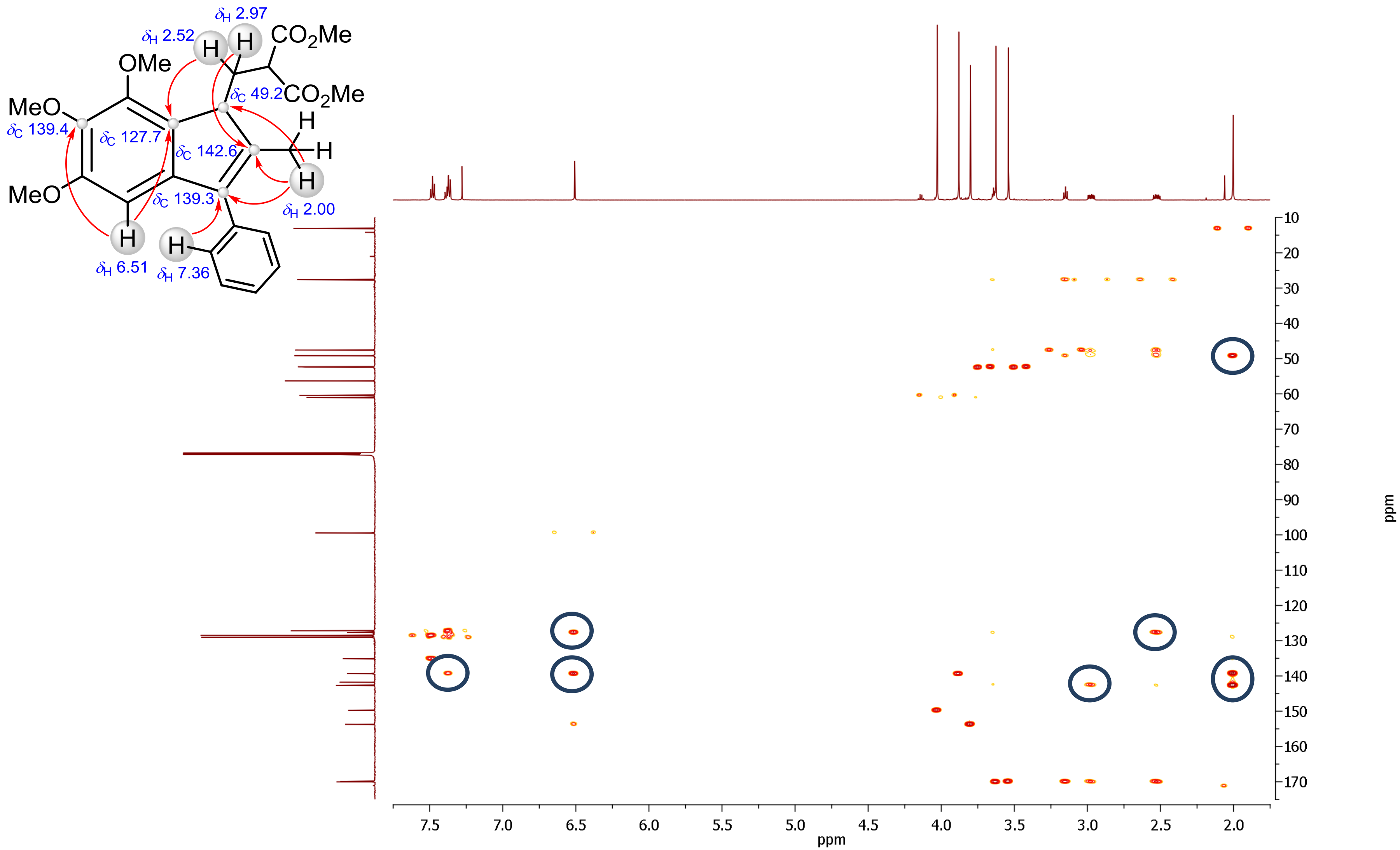
^{13}C NMR ($CDCl_3$, 150 MHz)





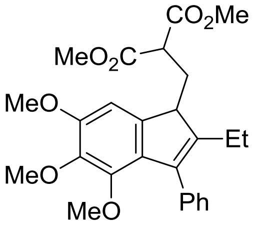
Dimethyl 2-[(5,6,7-trimethoxy-2-methyl-3-phenyl-1*H*-inden-1-yl)methyl]malonate (3q)

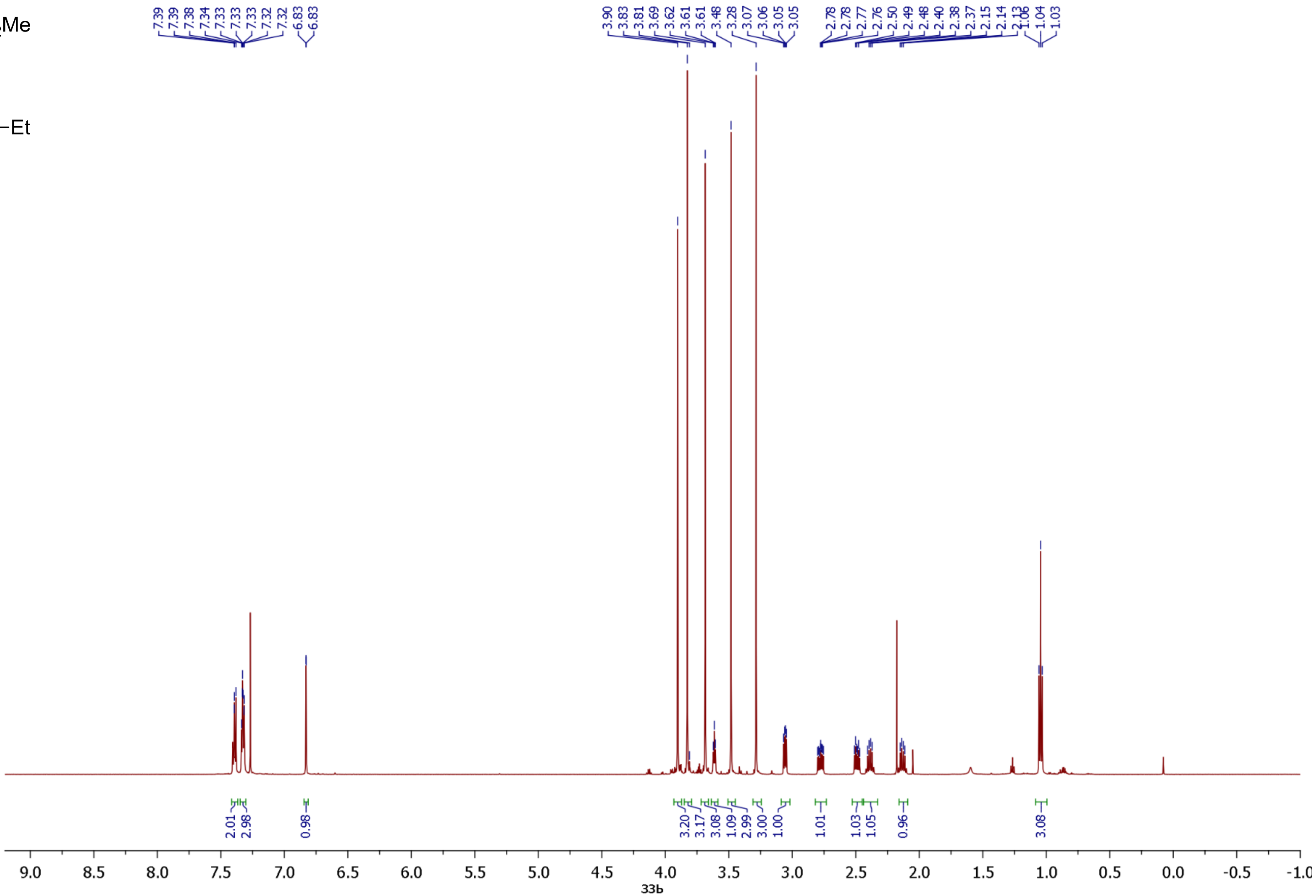
^{1}H-^{13}C HMBC ($CDCl_3$)



Dimethyl 2-[(2-ethyl-4,5,6-trimethoxy-3-phenyl-1H-inden-1-yl)methyl]malonate (3r)

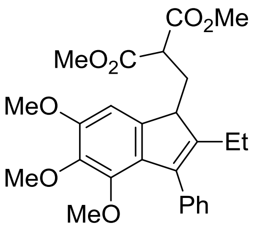
^{1}H NMR ($CDCl_3$, 600 MHz)

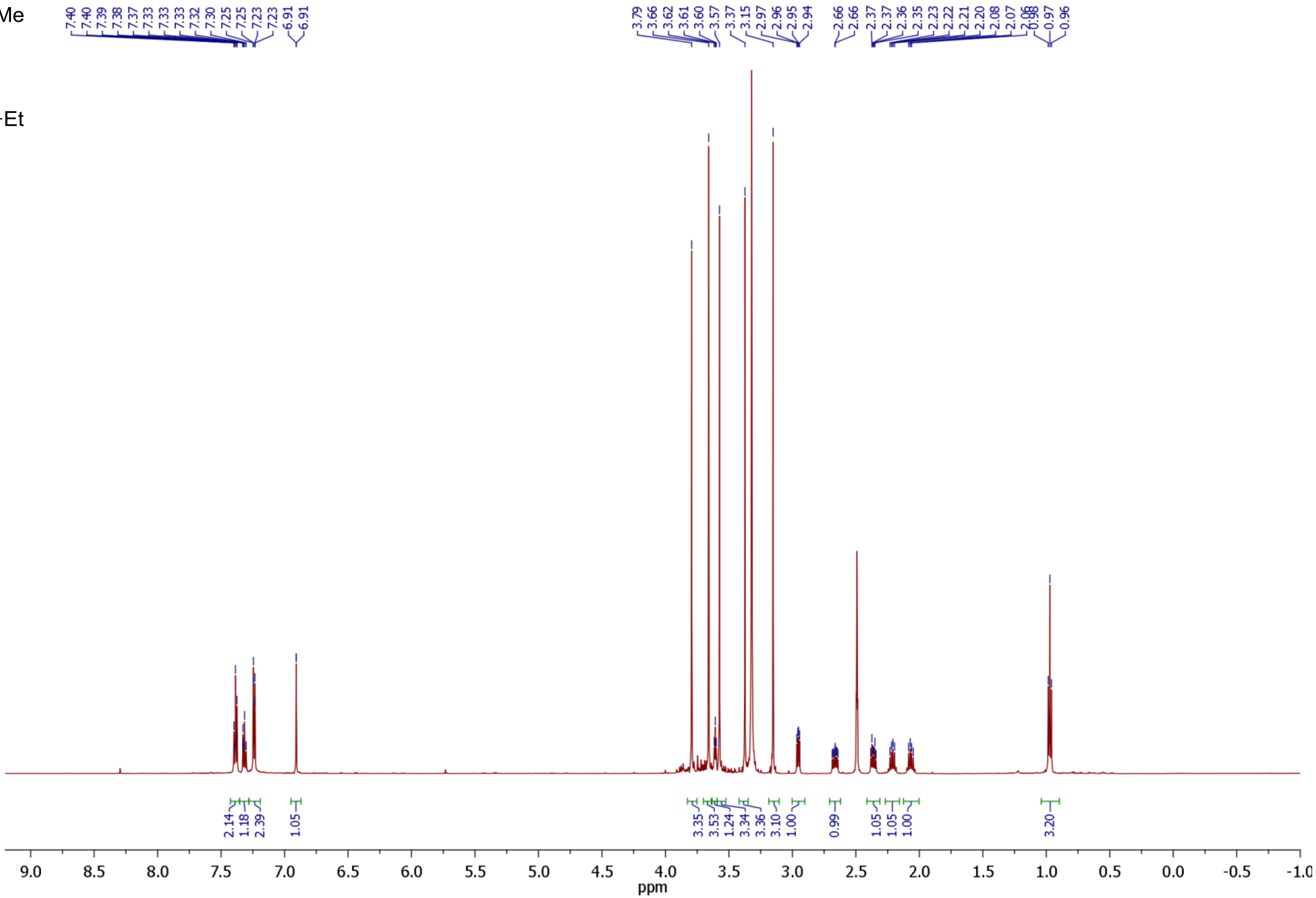




Dimethyl 2-[(2-ethyl-4,5,6-trimethoxy-3-phenyl-1H-inden-1-yl)methyl]malonate (3r)

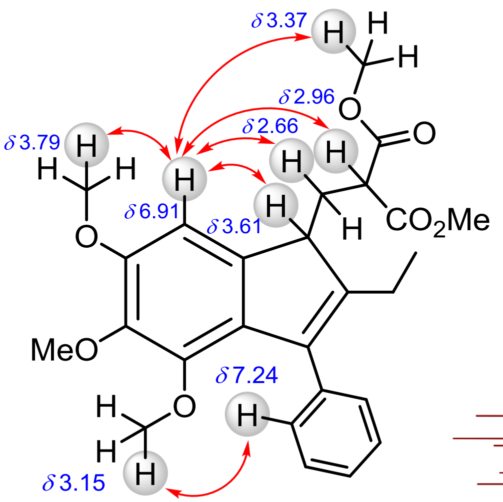
^{1}H NMR (DMSO-d$_6$, 600 MHz)

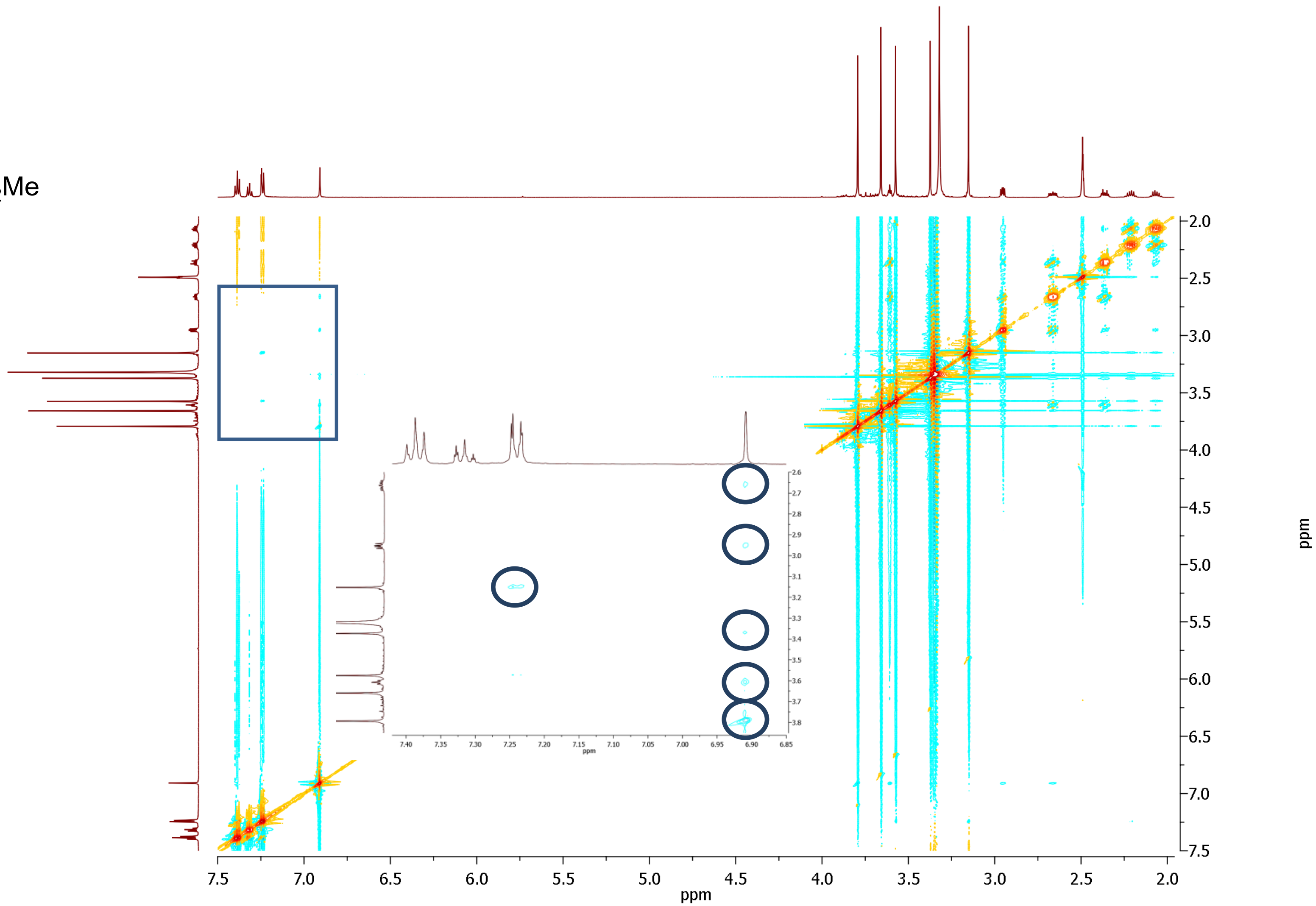




Dimethyl 2-[(2-ethyl-4,5,6-trimethoxy-3-phenyl-1H-inden-1-yl)methyl]malonate (3r)

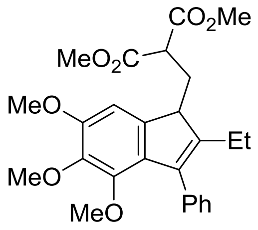
^{1}H-^{1}H NOESY (DMSO-d_6)

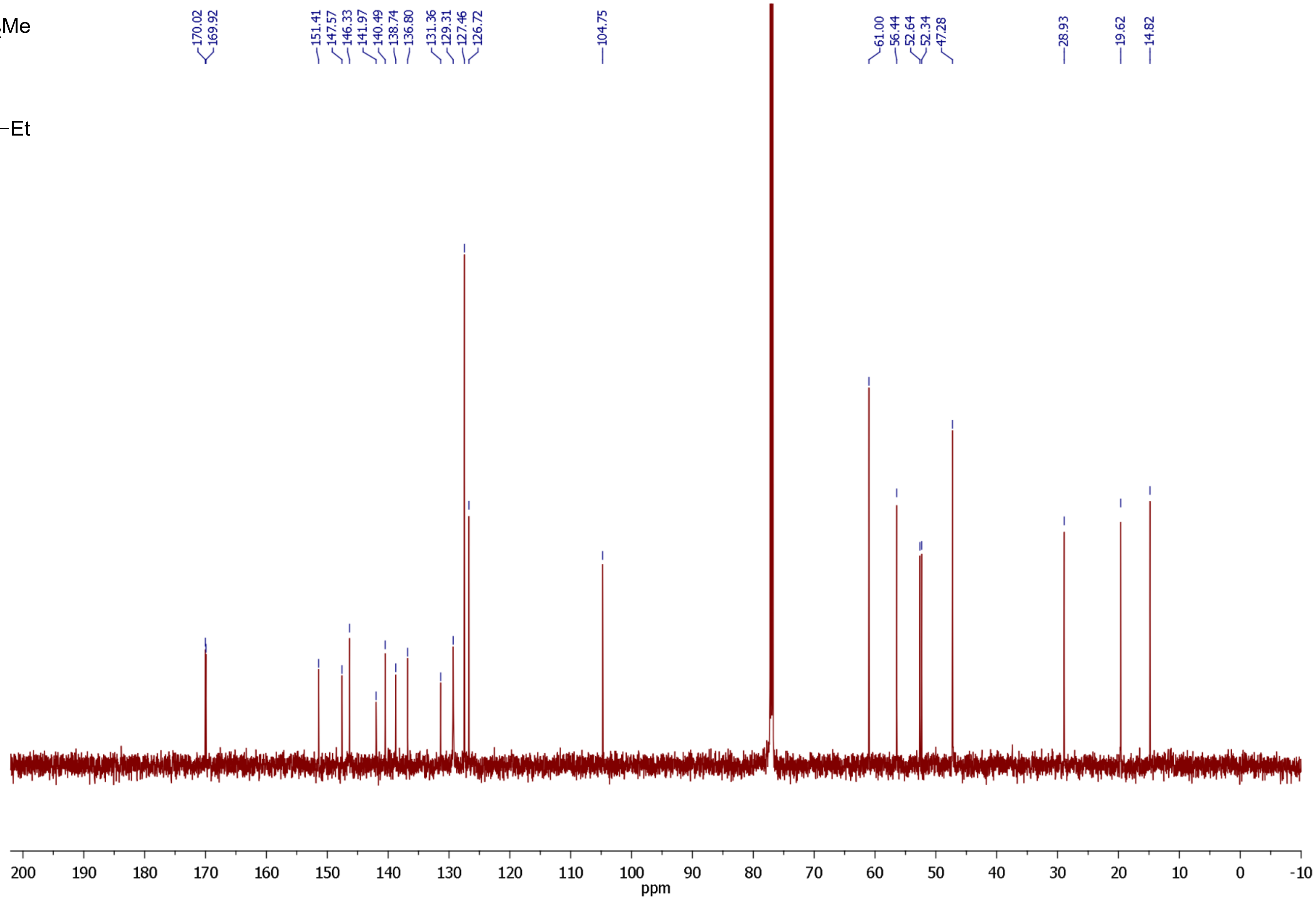




Dimethyl 2-[(2-ethyl-4,5,6-trimethoxy-3-phenyl-1H-inden-1-yl)methyl]malonate (3r)

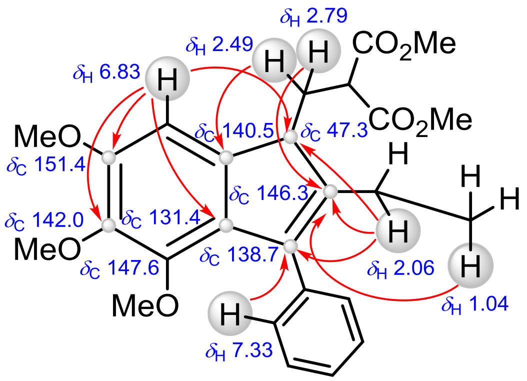
^{13}C NMR ($CDCl_3$, 150 MHz)

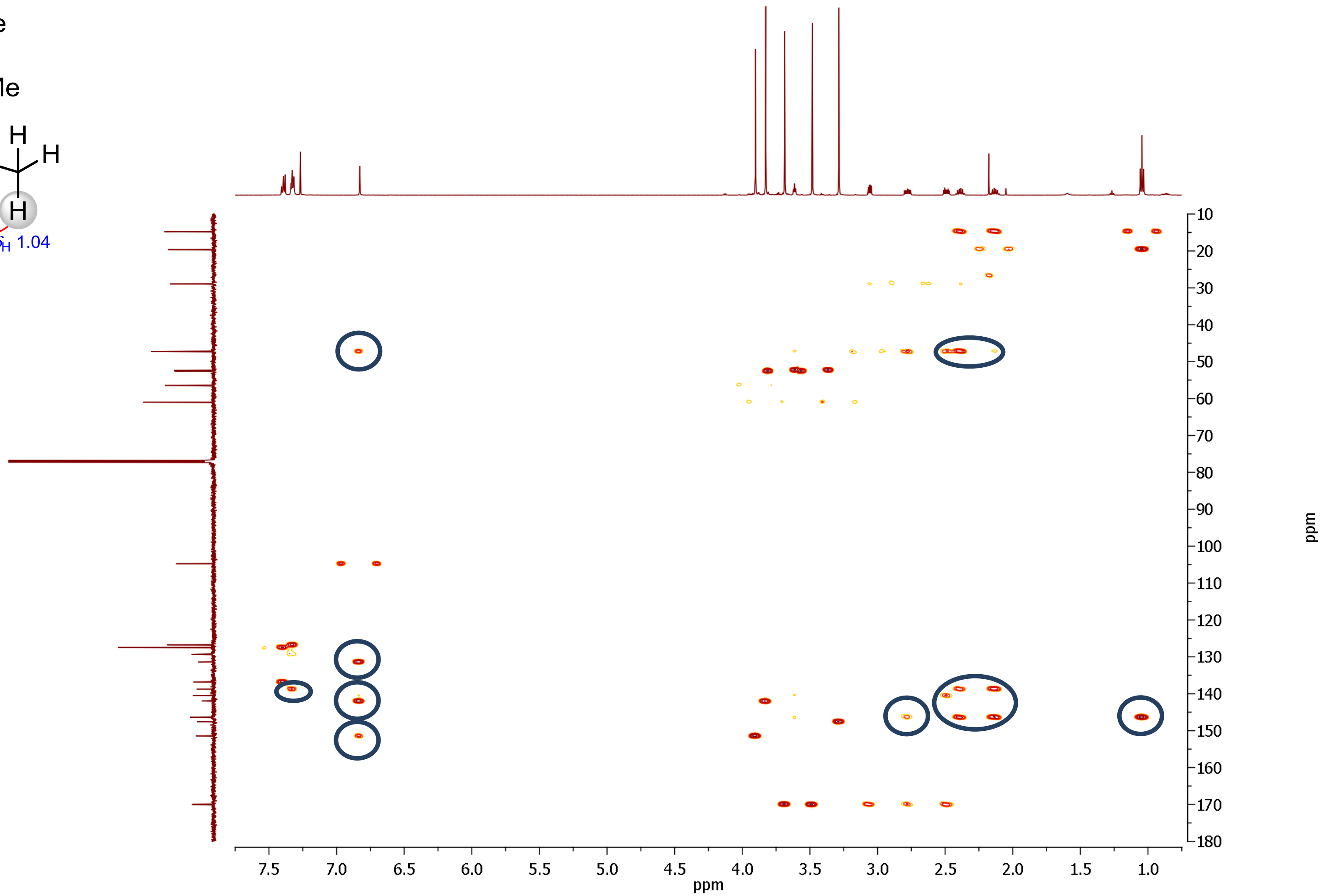




Dimethyl 2-[(2-ethyl-4,5,6-trimethoxy-3-phenyl-1H-inden-1-yl)methyl]malonate (3r)

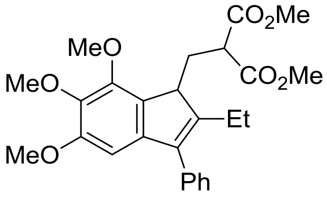
^{1}H-^{13}C HMBC ($CDCl_3$)

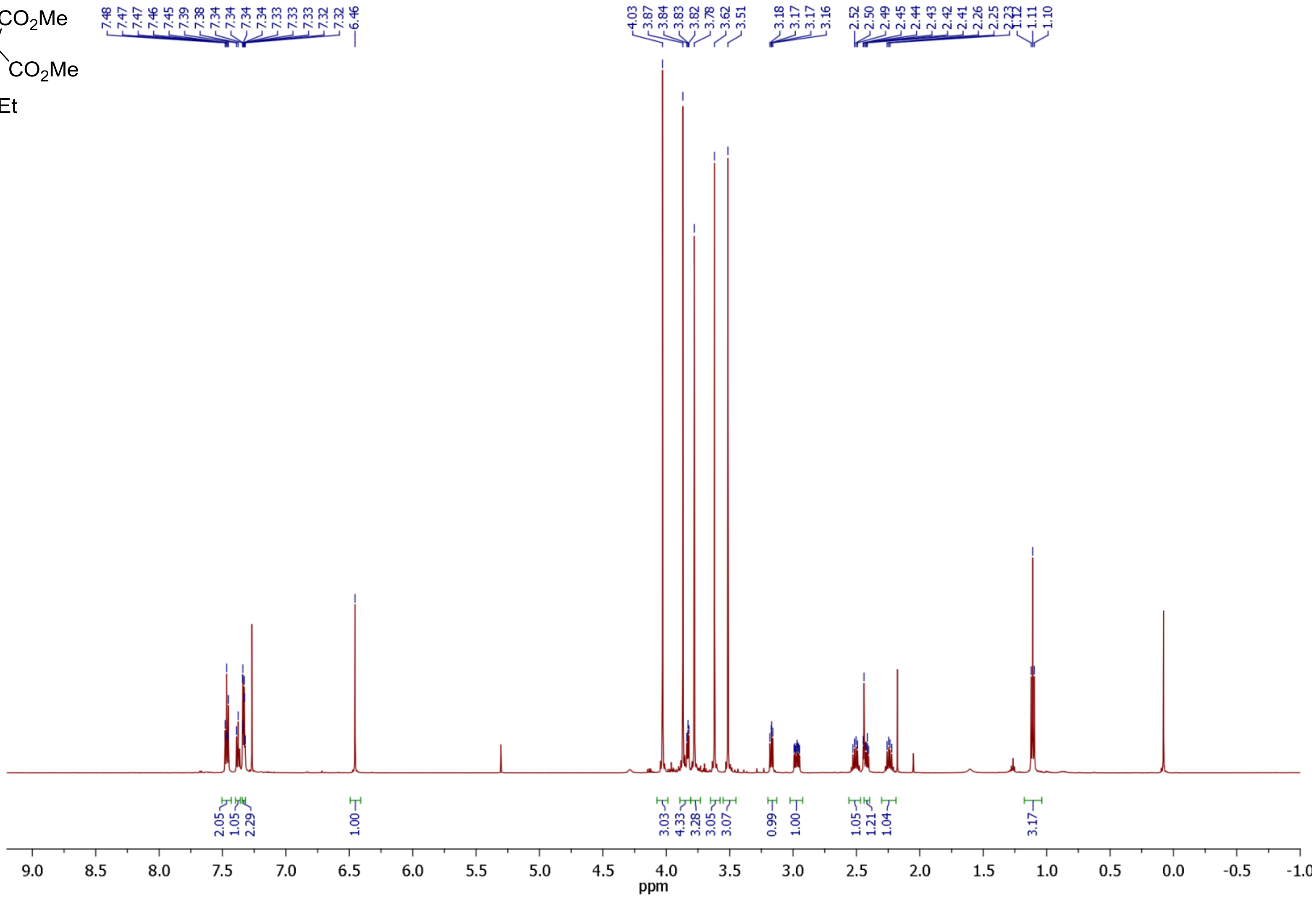




Dimethyl 2-[(2-ethyl-5,6,7-trimethoxy-3-phenyl-1H-inden-1-yl)methyl]malonate (3s)

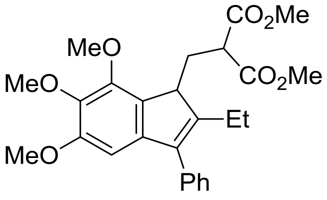
^{1}H NMR ($CDCl_3$, 600 MHz)

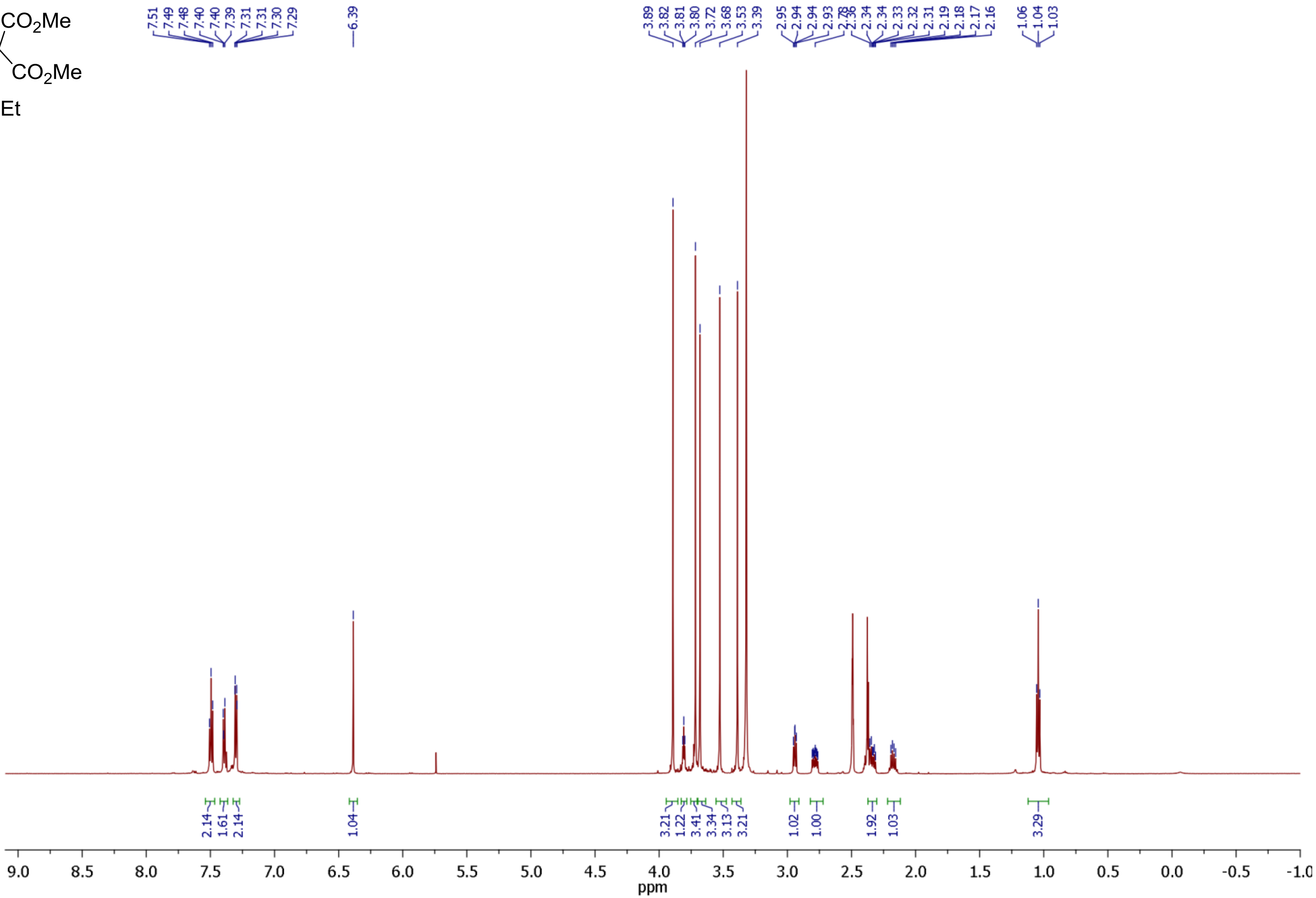




Dimethyl 2-[(2-ethyl-5,6,7-trimethoxy-3-phenyl-1H-inden-1-yl)methyl]malonate (3s)

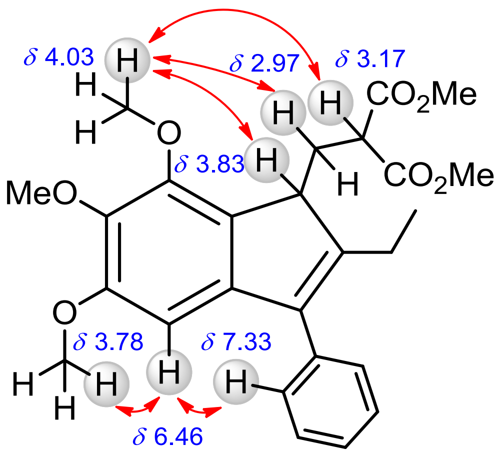
^{1}H NMR (DMSO-d$_6$, 600 MHz)

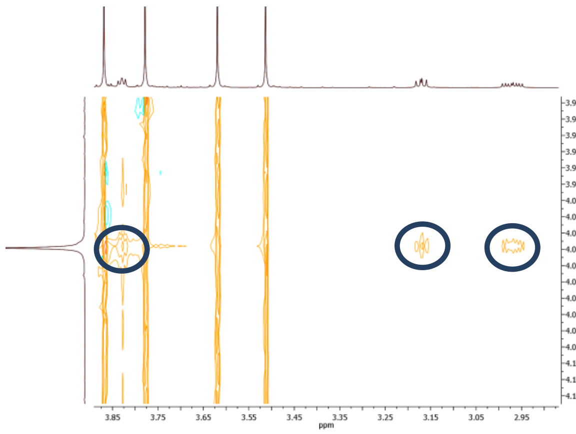


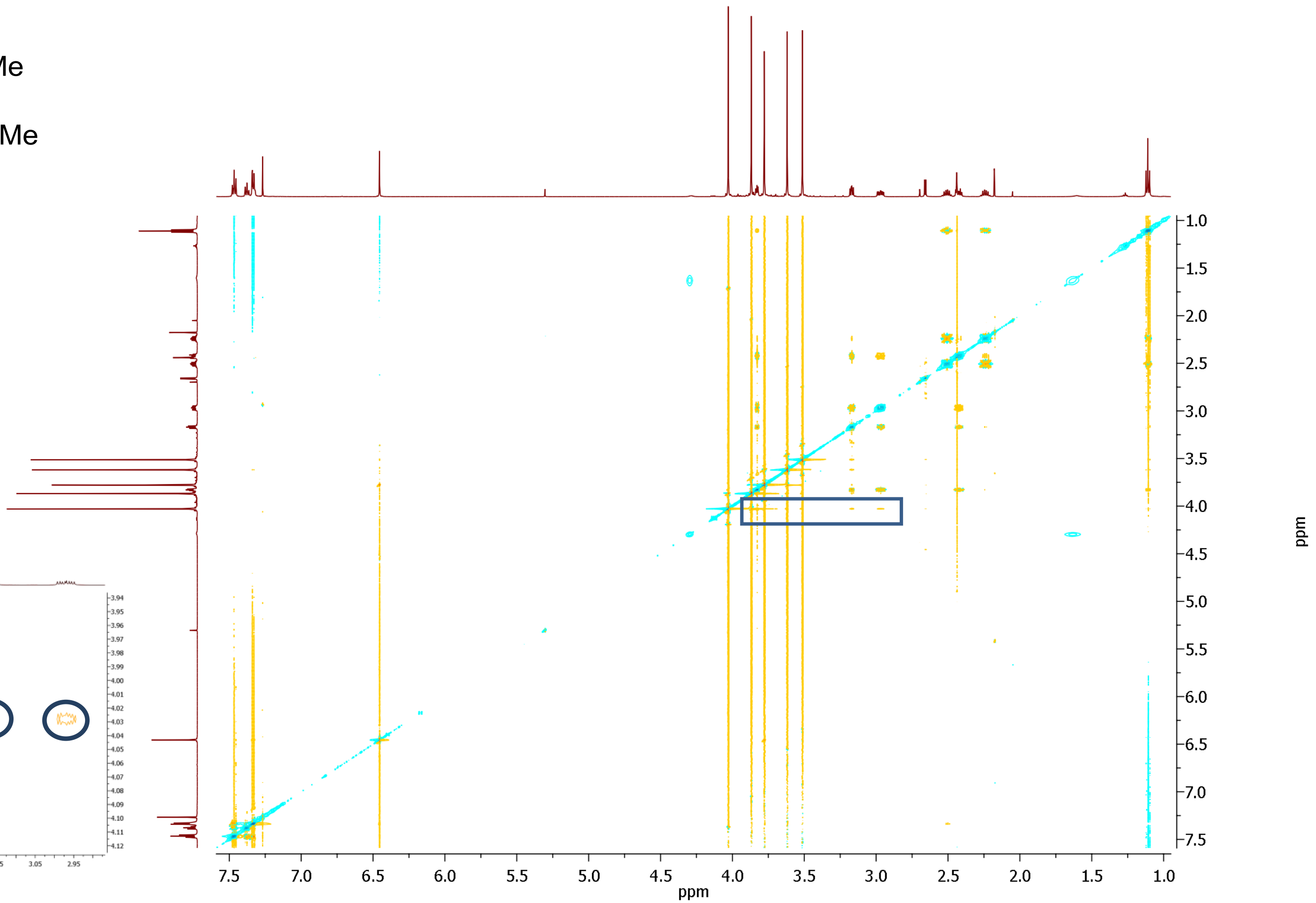


Dimethyl 2-[(2-ethyl-5,6,7-trimethoxy-3-phenyl-1H-inden-1-yl)methyl]malonate (3s)

^{1}H-^{1}H NOESY ($CDCl_3$)

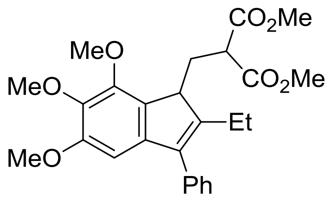


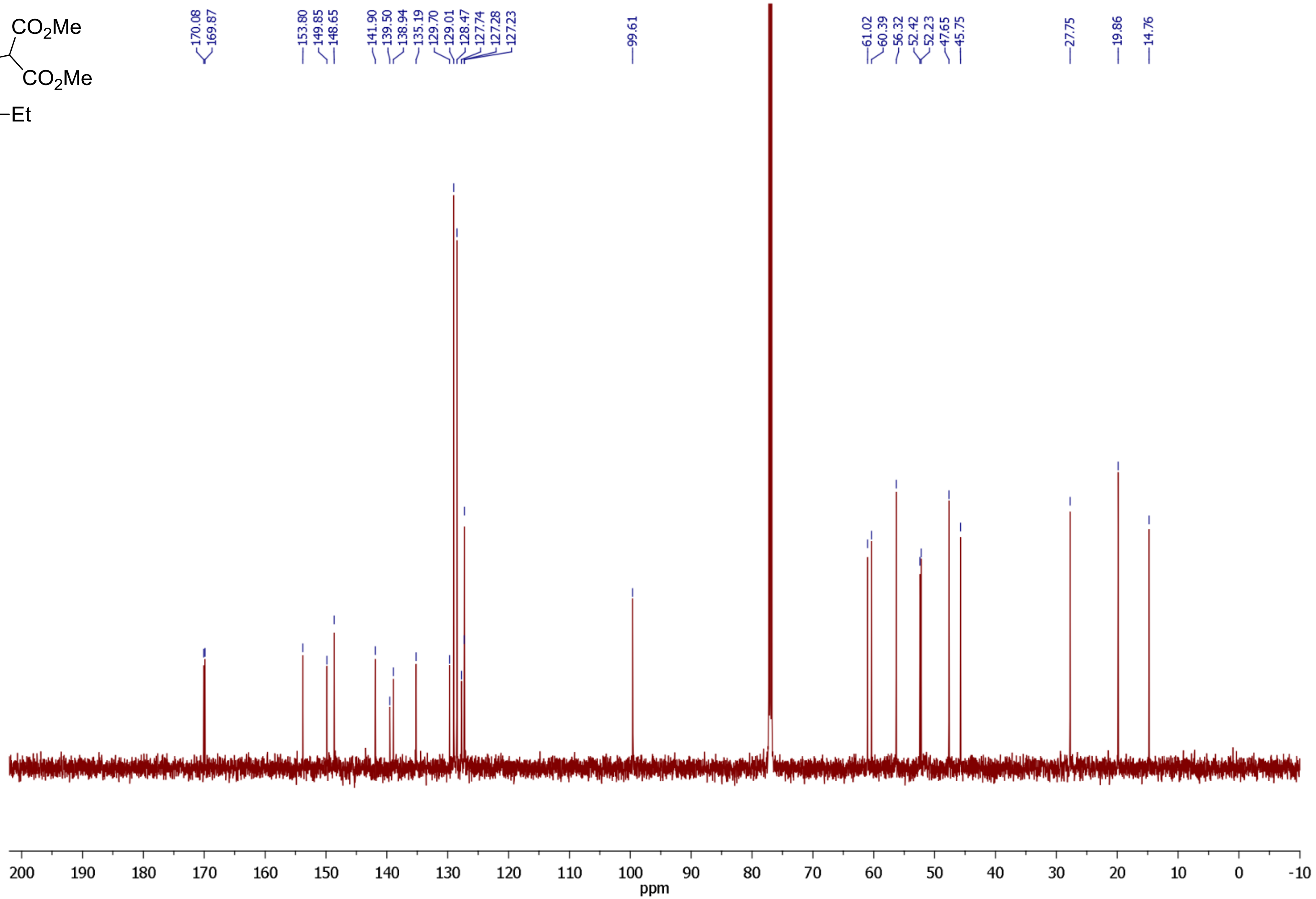




Dimethyl 2-[(2-ethyl-5,6,7-trimethoxy-3-phenyl-1H-inden-1-yl)methyl]malonate (3s)

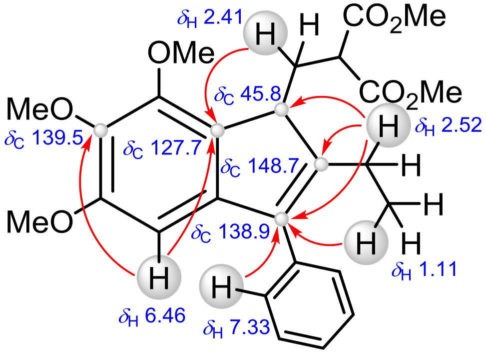
^{13}C NMR ($CDCl_3$, 150 MHz)

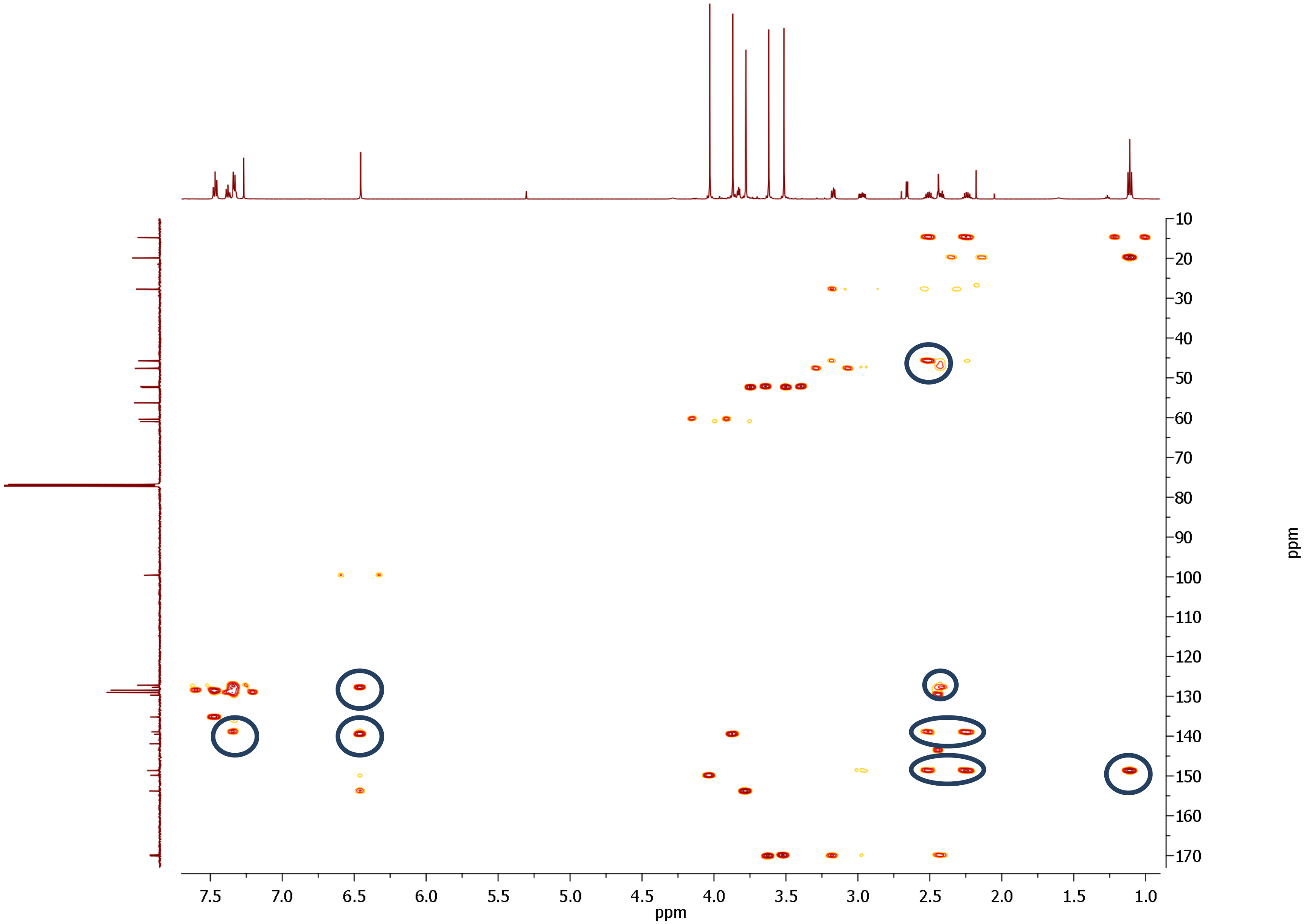




Dimethyl 2-[(2-ethyl-5,6,7-trimethoxy-3-phenyl-1H-inden-1-yl)methyl]malonate (3s)

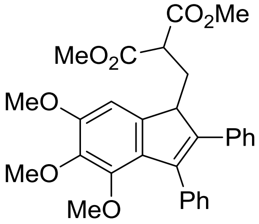
^{1}H-^{13}C HMBC ($CDCl_3$)

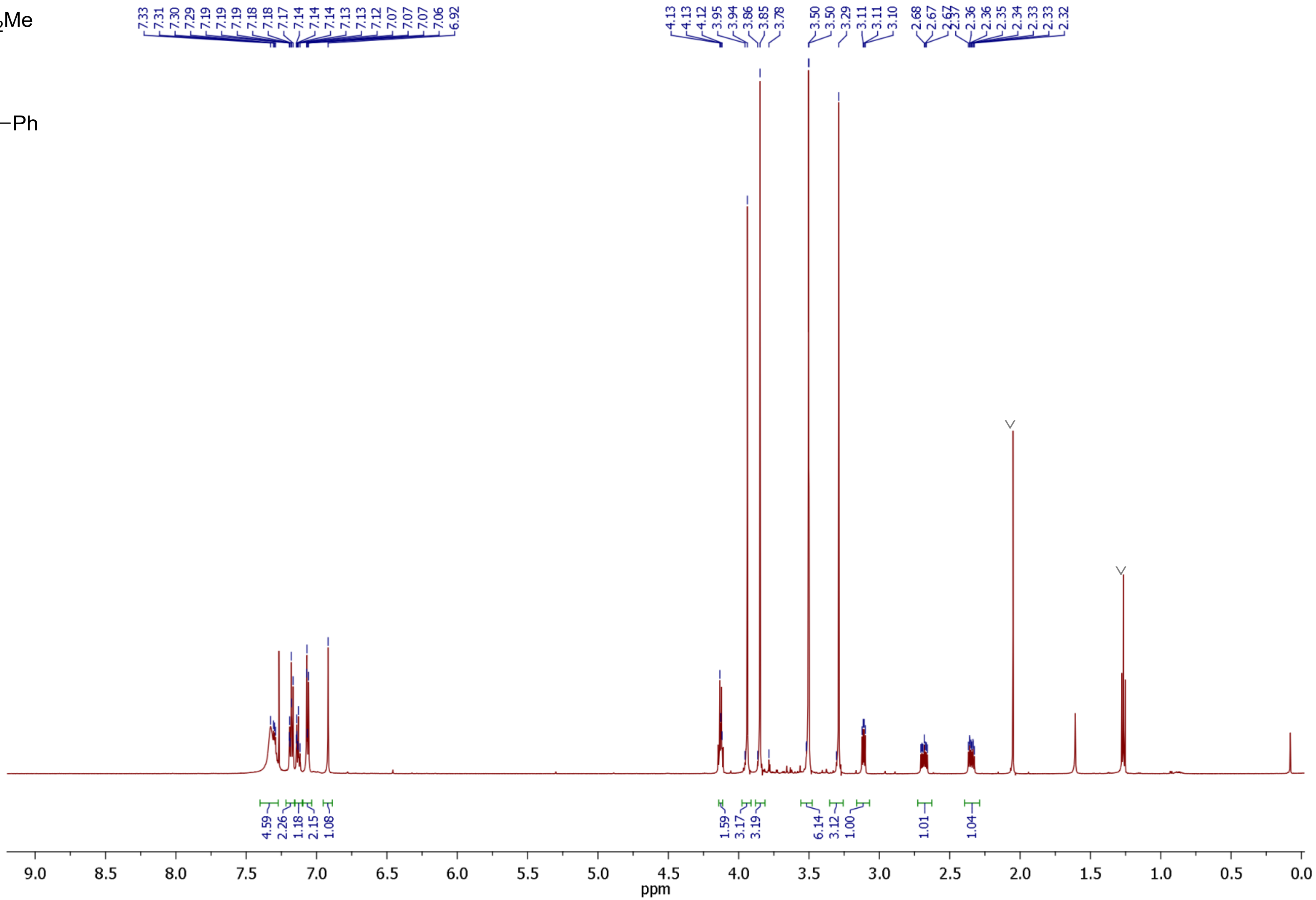




Dimethyl 2-[(4,5,6-trimethoxy-2,3-diphenyl-1H-inden-1-yl)methyl]malonate (3t)

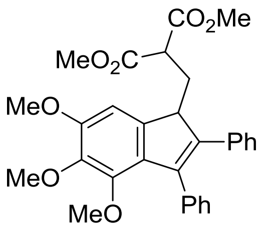
^{1}H NMR ($CDCl_3$, 600 MHz)

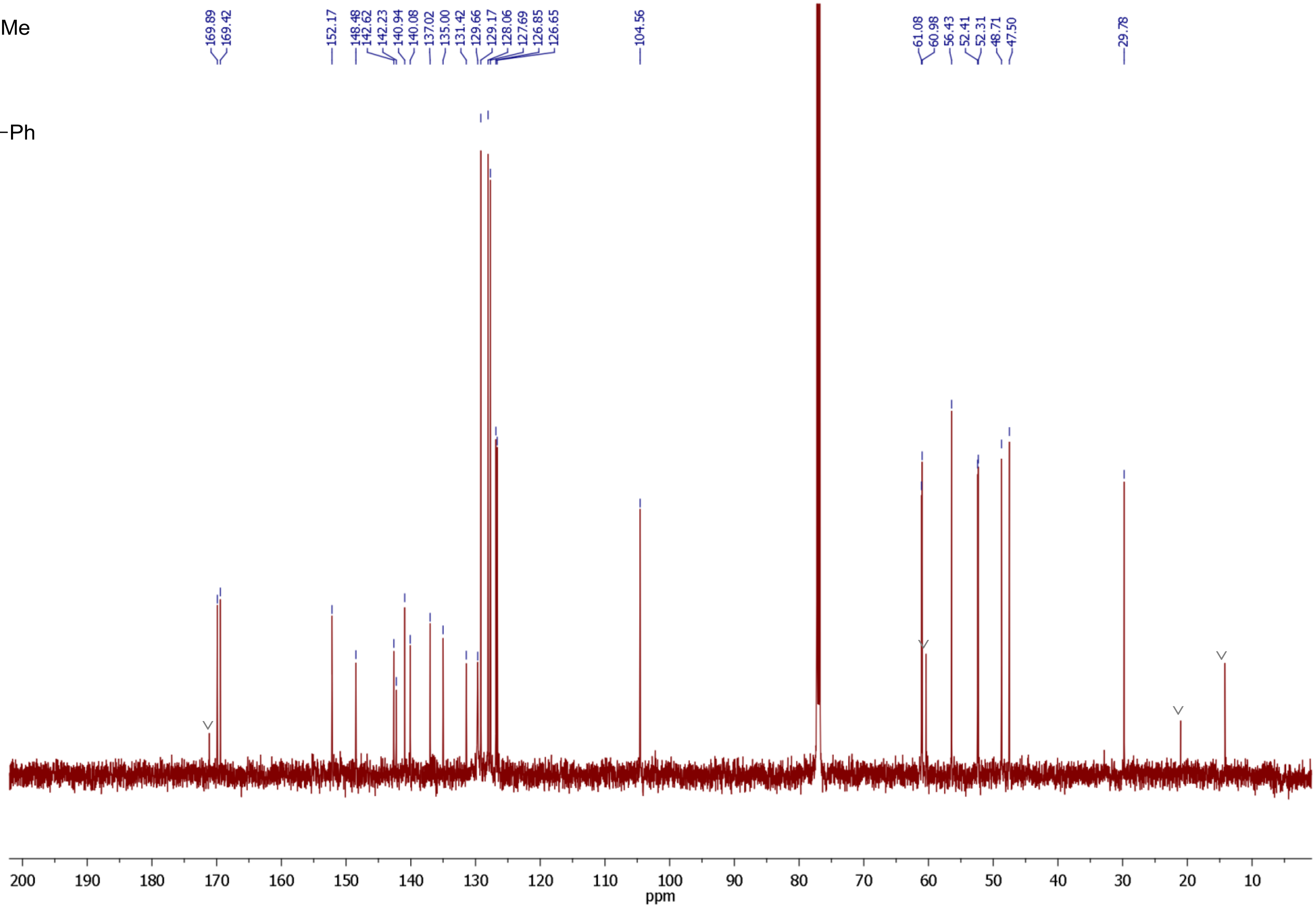




Dimethyl 2-[(4,5,6-trimethoxy-2,3-diphenyl-1H-inden-1-yl)methyl]malonate (3t)

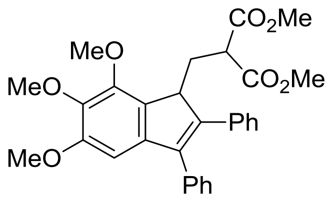
^{13}C NMR ($CDCl_3$, 150 MHz)

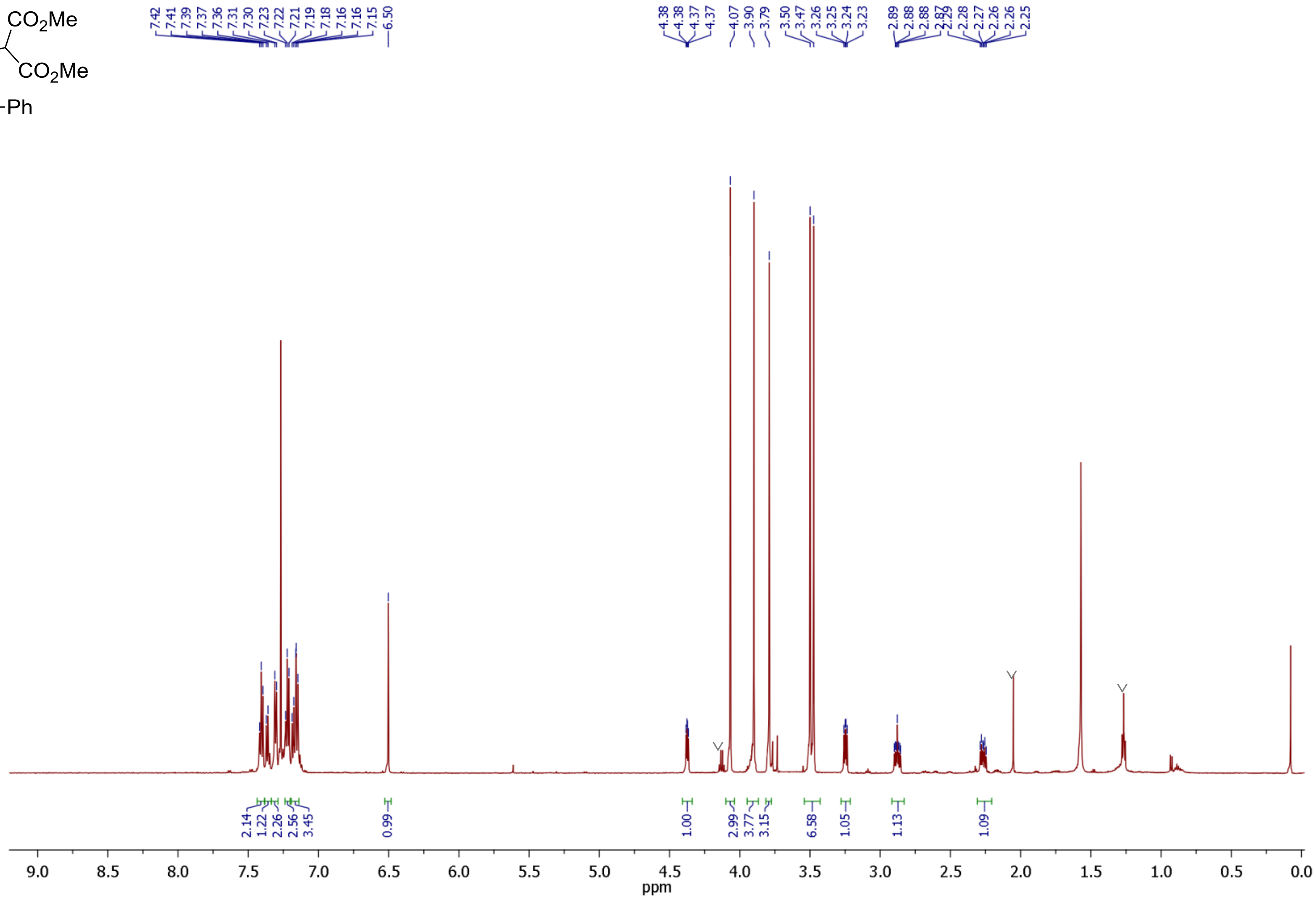




Dimethyl 2-[(4,5,6-trimethoxy-2,3-diphenyl-1H-inden-1-yl)methyl]malonate (3u)

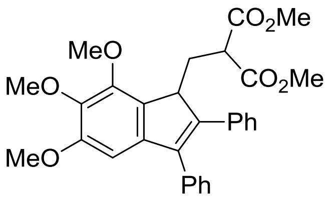
^{1}H NMR ($CDCl_3$, 600 MHz)

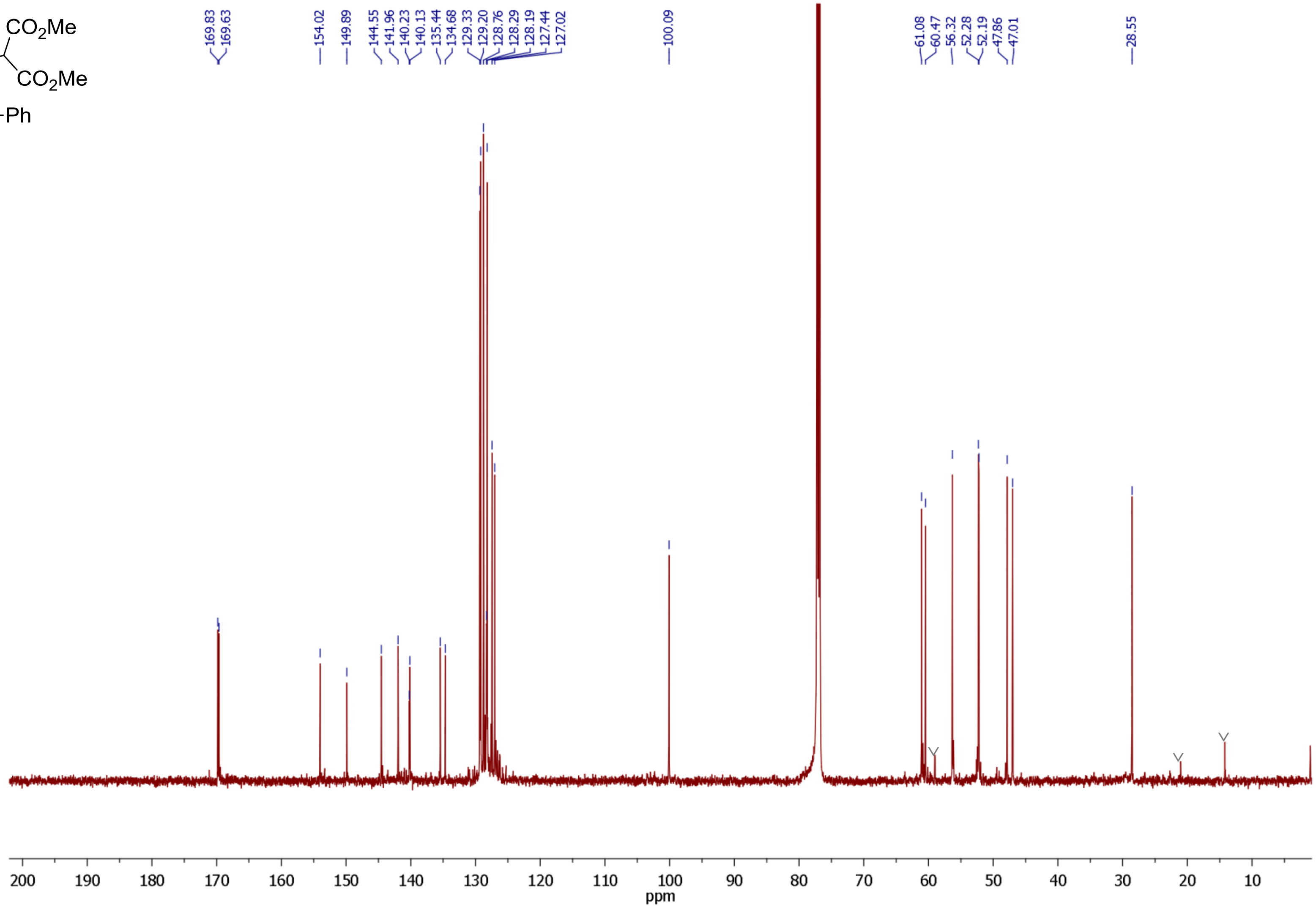




Dimethyl 2-[(4,5,6-trimethoxy-2,3-diphenyl-1H-inden-1-yl)methyl]malonate (3u)

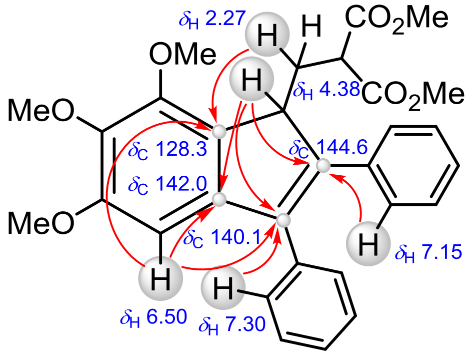
^{13}C NMR ($CDCl_3$, 150 MHz)

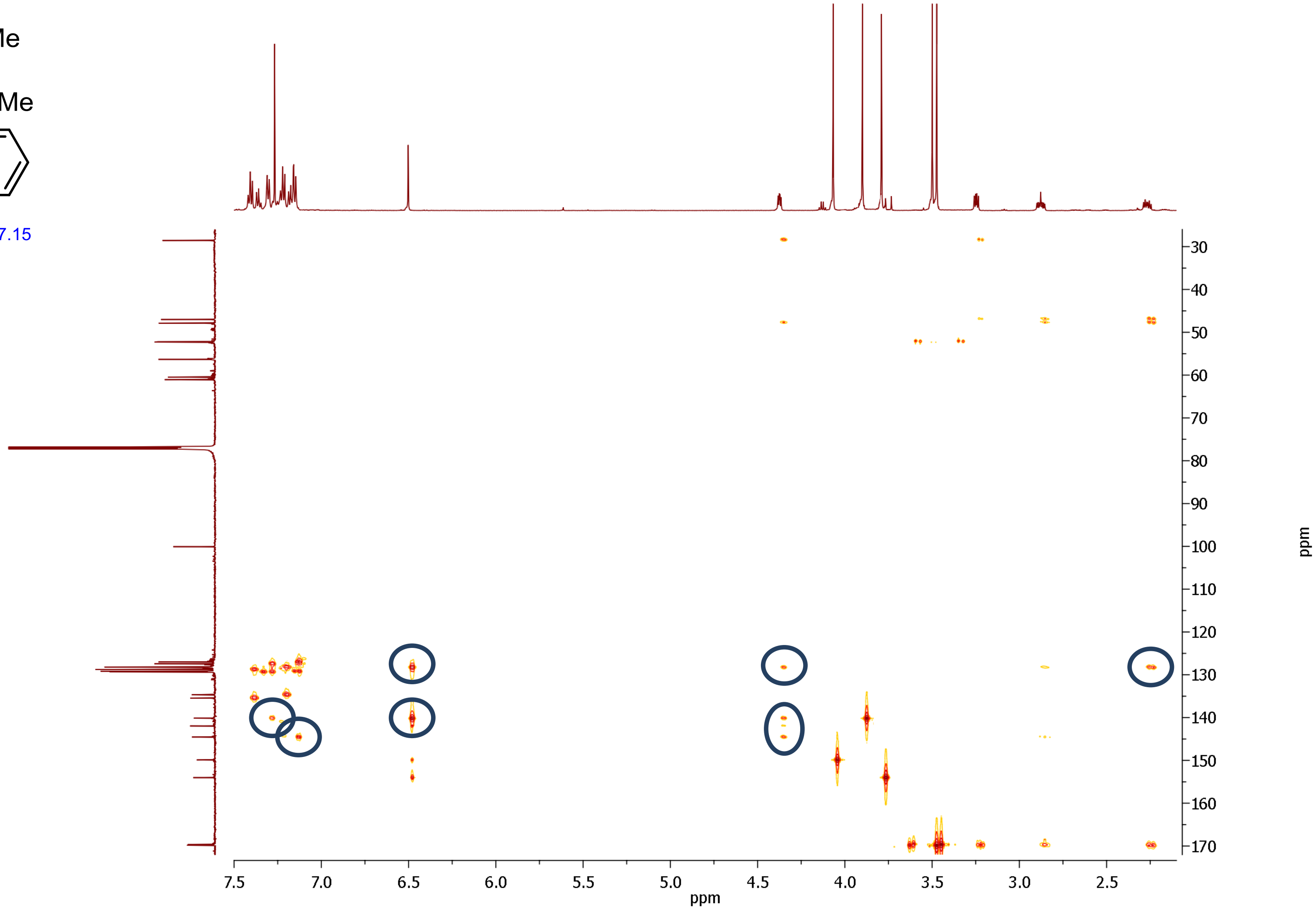




Dimethyl 2-[(4,5,6-trimethoxy-2,3-diphenyl-1H-inden-1-yl)methyl]malonate (3u)

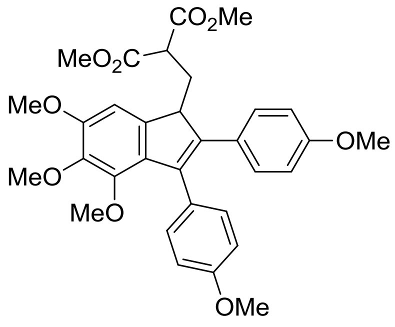
[1]H-[13]C HMBC ($CDCl_3$)

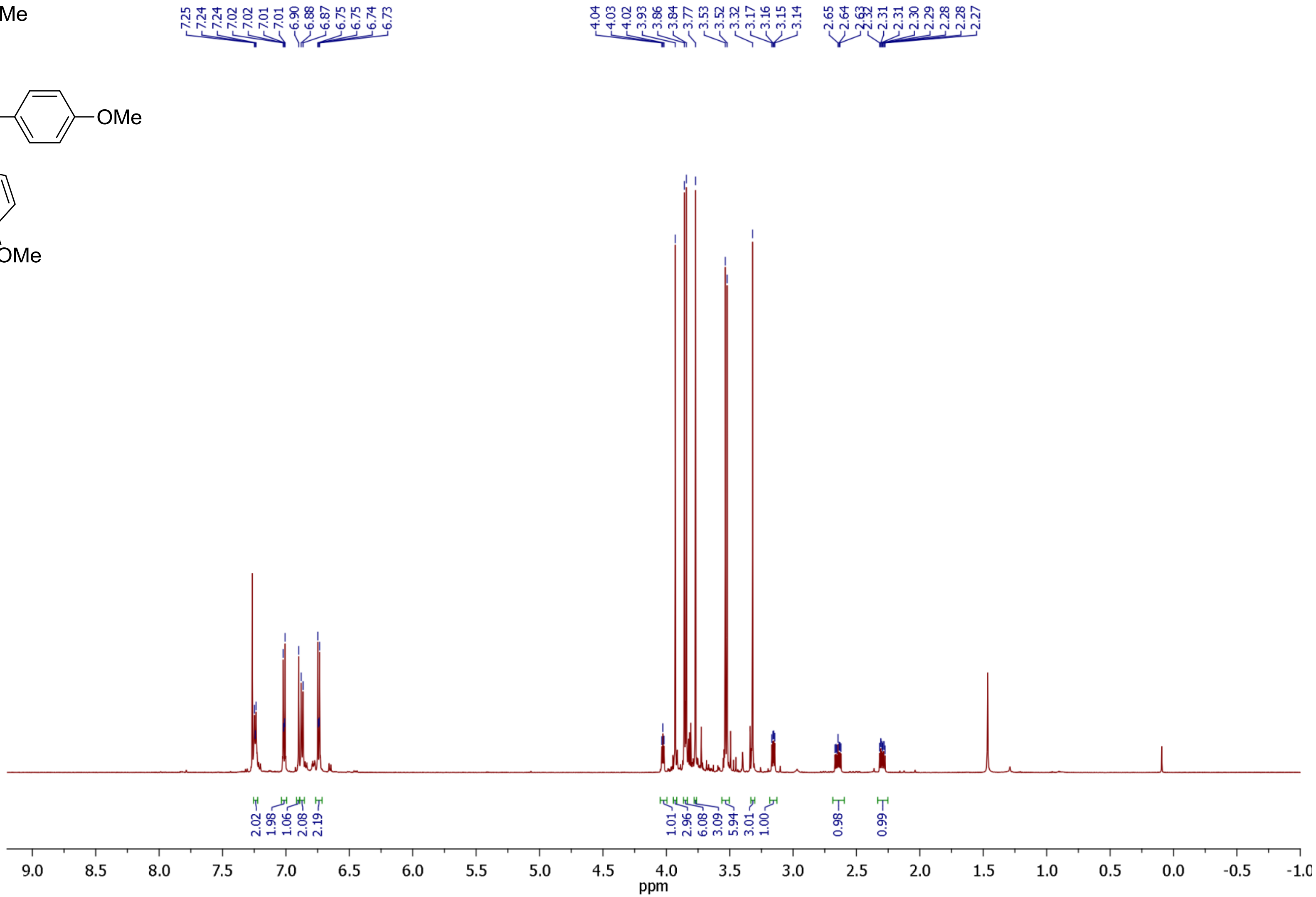




Dimethyl 2-{[4,5,6-trimethoxy-2,3-bis(4-methoxyphenyl)-1H-inden-1-yl]methyl}malonate (3v)

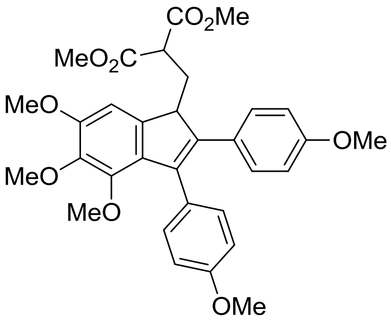
^{1}H NMR ($CDCl_3$, 600 MHz, 333 K)

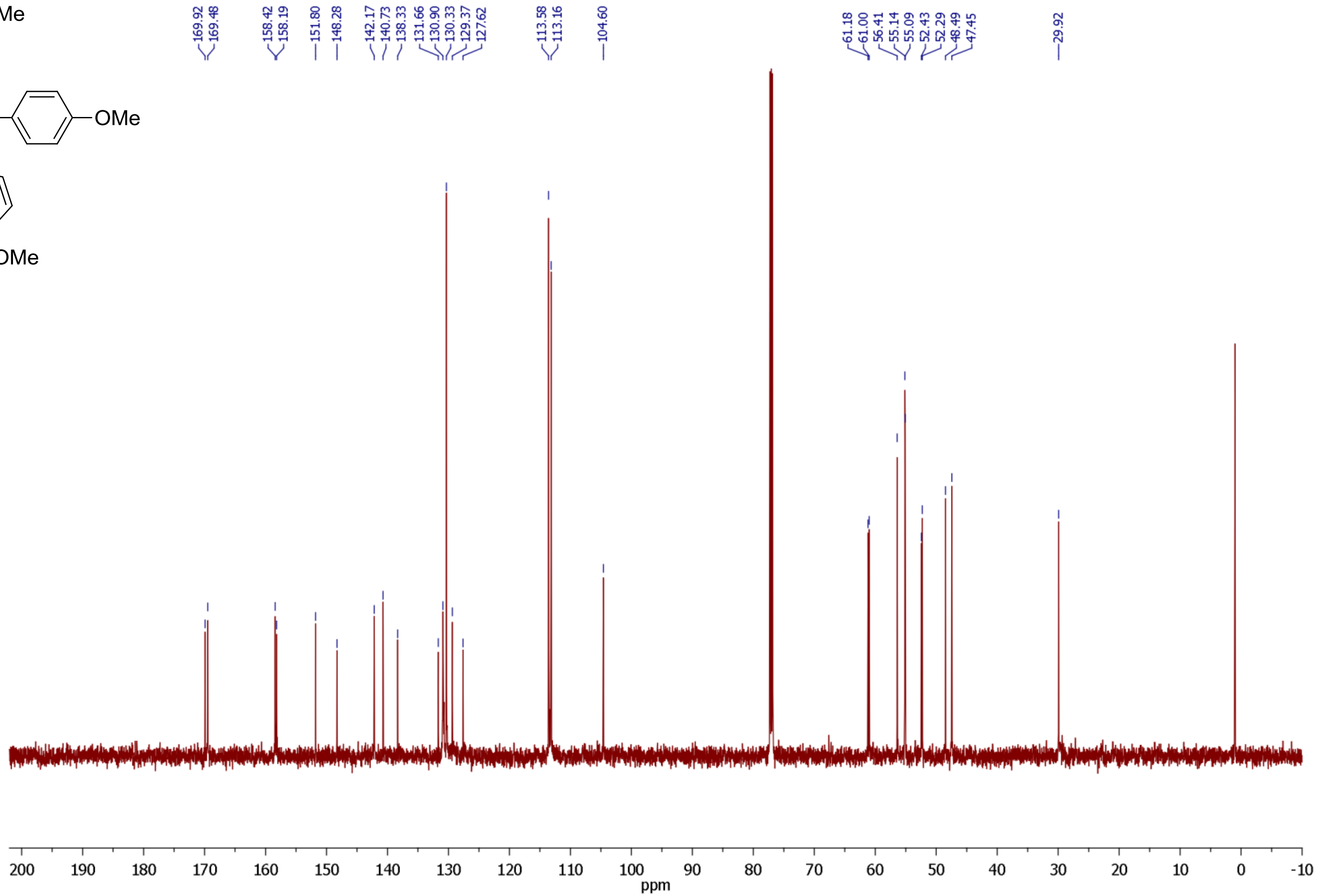




Dimethyl 2-{[4,5,6-trimethoxy-2,3-bis(4-methoxyphenyl)-1H-inden-1-yl]methyl}malonate (3v)

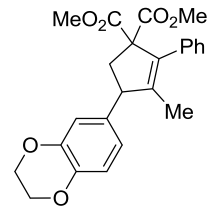
^{13}C NMR ($CDCl_3$, 150 MHz)

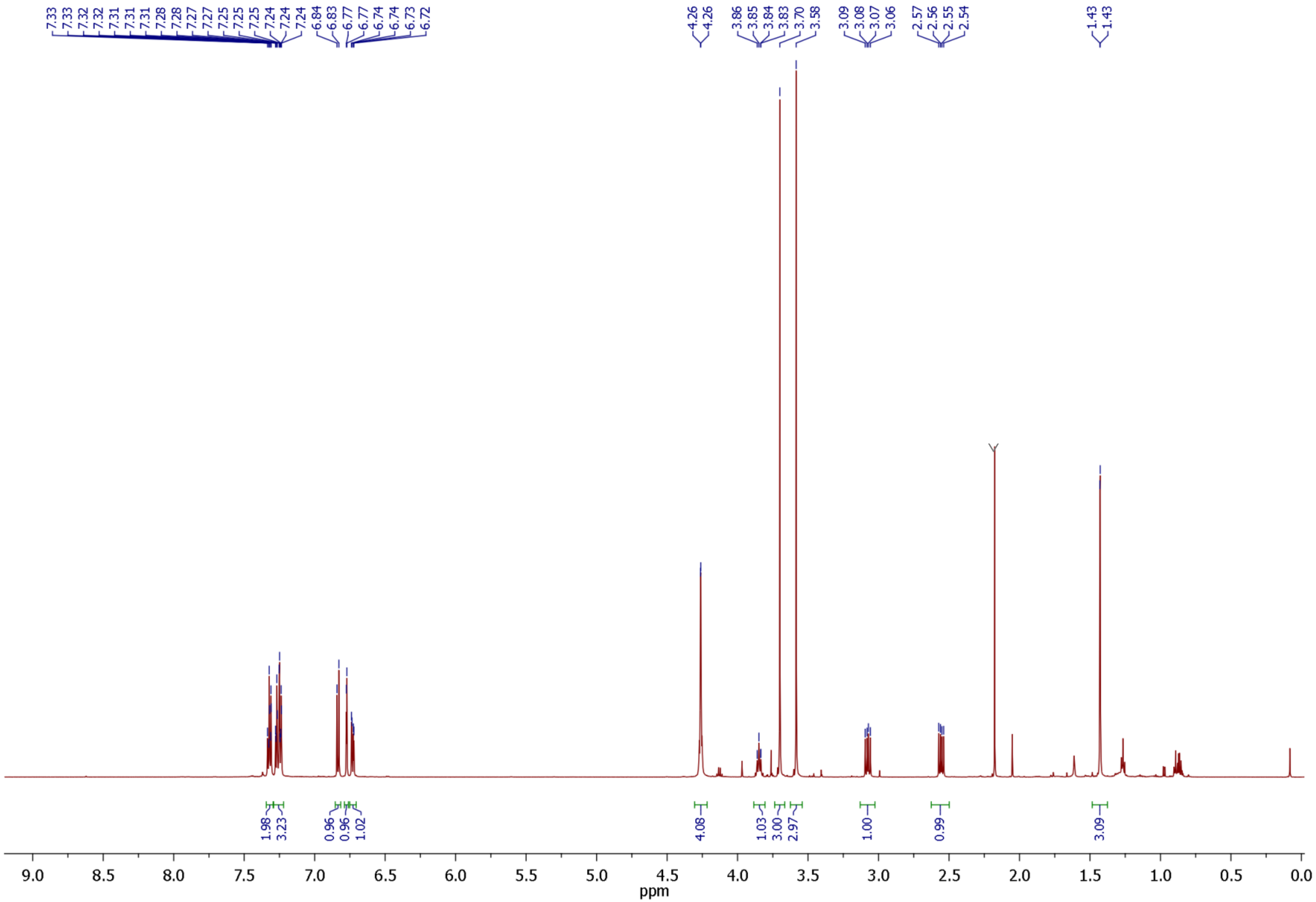




Dimethyl 4-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-3-methyl-2-phenylcyclopent-2-ene-1,1-dicarboxylate (4)

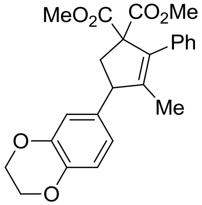
^{1}H NMR ($CDCl_3$, 600 MHz)

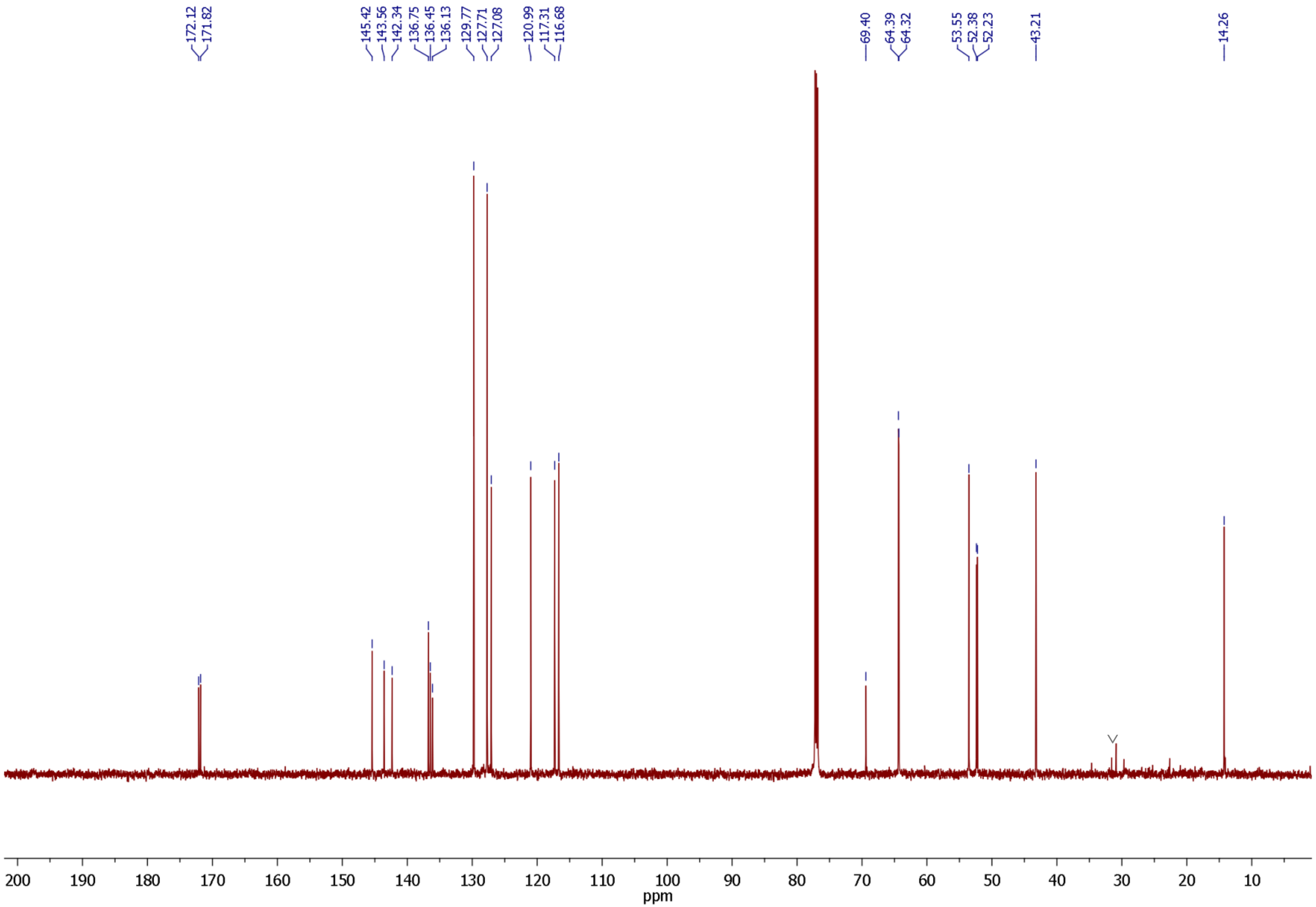




Dimethyl 4-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-3-methyl-2-phenylcyclopent-2-ene-1,1-dicarboxylate (4)

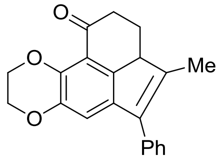
^{13}C NMR ($CDCl_3$, 150 MHz)

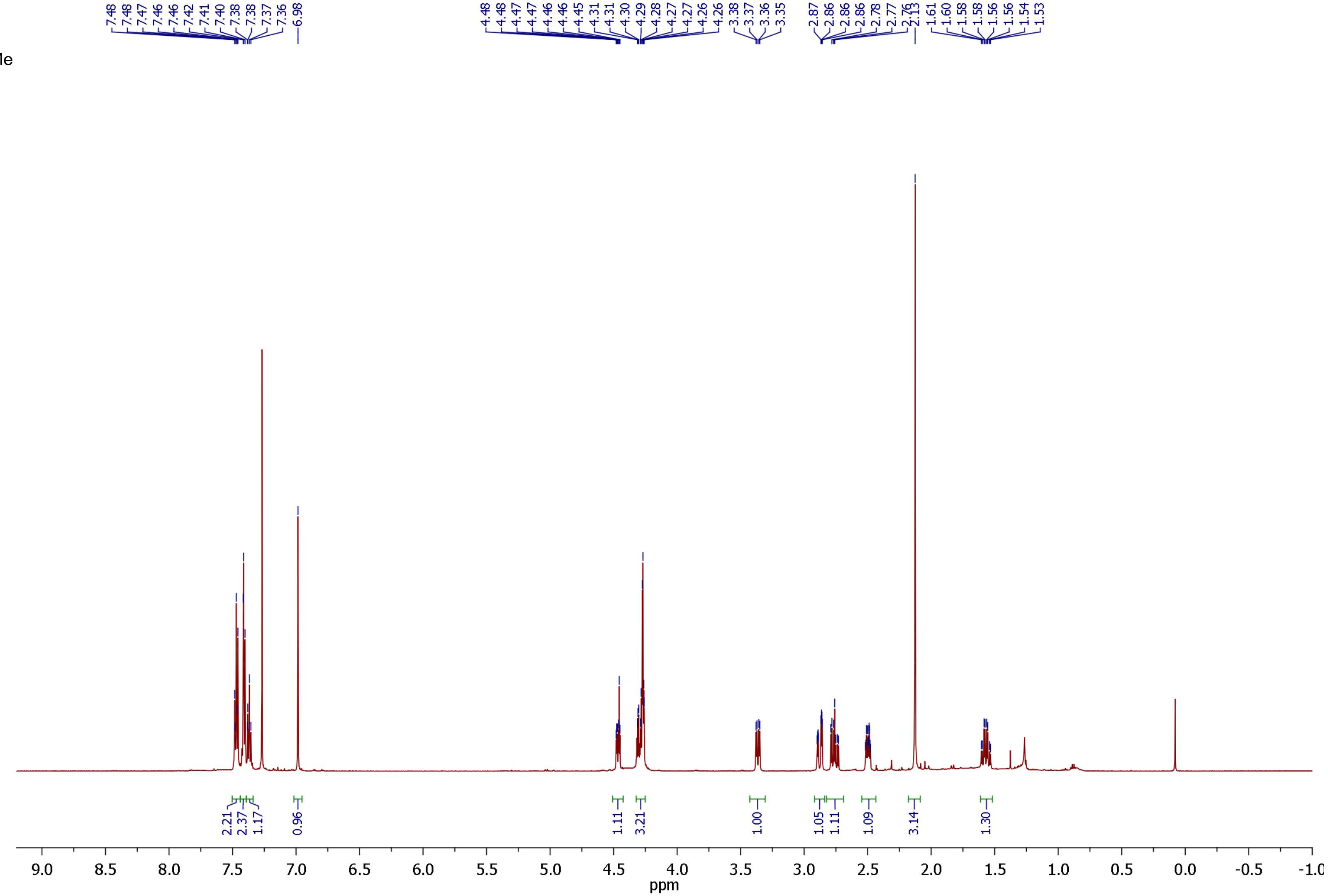




4-Methyl-5-phenyl-3,3a,8,9-tetrahydroacenaphtho[4,5-*b*][1,4]dioxin-1(2*H*)-one (5)

^{1}H NMR ($CDCl_3$, 600 MHz)





4-Methyl-5-phenyl-3,3a,8,9-tetrahydroacenaphtho[4,5-*b*][1,4]dioxin-1(2*H*)-one (5)

^{13}C NMR ($CDCl_3$, 150 MHz)