Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

# Alkene Cyclopropanation by Metallocarbenes Generated from Monocarbonyl Iodonium Ylides

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## General Experimental Details Methods

All reactions were carried out in flame-dried glassware under a dry nitrogen atmosphere, unless otherwise noted. All solvents were obtained pure and dry from a JC Meyer solvent purification system. All reagents were purchased from Sigma-Aldrich and used without further purification. $^{1}H$ NMR spectra were recorded on Bruker instruments at 300 MHz, and were referenced to residual $^{1}H$ shift in $CDCl_3$ (7.24 ppm). All $^{13}C$ [$^{1}H$] NMR were recorded at 75 MHz, and CDCl3 (77.0 ppm) was used as the internal reference. $^{31}P$ NMR spectra were recorded at 121 MHz, and referenced to the $H_3PO_4$ signal at 0 ppm. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br s = broad singlet. Reactions were monitored by thin-layer chromatography (TLC) on commercial silica pre-coated plates with a particle size of 60 Å and viewed by UV lamp (254 nm), by gas chromatography (HP5890A Series II) with a J&W Scientific 30m x 0.53mm DB624 column with 3 micron film thickness (run settings: 2.5 min at 75

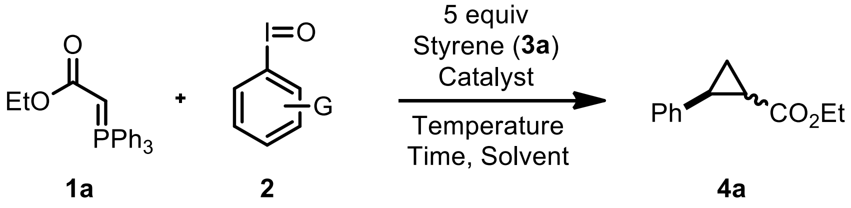
°C, 7.5 °C/min to 250 °C), and by $^{31}$P NMR. Flash chromatography was performed using 60Å (230-400 mesh) silica gel. Melting points were performed using a MeltTemp apparatus. InfraRed (IR) data was recorded using an ATR-FTIR (Attenuated Total Reflection Fourier Transform InfraRed) instrument. The following abbreviations were used to explain the IR peak intensities: (s) = strong, (m) = medium, (w) = weak. Positive ion electrospray ionization (ESI) was performed with a Thermo Scientific Q-Exactive hybrid mass spectrometer. Accurate mass determinations were performed at a mass resolution of 70,000. For ESI, samples were infused at 10 µL/min in 1:1 $CH_3OH/H_2O$ + 0.1% formic acid.

## General Procedure for Synthesis of Iodosoarenes (GP1)

Iodosoarenes **2a**-**2g** are all known compounds, and prepared over two steps from the corresponding aryliodides.[1]

## Table SI-1: Optimization of the Cyclopropanation Reaction

In a dry 10 mL round bottom flask containing $CHCl_3$ (3 mL) was added iodosoarene **2**, the catalyst and additive (if used) and this was stirred at room temperature. Wittig reagent **1** (1 equiv) in $CHCl_3$ (1 mL) was then added dropwise to the reaction mixture by syringe pump over 1 hour, and the reaction stirred for an additional until the indicated length of time at room temperature.



| Entry | Iodosoarene | **2** (Equiv) | Solvent | Temp. (°C) | Time (h) | Catalyst (mol %) | Yield (%) |
|---|---|---|---|---|---|---|---|
| 1 | G = H (**2a**) | 2 | $CHCl_3$ | 25 | 1.5 | Cu(tfacac)$_2$ (10) | 27 |
| 2 | G = *p*-Me (**2e**) | 2 | $CHCl_3$ | 25 | 1.5 | Cu(tfacac)$_2$ (10) | 53 |
| 3 | G = *p*-OMe (**2d**) | 2 | $CHCl_3$ | 25 | 1.5 | Cu(tfacac)$_2$ (10) | 0 |
| 4 | G = *p*-NO$_2$ (**2f**) | 2 | $CHCl_3$ | 25 | 1.5 | Cu(tfacac)$_2$ (10) | 48 |
| 5 | G = *p*-$^t$Bu (**2g**) | 2 | $CHCl_3$ | 25 | 1.5 | Cu(tfacac)$_2$ (10) | 45 |
| 6 | G = *o*-Me (**2c**) | 2 | $CHCl_3$ | 25 | 1.5 | Cu(tfacac)$_2$ (10) | 0 |
| 7 | G = *o*-SO$_2$$^t$Bu (**2b**) | 2 | $CHCl_3$ | 25 | 1.5 | Cu(tfacac)$_2$ (10) | 0 |
| 8 | **2e** | 1.2 | $CHCl_3$ | 25 | 1.5 | Cu(tfacac)$_2$ (10) | 34 |
| 9 | **2e** | 4 | $CHCl_3$ | 25 | 1.5 | Cu(tfacac)$_2$ (10) | 0 |
| 10 | **2e** | 2 | $CH_2Cl_2$ | 25 | 1.5 | Cu(tfacac)$_2$ (10) | 43 |
| 11 | **2e** | 2 | $CH_3CN$ | 25 | 1.5 | Cu(tfacac)$_2$ (10) | 0 |
| 12 | **2e** | 2 | $CHCl_3$ | 25 | 1.5 | Rh$_2$(OAc)$_4$ (5) | 0 |
| 13[a] | **2e** | 2 | $CHCl_3$ | 25 | 1.5 | Cu(tfacac)$_2$ (10) | 0 |
| 14[a] | **2e** | 1.2 | $CHCl_3$ | 25 | 3 | Cu(tfacac)$_2$ (10) | 0 |
| 15 | **2e** | 3 | $CHCl_3$ | 25 | 1 | Cu(tfacac)$_2$ (10) | 30 |

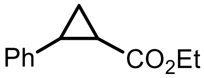
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 16 | **2c** | 1.2 | $CHCl_3$ | 25 | 1.5 | $Cu(tfacac)_2$ (10) | 0 |
| 17 | **2c** | 1.2 | $CHCl_3$ | 25 | 22 | $Cu(tfacac)_2$ (10) | 0 |
| 18 | **2b** | 1.2 | $CHCl_3$ | 25 | 1.5 | $Cu(tfacac)_2$ (10) | 0 |
| 19 | **2b** | 1.2 | $CHCl_3$ | 25 | 2 | $Rh_2(OAc)_4$ (5) | 0 |
| 20 | **2b** | 1.2 | $CHCl_3$ | 25 | 4.5 | $Rh_2(piv)_4$ (5) | 0 |
| 21 | **2b** | 1.2 | $CHCl_3$ | 25 | 5 | $Rh_2(tpa)_4$ (5) | 0 |
| 22 | **2b** | 1.2 | $CHCl_3$ | 25 | 2 | $Cu(hfacac)_2$ (10) | 0 |
| 23 | **2b** | 1.2 | $CHCl_3$ | 25 | 24 | $Cu(tfacac)_2$ (10) | 0 |
| 24 | **2b** | 1 | $CHCl_3$ | 25 | 20 | - | 0 |
| 25 | **2b** | 1.2 | $CHCl_3$ | -78 | 18 | $Cu(tfacac)_2$ (10) | 0 |
| 26 | **2b** | 1.2 | $CHCl_3$ | 25 | 20 | $Cu(acac)_2$ (10) | 0 |
| 27 | **2b** | 2 | $CHCl_3$ | 25 | 75 | $Cu(tfacac)_2$ (10) | 0 |
| 28 | **2b** | 1.2 | $CHCl_3$ | 25 | 75 | $Cu(acac)_2$ (10) | 0 |
| 29 | **2b** | 3 | $CHCl_3$ | 25 | 22 | $Cu(tfacac)_2$ (10) | 0 |
| 30[b] | **2b** | 1.2 | $CHCl_3$ | 25 | 19 | $Rh_2(piv)_4$ (5) | 0 |
| 31 | **2c** | 1.2 | $CHCl_3$ | 40 | 2 | $Cu(tfacac)_2$ (10) | 0 |
| 32 | **2c** | 1.2 | $CHCl_3$ | 25 | 2 | $Cu(tfacac)_2$ (10) | 0 |
| 33 | **2a** | 1.2 | AcOH | 70 | 2 | $Cu(tfacac)_2$ (10) | 0 |
| 34 | **2a** | 1.2 | $CHCl_3$ | 25 | 1.5 | $Cu(tfacac)_2$ (10) | 17 |
| 35 | $PhI(O)_2$ | 1.2 | $CHCl_3$ | 25 | 75 | $Cu(tfacac)_2$ (10) | 0 |
| 36 | $o\text{-}SO_2{}^t BuC_6H_4I(O)_2$ | 1.2 | $CHCl_3$ | 25 | 75 | $Cu(tfacac)_2$ (10) | 0 |
| 37[c] | **2e** | 1.2 | $CHCl_3$ | 25 | 1.5 | $Cu(tfacac)_2$ (10) | 0 |
| 38[d] | **2e** | 2 | $CHCl_3$ | 25 | 2 | $Cu(tfacac)_2$ (10) | 47 |
| 39[e] | **2e** | 2 | $CHCl_3$ | 25 | 2 | $Cu(tfacac)_2$ (10) | 51 |
| 40[f] | PhI | 0.25 | $CHCl_3$ | 25 | 2 | $Cu(tfacac)_2$ (10) | 0 |
| 41 | $PhI(OAc)_2$ | 1 | $CH_2Cl_2$ | 25 | 12 | $Cu(tfacac)_2$ (10) | 0 |
| 42[g] | PhI | 1 | $CH_2Cl_2$ | 25 | 12 | $Cu(tfacac)_2$ (10) | 0 |
| 43[h] | $PhI(OAc)_2$ | 1 | $CH_2Cl_2$ | 25 | 22 | $Cu(tfacac)_2$ (10) | 0 |
| 45[i] | **2e** | 2 | $CHCl_3$ | 25 | 2 | $Cu(tfacac)_2$ (10) | 48 |
| 46[j] | **2e** | 2 | $CHCl_3$ | 25 | 2 | $Cu(tfacac)_2$ (10) | 10 |

[a] Tri-*n*-butyl Wittig reagent used. [b] 4 Å Molecular Sieves used. [c] 4 Å Molecular Sieves and $HBF_4\bullet OEt_2$ used. [d] KBr (1 equiv) used. [e] ${}^nBu_4NI$ (0.1 equiv) used. [f] *m*CPBA (1.5 equiv) used. [g] $NaHCO_3$ (1 equiv) used. [h] $K_2CO_3$ (0.1 equiv) used. [i] Styrene (4 equiv) used. [j] Styrene (1 equiv) used.

## General Procedure for Synthesis of Cyclopropanes 4 (GP2)

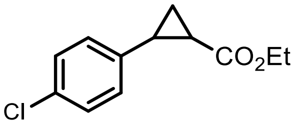
In a dry 10 mL round bottom flask, iodosoarene **2** (0.28 mmol, 2 equiv), $Cu(tfacac)_2$ (0.014 mml, 0.1 equiv), alkene **3** (0.70 mmol, 5 equiv), then $CHCl_3$ (3 mL) was stirred at room temperature. Wittig reagent **1** (0.14 mmol, 1 equiv) in $CHCl_3$ (1 mL) was then added to the solution by syringe pump addition over 1 hour, and the reaction stirred for an additional 0.5 hour (1.5 hours total time) at room temperature. The reaction was quenched with 10 % $K_2CO_3$ (2 mL) and transferred to a separatory funnel. Extraction of product using $CH_2Cl_2$ (3 x 10 mL), followed by washing the combined organic extracts with brine (2 x 10 mL). The organic extracts were dried over $MgSO_4$, filtered, concentrated on a rotory evaporator and then placed under high vacuum. The crude reaction mixture was loaded onto a column of silica gel using a minimal amount of $CH_2Cl_2$. Elution was accomplished using mixtures of EtOAc/hexanes.

**Ethyl 2-phenylcyclopropanecarboxylate (4a)**



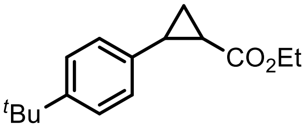
Synthesized according to **GP2** using iodosoarene **2e** (0.201 g, 0.86 mmol, 2 equiv), Cu(tfacac)$_2$ (0.016 g, 0.043 mmol, 0.1 equiv), styrene (0.247 mL, 2.15 mmol, 5 equiv), $CHCl_3$ (4.3 mL), and Wittig reagent **1a** (0.150 g, 0.43 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 8:1) led to the title compound isolated as a pale yellow oil (0.042 g, 53% yield) with a 2.3:1 *trans*:*cis* ratio. $R_f$ = 0.64 (hexanes:EtOAc 3:1). The characterization data matches what has been previously reported in the literature.[2]

**Ethyl 2-(4-chlorophenyl)cyclopropanecarboxylate (4b)**



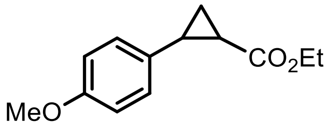
Synthesized according to **GP2** using iodosoarene **2e** (0.200 g, 0.86 mmol, 2 equiv), Cu(tfacac)$_2$ (0.016 g, 0.043 mmol, 0.1 equiv), 4-chlorostyrene (0.288 mL, 2.15 mmol, 5 equiv), $CHCl_3$ (4.3 mL), and Wittig reagent **1a** (0.150 g, 0.43 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 10:1) led to the title compound isolated as a pale yellow oil (0.040 g, 42% yield) with a 2.3:1 *trans*:*cis* ratio. $R_f$ = 0.30 (hexanes:$Et_2O$ 10:1). The characterization data matches what has been previously reported in the literature.[3]

**Ethyl 2-(4-(tert-butyl)phenyl)cyclopropanecarboxylate (4c)**



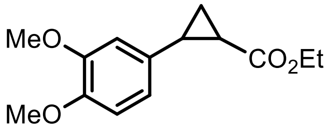
Synthesized according to **GP2** using iodosoarene **2e** (0.066 g, 0.28 mmol, 2 equiv), Cu(tfacac)$_2$ (0.005 g, 0.014 mmol, 0.1 equiv), 4-*tert*-butylstyrene (0.128 mL, 0.70 mmol, 5 equiv), $CHCl_3$ (1.9 mL), and Wittig reagent **1a** (0.050 g, 0.14 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 10:1) led to the title compound isolated as a pale yellow oil (0.013 g, 38% yield) with a 2.4:1 *trans*:*cis* ratio. $R_f = 0.63$ (hexanes:EtOAc 3:1). The characterization data matches what has been previously reported in the literature.[4]

### Ethyl 2-(4-methoxyphenyl)cyclopropanecarboxylate (4d)



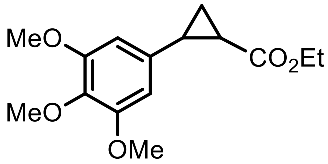
Synthesized according to **GP2** using iodosoarene **2e** (0.201 g, 0.86 mmol, 2 equiv), Cu(tfacac)$_2$ (0.016 g, 0.043 mmol, 0.1 equiv), 4-methoxystyrene (0.286 mL, 2.15 mmol, 5 equiv), $CHCl_3$ (4.3 mL), and Wittig reagent **1a** (0.150 g, 0.43 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 9:1) led to the title compound isolated as a pale yellow oil (0.054 g, 57% yield) with a 2.3:1 *trans*:*cis* ratio. $R_f = 0.59$ (hexanes:EtOAc 3:1). The characterization data matches what has been previously reported in the literature.[3]

### Ethyl 2-(3,4-dimethoxyphenyl)cyclopropanecarboxylate (4e)



Synthesized according to **GP2** using iodosoarene **2e** (0.065 g, 0.28 mmol, 2 equiv), Cu(tfacac)$_2$ (0.005 g, 0.014 mmol, 0.1 equiv), 3,4-dimethoxystyrene (0.115 g, 0.70 mmol, 5 equiv), $CHCl_3$ (3.0 mL), and Wittig reagent **1a** (0.050 g, 0.14 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 12:1) led to the title compound isolated as a pale yellow oil (0.024 g, 68% yield) with a 2.3:1 *trans*:*cis* ratio. $R_f = 0.34$ (hexanes:EtOAc 3:1). The characterization data matches what has been previously reported in the literature.[5]

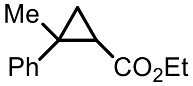
### Ethyl 2-(3,4,5-trimethoxyphenyl)cyclopropanecarboxylate (4f)



Synthesized according to **GP2** using iodosoarene **2e** (0.065 g, 0.28 mmol, 2 equiv), Cu(tfacac)$_2$ (0.005 g, 0.014 mmol, 0.1 equiv), 3,4,5-trimethoxystyrene (0.136 g, 0.70 mmol, 5 equiv), $CHCl_3$ (3.0 mL), and Wittig reagent **1a** (0.050 g, 0.14 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 12:1 to 8:1) led to the title compound isolated as a pale yellow oil (0.029 g, 74% yield) with a 1.9:1 *trans*:*cis* ratio. $R_f = 0.28$

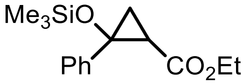
(hexanes:EtOAc 3:1). The characterization data matches what has been previously reported in the literature.[6]

### Ethyl 2-methyl-2-phenylcyclopropanecarboxylate (4g)



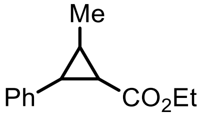
Synthesized according to **GP2** using iodosoarene **2e** (0.135 g, 0.58 mmol, 2 equiv), Cu(tfacac)$_2$ (0.010 g, 0.029 mmol, 0.1 equiv), α-Methylstyrene (0.189 mL, 1.45 mmol, 5 equiv), CHCl$_3$ (4.0 mL), and Wittig reagent **1a** (0.100 g, 0.29 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 12:1 to 10:1) led to the title compound isolated as a pale yellow oil (0.037 g, 63% yield) with a 1.4:1 *trans*:*cis* ratio. R$_f$ = 0.62 (hexanes:EtOAc 3:1). The characterization data matches what has been previously reported in the literature.[7]

### Ethyl 2-phenyl-2-((trimethylsilyl)oxy)cyclopropanecarboxylate (4h)



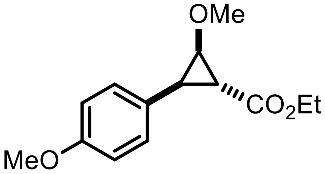
Synthesized according to **GP2** using iodosoarene **2e** (0.201 g, 0.86 mmol, 2 equiv), Cu(tfacac)$_2$ (0.016 g, 0.043 mmol, 0.1 equiv), α-(Trimethylsiloxy)styrene (0.410 g, 2.15 mmol, 5 equiv), CHCl$_3$ (5.0 mL), and Wittig reagent **1a** (0.150 g, 0.43 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 9:1) led to the title compound isolated as a pale yellow oil (0.067 g, 56% yield) with a 1:1 *trans*:*cis* ratio. R$_f$ = 0.36 (hexanes:EtOAc 9:1). The characterization data matches what has been previously reported in the literature.[8]

### Ethyl 2-methyl-3-phenylcyclopropanecarboxylate (4i)



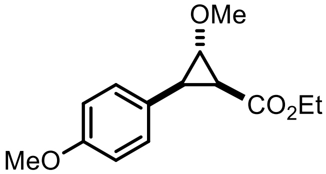
Synthesized according to **GP2** using iodosoarene **2e** (0.065 g, 0.28 mmol, 2 equiv), Cu(tfacac)$_2$ (0.005 g, 0.014 mmol, 0.1 equiv), β-Methylstyrene (0.091 mL, 0.70 mmol, 5 equiv), CHCl$_3$ (4.0 mL), and Wittig reagent **1a** (0.050 g, 0.14 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 6:1 to 5:1) led to the title compound isolated as a pale yellow oil (0.017 g, 59% yield) with a 2.5:1 *trans*:*cis* ratio. R$_f$ = 0.51 (hexanes:EtOAc 3:1). The characterization data matches what has been previously reported in the literature.[9]

### Ethyl 2-methoxy-3-(4-methoxyphenyl)cyclopropanecarboxylate (4k)



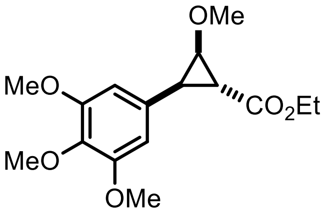
Synthesized according to **GP2** using iodosoarene **2e** (0.131 g, 0.56 mmol, 2 equiv), Cu(tfacac)$_2$ (0.010 g, 0.029 mmol, 0.1 equiv), (Z)-1-methoxy-4-(2-methoxyvinyl)benzene (0.230 g, 1.4 mmol, 5 equiv), CHCl$_3$ (4.0 mL), and Wittig reagent **1a** (0.100 g, 0.29 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 10:1 to 8:1) led to the title compound isolated as a pale yellow oil (0.042 g, 60% yield). R$_f$ = 0.53 (hexanes:EtOAc 3:1); IR: 2935 (w), 1717 (s), 1515 (s), 1287 (m), 830 (s) cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) 7.18 (d, *J* = 9.0 Hz, 2H), 6.83 (d, *J* = 9.0 Hz, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.77 - 3.80 (m, 4H), 3.30 (s, 3H), 2.65 (dd, *J* = 6.3, 6.3 Hz, 1H), 2.11 (dd, *J* = 6.0, 2.7 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) 175.1, 161.3, 132.2, 129.6, 116.5, 68.8, 63.7, 61.6, 58.1, 34.8, 30.9, 17.1; HRMS: ESI$^+$ [M+H]$^+$ calcd for $C_{14}H_{19}O_4$ 251.1278, found 251.1278.

### Ethyl 2-methoxy-3-(4-methoxyphenyl)cyclopropanecarboxylate (4l)



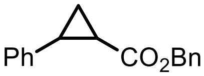
Synthesized according to **GP2** using iodosoarene **2e** (0.140 g, 0.60 mmol, 2 equiv), Cu(tfacac)$_2$ (0.011 g, 0.030 mmol, 0.1 equiv), (E)-1-methoxy-4-(2-methoxyvinyl)benzene (0.246 g, 1.50 mmol, 5 equiv), CHCl$_3$ (4.0 mL), and Wittig reagent **1a** (0.104 g, 0.30 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 20:1 to 8:1) led to the title compound isolated as a pale yellow oil (0.046 g, 61% yield) with a 1:2.9 *trans*:*cis* ratio. R$_f$ = 0.40 (hexanes:EtOAc 3:1); IR: 2935 (w), 1732 (s), 1515 (s), 1243 (s) cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) 7.31 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 4.02 (dq, *J* = 7.1, 4.1 Hz, 2H), 3.74 - 3.83 (m, 4H), 3.40 (s, 3H), 2.51 (dd, *J* = 10.1, 7.1 Hz, 1H), 1.97 (dd, *J* = 10.1, 6.1 Hz, 1H), 1.29 (*t*, J = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) 171.1, 161.1, 134.1, 128.4, 116.2, 66.2, 62.9, 62.0, 58.0, 30.6, 26.7, 17.1; HRMS: ESI$^+$ [M+H]$^+$ calcd for $C_{14}H_{19}O_4$ 251.1278, found 251.1275.

### Ethyl 2-methoxy-3-(3,4,5-trimethoxyphenyl)cyclopropanecarboxylate (4m)



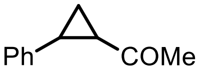
Synthesized according to **GP2** using iodosoarene **2e** (0.065 g, 0.28 mmol, 2 equiv), Cu(tfacac)$_2$ (0.005 g, 0.014 mmol, 0.1 equiv), (Z)-1,2,3-trimethoxy-5-(2-methoxyvinyl)benzene (0.157 g, 0.70 mmol, 5 equiv), $CHCl_3$ (4.0 mL), and Wittig reagent **1a** (0.050 g, 0.14 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 12:1 to 8:1) led to the title compound isolated as a pale yellow oil (0.035 g, 81% yield). $R_f$ = 0.27 (hexanes:EtOAc 3:1); IR: 2936 (w), 1718 (s), 1587 (m), 1123 (s), 834 (w) cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$) 6.49 (s, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.78 - 3.89 (m, 10H), 3.34 (s, 3H), 2.62 (dd, *J* = 6.3, 6.3 Hz, 1H), 2.13 (dd, *J* = 6.0, 2.7 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) 172.1, 153.1, 137.0, 130.7, 105.6, 66.2, 61.1, 59.0, 56.3, 32.8, 28.7, 14.4; HRMS: ESI$^+$ [M+H]$^+$ calcd for $C_{16}H_{23}O_6$ 311.1489, found 311.1487.

**Benzyl 2-phenylcyclopropanecarboxylate (4n)**



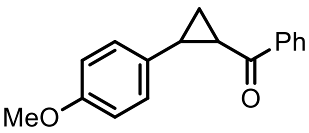
Synthesized according to **GP2** using iodosoarene **2e** (0.112 g, 0.48 mmol, 2 equiv), Cu(tfacac)$_2$ (0.009 g, 0.024 mmol, 0.1 equiv), styrene (0.137 mL, 1.20 mmol, 5 equiv), $CHCl_3$ (4.0 mL), and Wittig reagent **1b** (0.100 g, 0.24 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 9:1 to 3:1) led to the title compound isolated as a pale yellow oil (0.033 g, 55% yield) with a 3:1 *trans*:*cis* ratio. $R_f$ = 0.56 (hexanes:EtOAc 3:1). The characterization data matches what has been previously reported in the literature.[10]

**1-(2-Phenylcyclopropyl)ethanone (4o)**



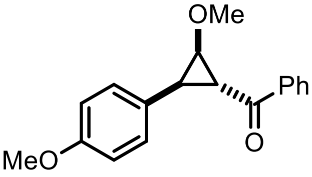
Synthesized according to **GP2** using iodosoarene **2e** (0.112 g, 0.48 mmol, 2 equiv), Cu(tfacac)$_2$ (0.009 g, 0.024 mmol, 0.1 equiv), styrene (0.137 mL, 1.20 mmol, 5 equiv), $CHCl_3$ (2.5 mL), and Wittig reagent **1c** (0.075 g, 0.24 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 10:1) led to the title compound isolated as a pale yellow oil (0.018 g, 46% yield) with a 2:1 *trans*:*cis* ratio. $R_f$ = 0.73 (hexanes:EtOAc 2:1). The characterization data matches what has been previously reported in the literature.[11]

**(2-(4-Methoxyphenyl)cyclopropyl)(phenyl)methanone (4p)**



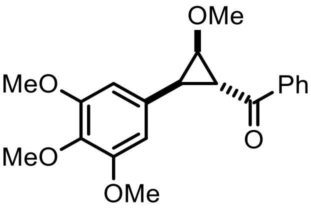
Synthesized according to **GP2** using iodosoarene **2e** (0.182 g, 0.78 mmol, 2 equiv), Cu(tfacac)$_2$ (0.014 g, 0.039 mmol, 0.1 equiv), 4-methoxystyrene (0.250 mL, 1.95 mmol, 5 equiv), CHCl$_3$ (3.5 mL), and Wittig reagent **1d** (0.150 g, 0.39 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 10:1) led to the title compound isolated as a pale yellow oil (0.029 g, 30% yield) with a 2:1 *trans*:*cis* ratio. R$_f$ = 0.58 (hexanes:EtOAc 3:1). The characterization data matches what has been previously reported in the literature.[12]

**2-Methoxy-3-(4-methoxyphenyl)cyclopropyl)(phenyl)methanone (4q)**



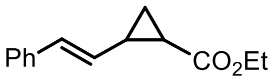
Synthesized according to **GP2** using iodosoarene **2e** (0.031 g, 0.13 mmol, 2 equiv), Cu(tfacac)$_2$ (0.002 g, 0.007 mmol, 0.1 equiv), (Z)-1-methoxy-4-(2-methoxyvinyl)benzene (0.054 g, 0.33 mmol, 5 equiv), CHCl$_3$ (3.0 mL), and Wittig reagent **1d** (0.025 g, 0.07 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 10:1 to 8:1) led to the title compound isolated as a pale yellow oil (0.010 g, 54% yield). R$_f$ = 0.51 (hexanes:EtOAc 3:1); IR: 2934 (w), 1658 (m), 1245 (s), 1178 (m), 832 (m), 690 (s) cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) 8.02 (d, $J$ = 7.5 Hz, 2H), 7.58 (t, $J$ = 7.2 Hz, 1H), 7.48 (app. t, $J$ = 7.5 Hz, 2H), 7.28 (d, $J$ = 8.4 Hz, 2H), 6.86 (d, $J$ = 8.1 Hz, 2H), 3.98 (dd, $J$ = 6.6, 3.0 Hz, 1H), 3.79 (s, 3H), 3.36 (s, 3H), 3.14 (dd, $J$ = 6.0, 2.4 Hz, 1H), 2.98 (dd, $J$ = 6.0, 6.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) 200.4, 161.4, 140.3, 135.9, 132.3, 131.5, 130.9, 130.2, 116.6, 72.5, 61.8, 58.2, 38.0, 36.6; HRMS: ESI$^+$ [M+H]$^+$ calcd for $C_{18}H_{19}O_3$ 283.1329, found 283.1332.

**2-Methoxy-3-(3,4,5-trimethoxyphenyl)cyclopropyl)(phenyl)methanone (4r)**



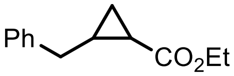
Synthesized according to **GP2** using iodosoarene **2e** (0.164 g, 0.70 mmol, 2 equiv), Cu(tfacac)$_2$ (0.013 g, 0.035 mmol, 0.1 equiv), (Z)-1,2,3-trimethoxy-5-(2-methoxyvinyl)benzene (0.392 g, 1.75 mmol, 5 equiv), $CHCl_3$ (4.0 mL), and Wittig reagent **1d** (0.133 g, 0.35 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 20:1 to 8:1) led to the title compound isolated as a pale yellow oil (0.093 g, 78% yield). $R_f = 0.19$ (hexanes:EtOAc 3:1); IR: 2932 (w), 1669 (m), 1587 (m), 1448(m), 1217 (m), 1124 (s), 1008 (s), 689 (m) cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$) 8.09 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.1 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 6.40 (s, 2H), 3.98 (dd, *J* = 6.4, 4.4 Hz, 1H), 3.90 (s, 6H), 3.85 (s, 3H), 3.46 (dd, *J* = 5.0, 4.4 Hz, 1H), 3.30 (s, 3H), 3.05 (dd, *J* = 6.5, 6.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) 195.7, 156.2, 141.1, 139.9, 136.8, 135.8, 131.5, 131.0, 107.0, 72.4, 63.8, 62.0, 59.1, 38.4, 34.2; HRMS: ESI$^+$ [M+H]$^+$ calcd for $C_{20}H_{23}O_5$ 343.1540, found 343.1538.

### (E)-Ethyl 2-styrylcyclopropanecarboxylate (4s)



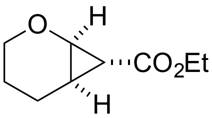
Synthesized according to **GP2** using iodosoarene **2e** (0.066 g, 0.28 mmol, 2 equiv), Cu(tfacac)$_2$ (0.005 g, 0.014 mmol, 0.1 equiv), (E)-1-phenyl-1,3-butadiene (0.091 g, 0.70 mmol, 5 equiv), $CHCl_3$ (3.0 mL), and Wittig reagent **1a** (0.050 g, 0.14 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 8:1) led to the title compound isolated as a pale yellow oil (0.018 g, 61% yield) with a 1.6:1 *trans*:*cis* ratio. $R_f = 0.45$ (hexanes:EtOAc 3:1). The characterization data matches what has been previously reported in the literature.[13]

### Ethyl 2-benzylcyclopropanecarboxylate (4t)



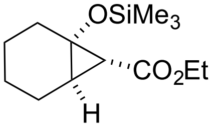
Synthesized according to **GP2** using iodosoarene **2e** (0.065 g, 0.28 mmol, 2 equiv), Cu(tfacac)$_2$ (0.005 g, 0.014 mmol, 0.1 equiv), allylbenzene (0.082 g, 0.70 mmol, 5 equiv), $CHCl_3$ (3.0 mL), and Wittig reagent **1a** (0.050 g, 0.14 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 20:1 to 10:1) led to the title compound isolated as a pale yellow oil (0.014 g, 49% yield) with a 1.9:1 *trans*:*cis* ratio. $R_f = 0.68$ (hexanes:EtOAc 3:1). The characterization data matches what has been previously reported in the literature.[14]

### Ethyl 2-oxabicyclo[4.1.0]heptane-7-carboxylate (4u)



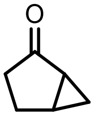
Synthesized according to **GP2** using iodosoarene **2e** (0.066 g, 0.28 mmol, 2 equiv), Cu(tfacac)$_2$ (0.005 g, 0.014 mmol, 0.1 equiv), dihydropyran (0.064 mL, 0.70 mmol, 5 equiv), CHCl$_3$ (2.5 mL), and Wittig reagent **1a** (0.050 g, 0.14 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 8:1 to 3:1) led to the title compound isolated as a pale yellow oil (0.014 g, 60% yield) as a 3:1 *trans*:*cis* ratio. R$_f$ = 0.80 (EtOAc:Petroleum ether 1:4). The characterization data matches what has been previously reported in the literature.[15]

### Ethyl 1-((trimethylsilyl)oxy)bicyclo[4.1.0]heptane-7-carboxylate (4v)



Synthesized according to **GP2** using iodosoarene **2e** (0.135 g, 0.58 mmol, 2 equiv), Cu(tfacac)$_2$ (0.010 g, 0.029 mmol, 0.1 equiv), 1-(Trimethylsiloxy)cyclohexene (0.286 mL, 1.45 mmol, 5 equiv), CHCl$_3$ (4.0 mL), and Wittig reagent **1a** (0.100 g, 0.29 mmol, 1 equiv). Purification by flash chromatography through a column of silica gel (hexanes:EtOAc 20:1 to 10:1) led to the title compound isolated as a pale yellow oil (0.047 g, 63% yield) as a 1:1.7 *trans*:*cis* ratio. R$_f$ = 0.53 (hexanes:EtOAc 9:1). The characterization data matches what has been previously reported in the literature.[8]

### Bicyclo[3.1.0]hexan-2-one (4w)



To a dry 10 mL round bottom flask was added iodosoarene **2e** (0.102 g, 0.44 mmol, 2 equiv), Cu(tfacac)$_2$ (0.008 g, 0.022 mml, 0.1 equiv), Wittig reagent **1e** (0.080 g, 0.22 mmol, 1 equiv), then CHCl$_3$ (4 mL), and the resulting mixture stirred at room temperature for 3.5 hours. The reaction was quenched with 10 % K$_2$CO$_3$ (2 mL), transferred to a seperatory funnel and extracted using CH$_2$Cl$_2$ (3 x 10 mL). The combined organic extracts were washed with brine (2 x 10 mL), dried over MgSO$_4$, filtered, and concentrated by rotary evaporation (keeping the bath temperature below 30 °C). The crude reaction mixture was loaded onto a column of silica gel using a minimal amount of CH$_2$Cl$_2$ and elution was accomplished using (hexanes:EtOAc 10:1 to 5:1), which gave 0.013 g of **4w** as a pale yellow oil in 63% yield. The characterization data matches what has been previously reported in the literature.[16]

# References

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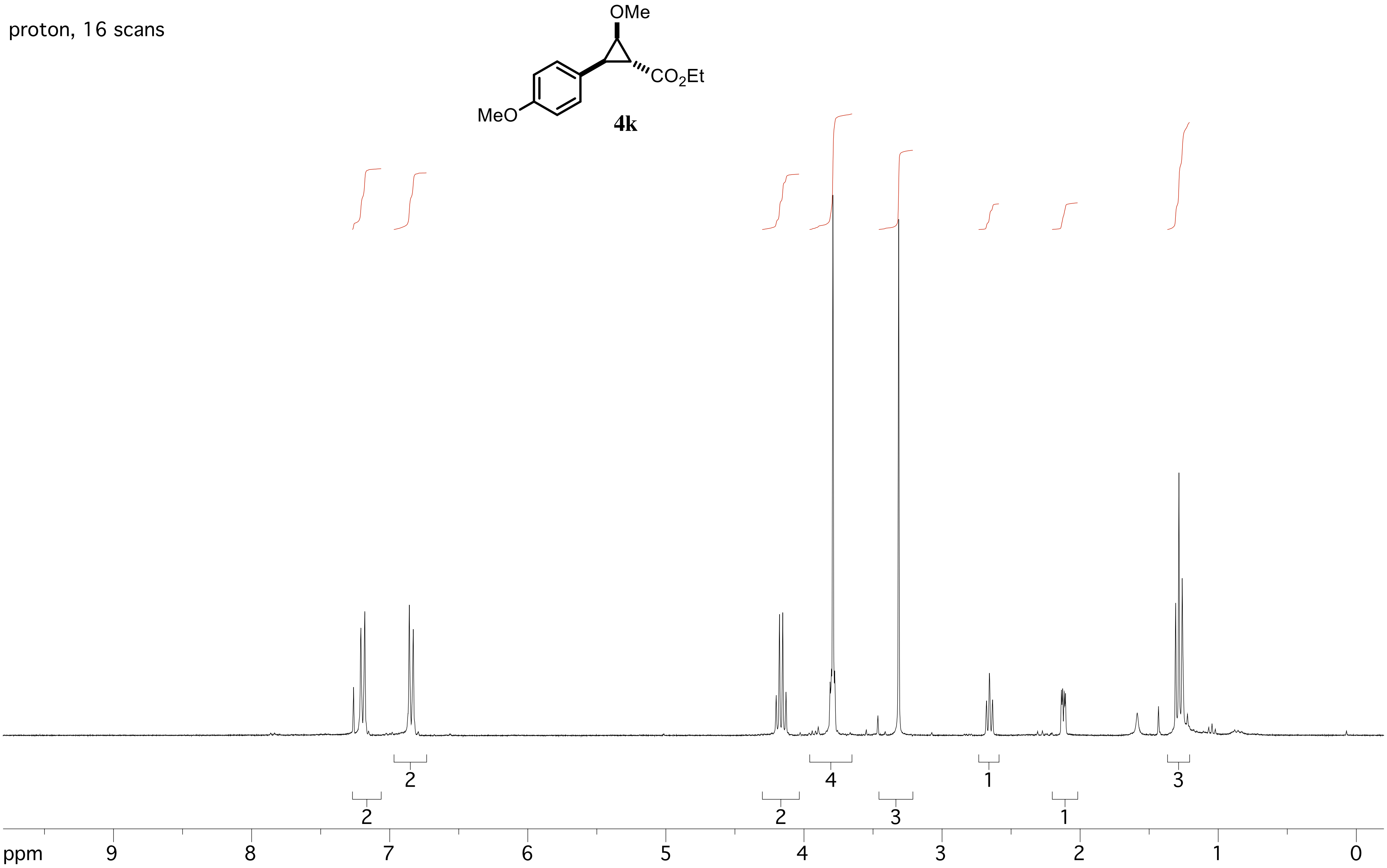
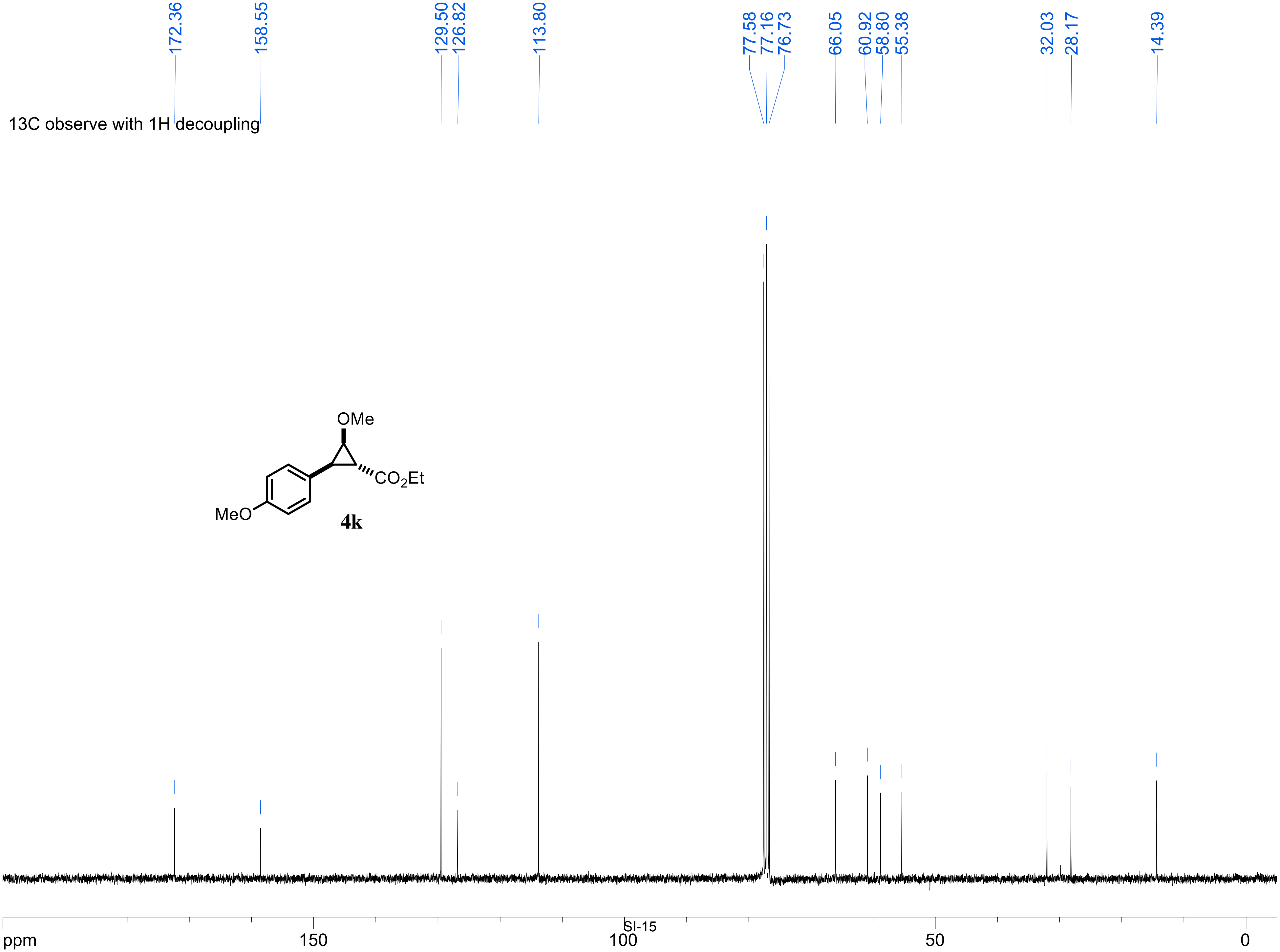
# NMR Spectra of New Compounds

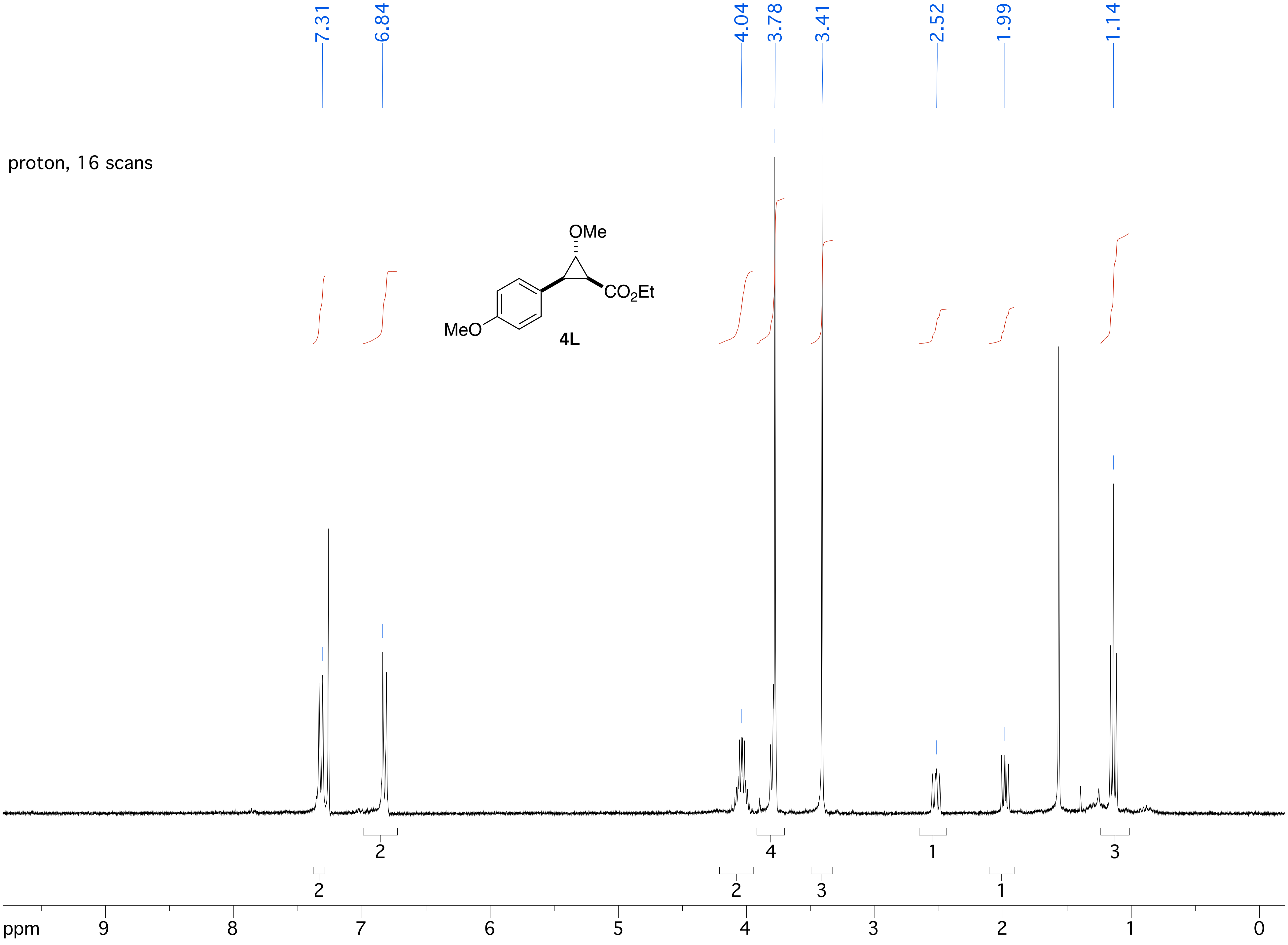
proton, 16 scans

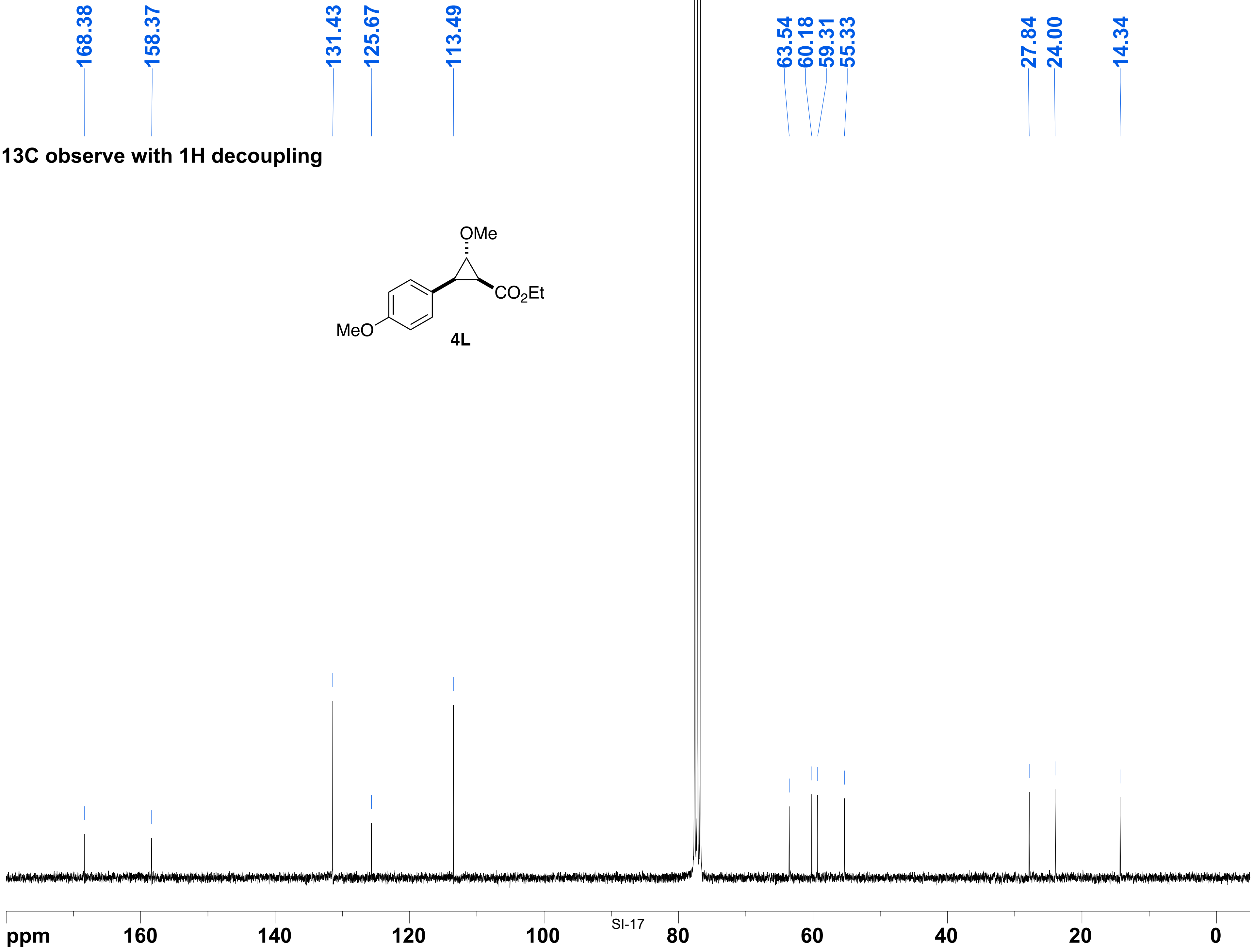


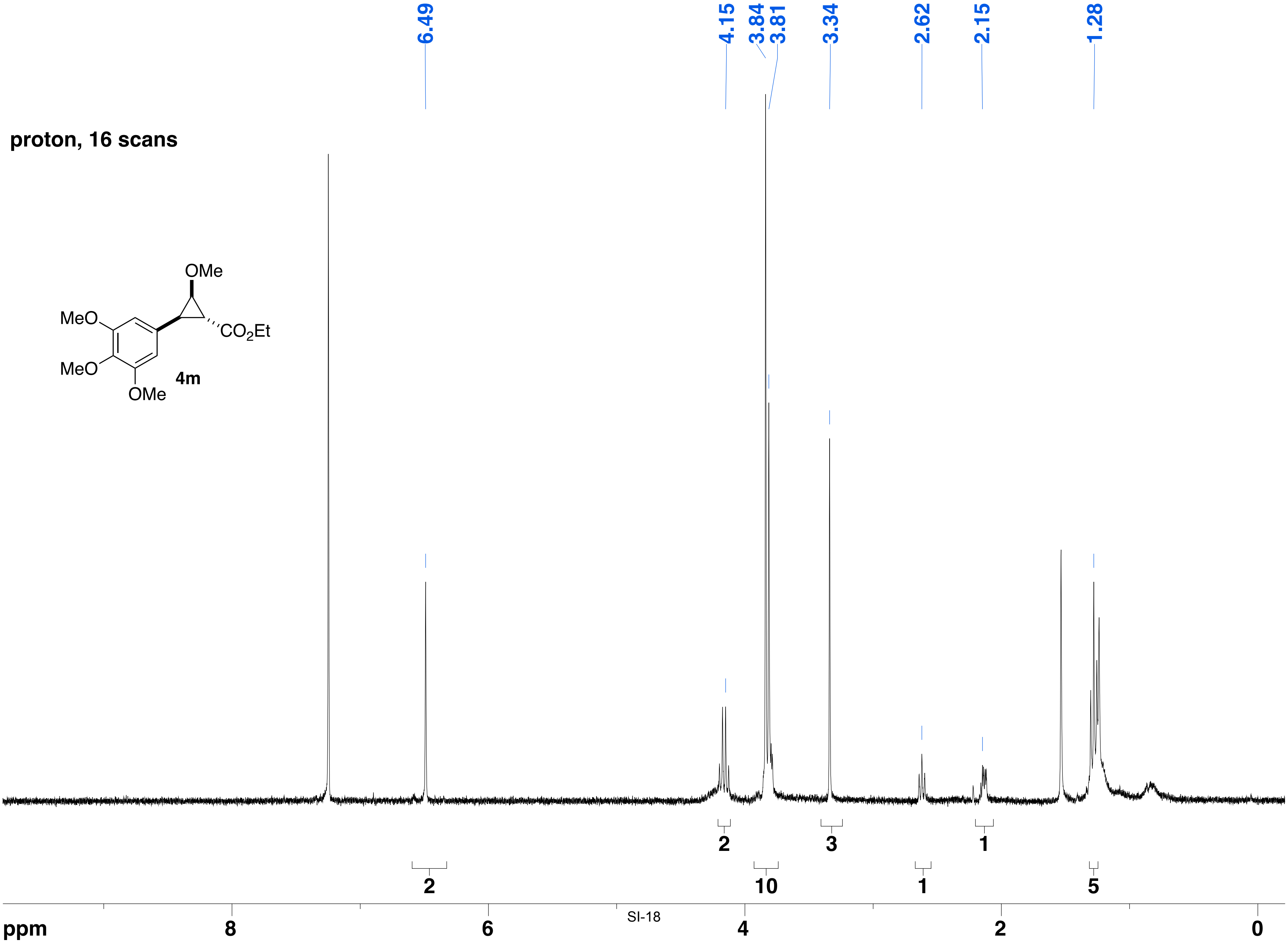
**4k**

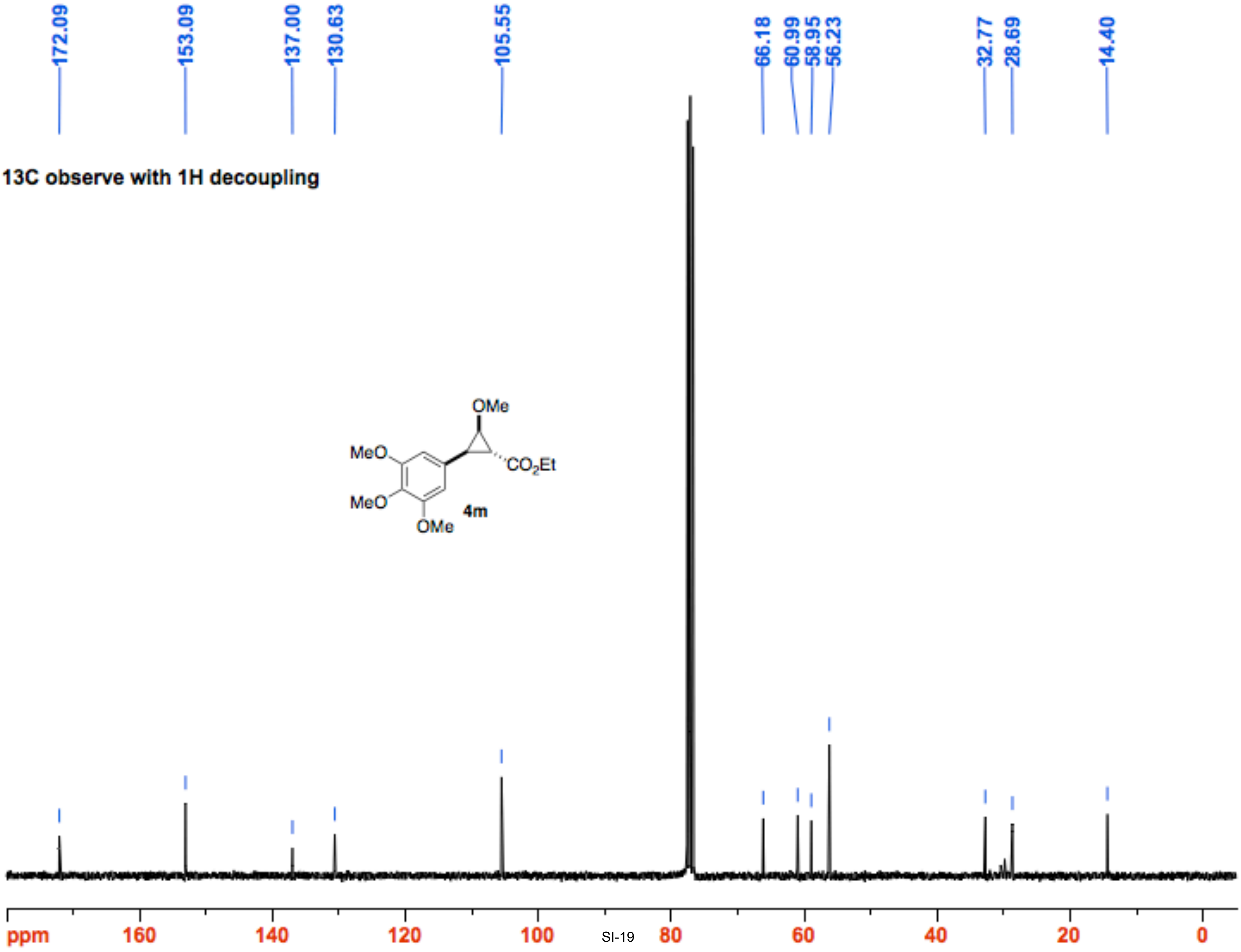

172.36
158.55
129.50
126.82
113.80
77.58
77.16
76.73
66.05
60.92
58.80
55.38
32.03
28.17
14.39
13C observe with 1H decoupling
OMe
$CO_2Et$
MeO
ppm
150
100
50
0

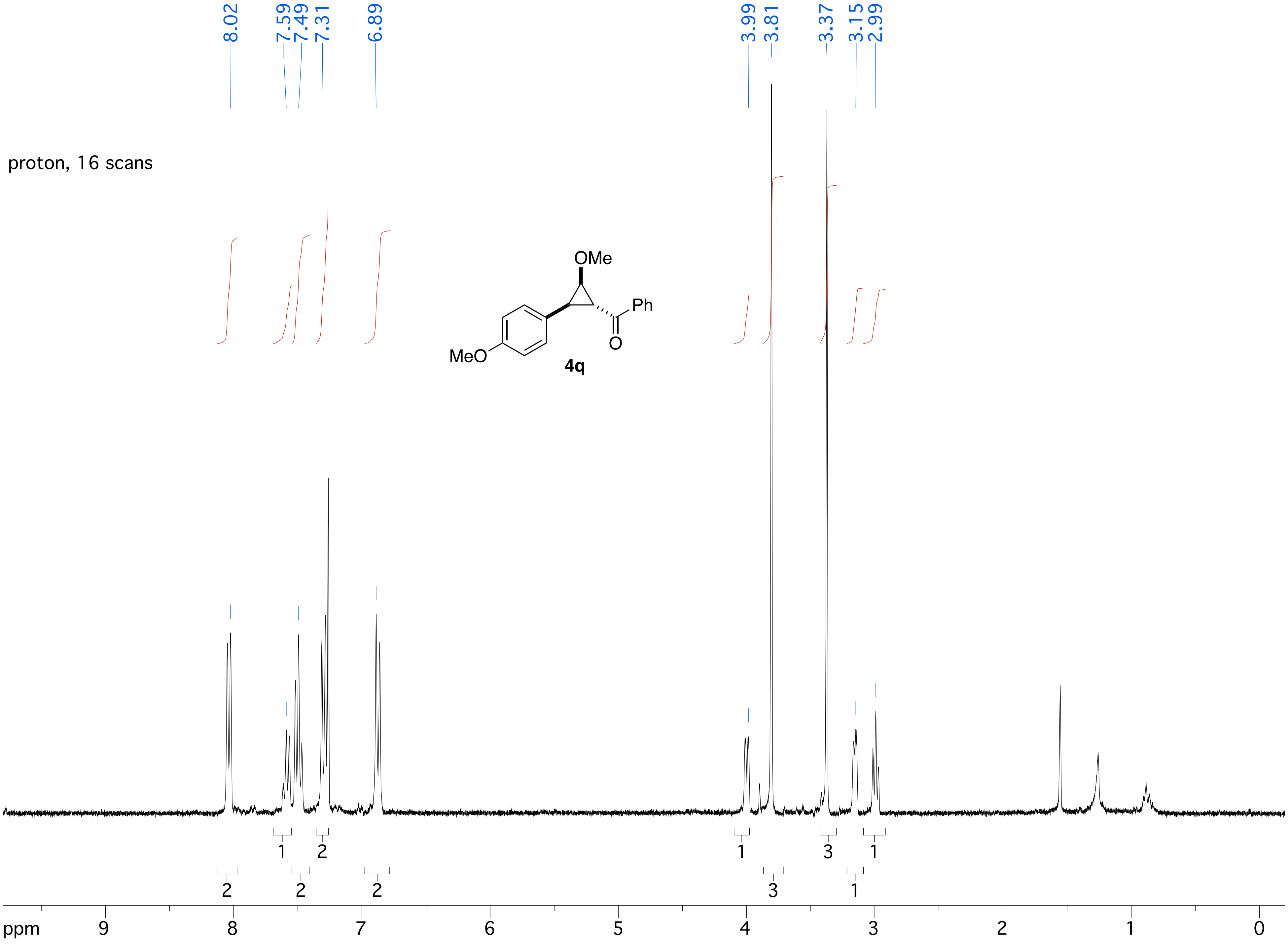
**4k**

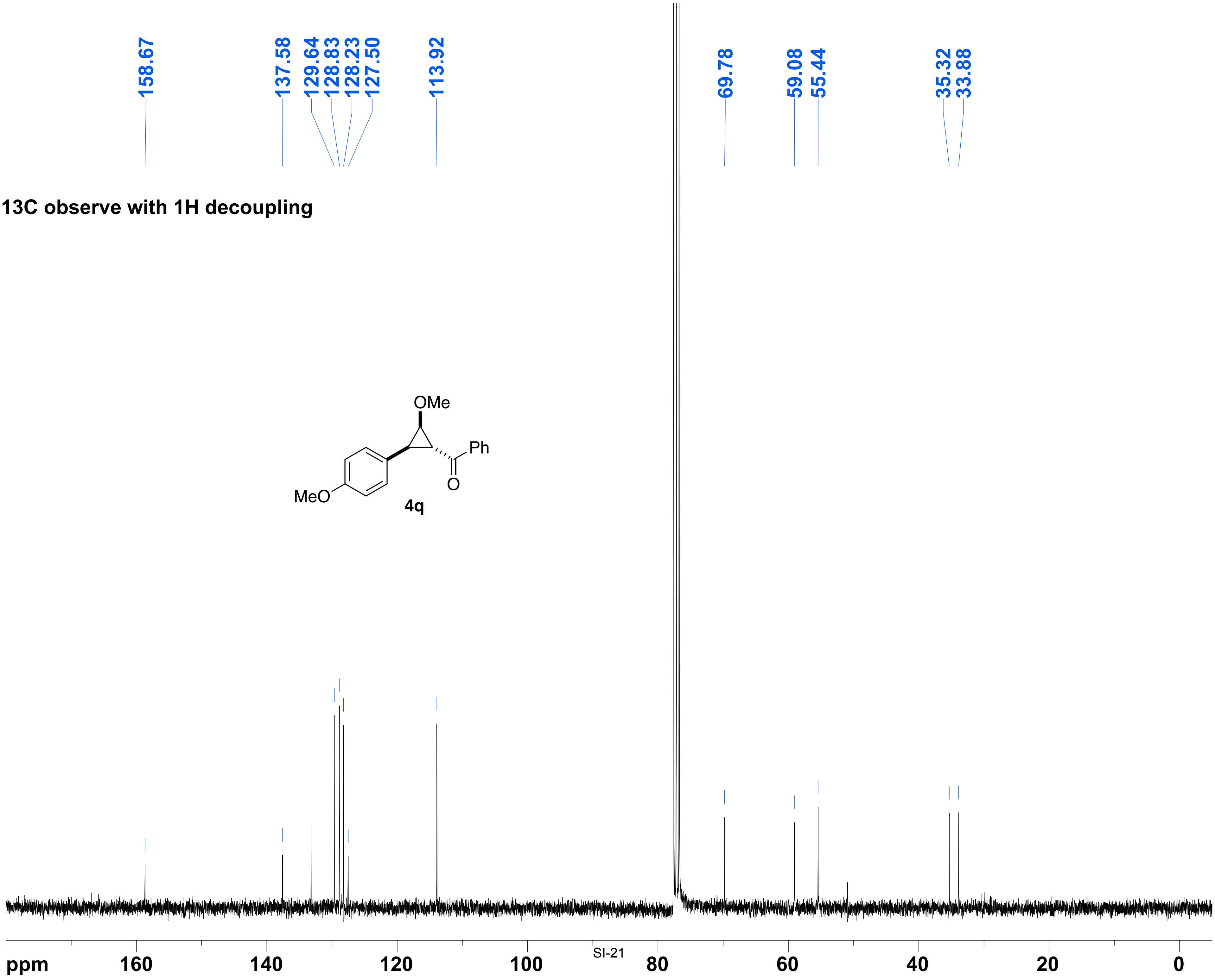

7.31
6.84
4.04
3.78
3.41
2.52
1.99
1.14
proton, 16 scans
OMe
CO2Et
MeO
4L
2
2
2
4
3
1
1
3
ppm
9
8
7
6
5
4
3
2
1
0


168.38
158.37
131.43
125.67
113.49
63.54
60.18
59.31
55.33
27.84
24.00
14.34
13C observe with 1H decoupling
OMe
CO2Et
MeO
4L
ppm
160
140
120
100
80
60
40
20
0

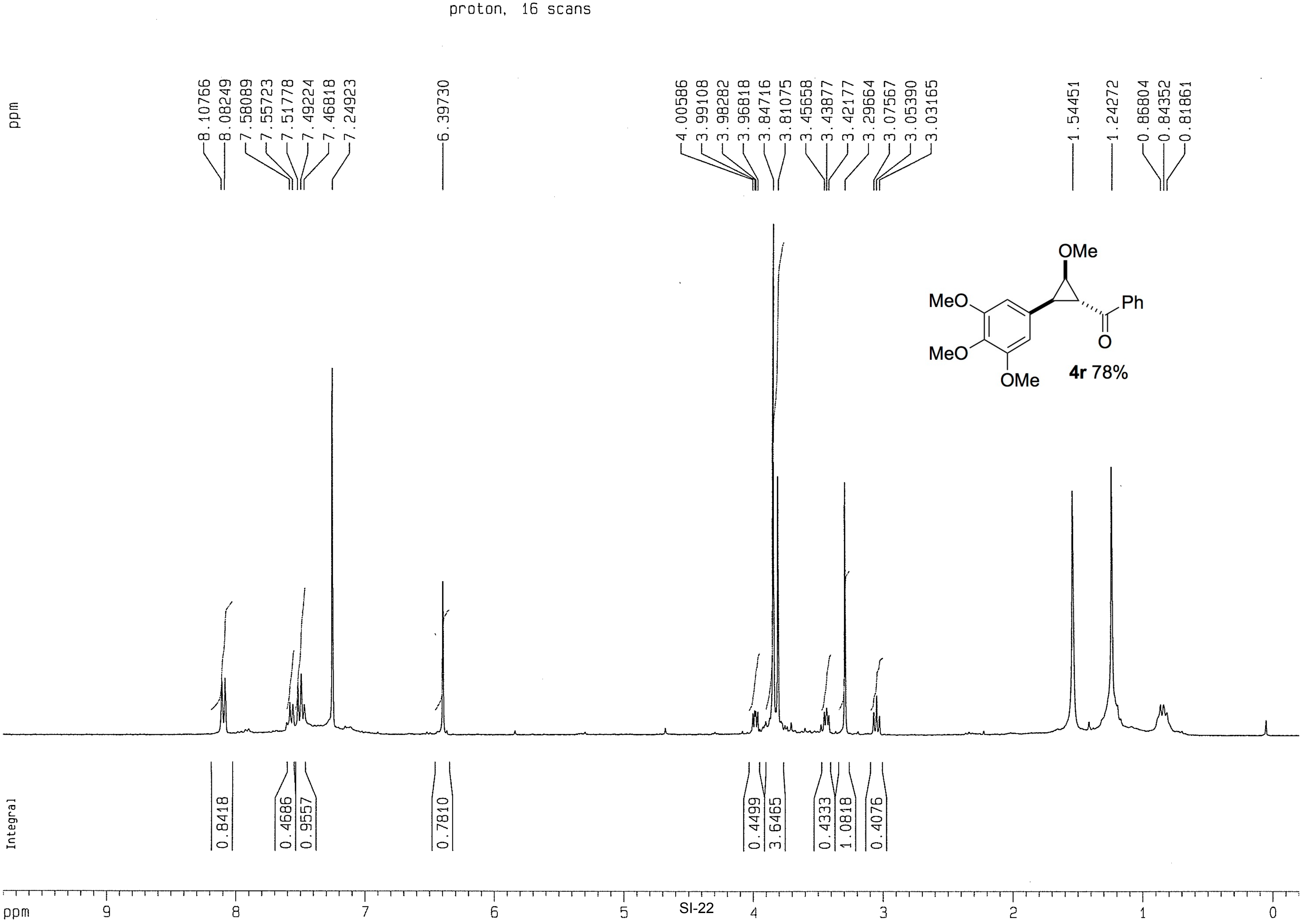

6.49
4.15
3.84
3.81
3.34
2.62
2.15
1.28
proton, 16 scans
OMe
MeO
MeO
OMe
CO2Et
4m
2
3
1
2
10
1
5
ppm
8
6
4
2
0


172.09
153.09
137.00
130.63
105.55
66.18
60.99
58.95
56.23
32.77
28.69
14.40
13C observe with 1H decoupling
OMe
MeO
$CO_2Et$
MeO
OMe
4m
ppm
160
140
120
100
80
60
40
20
0


8.02
7.59
7.49
7.31
6.89
3.99
3.81
3.37
3.15
2.99
proton, 16 scans
OMe
Ph
O
MeO
4q
1
2
1
3
1
2
2
2
3
1
ppm
9
8
7
6
5
4
3
2
1
0


158.67
137.58
129.64
128.83
128.23
127.50
113.92
69.78
59.08
55.44
35.32
33.88
13C observe with 1H decoupling
OMe
Ph
MeO
O
ppm
160
140
120
100
80
60
40
20
0

**4q**


proton, 16 scans
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8.08249
7.58089
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7.51778
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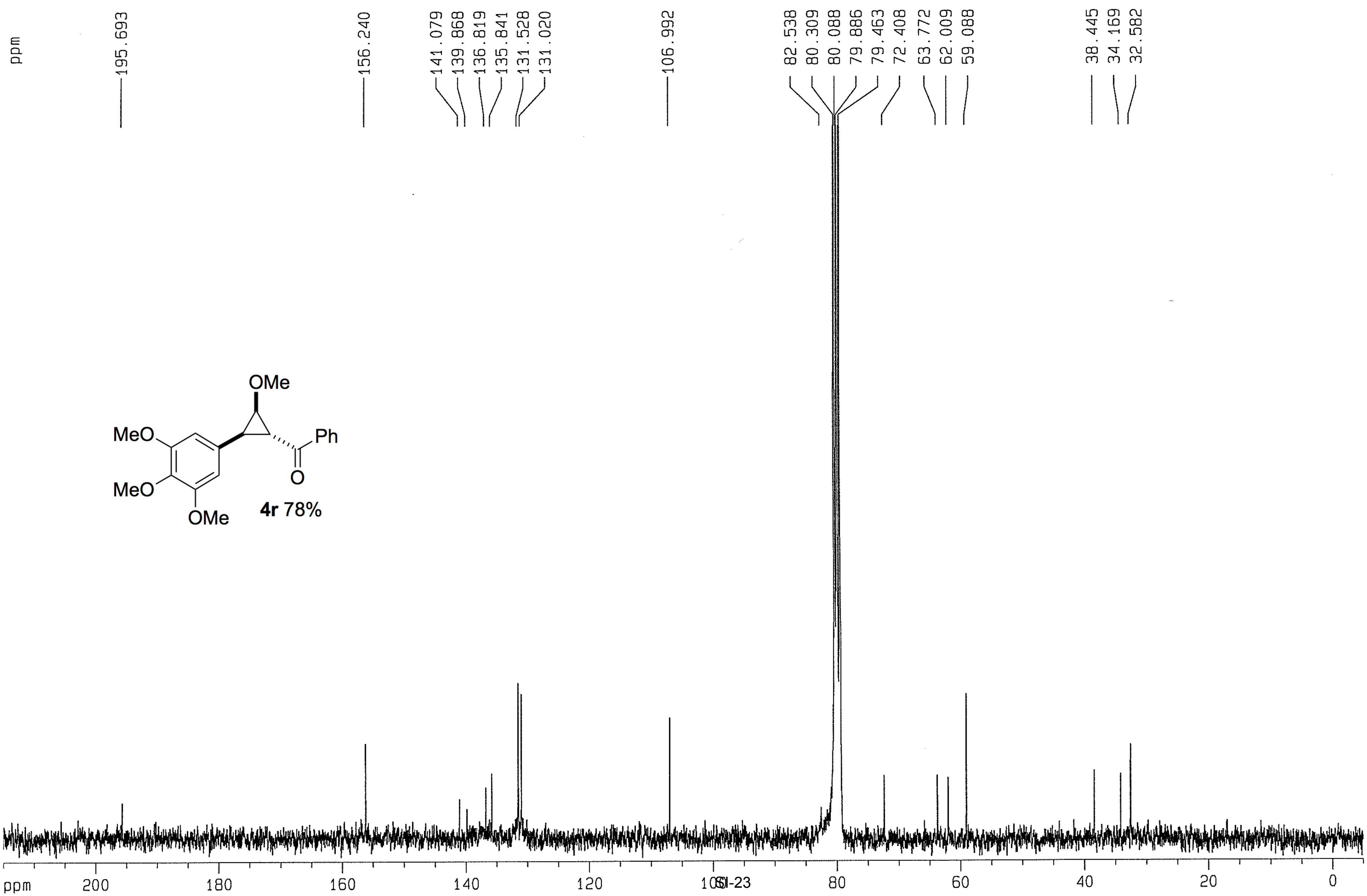
7.46818
7.24923
6.39730
4.00586
3.99108
3.98282
3.96818
3.84716
3.81075
3.45658
3.43877
3.42177
3.29664
3.07567
3.05390
3.03165
1.54451
1.24272
0.86804
0.84352
0.81861
OMe
MeO
Ph
O
MeO
OMe
4r 78%
Integral
0.8418
0.4686
0.9557
0.7810
0.4499
3.6465
0.4333
1.0818
0.4076
ppm
9
8
7
6
5
4
3
2
1
0


13C observe with 1H decoupling
ppm
195.693
156.240
141.079
139.868
136.819
135.841
131.528
131.020
106.992
82.538
80.309
80.088
79.886
79.463
72.408
63.772
62.009
59.088
38.445
34.169
32.582
OMe
MeO
MeO
OMe
Ph
O
ppm
200
180
160
140
120
100
80
60
40
20
0

**4r** 78%