

Supporting Information

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

Katsuya Shimomaki,[†] Kei Murata,[†] Ruben Martin^{‡, §} and Nobuharu Iwasawa^{†,*}

[†] Department of Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8551, Japan

[‡] Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology, Av. Països Catalans 16, 43007 Tarragona, Spain

[§] Catalan Institution for Research and Advanced Studies (ICREA), Passeig Lluís Companys, 23, 08010, Barcelona, Spain

| Contents | Table, Figure, Scheme | Page |
|---|-----------------------------------|--------|
| General | | S2 |
| Procedure for Screening of Reaction Conditions | | S3 |
| General Procedure of Substrate Scope | | S3 |
| Control Experiments | Table S1. | S4 |
| Optimization for the Carboxylation of Aryl Bromides with Carbon Dioxide (CO ₂) | Table S2~12 | S5~11 |
| Optimization for the Carboxylation of Electron-Withdrawing Aryl Bromides with Carbon Dioxide (CO ₂) | Table S13,14 | S12~13 |
| Optimization for the Carboxylation of Aryl Chloride 6e with Carbon Dioxide (CO ₂) | Table S15 | S13 |
| Mechanistic Study of Carboxylation Reaction | Figure S1~4 Scheme S1,2 | S14~20 |
| Mechanistic Study of Reduction Reaction | Table S16, Figure S5 Scheme S3 | S21~24 |
| The Carboxylation of Aryl Bromides | | S24~27 |
| The Carboxylation of Aryl Chlorides | | S28~29 |
| References | | S30 |
| Spectral Data | | S31~54 |

General

All operations were performed under an argon, N₂ or CO₂ atmosphere unless otherwise noted. ¹H NMR spectra were recorded on JEOL ECZ-500 and ECX-500 (500 MHz) spectrometers in CDCl₃ using residual CHCl₃ (for ¹H, δ = 7.26) as an internal standard. ¹³C NMR spectra were recorded on JEOL ECZ-500 and ECX-500 (125 MHz) spectrometer in CDCl₃ using CDCl₃ (for ¹³C, δ = 77.0) as an internal standard. ³¹P NMR chemical shift was calibrated using external 85% H₃PO₄ (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 cm²) 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_{irr.} = 425 ± 15 nm) for photocatalytic reactions.

Et₂O 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 N₂. CO₂ gas was purchased from Taiyo Nippon Sanso Corporation.

Palladium acetate (Pd(OAc)₂), 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),¹ Ru(bpy)₃(PF₆)₂ **4a**,² Ir(dF(CF₃)ppy)₂(dtbpy)(PF₆) **4b**,³ Ir(ppy)₂(dtbpy)(PF₆) **4c**,⁴ Ir(ppy)₂(dmobpy)(PF₆) **4d**,⁵ Ir(ppy)₂(bp bpy)(PF₆) **4e**,⁶ Ir(ppy)₂(phen)(PF₆) **4f**,⁷ Ir(ppy)₂(Me₄phen)(PF₆) **4g**,⁷ *fac*-Ir(ppy)₃ **4h**,⁸ TMSCHN₂,⁹ (COD)Pd(CH₂TMS)₂¹⁰ and compounds **1h**,¹¹ **1k**,¹² **1l**,¹³ **1q**,¹⁴ and **6d**,¹⁵ 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)

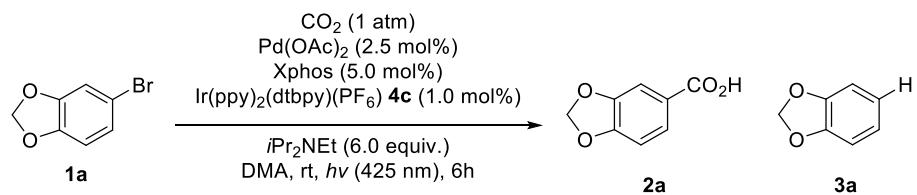
A DMA solution (1.0 mL) of 3,4-methylenedioxybromobenzene **1a** (24 μ L, 0.20 mmol) with palladium acetate (1.1 mg, 0.005 mmol, 2.5 mol%), a ligand (0.01 mmol, 5.0 mol%), a photoredox catalyst (0.002 mmol, 1.0 mol%), additive and *i*Pr₂NEt (0.21 mL, 1.2 mmol, 6.0 equiv. or 0.10 mL, 0.60 mmol, 3.0 equiv.) was prepared in a test tube under a nitrogen atmosphere. Then the gas phase was replaced by atmospheric pressure of CO₂, 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 H₂O and then the mixture was extracted with Et₂O three times. The combined organic layer was washed with H₂O and dried over Na₂SO₄. After the filtration of the drying agent, the filtrate was evaporated, and the crude product was analyzed by ¹H-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 Et₂O three times. The combined organic layer was dried over Na₂SO₄, filtrated and evaporated under reduced pressure to give the carboxylic acid **2a**. The NMR yield of **2a** was determined by ¹H-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)₂(dtbpy)(PF₆) **4c** (4.6 mg, 0.005 mmol, 2.5 mol%), Cs₂CO₃ (195 mg, 0.60 mmol, 3.0 equiv.) and *i*Pr₂NEt (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 CO₂, 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 H₂O and then the mixture was extracted with Et₂O three times. The organic layer was washed with H₂O. The combined aqueous layer was acidified with 1N HCl aq., and then extracted with Et₂O three times. The combined organic layer was dried over Na₂SO₄, filtrated and evaporated under reduced pressure to give the carboxylic acid. The product was dissolved in Et₂O (2.0 mL) and MeOH (0.5 mL), and a Et₂O solution of TMSCHN₂ (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



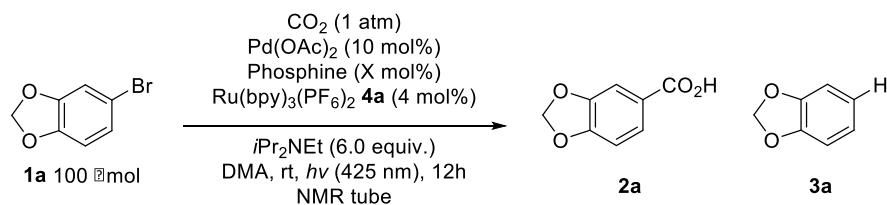
| Entry | Conditions | Conv. /% ^a | 2a /% ^a | 3a /% ^a |
|-------|---|-----------------------|--------------------|--------------------|
| 1 | standard conditions | 100 | 48 | 45 |
| 2 | without Pd(OAc) ₂ and Xphos | 76 | — | 75 |
| 3 | without Ir(ppy) ₂ (dtbpyp)(PF ₆) 4c | 2 | — | 2 |
| 4 | without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

^a Determined by ¹H-NMR spectra.

In this carboxylation reaction, palladium catalyst, photoredox catalyst, amine, photo-irradiation and CO₂ gas were all necessary, and lack of one component suppressed the reaction.

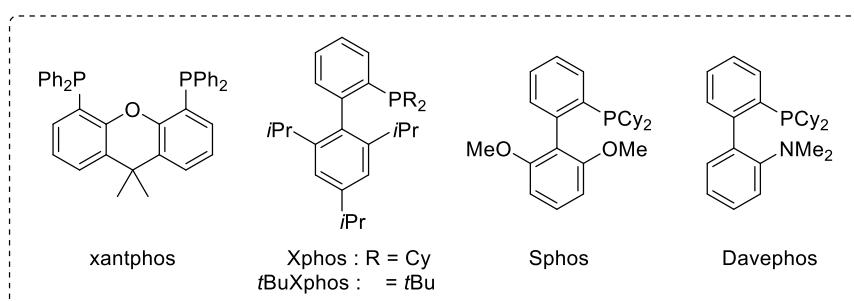
Optimization for the Carboxylation of Aryl Bromides with Carbon Dioxide (CO₂)

Table S2. The screening of phosphine ligands



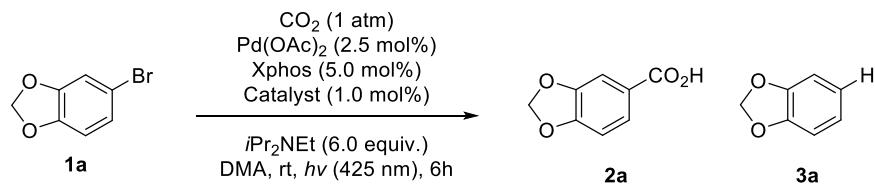
| Entry | Phosphine (X mol%) | Conv. /% ^a | 2a /% ^a | 3a /% ^a |
|-------|--|-----------------------|--------------------|--------------------|
| 1 | PPh ₃ (20) | 100 | — | 100 |
| 2 | PMes ₃ (20) | 30 | — | 14 |
| 3 | PCy ₃ (20) | 5 | — | 8 |
| 4 | PtBu ₃ -HBF ₄ (20) | 49 | — | 19 |
| 5 | dppe (10) | 22 | — | 23 |
| 6 | Xantphos (10) | 65 | 14 | 35 |
| 7 | Xphos (20) | 42 | 15 | 28 |
| 8 | tBuXphos (20) | 100 | 29 | 36 |
| 9 | Sphos (20) | 32 | 6 | 31 |
| 10 | Davephos (20) | 71 | 10 | 33 |

^a Determined by ¹H-NMR spectra.



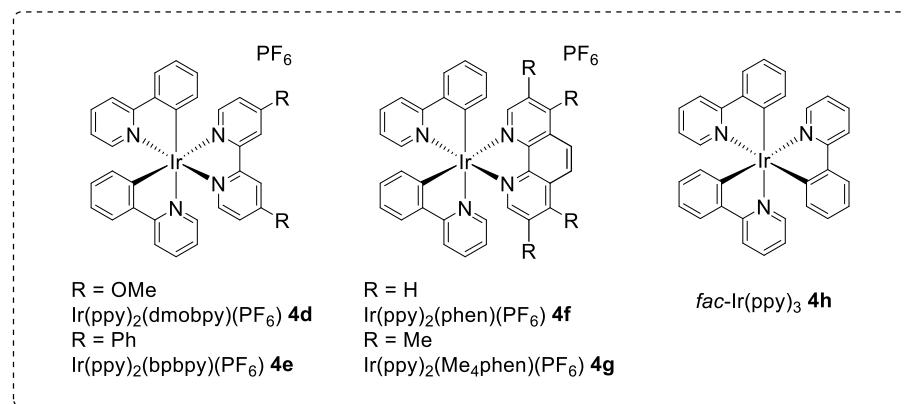
The desired carboxylic acid **2a** was produced by using xantphos and monodentate phosphine ligands containing a biphenyl moiety (entries 6~10). Xphos containing a 2,4,6-triisopropylbiphenyl moiety was preferable to Sphos or Davephos (entries 7,9,10).

Table S3. The screening of other photoredox catalysts

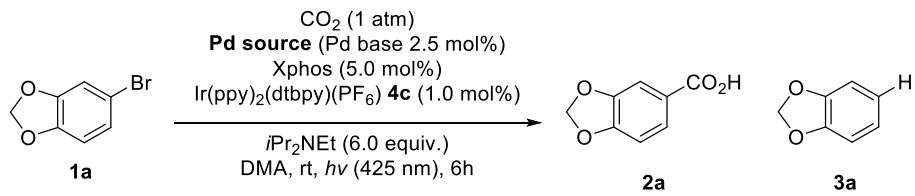


| Entry | Catalyst | Conv. /% ^a | 2a /% ^a | 3a /% ^a |
|-------|--|-----------------------|---------------------------|---------------------------|
| 1 | Ru(bpy) ₃ (PF ₆) ₂ 4a | 12 | 3 | 9 |
| 2 | Ir(dF(CF ₃)ppy) ₂ (dtbpy)(PF ₆) 4b | 48 | 12 | 25 |
| 3 | Ir(ppy) ₂ (dtbpy)(PF ₆) 4c | 100 | 48 | 45 |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

^a Determined by ¹H-NMR spectra.

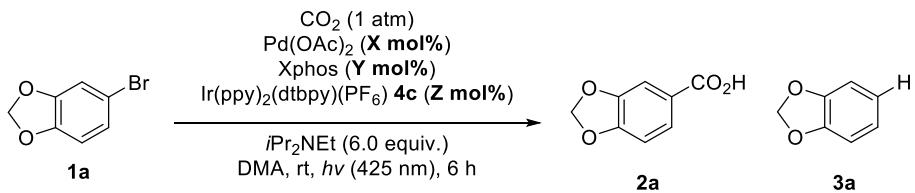


The conversion of substrate **1a** and the yield of carboxylic acid **2a** were improved with $\text{Ir}(\text{ppy})_2(\text{dtbpy})(\text{PF}_6)$ **4c** and $\text{Ir}(\text{ppy})_2(\text{dmobpy})(\text{PF}_6)$ **4d** having higher reduction potentials.

Table S4. The screening of Pd sources

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

^a Determined by ¹H-NMR spectra.

Table S5. The amount of Pd and photoredox catalysts

| | Entry | X mol% | Y mol% | Z mol% | Conv. /% ^a | 2a /% ^a | 3a /% ^a |
|--------------------|-------|--------|--------|--------|-----------------------|--------------------|--------------------|
| 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 |

^a Determined by ¹H-NMR spectra.

This carboxylation reaction necessitated the use of two molar amounts of phosphine ligand for Pd(OAc)₂ (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

| Entry | e ⁻ donor (X equiv.) | Conv. /% ^a | 2a /% ^a | 3a /% ^a |
|-------|---------------------------------|-----------------------|--------------------|--------------------|
| 1 | iPr ₂ NEt (6.0) | 100 | 48 | 45 |
| 2 | NEt ₃ (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 |

^a Determined by ¹H-NMR spectra.

The carboxylic acid **2a** was produced in a higher yield by using *i*Pr₂NEt as a sacrificial electron-donor (entry 1).

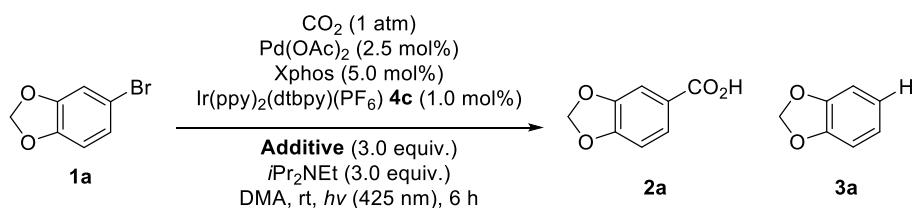
Table S7. The screening of solvents

| Entry | Solvent | Conv. /% ^a | 2a /% ^a | 3a /% ^a |
|-------|---------|-----------------------|--------------------|--------------------|
| 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 |

^a Determined by ¹H-NMR spectra.

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

Table S8. The screening of additives

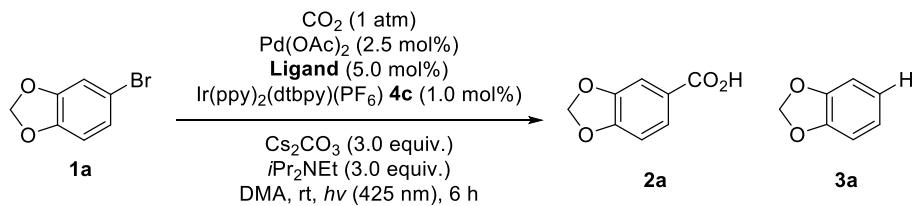


| Entry | Additive | Conv. /% ^a | 2a /% ^a | 3a /% ^a |
|----------------|---------------------------------|-----------------------|--------------------|--------------------|
| 1 ^b | none | 100 | 48 | 45 |
| 2 ^b | TFA (1.0 equiv.) | 98 | 34 | 53 |
| 3 ^b | TFA (2.0 equiv.) | 78 | 16 | 47 |
| 4 | Na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

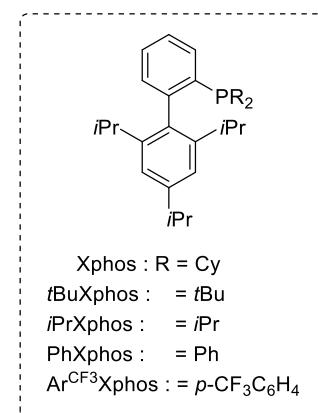
^a Determined by ¹H-NMR spectra. ^b Using *i*Pr₂NEt (6.0 equiv.)

This carboxylation reaction was improved by the addition of Cs₂CO₃ 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. /% ^a | 2a /% ^a | 3a /% ^a |
|----------------|-------------------------|-----------------------|--------------------|--------------------|
| 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 ^{CF3} Xphos | 99 | 75 | 9 |
| 6 ^b | PhXphos | 100 | 88 | 6 |



^a Determined by ¹H-NMR spectra. ^b Using Ir 4c (2.5 mol%)

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

Table S10. The effect of CO₂ pressure

| 1a | CO ₂ (X atm) Pd(OAc) ₂ (2.5 mol%) Xphos (5.0 mol%) Ir(ppy) ₂ (dtbpy)(PF ₆) 4c (1.0 mol%) iPr ₂ NEt (6.0 equiv.) DMA, rt, h (425 nm), 1 h in a pressure tight vessel | 2a | 3a | |
|-------|--|-----------------------|--------------------|--------------------|
| Entry | X atm | Conv. /% ^a | 2a /% ^a | 3a /% ^a |
| 1 | 1.0 | 55 | 35 | 19 |
| 2 | 5.0 | 60 | 38 | 16 |
| 3 | 10.0 | 58 | 37 | 14 |

^a Determined by ¹H-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.

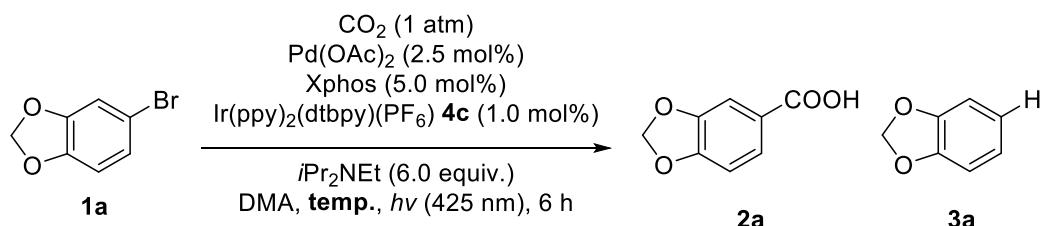
Table S11. The effect of photon flux

| 1a | CO ₂ (1 atm) Pd(OAc) ₂ (2.5 mol%) Xphos (5.0 mol%) Ir(ppy) ₂ (dtbpy)(PF ₆) 4c (1.0 mol%) none or Cs ₂ CO ₃ iPr ₂ NEt (6.0 equiv.) DMA, rt, 2 h h (425 nm) X sockets | 2a | 3a | | |
|----------------|---|---------------------------------|-----------------------|--------------------|--------------------|
| Entry | X sockets | Cs ₂ CO ₃ | Conv. /% ^a | 2a /% ^a | 3a /% ^a |
| 1 | 1 | none | 59 | 40 | 16 |
| 2 | 2 (standard) | none | 73 | 44 | 24 |
| 3 | 4 | none | 100 | 47 | 52 |
| 4 ^b | 1 | 3.0 equiv. | 61 | 46 | 9 |
| 5 ^b | 2 (standard) | 3.0 equiv. | 81 | 58 | 12 |
| 6 ^b | 4 | 3.0 equiv. | 93 | 58 | 22 |

^a Determined by ¹H-NMR spectra. ^b Using *i*Pr₂NEt (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



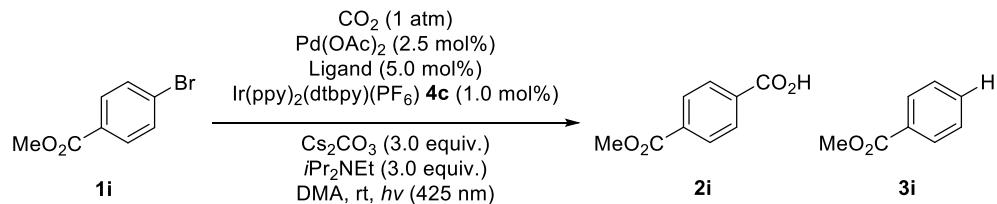
| Entry | temp. | Cs ₂ CO ₃ | Conv. /% ^a | 2a /% ^a | 3a /% ^a |
|-------|-------------|---------------------------------|-----------------------|---------------------------|---------------------------|
| 1 | 0 °C | none | 77 | 47 | 25 |
| 2 | 0 °C (12 h) | none | 92 | 45 | 48 |
| 3 | rt | none | 100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

^a Determined by ¹H-NMR spectra. ^b Using *i*Pr₂NEt (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 CO₂ and/or decomposition of the Pd complex.

Optimization for the Carboxylation of Electron-Withdrawing Aryl Bromides with Carbon Dioxide (CO_2)

Table S13. The screening of phosphine ligands



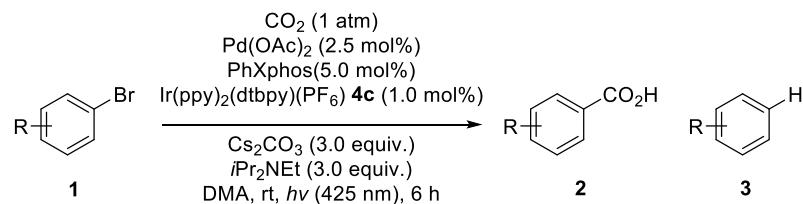
| Entry | Ligand | Conv. /% ^a | 2i /% ^a | 3i /% ^a |
|----------------|------------------|-----------------------|---------------------------|---------------------------|
| 1 | PhXphos | 100 | 40 | 48 |
| 2 ^b | PhXphos | 100 | 51 | 46 |
| 3 | Xphos | 100 | 21 | 64 |
| 4 | <i>t</i> BuXphos | 100 |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

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

^c 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



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

^a Determined by ¹H-NMR spectra.

^b Using Ir(dF(CF₃)ppy)₂(dtbpy)(PF₆) **4b** instead of Ir(ppy)₂(dtbpy)(PF₆) **4c**.

^c Using Ir(ppy)₂(dtbpy)(PF₆) **4c** (2.5 mol%).

Optimization for the Carboxylation of Aryl Chloride **6e** with Carbon Dioxide (CO₂)

Table S15. The screening of phosphine ligands

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

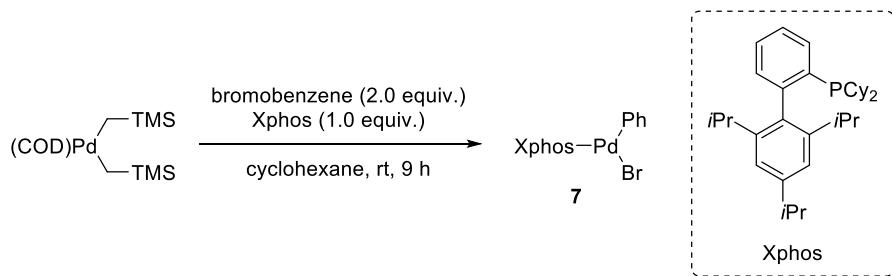
^a Determined by ¹H-NMR spectra. ^b Reaction time is 12 h.

^c 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 μ L, 0.20 mmol, 2.0 equiv.) with Xphos (48 mg, 0.10 mmol, 1.0 equiv.) and $(\text{COD})\text{Pd}(\text{CH}_2\text{TMS})_2^{10}$ (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.

$^1\text{H-NMR}$ (500 MHz in CDCl_3): δ = 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

$^{13}\text{C-NMR}$ (125 MHz in CDCl_3): δ = 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

$^{31}\text{P-NMR}$ (202 MHz in CDCl_3): δ = 26.5 ppm

Observation of the Reaction Intermediate under the Catalytic Conditions

A DMA solution (0.5 mL) of bromobenzene (10.5 μ 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%), $\text{Ir}(\text{ppy})_2(\text{dtbpy})(\text{PF}_6)$ **4c** (1.8 mg, 0.002 mmol, 2.0 mol%), and $i\text{Pr}_2\text{NEt}$ (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_2 atmosphere at room temperature for 5 min. Arylpalladium bromide complex 7 was observed as the resting state.

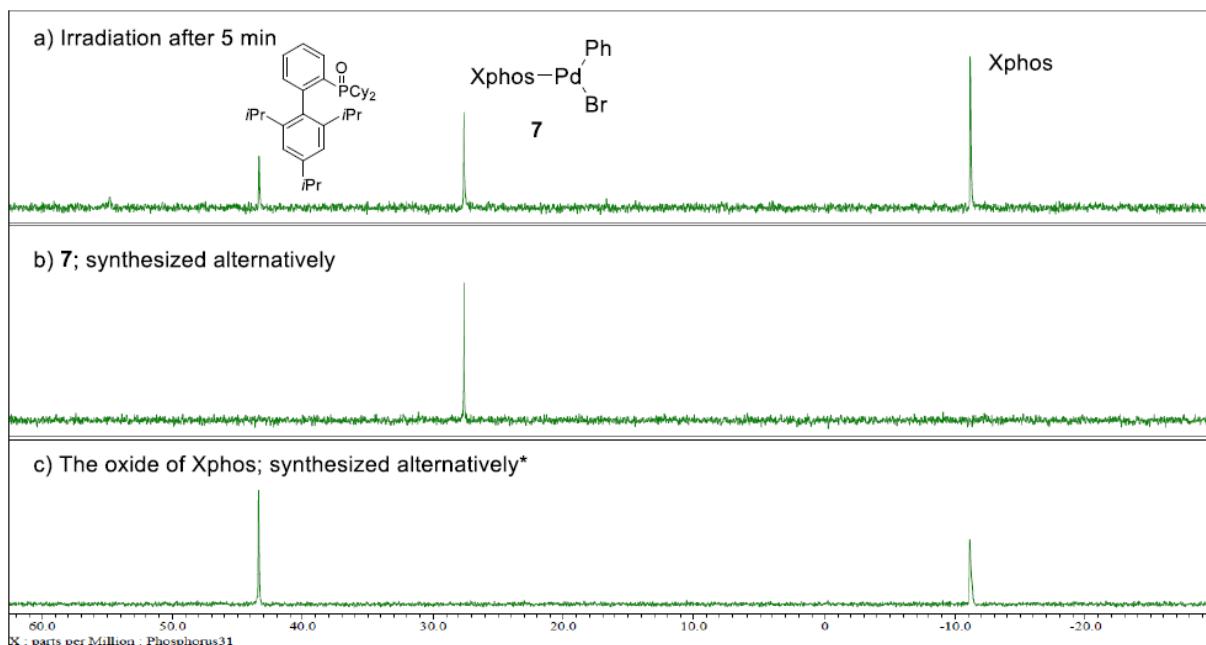


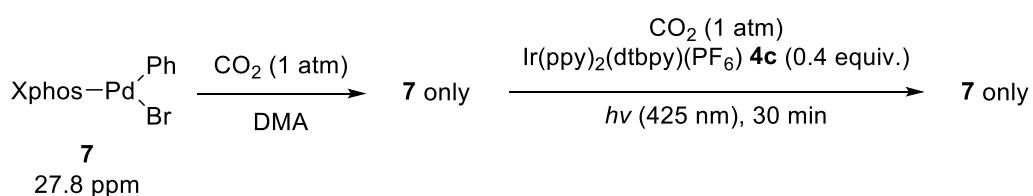
Figure S1. ^{31}P -NMR Spectra under the Catalytic Carboxylation Conditions
(202 MHz, DMA (0.5 mL) and $i\text{Pr}_2\text{NEt}$ (0.1 mL))

* The oxide of Xphos was prepared in toluene under O_2 atmosphere at 100 °C for 11 h.

Reactivity of Arylpalladium Bromide Complex 7

Reaction of Arylpalladium Bromide Complex 7 with 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 CO_2 atmosphere at room temperature. No change was observed by ^{31}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 CO_2 atmosphere at room temperature for 30 min. However, a new peak wasn't detected by ^{31}P -NMR spectrum in the absence of $i\text{Pr}_2\text{NEt}$.



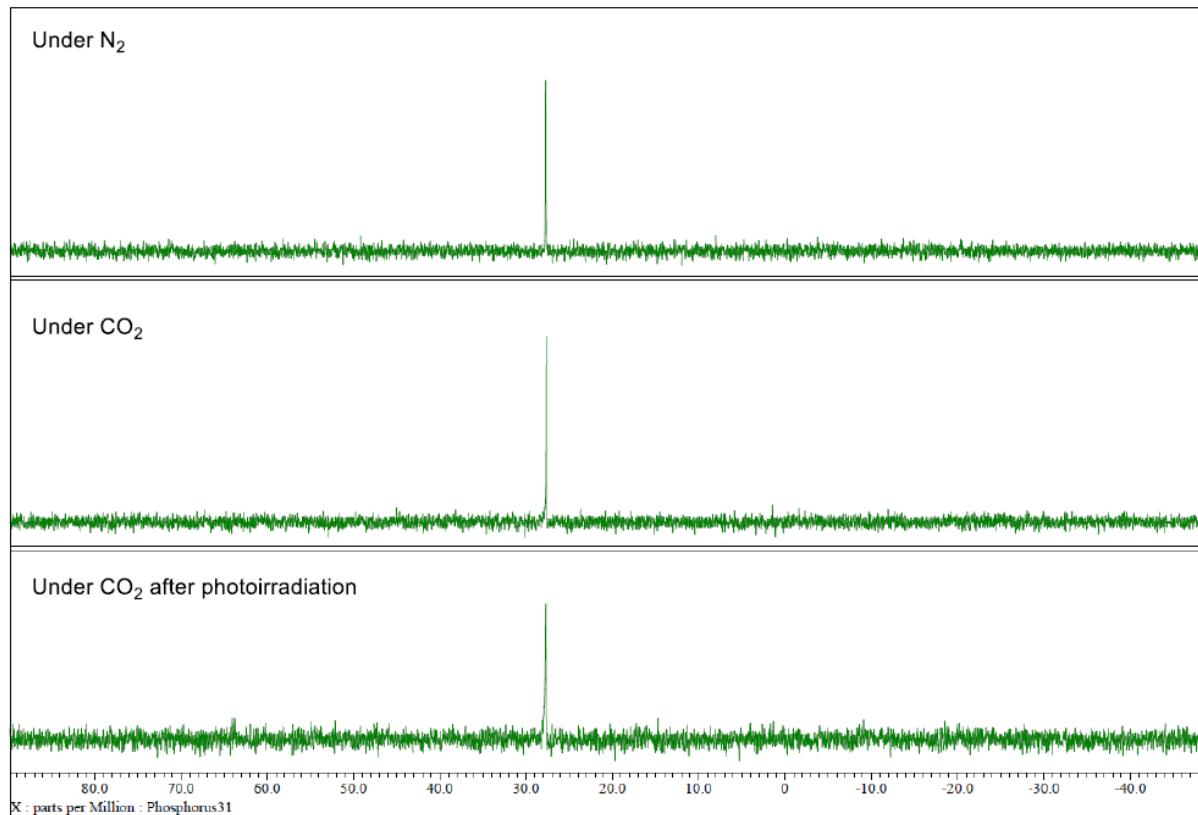


Figure S2. ³¹P-NMR Spectra under CO₂ atmosphere

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 (NaBAr^F, 5.3 mg, 0.006 mmol) in CH₂Cl₂ (0.6 mL) was put in a J. Young NMR tube under a nitrogen atmosphere at room temperature. After 40 min, ³¹P-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.¹⁶

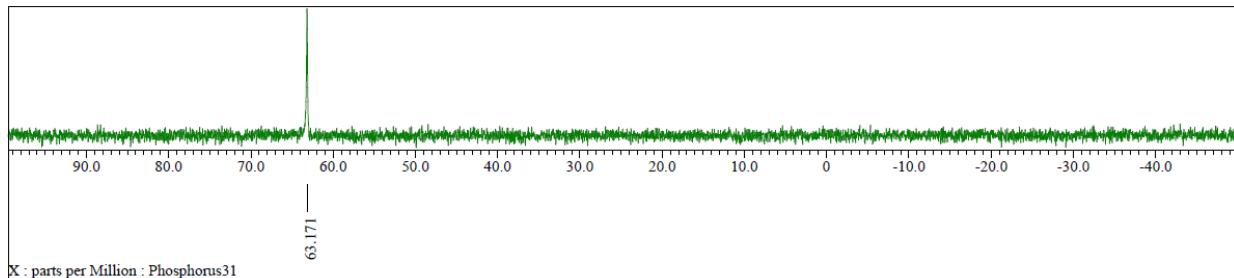
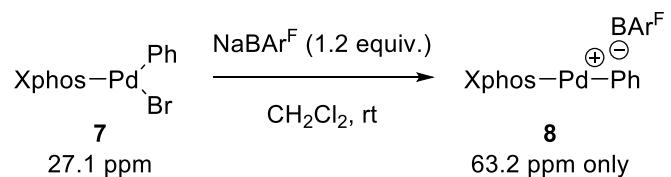


Figure S3. ^{31}P -NMR Spectra of arylpalladium cation 8 *in situ*

Cyclic Voltammograms of Aryl palladium complexes 7 and 8

All voltammograms were measured at room temperature using Ag/AgNO₃ reference electrode, a platinum (Pt) counter and working electrode. The conditions of the experiments were as follows: a THF or a CH₂Cl₂ solution of 100 mM tetrabutylammonium hexafluorophosphate (NBu₄PF₆) 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 ($E_{p/2}$) since the reduction was non-reversible. To convert the potentials from Ag/AgNO₃ to Fc/Fc⁺ reference, ferrocene was measured under the above conditions in a THF or a CH₂Cl₂ solution, and -0.15 V (THF) or -0.06 V (CH₂Cl₂) were subtracted from the measured values.

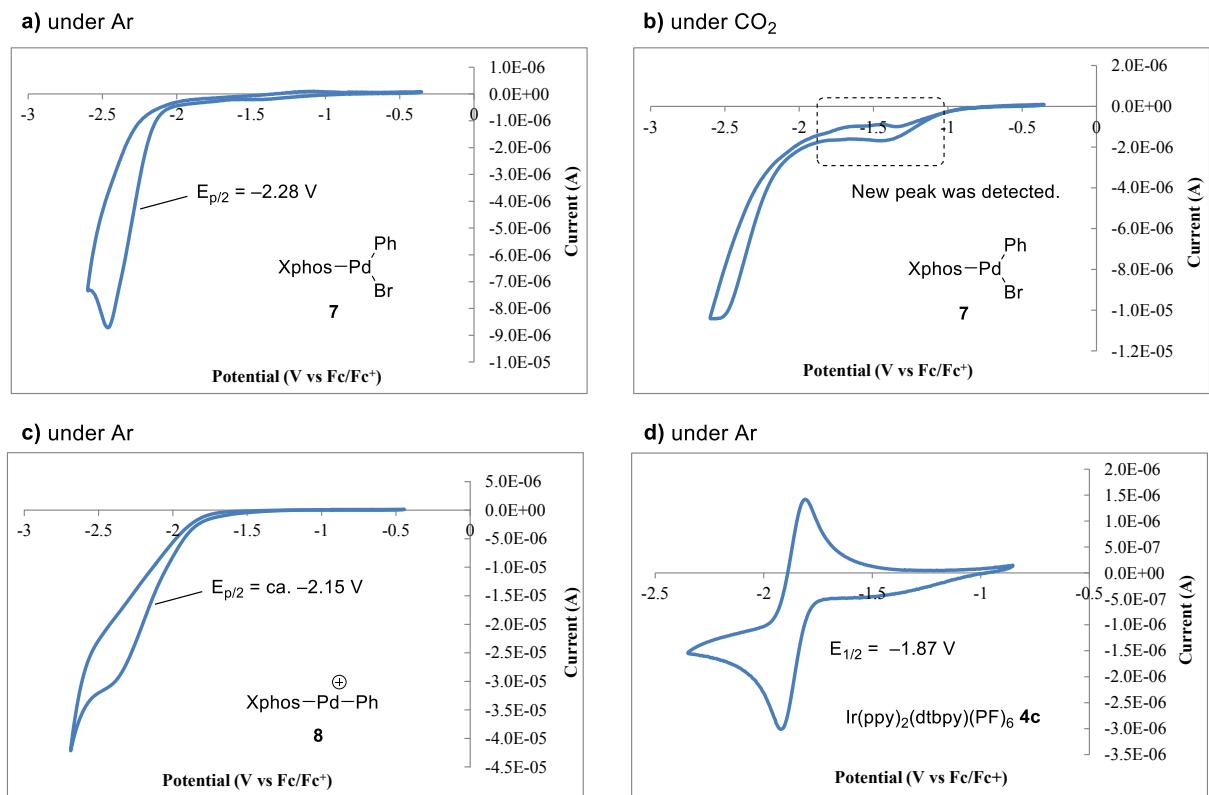


Figure S4 : Cyclic voltammograms a) Arylpalladium bromide **7** (2.0 mM) in THF under Ar. b) Arylpalladium bromide **7** (2.0 mM) in THF under CO_2 . c) Arylpalladium cation **8** (1.0 mM) generated from arylpalladium bromide **7** (3.7 mg, 0.005 mmol) and NaBAr^{F} (NaBAr^{F} , 5.3 mg, 0.006 mmol) in CH_2Cl_2 *in situ* (see. Figure S3). d) $\text{Ir}(\text{ppy})_2(\text{dtbbpy})(\text{PF}_6)$ **4c** (1.0 mM) in THF.

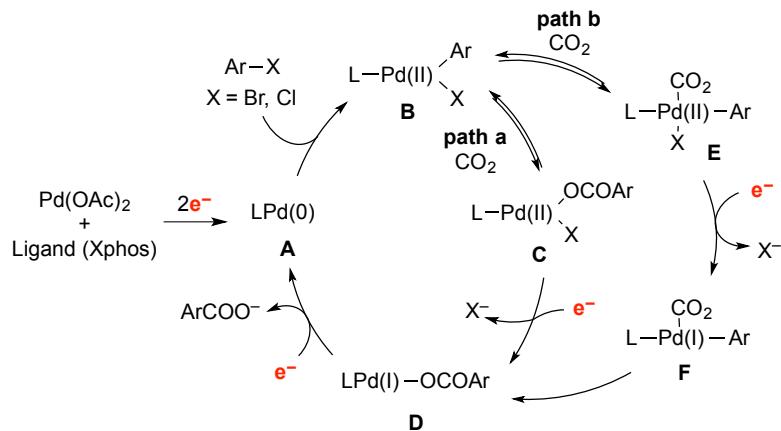
Figure S4b showed a new peak around -1.4 V by measuring under CO_2 . Although this new peak was rather weak, repeated experiments confirmed its presence. Furthermore, by bubbling Ar after CV measurement under CO_2 , the CV changed to the one shown in Figure S4a. Thus, a new species is thought to be generated by exposing arylpalladium bromide **7** to CO_2 .

Proposed Mechanism (Carboxylation Reaction)

As the resting state of this reaction, aryl palladium **B** was observed by a ^{31}P -NMR spectrum under the catalytic reaction conditions (Figure S1). It was also found that the reduction potential of isolated $\text{PhPd}(\text{II})\text{Br}(\text{Xphos})$ **7** was quite low ($E_{\text{p/2}} = -2.28 \text{ V}$ vs Fc/Fc^+) and this complex by itself could not be reduced under argon by the reduced form of Ir catalyst ($E_{1/2} = -1.87 \text{ V}$ vs Fc/Fc^+) (Figure S4a vs d). The reduction potential of $[\text{PhPd}(\text{Xphos})]^+$ **8** was also lower ($E_{\text{p/2}} = -2.15 \text{ V}$ vs Fc/Fc^+) than the Ir catalyst, and direct reduction of these species is not likely (Figure S4c). Interestingly, CV measurement of this complex under CO_2 atmosphere showed a new peak at about -1.4 V (Figure S4b).

This means under CO_2 atmosphere, a new species, which can be reduced by the reduced form of Ir catalyst, appeared. However, when $\text{PhPdBr}(\text{Xphos})$ 7 was subjected to CO_2 atmosphere, a new peak wasn't detected by ^{31}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.

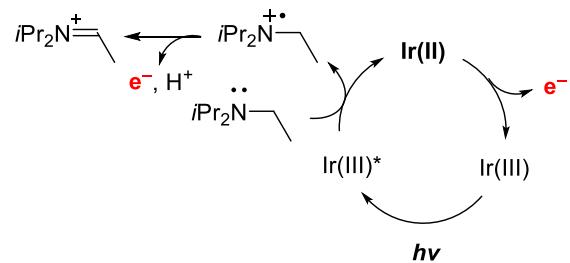
Scheme S1. Proposed mechanism of carboxylation reaction



The first one is $(\text{ArCOO})\text{Pd}(\text{II})\text{X}(\text{Xphos})$ **C** generated in a small amount in equilibrium with $\text{ArPd}(\text{II})\text{X}(\text{Xphos})$ **B** under CO_2 as shown in Scheme S1 (path a). Photoredox-catalyzed one-electron reduction of $(\text{ArCOO})\text{Pd}(\text{II})\text{X}(\text{Xphos})$ **C** would give $(\text{ArCOO})\text{Pd}(\text{I})(\text{Xphos})$ **D** and X^- , and the generated $(\text{ArCOO})\text{Pd}(\text{I})(\text{Xphos})$ **D** would undergo further one-electron reduction to give $\text{Pd}(0)(\text{Xphos})_2$ and ArCOO^- . As no detectable formation of $(\text{ArCOO})\text{PdX}(\text{Xphos})$ **C** was observed when $\text{ArPdX}(\text{Xphos})$ **B** was subjected to CO_2 atmosphere, it is possible that there is an equilibrium between $\text{ArPdX}(\text{Xphos})$ **B** and $(\text{ArCOO})\text{PdX}(\text{Xphos})$ **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_2 -coordinated $\text{ArPd}(\text{II})\text{X}(\text{Xphos})$ **E**, again generated in a small amount, and this species would be able to undergo one-electron reduction to give a CO_2 -coordinated $\text{ArPd}(\text{I})(\text{Xphos})$ species **F**, which would have higher ability to undergo addition to CO_2 to give $(\text{ArCOO})\text{Pd}(\text{I})(\text{Xphos})$ **D**. This would then undergo the similar process as described above (Scheme S1 (path b)). The additional one-electron reduction of $\text{ArPd}(\text{I})(\text{Xphos})$ **F** to $[\text{ArPd}(0)(\text{Xphos})]^-$ **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 $\text{Ir}(\text{III})^*$ species by $i\text{Pr}_2\text{NEt}$ produced $\text{Ir}(\text{II})$ as a reductive species and an amine radical cation. The one-electron reduction of Pd species proceeded by electron-transfer from the $\text{Ir}(\text{II})$ 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 (ArCOO^- and X^-) is both protons generated from the oxidized amine, and these two acids are neutralized with the excess Cs_2CO_3 and/or amine.

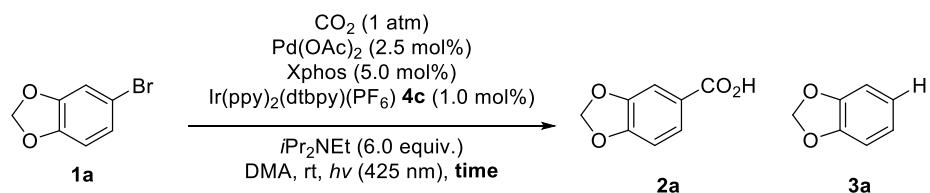
Mechanistic Study of Reduction Reaction

The hydrogenated products **3** could be produced by the direct photo-redox catalyzed reduction using *iPr*₂NEt 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**

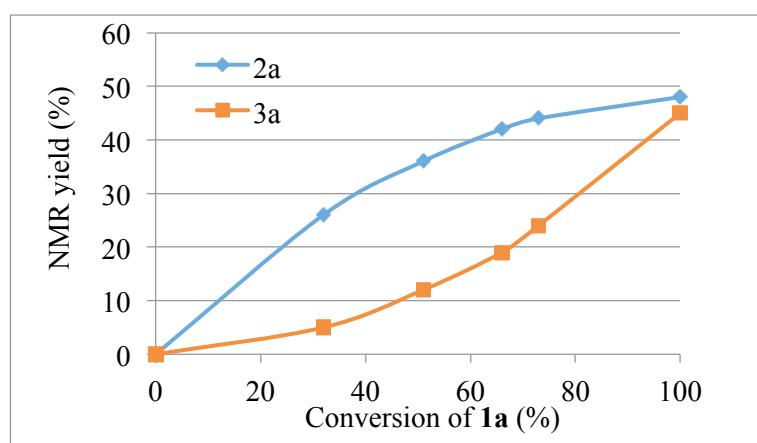
A DMA solution (1.0 mL) of **1a** (24 μ L, 0.20 mmol) with palladium acetate (1.1 mg, 0.005 mmol, 2.5 mol%), Xphos (4.8 mg, 0.01 mmol, 5.0 mol%), Ir(ppy)₂(dtbpy)(PF₆) **4c** (1.8 mg, 0.002 mmol, 1.0 mol%), and *iPr*₂NEt (0.21 mL, 1.2 mmol, 6.0 equiv.) was prepared in a test tube under nitrogen atmosphere. Then the gas phase was replaced by atmospheric pressure of CO₂, 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 15, 30, 60, 120 and 360 min respectively in the closed system. The product mixture was analyzed by ¹H 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. /% ^a | 2a /% ^a | 3a /% ^a |
|-------|-----------|-----------------------|---------------------------|---------------------------|
| 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 |

^a Determined by ¹H-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 $\text{THF}-d_8$ (0.6 mL) was put in a J. Young NMR tube under N_2 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 ^{31}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 ^{31}P -NMR.

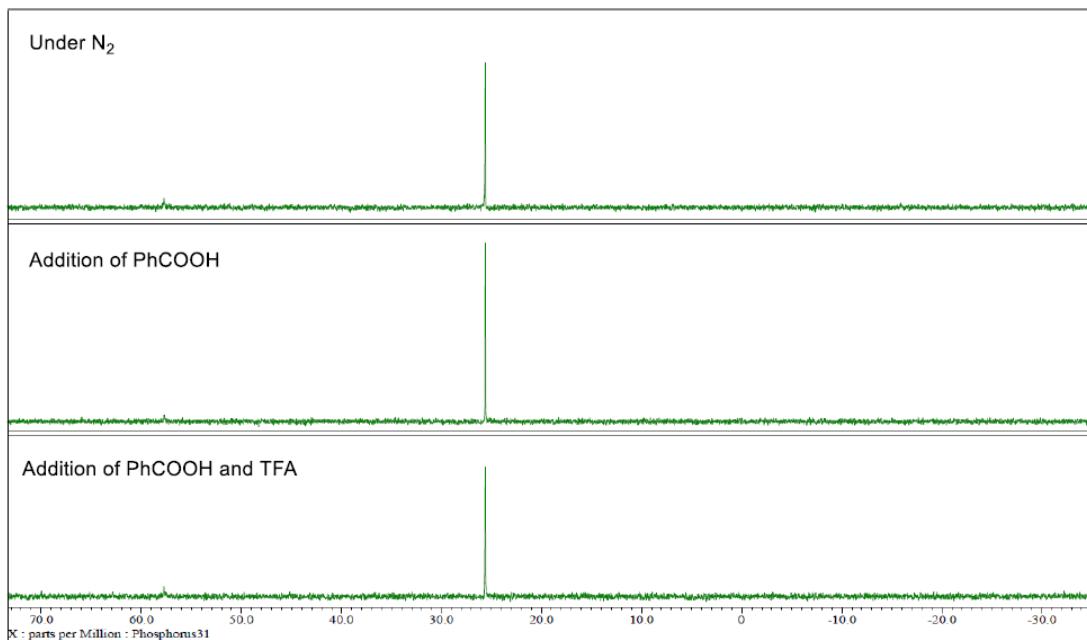
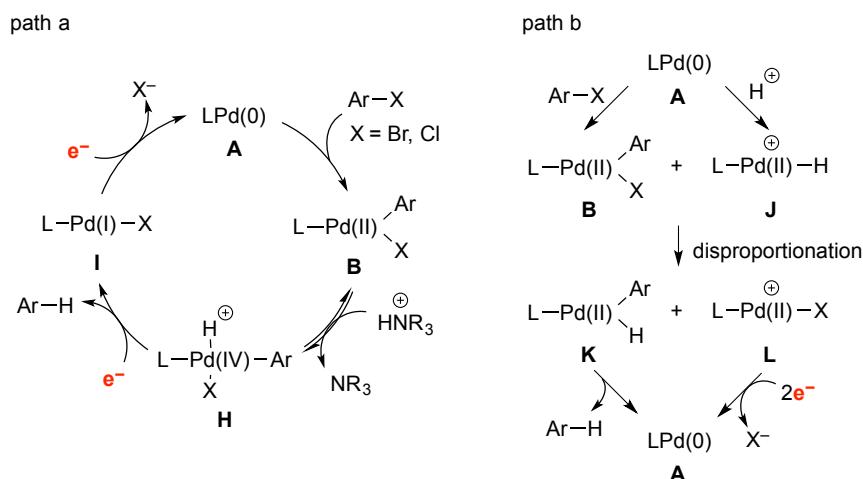


Figure S5. ^{31}P -NMR Spectra with Brønsted acids

Proposed Mechanism (Reduction Reaction)

The time-dependence of the ratio of the carboxylation and reduction products in the absence of Cs_2CO_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 Cs_2CO_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



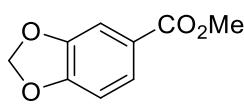
The first one is the protonation of ArPd(II)X(Xphos) intermediate to give $[\text{ArPd(IV)(H)(Br)(Xphos)}]^+$ **H**, which would give $(\text{Xphos})\text{Pd(I)X}$ **I** by photoredox-catalyzed one-electron reduction to release the hydrogenated product. The generated $(\text{Xphos})\text{Pd(I)X}$ would undergo further one-electron reduction to give Pd(0)(Xphos) and halide anion. It might be possible that two successive electron-transfer occurs first to give to ArPd(II)H(Xphos) , which undergoes the reductive elimination to give the hydrogenated product. Although no formation of PdH species nor benzene was observed by the addition of TFA to PhPdBr(Xphos) in $\text{THF}-d_8$ at rt to 60 °C (Figure S5), this does not necessarily mean that the reduction pathway through 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 ArX , Pd(0) would react with the acid generated, thus generating a Pd(II)-hydride **J** on one end and 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

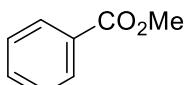
The Carboxylation of Aryl Bromides



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.¹⁷

¹H-NMR (500 MHz in CDCl₃): δ = 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

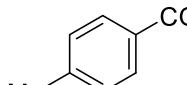
¹³C-NMR (125 MHz in CDCl₃): δ = 52.0, 101.7, 107.9, 109.5, 124.1, 125.3, 147.7, 151.5, 166.4 ppm



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.¹⁸

¹H-NMR (500 MHz in CDCl₃): δ = 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

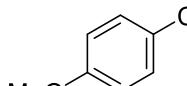
¹³C-NMR (125 MHz in CDCl₃): δ = 52.1, 128.3, 129.5, 130.1, 132.9, 167.1 ppm



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.¹⁸

¹H-NMR (500 MHz in CDCl₃): δ = 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

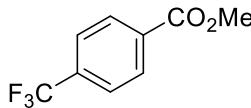
¹³C-NMR (125 MHz in CDCl₃): δ = 21.6, 51.9, 127.4, 129.0, 129.6, 143.5, 167.2 ppm



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.¹⁸

¹H-NMR (500 MHz in CDCl₃): δ = 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

¹³C-NMR (125 MHz in CDCl₃): δ = 51.8, 55.4, 113.5, 122.5, 131.5, 163.3, 166.8 ppm

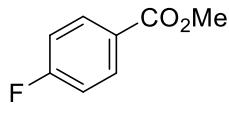


With PhXphos, **1e** (0.2 mmol, 45.0 mg) provided 33.8 mg (83% yield) of the corresponding compound **5e** as colorless oil. The spectroscopic data coincided

with those of the literature.¹⁷

¹H-NMR (500 MHz in CDCl₃): 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

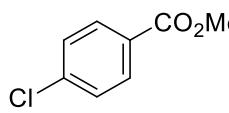
¹³C-NMR (125 MHz in CDCl₃): δ = 52.5, 123.6 (q, J = 274 Hz), 125.4 (q, J = 4 Hz), 129.6, 133.3, 134.4 (q, J = 33 Hz), 165.9 ppm



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.¹⁸

¹H-NMR (500 MHz in CDCl₃): δ = 3.91 (s, 3 H), 7.08-7.13 (m, 2 H), 8.03-8.07 (m, 2 H) ppm

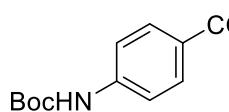
¹³C-NMR (125 MHz in CDCl₃): δ = 52.2, 115.5 (d, J = 23 Hz), 126.3 (d, J = 2 Hz), 132.1 (d, J = 8 Hz), 165.7 (d, J = 255 Hz), 166.1 ppm



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.¹⁸

¹H-NMR (500 MHz in CDCl₃): 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

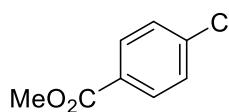
¹³C-NMR (125 MHz in CDCl₃): δ = 52.3, 128.5, 128.7, 130.9, 139.3, 166.2 ppm



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.¹⁹

¹H-NMR (500 MHz in CDCl₃): 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

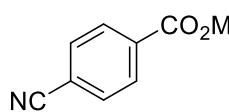
¹³C-NMR (125 MHz in CDCl₃): δ = 28.2, 51.9, 81.2, 117.3, 124.3, 130.9, 142.7, 152.2, 166.7 ppm



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.¹⁷

¹H-NMR (500 MHz in CDCl₃): δ = 3.94 (s, 6 H), 8.10 (s, 4 H) ppm

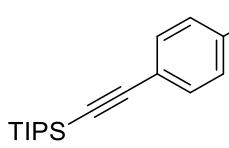
¹³C-NMR (125 MHz in CDCl₃): δ = 52.4, 129.5, 133.9, 166.3 ppm



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.²⁰

¹H-NMR (500 MHz in CDCl₃): 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

¹³C-NMR (125 MHz in CDCl₃): δ = 52.7, 116.4, 118.0, 130.1, 132.2, 133.9, 165.4 ppm



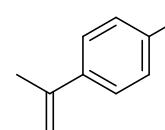
With PhXphos, **1k** (0.2 mmol, 67.5 mg) provided 54.0 mg (85% yield) of the corresponding compound **5k** as colorless oil.

IR (neat): 2944, 2866, 2156, 1605, 1463, 1436, 1276, 1107, 844, 680 cm⁻¹

¹H-NMR (500 MHz in CDCl₃): 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

¹³C-NMR (125 MHz in CDCl₃): δ = 11.2, 18.6, 52.2, 94.3, 106.1, 128.1, 129.3, 129.5, 131.9, 166.5 ppm

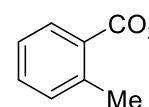
HRMS(FD⁺): Calcd. C₁₉H₂₈O₂Si [M]⁺: 316.1859, Found: 316.1841 m/z.



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.²¹

¹H-NMR (500 MHz in CDCl₃): 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

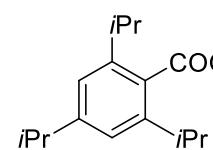
¹³C-NMR (125 MHz in CDCl₃): δ = 21.6, 52.0, 114.6, 125.4, 128.9, 129.5, 142.4, 145.6, 166.9 ppm



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.²²

¹H-NMR (500 MHz in CDCl₃): 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

¹³C-NMR (125 MHz in CDCl₃): δ = 21.7, 51.8, 125.7, 129.5, 130.5, 131.7, 131.9, 140.2, 168.1 ppm



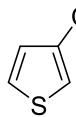
With PhXphos, **1n** (0.2 mmol, 56.6 mg) provided 39.9 mg (76% yield) of the corresponding compound **5n** as a white solid.

IR (neat): 2962, 2871, 1726, 1606, 1460, 1430, 1254, 1078, 876, 772 cm⁻¹

¹H-NMR (500 MHz in CDCl₃): 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

¹³C-NMR (125 MHz in CDCl₃): δ = 23.9, 24.1, 31.6, 34.4, 51.8, 120.8, 130.3, 144.8, 150.2, 171.4 ppm

HRMS(FD⁺): Calcd. C₁₇H₂₆O₂ [M]⁺: 262.1933, Found: 262.1887 m/z.

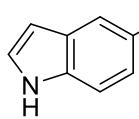


CO₂Me With PhXphos, **1o** (0.2 mmol, 32.6 mg) provided 20.6 mg (72% yield) of the corresponding compound **5o** as colorless oil. The spectroscopic data coincided with those of the literature.¹⁸

¹H-NMR (500 MHz in CDCl₃): 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

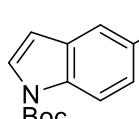
¹³C-NMR (125 MHz in CDCl₃): δ = 51.8, 126.0, 127.9, 132.7, 133.5, 163.2 ppm



CO₂Me 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.²³

¹H-NMR (500 MHz in CDCl₃): 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

¹³C-NMR (125 MHz in CDCl₃): δ = 51.9, 104.0, 110.7, 121.8, 123.3, 123.8, 125.5, 127.4, 138.3, 168.3 ppm



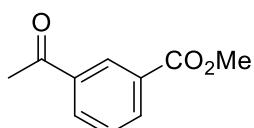
CO₂Me With PhXphos, **1q** (0.2 mmol, 59.2 mg) provided 39.5 mg (72% yield) of the corresponding compound **5q** as colorless oil.

IR (neat): 3152, 2980, 1739, 1718, 1615, 1438, 1237, 1092, 1024, 758 cm⁻¹

¹H-NMR (500 MHz in CDCl₃): 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

¹³C-NMR (125 MHz in CDCl₃): 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⁺): Calcd. C₁₅H₁₇NO₄ [M]⁺: 275.1158, Found: 275.1123 m/z.

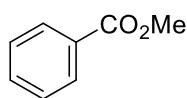


CO₂Me With *t*BuXphos, **1r** (0.2 mmol, 39.8 mg) provided 23.8 mg (67% yield) of the corresponding compound **5r** as a white solid. The spectroscopic data coincided with those of the literature.²⁴

¹H-NMR (500 MHz in CDCl₃): 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

¹³C-NMR (125 MHz in CDCl₃): δ = 26.7, 52.4, 128.8, 129.5, 130.6, 132.3 133.9, 137.2, 166.2, 197.2 ppm

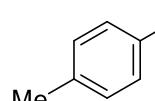
The Carboxylation of Aryl Chlorides



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.¹⁸

¹H-NMR (500 MHz in CDCl₃): δ = 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

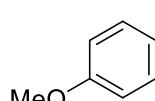
¹³C-NMR (125 MHz in CDCl₃): δ = 52.1, 128.3, 129.5, 130.1, 132.9, 167.1 ppm



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.¹⁸

¹H-NMR (500 MHz in CDCl₃): δ = 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

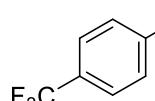
¹³C-NMR (125 MHz in CDCl₃): δ = 21.6, 51.9, 127.4, 129.0, 129.6, 143.5, 167.2 ppm



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.¹⁸

¹H-NMR (500 MHz in CDCl₃): δ = 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

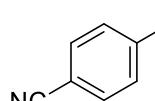
¹³C-NMR (125 MHz in CDCl₃): δ = 51.8, 55.4, 113.5, 122.5, 131.5, 163.3, 166.8 ppm



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.¹⁷

¹H-NMR (500 MHz in CDCl₃): 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

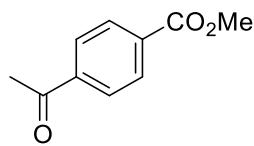
¹³C-NMR (125 MHz in CDCl₃): δ = 52.5, 123.6 (q, *J* = 274 Hz), 125.4 (q, *J* = 4 Hz), 129.6, 133.3, 134.4 (q, *J* = 33 Hz), 165.9 ppm



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

¹H-NMR (500 MHz in CDCl₃): 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

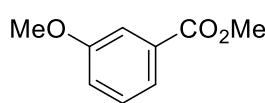
¹³C-NMR (125 MHz in CDCl₃): δ = 52.7, 116.4, 118.0, 130.1, 132.2, 133.9, 165.4 ppm



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.²⁴

¹H-NMR (500 MHz in CDCl₃): δ = 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

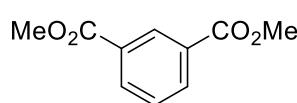
¹³C-NMR (125 MHz in CDCl₃): δ = 26.9, 52.5, 128.2, 129.8, 133.9, 140.2, 166.2, 197.6 ppm



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.²²

¹H-NMR (500 MHz in CDCl₃): δ = 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

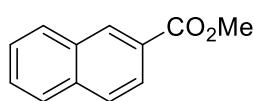
¹³C-NMR (125 MHz in CDCl₃): δ = 52.2, 55.4, 113.9, 119.5, 121.9, 129.4, 131.4, 159.5, 167.0 ppm



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.²⁵

¹H-NMR (500 MHz in CDCl₃): δ = 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

¹³C-NMR (125 MHz in CDCl₃): δ = 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.²⁰

¹H-NMR (500 MHz in CDCl₃): δ = 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

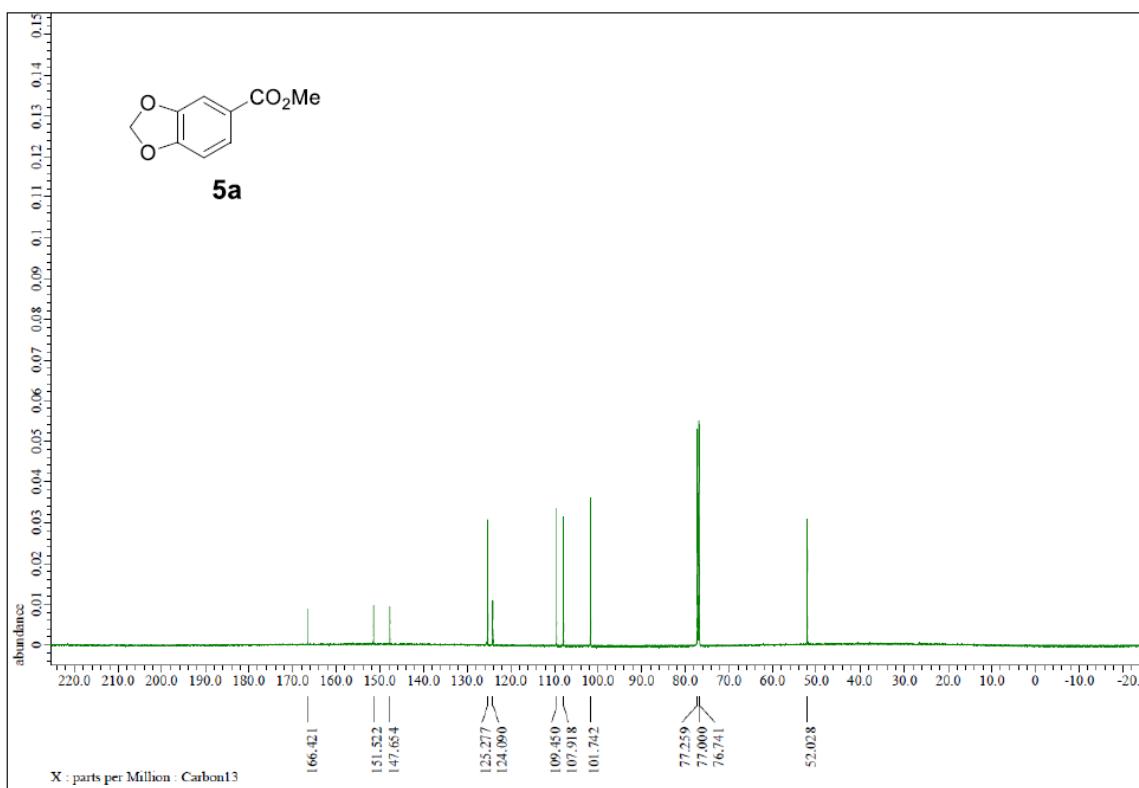
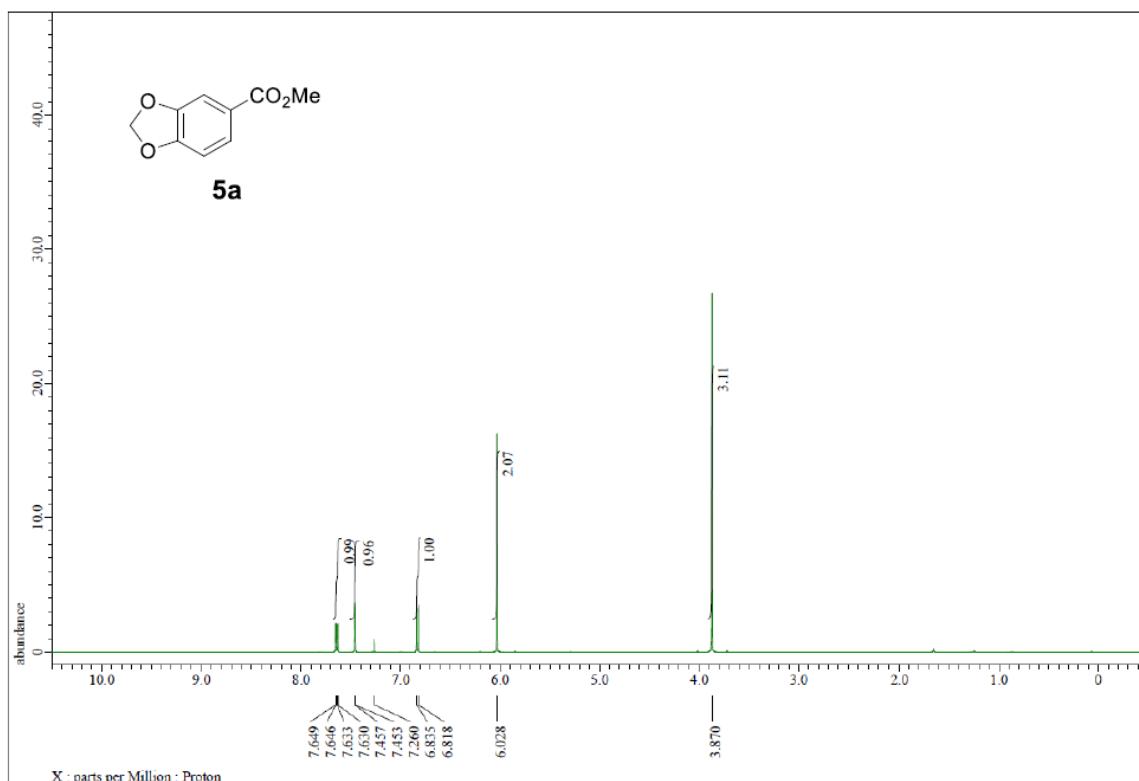
¹³C-NMR (125 MHz in CDCl₃): δ = 52.2, 125.2, 126.6, 127.3, 127.7, 128.1, 128.2, 129.3, 131.0, 132.4, 135.5, 167.2 ppm

References

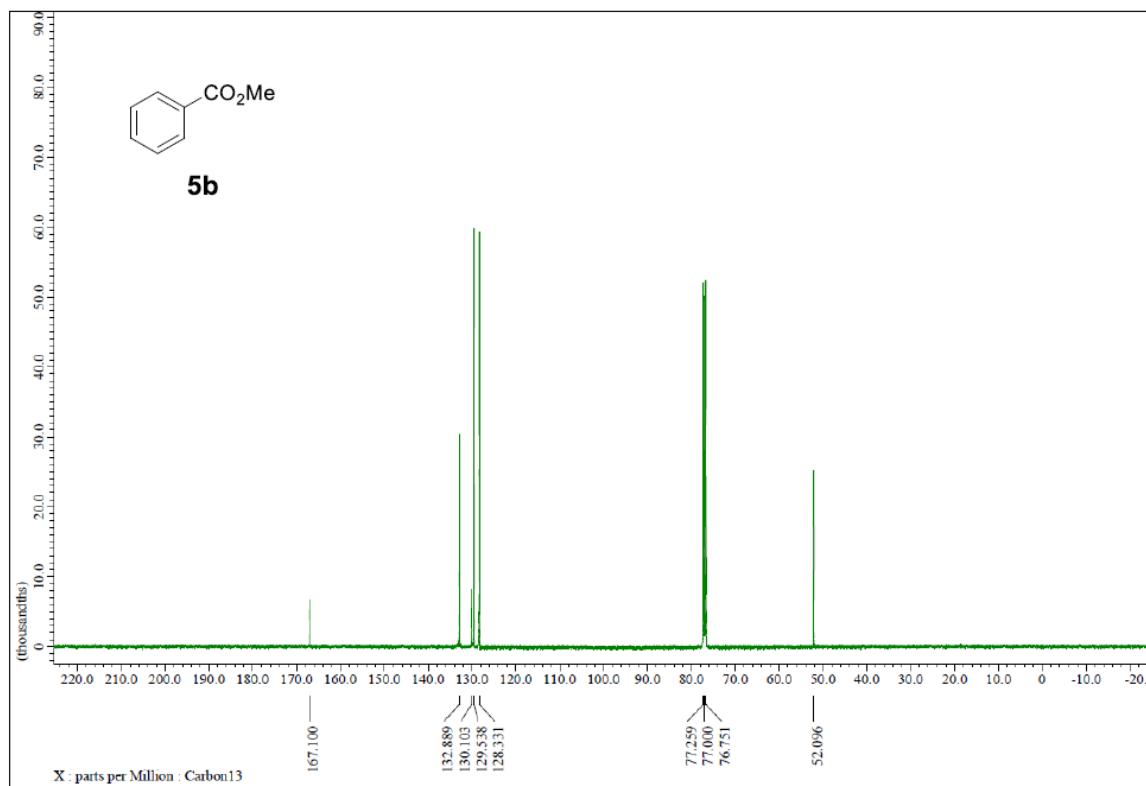
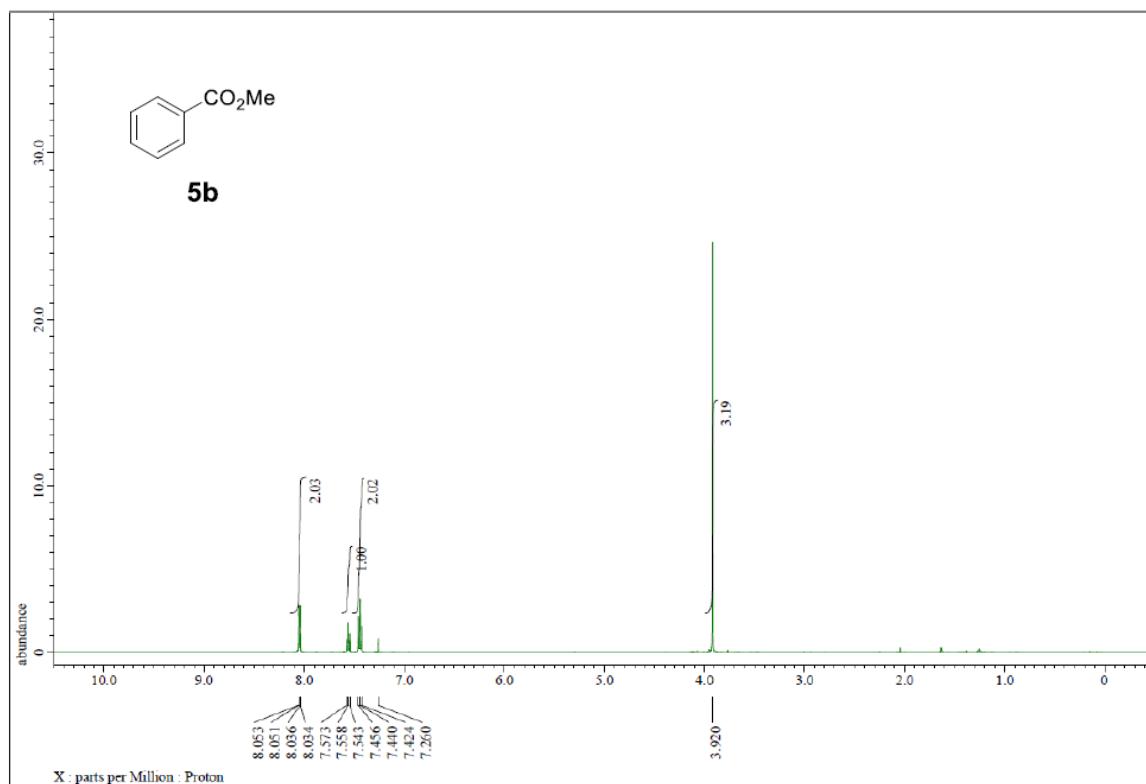
- (1) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685.
- (2) Damrauer, N. H.; Boussie, T. R.; Devenney, M.; McCusker, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 8253.
- (3) Oderinde, M. S.; Alvarez, A. V.; Aquila, B.; Robbins, D. W.; Johannes, J. W. *J. Org. Chem.* **2015**, *80*, 7642.
- (4) Perepichka, I.; Kundu, S.; Hearne, Z.; Li, C. *J. Org. Biomol. Chem.* **2015**, *13*, 447.
- (5) Ma, D. L.; Liu, L. J.; Leung, K. H.; Chen, Y. T.; Zhong, H. J.; Chan, D. S. H.; Wang, H. M. D.; Leung, C. H. *Angew. Chem. Int. Ed.* **2014**, *53*, 9178.
- (6) Whang, D. R.; Sakai, K.; Park S. Y. *Angew. Chem. Int. Ed.* **2013**, *52*, 11612.
- (7) Lowry, M. S.; Hudson, W. R.; Pascal, Jr., R. A.; Bernhard, S. *J. Am. Chem. Soc.* **2004**, *126*, 14129.
- (8) Tamayo, A. B.; Alleyne, B. D.; Djurovich, P. I.; Lamansky, S.; Tsyba, I.; Ho, N. N.; Bau, R.; Thompson, M. E. *J. Am. Chem. Soc.* **2003**, *125*, 7377.
- (9) Presser, A.; Hüfner, A. *Monatsh. Chem.* **2004**, *135*, 1015.
- (10) McAtee, J. R.; Martin, S. E. S.; Ahneman, D. T.; Johnson, K. A.; Watson, D. A. *Angew. Chem. Int. Ed.* **2012**, *51*, 3663.
- (11) Lamothe, M.; Pauwels, P. J.; Belliard, K.; Schambel, P.; Halazy, S. *J. Med. Chem.* **1997**, *40*, 3542.
- (12) Onitsuka, K.; Fujimoto, M.; Kitajima, H.; Ohshiro, N.; Takei, F.; Takahashi, S. *Chem. Eur. J.* **2004**, *10*, 6433.
- (13) Zhang, L.; Dolbier Jr., W. R.; Sheeller, B.; Ingold, K. U. *J. Am. Chem. Soc.* **2002**, *124*, 6362.
- (14) Furuya, T.; Strom, A. E.; Ritter, T. *J. Am. Chem. Soc.* **2009**, *131*, 1662.
- (15) Bouider, N.; Fhayli, W.; Ghandour, Z.; Boyer, M.; Harrouche, K.; Florence, X.; Pirotte, B.; Lebrun, P.; Faury, G.; Khelili, S. *Bio. Med. Chem.* **2015**, *23*, 1735.
- (16) McGarry, K. R.; McDaniel, M.; Chan, B. C.; O'Connor, A. R. *Polyhedron*, **2016**, *114*, 101.
- (17) Powell, A. B.; Stahl, S. S. *Org. Lett.* **2013**, *15*, 5072.
- (18) Jiang, Q.; Zhao, A.; Xu, B.; Jia, J.; Liu, X.; Guo, C. *J. Org. Chem.* **2014**, *79*, 2709.
- (19) Streit, U.; Birbaum, F.; Quattropani, A.; Bochet, C. G. *J. Org. Chem.* **2013**, *78*, 6890.
- (20) Lerebours, R.; Wolf, C. *J. Am. Chem. Soc.* **2006**, *128*, 13052.
- (21) Braisted, A. C.; Schultz, P. G. *J. Am. Chem. Soc.* **1994**, *116*, 2211.
- (22) Xia, J.; Shao, A.; Tang, S.; Gao, X.; Gao, M.; Lei, A. *Org. Biomol. Chem.* **2015**, *13*, 6154.
- (23) Mita, T.; Suga, K.; Sato, K.; Sato, Y. *Org. Lett.* **2015**, *17*, 5276.
- (24) Lee, J. J.; Kraus, G. A. *Green Chem.* **2014**, *16*, 2111.
- (25) Discekici, E. H.; Treat, N. J.; Poelma, S. O.; Mattson, K. M.; Hudson, Z. M.; Luo, Y.; Hawker, C. J.; Alaniz, J. R. *Chem. Commun.* **2015**, *51*, 11705.

Spectral Data

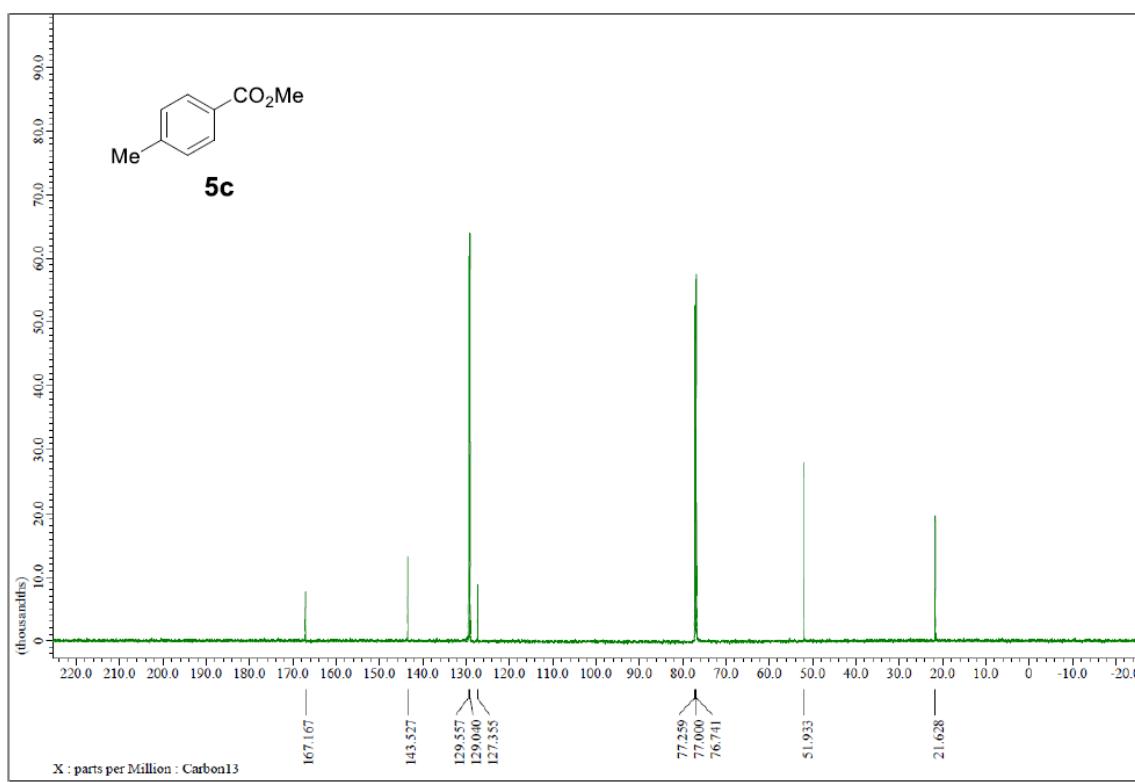
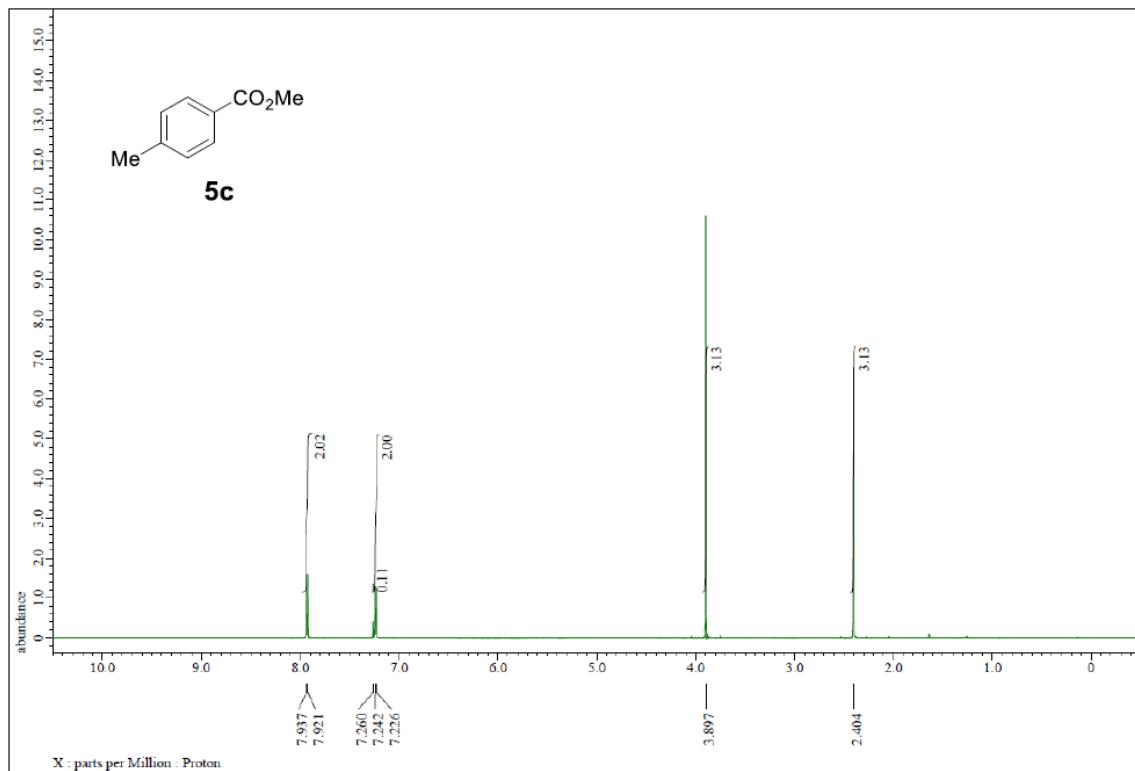
^1H and ^{13}C NMR Spectra of Compounds 5a



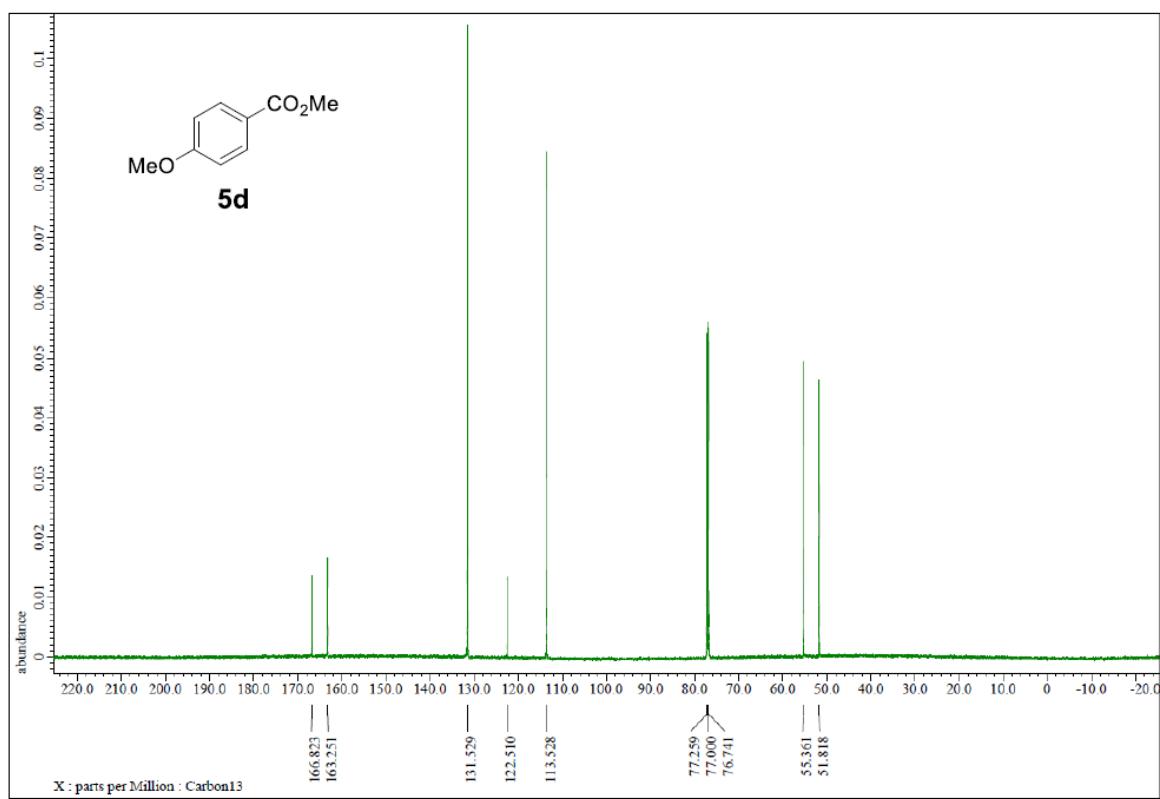
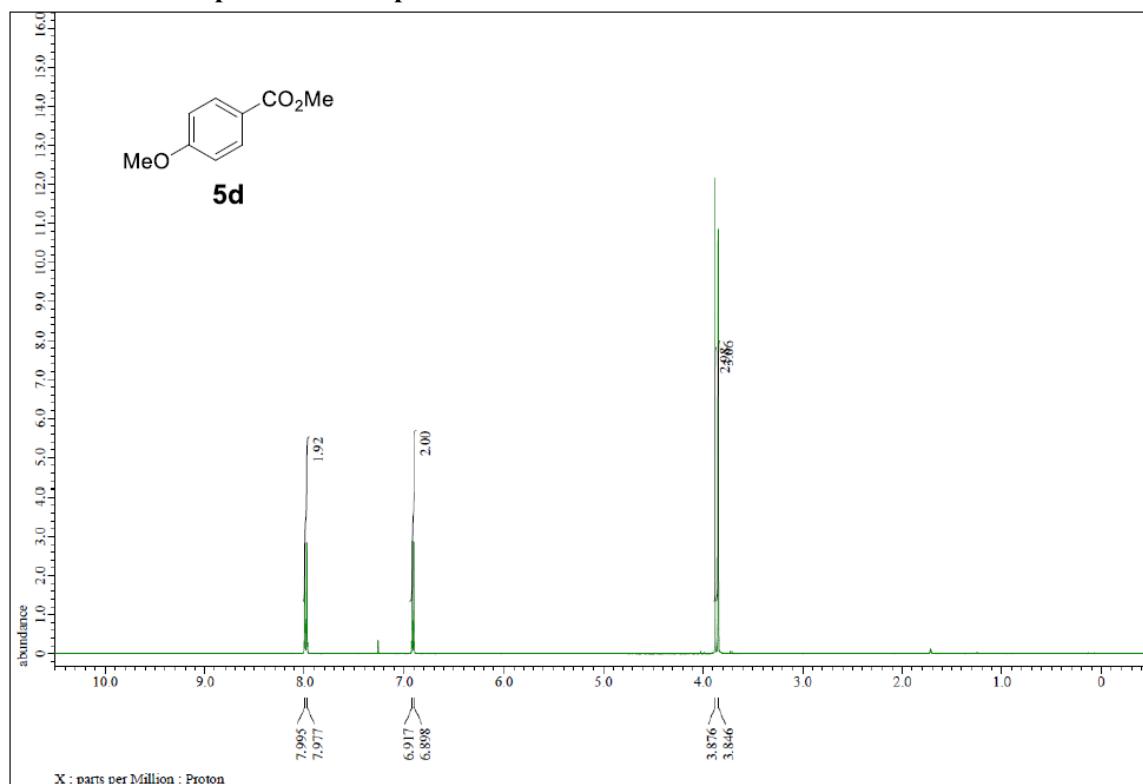
¹H and ¹³C NMR Spectra of Compounds 5b



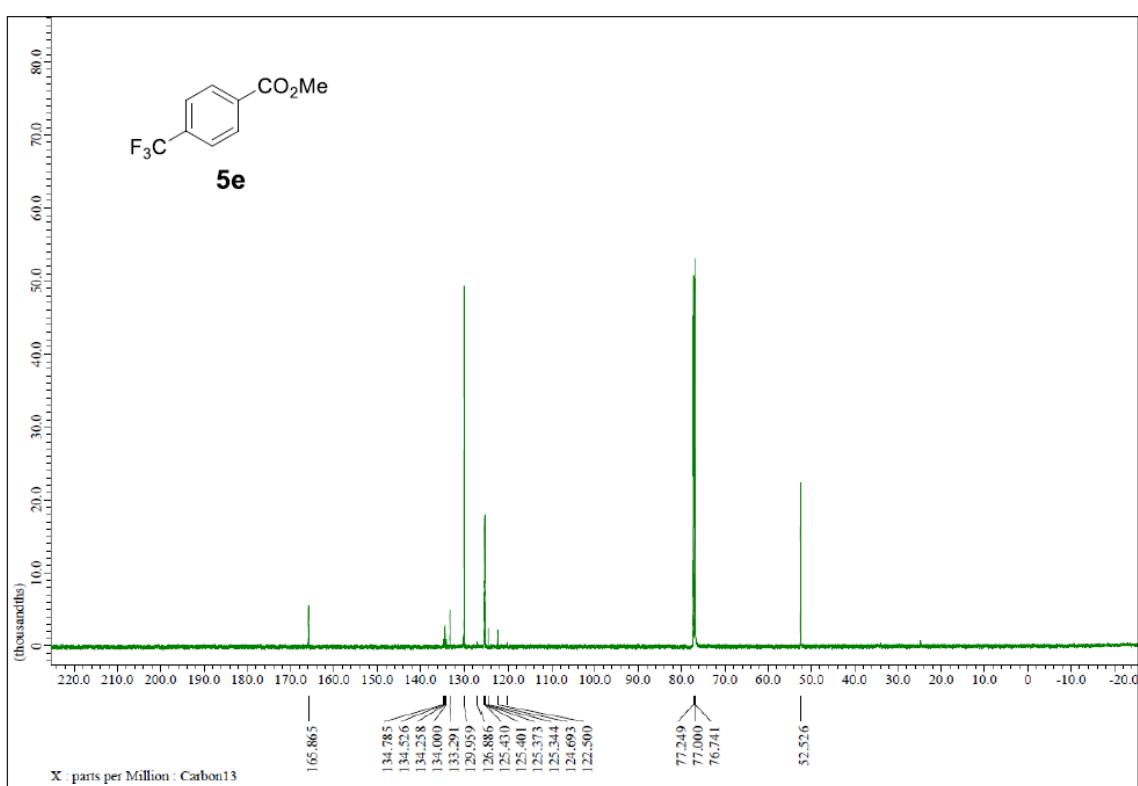
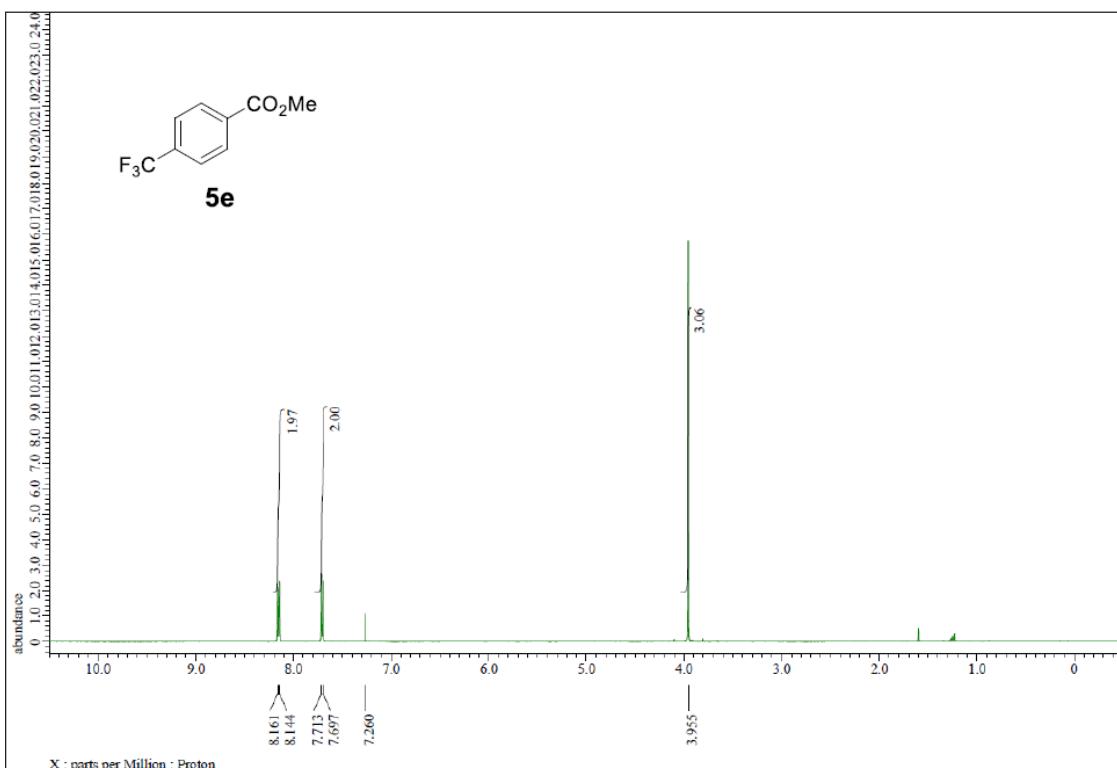
¹H and ¹³C NMR Spectra of Compounds 5c



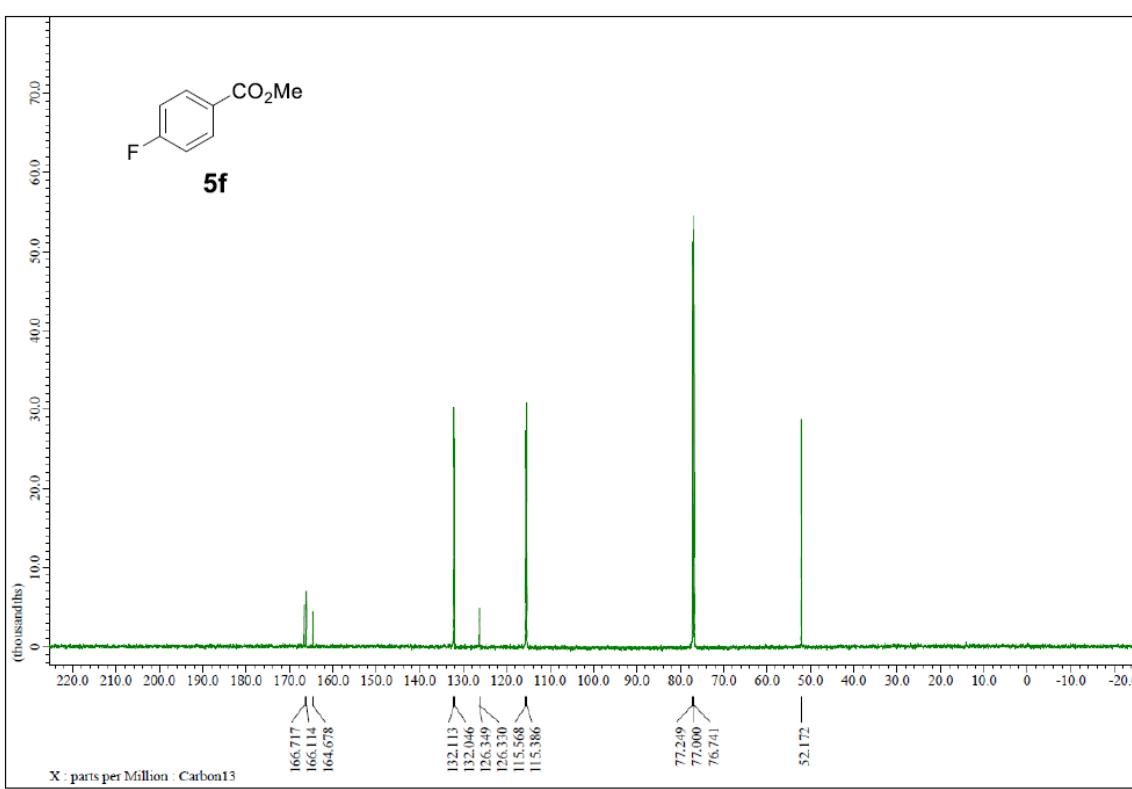
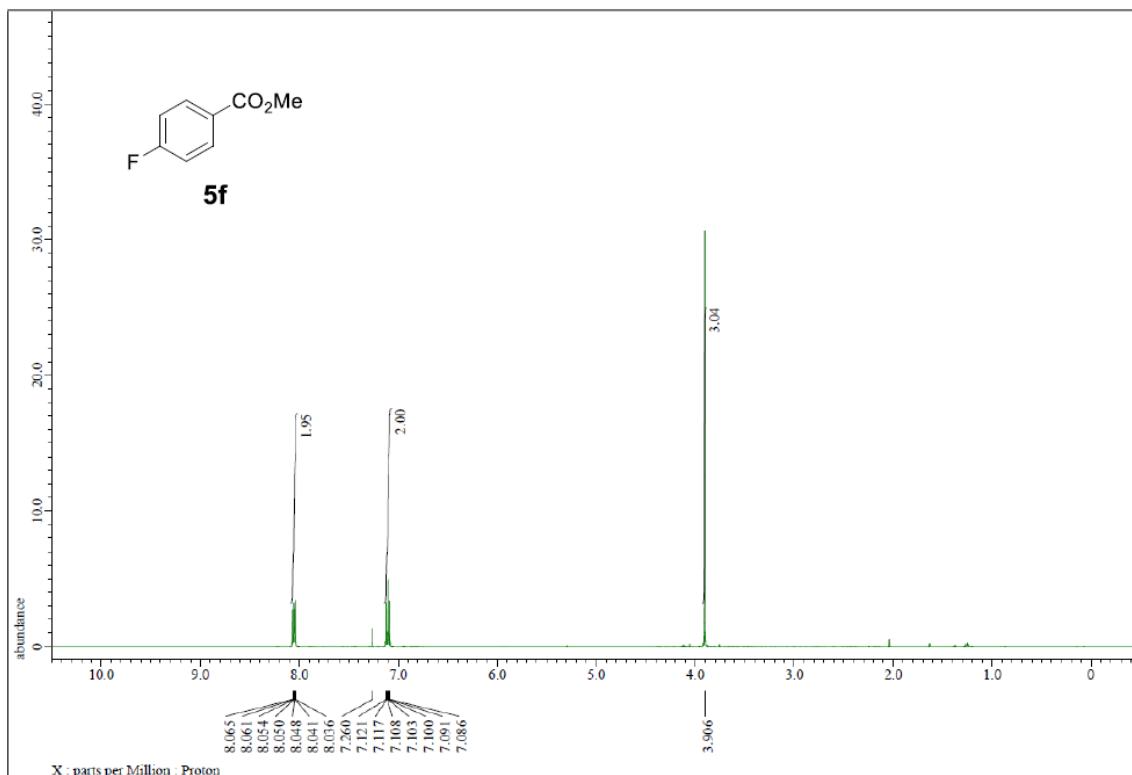
¹H and ¹³C NMR Spectra of Compounds 5d



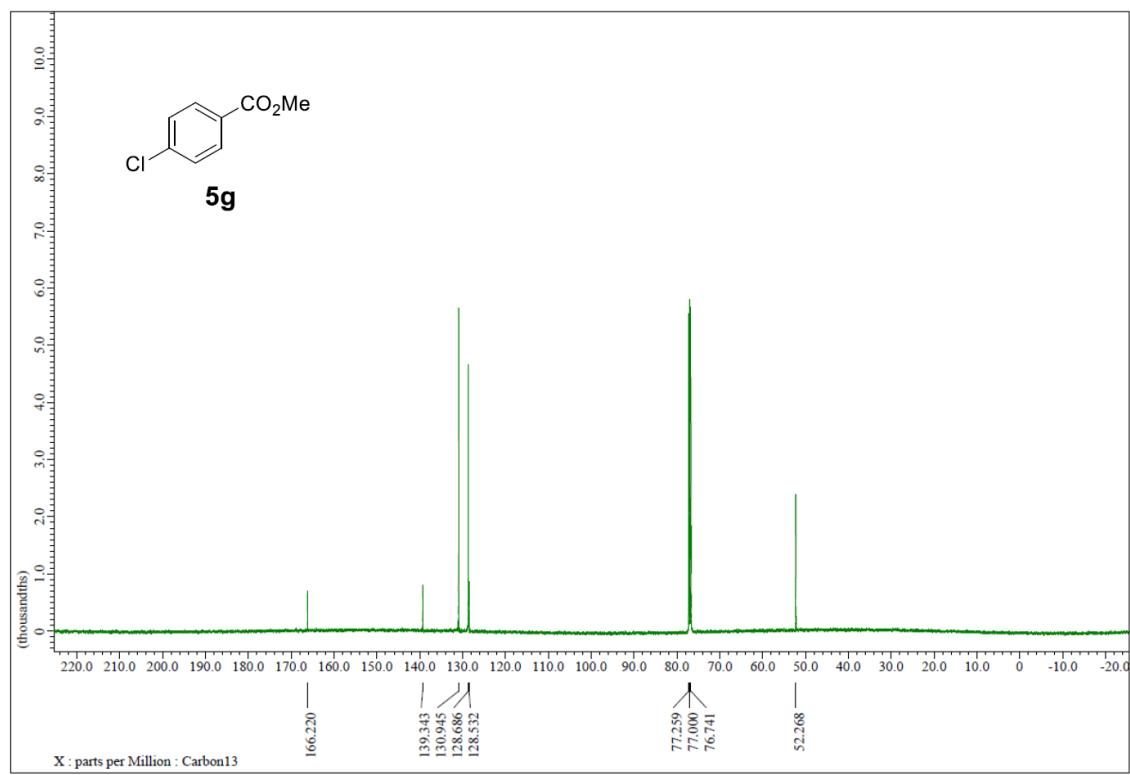
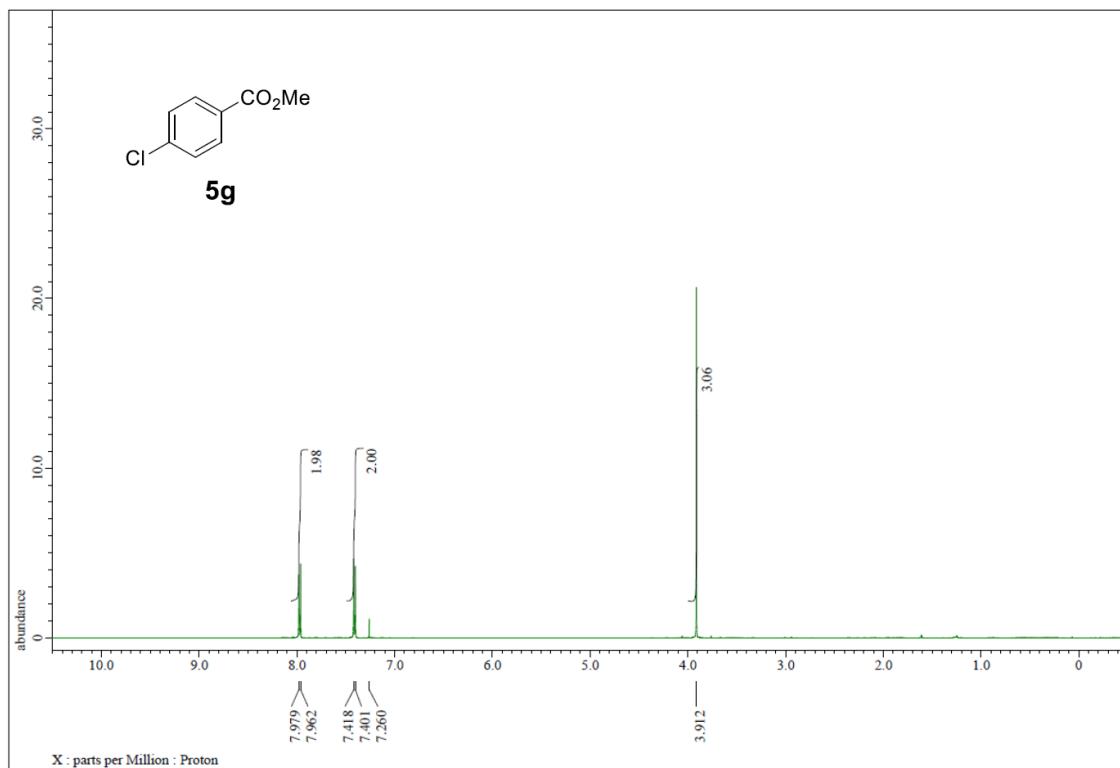
¹H and ¹³C NMR Spectra of Compounds 5e



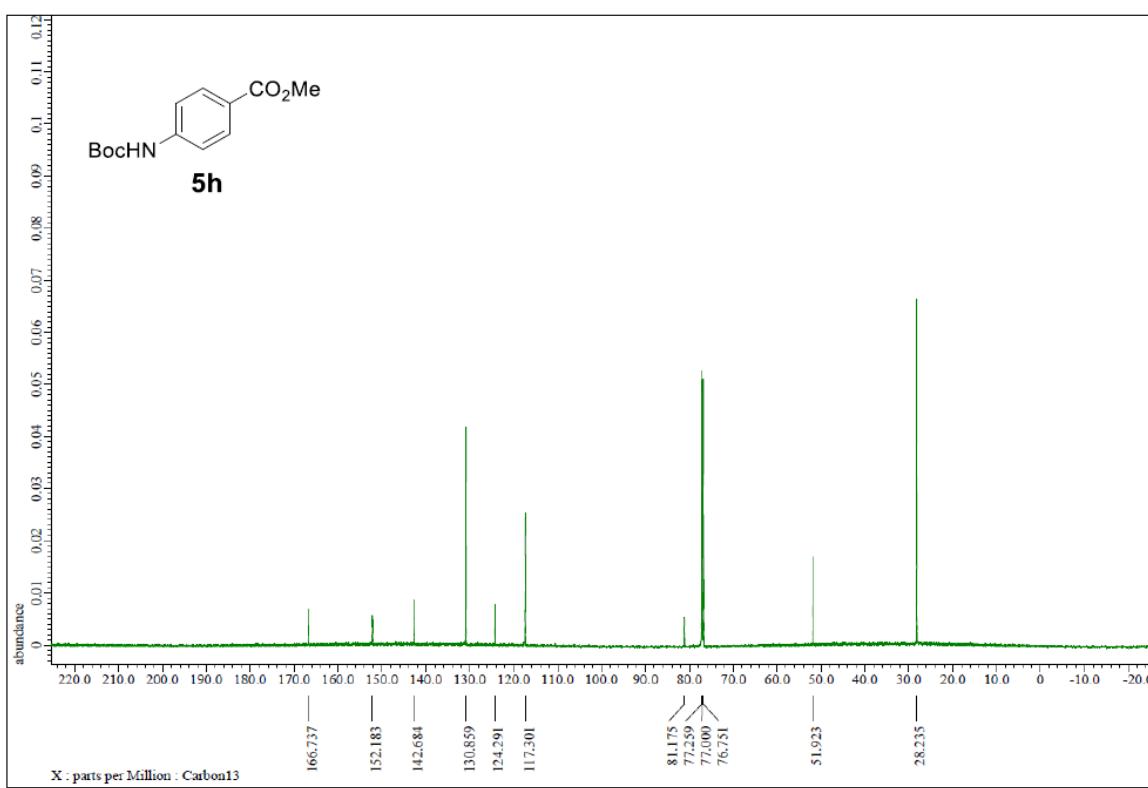
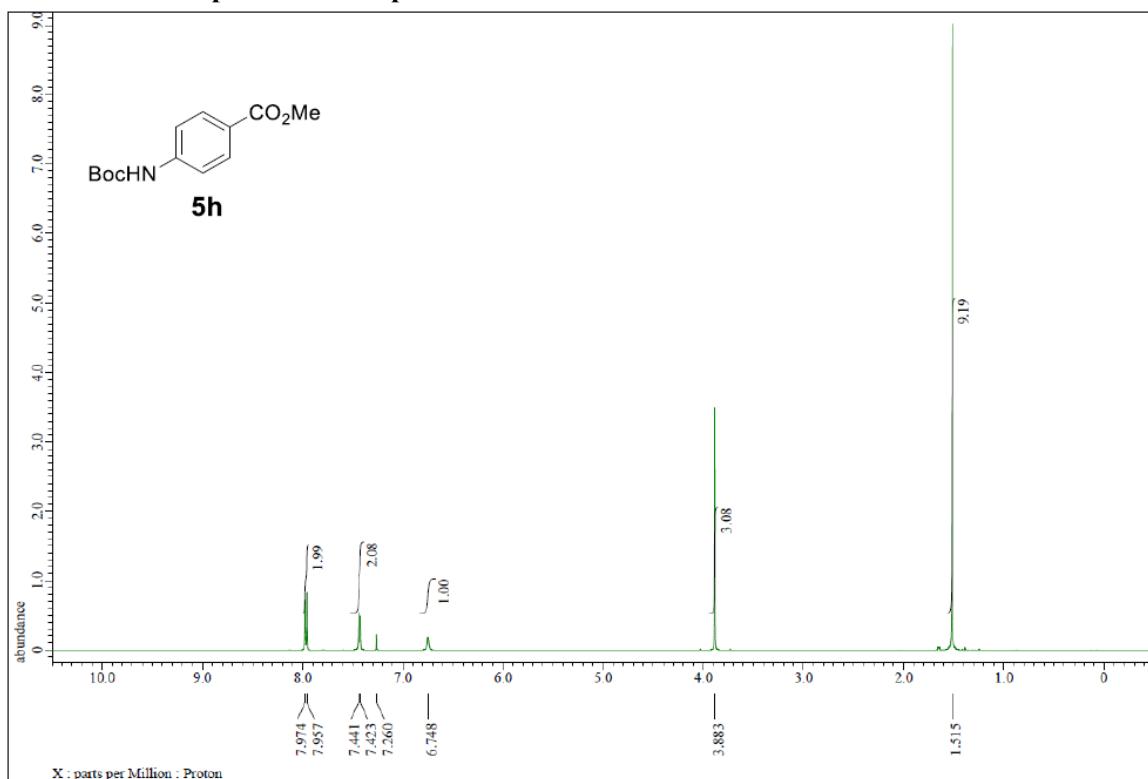
¹H and ¹³C NMR Spectra of Compounds 5f



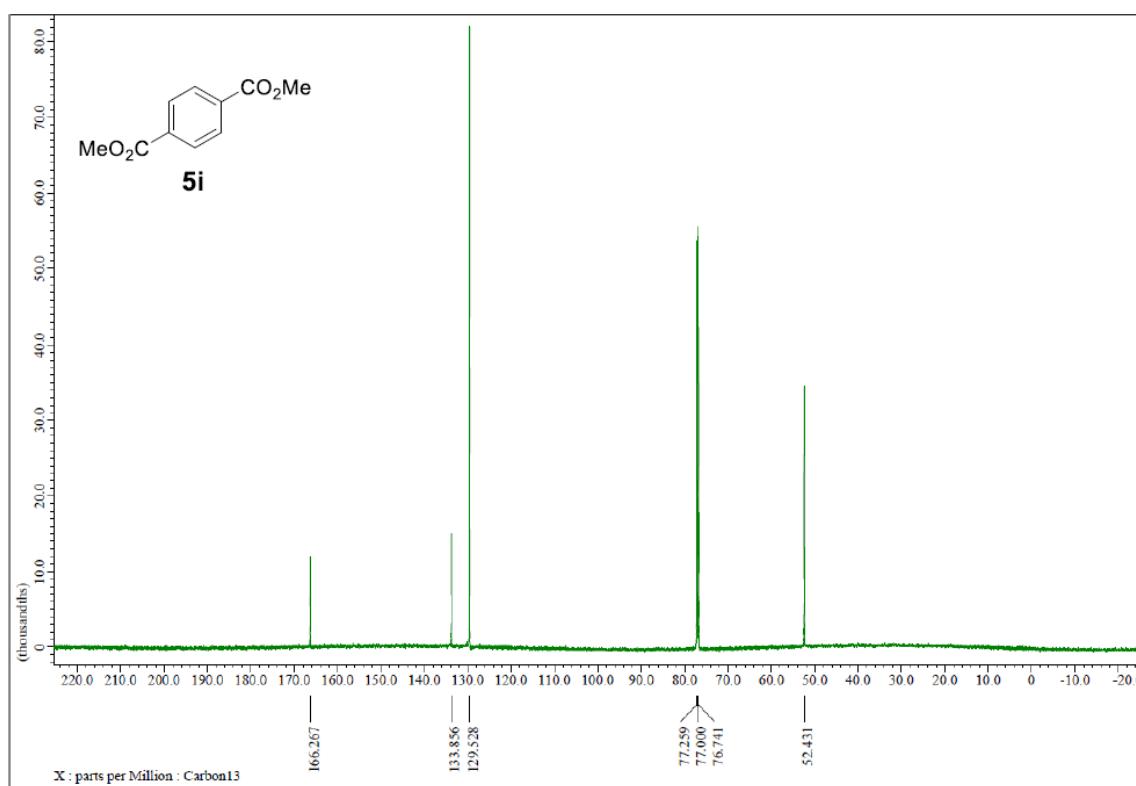
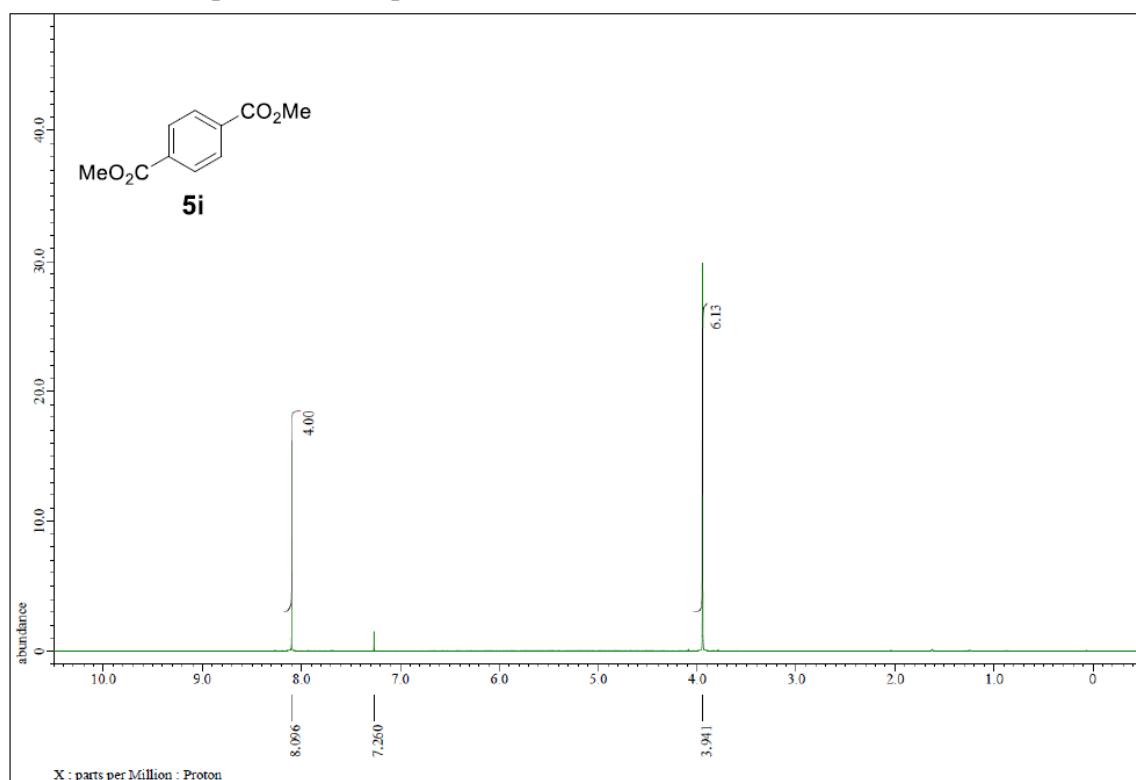
¹H and ¹³C NMR Spectra of Compounds 5g



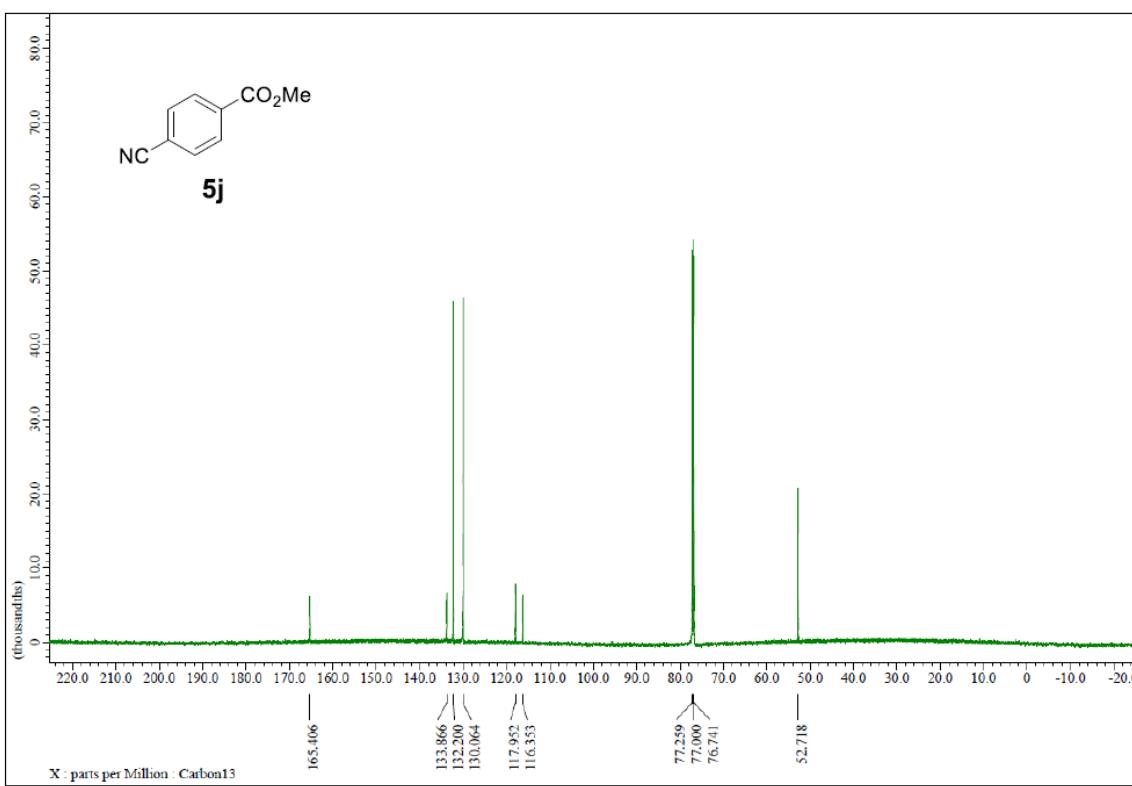
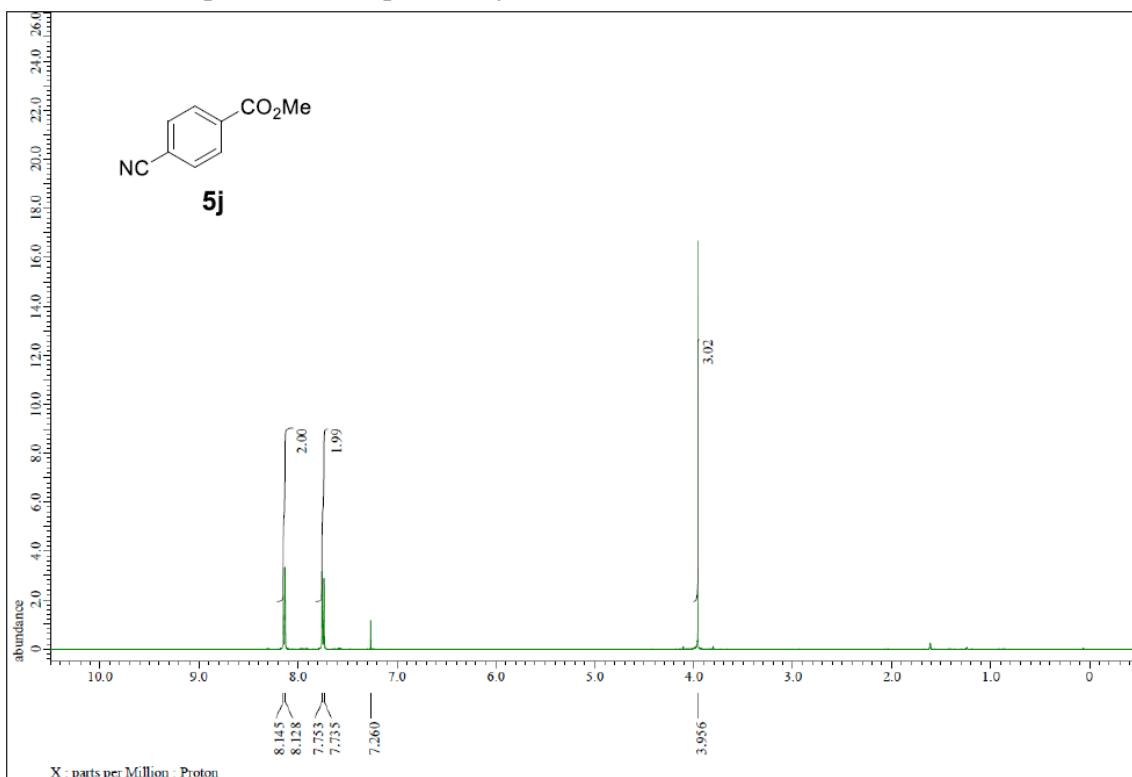
¹H and ¹³C NMR Spectra of Compounds 5h



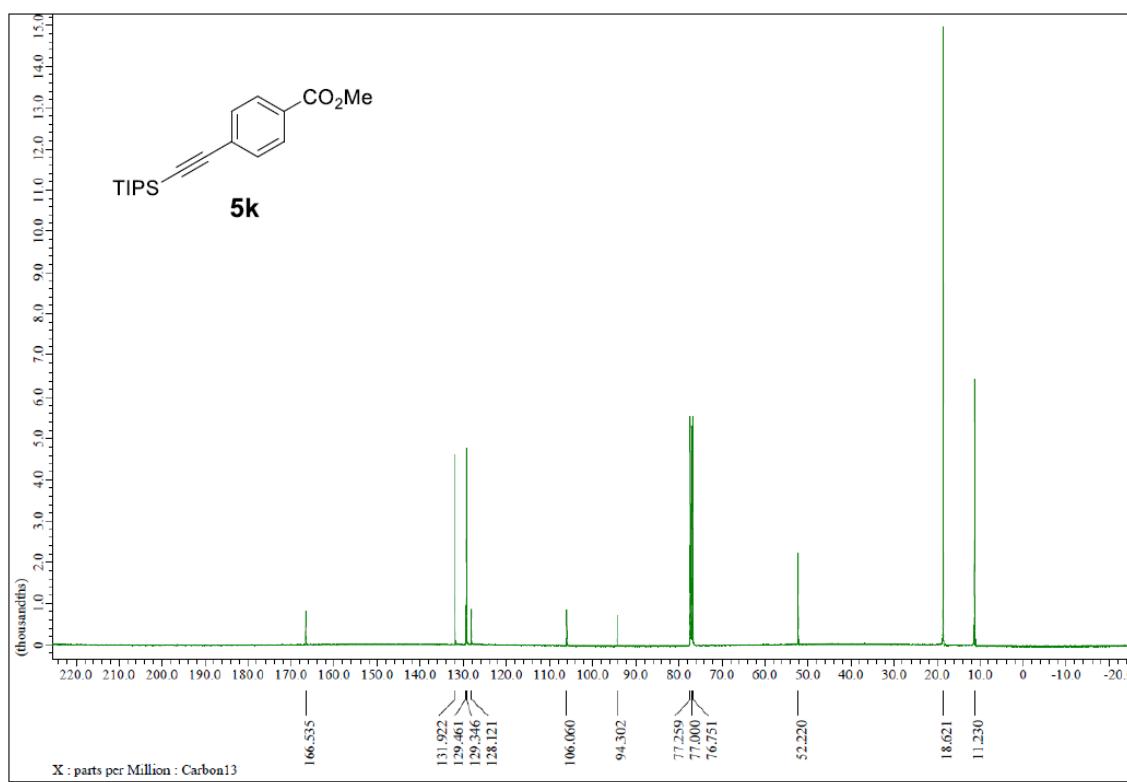
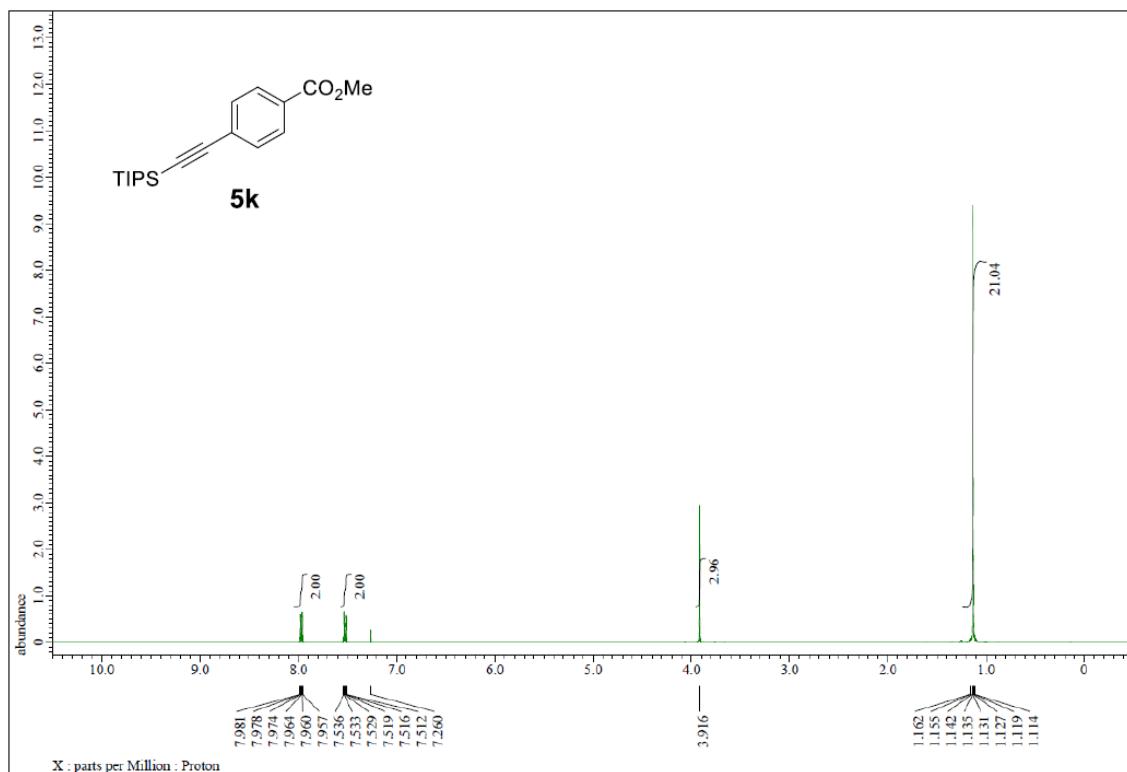
¹H and ¹³C NMR Spectra of Compounds 5i



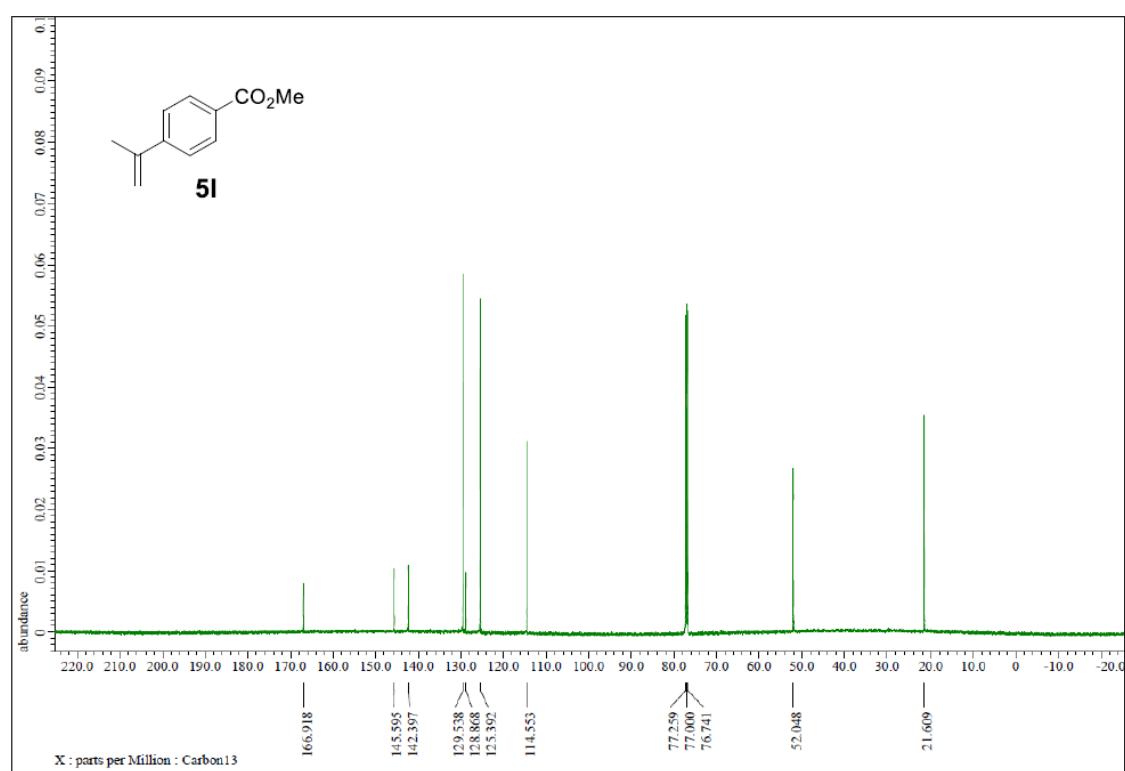
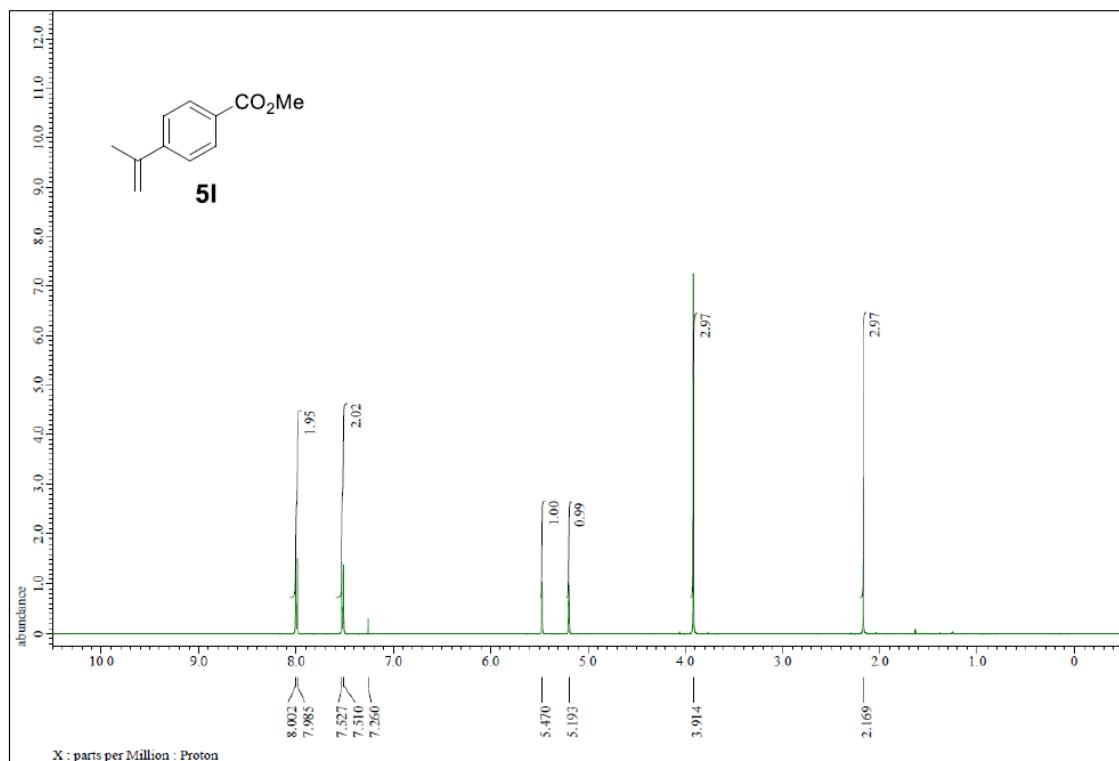
¹H and ¹³C NMR Spectra of Compounds 5j



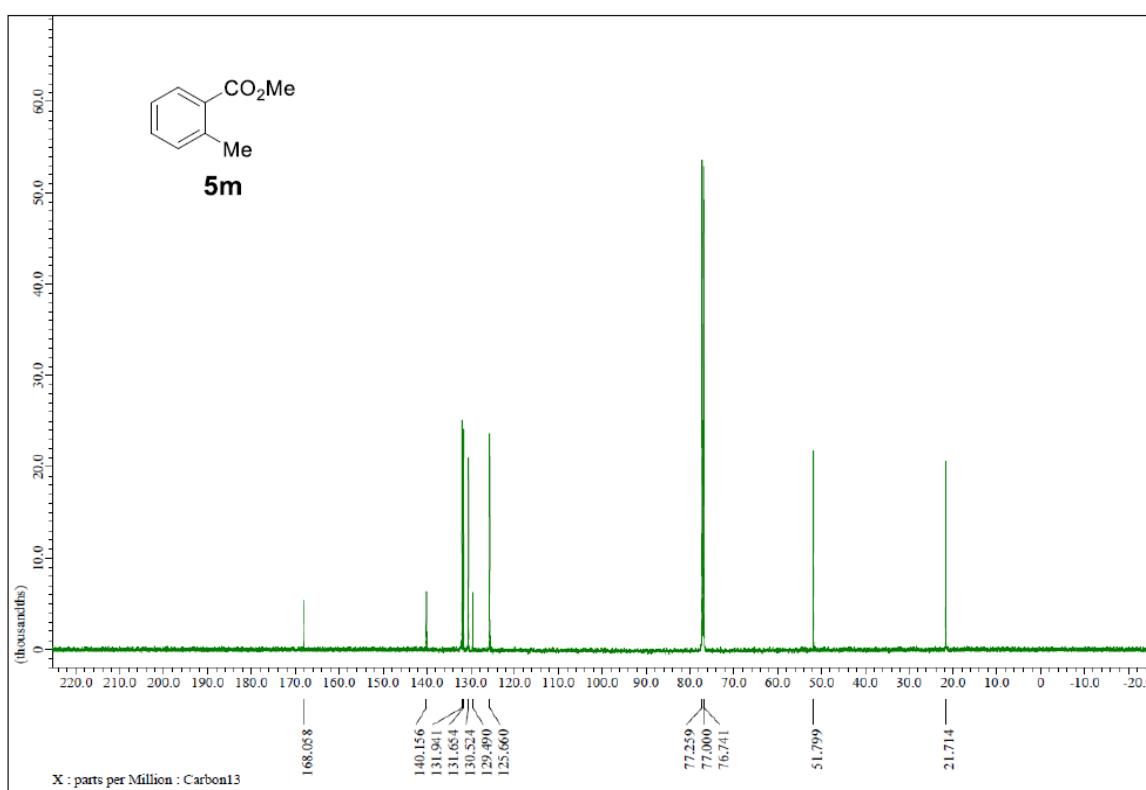
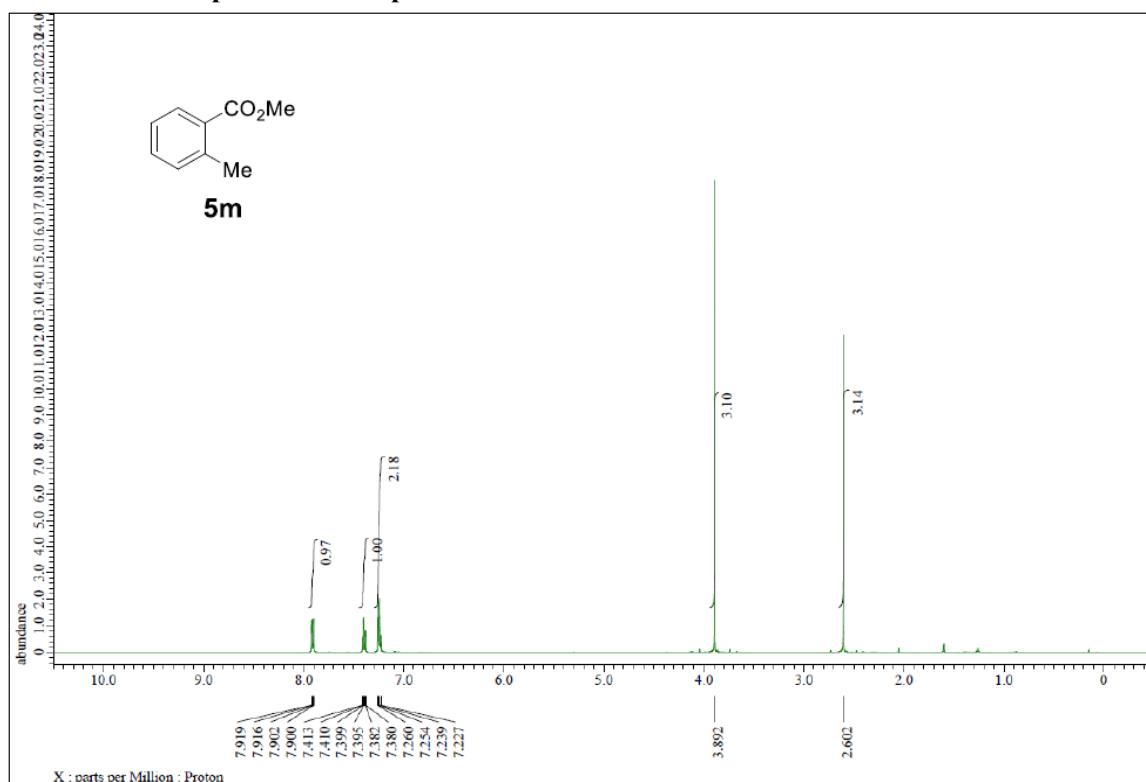
¹H and ¹³C NMR Spectra of Compounds 5k



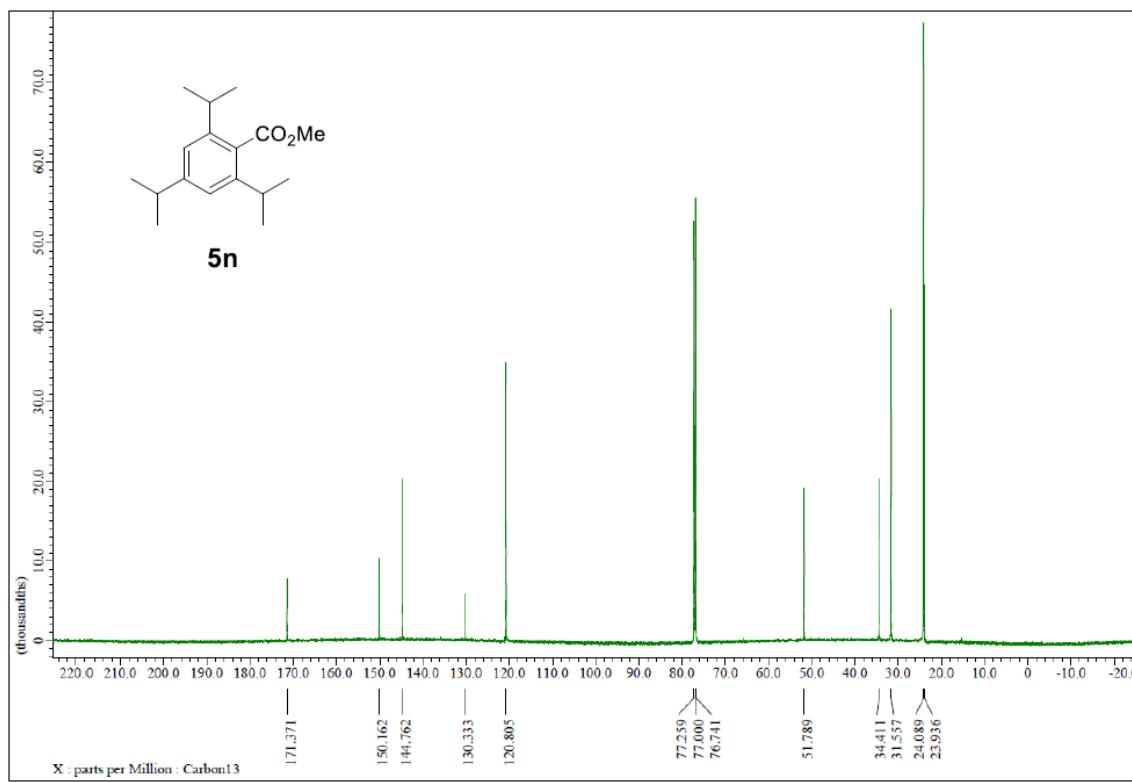
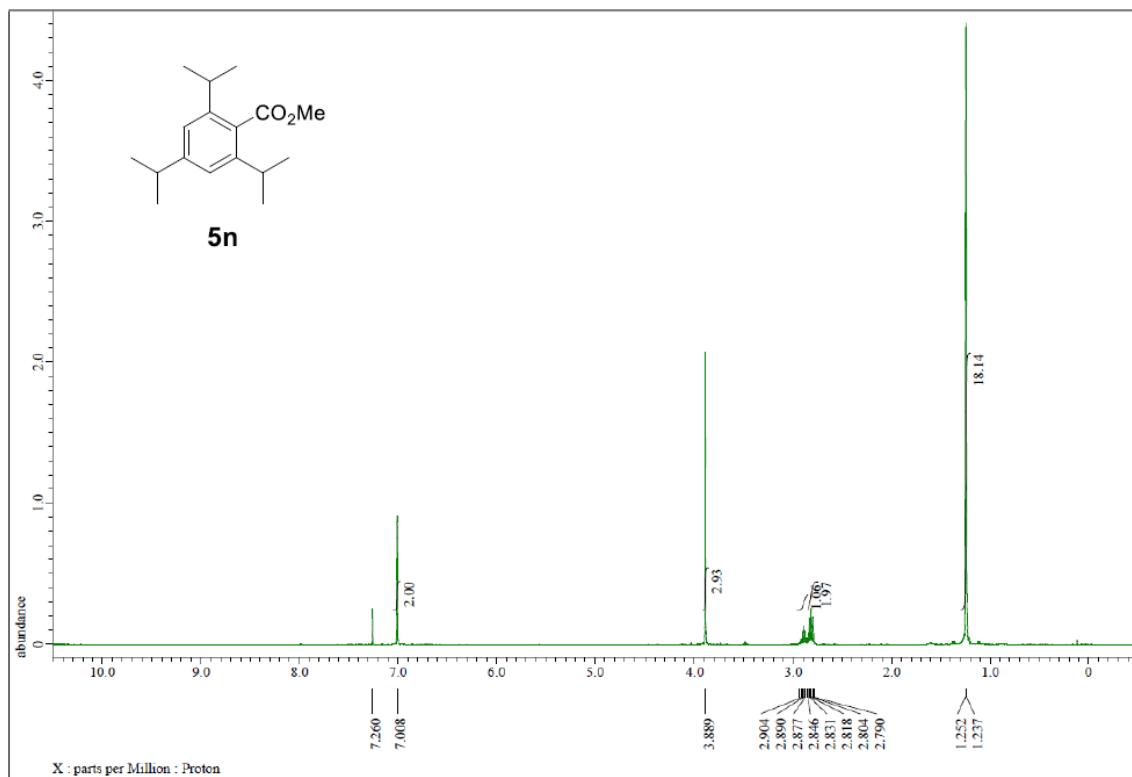
¹H and ¹³C NMR Spectra of Compounds 5l



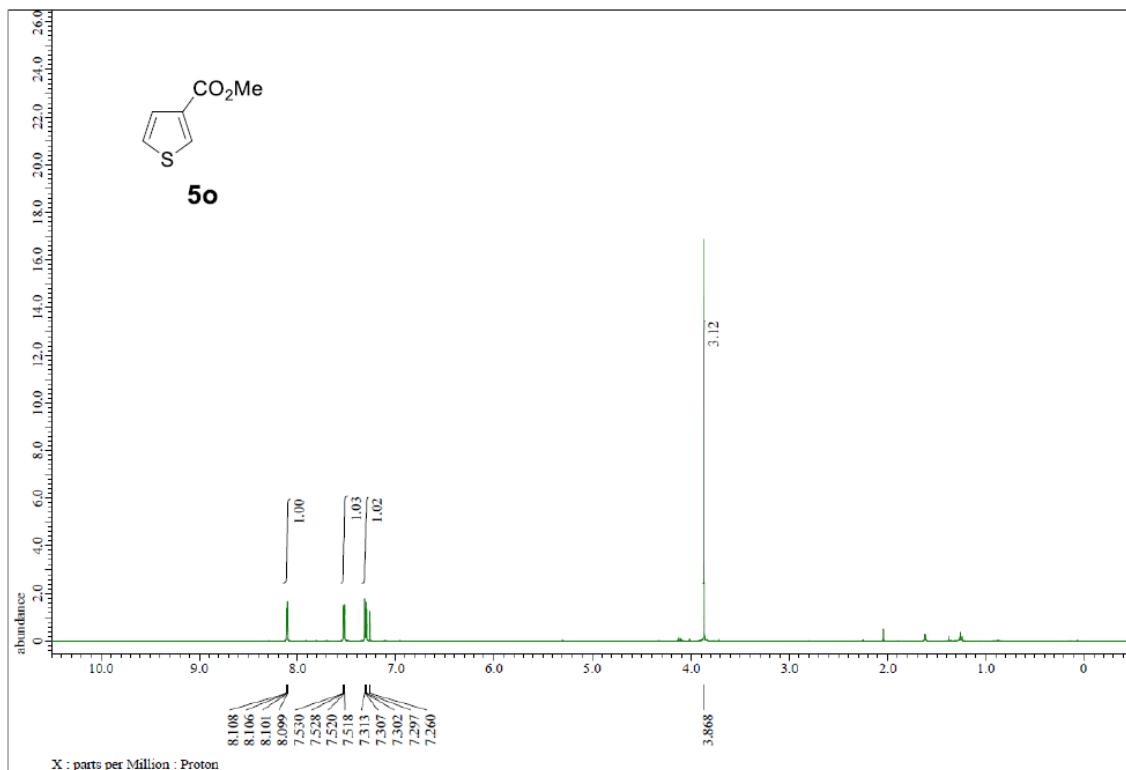
¹H and ¹³C NMR Spectra of Compounds 5m



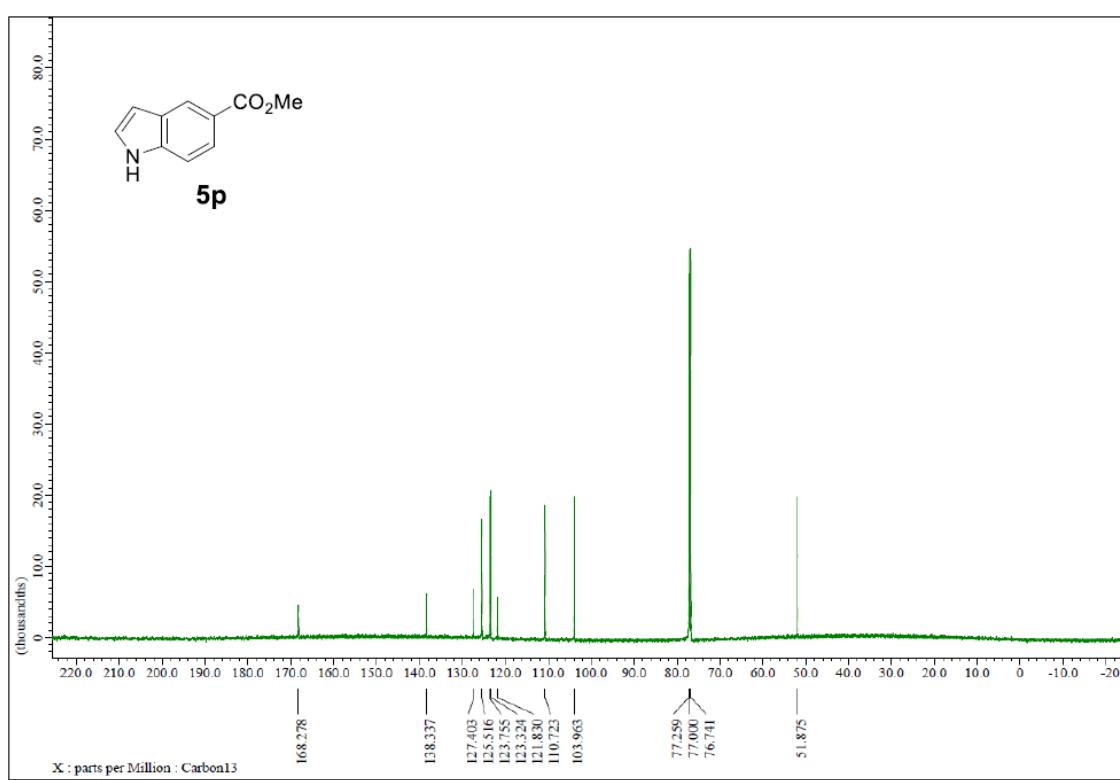
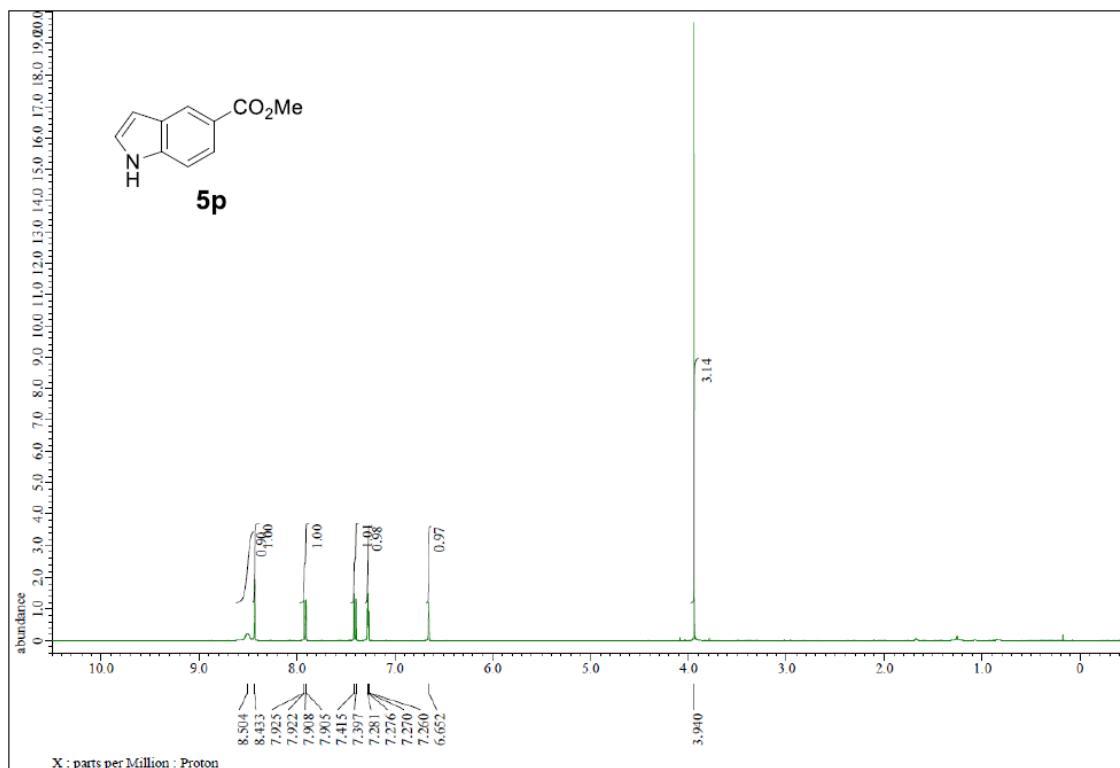
¹H and ¹³C NMR Spectra of Compounds 5n



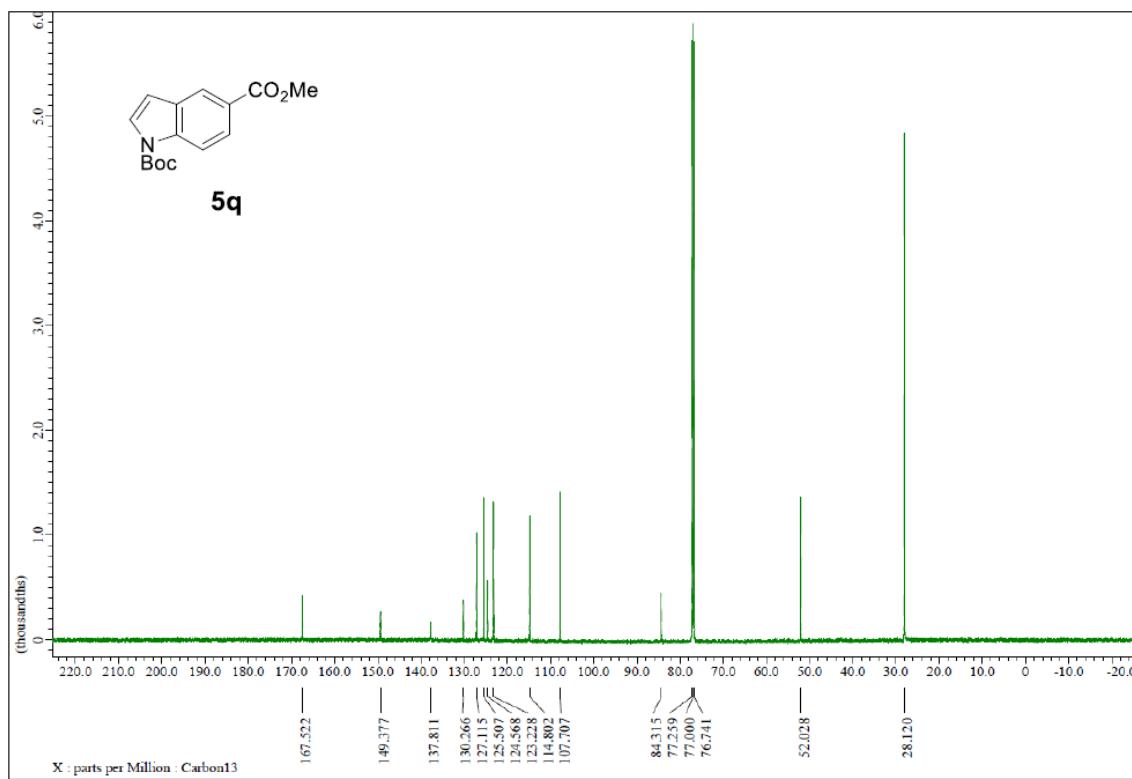
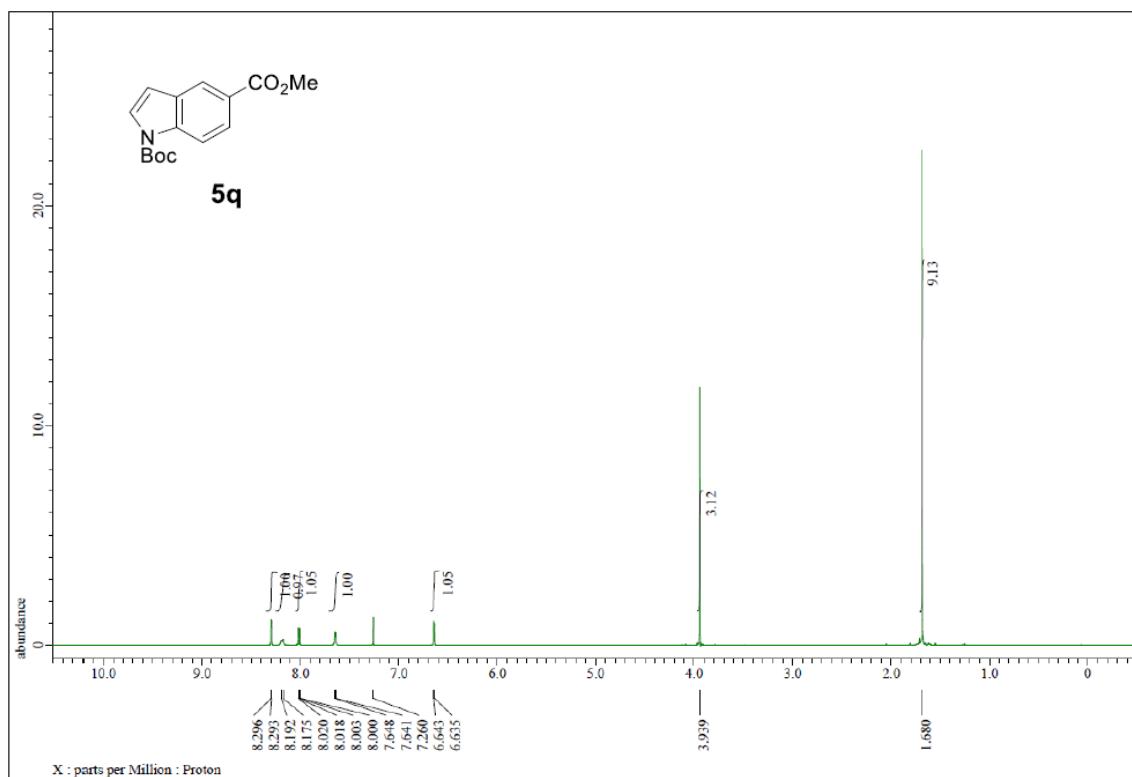
¹H and ¹³C NMR Spectra of Compounds 5o



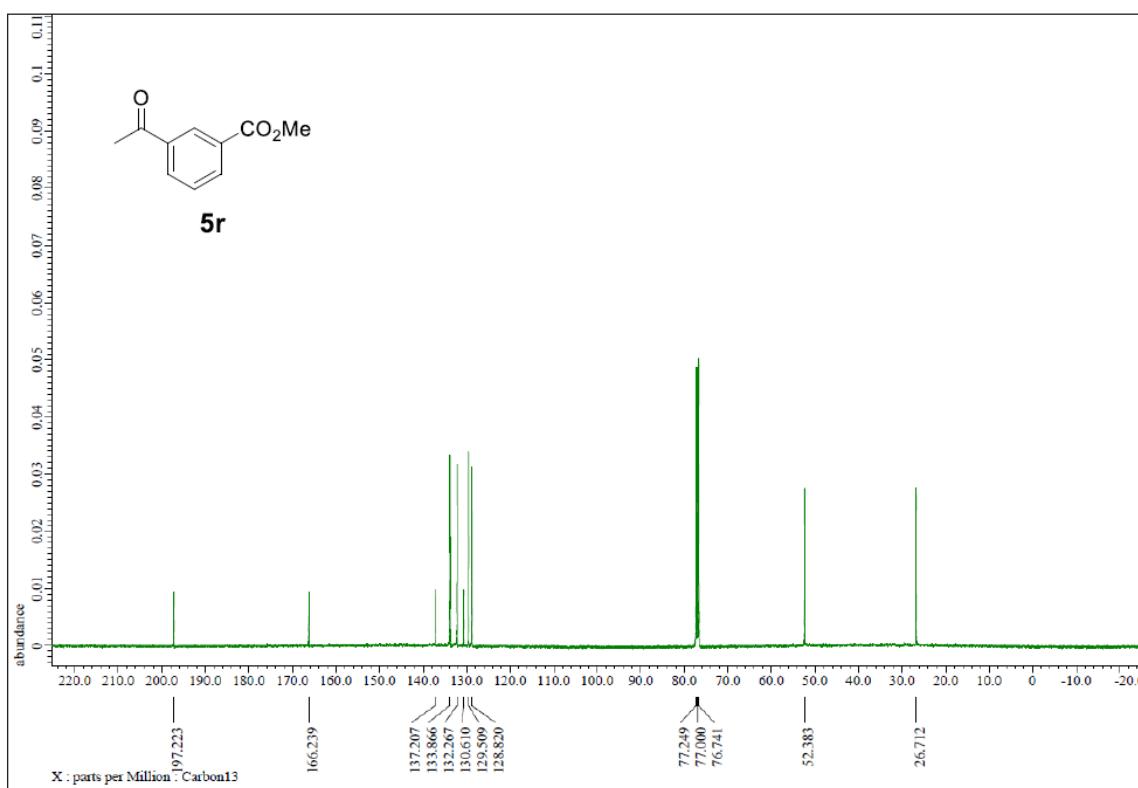
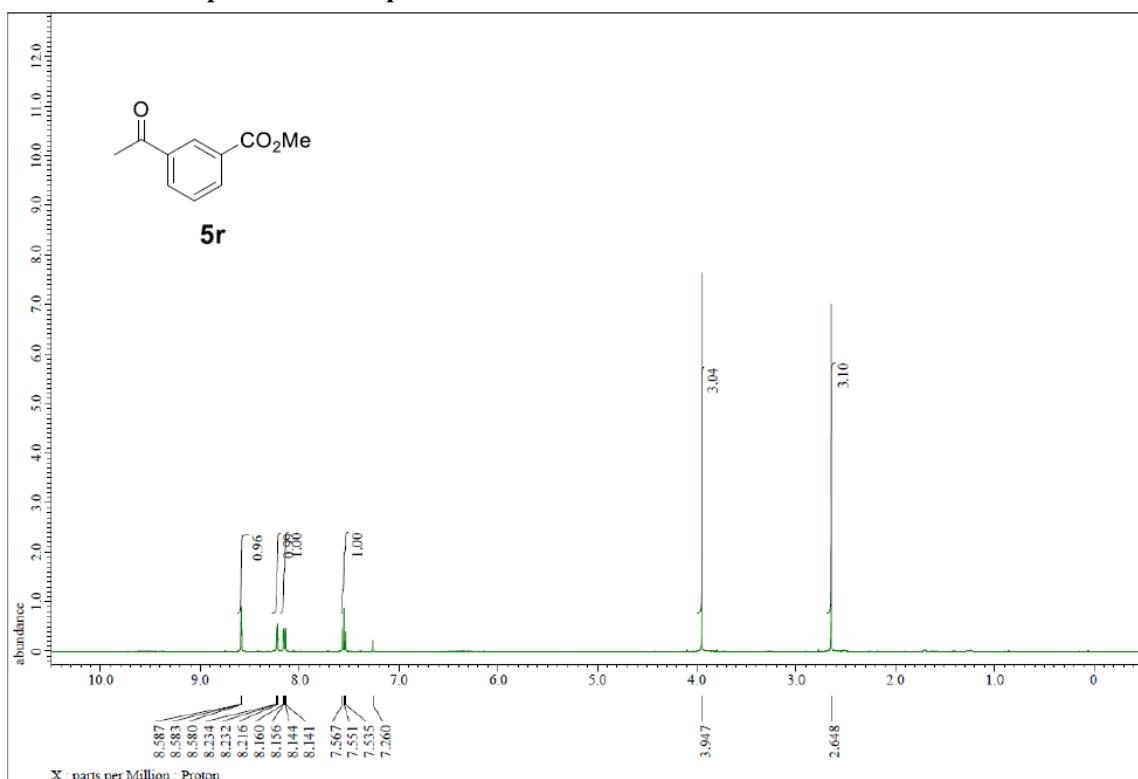
¹H and ¹³C NMR Spectra of Compounds 5p



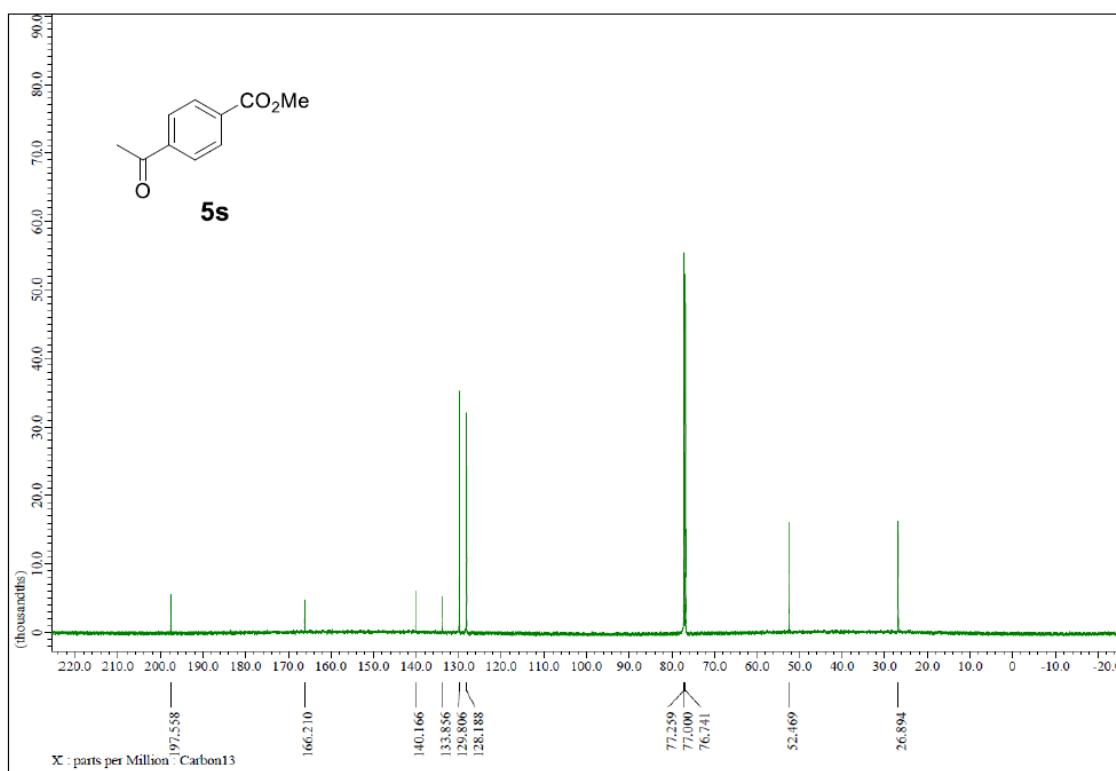
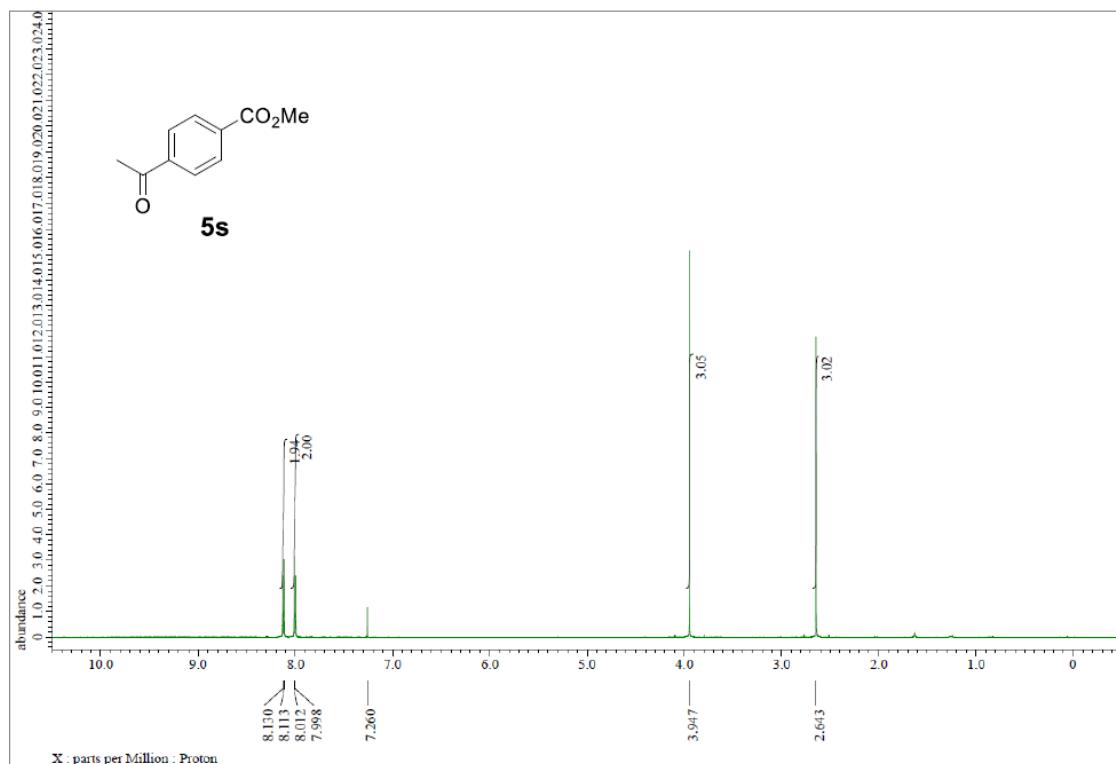
¹H and ¹³C NMR Spectra of Compounds 5q



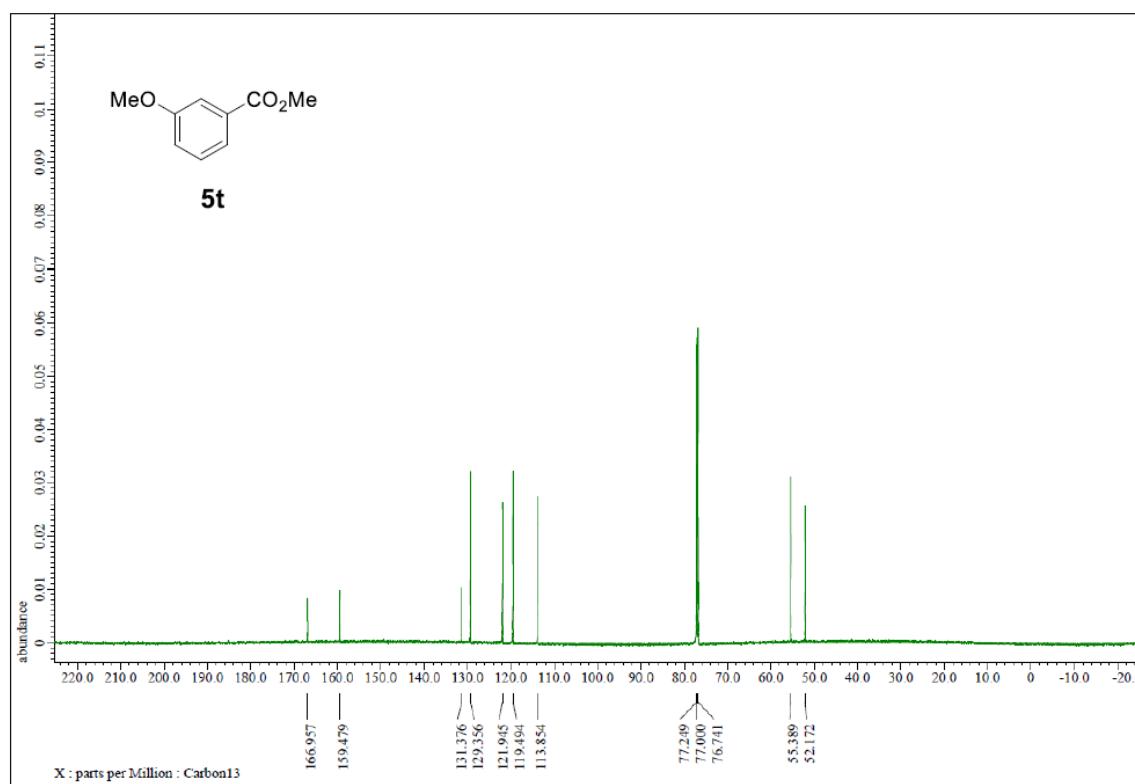
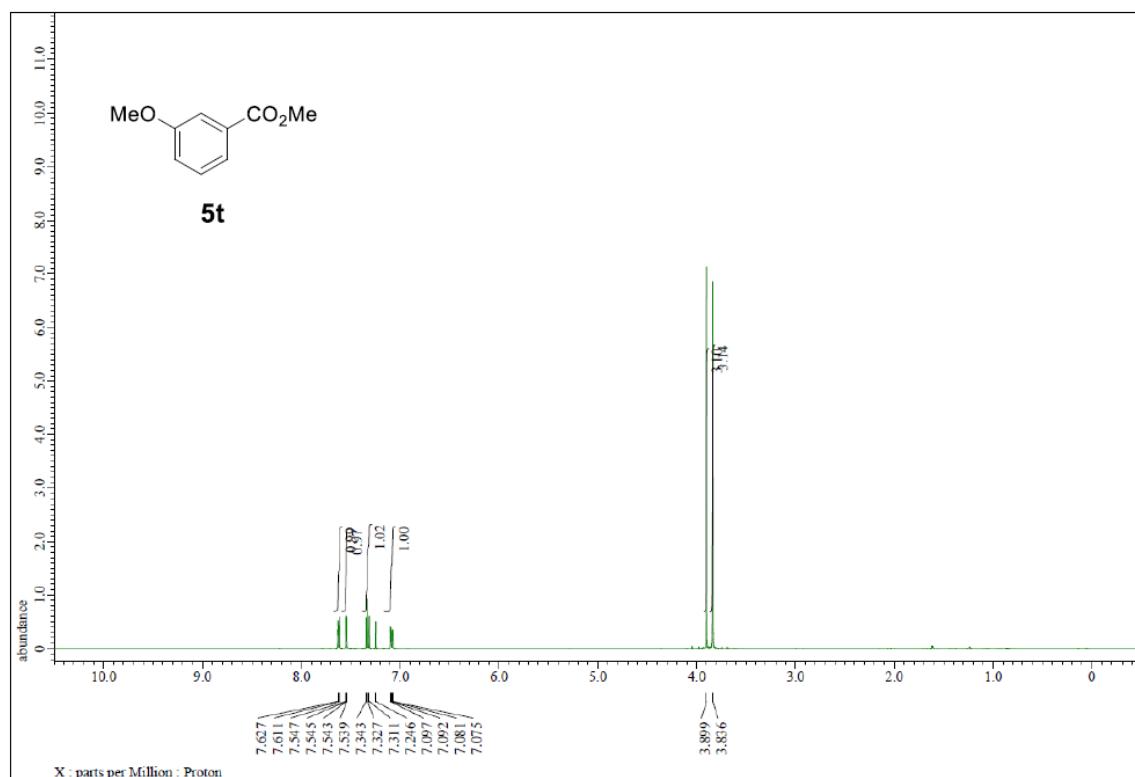
¹H and ¹³C NMR Spectra of Compounds 5r



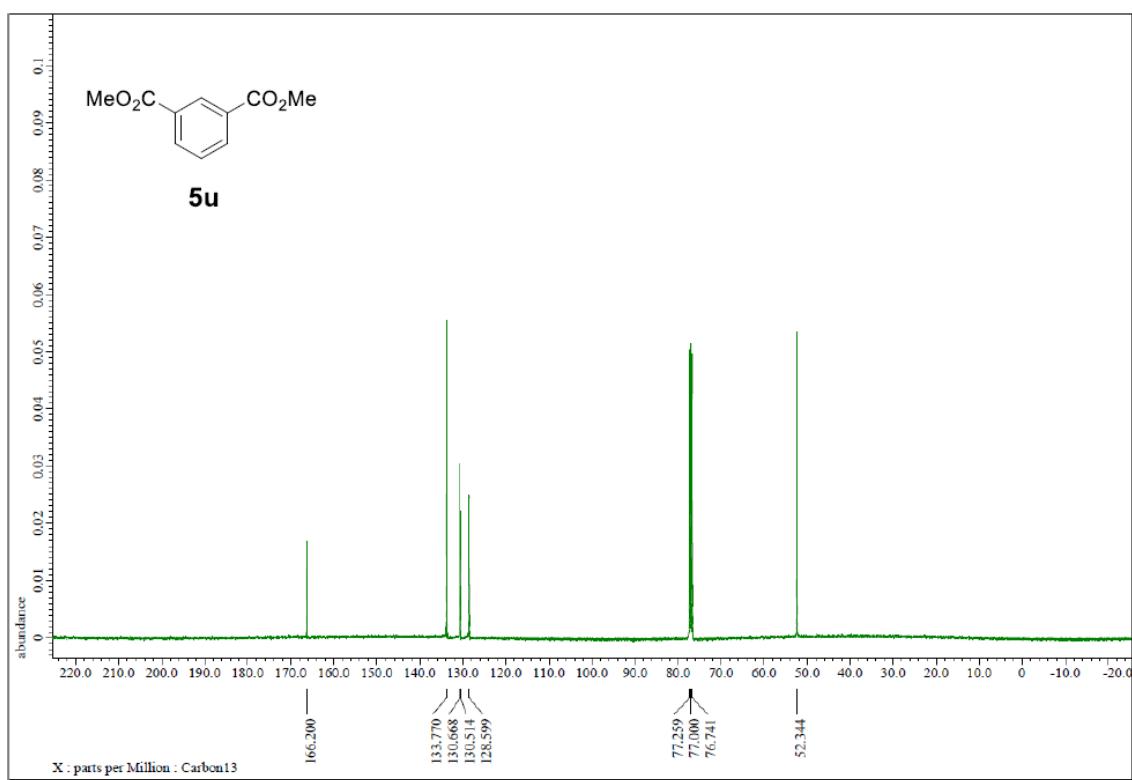
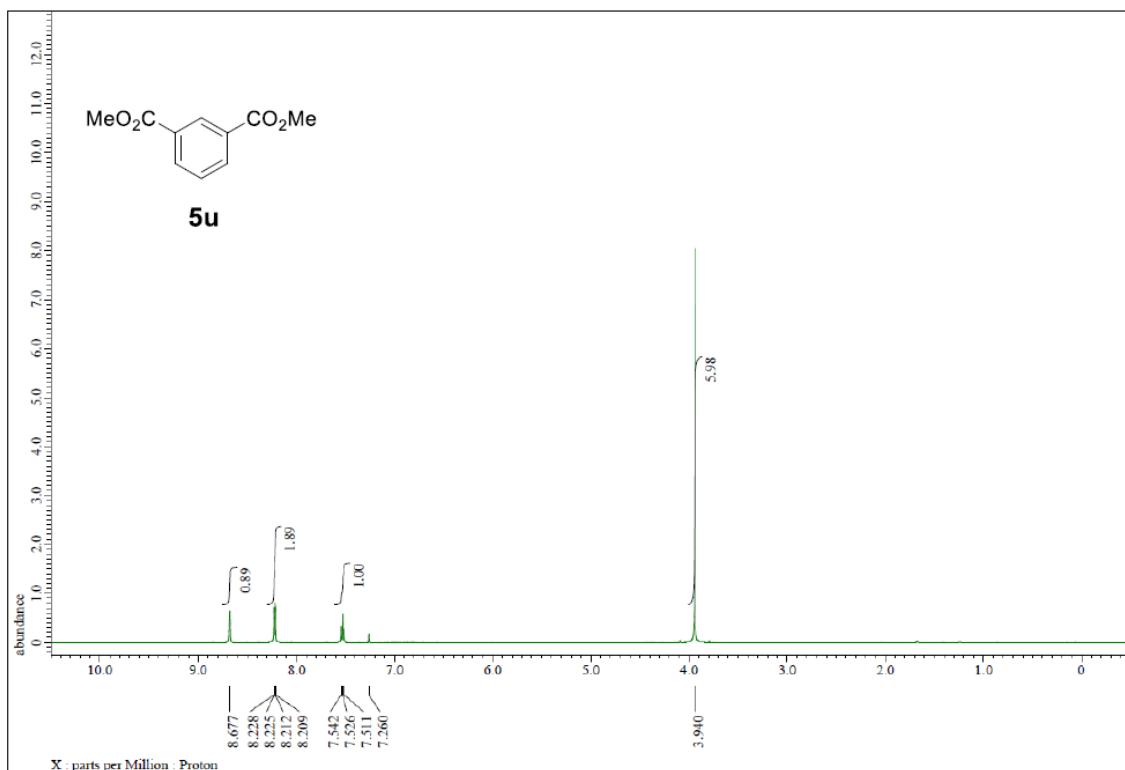
¹H and ¹³C NMR Spectra of Compounds 5s



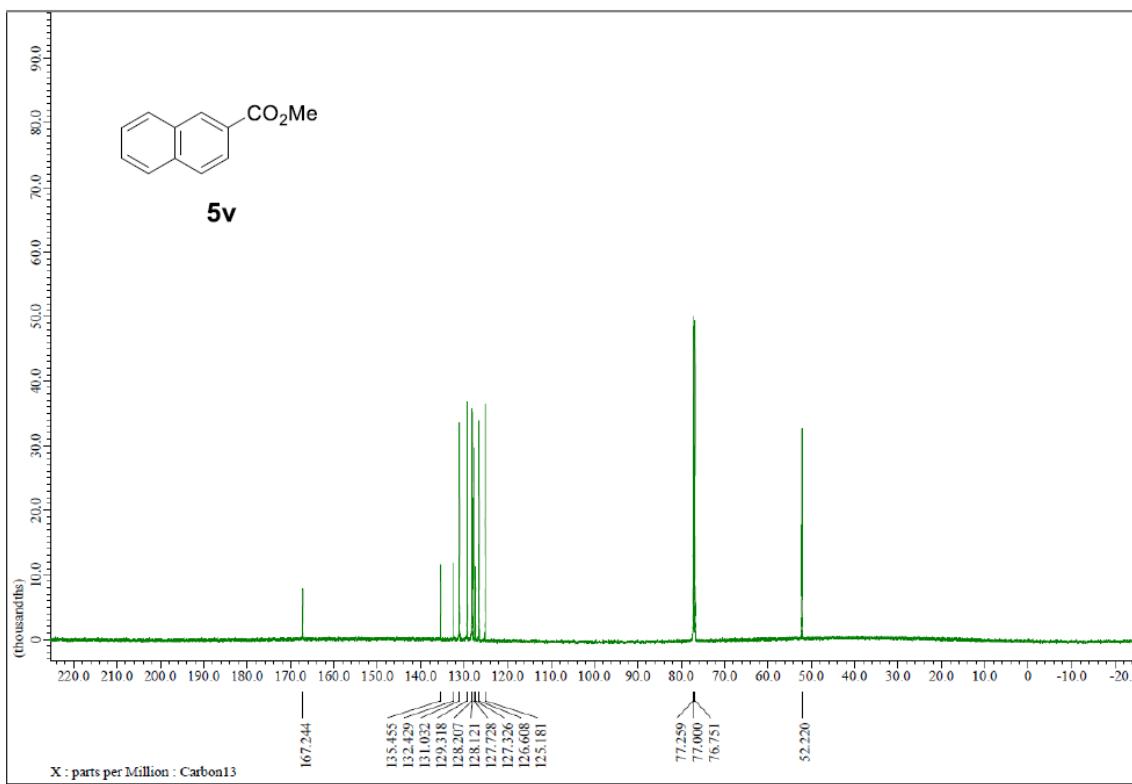
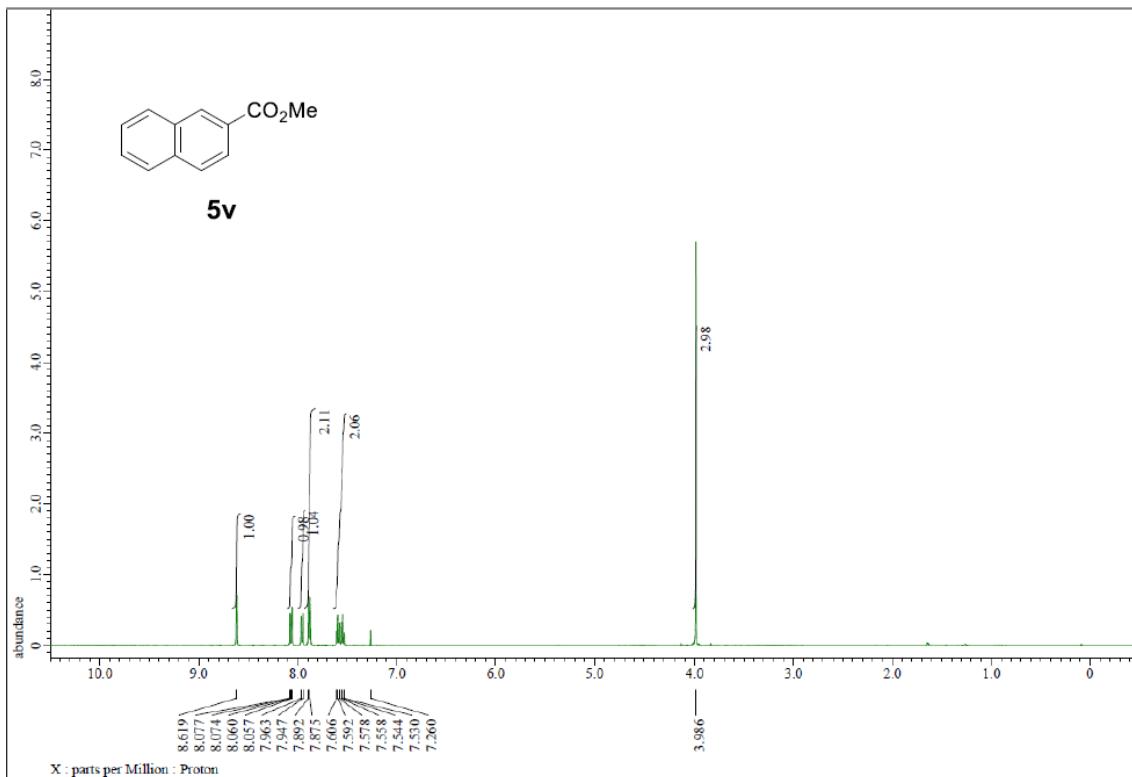
¹H and ¹³C NMR Spectra of Compounds 5t



¹H and ¹³C NMR Spectra of Compounds 5u



¹H and ¹³C NMR Spectra of Compounds 5v



¹H, ¹³C and ³¹P NMR Spectra of Compounds 7

