Anthracene-based covalent organic framework supported palladium nanoparticles for visible-light-mediated Suzuki-Miyaura cross-coupling

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Experimental

Synthesis of AntCOF

Ant (46.0 mg, 0.128 mmol) and 1,3,5-triformylphloroglucinol (18.0 mg, 0.086 mmol) were added sequentially to a 25 mL Pyrex tube with homogenization of the mixture by ultrasonication. After three freeze-pump-thaw cycles, the reaction flask was sealed under vacuum and placed in an oil bath at 150 °C for 72 h. After cooling to room temperature, the solids were collected by centrifugation, and the precipitates were washed with anhydrous N,N-dimethylacetamide, tetrahydrofuran, and acetone, and then dried under vacuum at 80 °C overnight to obtain a light yellow powder, AntCOF. Yield: 40 mg (62.5%).

Synthesis of Pd/AntCOF

AntCOF (100 mg), $Pd(OAc)_2$ (22.4 mg, 0.1 mmol) and anhydrous ethanol (25 mL) were added to a 100 mL round bottom flask. The mixture was ultrasonically dispersed and stirred at room temperature for 1 h. An ethanol solution of sodium borohydride (0.1 M, 5.0 mL) was then added and the reaction was continued for 4 h. A green precipitate was obtained by centrifugation, and the solids were washed sequentially with ethanol and ether, and dried under vacuum at 80 °C to obtain the green solid powder, Pd/AntCOF.

Typical procedure for Suzuki-Miyaura cross-coupling reaction

Aryl bromide (0.2 mmol), arylboronic acid (0.3 mmol), Pd/AntCOF (8 mg), K_3PO_4 (0.3 mmol), and water (5 mL) were sequentially added to a 15 mL quartz tube under a nitrogen atmosphere. The mixture was stirred under a blue LED (410-430 nm) lamp at ambient temperature for 12 h with fan cooling. After this period, the solid was filtered and washed with ethyl acetate and water. The solution was extracted three times with ethyl acetate (3 × 5 mL). The combined organic layers were washed with brine, dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography using petroleum ether and ethyl acetate as the eluent.

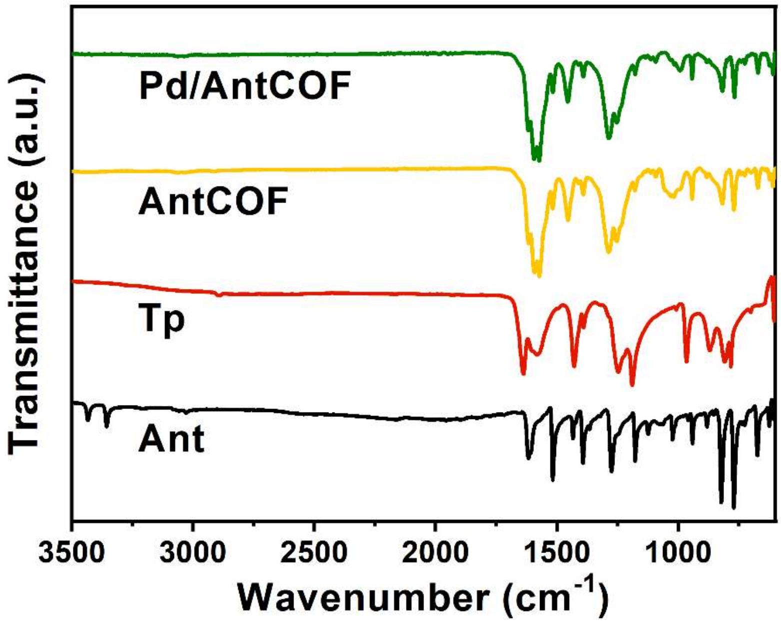


Fig. S1 FT-IR spectra of Tp, Ant, AntCOF and Pd/AntCOF.

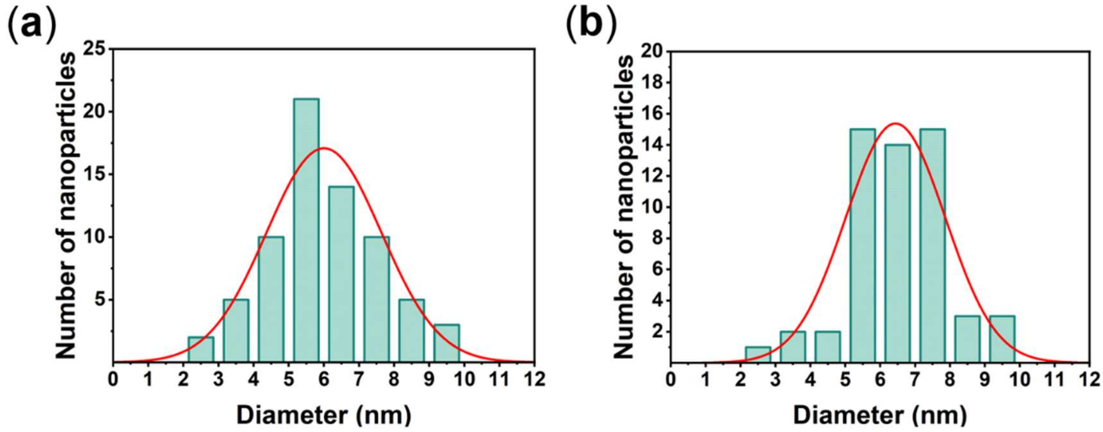


Fig. S2 Histogram illustrating the particle size distribution before (a) and after (b) photocatalytic reaction.

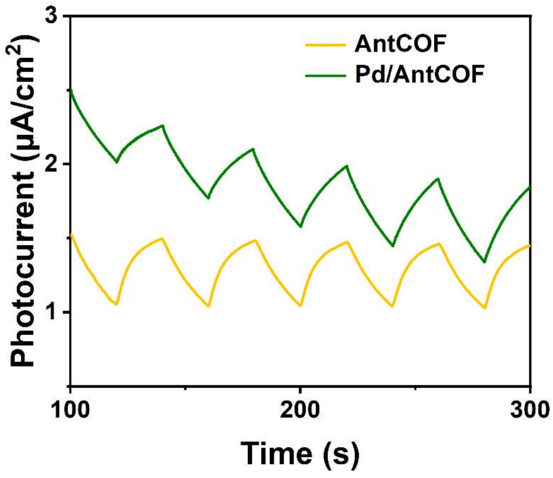


Fig. S3 Photocurrent spectra of AntCOF and Pd/AntCOF.

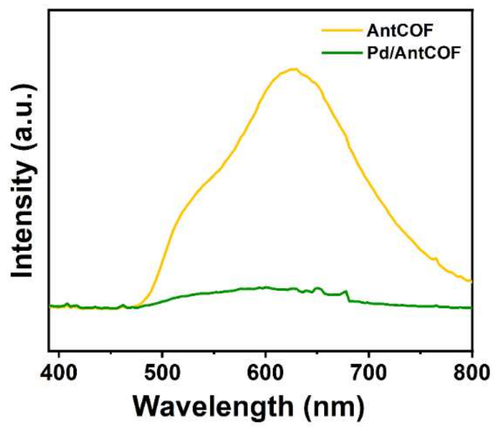


Fig. S4 The emission spectra of AntCOF and Pd/AntCOF in EtOH.

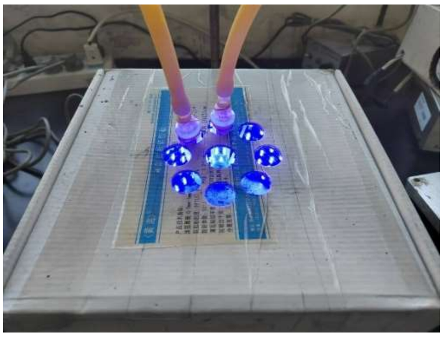
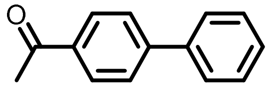


Fig. S5 The reaction set-up with blue LEDs

Analytical data of the products

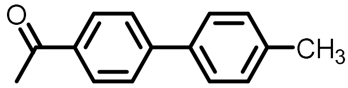
1-([1,1'-biphenyl]-4-yl)ethan-1-one (3a)[S1]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 2.64 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 145.8, 139.9, 135.9, 129.0, 128.9, 128.3, 127.3, 127.3, 127.3, 26.7.

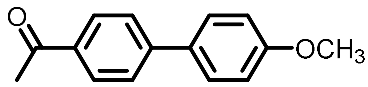
1-(4'-methyl-[1,1'-biphenyl]-4-yl)ethan-1-one (3b)[S2]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 2.62 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 145.7, 138.3, 137.0, 135.6, 129.7, 128.9, 127.1, 127.0, 26.7, 21.2.

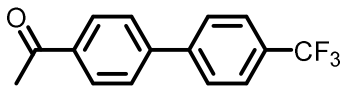
1-(4'-methoxy-[1,1'-biphenyl]-4-yl)ethan-1-one (3c)[S2]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 2.63 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 159.9, 145.4, 135.3, 132.3, 129.0, 128.4, 126.6, 114.4, 55.4, 26.6.

1-(4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)ethan-1-one (3d)[S3]

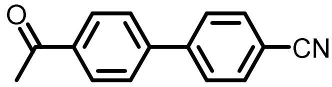


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.81–7.62 (m, 6H), 2.65 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 144.2, 143.4, 136.6, 130.4, 130.1, 129.1, 127.6, 127.5, 126.0, 125.9, 125.9, 125.95, 125.5, 122.8, 26.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.54.

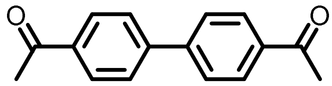
4'-acetyl-[1,1'-biphenyl]-4-carbonitrile (3e)[S2]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.3 Hz, 2H), 7.80–7.71 (m, 4H), 7.69 (d, J = 8.4 Hz, 2H), 3.12–2.16 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 144.3, 143.6, 136.9, 132.8, 129.1, 128.0, 127.5, 118.7, 111.9, 26.7.

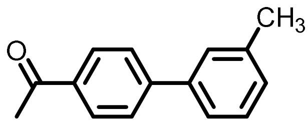
1,1'-([1,1'-biphenyl]-4,4'-diyl)bis(ethan-1-one) (3f)[S4]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13–8.00 (m, 4H), 7.78–7.67 (m, 4H), 2.66 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 144.4, 136.6, 129.0, 127.5, 26.7.

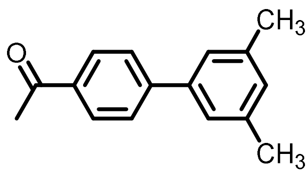
1-(3'-methyl-[1,1'-biphenyl]-4-yl)ethan-1-one (3g)[S4]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.37 (t, J = 7.9 Hz, 1H), 7.20 (d, J = 7.7 Hz, 1H), 7.14 (s, 1H), 6.94 (dd, J = 8.2, 2.0 Hz, 1H), 3.86 (s, 3H), 2.62 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 146.0, 139.9, 138.6, 135.8, 129.0, 128.9, 128.1, 127.2, 124.4, 26.7, 21.6.

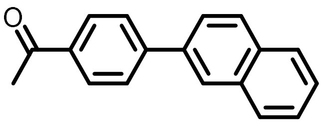
1-(3',5'-dimethyl-[1,1'-biphenyl]-4-yl)ethan-1-one (3h)[S5]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.5 Hz, 2H), 7.93 (t, J = 9.2 Hz, 2H), 7.81 (d, J = 8.3 Hz, 2H), 7.76 (dd, J = 8.5, 1.7 Hz, 1H), 7.52 (dd, J = 6.4, 2.6 Hz, 3H), 2.65 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 145.7, 137.2, 135.9, 133.6, 133.0, 129.0, 128.7, 128.4, 127.7, 127.5, 126.6, 126.5, 126.4, 125.2, 26.7.

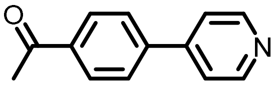
1-(4-(naphthalen-2-yl)phenyl)ethan-1-one (3i)[S2]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.5 Hz, 3H), 7.93 (t, *J* = 9.2 Hz, 3H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.76 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.52 (dd, *J* = 6.4, 2.6 Hz, 2H), 2.65 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 172.2, 145.7, 137.2, 135.9, 133.6, 133.04, 129.0, 128.7, 128.4, 127.7, 127.5, 126.6, 126.5, 126.4, 125.2, 26.7.

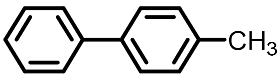
1-(4-(pyridin-4-yl)phenyl)ethan-1-one (3j)[S6]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 3.5 Hz, 2H), 8.20–7.91 (m, 2H), 7.82–7.64 (m, 2H), 7.54 (dd, *J* = 4.6, 1.5 Hz, 2H), 2.66 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 150.5, 147.1, 142.6, 137.3, 129.1, 127.3, 121.7, 26.8.

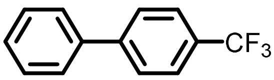
4-methyl-1,1'-biphenyl (3k)[S1]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.9 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.27–7.23 (m, 2H), 2.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 138.4, 137.1, 129.5, 128.8, 127.1, 127.0, 21.2.

4-(trifluoromethyl)-1,1'-biphenyl (3l)[S1]

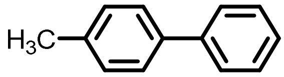


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 5.6 Hz, 4H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 139.8, 129.5, 129.2, 129.0, 128.2, 127.4, 127.3, 125.8, 125.7, 125.7, 125.7, 123.0.

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.38.

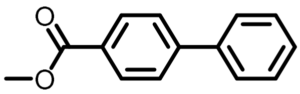
4-methyl-1,1'-biphenyl (3m)[S1]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.9 Hz, 2H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 6.2 Hz, 2H), 2.39 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 138.4, 137.1, 129.5, 128.8, 127.1, 127.0, 21.2.

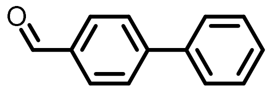
methyl [1,1'-biphenyl]-4-carboxylate (3n)[S1]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.5 Hz, 2H), 7.63 (dd, *J* = 14.8, 7.8 Hz, 4H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 3.93 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 145.7, 140.0, 130.1, 129.0, 128.2, 127.3, 127.2, 52.1.

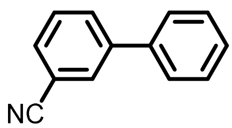
methyl [1,1'-biphenyl]-4-carboxylate (3o)[S4]



^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 7.1 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 147.2, 139.7, 135.2, 130.3, 129.0, 128.5, 127.7, 127.4.

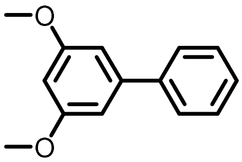
[1,1'-biphenyl]-3-carbonitrile (3p)[S1]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.55 (dt, *J* = 11.1, 4.8 Hz, 3H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 138.9, 131.5, 130.7, 130.7, 129.6, 129.2, 128.4, 127.1, 118.9, 113.0.

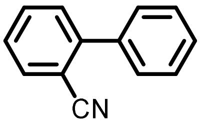
3,5-dimethoxy-1,1'-biphenyl (3q)[S7]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dt, *J* = 8.3, 1.8 Hz, 2H), 7.47–7.40 (m, 2H), 7.39–7.32 (m, 1H), 6.73 (d, *J* = 2.3 Hz, 2H), 6.47 (t, *J* = 2.3 Hz, 1H), 3.85 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 143.5, 141.2, 128.7, 127.6, 127.2, 105.5, 99.3, 55.4.

[1,1'-biphenyl]-2-carbonitrile (3r)[S8]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.72 (m, 1H), 7.62 (td, *J* = 7.7, 1.4 Hz, 1H), 7.58–7.53 (m, 2H), 7.52–7.39 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 138.2, 133.8, 132.9, 130.1, 128.8, 128.8, 127.6, 118.8, 111.3.

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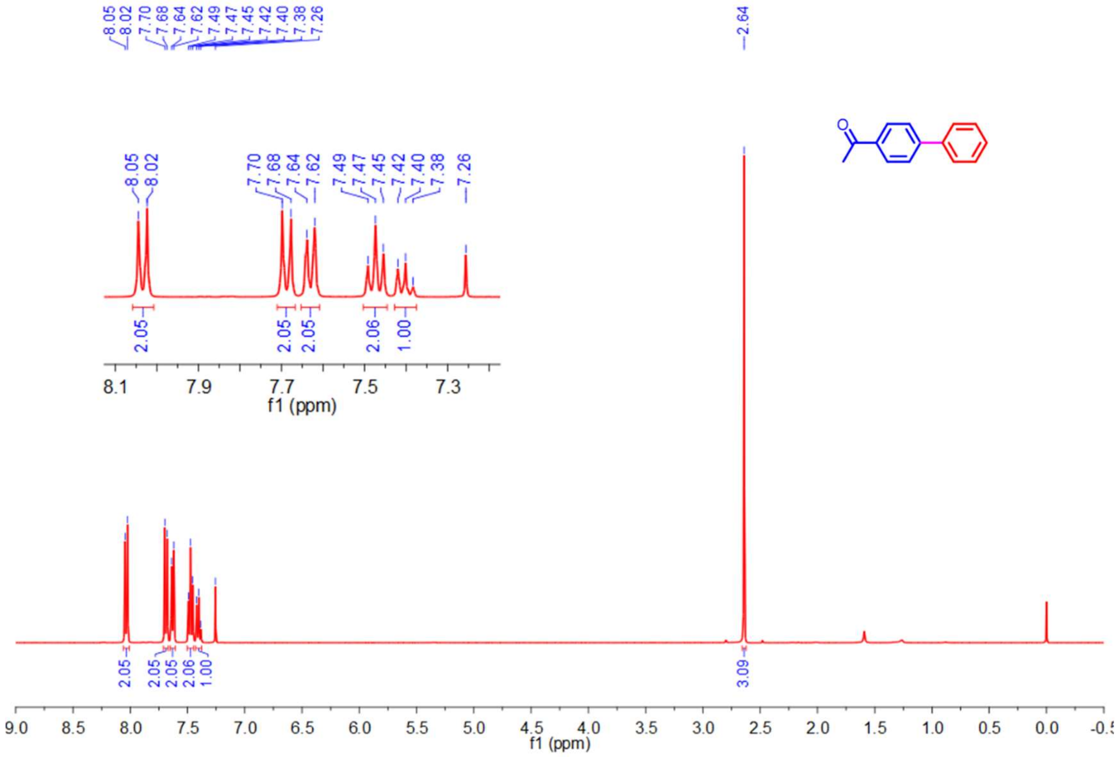
S7 C. Zhong, M. Liu, X. Qiu, H. Wei, B. Cui, Y. Shi and C. Cao, *J. Org. Chem.*, **2023**, *88*, 13418-13426.

S8 Y. Yan, J. Sun, G. Li, L. Yang, W. Zhang, R. Cao, C. Wang, J. Xiao and D. Xue, *Org Lett*., **2022**, *24*, 2271-2275.

Fig. S6 ^{1}H and ^{13}C NMR spectra of **3a**



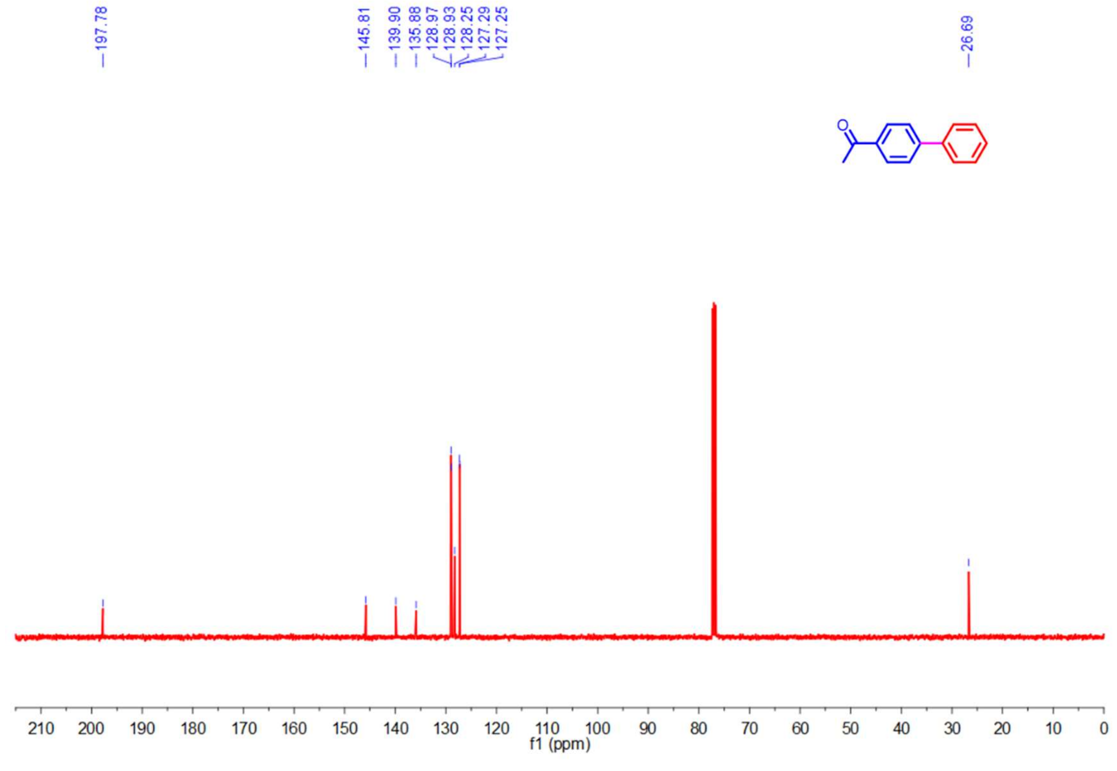
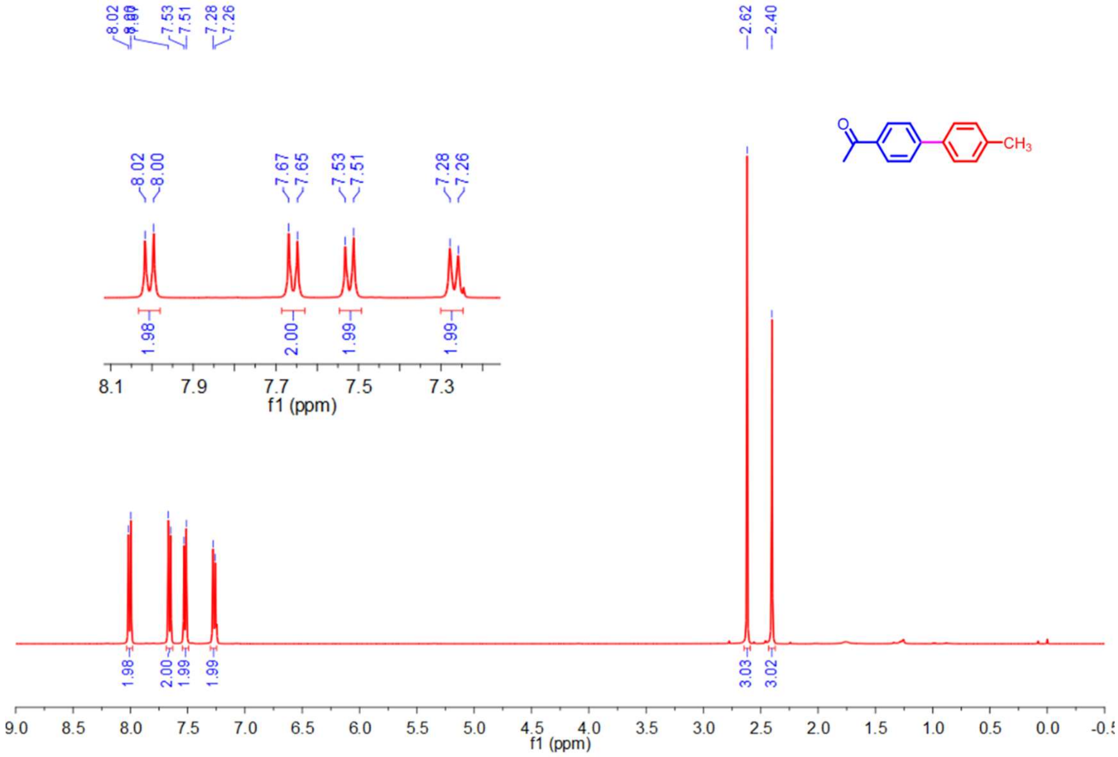


Fig. S7 ^{1}H and ^{13}C NMR spectra of **3b**



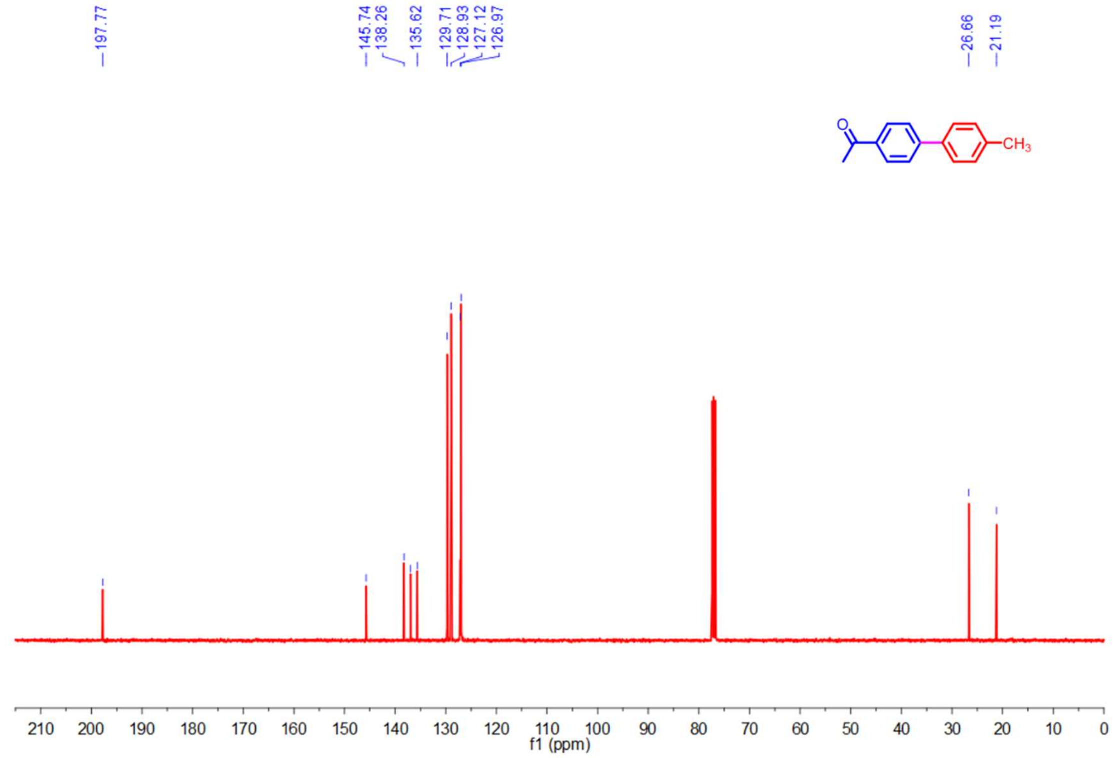
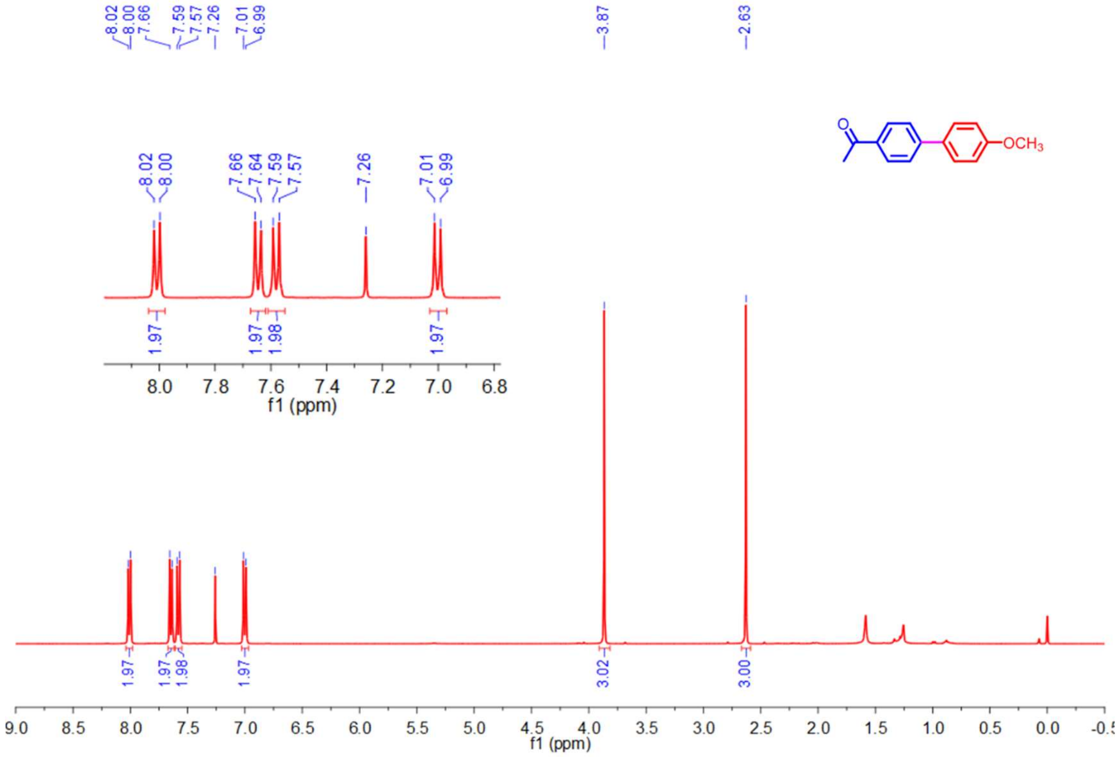


Fig. S8 ^{1}H, ^{13}C and ^{19}F NMR spectra of **3c**



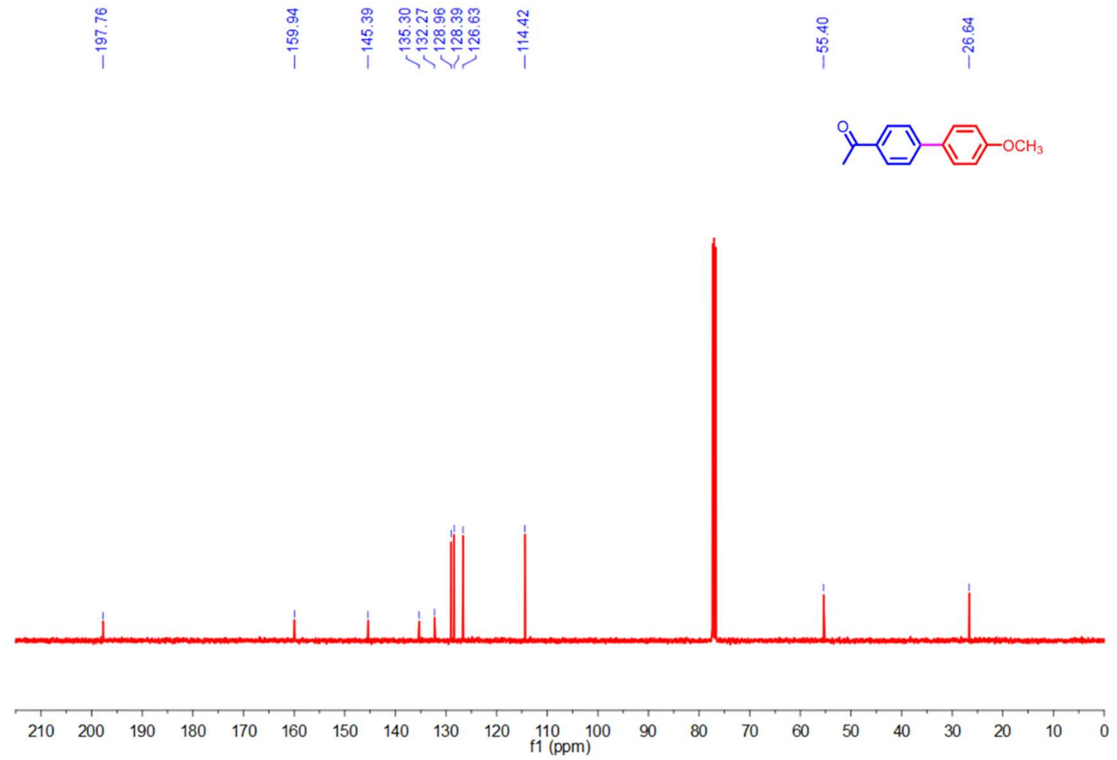
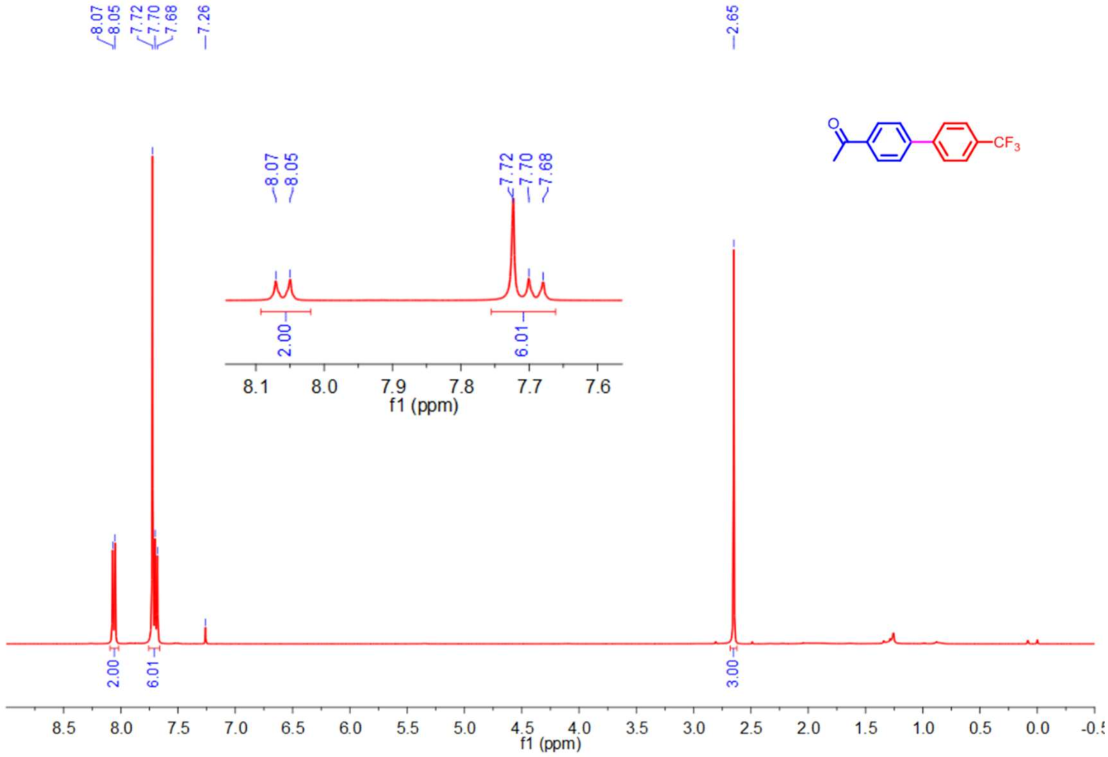
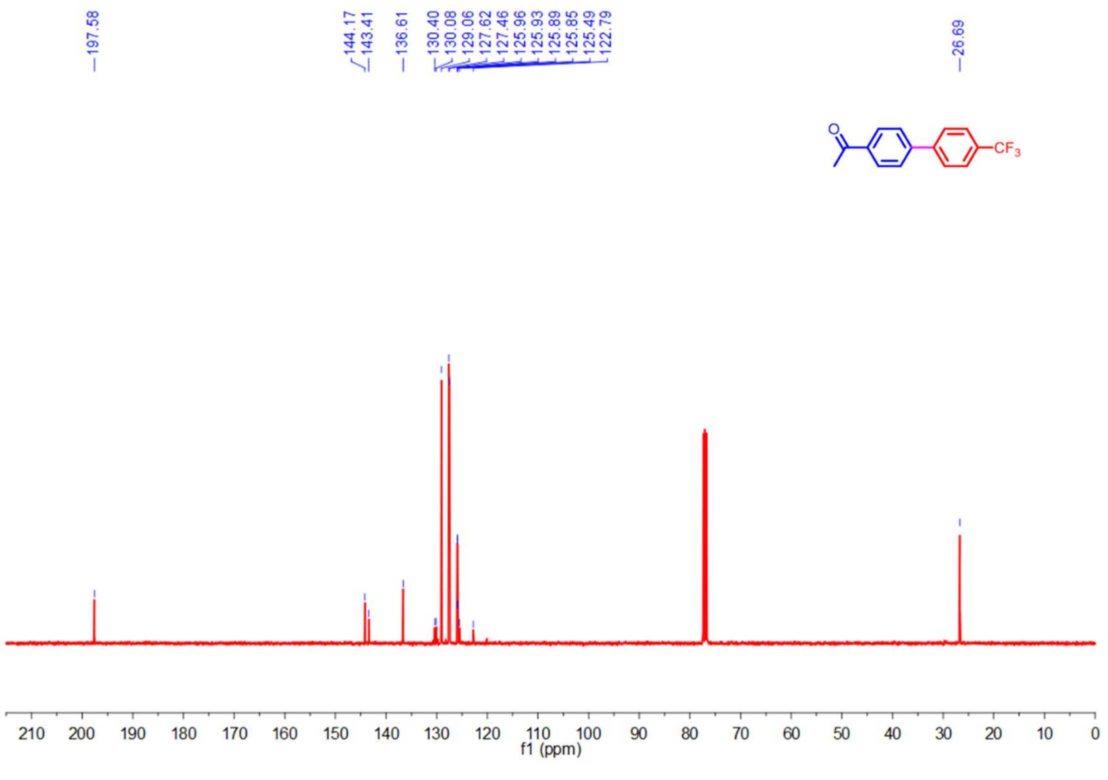


Fig. S9 ^{1}H and ^{13}C NMR spectra of **3d**





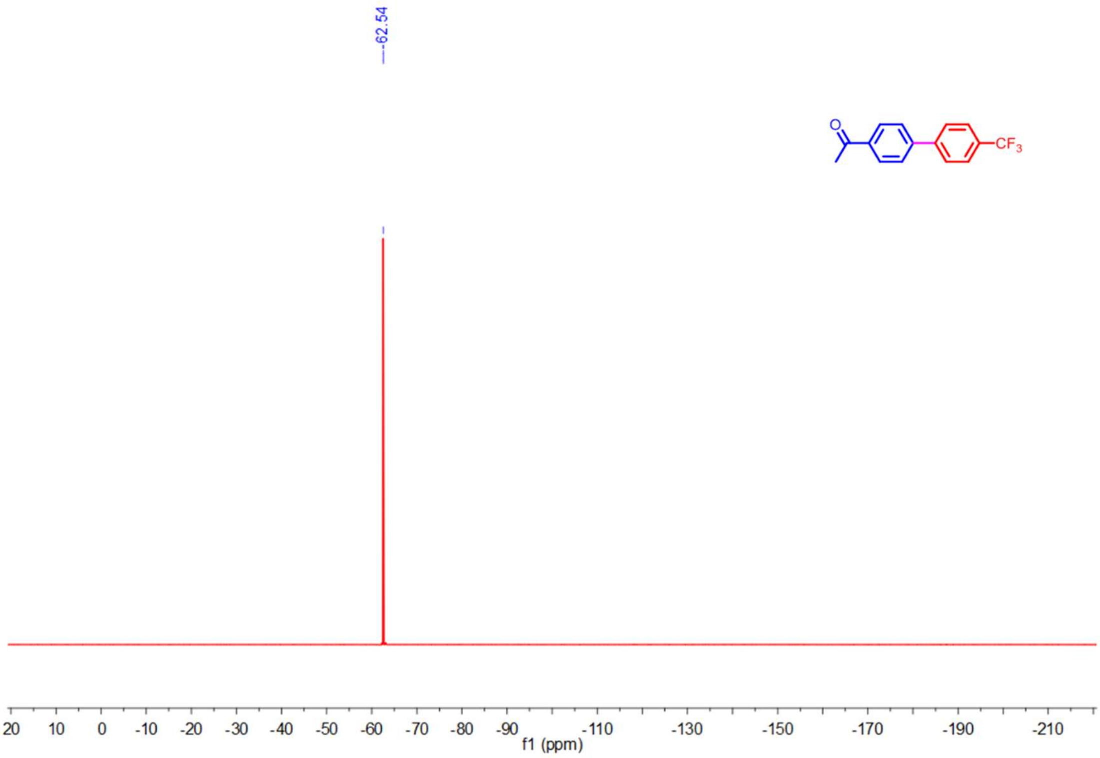
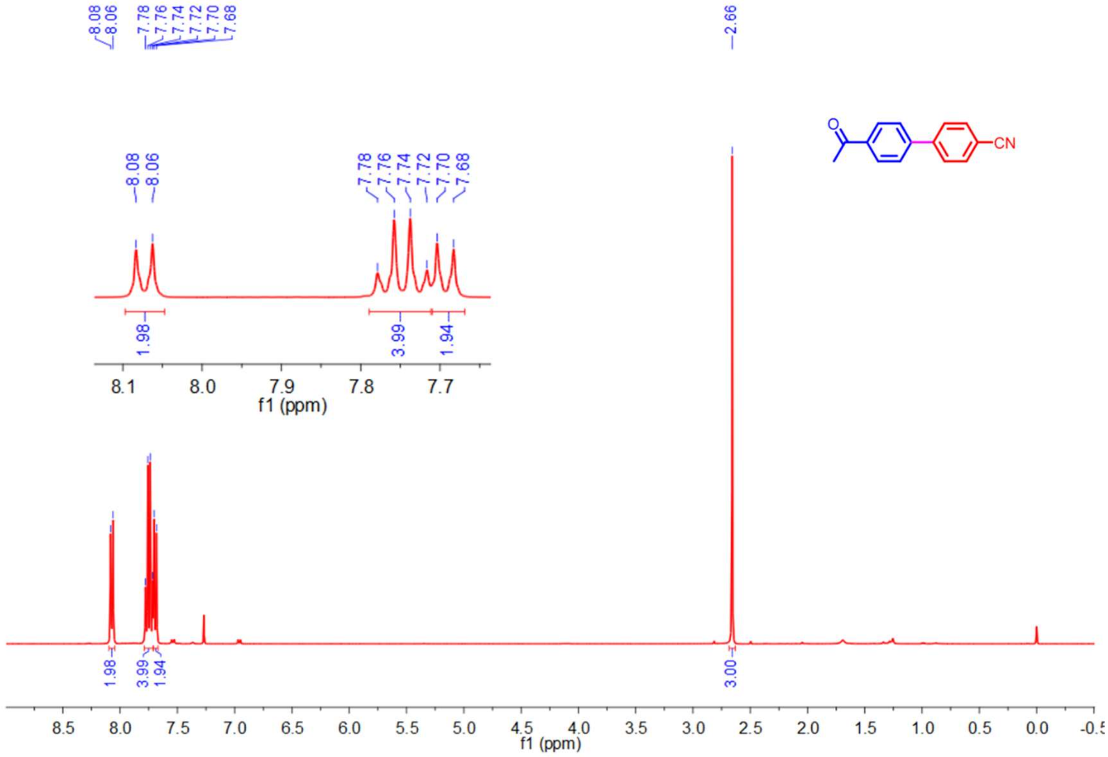

-62.54
CF3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

Fig. S10 ^{1}H and ^{13}C NMR spectra of **3e**



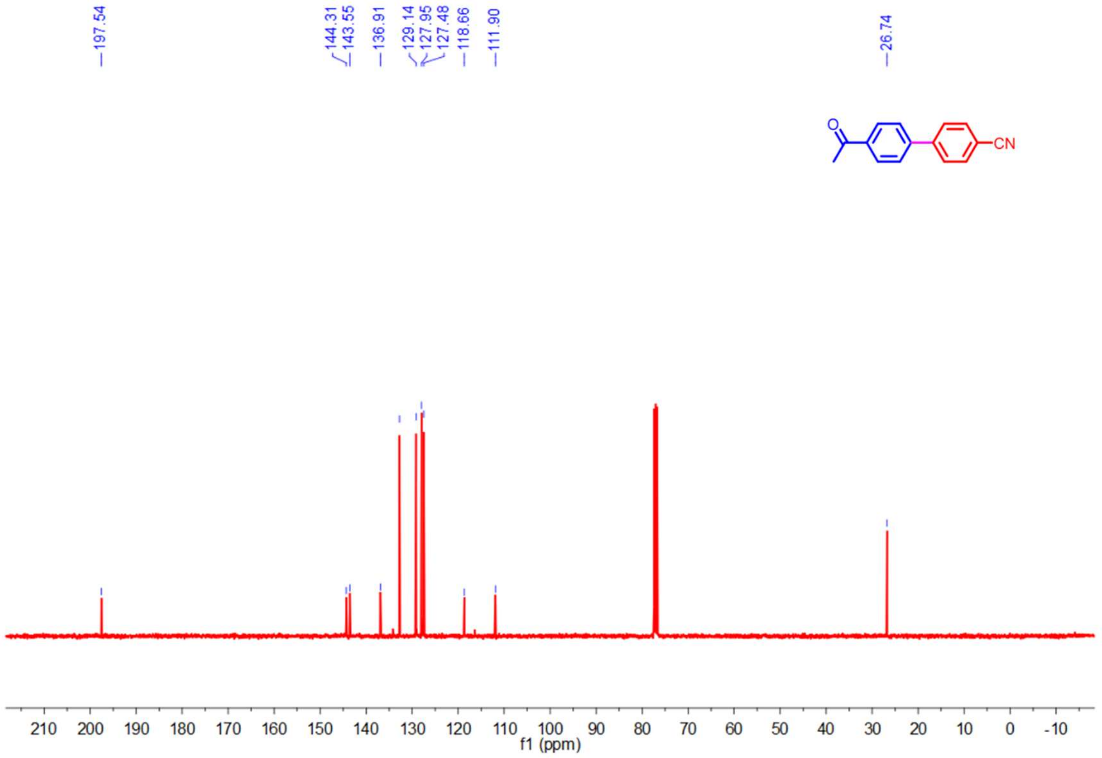
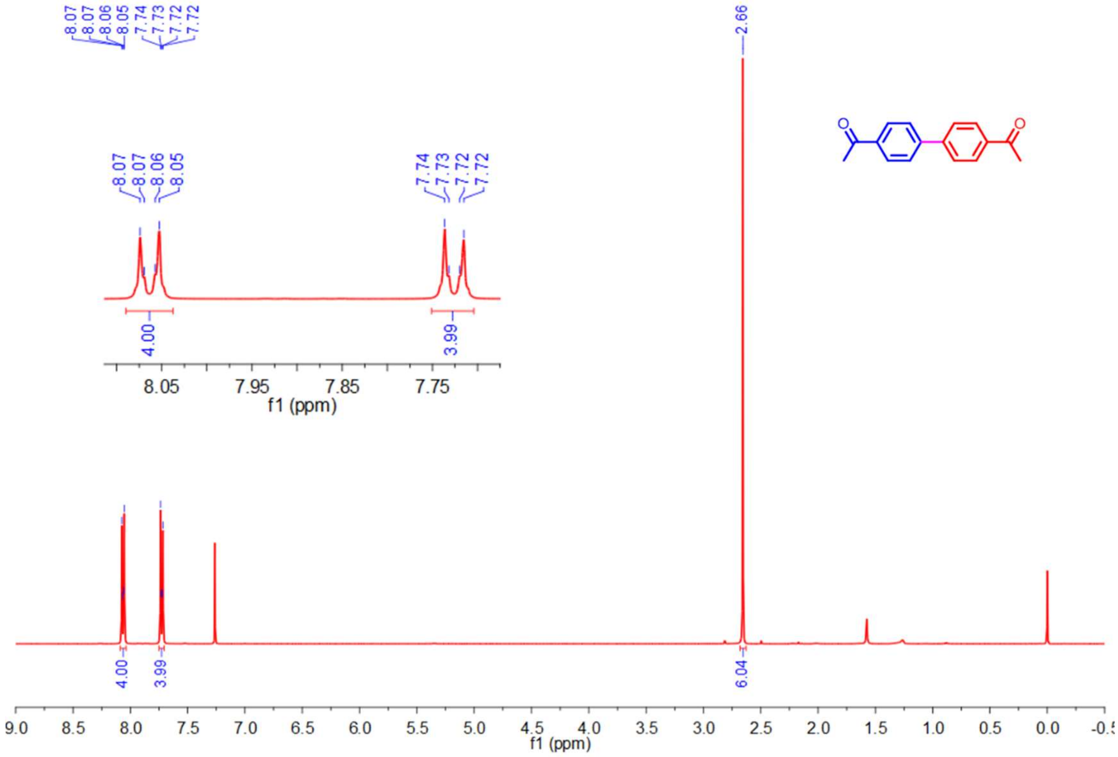


Fig. S11 [1]H and [13]C NMR spectra of **3f**



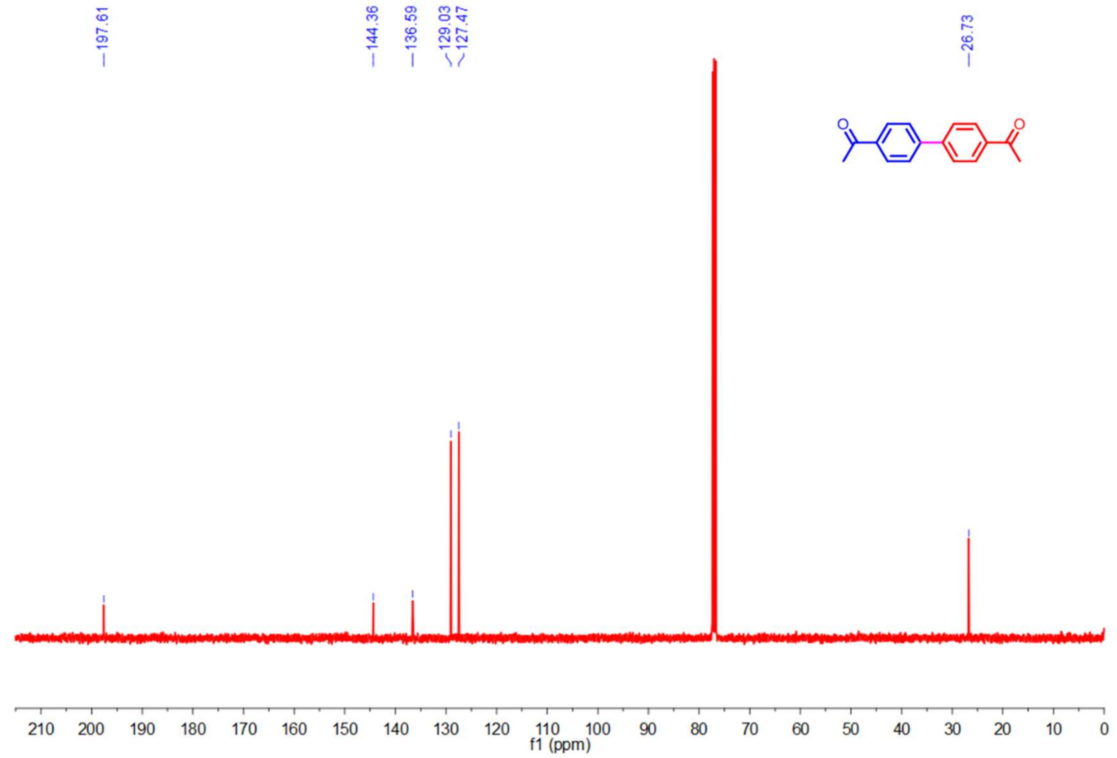
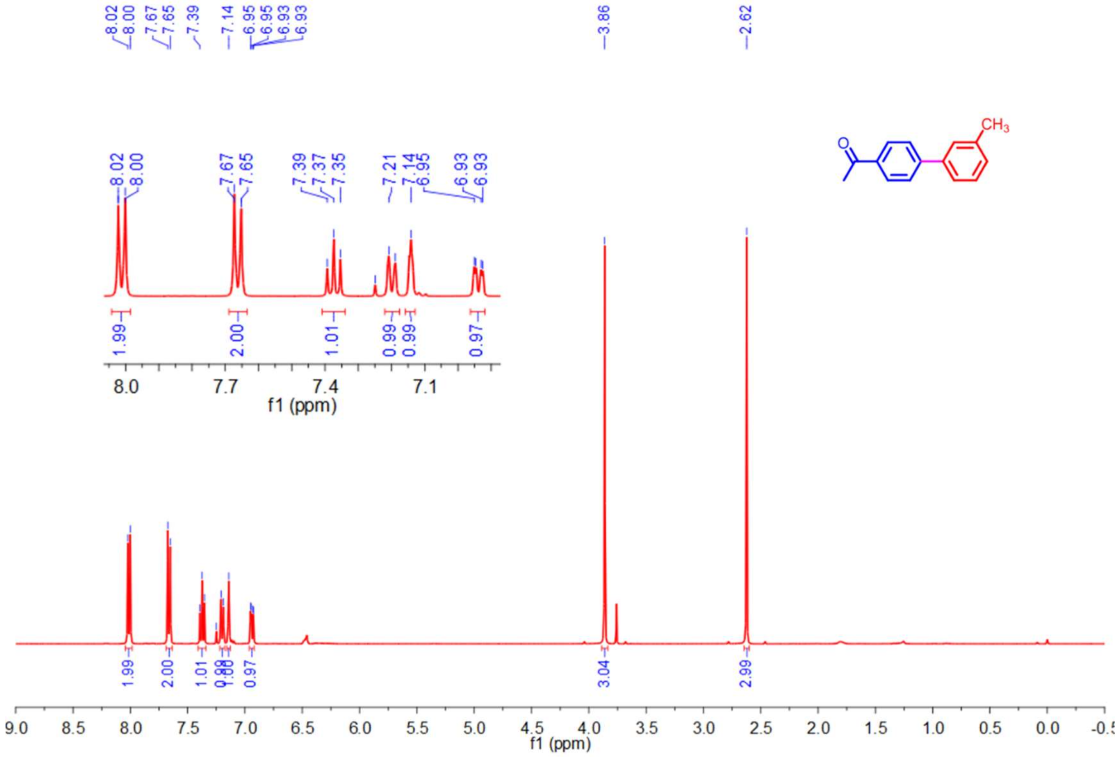


Fig. S12 ^{1}H and ^{13}C NMR spectra of **3g**



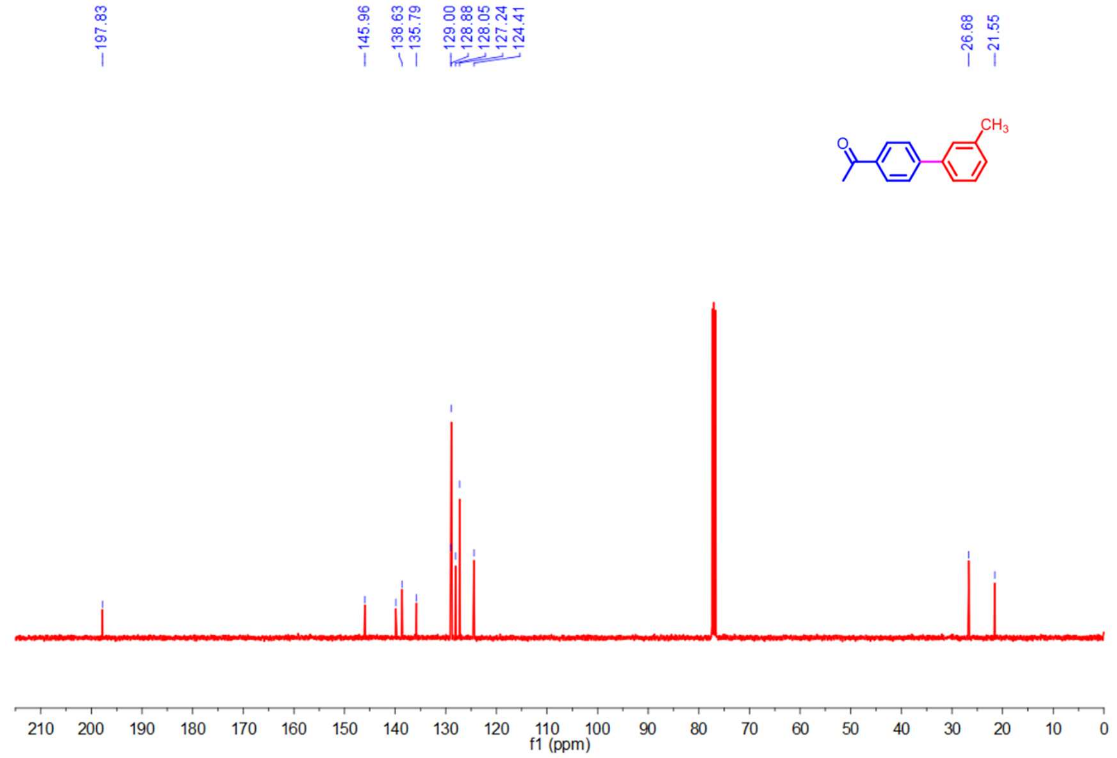
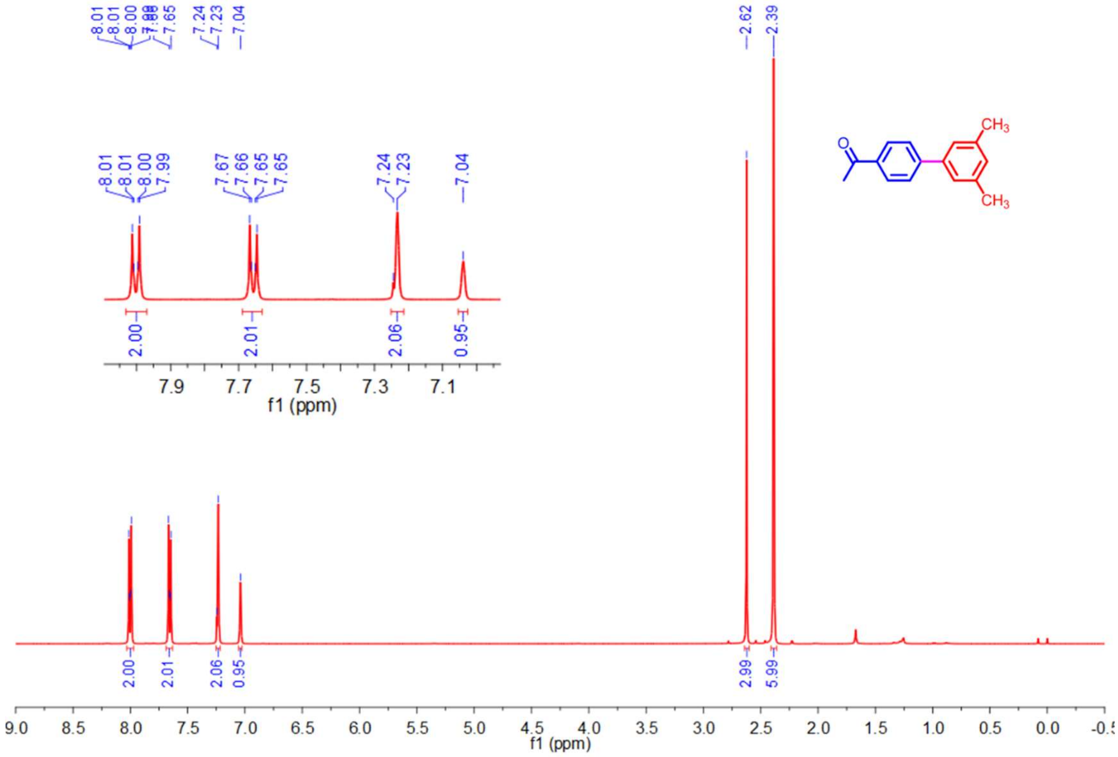


Fig. S13 ^{1}H and ^{13}C NMR spectra of **3h**



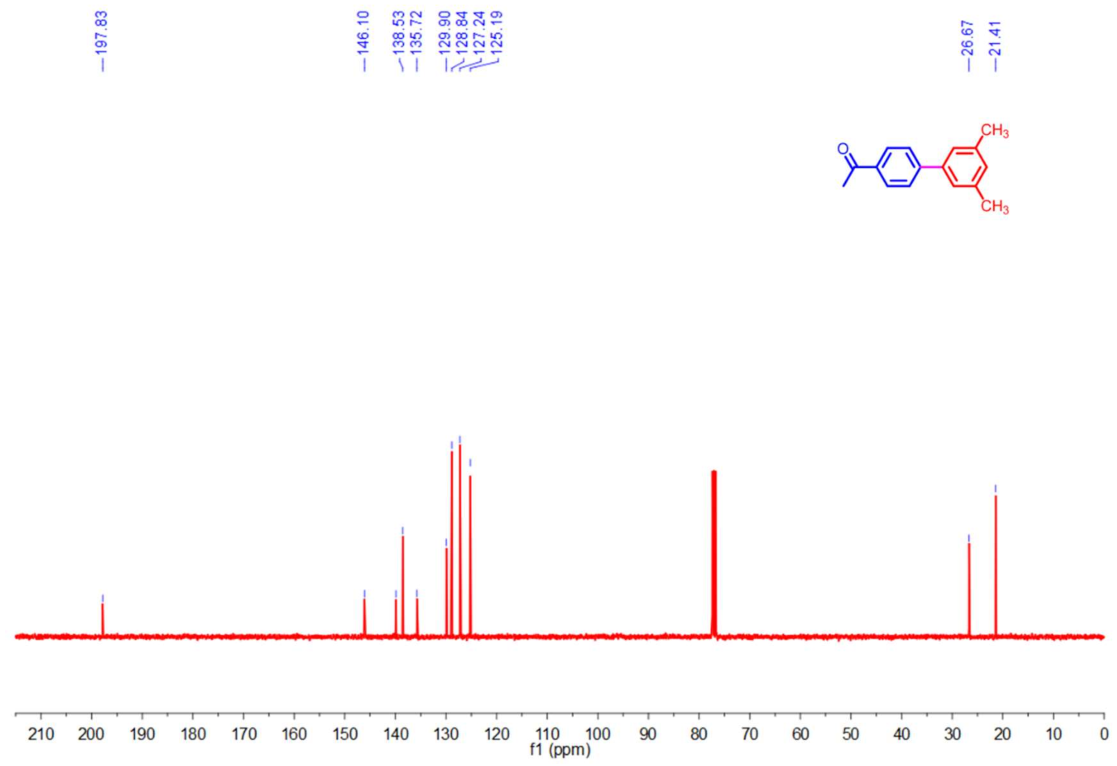
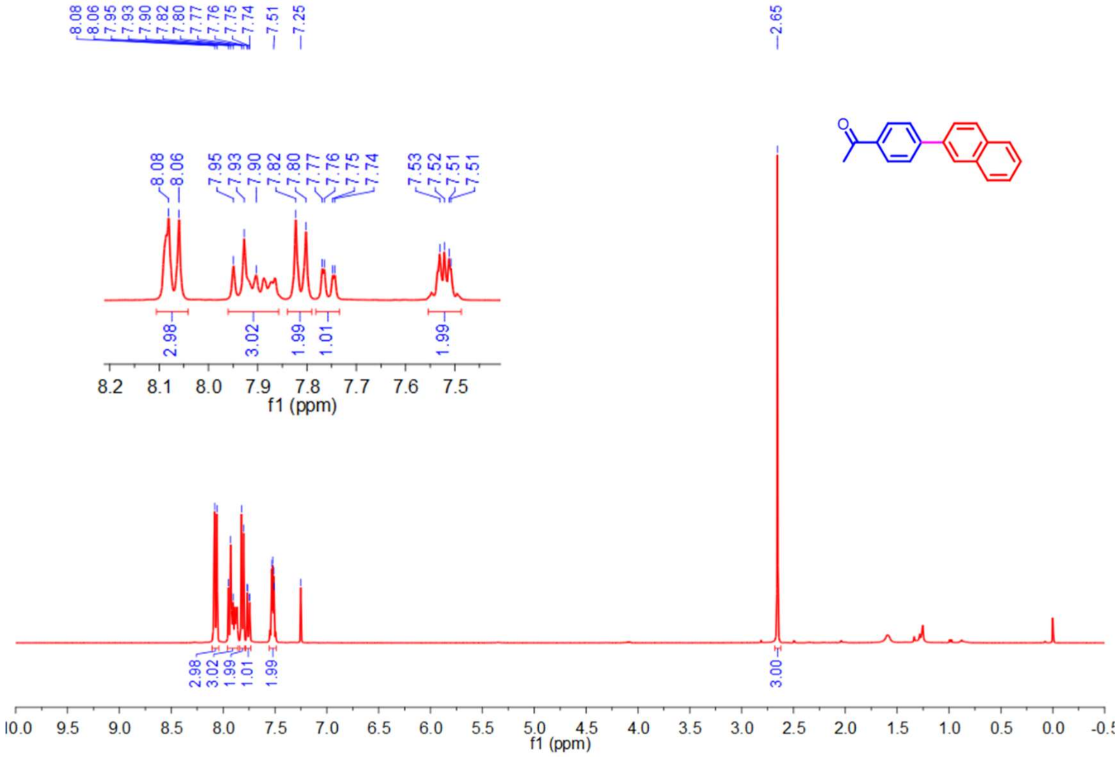


Fig. S14 ^{1}H and ^{13}C NMR spectra of **3i**



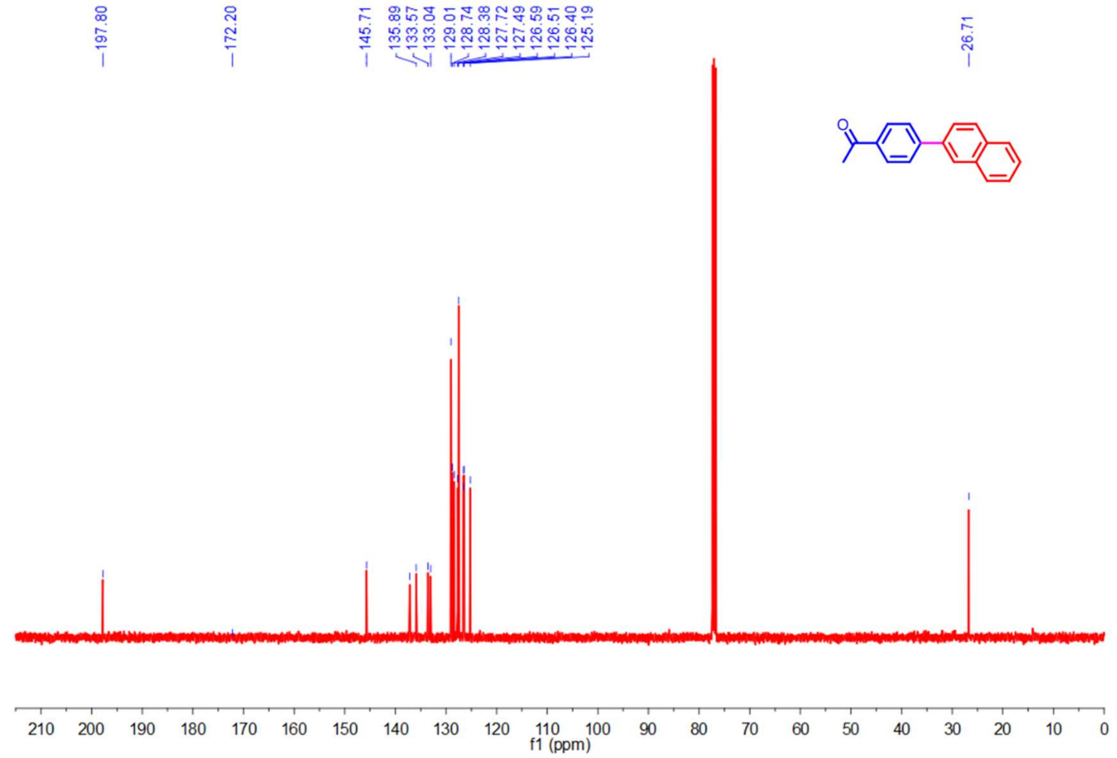


Fig. S15 ^{1}H and ^{13}C NMR spectra of **3j**

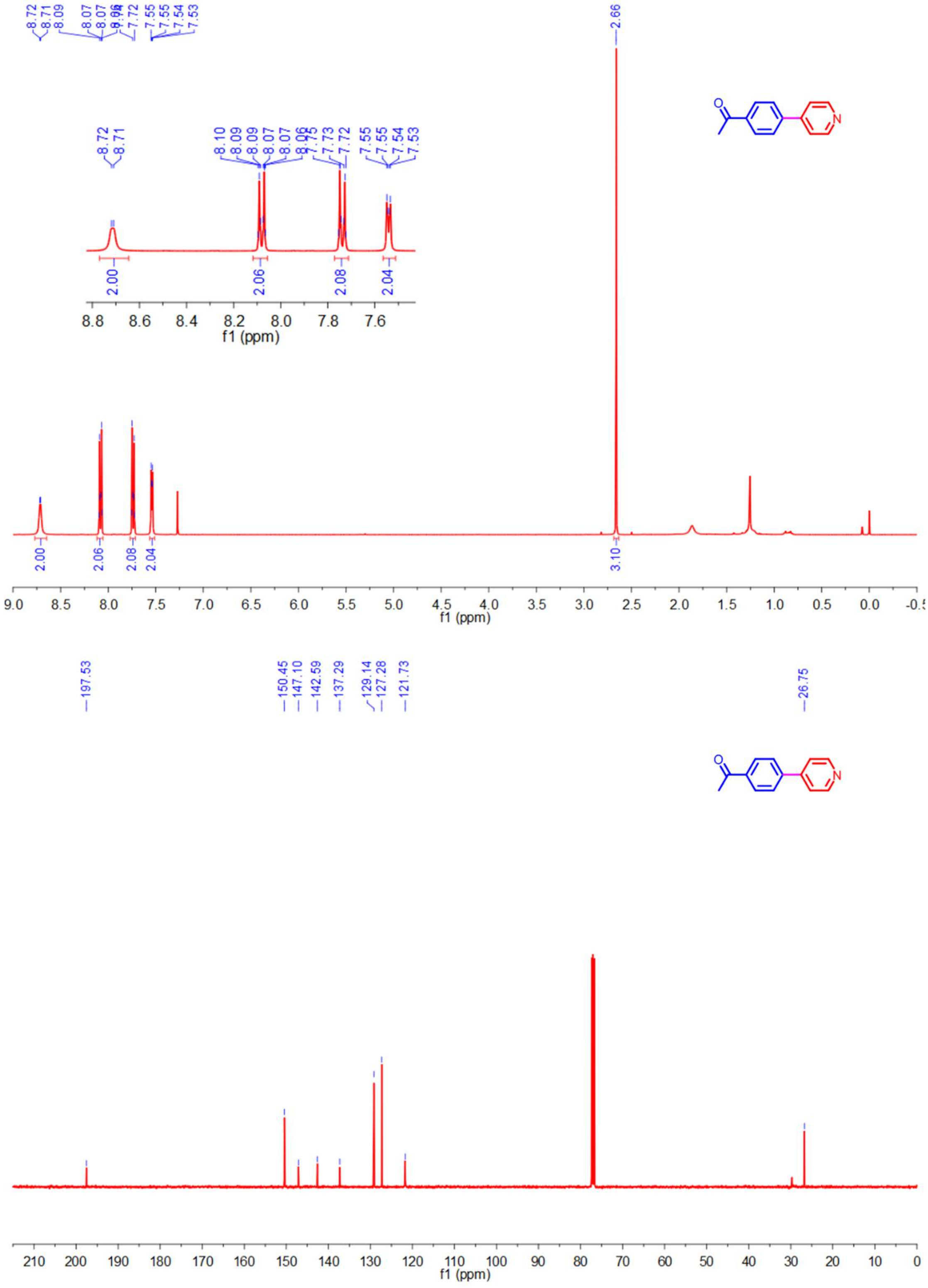
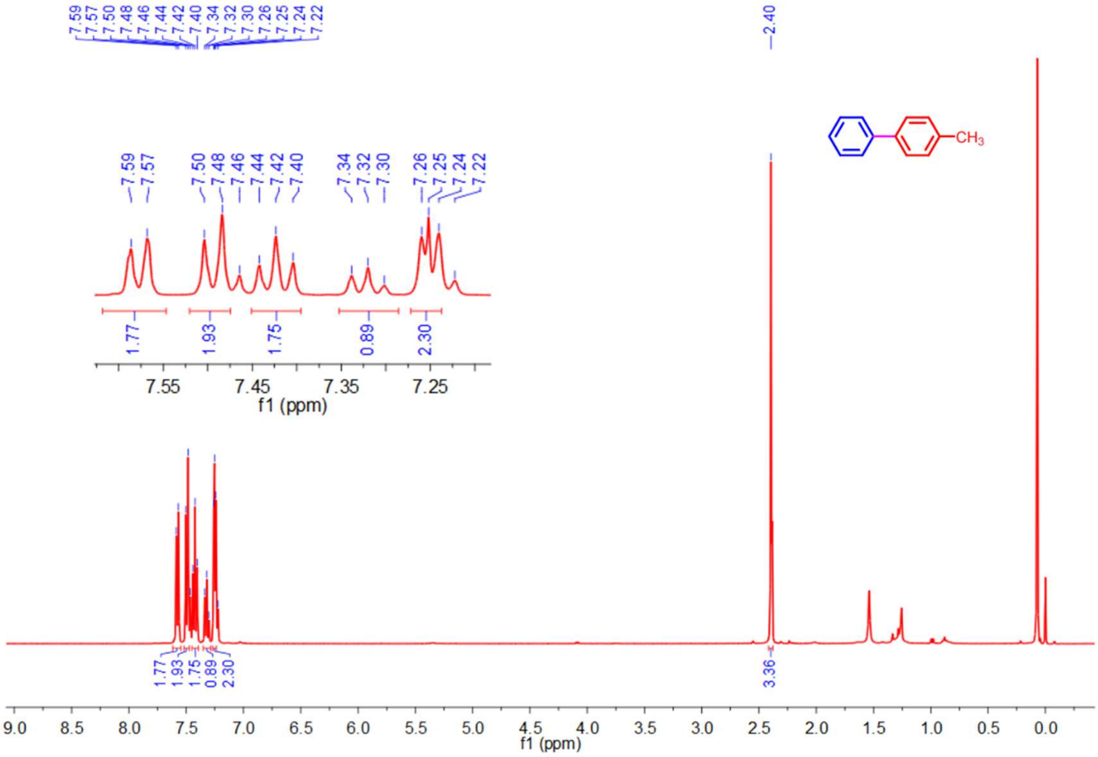


Fig. S16 ^{1}H and ^{13}C NMR spectra of **3k**



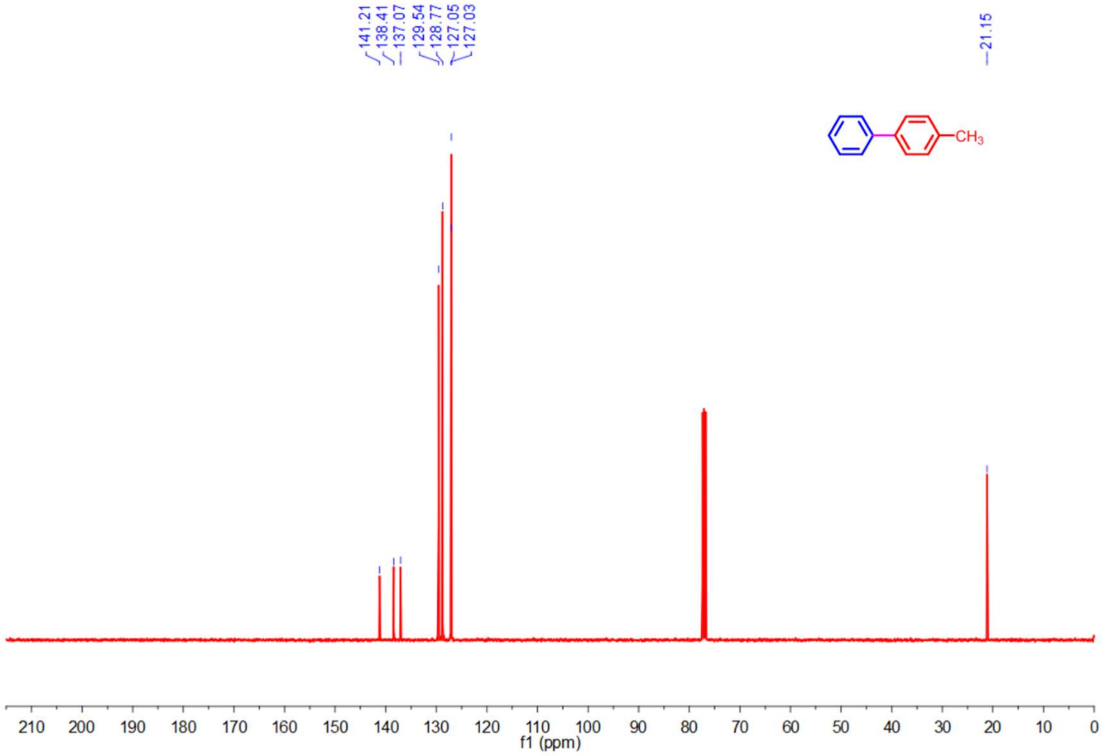
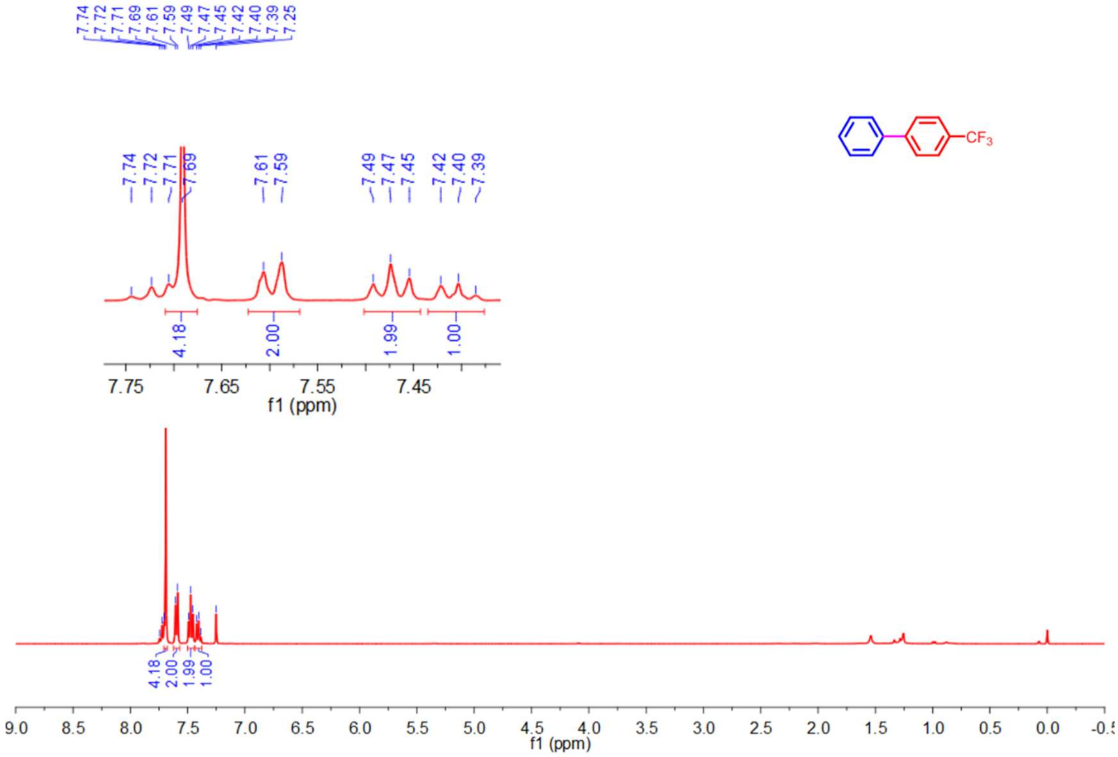
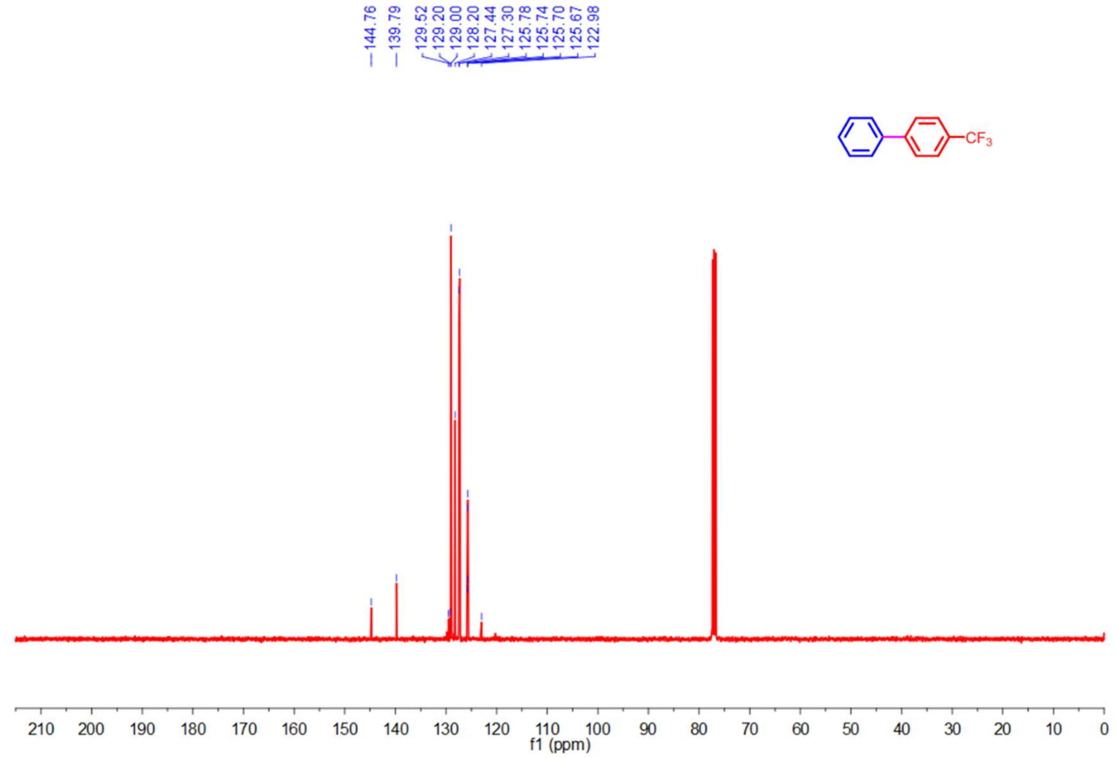


Fig. S17 ^{1}H and ^{13}C NMR spectra of **3l**





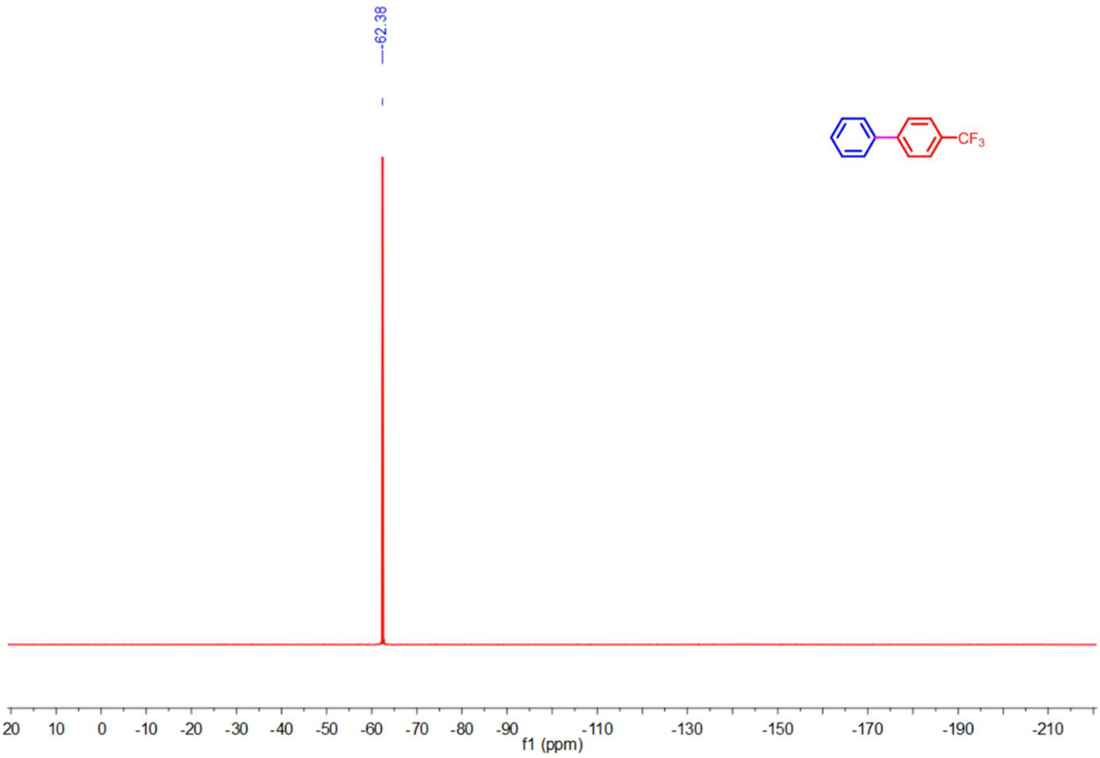
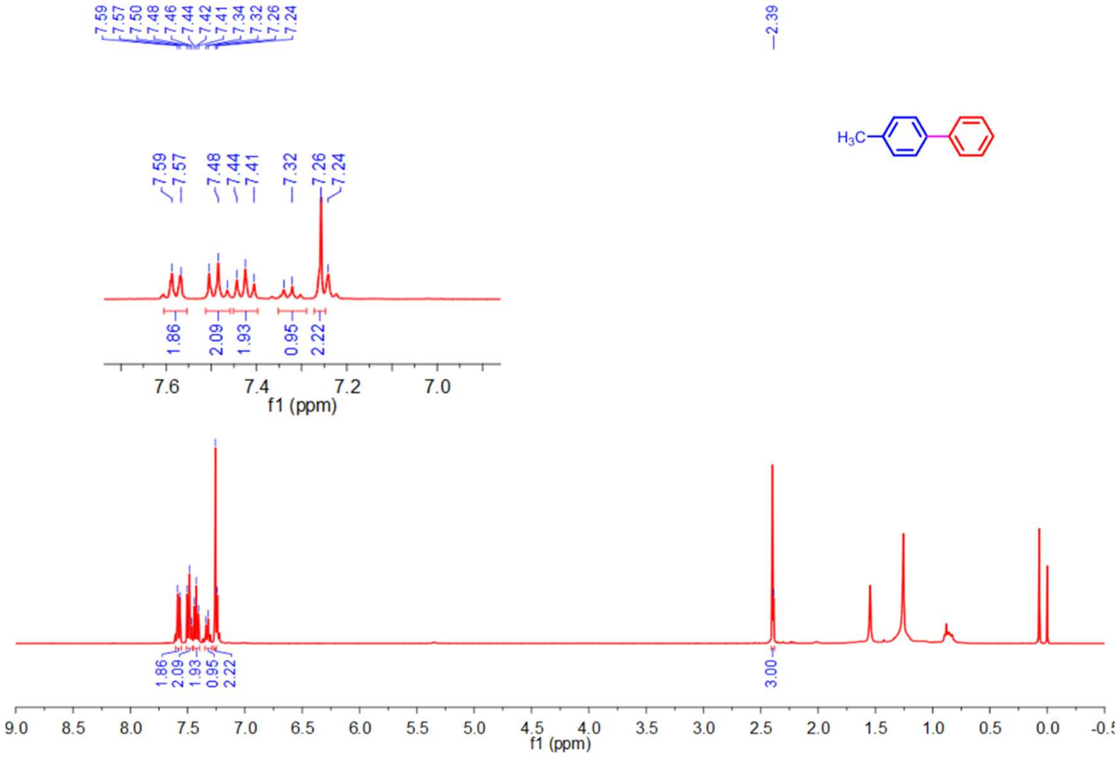

-62.38
CF3
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

Fig. S18 ^{1}H and ^{13}C NMR spectra of **3m**



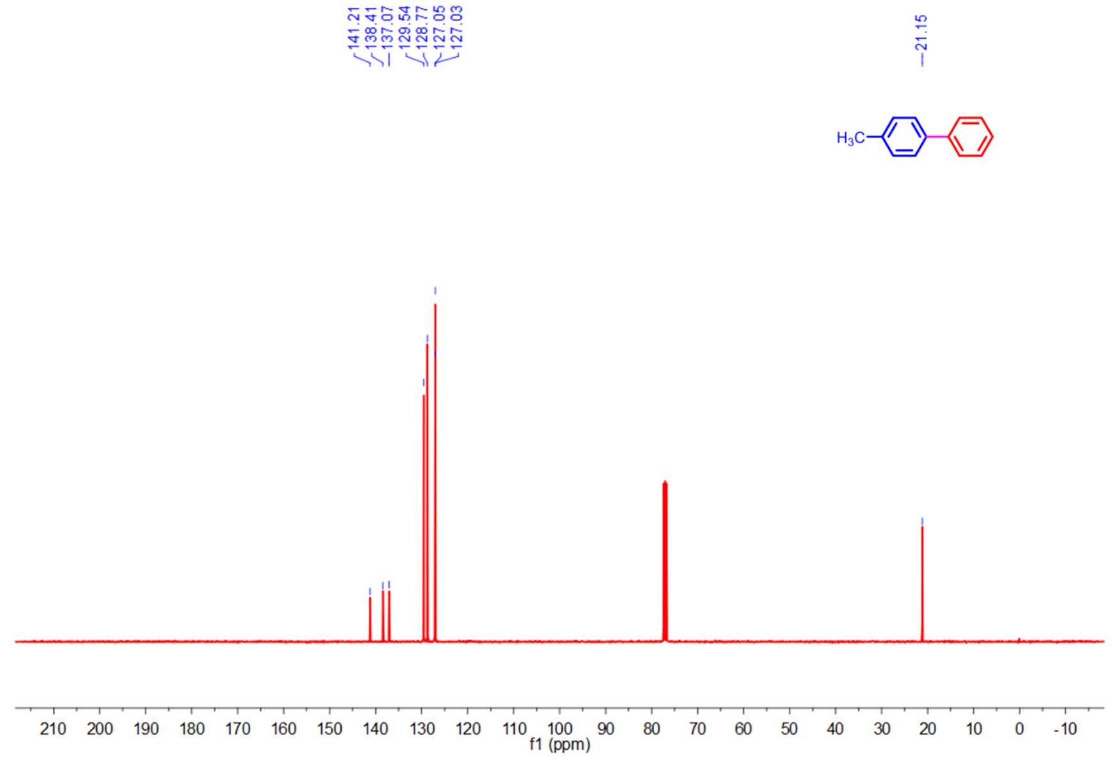
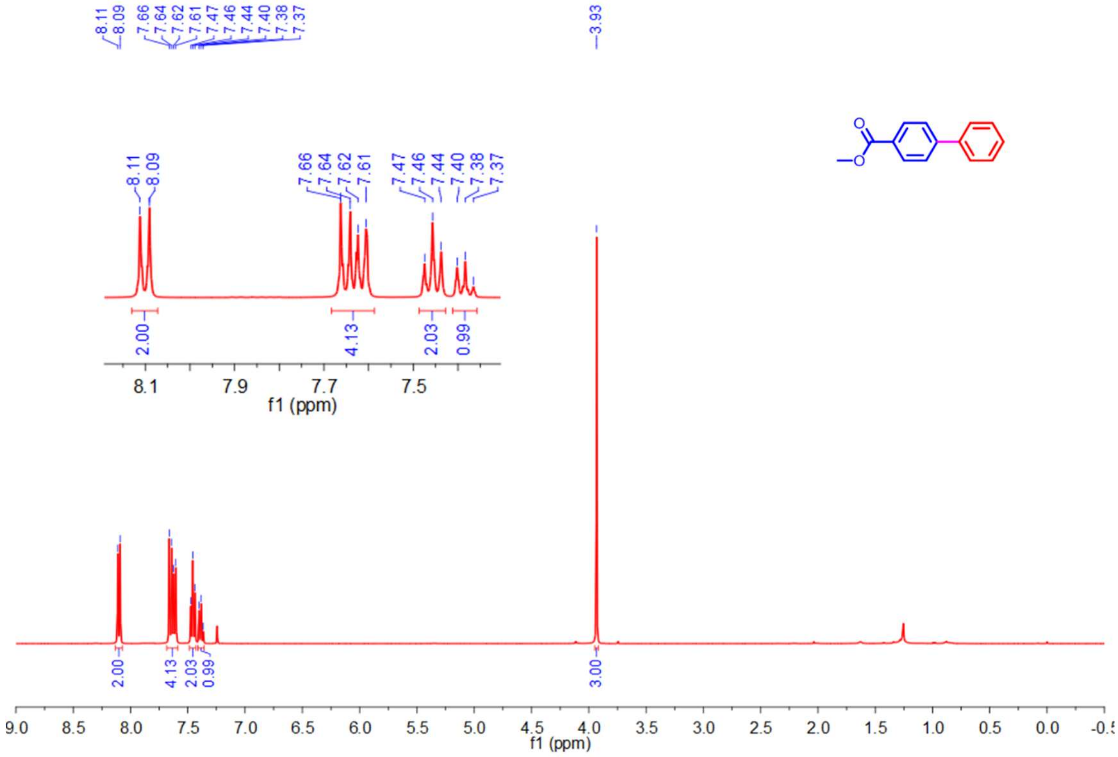


Fig. S19 ^{1}H and ^{13}C NMR spectra of **3n**



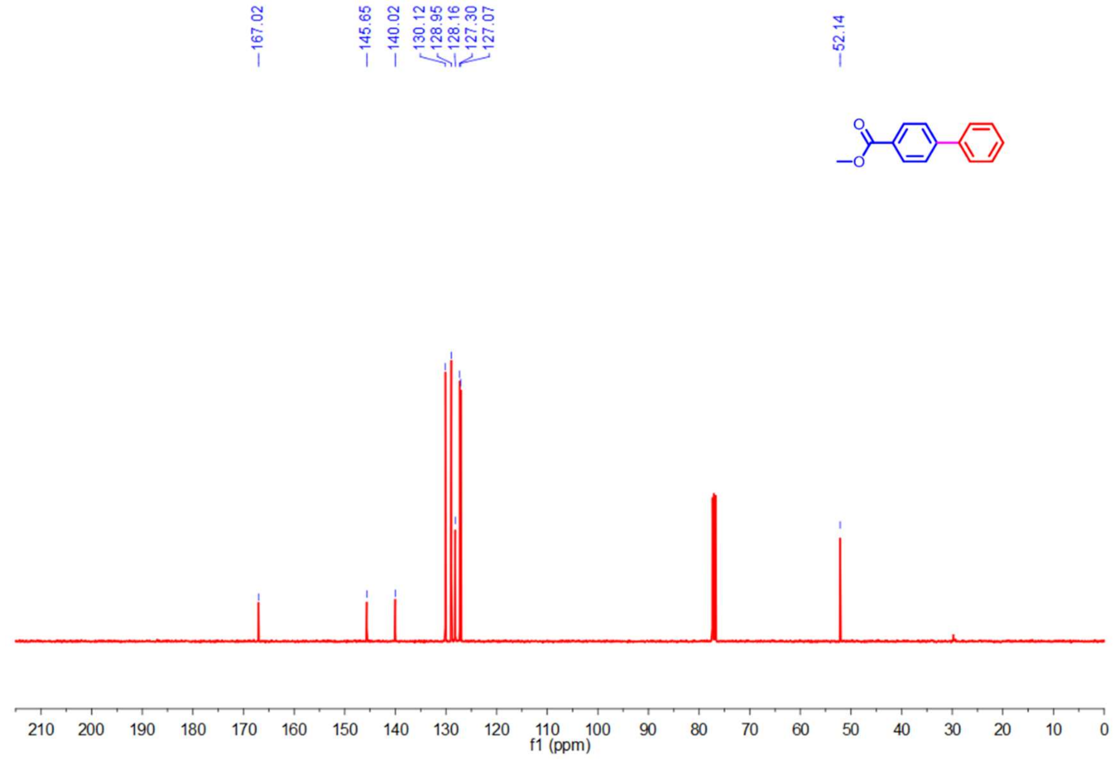
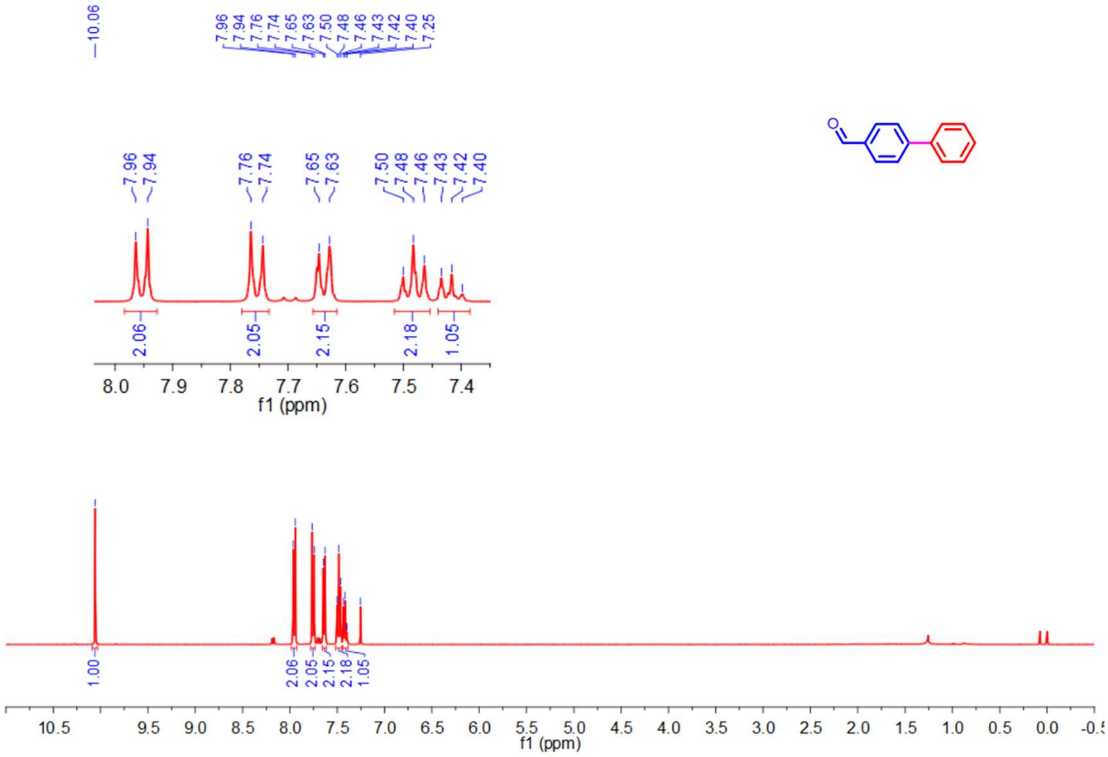


Fig. S20 ^{1}H and ^{13}C NMR spectra of **3o**



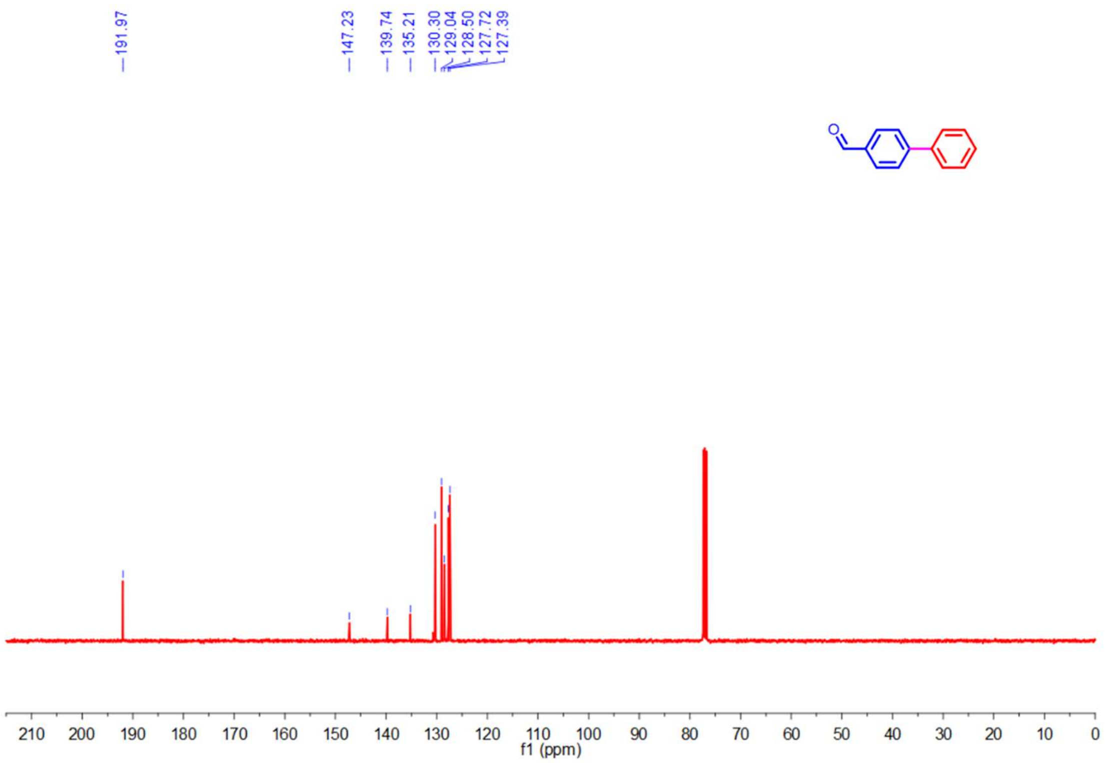
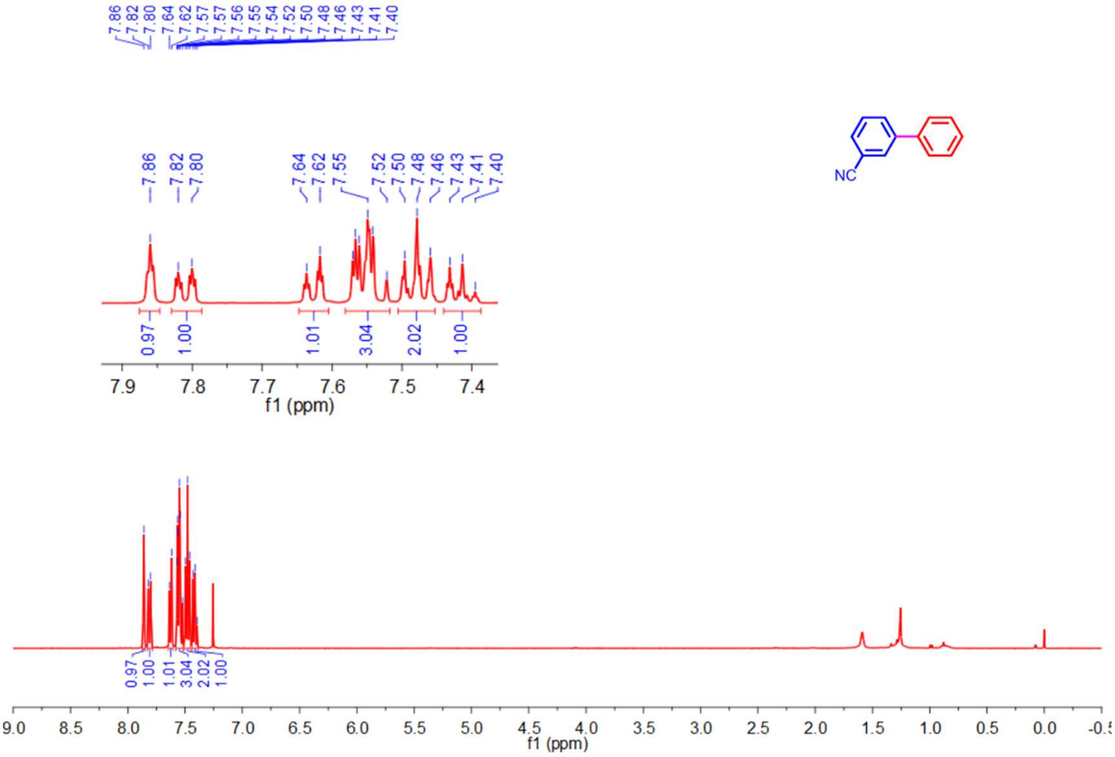


Fig. S21 ^{1}H and ^{13}C NMR spectra of **3p**



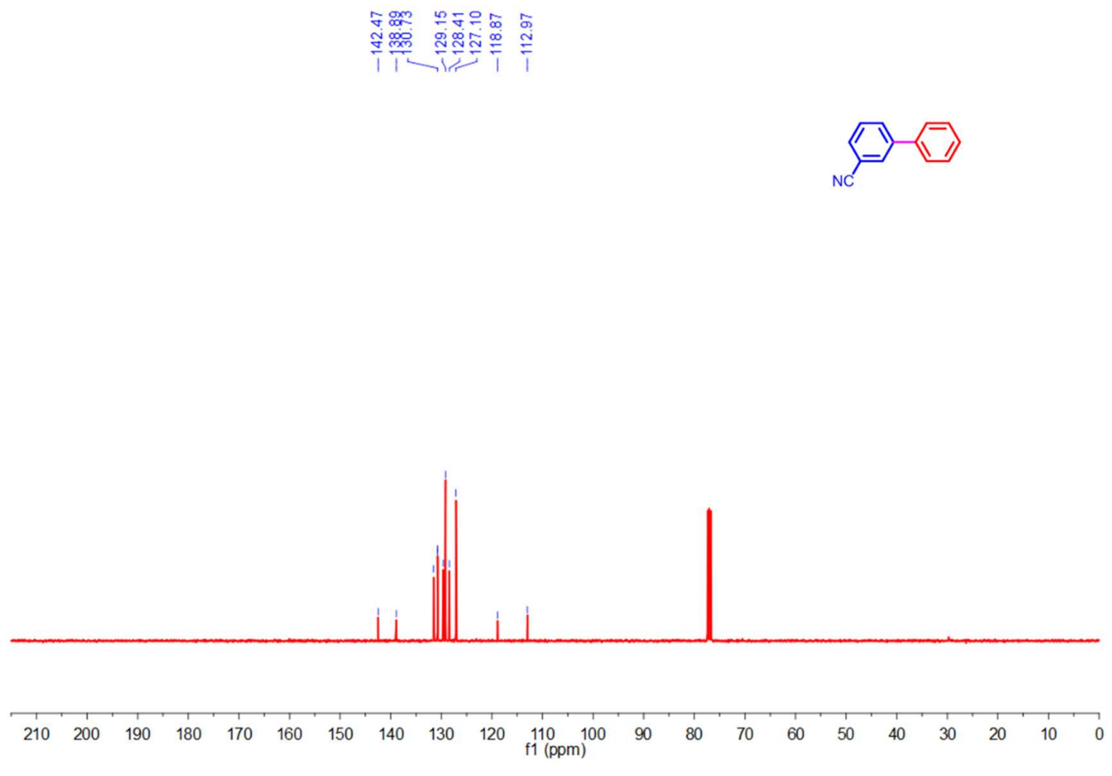
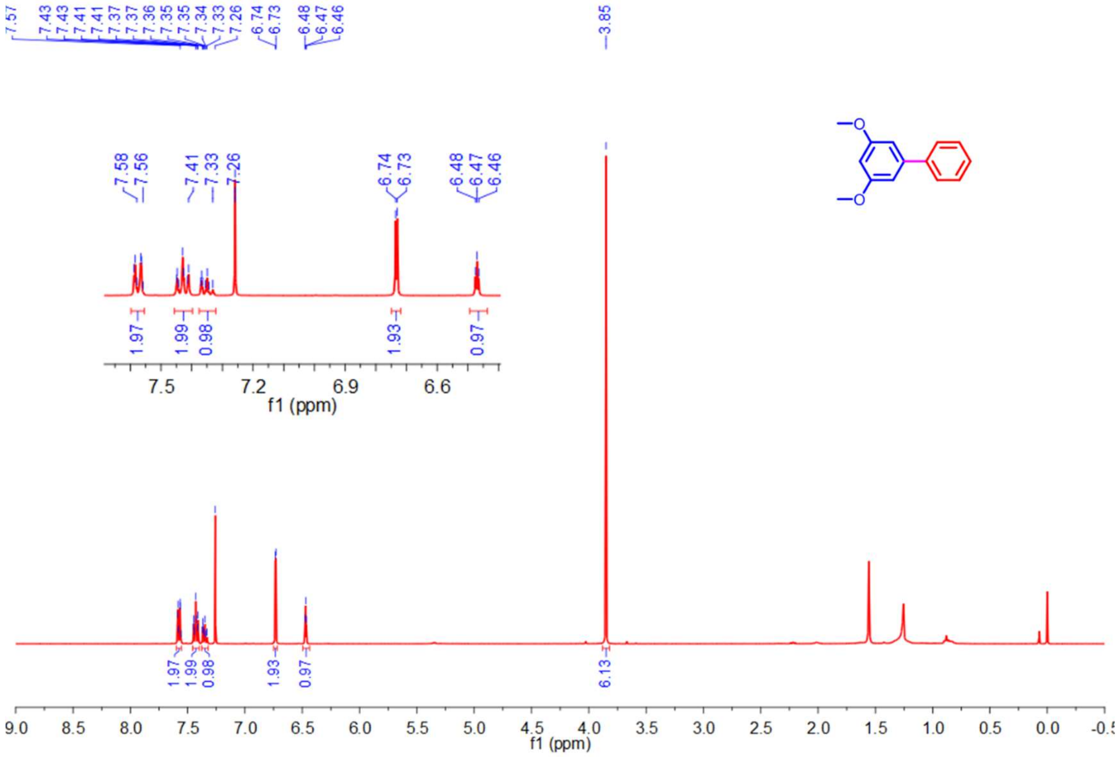


Fig. S22 ^{1}H and ^{13}C NMR spectra of **3q**



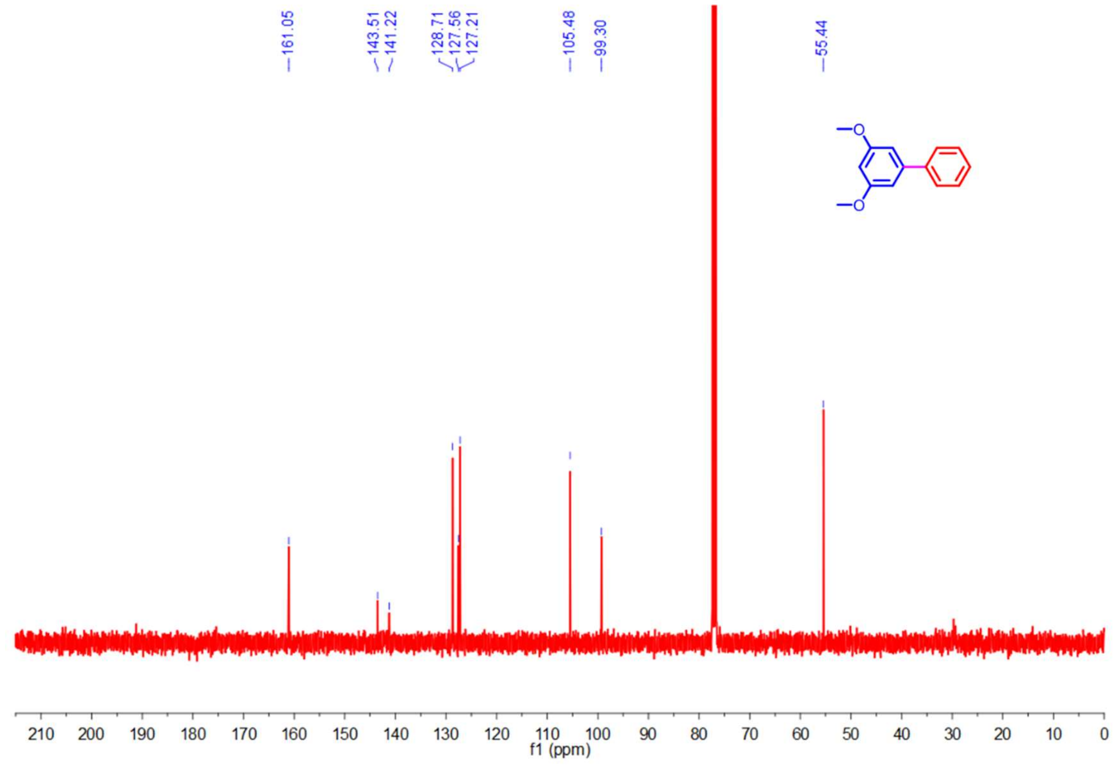


Fig. S23 ^{1}H and ^{13}C NMR spectra of **3r**