Supporting Information

Synthesis of fluorenones by using Pd/Mg-La mixed oxide catalyst

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CONTENTS

A. General Information

All reagents were commercial grade materials and were used without further purification. All solvents were dried and distilled by standard methods as described in the literature. Thin layer chromatography was performed on pre-coated silica gel 60-F_{254} plates. The ^{1}H NMR and ^{13}C NMR spectra were recorded on 200, 300 and 500 MHz spectrometer. Chemical shifts (δ) are reported in ppm, using TMS as an internal standard in $CDCl_3$ solvent. The X-ray diffraction (XRD) patterns of the fresh and used samples were obtained on a Rigaku Miniflex X-ray diffractometer using Ni filtered Cu K_α radiation (λ= 0.15406 nm) from 2θ = 15 to 70°, at a scan rate of 2° min^{-1}, with the beam voltage and beam current of 30 kV and 15 mA respectively. Transmission electron micrographs were carried out in a Philips Tecnai G^2 FEI F12 electron microscope for probing particle size. The samples were ultrasonically dispersed in ethanol before loading onto a carbon coated copper grid and then allowed to dry at room temperature before recording the micrographs. **The CO_2 pulse chemisorption was studied in order to measure the basicity of the catalysts. In a typical method about 100 mg catalyst loaded in vertical quartz reactor interfaced to an online gas chromatograph equipped with TCD. The sample was degassed and reductively pre-treated using H_2/Ar at 450 ºC/2h followed by flushing the sample in He gas and subsequently brought the temperature down to 50 ºC. The 5%CO_2/He was injected in sequential pulses and estimated the amount of CO_2 adsorbed on the catalyst sample.** The elemental analysis of the fresh and used Pd(II)/Mg-La mixed oxide samples were analysed by The Agilent 7700 Series Inductively Coupled Plasma-Mass Spectrometer (ICP-MS).

B. Typical Experimental Procedures

Preparation of Pd(II)/Mg-La mixed oxide

The Mg-La mixed oxide was obtained by co-precipitation of Mg and La nitrates (0.39 mol and 0.13 mol respectively, in 0.5 L water for an atomic ratio Mg/La = 3) at a constant *p*H = 10.0 using a mixture of KOH (1 mol) and K_2CO_3 (0.26 mol) in 0.52 L of distilled water.[1] The gel was washed until the *p*H reached to 7 followed by oven drying at 120 °C for 16 h. It is then calcined in static air at 750 °C/5 h at a ramping rate of 10 °C/min. The Pd(II)/Mg-La mixed oxide catalyst was prepared by impregnation method.[2] In a typical procedure, Mg-La mixed oxide (1.5 g) was suspended in 150 mL of aqueous palladium (II) nitrate (Pd $(NO_3)_2.xH_2O$) [0.345 g, 1.5 mmol]

solution and stirred at 25 °C for 12 h under nitrogen atmosphere. The solid catalyst was filtered, washed thoroughly with 500 mL of water, and vacuum-dried and calcined at 350 °C for 5h to obtain brown Pd(II)/Mg-La mixed oxide (9.6 % of Pd determined by ICP-MS).

Typical procedure for synthesis of fluorenones by using Pd(II)/Mg-La mixed oxide catalyst

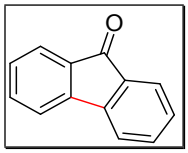
A 10 mL round bottom flask was charged with benzophenone (91.1 mg, 0.5 mmol), Pd(II)/Mg-La mixed oxide (30 mg, 5.3 mol % of Pd), Ag_2O (231.7 mb, 2 equiv., 1mmol) and TFA/H_2O (1:1 v/v %, 1 mL). The round bottom flask was kept stirring at 130 ^oC for 24 h. After the completion of the reaction, as monitored by TLC, the catalyst was separated by simple centrifugation, washed with distilled water for 5 times, dried at 100 ºC and directly used for the next cycle without any further purification. The reaction mixture was cooled and extracted with dichloromethane (3x5 mL). The combined filtrate was dried with Na_2SO_4 then concentrated and separated on a silica gel column using hexane/EtOAc (15:1) as eluent gave the corresponding pure fluorenone product with 82% yield.

Table S1: Basicity of catalysts estimated by pulse CO_2 chemisorption

Catalyst	**CO_2 uptake µmol/$g_{catalyst}$**
Pd(II)/MgO	55.8
Pd(II)/La_2O_3	49.3
Pd(II)/Mg-La	98.5

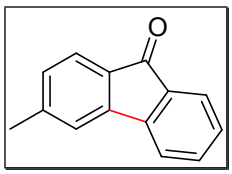
C. Analytical Data of the Products

9*H*-Fluoren-9-one (Table 2, entry 1)[3]



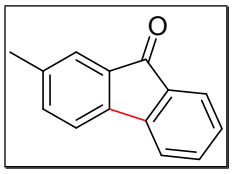
^{1}H NMR ($CDCl_3$, 600 MHz, ppm): δ 7.65 (d, J = 7.1 Hz, 2H), 7.51 (d, J = 7.1 Hz, 2H), 7.48 (t, J = 7.5 Hz, 2H), 7.29 (t, J = 7.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 193.7, 144.2, 134.5, 134.1, 128.9, 124.1, 120.2; MS (ESI) 181 (M+H); HRMS calcd. for: $C_{13}H_8O$ $[M+H]^+$ 181.06479, found 181.06471.

3-Methylfluoren-9-one (Table 2, entry 2)[3]



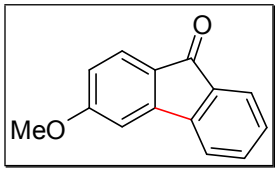
^{1}H NMR ($CDCl_3$, 600 MHz, ppm): δ 7.58 (d, J = 7.3 Hz, 1H), 7.47 (d, J = 7.5 Hz, 1H), 7.40-7.39 (m, 2H), 7.26-7.19 (m, 2H), 7.01 (d, J = 7.5 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 193.6, 145.6, 144.6, 144.1, 134.5, 134.2, 131.6, 129.3, 128.7, 124.0, 123.9, 121.0, 119.9, 21.9; MS (ESI) 195 (M+H); HRMS calcd. for: C_{14} H_{11} O $[M+H]^+$ 95.08044, found 195.08034.

2-Methyl-9*H*-fluoren-9-one (Table 2, entry 3)[3]



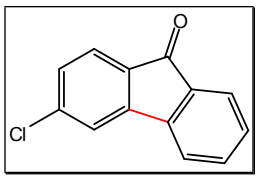
^{1}H NMR ($CDCl_3$, 600 MHz, ppm): δ 7.60 (d, J = 7.3 Hz, 1H), 7.43-7.42 (m, 3H), 7.35 (d, J = 7.5 Hz, 1H), 7.25-7.20 (m, 2H), 2.35 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 194.0, 144.5, 141.7, 139.1, 134.9, 134.5, 134.3, 134.1, 128.4, 124.8, 124.0, 120.0, 119.8, 21.2; MS (ESI) 195 (M+H); HRMS calcd. for: C_{14} H_{11} O $[M+1]^+$ 195.08044, found 195.08028.

3-Methoxy-9*H*-fluoren-9-one (Table 2, entry 5)[4]



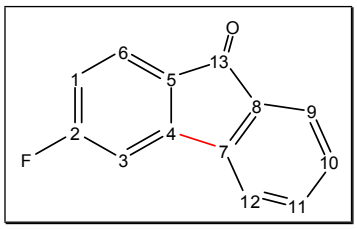
^{1}H NMR ($CDCl_3$, 600 MHz, ppm): δ 7.62-7.58 (m, 2H), 7.46-7.44 (m, 2H), 7.31-7.25 (m, 1H), 7.0 (s, 1H), 6.72 (dd, J = 2.0 Hz, J = 8.3 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 192.4, 165.3, 146.9, 143.3, 135.3, 134.0, 129.2, 127.1, 126.2, 123.8, 120.0, 112.9, 107.0, 55.7.

3-Chloro-9*H*-fluoren-9-one (Table 2, entry 6)[3]



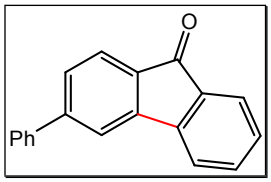
^{1}H NMR ($CDCl_3$, 600 MHz, ppm): δ 7.68-7.66 (m, 1H), 7.58 (d, J = 7.9 Hz, 1H), 7.51-7.49 (m, 3H), 7.35-7.32 (m, 1H), 7.27 (d, J = 1.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 192.3, 146.0, 143.0, 140.9, 134.7, 134.3, 132.3, 129.7, 128.9, 125.3, 124.5, 120.9, 120.5.

3-Fluoro-9*H*-fluoren-9-one (Table 2, entry 7)[3]



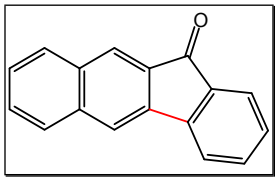
^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.67-7.63 (m, 2H,), 7.53- 7.47 (m,2H) 7.38-7.30 (m, 1H), 7.21-7.17 (m, 1H), 6.98-6.91(m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 191.9 (C13), 167.2 (d, J_{CF} = 254.2Hz, C2), 147.3 (d, J_{CF} = 9.9 Hz, C4), 142.7 (C7), 134.6 (C8), 134.5 (C9), 130.1 (d, J_{CF} = 1.8 Hz, C5), 129.7 (C10), 126.3 (d, J_{CF} = 10.8 Hz, C6), 124.2 (C12), 120.4 (C11), 115.4 (d, J_{CF} = 22.7 Hz, C3), 108.3 (d, J_{CF} = 24.5 Hz, C1).

3-Phenyl-9*H*-fluoren-9-one (Table 2, entry 8)[5]



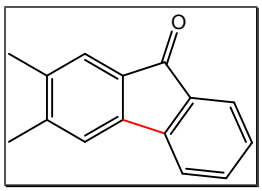
^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.73-7.69 (m, 2H), 7.67-7.64 (m,3H), 7.60-7.58 (m, 1H), 7.52-7.48 (m,4H), 7.46-7.44 (m, 1H), 7.34-7.29 (m,1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 193.2, 147.5, 144.9, 143.8, 139.9, 134.4, 134.4, 132.7, 129.0,128.7, 128.2, 127.6, 127.0, 124.4, 123.9, 120.1, 119.0.

11-*H*-benzo[*b*]fluoren-11-one (Table 2, entry 9)[3]



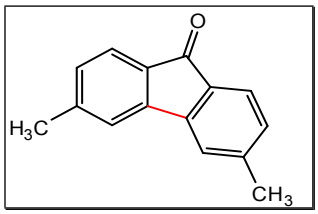
^{1}H NMR ($CDCl_3$, 600 MHz, ppm): δ 8.17 (s, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.86 (s, 1H), 7.83 (d, J = 7.6 Hz, 1H), 7.76-7.74 (m, 1H), 7.72-7.71 (m, 1H), 7.57-7.53 (m, 2H), 7.48-7.45 (m, 1H), 7.36-7.33 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.1, 144.8, 138.3, 136.9, 136.1, 135.0, 133.6, 132.7, 130.8, 129.1, 129.0, 128.7, 126.9, 125.7, 124.4, 121.0, 119.1.

2,3-Dimethyl-9*H*-fluoren-9-one (Table 2, entry 10)[6]



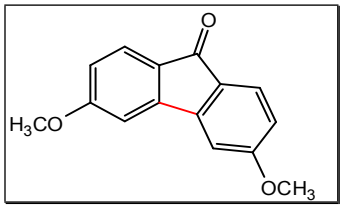
^{1}H NMR ($CDCl_3$, 600 MHz, ppm): δ 7.59 (d, 1H), 7.43-7.41 (m, 3H), 7.26-7.20 (m, 2H), 2.31 (s, 3H), 2.26 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.9, 144.5, 144.0, 142.4, 137.4, 134.5, 134.2, 132.2, 128.4, 125.4, 123.9, 121.7, 119.7, 20.6, 19.8; MS (ESI) 209 (M+H).

3,6-Dimethyl-9*H*-fluoren-9-one (Table 2, entry 11)[4,7]



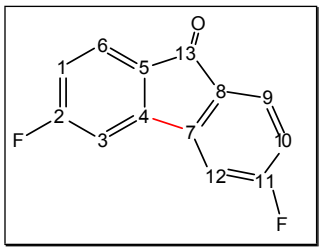
^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.50 (d, J = 7.4 Hz, 2H), 7.27 (s, 2H), 7.05 (d, J = 7.4 Hz, 2H), 2.4 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 193.2, 145.3, 144.5, 132.2, 129.3, 123.9, 120.9, 22.0.

3,6-Dimethoxyfluoren-9-one (Table 2, entry 12)[4]



^{1}H NMR ($CDCl_3$, 600 MHz, ppm): δ 7.57 (d, J = 8.2 Hz, 2H), 6.98 (d, J = 2.2 Hz, 2H), 6.73 (dd, $J1$ = 8.2 Hz, $J2$ = 2.2 Hz, 2H), 3.89 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 191.3, 164.9, 145.8, 128.2, 125.6, 112.9, 107.0, 55.7; MS (ESI) 241 (M+H); HRMS calcd. for: C_{15} H_{13} O_3 $[M+H]^+$ 241.08592, found 241.08557.

3,6-Difluoro-9*H*-fluoren-9-one (Table 2, entry 13)[7]



^{1}H NMR ($CDCl_3$, 600 MHz, ppm): δ 7.68-7.65 (m, 2H, H6, H9), 7.19-7.17 (m, 2H, H3, H12), 7.02-6.98 (m, 2H, H1, H10). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 190.2 (C13), 167.2 (d, J_{CF} = 255 Hz, C2, C11), 145.8 (C5, C8), 130.7 (C4, C7), 126.4 (d, J_{CF} =10 Hz, C6, C9), 116.2 (d, J_{CF} = 23 Hz, C1, C10), 108.7 (d, J_{CF} = 24 Hz, C3, C12), MS (ESI) 217 (M+H);

D. References

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3 V. S. Thirunavukkarasu and C. -H Cheng, *Chem. Eur. J.*, 2011, **17**, 14723 – 14726

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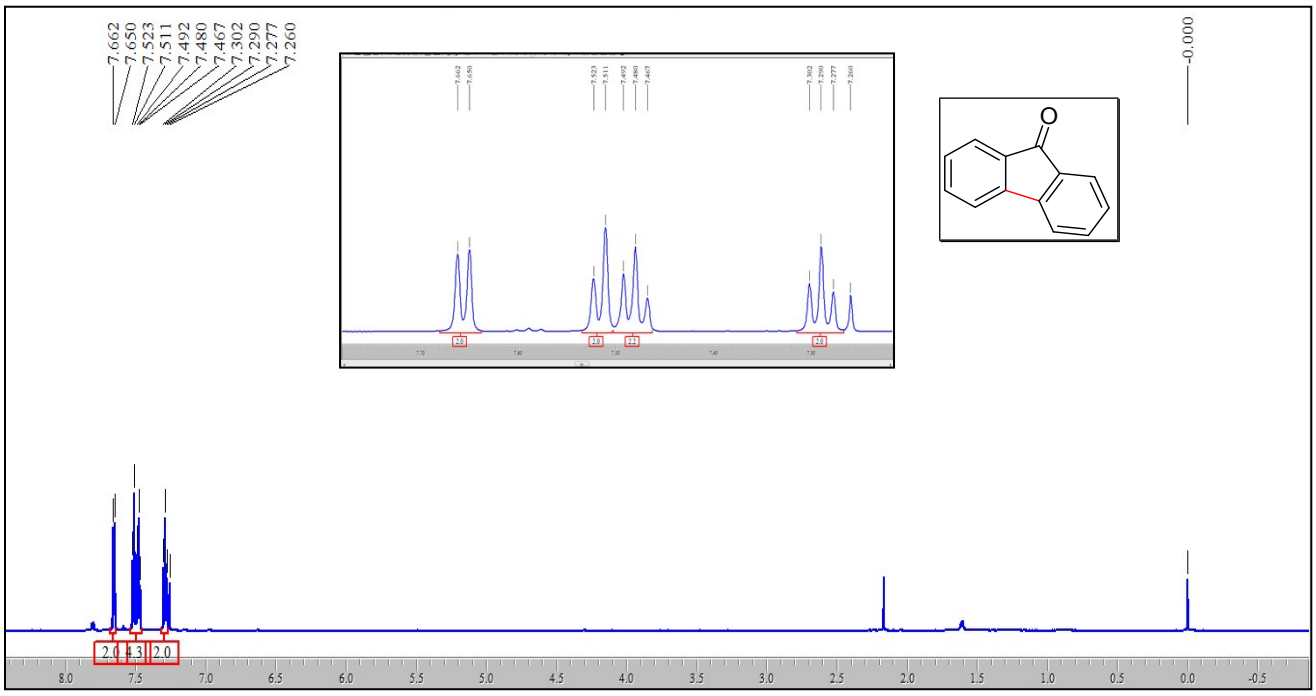
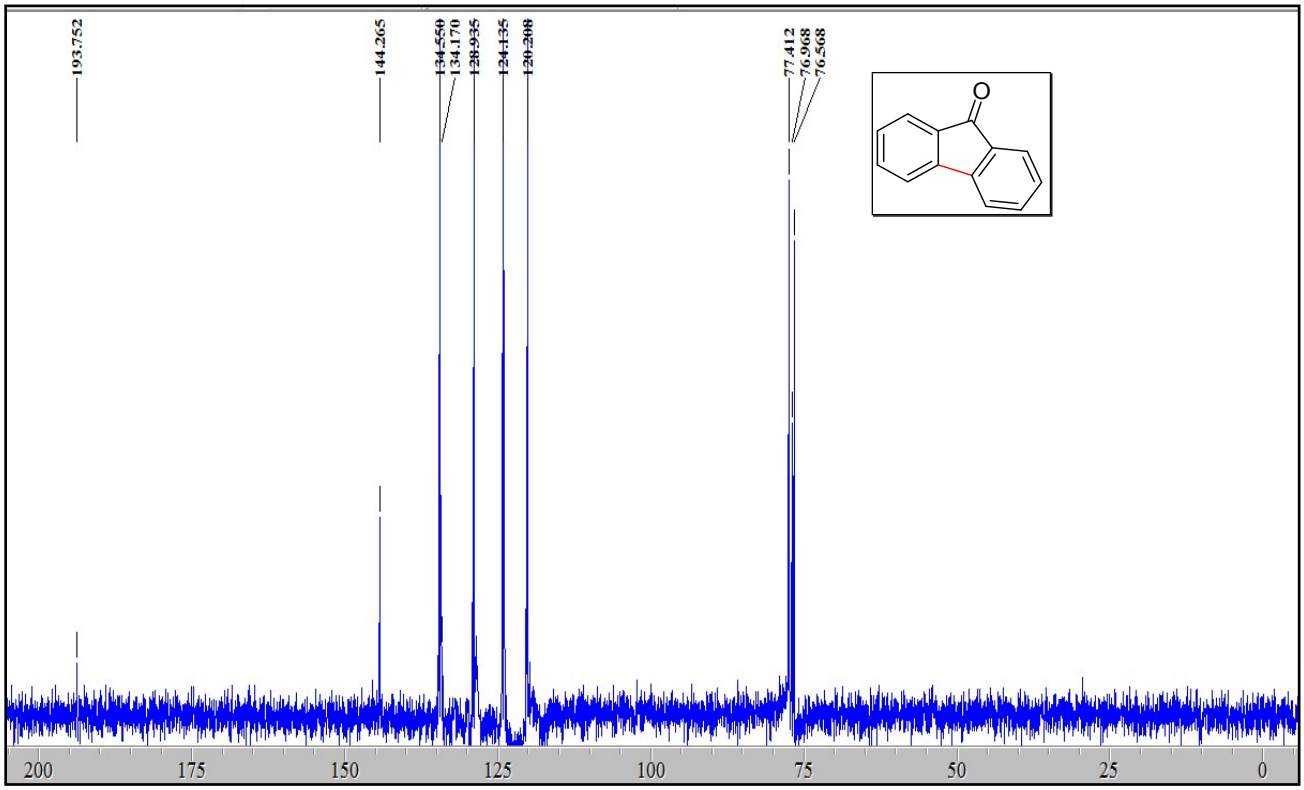
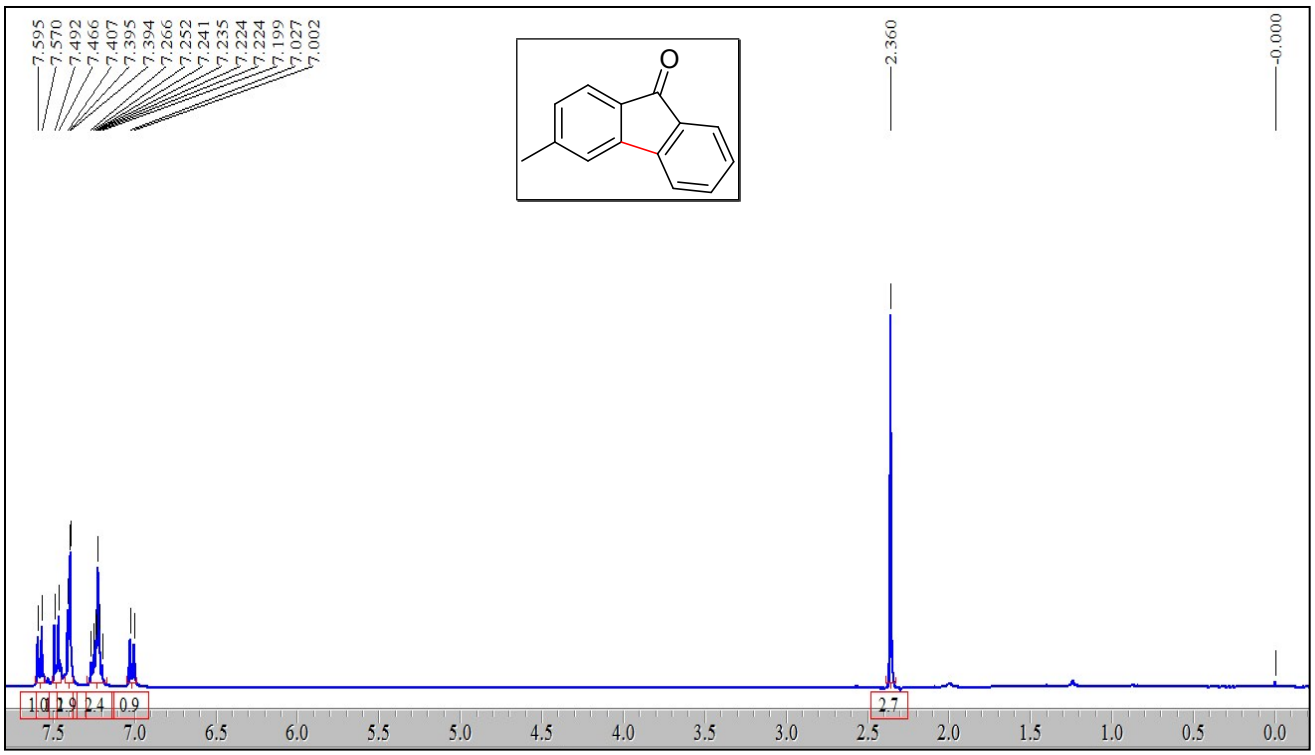
E ^{1}H and ^{13}C NMR Spectra of the Products

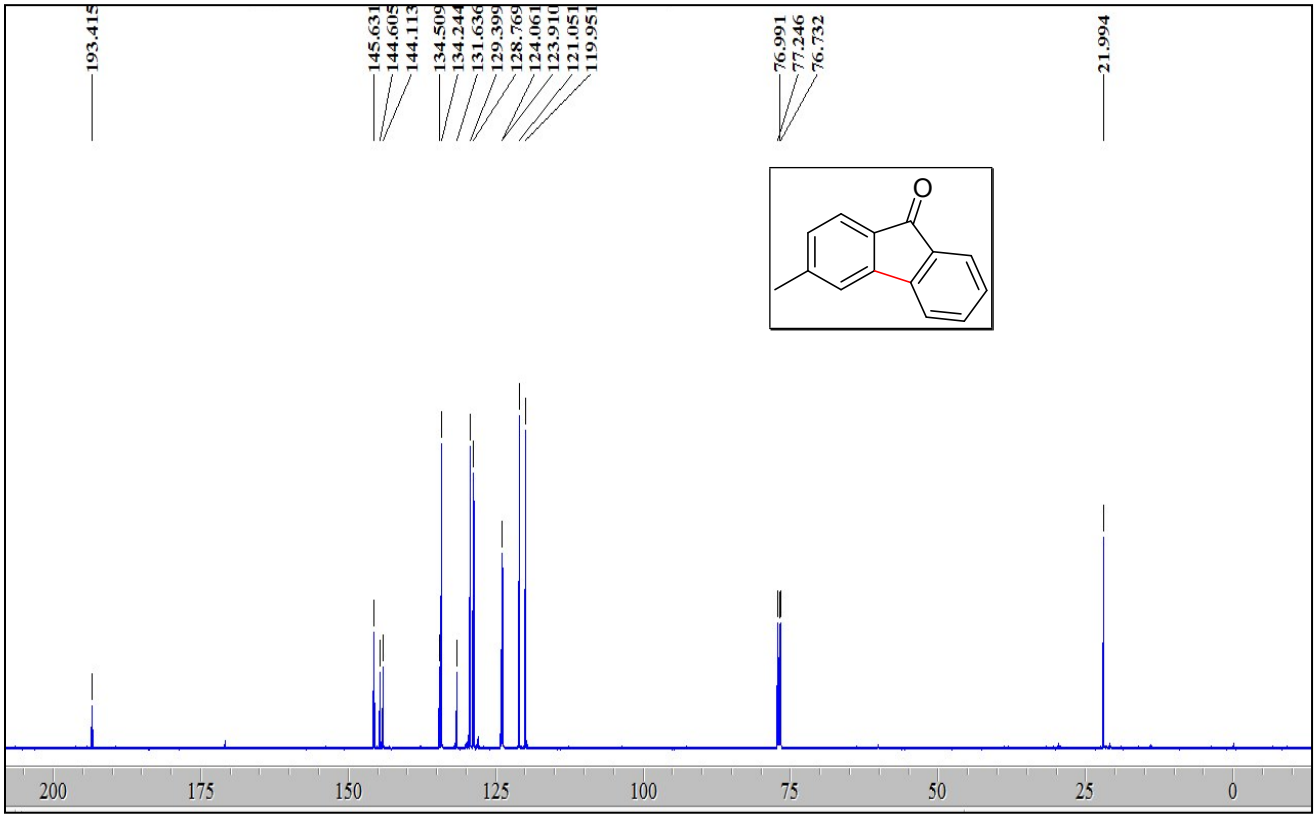
^{1}H and ^{13}C NMR Spectra of 9*H*-Fluoren-9-one (Table 2, entry 1)



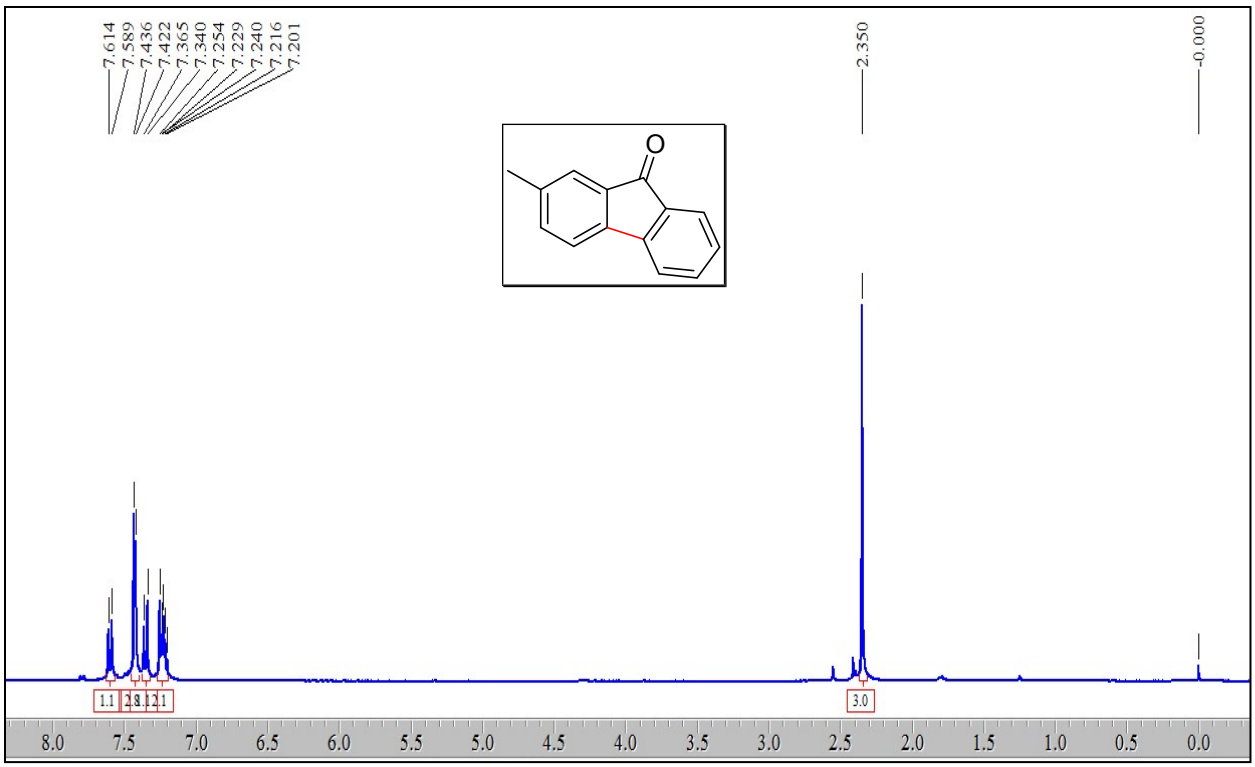


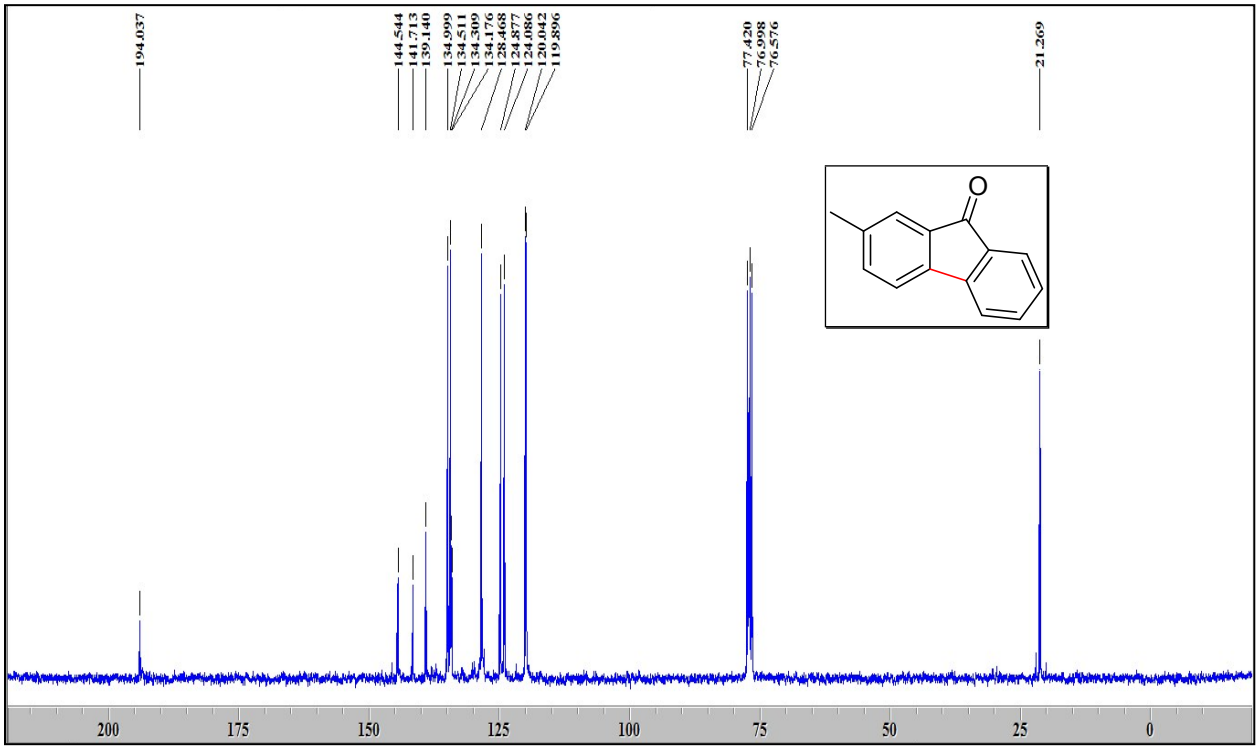
^{1}H and ^{13}C NMR Spectra of 3-Methylfluoren-9-one (Table 2, entry 2)



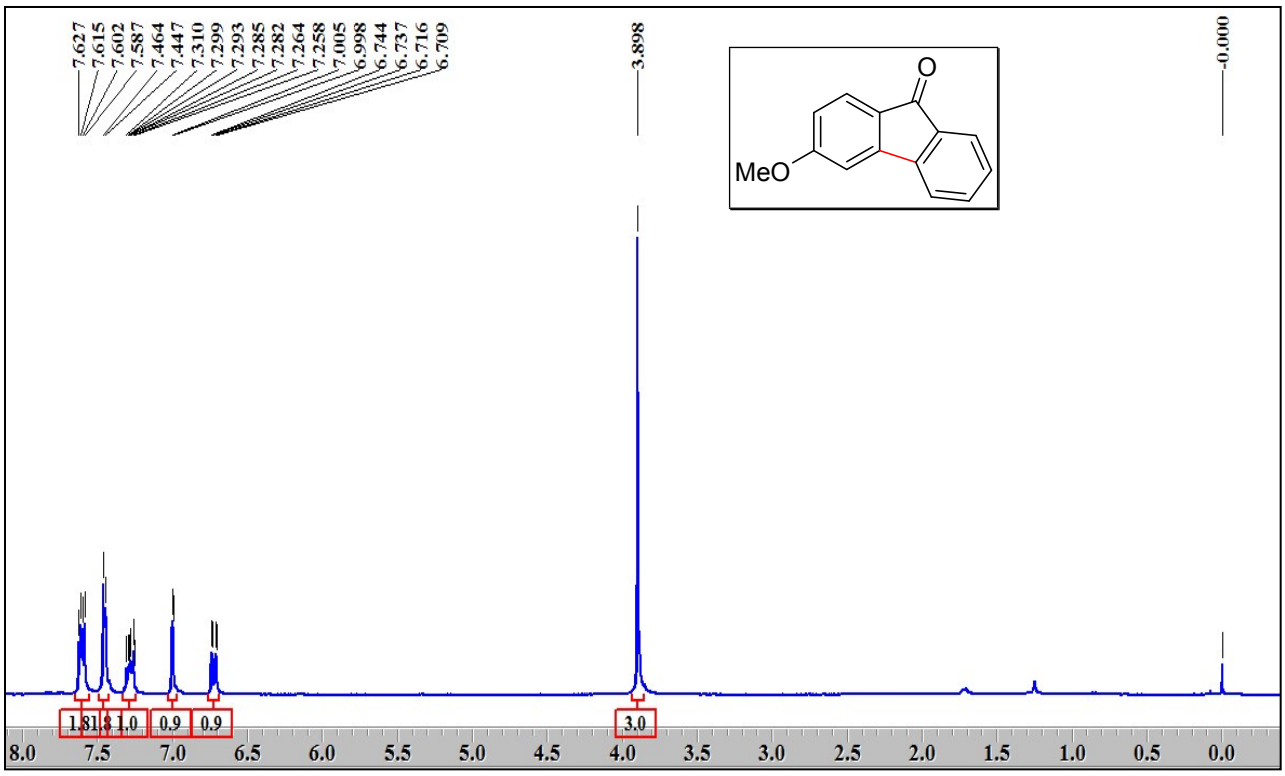


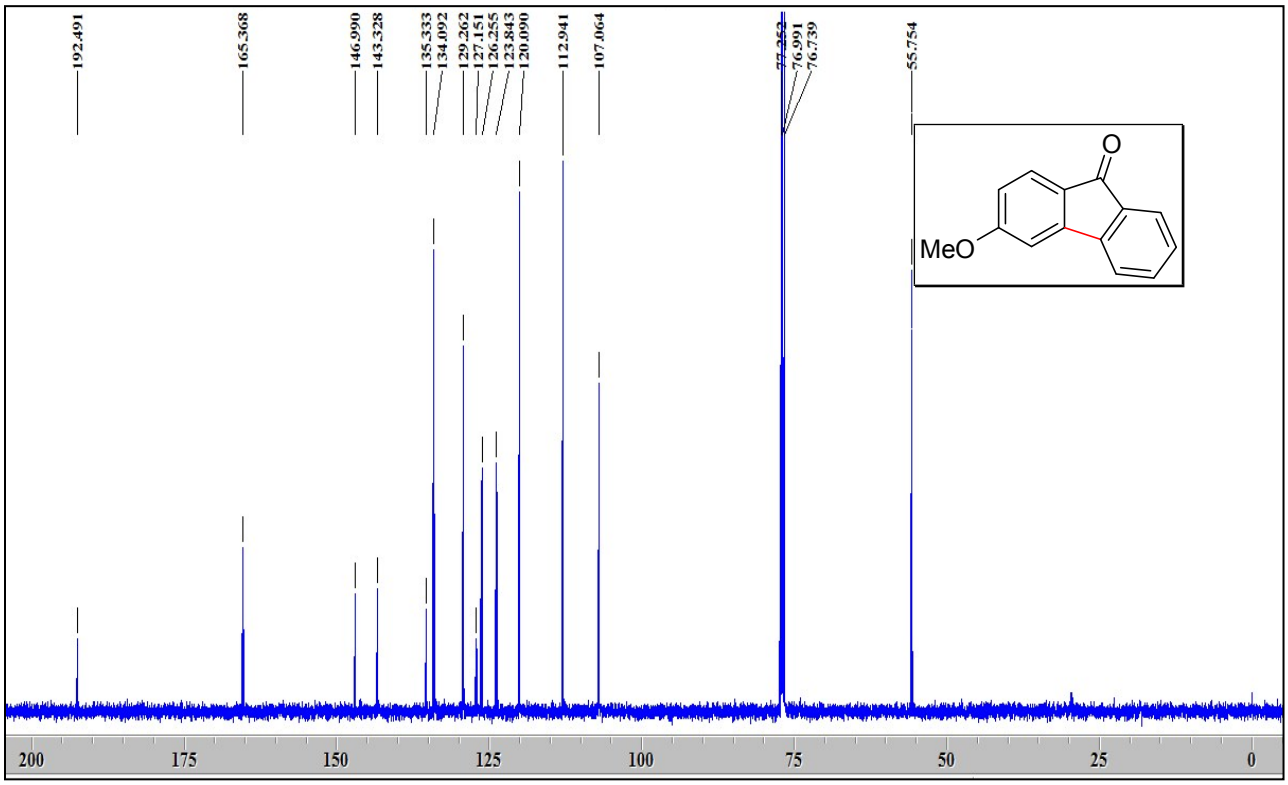
^{1}H and ^{13}C NMR Spectra of 2-Methyl-9*H*-fluoren-9-one (Table 2, entry 3)



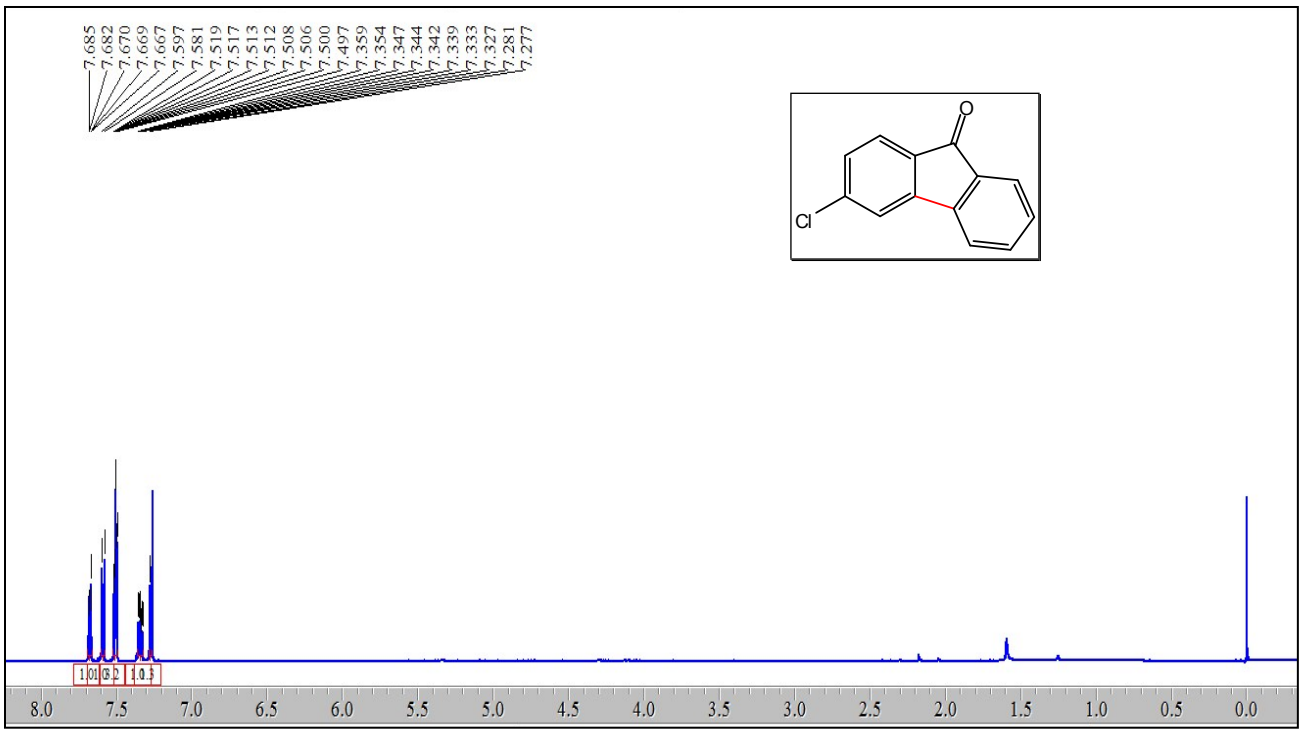


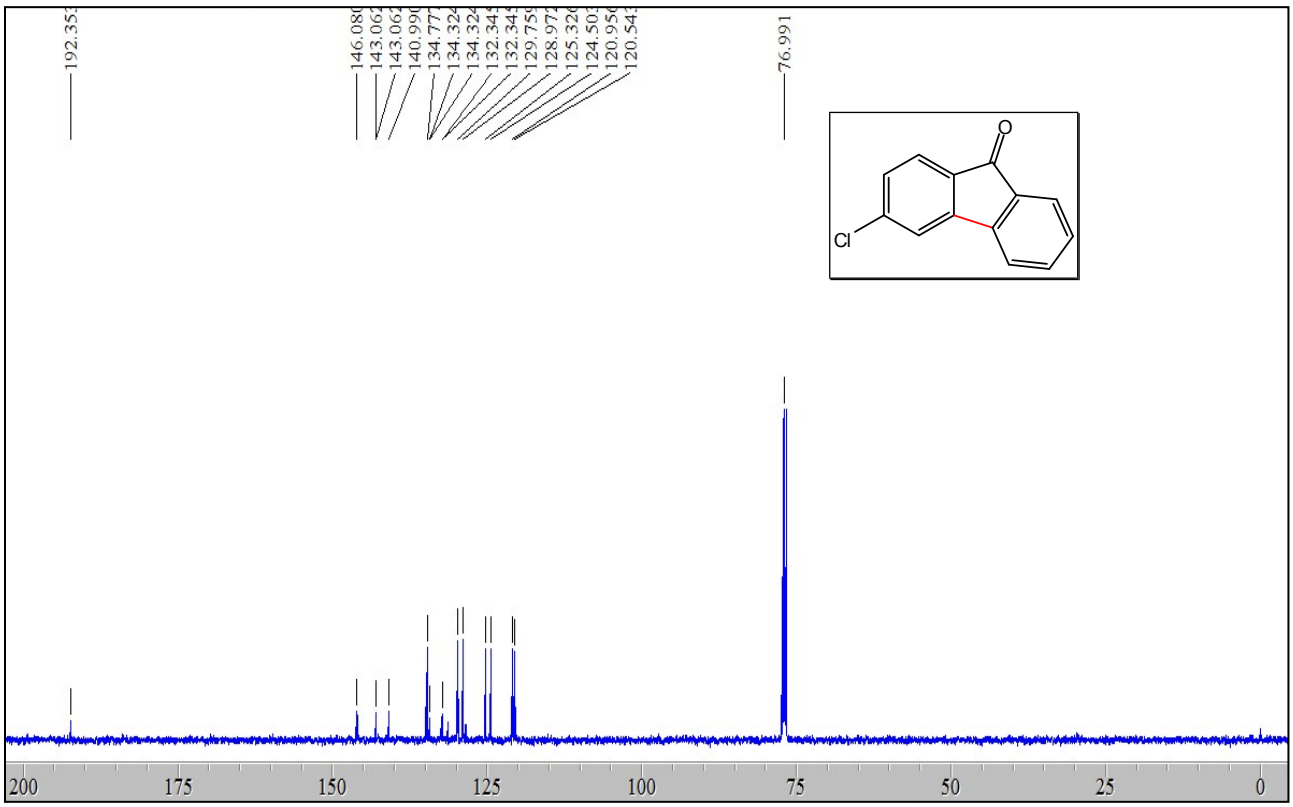
^{1}H and ^{13}C NMR Spectra of 3-Methoxy-9*H*-fluoren-9-one (Table 2, entry 5)



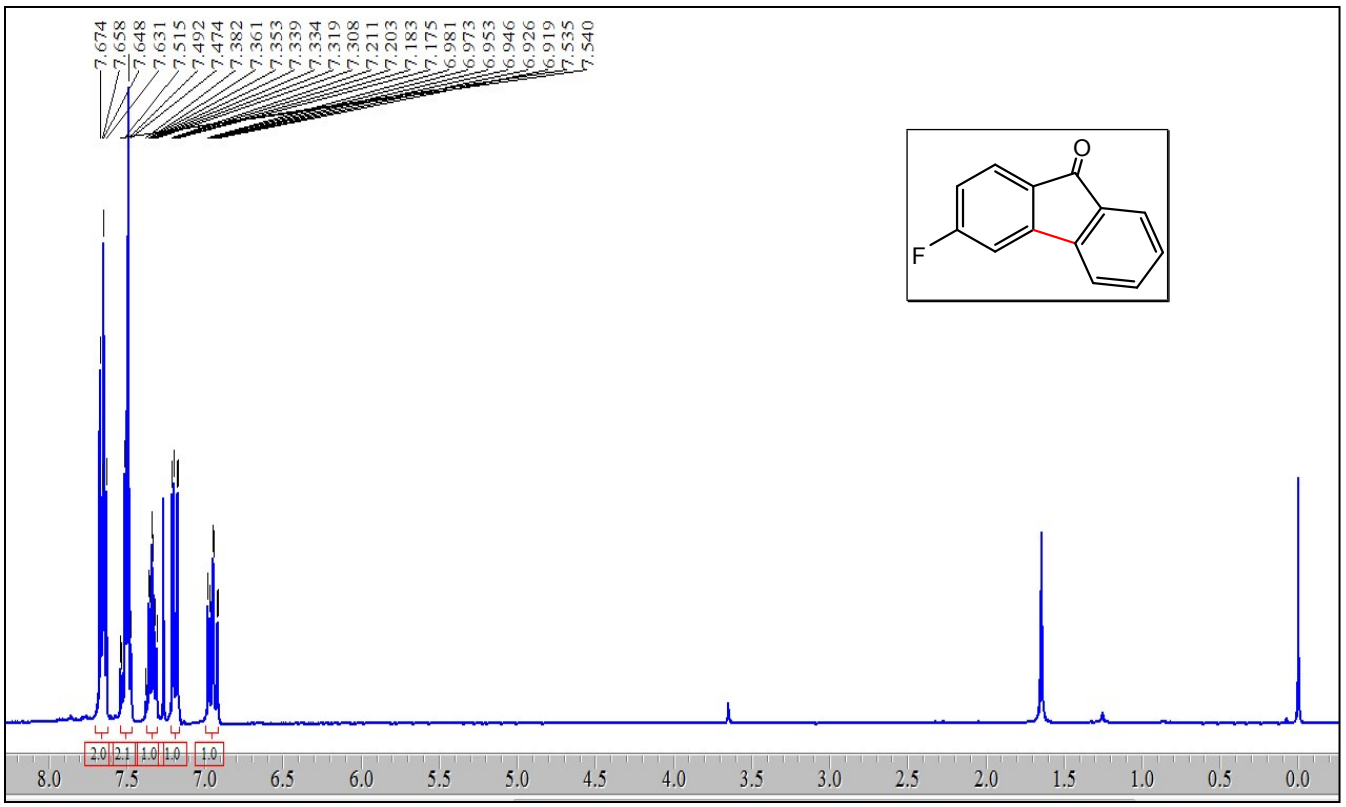


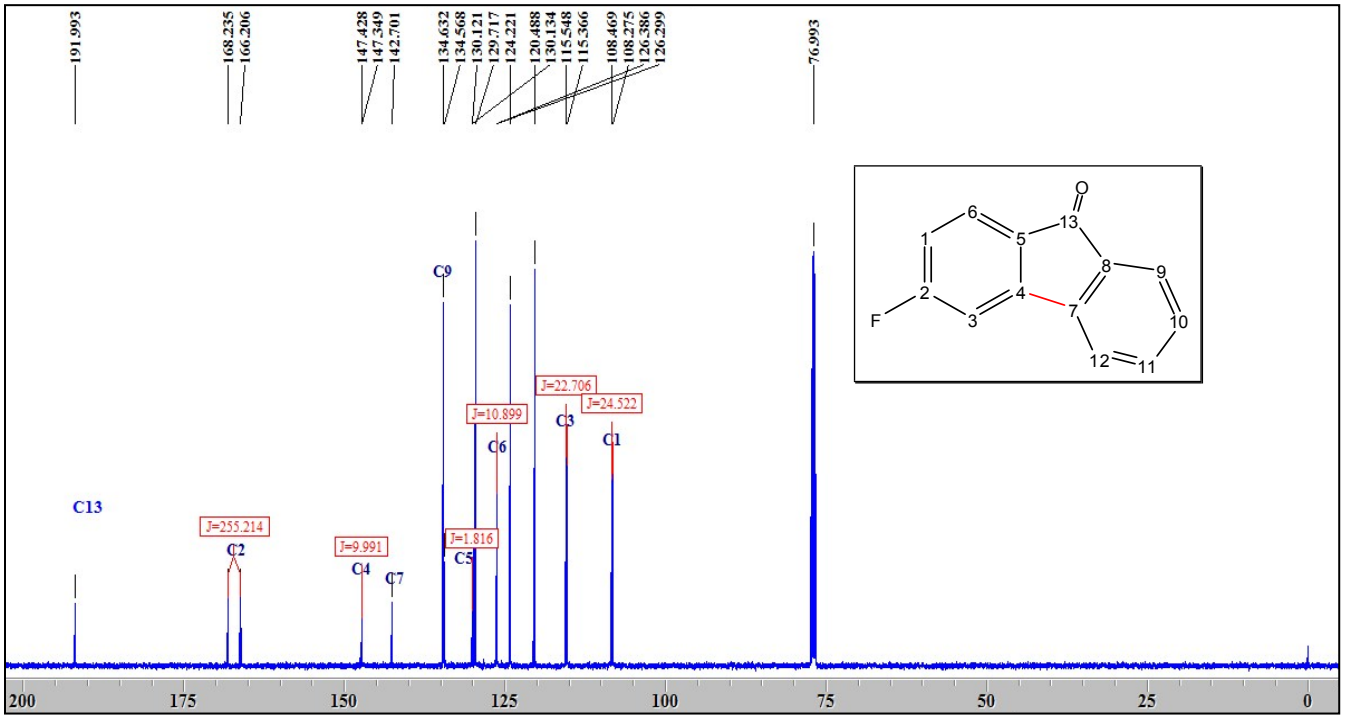
^{1}H and ^{13}C NMR Spectra of 3-Chloro-9*H*-fluoren-9-one (Table 2, entry 6)



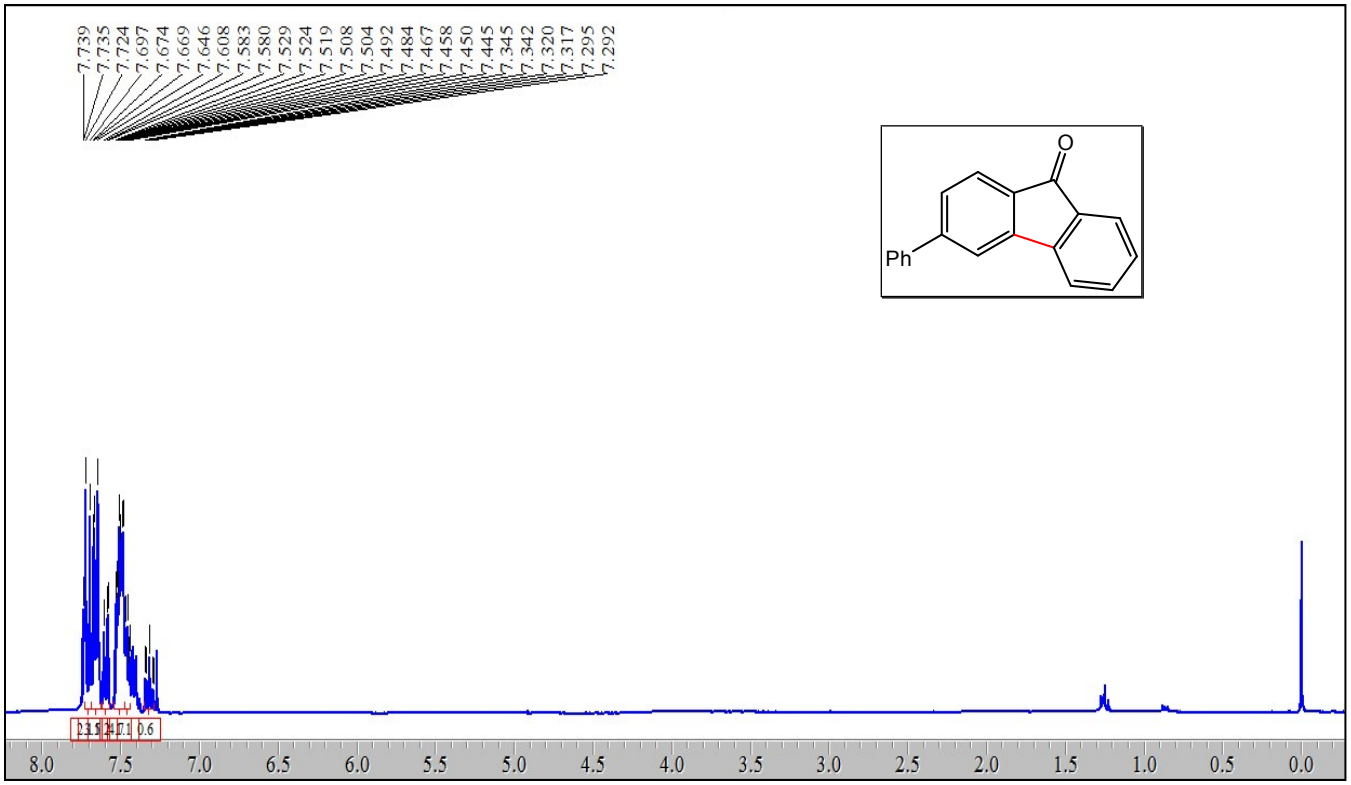


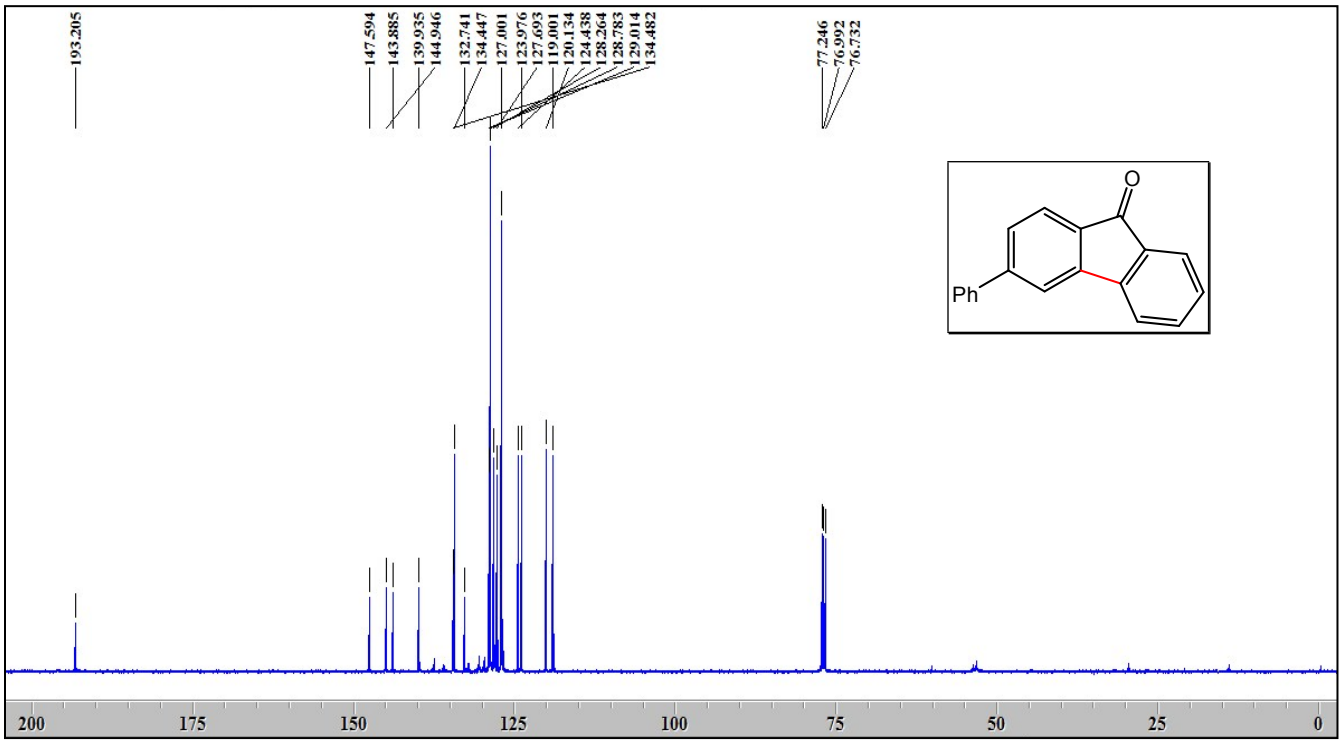
^{1}H and ^{13}C NMR Spectra of 3-Fluoro-9*H*-fluoren-9-one (Table 2, entry 7)



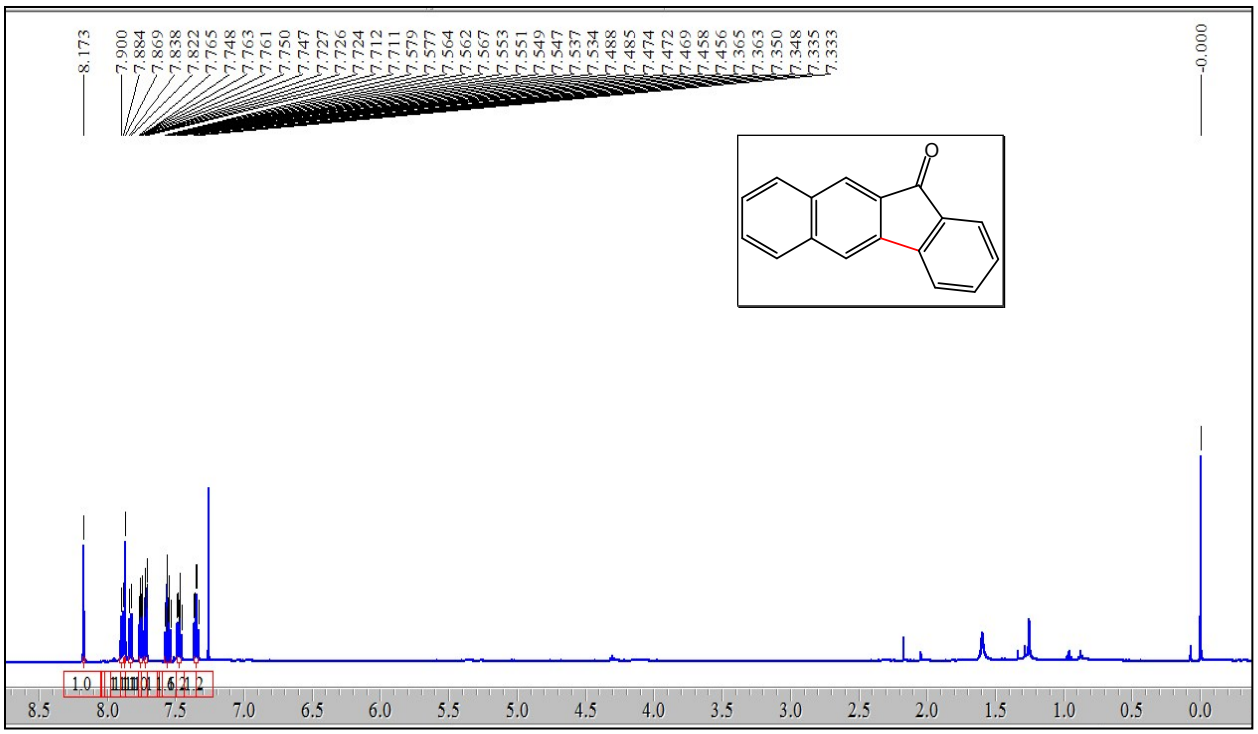


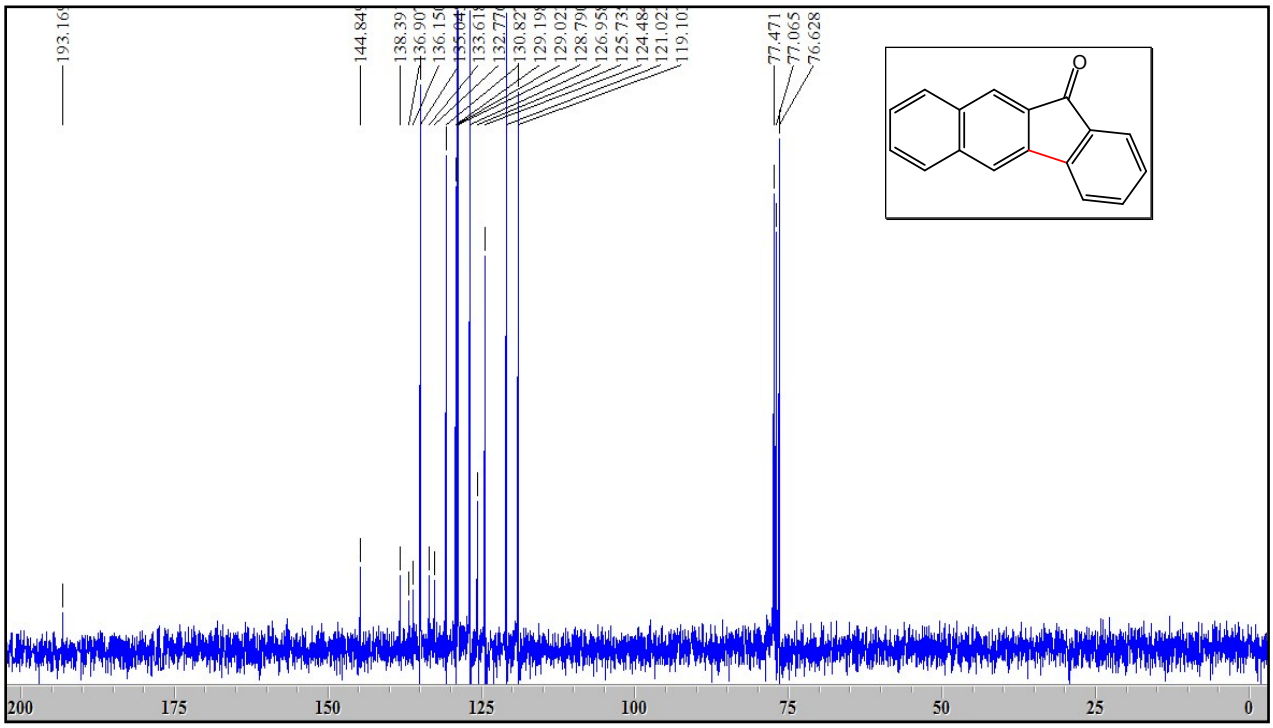
^{1}H and ^{13}C NMR Spectra of 3-Phenyl-9*H*-fluoren-9-one (Table 2, entry 8)



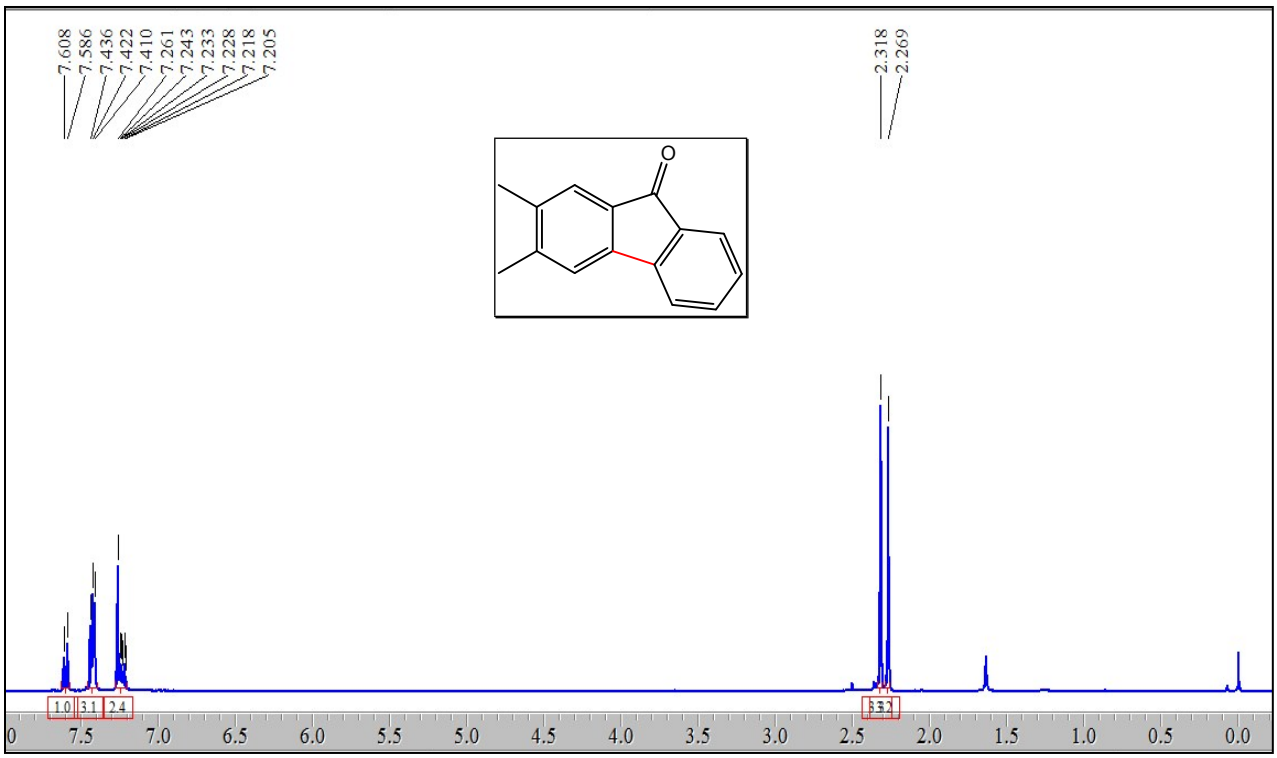


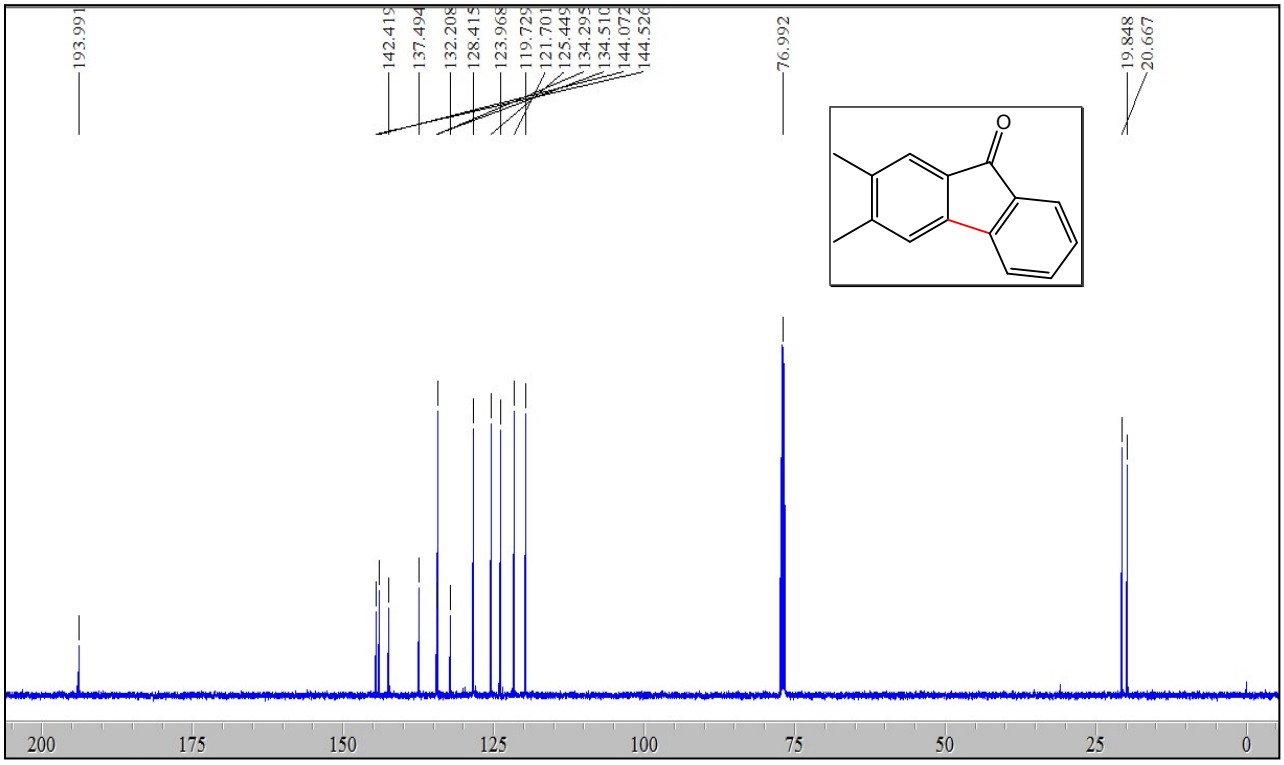
[1]H Spectrum of 11-*H*-benzo[*b*]fluoren-11-one (Table 2, entry 9)



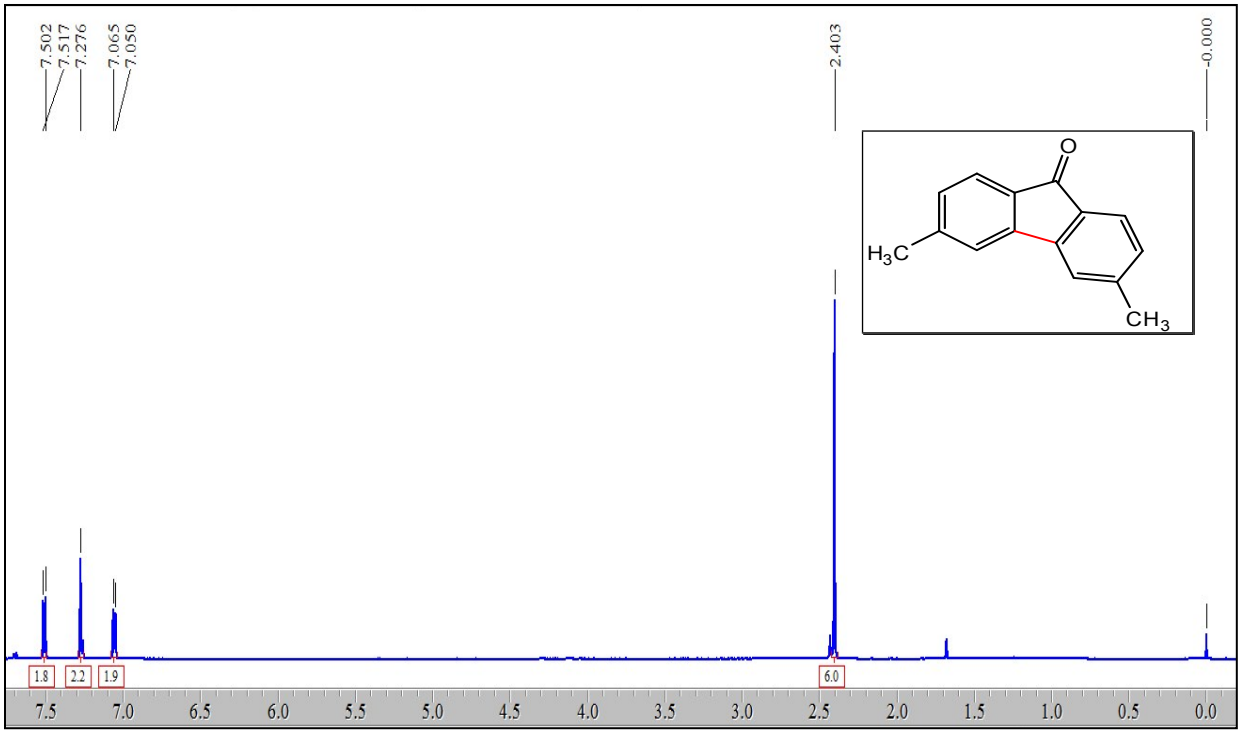


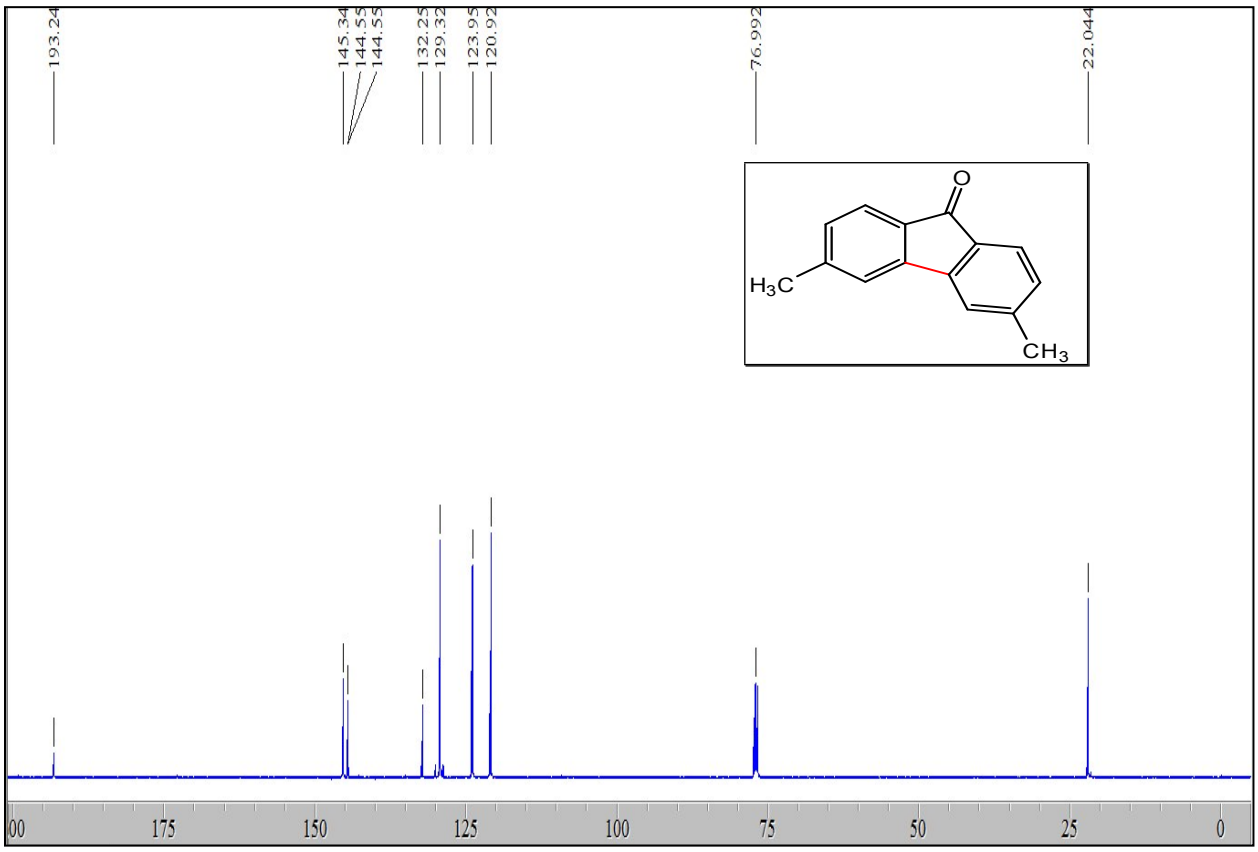
^{1}H and ^{13}C NMR Spectra of 2, 3-Dimethyl-9*H*-fluoren-9-one (Table 2, entry 10)



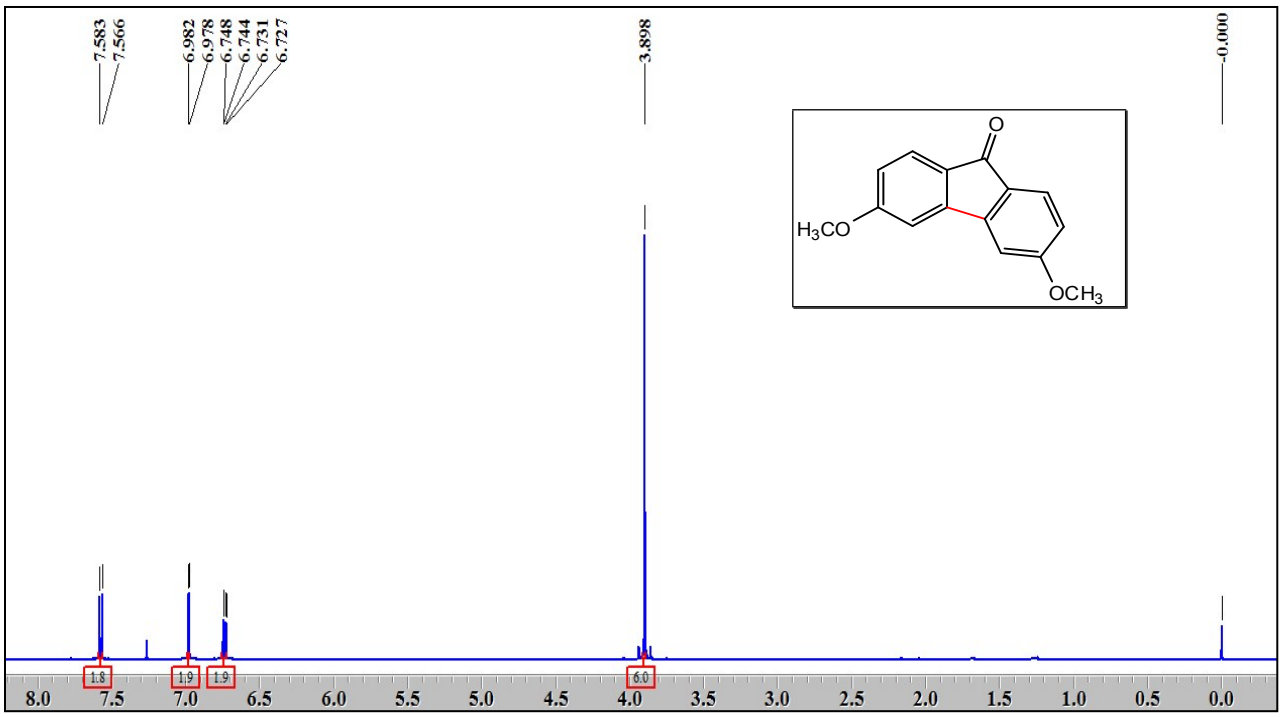


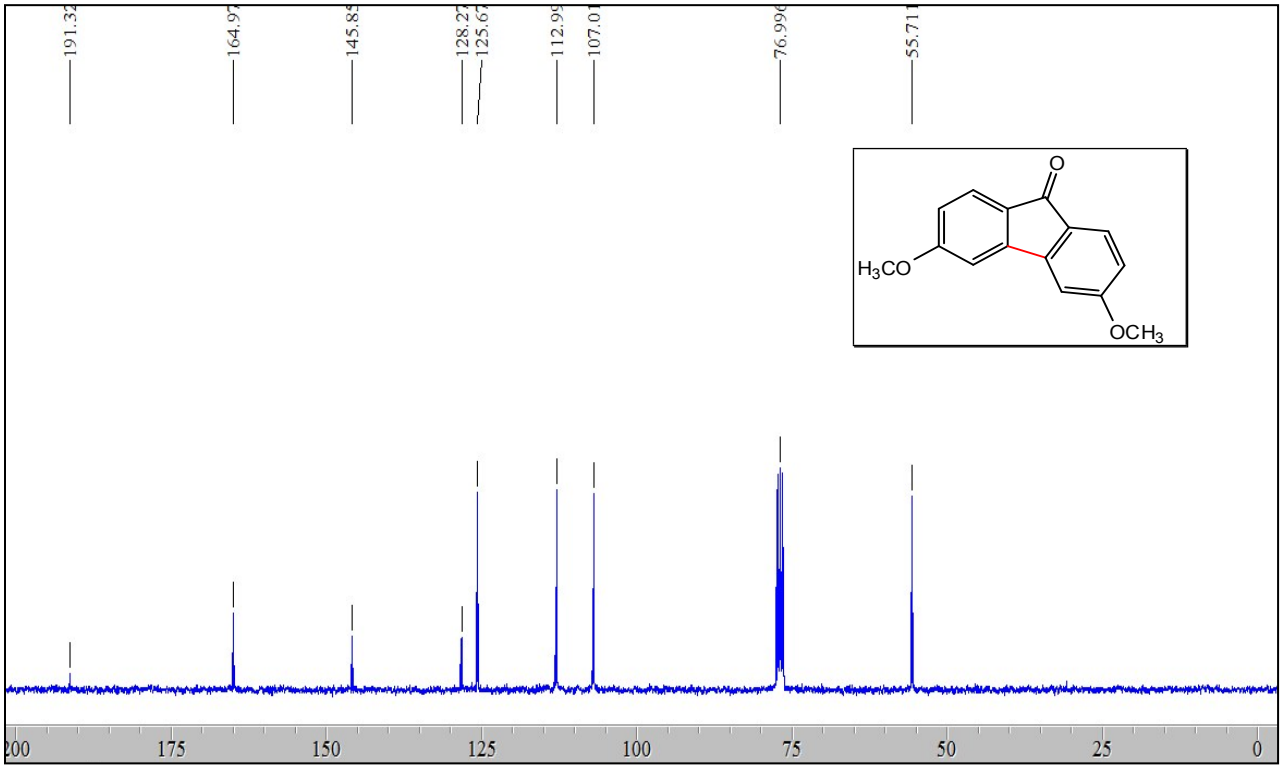
^{1}H and ^{13}C NMR Spectra of 3,6-Dimethyl-9*H*-fluoren-9-one (Table 2, entry 11)





^{1}H and ^{13}C NMR Spectra of 3,6-Dimethoxyfluoren-9-one (Table 2, entry 12)





^{1}H and ^{13}C NMR Spectra of 3, 6-Difluoro-9*H*-fluoren-9-one (Table 2, entry 13)