Rhodium-Catalyzed *ortho*-Acrylation of Aryl Ketone *O*-Methyl Oximes with Cyclopropenones

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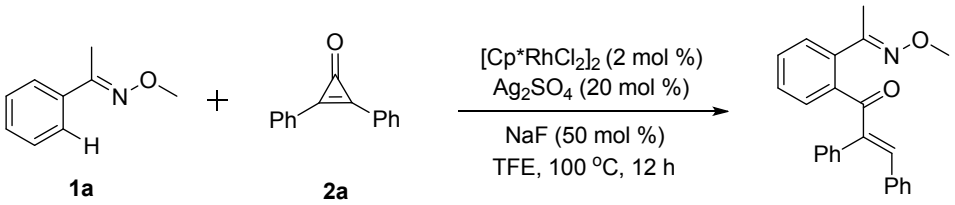
Supporting Information

General remark

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400M and Mercury 300M in $CDCl_3$. All ^{1}H NMR and ^{13}C NMR chemical shifts were given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. ^{1}H NMR and ^{13}C NMR spectra of all compounds were provided. Products were purified by flash chromatography on 200-300 mesh silica gels. All melting points were determined without correction. All reagents were purchased commercially and used as received, unless otherwise noted.

General procedure for the synthesis of 3aa

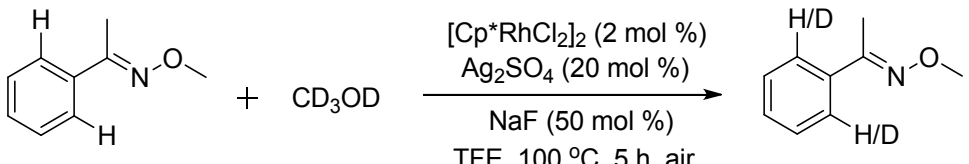


1a **2a** **3aa**

A mixture of (*E*)-acetophenone *O*-methyl oxime (**1a**, 0.20 mmol), diphenylcyclopropenone (**2a**, 0.30 mmol), $[Cp^*RhCl_2]_2$ (0.004mmol), Ag_2SO_4 (0.04mmol) and NaF (0.10 mmol) in TFE (2 mL) was stirred at 100 °C for 12 h. After the reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure to obtain the crude product. The residue was purified by silica gel chromatography (eluent: petroleum/ethyl acetate = 10/1) to obtain the desired product **3aa** as light yellow liquid (61.0 mg, 86 % yield).

Mechanitic studies

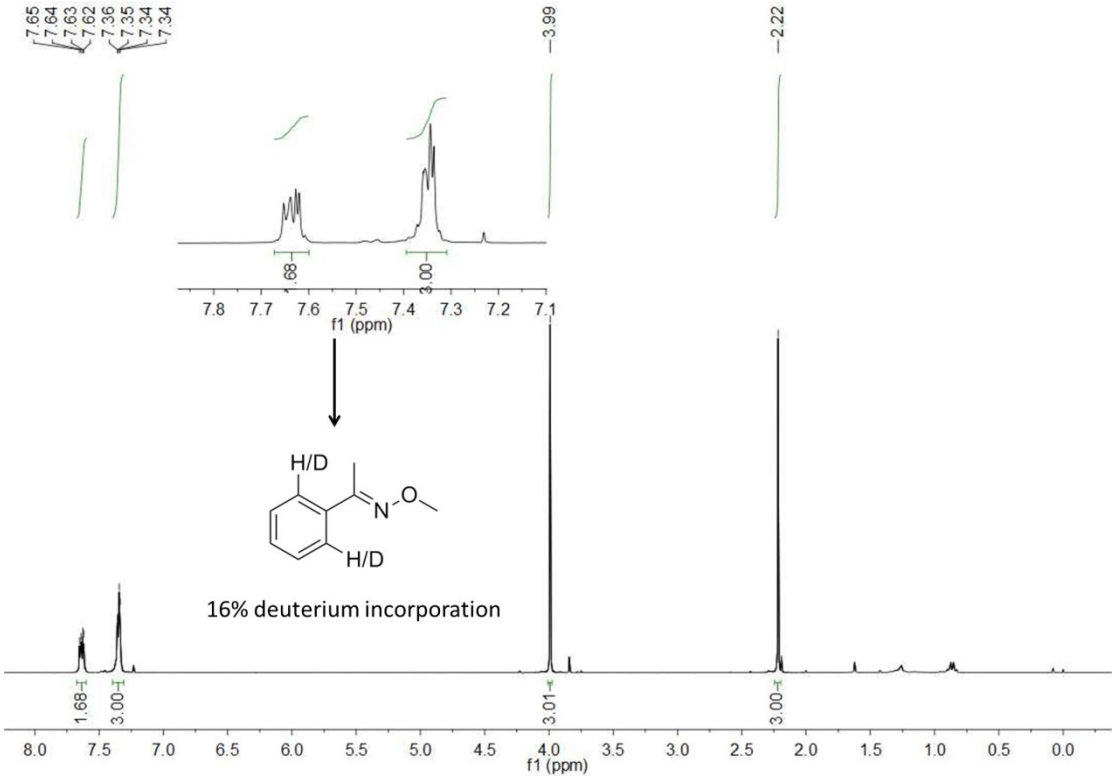
(a) H/D exchange experiment



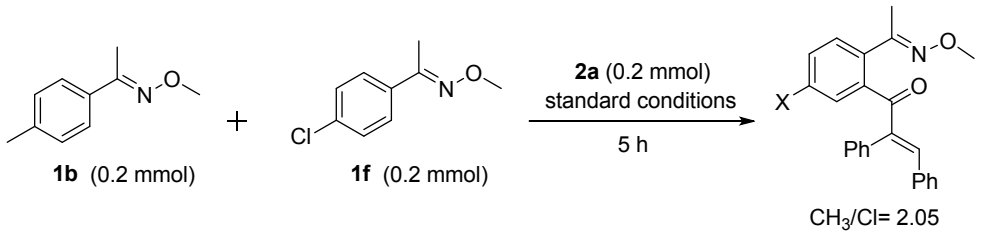
1a 16% D

A mixture of (*E*)-acetophenone *O*-methyl oxime (**1a**, 0.20 mmol), CD_3OD (0.1 mL), $[Cp^*RhCl_2]_2$ (0.004 mmol), Ag_2SO_4 (0.04 mmol) and NaF (0.10 mmol) in TFE (2 mL) was stirred at 100 °C for 5 h. After the reaction mixture was cooled to room

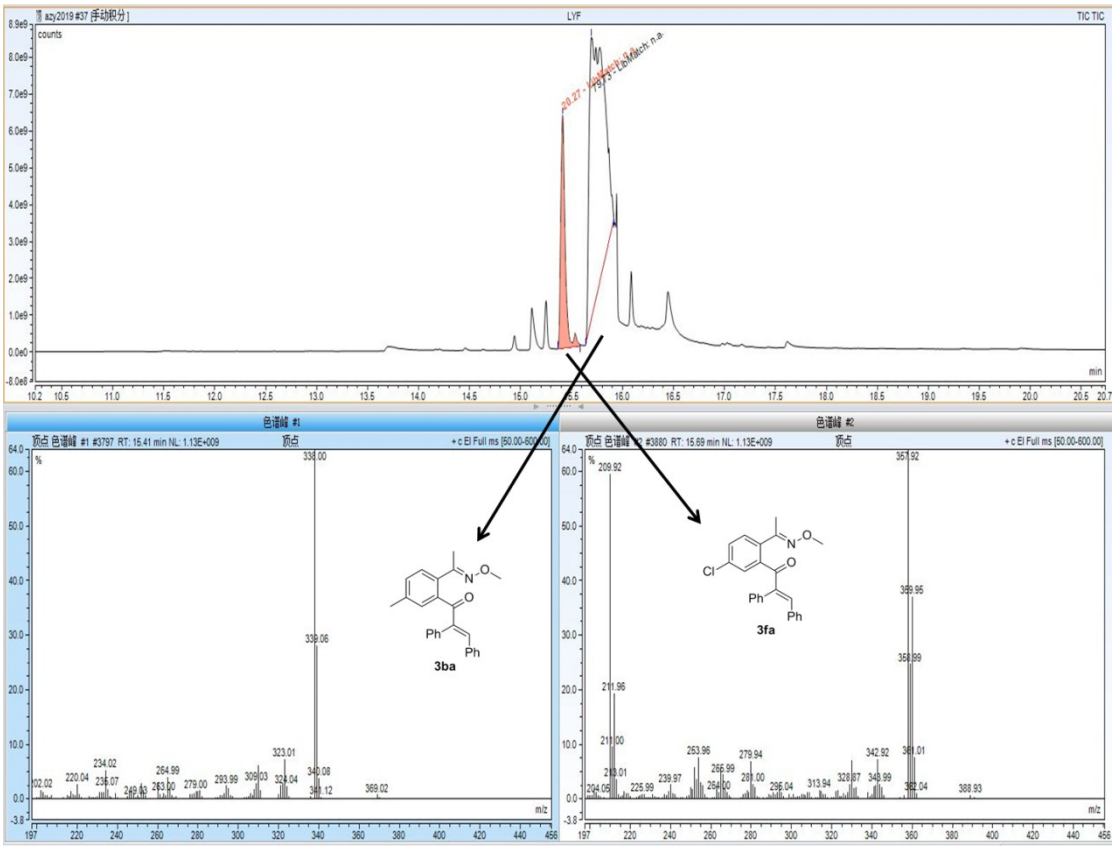
temperature, the solvent was removed under reduced pressure to obtain the crude product. The residue was purified by silica gel chromatography (eluent: petroleum/ethyl acetate = 40/1), the deuterium incorporation was estimated to be 16% at *ortho* position by ^{1}H NMR analysis.



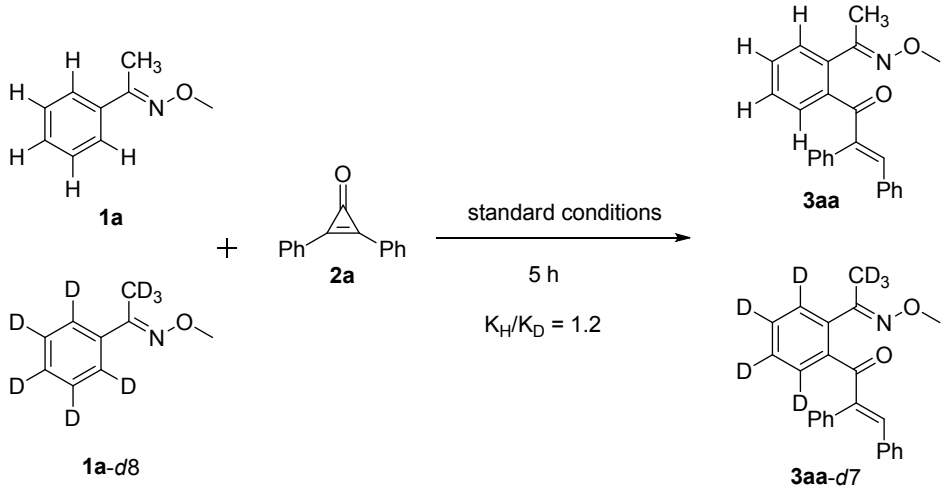
(b) Intermolecular competition experiment between different oximes **1**



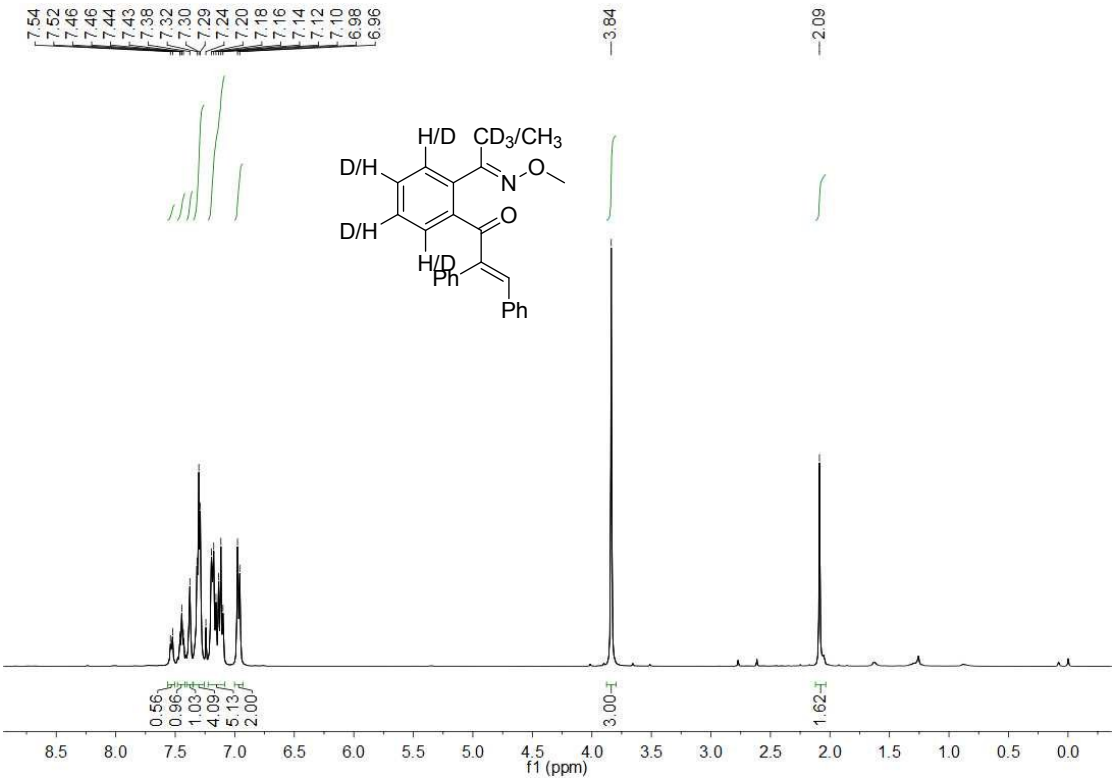
A mixture of **1b** (32.6 mg, 0.20 mmol), **1f** (36.6 mg, 0.20 mmol), diphenylcyclopropenone **2a** (41.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (0.004mmol), Ag_2SO_4 (0.04 mmol) and NaF (0.10 mmol) in TFE (2 mL) was stirred at 100 ^oC for 5 h. After the reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure to obtain the crude product. The residue was purified by silica gel chromatography (eluent: petroleum/ethyl acetate = 10/1). The product was detected by GC-MS. As shown in pictures below, products **3ba** and **3fa** were obtained in this reaction, and the ratio of **3ba** : **3fa**= 3.93



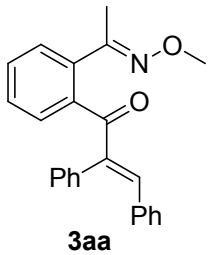
(c) Kinetic isotope study



A mixture of **1a** (29.8 mg, 0.20 mmol), **1a**-*d*8 (31.4 mg, 0.20 mmol), diphenylcyclopropenone **2a** (41.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (0.004 mmol), Ag_2SO_4 (0.04 mmol) and NaF (0.10 mmol) in TFE (2 mL) was stirred at 100 °C for 5 h. After the reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure to obtain the crude product. The residue was purified by silica gel chromatography (eluent: petroleum/ethyl acetate = 10/1). KIE value (K_H/K_D = 1.2) was determined on the basis of ^{1}H NMR analysis.

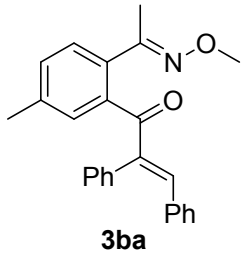

7.54
7.52
7.46
7.46
7.44
7.43
7.38
7.32
7.30
7.29
7.24
7.20
7.18
7.16
7.14
7.12
7.10
6.98
6.96
3.84
2.09
H/D
CD3/CH3
D/H
N
O
D/H
O
H/D
Ph
Ph
0.56
0.96
1.03
4.09
5.13
2.00
3.00
1.62
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

The data of products



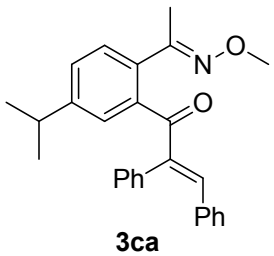
3aa

(*E*)-1-(2-((*E*)-1-(methoxyimino)ethyl)phenyl)-2,3-diphenylprop-2-en-1-one (**3aa**)[1]
Light yellow liquid (61.0 mg, 86% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 1H), 7.48 – 7.41 (m, 2H), 7.40 – 7.36 (m, 1H), 7.34 – 7.27 (m, 4H), 7.22 – 7.08 (m, 5H), 6.97 (dd, *J* = 8.3, 1.2 Hz, 2H), 3.84 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.1, 154.7, 141.8, 141.4, 139.4, 136.1, 135.8, 134.8, 130.4, 130.0, 129.8, 129.0, 128.5, 128.3, 128.1, 127.7, 127.4, 61.8, 14.7. ESI calcd for $C_{24}H_{22}NO_2$ $[M+H]^+$ 356.1645; found: 356.1651.



3ba

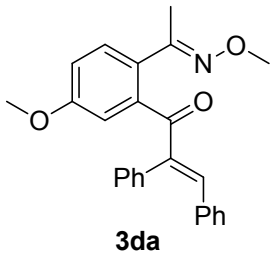
(*E*)-1-(2-((*E*)-1-(methoxyimino)ethyl)-5-methylphenyl)-2,3-diphenylprop-2-en-1-one (**3ba**)
Yellow liquid (52.3 mg, 71% yield). ^{1}H NMR (300 MHz, CDCl3) δ 7.35 – 7.25 (m, 7H), 7.22 – 7.18 (m, 2H), 7.14 (dd, *J* = 10.7, 7.2 Hz, 3H), 7.00 – 6.92 (m, 2H), 3.81 (s, 3H), 2.40 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.2, 154.7, 141.7, 141.5, 139.3, 138.7, 135.8, 134.9, 133.4, 130.5, 130.4, 130.1, 129.6, 128.9, 128.3, 128.1, 127.6, 127.3, 61.7, 21.1, 14.7. ESI calcd for $C_{25}H_{24}NO_2$ $[M+H]^+$ 370.1802; found: 370.1795.



3ca

(*E*)-1-(5-isopropyl-2-((*E*)-1-(methoxyimino)ethyl)phenyl)-2,3-diphenylprop-2-en-1-one (**3ca**)
Yellow liquid (46.8 mg, 59% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.33 – 7.27 (m, 5H), 7.25 – 7.07 (m, 6H), 6.97 (d, *J* = 7.0 Hz, 2H), 3.81 (s, 3H), 2.95 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.09 (s, 3H), 1.26 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.3, 154.7, 149.5, 141.6, 141.5, 139.2, 135.8, 134.8, 133.7, 130.4, 129.9, 128.9,

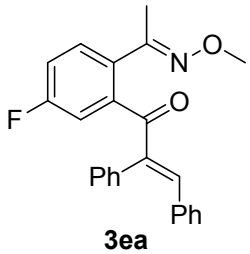
128.3, 128.1, 127.9, 127.5, 127.3, 127.1, 61.9, 33.8, 23.7, 14.7. ESI calcd for $C_{27}H_{28}NO_2$ $[M+H]^+$ 398.2115; found: 398.2122.



3da

(*E*)-1-(5-methoxy-2-((*E*)-1-(methoxyimino)ethyl)phenyl)-2,3-diphenylprop-2-en-1-one (**3da**)

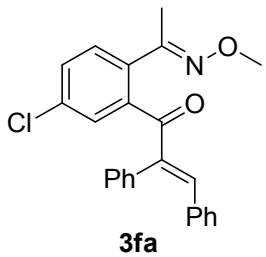
Yellow liquid (48.5 mg, 63% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 5H), 7.22 – 7.17 (m, 2H), 7.15 (dd, *J* = 7.4, 4.6 Hz, 3H), 7.04 (d, *J* = 2.6 Hz, 1H), 6.97 (dd, *J* = 8.8, 6.0 Hz, 3H), 3.83 (d, *J* = 13.1 Hz, 6H), 2.06 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.7, 159.7, 154.3, 141.7, 141.3, 140.8, 135.8, 134.9, 130.5, 130.1, 128.9, 128.7, 128.6, 128.3, 128.1, 127.7, 115.7, 114.1, 61.7, 55.5, 14.6. ESI calcd for $C_{25}H_{24}NO_3$ $[M+H]^+$ 386.1751; found: 386.1764.



3ea

(*E*)-1-(5-fluoro-2-((*E*)-1-(methoxyimino)ethyl)phenyl)-2,3-diphenylprop-2-en-1-one (**3ea**)

Yellow liquid (58.9 mg, 79% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 5H), 7.23 – 7.08 (m, 7H), 6.98 (d, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.4, 164.1-160.8 (d, *J* = 249.8 Hz, 1 C), 153.7, 142.2, 141.6-141.5 (d, *J* = 6 Hz, 1 C), 140.8, 135.5, 134.6, 132.2, 130.5, 130.0, 129.3, 129.2, 128.4, 128.2, 127.8, 116.8-116.5 (d, *J* = 21.0 Hz, 1 C), 116.3-116.0 (d, *J* = 23.3 Hz, 1 C), 61.9, 14.6. ESI calcd for $C_{24}H_{21}FNO_2$ $[M+H]^+$ 374.1551; found: 374.2060.

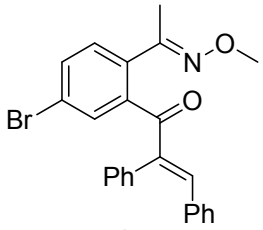


3fa

(*E*)-1-(5-chloro-2-((*E*)-1-(methoxyimino)ethyl)phenyl)-2,3-diphenylprop-2-en-1-one (**3fa**)

Yellow liquid (62.2 mg, 80% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, *J* = 2.0 Hz, 1H), 7.32 (dd, *J* = 6.6, 3.8 Hz, 1H), 7.23 (d, *J* = 1.5 Hz, 5H), 7.12 – 6.99 (m, 5H), 6.89 (d, *J* = 6.9 Hz, 2H), 3.75 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ

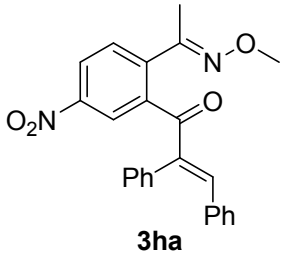
196.4, 153.6, 142.3, 140.9, 140.8, 135.4, 134.7, 134.5, 134.3, 130.5, 130.0, 129.7, 129.2, 128.9, 128.6, 128.4, 128.2, 127.8, 61.9, 14.4. ESI calcd for $C_{24}H_{21}ClNO_2$ $[M+H]^+$ 390.1256; found: 390.1301.



3ga

(*E*)-1-(5-bromo-2-((*E*)-1-(methoxyimino)ethyl)phenyl)-2,3-diphenylprop-2-en-1-one (**3ga**)

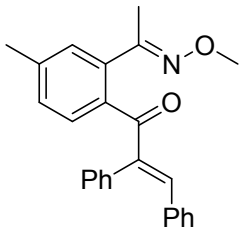
Yellow liquid (62.3 mg, 72% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.57 (d, *J* = 8.3 Hz, 1H), 7.31 (s, 4H), 7.27 – 7.08 (m, 6H), 6.97 (d, *J* = 7.3 Hz, 2H), 3.83 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.3, 153.7, 142.3, 141.1, 140.8, 135.4, 134.8, 134.6, 132.7, 131.8, 130.5, 130.0, 129.2, 128.8, 128.5, 128.2, 127.8, 122.8, 61.9, 14.4. ESI calcd for $C_{24}H_{21}BrNO_2$ $[M+H]^+$ 434.0750; found: 434.0717.



3ha

(*E*)-1-(2-((*E*)-1-(methoxyimino)ethyl)-5-nitrophenyl)-2,3-diphenylprop-2-en-1-one (**3ha**)

Yellow liquid (66.4 mg, 83% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (d, *J* = 2.3 Hz, 1H), 8.24 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.42 (s, 1H), 7.30 (dd, *J* = 5.0, 1.7 Hz, 3H), 7.15 (ddd, *J* = 10.7, 8.8, 7.1 Hz, 5H), 7.00 (d, *J* = 7.6 Hz, 2H), 3.89 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.3, 152.6, 147.1, 142.4, 141.2, 140.6, 139.9, 135.1, 134.1, 130.4, 129.9, 129.4, 128.4, 128.2, 128.1, 127.8, 124.2, 123.7, 62.1, 13.9. ESI calcd for $C_{24}H_{21}N_2O_4$ $[M+H]^+$ 401.1496; found: 401.2037.

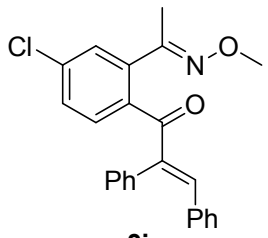


3ia

(*E*)-1-(2-((*E*)-1-(methoxyimino)ethyl)-4-methylphenyl)-2,3-diphenylprop-2-en-1-one (**3ia**)

Yellow liquid (41.3 mg, 56% yield). ^{1}H NMR (400 MHz,) δ 7.45 (d, *J* = 7.8 Hz, 1H), 7.30 (dd, *J* = 5.2, 3.5 Hz, 3H), 7.26 (s, 1H), 7.21 (ddd, *J* = 10.0, 4.5, 1.7 Hz, 4H), 7.16

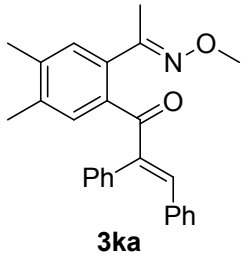
– 7.08 (m, 3H), 7.00 – 6.94 (m, 2H), 3.82 (s, 3H), 2.40 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (101 MHz,) δ 198.1, 155.2, 141.6, 141.6, 140.2, 136.5, 135.9, 134.8, 130.4, 130.0, 129.3, 129.2, 128.9, 128.3, 128.2, 128.1, 127.6, 61.7, 21.3, 15.1. ESI calcd for $C_{25}H_{24}NO_2$ $[M+H]^+$ 370.1802; found: 370.1809.



3ja

(*E*)-1-(4-chloro-2-((*E*)-1-(methoxyimino)ethyl)phenyl)-2,3-diphenylprop-2-en-1-one (**3ja**)

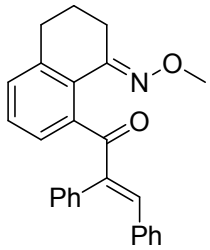
Yellow liquid (48.2 mg, 62% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 2H), 7.25 (dd, *J* = 12.4, 2.6 Hz, 5H), 7.12 – 7.01 (m, 5H), 6.90 (d, *J* = 7.2 Hz, 2H), 3.77 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.9, 153.6, 142.0, 141.0, 137.8, 137.7, 135.8, 135.6, 134.6, 130.5, 130.4, 130.0, 129.2, 128.6, 128.4, 128.2, 127.8, 127.5, 62.0, 14.6. ESI calcd for $C_{24}H_{21}ClNO_2$ $[M+H]^+$ 390.1256; found: 390.1312.



3ka

(*E*)-1-(2-((*E*)-1-(methoxyimino)ethyl)-4,5-dimethylphenyl)-2,3-diphenylprop-2-en-1-one (**3ka**)

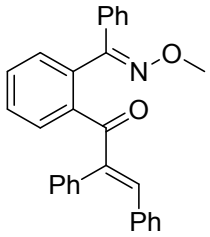
Yellow liquid (68.1 mg, 89% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, *J* = 4.0 Hz, 4H), 7.27 – 7.18 (m, 3H), 7.18 – 7.07 (m, 4H), 6.96 (d, *J* = 7.3 Hz, 2H), 3.81 (s, 3H), 2.31 (s, 6H), 2.07 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.3, 155.2, 141.7, 138.8, 137.3, 136.7, 135.9, 134.9, 134.0, 130.4, 130.0, 128.9, 128.7, 128.3, 128.1, 127.6 , 61.7, 19.8, 19.5, 15.1. ESI calcd for $C_{26}H_{26}NO_2$ $[M+H]^+$ 384.1958; found: 384.2001.



3la

(*E*)-1-((*E*)-8-(methoxyimino)-5,6,7,8-tetrahydronaphthalen-1-yl)-2,3-diphenylprop-2-en-1-one (**3la**)

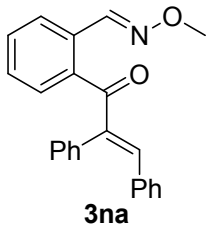
Yellow liquid (57.9 mg, 76% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.35 – 7.28 (m, 2H), 7.25 – 7.19 (m, 3H), 7.18 – 7.09 (m, 4H), 7.08 – 6.98 (m, 4H), 3.91 (s, 3H), 2.58 (t, *J* = 5.9 Hz, 2H), 2.49 (t, *J* = 6.7 Hz, 2H), 1.50 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.7, 152.9, 140.4, 140.2, 139.3, 139.0, 136.4, 135.1, 130.3, 130.2, 129.1, 128.6, 128.5, 128.2, 127.9, 127.9, 127.2, 126.7, 61.9, 30.1, 24.6, 20.7. ESI calcd for $C_{26}H_{24}NO_2$ $[M+H]^+$ 382.1802; found: 3382.2336.



3ma

(*E*)-1-(2-((*E*)-(methoxyimino)(phenyl)methyl)phenyl)-2,3-diphenylprop-2-en-1-one (**3ma**)

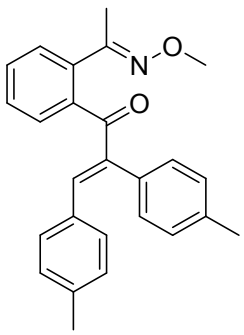
Yellow liquid (56.7 mg, 68% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.3 Hz, 1H), 7.45 (s, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.33 (s, 6H), 7.26 (dd, *J* = 23.9, 7.3 Hz, 5H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 5.8 Hz, 2H), 6.96 (d, *J* = 7.6 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.9, 155.4, 142.5, 141.4, 140.8, 135.9, 135.7, 134.9, 132.8, 130.5, 130.2, 130.2, 129.9, 129.5, 129.2, 129.0, 128.9, 128.6, 128.4, 128.1, 127.8, 127.6, 62.3. ESI calcd for $C_{29}H_{24}NO_2$ $[M+H]^+$ 418.1802; found: 418.1827.



3na

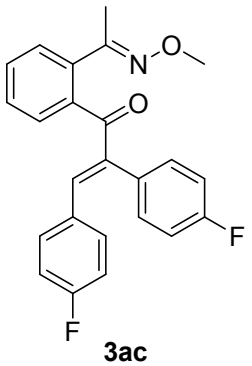
(*E*)-2-((*E*)-2,3-diphenylacryloyl)benzaldehyde *O*-methyl oxime (**3na**)

Yellow liquid (53.1 mg, 78% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.84 – 7.79 (m, 1H), 7.51 – 7.33 (m, 6H), 7.25 (dd, *J* = 10.2, 4.7 Hz, 3H), 7.20 – 7.09 (m, 3H), 6.99 (d, *J* = 7.2 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.1, 146.5, 144.3, 141.5, 139.1 135.5, 134.4, 130.6, 130.5, 129.9, 129.8, 129.4, 128.9, 128.6, 128.6, 128.2, 127.9, 127.2, 62.1. ESI calcd for $C_{23}H_{20}NO_2$ $[M+H]^+$ 342.1489; found: 342.1503.



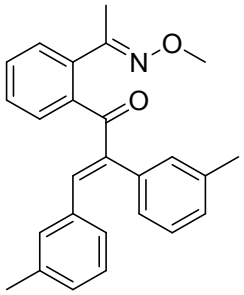
3ab

(*E*)-1-(2-((*E*)-1-(methoxyimino)ethyl)phenyl)-2,3-di-*p*-tolylprop-2-en-1-one (**3ab**)
Yellow liquid (68.1 mg, 89% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 2.3 Hz, 1H), 7.45 – 7.34 (m, 3H), 7.22 (s, 1H), 7.20 – 7.07 (m, 4H), 6.91 (dd, *J* = 14.4, 8.7 Hz, 4H), 3.84 (s, 3H), 2.34 (s, 3H), 2.23 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.3, 154.8, 142.1, 140.5, 139.5, 139.2, 137.2, 136.2, 132.9, 132.0, 130.4, 129.8, 129.6, 129.1, 128.9, 128.8, 128.4, 127.4, 61.7, 21.2, 21.2, 14.8. ESI calcd for $C_{26}H_{26}NO_2$ $[M+H]^+$ 384.1958; found: 384.2510.



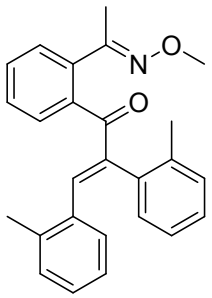
3ac

(*E*)-2,3-bis(4-fluorophenyl)-1-(2-((*E*)-1-(methoxyimino)ethyl)phenyl)prop-2-en-1-one (**3ac**)
Yellow liquid (64.1 mg, 82% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 – 7.36 (m, 4H), 7.30 – 7.12 (m, 3H), 7.08 – 6.90 (m, 4H), 6.83 (t, *J* = 8.4 Hz, 2H), 3.82 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.7, 164.5-161.1 (d, *J* = 249.8 Hz, 1 C), 163.9-160.7 (d, *J* = 245.3 Hz, 1 C), 154.7, 140.6, 140.2, 139.1, 136.0, 132.3-132.2 (d, *J* = 8.3 Hz, 1 C), 131.9-131.8 (d, *J* = 8.3 Hz, 1 C), 129.9, 128.9, 128.6, 127.4, 115.7-115.4 (d, *J* = 21.0 Hz, 1 C), 115.5-115.2 (d, *J* = 21.8 Hz, 1 C), 61.8, 14.7. ESI calcd for $C_{24}H_{20}F_2NO_2$ $[M+H]^+$ 392.1457; found: 392.1469.



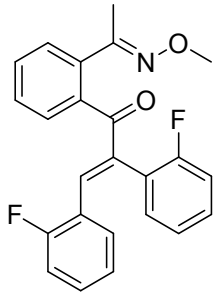
3ad

(*E*)-1-(2-((*E*)-1-(methoxyimino)ethyl)phenyl)-3-(*m*-tolyl)-2-(*p*-tolyl)prop-2-en-1-one (**3ad**)
Yellow liquid (70.4 mg, 92% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.42 (d, *J* = 12.2 Hz, 3H), 7.20 (s, 2H), 7.11 (d, *J* = 7.8 Hz, 1H), 7.06 – 6.94 (m, 4H), 6.77 (d, *J* = 17.5 Hz, 2H), 3.85 (s, 3H), 2.31 (s, 3H), 2.12 (d, *J* = 13.6 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.2, 154.9, 142.1, 141.4, 139.4, 137.8, 137.6, 136.2, 135.8, 134.6, 131.5, 130.4, 129.8, 129.7, 128.9, 128.5, 128.3, 128.2, 127.9, 127.4, 126.9, 61.7, 21.6, 21.1, 14.9. ESI calcd for $C_{26}H_{26}NO_2$ $[M+H]^+$ 384.1958; found: 384.1984.



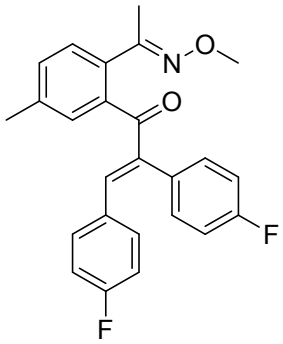
3ae

(*E*)-1-(2-((*E*)-1-(methoxyimino)ethyl)phenyl)-2,3-di-o-tolylprop-2-en-1-one (**3ae**)
Yellow liquid (59.7 mg, 78% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.48 (d, *J* = 22.3 Hz, 4H), 7.26 – 7.02 (m, 6H), 6.81 (s, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 3.89 (s, 3H), 2.26 – 2.14 (m, 6H), 2.08 (d, *J* = 5.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.2, 154.9, 142.7, 141.5, 139.8, 137.5, 136.6, 135.2, 133.9, 131.5, 130.2, 130.1, 130.0, 129.6, 128.9, 128.8, 128.5, 128.1, 127.9, 127.8, 125.7, 125.5, 61.8, 19.9, 19.7, 15.1. ESI calcd for $C_{26}H_{26}NO_2$ $[M+H]^+$ 384.1958; found: 384.1923.



3af

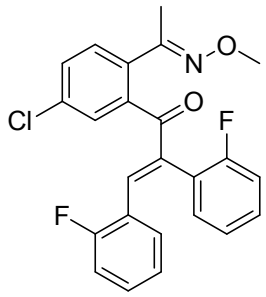
(*E*)-2,3-bis(2-fluorophenyl)-1-(2-((*E*)-1-(methoxyimino)ethyl)phenyl)prop-2-en-1-one (**3af**)
Yellow liquid (51.6 mg, 66% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.60 – 7.52 (m, 1H), 7.49 – 7.33 (m, 3H), 7.31 – 6.94 (m, 6H), 6.80 (d, *J* = 4.6 Hz, 2H), 3.87 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.7, 162.5-159.2 (d, *J* = 249.8 Hz, 1 C), 161.6-158.3 (d, *J* = 246.0 Hz, 1 C), 154.3, 138.8, 137.2, 135.9-135.5 (d, *J* = 35.3 Hz, 1 C), 135.6, 131.8-131.7 (d, *J* = 3.0 Hz, 1 C), 130.9, 130.9, 130.1, 129.9, 129.6, 129.2, 128.4, 127.2, 124.1-124.0 (d, *J* = 2.8 Hz, 1 C), 123.7-123.6 (d, *J* = 3.0 Hz, 1 C), 123.1, 115.8-115.5 (d, *J* = 21.8 Hz, 1 C), 115.6-115.3 (d, *J* = 21.8 Hz, 1 C), 61.8, 14.3. ESI calcd for $C_{24}H_{20}F_2NO_2$ $[M+H]^+$ 392.1457; found: 392.1502.



3bc

(*E*)-2,3-bis(4-fluorophenyl)-1-(2-((*E*)-1-(methoxyimino)ethyl)-5-methylphenyl)prop-2-en-1-one (**3bc**)

Yellow liquid (63.9 mg, 79% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (t, *J* = 8.9 Hz, 3H), 7.23 – 7.13 (m, 3H), 7.03 (t, *J* = 8.7 Hz, 2H), 6.98 – 6.90 (m, 2H), 6.83 (t, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 2.41 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.9, 164.4-161.1 (d, *J* = 249.8 Hz, 1 C), 163.9-160.7 (d, *J* = 245.3 Hz, 1 C), 154.6, 140.5, 140.3, 138.9, 138.8, 133.2, 132.3-132.2 (d, *J* = 8.3 Hz, 1 C), 131.9-131.8 (d, *J* = 8.3 Hz, 1 C), 131.4, 130.8, 130.7, 129.5, 127.3, 115.6-115.4 (d, *J* = 21.8 Hz, 1 C), 115.5-115.2 (d, *J* = 21.0 Hz, 1 C), 61.7, 21.1, 14.6. ESI calcd for $C_{25}H_{22}F_2NO_2$ $[M+H]^+$ 406.1613; found: 406.1624.

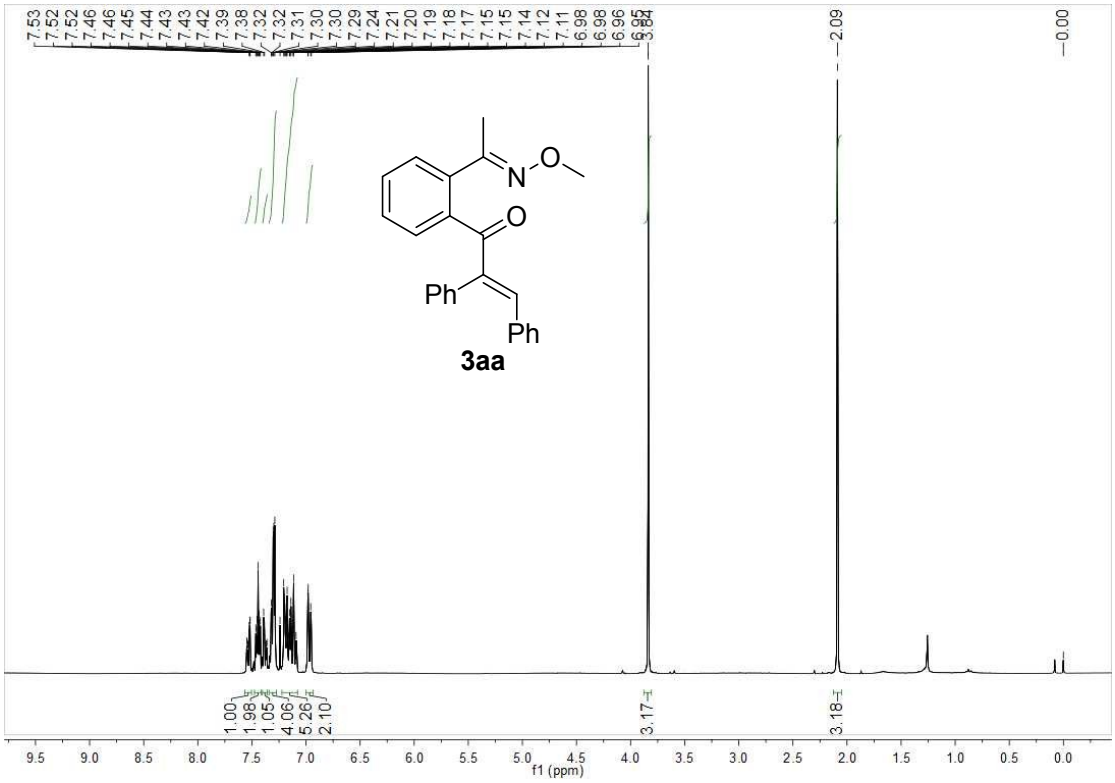


3ff

(*E*)-1-(5-chloro-2-((*E*)-1-(methoxyimino)ethyl)phenyl)-2,3-bis(2-fluorophenyl)prop-2-en-1-one (**3ff**)

Yellow liquid (62.0 mg, 73% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.53 (d, *J* = 1.8 Hz, 1H), 7.41 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.35 – 7.16 (m, 3H), 7.05 (dt, *J* = 18.2, 8.6 Hz, 4H), 6.79 (t, *J* = 6.8 Hz, 2H), 3.86 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.1, 162.6-159.2 (d, *J* = 250.5 Hz, 1 C),161.6-158.3 (d, *J* = 246.0 Hz, 1 C), 153.1, 140.3, 136.6, 136.0, 135.9, 134.6, 134.2, 131.7, 131.2-131.1 (d, *J* = 9.0 Hz, 1 C), 130.3-130.2 (d, *J* = 7.5 Hz, 1 C), 129.9, 129.6, 129.1, 128.4, 124.1, 123.7, 123.3-123.1 (d, *J* = 16.5 Hz, 1 C), 122.8-122.6 (d, *J* = 12.0 Hz, 1 C), 115.8-115.5 (d, *J* = 22.5 Hz, 1 C),115.6-115.4 (d, *J* = 21.8 Hz, 1 C), 61.9, 13.9. ESI calcd for $C_{24}H_{19}ClF_2NO_2$ $[M+H]^+$ 426.1067; found: 426.0988.

[1] S. J. Yu and X. W. Li, *Org. Lett.,* 2014, **16**, 1220.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7.29
7.24
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7.20
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7.15
7.14
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7.11
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6.98
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6.95
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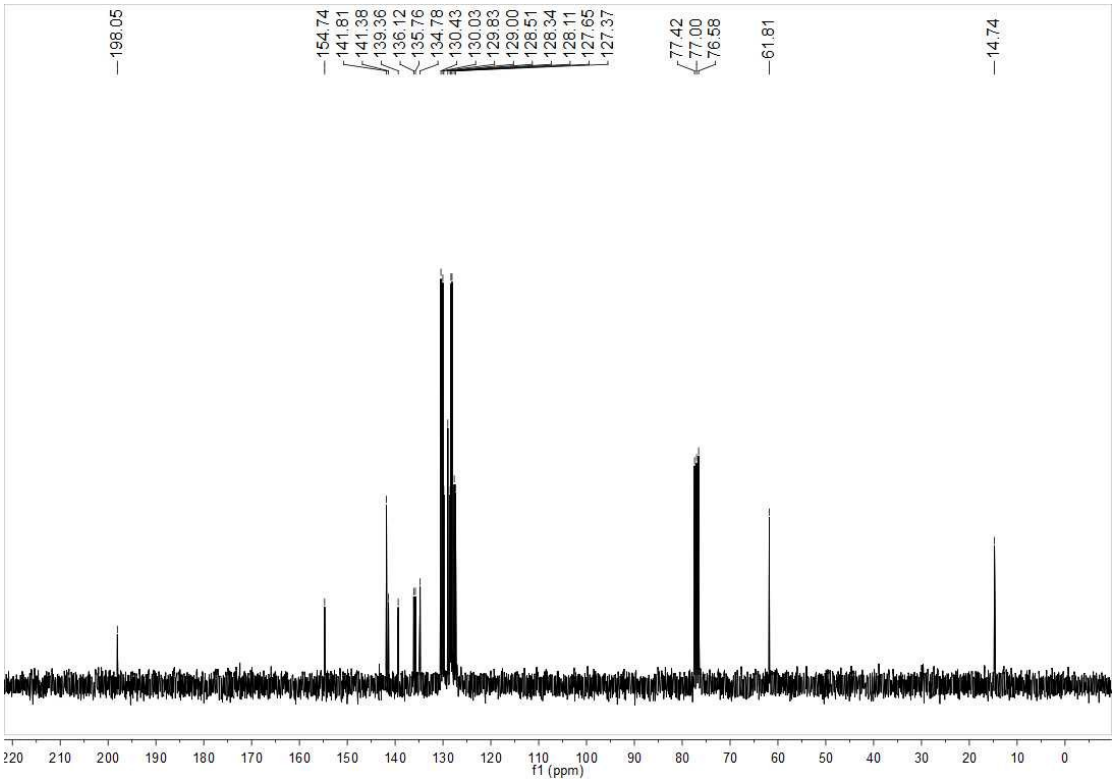
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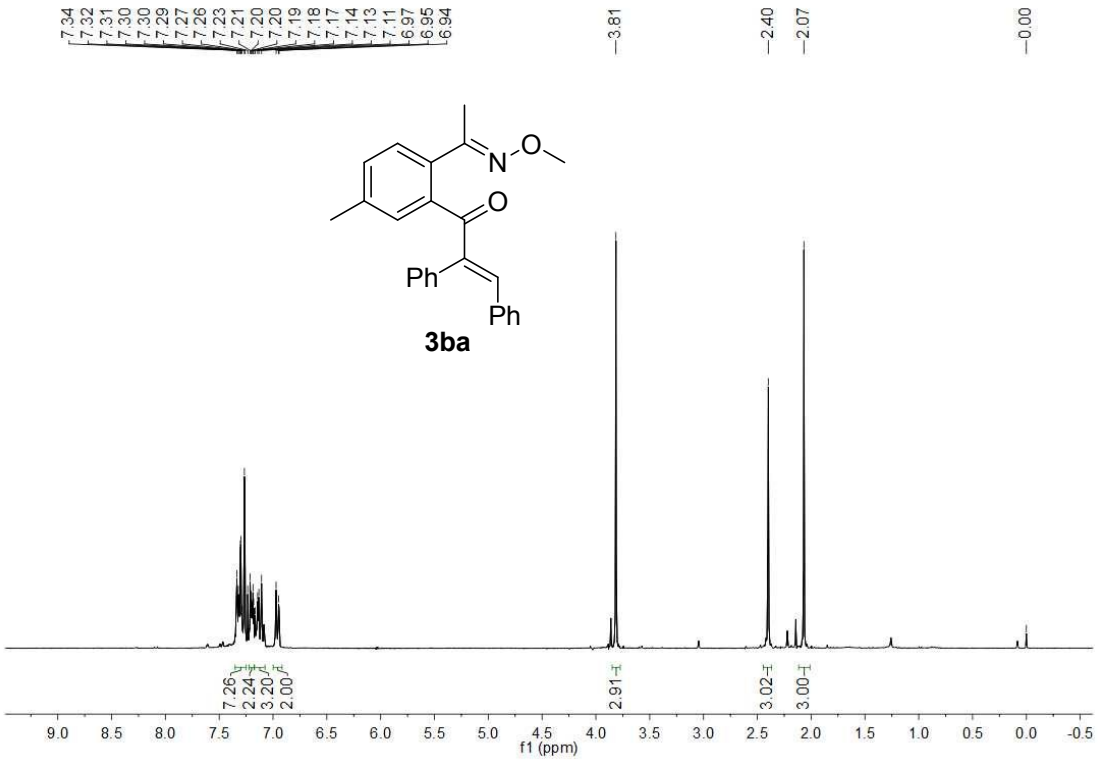
f1 (ppm)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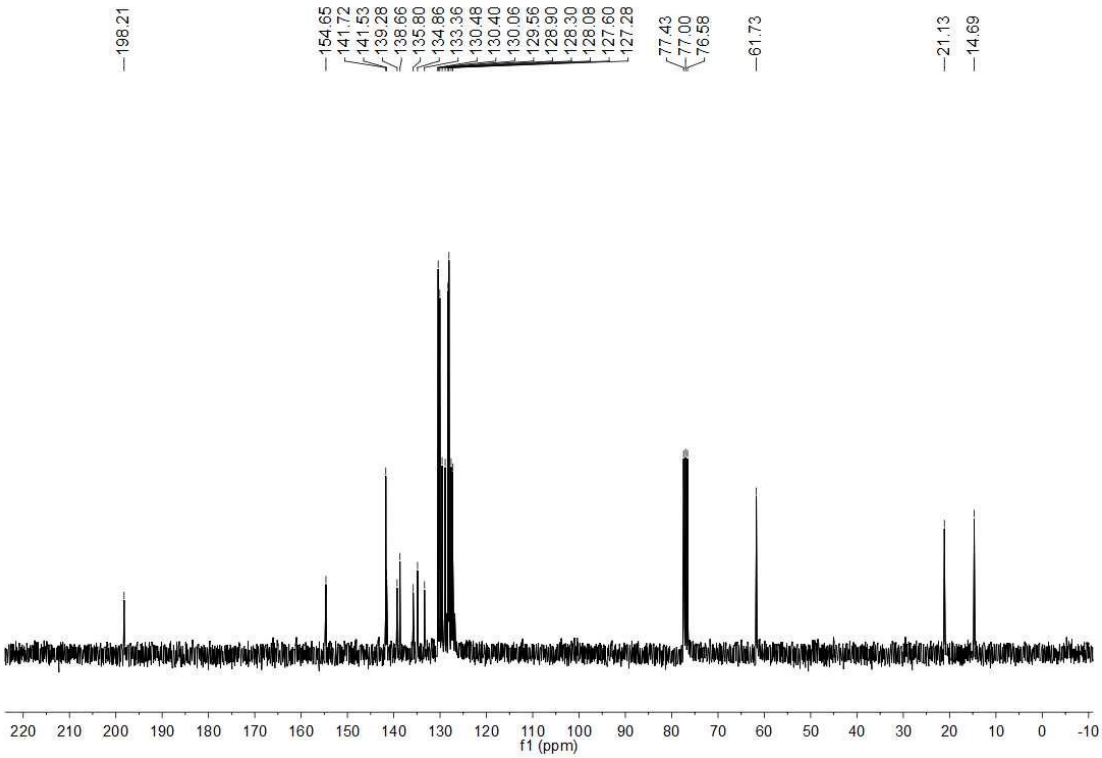
f1 (ppm)

3ba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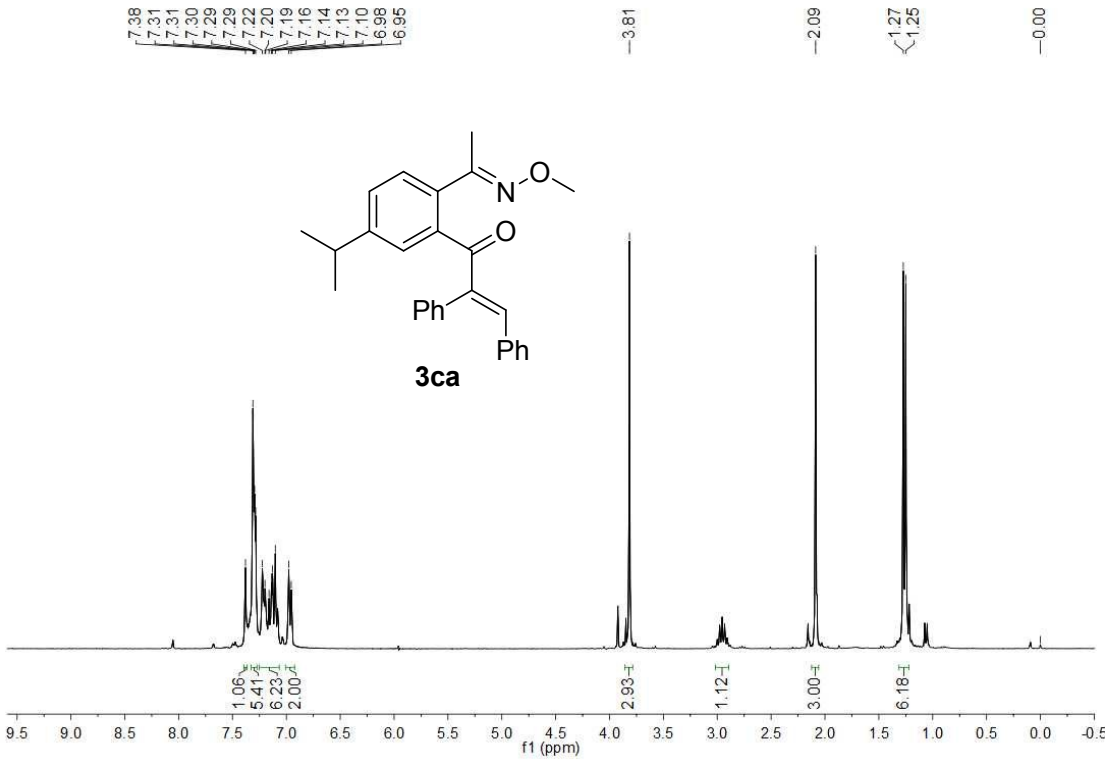
f1 (ppm)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1.25
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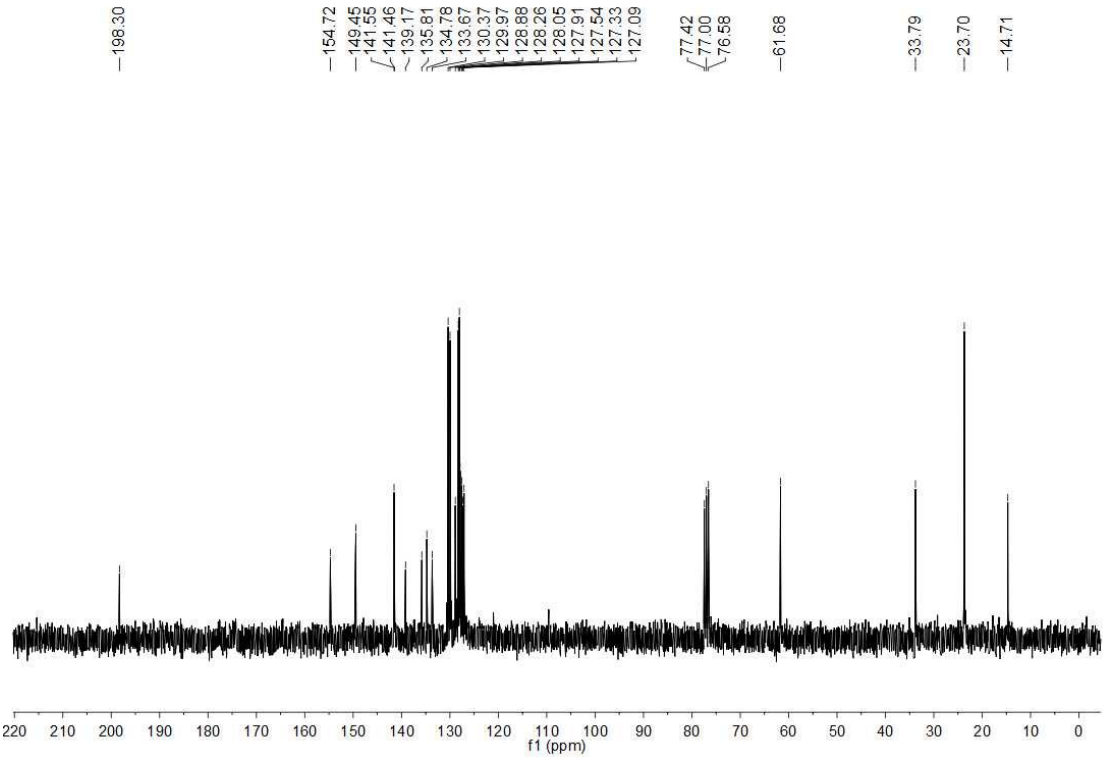
f1 (ppm)

3ca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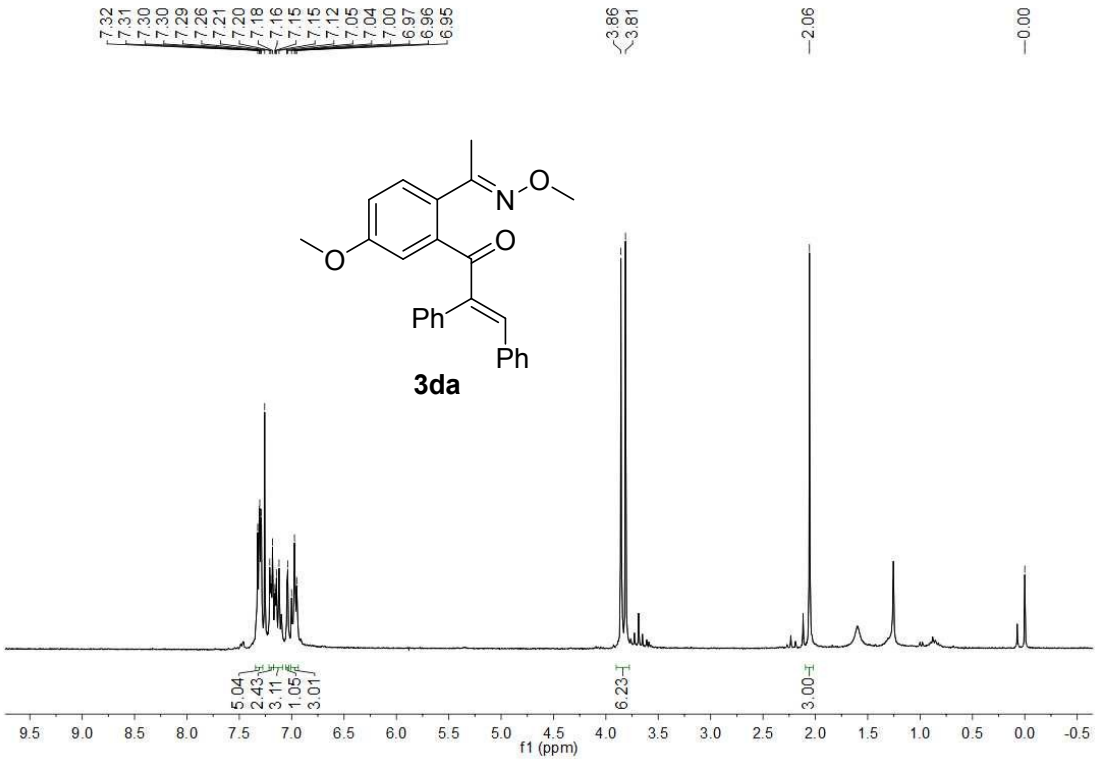
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6.95
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3.81
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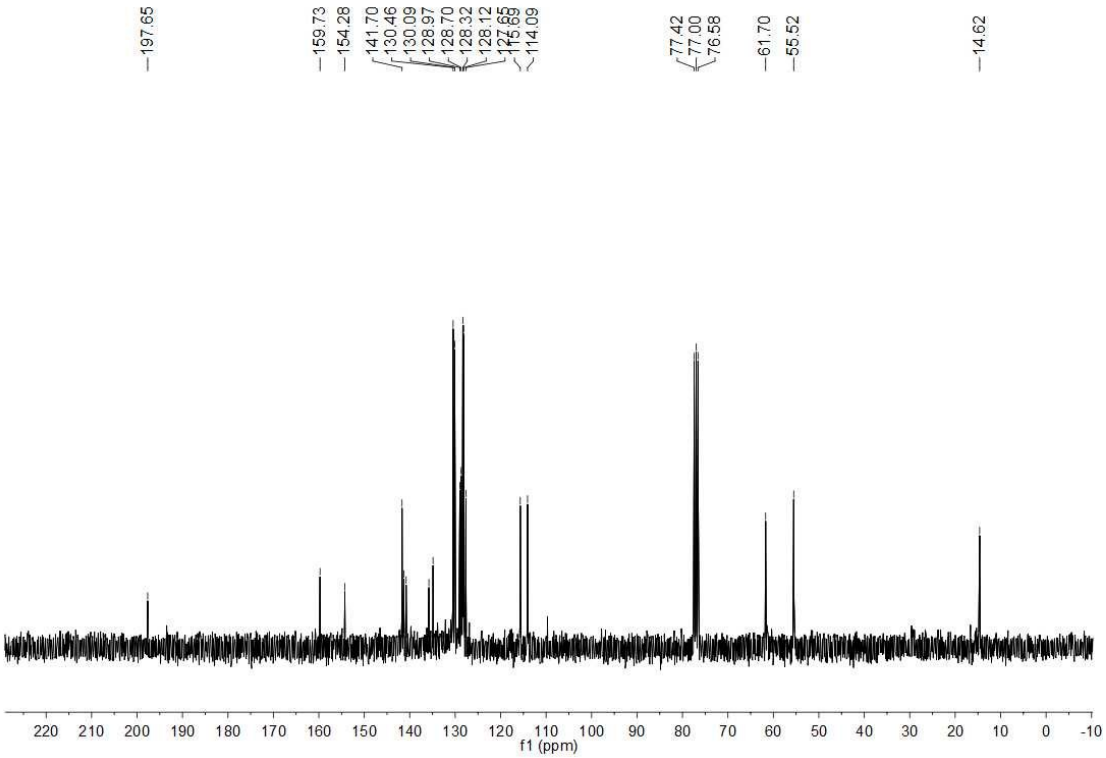
f1 (ppm)

3da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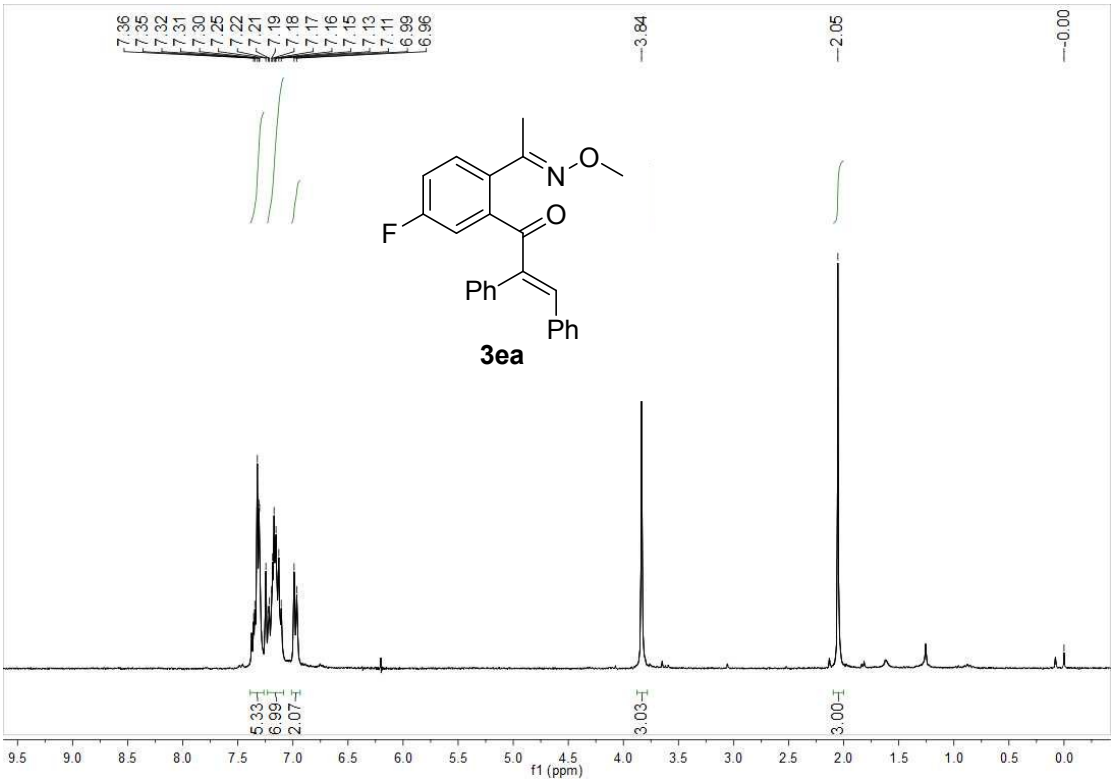
14.62
f1 (ppm)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7.13
7.11
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6.96
3.84
2.05
0.00
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N
O
Ph
Ph
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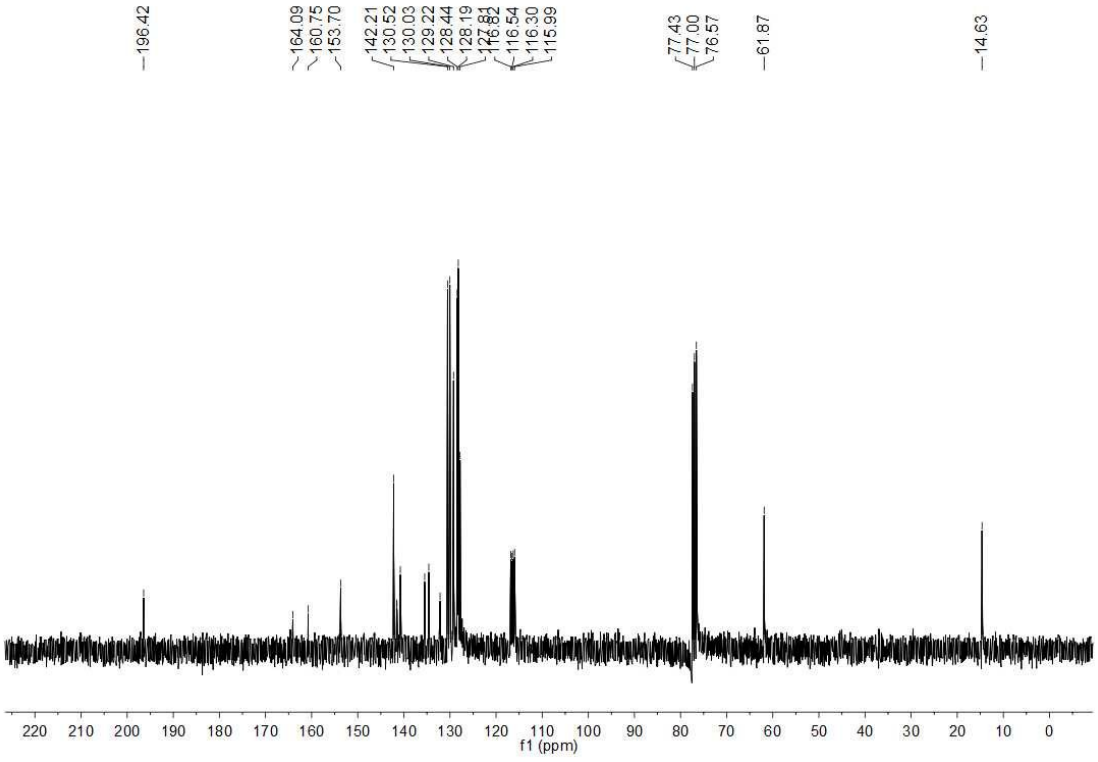
6.99
2.07
3.03
3.00
f1 (ppm)

3ea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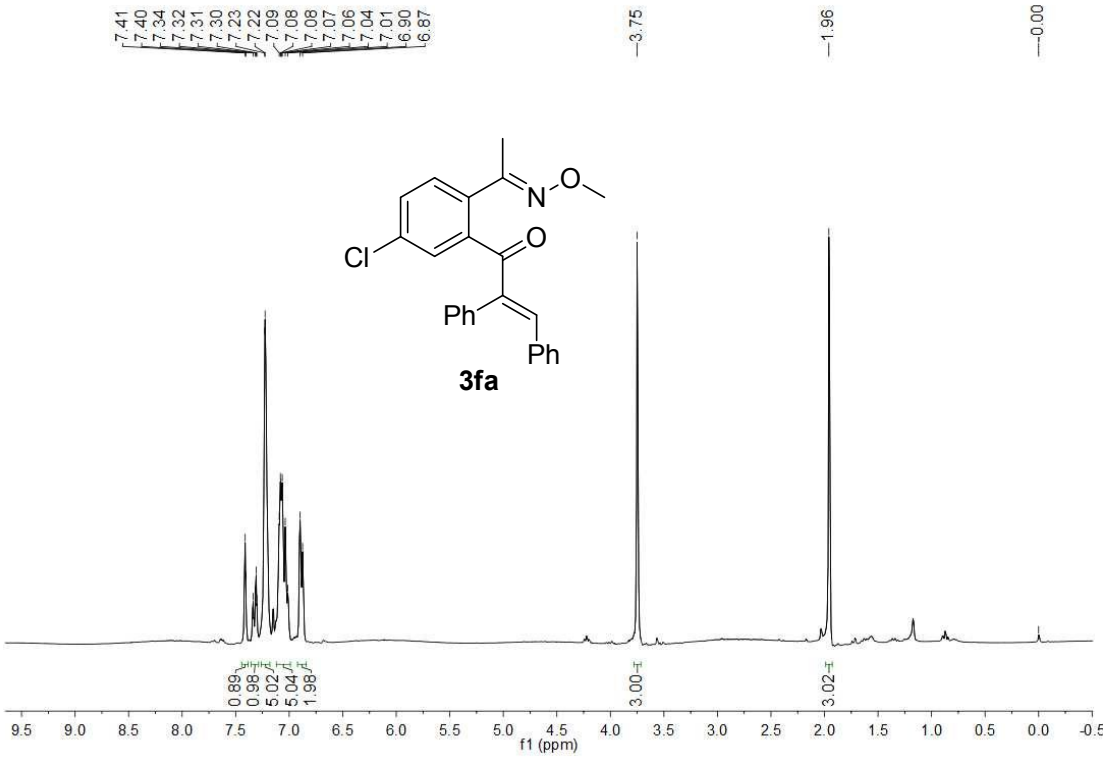
f1 (ppm)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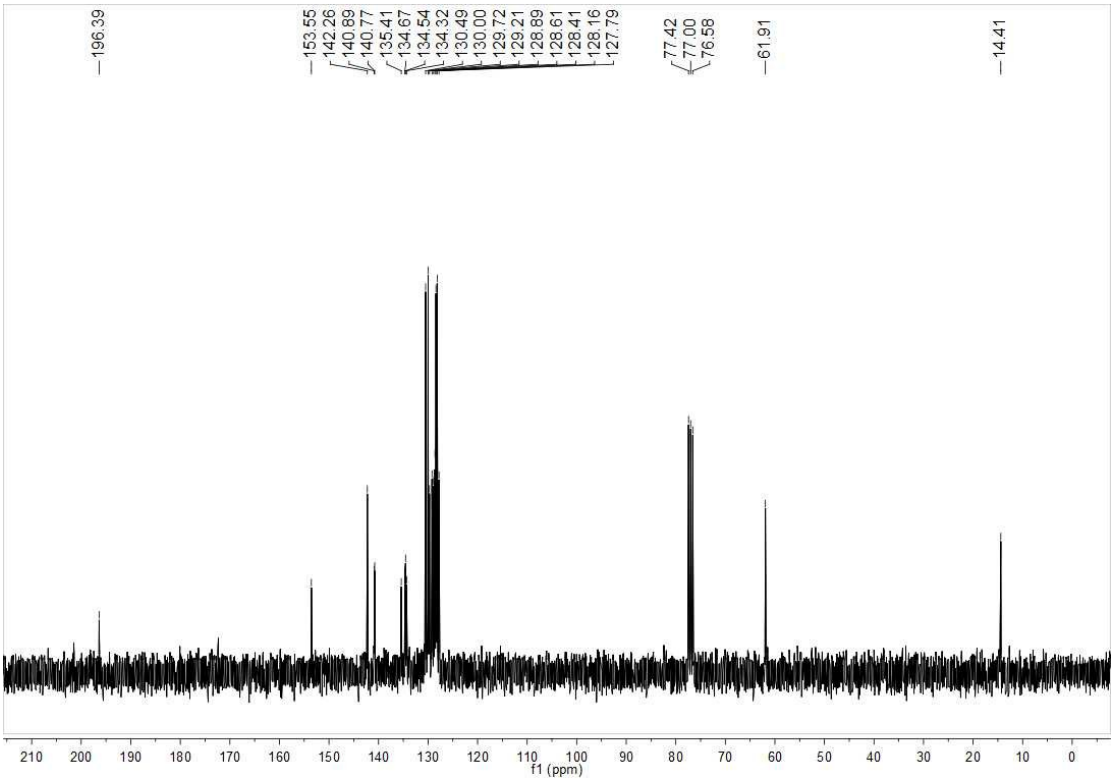
f1 (ppm)

3fa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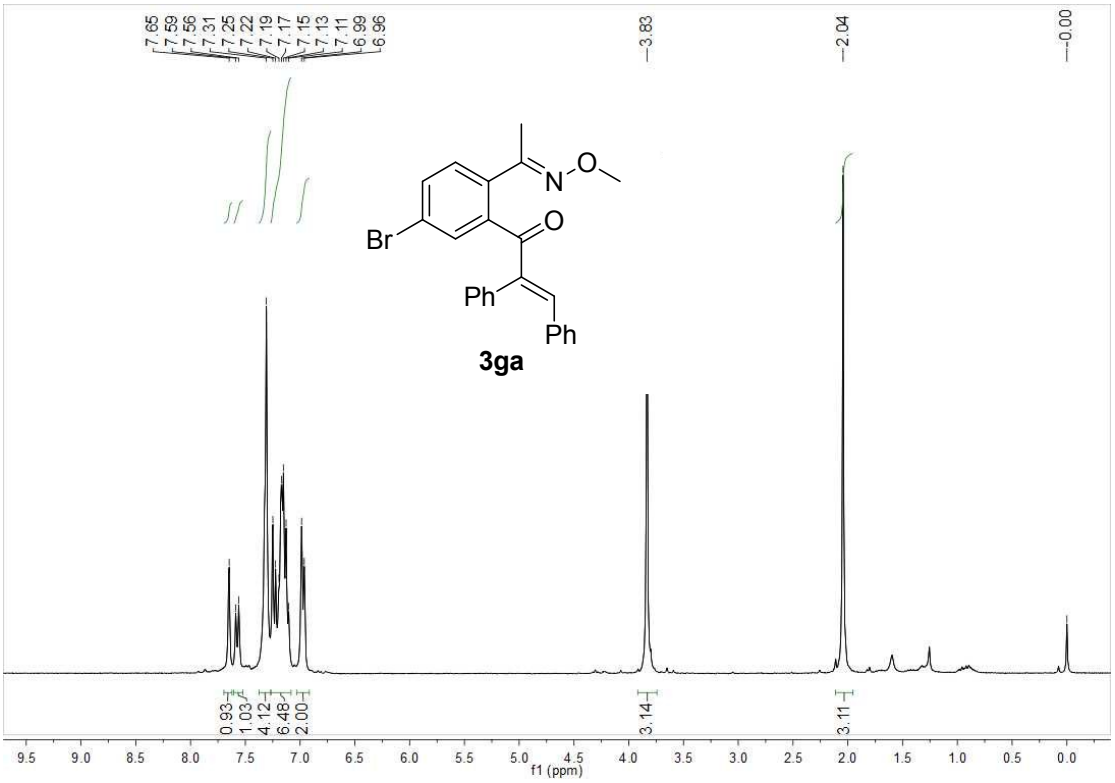
f1 (ppm)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7.15
7.13
7.11
6.99
6.96
3.83
2.04
0.00
Br
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O
Ph
Ph
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1.03
4.12
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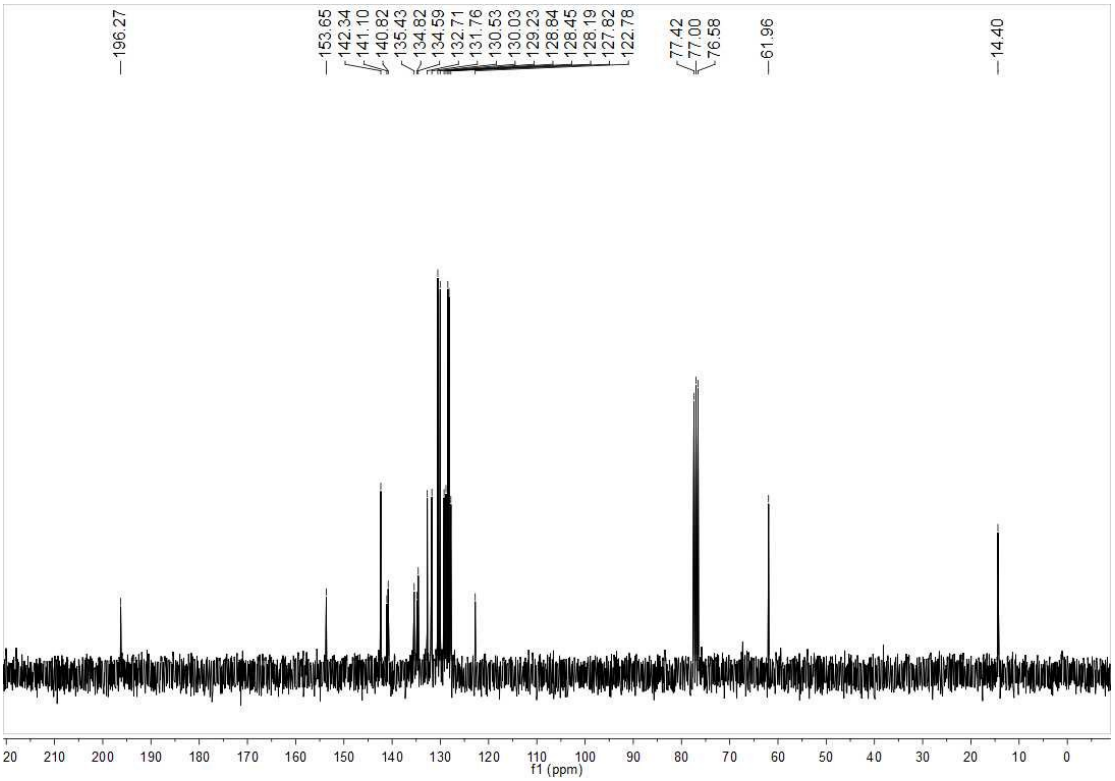
2.00
3.14
3.11
f1 (ppm)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135.43
134.82
134.59
132.71
131.76
130.53
130.03
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128.19
127.82
122.78
77.42
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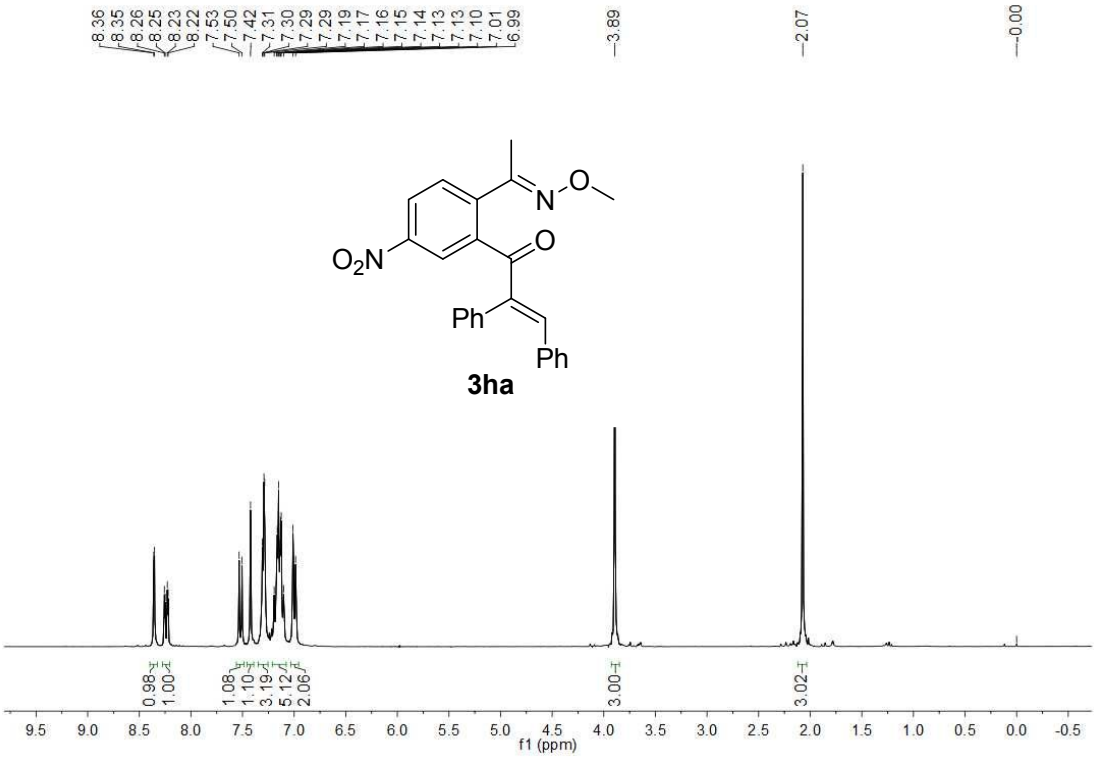
76.58
61.96
14.40
f1 (ppm)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7.50
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7.31
7.30
7.29
7.29
7.19
7.17
7.16
7.15
7.14
7.13
7.13
7.10
7.01
6.99
3.89
2.07
0.00
N
O
O2N
O
Ph
Ph
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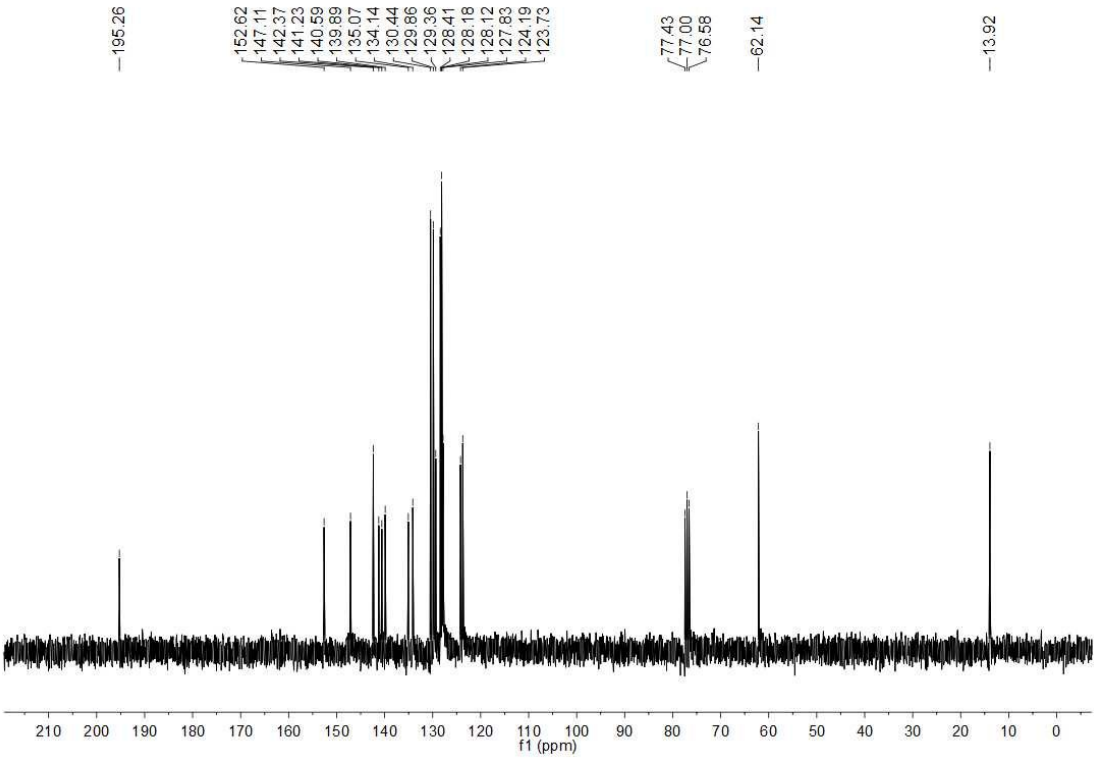
1.08
1.10
3.19
5.12
2.06
3.00
3.02
f1 (ppm)

3ha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140.59
139.89
135.07
134.14
130.44
129.86
129.36
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128.18
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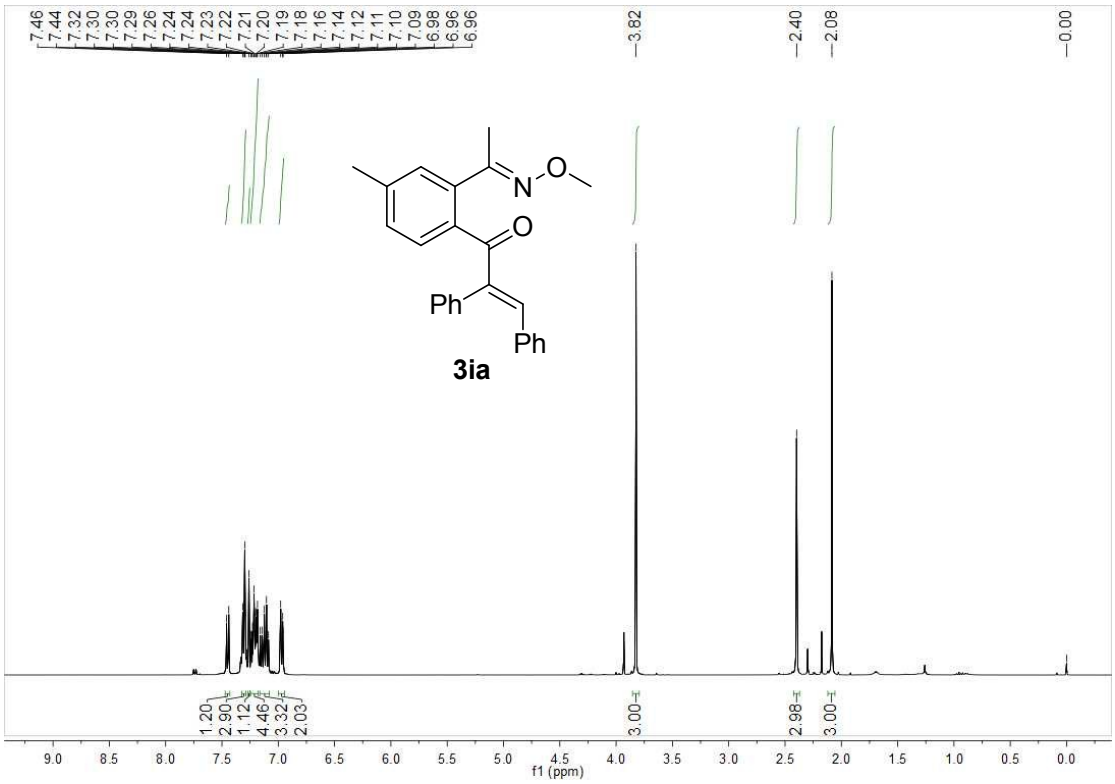
127.83
124.19
123.73
77.43
77.00
76.58
62.14
13.92
f1 (ppm)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7.24
7.24
7.23
7.22
7.21
7.20
7.19
7.18
7.16
7.14
7.12
7.11
7.10
7.09
6.98
6.96
6.96
3.82
2.40
2.08
0.00
N
O
O
Ph
Ph
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1.12
4.46
3.32
2.03
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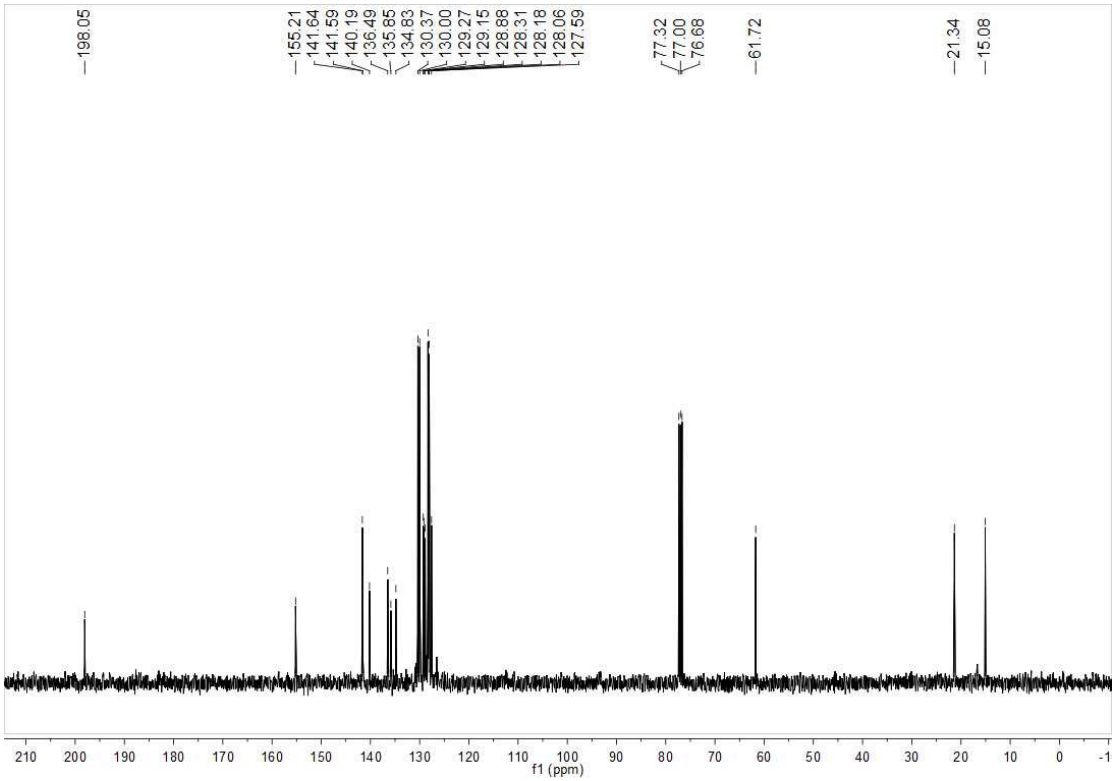
3.00
f1 (ppm)

3ia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134.83
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130.00
129.27
129.15
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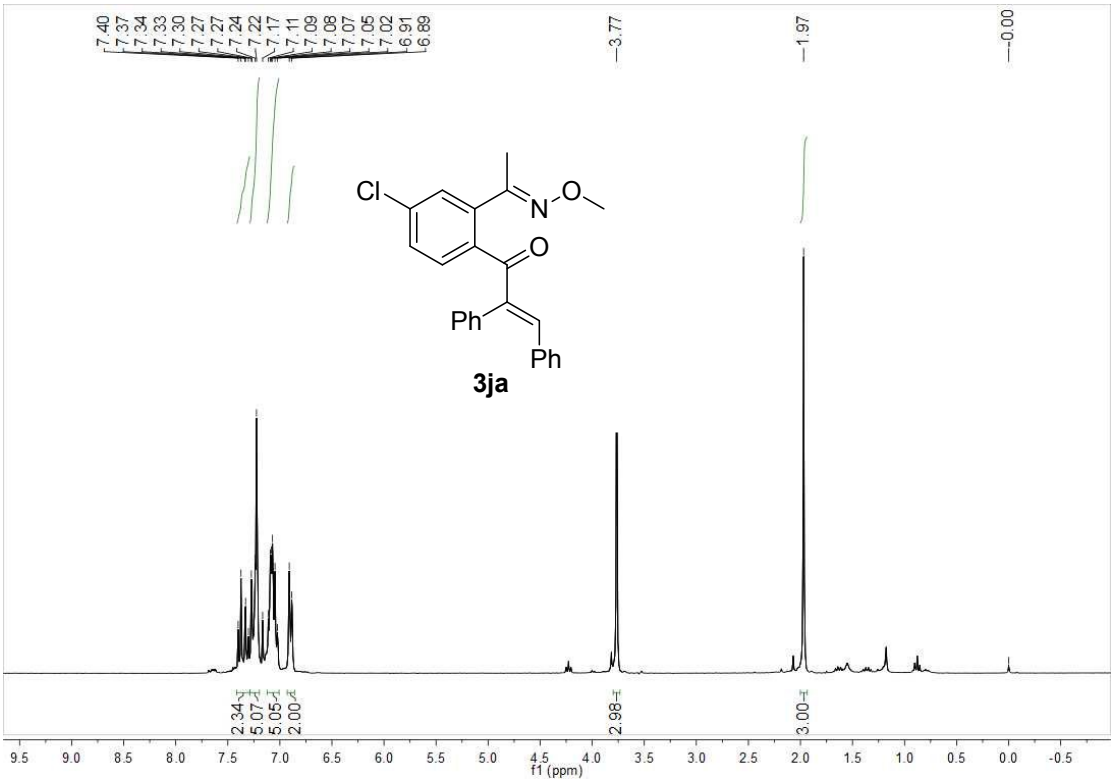
128.06
127.59
77.32
77.00
76.68
61.72
21.34
15.08
f1 (ppm)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7.27
7.24
7.22
7.17
7.11
7.09
7.08
7.07
7.05
7.02
6.91
6.89
3.77
1.97
0.00
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O
Ph
Ph
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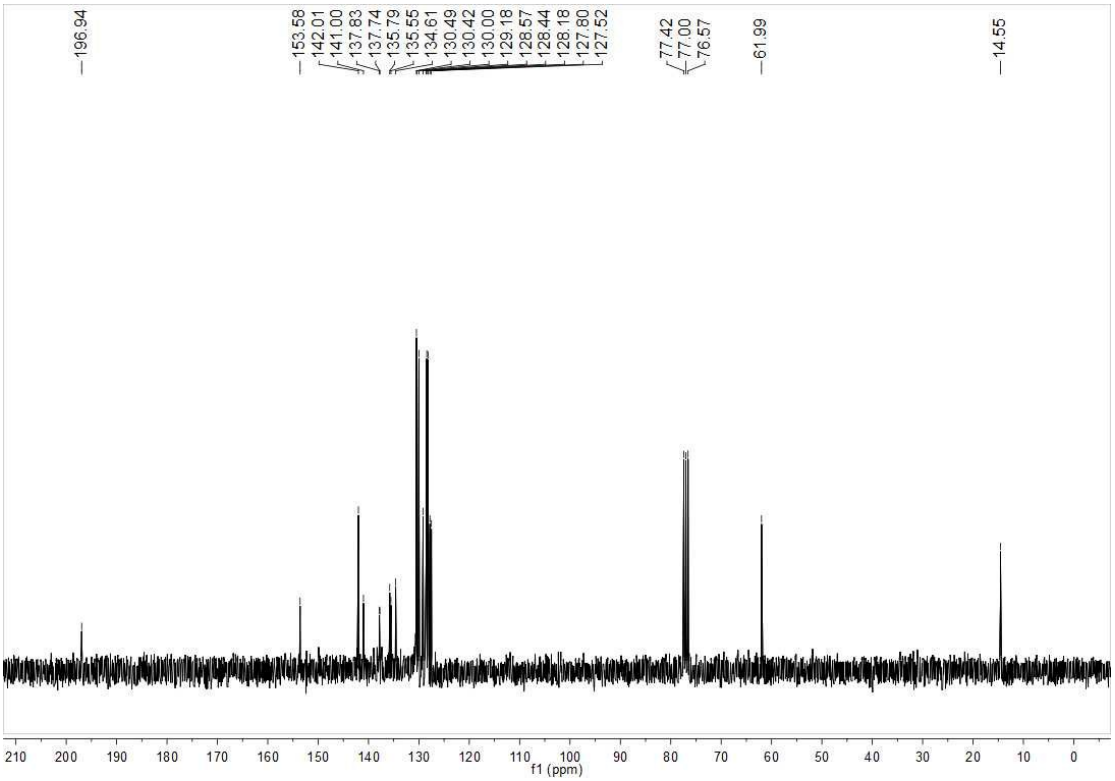
5.07
5.05
2.00
2.98
3.00
f1 (ppm)

3ja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130.00
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128.18
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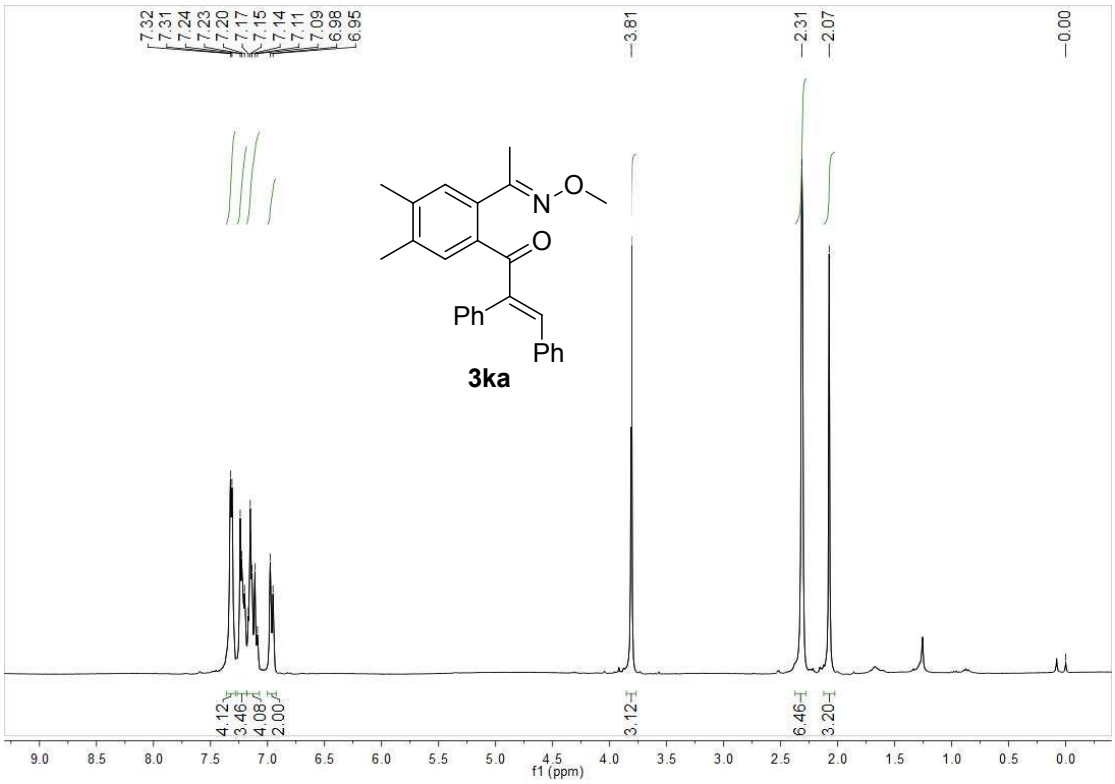
127.52
77.42
77.00
76.57
61.99
14.55
f1 (ppm)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7.31
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7.23
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7.17
7.15
7.14
7.11
7.09
6.98
6.95
3.81
2.31
2.07
0.00
N
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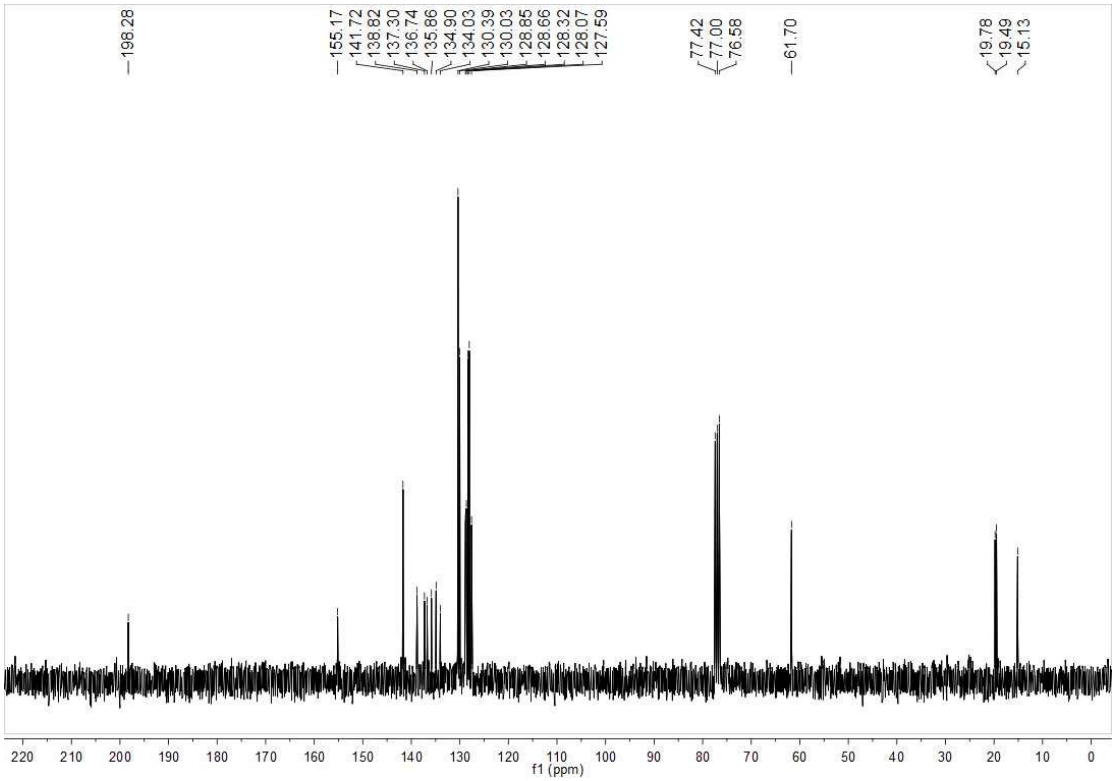
O
Ph
Ph
4.12
3.46
4.08
2.00
3.12
6.46
3.20
f1 (ppm)

3ka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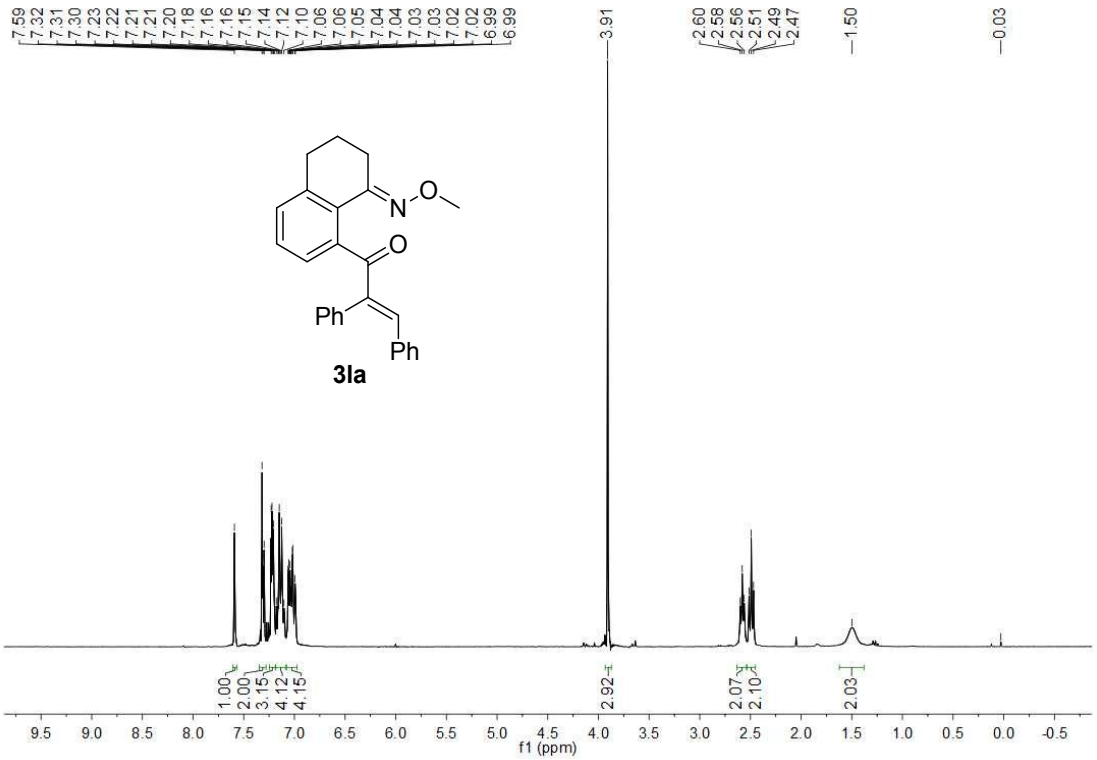
136.74
135.86
134.90
134.03
130.39
130.03
128.85
128.66
128.32
128.07
127.59
77.42
77.00
76.58
61.70
19.78
19.49
15.13
f1 (ppm)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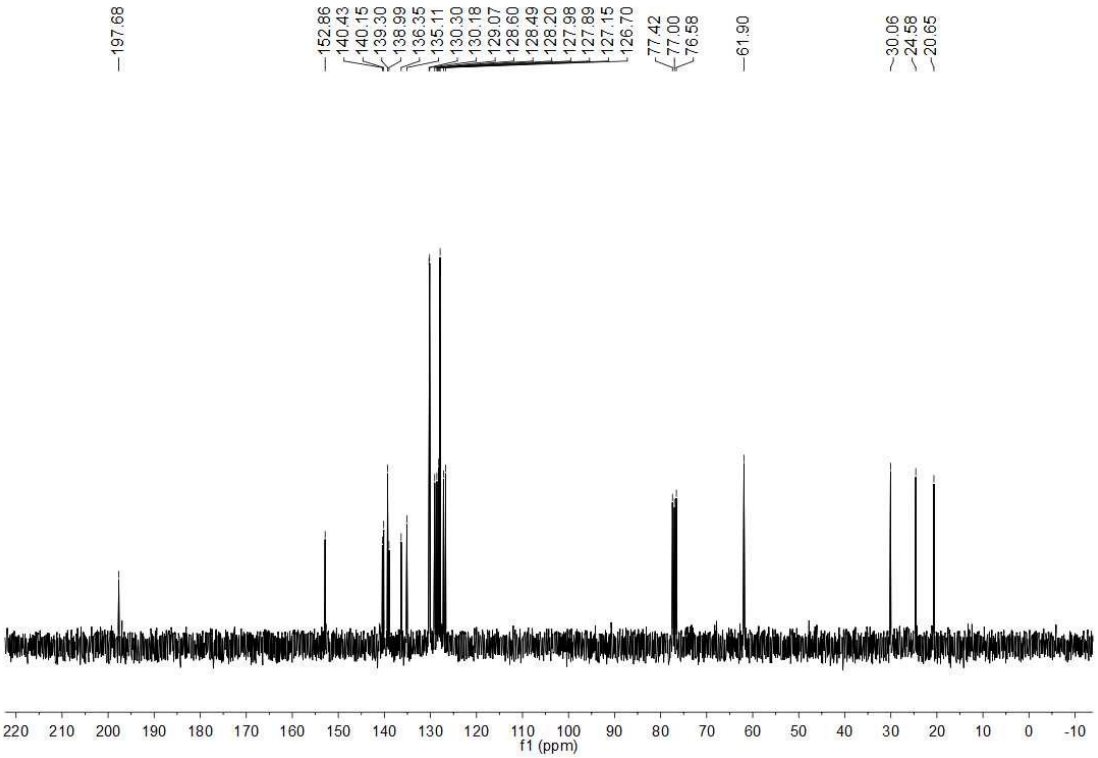
7.21
7.20
7.18
7.16
7.16
7.15
7.14
7.12
7.10
7.06
7.06
7.05
7.04
7.04
7.03
7.03
7.02
7.02
6.99
6.99
3.91
2.60
2.58
2.56
2.51
2.49
2.47
1.50
0.03
N
O
O
Ph
Ph
1.00
2.00
3.15
4.12
4.15
2.92
2.07
2.10
2.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

3la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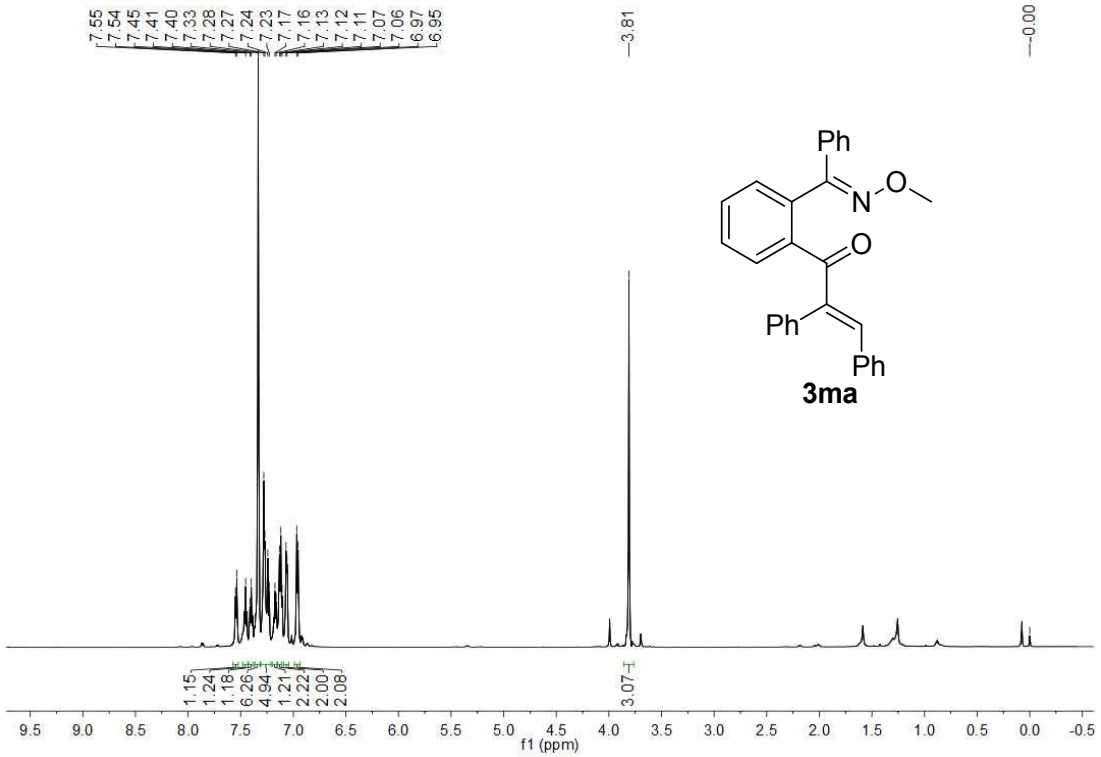
152.86
140.43
140.15
139.30
138.99
136.35
135.11
130.30
130.18
129.07
128.60
128.49
128.20
127.98
127.89
127.15
126.70
77.42
77.00
76.58
61.90
30.06
24.58
20.65
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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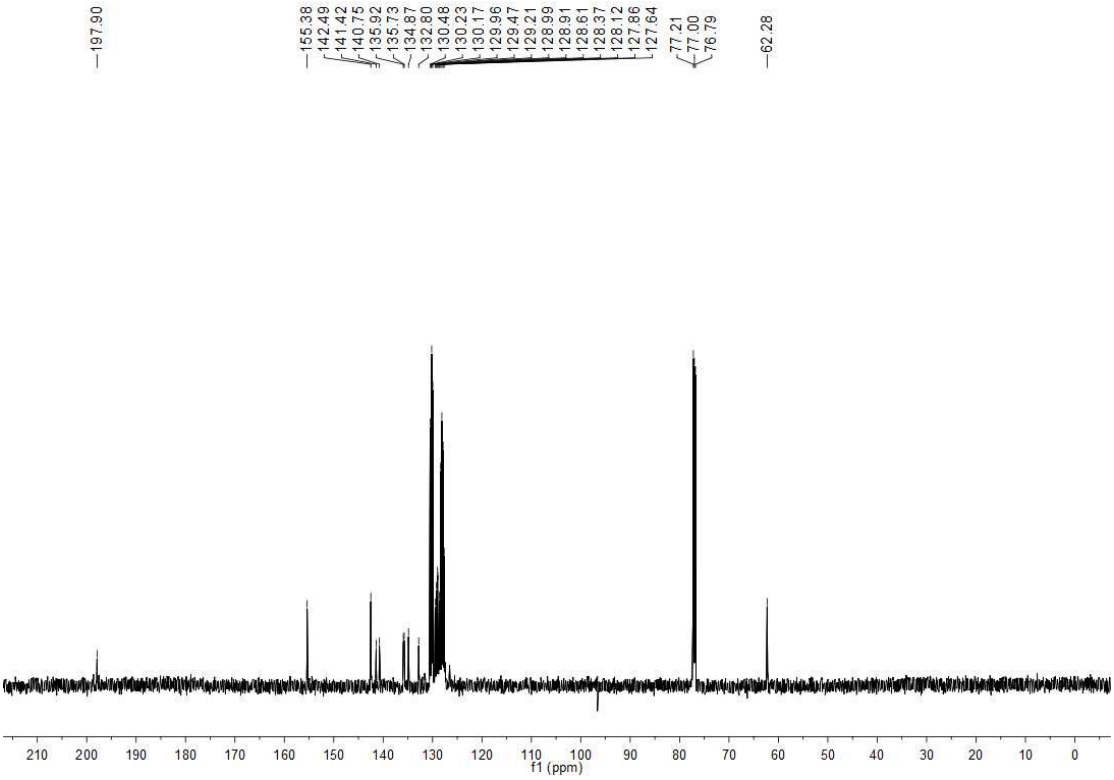
7.54
7.45
7.41
7.40
7.33
7.28
7.27
7.24
7.23
7.17
7.16
7.13
7.12
7.11
7.07
7.06
6.97
6.95
3.81
0.00
1.15
1.24
1.18
6.26
4.94
1.21
2.22
2.00
2.08
3.07
f1 (ppm)

Ph
N
O
O
Ph
Ph

3ma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134.87
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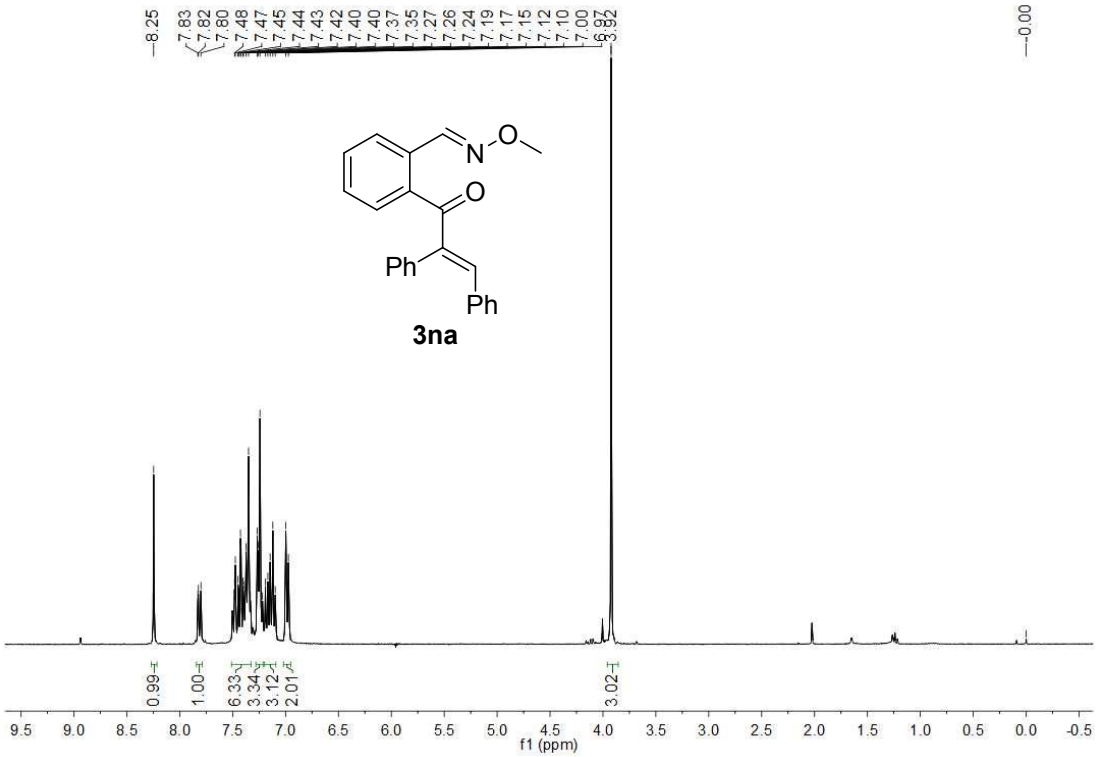
130.48
130.23
130.17
129.96
129.47
129.21
128.99
128.91
128.61
128.37
128.12
127.86
127.64
77.21
77.00
76.79
62.28
f1 (ppm)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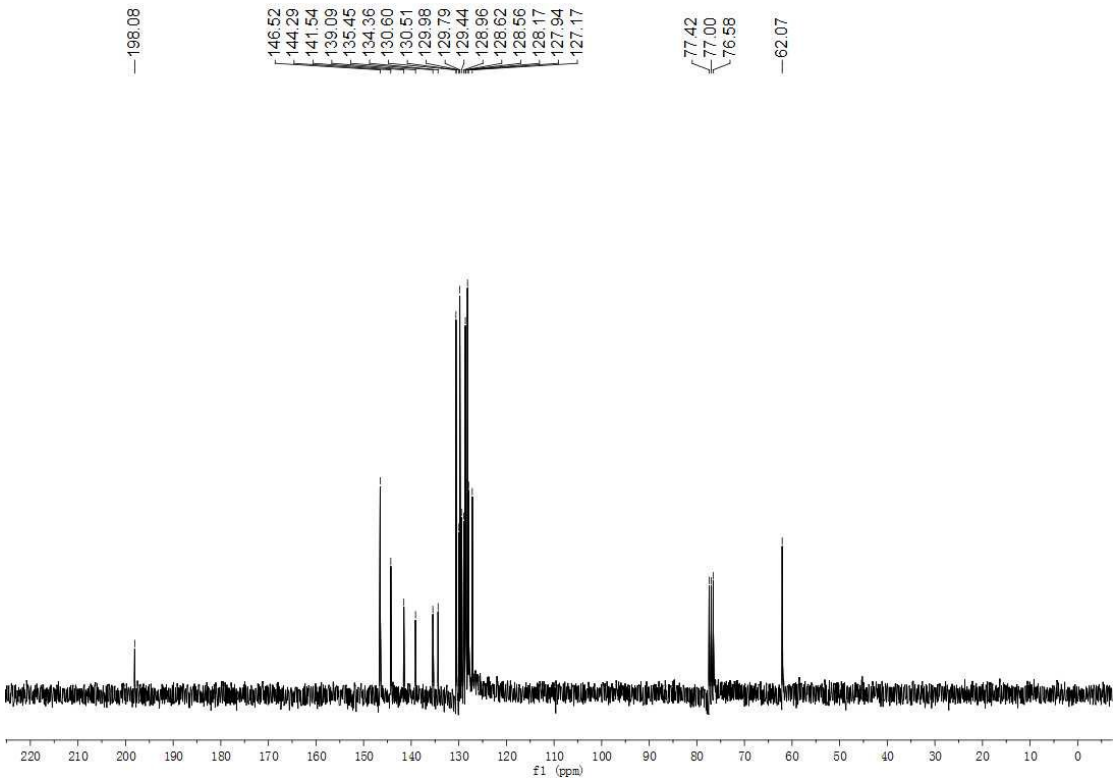
7.47
7.45
7.44
7.43
7.42
7.40
7.40
7.37
7.35
7.27
7.26
7.24
7.19
7.17
7.15
7.12
7.10
7.00
6.97
6.92
0.00
N
O
O
Ph
Ph
0.99
1.00
6.33
3.34
3.12
2.01
3.02
f1 (ppm)

3na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130.60
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129.98
129.79
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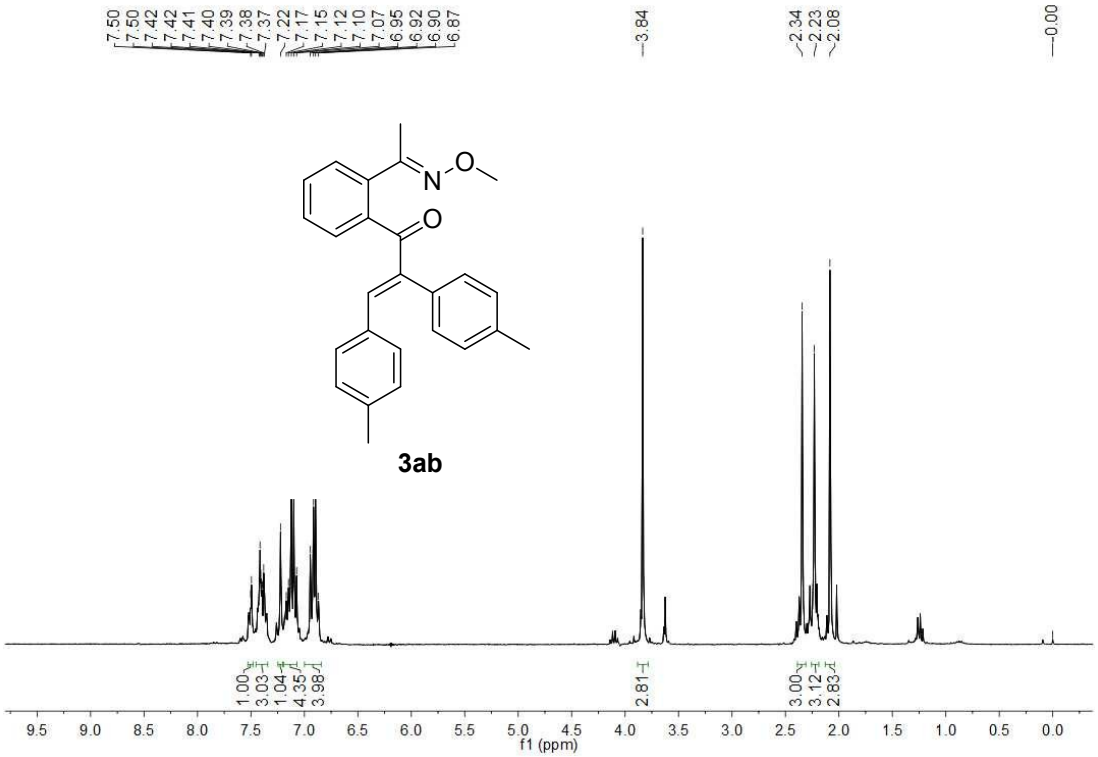
128.56
128.17
127.94
127.17
77.42
77.00
76.58
62.07
f1 (ppm)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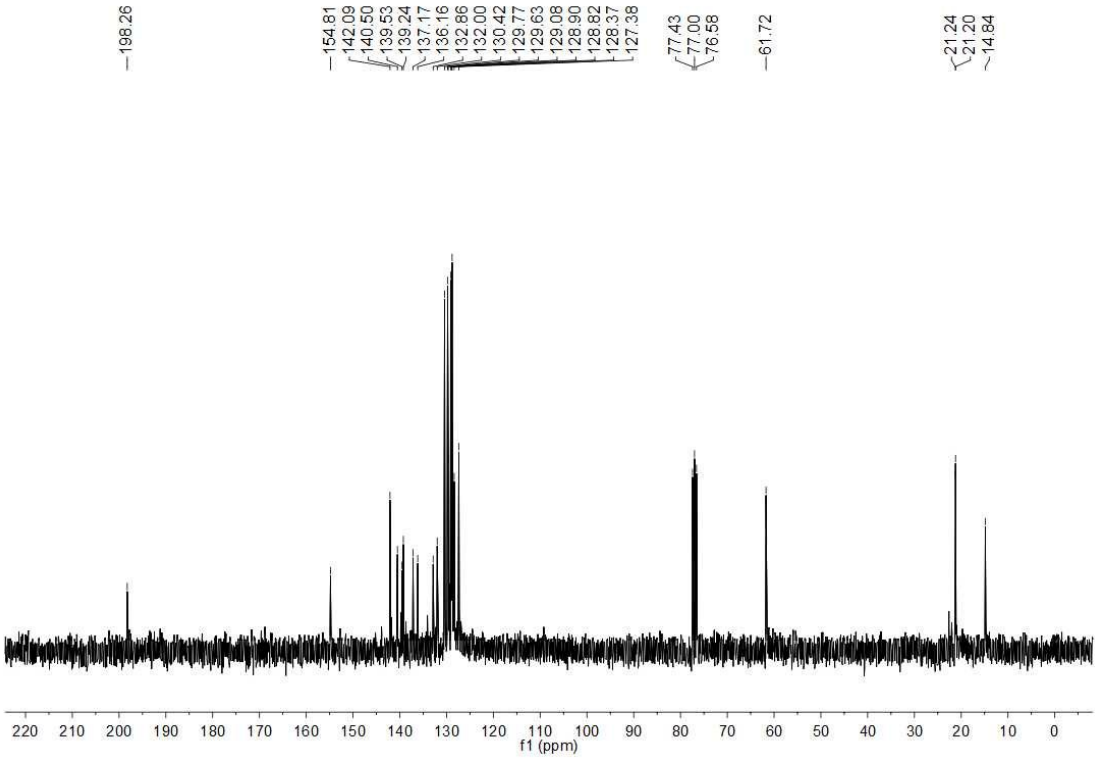
7.40
7.39
7.38
7.37
7.22
7.17
7.15
7.12
7.10
7.07
6.95
6.92
6.90
6.87
3.84
2.34
2.23
2.08
0.00
N
O
O
1.00
3.03
1.04
4.35
3.98
2.81
3.00
3.12
2.83
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3ab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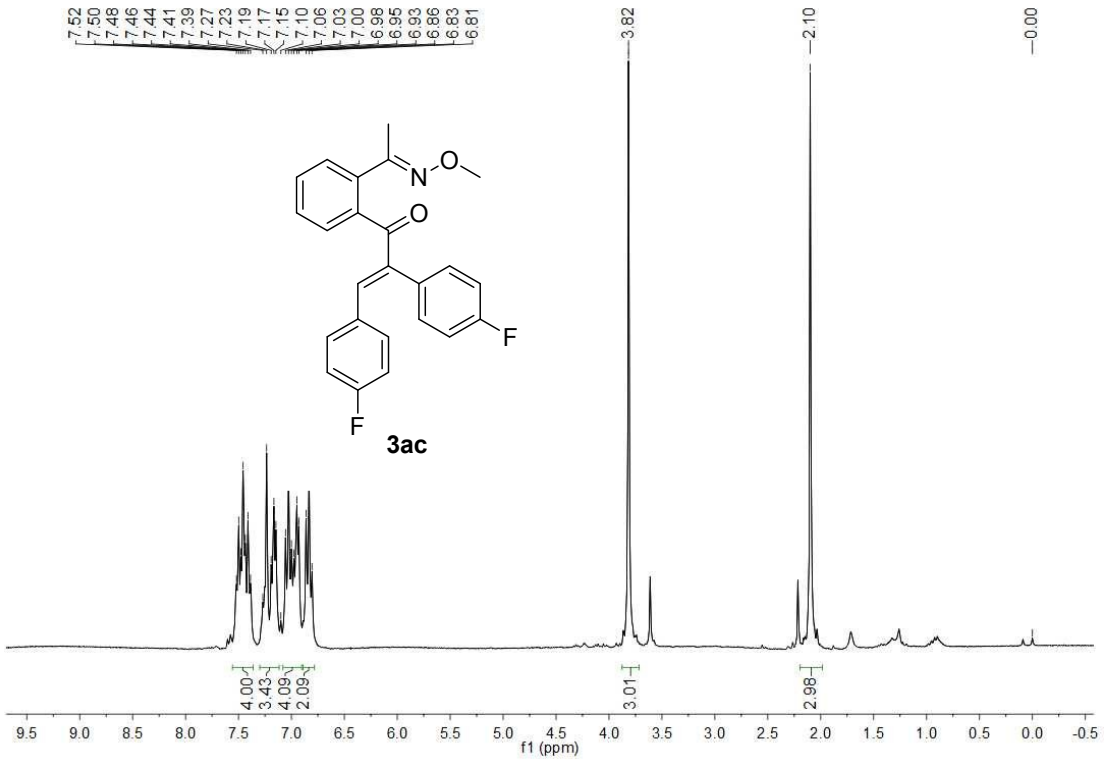
140.50
139.53
139.24
137.17
136.16
132.86
132.00
130.42
129.77
129.63
129.08
128.90
128.82
128.37
127.38
77.43
77.00
76.58
61.72
21.24
21.20
14.84
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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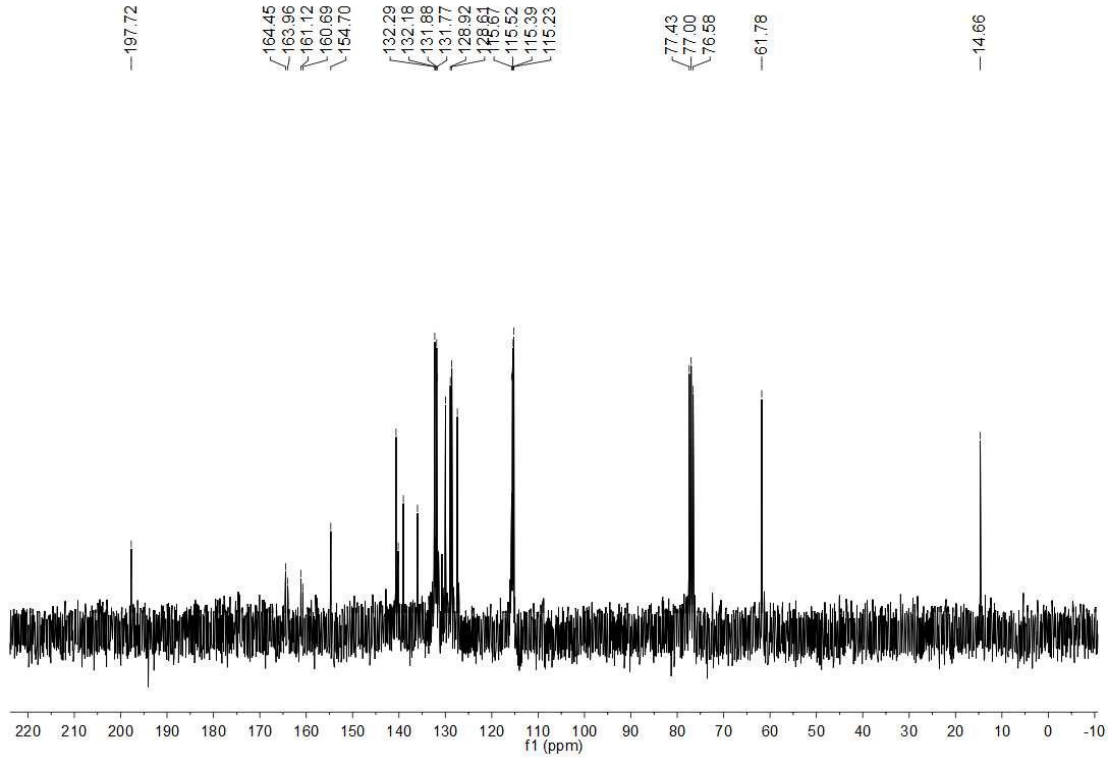
7.41
7.39
7.27
7.23
7.19
7.17
7.15
7.10
7.06
7.03
7.00
6.98
6.95
6.93
6.86
6.83
6.81
3.82
2.10
0.00
N
O
O
F
F
4.00
3.43
4.09
2.09
3.01
2.98
f1 (ppm)

3ac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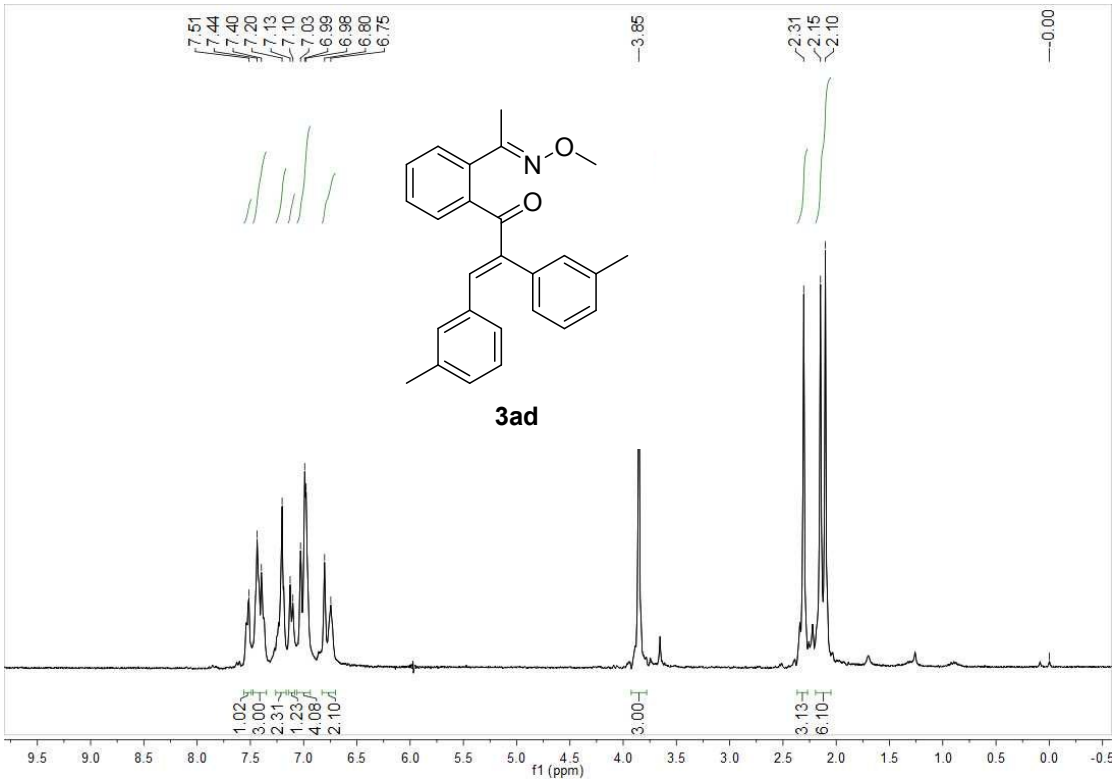
161.12
160.69
154.70
132.29
132.18
131.88
131.77
128.92
115.52
115.39
115.23
77.43
77.00
76.58
61.78
14.66
f1 (ppm)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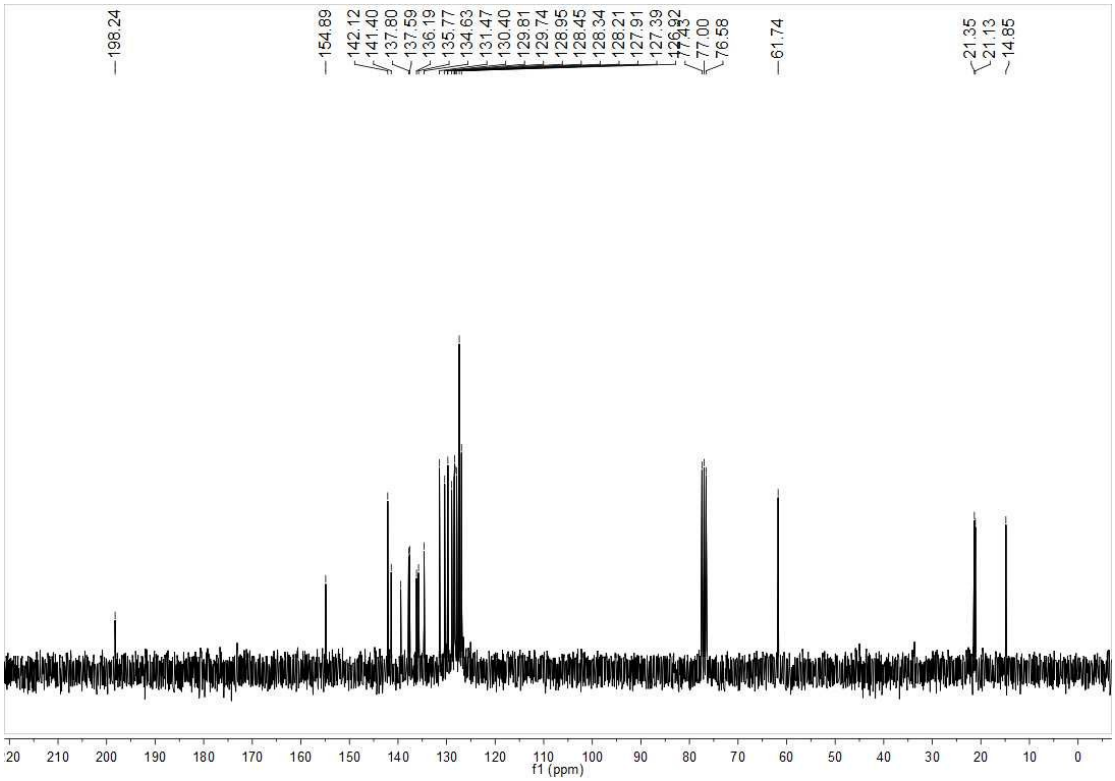
7.20
7.13
7.10
7.03
6.99
6.98
6.80
6.75
3.85
2.31
2.15
2.10
0.00
N
O
O
1.02
3.00
2.31
1.23
4.08
2.10
3.00
3.13
6.10
f1 (ppm)

3ad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136.19
135.77
134.63
131.47
130.40
129.81
129.74
128.95
128.45
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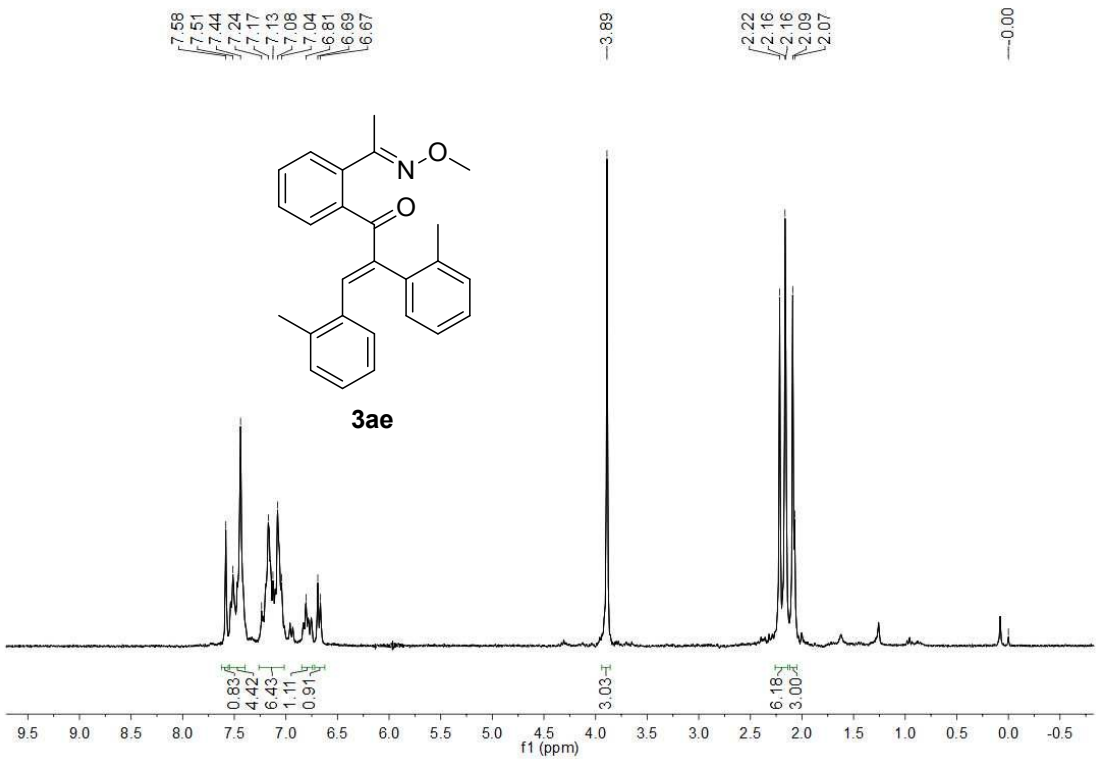
127.91
127.39
77.00
76.58
61.74
21.35
21.13
14.85
f1 (ppm)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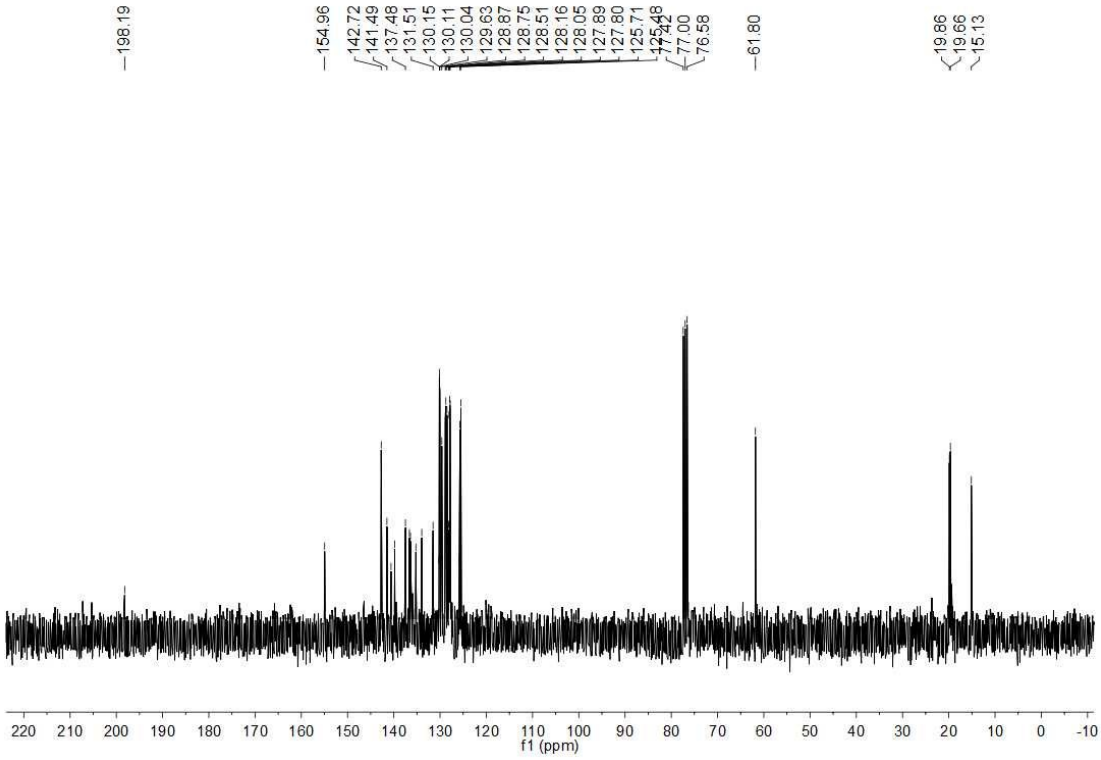
7.24
7.17
7.13
7.08
7.04
6.81
6.69
6.67
3.89
2.22
2.16
2.16
2.09
2.07
0.00
N
O
O
0.83
4.42
6.43
1.11
0.91
3.03
6.18
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

3ae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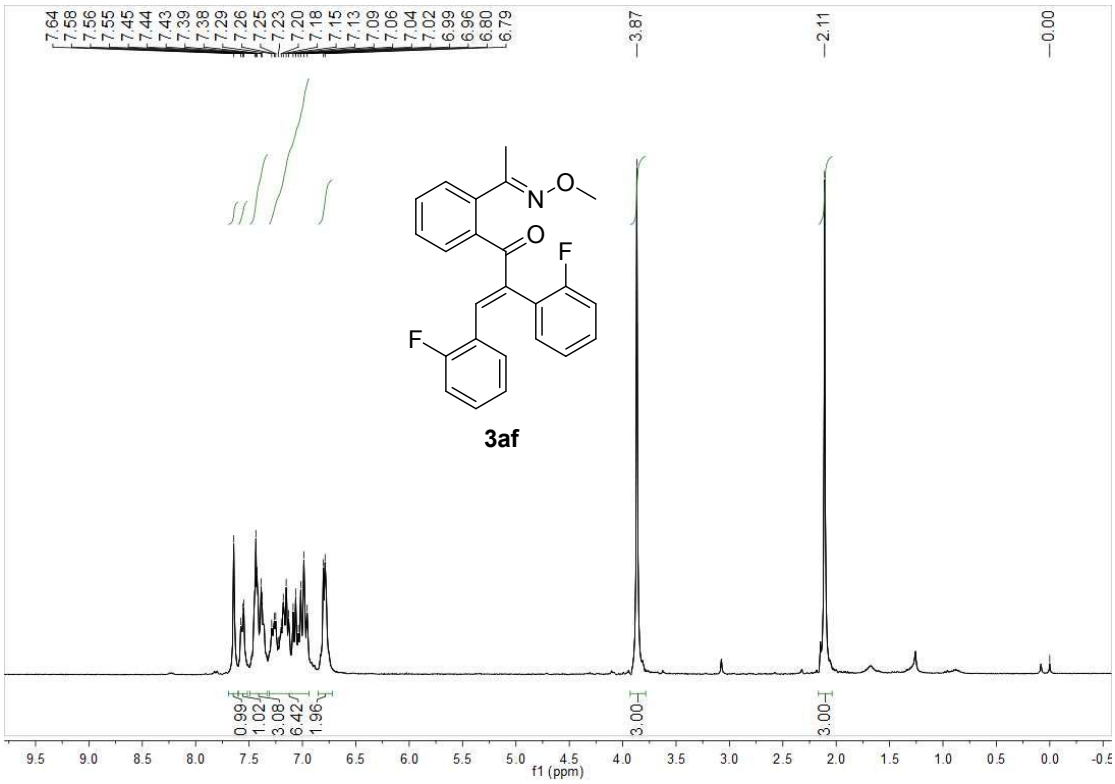
141.49
137.48
131.51
130.15
130.11
130.04
129.63
128.87
128.75
128.51
128.16
128.05
127.89
127.80
125.71
125.48
77.42
77.00
76.58
61.80
19.86
19.66
15.13
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.38
7.29
7.26
7.25
7.23
7.20
7.18
7.15
7.13
7.09
7.06
7.04
7.02
6.99
6.96
6.80
6.79
3.87
2.11
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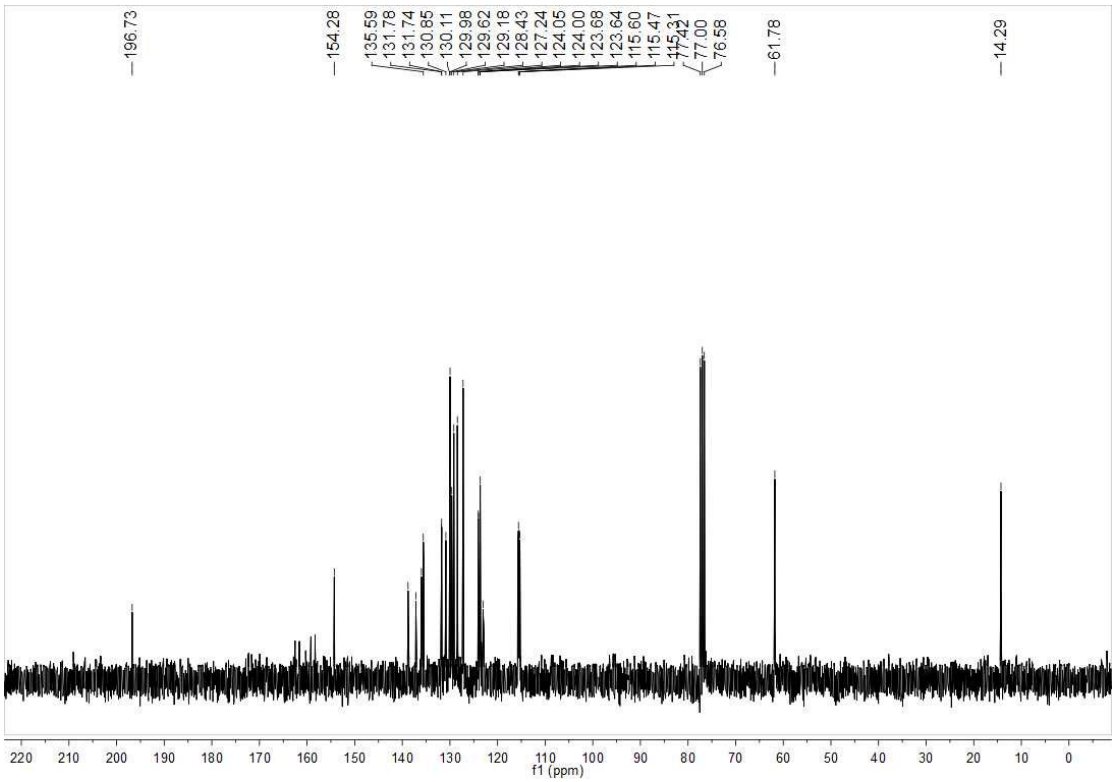
0.99
1.02
3.08
6.42
1.96
3.00
3.00
f1 (ppm)

3af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131.78
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130.85
130.11
129.98
129.62
129.18
128.43
127.24
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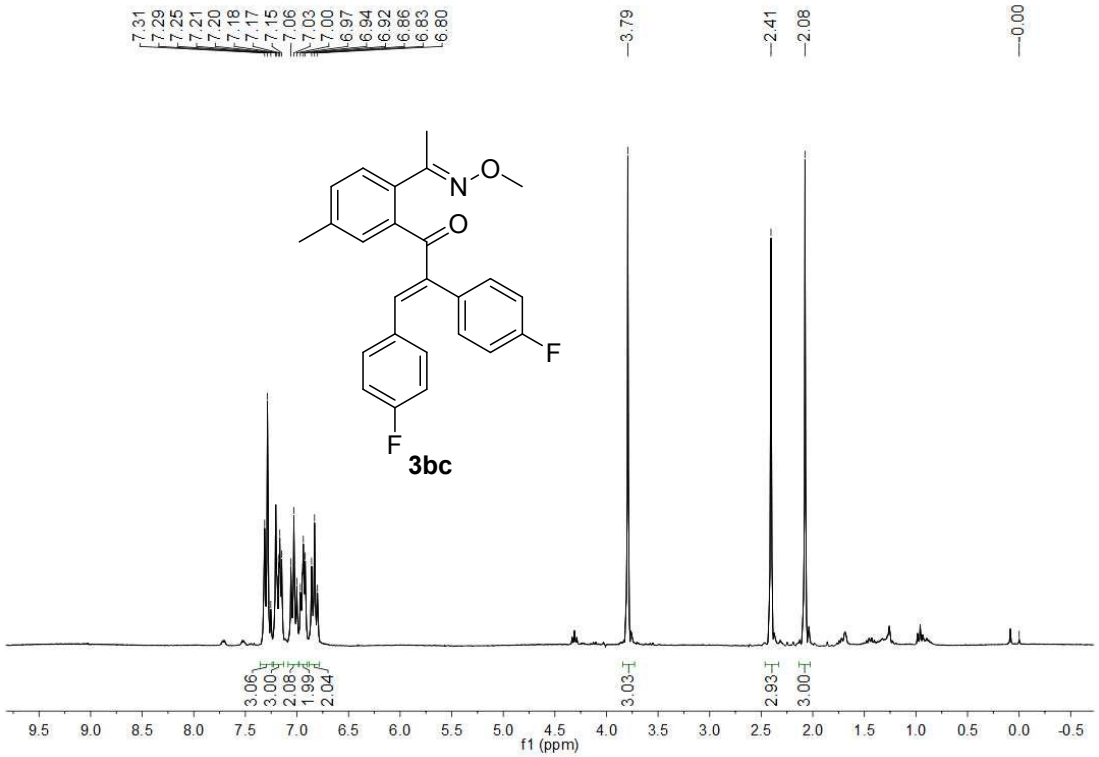
61.78
14.29
f1 (ppm)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7.21
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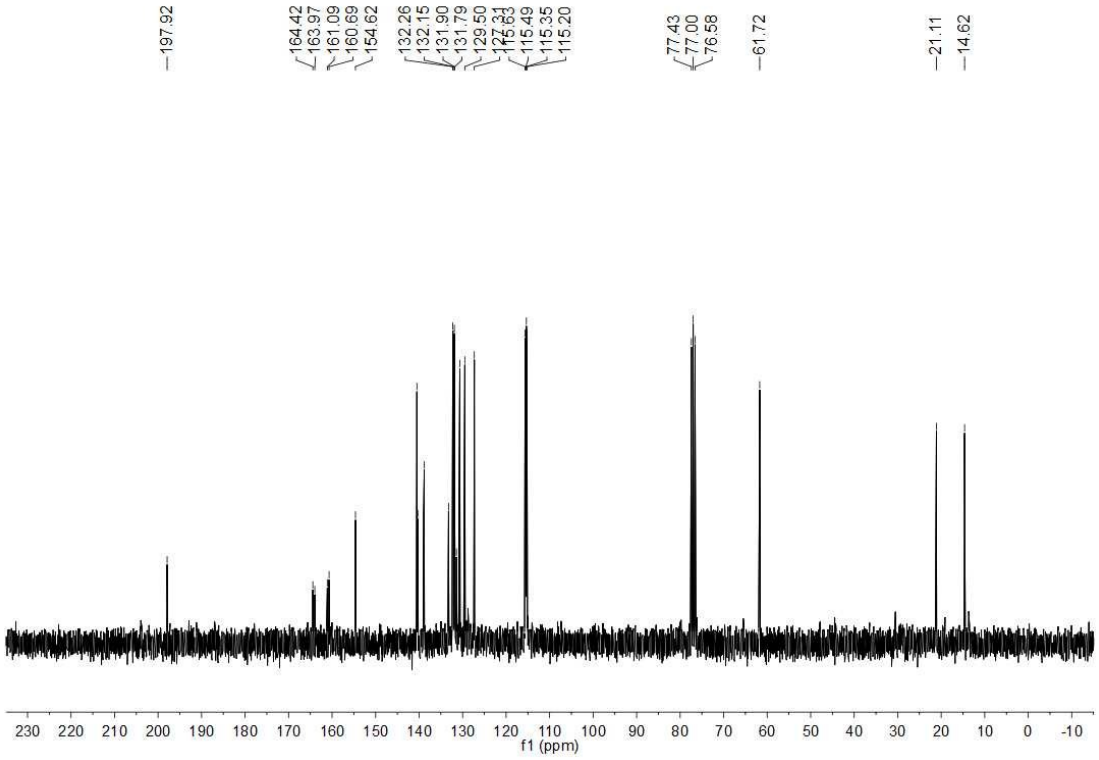
7.18
7.17
7.15
7.06
7.03
7.00
6.97
6.94
6.92
6.86
6.83
6.80
3.79
2.41
2.08
0.00
N
O
O
F
F
3bc
3.06
3.00
2.08
1.99
2.04
3.03
2.93
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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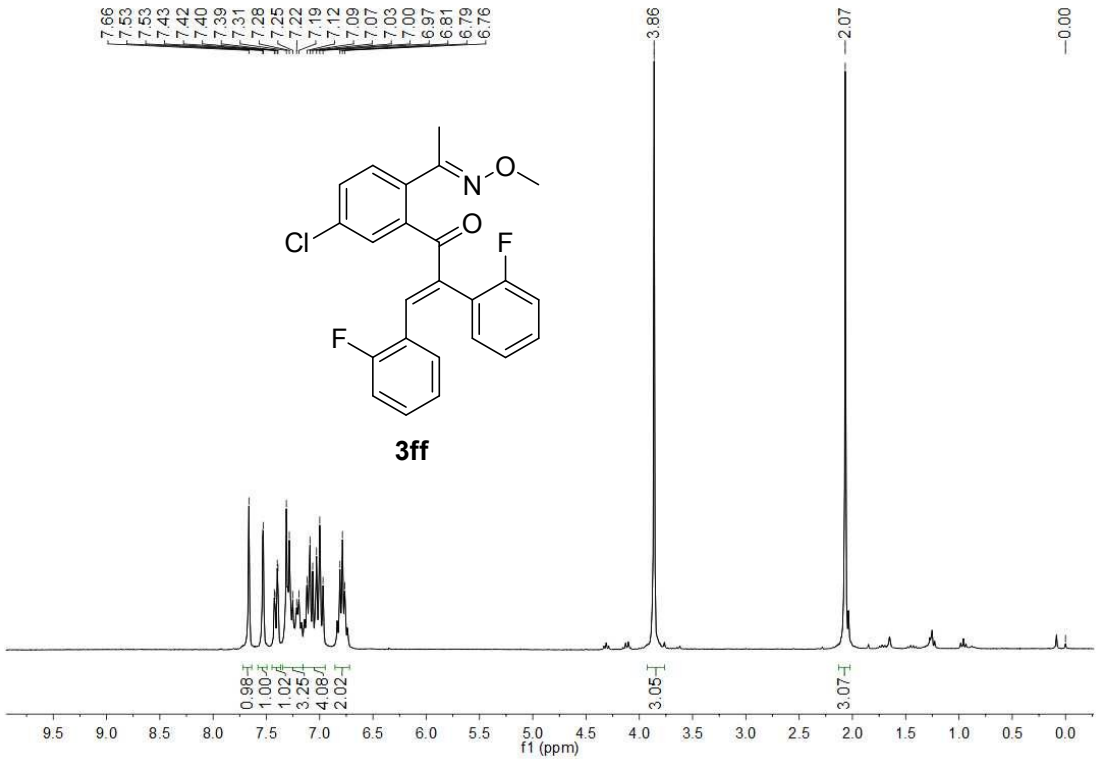
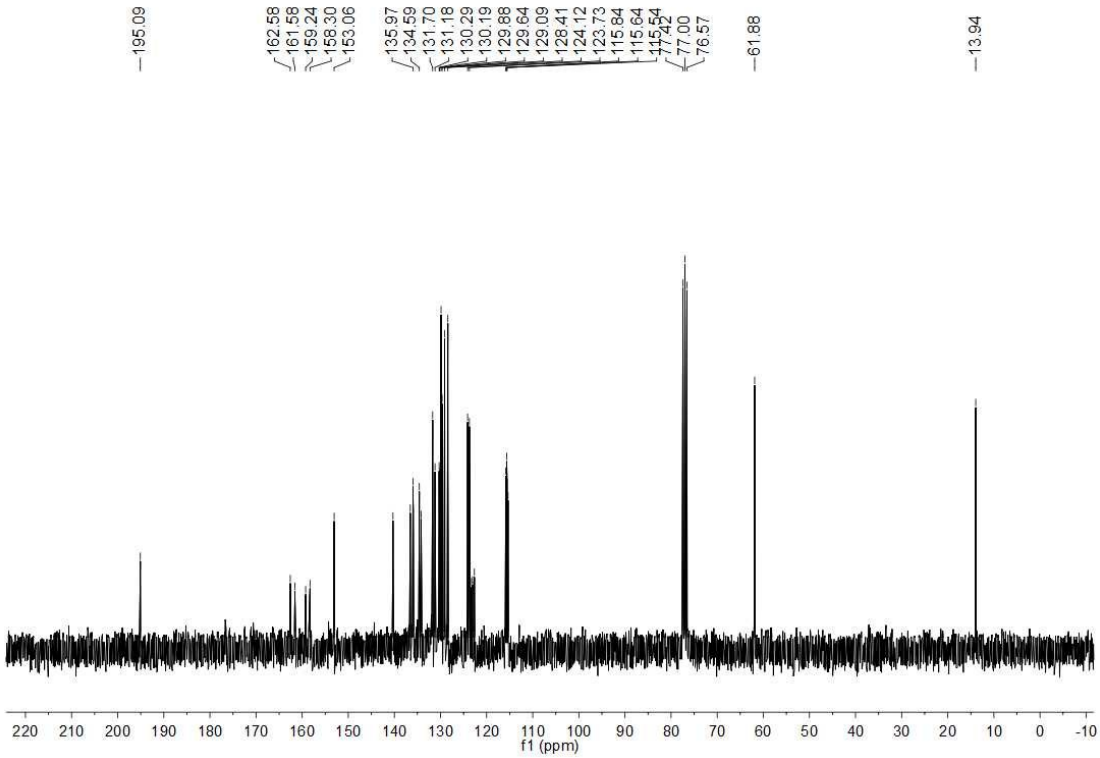
161.09
160.69
154.62
132.26
132.15
131.90
131.79
129.50
127.33
125.83
115.49
115.35
115.20
77.43
77.00
76.58
61.72
21.11
14.62
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.66
7.53
7.53
7.43
7.42
7.40
7.39
7.31
7.28
7.25
7.22
7.19
7.12
7.09
7.07
7.03
7.00
6.97
6.81
6.79
6.76
3.86
2.07
0.00
Cl
N
O
O
F
F
0.98
1.00
1.02
3.25
4.08
2.02
3.05
3.07
f1 (ppm)

3ff


195.09
162.58
161.58
159.24
158.30
153.06
135.97
134.59
131.70
131.18
130.29
130.19
129.88
129.64
129.09
128.41
124.12
123.73
115.84
115.64
115.54
77.42
77.00
76.57
61.88
13.94
f1 (ppm)