**Electronic Supplementary Information**

*for*

# Photochemically synthesized palladium nanoparticles with catalytic activity at ppb levels for C-C coupling reactions

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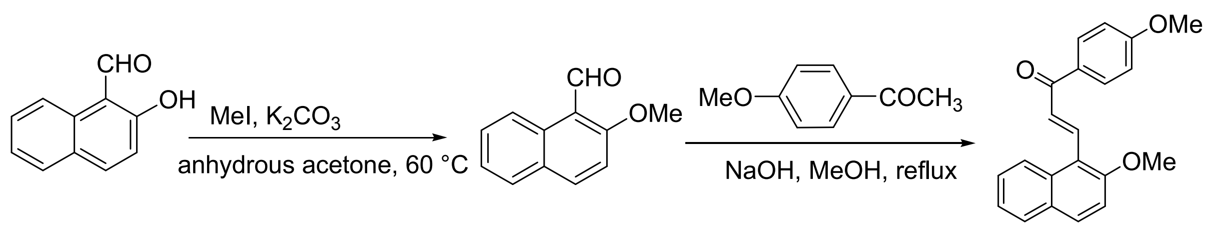
# Table of Contents

## General Procedures

The starting materials and all solvents used were purchased from commercial sources and used without further purification. Solvents were dried using standard methods. TLC was performed on pre-coated aluminum plates of silica gel 60 F254. TLC spots of the compound were visualized by UV light (254 nm). All the $^{1}$H-NMR and $^{13}$C-NMR spectrum were recorded on 300,400 and 500 MHz NMR spectrometer in solution of $CDCl_3$ using tetramethylsilane as the internal standard, $\delta$ values are given in parts per million(ppm) and coupling constants (J) in hertz(Hz).

## Experimental

**Synthesis of (*E*)-3-(2-methoxynaphthalen-1-yl)-1-(4-methoxyphenyl)prop-2-en-1-one (1)**.Compound **1** was synthesized by reported procedure.[1]




**1**

**Scheme 1.** Synthesis of **1**

To a solution of 2-hydroxynapthaldehyde **1** (3.0 g, 17.4 mmol) in anhydrous acetone (30mL) was added anhydrous $K_2CO_3$ (2.97 g, 21.5 mmol) and methyliodide (5.43 g, 38.2 mmol) and the resulting mixture was heated to 60 °C (bath temperature) under argon for 2 hours. After completion of the reaction (monitored by TLC), the solvent was removed *in vacuo* and the residue worked up in the usual way using ethyl acetate and water to yield the crude 2-methoxynapthaldehyde (3.0 gm). The crude **2** was used for the next step without further purification.

The crude product **2** from the previous step was taken in a RB flask and dissolved in MeOH (30 mL) followed by addition of 4-methoxyacetophenone (2.42 g, 16.1 mmol) and NaOH (2.1g, 5 mmol). The mixture was then refluxed for 3 hours after which the reaction was found to be completed as monitored by TLC. The reaction mixture was then cooled and the MeOH evaporated *in vacuo*. The resulting mixture was worked up by addition of water followed by extraction with ethyl acetate (3x50mL). The combined ethyl acetate layers was washed with brine till neutral, after which it was concentrated *in vacuo*. The residue was then chromatographed over a column of silica-gel (60-120 mesh) using 10% ethyl acetate-petroleum ether as eluent to afford the (*E*)-3-(2-methoxynaphthalen-1-yl)-1-(4-methoxyphenyl)prop-2-en-1-one (**3**, 3.1 g, 56%). M. p. 100-102 °C; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$3.83 (s, 3H), 3.99 (s, 3H), 6.96 (d, J = 9 Hz), 7.26 (d, J = 9 Hz), 7.36 (dd, J = 8, 8 Hz), 7.51 (dd, J = 8, 8 Hz), 7.76 (d, J = 8 Hz), 7.82 (d, J = 9 Hz), 7.89 (d, J = 16 Hz), 8.07 (d, J = 9 Hz), 8.26 (d, J = 9 Hz),8.48 (d, J = 16 Hz); $^{13}$C-NMR (75 MHz, $CDCl_3$): $\delta$55.6, 56.4, 112.9, 113.9, 117.7, 123.6, 124.0, 127.3, 127.5, 128.7, 129.1, 131.0, 131.6, 131.7, 133.1, 137.1, 157.0, 163.4, 189.7.

**Procedure for the synthesis of Pd nanoparticles**

A solution of 1 (63.6mg, 0.2 mmol) in MeOH (120 mL) was deaerated by bubbling argon for 30 minutes after which $Pd(OAc)_2$ (4.49 mg, 0.02 mmol) was added. The solution was then photolyzed in an immersion well at 4 °C with a 450 W medium pressure Hg-vapour lamp for 30 minutes. The resulting dark solution was then characterized for PdNPs through TEM and used directly for catalytic studies.

**General Experimental Procedure for the Suzuki-Miyaura Cross Coupling Reaction**

To a solution of aryl halide (10 mmol) in 25 ml MeOH-$H_2O$ (1:1) ($H_2O$ for ArBr/ArCl) mixture was added aryl boronic acid (15mmol) and anhydrous $K_2CO_3$(10 mmol) and 5μl catalyst and the resulting mixture was deaerated by bubbling argon for 5minutes.Then the mixture was heated at $60^0$(100 °C for aryl bromides and chlorides) C under argon atmosphere till the reaction was complete. After completion of the reaction (monitored by TLC), the mixture was cooled and was worked up by adding water followed by the extraction with ether. The ether extract was dried over anhydrous $Na_2SO_4$. The extract was then concentrated under reduced pressure and the residue was chromatographed over a column of silica-gel (100-200 mesh) using ethyl acetate-petroleum ether as eluent to afford the desired biaryl compounds.

## General Experimental Procedure for the Mizoroki-Heck Reaction

To a solution of aryl halide (10 mmol) in anhydrous DMF (20ml) was added methyl acrylate (12 mmol) and triethylamine (10 mmol) and catalyst (5μl).The resulting mixture deaerated by bubbling argon for 5minutes after that the resulting mixture was heated at $130^0$ C under argon atmosphere for appropriate time. After completion of the reaction (monitored by TLC),the mixture was cooled and then water was added to it. It was then extracted with ethyl acetate and the ethylacetate extract dried over anhydrous $Na_2SO_4$. Then the ethyl acetate extract was concentrated under reduced pressure. The residue was then subjected to column chromatography on silica-gel (100-200 mesh) using ethyl acetate-petroleum ether as eluent to afford the desired product.

## General Experimental Procedure for the Hiyama Coupling Reaction

A mixture of arylsiloxane (40 mmol) and NaOH (50 mmol) in 30 ml $H_2O$ was deaerated by bubbling argon for 5minutes after which it was stirred at room temperature for 5 minutes under argon atmosphere. After that aryl halide (10 mmol) was added followed by the addition of 5μl of the catalyst and the resulting mixture was heated at $100^0$ C under argon atmosphere for 3 hours. After completion of the reaction (monitored by TLC), the mixture was cooled. The resulting mixture was extractedwith ethyl acetate.The ethyl acetate extract was dried over $Na_2SO_4$, after which it was concentrated under reduced pressure. The residue was then chromatographed over a column of silica-gel (100-200 mesh) using ethyl acetate-petroleum ether as eluent to afford the desired biaryl compound.

## Additional Characterization of PdNPs

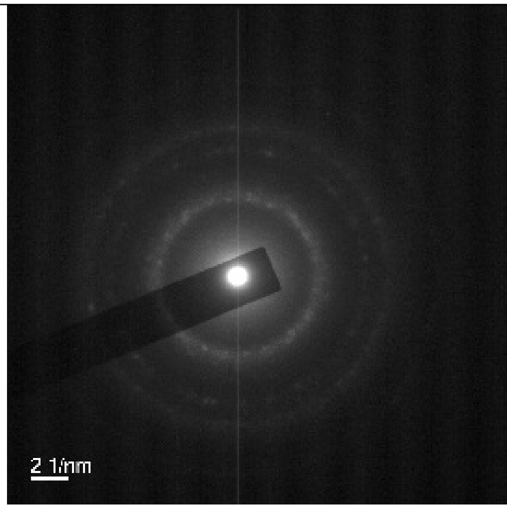



**Figure S1**. SAED image of a PdNP

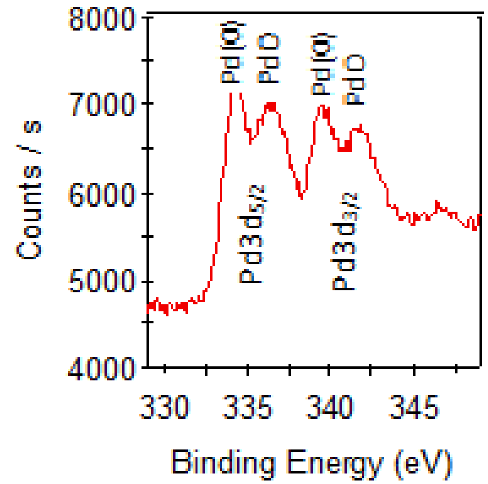



**Figure S2**. XPS spectra of the PdNP

## Compound Characterization data

Biphenyl[2] (**6a**): $^1$H-NMR (500 MHz, $CDCl_3$) δ 7.35-7.37(m, 1H), 7.43-7.46(m, 2H), 7.59-7.61(m, 2H) ; $^{13}$C-NMR(75 MHz, $CDCl_3$) δ 127.4, 127.5, 129.0, 141.4.

4-methoxybiphenyl[2,3,4](**6b**): $^1$H-NMR (400 MHz, $CDCl_3$) δ 3.86(s, 3H), 6.99(dd, *J*=2 Hz and 2 Hz, 2H), 7.29-7.33(m, 1H), 7.40-7.44(m, 2H), 7.53-7.57(m, 4H); $^{13}$C-NMR (100 MHz, $CDCl_3$) 55.4,114.3,126.7,126.8, 128.2, 128.8, 133.8, 140.9, 159.2.

4-chlorobiphenyl[4](**6c**): $^1$H-NMR (500 MHz, $CDCl_3$) δ 7.32-7.42(m, 5H), 7.43-7.50(m, 2H), 7.51-7.57(m,2H); $^{13}$C-NMR (100 MHz, $CDCl_3$)δ 127.0, 127.6,128.0, 128.4, 128.9, 129.0, 133.4, 139.7, 140.0.

4-methylbiphenyl[2,4](**6d**): $^1$H-NMR (400 MHz, $CDCl_3$) δ 2.33(s, 3H), 7.18(t, *J* = 3.6 Hz, 3H), 7.25(t, *J* = 7.4 Hz, 1H), 7.35(t, *J* = 7.6 Hz, 2H), 7.42(d, *J* = 8 Hz, 2H), 7.51(d, *J* = 7.6 Hz, 1H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 21.2, 127.1, 128.8, 129.6, 137.1, 138.4, 141.2.

4-methoxy-4'-methylbiphenyl[5](**6e**): $^1$H-NMR (400 MHz, $CDCl_3$) δ 2.34(s, 3H), 3.81(s, 3H), 6.93(d, *J* = 8.8 Hz, 2H), 7.19(d, *J* = 8.0 Hz, 2H), 7.41(d, *J* = 8 Hz, 2H), 7.47(d, *J* = 8.8 Hz, 2H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 21.0, 55.3, 114.2, 126.6, 127.9, 129.4, 133.8, 136.3, 138.0, 158.9.

4-chloro-4'-methylbiphenyl[2](**6f**): $^1$H-NMR (500 MHz, $CDCl_3$) δ 2.40(s, 3H), 7.25(d, *J* = 8.6 Hz, 2H), 7.39(d, *J* = 8.6 Hz, 2H), 7.46(d, *J* = 8.4 Hz, 2H), 7.49(d, *J* = 4.6 Hz, 2H), 7.51(d, *J* = 2.6 Hz, 2H); $^{13}$C-NMR (75 MHz, $CDCl_3$) δ 21.3, 127.0, 128.4,129.0, 129.8, 133.2, 137.3, 137.6, 139.7.

4-chloro-4'-methoxybiphenyl[3](**6g**): $^1$H-NMR (500 MHz, $CDCl_3$) δ 3.85(s, 3H), 6.98(d, *J* = 9.8 Hz, 2H), 7.38(d, *J* = 9.1 Hz, 2H), 7.46-7.50(m, 4H); $^{13}$C-NMR (75 MHz, $CDCl_3$) δ 55.6, 114.5, 128.1, 128.2, 129.0, 132.6, 132.8, 139.4, 159.5.

4-amino-4-methoxybiphenyl[2](**6h**): $^1$H-NMR (300 MHz, $CDCl_3$) δ 3.86(s, 3H), 6.74(d, *J* = 8.4 Hz, 2H), 6.94(d, *J* = 9.0 Hz, 2H), 7.36(d, *J* = 8.4 Hz, 2H), 7.45(d, *J* = 8.4 Hz, 2H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 55.4, 114.1, 115.5, 127.4, 127.6, 131.4, 133.9, 145.3, 158.4

Methyl(4-phenyl)benzoate[6](**6i**): $^1$H-NMR (400 MHz, $CDCl_3$) δ 3.94(s, 3H), 7.40(t, *J* = 5.6 Hz, 1H), 7.47(t, *J* = 6 Hz, 2H), 7.65(dd, *J* = 6 Hz and 6 Hz, 4H), 8.11(d, *J* = 6.8 Hz, 2H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 52.2, 127.1, 127.3, 128.2, 128.9, 129.0, 130.1, 140.0, 145.7, 167.0.

4-methylcarboxylato-4'-chlorobiphenyl[3](**6j**): $^1$H-NMR (400 MHz, $CDCl_3$) δ 3.94(s, 3H), 7.43(d, *J* = 8 Hz, 2H), 7.55(d, *J* = 8 Hz, 2H), 7.62(d, *J* = 8 Hz, 2H), 8.10(d, *J* = 8 Hz, 2H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 52.2, 126.9, 128.6, 129.1, 130.2, 134.4, 138.4, 144.3, 166.9.

4-acetylbiphenyl[4](**6k**): $^1$H-NMR (400 MHz, $CDCl_3$) δ 2.57(s, 3H), 7.33(t, *J* = 8 Hz, 1H), 7.40(d, *J* = 8 Hz, 2H), 7.56(d, *J* = 8 Hz, 2H),7.61(d, *J* = 8 Hz, 2H), 7.96(d, *J* = 8 Hz, 2H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 26.7, 127.2, 127.3, 128.3, 128.9, 129.0, 135.8, 139.9, 145.8, 197.8.

4-chloro-4'-acetylbiphenyl[2](**6l**): $^{1}$H-NMR (400 MHz, $CDCl_3$) δ 2.55(s, 3H), 7.35(d, *J* = 12 Hz, 2H), 7.46(d, *J* = 8 Hz, 2H), 7.55(d, *J* = 8 Hz, 2H), 7.94(d, *J* = 8 Hz, 2H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 26.7, 127.1, 128.5, 129.0, 129.2, 134.5, 136.1, 138.3, 144.5, 197.7.

4-fluoro-4'-acetylbiphenyl[4](**6m**): $^{1}$H-NMR (400 MHz, $CDCl_3$) δ 2.56(s, 3H), 7.07(t, *J* = 8 Hz, 2H), 7.49-7.56(m, 4H), 7.94(d, *J* = 12 Hz, 2H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 26.7, 115.8, 116.0, 127.1, 128.9, 129.0, 135.8, 136.0, 144.7, 161.8, 164.2, 197.7.

4-fluorobiphenyl[4,5](**6n**): $^{1}$H-NMR (400 MHz, $CDCl_3$) δ 7.11-7.16(m, 2H), 7.34-7.37(m, 1H), 7.43-7.46(m, 2H), 7.53-7.57(m, 4H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 115.6, 115.8, 127.1, 127.3, 128.7, 128.8, 128.9, 137.3, 137.4, 140.3, 161.3, 163.7.

(*E*)-methylcinnamate[3](**9a**): $^{1}$H-NMR (400 MHz, $CDCl_3$) δ 3.81(s, 3H), 6.45(d, *J* = 16 Hz, 1H), 7.38(t, *J* = 4 Hz, 3H), 7.51-7.54(m, 2H), 7.70(d, *J* = 16 Hz, 1H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 50.7, 116.8, 127.0, 127.9, 129.3, 133.3, 143.9, 166.4.

(*E*)-methyl-3-*p*-tolylacrylate[3](**9b**): $^{1}$H-NMR (500 MHz, $CDCl_3$) δ 2.37(s, 3H), 3.80(s, 3H), 6.40(d, J = 16 Hz, 1H), 7.19(d, *J* = 8 Hz, 2H), 7.42(d, J=8.1 Hz, 2H), 7.67(d, J=16 Hz, 1H); $^{13}$C-NMR (75MHz, $CDCl_3$) δ 21.7, 51.9, 116.8, 128.3, 129.8, 131.8, 140.9, 145.1, 167.9.

(*E*)-methyl-3-(4-methoxyphenyl)acrylate[4](**9c**): $^{1}$H-NMR (500 MHz, $CDCl_3$) δ 3.79(s, 3H), 3.84(s, 3H), 6.31(d, *J* = 16 Hz, 1H), 6.91(d, J = 8.8 Hz, 2H), 7.48(d, *J* = 8.8 Hz, 2H), 7.65(d, *J* = 16 Hz, 1H); ); $^{13}$C-NMR (75MHz, $CDCl_3$) δ 51.8,55.6, 114.5, 115.4, 127.2, 129.9, 144.8, 161.5, 168.0.

(*E*)-methyl-3-(4-aminophenyl)acrylate[8](**9d**): $^{1}$H-NMR (500 MHz, $CDCl_3$) δ 3.76(s, 3H), 6.24(d, *J* = 16 Hz, 1H), 6.65(d, *J* = 8.5 Hz, 2H), 7.35(d, *J* = 8.5 Hz, 2H), 7.60(d, *J* = 16 Hz, 1H); $^{13}$C-NMR (75MHz, $CDCl_3$) δ 52.0, 112.9, 113.4, 115.0, 124.9, 130.1, 145.3, 149.0,168.3.

methyl-4-((*E*)-2-(methoxycarbonyl)vinyl)benzoate[3](**9e**): $^{1}$H-NMR (400 MHz, $CDCl_3$) δ 3.75(s, 3H), 3.86(s, 3H), 6.45(d, *J* = 16 Hz, 1H), 7.51(d, *J* = 8 Hz, 2H), 7.63(d, *J* = 16 Hz, 1H), 7.97(d, J=8 Hz, 2H); $^{13}$C-NMR (100MHz, $CDCl_3$) δ 51.9, 52.3, 120.2, 127.9, 130.1, 131.4, 138.6, 143.5, 166.4, 167.0.

(*E*)-methyl-3-(4-acetylphenyl)acrylate[7](**9f**): $^{1}$H-NMR (400 MHz, $CDCl_3$) δ 2.62(s, 3H), 3.83(s, 3H), 6.53(d, *J* = 16 Hz, 1H), 7.61(d, *J* = 8 Hz,2H), 7.71(d, *J* = 16 Hz, 1H), 7.97(d, *J* = 8 Hz, 2H); $^{13}$C-NMR (100MHz, $CDCl_3$) δ 26.7, 51.9, 120.3, 128.1, 128.5, 128.9, 138.0,138.7, 143.3, 166.9, 197.3.

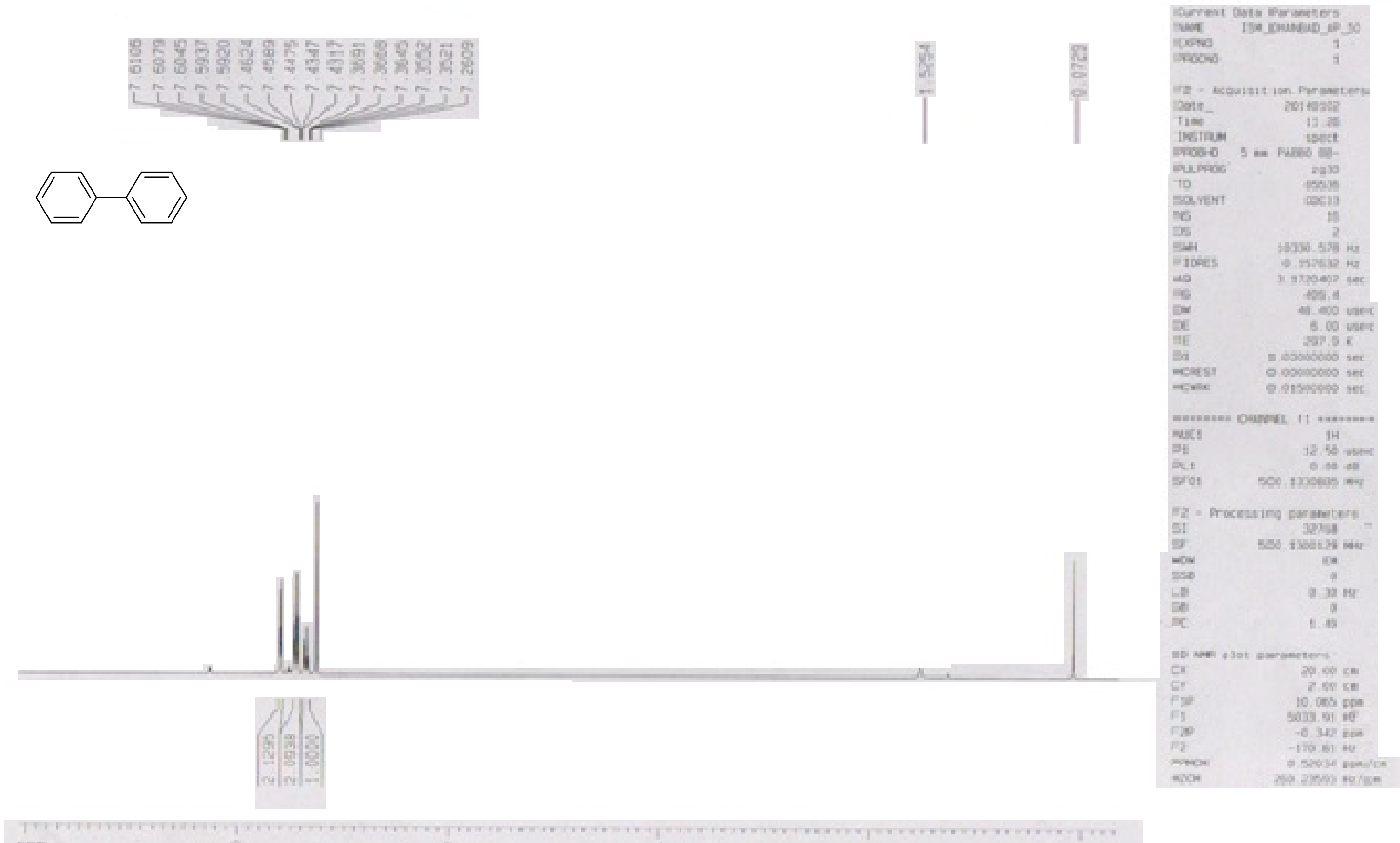


**Figure S3**. $^{1}$H-NMR (500 MHz, $CDCl_3$) of **6a.**

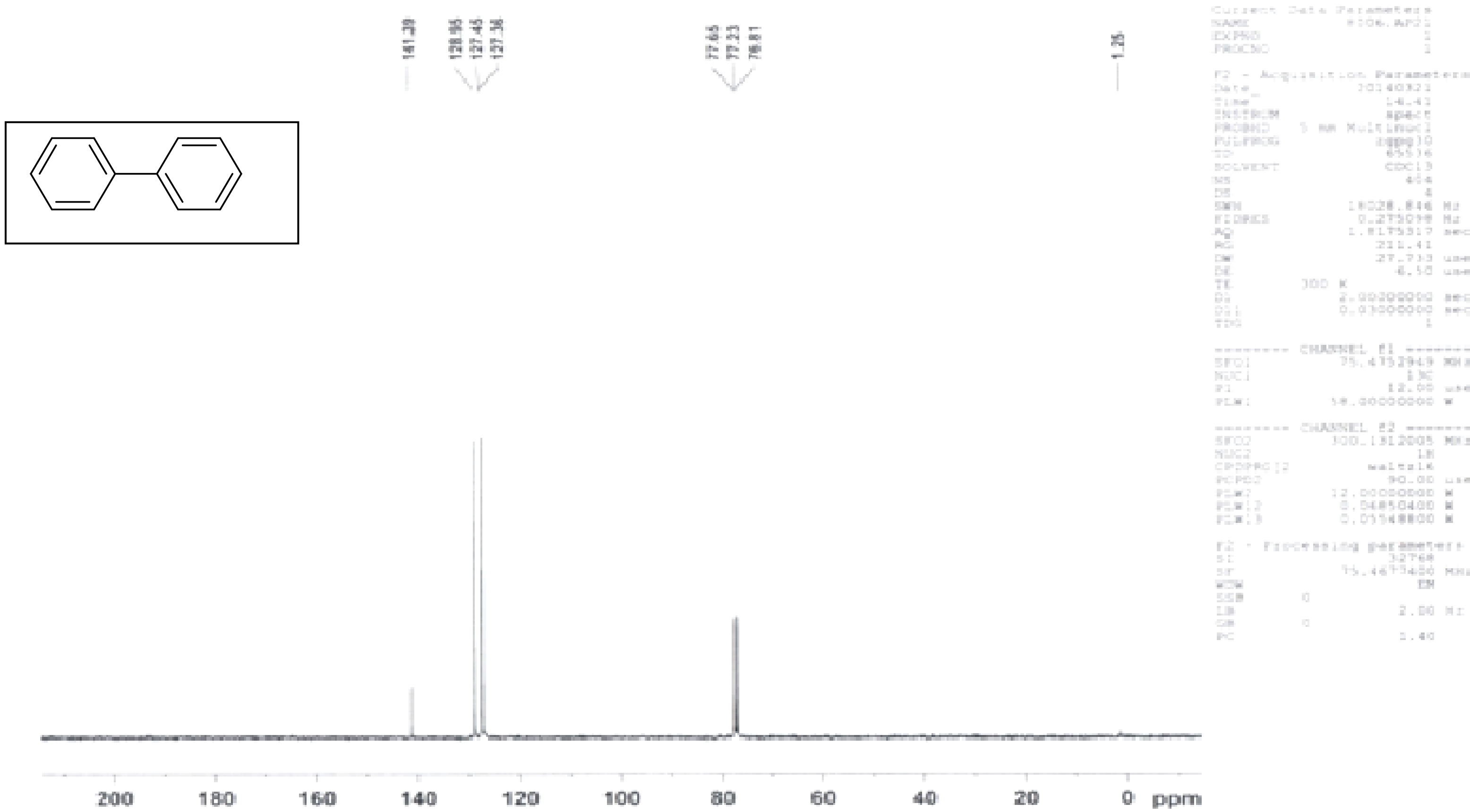



**Figure S4**. $^{13}C$-NMR (75 MHz, $CDCl_3$) of **6a.**

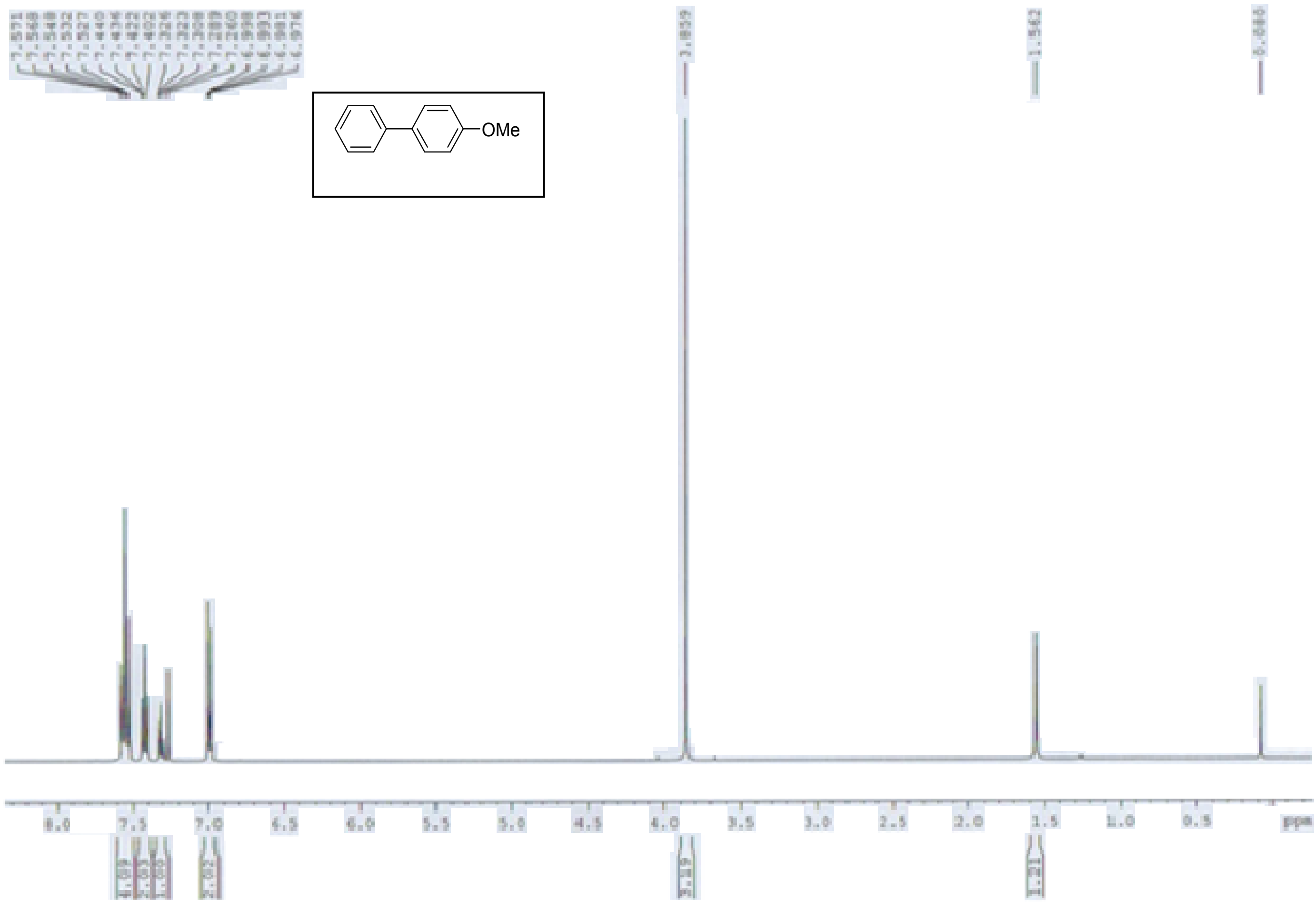


**Figure S5**. $^{1}$H-NMR (400 MHz, $CDCl_3$) of **6b.**

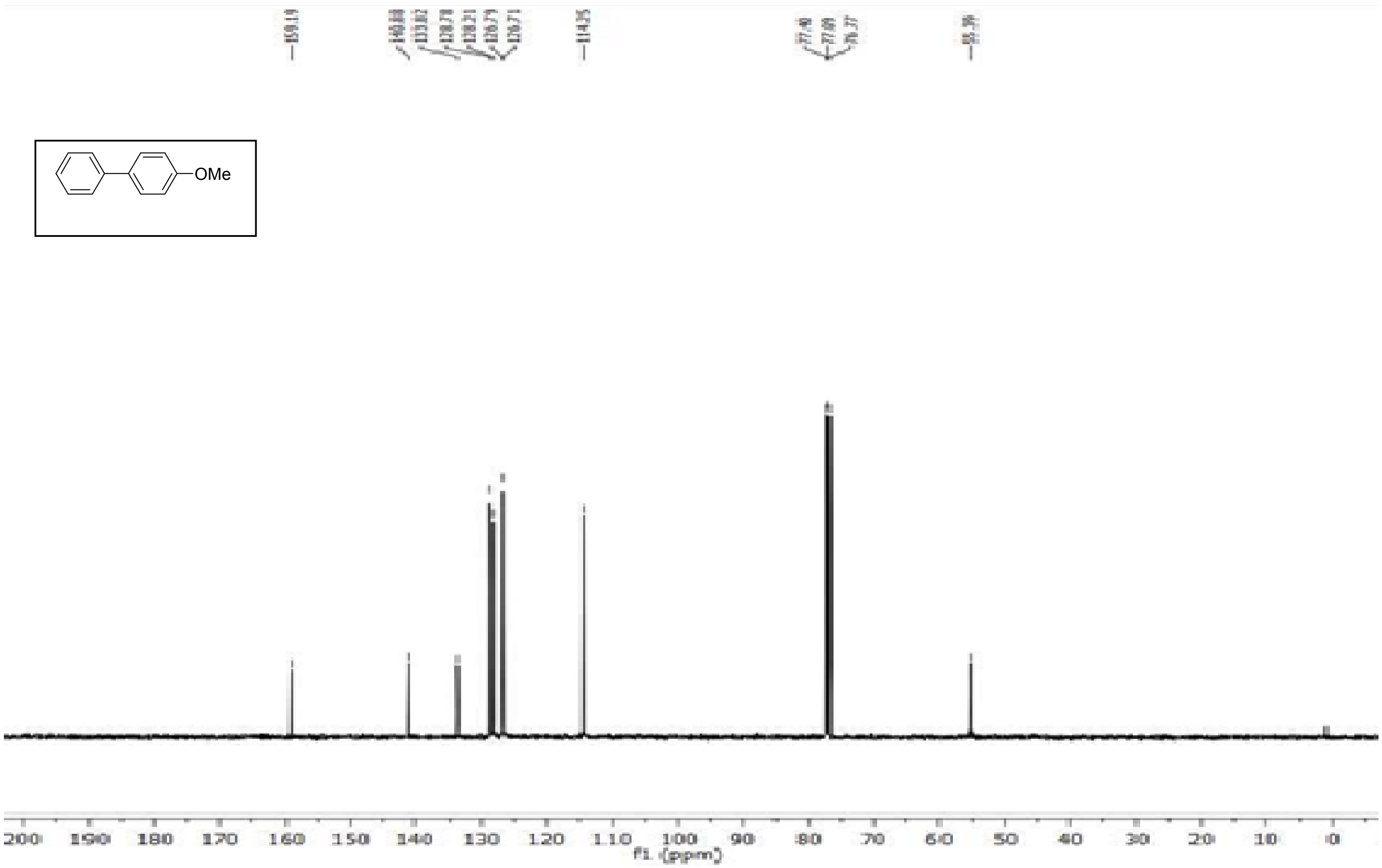


**Figure S6**. $^{13}$C-NMR (100 MHz, $CDCl_3$) of **6b.**

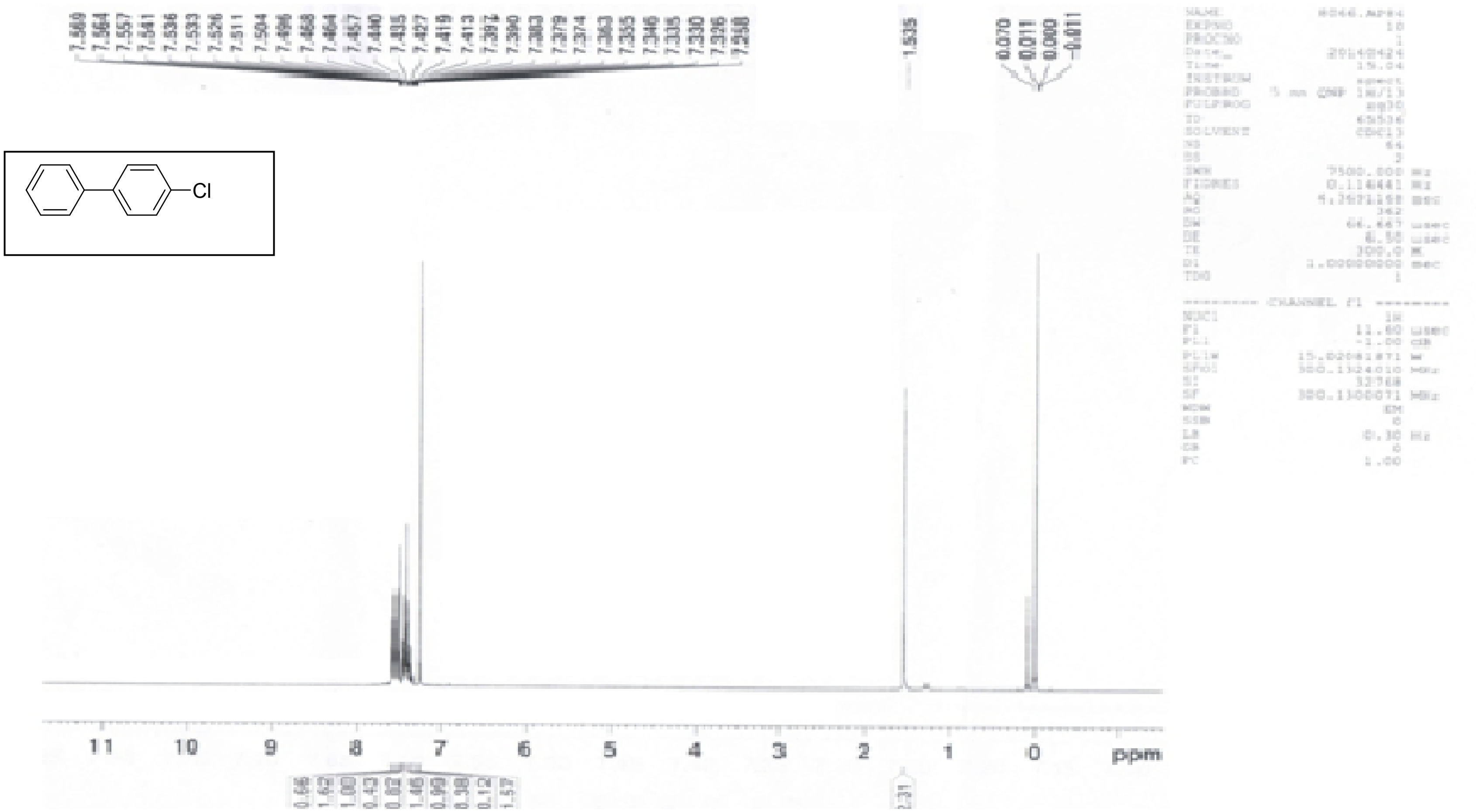



**Figure S7.** ¹H-NMR (400 MHz, $CDCl_3$) of **6c.**

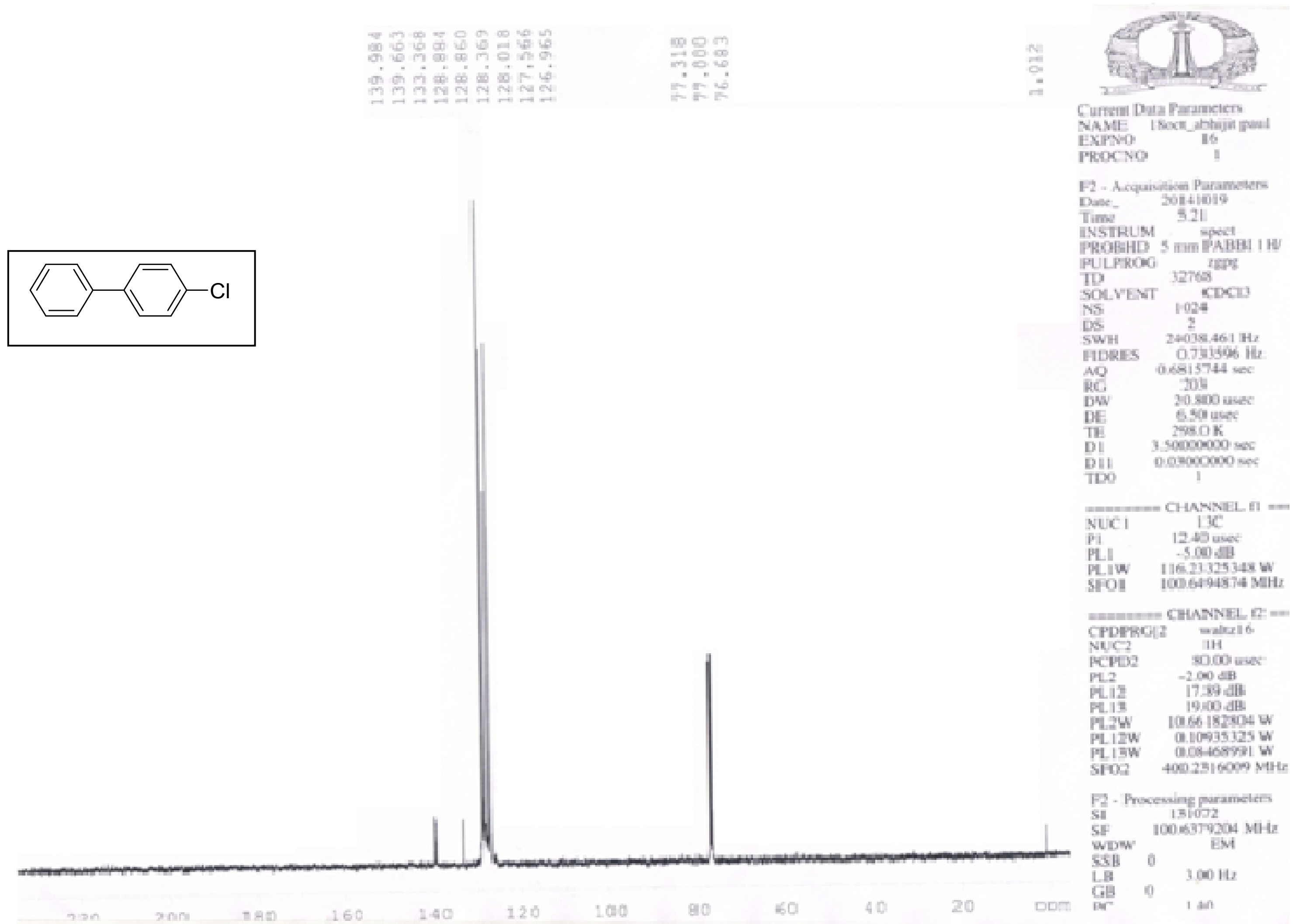


**Figure S8.** $^{13}$C-NMR (100 MHz, $CDCl_3$) of **6c.**

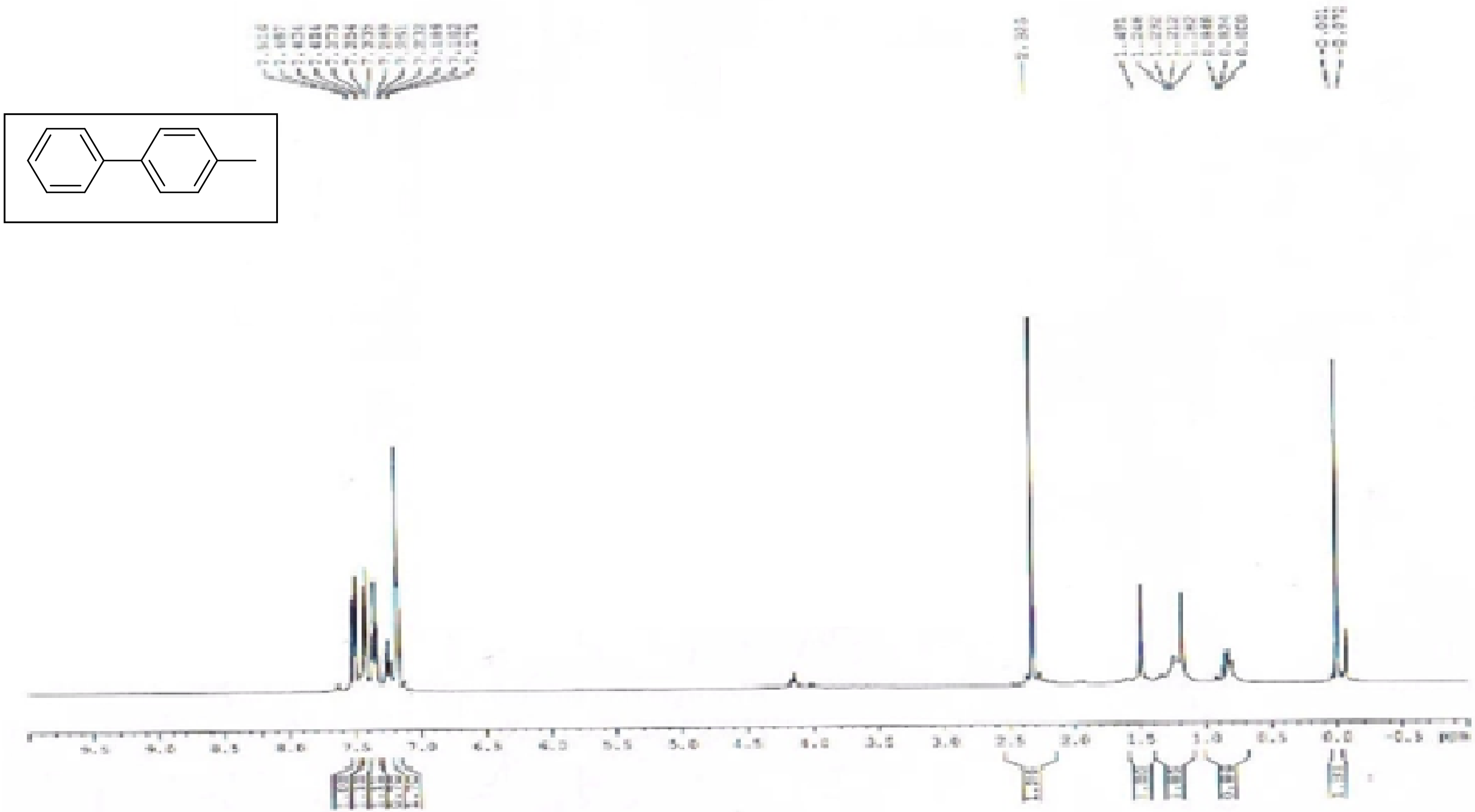


**Figure S9.** $^{1}$H-NMR (400 MHz, $CDCl_3$) of **6d.**

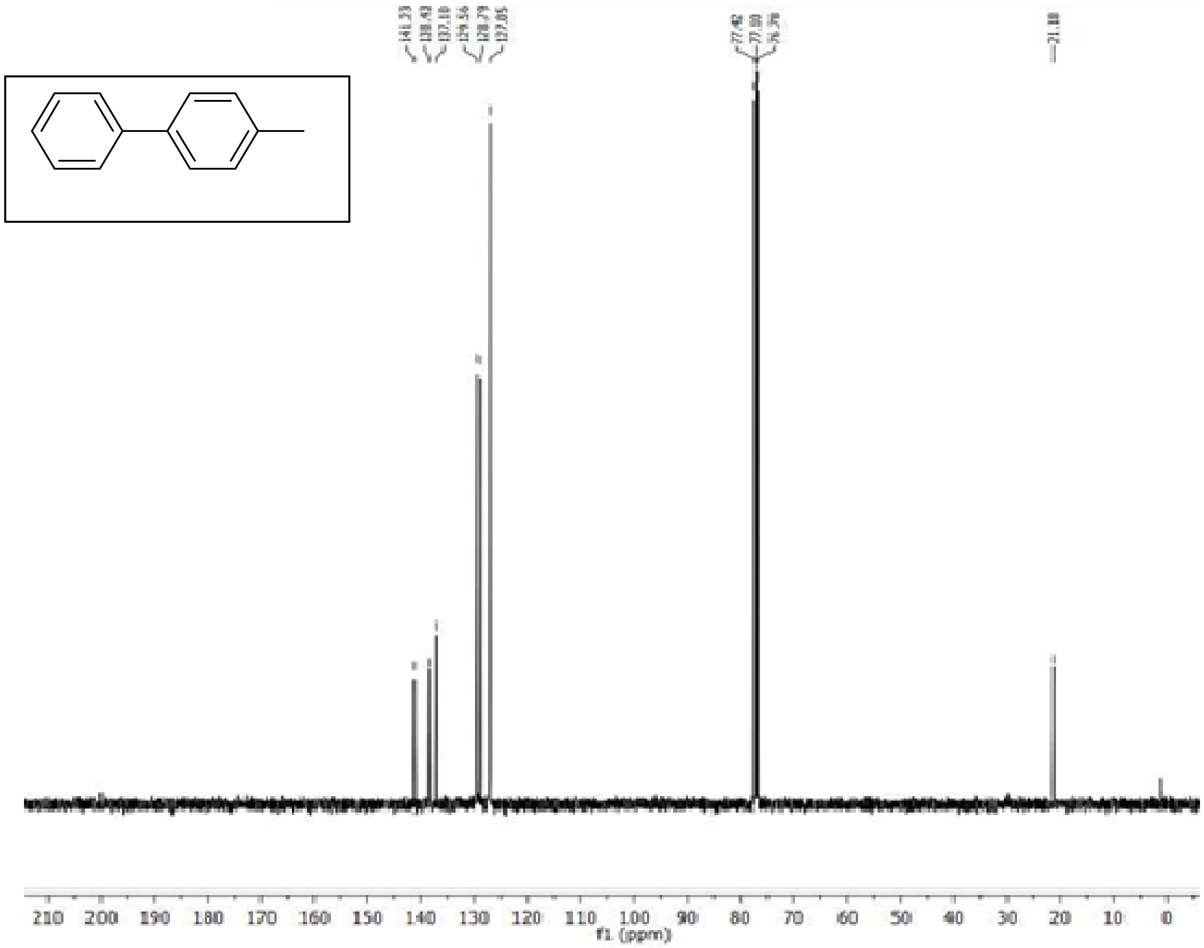



**Figure S10.** $^{13}$C-NMR (100 MHz, $CDCl_3$) of **6d.**

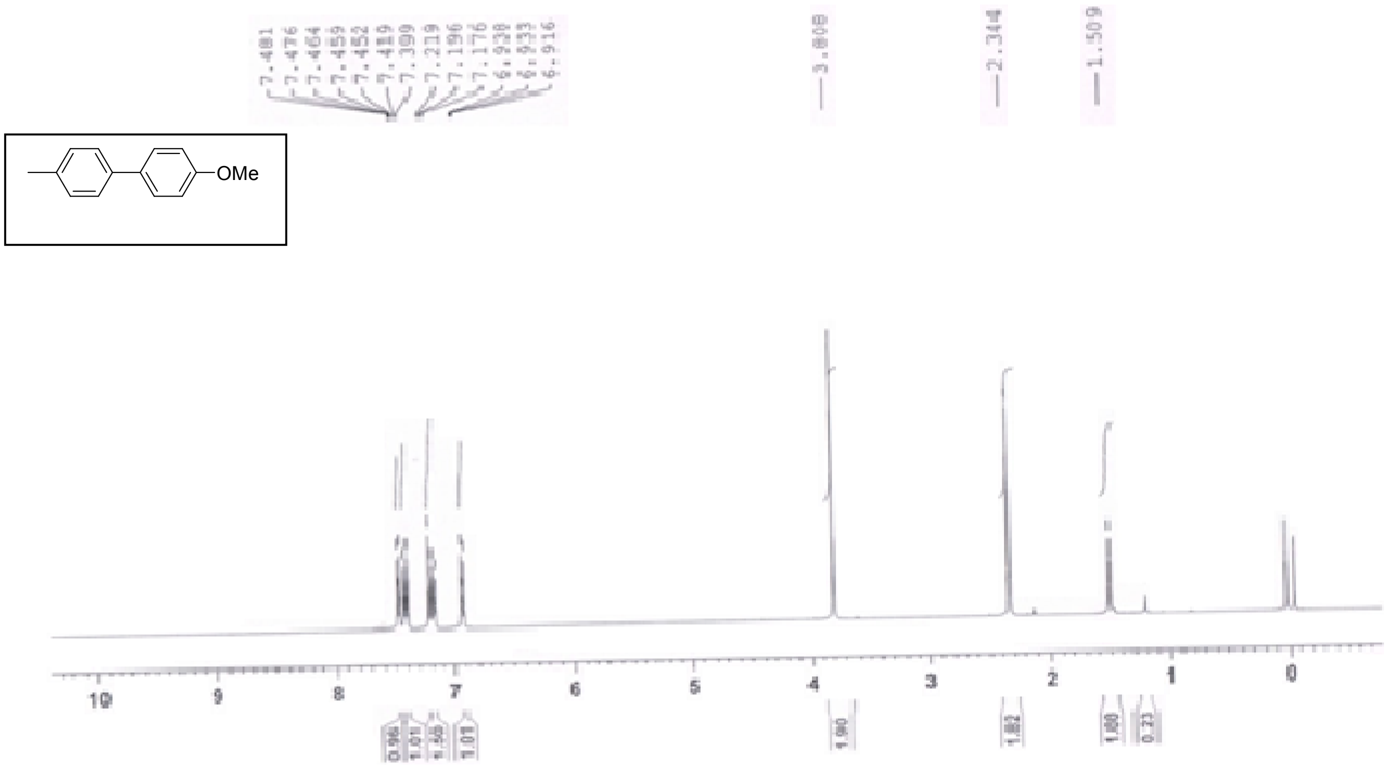


**Figure S11.** $^{1}$H-NMR (400 MHz, $CDCl_3$) of **6e.**

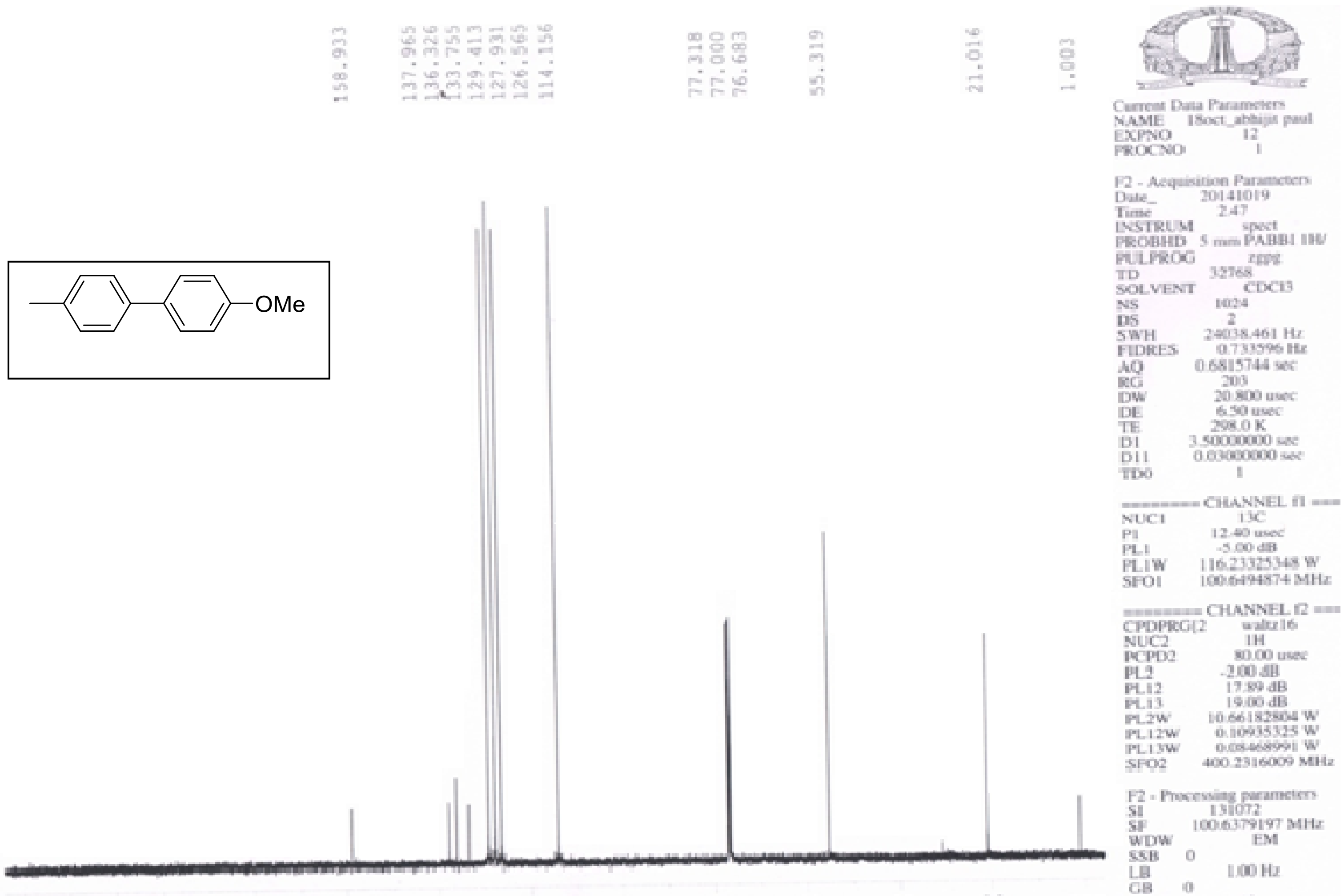


Figure S12. $^{13}$C-NMR (100 MHz, $CDCl_3$) of **6e.**

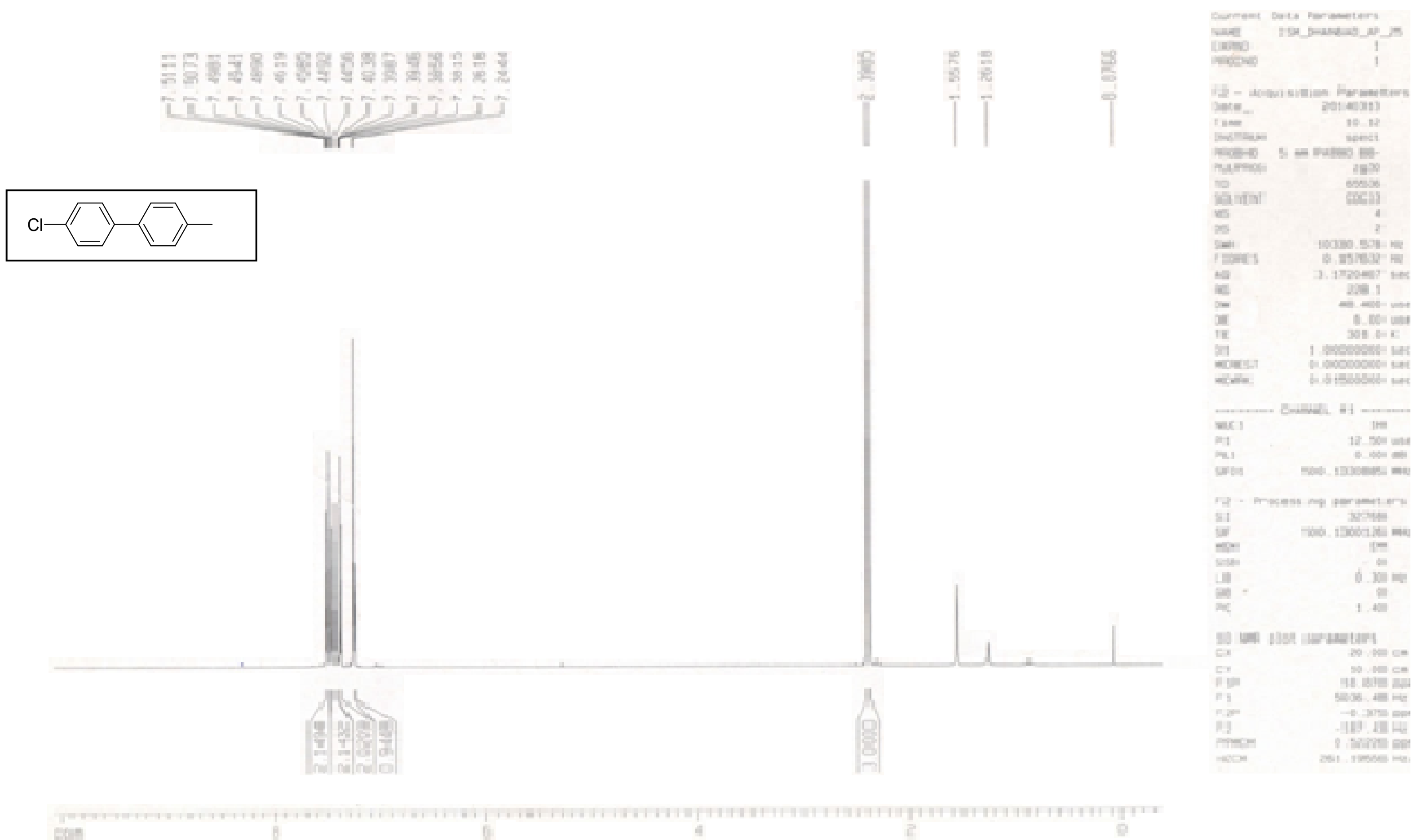


**Figure S13**. $^{1}$H-NMR (500 MHz, $CDCl_3$) of **6f.**

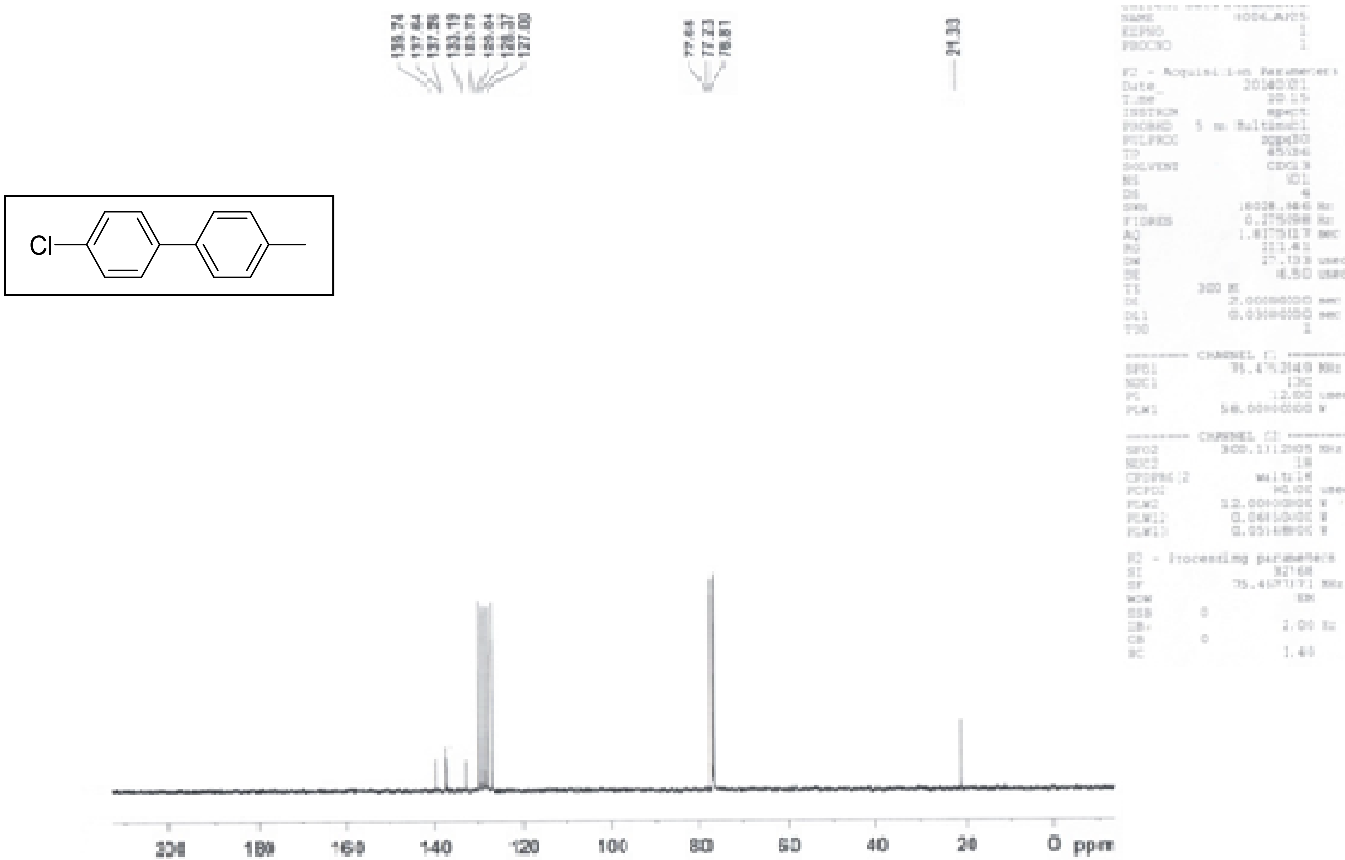



**Figure S14**. $^{13}$C-NMR (75 MHz, $CDCl_3$) of **6f.**

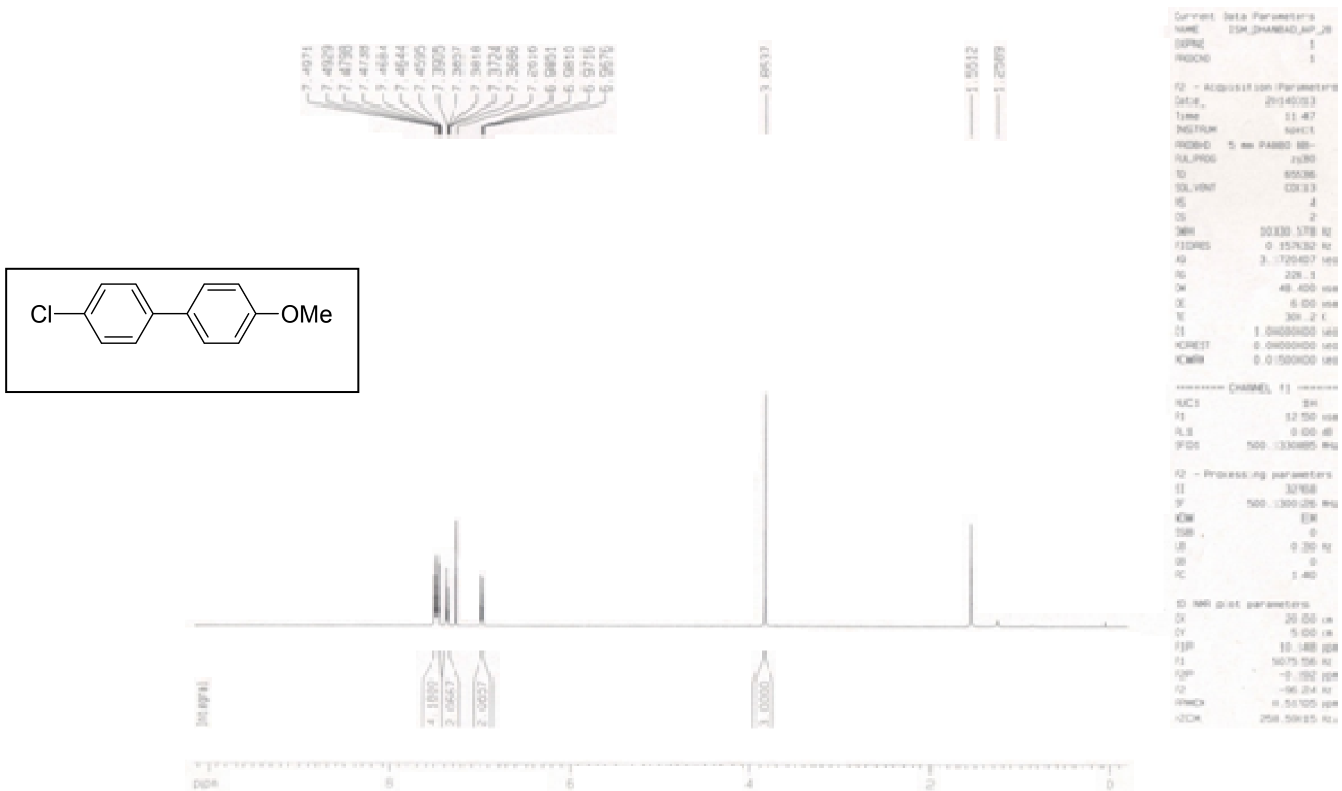



**Figure S15.** $^1$H-NMR (500 MHz, $CDCl_3$) of **6g.**

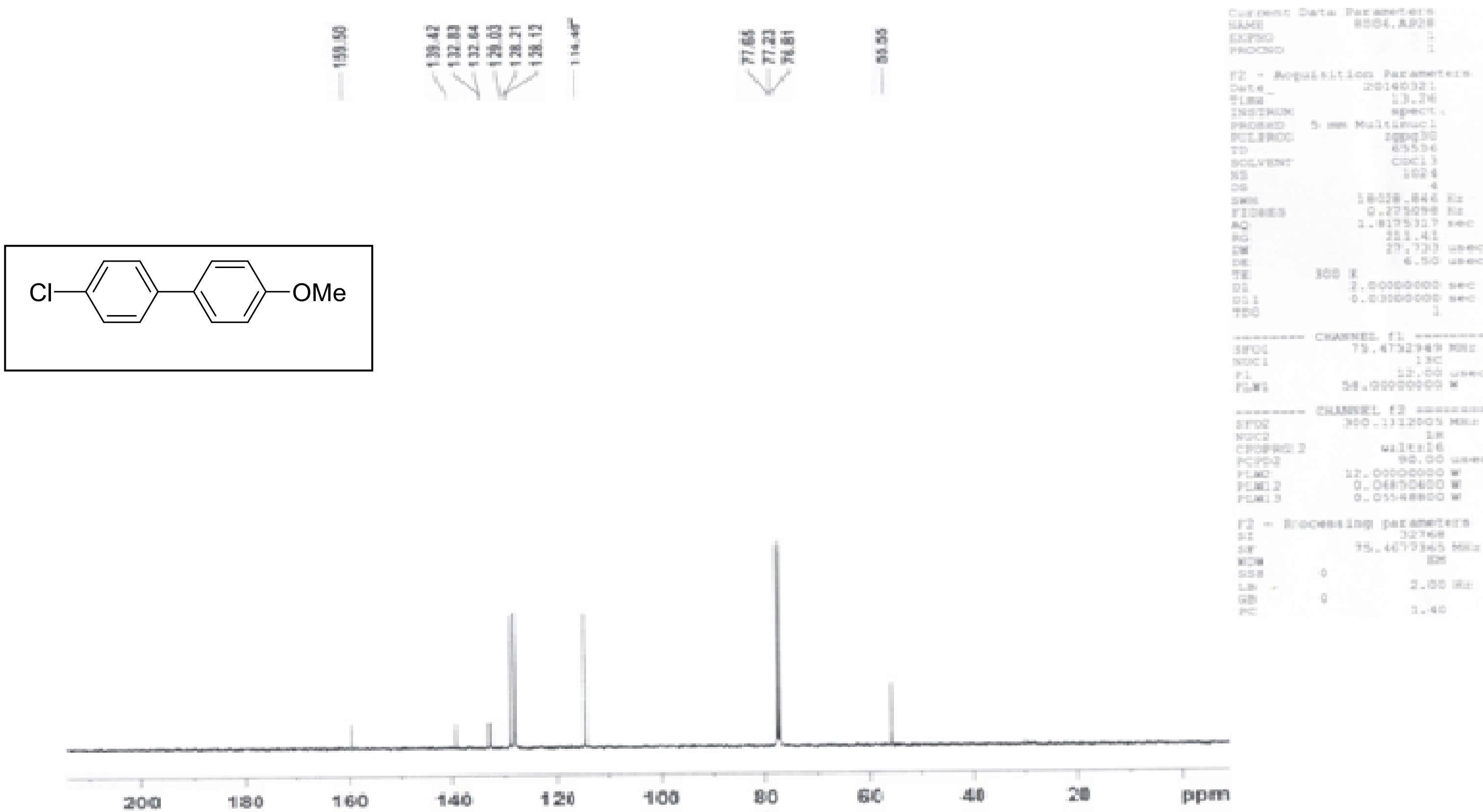



**Figure S16.** $^{13}$C-NMR (75 MHz, $CDCl_3$) of **6g.**

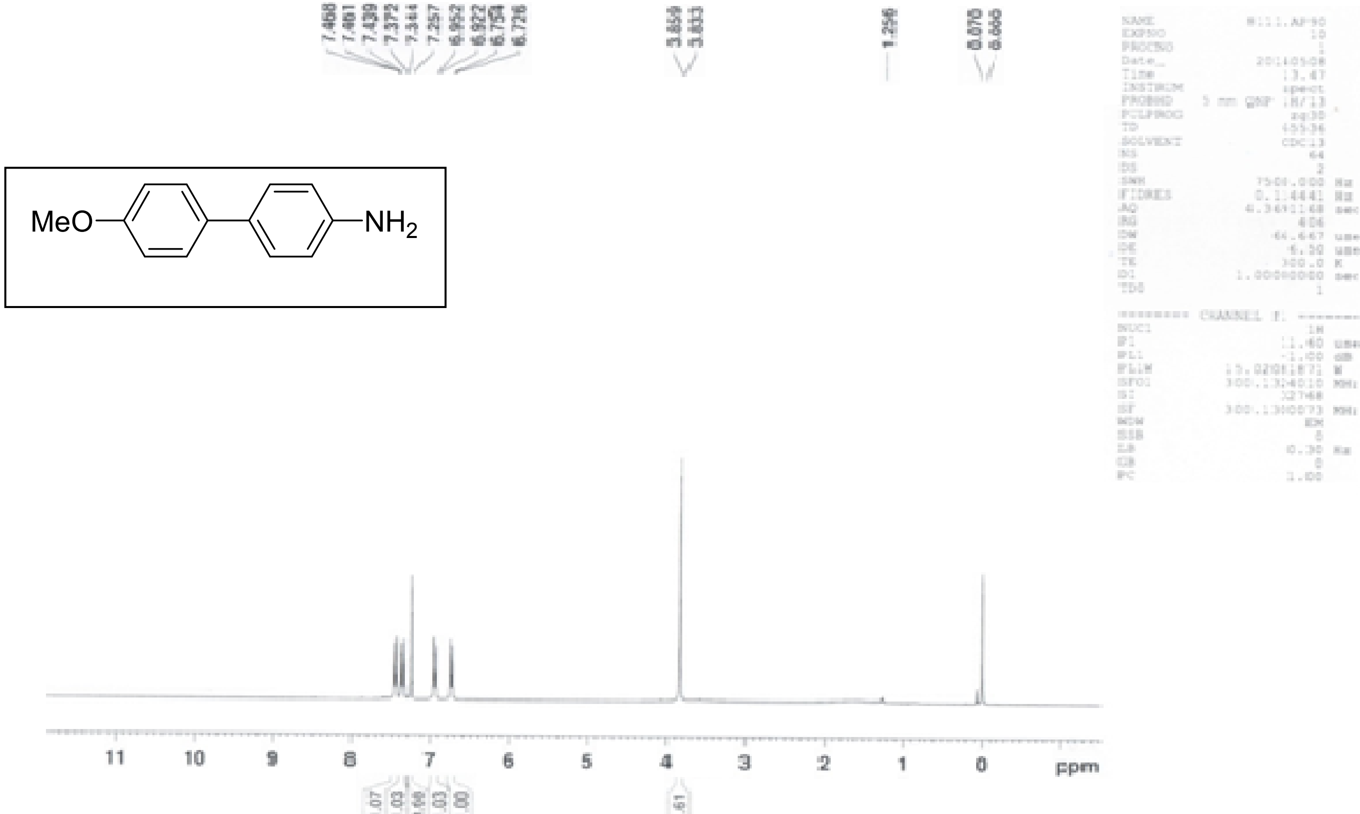


**Figure S17.** $^{1}H$-NMR (300 MHz, $CDCl_3$) of **6h.**

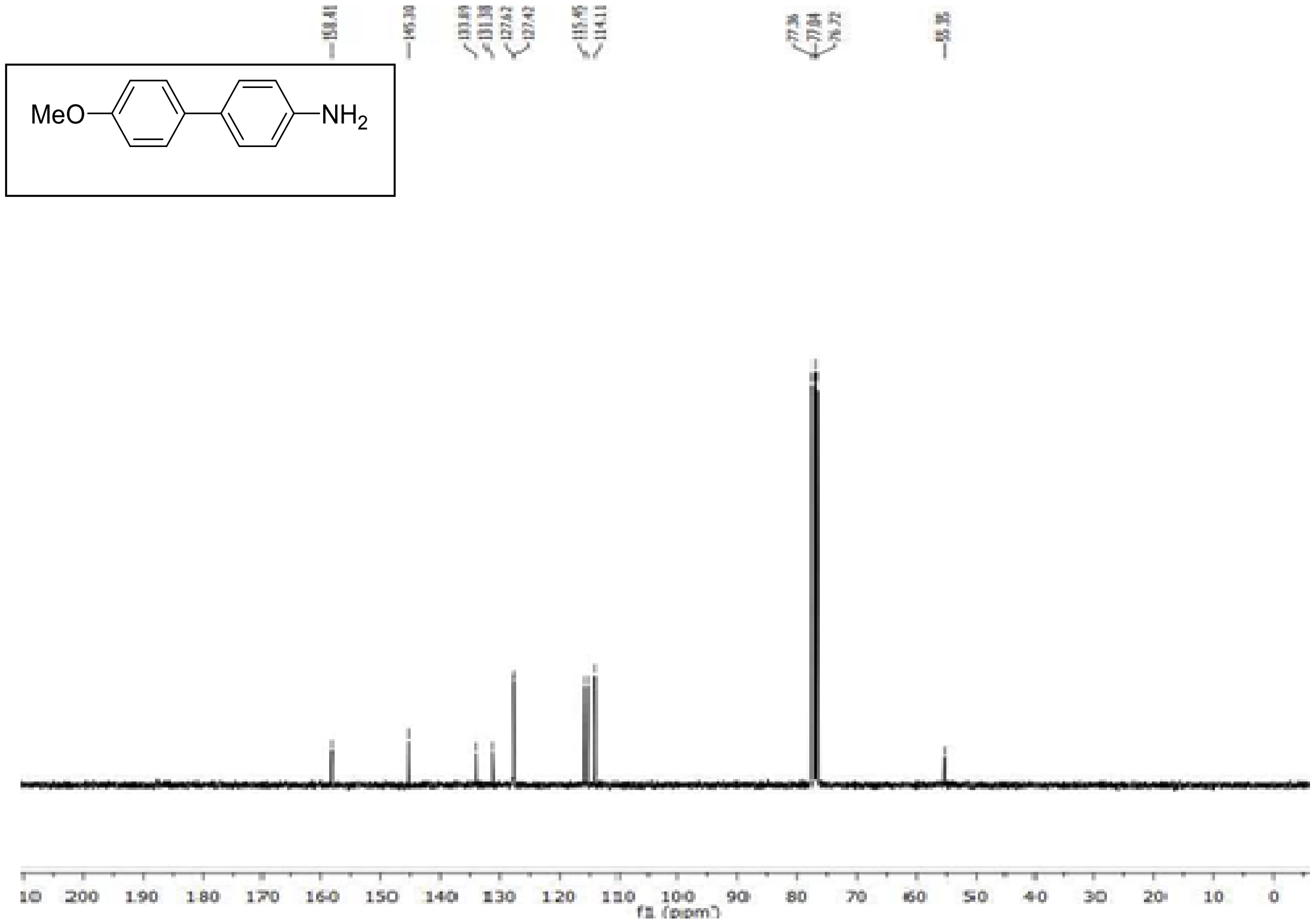



**Figure S18.** $^{13}$C-NMR (100 MHz, $CDCl_3$) of **6h.**

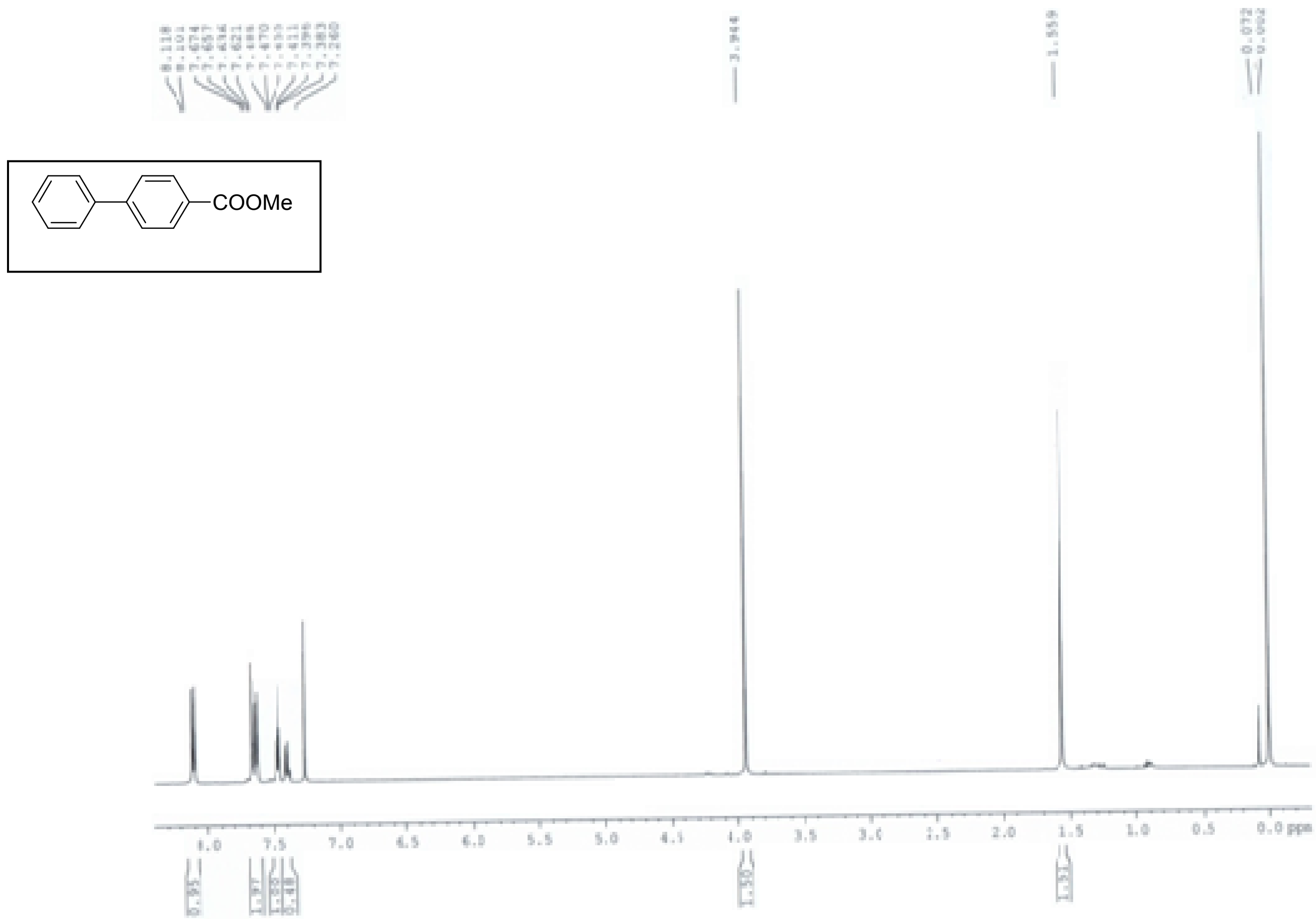



**Figure S19.** $^{1}$H-NMR (400 MHz, $CDCl_3$) of **6i.**

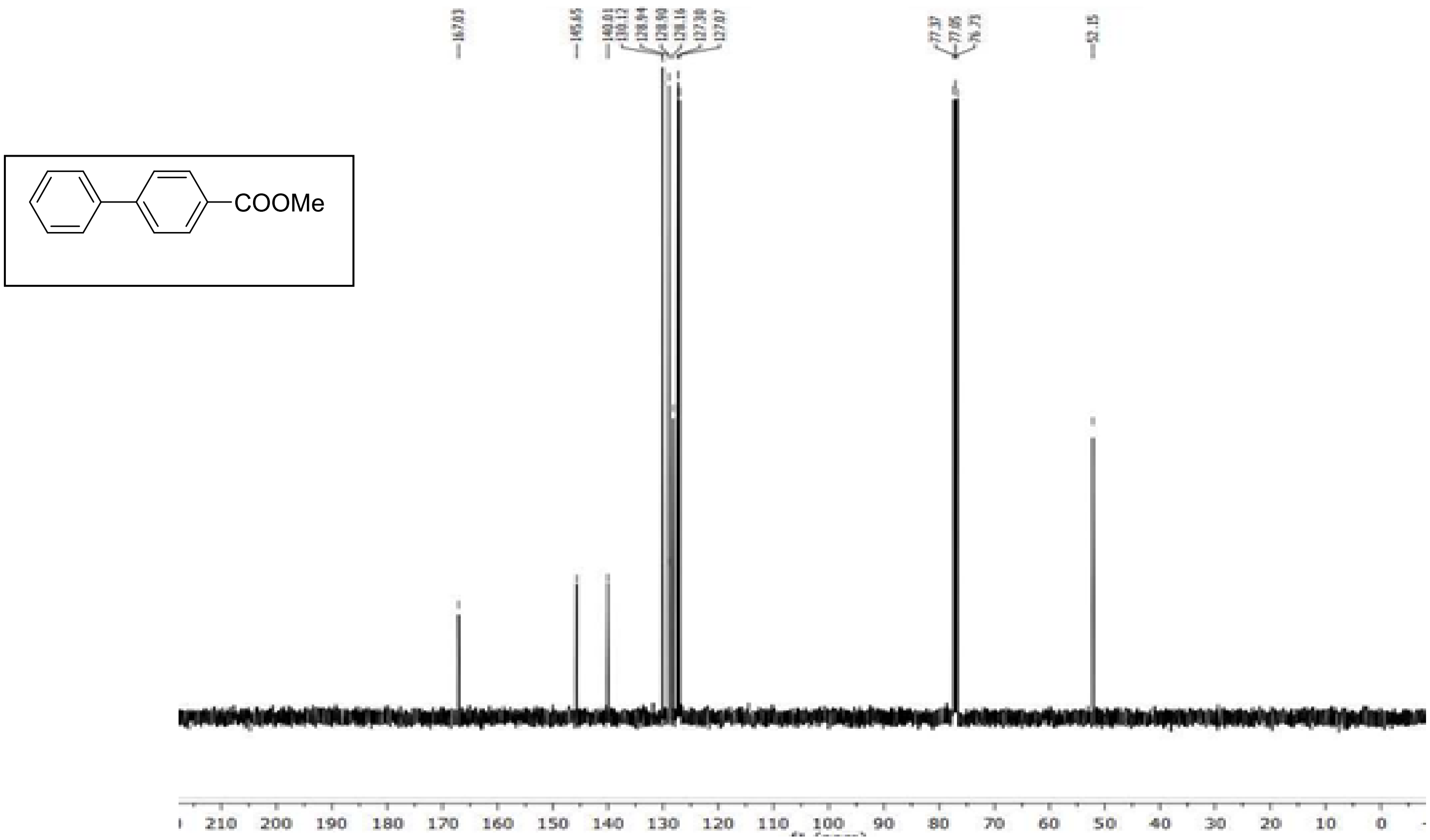



**Figure S20.** $^{13}$C-NMR (100 MHz, $CDCl_3$) of **6i.**

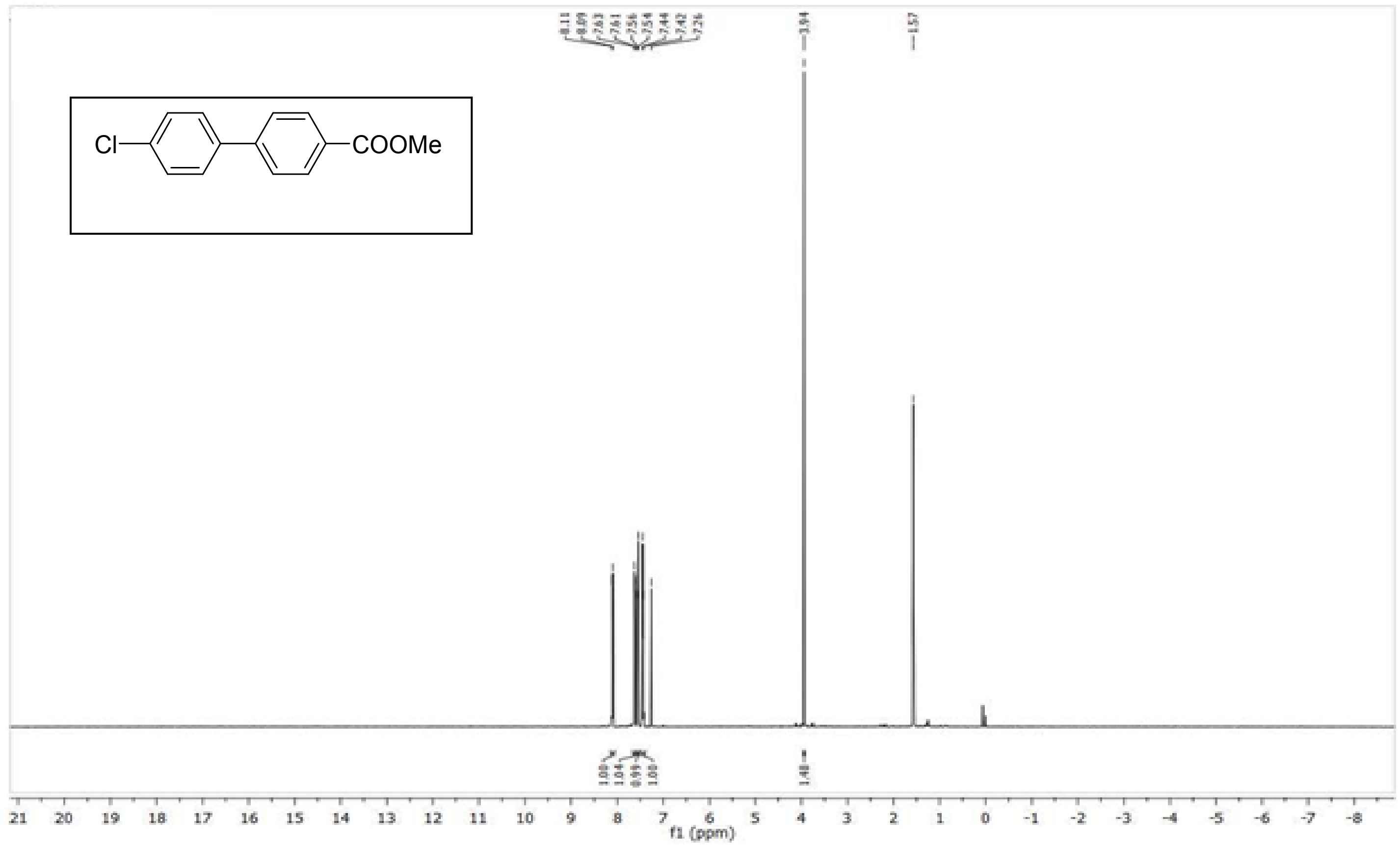



**Figure S21.** $^1$H-NMR (400 MHz, $CDCl_3$) of **6j.**

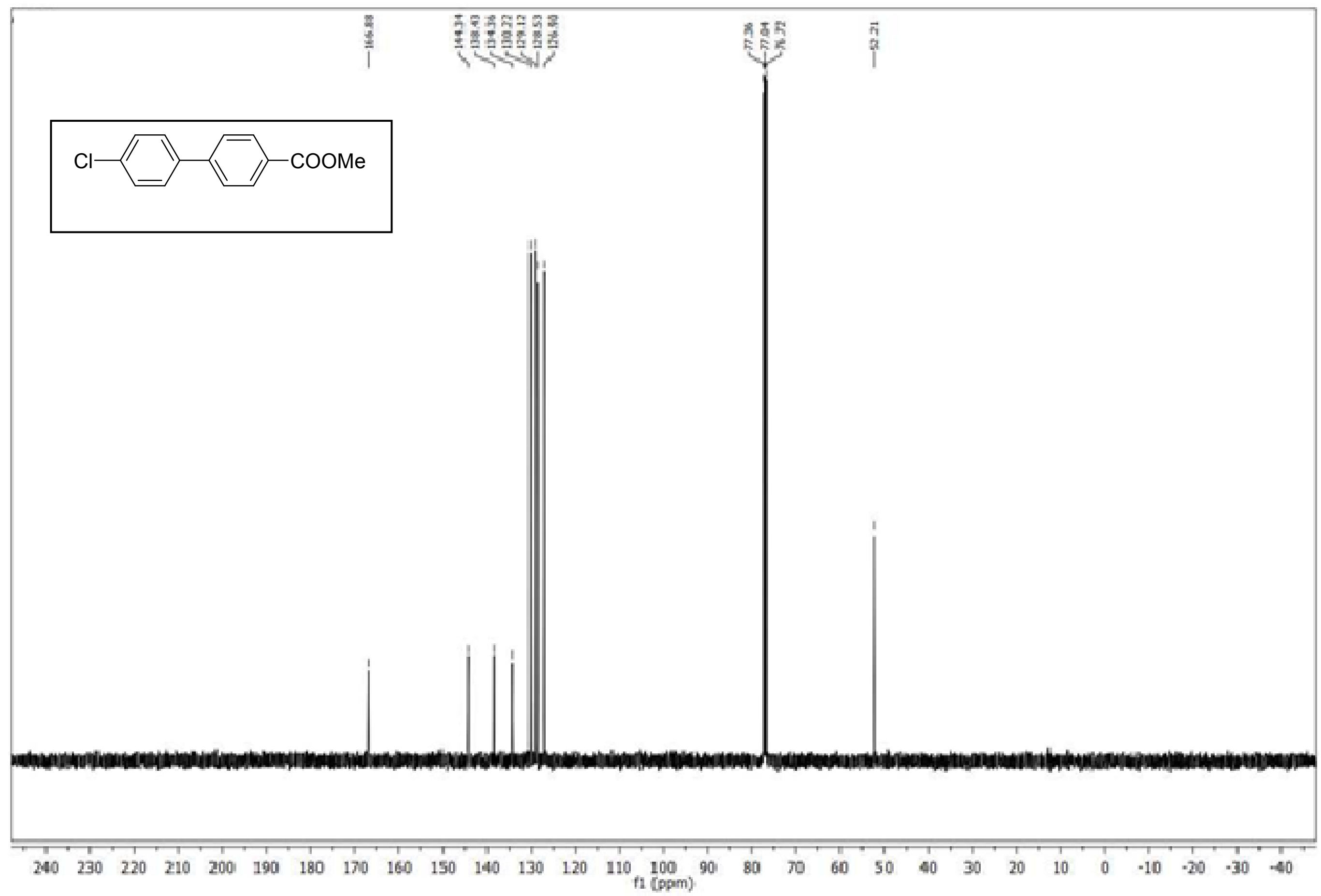



**Figure S22.** $^{13}$C-NMR (100 MHz, $CDCl_3$) of **6j.**

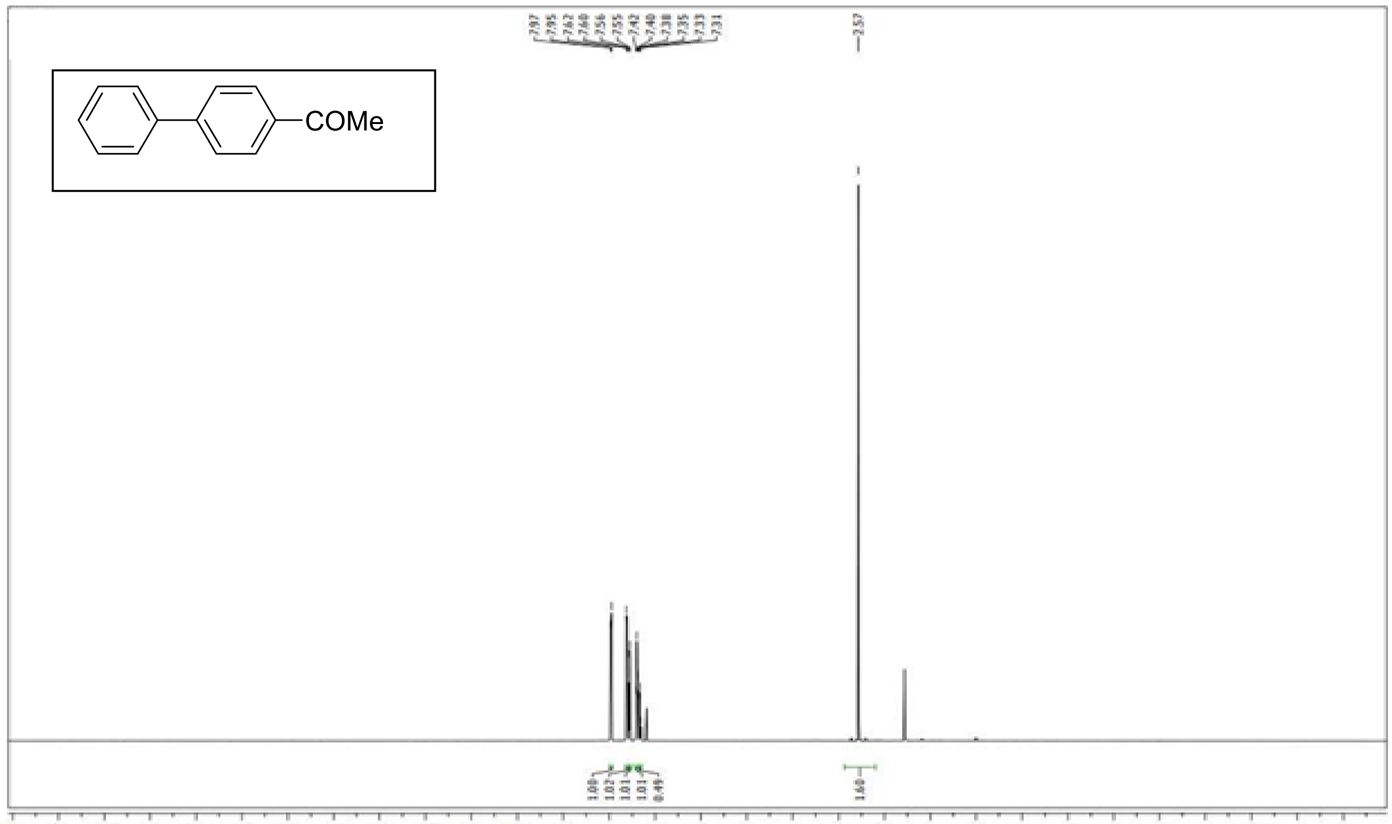



**Figure S23.** $^{1}$H-NMR (400 MHz, $CDCl_3$) of **6k.**

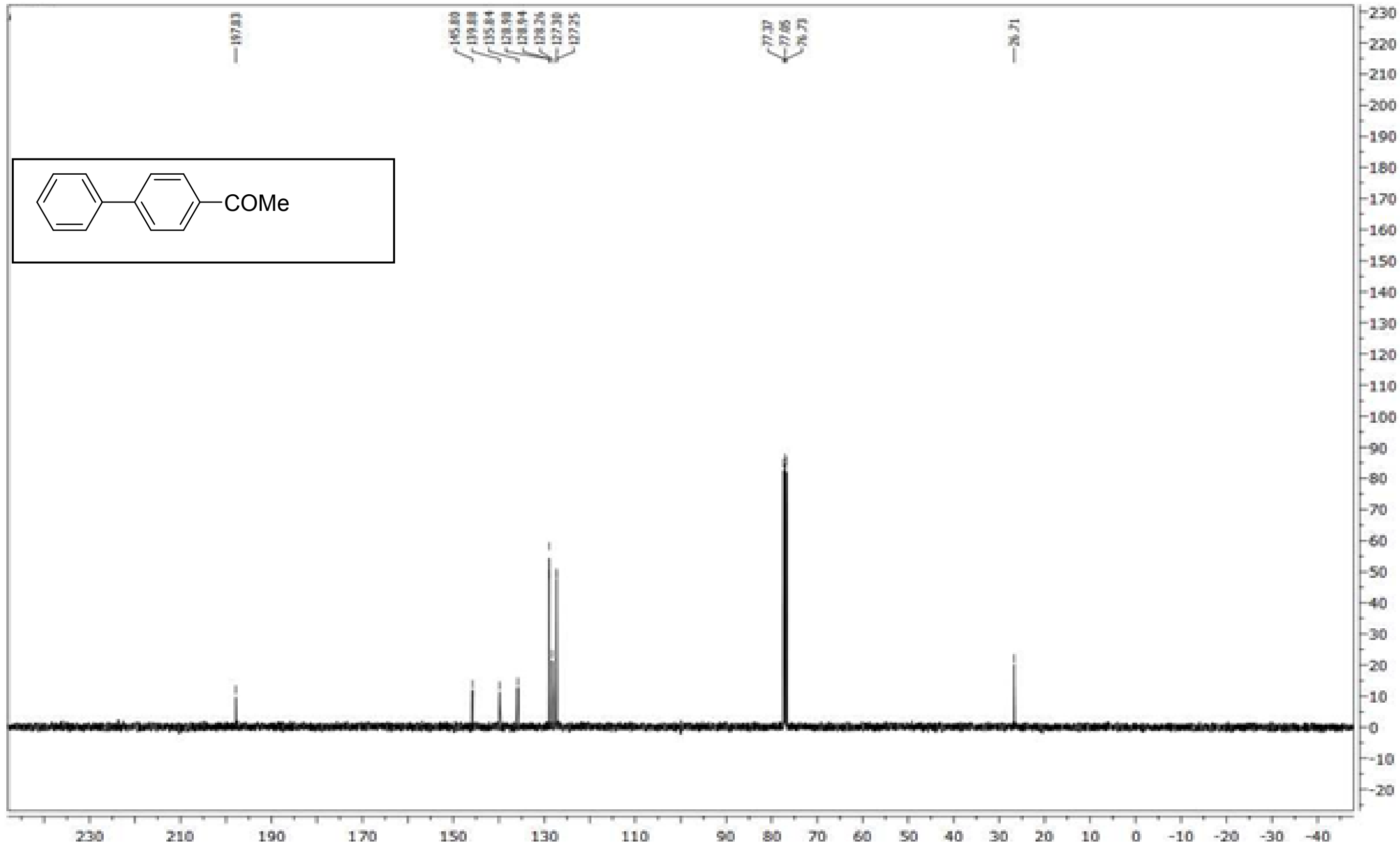



**Figure S24**. $^{13}C$-NMR (100 MHz, $CDCl_3$) of **6k.**

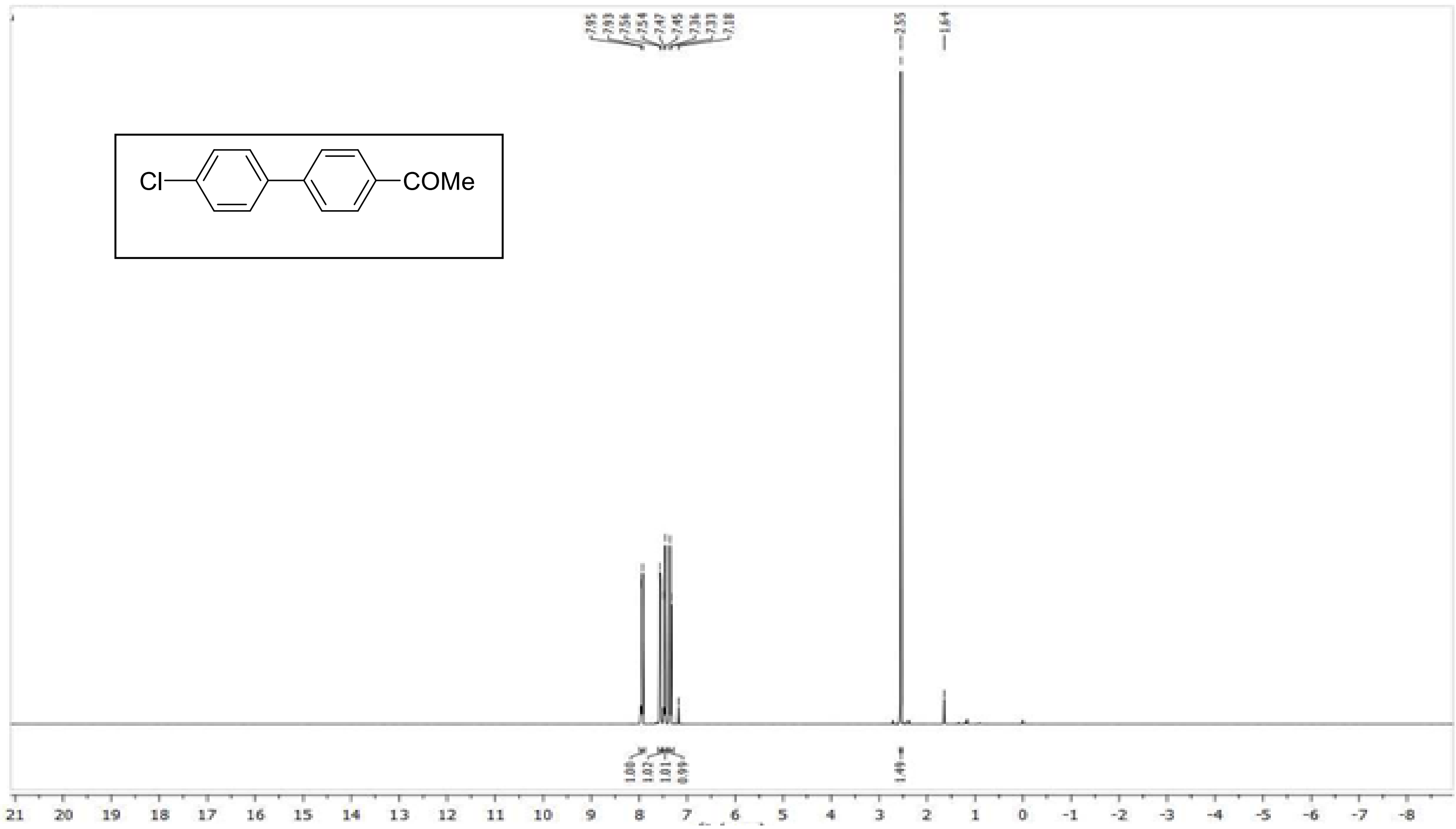



**Figure S25.** $^1$H-NMR (400 MHz, $CDCl_3$) of **6l.**

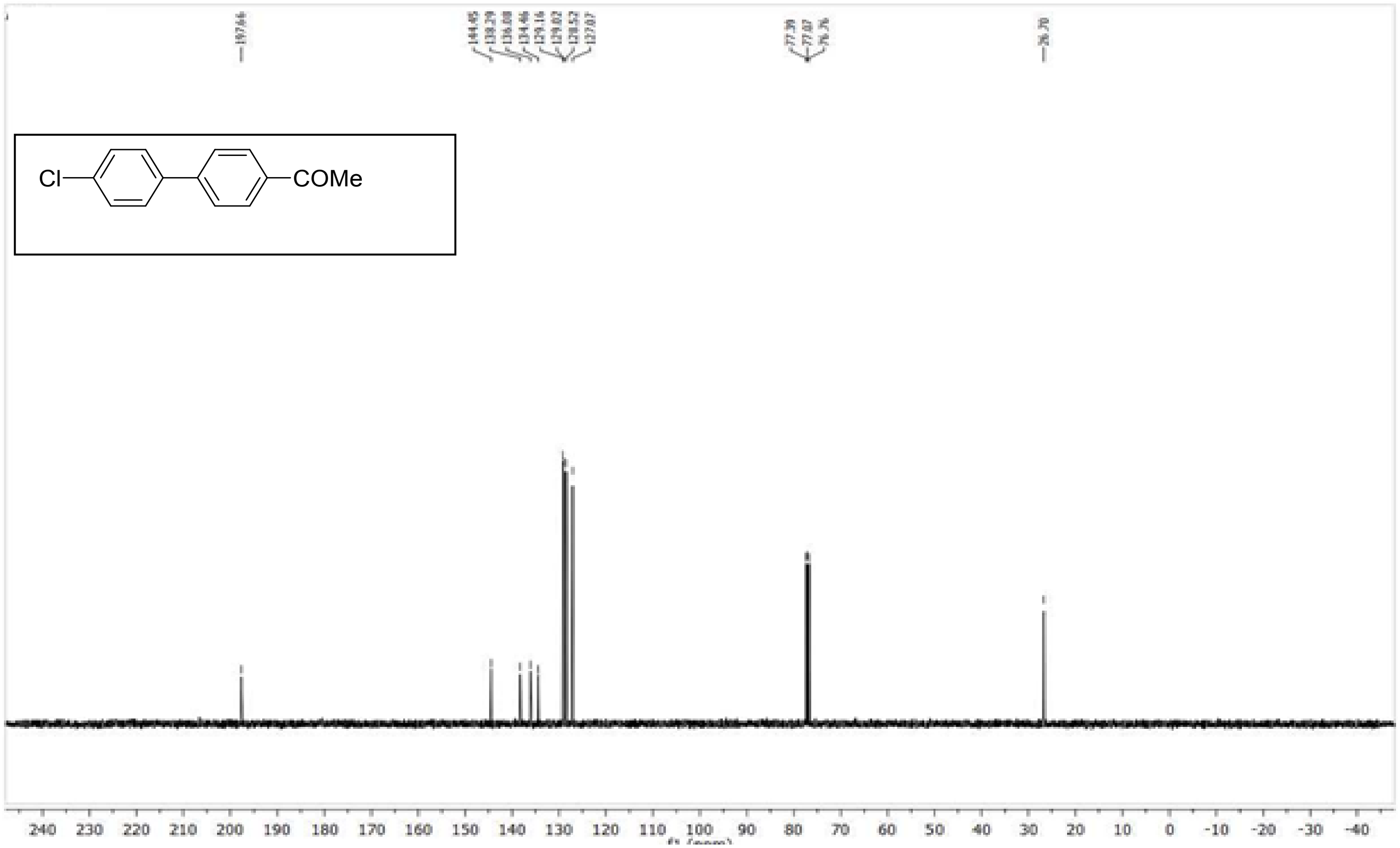



**Figure S26**. $^{13}$C-NMR (100 MHz, $CDCl_3$) of **6l.**

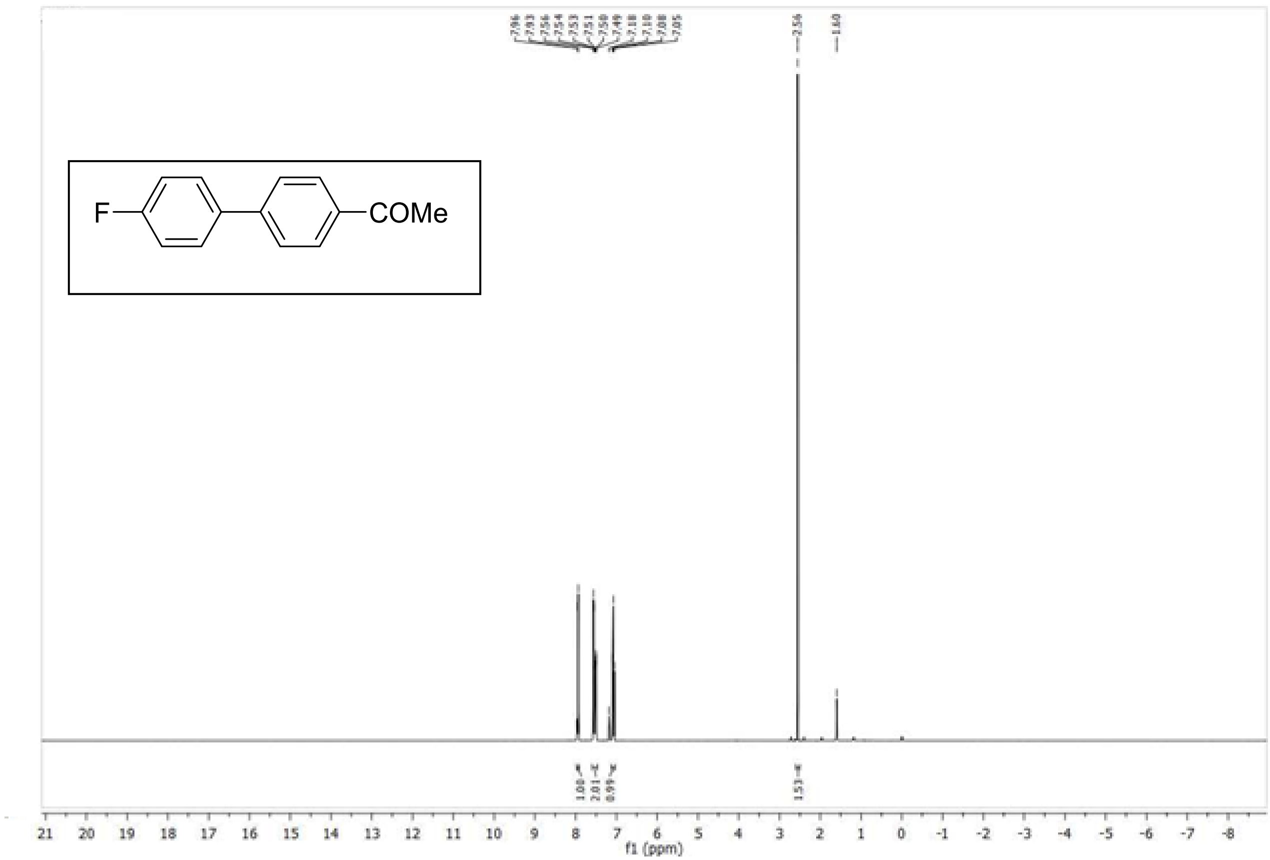



**Figure S27.** $^{1}$H-NMR (400 MHz, $CDCl_3$) of **6m.**

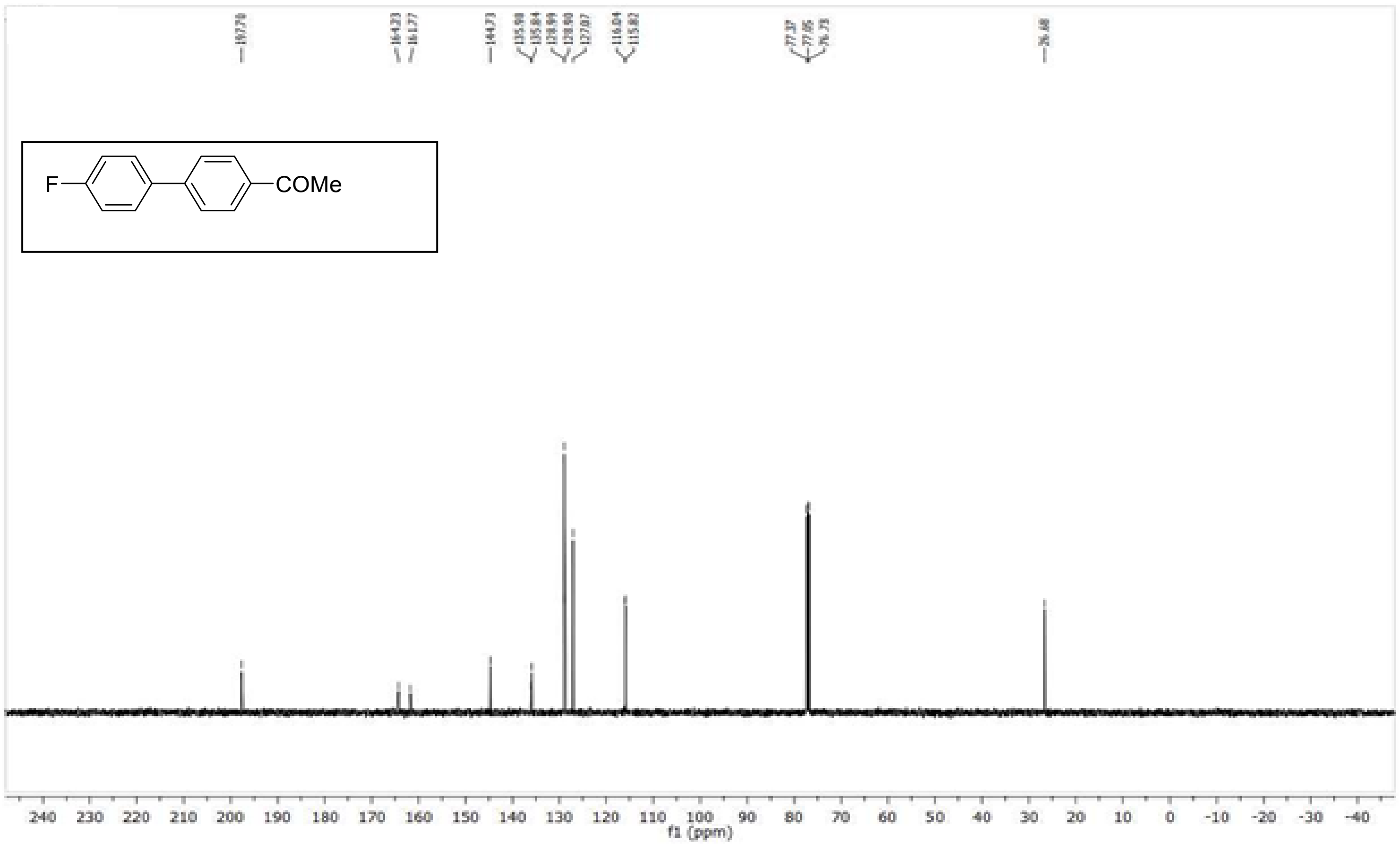



**Figure S28**. $^{13}$C-NMR (100 MHz, $CDCl_3$) of **6m.**

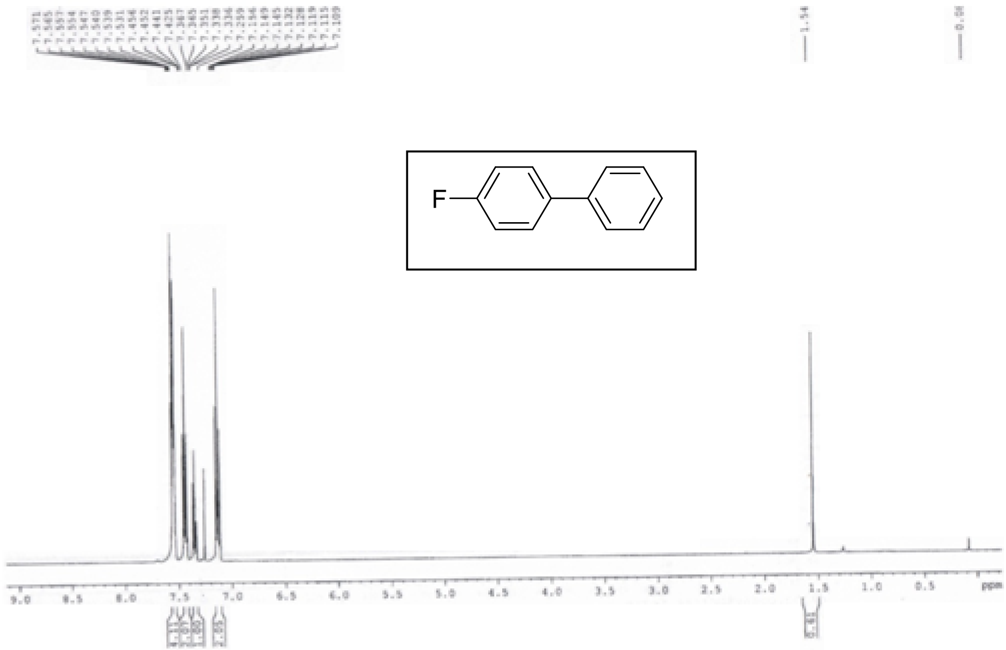


Figure S29. $^1$H-NMR (400 MHz, $CDCl_3$) of **6n.**

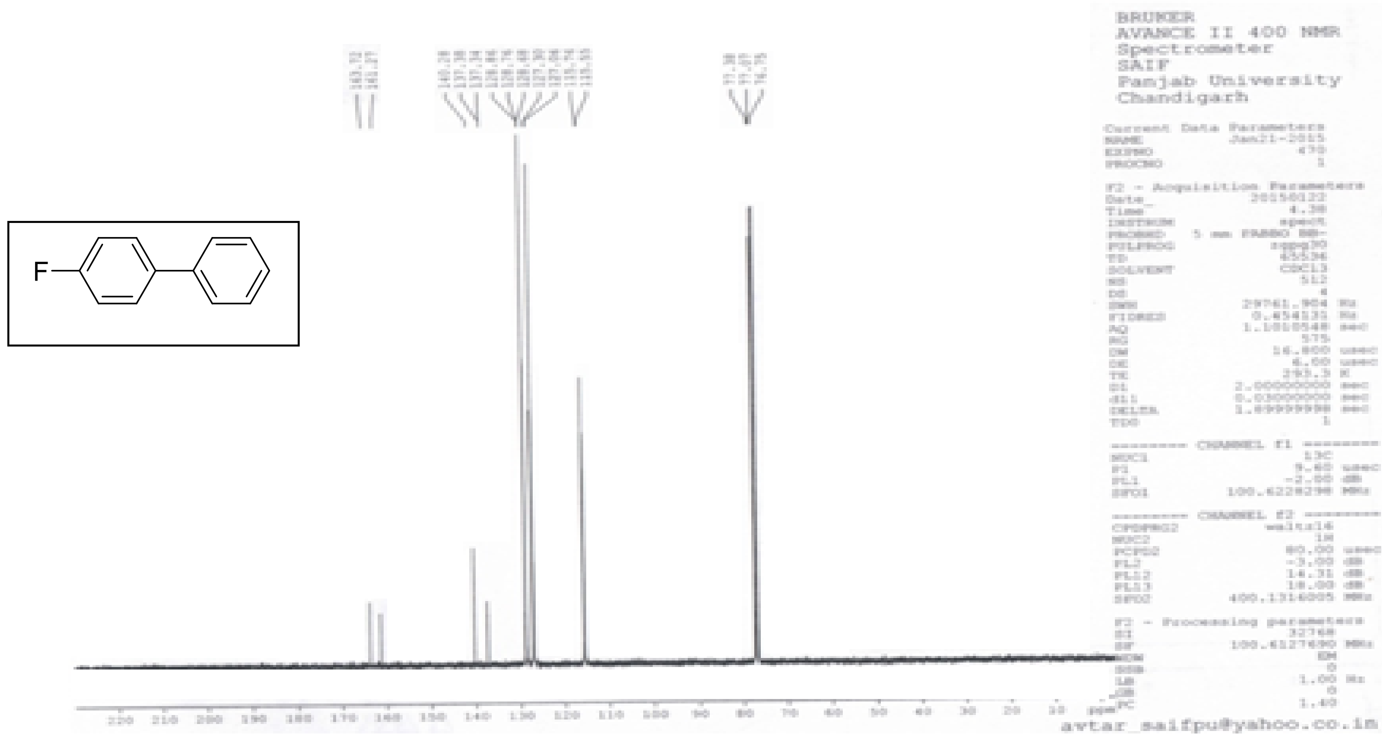



**Figure S30.** $^{13}$C-NMR (100 MHz, $CDCl_3$) of **6n.**

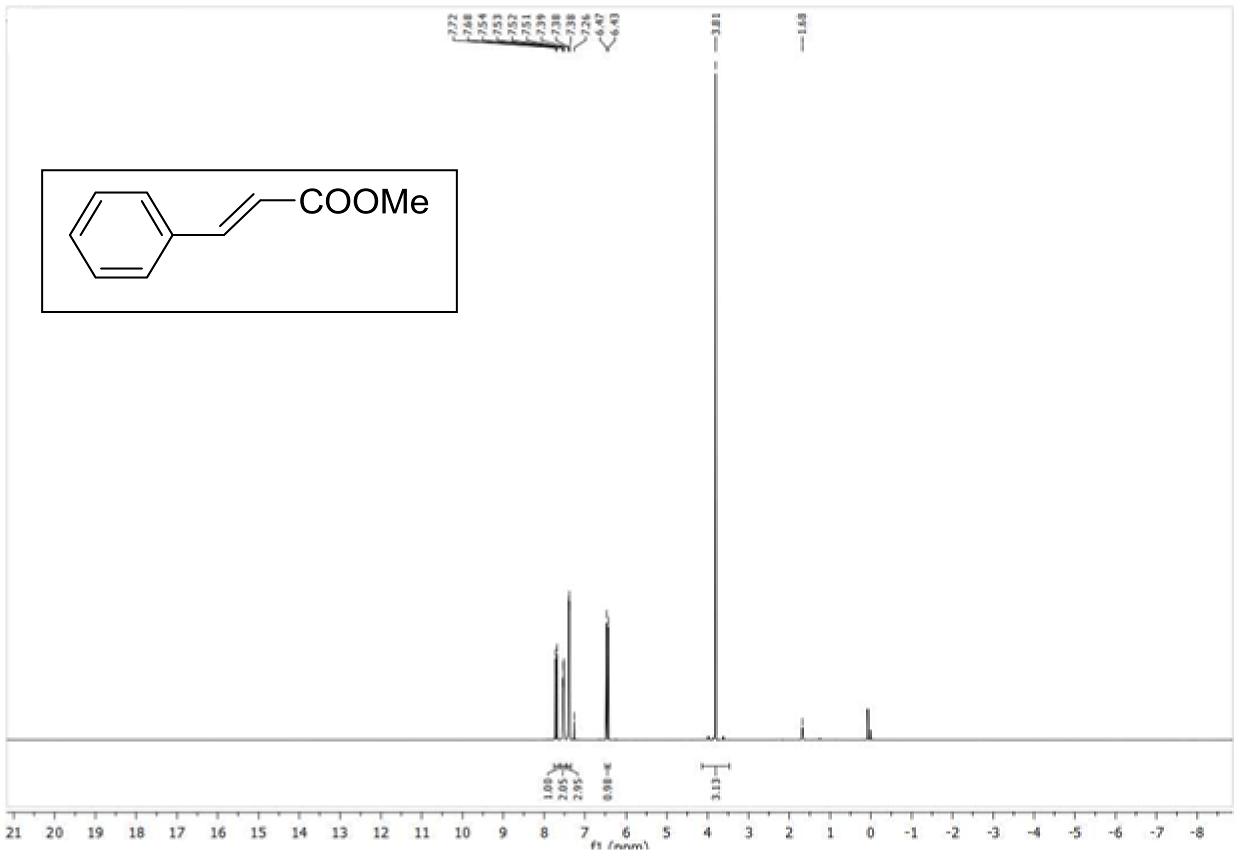



**Figure S31**. $^1$H-NMR (400 MHz, $CDCl_3$) of **9a.**

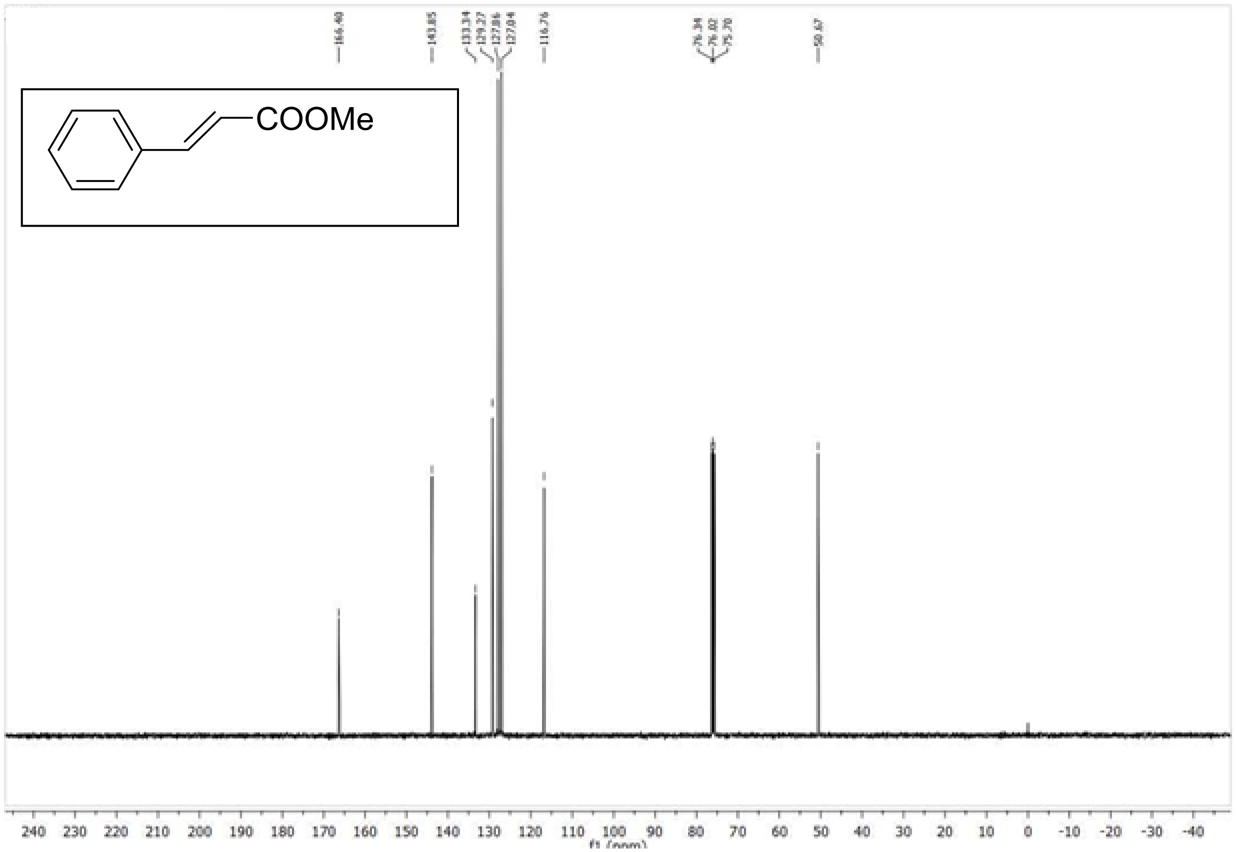



**Figure S32**. $^{13}$C-NMR (100 MHz, $CDCl_3$) of **9a.**

**Figure S33**. $^1$H-NMR (500 MHz, $CDCl_3$) of **9b.**

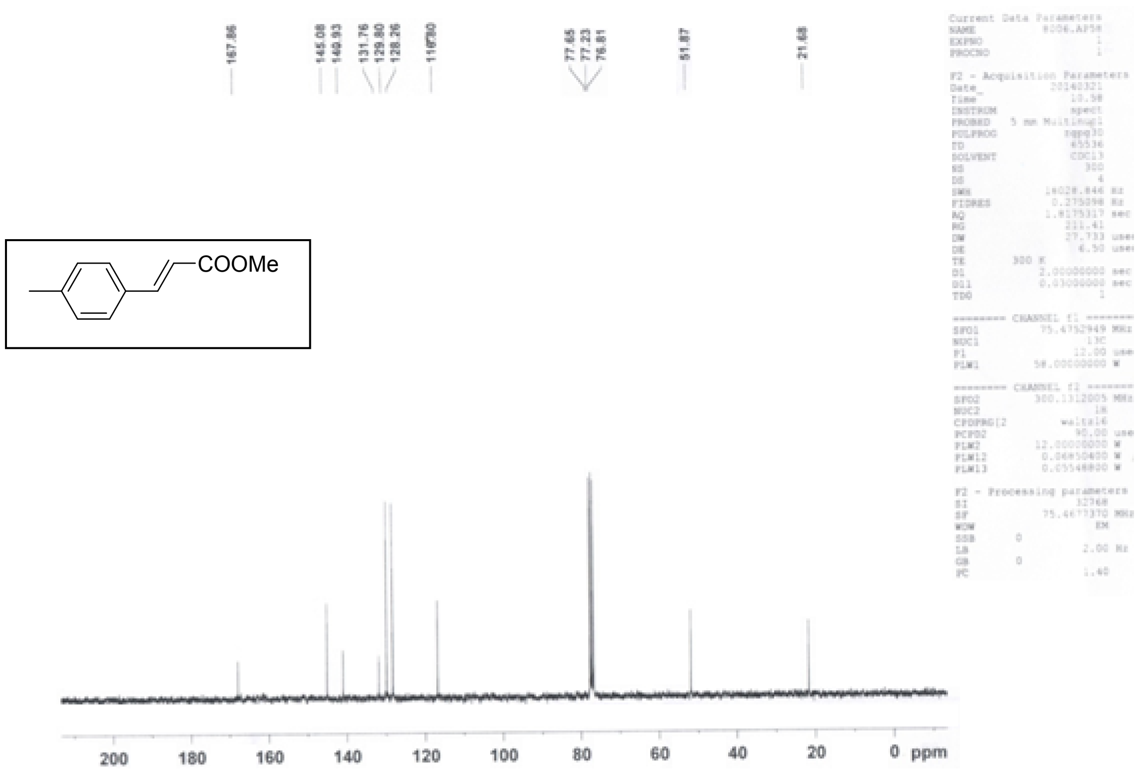



**Figure S34**. $^{13}$C-NMR (75 MHz, $CDCl_3$) of **9b.**

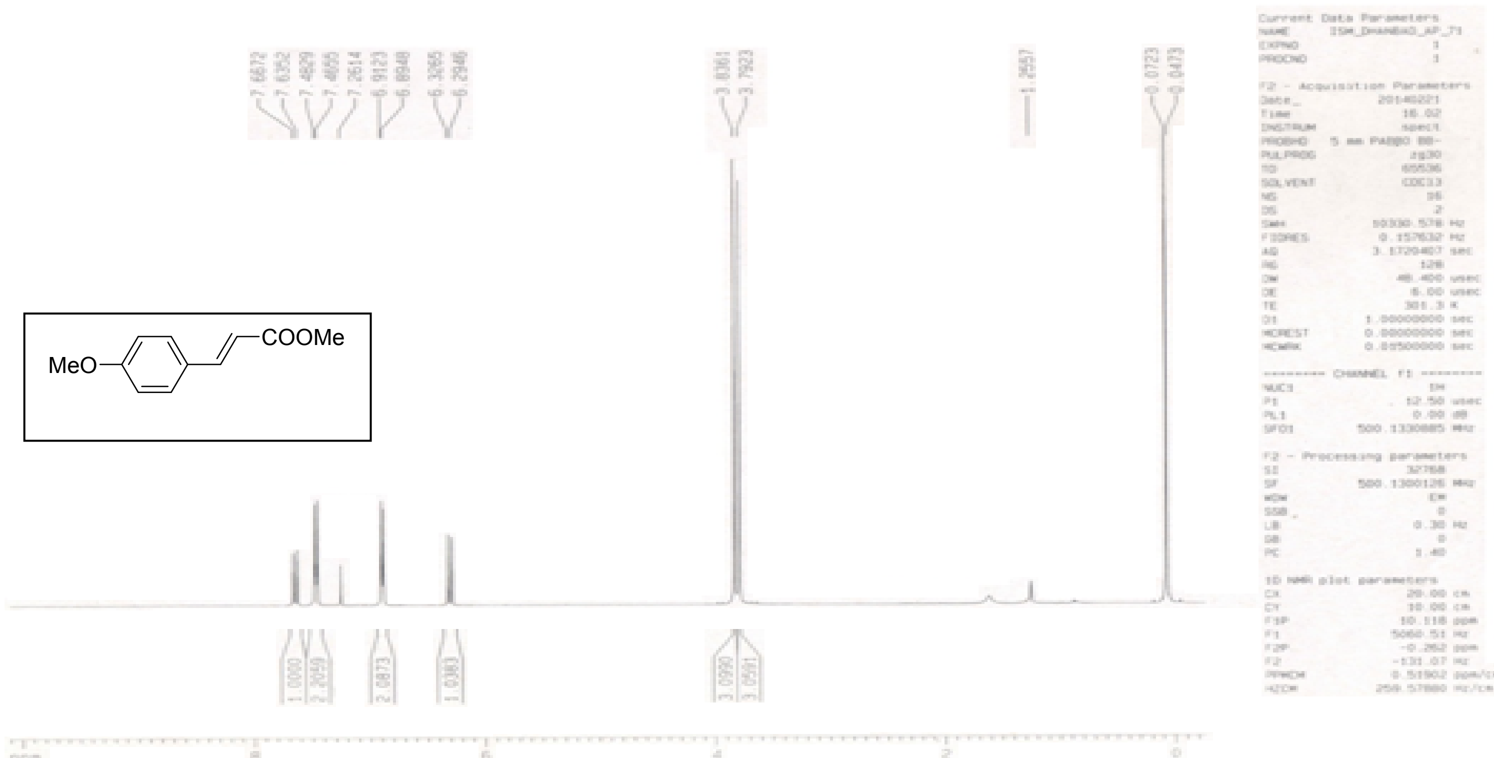



**Figure S35**. $^{1}$H-NMR (500 MHz, $CDCl_3$) of **9c.**

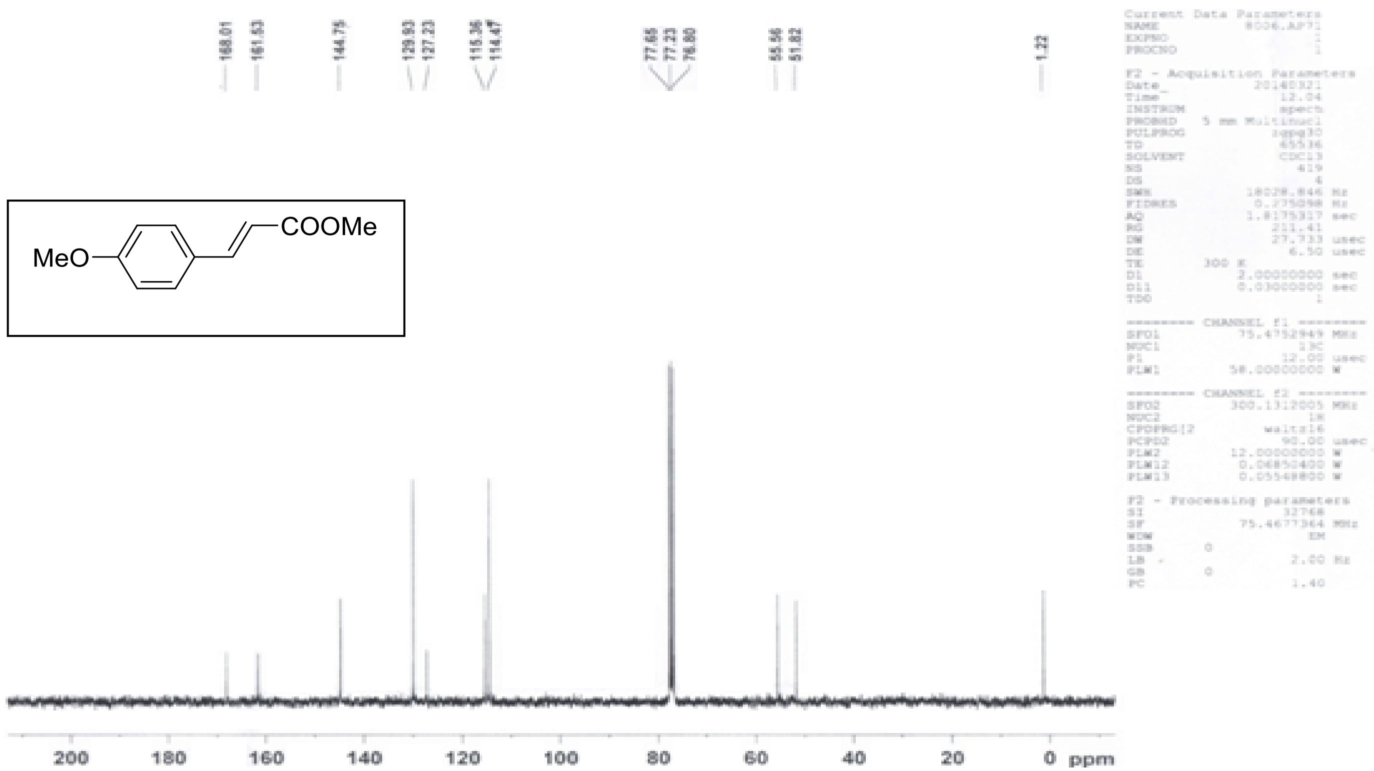


**Figure S36**. $^{13}$C-NMR (75 MHz, $CDCl_3$) of **9c.**

**Figure S37**. [1]H-NMR (500 MHz, $CDCl_3$) of **9d.**

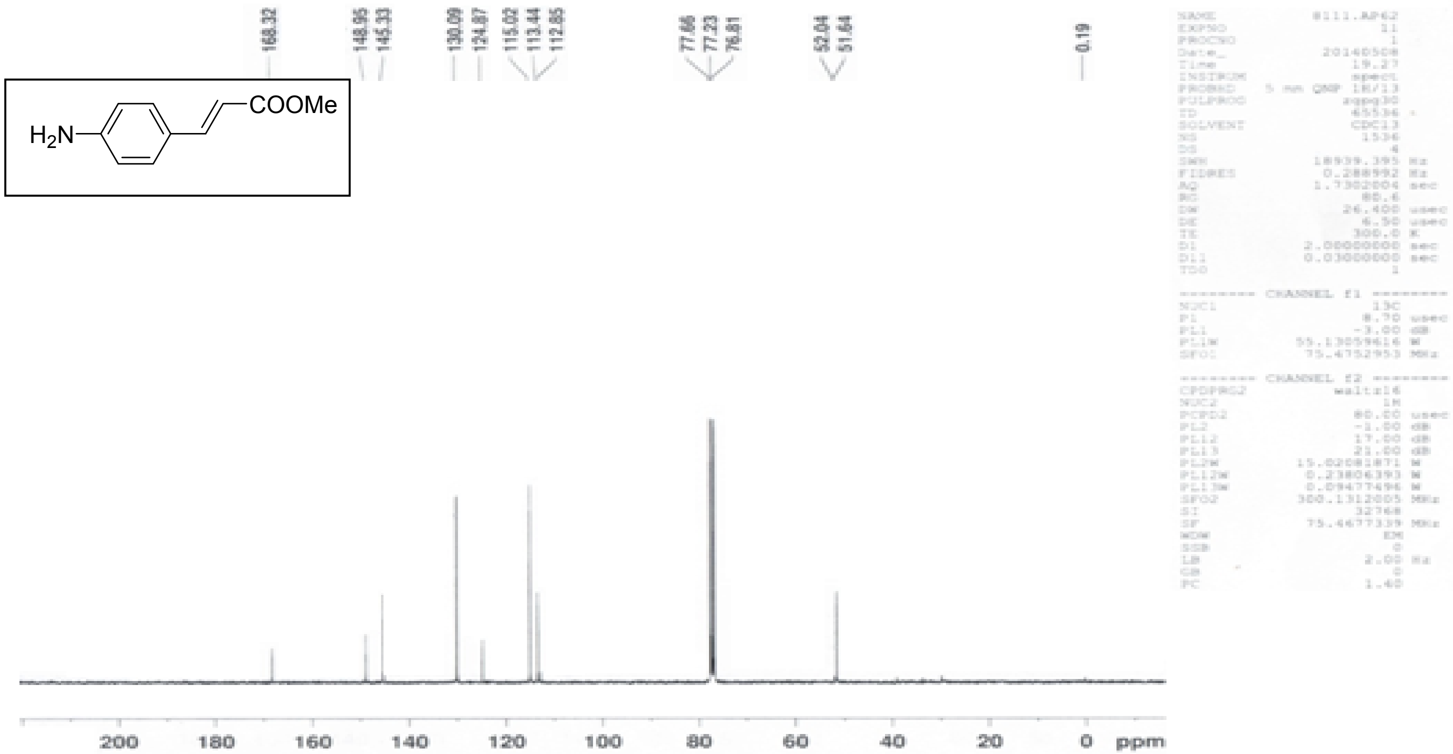



**Figure S38.** $^{13}$C-NMR (75 MHz, $CDCl_3$) of **9d.**

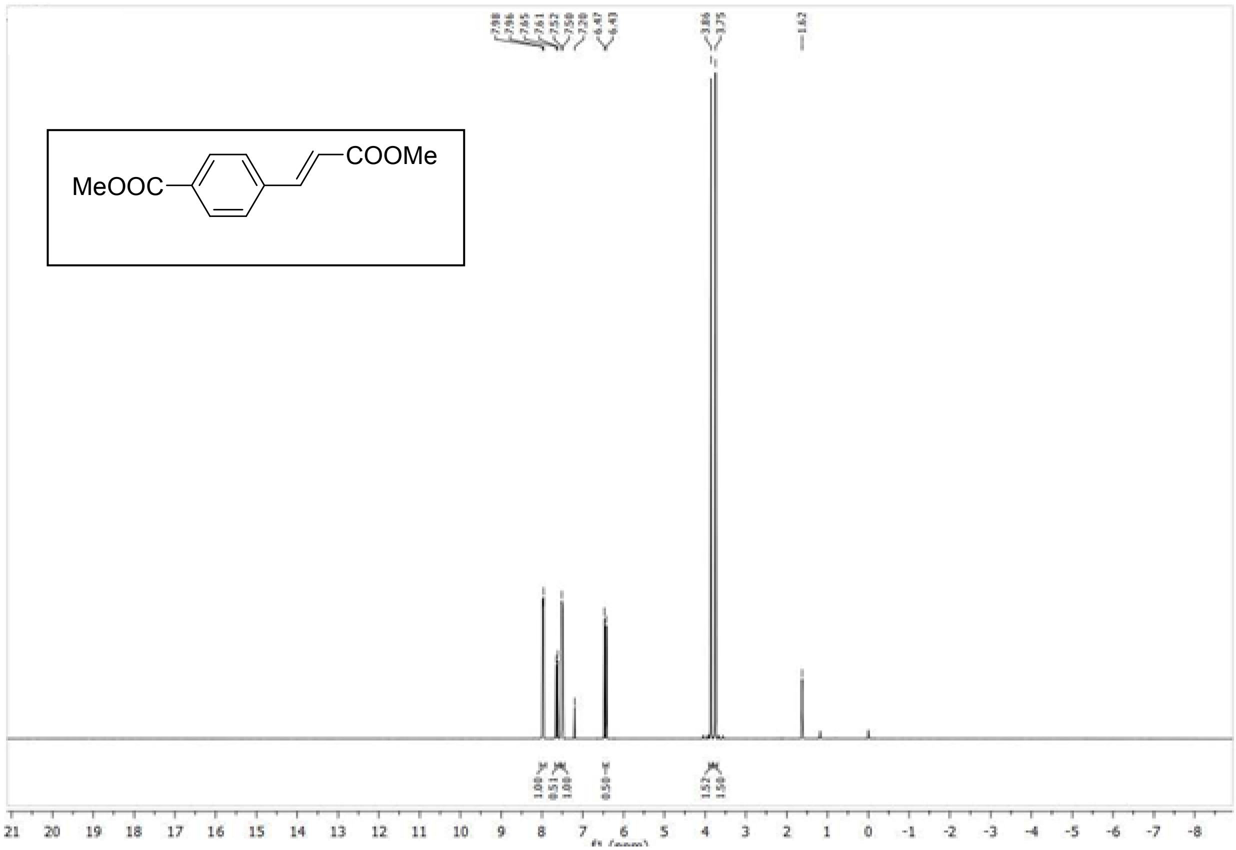



**Figure S39**. $^1$H-NMR (400 MHz, $CDCl_3$) of **9e.**

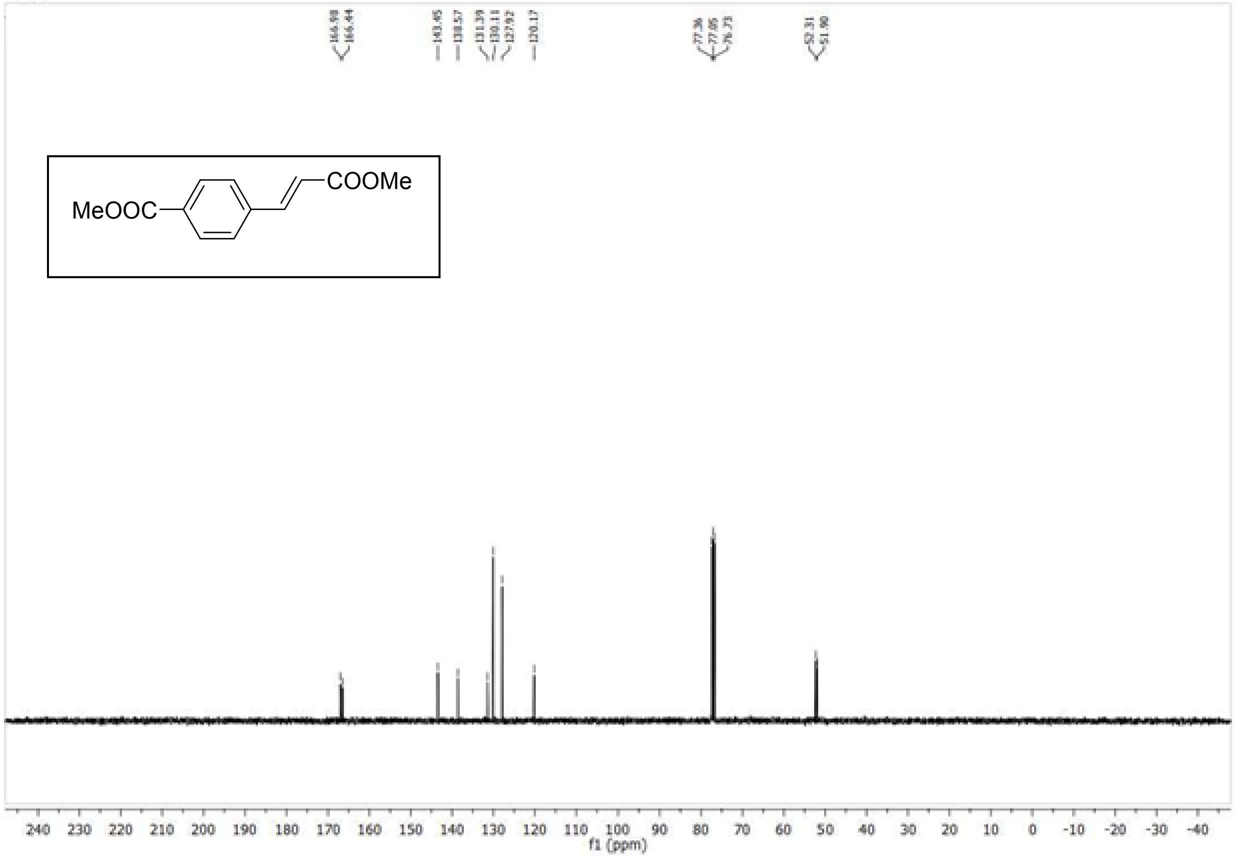



**Figure S40**. $^{13}$C-NMR (100 MHz, $CDCl_3$) of **9e.**

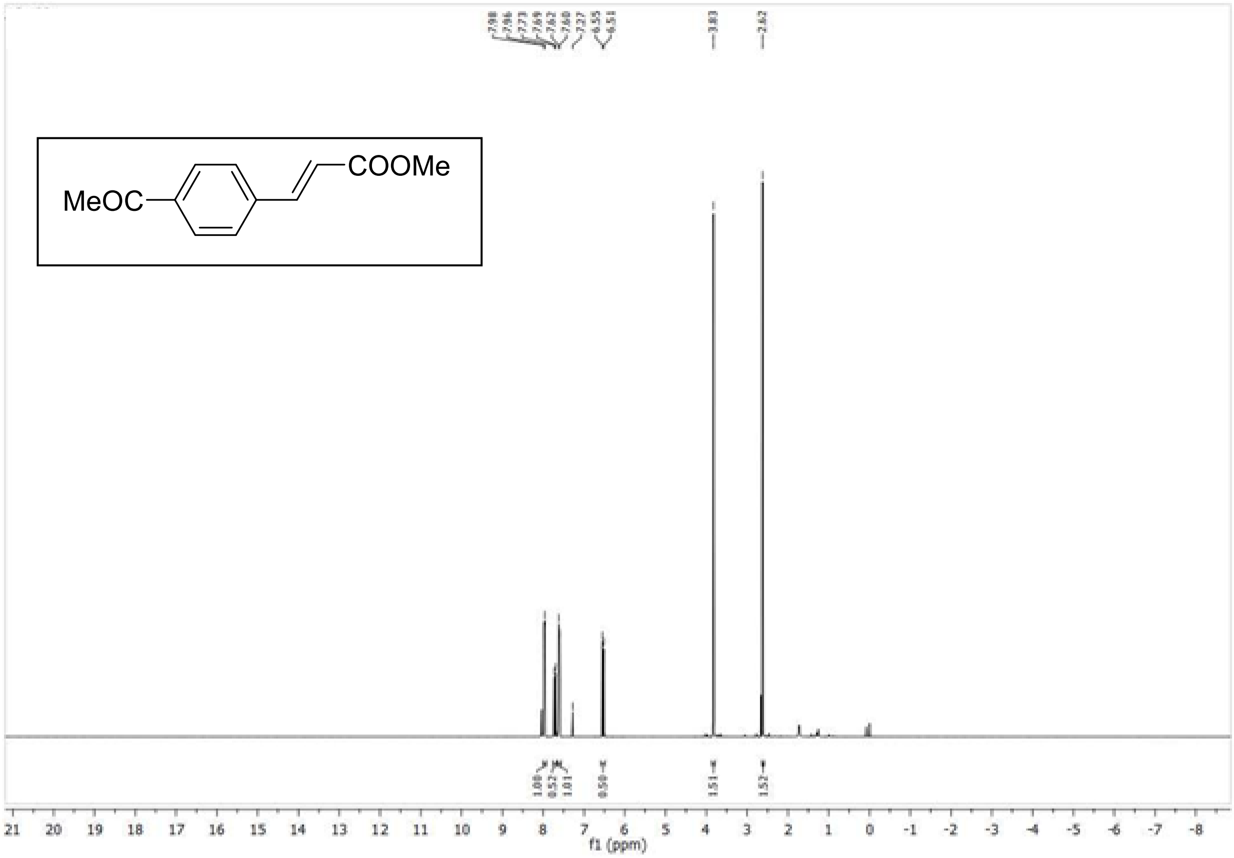


**Figure S41**. $^{1}$H-NMR (400 MHz, $CDCl_3$) of **9f.**

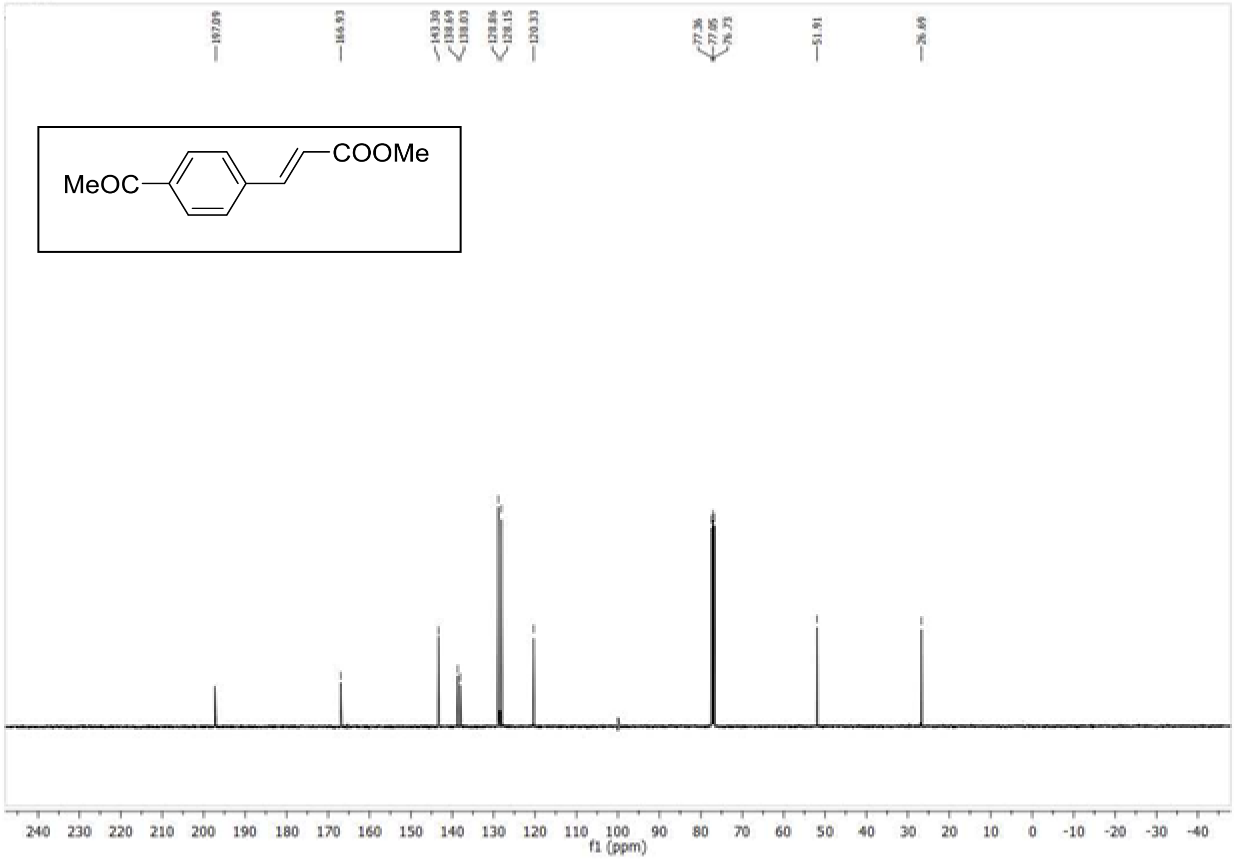



**Figure S42**. $^{13}$C-NMR (100 MHz, $CDCl_3$) of **9f**.

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