Supporting Information

Palladium-catalysed oxidative esterification between two alcohols

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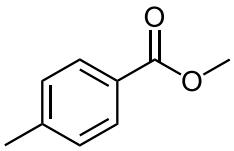
General information

All reactions were isolated from moisture and oxygen by a nitrogen atmosphere with a balloon fitted on a Schlenk tube. All glassware was oven dried at 110 °C for hours and cooled down under vacuum. THF was purified by distillation with sodium. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 °C). Gas chromatographic analyses were performed on Varian GC 2000 gas chromatography instrument with a FID detector and naphthalene was added as internal standard. ^{1}H and ^{13}C NMR data were recorded with Bruker Advance III (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks (77.00 ppm, chloroform), respectively.

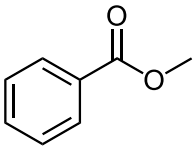
General procedure

$PdCl_2(PPh_3)_2$ (17.5 mg, 0.025 mmol) and K_2CO_3 (139.0 mg, 1.0 mmol) were placed in a Shlenck tube, which was filled with nitrogen by using standard Schlenk techniques. THF (2.0 mL), benzyl chloride (126.6 mg, 1.0 mmol), benzyl alcohol **1** (0.50 mmol) and aliphatic alcohol **2** (5.0 mmol) were consequently added to the reaction tube. The reaction mixture was stirred at 65-70 °C for 20 h. Then the suspension solution was extracted by ethyl acetate (3 x 5 mL), and the resulting mixture was quenched with water. The organic layers were combined, and dried over sodium sulfate. The pure product was obtained by flash column chromatography on silica gel (petroleum : ethyl acetate = 50:1)

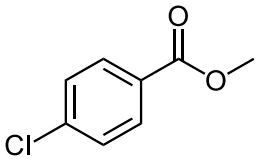
Detail descriptions for products



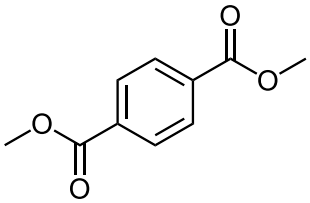
Methyl 4-methylbenzoate (3a):[1] pale yellow oil was obtained in 99% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.92 (d, *J* = 8.2 Hz, 2H),7.22 (d, *J* = 8.2 Hz, 2H), 3.89 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 167.07, 143.44, 129.50, 128.97, 127.33, 51.83, 21.54.



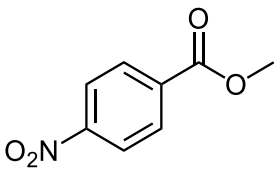
Methyl benzoate (3b):[1] pale yellow oil was obtained in 99% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.04 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.53(d, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 167.09, 132.88, 130.11, 129.67, 129.53, 128.56, 128.32, 52.08.



Methyl 4-chlorobenzoate (3c):[2] pale yellow oil was obtained in 98% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.96 (d, *J* = 8.7 Hz, 2H),7.40 (d, *J* = 8.7 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 166.11, 139.27,130.88, 128.62, 128.49, 52.18.

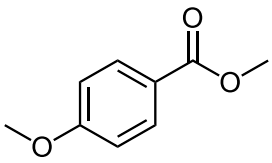


Dimethyl terephthalate (3d):[2] pale yellow oil was obtained in 84% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.09 (s, 4H), 3.94 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 166.21, 133.82, 129.48, 77.32, 77.00, 76.68, 52.39.

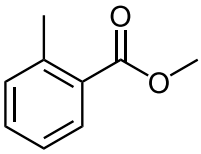


Methyl 4-nitrobenzoate (3e):[1] pale yellow oil was obtained in 50 % isolated yield. ^{1}H NMR (400

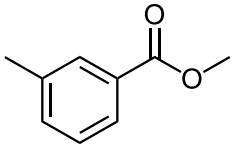
MHz, $CDCl_3$) δ_H 8.30 (d, *J* = 8.9 Hz, 2H),8.22 (d, *J* = 8.9 Hz, 2H), 3.99 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 165.16, 150.54, 135.48, 130.69, 123.53, 52.81.



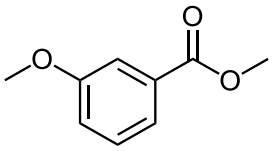
Methyl 4-methoxybenzoate (3f):[1] pale yellow oil was obtained in 98% isolated yield. ^1H NMR (400 MHz, $CDCl_3$) δ_H 8.00 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H), 3.86 (s, 3H) ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 166.85, 163.28, 131.55, 122.55, 113.56, 55.38, 51.84.



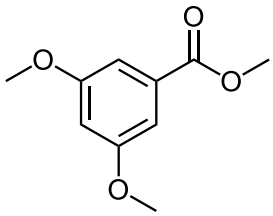
Methyl 2-methylbenzoate (3g):[2] pale yellow oil was obtained in 86% isolated yield. ^1H NMR (400 MHz, $CDCl_3$) δ_H 7.91 (d, *J* = 8.4 Hz, 1H),7.39 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 2H), 3.88 (s, 3H), 2.60 (s, 3H). ^{13}C NMR(101 MHz, $CDCl_3$) δ_C 168.00, 140.11, 131.89, 131.61, 130.50, 129.48, 125.62, 51.73,21.67.



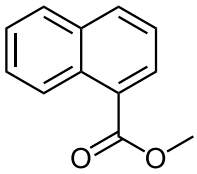
Methyl 3-methylbenzoate (3h):[1] pale yellow oil was obtained in 98% isolated yield. ^1H NMR (400 MHz, $CDCl_3$) δ_H 7.90 – 7.80 (m, 2H), 7.40– 7.29 (m, 2H), 3.91 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 167.24, 138.09, 133.62, 130.07, 128.21, 126.66, 51.99, 21.21.



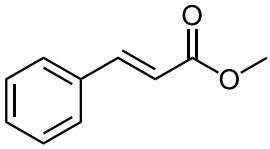
Methyl 3-methoxybenzoate (3i):[1] pale yellow oil was obtained in 95% isolated yield. ^1H NMR (400 MHz, $CDCl_3$) δ_H 7.65 – 7.45 (m, 2H), 7.24 (t, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 2.6 Hz, 1H), 3.82 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 166.84, 159.43, 131.32, 129.27, 121.85, 119.36, 113.84,55.28, 52.05.



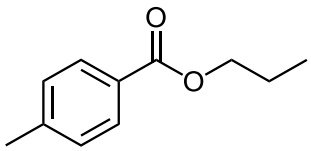
Methyl 3,5-dimethoxybenzoate (3j)[3]: pale yellow oil was obtained in 98% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.18 (d, *J* = 2.3 Hz,2H), 6.64 (t, *J* = 2.3 Hz, 1H), 3.90 (s, 3H), 3.82 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 166.79, 160.56, 131.92, 107.03, 105.69, 55.49, 52.18.



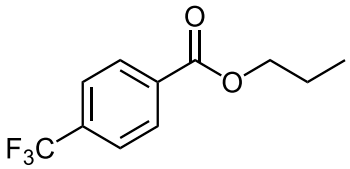
Methyl 1-naphthoate (3k):[3] pale yellow oil was obtained in 91% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.91 (d, *J* = 8.7 Hz, 1H), 8.17(dd, *J* = 7.3, 1.1 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.60 (t, *J* =8.4 Hz, 1H), 7.54 – 7.42 (m, 2H), 3.98 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 167.93, 133.74, 133.29, 131.24, 130.15, 128.46, 127.68, 126.95, 126.12, 125.73, 124.39, 52.06.



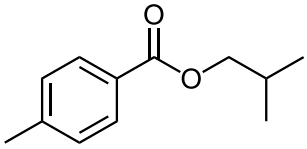
Methyl cinnamate (3l):[1] pale yellow oil was obtained in 78% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.70 (d, *J* = 16.0 Hz, 1H), 7.56 – 7.48(m, 2H), 7.42 – 7.34 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR(101 MHz, $CDCl_3$) δ_C 167.36, 144.82, 134.36, 130.23, 128.83, 128.01, 117.78, 51.62.



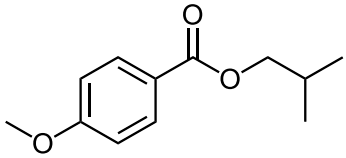
Propyl 4-methylbenzoate (3m):[4] pale yellow oil was obtained in 76% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.97 (d, *J* = 8.2 Hz, 2H),7.26 (d, *J* = 8.0 Hz, 2H), 4.29 (t, *J* = 6.7 Hz, 2H), 2.43 (s, 3H), 1.81 (m, *J* = 14.2, 7.0 Hz, 2H), 1.05 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 166.69, 143.33, 129.50,128.96, 127.74, 66.28, 22.09, 21.57, 10.47.



Propyl 4-(trifluoromethyl)benzoate (3n):[5] pale yellow oil was obtained in 60% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.16 (d, *J* =8.1Hz,2H), 7.70 (d, *J* = 8.2 Hz, 2H), 4.32 (t, *J* = 6.7 Hz, 2H), 1.89 – 1.74 (m, 2H),1.04 (t, *J* = 7.4 Hz, 3H). ^{13}CNMR (101 MHz, $CDCl_3$) δ_C ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.29, 165.42, 134.78, 134.46, 134.14, 133.81, 133.71, 129.91, 128.30, 127.72, 125.39, 125.36, 125.32, 125.28, 125.00, 122.30, 119.59, 67.07, 22.03, 10.43.



isobutyl 4-Methylbenzoate (3o):[6] pale yellow oil was obtained in 68% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.94 (d, *J* = 8.2 Hz, 2H),7.22 (d, *J* = 8.0 Hz, 2H), 4.09 (d, *J* = 6.6 Hz, 2H), 2.39 (s, 3H), 2.20 – 1.95 (m, 1H), 1.01 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 166.59, 143.32, 129.47, 128.95, 127.70, 70.72, 27.84, 21.54, 19.12.



Isobutyl 4-Methoxybenzoate (3p):[7] pale yellow oil was obtained in 70% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.01 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 4.07 (d, *J* = 6.6 Hz, 2H), 3.84 (s, 3H), 2.20 – 1.95 (m, 1H), 1.01 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 166.27, 163.16,131.42, 122.85, 113.46, 70.60, 55.28, 27.84, 19.12.

References

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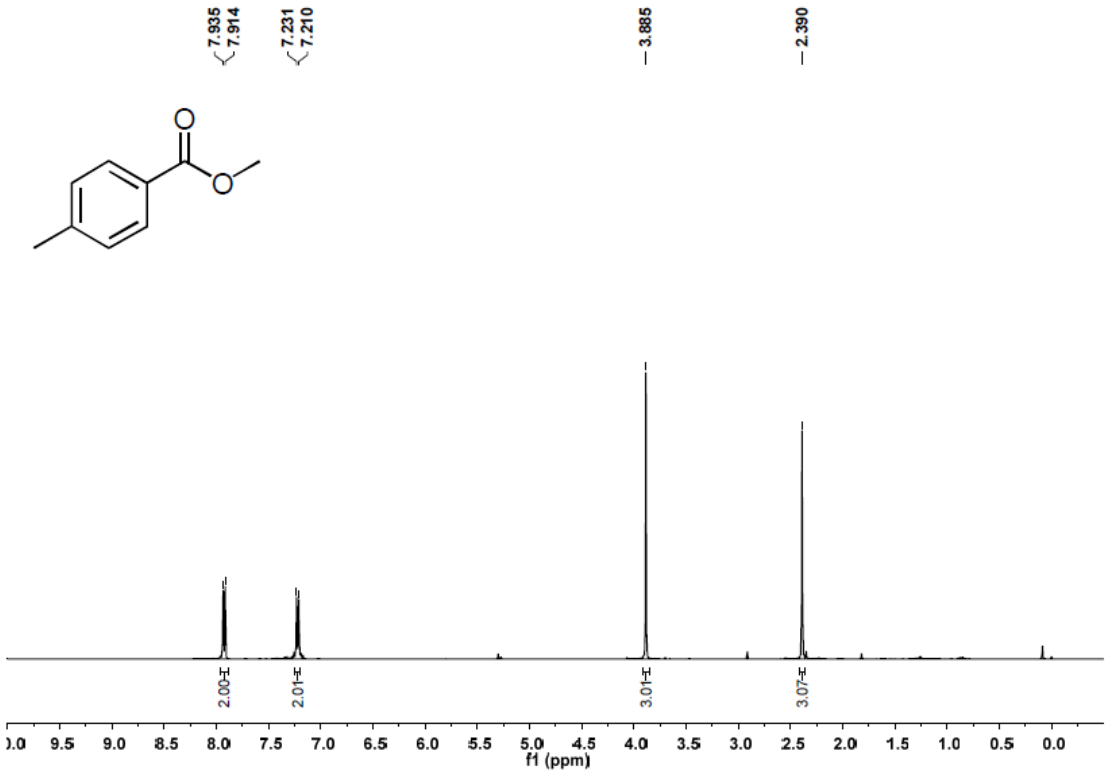
7. J. I. Lee, *B. Kor. Chem. Soc.*, 2011, **32**, 1765-1768.

Copies of product NMR Spectra

3a

^{1}H NMR



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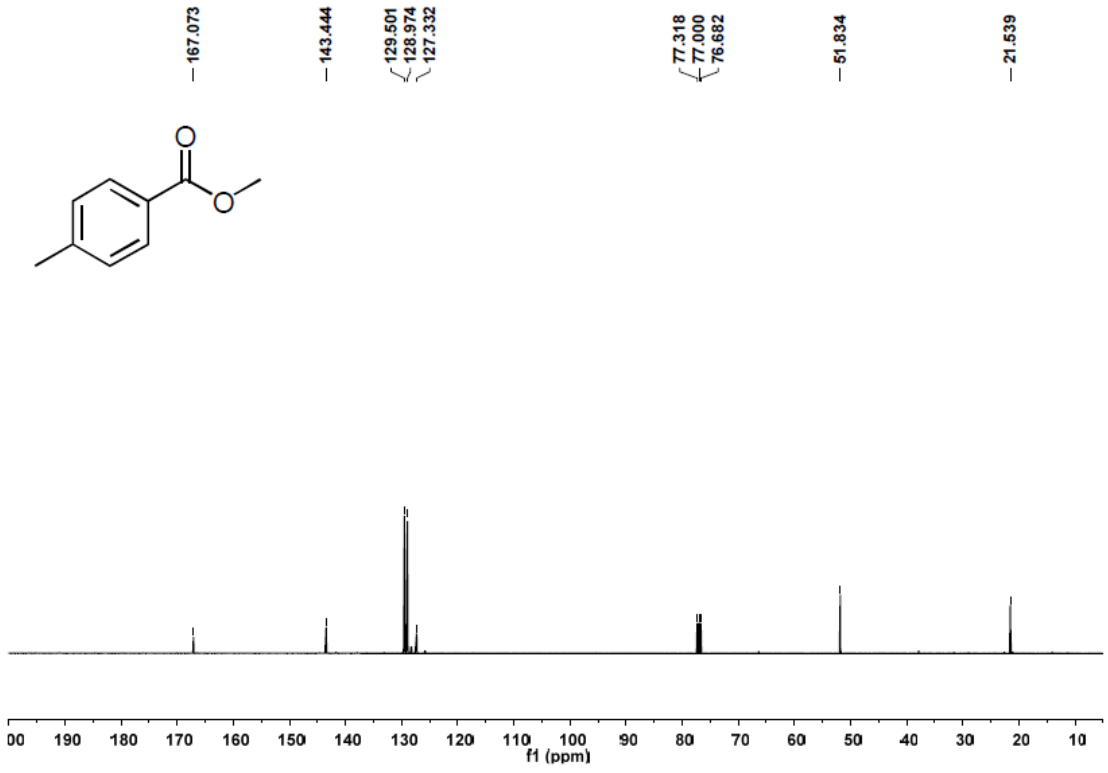

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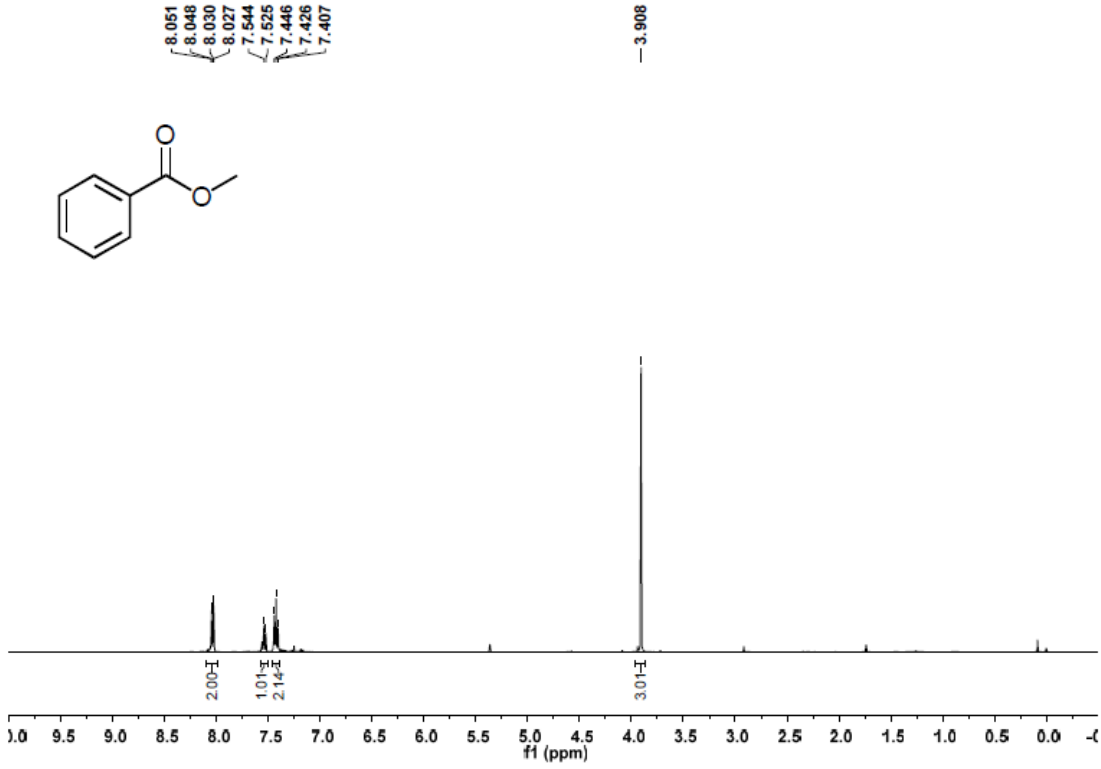

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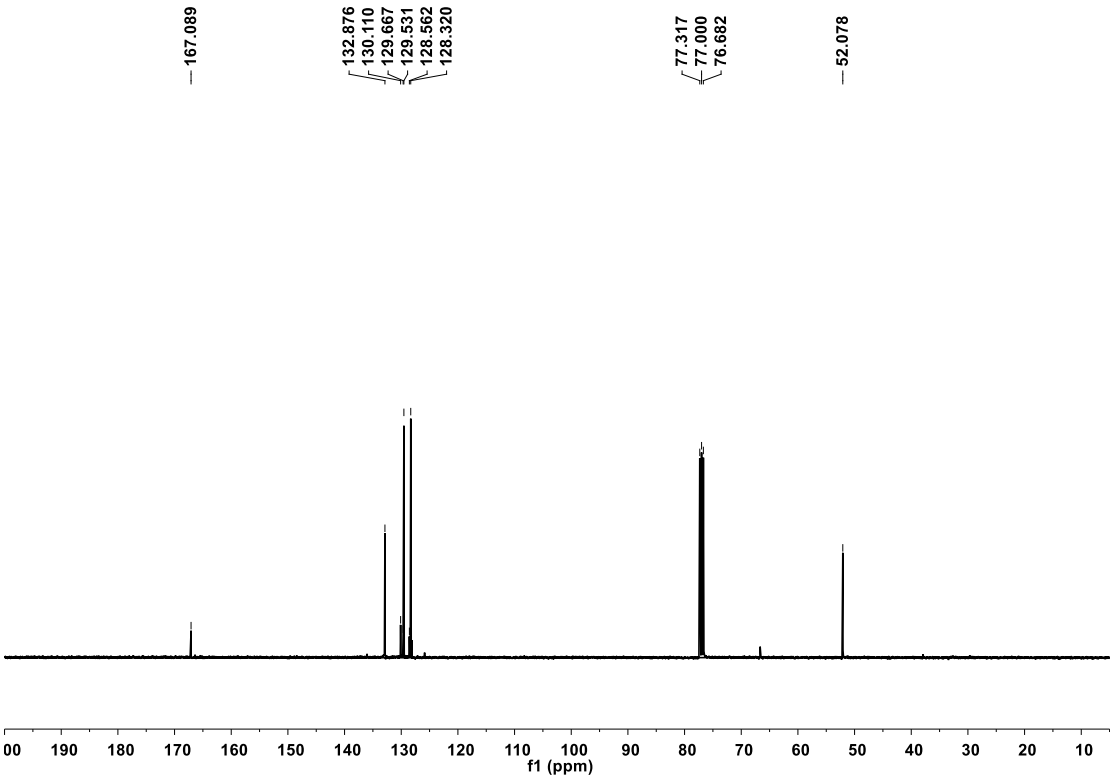

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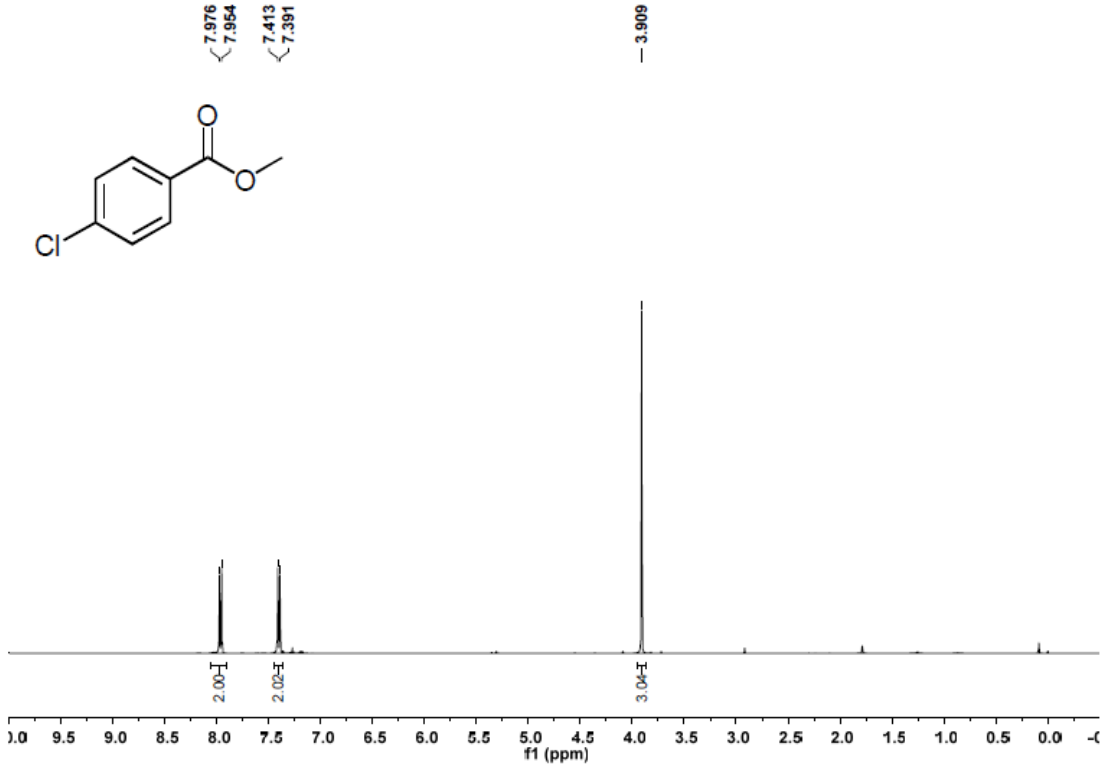

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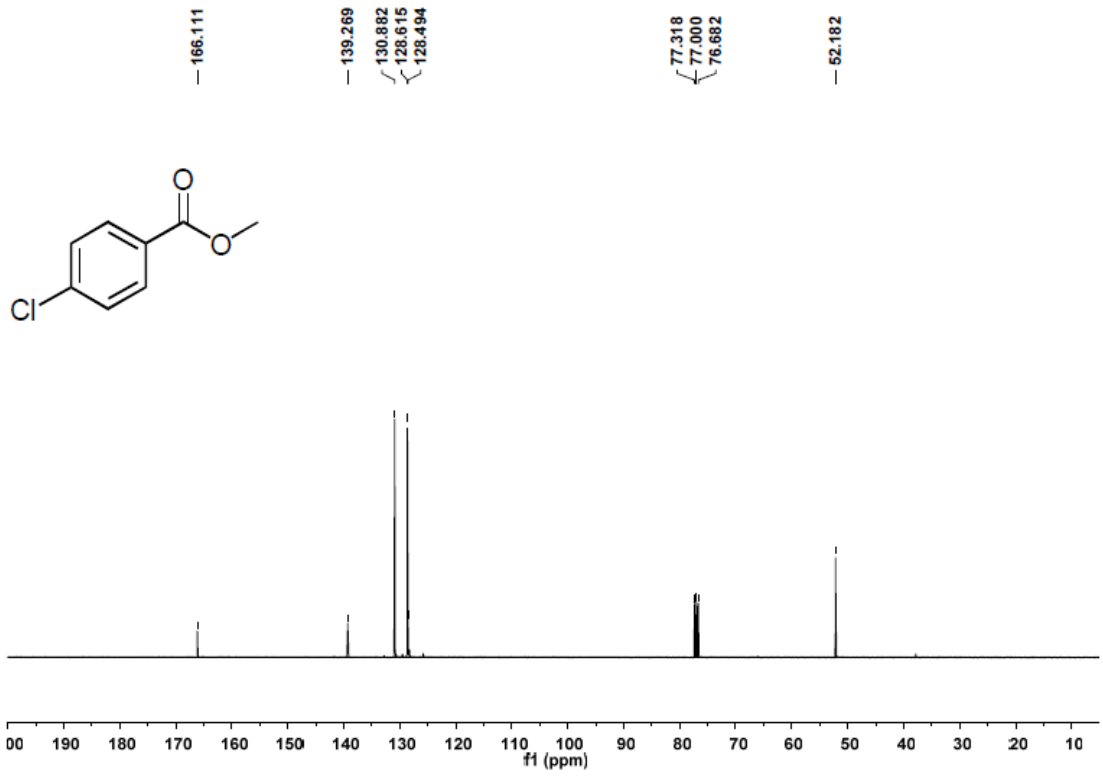

3d

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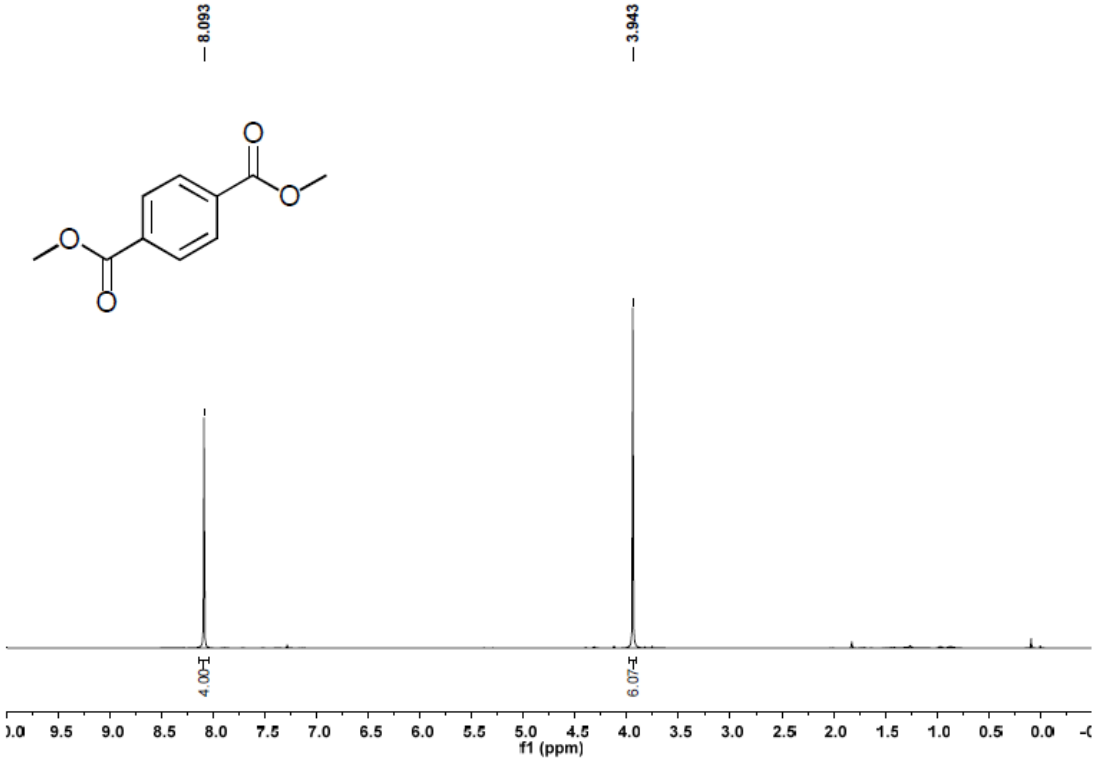

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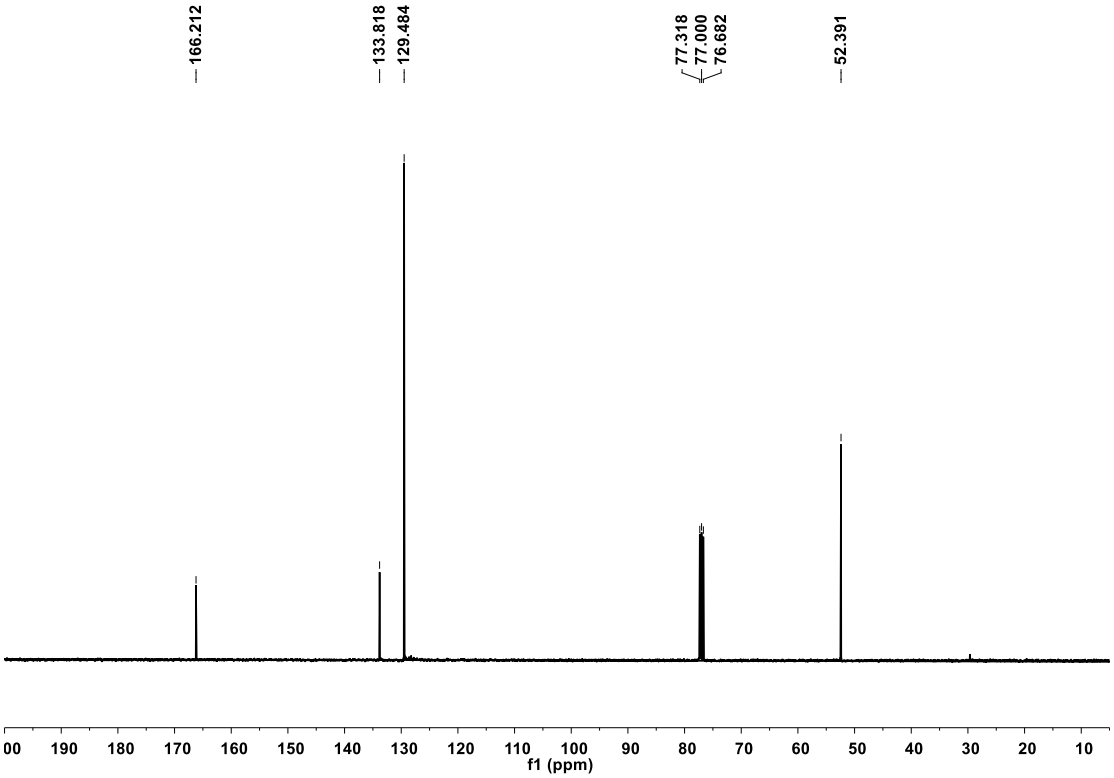

3e

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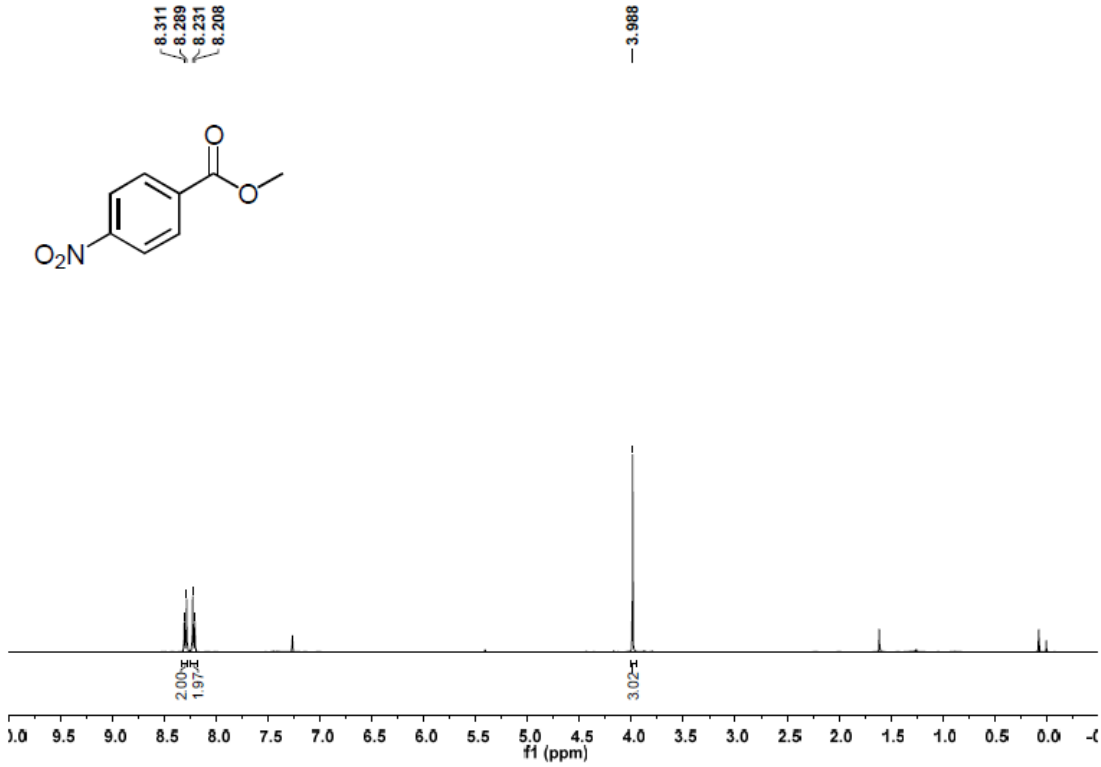

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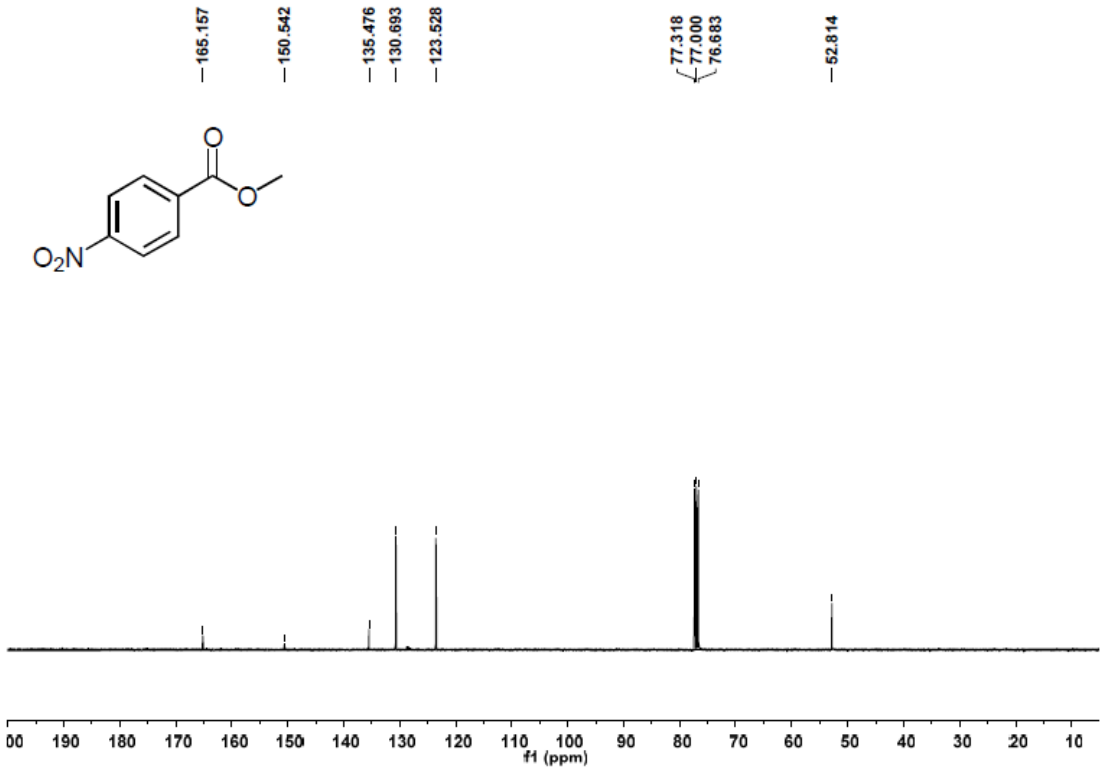

3f

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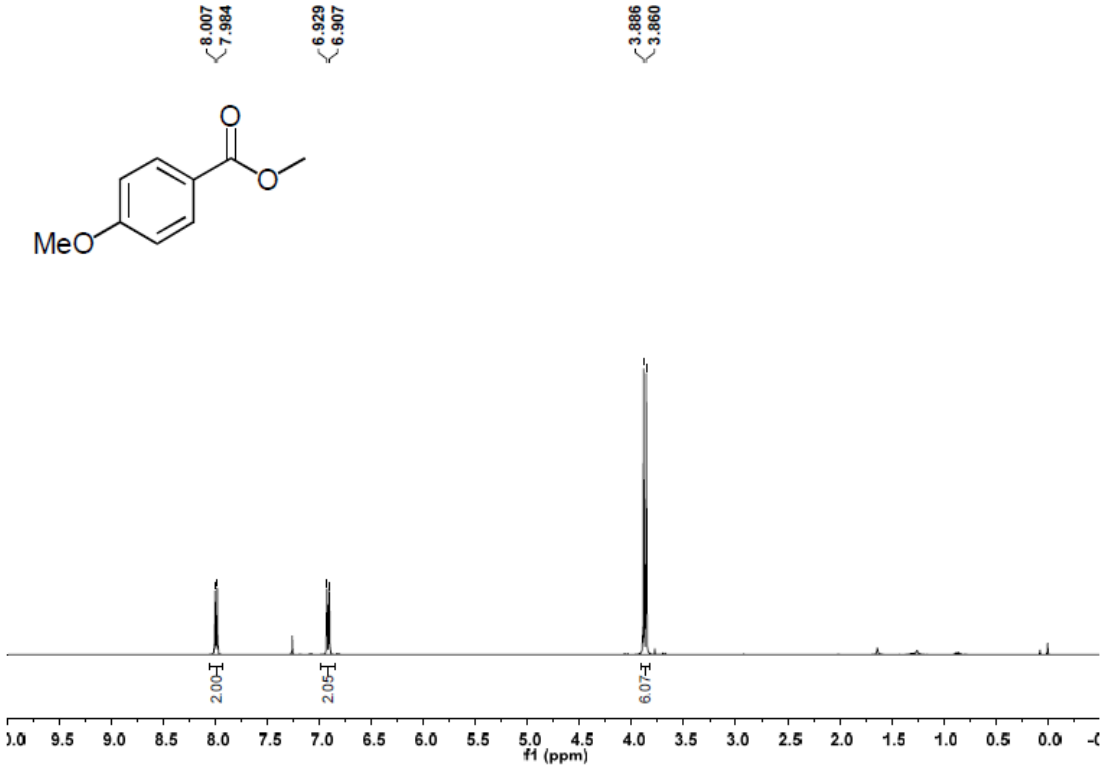

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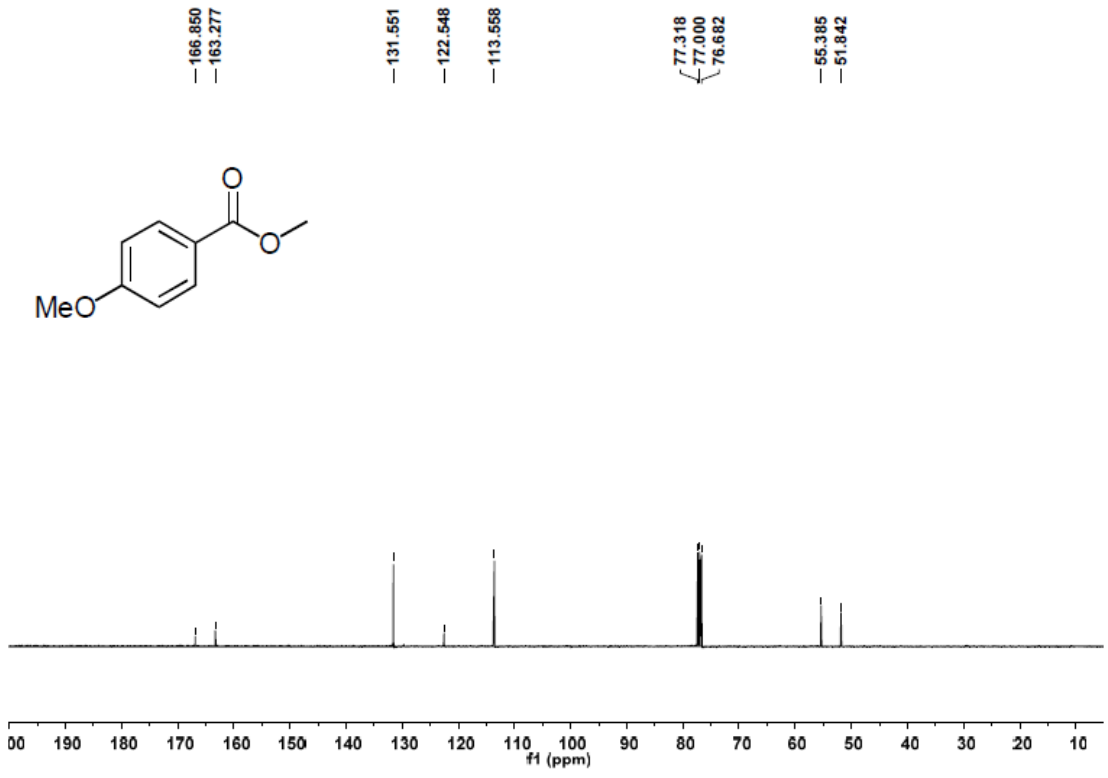

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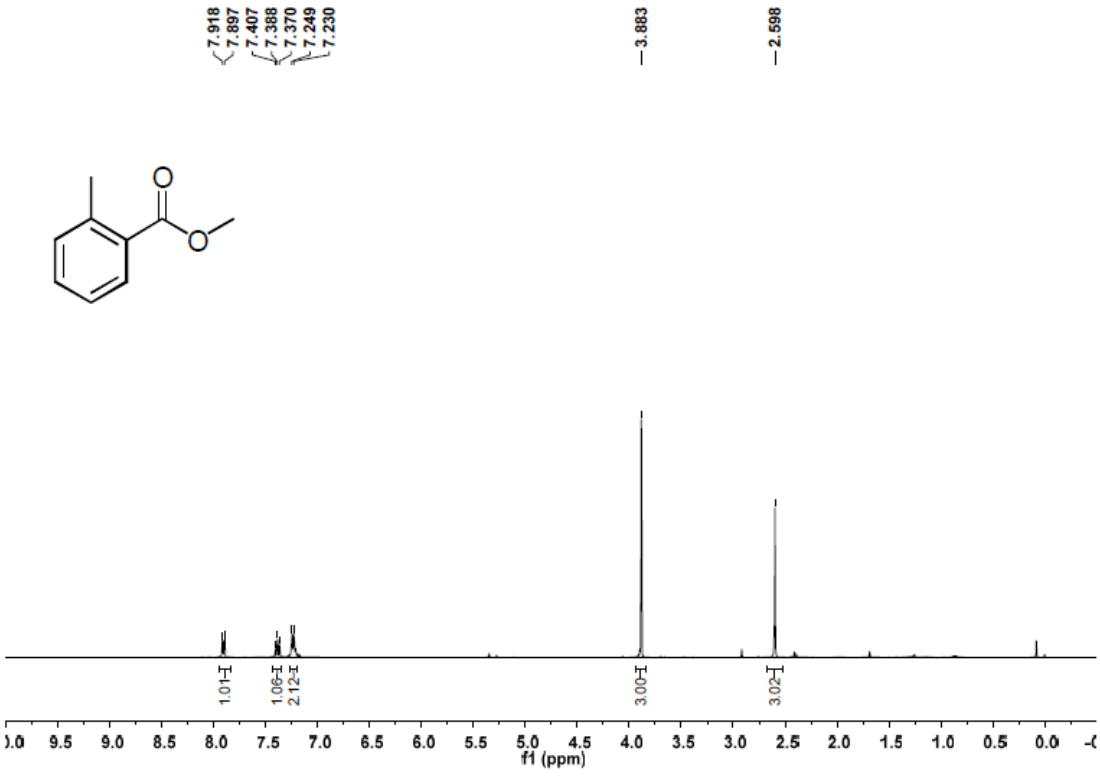

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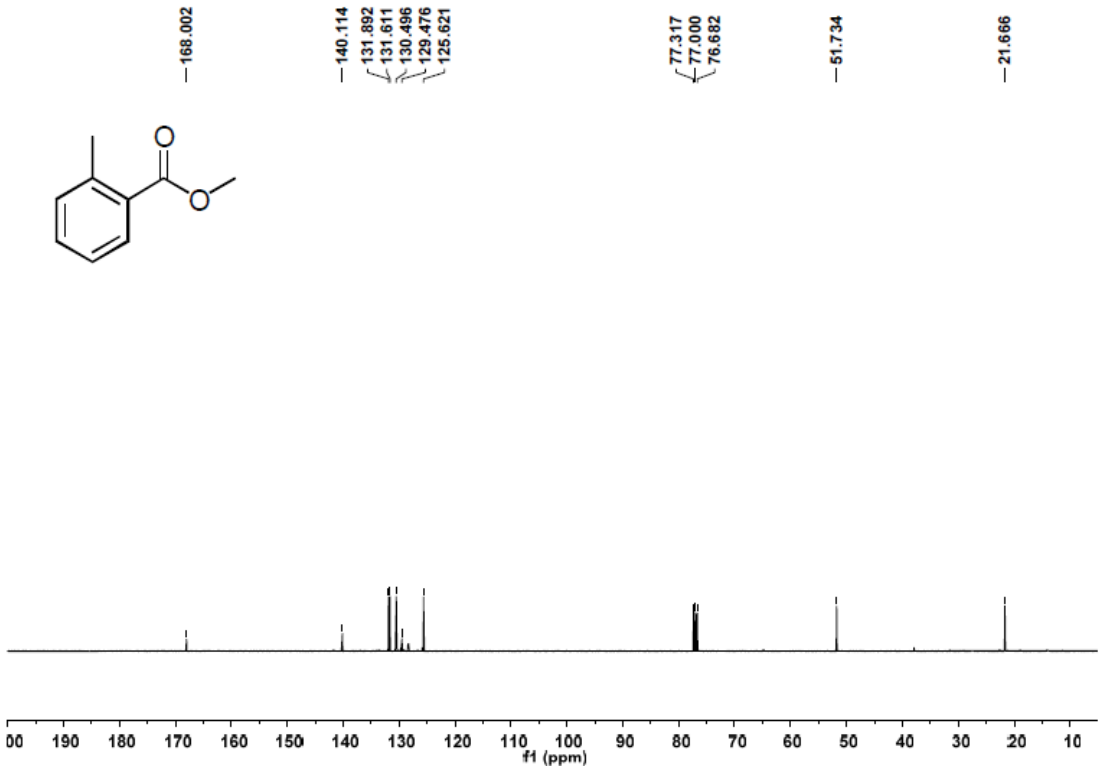

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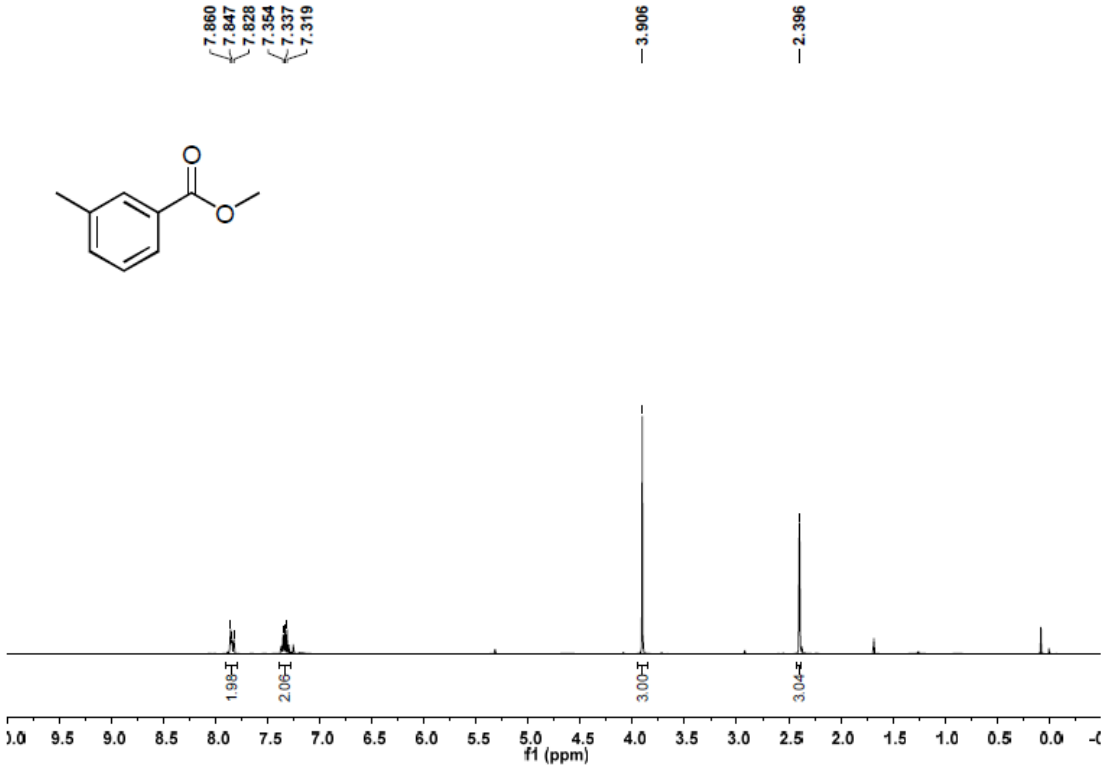

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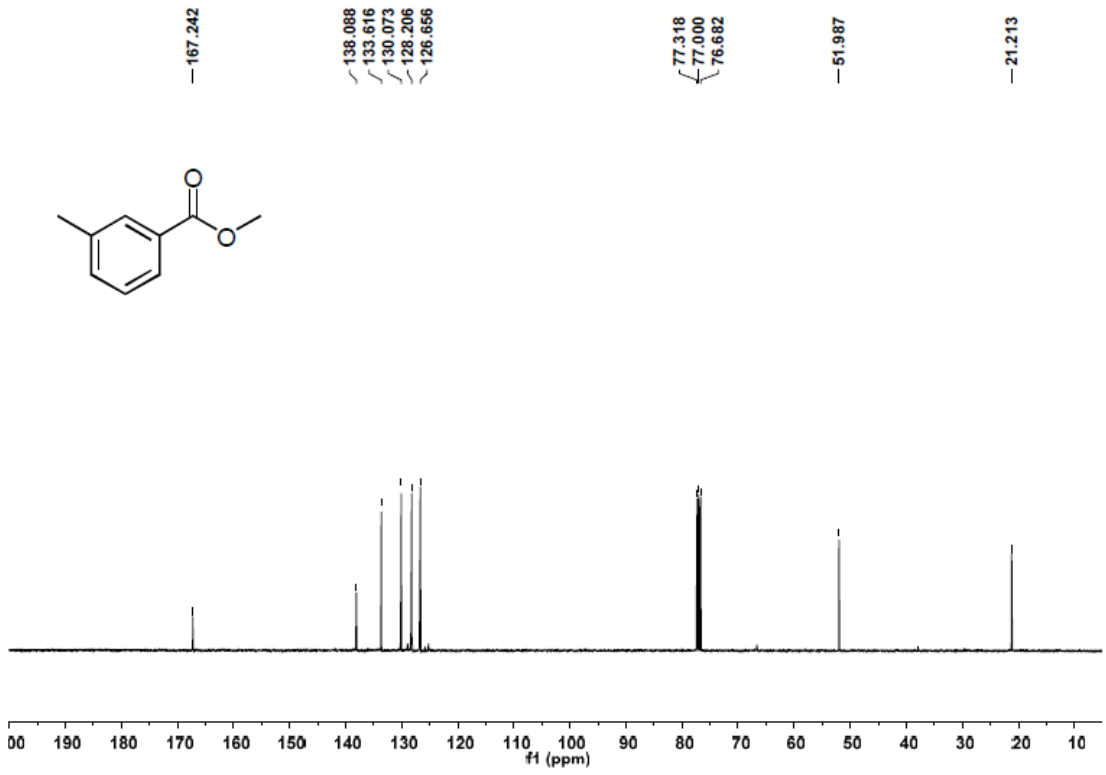

3i

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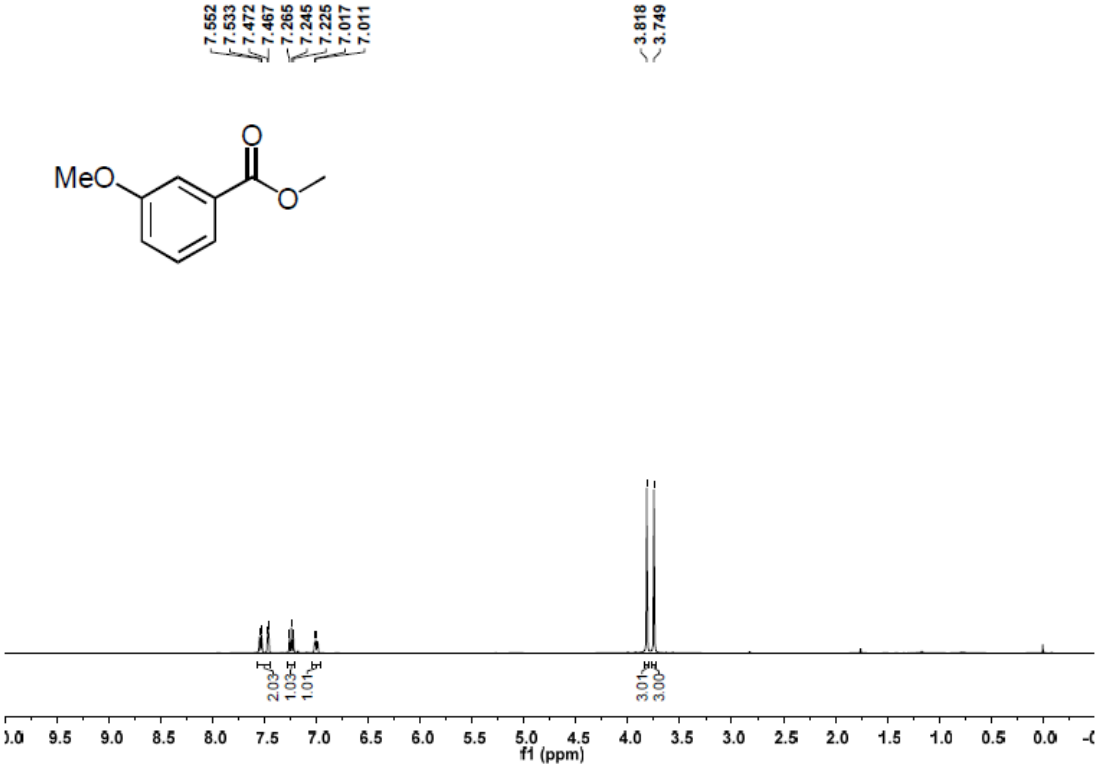
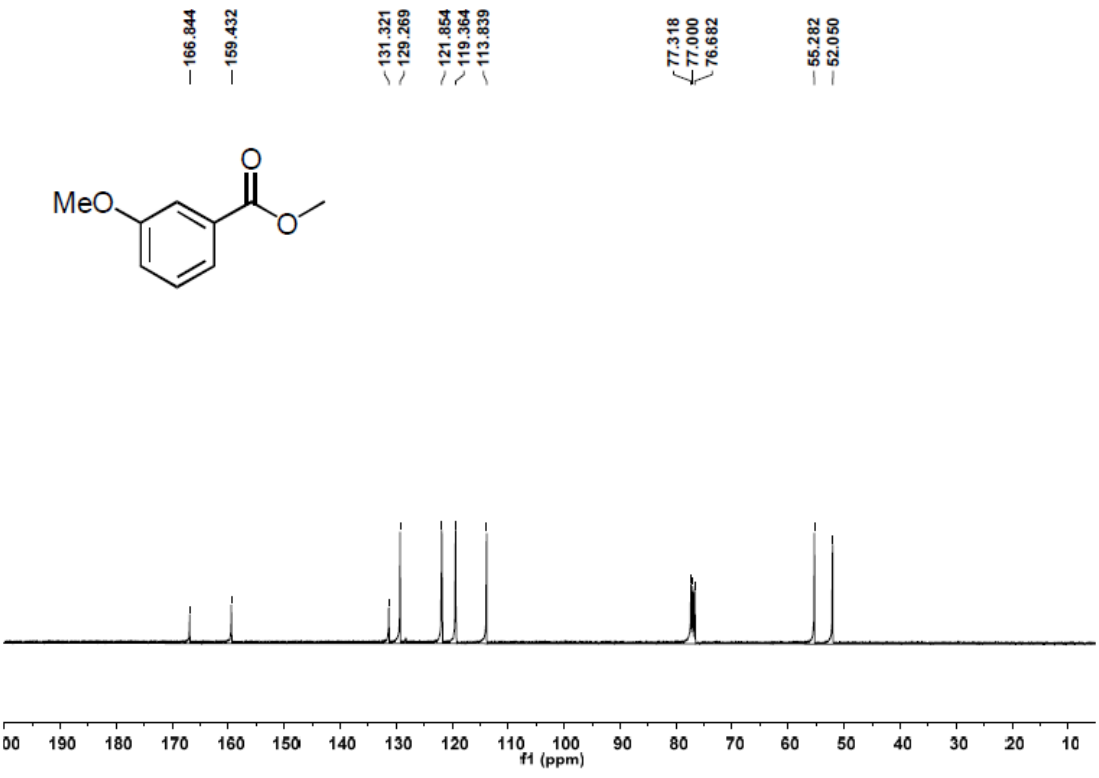
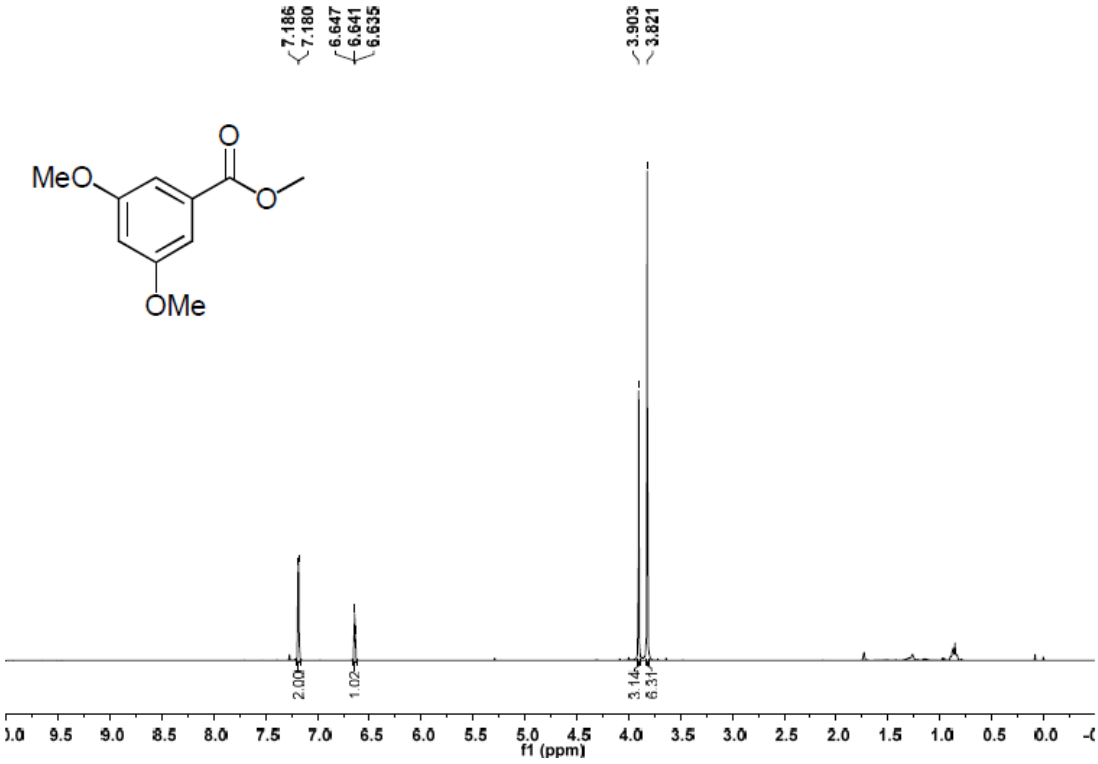


^{13}C NMR

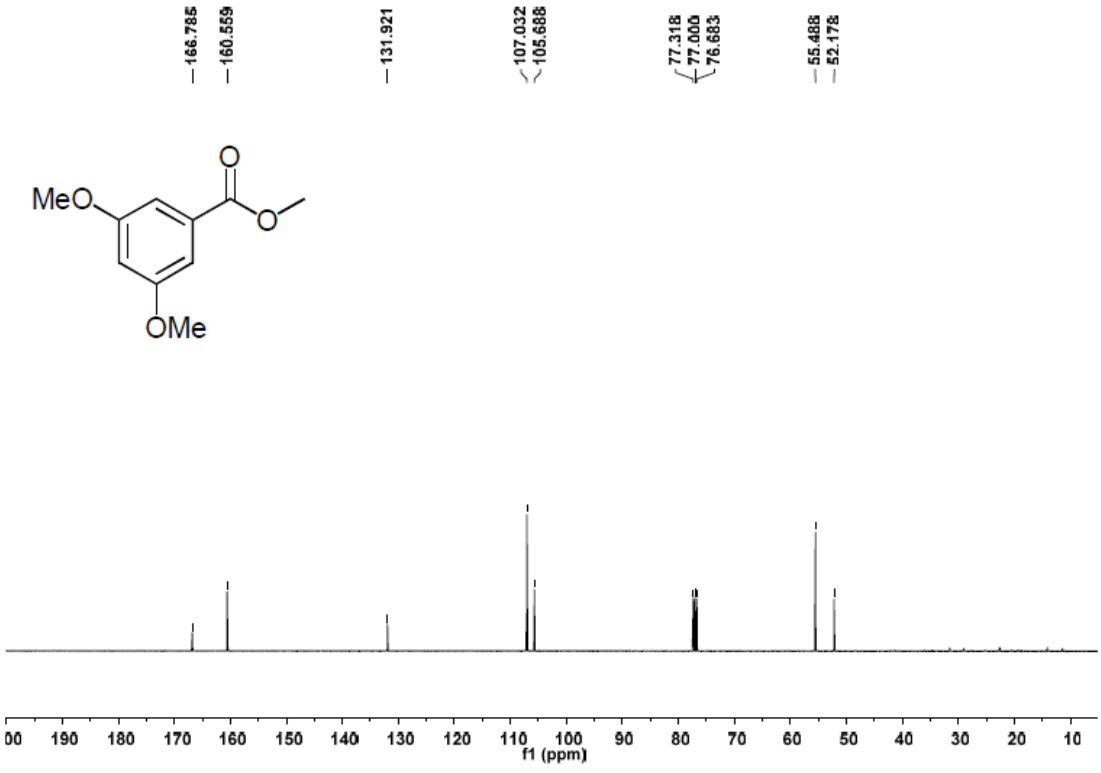


3j

^{1}H NMR

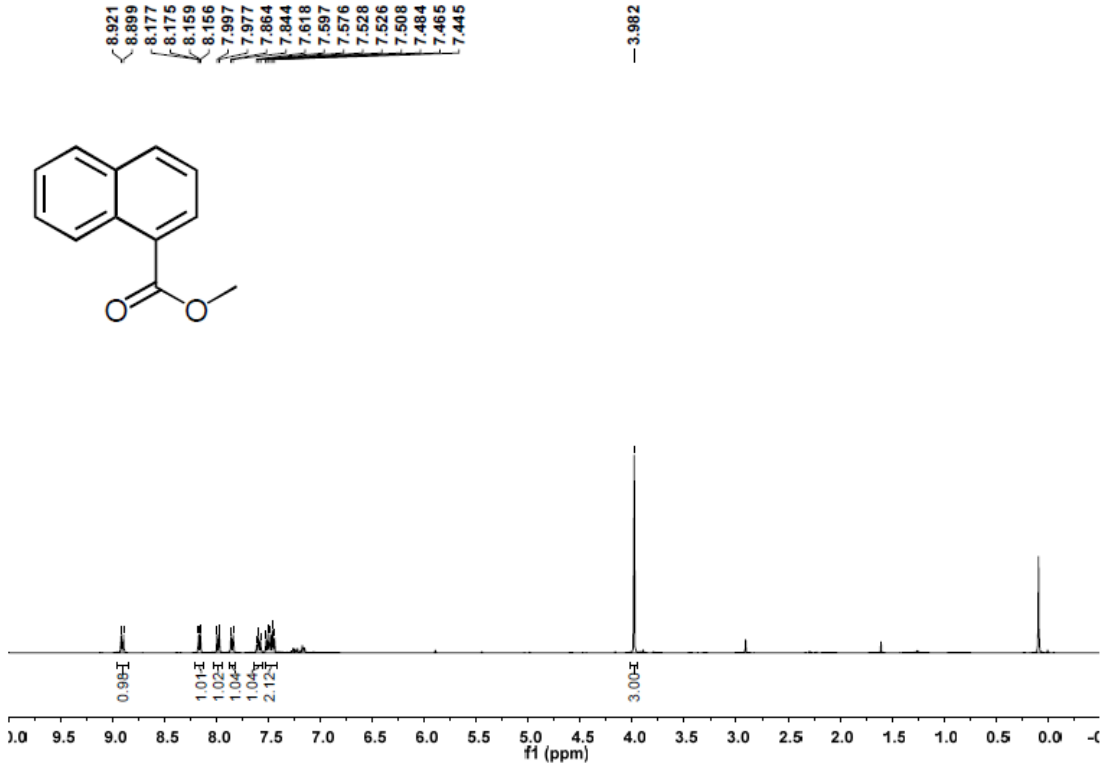


^{13}C NMR

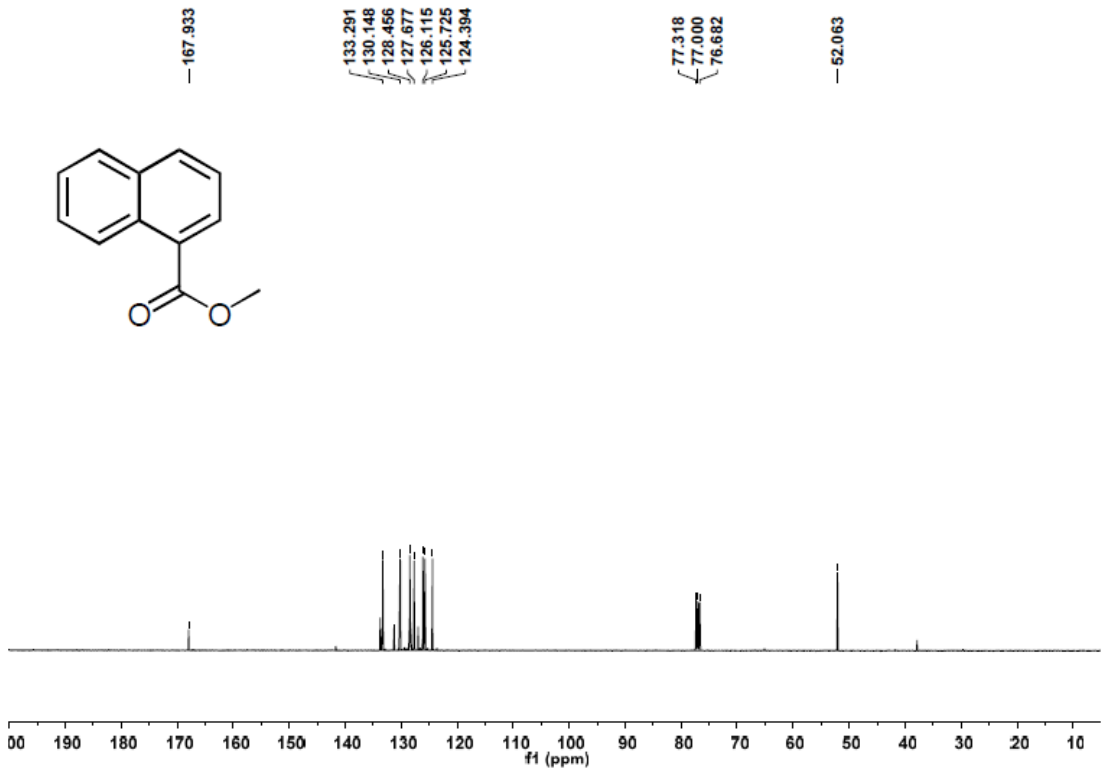


3k

^{1}H NMR

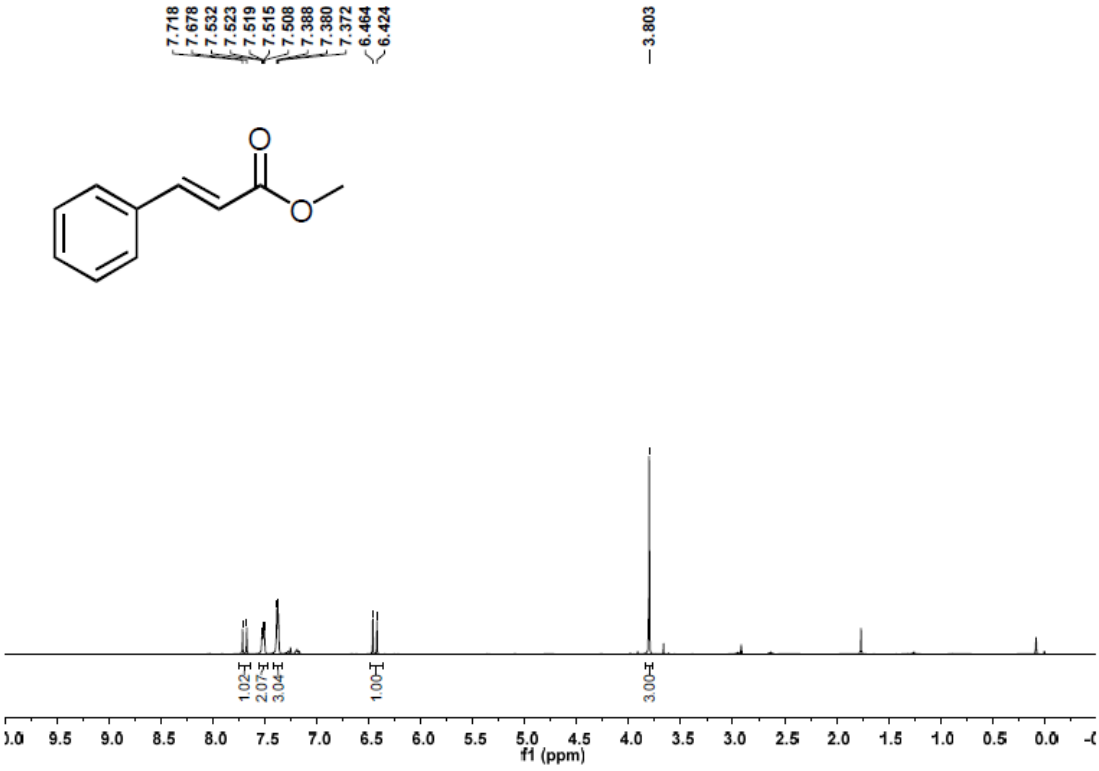


^{13}C NMR

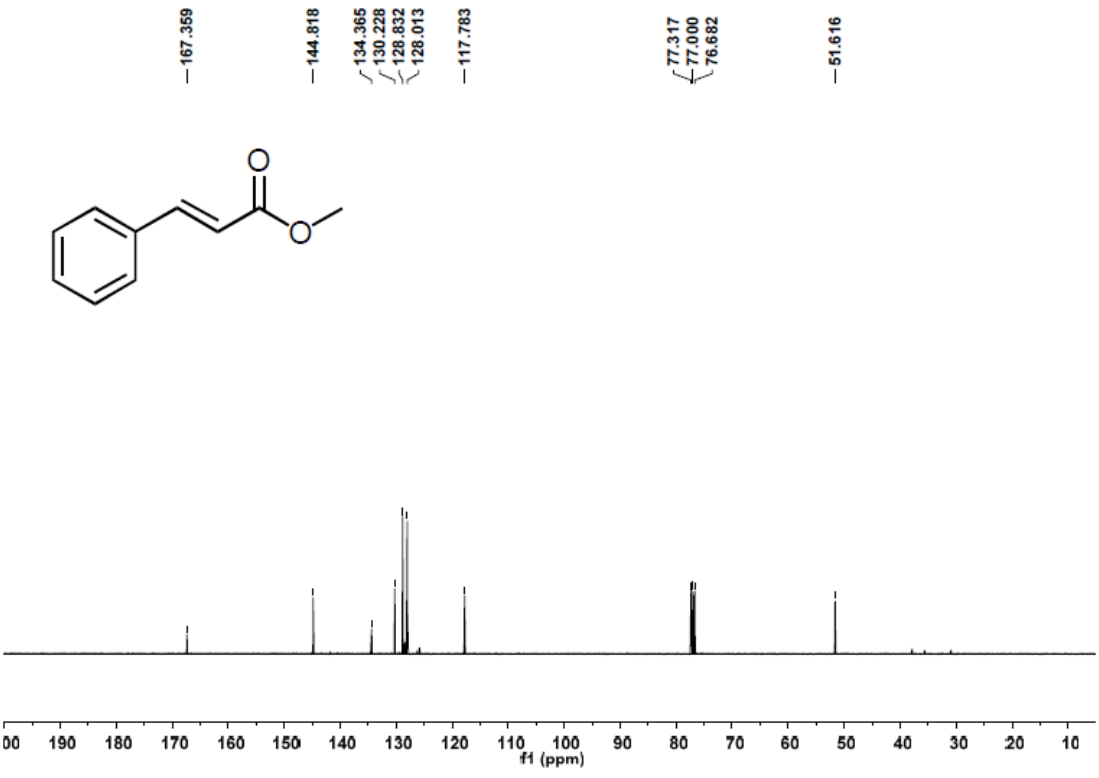


3l

^{1}H NMR

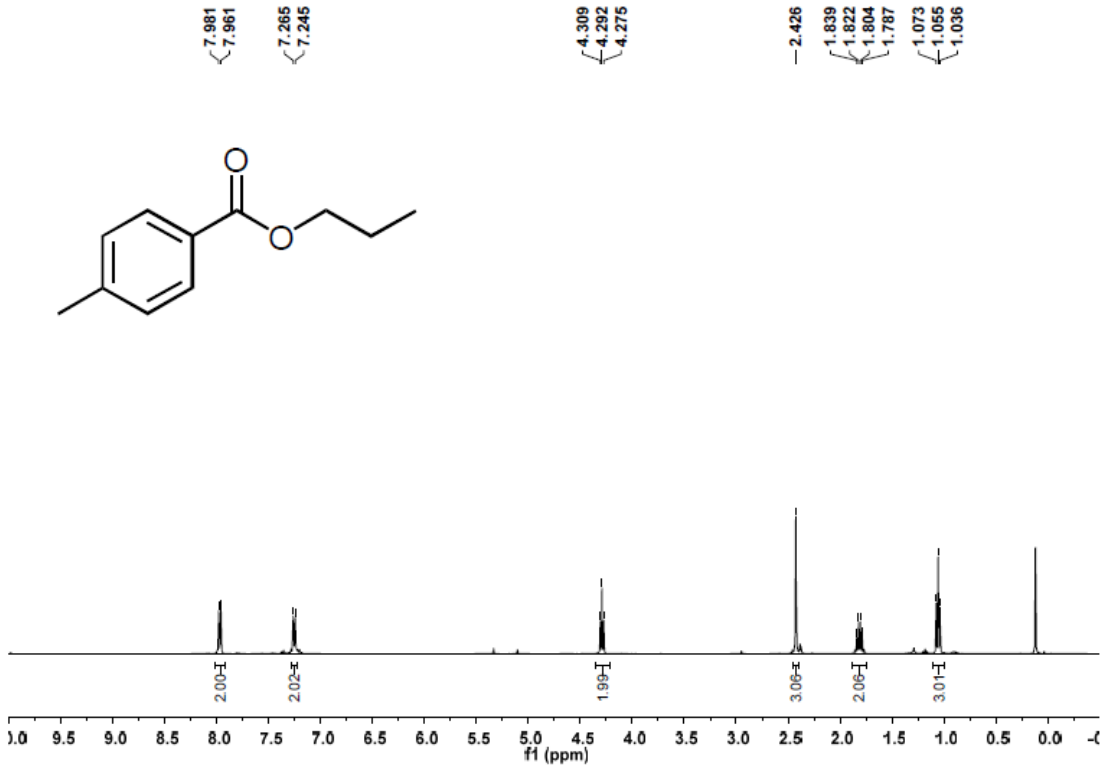


^{13}C NMR

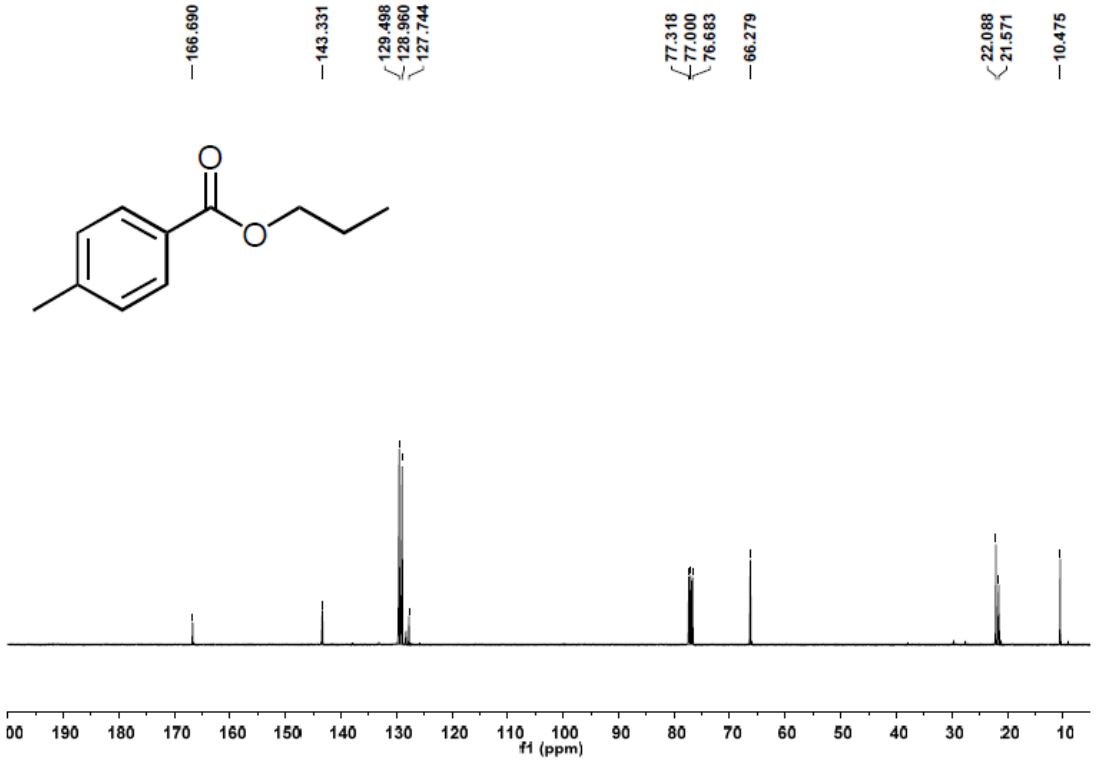


3m

^{1}H NMR

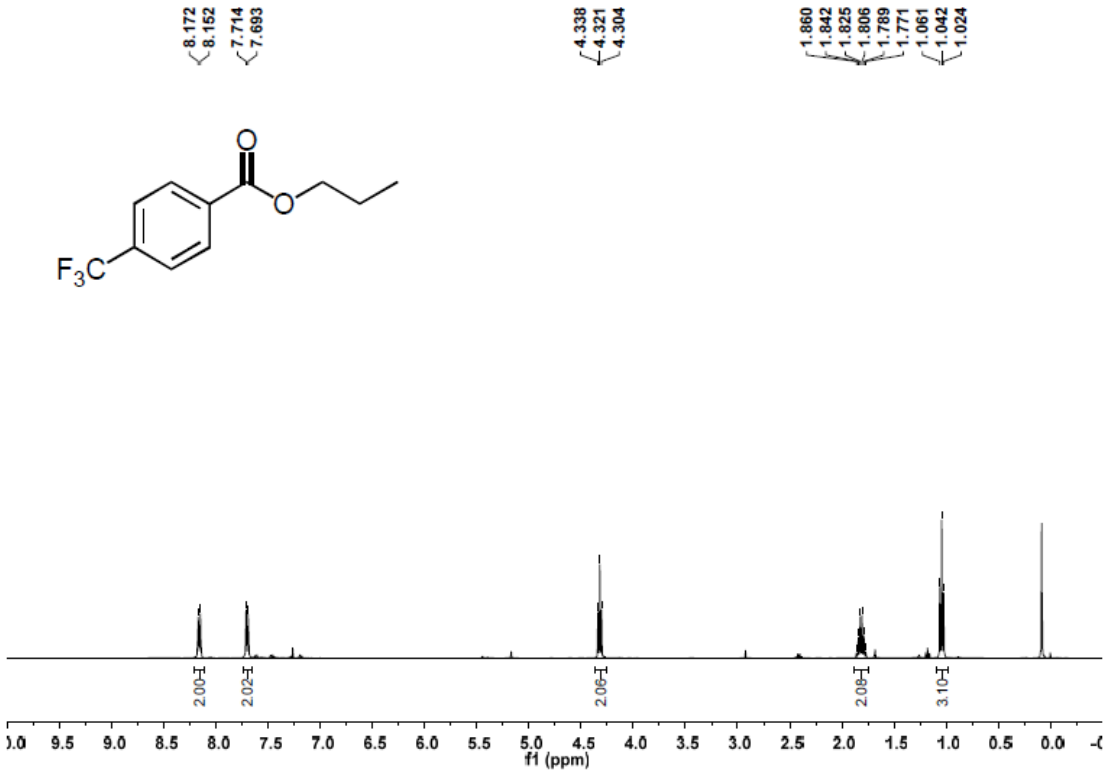


^{13}C NMR

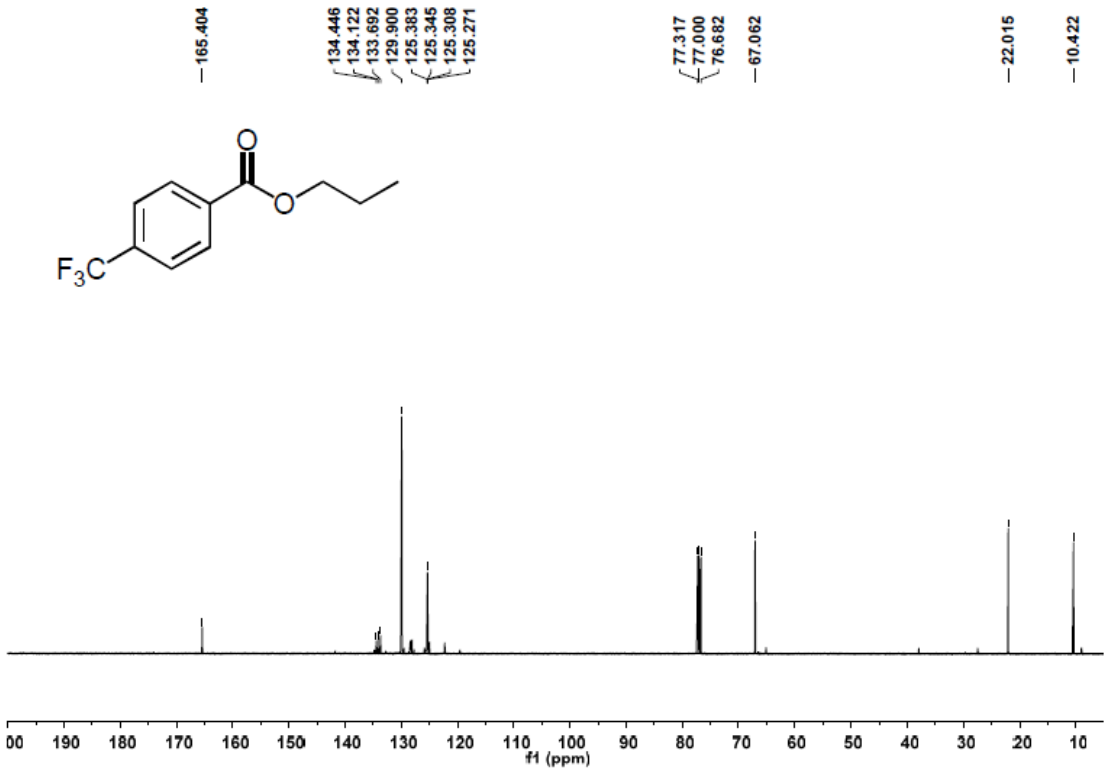


3n

^{1}H NMR

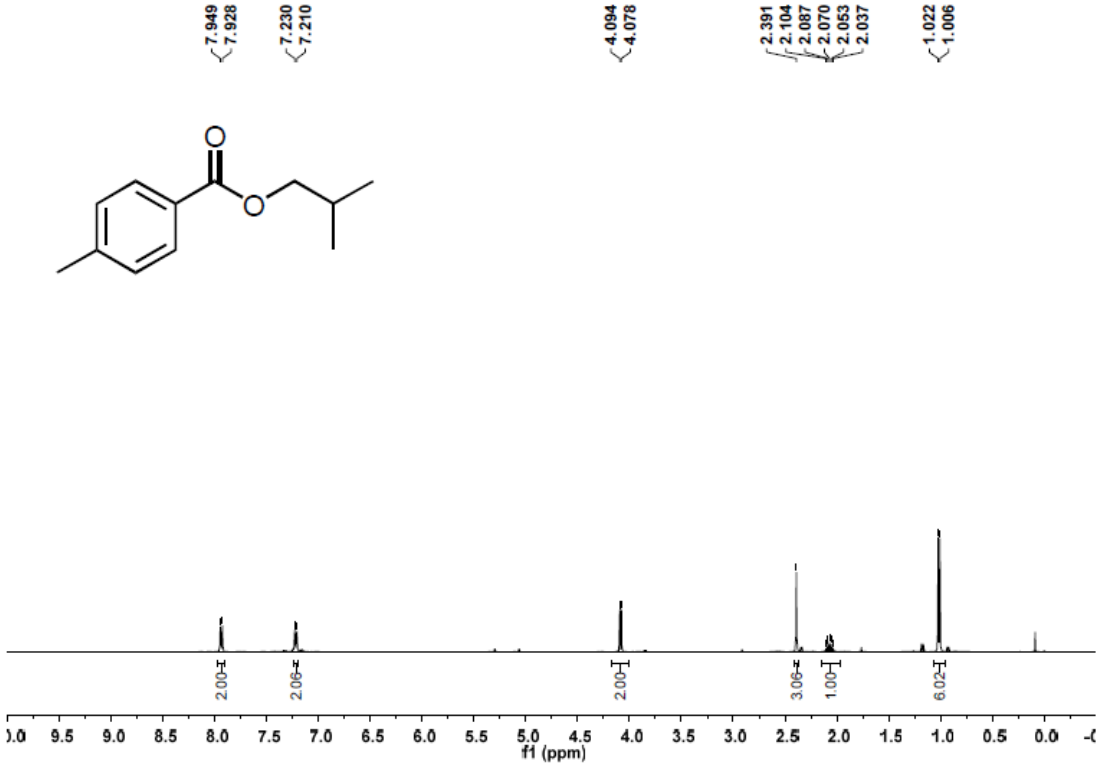


^{13}C NMR

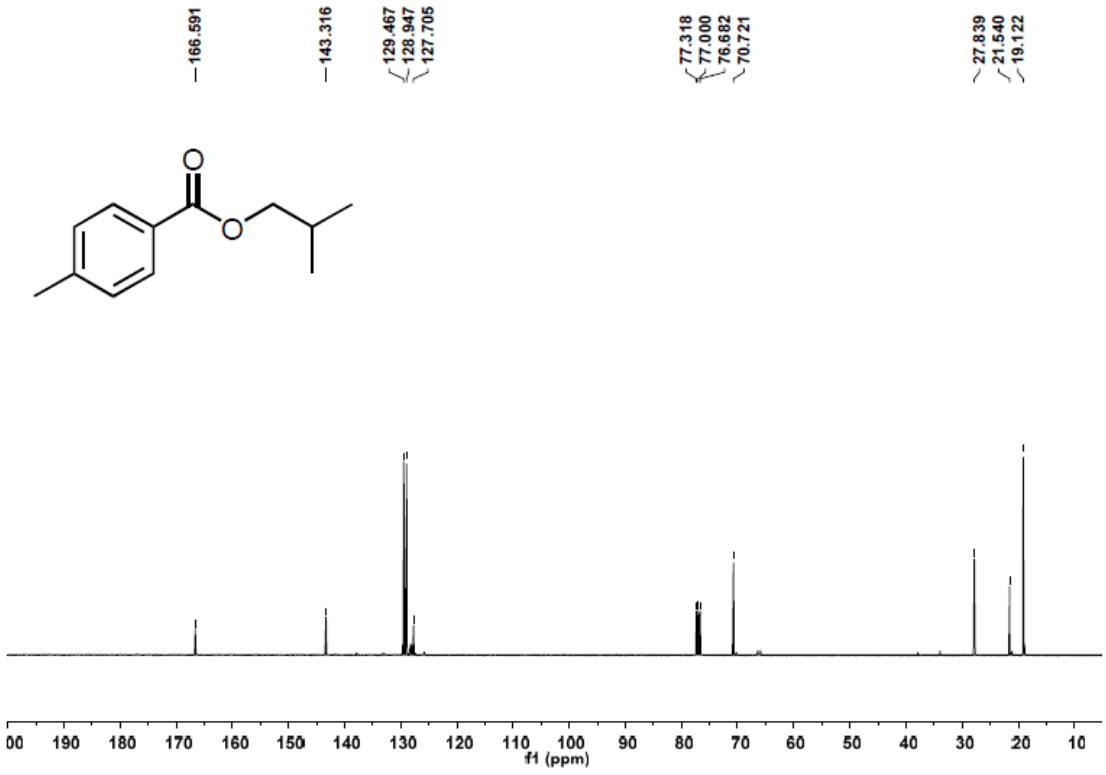


3o

^{1}H NMR

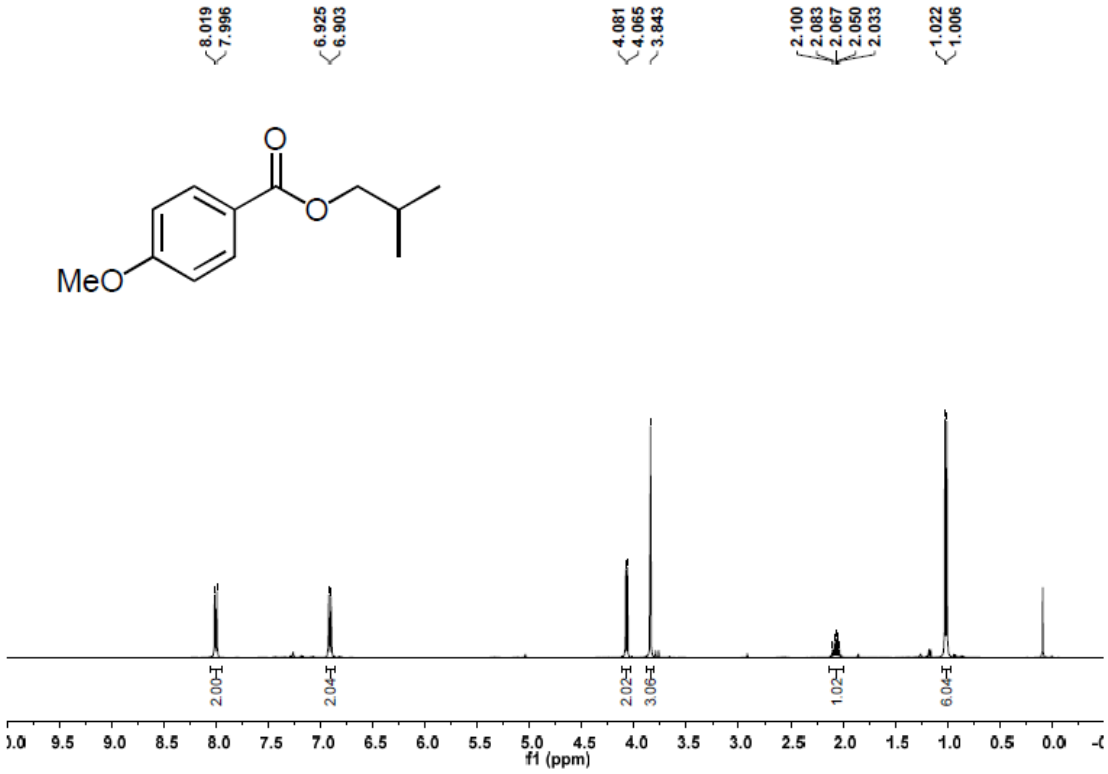


^{13}C NMR



3p

^{1}H NMR



^{13}C NMR