Supporting Information

B_2pin_2-catalyzed oxidative cleavage of a C=C double bond with molecular oxygen

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1. Materials and methods

General. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Varian Inova-400 (400 MHz, 100 MHz and 376 MHz, respectively) spectrometer. ^{1}H and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 or $CDCl_3$ (δ(^{1}H), 7.26 ppm; δ(^{13}C), 77.16 ppm) and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as internal standard. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. The HRMS analysis was obtained on a Agilent 6540 UHD Q-TOF mass spectrometer. The melting point was recorded on BÜCHI (M-560) and uncorrected. Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel 60 F254 plates and viewed by UV light (254 nm). Column chromatographic purification was performed using 200-300 mesh silica gel.

Materials. All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. Starting materials **1b-e**,[1] **1g-t**,[1] **3**,[1] **5**[2] are known compounds and synthesized according to the reported method. Their spectroscopic features are in good agreement with those reported in the literatures. Starting materials **1f**,[1] **1u-x**,[1] **1y**[3] are new compounds and prepared by the reported procedure.

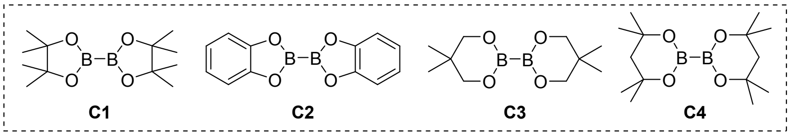
2. Experimental procedures

2.1 Optimization of reaction conditions[a]

Table S1:

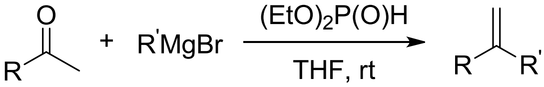
Entry	[B]/(mol%)	T (°C)	Solvent	Yield (%)[b]
1	C1 (10)	100	DMSO/H_2O	66
2	C2 (10)	100	DMSO/H_2O	15
3	C3 (10)	100	DMSO/H_2O	32
4	C4 (10)	100	DMSO/H_2O	28
5	C1 (10)	100	DMSO	56
6	C1 (10)	100	H_2O	0
7	C1 (10)	100	1,4-dioxane	11
8	C1 (10)	100	DMF	16
9	C1 (10)	100	Glycerol	36
10	C1 (10)	100	NMP	77
11	C1 (20)	100	NMP	74
12	C1 (5)	100	NMP	74
13	C1 (10)	120	NMP	80
14	C1 (10)	80	NMP	60
15[c]	**C1 (10)**	**100**	**NMP**	**90**
16	C1 (0)	100	NMP	37
17	C1 (0)	100	DMSO/H_2O	32
18[d]	C1 (10)	100	NMP	3
19[e]	C1 (10)	100	NMP	17
20[d]	C1 (0)	100	NMP	0

[a] Reaction conditions: **1a** (0.5 mmol), [B] catalyst, solvent (1.0 mL), O_2 (1 atm), 100 °C, 22 h. [b] Isolated yields. [c] 30 h. [d] Under Ar. [e] Under air.



2.2 General procedure for synthesis of substrates

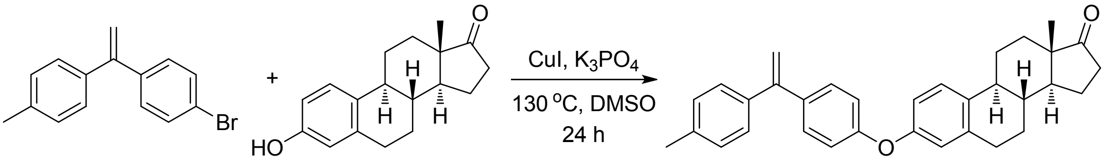
2.2.1 A typical procedure for the synthesis of 1 (except 1y):



Under a nitrogen atmosphere, a solution of Grignard reagents (8.8 mL, 1.0 M in

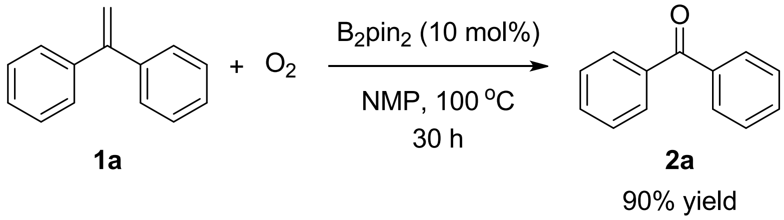
THF, 8.8 mmol) was added dropwise to a solution of carbonyl compounds (4.0 mmol) in dry THF (12 mL) at room temperature. After 0.5 h stirring, diethylphosphite (0.62 mL, 4.8 mmol) was added. The reaction mixture was stirred and monitored by TLC analysis. The reaction was then quenched with water and extracted with EtOAc (3×20 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered, and all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)).

2.2.2 A typical procedure for the synthesis of 1y:



Under a nitrogen atmosphere, the schlenk tube was loaded with K_3PO_4 (2 equiv) and estrone (2 equiv). Then, CuI (10 mol%) in DMSO and the aryl bromide (2 equiv) were added. The tube was sealed. After the reaction was stirred at 130 °C for 24 h, the mixture was extracted with EtOAc for 3 times. The combined organic phase was dried over anhydrous $MgSO_4$, filtered, and all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/EtOAc).

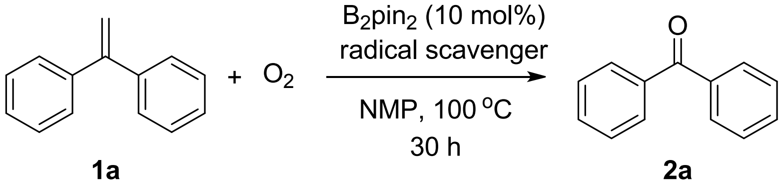
2.3 General procedure for synthesis of products (taking 2a as an example)



A mixture of 1,1-diphenylethylene **1a** (90 mg, 0.50 mmol), B_2pin_2 (13 mg, 0.05 mmol) and NMP (1.0 mL) were added to a 10 mL Schlenk tube. The reaction tube was flushed with O_2 for 1.0 minute and then equipped with a O_2 balloon. The reaction was stirred at 100 °C for 30 h. After cooling to ambient temperature, the resulting mixture was extracted with EtOAc (3×10 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered, and all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (35-60 °C)/EtOAc = 80:1, v/v) to afford the desired product **2a** in 90% yield.

3. Mechanistic studies

3.1 Radical trapping experiments

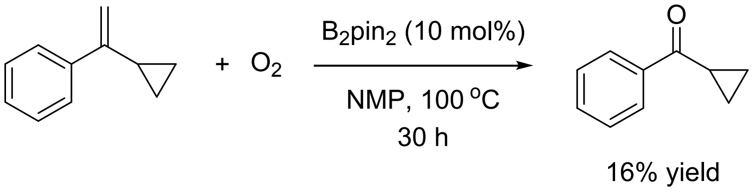


1a **2a**

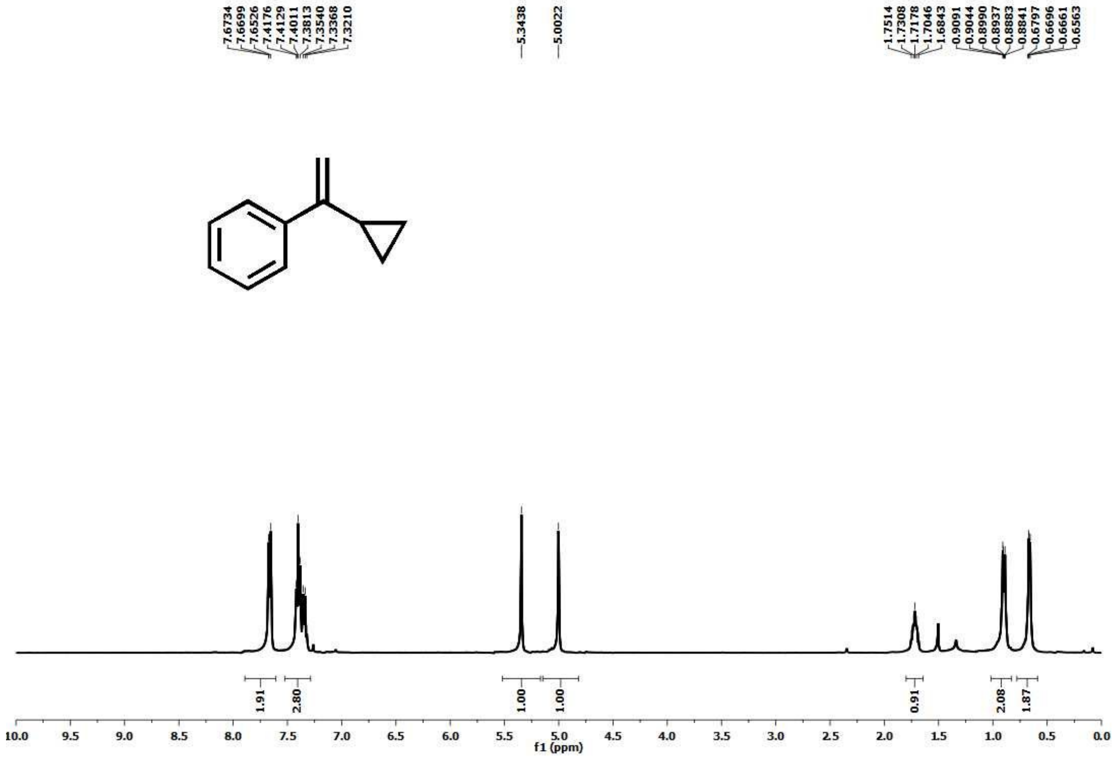
Entry	Radical scavenger (equiv)	Yield of **2a** (%)
1	TEMPO (2.0)	23
2	TEMPO (4.0)	10
3	BHT (2.0)	10
4	BHT (4.0)	0
5	PhSeSePh (2.0)	25

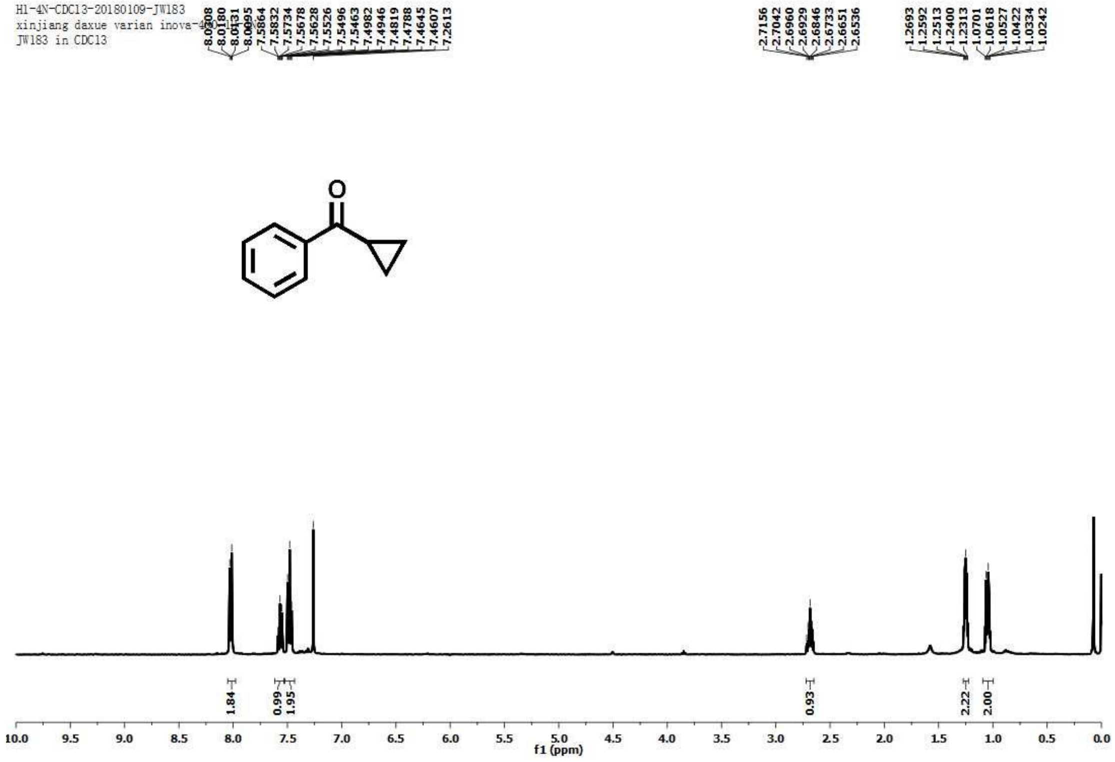
A mixture of 1,1-diphenylethylene **1a** (90 mg, 0.50 mmol), B_2pin_2 (13 mg, 0.05 mmol), radical scavenger TEMPO, BHT or PhSeSePh (1.0 mmol or 2.0 mmol) and NMP (1.0 mL) were added to a 10 mL Schlenk tube. The reaction tube was flushed with O_2 for 1.0 minute and then equipped with a O_2 balloon. The reaction was stirred at 100 °C for 30 h. After cooling to ambient temperature, the resulting mixture was extracted with EtOAc (3×10 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered, and all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (35-60 °C)/EtOAc = 80:1, v/v).

3.2 Radical clock experiment



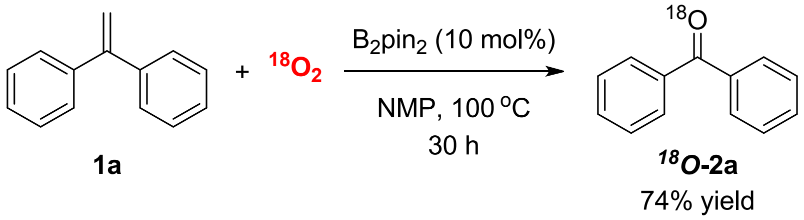
A mixture of (1-cyclopropylvinyl)benzene (36 mg, 0.25 mmol), B_2pin_2 (6.5 mg, 0.025 mmol) and NMP (0.5 mL) were added to a 10 mL Schlenk tube. The reaction tube was flushed with O_2 for 1.0 minute and then equipped with a O_2 balloon. The reaction was stirred at 100 °C for 30 h. After cooling to ambient temperature, the resulting mixture was extracted with EtOAc (3×10 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered, and all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (35-60 °C)/EtOAc) to afford cyclopropyl(phenyl)methanone in 16% yield.



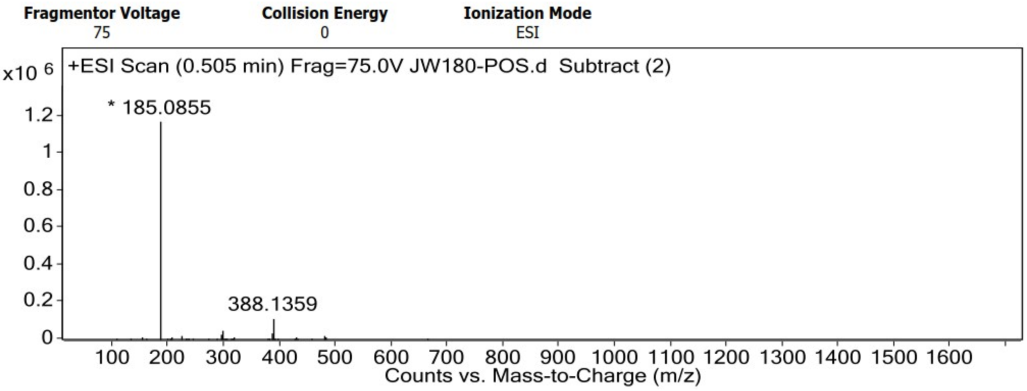


3.3 Isotope labeling experiments

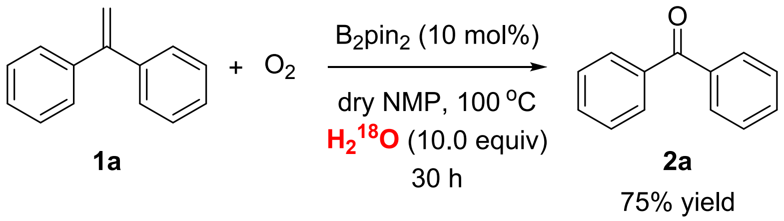
3.3.1 Isotope labeling experiment with $^{18}O_2$



A mixture of 1,1-diphenylethylene **1a** (90 mg, 0.50 mmol), B_2pin_2 (13 mg, 0.05 mmol) and NMP (1.0 mL) were added to a 10 mL Schlenk tube. The reaction tube was then equipped with a $^{18}O_2$ balloon. The reaction was stirred at 100 °C for 30 h. After cooling to ambient temperature, the resulting mixture was extracted with EtOAc (3×10 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered, and all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (35-60 °C)/EtOAc = 80:1, v/v) to afford the desired product in 74% yield. Then the product was analyzed by HRMS. **HRMS** (ESI) m/z Calcd for $C_{13}H_{11}{}^{18}O$ $[M+H]^+$: 185.0852; Found: 185.0855.

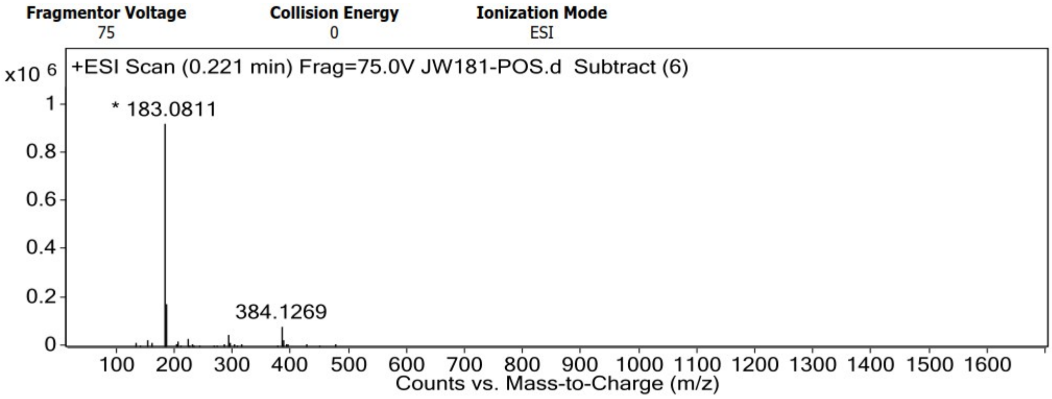


3.3.2 Isotope labeling experiment with $H_2{}^{18}O$

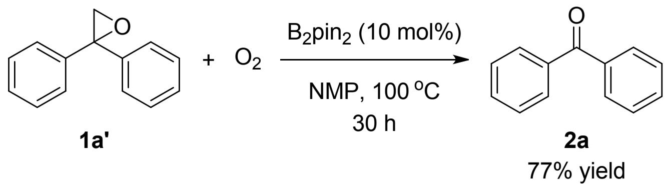


A mixture of 1,1-diphenylethylene **1a** (90 mg, 0.50 mmol), B_2pin_2 (13 mg, 0.05 mmol), dry NMP (1.0 mL) and $H_2{}^{18}O$ (100 mg, 5.0 mmol) were added to a 10 mL

Schlenk tube. The reaction tube was flushed with O_2 for 1.0 minute and then equipped with a O_2 balloon. The reaction was stirred at 100 °C for 30 h. After cooling to ambient temperature, the resulting mixture was extracted with EtOAc (3×10 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered, and all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (35-60 °C)/EtOAc = 80:1, v/v) to afford the desired product in 75% yield. Then the product was analyzed by HRMS. **HRMS** (ESI) m/z Calcd for $C_{13}H_{11}O$ $[M+H]^+$: 183.0810; Found: 183.0811.

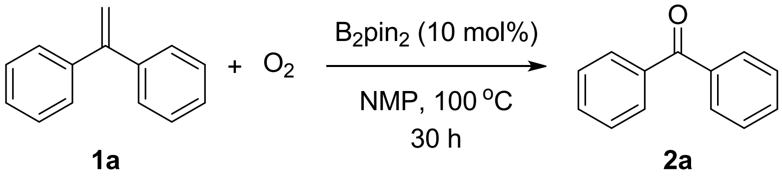


3.4 Intermediate probe experiment

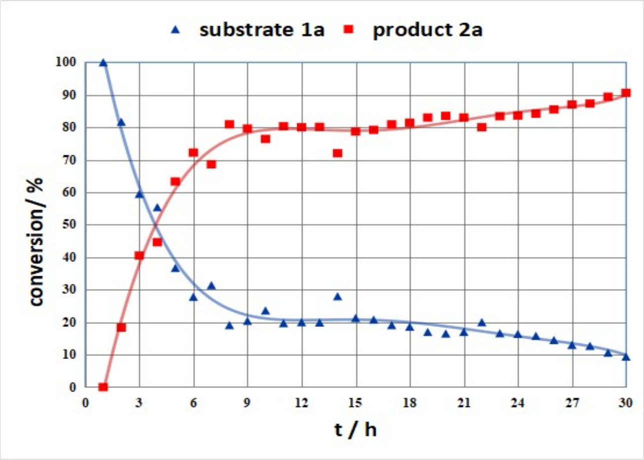


A mixture of 2,2-diphenyloxirane **1a'** (98 mg, 0.50 mmol), B_2pin_2 (13 mg, 0.05 mmol) and NMP (1.0 mL) were added to a 10 mL Schlenk tube. The reaction tube was then equipped with a O_2 balloon. The reaction was stirred at 100 °C for 30 h. After cooling to ambient temperature, the resulting mixture was extracted with EtOAc (3×10 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered, and all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (35-60 °C)/EtOAc = 80:1, v/v) to afford the desired product in 77% yield.

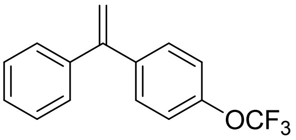
3.5 Kinetic experiment



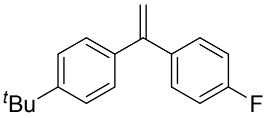
A mixture of 1,1-diphenylethylene **1a** (90 mg, 0.50 mmol), B_2pin_2 (13 mg, 0.05 mmol) and NMP (1.0 mL) were added to a 10 mL Schlenk tube. The reaction tube was flushed with O_2 for 1.0 minute and then equipped with a O_2 balloon. During the reaction, 0.05 mL of the reaction mixture was sampled every hour and immediately diluted with 0.5 mL of DCM at ambient temperature for GC analysis.



4. Analytical data

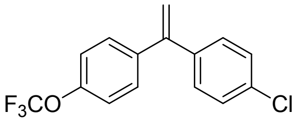


1-(1-Phenylvinyl)-4-(trifluoromethoxy)benzene (1f): New compound. 806 mg, 76% yield. Colorless oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.42-7.35 (m, 7H), 7.23-7.20 (m, 2H), 5.53 (d, *J* = 1.0 Hz, 1H), 5.50 (d, *J* = 1.0 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 149.0 x 2, 141.1, 140.4, 129.8, 128.5, 128.3, 128.1, 120.8, 120.7 (d, *J* = 256.0 Hz), 115.1; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -57.77. **HRMS** (ESI) m/z Calcd for $C_{15}H_{12}F_3O$ $[M+H]^+$: 265.0840; Found: 265.0835.

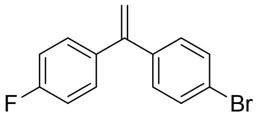


1-(*tert*-Butyl)-4-(1-(4-fluorophenyl)vinyl)benzene (1u): New compound. 954 mg, 94% yield. White solid. m.p.: 48.9-51.0 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.44-

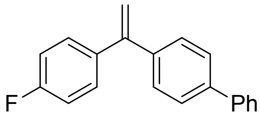
7.33 (m, 6H), 7.08 (t, *J* = 8.8 Hz, 2H), 5.51 (s, 1H), 5.43 (s, 1H), 1.42 (s, 9H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ 162.6 (d, *J* = 245.0 Hz), 151.0, 149.0, 138.4, 137.9 (d, *J* = 4.0 Hz), 130.1 (d, *J* = 8.0 Hz), 128.0, 125.3, 115.1 (d, *J* = 21.0 Hz), 113.8, 34.7, 31.5; **^{19}F NMR** (CDCl$_3$, 376 MHz) δ -114.88. **HRMS** (ESI) m/z Calcd for $C_{18}H_{20}F$ [M+H]$^+$: 255.1549; Found: 255.1547.



1-Chloro-4-(1-(4-(trifluoromethoxy)phenyl)vinyl)benzene (1v): New compound. 824 mg, 69% yield. Colorless oil. **^{1}H NMR** (CDCl$_3$, 400 MHz) δ 7.38-7.21 (m, 8H), 5.51 (s, 1H), 5.49 (s, 1H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ 149.1 (d, *J* = 1.0 Hz), 147.9, 139.8, 139.6, 134.1, 129.7, 129.6, 128.7, 123.1 (q, *J* = 261.0 Hz), 120.9, 115.5; **^{19}F NMR** (CDCl$_3$, 376 MHz) δ -57.78. **HRMS** (ESI) m/z Calcd for $C_{15}H_{11}ClF_3O$ [M+H]$^+$: 299.0451; Found: 299.0445.

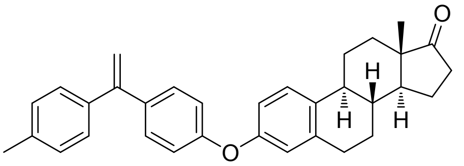


1-Bromo-4-(1-(4-fluorophenyl)vinyl)benzene (1w): New compound. 885 mg, 80% yield. Colorless oil. **^{1}H NMR** (CDCl$_3$, 400 MHz) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.31-7.29 (m, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.05 (t, *J* = 8.7 Hz, 2H), 5.45 (s, 2H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ 162.7 (d, *J* = 246.0 Hz), 148.1, 140.3, 137.1 (d, *J* = 3.0 Hz), 131.5, 130.0, 129.9, 122.1, 115.3 (d, *J* = 22.0 Hz), 114.8; **^{19}F NMR** (CDCl$_3$, 376 MHz) δ -114.16. **HRMS** (ESI) m/z Calcd for $C_{14}H_{11}BrF$ [M+H]$^+$: 277.0028; Found: 277.0023.

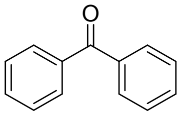


4-(1-(4-Fluorophenyl)vinyl)-1,1'-biphenyl (1x): New compound. 897 mg, 82% yield. White solid. m.p.: 109.0-110.3 °C. **^{1}H NMR** (CDCl$_3$, 400 MHz) δ 7.72-7.65 (m, 4H), 7.56-7.42 (m, 7H), 7.12 (t, *J* = 8.7 Hz, 2H), 5.59 (s, 1H), 5.52 (s, 1H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ 162.7 (d, *J* = 245.0 Hz), 148.7, 140.8 (d, *J* = 8.0 Hz), 140.3, 137.6 x 2, 130.1 (d, *J* = 8.0 Hz), 128.9, 128.7, 127.5, 127.1 (d, *J* = 6.0 Hz), 115.8 (d, *J* = 22.0 Hz), 115.2 (d, *J* = 21.0 Hz), 114.3; **^{19}F NMR** (CDCl$_3$, 376 MHz) δ -114.57.

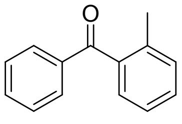
HRMS (ESI) m/z Calcd for $C_{20}H_{16}F$ $[M+H]^+$: 275.1236; Found: 275.1233.



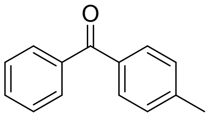
(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(4-(1-(*p*-tolyl)vinyl)phenoxy)-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[*a*]phenanthren-17(14*H*)-one (1y): New compound. 477 mg, 50% yield. White solid. m.p.: 170.0-172.0 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.31-7.27 (m, 2H), 7.26-7.24 (m, 3H), 7.16 (s, 1H), 7.14 (s, 1H), 6.96-6.93 (m, 2H), 6.83 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.79-6.78 (m, 1H), 5.37 (s, 2H), 2.91-2.87 (m, 2H), 2.54-2.48 (m, 1H), 2.37 (s, 3H), 2.17-2.13 (m, 1H), 2.10-1.96 (m, 3H), 1.63-1.46 (m, 8H), 0.93 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 220.9, 157.3, 155.0, 149.4, 138.8, 138.4, 137.7, 136.5, 135.0, 129.7, 129.0, 128.3, 126.8, 119.3, 118.2, 116.6, 113.1, 50.6, 48.1, 44.3, 38.4, 36.0, 31.7, 29.7, 26.6, 26.0, 21.8, 21.3, 14.0. **HRMS** (ESI) m/z Calcd for $C_{33}H_{35}O_2$ $[M+H]^+$: 463.2637; Found: 463.2596.



Benzophenone (2a)[4]: Known compound. 82 mg, 90% yield. Colorless oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.80 (d, *J* = 8.1 Hz, 4H), 7.60-7.56 (m, 2H), 7.49-7.45 (m, 4H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 196.8, 137.7, 132.5, 130.1, 128.4.

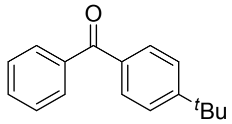


Phenyl(*o*-tolyl)methanone (2b)[4]: Known compound. 35 mg, 36% yield. Yellow oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.82-7.79 (m, 2H), 7.60-7.56 (m, 1H), 7.48-7.44 (m, 2H), 7.42-7.37 (m, 1H), 7.33-7.23 (m, 3H), 2.34 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 198.8, 138.7, 137.8, 136.9, 133.3, 131.1, 130.4, 130.3, 128.6 x 2, 125.3, 20.1.

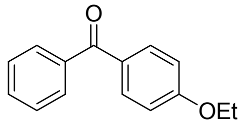


Phenyl(*p*-tolyl)methanone (2c)[4]: Known compound. 78 mg, 80% yield. White solid. m.p.: 54.0-56.0 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.80-7.77 (m, 2H), 7.73 (d, *J*

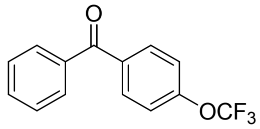
= 8.2 Hz, 2H), 7.59-7.55 (m, 1H), 7.49-7.45 (m, 2H), 7.27 (t, J = 7.9 Hz, 2H), 2.44 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 196.6, 143.3, 138.1, 135.0, 132.3, 130.4, 130.0, 129.1, 128.3, 21.8.



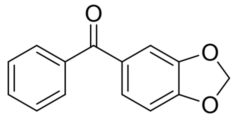
(4-(*tert*-Butyl)phenyl)(phenyl)methanone (2d)[5]: Known compound. 87 mg, 81%. Colorless oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.83-7.76 (m, 4H), 7.60-7.55 (m, 1H), 7.52-7.45 (m, 4H), 1.37 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 196.5, 156.3, 138.0, 134.9, 132.3, 130.2, 130.1, 128.3, 125.3, 35.2, 31.3.



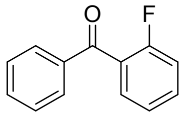
(4-Ethoxyphenyl)(phenyl)methanone (2e)[6]: Known compound. 93 mg, 82% yield. White solid. m.p.: 38.8-39.6 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.81 (dt, J = 8.7, 2.8 Hz, 2H), 7.76-7.73 (m, 2H), 7.57-7.52 (m, 1H), 7.48-7.43 (m, 2H), 6.93 (dt, J = 8.8, 2.7 Hz, 2H), 4.09 (q, J = 7.0 Hz, 2H), 1.44 (t, J = 7.0 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 195.6, 162.7, 138.4, 132.6, 131.9, 130.0, 129.7, 128.2, 114.0, 63.8, 14.8.



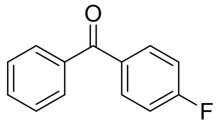
Phenyl(4-(trifluoromethoxy)phenyl)methanone (2f)[7]: Known compound. 104 mg, 78%. White solid. m.p.: 53.4-54.4 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.86 (td, J = 8.9, 2.6 Hz, 2H), 7.80-7.77 (m, 2H), 7.62-7.58 (m, 1H), 7.51-7.47 (m, 2H), 7.33-7.30 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 195.2, 152.2, 137.3, 136.0, 132.8, 132.1, 130.1, 128.6, 120.5 (q, J = 258.0 Hz), 120.3; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -57.58.



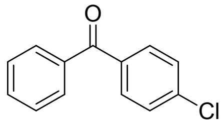
Benzo[d][1,3]dioxol-5-yl(phenyl)methanone (2g)[5]: Known compound. 87 mg, 77%. Yellow oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.75-7.72 (m, 2H), 7.56-7.54 (m, 1H), 7.48-7.44 (m, 2H), 7.38-7.36 (m, 2H), 6.86-6.84 (m, 1H), 6.05 (s, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 195.2, 151.6, 148.0, 138.2, 132.1, 132.0, 129.8, 128.3, 127.0, 110.0, 107.8, 102.0.



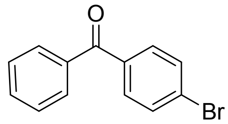
(2-Fluorophenyl)(phenyl)methanone (2h)[5]: Known compound. 66 mg, 66%. Colorless oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.86-7.83 (m, 2H), 7.60-7.38 (m, 5H), 7.29-7.25 (m, 1H), 7.18-7.13 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 193.6, 160.2 (d, J = 251.0 Hz), 137.5, 133.5, 133.2 (d, J = 9.0 Hz), 130.9 (d, J = 3.0 Hz), 129.9, 128.6, 127.1 (d, J = 11.0 Hz), 124.4 (d, J = 4.0 Hz), 116.4 (d, J = 21.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -111.03.



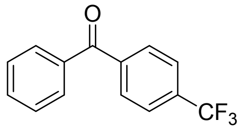
(4-Fluorophenyl)(phenyl)methanone (2i)[6]: Known compound. 75 mg, 75%. Yellow oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.87-7.82 (m, 2H), 7.78-7.76 (m, 2H), 7.61-7.57 (m, 1H), 7.51-7.46 (m, 2H), 7.18-7.13 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 195.4, 165.5 (d, J = 252.0 Hz), 137.6, 133.9 (d, J = 3.0 Hz), 132.8 (d, J = 10.0 Hz), 132.6, 130.0, 128.5, 115.6 (d, J = 22.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -105.95.



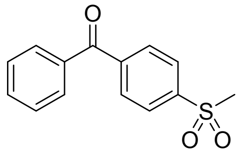
(4-Chlorophenyl)(phenyl)methanone (2j)[4]: Known compound. 81 mg, 75% yield. White solid. m.p.: 73.0-73.2 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.79-7.74 (m, 4H), 7.62-7.57 (m, 1H), 7.51-7.44 (m, 4H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 195.5, 139.0, 137.3, 135.9, 132.7, 131.5, 130.0, 128.7, 128.5.



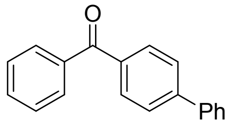
(4-Bromophenyl)(phenyl)methanone (2k)[6]: Known compound. 90 mg, 69% yield. White solid. m.p.: 79.4-79.8 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.77-7.75 (m, 2H), 7.68-7.66 (m, 2H), 7.62-7.57 (m, 3H), 7.48 (t, J = 7.8 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 195.6, 137.2, 136.3, 132.7, 131.7, 131.6, 130.0, 128.5, 127.6.



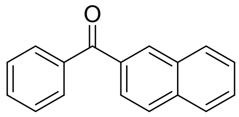
Phenyl(4-(trifluoromethyl)phenyl)methanone (2l)[5]: Known compound. 78 mg, 66% yield. White solid. m.p.: 112.8-113.5 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 195.6, 140.8, 136.8, 133.8 (q, *J* = 33.0 Hz), 133.2, 130.3, 130.2, 128.6, 125.5 (q, *J* = 4.0 Hz), 123.8 (q, *J* = 271.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -63.00.



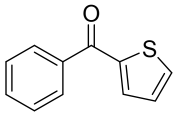
(4-(ethylsulfonyl)phenyl)(phenyl)methanone (2m)[8]: Known compound. 91 mg, 70% yield. White solid. m.p.: 139.5-140.7 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.04 (d, *J* = 8.1 Hz, 2H), 7.91 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 7.7 Hz, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 3.09 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 195.1, 143.4, 142.3, 136.3, 133.4, 130.5, 130.1, 128.6, 127.4, 44.3.



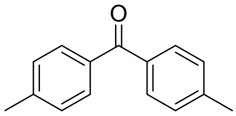
[1,1'-Biphenyl]-4-yl(phenyl)methanone (2n)[5]: Known compound. 90 mg, 70% yield. White solid. m.p.: 99.4-100.9 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.93-7.90 (m, 2H), 7.87-7.85 (m, 2H), 7.73-7.70 (m, 2H), 7.68-7.66 (m, 2H), 7.64-7.59 (m, 1H), 7.53-7.48 (m, 4H), 7.44-7.40 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 196.4, 145.3, 140.1, 137.9, 136.3, 132.5, 130.8, 130.1, 129.1, 128.4, 128.3, 127.4, 127.1.



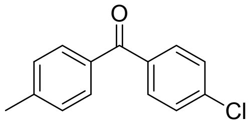
Naphthalen-2-yl(phenyl)methanone (2o)[4]: Known compound. 95 mg, 82% yield. Yellow oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.28 (s, 1H), 7.96-7.95 (m, 2H), 7.93-7.90 (m, 2H), 7.89-7.88 (m, 1H), 7.88-7.87 (m, 1H), 7.63-7.59 (m, 2H), 7.57-7.50 (m, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 196.8, 138.0, 135.3, 134.9, 132.5, 132.3, 132.0, 130.2, 129.5, 128.4 x 2, 127.9, 126.9, 125.8.



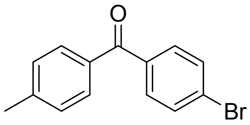
Phenyl(thiophen-2-yl)methanone (2p)[4]: Known compound. 38 mg, 40% yield. Yellow oil. **^{1}H NMR** (CDCl$_3$, 400 MHz) δ 7.88-7.86 (m, 2H), 7.72 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.65 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.62-7.57 (m, 2H), 7.52-7.48 (m, 2H), 7.16 (dd, *J* = 5.0, 3.8 Hz, 1H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ 188.3, 143.8, 138.3, 135.0, 134.3, 132.4, 129.3, 128.5, 128.1.



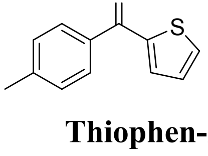
Di-*p*-tolylmethanone (2q)[4]: Known compound. 81 mg, 77% yield. White solid. m.p.: 79.0-81.0 °C. **^{1}H NMR** (CDCl$_3$, 400 MHz) δ 7.71 (d, *J* = 8.1 Hz, 4H), 7.27 (dd, *J* = 8.4, 0.6 Hz, 4H), 2.44 (s, 6H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ 196.4, 143.0, 135.3, 130.3, 129.0, 21.7.



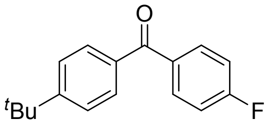
(4-Chlorophenyl)(*p*-tolyl)methanone (2r)[4]: Known compound. 81 mg, 70% yield. White solid. m.p.: 120.0-121.0 °C. **^{1}H NMR** (CDCl$_3$, 400 MHz) δ 7.73 (dt, *J* = 8.7, 2.3 Hz, 2H), 7.69 (dt, *J* = 8.1, 1.8 Hz, 2H), 7.45 (dt, *J* = 8.7, 2.3 Hz, 2H), 7.28 (dd, *J* = 8.5, 0.6 Hz, 2H), 2.44 (s, 3H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ 195.3, 143.6, 138.7, 136.4, 134.7, 131.5, 130.3, 129.2, 128.7, 21.8.



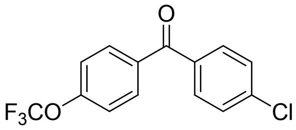
(4-Bromophenyl)(*p*-tolyl)methanone (2s)[9]: Known compound. 101 mg, 73% yield. White solid. m.p.: 136.0-138.0 °C. **^{1}H NMR** (CDCl$_3$, 400 MHz) δ 7.70-7.66 (m, 3H), 7.65-7.62 (m, 3H), 7.28 (d, *J* = 7.9 Hz, 2H), 2.44 (s, 3H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ 195.5, 143.7, 136.8, 134.6, 131.7, 131.6, 130.3, 129.2, 127.3, 21.8.



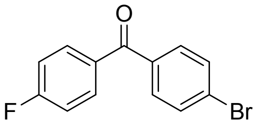
Thiophen-2-yl(*p*-tolyl)methanone (2t)[4]: Known compound. 33 mg, 31% yield, Yellow oil. **^{1}H NMR** (CDCl$_3$, 400 MHz) δ 7.79 (dt, *J* = 8.2, 1.9 Hz, 2H), 7.70 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.65 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.31-7.28 (m, 2H), 7.16 (dd, *J* = 5.0, 3.8 Hz, 1H), 2.44 (s, 3H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ 188.0, 143.9, 143.2, 135.6, 134.6, 133.9, 129.5, 129.2, 128.0, 21.8.



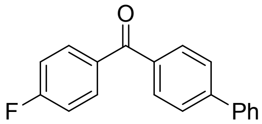
(4-(*tert*-Butyl)phenyl)(4-fluorophenyl)methanone (2u)[10]: Known compound. 90 mg, 70% yield. White solid. m.p.: 70.2-71.8 °C. **^{1}H NMR** (CDCl$_3$, 400 MHz) δ 7.87-7.82 (m, 2H), 7.74-7.72 (m, 2H), 7.51-7.49 (m, 2H), 7.17-7.12 (m, 2H), 1.36 (s, 9H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ 195.0, 165.3 (d, *J* = 253.0 Hz), 156.3, 134.8, 134.2 (d, *J* = 3.0 Hz), 132.7 (d, *J* = 9.0 Hz), 130.1, 125.4, 115.4 (d, *J* = 22.0 Hz), 35.2, 31.2; **^{19}F NMR** (CDCl$_3$, 376 MHz) δ -106.45.



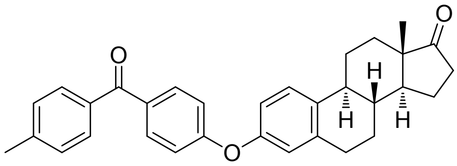
(4-Chlorophenyl)(4-(trifluoromethoxy)phenyl)methanone (2v)[11]: Known compound. 105 mg, 70% yield, White solid. m.p.: 73.2-73.7 °C. **^{1}H NMR** (CDCl$_3$, 400 MHz) δ 7.83 (dt, *J* = 8.8, 2.6 Hz, 2H), 7.75-7.72 (m, 2H), 7.49-7.45 (m, 2H), 7.34-7.30 (m, 2H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ 194.0, 152.4 (q, *J* = 2.0 Hz), 139.4, 135.6, 135.5, 132.0, 131.5, 128.9, 120.4 (d, *J* = 258.0 Hz), 120.5 (d, *J* = 1.0 Hz); **^{19}F NMR** (CDCl$_3$, 376 MHz) δ -57.59.



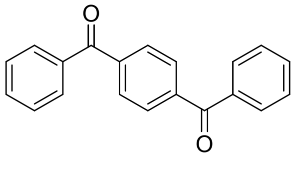
(4-Bromophenyl)(4-fluorophenyl)methanone (2w)[12]: Known compound. 99 mg, 71% yield, White solid. m.p.: 109.3-109.8 °C. **^{1}H NMR** (CDCl$_3$, 400 MHz) δ 7.84-7.79 (m, 2H), 7.63 (s, 4H), 7.19-7.13 (m, 2H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ 194.2, 165.6 (d, *J* = 254.0 Hz), 136.3, 133.5 (d, *J* = 3.0 Hz), 132.7 (d, *J* = 9.0 Hz), 131.8, 131.5, 127.7, 115.7 (d, *J* = 22.0 Hz); **^{19}F NMR** (CDCl$_3$, 376 MHz) δ -105.33.



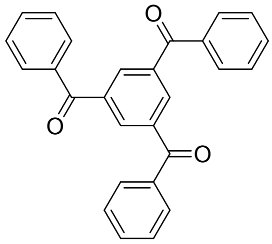
[1,1'-Biphenyl]-4-yl(4-fluorophenyl)methanone (2x)[13]: Known compound. 111 mg, 80% yield. White solid. m.p.: 146.8-148.0 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.91-7.86 (m, 4H), 7.73-7.71 (m, 2H), 7.67-7.65 (m, 2H), 7.51-7.47 (m, 2H), 7.44-7.40 (m, 1H), 7.21-7.15 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 194.9, 165.4 (d, J = 253.0 Hz), 145.3, 139.9, 136.1, 134.0 (d, J = 3.0 Hz), 132.7 (d, J = 10.0 Hz), 130.6, 129.0, 128.3, 127.3, 127.1, 115.5 (d, J = 21.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -106.02.



(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(4-(4-methylbenzoyl)phenoxy)-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[*a*]phenanthren-17(14*H*)-one (2y): New compound. 67 mg, 29% yield. White solid. m.p.: 165.0-168.0 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.82-7.79 (m, 2H), 7.72-7.70 (m, 2H), 7.32-7.27 (m, 3H), 7.08-7.00 (m, 2H), 6.90-6.88 (m, 1H), 6.88-6.83 (m, 1H), 2.92-2.87 (m, 2H), 2.54-2.50 (m, 1H), 2.45 (s, 3H), 2.19-2.01 (m, 6H), 1.68-1.48 (m, 6H), 0.95 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 220.9, 195.5, 161.8, 153.6, 143.0, 138.8, 136.2, 135.3, 132.4, 130.2, 129.1, 127.0, 125.9, 120.3, 117.6, 117.1, 50.6, 48.1, 44.3, 38.3, 36.0, 31.7, 29.6, 26.5, 26.0, 22.7, 21.8, 14.0. **HRMS** (ESI) m/z Calcd for $C_{32}H_{33}O_3$ $[M+H]^+$: 465.2430; Found: 465.2415.



1,4-Phenylenebis(phenylmethanone) (4)[14]: Known compound. 82 mg, 57% yield, White solid. m.p.: 150-152 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.89 (s, 4H), 7.85-7.83 (m, 4H), 7.65-7.61 (m, 2H), 7.55-7.49 (m, 4H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 196.1, 140.7, 137.0, 133.1, 130.2, 129.8, 128.6.



Benzene-1,3,5-triyltris(phenylmethanone) (6)[15]: Known compound. 86 mg, 44% yield, White solid. m.p.: 113-114 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.40 (s, 3H), 7.87-7.84 (m, 6H), 7.65-7.61 (m, 3H), 7.54-7.50 (m, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 195.0, 138.4, 136.6, 134.2, 133.4, 130.2, 128.8.

5. References

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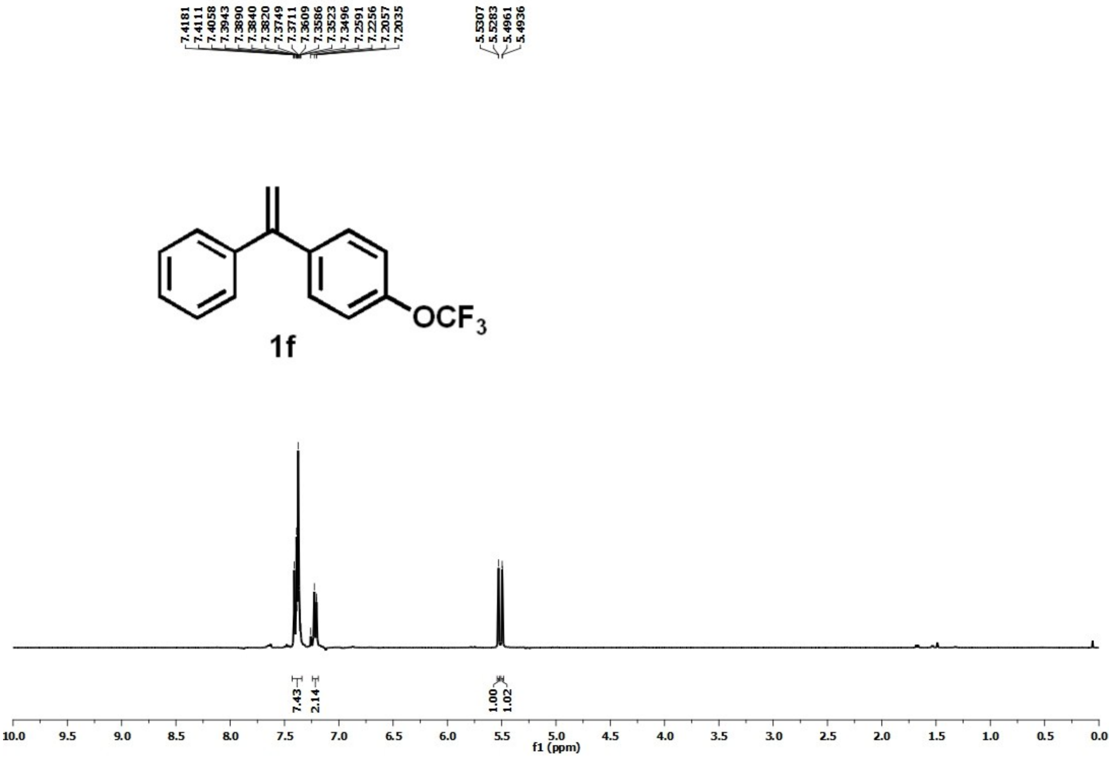
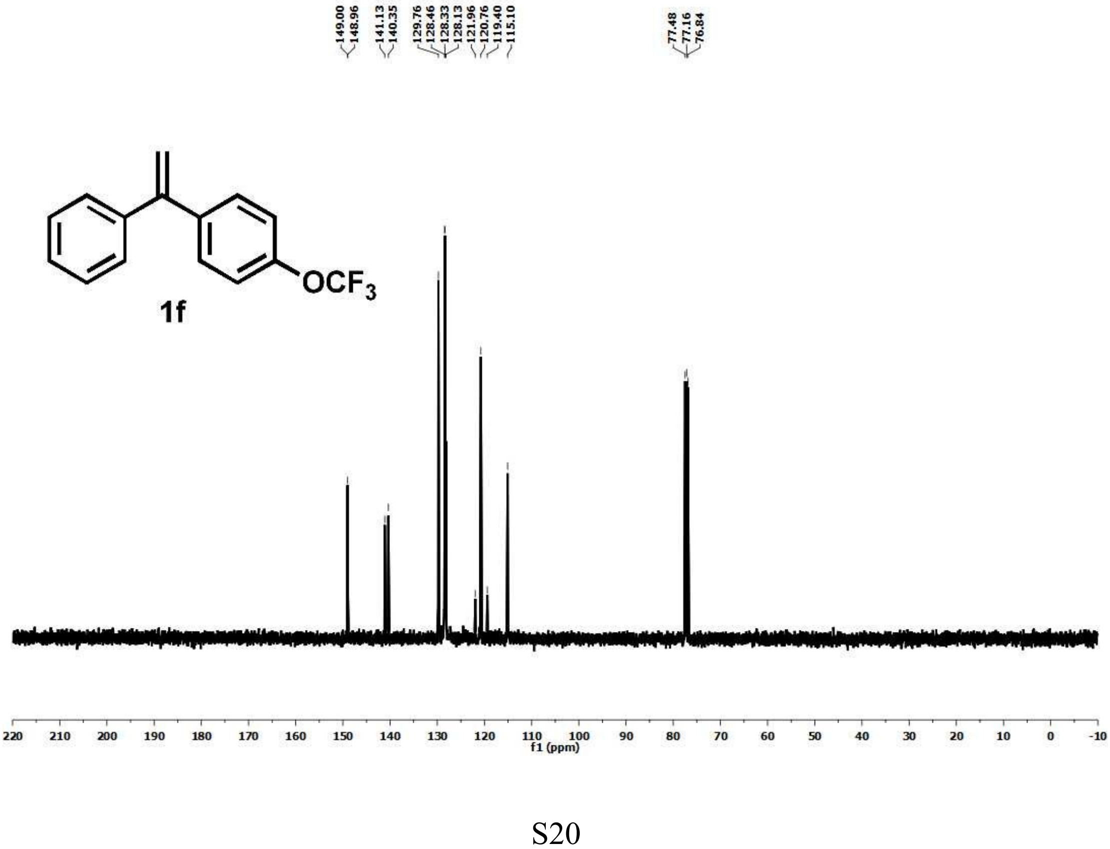
6. Copies of NMR spectra (the new starting materials and all products)

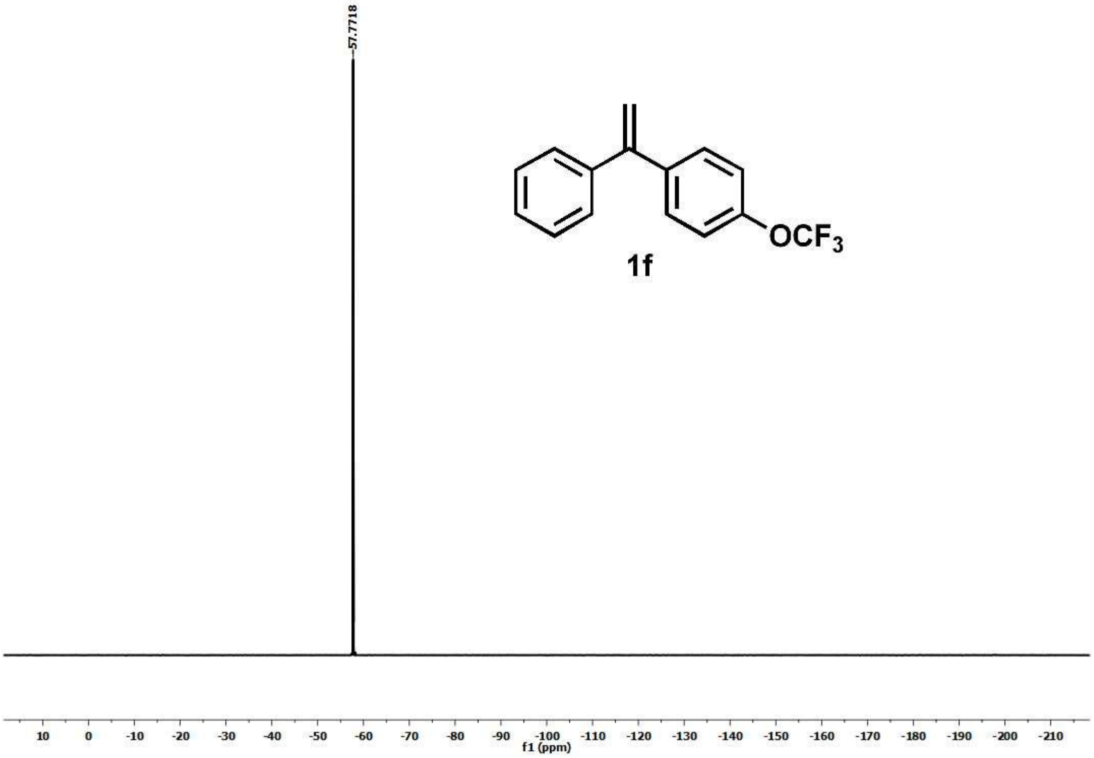
^{1}H NMR of new starting material 1f in $CDCl_3$ (400 MHz)



^{13}C NMR of new starting material 1f in $CDCl_3$ (100 MHz)



^{19}F NMR of new starting material 1f in $CDCl_3$ (376 MHz)



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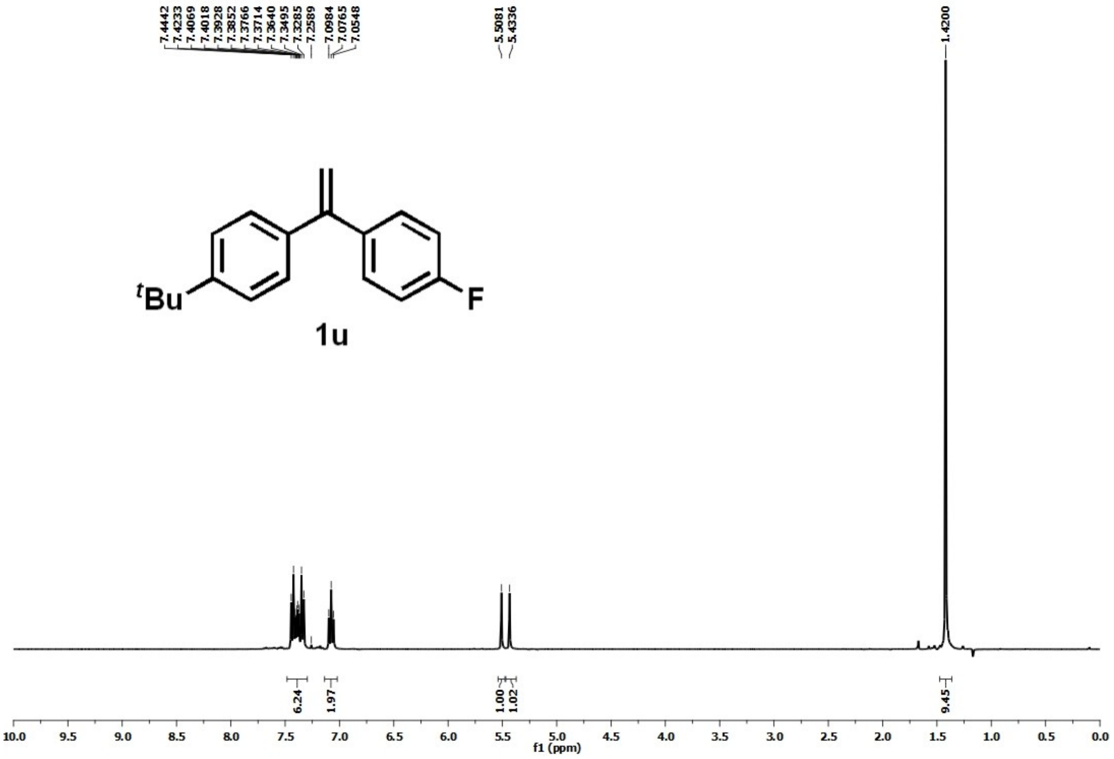
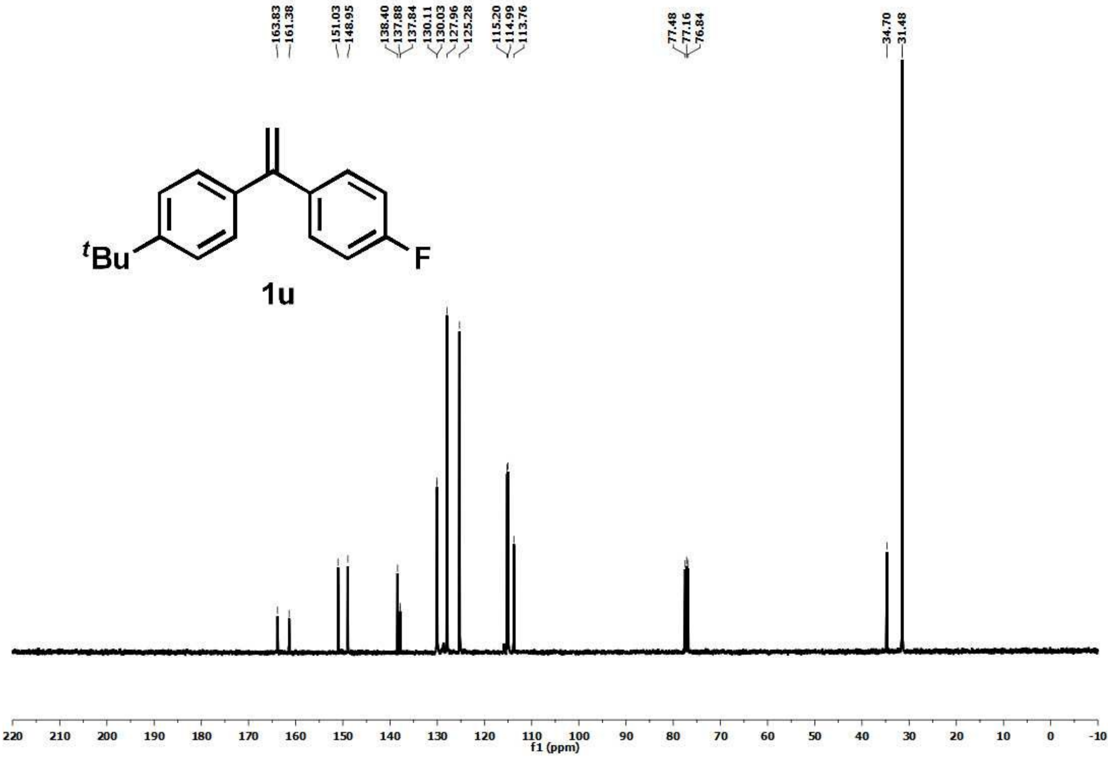
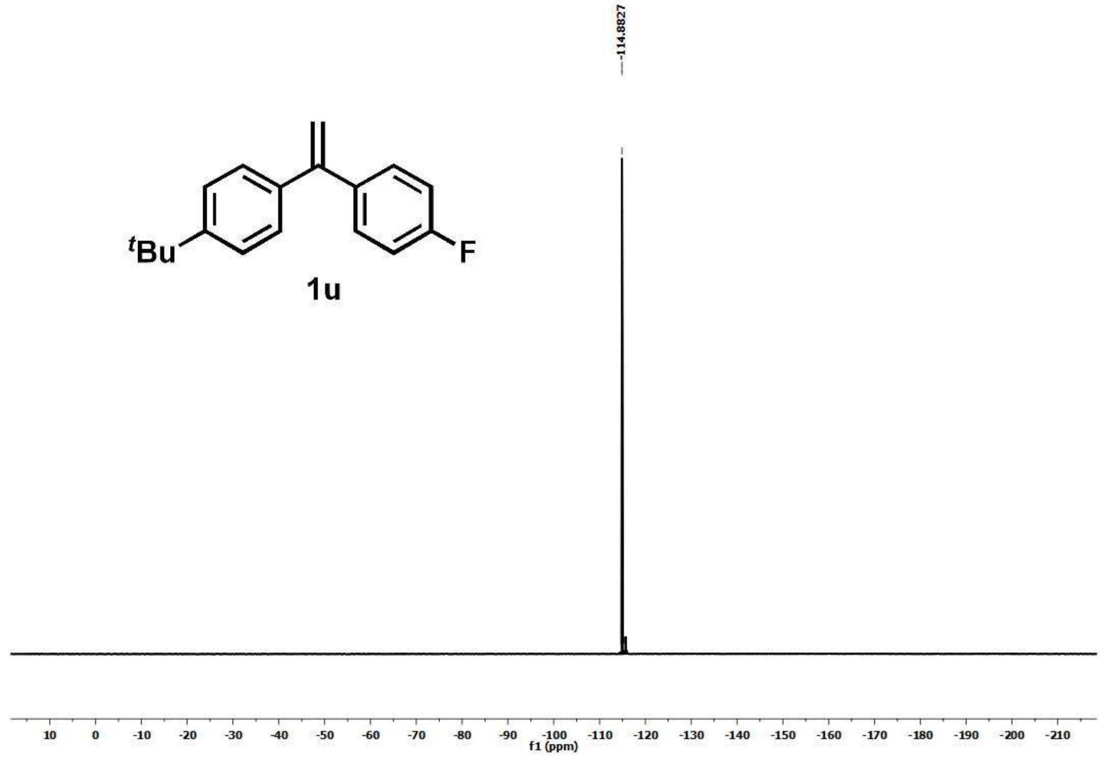


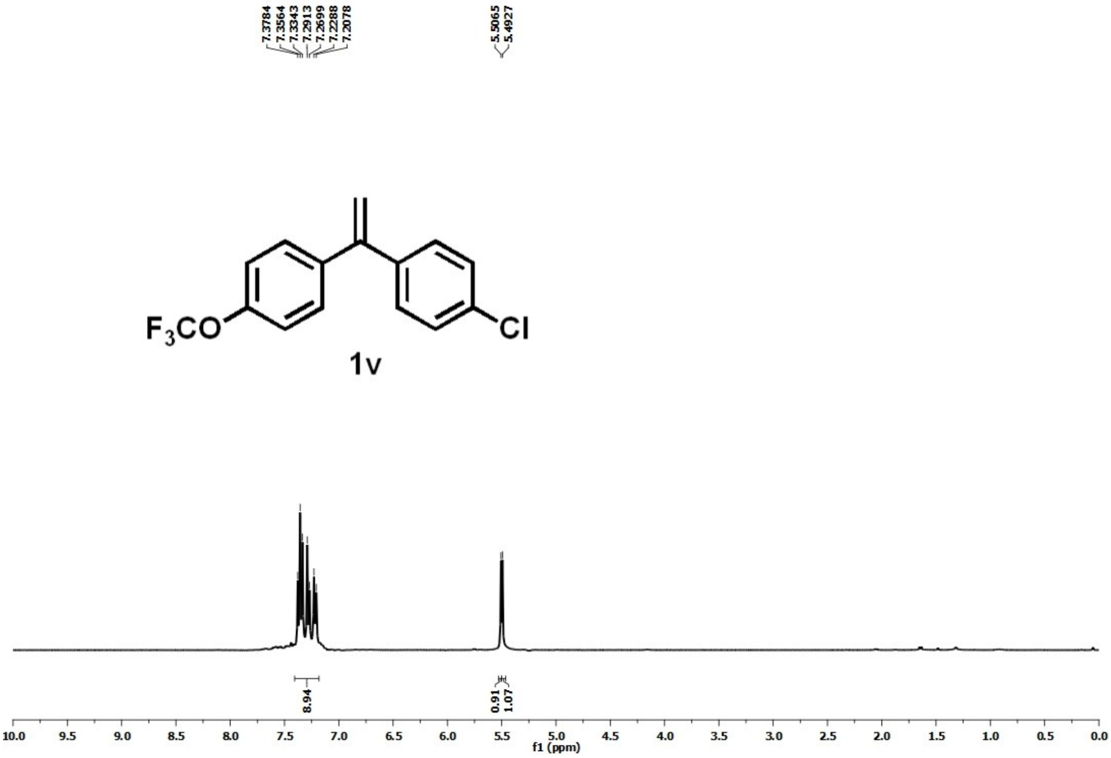
^{13}C NMR of new starting material 1u in CDCl$_3$ (100 MHz)



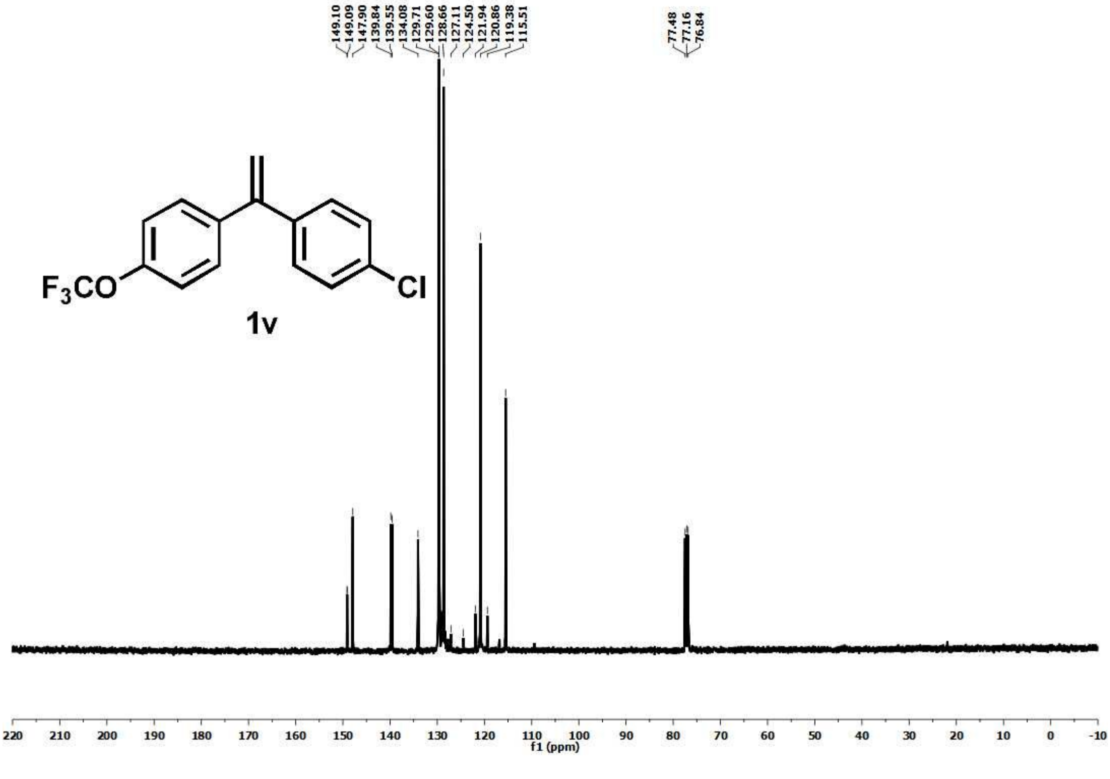
^{19}F NMR of new starting material 1u in CDCl$_3$ (376 MHz)



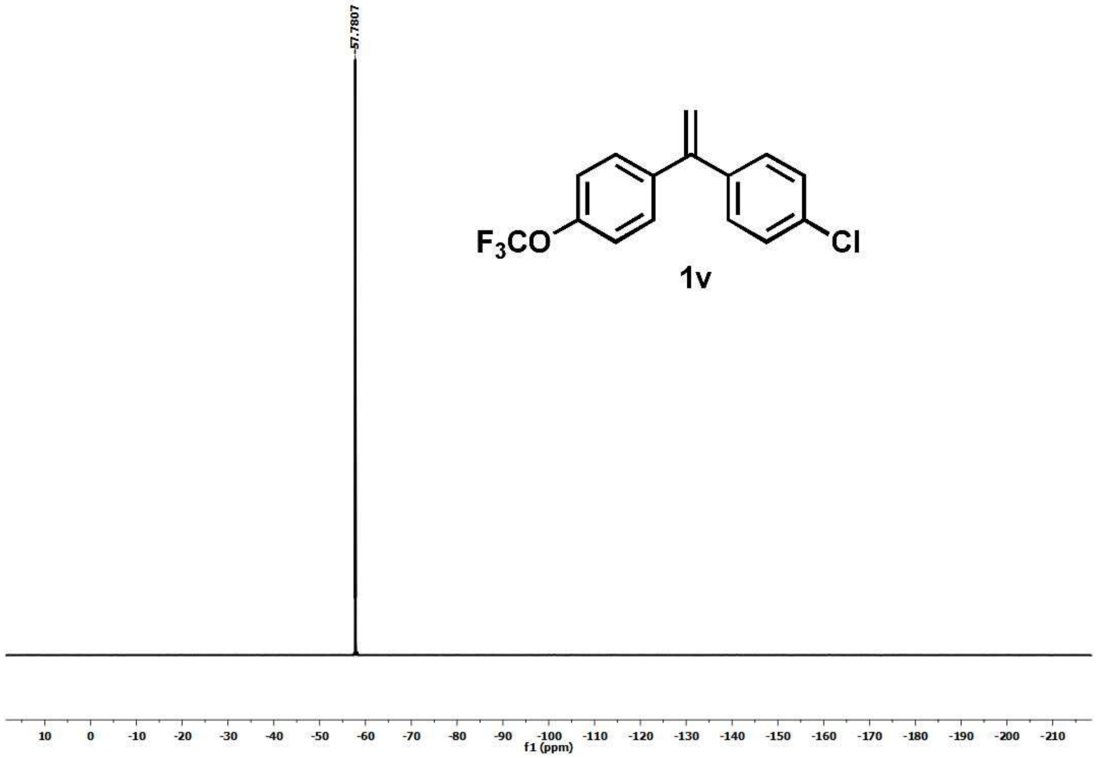
^{1}H NMR of new starting material 1v in CDCl$_3$ (400 MHz)



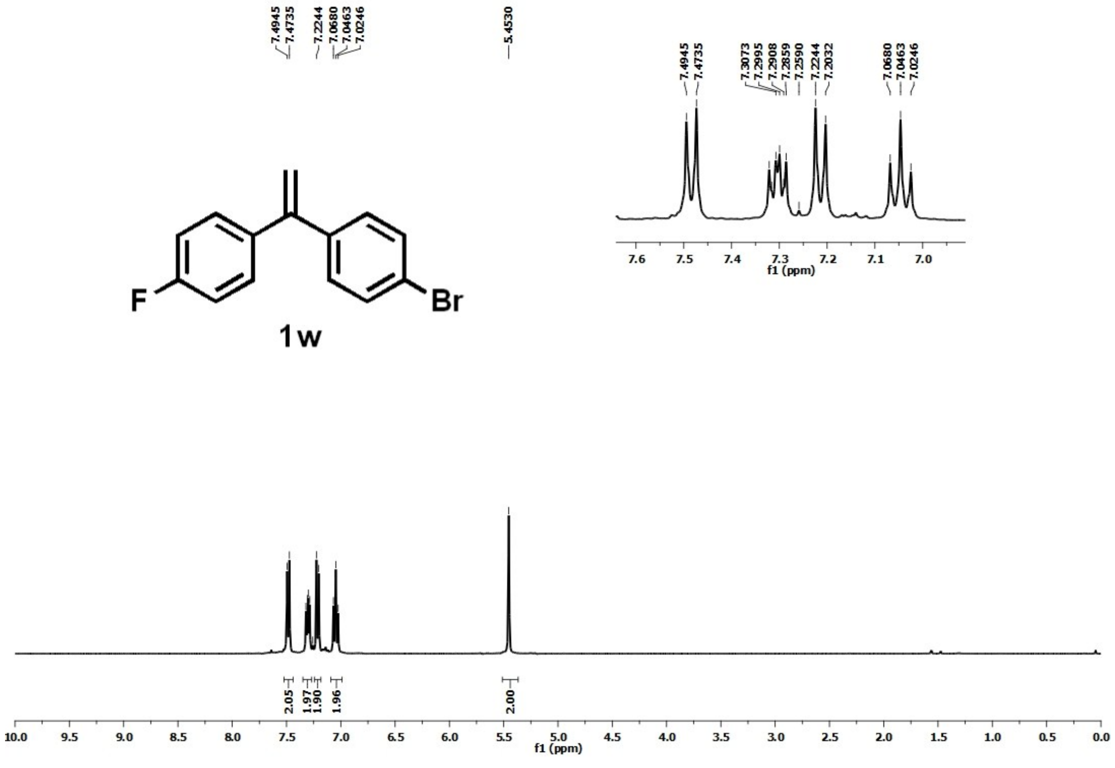
^{13}C NMR of new starting material 1v in CDCl$_3$ (100 MHz)



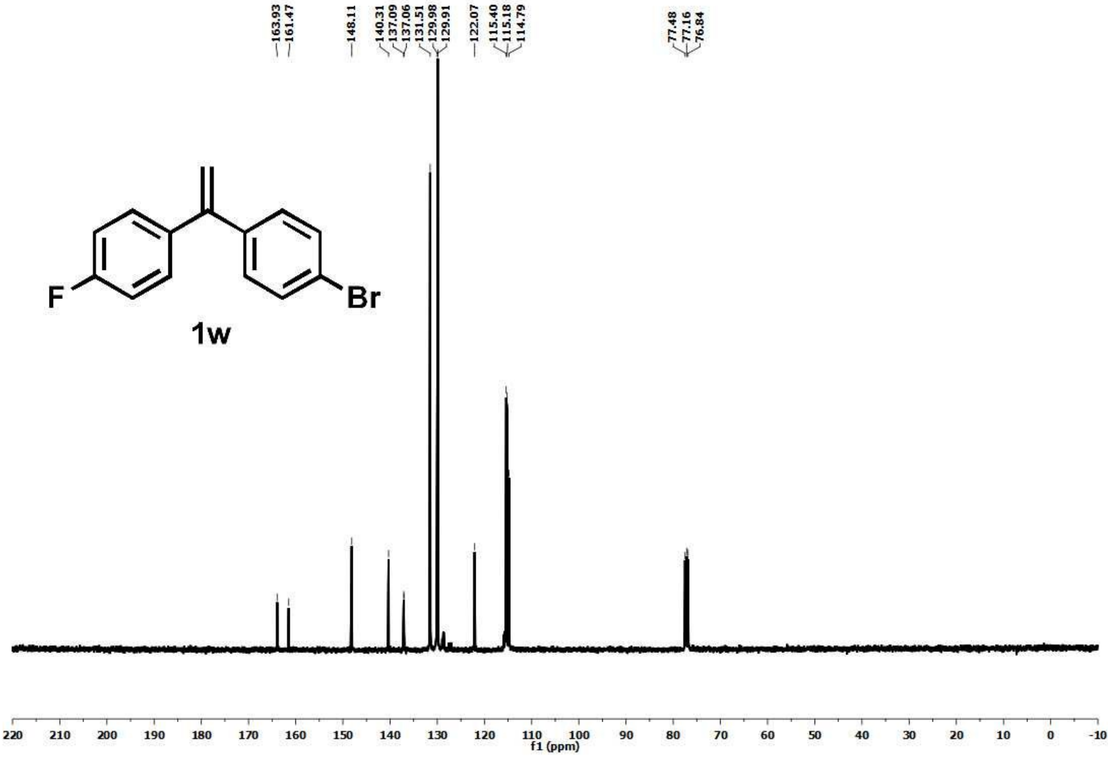
^{19}F NMR of new starting material 1v in CDCl$_3$ (376 MHz)



^{1}H NMR of new starting material 1w in CDCl$_3$ (400 MHz)



^{13}C NMR of new starting material 1w in CDCl$_3$ (100 MHz)



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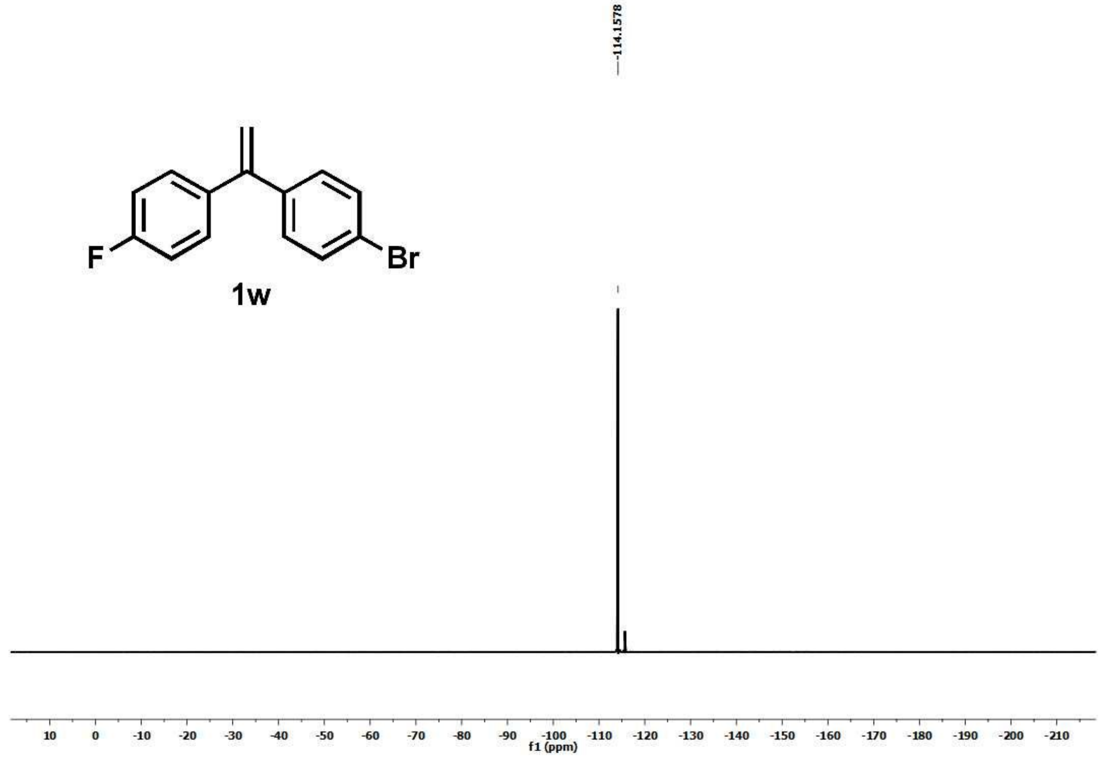
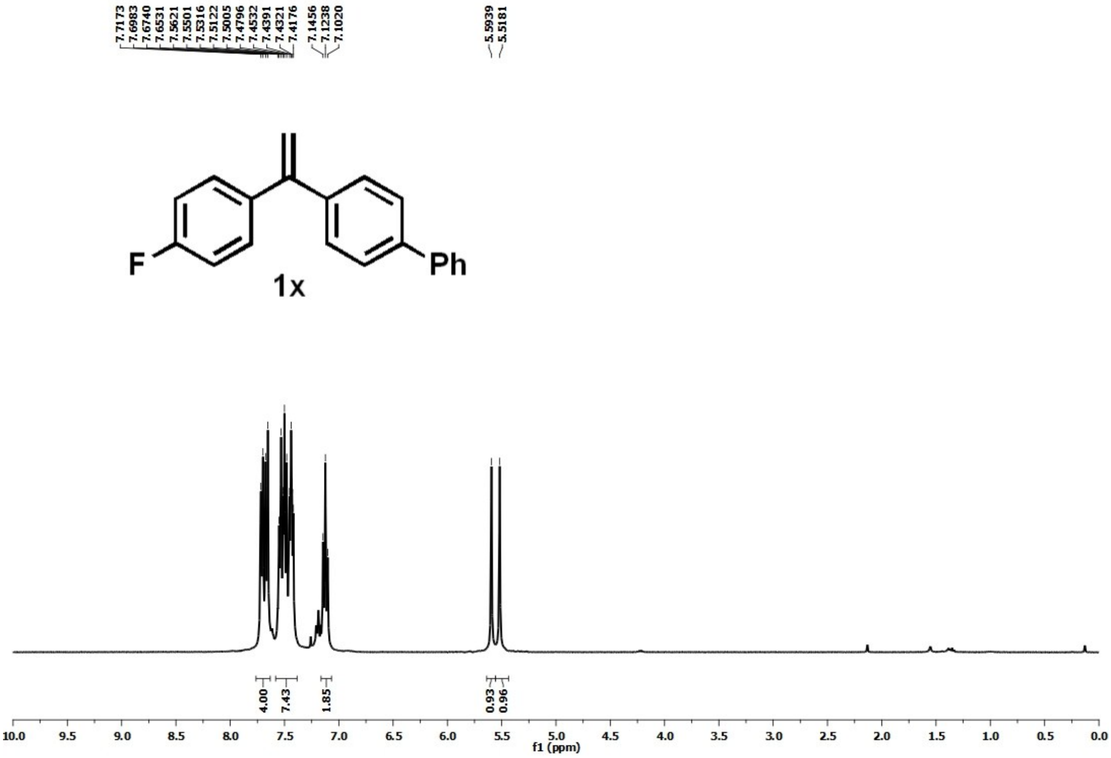


^{1}H NMR of new starting material 1x in CDCl$_3$ (400 MHz)



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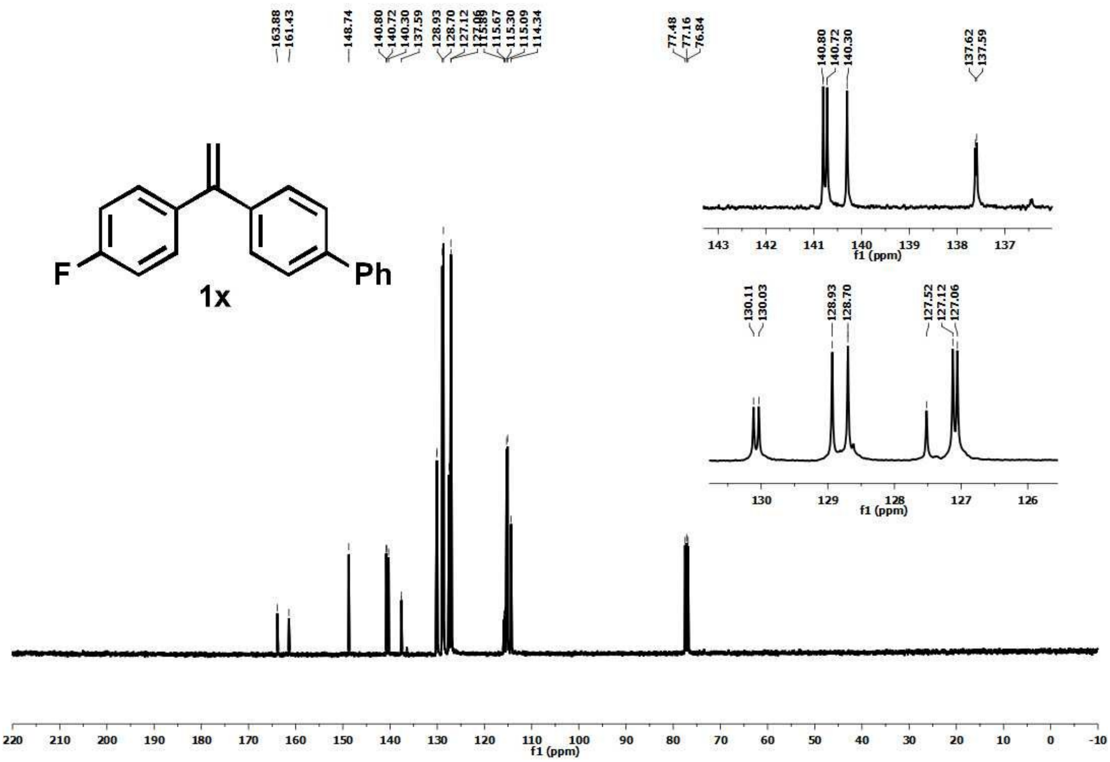
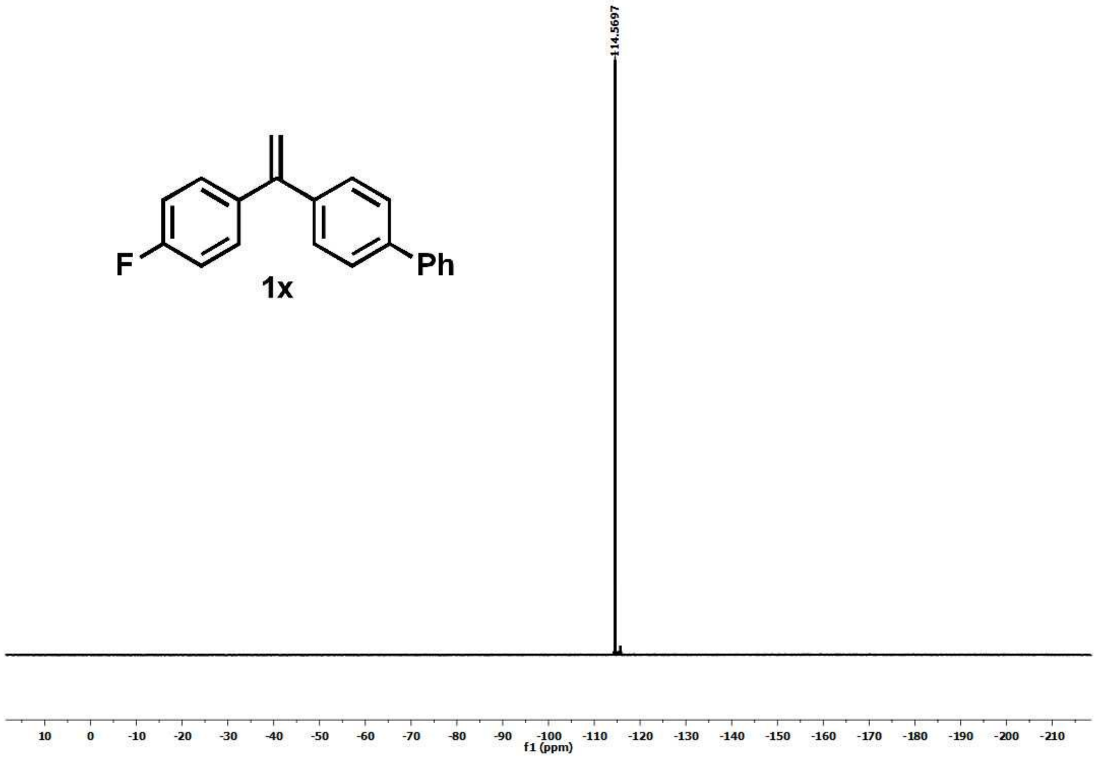
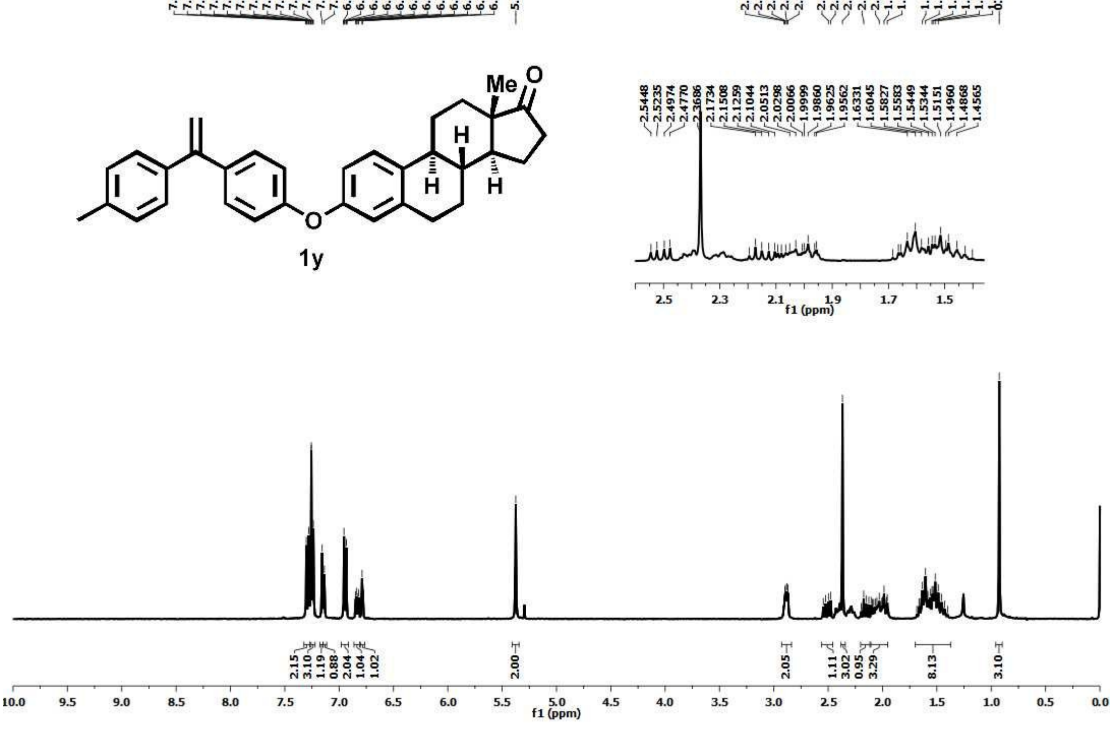


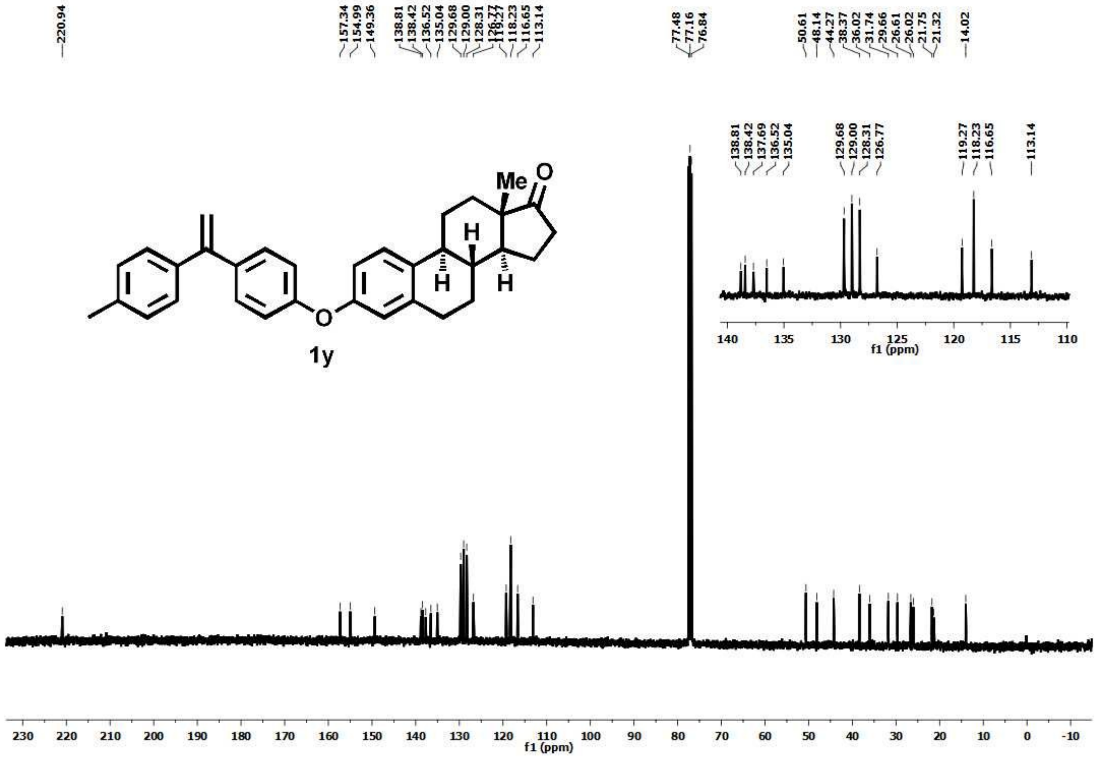
^{19}F NMR of new starting material 1x in CDCl$_3$ (376 MHz)



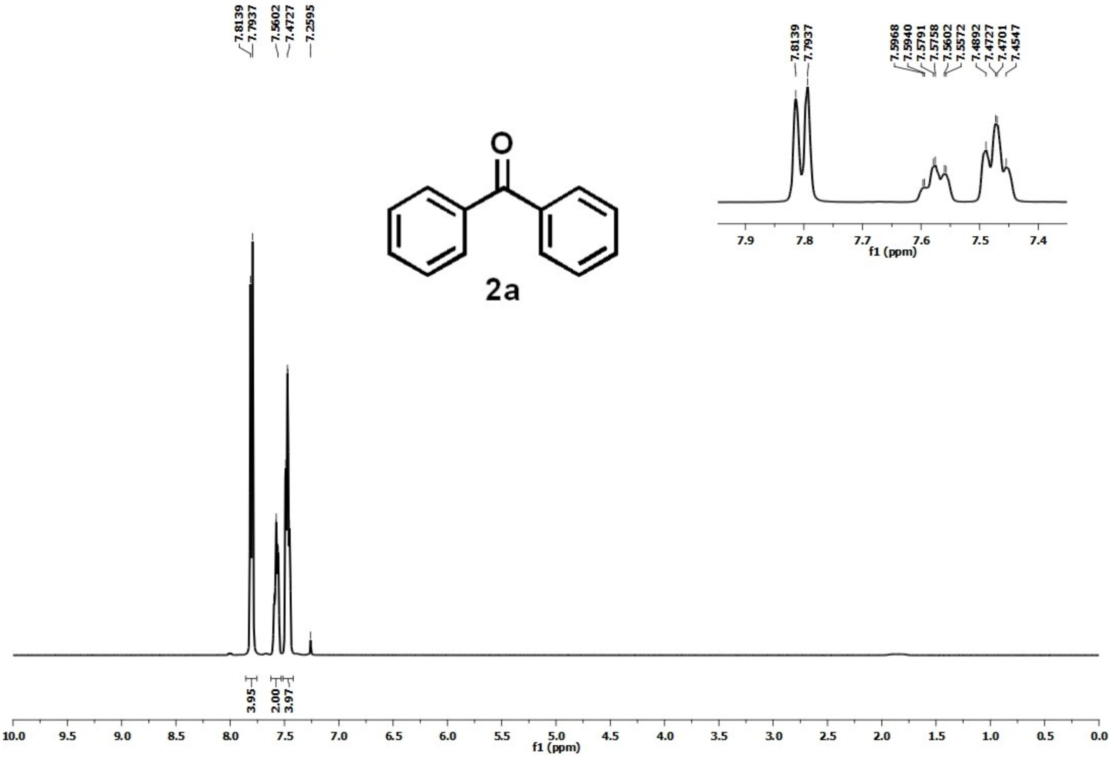
^{1}H NMR of new starting material 1y in CDCl$_3$ (400 MHz)



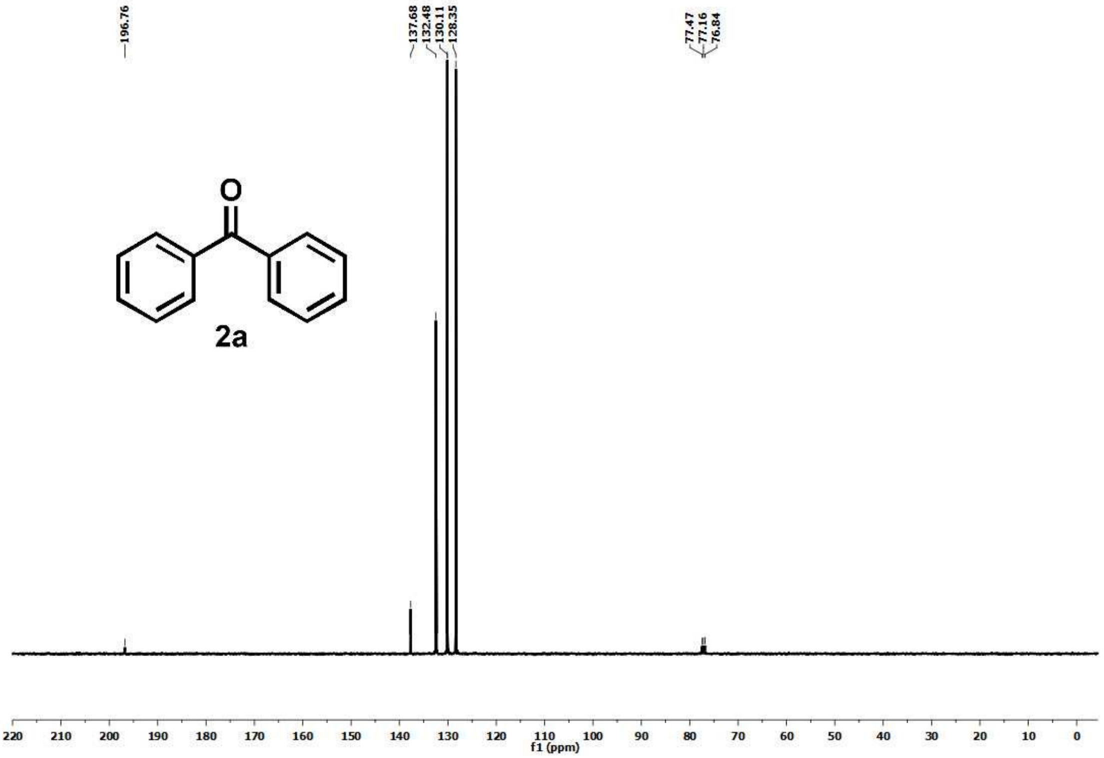
^{13}C NMR of new starting material 1y in CDCl$_3$ (100 MHz)



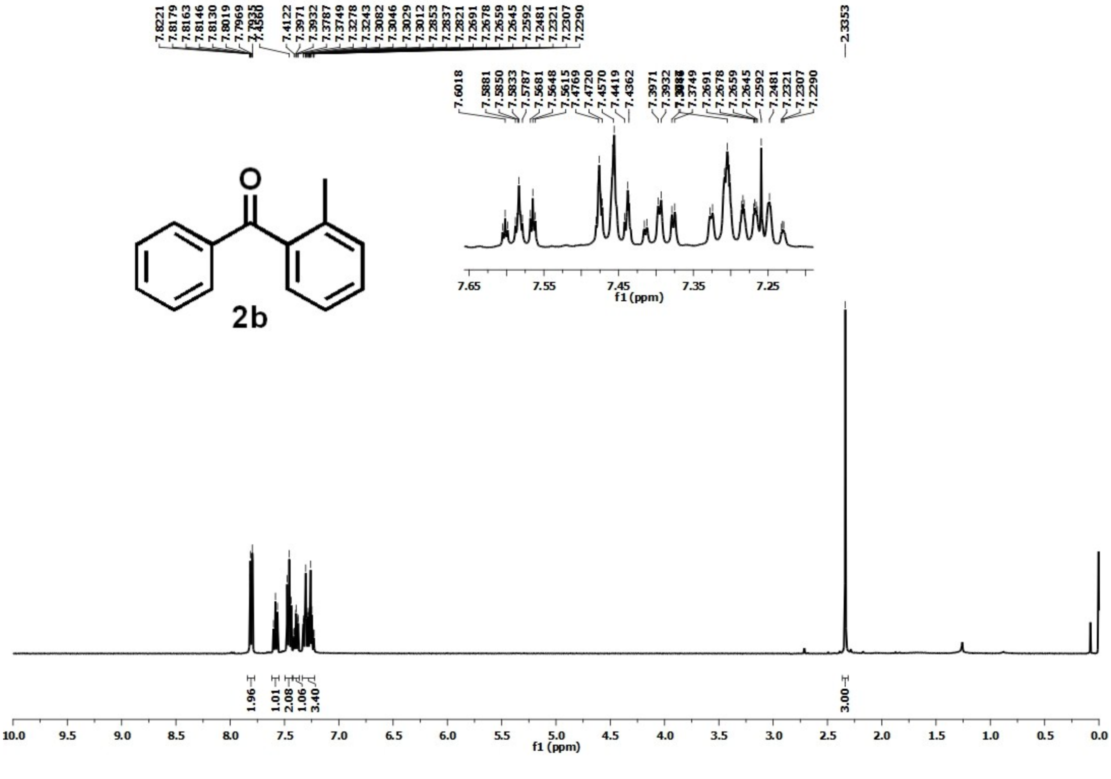
^{1}H NMR of product 2a in CDCl$_3$ (400 MHz)



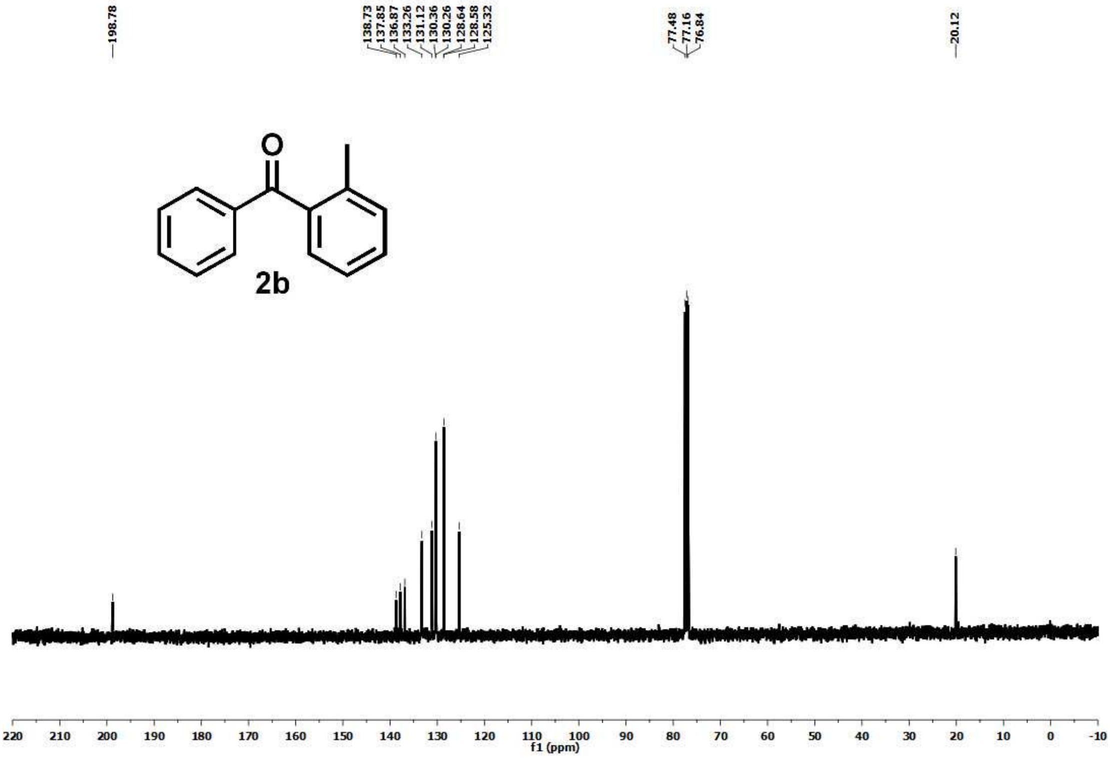
^{13}C NMR of product 2a in CDCl$_3$ (100 MHz)



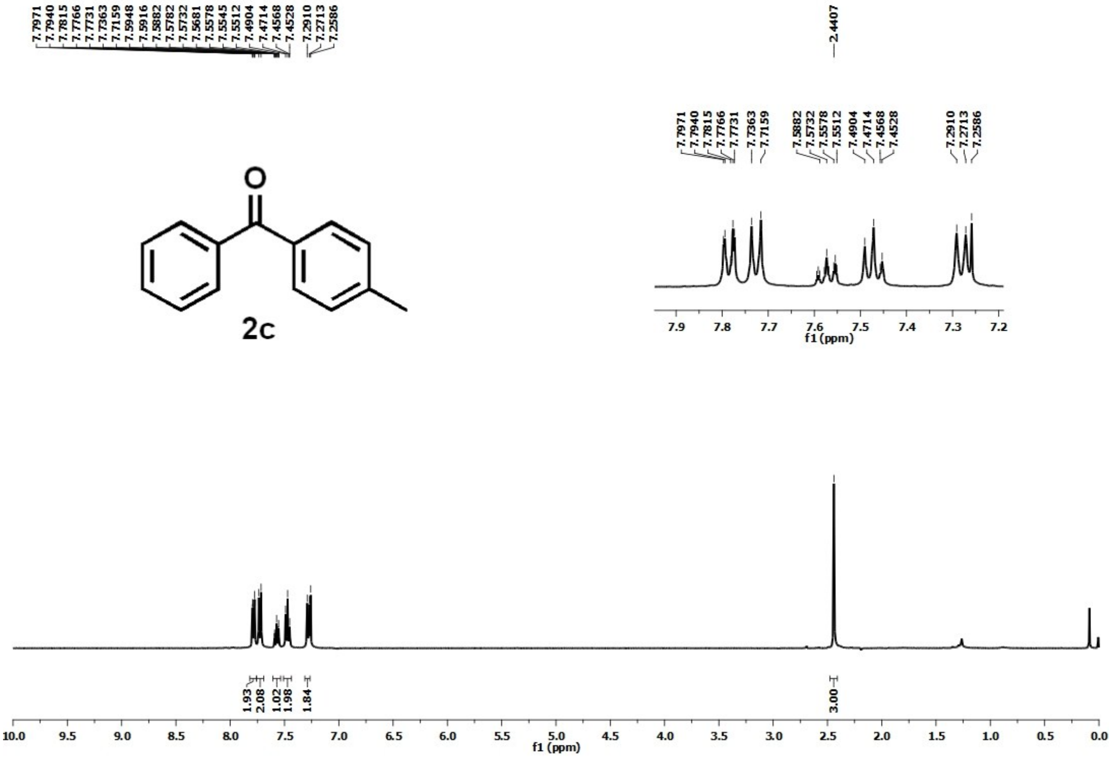
^{1}H NMR of product 2b in CDCl$_3$ (400 MHz)



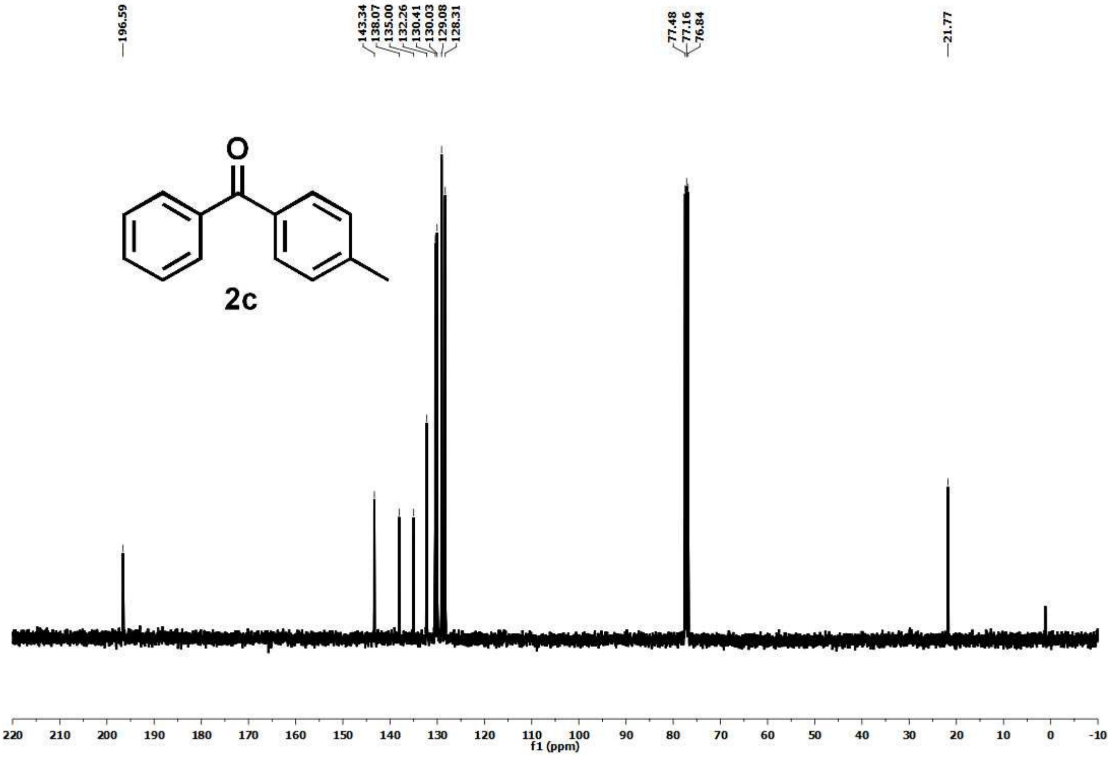
^{13}C NMR of product 2b in $CDCl_3$ (100 MHz)



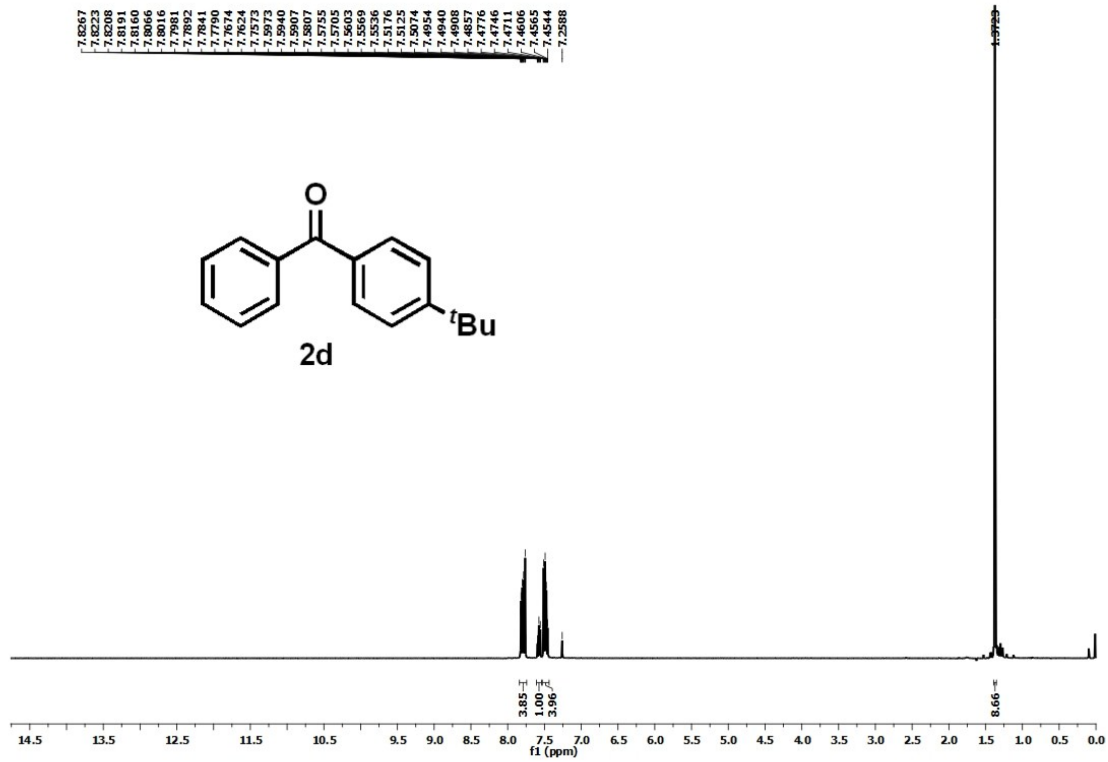
^{1}H NMR of product 2c in $CDCl_3$ (400 MHz)



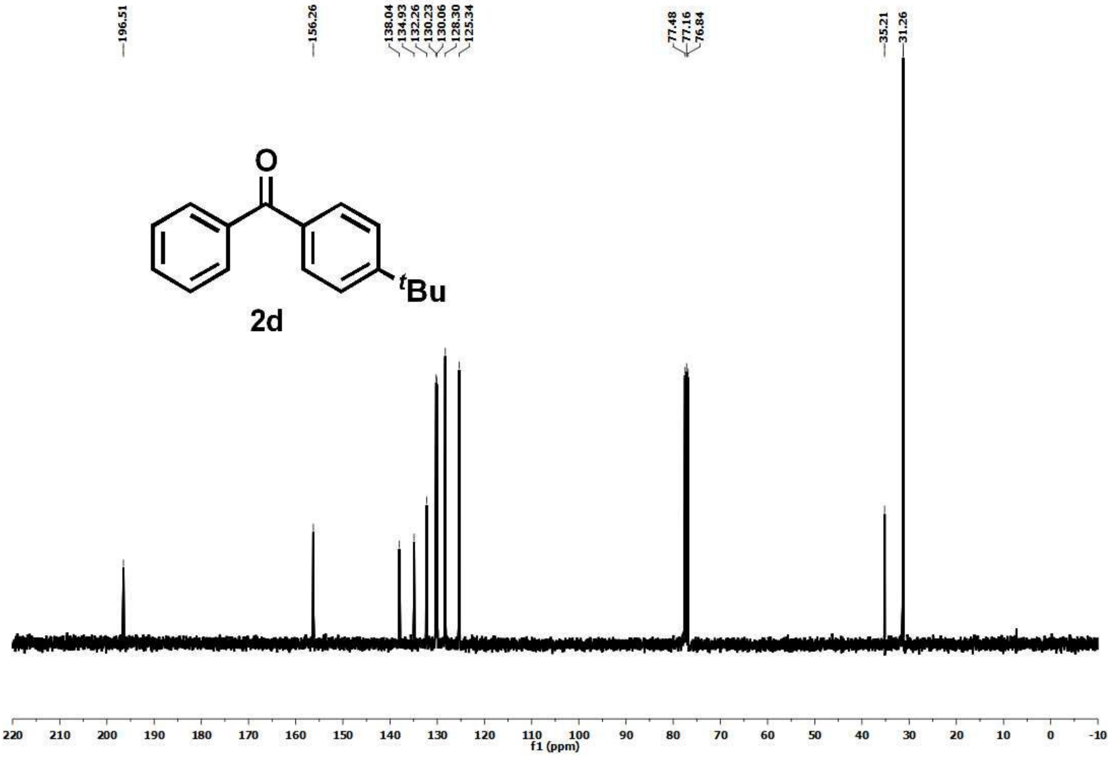
^{13}C NMR of product 2c in CDCl$_3$ (100 MHz)



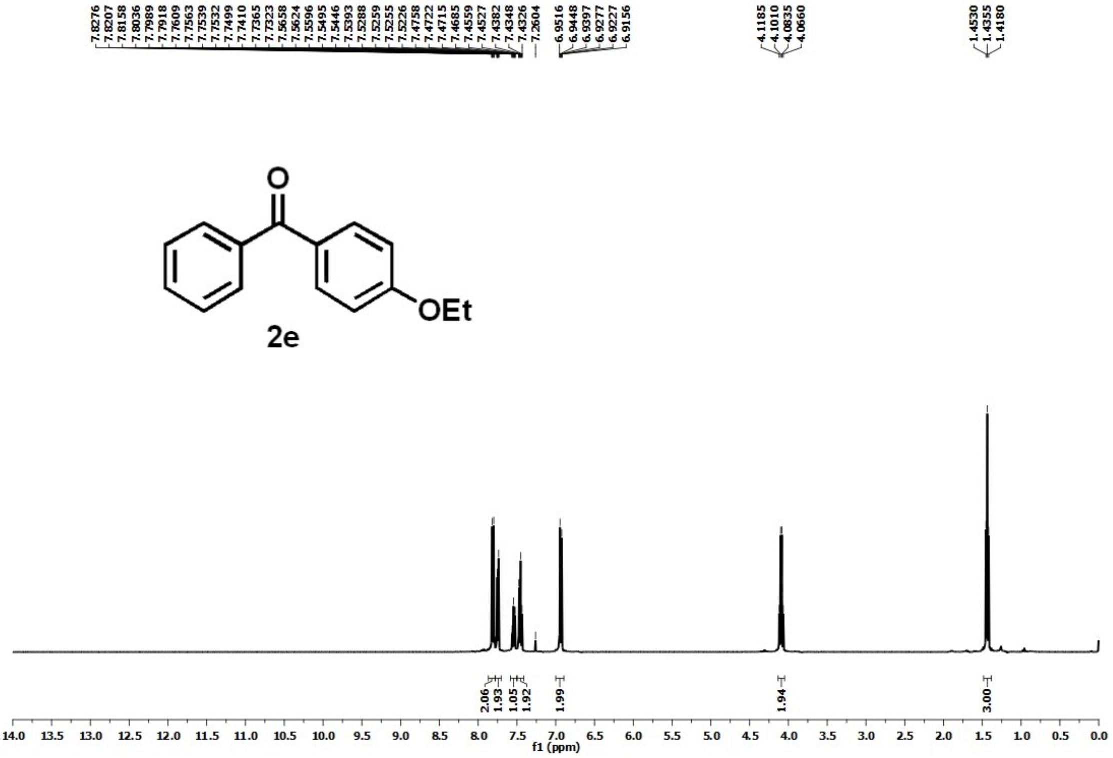
^{1}H NMR of product 2d in CDCl$_3$ (400 MHz)



^{13}C NMR of product 2d in $CDCl_3$ (100 MHz)



^{1}H NMR of product 2e in $CDCl_3$ (400 MHz)



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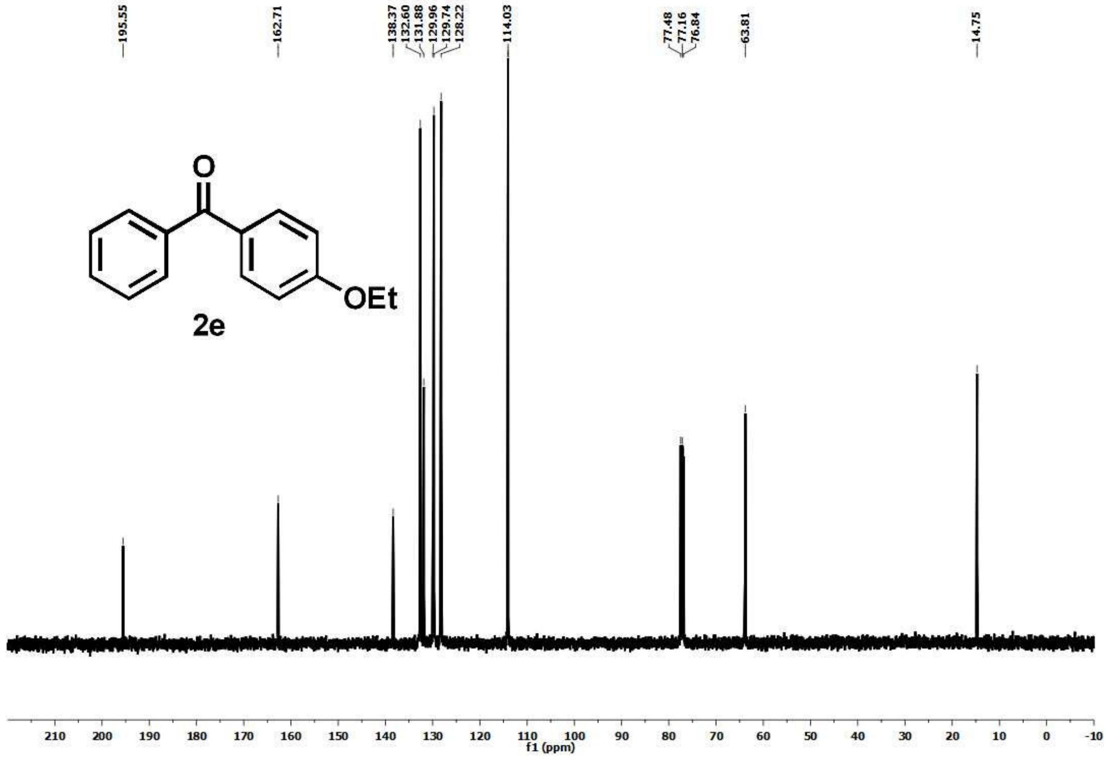
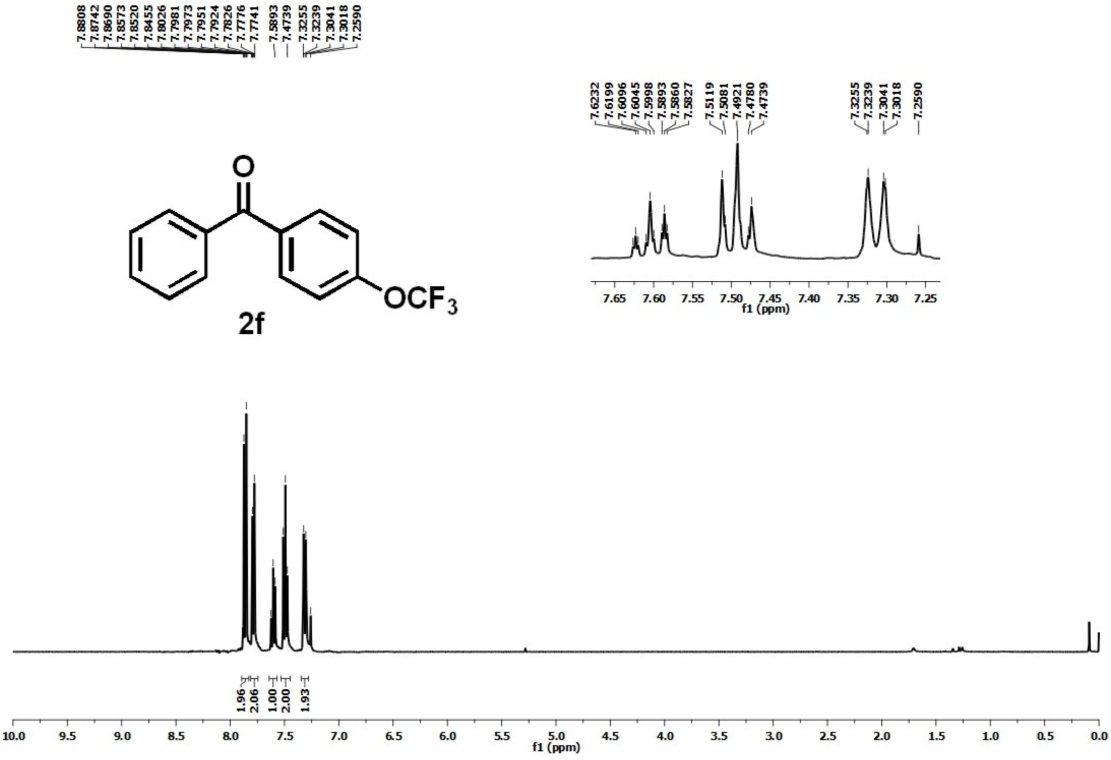
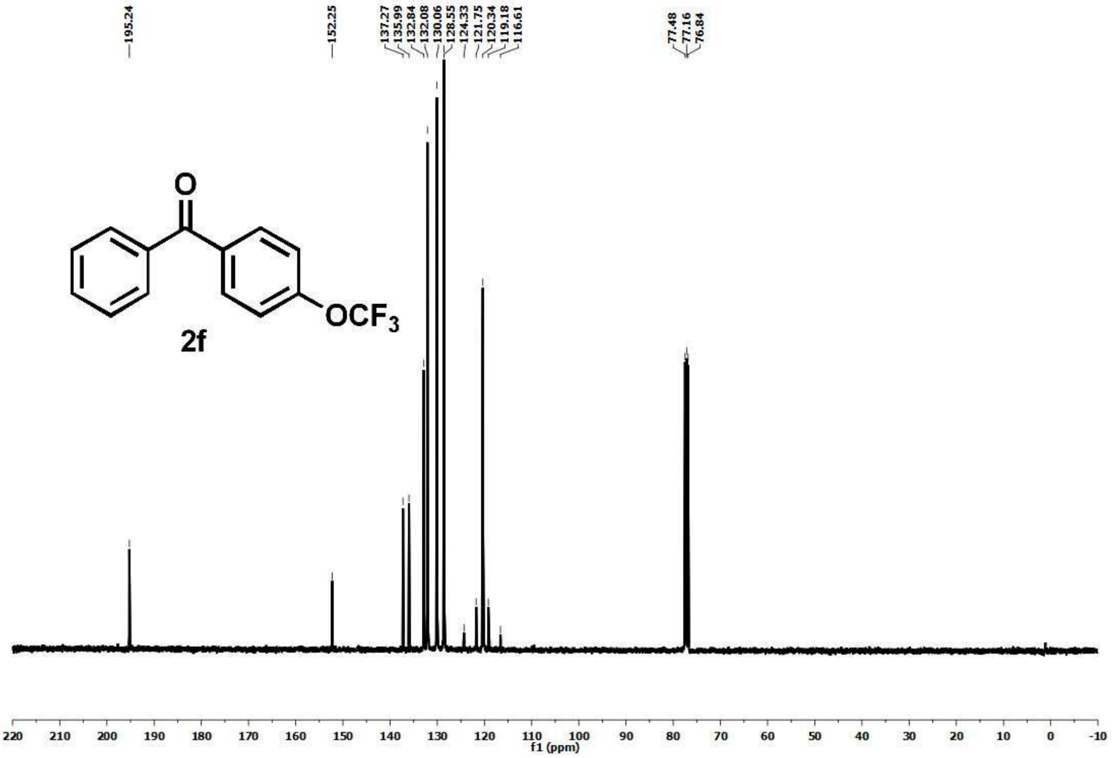


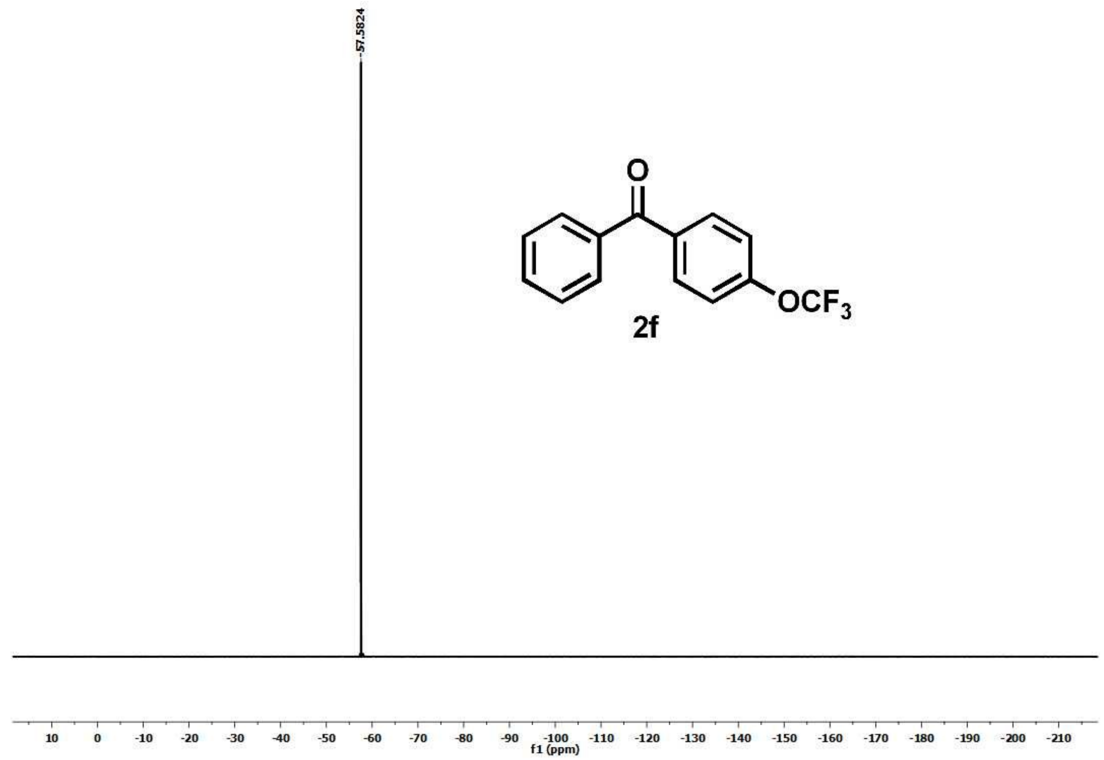
^{1}H NMR of product 2f in CDCl$_3$ (400 MHz)



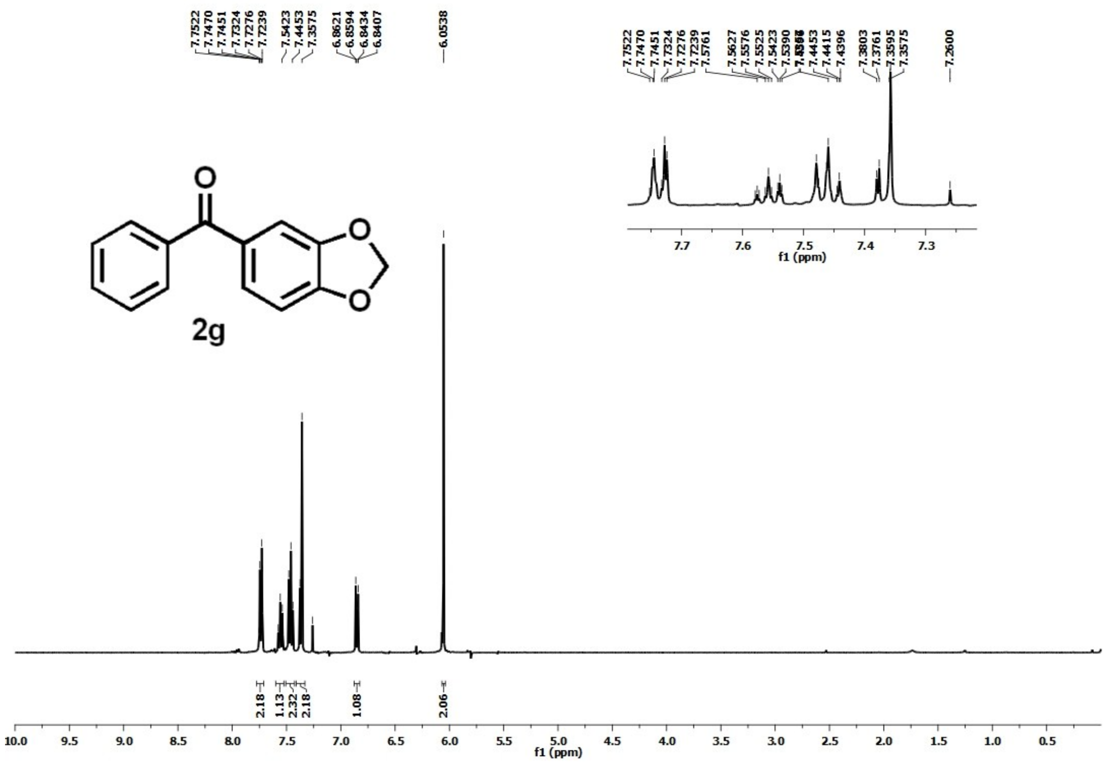
^{13}C NMR of product 2f in CDCl$_3$ (100 MHz)



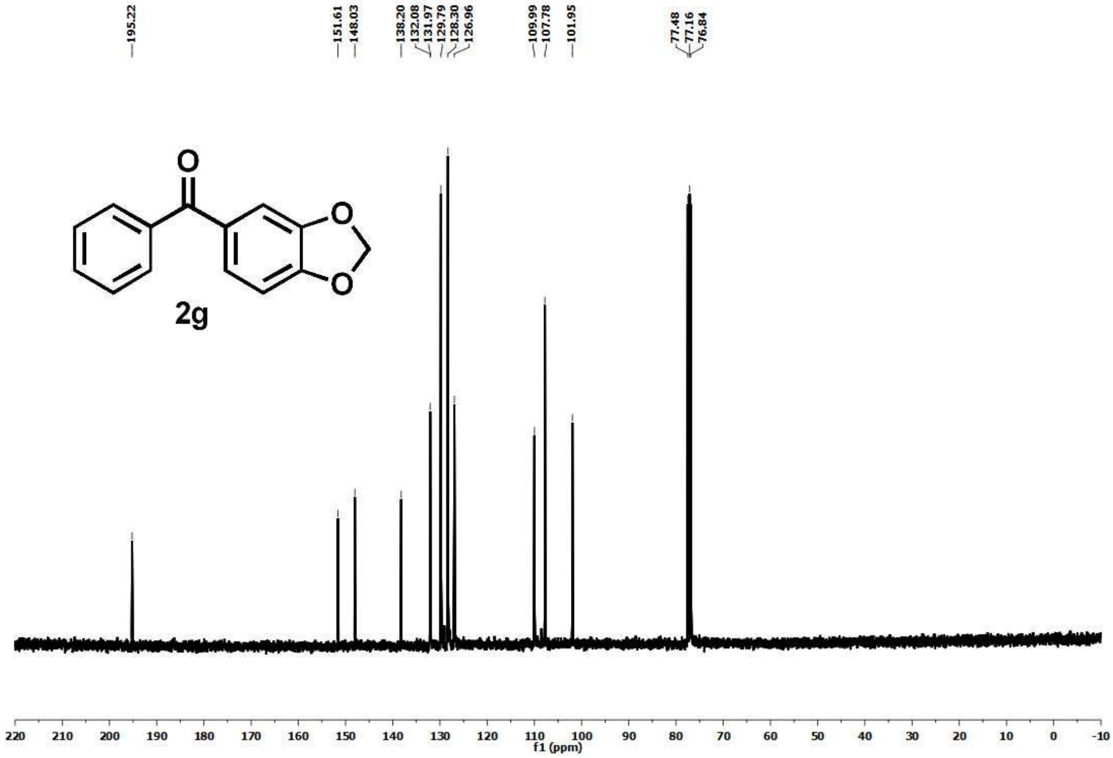
^{19}F NMR of product 2f in CDCl$_3$ (376 MHz)



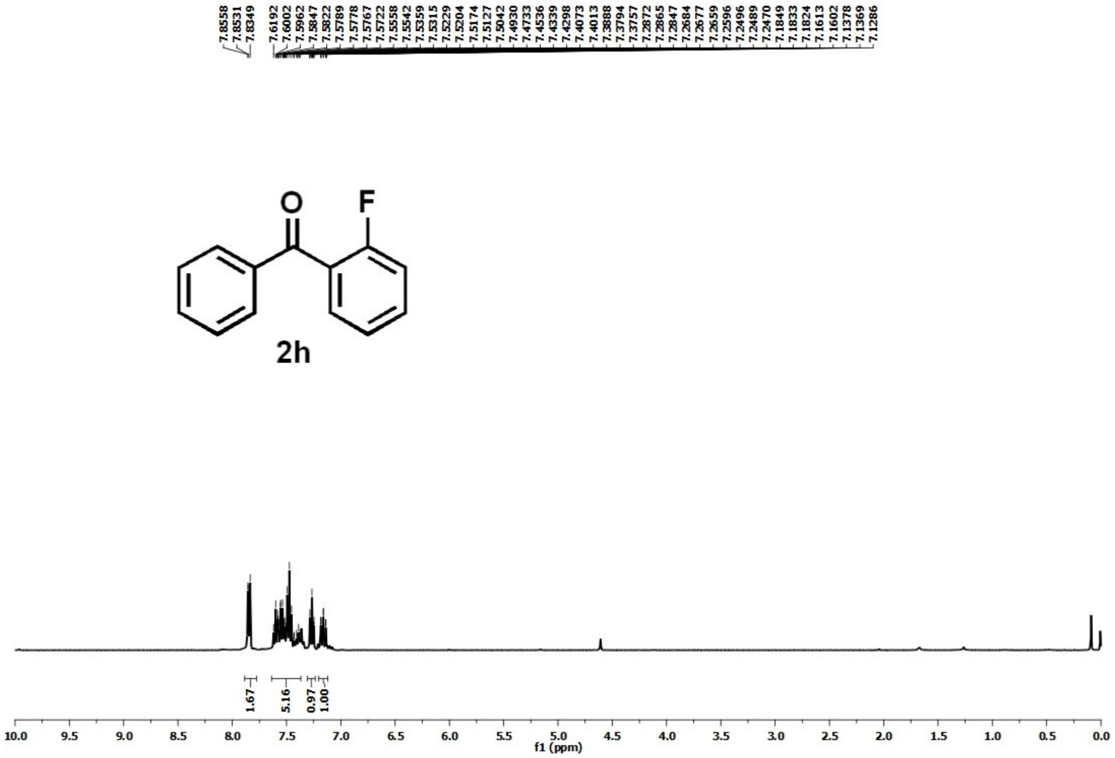
^{1}H NMR of product 2g in CDCl$_3$ (400 MHz)



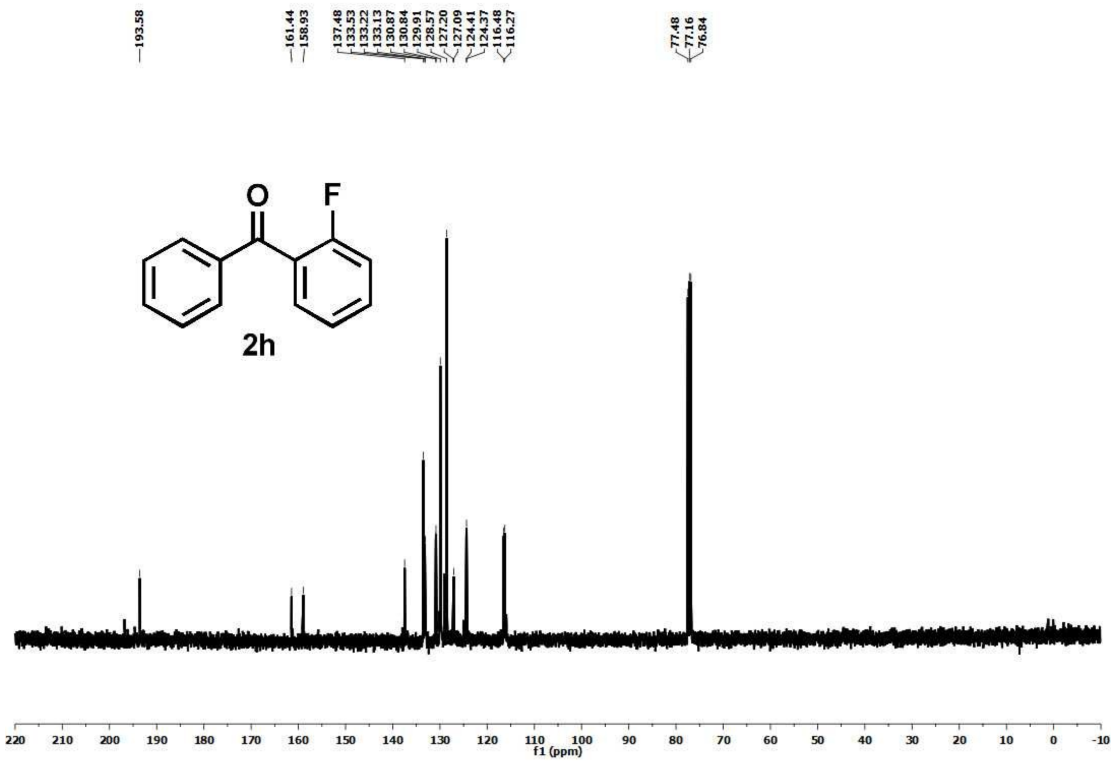
^{13}C NMR of product 2g in CDCl$_3$ (100 MHz)



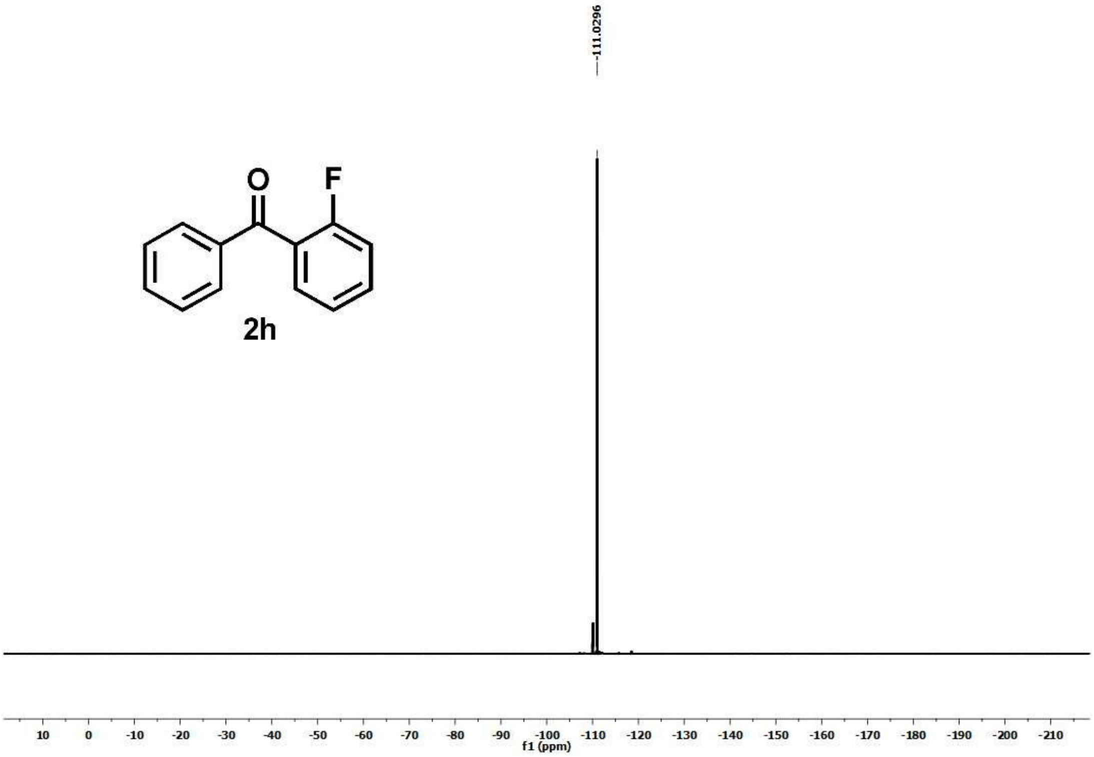
^{1}H NMR of product 2h in $CDCl_3$ (400 MHz)



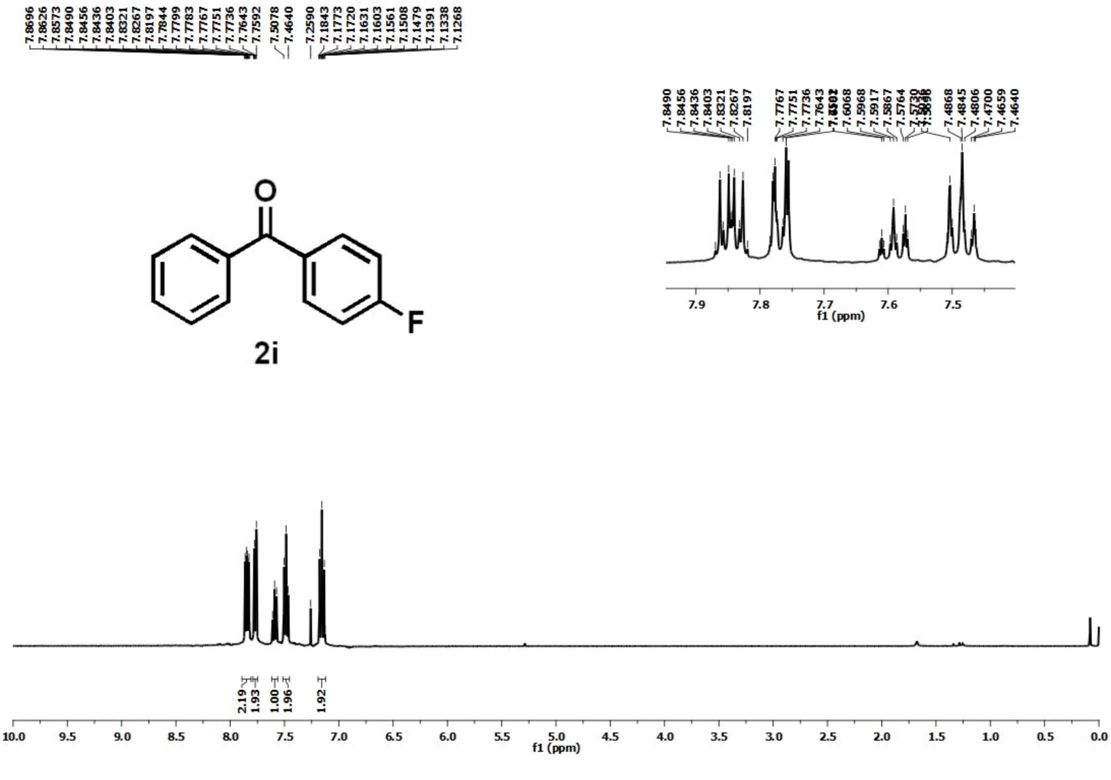
^{13}C NMR of product 2h in $CDCl_3$ (100 MHz)



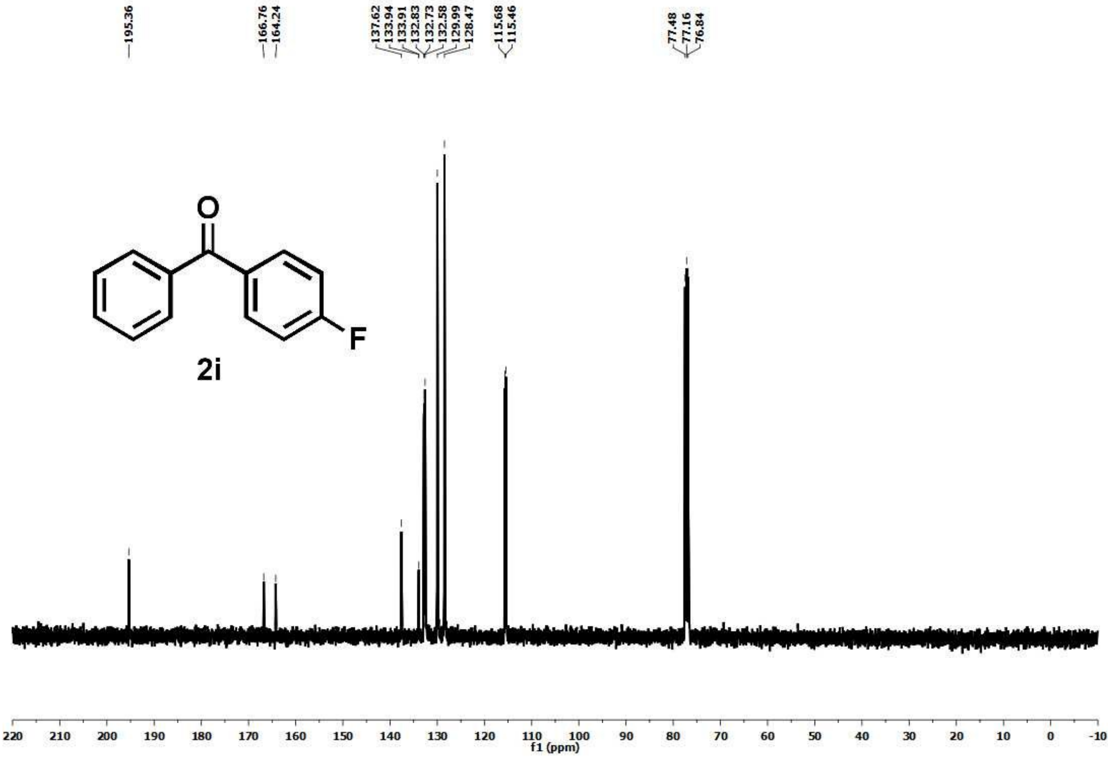
^{19}F NMR of product 2h in CDCl$_3$ (376 MHz)



^{1}H NMR of product 2i in CDCl$_3$ (400 MHz)



^{13}C NMR of product 2i in CDCl$_3$ (100 MHz)



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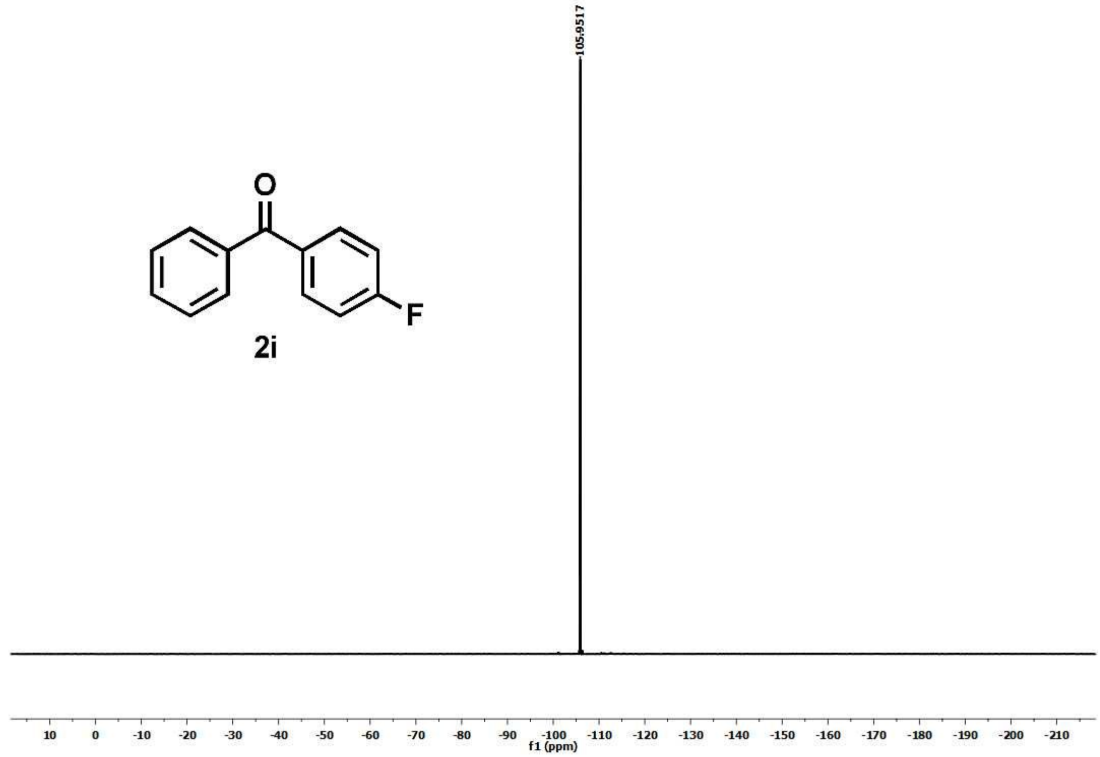

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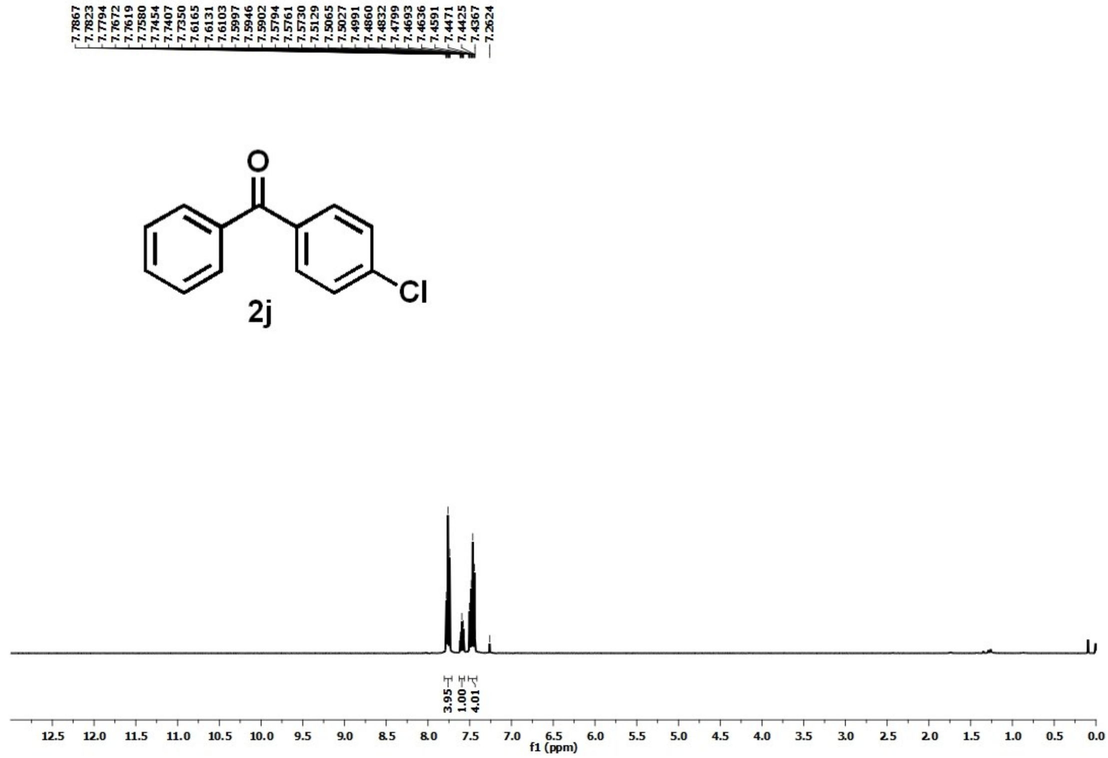

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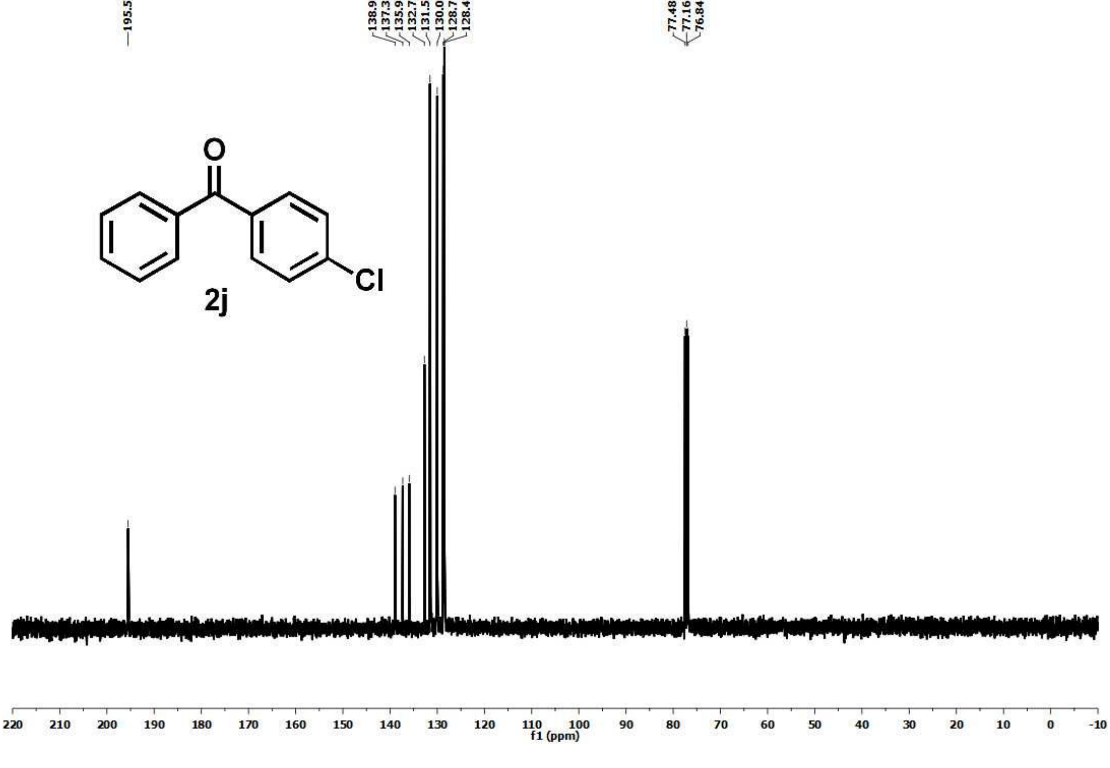

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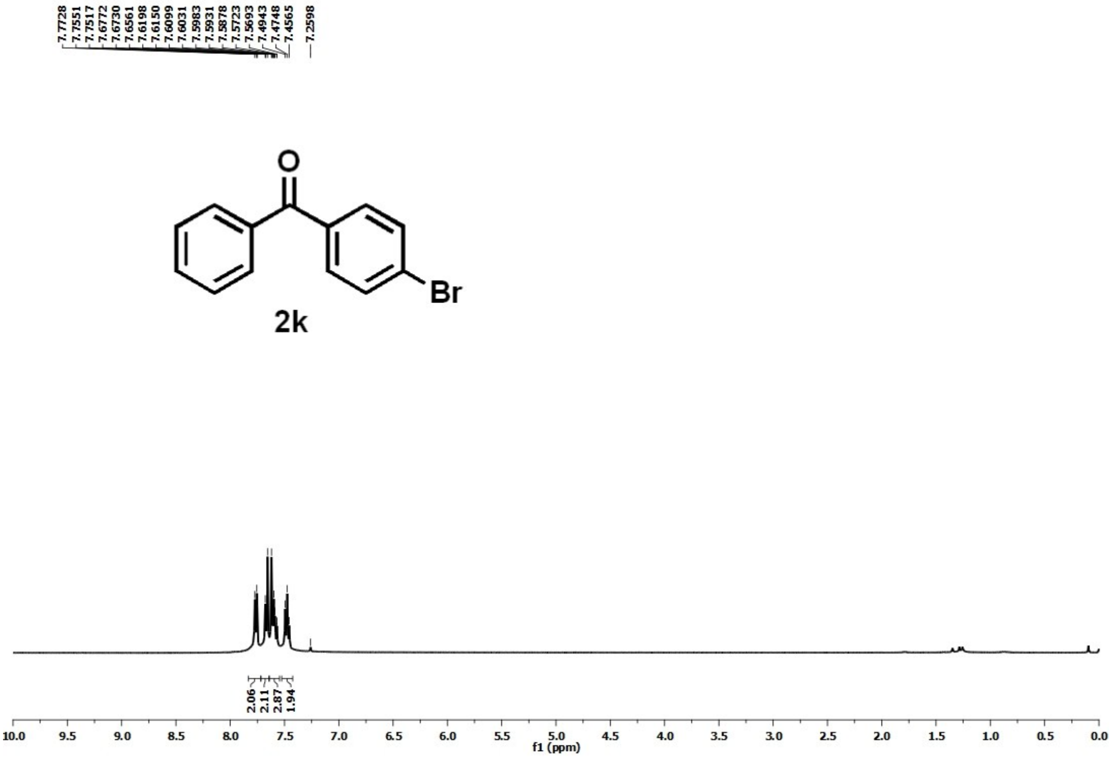

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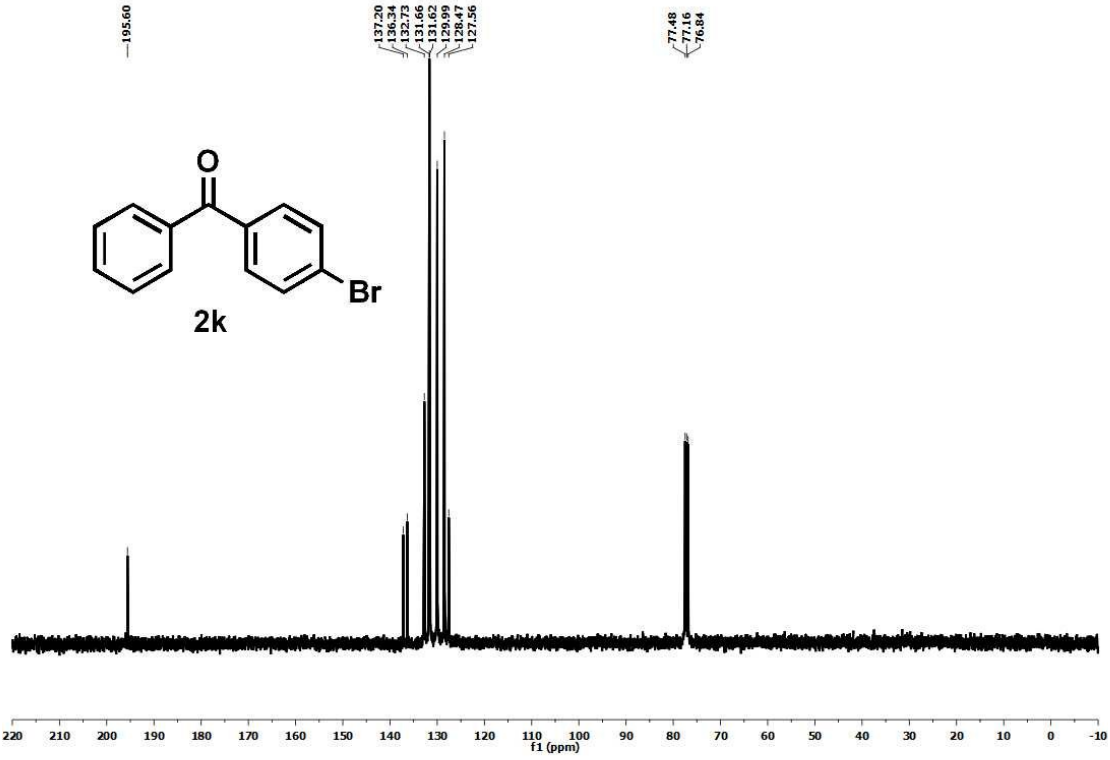

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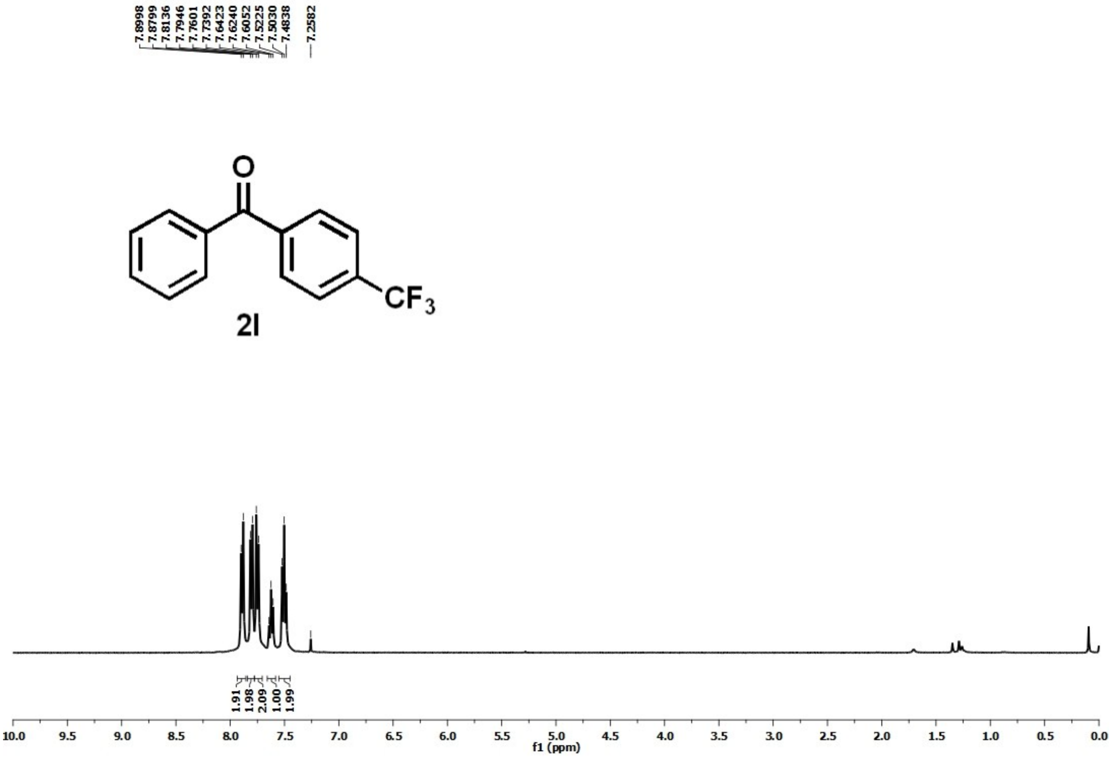

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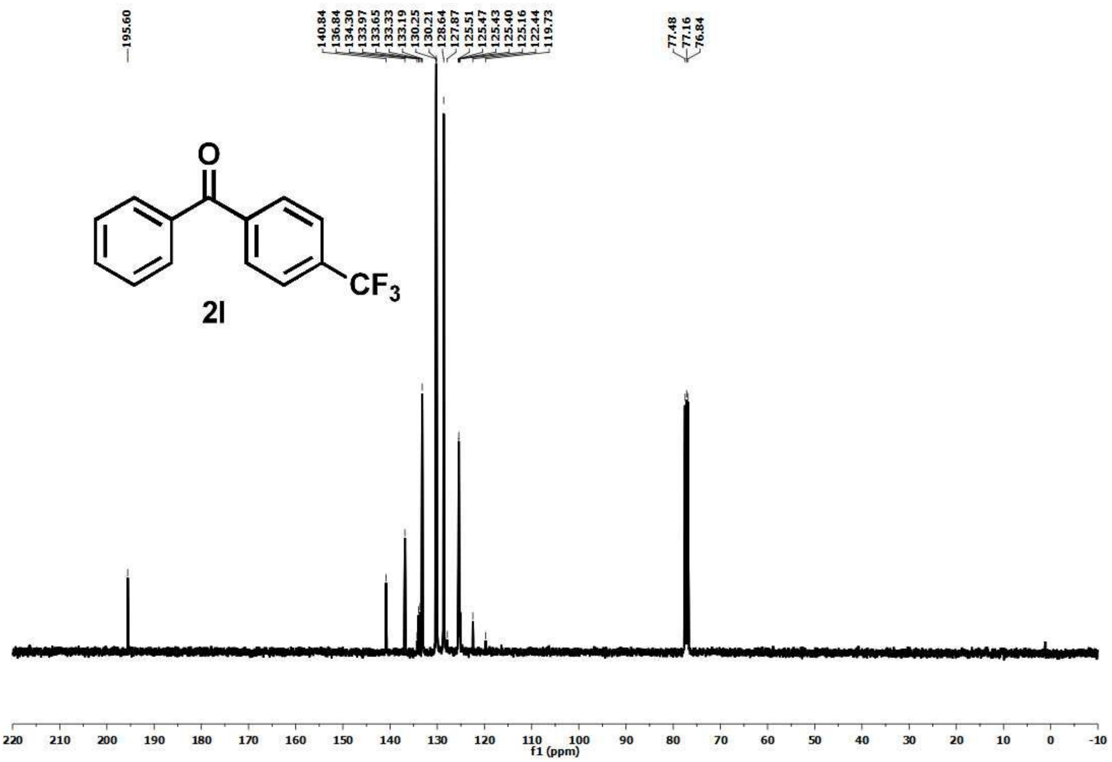
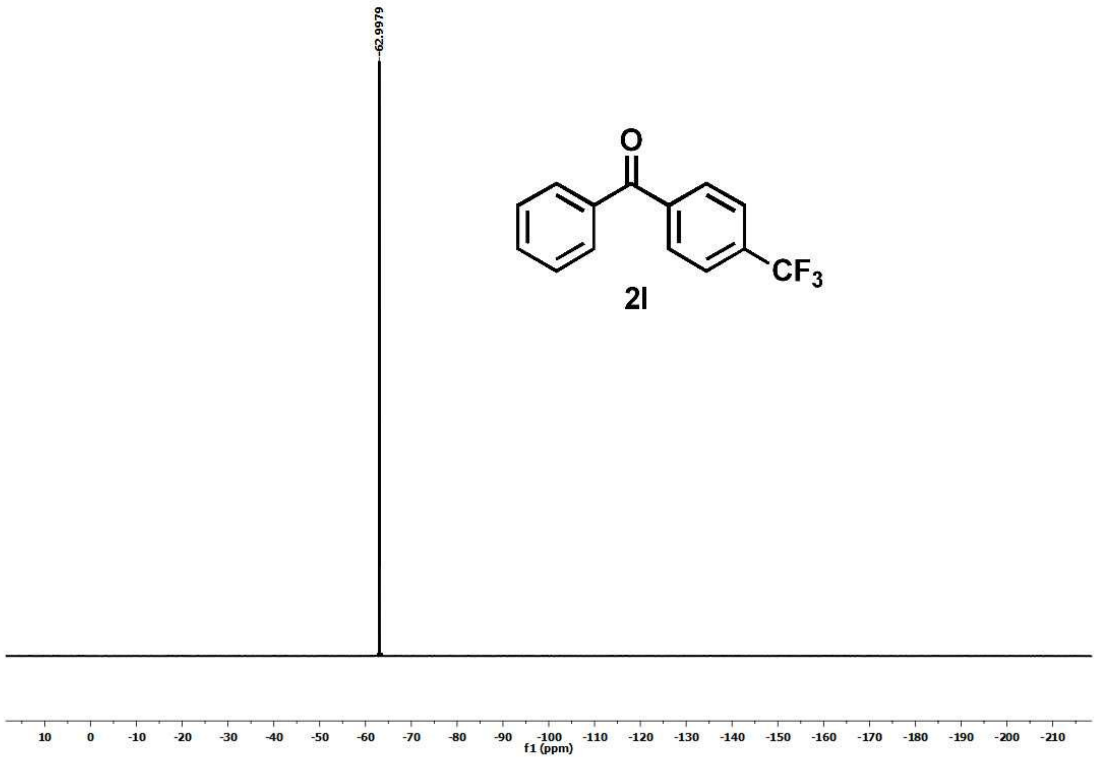


^{19}F NMR of product 2l in $CDCl_3$ (376 MHz)



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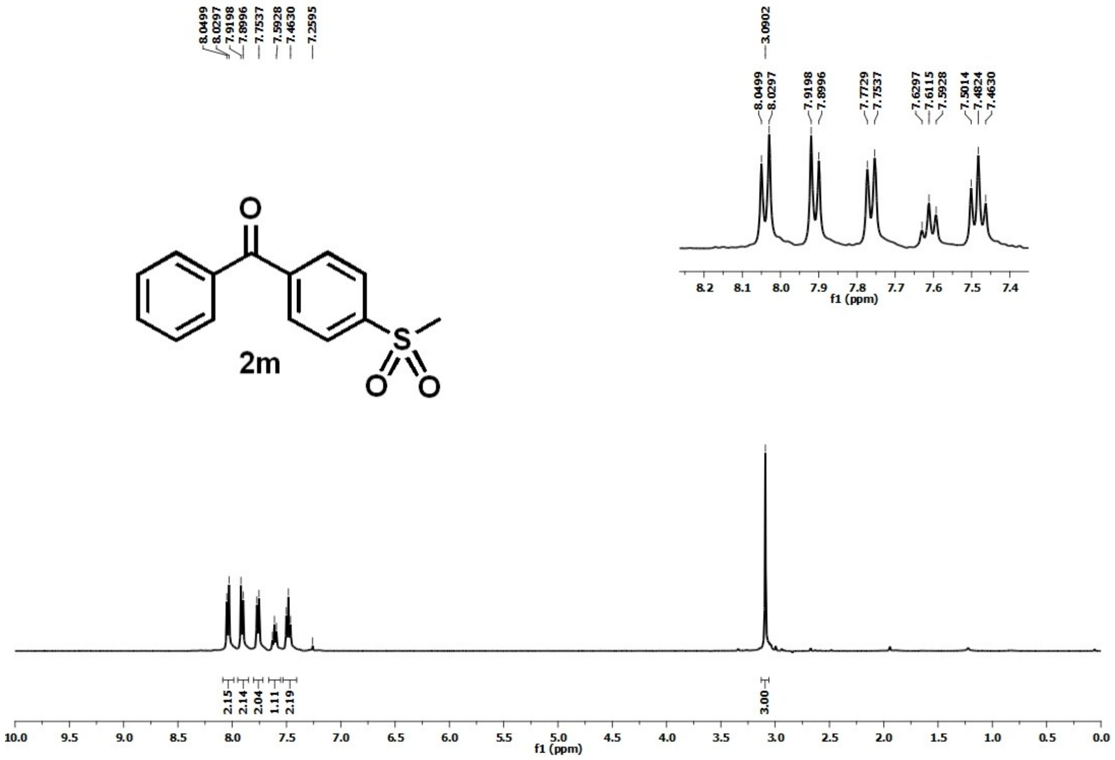

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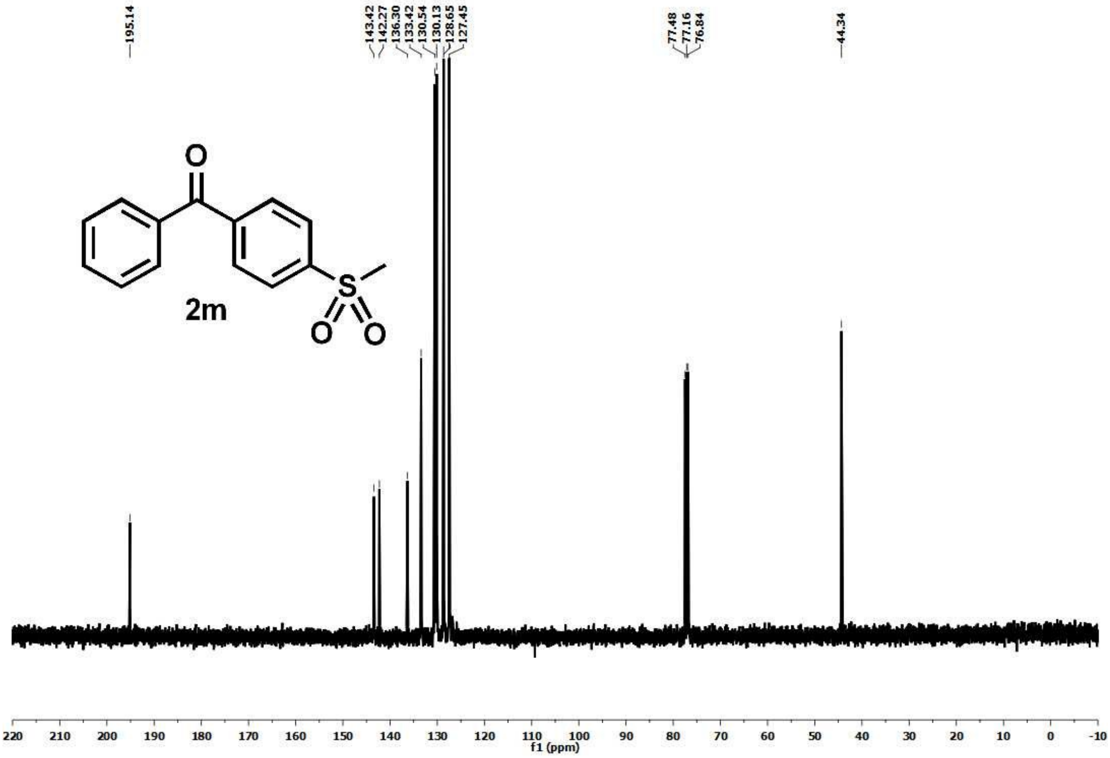

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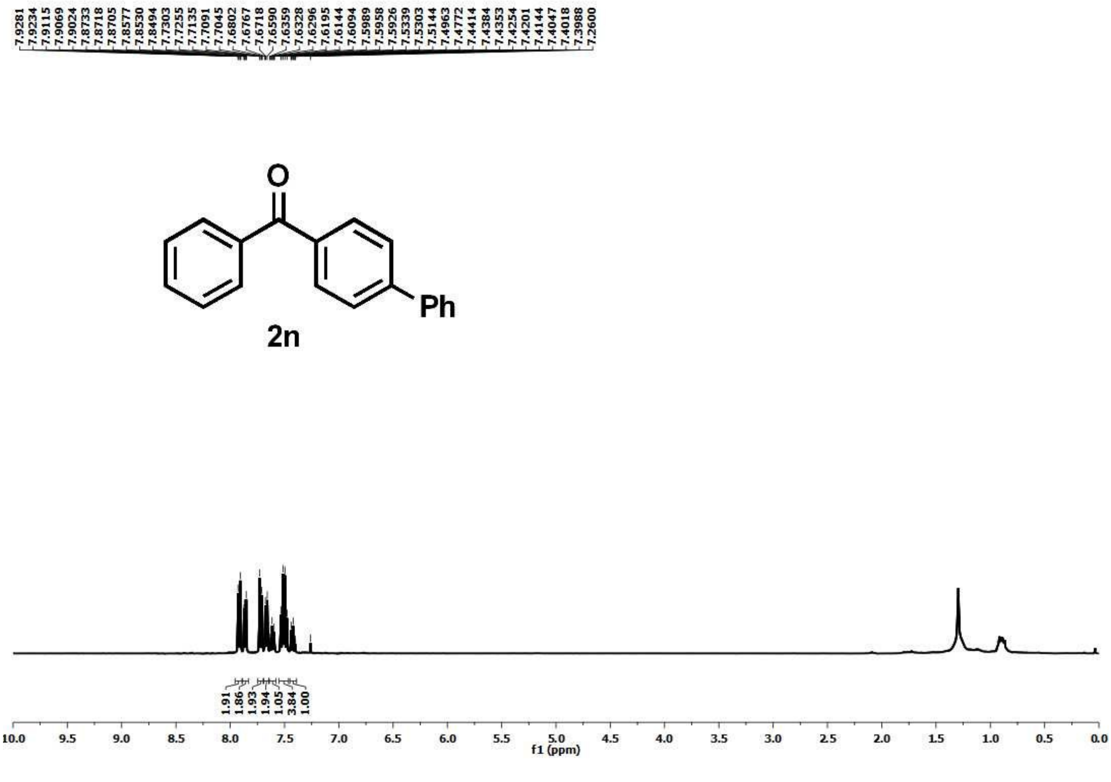

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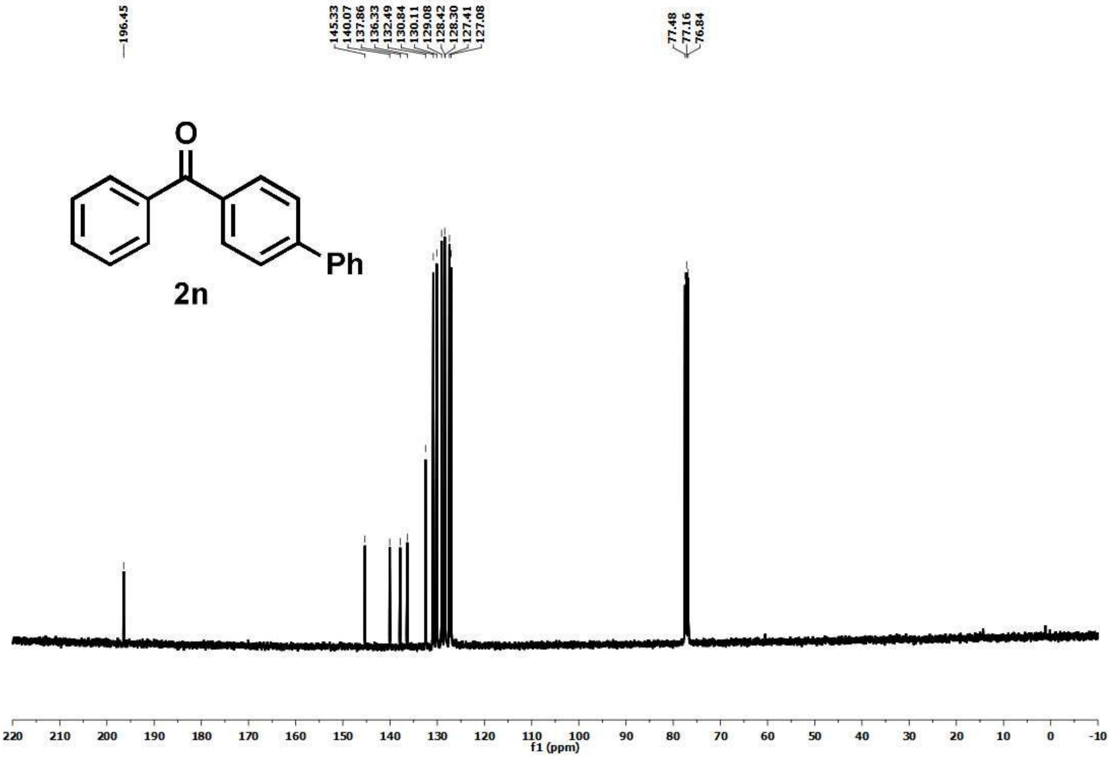

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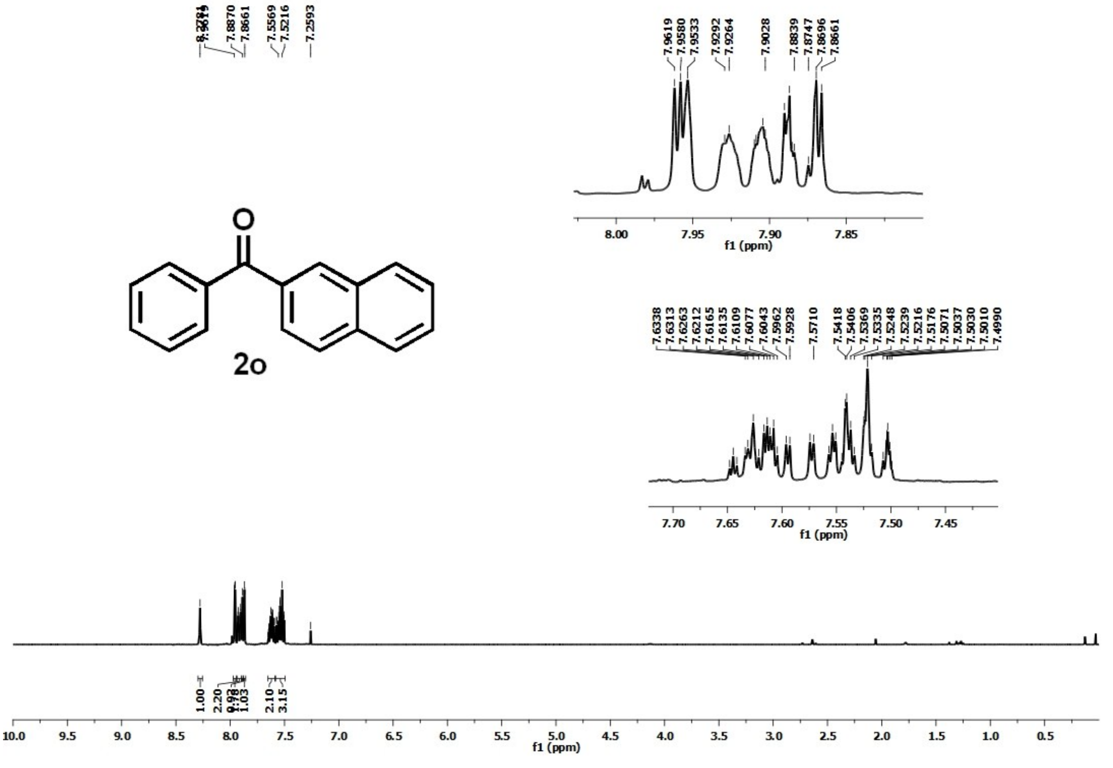
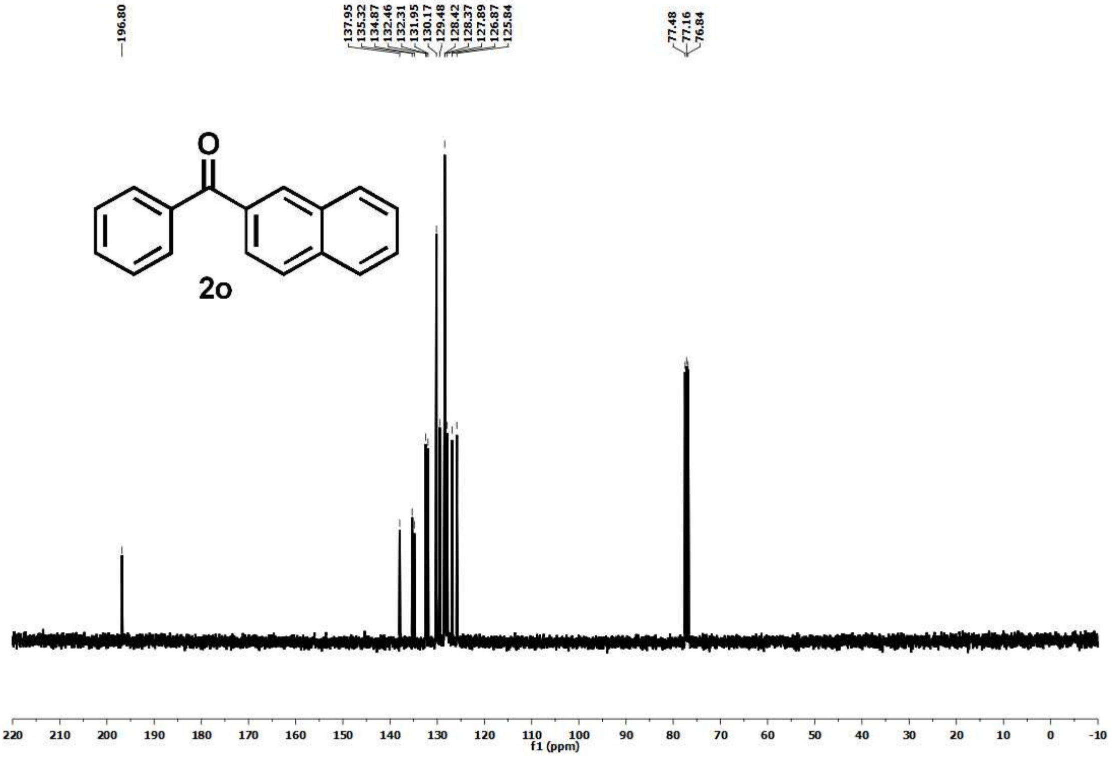
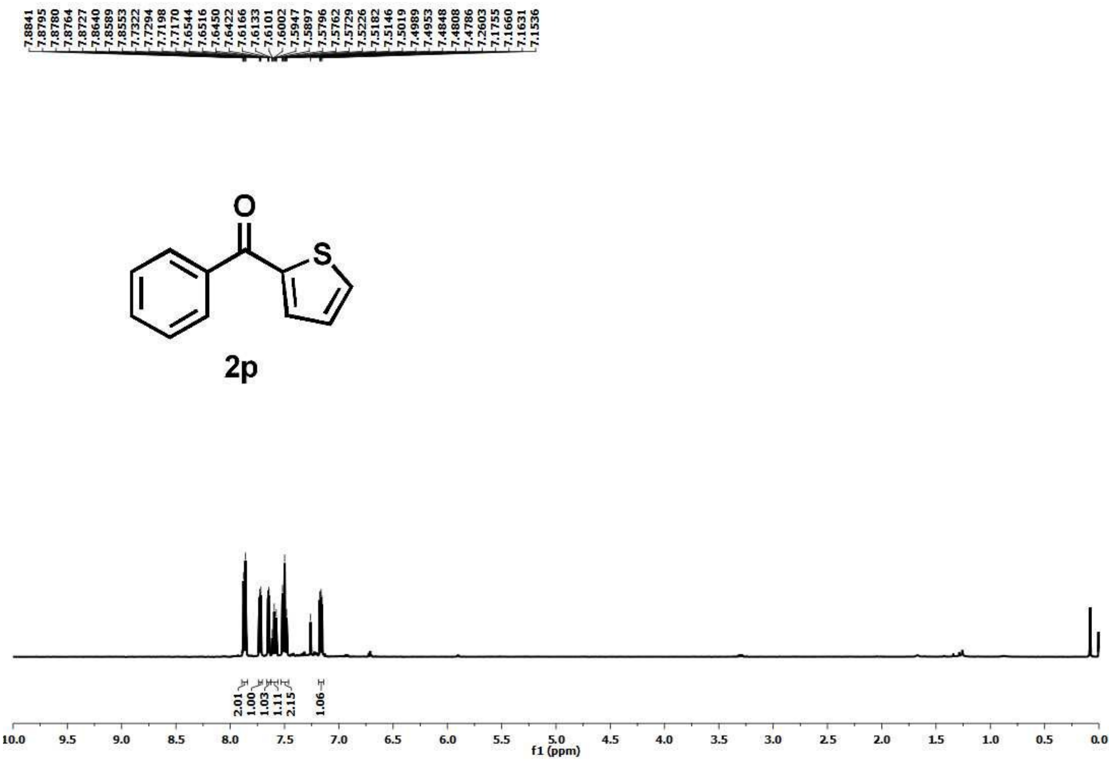


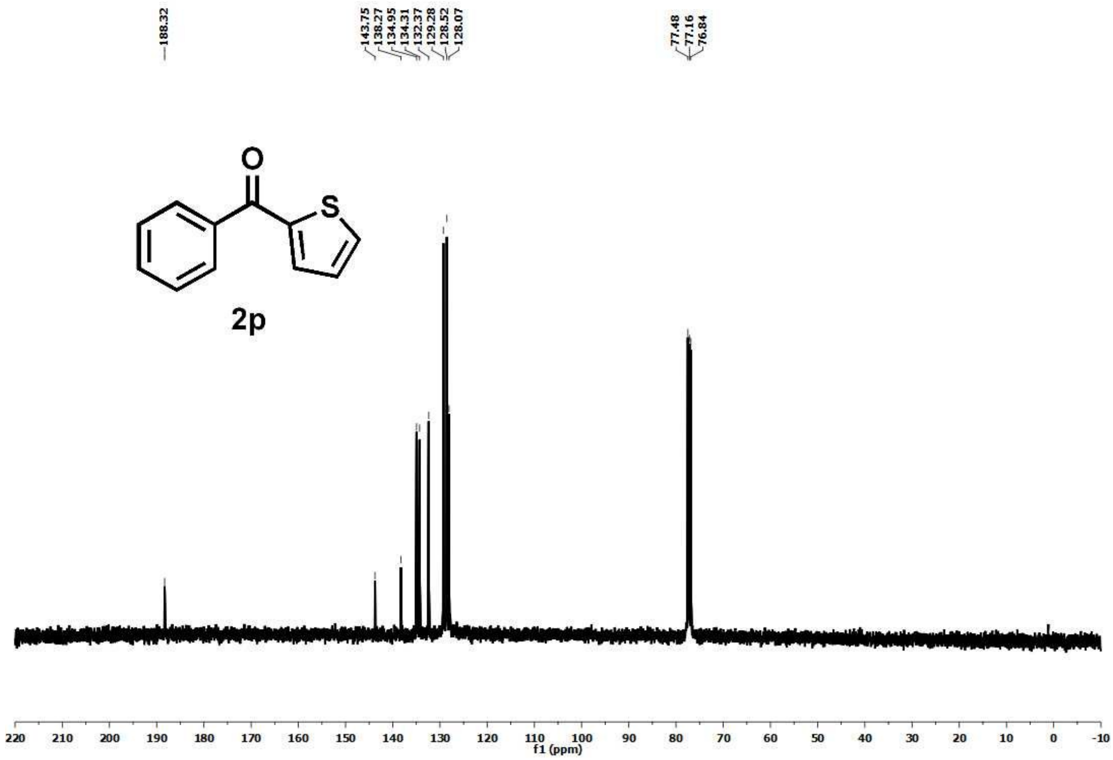
^{13}C NMR of product 2o in $CDCl_3$ (100 MHz)



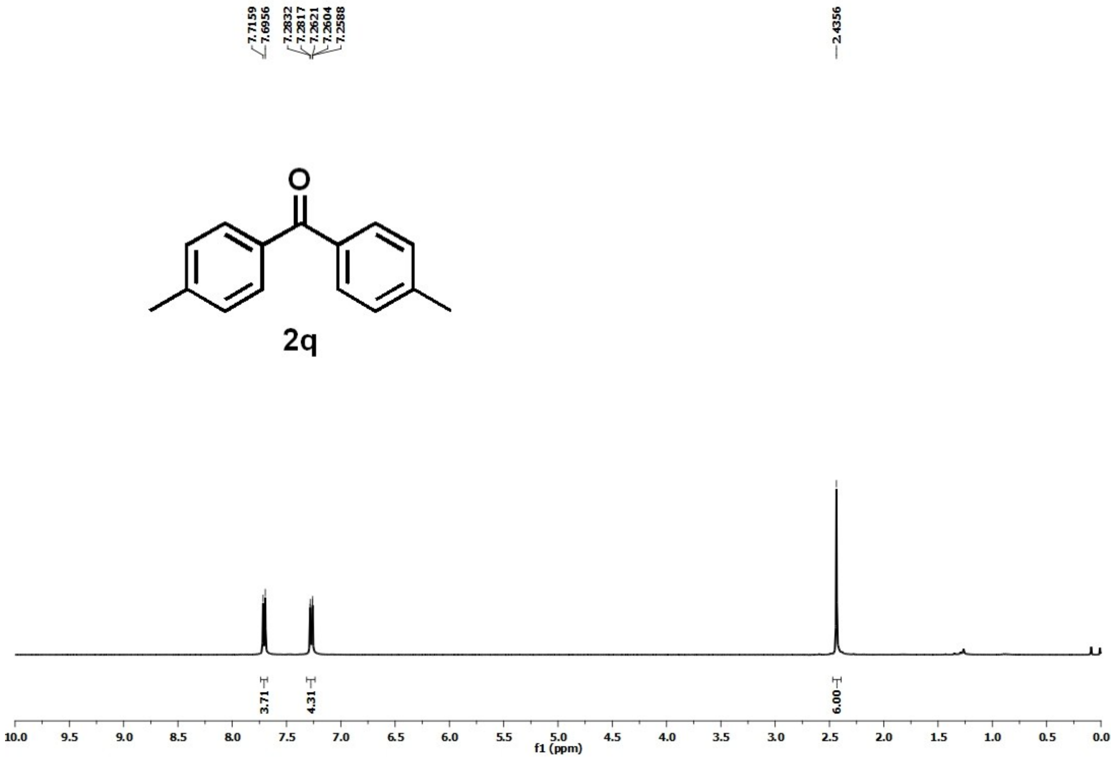
^1H NMR of product 2p in $CDCl_3$ (400 MHz)



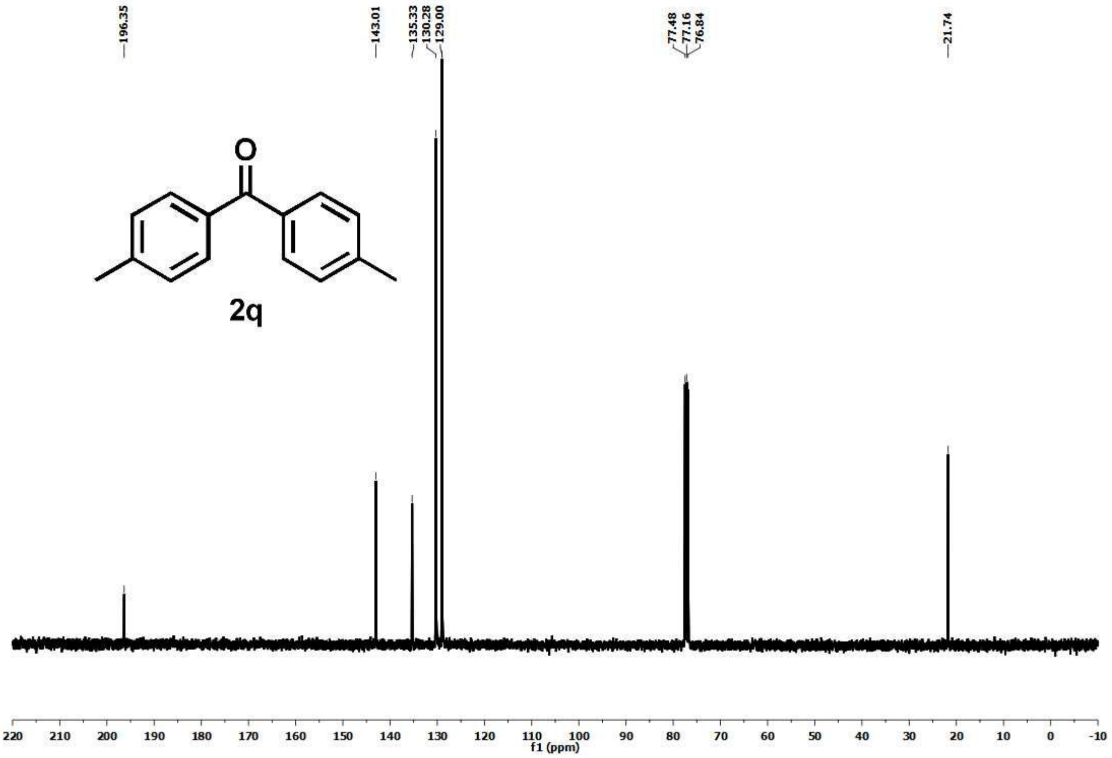
^{13}C NMR of product 2p in $CDCl_3$ (100 MHz)



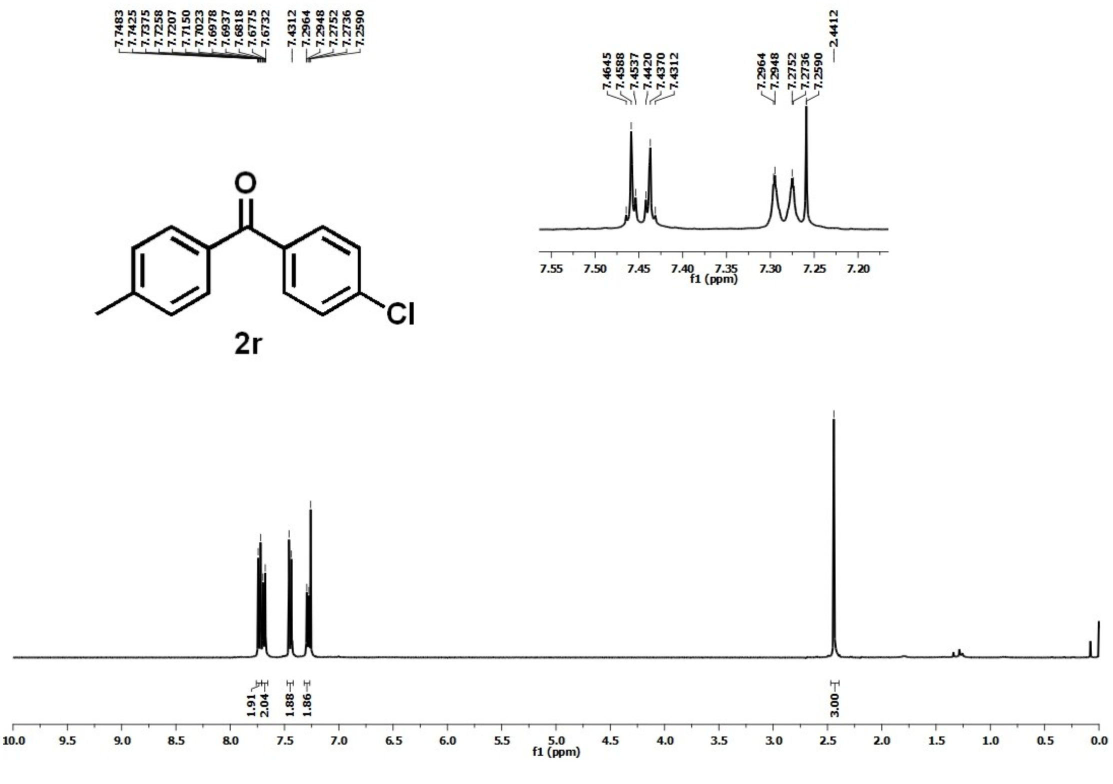
^{1}H NMR of product 2q in $CDCl_3$ (400 MHz)



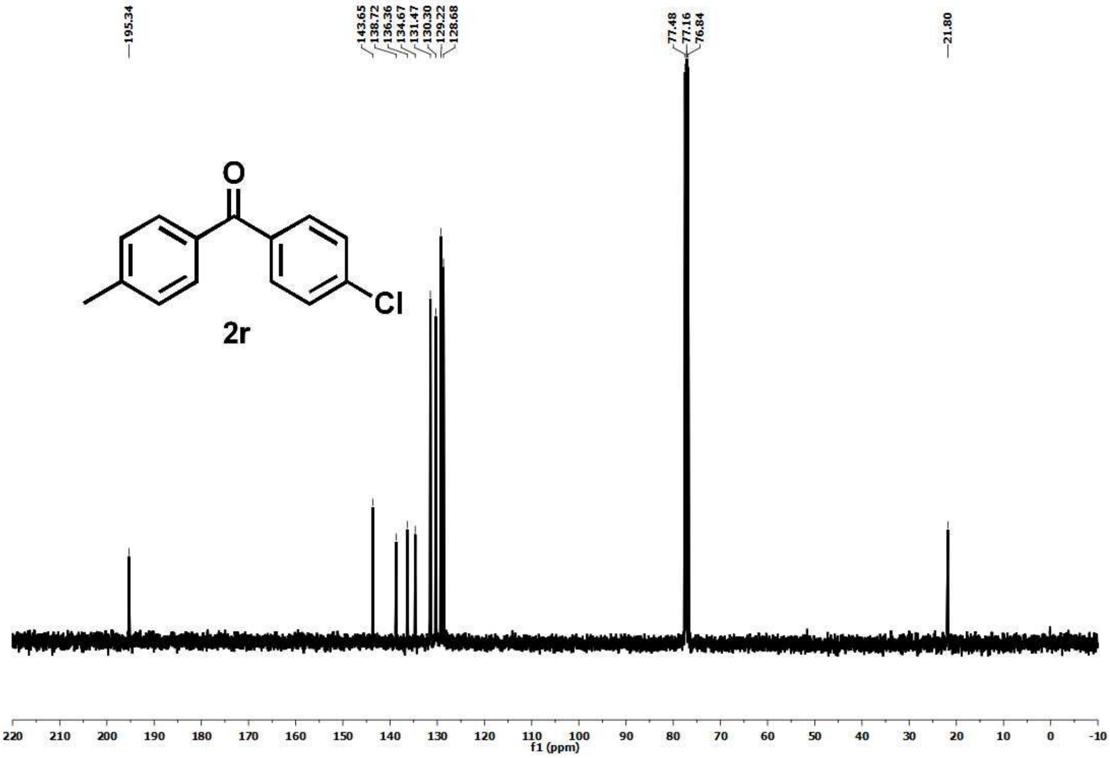
^{13}C NMR of product 2q in $CDCl_3$ (100 MHz)



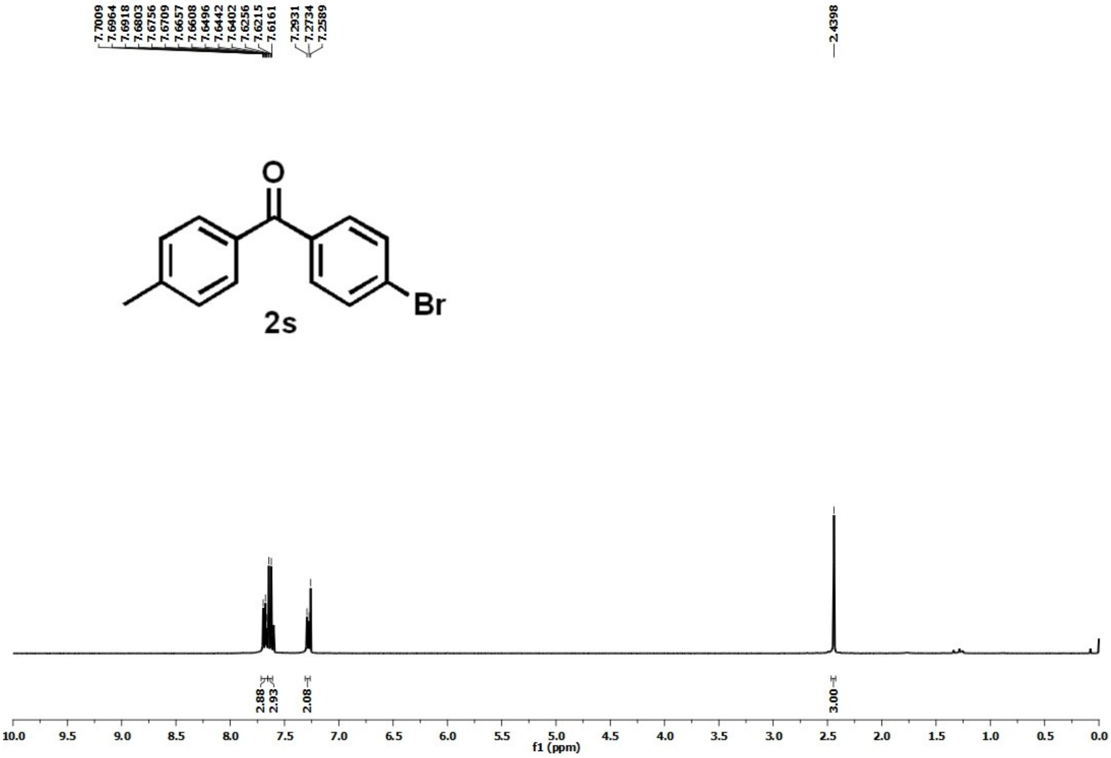
^1H NMR of product 2r in $CDCl_3$ (400 MHz)



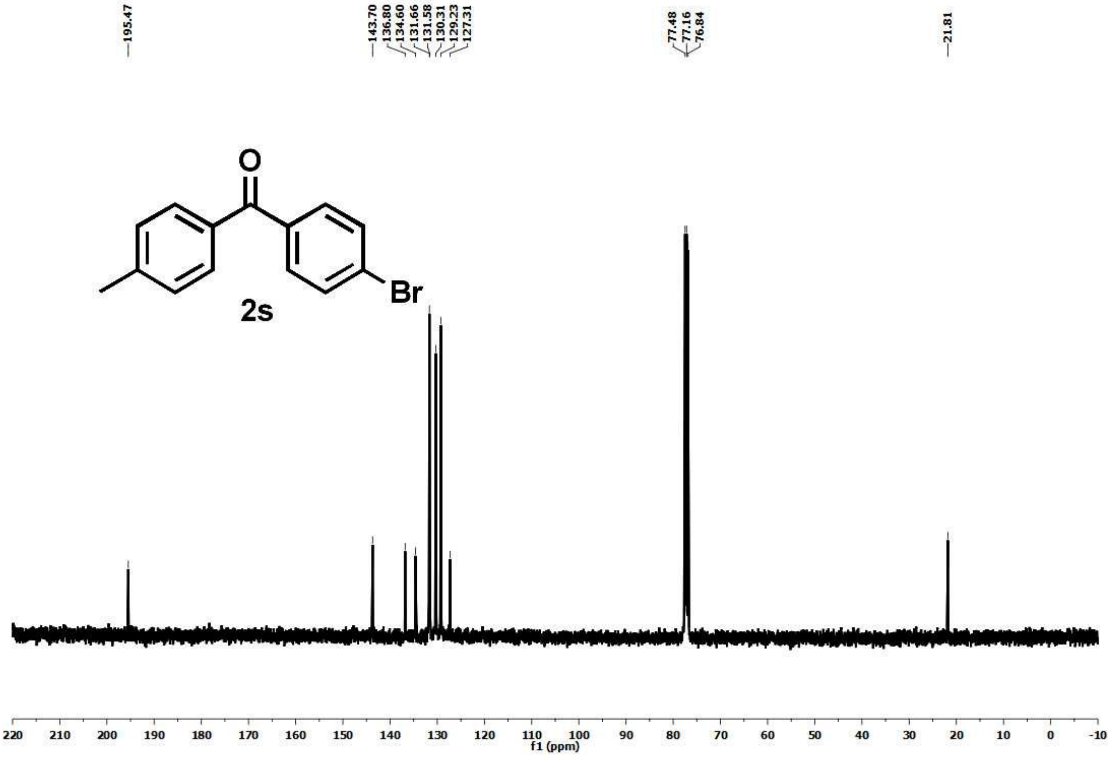
^{13}C NMR of product 2r in $CDCl_3$ (100 MHz)



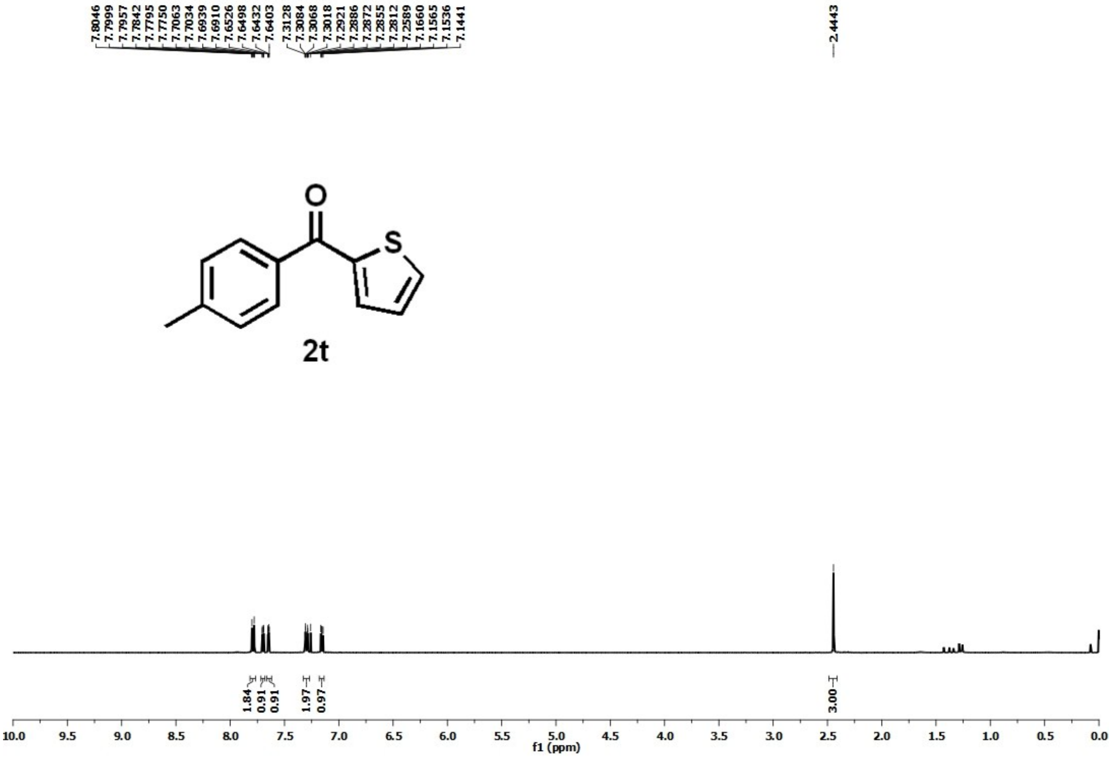
^{1}H NMR of product 2s in $CDCl_3$ (400 MHz)



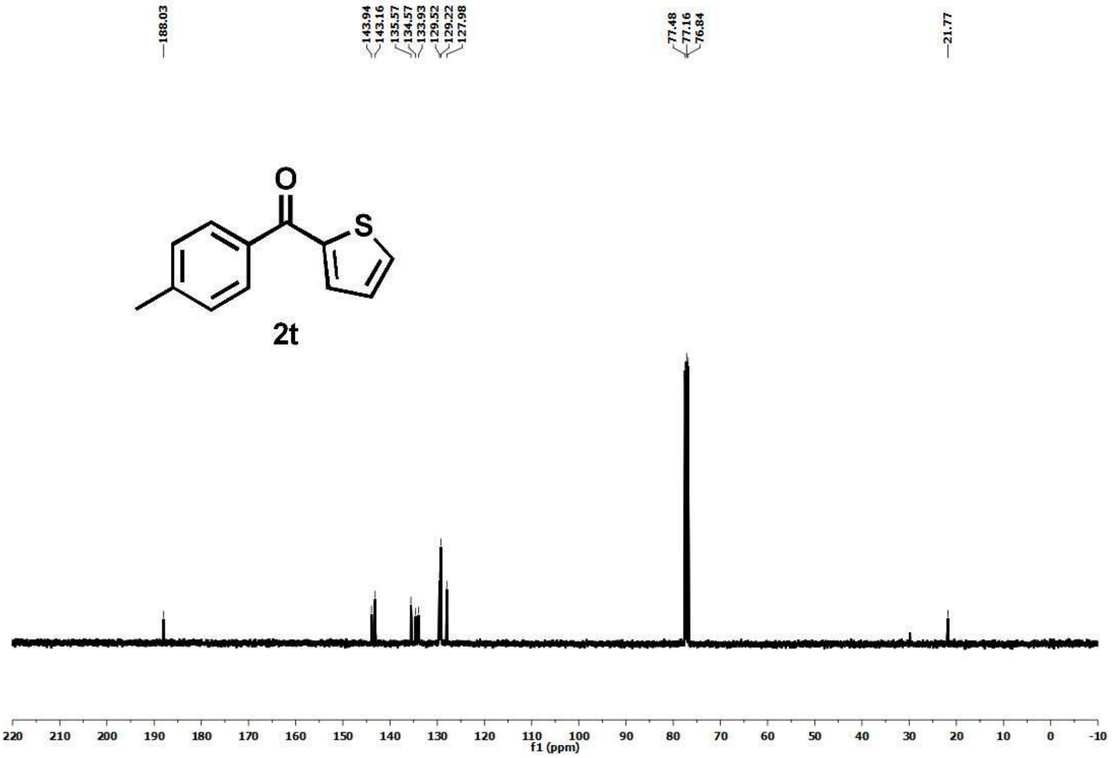
^{13}C NMR of product 2s in $CDCl_3$ (100 MHz)



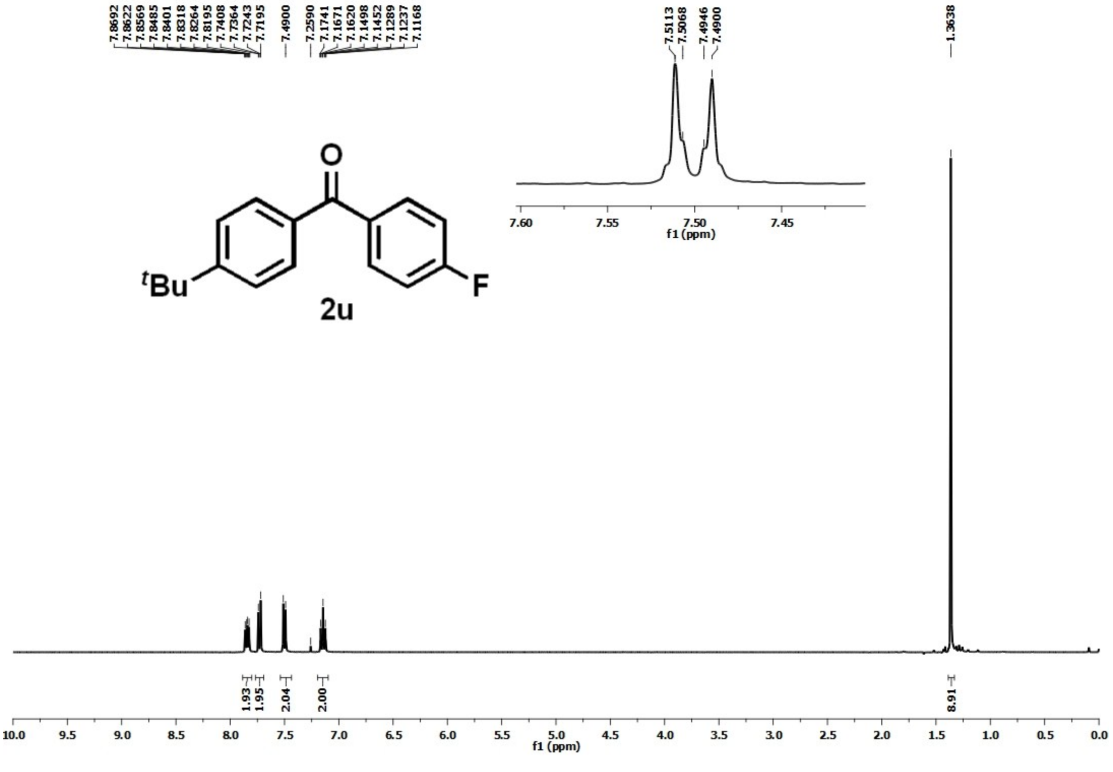
^{1}H NMR of product 2t in $CDCl_3$ (400 MHz)



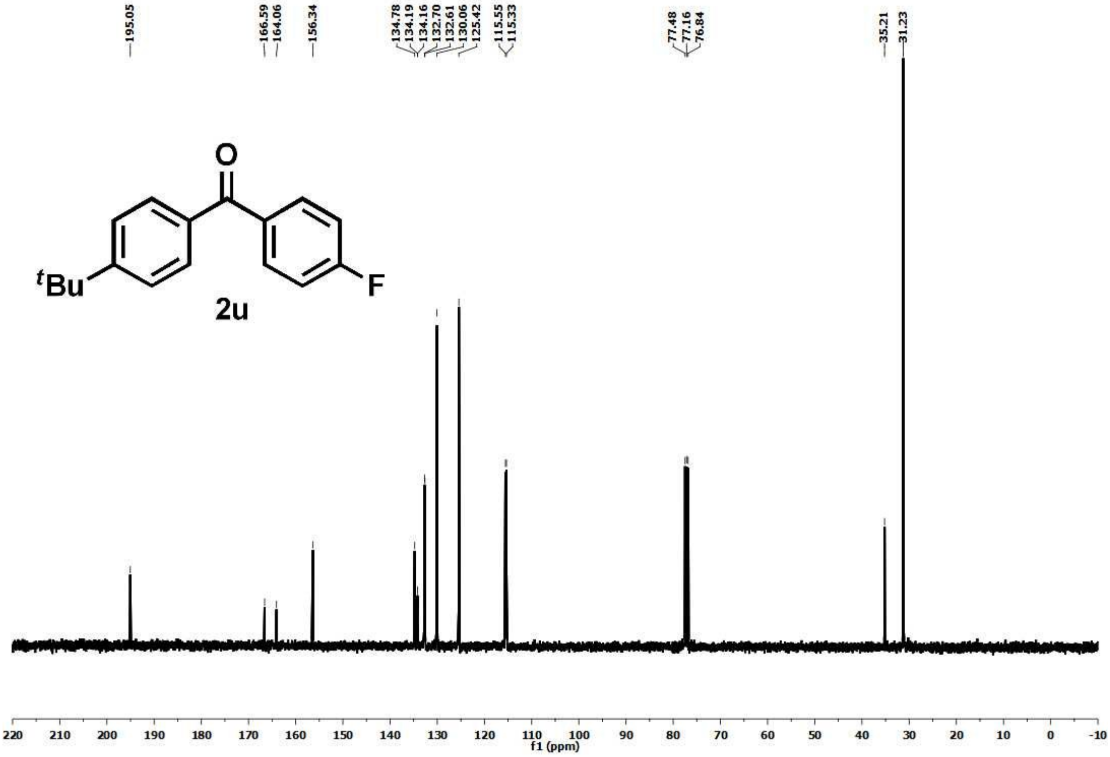
^{13}C NMR of product 2t in CDCl$_3$ (100 MHz)



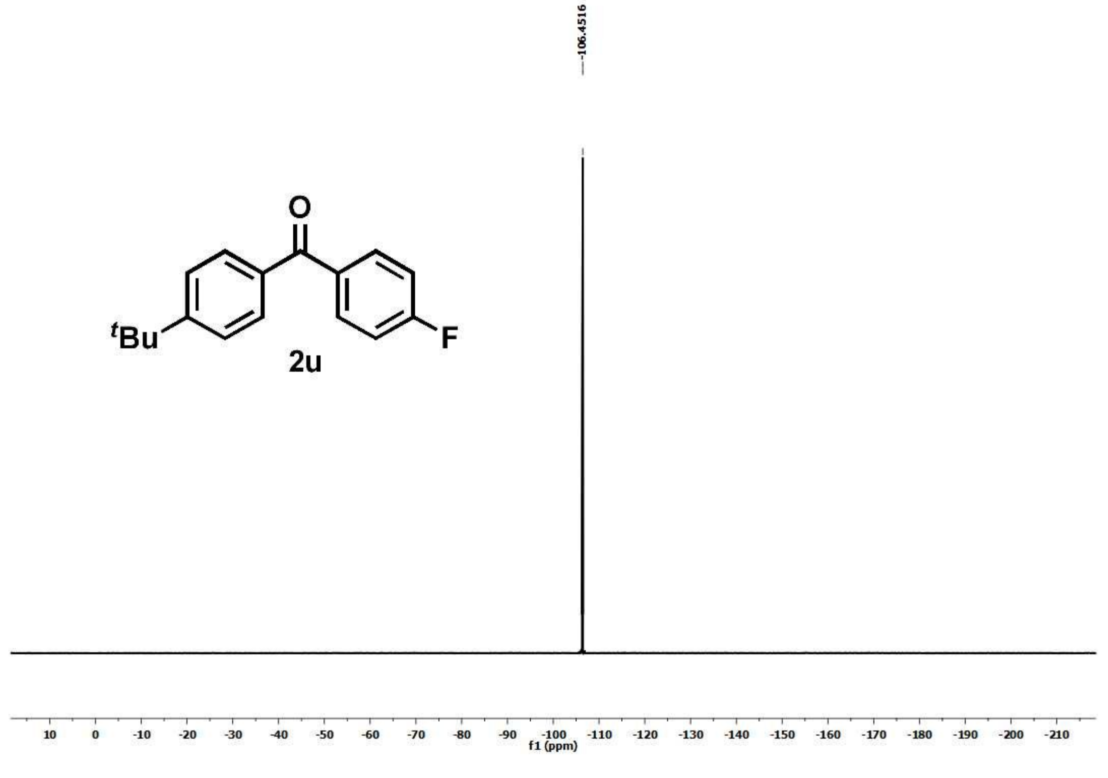
^{1}H NMR of product 2u in CDCl$_3$ (400 MHz)



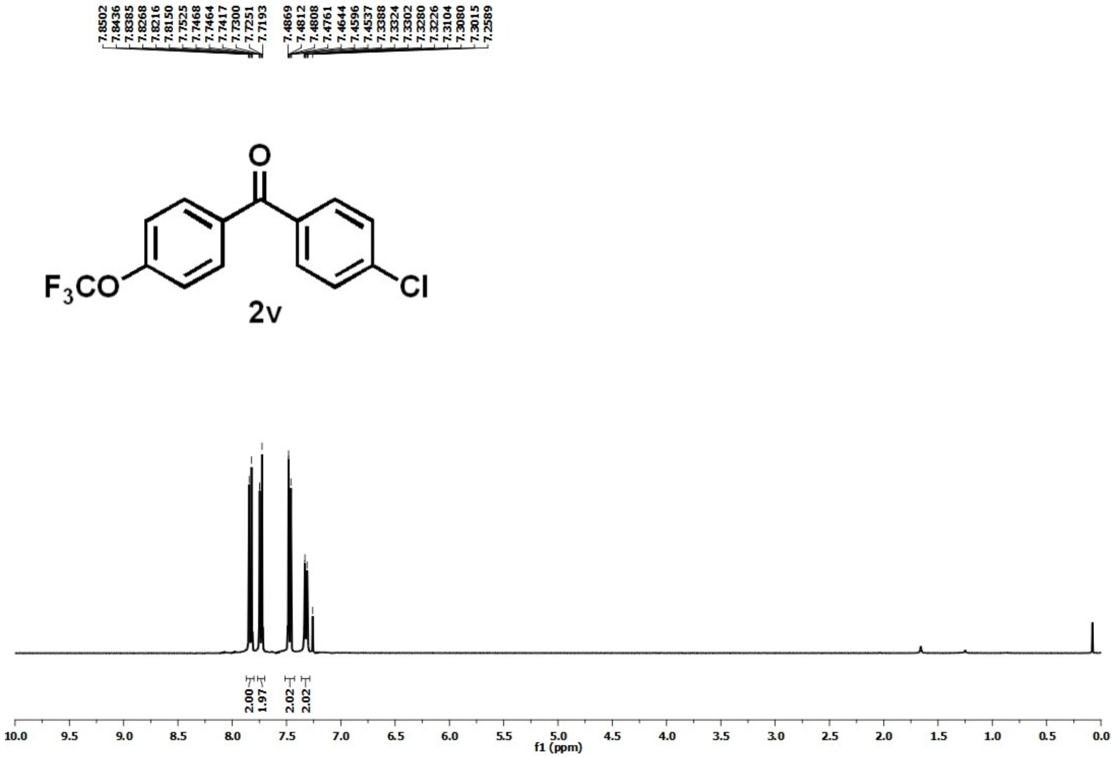
^{13}C NMR of product 2u in CDCl$_3$ (100 MHz)



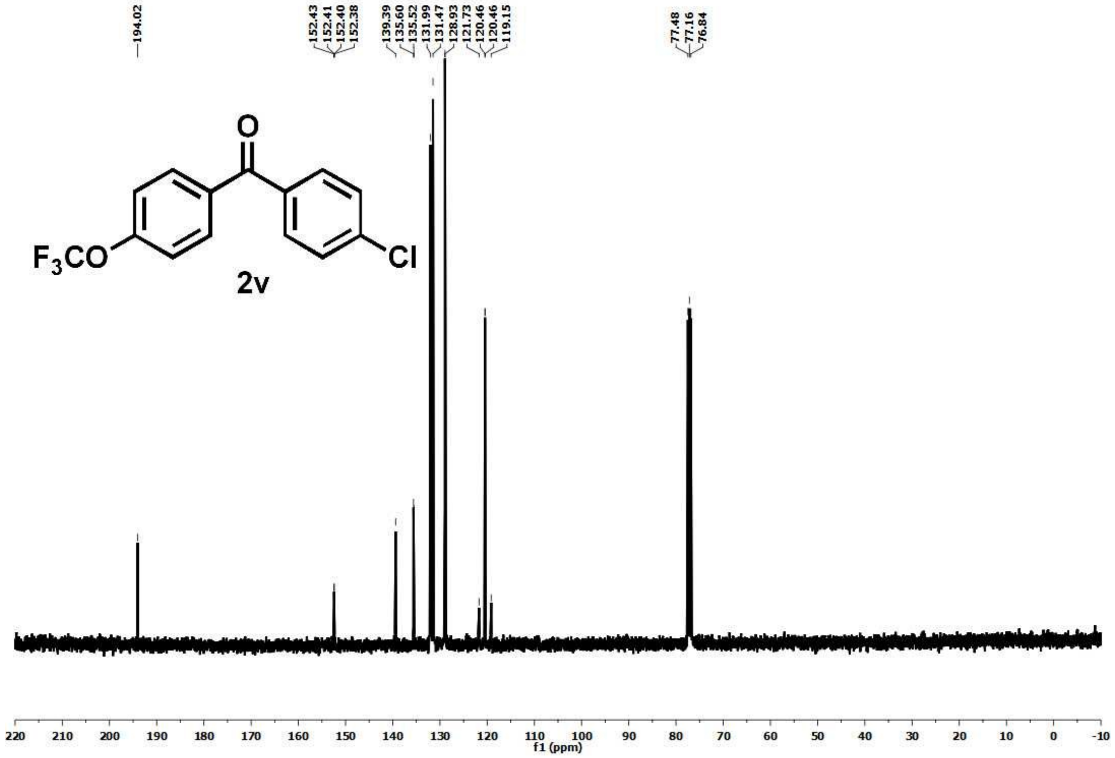
^{19}F NMR of product 2u in CDCl$_3$ (376 MHz)



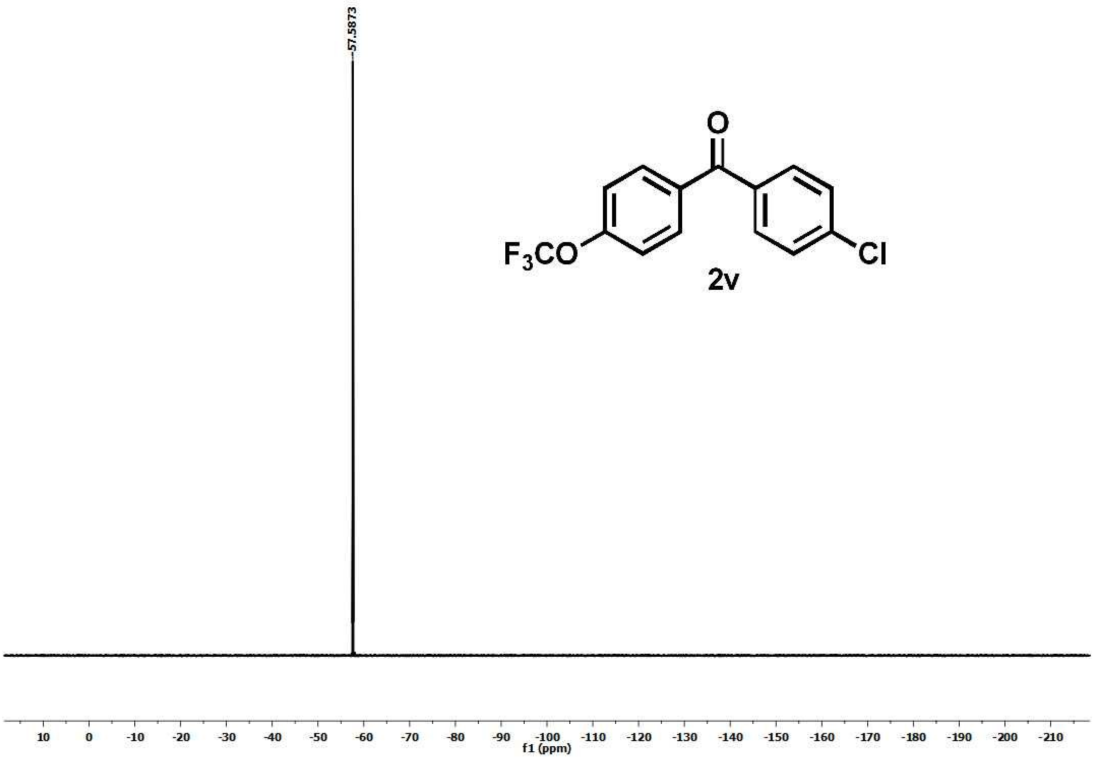
^1H NMR of product 2v in $CDCl_3$ (400 MHz)



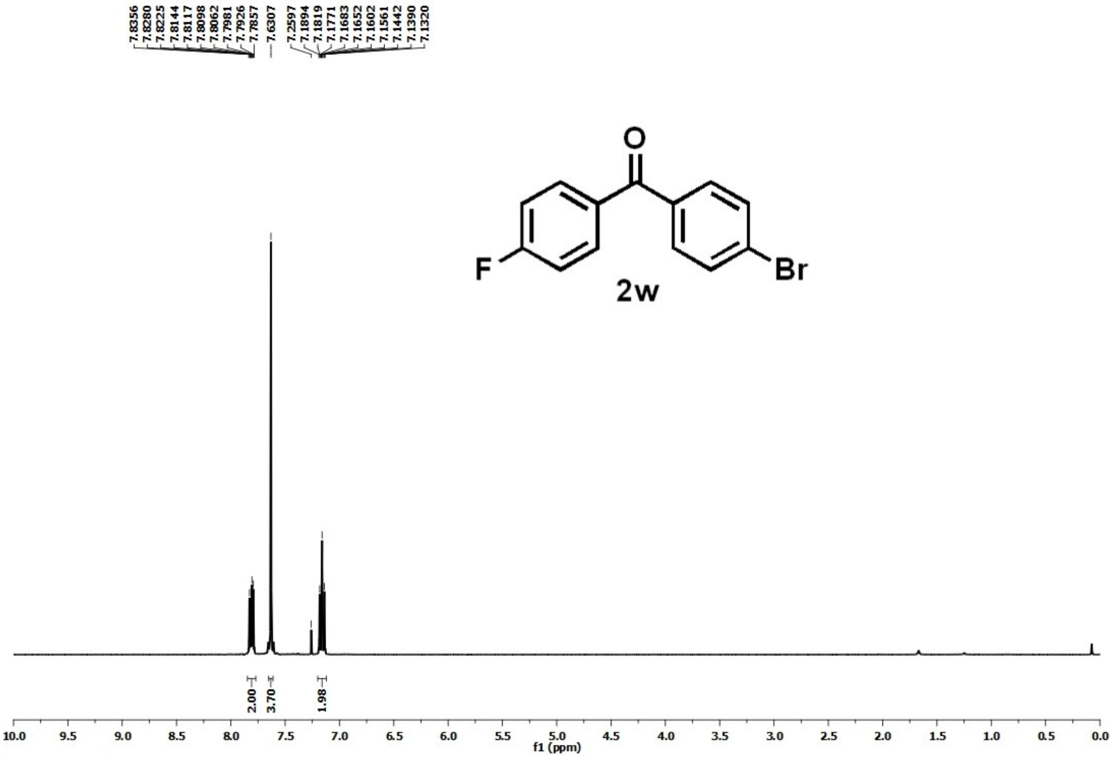
^{13}C NMR of product 2v in $CDCl_3$ (100 MHz)



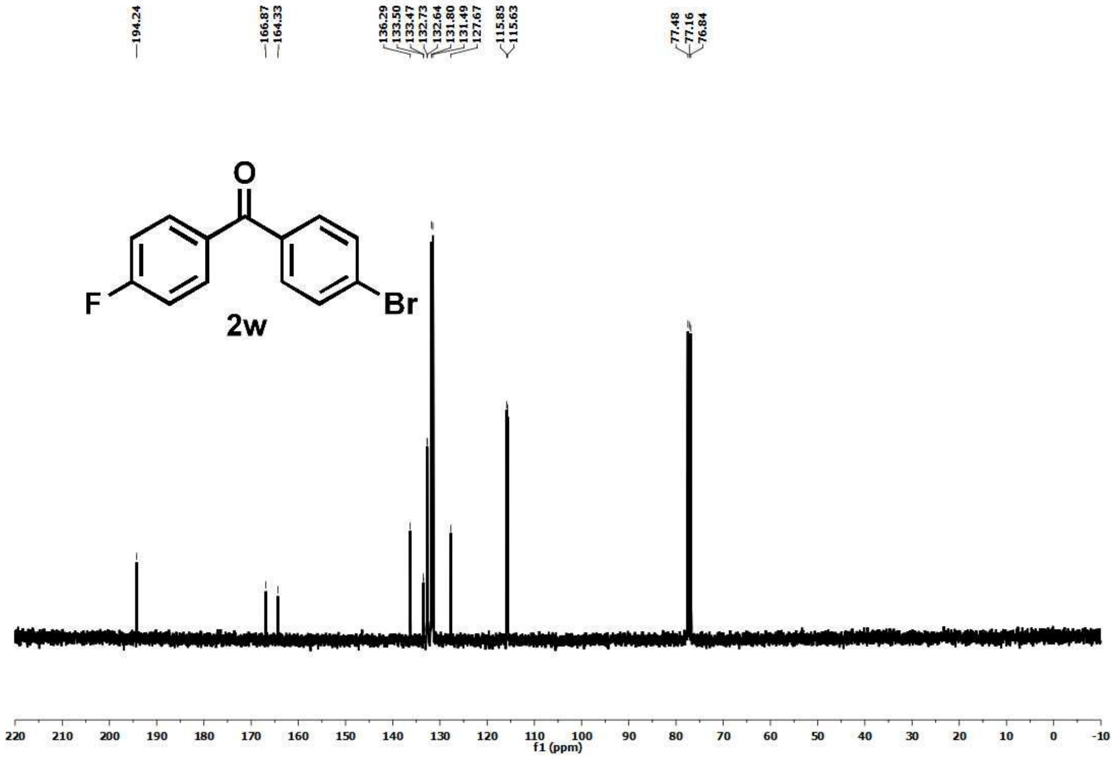
^{19}F NMR of product 2v in $CDCl_3$ (376 MHz)



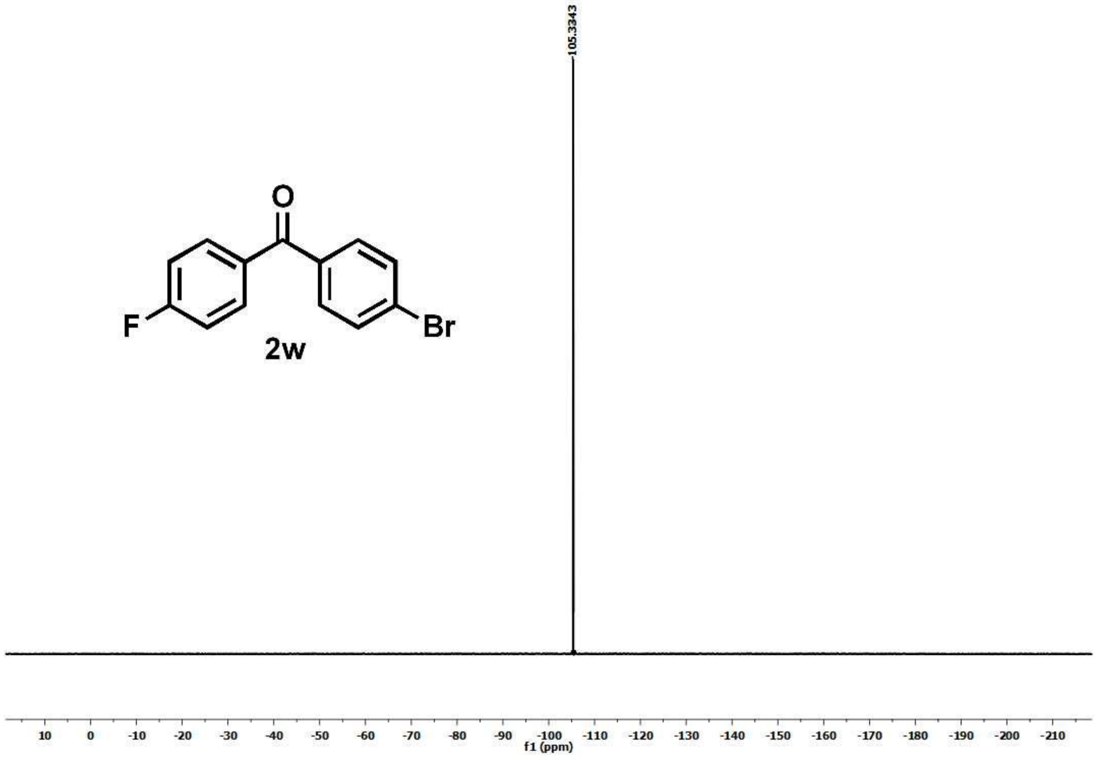
^{1}H NMR of product 2w in $CDCl_3$ (400 MHz)



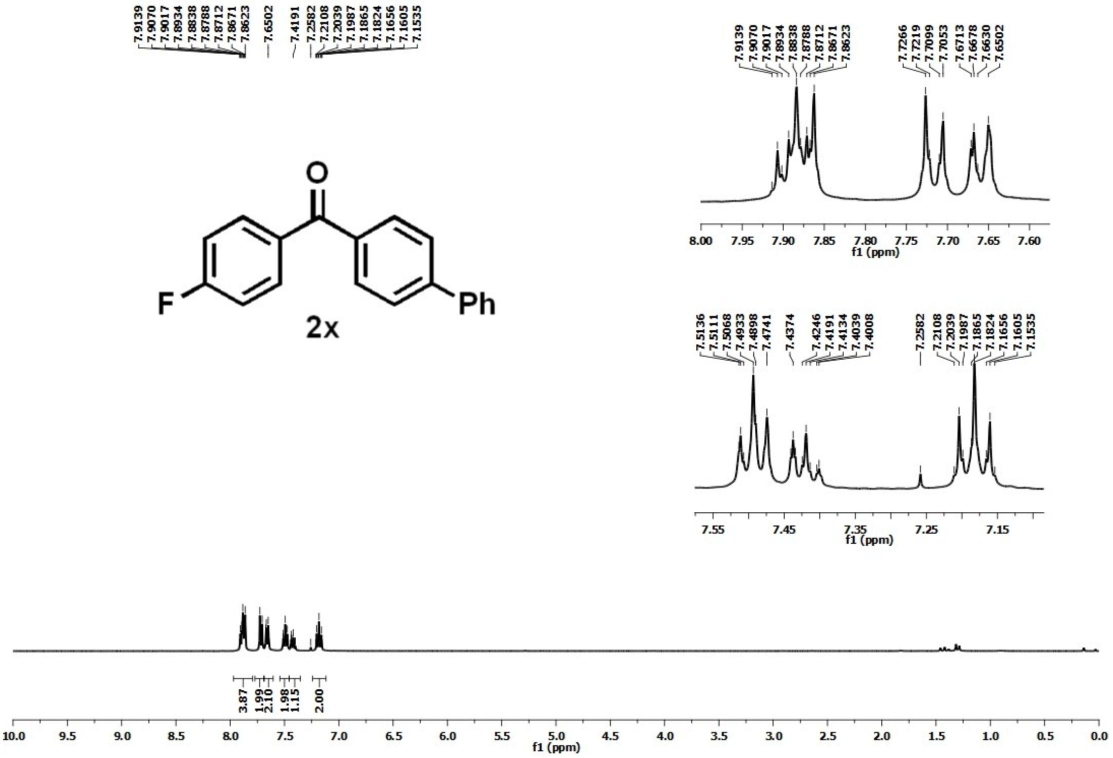
^{13}C NMR of product 2w in CDCl$_3$ (100 MHz)



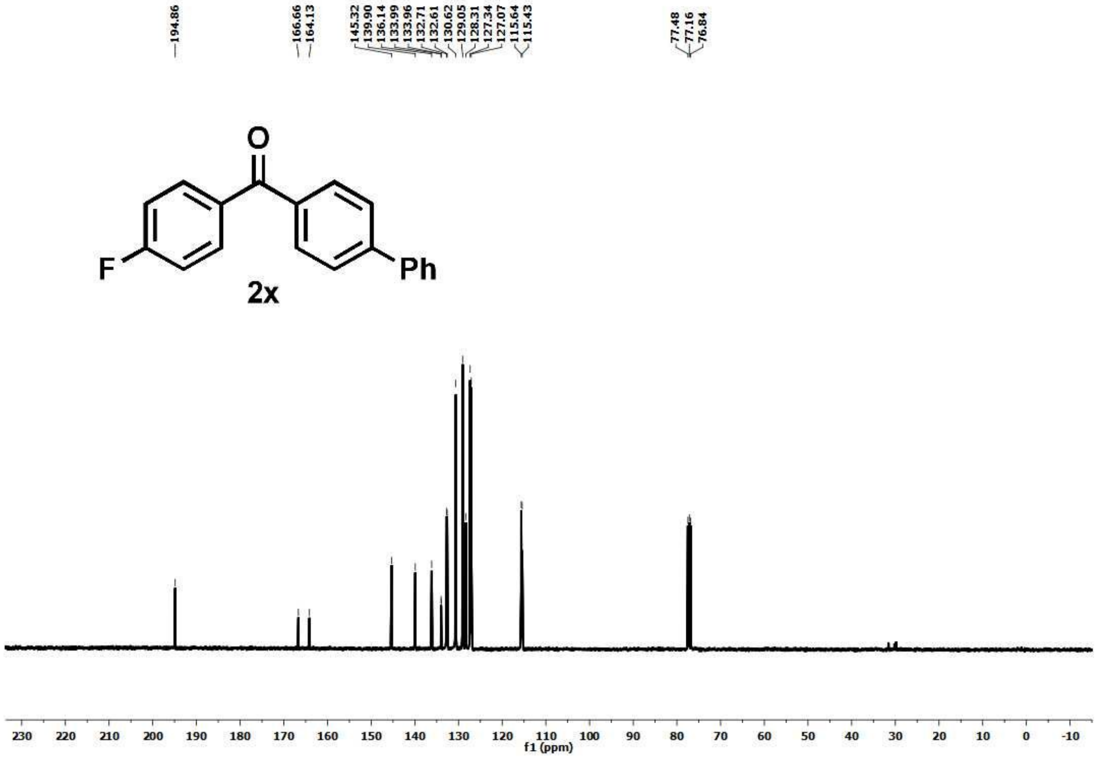
^{19}F NMR of product 2w in CDCl$_3$ (376 MHz)



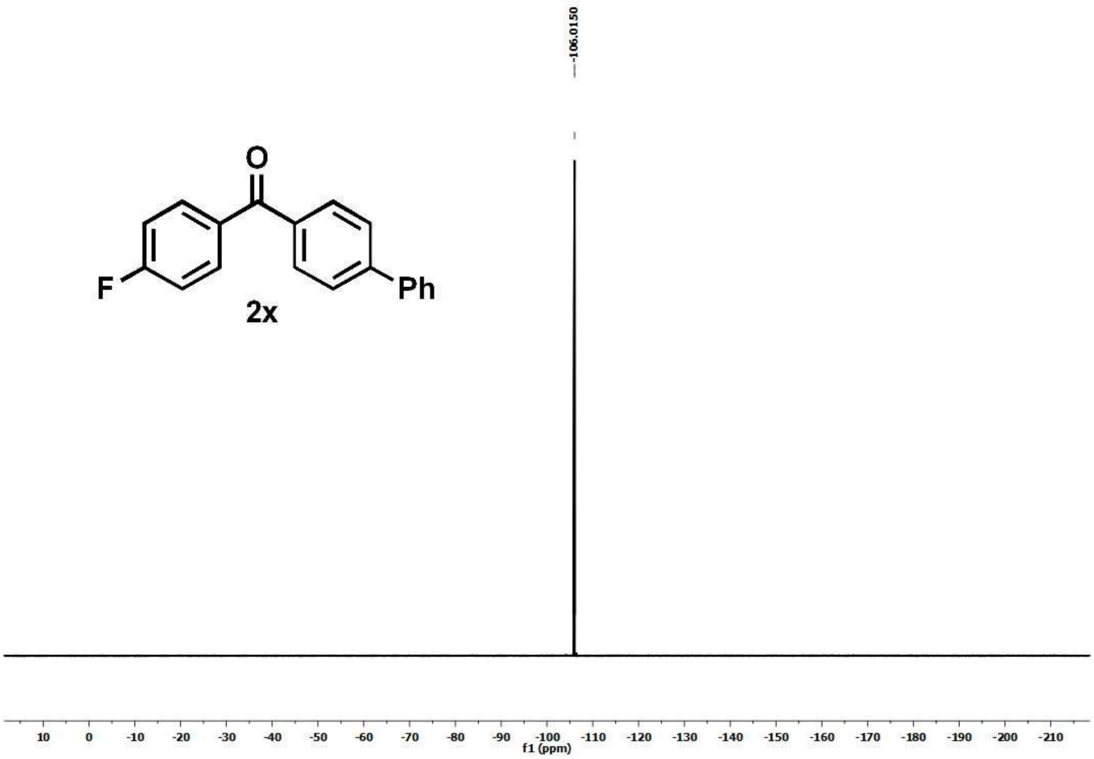
^{1}H NMR of product 2x in CDCl$_3$ (400 MHz)



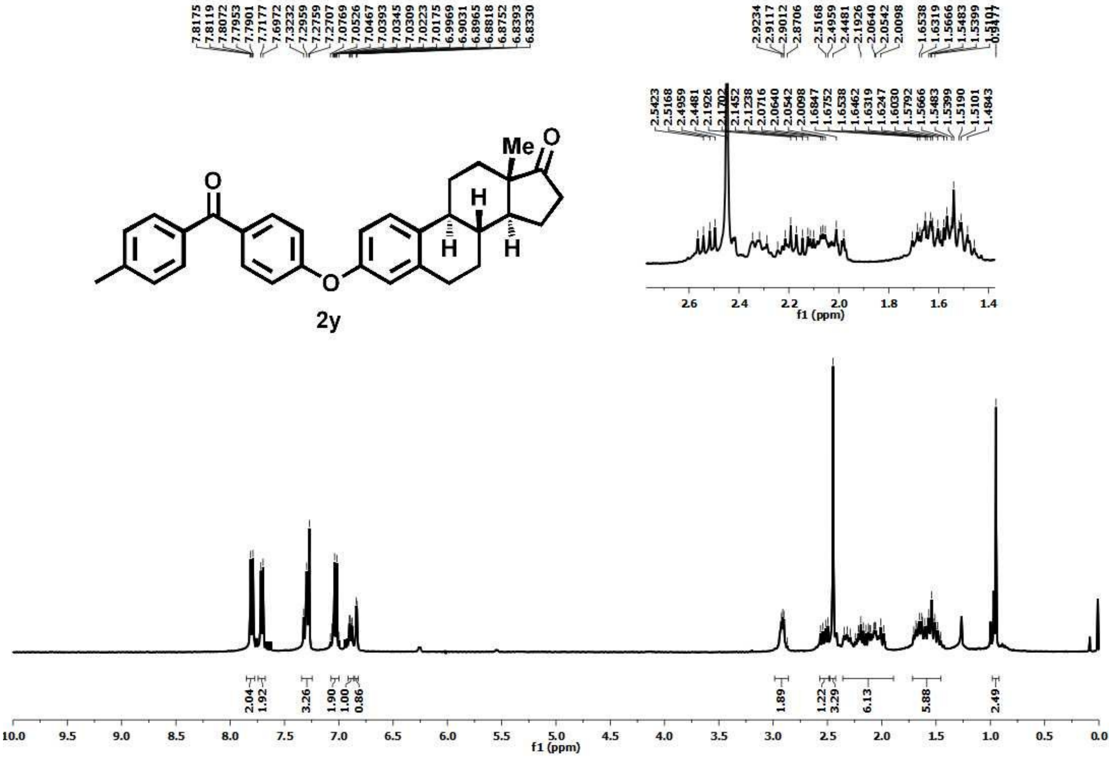
^{13}C NMR of product 2x in CDCl$_3$ (100 MHz)



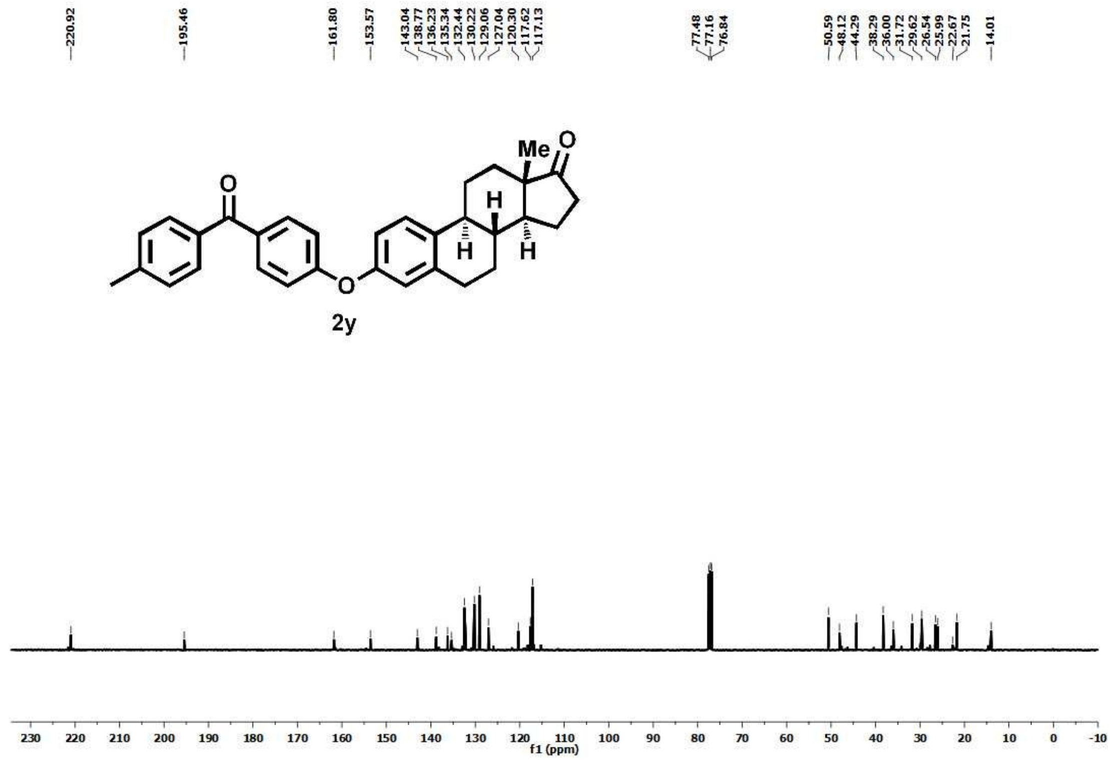
^{19}F NMR of product 2x in $CDCl_3$ (376 MHz)



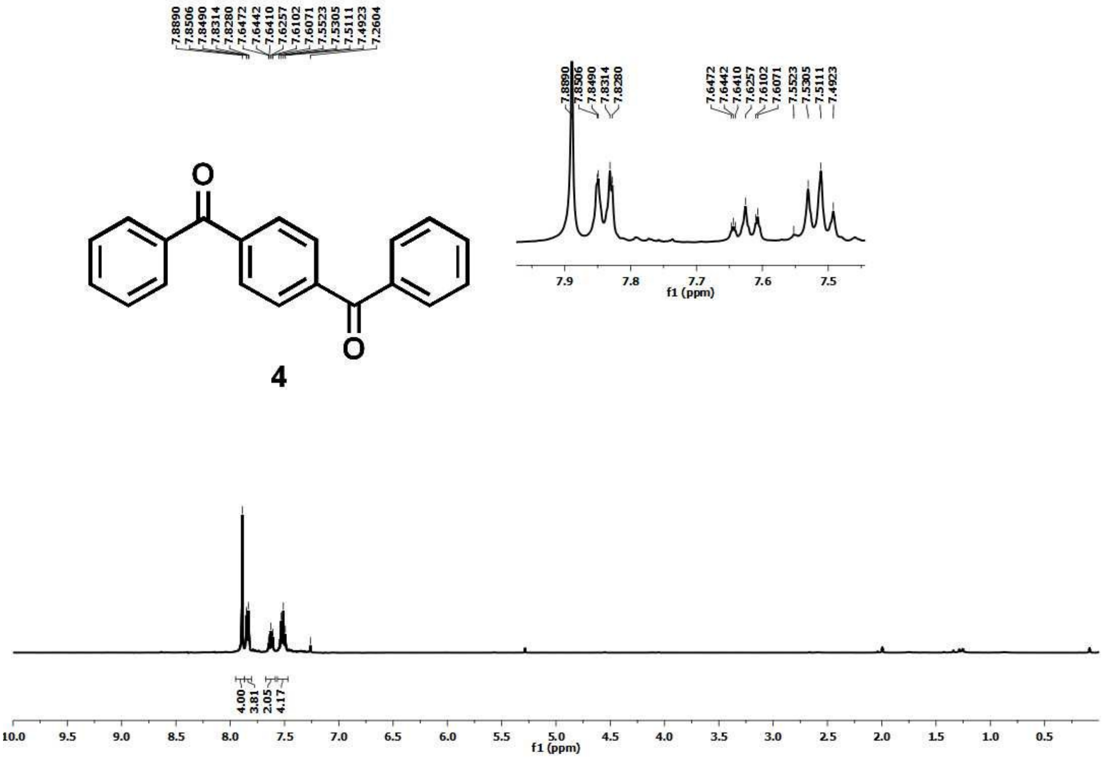
^1H NMR of product 2y in $CDCl_3$ (400 MHz)



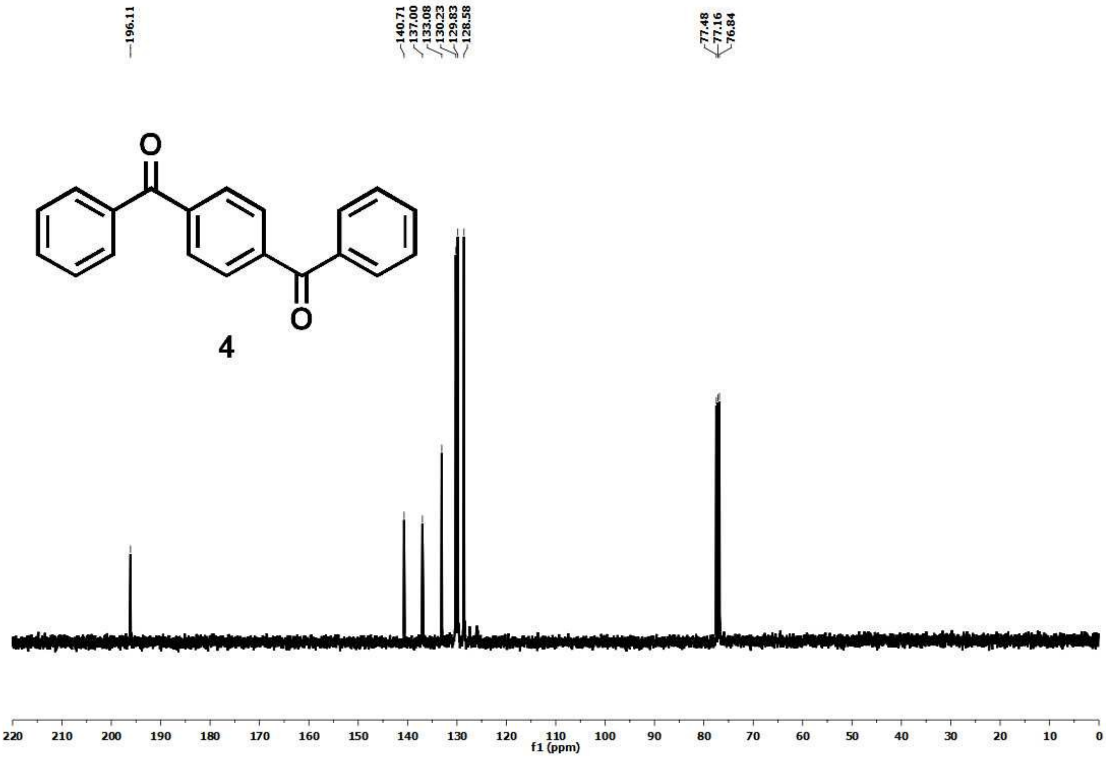
^{13}C NMR of product 2y in $CDCl_3$ (100 MHz)



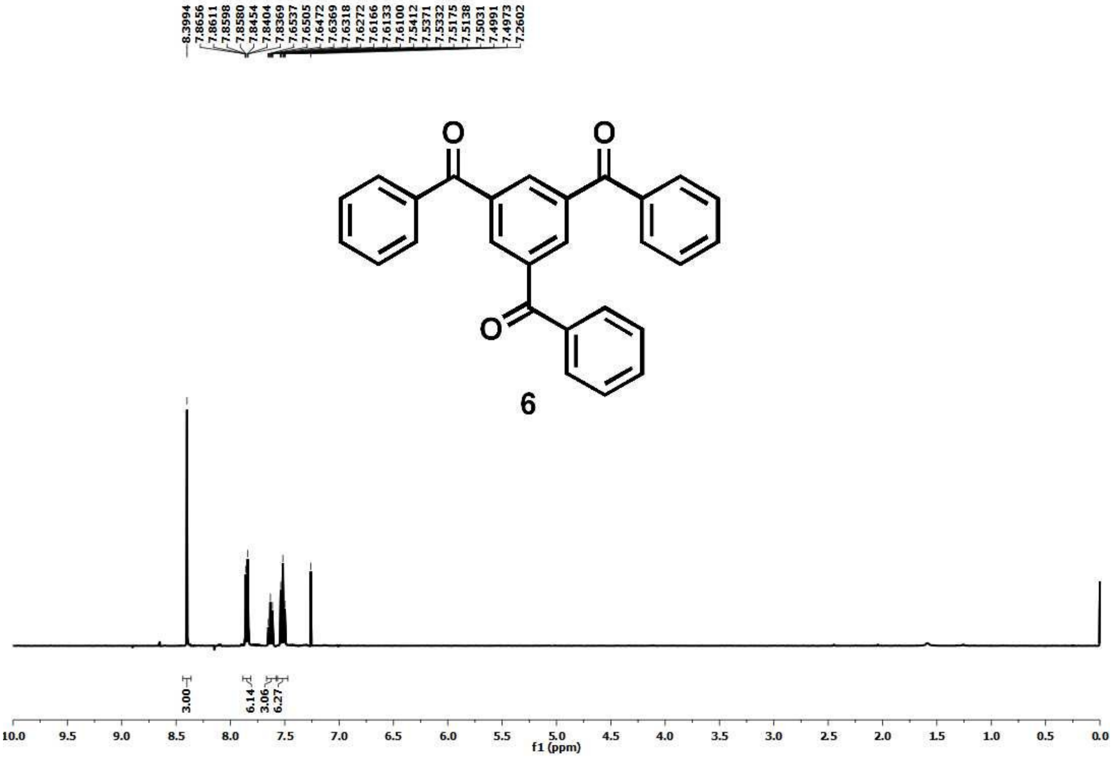
^1H NMR of product 4 in $CDCl_3$ (400 MHz)



^{13}C NMR of product 4 in CDCl$_3$ (100 MHz)



^{1}H NMR of product 6 in CDCl$_3$ (400 MHz)



^{13}C NMR of product 6 in CDCl$_3$ (100 MHz)