Supporting Information for:

# Palladium-Catalyzed Cross-Coupling of α-Bromocarbonyls and Allylic Alcohols for the Synthesis of α-Aryl Dicarbonyl Compounds

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## Materials and Methods

All reactions were carried out in capped reaction vials with magnetic stirring unless otherwise indicated. Commercially obtained reagents were used as received. Solvents were dried by passage through an activated alumina column under argon. Liquids and solutions were transferred via syringe. All reactions were monitored by thin-layer chromatography with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). All flash chromatography purifications were performed on a Teledyne Isco CombiFlash® Rf unless otherwise indicated. $^{1}H$ and $^{13}C$ NMR spectra were recorded on Varian Inova-400 or 500 spectrometers. Data for $^{1}H$ NMR spectra are reported relative to chloroform or benzene as an internal standard (7.26 ppm or 7.10 ppm) and are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Data for $^{13}C$ NMR spectra are reported relative to chloroform or benzene as an internal standard (77.23 ppm or 128.39 ppm) and are reported in terms of chemical shift (δ ppm). Infrared spectra were recorded on a Perkin-Elmer 1000 series FTIR. Chiral HPLC analyses were performed on an Agilent 1200 Series system. LRMS data were measured using an Agilent 1200 series LC/MS. HRMS data were obtained at The Scripps Center for Mass Spectrometry.

## Optimization of Reaction Parameters

### *(a) Effect of Varying the Palladium Source*

Standard Procedure: A solution of allylic alcohol **1** (0.10 mmol, 1.0 equiv), palladium source (5 mol%), dppe (10 mol%), and $Ag_2CO_3$ (0.20 mmol, 2.0 equiv), in toluene (1 mL) was treated with ethyl bromoacetate **2** (0.20 mmol, 2.0 equiv) and stirred at 110 °C for 12 h. The

mixture was concentrated under reduced pressure. The yield was determined by $^1$H NMR spectroscopy using 1,4-Dimethoxybenzene as an internal standard.

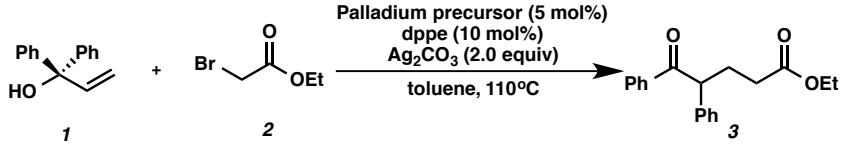



Table S1

| Entry | Palladium Source (5 mol%) | Ligand (10 mol%) | Additive (2 equiv) | Solvent | Temp (°C) | Yield (%) |
|---|---|---|---|---|---|---|
| 1 | $PdCl_2$ | dppe | $Ag_2CO_3$ | PhMe | 110 | trace |
| 2 | $Pd(OAc)_2$ | dppe | $Ag_2CO_3$ | PhMe | 110 | 50 |
| 3 | $Pd(dba)_2$ | dppe | $Ag_2CO_3$ | PhMe | 110 | 35 |
| 4 | $Pd(PPh_3)_4$ | dppe | $Ag_2CO_3$ | PhMe | 110 | 40 |
| 5 | $PdCl_2(nbd)_2$ | dppe | $Ag_2CO_3$ | PhMe | 110 | 64 |
| 6 | $[PdCl_2(MeCN)_2]$ | dppe | $Ag_2CO_3$ | PhMe | 110 | 58 |
| 7 | $[PdCl_2(PhCN)_2]$ | dppe | $Ag_2CO_3$ | PhMe | 110 | 66 |
| 8 | - | dppe | $Ag_2CO_3$ | PhMe | 110 | 0 |

dba = dibenzylideneacetone
nbd = Bicyclo[2.2.1]hepta-2,5-diene.

### *(b) Effect of Varying the Ligands*

Standard Procedure: A solution of allylic alcohol **1** (0.10 mmol, 1.0 equiv), $[PdCl_2(PhCN)_2]$ (5 mol%), ligand (10 mol%), and $Ag_2CO_3$ (0.20 mmol, 2.0 equiv) in toluene (1 mL) was treated with ethyl bromoacetate **2** (0.20 mmol, 2.0 equiv) and stirred at 110 °C for 12 h. The mixture was concentrated under reduced pressure. The yield was determined by $^1$H NMR spectroscopy using 1,4-Dimethoxybenzene as an internal standard.

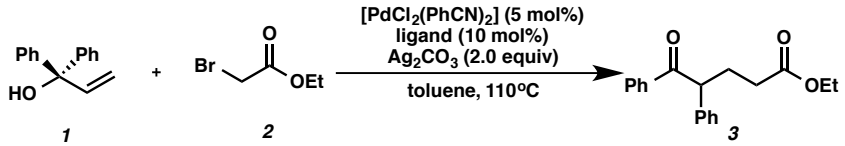



Table S2

| Entry | Palladium Source (5 mol%) | Ligand (10 mol%) | Additive (2 equiv) | Solvent | Temp (°C) | Yield (%) |
|---|---|---|---|---|---|---|
| 1 | $[PdCl_2(PhCN)_2]$ | dppe | $Ag_2CO_3$ | PhMe | 110 | 66 |
| 2 | $[PdCl_2(PhCN)_2]$ | - | $Ag_2CO_3$ | PhMe | 110 | 22 |
| 3 | $[PdCl_2(PhCN)_2]$ | $PPh_3$ | $Ag_2CO_3$ | PhMe | 110 | 63 |
| 4 | $[PdCl_2(PhCN)_2]$ | P(*p*-Tol)$_3$ | $Ag_2CO_3$ | PhMe | 110 | 55 |
| 5 | $[PdCl_2(PhCN)_2]$ | P(*o*-Tol)$_3$ | $Ag_2CO_3$ | PhMe | 110 | 43 |
| 6 | $[PdCl_2(PhCN)_2]$ | P(*o*-MeOPh)$_3$ | $Ag_2CO_3$ | PhMe | 110 | trace |
| 7 | $[PdCl_2(PhCN)_2]$ | $PCy_3$ | $Ag_2CO_3$ | PhMe | 110 | 47 |
| 8 | $[PdCl_2(PhCN)_2]$ | JohnPhos | $Ag_2CO_3$ | PhMe | 110 | trace |

JohnPhos = (2-Biphenyl)di-tert-butylphosphine.

### *(c) Effect of Varying the Additive*

Standard Procedure: A solution of allylic alcohol **1** (0.10 mmol, 1.0 equiv), [$PdCl_2(PhCN)_2$] (5 mol%), dppe (10 mol%), and additive (0.20 mmol, 2.0 equiv) in toluene (1 mL) was treated with ethyl bromoacetate **2** (0.20 mmol, 2.0 equiv) and stirred at 110 °C for 12 h. The mixture was concentrated under reduced pressure. The yield was determined by $^1$H NMR spectroscopy using 1,4-Dimethoxybenzene as an internal standard.

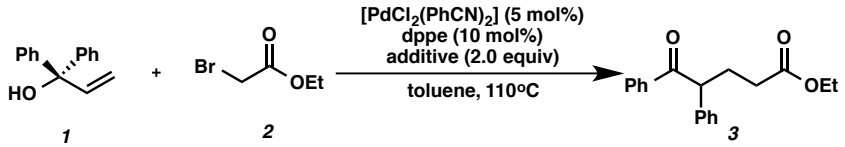



Table S3

| Entry | Palladium Source (5 mol%) | Ligand (10 mol%) | Additive (2 equiv) | Solvent | Temp (°C) | Yield (%) |
|---|---|---|---|---|---|---|
| 1 | $[PdCl_2(PhCN)_2]$ | dppe | NaOAc | PhMe | 110 | 0 |
| 2 | $[PdCl_2(PhCN)_2]$ | dppe | $Cu(OAc)_2$ | PhMe | 110 | 0 |
| 3 | $[PdCl_2(PhCN)_2]$ | dppe | AgOAc | PhMe | 110 | 24 |
| 4 | $[PdCl_2(PhCN)_2]$ | dppe | $PhI(OAc)_2$ | PhMe | 110 | trace |
| 5 | $[PdCl_2(PhCN)_2]$ | dppe | $Cs_2CO_3$ | PhMe | 110 | 2 |
| 6 | $[PdCl_2(PhCN)_2]$ | dppe | $Ag_2CO_3$ | PhMe | 110 | 66 |
| 7 | $[PdCl_2(PhCN)_2]$ | dppe | $Ag_2O$ | PhMe | 110 | 80 |
| 8 | $[PdCl_2(PhCN)_2]$ | dppe | - | PhMe | 110 | 0 |

### *(d) Effect of Varying the Solvents*

Standard Procedure: allylic alcohol **1** (0.10 mmol, 1.0 equiv), [$PdCl_2(PhCN)_2$] (5 mol%), dppe (10 mol%), and additive (0.20 mmol, 2.0 equiv) in the designated solvent (1 mL) was treated with ethyl bromoacetate **2** (0.20 mmol, 2.0 equiv) and stirred at 110 °C for 12 h. The mixture was concentrated under reduced pressure. The yield was determined by $^1$H NMR spectroscopy using 1,4-Dimethoxybenzene as an internal standard.

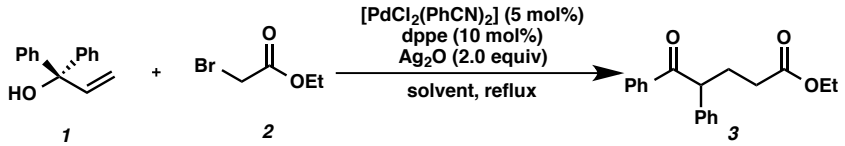



Table S4

| Entry | Palladium Source (5 mol%) | Ligand (10 mol%) | Additive (2 equiv) | Solvent | Temp (°C) | Yield (%) |
|---|---|---|---|---|---|---|
| 1 | $[PdCl_2(PhCN)_2]$ | dppe | $Ag_2CO_3$ | PhMe | 110 | 66 |
| 2 | $[PdCl_2(PhCN)_2]$ | dppe | $Ag_2CO_3$ | *o*-Xylene | 140 | 37 |
| 3 | $[PdCl_2(PhCN)_2]$ | dppe | $Ag_2CO_3$ | *m*-Xylene | 135 | 60 |
| 4 | $[PdCl_2(PhCN)_2]$ | dppe | $Ag_2CO_3$ | *p*-Xylene | 138 | 42 |
| 5 | $[PdCl_2(PhCN)_2]$ | dppe | $Ag_2CO_3$ | DMF | 120 | 0 |
| 6 | $[PdCl_2(PhCN)_2]$ | dppe | $Ag_2CO_3$ | Dioxane | 100 | 63 |
| 7 | $[PdCl_2(PhCN)_2]$ | dppe | $Ag_2CO_3$ | $PhCF_3$ | 120 | 93 |
| 8 | $[PdCl_2(PhCN)_2]$ | dppe | $Ag_2O$ | $PhCF_3$ | 120 | 94 |

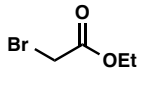
## Synthesis of Starting Materials

### *(a) Allylic Alcohols*

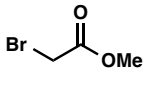
All allylic alcohols in Tables 1-3 were synthesized according to literature precedence. Spectroscopic data matched the reported data in the literature.[1]

### *(b) α-Bromoesters*

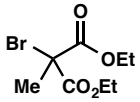
α-Bromoesters **2**, **5**, and **7a-d** were purchased from Sigma-Aldrich.



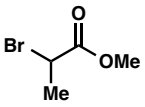
*2*



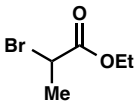
*5*



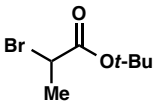
*7a*



*7b*



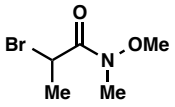
*7c*



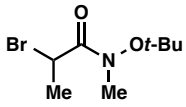
*7d*

### *(b) Weinreb Amides*

Weinreb amides **7e-f** were synthesized according to literature precedence. Spectroscopic data matched the reported data in the literature.[2]



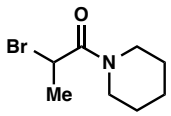
*7e*



*7f*

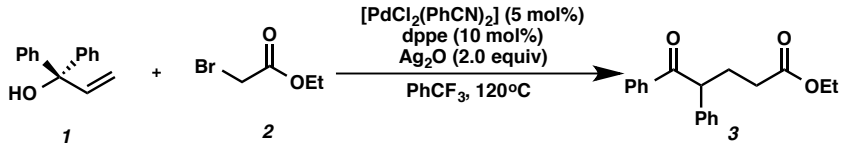
### *(c) α-Methyl-α-Bromoamide*

α-Methyl-α-bromoamide **7g** was synthesized according to literature precedence. Spectroscopic data matched the reported data in the literature.[3]



*7g*

## General Procedure for the Synthesis of α-Aryl Dicarbonyl Compounds



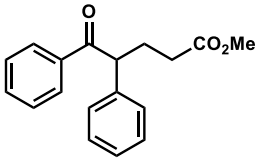

*1* *2* *3*

**Table 1, entry 14:** In an 8-mL reaction vial, a solution of 1,1-diphenylprop-2-en-1-ol **1** (0.200 mmol, 42.0 mg, 1.0 equiv), $Pd(PhCN)_2Cl_2$ (3.80 mg, 5mol %), dppe (8.0 mg, 10 mol%), and $Ag_2O$ (0.400 mmol, 92.7 mg, 2.0 equiv), in α,α,α-Trifluorotoluene (1.0 mL, 0.2 M) was treated with ethyl bromoacetate **2** (0.400 mmol, 66.9 mg, 2.0 equiv). The reaction vial was charged with nitrogen for 5 minutes and then sealed. The mixture was stirred at

120 °C for 12 h. After the reaction was finished, the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The resulting residue was purified by silica gel flash chromatography (gradient eluent pentane/diethyl ether) to afford the desired product **3** (49.2 mg, 83% yield) as a clear oil:
$^1$H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.85 (m, 2H), 7.51 – 7.42 (m, 1H), 7.37 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.34 – 7.22 (m, 4H), 7.23 – 7.17 (m, 1H), 4.68 (t, *J* = 7.3 Hz, 1H), 4.15 – 4.03 (m, 2H), 2.50 – 2.41 (m, 1H), 2.34 – 2.24 (m, 2H), 2.21 – 2.14 (m, 1H), 1.22 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 199.27, 173.24, 138.79, 136.56, 132.92, 129.03, 128.71, 128.50, 128.30, 127.26, 60.35, 52.39, 31.83, 28.78, 14.21. IR (thin film): 2981, 2937, 1731, 1681, 1598, 1581, 1448, 1374, 1178, 1030, 860, 758, 699 cm$^{-1}$. HRMS (ESI) calcd for $[C_{19}H_{21}O_3]^+$([M+H]$^+$): 297.1412, found 297.1489.

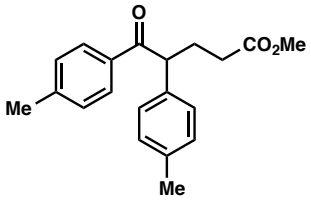
**Characterization Data for Products**

**Table 2, entry 1:** Following the general procedure for the synthesis of α-aryl dicarbonyl compounds, purification by flash chromatography afforded the desired product (47.4 mg, 84% yield) as a clear oil:



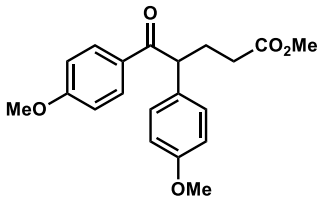

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.96 (m, *J* = 7.2, 1.4 Hz, 2H), 7.50 – 7.43 (m, 1H), 7.42 – 7.31 (m, 2H), 7.29 (d, *J* = 4.4 Hz, 4H), 7.20 (ddd, *J* = 8.7, 5.0, 3.9 Hz, 1H), 4.67 (t, *J* = 7.3 Hz, 1H), 3.64 (s, 3H), 2.49-2.41 (m, 1H), 2.31 (dd, *J* = 8.0, 6.3 Hz, 2H), 2.22-2.13 (m, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 199.21, 173.69, 138.75, 136.52, 132.93, 129.05, 128.72, 128.50, 128.29, 127.28, 52.39, 51.56, 31.54, 28.73. IR (thin film): 2951, 1735, 1682, 1597, 1580, 1447, 1368, 1175, 1001, 886, 758, 699 cm$^{-1}$. MS (ES-API) calcd for $[C_{18}H_{19}O_3]^+$([M+H]$^+$): 283.1, found 283.1.

**Table 2, entry 2:** Following the general procedure for the synthesis of α-aryl dicarbonyl compounds, purification by flash chromatography afforded the desired product (37.4 mg, 56% yield) as a clear oil:



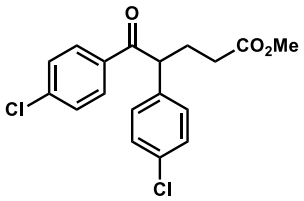

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.89 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 4H), 7.08 (d, *J* = 7.8 Hz, 2H), 4.60 (t, *J* = 7.3 Hz, 1H), 3.64 (s, 3H), 2.39 – 2.46 (m, 1H), 2.33 (s, 3H), 2.28 – 2.32 (m, 2H), 2.27 (s, 3H), 2.10 – 2.18 (m, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 198.93, 173.79, 143.65, 136.82, 135.93, 134.03, 129.70, 129.17, 128.85, 128.11, 51.85, 51.53, 31.60, 28.68, 21.57, 21.01. IR (thin film): 2951, 1738, 1681, 1606, 1513, 1436, 1326, 1176, 1020, 813, 778, 662 cm$^{-1}$. MS (ES-API) calcd for $[C_{20}H_{22}O_3Na]^+$([M+Na]$^+$): 333.1, found 332.8.

**Table 2, entry 3:** Following the general procedure for the synthesis of α-aryl dicarbonyl compounds, purification by flash chromatography afforded the desired product (58.2 mg, 85% yield) as a clear oil:



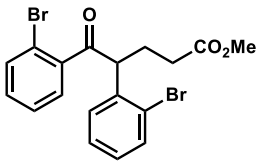

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.85 (m, 2H), 7.24 – 7.11 (m, 2H), 6.94 – 6.70 (m, 4H), 4.56 (t, *J* = 7.3 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 3.63 (s, 3H), 2.44 – 2.35 (m, 1H), 2.28 (t, *J* = 7.1 Hz, 2H), 2.16 – 2.07 (m, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.91, 173.80, 163.24, 158.65, 131.14, 130.98, 129.51, 129.23, 114.36, 113.64, 55.38, 55.16, 51.51, 51.10, 31.57, 28.75. IR (thin film): 2953, 1735, 1670, 1600, 1511, 1440, 1253, 1170, 1030, 824, 785, 713 cm$^{-1}$. MS (ES-API) calcd for $[C_{20}H_{22}O_5Na]^+$([M+Na]$^+$): 365.1, found 365.0.

**Table 2, entry 4:** Following the general procedure for the synthesis of α-aryl dicarbonyl compounds, purification by flash chromatography afforded the desired product (46.2 mg, 66% yield) as a clear oil:




$^1$H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.93 (m, 2H), 7.93 – 7.42 (m, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 4.62 (t, *J* = 7.3 Hz, 1H), 3.64 (s, 3H), 2.41 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.24 – 2.34 (m, 2H), 2.12 (dt, *J* = 13.9, 7.1 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.70, 173.49, 139.61, 136.89, 134.53, 133.41, 130.08, 129.58, 129.32, 128.93, 51.64, 51.55, 31.21, 28.53. IR (thin film): 2951, 1738, 1682, 1589, 1489, 1436, 1214, 1174, 1093, 812, 745, 689 cm$^{-1}$. MS (ES-API) calcd for $[C_{18}H_{15}Cl_2O_3]^+$([M-H]$^-$): 349.0, found 349.0.

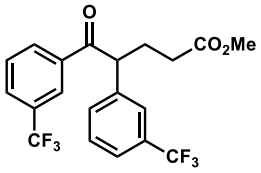
**Table 2, entry 5:** Following the general procedure for the synthesis of α-aryl dicarbonyl compounds, purification by flash chromatography afforded the desired product (36.8 mg, 42% yield) as a clear oil:




$^1$H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.56 (m, 2H), 7.26 – 7.32 (m, 2H), 7.17 – 7.23 (m, 2H), 7.13 – 7.17 (m, 1H), 7.04 – 7.11 (m, 1H), 5.12 (t, *J* = 7.3 Hz, 1H), 3.66 (s, 3H), 2.55 (ddd, *J* = 13.9, 6.8, 1.9 Hz, 1H), 2.38 – 2.46 (m, 1H), 2.30 – 2.38 (m, 1H), 2.11 – 2.20 (m, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 201.72, 173.35, 140.61, 136.62, 133.59, 133.23, 131.50, 129.30, 129.12, 128.62, 128.03, 127.06, 125.76, 119.30, 54.35, 51.68, 31.35, 27.18. IR (thin film):

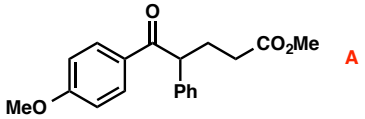
2950, 1738, 1704, 1588, 1469, 1435, 1211, 1160, 1024, 892, 757, 736 $cm^{-1}$. MS (ES-API) calcd for $[C_{18}H_{16}Br_2O_3Na]^+$($[M+Na]^+$): 460.9, found 460.6.

**Table 2, entry 6:** Following the general procedure for the synthesis of α-aryl dicarbonyl compounds, purification by flash chromatography afforded the desired product (73.6 mg, 88% yield) as a clear oil:



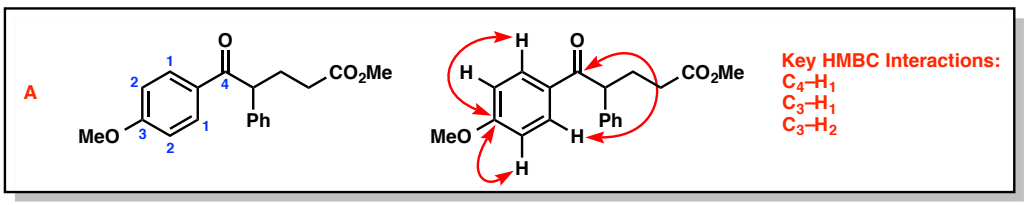

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.12 (d, $J$ = 7.8 Hz, 1H), 7.76 (d, $J$ = 7.7 Hz, 1H), 7.37 – 7.63 (m, 5H), 4.81 (t, $J$ = 7.3 Hz, 1H), 3.66 (s, 3H), 2.50 (dq, $J$ = 14.0, 7.0 Hz, 1H), 2.32 (td, $J$ = 6.9, 2.8 Hz, 2H), 2.19 (dt, $J$ = 13.9, 7.1 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.36, 173.31, 139.05, 136.60, 131.75, 131.70, 131.63, 131.51, 131.38, 131.18, 129.71, 129.69, 129.66, 129.62, 129.39, 125.58, 125.54, 125.50, 125.46, 125.12, 125.07, 125.04, 125.00, 124.62, 124.58, 124.54, 124.51, 122.41, 122.15, 52.02, 51.67, 31.15, 28.65. IR (thin film): 2957, 1732, 1694, 1612, 1440, 1331, 1168, 1127, 1074, 904, 806, 774, 704, 694, 658 $cm^{-1}$. MS (ES-API) calcd for $[C_{20}H_{15}F_6O_3]^+$($[M-H]^-$): 417.1, found 417.2.

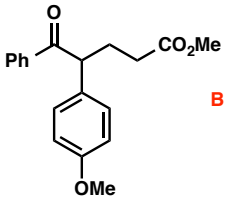
**Table 2, entry 7:** Following the general procedure for the synthesis of α-aryl dicarbonyl compounds, purification by flash chromatography afforded the desired products as a separable mixture of A and B (41.2 mg, 66% yield, A:B = 1.7:1) as clear oils:




$^1$H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.98 (m, 2H), 7.28 (d, $J$ = 4.3 Hz, 4H), 7.19 (p, $J$ = 4.4 Hz, 1H), 6.80 – 6.89 (m, 2H), 4.62 (t, $J$ = 7.3 Hz, 1H), 3.80 (s, 3H), 3.64 (s, 3H), 2.43 (dt, $J$ = 14.5, 7.1 Hz, 1H), 2.26 – 2.33 (m, 2H), 2.12 – 2.19 (m, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.70, 173.76, 163.31, 139.21, 131.03, 129.51, 128.98, 128.20, 127.16, 113.67, 55.40, 52.02, 51.54, 31.61, 28.78. IR (thin film): 2952, 1732, 1668, 1600, 1574, 1511, 1455, 1259, 1169, 1030, 841, 749, 703 $cm^{-1}$. MS (ES-API) calcd for $[C_{19}H_{20}O_4Na]^+$($[M+Na]^+$): 335.1, found 334.8.

*2D NMR Data:*






B

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.91 – 8.00 (m, 2H), 7.44 – 7.50 (m, 1H), 7.37 (td, *J* = 7.6, 1.5 Hz, 2H), 7.14 – 7.23 (m, 2H), 6.78 – 6.87 (m, 2H), 4.61 (t, *J* = 7.3 Hz, 1H), 3.74 (s, 3H), 3.64 (s, 3H), 2.37 – 2.45 (m, 1H), 2.30 (t, *J* = 7.1 Hz, 2H), 2.15 (dt, *J* = 13.4, 4.3 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 199.43, 173.76, 158.74, 136.55, 132.85, 130.64, 129.33, 128.70, 128.48, 14.44, 55.19, 51.55, 51.48, 31.51, 28.69. IR (thin film): 2952, 1736, 1681, 1608, 1511, 1448, 1252, 1178, 1034, 824, 737, 691 cm$^{-1}$. MS (ES-API) calcd for $[C_{19}H_{20}O_4Na]^+$([M+Na]$^+$): 335.1, found 335.0.

*2D NMR Data:*

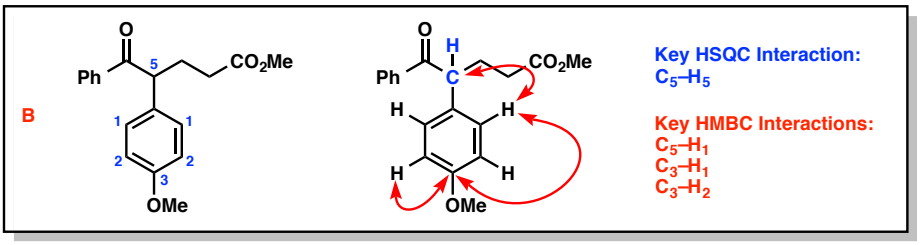
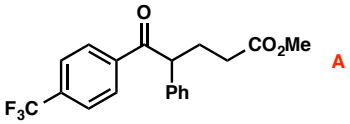
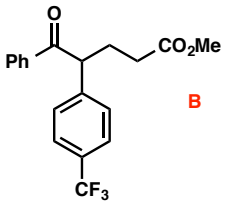



**Table 2, entry 8:** Following the general procedure for the synthesis of α-aryl dicarbonyl compounds, purification by flash chromatography afforded the desired products as a separable mixture of A and B (56.7 mg, 81% yield, A:B = 1:8) as clear oils:




A

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.29 – 7.29 (m, 2H), 7.22 – 7.26 (m, 3H), 4.66 (t, *J* = 7.3 Hz, 1H), 3.65 (s, 3H), 2.46 (ddd, *J* = 12.3, 6.5, 1.1 Hz, 1H), 2.31 (t, *J* = 7.0 Hz, 2H), 2.12 – 2.21 (m, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 198.25, 173.61, 139.17, 138.01, 129.26, 129.03, 128.48, 128.45, 128.26, 127.89, 127.60, 127.22, 127.06, 125.62, 125.58, 125.55, 125.51, 52.81, 51.63, 31.29, 28.50. IR (thin film): 2954, 1738, 1689, 1619, 1601, 1582, 1493, 1439, 1410, 1324, 1168, 1128, 1067, 1016, 838, 751, 702 cm$^{-1}$. MS (ES-API) calcd for $[C_{19}H_{16}F_3O_3]^+$([M-H]$^-$): 349.1, found 349.2.




B

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.47 – 7.52 (m, 1H), 7.33 – 7.48 (m, 4H), 4.80 (t, *J* = 7.3 Hz, 1H), 3.64 (s, 3H), 2.44 – 2.54 (m, 1H), 2.31 (t, *J* = 7.0 Hz, 2H), 2.12 – 2.21 (m, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 198.61, 173.42, 142.80, 142.79, 136.17, 133.33, 129.73, 129.40, 128.69, 128.68, 126.02, 125.98, 125.94, 125.91, 125.33, 122.62, 51.88, 51.62, 31.34, 28.73. IR (thin film): 2953, 1736, 1682, 1618,

1597, 1448, 1420, 1325, 1164, 1123, 1068, 1018, 822, 699 $cm^{-1}$. MS (ES-API) calcd for $[C_{19}H_{16}F_3O_3]^+$([M-H$^-$]): 349.1, found 349.2.

*2D NMR Data:*

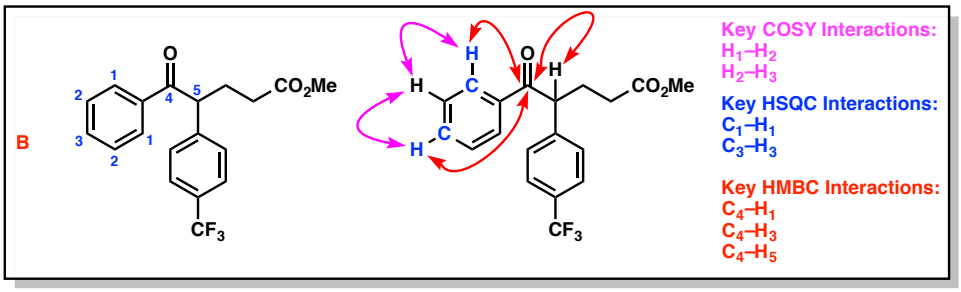
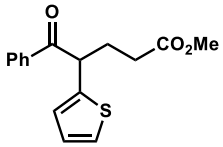



**Table 2, entry 9:** Following the general procedure for the synthesis of α-aryl dicarbonyl compounds, purification by flash chromatography afforded the desired product (26.5 mg, 46% yield) as a clear oil:




$^1$H NMR (400 MHz, $CDCl_3$) δ 7.97 – 8.07 (m, 2H), 7.50 – 7.55 (m, 1H), 7.43 (dd, *J* = 8.5, 7.0 Hz, 2H), 7.12 – 7.23 (m, 1H), 6.82 – 6.98 (m, 2H), 5.02 – 5.07 (m, 1H), 3.66 (s, 3H), 2.45 (ddd, *J* = 12.8, 7.9, 6.2 Hz, 1H), 2.32 – 2.39 (m, 2H), 2.18 – 2.26 (m, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 198.24, 173.52, 140.74, 136.02, 133.27, 128.76, 128.64, 126.97, 126.08, 125.25, 51.63, 46.63, 31.21, 29.51. IR (thin film): 2951, 1733, 1682, 1596, 1580, 1448, 1436, 1368, 1211, 1172, 1011, 850, 828, 804, 701 $cm^{-1}$. MS (ES-API) calcd for $[C_{16}H_{17}O_3S]^+$([M+H]$^+$): 289.1, found 289.1.

*2D NMR Data:*

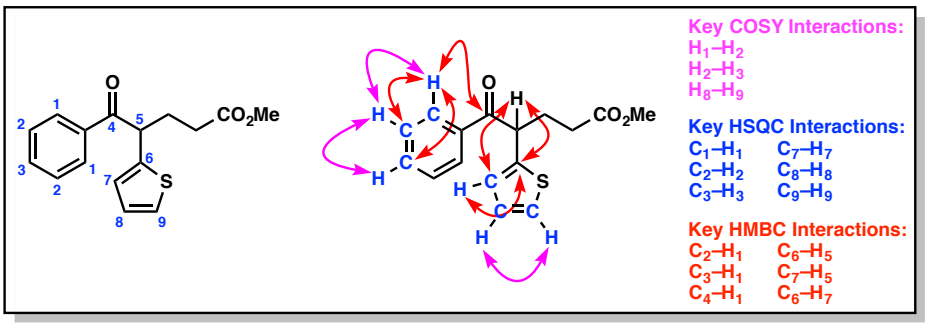
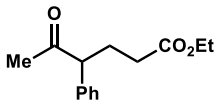


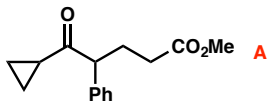

**Table 2, entry 10:** Following the general procedure for the synthesis of α-aryl dicarbonyl compounds, purification by flash chromatography afforded the desired product (24.8 mg, 53% yield) as a clear oil:



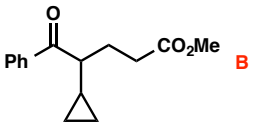

$^1$H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.37 (m, 2H), 7.25 – 7.29 (m, 1H), 7.14 – 7.21 (m, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.70 (dd, *J* = 8.3, 6.6 Hz, 1H), 2.32 (ddd, *J* = 13.6, 7.0, 1.3

Hz, 1H), 2.18 (dd, *J* = 7.9, 6.5 Hz, 2H), 2.04 (s, 3H), 1.94 – 2.02 (m, 1H), 1.22 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 207.68, 173.16, 138.10, 129.06, 128.31, 127.52, 60.34, 58.38, 31.73, 29.09, 26.81, 14.20. IR (thin film): 2982, 1732, 1714, 1600, 1493, 1454, 1374, 1356, 1200, 1173, 1029, 859, 764, 703 cm$^{-1}$. MS (ES-API) calcd for $[C_{14}H_{19}O_3]^+$([M+H]$^+$): 235.1, found 235.2.

**Table 2, entry 11:** Following the general procedure for the synthesis of α-aryl dicarbonyl compounds, purification by flash chromatography afforded the desired products as a separable mixture of A and B (21.2 mg, 43% yield, A:B = 2.5:1) as clear oils:




$^1$H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.7 Hz, 2H), 7.26 – 7.29 (m, 1H), 7.16 – 7.25 (m, 2H), 3.86 (t, *J* = 7.4 Hz, 1H), 3.64 (s, 3H), 2.31 – 2.39 (m, 1H), 2.23 (t, *J* = 7.3 Hz, 2H), 1.96 – 2.04 (m, 1H), 1.80 – 1.88 (m, 1H), 0.98 (dddd, *J* = 18.7, 7.8, 6.1, 4.2 Hz, 2H), 0.78 – 0.84 (m, 1H), 0.67 – 0.73 (m, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 209.65, 173.69, 138.31, 128.94, 128.57, 127.36, 58.39, 51.54, 31.54, 27.06, 20.42, 11.49, 11.35. IR (thin film): 2952, 2851, 1732, 1694, 1493, 1454, 1436, 1381, 1198, 1166, 1077, 1041, 752, 701 cm$^{-1}$. MS (ES-API) calcd for $[C_{15}H_{19}O_3]^+$([M+H]$^+$): 247.1, found 247.1.




$^1$H NMR (400 MHz, $CDCl_3$) δ 7.80 – 8.05 (m, 2H), 7.57 (td, *J* = 7.5, 1.6 Hz, 1H), 7.47 (td, *J* = 7.6, 1.5 Hz, 2H), 3.64 (s, 3H), 2.78 – 2.89 (m, 1H), 2.43 – 2.53 (m, 1H), 2.32 (ddd, *J* = 7.1, 5.5, 1.6 Hz, 1H), 2.18 – 2.23 (m, 1H), 1.97 – 2.03 (m, 1H), 0.98 (dq, *J* = 12.1, 4.4, 3.6 Hz, 1H), 0.56 – 0.66 (m, 1H), 0.38 – 0.49 (m, 1H), 0.24 (dq, *J* = 10.7, 5.7 Hz, 1H), 0.06 – 0.15 (m, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 203.26, 173.78, 133.06, 128.98, 128.63, 128.33, 51.55, 49.25, 31.45, 27.64, 13.39, 4.45, 3.57. IR (thin film): 2923, 2853, 2359, 1732, 1681, 1446, 1382, 1198, 1164, 1038, 830, 698 cm$^{-1}$. MS (ES-API) calcd for $[C_{15}H_{19}O_3]^+$([M+H]$^+$): 247.1, found 247.1.

*2D NMR Data:*

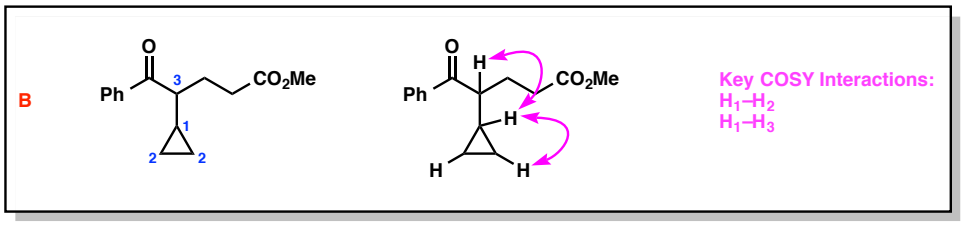
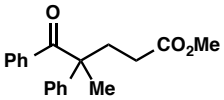
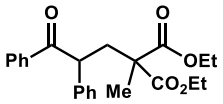



**Table 2, entry 12:** Following the general procedure for the synthesis of α-aryl dicarbonyl compounds, purification by flash chromatography afforded the desired product (43.2 mg, 73% yield) as a clear oil:



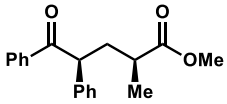
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.45 (dt, *J* = 8.4, 1.3 Hz, 2H), 7.32 – 7.41 (m, 3H), 7.26 – 7.32 (m, 3H), 7.21 (t, *J* = 7.8 Hz, 2H), 3.60 (s, 3H), 2.38 (ddt, *J* = 11.0, 5.6, 1.4 Hz, 2H), 2.14 – 2.20 (m, 2H), 1.61 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 202.84, 173.88, 142.98, 136.26, 131.82, 129.55, 129.06, 128.01, 127.15, 126.29, 53.90, 51.59, 35.24, 29.54, 23.45. IR (thin film): 2951, 1738, 1674, 1598, 1578, 1495, 1445, 1377, 1245, 1197, 1177, 1079, 966, 852, 764, 703 cm$^{-1}$. MS (ES-API) calcd for $[C_{19}H_{20}O_3Na]^+$([M+Na]$^+$): 319.1, found 320.0.

**Table 3, entry 1:** Following the general procedure for the synthesis of α-aryl dicarbonyl compounds, purification by flash chromatography afforded the desired product (55.0 mg, 72% yield) as a clear oil:



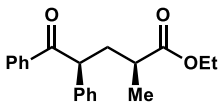

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.87 – 8.01 (m, 2H), 7.42 – 7.48 (m, 1H), 7.36 (dd, *J* = 8.3, 6.8 Hz, 2H), 7.22 – 7.33 (m, 4H), 7.14 – 7.19 (m, 1H), 4.93 (dd, *J* = 8.7, 3.2 Hz, 1H), 4.13 (qd, *J* = 7.1, 2.9 Hz, 2H), 4.02 – 4.10 (m, 1H), 3.75 (dt, *J* = 10.7, 7.1 Hz, 1H), 3.03 (dd, *J* = 14.4, 8.6 Hz, 1H), 2.29 (dd, *J* = 14.4, 3.2 Hz, 1H), 1.41 (2, 3H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 198.50, 172.27, 171.64, 139.99, 136.37, 132.82, 128.98, 128.72, 128.49, 128.15, 127.05, 61.29, 61.24, 49.59, 39.30, 34.11, 13.98, 13.66. IR (thin film): 2984, 1732, 1683, 1598, 1581, 1493, 1448, 1380, 1259, 1192, 1106, 1024, 939, 860, 757, 701 cm$^{-1}$. MS (ES-API) calcd for $[C_{23}H_{26}O_5Na]^+$([M+Na]$^+$): 405.2, found 404.8.

**Table 3, entry 2:** Following the general procedure for the synthesis of α-aryl dicarbonyl compounds, purification by flash chromatography afforded the desired products as an inseparable 1.3:1 mixture of diastereomers (58.0 mg, 98% yield) as clear oils:



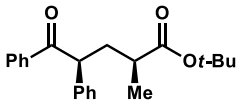

$^1$H NMR (400 MHz, Benzene-$d_6$) δ 7.94 – 8.01 (m, 2H), 7.17 – 7.34 (m, 2H), 6.76 – 7.12 (m, 6H), 4.74 (dd, *J* = 8.4, 6.1 Hz, 0.57H), 4.69 (dd, *J* = 9.1, 5.4 Hz, 0.43H), 3.25 – 3.31 (m, 3H), 2.65 – 2.71 (m, 0.57H), 2.50 – 2.57 (m, 0.43H), 2.41 – 2.48 (m, 0.43H), 2.31 – 2.39 (m, 0.57H), 2.16 – 2.23 (m, 0.43H), 1.97-2.04 (m, 0.57H), 1.03 – 1.05 (m, 1.29H), 0.90 – 0.94 (m, 1.71H). $^{13}$C NMR (101 MHz, Benzene-$d_6$) δ 198.27, 198.14, 175.86, 175.74, 139.60, 139.29, 136.97, 136.71, 132.38, 132.35, 128.93, 128.88, 128.60, 128.55, 128.37, 128.28, 128.04, 127.89, 127.01, 126.94, 51.42, 51.27, 50.86, 50.77, 38.27, 37.68, 37.61, 37.01, 17.53, 17.42. IR (thin film): 2950, 1727, 1678, 1596, 1579, 1492, 1447, 1364, 1250, 1206, 1164, 1128, 1026, 967, 834, 751, 696 cm$^{-1}$. MS (ES-API) calcd for $[C_{19}H_{20}O_3Na]^+$([M+Na]$^+$): 319.1, found 318.8.

**Table 3, entry 3:** Following the general procedure for the synthesis of α-aryl dicarbonyl compounds, purification by flash chromatography afforded the desired products as an inseparable 1.3:1 mixture of diastereomers (61.4 mg, 99% yield) as clear oils:



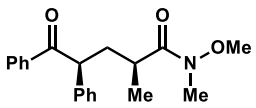
$^1$H NMR (400 MHz, Benzene-$d_6$) δ 7.96 – 8.02 (m, 2H), 7.22 – 7.29 (m, 2H), 6.86 – 7.02 (m, 6H), 4.78 (dd, $J$ = 8.6, 6.0 Hz, 0.57H), 4.73 (dd, $J$ = 9.4, 5.2 Hz, 0.43H), 3.87 – 3.95 (m, 1.14H), 3.79 – 3.84 (m, 0.86H), 2.66 – 2.71 (m, 0.57H), 2.54 – 2.58 (m, 0.43H), 2.44 – 2.51 (m, 0.43H), 2.32 – 2.40 (m, 0.57H), 2.15 – 2.22 (m, 0.43H), 2.00 – 2.07 (m, 0.57H), 1.07 (d, $J$ = 6.9 Hz, 1.29H), 0.94 (d, $J$ = 7.0 Hz, 1.71H), 0.86 – 0.90 (m, 1.71H), 0.86 – 0.90 (m, 1.29H). $^{13}$C NMR (101 MHz, Benzene-$d_6$) δ 198.29, 198.18, 175.52, 175.36, 139.72, 139.30, 137.03, 136.73, 132.38, 132.36, 128.94, 128.86, 128.59, 128.55, 128.41, 128.29, 128.26, 128.00, 127.01, 126.93, 59.80, 59.71, 51.45, 51.24, 38.48, 37.78, 37.68, 37.12, 17.61, 17.52, 13.87, 13.74. IR (thin film): 2979, 1732, 1682, 1597, 1580, 1493, 1448, 1378, 1252, 1208, 1175, 1129, 1028, 970, 860, 758, 700 cm$^{-1}$. MS (ES-API) calcd for $[C_{20}H_{22}O_3Na]^+$([M+Na]$^+$): 333.2, found 333.0.

**Table 3, entry 4:** Following the general procedure for the synthesis of α-aryl dicarbonyl compounds, purification by flash chromatography afforded the desired products as an inseparable 1.7:1 mixture of diastereomers (46.7 mg, 69% yield) as clear oils:



$^1$H NMR (500 MHz, Benzene-$d_6$) δ 8.03 – 8.08 (m, 1.26H), 8.01 – 8.03 (m, 0.74H), 7.29 – 7.41 (m, 1.26H), 7.26 – 7.29 (m, 0.74H), 6.85 – 7.08 (m, 6H), 4.86 (dd, $J$ = 9.2, 5.6 Hz, 0.63H), 4.83 (dd, $J$ = 9.7, 4.5 Hz, 0.37H), 2.63 – 2.69 (m, 0.63H), 2.54 – 2.58 (m, 0.37H), 2.49 – 2.52 (m, 0.37H), 2.29 – 2.33 (m, 0.63H), 2.14 – 2.18 (m, 0.37H), 2.04 – 2.10 (m, 0.63H), 1.33 (s, 5.67H), 1.24 (s, 3.33H), 1.08 (d, $J$ = 6.7 Hz, 1.11H), 0.95 (d, $J$ = 7.0 Hz, 1.89H). $^{13}$C NMR (101 MHz, Benzene-$d_6$) δ 198.42, 198.35, 175.18, 175.03, 139.99, 139.31, 137.21, 136.80, 132.37, 128.98, 128.83, 128.57, 128.51, 128.30, 128.25, 127.93, 127.01, 126.92, 79.27, 79.23, 51.57, 51.22, 38.90, 38.77, 37.97, 37.74, 27.70, 27.59, 17.82, 17.73. IR (thin film): 2976, 1724, 1683, 1598, 1580, 1493, 1449, 1367, 1253, 1213, 1150, 1071, 970, 849, 758, 699 cm$^{-1}$. MS (ES-API) calcd for $[C_{22}H_{26}O_3Na]^+$([M+Na]$^+$): 361.2, found 360.8.

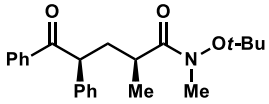
**Table 3, entry 5:** Following the general procedure for the synthesis of α-aryl dicarbonyl compounds, purification by flash chromatography afforded the desired products as an inseparable 3:1 mixture of diastereomers (59.8 mg, 92% yield) as clear oils:



$^1$H NMR (400 MHz, Chloroform-$d$) δ 8.01 (d, $J$ = 7.5 Hz, 1.5H), 7.93 (d, $J$ = 7.7 Hz, 0.5H), 7.43 – 7.50 (m, 1H), 7.34 – 7.41 (m, 2H), 7.25 – 7.31 (m, 4H), 7.17 – 7.22 (m, 1H), 4.73 (dd, $J$ = 9.8, 5.4 Hz, 0.75H), 4.63 (dd, $J$ = 9.4, 5.4 Hz, 0.25H), 3.32 (m, 3H), 3.17 (s, 2.25H), 3.09 (s, 0.75H), 2.88 (brd, 0.25H), 2.64 (brd, 0.75H), 2.42 – 2.50 (m, 0.75H), 2.26 – 2.32 (m, 0.25H), 2.10 – 2.17 (m, 0.25H), 2.01 – 2.08 (m, 0.75H), 1.17 (d, $J$ = 6.9 Hz, 0.75H), 1.11 (d, $J$ = 6.8 Hz, 2.25H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 199.76, 199.64, 139.50, 138.71,

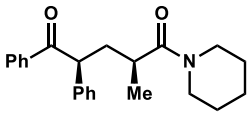
136.82, 136.51, 132.86, 128.89, 128.78, 128.61, 128.49, 128.47, 128.13, 127.14, 127.04, 61.04, 60.96, 51.12, 50.83, 38.16, 36.55, 33.41, 33.23, 32.32, 17.99, 17.72. IR (thin film): 3445, 2970, 2935, 1681, 1652, 1597, 1579, 1493, 1448, 1386, 1327, 1264, 1209, 1176, 1116, 1072, 996, 756, 699 $cm^{-1}$. MS (ES-API) calcd for $[C_{20}H_{23}NO_3Na]^+$($[M+Na]^+$): 348.2, found 347.8.

**Table 3, entry 6:** Following the general procedure for the synthesis of α-aryl dicarbonyl compounds, purification by flash chromatography afforded the desired products as an inseparable 3.6:1 mixture of diastereomers (55.1 mg, 75% yield) as clear oils:




$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.00 – 8.04 (m, 1.56H), 7.92 – 7.94 (m, 0.44H), 7.48 – 7.52 (m, 0.78H), 7.45 – 7.48 (m, 0.22H), 7.40 – 7.43 (m, 1.56H), 7.35 – 7.38 (m, 0.44H), 7.27 – 7.34 (m, 4H), 7.17 – 7.21 (m, 1H), 4.67 – 4.78 (m, 0.78H), 4.55 – 4.59 (m, 0.22H), 3.20 – 3.23 (m, 3H), 2.96 – 3.08 (m, 1H), 2.54 (dt, *J* = 14.7, 7.1 Hz, 0.78H), 2.30 – 2.34 (m, 0.22H), 2.06(m, 0.22H), 1.97 – 2.02 (m, 0.78H), 1.03 – 1.28 (m, 12H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 199.62, 199.19, 139.69, 138.88, 136.66, 136.58, 132.85, 132.72, 128.95, 128.78, 128.73, 128.63, 128.50, 128.31, 128.04, 127.07, 126.99, 53.43, 51.10, 50.74, 39.59, 38.40, 37.37, 33.81, 27.55, 27.30, 17.33. IR (thin film): 2979, 2935, 1682, 1651, 1597, 1580, 1494, 1448, 1367, 1265, 1208, 1176, 1159, 1070, 968, 848, 760, 700 $cm^{-1}$. MS (ES-API) calcd for $[C_{23}H_{29}NO_3Na]^+$($[M+Na]^+$): 390.2, found 389.8.

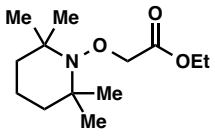
**Table 3, entry 7:** Following the general procedure for the synthesis of α-aryl dicarbonyl compounds, purification by flash chromatography afforded the desired products as an inseparable 5:1 mixture of diastereomers (66.3 mg, 95% yield) as clear oils:




$^1$H NMR (500 MHz, Benzene-$d_6$) δ 8.16 – 8.20 (m, 1.66H), 8.01 – 8.03 (m, 0.34H), 7.36 – 7.39 (m, 0.34H), 7.28 – 7.31 (m, 1.66H), 7.01 – 7.09 (m, 2H), 6.94 – 7.01 (m, 4H), 4.94 – 4.99 (m, 1H), 3.54 – 3.69 (m, 0.83H), 3.53 – 3.57 (m, 0.17H), 3.35 – 3.41 (m, 0.83H), 3.23 – 3.29 (m, 0.17H), 2.75 – 2.81 (m, 2H), 2.63 – 2.68 (m, 1H), 2.48 – 2.54 (m, 0.17H), 2.40 – 2.44 (m, 0.17H), 2.31 – 2.38 (m, 0.83H), 2.07 – 2.13 (m, 0.83H), 1.22 (m, 3H), 1.09 – 1.15 (m, 1H), 1.05 (d, *J* = 6.9 Hz, 0.51H), 0.97 (m, 2H), 0.91 (d, *J* = 7.0 Hz, 2.49H). $^{13}$C NMR (101 MHz, Benzene-$d_6$) δ 199.41, 199.07, 173.03, 172.88, 140.48, 139.54, 137.28, 136.91, 132.36, 128.86, 128.83, 128.79, 128.59, 128.34, 128.27, 126.78, 51.01, 45.57, 42.39, 39.31, 37.96, 33.29, 32.89, 26.22, 25.63, 24.47, 24.34, 17.95. IR (thin film): 2936, 2855, 1682, 1634, 1598, 1580, 1493, 1445, 1355, 1248, 1230, 1178, 1120, 1010, 976, 852, 756, 700 $cm^{-1}$. MS (ES-API) calcd for $[C_{23}H_{27}NO_2Na]^+$($[M+Na]^+$): 372.2, found 371.8.

**Mechanistic Studies**

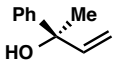
***(a) TEMPO Adduct 14***




***14***

In an 8-mL reaction vial, a solution of 1,1-diphenylprop-2-en-1-ol **1** (0.200 mmol, 42.0 mg, 1.0 equiv), $Pd(PhCN)_2Cl_2$ (3.80 mg, 5mol %), dppe (8.0 mg, 10 mol%), $Ag_2O$ (0.400 mmol, 92.7 mg, 2.0 equiv), and **TEMPO** (78.1 mg, 2.5 equiv) in α,α,α-Trifluorotoluene (1.0 mL, 0.2 M) was treated with ethyl bromoacetate **2** (0.400 mmol, 66.9 mg, 2.0 equiv). The reaction vial was charged with nitrogen for 5 minutes and then sealed. The mixture was stirred at 120 °C for 12 h. After the reaction was finished, the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The resulting residue was purified by silica gel flash chromatography (gradient eluent pentane/diethyl ether) to afford the desired product **3** (5.0 mg, 8% yield) and TEMPO adduct **14** (87.6 mg, 90% yield). Spectroscopic data for TEMPO adduct **14** matched the reported data in the literature.[4]

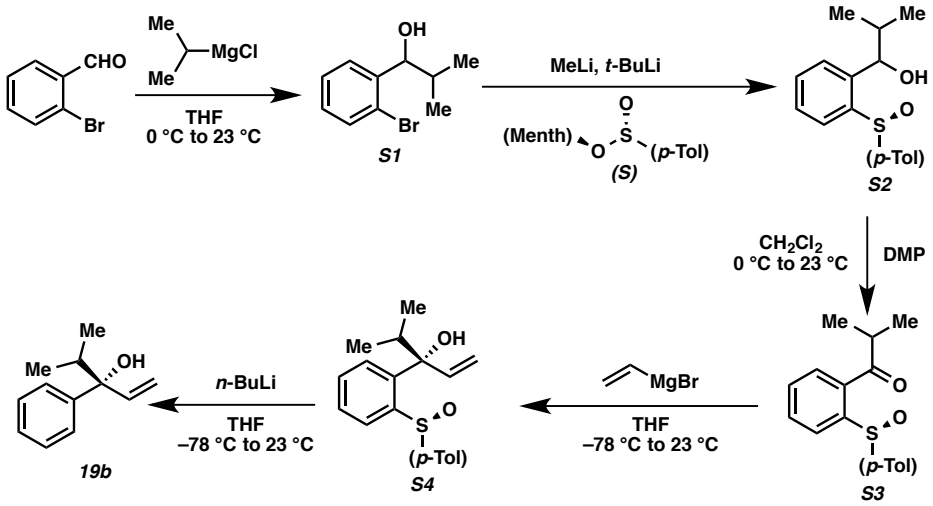
***(b) Enantioenriched Allylic Alcohol 19a***




***19a***

Enantioenriched **19a** was synthesized according to literature precedence.[5] The product was isolated as a clear oil (148.3 mg, 69% yield): ee = 96%; $[\alpha]_D$ = +25.4°, (c = 1.0, $CHCl_3$). $^1H$ NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.45 (m, 2H), 7.33 – 7.42 (m, 2H), 7.25 – 7.25 (m, 1H), 6.19 (dd, J = 17.3, 10.6 Hz, 1H), 5.32 (dd, J = 17.2, 1.1 Hz, 1H), 5.17 (dd, J = 10.6, 1.1 Hz, 1H), 2.24 (s, 1H), 1.68 (s, 3H); $^{13}C$ NMR (101 MHz, Chloroform-*d*) δ 146.45, 144.85, 128.24, 127.00, 125.23, 112.38, 74.81, 29.31. HPLC condition: Chiral IA-H column, 1% isopropanol in hexane, 1.0 mL/min, TR= 17.7 (major), 18.7 (minor). Spectroscopic data matched the reported data in the literature.[5]

### *(c) Enantioenriched Allylic Alcohol 19b*




Based on a method developed by Ready and co-workers,[6] known alcohol **S1**[7] was converted to enantioenriched **19b** through a series of steps.

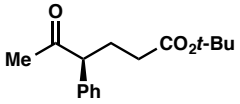
**S2** was isolated as a mixture of diastereoisomers (1:1) in 68 % yield (778 mg): $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.79 – 7.84 (m, 1H), 7.38 – 7.55 (m, 10H), 7.24 (d, *J* = 12.4 Hz, 4H), 4.81 (dd, *J* = 7.4, 3.5 Hz, 1H), 4.76 (dd, *J* = 7.7, 3.8 Hz, 1H), 2.36 (d, *J* = 4.3 Hz, 6H), 2.11 (q, *J* = 6.9 Hz, 1H), 1.94 – 2.03 (m, 1H), 1.04 (dd, *J* = 6.6, 1.6 Hz, 6H), 0.79 (d, *J* = 6.8 Hz, 3H), 0.64 (dd, *J* = 7.0, 3.0 Hz, 3H); MS (ES-API): 310.8 [M + Na]$^+$.

**S3** was isolated in 87% yield (670 mg): $^1$H NMR (400 MHz, $CDCl_3$) δ 8.51 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.83 - 7.91 (m, 1H), 7.77 - 7.83 (m, 1H), 7.49 - 7.64 (m, 3H), 7.12 - 7.18 (m, 2H), 3.44 (hept, *J* = 6.8 Hz, 1H), 2.30 (d, *J* = 0.9 Hz, 3H), 1.15 (dd, *J* = 6.9, 0.8 Hz, 3H), 0.99 (dd, *J* = 6.7, 0.9 Hz, 3H); MS (ES-API): 308.8 [M + Na]$^+$.

**S4** was isolated as the pure ($S_S$, R)–isomer (d.r. > 50:1) in 99 % yield (338 mg): $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.14 – 8.21 (m, 1H), 7.49 – 7.49 (m, 2H), 7.43 (qdd, *J* = 7.2, 4.5, 1.9 Hz, 2H), 7.30 – 7.37 (m, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.15 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.29 (d, *J* = 17.2 Hz, 1H), 5.17 (dd, *J* = 10.8, 1.7 Hz, 1H), 2.43 – 2.29 (m, 5H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.54 (d, *J* = 6.7 Hz, 3H); MS: MS (ES-API): 336.8 [M + Na]$^+$.

Enantioenriched **19b** was isolated in 70% yield (123 mg): ee = 96%; $[\alpha]_D$ = +67.4$^o$, (c = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.51 (m, 2H), 7.32 – 7.36 (m, 2H), 7.20– 7.26 (m, 1H), 6.30 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.33 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.19 (dd, *J* = 10.8, 1.2 Hz, 1H), 2.19 (p, *J* = 6.8 Hz, 1H), 1.79 (s, 1H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.78 (d, *J* = 6.8 Hz, 3H); $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 145.67, 143.18, 128.06, 126.57, 125.43, 112.65, 79.28, 37.26, 17.08, 16.70; MS (ES-API): [M-H]$^-$ 175.1. HPLC condition: Chiracel IA-H column, 1% isopropanol in hexane, 1.0 mL/min, TR= 11.4 (major), 13.6 (minor).

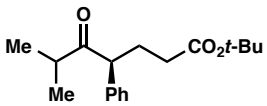
***(d) Enantioenriched Product 20a***




***20a***

Following the general procedure for the synthesis of α-aryl dicarbonyl compounds, purification by flash chromatography afforded **20b** (36.0 mg, 46% yield) as a clear oil: ee = 30%; $[\alpha]_D$ = -49.4°, (c = 1.7, $CHCl_3$). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.38 (m, 2H), 7.24 – 7.28 (m, 1H), 7.11 – 7.22 (m, 2H), 3.67 – 3.73 (m, 1H), 2.28 (ddd, *J* = 13.3, 7.1, 0.9 Hz, 1H), 2.10 (td, *J* = 7.1, 1.3 Hz, 2H), 2.04 (s, 3H), 1.94 (ddd, *J* = 13.7, 6.8, 1.2 Hz, 1H), 1.42 (s, 9H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 207.77, 172.49, 138.22, 129.02, 128.31, 127.45, 80.25, 58.37, 32.89, 29.12, 28.08, 26.97. IR (thin film): 2978, 2932, 1728, 1716, 1601, 1494, 1455, 1368, 1255, 1148, 952, 848, 746, 702 cm$^{-1}$. MS (ES-API) calcd for $[C_{16}H_{22}O_3Na]^+$([M+Na]$^+$): 285.2, found 285.1. HPLC condition: Chiral OD-H column, 2% isopropanol in hexane, 0.8 mL/min, TR= 8.3 (major), 9.1 (minor).

***(e) Enantioenriched Product 20b***




***20b***

Following the general procedure for the synthesis of α-aryl dicarbonyl compounds, purification by flash chromatography afforded **20a** (34.1 mg, 65% yield) as a clear oil: ee = 50%; $[\alpha]_D$ = -104.8°, (c = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.33 (m, 2H), 7.23 – 7.26 (m, 1H), 7.15 – 7.23 (m, 2H), 3.89 (td, *J* = 7.3, 1.6 Hz, 1H), 2.63 (pd, *J* = 6.9, 1.5 Hz, 1H), 2.21 – 2.29 (m, 1H), 2.05 – 2.14 (m, 2H), 1.94 (ddd, *J* = 13.9, 6.3, 1.5 Hz, 1H), 1.43 (s, 9H), 1.08 (dd, *J* = 7.1, 1.6 Hz, 3H), 0.90 (dd, *J* = 6.7, 1.6 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 213.66, 172.52, 138.36, 128.89, 128.42, 127.29, 80.23, 55.73, 39.84, 33.05, 28.09, 27.86, 18.94, 18.04. IR (thin film): 2974, 2934, 1728, 1714, 1600, 1493, 1454, 1367, 1254, 1150, 1012, 850, 748, 701 cm$^{-1}$. MS (ES-API) calcd for $[C_{18}H_{26}O_3Na]^+$([M+Na]$^+$): 313.2, found 313.2. HPLC condition: Chiracel AD-H column, 2% isopropanol in hexane, 0.6 mL/min, TR= 9.3 (major), 10.8 (minor).

**Determination of Relative Stereochemistry of Products (Table 3, entry 7)**

A sample of α-aryl dicarbonyl product from Table 3, entry 7 was recrystallized from $CH_2Cl_2$/$Et_2O$/Pentanes (slow evaporation). The resulting crystals were suitable for X-ray diffraction and the structure was solved (Figure S1). This structure allowed the assignment of relative configuration as shown. The relative configurations of all other α-aryl dicarbonyl compounds in Table 3 were assigned by analogy. We thank Dr. Vincent Lynch (Manager of the X-ray Diffraction Lab at UT Austin) for the X-ray structural analysis. The CIF file is available as a separate file in the supporting information.

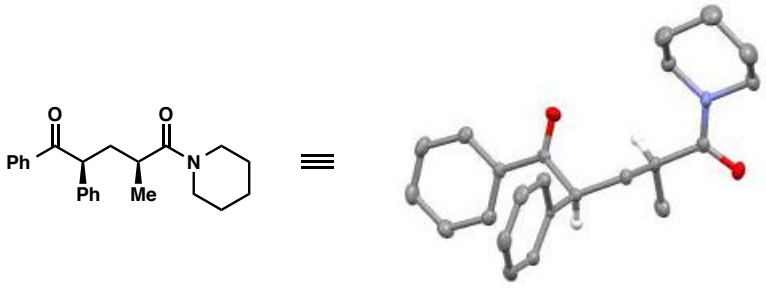
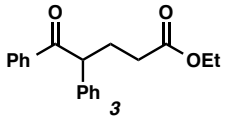



**Figure S1**

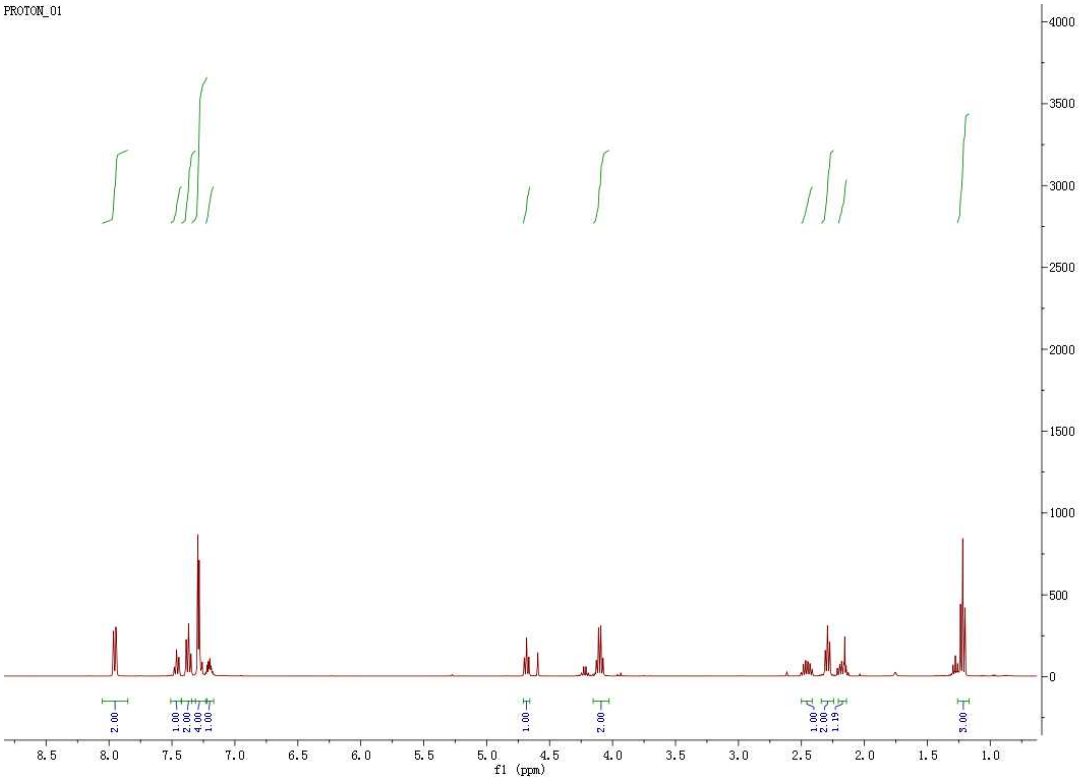
## References

1. (a) Rosa, D.; Orellana, A. *Org. Lett.* **2011**, *13*, 3648–3651. (b) Hayashi, S.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2009**, *131*, 2052–2053. (c) Zheng, H.; Lejkowski, M.; Hall, D. *Chem. Sci.* **2011**, *2*, 1305–1310.
2. (a) Donohoe, T. J.; Fishlock, L. P.; Basutto, J. A.; Bower, J. F.; Procopiou, P. A.; Thompsonz, A. L. *Chem. Commun.* **2009**, 3008–3010. (b) Hirner, S.; Kirchner, D. K.; Somfai, P. *Eur. J. Org. Chem.* **2008**, 5583–5589.
3. Sakurai, Y.; Matsui, E. *Chem. Pharm. Bull.* **1965**, *13*, 594–598.
4. Sumino, S; Fusano, A.; Ryu, I. *Org. Lett.* **2013**, *15*, 2826–2829.
5. Stymiest, J. L.; Bagutski, V.; French, R.M.; Aggarwal, V. K. *Nature* **2008**, *456*, 778–782.
6. Antczak, M. I.; Cai, F.; Ready, J. M. *Org. Lett.* **2011**, *13*, 184–187.
7. Schulte, B.; Fröhlich, R.; Studer, A. *Tetrahedron* **2008**, *64*, 11852–11859.

## NMR Spectra




*3*



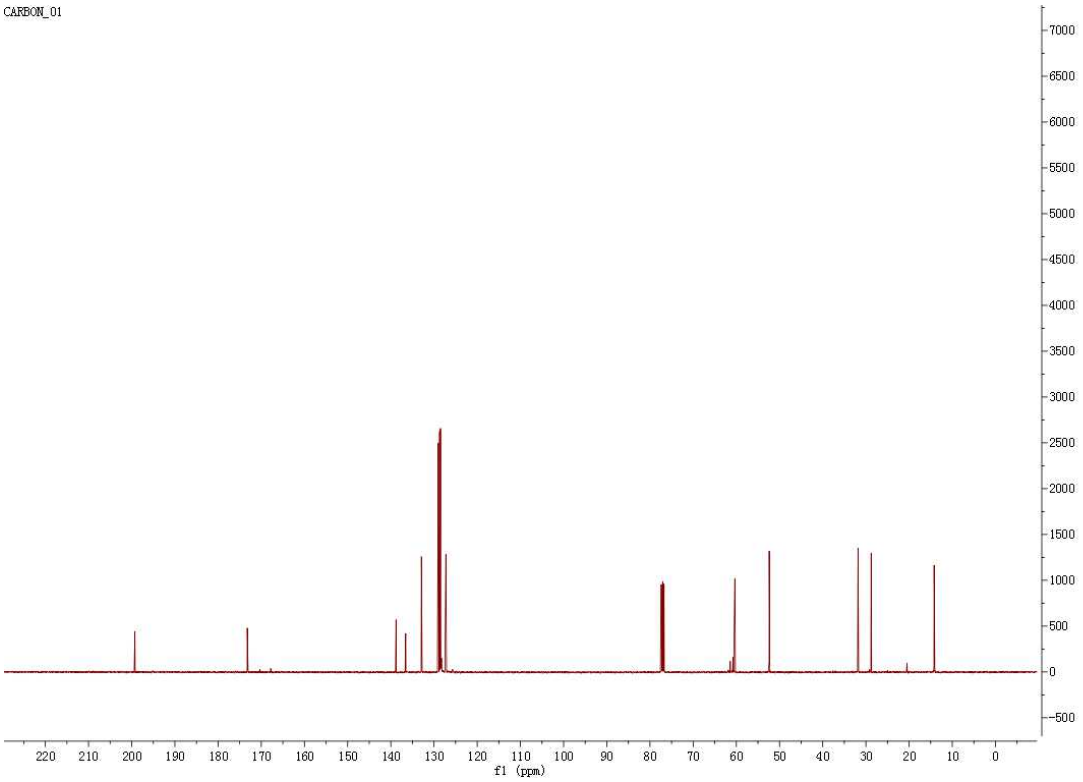
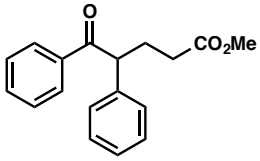
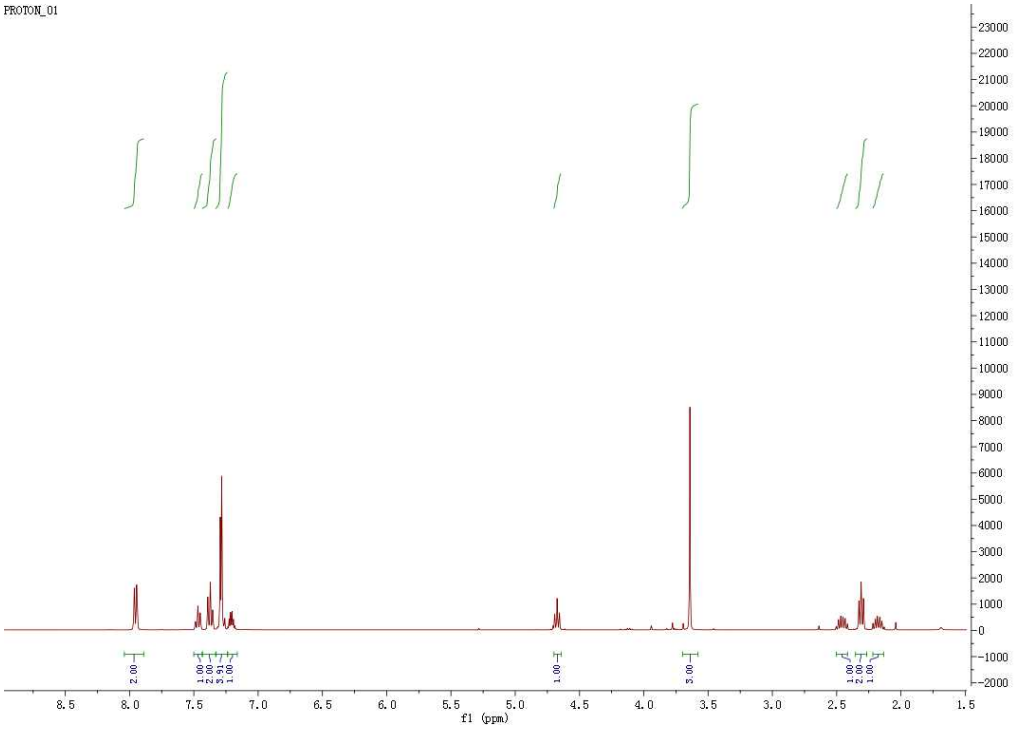



*Table 2, Entry 1*



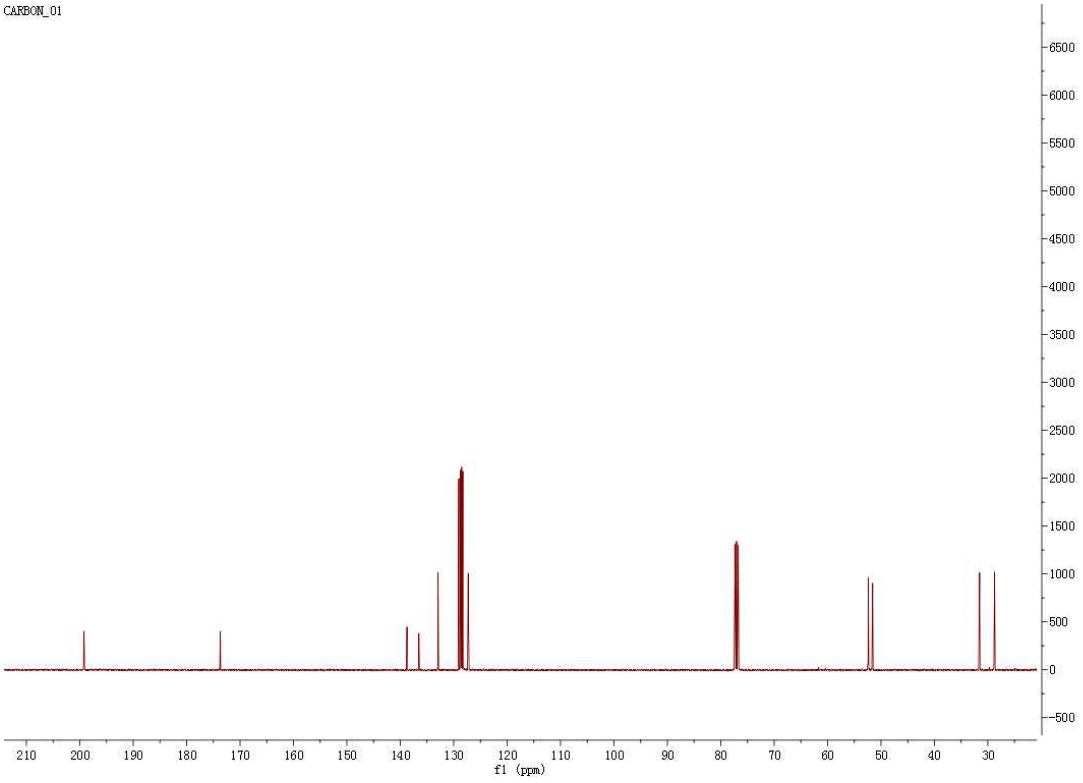
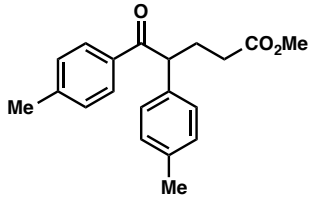
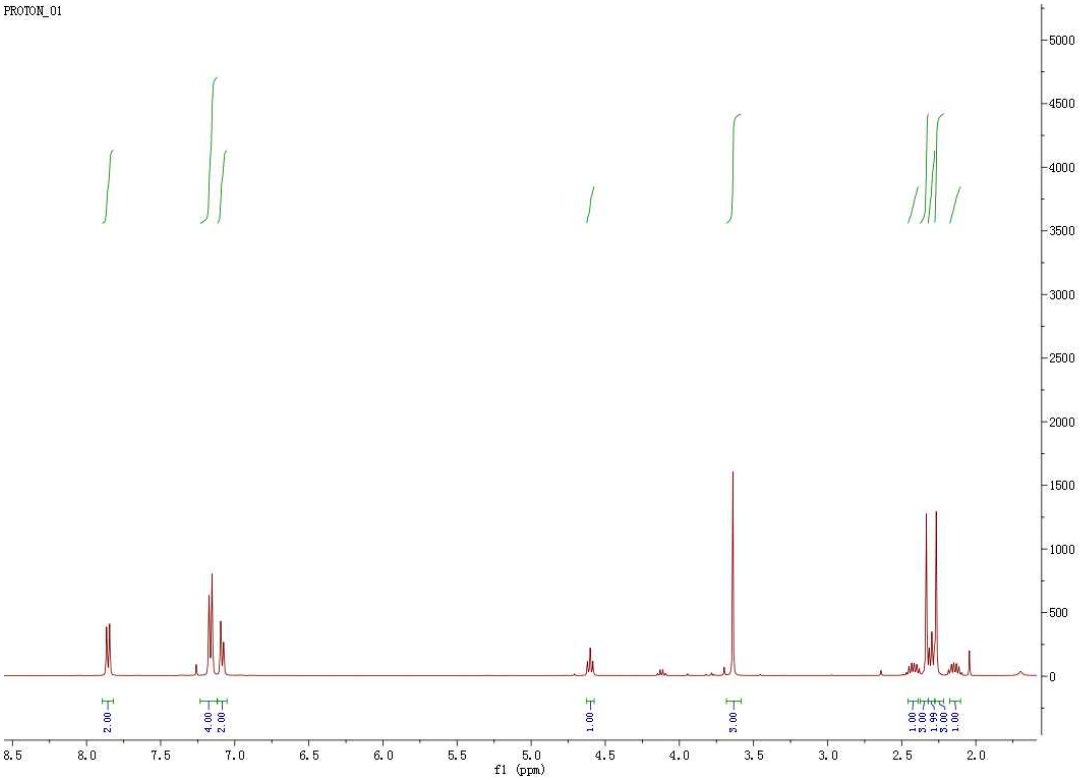
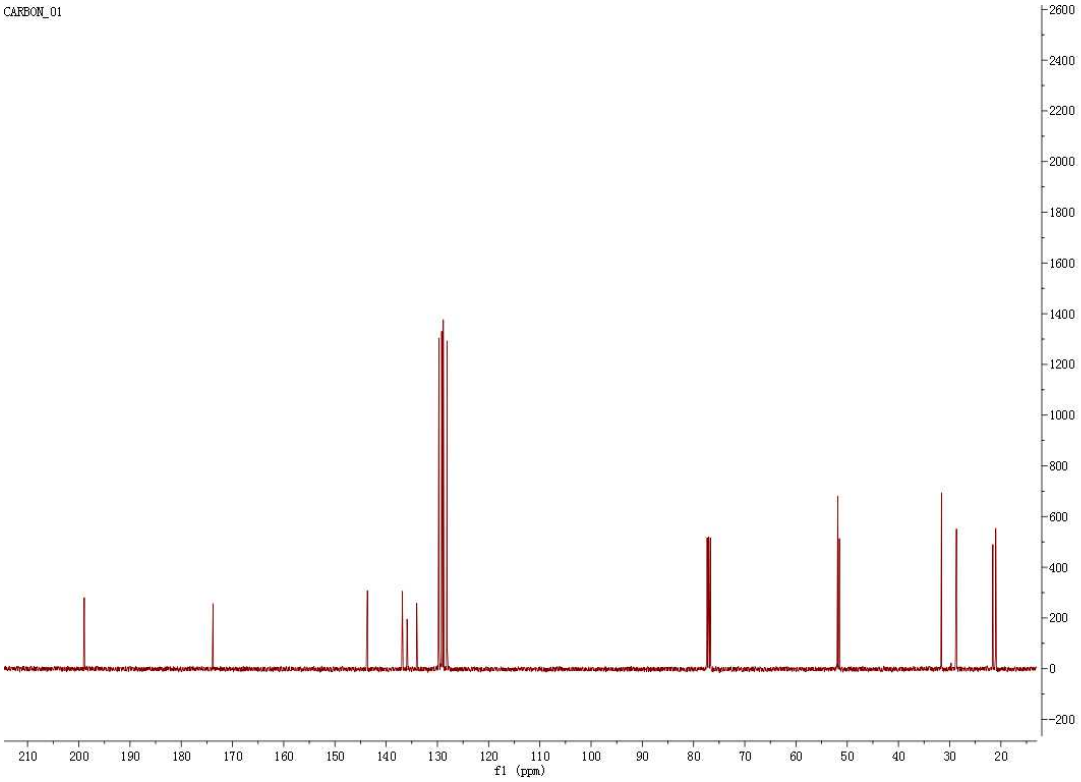



*Table 2, Entry 2*



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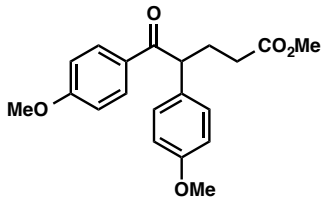


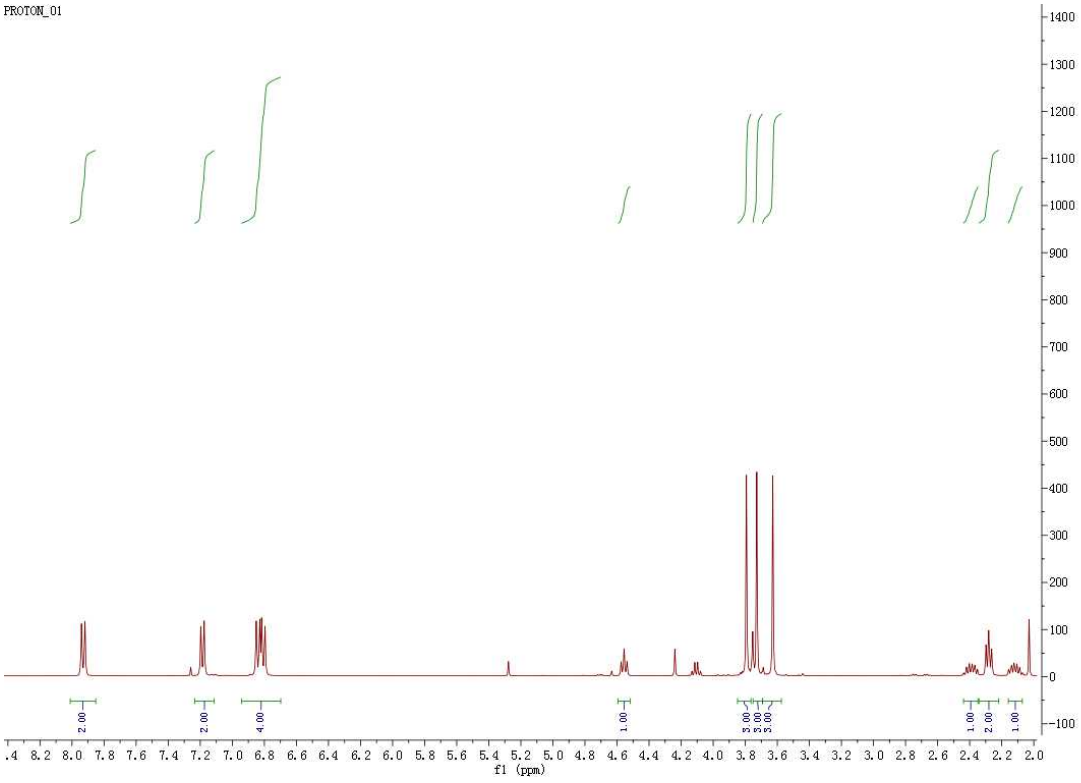


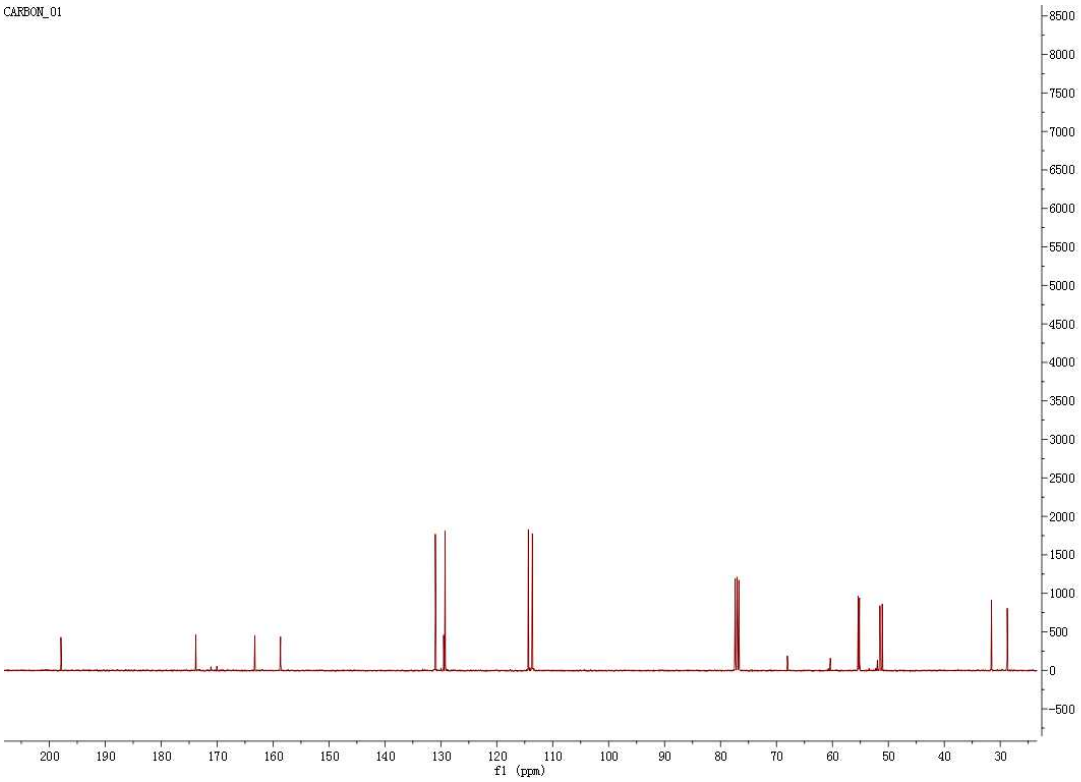

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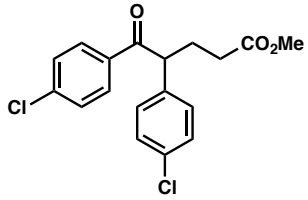


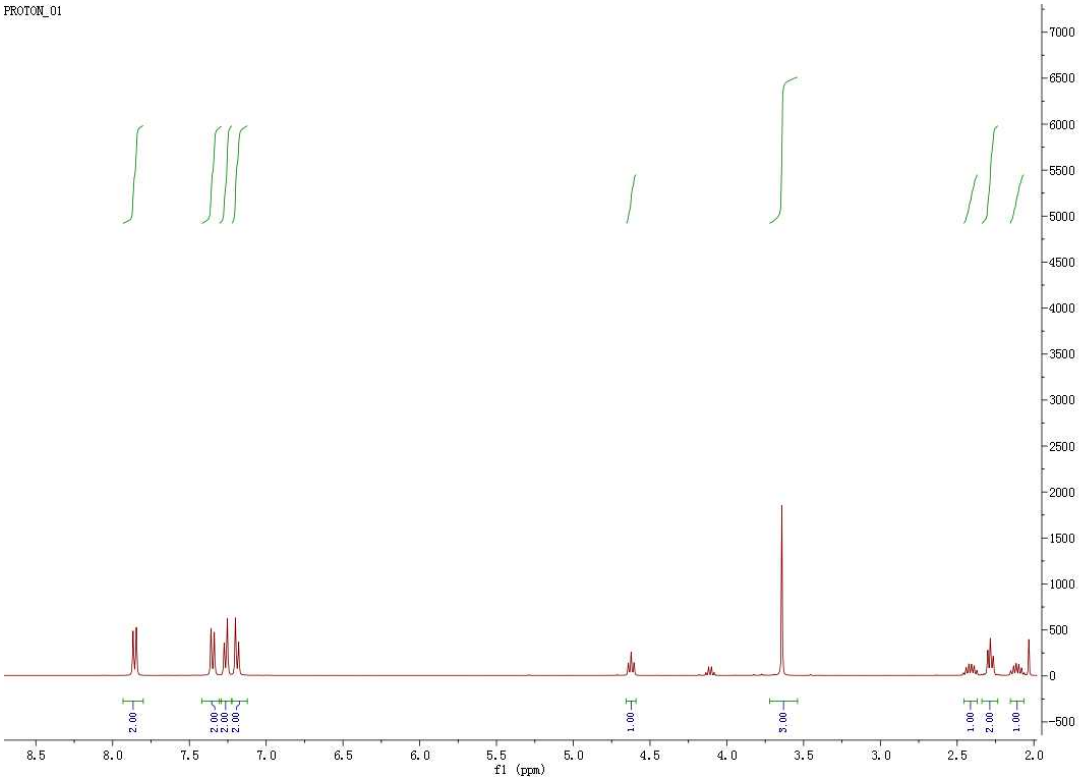


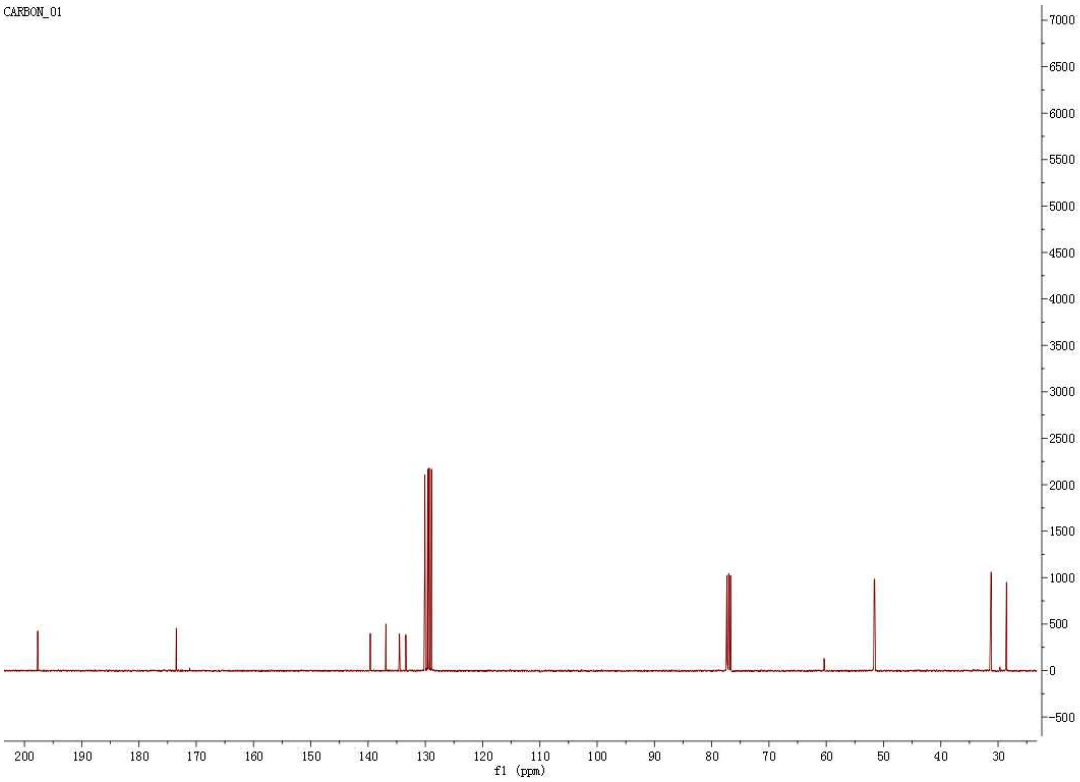

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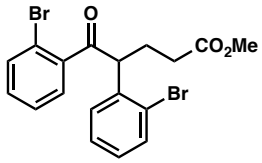


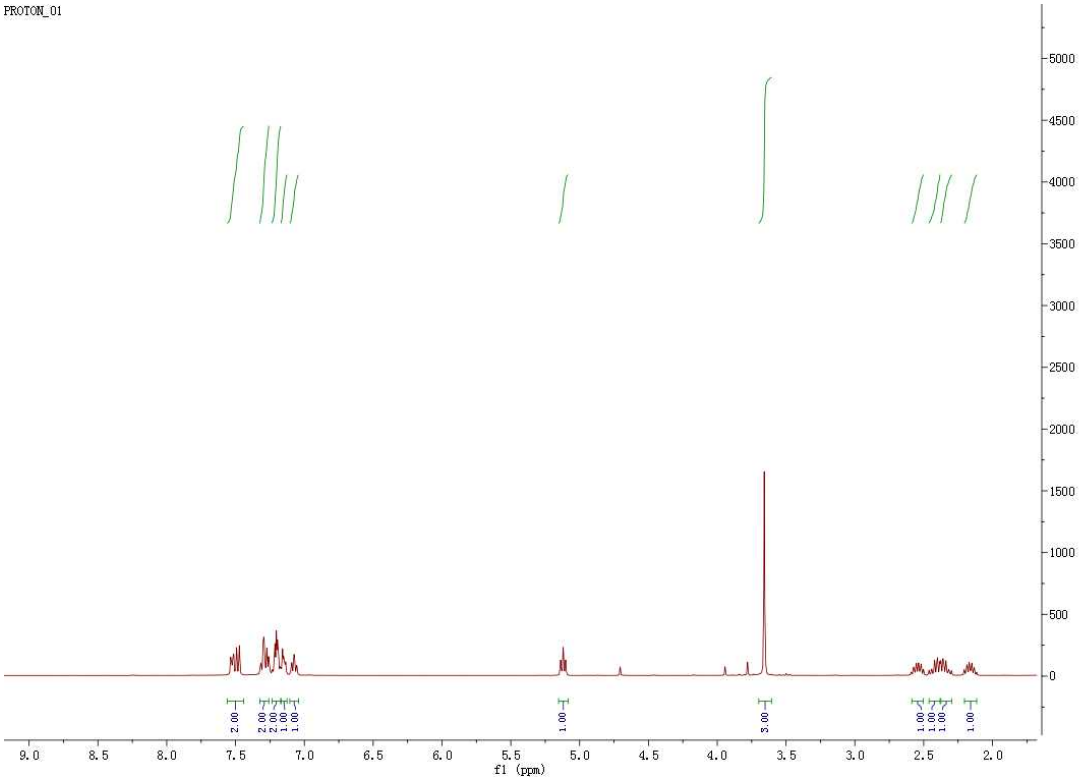


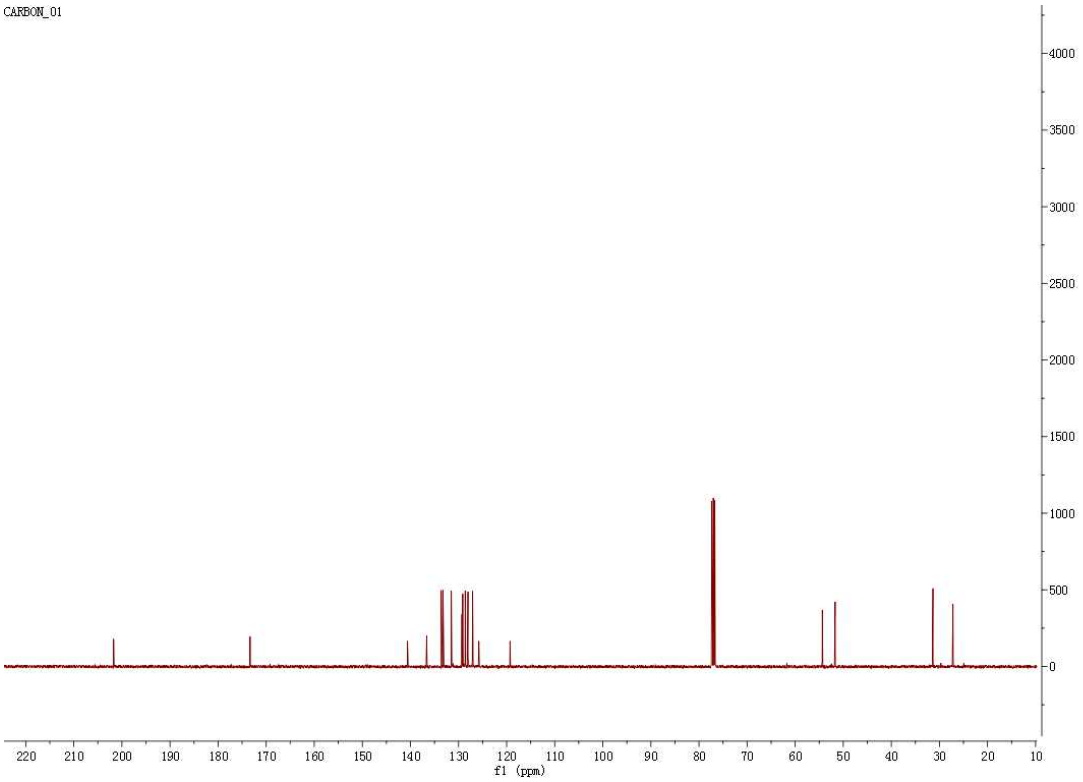

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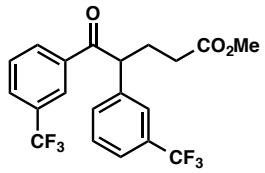


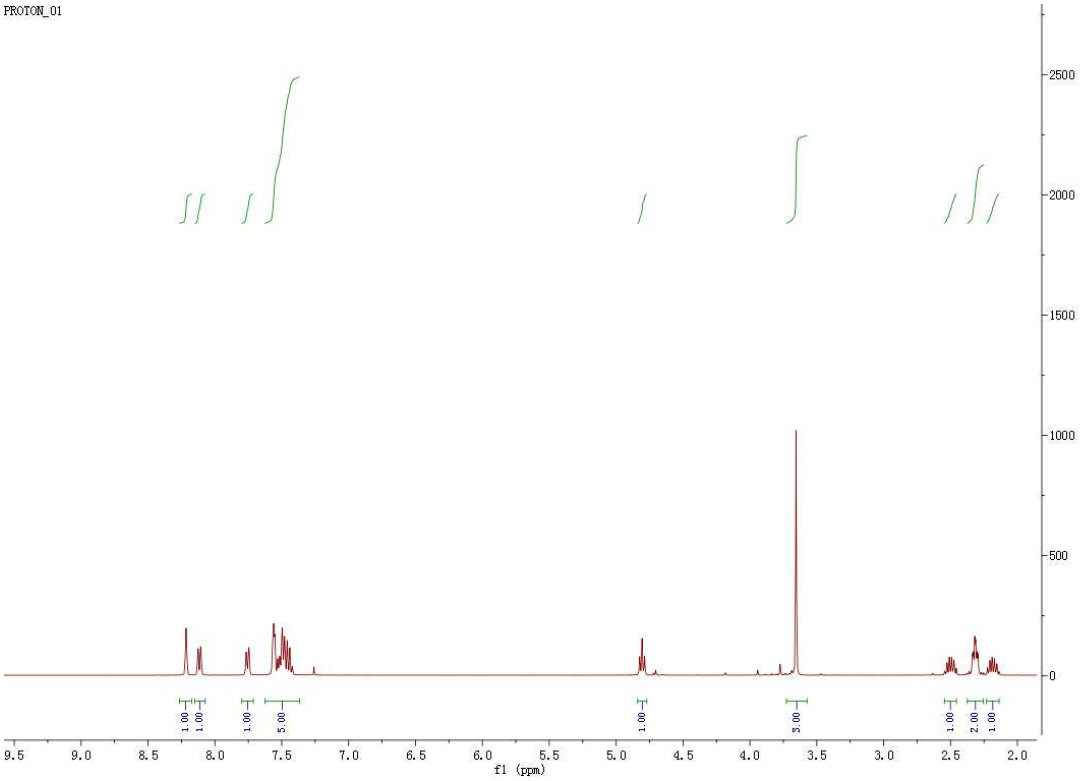


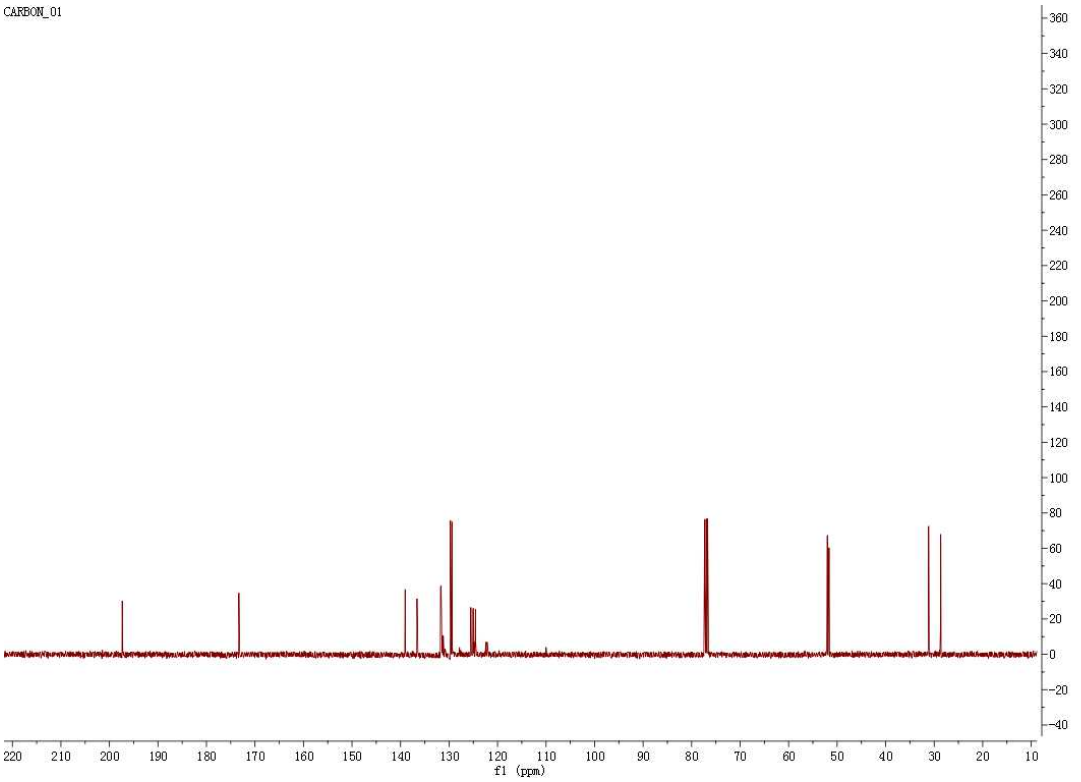

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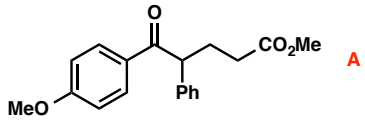


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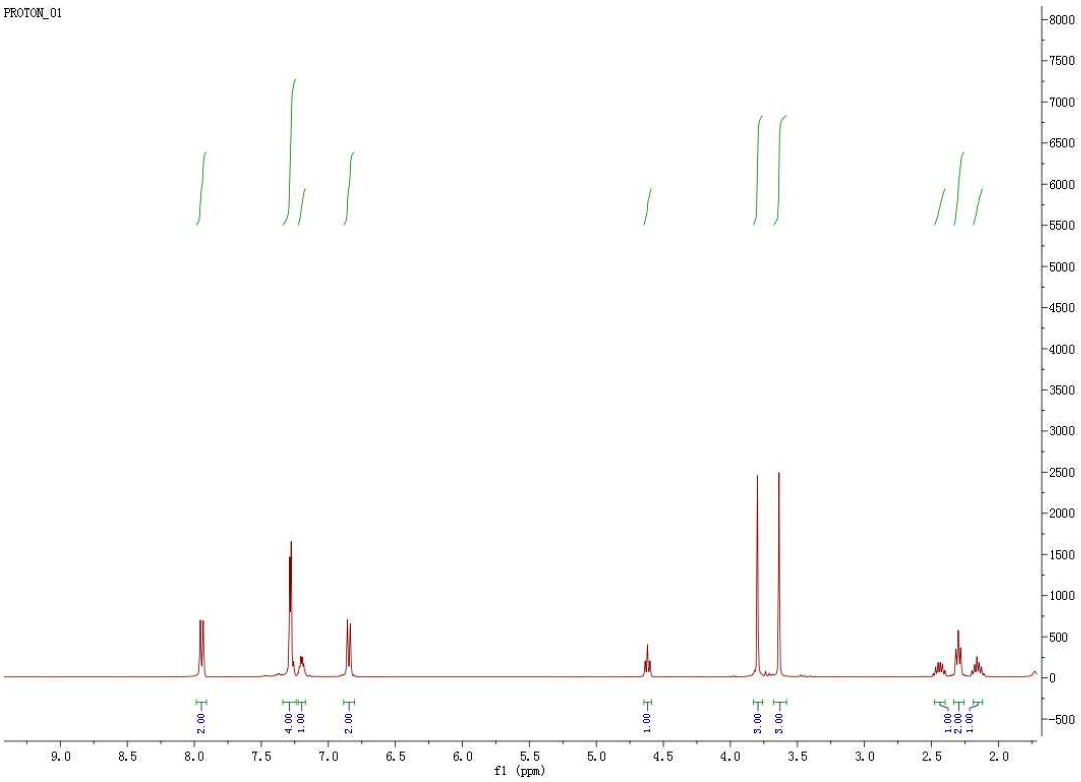


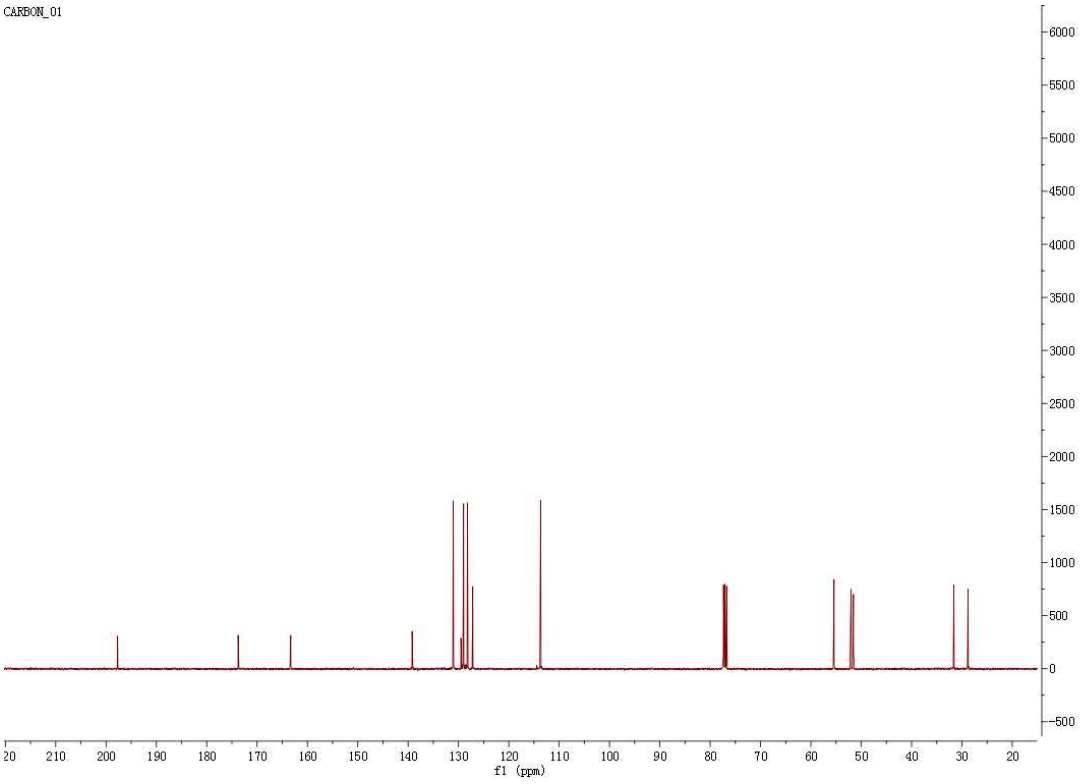
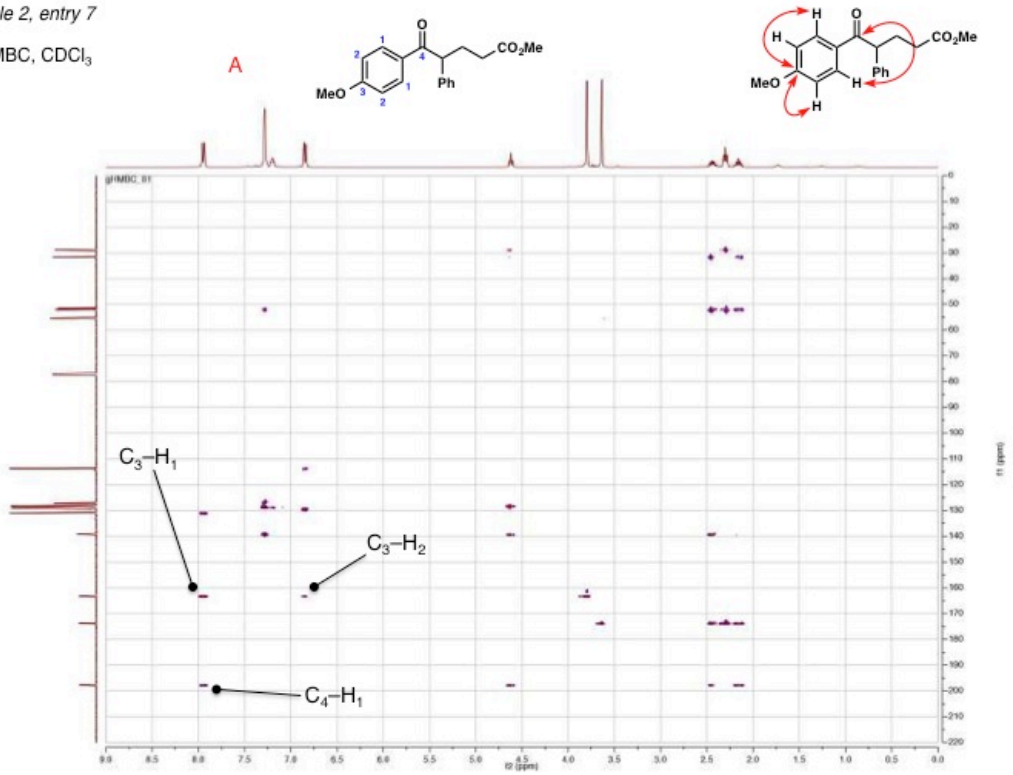



*Table 2, entry 7*

HMBC, $CDCl_3$



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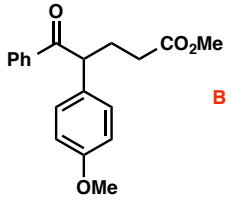


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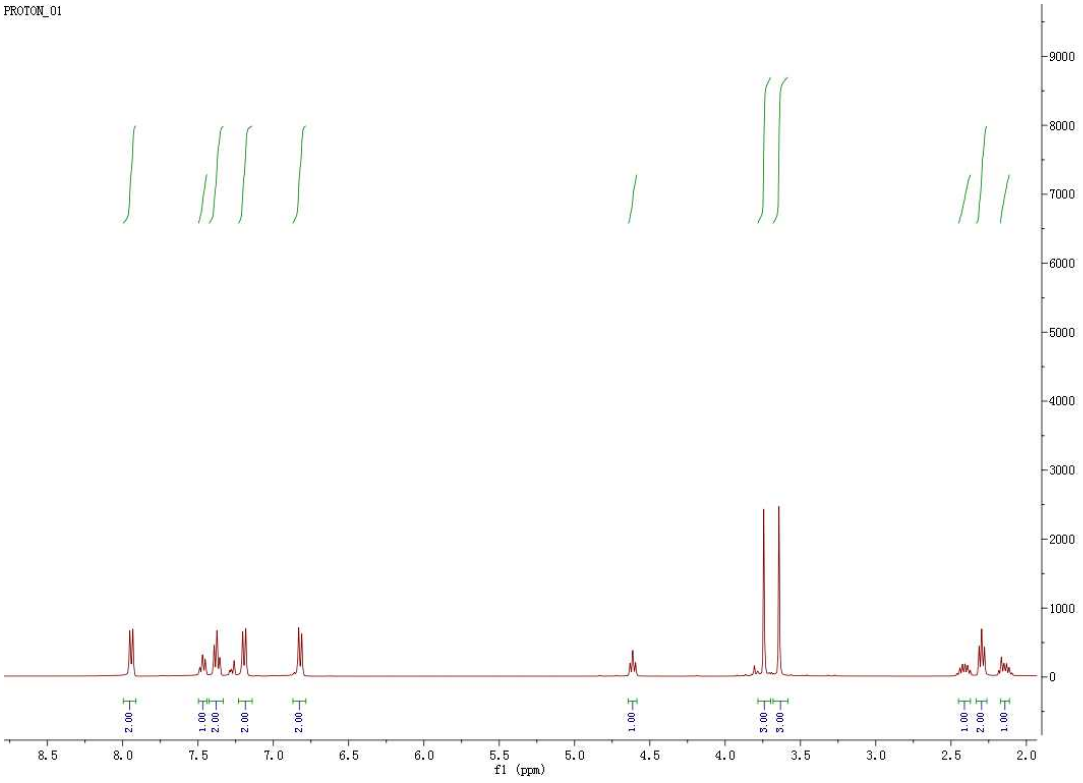


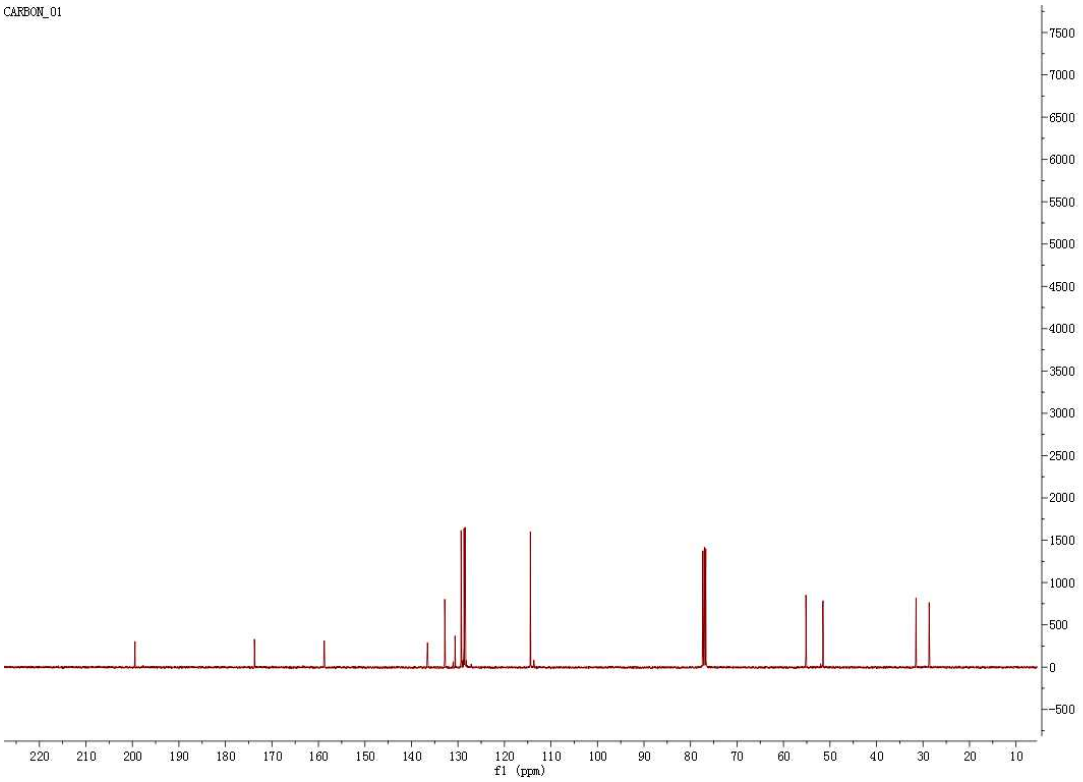



*Table 2, entry 7*

HSQC, $CDCl_3$

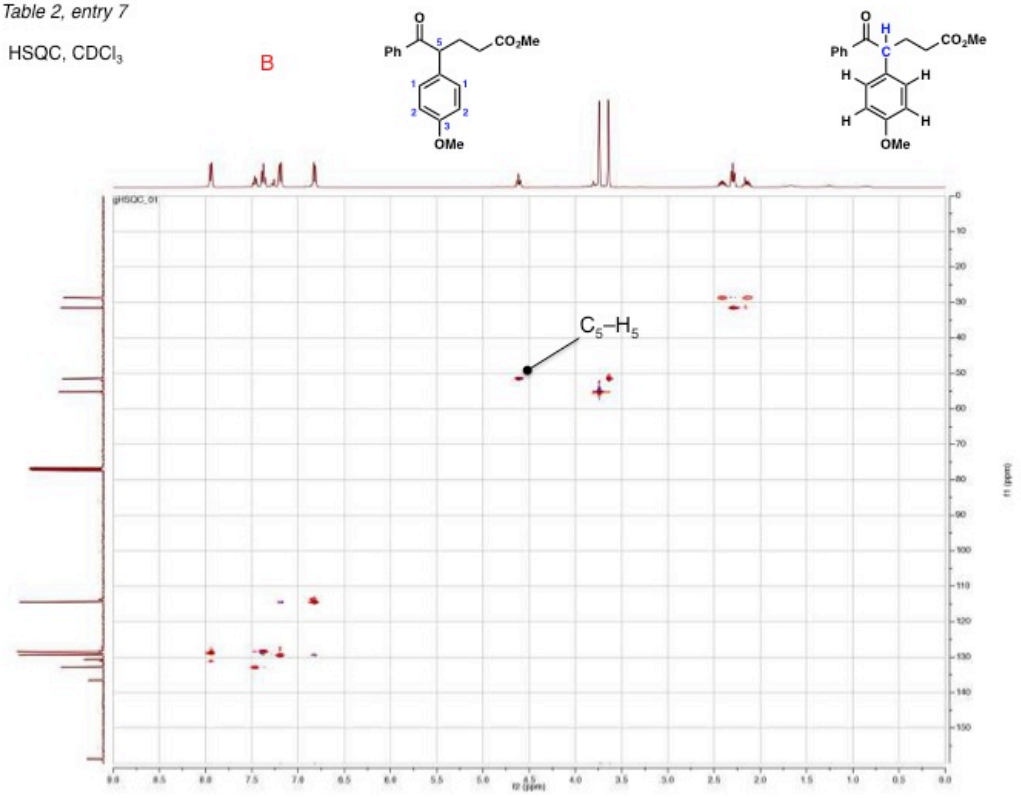
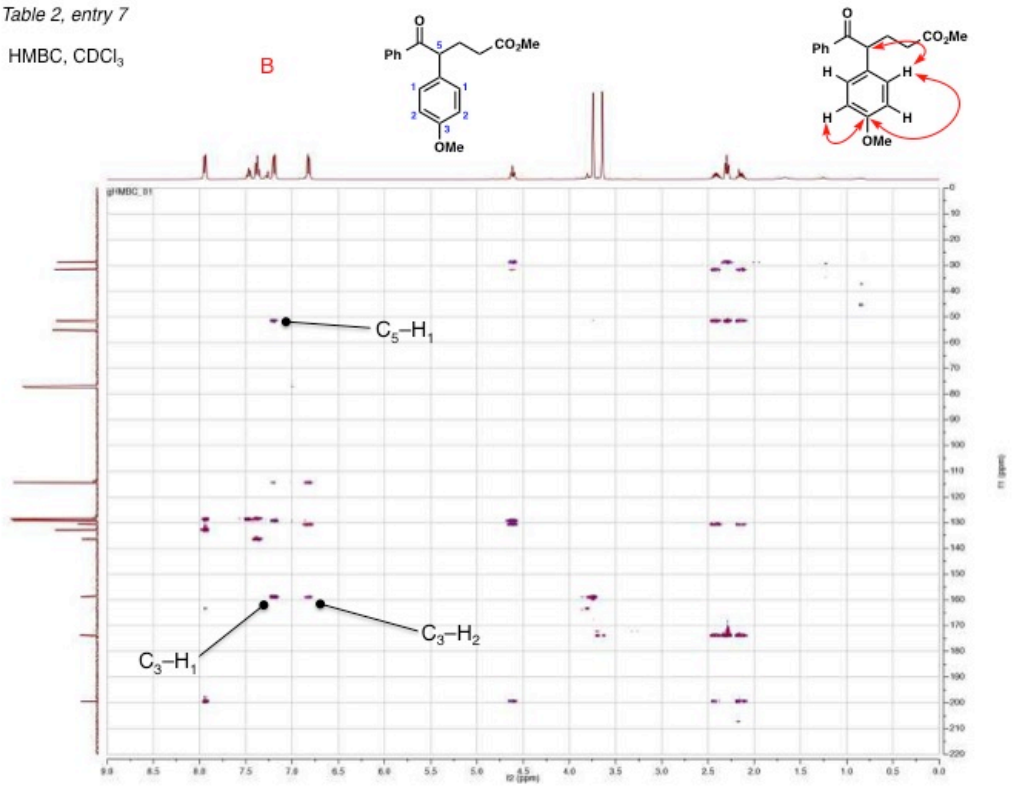



*Table 2, entry 7*

HMBC, $CDCl_3$



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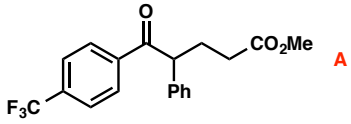
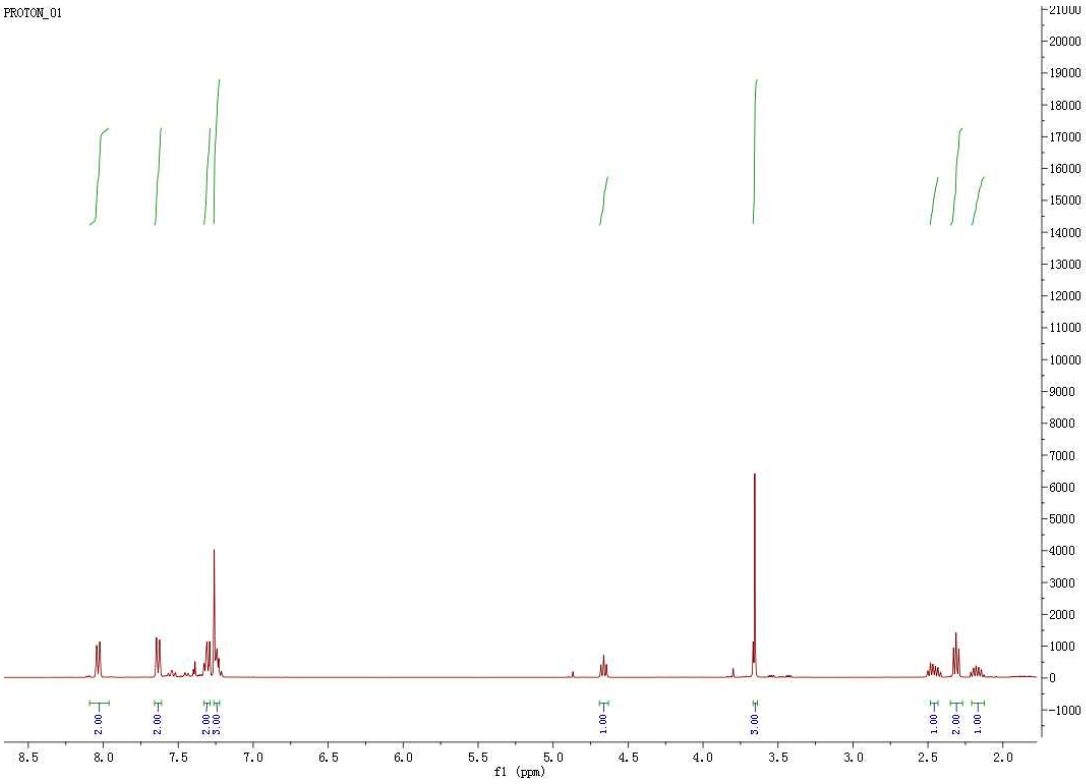
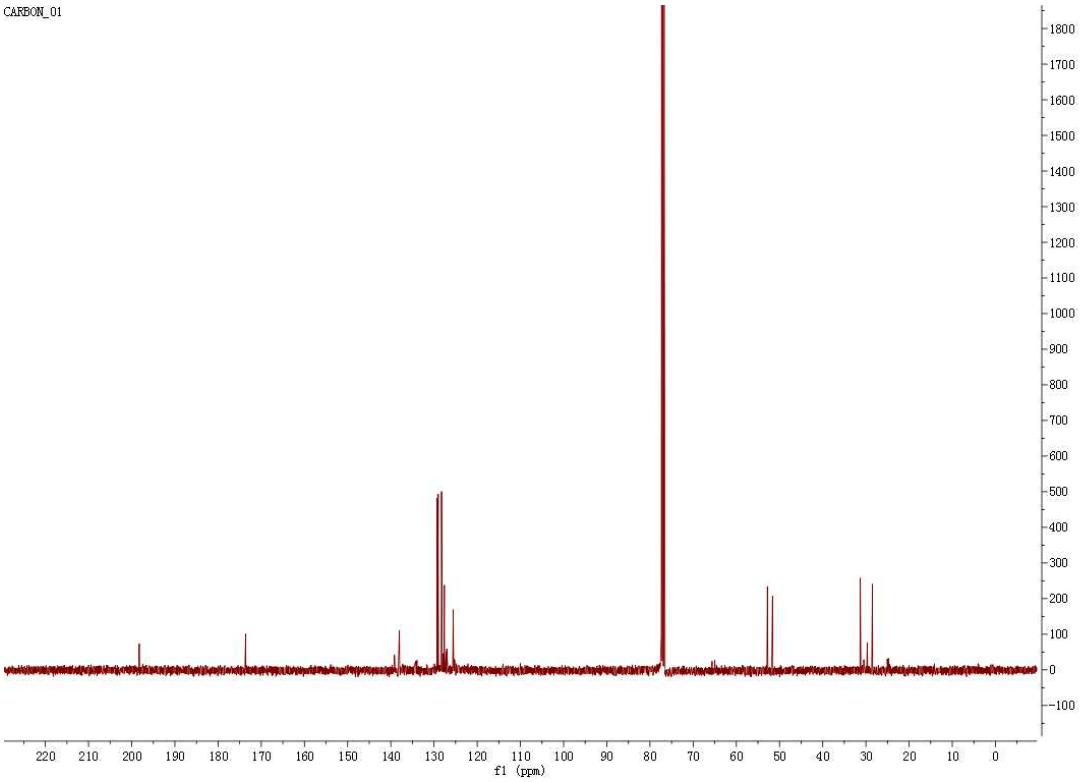



A



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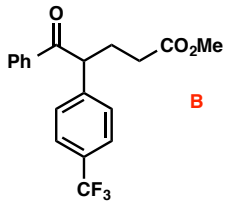
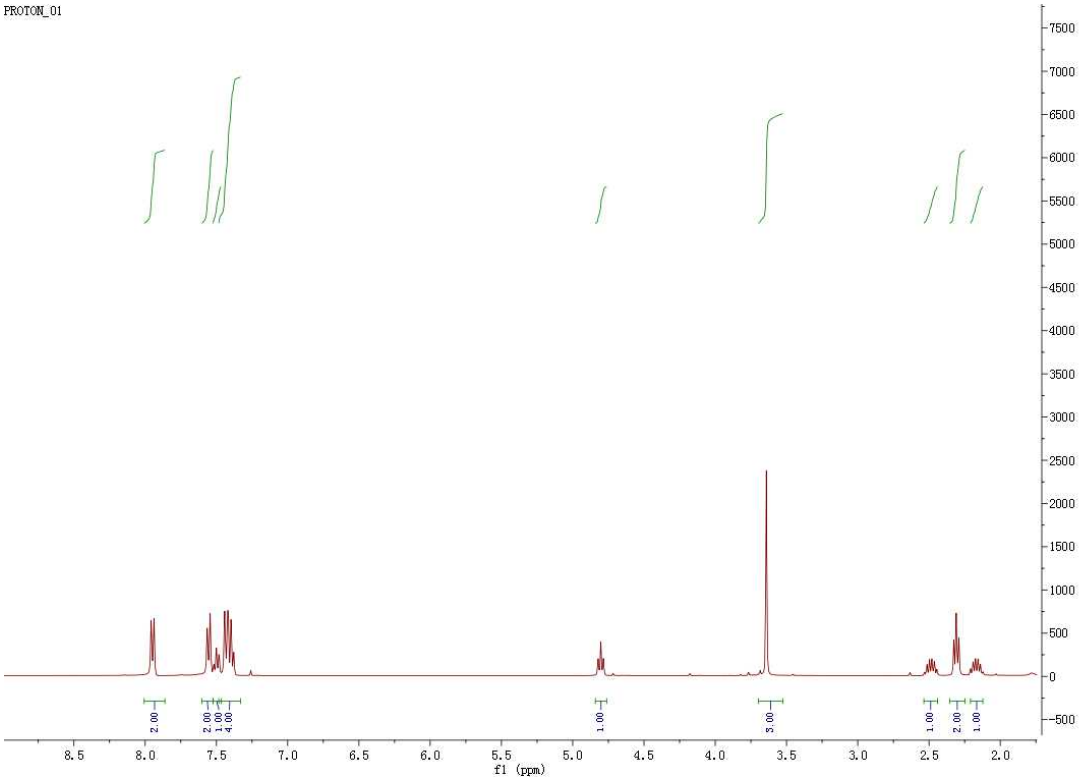


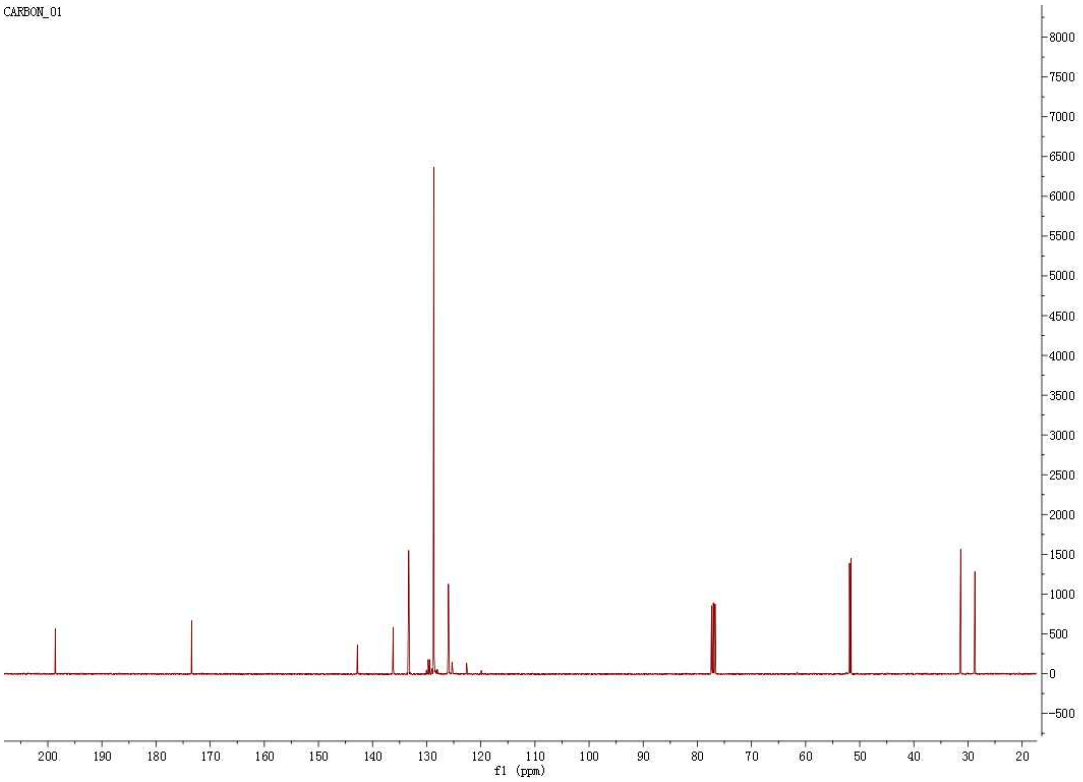



*Table 2, entry 8*

COSY, $CDCl_3$

B

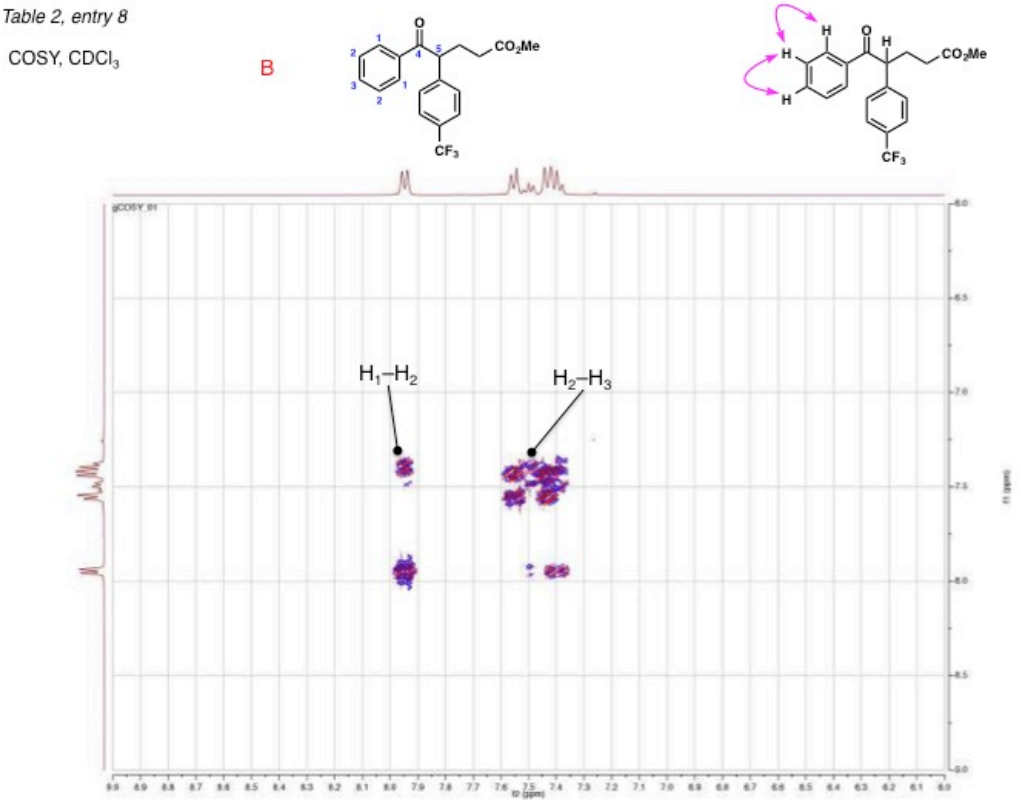



*Table 2, entry 8*

HSQC, $CDCl_3$

B

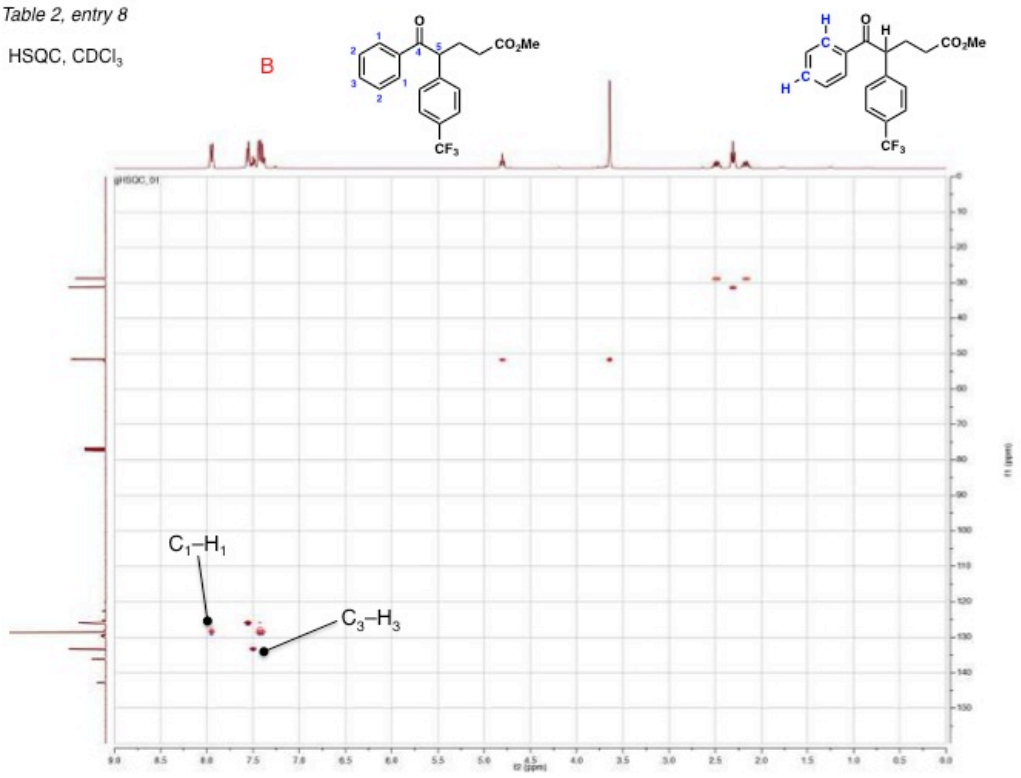
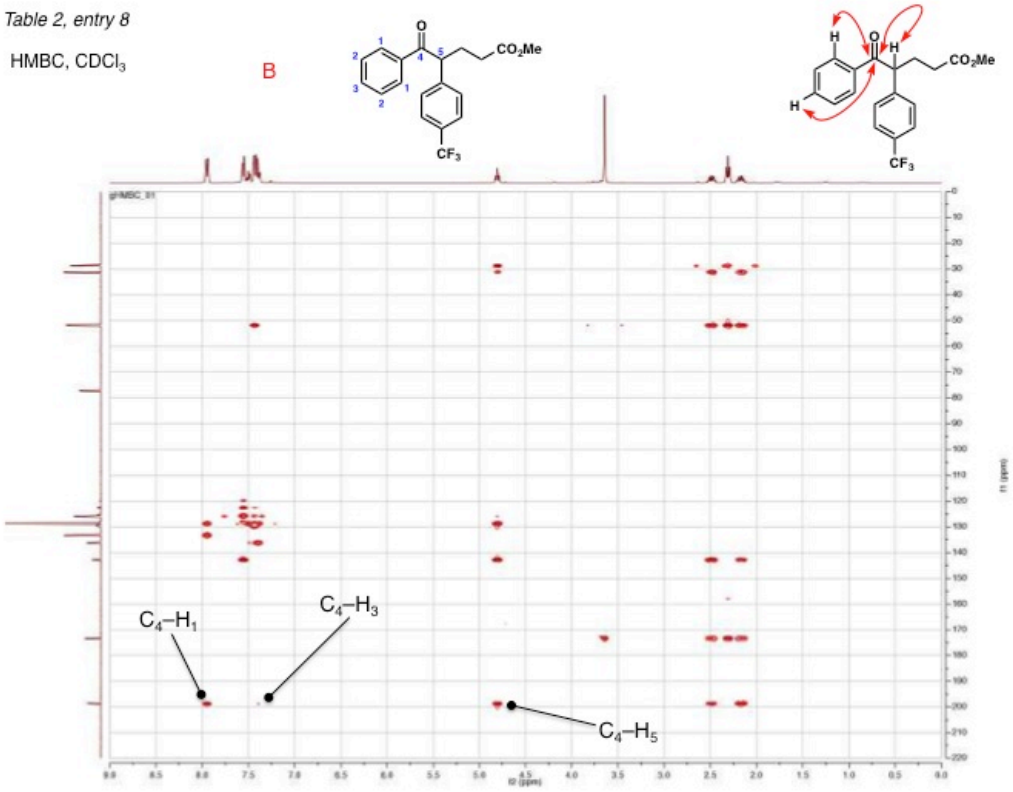


*Table 2, entry 8*

HMBC, $CDCl_3$

B



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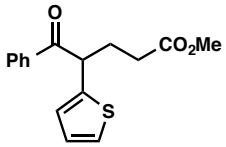


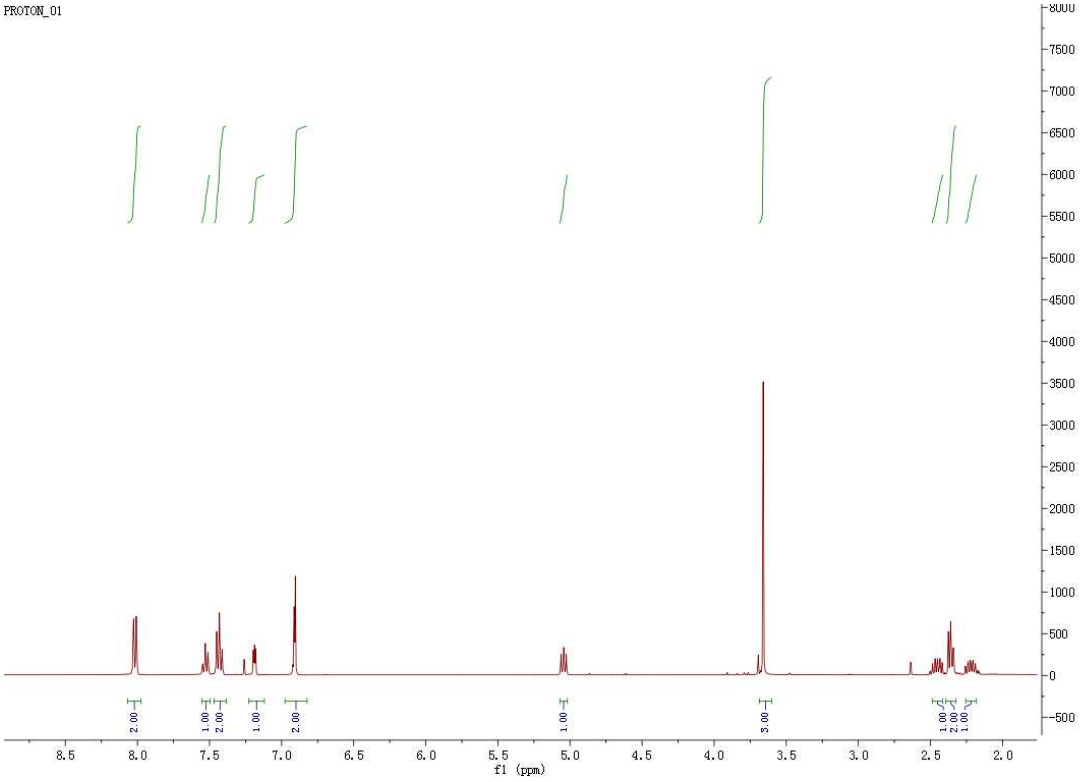


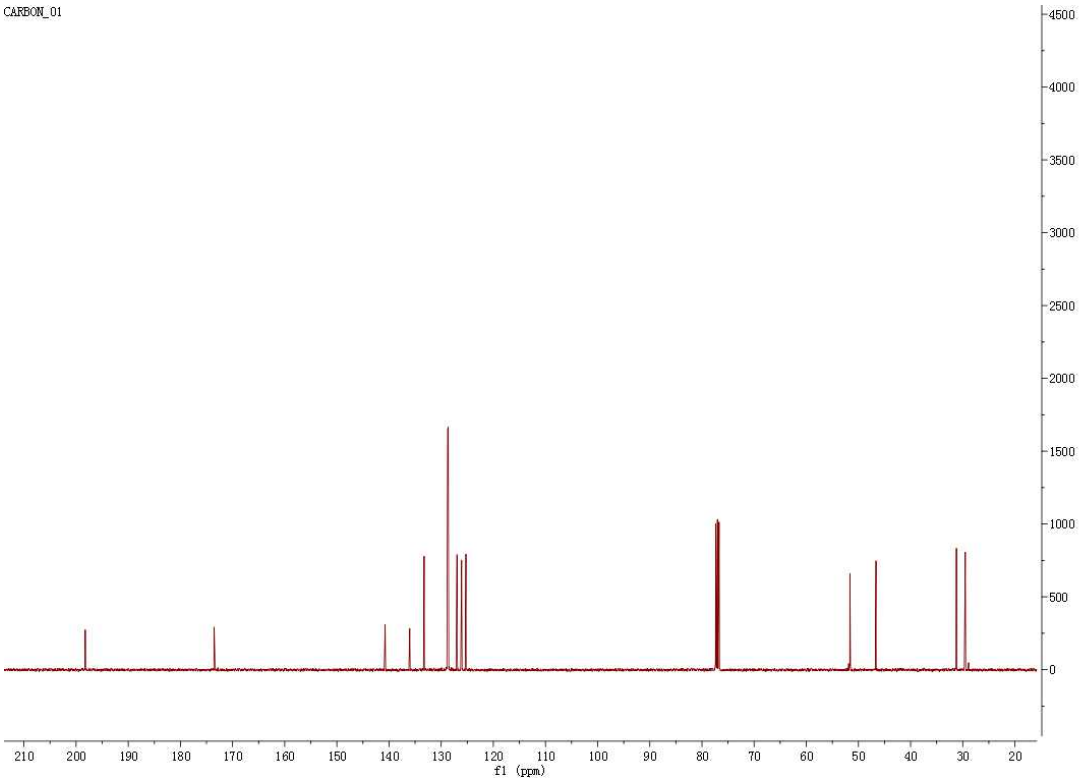

*Table 2, entry 9*

COSY, $CDCl_3$

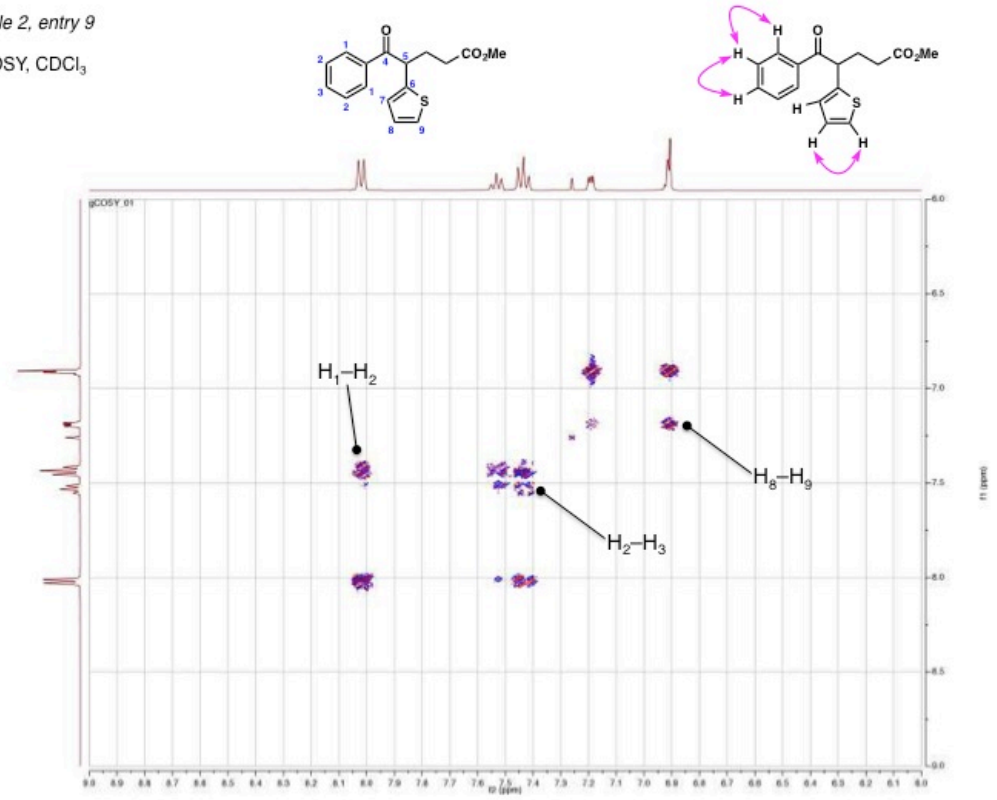


*Table 2, entry 9*

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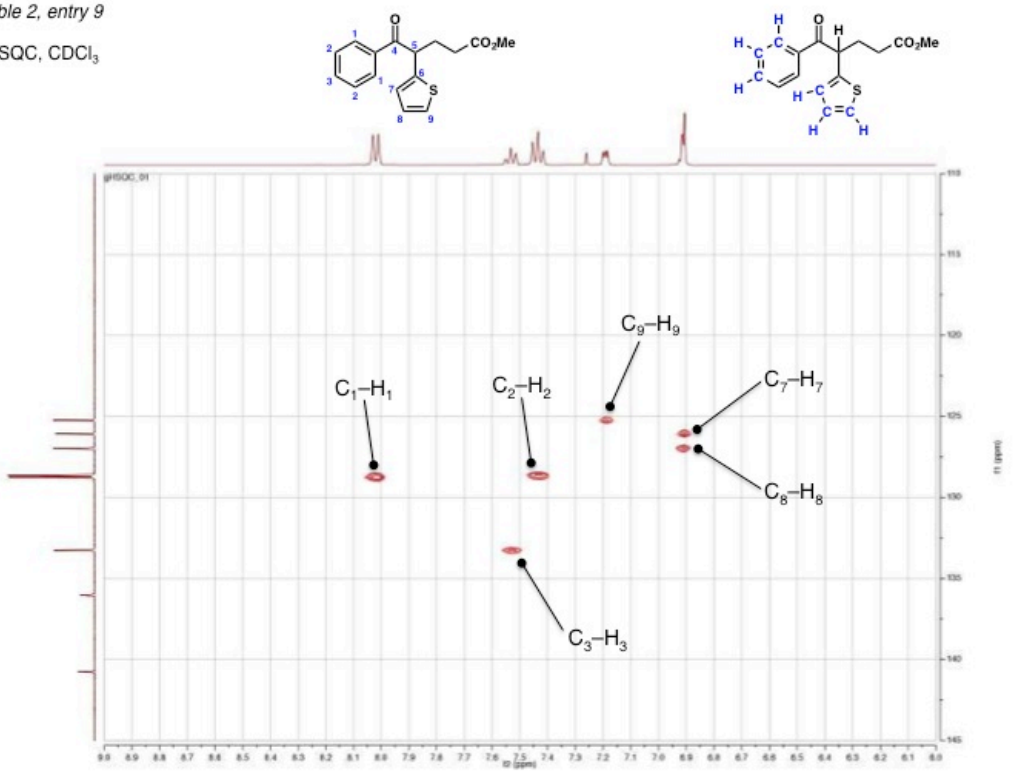
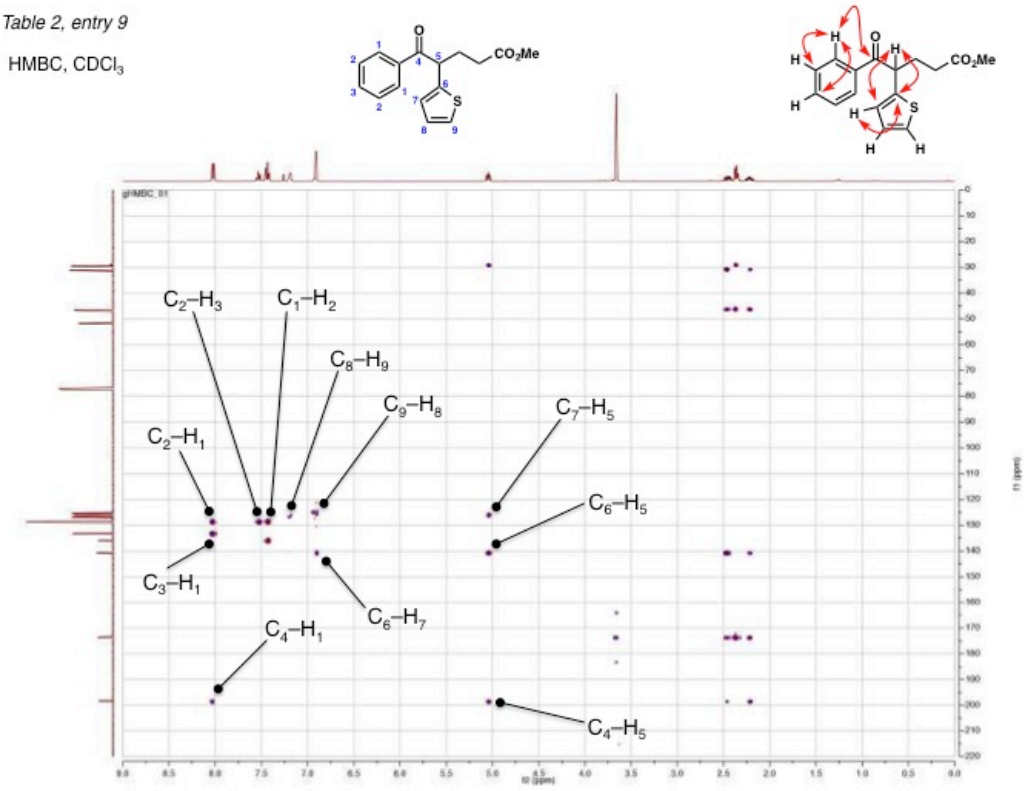


*Table 2, entry 9*

HMBC, $CDCl_3$



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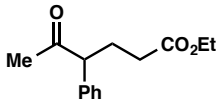
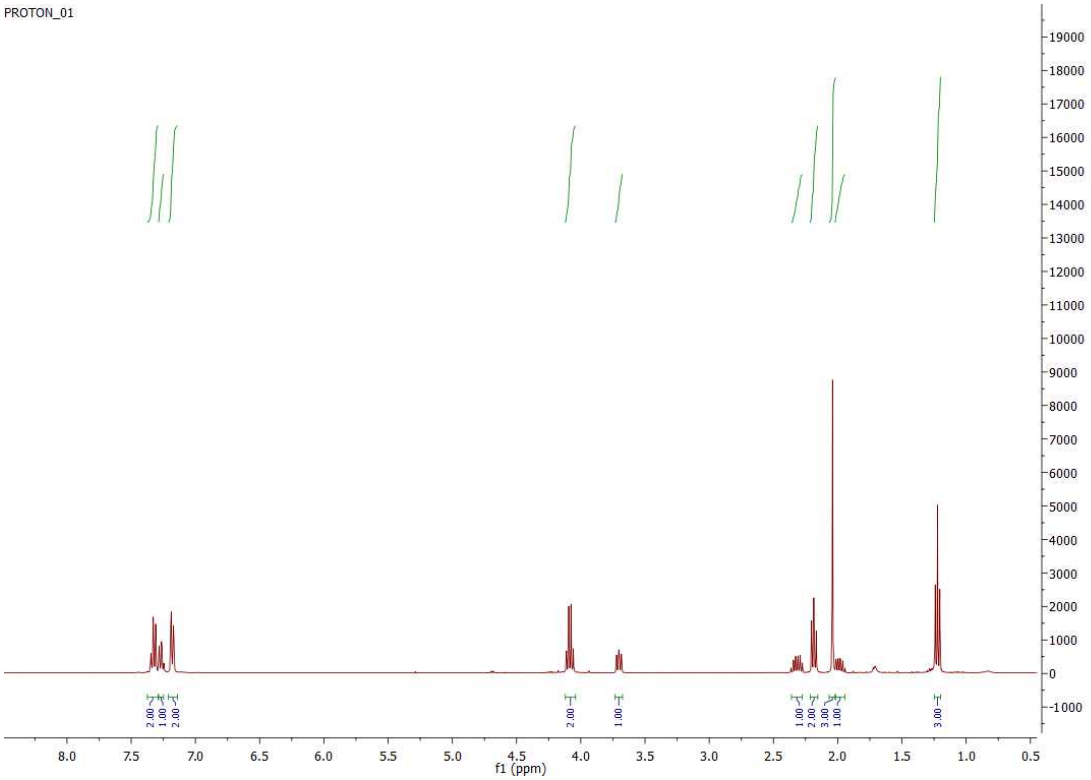


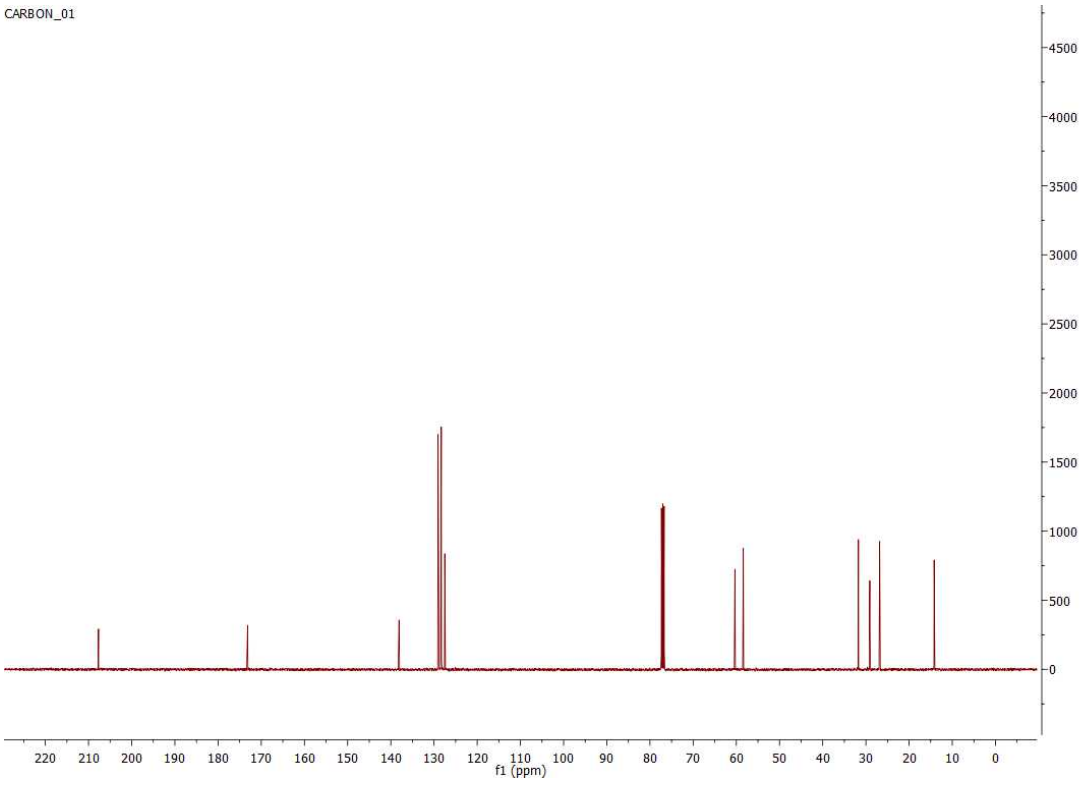
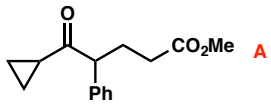



*Table 2, Entry 11*

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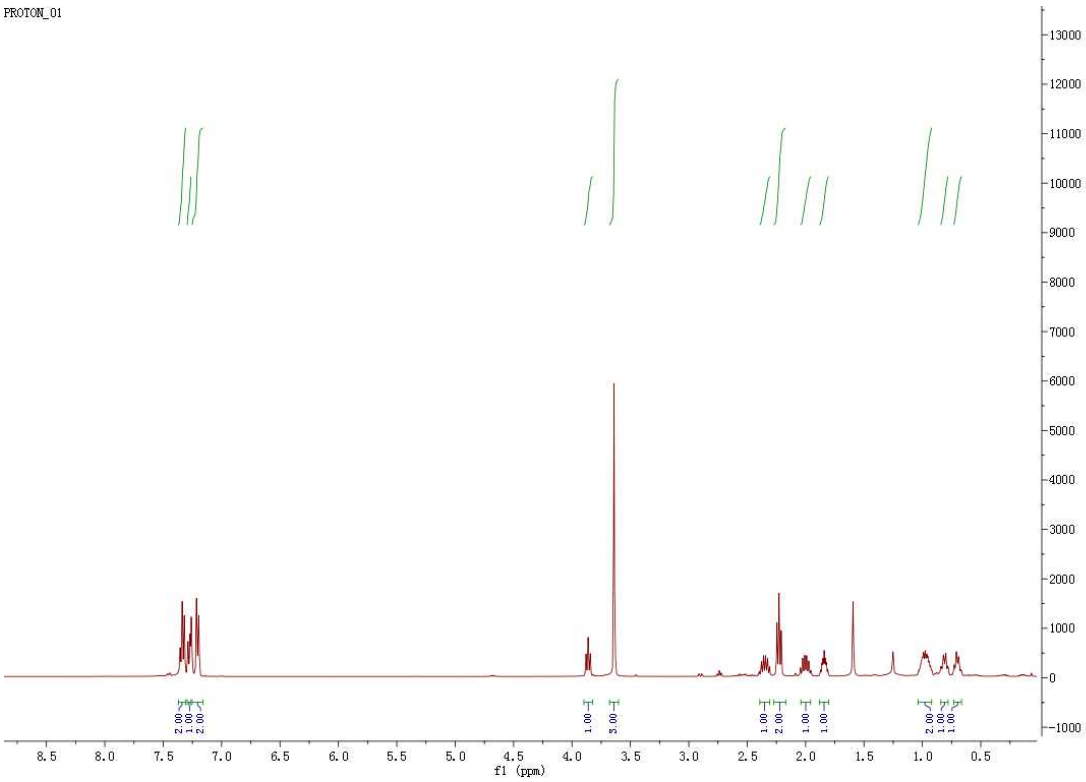


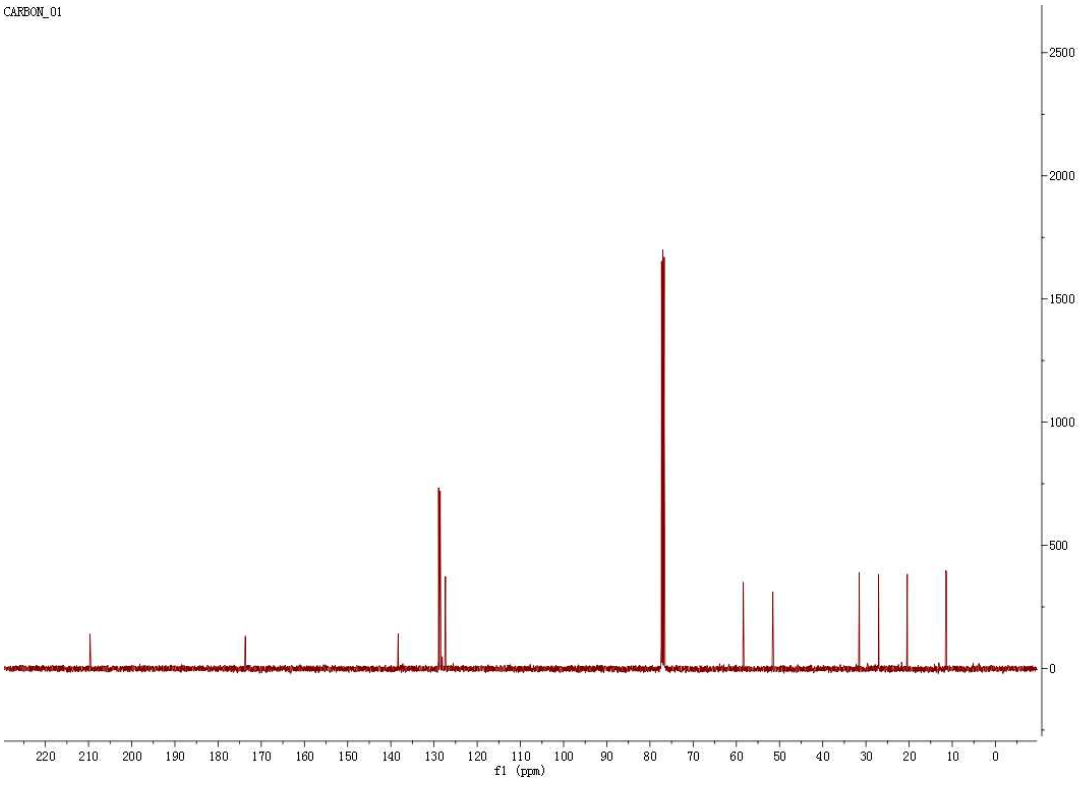

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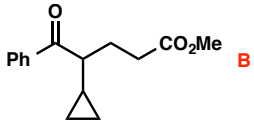


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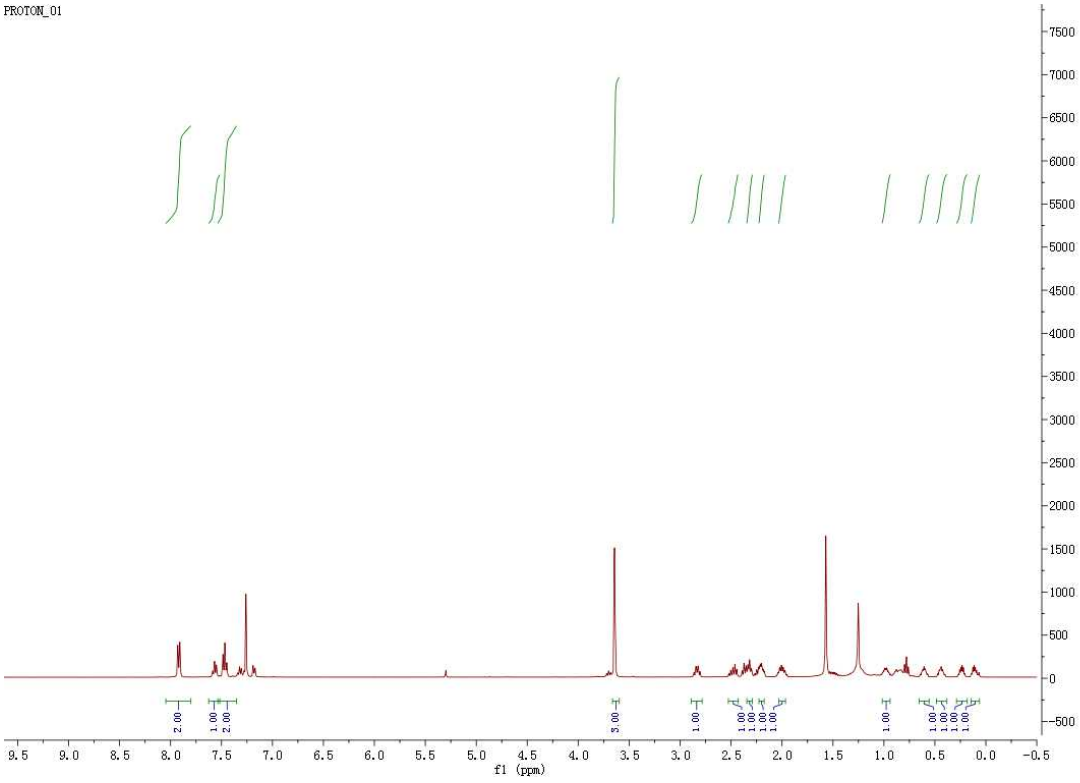


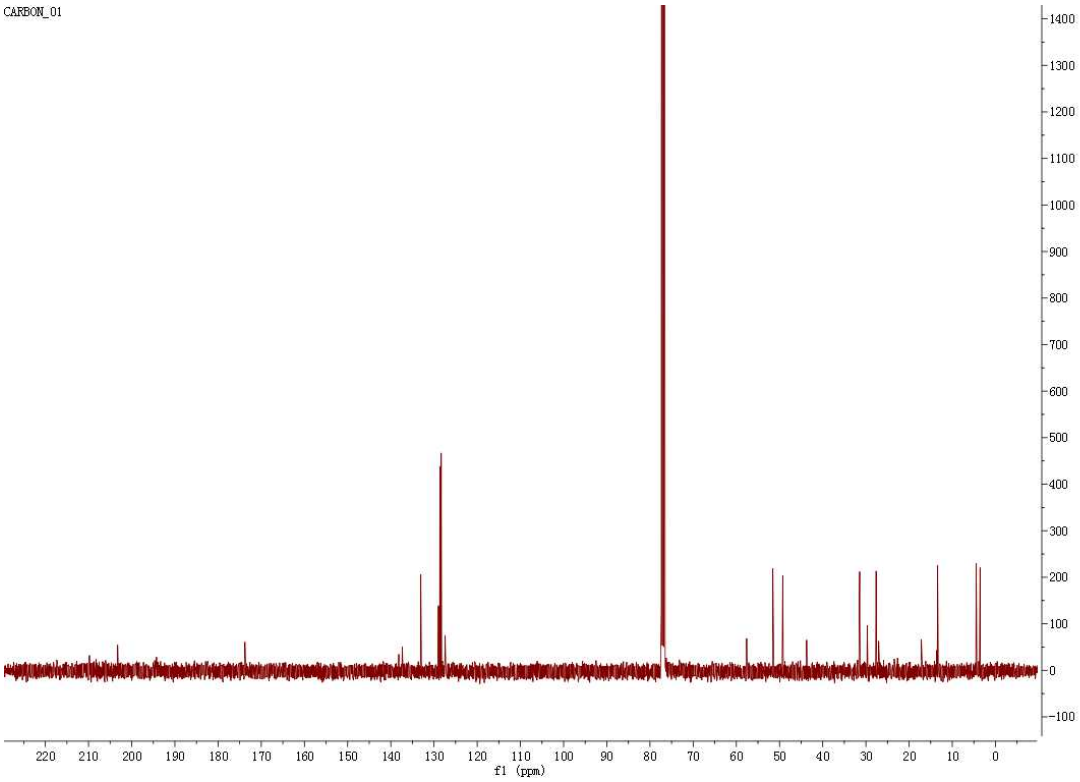
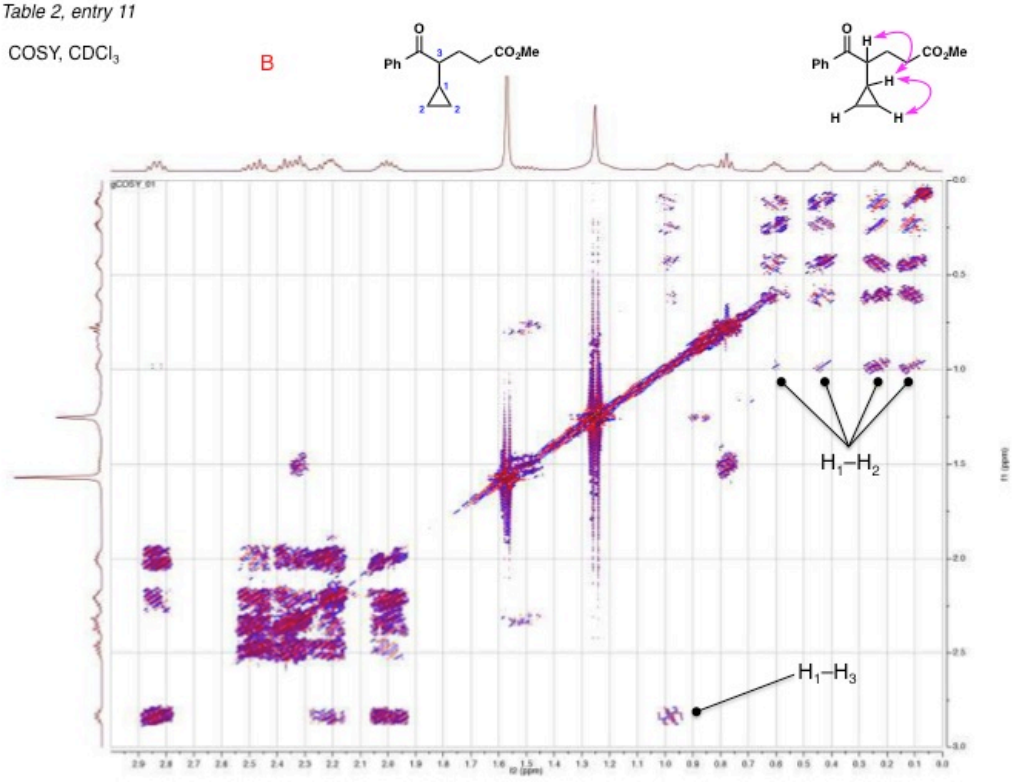



*Table 2, entry 11*

COSY, $CDCl_3$

B



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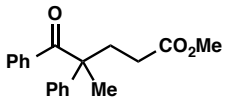


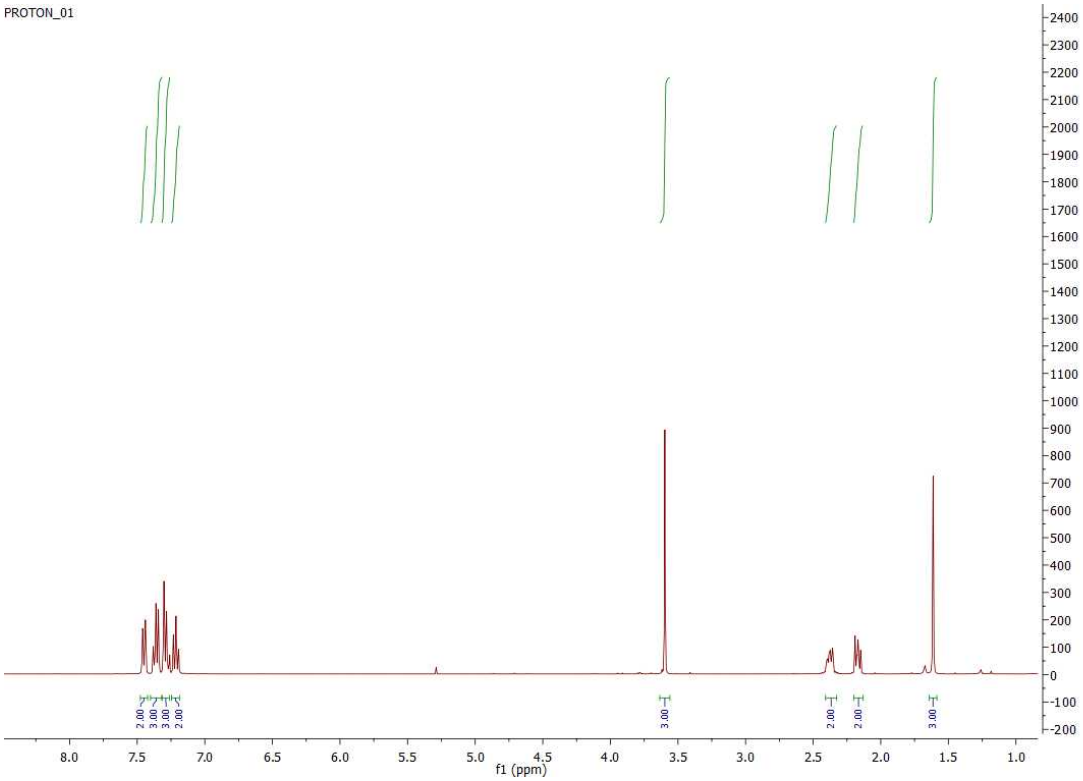


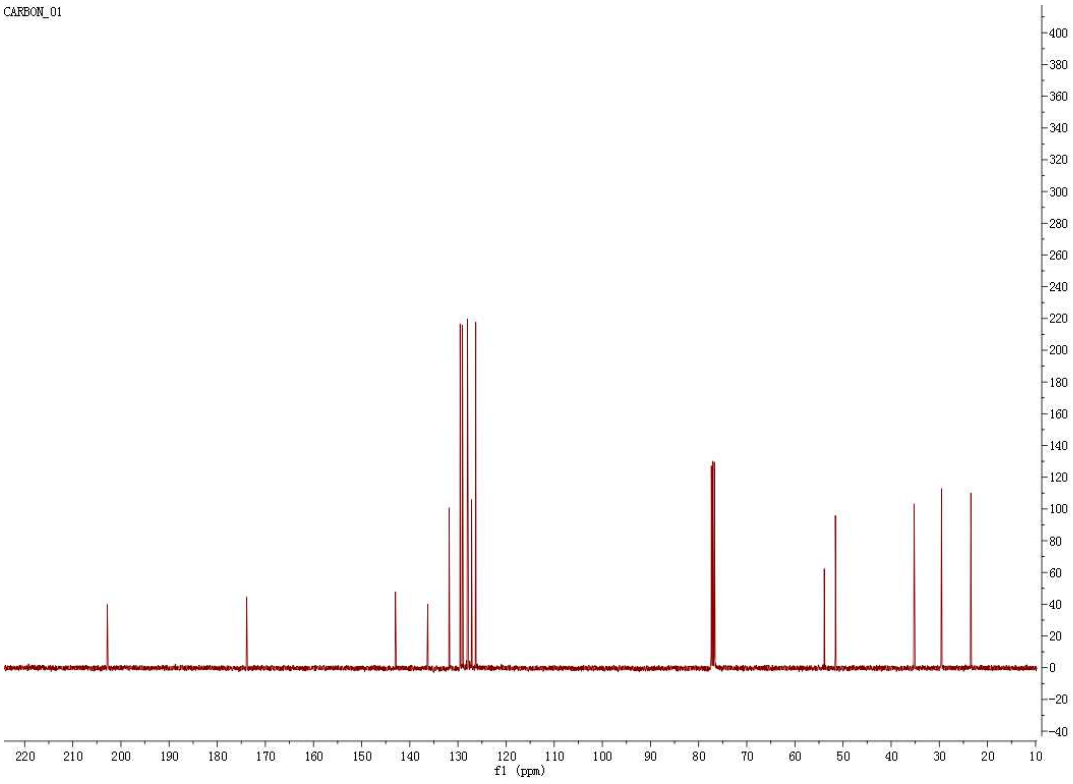

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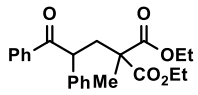


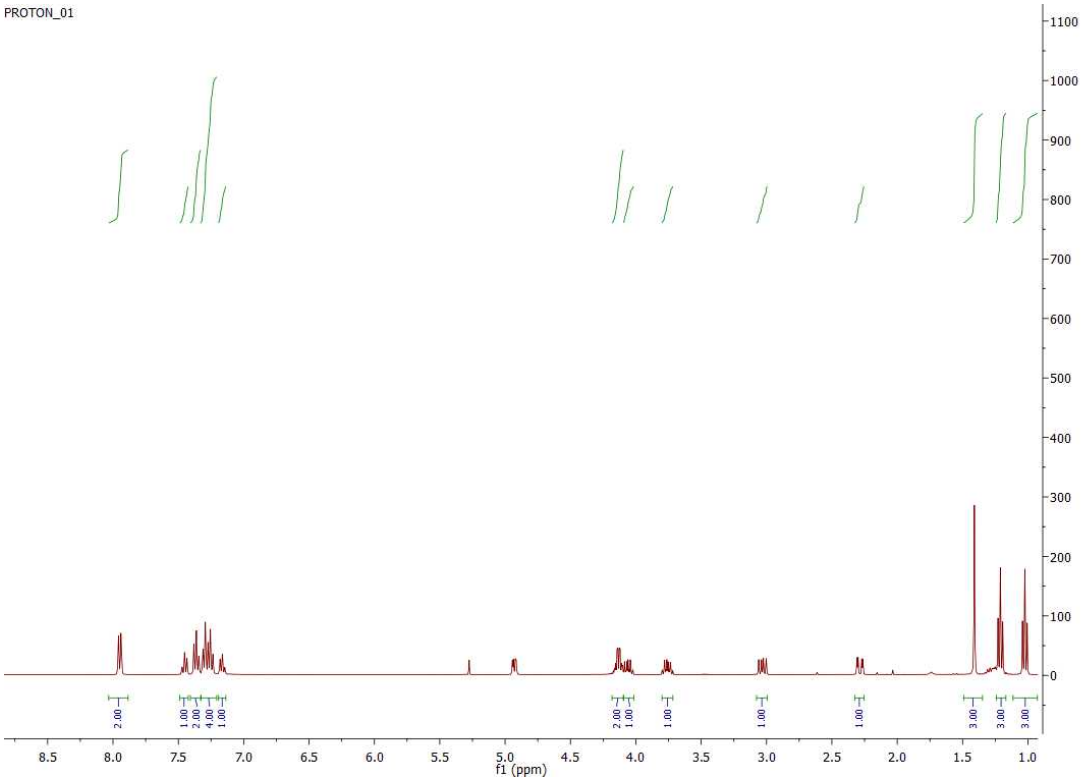


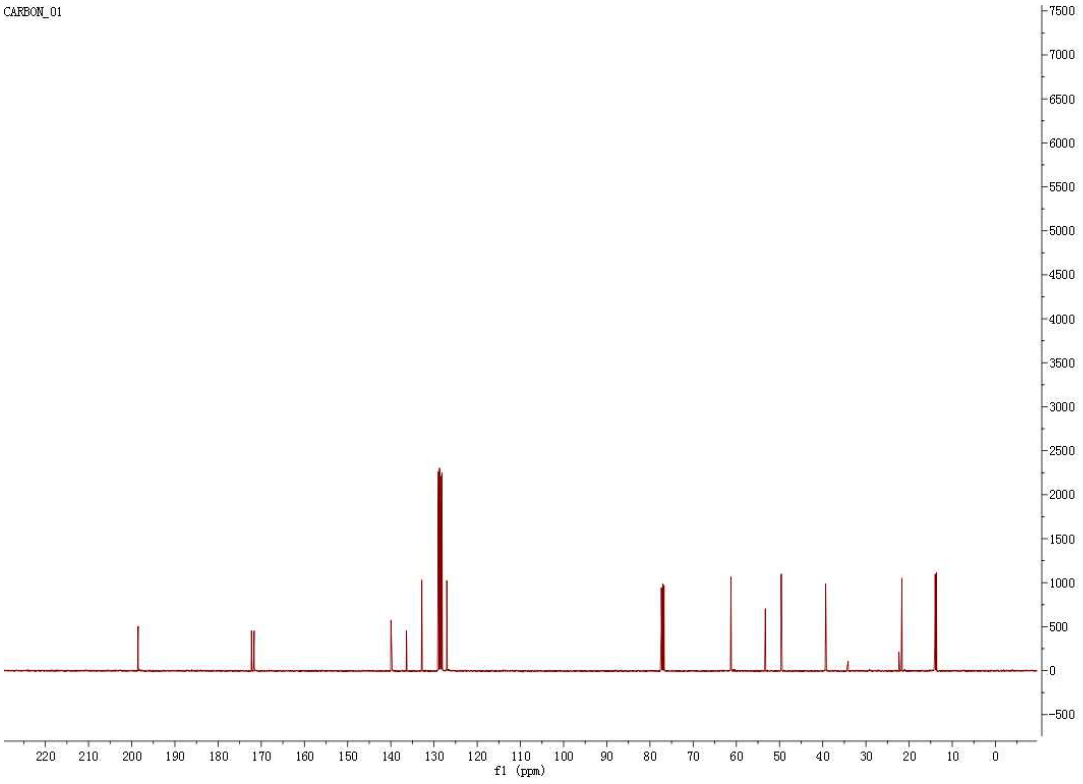

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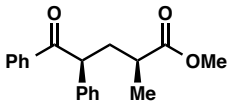


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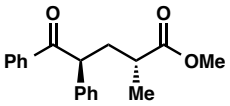


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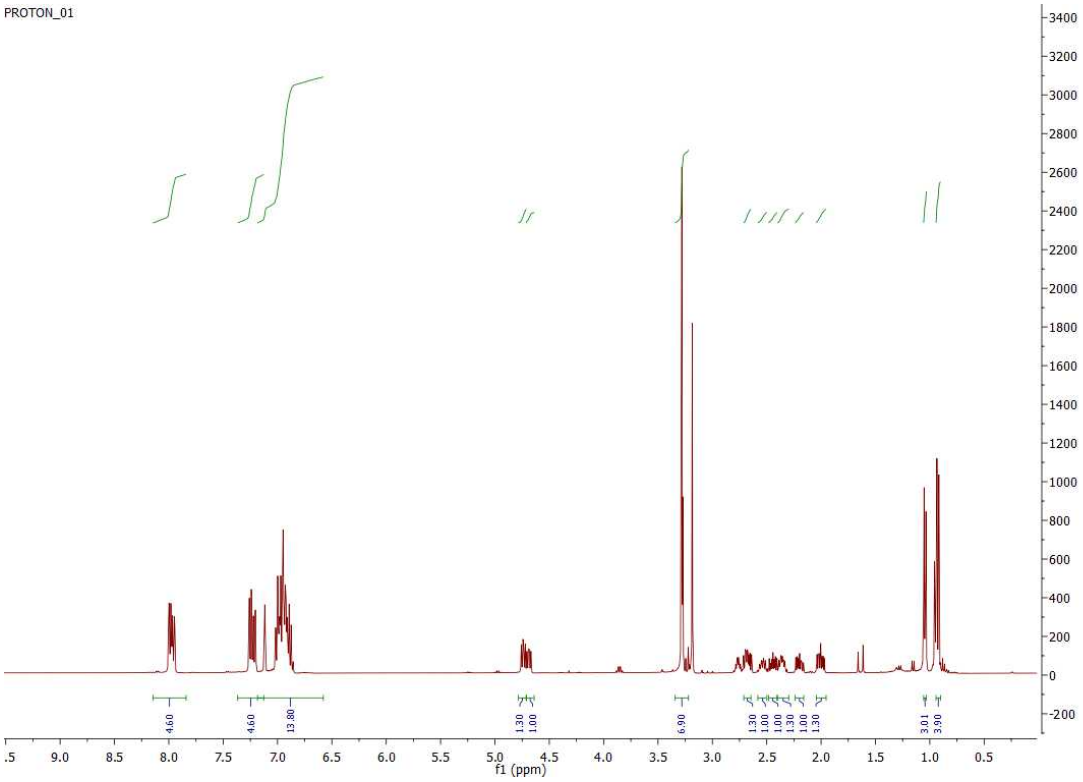


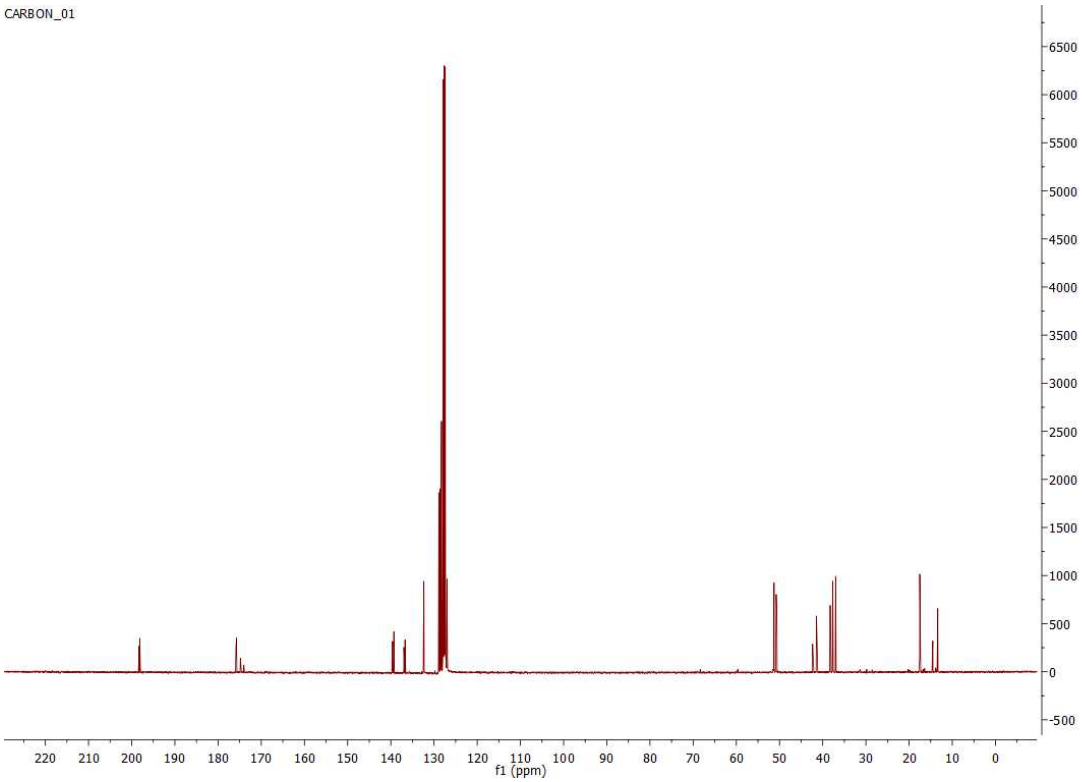
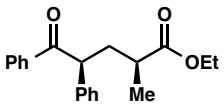
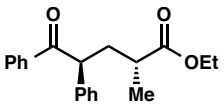



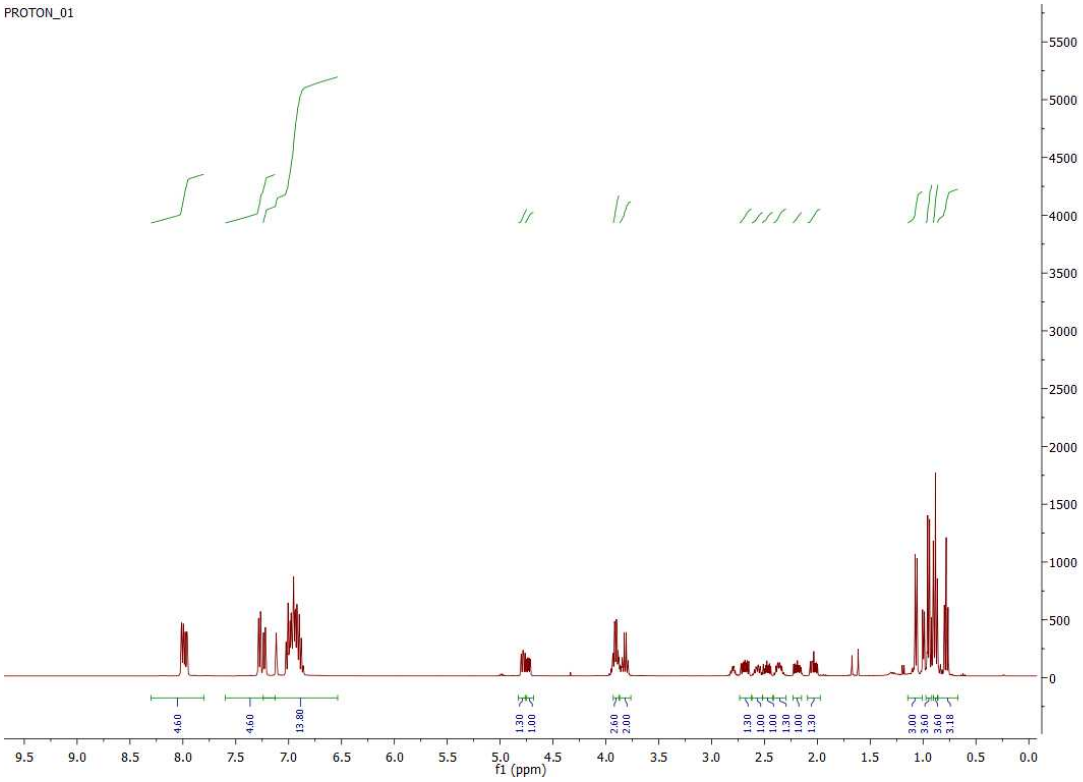
*Table 3, Entry 3*




***major***




***minor***



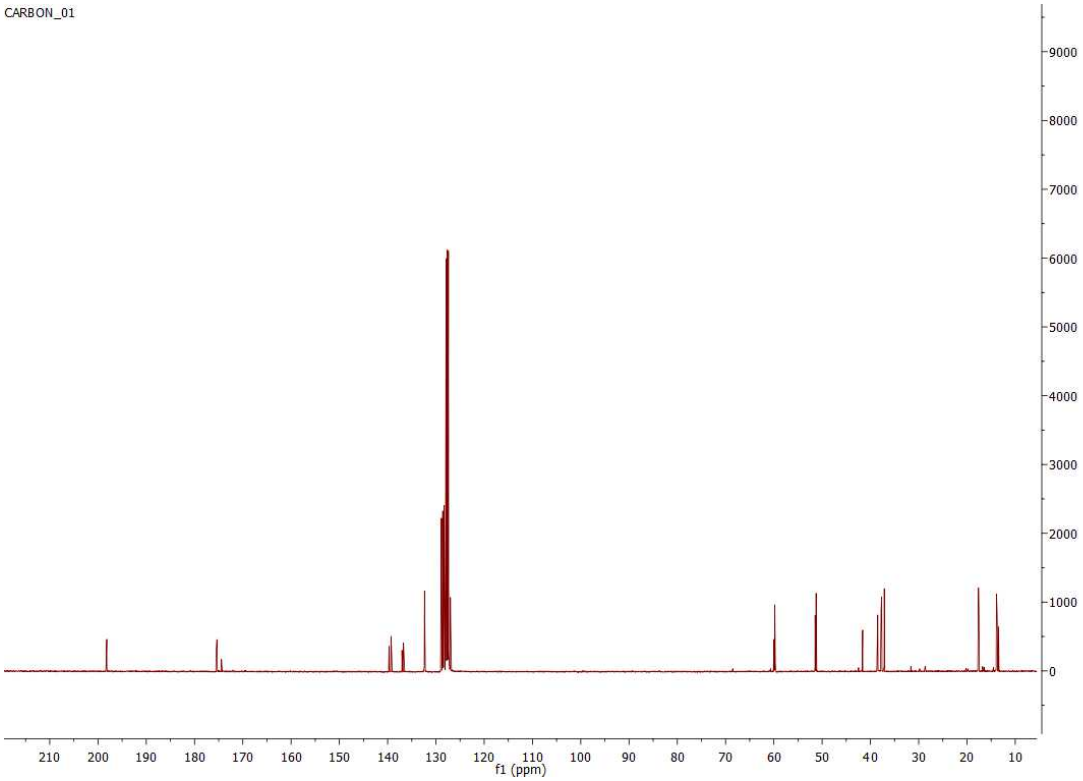
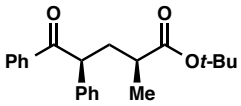
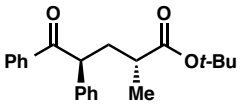



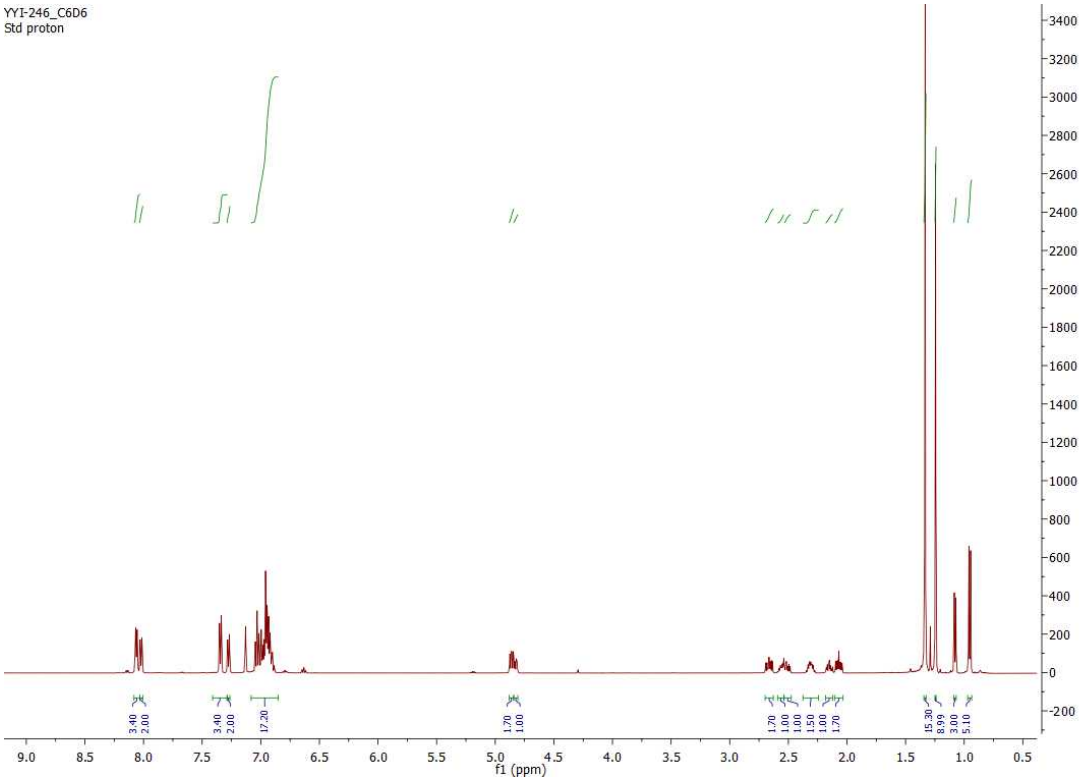
*Table 3, entry 4:*




***major***




***minor***



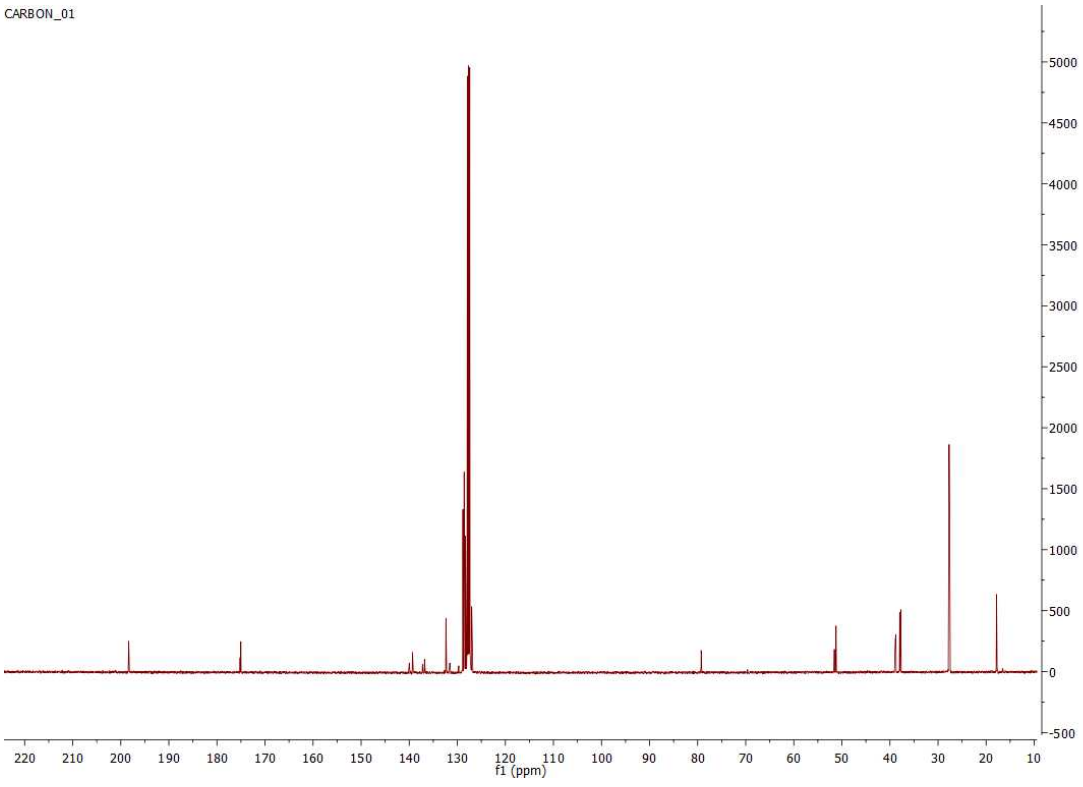
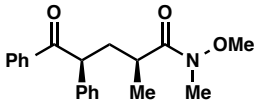
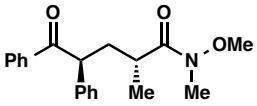



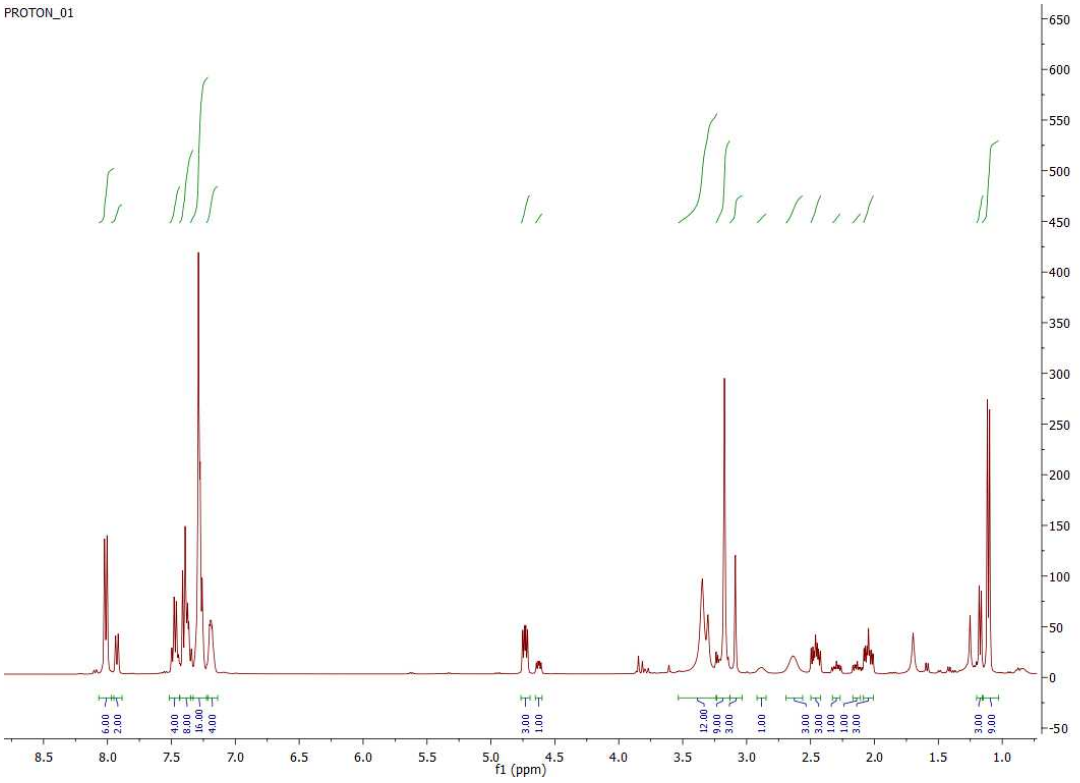
*Table 3, entry 5:*




***major***




***minor***



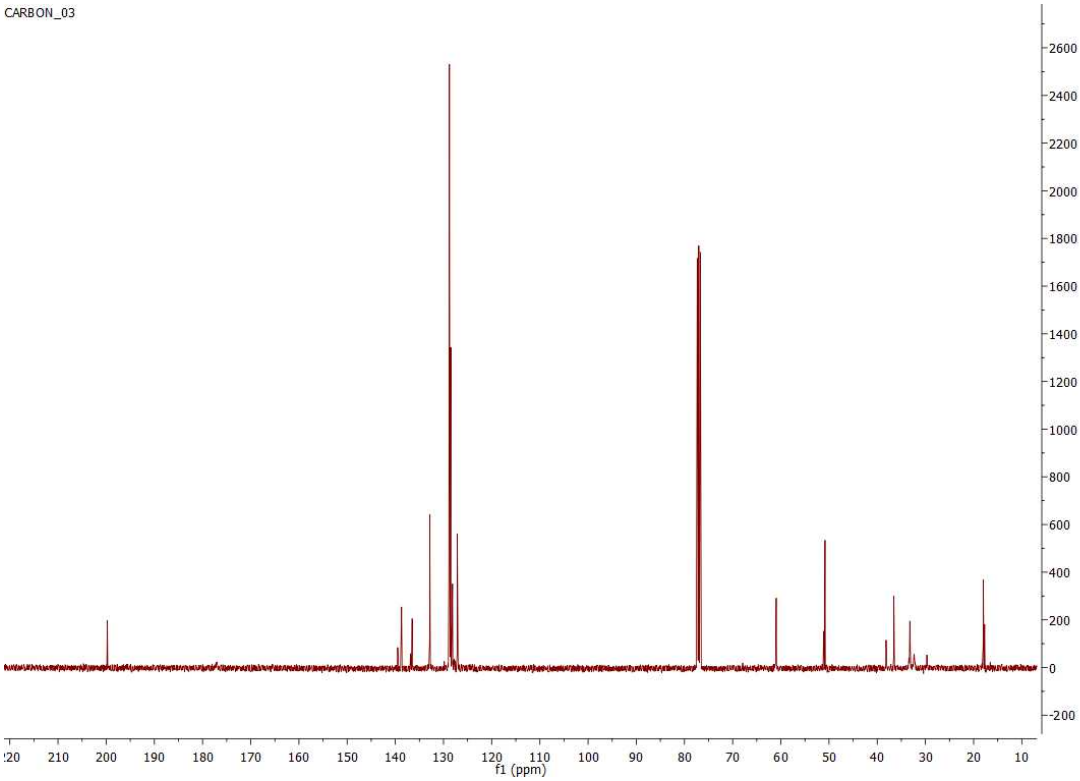
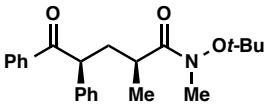
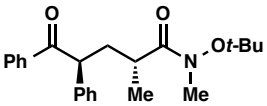



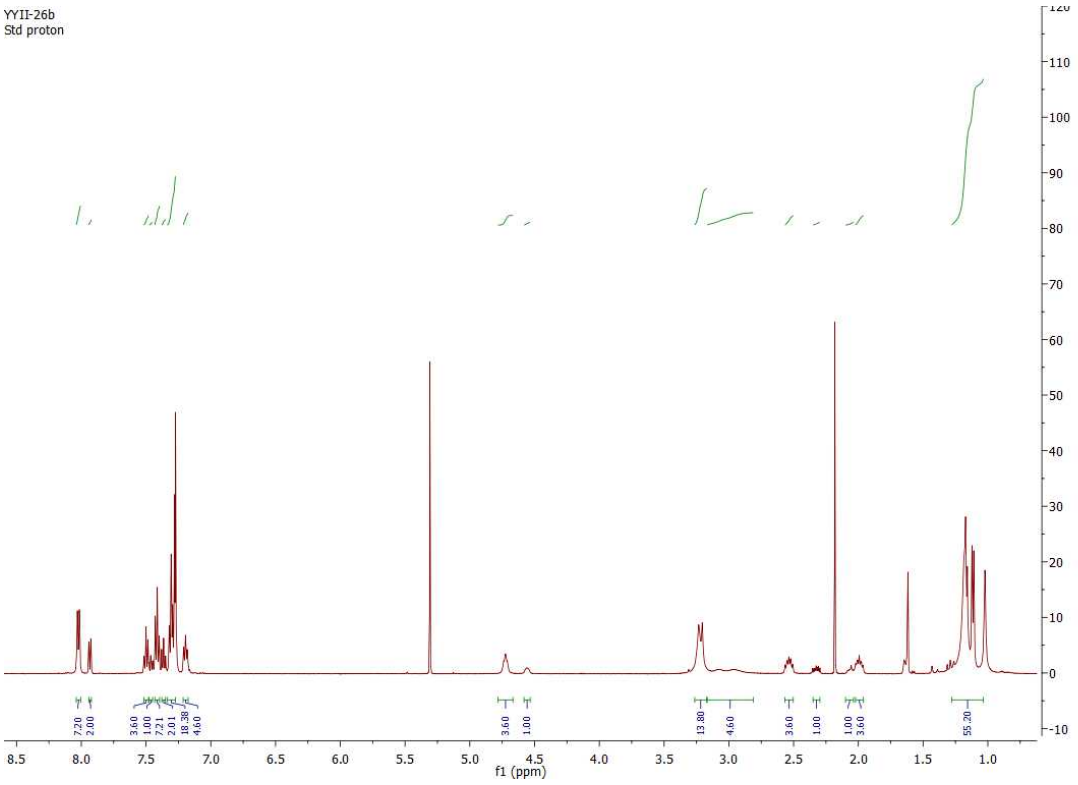
*Table 3, entry 6:*




***major***




***minor***



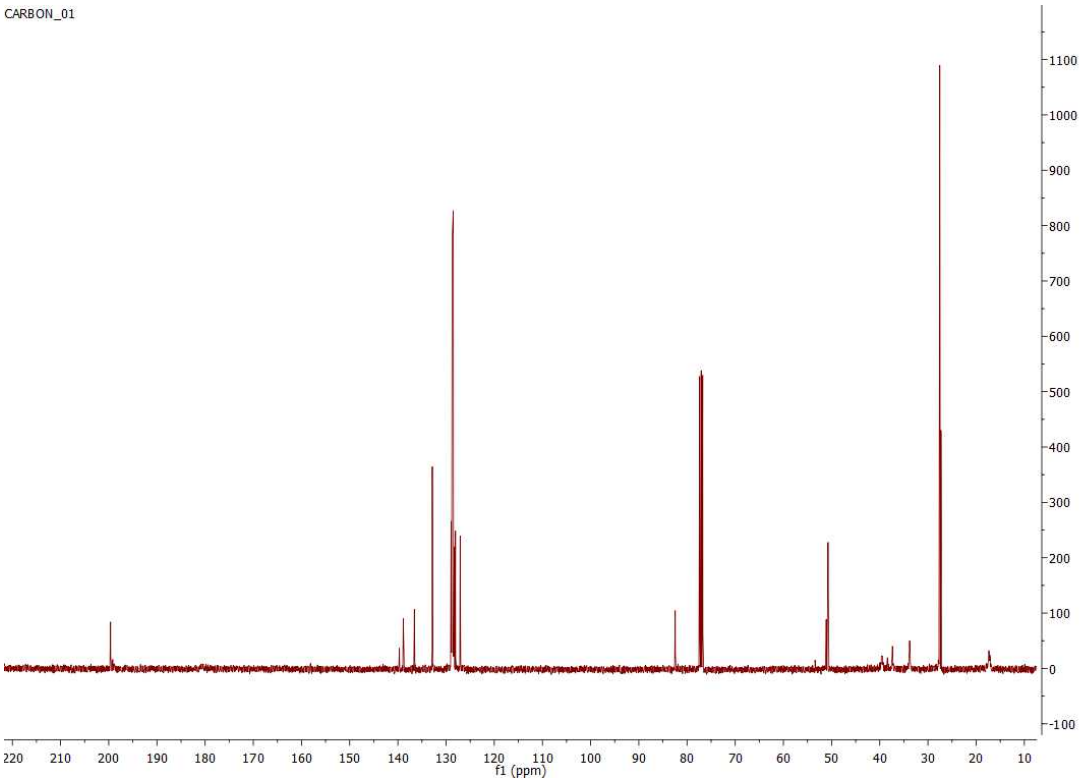
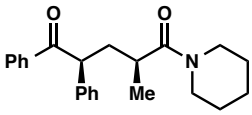
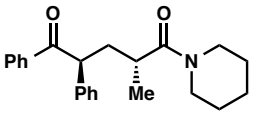



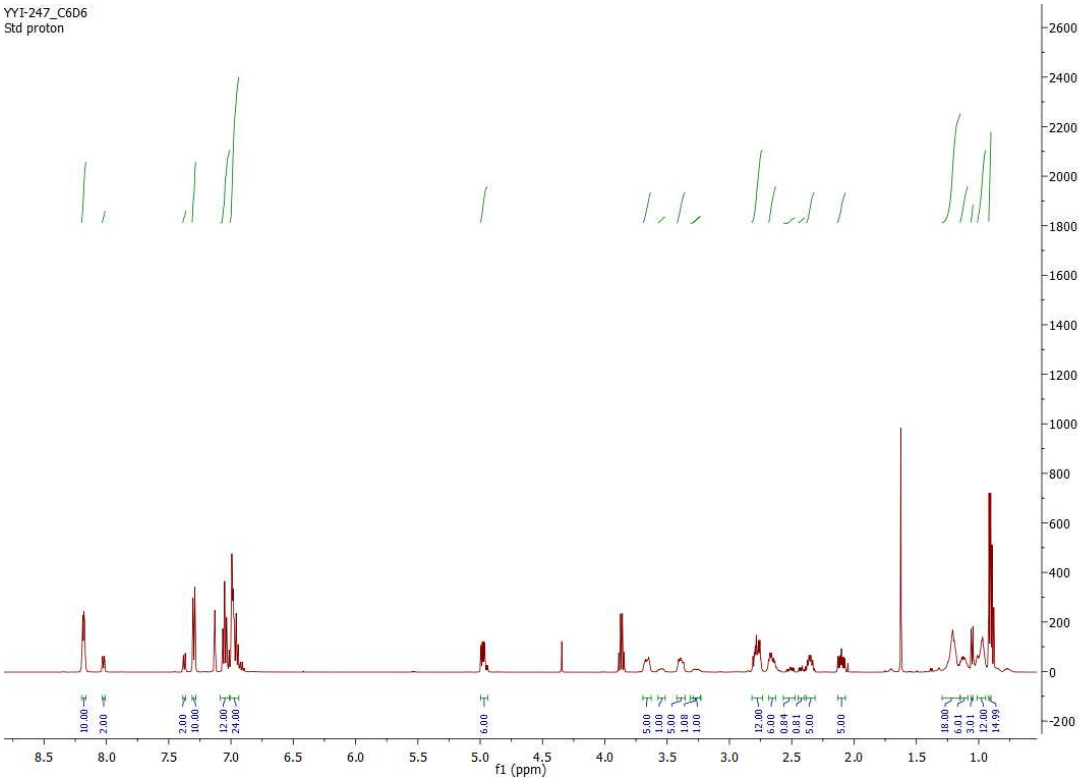
*Table 3, entry 7:*

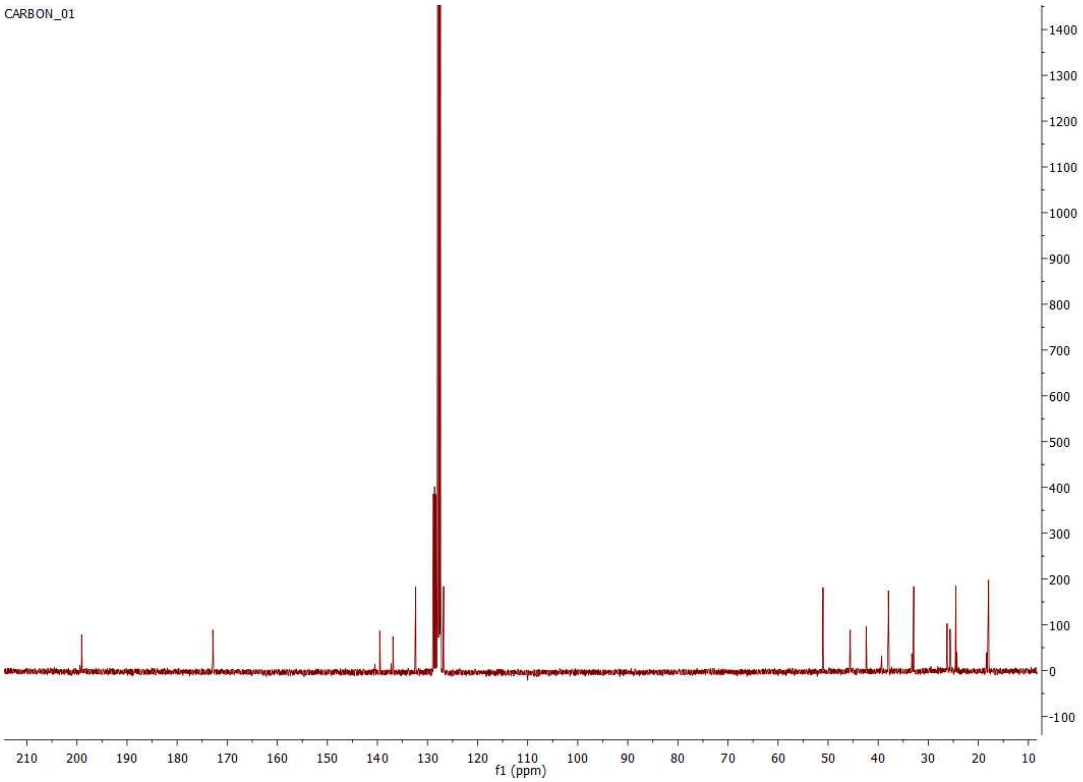


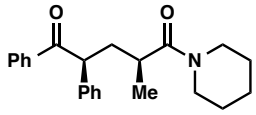

***major***



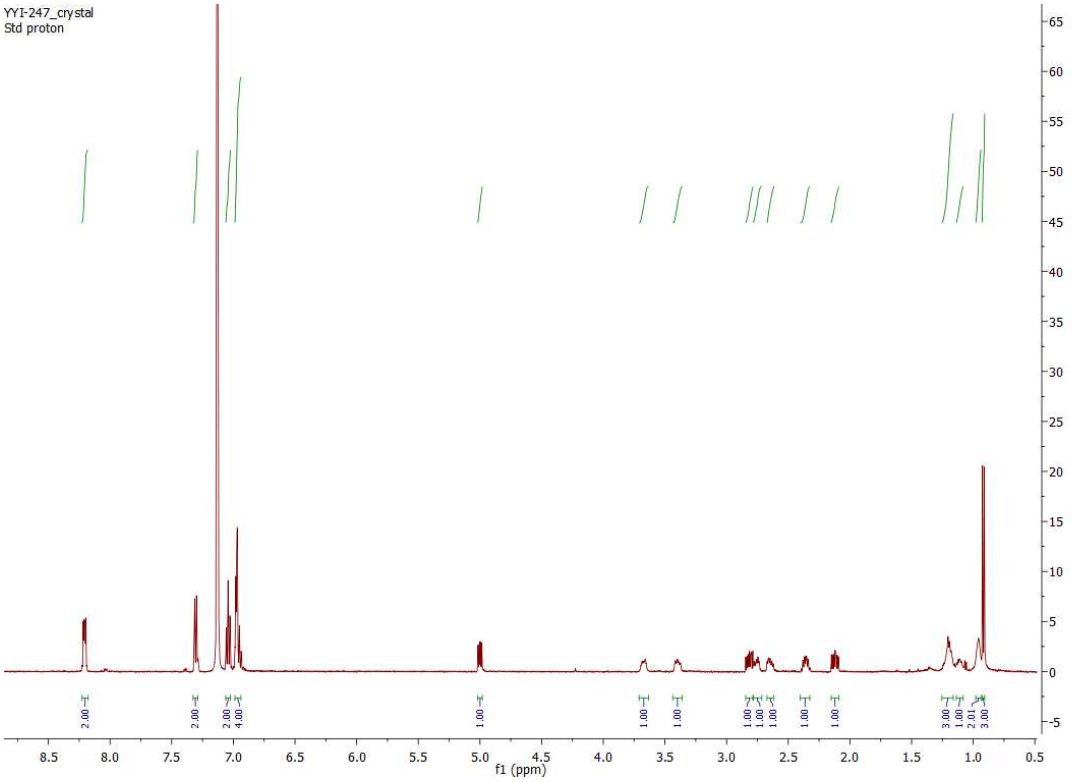

***minor***



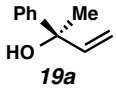





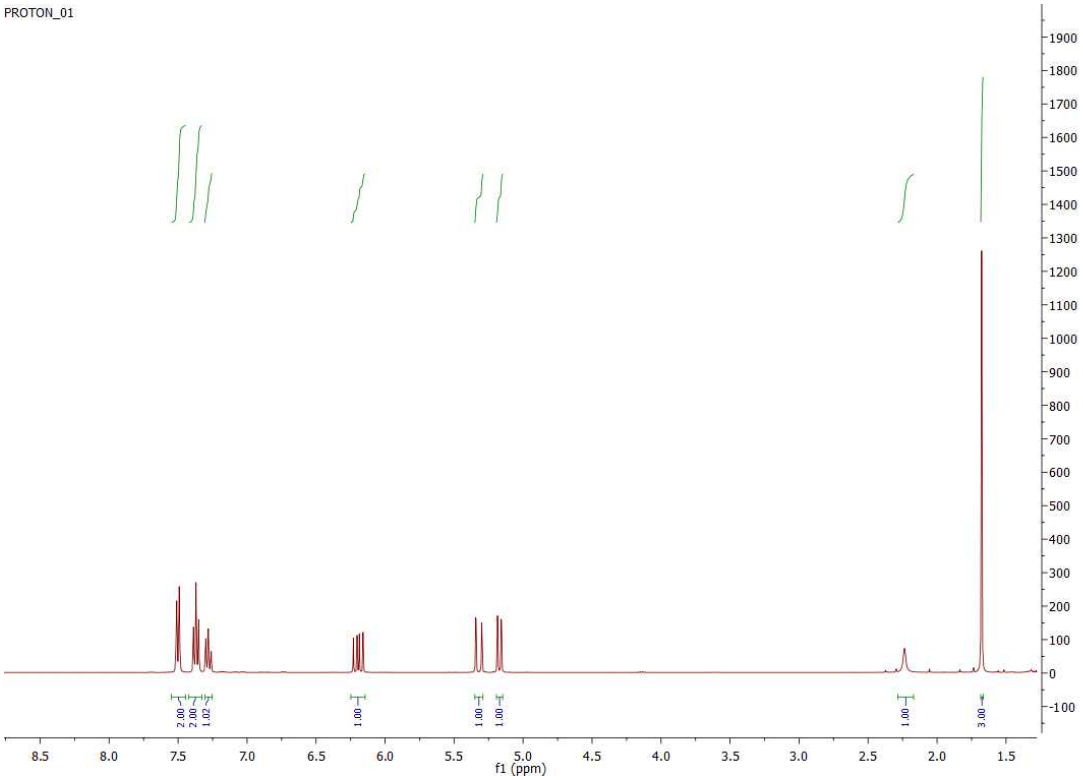

recrystallized from
$CH_2Cl_2/Et_2O$/Pentanes
(slow evaporation)

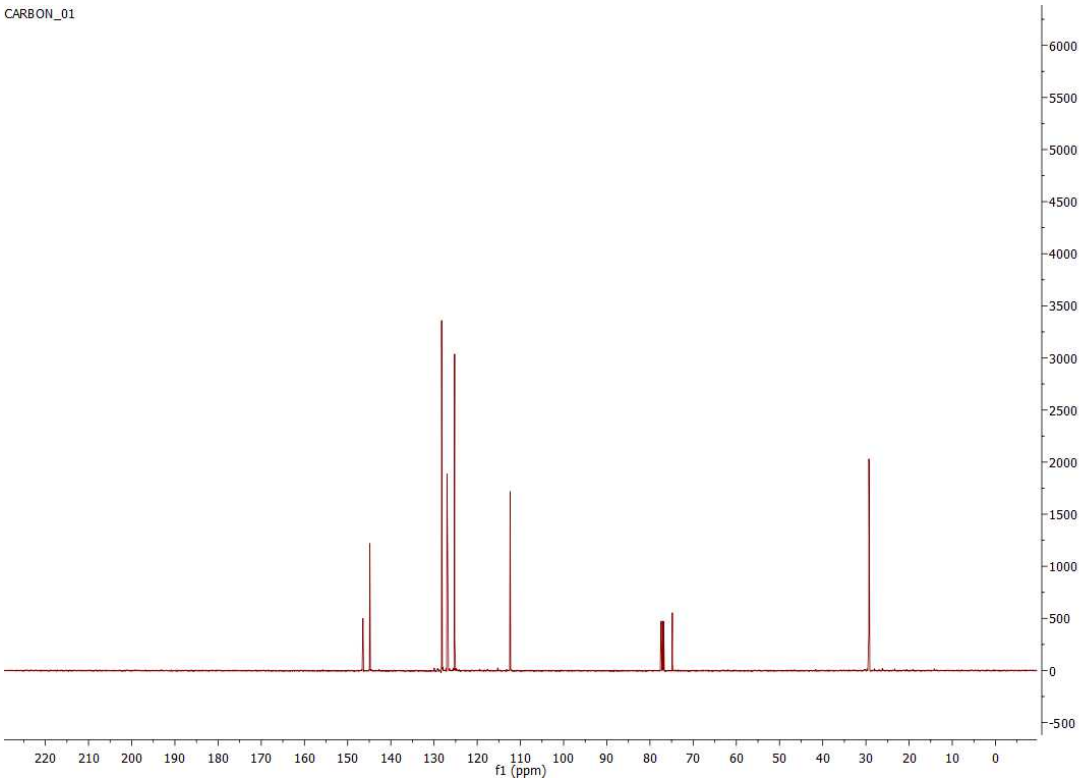


*Scheme 2,* ***19a***

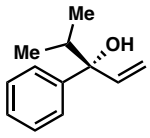



***19a***

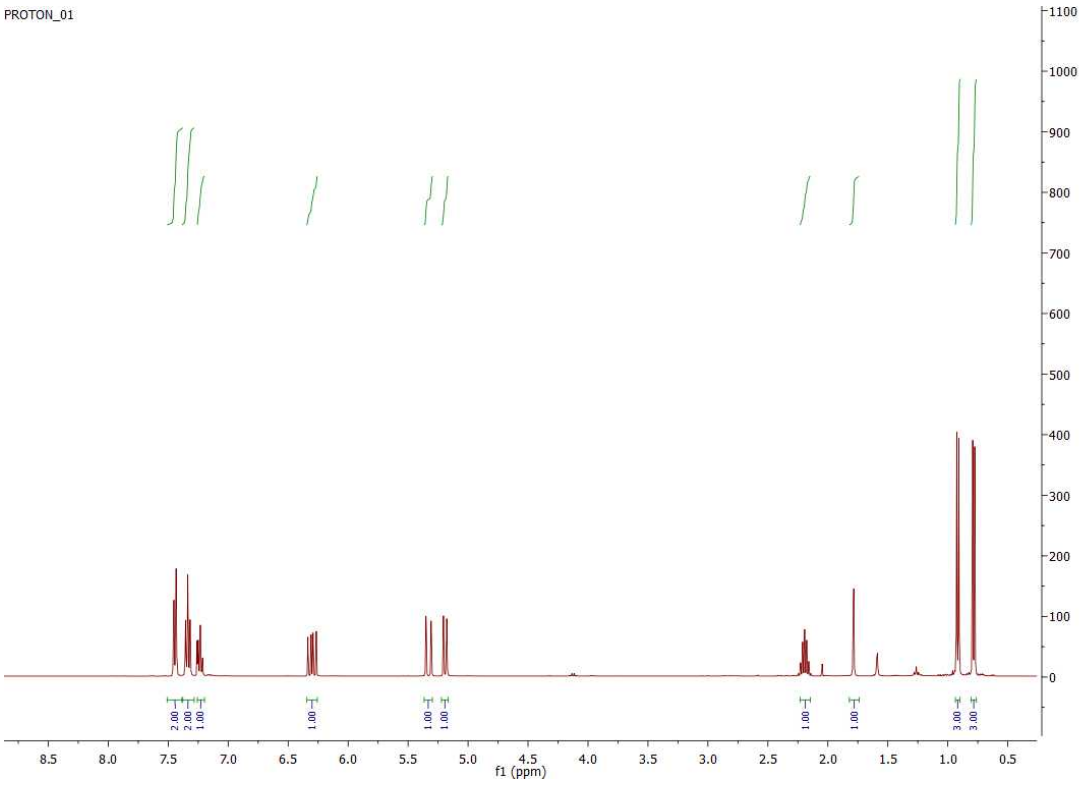


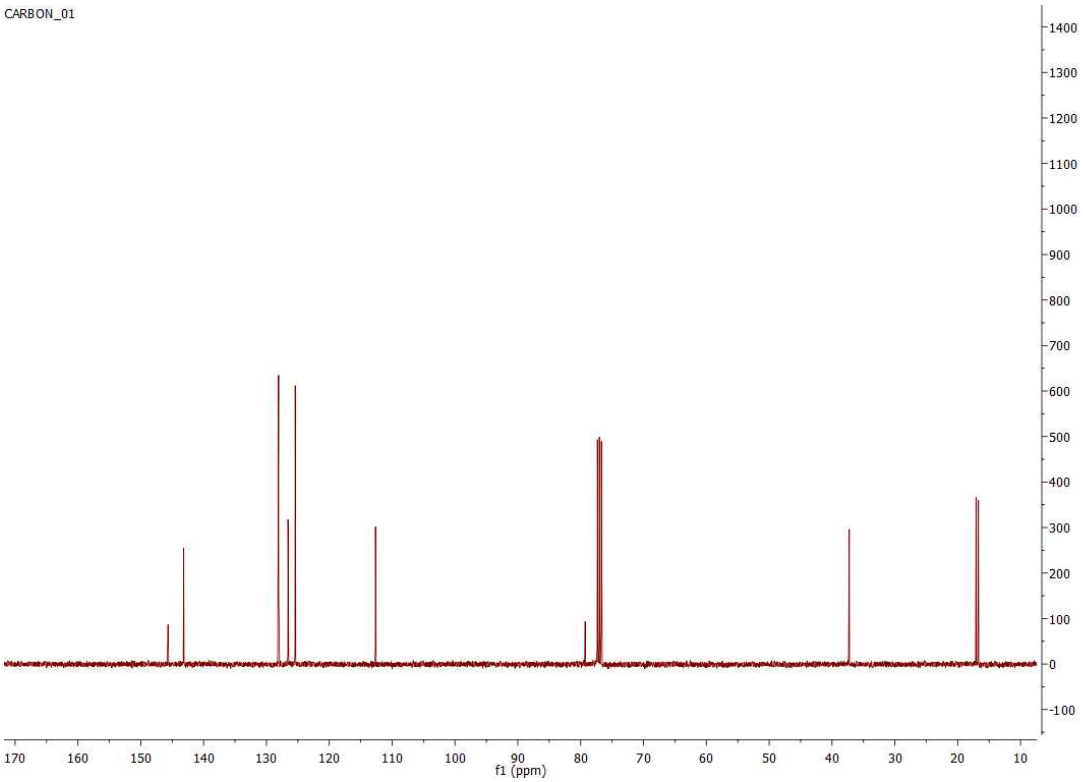



*Scheme 2,* ***19b***

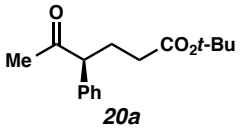



***19b***

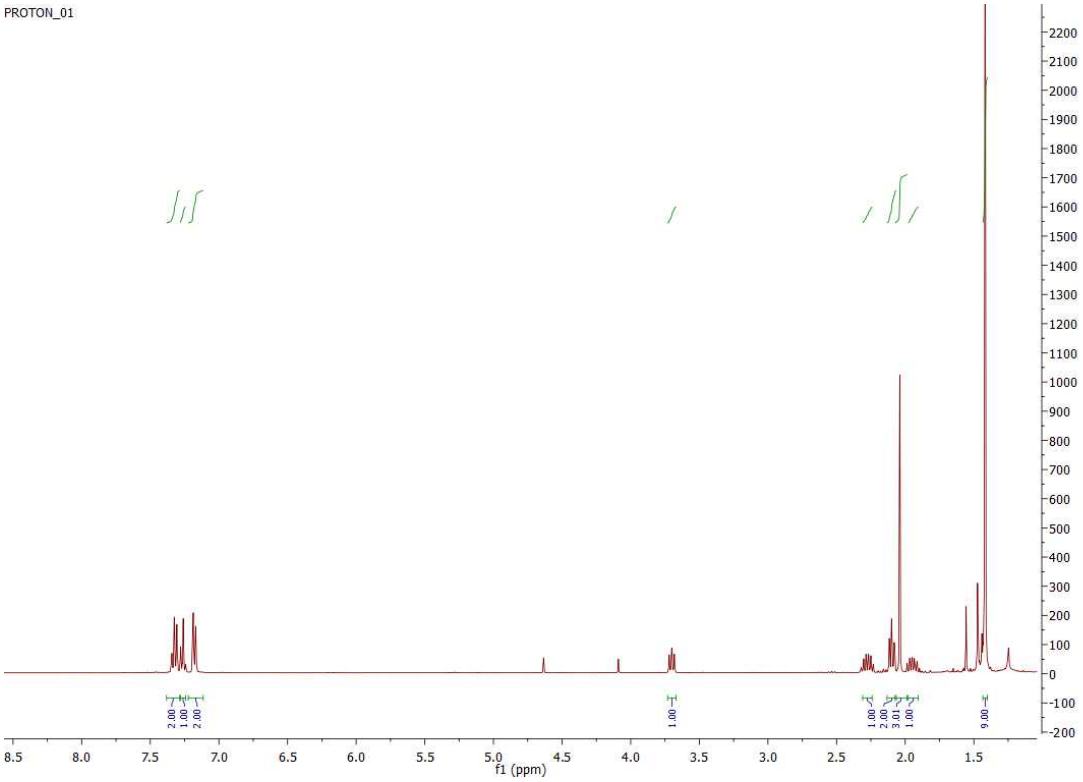


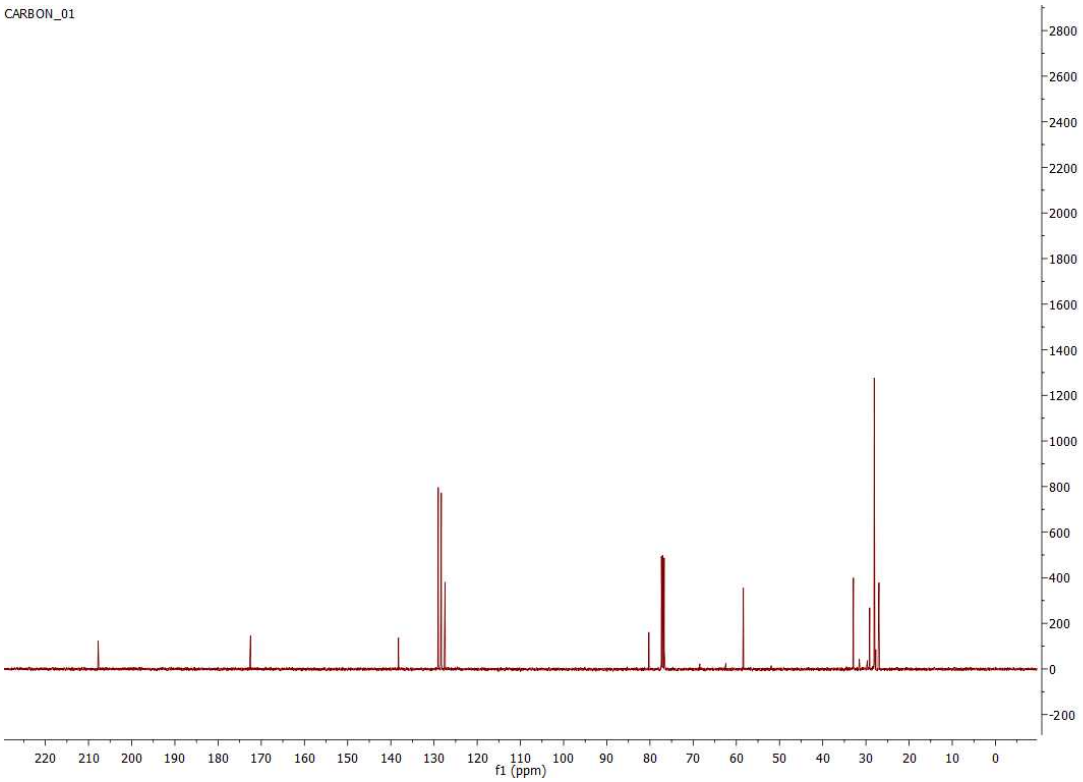



*Scheme 2,* ***20a***

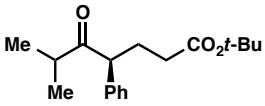



***20a***

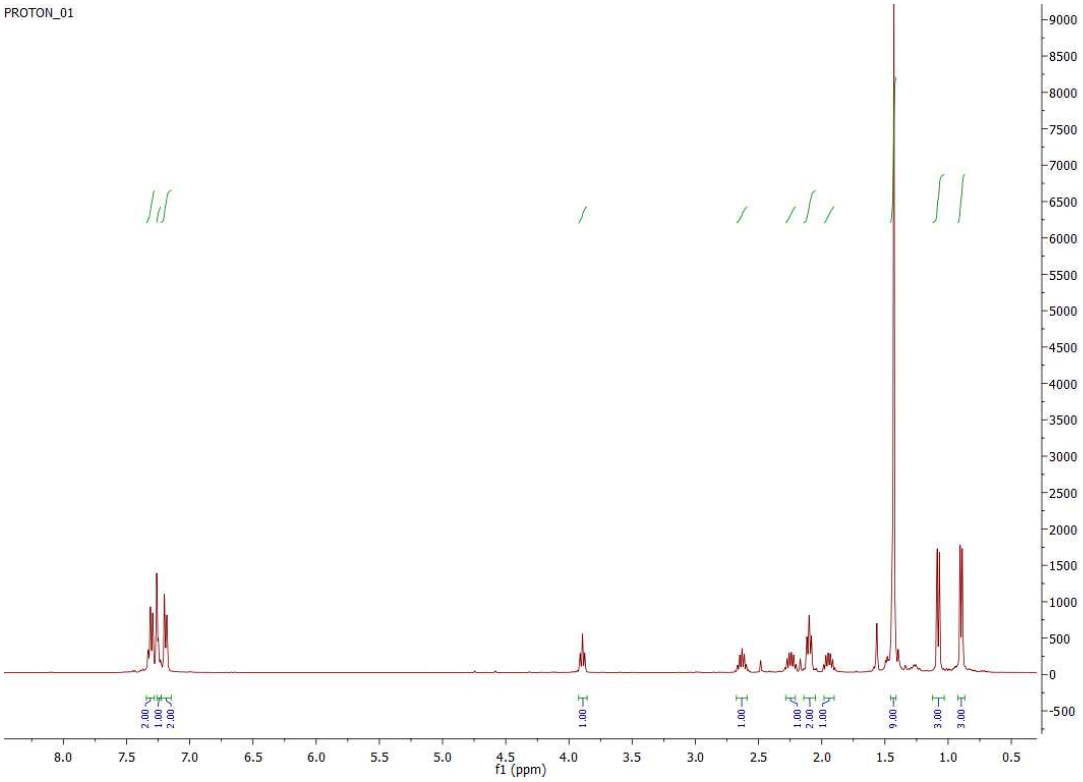


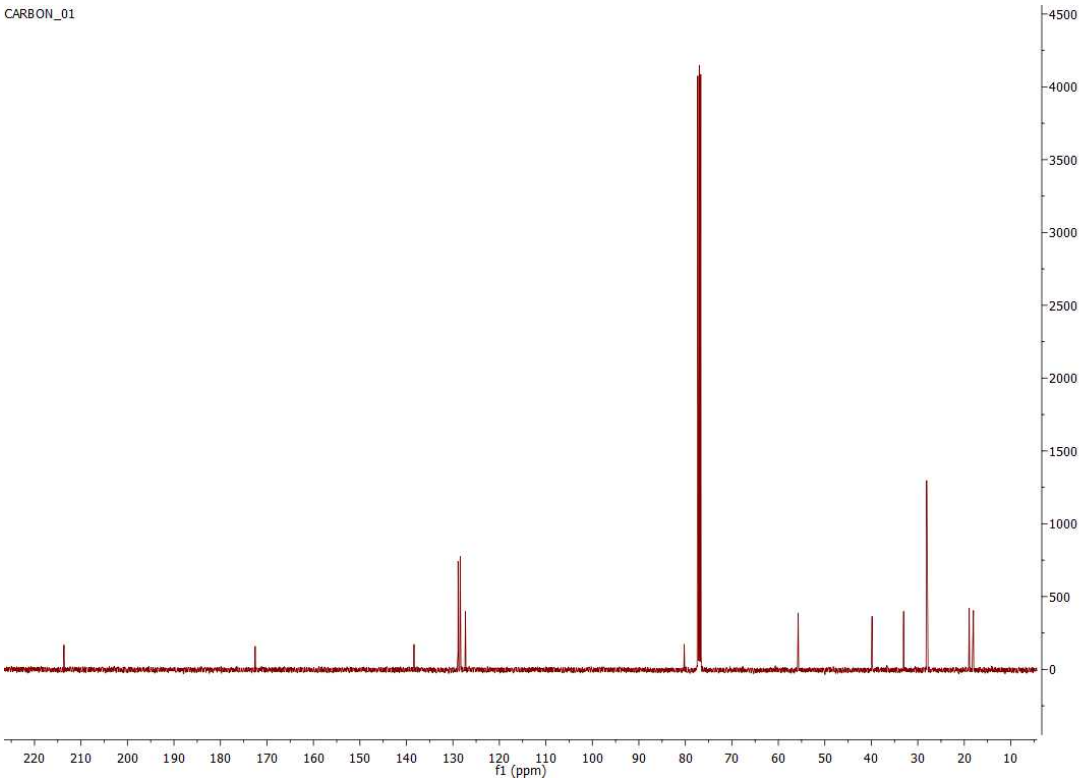



*Scheme 2,* ***20b***



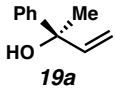

***20b***



## Chiral HPLC Data

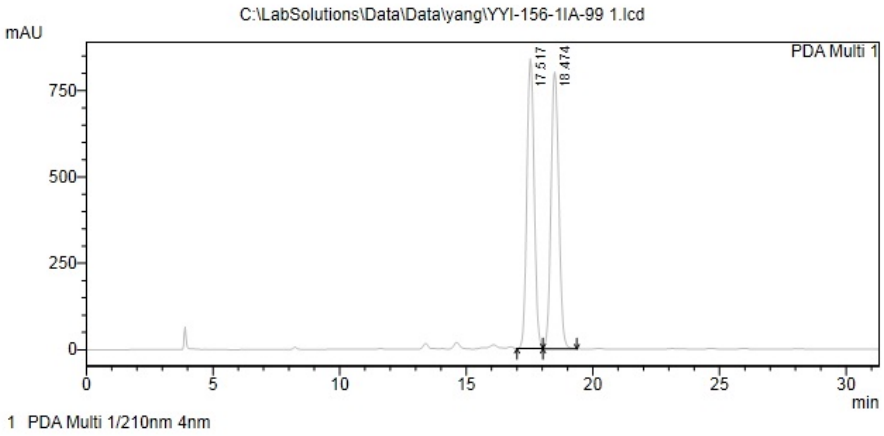
*Scheme 2,* ***19a***




***19a***

IA-H, 99/1 Hex/iPrOH, 1.0 mL/min, 96% ee.

<Chromatogram>



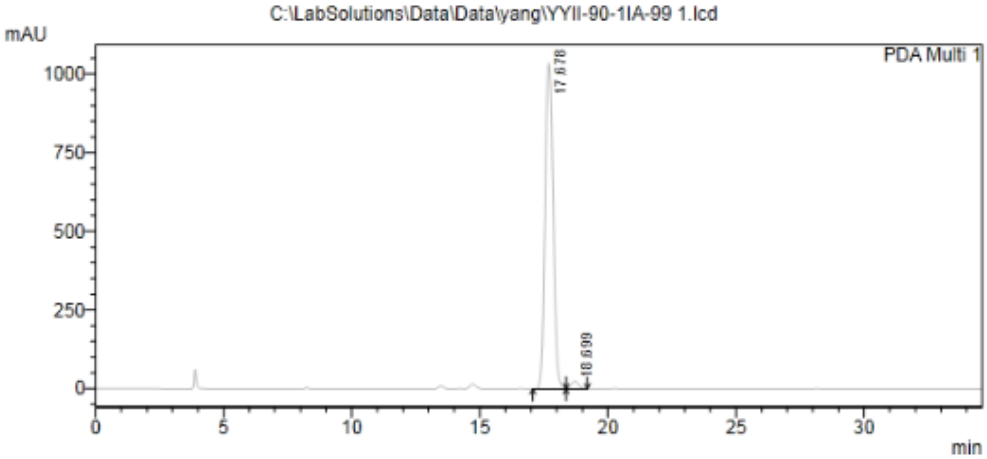

1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 17.517 | 16895142 | 839709 | 49.596 | 51.153 |
| 2 | 18.474 | 17170701 | 801854 | 50.404 | 48.847 |
| Total | | 34065843 | 1641562 | 100.000 | 100.000 |

<Chromatogram>



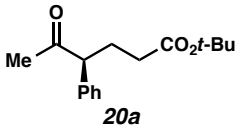

1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

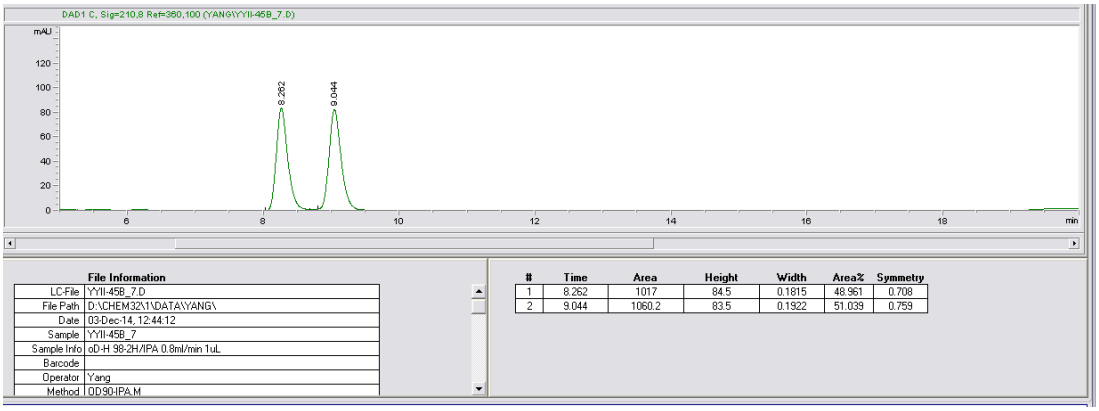
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 17.678 | 22871940 | 1036034 | 97.854 | 97.695 |
| 2 | 18.699 | 501710 | 24446 | 2.146 | 2.305 |
| Total | | 23373651 | 1060480 | 100.000 | 100.000 |

*Scheme 2,* ***20a***



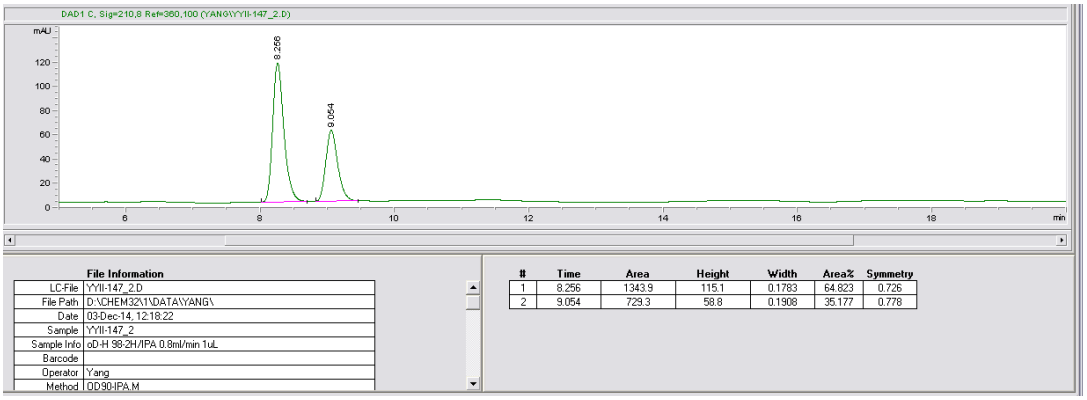

***20a***

OD-H, 98/2 Hex/iPrOH, 0.8 mL/min, 30% ee.




| File Information | |
|---|---|
| LC-File | YYII-45B_7.D |
| File Path | D:\CHEM32\1\DATA\YANG\ |
| Date | 03-Dec-14, 12:44:12 |
| Sample | YYII-45B_7 |
| Sample Info | oD-H 98-2H/IPA 0.8ml/min 1uL |
| Barcode | |
| Operator | Yang |
| Method | OD90-IPA.M |

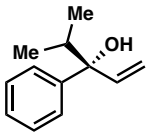
| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 8.262 | 1017 | 84.5 | 0.1815 | 48.961 | 0.708 |
| 2 | 9.044 | 1060.2 | 83.5 | 0.1922 | 51.039 | 0.759 |




| File Information | |
|---|---|
| LC-File | YYII-147_2.D |
| File Path | D:\CHEM32\1\DATA\YANG\ |
| Date | 03-Dec-14, 12:18:22 |
| Sample | YYII-147_2 |
| Sample Info | oD-H 98-2H/IPA 0.8ml/min 1uL |
| Barcode | |
| Operator | Yang |
| Method | OD90-IPA.M |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 8.256 | 1343.9 | 115.1 | 0.1783 | 64.823 | 0.726 |
| 2 | 9.054 | 729.3 | 58.8 | 0.1908 | 35.177 | 0.778 |

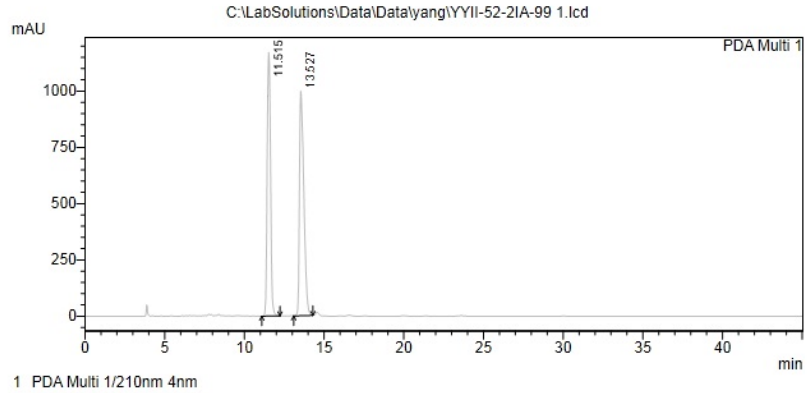
*Scheme 2,* ***19b***




***19b***

IA-H, 99/1 Hex/iPrOH, 1.0 mL/min, 96% ee.

**<Chromatogram>**



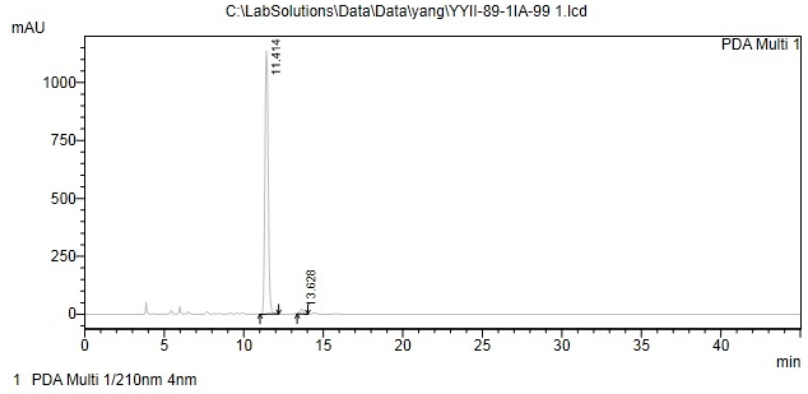

1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 11.515 | 17191389 | 1171286 | 47.451 | 54.001 |
| 2 | 13.527 | 19038150 | 997734 | 52.549 | 45.999 |
| Total | | 36229539 | 2169019 | 100.000 | 100.000 |

**<Chromatogram>**



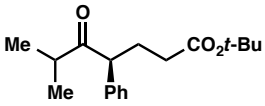

1 PDA Multi 1/210nm 4nm

PeakTable

PDA Ch1 210nm 4nm

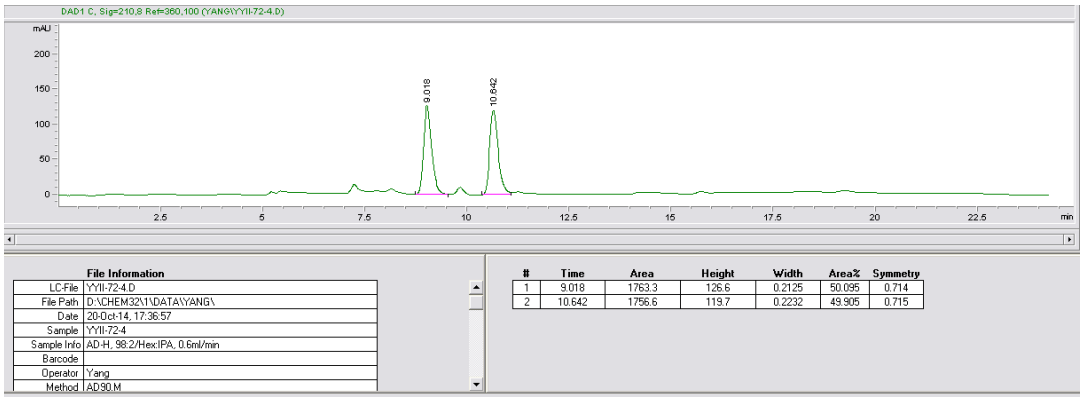
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 11.414 | 16395126 | 1136055 | 98.149 | 98.068 |
| 2 | 13.628 | 309161 | 22380 | 1.851 | 1.932 |
| Total | | 16704287 | 1158435 | 100.000 | 100.000 |

*Scheme 2,* ***20b***



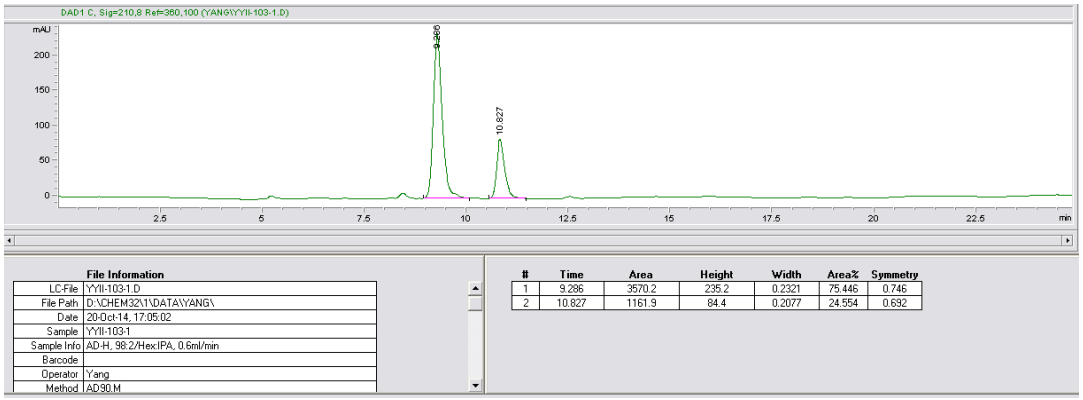

***20b***

AD-H, 98/2 Hex/iPrOH, 0.6 mL/min, 50% ee.




| File Information | |
|---|---|
| LC-File | YYII-72-4.D |
| File Path | D:\CHEM32\1\DATA\YANG\ |
| Date | 20-Oct-14, 17:36:57 |
| Sample | YYII-72-4 |
| Sample Info | AD-H, 98:2/Hex:IPA, 0.6ml/min |
| Barcode | |
| Operator | Yang |
| Method | AD90.M |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 9.018 | 1763.3 | 126.6 | 0.2125 | 50.095 | 0.714 |
| 2 | 10.642 | 1756.6 | 119.7 | 0.2232 | 49.905 | 0.715 |




| File Information | |
|---|---|
| LC-File | YYII-103-1.D |
| File Path | D:\CHEM32\1\DATA\YANG\ |
| Date | 20-Oct-14, 17:05:02 |
| Sample | YYII-103-1 |
| Sample Info | AD-H, 98:2/Hex:IPA, 0.6ml/min |
| Barcode | |
| Operator | Yang |
| Method | AD90.M |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 9.286 | 3570.2 | 235.2 | 0.2321 | 75.446 | 0.746 |
| 2 | 10.827 | 1161.9 | 84.4 | 0.2077 | 24.554 | 0.692 |