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Rongalite-promoted synthesis of β-keto sulfones *via* radical cascade reaction

Min-xiao Xu and Kai-ming Zhang

Contents

General experimental

Unless otherwise noted, all chemicals were purchased from commercial suppliers (Aladdin) and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance III 400 analyzer in $CDCl_3$ or DMSO-d_6 using TMS as an internal standard. Chemical shifts are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ or DMSO-d_6 as the internal standard. The coupling constants *J* are given in Hz. Mass spectrometry was performed on an LCMS-2010 EV (Shimadzu) instrument with an ESI source. Column chromatography was performed using EM Silica gel 60 (300-400 mesh). All the products are known compounds and were identified by comparing their physical and spectra data with those reported in the literature.

Experimental procedures, spectral and analytical data

General procedure for the synthesis of 3a-n

A sealed tube equipped with a magnetic stirrer bar was charged with aryl iodide **1** (0.3 mmol), $Na_2S_2O_5$ (0.6 mmol, 114 mg), alkene **2** (0.2 mmol), rongalite (0.6 mmol, 93 mg), KOH (0.6 mmol, 34 mg) and DMSO/H_2O (2:1, 2 ml). The reaction mixture was then heated to 80 °C and stirred overnight under air. Upon reaction completion, the resulting solution was quenched with water and extracted by ethyl acetate. The collected organic extracts were dried over Na_2SO_4. The solvent was then removed under reduced pressure and the residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (8:1, *v*/*v*) as eluent to afford product **3a-n**.

Characterization data of products 3

2-((4-Nitrophenyl)sulfonyl)-1-phenylethan-1-one (**3a**).[S1] Yellow solid (44 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.8 Hz, 2H), 8.14 (d, *J* = 8.8 Hz, 2H), 7.97 – 7.95 (m, 2H), 7.67 – 7.52 (m, 3H), 4.84 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 151.1, 144.1, 135.4, 134.9, 130.3, 129.2, 129.1, 124.3, 63.0. MS-ESI: *m/z* = 328.0 $[M + Na]^+$.

1-Phenyl-2-tosylethan-1-one (**3b**).[S2] White solid (39 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.74 (s, 2H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 145.4, 135.8 (overlapped), 134.3, 129.8, 129.4, 128.9, 128.6, 63.6, 21.7. MS-ESI: *m/z* = 297.1 $[M + Na]^+$.

2-((4-Methoxyphenyl)sulfonyl)-1-phenylethan-1-one (**3c**).[S3] Yellow solid (44 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.86 (m, 2H), 7.82 (d, *J* = 9.0 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 9.0 Hz, 2H), 4.74 (s, 2H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3, 164.2, 135.8, 134.3, 130.9, 130.2, 129.3, 128.8, 114.4, 63.8, 55.7. MS-ESI: *m/z* = 313.0 $[M + Na]^+$.

2-((4-Bromophenyl)sulfonyl)-1-phenylethan-1-one (**3d**).[S4] Yellow solid (43 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 2H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.75 – 7.64 (m, 3H), 7.52 (t, *J* = 7.8 Hz, 2H), 4.76 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.9, 137.7, 135.6, 135.5, 132.5, 130.2, 129.8, 129.3, 129.0, 63.3. MS-ESI: *m/z* = 360.9 $[M + Na]^+$.

2-((4-Chlorophenyl)sulfonyl)-1-phenylethan-1-one (**3e**).[S2] White solid (42 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.4 Hz, 2H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.59 – 7.45 (m, 4H), 4.77 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.9, 141.1, 137.1, 135.6, 134.6, 130.2, 129.5, 129.3, 129.0, 63.4. MS-ESI: *m/z* = 317.0 $[M + Na]^+$.

((2-Chlorophenyl)sulfonyl)-1-phenylethan-1-one (**3f**).[S5] White solid (30 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.06 (m, 1H), 7.96 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.65 – 7.57 (m, 3H), 7.54 – 7.45 (m, 3H), 5.08 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.8, 136.5, 135.8, 135.2, 134.5, 132.7, 132.1, 131.9, 129.2, 128.9, 127.5, 61.0. MS-ESI: *m/z* = 317.0 $[M + Na]^+$.

((3-Chlorophenyl)sulfonyl)-1-phenylethan-1-one (**3g**).[S6] White solid (34 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.91 (m, 3H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 3H), 4.78 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.7, 140.4, 135.6, 135.5, 134.6, 134.4, 130.5, 129.2, 129.0, 128.7, 126.9, 63.3. MS-ESI: *m/z* = 317.0 $[M + Na]^+$.

Ethyl-4-((2-oxo-2-phenylethyl)sulfonyl)benzoate (**3h**).[S6] White solid (46 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.6 Hz, 2H), 8.08 – 7.95 (m, 4H), 7.69 – 7.62 (m, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 4.80 (s, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.8, 158.7, 142.3, 136.1, 135.6, 134.6, 130.3, 129.3, 129.0, 128.7, 63.3, 61.8, 14.2. MS-ESI: *m/z* = 355.1 $[M + Na]^+$.

1-Phenyl-2-(pyridin-3-ylsulfonyl)ethan-1-one (**3i**).[S2] White solid (33 mg, 63%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.07 (d, *J* = 2.2 Hz, 1H), 8.91 (d, *J* = 3.9 Hz, 1H), 8.33 (d, *J* = 8.0 Hz, 1H), 8.07 – 7.89 (m, 2H), 7.80 – 7.63 (m, 2H), 7.53 (t, *J* = 7.8 Hz, 2H), 5.57 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 189.7, 154.8, 149.2, 136.9, 136.5, 136.0, 134.8, 129.4, 129.3, 124.6, 62.6. MS-ESI: *m/z* = 284.0 $[M + Na]^+$.

1-(4-Chlorophenyl)-2-((4-nitrophenyl)sulfonyl)ethan-1-one (**3j**).[S5] White solid (47 mg, 70%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.44 (d, *J* = 8.9 Hz, 2H), 8.20 (d, *J* = 8.9 Hz, 2H), 7.96 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 5.56 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 188.5, 151.0, 145.0, 140.0, 134.5, 131.3, 130.4, 129.4, 124.8, 62.3. MS-ESI: *m/z* = 362.0 $[M + Na]^+$.

2-((4-Nitrophenyl)sulfonyl)-1-(p-tolyl)ethan-1-one (**3k**).[S3] White solid (47 mg, 74%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.45 (d, *J* = 8.9 Hz, 2H), 8.21 (d, *J* = 8.9 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 5.56 (s, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 188.9, 151.0, 145.6, 145.4, 133.5, 130.3, 129.8, 129.6, 124.8, 62.2, 21.7. MS-ESI: *m/z* = 342.0 $[M + Na]^+$.

1-(4-Methoxyphenyl)-2-((4-nitrophenyl)sulfonyl)ethan-1-one (**3l**).[S3] Yellow solid (52 mg, 77%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.45 (d, *J* = 8.8 Hz, 2H), 8.20 (d, *J* = 8.8 Hz, 2H), 7.95 (d, *J* = 8.9 Hz, 2H), 7.05 (d, *J* = 8.9 Hz, 2H), 5.53 (s, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 187.6, 164.6, 151.0, 145.4, 132.1, 130.3, 128.9, 124.8, 114.6, 62.1, 56.2. MS-ESI: *m/z* = 358.0 $[M + Na]^+$.

((4-Nitrophenyl)sulfonyl)-1-(m-tolyl)ethan-1-one (**3m**).[S3] White solid (43 mg, 68%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.45 (d, *J* = 8.9 Hz, 2H), 8.21 (d, *J* = 8.9 Hz, 2H), 7.76 (d, *J* = 6.4 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 5.59 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 189.6, 151.0, 145.3, 138.8, 136.0, 135.5, 130.4, 129.8, 129.2, 126.7, 124.8, 62.3, 21.2. MS-ESI: *m/z* = 342.0 $[M + Na]^+$.

2-((4-Nitrophenyl)sulfonyl)-1-(thiophen-2-yl)ethan-1-one (**3n**).[S5] White solid (37 mg, 60%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.45 (d, *J* = 8.9 Hz, 2H), 8.19 (d, *J* = 8.9 Hz, 2H), 8.10 (d, *J* = 4.7 Hz, 2H), 7.30 – 7.21 (m, 1H), 5.43 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 181.6, 151.1, 144.9, 143.1, 138.1, 137.2, 130.4, 129.6, 124.9, 62.5. MS-ESI: *m/z* = 334.0 $[M + Na]^+$.

References

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S2. X. Gong, Y. Ding, X. Fan and J. Wu, *Adv. Synth. Catal.*, 2017, **359**, 2999.
S3. M. Kumar, R. Ahmed, M. Singh, S. Sharma, T. Thatikonda and P. Singh, *J. Org. Chem.*, 2020, **85**, 716.
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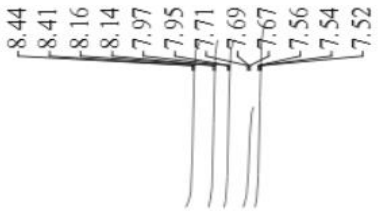
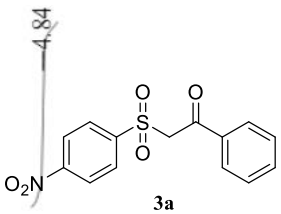
S5. B. Ni, B. Zhang, J. Han, B. Peng, Y. Shan and T. Niu, *Org. Lett.*, 2020, **22**, 670.
S6. J. Yu, R. Mao, Q. Wang and J. Wu, *Org. Chem. Front.*, 2017, **4**, 617.

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





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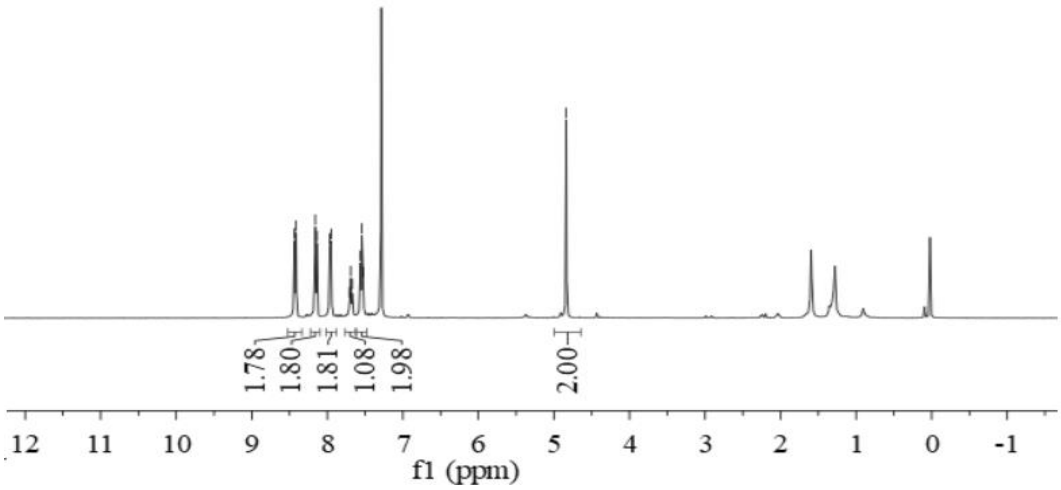

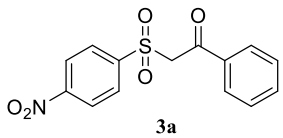

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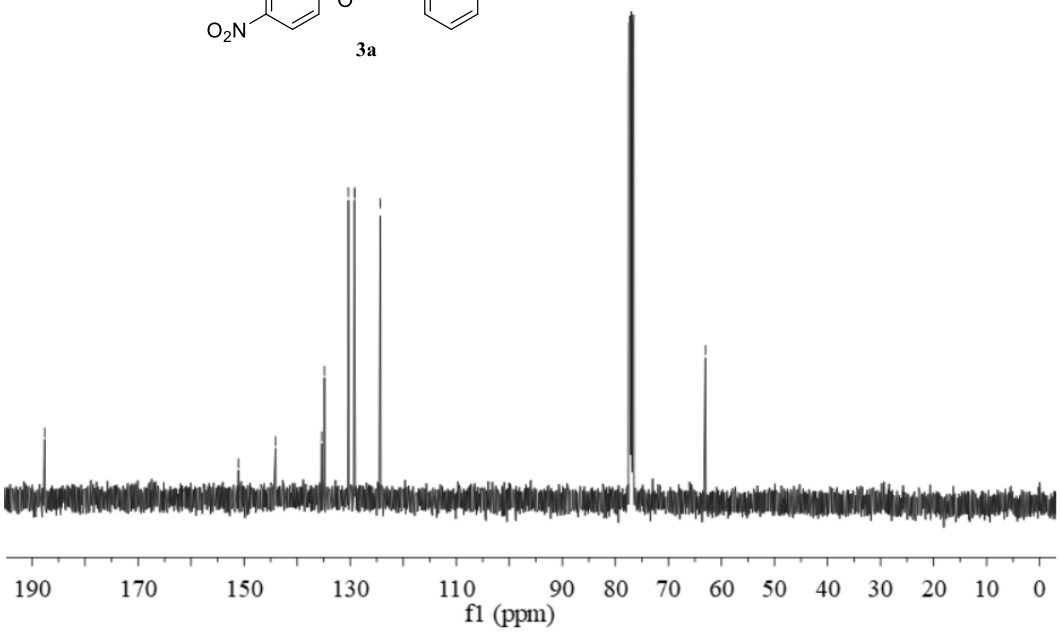

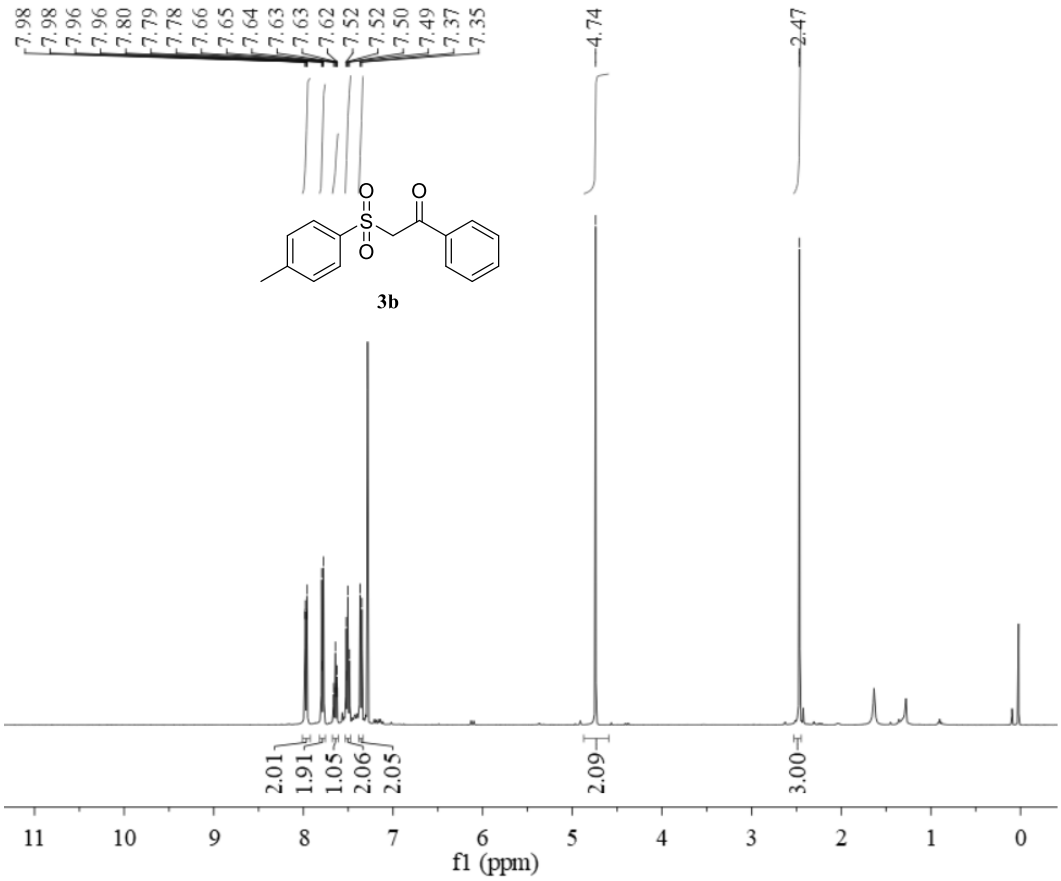
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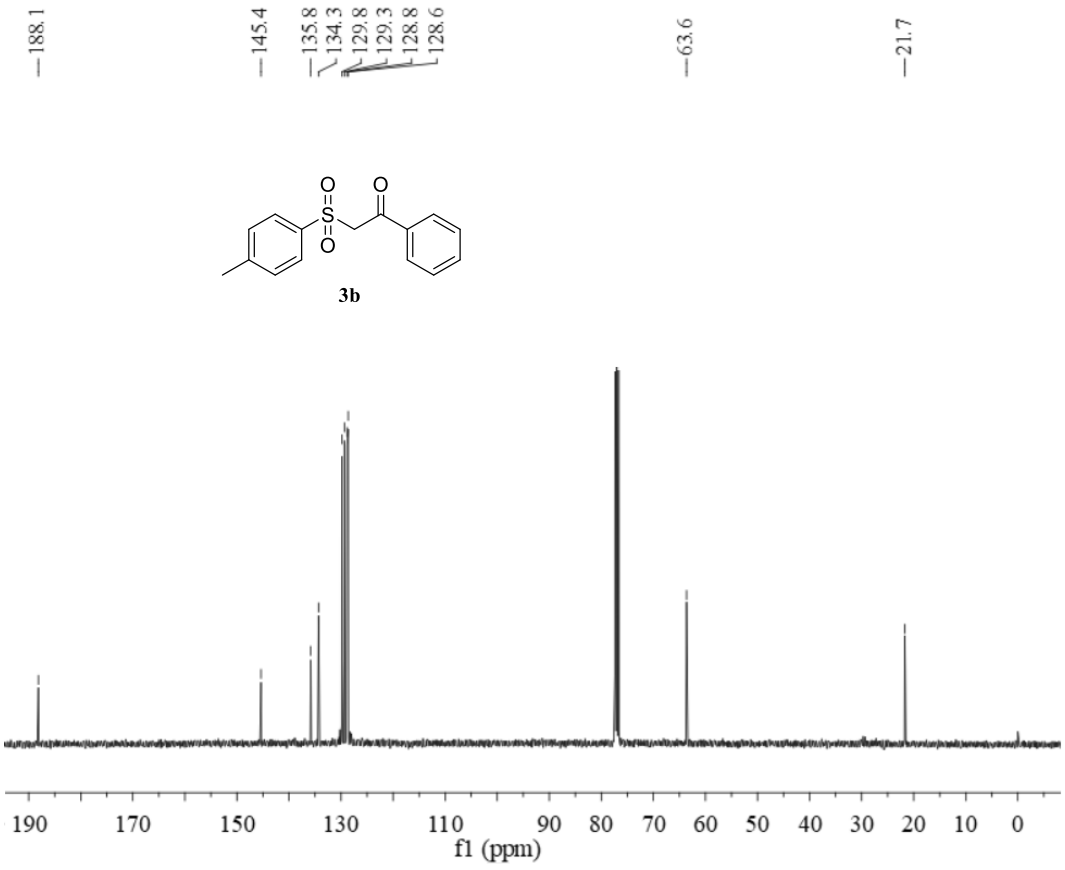
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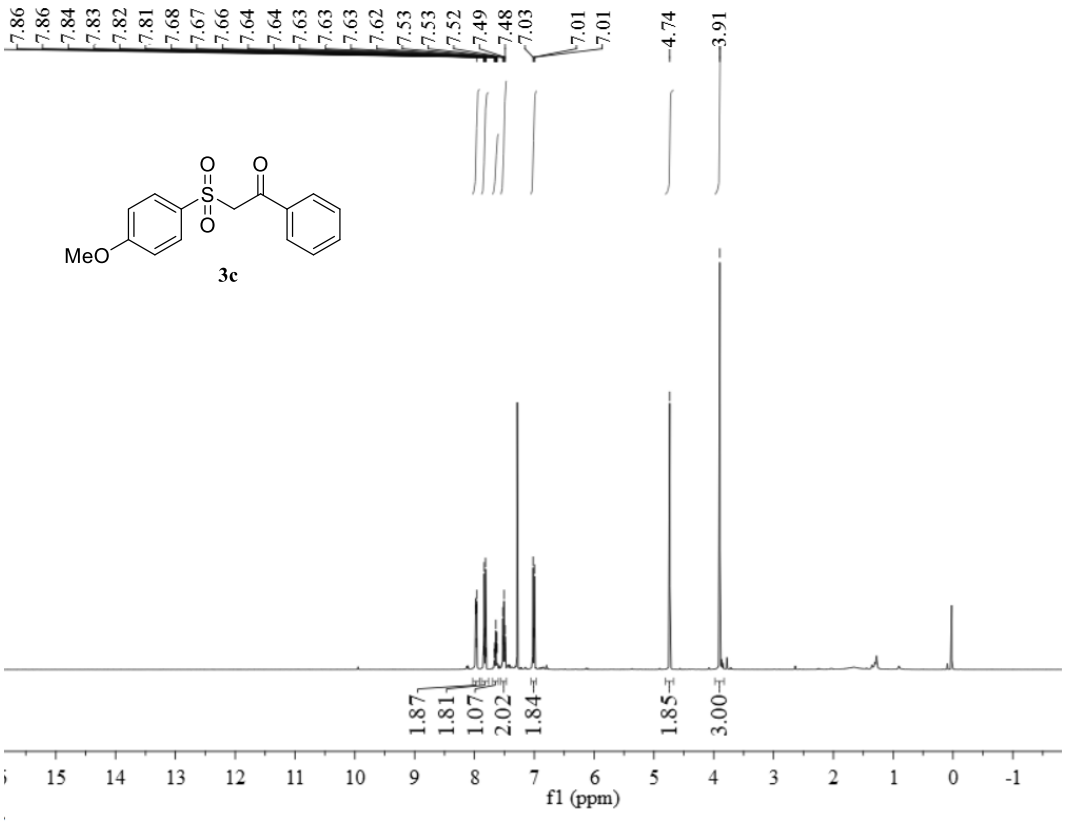
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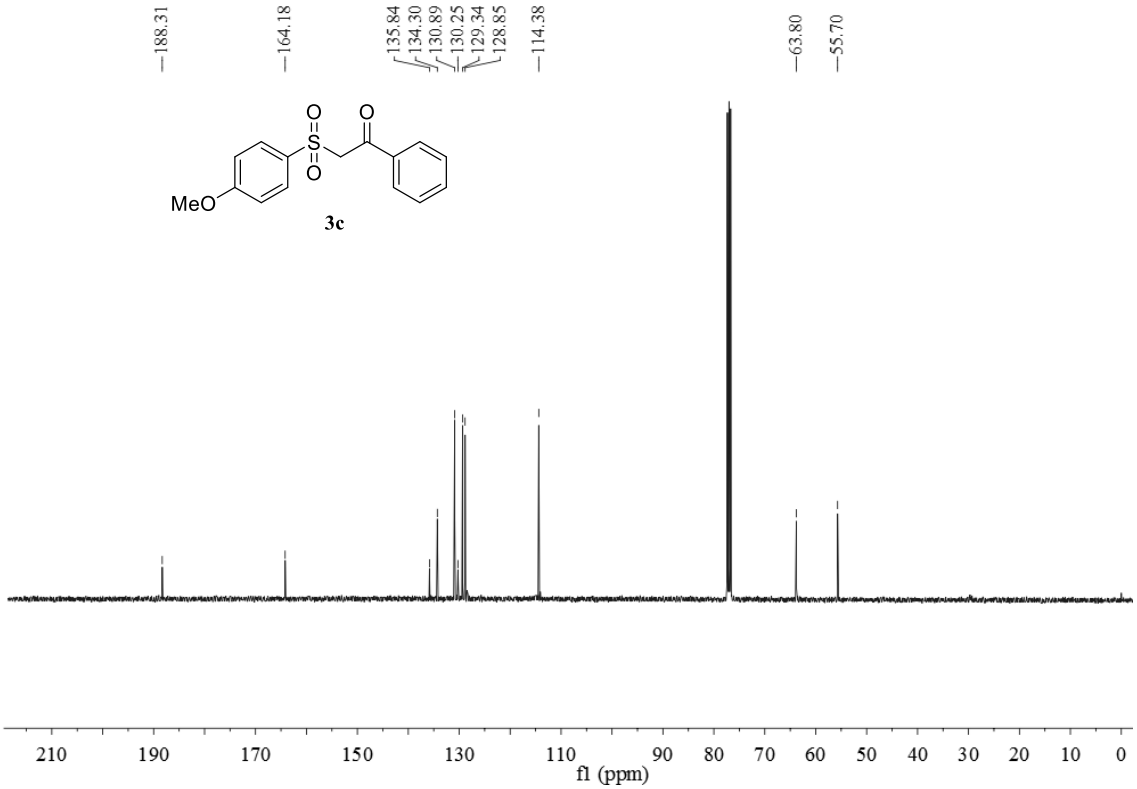
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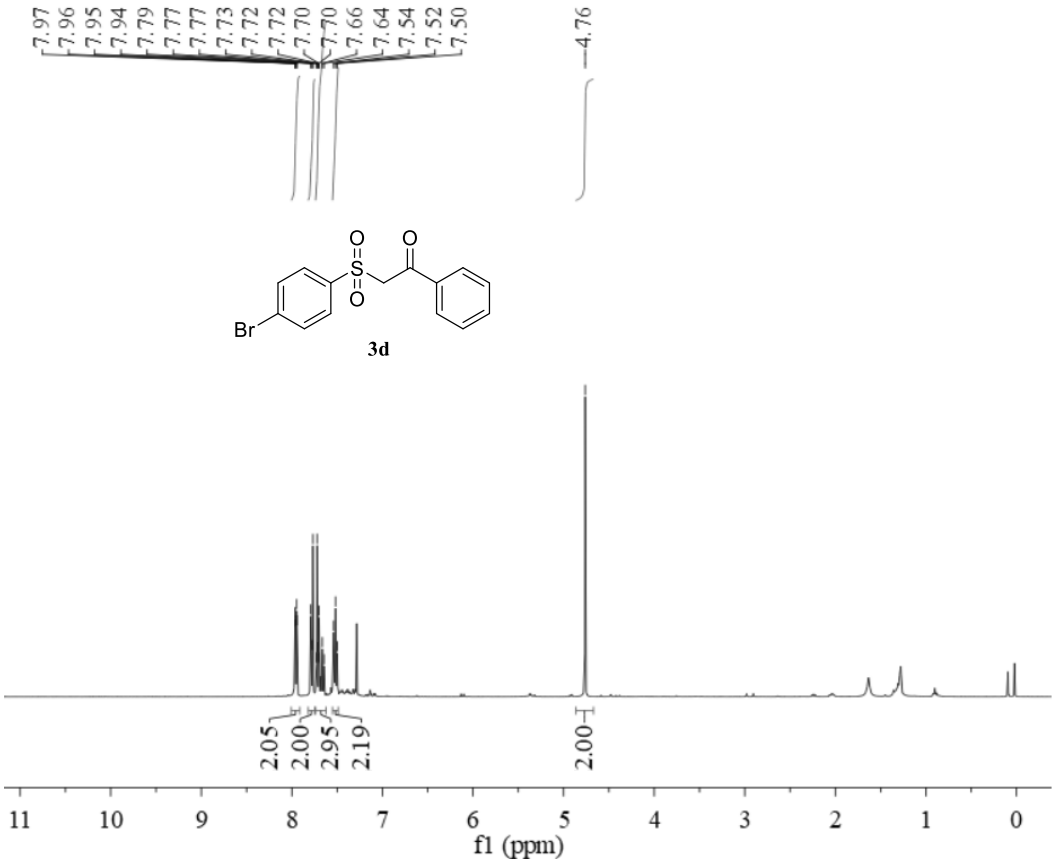
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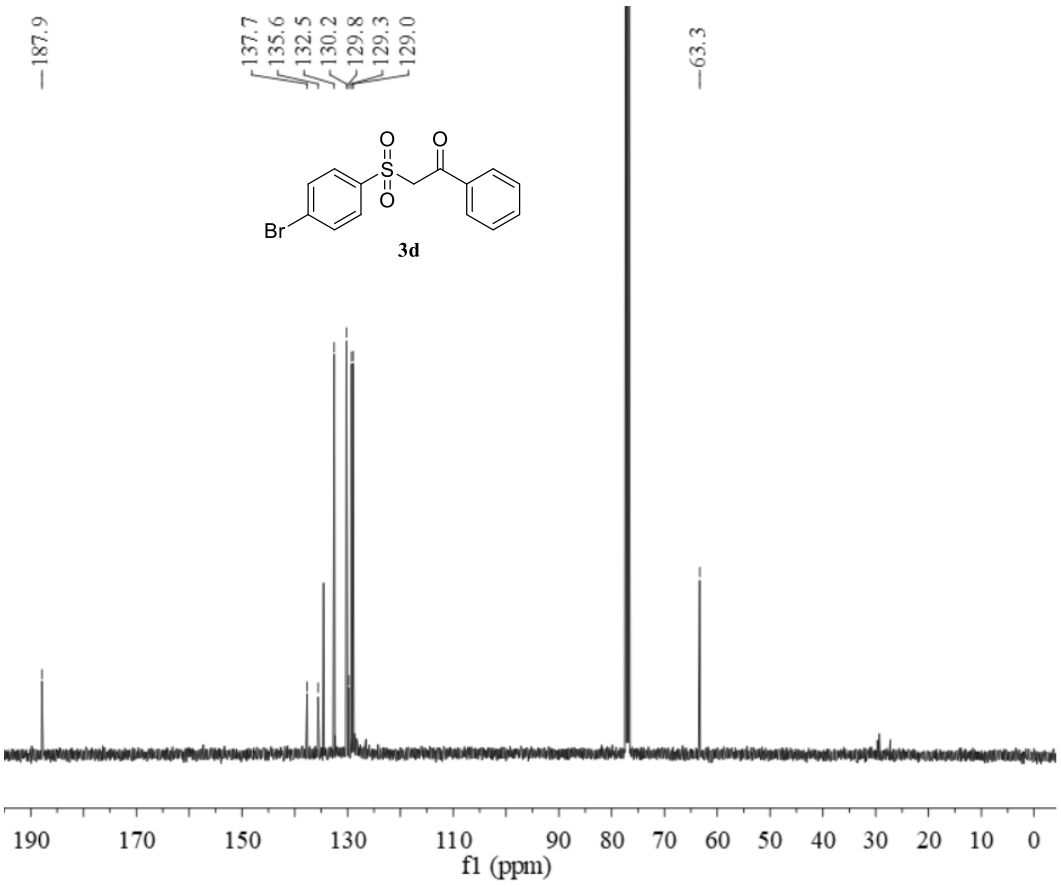
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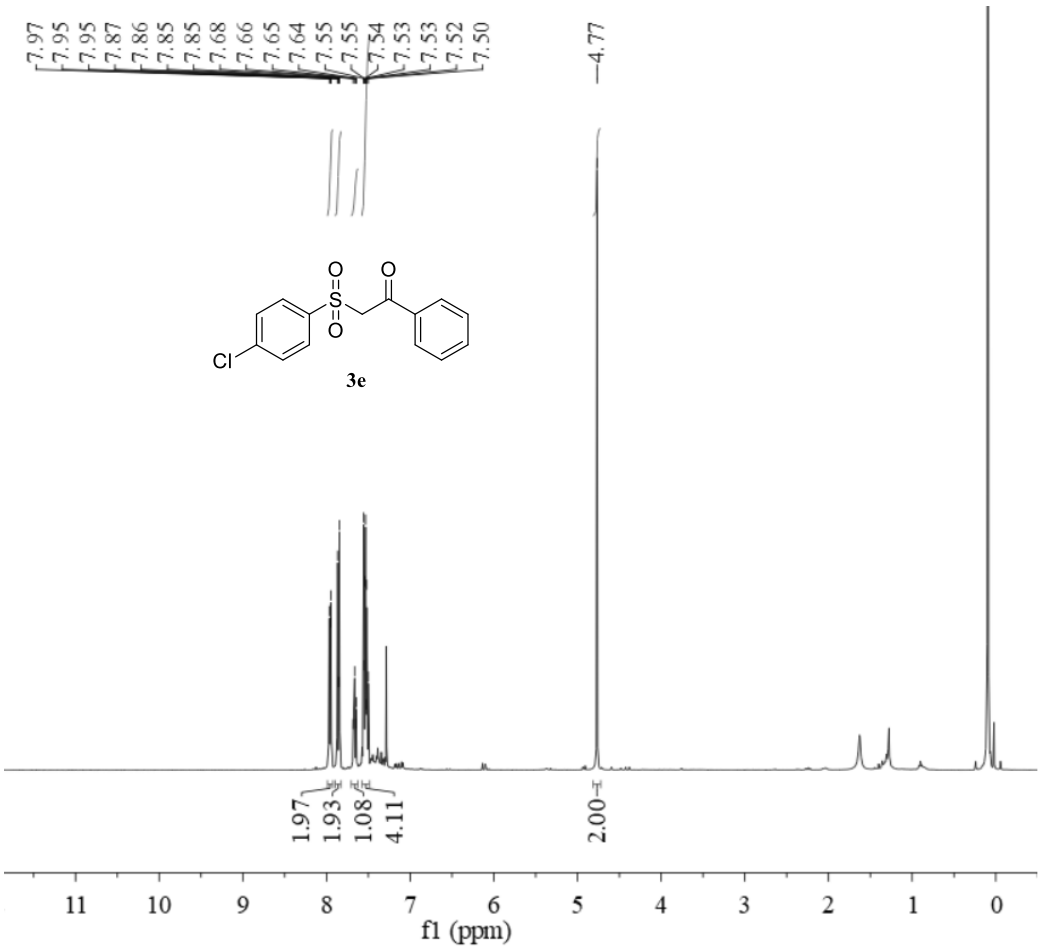
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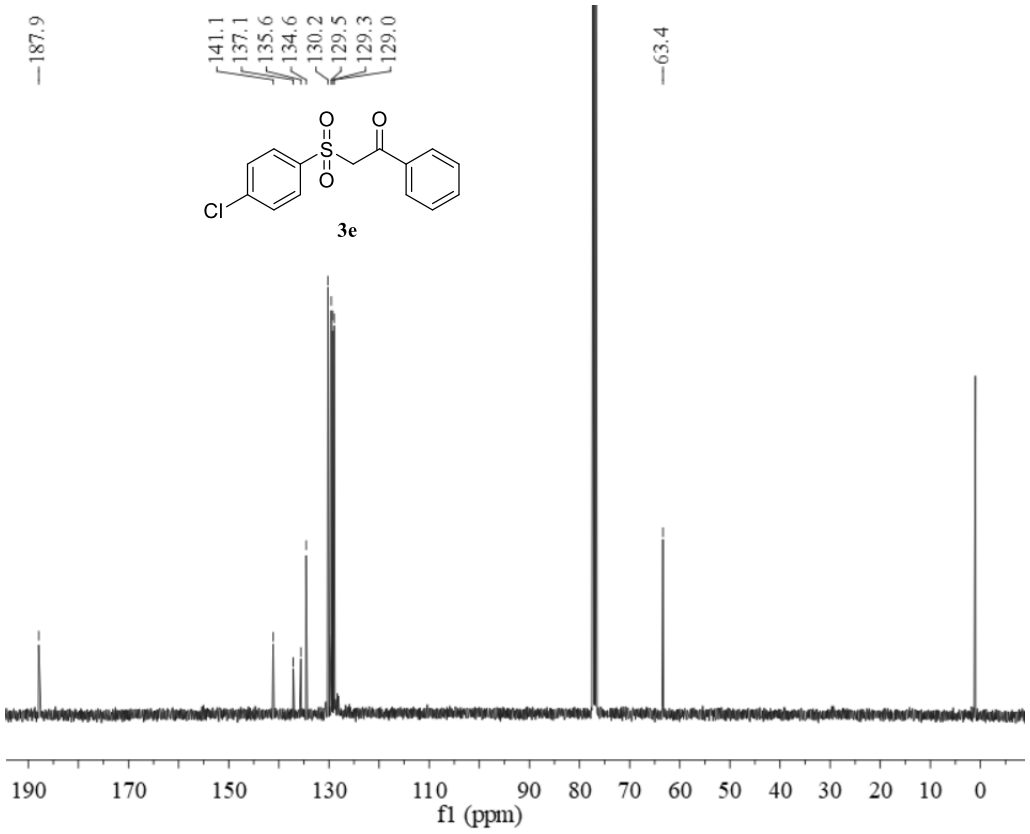
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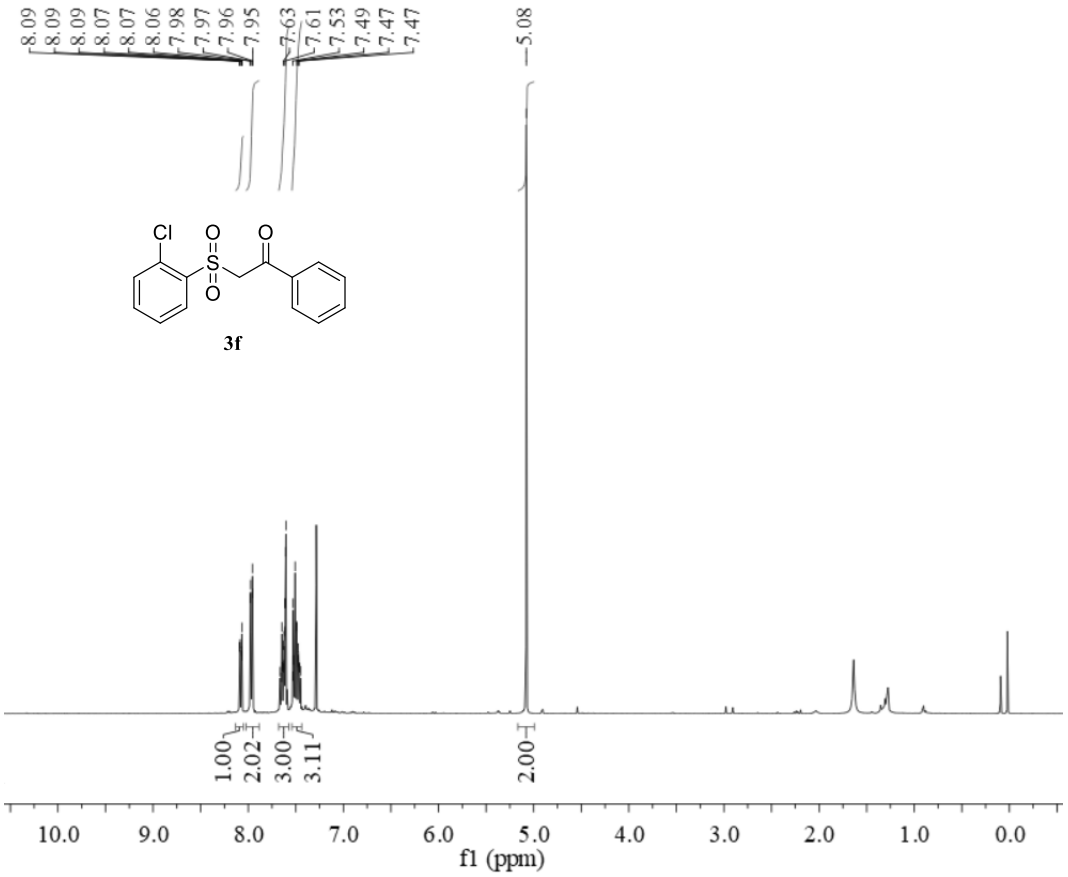
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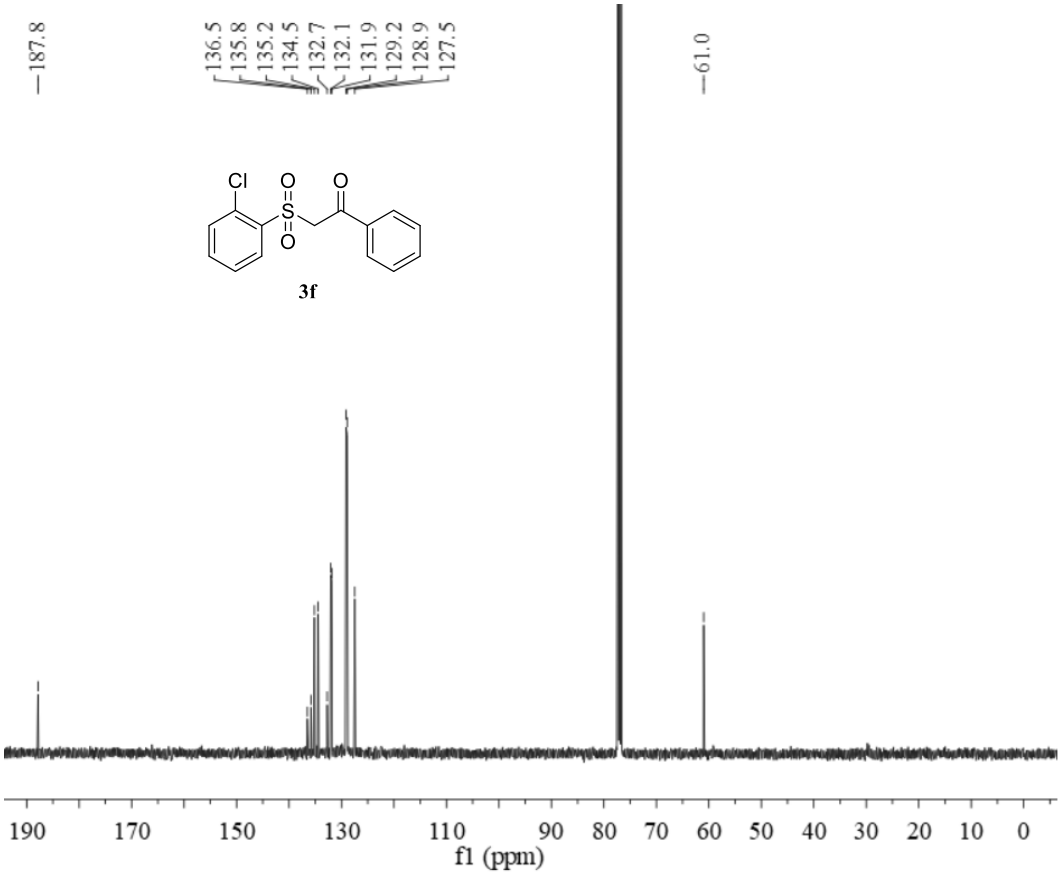
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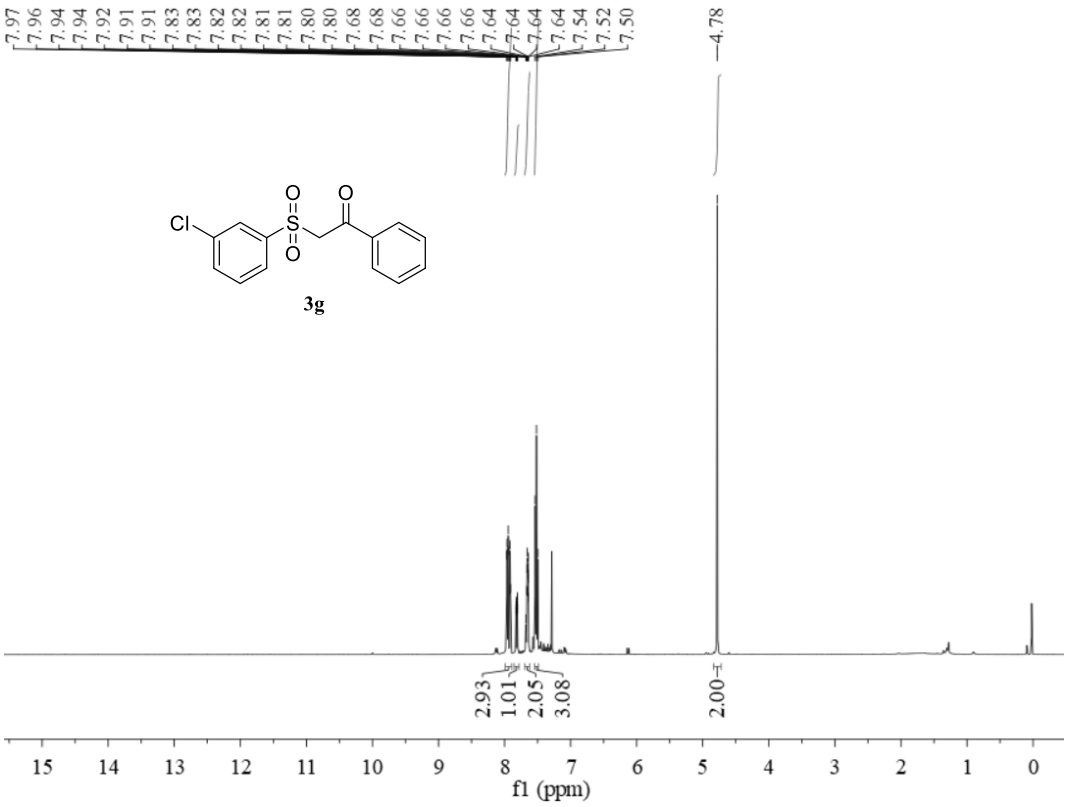
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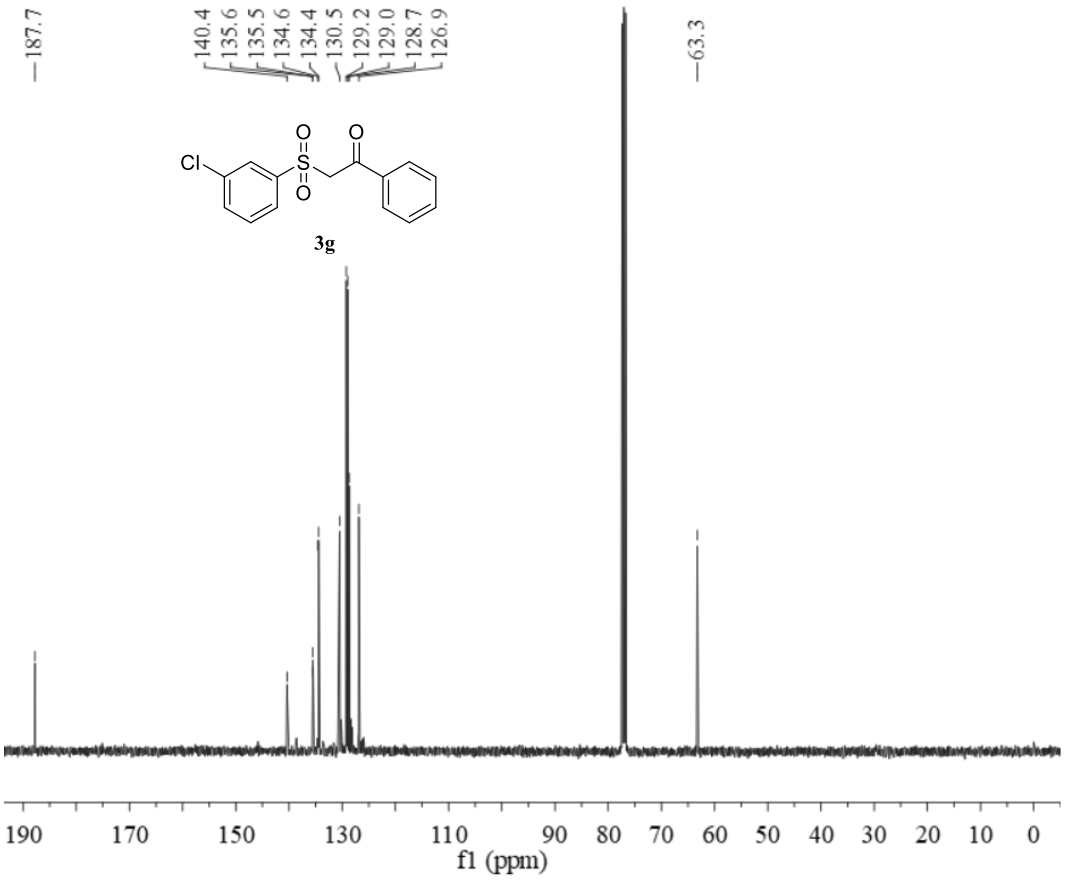
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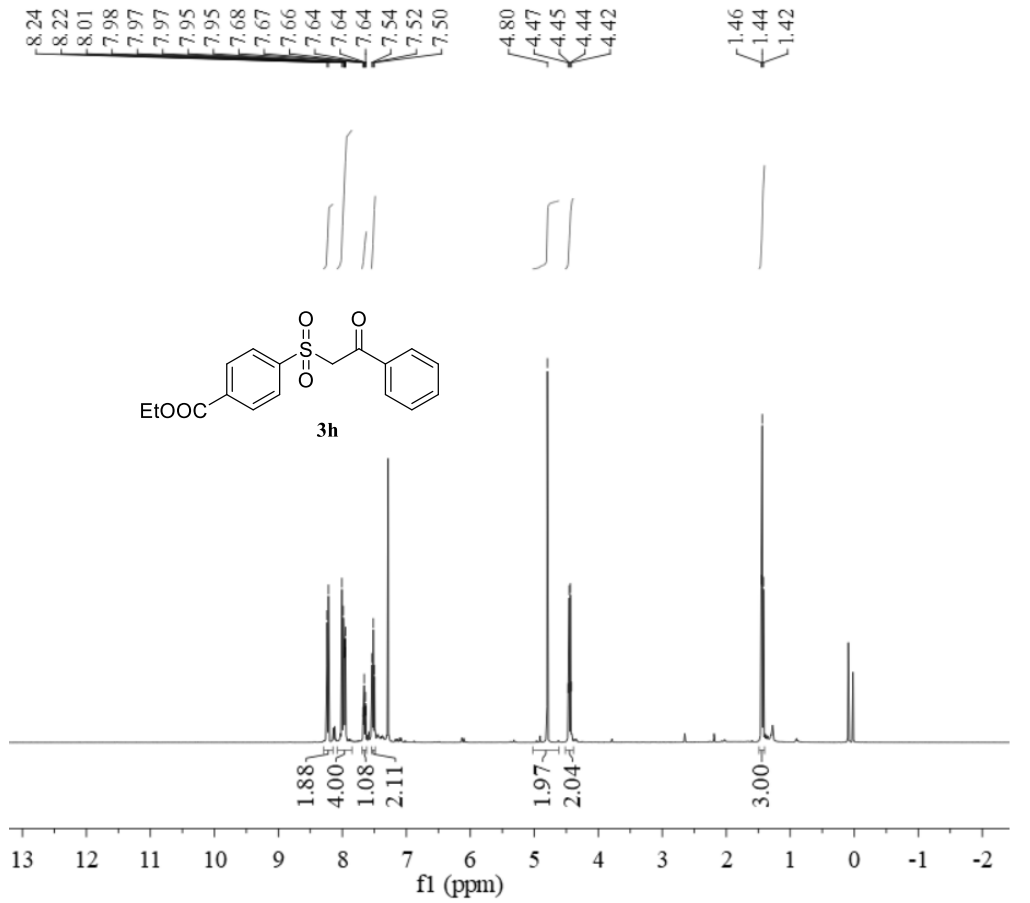
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2.04
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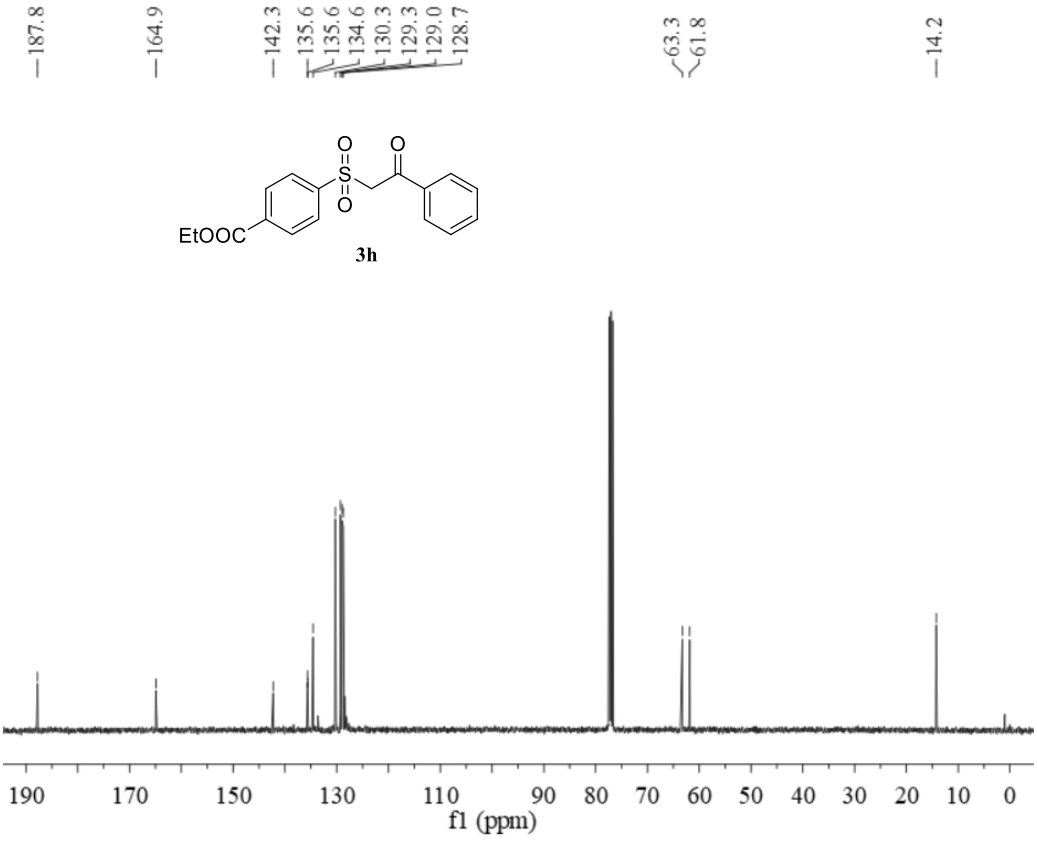
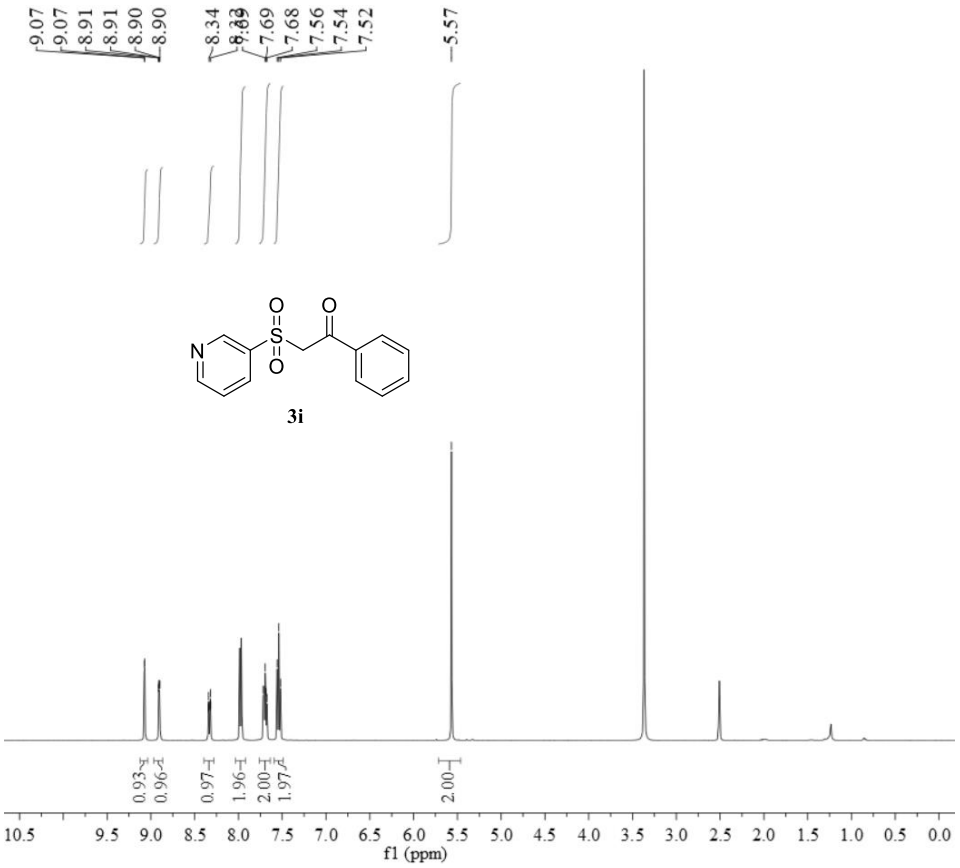
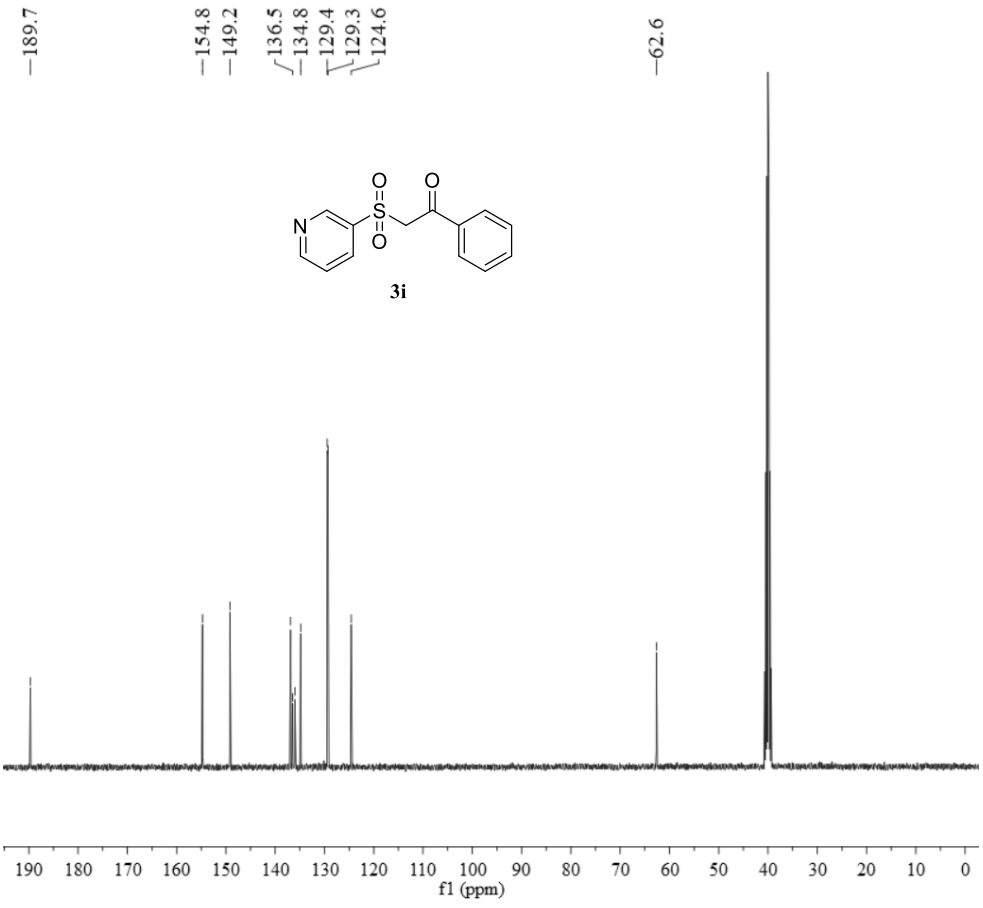
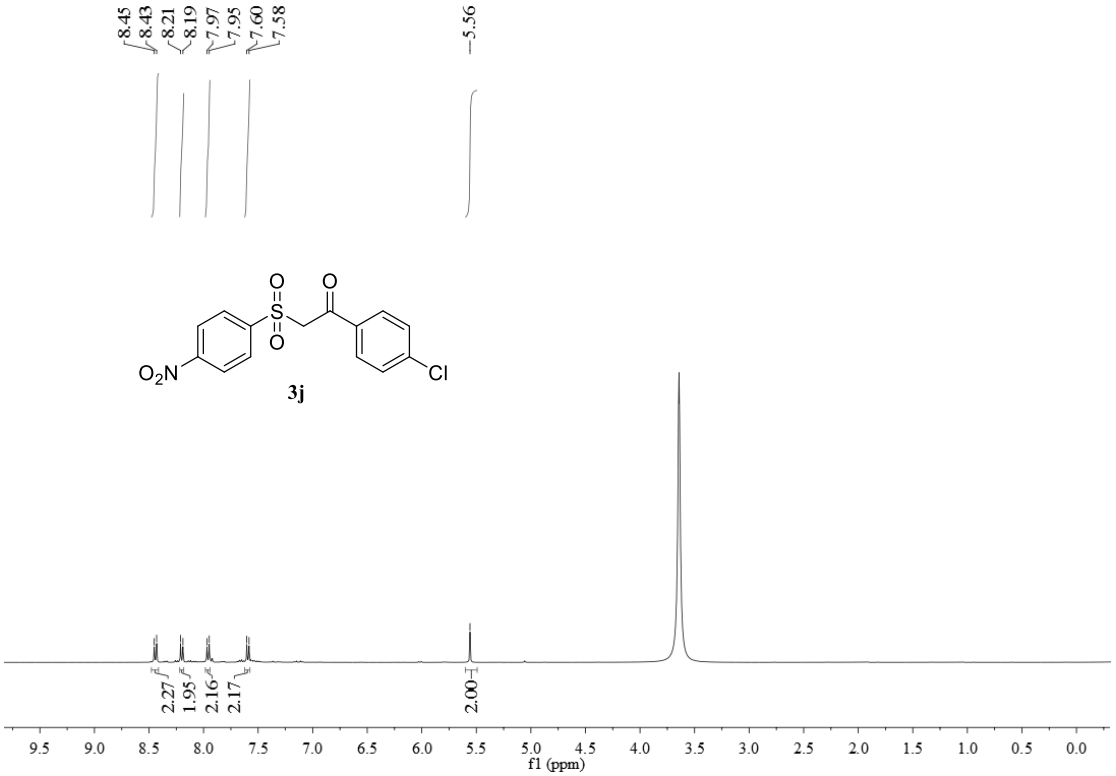
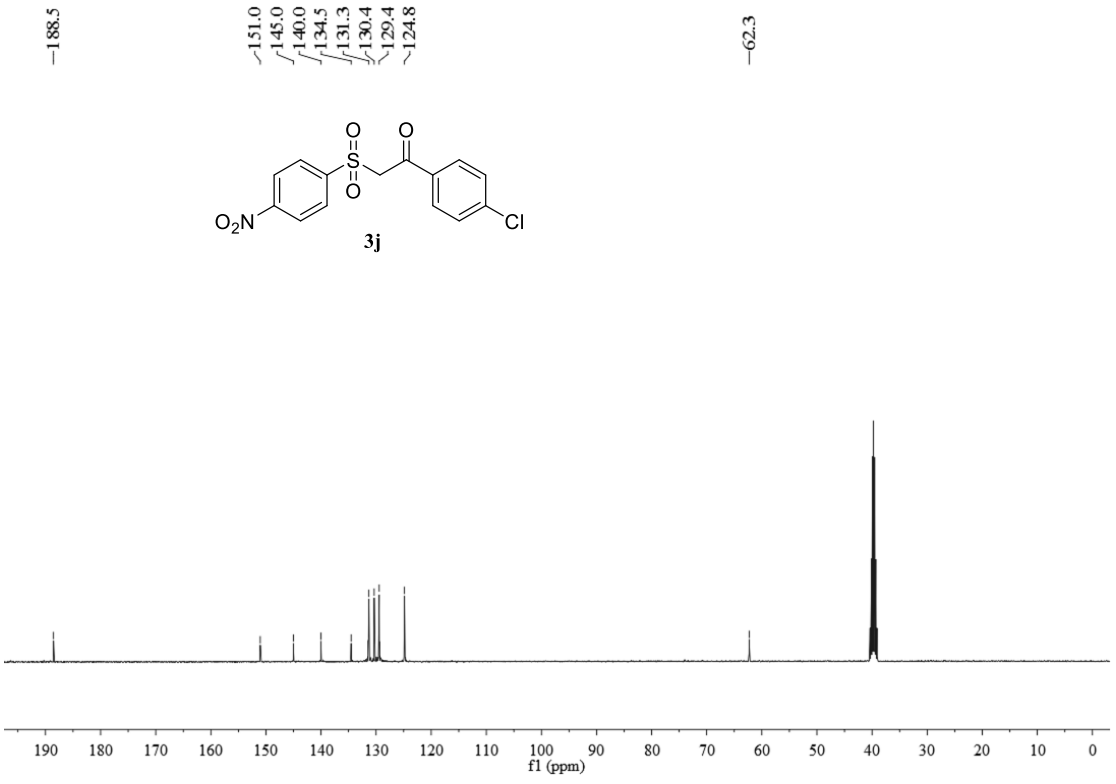
f1 (ppm)

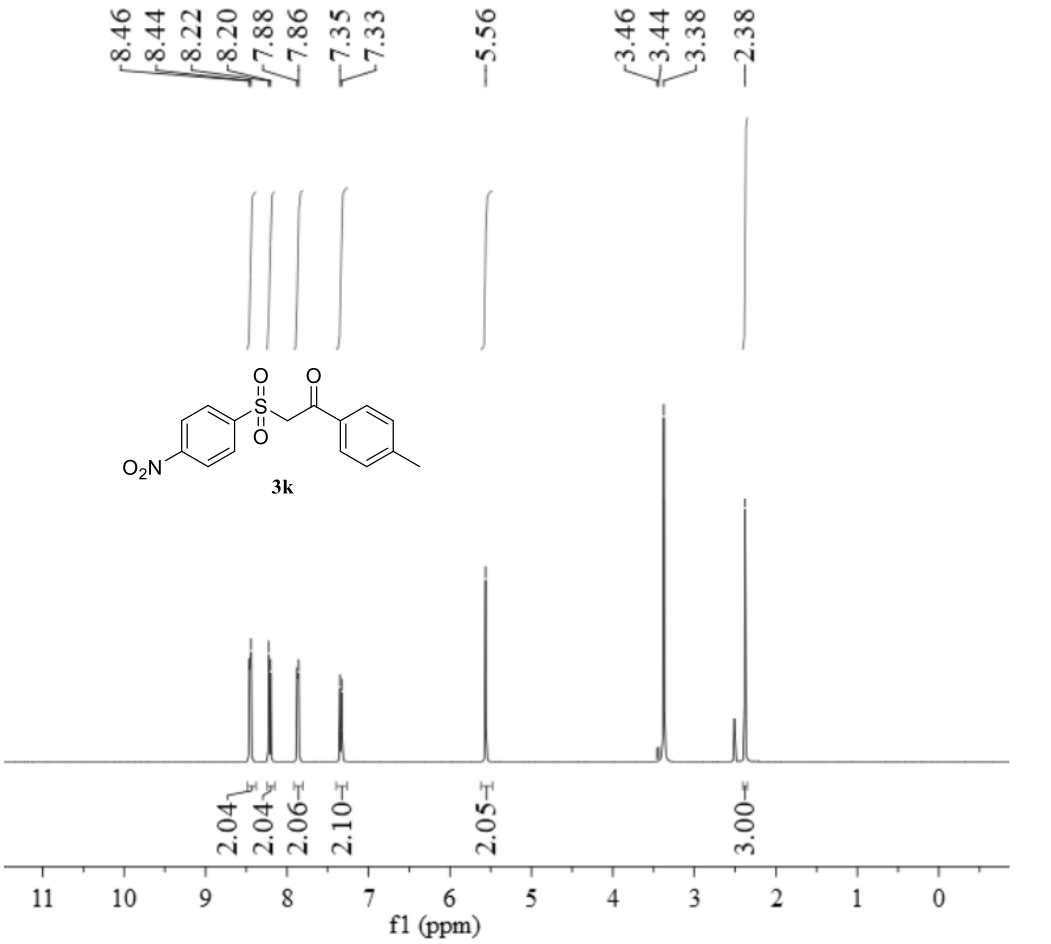

187.8
164.9
142.3
135.6
135.6
134.6
130.3
129.3
129.0
128.7
63.3
61.8
14.2
EtOOC
3h
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

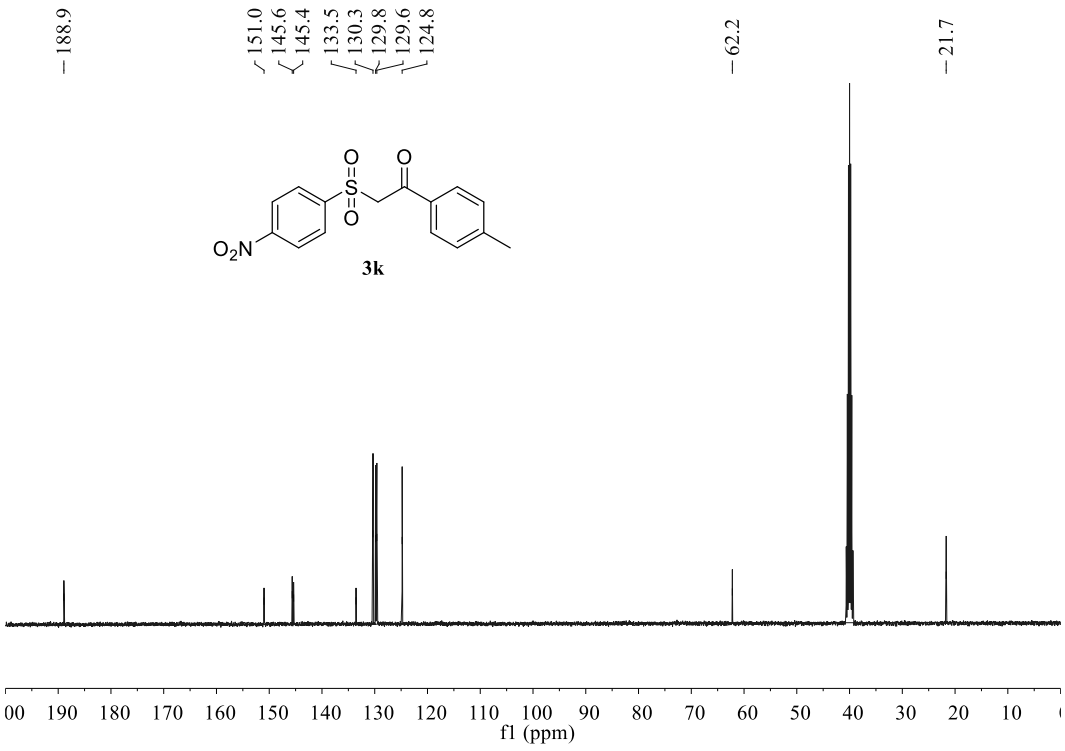

9.07
9.07
8.91
8.91
8.90
8.90
8.34
7.69
7.68
7.56
7.54
7.52
5.57
O
O
S
O
N
3i
0.93
0.96
0.97
1.96
2.00
1.97
2.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

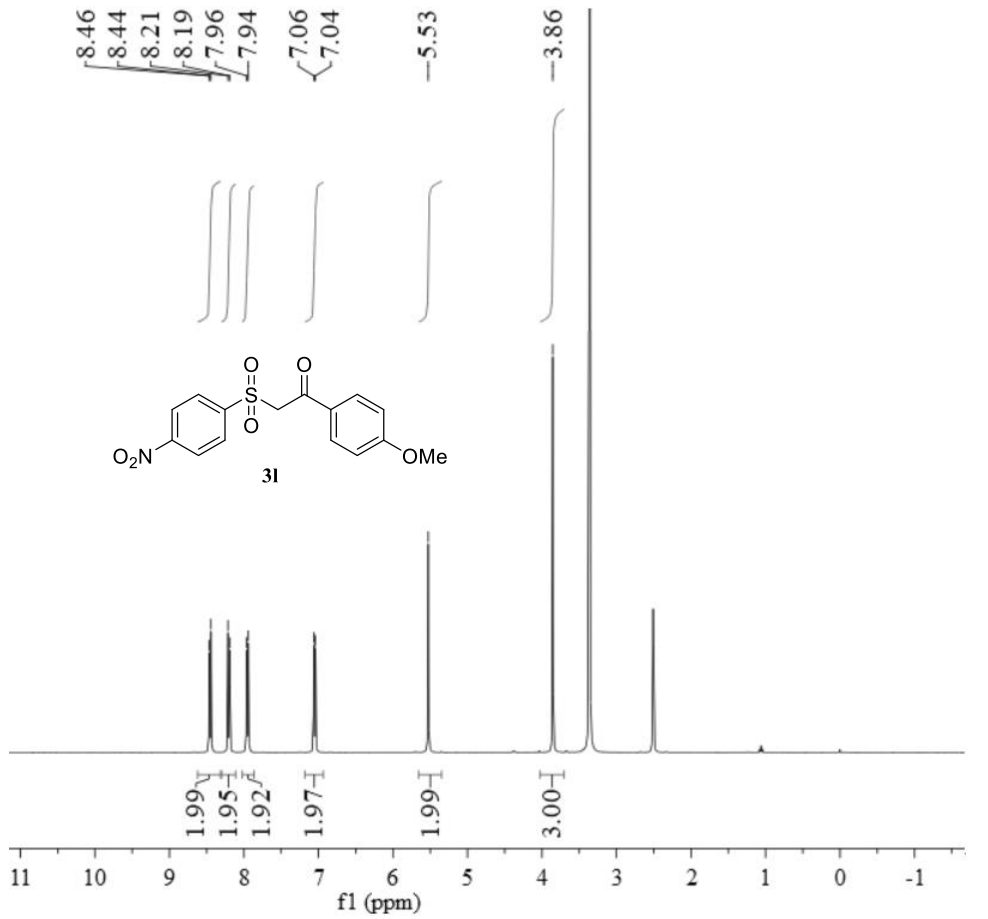

189.7
154.8
149.2
136.5
134.8
129.4
129.3
124.6
62.6
O
O
S
O
N
3i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

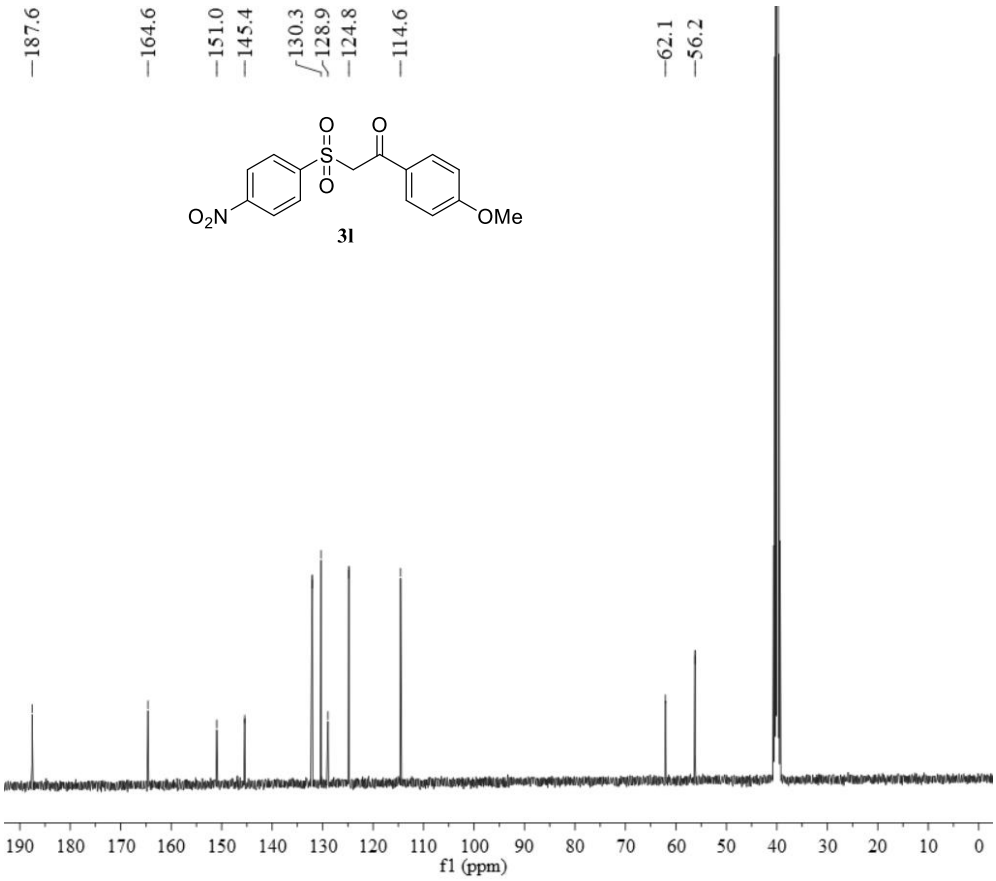

8.45
8.43
8.21
8.19
7.97
7.95
7.60
7.58
5.56
O
O
S
O
O
O2N
Cl
3j
2.27
1.95
2.16
2.17
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

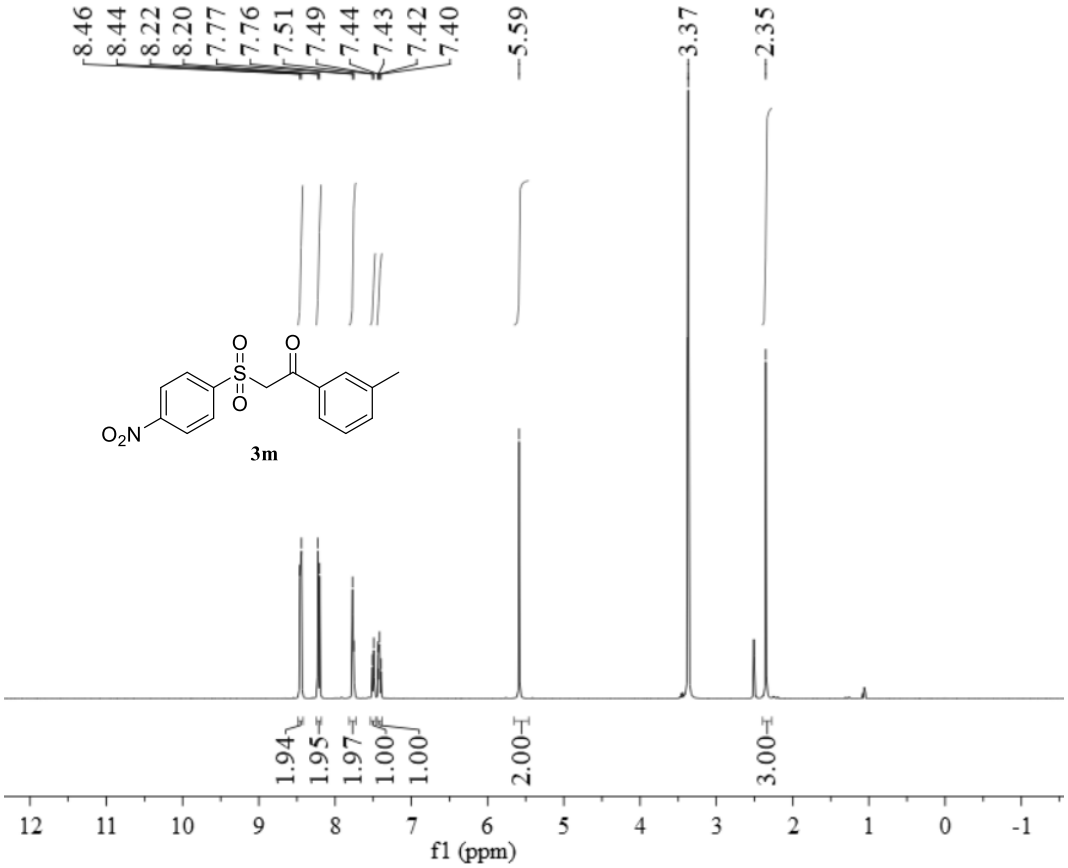

188.5
151.0
145.0
140.0
134.5
131.3
130.4
129.4
124.8
62.3
O
O
S
O
O
O2N
Cl
3j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.46
8.44
8.22
8.20
7.88
7.86
7.35
7.33
5.56
3.46
3.44
3.38
2.38
O
O
S
O
O
O_2N
3k
2.04
2.04
2.06
2.10
2.05
3.00
11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


188.9
151.0
145.6
145.4
133.5
130.3
129.8
129.6
124.8
62.2
21.7
O
O
S
O
O
O_2N
3k
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


8.46
8.44
8.21
8.19
7.96
7.94
7.06
7.04
5.53
3.86
O
O
S
O
O
O2N
OMe
3l
1.99
1.95
1.92
1.97
1.99
3.00
11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


187.6
164.6
151.0
145.4
130.3
128.9
124.8
114.6
62.1
56.2
O
O
S
O
O
O2N
OMe
3l
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.46
8.44
8.22
8.20
7.77
7.76
7.51
7.49
7.44
7.43
7.42
7.40
5.59
3.37
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1.95
1.97
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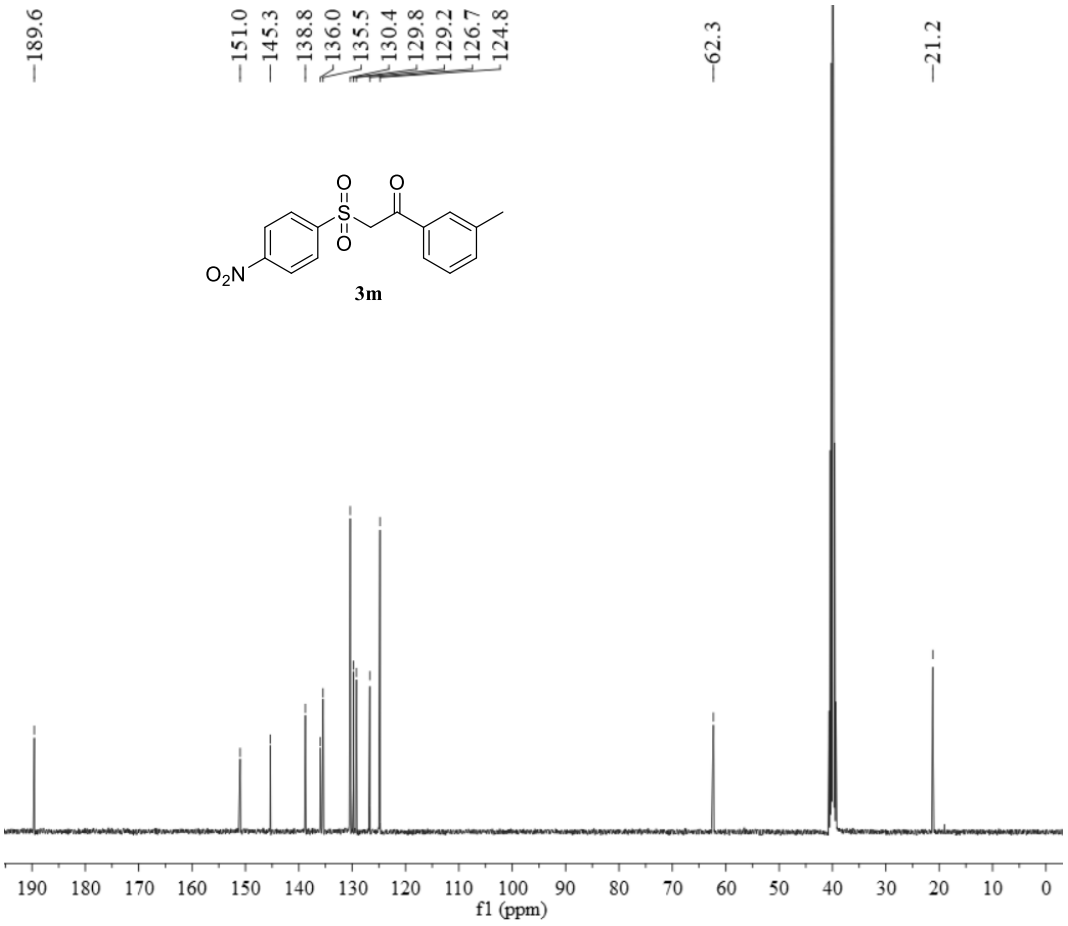
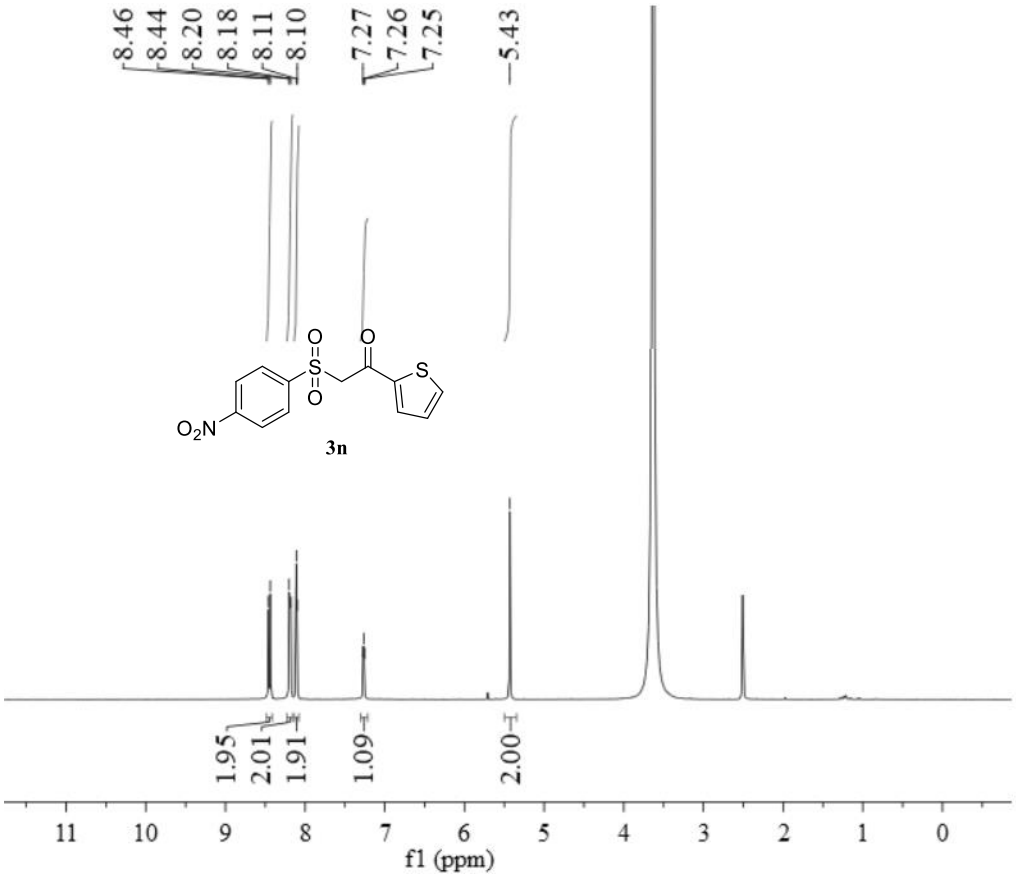
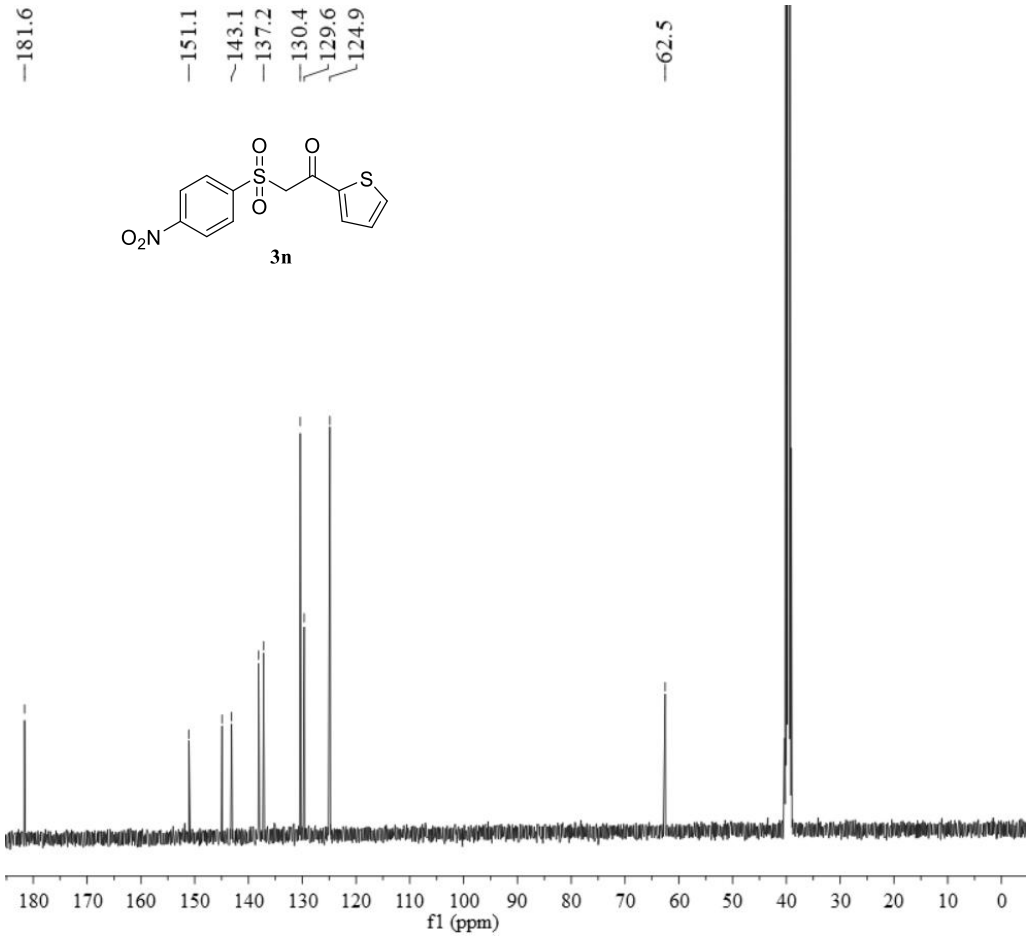
1.00
2.00
3.00
O2N
3m
f1 (ppm)


189.6
151.0
145.3
138.8
136.0
135.5
130.4
129.8
129.2
126.7
124.8
62.3
21.2
O2N
3m
f1 (ppm)


8.46
8.44
8.20
8.18
8.11
8.10
7.27
7.26
7.25
5.43
1.95
2.01
1.91
1.09
2.00
11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

3n


181.6
151.1
143.1
137.2
130.4
129.6
124.9
62.5
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3n