Electronic Supplementary Material (ESI) for Green Chemistry.

# Pd-Catalysed Carbonylative Suzuki-Miyaura Cross-couplings using $Fe(CO)_5$ under mild conditions: generation of a highly active, recyclable and scalable 'Pd-Fe' nanocatalyst

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## Supplementary Information

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## 1. General information

**General Methods and Materials.** All manipulations were performed under an atmosphere of air. All reagents and solvents were purchased from commercial suppliers and used without further purification, unless specified otherwise. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system according to standard techniques; analytical thin layer chromatography was carried out using 250 μm commercial silica gel plates. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker EQUINX55 (400 MHz for $^1$H; 101 MHz for $^{13}$C) spectrometer in $CDCl_3$. For $^1$H NMR, tetramethylsilane (TMS) served as internal standard ($\delta = 0$) and $^1$H NMR chemical shifts are reported in ppm downfield of tetramethylsilane and referenced to residual solvent peak ($CDCl_3$ at 7.26 ppm) unless otherwise noted. The data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet), and coupling constants in Hz.v For $^{13}$C NMR, $CDCl_3$ was used as internal standard ($\delta = 77.16$) and spectra were obtained with full proton decoupling. SEM images were obtained using a JEOL JSM-7600F scanning electron microscope set 5 kV as acceleration voltage. TEM images were obtained using a JEOL 100CXII Transmission Electron Microscope. X-ray Photoelectron Spectroscopy (XPS) was carried out on a VG ESCALAB 250 XPS system with a monochromatized Al Kα X-ray source (15 kV, 200 W). EDAX mapping analysis was carried out on a TEM-EDAX TEAM system.

**General Method for Carbonylation of Aryl halide with Arylboronic Acids.** To an appropriate reaction flask were added aryl halide (0.434 mmol, 1.00 equiv), arylboronic acid (0.75 mmol, 1.75 equiv), $K_2CO_3$ (0.86 mmol, 2.0 equiv) and $Pd(OAc)_2$ (0.00434 mmol, 1 mol%), without protection from air. Anisole (3 mL) was added and then the reaction flask was fitted and sealed with a rubber Suba-seal. $Fe(CO)_5$ (0.15 mmol, 0.35 equiv) was added to the reaction mixture *via* syringe. The reaction mixture was stirred and heated at 80 °C for 12 h. The crude reaction mixtures were then evaporated onto silica gel *in vacuo* and purified with flash column chromatography (0–10 %, EtOAc/petroleum ether) to yield the desired carbonylated organic product.

## 2. Optimization of Reaction Conditions

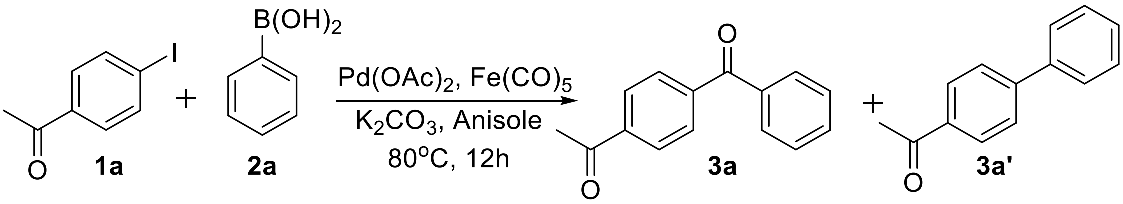


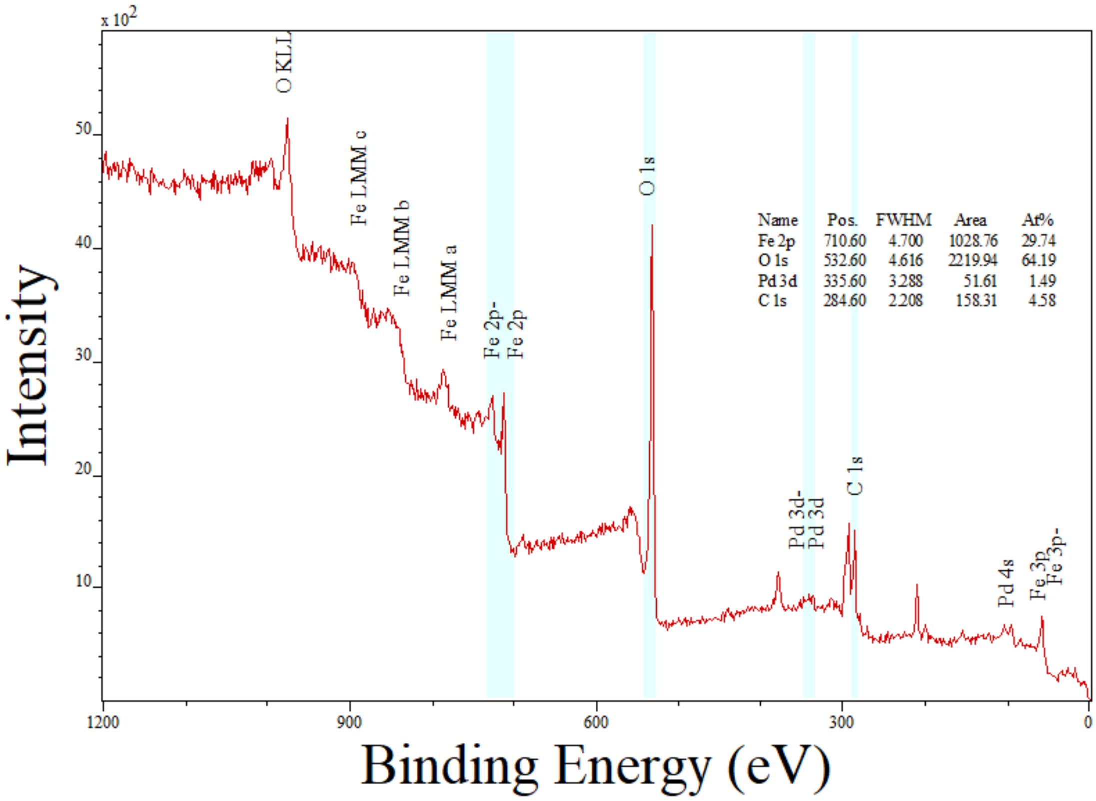
**Table S1.** Variation in substrate **2a** / Fe(CO)$_5$ amounts on Suzuki carbonylation.

| Entry | Catalyst | **2a**/eq | Fe(CO)$_5$/% | **3a** (%) | **3a'** (%) | Selec. (%) |
|---|---|---|---|---|---|---|
| 1 | Pd(OAc)$_2$ | 1.00 | 35 | 50 | 3 | 94 |
| 2 | Pd(OAc)$_2$ | 1.10 | 35 | 60 | 3 | 94 |
| 3 | Pd(OAc)$_2$ | 1.30 | 35 | 67 | 3 | 96 |
| 4 | Pd(OAc)$_2$ | 1.50 | 35 | 84 | 10 | 89 |
| 5 | Pd(OAc)$_2$ | 1.75 | 35 | 90 | 7 | 93 |
| 6 | Pd(OAc)$_2$ | 1.75 | 32 | 74 | 5 | 94 |
| 7 | Pd(OAc)$_2$ | 1.75 | 28 | 63 | 4 | 94 |
| 8 | Pd(OAc)$_2$ | 1.75 | 24 | 81 | 4 | 95 |
| 9 | Pd(OAc)$_2$ | 1.75 | 20 | 67 | 7 | 91 |

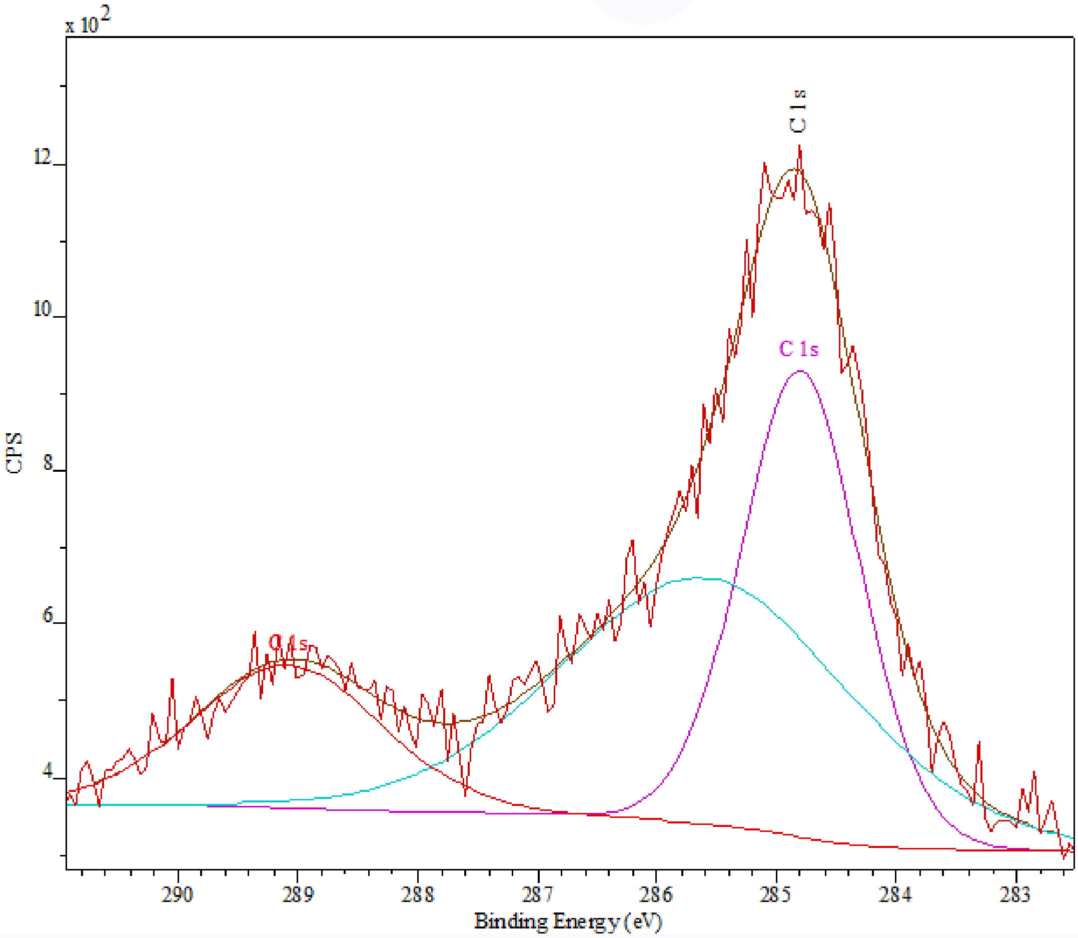
**Table S2.** Effect of the different CORMs in Suzuki carbonylation.

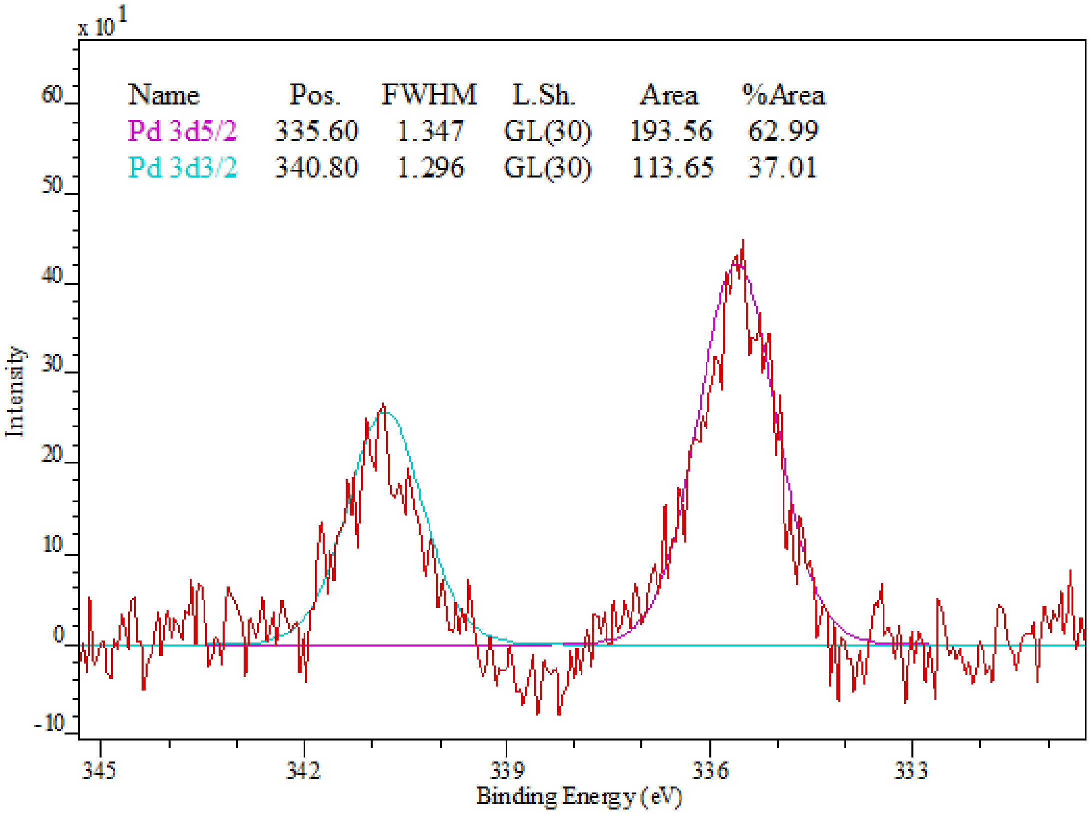
| Entry | Catalyst | CORMs | **3a** (%) | **3a'** (%) | Selec. (%) |
|---|---|---|---|---|---|
| 15 | Pd(OAc)$_2$ | Fe$_2$(CO)$_9$ | 88 | 2 | 98 |
| 16 | Pd(OAc)$_2$ | Fe$_3$(CO)$_{12}$ | 73 | 4 | 95 |
| 17 | Pd(OAc)$_2$ | Mo(CO)$_6$ | 77 | 21 | 79 |
| 18 | Pd(OAc)$_2$ | Cr(CO)$_6$ | 75 | 11 | 87 |
| 19 | Pd(OAc)$_2$ | CO(balloon) | 13 | 79 | 14 |

## 3. XPS details of Fe-Pd NPs

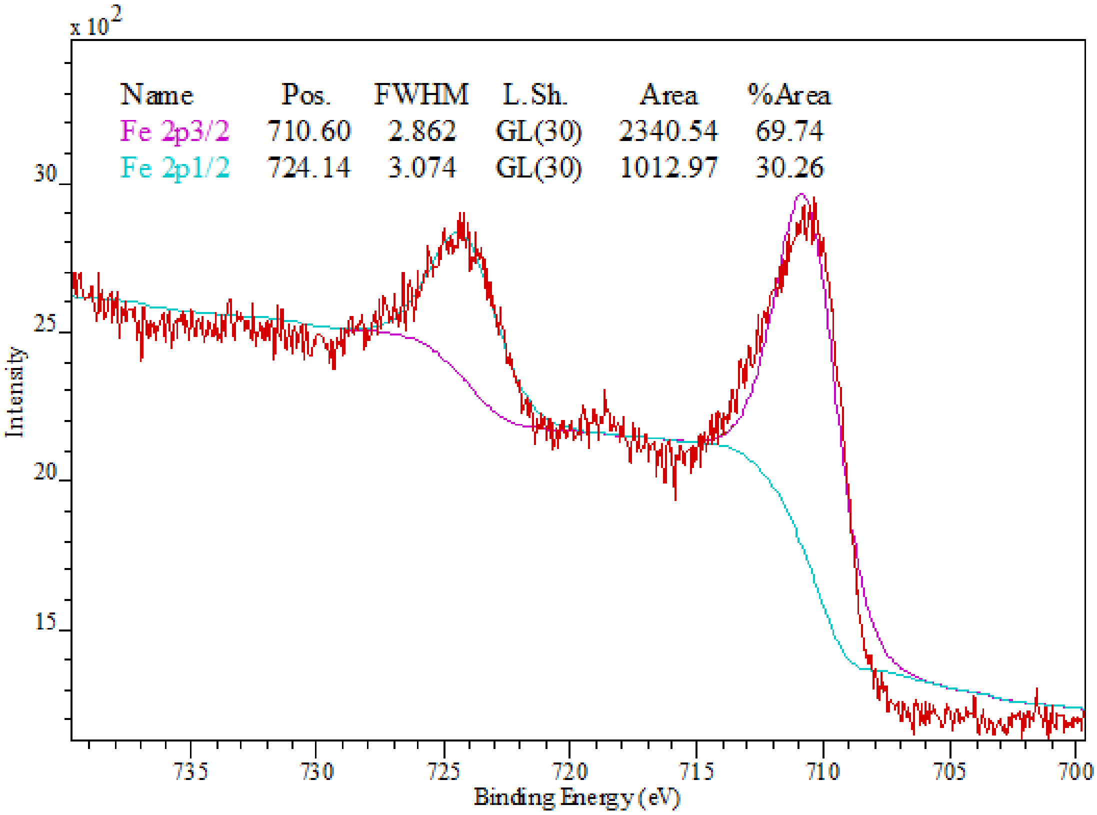


| Name | Pos. | FWHM | Area | At% |
|---|---|---|---|---|
| Fe 2p | 710.60 | 4.700 | 1028.76 | 29.74 |
| O 1s | 532.60 | 4.616 | 2219.94 | 64.19 |
| Pd 3d | 335.60 | 3.288 | 51.61 | 1.49 |
| C 1s | 284.60 | 2.208 | 158.31 | 4.58 |



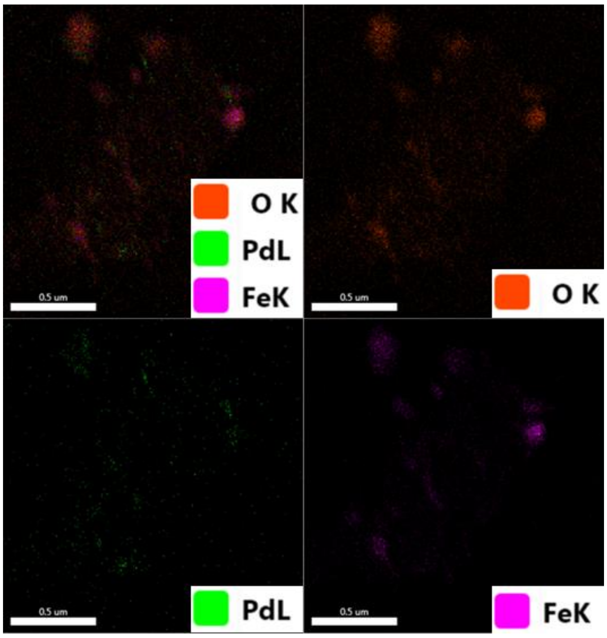


| Name | Pos. | FWHM | L.Sh. | Area | %Area |
|---|---|---|---|---|---|
| Pd 3d5/2 | 335.60 | 1.347 | GL(30) | 193.56 | 62.99 |
| Pd 3d3/2 | 340.80 | 1.296 | GL(30) | 113.65 | 37.01 |



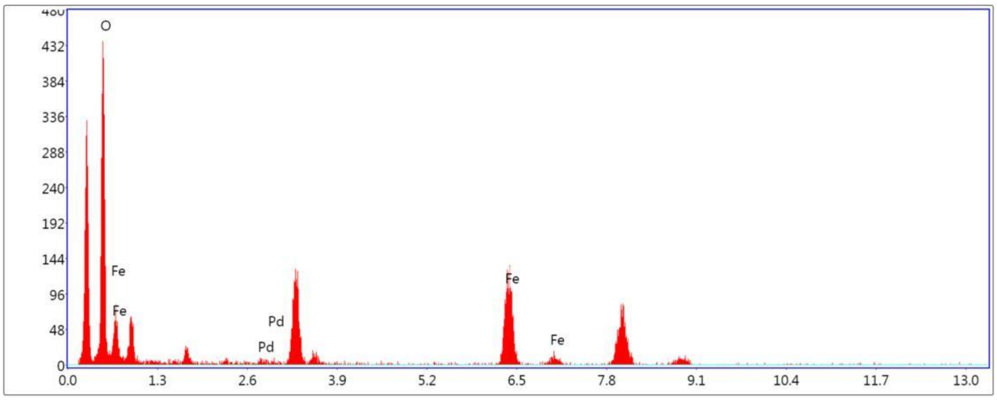
| Name | Pos. | FWHM | L.Sh. | Area | %Area |
|---|---|---|---|---|---|
| Fe 2p3/2 | 710.60 | 2.862 | GL(30) | 2340.54 | 69.74 |
| Fe 2p1/2 | 724.14 | 3.074 | GL(30) | 1012.97 | 30.26 |

## 4. EDAX mapping details of Fe-Pd NPs



kV: 200 Mag: 40000 Takeoff: 14.8 Live Time(s): 7.6 Amp Time(µs): 7.68 Resolution(eV): 127.6

**Phase: O K/FeK**

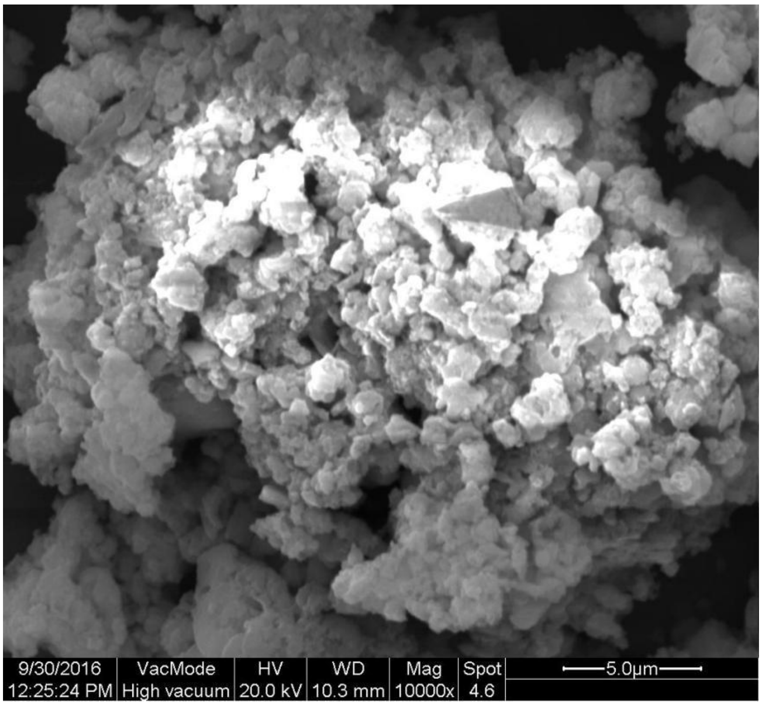


Lsec: 7.6 0 Cnts 0.000 keV Det: Apollo XLT2 SUTW Det

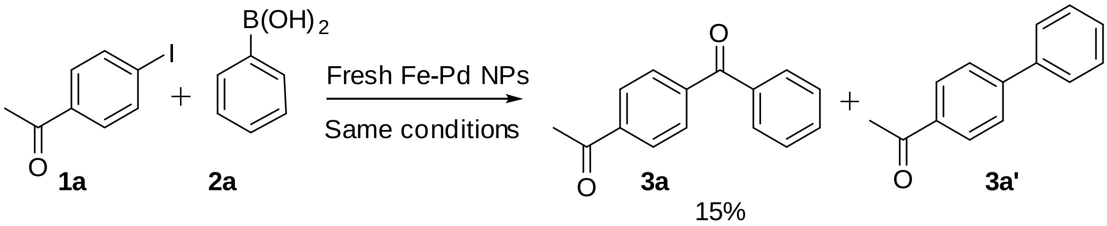
**MThin Smart Quant Results (Theoretical)**

| Element | Weight % | Atomic % | Net Int. | Net Error% | KABFactor |
|---|---|---|---|---|---|
| O K | 52.99 | 80.36 | 333.4 | 2.12 | 1 |
| PdL | 3.77 | 0.86 | 7.2 | 6.70 | 3.3 |
| FeK | 43.24 | 18.78 | 218.3 | 3.18 | 1.25 |

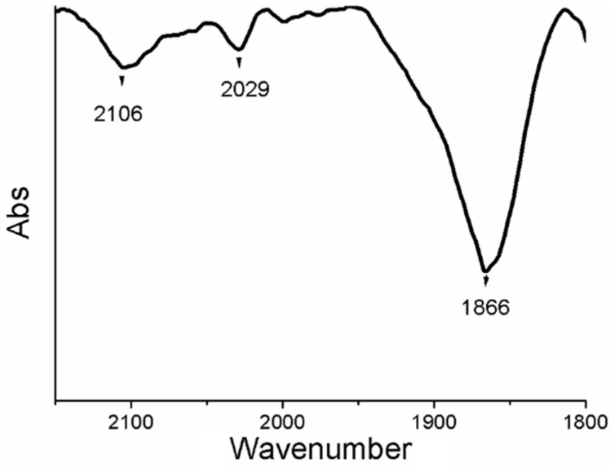
## 5. SEM images of Fe-Pd NPs



## 6. FT-IR and Reactivity of Fresh Isolated Fe-Pd NPs (I)



IR spectrum of iron carbonyl region:



$Fe(CO)_5$: 2022, 1999 ($cm^{-1}$)

$Fe_3(CO)_{12}$: 2047, 2028 ($cm^{-1}$)

T. S. Chong, S. T. Ta, and W. Y. Fan, *Chem. Eur. J.*, 2006, **12**, 5128.

Pd(CO): 2050 (nm)

CO: 2150 (nm)

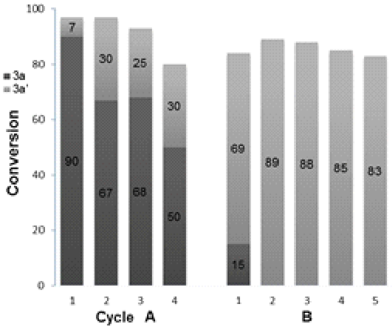
T. Mehner, R. Köppe, and H. Schnöckel, *Angew. Chem.*, 1992, **104**, 653.

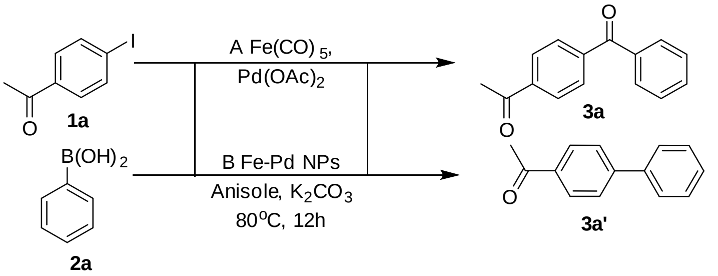
CO-Pd@MMT: 2179, 2125 (nm)

CO-Pd/Cu@MMT: 2119, 2063 (nm)

W. Xu, H. Sun, B.Yu, G. Zhang, W. Zhang, and Z. Gao, *ACS Appl. Mater. Interfaces*, 2014, **6**, 20261.

## 8. Recycling experiment of Fe-Pd NPs





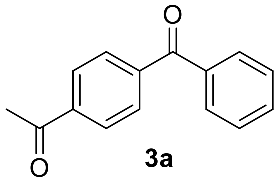
**Recycle A1:** 1-(4-Iodophenyl)ethan-1-one (**1a**, 0.434 mmol, 1.00 equiv), phenylboronic acid (**2b**, 0.75 mmol, 1.75 equiv), $K_2CO_3$ (0.86 mmol, 2.00 equiv), $Fe(CO)_5$ (0.15 mmol, 35 mol%) and $Pd(OAc)_2$ (0.0434 mmol, 1 mol %) were added to a Schlenk tube in anisole (3 mL) with a magnetic stir bar, and then heated at 80 °C for 12 h. The crude reaction mixture was extracted three times with EtOAc, leaving a residual solid (note: the catalyst/salt mixture). After the combined solvent fractions were removed *in vacuo*, the organic residue was purified using flash column chromatography on silica gel (0 – 10 %, EtOAc/petroleum ether as eluent) to yield the desired product(s). The combined extracts consisted of **3a** (90% and **3a'** (7%). The remaining residual residue was washed three times with distilled water to remove any base / salts. Then, the semi-purified Pd-Fe NPs were filtered and reused for the next cycle.

**Recycle A2-A4:** Using the conditions described in **A1** and replacing $Pd(OAc)_2$ with the Pd-Fe NPs obtained by method **A1**, the catalyst system was recycled three additional times with the % yields of **3a**:**3a'** being 67:30 (**A2**), 68:25 (**A3**) to 50:30 (**A4**), respectively.

**Recycle B1:** Using the conditions described in **A1** and replacing $Fe(CO)_5$ and $Pd(OAc)_2$ with the Pd-Fe NPs obtained by method **A1** – **3a'** was obtained in 69 % yield and **3a** in 15 % yield.

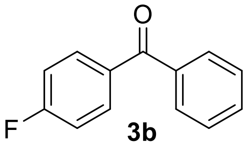
**Recycle B2-B5:** Using the conditions described in **A1** and replacing $Fe(CO)_5$ and $Pd(OAc)_2$ with the Pd-Fe NPs obtained by the method of **A1** in the last recycle (**B1-B4**), only **3a'** was obtained and the yields were found to be comparatively high – 89 % (**B1**), 88 % (**B2**), 85 % (**B3**)to 83 % (**B4**) over the four reactions.

## 9. Characterization of the Products



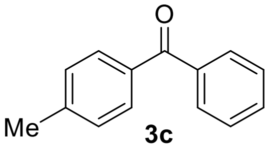
**3a**

**1-(4-Benzoylphenyl)ethan-1-one (3a).** General Method with 1-(4-iodophenyl)ethan-1-one and phenylboronic acid gave 0.0876 g (90% yield) of the title compound. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.06 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 7.3 Hz, 3H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 2.67 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm): δ 197.48, 195.92, 141.33139.57, 136.92, 132.97, 130.08, 130.03, 128.47, 128.15, 26.88.



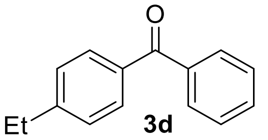
**3b**

**(4-fluorophenyl)(phenyl)methanone (3b)**. (1) General Method with 1-fluoro-4-iodobenzene and phenylboronic acid gave 0.0685 g (79 % yield) of the title compound. (2) General Method with iodobenzene and (4-fluorophenyl)boronic acid gave 0.0730 g (84 % yield) of the title compound. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.89 – 7.81 (m, 2H), 7.80 – 7.73 (m, 2H), 7.61 – 7.56 (m, 1H), 7.51 – 7.46 (m, 2H), 7.20 – 7.10 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm): 195.32, 165.48 (d, *J* = 254.1 Hz), 137.60, 133.92, 132.76 (d, *J* = 9.1 Hz), 132.56, 129.96, 128.45, 115.54 (d, *J* = 21.9 Hz).



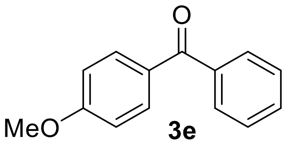
**3c**

**Phenyl(4-tolyl)methanone (3c)**. (1) General Method with 1-iodo-4-methylbenzene and phenylboronic acid gave 0.0715 g (84 % yield) of the title compound. (2) General Method with iodobenzene and 4-tolylboronic acid acid gave 0.0750 g (88 % yield) of the title compound.$^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.81 – 7.77 (m, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.62 – 7.52 (m, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm): 196.46, 143.23, 137.97, 134.90, 132.16, 130.30, 129.92, 128.98, 128.21, 21.66.



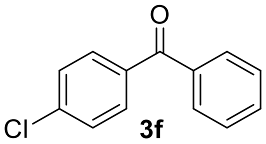
**3d**

**(4-Ethylphenyl)(phenyl)methanone (3d)**. General Method with 1-ethyl-4-iodobenzene and phenylboronic acid gave 0.0603 g (66 % yield) of the title compound. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.78 (dd, *J* = 16.5, 7.7 Hz, 4H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm): 196.55, 149.48, 138.05, 135.20, 132.23, 130.48, 130.02, 128.29, 127.88, 29.06, 15.35.



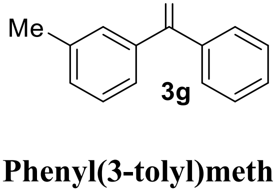
**3e**

**(4-Methoxyphenyl)(phenyl)methanone (3e).** (1) General Method with 1-iodo-4-methoxybenzene and phenylboronic acid gave 0.0678 g (74 % yield) of the title compound. (2) General Method with iodobenzene and (4-methoxyphenyl)boronic acid gave 0.0737 g (80 % yield) of the title compound. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.85 – 7.80 (m, 2H), 7.79 – 7.72 (m, 2H), 7.58 – 7.53 (m, 1H), 7.46 (td, *J* = 6.9, 1.4 Hz, 2H), 7.00 – 6.91 (m, 3H), 3.87 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm): 195.52, 163.23, 138.30, 132.55, 131.88, 130.16, 129.71, 128.18, 113.56, 55.49.



**3f**

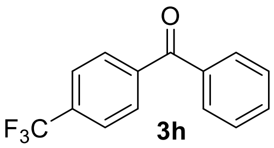
**(4-Chlorophenyl)(phenyl)methanone (3f)**. (1) General Method with 1-chloro-4-iodobenzene and phenylboronic acid gave 0.0690 g (73 % yield) of the title compound. (2) General Method with iodobenzene and (4-chlorophenyl)boronic acid gave 0.0841 g (89 % yield) of the title compound. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.84 – 7.69 (m, 4H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.53 – 7.42 (m, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm): 195.46, 138.89, 137.25, 135.88, 132.63, 131.45, 129.92, 128.63, 128.40.



**3g**

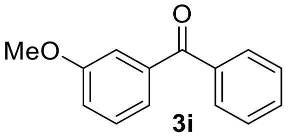
**Phenyl(3-tolyl)methanone (3g)**. General Method with 1-iodo-3-methylbenzenee and phenylboronic acid gave 0.0630 g (74 % yield) of the title compound. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.82 – 7.79 (m, 2H), 7.63 (s, 1H), 7.61 – 7.56 (m, 2H), 7.50 – 7.45 (m, 2H), 7.42 – 7.33 (m, 2H), 2.42 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm):

196.94, 138.15, 137.78, 137.65, 133.18, 132.32, 130.45, 130.03, 128.24, 128.09, 127.36, 21.36.



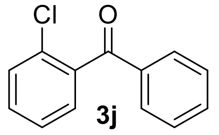
**3h**

**Phenyl(4-(trifluoromethyl)phenyl)methanone (3h)**. General Method with 1-iodo-4-(trifluoromethyl)benzene and phenylboronic acid gave 0.0630 g (74 % yield) of the title compound. $^{1}$H NMR (400 MHz, CDCl$_3$) δ (ppm): $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.81 (d, *J* = 7.4 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ (ppm): 195.64, 140.88, 136.88, 133.86 (d, *J* = 32.6 Hz), 133.21, 130.27, 130.23, 128.66, 125.48 (q, *J* = 3.7 Hz), 123.82 (d, *J* = 272.7 Hz).



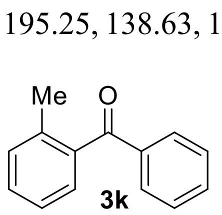
**3i**

**(3-Methoxyphenyl)(phenyl)methanone (3i)**. General Method with 1-iodo-3-methoxybenzene and phenylboronic acid gave 0.0486 g (53 % yield) of the title compound. $^{1}$H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.81 (d, *J* = 7.3 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.42 – 7.30 (m, 3H), 7.18 – 7.08 (m, 1H), 3.85 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ (ppm): 196.47, 159.58, 138.90, 137.62, 132.42, 130.03, 129.21, 128.25, 122.85, 118.83, 114.35, 55.46.



**3j**

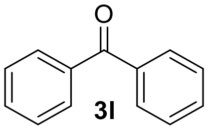
**(2-Chlorophenyl)(phenyl)methanone (3j)**. General Method with 1-chloro-2-iodobenzene and phenylboronic acid gave 0.0470 g (50 % yield) of the title compound. $^{1}$H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.82 (d, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.52 – 7.42 (m, 4H), 7.38 (t, *J* = 2.8 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ (ppm): 195.25, 138.63, 136.50, 133.68, 131.33, 131.11, 130.07, 129.12, 128.60, 128.27, 126.67.



**3k**

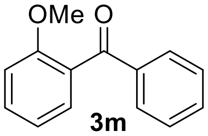
**Phenyl(2-tolyl)methanone (3k)**. General Method with 1-iodo-2-methylbenzene and phenylboronic acid gave 0.0613 g (72 % yield) of the title compound. $^{1}$H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.84 – 7.78 (m, 2H), 7.61 – 7.55 (m, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.42 – 7.36 (m, 1H), 7.34 – 7.28 (m, 2H), 7.24 (t, J = 7.6 Hz, 1H), 2.34 (s, 3H).

$^{13}C$ NMR (101 MHz, $CDCl_3$) δ (ppm): 198.77, 138.78, 137.90, 136.88, 133.26, 131.13, 130.37, 130.27, 128.65, 128.59, 125.33, 20.12.



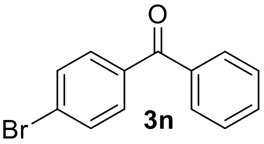
3l

**Benzophenone (4g)**. General Method with iodobenzene and phenylboronic acid gave 0.0576 g (73 % yield) of the title compound. $^{1}H$ NMR (400 MHz, $CDCl_3$) δ (ppm): 7.86 – 7.77 (m, 4H), 7.62 – 7.56 (m, 2H), 7.48 (t, *J* = 7.6 Hz, 4H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ (ppm): 196.73, 137.61, 132.41, 130.05, 128.27.



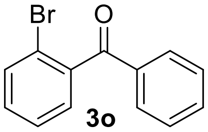
3m

**(2-Methoxyphenyl)(phenyl)methanone (3m)**. General Method with 1-iodo-2-methoxybenzene and phenylboronic acid gave 0.0716 g (78 % yield) of the title compound. $^{1}H$ NMR (400 MHz, $CDCl_3$) δ (ppm): 7.81 (d, J = 7.3 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.49 – 7.40 (m, 3H), 7.36 (d, J = 6.0 Hz, 1H), 7.08 – 6.97 (m, 2H), 3.72 (s, 3H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ (ppm): 196.44, 157.36, 137.84, 132.90, 131.87, 129.81, 129.57, 128.89, 128.21, 120.49, 111.48, 55.61.



3n

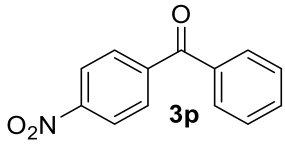
**(4-Bromophenyl)(phenyl)methanone (3n)**. (1) General Method with 1-bromo-4-iodobenzene and phenylboronic acid gave 0.0907 g (80 % yield) of the title compound. (2) General Method with iodobenzene and (4-bromophenyl)boronic acid gave 0.0838 g (74 % yield) of the title compound. $^{1}H$ NMR (400 MHz, $CDCl_3$) δ (ppm): 7.77 (d, J = 7.6 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.66 – 7.55 (m, 5H), 7.48 (t, J = 7.6 Hz, 2H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ (ppm): 194.68, 136.29, 135.43, 131.77, 130.72, 130.66, 129.03, 127.51, 126.61.



3o

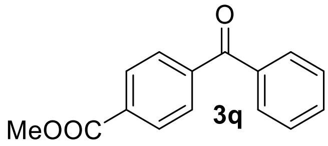
**(2-Bromophenyl)(phenyl)methanone (3o)**. General Method with 1-bromo-2-iodobenzene and phenylboronic acid gave 0.0343 g (30 % yield) of the title compound. $^{1}H$ NMR (400 MHz, $CDCl_3$) δ (ppm): 7.82 (d, *J* = 7.3 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.1

Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ (ppm): 195.78, 140.66, 136.10, 133.66, 133.14, 131.08, 130.16, 128.94, 128.58, 127.13, 119.49.



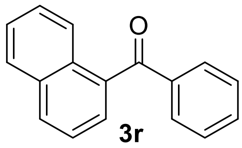
**3p**

**(4-Nitrophenyl)(phenyl)methanone (3p)**. General Method with 1-iodo-4-nitrobenzene and phenylboronic acid gave 0.0639 g (65 % yield) of the title compound. $^{1}$H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.34 (d, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.65 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H).$^{13}$C NMR (101 MHz, CDCl$_3$) δ (ppm): 194.76, 149.83, 142.88, 136.29, 133.46, 130.68, 130.09, 128.68, 123.53.



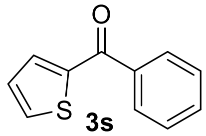
**3q**

**Methyl 4-benzoylbenzoate (3q)**. (1) General Method with methyl 4-iodobenzoate and phenylboronic acid gave 0.0839 g (80 % yield) of the title compound. (2) General Method with iodobenzene and (4-(methoxycarbonyl)phenyl)boronic acid gave 0.0440 g (42 % yield) of the title compound. $^{1}$H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.15 (d, *J* = 8.3 Hz, 2H), 7.82 (dd, *J* = 15.3, 8.4 Hz, 4H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 3.97 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ (ppm): 196.16, 166.46, 141.49, 137.13, 133.39, 133.08, 130.25, 129.91, 129.65, 128.61, 52.61.



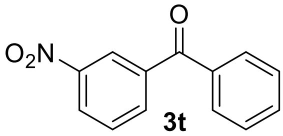
**3r**

**Naphthalen-1-yl(phenyl)methanone (3r)**. General Method with 1-iodonaphthalene and phenylboronic acid gave 0.0558 g (55 % yield) of the title compound. $^{1}$H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.12 (d, J = 7.9 Hz, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.96 – 7.91 (m, 1H), 7.88 (d, J = 7.3 Hz, 2H), 7.63 – 7.57 (m, 2H), 7.55 – 7.44 (m, 5H).$^{13}$C NMR (101 MHz, CDCl$_3$) δ (ppm): 197.97, 138.28, 136.32, 133.68, 133.19, 131.22, 130.92, 130.36, 128.41, 127.73, 127.22, 126.42, 125.65, 124.30.



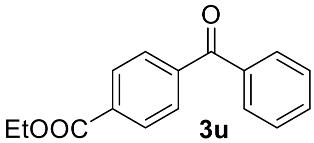
**3s**

**Phenyl(thiophen-2-yl)methanone (3s)**. (1) General Method with 2-iodothiophene and phenylboronic acid gave 0.0444 g (54 % yield) of the title compound. (2) General Method with iodobenzene and thiophen-2-ylboronic acid gave 0.0444 g (54 % yield) of the title compound. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.93 (d, *J* = 2.8 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.59 (dd, *J* = 10.4, 6.1 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.39 (dd, *J* = 4.9, 3.0 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm): 190.00, 141.31, 138.64, 133.90, 132.29, 129.36, 128.61, 128.37, 126.19.



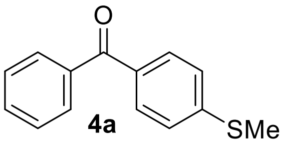
**3t**

**(3-Nitrophenyl)(phenyl)methanone (3t)**. General Method with 1-iodo-3-nitrobenzene and phenylboronic acid gave 0.0639 g (65 % yield) of the title compound. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.59 (s, 1H), 8.42 (dd, *J* = 8.7, 1.5 Hz, 1H), 8.12 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.67 (dt, *J* = 20.9, 7.6 Hz, 2H), 7.51 (t, *J* = 7.7 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm): 194.21, 148.14, 139.08, 136.30, 135.51, 133.42, 130.06, 129.71, 128.78, 126.76, 124.72.



**3u**

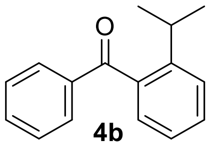
**4-Benzoylphenyl propionate (3u)**. General Method with 4-iodophenyl propionate and phenylboronic acid gave 0.0806 g (73 % yield) of the title compound. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.13 (d, *J* = 8.2 Hz, 2H), 7.80 (dd, *J* = 13.7, 8.2 Hz, 4H), 7.60 (d, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm): 196.01, 165.82, 141.25, 137.03, 133.63, 132.95, 130.13, 129.77, 129.49, 128.49, 61.46, 14.36.



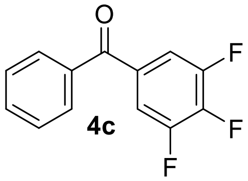
**4a**

**(4-(Methylthio)phenyl)(phenyl)methanone (4a)**. General Method with iodobenzene and (4-(methylthio)phenyl)boronic acid gave 0.0640 g (65 % yield) of the title compound. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.75 (t, *J* = 7.6 Hz, 4H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.28 (d, *J* = 7.7 Hz, 2H), 2.52 (s, 3H). $^{13}$C NMR

(101 MHz, $CDCl_3$) δ (ppm): 195.77, 145.29, 137.87, 133.65, 132.18, 130.64, 129.82, 128.26, 124.85, 14.86.

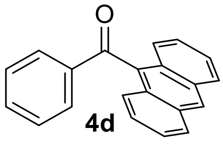

**4b**

**(2-Isopropylphenyl)(phenyl)methanone (4b).** General Method with iodobenzene and (2-isopropylphenyl)boronic acid gave 0.0701 g (72 % yield) of the title compound. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.83 (d, $J$ = 7.2 Hz, 2H), 7.58 (t, $J$ = 7.4 Hz, 1H), 7.48 – 7.42 (m, 4H), 7.27 – 7.21 (m, 2H), 3.06 (p, $J$ = 6.8 Hz, 1H), 1.21 (d, $J$ = 6.8 Hz, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm): 199.11, 147.24, 138.46, 137.91, 133.41, 130.26, 128.54, 127.62, 126.10, 125.25, 30.33, 24.18.

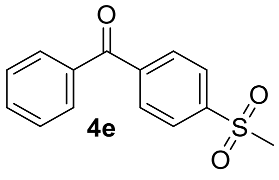


**4c**

**Phenyl(3,4,5-trifluorophenyl)methanone (4c)**. General Method with iodobenzene and (3,4,5-trifluorophenyl)boronic acid gave 0.0236 g (23 % yield) of the title compound. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.76 (d, $J$ = 7.9 Hz, 2H), 7.64 (t, $J$ = 7.4 Hz, 1H), 7.54 – 7.44 (m, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm): 192.88, 152.22 (dd, $J$ = 10.3, 3.4 Hz), 149.70 (dd, $J$ = 10.2, 3.4 Hz), 136.19, 133.11, 129.79, 128.62, 114.63 (d, $J$ = 6.2 Hz), 114.48 (d, $J$ = 6.2 Hz).

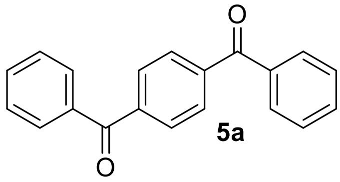

**4d**

**Anthracen-9-yl(phenyl)methanone (4d)**. General Method with iodobenzene and anthracen-9-ylboronic acid gave 0.0907 g (74 % yield) of the title compound. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.57 (s, 1H), 8.07 (d, $J$ = 8.5 Hz, 2H), 7.83 (d, $J$ = 7.5 Hz, 2H), 7.74 (d, $J$ = 8.7 Hz, 2H), 7.58 (t, $J$ = 7.4 Hz, 1H), 7.48 (t, 2H), 7.43 – 7.37 (m, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm): 200.16, 138.11, 134.00, 133.91, 131.00, 130.03, 128.80, 128.60, 128.59, 128.33, 126.49, 125.45, 125.27.



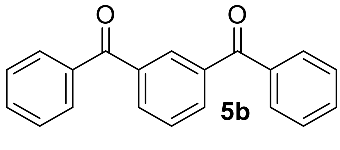
4e

**(4-(Methylsulfonyl)phenyl)(phenyl)methanone (4e)**. General Method with iodobenzene and (4-(methylsulfonyl)phenyl)boronic acid gave 0.0418 g (37 % yield) of the title compound. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.09 (d, $J$ = 8.3 Hz, 2H), 7.96 (d, $J$ = 8.3 Hz, 2H), 7.82 (d, $J$ = 7.4 Hz, 2H), 7.66 (t, $J$ = 7.4 Hz, 1H), 7.53 (t, $J$ = 7.7 Hz, 2H), 3.13 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm): 195.24, 143.56, 142.45, 136.46, 133.51, 130.65, 130.24, 128.76, 127.57, 44.49.



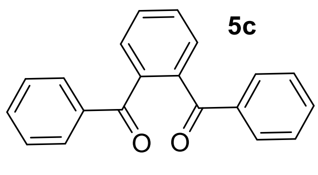
5a

**1,4-Phenylenebis(phenylmethanone) (5a)**. General Method with 1,4-diiodobenzene and phenylboronic acid gave 0.0800 g (64 % yield) of the title compound. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.88 (s, 4H), 7.83 (d, $J$ = 7.5 Hz, 4H), 7.61 (t, $J$ = 7.3 Hz, 2H), 7.50 (t, $J$ = 7.5 Hz, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm): 195.95, 140.65, 136.96, 132.96, 130.12, 129.73, 128.49.



5b

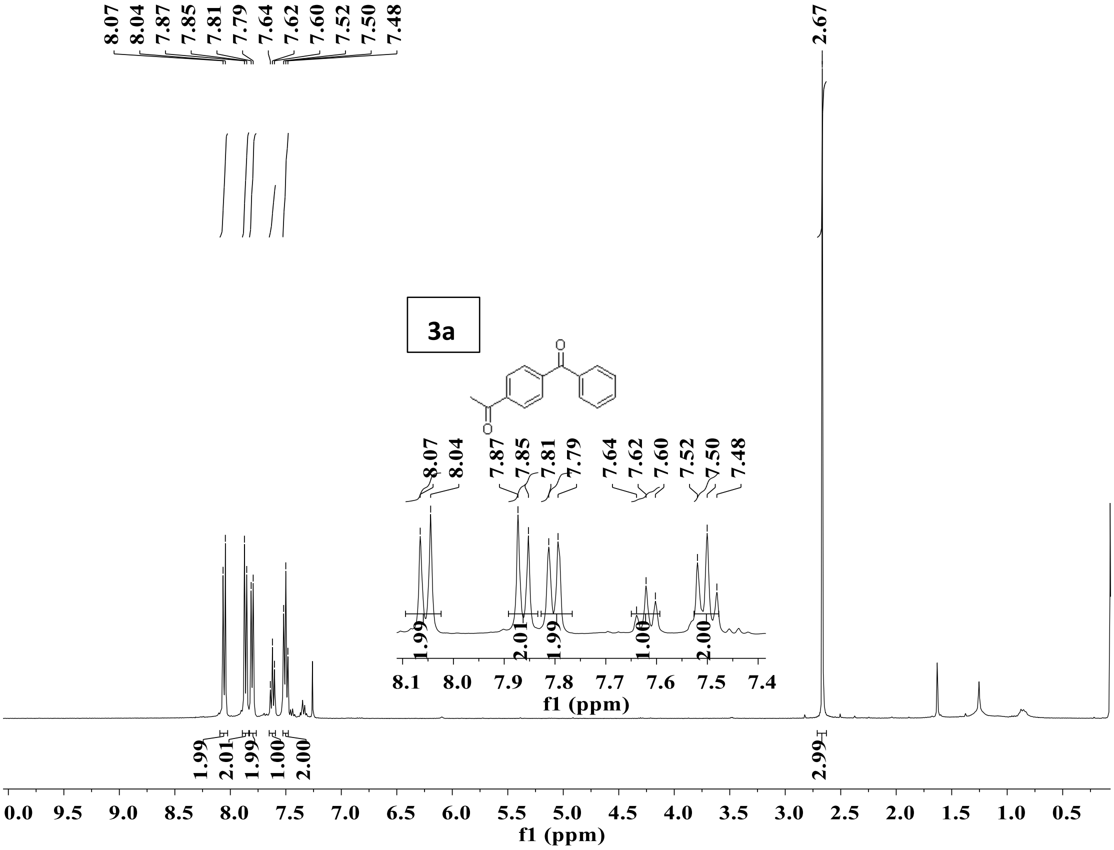
**1,3-Phenylenebis(phenylmethanone) (5b)**. General Method with 1,3-diiodobenzene and phenylboronic acid gave 0.1068 g (86 % yield) of the title compound. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.20 (s, 1H), 8.02 (dd, 2H), 7.82 (d, $J$ = 7.3 Hz, 4H), 7.64 – 7.57 (m, 3H), 7.49 (t, $J$ = 7.6 Hz, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm): 195.86, 137.80, 136.95, 133.51, 132.92, 131.23, 130.09, 128.55, 128.50.

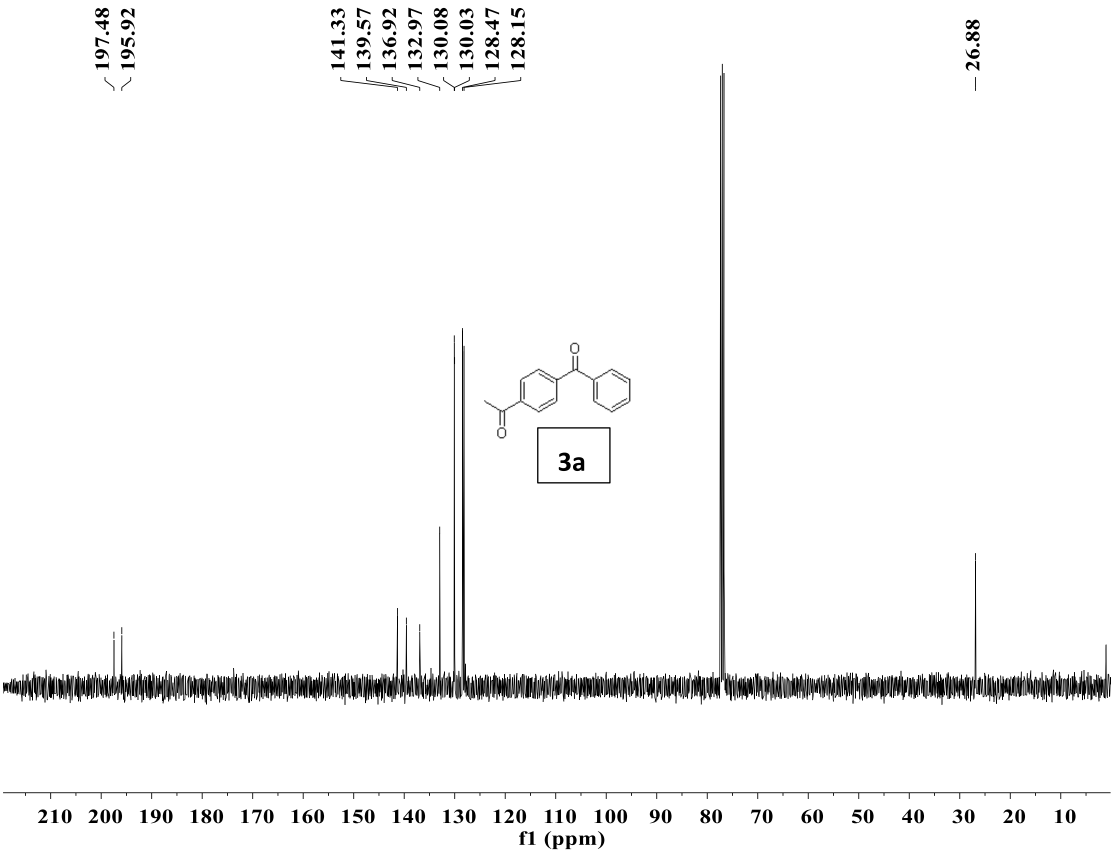


5c

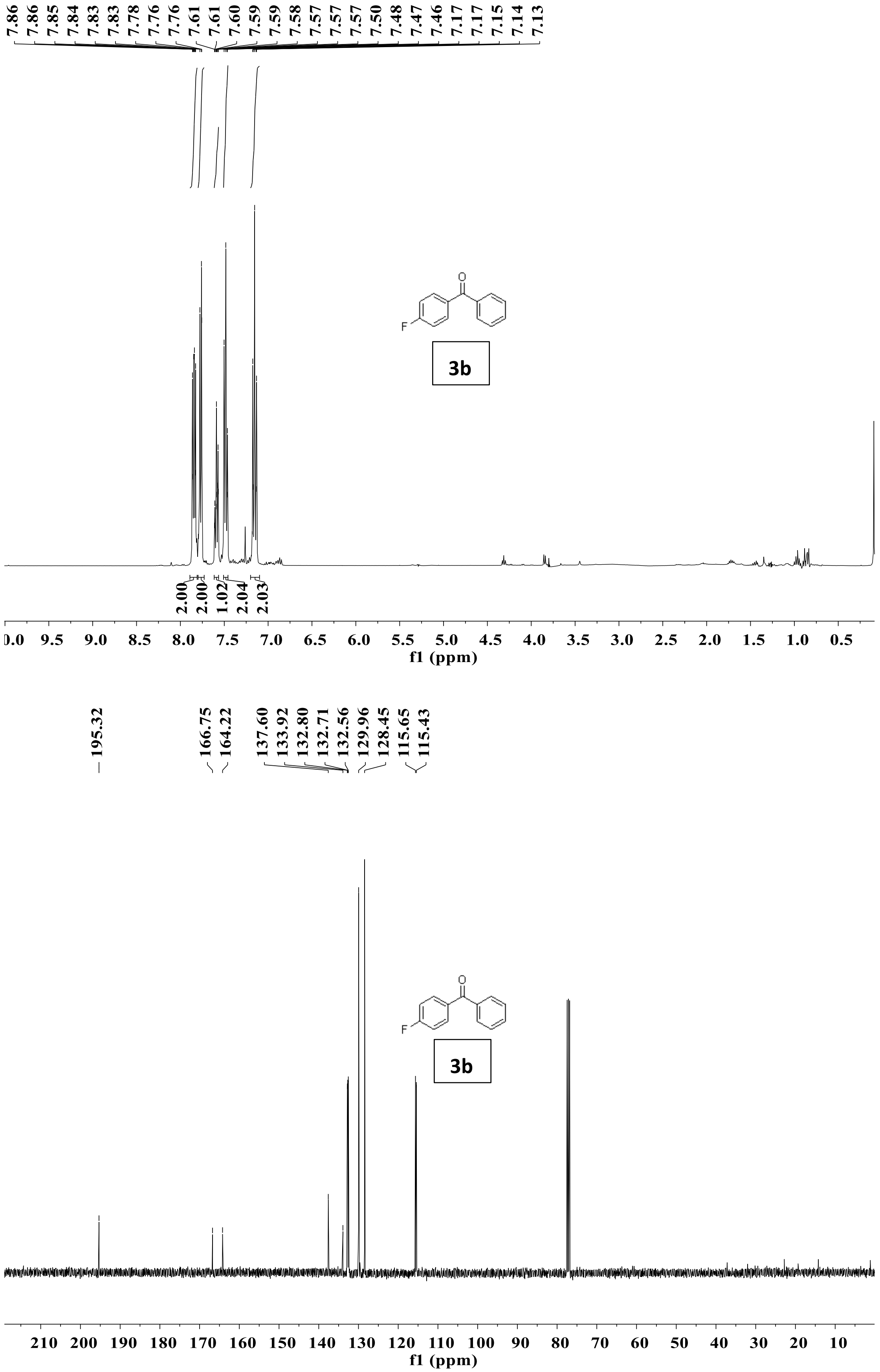
**1,2-Phenylenebis(phenylmethanone) (5c)**. General Method with 1,2-diiodobenzene and phenylboronic acid gave 0.0434 g (35 % yield) of the title compound. $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.70 (d, $J$ = 7.3 Hz, 4H), 7.62 (s, 4H), 7.52 (t, $J$ = 7.4 Hz, 2H), 7.37 (t, $J$ = 7.7 Hz, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm): 196.57, 140.02, 137.20, 132.98, 130.35, 129.83, 129.66, 128.32.

## 10. Copies of $^1$H-NMR and $^{13}$C-NMR Spectra (Representative Data; note that some impurities are seen by $^1$H NMR for these relatively non-polar compounds).

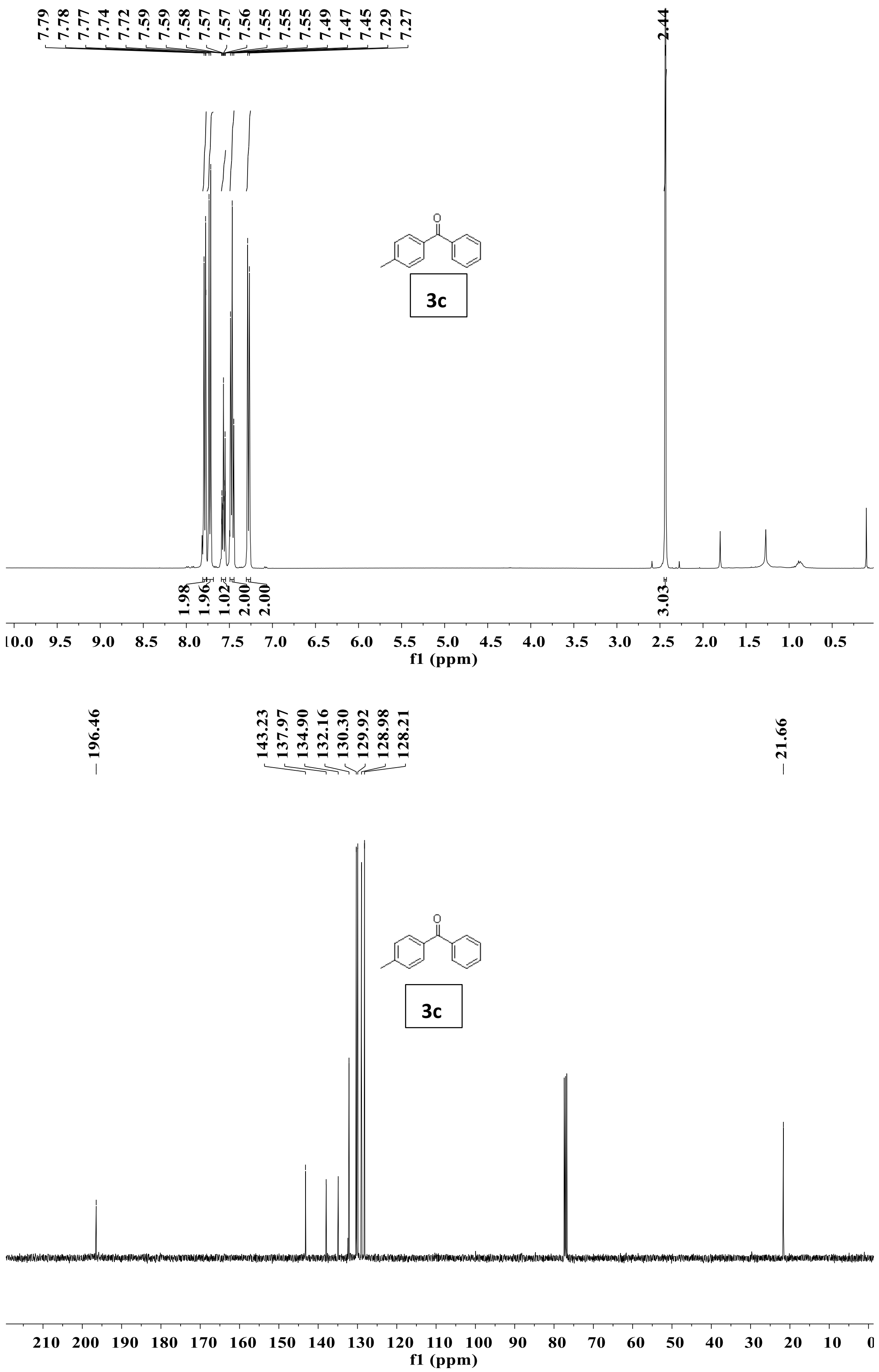




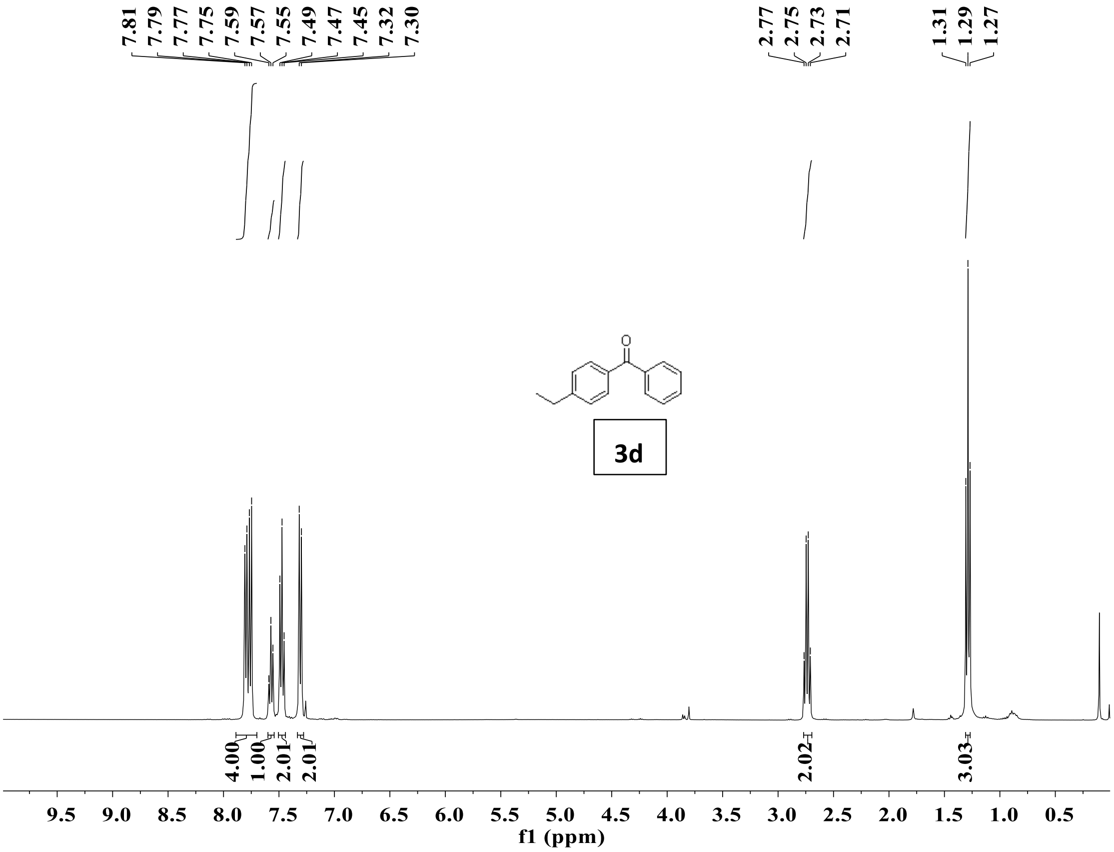
$^1$H **NMR** (400 MHz) and $^{13}$C{$^1$H} **NMR** (101 MHz) spectra of 1-(4-benzoylphenyl)ethan-1-one (CDCl$_3$).

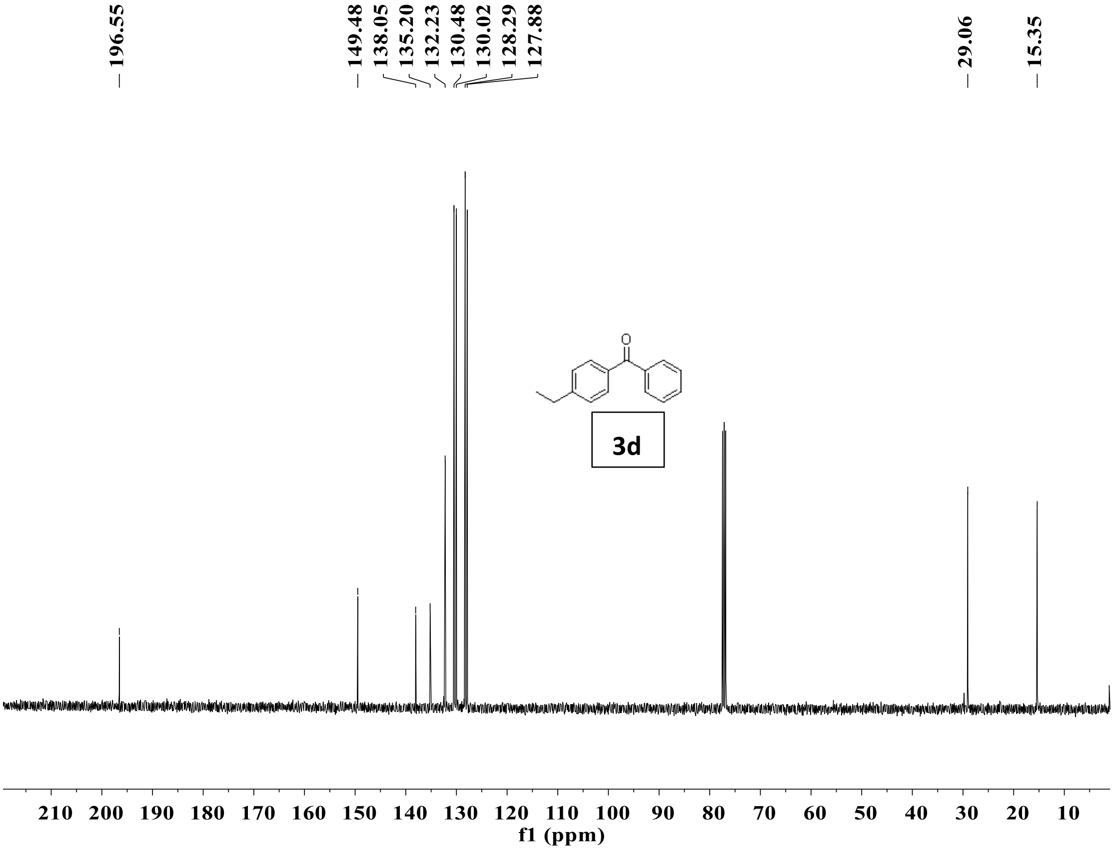


$^1$H **NMR** (400 MHz) and $^{13}$C{$^1$H} **NMR** (101 MHz) spectra of (4-fluorophenyl)(phenyl)methanone ($CDCl_3$).

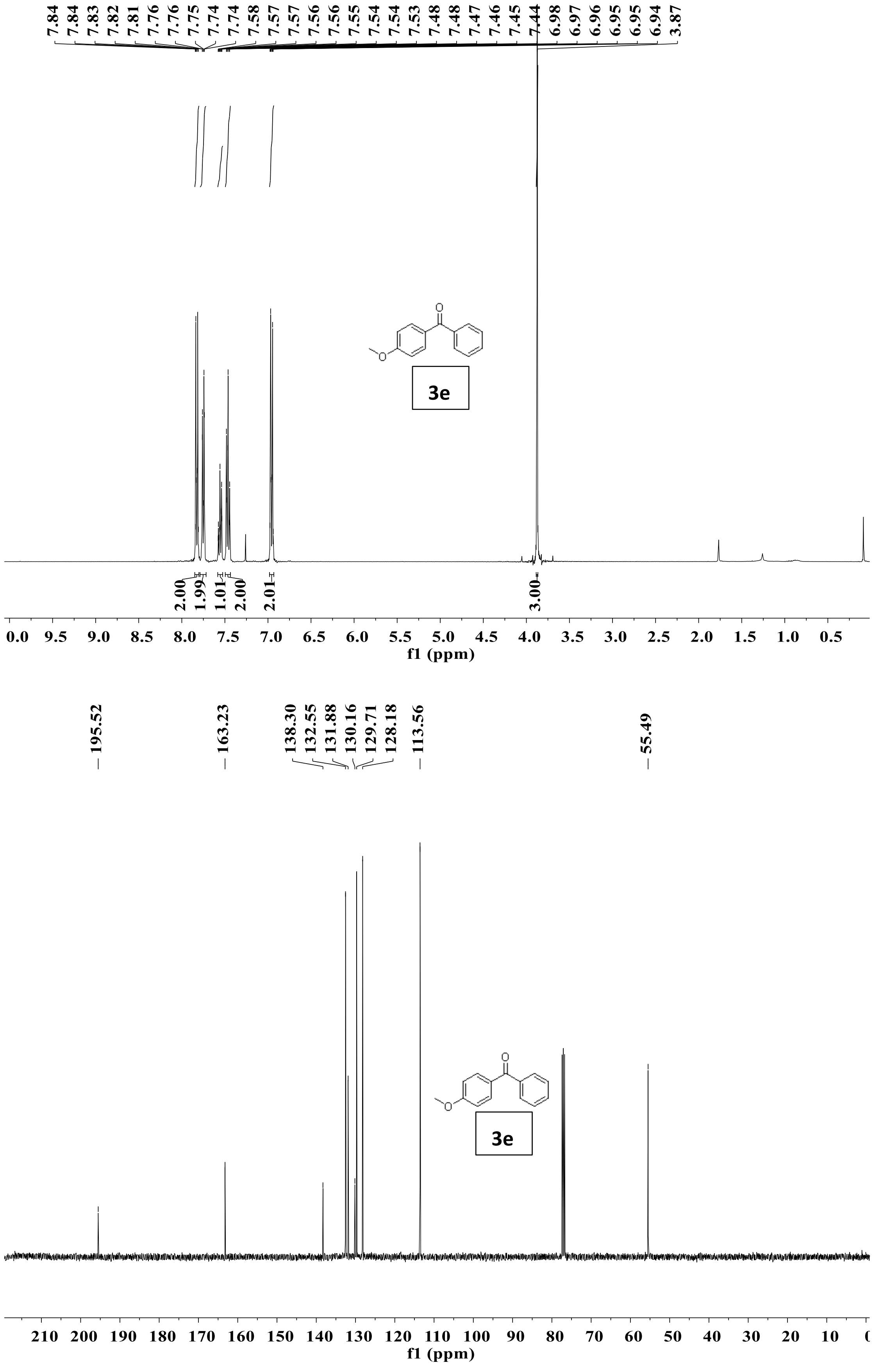


$^1$H **NMR** (400 MHz) and $^{13}$C{$^1$H} **NMR** (101 MHz) spectra of phenyl(p-tolyl)methanone ($CDCl_3$).

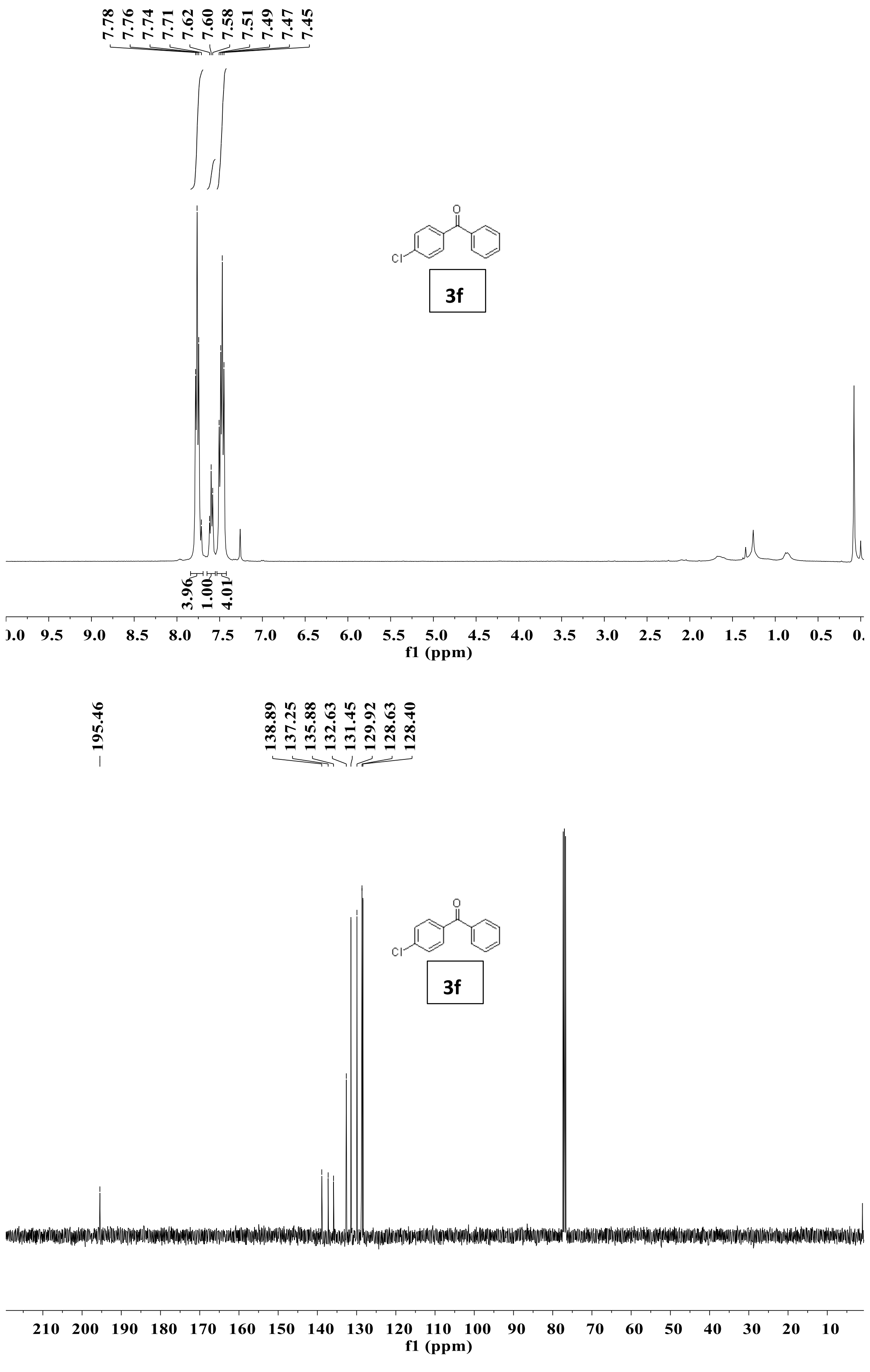




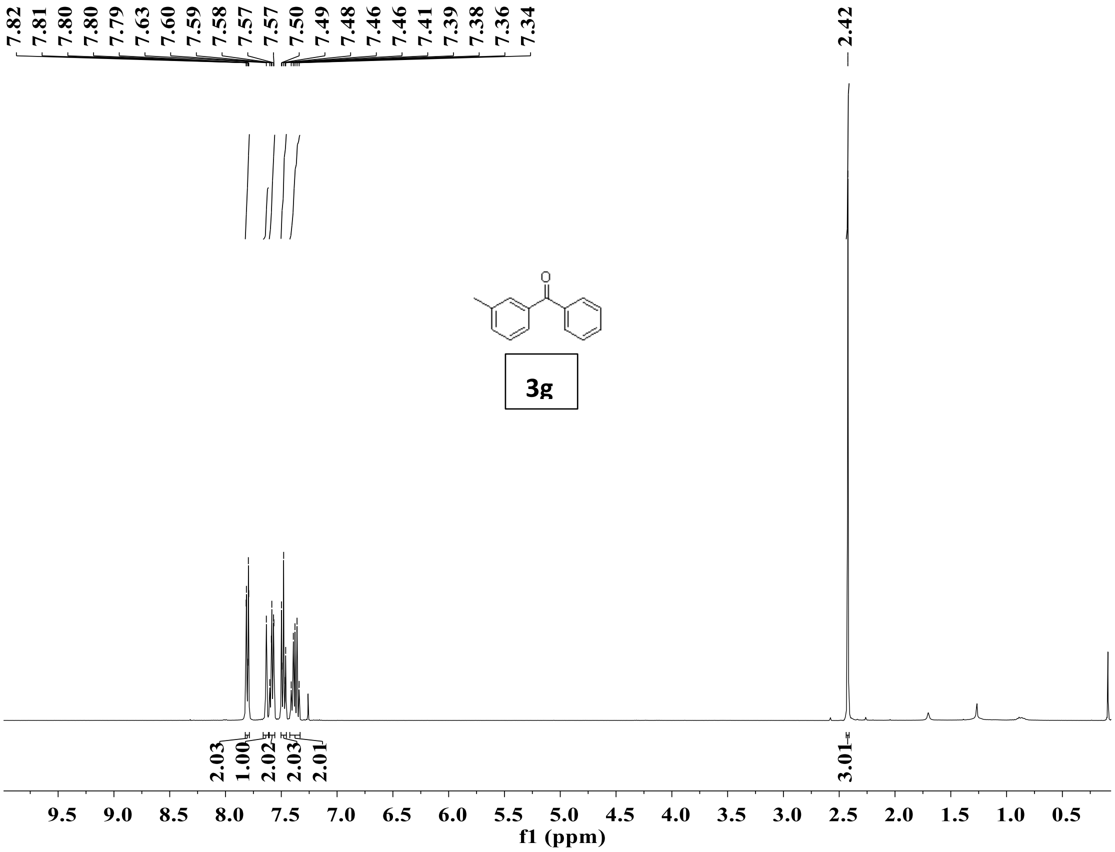
$^1$H **NMR** (400 MHz) and $^{13}$C{$^1$H} **NMR** (101 MHz) spectra of (4-ethylphenyl)(phenyl)methanone (CDCl$_3$).

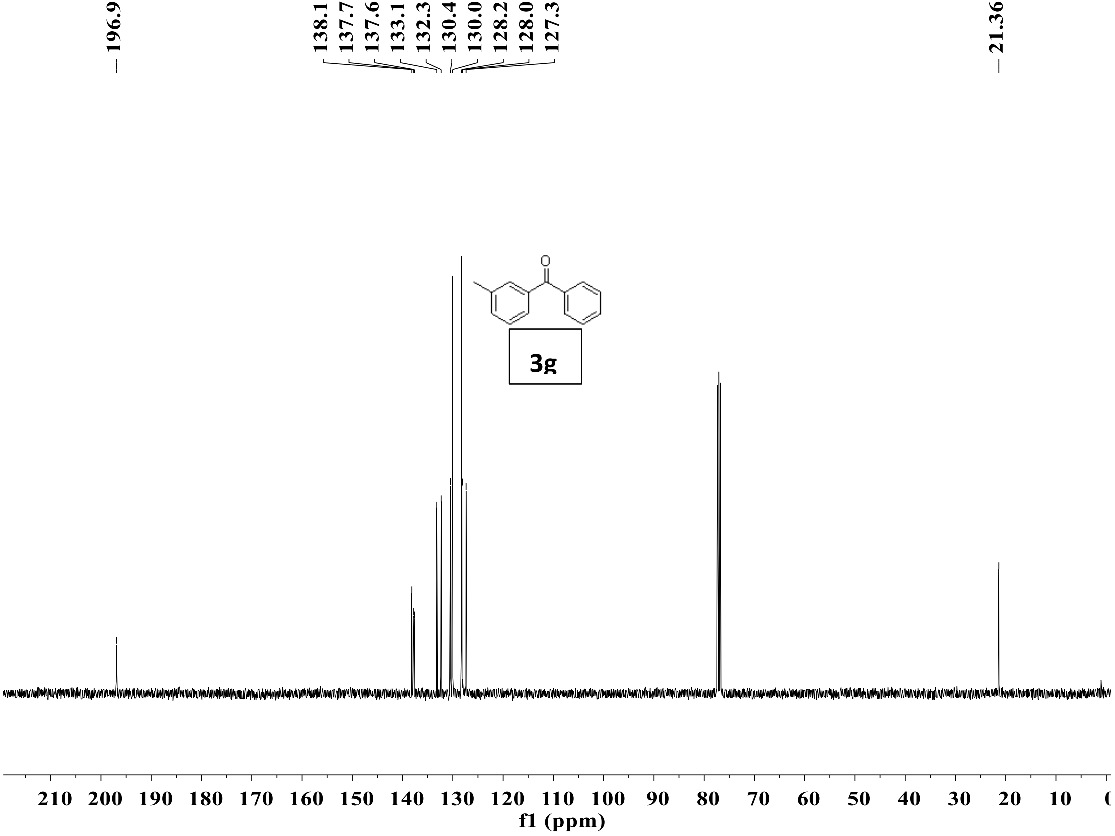


$^1$H **NMR** (400 MHz) and $^{13}$C{$^1$H} **NMR** (101 MHz) spectra of (4-methoxyphenyl)(phenyl)methanone (CDCl$_3$).

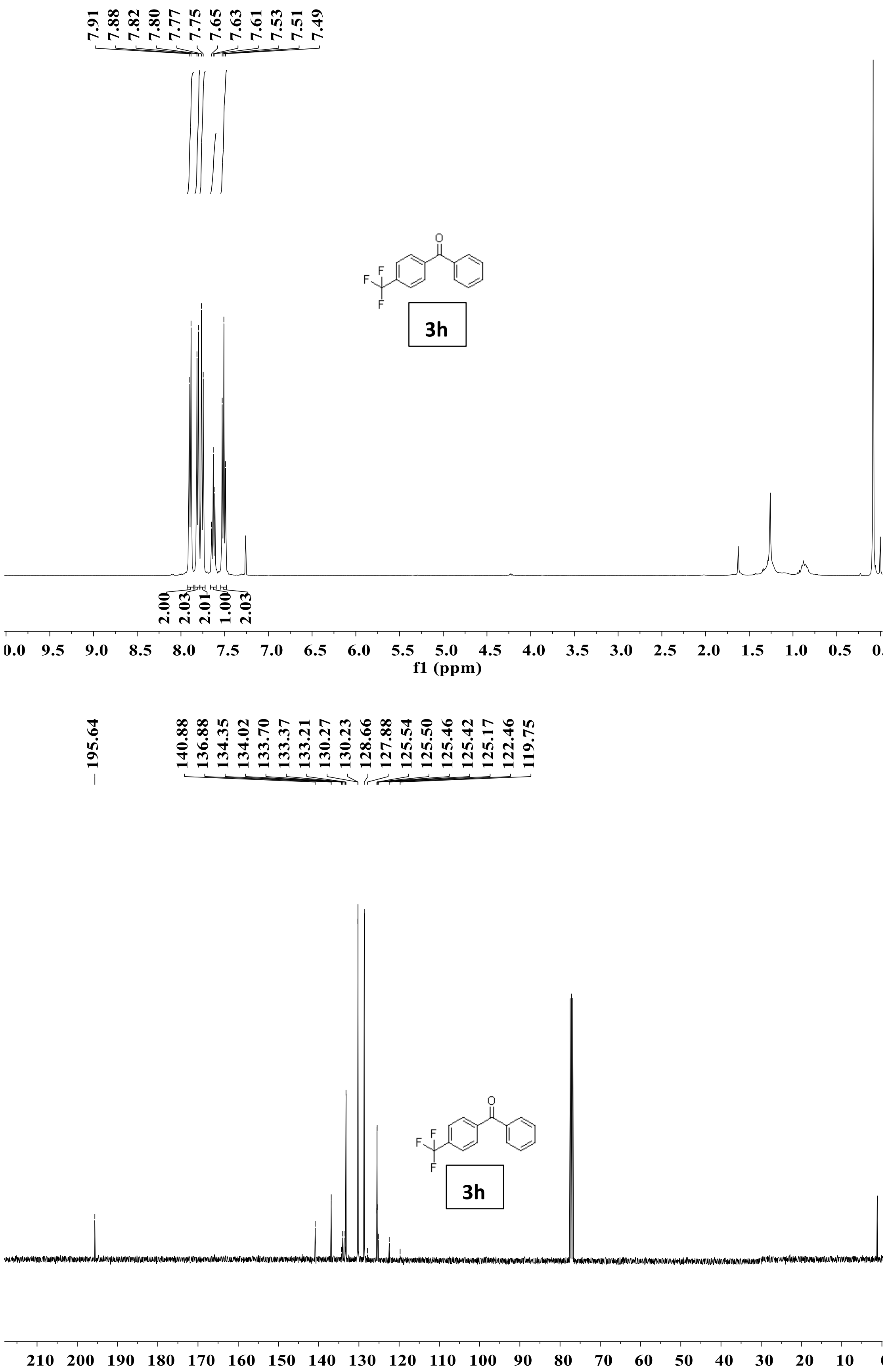


$^1$H **NMR** (400 MHz) and $^{13}$C{$^1$H} **NMR** (101 MHz) spectra of (4-chlorophenyl)(phenyl)methanone ($CDCl_3$).

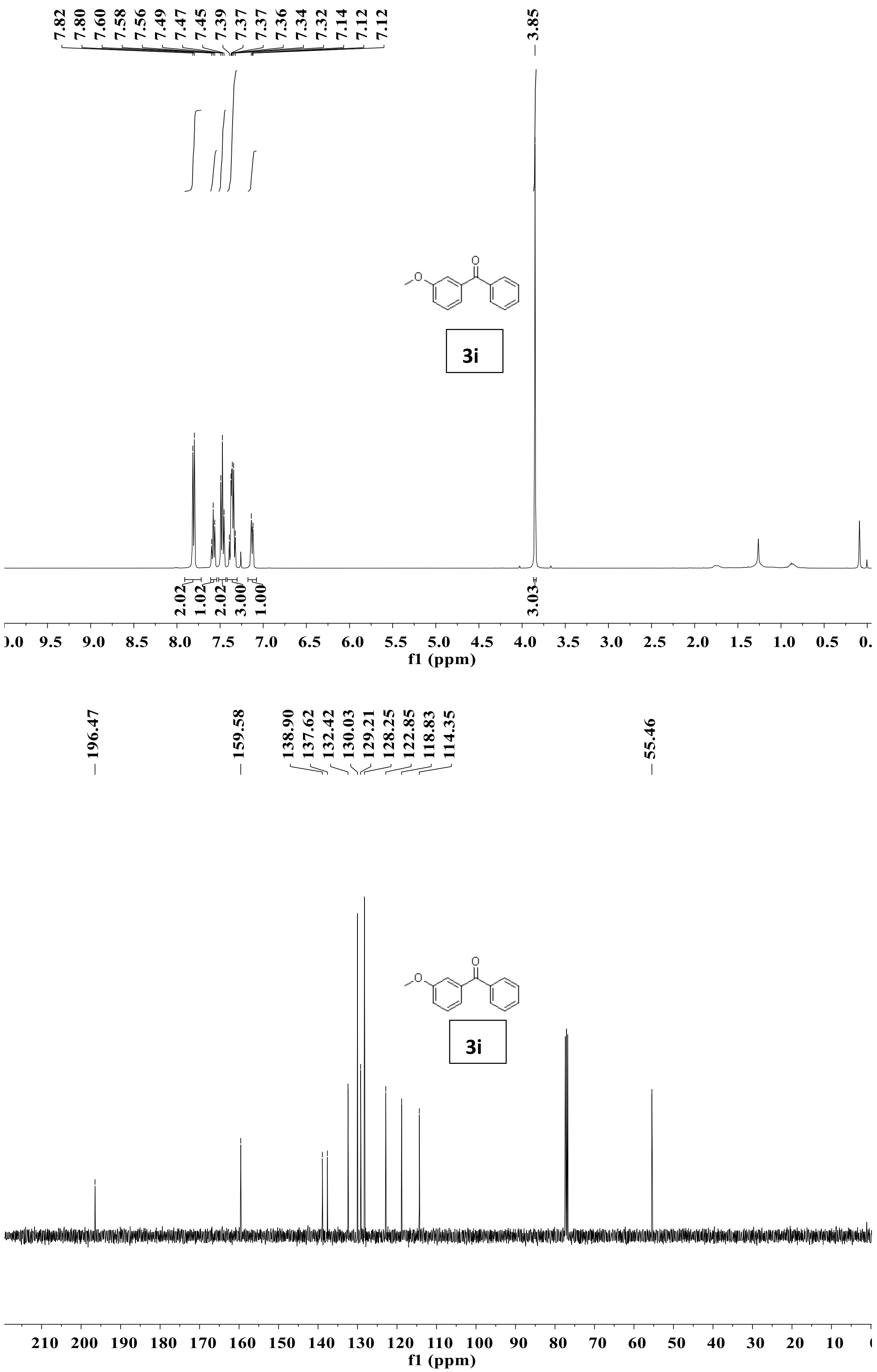




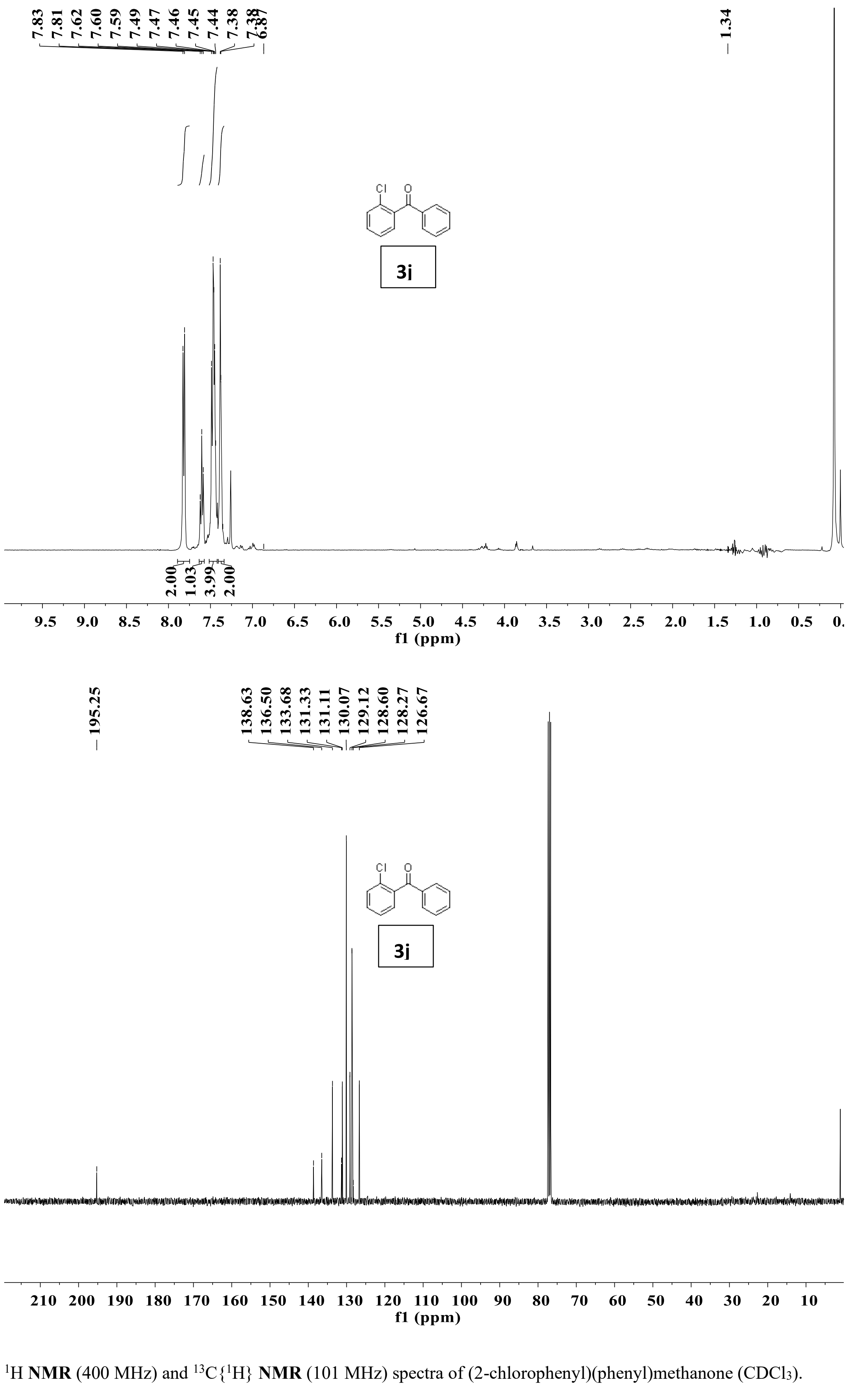
$^{1}$H **NMR** (400 MHz) and $^{13}$C{$^{1}$H} **NMR** (101 MHz) spectra of phenyl(3-tolyl)methanone (CDCl$_3$).



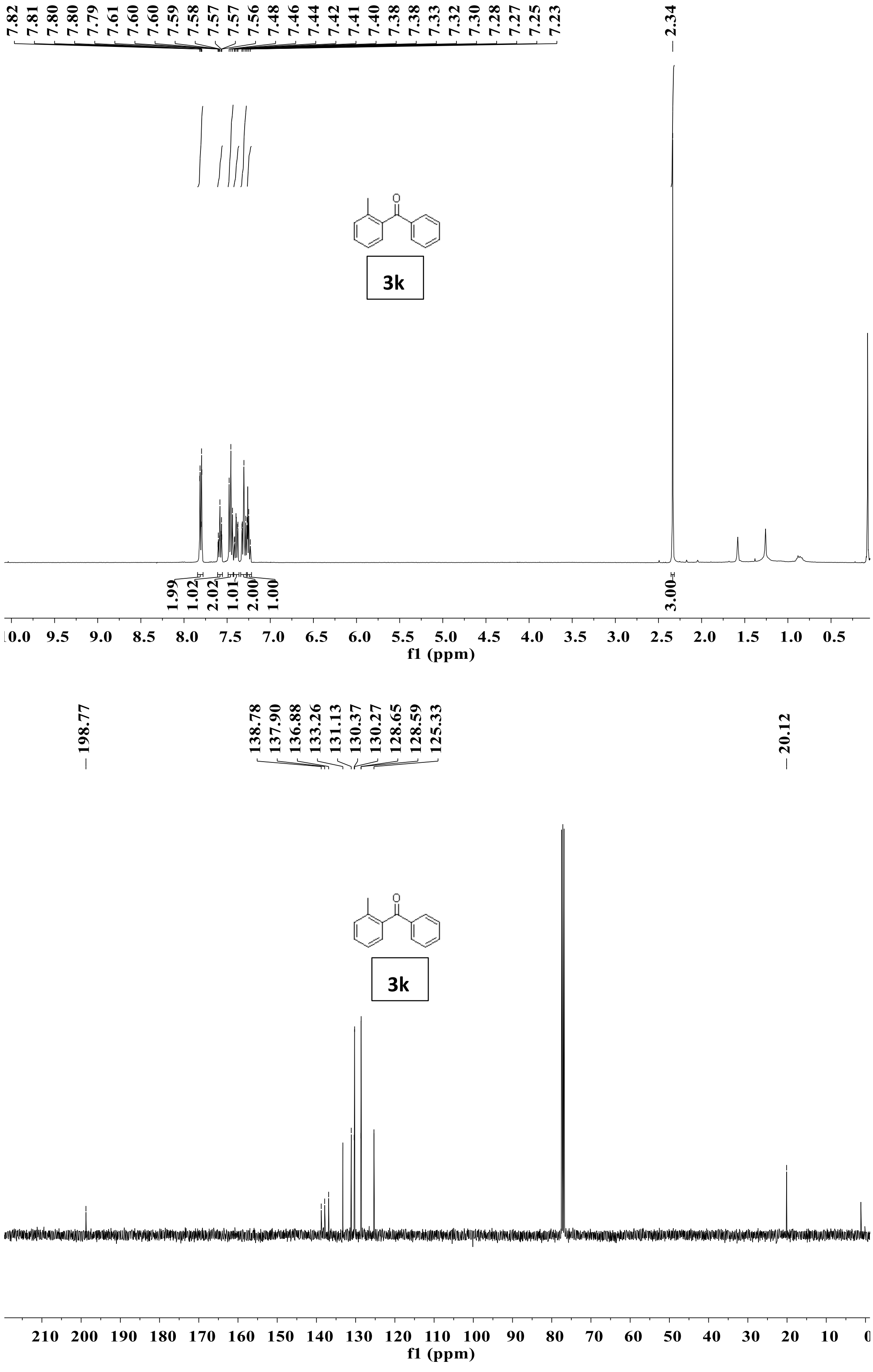
$^{1}$H (400 MHz) and $^{13}$C{$^{1}$H} (101 MHz) **NMR** spectra of phenyl(4-(trifluoromethyl)phenyl)methanone ($CDCl_3$).



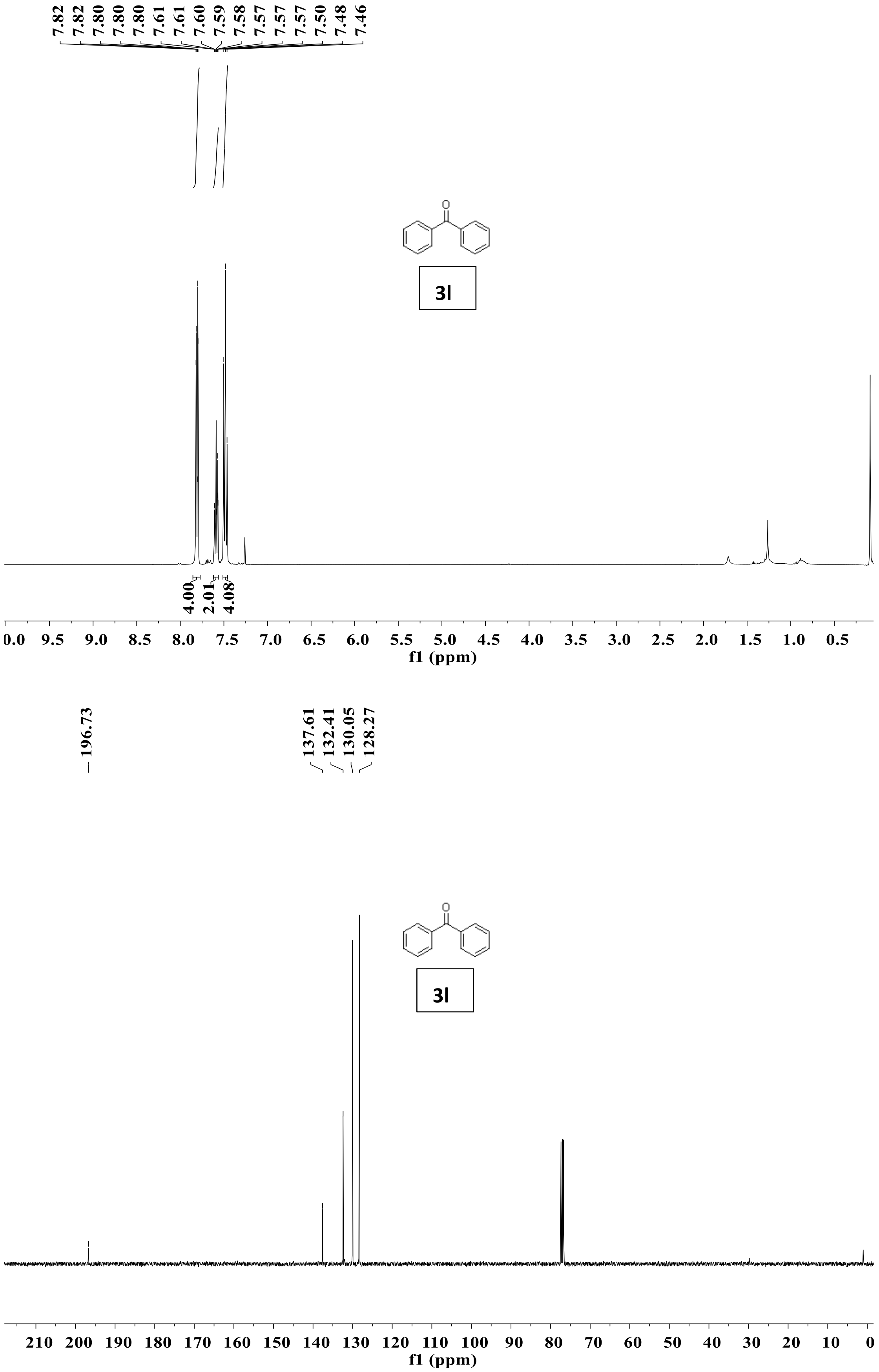
$^{1}$H **NMR** (400 MHz) and $^{13}$C{$^{1}$H} **NMR** (101 MHz) spectra of (3-methoxyphenyl)(phenyl)methanone (CDCl$_3$).



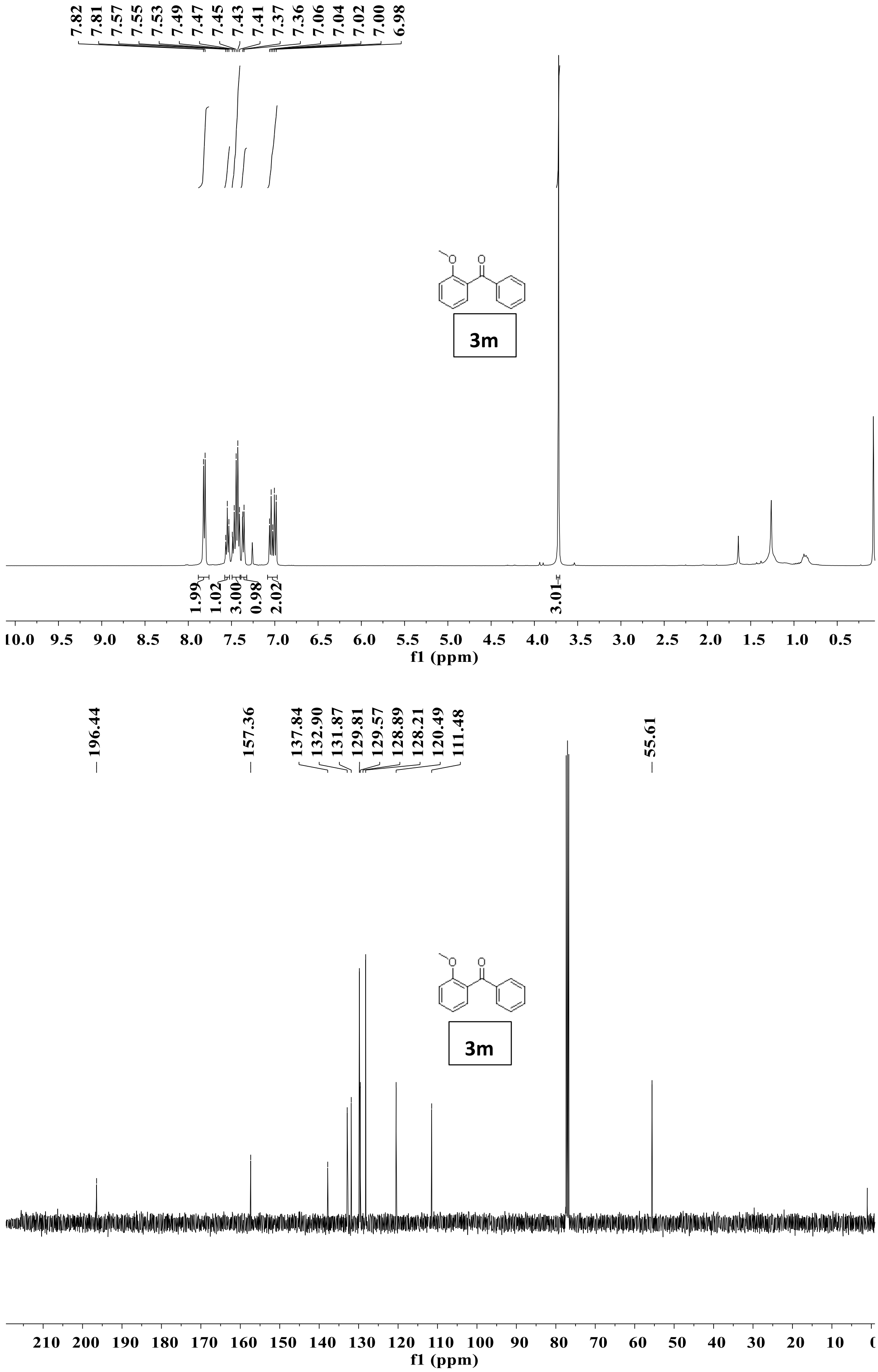
$^{1}$H **NMR** (400 MHz) and $^{13}$C{$^{1}$H} **NMR** (101 MHz) spectra of (2-chlorophenyl)(phenyl)methanone ($CDCl_3$).



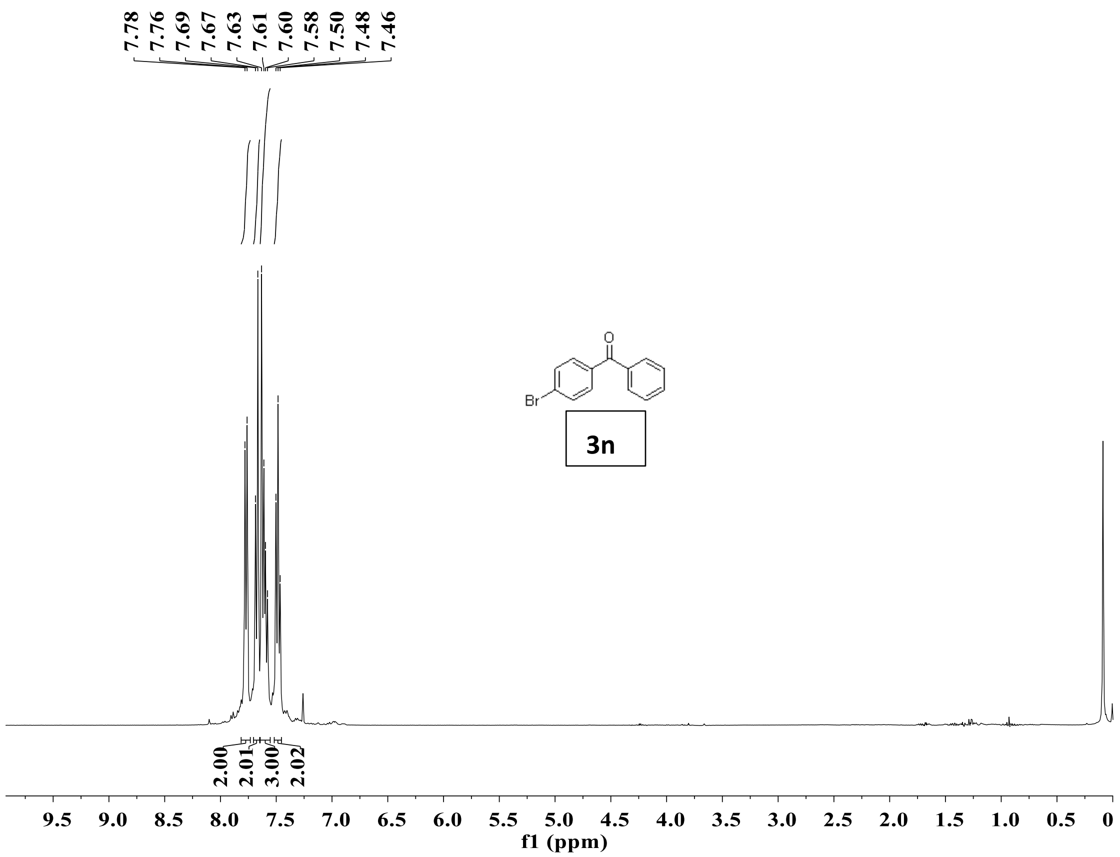
$^1$H **NMR** (400 MHz) and $^{13}$C{$^1$H} **NMR** (101 MHz) spectra of phenyl(2-tolyl)methanone ($CDCl_3$).

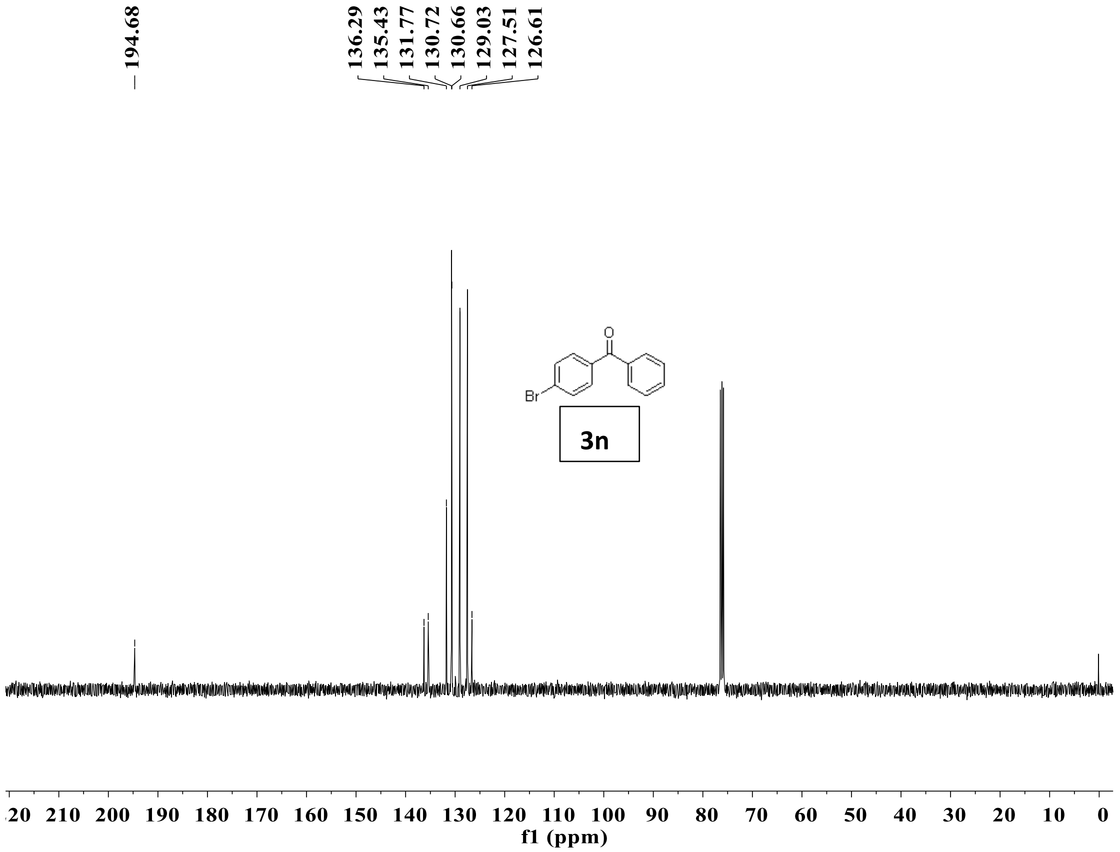


$^1$H **NMR** (400 MHz) and $^{13}$C{$^1$H} **NMR** (101 MHz) spectra of benzophenone (CDCl$_3$).

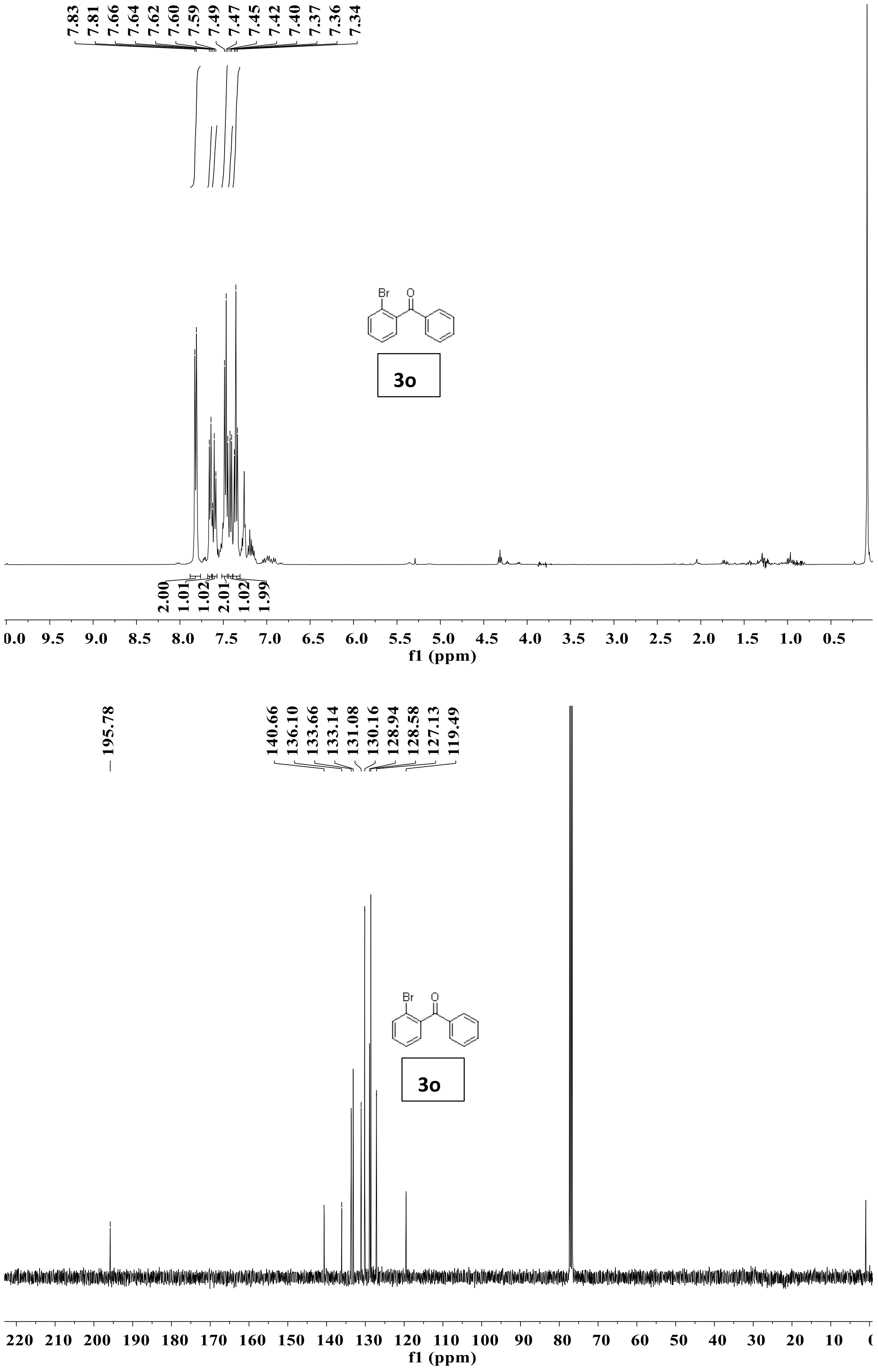


$^1$H **NMR** (400 MHz) and $^{13}$C{$^1$H} **NMR** (101 MHz) spectra of (2-methoxyphenyl)(phenyl)methanone ($CDCl_3$).

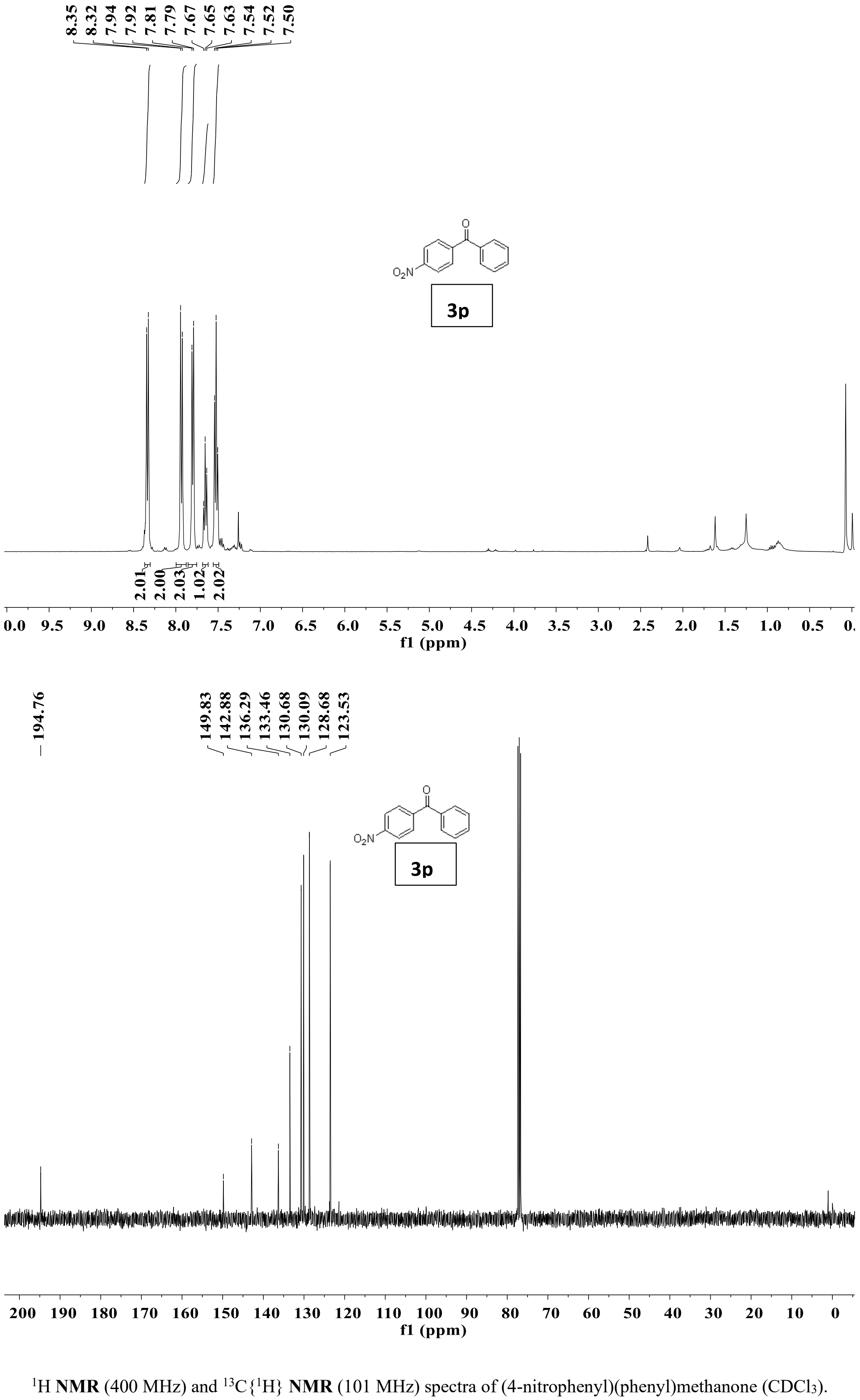




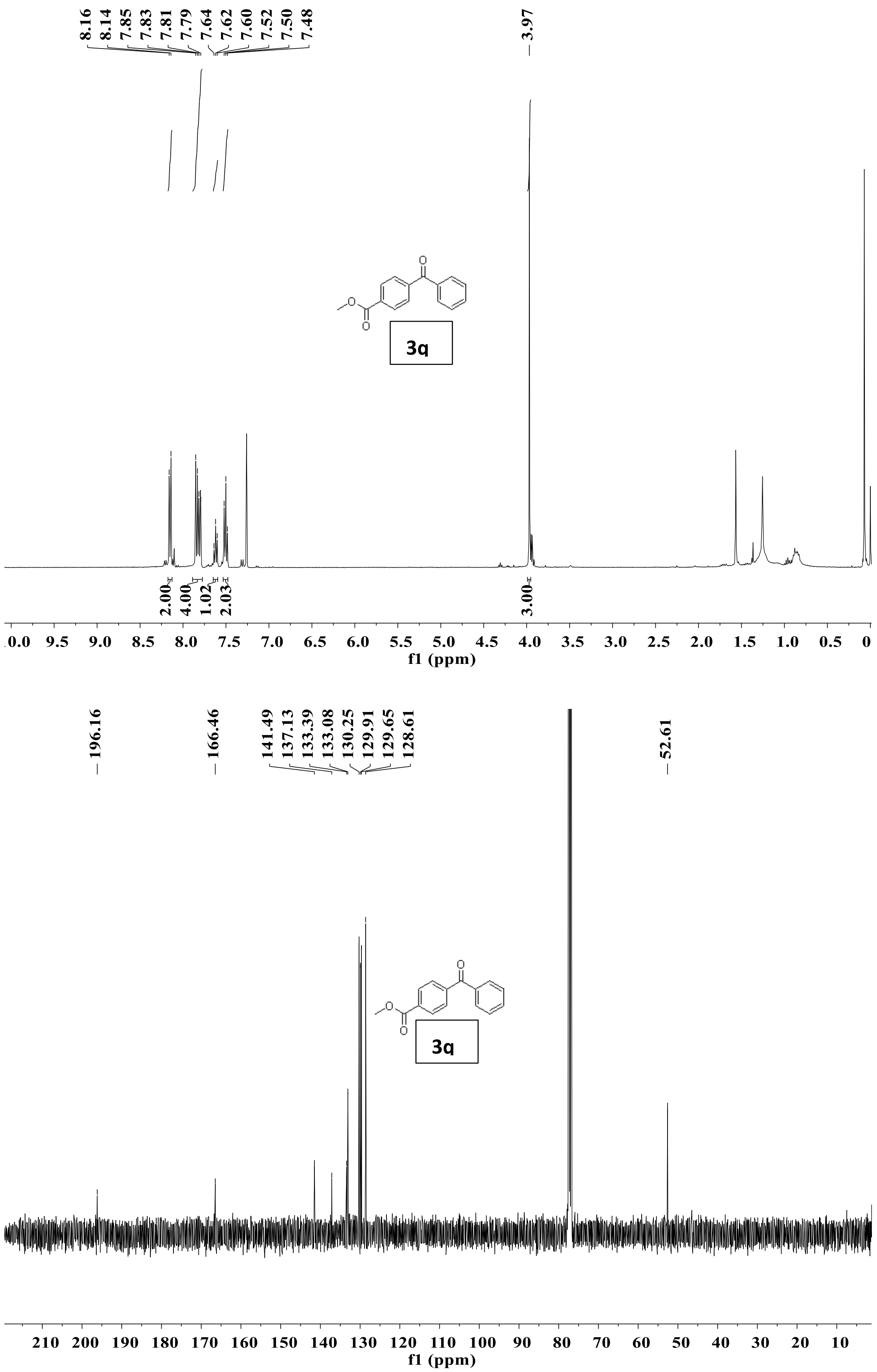
$^1$H **NMR** (400 MHz) and $^{13}$C{$^1$H} **NMR** (101 MHz) spectra of (4-bromophenyl)(phenyl)methanone (CDCl$_3$).



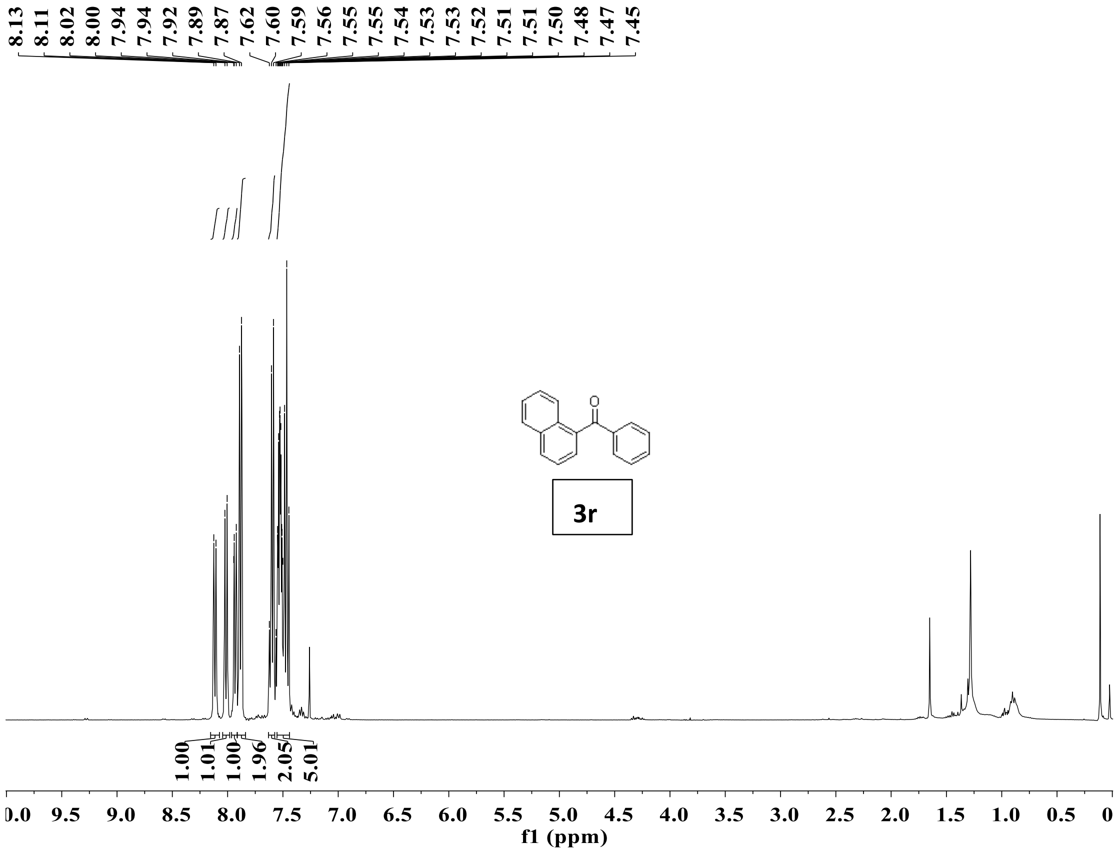
$^{1}$H **NMR** (400 MHz) and $^{13}$C{$^{1}$H} **NMR** (101 MHz) spectra of (2-bromophenyl)(phenyl)methanone (CDCl$_3$).

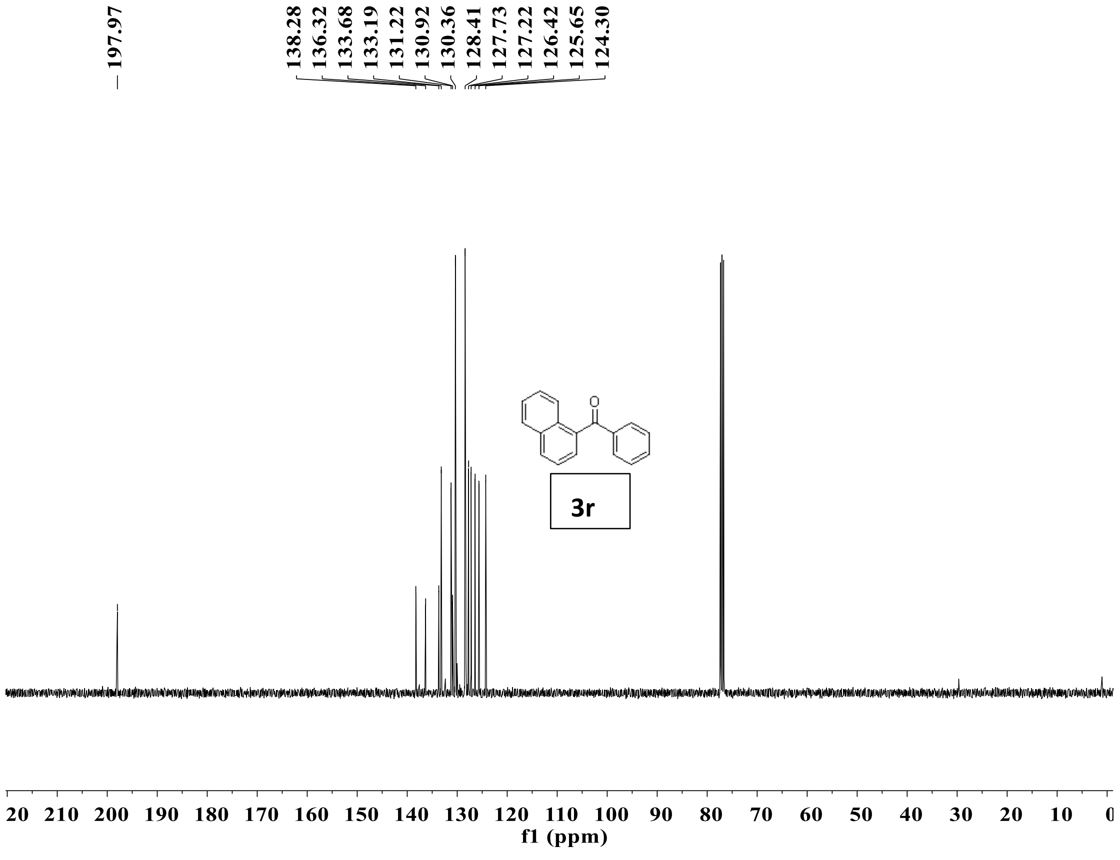


$^{1}$H **NMR** (400 MHz) and $^{13}$C{$^{1}$H} **NMR** (101 MHz) spectra of (4-nitrophenyl)(phenyl)methanone (CDCl$_3$).

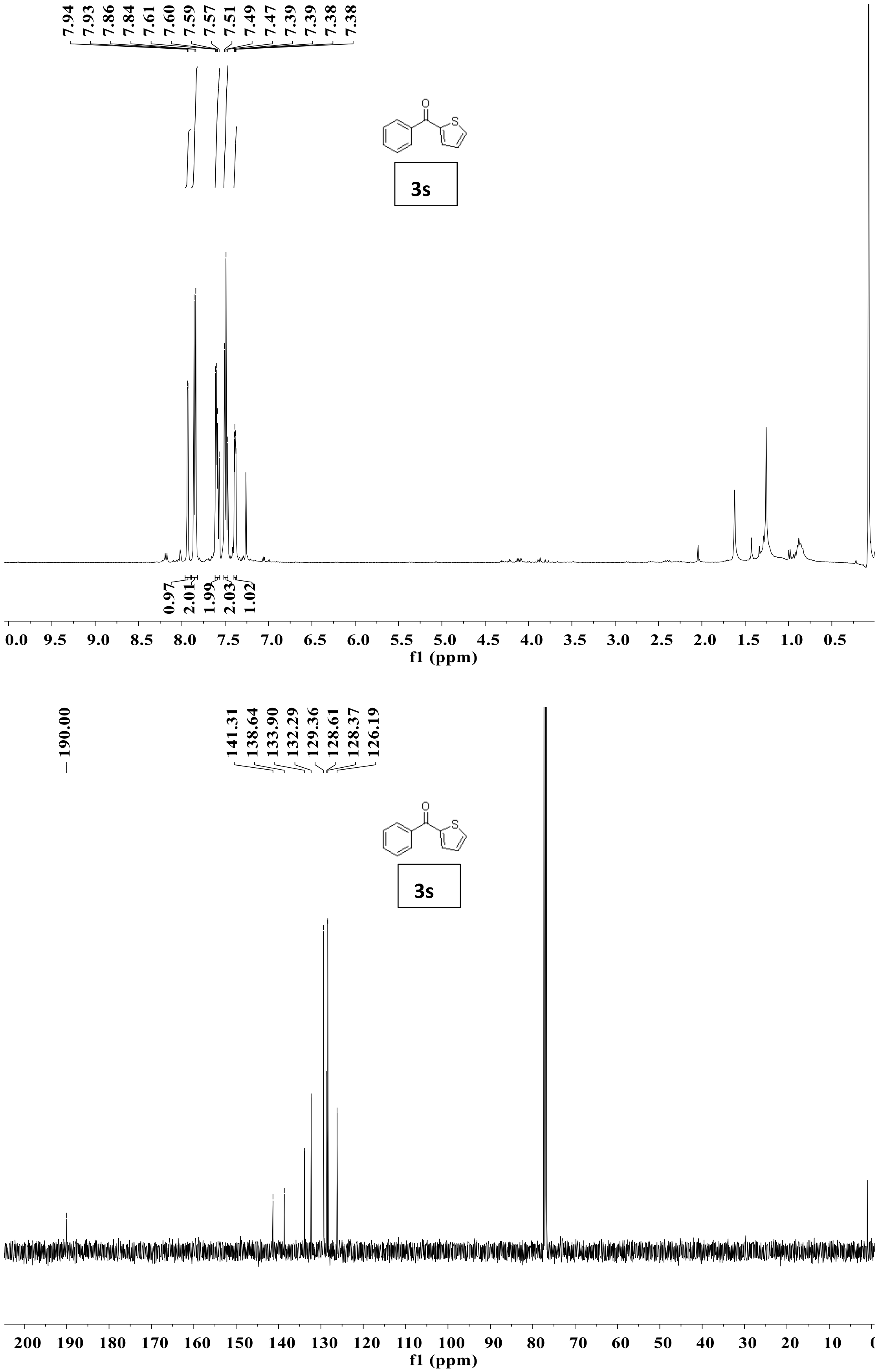


$^{1}$H **NMR** (400 MHz) and $^{13}$C{$^{1}$H} **NMR** (101 MHz) spectra of methyl 4-benzoylbenzoate ($CDCl_3$).

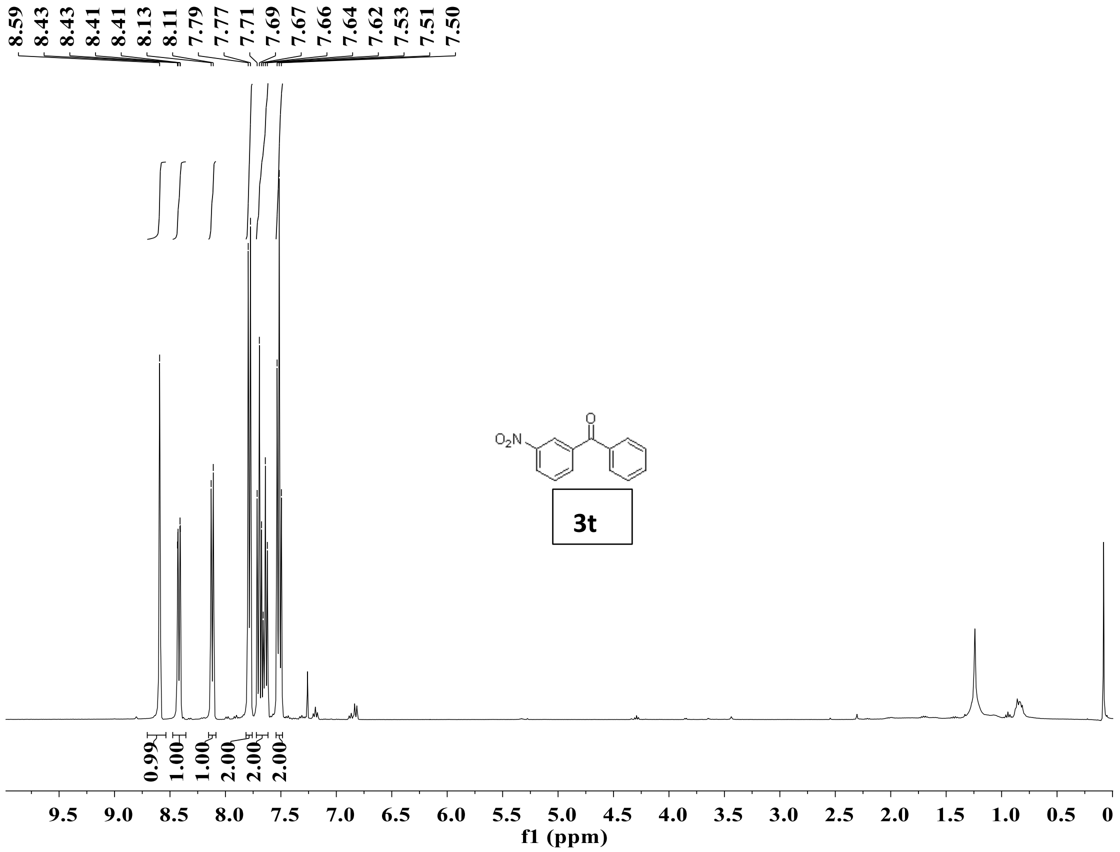


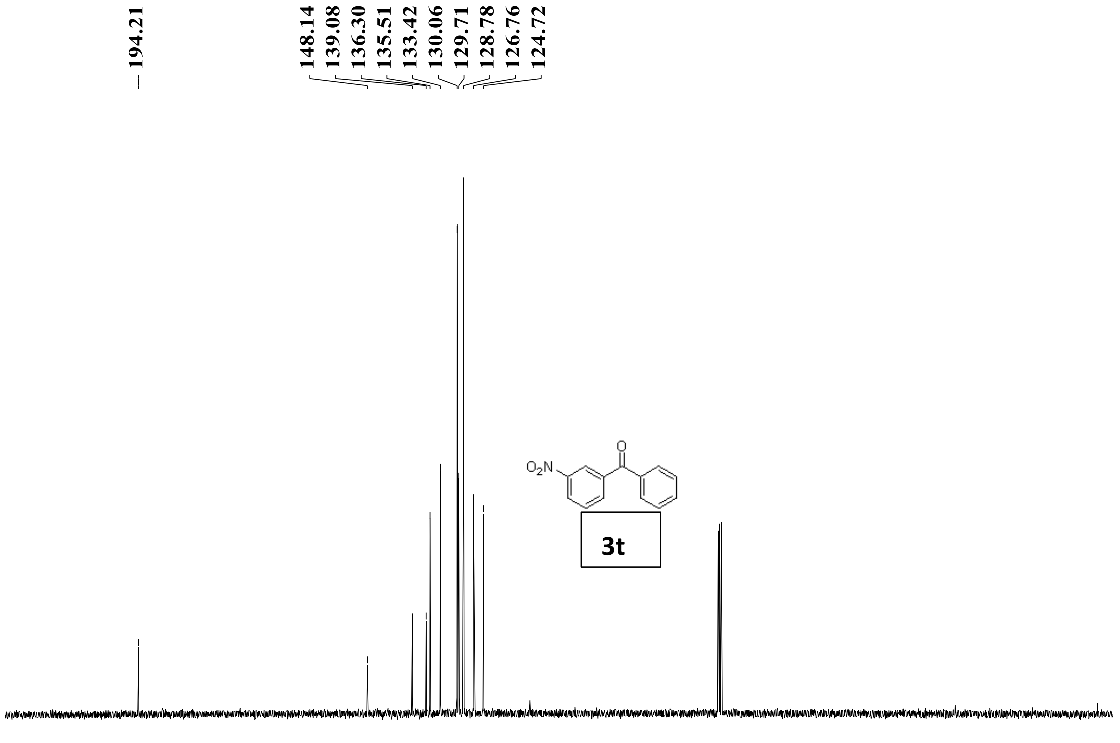


$^{1}$H **NMR** (400 MHz) and $^{13}$C{$^{1}$H} **NMR** (101 MHz) spectra of naphthalen-1-yl(phenyl)methanone (CDCl$_3$).

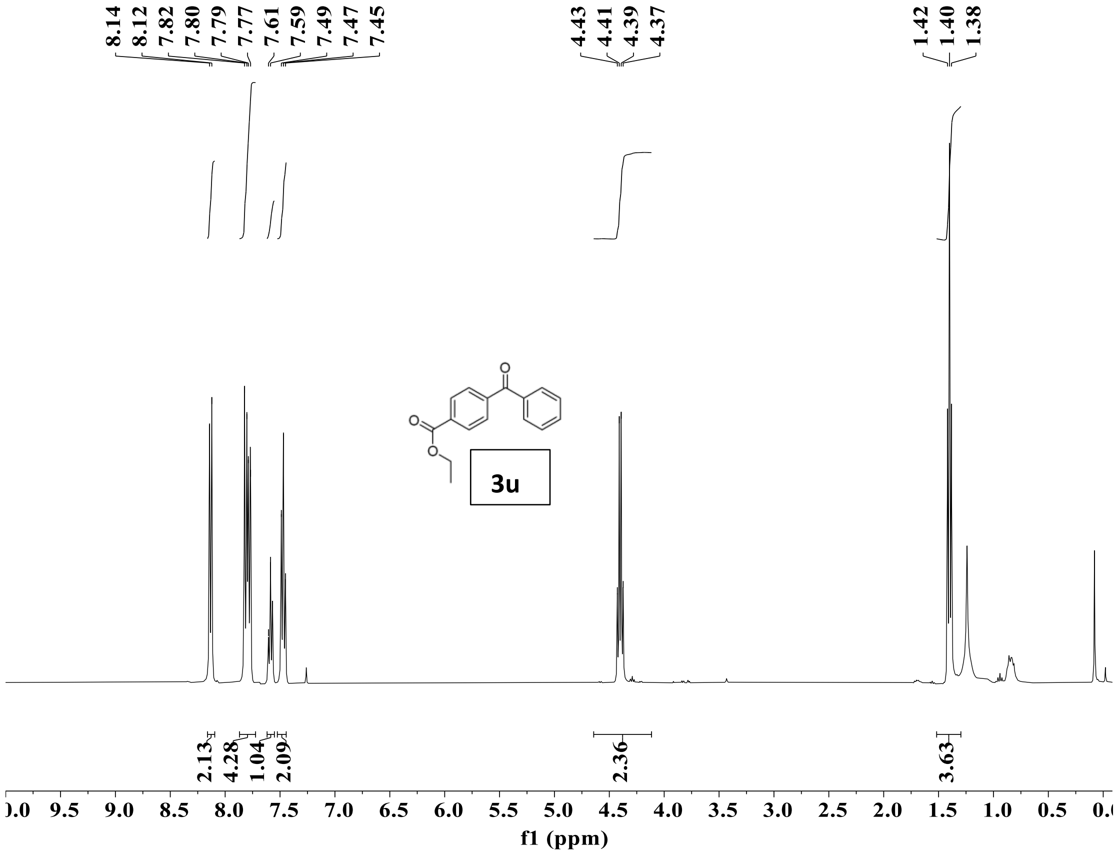


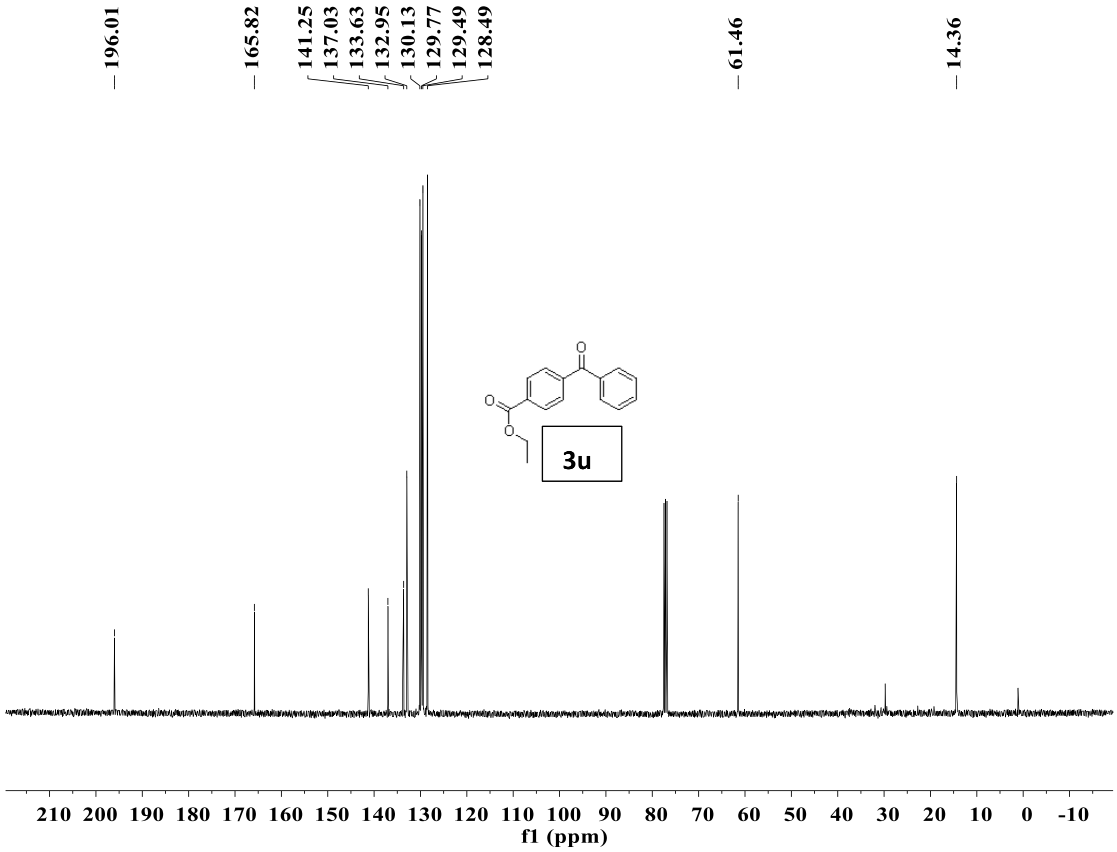
$^1$H **NMR** (400 MHz) and $^{13}$C{$^1$H} **NMR** (101 MHz) spectra of phenyl(thiophen-2-yl)methanone (CDCl$_3$).



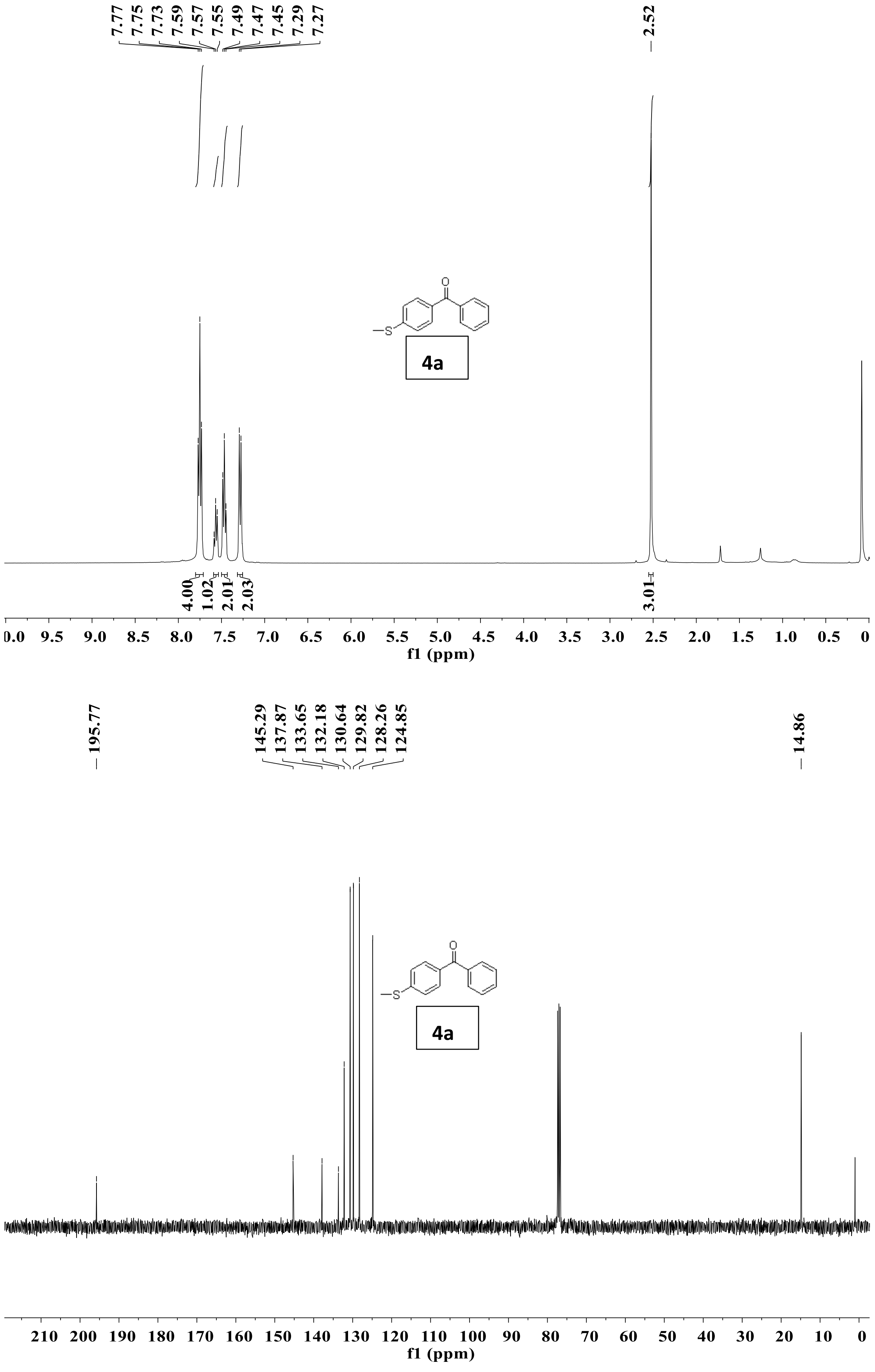


$^1$H **NMR** (400 MHz) and $^{13}$C{$^1$H} **NMR** (101 MHz) spectra of (3-nitrophenyl)(phenyl)methanone ($CDCl_3$).

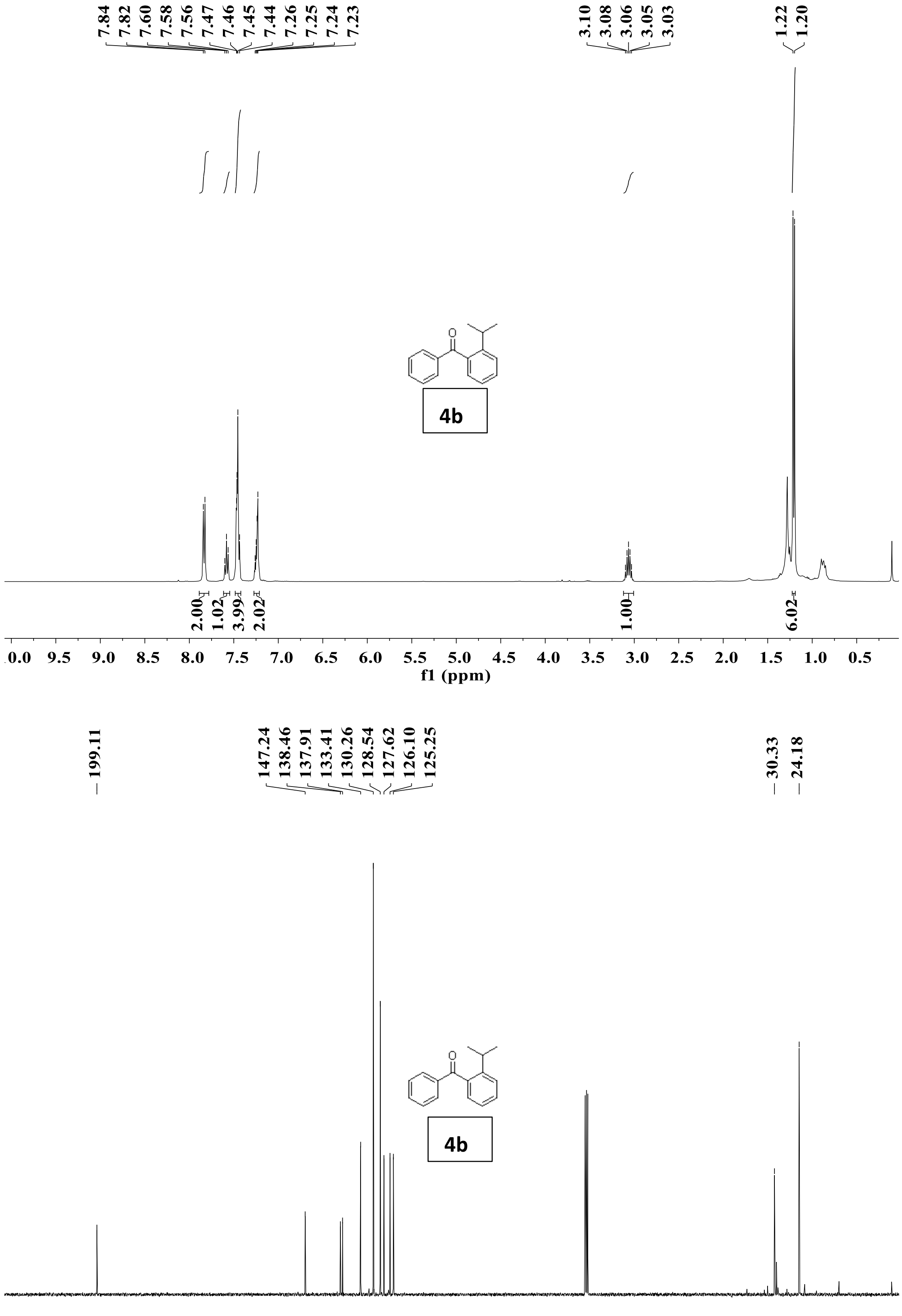




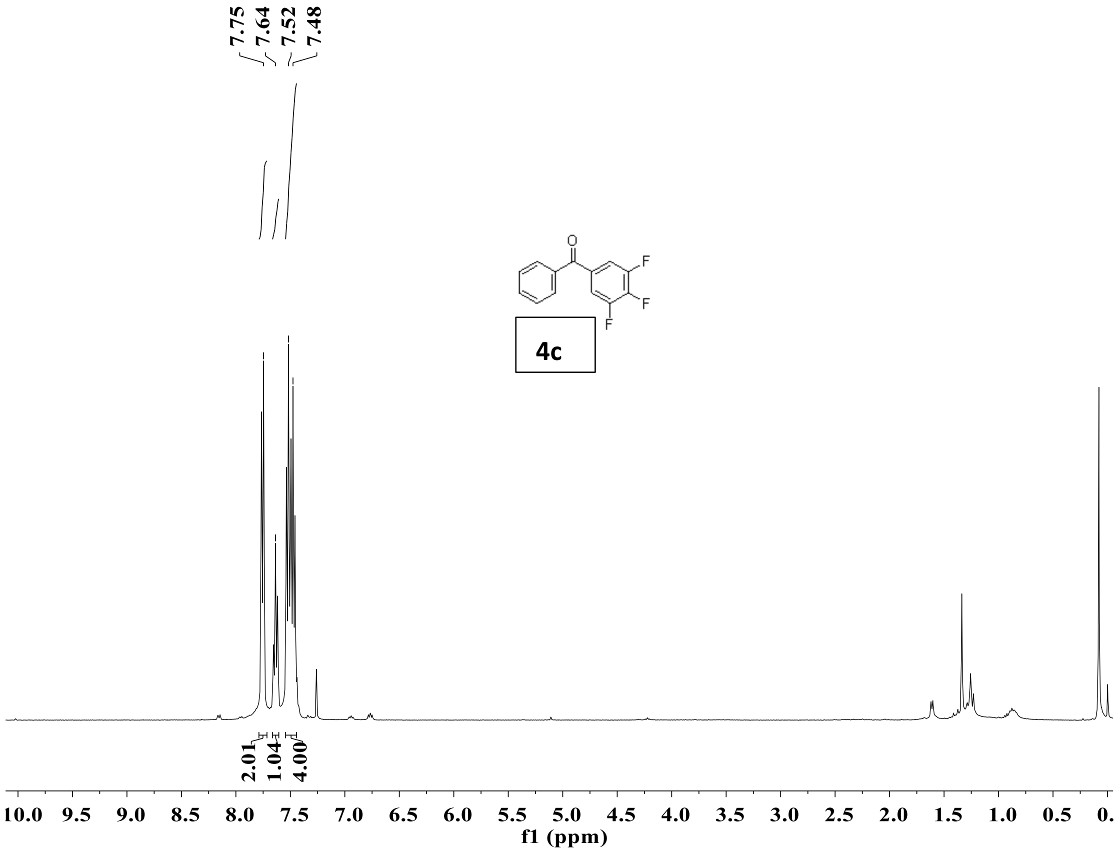
$^1$H **NMR** (400 MHz) and $^{13}$C{$^1$H} **NMR** (101 MHz) spectra of 4-benzoylphenyl propionate (CDCl$_3$).

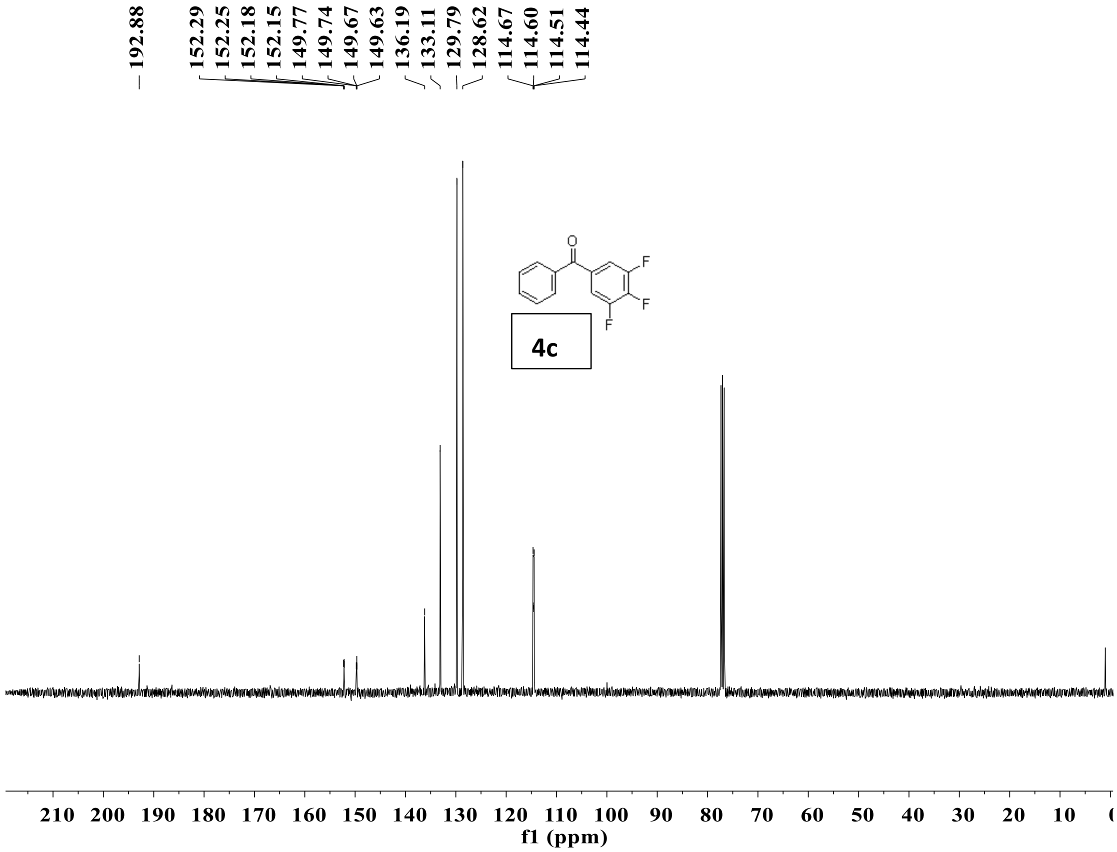


$^1$H (400 MHz) and $^{13}$C{$^1$H} (101 MHz) **NMR** spectra of (4-(methylthio)phenyl)(phenyl)methanone (CDCl$_3$).

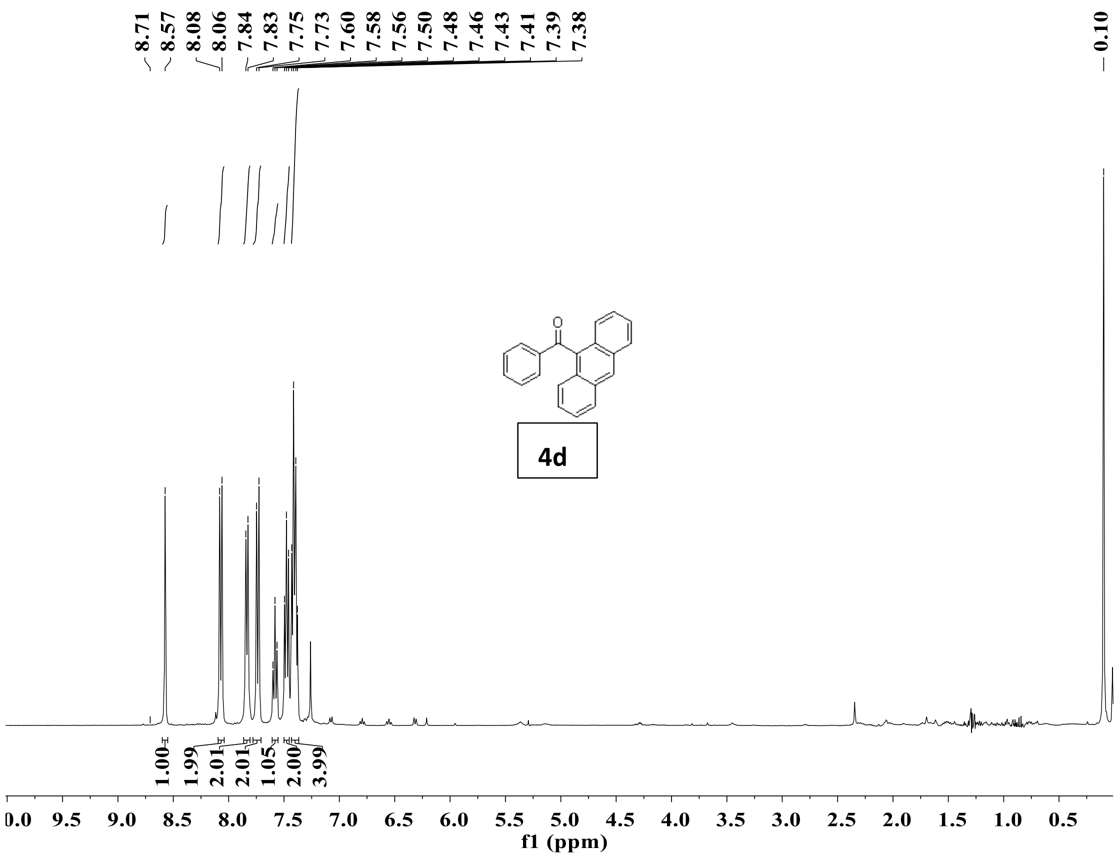


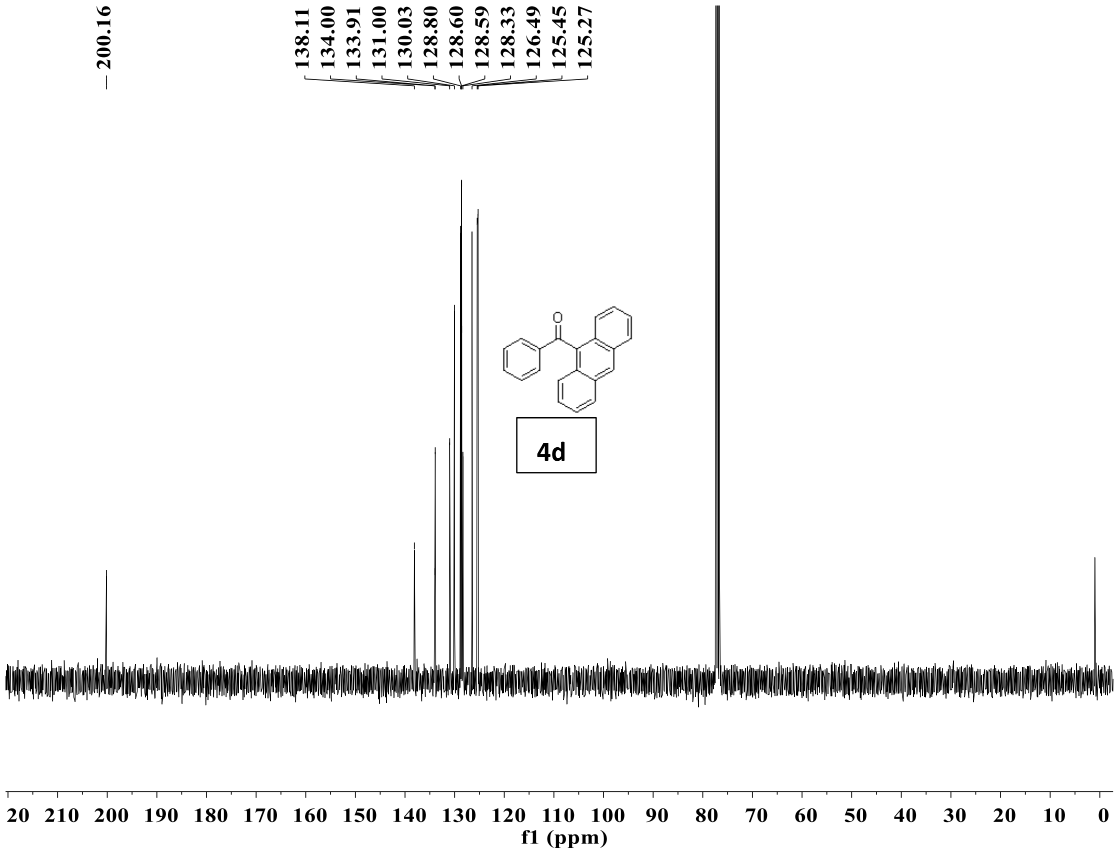
$^1$H **NMR** (400 MHz) and $^{13}$C{$^1$H} **NMR** (101 MHz) spectra of (2-isopropylphenyl)(phenyl)methanone (CDCl$_3$).



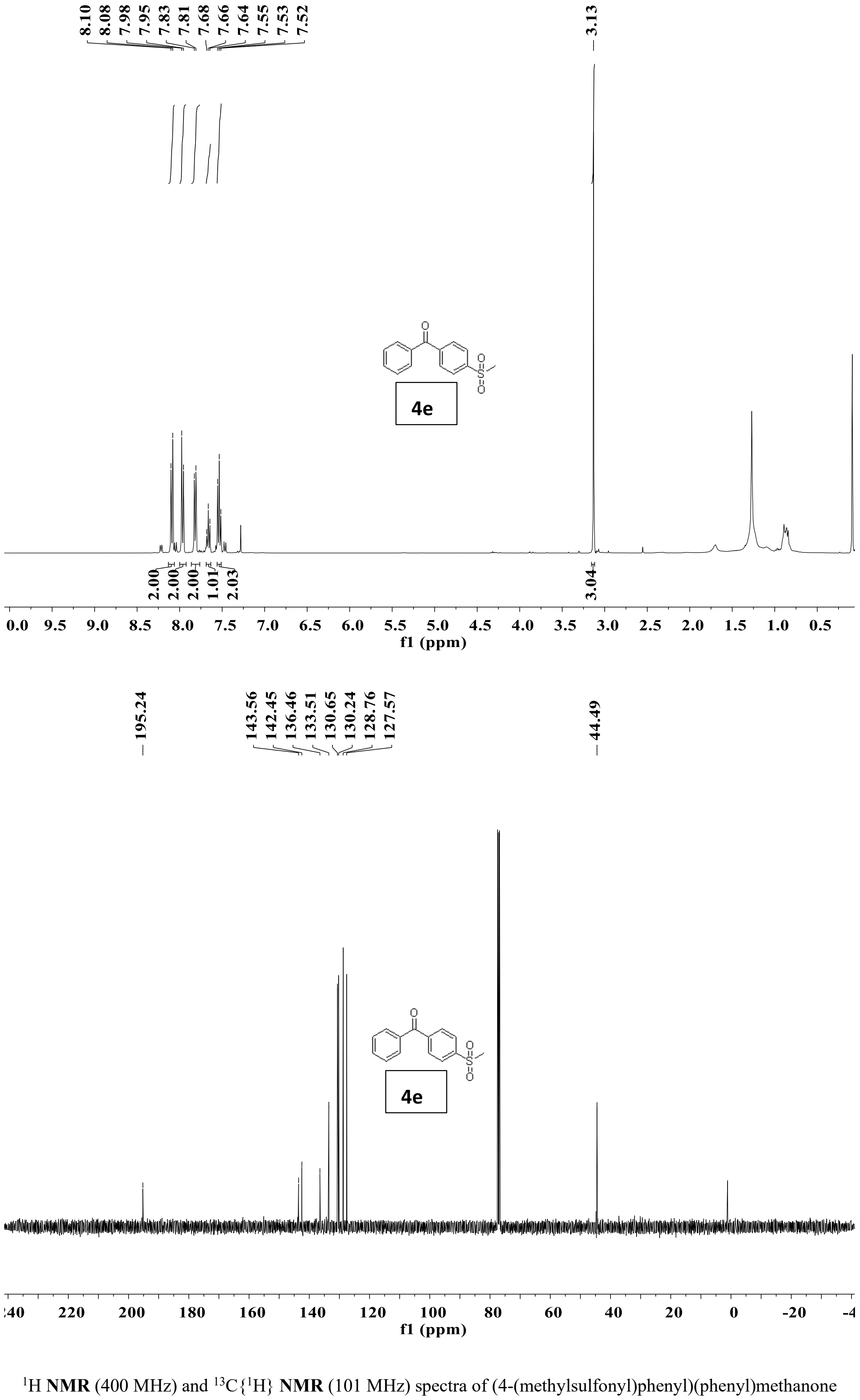


$^{1}$H **NMR** (400 MHz) and $^{13}$C{$^{1}$H} **NMR** (101 MHz) spectra of phenyl(3,4,5-trifluorophenyl)methanone (CDCl$_3$).

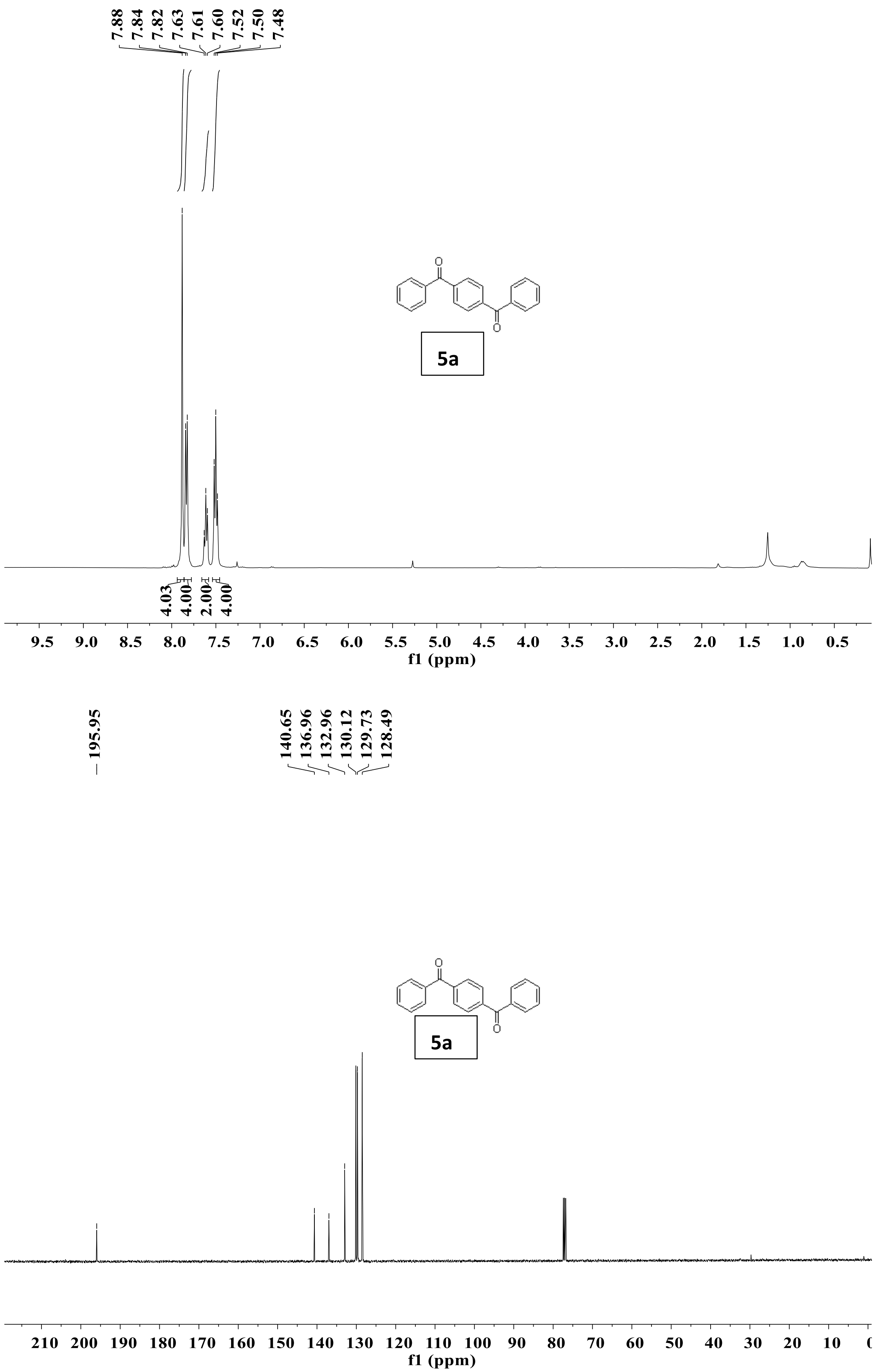




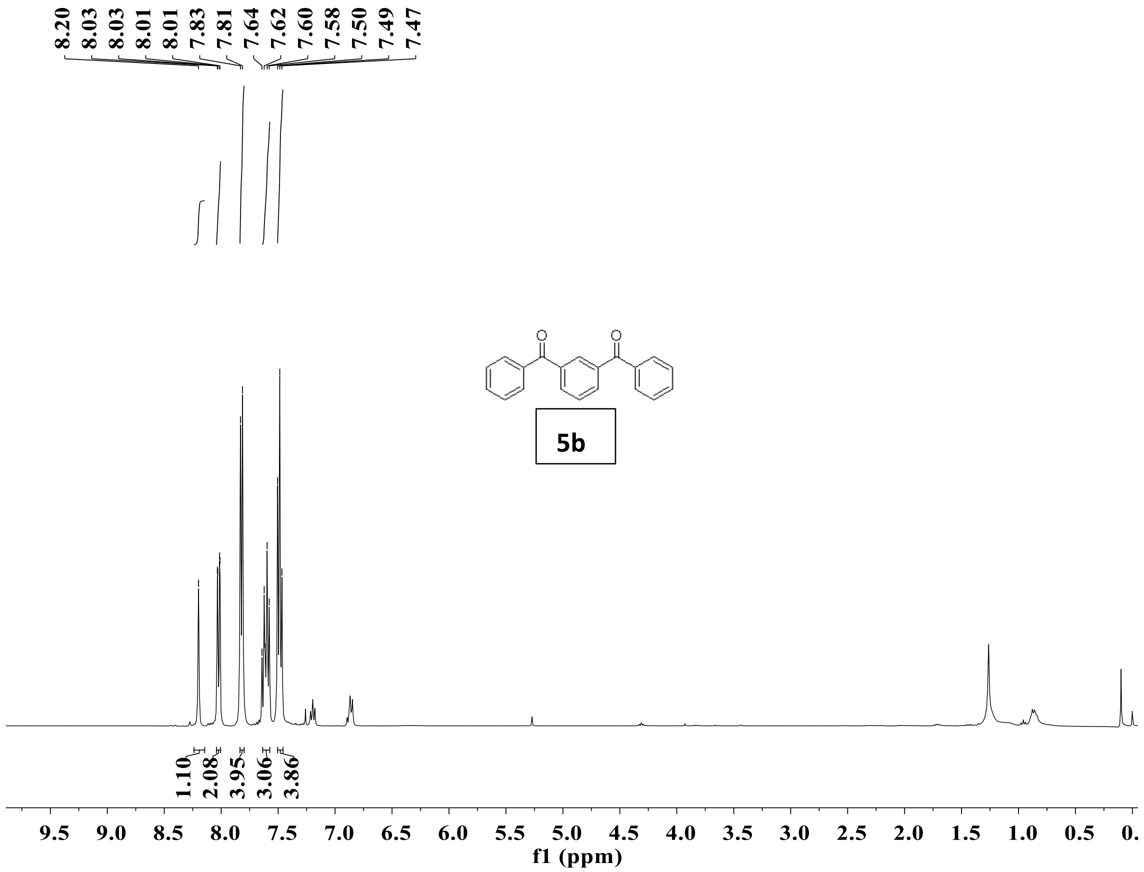
$^1$H **NMR** (400 MHz) and $^{13}$C{$^1$H} **NMR** (101 MHz) spectra of anthracen-9-yl(phenyl)methanone (CDCl$_3$).

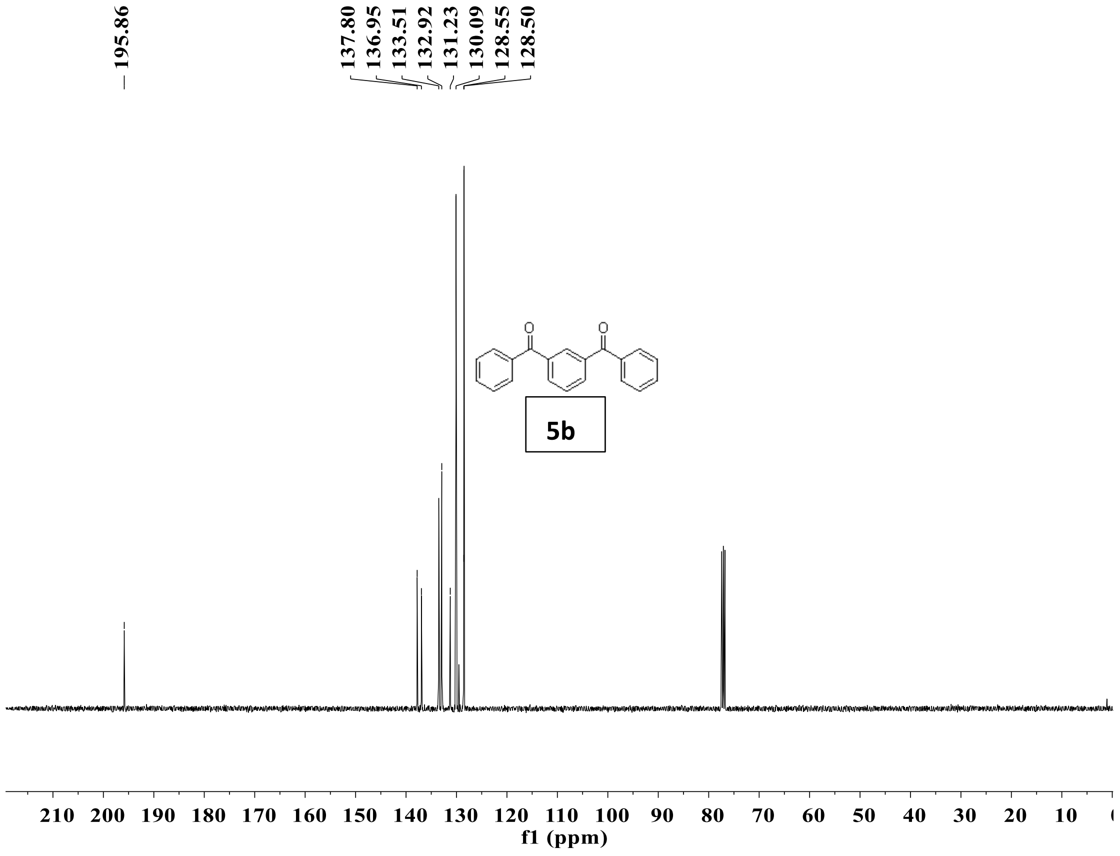


$^{1}$H **NMR** (400 MHz) and $^{13}$C{$^{1}$H} **NMR** (101 MHz) spectra of (4-(methylsulfonyl)phenyl)(phenyl)methanone (CDCl$_3$).

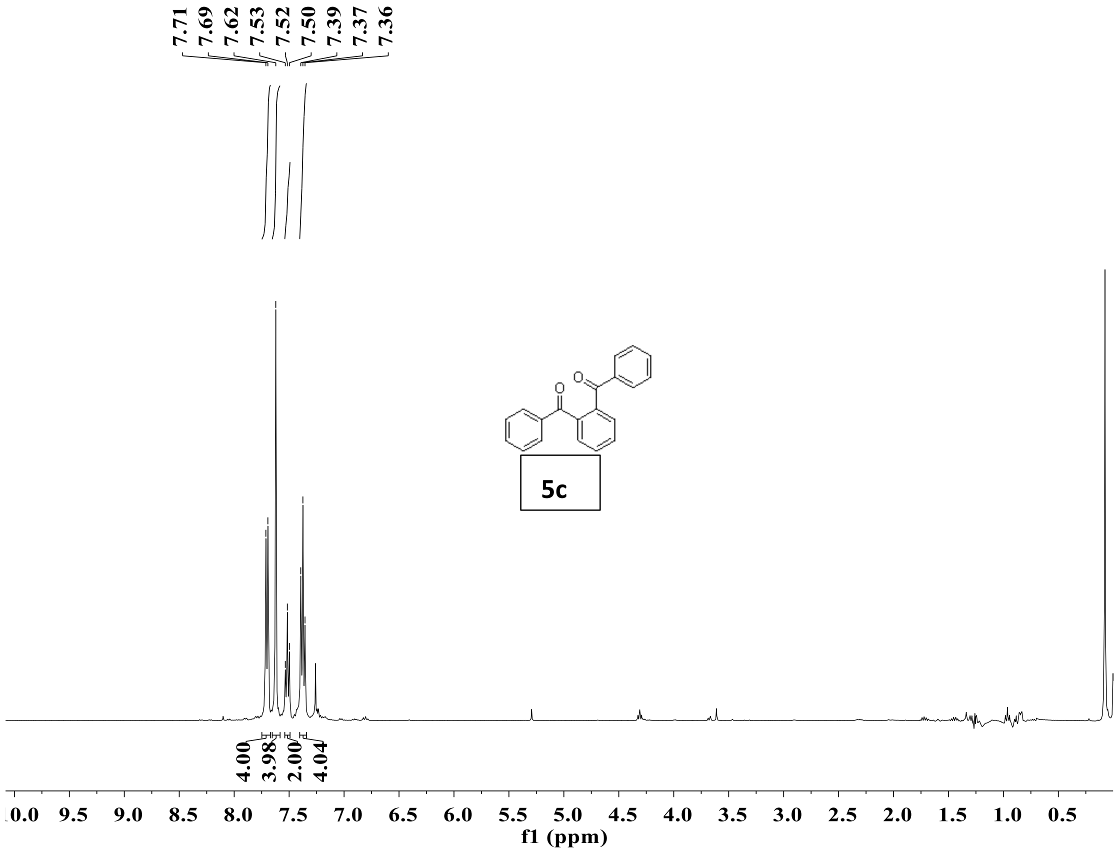


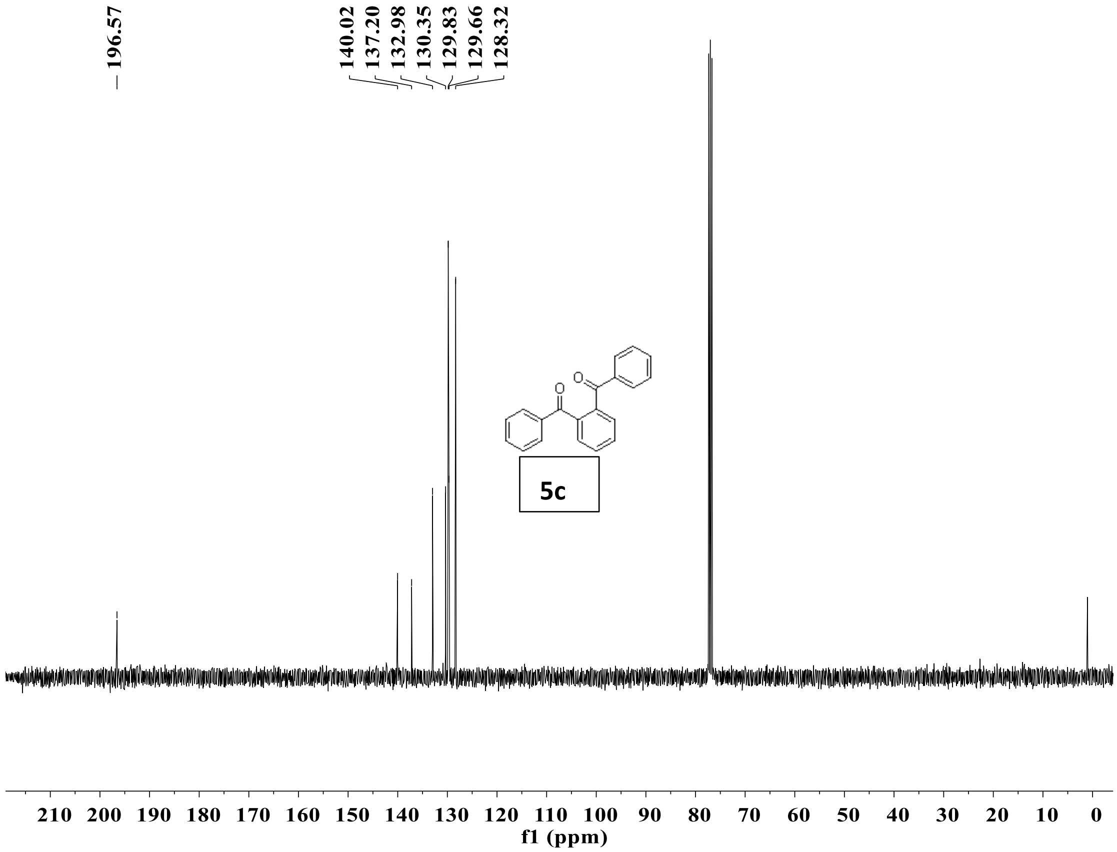
$^{1}$H **NMR** (400 MHz) and $^{13}$C{$^{1}$H} **NMR** (101 MHz) spectra of 1,4-phenylenebis(phenylmethanone) ($CDCl_3$).





$^{1}$H **NMR** (400 MHz) and $^{13}$C{$^{1}$H} **NMR** (101 MHz) spectra of 1,3-phenylenebis(phenylmethanone) (CDCl$_3$).





$^{1}$H **NMR** (400 MHz) and $^{13}$C{$^{1}$H} **NMR** (101 MHz) spectra of 1,2-phenylenebis(phenylmethanone) (CDCl$_3$).