

## Supporting Information

# Visible Light-Driven Carboxylation of Aryl Halides by the Combined Use of Palladium and Photoredox Catalysts

Katsuya Shimomaki,<sup>†</sup> Kei Murata,<sup>†</sup> Ruben Martin<sup>‡, §</sup> and Nobuharu Iwasawa<sup>†,\*</sup>

<sup>†</sup> Department of Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8551, Japan

<sup>‡</sup> Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology, Av. Països Catalans 16, 43007 Tarragona, Spain

<sup>§</sup> Catalan Institution for Research and Advanced Studies (ICREA), Passeig Lluís Companys, 23, 08010, Barcelona, Spain

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## General

All operations were performed under an argon, N<sub>2</sub> or CO<sub>2</sub> atmosphere unless otherwise noted. <sup>1</sup>H NMR spectra were recorded on JEOL ECZ-500 and ECX-500 (500 MHz) spectrometers in CDCl<sub>3</sub> using residual CHCl<sub>3</sub> (for <sup>1</sup>H, δ = 7.26) as an internal standard. <sup>13</sup>C NMR spectra were recorded on JEOL ECZ-500 and ECX-500 (125 MHz) spectrometer in CDCl<sub>3</sub> using CDCl<sub>3</sub> (for <sup>13</sup>C, δ = 77.0) as an internal standard. <sup>31</sup>P NMR chemical shift was calibrated using external 85% H<sub>3</sub>PO<sub>4</sub> (δ: 0.0 ppm). IR spectra were recorded on an SC-100-VIR (JASCO Co., Ltd.). FD-MS spectra were recorded on a JMS-T100 spectrometer. Cyclic voltammograms were recorded on Hokuto-Denko HSV-110. Merck Kiesel gel 60 F254 plate (0.25 mm thickness, coated on glass 20x20 cm<sup>2</sup>) was used for analytical thin layer chromatography (TLC), and Wakogel B-5F coated on glass in a thickness of 0.9 mm was used for preparative TLC. Visible light irradiation was performed with a Relyon Twin LED Light (3W × 2, λ<sub>irr.</sub> = 425 ± 15 nm) for photocatalytic reactions.

Et<sub>2</sub>O was dried by passing through a column of activated alumina (A-2, Purify) followed by a column of Q-5 scavenger (Engelhard). Dehydrated acetone, acetonitrile (MeCN), dimethylacetamide (DMA), dimethylformamide (DMF), methanol (MeOH) and *N*-methylpyrrolidone (NMP) were purchased from Kanto Chemical Co., Inc. (acetone, MeCN, DMA, DMF, MeOH) and Sigma-Aldrich (NMP), and degassed by argon bubbling before use. Tertiary amines were distilled, degassed three times by freeze-pump-thaw method and stored under N<sub>2</sub>. CO<sub>2</sub> gas was purchased from Taiyo Nippon Sanso Corporation.

Palladium acetate (Pd(OAc)<sub>2</sub>), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (Xphos), 2-Di-*tert*-butylphosphino-2',4',6'-triisopropylbiphenyl (*t*Buphos) and compounds **1b**, **r** and **6u**, were purchased from Sigma-Aldrich.

Compounds **1a**, **c**~**g**, **i**, **j**, **m**~**o** and **6b**, **c**, **e**, **j**, **s**, **t**, **v** were purchased from Tokyo Chemical Industry.

Cesium carbonate and **1p** were purchased from Wako Chemical Pure Industries.

2-Diphenylphosphino-2',4',6'-triisopropylbiphenyl (PhXphos),<sup>1</sup> Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> **4a**,<sup>2</sup> Ir(dF(CF<sub>3</sub>)ppy)<sub>2</sub>(dtbpy)(PF<sub>6</sub>) **4b**,<sup>3</sup> Ir(ppy)<sub>2</sub>(dtbpy)(PF<sub>6</sub>) **4c**,<sup>4</sup> Ir(ppy)<sub>2</sub>(dmobpy)(PF<sub>6</sub>) **4d**,<sup>5</sup> Ir(ppy)<sub>2</sub>(bpbpy)(PF<sub>6</sub>) **4e**,<sup>6</sup> Ir(ppy)<sub>2</sub>(phen)(PF<sub>6</sub>) **4f**,<sup>7</sup> Ir(ppy)<sub>2</sub>(Me<sub>4</sub>phen)(PF<sub>6</sub>) **4g**,<sup>7</sup> *fac*-Ir(ppy)<sub>3</sub> **4h**,<sup>8</sup> TMSCHN<sub>2</sub>,<sup>9</sup> (COD)Pd(CH<sub>2</sub>TMS)<sub>2</sub><sup>10</sup> and compounds **1h**,<sup>11</sup> **1k**,<sup>12</sup> **1l**,<sup>13</sup> **1q**<sup>14</sup> and **6d**<sup>15</sup> were prepared according to the published methods.

The liquid materials **1a**~**f**, **m**, **o**, **r** and **6b**~**e**, **s**~**u** were distilled and stored under Ar.

### Procedure for Screening of Reaction Conditions (Table 1)

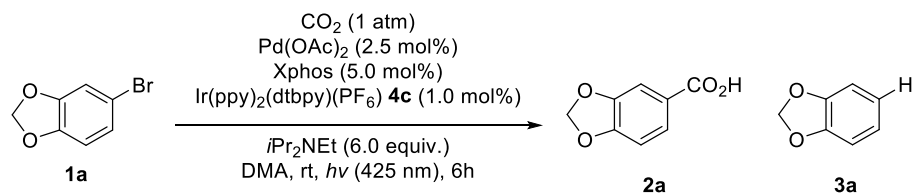
A DMA solution (1.0 mL) of 3,4-methylenedioxybromobenzene **1a** (24  $\mu$ L, 0.20 mmol) with palladium acetate (1.1 mg, 0.005 mmol, 2.5 mol%), a ligand (0.01 mmol, 5.0 mol%), a photoredox catalyst (0.002 mmol, 1.0 mol%), additive and *i*Pr<sub>2</sub>NEt (0.21 mL, 1.2 mmol, 6.0 equiv. or 0.10 mL, 0.60 mmol, 3.0 equiv.) was prepared in a test tube under a nitrogen atmosphere. Then the gas phase was replaced by atmospheric pressure of CO<sub>2</sub>, and the reaction vessel was put in a water bath placed at a distance of 10 mm from light sources. The mixture was irradiated with visible light ( $\lambda_{\text{irr.}}$  = 425 nm) using two sockets of blue LED lamp for 6 h in the closed system. After irradiation, the reaction was quenched with H<sub>2</sub>O and then the mixture was extracted with Et<sub>2</sub>O three times. The combined organic layer was washed with H<sub>2</sub>O and dried over Na<sub>2</sub>SO<sub>4</sub>. After the filtration of the drying agent, the filtrate was evaporated, and the crude product was analyzed by <sup>1</sup>H-NMR spectroscopy to determine the recovery of the starting material **1a** and the amount of the hydrogenated product **3a** (internal standard : dibromomethane). The combined aqueous layer was acidified with 1N HCl aq., and then extracted with Et<sub>2</sub>O three times. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated and evaporated under reduced pressure to give the carboxylic acid **2a**. The NMR yield of **2a** was determined by <sup>1</sup>H-NMR spectroscopy (internal standard : 1,4-dioxane).

### General Procedure of Substrate Scope (Table 2, 3)

A DMA solution (1.0 mL) of an aryl halide (0.20 mmol) with palladium acetate (1.1 mg, 0.005 mmol, 2.5 mol%), a ligand (0.01 mmol, 5.0 mol%), Ir(ppy)<sub>2</sub>(dtbpy)(PF<sub>6</sub>) **4c** (4.6 mg, 0.005 mmol, 2.5 mol%), Cs<sub>2</sub>CO<sub>3</sub> (195 mg, 0.60 mmol, 3.0 equiv.) and *i*Pr<sub>2</sub>NEt (0.10 mL, 0.60 mmol, 3.0 equiv.) was prepared in a test tube under a nitrogen atmosphere. Then the gas phase was replaced by atmospheric pressure of CO<sub>2</sub>, and the reaction vessel was put in a water bath placed at a distance of 10 mm from light sources. The mixture was irradiated with visible light ( $\lambda_{\text{irr.}}$  = 425 nm) using two sockets of blue LED lamp for 6 h in the closed system. After irradiation, the reaction was quenched with H<sub>2</sub>O and then the mixture was extracted with Et<sub>2</sub>O three times. The organic layer was washed with H<sub>2</sub>O. The combined aqueous layer was acidified with 1N HCl aq., and then extracted with Et<sub>2</sub>O three times. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated and evaporated under reduced pressure to give the carboxylic acid. The product was dissolved in Et<sub>2</sub>O (2.0 mL) and MeOH (0.5 mL), and a Et<sub>2</sub>O solution of TMSCHN<sub>2</sub> (2.0 equiv.) was added at 0 °C. The mixture was stirred at 0 °C for 30 min and the solvent was removed under reduced pressure. The crude product was purified by preparative TLC to give the corresponding methyl ester.

## Control experiments

**Table S1.** Control experiments



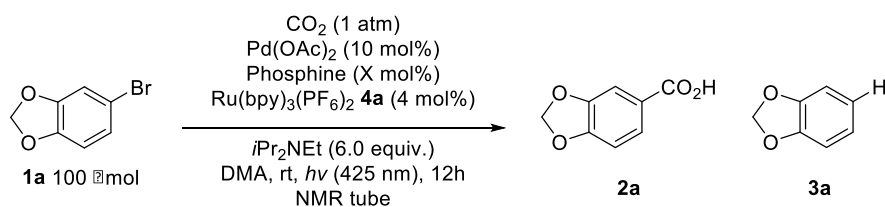
| Entry | Conditions   | Conv. /% <sup>a</sup> | <b>2a</b> /% <sup>a</sup> | <b>3a</b> /% <sup>a</sup> |
|-------|--|-----------------------|---------------------------|---------------------------|
| 1     | standard conditions  | 100                   | 48                        | 45                        |
| 2     | without $\text{Pd}(\text{OAc})_2$ and Xphos                            | 76                    | —                         | 75                        |
| 3     | without $\text{Ir}(\text{ppy})_2(\text{dtbpy})(\text{PF}_6)$ <b>4c</b> | 2                     | —                         | 2                         |
| 4     | without $i\text{Pr}_2\text{NEt}$                                       | 0                     | —                         | —                         |
| 5     | under dark   | 0                     | —                         | —                         |
| 6     | under $\text{N}_2$ instead of $\text{CO}_2$                            | 100                   | —                         | 95                        |
| 7     | under CO instead of $\text{CO}_2$                                      | 20                    | —                         | 19                        |

<sup>a</sup> Determined by  $^1\text{H}$ -NMR spectra.

In this carboxylation reaction, palladium catalyst, photoredox catalyst, amine, photo-irradiation and  $\text{CO}_2$  gas were all necessary, and lack of one component suppressed the reaction.

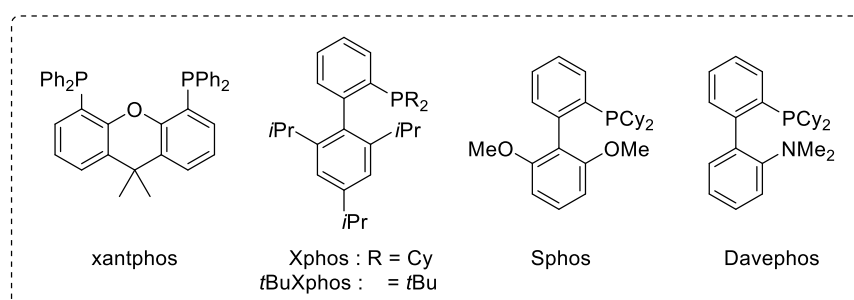
## Optimization for the Carboxylation of Aryl Bromides with Carbon Dioxide (CO<sub>2</sub>)

**Table S2.** The screening of phosphine ligands



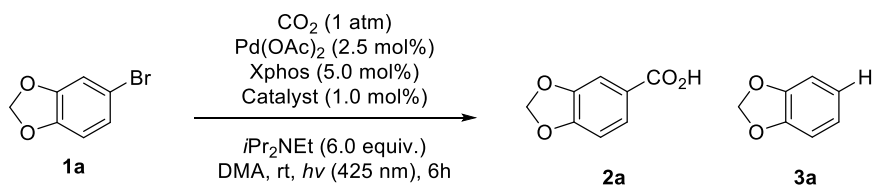
| Entry | Phosphine (X mol%)                               | Conv. /% <sup>a</sup> | <b>2a</b> /% <sup>a</sup> | <b>3a</b> /% <sup>a</sup> |
|-------|--|-----------------------|---------------------------|---------------------------|
| 1     | PPh <sub>3</sub> (20)                            | 100                   | —                         | 100                       |
| 2     | PMeS <sub>3</sub> (20)                           | 30                    | —                         | 14                        |
| 3     | PCy <sub>3</sub> (20)                            | 5                     | —                         | 8                         |
| 4     | <i>Pt</i> Bu <sub>3</sub> -HBF <sub>4</sub> (20) | 49                    | —                         | 19                        |
| 5     | dppe (10)  | 22                    | —                         | 23                        |
| 6     | Xantphos (10)                                    | 65                    | 14                        | 35                        |
| 7     | Xphos (20)                                       | 42                    | 15                        | 28                        |
| 8     | <i>t</i> BuXphos (20)                            | 100                   | 29                        | 36                        |
| 9     | Sphos (20)                                       | 32                    | 6                         | 31                        |
| 10    | Davephos (20)                                    | 71                    | 10                        | 33                        |

<sup>a</sup> Determined by <sup>1</sup>H-NMR spectra.



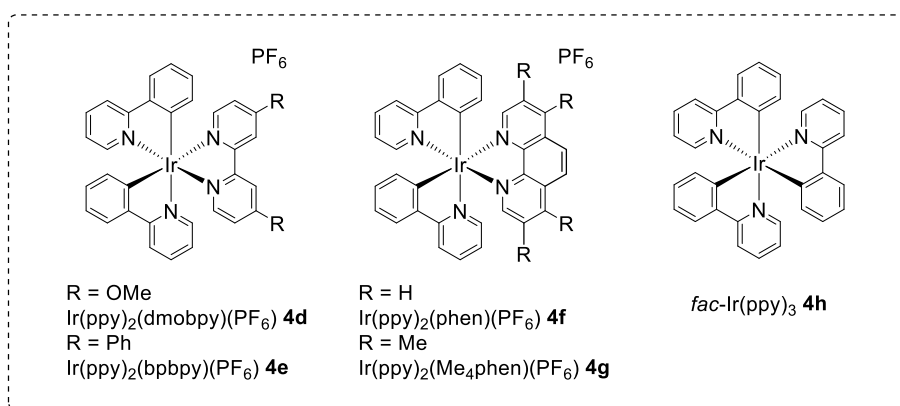
The desired carboxylic acid **2a** was produced by using xantphos and monodentate phosphine ligands containing a biphenyl moiety (entries 6~10). Xphos containing a 2,4,6-triisopropylbiphenyl moiety was preferable to Sphos or Davephos (entries 7,9,10).

**Table S3.** The screening of other photoredox catalysts

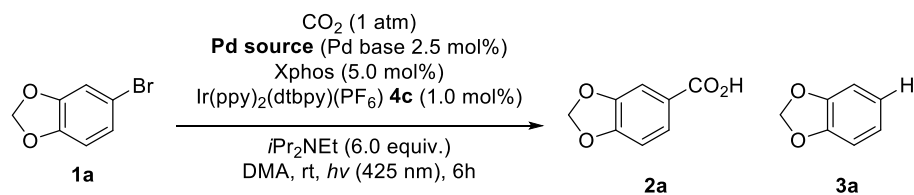


| Entry | Catalyst   | Conv. /% <sup>a</sup> | <b>2a</b> /% <sup>a</sup> | <b>3a</b> /% <sup>a</sup> |
|-------|--|-----------------------|---------------------------|---------------------------|
| 1     | $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ <b>4a</b>                                   | 12                    | 3                         | 9                         |
| 2     | $\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})(\text{PF}_6)$ <b>4b</b> | 48                    | 12                        | 25                        |
| 3     | $\text{Ir}(\text{ppy})_2(\text{dtbpy})(\text{PF}_6)$ <b>4c</b>                       | 100                   | 48                        | 45                        |
| 4     | $\text{Ir}(\text{ppy})_2(\text{dmobpy})(\text{PF}_6)$ <b>4d</b>                      | 100                   | 40                        | 55                        |
| 5     | $\text{Ir}(\text{ppy})_2(\text{bpbpy})(\text{PF}_6)$ <b>4e</b>                       | 54                    | 12                        | 25                        |
| 6     | $\text{Ir}(\text{ppy})_2(\text{phen})(\text{PF}_6)$ <b>4f</b>                        | 13                    | 3                         | 10                        |
| 7     | $\text{Ir}(\text{ppy})_2(\text{Me}_4\text{phen})(\text{PF}_6)$ <b>4g</b>             | 68                    | 28                        | 34                        |
| 8     | <i>fac</i> - $\text{Ir}(\text{ppy})_3$ <b>4h</b>                                     | 23                    | —                         | 8                         |

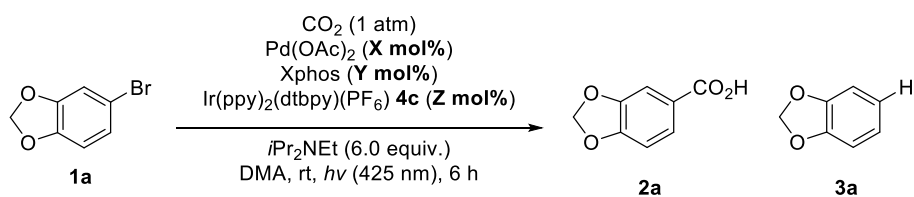
<sup>a</sup> Determined by  $^1\text{H}$ -NMR spectra.



The conversion of substrate **1a** and the yield of carboxylic acid **2a** were improved with  $\text{Ir}(\text{ppy})_2(\text{dtbpy})(\text{PF}_6)$  **4c** and  $\text{Ir}(\text{ppy})_2(\text{dmobpy})(\text{PF}_6)$  **4d** having higher reduction potentials.

**Table S4.** The screening of Pd sources

| Entry | Pd source                  | Conv. /% <sup>a</sup> | <b>2a</b> /% <sup>a</sup> | <b>3a</b> /% <sup>a</sup> |
|-------|----------------------------|-----------------------|---------------------------|---------------------------|
| 1     | Pd(OAc) <sub>2</sub>       | 100                   | 48                        | 45                        |
| 2     | PdCl <sub>2</sub>          | 37                    | —                         | 21                        |
| 3     | [(allyl)PdCl] <sub>2</sub> | 90                    | 25                        | 48                        |

<sup>a</sup> Determined by <sup>1</sup>H-NMR spectra.**Table S5.** The amount of Pd and photoredox catalysts

|                    | Entry | X mol% | Y mol% | Z mol% | Conv. /% <sup>a</sup> | <b>2a</b> /% <sup>a</sup> | <b>3a</b> /% <sup>a</sup> |
|--------------------|-------|--------|--------|--------|-----------------------|---------------------------|---------------------------|
| Standard condition | 1     | 2.5    | 5.0    | 1.0    | 100                   | 48                        | 45                        |
| Pd : Xphos         | 2     | 2.5    | 2.5    | 1.0    | 54                    | trace                     | 37                        |
|                    | 3     | 2.5    | 7.5    | 1.0    | 94                    | 43                        | 51                        |
| Catalyst amount    | 4     | 5.0    | 10.0   | 2.0    | 100                   | 69                        | 27                        |
|                    | 5     | 10.0   | 20.0   | 4.0    | 100                   | 72                        | 22                        |
| Pd : Ir            | 6     | 2.5    | 5.0    | 0.5    | 80                    | 26                        | 50                        |
|                    | 7     | 2.5    | 5.0    | 2.5    | 100                   | 71                        | 28                        |

<sup>a</sup> Determined by <sup>1</sup>H-NMR spectra.

This carboxylation reaction necessitated the use of two molar amounts of phosphine ligand for Pd(OAc)<sub>2</sub> (entries 1~3). The carboxylic acid **2a** was produced in good yield by increasing the amount of Pd and Ir catalysts (entries 4,5,7).

**Table S6.** The screening of sacrificial electron donors

| $\text{CO}_2$ (1 atm)<br>$\text{Pd}(\text{OAc})_2$ (2.5 mol%)<br>$\text{Xphos}$ (5.0 mol%)<br>$\text{Ir}(\text{ppy})_2(\text{dtbpy})(\text{PF}_6)$ <b>4c</b> (1.0 mol%)<br>$\text{e}^-$ donor ( <b>X equiv.</b> )<br>DMA, rt, $h\nu$ (425 nm), 6 h |  |                       |                           |                           |
|--|--|-----------------------|---------------------------|---------------------------|
|  |  |                       |                           |                           |
| Entry  | $\text{e}^-$ donor ( <b>X equiv.</b> ) | Conv. /% <sup>a</sup> | <b>2a</b> /% <sup>a</sup> | <b>3a</b> /% <sup>a</sup> |
| 1  | <i>i</i> Pr <sub>2</sub> NEt (6.0)     | 100                   | 48                        | 45                        |
| 2  | NEt <sub>3</sub> (6.0)                 | 23                    | 6                         | 12                        |
| 3  | TEOA (6.0)                             | 72                    | trace                     | 53                        |
| 4  | Et-TMP (6.0)                           | 17                    | trace                     | 12                        |
| 5  | Sodium L-Ascorbate (3.0)               | 17                    | —                         | 6                         |

TEOA

Et-TMP

Sodium L-Ascorbate

<sup>a</sup> Determined by <sup>1</sup>H-NMR spectra.

The carboxylic acid **2a** was produced in a higher yield by using *i*Pr<sub>2</sub>NEt as a sacrificial electron-donor (entry 1).

**Table S7.** The screening of solvents

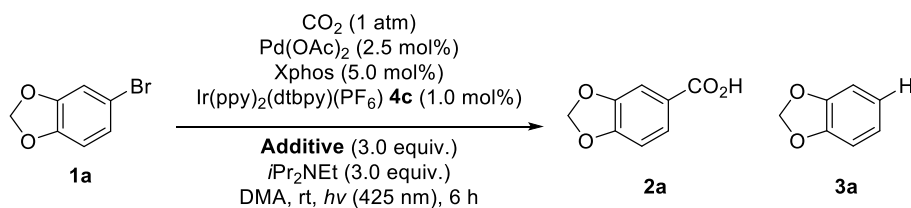
| $\text{CO}_2$ (1 atm)<br>$\text{Pd}(\text{OAc})_2$ (2.5 mol%)<br>$\text{Xphos}$ (5.0 mol%)<br>$\text{Ir}(\text{ppy})_2(\text{dtbpy})(\text{PF}_6)$ <b>4c</b> (1.0 mol%)<br><i>i</i> Pr <sub>2</sub> NEt (6.0 equiv.)<br><b>Solvent</b><br>rt, $h\nu$ (425 nm), 6 h |         |                       |                           |                           |
|--|---------|-----------------------|---------------------------|---------------------------|
|  |         |                       |                           |                           |
| Entry  | Solvent | Conv. /% <sup>a</sup> | <b>2a</b> /% <sup>a</sup> | <b>3a</b> /% <sup>a</sup> |
| 1  | DMF     | 97                    | 36                        | 52                        |
| 2  | NMP     | 94                    | 35                        | 54                        |
| 3  | MeCN    | 65                    | 7                         | 52                        |
| 4  | acetone | 100                   | 34                        | 61                        |
| 5  | THF     | 55                    | 14                        | 28                        |
| 6  | DMA     | 100                   | 48                        | 45                        |

<sup>a</sup> Determined by <sup>1</sup>H-NMR spectra.

A better result was obtained in DMA (entry 6),

**Table S8.** The screening of additives



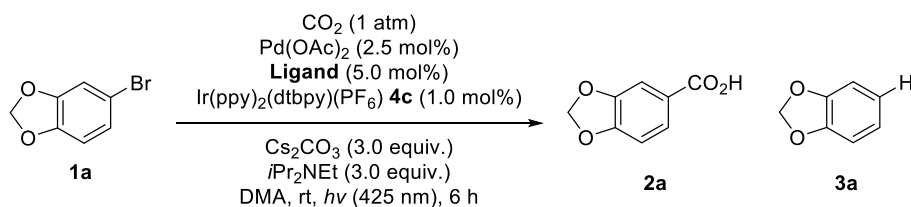


| Entry          | Additive                        | Conv. /% <sup>a</sup> | <b>2a</b> /% <sup>a</sup> | <b>3a</b> /% <sup>a</sup> |
|----------------|---------------------------------|-----------------------|---------------------------|---------------------------|
| 1 <sup>b</sup> | none                            | 100                   | 48                        | 45                        |
| 2 <sup>b</sup> | TFA (1.0 equiv.)                | 98                    | 34                        | 53                        |
| 3 <sup>b</sup> | TFA (2.0 equiv.)                | 78                    | 16                        | 47                        |
| 4              | Na <sub>2</sub> CO <sub>3</sub> | 82                    | 35                        | 37                        |
| 5              | K <sub>2</sub> CO <sub>3</sub>  | 74                    | 40                        | 24                        |
| 6              | Cs <sub>2</sub> CO <sub>3</sub> | 93                    | 58                        | 28                        |

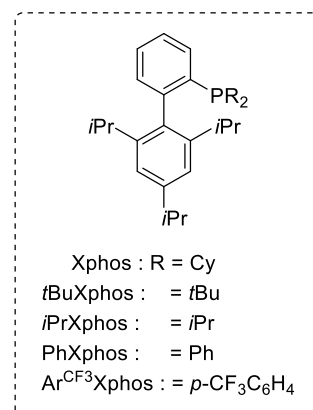
<sup>a</sup> Determined by <sup>1</sup>H-NMR spectra. <sup>b</sup> Using *i*Pr<sub>2</sub>NEt (6.0 equiv.)

This carboxylation reaction was improved by the addition of Cs<sub>2</sub>CO<sub>3</sub> as a base (entry 6). The effect of base is discussed in Mechanistic Study of Reduction Reaction section.

**Table S9.** The examination of Xphos type ligands under optimized conditions



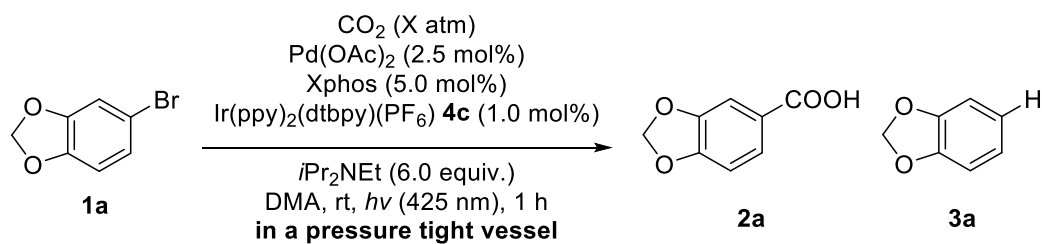
| Entry          | Ligand                  | Conv. /% <sup>a</sup> | <b>2a</b> /% <sup>a</sup> | <b>3a</b> /% <sup>a</sup> |
|----------------|-------------------------|-----------------------|---------------------------|---------------------------|
| 1              | Xphos                   | 93                    | 58                        | 28                        |
| 2              | <i>t</i> BuXphos        | 100                   | 65                        | 13                        |
| 3              | <i>i</i> PrXphos        | 94                    | 75                        | 18                        |
| 4              | PhXphos                 | 93                    | 75                        | 10                        |
| 5              | Ar <sup>CF3</sup> Xphos | 99                    | 75                        | 9                         |
| 6 <sup>b</sup> | PhXphos                 | 100                   | 88                        | 6                         |



<sup>a</sup> Determined by <sup>1</sup>H-NMR spectra. <sup>b</sup> Using Ir **4c** (2.5 mol%)

Use of 2.5 mol% each of Pd(OAc)<sub>2</sub> and Ir catalyst with PhXphos gave the best result (entry 6).

**Table S10.** The effect of CO<sub>2</sub> pressure

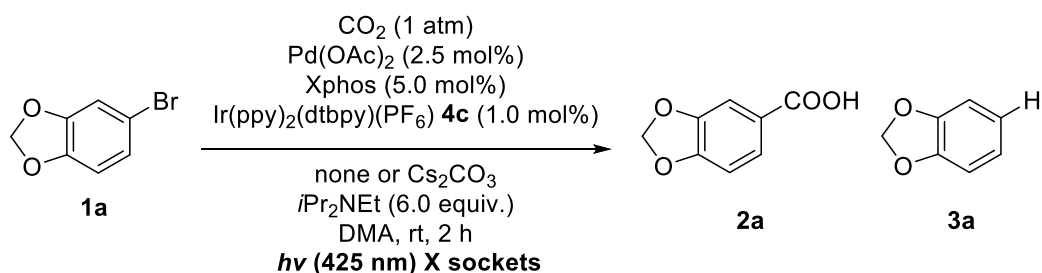


| Entry | X atm | Conv. /% <sup>a</sup> | <b>2a</b> /% <sup>a</sup> | <b>3a</b> /% <sup>a</sup> |
|-------|-------|-----------------------|---------------------------|---------------------------|
| 1     | 1.0   | 55                    | 35                        | 19                        |
| 2     | 5.0   | 60                    | 38                        | 16                        |
| 3     | 10.0  | 58                    | 37                        | 14                        |

<sup>a</sup> Determined by <sup>1</sup>H-NMR spectra.

These results were obtained using a pressure tight vessel and weren't directly comparable to the above examinations carried out in a test tube (Table S2~S9) as the vessels are different in the volume and the efficiency of photo-irradiation is also different. This reaction was run for 1 h to compare the rate of the reaction. Rather unexpectedly, all the reactions gave almost the same results. Although it is necessary to carry out more detailed examinations, it might be possible that the turnover-limiting step of this reaction is the generation of the Ir(II) species.

**Table S11.** The effect of photon flux

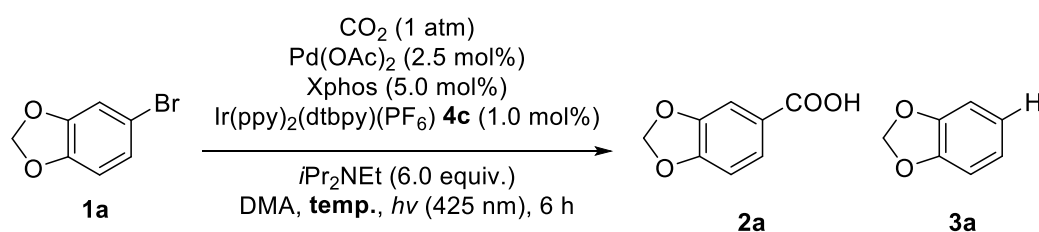


| Entry          | X sockets    | $\text{Cs}_2\text{CO}_3$ | Conv. /% <sup>a</sup> | <b>2a</b> /% <sup>a</sup> | <b>3a</b> /% <sup>a</sup> |
|----------------|--------------|--------------------------|-----------------------|---------------------------|---------------------------|
| 1              | 1            | none                     | 59                    | 40                        | 16                        |
| 2              | 2 (standard) | none                     | 73                    | 44                        | 24                        |
| 3              | 4            | none                     | 100                   | 47                        | 52                        |
| 4 <sup>b</sup> | 1            | 3.0 equiv.               | 61                    | 46                        | 9                         |
| 5 <sup>b</sup> | 2 (standard) | 3.0 equiv.               | 81                    | 58                        | 12                        |
| 6 <sup>b</sup> | 4            | 3.0 equiv.               | 93                    | 58                        | 22                        |

<sup>a</sup> Determined by <sup>1</sup>H-NMR spectra. <sup>b</sup> Using *i*Pr<sub>2</sub>NEt (3.0 equiv.)

By using 1,2 and 4 sockets of blue LED lamp, this reaction was run for 2 h to compare the rate of the reaction. The conversion of the starting material increased by using more number of sockets of blue LED lamp but the yield of the carboxylation products increased slightly and the reduction product increased considerably. This result can be explained by the fact that the ratio of the reduction product increases as the reaction proceeds more (Table S16). Increase of the conversion coincides with the assumption that generation of the Ir(II) species is the turnover-limiting step.

**Table S12.** The effect of reaction temperature



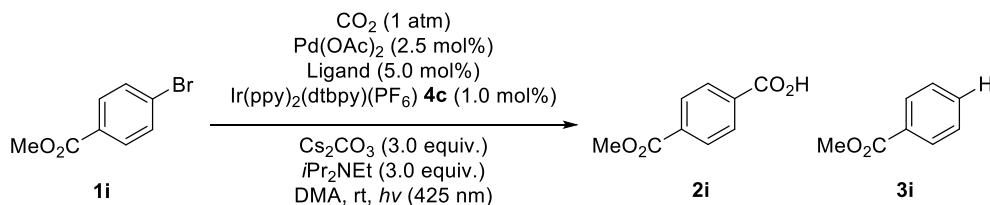
| Entry | temp.       | Cs <sub>2</sub> CO <sub>3</sub> | Conv. /% <sup>a</sup> | <b>2a</b> /% <sup>a</sup> | <b>3a</b> /% <sup>a</sup> |
|-------|-------------|---------------------------------|-----------------------|---------------------------|---------------------------|
| 1     | 0 °C        | none                            | 77                    | 47                        | 25                        |
| 2     | 0 °C (12 h) | none                            | 92                    | 45                        | 48                        |
| 3     | rt          | none                            | 100                   | 48                        | 45                        |
| 4     | 60 °C       | none                            | 100                   | 28                        | 67                        |

<sup>a</sup> Determined by <sup>1</sup>H-NMR spectra. <sup>b</sup> Using *i*Pr<sub>2</sub>NEt (3.0 equiv.)

The reaction at 0 °C and room temperature gave almost the same results, and at 60 °C, the yield of the product decreased and the hydrogenation product increased (entry 4). It is not necessarily easy to interpret the result, but it might be due to the lower concentration of CO<sub>2</sub> and/or decomposition of the Pd complex.

## Optimization for the Carboxylation of Electron-Withdrawing Aryl Bromides with Carbon Dioxide (CO<sub>2</sub>)

**Table S13.** The screening of phosphine ligands



| Entry          | Ligand           | Conv. /% <sup>a</sup> | <b>2i</b> /% <sup>a</sup> | <b>3i</b> /% <sup>a</sup> |
|----------------|------------------|-----------------------|---------------------------|---------------------------|
| 1              | PhXphos          | 100                   | 40                        | 48                        |
| 2 <sup>b</sup> | PhXphos          | 100                   | 51                        | 46                        |
| 3              | Xphos            | 100                   | 21                        | 64                        |
| 4              | <i>t</i> BuXphos | 100                   | 75                        | 8                         |
| 5 <sup>b</sup> | <i>t</i> BuXphos | 100                   | 80 (76) <sup>c</sup>      | 7                         |

<sup>a</sup> Determined by <sup>1</sup>H-NMR spectra. <sup>b</sup> Using Ir catalyst **4c** (2.5 mol%)

<sup>c</sup> Isolated yield after methyl esterification.

The hydrogenated product **2i** was produced more than other bromobenzenes under the conditions using PhXphos (entry 1,2). The desired carboxylic acid **3i** was obtained in good yield by using *t*BuXphos as an electron-rich phosphine ligand (entry 4, 5).

**Table S14.** The carboxylation of electron-withdrawing aryl bromides with PhXphos

Reaction scheme showing the carboxylation of aryl bromide **1** to carboxylic acid **2** and aryl bromide **3**. The reaction conditions are: CO<sub>2</sub> (1 atm), Pd(OAc)<sub>2</sub> (2.5 mol%), PhXphos (5.0 mol%), Ir(ppy)<sub>2</sub>(dtbbpy)(PF<sub>6</sub>) **4c** (1.0 mol%), Cs<sub>2</sub>CO<sub>3</sub> (3.0 equiv.), *i*Pr<sub>2</sub>NEt (3.0 equiv.), DMA, rt, *hν* (425 nm), 6 h.

| Entry          | R                              | <b>2</b> /% <sup>a</sup> | <b>3</b> /% <sup>a</sup> |
|----------------|--------------------------------|--------------------------|--------------------------|
| 1              | 4-CO <sub>2</sub> Me <b>1i</b> | 40                       | 48                       |
| 2              | 4-CN <b>1j</b>                 | 44                       | 39                       |
| 3 <sup>b</sup> | 3-COMe <b>1r</b>               | 18                       | 64                       |
| 4 <sup>c</sup> | 4-NHBoc <b>1h</b>              | 68                       | 13                       |

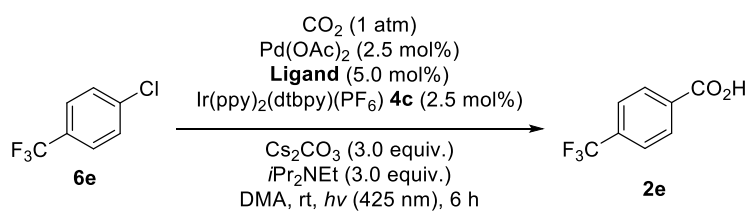
<sup>a</sup> Determined by <sup>1</sup>H-NMR spectra.

<sup>b</sup> Using Ir(dF(CF<sub>3</sub>)ppy)<sub>2</sub>(dtbpy)(PF<sub>6</sub>) **4b** instead of Ir(ppy)<sub>2</sub>(dtbpy)(PF<sub>6</sub>) **4c**.

<sup>c</sup> Using Ir(ppy)<sub>2</sub>(dtbpy)(PF<sub>6</sub>) **4c** (2.5 mol%).

### Optimization for the Carboxylation of Aryl Chloride **6e** with Carbon Dioxide (CO<sub>2</sub>)

**Table S15.** The screening of phosphine ligands



| Entry          | Ligand           | Conv. /% <sup>a</sup> | <b>2e</b> /% <sup>a</sup> |
|----------------|------------------|-----------------------|---------------------------|
| 1 <sup>b</sup> | PhXphos          | 72                    | 31                        |
| 2              | Xphos            | 70                    | 47                        |
| 3              | <i>t</i> BuXphos | 100                   | 96 (96) <sup>c</sup>      |

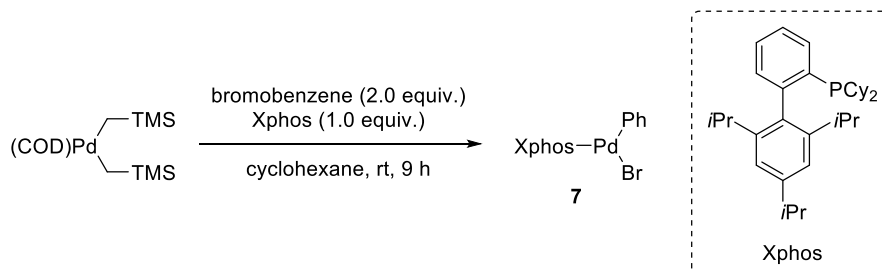
<sup>a</sup> Determined by <sup>1</sup>H-NMR spectra. <sup>b</sup> Reaction time is 12 h.

<sup>c</sup> Isolated yield after methyl esterification.

By using *t*BuXphos as an electron-rich ligand, the carboxylic acid **2e** was obtained in 96% yield probably due to the acceleration of the oxidative addition step.

## Mechanistic Study of Carboxylation Reaction

### Preparation of Arylpalladium Bromide Complex 7



In an argon-filled glovebox, a cyclohexane solution (2.0 mL) of bromobenzene (21  $\mu$ L, 0.20 mmol, 2.0 equiv.) with Xphos (48 mg, 0.10 mmol, 1.0 equiv.) and (COD)Pd(CH<sub>2</sub>TMS)<sub>2</sub><sup>10</sup> (39 mg, 0.10 mmol, 1.0 equiv.) was prepared in a screw vial containing a magnetic stirring bar. The resulting mixture was stirred at room temperature for 9 h. At the end of the reaction, the mixture was diluted with pentane (2 mL) and kept in  $-30$  °C freezer for 1 h. The precipitate that was formed was filtered through a fritted glass filter funnel, and washed with pentane. The precipitate was collected to give the target compound **7** as a white solid (31 mg, 42%), which was used without further purification.

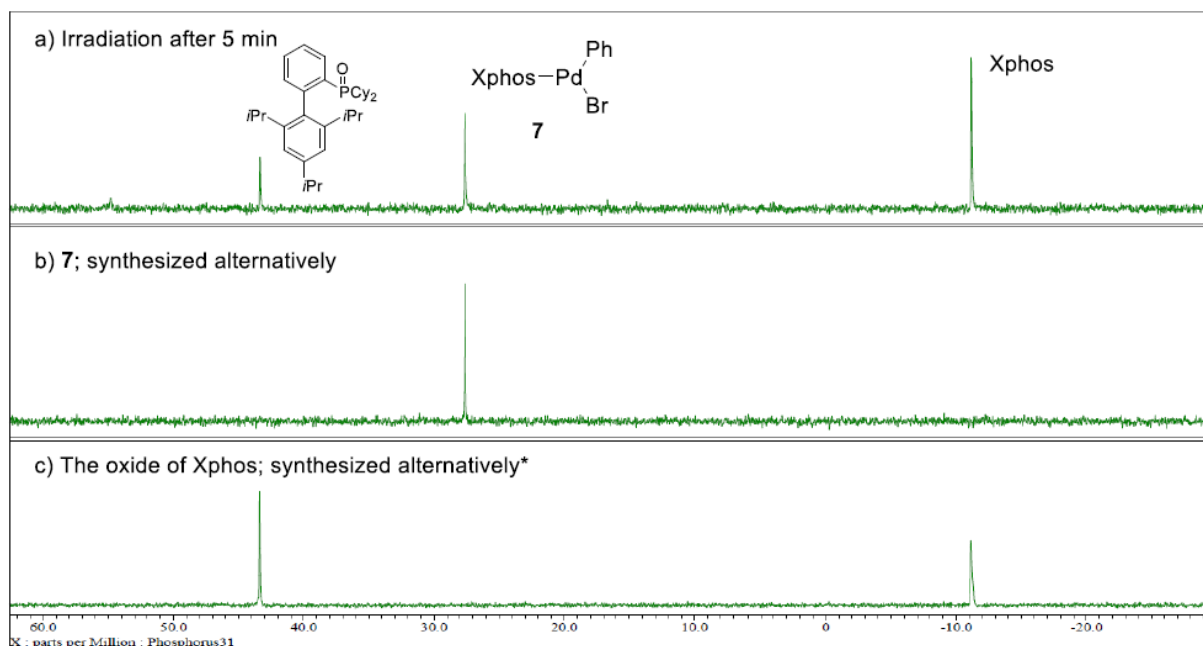
<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>):  $\delta$  = 0.55-0.67 (m, 2 H), 0.90 (d,  $J$  = 6.6 Hz, 6 H), 1.07-1.28 (m, 6 H), 1.39 (d,  $J$  = 6.9 Hz, 6 H), 1.57-1.74 (m, 14 H), 1.76-1.83 (m, 2 H), 1.91-1.99 (brs, 2 H), 2.18-2.27 (m, 2 H), 2.45 (septet,  $J$  = 6.7 Hz, 2 H), 3.12 (septet,  $J$  = 6.9 Hz, 1 H), 6.80 (t,  $J$  = 7.0 Hz, 1 H), 6.86-6.92 (m, 3 H), 7.03 (d,  $J$  = 6.3 Hz, 2 H), 7.13 (s, 2 H), 7.39-7.43 (m, 2 H), 7.67 (dt,  $J$  = 3.2, 6.3 Hz, 1 H) ppm

<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>):  $\delta$  = 24.4, 24.7, 25.5, 25.8, 27.3 (d,  $J$  = 10.7 Hz), 27.5-27.8 (m), 28.1, 31.5, 34.2, 35.0, 35.2, 123.3, 124.7, 125.7 (d,  $J$  = 3.6 Hz), 126.7 (d,  $J$  = 4.8 Hz), 127.2, 130.3, 131.8, 133.5 (d,  $J$  = 10.7 Hz), 134.38, 134.40 (d,  $J$  = 31.0 Hz), 136.8 (d,  $J$  = 3.6 Hz), 147.6 (d,  $J$  = 19.1 Hz), 149.1, 155.9 ppm

<sup>31</sup>P-NMR (202 MHz in CDCl<sub>3</sub>):  $\delta$  = 26.5 ppm

### Observation of the Reaction Intermediate under the Catalytic Conditions

A DMA solution (0.5 mL) of bromobenzene (10.5  $\mu$ L, 0.10 mmol) with palladium acetate (1.1 mg, 0.005 mmol, 5.0 mol%), Xphos (4.8 mg, 0.01 mmol, 10.0 mol%), Ir(ppy)<sub>2</sub>(dtbpy)(PF<sub>6</sub>) **4c** (1.8 mg, 0.002 mmol, 2.0 mol%), and *i*Pr<sub>2</sub>NEt (0.10 mL, 0.60 mmol, 6.0 equiv.) was prepared in a J. Young NMR tube. The mixture was irradiated with visible light ( $\lambda_{\text{irr.}}$  = 425 nm) using two sockets of blue LED lamp under CO<sub>2</sub> atmosphere at room temperature for 5 min. Arylpalladium bromide complex **7** was observed as the resting state.



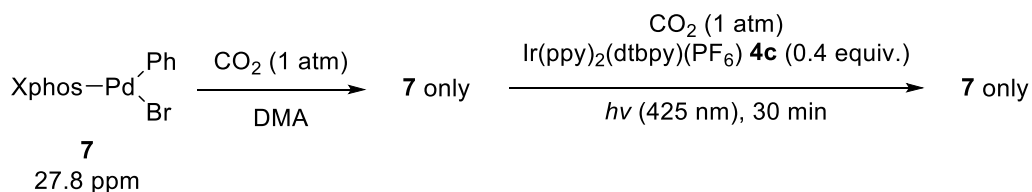
**Figure S1.**  $^{31}\text{P}$ -NMR Spectra under the Catalytic Carboxylation Conditions  
(202 MHz, DMA (0.5 mL) and  $i\text{Pr}_2\text{NEt}$  (0.1 mL))

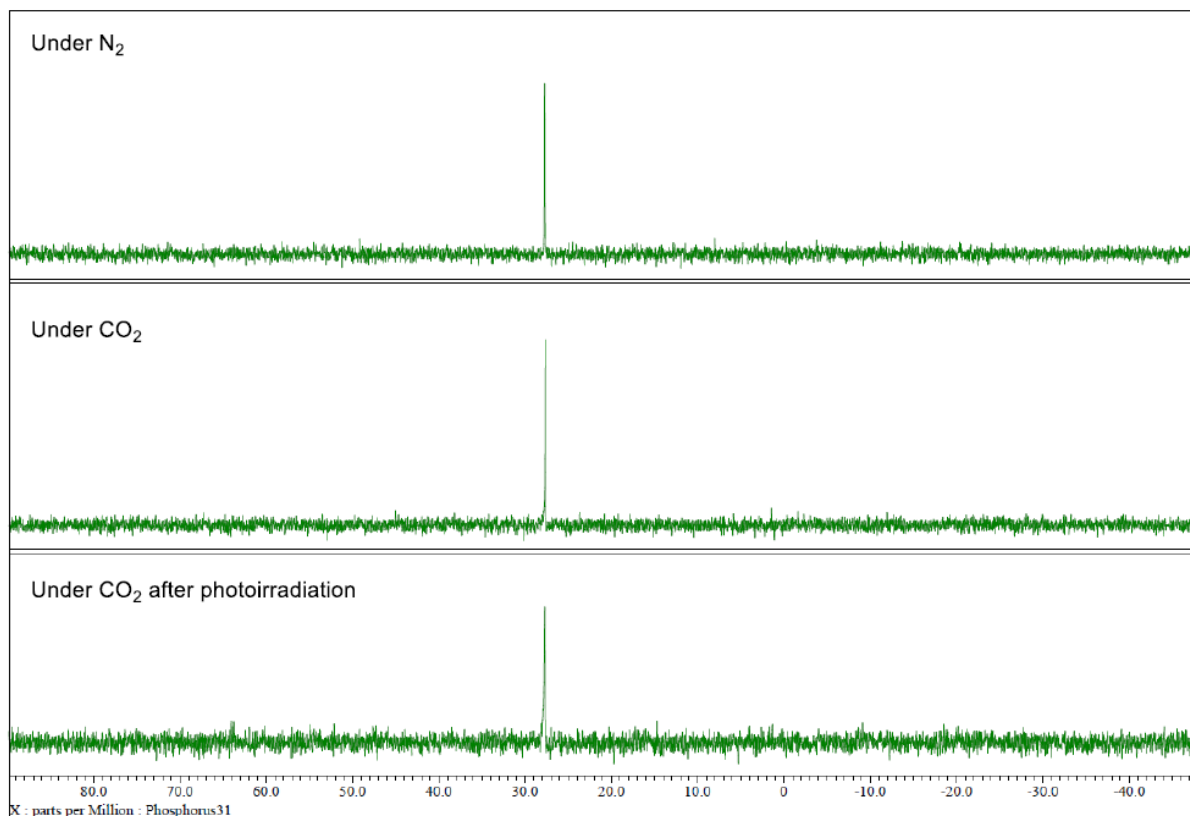
\* The oxide of Xphos was prepared in toluene under  $\text{O}_2$  atmosphere at 100 °C for 11 h.

### Reactivity of Arylpalladium Bromide Complex **7**

#### Reaction of Arylpalladium Bromide Complex **7** with $\text{CO}_2$ in the absence of $i\text{Pr}_2\text{NEt}$

A solution of arylpalladium bromide **7** (3.7 mg, 0.005 mmol) in DMA (0.6 mL) was put in a J. Young NMR tube under  $\text{CO}_2$  atmosphere at room temperature. No change was observed by  $^{31}\text{P}$  NMR. Then  $\text{Ir}(\text{ppy})_2(\text{dtbpy})(\text{PF}_6)$  **4c** (1.8 mg, 0.002 mmol) was added, and the mixture was irradiated with visible light ( $\lambda_{\text{irr.}} = 425 \text{ nm}$ ) under  $\text{CO}_2$  atmosphere at room temperature for 30 min. However, a new peak wasn't detected by  $^{31}\text{P}$ -NMR spectrum in the absence of  $i\text{Pr}_2\text{NEt}$ .



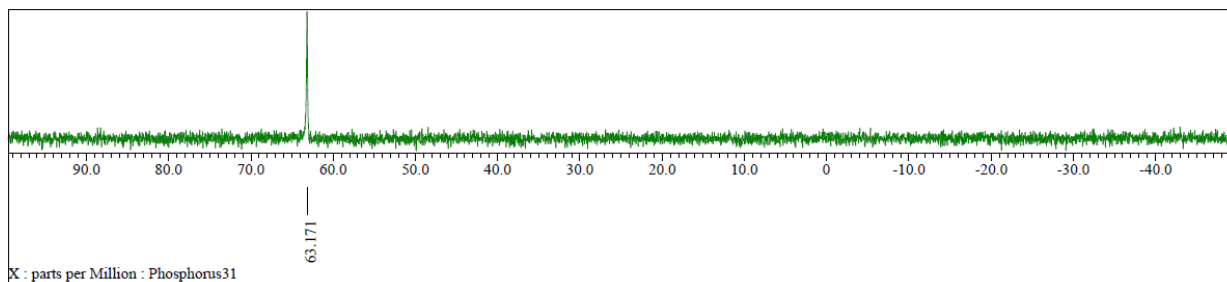
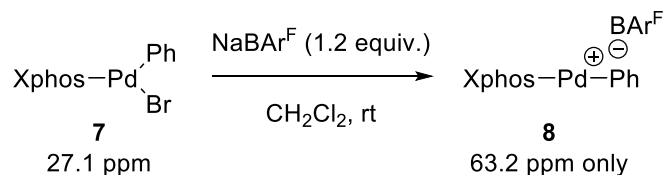


**Figure S2.**  $^{31}\text{P}$ -NMR Spectra under  $\text{CO}_2$  atmosphere

### Preparation of Cationic Arylpalladium Complex **8**

A solution of arylpalladium bromide **7** (3.7 mg, 0.005 mmol) and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ( $\text{NaBAR}^{\text{F}}$ , 5.3 mg, 0.006 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.6 mL) was put in a J. Young NMR tube under a nitrogen atmosphere at room temperature. After 40 min,  $^{31}\text{P}$ -NMR was measured and clean formation of a new signal was observed, which was thought to belong to arylpalladium cation **8** based on the similarity of the chemical shift of related species.<sup>16</sup>

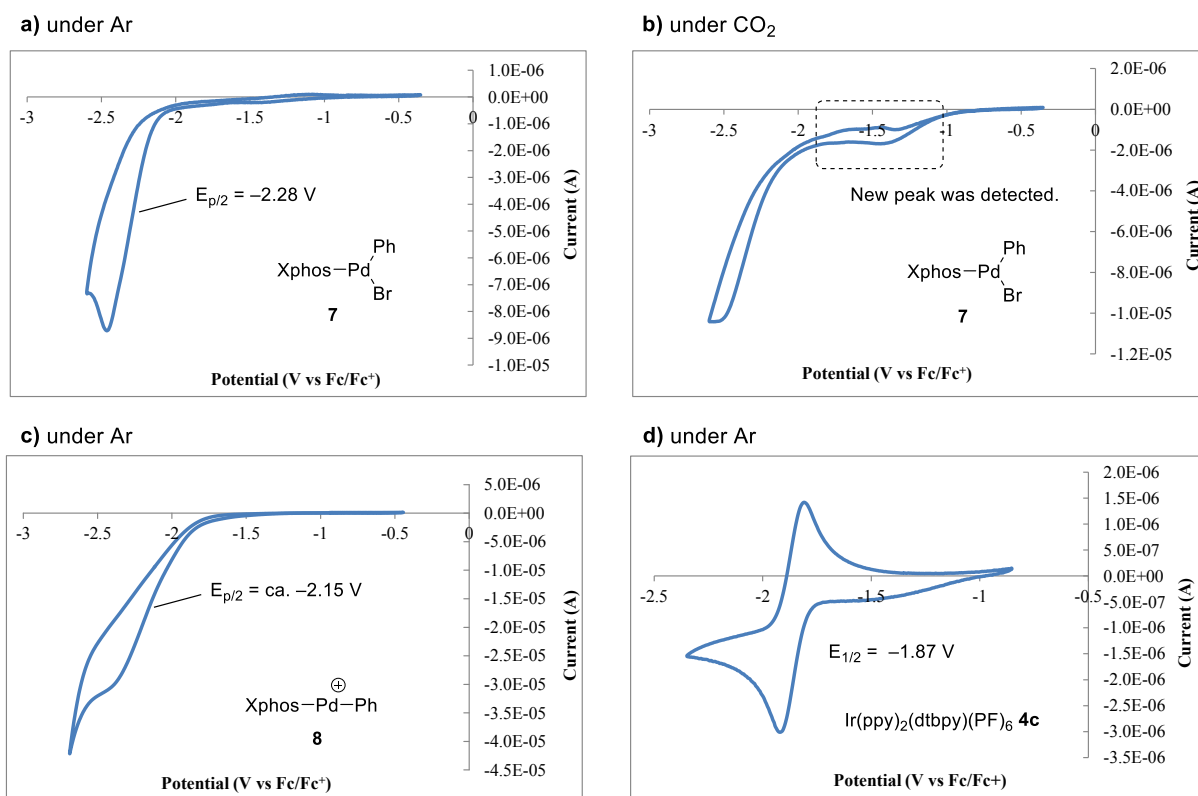




**Figure S3.**  $^{31}\text{P}$ -NMR Spectra of arylpalladium cation **8** *in situ*

### Cyclic Voltammograms of Aryl palladium complexes **7** and **8**

All voltammograms were measured at room temperature using  $\text{Ag}/\text{AgNO}_3$  reference electrode, a platinum (Pt) counter and working electrode. The conditions of the experiments were as follows: a THF or a  $\text{CH}_2\text{Cl}_2$  solution of 100 mM tetrabutylammonium hexafluorophosphate ( $\text{NBu}_4\text{PF}_6$ ) and a scan rate of 50 mV/s. The potentials of arylpalladium bromide **7** and cationic species **8** were taken at half-height of the peak ( $E_{\text{p}/2}$ ) since the reduction was non-reversible. To convert the potentials from  $\text{Ag}/\text{AgNO}_3$  to  $\text{Fc}/\text{Fc}^+$  reference, ferrocene was measured under the above conditions in a THF or a  $\text{CH}_2\text{Cl}_2$  solution, and  $-0.15 \text{ V}$  (THF) or  $-0.06 \text{ V}$  ( $\text{CH}_2\text{Cl}_2$ ) were subtracted from the measured values.



**Figure S4** : Cyclic voltammograms a) Arylpalladium bromide **7** (2.0 mM) in THF under Ar. b) Arylpalladium bromide **7** (2.0 mM) in THF under CO<sub>2</sub>. c) Arylpalladium cation **8** (1.0 mM) generated from arylpalladium bromide **7** (3.7 mg, 0.005 mmol) and NaBAR<sup>F</sup> (NaBAR<sup>F</sup>, 5.3 mg, 0.006 mmol) in CH<sub>2</sub>Cl<sub>2</sub> *in situ* (see. Figure S3). d) Ir(ppy)<sub>2</sub>(dtbpy)(PF<sub>6</sub>) **4c** (1.0 mM) in THF.

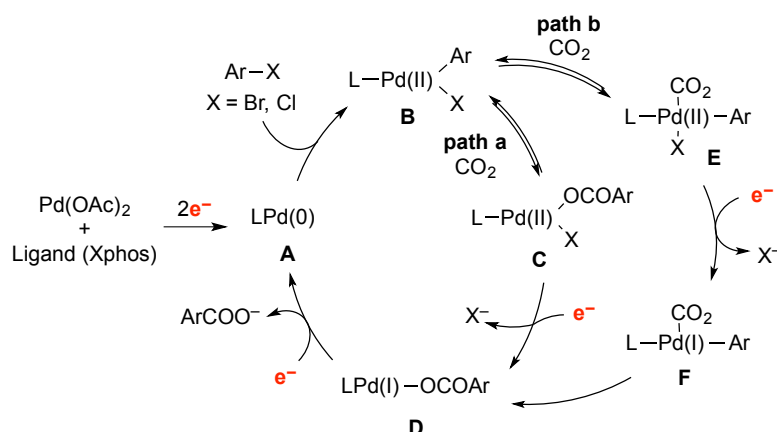
Figure S4b showed a new peak around -1.4 V by measuring under CO<sub>2</sub>. Although this new peak was rather weak, repeated experiments confirmed its presence. Furthermore, by bubbling Ar after CV measurement under CO<sub>2</sub>, the CV changed to the one shown in Figure S4a. Thus, a new species is thought to be generated by exposing arylpalladium bromide **7** to CO<sub>2</sub>.

### Proposed Mechanism (Carboxylation Reaction)

As the resting state of this reaction, aryl palladium **B** was observed by a <sup>31</sup>P-NMR spectrum under the catalytic reaction conditions (Figure S1). It was also found that the reduction potential of isolated PhPd(II)Br(Xphos) **7** was quite low ( $E_{p/2} = -2.28$  V vs Fc/Fc<sup>+</sup>) and this complex by itself could not be reduced under argon by the reduced form of Ir catalyst ( $E_{1/2} = -1.87$  V vs Fc/Fc<sup>+</sup>) (Figure S4a vs d). The reduction potential of [PhPd(Xphos)]<sup>+</sup> **8** was also lower ( $E_{p/2} = -2.15$  V vs Fc/Fc<sup>+</sup>) than the Ir catalyst, and direct reduction of these species is not likely (Figure S4c). Interestingly, CV measurement of this complex under CO<sub>2</sub> atmosphere showed a new peak at about -1.4 V (Figure S4b).

This means under CO<sub>2</sub> atmosphere, a new species, which can be reduced by the reduced form of Ir catalyst, appeared. However, when PhPdBr(Xphos) **7** was subjected to CO<sub>2</sub> atmosphere, a new peak wasn't detected by <sup>31</sup>P-NMR spectrum (Figure S2). From these data, we currently assume that there are two major possibilities for the actual palladium species reduced during the reaction.

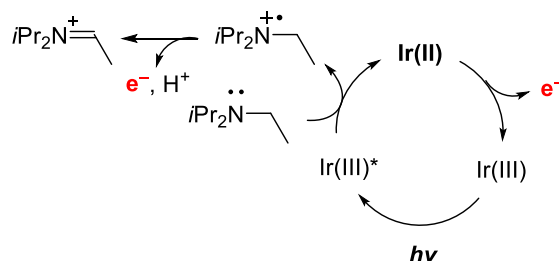
**Scheme S1.** Proposed mechanism of carboxylation reaction



The first one is (ArCOO)Pd(II)X(Xphos) **C** generated in a small amount in equilibrium with ArPd(II)X(Xphos) **B** under CO<sub>2</sub> as shown in Scheme S1 (path a). Photoredox-catalyzed one-electron reduction of (ArCOO)Pd(II)X(Xphos) **C** would give (ArCOO)Pd(I)(Xphos) **D** and X<sup>-</sup>, and the generated (ArCOO)Pd(I)(Xphos) **D** would undergo further one-electron reduction to give Pd(0)(Xphos)<sub>2</sub> and ArCOO<sup>-</sup>. As no detectable formation of (ArCOO)PdX(Xphos) **C** was observed when ArPdX(Xphos) **B** was subjected to CO<sub>2</sub> atmosphere, it is possible that there is an equilibrium between ArPdX(Xphos) **B** and (ArCOO)PdX(Xphos) **C**, the former of which is thermodynamically more stable. Therefore, through the reduction of the carboxylate complex **C** generated in a small amount from **B**, the equilibrium is shifted and the carboxylation reaction would proceed catalytically. It is noted that the decarboxylation of palladium carboxylates is a well-known process, although usually higher temperature (over 70 °C) is required (see reference 13 in the main text).

The other possibility of the reducible species is a CO<sub>2</sub>-coordinated ArPd(II)X(Xphos) **E**, again generated in a small amount, and this species would be able to undergo one-electron reduction to give a CO<sub>2</sub>-coordinated ArPd(I)(Xphos) species **F**, which would have higher ability to undergo addition to CO<sub>2</sub> to give (ArCOO)Pd(I)(Xphos) **D**. This would then undergo the similar process as described above (Scheme S1 (path b)). The additional one-electron reduction of ArPd(I)(Xphos) **F** to [ArPd(0)(Xphos)]<sup>-</sup> **G** is also possible, which might work as the actual carboxylation species.

**Scheme S2.** Reductive quenching cycle of  $[\text{Ir}(\text{ppy})_2(\text{dtbpy})]^+$



The reductive quenching of the photoexcited Ir(III)\* species by  $i\text{Pr}_2\text{NEt}$  produced Ir(II) as a reductive species and an amine radical cation. The one-electron reduction of Pd species proceeded by electron-transfer from the Ir(II) species. The produced amine radical cation likely released one or two protons and an electron to generate an iminium cation and/or enamine. In the proposed mechanism of carboxylation reaction, the counter cation of the two anions ( $\text{ArCOO}^-$  and  $\text{X}^-$ ) is both protons generated from the oxidized amine, and these two acids are neutralized with the excess  $\text{Cs}_2\text{CO}_3$  and/or amine.

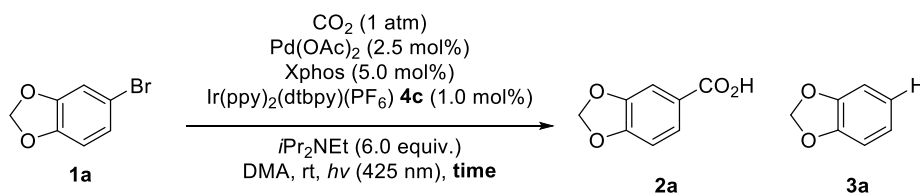
### Mechanistic Study of Reduction Reaction

The hydrogenated products **3** could be produced by the direct photo-redox catalyzed reduction using *i*Pr<sub>2</sub>NEt as an electron-donor as shown in Table S1. However, it is likely that there is also a Pd-catalyzed pathway for the production of the hydrogenated products **3**. We have carried out several experiments to clarify this point.

### Dependency of the Ratio of **2a** and **3a** on the Conversion of **1a**

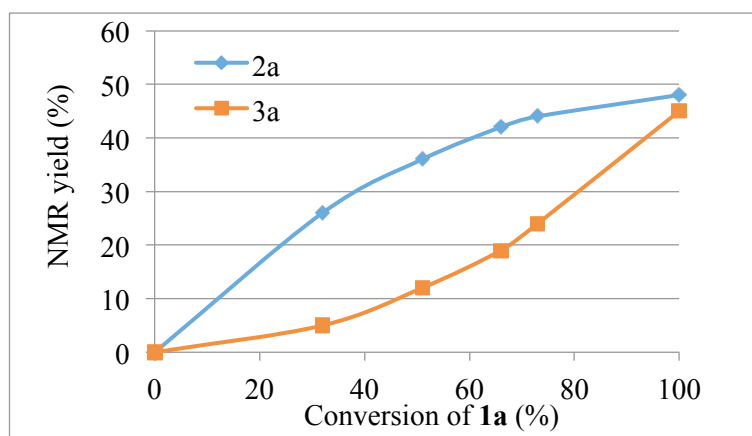
A DMA solution (1.0 mL) of **1a** (24  $\mu$ L, 0.20 mmol) with palladium acetate (1.1 mg, 0.005 mmol, 2.5 mol%), Xphos (4.8 mg, 0.01 mmol, 5.0 mol%), Ir(ppy)<sub>2</sub>(dtbpy)(PF<sub>6</sub>) **4c** (1.8 mg, 0.002 mmol, 1.0 mol%), and *i*Pr<sub>2</sub>NEt (0.21 mL, 1.2 mmol, 6.0 equiv.) was prepared in a test tube under nitrogen atmosphere. Then the gas phase was replaced by atmospheric pressure of CO<sub>2</sub>, and the reaction vessel was put in a water bath placed at a distance of 10 mm from light sources. The mixture was irradiated with visible light ( $\lambda_{irr.}$  = 425 nm) using two sockets of blue LED lamp for 15, 30, 60, 120 and 360 min respectively in the closed system. The product mixture was analyzed by <sup>1</sup>H NMR to determine the NMR yields of the starting material **1a**, the carboxylic acid **2a** and the hydrogenated product **3a**, respectively (internal standard : 1,4-dioxane).

**Table S16** The effect of the reaction time on the product distribution



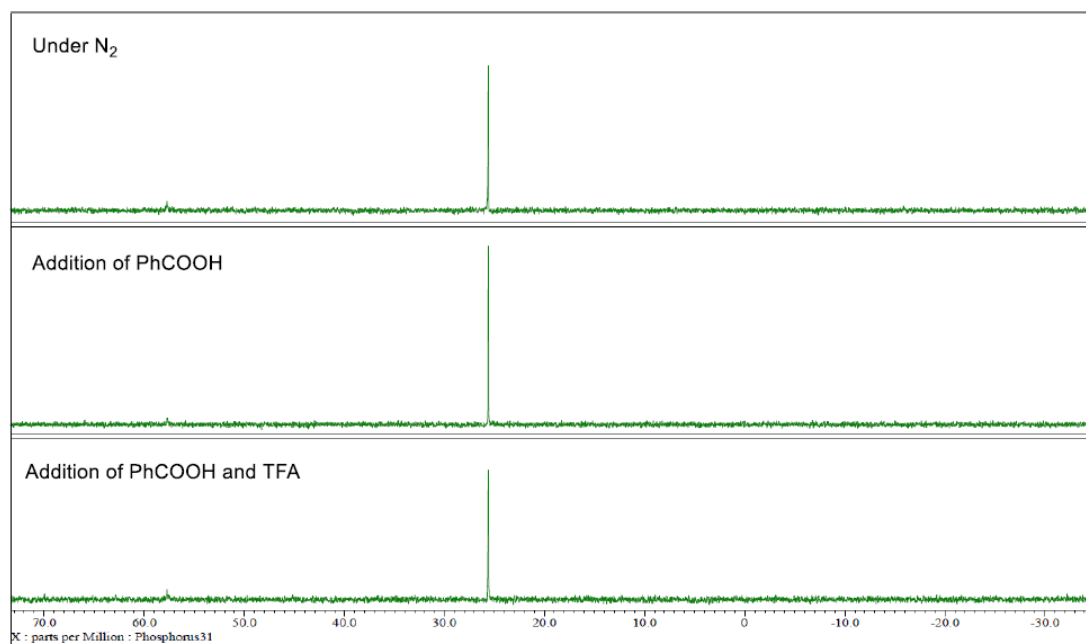
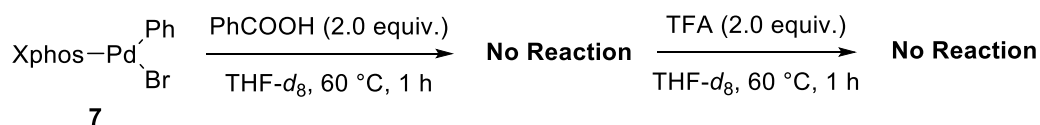
| Entry | Time/min. | Conv. /% <sup>a</sup> | <b>2a</b> /% <sup>a</sup> | <b>3a</b> /% <sup>a</sup> |
|-------|-----------|-----------------------|---------------------------|---------------------------|
| 1     | 15        | 32                    | 26                        | 5                         |
| 2     | 30        | 51                    | 36                        | 12                        |
| 3     | 60        | 66                    | 42                        | 19                        |
| 4     | 120       | 73                    | 44                        | 24                        |
| 5     | 360       | 100                   | 48                        | 45                        |

<sup>a</sup> Determined by <sup>1</sup>H-NMR spectra.



### Reaction of Arylpalladium Bromide Complex **7** with Benzoic Acid or TFA

A solution of arylpalladium bromide **7** (3.0 mg, 0.004 mmol) in THF-*d*<sub>8</sub> (0.6 mL) was put in a J. Young NMR tube under N<sub>2</sub> atmosphere at room temperature. Then benzoic acid (1.0 mg, 0.008 mmol, 2.0 equiv.) was added and the mixture was heated at 60 °C for 1 h. As no change was observed by <sup>31</sup>P NMR, trifluoroacetic acid (0.6 μL, 0.008 mmol, 2.0 equiv.) was further added and the mixture was heated at 60 °C for 1 h. However, a new peak wasn't detected by <sup>31</sup>P-NMR.

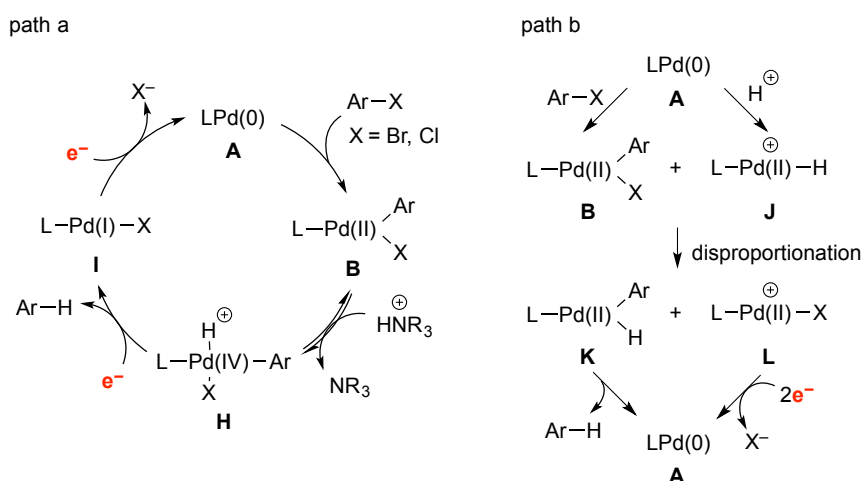


**Figure S5.** <sup>31</sup>P-NMR Spectra with Brønsted acids

### Proposed Mechanism (Reduction Reaction)

The time-dependence of the ratio of the carboxylation and reduction products in the absence of  $\text{Cs}_2\text{CO}_3$  (Table S16) showed that initially the carboxylation product was the major product and gradually the ratio of the reduction product increased. This result strongly supports that the produced ammonium salts of HBr and carboxylic acid play an important role in the formation of the reduction product. And also, the hydrogenated product **3a** was produced more by using TFA as a proton source (Table S8, entries 2,3). In contrast, this carboxylation reaction was improved by the addition of  $\text{Cs}_2\text{CO}_3$  as a base (Table S8, entry 6). It is likely that the protonation process is included in the mechanism of reduction reaction. From these data, we currently assume that there are two major possibilities for the Pd-catalyzed production of hydrogenated product.

**Scheme S3** Proposed mechanism of reduction reaction



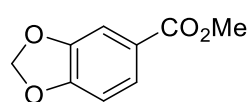
The first one is the protonation of  $\text{ArPd(II)X(Xphos)}$  intermediate to give  $[\text{ArPd(IV)(H)(Br)(Xphos)}]^+$  **H**, which would give  $(\text{Xphos})\text{Pd(I)X} **I** by photoredox-catalyzed one-electron reduction to release the hydrogenated product. The generated  $(\text{Xphos})\text{Pd(I)X} would undergo further one-electron reduction to give  $\text{Pd(0)(Xphos)}$  and halide anion. It might be possible that two successive electron-transfer occurs first to give to  $\text{ArPd(II)H(Xphos)}$ , which undergoes the reductive elimination to give the hydrogenated product. Although no formation of  $\text{PdH}$  species nor benzene was observed by the addition of TFA to  $\text{PhPdBr(Xphos)}$  in  $\text{THF-}d_8$  at rt to  $60^\circ\text{C}$  (Figure S5), this does not necessarily mean that the reduction pathway through  $\text{ArPdX(Xphos)}$  **B** does not exist because the reaction might be able to proceed through a small amount of the protonated species **H** generated *in situ* (Scheme S3, path a).$$

The other possibility is that in addition to oxidative addition of  $\text{ArX}$ ,  $\text{Pd(0)}$  would react with the acid generated, thus generating a  $\text{Pd(II)-hydride}$  **J** on one end and  $\text{ArPd(II)X}$  **B** on the other end. An

intermolecular event would generate the reduced product (Scheme S3, path b).

## Spectral Data of the Products

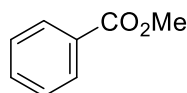
### The Carboxylation of Aryl Bromides



With PhXphos, **1a** (0.2 mmol, 40.5 mg) provided 32.9 mg (91% yield) of the corresponding compound **5a** as a white solid. The spectroscopic data coincided with those of the literature.<sup>17</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>):  $\delta$  = 3.87 (s, 3 H), 6.03 (s, 2 H), 6.83 (d,  $J$  = 8.5 Hz, 1 H), 7.46 (d,  $J$  = 2.0 Hz, 1 H), 7.64 (dd,  $J$  = 1.5, 8.0 Hz, 1 H) ppm

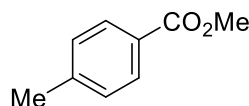
<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>):  $\delta$  = 52.0, 101.7, 107.9, 109.5, 124.1, 125.3, 147.7, 151.5, 166.4 ppm



With PhXphos, **1b** (0.2 mmol, 31.3 mg) provided 23.2 mg (85% yield) of the corresponding compound **5b** as colorless oil. The spectroscopic data coincided with those of the literature.<sup>18</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>):  $\delta$  = 3.92 (s, 3 H), 7.44 (t,  $J$  = 8.0 Hz, 2 H), 7.56 (t,  $J$  = 7.5 Hz, 1 H), 8.04 (d,  $J$  = 8.5 Hz, 2 H) ppm

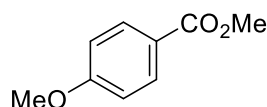
<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>):  $\delta$  = 52.1, 128.3, 129.5, 130.1, 132.9, 167.1 ppm



With PhXphos, **1c** (0.2 mmol, 34.1 mg) provided 26.3 mg (88% yield) of the corresponding compound **5c** as colorless oil. The spectroscopic data coincided with those of the literature.<sup>18</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>):  $\delta$  = 2.40 (s, 3 H), 3.90 (s, 3 H), 7.23 (d,  $J$  = 8.0 Hz, 2 H), 7.93 (d,  $J$  = 8.0 Hz, 2 H) ppm

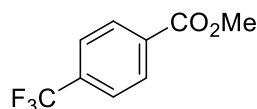
<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>):  $\delta$  = 21.6, 51.9, 127.4, 129.0, 129.6, 143.5, 167.2 ppm



With PhXphos, **1d** (0.2 mmol, 37.3 mg) provided 30.3 mg (91% yield) of the corresponding compound **5d** as a white solid. The spectroscopic data coincided with those of the literature.<sup>18</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>):  $\delta$  = 3.85 (s, 3 H), 3.88 (s, 3 H), 6.91 (d,  $J$  = 9.5 Hz, 2 H), 7.99 (d,  $J$  = 9.0 Hz, 2 H) ppm

<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>):  $\delta$  = 51.8, 55.4, 113.5, 122.5, 131.5, 163.3, 166.8 ppm



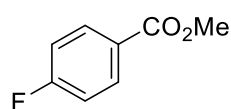
With PhXphos, **1e** (0.2 mmol, 45.0 mg) provided 33.8 mg (83% yield) of the corresponding compound **5e** as colorless oil. The spectroscopic data coincided



with those of the literature.<sup>17</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>): δ = 3.96 (s, 3 H), 7.71 (d, *J* = 8.0 Hz, 2 H), 8.15 (d, *J* = 8.5 Hz, 2 H) ppm

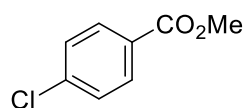
<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>): δ = 52.5, 123.6 (q, *J* = 274 Hz), 125.4 (q, *J* = 4 Hz), 129.6, 133.3, 134.4 (q, *J* = 33 Hz), 165.9 ppm



With PhXphos, **1f** (0.2 mmol, 35.0 mg) provided 29.7 mg (96% yield) of the corresponding compound **5f** as colorless oil. The spectroscopic data coincided with those of the literature.<sup>18</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>): δ = 3.91 (s, 3 H), 7.08-7.13 (m, 2 H), 8.03-8.07 (m, 2 H) ppm

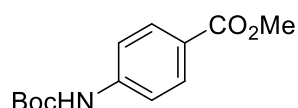
<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>): δ = 52.2, 115.5 (d, *J* = 23 Hz), 126.3 (d, *J* = 2 Hz), 132.1 (d, *J* = 8 Hz), 165.7 (d, *J* = 255 Hz), 166.1 ppm



With PhXphos, **1g** (0.2 mmol, 38.4 mg) for 6 h provided 30.8 mg (90% yield) of the corresponding compound **5g** as a white solid. The spectroscopic data coincided with those of the literature.<sup>18</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>): δ = 3.91 (s, 3 H), 7.41 (d, *J* = 8.5 Hz, 2 H), 7.97 (d, *J* = 8.5 Hz, 2 H) ppm

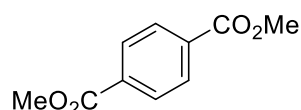
<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>): δ = 52.3, 128.5, 128.7, 130.9, 139.3, 166.2 ppm



With *t*BuXphos, **1h** (0.2 mmol, 54.4 mg) provided 38.7 mg (77% yield) of the corresponding compound **5h** as a white solid. The spectroscopic data coincided with those of the literature.<sup>19</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>): δ = 1.51 (s, 9 H), 3.88 (s, 3 H), 6.75 (s, 1 H), 7.43 (d, *J* = 9.0 Hz, 2 H), 7.97 (d, *J* = 8.5 Hz, 2 H) ppm

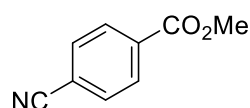
<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>): δ = 28.2, 51.9, 81.2, 117.3, 124.3, 130.9, 142.7, 152.2, 166.7 ppm



With *t*BuXphos, **1i** (0.2 mmol, 43.0 mg) provided 29.3 mg (76% yield) of the corresponding compound **5i** as a white solid. The spectroscopic data coincided with those of the literature.<sup>17</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>): δ = 3.94 (s, 6 H), 8.10 (s, 4 H) ppm

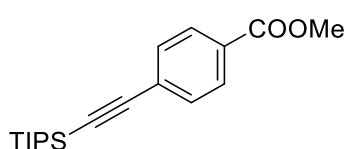
<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>): δ = 52.4, 129.5, 133.9, 166.3 ppm



With *t*BuXphos, **1j** (0.2 mmol, 36.4 mg) provided 24.4 mg (76% yield) of the corresponding compound **5j** as a white solid. The spectroscopic data coincided with those of the literature.<sup>20</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>): δ = 3.96 (s, 3 H), 7.74 (d, *J* = 9.0 Hz, 2 H), 8.14 (d, *J* = 8.5 Hz, 2 H) ppm

<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>): δ = 52.7, 116.4, 118.0, 130.1, 132.2, 133.9, 165.4 ppm



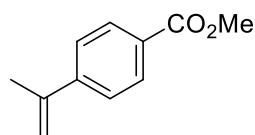
With PhXphos, **1k** (0.2 mmol, 67.5 mg) provided 54.0 mg (85% yield) of the corresponding compound **5k** as colorless oil.

IR (neat): 2944, 2866, 2156, 1605, 1463, 1436, 1276, 1107, 844, 680 cm<sup>-1</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>): δ = 1.12-1.15 (m, 21 H), 3.92 (s, 3 H), 7.50-7.54 (m, 2 H), 7.95-7.98 (m, 2 H) ppm

<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>): δ = 11.2, 18.6, 52.2, 94.3, 106.1, 128.1, 129.3, 129.5, 131.9, 166.5 ppm

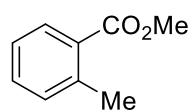
HRMS(FD<sup>+</sup>): Calcd. C<sub>19</sub>H<sub>28</sub>O<sub>2</sub>Si [M]<sup>+</sup>: 316.1859, Found: 316.1841 m/z.



With PhXphos, **1l** (0.2 mmol, 39.5 mg) provided 29.0 mg (82% yield) of the corresponding compound **5l** as a white solid. The spectroscopic data coincided with those of the literature.<sup>21</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>): δ = 2.17 (s, 3 H), 3.91 (s, 3 H), 5.19 (s, 1 H), 5.47 (s, 1 H), 7.52 (d, *J* = 8.5 Hz, 2 H), 7.99 (d, *J* = 8.5 Hz, 2 H) ppm

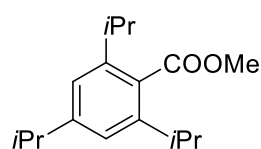
<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>): δ = 21.6, 52.0, 114.6, 125.4, 128.9, 129.5, 142.4, 145.6, 166.9 ppm



With PhXphos, **1m** (0.2 mmol, 34.2 mg) provided 24.0 mg (80% yield) of the corresponding compound **5m** as colorless oil. The spectroscopic data coincided with those of the literature.<sup>22</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>): δ = 2.60 (s, 3 H), 3.89 (s, 3 H), 7.22-7.27 (m, 2 H), 7.40 (dt, *J* = 1.5, 7.5 Hz, 1 H), 7.91 (dd, *J* = 1.3, 8.3 Hz, 1 H) ppm

<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>): δ = 21.7, 51.8, 125.7, 129.5, 130.5, 131.7, 131.9, 140.2, 168.1 ppm



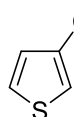
With PhXphos, **1n** (0.2 mmol, 56.6 mg) provided 39.9 mg (76% yield) of the corresponding compound **5n** as a white solid.

IR (neat): 2962, 2871, 1726, 1606, 1460, 1430, 1254, 1078, 876, 772 cm<sup>-1</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>): δ = 1.24 (d, *J* = 7.5 Hz, 18 H), 2.82 (septet, *J* = 7.0 Hz, 2 H), 2.89 (septet, *J* = 7.0 Hz, 1 H), 3.89 (s, 3 H), 7.01 (s, 2 H) ppm

<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>): δ = 23.9, 24.1, 31.6, 34.4, 51.8, 120.8, 130.3, 144.8, 150.2, 171.4 ppm

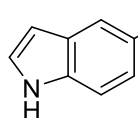
HRMS(FD<sup>+</sup>): Calcd. C<sub>17</sub>H<sub>26</sub>O<sub>2</sub> [M]<sup>+</sup>: 262.1933, Found: 262.1887 m/z.



With PhXphos, **1o** (0.2 mmol, 32.6 mg) provided 20.6 mg (72% yield) of the corresponding compound **5o** as colorless oil. The spectroscopic data coincided with those of the literature.<sup>18</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>): δ = 3.89 (s, 3 H), 7.30 (dd, *J* = 2.8, 5.3 Hz, 1 H), 7.52 (dd, *J* = 1.0, 5.0 Hz, 1 H), 8.10 (dd, *J* = 1.0, 3.5 Hz, 1 H) ppm

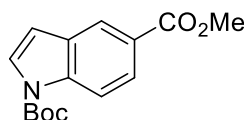
<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>): δ = 51.8, 126.0, 127.9, 132.7, 133.5, 163.2 ppm



With PhXphos, **1p** (0.2 mmol, 39.1 mg) provided 15.7 mg (45% yield) of the corresponding compound **5p** as a white solid. The spectroscopic data coincided with those of the literature.<sup>23</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>): δ = 3.94 (s, 3 H), 6.65 (s, 1 H), 7.28 (t, *J* = 2.8 Hz, 1 H), 7.41 (d, *J* = 9.0 Hz, 1 H), 7.92 (dd, *J* = 1.5, 8.5 Hz, 1 H), 8.43 (s, 1 H), 8.50 (br, 1 H) ppm

<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>): δ = 51.9, 104.0, 110.7, 121.8, 123.3, 123.8, 125.5, 127.4, 138.3, 168.3 ppm



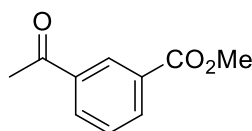
With PhXphos, **1q** (0.2 mmol, 59.2 mg) provided 39.5 mg (72% yield) of the corresponding compound **5q** as colorless oil.

IR (neat): 3152, 2980, 1739, 1718, 1615, 1438, 1237, 1092, 1024, 758 cm<sup>-1</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>): δ = 1.68 (s, 9 H), 3.94 (s, 3 H), 6.64 (d, *J* = 4.0 Hz, 1 H), 7.64 (d, *J* = 4.0 Hz, 1 H), 8.01 (dd, *J* = 1.5, 8.5 Hz, 1 H), 8.18 (brd, *J* = 8.5 Hz, 1 H), 8.29 (d, *J* = 1.5 Hz, 1 H) ppm

<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>): δ = 28.1, 52.0, 84.3, 107.7, 114.8, 123.2, 124.6, 125.5, 127.1, 130.3, 137.8, 149.4, 167.5 ppm

HRMS(FD<sup>+</sup>): Calcd. C<sub>15</sub>H<sub>17</sub>NO<sub>4</sub> [M]<sup>+</sup>: 275.1158, Found: 275.1123 m/z.

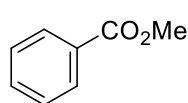


With *t*BuXphos, **1r** (0.2 mmol, 39.8 mg) provided 23.8 mg (67% yield) of the corresponding compound **5r** as a white solid. The spectroscopic data coincided with those of the literature.<sup>24</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>): δ = 2.65 (s, 3 H), 3.95 (s, 3 H), 7.55 (t, *J* = 8.0 Hz, 1 H), 8.15 (td, *J* = 1.5, 8.0 Hz, 1 H), 8.22 (td, *J* = 1.5, 8.0 Hz, 1 H), 8.58 (t, *J* = 1.8 Hz, 1 H) ppm

<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>): δ = 26.7, 52.4, 128.8, 129.5, 130.6, 132.3, 133.9, 137.2, 166.2, 197.2 ppm

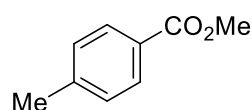
## The Carboxylation of Aryl Chlorides



**6b** (0.2 mmol, 22.3 mg) provided 21.7 mg (80% yield) of the corresponding compound **5b** as colorless oil. The spectroscopic data coincided with those of the literature.<sup>18</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>):  $\delta$  = 3.92 (s, 3 H), 7.44 (t,  $J$  = 8.0 Hz, 2 H), 7.56 (t,  $J$  = 7.5 Hz, 1 H), 8.04 (d,  $J$  = 8.5 Hz, 2 H) ppm

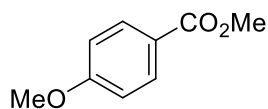
<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>):  $\delta$  = 52.1, 128.3, 129.5, 130.1, 132.9, 167.1 ppm



**6c** (0.2 mmol, 25.3 mg) provided 18.4 mg (61% yield) of the corresponding compound **5c** as colorless oil. The spectroscopic data coincided with those of the literature.<sup>18</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>):  $\delta$  = 2.40 (s, 3 H), 3.90 (s, 3 H), 7.23 (d,  $J$  = 8.0 Hz, 2 H), 7.93 (d,  $J$  = 8.0 Hz, 2 H) ppm

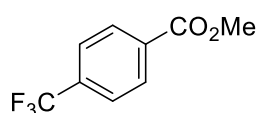
<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>):  $\delta$  = 21.6, 51.9, 127.4, 129.0, 129.6, 143.5, 167.2 ppm



**6d** (0.2 mmol, 28.5 mg) provided 19.5 mg (59% yield) of the corresponding compound **5d** as a white solid. The spectroscopic data coincided with those of the literature.<sup>18</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>):  $\delta$  = 3.85 (s, 3 H), 3.88 (s, 3 H), 6.91 (d,  $J$  = 9.5 Hz, 2 H), 7.99 (d,  $J$  = 9.0 Hz, 2 H) ppm

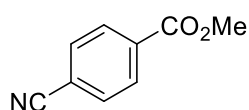
<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>):  $\delta$  = 51.8, 55.4, 113.5, 122.5, 131.5, 163.3, 166.8 ppm



**6e** (0.2 mmol, 35.9 mg) provided 39.1 mg (96% yield) of the corresponding compound **5e** as colorless oil. The spectroscopic data coincided with those of the literature.<sup>17</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>):  $\delta$  = 3.96 (s, 3 H), 7.71 (d,  $J$  = 8.0 Hz, 2 H), 8.15 (d,  $J$  = 8.5 Hz, 2 H) ppm

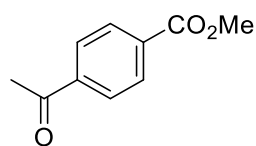
<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>):  $\delta$  = 52.5, 123.6 (q,  $J$  = 274 Hz), 125.4 (q,  $J$  = 4 Hz), 129.6, 133.3, 134.4 (q,  $J$  = 33 Hz), 165.9 ppm



**6j** (0.2 mmol, 27.6 mg) provided 28.9 mg (90% yield) of the corresponding compound **5j** as a white solid.<sup>20</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>):  $\delta$  = 3.96 (s, 3 H), 7.74 (d,  $J$  = 9.0 Hz, 2 H), 8.14 (d,  $J$  = 8.5 Hz, 2 H) ppm

<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>):  $\delta$  = 52.7, 116.4, 118.0, 130.1, 132.2, 133.9, 165.4 ppm

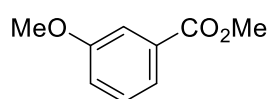


**6s** (0.2 mmol, 31.1 mg) provided 17.0 mg (48% yield) of the corresponding compound **5s** as a white solid. The spectroscopic data coincided with those of the literature.<sup>24</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>):  $\delta$  = 2.64 (s, 3 H), 3.95 (s, 3 H), 8.01 (d,  $J$  = 7.0

Hz, 2 H), 8.12 (d,  $J$  = 8.5 Hz, 2 H) ppm

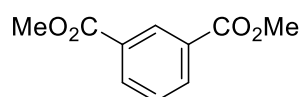
<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>):  $\delta$  = 26.9, 52.5, 128.2, 129.8, 133.9, 140.2, 166.2, 197.6 ppm



**6t** (0.2 mmol, 28.3 mg) provided 25.2 mg (76% yield) of the corresponding compound **5t** as colorless oil. The spectroscopic data coincided with those of the literature.<sup>22</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>):  $\delta$  = 3.84 (s, 3 H), 3.90 (s, 3 H), 7.09 (dd,  $J$  = 2.8, 8.3 Hz, 1 H), 7.33 (t,  $J$  = 8.0 Hz, 1 H), 7.54 (dd,  $J$  = 1.5, 2.5 Hz, 1 H), 7.62 (d,  $J$  = 8.0 Hz, 1 H) ppm

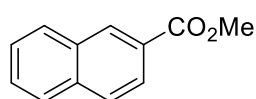
<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>):  $\delta$  = 52.2, 55.4, 113.9, 119.5, 121.9, 129.4, 131.4, 159.5, 167.0 ppm



**6u** (0.2 mmol, 34.1 mg) provided 34.2 mg (88% yield) of the corresponding compound **5u** as a white solid. The spectroscopic data coincided with those of the literature.<sup>25</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>):  $\delta$  = 3.94 (s, 3 H), 7.53 (t,  $J$  = 7.3 Hz, 1 H), 8.22 (dd,  $J$  = 1.5, 8.0 Hz, 2 H), 8.68 (s, 1 H) ppm

<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>):  $\delta$  = 52.3, 128.6, 130.5, 130.7, 133.8, 166.2 ppm



**6v** (0.2 mmol, 32.5 mg) provided 35.5 mg (95% yield) of the corresponding compound **5v** as a white solid. The spectroscopic data coincided with those of the literature.<sup>20</sup>

<sup>1</sup>H-NMR (500 MHz in CDCl<sub>3</sub>):  $\delta$  = 3.99 (s, 3 H), 7.57 (td,  $J$  = 7.0, 14.0 Hz, 2 H), 7.88 (d,  $J$  = 8.5 Hz, 2 H), 7.96 (d,  $J$  = 8.0 Hz, 1 H), 8.07 (dd,  $J$  = 1.5, 8.5 Hz, 1 H), 8.62 (s, 1 H) ppm

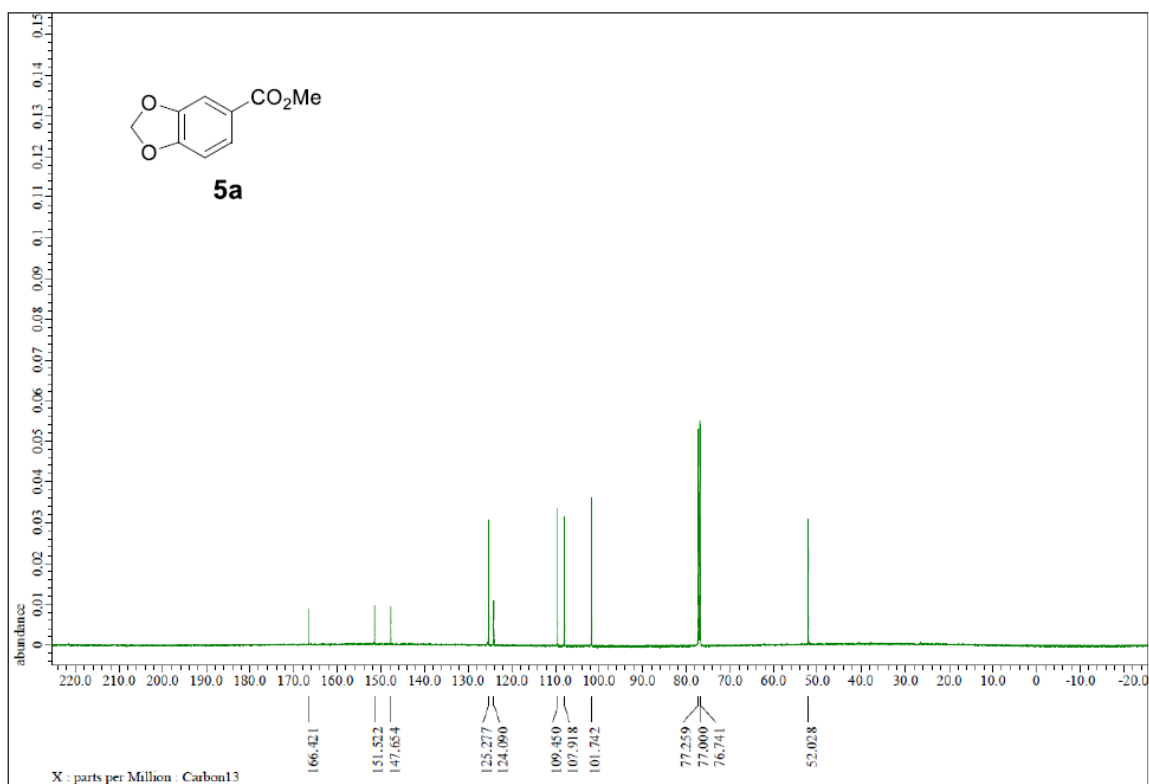
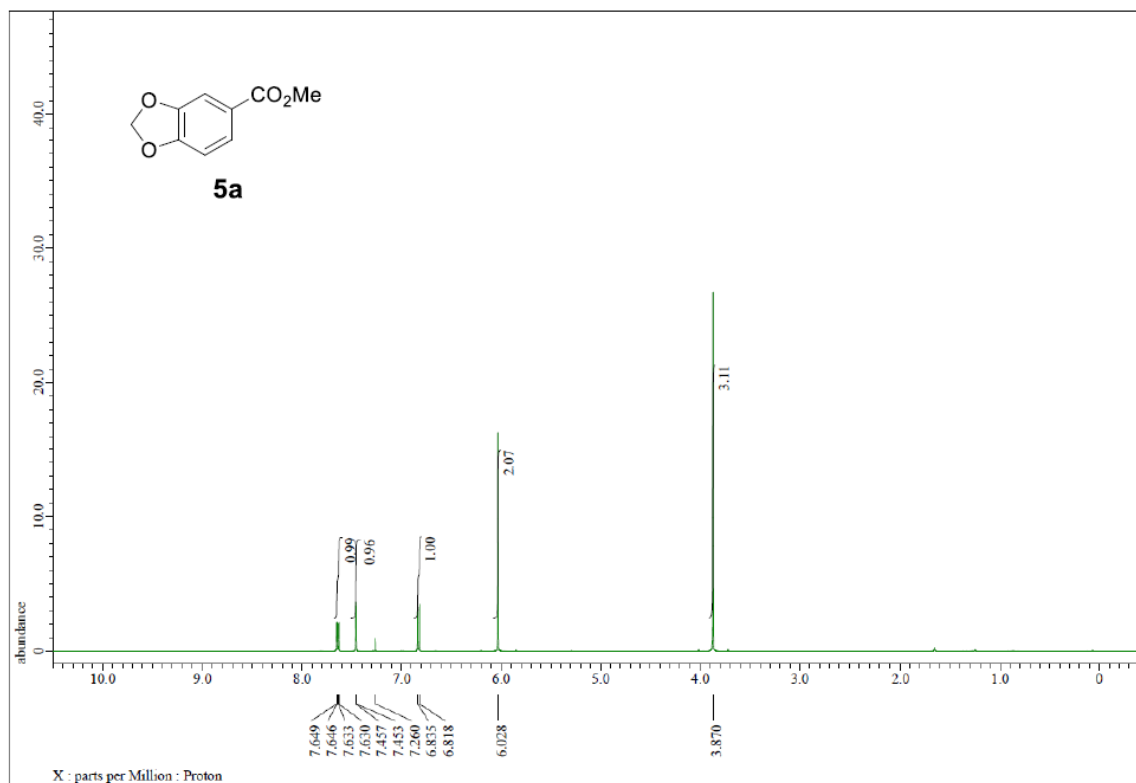
<sup>13</sup>C-NMR (125 MHz in CDCl<sub>3</sub>):  $\delta$  = 52.2, 125.2, 126.6, 127.3, 127.7, 128.1, 128.2, 129.3, 131.0, 132.4, 135.5, 167.2 ppm

## References

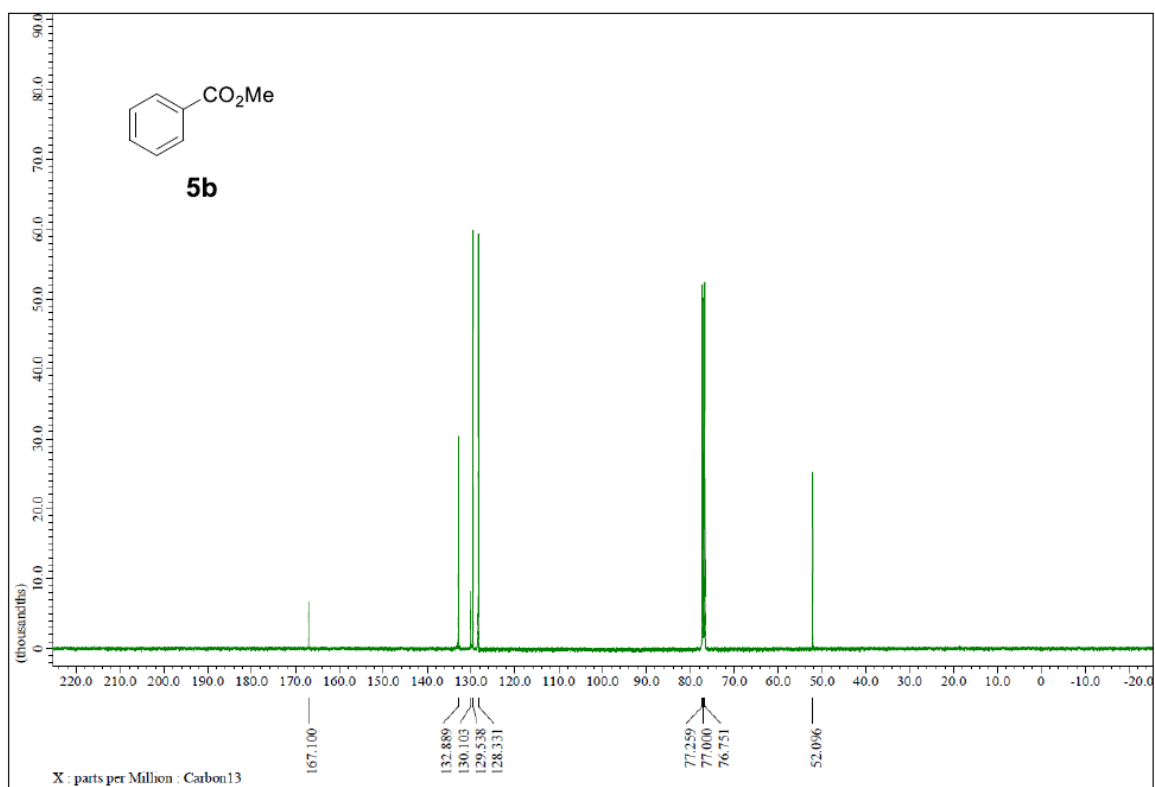
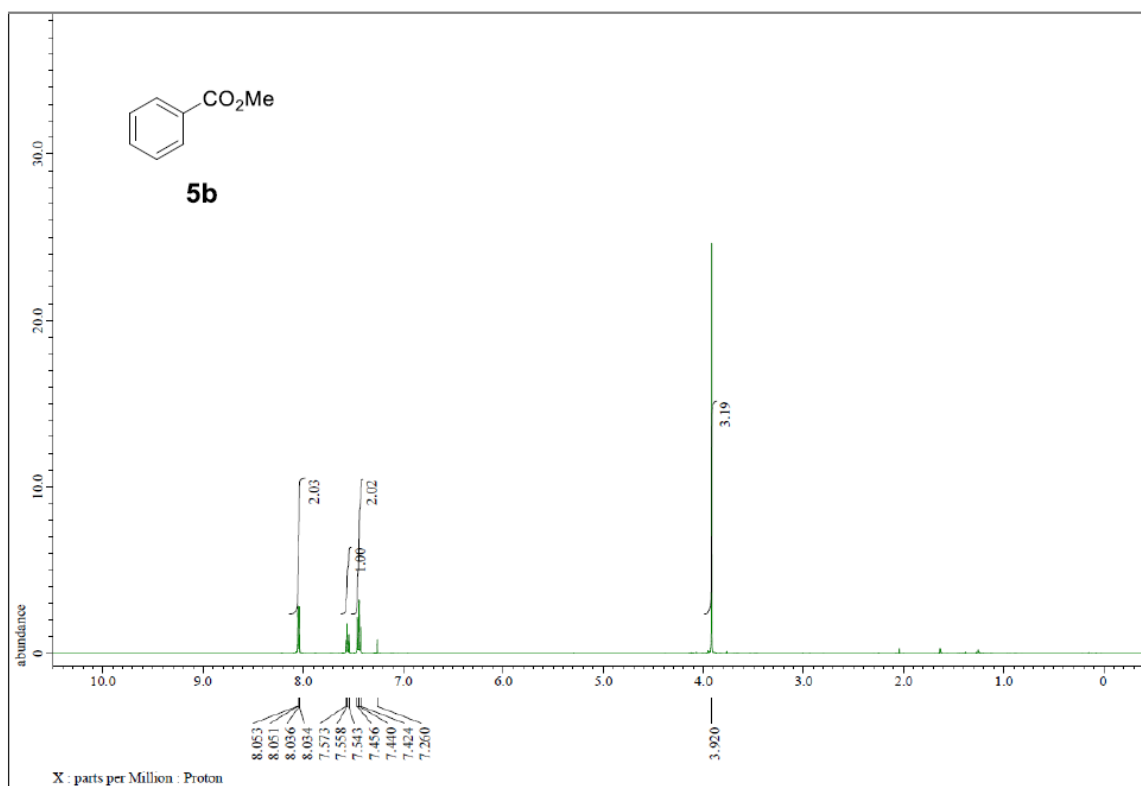
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## Spectral Data

### $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Compounds 5a

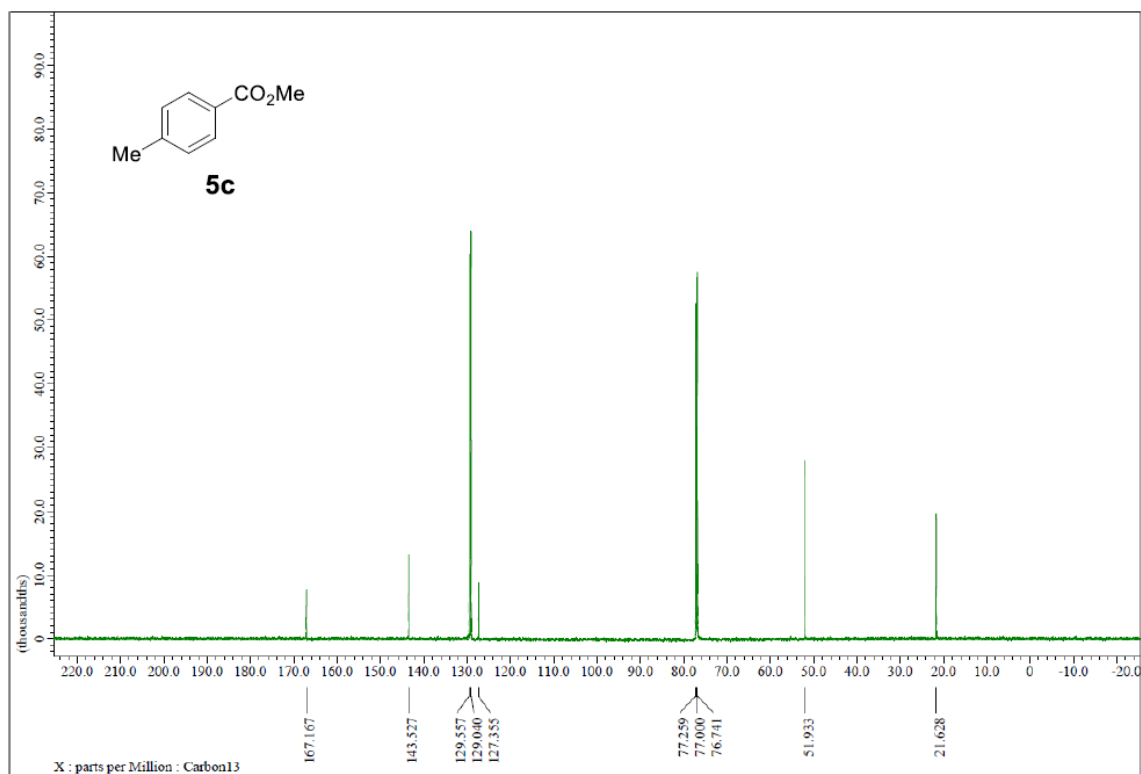
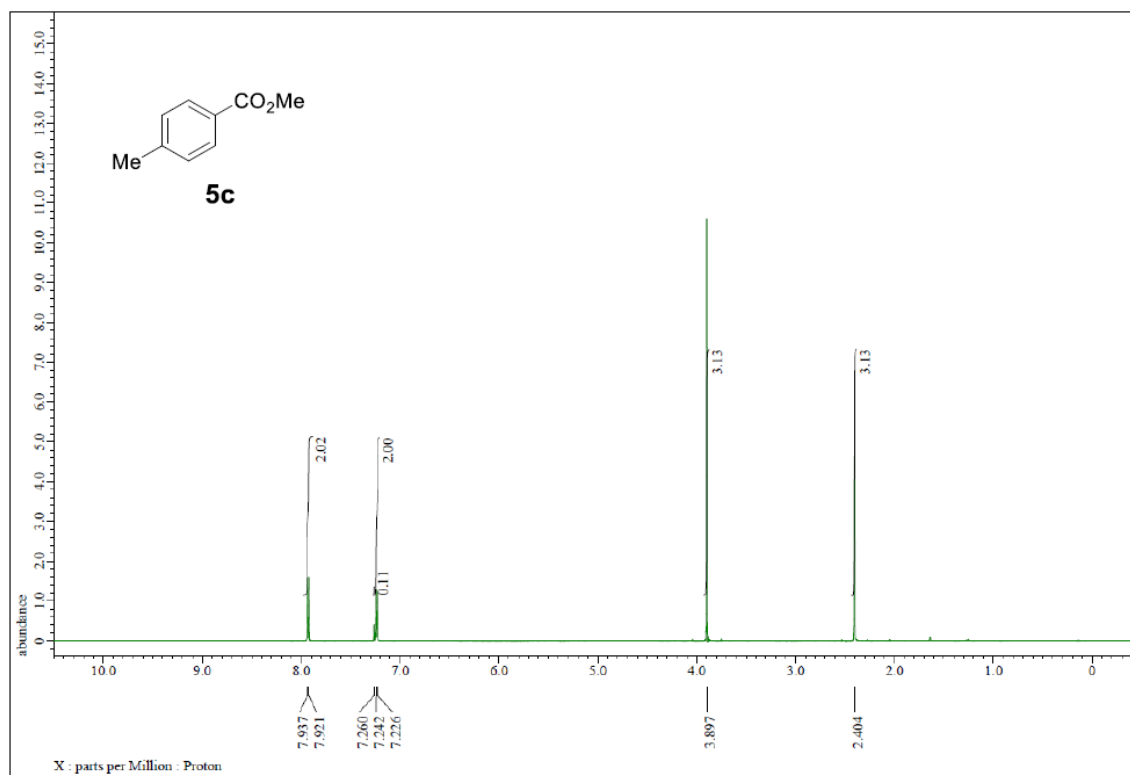


# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compounds 5b

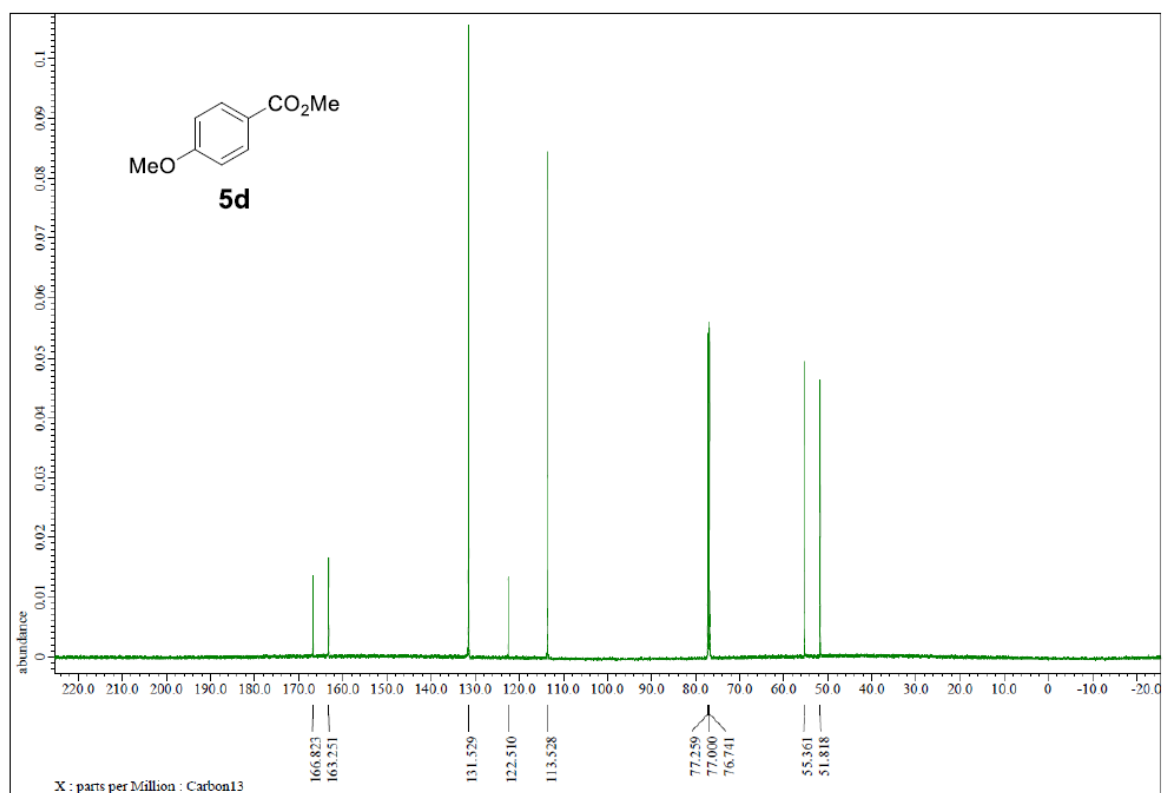
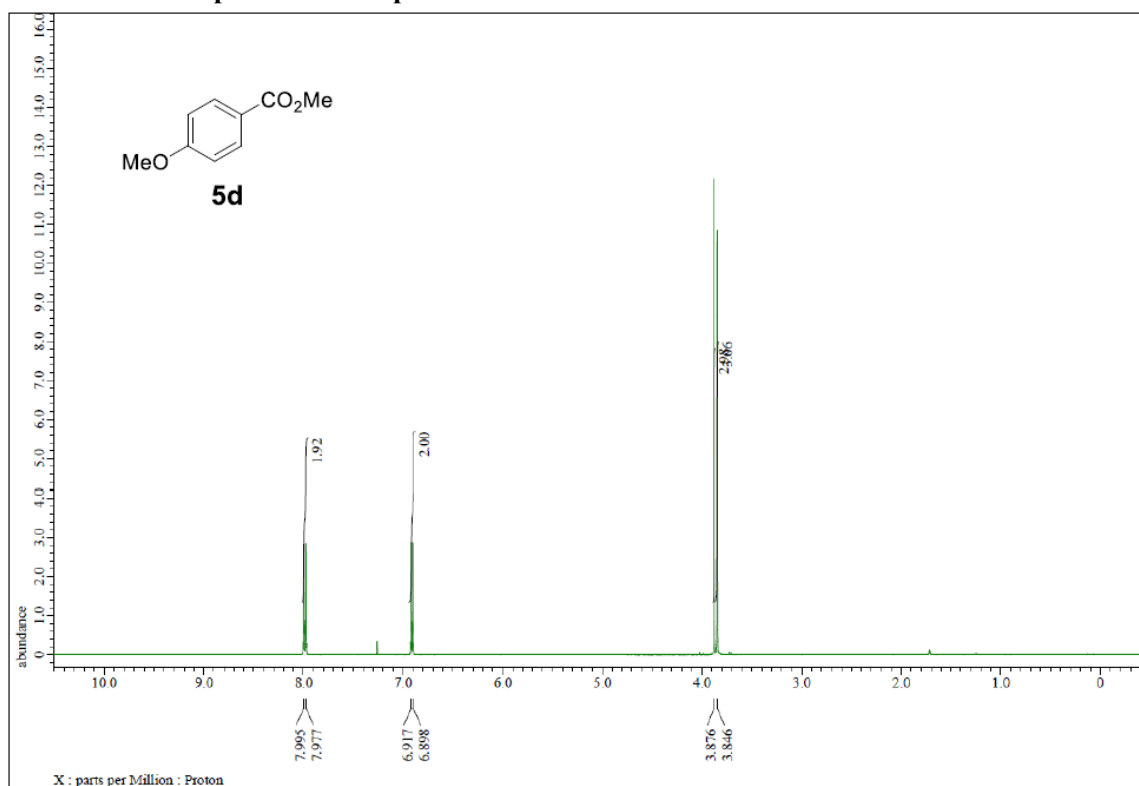




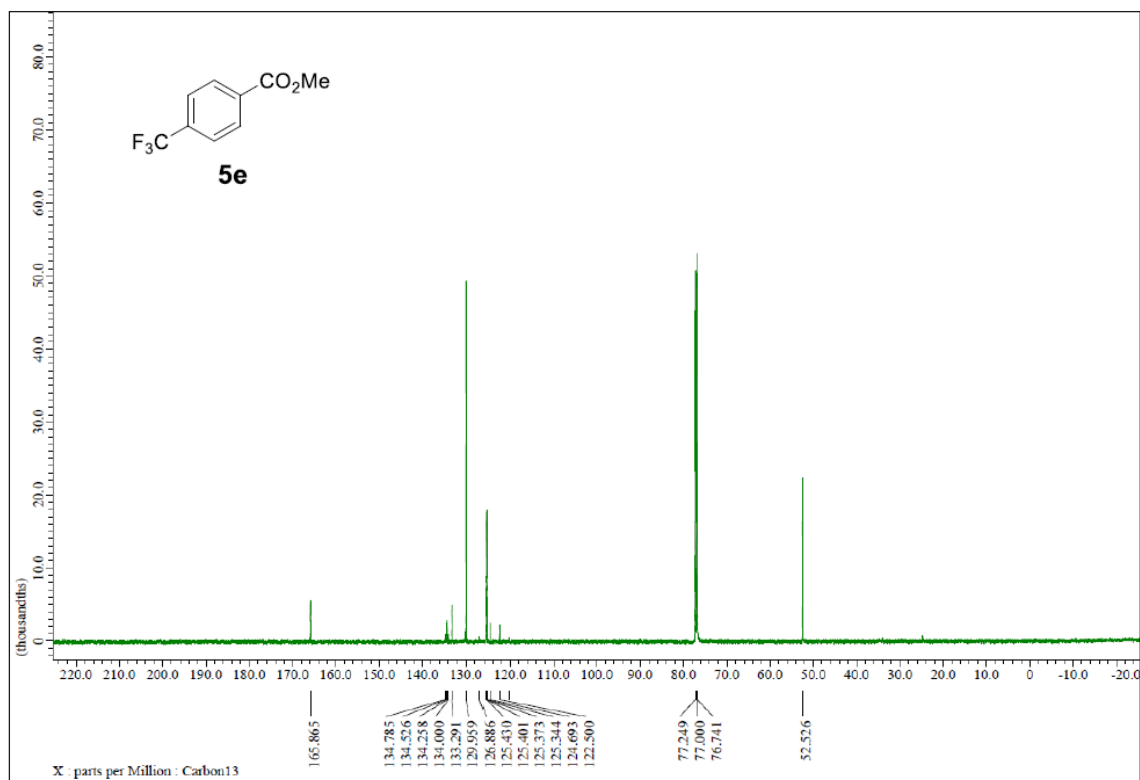
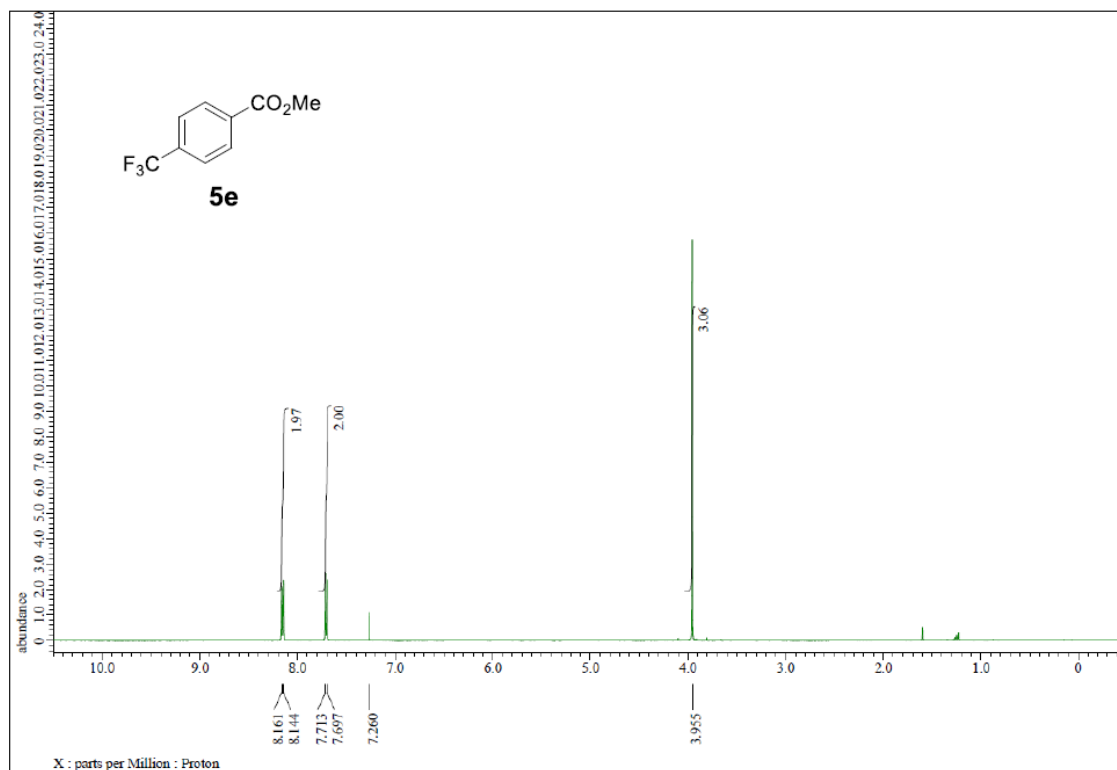
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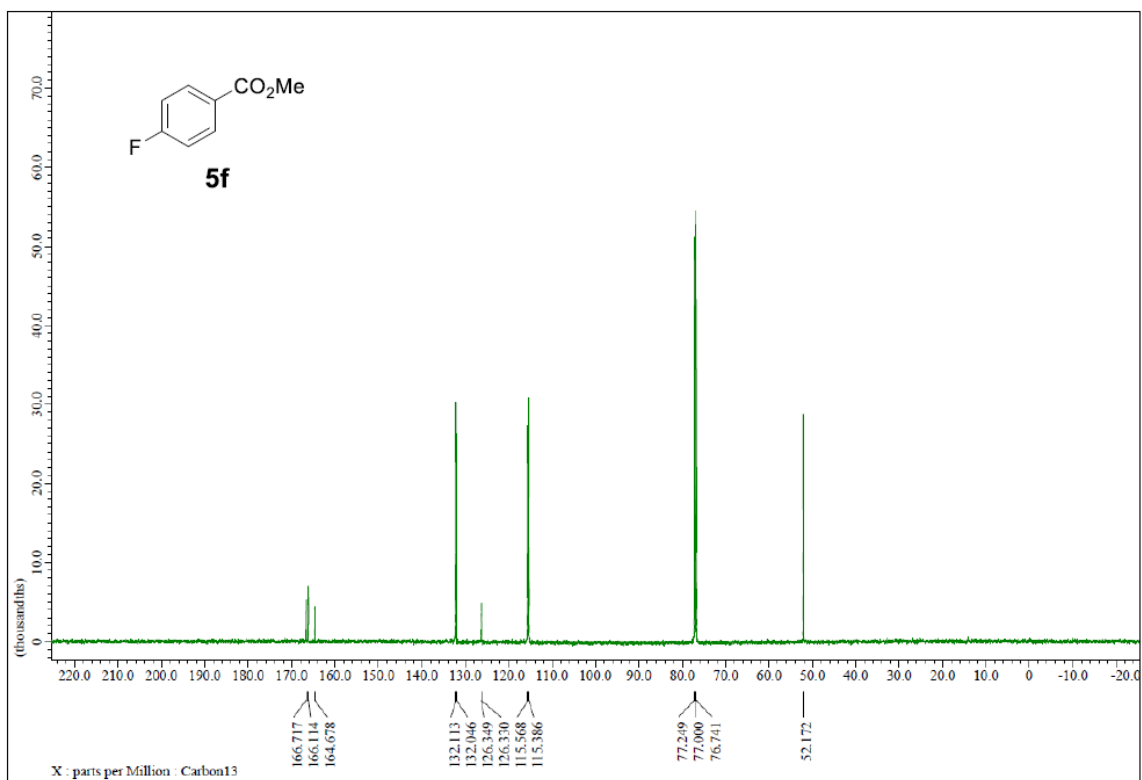
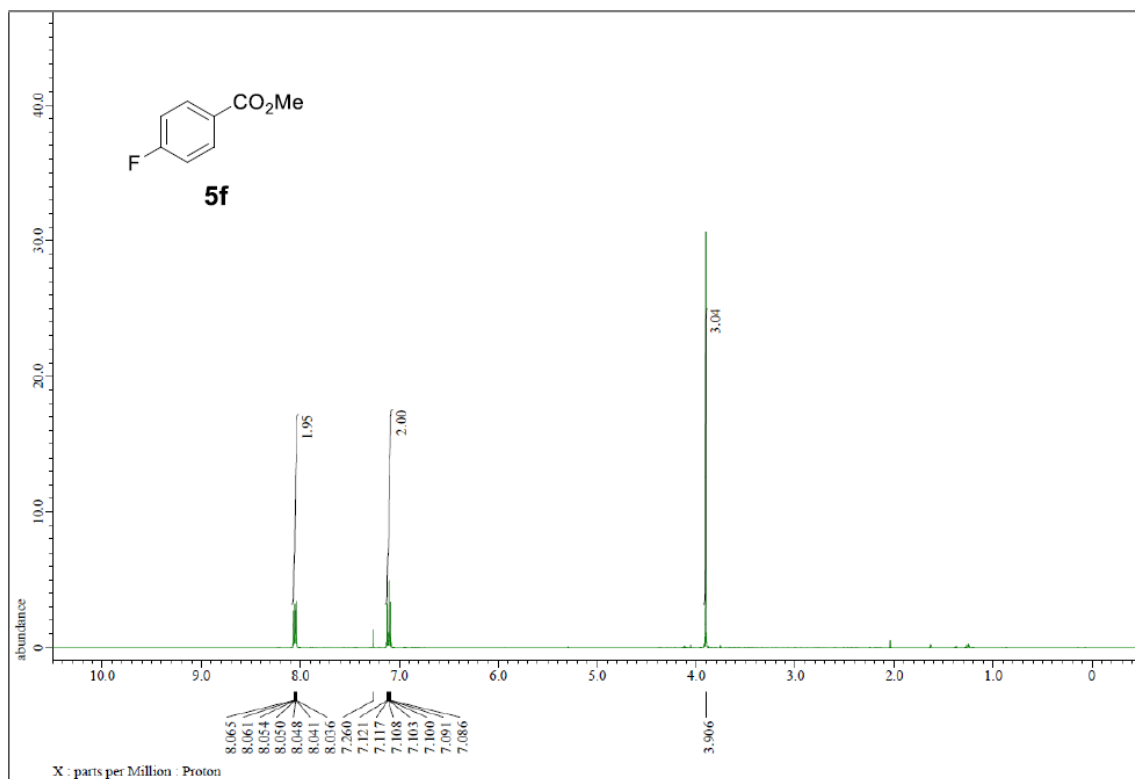
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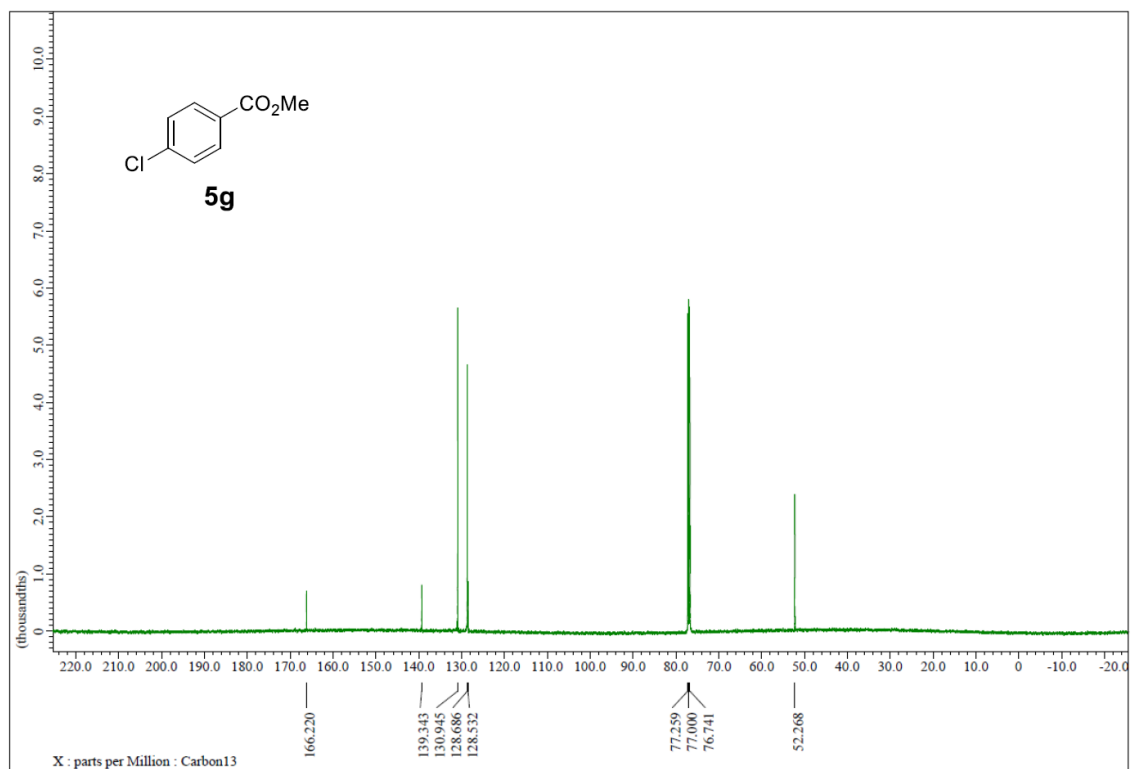
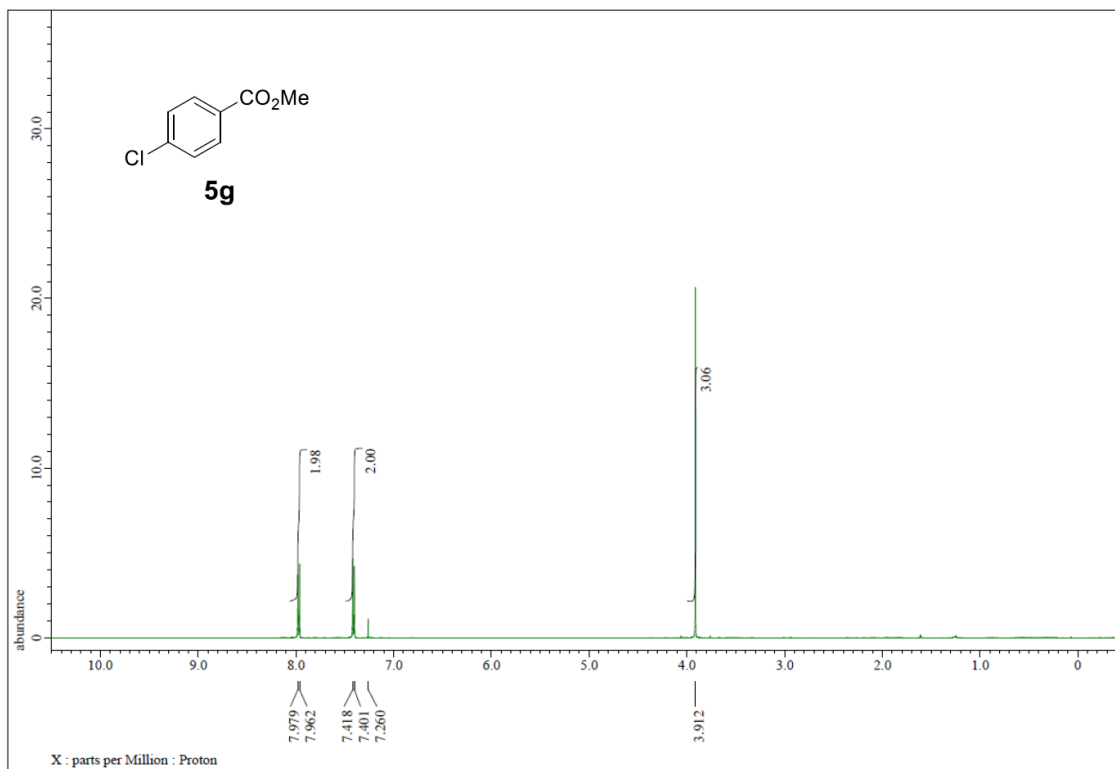
# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compounds 5e



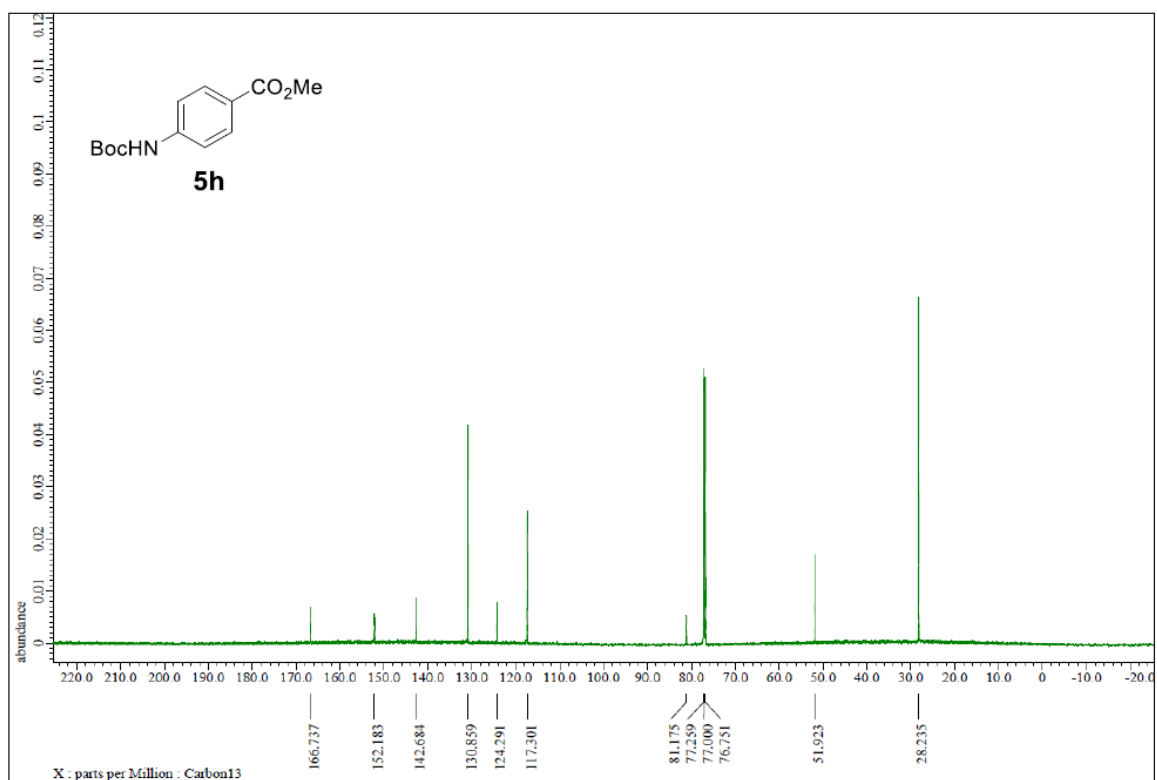
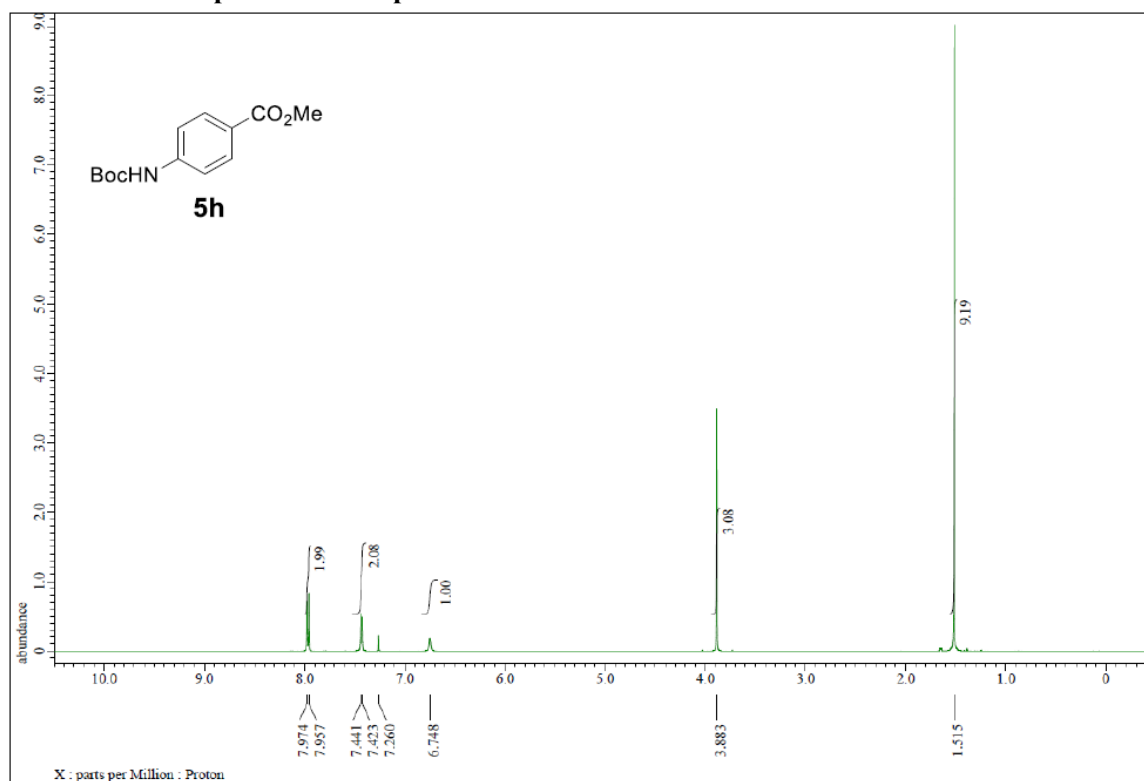
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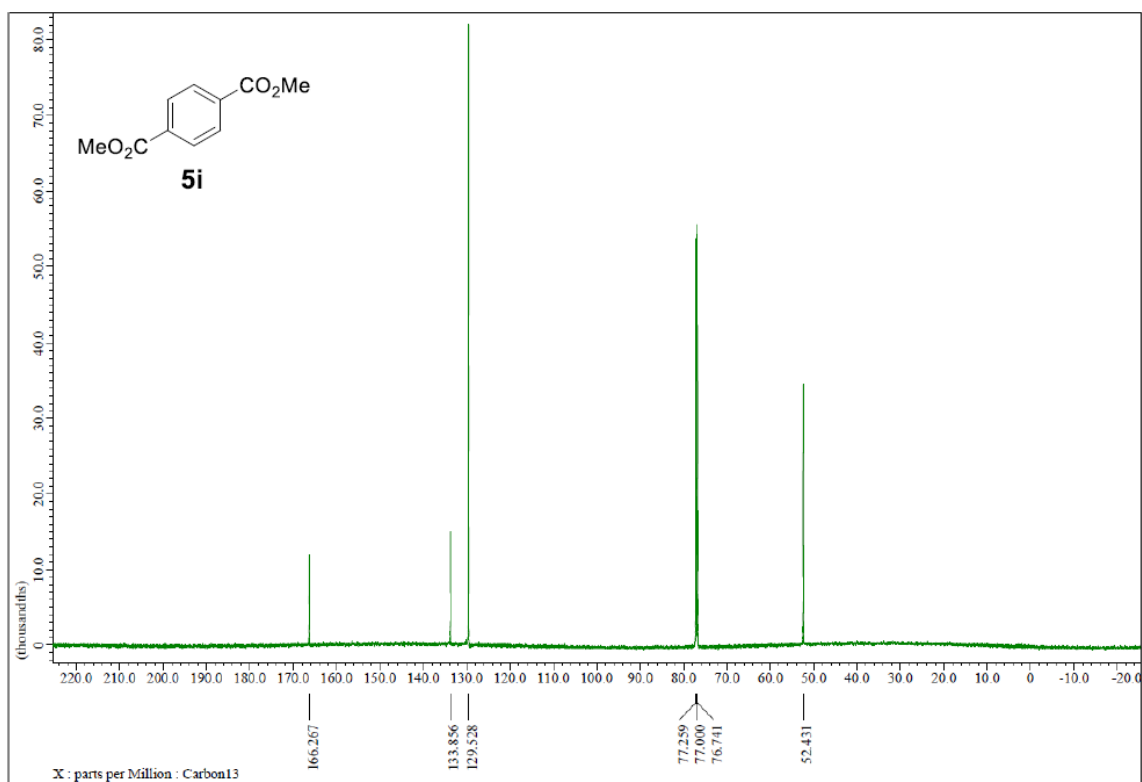
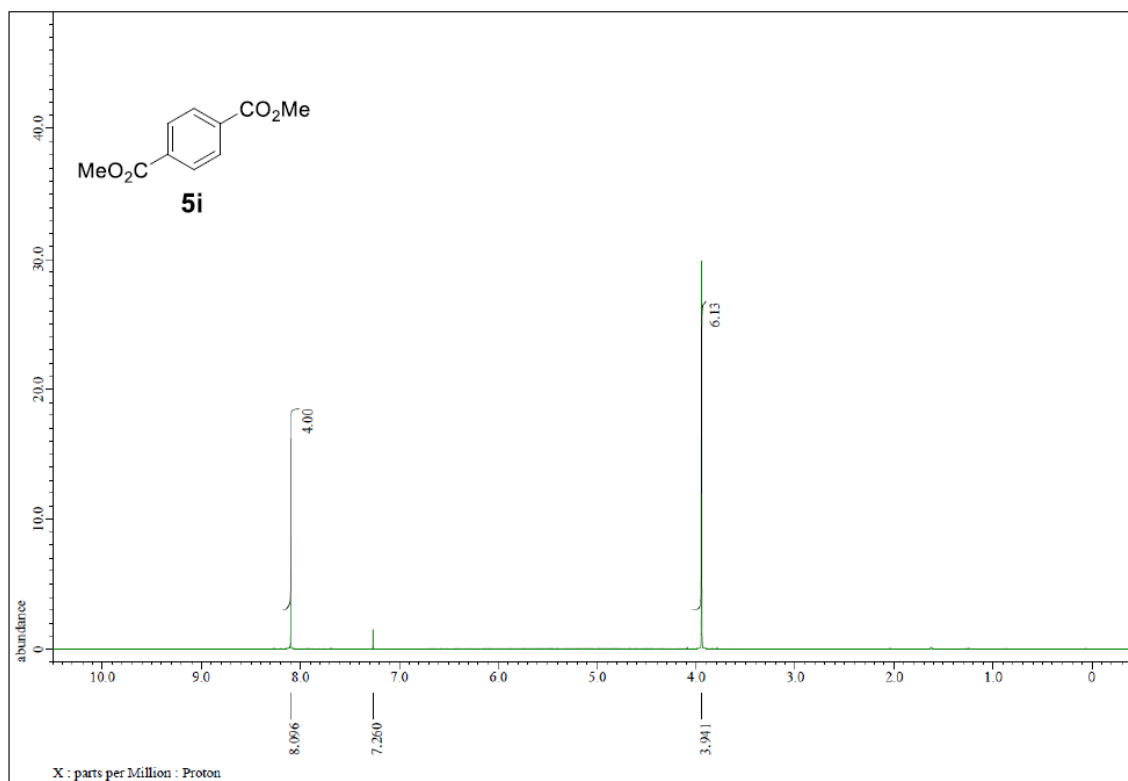
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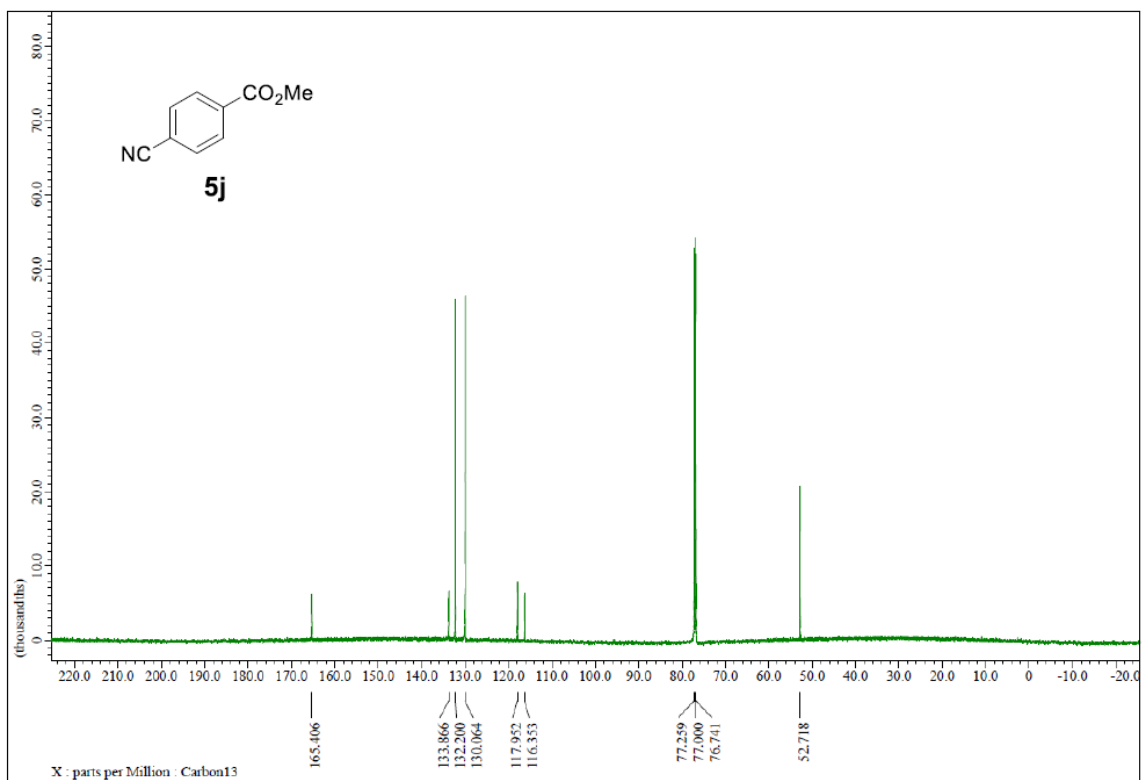
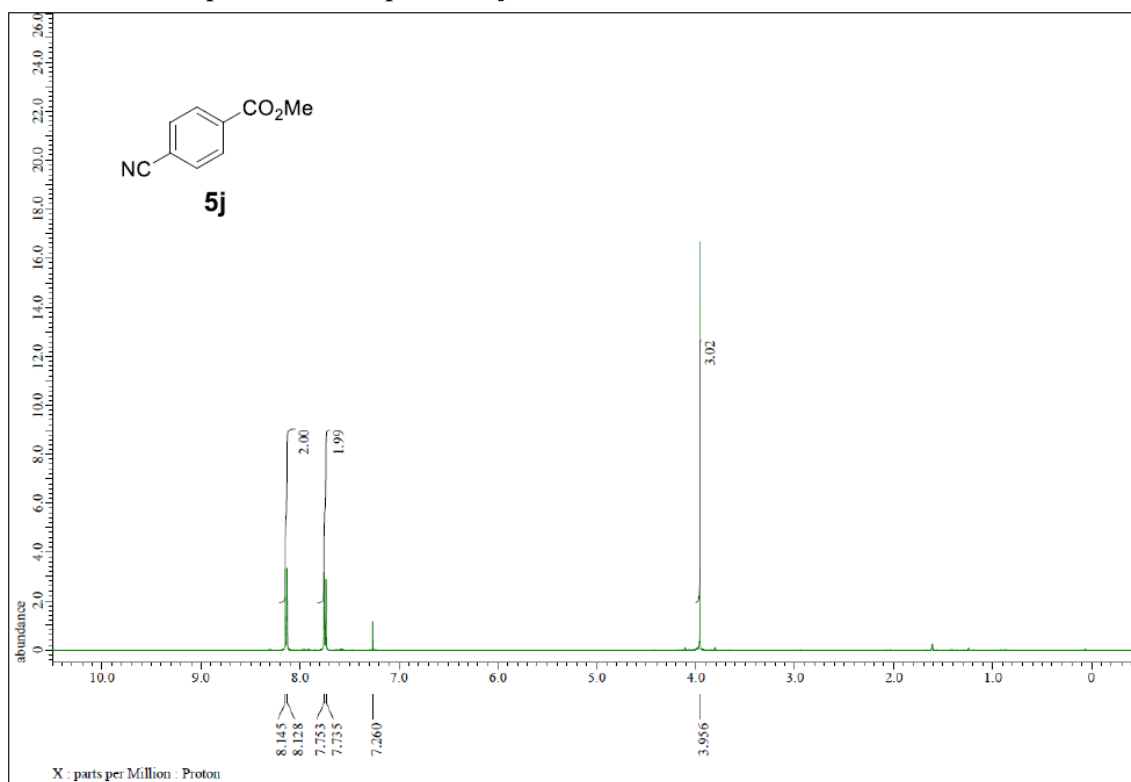
# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compounds 5h



# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compounds 5i

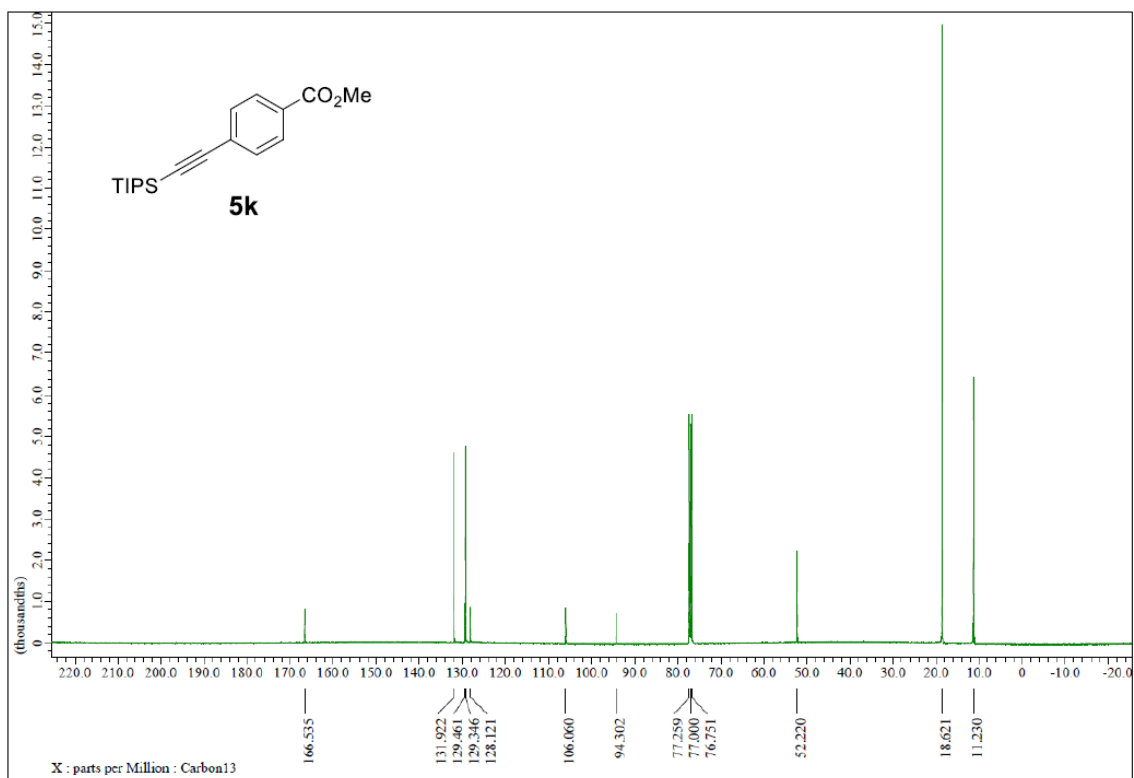
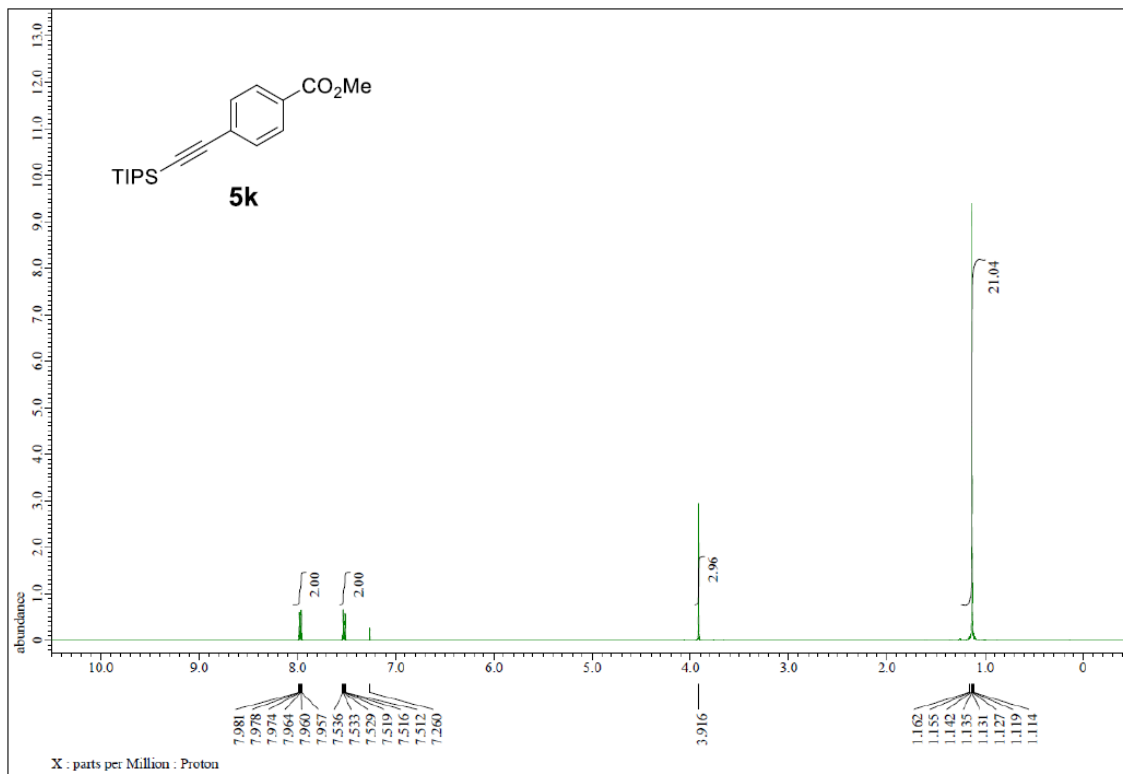


# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compounds 5j

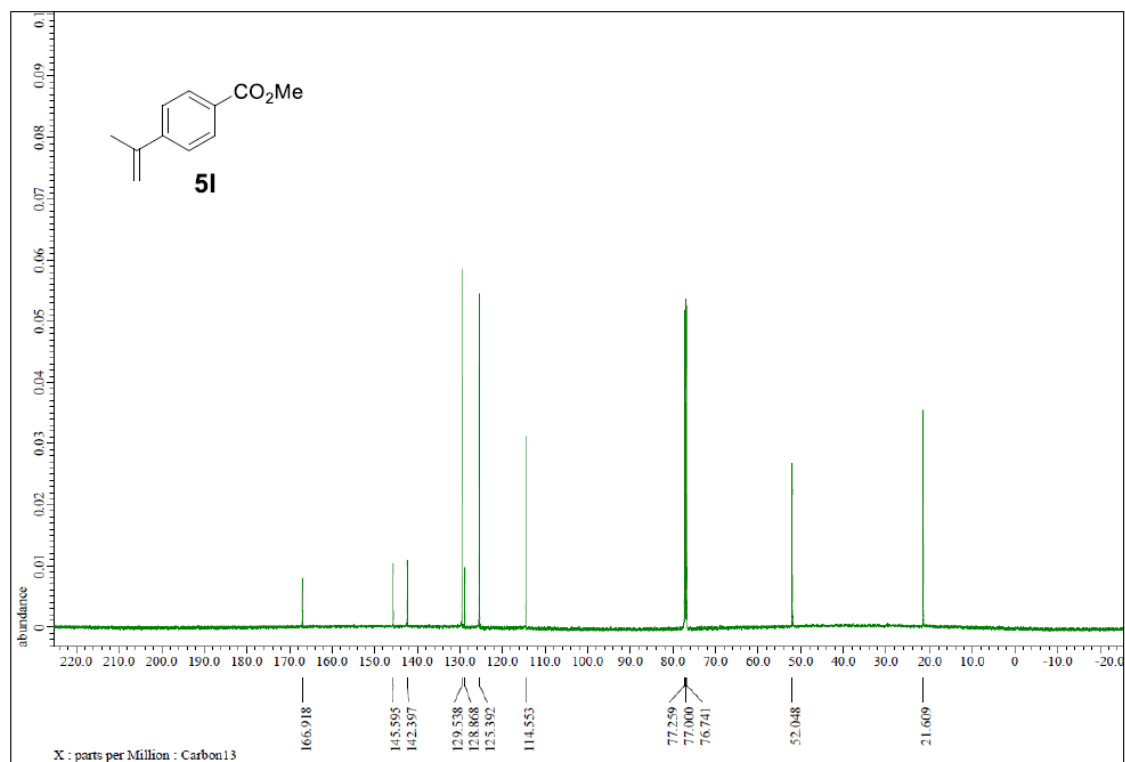
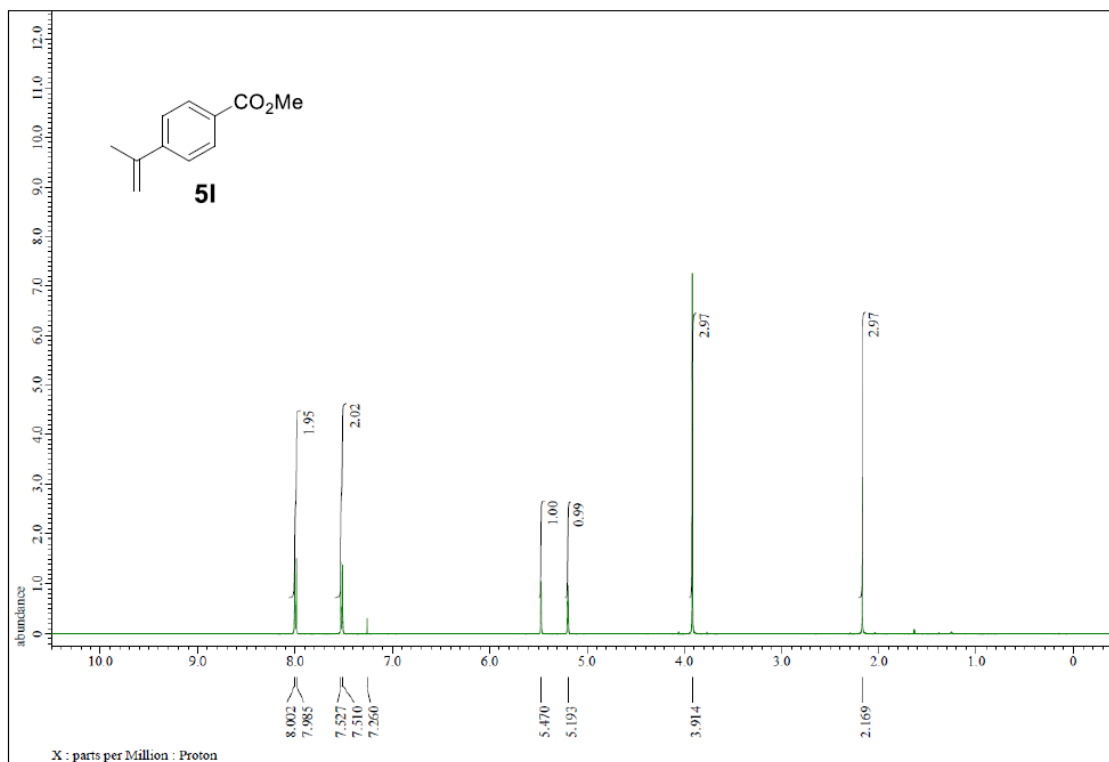




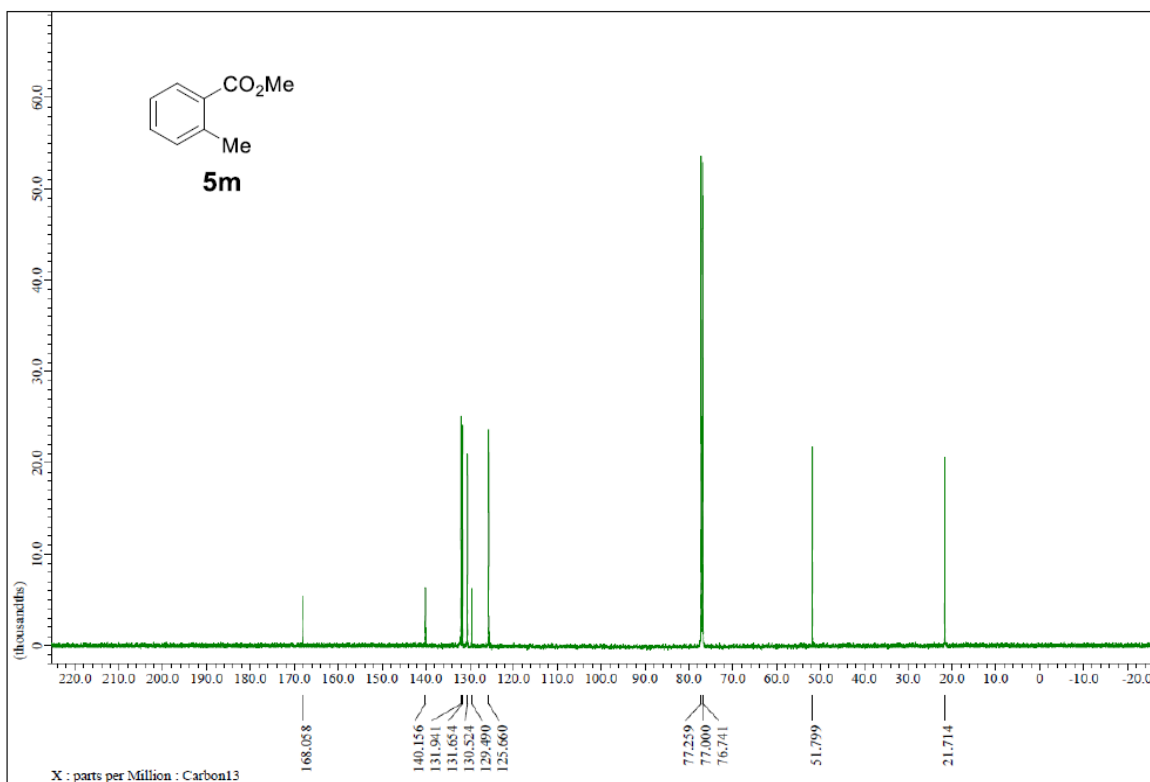
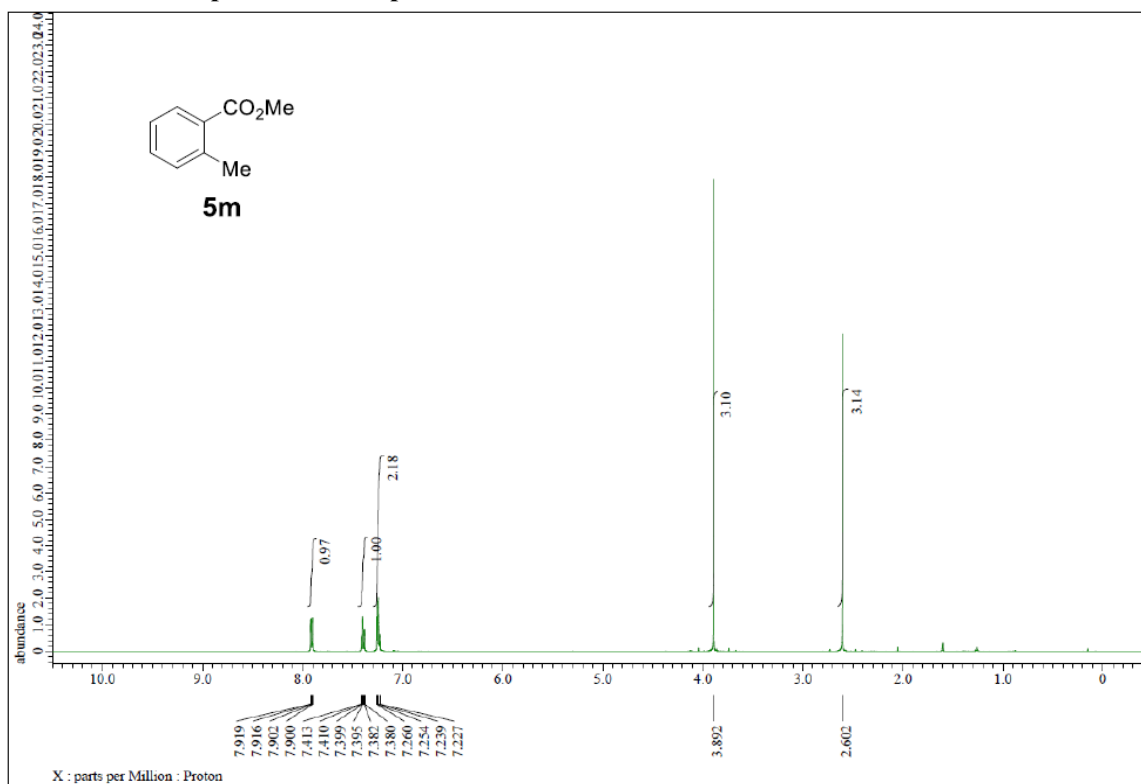
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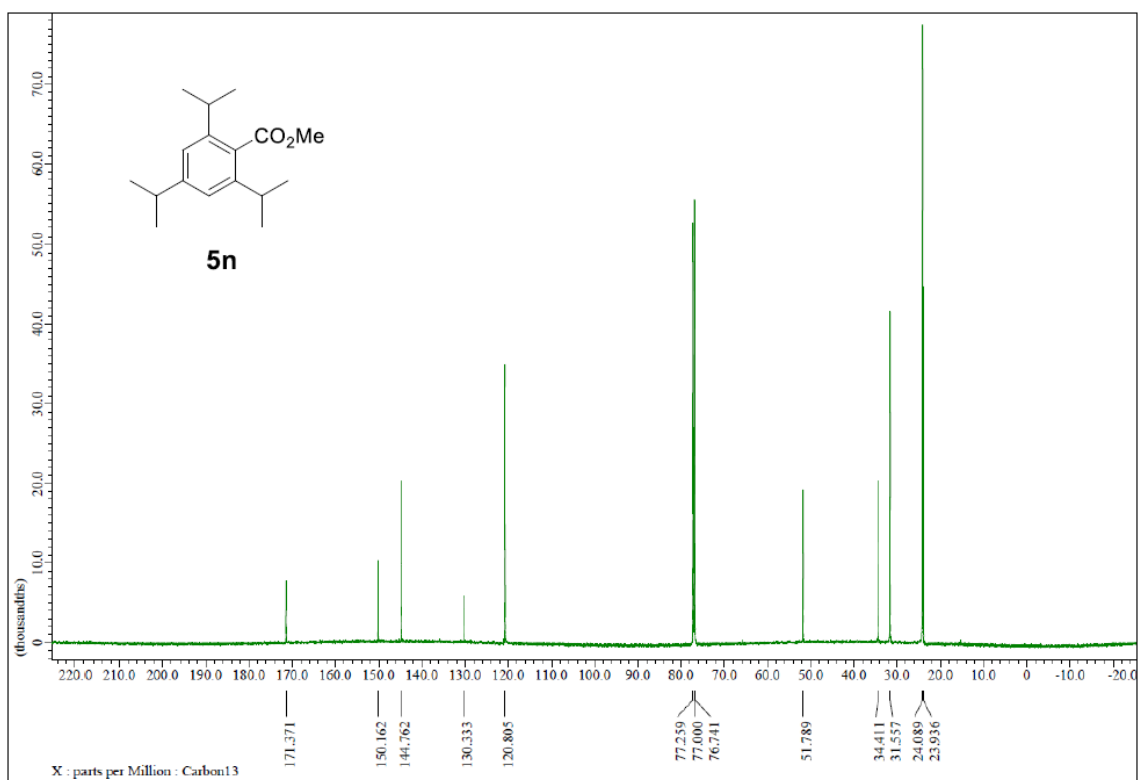
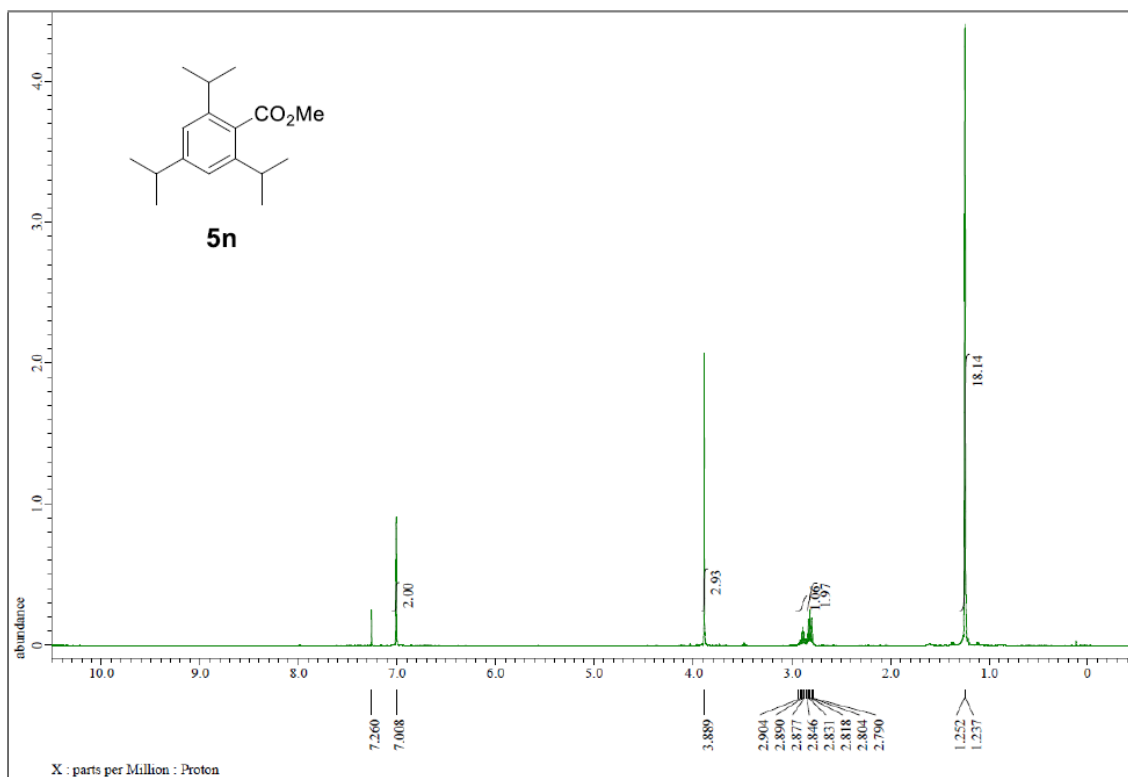
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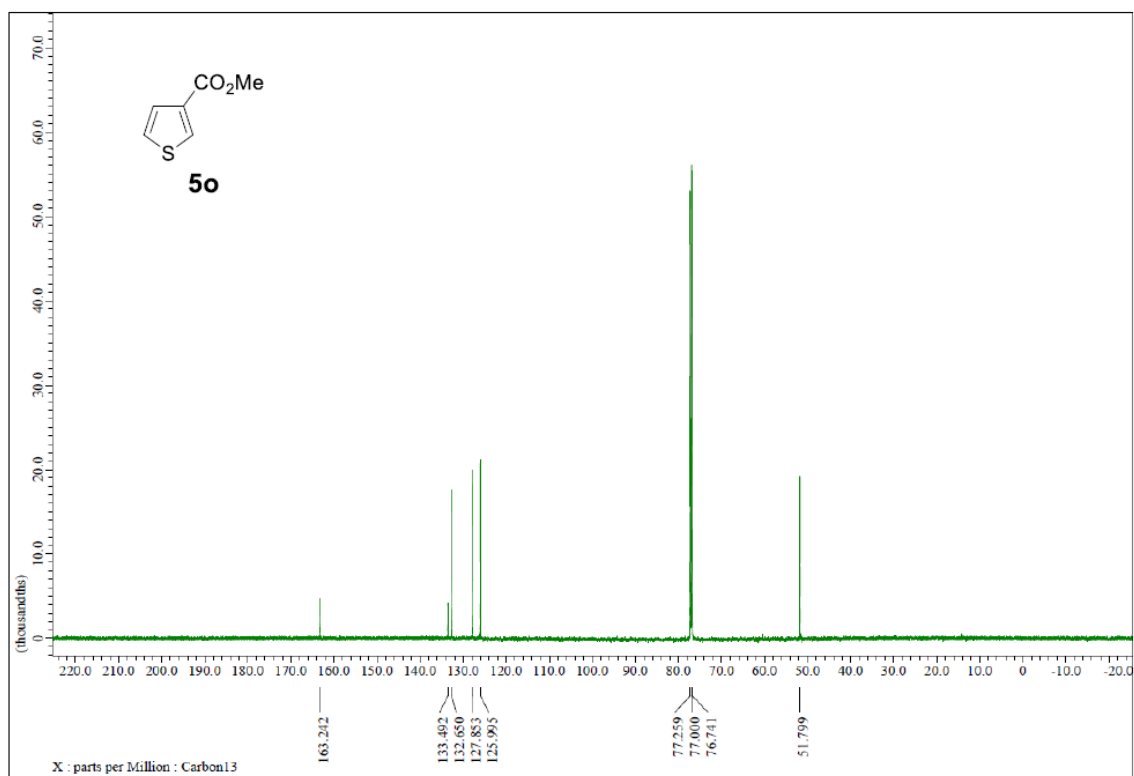
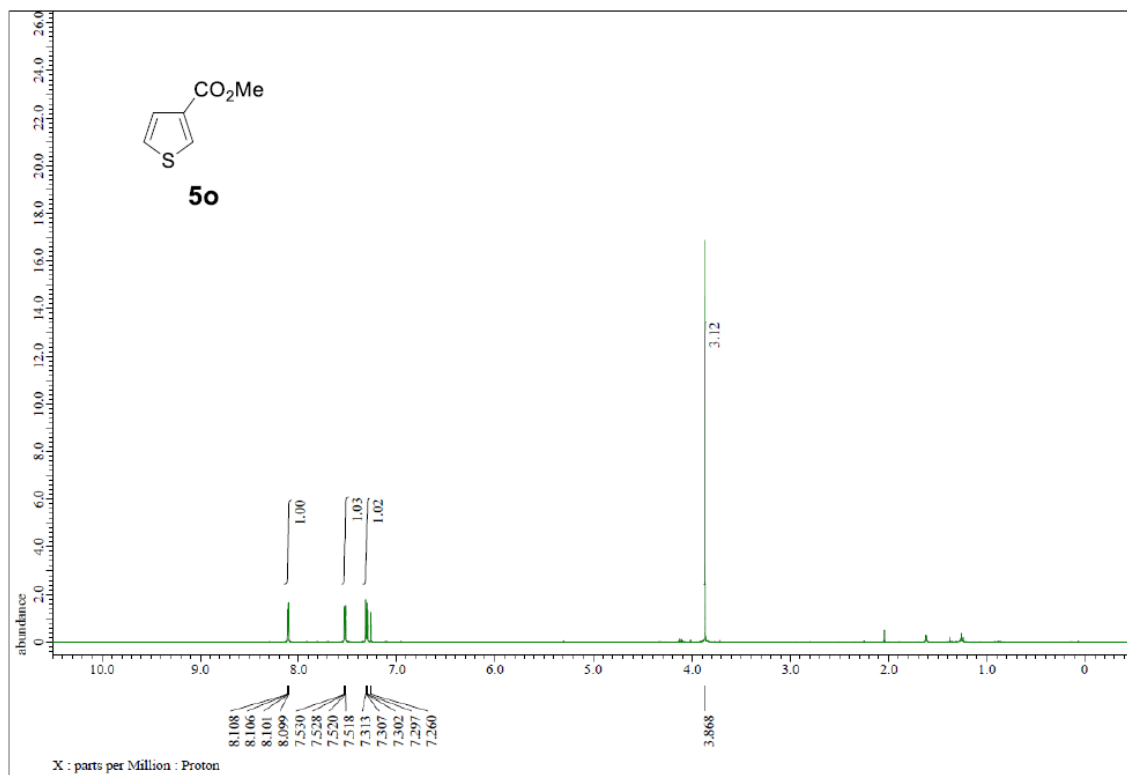
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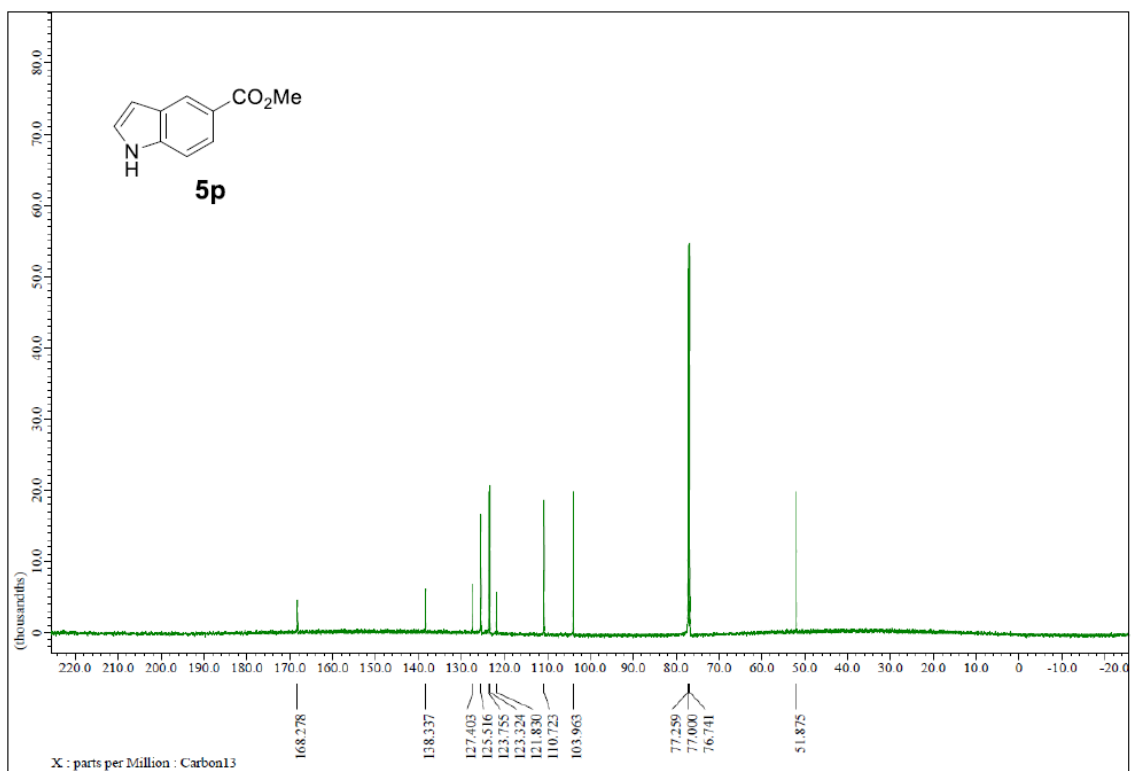
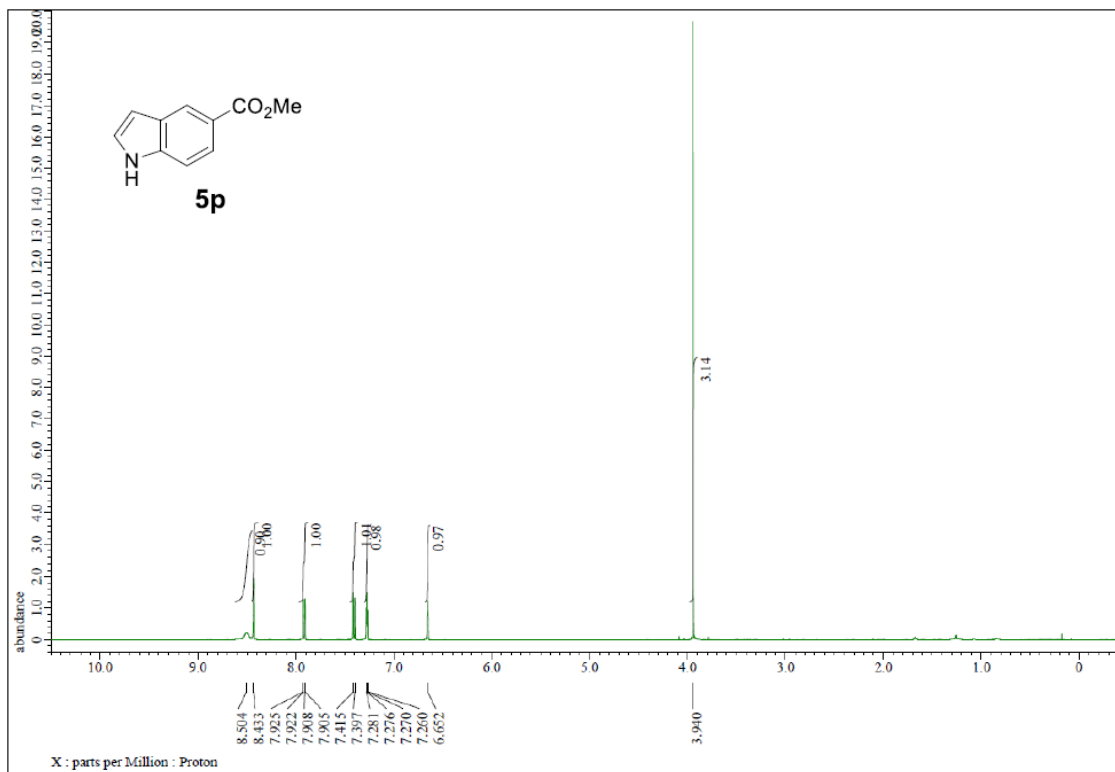
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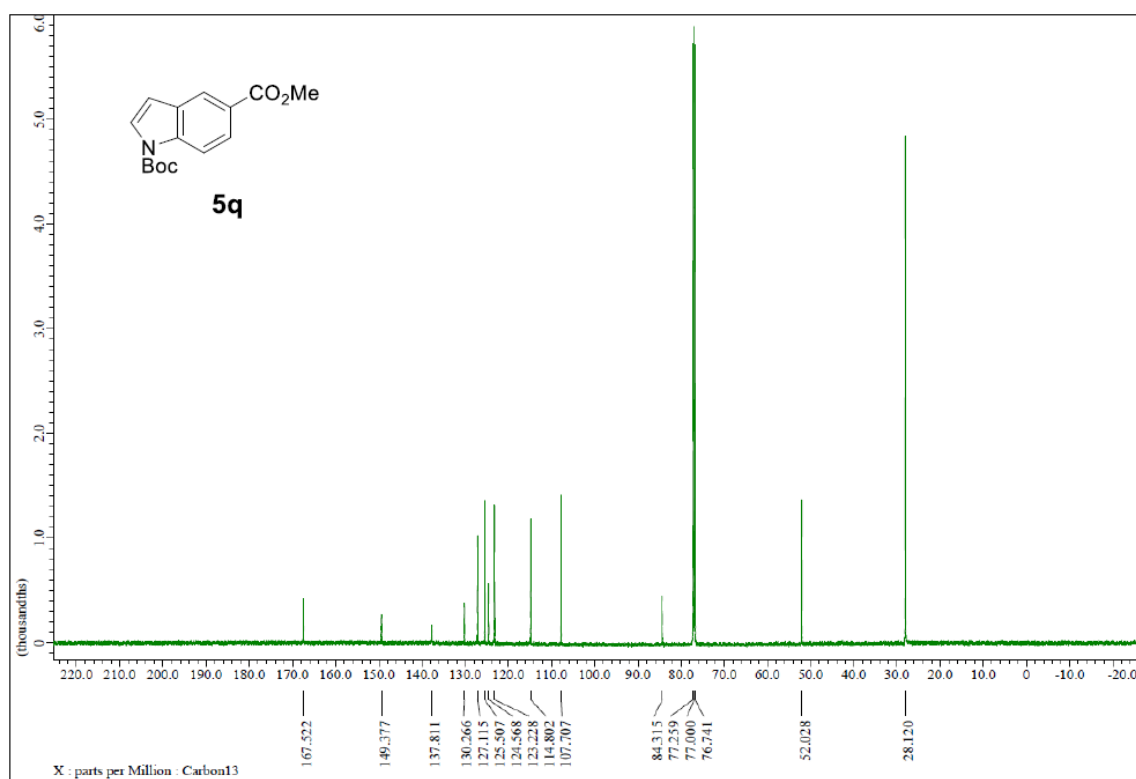
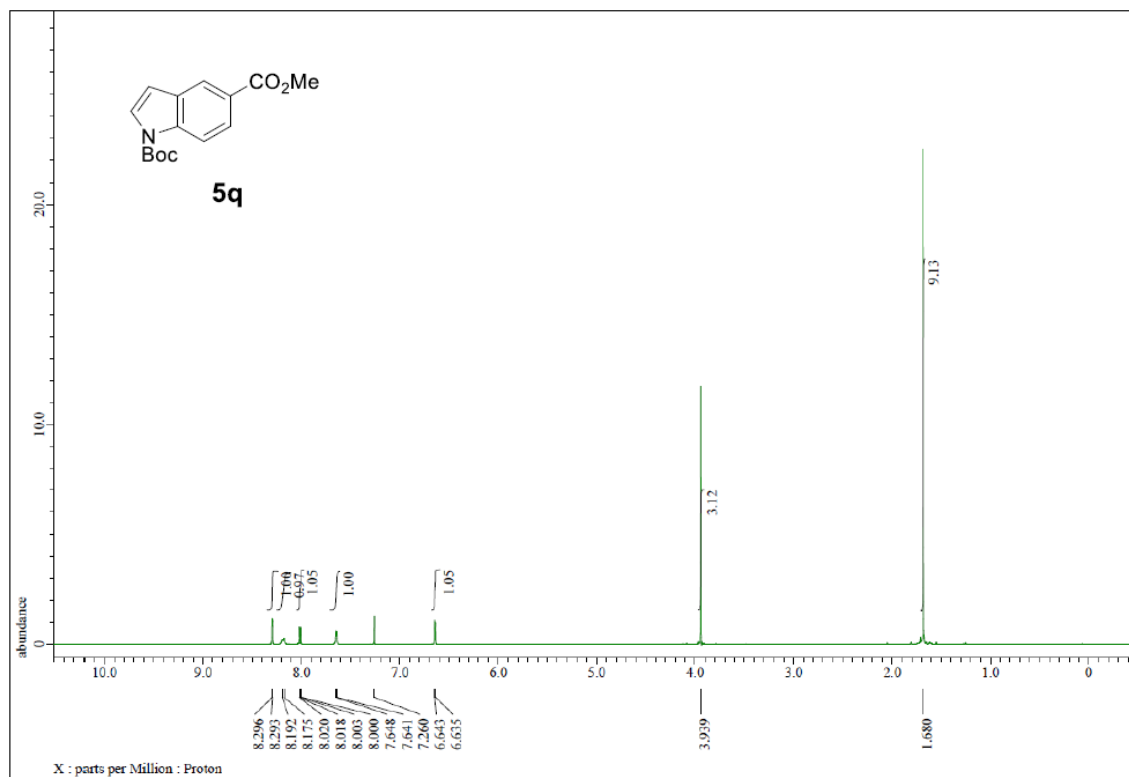
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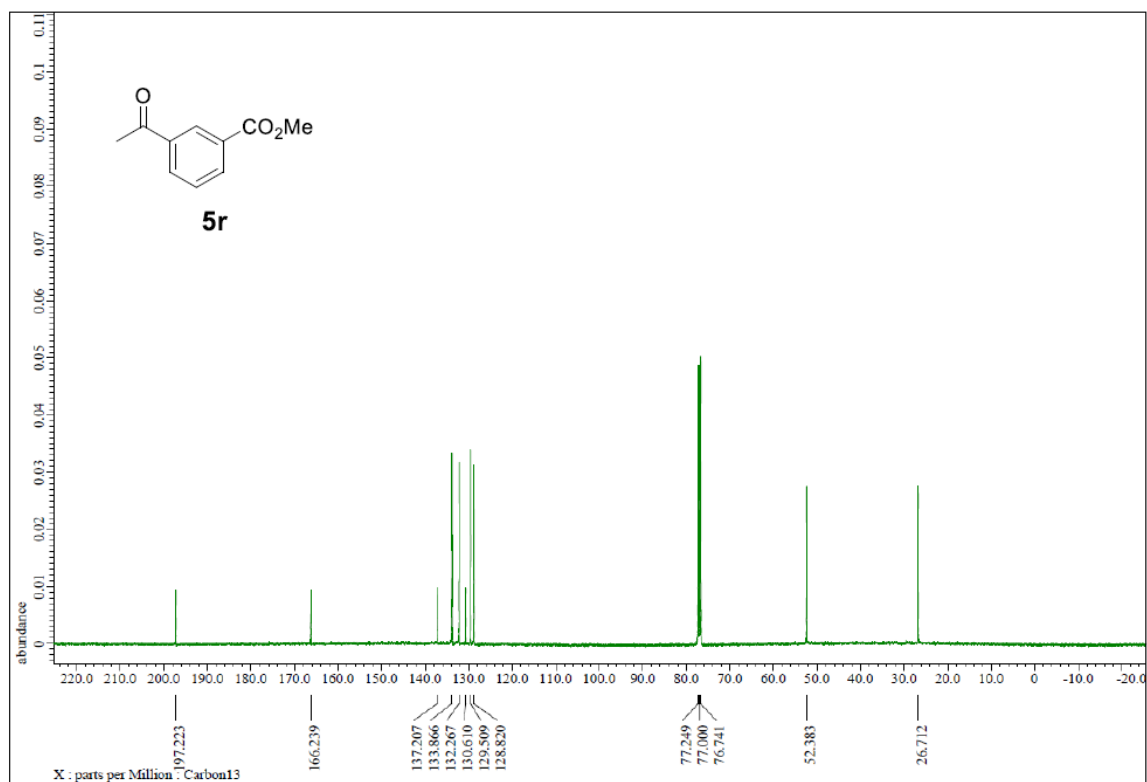
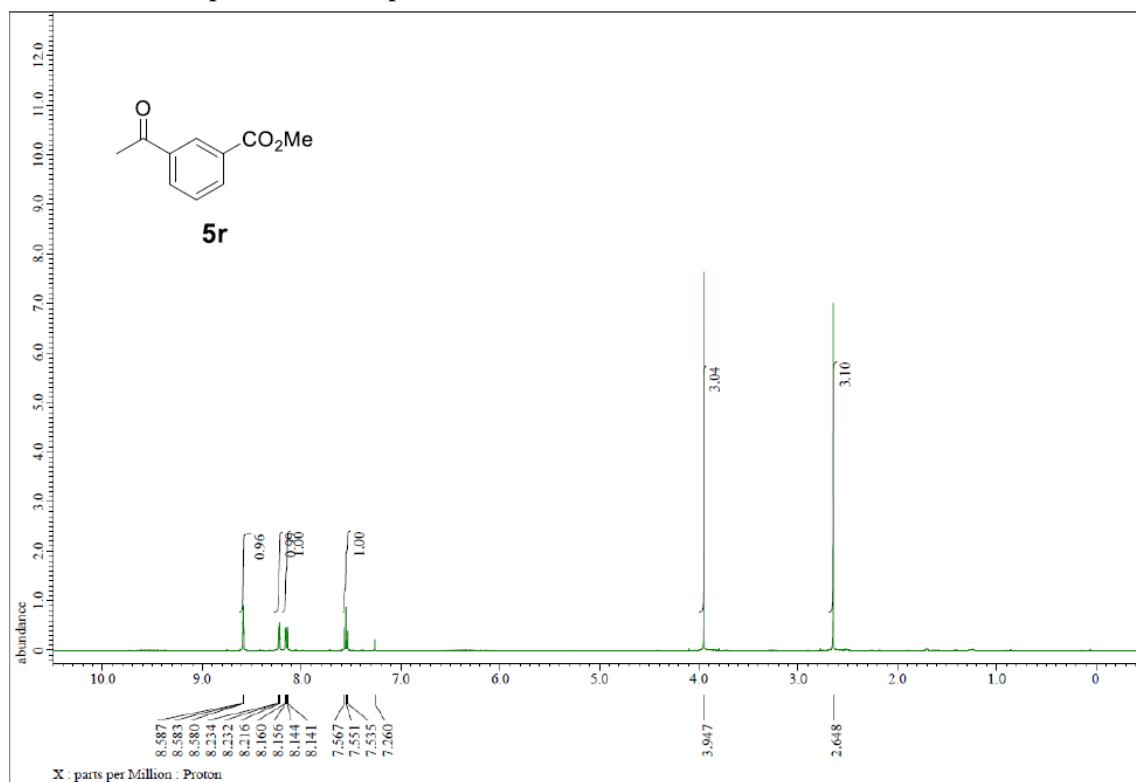
# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compounds 5p



# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compounds 5q

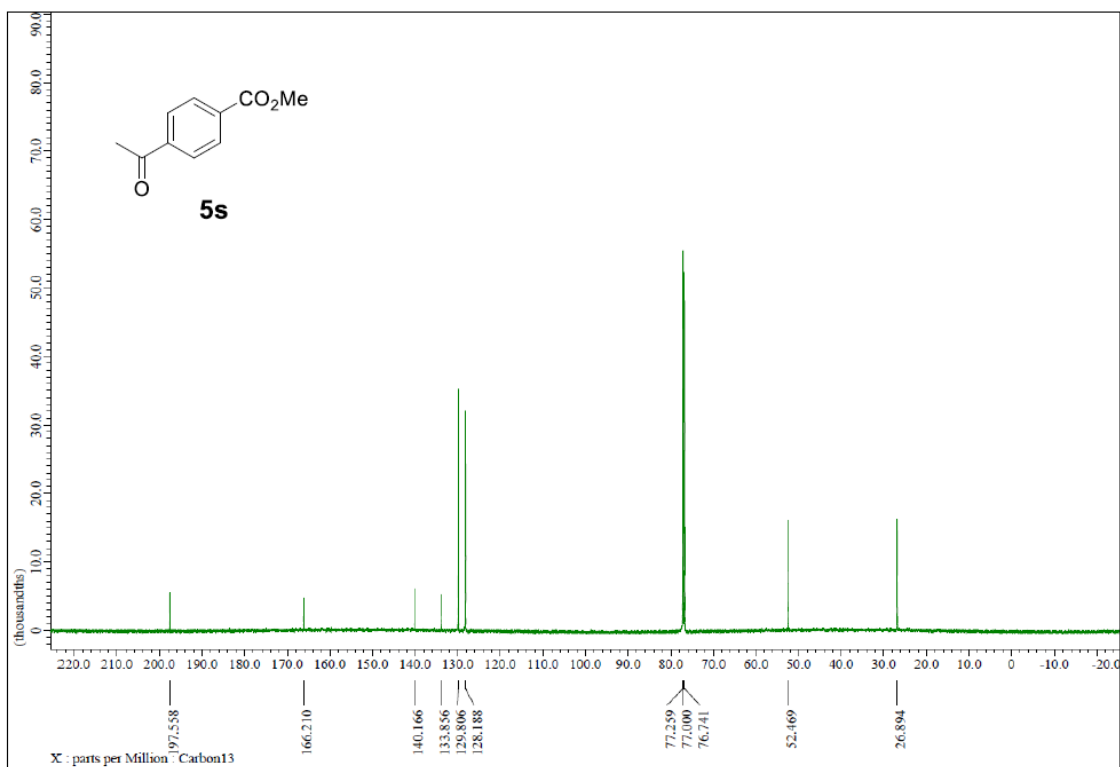
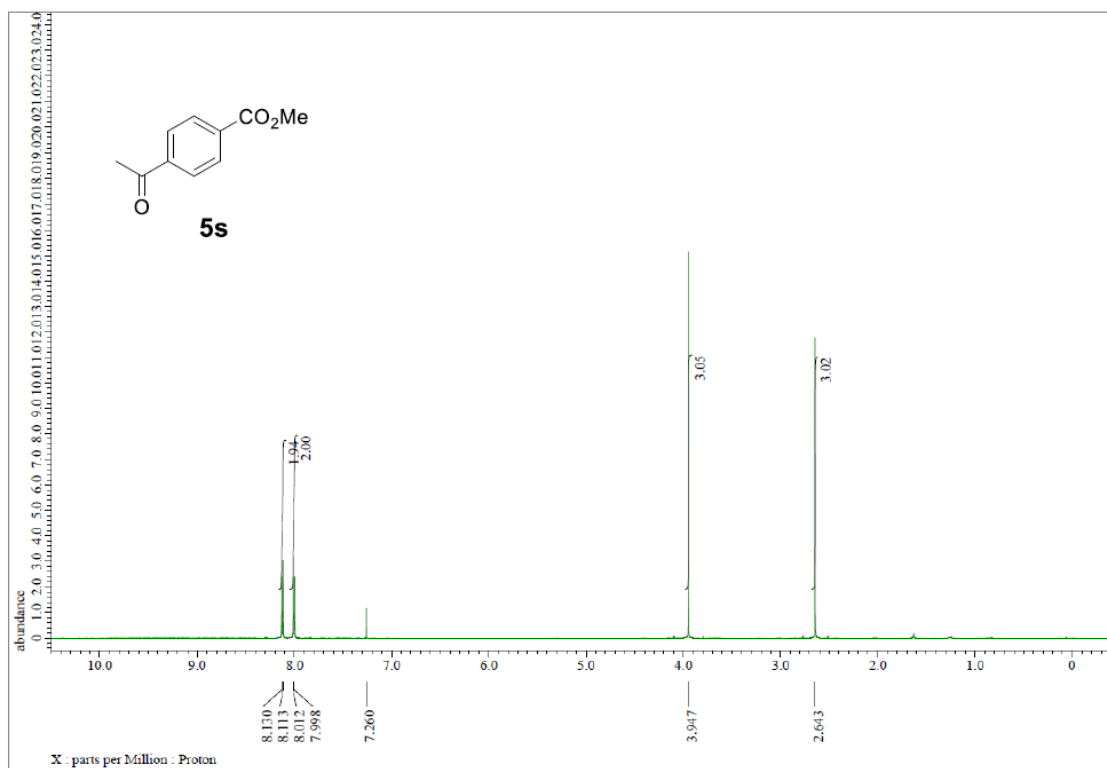


# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compounds 5r

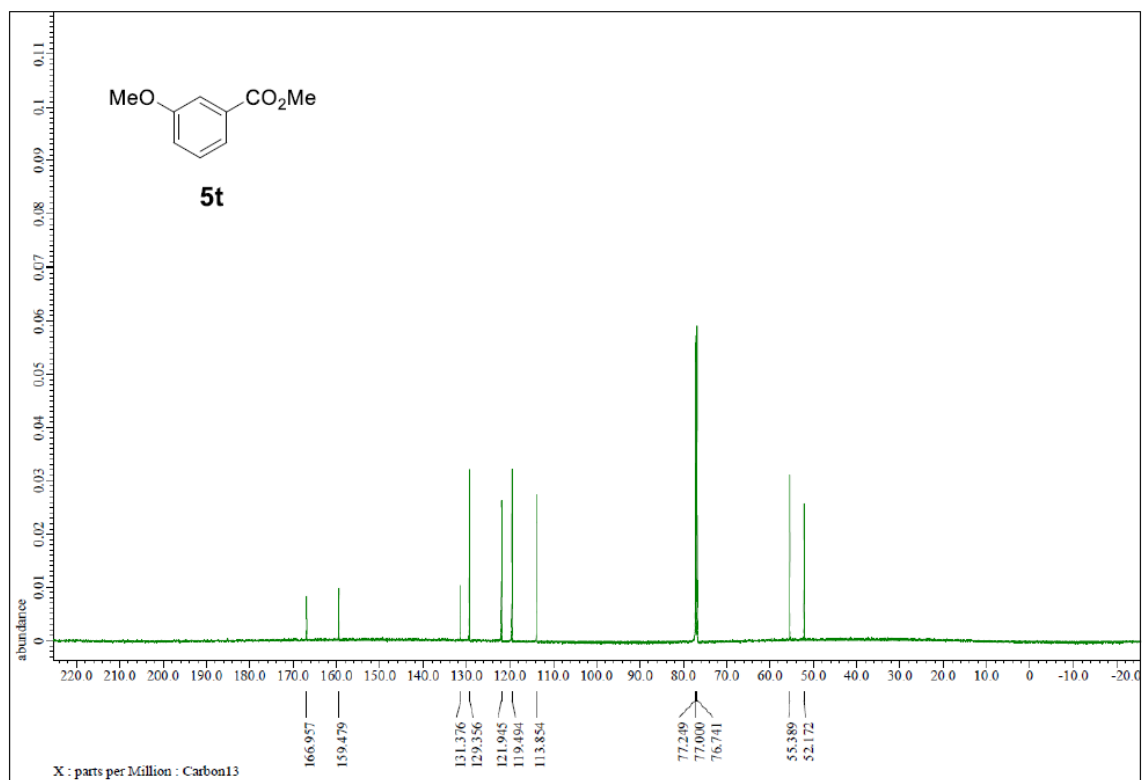
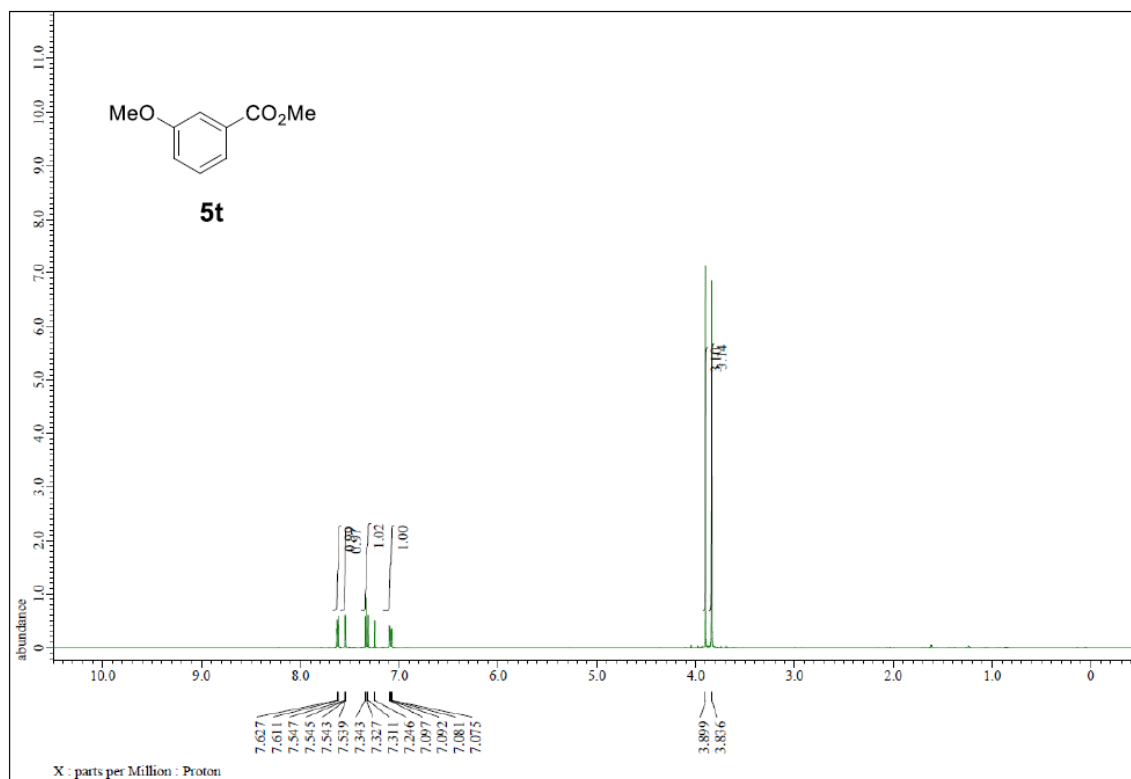




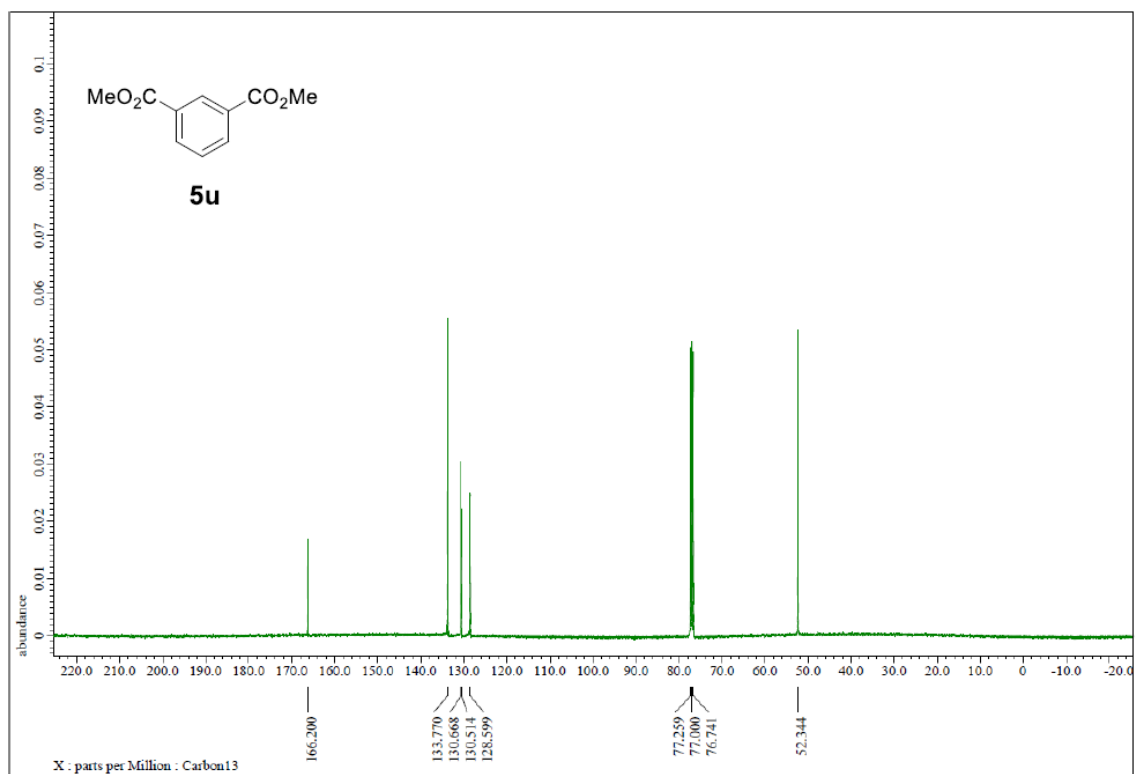
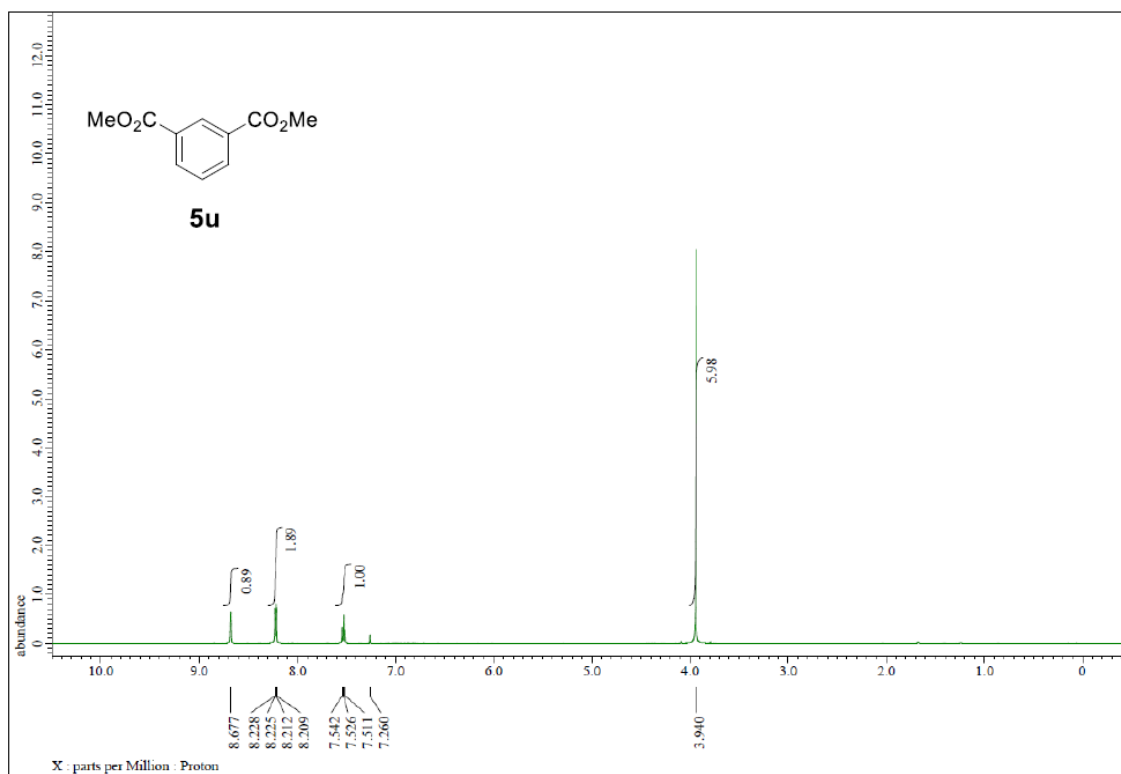
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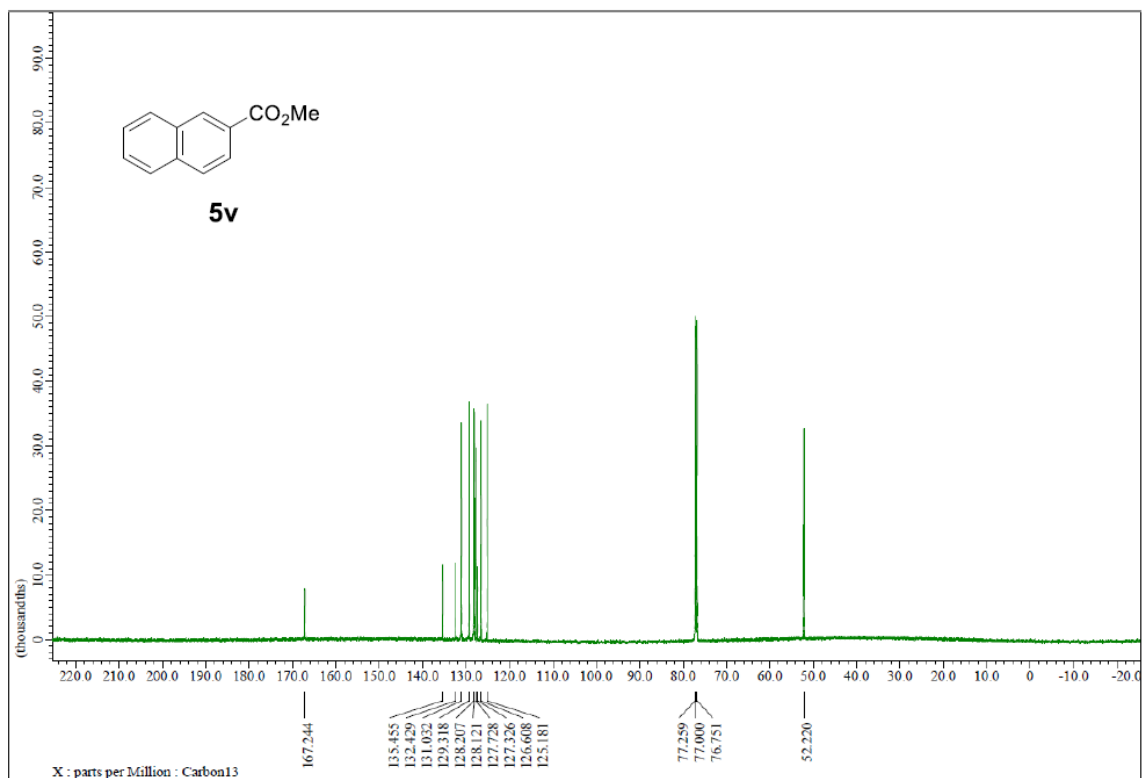
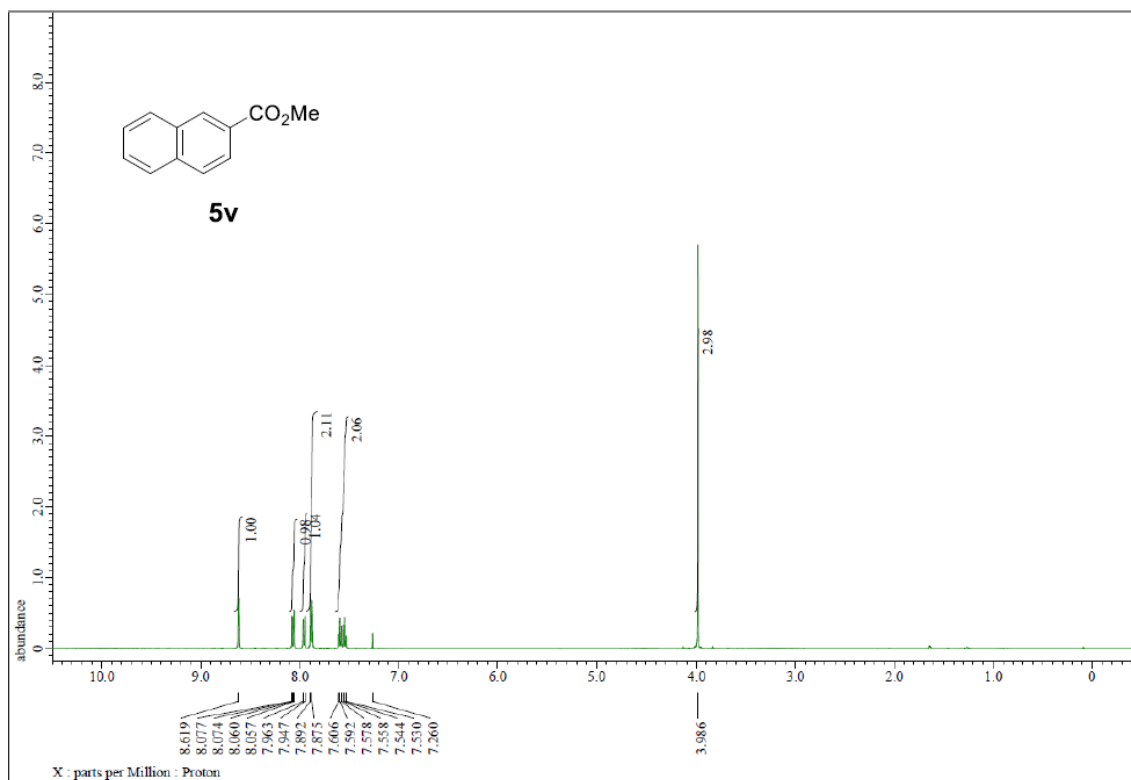
# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compounds 5t



# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compounds 5u



# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compounds 5v



# <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR Spectra of Compounds 7

