Supporting Information

Copper-Catalyzed Carbonylative Suzuki Coupling of Aryl iodides with Arylboronic Acids under Ambient Pressure of Carbon Monoxide

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1. General Information

Reagent Information. All the aryl halides and the arylboronic acids were purchased from Alfa Aesar and Accela ChemBio Co., Ltd. and were used as received. PEG-400 (bought from Acros) was pre-dried (toluene azeotrope) and pre-deoxygenated. The following nanocopper, bases, and *t*BuCOOH were used: nanocopper (99.9%, aladdin; 10-30 nm), K_3PO_4 (99%, Alfa Aesar), KF (99%, Accela), and *t*BuCOOH (99%, Alfa Aesar).

Analytical methods. ^{1}H and ^{13}C NMR spectra of solutions in $CDCl_3$ were recorded on a Bruker Avance 400 instrument. Chemical shifts were expressed in parts per million (ppm) downfield from tetramethylsilane and refer to the solvent signals ($CDCl_3$: H 7.24 and C 77.0 ppm) . The signals of water were observed at about 1.58 ppm in $CDCl_3$, respectively. Abbreviations for signal couplings are: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet; dd, doublet of doublets; dt, triplet of doublets; td, doublet of triplets; tt, triplet of triplets; ddd, doublet of doublet of doublets; tdd, doublet of doublet of triplets. Coupling constants, *J,* were reported in hertz unit (Hz). Infrared spectra of neat substances were recorded on a Thermo Nicolet Corporation GC-FTIR NEXUS670 spectrometer. HRMS was performed on a Bruker's *solarix 94* (ESI-*FTICR-MS*) mass spectrometer.

2. General Procedures for Copper-Catalyzed Carbonylative Suzuki Reactions

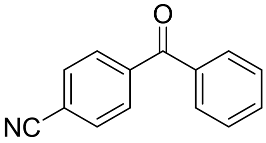
General Procedure A: A 25 mL Schlenk flask was charged with arylboronic acid (0.75mmol), nanocopper (0.1 mmol, 6.4 mg), K_3PO_4 (1.0 mmol, 218.8 mg), *t*BuCOOH (0.25 mmol, 25.8 mg), and PEG-400 (2.0 mL) before standard cycles of evacuation and back-filling with dry and pure carbon monoxide. Corresponding aryl iodide (0.5 mmol) was added successively. The mixture was stirred at 80 °C for the indicated time. At the end of the reaction, the reaction mixture was poured into a saturated aqueous NaCl solution (15 mL) and extracted with ethyl acetate (3 × 15 mL). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. The crude product was purified by column chromatography on silica gel (petroleum ether: diethyl ether = 25 : 1).

In the recycling experiment, the reaction mixture was extracted with ethyl acetate (2 × 15 mL), and the residue was subjected to a second run by charging it with the same substrates as mentioned above without further addition of $Pd(OAc)_2$ and PEG 400 under 1 atm of carbon monoxide. In the third, sixth, and eighth runs, another 0.5 mL of PEG-400 was added to the reaction mixture.

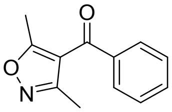
General Procedure B: A 25 mL Schlenk flask was charged with arylboronic acid (0.75mmol), nanocopper (0.1 mmol, 6.4 mg), K_3PO_4 (0.5 mmol, 109.4 mg), KF (0.25 mmol, 14.7 mg), *t*BuCOOH (0.25 mmol, 25.8 mg), and PEG-400 (2.0 mL) before standard cycles of evacuation and back-filling with dry and pure carbon monoxide. Corresponding aryl iodide (0.5 mmol) was added successively. The mixture was stirred at 100 °C for the indicated time. At the end of the reaction, the reaction mixture was poured into a saturated aqueous NaCl solution (15 mL) and extracted with ethyl acetate (3 × 15 mL). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. The crude product was purified by column chromatography on silica gel (petroleum ether: diethyl ether = 25 : 1).

3. Analytical Data of Products

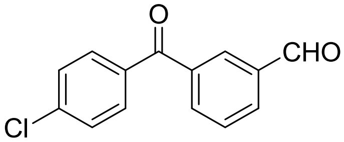
The products, **3aa**-**3fa**, **3ha**-**3na**, **3pa**-**3qa**, **3ab**-**3ae**, **3ii**-**3ij**, **3ie**, **3ki**-**3kj**, **3ke**, and **3kh** were identified by comparison of their spectral data with those of our previous reports.[S1-S2]



4-Benzoylbenzonitrile (3ga): Following *general procedure B*, **3ga** was isolated as a white solid. Known compound; the NMR spectroscopic data agree with those described in ref..[S3] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J*=8.0 Hz, 2 H), 7.77 (d, *J*=8.0 Hz, 2 H), 7.76-7.75 (m, 2 H), 7.62 (tt, *J*=8.0, 1.2 Hz, 1 H), 7.51-7.47 ppm (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.0, 141.2, 136.3, 133.3, 132.1, 130.2, 130.0, 128.6, 117.9, 115.6, 116.6 ppm.

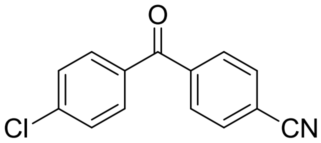


(3,5-Dimethylisoxazol-4-yl)(phenyl)methanone (3oa): Following *general procedure B*, **3oa** was isolated as a colorless liquid. Known compound; the NMR spectroscopic data agree with those described in ref..[S4] ^{1}H NMR (400 MHz, $CDCl_3$): δ7.70–7.68 (m, 2 H), 7.59 (tt, *J*=8.0, 1.2 Hz, 1H), 7.50–7.46 (m, 2 H), 2.31 (s, 3 H), 2.28 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.4, 172.3, 159.6, 138.4, 133.2, 128.9, 128.7, 116.4, 13.3, 11.3 ppm.

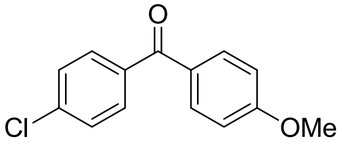


3-(4’-Chlorobenzoyl)benzaldehyde (3cf) : Following *general procedure B*, **3cf** was isolated as a white solid. Known compound; the NMR spectroscopic data agree with those described in ref..[S5] ^{1}H NMR (400 MHz, $CDCl_3$): δδ 10.07 (s, 1 H), 8.22 (t, *J*=4.0 Hz, 1 H), 8.10 (dt, *J*=8.0, 4.0 Hz, 1 H), 8.03 (dt, *J*=8.0, 4.0 Hz, 1 H), 7.74 (d, *J*=8.0 Hz, 2 H), 7.67 (t, *J*=8.0 Hz, 1 H), 7.47 ppm (d, *J*=8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.2, 191.2, 139.6, 138.1, 136.4, 135.2, 135.1, 132.9, 131.4, 131.0, 129.4, 128.9 ppm;

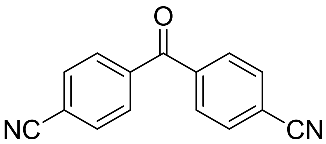
mp 93.5-94.3 °C.



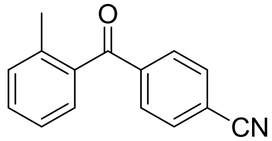
4-(4-Chlorobenzoyl)benzonitrile (3cg): Following *general procedure B*, **3cg** was isolated as a white solid. Known compound; the NMR spectroscopic data agree with those described in ref..[S3] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J*=8.0 Hz, 2 H), 7.78 (d, *J*=8.0 Hz, 2 H), 7.72 (d, *J*=8.0 Hz, 2 H), 7.47 ppm (d, *J*=8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.8, 140.8, 139.9, 134.6, 132.3, 131.4, 130.1, 129.0, 117.9, 115.9 ppm.



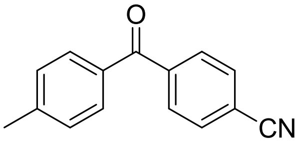
(4-Chlorophenyl)(4-methoxyphenyl)methanone (3ch): Following *general procedure B*, **3ch** was isolated as a white solid. Known compound; the NMR spectroscopic data agree with those described in ref..[S6] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J*=8.0 Hz, 2 H), 7.69 (d, *J*=8.0 Hz, 2 H), 7.43 (d, *J*=8.0 Hz, 2 H), 6.95 (d, *J*=8.0 Hz, 2 H), 3.87 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.3, 163.4, 138.3, 136.6, 132.4, 131.1, 129.8, 128.5, 113.7, 55.5 ppm; mp 123.3-124.0 °C.



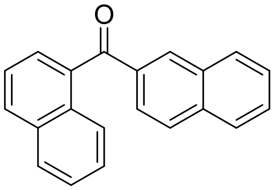
4,4'-Carbonyldibenzonitrile (3gg): Following *general procedure A*, **3gg** was isolated as a white solid. Known compound; the NMR spectroscopic data agree with those described in ref..[S7] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J*=8.0 Hz, 4 H), 7.81 ppm (d, *J*=8.0 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.4, 139.7, 132.5, 130.2, 117.7, 116.6 ppm.



4-(2-Methylbenzoyl)benzonitrile (3ig): Following *general procedure B*, **3ig** was isolated as a colorless liquid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.86 (d, *J*=8.0 Hz, 2 H), 7.74 (d, *J*=8.0 Hz, 2 H), 7.44–7.40 (m, 1 H), 7.31–7.23 (m, 3 H), 2.34 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 196.8, 141.1, 137.5, 136.9, 132.3, 131.4, 131.2, 130.3, 128.9, 125.4, 117.9, 116.2, 20.1 ppm.

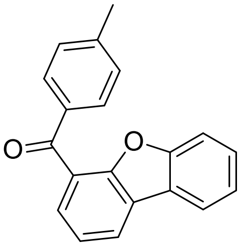


4-(4-Methylbenzoyl)benzonitrile (3kg): Following *general procedure B*, **3kg** was isolated as a white solid. Known compound; the NMR spectroscopic data agree with those described in ref..[S3] ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.83 (d, *J*=8.0 Hz, 2 H), 7.76 (d, *J*=8.0 Hz, 2 H), 7.67 (d, *J*=8.0 Hz 2 H), 7.29 (d, *J*=8.0 Hz, 2 H), 2.43 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 196.8, 144.4, 141.6, 133.6, 132.1, 130.3, 130.1, 129.3, 118.0, 115.3, 21.7 ppm.



Naphthalen-1-yl(naphthalen-2-yl)methanone (3nk): Following *general procedure B*, **3nk** was isolated as a white solid. Known compound; the NMR spectroscopic data agree with those described in ref..[S8] ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.24 (s, 1 H), 8.10 (d, *J*=8.0 Hz, 1 H), 8.07 (dd, *J*=8.0, 2.0 Hz, 1 H), 8.03 (d, *J*=8.0 Hz, 1 H), 7.95-7.92 (m, 2 H), 7.89 (d, *J*=8.0 Hz, 1 H), 7.82 (d, *J*=8.0 Hz, 1 H), 7.64 (dd, *J*=8.0, 1.2 Hz, 1 H), 7.61-7.57 (m, 1 H), 7.55 (d, *J*=8.0 Hz, 1 H), 7.53 (d, *J*=8.0 Hz, 1 H), 7.51-7.46 ppm (m, 2 H); ^{13}C

NMR (100 MHz, $CDCl_3$): δ 198.0, 136.6, 135.7, 135.6, 133.7, 132.9, 132.3, 131.2, 131.0, 129.7, 128.7, 128.42, 128.4, 127.8, 127.7, 127.3, 126.8, 126.5, 125.7, 125.4, 124.4 ppm; mp 132.7-133.2 °C.



Dibenzofuran-4-yl(p-tolyl)methanone (3km): Following *general procedure B*, **3km** was isolated as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 8.11 (dd, *J*=8.0, 1.2 Hz, 1 H), 7.97 (d, *J*=8.0 Hz, 1 H), 7.81 (d, *J*=8.0 Hz, 2 H), 7.67 (dd, *J*=8.0, 1.2 Hz, 1 H), 7.52 (d, *J*=8.0 Hz, 1 H), 7.46-7.39 (m, 2 H), 7.37-7.33 (m, 1 H), 7.26 (d, *J*=8.0 Hz, 2 H), 2.43 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.5, 156.3, 153.7, 144.0, 134.9, 130.4, 129.0, 128.4, 127.7, 125.4, 123.8, 123.5, 123.3, 123.1, 122.4, 120.6, 112.1, 21.7 ppm; IR ν_{max} (KBr)/cm^{-1} 3065, 2915, 1657, 1594, 1487, 1449, 1418, 1377, 1292, 1179, 846, 746; HRMS (ESI) calcd. for $C_{20}H_{15}O_2$ [M + H] 287.1072, found 287.1065; mp 96.5-97.1 °C.

4. Hg(0) Poisoning Test

As *general procedure B*, a reactions of 4-iodotoluene **1k** (0.5 mmol, 66.3 μL), phenylboronic acid **2a** (0.75 mmol, 92.4 mg), nanocopper (0.1 mmol, 6.4 mg), K_3PO_4 (0.5 mmol, 109.4 mg), KF (0.25 mmol, 14.7 mg), and *t*$BuCO_2H$ (0.25 mmol, 25.8 mg) in PEG-400 (2.0 mL), with the addition of elemental mercury (20mmol, 4.0 g) (relative to copper) was conducted. Following the reaction for 9 h at 100 °C, the isolated yield of the desired product **3aa** was less than 5%, suggesting that the reaction is inhibited by the introduction of Hg(0).

5. References

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[S2] Q. Zhou, S. H. Wei, W. Han, *J. Org. Chem*. **2014**, *79*, 1454-1460.

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[S4] R. R. Sauers, L. M. Hadel, A. A. Scimone, T. A. Stevenson, *J. Org. Chem.* **1990**, *55*, 4011-4019.

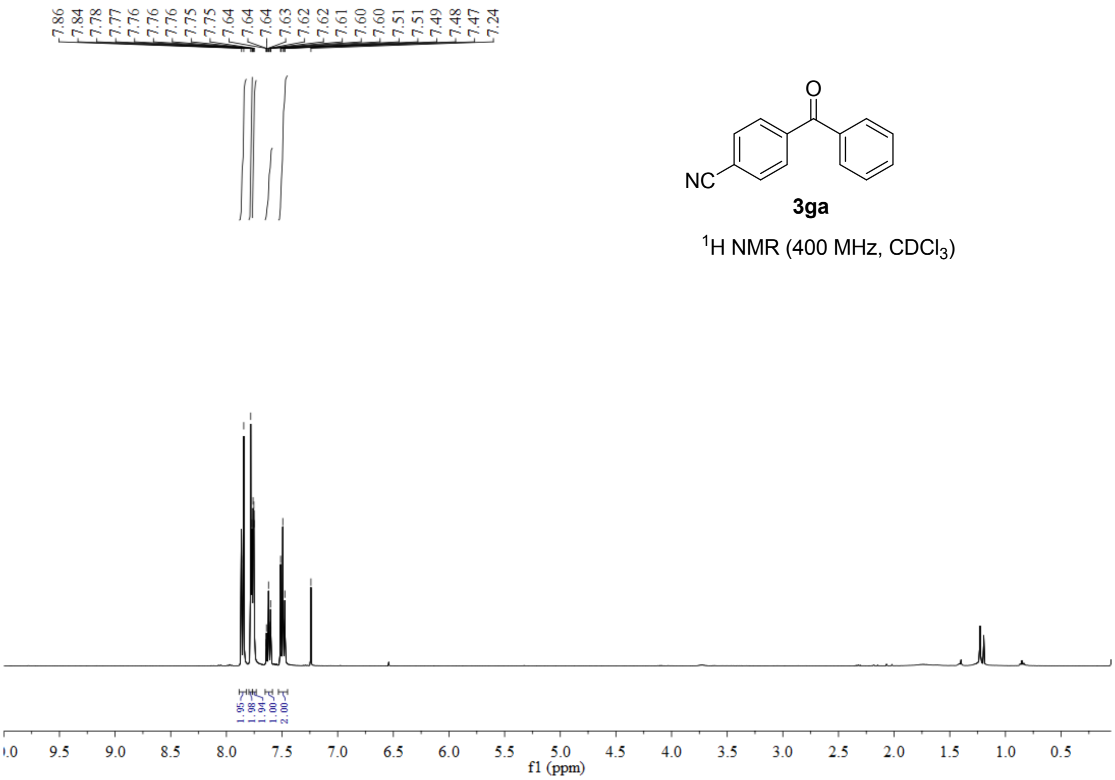
[S5] Y. Yamazaki, M. Sumikura, Y. Masuda, Y. Hayashi, H. Yasui, Y. Kiso, T. Chinen, T. Usui, F. Yakushiji, B. Potts, S. Neuteboome, M. Palladino, G. K. Lloyd, Y. Hayashi, *Bioorg. Med. Chem.* **2012**, *20*, 4279-4289.

[S6] J. R. Niu, M. M. Liu, P. Wang, Y. Long, M. Xie, R. Li, J. T. Ma, *New J. Chem.* **2014**, *38*, 1471-1476.

[S7] K. Kobayashi, Y. Nishimura, F. X. Gao, K. Gotoh, Y. Nishihara, K. Takagi, *J. Org. Chem.* **2011**, *76*, 1949-1952.

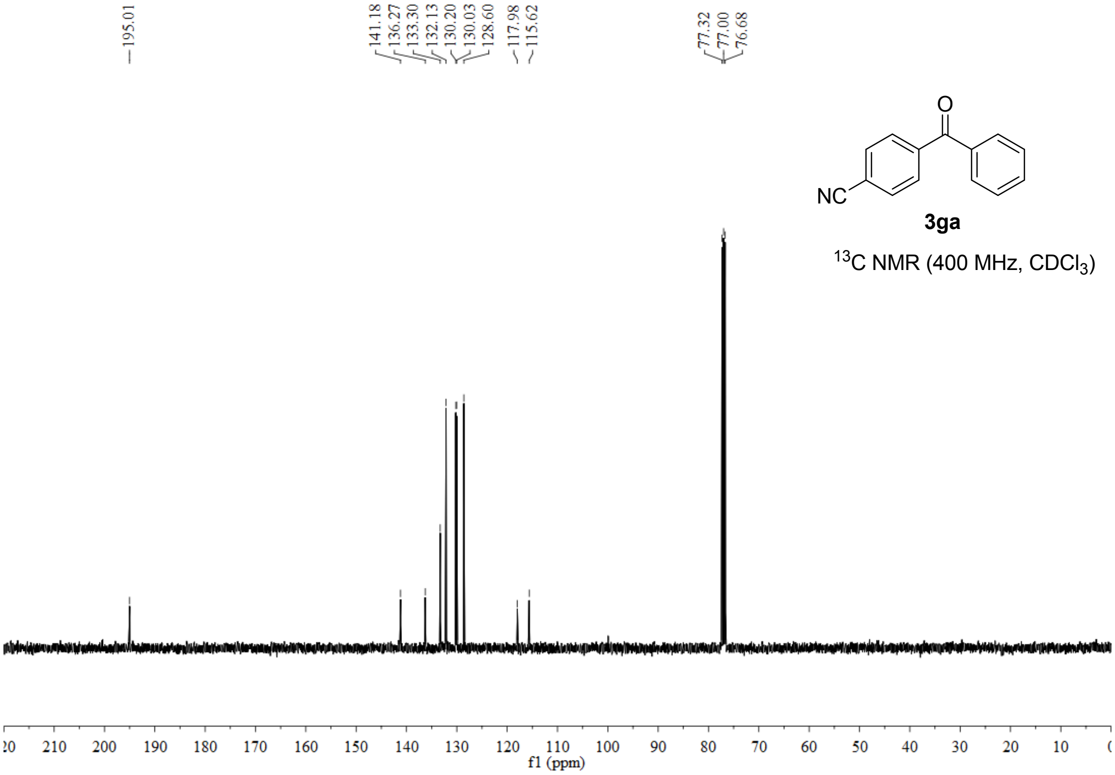
[S8] N. Assadi, S. Pogodin, S. Cohen, I. Agranat, *Struct. Chem.* **2012**, *23*, 771-790.

6. NMR Spectra for Products



3ga

^{1}H NMR (400 MHz, $CDCl_3$)



3ga

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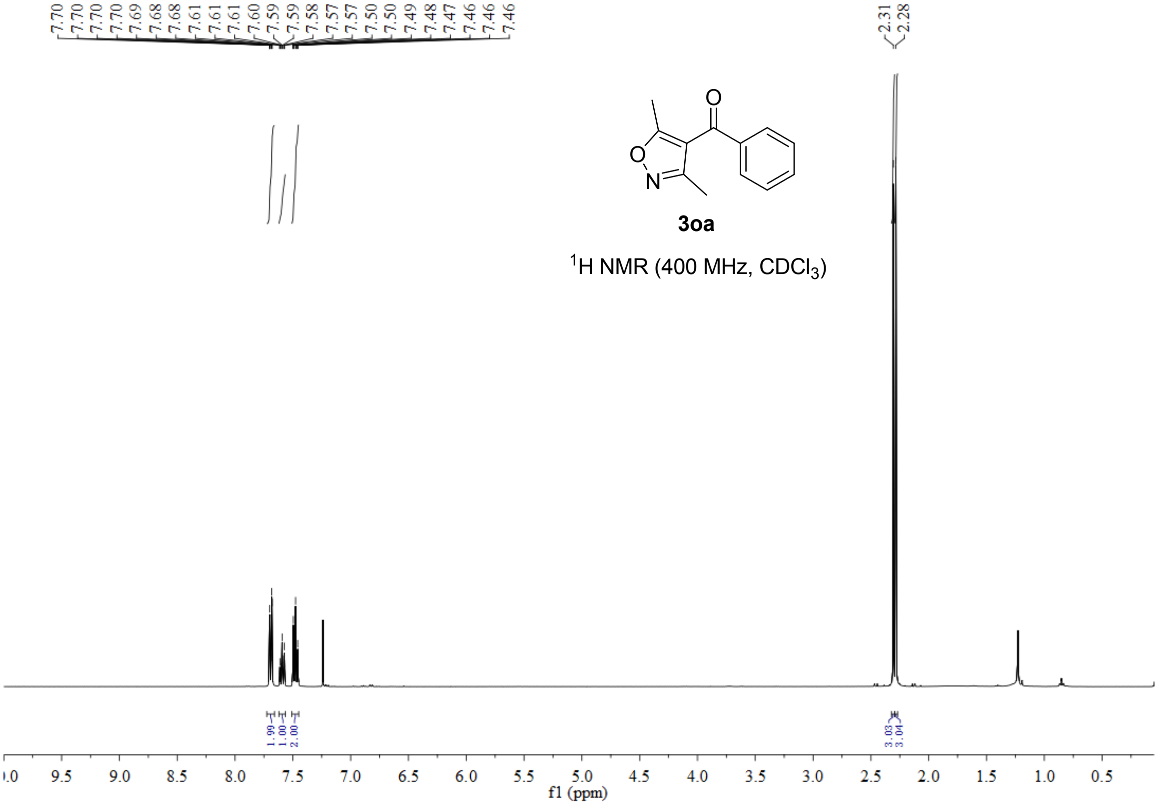
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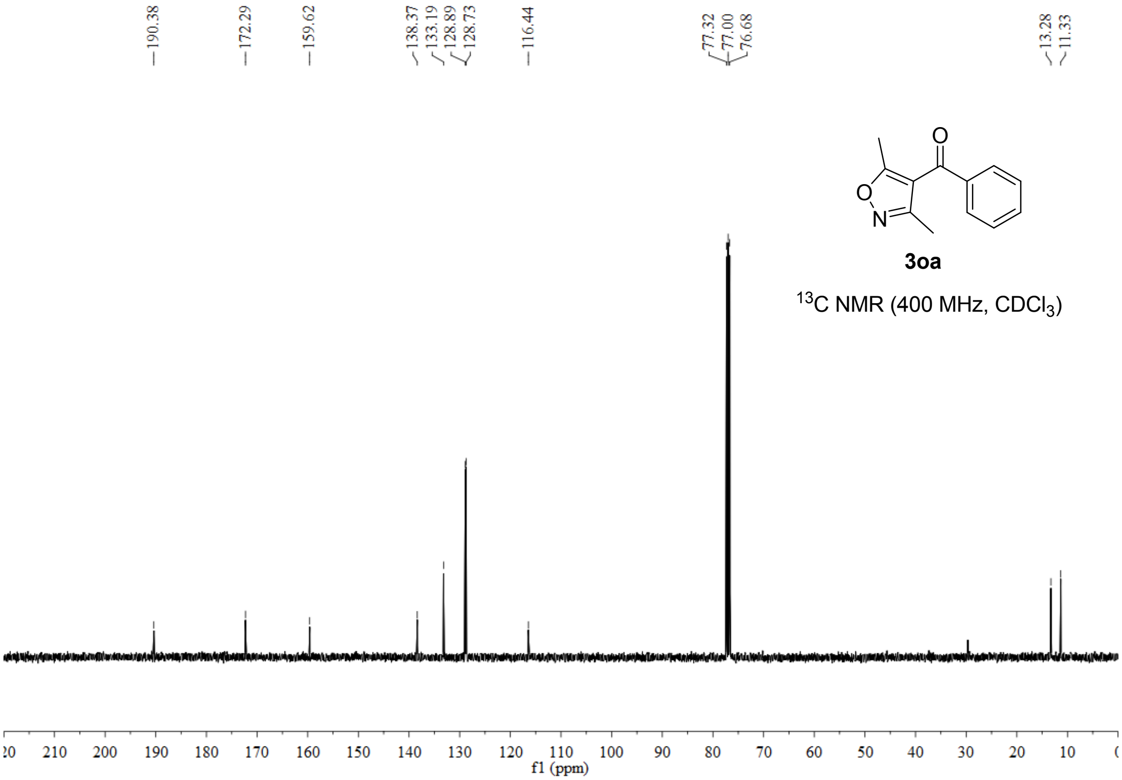
7.70
7.70
7.70
7.69
7.68
7.68
7.61
7.61
7.61
7.60
7.59
7.59
7.58
7.57
7.57
7.50
7.50
7.49
7.48
7.47
7.46
7.46
2.31
2.28
O
O
N
3oa
^{1}H NMR (400 MHz, CDCl$_3$)
1.99
1.00
2.00
3.03
3.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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172.29
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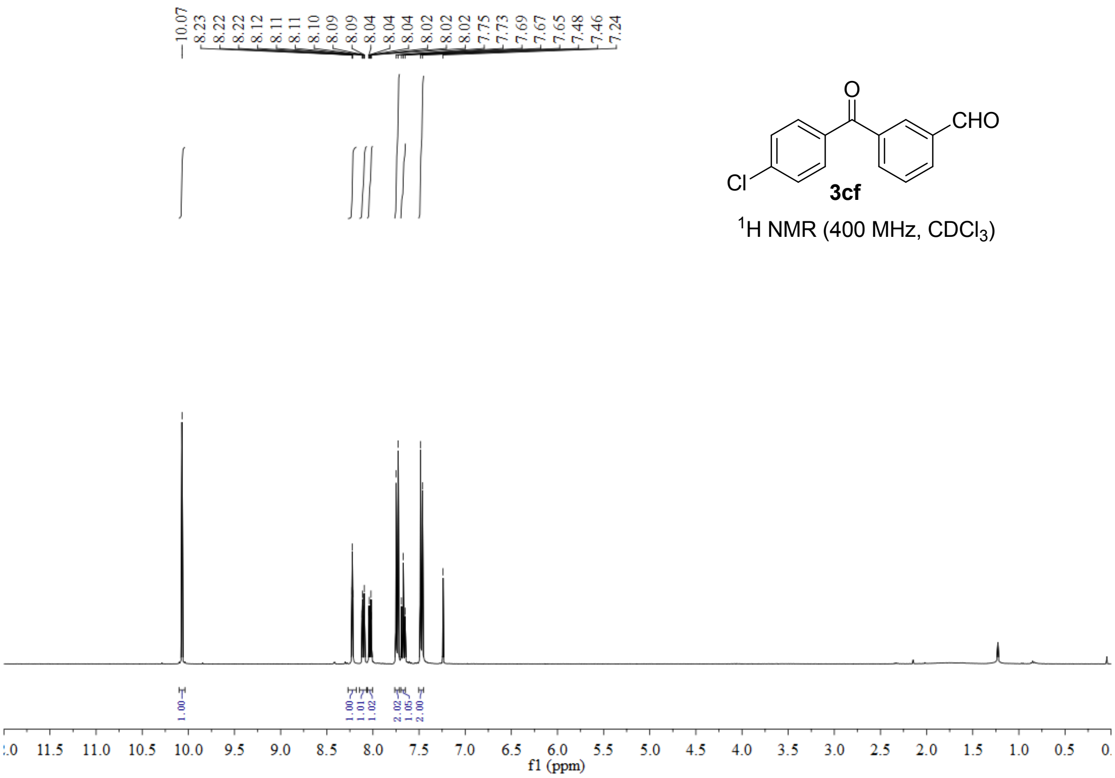
133.19
128.89
128.73
116.44
77.32
77.00
76.68
13.28
11.33
O
O
N
3oa
^{13}C NMR (400 MHz, CDCl$_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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8.11
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8.09
8.04
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8.04
8.02
8.02
8.02
7.75
7.73
7.69
7.67
7.65
7.48
7.46
7.24
O
CHO
Cl
3cf
^{1}H NMR (400 MHz, CDCl$_3$)
1.00
1.00
1.01
1.02
2.02
1.05
2.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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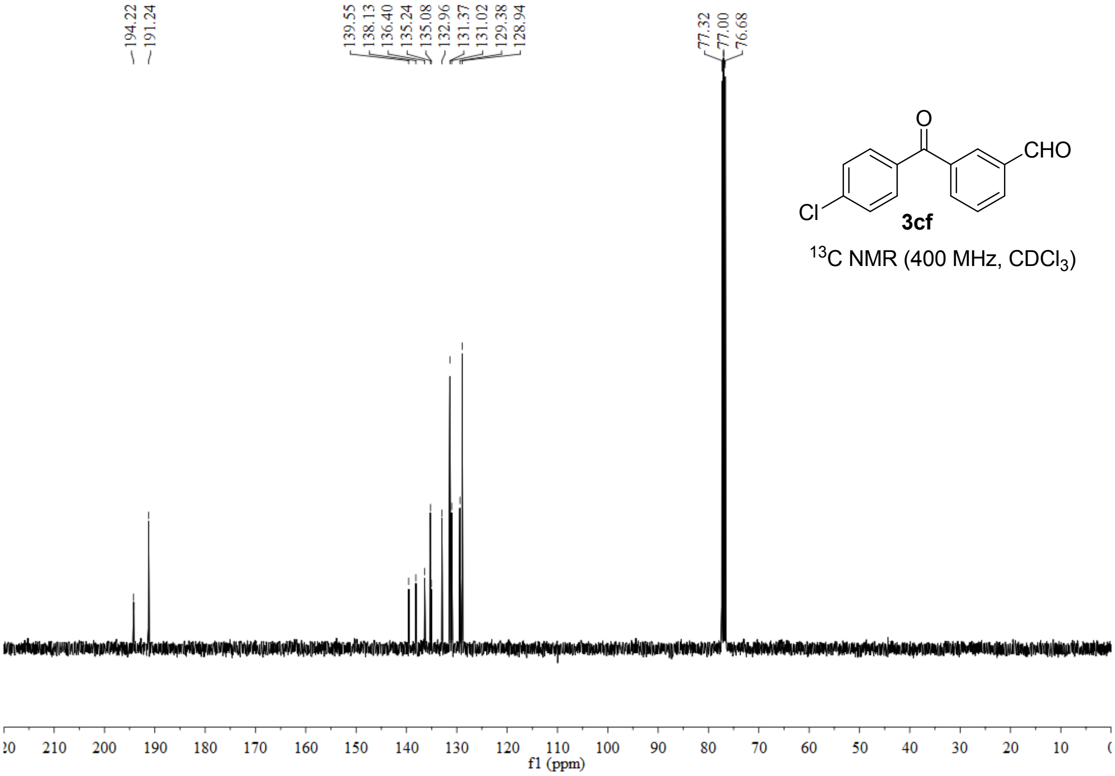
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)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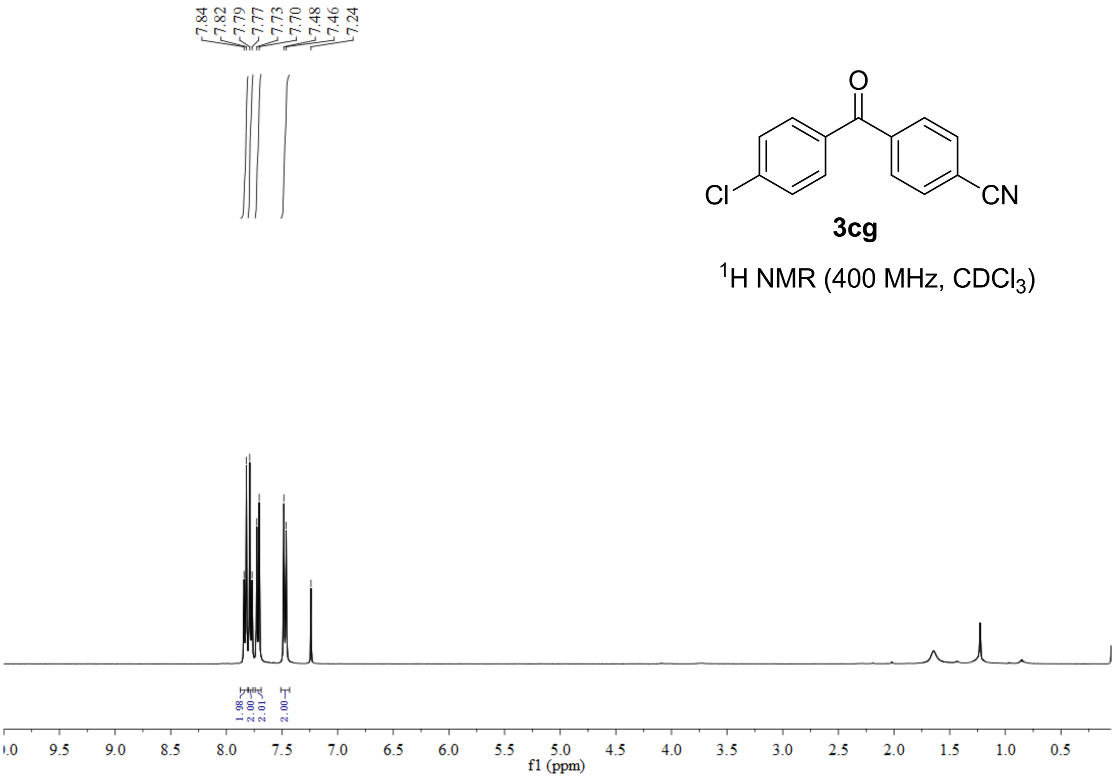
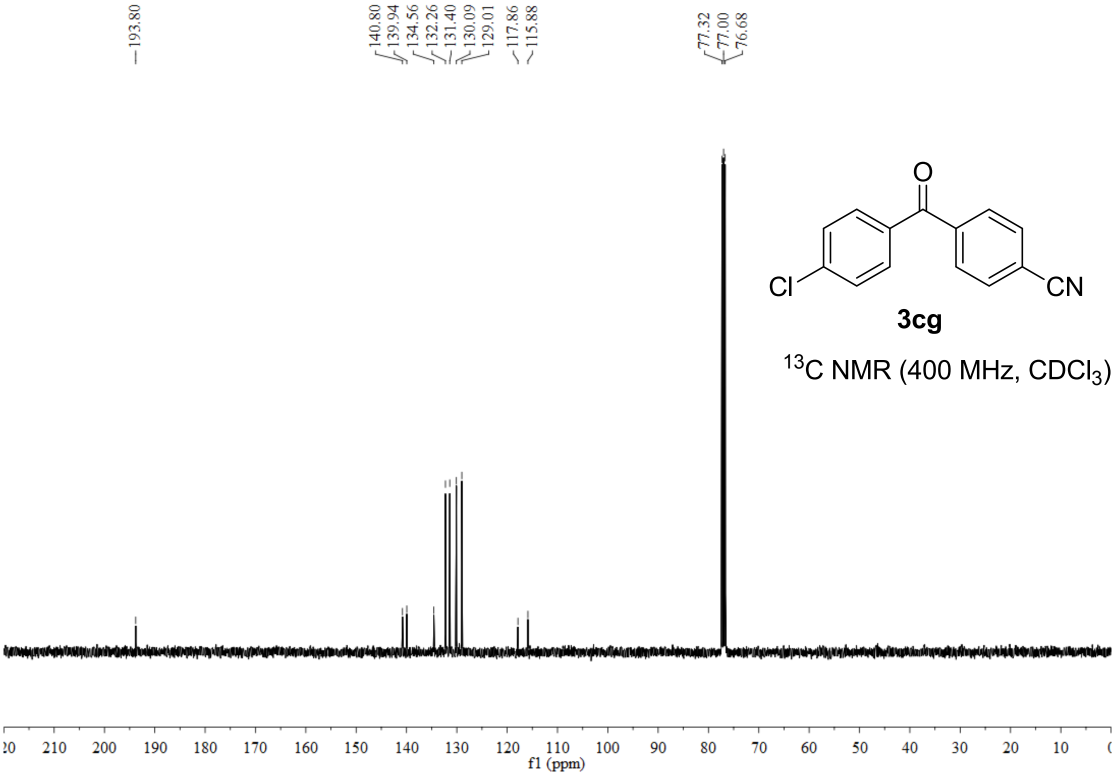
139.55
138.13
136.40
135.24
135.08
132.96
131.37
131.02
129.38
128.94
77.32
77.00
76.68
O
CHO
Cl
3cf
^{13}C NMR (400 MHz, CDCl$_3$)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



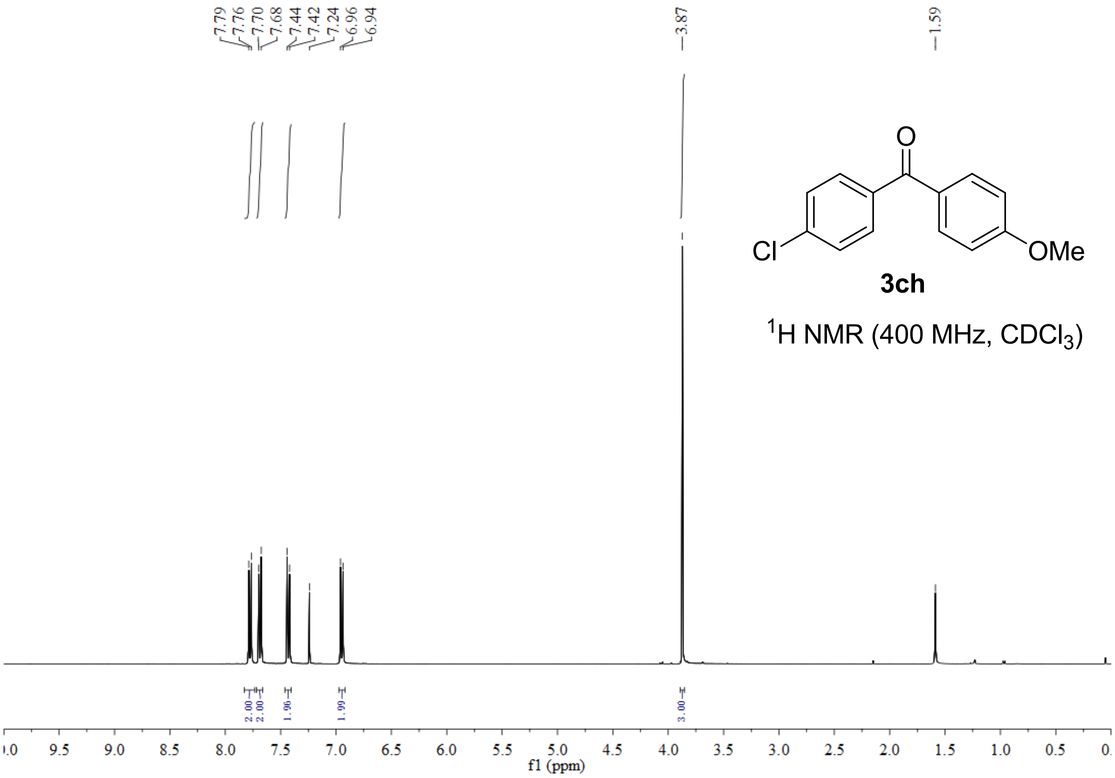
3cg

^{1}H NMR (400 MHz, $CDCl_3$)



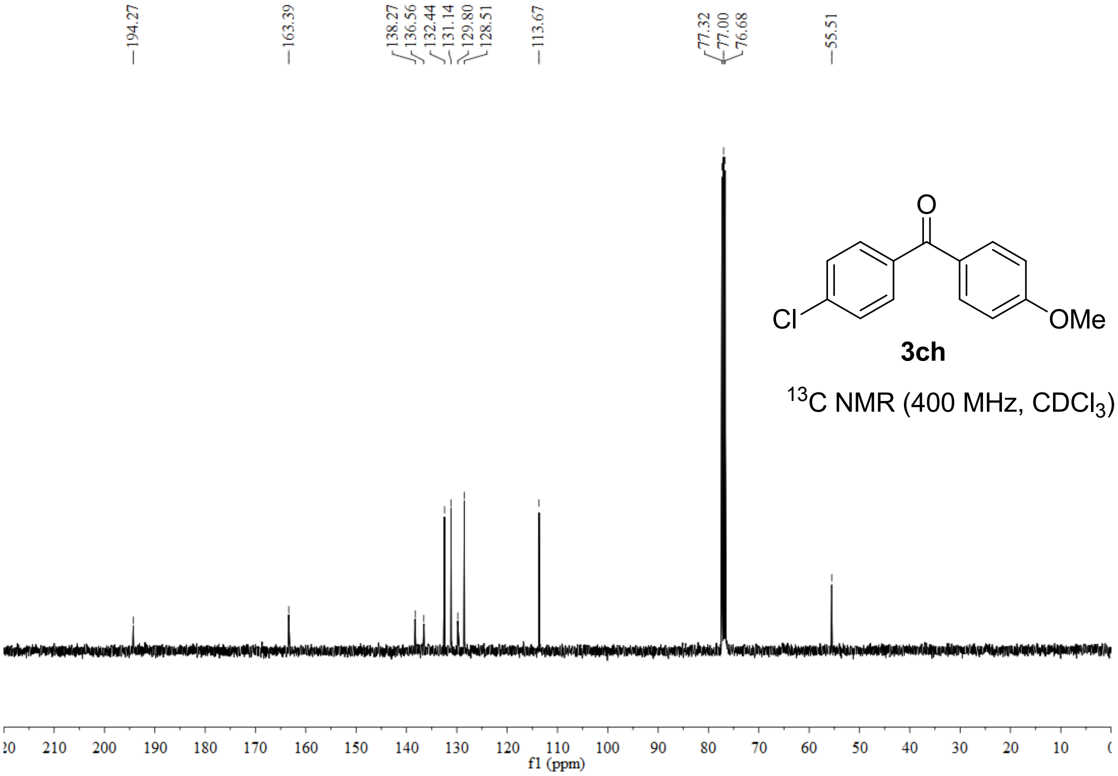
3cg

^{13}C NMR (400 MHz, $CDCl_3$)



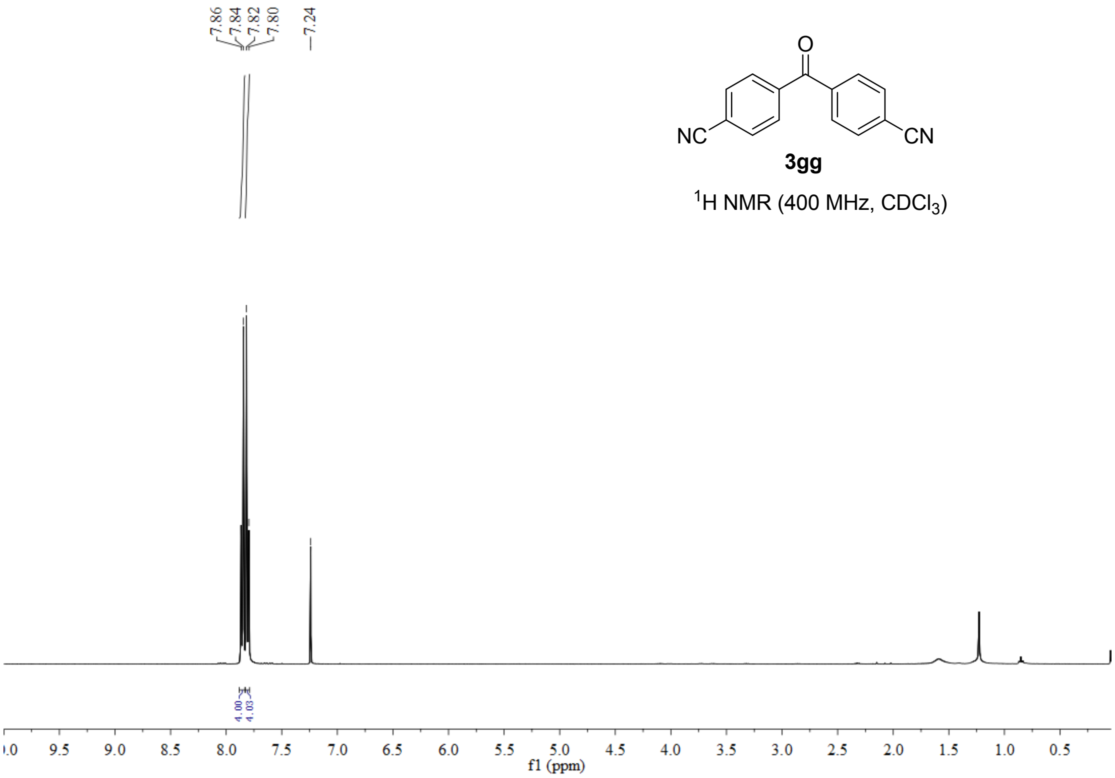
3ch

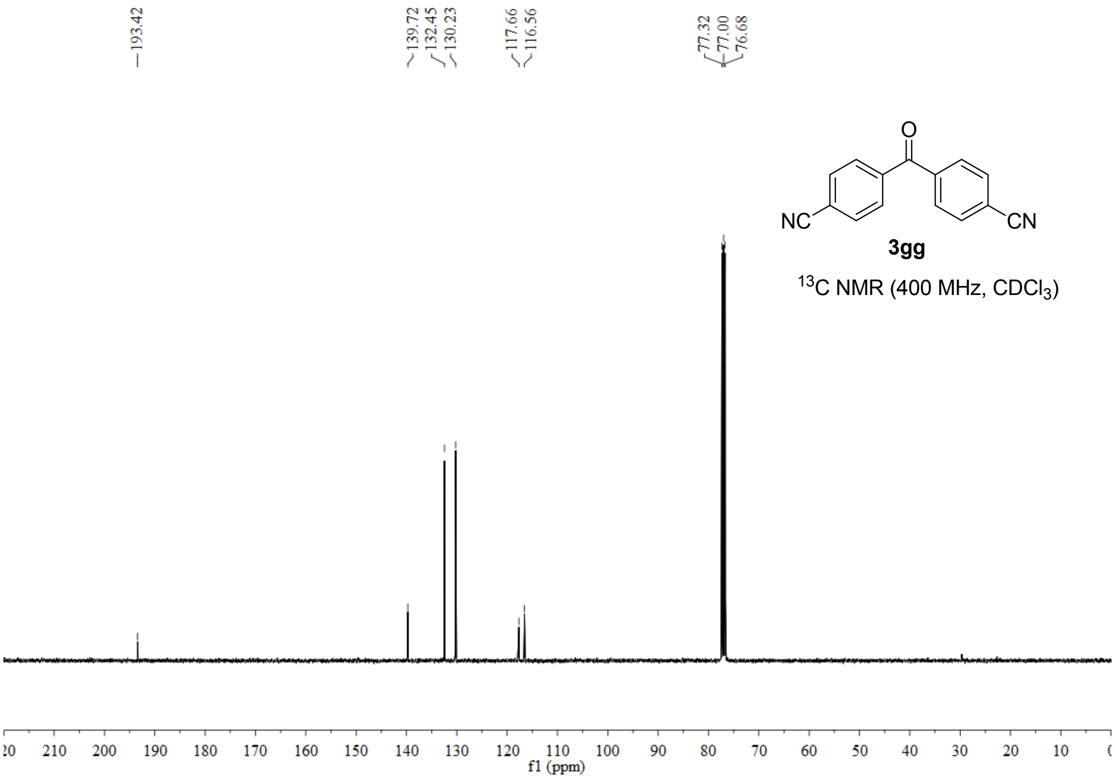
^{1}H NMR (400 MHz, CDCl$_3$)

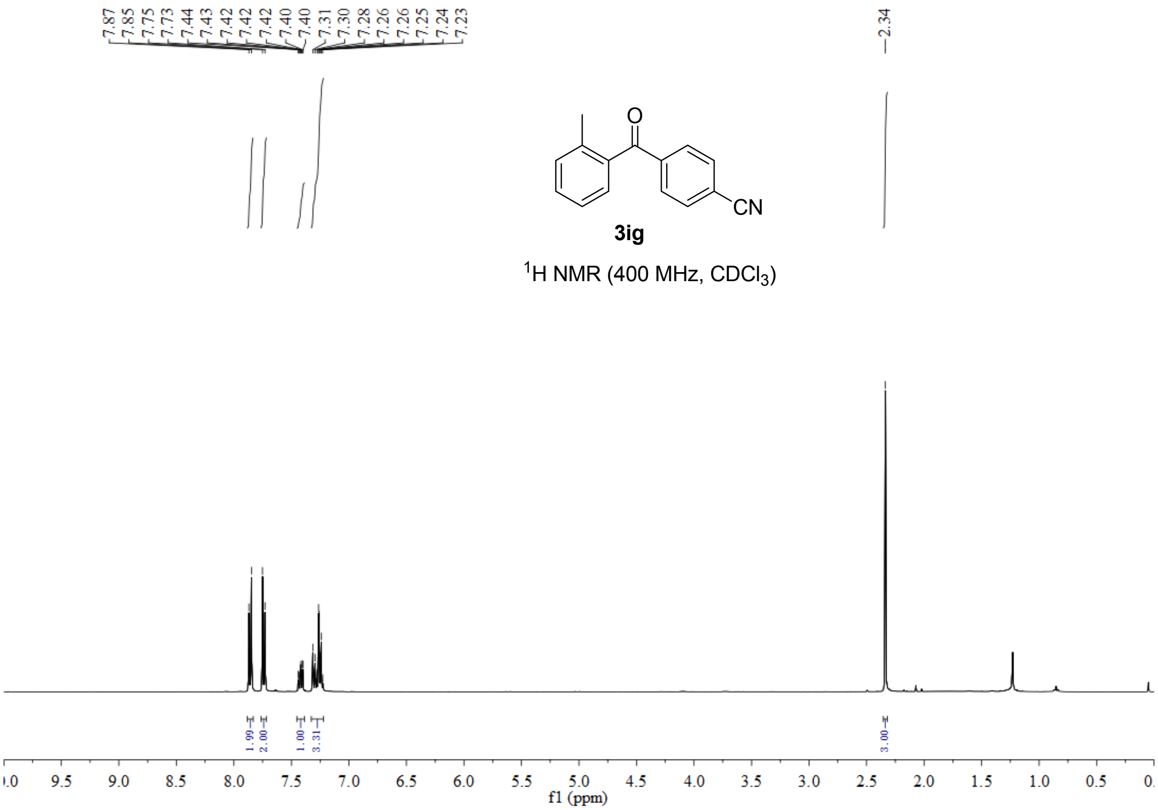


3ch

^{13}C NMR (400 MHz, CDCl$_3$)


7.86
7.84
7.82
7.80
7.24
O
NC
CN
3gg
^{1}H NMR (400 MHz, CDCl$_3$)
4.00
4.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


193.42
139.72
132.45
130.23
117.66
116.56
77.32
77.00
76.68
O
NC
CN
3gg
^{13}C NMR (400 MHz, CDCl$_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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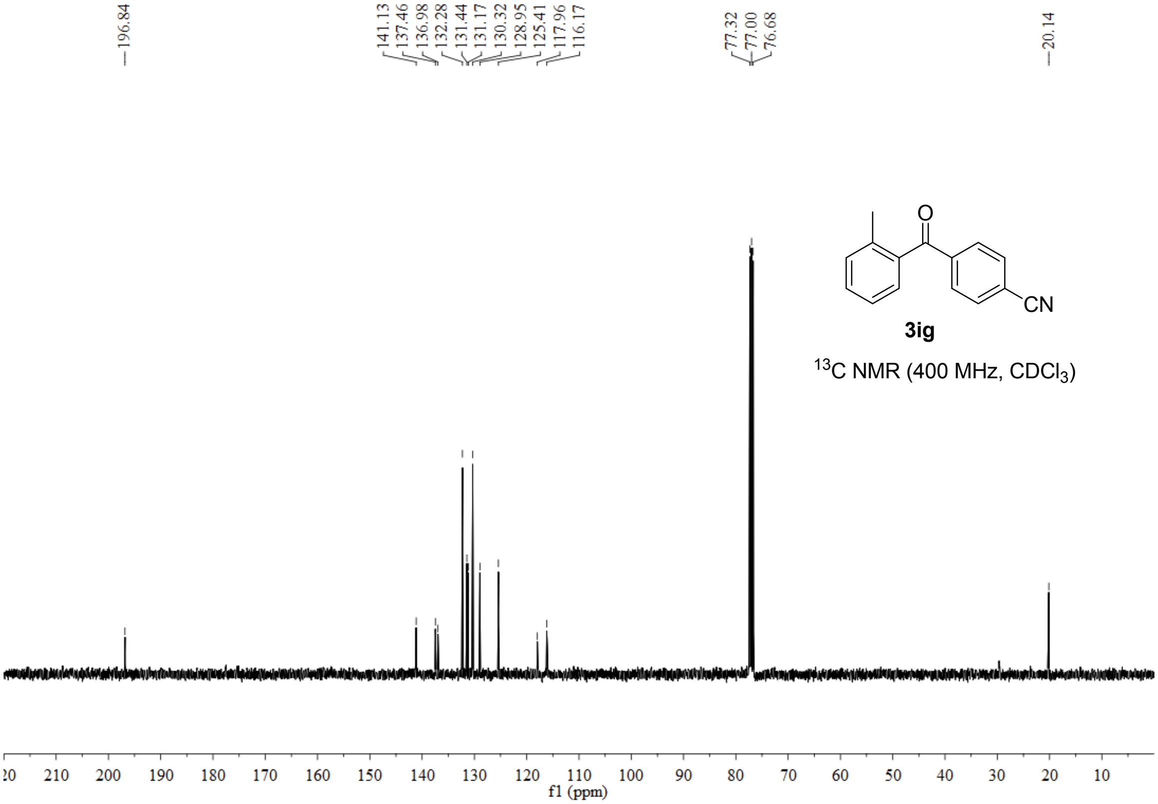
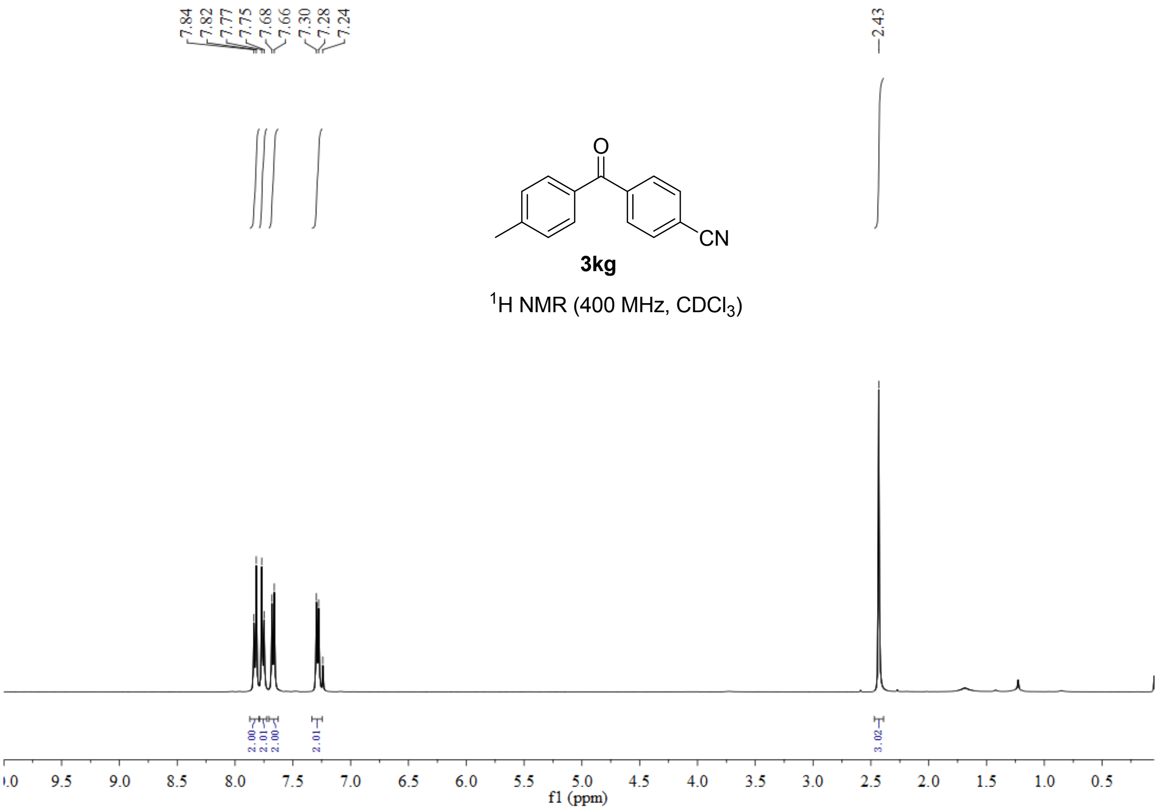
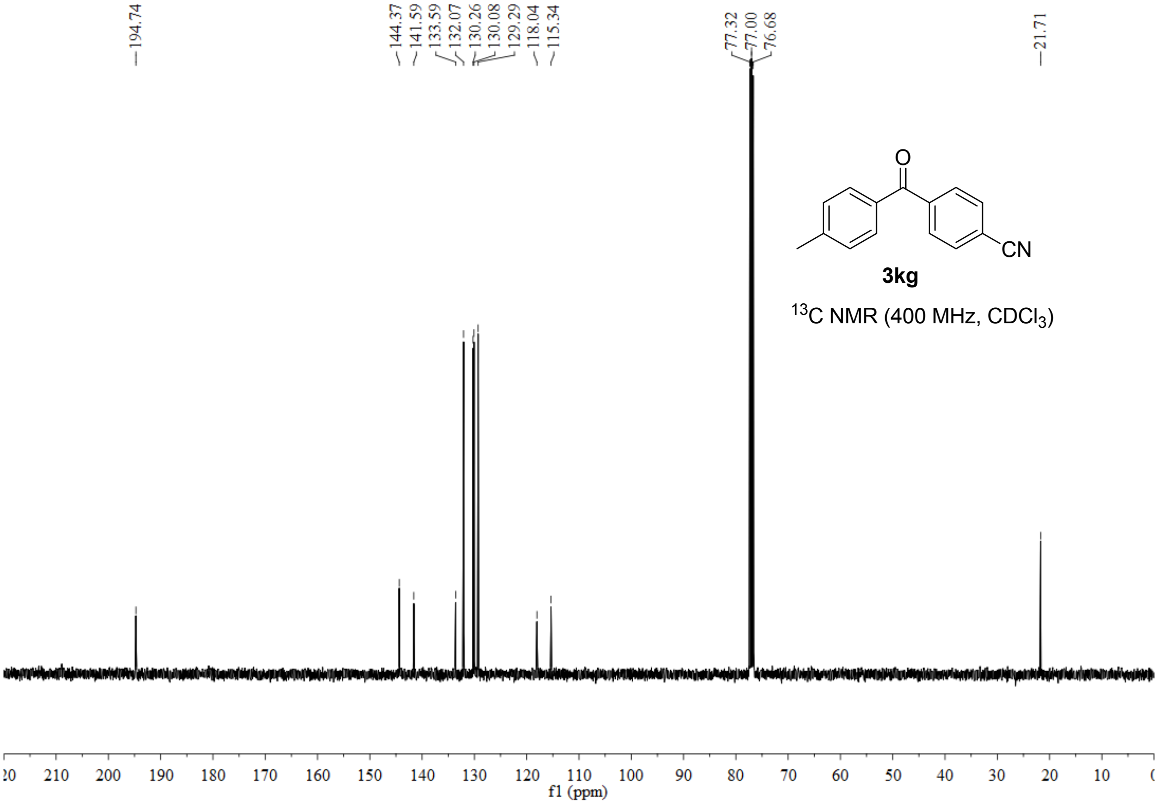
7.44
7.43
7.42
7.42
7.42
7.40
7.40
7.31
7.30
7.28
7.26
7.26
7.25
7.24
7.23
2.34
O
CN
3ig
^{1}H NMR (400 MHz, CDCl$_3$)
1.99
2.00
1.00
3.31
3.00
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)


196.84
141.13
137.46
136.98
132.28
131.44
131.17
130.32
128.95
125.41
117.96
116.17
77.32
77.00
76.68
20.14
O
CN
3ig
^{13}C NMR (400 MHz, CDCl$_3$)
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



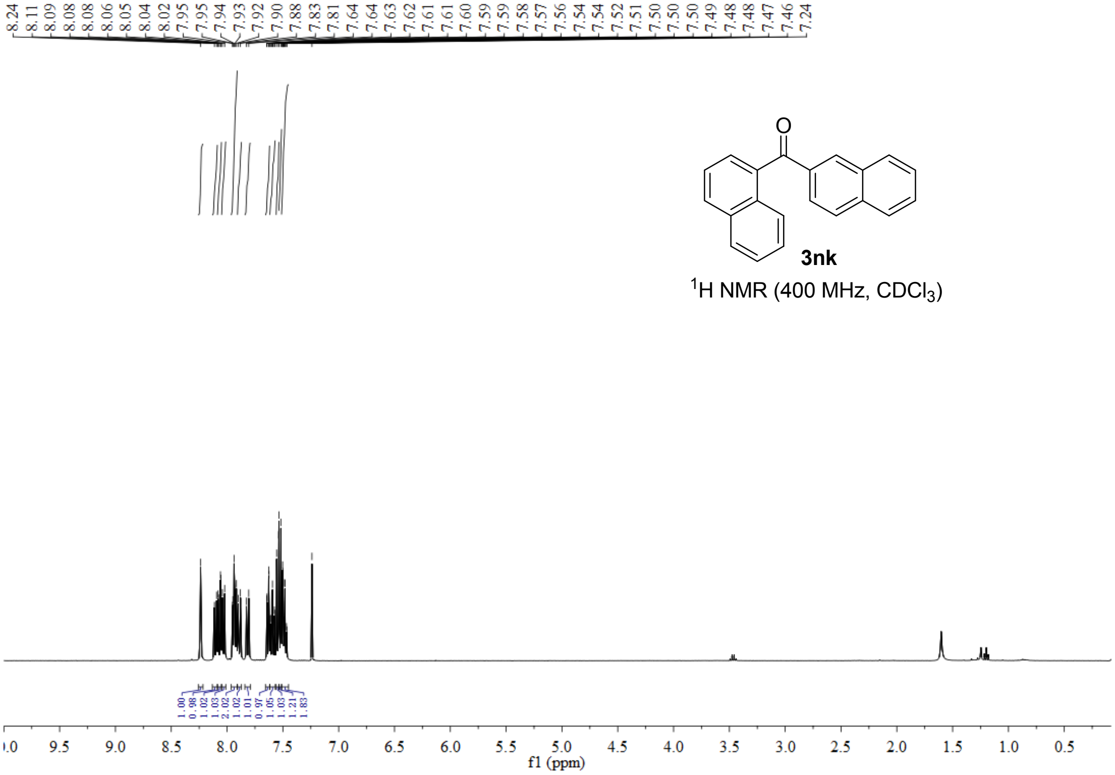
3kg

^{1}H NMR (400 MHz, $CDCl_3$)



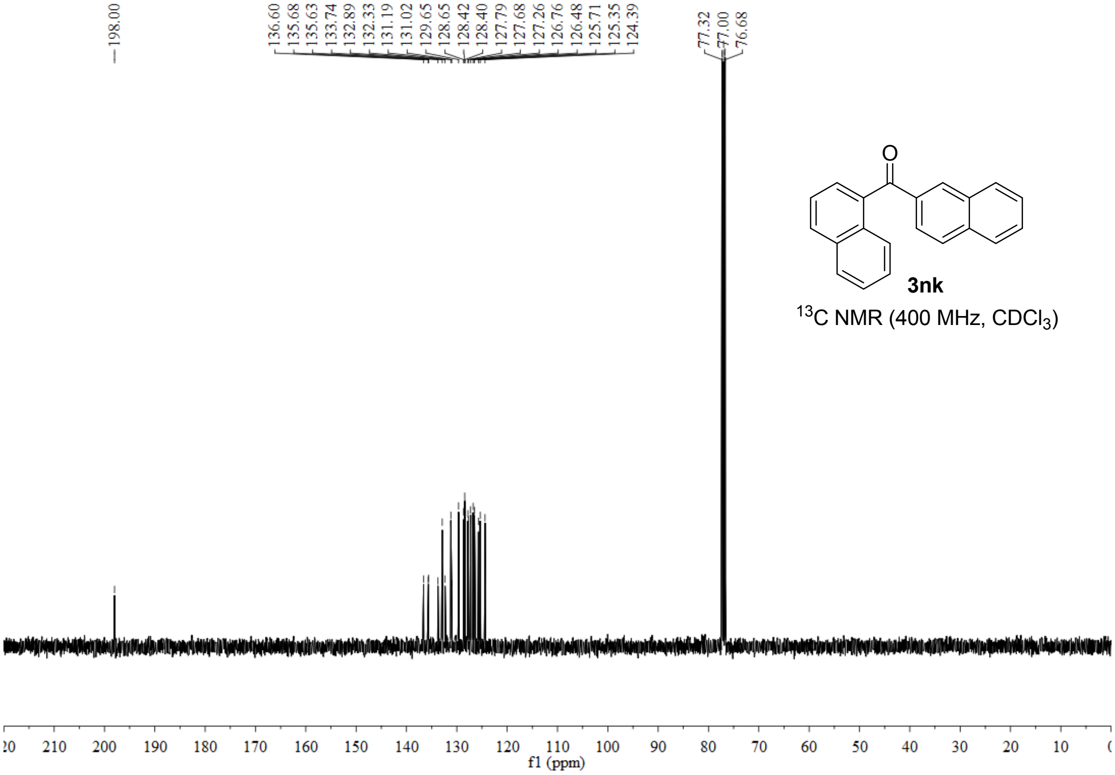
3kg

^{13}C NMR (400 MHz, $CDCl_3$)



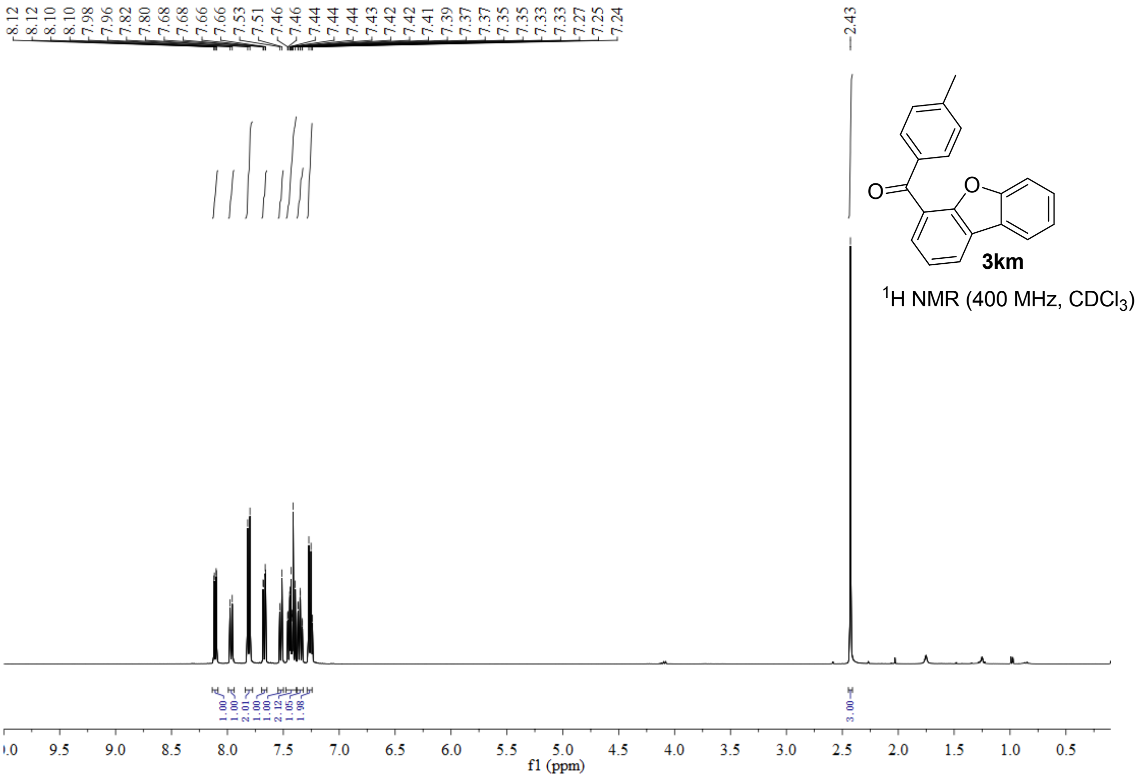
3nk

^{1}H NMR (400 MHz, $CDCl_3$)



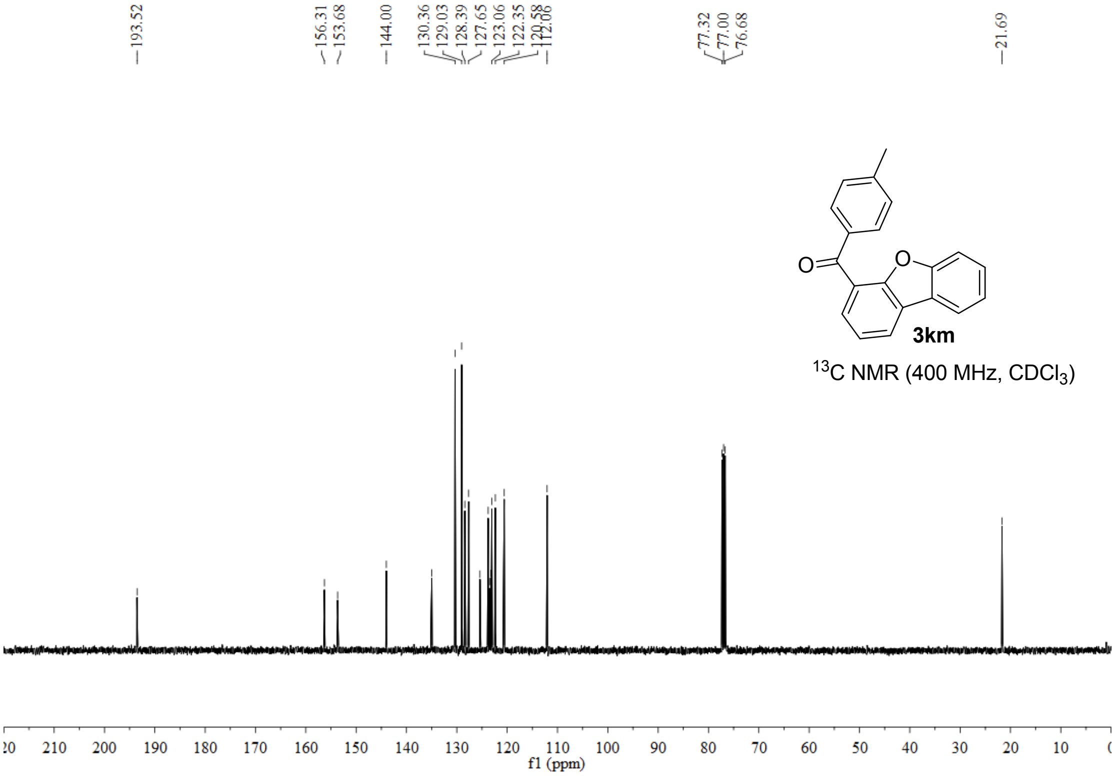
3nk

^{13}C NMR (400 MHz, $CDCl_3$)



3km

^{1}H NMR (400 MHz, $CDCl_3$)



3km

^{13}C NMR (400 MHz, $CDCl_3$)