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Magnetically recyclable Cu-BTC@Fe_3O_4-catalyzed synthesis of aryl α-chlorobenzyl ketones

Liang Wang, Ya-Juan Fan, Yu-Tao Sun and Xin He

Contents

General Experimental

Unless otherwise noted, all chemicals were purchased from commercial suppliers (Aladdin) and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a Bruker AVANCE III 300 spectrometer. Chemical shifts are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (7.26 or 77.0 ppm) as the internal standard. The coupling constants *J* are given in Hz. Column chromatography was performed using EM Silica gel 60 (300-400 mesh). Chromato-mass spectrometry (LCMS) was performed on a Shimadzu LCMS-2020 instrument with an ESI source. Fourier transform (FT) Infrared data were recorded on an AVATAR-370 (Nicolet) spectrometer by transmission through the sample deposited on a KBr pellet. Powder X-ray diffraction (PXRD) patterns of the as-synthesized and recycled samples were obtained using a Rigaku D/max 2500 PC X-ray diffractometer with Cu Kα (1.5406 Å) radiation at 10 min^{-1}. Thermogravimetric analysis (TGA) experiments were carried out on a TG/DTA 6300 thermoanalyzer from room temperature to 800 °C under nitrogen atmosphere at a heating rate of 10 °C/min. Field-emission Scanning Electron Microscopy (SEM) images of the samples were taken at 30 kV with a ZEISS Supra 55 microscope. The compositions of samples were analyzed by ICP (inductively coupled plasma) analysis (Varian Vista-AX). N_2 adsorption isotherms were obtained using a Micromeritics ASAP 2460 instrument.

Preparation of Cu-BTC@Fe_3O_4 composite

Cu-BTC@Fe_3O_4 was prepared through a secondary growth strategy according to the literature.[S1] PVP (0.2 g, 0.005 mmol) and $Cu(OAc)_2·H_2O$ (0.1 g, 0.5 mmol) were uniformly dissolved in a mixed solution of EtOH/H_2O (2:1, 90 mL) in a 150 ml round-bottom flask under mechanical stirring (600 rpm). Then 0.2 g carboxyl functionalized Fe_3O_4 was gradually added to the mixed solution with high-speed mechanical stirring of 900 rpm and kept for 10 min. The reaction system was stirred for another 12 h upon the addition of trimesic acid (0.3 g, 1.428 mmol) and $Cu(OAc)_2·H_2O$ (0.1 g, 0.5 mmol). The product was obtained by centrifugation and then washed with EtOH/H_2O (2:1, 3 × 20 ml) and EtOH (3 × 20 ml). Finally, the obtained product was dried at 60 °C under vacuum for 10 h and stored in a desiccator.

Characterization of the composites

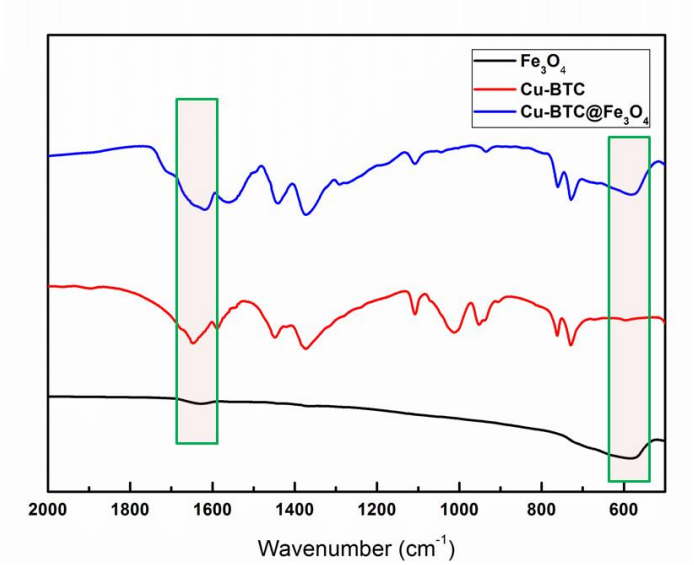
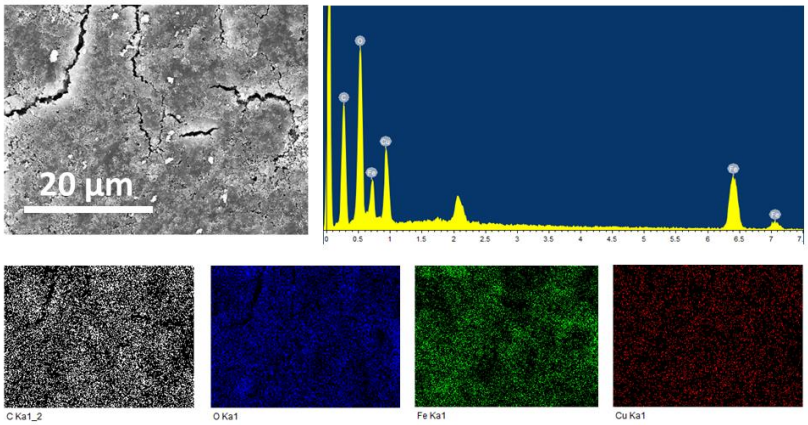


Figure S1. IR spectra of carboxyl functionalized Fe_3O_4 (black), Cu-BTC (red) and Cu-BTC@Fe_3O_4 (blue).



Element	C	O	Fe	Cu
Weight Percentage (%)	39.51	35.42	12.89	12.18
Atomic Percentage (%)	55.51	37.36	3.90	3.24

Figure S2. The EDS element analysis of Cu-BTC@Fe_3O_4, the scale bar is 20 µm.

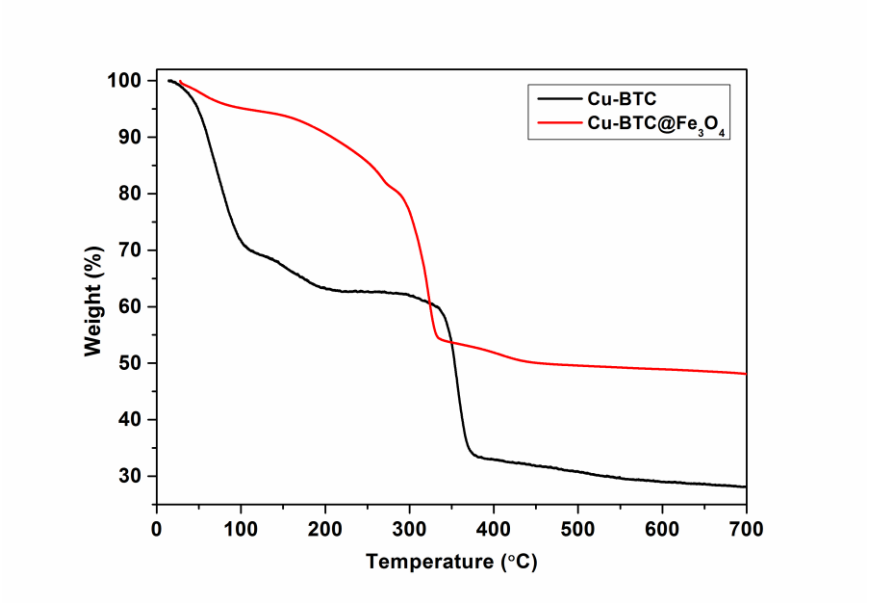


Figure S3. The TG curves of Cu-BTC and Cu-BTC@ Fe_3O_4.

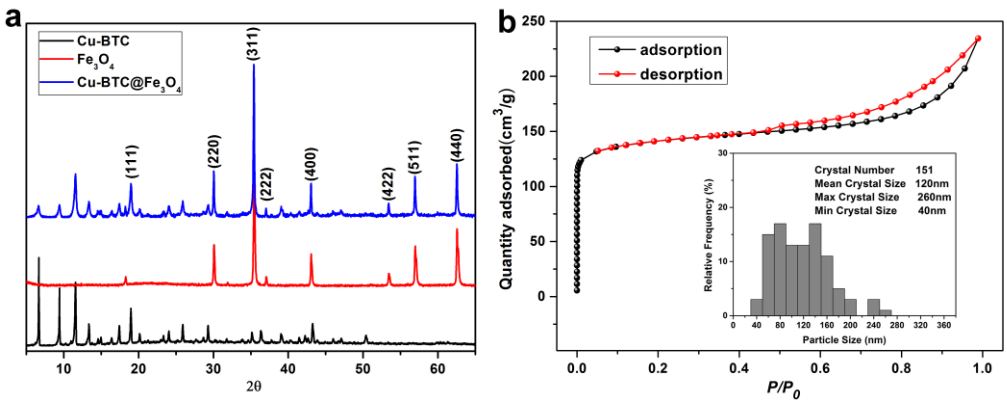


Figure S4. The PXRD patterns of Cu-BTC, Fe_3O_4 and Cu-BTC@Fe_3O_4 samples. (b) N_2 adsorption/desorption isotherms and particle size distribution of Cu-BTC@Fe_3O_4

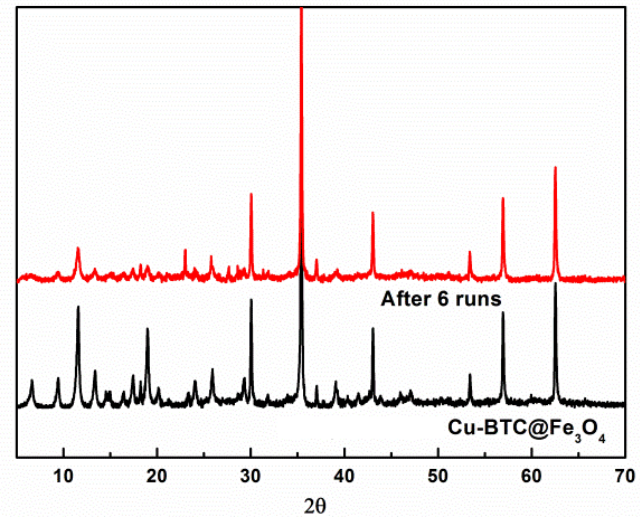
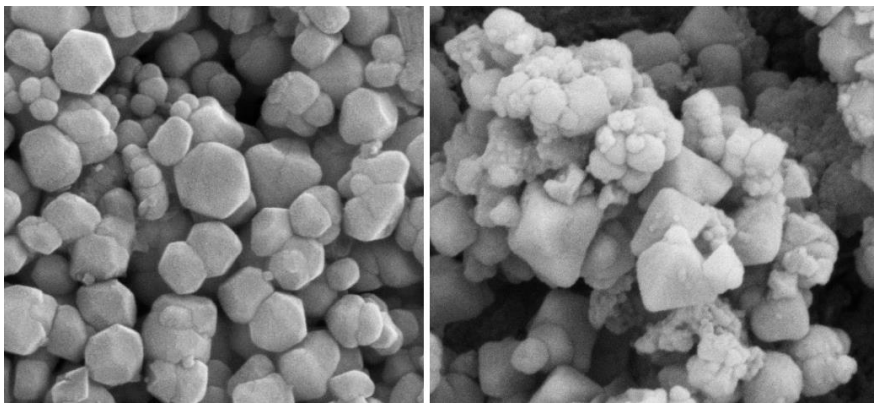


Figure S5. The PXRD patterns of Cu-BTC@Fe_3O_4 before and after catalysis reaction.



Fresh catalyst Recovered catalyst after 6 runs

Figure S6. SEM of Cu-BTC@Fe_3O_4 before and after reaction

Experimental Procedures, Spectral and Analytical data

*General procedure for the synthesis of **3a~l***

A sealed tube equipped with a magnetic stirrer bar was charged with arenediazonium salt **1** (0.5 mmol), arylacetylene **2** (0.6 mmol), aqueous HCl (1 mmol, *conc*. 37%), Cu-BTC@Fe_3O_4 composite (15 mg) and acetonitrile (2 ml). The reaction mixture was stirred under oxygen atmosphere overnight. After reaction, the Cu-BTC@Fe_3O_4 was recovered with an external magnet, and washed with EtOAc and water. The reaction mixture was extracted with EtOAc (3 × 5 ml) and dried over Na_2SO_4. The organic phase was then concentrated under reduced pressure to give the crude product, which was further purified by column chromatography using petroleum ether/ethyl acetate (10:1, *v*/*v*) as eluent to afford product **3a~l**.

Characterization data of product

*2-Chloro-2-(4-nitrophenyl)-1-phenylethan-1-one (**3a**)*.[S2] Yellow solid (111 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, J = 8.8 Hz, 2H), 7.98 (d, J = 7.2 Hz, 2H), 7.67 (d, J = 8.7 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 6.37 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.5, 148.0, 142.4, 134.3, 133.6, 129.6, 129.1, 128.9, 123.9, 59.2.

*1-(4-Chlorophenyl)-2-chloro-2-(4-nitrophenyl)ethan-1-one (**3b**)*.[S2] Yellow solid (113 mg, 73%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 – 8.22 (m, 2H), 7.95 – 7.90 (m, 2H), 7.68 – 7.64 (m, 2H), 7.48 – 7.43 (m, 2H), 6.27 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.5, 148.1, 142.0, 141.0, 131.9, 130.5, 129.6, 129.4, 124.1, 59.1.

*1-(4-Bromophenyl)-2-chloro-2-(4-nitrophenyl)ethan-1-one (**3c**)*.[S2] Yellow solid (118 mg, 67%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, J = 8.8 Hz, 2H), 7.84 (d, J = 8.7 Hz, 2H), 7.67 - 7.60 (m, 4H), 6.27 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.7, 148.1, 142.0, 132.6, 132.3, 130.56, 129.7, 129.6, 124.0, 59.1.

*4-(2-Chloro-2-(4-nitrophenyl)acetyl)benzonitrile (**3d**)*.[S2] Yellow solid (112 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, J = 6.6 Hz, 2H), 8.08 (d, J = 6.4 Hz, 2H), 7.80 (d, J = 6.4 Hz, 2H), 7.67 (d, J = 6.5 Hz, 2H), 6.25 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ189.4, 148.4, 141.3, 136.7, 132.7, 129.6 (doublet), 124.2, 117.4 (doublet), 59.1.

*Methyl 4-(2-chloro-2-(4-nitrophenyl)acetyl)benzoate (**3e**)*.[S2] Yellow solid (113 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (d, J = 8.7 Hz, 2H), 8.13 (d, J = 8.4 Hz, 2H), 8.03 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.7 Hz, 2H), 6.32 (s, 1H), 3.94 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.2, 165.7, 148.2, 141.9, 137.0, 134.9, 130.1, 129.6, 129.1, 124.1, 59.3, 52.6.

*2-Chloro-2-(4-nitrophenyl)-1-(m-tolyl)ethan-1-one (**3f**)*.[S2] Yellow solid (94 mg, 65%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 – 8.19 (m, 2H), 7.79 – 7.75 (m, 2H), 7.69 – 7.65 (m, 2H), 7.38 (dt, J = 15.1, 7.5 Hz, 2H), 6.36 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.7, 148.0, 142.5, 139.0, 135.1, 133.7, 129.6, 129.5, 128.8, 126.2, 123.9, 59.2, 21.3.

*2-Chloro-1-(2-chlorophenyl)-2-(4-nitrophenyl)ethan-1-one (**3g**)*.[S2] Yellow solid (94 mg, 61%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 7.44 – 7.39 (m, 2H), 7.38 – 7.27 (m, 2H), 6.28 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.8, 148.1, 141.4, 136.3, 132.7, 130.7, 130.5, 129.7, 129.6, 127.1, 123.9, 62.5.

*4-(1-Chloro-2-oxo-2-phenylethyl)benzonitrile (**3h**)*.[S2] Yellow solid (102 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H), 7.70 – 7.65 (m, 2H), 7.62 – 7.57 (m, 3H), 7.50 – 7.45 (m, 2H), 6.31 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.6, 140.6, 134.2, 133.7, 132.6, 129.3, 129.1, 128.9, 118.1, 112.9, 59.7.

*Ethyl 4-(1-chloro-2-oxo-2-phenylethyl)benzoate (**3i**)*.[S2] White solid (99 mg, 66%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 – 8.01 (m, 2H), 7.97 – 7.93 (m, 2H), 7.58 – 7.52 (m, 3H), 7.45 – 7.39 (m, 2H), 6.34 (s, 1H), 4.35 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.0, 165.8, 140.3, 134.2, 133.6, 131.0, 130.4, 129.9, 129.3, 128.8, 61.1, 60.9, 14.2.

*2-Chloro-2-(4-chlorophenyl)-1-phenylethan-1-one (**3j**)*.[S2] White solid (67 mg, 53%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 2H), 7.61 – 7.54 (m, 1H), 7.48 – 7.40 (m, 4H), 7.38 – 7.32 (m, 2H), 6.28 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.1, 135.2, 134.3, 134.0, 133.9, 129.8, 129.3, 129.1, 128.8, 60.8.

*2-(4-Acetylphenyl)-2-chloro-1-phenylethan-1-one (**3k**)*.[S2] Yellow solid (82 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 – 7.95 (m, 2H), 7.94 – 7.91 (m, 2H), 7.61 – 7.52 (m, 3H), 7.48 – 7.38 (m, 2H), 6.35 (s, 1H), 2.57 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.3, 190.9, 140.5, 137.3, 134.0, 133.9, 129.0, 128.9, 128.8,128.7, 60.8, 26.6.

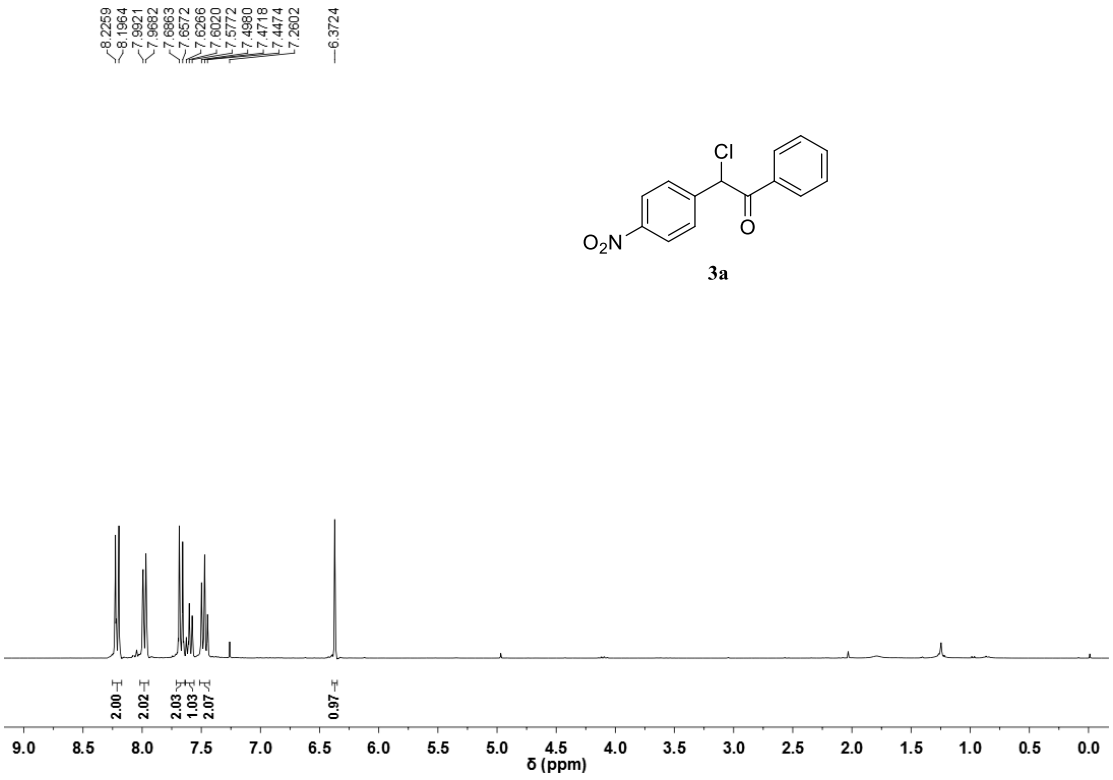
*2-Chloro-2-(3-nitrophenyl)-1-phenylethan-1-one (**3l**)*.[S2] Yellow solid (99 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (t, J = 2.0 Hz, 1H), 8.23 – 8.19 (m, 1H), 8.02 – 7.98 (m, 2H), 7.87 – 7.81 (m, 1H), 7.65 – 7.56 (m, 2H), 7.52 – 7.46 (m, 2H), 6.36 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.6, 148.3, 137.6, 134.7, 134.3, 133.6, 129.9, 129.1, 129.0, 124.0, 123.7, 58.8.

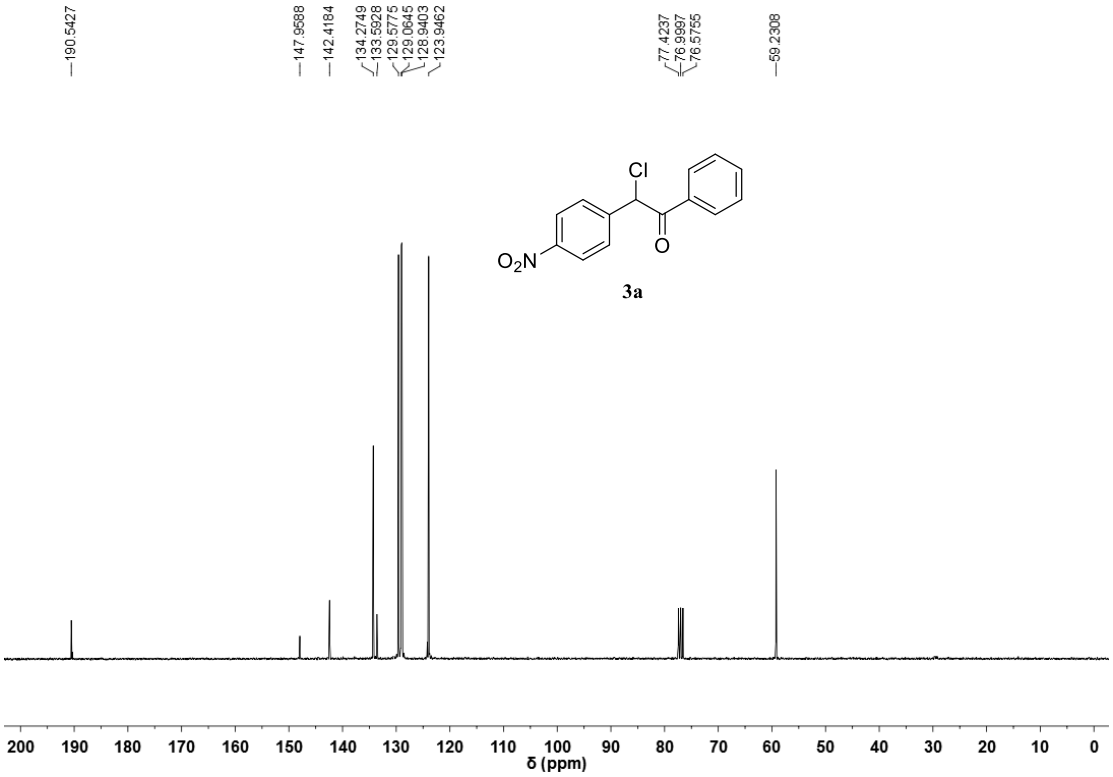
References

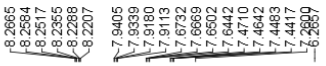
S1. Y. F. Chen, X. Q. Huang, S. H. Zhang, S. Q. Li, S. J. Cao, X. K. Pei, J. W. Zhou, X. Feng, B. Wang, *J. Am. Chem. Soc.*, 2016, **138**, 10810.

S2. T. Niu, D. Jiang, S. Li, B. Ni, L. Wang, *Chem. Commun*., 2016, **52**, 13105.

Copies of ^{1}H and ^{13}C NMR Spectra



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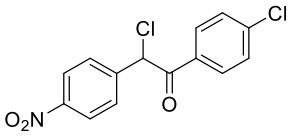
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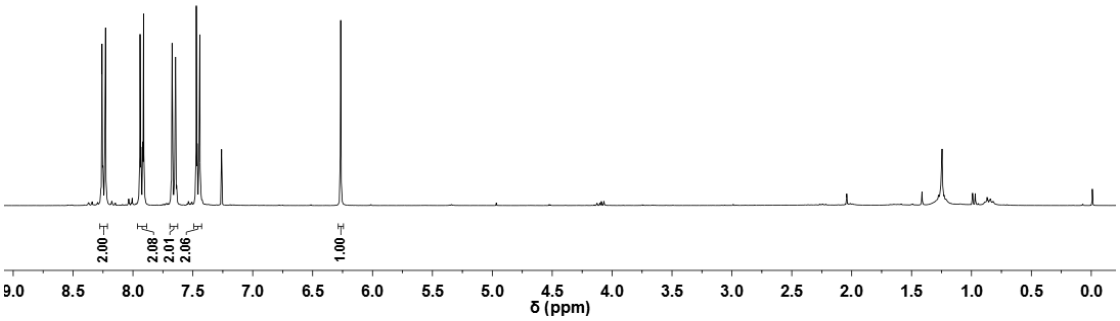
O2N

3b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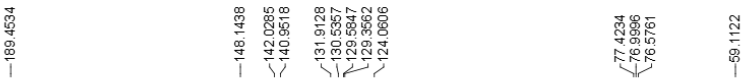
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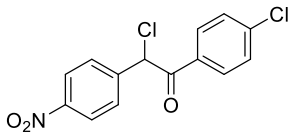
Cl
Cl
O
O2N

3b

190
180
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140
130
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100
90
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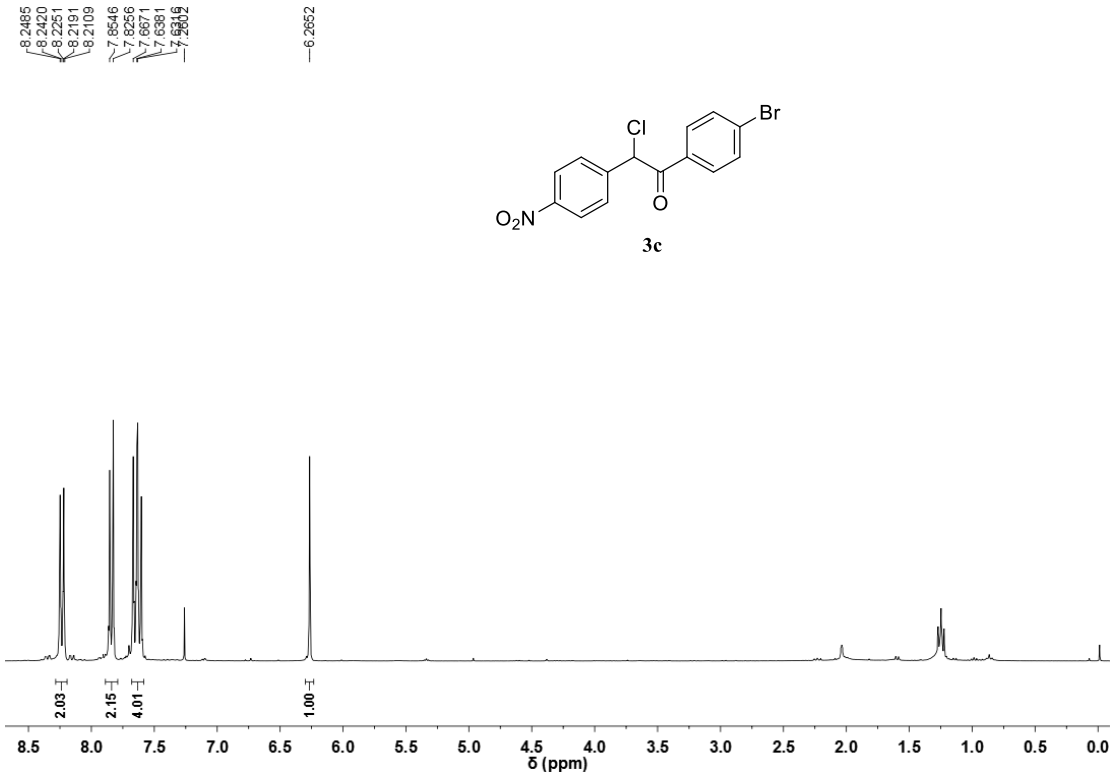
60
50
40
30
20
10
0
δ (ppm)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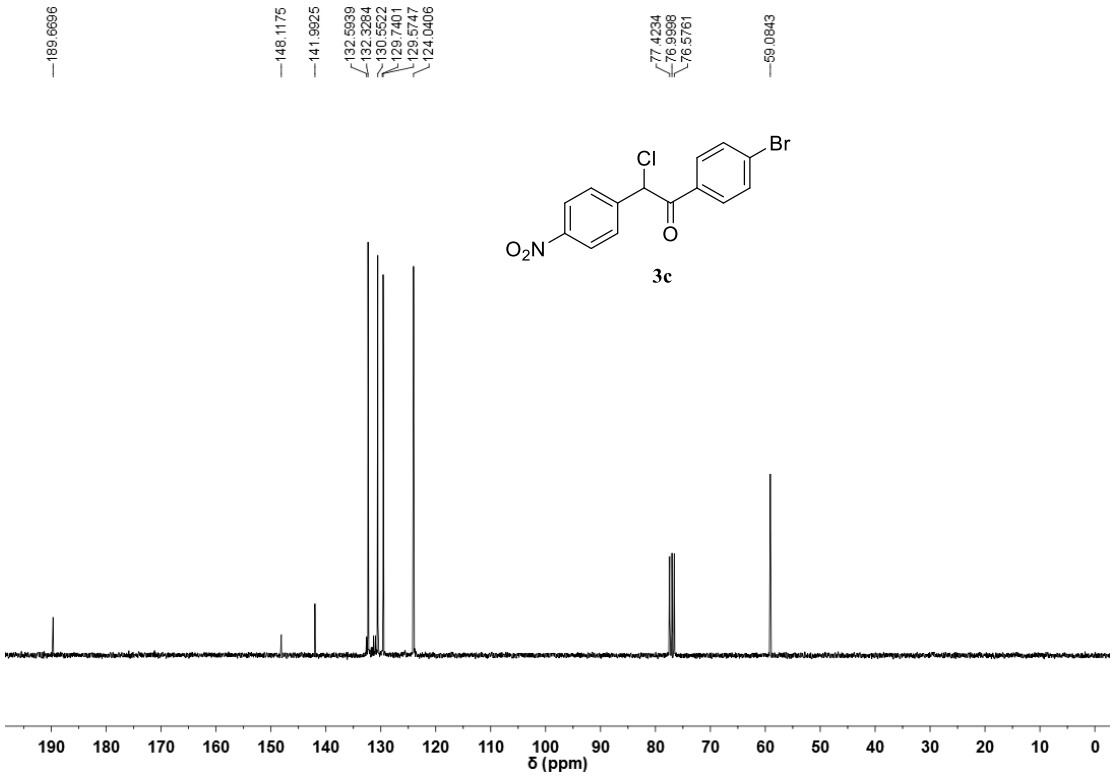
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δ (ppm)


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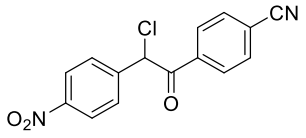
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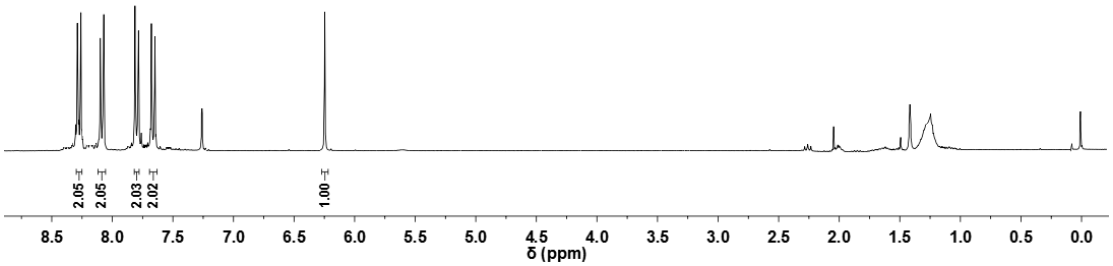
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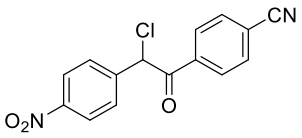
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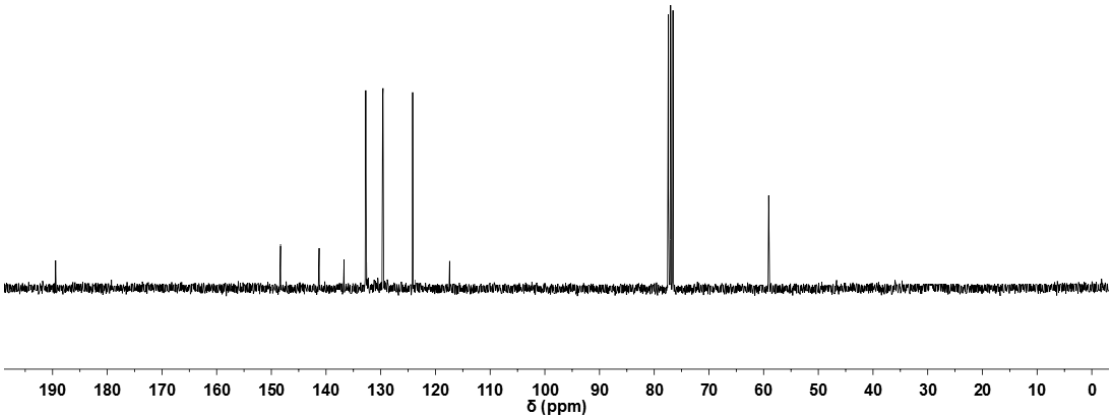
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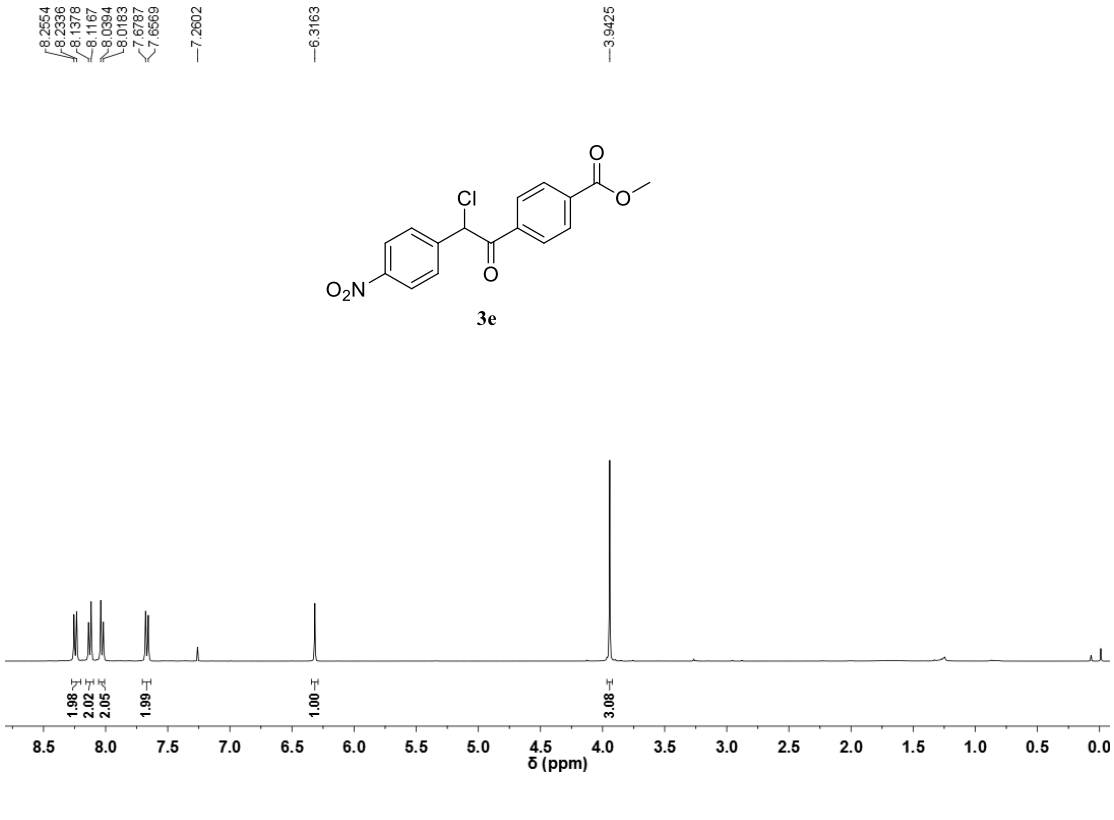
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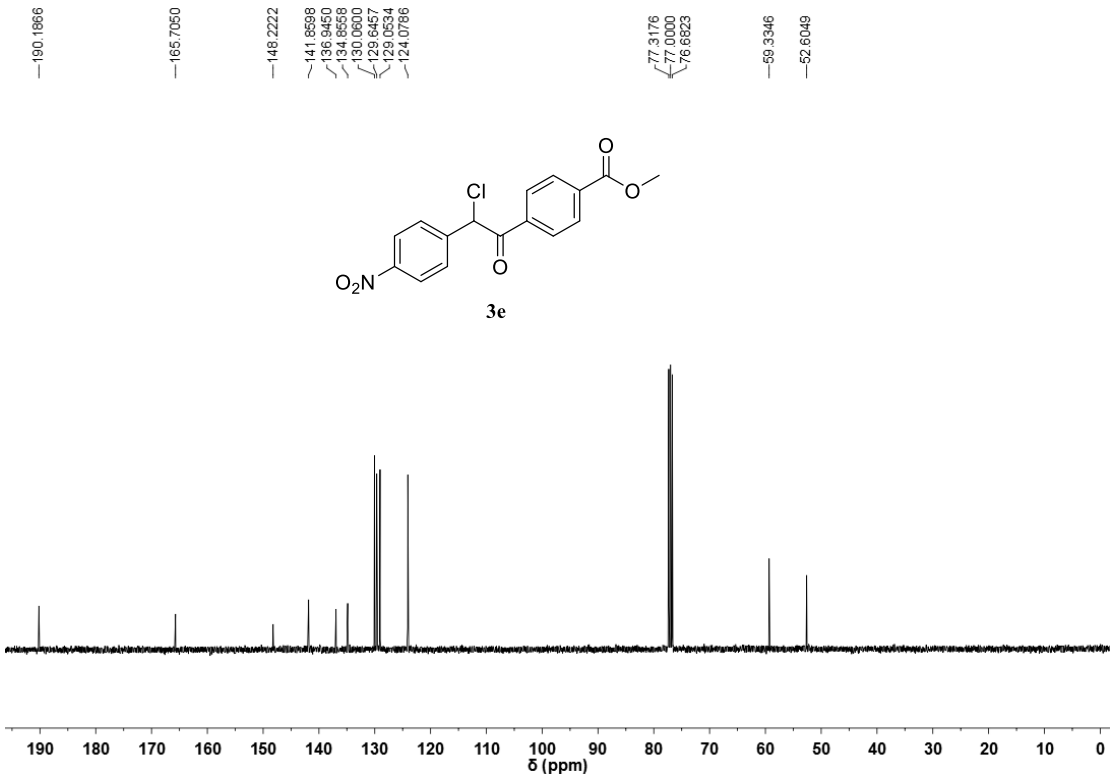
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O2N
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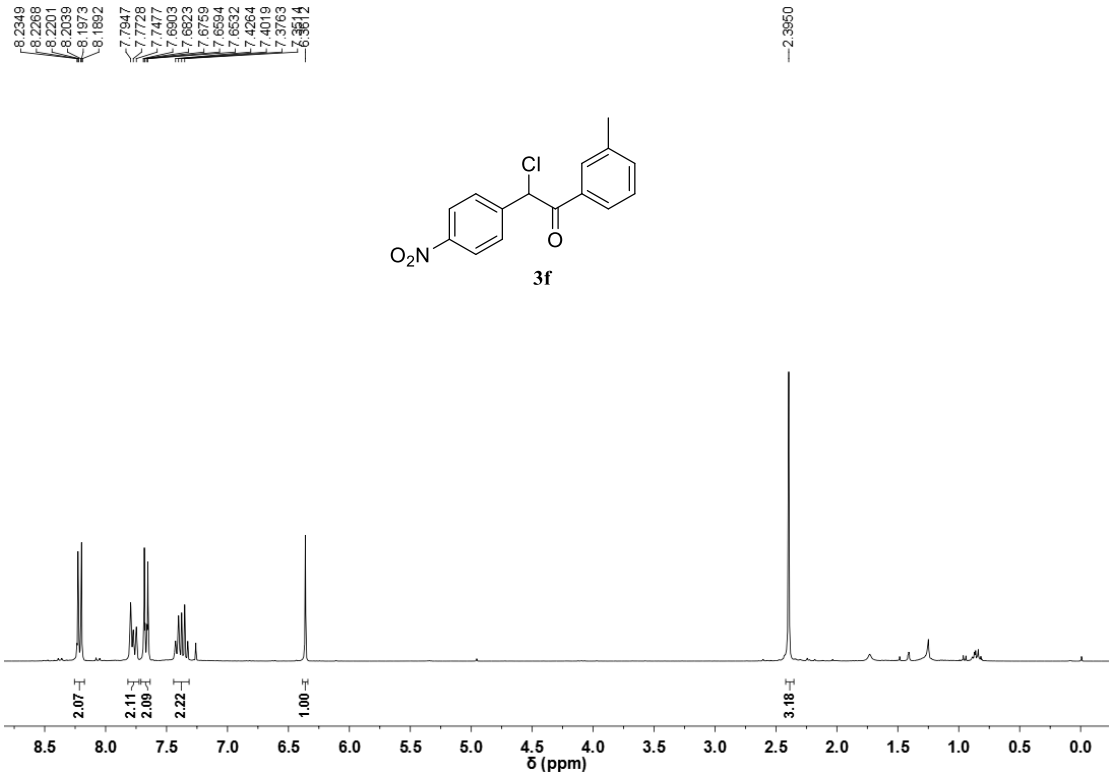
3e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O2N
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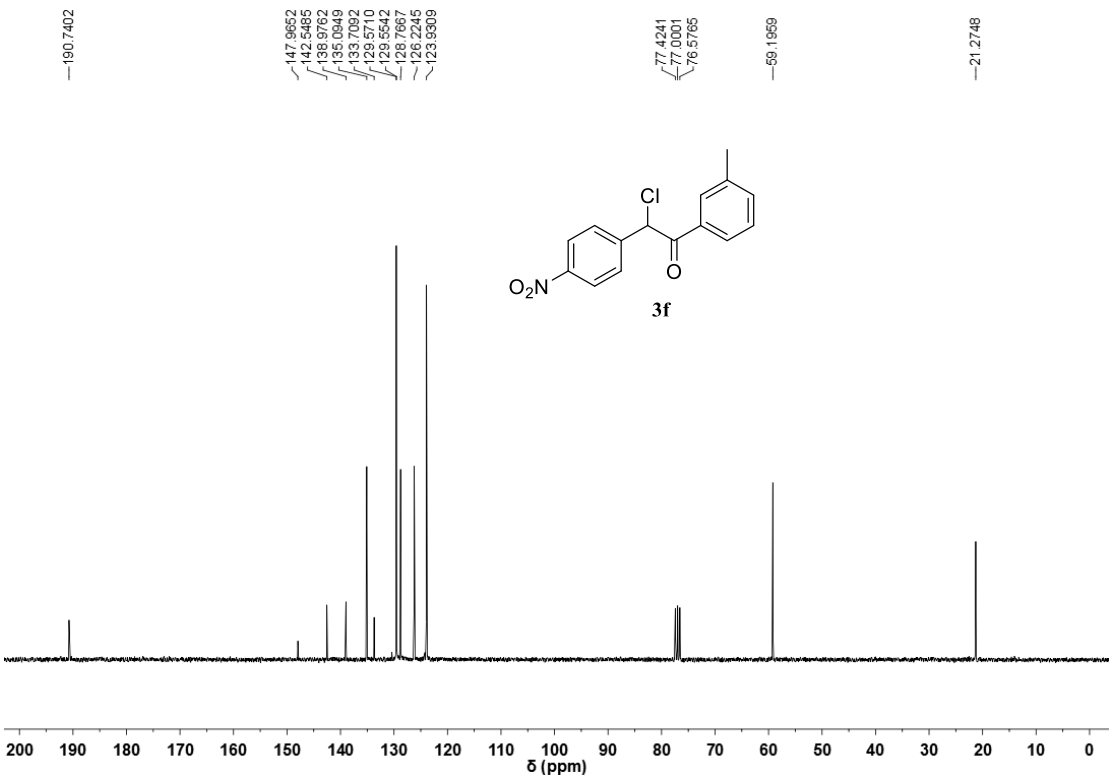
δ (ppm)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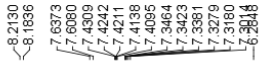
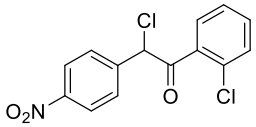
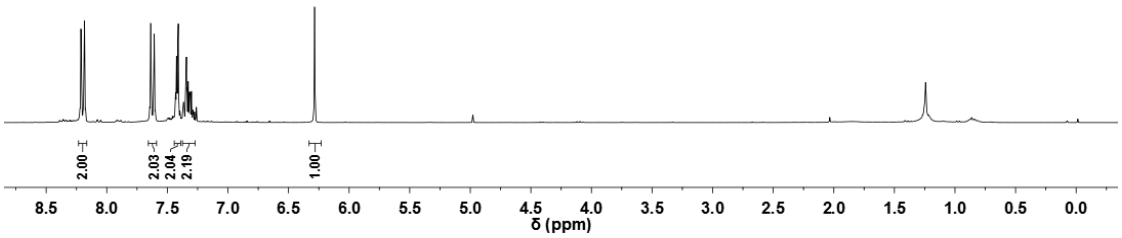
3f
δ (ppm)


8.2130
8.1836
7.6373
7.6080
7.4309
7.4242
7.4211
7.4138
7.4095
7.3464
7.3423
7.3381
7.3279
7.3180
7.3014
7.2848


Cl
O
Cl
O2N

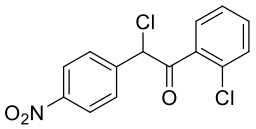
3g


2.00
2.03
2.04
2.19
1.00
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
0.0
δ (ppm)

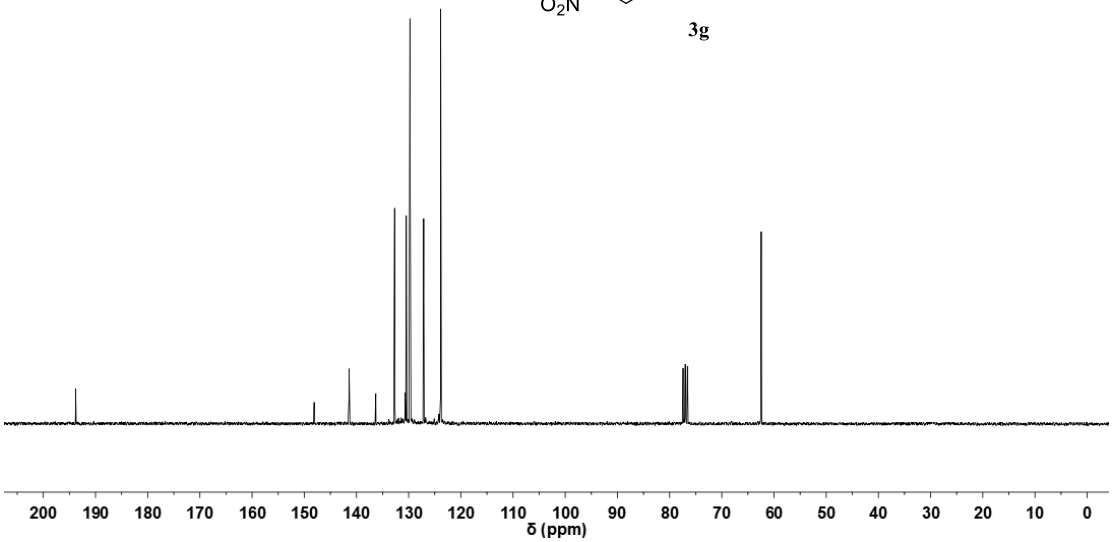

193.8060

148.1056
141.4207
136.2956
132.6882
130.6992
130.4590
129.7452
129.6933
127.1139
123.8663

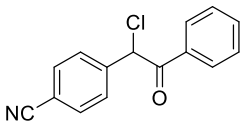

77.4243
77.0002
76.5764
62.4479


Cl
O
Cl
O2N

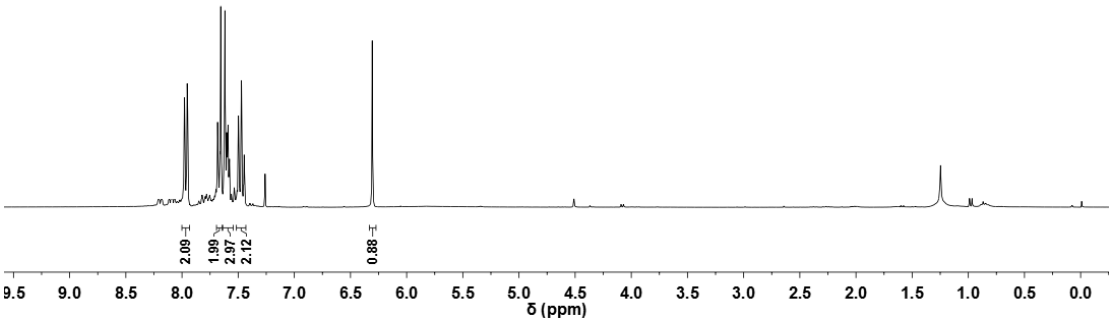
3g

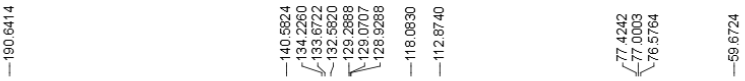

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

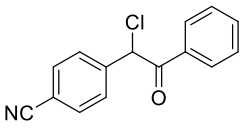

7.9780
7.9540
7.9492
7.6974
7.6832
7.6775
7.6616
7.6551
7.6179
7.6110
7.6022
7.5955
7.5898
7.5817
7.5774
7.5738
7.4973
7.4710
7.4516
7.4464
6.3064


Cl
O
NC

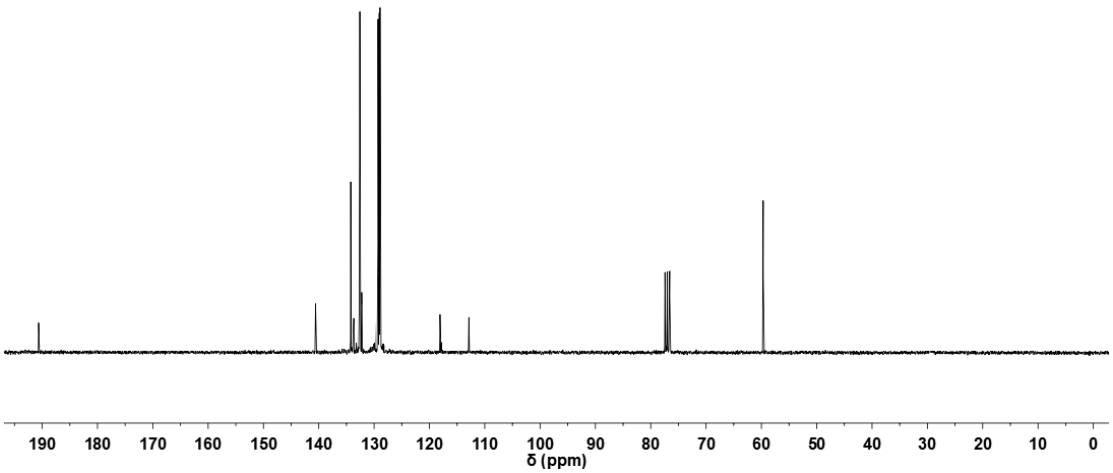
3h

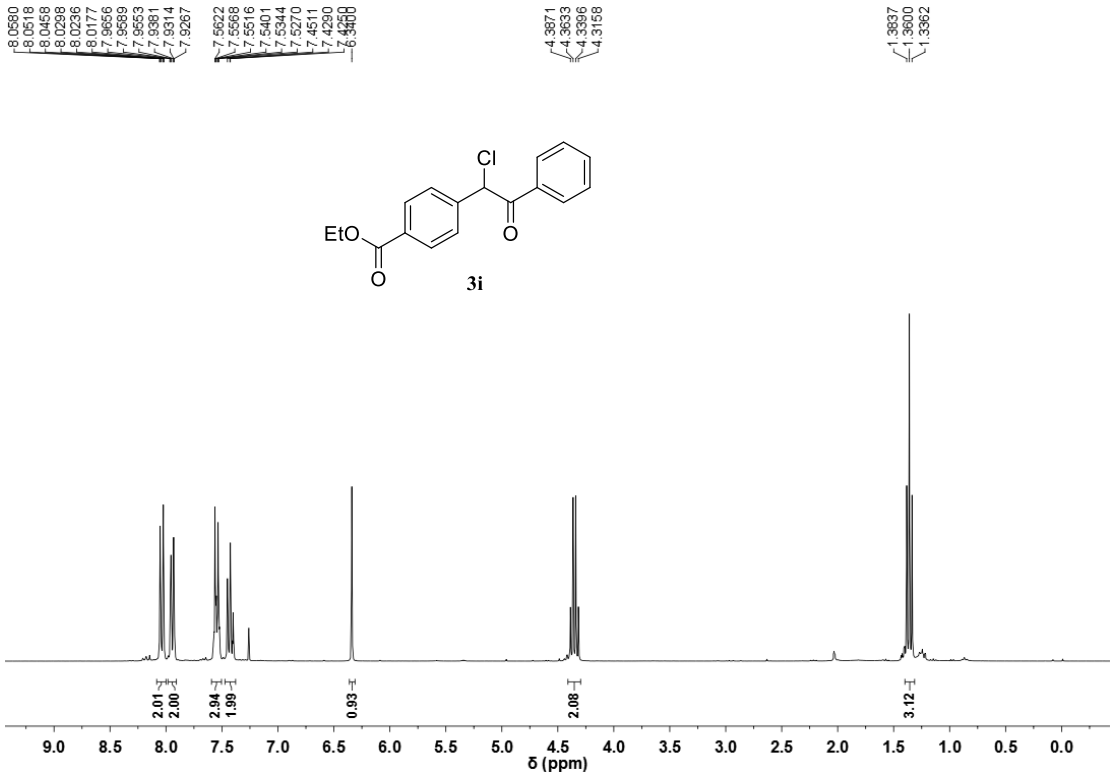

2.09
1.99
2.97
2.12
0.88
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

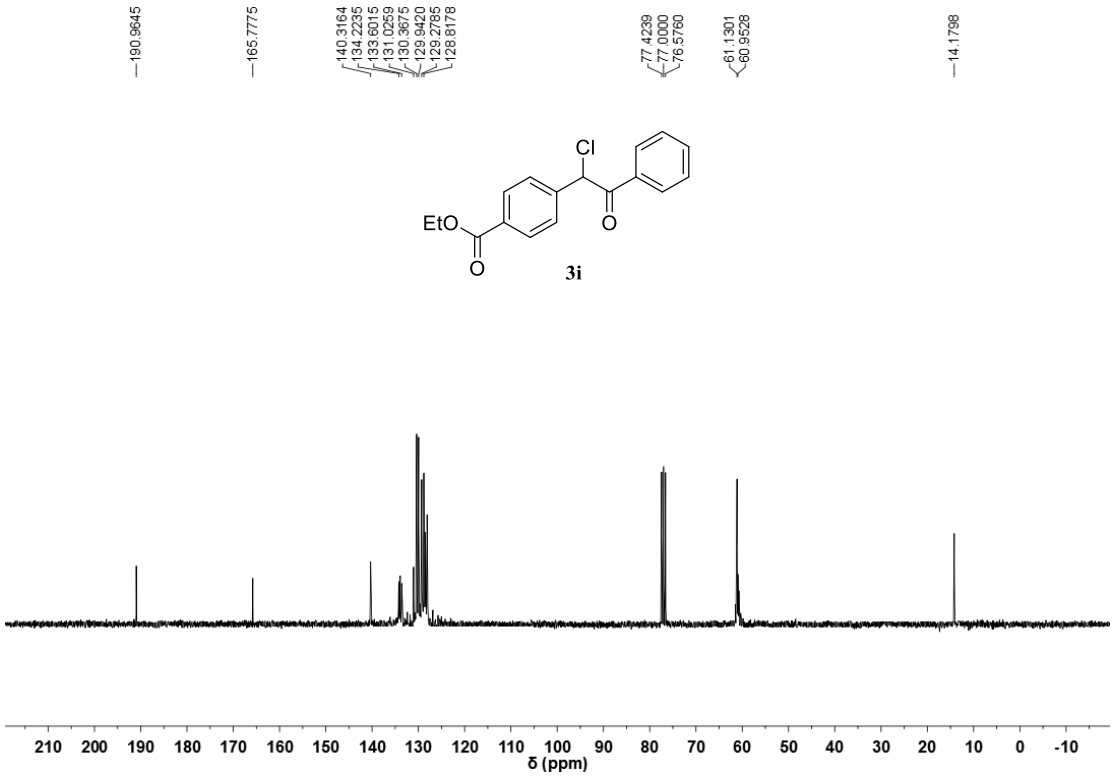

190.6414
140.5824
134.2260
133.6722
132.5820
129.2888
129.0707
128.9288
118.0830
112.8740
77.4242
77.0003
76.5764
59.6724


Cl
O
NC

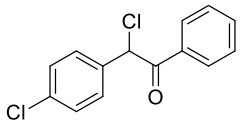
3h


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

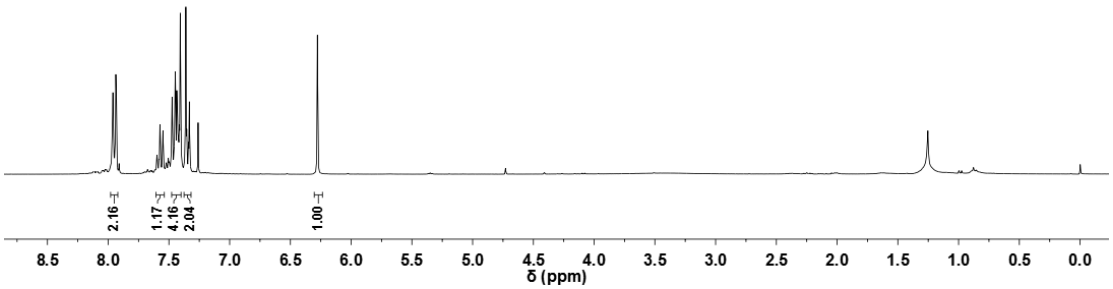

8.0580
8.0518
8.0458
8.0298
8.0236
8.0177
7.9656
7.9589
7.9553
7.9381
7.9314
7.9267
7.5622
7.5568
7.5516
7.5401
7.5344
7.5270
7.4511
7.4290
6.3400
4.3871
4.3633
4.3396
4.3158
1.3837
1.3600
1.3362
Cl
EtO
O
O
3i
2.01
2.00
2.94
1.99
0.93
2.08
3.12
δ (ppm)


190.9645
165.7775
140.3164
134.2235
133.8015
131.0259
130.3675
129.9420
128.2785
128.8178
77.4239
77.0000
76.5760
61.1301
60.9528
14.1798
Cl
EtO
O
O
3i
δ (ppm)


7.9778
7.9609
7.9499
7.9433
7.9371
7.9322
7.5738
7.4738
7.4515
7.4477
7.4353
7.4289
7.4234
7.4066
7.3606
7.3317
7.2596
6.2776


Cl
Cl
O

3j

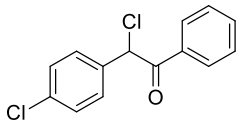

2.16
1.17
4.16
2.04
1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)


191.1169

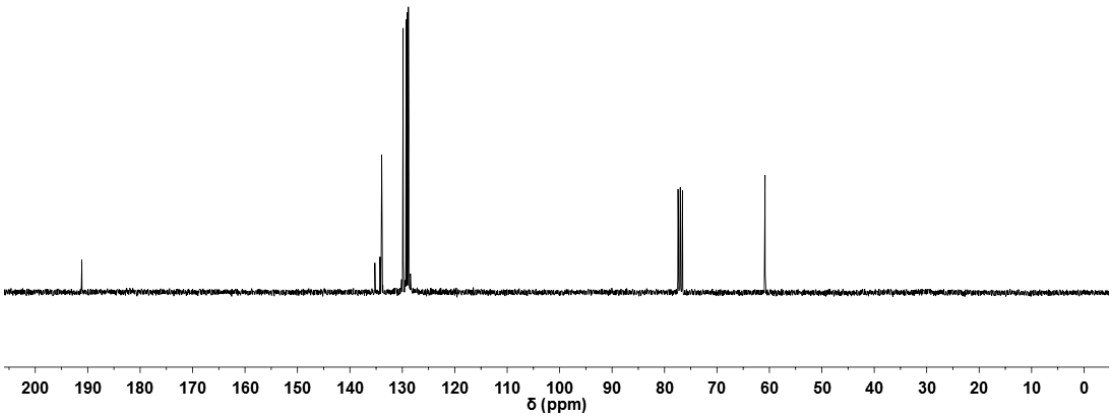
135.2283
134.2577
134.0017
133.9296
129.8438
129.2837
129.0701
128.8435

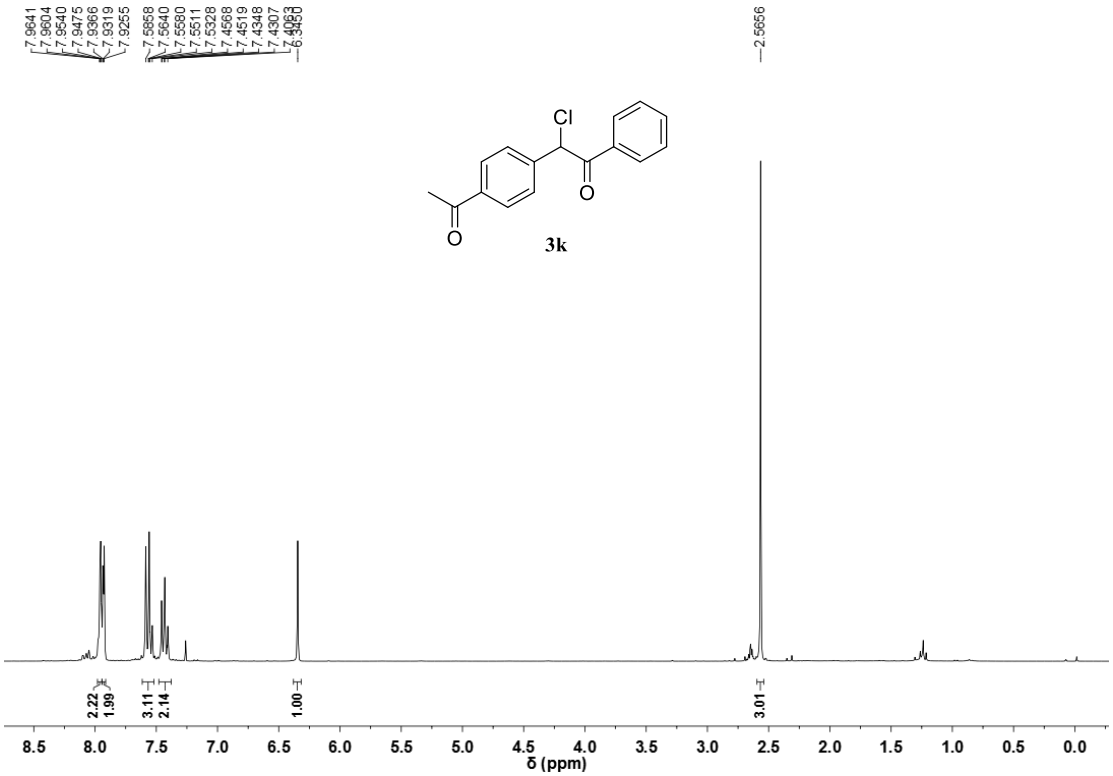

77.4238
77.0004
76.5767

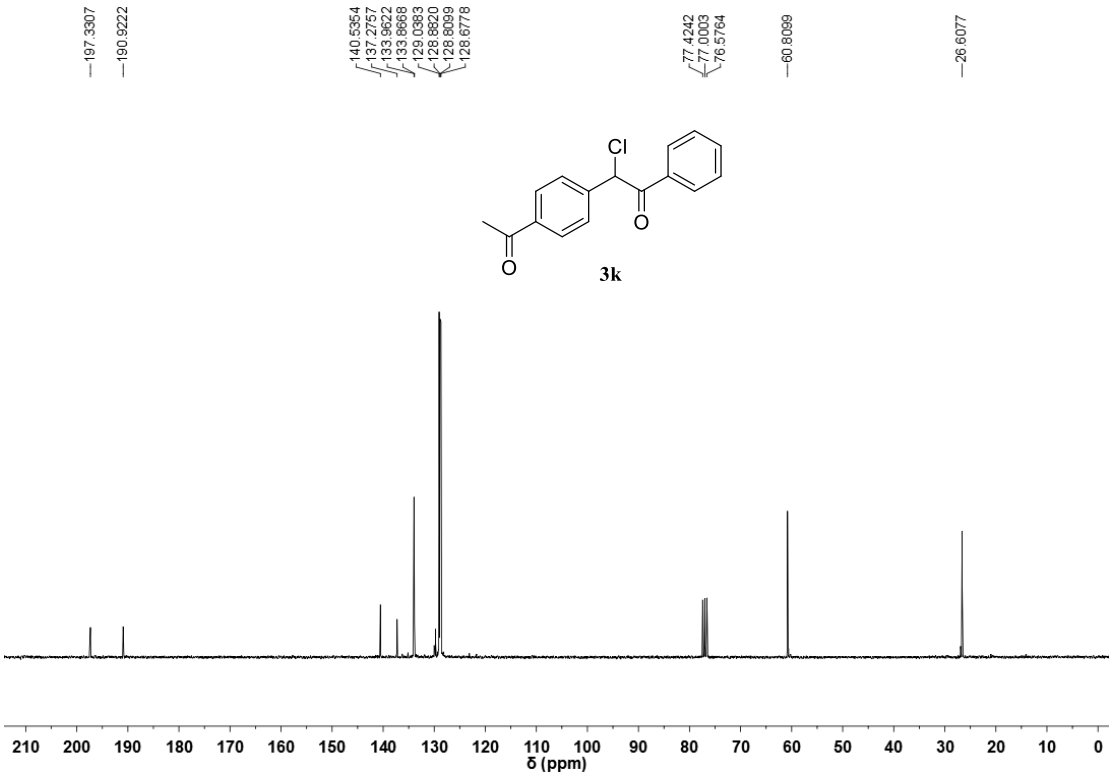
60.8237

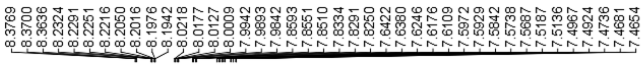

Cl
Cl
O

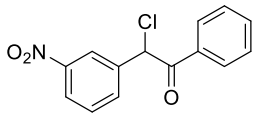
3j


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

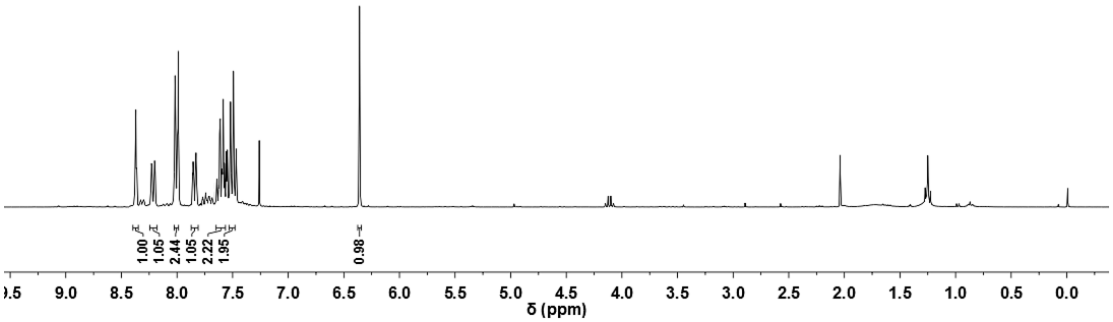

7.9641
7.9604
7.9540
7.9475
7.9366
7.9319
7.9255
7.5858
7.5640
7.5580
7.5511
7.5328
7.4568
7.4519
7.4348
7.4307
6.3450
2.5656
Cl
O
O
3k
2.22
1.99
3.11
2.14
1.00
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

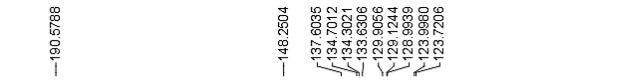

197.3307
190.9222
140.5354
137.2757
133.9622
133.8668
129.0383
128.8820
128.8099
128.6778
77.4242
77.0003
76.5764
60.8099
26.6077
Cl
O
O
3k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

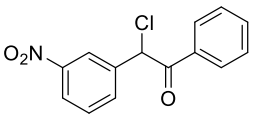

8.3769
8.3700
8.3636
8.2324
8.2291
8.2251
8.2216
8.2050
8.2016
8.1976
8.1942
8.0218
8.0177
8.0127
8.0009
7.9942
7.9893
7.9842
7.8593
7.8551
7.8510
7.8334
7.8291
7.8250
7.6422
7.6380
7.6246
7.6176
7.6109
7.5972
7.5929
7.5842
7.5738
7.5687
7.5187
7.5136
7.4967
7.4924
7.4736
7.4681
7.4654


Cl
O2N
O

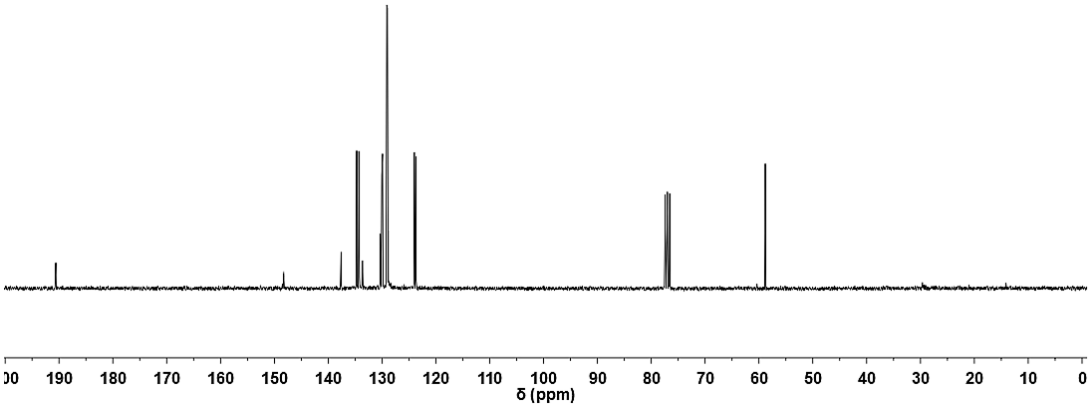
3l


1.00
1.05
2.44
1.05
2.22
1.95
0.98
δ (ppm)


190.5788
148.2504
137.6035
134.7012
134.3021
133.6306
129.9056
129.1244
128.9939
123.9960
123.7206
77.4242
77.0002
76.5768
58.8291


Cl
O2N
O

3l


δ (ppm)