Oxidative Cross-coupling Reaction of Catechols with Active Methylene Compounds in an Aqueous Medium Using $AlPO_4$-supported Ru Catalyst

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Electronic Supporting Information

General

$Ru(acac)_3$, $Pd(acac)_2$, $Rh(acac)(CO)_2$, $K_3[IrCl_6]$, and $Pt(acac)_2$ (N.E. Chemcat, Co.), MgO (Ube Industries, Ltd.), and SiO_2 (Q-3, Fuji Silysia Chemical, Ltd) were used as received. $AlPO_4$ (Wako Pure Chemical, Co.), AlOOH (Sasol North America, Inc.), $Mg_3(PO_4)_2$ (Kishida Chemicals Co., Ltd.) were purchased. All other chemicals were purchased from Wako Pure Chemical, Co., Ltd., the Tokyo Kasei Co., and Sigma-Aldrich Inc..^{1}H NMR and ^{13}C NMR spectra were obtained using a JNM-ESC400 spectrometer and chemical shifts (δ) are reported in ppm relative to tetramethylsilane. Ru K-edge X-ray absorption data were collected in quick mode and recorded in transmission mode using a BL01B1 station attached to a Si(311) monochromator at the SPring-8 (JASRI) facility in Harima, Japan (Proposal No. 2017B1155). Data analysis was carried out using the REX2000 program (ver. 2.5.7, Rigaku). Powder X-ray diffraction (XRD) patterns were recorded using a Philips X'Pert-MPD with Cu-Kα radiation. X-ray fluorescence (XRF) measurements were carried out using a Supermini benchtop wavelength-dispersive X-ray fluorescence spectrometer (Rigaku). Transmission electron microscopy (TEM) images were obtained using a Hitachi HF-2000 type microscope, operating at 200 kV, at the Research Center for Ultra-High Voltage Electron Microscopy, Osaka University.

Preparation of $AlPO_4$ supported catalysts

The mixture of tridymite-type $AlPO_4$ (1.5 g) and $Ru(acac)_3$ (0.0896 g) in acetone (50 mL) was stirred for 3 h at room temperature, and then evaporated to remove acetone. The obtained solid was calcined at 500 ºC under air for 3 h to afford a greenish gray powder, which was further treated in H_2O at 50 ºC, separated by filtration, and then re-calcined at 500 ºC for 3 h, to give $Ru/AlPO_4$.

Preparation of other supported Ru catalysts

The other supported Ru catalysts and $AlPO_4$-supported Ru catalysts were prepared through similar procedures using MgO, SiO_2, $AlPO_4$, AlOOH, and $Mg_3(PO_4)_2$ as supports and $Ru(acac)_3$,

$Pd(acac)_2$, $Rh(acac)(CO)_2$, $K_3[IrCl_6]$, and $Pt(acac)_2$ as precursors.

Typical procedure of oxidative coupling reactions

The oxidative coupling of a catechol **1a** (1.0 mmol) with an active methylene compound **2a** (1.0 mmol) was conducted under O_2 (1 atm) in a Schlenk flask using $Ru/AlPO_4$ (Ru: 50 μmol) in H_2O (4 mL) at 50 ºC. After the reaction, dimethyl sulfone (internal standard) and acetone (solvent to solve the products) were added, and the $Ru/AlPO_4$ was separated by filtration. The filtrate was evaporated to remove solvents. The resulting solid was solved in $CDCl_3$ and analysed by ^{1}HNMR.

Reaction of coupling product using $AlPO_4$-supported metal catalyst

To elucidate the high selectivity of $Ru/AlPO_4$, the reaction of the cross-coupling product **3aa** (0.4 mmol) was carried out under O_2 (1 atm) in a Schlenk flask using $Ru/AlPO_4$ or $Ru/AlPO_4$ (Ru or Pt: 20 μmol) in H_2O (2 mL) at 50 ºC for 12 h. After the reaction, dimethyl sulfone (internal standard) and acetone were added, and the catalyst was separated by filtration. The filtrate was evaporated to remove solvents. The resulting solid was solved in $CDCl_3$ and analysed by ^{1}HNMR.

Reuse experiment

After the coupling reaction of **1a** with **2a**, the catalyst was separated by filtration, washed with acetone, dried, and then calcined at 500 ºC for 3h. After that, the above catalyst was reused for another coupling reaction.

Reaction of 3-methoxy-1,2-benzoquinone (5a) with active methylene compound 2a

The synthesis of **5a** was conducted from **1a** using Ag_2O according to the reported procedure (M. Y. Zhang and R. A. Barrow, *Org. Lett*., 2017, **19**, 2302.). The obtained **5a** (0.26 mmol) was dissolved in $CDCl_3$ (2 mL) containing hexadecane (internal standard), and then reacted with 2a (0.5 mmol) in the presence of $AlPO_4$ (0.167 g) at r.t. After the reaction, a 4 mL of saturated $Na_2S_2O_4$ aq. was added. The organic phase was extracted for ^{1}H NMR measurement.

Product identification

All products were isolated as follows. After the reaction, EtOAc was added to solve the products. The catalyst was separated by filtration The organic phase was extracted, evaporated, and then purified by column chromatography (Wakogel, C-200, eluent: EtOAc/hexane).

The reaction products (**3aa**, **3ba**, **3ba'**, **3ca**, **3ca'**, **3ea**, **3ab**, **3ac**, and **3ad**) were identified by ^{1}H NMR spectroscopy and, in each case, the chemical shifts of the products corresponded with those reported in the literature, as summarized below. The other products (**3da, 3da'**, **3fa**,

3fa') were identified by ^{1}H and ^{13}C NMR spectroscopies and FTIR and HRMS measurements.

Figures

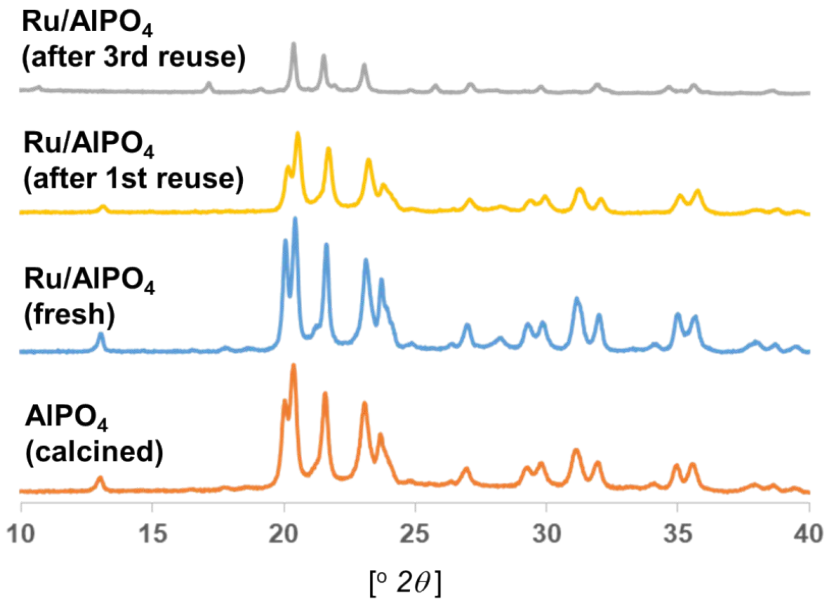


Figure S1. XRD spectra of tridimite-type $AlPO_4$, $Ru/AlPO_4$ (fresh), and the $Ru/AlPO_4$ after the 1st and 3rd reuse experiment.

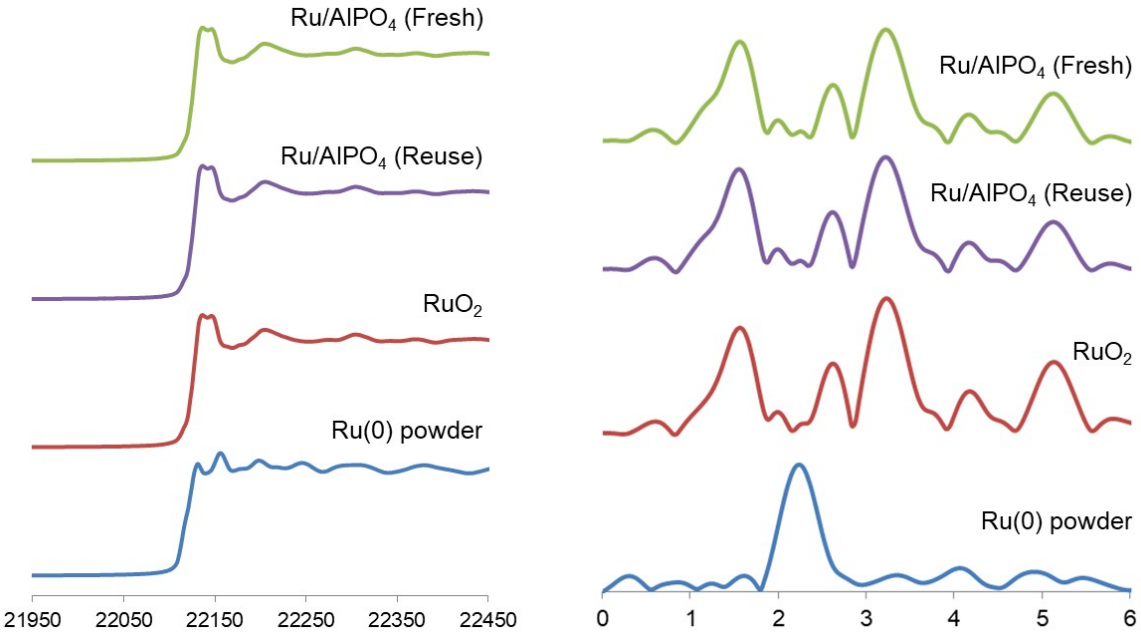


Figure S2. XANES and EXAFS spectra of $Ru/AlPO_4$ (fresh), the $Ru/AlPO_4$ after the reuse

experiment, RuO_2, and Ru(0) powder.

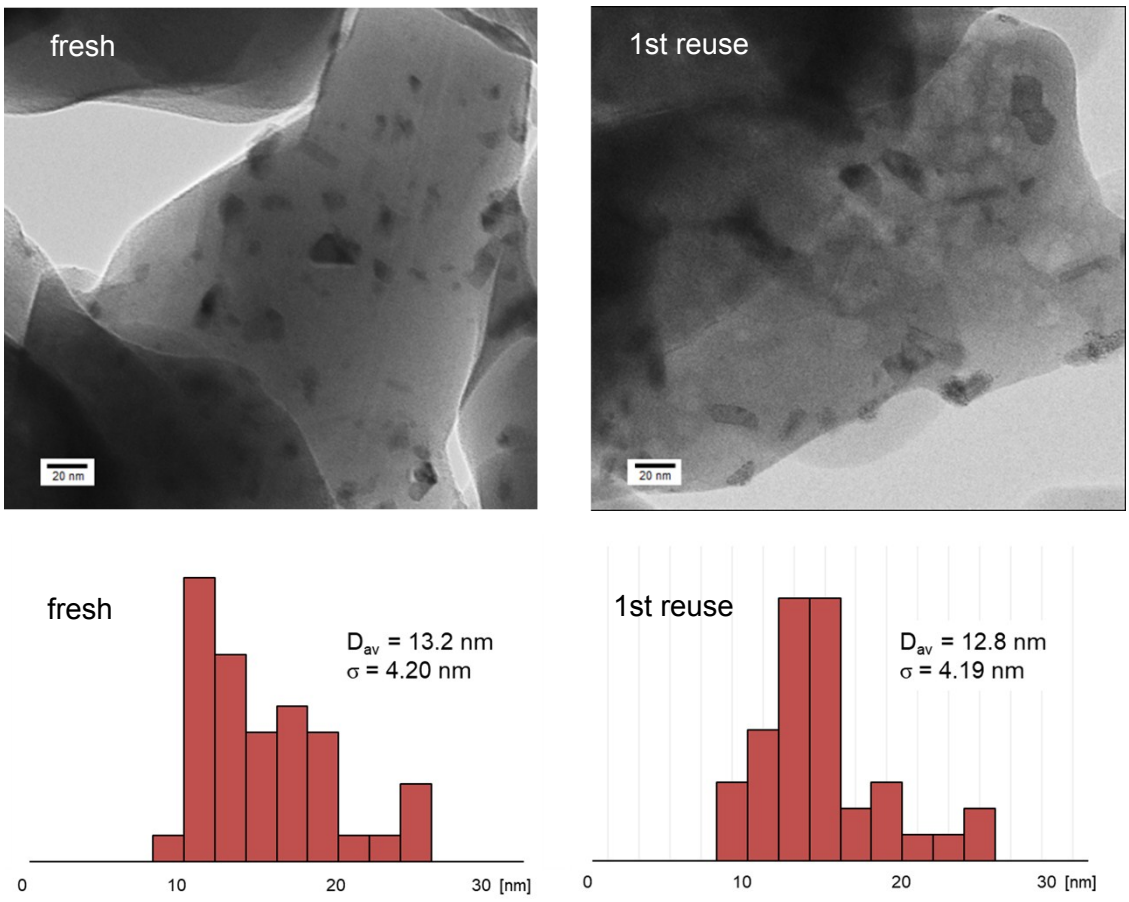


Figure S3. TEM images and size distributions of $Ru/AlPO_4$ (fresh), and the $Ru/AlPO_4$ after the reuse experiment.

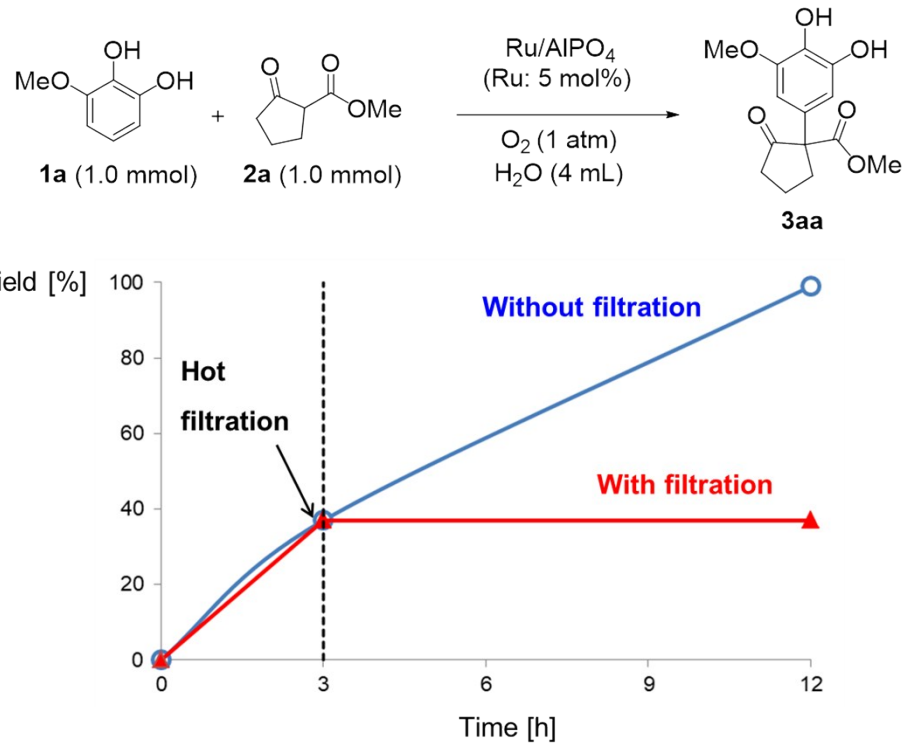


Figure S4. Time course of hot filtration test.

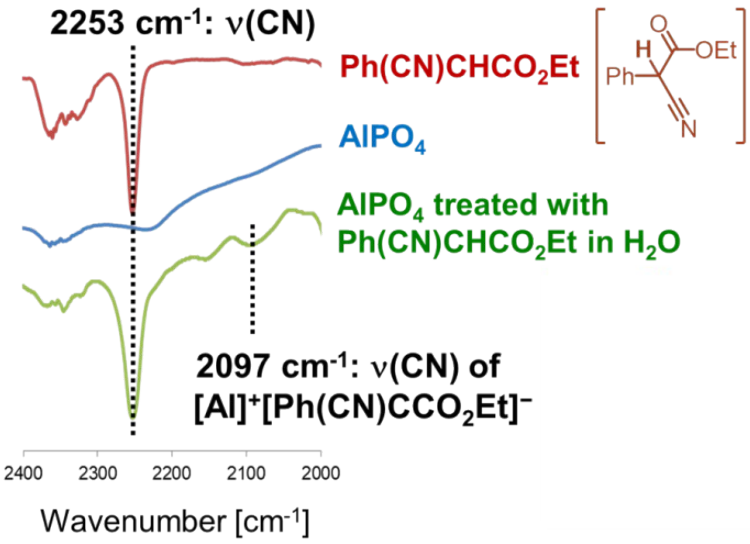
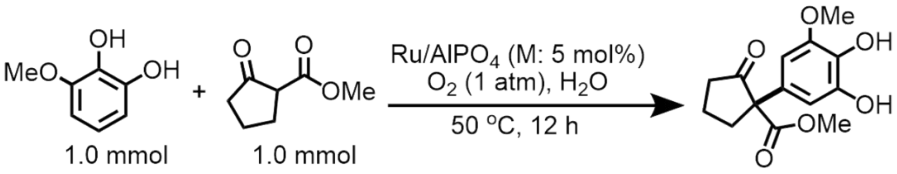


Figure S5 FTIR spectra of $Ph(CN)CHCO_2Et$, $AlPO_4$ (calcined), and the $Ph(CN)CHCO_2Et$ after treatment with $AlPO_4$.

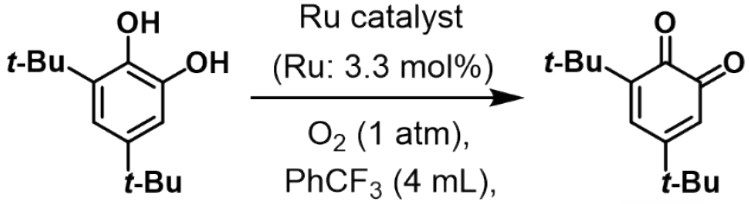
Tables

Table S1 Reuse experiment of $Ru/AlPO_4$ in the model reaction



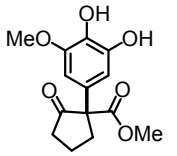
Catalyst	Conv. [%]	Yield [%]
Fresh	>99	99
1st Reuse	>99	98
2nd Reuse	42	42
3rd Reuse	29	29
4th Reuse (800 °C calcined)	35	35
5th Reuse (24 h)	63	62

Table S2 Aerobic dehydrogenation of di-*tert*-butylcatechol using Ru catalysts



Ru catalyst	Conv. [%]	Yield [%]	Sel. [%]
$RuO_2/AlPO_4$	52	52	**100**
$RuO_2/AlOOH$	>99	75	**75**
$RuO_2/Mg_3(PO_4)_2$	>99	69	**69**
RuO_2/MgO	50	14	**28**

Spectrum data

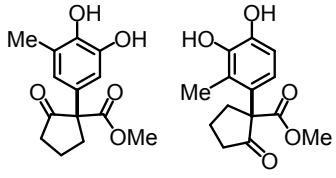


Methyl 1-(3,4-dihydroxy-5-methoxyphenyl)-2-oxocyclopentane –carboxylate (**3aa**) [CAS No. 959151-78-1]

^{1}H NMR: (400 MHz, $CDCl_3$): δ = 6.62 (d, J = 1.8 Hz, 1 H, H-2′), 6.57 (d, J = 1.8 Hz, 1 H, H-6′), 5.46 (s, 1H, OH), 5.40 (s, 1H, OH), 3.86 (s, 3H, -OCH_3), 3.70 (s, 3H, -CO_2CH_3) 2.84–2.76 (m, 1 H, H-5), 2.53–2.47 (m, 1 H, H-5), 2.48–2.43 (m, 1 H, H-3), 2.40–2.31 (m, 1 H, H-3), 2.02–1.87 (m, 2 H, H-4) ppm.

^{13}C NMR: (100 MHz, $CDCl_3$): δ= 212.2 (C=O), 171.3 (CO_2Me), 146.9 (C-5′), 144.0 (C-3′), 132.1 (C-4′), 127.5 (C-1′), 108.1 (C-2′), 103.1 (C-6′), 64.5 (C-1), 56.3 ($ArOCH_3$), 53.0 (CO_2CH_3), 37.8 (C-3), 35.0 (C-5), 19.22 (C-4) ppm.

^{1}HNMR and ^{13}C NMR results were consistent with previously reported values. See ref 4(a).



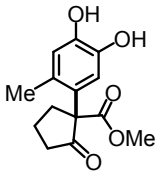
3ba **3ba'**

Methyl 1-(3,4-dihydroxy-5-methylphenyl)-2-oxocyclopentane - carboxylate (**3ba**) [CAS No. 1397495-63-4]
and its regiomer (**3ba'**) [CAS No. 1397495-77-0]

^{1}H NMR (400 MHz, $CDCl_3$): δ =6.80 (s, 1 H, H-2′, for **3ba**'), 6.68 (s, 1 H, H-6′, for **3ba**), 6.57 (d, J = 8.2 Hz, 1 H, H-6′, for **3ba**'), 6.36 (d, J = 8.2 Hz, 1 H, H-5′, for **3ba**') 5.60 (brs, 1 H, OH, for **3ba**, and 1 H, OH, for **3ba**'), 5.28 (brs, 1 H, OH, for **3ba**, and 1 H, OH, for **3ba**'), 3.71 (s, 3 H, CO_2CH_3, for **3ba**, and 3 H, CO_2CH_3, for **3ba**'), 2.83–2.76 (m, 1 H, H-5, for **3ba**, and 1 H, H-5, for **3ba**'), 2.54–2.47 (m, 1 H, H-5, for **3ba**, and 1 H, H-5, for **3ba**'), 2.46–2.34 (m,2 H, H-3, for **3ba**, and 2 H, H-3, for **3ba**'), 2.23 (s, 3 H, CH_3, for **3ba**, and 3 H, CH_3, for **3ba**'), 2.02–1.90 (m, 2 H, H-4, for **3ba**, and 2 H, H-4, for **3ba**') ppm.

^{13}C NMR for **3ba** and **3ba'** (100 MHz, $CDCl_3$): δ = 213.3, 171.7, 167.8, 143.1, 142.3, 130.9, 128.8, 126.7, 124.5, 121.3, 118.5, 112.5, 111.9, 68.3, 64.4, 53.0, 38.7, 37.7, 34.9, 30.4, 29.0, 23.7, 23.0, 19.2, 15.7 ppm.

^{1}HNMR and ^{13}C NMR results were consistent with previously reported values. See ref 4(a).

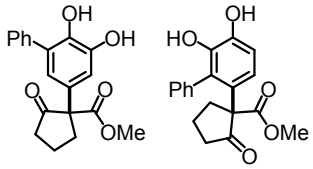


Methyl 1-(4,5-dihydroxy-2-methylphenyl)-2-oxocyclopentane-carboxylate (**3ca**) [CAS No. 1400975-93-0]

^{1}H NMR: (400 MHz, $CDCl_3$): δ = 6.68 (s, 1 H, H-6′), 6.45 (s, 1 H, H-3′), 5.68 (brs, 1 H, OH), 5.50 (brs, 1 H, OH), 3.75 (s, 3 H, CO_2CH_3), 3.02‑2.95 (m, 1 H, H-5), 2.52‑2.47 (m, 2 H, H-3), 2.31‑2.23 (m, 1 H, H-5), 2.13‑2.00 (m, 1 H, H-4), 2.06 (s, 3 H, CH_3), 1.89-1.78 (m, 1 H, H-4) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 215.2 (C=O), 172.0 (CO_2Me), 143.0 (COH), 141.1 (COH), 129.3, 129.0, 119.3 (C-5′), 114.8 (C-2′), 66.2 (C-1), 53.3 (CO_2CH_3), 39.0 (C-2), 35.8 (C-5), 19.6 (C-4), 19.3 ($ArCH_3$) ppm.

^{1}HNMR and ^{13}C NMR results were consistent with previously reported values. See ref 4(a).



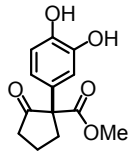
Methyl 1-(5,6-dihydroxy-[1,1'-biphenyl]-3-yl)-2-oxocyclopentane-1-carboxylate (**3da**) and its regiomer (**3da**')

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52-7.44 (m, 5 H, Ar-H, for **3da**'), 7.43-7.37 (m, 5 H, Ar-H, for **3da**'), 7.00 (d, J = 2.3 Hz, 1 H, H-2′, for **3da**), 6.88 (d, J = 8.7 Hz, 1 H, H-6′, for **3da**'), 6.84 (d, J = 2.3 Hz, 1 H, H-5′, for **3da**), 6.63 (d, J = 8.7 Hz, 1 H, H-6′, for **3da**'), 5.49 (brs, 1H, OH, for **3da**, and 1H, OH, for **3da**'), 5.34 (brs, 1H, OH, for **3da** and 1H, OH, for **3da**'), 3.72 (s, 3H, -CO_2CH_3, for **3da**), 3.50 (s, 3H, -CO_2CH_3, for **3da**'), 2.87–2.81 (m, 1 H, H-5, for **3da**, and 1 H, H-5, for **3da**'), 2.62–2.49 (m, 1 H, H-5, for **3da**, and 1 H, H-5, for **3da**'), 2.48–2.44 (m, 1 H, H-3, for **3da**, and 1 H, H-3, for **3da**'), 2.42–2.24 (m, 1 H, H-3, for **3da**, and 1 H, H-3, for **3da**'), 2.02–1.91 (m, 2 H, H-4, for **3da**, and 2 H, H-4, for **3da**') ppm.

^{13}C NMR for **3ca** and **3ca**' (100 MHz, $CDCl_3$): δ = 213.4, 212.2,171.4, 170.3, 144.1, 143.5, 141.2, 140.1, 136.8, 131.5, 131.2, 129.1, 129.0, 127.9, 120.7, 120.1, 114.3, 114.1, 66.1, 64.4, 53.0, 52.6, 39.0, 37.8, 35.0, 19.5, 19.3 ppm.

IR (neat, cm^{-1}): 3421 (OH stretch), 3276 (C_{aryl}-H stretch), 2971 (CH_2 stretch), 2951 (CH_2 stretch), 1725 (C=O stretch), 1617 (C=C stretch), 1420 (C=C stretch), 1310, 1279, 1239 (C(=O)-O stretch), 1173 (C(=O)-O stretch), 803 (C_{aryl}-H bending).

HRMS (FAB): calculated (for $C_{19}H_{17}O_5$) 325.1076, found 325.1068 $[M-H]^-$.

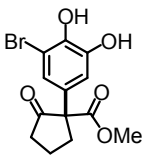


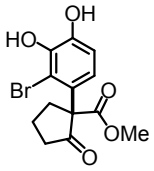
Methyl 1-(3,4-dihydroxyphenyl)-2-oxocyclopentane-carboxylate (**3ea**) [CAS No. 1245654-29-8]]

^{1}H NMR: (400 MHz, $CDCl_3$): δ= 6.96 (d, J = 4.1 Hz, 1 H, H-2′), 6.80 (t, J = 11.2 Hz, 2 H, H-1′, H-6′) , 5.82 (s, 1H, OH), 5.52 (s, 1H, OH), 3.71(s, 3H, -CO_2CH_3) 2.84–2.77 (m, 1 H, H-5), 2.55–2.48 (m, 1 H, H-5), 2.48–2.43 (m, 1 H, H-3), 2.41–2.32 (m, 1 H, H-3), 2.03–1.87 (m, 2 H, H-4) ppm.

^{13}C NMR: (100 MHz, $CDCl_3$): δ= 213.2 (C=O), 172.0 (CO_2Me), 143.8 (2C, C-3′and C-4′) 128.1 (C-1′), 119.7 (C-6′), 115.3 (C-5′), 115.0 (C-2′), 64.3 (C-1), 53.1 (CO_2CH_3), 37.8 (C-3), 35.0 (C-5), 19.2 (C-4) ppm.

^{1}HNMR and ^{13}C NMR results were consistent with previously reported values. See ref 4(a).





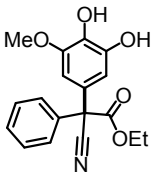
Methyl 1-(3-bromo-4,5-dihydroxyphenyl)-2-oxocyclopentane -carboxylate(**3fa**) and its regiomer (**3fa**')

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.06 (d, J = 1.8 Hz, 1 H, H-2′, for **3fa**), 6.96 (d, J = 1.8 Hz, 1 H, H-6′, for **3fa**), 6.80 (d, J = 8.2 Hz, 1 H, H-6′, for **3fa**'), 6.51 (d, J = 8.2 Hz, 1 H, H-5′, for **3fa**'), 5.70 (brs, 1H, OH, for **3fa**, and 1H, OH, for **3fa**'), 5.53 (brs, 1H, OH, for **3fa**, and 1H, OH, for **3fa′**), 3.74 (s, 3H, -CO_2CH_3, for **3fa**'), 3.72 (s, 3H, -CO_2CH_3, for **3fa**), 2.86–2.79 (m, 1 H, H-5, for **3fa**, and 1 H, H-5, for **3fa'**), 2.54-2.47 (m, 1 H, H-5, for **3fa**, and 1 H, H-5, for **3fa**'), 2.47–2.44 (m, 1 H, H-3, for **3fa**, and 1 H, H-3, for **3fa**'), 2.40–2.20 (m, 1 H, H-3, for **3fa**, and 1 H, H-3, for **3fa**'), 2.11–1.89 (m, 1 H, H-4, for **3fa**, and 1 H, H-4, for **3fa**') 1.80-1.73 (m, 1 H, H-4, for **3fa**, and 1 H, H-4, for **3fa**')ppm.

^{13}C NMR for **3fa** and **3fa′** (100 MHz, $CDCl_3$): δ = 213.3, 211.6, 170.4, 144.5, 143.9, 141.5, 140.1, 130.4, 129.9, 122.3, 120.7, 114.6, 113.9, 111.4, 109.5, 67.7, 63.8, 60.5, 53.5, 53.2, 39.2, 38.1, 37.7, 35.6, 34.9, 32.8, 27.4, 21.1, 19.4, 19.3, 14.2 ppm.

IR (neat, cm^{-1}): 3423 (OH stretch), 2962 (C_{aryl}-H stretch), 2884 (CH_2 stretch), 2838 (CH_2 stretch), 1751 (C=O stretch), 1609 (C=C stretch), 1499 (C=C stretch), 1457 (C=C stretch), 1285 (C(=O)-O stretch), 1132, 1106, 1038, 862, 803 (C_{aryl}-H bending).

HRMS (FAB): calculated (for $C_{13}H_{12}BrO_5$) 326.9868, found 326.9865 $[M-H]^-$.

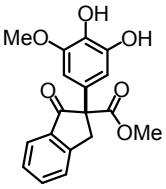


Ethyl 2-cyano-2-(3,4-dihydroxy-5-methoxyphenyl)-2-phenylacetate (**3ab**) [CAS No. 959151-83-8]

^{1}H NMR: (400 MHz, $CDCl_3$): δ= 7.44-7.36 (m, 5 H, -Ph), 6.63 (s, 1 H, H-2´), 6.56 (s, 1H, H-6´), 5.47 (brs, 1H, OH), 5.32 (brs, 1H, OH), 4.35 (q, 2H, -CO_2CH_2), 3.84 (s, 3H, -OCH_3) 1.33 (t, J = 7.1 Hz, 3 H, -$CO_2CH_2CH_3$) ppm.

^{13}C NMR: (100 MHz, $CDCl_3$): δ= 167.2, 146.8, 144.0, 135.8, 132.8 129.0, 128.9, 128.1, 118.9, 109.1, 103.2, 63.5, 56.3, 14.0 ppm.

^{1}HNMR and ^{13}C NMR results were consistent with previously reported values. See ref 3(c).

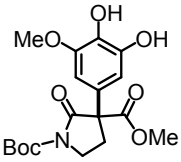


Methyl 2-(3,4-dihydroxy-5-methoxyphenyl)-1-oxo-2,3-dihydro -1H-indene-2-carboxylate (**3ac**) [CAS No. 959151-79-2]

^{1}H NMR: (400 MHz, $CDCl_3$): δ= 7.80 (d, J = 7.8 Hz, 1 H), 7.62 (t, J = 7.5 Hz, 1 H), 7.46 (d, J = 7.8 Hz, 1 H), 7.39 (t, J = 7.4 Hz, 1 H), 6.63 (d, J = 1.8 Hz, 1 H, H-6´), 6.58 (d, J = 2.3 Hz, 1 H, H-6´), 5.41 (s, 2 H, OH), 4.15 (d, J = 17.4 Hz, 1 H), 3.84 (s, 3H, -OCH_3), 3.72 (s, 3H, -CO_2CH_3) ppm.

^{13}C NMR: (100 MHz, $CDCl_3$): 200.1, 171.0, 146.8, 143.7, 135.6, 134.9, 132.0, 130.0, 127.9, 126.1, 125.1, 108.0, 102.8, 64.7, 56.2, 53.2, 40.7 ppm.

^{1}HNMR and ^{13}C NMR results were consistent with previously reported values. See ref 3(c)



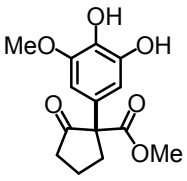
1-*tert*-butyl 3-methyl 3-(3,4-dihydroxy-5-methoxyphenyl) -2-oxopyrrolidine-1,3-dicarboxylate (**3ad**) [CAS No. 1397496-03-5]

^{1}H NMR: (400 MHz, $CDCl_3$): δ= 6.73 (d, J = 1.8 Hz, 1 H, H-2´), 6.63(d, J =1.8 Hz, 1 H, H-6´), 5.58 (brs, 1H, OH), 5.47 (brs, 1H, OH), 3.86 (s, 3H, -OCH_3), 3.79-3.68 (m, 1 H, H-4), 3.75 (s, 3H, -CO_2CH_3), 3.68-3.62 (m, 1 H, H-4), 2.93-2.87 (m, 1 H, H-5), 2.46-2.39 (m, 1 H, H-5), 1.53 (s, 9 H, $C(CH_3)_3$) ppm.

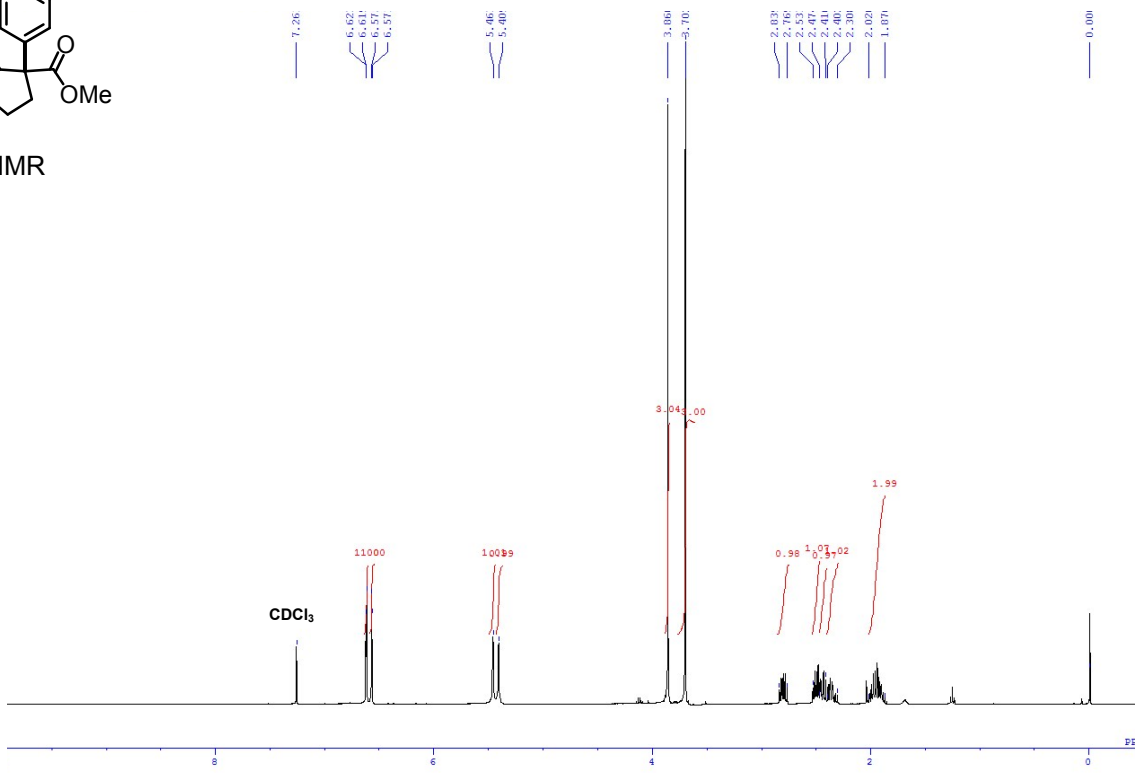
^{13}C NMR: (100 MHz, $CDCl_3$): 170.2, 169.6, 150.0 ($NCO_2{}^t$Bu), 147.0 (COH), 143.8 (COH),

127.5 (C-1'), 119.7 (C-6'), 107.7 (C-5'), 102.2 (C-2'), 83.5 ($CO_2C(CH_3)_3$), 61.2 (C-3), 53.3 (CO_2CH_3), 43.3 (C-5), 30.2 (C-4), 28.0 (3C, $CO_2C(CH_3)_3$) ppm.

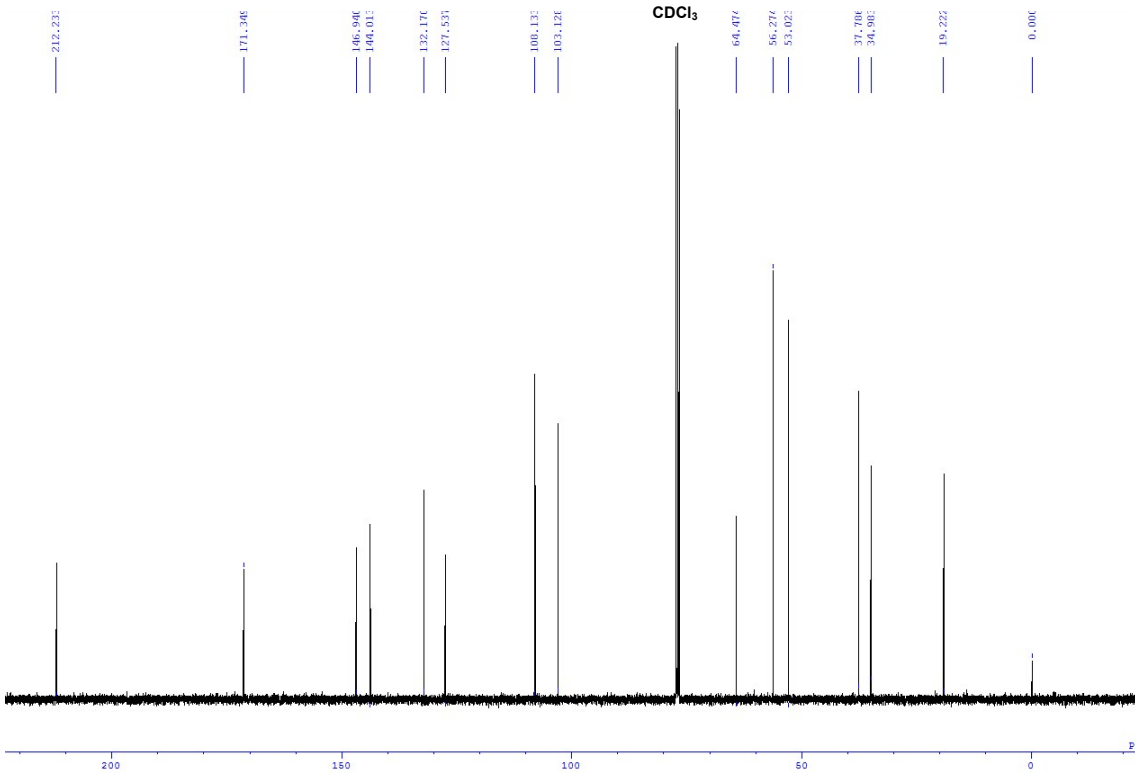
^{1}HNMR and ^{13}C NMR results were consistent with previously reported values. See ref 4(a).

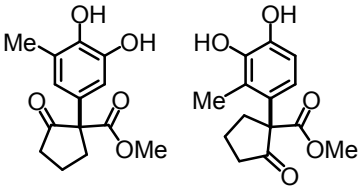


^{1}HNMR



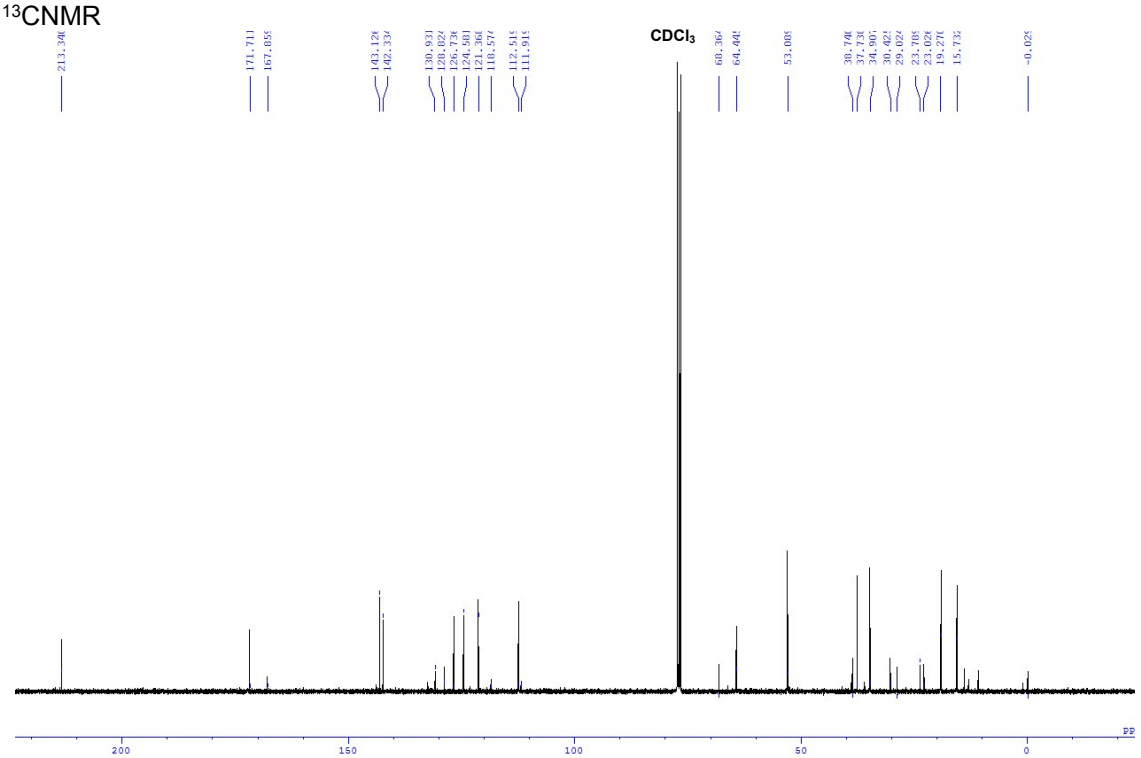
^{13}CNMR

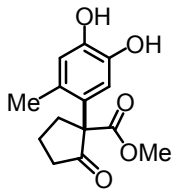




^{1}HNMR

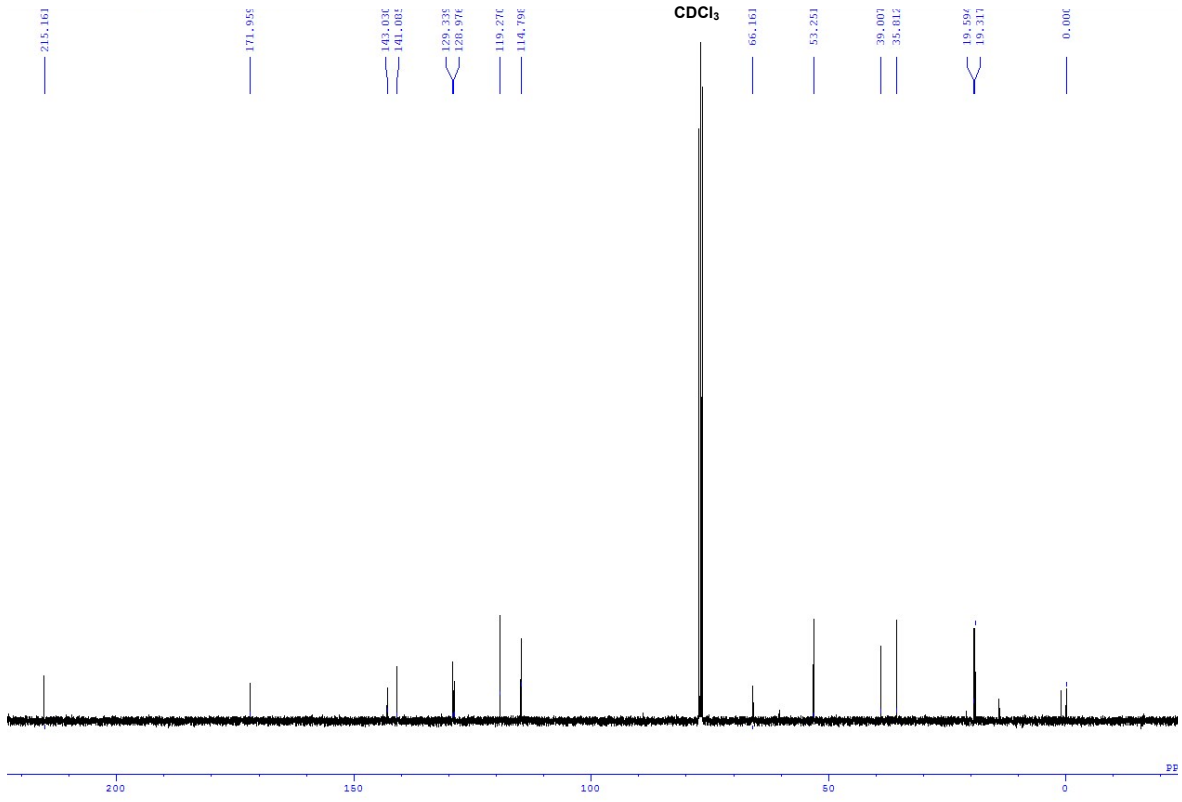
^{13}CNMR

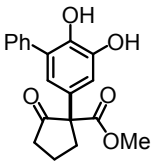


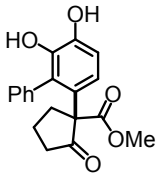


^{1}HNMR

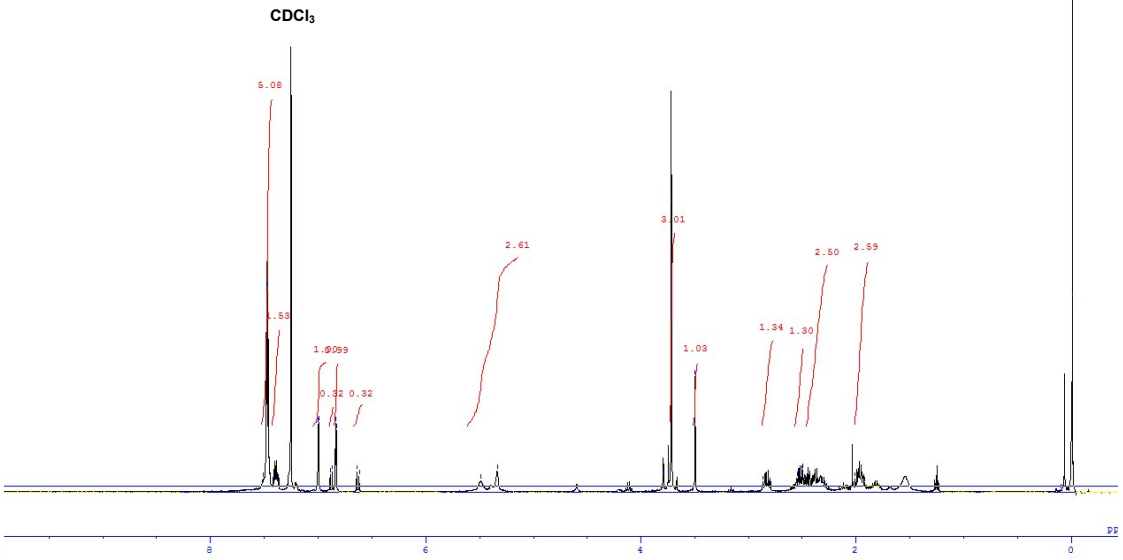
^{13}CNMR



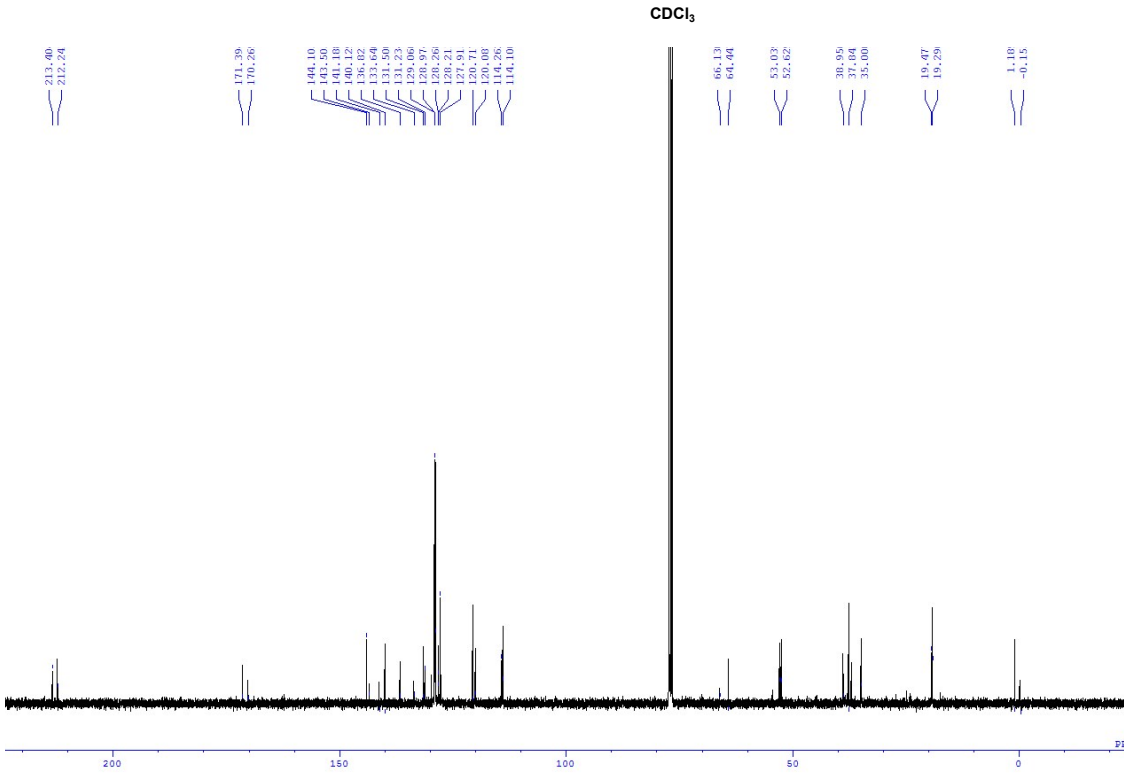


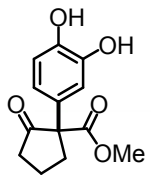


^{1}HNMR

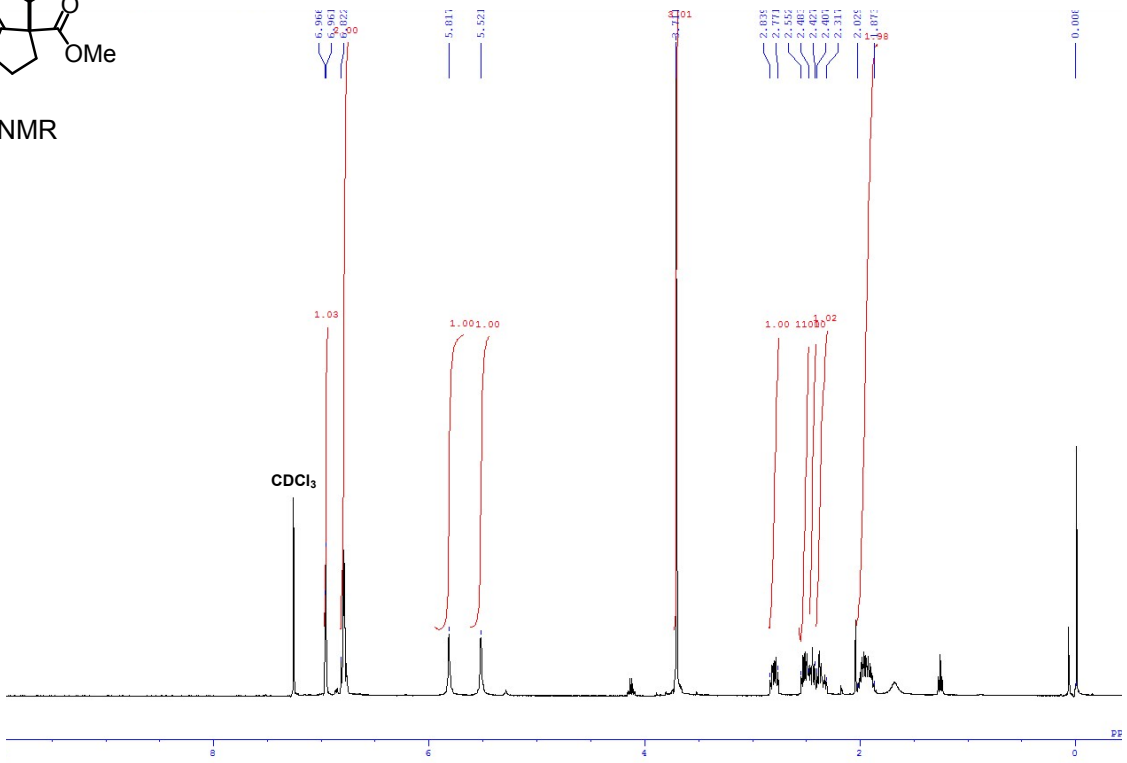


^{13}CNMR

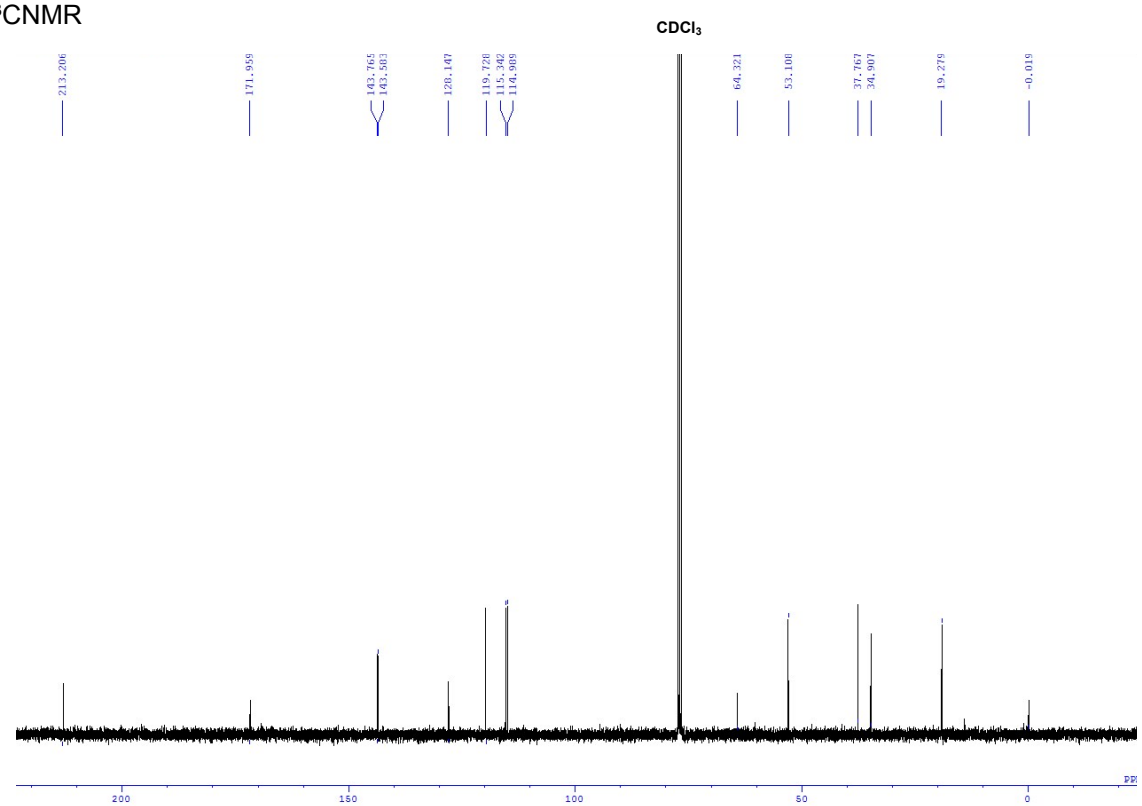


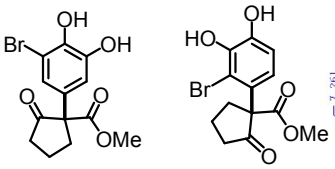


^{1}HNMR



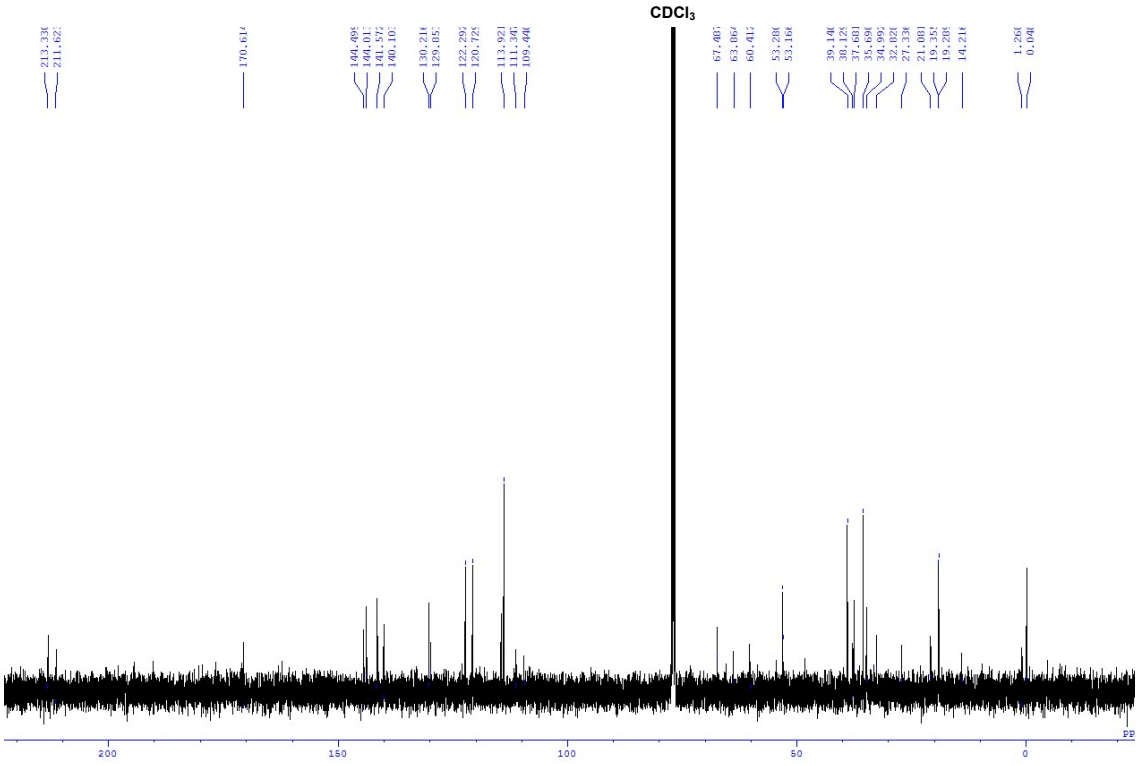
^{13}CNMR

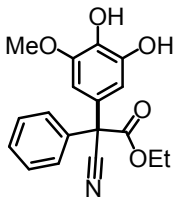




^{1}HNMR

^{13}CNMR





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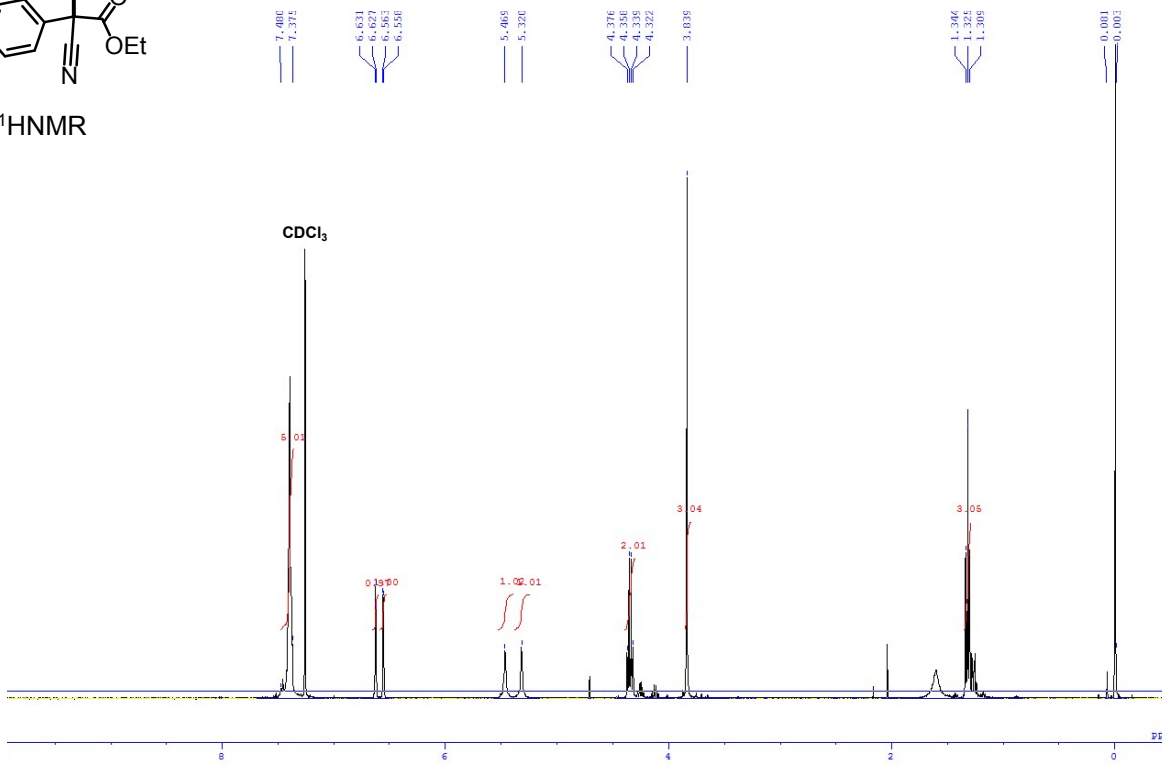

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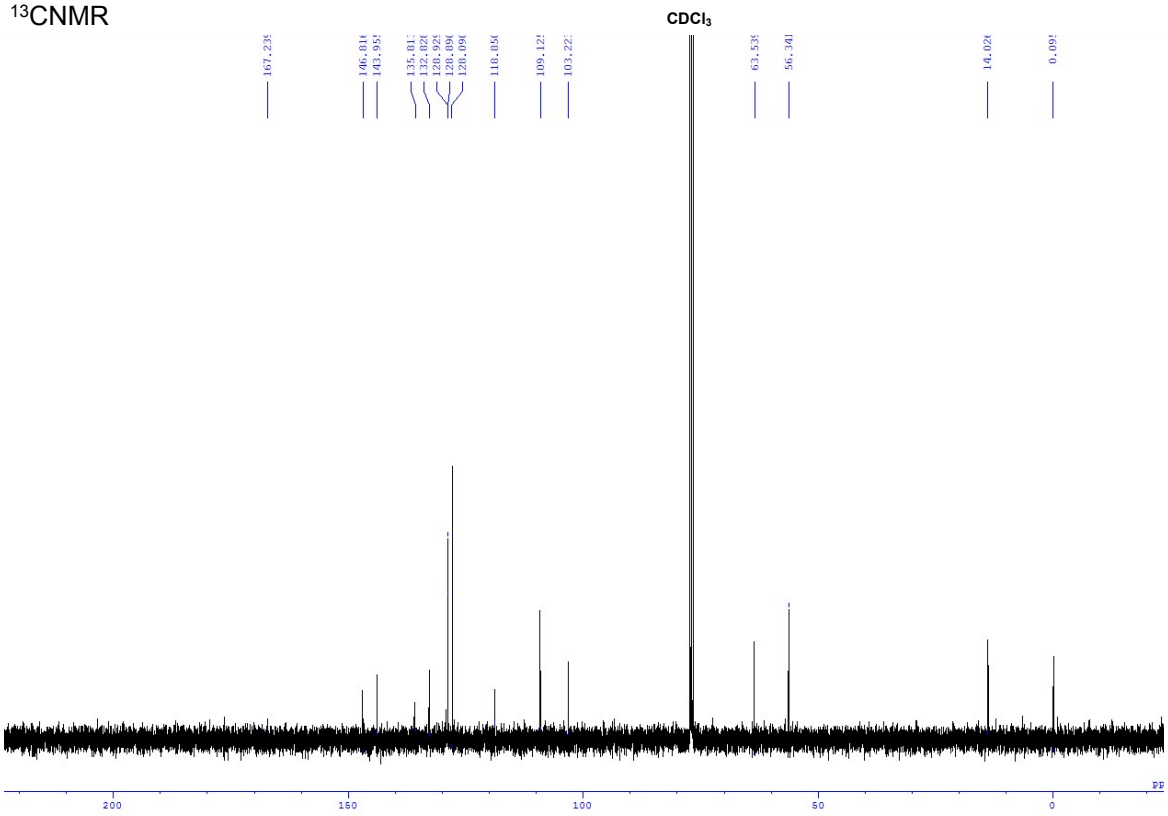
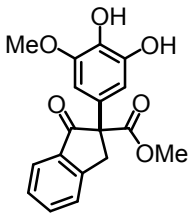
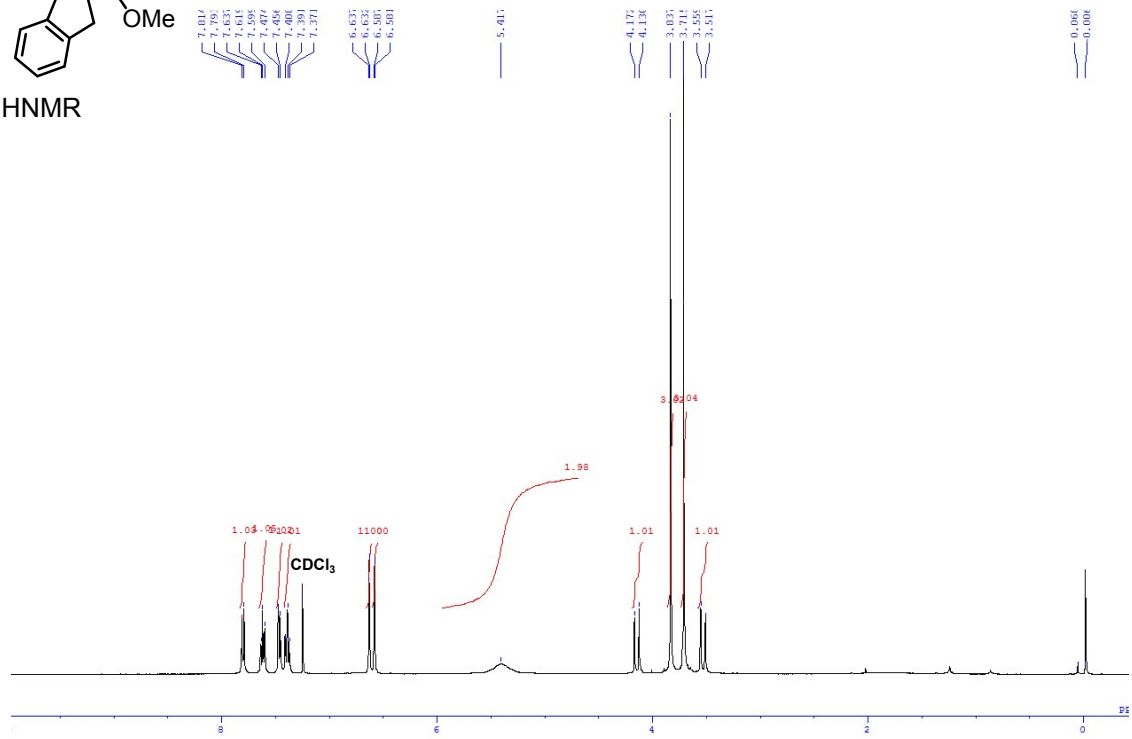




^{1}HNMR



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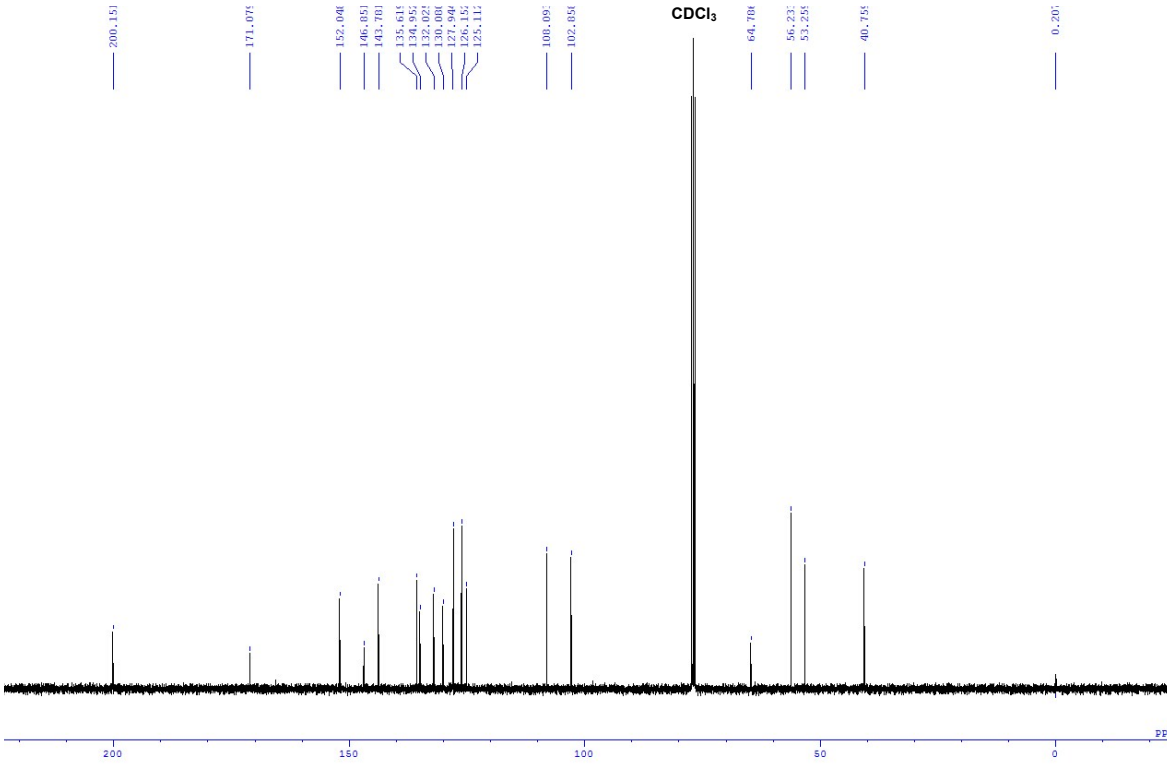
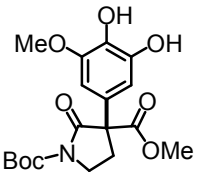
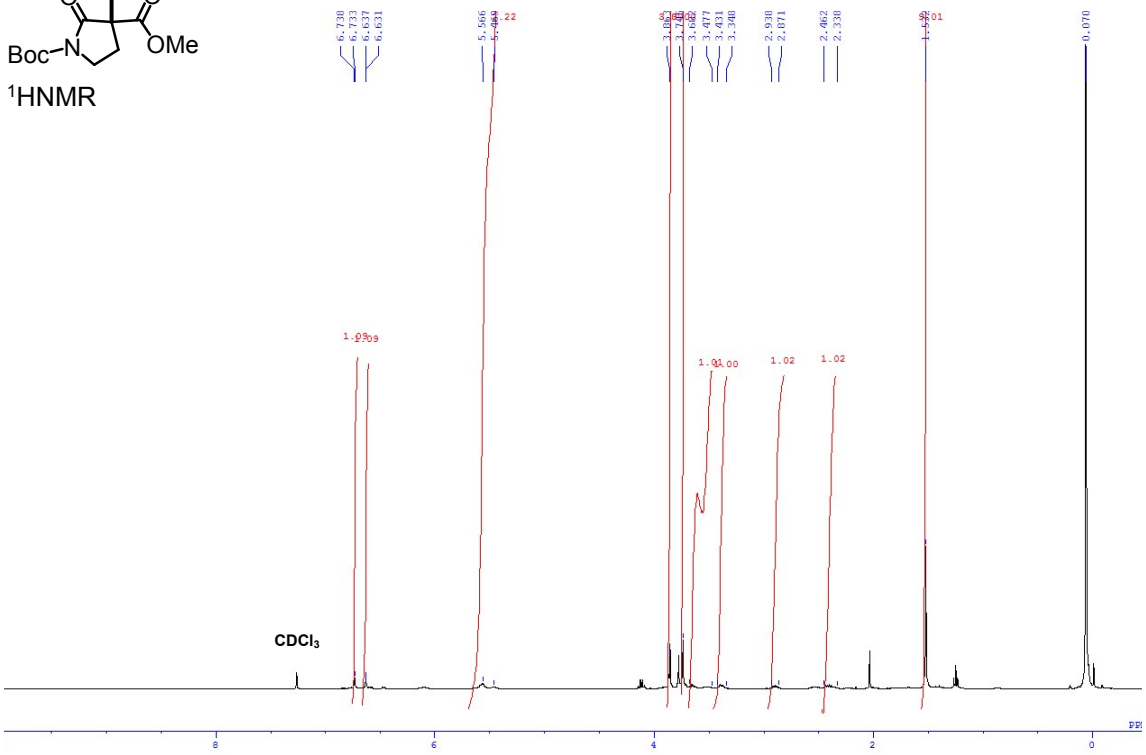




^{1}HNMR



^{13}CNMR