Supplementary Material (ESI) for Chemical Communications

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Supporting Information

Copper-promoted decarboxylative direct C3-acylation of *N*-substituted indoles with α-oxocarboxylic acids

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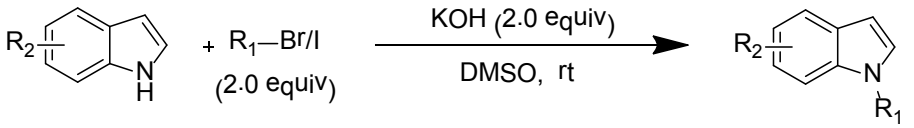
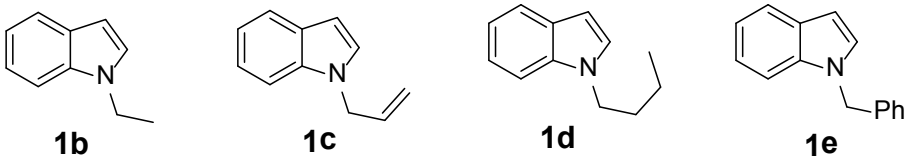
1. General considerations

All reactions were carried out under air. Acetonitrile was distillated over CaH_2 prior to use. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker Avance NMR spectrometer (400 MHz or 100 MHz, respectively) in $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, J, are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on a Waters Micromass GCT instrument.

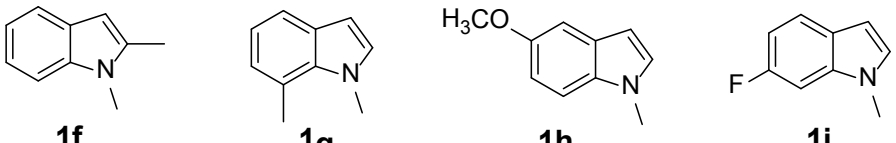
2. Starting materials

For this study, 1-methyl-1*H*-indole (**1a**) and benzoylformic acid (**2a**) were purchased from commercial sources. *N*-Protected indoles (**1b–l**) were prepared from substituted indoles with alkyl bromides (iodomethane used for methyl-protected reagent).[1]

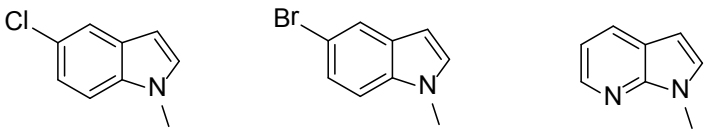




1b **1c** **1d** **1e**

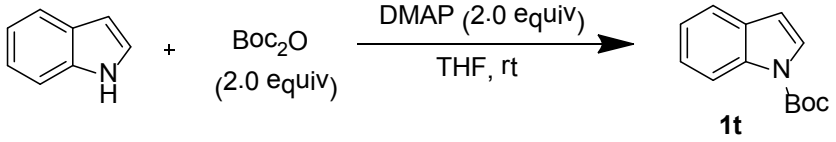


1f **1g** **1h** **1i**



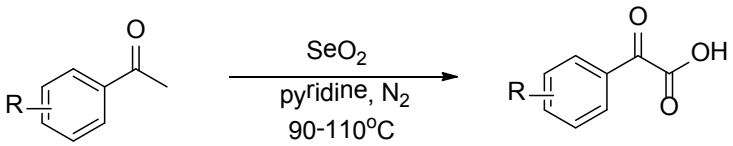
1j **1k** **1l**

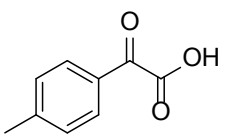
Synthesis of *N*-Boc-indole (**1t**) from indole with di-*tert*-butyl dicarbonate was according to the literature.[1]



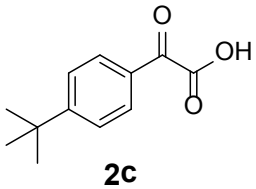
1t

Other α-oxocarboxylic acids (**2b–h**) were prepared from the oxidation of corresponding methyl ketones with SeO_2 according to the reported procedure.[2]

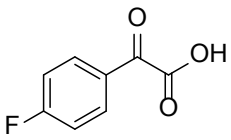




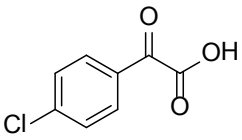
2b



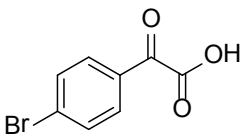
2c



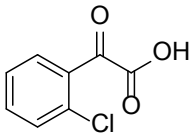
2d



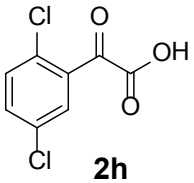
2e



2f

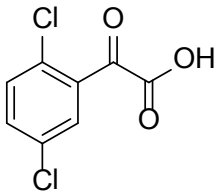


2g

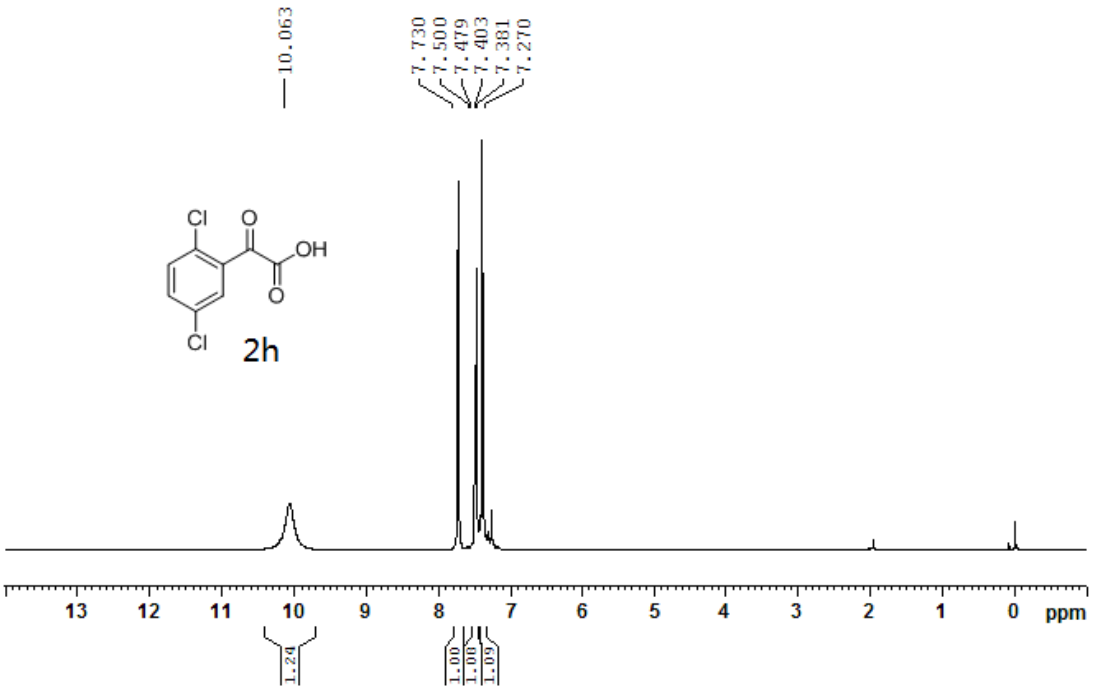


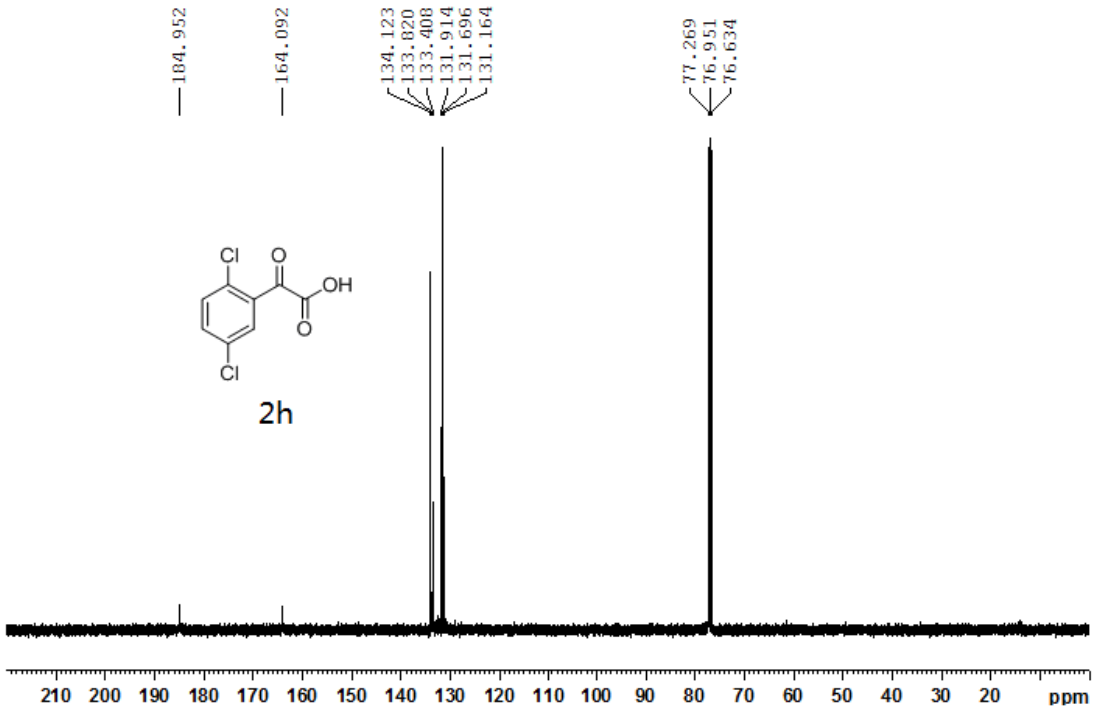
2h

α-Oxocarboxylic acids (**2b–g**) are known compounds, and their ^{1}H and ^{13}C NMR spectra are matched with literatures.[2] 2-(2,5-Dichlorophenyl)-2-oxoacetic acid (**2h**) is an new compound, and its ^{1}H and ^{13}C NMR data and HRMS are as following.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.0 (br, 1H), 7.73 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.39 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.9, 164.0, 134.1, 133.8, 133.4, 131.9, 131.6, 131.1. HRMS (EI) ($[M]^{+}$): Calcd. for $C_8H_4Cl_2O_3$: 217.9537. Found 217.9541.

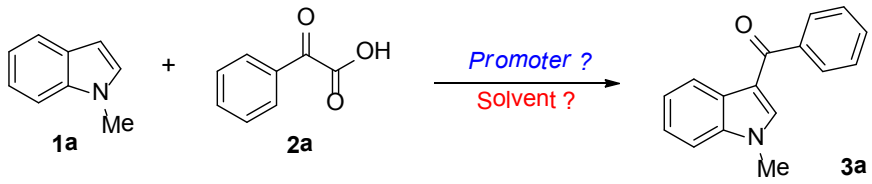

10.063
7.730
7.500
7.479
7.403
7.381
7.270
Cl
O
OH
O
Cl
2h
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.24
1.00
1.00
1.09


184.952
164.092
134.123
133.820
133.408
131.914
131.696
131.164
77.269
76.951
76.634
Cl
O
OH
O
Cl
2h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

3. General procedure

A 10-mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with $Cu(OAc)_2 \cdot H_2O$ (60 mg, 0.30 mmol) and benzoylformic acid (**2a**, 75 mg, 0.5 mmol). 1-Methyl-1*H*-indole (**1a**, 32 mg, 0.25 mmol) and CH_3CN (2.0 mL) were added to the sealed reaction vessel by syringe. The resulting solution was stirred at 110 °C for 10 h. After cooling to room temperature, the suspension was diluted with ethyl acetate then washed with 0.5 mmol/L NaOH aqueous solution (5.0 mL×3), dried over by $MgSO_4$. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate= 4:1 to 10:1) to give **3a** as an oil.

4. Effect of promoter and solvent on the model reaction[a] (Table S1)

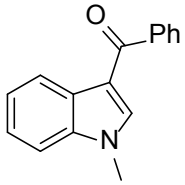


Entry	Promoter	Solvent	Yield of **3a** (%)[b]
1	$Cu(OAc)_2·H_2O$	CH_3CN	75
2	$Cu(NO_3)_2·3H_2O$	CH_3CN	53
3	$(NH_4)_2S_2O_8$	CH_3CN	41
4	Ag_2CO_3	CH_3CN	32
5	$CuSO_4·5H_2O$	CH_3CN	32
6	$CuBr_2$	CH_3CN	trace
7	$Cu(acac)_2$	CH_3CN	trace
8	$Cu(OH)_2$	CH_3CN	NR
9	$CuCl·2H_2O$	CH_3CN	NR
10	Cu	CH_3CN	NR
11	$K_2S_2O_8$	CH_3CN	NR
12	TBHP	CH_3CN	NR
13	$Cu(OAc)_2·H_2O$	chlorobenzene	55
14	$Cu(OAc)_2·H_2O$	methanol	44
15	$Cu(OAc)_2·H_2O$	dioxane	41
16	$Cu(OAc)_2·H_2O$	DMSO	35
17	$Cu(OAc)_2·H_2O$	toluene	30
18	$Cu(OAc)_2·H_2O$	*p*-xylene	26
19	$Cu(OAc)_2·H_2O$	CH_3CH_2OH	19
20	$Cu(OAc)_2·H_2O$	EtOAc	13
21	$Cu(OAc)_2·H_2O$	CH_3NO_2	trace
22	$Cu(OAc)_2·H_2O$	DCE	trace
23	$Cu(OAc)_2·H_2O$	THF	NR
24	$Cu(OAc)_2·H_2O$	NMP	NR
25	$Cu(OAc)_2·H_2O$	H_2O	NR
26	$Cu(OAc)_2·H_2O$	CH_3CN	75[c]
27	$Cu(OAc)_2·H_2O$	CH_3CN	75[d]
28	$Cu(OAc)_2·H_2O$	CH_3CN	72[e]
29	$Cu(OAc)_2·H_2O$	CH_3CN	64[f]

[a] Reaction conditions: *N*-methylindole (**1a**, 0.25 mmol), benzoylformic acid (**2a**, 0.50 mmol), promoter (0.30 mmol, 1.2 equiv), solvent (2.0 mL), 110 °C, 10 h. [b] Isolated yields. [c] $Cu(OAc)_2·H_2O$ (2.0 equiv). [d] 120 °C. [e] 100 °C. [f] 90 °C.

5. Characterization data for the products

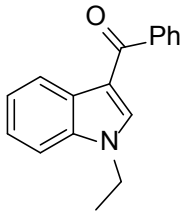
(1-Methyl-1*H*-indol-3-yl)(phenyl)methanone (3a)



Oil.[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45–8.43 (m, 1H), 7.82 (d, *J* = 7.2 Hz, 2H), 7.57–7.47 (m, 4H), 7.37–7.35 (m, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.8, 140.9, 137.8, 137.5, 131.0, 128.6, 128.2, 127.2, 123.6, 122.7, 122.6, 115.6, 109.5, 33.5.

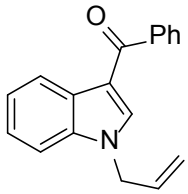
(1-Ethyl-1*H*-indol-3-yl)(phenyl)methanone (3b)



Yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46–8.44 (m, 1H), 7.83 (d, *J* = 7.2 Hz, 2H), 7.60–7.48 (m, 4H), 7.42–7.34 (m, 3H), 4.22 (q, *J* = 7.2 Hz, 2H), 1.52 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.8, 141.0, 136.6, 136.1, 131.0, 128.6, 128.2, 127.4, 123.5, 122.8, 122.6, 115.7, 109.7, 41.7, 15.1. IR (KBr, cm^{-1}): 1621 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{17}H_{16}NO$: 250.1232. Found 250.1234.

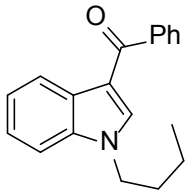
(1-Allyl-1*H*-indol-3-yl)(phenyl)methanone (3c)



Yellow solid, mp 98.4–99.7 ℃.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47–8.45 (m, 1H), 7.83 (d, *J* = 6.8 Hz, 2H), 7.58–7.47 (m, 4H), 7.39–7.34 (m, 3H), 6.05–5.96 (m, 1H), 5.28 (d, *J* = 10.0 Hz, 1H), 5.17 (d, *J* = 17.2 Hz, 1H), 4.77 (d, *J* = 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.9, 140.8, 136.9, 136.8, 132.0, 131.1, 128.7, 128.3, 127.3, 123.6, 122.8, 122.7, 118.5, 115.9, 110.1, 49.4. IR (KBr, cm^{-1}): 1622 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{18}H_{16}NO$: 262.1232. Found 262.1231.

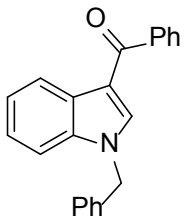
(1-Butyl-1*H*-indol-3-yl)(phenyl)methanone (3d)



Yellow solid, mp 79.0–80.8 ℃.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49–8.47 (m, 1H), 7.84 (d, *J* = 7.2 Hz, 2H), 7.58–7.48 (m, 4H), 7.42–7.34 (m, 3H), 4.15 (t, *J* = 6.8 Hz, 2H), 1.89–1.82 (m, 2H), 1.40–1.34 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.9, 140.9, 137.0, 136.8, 131.0, 128.7, 128.3, 127.4, 123.5, 122.8, 122.6, 115.5, 109.9, 46.9, 31.9, 20.1, 13.6. IR (KBr, cm^{-1}): 1622 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{19}H_{20}NO$: 278.1545. Found 278.1546.

(1-Benzyl-1*H*-indol-3-yl)(phenyl)methanone (3e)

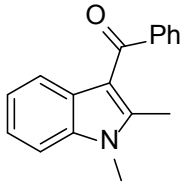


Yellow solid, mp 148.7–149.9 ℃.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.64 (br, 1H), 7.57–7.47 (m, 3H), 7.38–7.29 (m, 6H), 7.16–7.14 (m, 2H), 5.35 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.9, 140.8, 137.2, 137.1, 135.8, 131.2,

129.0, 128.7, 128.3, 128.1, 127.4, 126.8, 123.8, 122.8, 116.1, 110.3, 50.8. IR (KBr, cm^{-1}): 1621 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{22}H_{18}NO$: 312.1388. Found 312.1390.

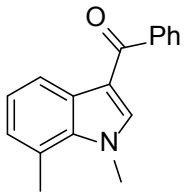
(1,2-Dimethyl-1*H*-indol-3-yl)(phenyl)methanone (3f)



Yellow solid, mp 140.9–141.2 ℃.[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 7.2 Hz, 2H), 7.58–7.54 (m, 1H), 7.48–7.45 (m, 2H), 7.37–7.31 (m, 2H), 7.24–7.21 (m, 1H), 7.11–7.07 (m, 1H), 3.71 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.9, 144.7, 141.5, 136.6, 131.4, 129.0, 128.2, 127.1, 122.0, 121.4, 120.9, 113.6, 109.1, 29.6, 12.5.

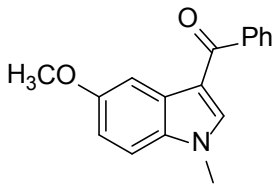
(1,7-Dimethyl-1*H*-indol-3-yl)(phenyl)methanone (3g)



Yellow solid, mp 134.6–135.4 ℃.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 7.2 Hz, 2H), 7.54–7.46 (m, 3H), 7.37 (br, 1H), 7.22–7.18 (m, 1H), 7.03 (d, *J* = 7.2 Hz, 1H), 4.02 (s, 3H), 2.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.7, 141.0, 139.6, 136.2, 131.0, 128.6, 128.3, 128.2, 126.3, 122.8, 121.5, 120.7, 115.0, 37.6, 19.5. IR (KBr, cm^{-1}): 1617 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{17}H_{16}NO$: 250.1232. Found 250.1231.

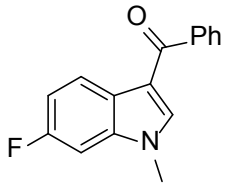
(5-Methoxy-1-methyl-1*H*-indol-3-yl)(phenyl)methanone (3h)



Yellow oil.[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 2.4 Hz, 1H), 7.81 (d, *J* = 6.8 Hz, 2H), 7.54–7.46 (m, 4H), 7.23 (d, *J* = 8.8 Hz, 1H), 7.00–6.97 (m, 1H), 3.92 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.8, 156.6, 141.0, 137.9, 132.5, 130.9, 128.5, 128.2, 128.0, 115.1, 114.1, 110.5, 103.9, 55.8, 33.6.

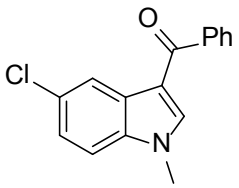
(6-Fluoro-1-methyl-1*H*-indol-3-yl)(phenyl)methanone (3i)



Yellow solid, mp 147.2–148.3 ℃.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39–8.36 (m, 1H), 7.80 (d, *J* = 7.2 Hz, 2H), 7.57–7.46 (m, 4H), 7.12–7.06 (m, 1H), 7.04–7.01 (m, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.6, 160.5 (d, *J* = 239.6 Hz), 140.6, 138.1 (d, *J* = 2.8 Hz), 137.7 (d, *J* = 11.7 Hz), 131.2, 128.5, 128.3, 123.8 (d, *J* = 9.8 Hz), 123.5 (d, *J* = 1.2 Hz), 115.6, 111.1 (d, *J* = 23.7 Hz), 96.2 (d, *J* = 26.2 Hz), 33.5. IR (KBr, cm^{-1}): 1621 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{16}H_{13}FNO$: 254.0981. Found 254.0980.

(5-Chloro-1-methyl-1*H*-indol-3-yl)(phenyl)methanone (3j)

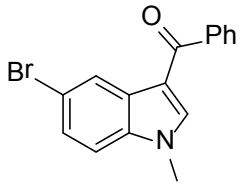


Yellow solid, mp 150.0–151.6 ℃.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, *J* = 1.12 Hz, 1H), 7.77 (d, *J* = 7.2 Hz, 2H), 7.56–7.45 (m, 4H), 7.26–7.23 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ

= 190.4, 140.4, 138.6, 135.8, 131.2, 128.6, 128.5, 128.3, 128.1, 123.9, 122.1, 115.0, 110.7, 33.7. IR (KBr, cm^{-1}): 1623 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{16}H_{13}ClNO$: 270.0686. Found 270.0683.

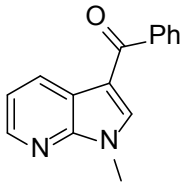
(5-Bromo-1-methyl-1*H*-indol-3-yl)(phenyl)methanone (3k)



Yellow solid, mp 174.4–175.1 ℃.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.59 (d, *J* = 1.64 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.56–7.45 (m, 4H), 7.39–7.36 (m, 1H), 7.17 (d, *J* = 8.8 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.3, 140.4, 138.4, 136.1, 131.2, 128.7, 128.5, 128.3, 126.5, 125.2, 116.3, 114.9, 111.1, 33.6. IR (KBr, cm^{-1}): 1606 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{16}H_{13}BrNO$: 314.0181. Found 314.0179.

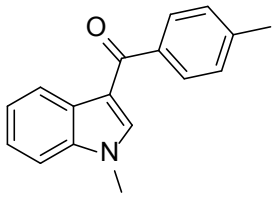
(1-Methyl-1*H*-pyrrolo[2,3-b]pyridin-3-yl)(phenyl)methanone (3l)



Yellow solid, mp 166.3–166.9 ℃.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.64 (d, *J* = 8.0 Hz, 1H), 8.43 (d, *J* = 4.4 Hz, 1H), 7.80 (d, *J* = 7.2 Hz, 2H), 7.68 (br, 1H), 7.56–7.46 (m, 3H), 7.28–7.25 (m, 1H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.5, 148.3, 144.6, 140.0, 137.4, 131.4, 131.1, 128.6, 128.4, 119.7, 118.5, 113.9, 31.9. IR (KBr, cm^{-1}): 1622 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{15}H_{13}N_2O$: 237.1028. Found 237.1025.

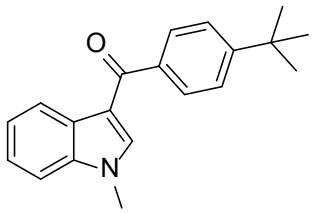
(1-Methyl-1*H*-indol-3-yl)(*p*-tolyl)methanone (3m)



Yellow solid, mp 134.0–134.9 ℃.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44–8.42 (m, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.53 (br, 1H), 7.36–7.33 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.6, 141.5, 138.2, 137.55, 137.52, 128.9, 128.8, 127.2, 123.5, 122.7, 122.5, 115.7, 109.5, 33.4, 21.5. IR (KBr, cm^{-1}): 1618 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{17}H_{16}NO$: 250.1232. Found 250.1233.

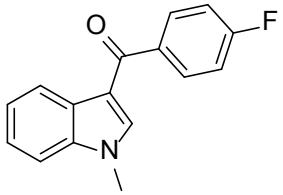
(4-(*tert*-Butyl)phenyl)(1-methyl-1*H*-indol-3-yl)methanone (3n)



Yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.48–8.46 (m, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.57 (br, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.36–7.34 (m, 3H), 3.84 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.6, 154.5, 138.1, 137.6, 137.5, 128.6, 127.2, 125.2, 123.5, 122.7, 122.5, 115.7, 109.5, 33.4, 31.2. IR (KBr, cm^{-1}): 1621 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{20}H_{22}NO$: 292.1701. Found 292.1702.

(4-Fluorophenyl)(1-methyl-1*H*-indol-3-yl)methanone (3o)

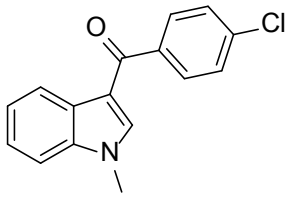


Yellow solid, mp 138.8–140.7 ℃.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42–8.39 (m, 1H), 7.83–7.80 (m, 2H), 7.47 (br,

1H), 7.35–7.32 (m, 3H), 7.16–7.12 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.2, 164.5 (d, *J* = 249.8 Hz), 137.57, 137.56, 137.0 (d, *J* = 3.2 Hz), 131.0, 130.9, 127.1, 123.6, 122.7, 122.5, 115.2 (d, *J* = 21.5 Hz), 109.7, 33.5. IR (KBr, cm^{-1}): 1617 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{16}H_{13}FNO$: 254.0981. Found 254.0987.

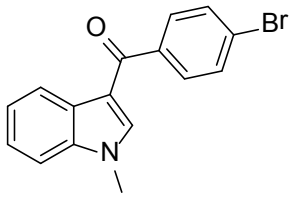
(4-Chlorophenyl)(1-methyl-1*H*-indol-3-yl)methanone (3p)



Yellow solid, mp 135.2–136.4 ℃.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41–8.39 (m, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.49 (br, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.36–7.33 (m, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.3, 139.1, 137.7, 137.5, 137.2, 130.0, 128.5, 127.0, 123.7, 122.8, 122.6, 115.3, 109.7, 33.5. IR (KBr, cm^{-1}): 1616 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{16}H_{13}ClNO$: 270.0686. Found 270.0690.

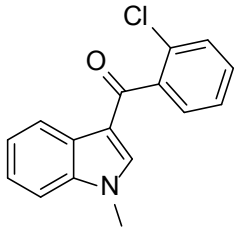
(4-Bromophenyl)(1-methyl-1*H*-indol-3-yl)methanone (3q)



Yellow solid, mp 138.9–141.5 ℃.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40–8.39 (m, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.49 (br, 1H), 7.36–7.32 (m, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.4, 139.6, 137.6, 137.5, 131.5, 130.2, 127.0, 125.7, 123.8, 122.8, 122.6, 115.3, 109.7, 33.5. IR (KBr, cm^{-1}): 1614 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{16}H_{13}BrNO$: 314.0181. Found 314.0175.

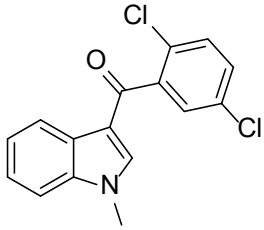
(2-Chlorophenyl)(1-methyl-1*H*-indol-3-yl)methanone (3r)



Yellow solid, mp 164.7–165.5 ℃.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40–8.38 (m, 1H), 7.47–7.37 (m, 3H), 7.36–7.32 (m, 4H), 7.29 (br, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.7, 140.5, 138.8, 137.8, 130.9, 130.3, 130.0, 128.7, 126.48, 126.45, 123.8, 123.0, 122.6, 116.3, 109.8, 33.5. IR (KBr, cm^{-1}): 1626 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{16}H_{13}ClNO$: 270.0686. Found 270.0687.

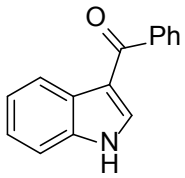
(2,5-Dichlorophenyl)(1-methyl-1*H*-indol-3-yl)methanone (3s)



Yellow solid, mp 180.2–181.6 ℃.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38–8.36 (m, 1H), 7.43–7.41 (m, 1H), 7.39–7.34 (m, 5H), 7.32 (br, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.8, 141.8, 138.8, 137.8, 132.5, 131.2, 130.3, 129.3, 128.5, 126.3, 124.0, 123.2, 122.5, 115.9, 109.9, 33.6. IR (KBr, cm^{-1}): 1633 ($\nu_{C=O}$). HRMS (ESI) ($[M+H]^+$): Calcd. for $C_{16}H_{12}Cl_2NO$: 304.0296. Found 304.0296.

(1*H*-Indol-3-yl)(phenyl)methanone (3t)



White solid, mp 243.3–244.9 ℃.[4]

^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.0 (s, 1H), 8.24 (d, *J* = 7.2 Hz, 1H), 7.91 (br, 1H), 7.77 (d, *J* = 7.2 Hz, 2H), 7.60–7.50 (m, 4H), 7.25–7.20 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 190.5, 140.9, 137.1, 136.2, 131.5, 128.86, 128.81, 126.6, 123.6, 122.3, 121.9, 115.4, 112.7.

6. References

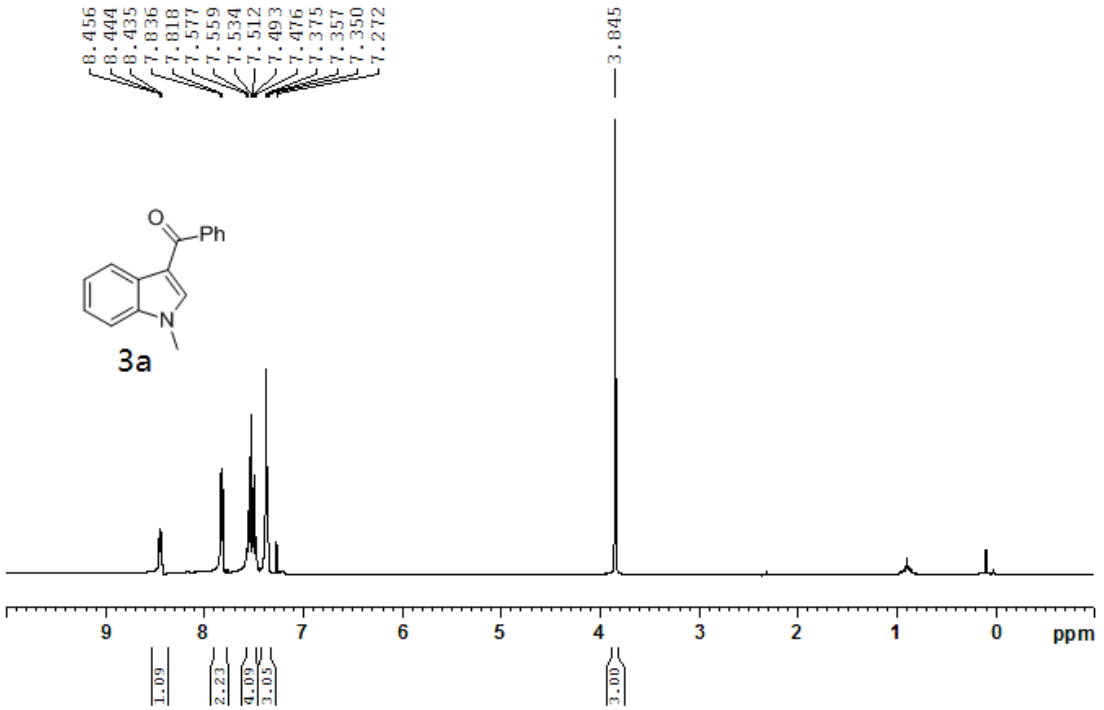
[1] L. Zhang, C. Peng, D. Zhao, Y. Wang, H.-J. Fu, Q. Shen and J.-X. Li, *Chem. Commun.* 2012, **48**, 5928.

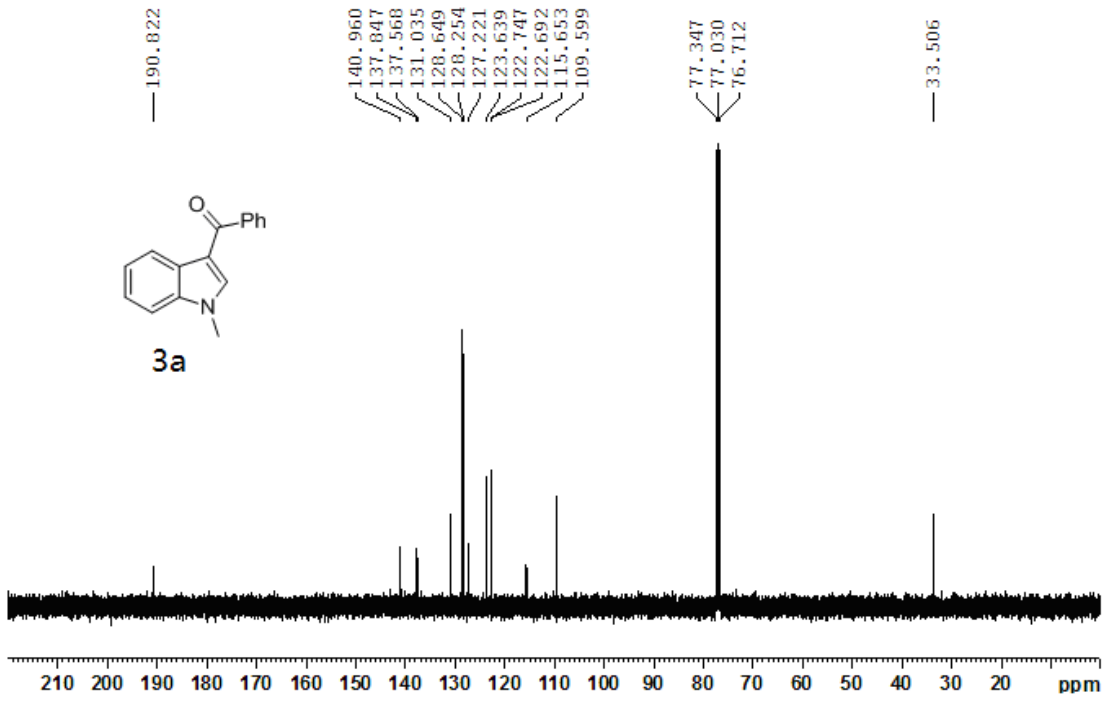
[2] (a) K. Wadhwa, C. X. Yang, P. R. West, K. C. Deming, S. R. Chemburkar and R. E. Reddy, *Synth. Commun*., 2008, **38**, 4434; (b) P. Fang, M. Li and H. Ge, *J. Am. Chem. Soc*., 2010, **132**, 11898.

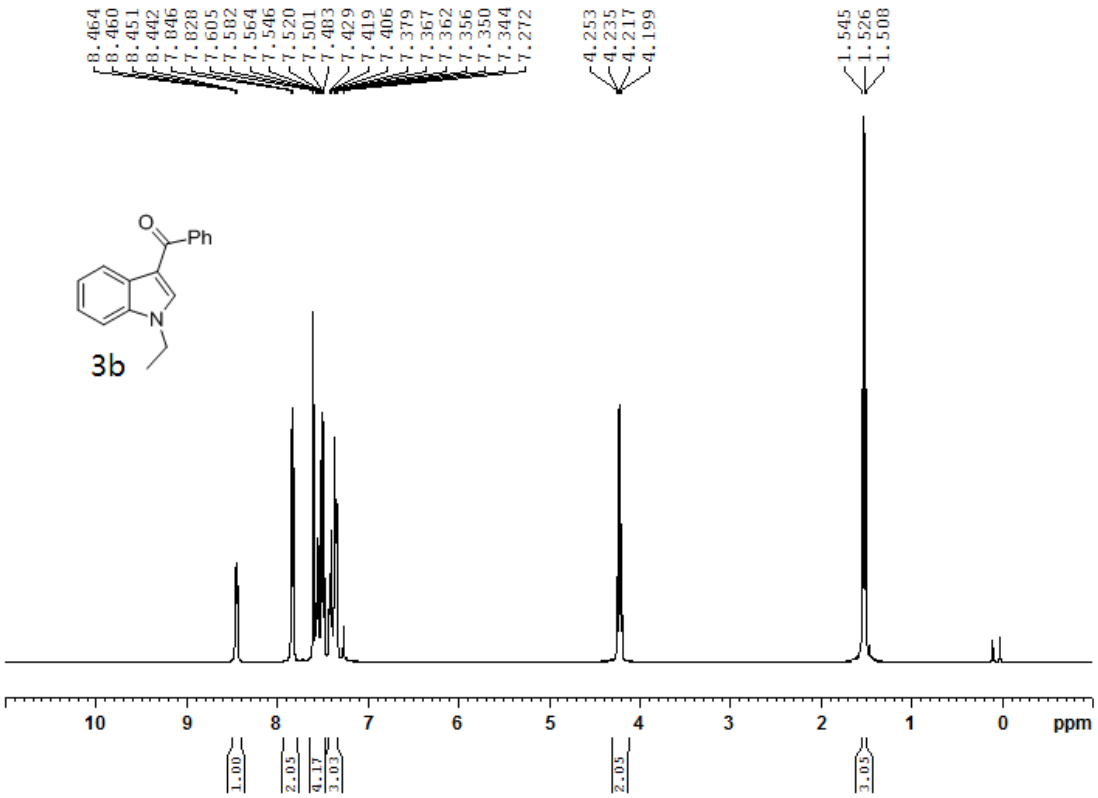
[3] J. E. Taylor, M. D. Jones, J. M. J. Williams and S. D. Bull, *Org. Lett.* 2010, **12**, 5740.

[4] S. K. Guchhait, M. Kashyap and H. Kamble, *J. Org. Chem.* 2011, **76**, 4753.

7. ^{1}H NMR and ^{13}C NMR spectra of the products



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8.451
8.442
7.846
7.828
7.605
7.582
7.564
7.546
7.520
7.501
7.483
7.429
7.419
7.406
7.379
7.367
7.362
7.356
7.350
7.344
7.272
4.253
4.235
4.217
4.199
1.545
1.526
1.508
O
Ph
N
3b
10
9
8
7
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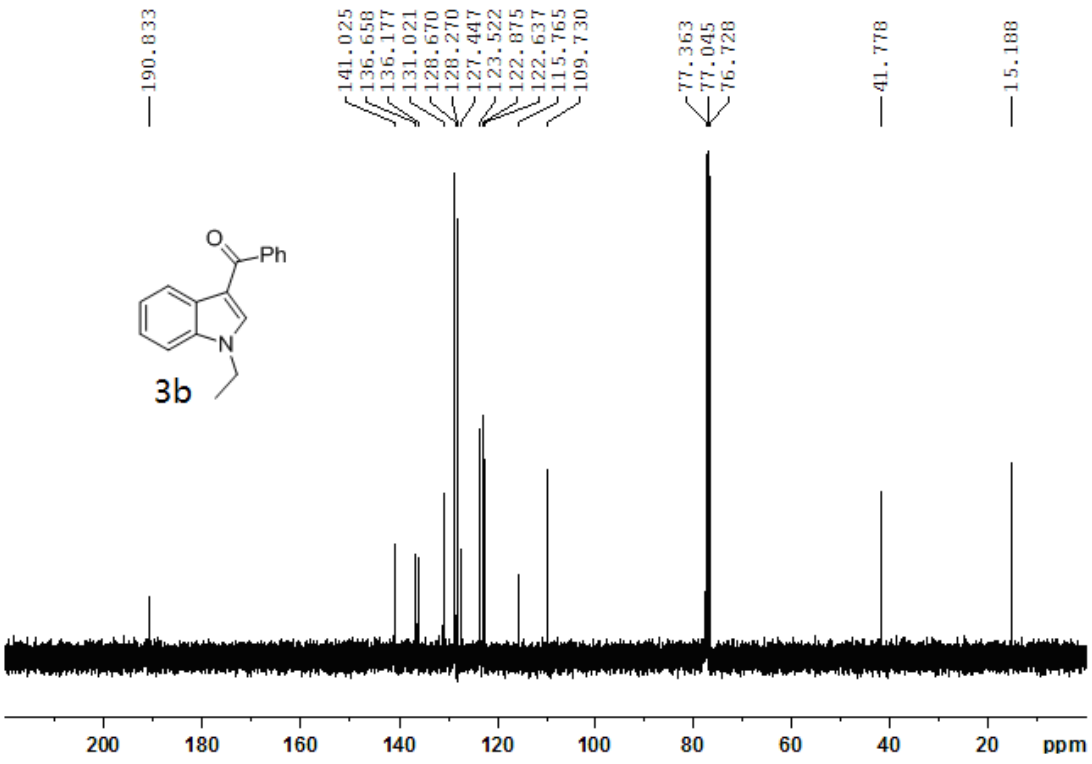
4
3
2
1
0
ppm
1.00
2.05
4.17
3.03
2.05
3.05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77.045
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Ph
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3b
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140
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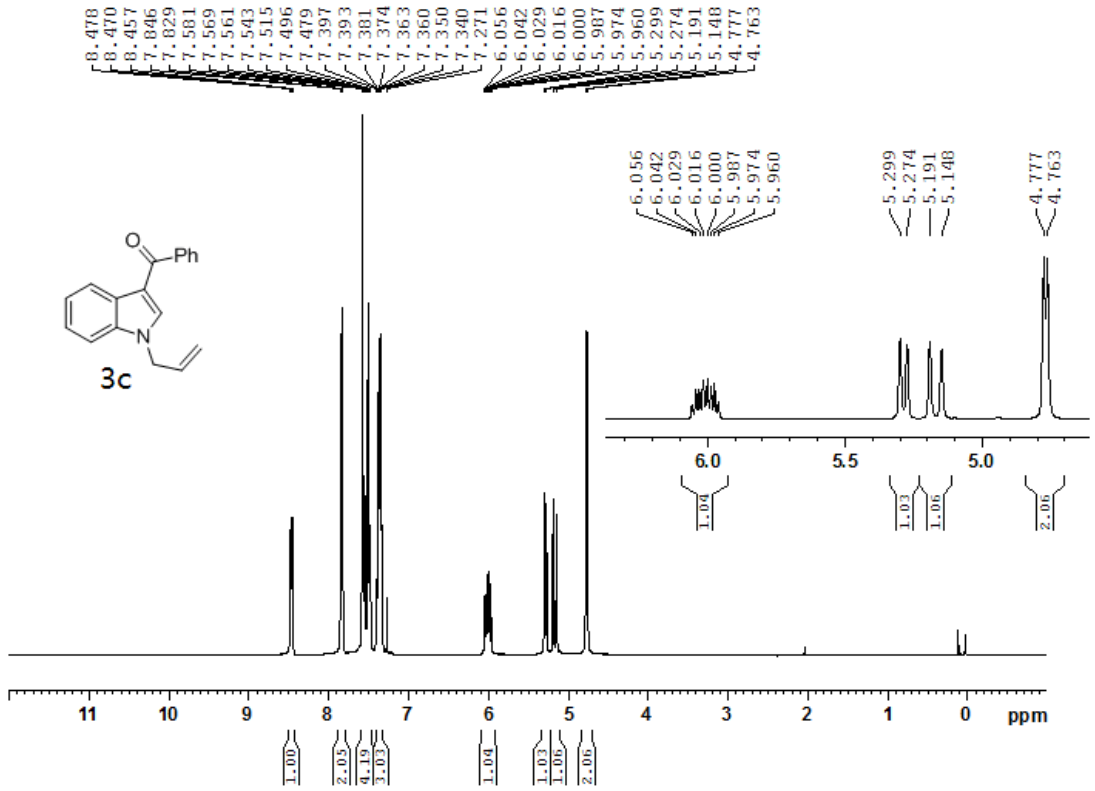
80
60
40
20
ppm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8.457
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7.496
7.479
7.397
7.393
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7.350
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6.042
6.029
6.016
6.000
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5.148
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Ph
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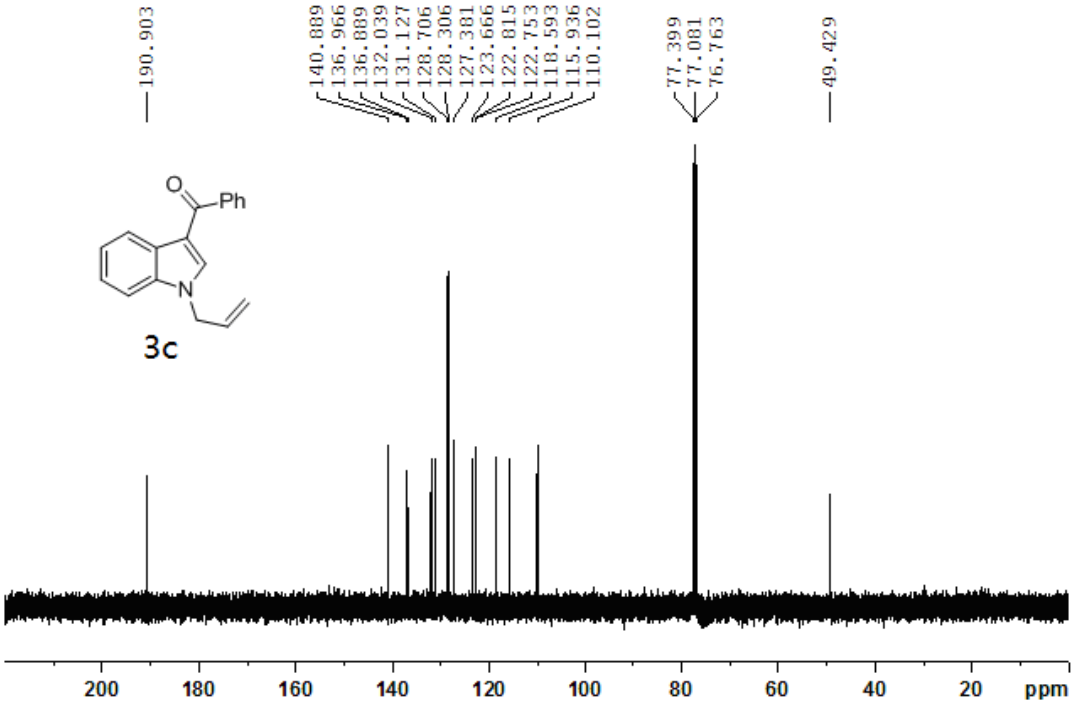
2.06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140.889
136.966
136.889
132.039
131.127
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128.306
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118.593
115.936
110.102
77.399
77.081
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O
Ph
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3c
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140
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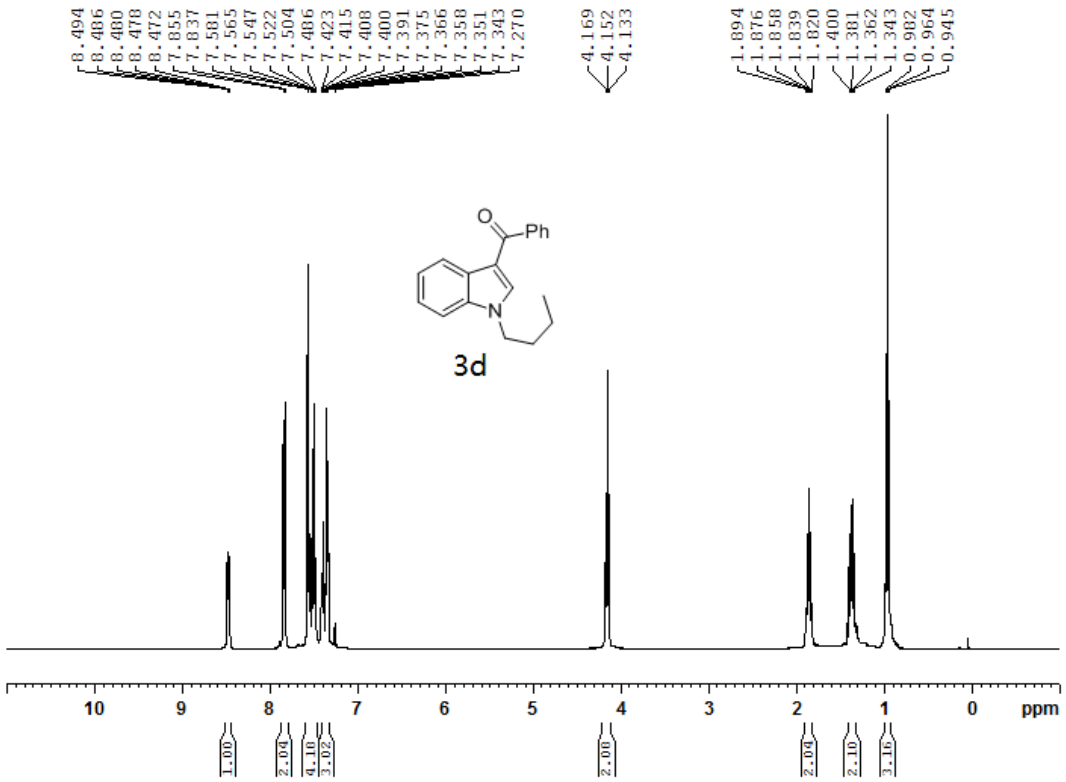
80
60
40
20
ppm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8.478
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7.581
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7.486
7.423
7.415
7.408
7.400
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7.366
7.358
7.351
7.343
7.270
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4.152
4.133
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1.876
1.858
1.839
1.820
1.400
1.381
1.362
1.343
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0.964
0.945
O
Ph
N
3d
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9
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7
6
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3.02
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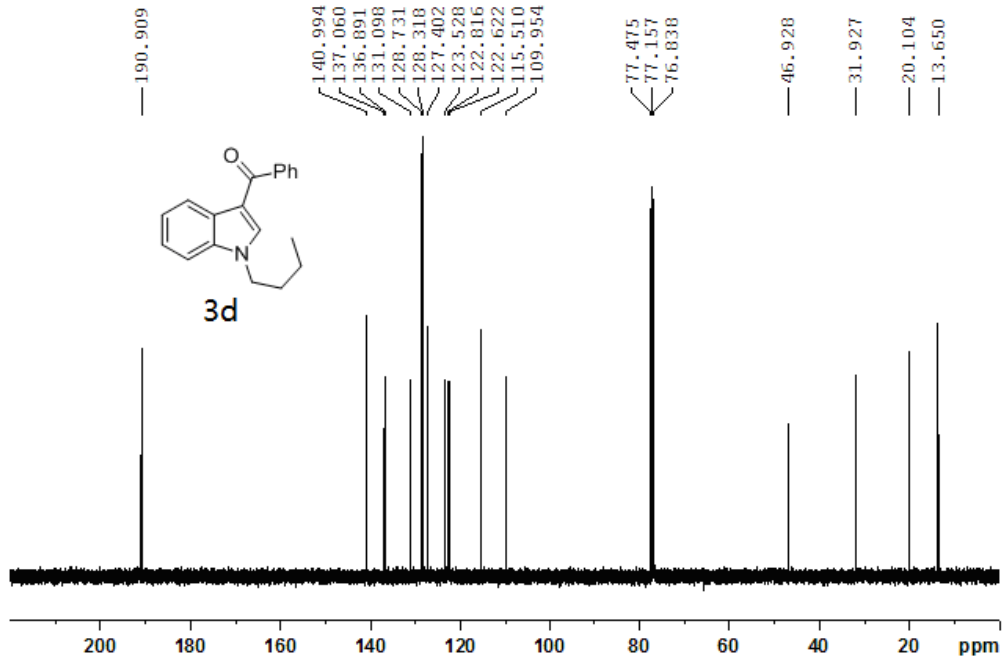
2.10
3.16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136.891
131.098
128.731
128.318
127.402
123.528
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122.622
115.510
109.954
77.475
77.157
76.838
46.928
31.927
20.104
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Ph
N
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200
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140
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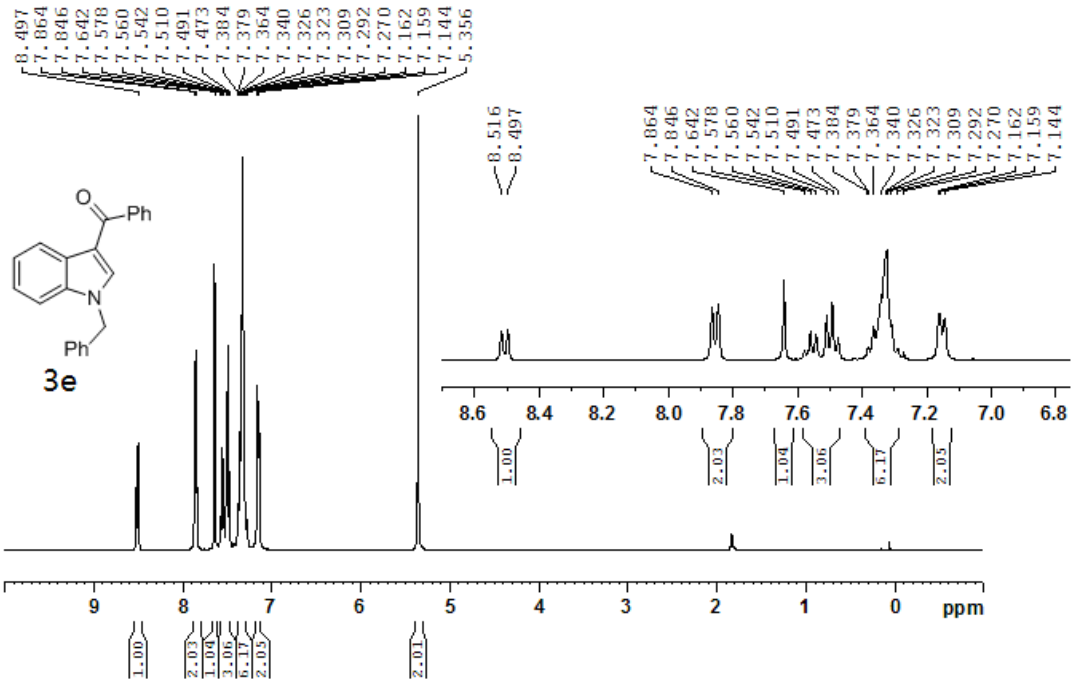
80
60
40
20
ppm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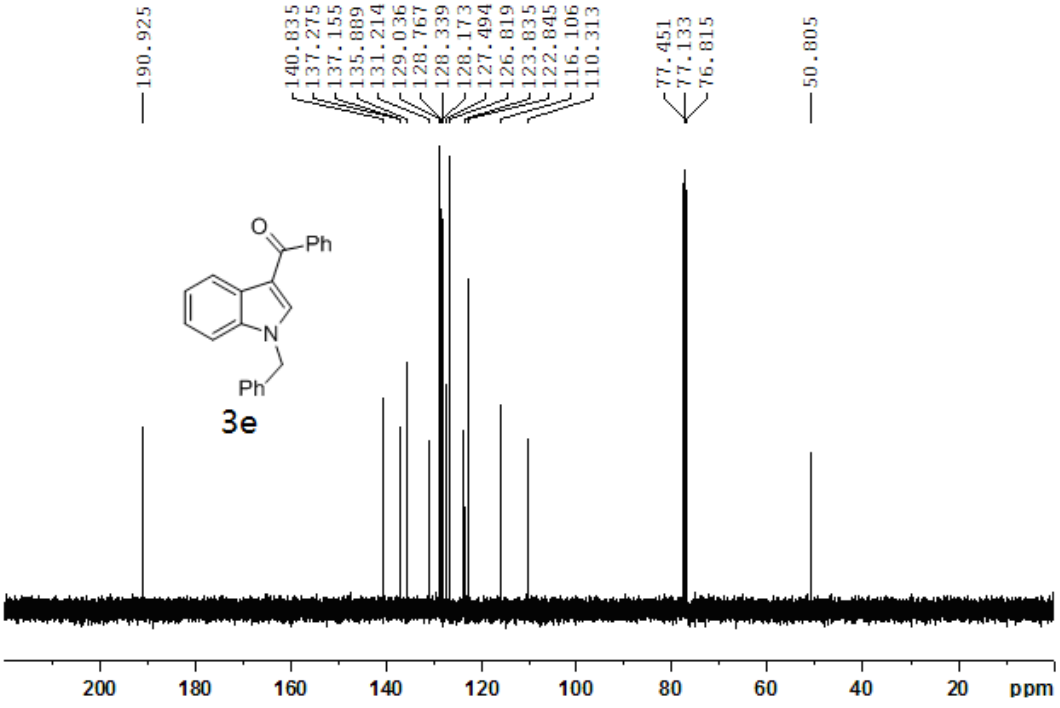
7.846
7.642
7.578
7.560
7.542
7.510
7.491
7.473
7.384
7.379
7.364
7.340
7.326
7.323
7.309
7.292
7.270
7.162
7.159
7.144
5.356
8.516
8.497
O
Ph
N
Ph
3e
ppm
1.00
2.03
1.04
3.06
6.17
2.05
2.01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128.767
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116.106
110.313
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77.133
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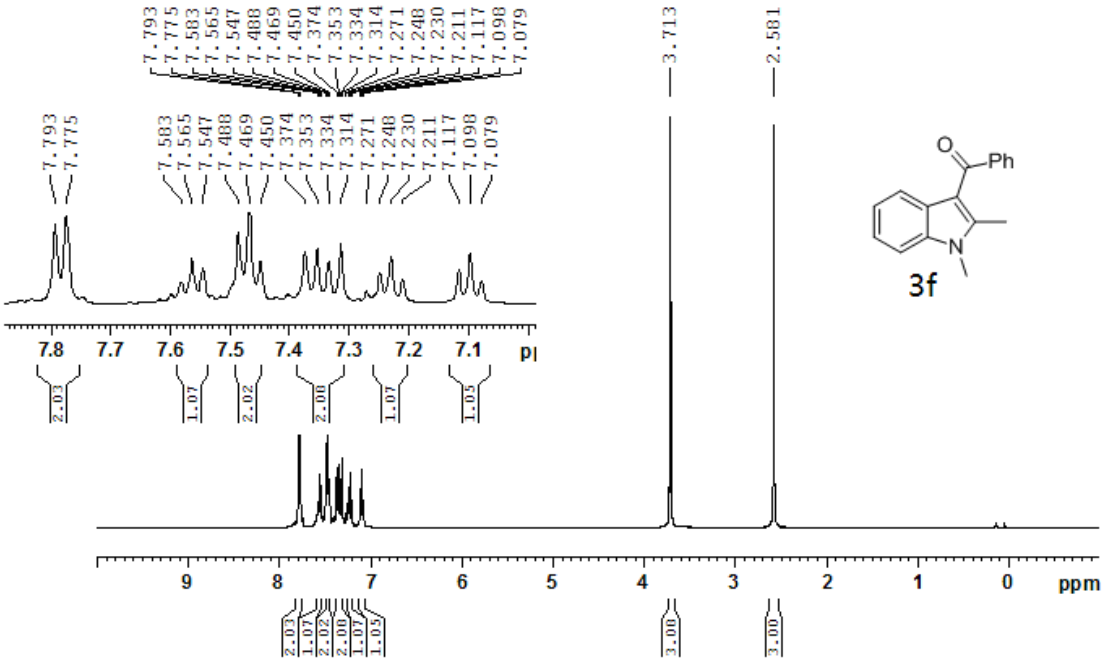
Ph
3e
ppm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7.450
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7.271
7.248
7.230
7.211
7.117
7.098
7.079
3.713
2.581
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Ph
N
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7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
2.03
1.07
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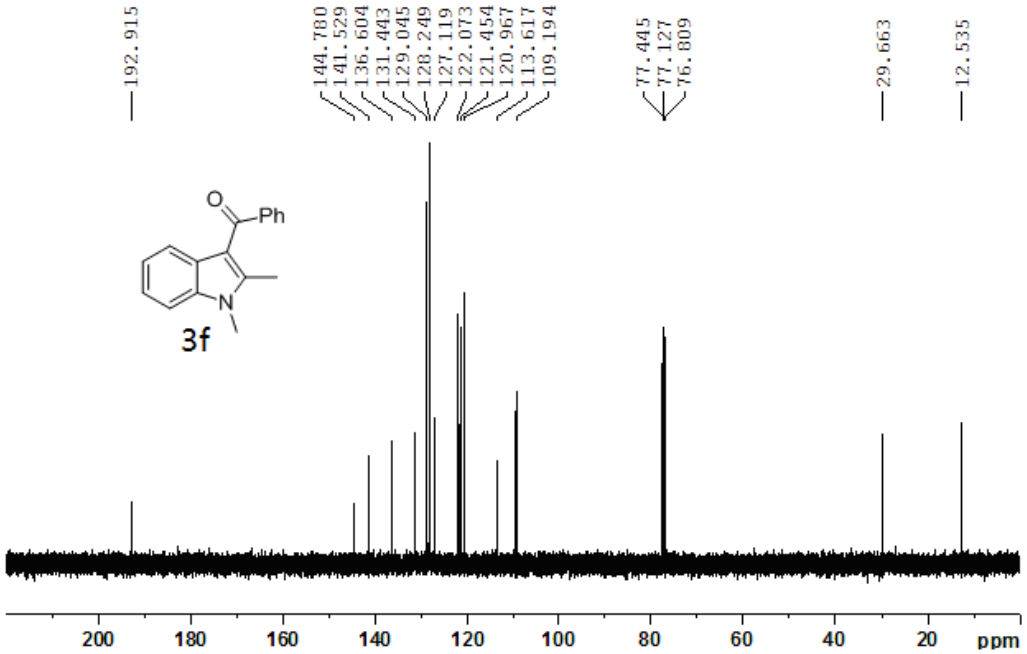
3.00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77.127
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O
Ph
N
3f
200
180
160
140
120
100
80
60
40
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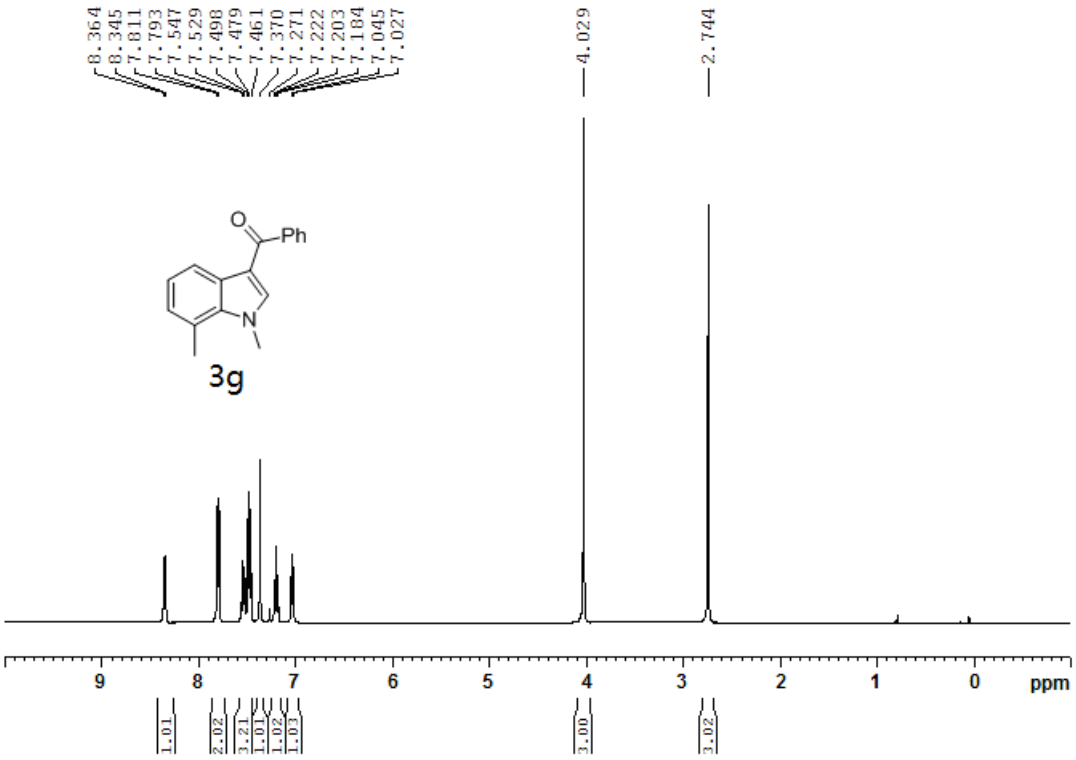
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7.461
7.370
7.271
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7.203
7.184
7.045
7.027
4.029
2.744
O
Ph
N
3g
9
8
7
6
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ppm
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2.02
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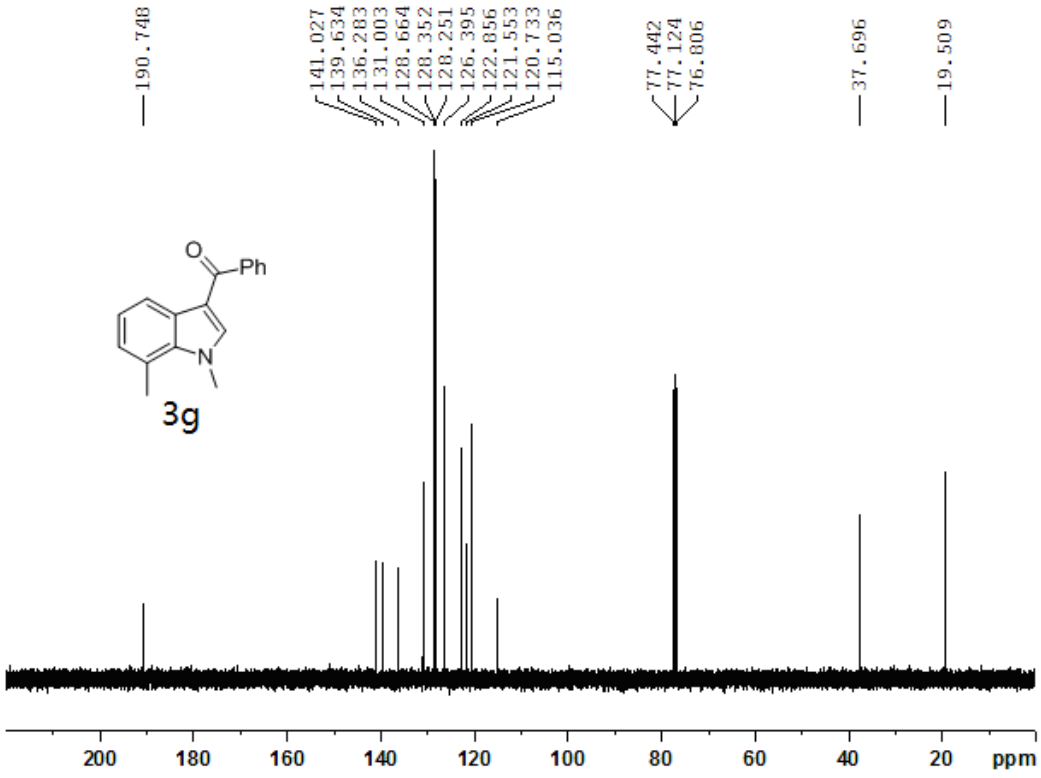
1.01
1.02
1.03
3.00
3.02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115.036
77.442
77.124
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O
Ph
N
3g
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60
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20
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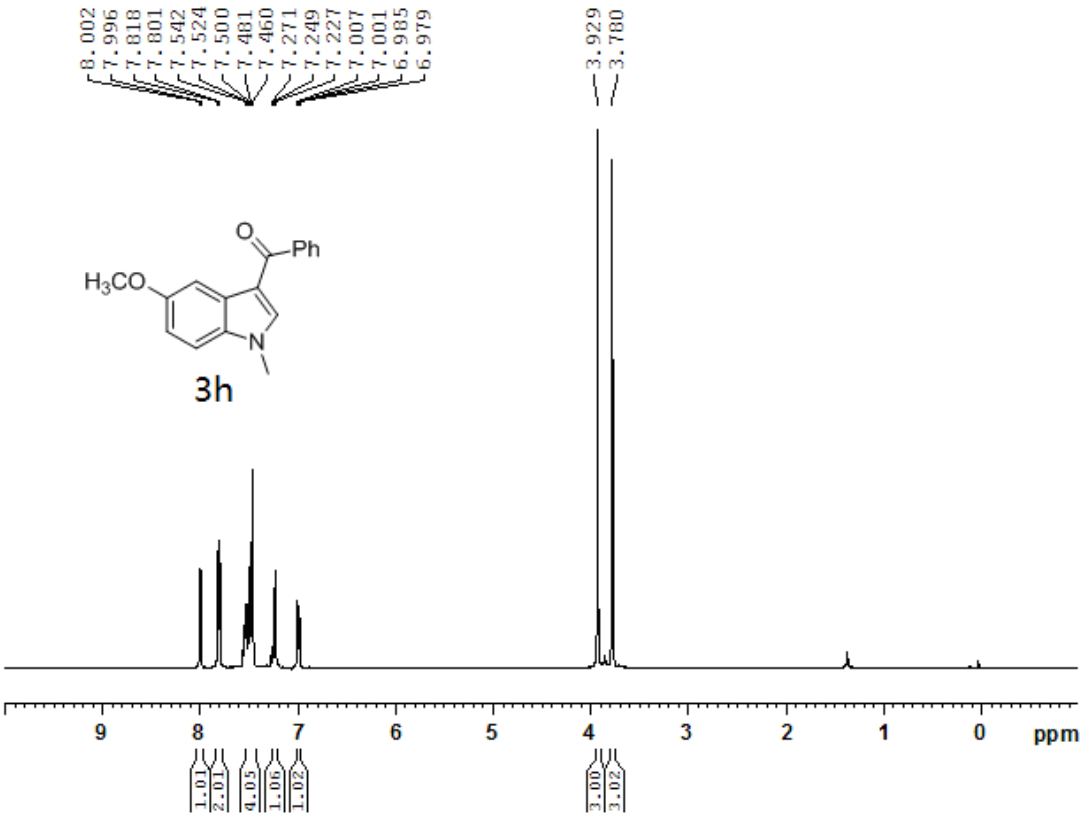
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7.007
7.001
6.985
6.979
3.929
3.780
O
Ph
H3CO
N
3h
9
8
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5
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2
1
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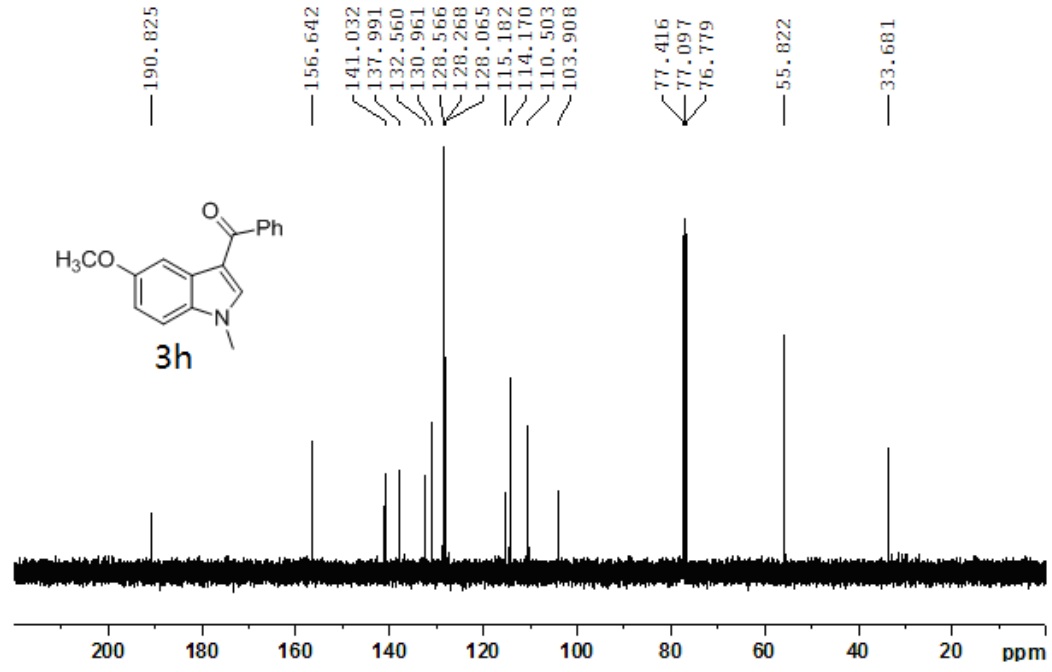
3.02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77.416
77.097
76.779
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Ph
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N
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20
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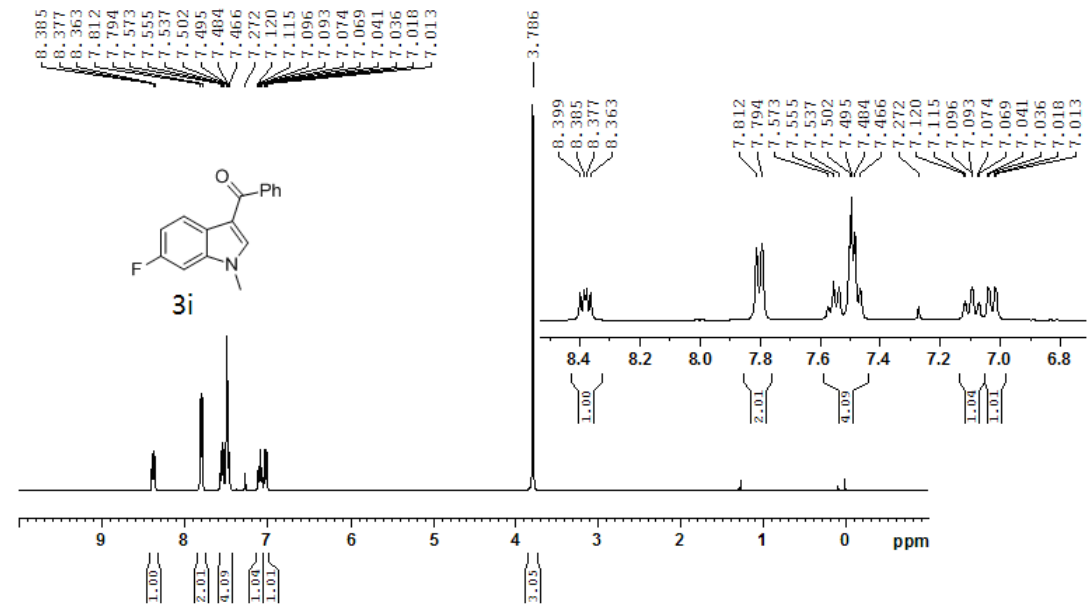
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7.537
7.502
7.495
7.484
7.466
7.272
7.120
7.115
7.096
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7.041
7.036
7.018
7.013
3.786
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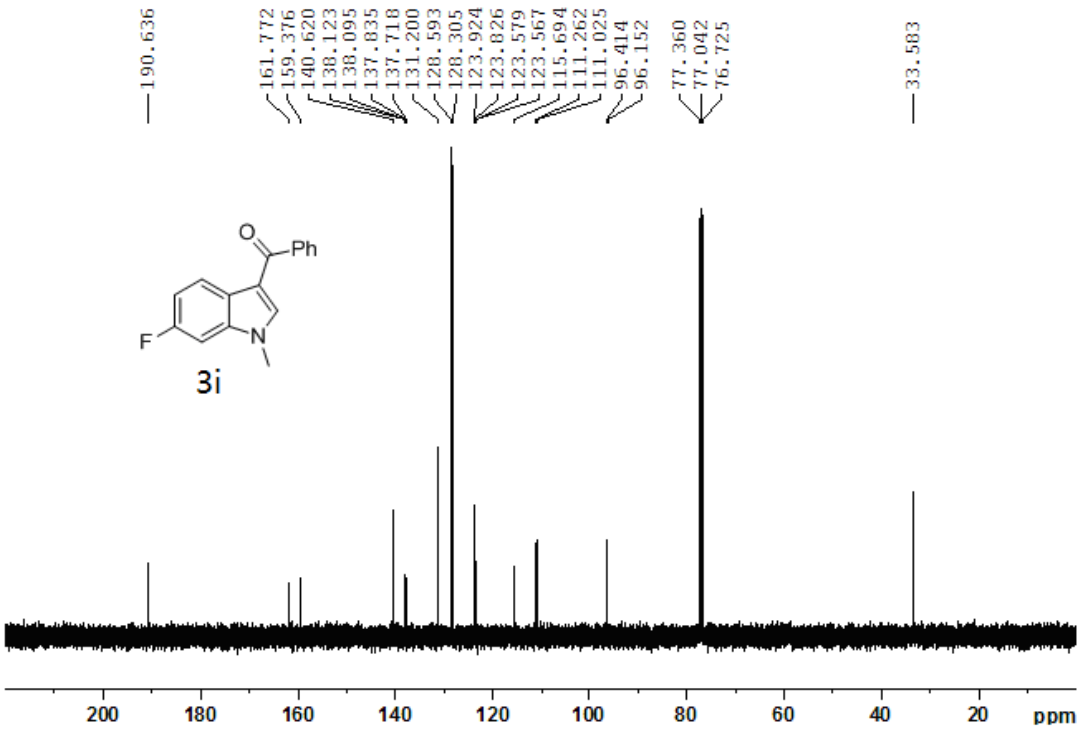
Ph
F
N
3i
ppm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159.376
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128.305
123.924
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123.579
123.567
115.694
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96.152
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76.725
33.583
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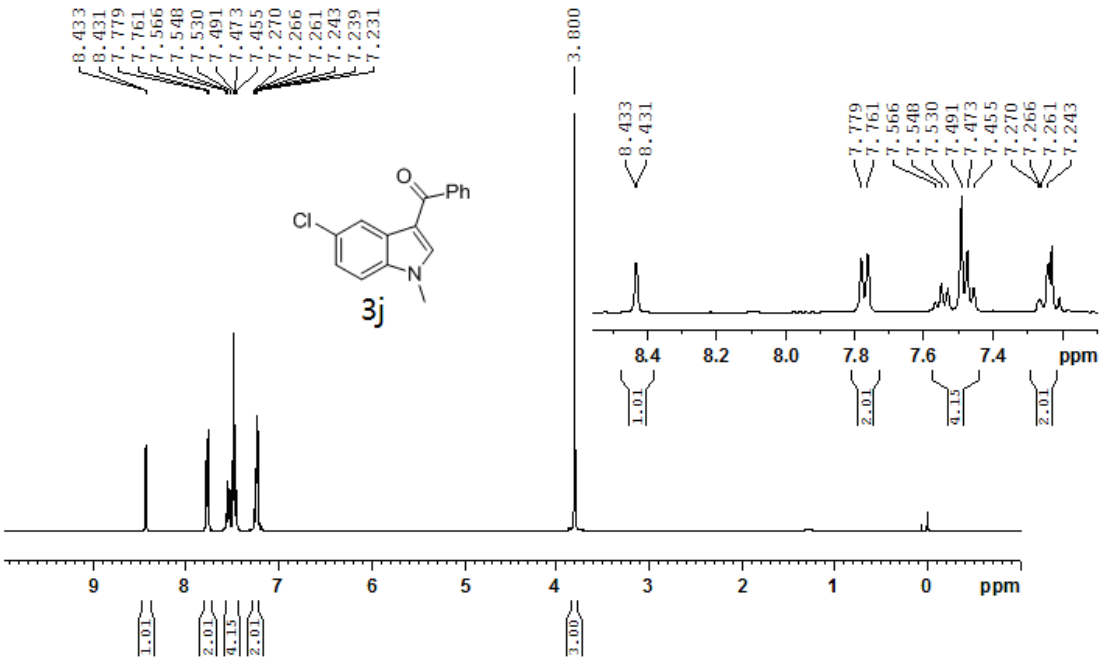
Ph
F
N
3i
ppm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7.761
7.566
7.548
7.530
7.491
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7.455
7.270
7.266
7.261
7.243
7.239
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3.800
O
Ph
Cl
N
3j
ppm
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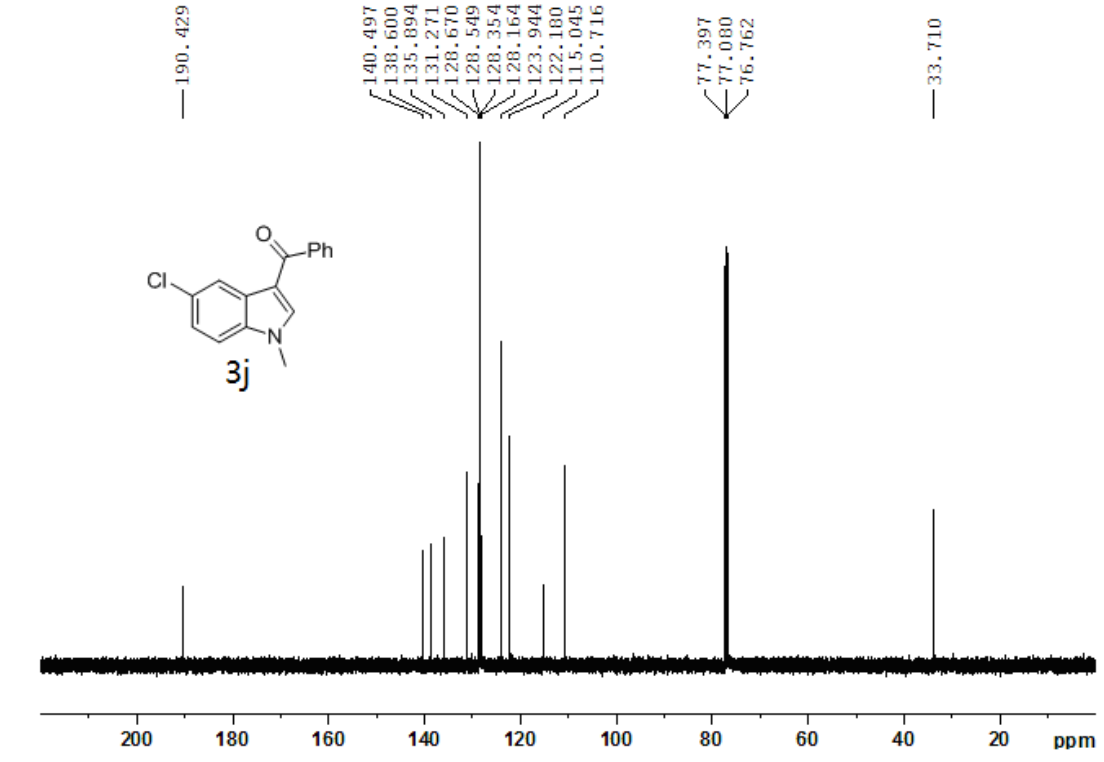
2.01
4.15
2.01
3.00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128.670
128.549
128.354
128.164
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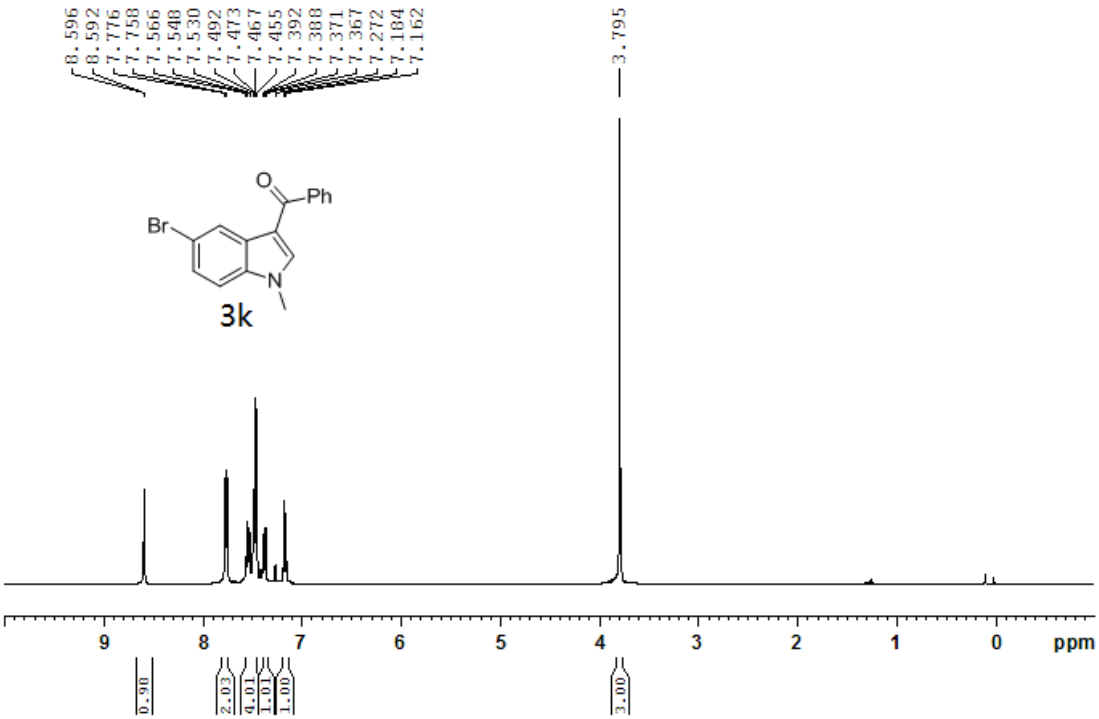
115.045
110.716
77.397
77.080
76.762
33.710
O
Ph
Cl
N
3j
ppm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7.566
7.548
7.530
7.492
7.473
7.467
7.455
7.392
7.388
7.371
7.367
7.272
7.184
7.162
3.795
O
Ph
Br
N
3k
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4
3
2
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ppm
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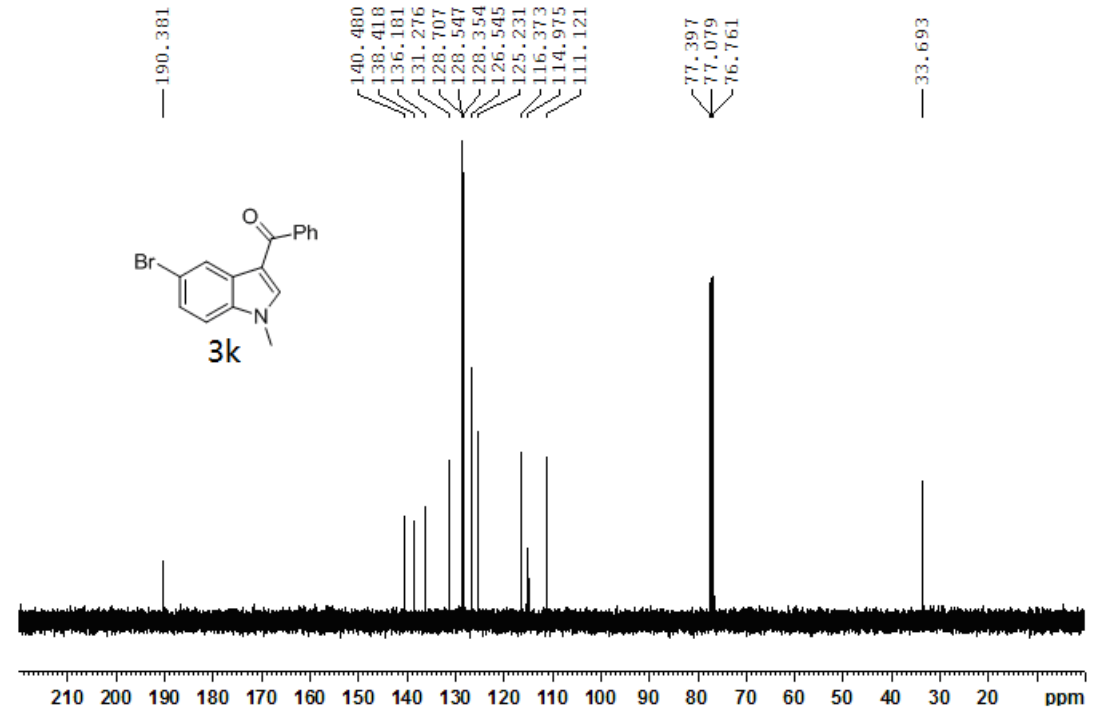
2.03
4.01
1.01
1.00
3.00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128.547
128.354
126.545
125.231
116.373
114.975
111.121
77.397
77.079
76.761
33.693
O
Ph
Br
N
3k
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160
150
140
130
120
110
100
90
80
70
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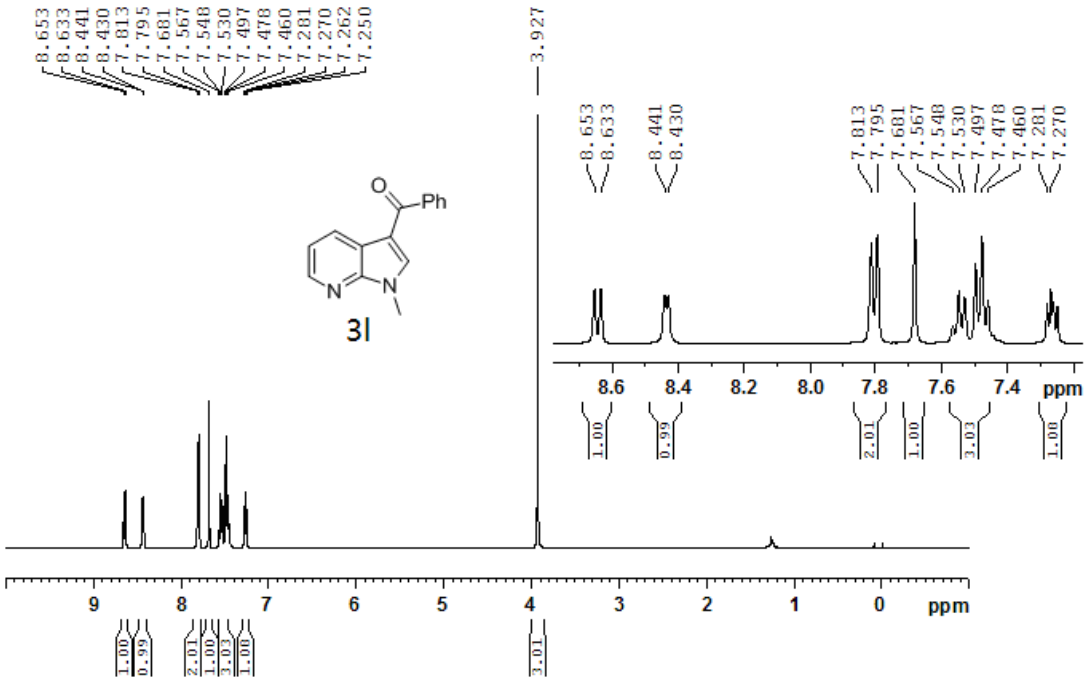
50
40
30
20
ppm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7.567
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7.530
7.497
7.478
7.460
7.281
7.270
7.262
7.250
3.927
O
Ph
N
N
3l
ppm
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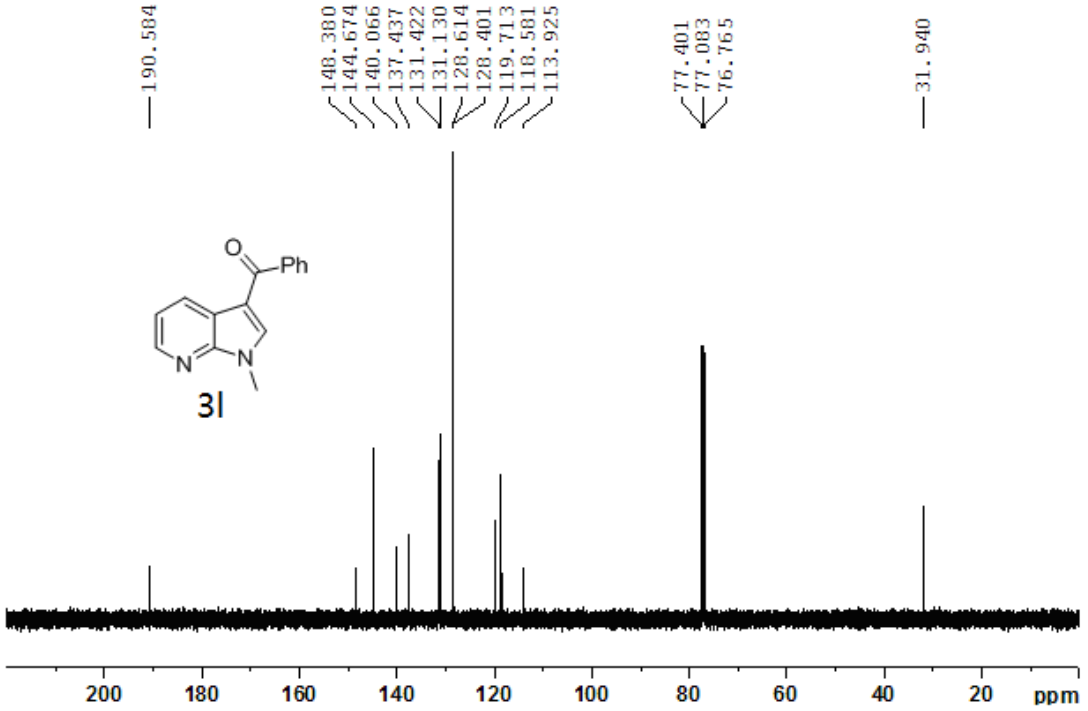
0.99
2.01
1.00
3.03
1.00
3.01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128.614
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113.925
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77.083
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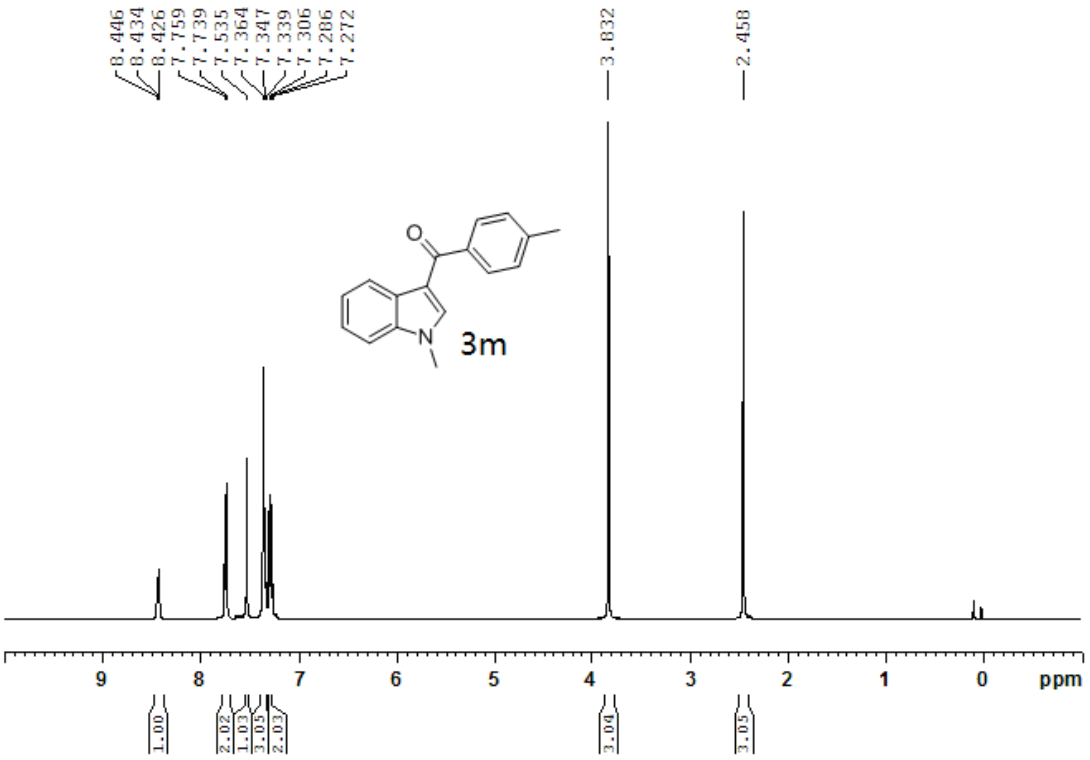
31.940
O
Ph
N
N
3l
ppm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7.535
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7.347
7.339
7.306
7.286
7.272
3.832
2.458
3m
9
8
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2
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ppm
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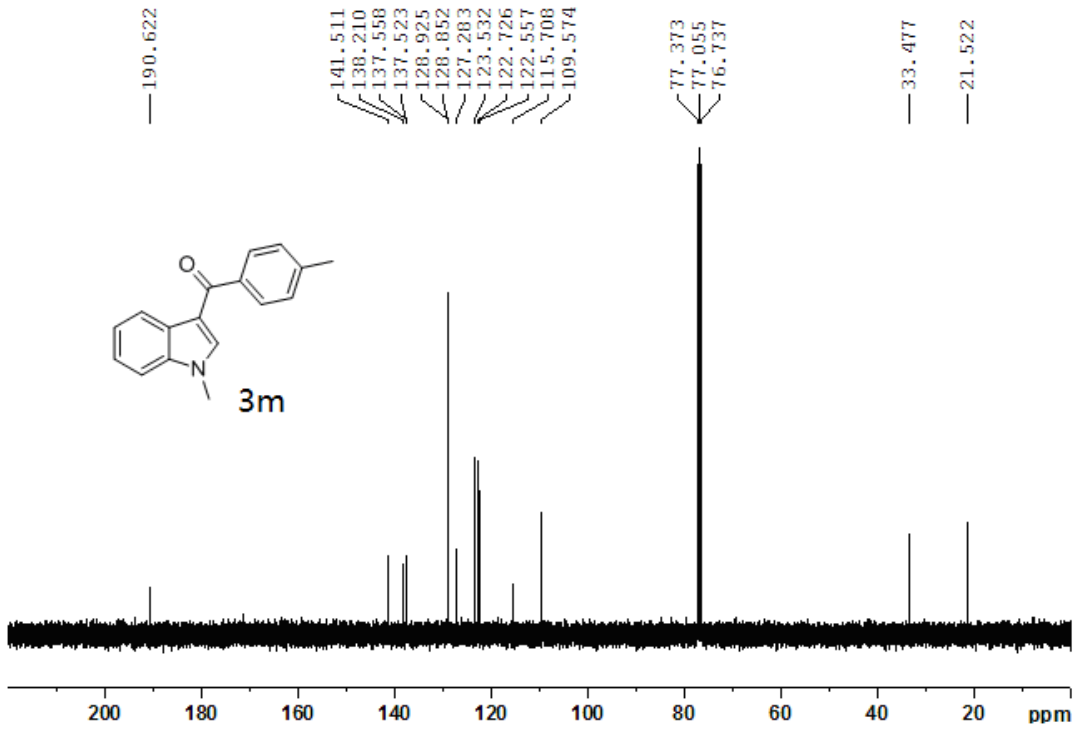
1.03
3.05
2.03
3.04
3.05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137.523
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128.852
127.283
123.532
122.726
122.557
115.708
109.574
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77.055
76.737
33.477
21.522
3m
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140
120
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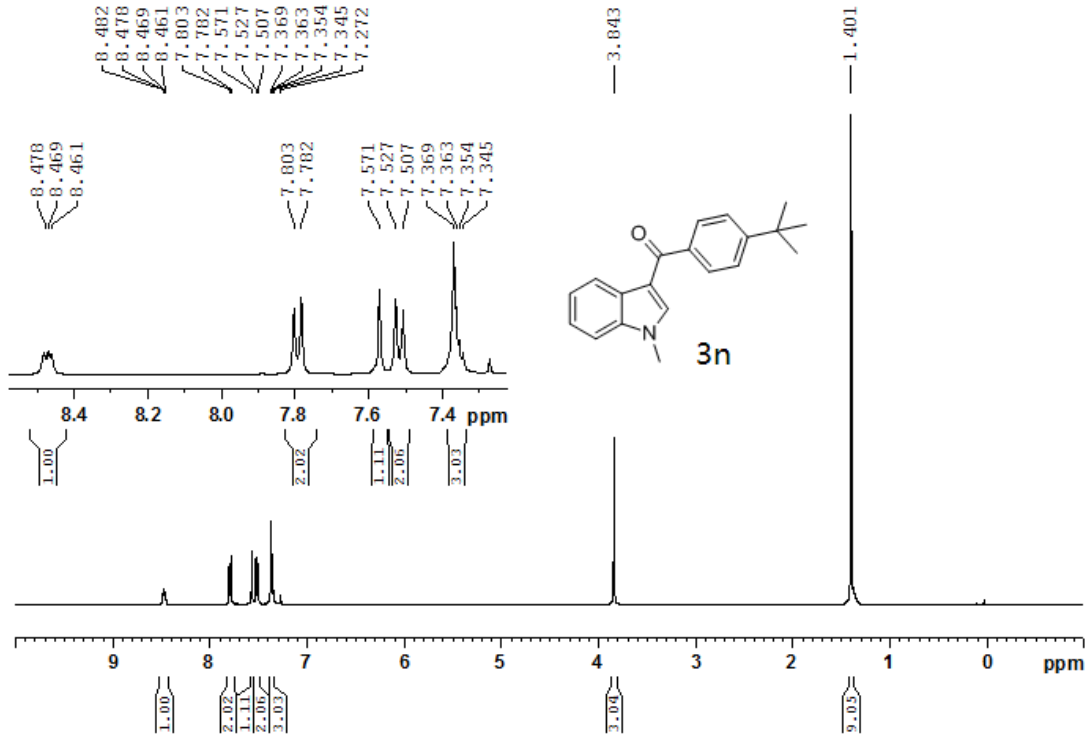
60
40
20
ppm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7.363
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7.345
7.272
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3n
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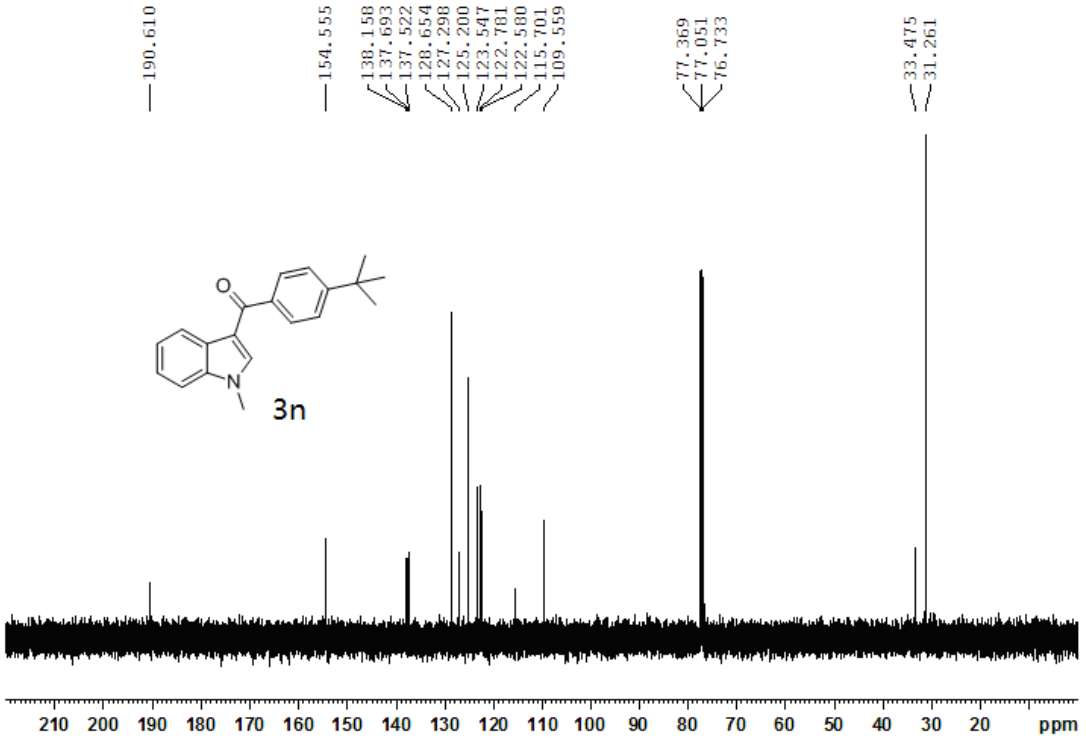
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76.733
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3n
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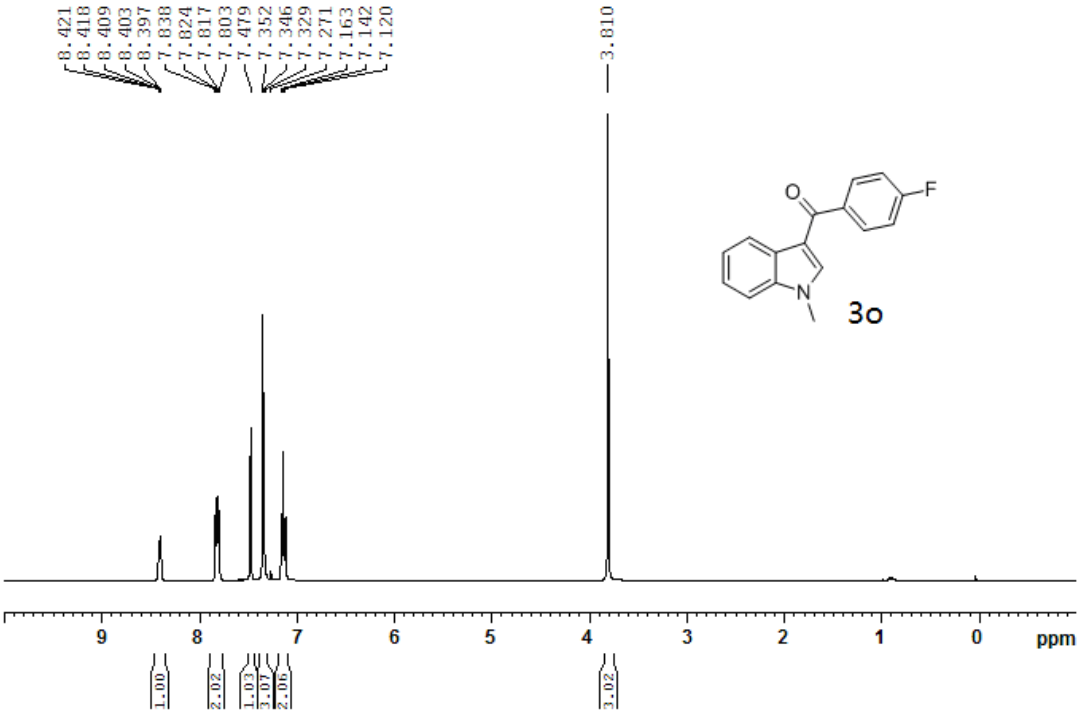
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7.838
7.824
7.817
7.803
7.479
7.352
7.346
7.329
7.271
7.163
7.142
7.120
3.810
O
F
N
3o
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8
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4
3
2
1
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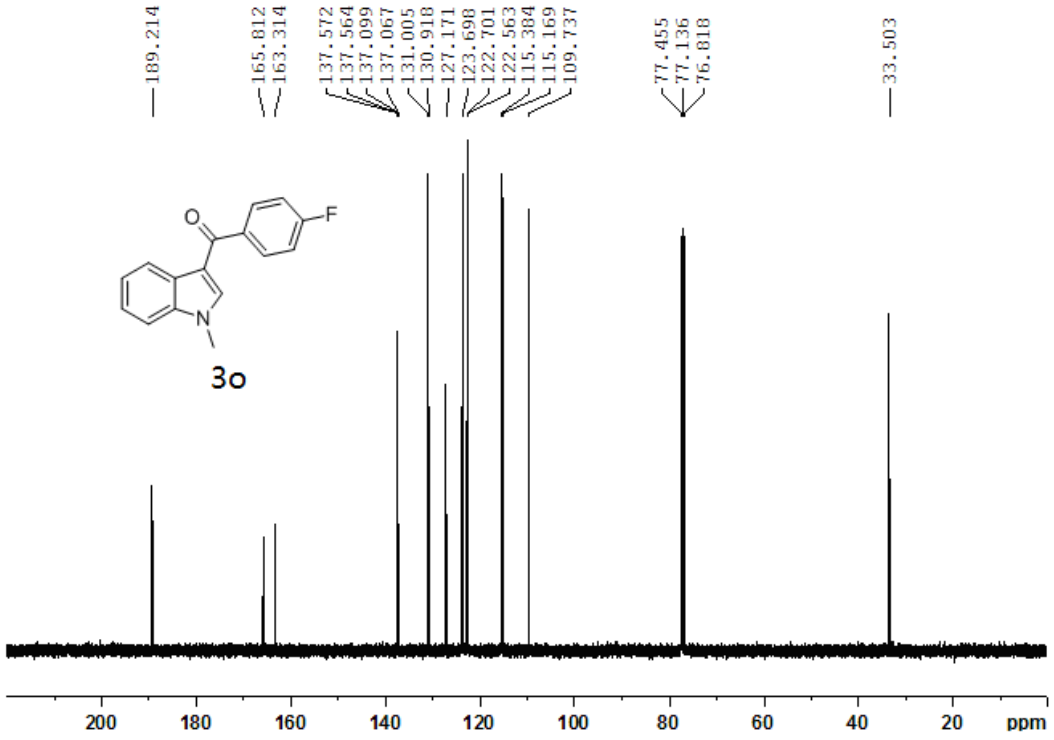
2.02
1.03
3.07
2.06
3.02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131.005
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123.698
122.701
122.563
115.384
115.169
109.737
77.455
77.136
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F
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60
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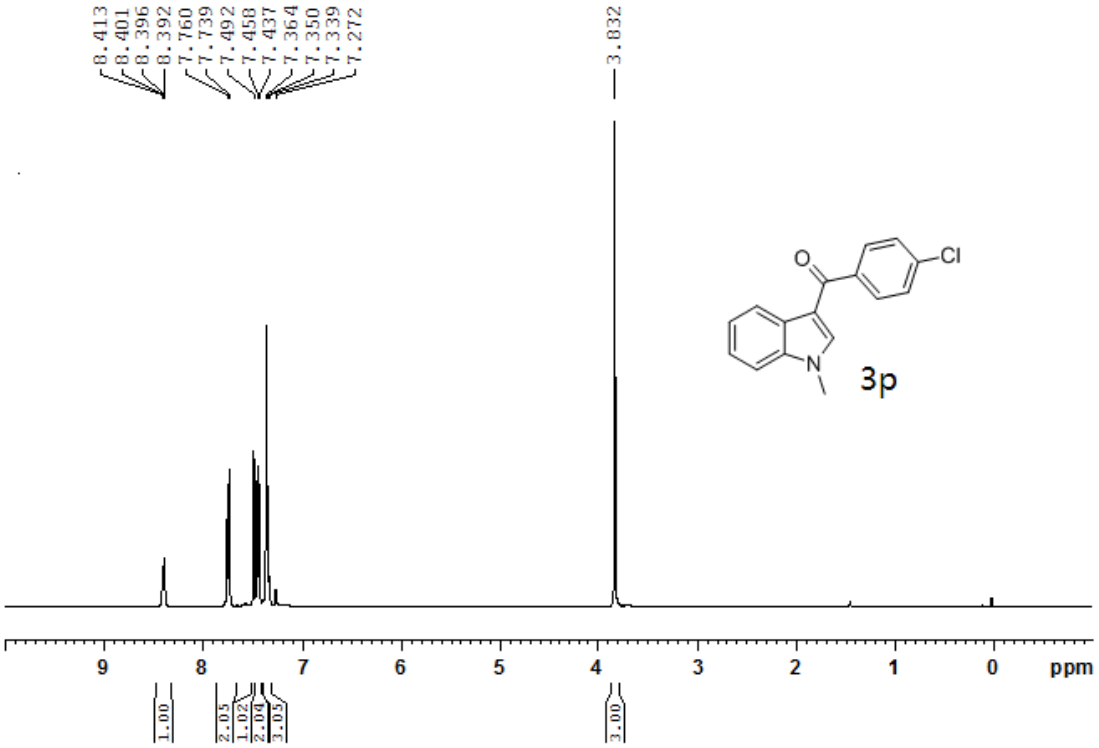
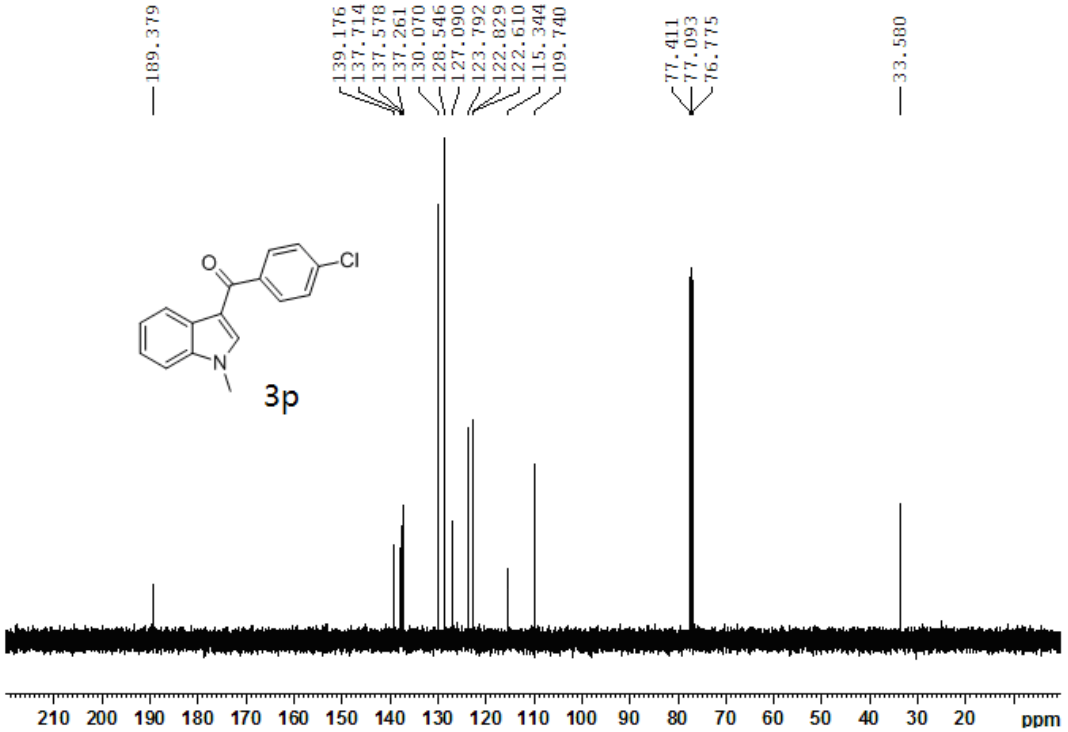
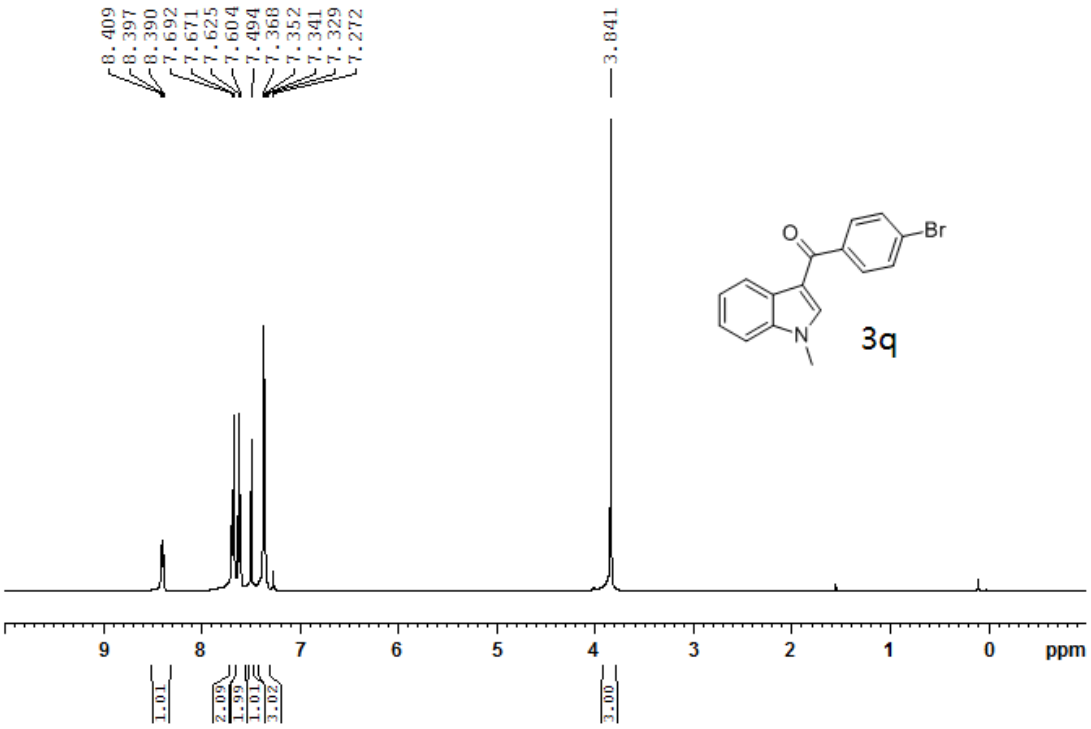
20
ppm



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7.341
7.329
7.272
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Br
O
N
3q
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4
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2
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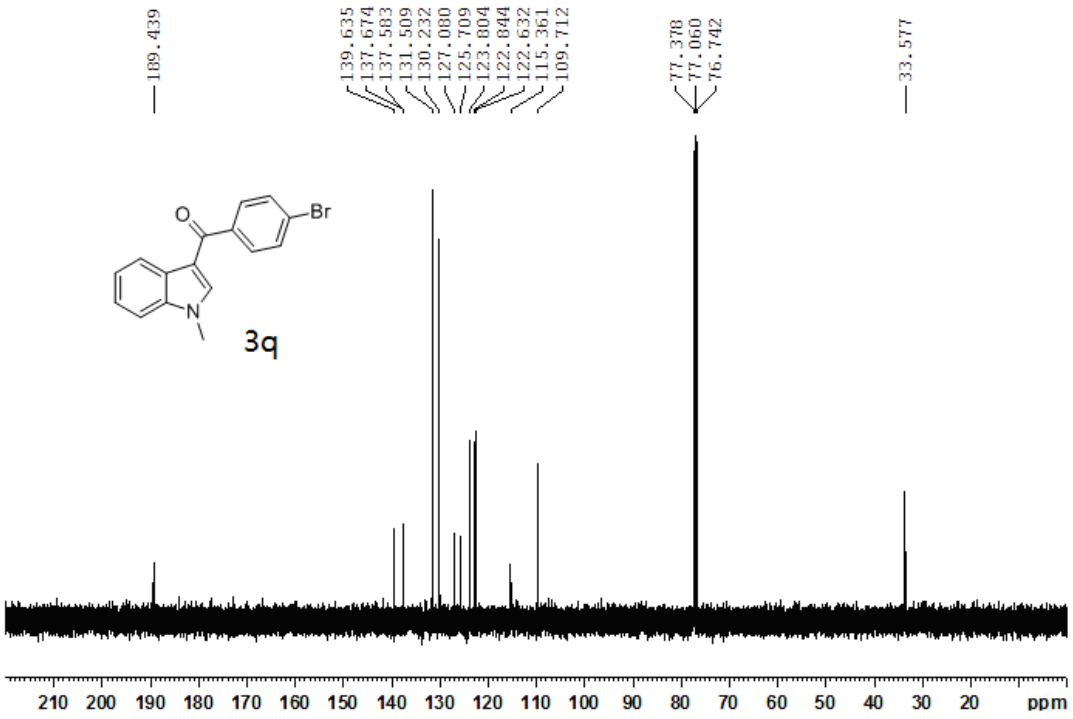
3.00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125.709
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109.712
77.378
77.060
76.742
33.577
Br
O
N
3q
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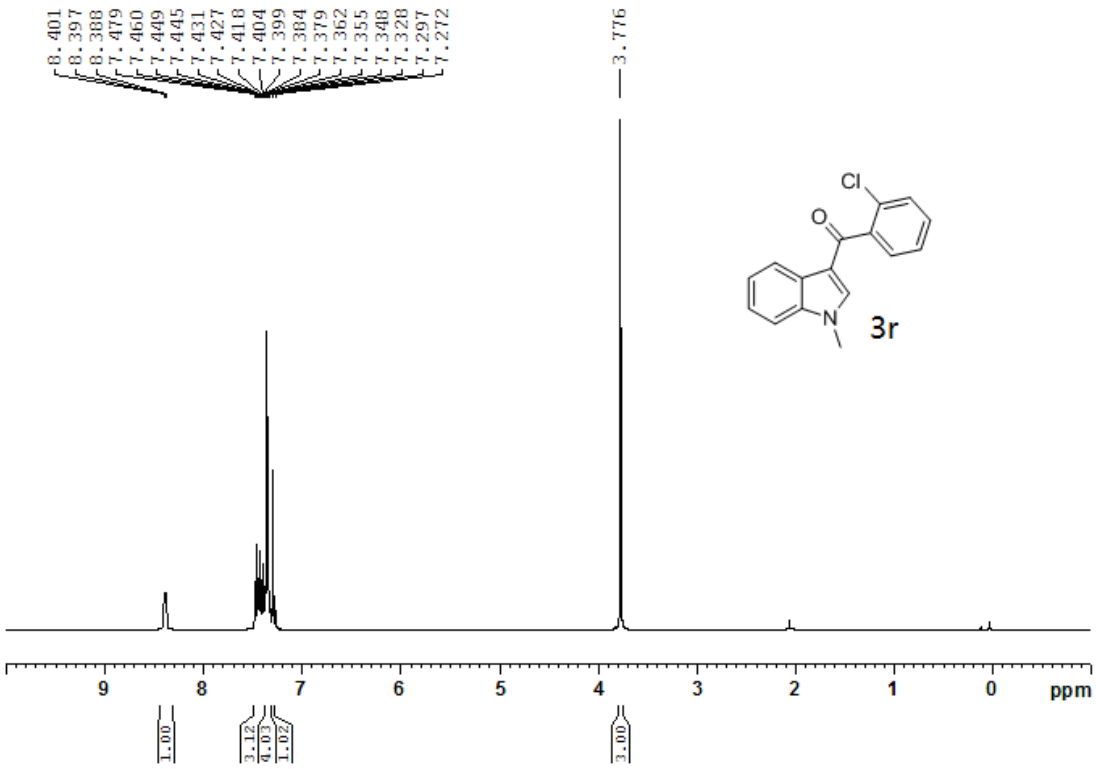
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.404
7.399
7.384
7.379
7.362
7.355
7.348
7.328
7.297
7.272
3.776
Cl
O
N
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6
5
4
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2
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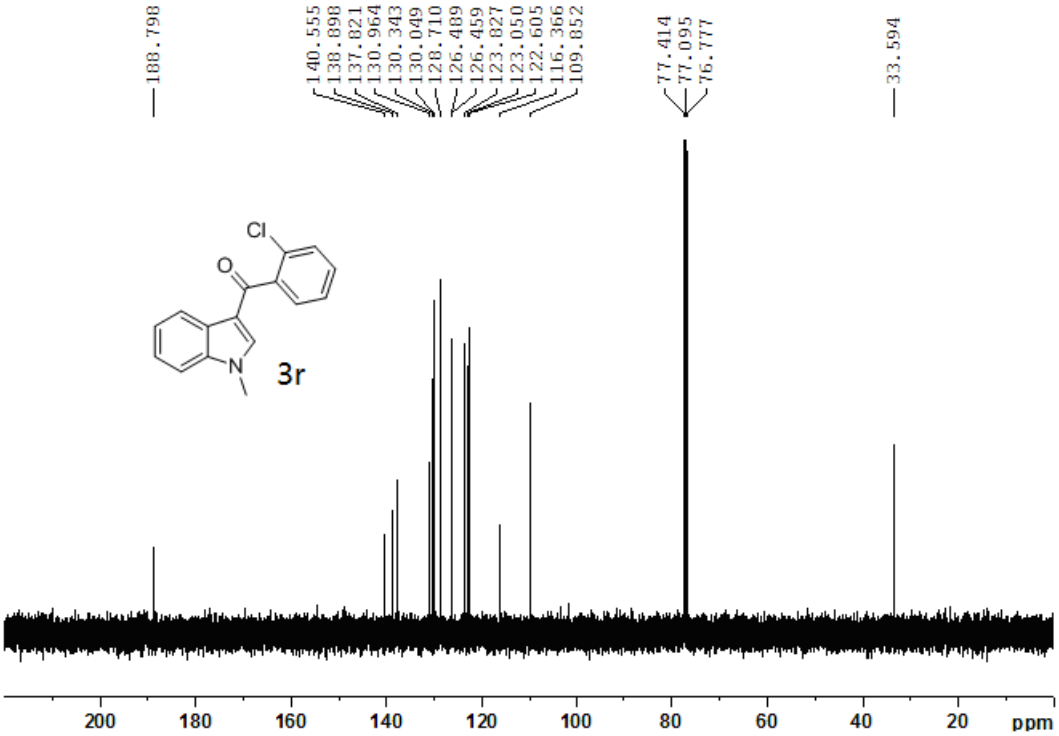
1.00
3.12
4.03
1.02
3.00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122.605
116.366
109.852
77.414
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76.777
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Cl
O
N
3r
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180
160
140
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100
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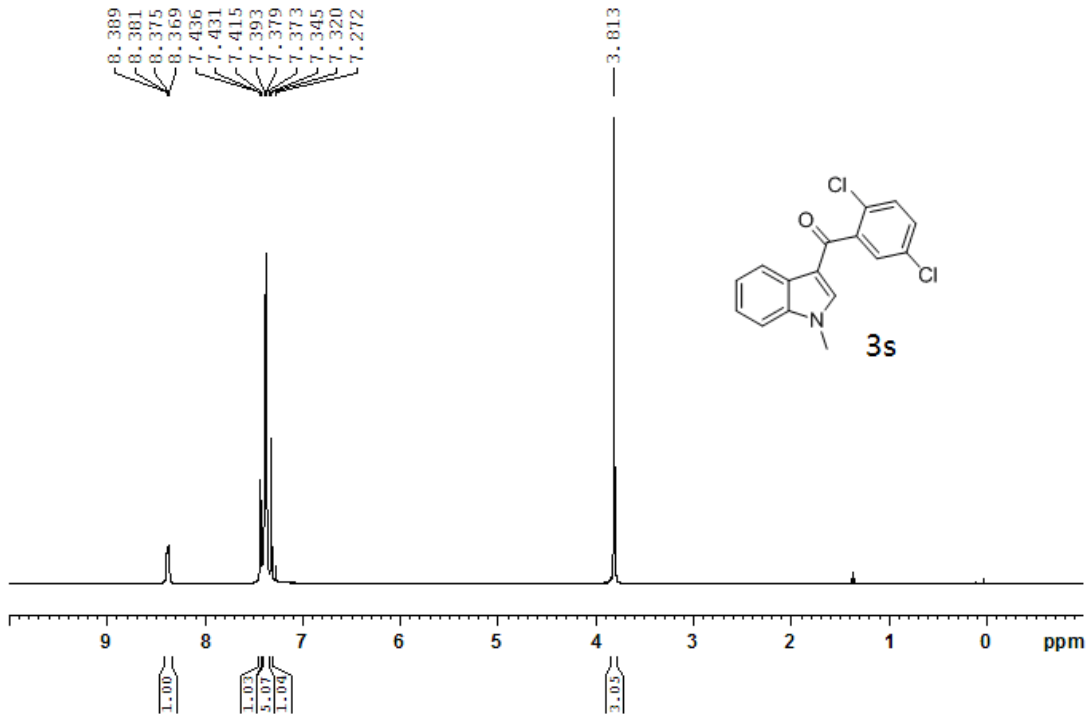
60
40
20
ppm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7.373
7.345
7.320
7.272
3.813
Cl
O
Cl
N
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5
4
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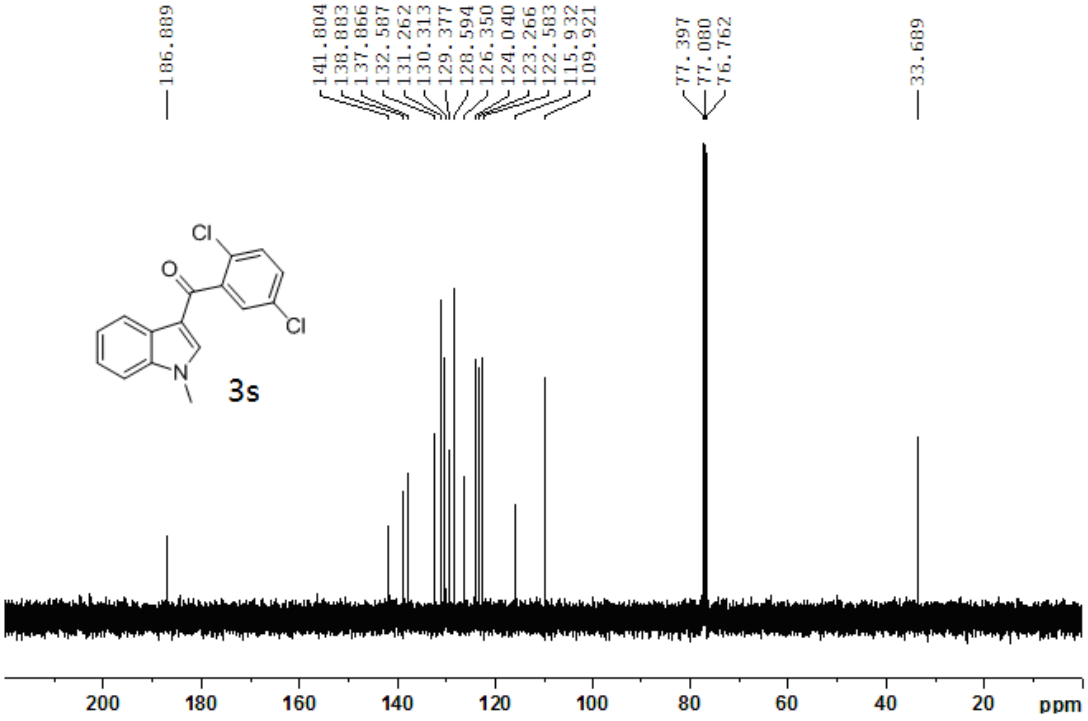
1.03
5.07
1.04
3.05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115.932
109.921
77.397
77.080
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O
Cl
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140
120
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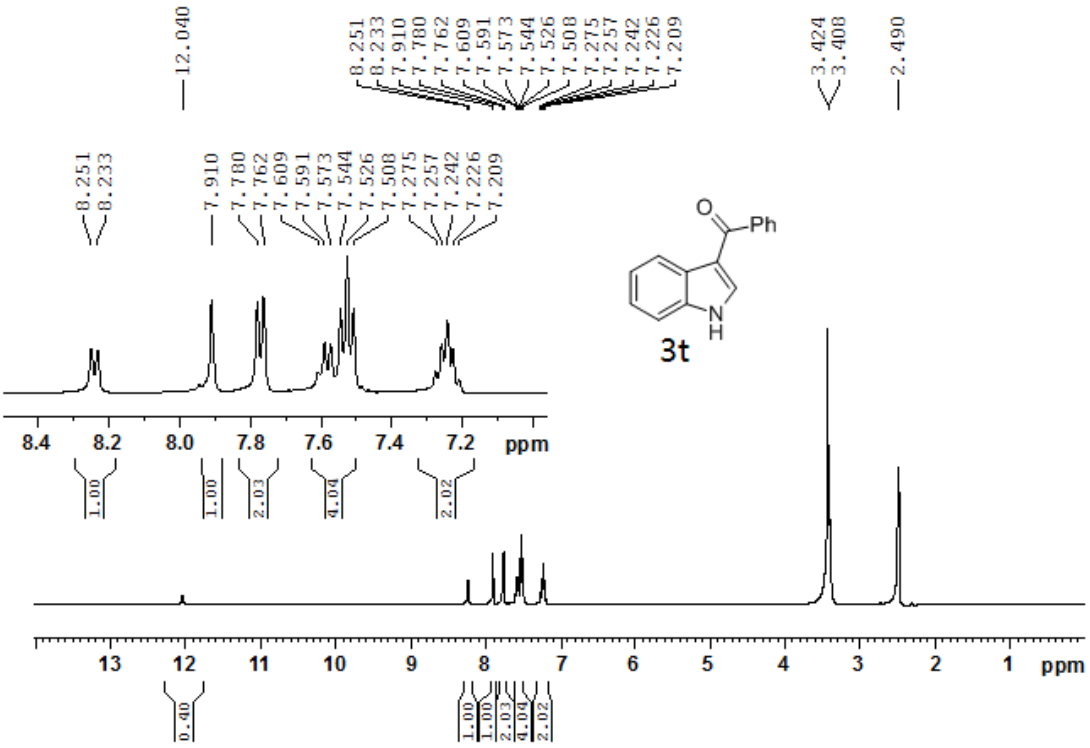
60
40
20
ppm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7.762
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7.544
7.526
7.508
7.275
7.257
7.242
7.226
7.209
3.424
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Ph
O
N
H
3t
ppm
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1.00
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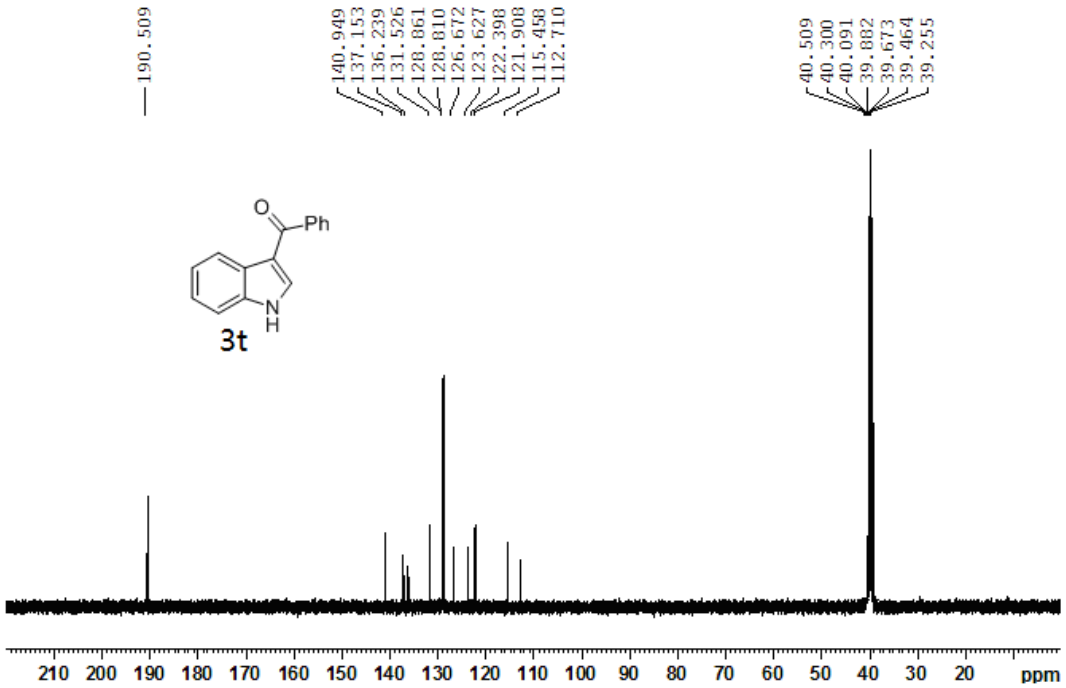
4.04
2.02
0.40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112.710
40.509
40.300
40.091
39.882
39.673
39.464
39.255
Ph
O
N
H
3t
ppm