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Supporting Information for

DABCO Catalyzed [4+2] Annulations of Morita−Baylis−Hillman Carbonates with Isocyanates

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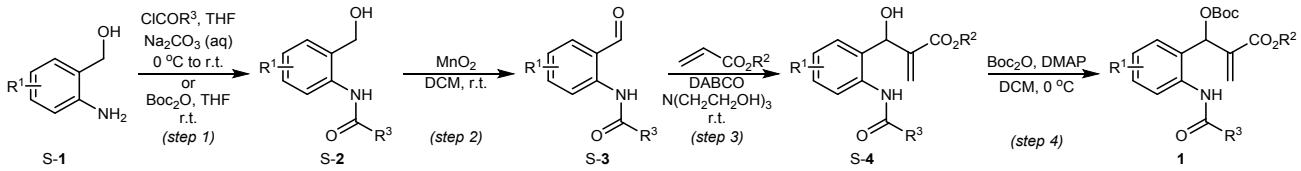
CONTENTS

1. General methods

^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) were recorded on a Bruker AV 400 (400 MHz) spectrometer with $CDCl_3$ as solvent (Unless otherwise noted, records are all performed at ambient temperature). Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton ($CDCl_3$: δ 7.26 ppm), carbon ($CDCl_3$: δ 77.07 ppm) or tetramethylsilane (TMS δ 0.00). Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), m (multiplet). Coupling constants *J* are reported in Hz. HRMS were obtained on Agilent 6520 Q-TOF LC/MS with ESI resource. Melting points were measured on a RY-I apparatus and are reported uncorrected. Column chromatography was performed on silica gel 200-300 mesh.

All reactions were carried out under nitrogen or argon atmosphere. Unless otherwise noted, analytical grade solvents and commercially available reagents were used without further purification. All isocyanates used in the article are commercially available.

2. Synthesis of *o*-amino-acylation aryl MBH carbonates 1



General procedure for the synthesis of substituted *o*-amino-acylation aryl MBH carbonates

o-amino-acylation aryl MBH carbonates were synthesized following the general procedure shown in the figure above. Depending on which substrates were commercial available, the starting point for the synthesis was *o*-amino benzyl alcohol (S-**1**) (Commercially available or reduced from *o*-amino benzoic acid[1]). Analogues of S-**4** have been reported earlier[2]. Step 4 is the classic hydroxyl protection[3].

21 kinds of substituted *o*-amino-acylation aryl MBH carbonates were prepared according to the above method (Supplementary Fig. 1).

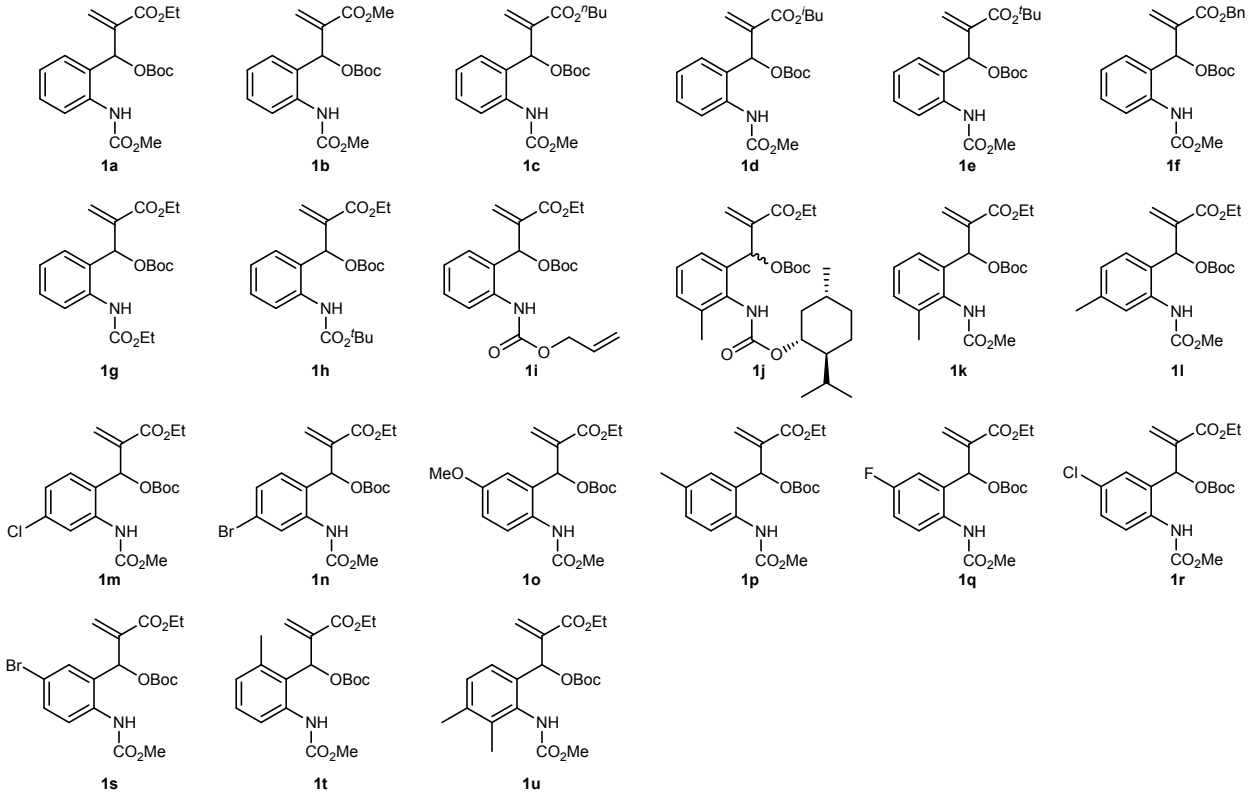
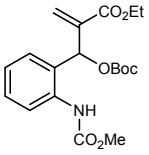


Figure S1. Scopes of *o*-amino-acylation aryl MBH carbonates.

[1] L. A. Leth, F. Glaus, M. Meazza, L. Fu, M. K. Thøgersen, E. A. Bitsch and K. A. Jørgensen, *Angew. Chem. Int. Ed.*, 2016, **55**, 15272-15276. [2] H. N. Lim, Y. S. Song and K.-J. Lee, *Synthesis*, 2007, **2007**, 3376-3384. [3] Y. Du, X. Lu and C. Zhang, *Angew. Chem., Int. Ed.*, 2003**, 42**, 1035-1037.

2.2 Characterization Data of o-amino-acylation aryl MBH carbonates

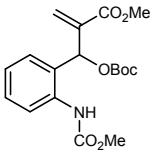
ethyl 2-(((tert-butoxycarbonyl)oxy)(2-((methoxycarbonyl)amino)phenyl)methyl)acrylate (1a)



1a

7.9 g, 52% yield (4 steps). White solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 7.84 – 7.71 (m, 1H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.16 – 7.08 (m, 1H), 6.58 (s, 1H), 6.43 (s, 1H), 6.13 – 6.08 (m, 1H), 4.23 – 4.08 (m, 2H), 3.81 (s, 3H), 1.46 (s, 9H), 1.21 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.3, 154.8, 152.6, 139.0, 135.9, 129.3, 129.2, 128.1, 125.1, 124.5, 83.2, 71.2, 61.4, 52.3, 27.7, 13.9. (There is a carbon signal missing, and this situation often occurs later, so no reminder will be given) **HRMS(ESI)** m/z: $[M + Na]^+$ calcd for $C_{19}H_{25}NNaO_7^+$ 402.1523; Found: 402.1520.

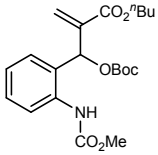
methyl 2-(((tert-butoxycarbonyl)oxy)(2-((methoxycarbonyl)amino)phenyl)methyl)acrylate (1b)



1b

7.0 g, 48% yield (4 steps). White solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 7.76 (s, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.58 (s, 1H), 6.43 (s, 1H), 6.13 (s, 1H), 3.81 (s, 3H), 3.70 (s, 3H), 1.46 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.9, 154.8, 152.5, 138.8, 135.8, 129.3, 128.1, 125.4, 124.6, 123.7, 83.2, 71.0, 52.4, 27.7. **HRMS(ESI)** m/z: $[M + Na]^+$ calcd for $C_{18}H_{23}NNaO_7^+$ 388.1367; Found: 388.1362.

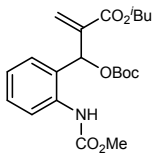
butyl 2-(((tert-butoxycarbonyl)oxy)(2-((methoxycarbonyl)amino)phenyl)methyl)acrylate (1c)



1c

5.2 g, 32% yield (4 steps). White solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.77 (s, 1H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.57 (s, 1H), 6.42 (s, 1H), 6.17 – 6.06 (m, 1H), 4.09 (qt, *J* = 10.8, 6.7 Hz, 2H), 3.80 (s, 3H), 1.60 – 1.51 (m, 2H), 1.45 (s, 9H), 1.28 (dq, *J* = 14.7, 7.4 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 154.8, 152.6, 139.1, 135.9, 129.3, 128.1, 125.1, 124.5, 123.4, 83.2, 71.2, 65.3, 52.3, 30.4, 27.7, 19.0, 13.7. **HRMS(ESI)** m/z: $[M + Na]^+$ calcd for $C_{21}H_{29}NNaO_7^+$ 430.1836; Found: 430.1831.

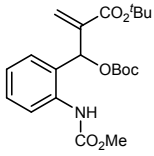
isobutyl 2-(((tert-butoxycarbonyl)oxy)(2-((methoxycarbonyl)amino)phenyl)methyl)acrylate (1d)



1d

5.9 g, 36% yield (4 steps). White solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.15 (s, 1H), 7.77 (s, 1H), 7.31 (t, *J* = 8.1 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.57 (s, 1H), 6.43 (s, 1H), 6.10 (s, 1H), 3.93 – 3.81 (m, 2H), 3.79 (s, 3H), 1.89 (dp, *J* = 13.4, 6.7 Hz, 1H), 1.44 (s, 9H), 0.86 (dd, *J* = 6.7, 2.7 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 154.8, 152.6, 139.0, 135.9, 129.3, 128.1, 125.2, 124.5, 123.4, 83.3, 71.4, 71.1, 52.3, 27.7, 27.6, 19.0. **HRMS(ESI)** m/z: $[M + Na]^+$ calcd for $C_{21}H_{29}NNaO_7^+$ 430.1836; Found: 430.1833.

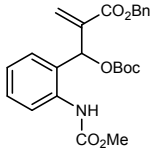
tert-butyl 2-(((tert-butoxycarbonyl)oxy)(2-((methoxycarbonyl)amino)phenyl)methyl)acrylate (1e)



1e

5.4 g, 33% yield (4 steps). White solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.75 (s, 1H), 7.22 (d, *J* = 7.3 Hz, 2H), 7.01 (d, *J* = 6.7 Hz, 1H), 6.46 (s, 1H), 6.26 (s, 1H), 5.91 (s, 1H), 3.71 (s, 3H), 1.38 (s, 9H), 1.26 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.5, 154.7, 152.9, 140.2, 136.1, 129.3, 128.3, 124.3, 124.2, 123.0, 83.2, 82.1, 71.5, 52.2, 27.8, 27.7. **HRMS(ESI)** m/z: $[M + Na]^+$ calcd for $C_{21}H_{29}NNaO_7^+$ 430.1836; Found: 430.1832.

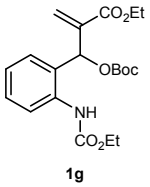
benzyl 2-(((tert-butoxycarbonyl)oxy)(2-((methoxycarbonyl)amino)phenyl)methyl)acrylate (1f)



1f

4.9 g, 28% yield (4 steps). White solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.77 (s, 1H), 7.33 (ddd, *J* = 7.9, 4.2, 2.0 Hz, 5H), 7.24 (dd, *J* = 7.1, 2.4 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.60 (s, 1H), 6.46 (s, 1H), 6.13 (s, 1H), 5.16 – 5.07 (m, 2H), 3.78 (s, 3H), 1.44 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 154.8, 152.6, 146.8, 138.7, 135.9, 135.2, 129.3, 128.6, 128.3, 128.2, 125.7, 124.6, 83.3, 71.2, 67.1, 52.3, 27.7, 27.4. **HRMS(ESI)** m/z: $[M + Na]^+$ calcd for $C_{24}H_{27}NNaO_7^+$ 464.1680; Found: 464.1677.

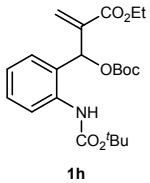
ethyl 2-(((tert-butoxycarbonyl)oxy)(2-((ethoxycarbonyl)amino)phenyl)methyl)acrylate (1g)



1g

7.9 g, 50% yield (4 steps). White solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.04 8.00 (s, 1H), 7.75 (s, 1H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.57 (s, 1H), 6.43 (s, 1H), 6.08 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.19 – 4.07 (m, 2H), 1.45 (s, 9H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.3, 154.4, 152.6, 139.0, 136.0, 129.2, 128.2, 125.1, 124.4, 123.7, 123.6, 83.2, 71.3, 61.4, 61.2, 27.7, 14.6, 13.9. **HRMS(ESI)** m/z: $[M + Na]^+$ calcd for $C_{20}H_{27}NNaO_7^+$ 416.1680; Found: 416.1675.

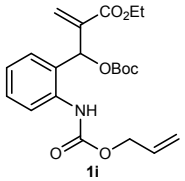
ethyl 2-((2-((tert-butoxycarbonyl)amino)phenyl)((tert-butoxycarbonyl)oxy)methyl)acrylate (1h)



1h

9.3 g, 55% yield (4 steps). White solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.81 – 7.67 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.14 – 7.05 (m, 1H), 6.59 (s, 1H), 6.44 (s, 1H), 6.12 – 6.02 (m, 1H), 4.24 – 4.07 (m, 2H), 1.55 (s, 9H), 1.47 (s, 9H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 153.5, 152.5, 139.0, 136.3, 129.1, 128.2, 125.1, 124.1, 123.7, 83.1, 80.2, 71.4, 61.3, 28.4, 27.7, 13.9. **HRMS(ESI)** m/z: $[M + Na]^+$ calcd for $C_{22}H_{31}NNaO_7^+$ 444.1993; Found: 444.1987.

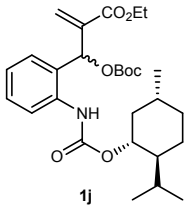
ethyl 2-((2-(((allyloxy)carbonyl)amino)phenyl)((tert-butoxycarbonyl)oxy)methyl)acrylate (1i)



1i

7.6 g, 47% yield (4 steps). White solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.03 (s, 1H), 7.68 (s, 1H), 7.23 (t, J = 7.6 Hz, 2H), 7.03 (t, J = 7.4 Hz, 1H), 6.50 (s, 1H), 6.35 (s, 1H), 6.01 (s, 1H), 5.93 (ddt, J = 16.2, 10.8, 5.6 Hz, 1H), 5.30 (d, J = 17.1 Hz, 1H), 5.17 (d, J = 10.3 Hz, 1H), 4.62 (d, J = 5.5 Hz, 2H), 4.13 – 3.98 (m, 2H), 1.37 (s, 9H), 1.11 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.3, 154.0, 152.6, 139.0, 135.9, 132.8, 129.2, 128.2, 125.1, 124.6, 123.6, 117.8, 83.2, 71.2, 65.9, 65.8, 61.4, 27.7, 13.9. **HRMS(ESI)** m/z: $[M + Na]^+$ calcd for $C_{21}H_{27}NNaO_7^+$ 428.1680; Found: 428.1676.

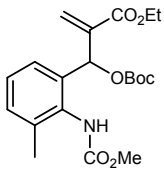
ethyl 2-(((tert-butoxycarbonyl)oxy)(2-(((((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)amino)-3-methylphenyl)methyl)acrylate (1j)



1j

4.6 g, 23% yield (4 steps). Colorless viscous oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 11.4 Hz, 2H), 7.30 (t, *J* = 6.9 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.58 (d, *J* = 7.1 Hz, 1H), 6.42 (d, *J* = 3.7 Hz, 1H), 6.05 (s, 1H), 4.68 (tt, *J* = 10.5, 4.6 Hz, 1H), 4.13 (dddt, *J* = 14.8, 10.8, 7.3, 3.8 Hz, 2H), 2.17 – 2.10 (m, 1H), 2.07 – 1.99 (m, 1H), 1.69 (d, *J* = 11.2 Hz, 2H), 1.53 (s, 3H), 1.47 – 1.39 (m, 10H), 1.28 – 1.03 (m, 6H), 0.93 (d, *J* = 6.5 Hz, 6H), 0.83 (dd, *J* = 6.9, 3.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 154.2, 152.5, 146.7, 138.9, 138.9, 136.2, 129.2, 129.2, 128.4, 128.2, 125.2, 125.1, 124.2, 123.5, 83.1, 75.1, 75.0, 71.6, 71.5, 61.3, 47.3, 47.2, 41.4, 41.3, 34.3, 31.4, 31.4, 27.7, 27.7, 27.4, 26.4, 26.3, 23.7, 23.6, 22.1, 20.8, 20.8, 16.6, 16.6, 13.9, 13.9. **HRMS(ESI)** m/z: $[M + Na]^+$ calcd for $C_{28}H_{41}NNaO_7^+$ 526.2775; Found: 526.2770.

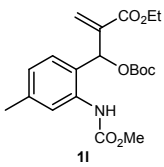
ethyl 2-(((tert-butoxycarbonyl)oxy)(2-((methoxycarbonyl)amino)-3-methylphenyl)methyl)acrylate (1k)



1k

5.7 g, 36% yield (4 steps). White solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.57 (s, 1H), 7.22 (dt, *J* = 14.7, 6.7 Hz, 3H), 6.71 (s, 1H), 6.45 (s, 1H), 6.08 (s, 1H), 4.17 (dtd, *J* = 10.8, 7.1, 3.7 Hz, 2H), 3.82 (s, 3H), 2.35 (s, 3H), 1.48 (s, 9H), 1.23 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 154.6, 152.6, 139.3, 136.8, 133.8, 133.7, 131.3, 126.9, 125.8, 125.1, 82.9, 71.6, 61.2, 52.4, 27.7, 18.5, 14.0. **HRMS(ESI)** m/z: $[M + Na]^+$ calcd for $C_{20}H_{27}NNaO_7^+$ 416.1680; Found: 416.1676.

ethyl 2-(((tert-butoxycarbonyl)oxy)(2-((methoxycarbonyl)amino)-4-methylphenyl)methyl)acrylate (1l)

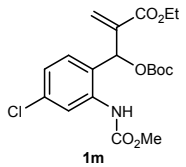


1l

7.2 g, 46% yield (4 steps). White solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 7.57 (d, *J* = 21.2 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.55 (s, 1H), 6.42 (s, 1H),

6.10 (s, 1H), 4.15 (qt, *J* = 10.7, 5.4 Hz, 2H), 3.81 (s, 3H), 2.34 (s, 3H), 1.46 (s, 9H), 1.21 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.4, 154.8, 152.7, 139.4, 139.1, 135.7, 128.0, 125.5, 124.9, 124.0, 83.1, 71.1, 61.4, 52.3, 27.7, 21.4, 13.9. **HRMS(ESI)** m/z: $[M + Na]^+$ calcd for $C_{20}H_{27}NNaO_7^+$ 416.1680; Found: 416.1677.

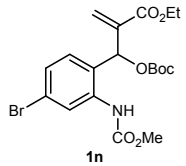
ethyl 2-(((tert-butoxycarbonyl)oxy)(4-chloro-2-((methoxycarbonyl)amino)phenyl)methyl)acrylate (1m)



1m

8.1 g, 49% yield (4 steps). White solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.24 (s, 1H), 7.86 (s, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.07 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.50 (s, 1H), 6.44 (s, 1H), 6.15 – 6.10 (m, 1H), 4.25 – 4.06 (m, 2H), 3.81 (s, 3H), 1.45 (s, 9H), 1.21 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.3, 154.4, 152.5, 138.7, 137.1, 135.0, 129.2, 126.6, 125.3, 124.6, 123.0, 83.5, 70.5, 61.5, 52.5, 27.7, 13.9. **HRMS(ESI)** m/z: $[M + Na]^+$ calcd for $C_{19}H_{24}ClNNaO_7^+$ 436.1133; Found: 436.1130.

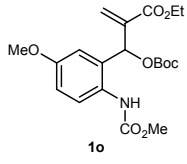
ethyl 2-((4-bromo-2-((methoxycarbonyl)amino)phenyl)((tert-butoxycarbonyl)oxy)methyl)acrylate (1n)



1n

6.4 g, 35% yield (4 steps). White solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.16 (s, 1H), 7.94 (s, 1H), 7.17 – 7.13 (m, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 6.42 (s, 1H), 6.36 (s, 1H), 6.05 (s, 1H), 4.06 (qt, *J* = 10.8, 5.4 Hz, 2H), 3.73 (s, 3H), 1.38 (s, 9H), 1.14 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.3, 154.4, 152.5, 146.8, 138.6, 137.2, 129.5, 127.5, 126.1, 125.3, 123.0, 83.5, 70.5, 61.5, 52.5, 27.7, 13.9. **HRMS(ESI)** m/z: $[M + Na]^+$ calcd for $C_{19}H_{24}BrNNaO_7^+$ 480.0628; Found: 480.0624.

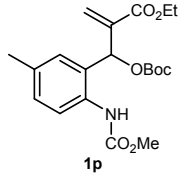
ethyl 2-(((tert-butoxycarbonyl)oxy)(5-methoxy-2-((methoxycarbonyl)amino)phenyl)methyl)acrylate (1o)



1o

7.2 g, 44% yield (4 steps). White solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.53 (s, 1H), 6.80 (dd, *J* = 15.4, 5.9 Hz, 2H), 6.53 – 6.47 (m, 1H), 6.37 (d, *J* = 5.6 Hz, 1H), 6.03 (d, *J* = 5.0 Hz, 1H), 4.08 (q, *J* = 7.4 Hz, 2H), 3.76 – 3.65 (m, 6H), 1.39 (d, *J* = 7.9 Hz, 9H), 1.14 (q, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 156.7, 155.2, 152.5, 139.0, 130.6, 128.8, 125.7, 125.2, 114.7, 113.1, 83.2, 70.9, 61.3, 55.4, 52.2, 27.7, 13.9. **HRMS(ESI)** m/z: $[M + Na]^+$ calcd for $C_{20}H_{27}NNaO_8^+$ 432.1629; Found: 432.1624.

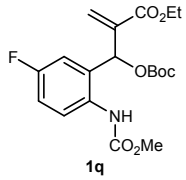
ethyl 2-(((tert-butoxycarbonyl)oxy)(2-((methoxycarbonyl)amino)-5-methylphenyl)methyl)acrylate (1p)



1p

8.0 g, 51% yield (4 steps). White solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.73 (s, 1H), 7.25 (d, *J* = 8.3 Hz, 2H), 6.68 (s, 1H), 6.55 (s, 1H), 6.22 (s, 1H), 4.34 – 4.20 (m, 2H), 3.92 (s, 3H), 2.42 (s, 3H), 1.59 (s, 9H), 1.33 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.4, 155.0, 152.6, 149.8, 139.1, 133.3, 130.1, 128.4, 125.0, 123.8, 83.2, 71.2, 61.4, 52.3, 27.7, 20.9, 13.9. **HRMS(ESI)** m/z: $[M + Na]^+$ calcd for $C_{20}H_{27}NNaO_7^+$ 416.1680; Found: 416.1676.

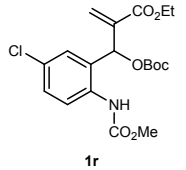
ethyl 2-(((tert-butoxycarbonyl)oxy)(5-fluoro-2-((methoxycarbonyl)amino)phenyl)methyl)acrylate (1q)



1q

6.7 g, 42% yield (4 steps). White solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 7.82 – 7.57 (m, 1H), 7.06 – 6.98 (m, 2H), 6.57 – 6.50 (m, 1H), 6.45 (s, 1H), 6.18 – 6.12 (m, 1H), 4.16 (tdd, *J* = 10.9, 9.0, 5.4 Hz, 2H), 3.79 (s, 3H), 1.53 (s, 3H), 1.46 (s, 9H), 1.21 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 155.0, 152.4, 146.7, 138.7, 131.8, 125.4, 116.2 (d, *J* = 22.3 Hz), 114.4 (d, *J* = 23.5 Hz), 85.2, 83.5, 70.4, 61.5, 52.4, 27.7, 27.4, 13.9. **^{19}F NMR** (377 MHz, Chloroform-d) δ -117.25. **HRMS(ESI)** m/z: $[M + Na]^+$ calcd for $C_{19}H_{24}FNNaO_7^+$ 420.1429; Found: 420.1424.

ethyl 2-(((tert-butoxycarbonyl)oxy)(5-chloro-2-((methoxycarbonyl)amino)phenyl)methyl)acrylate (1r)

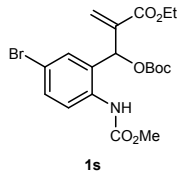


1r

7.3 g, 44% yield (4 steps). White solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.17 (s, 1H), 7.72 (s, 1H), 7.27 (d, *J* = 6.8 Hz, 2H), 6.50 (s, 1H), 6.46 (s, 1H), 6.17 – 6.12 (m, 1H), 4.22 – 4.08 (m,

2H), 3.80 (s, 3H), 1.46 (s, 9H), 1.22 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.3, 154.7, 152.4, 138.6, 134.5, 129.7, 129.4, 127.9, 125.6, 124.9, 83.6, 70.3, 61.6, 52.4, 27.7, 13.9. **HRMS(ESI)** m/z: $[M + Na]^+$ calcd for $C_{19}H_{24}ClNNaO_7^+$ 436.1133; Found: 436.1128.

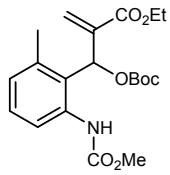
ethyl 2-((5-bromo-2-((methoxycarbonyl)amino)phenyl)((tert-butoxycarbonyl)oxy)methyl)acrylate (1s)



1s

5.7 g, 31% yield (4 steps). White solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.15 (s, 1H), 7.67 (s, 1H), 7.41 (d, J = 8.0 Hz, 2H), 6.50 (s, 1H), 6.46 (s, 1H), 6.14 (s, 1H), 4.16 (qd, J = 10.9, 5.5 Hz, 2H), 3.80 (s, 3H), 1.46 (s, 9H), 1.22 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 154.6, 152.4, 138.6, 135.0, 132.2, 130.8, 130.6, 125.6, 125.1, 117.3, 83.6, 70.3, 61.6, 52.4, 27.7, 13.9. **HRMS(ESI)** m/z: $[M + Na]^+$ calcd for $C_{19}H_{24}BrNNaO_7^+$ 480.0628; Found: 480.0623.

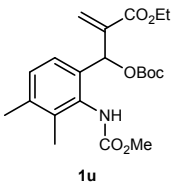
ethyl 2-(((tert-butoxycarbonyl)oxy)(2-((methoxycarbonyl)amino)-6-methylphenyl)methyl)acrylate (1t)



1t

7.5 g, 48% yield (4 steps). White solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.67 (s, 1H), 7.58 (s, 1H), 7.23 (t, J = 7.9 Hz, 1H), 6.94 (d, J = 7.5 Hz, 1H), 6.90 (s, 1H), 6.39 (s, 1H), 5.68 (s, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.75 (s, 3H), 2.45 (s, 3H), 1.46 (s, 9H), 1.25 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.3, 154.6, 152.2, 138.2, 137.3, 137.1, 129.2, 127.2, 126.9, 121.6, 83.1, 72.2, 61.2, 52.3, 27.7, 20.2, 14.0. **HRMS(ESI)** m/z: $[M + Na]^+$ calcd for $C_{20}H_{27}NNaO_7^+$ 416.1680; Found: 416.1675.

ethyl 2-(((tert-butoxycarbonyl)oxy)(2-((methoxycarbonyl)amino)-3,4-dimethylphenyl)methyl)acrylate (1u)

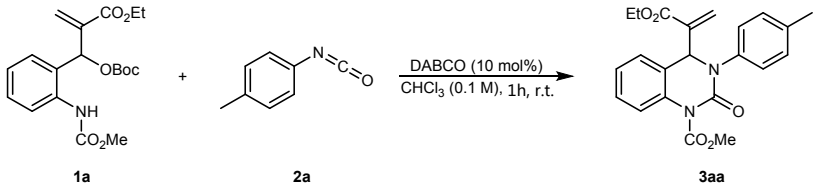


1u

8.0 g, 49% yield (4 steps). White solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.51 (s, 1H), 7.08 (q, J = 7.9 Hz, 2H), 6.64 (s, 1H), 6.39 (s, 1H), 6.03 (s, 1H), 4.13 (q, J = 7.0 Hz, 2H), 3.73 (d, J = 43.5 Hz, 3H), 2.27 (s, 3H), 2.18 (s, 3H), 1.44 (s, 9H), 1.19 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 154.9, 152.7, 139.3, 138.6, 135.3, 133.6, 131.2, 128.6, 125.1, 124.9, 82.8, 71.9, 61.1, 52.4, 27.7, 20.6, 15.0, 14.0. **HRMS(ESI)** m/z: $[M + Na]^+$ calcd for $C_{21}H_{29}NNaO_7^+$ 430.1836; Found: 430.1831.

General Procedure of Optimization and Substrate Scope

General procedure 1 (GP1) for the synthesis of 3,4-dihydroquinazolinone

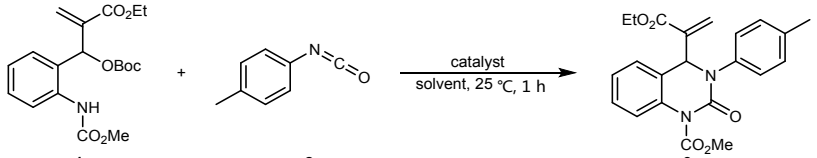


1a **2a** **3aa**

o-amino-acylation aryl MBH carbonate **1a** (0.1 mmol, 1.0 eq.) and isocyanate **2a** (0.2 mmol, 2.0 eq.) and $CHCl_3$ (0.5 mL) were added to a dry flask at room temperature, then DABCO (0.01 mmol, 0.1 eq.) in $CHCl_3$ (0.5 mL) was added to the above solution in one portion. This solution was stirred at until the complete consumption of the starting materials monitored by TLC. After the removal of the solvent, the residue was purified by flash column chromatography (petroleum ether/ethyl acetate 3:1) to afford product **3aa.**

3.3. Optimization of intermolecular cycloaddition reaction conditions

Table S1 | Optimization of intermolecular cycloaddition on 1a and 2a



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

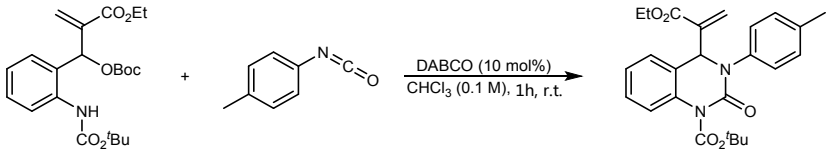
Entry	1a/2a	Solvent	Catalyst	Yield of 3aa (%)[b]
1	1:1	$CHCl_3$	—	no reaction
2	1:1	$CHCl_3$	DABCO	63
3	1:0.8	$CHCl_3$	DABCO	61
4	1:1.2	$CHCl_3$	DABCO	72
5	1:1.5	$CHCl_3$	DABCO	87
6	1:2	$CHCl_3$	DABCO	**96**
7	1:2	$CHCl_3$	Et_3N	mess
8	1:2	$CHCl_3$	DMAP	87
9	1:2	$CHCl_3$	DBU	92
10	1:2	$CHCl_3$	quinine	no reaction
11	1:2	$CHCl_3$	PPh_3	no reaction
12	1:2	MeCN	DABCO	94
13	1:2	toluene	DABCO	93
14	1:2	EtOAc	DABCO	94
15	1:2	THF	DABCO	no reaction

[a] 1 mL, [b] 0.01 mmol, [c] Isolated yield.

4. Gram scale reactions and synthetic transformations

Gram scale reactions

Synthesis of 3,4-dihydroquinazolinone 3ha

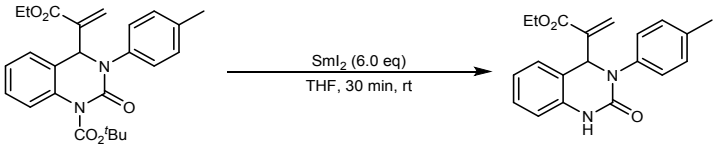


1h **2a** **3ha**

o-amino-acylation aryl MBH carbonate **1h** (1.69 g, 4 mmol, 1.0 eq.) and isocyanate **2a** (1.01 mL, 8 mmol, 2.0 eq.) and $CHCl_3$ (35 mL) were added to a 100 mL dry flask at room temperature, then DABCO (44.9 mg, 0.4 mmol, 0.1 eq.) in $CHCl_3$ (5 mL) was added to the above solution in one portion. The resulting solution of the reaction mixture was stirred at room temperature for 1 h. The solvent was evaporated to give the crude product, which was directly purified by flash chromatography (petroleum ether/ethyl acetate 6:1) to provide the desired product **3ha** as a white solid (1.55 g, 89% yield). The analytical data of the gram scale reaction of **3ha** are consistent with those of the 0.1 mmol scale experiment.

4.2. Synthetic transformations

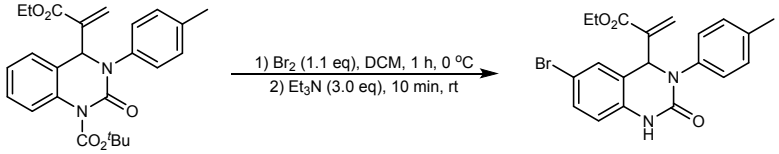
3ha to 4a (Removal of $CO_2{}^tBu$)



3ha **4a**, yield = 74%

To a stirred solution of **3ha** (43.6 mg, 0.1 mmol, 1.0 eq.) in 3 mL THF was added SmI_2 (6 mL, 0.1 M in THF, 6.0 eq.) in one portion at room temperature. The resulting solution of the reaction mixture was stirred for 30 min then evaporated to give the crude product, which was purified by flash chromatography (petroleum ether/ethyl acetate 2:1) to provide the desired product **4a** (24.9 mg, 74% yield).

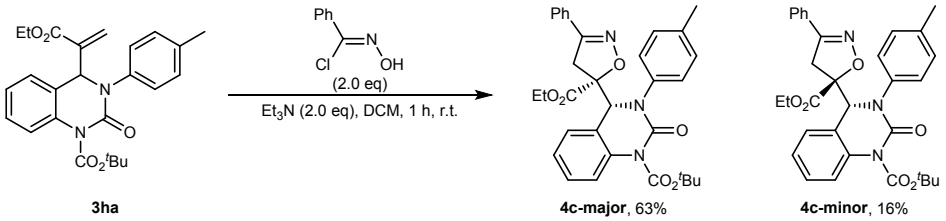
3ha to 4b (Bromination/Removal of $CO_2{}^tBu$)



3ha **4b**, yield = 87%

To a stirred solution of **3ha** (43.6 mg, 0.1 mmol, 1.0 eq.) in 1 mL DCM was added solution of Br_2 (5.6 μL, 0.11 mmol, 1.1 eq.) in 1mL DCM dropwise at 0 ℃. After stirred 1 h, Et_3N (41.7 μL, 0.3 mmol, 3.0 eq.) was added in one portion. Then the reaction solution was allowed to gradually warm to room temperature and was stirred for 10 min. The solvent was evaporated to give the crude product, which was purified by flash chromatography (petroleum ether/ethyl acetate 2:1) to provide the desired product **4b** (36.1 mg, 89% yield).

3ha to 4c (3+2 cycloaddition)



3ha **4c-major**, 63% **4c-minor**, 16%

To a stirred solution of N-hydroxybenzimidoyl chloride (31.1 mg, 0.2 mmol, 2.0 eq.) in 1 mL DCM was added Et_3N (27.8 μL, 0.2 mmol, 2.0 eq.) at room temperature. After stirred for 10 min, **3ha** (43.6 mg, 0.1 mmol, 1.0 eq.) in 1 mL DCM was added to the solution. The resulting mixture was stirred for 1 h then evaporated to give the crude product, which was purified by flash chromatography (petroleum ether/ethyl acetate 3:1) to provide the desired product **4c** (43.9 mg, 79% yield, d.r. = 4:1, separable).

5. Density Functional Theory (DFT) Calculations

Computational Methods

Density functional theory (DFT) investigations were performed to delineate the detailed mechanism of the Lewis base-catalyzed [4+2] annulations of *o*-amino-acylation aryl MBH carbonates with isocyanates. All DFT calculations were carried out with the Gaussian 09 programs.[4] The geometry optimizations of the reactants, transition states, and products were performed with the M06-2X/6-31G(d) level.[5] The frequency calculations were carried out at the same level to conform that there was no imaginary frequency for ground state structures and only one imaginary frequency for transition state structures. The solvent ($CHCl_3$) effects were considered by single point energy calculations on the gas-phase stationary points using M06-2X functional with the def2-TZVP[6] basis set in a SMD continuum solvation model. The energies given in this work are M06-2X calculated Gibbs free energies in $CHCl_3$ solvent noted on figures.[7] In addition, we utilized a correction of (n-m)*1.89 kcal/mol for a process from m- to n-components to account for the Gibbs energy transition from gas to solution.

5.2. Calculated data

Table S2 | The absolute calculation energies, enthalpies and free energies of [4+2] annulation.

Geometry	$E_{(elec)}$[1]	$E_{(solv)}$[2]	$G_{(corr)}$[3]	$H_{(corr)}$[4]	IF[5]
1b	-1280.262547	-1281.1411271	0.344924	0.431572	
PhNCO	-399.491110	-399.730331266	0.072798	0.113236	
CO_2	-188.517761	-188.594609085	-0.008735	0.015525	
^{t}BuO$^-$	-232.826769	-233.115475297	0.093301	0.129250	
^{t}BuOH	-233.442156	-233.660746667	0.108428	0.145078	
DABCO	-345.018414	-345.313541488	0.155886	0.193762	
INT1	-1203.291034	-1204.1723119	0.384822	0.463060	
TS2	-1602.765875	-1603.91012163	0.482940	0.576777	-216.98
INT2	-1602.767490	-1603.92079617	0.484075	0.578424	
TS3	-1602.763167	-1603.90599768	0.484257	0.577439	-224.95
INT3	-1602.797738	-1603.93890157	0.488846	0.580273	
TS4	-1602.799239	-1603.93472055	0.486787	0.578380	-168.80
3	-1257.811614	-1258.62778561	0.302854	0.381959	

[1]The electronic energy calculated by M06-2x/6-31G(d) level in gas phase. [2]The solvation energy corrections calculated at the M06-2x/def2-TZVP level with the SMD solvation model for acetonitrile minus electronic energy in gas phase. [3]The thermal correction to Gibbs free energy calculated by M06-2x/6-31G(d) level in gas phase. [4]The thermal correction to enthalpy calculated by M06-2x/6-31G(d) level in gas phase. [5]The M06-2x/6-31G(d) level calculated imaginary frequencies for the transition states.

[4] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Jr. Montgomery, J. A.; J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

[5] (a) Y. Zhao and D. G. Truhlar, *Acc. Chem. Res.*, 2008, **41**, 157-167; (b) Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241; (c) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652; (d) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.

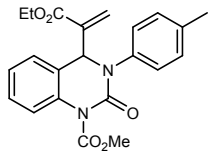
[6] F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-305.

[7] A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B.* 2009, **113**, 6378-6396.

6. Analytical Data

DABCO catalyzed [4+2] cycloadducts 3

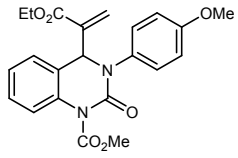
methyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2-oxo-3-(p-tolyl)-3,4-dihydroquinazoline-1(2H)-carboxylate (3aa)



3aa

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3aa** as white solid (37.8 mg, 96% yield, mp: 104-106 ℃). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.49 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.37 (td, *J* = 7.8, 1.6 Hz, 1H), 7.23 – 7.15 (m, 5H), 6.40 (d, *J* = 1.1 Hz, 1H), 6.07 (d, *J* = 1.6 Hz, 1H), 5.68 (s, 1H), 4.25 – 4.07 (m, 2H), 3.91 (s, 3H), 2.34 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 153.1, 151.9, 138.7, 138.0, 137.2, 135.3, 129.8, 128.4, 128.2, 126.8, 125.6, 125.3, 124.2, 123.1, 62.8, 61.4, 54.2, 21.1, 14.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{23}N_2O_5^+$ 395.1602; Found: 395.1603.

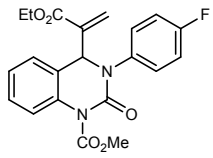
methyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-3-(4-methoxyphenyl)-2-oxo-3,4-dihydroquinazoline-1(2H)-carboxylate (3ab)



3ab

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3ab** as white solid (40.6 mg, 99% yield, mp: 136-138 ℃). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.49 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.37 (td, *J* = 7.6, 1.6 Hz, 1H), 7.26 – 7.15 (m, 3H), 6.95 – 6.81 (m, 2H), 6.40 (d, *J* = 1.1 Hz, 1H), 6.07 (d, *J* = 1.5 Hz, 1H), 5.65 (d, *J* = 1.2 Hz, 1H), 4.26 – 4.06 (m, 2H), 3.91 (s, 3H), 3.79 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 158.5, 153.1, 152.0, 138.0, 135.3, 134.1, 128.4, 128.2, 126.9, 126.8, 125.6, 124.2, 123.1, 114.4, 63.0, 61.4, 55.5, 54.1, 14.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{23}N_2O_6^+$ 411.1551; Found: 411.1554.

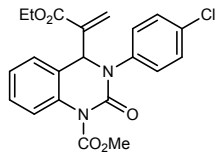
methyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-3-(4-fluorophenyl)-2-oxo-3,4-dihydroquinazoline-1(2H)-carboxylate (3ac)



3ac

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3ac** as colorless viscous oil (39.4 mg, 99% yield). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.2 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.44 – 7.37 (m, 1H), 7.31 (dd, *J* = 9.0, 4.7 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 8.7 Hz, 2H), 6.43 (s, 1H), 6.06 (s, 1H), 5.69 (s, 1H), 4.29 – 4.11 (m, 2H), 3.95 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.1, 161.2 (d, *J* = 247.5 Hz), 153.0, 151.9, 137.9, 137.2, 135.2, 128.6, 127.9, 127.3 (d, *J* = 8.6 Hz), 126.8, 125.7, 124.3, 123.0, 116.1 (d, *J* = 23.2 Hz), 62.8, 61.5, 54.2, 14.1. **^{19}F NMR** (377 MHz, Chloroform-*d*) δ -114.11 (dt, *J* = 13.9, 7.8 Hz). **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{21}H_{20}FN_2O_5^+$ 399.1351; Found: 399.1352.

methyl 3-(4-chlorophenyl)-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2-oxo-3,4-dihydroquinazoline-1(2H)-carboxylate (3ad)

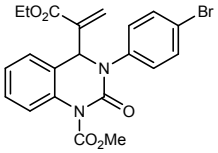


3ad

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3ad** as colorless viscous oil (41 mg, 99% yield). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.48 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.41 – 7.32 (m, 3H), 7.28 – 7.19 (m, 3H), 6.40 (d, *J* = 1.1 Hz, 1H), 6.01 (d, *J* = 1.5 Hz, 1H), 5.68 (d, *J* = 1.3 Hz, 1H), 4.27 – 4.09 (m, 2H), 3.92 (s, 3H),

1.27 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.1, 152.9, 151.8, 139.7, 137.8, 135.1, 132.6, 129.3, 128.6, 127.7, 126.8, 126.6, 125.7, 124.3, 123.0, 62.5, 61.5, 54.3, 14.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{21}H_{20}ClN_2O_5^+$ 415.1055; Found: 415.1058.

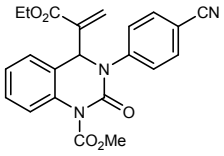
methyl 3-(4-bromophenyl)-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2-oxo-3,4-dihydroquinazoline-1(2H)-carboxylate (3ae)



3ae

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3ae** as colorless viscous oil (41.2 mg, 90% yield). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 (dd, J = 8.3, 1.0 Hz, 1H), 7.52 – 7.45 (m, 3H), 7.38 (td, J = 7.8, 1.7 Hz, 1H), 7.24 – 7.16 (m, 3H), 6.40 (d, J = 1.0 Hz, 1H), 6.01 (d, J = 1.6 Hz, 1H), 5.68 (s, 1H), 4.27 – 4.09 (m, 2H), 3.92 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.1, 152.9, 151.7, 140.2, 137.8, 135.0, 132.2, 128.6, 127.7, 126.9, 125.7, 124.3, 123.0, 120.5, 62.5, 61.5, 54.3, 14.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{21}H_{20}BrN_2O_5^+$ 459.0550; Found: 459.0547.

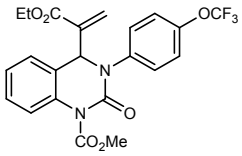
methyl 3-(4-cyanophenyl)-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2-oxo-3,4-dihydroquinazoline-1(2H)-carboxylate (3af)



3af

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3af** as colorless viscous oil (38.9 mg, 96% yield). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (d, J = 8.3 Hz, 1H), 7.67 (d, J = 7.3 Hz, 2H), 7.48 (dd, J = 15.7, 7.5 Hz, 3H), 7.40 (t, J = 7.8 Hz, 1H), 7.23 (t, J = 7.6 Hz, 1H), 6.42 (s, 1H), 5.97 (s, 1H), 5.76 (s, 1H), 4.21 (dhept, J = 14.4, 7.5 Hz, 2H), 3.93 (s, 3H), 1.29 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.9, 152.7, 151.6, 145.0, 137.5, 134.7, 133.8, 133.0, 128.9, 127.1, 127.0, 125.9, 124.9, 124.4, 122.8, 118.3, 114.4, 109.9, 61.9, 61.7, 54.4, 14.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{20}N_3O_5^+$ 406.1398; Found: 406.1401.

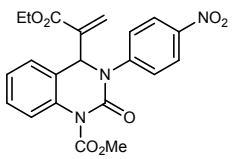
methyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2-oxo-3-(4-(trifluoromethoxy)phenyl)-3,4-dihydroquinazoline-1(2H)-carboxylate (3ag)



3ag

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3ag** as colorless viscous oil (45.9 mg, 99% yield). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 (dd, J = 8.3, 1.2 Hz, 1H), 7.51 (dd, J = 7.6, 1.7 Hz, 1H), 7.43 – 7.34 (m, 3H), 7.27 – 7.20 (m, 3H), 6.43 (d, J = 1.1 Hz, 1H), 6.04 (d, J = 1.5 Hz, 1H), 5.72 (t, J = 1.3 Hz, 1H), 4.30 – 4.11 (m, 2H), 3.94 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.1, 152.9, 151.8, 139.7, 137.8, 135.0, 128.6, 127.7, 126.8, 126.6, 125.7, 124.3, 122.9, 121.7, 119.1, 62.5, 61.5, 54.3, 14.0. **^{19}F NMR** (377 MHz, Chloroform-*d*) δ -57.97. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{20}F_3N_2O_6^+$ 465.1268; Found: 465.1273.

methyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-3-(4-nitrophenyl)-2-oxo-3,4-dihydroquinazoline-1(2H)-carboxylate (3ah)

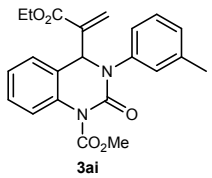


3ah

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3ah** as colorless viscous oil (37 mg, 87% yield). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.24 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 8.2 Hz, 1H), 7.51 (d, J = 8.5 Hz, 3H), 7.41 (t, J = 7.7 Hz, 1H), 7.24 (t, J = 7.4 Hz, 1H), 6.43 (s, 1H), 5.98 (s, 1H), 5.81 (s, 1H), 4.21 (tt, J = 17.8, 8.9 Hz, 2H), 3.94 (s, 3H),

1.29 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.9, 152.7, 151.6, 146.7, 145.3, 137.5, 134.7, 128.9, 127.0, 125.9, 124.7, 124.5, 124.4, 122.7, 61.9, 61.7, 54.4, 14.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{21}H_{20}N_3O_7^+$ 426.1296; Found: 426.1301.

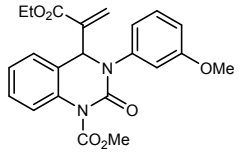
methyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2-oxo-3-(m-tolyl)-3,4-dihydroquinazoline-1(2H)-carboxylate (3ai)



3ai

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3ai** as colorless viscous oil (39 mg, 99% yield). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.1 Hz, 1H), 7.50 (d, *J* = 7.0 Hz, 1H), 7.41 – 7.34 (m, 1H), 7.24 (dt, *J* = 19.1, 7.6 Hz, 2H), 7.15 – 7.07 (m, 3H), 6.42 (s, 1H), 6.14 – 6.02 (m, 1H), 5.70 (s, 1H), 4.26 – 4.09 (m, 2H), 3.92 (s, 3H), 2.34 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 153.0, 152.0, 141.1, 139.2, 137.9, 135.2, 129.1, 128.5, 128.1, 126.9, 126.1, 125.6, 124.2, 123.1, 122.4, 62.8, 61.4, 54.2, 21.4, 14.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{23}N_2O_5^+$ 395.1602; Found: 395.1607.

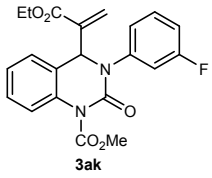
methyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-3-(3-methoxyphenyl)-2-oxo-3,4-dihydroquinazoline-1(2H)-carboxylate (3aj)



3aj

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3aj** as colorless viscous oil (40.6 mg, 99% yield). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.8 Hz, 1H), 7.49 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.37 (td, *J* = 8.2, 1.4 Hz, 1H), 7.27 (ddd, *J* = 8.4, 5.5, 2.4 Hz, 1H), 7.20 (td, *J* = 7.6, 1.0 Hz, 1H), 6.92 – 6.85 (m, 2H), 6.84 – 6.79 (m, 1H), 6.44 – 6.37 (m, 1H), 6.07 (d, *J* = 1.4 Hz, 1H), 5.71 (s, 1H), 4.27 – 4.09 (m, 2H), 3.92 (s, 3H), 3.78 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.1, 160.0, 153.0, 151.8, 142.3, 137.9, 135.2, 129.9, 128.5, 128.1, 126.9, 125.6, 124.2, 123.0, 117.3, 112.7, 111.4, 62.7, 61.4, 55.4, 54.2, 14.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{23}N_2O_6^+$ 411.1551; Found: 411.1554.

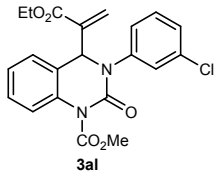
methyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-3-(3-fluorophenyl)-2-oxo-3,4-dihydroquinazoline-1(2H)-carboxylate (3ak)



3ak

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3ak** as colorless viscous oil (36.6 mg, 92% yield). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.2 Hz, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.35 (dt, *J* = 22.8, 7.9 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.13 – 7.04 (m, 2H), 6.98 (t, *J* = 8.2 Hz, 1H), 6.41 (s, 1H), 6.02 (s, 1H), 5.72 (s, 1H), 4.28 – 4.10 (m, 2H), 3.92 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.1, 162.7 (d, *J* = 247.0 Hz), 152.9, 151.7, 142.5 (d, *J* = 10.0 Hz), 137.8, 135.0, 130.2 (d, *J* = 9.2 Hz), 128.6, 127.7, 126.9, 125.7, 124.3, 122.9, 120.6 (d, *J* = 3.1 Hz), 114.0 (d, *J* = 21.0 Hz), 112.8 (d, *J* = 24.1 Hz), 62.5, 61.5, 54.3, 14.0. **^{19}F NMR** (377 MHz, Chloroform-*d*) δ -111.19 (q, *J* = 8.1 Hz). **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{21}H_{20}FN_2O_5^+$ 399.1351; Found: 399.1350.

methyl 3-(3-chlorophenyl)-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2-oxo-3,4-dihydroquinazoline-1(2H)-carboxylate (3al)

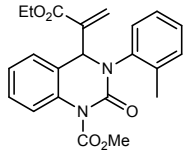


3al

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3al** as colorless viscous oil (38.1 mg, 92% yield). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.36 (s, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.28 (s,

1H), 7.24 (t, *J* = 7.7 Hz, 2H), 6.44 (s, 1H), 6.04 (s, 1H), 5.72 (s, 1H), 4.21 (dtt, *J* = 22.7, 7.2, 3.7 Hz, 2H), 3.95 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.1, 152.9, 151.7, 142.2, 137.7, 135.0, 134.6, 130.1, 128.6, 127.7, 127.3, 126.9, 125.7, 125.6, 124.4, 123.4, 123.0, 62.5, 61.5, 54.3, 14.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{21}H_{20}ClN_2O_5^+$ 415.1055; Found: 415.1059.

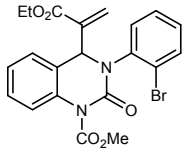
methyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2-oxo-3-(o-tolyl)-3,4-dihydroquinazoline-1(2H)-carboxylate (3am)



3am

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3am** as white solid (35.9 mg, 91% yield, d.r. = 6:1, mp: 155-157 ℃). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 (t, *J* = 8.5 Hz, 1H), 7.49 (d, *J* = 7.4 Hz, 1H), 7.43 – 7.33 (m, 1H), 7.31 – 7.17 (m, 6H), 6.48 (s, 1H), 6.35 (s, 0H), 6.28 – 6.19 (m, 1H), 5.76 (s, 0H), 5.73 (s, 0H), 5.44 (s, 1H), 4.27 – 4.08 (m, 2H), 3.93 (s, 3H), 2.32 (s, 0H), 1.97 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.13 (q, *J* = 9.3, 8.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 153.0, 151.6, 140.1, 138.2, 135.3, 134.9, 131.4, 128.5, 128.5, 128.4, 127.5, 126.9, 126.6, 125.6, 124.2, 123.1, 62.5, 61.4, 54.1, 17.9, 14.0. (Only one set of diastereoisomer peaks is labeled). **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{23}N_2O_5^+$ 395.1602; Found: 395.1597.

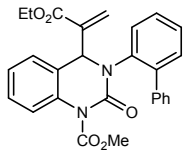
methyl 3-(2-bromophenyl)-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2-oxo-3,4-dihydroquinazoline-1(2H)-carboxylate (3an)



3an

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3an** as white solid (42.6 mg, 93% yield, d.r. = 10:1, mp: 220-222 ℃). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.3 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.39 (dt, *J* = 13.3, 7.6 Hz, 3H), 7.24 (q, *J* = 8.4, 7.7 Hz, 2H), 6.45 (s, 1H), 6.41 (s, 0H), 6.13 (s, 1H), 5.78 (s, 0H), 5.73 (s, 0H), 5.55 (s, 1H), 4.17 (qt, *J* = 14.4, 7.2 Hz, 2H), 3.95 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 0H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 153.0, 151.4, 139.8, 138.2, 135.1, 133.8, 130.6, 129.9, 128.3, 128.3, 126.8, 125.6, 124.6, 122.9, 122.3, 62.2, 61.4, 54.2, 14.0 (Only one set of diastereoisomer peaks is labeled). **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{21}H_{20}BrN_2O_5^+$ 459.0550; Found: 459.0550.

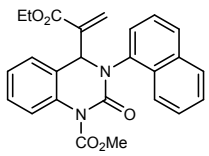
methyl 3-([1,1'-biphenyl]-2-yl)-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2-oxo-3,4-dihydroquinazoline-1(2H)-carboxylate (3ao)



3ao

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3ao** as white solid (43.8 mg, 96% yield, d.r. = 10:1, mp: 114-116 ℃). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 8.2 Hz, 1H), 7.46 (s, 1H), 7.43 (q, *J* = 5.5, 4.9 Hz, 3H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 2H), 6.98 (ddt, *J* = 22.0, 14.9, 7.4 Hz, 4H), 6.76 (d, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 7.9 Hz, 0H), 6.37 (s, 1H), 6.21 (s, 0H), 6.06 (s, 1H), 5.70 (s, 0H), 5.16 (s, 1H), 4.19 – 4.02 (m, 2H), 3.92 (s, 3H), 1.28 (s, 0H), 1.21 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 152.9, 152.0, 139.6, 138.7, 138.0, 137.6, 134.5, 131.1, 129.3, 128.6, 128.6, 128.3, 128.2, 128.1, 127.7, 127.6, 126.4, 125.2, 124.1, 123.0, 62.6, 61.2, 54.0, 14.0 (Only one set of diastereoisomer peaks is labeled). **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{27}H_{25}N_2O_5^+$ 457.1758; Found: 457.1762.

methyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-3-(naphthalen-1-yl)-2-oxo-3,4-dihydroquinazoline-1(2H)-carboxylate (3ap)

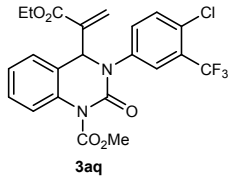


3ap

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded

dihydroquinazolinone **3ap** as white solid (38.3 mg, 89% yield, d.r. = 8:1, mp: 161-163 ℃). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.87 (q, *J* = 8.6 Hz, 4H), 7.49 (tt, *J* = 15.3, 7.4 Hz, 6H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 10.0 Hz, 3H), 6.49 (s, 1H), 6.35 (s, 0H), 6.29 (s, 1H), 5.83 (s, 0H), 5.65 (s, 0H), 5.58 (s, 1H), 4.23 – 4.03 (m, 2H), 3.96 (d, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H), 0.80 (t, *J* = 7.1 Hz, 0H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 153.2, 152.2, 138.2, 137.1, 135.5, 134.9, 129.1, 129.1, 128.8, 128.6, 128.3, 127.3, 126.9, 126.5, 126.4, 125.8, 125.4, 124.4, 123.2, 122.0, 62.7, 61.4, 54.2, 14.0 (Only one set of diastereoisomer peaks is labeled). **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{25}H_{23}N_2O_5^+$ 431.1602; Found: 431.1605.

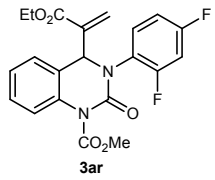
methyl 3-(4-chloro-3-(trifluoromethyl)phenyl)-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2-oxo-3,4-dihydroquinazoline-1(2H)-carboxylate (3aq)



3aq

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3aq** as colorless viscous oil (44.8 mg, 93% yield). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 2.3 Hz, 1H), 7.50 (t, *J* = 8.9 Hz, 2H), 7.46 – 7.37 (m, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 6.42 (s, 1H), 5.97 (s, 1H), 5.70 (s, 1H), 4.29 – 4.10 (m, 2H), 3.93 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.0, 152.8, 151.7, 139.8, 134.9, 132.1, 130.4, 129.3 (d, *J* = 14.3 Hz), 129.3 – 128.9 (m), 128.8, 127.2, 126.8, 125.9, 124.5 (d, *J* = 4.4 Hz), 122.9, 62.2, 61.6, 54.4, 14.0. **^{19}F NMR** (377 MHz, Chloroform-*d*) δ -62.88. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{19}ClF_3N_2O_5^+$ 483.0929; Found: 483.0932.

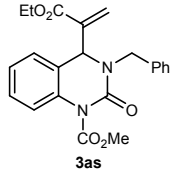
methyl 3-(2,6-difluorophenyl)-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2-oxo-3,4-dihydroquinazoline-1(2H)-carboxylate (3ar)



3ar

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3ar** as colorless viscous oil (30.4 mg, 73% yield). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.1 Hz, 1H), 7.39 (ddd, *J* = 34.4, 15.4, 7.7 Hz, 3H), 7.25 (t, *J* = 7.4 Hz, 1H), 6.93 (t, *J* = 8.3 Hz, 2H), 6.41 (s, 1H), 5.99 (s, 1H), 5.58 (s, 1H), 4.28 – 4.08 (m, 2H), 3.96 (s, 3H), 1.27 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 163.5 – 156.5 (m), 152.9, 151.3, 137.9, 135.2, 130.0 (d, *J* = 10.1 Hz), 128.6, 127.7, 126.5, 125.7, 125.0, 122.9, 111.8 (d, *J* = 18.9 Hz), 105.9 – 104.6 (m), 62.6, 61.4, 54.3, 14.0. **^{19}F NMR** (377 MHz, Chloroform-*d*) δ -108.78 (p, *J* = 7.7 Hz), -113.26. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{21}H_{19}F_2N_2O_5^+$ 417.1257; Found: 417.1260.

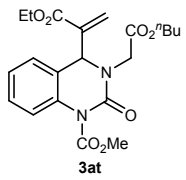
methyl 3-benzyl-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2-oxo-3,4-dihydroquinazoline-1(2H)-carboxylate (3as)



3as

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3as** as white solid (25.2 mg, 64% yield, mp: 64-66 ℃). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.29 (m, 1H), 7.28 – 7.23 (m, 3H), 7.22 – 7.19 (m, 1H), 7.18 – 7.14 (m, 2H), 7.14 – 7.08 (m, 1H), 6.24 (s, 1H), 5.67 (d, *J* = 1.2 Hz, 1H), 5.24 (d, *J* = 15.1 Hz, 2H), 4.25 – 4.12 (m, 3H), 3.92 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 153.1, 152.8, 137.5, 135.8, 135.4, 128.7, 128.2, 128.0, 127.8, 127.8, 126.4, 125.5, 124.6, 122.8, 61.3, 57.8, 54.1, 50.7, 14.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{23}N_2O_5^+$ 395.1601; Found: 395.1604.

methyl 3-(2-butoxy-2-oxoethyl)-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2-oxo-3,4-dihydroquinazoline-1(2H)-carboxylate (3at)

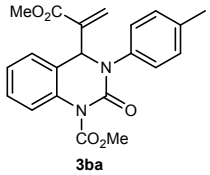


3at

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded

dihydroquinazolinone **3at** as colorless viscous oil (37.2 mg, 89% yield). R_f = 0.5 (petroleum ether/ethyl acetate = 6:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.2 Hz, 1H), 7.39 – 7.33 (m, 1H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 6.30 (s, 1H), 5.56 (s, 1H), 5.35 (s, 1H), 4.23 (q, *J* = 6.9 Hz, 2H), 4.14 – 3.99 (m, 3H), 3.89 (s, 3H), 1.48 (dt, *J* = 13.3, 6.6 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.23 (dq, *J* = 15.0, 7.6 Hz, 3H), 0.85 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.6, 165.8, 152.9, 152.3, 137.7, 135.4, 128.3, 127.9, 126.2, 126.0, 125.7, 123.1, 65.3, 61.5, 60.0, 54.1, 49.7, 30.4, 18.9, 14.1, 13.6. **HRMS(ESI)** m/z: $[M + Na]^+$ calcd for $C_{21}H_{26}N_2NaO_7^+$ 441.1632; Found: 441.1628

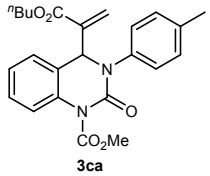
methyl 4-(3-methoxy-3-oxoprop-1-en-2-yl)-2-oxo-3-(p-tolyl)-3,4-dihydroquinazoline-1(2H)-carboxylate (3ba)



3ba

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3ba** as white solid (34.6 mg, 91% yield, mp: 102-104 ℃). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.2 Hz, 1H), 7.50 (d, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 9.5 Hz, 5H), 6.42 (s, 1H), 6.11 (s, 1H), 5.70 (s, 1H), 3.93 (s, 3H), 3.74 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.6, 153.0, 151.9, 138.7, 137.7, 137.1, 135.3, 129.8, 128.4, 128.2, 126.8, 125.6, 125.2, 124.4, 123.1, 62.8, 54.1, 52.2, 21.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{21}H_{21}N_2O_5^+$ 381.1445; Found: 381.1449.

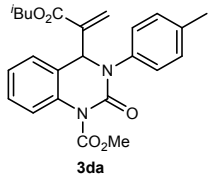
methyl 4-(3-butoxy-3-oxoprop-1-en-2-yl)-2-oxo-3-(p-tolyl)-3,4-dihydroquinazoline-1(2H)-carboxylate (3ca)



3ca

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3ca** as colorless viscous oil (41.8 mg, 99% yield). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.21 (s, 5H), 6.41 (s, 1H), 6.09 (s, 1H), 5.71 (s, 1H), 4.23 – 4.05 (m, 2H), 3.94 (s, 3H), 2.36 (s, 3H), 1.68 – 1.56 (m, 2H), 1.43 – 1.31 (m, 2H), 0.94 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.3, 153.1, 151.9, 138.7, 138.0, 137.1, 135.3, 129.8, 128.4, 128.2, 126.8, 125.6, 125.2, 124.0, 123.1, 65.2, 62.8, 54.1, 30.5, 21.1, 19.1, 13.7. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{24}H_{27}N_2O_5^+$ 423.1915; Found: 423.1922.

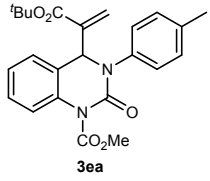
methyl 4-(3-isobutoxy-3-oxoprop-1-en-2-yl)-2-oxo-3-(p-tolyl)-3,4-dihydroquinazoline-1(2H)-carboxylate (3da)



3da

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3da** as colorless viscous oil (32.1 mg, 76% yield). R_f = 0.5 (petroleum ether/ethyl acetate = 6:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.2 Hz, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.23 – 7.13 (m, 5H), 6.39 (s, 1H), 6.08 (s, 1H), 5.69 (s, 1H), 3.97 – 3.82 (m, 5H), 2.34 (s, 3H), 1.93 (dp, *J* = 13.3, 6.7 Hz, 1H), 0.95 – 0.88 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 153.1, 151.9, 138.7, 138.1, 137.1, 135.3, 129.8, 128.4, 128.2, 126.9, 125.6, 125.2, 123.9, 123.0, 71.4, 62.8, 54.1, 27.7, 21.1, 19.1, 19.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{24}H_{27}N_2O_5^+$ 423.1915; Found: 423.1917.

methyl 4-(3-(tert-butoxy)-3-oxoprop-1-en-2-yl)-2-oxo-3-(p-tolyl)-3,4-dihydroquinazoline-1(2H)-carboxylate (3ea)

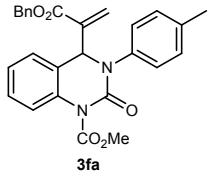


3ea

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3ea** as white solid (38.8 mg, 92% yield, mp: 83-85 ℃). R_f = 0.5 (petroleum ether/ethyl acetate = 6:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.2 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.23 (d, *J* = 8.7 Hz, 5H), 6.29 (s,

1H), 5.99 (s, 1H), 5.70 (s, 1H), 3.95 (s, 3H), 2.37 (s, 3H), 1.47 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.5, 153.2, 151.9, 139.3, 138.8, 137.0, 135.3, 129.8, 128.4, 128.3, 126.6, 125.4, 125.4, 123.0, 82.1, 62.7, 54.1, 28.0, 21.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{24}H_{27}N_2O_5^+$ 423.1915; Found: 423.1916.

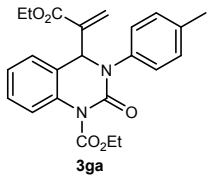
methyl 4-(3-(benzyloxy)-3-oxoprop-1-en-2-yl)-2-oxo-3-(p-tolyl)-3,4-dihydroquinazoline-1(2H)-carboxylate (3fa)



3fa

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3fa** as colorless viscous oil (21.9 mg, 48% yield). R_f = 0.5 (petroleum ether/ethyl acetate = 6:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.1 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 6.9 Hz, 4H), 7.32 – 7.28 (m, 2H), 7.25 (s, 1H), 7.16 (d, *J* = 5.9 Hz, 5H), 6.44 (s, 1H), 6.09 (s, 1H), 5.68 (s, 1H), 5.22 (d, *J* = 12.2 Hz, 1H), 5.06 (d, *J* = 12.2 Hz, 1H), 3.90 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.0, 153.1, 151.9, 138.7, 137.8, 137.2, 135.3, 135.2, 129.8, 129.5, 128.7, 128.5, 128.4, 128.1, 126.9, 125.6, 125.3, 124.7, 123.0, 67.2, 62.9, 54.1, 21.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{27}H_{25}N_2O_5^+$ 457.1758; Found: 457.1762.

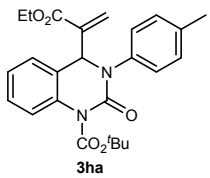
ethyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2-oxo-3-(p-tolyl)-3,4-dihydroquinazoline-1(2H)-carboxylate (3ga)



3ga

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3ga** as colorless viscous oil (40.4 mg, 99% yield). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.2 Hz, 1H), 7.50 (d, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 9.0 Hz, 5H), 6.43 (s, 1H), 6.12 (s, 1H), 5.70 (s, 1H), 4.48 – 4.30 (m, 2H), 4.28 – 4.12 (m, 2H), 2.36 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 152.5, 152.0, 138.8, 138.1, 137.0, 135.3, 129.7, 128.4, 128.2, 126.8, 125.4, 125.0, 124.1, 123.0, 63.4, 62.7, 61.4, 21.0, 14.3, 14.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{23}H_{25}N_2O_5^+$ 409.1758; Found: 409.1760.

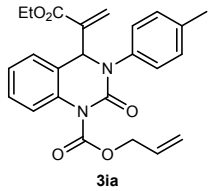
tert-butyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2-oxo-3-(p-tolyl)-3,4-dihydroquinazoline-1(2H)-carboxylate (3ha)



3ha

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3ha** as white solid (40.1 mg, 92% yield, mp: 73-75 ℃). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 7.5 Hz, 1H), 7.37 – 7.30 (m, 1H), 7.16 (d, *J* = 8.1 Hz, 5H), 6.42 (s, 1H), 6.12 (s, 1H), 5.67 (s, 1H), 4.27 – 4.10 (m, 2H), 2.33 (s, 3H), 1.55 (s, 9H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.3, 152.3, 151.1, 138.9, 138.4, 136.7, 135.4, 129.7, 128.3, 127.6, 126.8, 125.0, 124.9, 124.1, 122.3, 83.6, 62.5, 61.3, 28.0, 21.0, 14.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{25}H_{29}N_2O_5^+$ 437.2071; Found: 437.2071.

allyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2-oxo-3-(p-tolyl)-3,4-dihydroquinazoline-1(2H)-carboxylate (3ia)

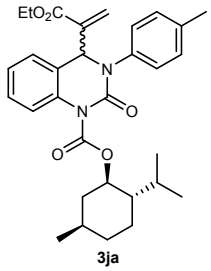


3ia

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3ia** as colorless viscous oil (37.8 mg, 90% yield). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.2 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.26 – 7.11 (m, 5H), 6.42 (s, 1H), 6.11 (s, 1H), 6.00 (ddt, *J* = 16.3, 10.7, 5.5 Hz, 1H), 5.71 (s, 1H), 5.45 (d, *J* = 17.1 Hz, 1H), 5.29 (d, *J* = 10.5 Hz, 1H), 4.83 (d, *J* = 5.0 Hz, 2H), 4.32 – 4.08 (m, 2H), 2.36 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 152.3, 151.8, 138.8, 138.2, 137.0, 135.3, 131.5, 129.7, 128.4, 128.2, 126.8, 125.5, 125.1, 124.1, 123.0, 118.9, 67.7, 62.8, 61.3, 21.0, 14.0. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{24}H_{25}N_2O_5^+$ 421.1758; Found:

421.1753.

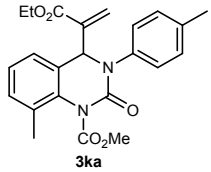
(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2-oxo-3-(p-tolyl)-3,4-dihydroquinazoline-1(2H)-carboxylate (3ja)



3ja

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3ja** as colorless viscous oil (44.1 mg, 85% yield, d.r. = 1:1). R_f = 0.5 (petroleum ether/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (dd, *J* = 54.2, 8.2 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.35 (q, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 5H), 6.36 (d, *J* = 10.3 Hz, 1H), 6.09 (d, *J* = 12.2 Hz, 1H), 5.66 (d, *J* = 10.1 Hz, 1H), 4.80 (td, *J* = 10.9, 4.3 Hz, 1H), 4.28 – 4.09 (m, 2H), 2.33 (s, 3H), 2.25 – 1.87 (m, 2H), 1.69 (d, *J* = 10.7 Hz, 2H), 1.56 – 1.43 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 4H), 1.06 (q, *J* = 11.8 Hz, 2H), 0.92 (d, *J* = 6.3 Hz, 4H), 0.84 (d, *J* = 7.0 Hz, 2H), 0.78 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 152.4, 152.1, 152.0, 151.8, 139.0, 138.4, 138.3, 136.9, 136.8, 135.4, 129.8, 129.7, 128.5, 128.4, 128.2, 127.8, 126.8, 126.7, 125.3, 125.2, 125.0, 124.8, 123.9, 123.5, 122.5, 78.1, 77.9, 77.3, 62.9, 62.6, 61.3, 61.3, 47.0, 46.7, 40.8, 40.1, 34.2, 34.1, 31.5, 31.5, 26.1, 25.7, 23.1, 23.1, 22.1, 22.0, 21.0, 20.9, 20.9, 16.1, 16.0, 14.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{31}H_{39}N_2O_5^+$ 519.2854; Found: 519.2850.

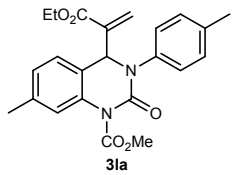
methyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-8-methyl-2-oxo-3-(p-tolyl)-3,4-dihydroquinazoline-1(2H)-carboxylate (3ka)



3ka

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3ka** as colorless viscous oil (40.4 mg, 99% yield). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 9.3 Hz, 1H), 7.22 (d, *J* = 6.0 Hz, 5H), 6.40 (s, 1H), 6.01 (s, 1H), 5.68 (s, 1H), 4.24 (dq, *J* = 10.9, 7.1 Hz, 1H), 4.18 – 4.08 (m, 1H), 3.88 (s, 3H), 2.42 – 2.33 (m, 6H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 152.2, 151.8, 138.7, 138.4, 137.1, 134.5, 134.4, 131.5, 131.1, 129.7, 126.8, 125.0, 124.8, 123.6, 63.7, 61.4, 53.9, 21.1, 18.3, 14.0. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{23}H_{25}N_2O_5^+$ 409.1758; Found: 409.1764.

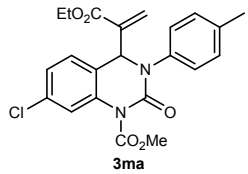
methyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-7-methyl-2-oxo-3-(p-tolyl)-3,4-dihydroquinazoline-1(2H)-carboxylate (3la)



3la

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3la** as white solid (40.4 mg, 99% yield, mp: 105-107 ℃). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59 (s, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.17 (s, 4H), 7.01 (d, *J* = 7.9 Hz, 1H), 6.37 (s, 1H), 6.04 (s, 1H), 5.64 (s, 1H), 4.25 – 4.07 (m, 2H), 3.91 (s, 3H), 2.39 (s, 3H), 2.33 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 153.2, 152.0, 138.8, 138.6, 138.2, 137.0, 135.2, 129.7, 126.6, 126.3, 125.4, 125.2, 123.9, 123.4, 62.6, 61.3, 54.1, 21.5, 21.0, 14.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{23}H_{25}N_2O_5^+$ 409.1758; Found: 409.1762.

methyl 7-chloro-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2-oxo-3-(p-tolyl)-3,4-dihydroquinazoline-1(2H)-carboxylate (3ma)

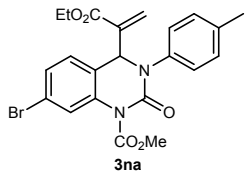


3ma

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3ma** as white solid (36 mg, 84% yield, mp: 137-139 ℃). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 2.1

Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.17 (d, *J* = 4.9 Hz, 5H), 6.42 (s, 1H), 6.08 (s, 1H), 5.65 (s, 1H), 4.26 – 4.09 (m, 2H), 3.93 (s, 3H), 2.34 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.0, 152.9, 151.4, 138.5, 137.6, 137.3, 136.2, 134.3, 129.8, 127.9, 126.4, 125.7, 125.2, 124.4, 123.0, 62.3, 61.5, 54.4, 21.1, 14.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{22}ClN_2O_5^+$ 429.1212; Found: 429.1216.

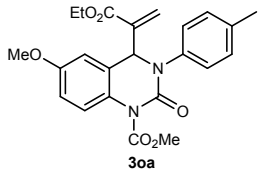
methyl 7-bromo-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2-oxo-3-(p-tolyl)-3,4-dihydroquinazoline-1(2H)-carboxylate (3na)



3na

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3na** as white solid (34.9 mg, 74% yield, mp: 111-113 ℃). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 2.0 Hz, 1H), 7.42 – 7.32 (m, 2H), 7.19 (s, 4H), 6.44 (d, *J* = 0.9 Hz, 1H), 6.11 (d, *J* = 1.7 Hz, 1H), 5.65 (s, 1H), 4.29 – 4.09 (m, 2H), 3.95 (s, 3H), 2.36 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.0, 152.9, 151.4, 138.5, 137.5, 137.3, 136.3, 129.8, 128.6, 128.2, 126.9, 125.8, 125.1, 124.4, 122.1, 62.4, 61.5, 54.4, 21.1, 14.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{22}BrN_2O_5^+$ 473.0707; Found: 473.0704.

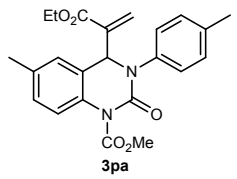
methyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-6-methoxy-2-oxo-3-(p-tolyl)-3,4-dihydroquinazoline-1(2H)-carboxylate (3oa)



3oa

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3oa** as colorless viscous oil (39.4 mg, 93% yield). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.9 Hz, 1H), 7.20 (s, 4H), 7.05 (d, *J* = 2.9 Hz, 1H), 6.93 (dd, *J* = 9.0, 2.9 Hz, 1H), 6.42 (s, 1H), 6.08 (s, 1H), 5.65 (s, 1H), 4.26 – 4.12 (m, 2H), 3.92 (s, 3H), 3.83 (s, 3H), 2.36 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 157.2, 153.1, 152.1, 138.8, 137.9, 137.1, 129.8, 129.3, 128.4, 125.3, 124.5, 124.1, 113.9, 111.8, 62.9, 61.4, 55.6, 54.0, 21.0, 14.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{23}H_{25}N_2O_6^+$ 425.1707; Found: 425.1708.

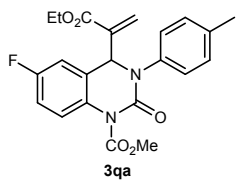
methyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-6-methyl-2-oxo-3-(p-tolyl)-3,4-dihydroquinazoline-1(2H)-carboxylate (3pa)



3pa

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3pa** as white solid (36.7 mg, 90% yield, mp: 40-42 ℃). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.3 Hz, 1H), 7.28 (s, 1H), 7.17 (d, *J* = 6.3 Hz, 5H), 6.41 – 6.36 (m, 1H), 6.04 (d, *J* = 1.3 Hz, 1H), 5.63 (s, 1H), 4.27 – 4.08 (m, 2H), 3.90 (s, 3H), 2.34 (d, *J* = 4.4 Hz, 6H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 153.1, 152.0, 138.8, 138.1, 137.1, 135.4, 132.9, 129.7, 129.0, 128.3, 127.2, 125.3, 124.1, 123.0, 62.8, 61.3, 54.1, 21.1, 21.0, 14.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{23}H_{25}N_2O_5^+$ 409.1758; Found: 409.1759.

methyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-6-fluoro-2-oxo-3-(p-tolyl)-3,4-dihydroquinazoline-1(2H)-carboxylate (3qa)

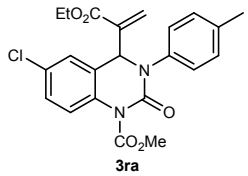


3qa

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3qa** as white solid (35.9 mg, 87% yield, mp: 44-46 ℃). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.75 (dd, *J* = 9.0, 4.8 Hz, 1H), 7.23 (dd, *J* = 8.2, 2.8 Hz, 1H), 7.18 (s, 4H), 7.07 (td, *J* = 8.8, 2.9 Hz, 1H),

6.43 (s, 1H), 6.13 – 6.06 (m, 1H), 5.62 (s, 1H), 4.19 (dddd, *J* = 18.0, 10.8, 7.2, 3.7 Hz, 2H), 3.91 (s, 3H), 2.34 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.0, 159.9 (d, *J* = 246.3 Hz), 153.0, 151.7, 138.5, 137.4, 137.3, 131.4, 130.2 (d, *J* = 8.1 Hz), 129.8, 125.2, 124.9 (d, *J* = 8.4 Hz), 124.5, 115.3 (d, *J* = 22.8 Hz), 113.8 (d, *J* = 24.2 Hz), 62.5, 61.5, 54.2, 21.1, 14.0. **^{19}F NMR** (377 MHz, Chloroform-*d*) δ -116.04 (td, *J* = 8.1, 5.0 Hz). **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{22}FN_2O_5^+$ 413.1507; Found: 413.1510.

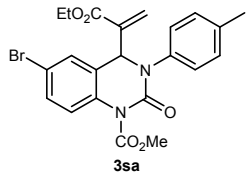
methyl 6-chloro-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2-oxo-3-(p-tolyl)-3,4-dihydroquinazoline-1(2H)-carboxylate (3ra)



3ra

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3ra** as white solid (42.4 mg, 99% yield, mp: 43-45 ℃). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.7 Hz, 1H), 7.50 (s, 1H), 7.37 – 7.30 (m, 1H), 7.17 (s, 4H), 6.44 (s, 1H), 6.08 (s, 1H), 5.62 (s, 1H), 4.32 – 4.09 (m, 2H), 3.91 (s, 3H), 2.34 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.9, 152.9, 151.5, 138.4, 137.4, 133.9, 131.0, 129.9, 129.7, 128.5, 126.9, 125.3, 124.7, 124.4, 62.4, 61.6, 54.3, 21.1, 14.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{22}ClN_2O_5^+$ 429.1212; Found: 429.1211.

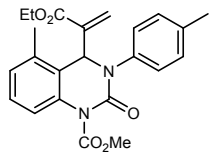
methyl 6-bromo-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2-oxo-3-(p-tolyl)-3,4-dihydroquinazoline-1(2H)-carboxylate (3sa)



3sa

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3sa** as white solid (34.5 mg, 73% yield, mp: 108-110 ℃). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.70 – 7.63 (m, 2H), 7.48 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.17 (s, 4H), 6.44 (s, 1H), 6.12 – 6.04 (m, 1H), 5.61 (s, 1H), 4.20 (dddd, *J* = 34.8, 14.3, 10.8, 7.1 Hz, 2H), 3.91 (s, 3H), 2.34 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.9, 152.8, 151.4, 138.4, 137.4, 137.4, 134.4, 131.4, 130.0, 129.9, 129.8, 125.3, 124.8, 124.6, 118.7, 62.3, 61.6, 54.3, 21.1, 14.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{22}BrN_2O_5^+$ 473.0707; Found: 473.0707.

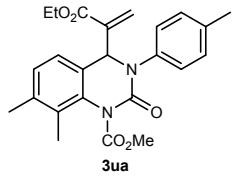
methyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-5-methyl-2-oxo-3-(p-tolyl)-3,4-dihydroquinazoline-1(2H)-carboxylate (3ta)



3ta

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3ta** as white solid (39.6 mg, 97% yield, mp: 92-94 ℃). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.17 (dq, *J* = 16.9, 7.7 Hz, 5H), 6.28 (s, 1H), 5.87 (s, 1H), 5.50 (s, 1H), 4.15 (dt, *J* = 14.4, 7.2 Hz, 1H), 4.00 (dq, *J* = 13.1, 6.4, 5.8 Hz, 1H), 3.93 (s, 3H), 2.37 (d, *J* = 6.3 Hz, 6H), 1.13 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7, 153.3, 151.3, 139.2, 137.9, 137.1, 136.4, 133.8, 129.7, 128.3, 127.8, 127.6, 126.5, 126.2, 121.5, 61.3, 59.6, 54.1, 21.1, 18.6, 13.8. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{23}H_{25}N_2O_5^+$ 409.1758; Found: 409.1766.

methyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-7,8-dimethyl-2-oxo-3-(p-tolyl)-3,4-dihydroquinazoline-1(2H)-carboxylate (3ua)



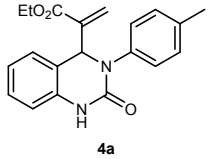
3ua

The reaction was conducted on a 0.1 mmol scale according to the GP2 and afforded dihydroquinazolinone **3ua** as colorless viscous oil (41.8 mg, 99% yield). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 4.9 Hz, 1H),

7.20 (s, 4H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.37 (s, 1H), 6.00 (s, 1H), 5.65 (s, 1H), 4.23 (dq, *J* = 14.2, 7.1 Hz, 1H), 4.17 – 4.06 (m, 1H), 3.87 (s, 3H), 2.35 (d, *J* = 5.2 Hz, 6H), 2.22 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.3, 152.4, 152.0, 138.7, 138.5, 138.3, 136.9, 134.3, 133.1, 129.7, 129.2, 128.2, 124.9, 124.1, 123.4, 63.6, 61.3, 53.9, 21.1, 20.3, 15.3, 14.0. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{24}H_{27}N_2O_5^+$ 423.1915; Found: 423.1920.

6.2. Products of derivatization

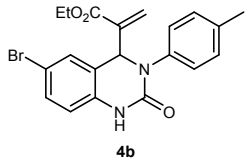
ethyl 2-(2-oxo-3-(p-tolyl)-1,2,3,4-tetrahydroquinazolin-4-yl)acrylate (4a)



4a

The reaction was conducted on a 0.1 mmol scale according to the corresponding procedure in section 5.2 and afforded **4a** as colorless viscous oil (24.9 mg, 74% yield). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.25 – 7.13 (m, 6H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 7.9 Hz, 1H), 6.27 (s, 1H), 5.86 (s, 1H), 5.82 (s, 1H), 4.23 – 4.09 (m, 2H), 2.34 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.4, 153.8, 140.0, 138.6, 136.4, 136.1, 129.6, 128.6, 126.4, 126.3, 125.6, 122.2, 120.0, 114.2, 62.8, 61.1, 21.0, 14.0. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{20}H_{21}N_2O_3^+$ 337.1547; Found: 337.1544.

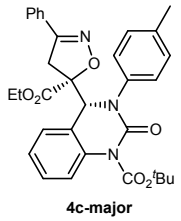
6-bromo-4-(prop-1-en-2-yl)-3-(p-tolyl)-3,4-dihydroquinazolin-2(1H)-one (4b)



4b

The reaction was conducted on a 0.1 mmol scale according to the corresponding procedure in section 5.2 and afforded **4b** as white solid (36 mg, 87% yield, mp: 210-212 ℃). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.16 (s, 1H), 7.35 (s, 1H), 7.23 (d, *J* = 8.5 Hz, 1H), 7.18 (s, 4H), 6.64 (d, *J* = 8.4 Hz, 1H), 6.31 (s, 1H), 5.86 (s, 1H), 5.75 (s, 1H), 4.18 (tdt, *J* = 14.4, 11.0, 5.4 Hz, 2H), 2.35 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.1, 154.0, 139.4, 138.3, 136.7, 135.4, 131.5, 129.8, 129.1, 126.4, 121.7, 116.2, 114.1, 62.4, 61.3, 21.1, 14.0. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{20}H_{20}BrN_2O_3^+$ 415.0652; Found: 415.0646.

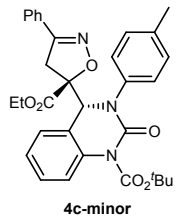
ethyl (R)-5-((R)-1-(tert-butoxycarbonyl)-2-oxo-3-(p-tolyl)-1,2,3,4-tetrahydroquinazolin-4-yl)-3-methyl-4,5-dihydroisoxazole-5-carboxylate (4c-major)



4c-major

The reaction was conducted on a 0.2 mmol scale according to the corresponding procedure in section 5.2 and afforded **4c-major** as pale-yellow solid (70.0 mg, 63% yield, mp: 112-114 ℃). R_f = 0.5 (petroleum ether/ethyl acetate = 4:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 6.9 Hz, 2H), 7.36 (dq, *J* = 19.8, 7.0 Hz, 5H), 7.17 (d, *J* = 6.7 Hz, 5H), 5.52 (s, 1H), 4.01 – 3.87 (m, 2H), 3.65 (dq, *J* = 10.6, 7.1 Hz, 1H), 3.49 (d, *J* = 17.4 Hz, 1H), 2.33 (s, 3H), 1.62 (s, 9H), 0.97 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.7, 156.8, 151.1, 139.2, 137.2, 136.6, 130.5, 129.6, 129.2, 128.7, 128.4, 128.0, 127.0, 126.7, 124.8, 122.8, 120.9, 91.1, 84.0, 65.0, 62.5, 38.7, 28.0, 21.0, 13.5. **HRMS(ESI)** m/z: $[M + Na]^+$ calcd for $C_{32}H_{33}N_3NaO_3^+$ 578.2261; Found: 578.2257.

ethyl (S)-5-((R)-1-(tert-butoxycarbonyl)-2-oxo-3-(p-tolyl)-1,2,3,4-tetrahydroquinazolin-4-yl)-3-phenyl-4,5-dihydroisoxazole-5-carboxylate (4c-minor)



4c-minor

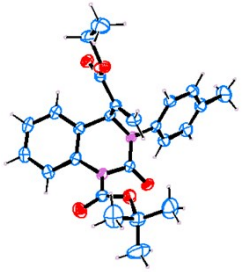
The reaction was conducted on a 0.2 mmol scale according to the corresponding procedure in section 5.2 and afforded **4c-minor** as pale yellow solid (17.8 mg, 16% yield, mp: 167-169 ℃). R_f = 0.4 (petroleum ether/ethyl acetate = 4:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.2 Hz, 1H), 7.61 (d, *J* = 6.6 Hz, 2H), 7.48 – 7.36 (m, 4H), 7.30 – 7.16 (m, 6H), 5.46 (s, 1H), 4.20 – 4.00 (m, 2H), 3.83 (d, *J* = 17.4 Hz, 1H), 3.71 (d, *J* = 17.4 Hz, 1H), 2.37 (s, 3H), 1.58 (s, 9H), 1.21

(t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.6, 157.0, 151.8, 151.1, 139.7, 137.4, 136.7, 130.6, 129.8, 129.3, 128.7, 128.5, 127.3, 126.8, 126.8, 124.6, 122.8, 121.4, 91.9, 84.0, 65.8, 62.6, 39.5, 27.9, 21.1, 13.8. **HRMS(ESI)** m/z: $[M + Na]^+$ calcd for $C_{32}H_{33}N_3NaO_3^+$ 578.2261; Found: 578.2257.

7. X-ray Crystallographic Analysis

DABCO catalyzed [4+2] cycloadduct - 3ha

Crystallographic data for **3ha** has been deposited with the Cambridge Crystallographic Data Centre as deposition number CCDC 2034954 (Experimental Crystal Structure Determination, 2020, DOI: 10.5517/ccdc.csd.cc25y2v2). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

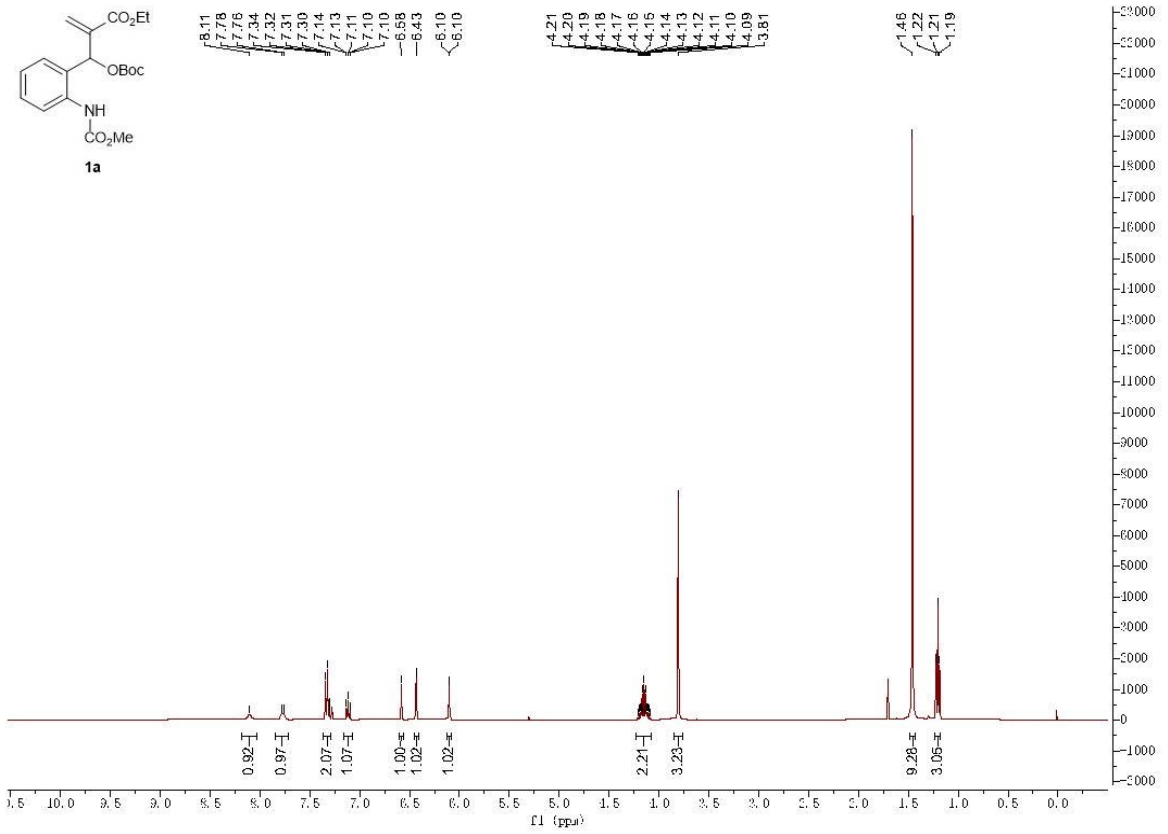


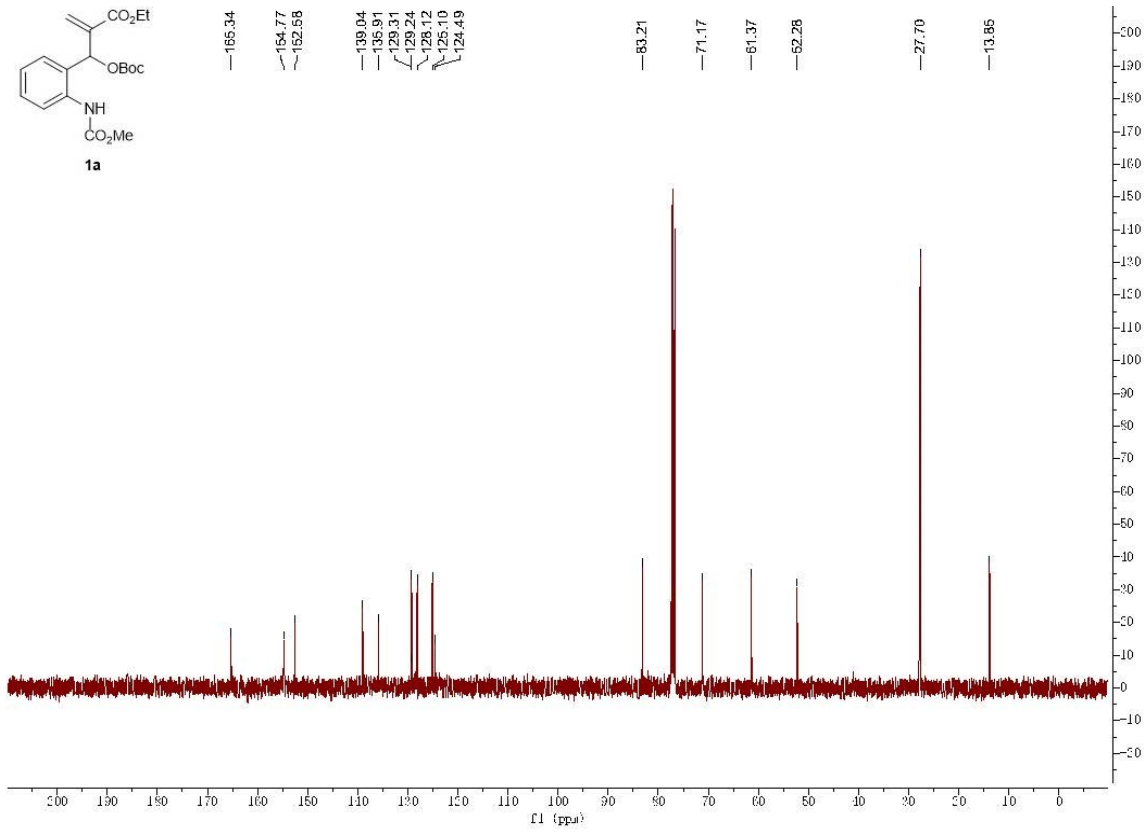
ORTEP diagram of **3ha**. Thermal ellipsoids are shown at the 50% probability level. A colorless stick-shaped crystal of **3ha** for X-ray diffraction was obtained by slowly volatilizing a saturated solution of 3fa in hexane/chloroform (5:1). The X-ray intensity data was measured on a Rigaku 007 Saturn 70 single crystal diffractometer.

CCDC number	2023954
Identification code	**3ha**
Empirical formula	$C_{25}H_{28}N_2O_5$
Formula weight	436.49
Temperature/K	113(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.2030(16)
b/Å	35.274(7)
c/Å	8.3403(17)
α/°	90
β/°	102.52(3)
γ/°	90
Volume/Å^3	2355.9(9)
Z	4
ρ_{calc}g/cm^3	1.231
μ/mm^{-1}	0.086
F(000)	928.0
Crystal size/mm^3	0.200 × 0.180 × 0.120
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.134 to 55.808
Index ranges	$-10 \le h \le 10$, $-46 \le k \le 46$, $-10 \le l \le 10$
Reflections collected	26220
Independent reflections	5622 [R_{int} = 0.0594, R_{sigma} = 0.0528]
Data/restraints/parameters	5622/0/295
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0551, wR_2 = 0.1329
Final R indexes [all data]	R_1 = 0.0812, wR_2 = 0.1476
Largest diff. peak/hole / e Å^{-3}	0.22/-0.21

8. NMR Spectra

o-Amino-acylation aryl MBH carbonates

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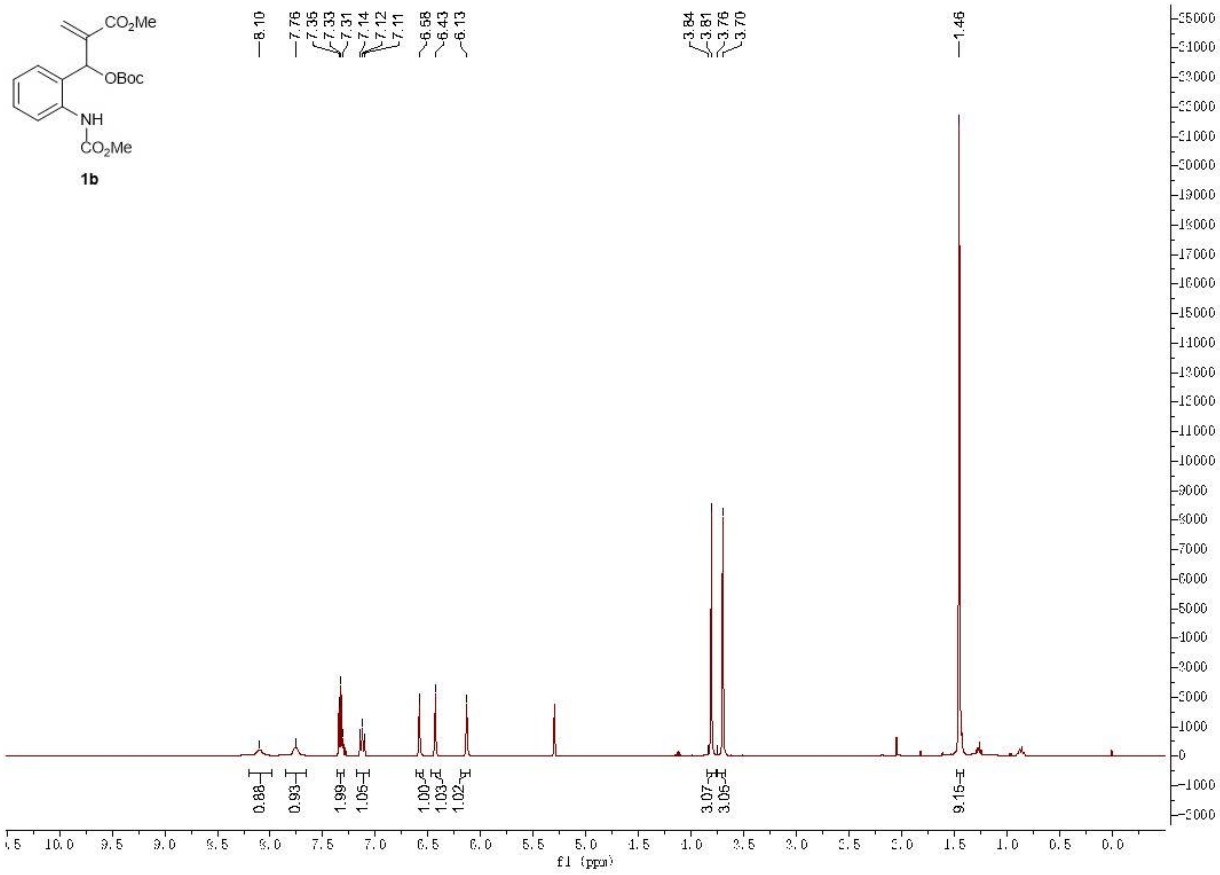
52.28
27.70
13.86
f1 (ppm)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6.58
6.43
6.13
3.84
3.81
3.76
3.70
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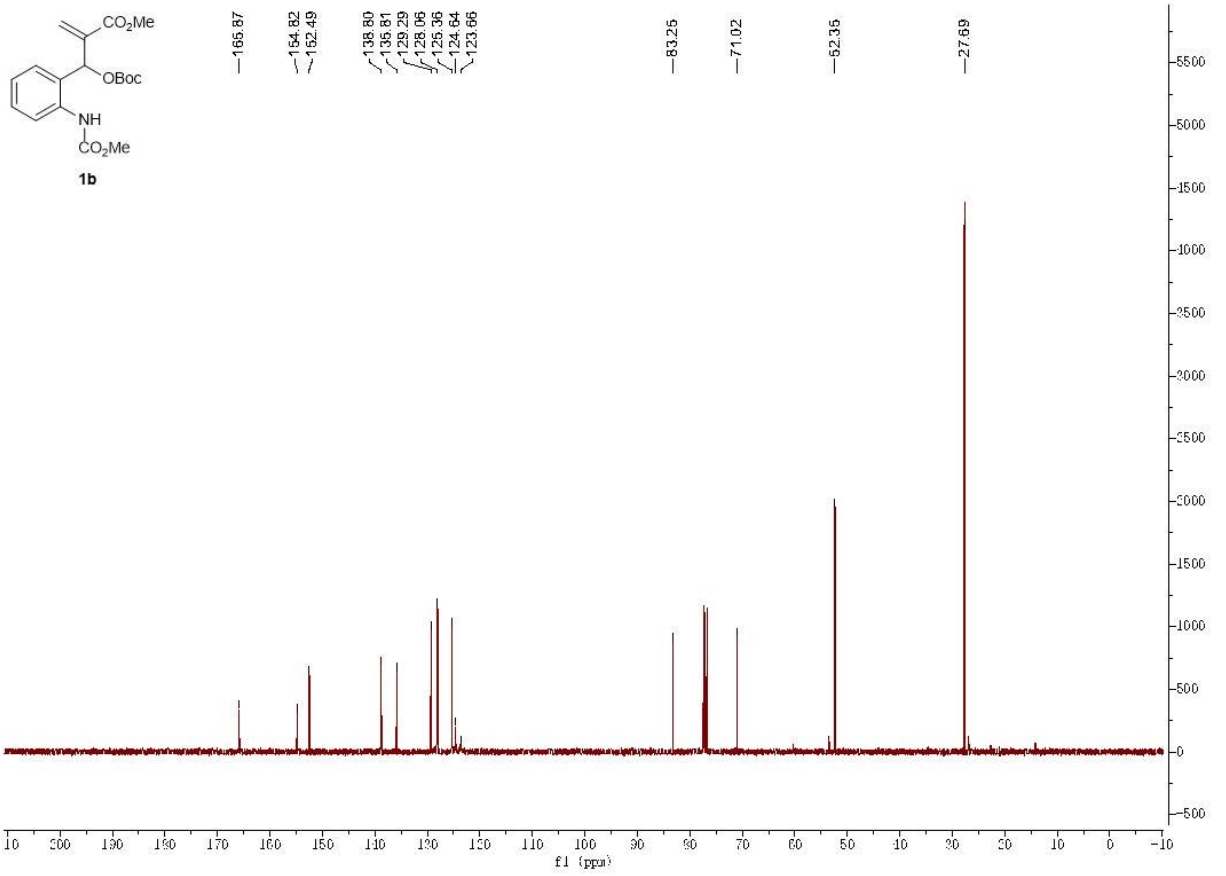
1.99
1.05
1.00
1.03
1.02
3.07
3.05
9.15
f1 (ppm)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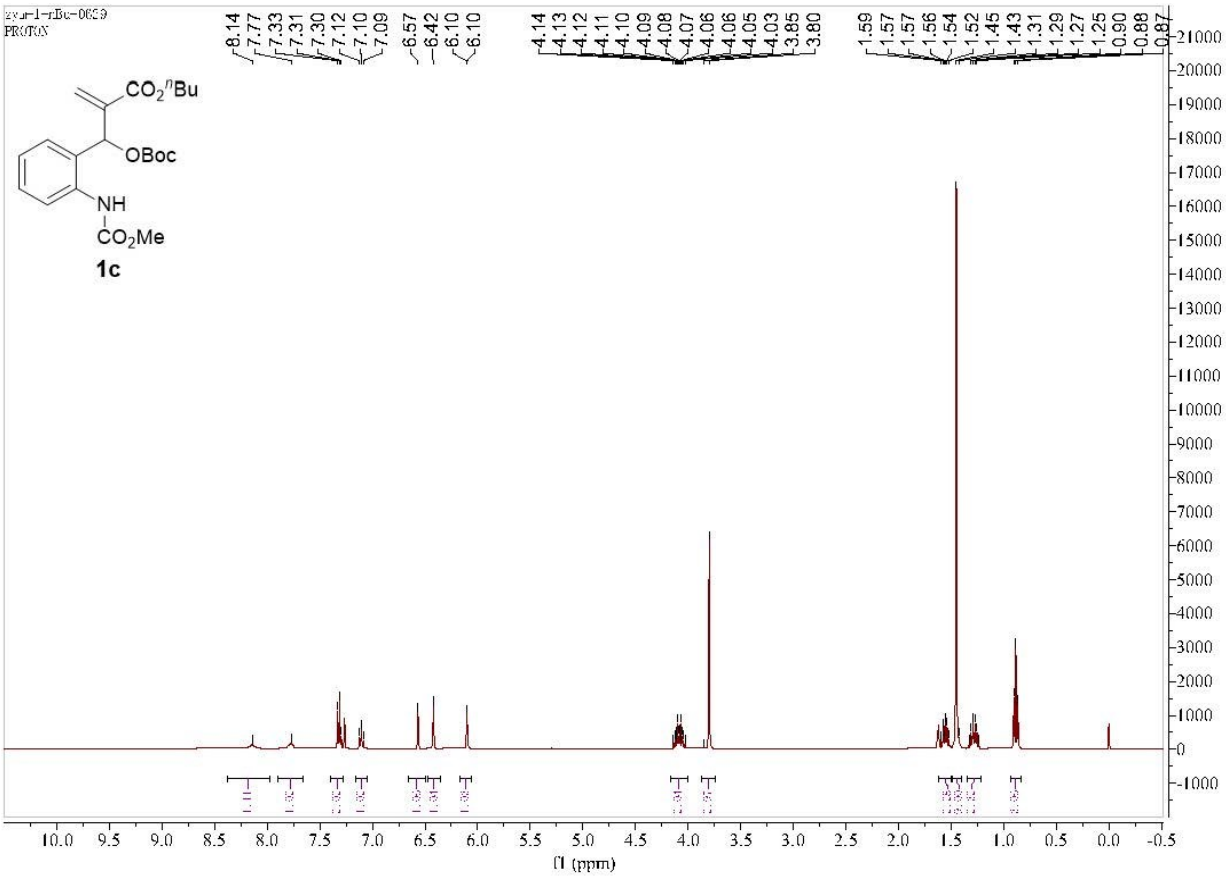
27.69
f1 (ppm)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7.09
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6.42
6.10
6.10
4.14
4.13
4.12
4.11
4.10
4.09
4.08
4.07
4.06
4.06
4.05
4.03
3.85
3.80
1.59
1.57
1.57
1.56
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1.52
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1.31
1.29
1.27
1.25
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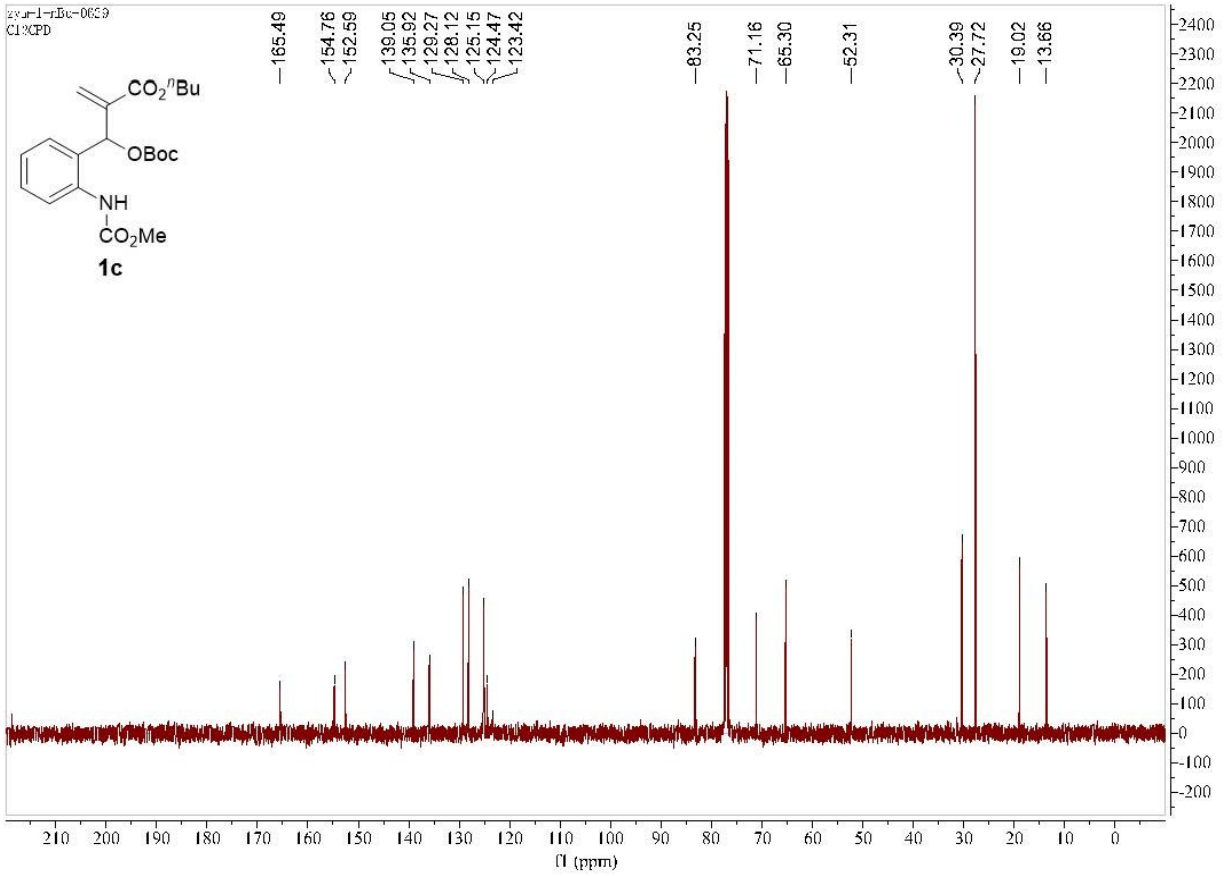
0.87
f1 (ppm)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NH
CO2Me
1c
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129.27
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30.39
27.72
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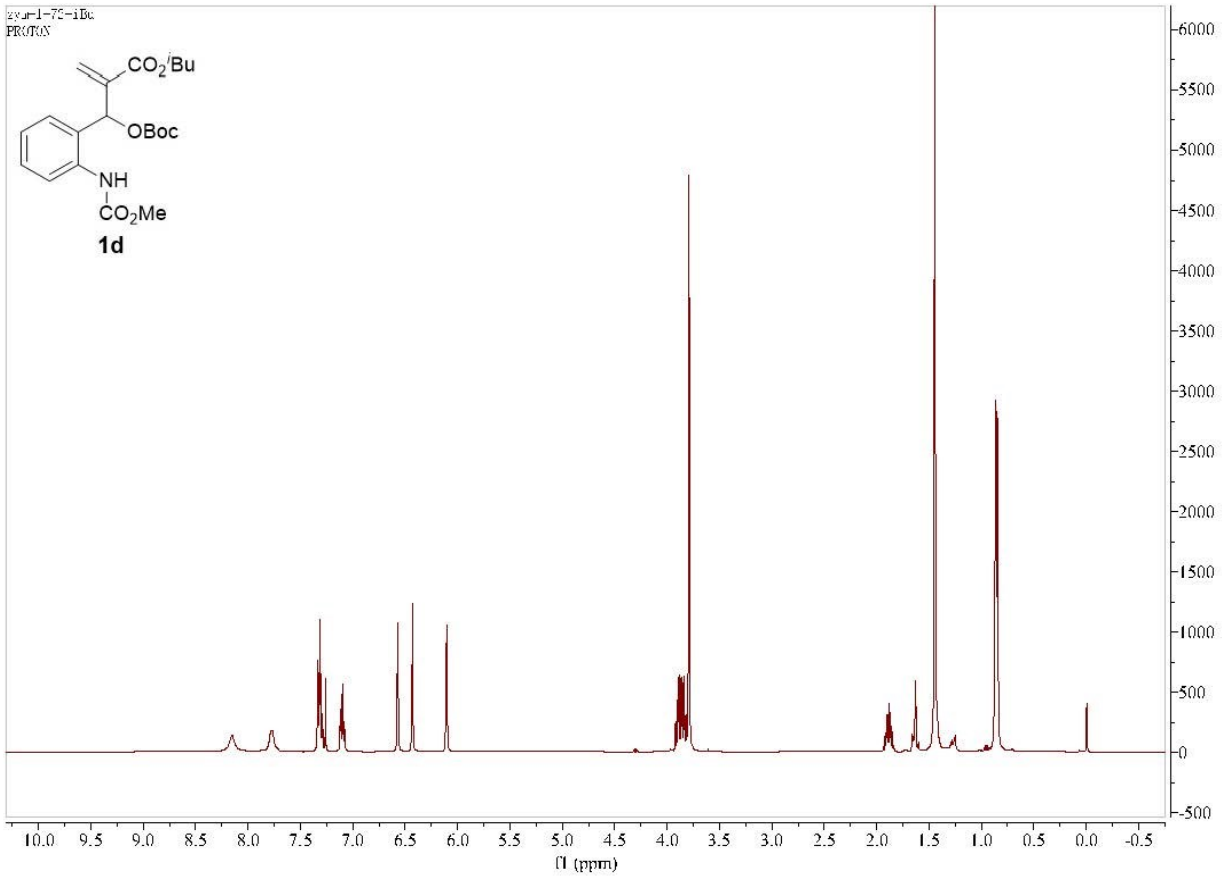
13.66
f1 (ppm)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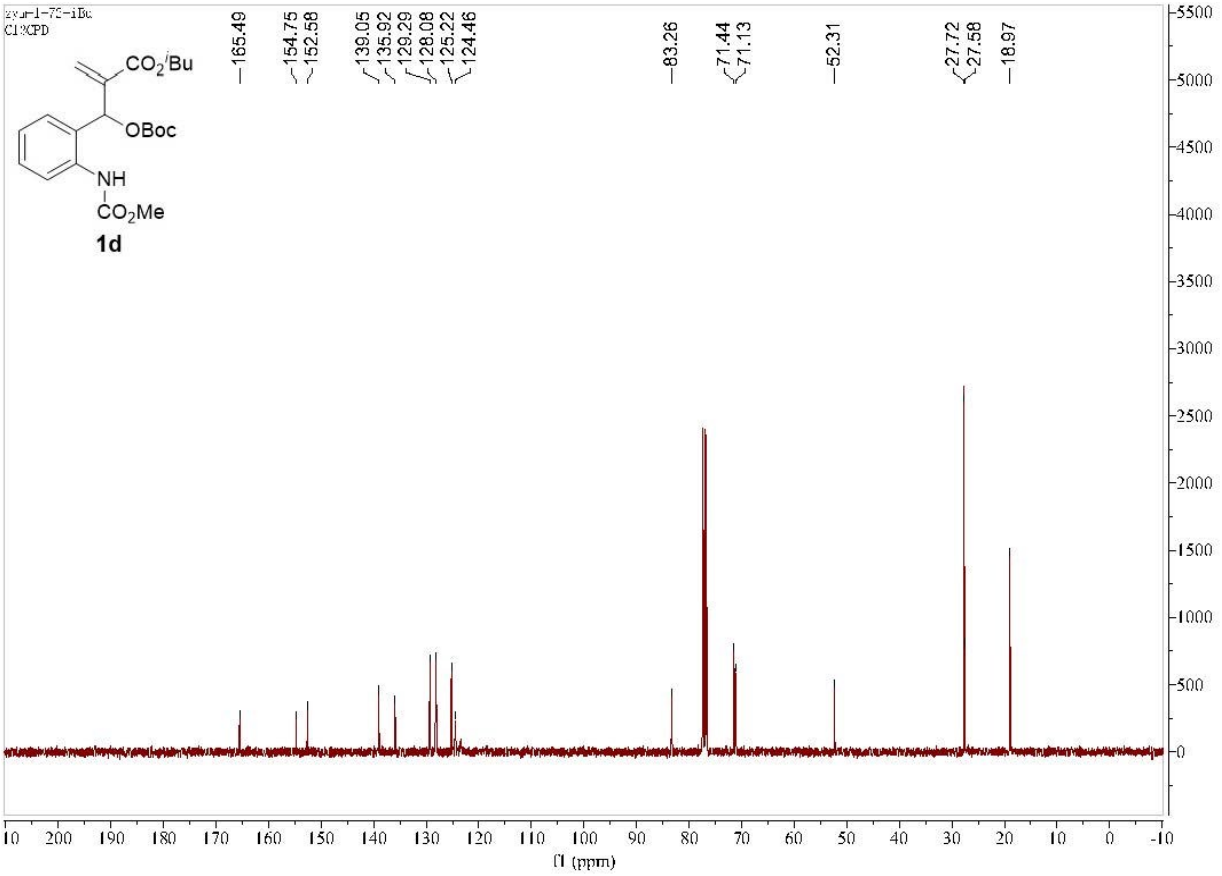
f1 (ppm)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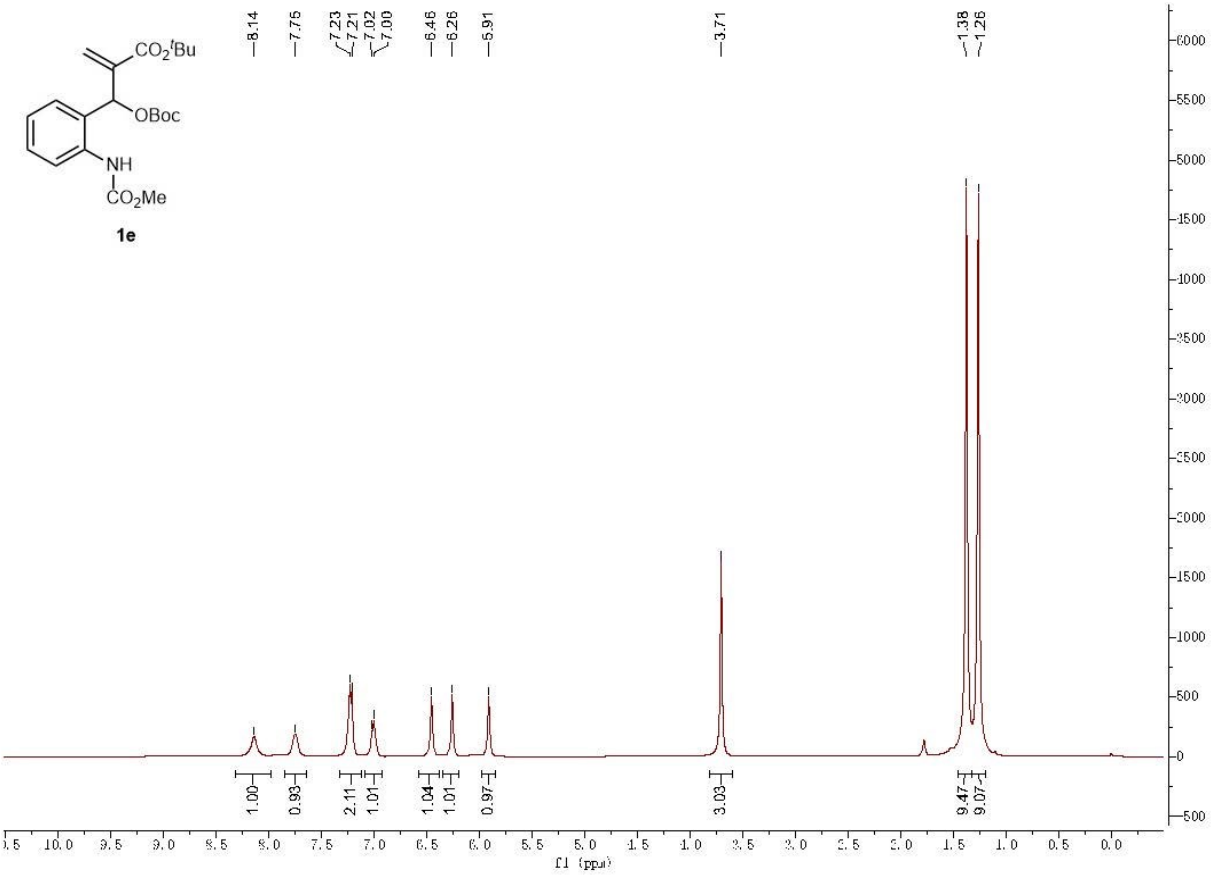
52.31
27.72
27.58
18.97
f1 (ppm)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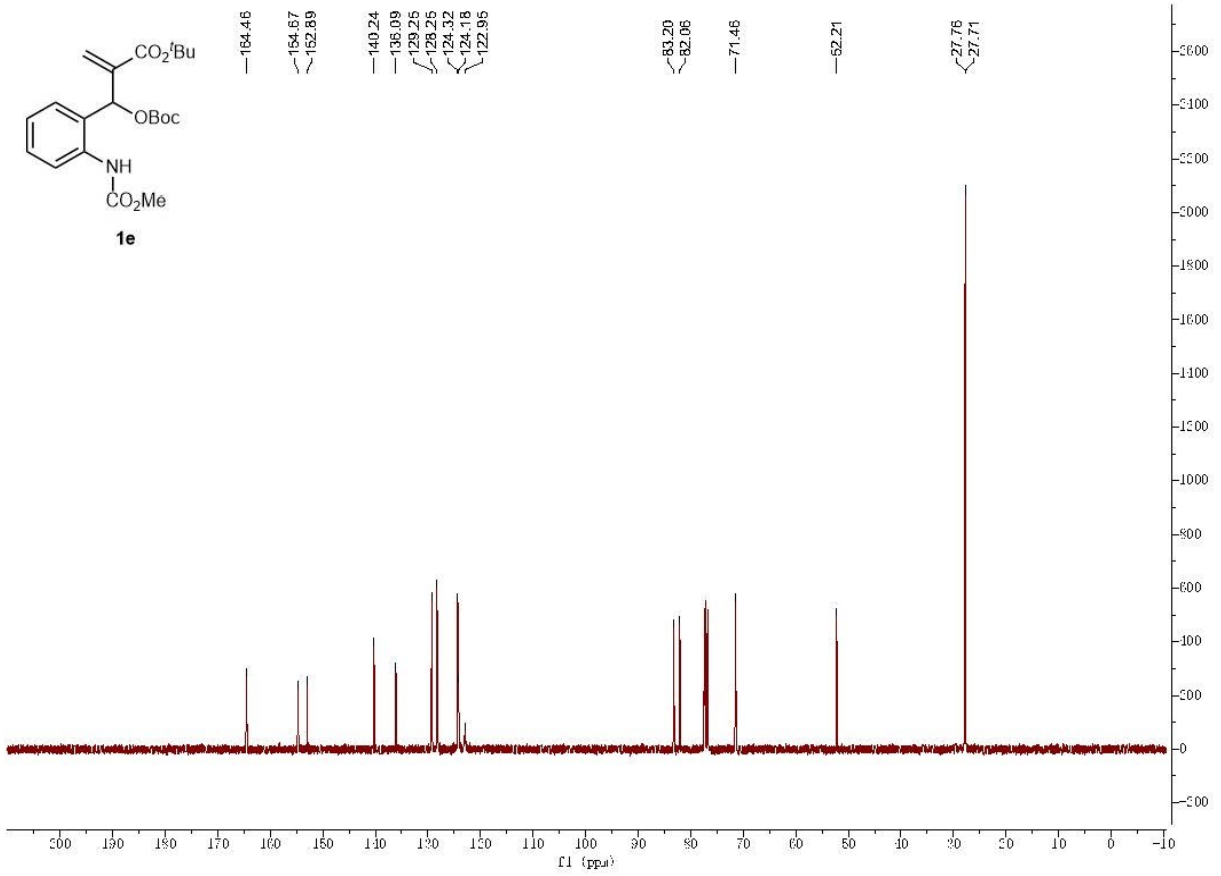
f1 (ppm)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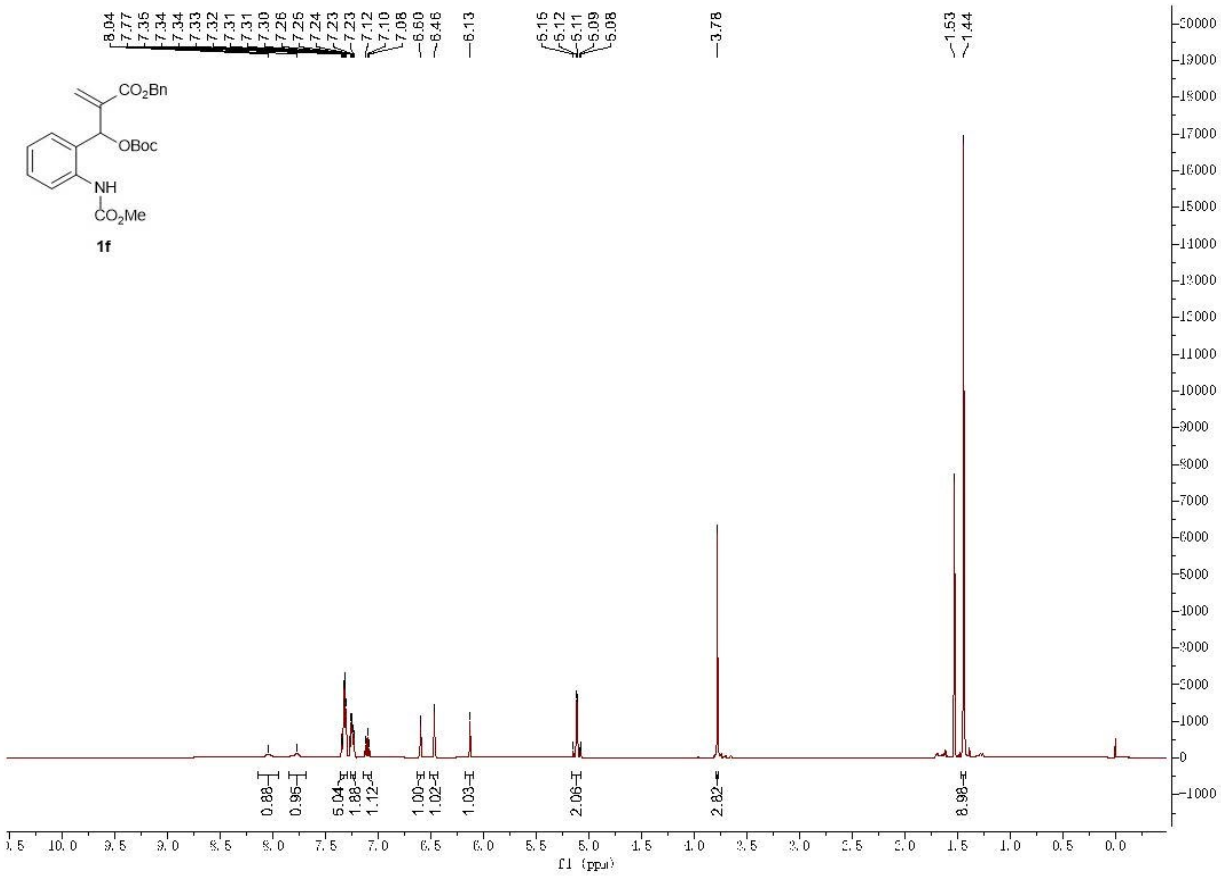
f1 (ppm)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7.08
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5.08
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OBoc
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CO2Me
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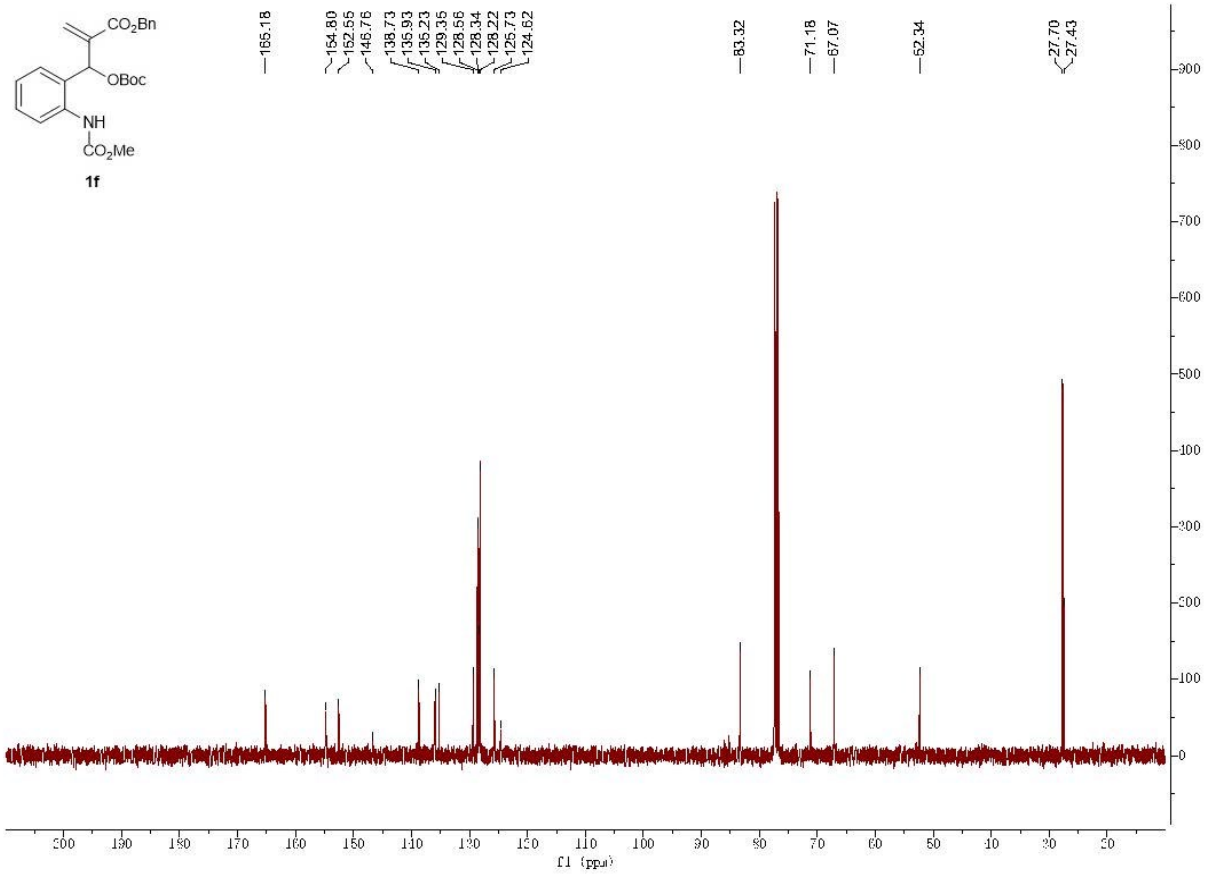
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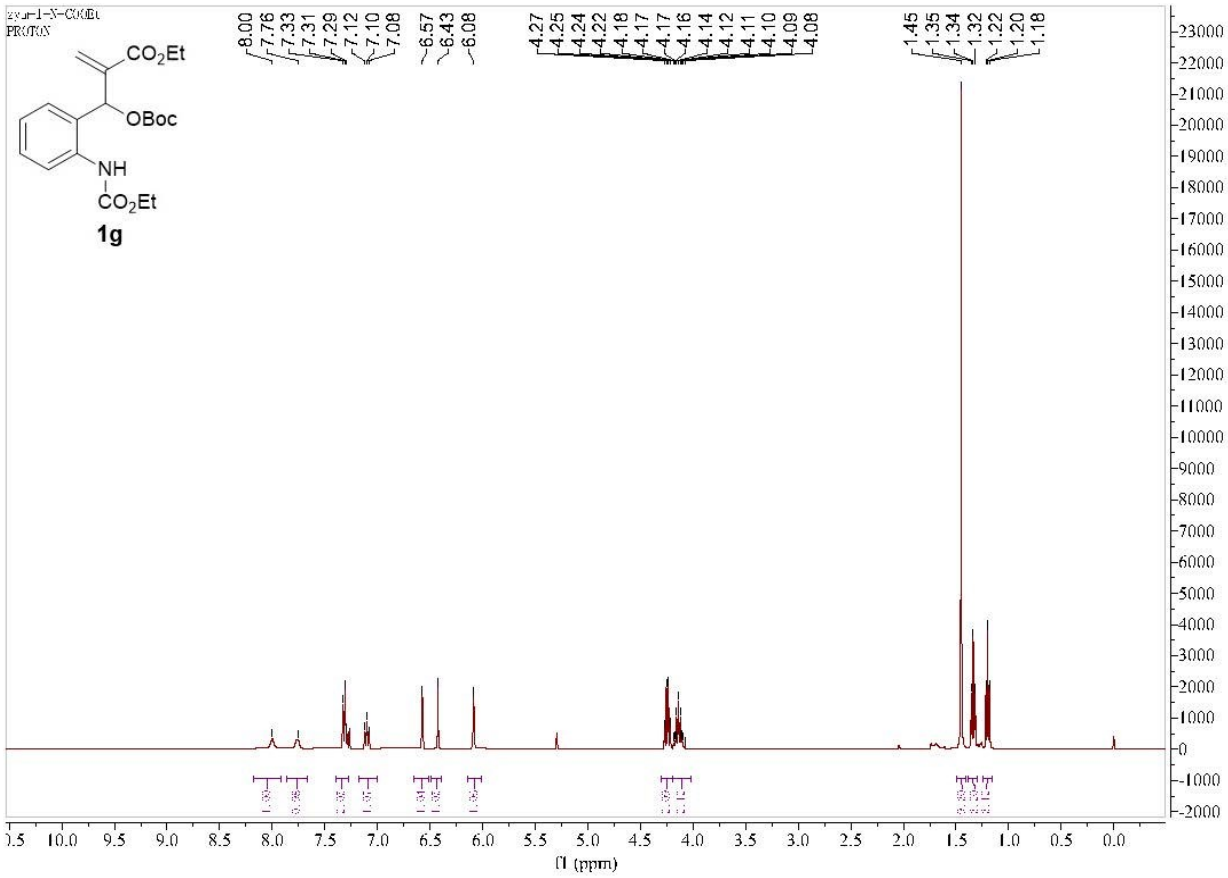
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4.16
4.14
4.12
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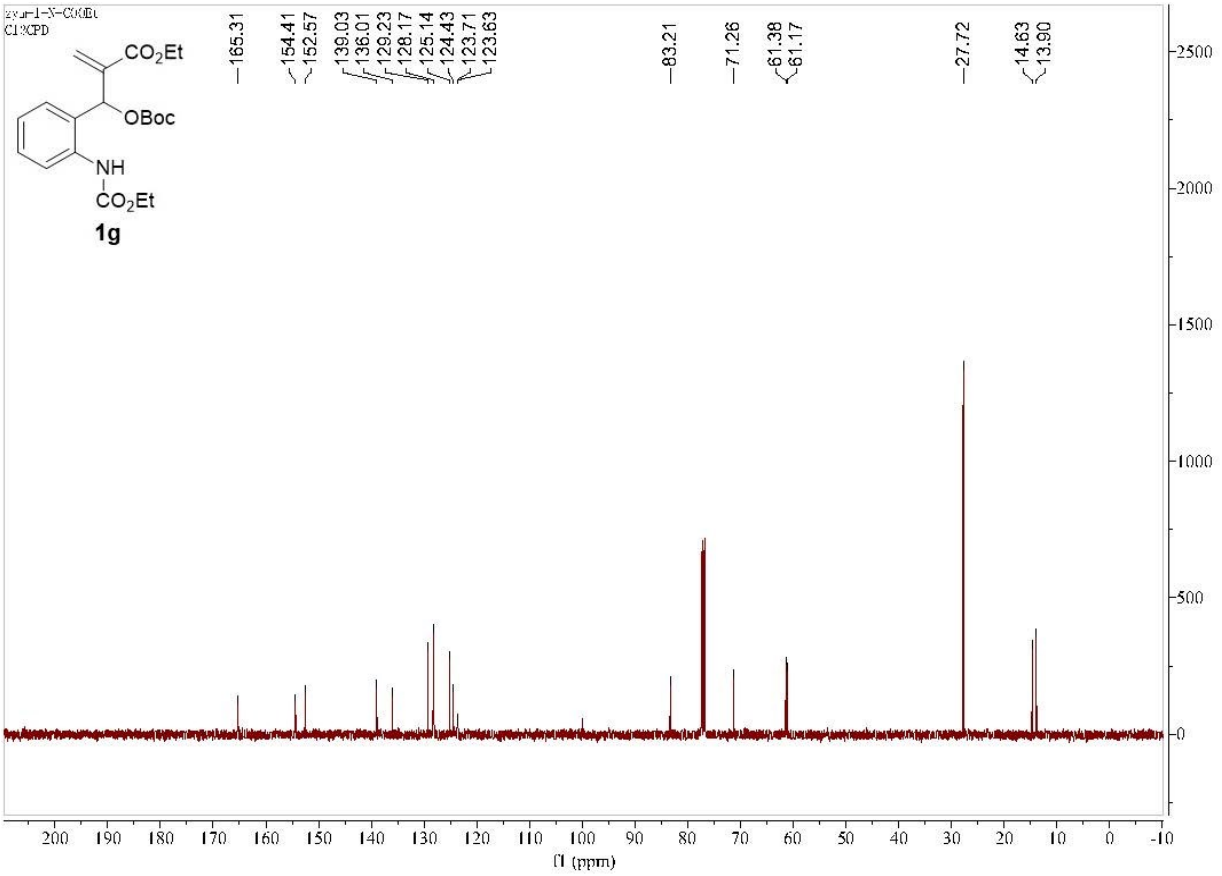
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13.90
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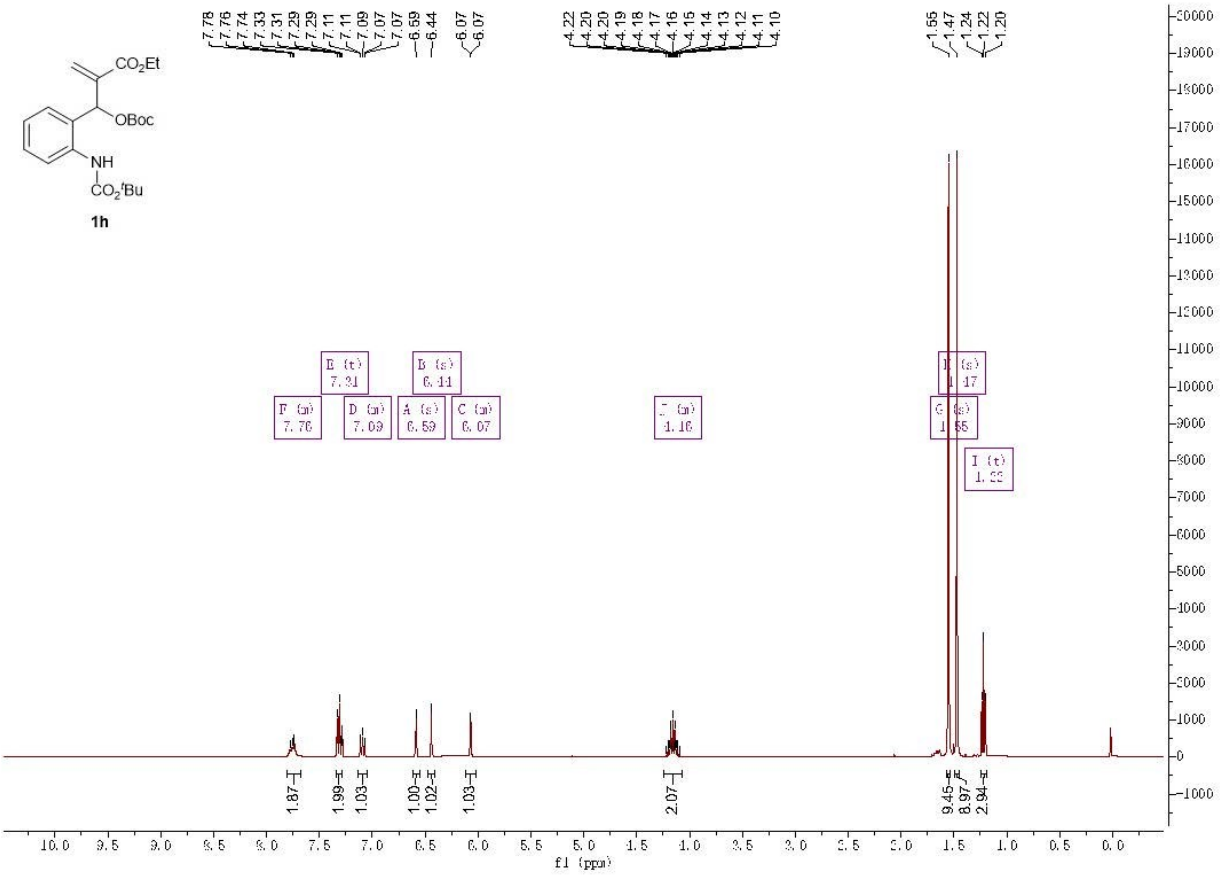
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6.07
6.07
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4.20
4.19
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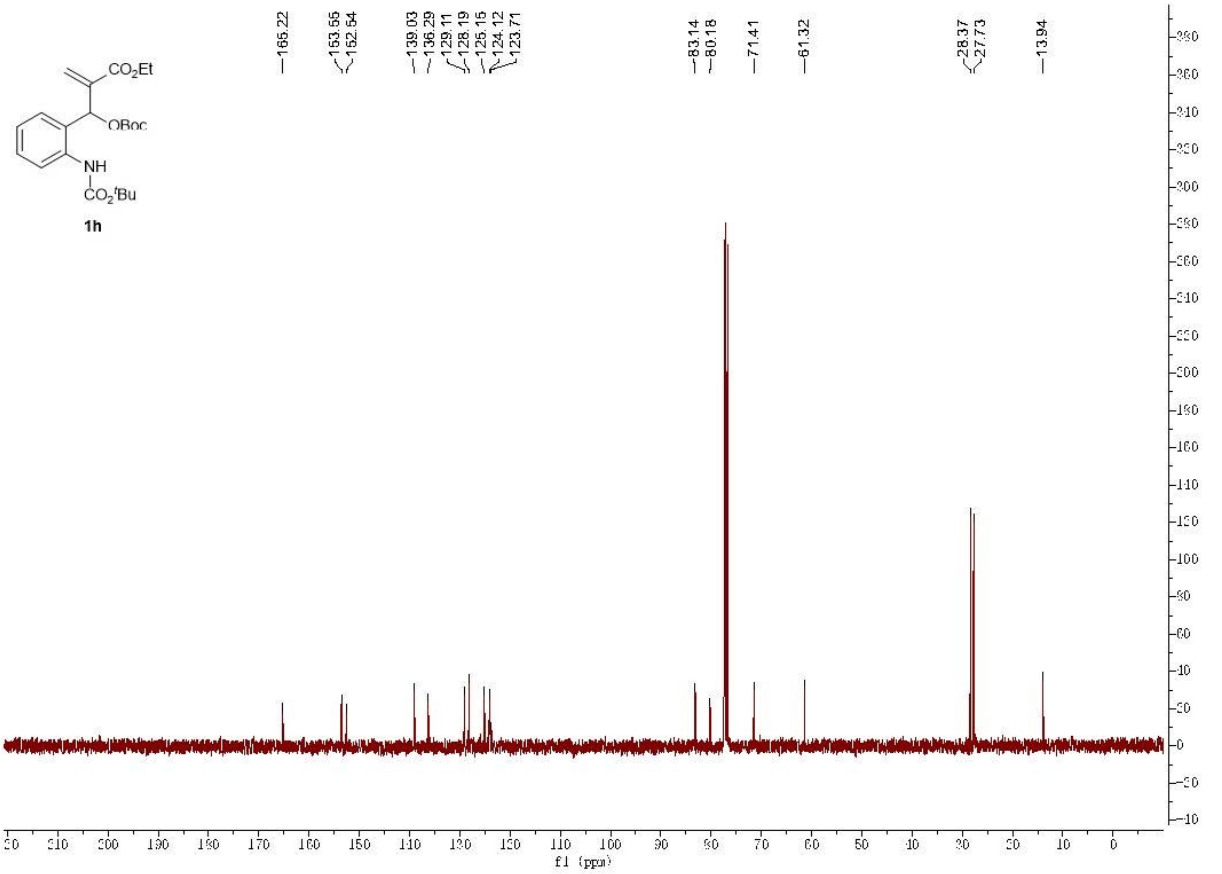
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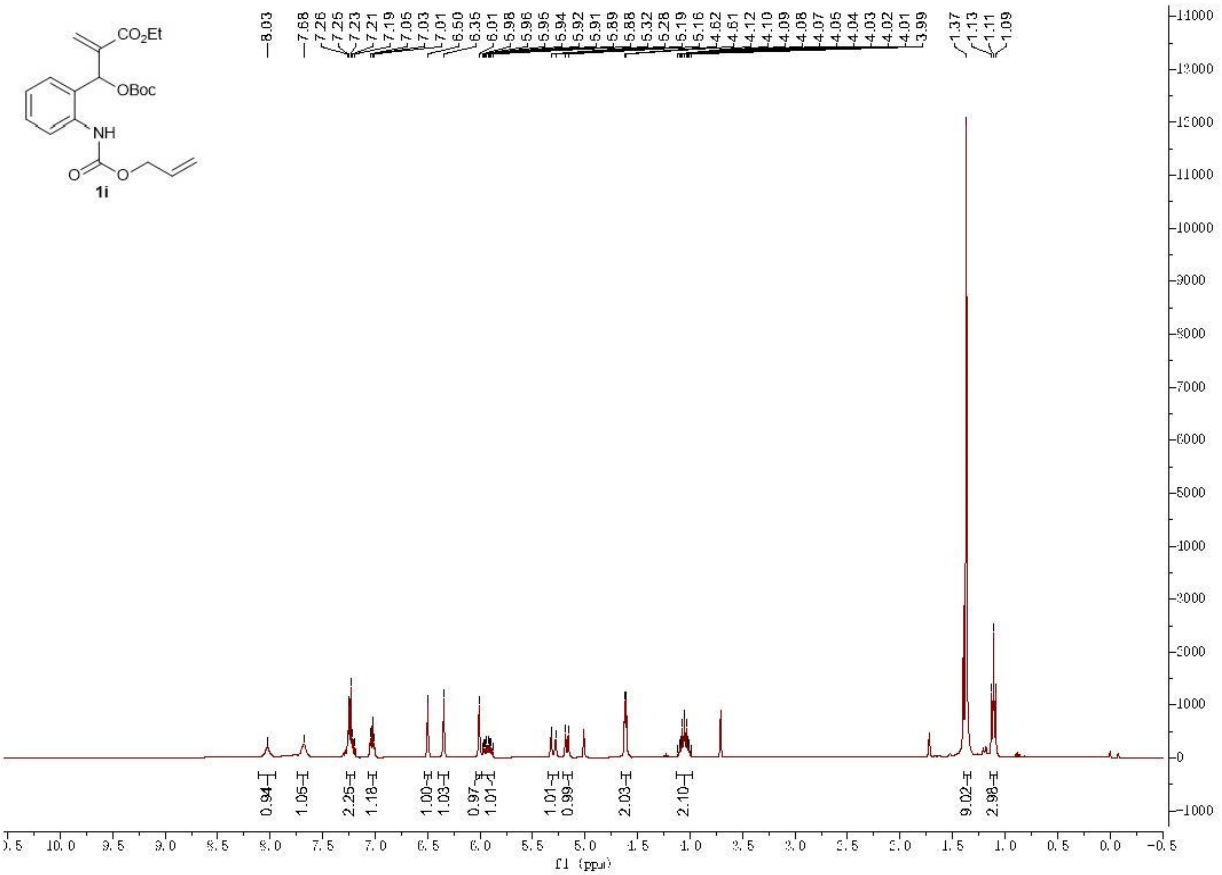
f1 (ppm)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OBoc
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4.08
4.07
4.05
4.04
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4.02
4.01
3.99
1.37
1.13
1.11
1.09
0.94
1.05
2.25
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2.03
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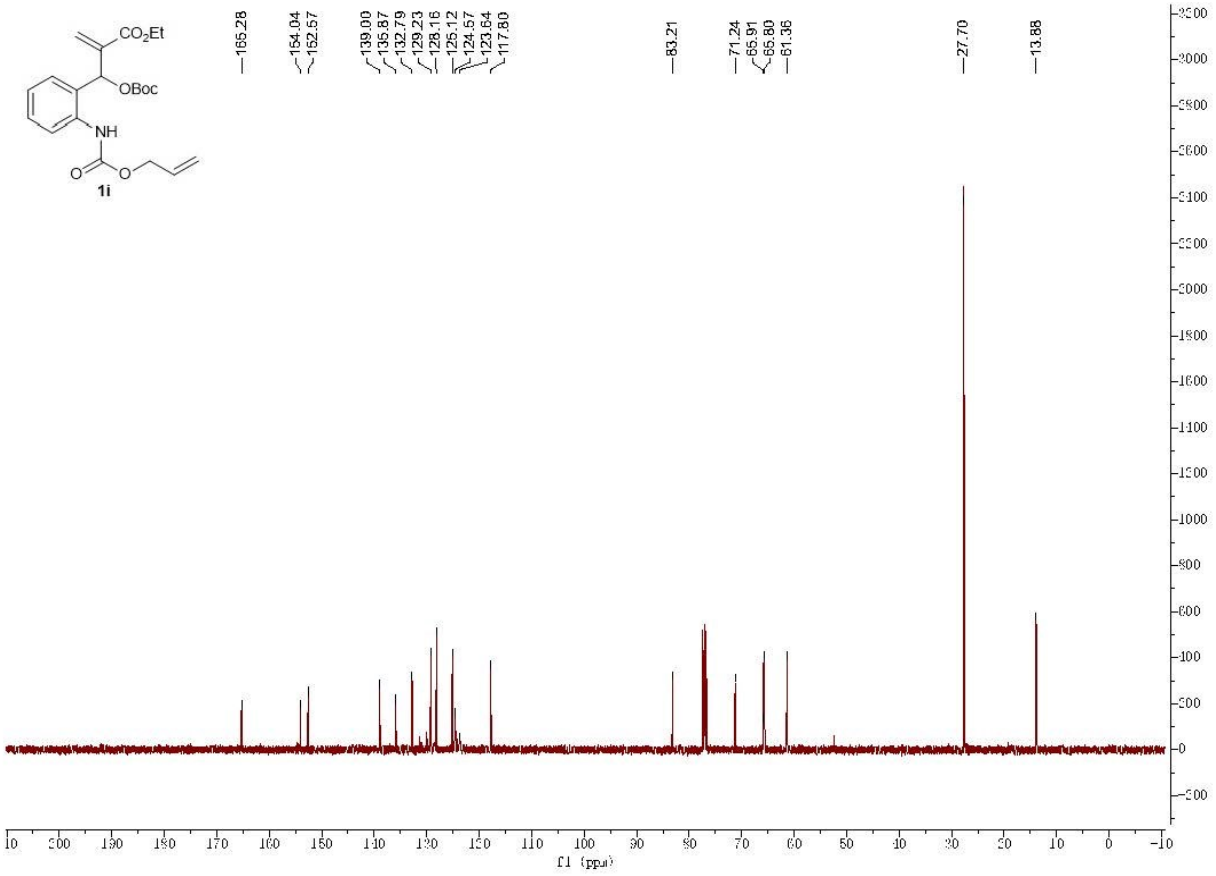
f1 (ppm)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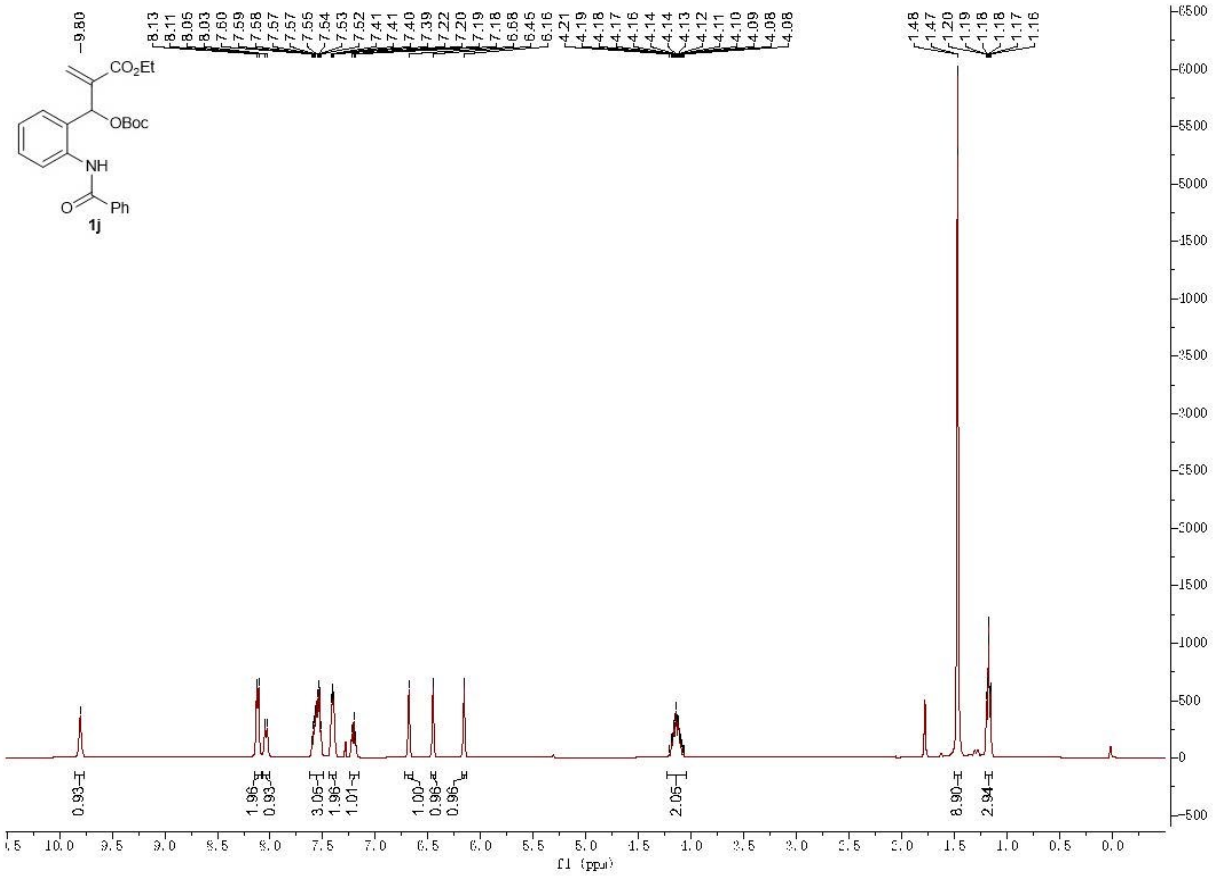
13.88
f1 (ppm)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7.22
7.20
7.19
7.18
6.88
6.45
5.16
4.21
4.19
4.18
4.17
4.16
4.14
4.14
4.13
4.12
4.11
4.10
4.09
4.08
4.08
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1.47
1.20
1.19
1.18
1.18
1.17
1.16
CO2Et
OBoc
NH
O
Ph
1j
0.93
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1.00
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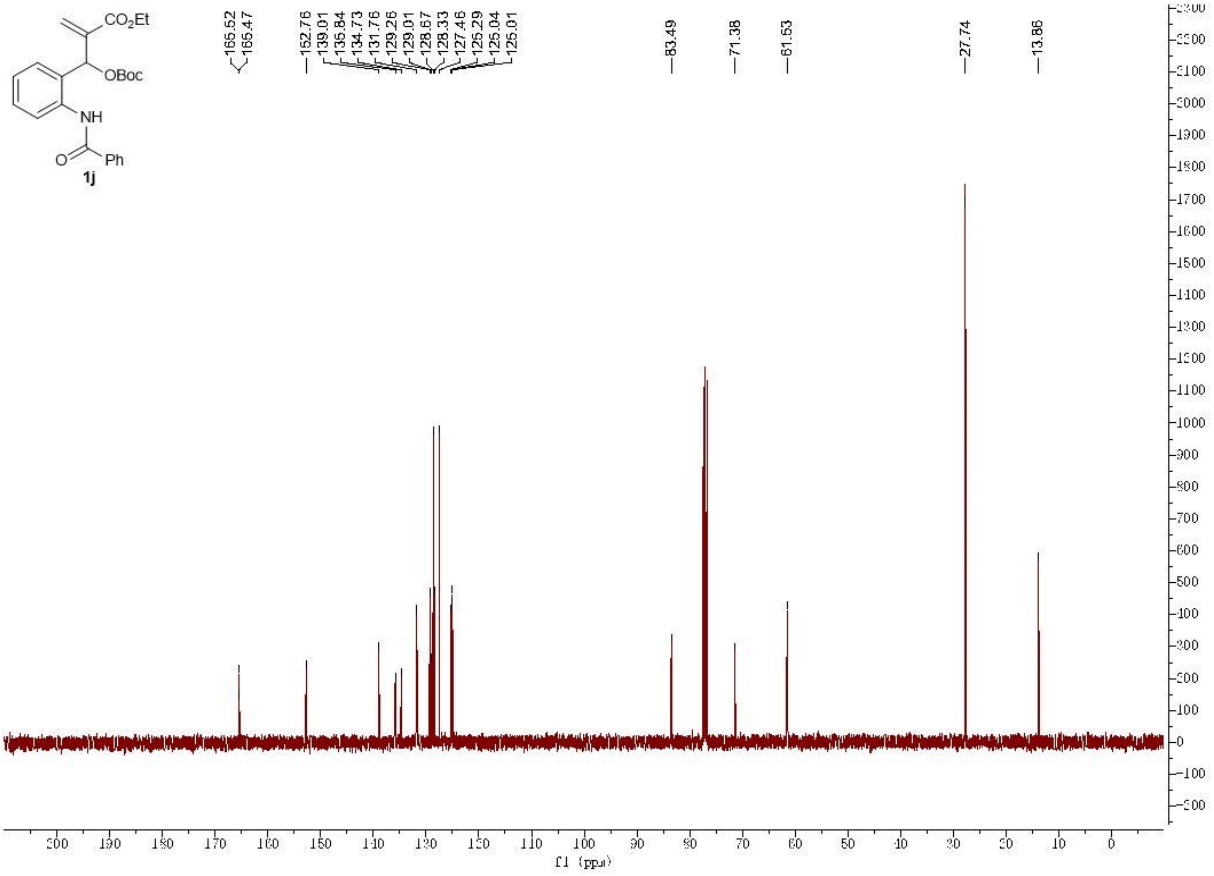
2.94
f1 (ppm)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129.01
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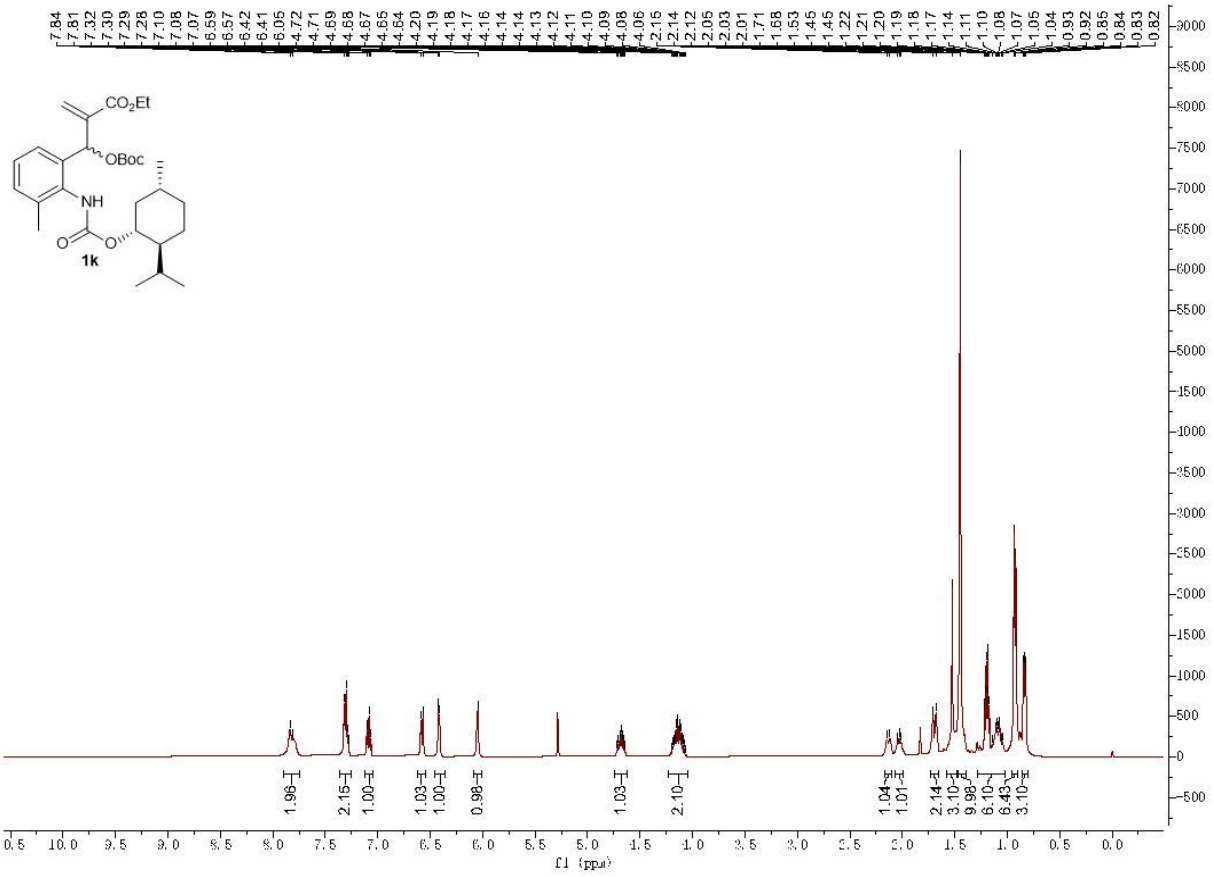
f1 (ppm)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O
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7.10
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7.07
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6.57
6.42
6.41
6.05
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4.71
4.69
4.68
4.67
4.65
4.64
4.20
4.19
4.18
4.17
4.16
4.14
4.14
4.13
4.12
4.11
4.10
4.09
4.08
4.06
2.15
2.14
2.12
2.05
2.03
2.01
1.71
1.68
1.53
1.45
1.45
1.22
1.21
1.20
1.19
1.18
1.17
1.14
1.11
1.10
1.08
1.07
1.05
1.04
0.93
0.92
0.85
0.84
0.83
0.82
1.96
2.15
1.00
1.03
1.00
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1.04
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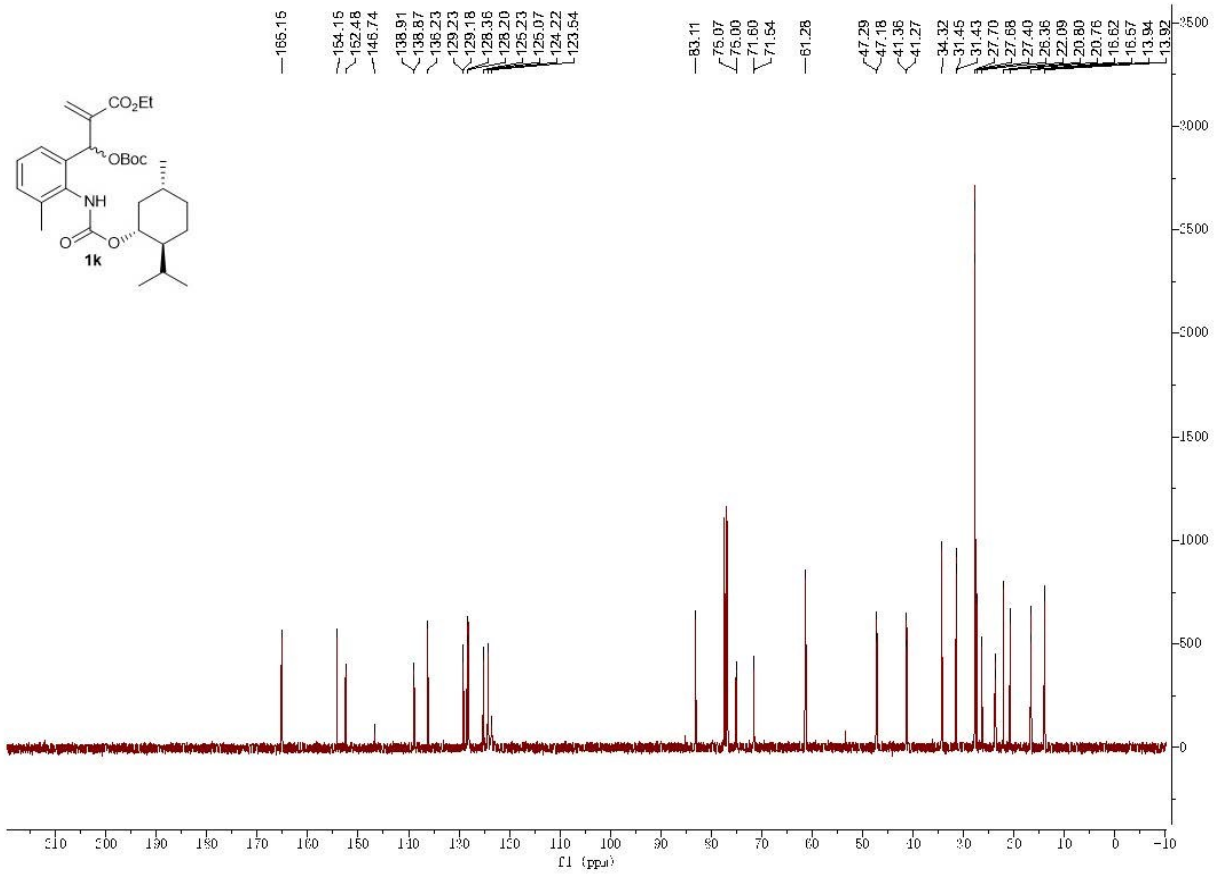
6.10
6.43
3.10
f1 (ppm)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O
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129.18
128.36
128.20
125.23
125.07
124.22
123.54
83.11
76.07
76.00
71.60
71.54
61.28
47.29
47.18
41.36
41.27
34.32
31.45
31.43
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20.80
20.76
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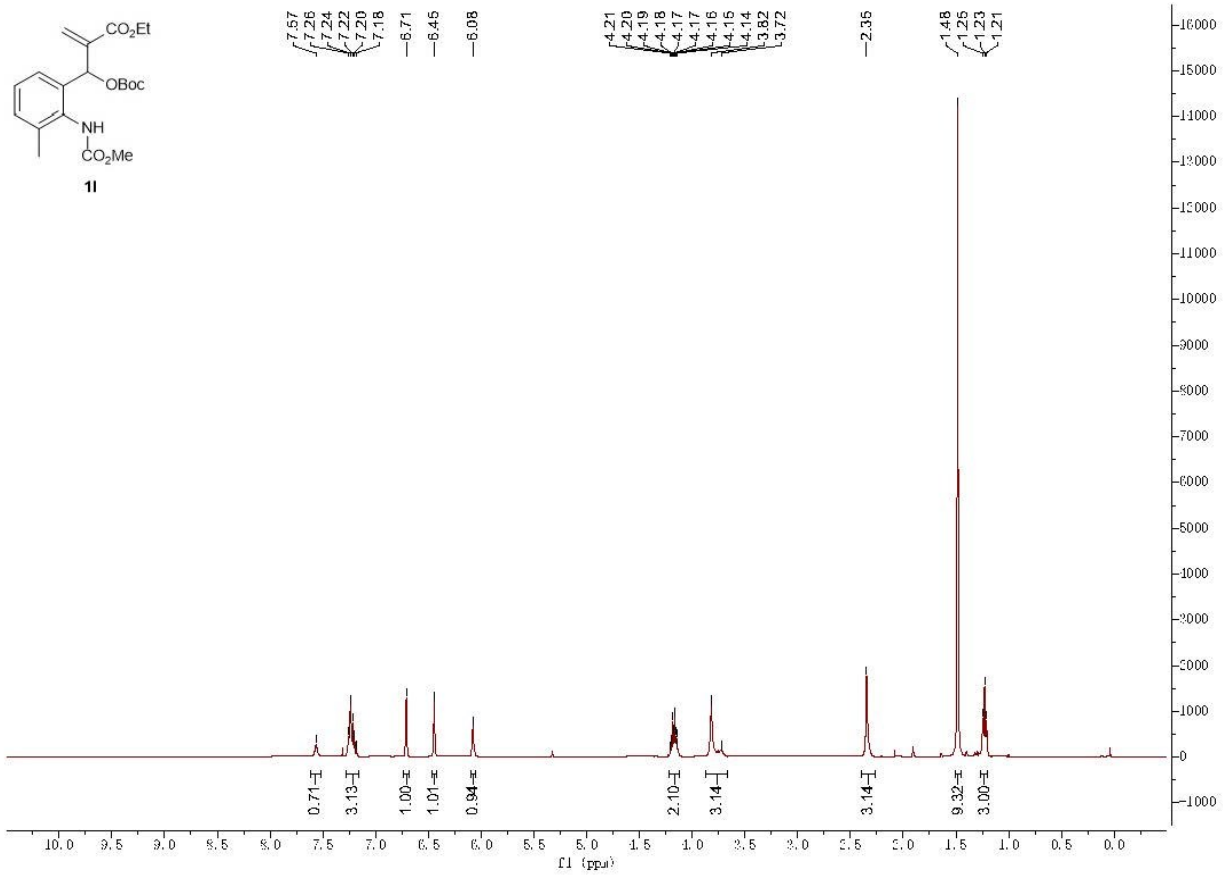
16.57
13.94
13.92
f1 (ppm)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NH
CO2Me
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7.18
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6.45
6.08
4.21
4.20
4.19
4.18
4.17
4.17
4.16
4.15
4.14
3.82
3.72
2.35
1.48
1.25
1.23
1.21
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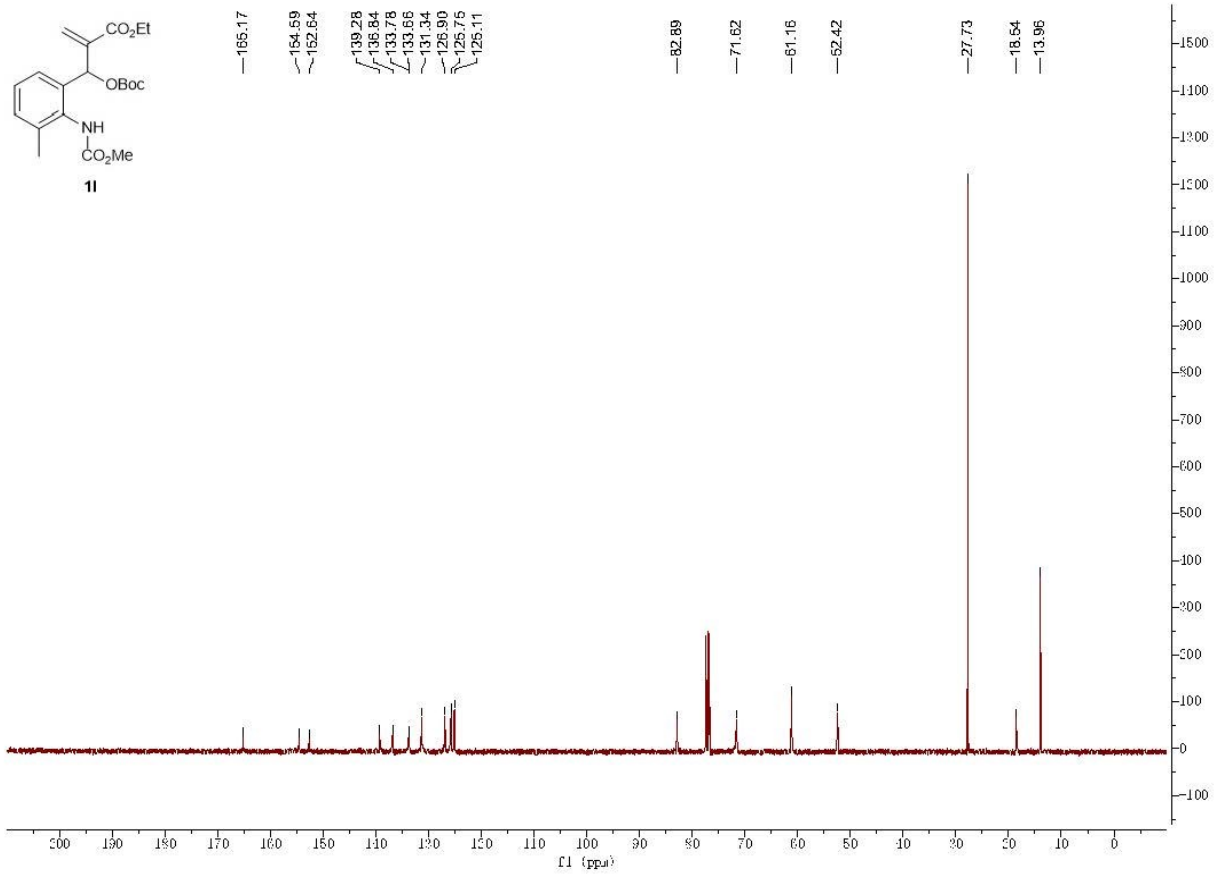
1.00
1.01
0.94
2.10
3.14
3.14
9.32
3.00
f1 (ppm)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OBoc
NH
CO2Me
1l
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152.64
139.28
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133.78
133.66
131.34
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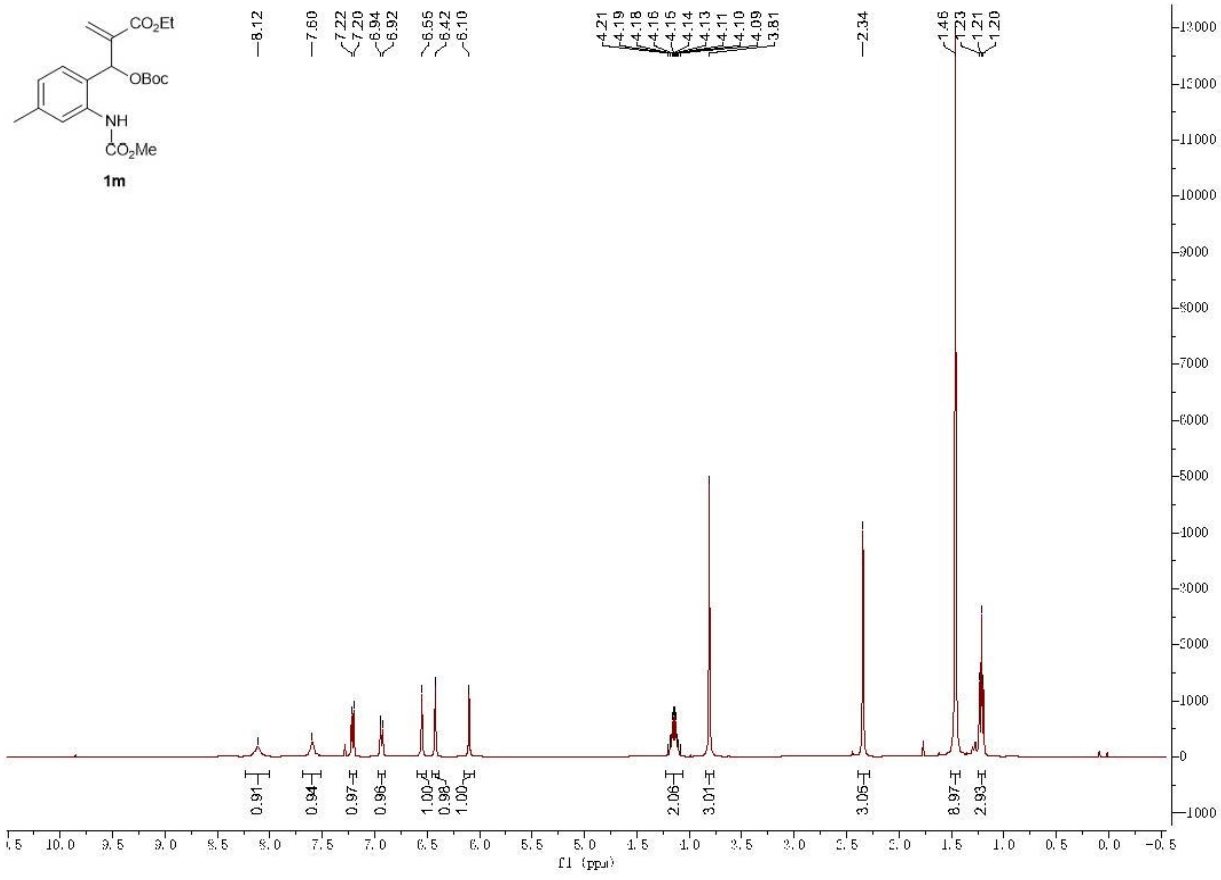
125.11
82.89
71.62
61.16
52.42
27.73
18.54
13.96
f1 (ppm)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OBoc
NH
CO2Me
1m
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7.22
7.20
6.94
6.92
6.55
6.42
6.10
4.21
4.19
4.18
4.16
4.15
4.14
4.13
4.11
4.10
4.09
3.81
2.34
1.46
1.23
1.21
1.20
0.91
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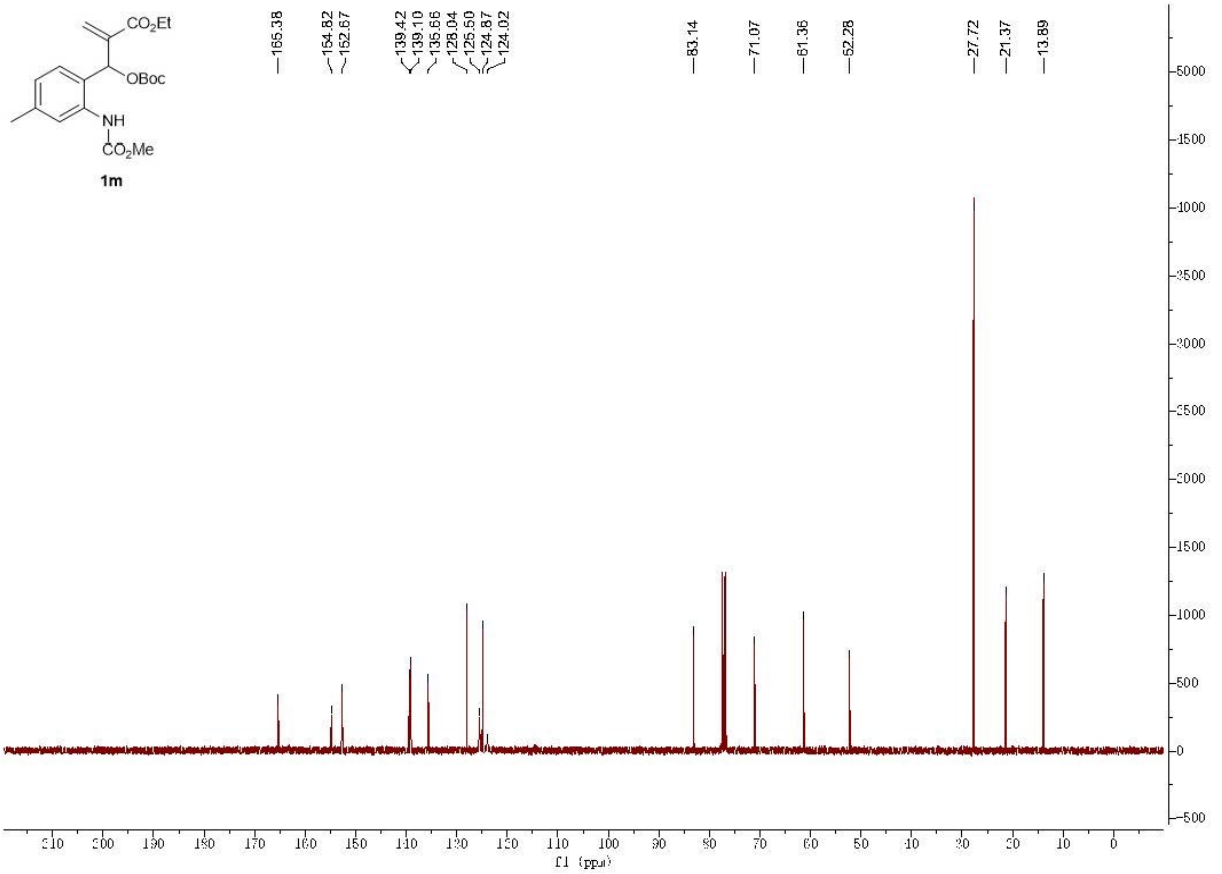
0.97
0.96
1.00
0.98
1.00
2.06
3.01
3.05
8.97
2.93
f1 (ppm)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CO2Me
1m
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135.66
128.04
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124.02
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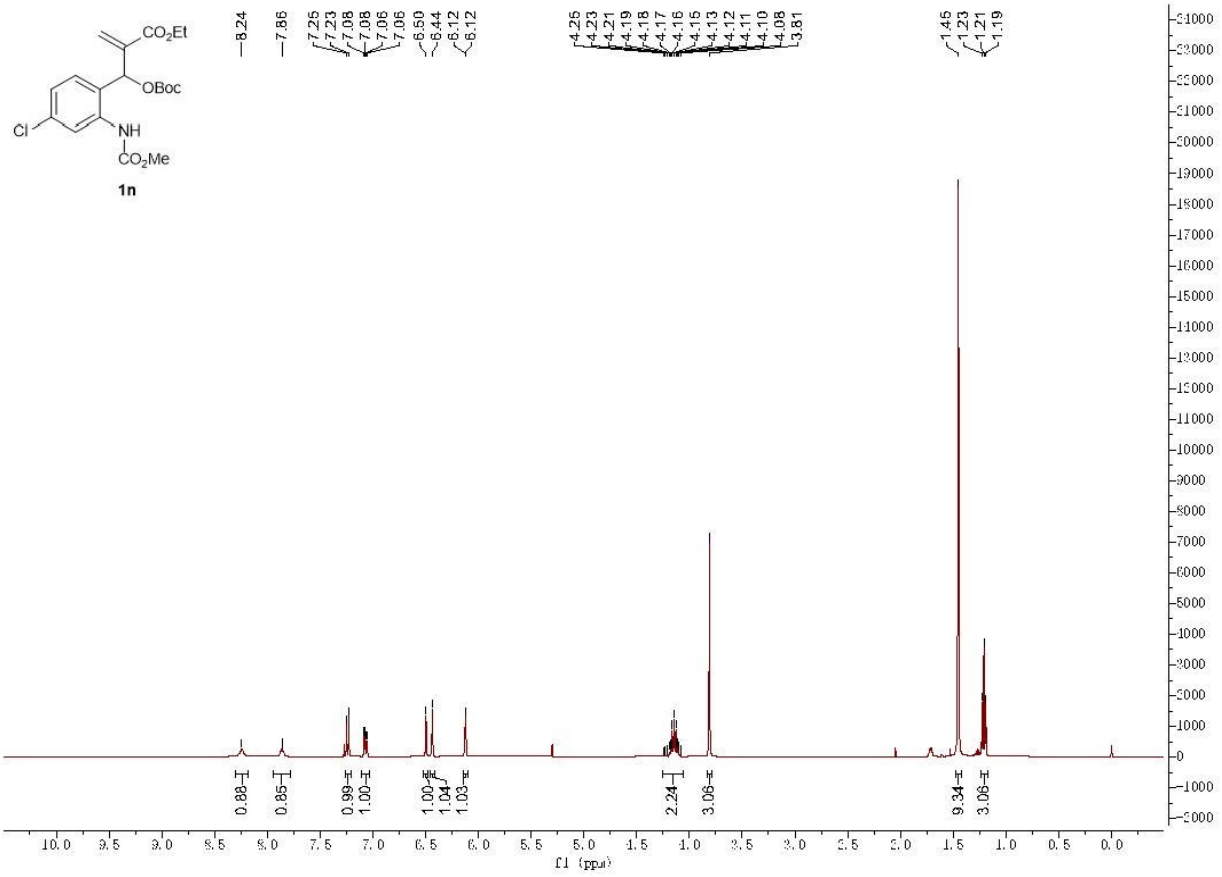
71.07
61.36
52.28
27.72
21.37
13.89
f1 (ppm)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OBoc
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NH
CO2Me
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7.08
7.08
7.06
7.06
6.50
6.44
6.12
6.12
4.25
4.23
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4.19
4.18
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4.15
4.13
4.12
4.11
4.10
4.08
3.81
1.45
1.23
1.21
1.19
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0.85
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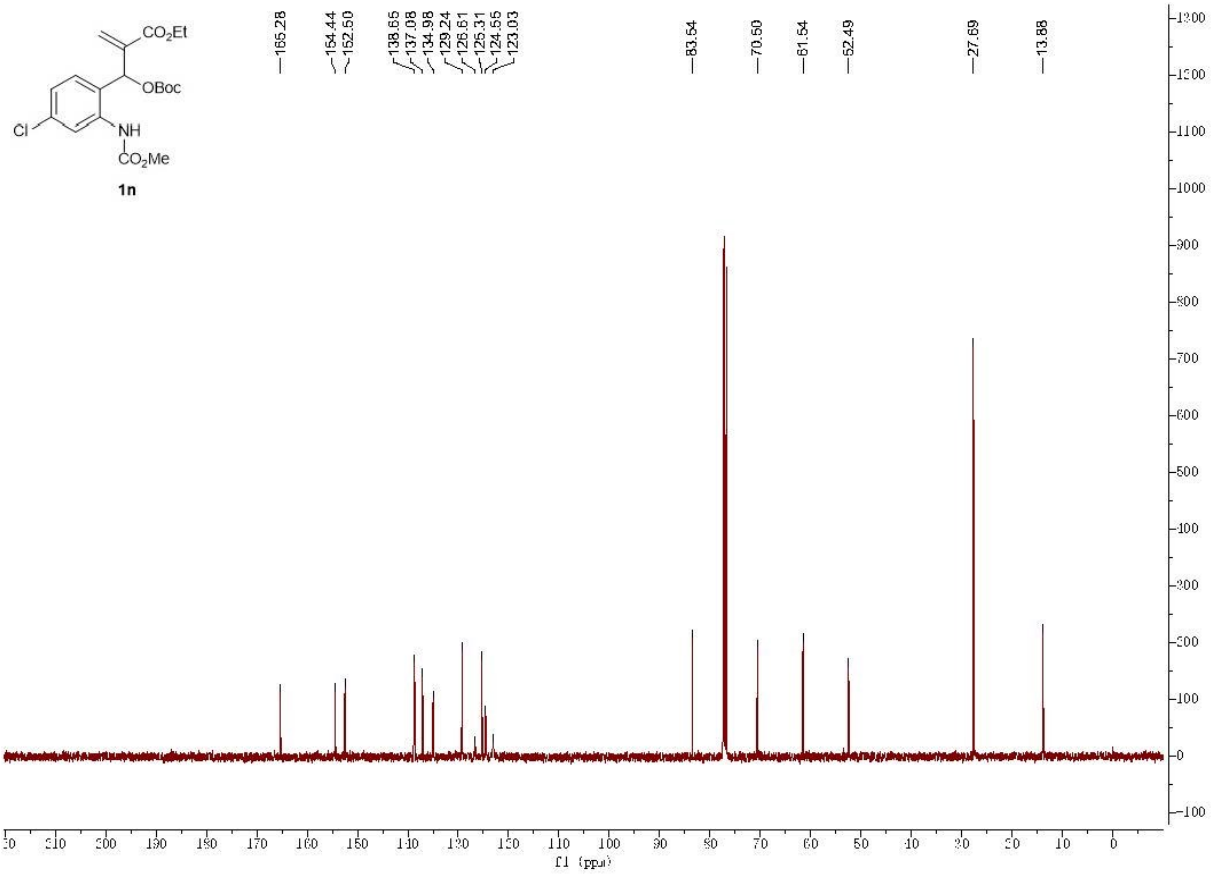
1.00
1.00
1.04
1.03
2.24
3.06
9.34
3.06
f1 (ppm)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OBoc
Cl
NH
CO2Me
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152.50
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137.08
134.98
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126.61
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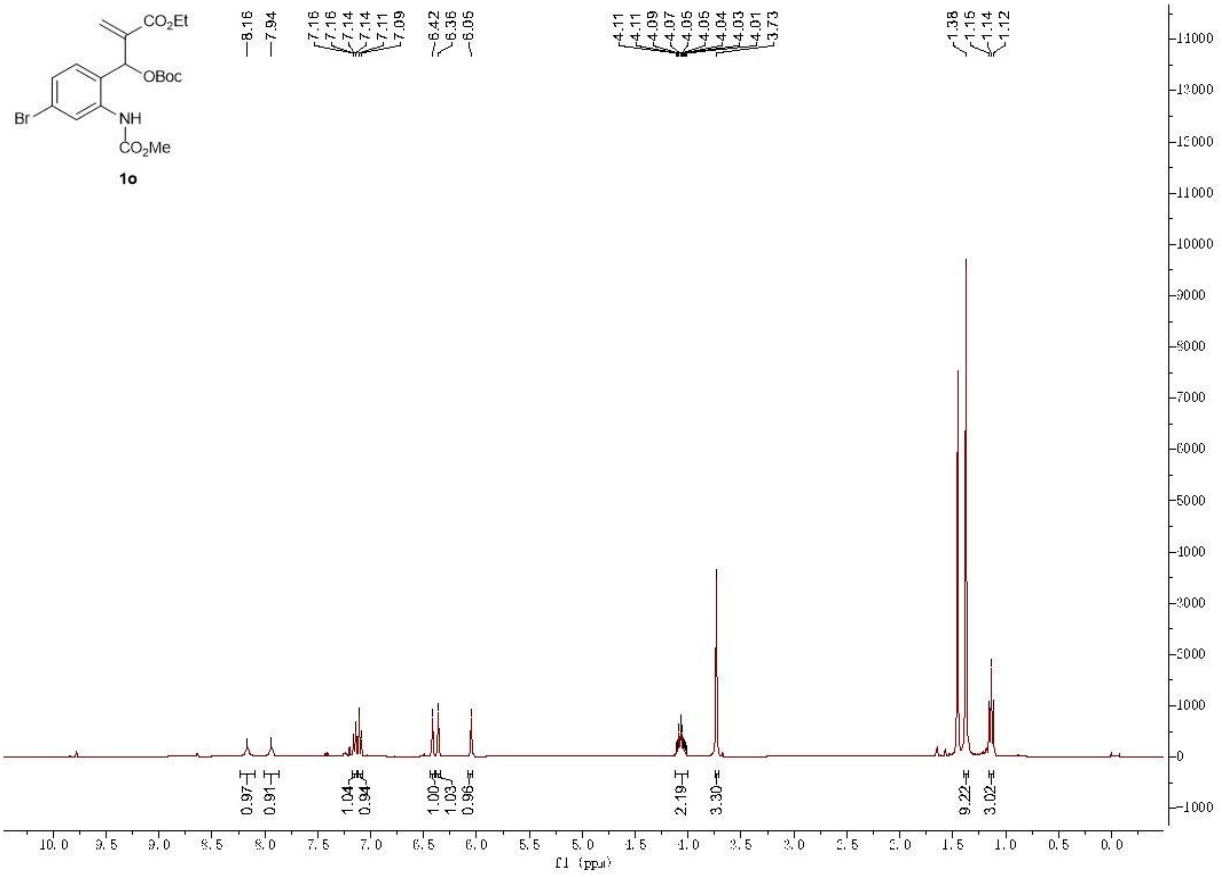
124.55
123.03
83.54
70.50
61.54
52.49
27.69
13.88
f1 (ppm)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OBoc
Br
NH
CO2Me
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7.16
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7.14
7.14
7.11
7.09
6.42
6.36
6.05
4.11
4.11
4.09
4.07
4.05
4.05
4.04
4.03
4.01
3.73
1.38
1.15
1.14
1.12
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0.94
1.00
1.03
0.96
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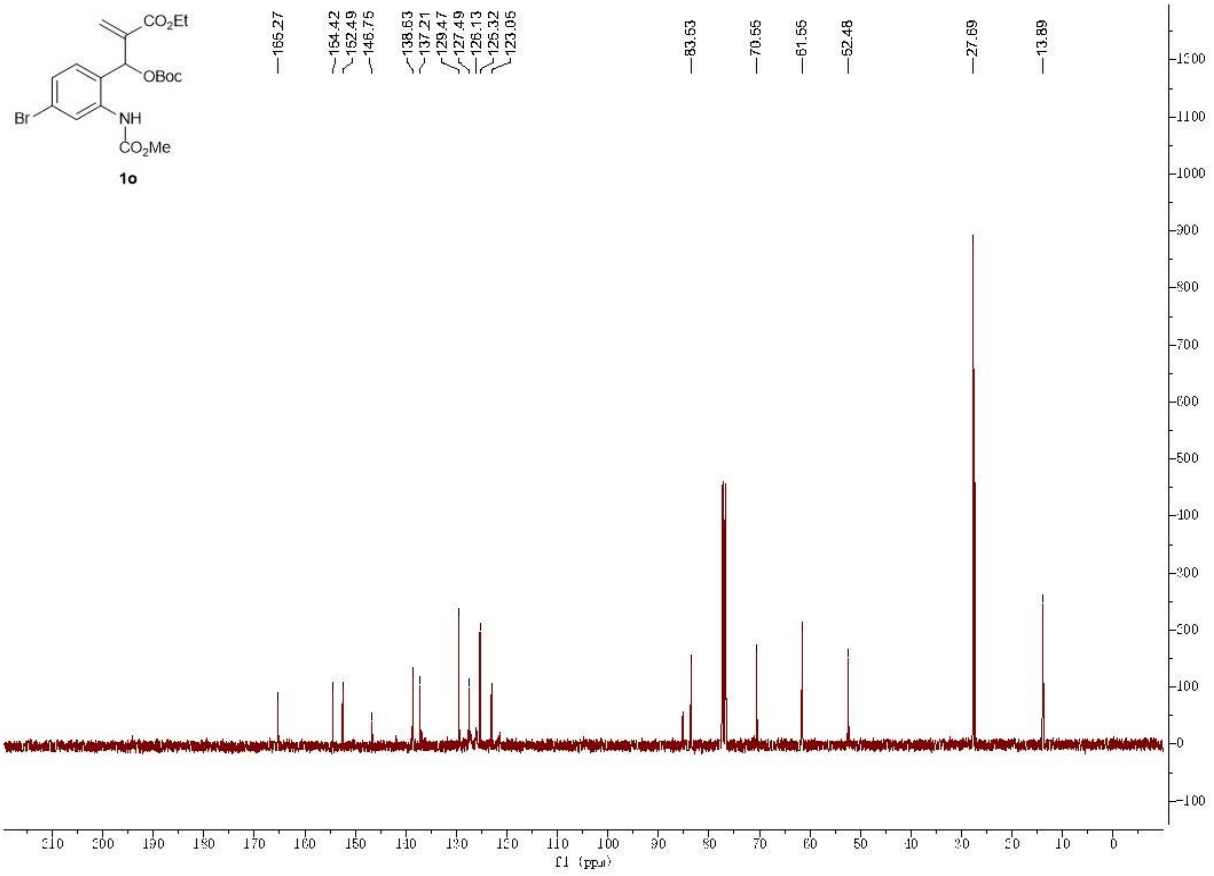
3.30
9.22
3.02
f1 (ppm)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OBoc
Br
NH
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137.21
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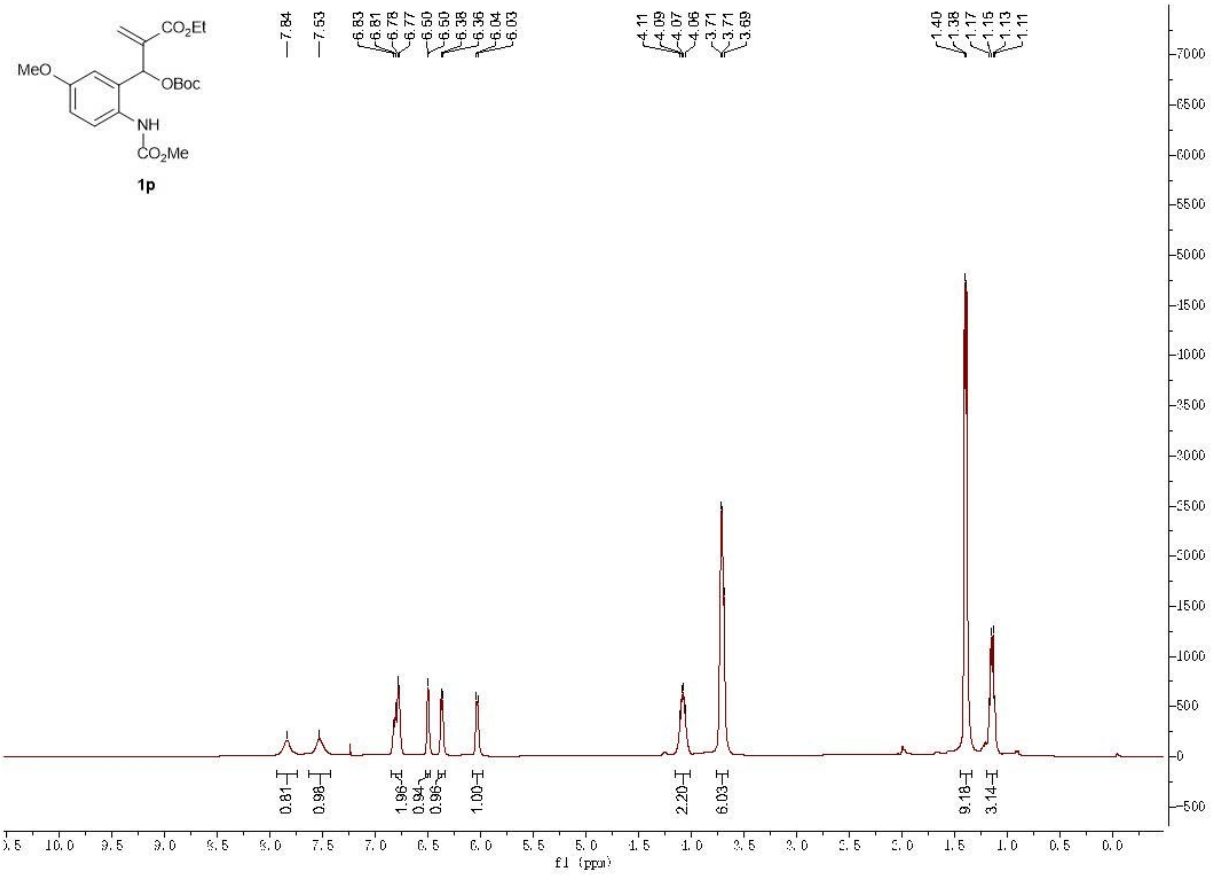
61.55
52.48
27.69
13.89
f1 (ppm)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6.03
4.11
4.09
4.07
4.06
3.71
3.71
3.69
1.40
1.38
1.17
1.15
1.13
1.11
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1.96
0.94
0.96
1.00
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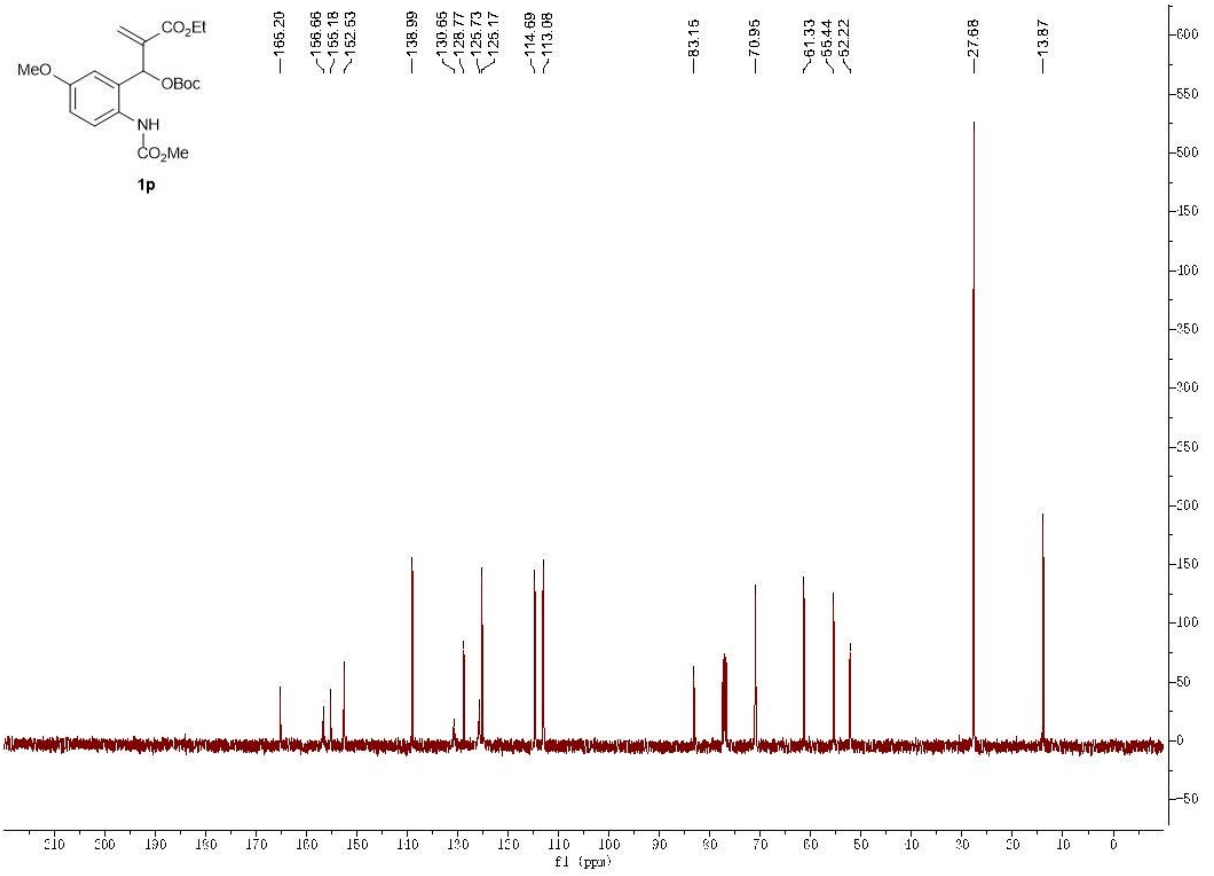
6.03
9.18
3.14
f1 (ppm)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NH
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130.65
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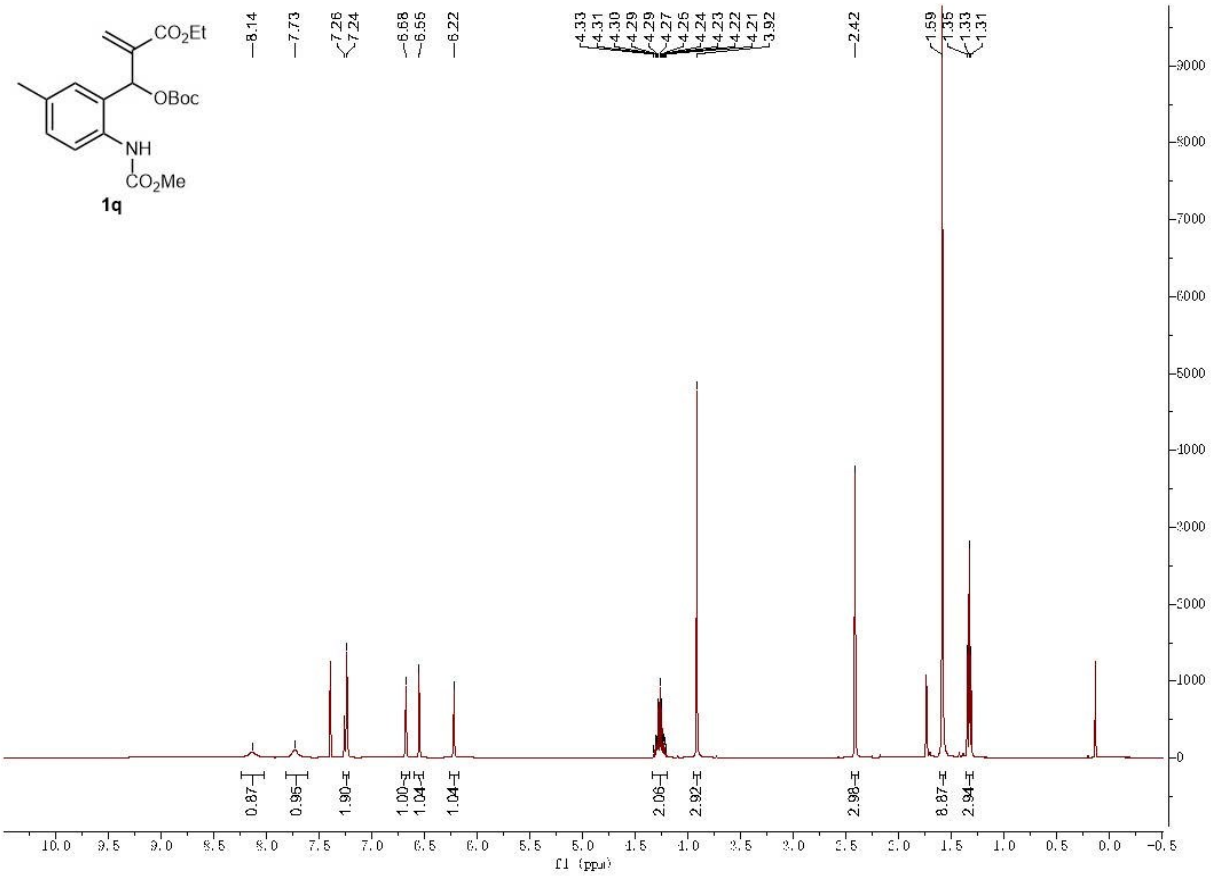
f1 (ppm)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4.31
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4.29
4.29
4.27
4.25
4.24
4.23
4.22
4.21
3.92
2.42
1.59
1.35
1.33
1.31
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1.00
1.04
1.04
2.06
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2.98
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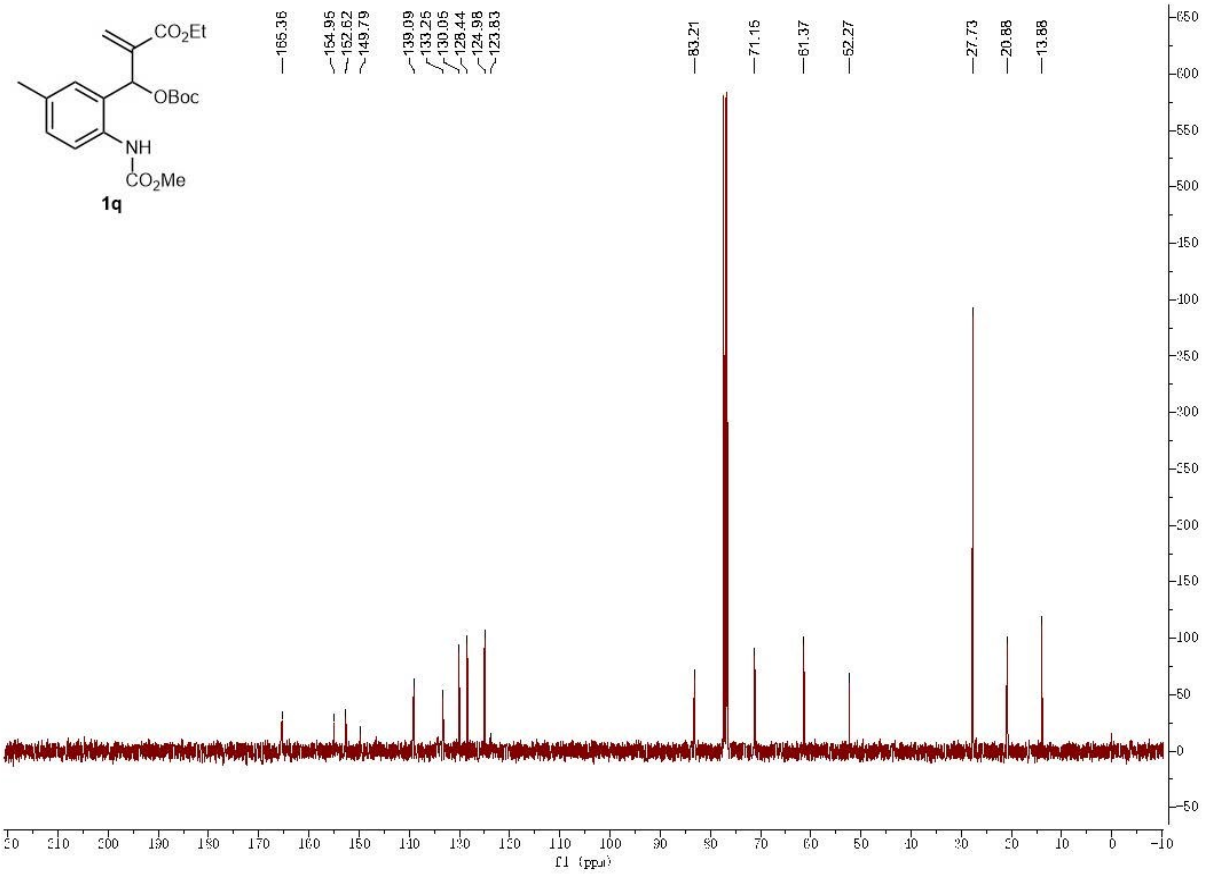
2.94
f1 (ppm)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NH
CO2Me
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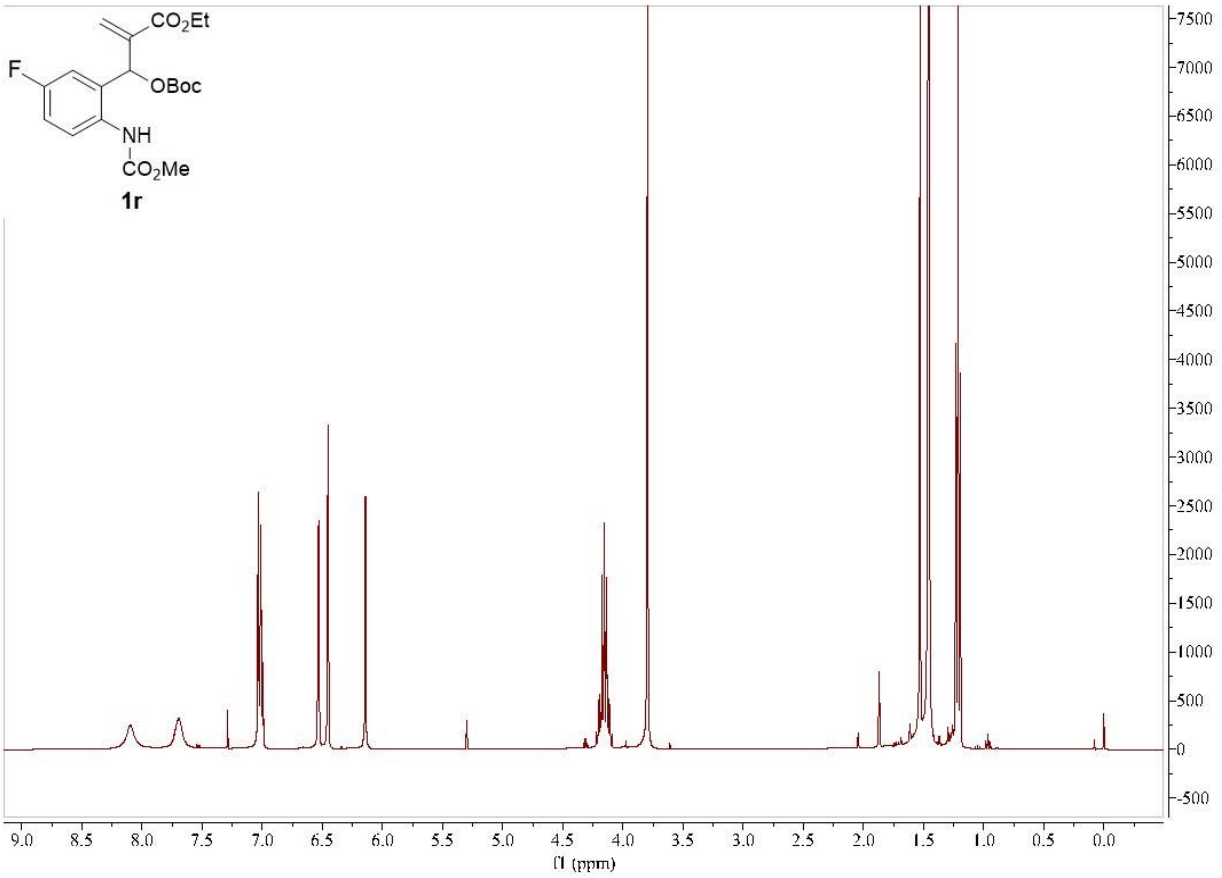
123.83
83.21
71.15
61.37
52.27
27.73
20.88
13.88
f1 (ppm)


CO2Et
F
OBoc
NH
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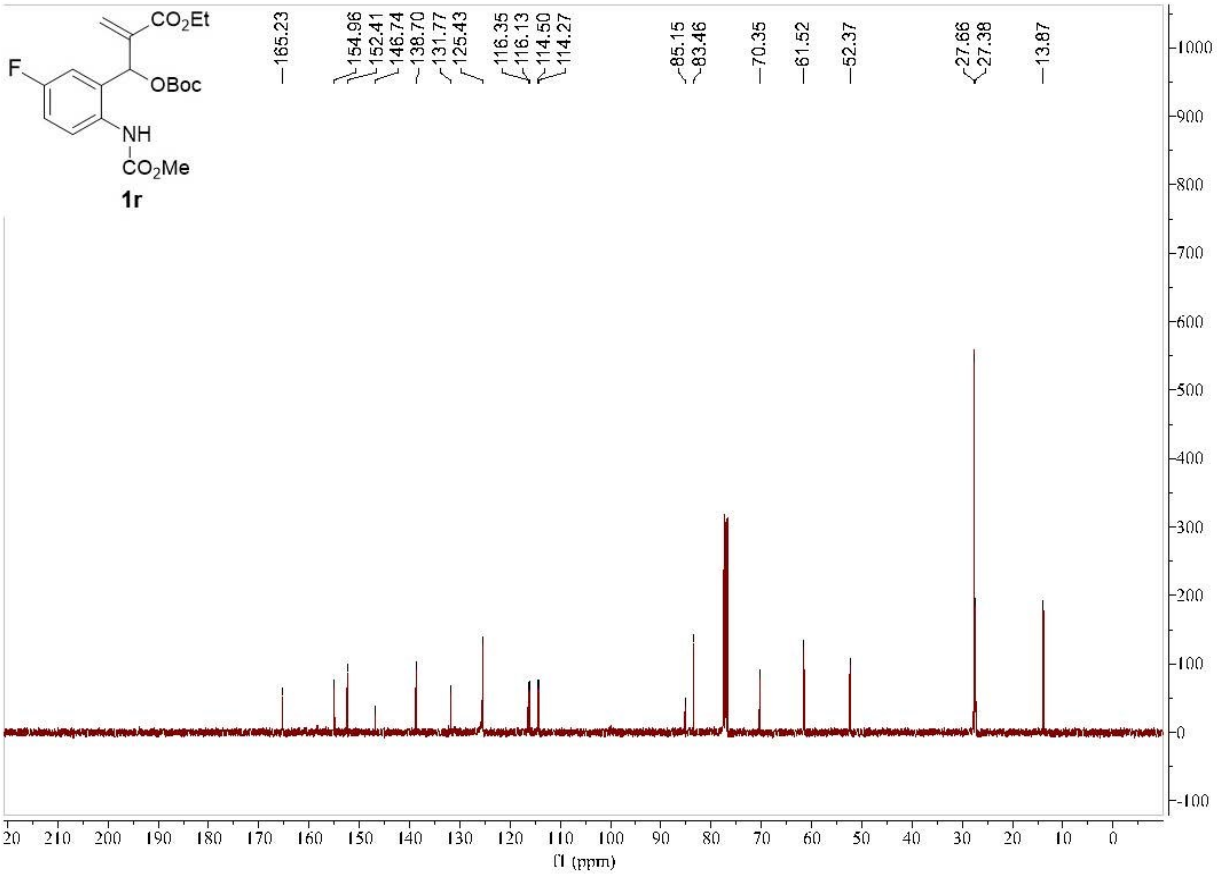
1r
f1 (ppm)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F
OBoc
NH
CO2Me
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61.52
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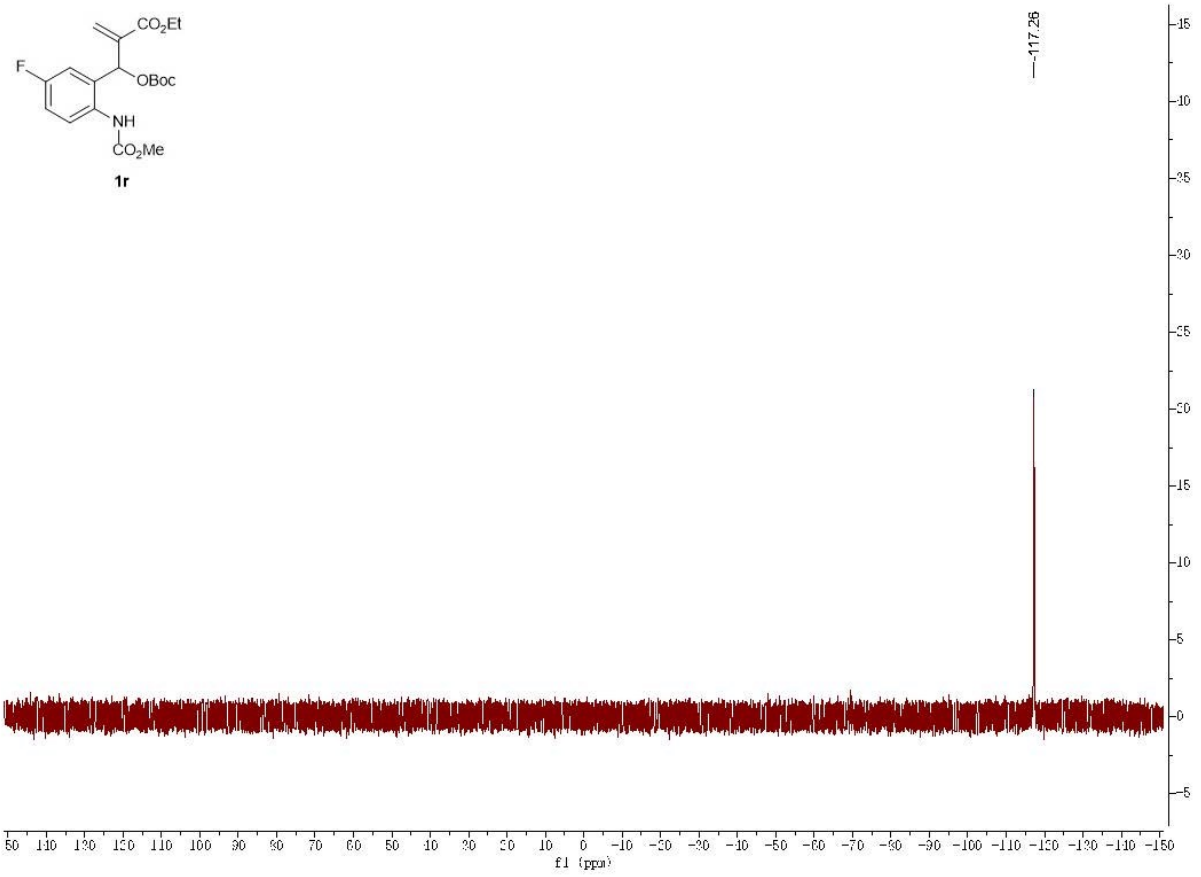
13.87
f1 (ppm)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NH
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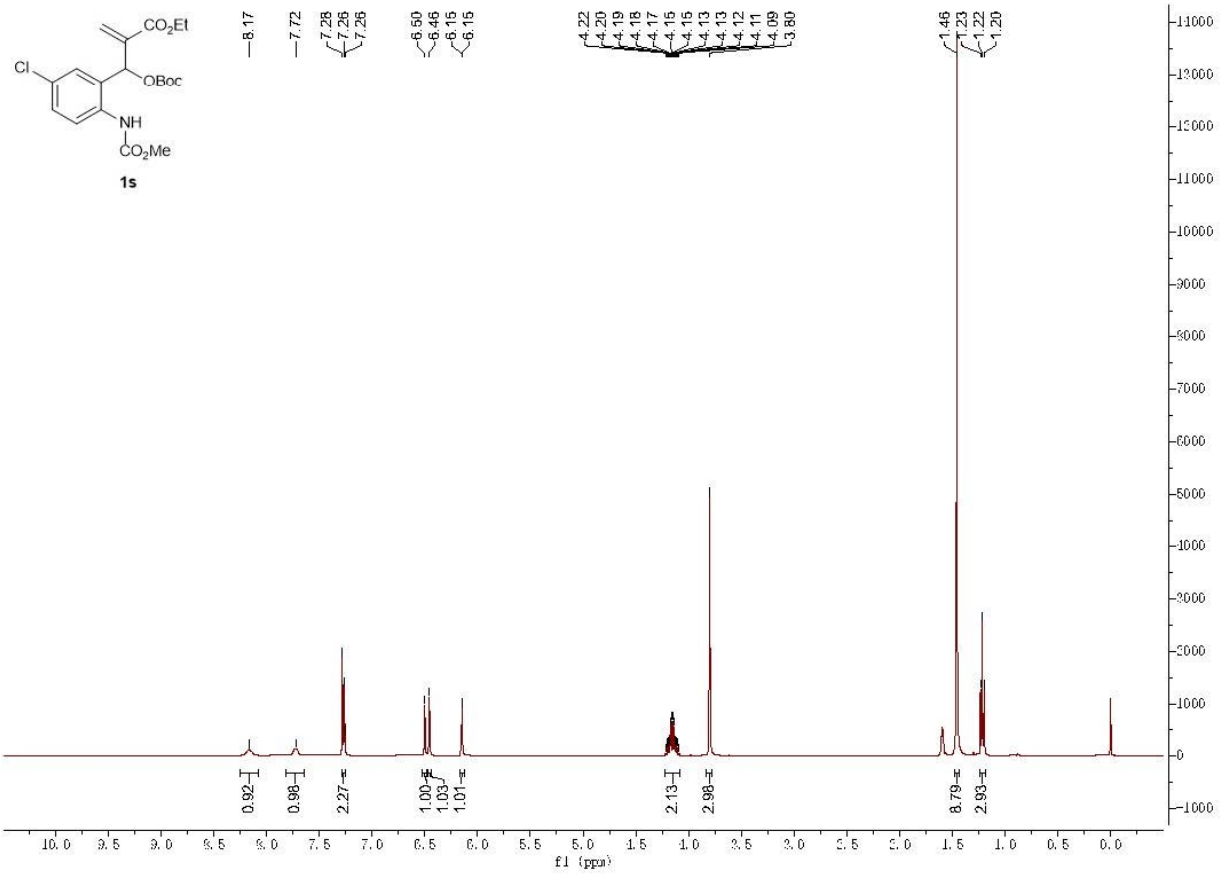
1r
-117.26
f1 (ppm)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Cl
OBoc
NH
CO2Me
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6.15
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4.18
4.17
4.15
4.15
4.13
4.13
4.12
4.11
4.09
3.80
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1.23
1.22
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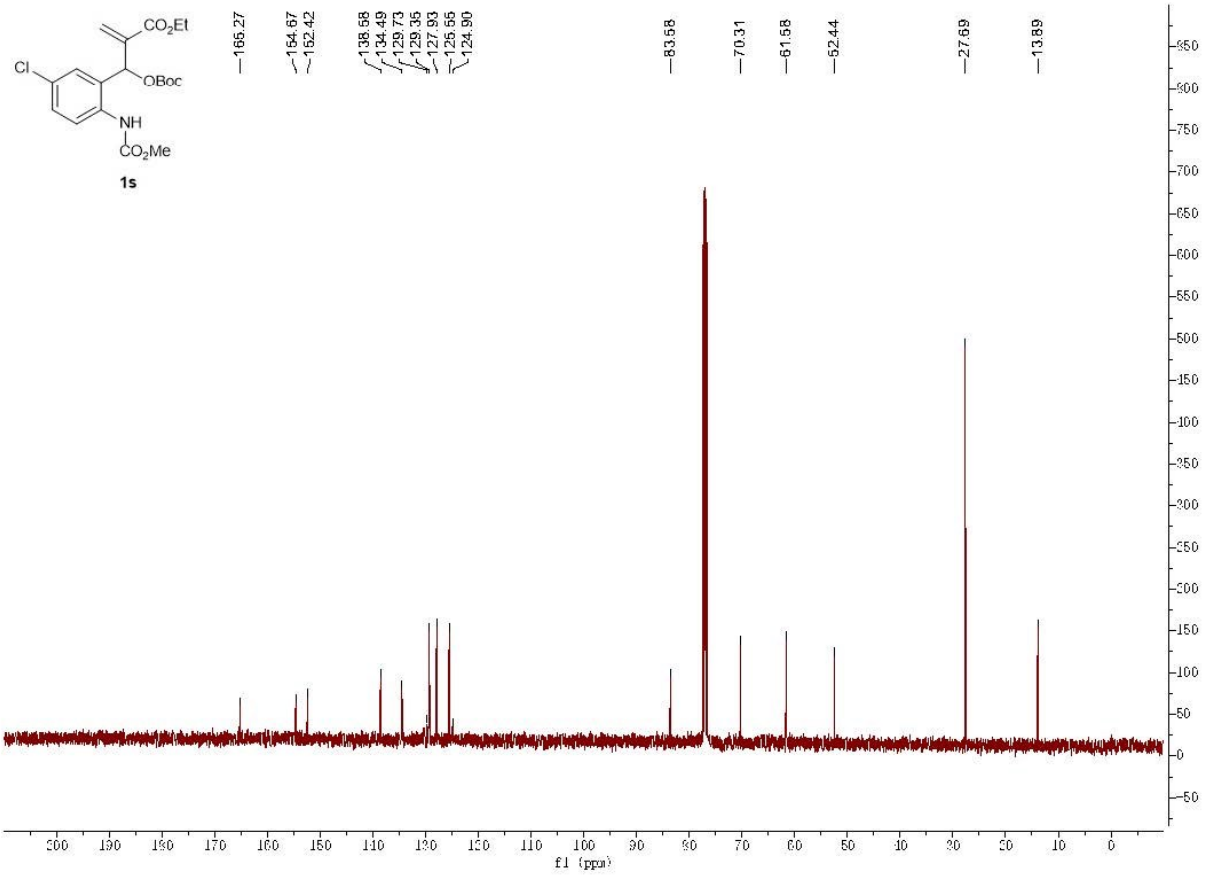
f1 (ppm)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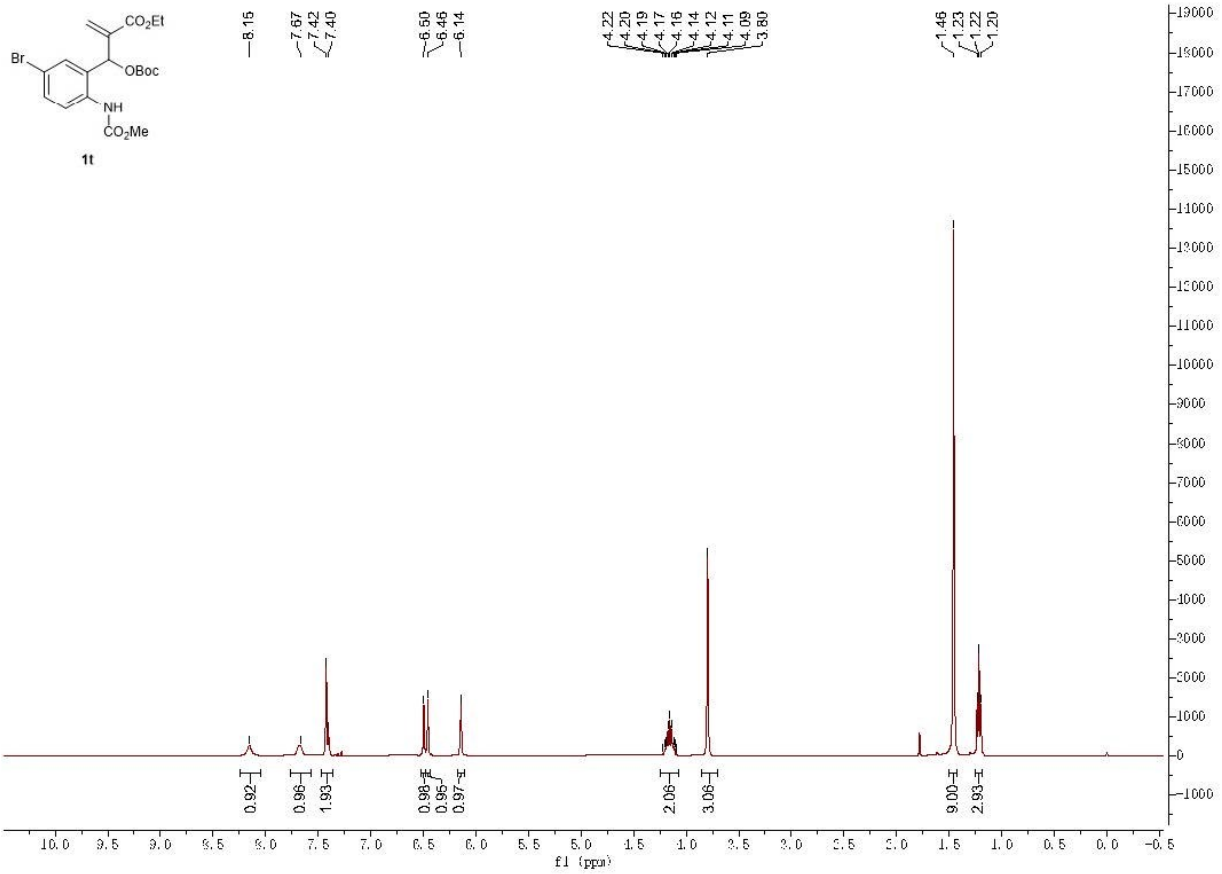
13.89
f1 (ppm)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OBoc
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4.20
4.19
4.17
4.16
4.14
4.12
4.11
4.09
3.80
1.46
1.23
1.22
1.20
0.92
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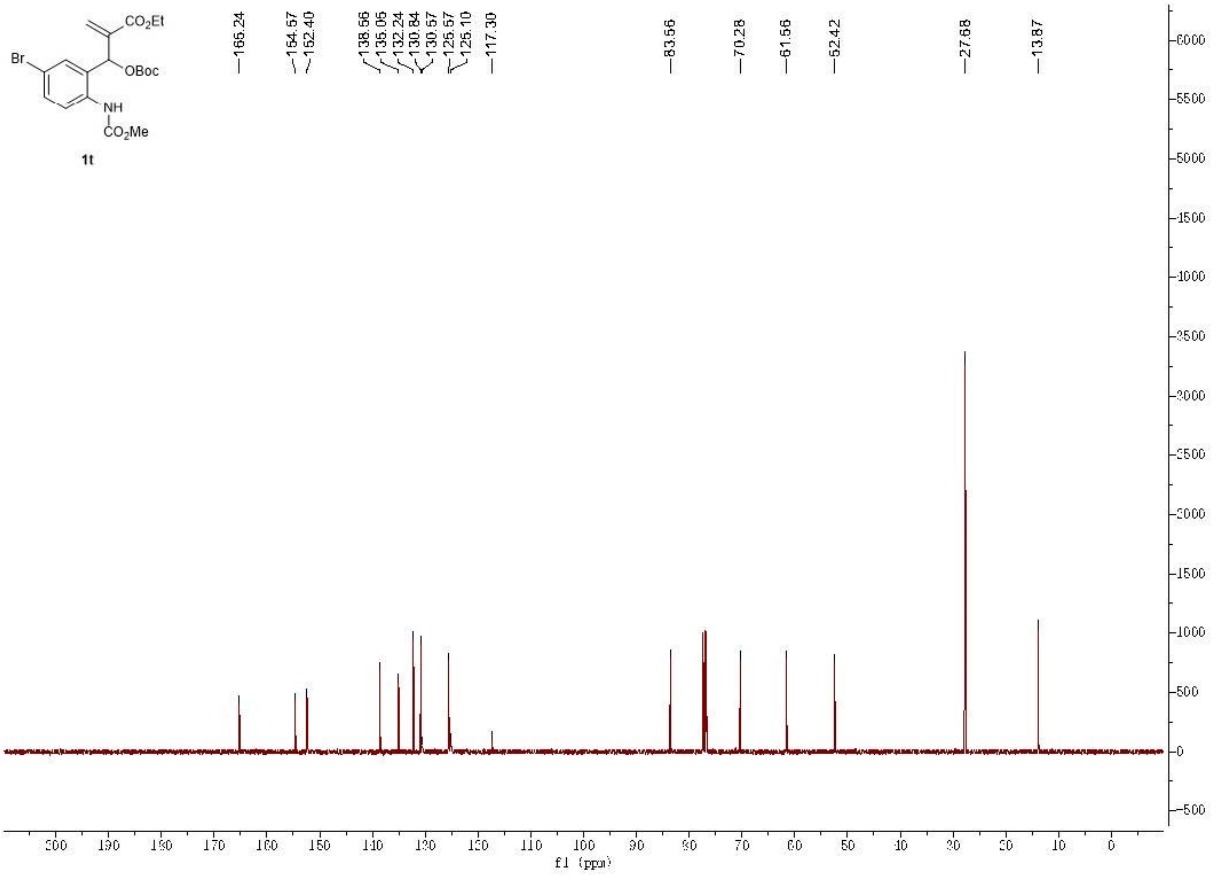
1.93
0.98
0.95
0.97
2.06
3.06
9.00
2.93
f1 (ppm)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Br
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NH
CO2Me
1t
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135.05
132.24
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130.57
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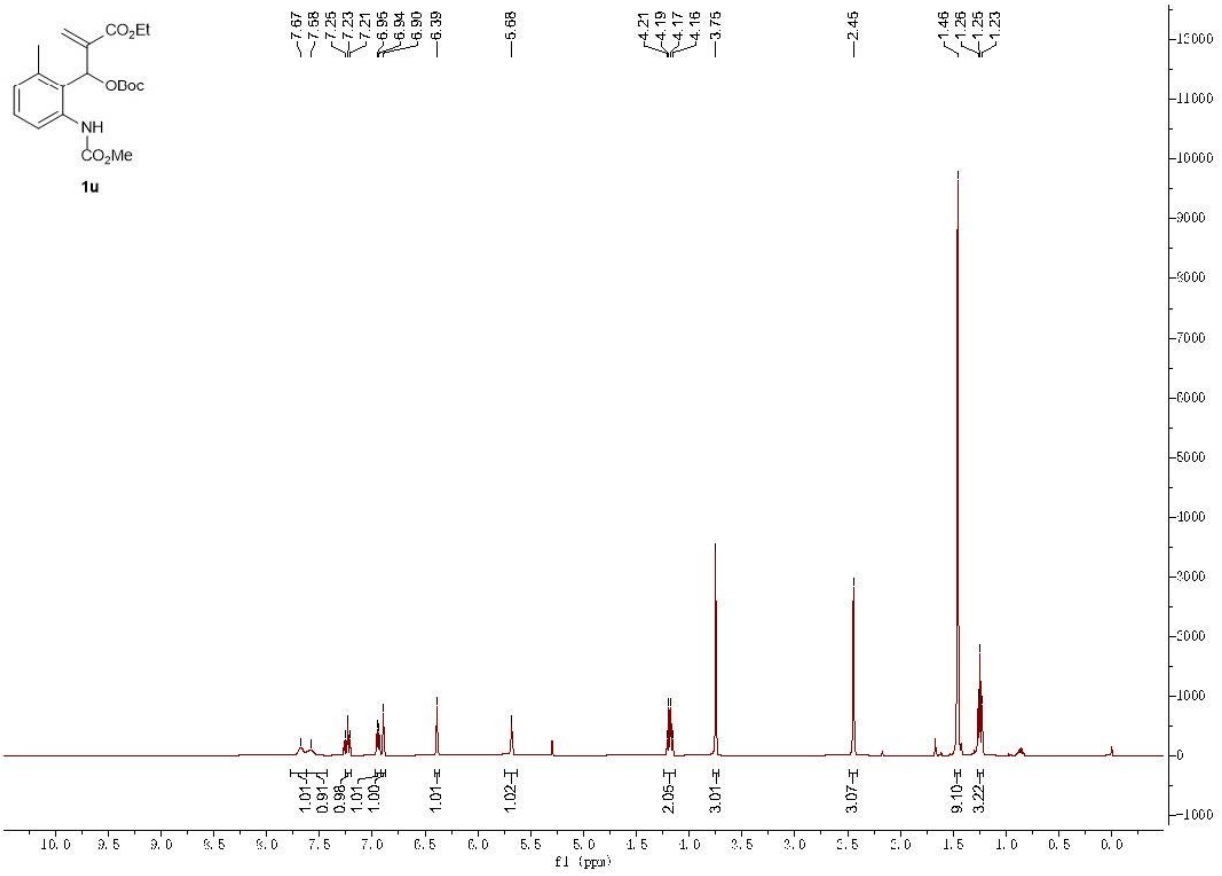
125.10
117.30
83.56
70.28
61.56
62.42
27.68
13.87
f1 (ppm)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NH
CO2Me
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5.68
4.21
4.19
4.17
4.16
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2.45
1.46
1.26
1.25
1.23
1.01
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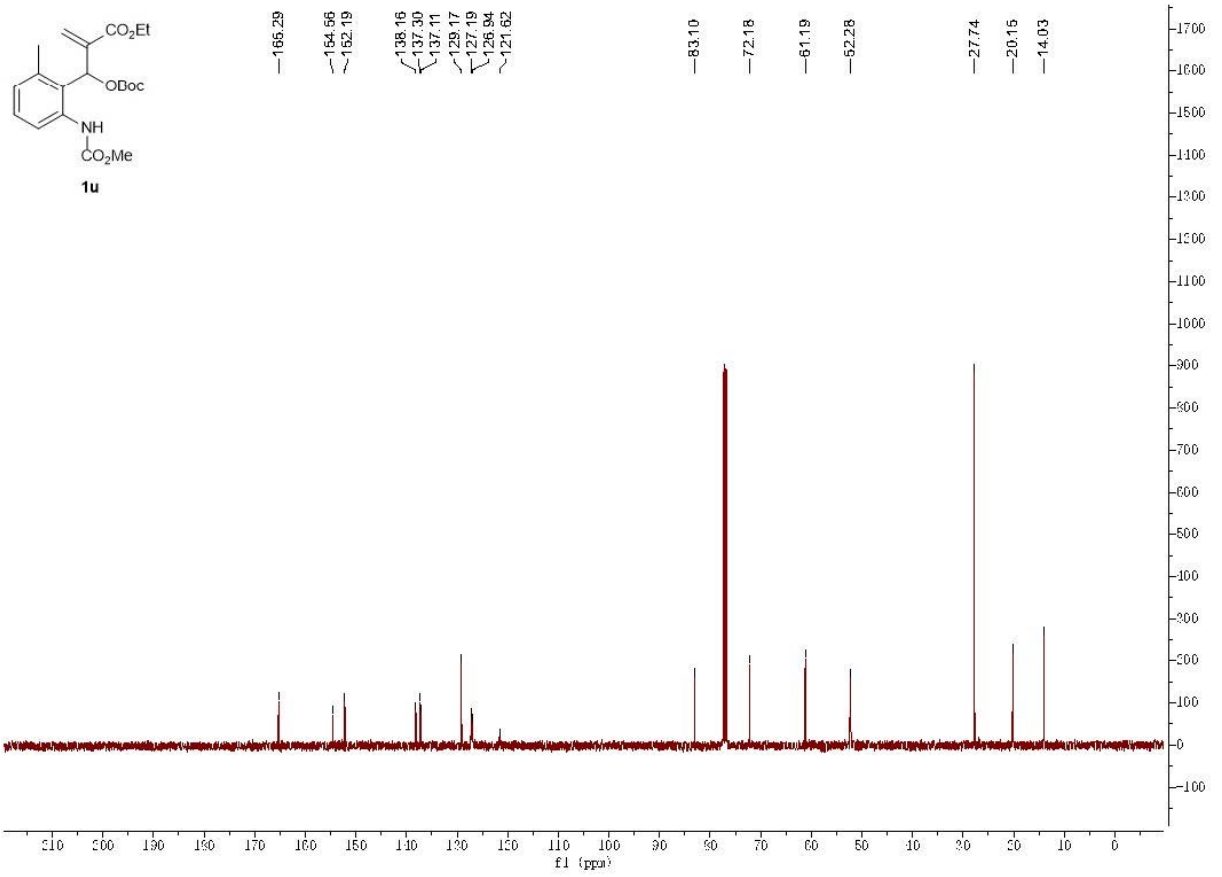
1.00
1.01
1.02
2.05
3.01
3.07
9.10
3.22
f1 (ppm)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121.62
83.10
72.18
61.19
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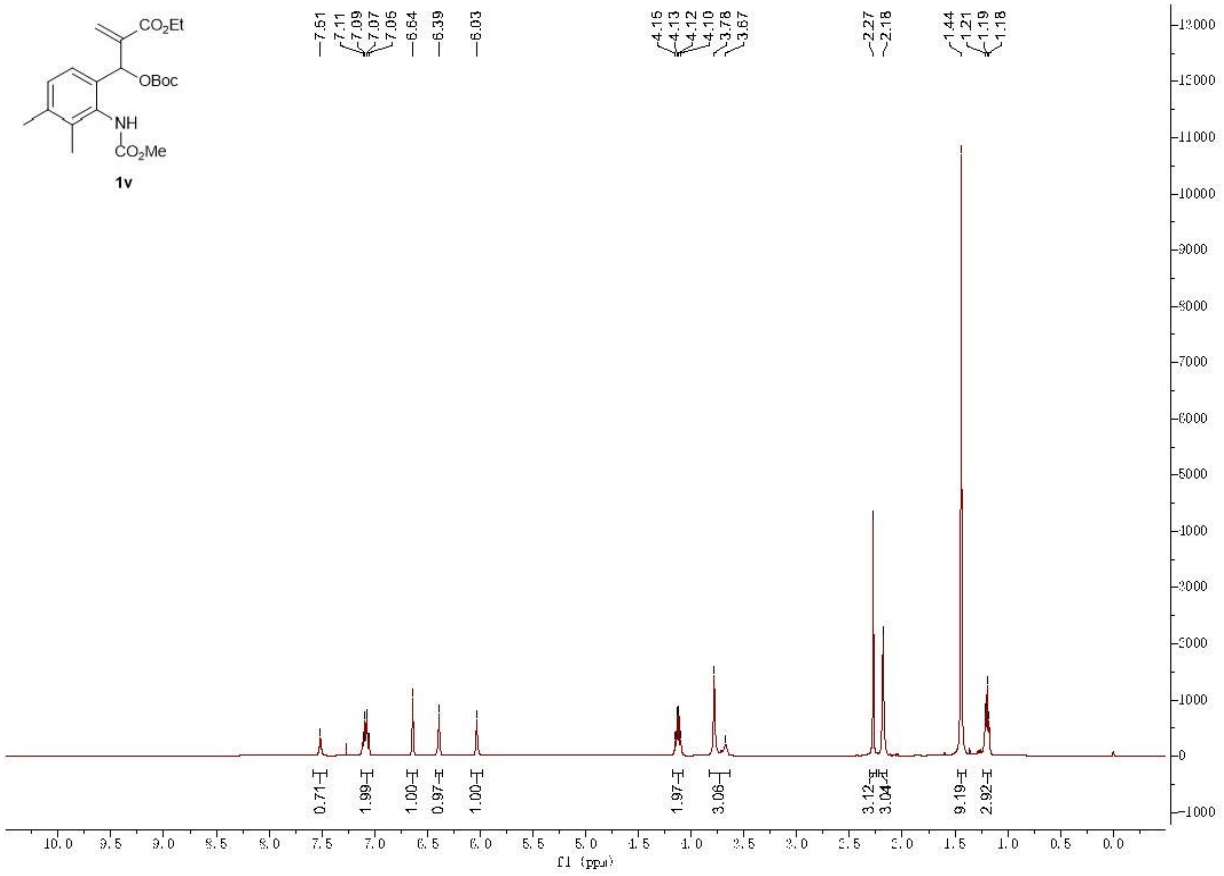
27.74
20.15
14.03
f1 (ppm)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4.15
4.13
4.12
4.10
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2.27
2.18
1.44
1.21
1.19
1.18
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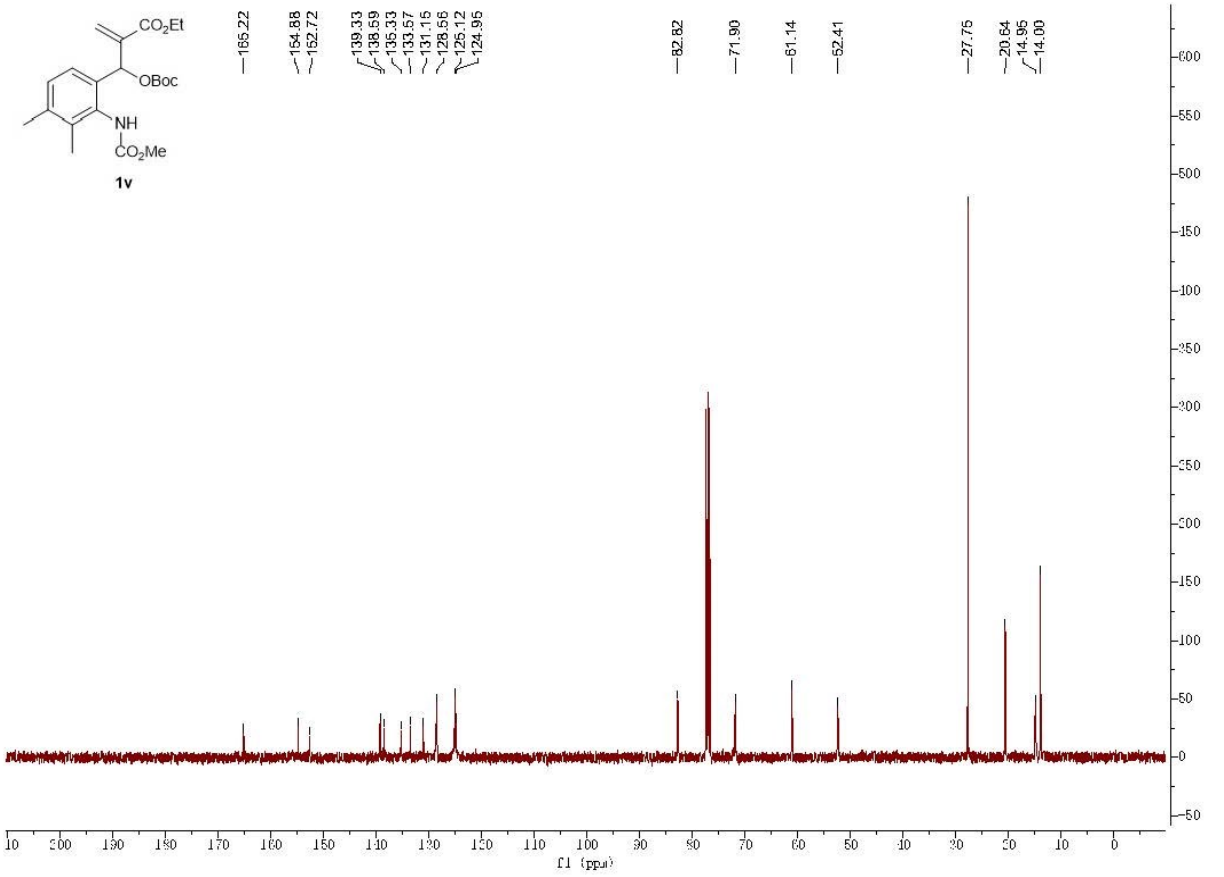
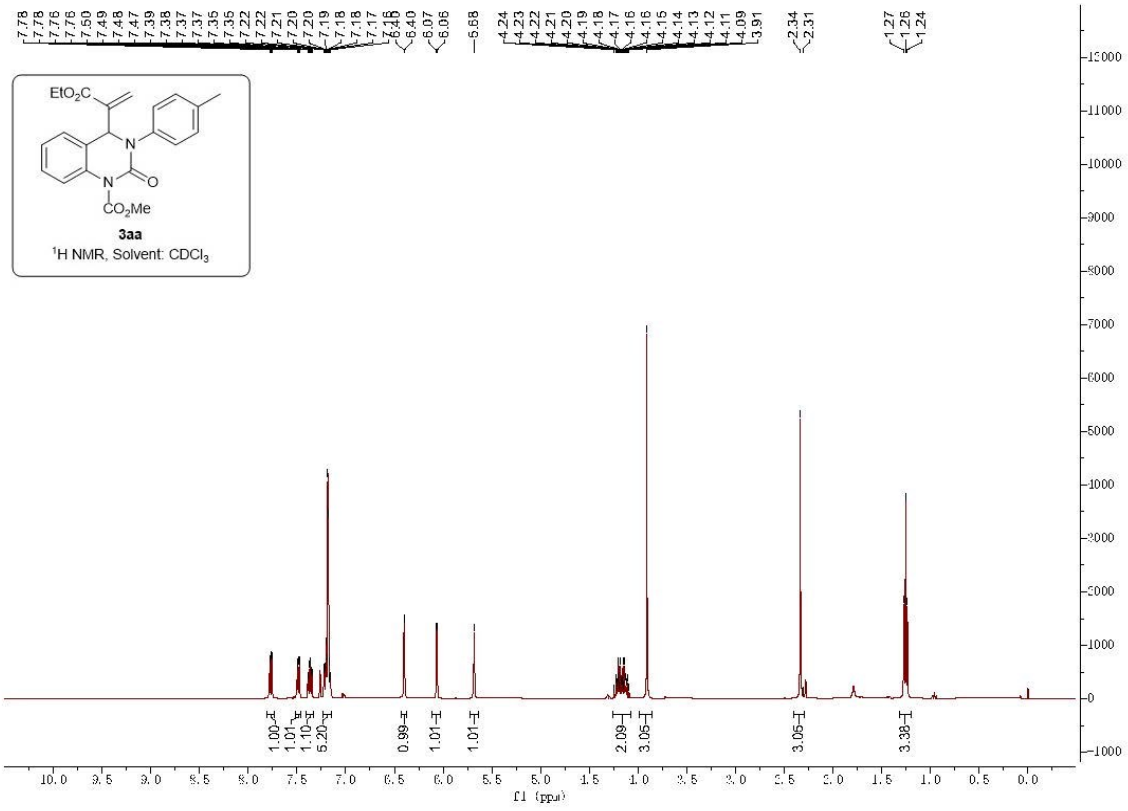
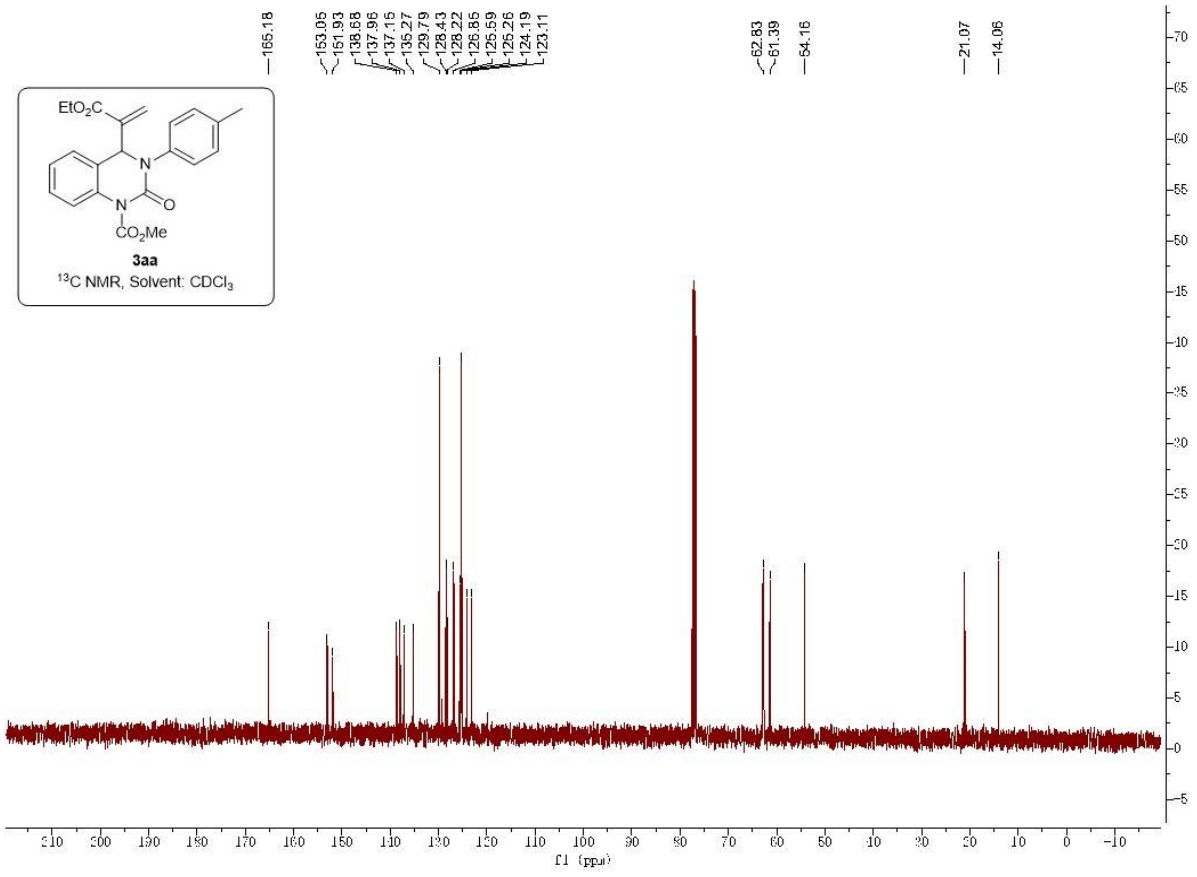
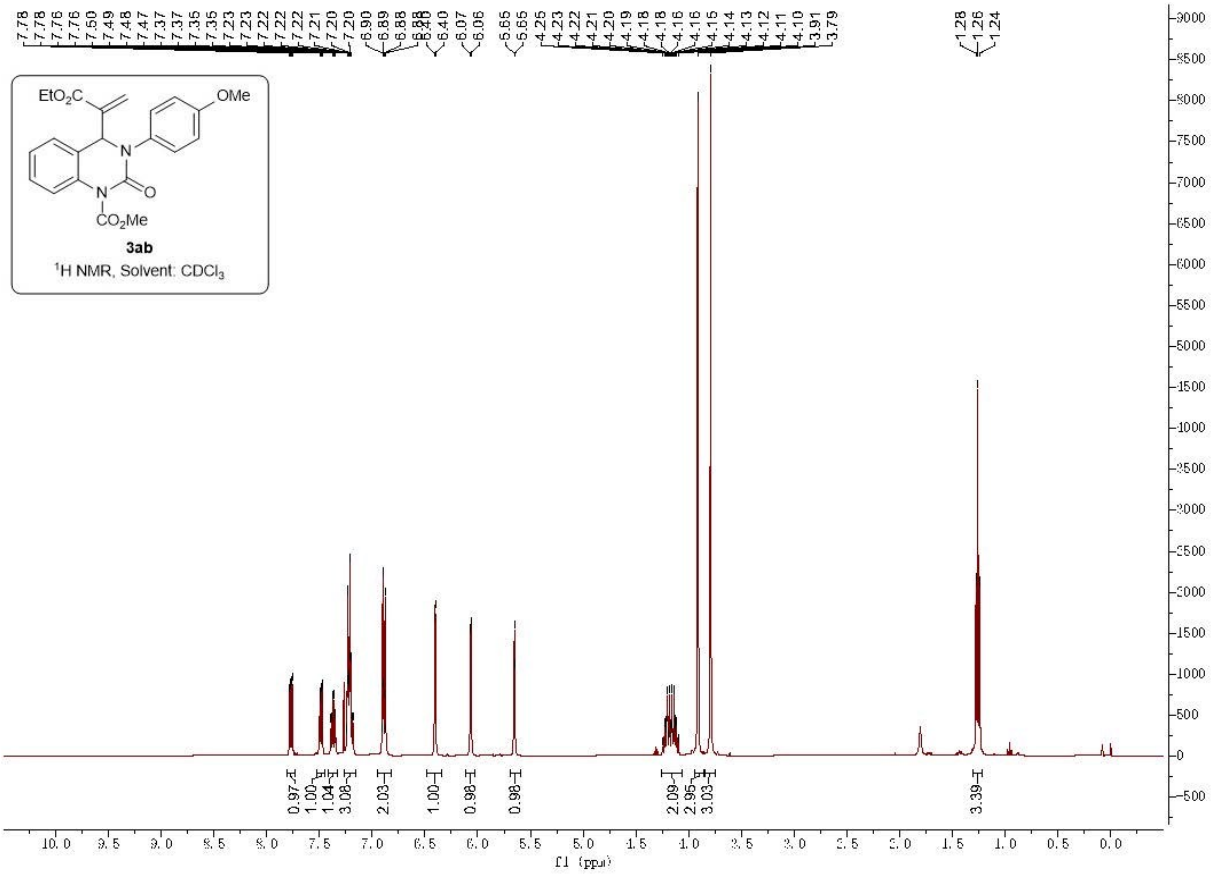
1.99
1.00
0.97
1.00
1.97
3.06
3.12
3.04
9.19
2.92
f1 (ppm)

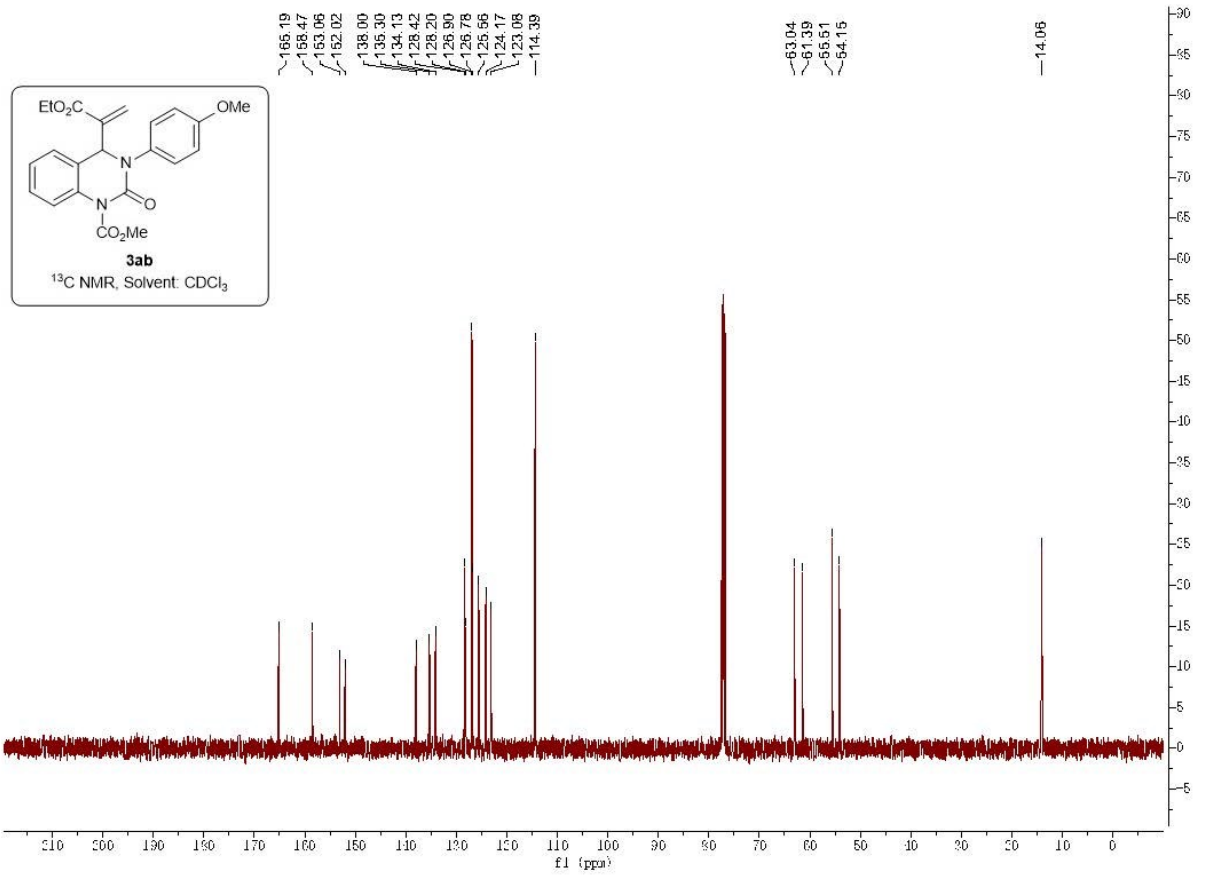

CO2Et
OBoc
NH
CO2Me
1v
165.22
154.88
152.72
139.33
138.59
135.33
133.57
131.15
128.56
125.12
124.95
82.82
71.90
61.14
52.41
27.75
20.64
14.95
14.00
f1 (ppm)

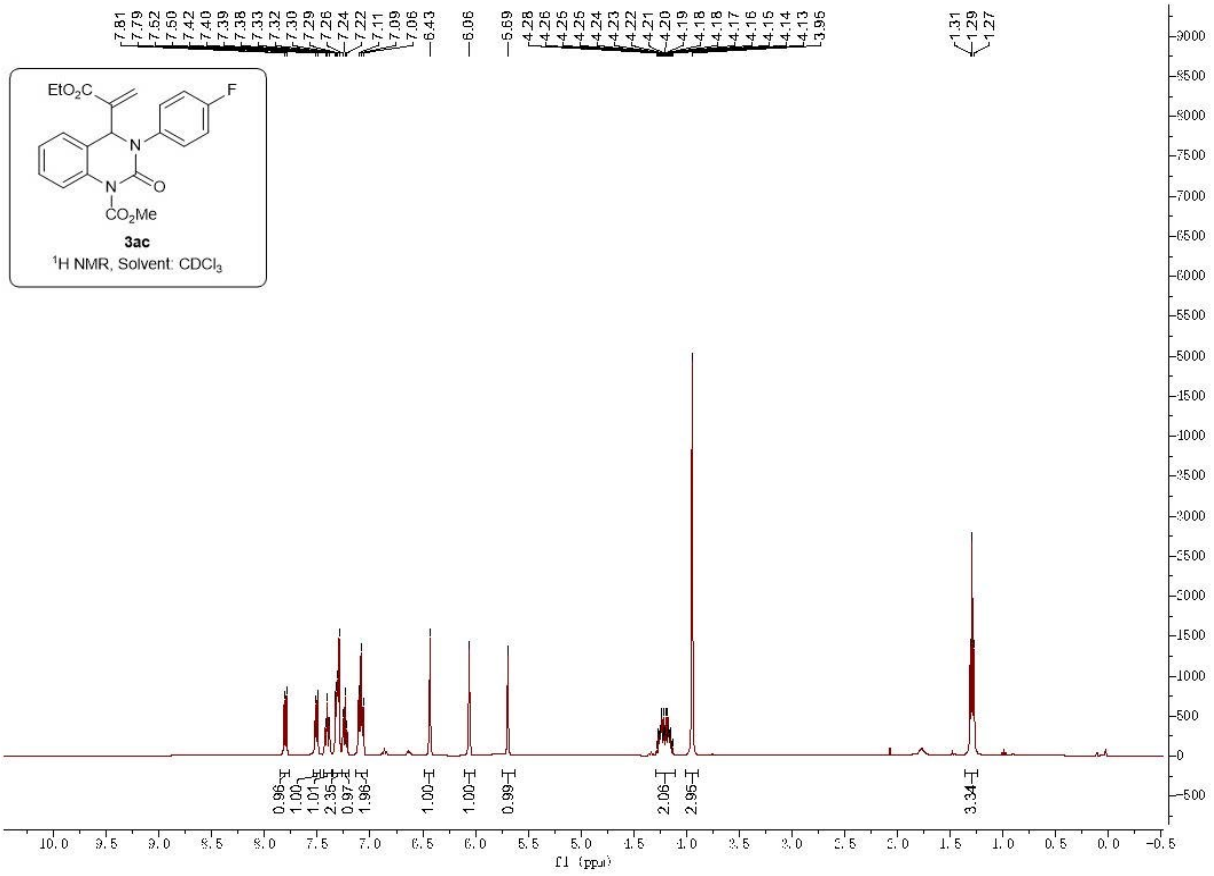
8.2. DABCO catalyzed [4+2] cycloadducts 3

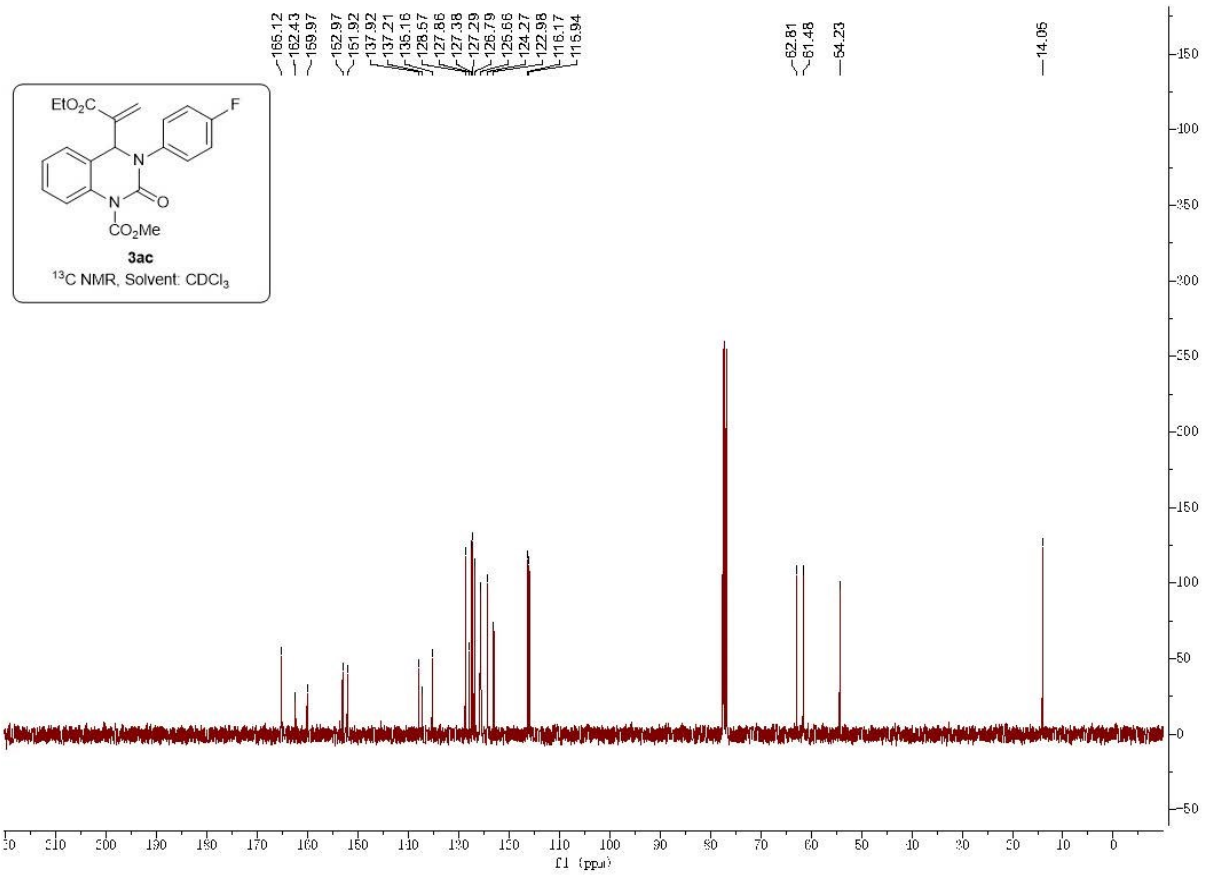


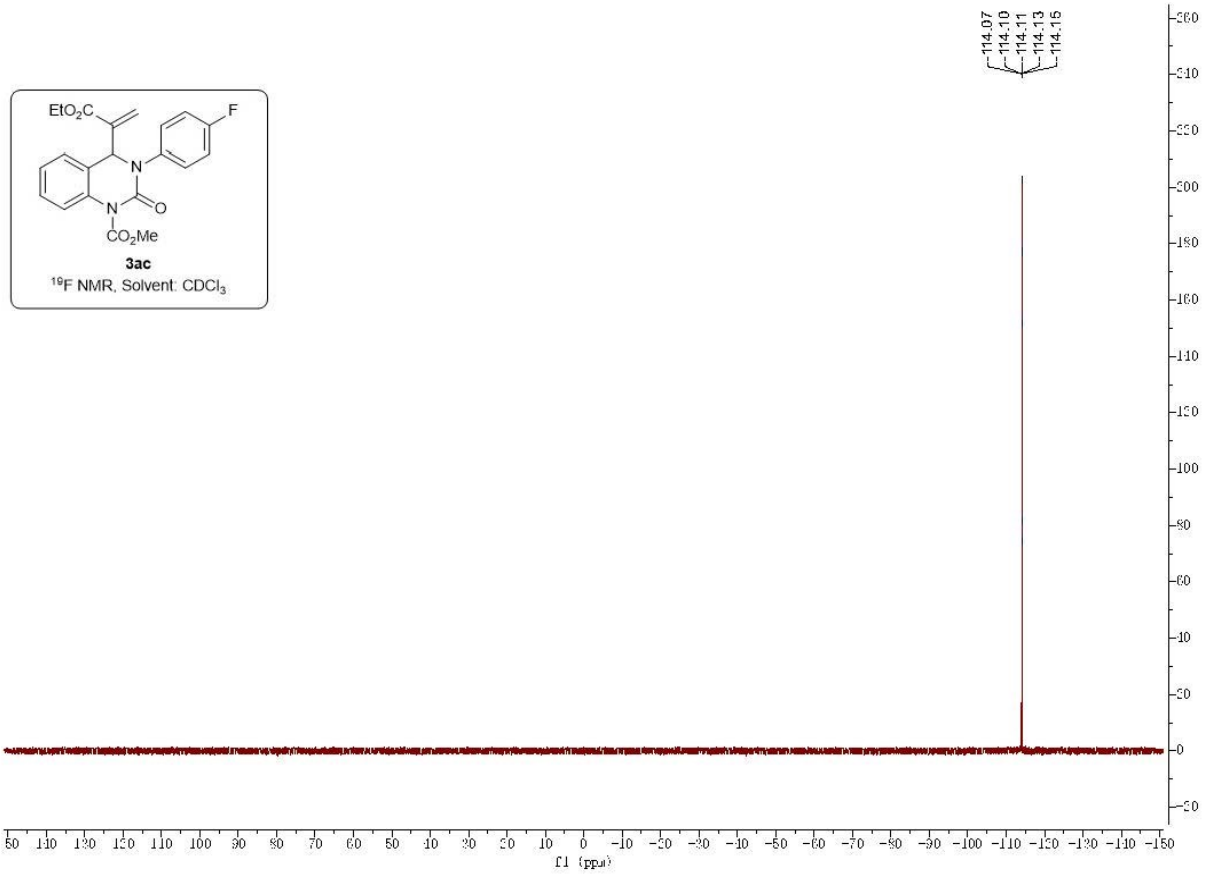


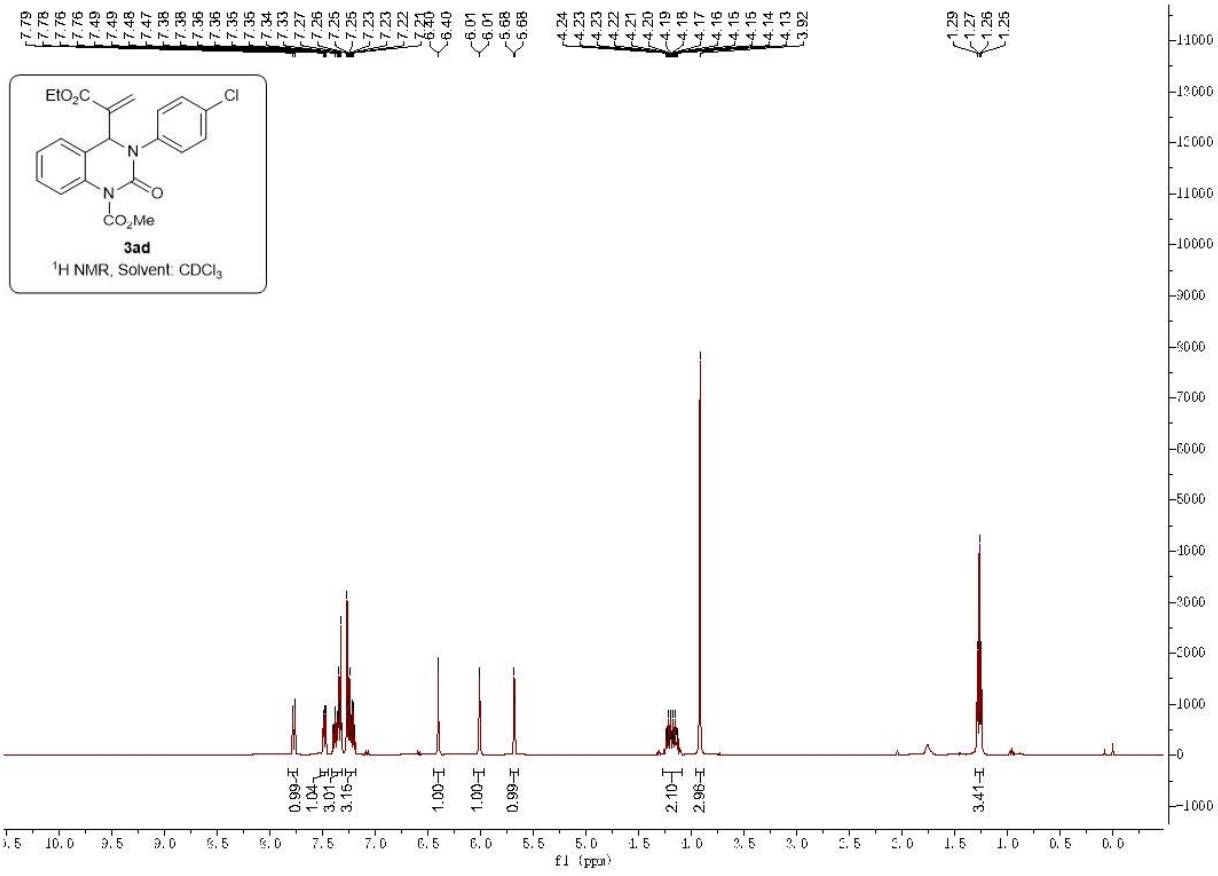

EtO2C
OMe
N
N
O
CO2Me
3ab
1H NMR, Solvent: CDCl3
f1 (ppm)

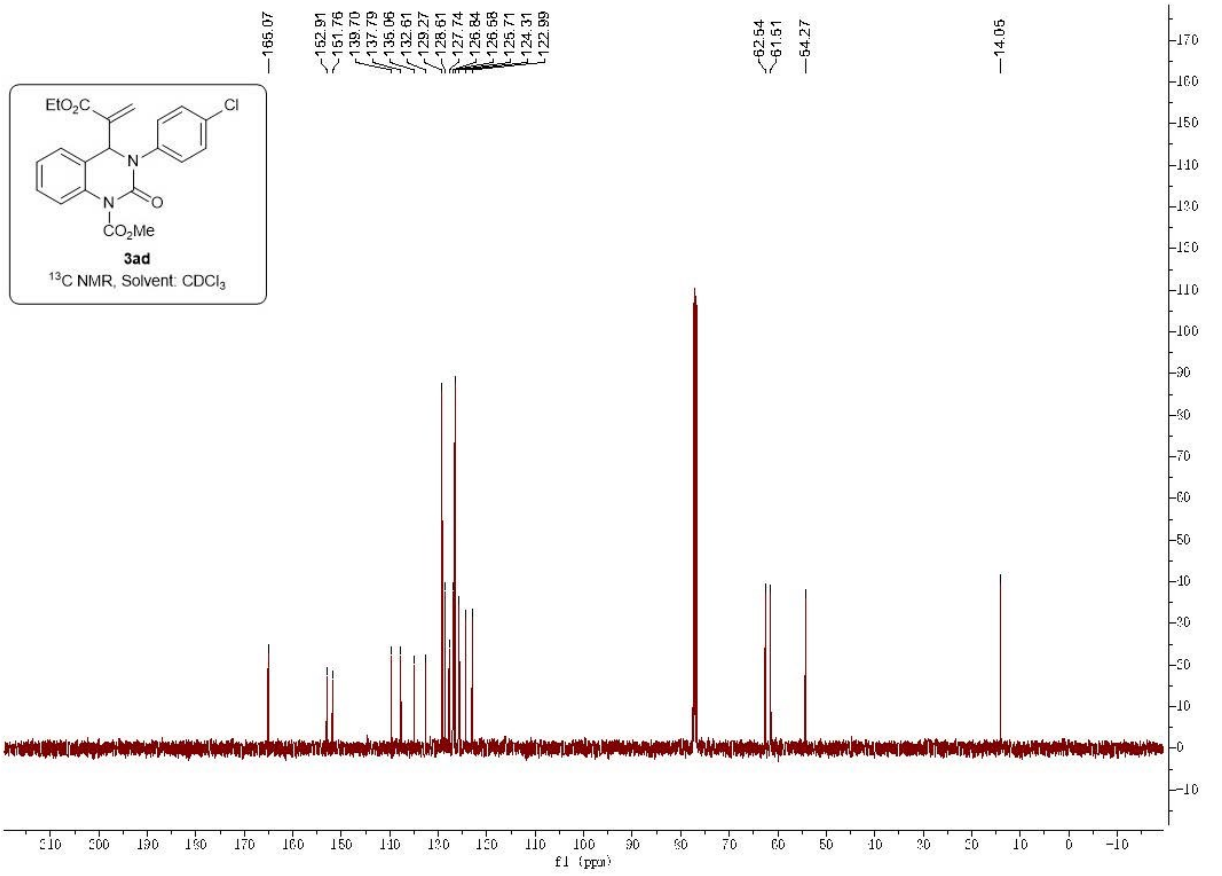

EtO2C
OMe
N
N
O
CO2Me
3ab
13C NMR, Solvent: CDCl3
f1 (ppm)

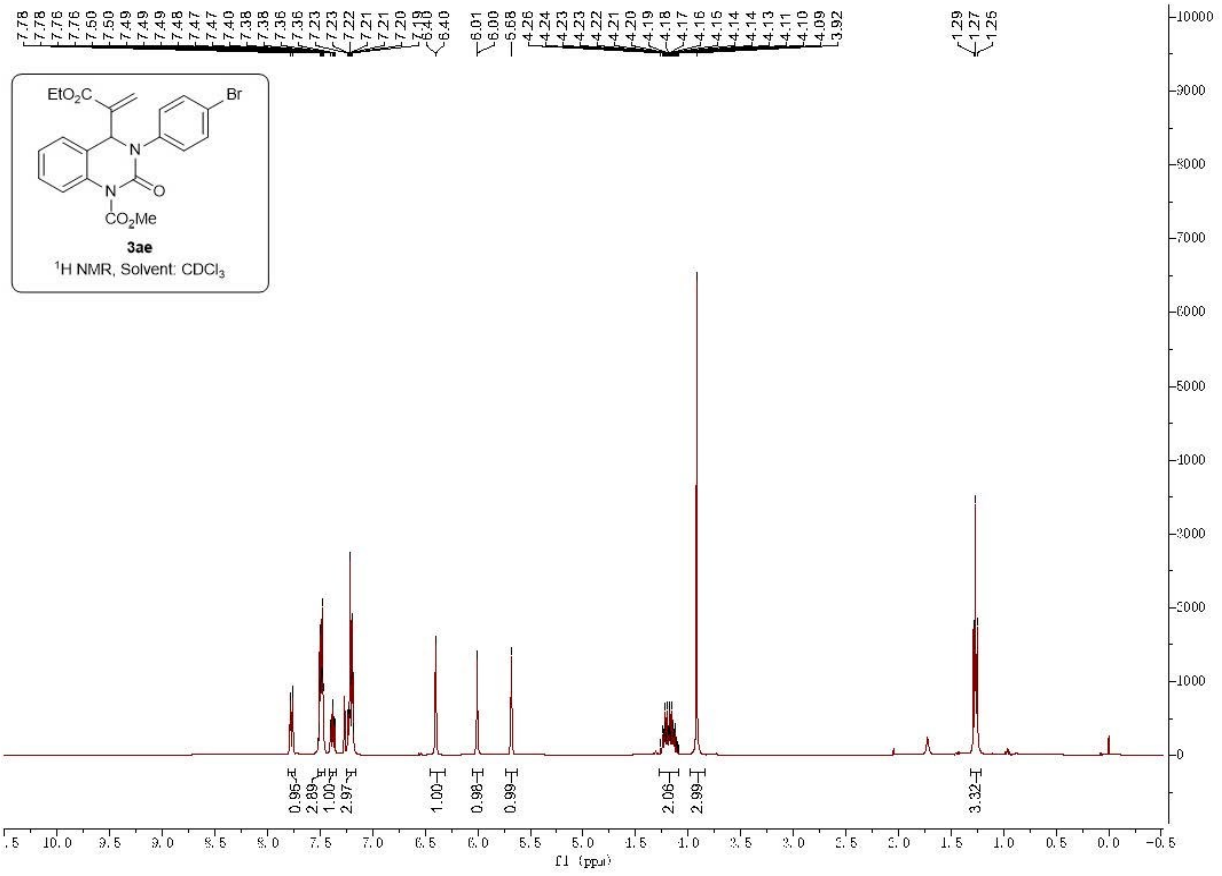

7.81
7.79
7.52
7.50
7.42
7.40
7.39
7.38
7.33
7.32
7.30
7.29
7.26
7.24
7.22
7.11
7.09
7.06
6.43
6.06
5.59
4.28
4.26
4.25
4.25
4.24
4.23
4.22
4.21
4.20
4.19
4.18
4.18
4.17
4.16
4.15
4.14
4.13
3.95
1.31
1.29
1.27
EtO2C
F
N
N
O
CO2Me
3ac
1H NMR, Solvent: CDCl3
0.96
1.00
1.01
2.35
0.97
1.96
1.00
1.00
0.99
2.06
2.95
3.34
f1 (ppm)

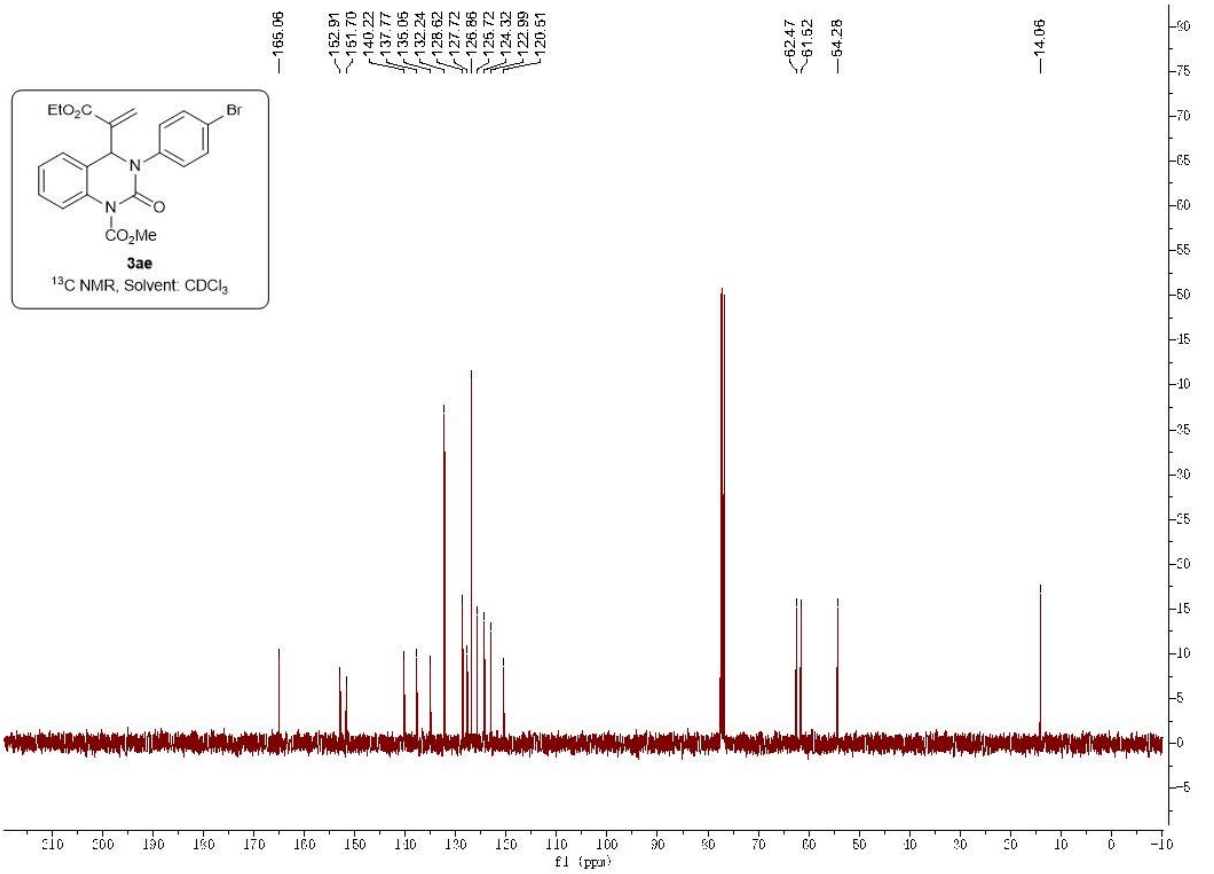

165.12
162.43
159.97
152.97
151.92
137.92
137.21
135.16
128.57
127.86
127.38
127.29
125.79
125.66
124.27
122.98
116.17
115.94
62.81
61.48
54.23
14.05
EtO2C
F
N
N
O
CO2Me
3ac
13C NMR, Solvent: CDCl3
f1 (ppm)

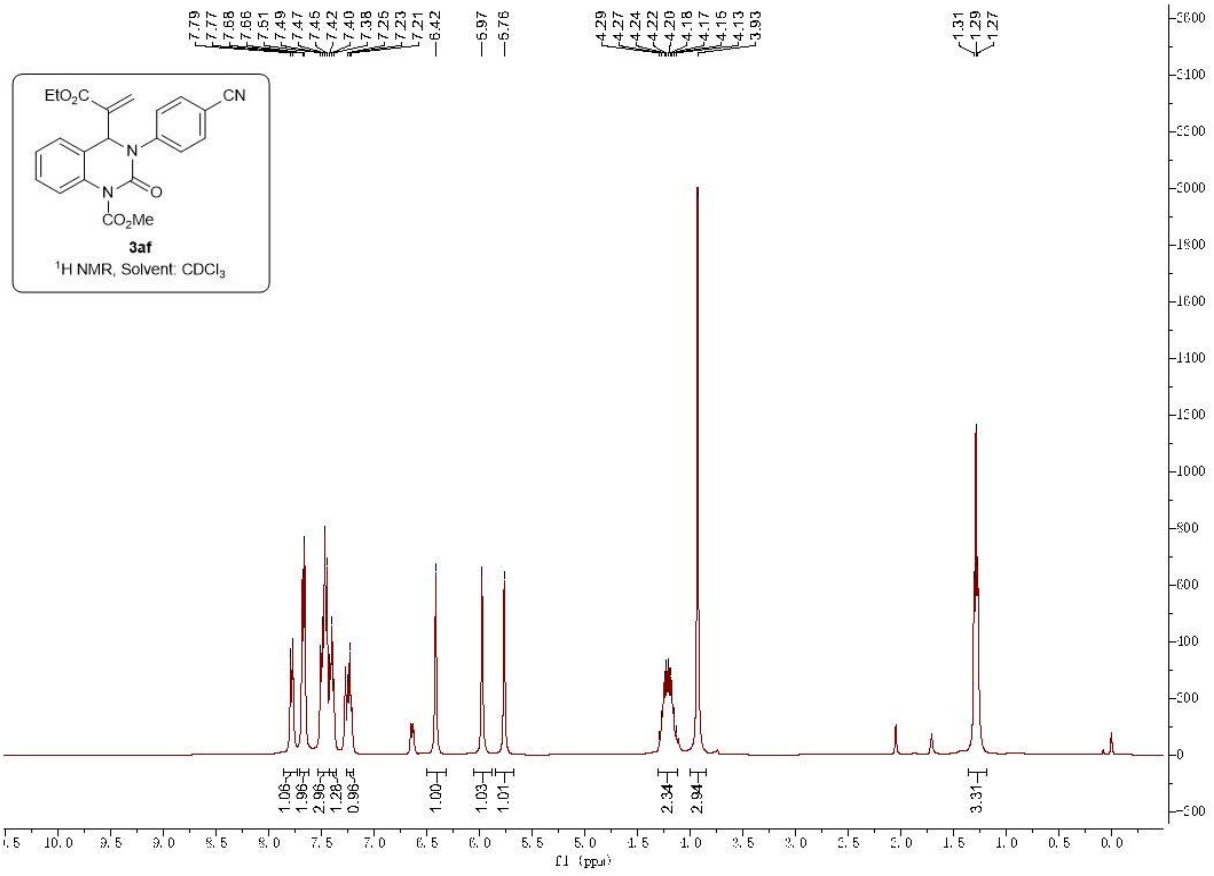

EtO2C
F
N
N
O
CO2Me
3ac
19F NMR, Solvent: CDCl3
114.07
114.10
114.11
114.13
114.15
f1 (ppm)

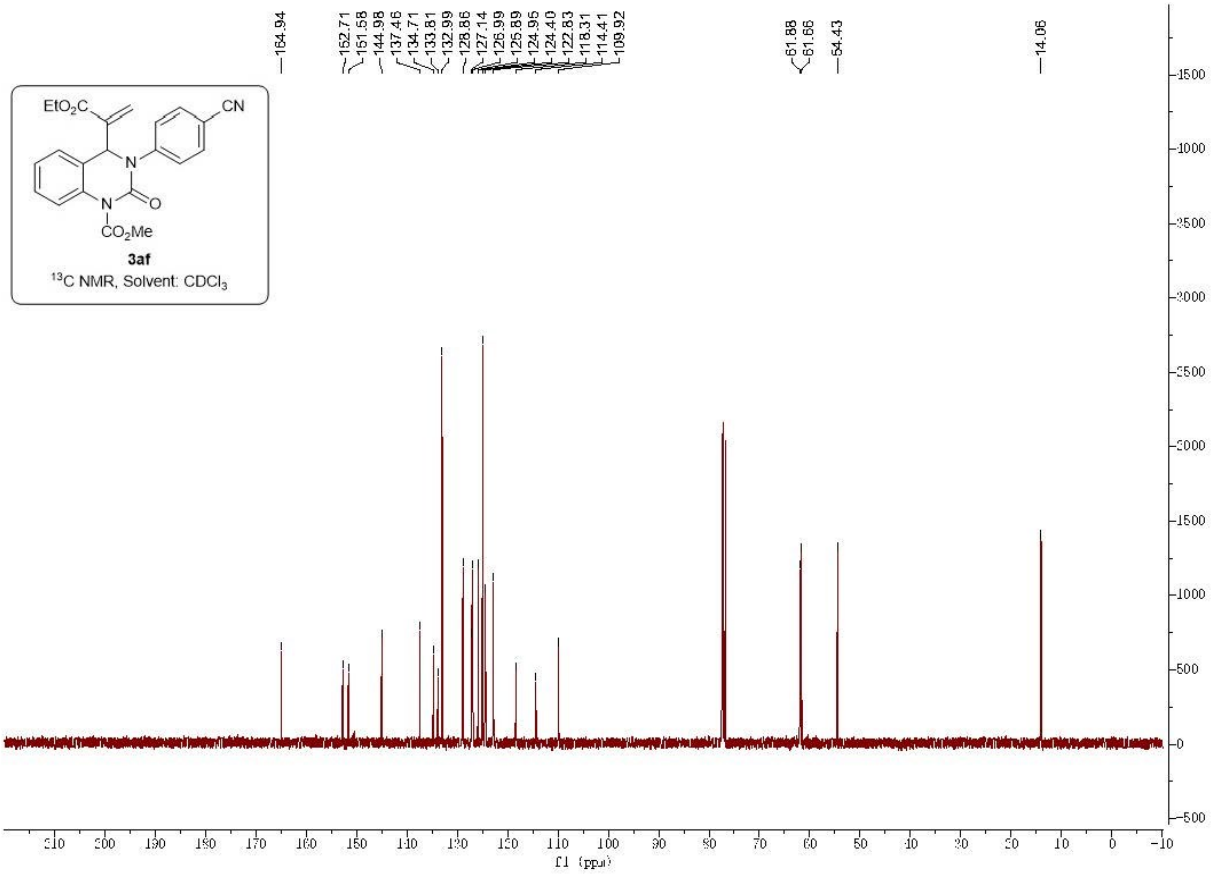

EtO2C
Cl
N
N
O
CO2Me
3ad
1H NMR, Solvent: CDCl3
7.79
7.78
7.76
7.76
7.49
7.49
7.48
7.47
7.38
7.38
7.36
7.36
7.35
7.35
7.34
7.33
7.27
7.26
7.25
7.25
7.23
7.23
7.22
7.21
6.40
6.01
6.01
5.68
5.68
4.24
4.23
4.23
4.22
4.21
4.20
4.19
4.18
4.17
4.16
4.15
4.15
4.14
4.13
3.92
1.29
1.27
1.26
1.25
0.99
1.04
3.01
3.15
1.00
1.00
0.99
2.10
2.96
3.41
f1 (ppm)

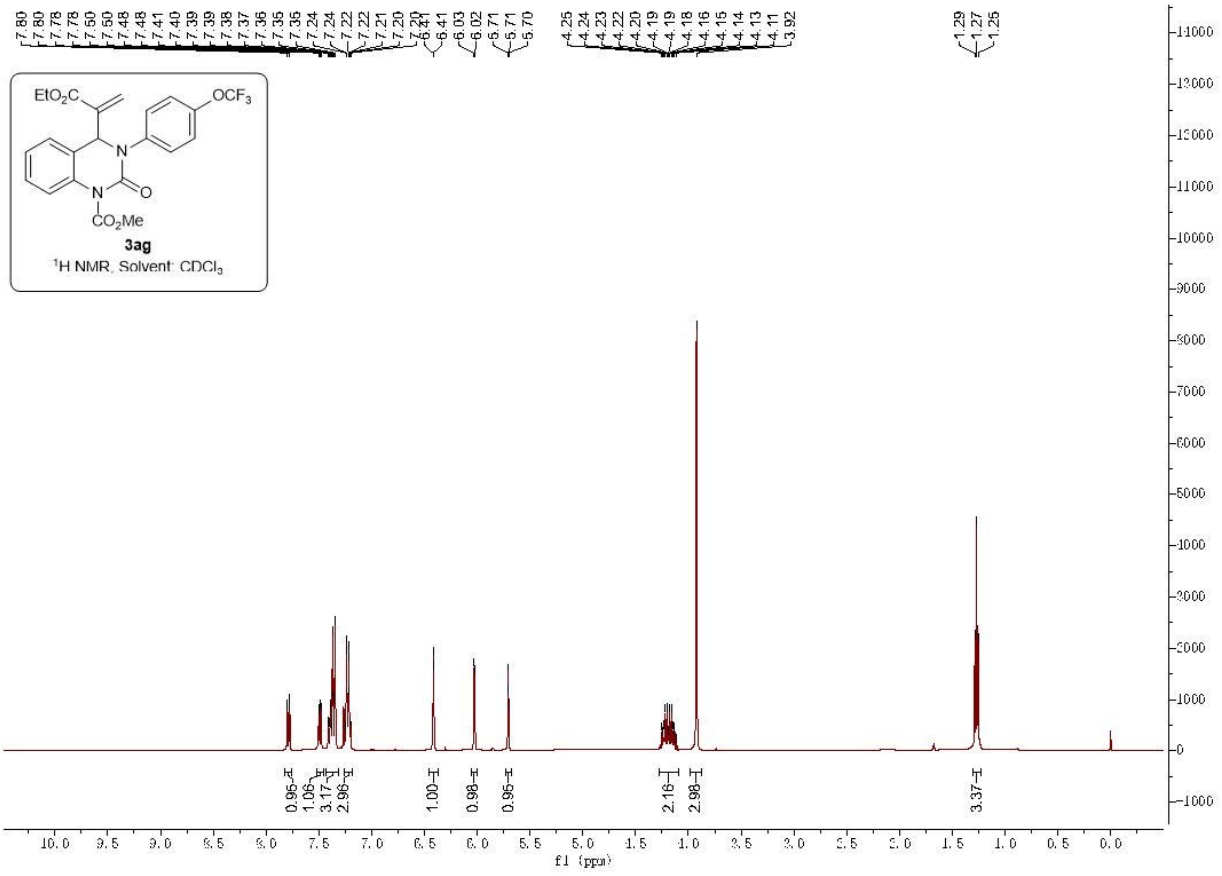

EtO2C
Cl
N
N
O
CO2Me
3ad
13C NMR, Solvent: CDCl3
166.07
152.91
151.78
139.70
137.79
135.06
132.61
129.27
128.61
127.74
126.84
126.58
125.71
124.31
122.99
62.54
61.51
54.27
14.05
f1 (ppm)

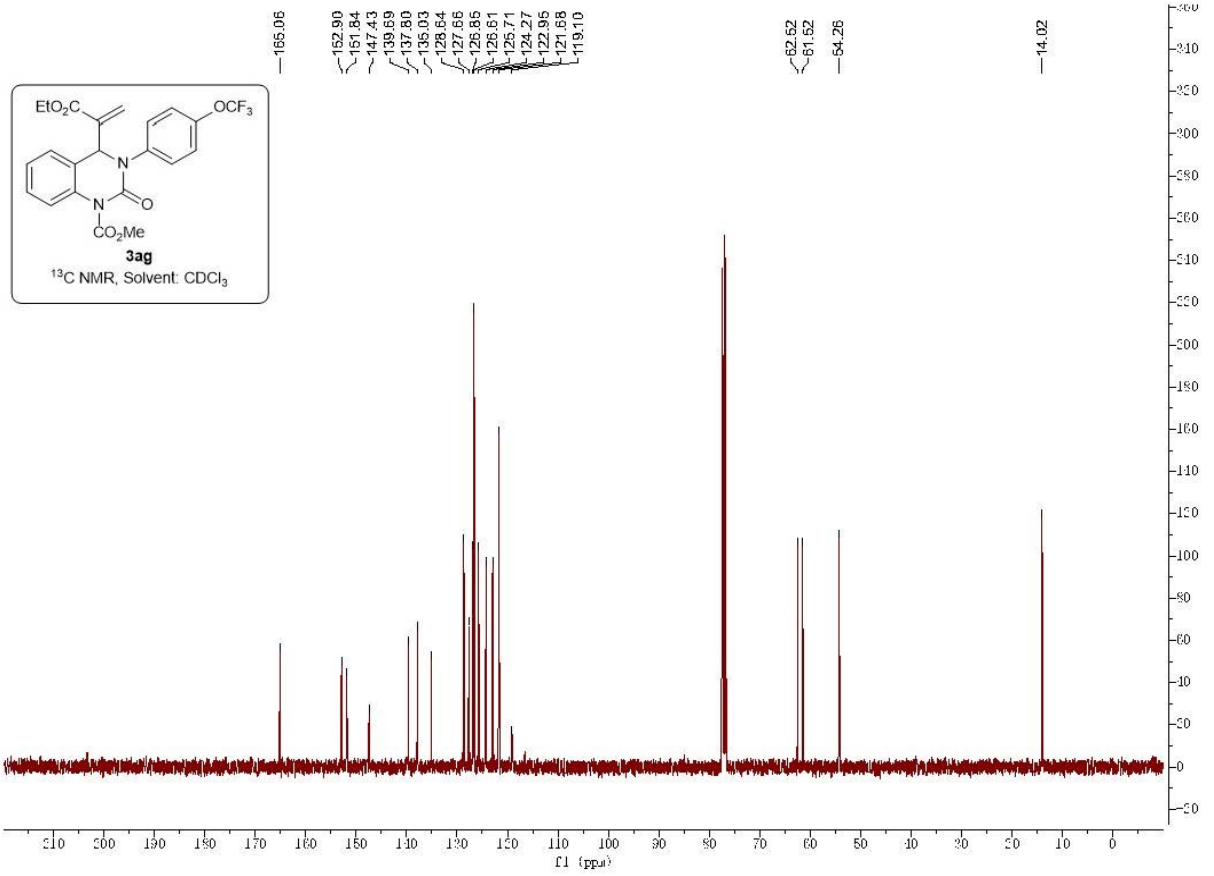

EtO2C
Br
N
N
O
CO2Me
3ae
1H NMR, Solvent: CDCl3
7.78
7.78
7.76
7.76
7.50
7.49
7.49
7.49
7.48
7.47
7.47
7.40
7.38
7.38
7.36
7.36
7.23
7.23
7.22
7.21
7.21
7.20
7.19
6.40
6.01
6.00
5.68
4.26
4.24
4.23
4.23
4.22
4.21
4.20
4.19
4.18
4.17
4.16
4.15
4.14
4.14
4.13
4.11
4.10
4.09
3.92
1.29
1.27
1.25
0.96
2.89
1.00
2.97
1.00
0.98
0.99
2.06
2.99
3.32
f1 (ppm)

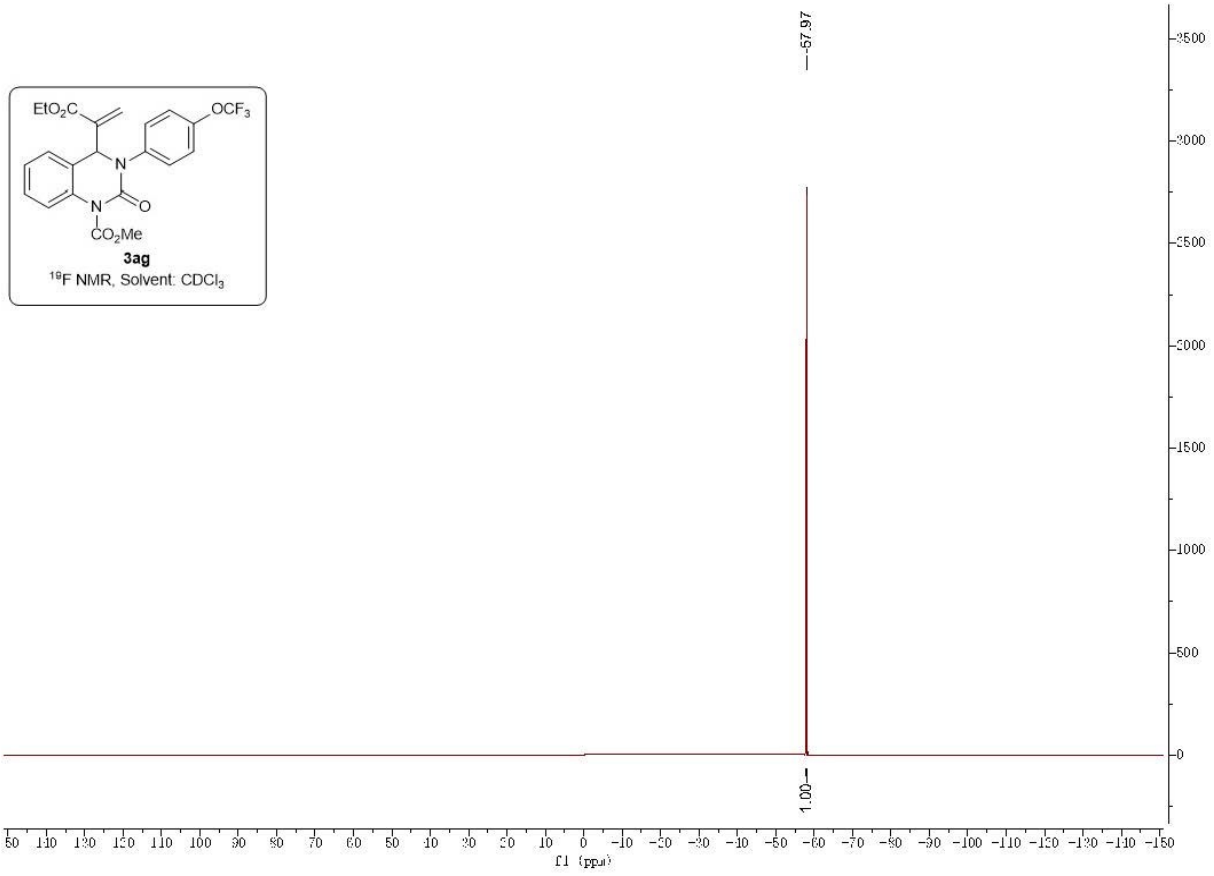

EtO2C
Br
N
N
O
CO2Me
3ae
13C NMR, Solvent: CDCl3
165.06
152.91
151.70
140.22
137.77
135.05
132.24
128.62
127.72
126.86
125.72
124.32
122.99
120.51
62.47
61.62
54.28
14.06
f1 (ppm)

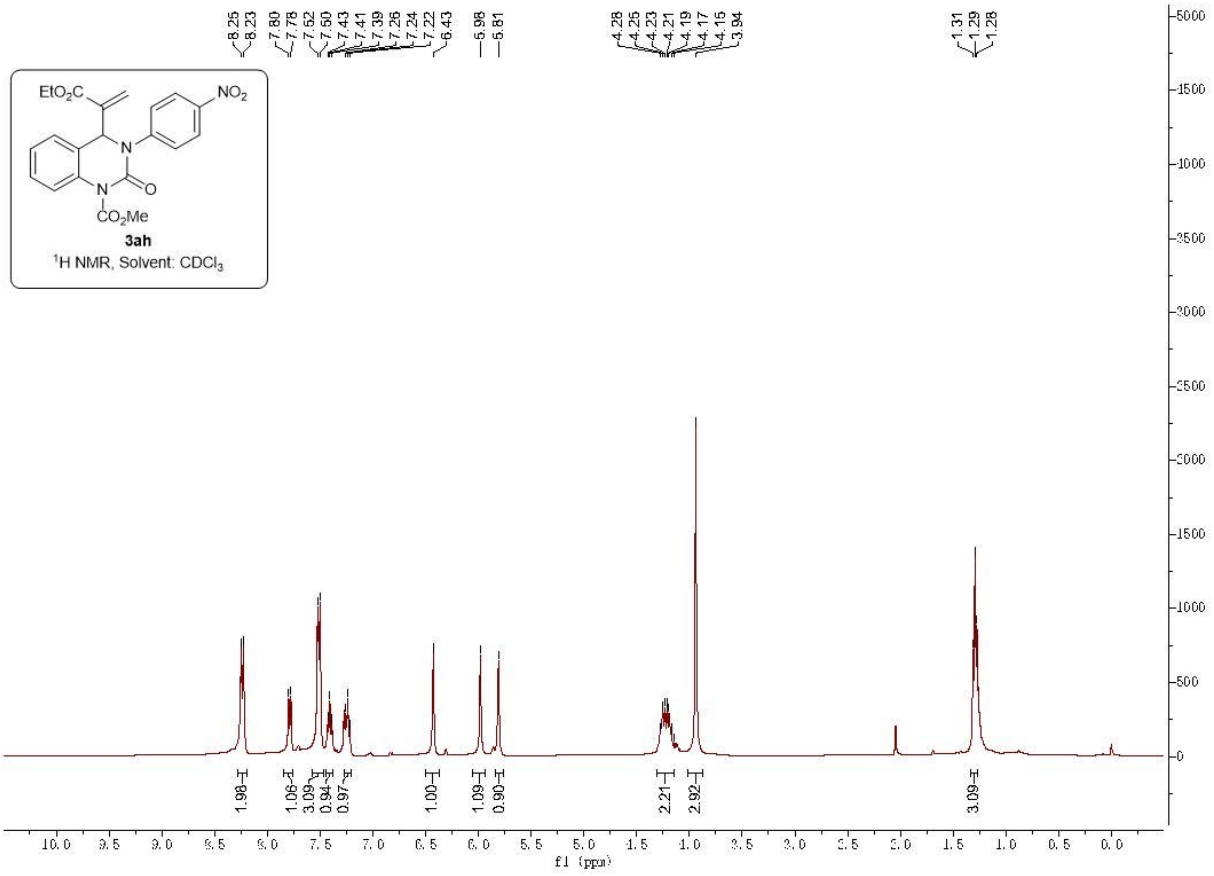

EtO2C
CN
N
N
O
CO2Me
3af
1H NMR, Solvent: CDCl3
7.79
7.77
7.68
7.66
7.51
7.49
7.47
7.45
7.42
7.40
7.38
7.25
7.23
7.21
6.42
5.97
5.76
4.29
4.27
4.24
4.22
4.20
4.18
4.17
4.15
4.13
3.93
1.31
1.29
1.27
1.06
1.96
2.96
1.28
0.98
1.00
1.03
1.01
2.34
2.94
3.31
f1 (ppm)


EtO2C
CN
N
O
CO2Me
3af
13C NMR, Solvent: CDCl3
164.94
152.71
151.58
144.98
137.46
134.71
133.81
132.99
128.86
127.14
126.99
125.89
124.95
124.40
122.83
118.31
114.41
109.92
61.88
61.66
54.43
14.06
f1 (ppm)


EtO2C
OCF3
N
O
CO2Me
3ag
1H NMR, Solvent: CDCl3
7.80
7.78
7.50
7.48
7.41
7.40
7.39
7.38
7.37
7.36
7.35
7.24
7.22
7.21
7.20
6.41
6.03
6.02
5.71
5.70
4.25
4.24
4.23
4.22
4.20
4.19
4.18
4.16
4.15
4.14
4.13
4.11
3.92
1.29
1.27
1.25
0.95
1.06
3.17
2.96
1.00
0.98
0.95
2.16
2.98
3.37
f1 (ppm)


165.06
152.90
151.84
147.43
139.69
137.80
135.03
128.64
127.66
126.85
126.61
125.71
124.27
122.95
121.88
119.10
62.62
61.52
54.26
14.02
EtO2C
OCF3
N
N
O
CO2Me
3ag
13C NMR, Solvent: CDCl3
f1 (ppm)


-57.97
1.00
EtO2C
OCF3
N
N
O
CO2Me
3ag
19F NMR, Solvent: CDCl3
f1 (ppm)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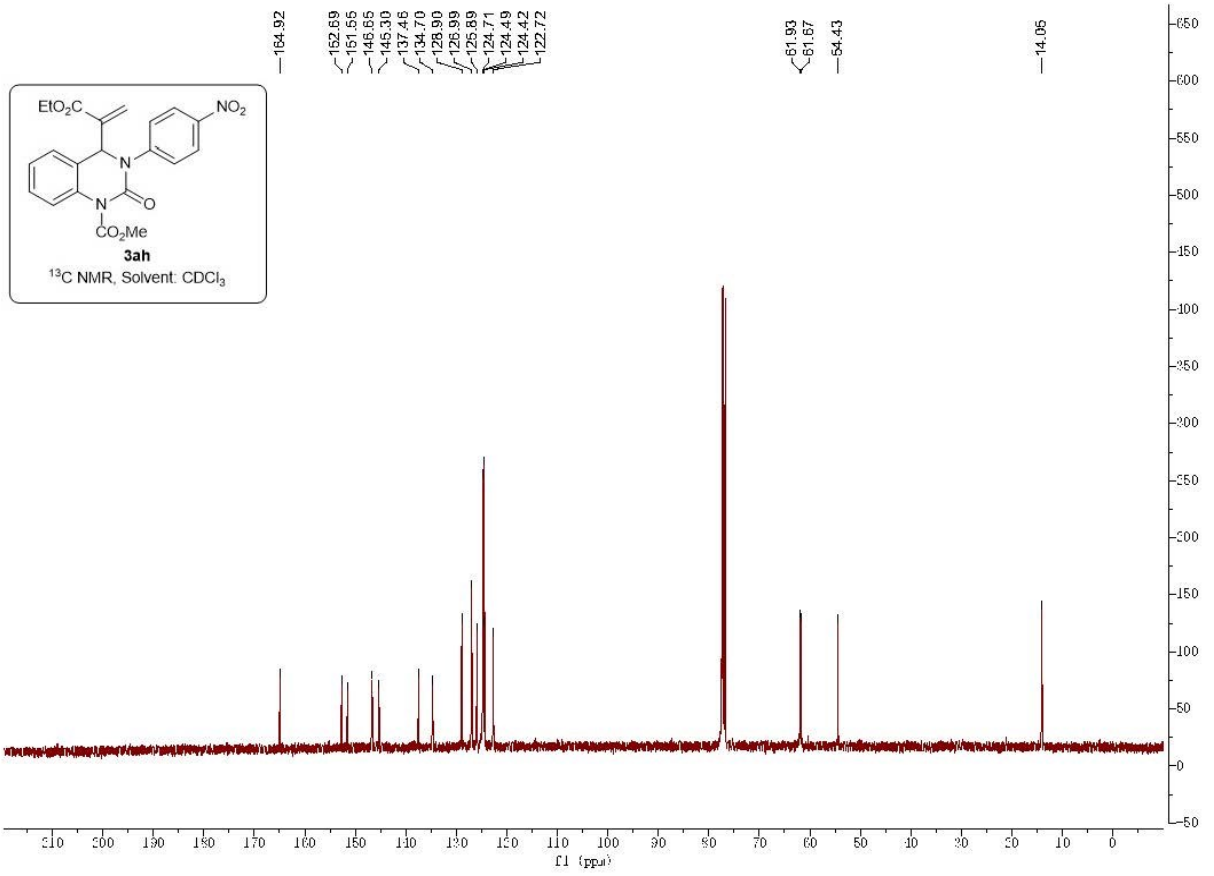
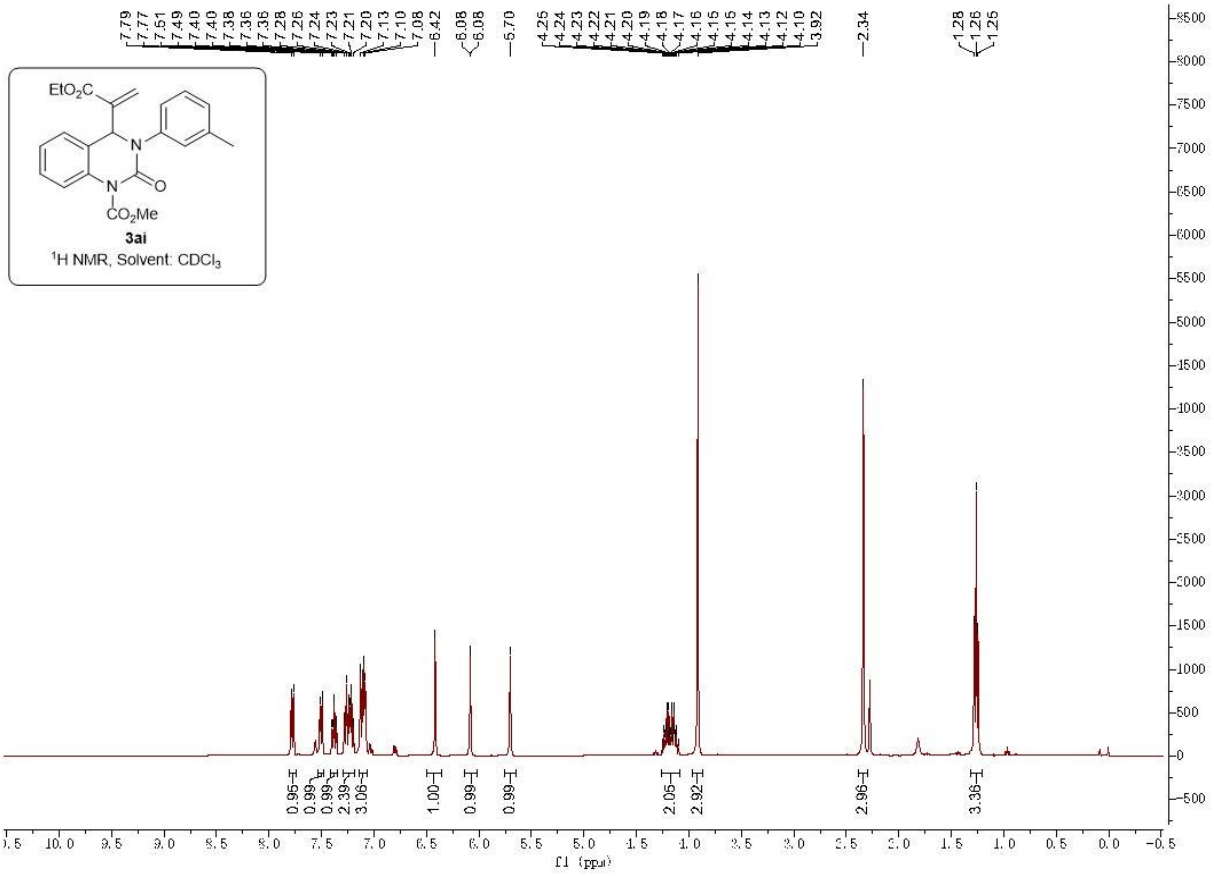
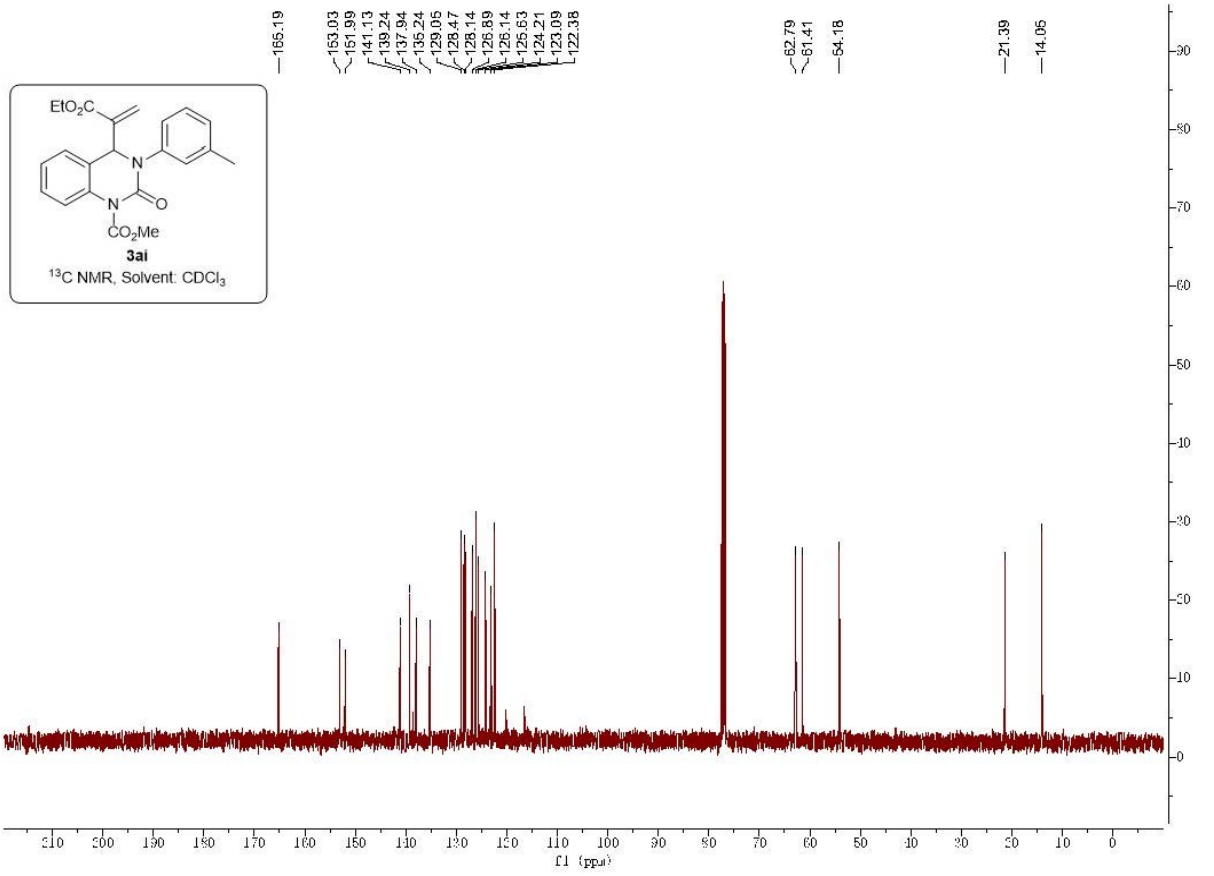
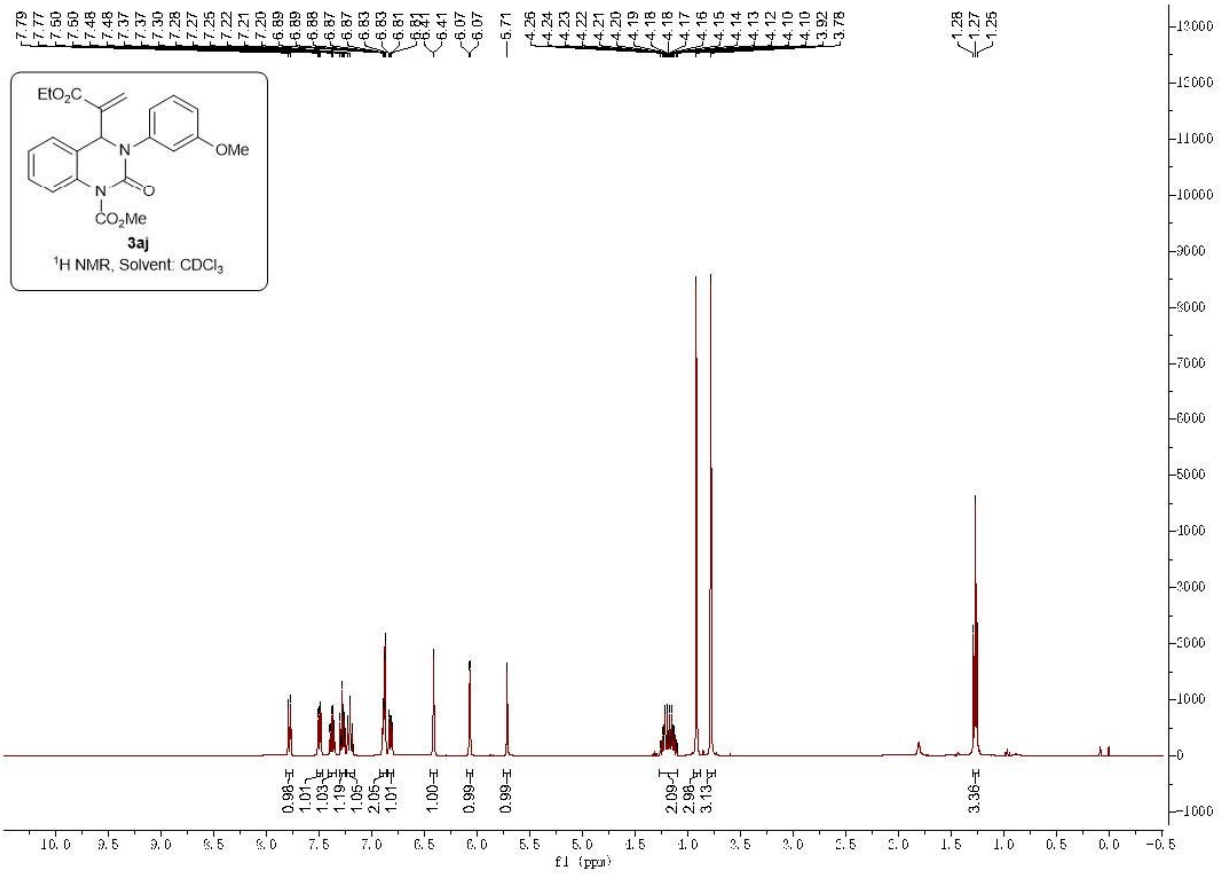
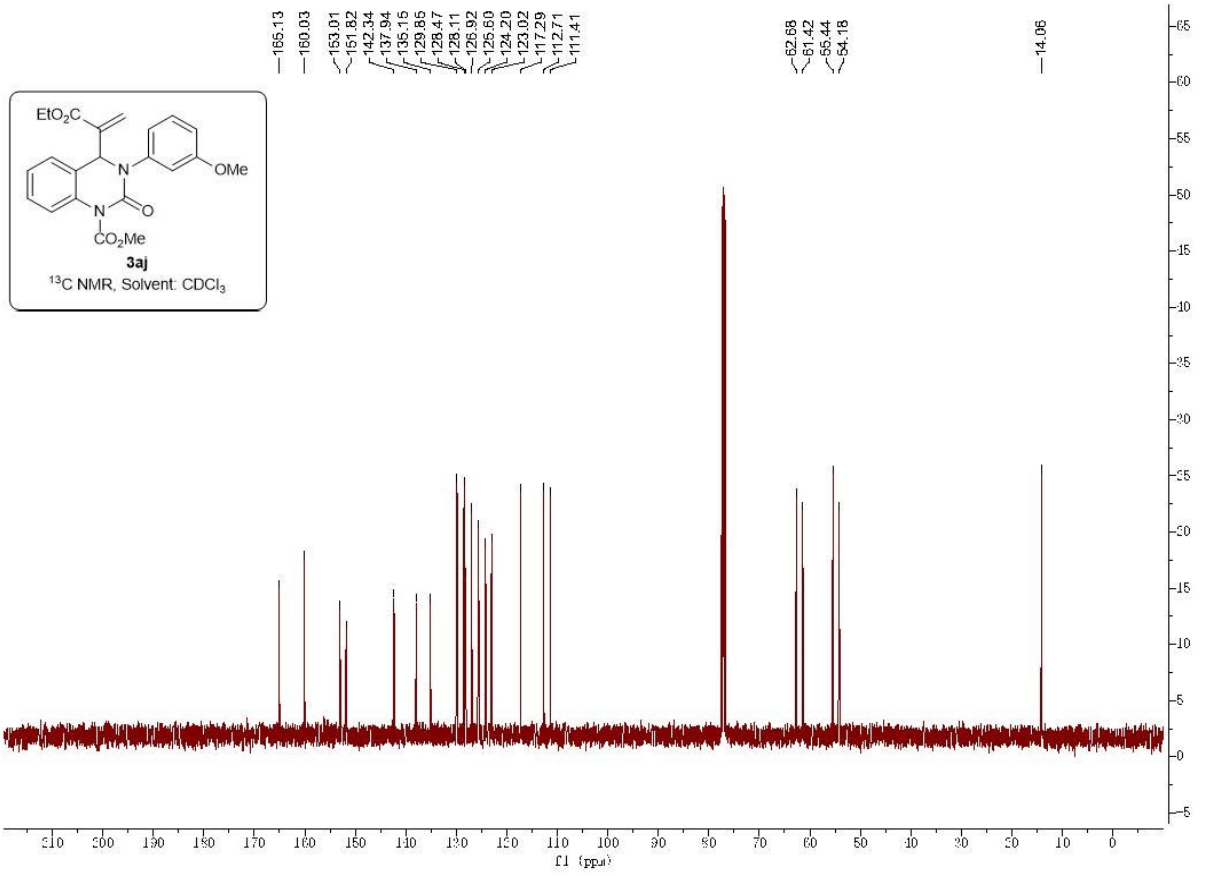
8.23
7.80
7.78
7.62
7.50
7.43
7.41
7.39
7.26
7.24
7.22
6.43
5.98
5.81
4.28
4.25
4.23
4.21
4.19
4.17
4.15
3.94
1.31
1.29
1.28
EtO2C
NO2
N
N
O
CO2Me
3ah
1H NMR, Solvent: CDCl3
1.98
1.06
3.09
0.94
0.97
1.00
1.09
0.90
2.21
2.92
3.09
f1 (ppm)

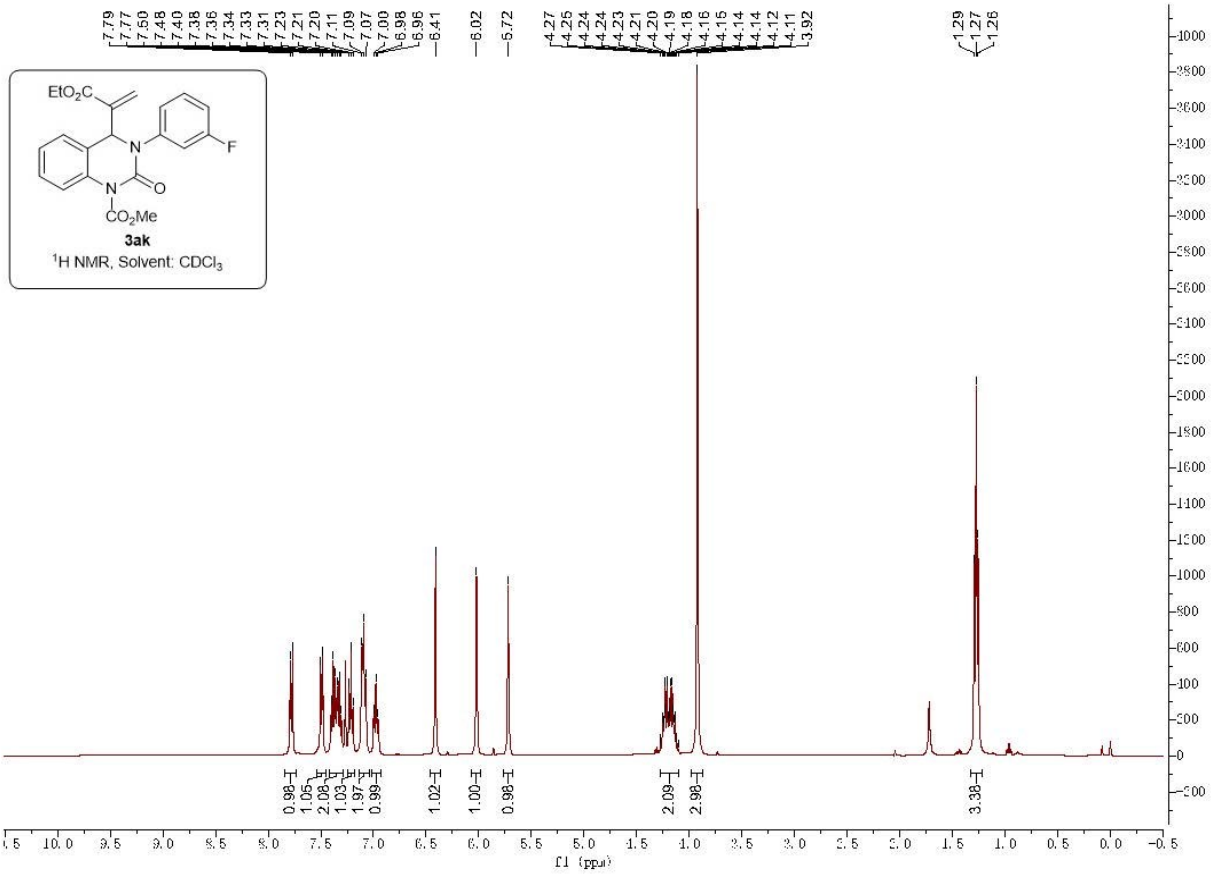

164.92
152.69
151.55
146.65
145.30
137.46
134.70
128.90
126.99
125.89
124.71
124.49
124.42
122.72
61.93
61.67
54.43
14.05
EtO2C
NO2
N
N
O
CO2Me
3ah
13C NMR, Solvent: CDCl3
f1 (ppm)


EtO2C
N
N
O
CO2Me
3ai
1H NMR, Solvent: CDCl3
7.79
7.77
7.51
7.49
7.40
7.40
7.38
7.36
7.36
7.28
7.26
7.24
7.23
7.21
7.20
7.13
7.10
7.08
6.42
6.08
6.08
5.70
4.25
4.24
4.23
4.22
4.21
4.20
4.19
4.18
4.17
4.16
4.15
4.14
4.13
4.12
4.10
3.92
2.34
1.28
1.26
1.25
0.95
0.99
0.99
2.39
3.06
1.00
0.99
0.99
2.05
2.92
2.96
3.36
f1 (ppm)


EtO2C
N
N
O
CO2Me
3ai
13C NMR, Solvent: CDCl3
165.19
153.03
151.99
141.13
139.24
137.94
135.24
129.06
128.47
128.14
126.89
126.14
125.63
124.21
123.09
122.38
62.79
61.41
54.18
21.39
14.06
f1 (ppm)


EtO2C
OMe
N
O
CO2Me
3aj
1H NMR, Solvent: CDCl3
f1 (ppm)


EtO2C
OMe
N
O
CO2Me
3aj
13C NMR, Solvent: CDCl3
f1 (ppm)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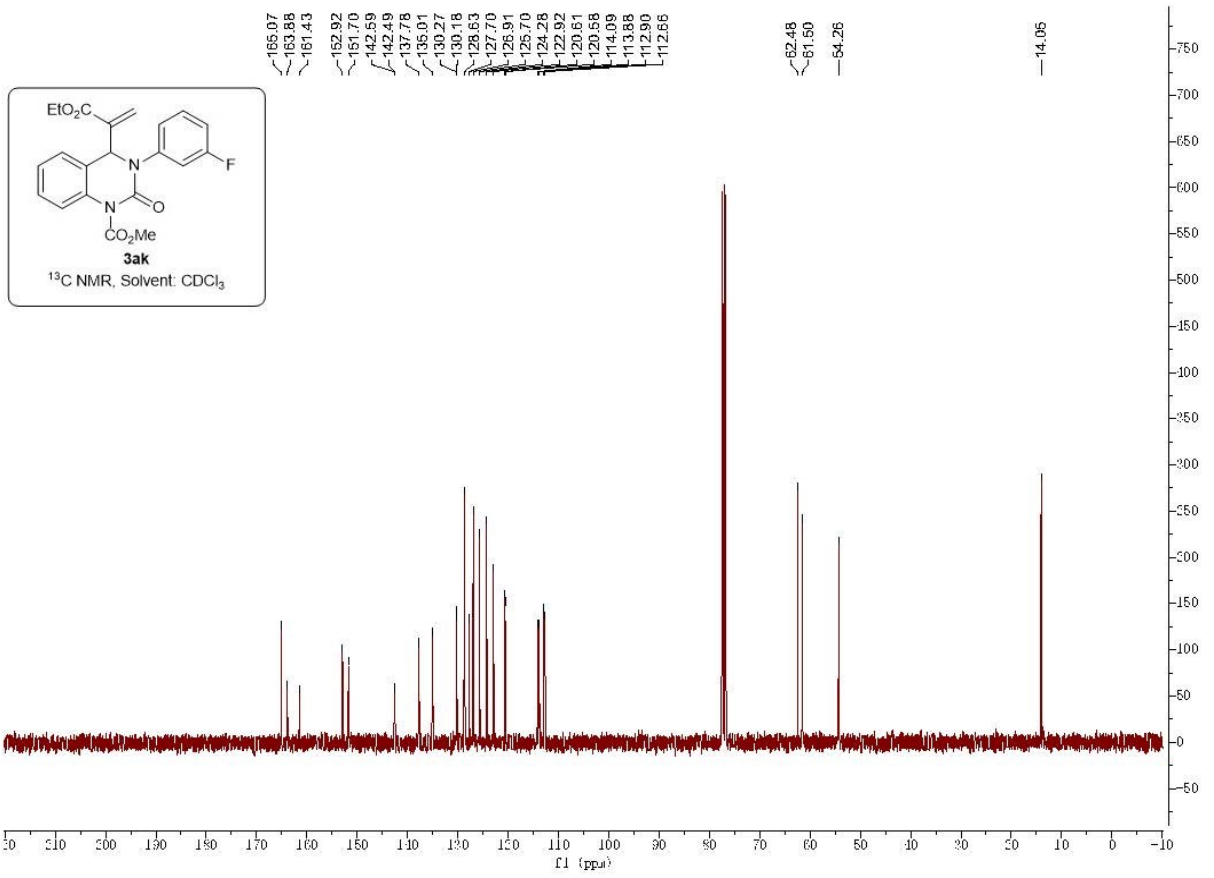
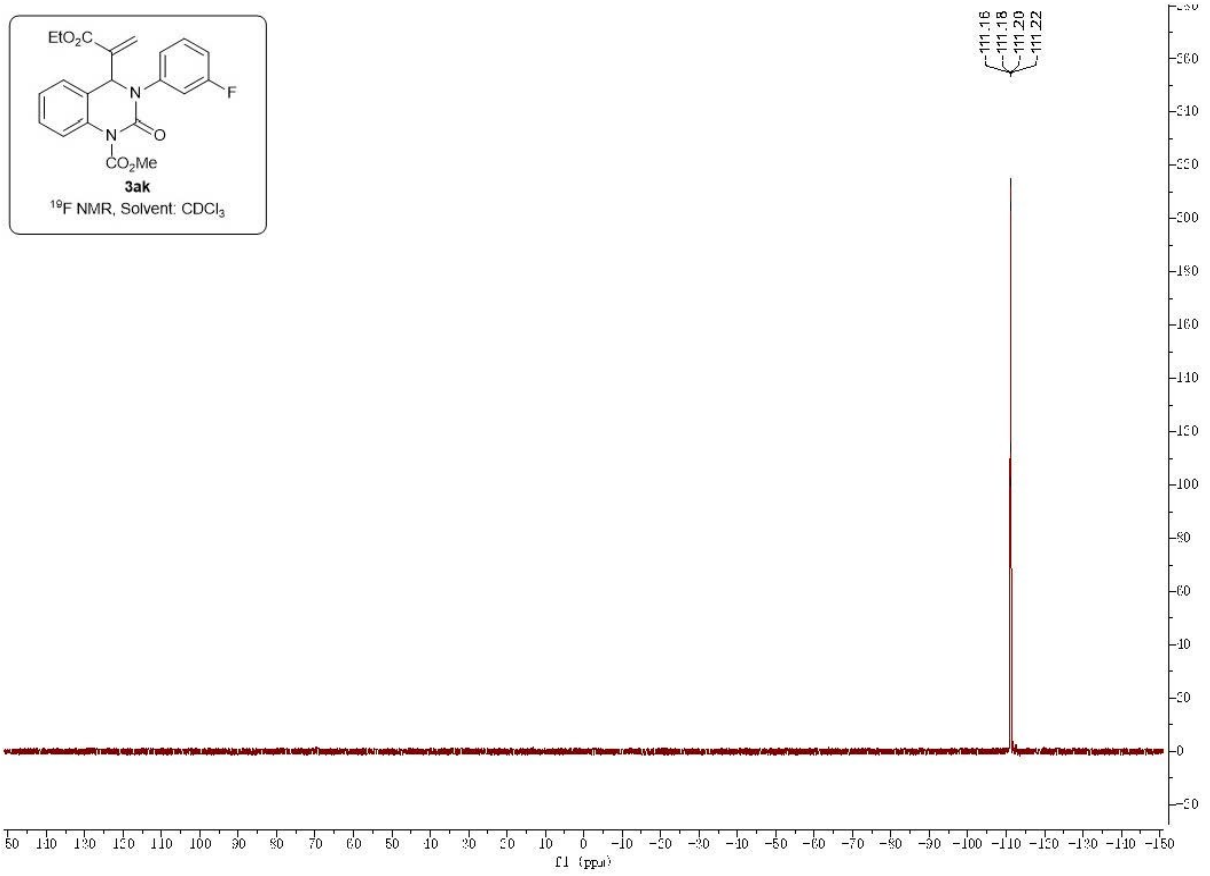
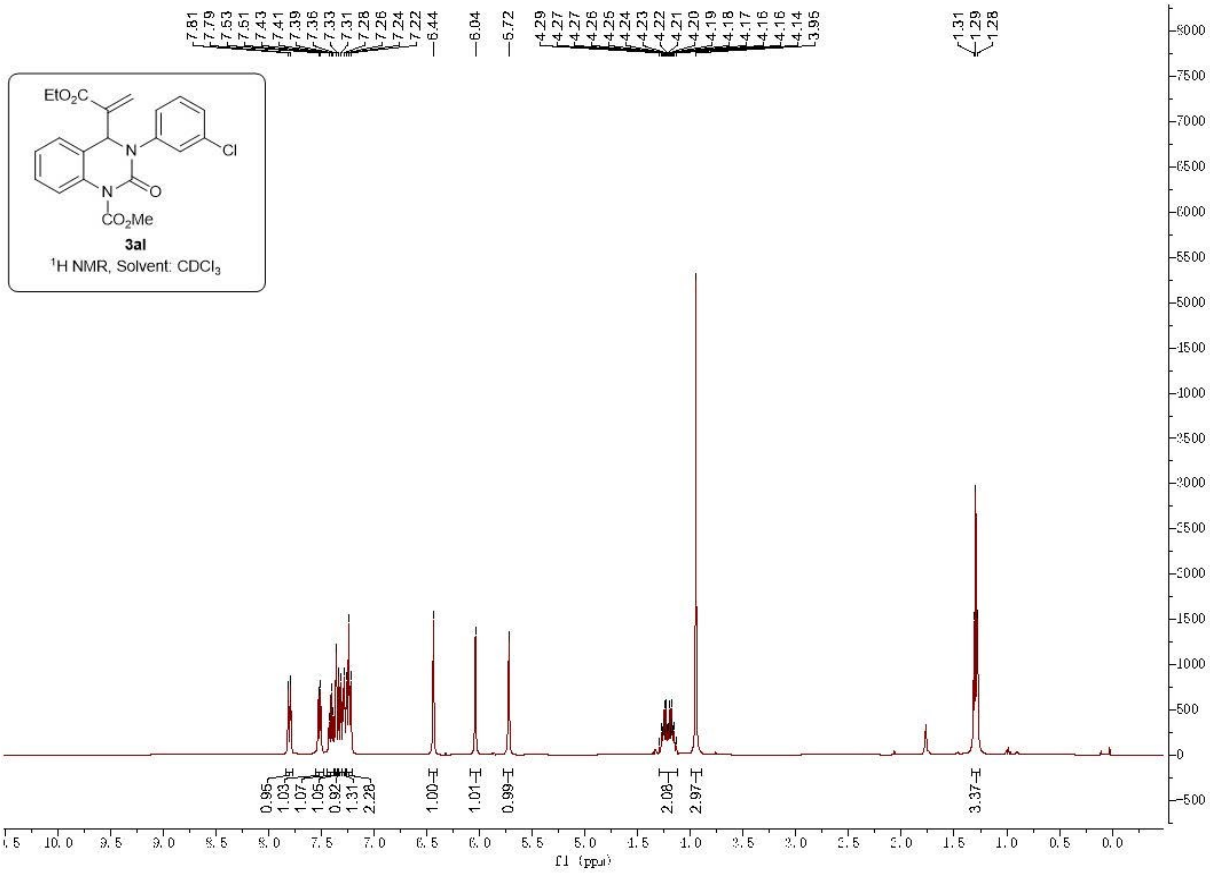
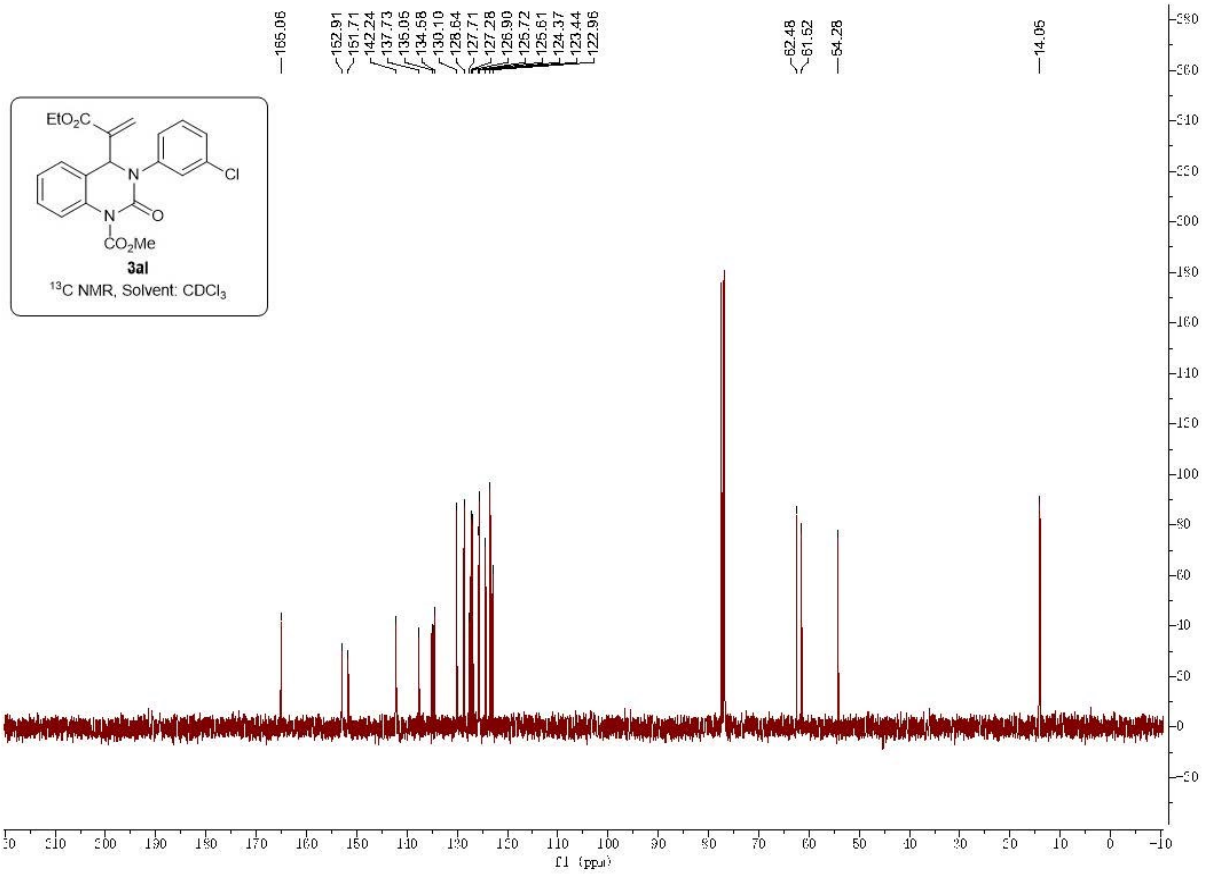
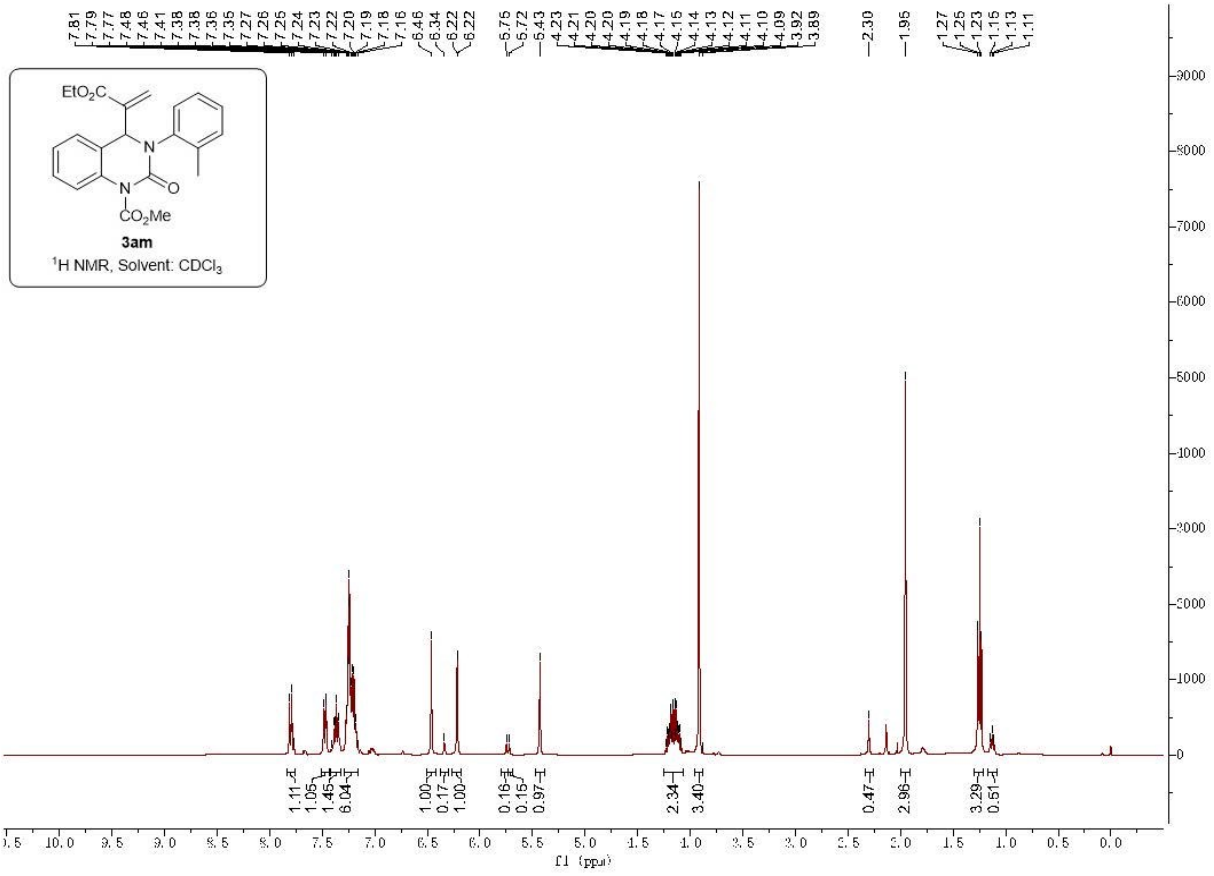
7.77
7.50
7.48
7.40
7.38
7.36
7.34
7.33
7.31
7.23
7.21
7.20
7.11
7.09
7.07
7.00
6.98
6.96
6.41
6.02
5.72
4.27
4.25
4.24
4.24
4.23
4.21
4.20
4.19
4.18
4.16
4.15
4.14
4.14
4.12
4.11
3.92
1.29
1.27
1.26
EtO2C
N
F
N
O
CO2Me
3ak
1H NMR, Solvent: CDCl3
0.98
1.05
2.08
1.03
1.97
0.99
1.02
1.00
0.98
2.09
2.98
3.38
f1 (ppm)


165.07
163.88
161.43
152.92
151.70
142.59
142.49
137.78
135.01
130.27
130.18
128.63
127.70
126.91
125.70
124.28
122.92
120.61
120.58
114.09
113.88
112.90
112.66
62.48
61.50
54.26
14.05
EtO2C
N
F
N
O
CO2Me
3ak
13C NMR, Solvent: CDCl3
f1 (ppm)


EtO2C
N
F
N
O
CO2Me
3ak
19F NMR, Solvent: CDCl3
111.16
111.18
111.20
111.22
f1 (ppm)


EtO2C
N
Cl
N
O
CO2Me
3al
1H NMR, Solvent: CDCl3
7.81
7.79
7.53
7.51
7.43
7.41
7.39
7.36
7.33
7.31
7.28
7.26
7.24
7.22
6.44
6.04
5.72
4.29
4.27
4.27
4.26
4.25
4.24
4.23
4.22
4.21
4.20
4.19
4.18
4.17
4.16
4.16
4.14
3.95
1.31
1.29
1.28
0.95
1.03
1.07
1.05
0.92
1.31
2.28
1.00
1.01
0.99
2.08
2.97
3.37
f1 (ppm)


EtO2C
N
Cl
N
O
CO2Me
3al
13C NMR, Solvent: CDCl3
165.06
152.91
151.71
142.24
137.73
135.05
134.58
130.10
128.64
127.71
127.28
126.90
125.72
125.61
124.37
123.44
122.96
62.48
61.52
54.28
14.05
f1 (ppm)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N
O
N
CO2Me
3am
1H NMR, Solvent: CDCl3
7.81
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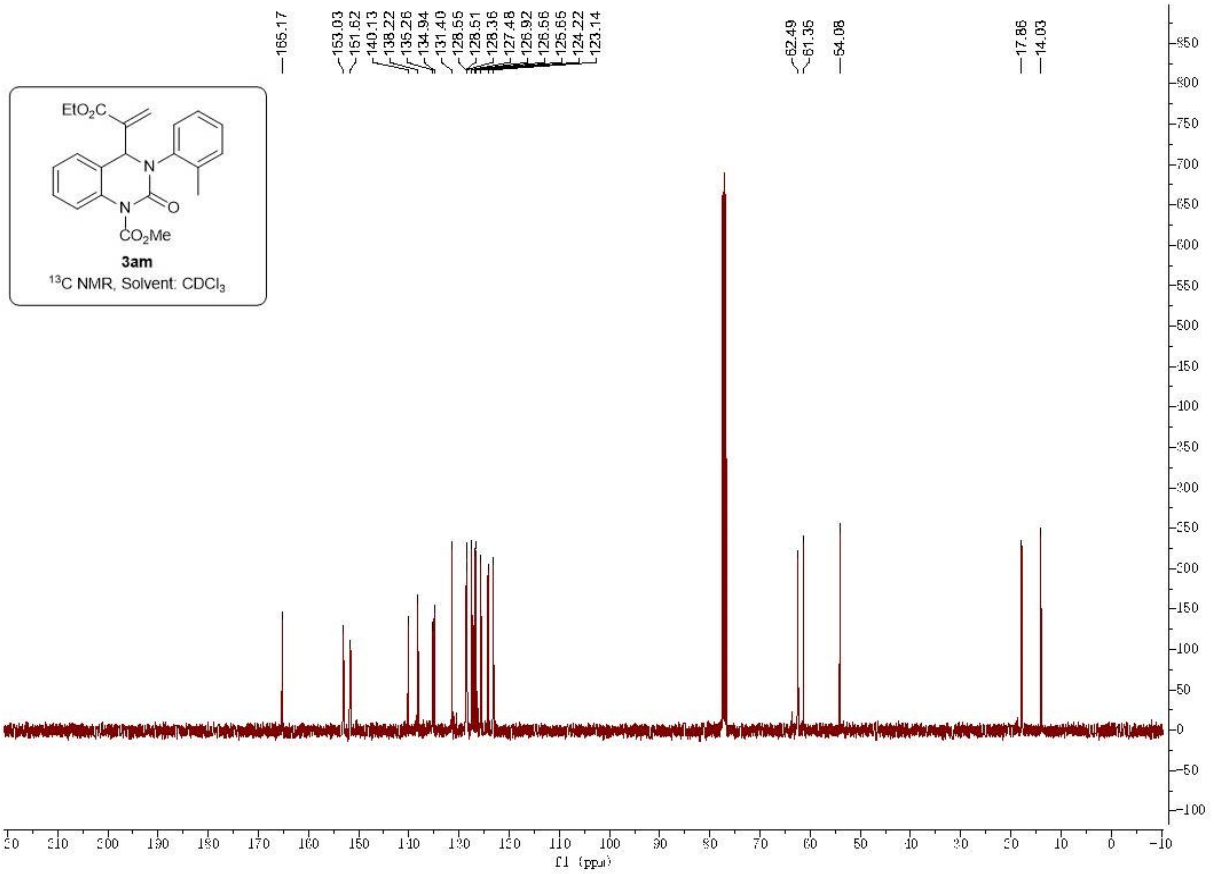
7.77
7.48
7.46
7.41
7.38
7.36
7.35
7.27
7.26
7.25
7.24
7.23
7.22
7.20
7.19
7.18
7.16
6.46
6.34
6.22
6.22
5.75
5.72
5.43
4.23
4.21
4.20
4.20
4.19
4.18
4.17
4.15
4.14
4.13
4.12
4.11
4.10
4.09
3.92
3.89
2.30
1.95
1.27
1.25
1.23
1.15
1.13
1.11
1.11
1.05
1.45
6.04
1.00
0.17
1.00
0.16
0.15
0.97
2.34
3.40
0.47
2.96
3.29
0.51
f1 (ppm)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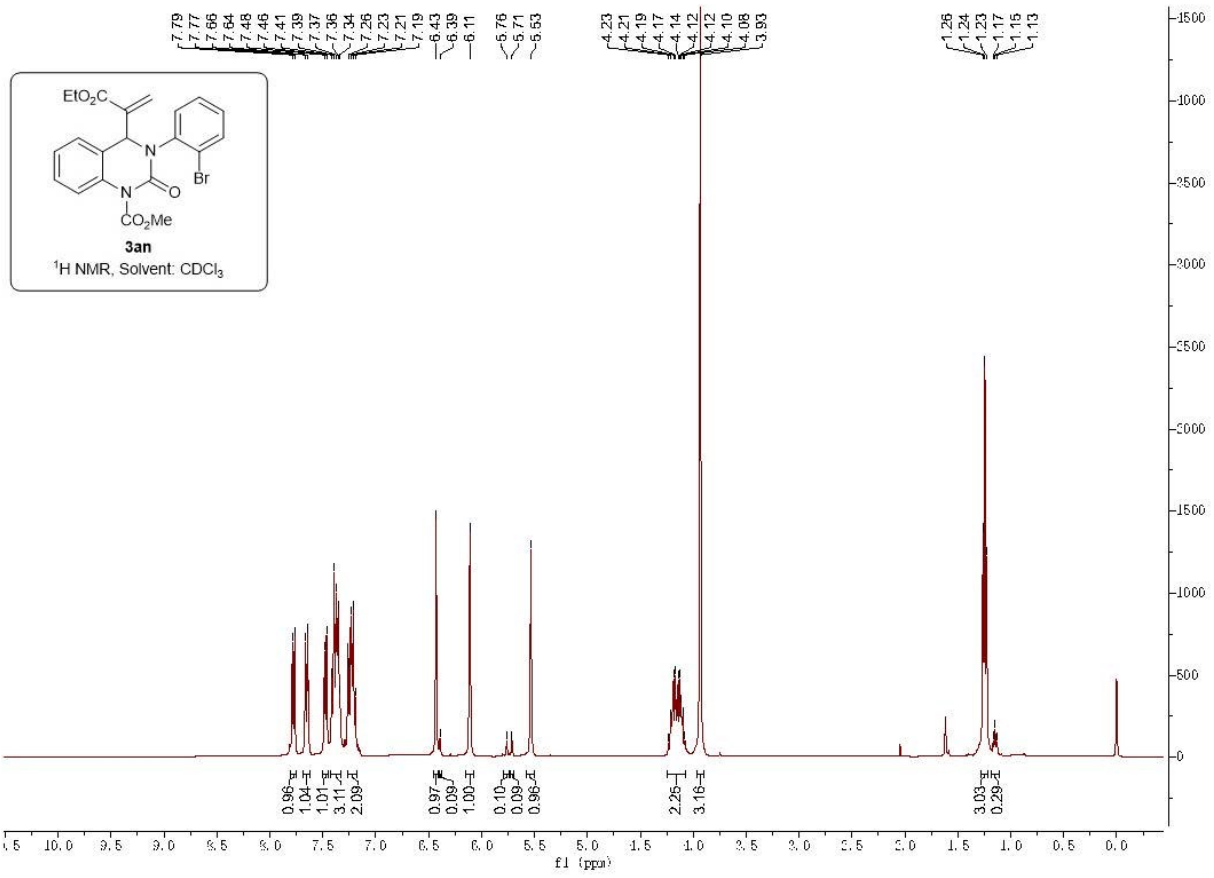
N
N
O
CO2Me
3am
13C NMR, Solvent: CDCl3
165.17
153.03
151.62
140.13
138.22
135.26
134.94
131.40
128.55
128.51
128.36
127.48
126.92
126.56
125.65
124.22
123.14
62.49
61.35
54.08
17.86
14.03
f1 (ppm)


EtO2C
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N
O
Br
CO2Me
3an
1H NMR, Solvent: CDCl3
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7.77
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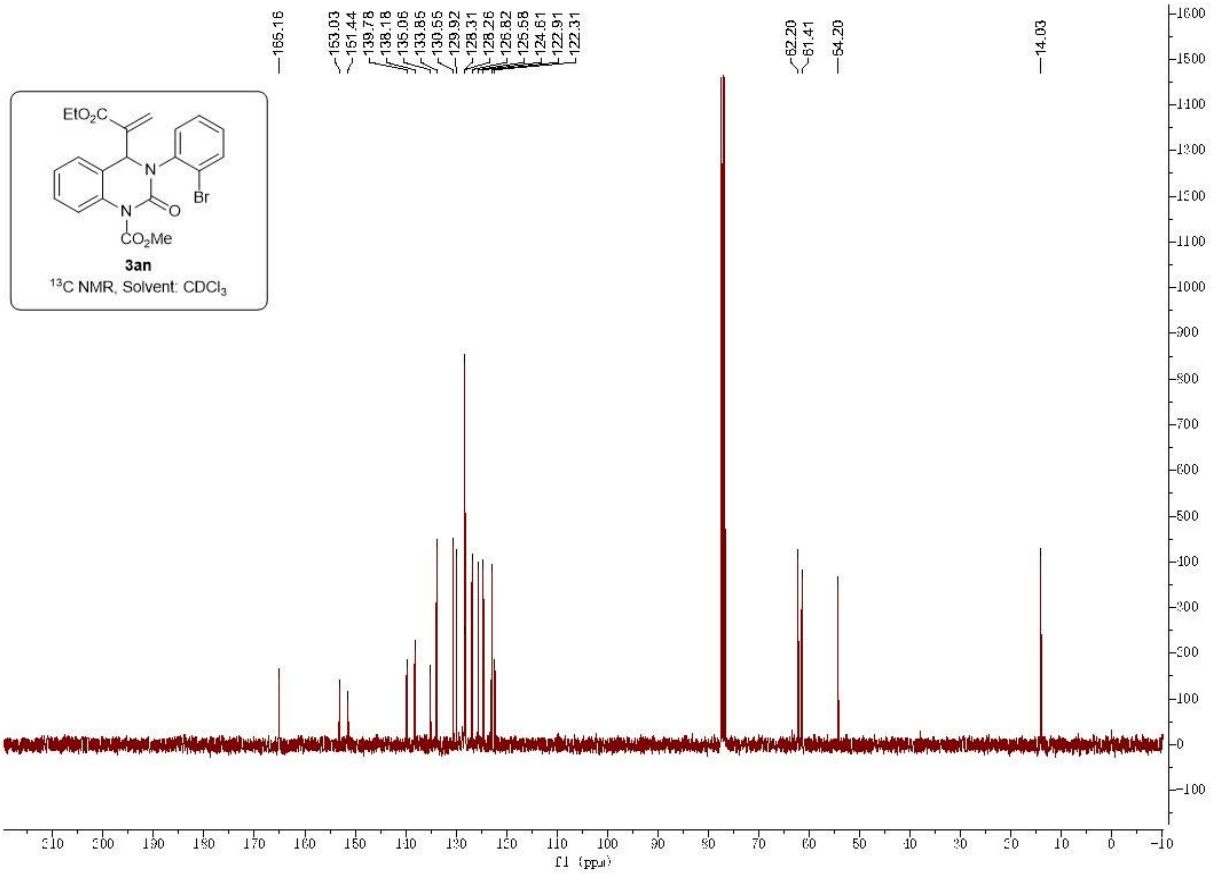
7.46
7.41
7.39
7.37
7.36
7.34
7.26
7.23
7.21
7.19
6.43
6.39
6.11
5.76
5.71
5.53
4.23
4.21
4.19
4.17
4.14
4.12
4.10
4.08
3.93
1.26
1.24
1.23
1.17
1.15
1.13
0.96
1.04
1.01
3.11
2.09
0.97
0.09
1.00
0.10
0.09
0.96
2.25
3.16
3.03
0.29
f1 (ppm)


EtO2C
N
Br
N
O
CO2Me
3an
13C NMR, Solvent: CDCl3
165.16
153.03
151.44
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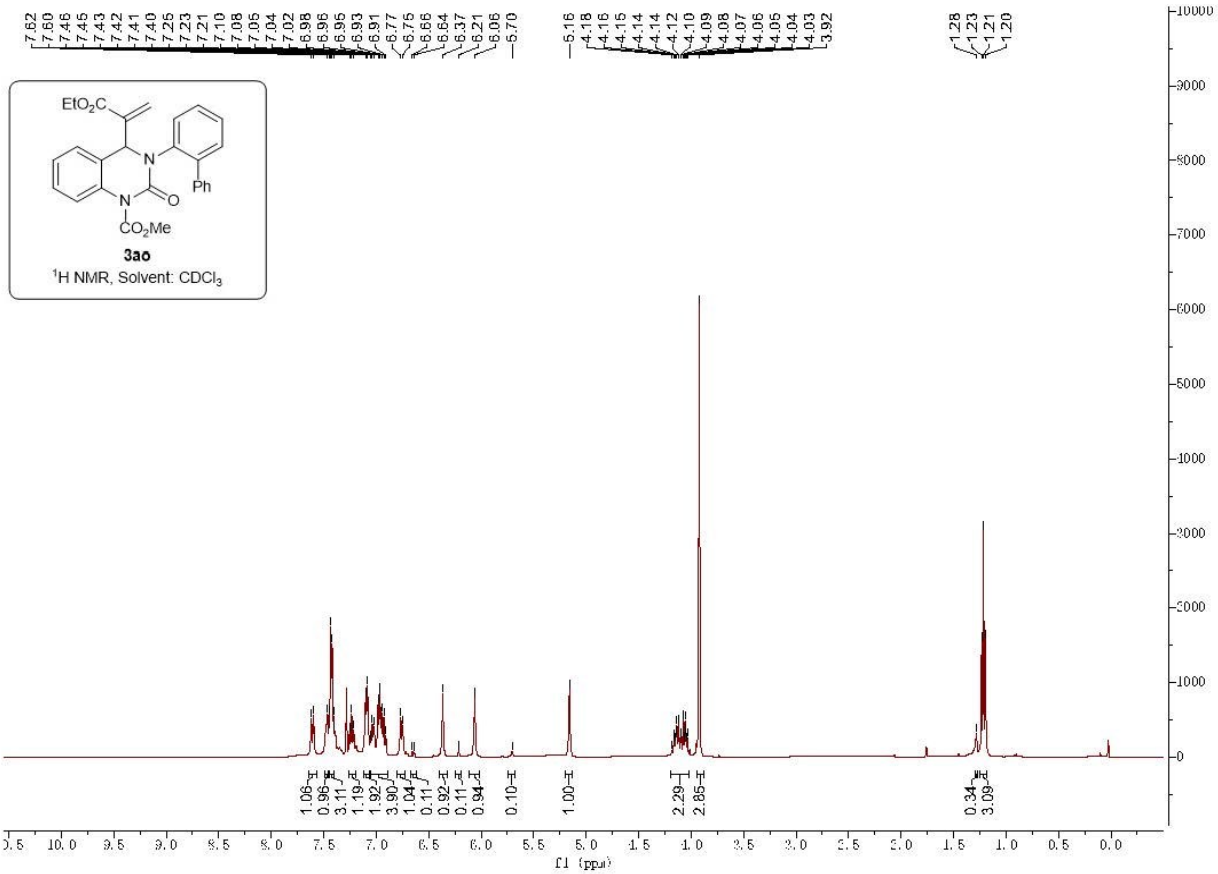
138.18
135.06
133.85
130.55
129.92
128.31
128.25
126.82
125.58
124.61
122.91
122.31
62.20
61.41
54.20
14.03
f1 (ppm)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Ph
N
O
CO2Me
3ao
1H NMR, Solvent: CDCl3
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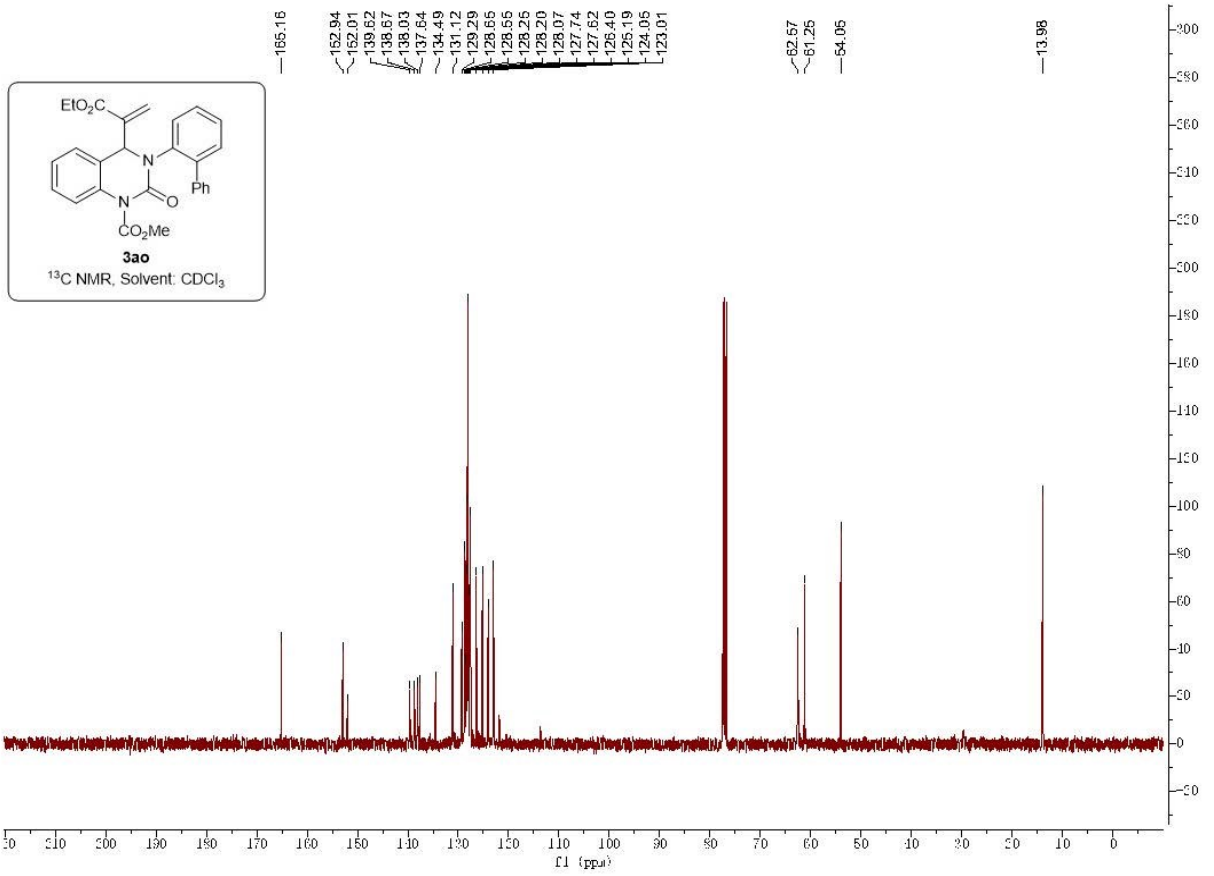
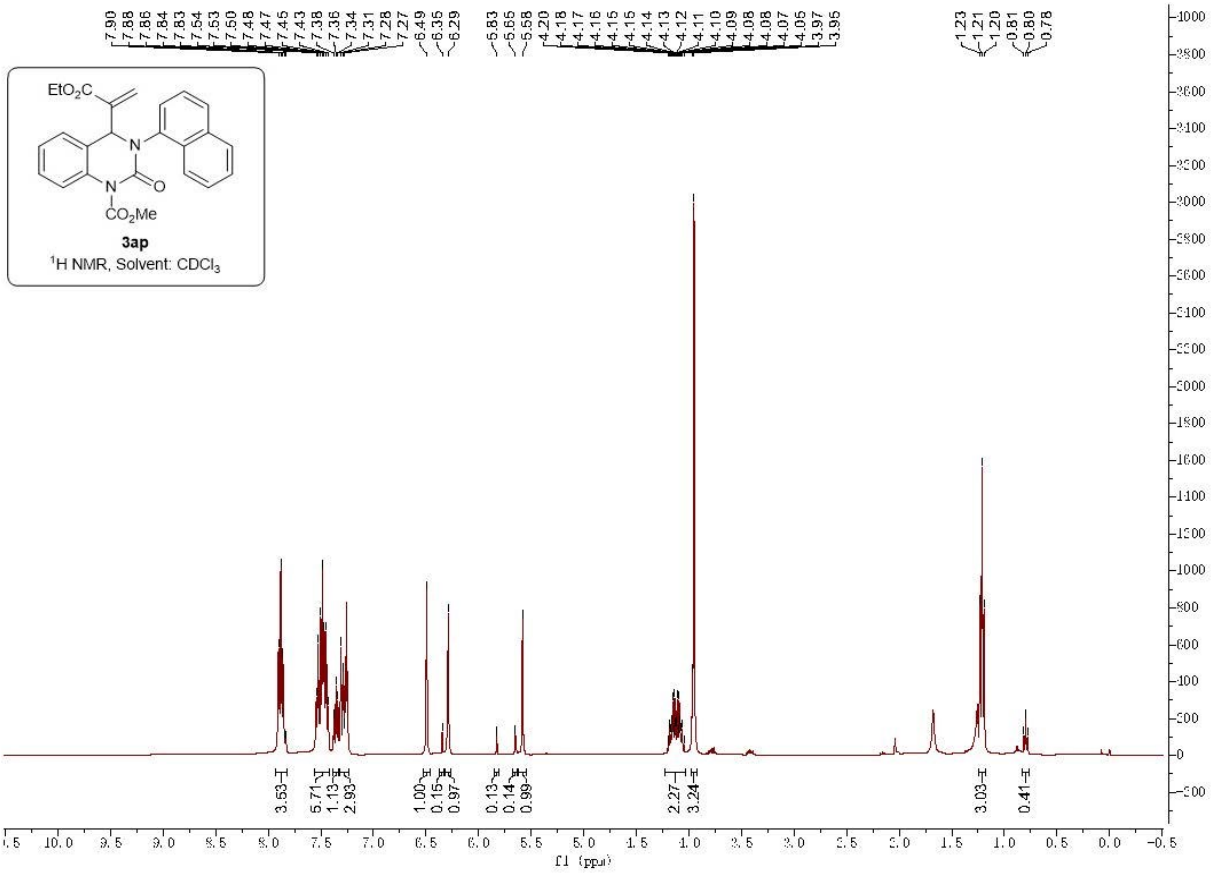
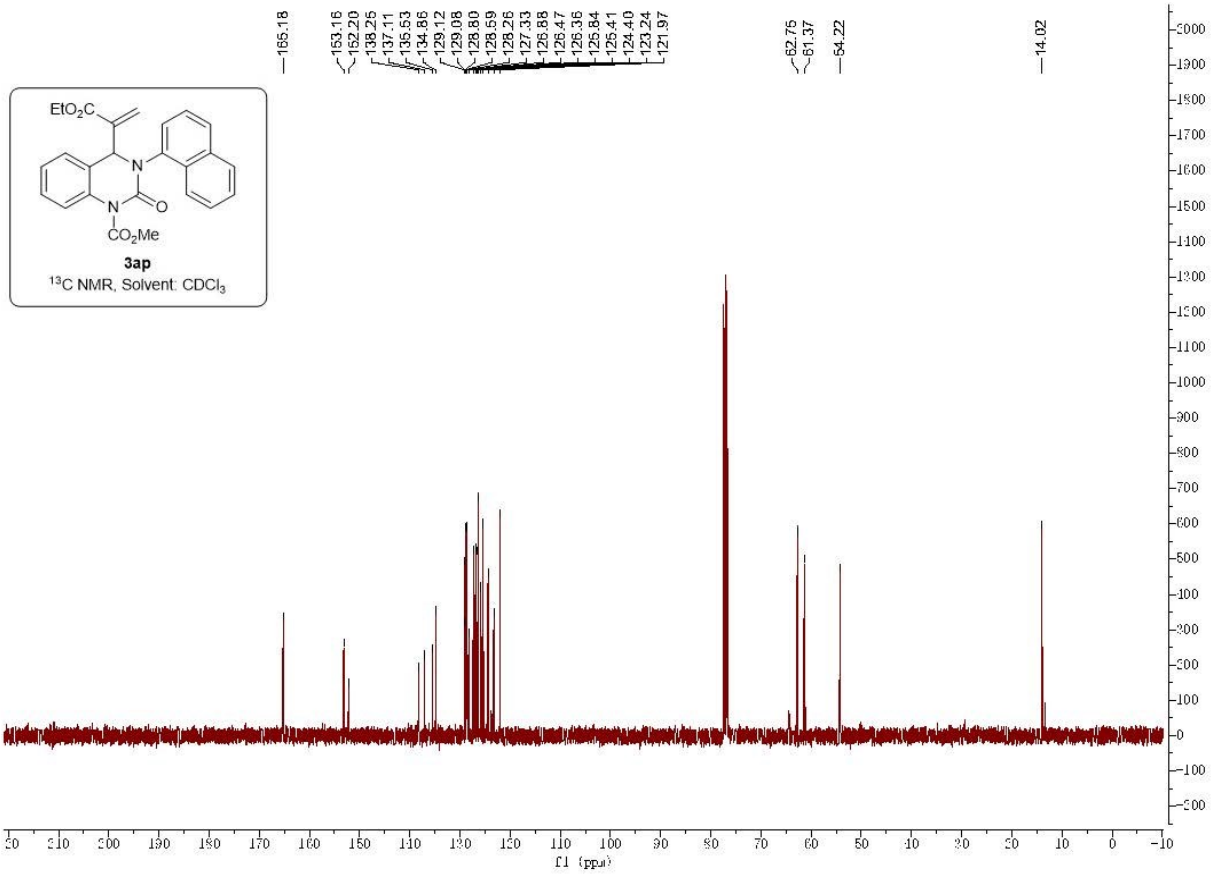
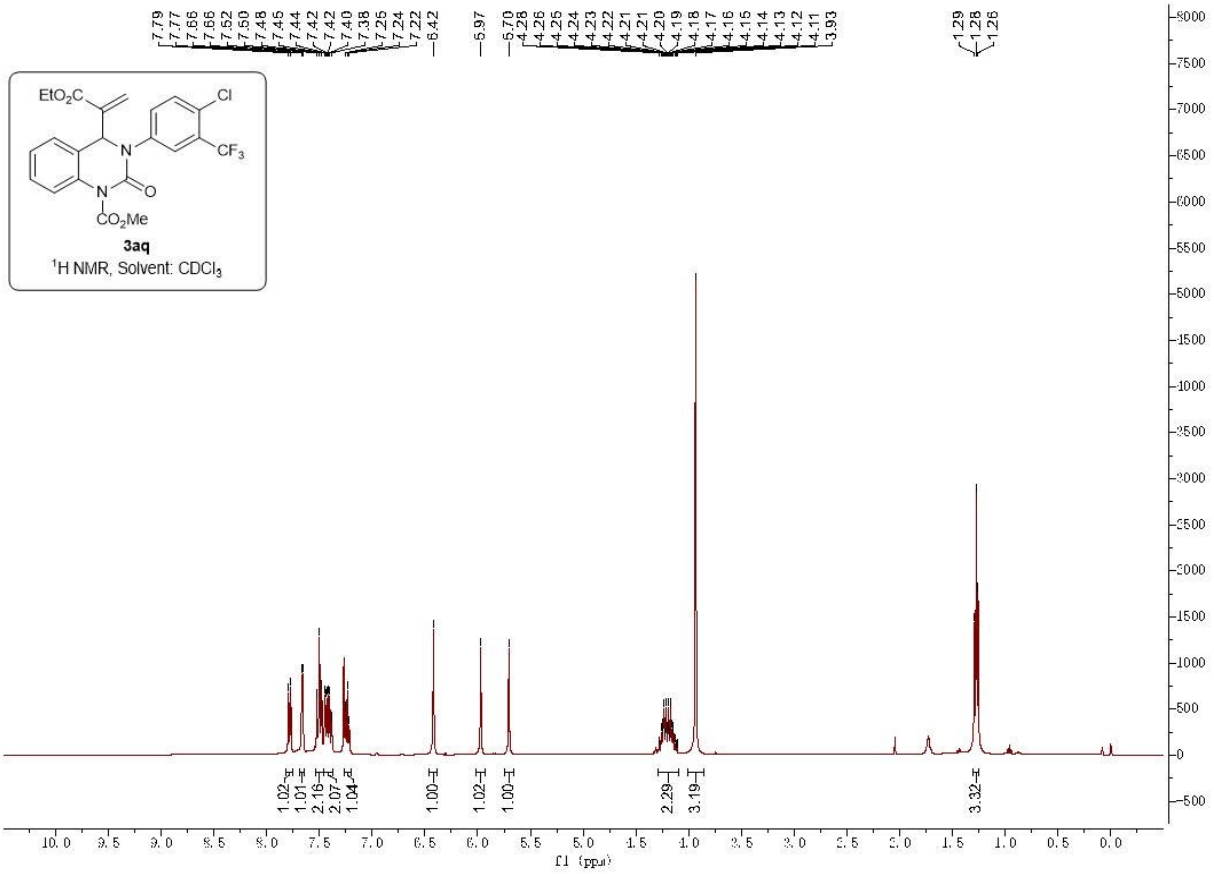
7.46
7.45
7.43
7.42
7.41
7.40
7.25
7.23
7.21
7.10
7.08
7.05
7.04
7.02
6.98
6.96
6.95
6.93
6.91
6.77
6.75
6.66
6.64
6.37
6.21
6.06
5.70
5.16
4.18
4.16
4.15
4.14
4.14
4.12
4.10
4.09
4.08
4.07
4.06
4.06
4.04
4.03
3.92
1.28
1.23
1.21
1.20
1.06
0.96
3.11
1.19
1.92
3.90
1.04
0.11
0.92
0.11
0.94
0.10
1.00
2.29
2.86
0.34
3.09
f1 (ppm)


EtO2C
N
N
O
Ph
CO2Me
3ao
13C NMR, Solvent: CDCl3
165.16
152.94
152.01
139.52
138.67
138.03
137.64
134.49
131.12
129.29
128.65
128.55
128.25
128.20
128.07
127.74
127.52
126.40
125.19
124.05
123.01
62.57
61.25
54.05
13.98
f1 (ppm)


EtO2C
N
N
O
CO2Me
3ap
1H NMR, Solvent: CDCl3
7.90
7.88
7.86
7.84
7.83
7.54
7.53
7.50
7.48
7.47
7.45
7.43
7.38
7.36
7.34
7.31
7.28
7.27
6.49
6.35
6.29
5.83
5.65
5.58
4.20
4.18
4.17
4.16
4.15
4.15
4.14
4.13
4.12
4.11
4.10
4.09
4.08
4.08
4.07
4.05
3.97
3.95
1.23
1.21
1.20
0.81
0.80
0.78
3.53
5.71
1.13
2.93
1.00
0.15
0.97
0.13
0.14
0.99
2.27
3.24
3.03
0.41
f1 (ppm)


EtO2C
N
N
O
CO2Me
3ap
13C NMR, Solvent: CDCl3
165.18
153.16
152.20
138.25
137.11
135.53
134.86
129.12
129.08
128.80
128.59
128.26
127.33
126.88
126.47
126.36
125.84
125.41
124.40
123.24
121.97
62.75
61.37
54.22
14.02
f1 (ppm)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Cl
CF3
N
N
O
CO2Me
3aq
1H NMR, Solvent: CDCl3
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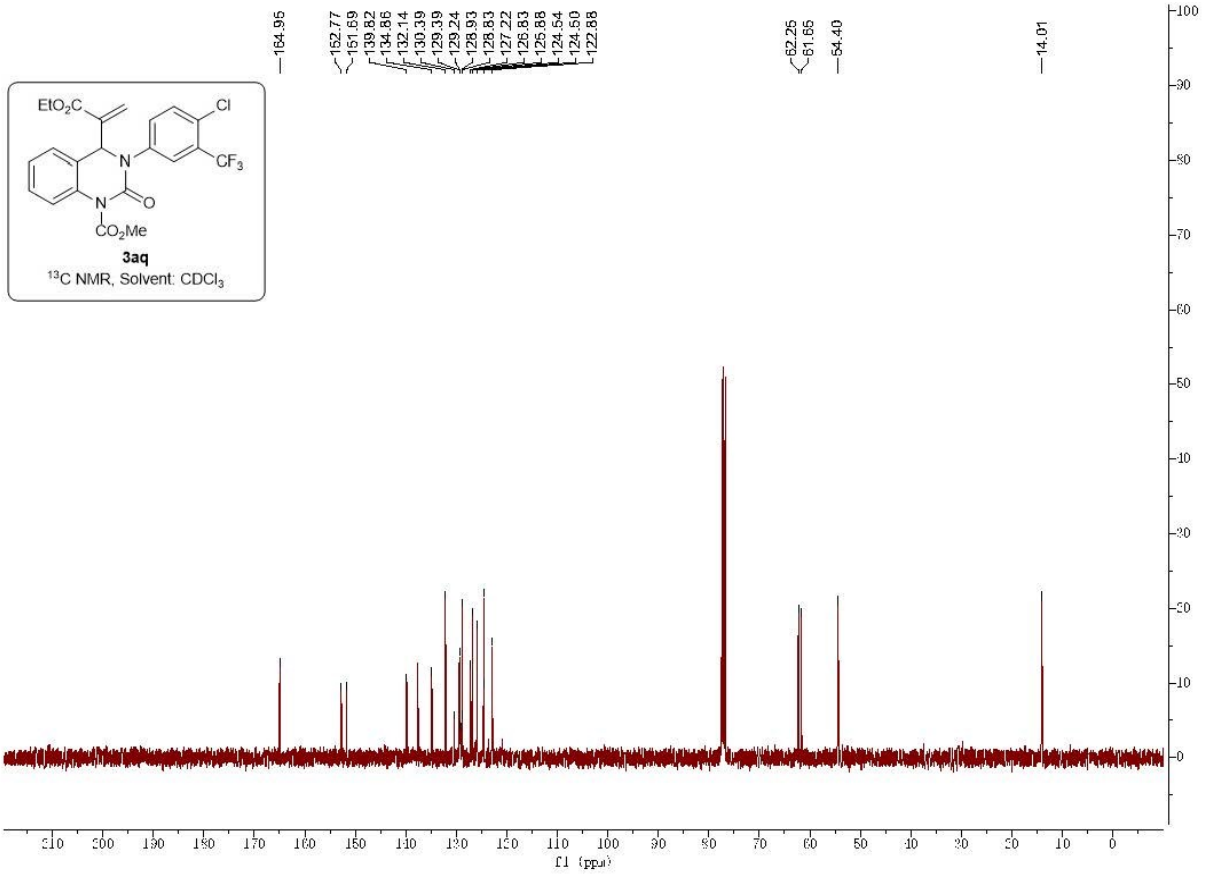
7.77
7.66
7.66
7.52
7.50
7.48
7.45
7.44
7.42
7.42
7.40
7.38
7.25
7.24
7.22
6.42
5.97
5.70
4.28
4.26
4.25
4.24
4.23
4.22
4.21
4.21
4.20
4.19
4.18
4.17
4.16
4.15
4.14
4.13
4.12
4.11
3.93
1.29
1.28
1.26
1.02
1.01
2.16
2.07
1.04
1.00
1.02
1.00
2.29
3.19
3.32
f1 (ppm)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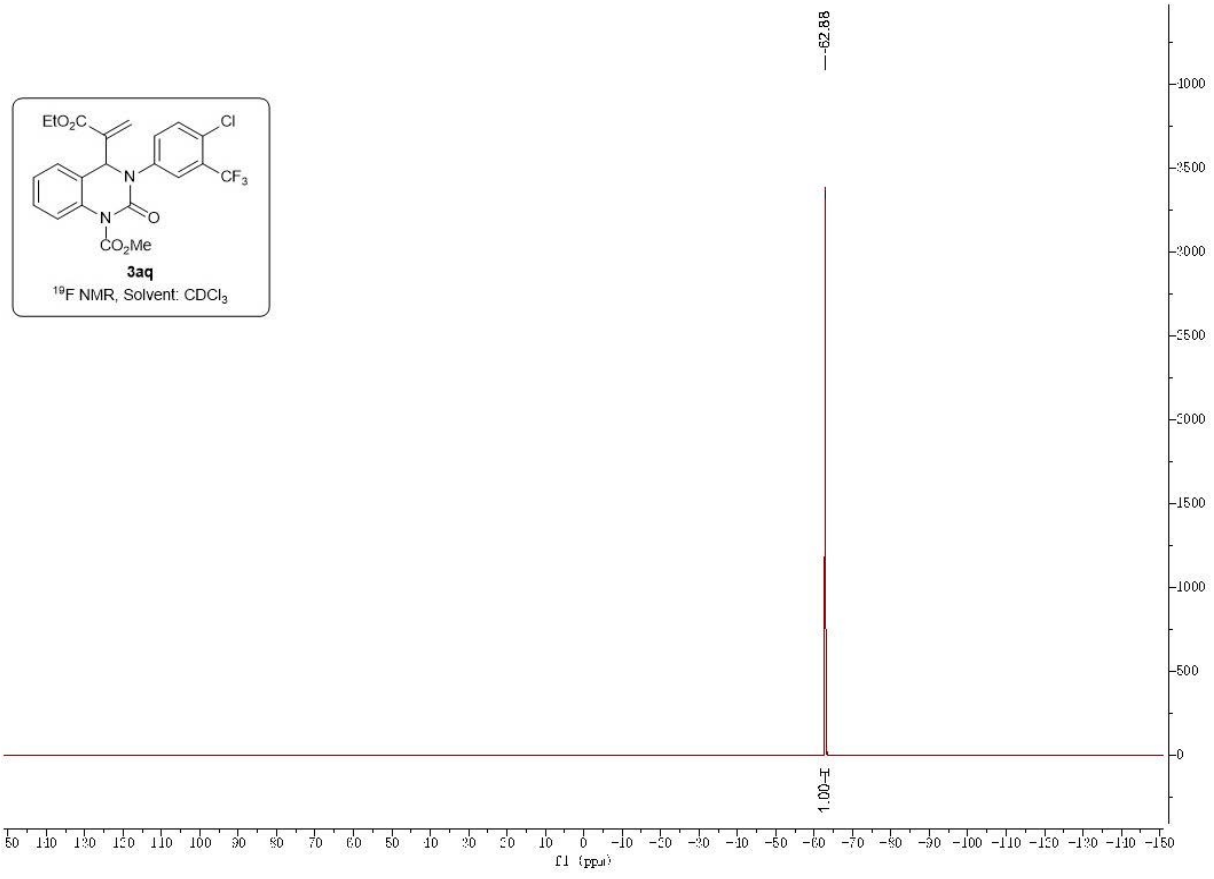
152.77
151.59
139.82
134.86
132.14
130.39
129.39
129.24
128.93
128.83
127.22
126.83
125.88
124.54
124.50
122.88
62.25
61.65
54.40
14.01
EtO2C
Cl
CF3
N
N
O
CO2Me
3aq
13C NMR, Solvent: CDCl3
f1 (ppm)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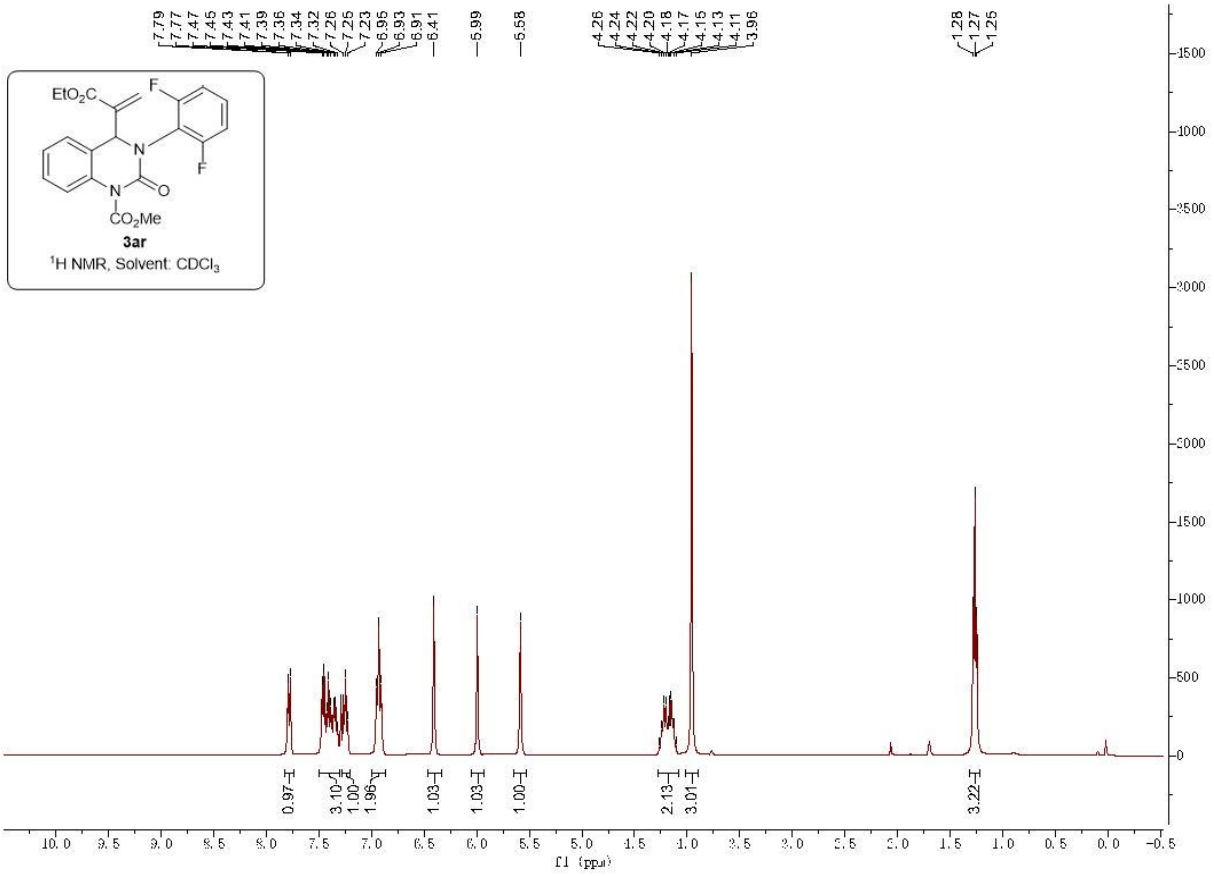
1.00
EtO2C
Cl
CF3
N
N
O
CO2Me
3aq
19F NMR, Solvent: CDCl3
f1 (ppm)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7.77
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7.45
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7.41
7.39
7.36
7.34
7.32
7.26
7.25
7.23
6.95
6.93
6.91
6.41
5.99
5.58
4.26
4.24
4.22
4.20
4.18
4.17
4.15
4.13
4.11
3.96
1.28
1.27
1.25
EtO2C
F
N
F
N
O
CO2Me
3ar
1H NMR, Solvent: CDCl3
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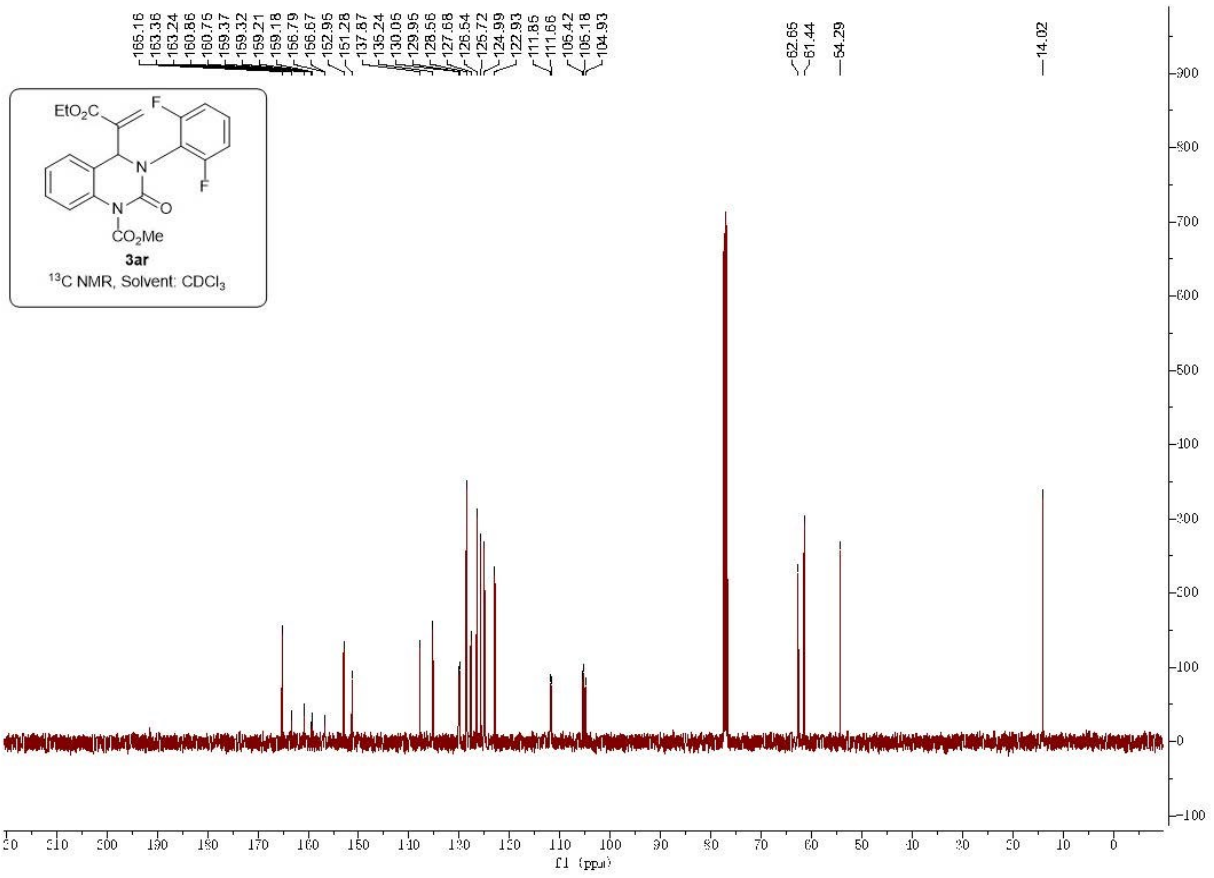
1.00
1.96
1.03
1.03
1.00
2.13
3.01
3.22
f1 (ppm)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163.36
163.24
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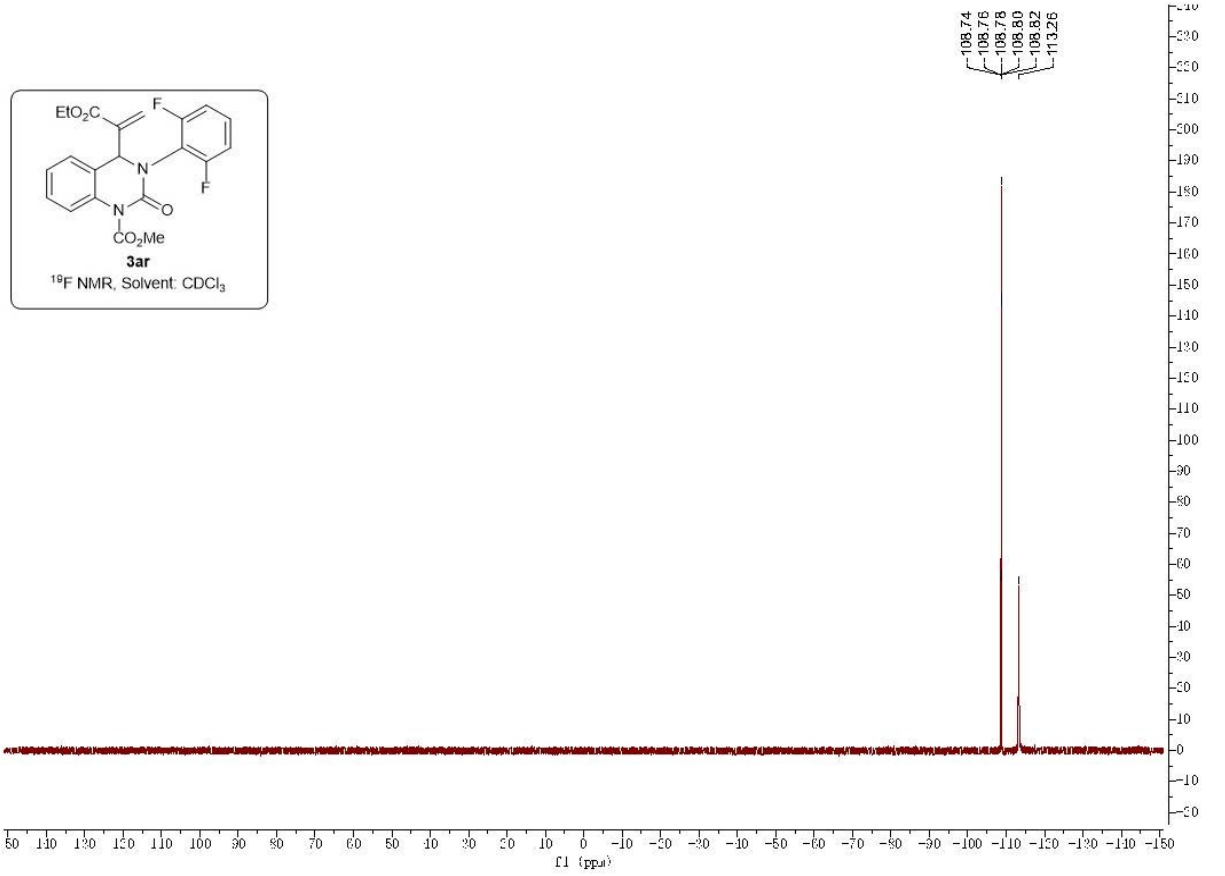
160.75
159.37
159.32
159.21
159.18
156.79
156.67
152.95
151.28
137.87
135.24
130.05
129.95
128.56
127.68
126.54
125.72
124.99
122.93
111.85
111.66
105.42
105.18
104.93
62.65
61.44
54.29
14.02
EtO2C
F
N
F
N
O
CO2Me
3ar
13C NMR, Solvent: CDCl3
f1 (ppm)


EtO2C
F
N
F
N
O
CO2Me
3ar
19F NMR, Solvent: CDCl3
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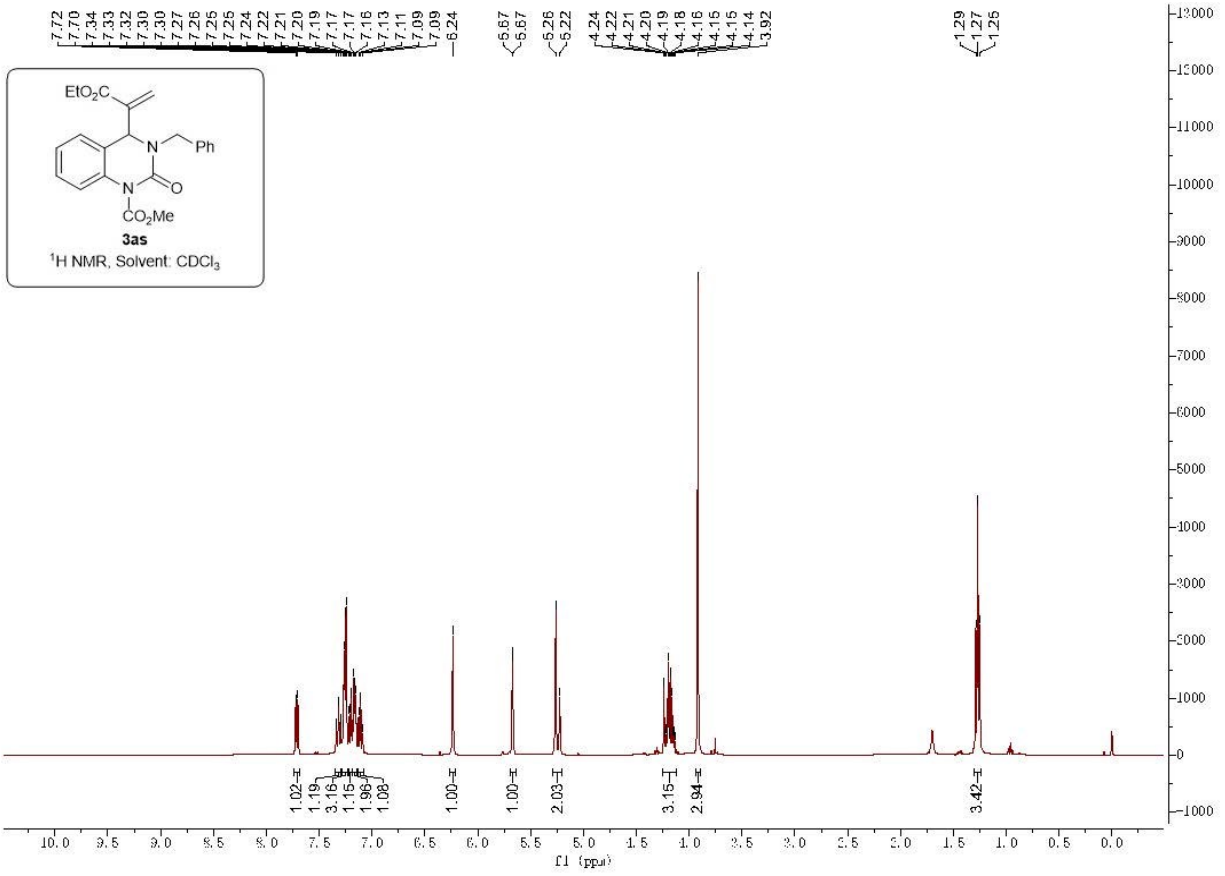
-108.76
-108.78
-108.80
-108.82
-113.26
f1 (ppm)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Ph
N
O
CO2Me
3as
1H NMR, Solvent: CDCl3
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7.70
7.34
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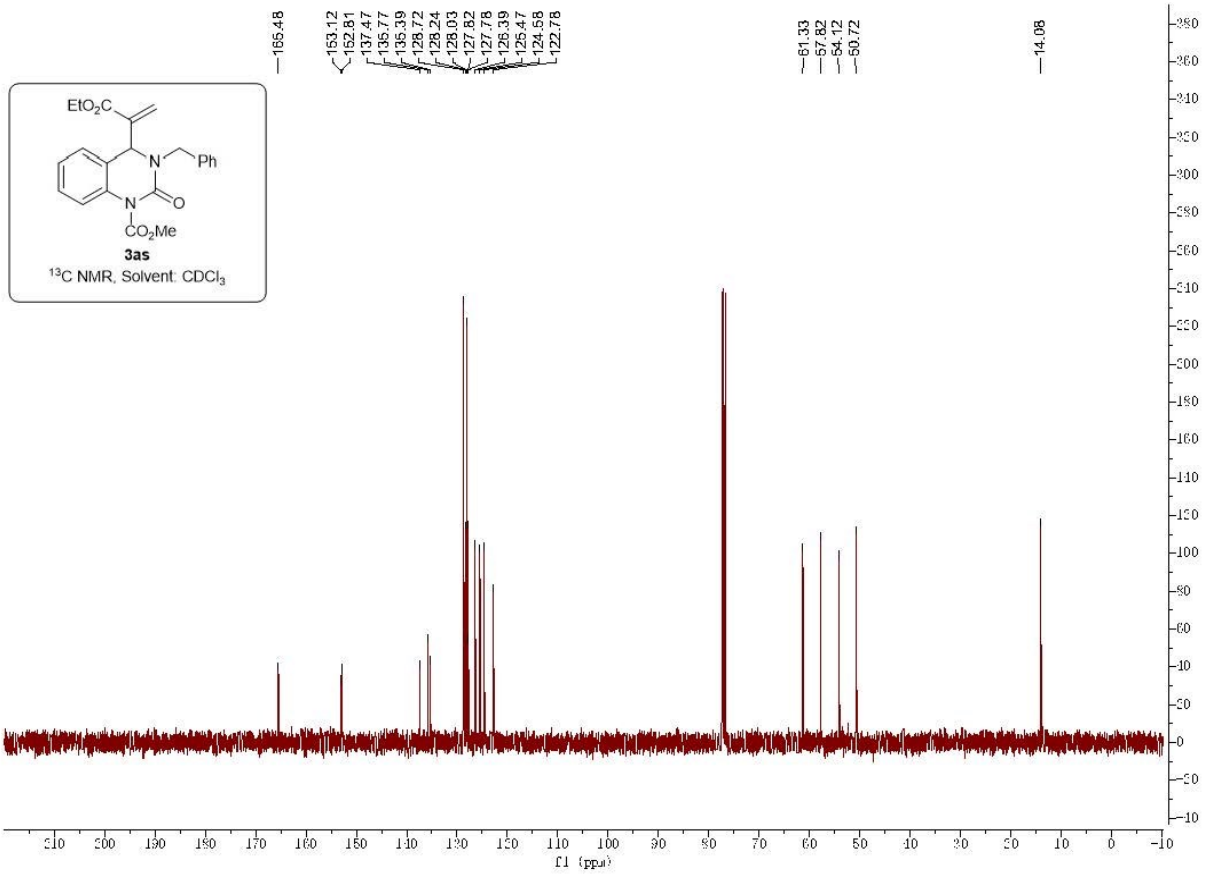
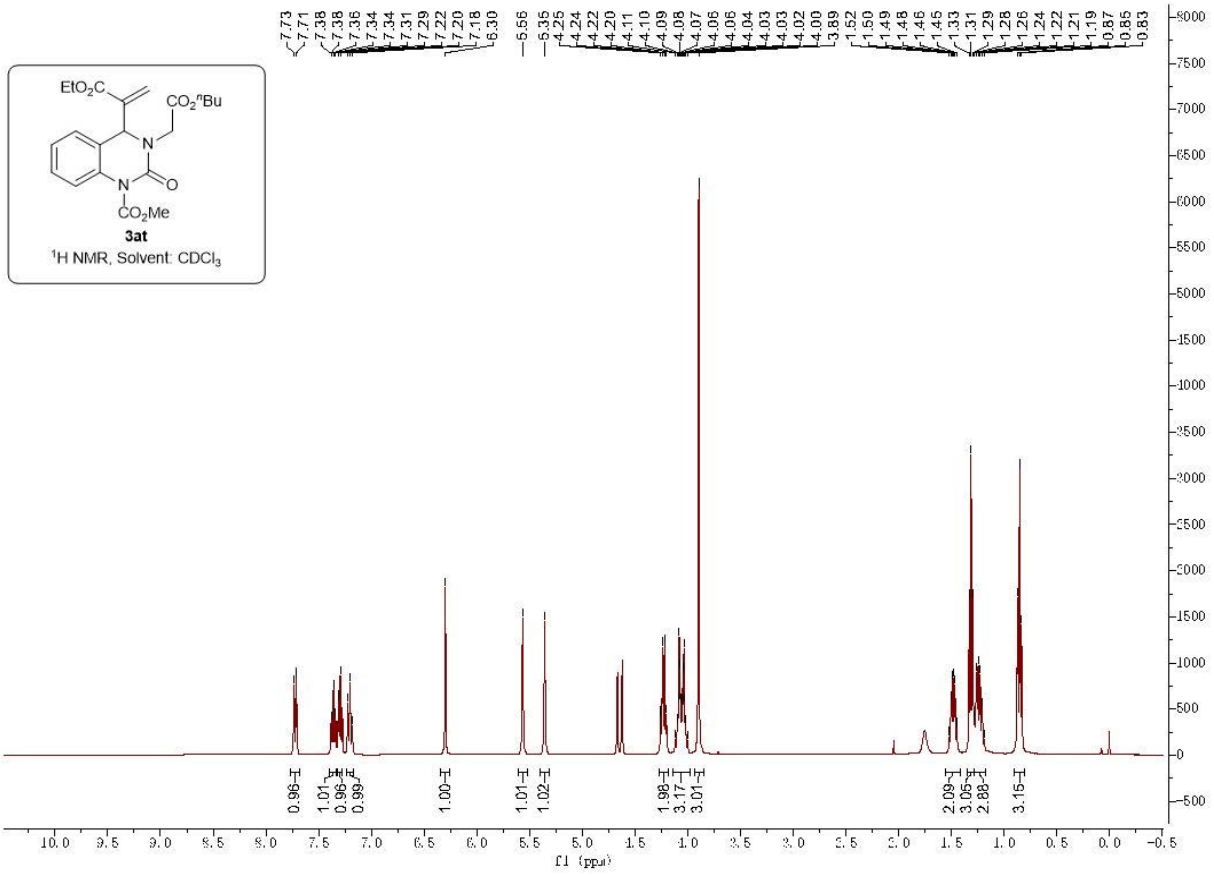
7.32
7.30
7.30
7.27
7.26
7.25
7.25
7.24
7.22
7.21
7.20
7.19
7.17
7.17
7.16
7.13
7.11
7.09
7.09
6.24
5.67
5.67
5.26
5.22
4.24
4.22
4.21
4.20
4.19
4.18
4.16
4.15
4.15
4.14
3.92
1.29
1.27
1.25
1.02
1.19
3.16
1.15
1.96
1.08
1.00
1.00
2.03
3.15
2.94
3.42
f1 (ppm)


EtO2C
N
Ph
N
O
CO2Me
3as
13C NMR, Solvent: CDCl3
165.48
153.12
152.81
137.47
135.77
135.39
128.72
128.24
128.03
127.82
127.78
126.39
125.47
124.58
122.78
61.33
57.82
54.12
50.72
14.08
f1 (ppm)


EtO2C
CO2nBu
N
N
O
CO2Me
3at
1H NMR, Solvent: CDCl3
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7.71
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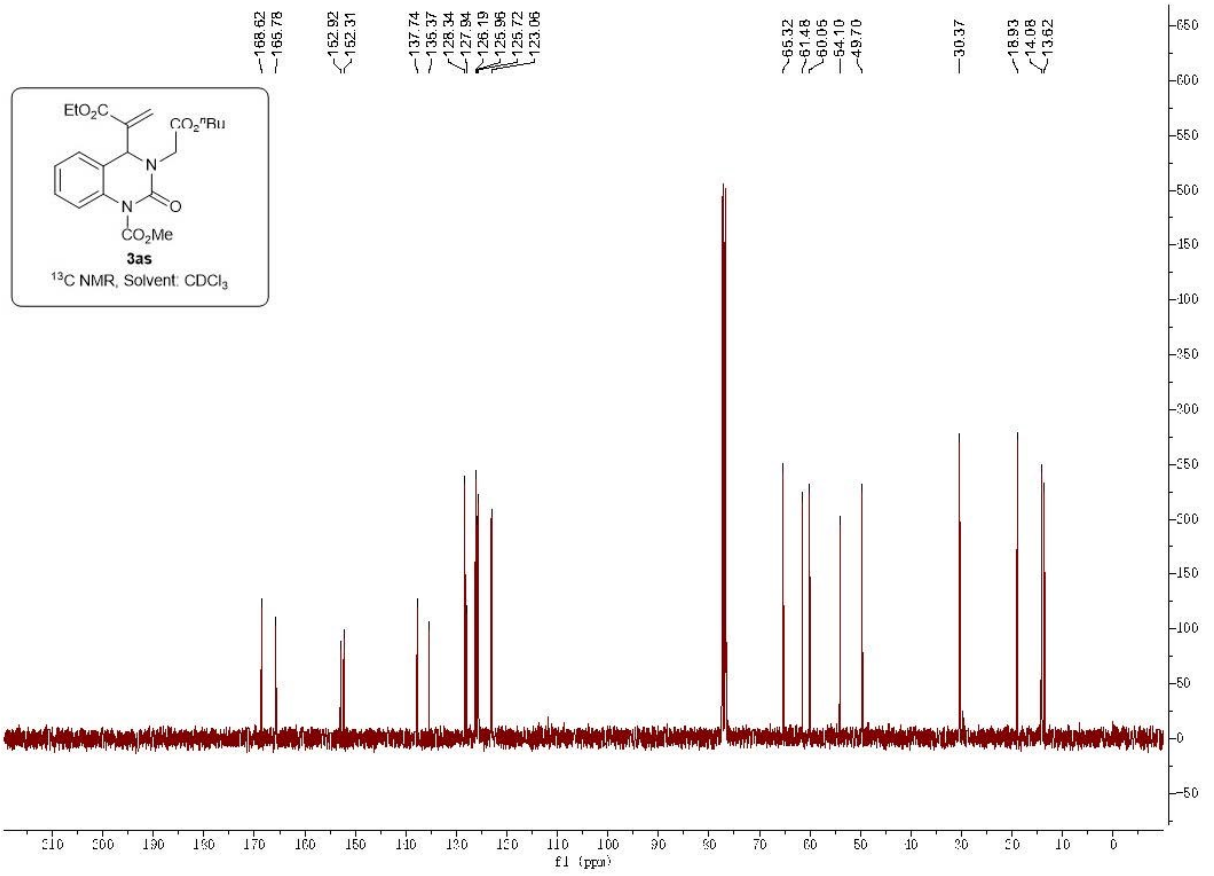
7.34
7.31
7.29
7.22
7.20
7.18
6.30
5.56
5.35
4.25
4.24
4.22
4.20
4.11
4.10
4.09
4.08
4.07
4.06
4.06
4.04
4.03
4.03
4.02
4.00
3.89
1.52
1.50
1.49
1.48
1.46
1.45
1.33
1.31
1.29
1.28
1.26
1.24
1.22
1.21
1.19
0.87
0.85
0.83
0.96
1.01
0.96
0.99
1.00
1.01
1.02
1.98
3.17
3.01
2.09
3.06
2.88
3.15
f1 (ppm)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152.31
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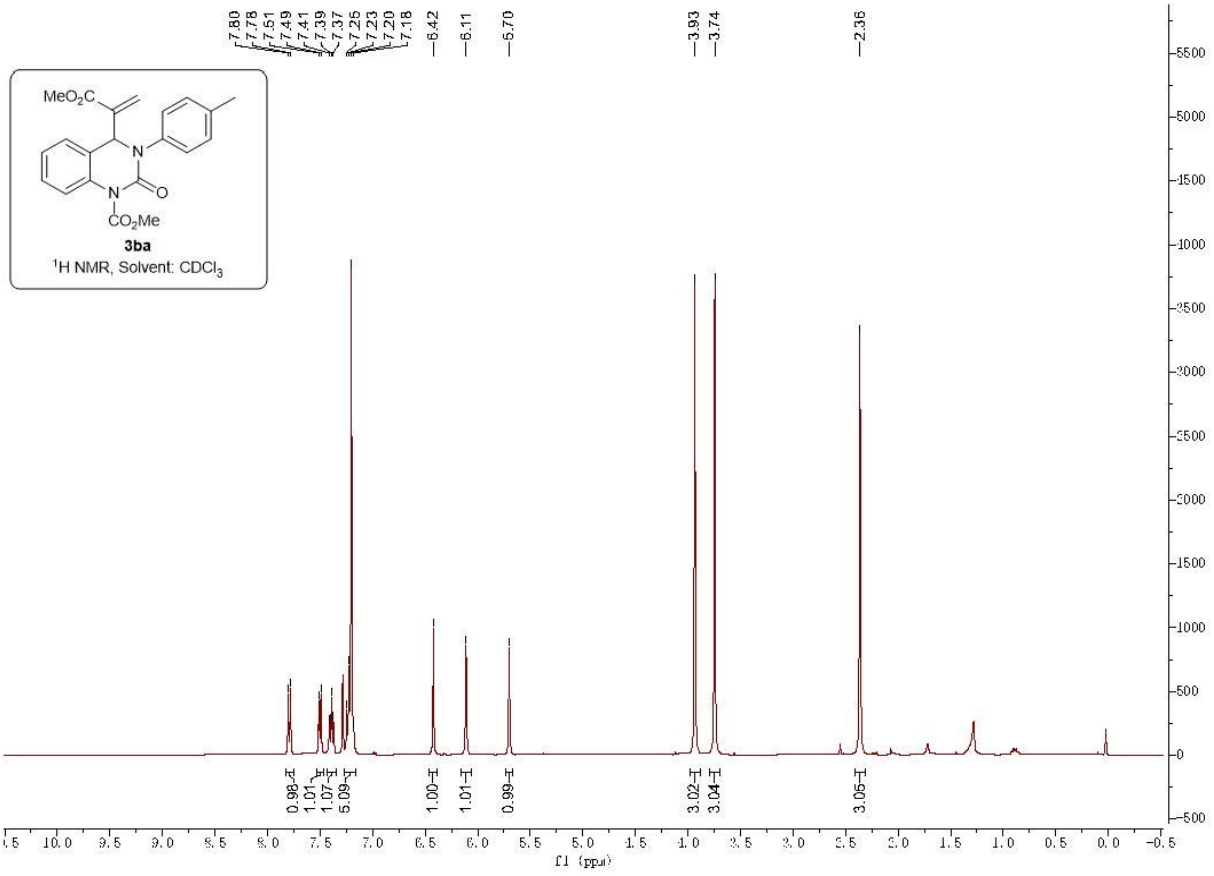
135.37
128.34
127.84
126.19
125.96
125.72
123.06
65.32
61.48
60.05
54.10
49.70
30.37
18.93
14.08
13.62
EtO2C
CO2nBu
N
N
O
CO2Me
3as
13C NMR, Solvent: CDCl3
f1 (ppm)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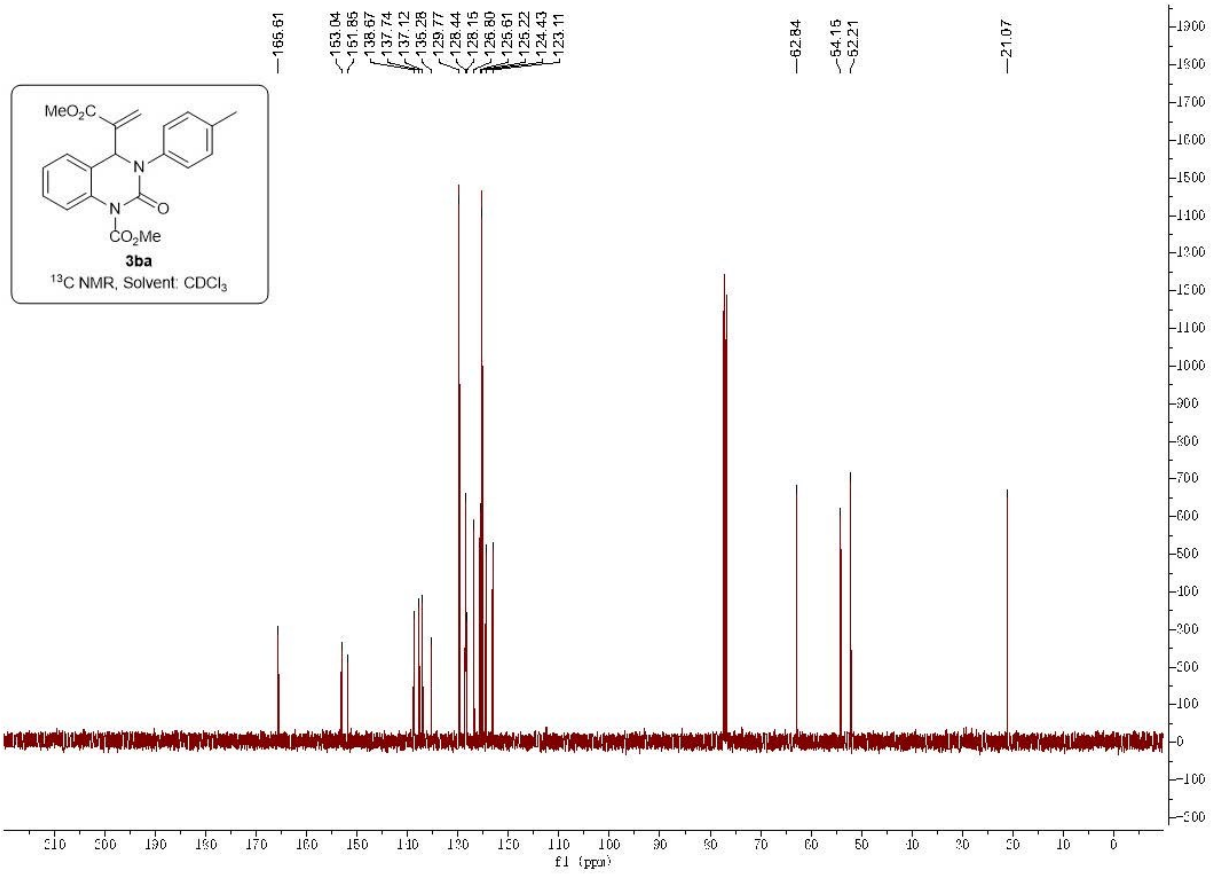
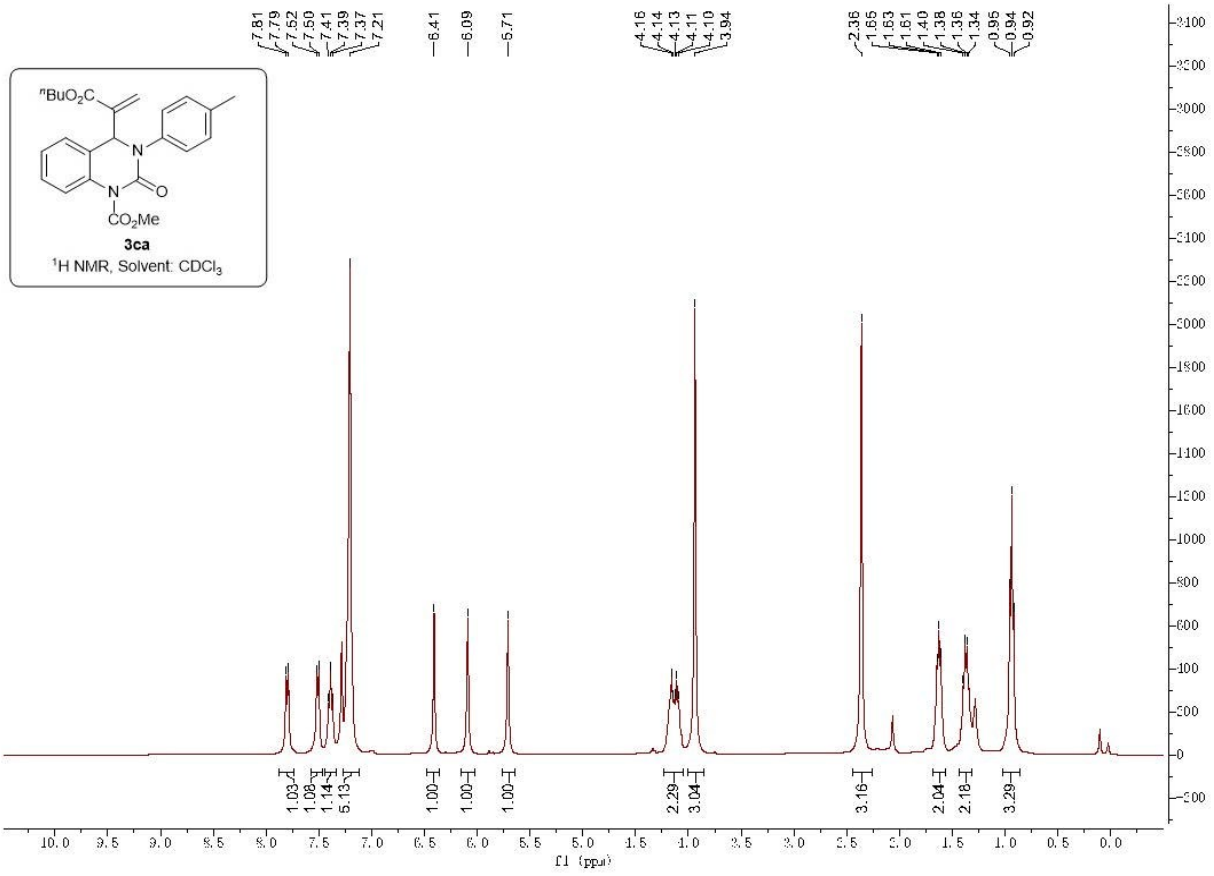
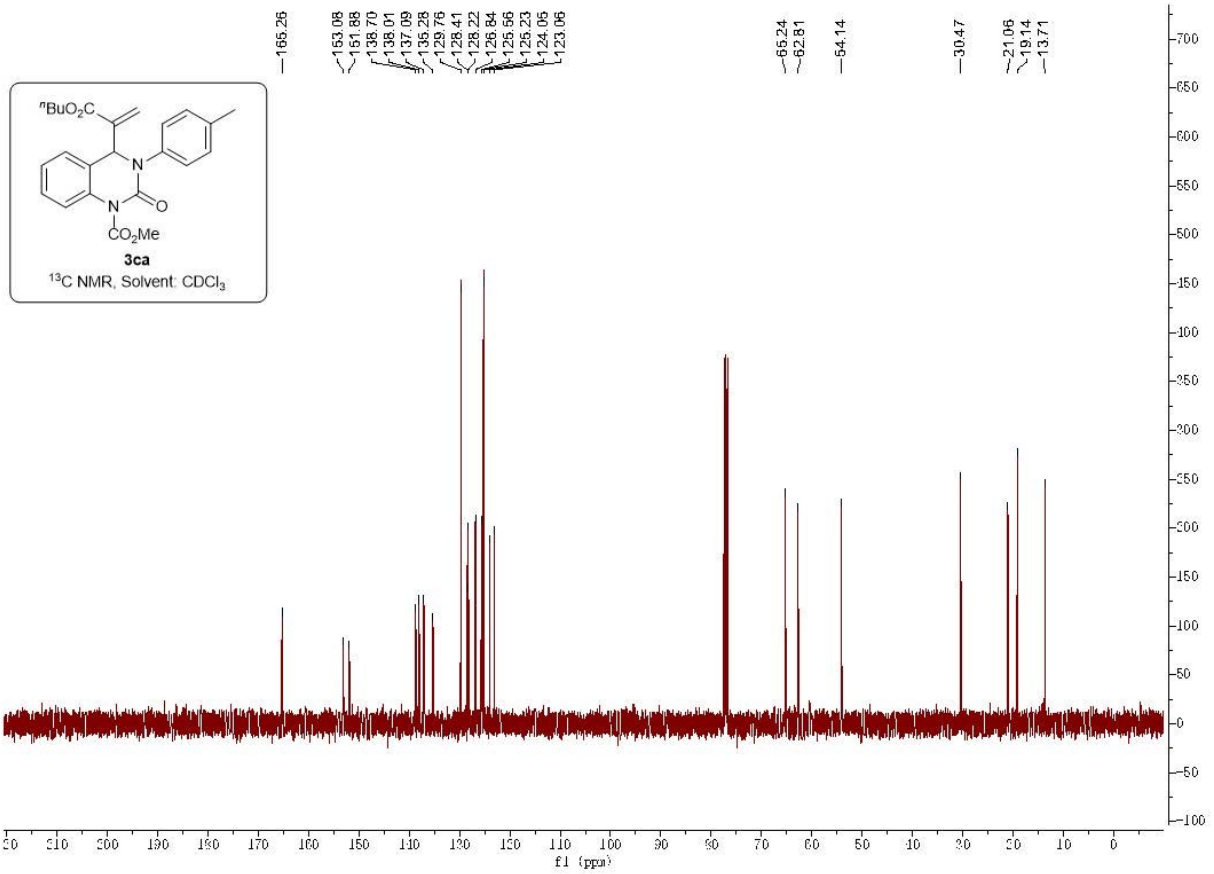
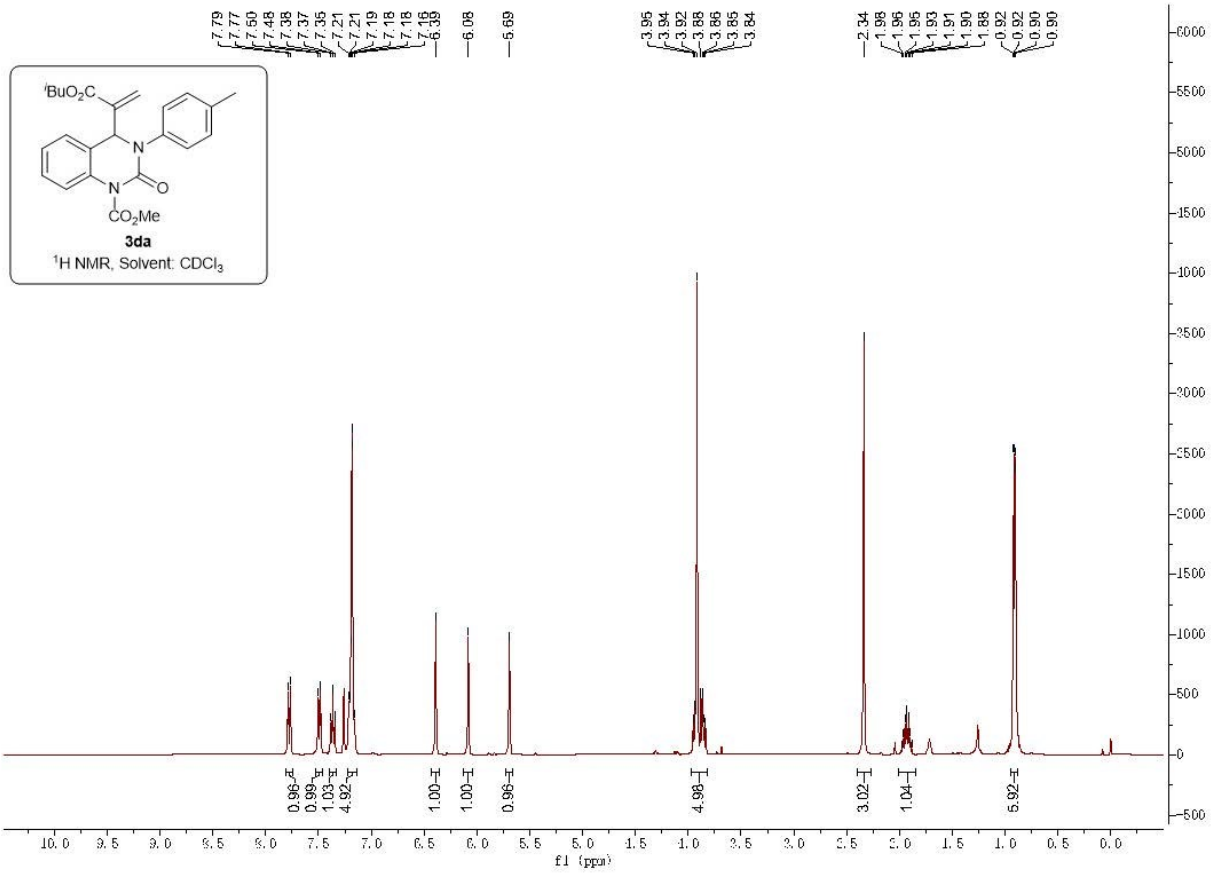
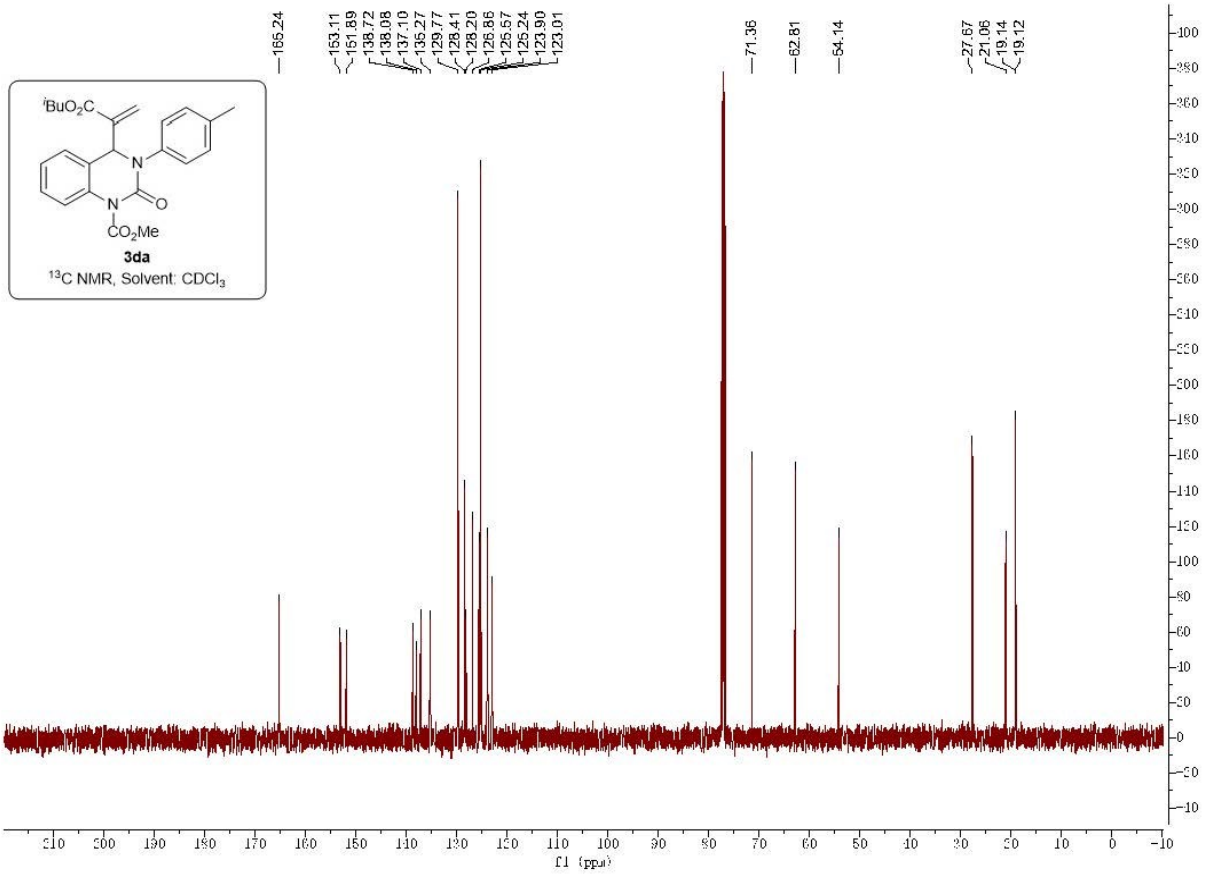
7.78
7.51
7.49
7.41
7.39
7.37
7.25
7.23
7.20
7.18
6.42
6.11
6.70
3.93
3.74
2.36
MeO2C
N
N
O
CO2Me
3ba
1H NMR, Solvent: CDCl3
0.98
1.01
1.07
5.09
1.00
1.01
0.99
3.02
3.04
3.05
f1 (ppm)

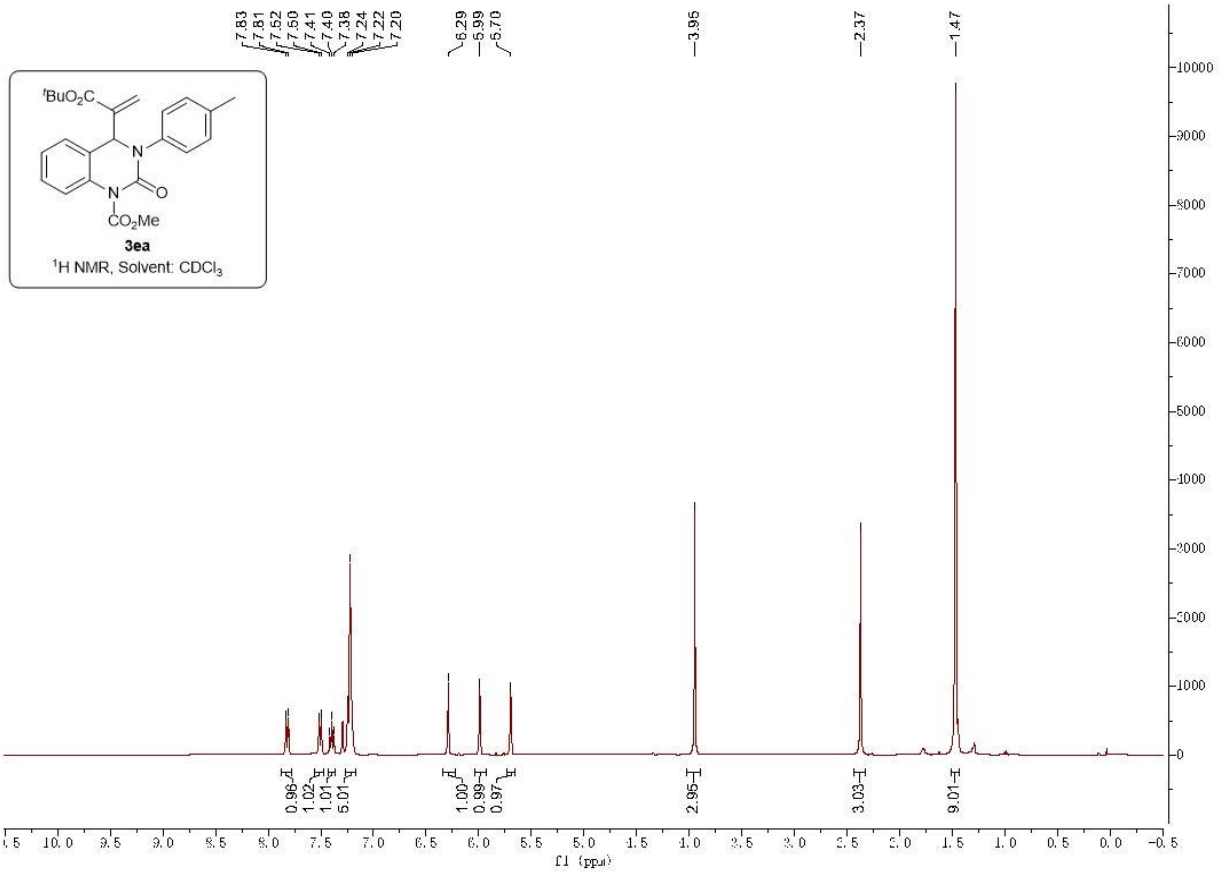

MeO2C
N
N
O
CO2Me
3ba
13C NMR, Solvent: CDCl3
166.61
153.04
151.86
138.67
137.74
137.12
135.28
129.77
128.44
128.15
126.80
125.61
125.22
124.43
123.11
62.84
54.15
52.21
21.07
f1 (ppm)

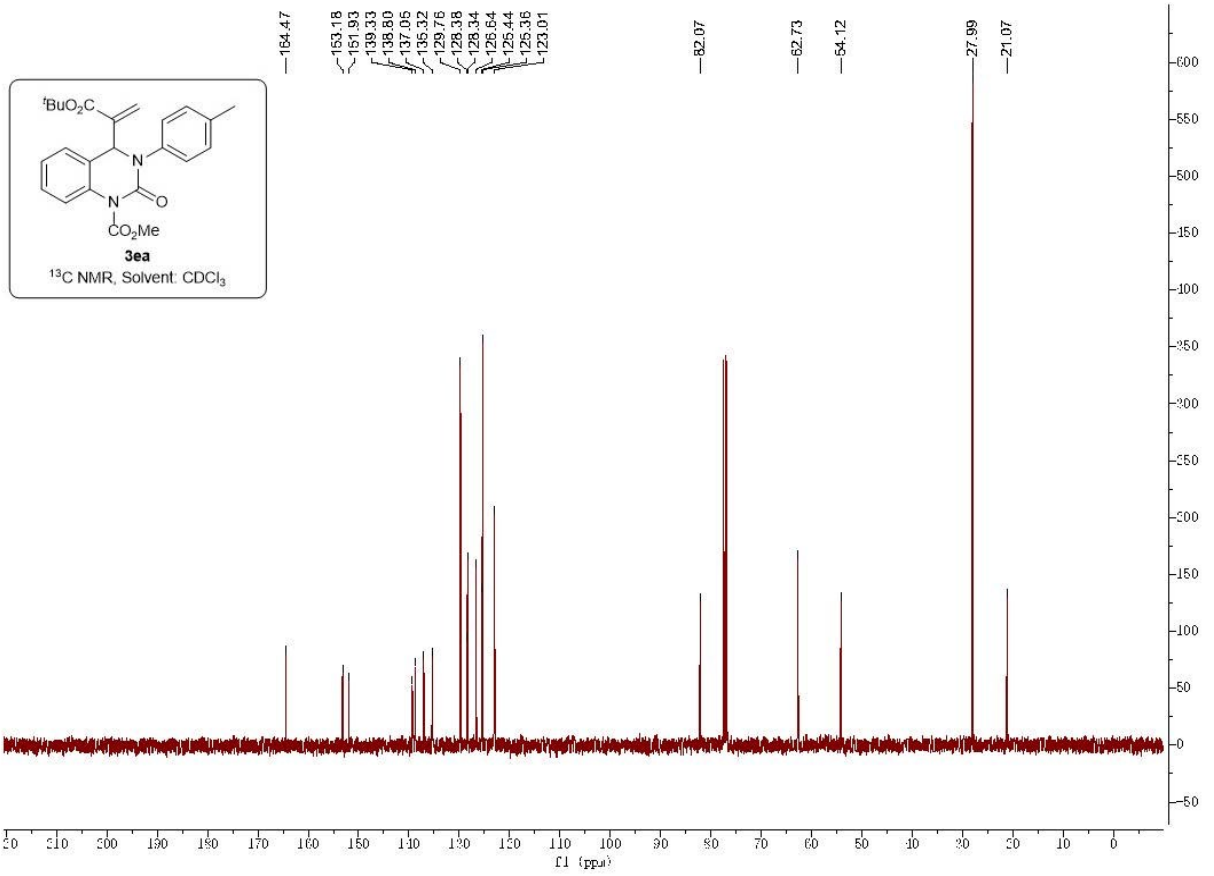

nBuO2C
N
N
O
CO2Me
3ca
1H NMR, Solvent: CDCl3
7.81
7.79
7.52
7.50
7.41
7.39
7.37
7.21
6.41
6.09
5.71
4.16
4.14
4.13
4.11
4.10
3.94
2.36
1.65
1.63
1.61
1.40
1.38
1.36
1.34
0.95
0.94
0.92
1.03
1.08
1.14
5.13
1.00
1.00
1.00
2.29
3.04
3.16
2.04
2.18
3.29
f1 (ppm)

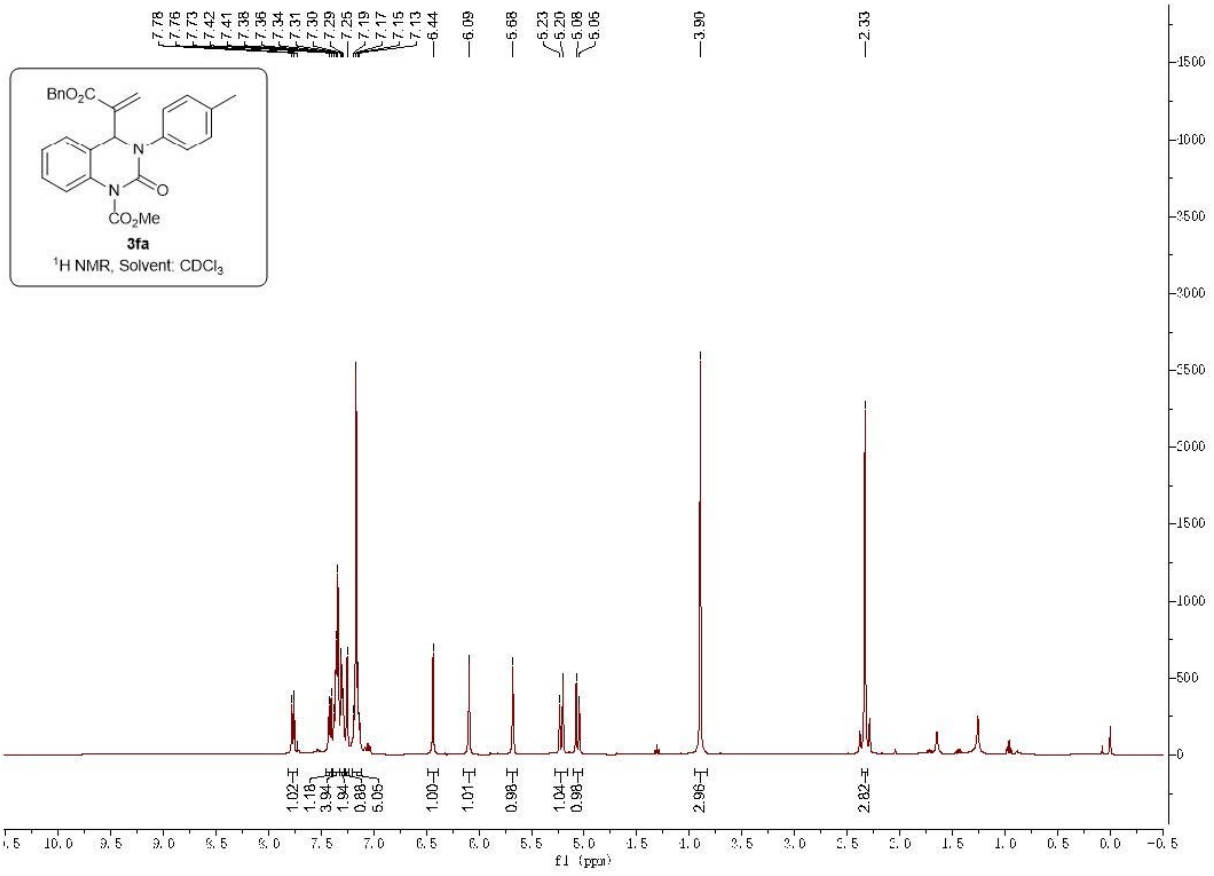

nBuO2C
N
N
O
CO2Me
3ca
13C NMR, Solvent: CDCl3
165.26
153.08
151.88
138.70
138.01
137.09
135.28
129.76
128.41
128.22
126.84
125.66
125.23
124.05
123.06
65.24
62.81
54.14
30.47
21.06
19.14
13.71
f1 (ppm)

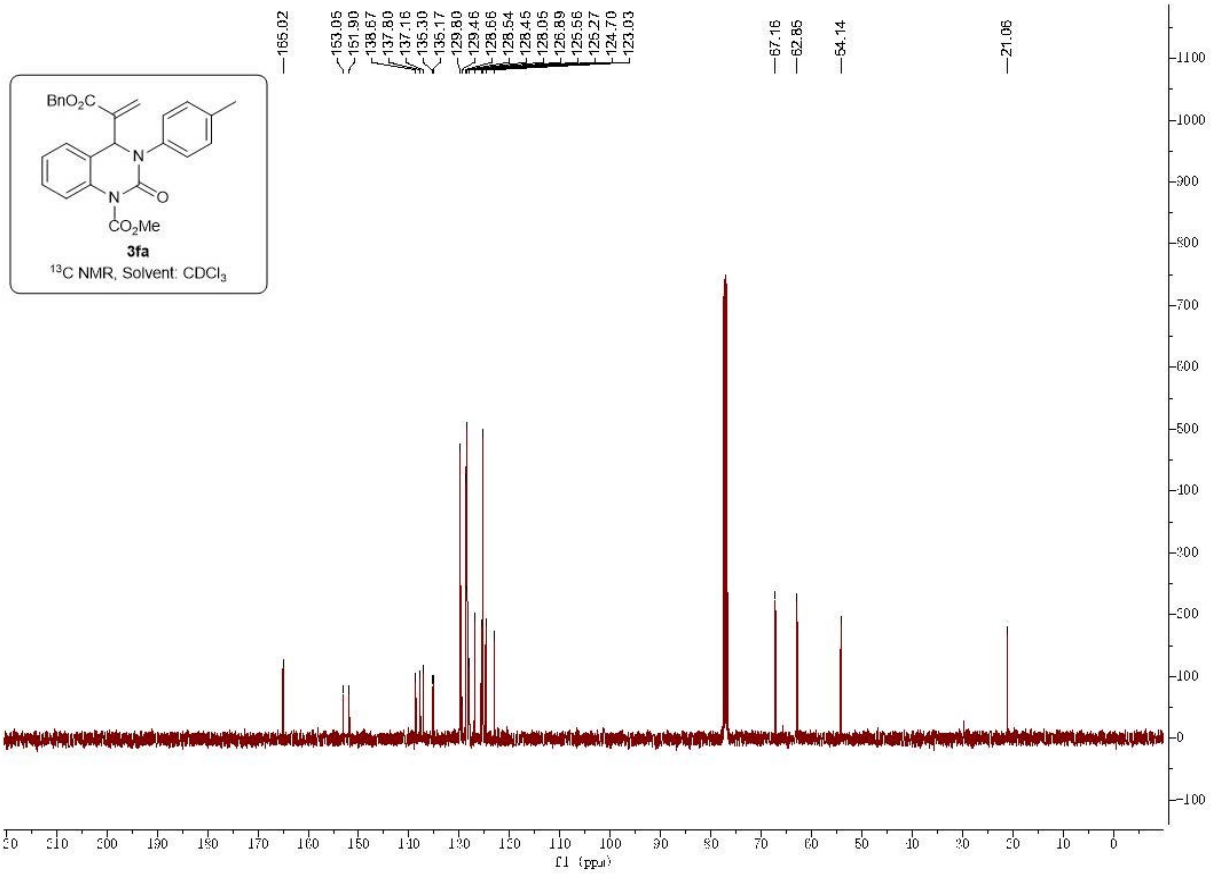

tBuO2C
N
N
O
CO2Me
3da
1H NMR, Solvent: CDCl3
7.79
7.77
7.60
7.48
7.38
7.37
7.35
7.21
7.21
7.19
7.18
7.18
7.16
6.39
6.08
6.69
3.95
3.94
3.92
3.88
3.86
3.85
3.84
2.34
1.98
1.96
1.95
1.93
1.91
1.90
1.88
0.92
0.92
0.90
0.90
0.96
0.99
1.03
4.92
1.00
1.00
0.96
4.98
3.02
1.04
5.92
f1 (ppm)

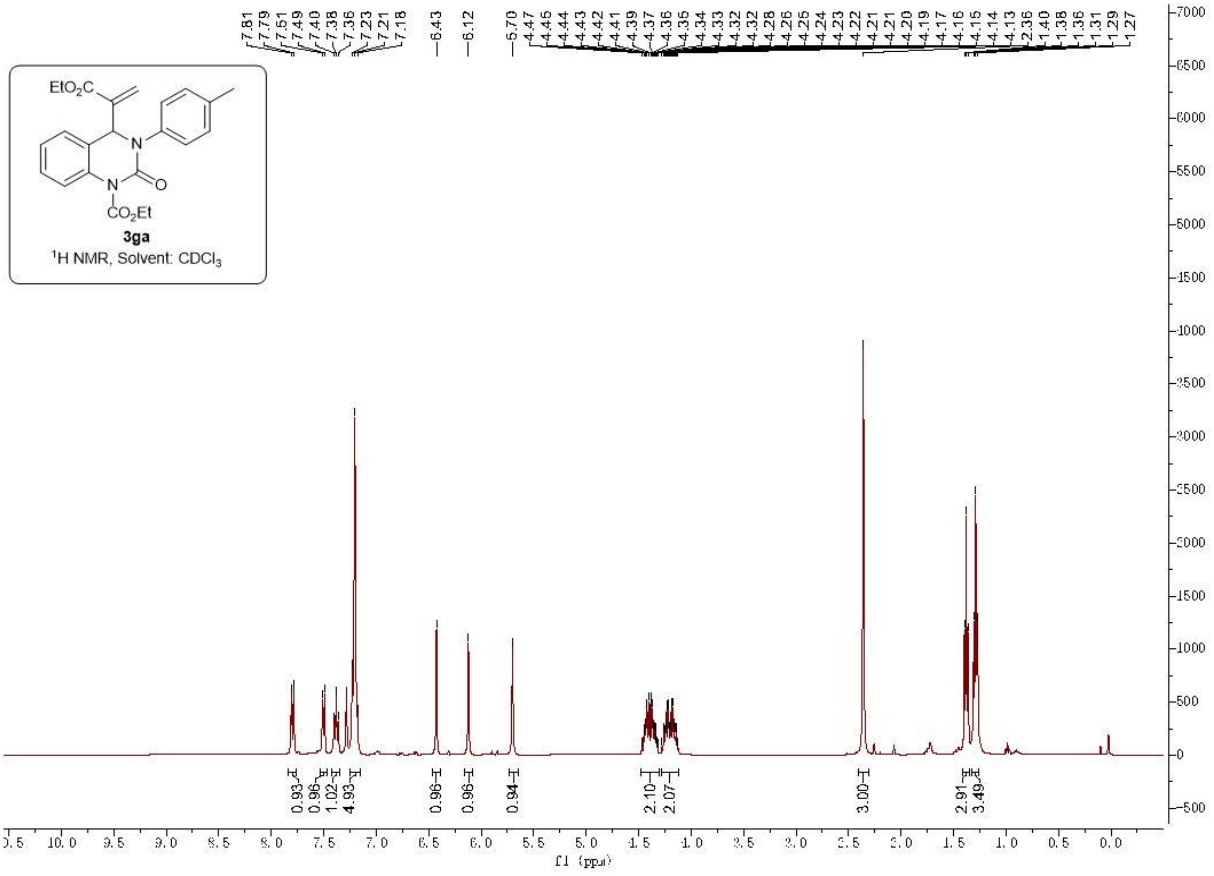

tBuO2C
N
N
O
CO2Me
3da
13C NMR, Solvent: CDCl3
165.24
153.11
151.89
138.72
138.08
137.10
135.27
129.77
128.41
128.20
126.86
125.57
125.24
123.90
123.01
71.36
62.81
54.14
27.67
21.06
19.14
19.12
f1 (ppm)

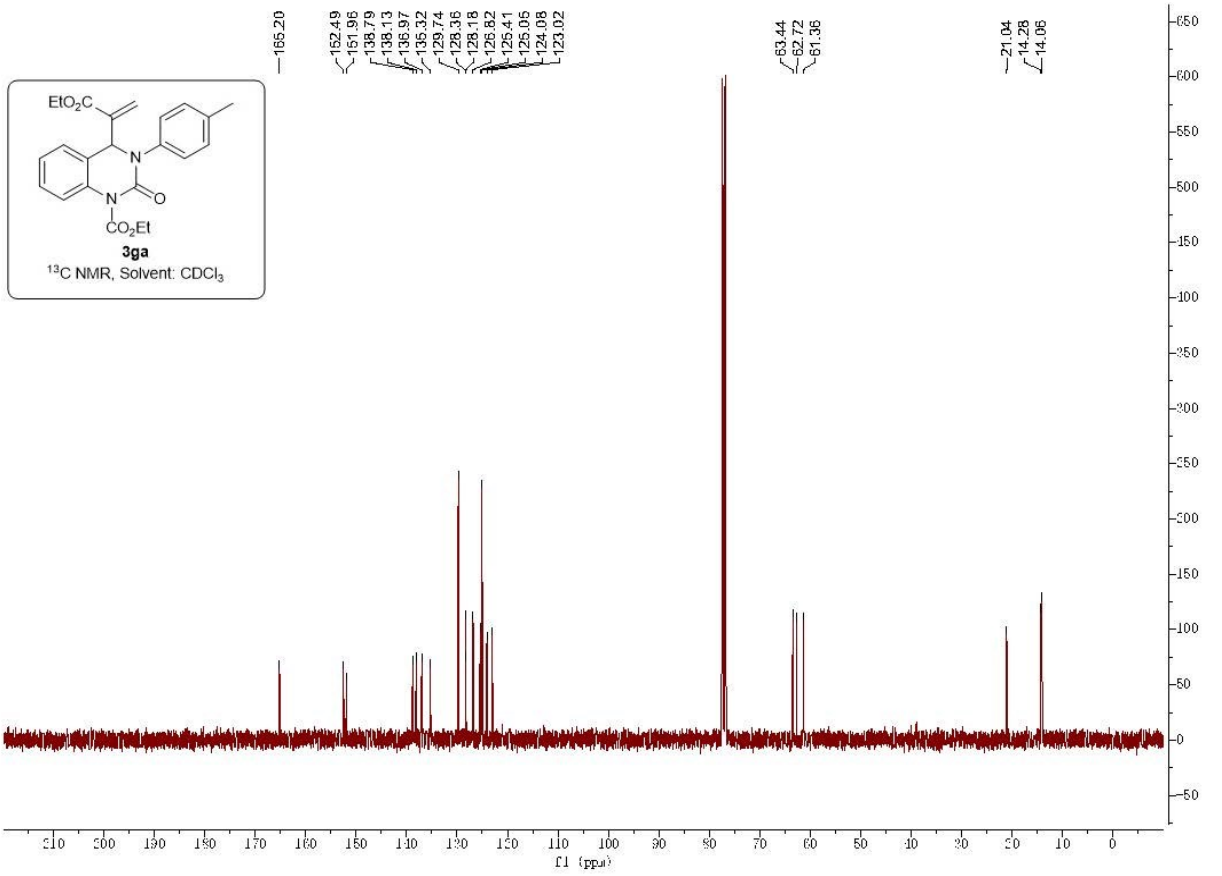

tBuO2C
N
N
O
CO2Me
3ea
1H NMR, Solvent: CDCl3
7.83
7.81
7.52
7.50
7.41
7.40
7.38
7.24
7.22
7.20
6.29
5.99
5.70
3.95
2.37
1.47
0.96
1.02
1.01
5.01
1.00
0.99
0.97
2.95
3.03
9.01
f1 (ppm)

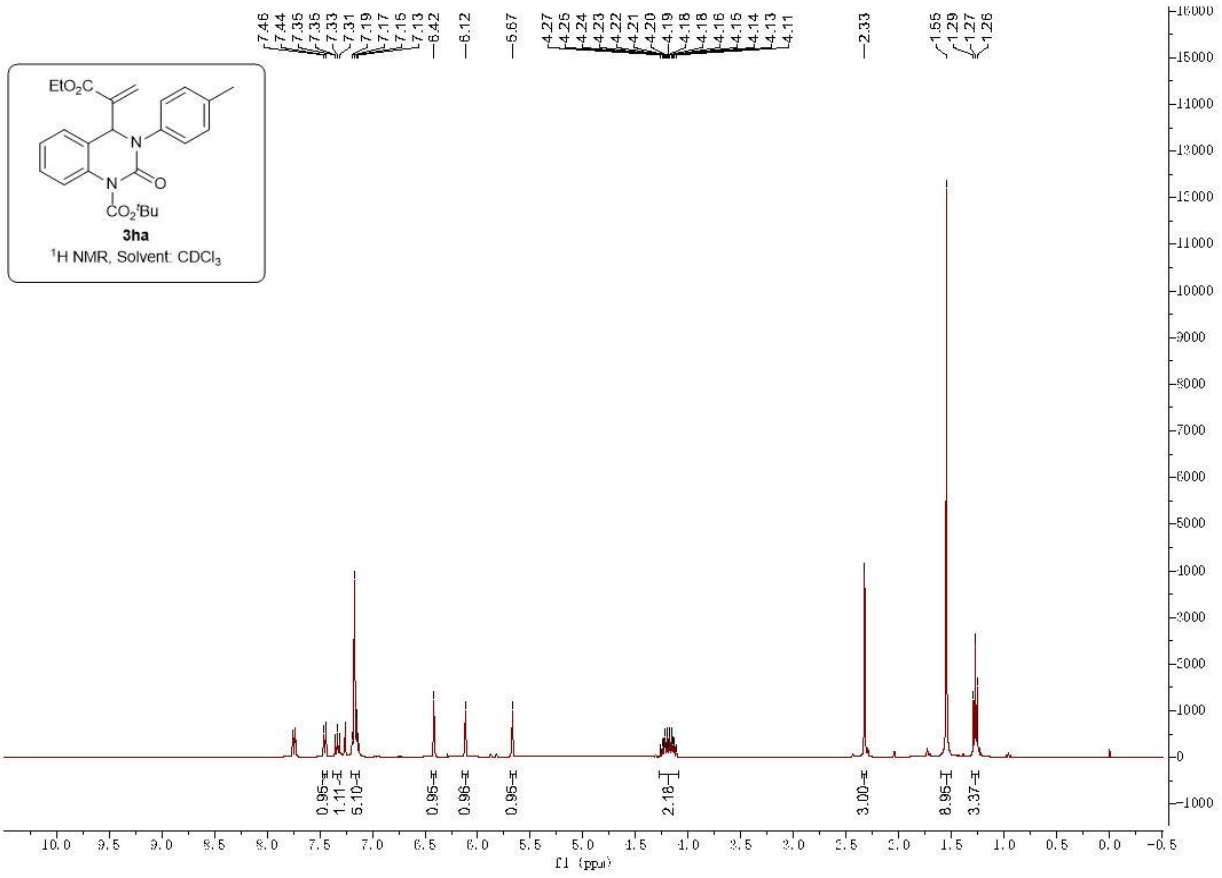

tBuO2C
N
N
O
CO2Me
3ea
13C NMR, Solvent: CDCl3
164.47
153.18
151.93
139.33
138.80
137.05
135.32
129.76
128.38
128.34
126.64
125.44
125.36
123.01
82.07
62.73
54.12
27.99
21.07
f1 (ppm)

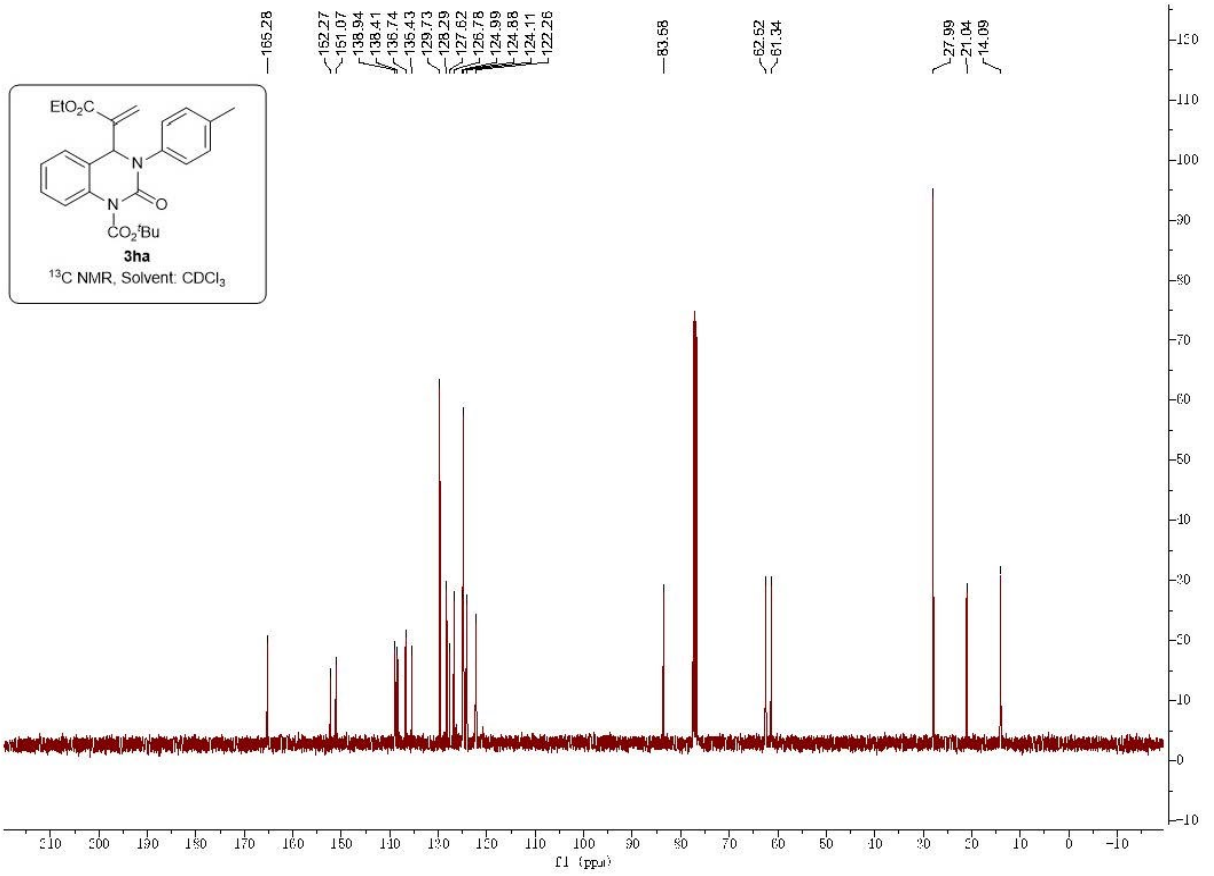

BnO2C
N
N
O
CO2Me
3fa
1H NMR, Solvent: CDCl3
7.78
7.76
7.73
7.42
7.41
7.38
7.36
7.34
7.31
7.30
7.29
7.25
7.19
7.17
7.15
7.13
6.44
6.09
5.68
5.23
5.20
5.08
5.05
3.90
2.33
1.02
1.18
3.94
1.94
0.88
5.05
1.00
1.01
0.98
1.04
0.98
2.96
2.82
f1 (ppm)

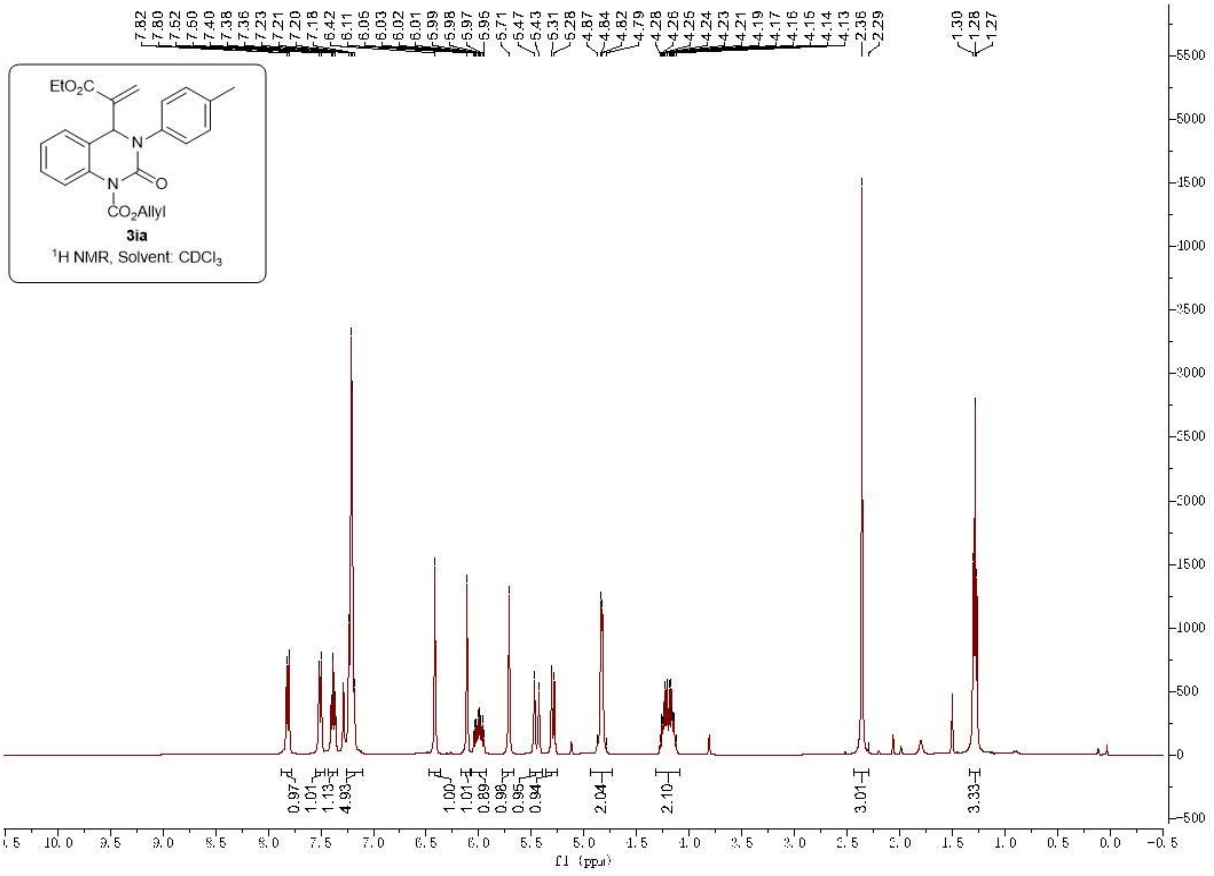

BnO2C
N
N
O
CO2Me
3fa
13C NMR, Solvent: CDCl3
165.02
153.05
151.90
138.67
137.80
137.16
136.30
135.17
129.80
129.46
128.66
128.54
128.45
128.05
126.89
125.56
125.27
124.70
123.03
67.16
62.85
54.14
21.06
f1 (ppm)

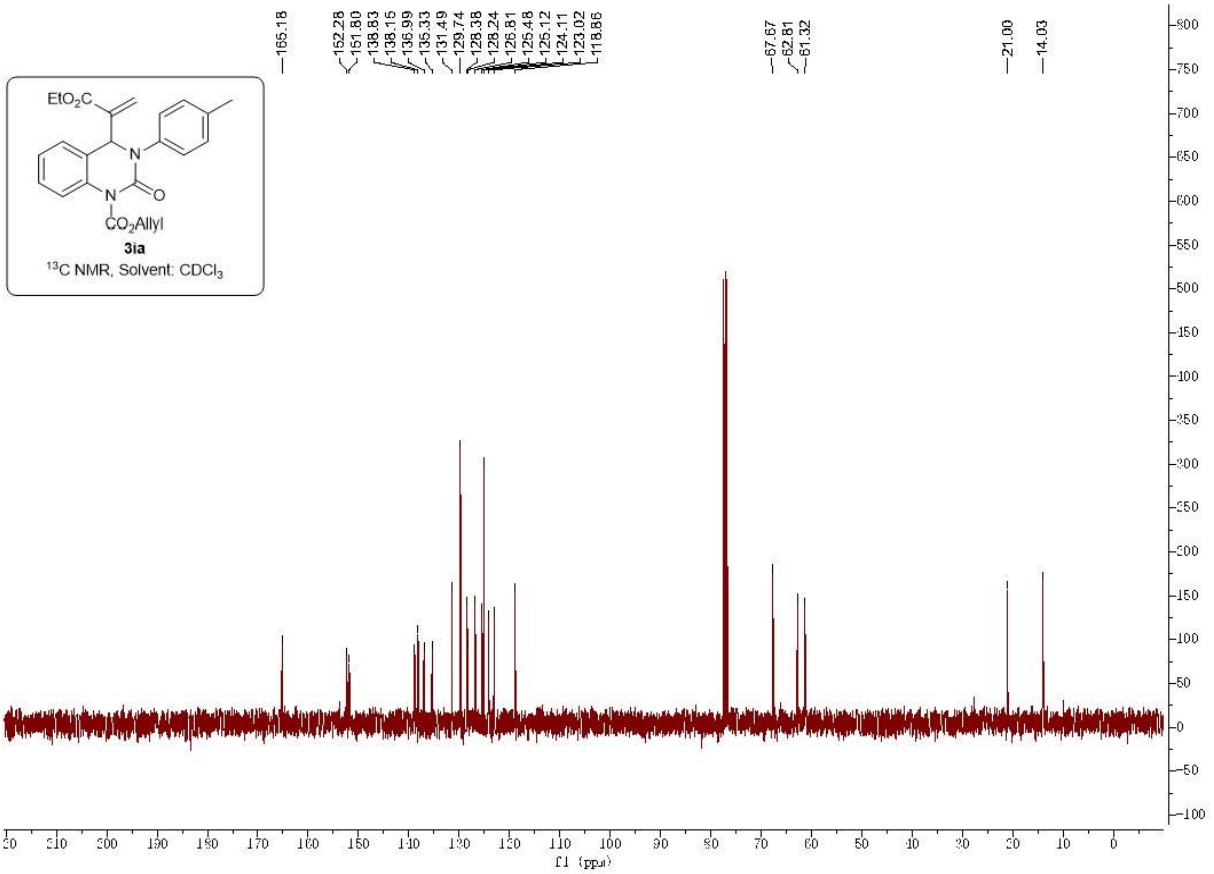

EtO2C
N
N
O
CO2Et
3ga
1H NMR, Solvent: CDCl3
7.81
7.79
7.51
7.49
7.40
7.38
7.36
7.23
7.21
7.18
6.43
6.12
5.70
4.47
4.45
4.44
4.43
4.42
4.41
4.39
4.37
4.36
4.35
4.34
4.33
4.32
4.28
4.26
4.25
4.24
4.23
4.22
4.21
4.21
4.20
4.19
4.17
4.16
4.15
4.14
4.13
2.36
1.40
1.38
1.36
1.31
1.29
1.27
0.93
0.96
1.02
4.93
0.96
0.96
0.94
2.10
2.07
3.00
2.91
3.49
f1 (ppm)

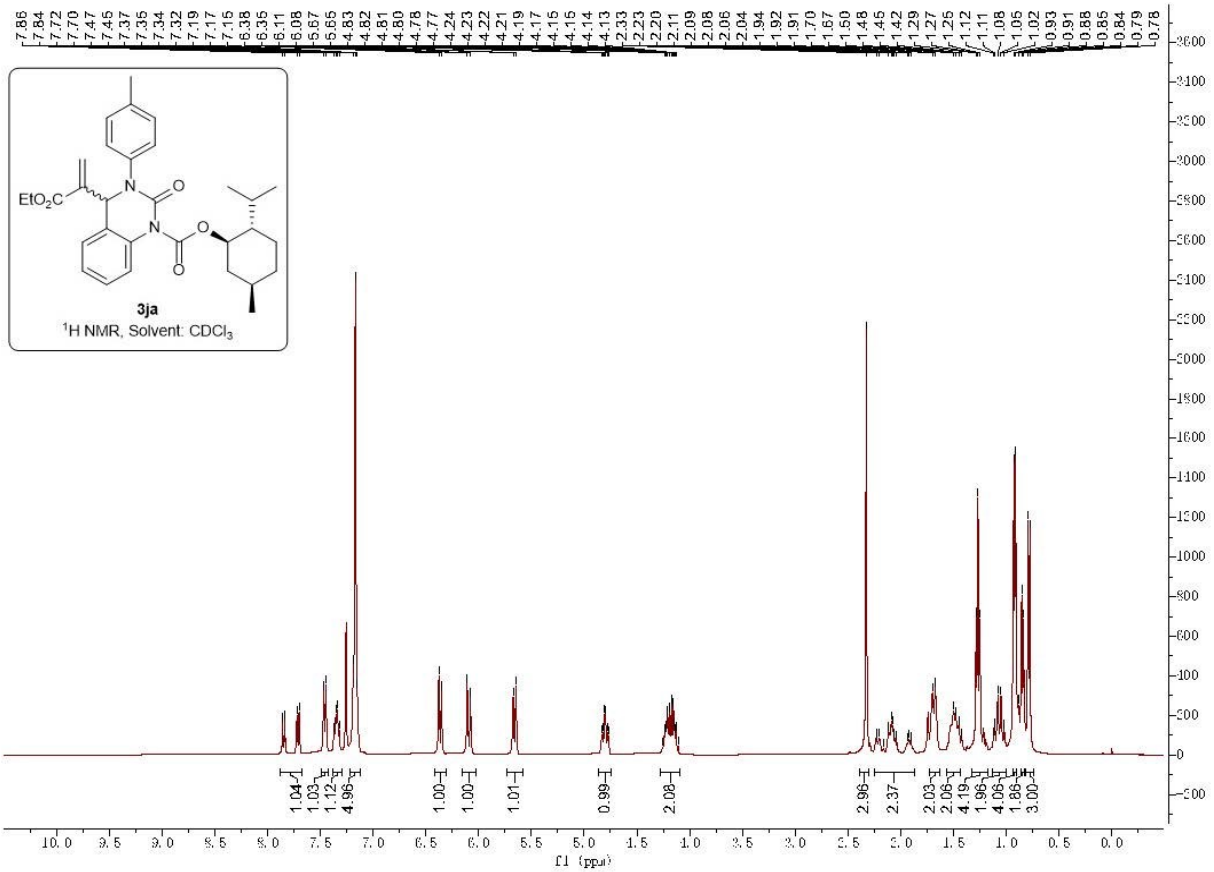

EtO2C
N
N
O
CO2Et
3ga
13C NMR, Solvent: CDCl3
165.20
152.49
151.96
138.79
138.13
136.97
135.32
129.74
128.36
128.18
126.82
125.41
125.05
124.08
123.02
63.44
62.72
61.36
21.04
14.28
14.06
f1 (ppm)

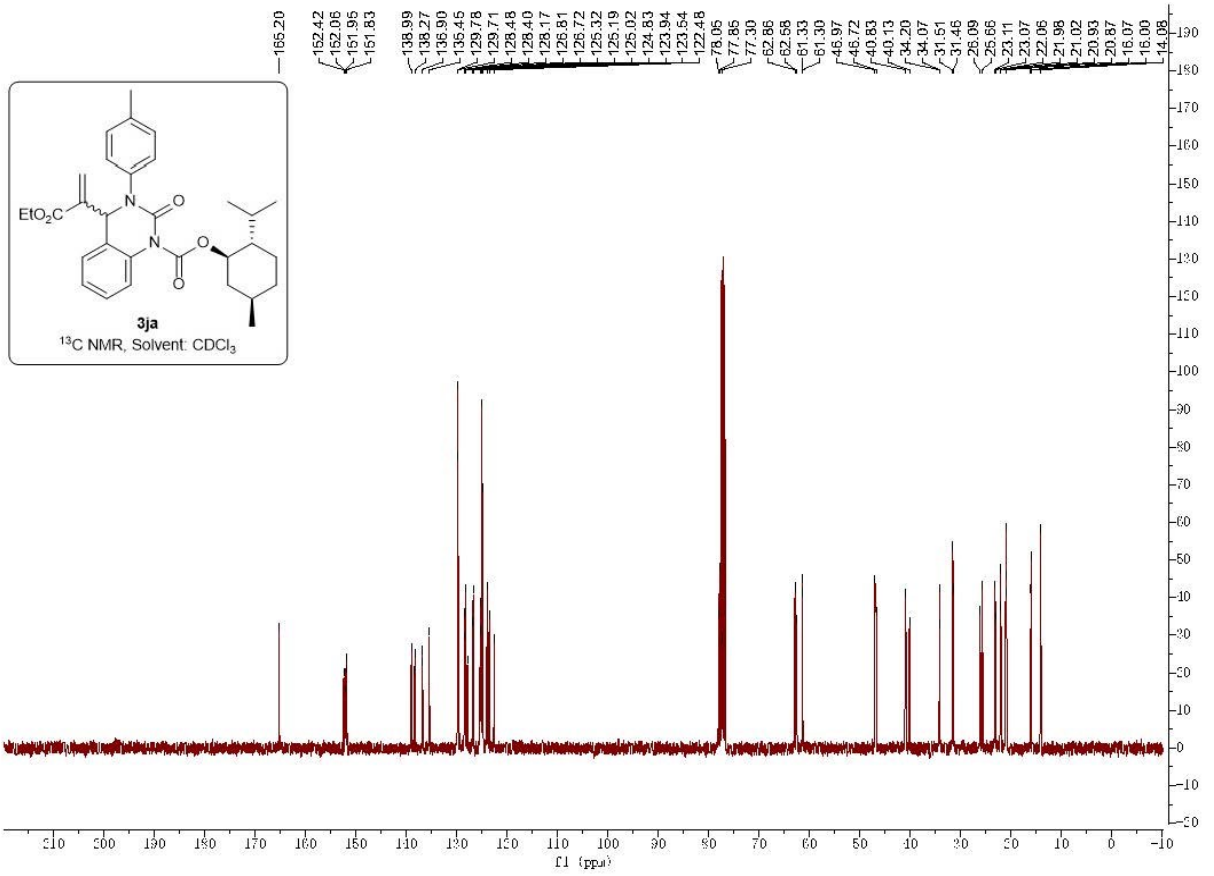

EtO2C
N
N
O
CO2tBu
3ha
1H NMR, Solvent: CDCl3
7.46
7.44
7.35
7.35
7.33
7.31
7.19
7.17
7.15
7.13
6.42
6.12
5.67
4.27
4.25
4.24
4.23
4.22
4.21
4.20
4.19
4.18
4.18
4.16
4.15
4.14
4.13
4.11
2.33
1.55
1.29
1.27
1.26
0.95
1.11
5.10
0.95
0.96
0.95
2.18
3.00
8.95
3.37
f1 (ppm)

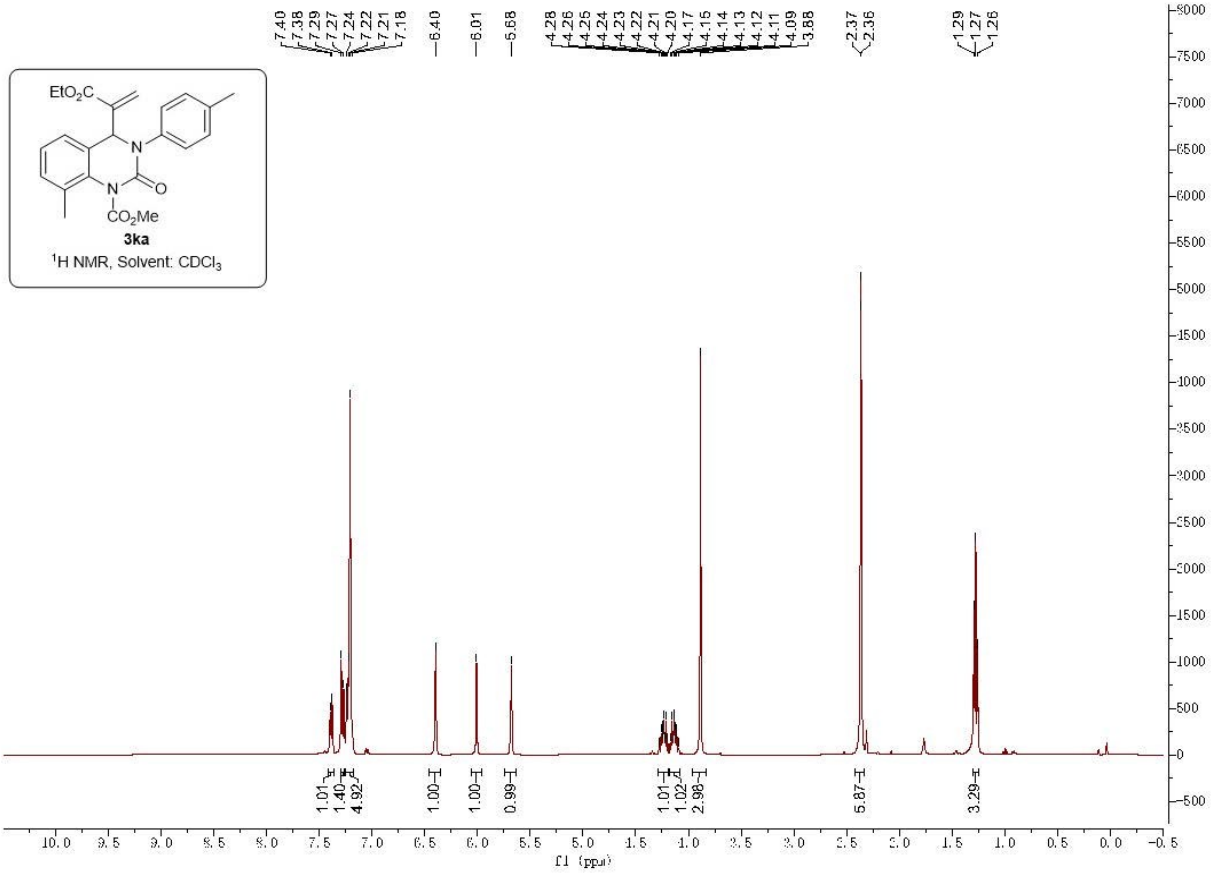

EtO2C
N
N
O
CO2tBu
3ha
13C NMR, Solvent: CDCl3
165.28
162.27
151.07
138.94
138.41
136.74
135.43
129.73
128.29
127.62
126.78
124.99
124.88
124.11
122.26
83.58
62.52
61.34
27.99
21.04
14.09
f1 (ppm)

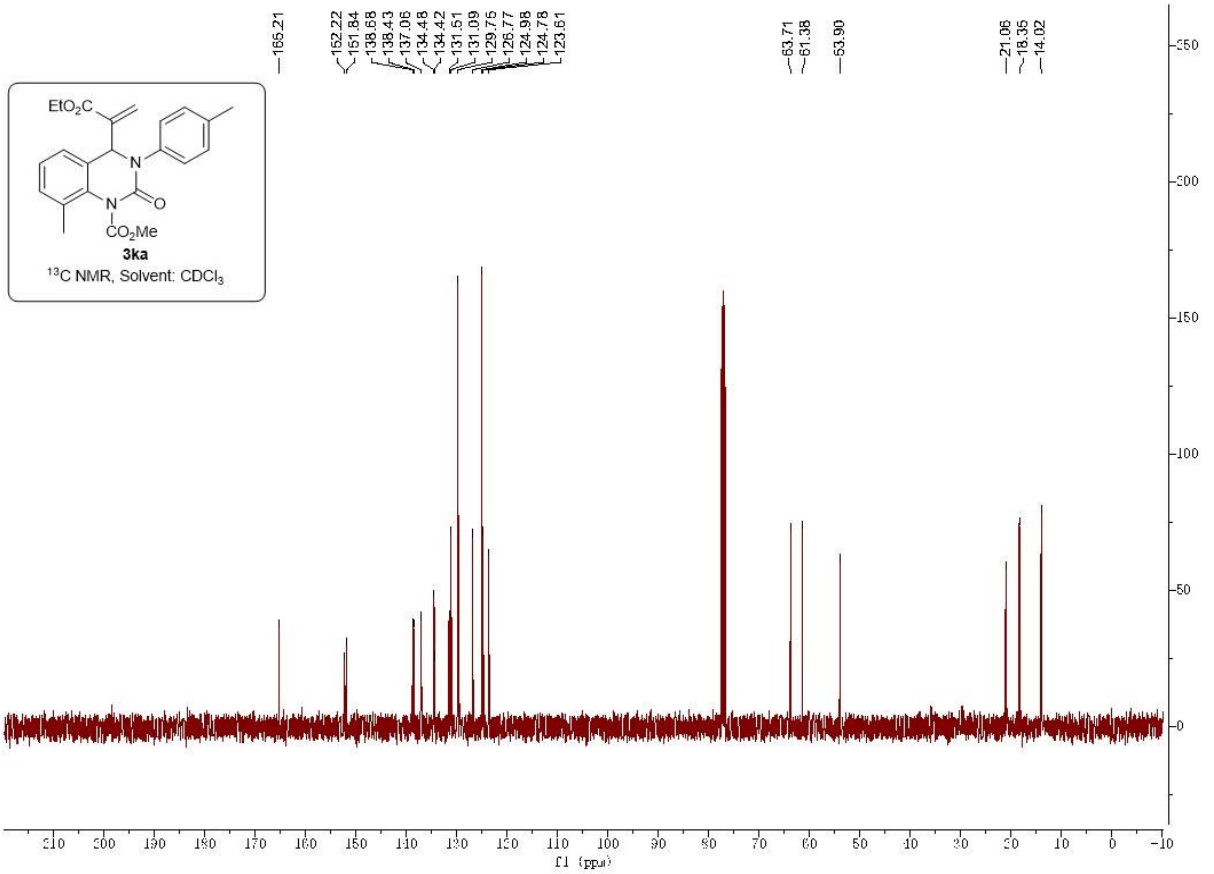

EtO2C
N
N
O
CO2Allyl
3ia
1H NMR, Solvent: CDCl3
7.82
7.80
7.52
7.50
7.40
7.38
7.36
7.23
7.21
7.20
7.18
6.42
6.11
6.05
6.03
6.02
6.01
5.99
5.98
5.97
5.95
5.71
5.47
5.43
5.31
5.28
4.87
4.84
4.82
4.79
4.28
4.26
4.25
4.24
4.23
4.21
4.19
4.17
4.16
4.15
4.14
4.13
2.36
2.29
1.30
1.28
1.27
0.97
1.01
1.13
4.93
1.00
1.01
0.89
0.98
0.95
0.94
2.04
2.10
3.01
3.33
f1 (ppm)

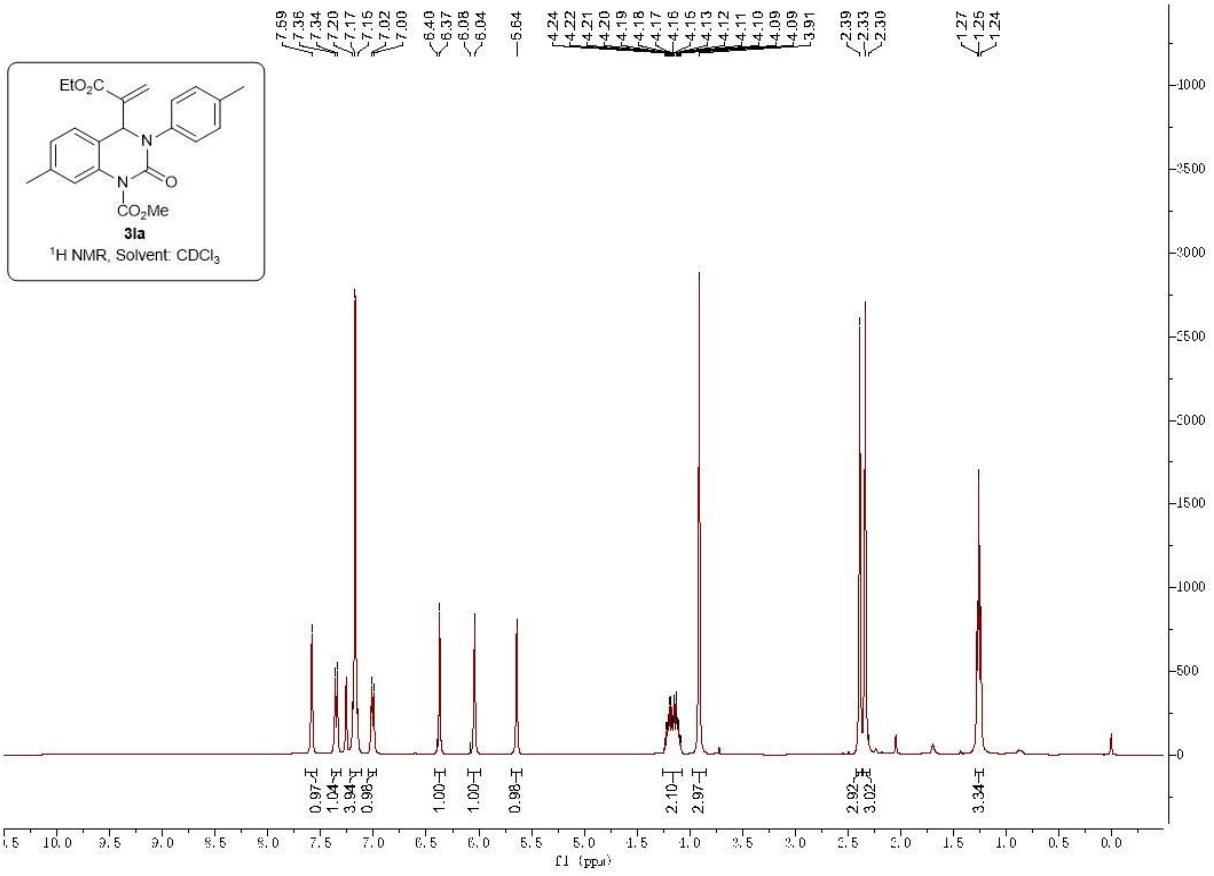

EtO2C
N
N
O
CO2Allyl
3ia
13C NMR, Solvent: CDCl3
165.18
152.28
151.80
138.83
138.15
136.99
135.33
131.49
129.74
128.38
128.24
126.81
125.48
125.12
124.11
123.02
118.86
67.67
62.81
61.32
21.00
14.03
f1 (ppm)

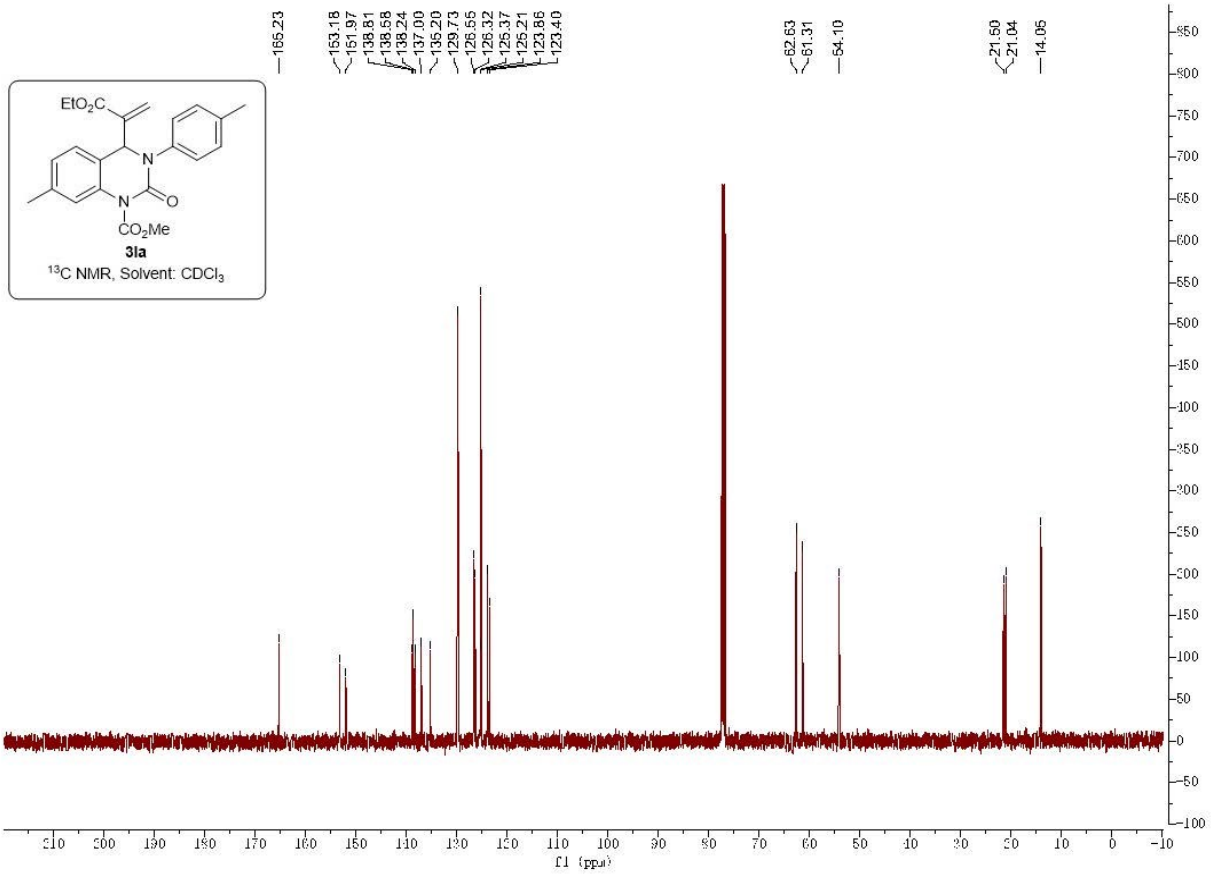

EtO2C
N
O
N
O
O
3ja
1H NMR, Solvent: CDCl3
7.86
7.84
7.72
7.70
7.47
7.45
7.37
7.36
7.34
7.32
7.19
7.17
7.15
6.38
6.35
6.11
6.08
5.67
5.65
4.83
4.82
4.81
4.80
4.78
4.77
4.24
4.23
4.22
4.21
4.19
4.17
4.15
4.15
4.14
4.13
2.33
2.23
2.20
2.11
2.09
2.08
2.06
2.04
1.94
1.92
1.91
1.70
1.67
1.50
1.48
1.45
1.42
1.29
1.27
1.25
1.12
1.11
1.08
1.05
1.02
0.93
0.91
0.88
0.85
0.84
0.79
0.78
1.04
1.03
1.12
4.96
1.00
1.00
1.01
0.99
2.08
2.96
2.37
2.03
2.06
4.19
1.96
4.06
1.88
3.00
f1 (ppm)

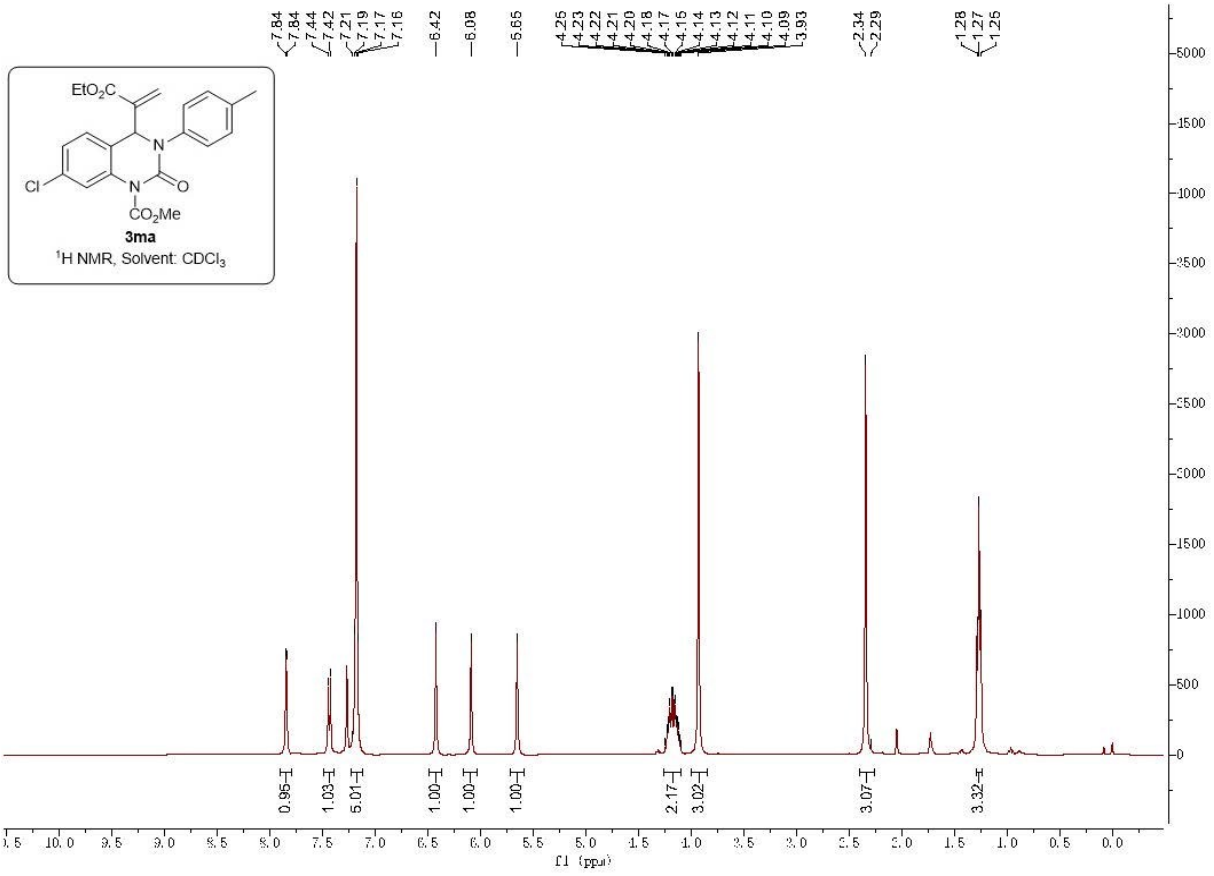

3ja
^{13}C NMR, Solvent: $CDCl_3$
f1 (ppm)

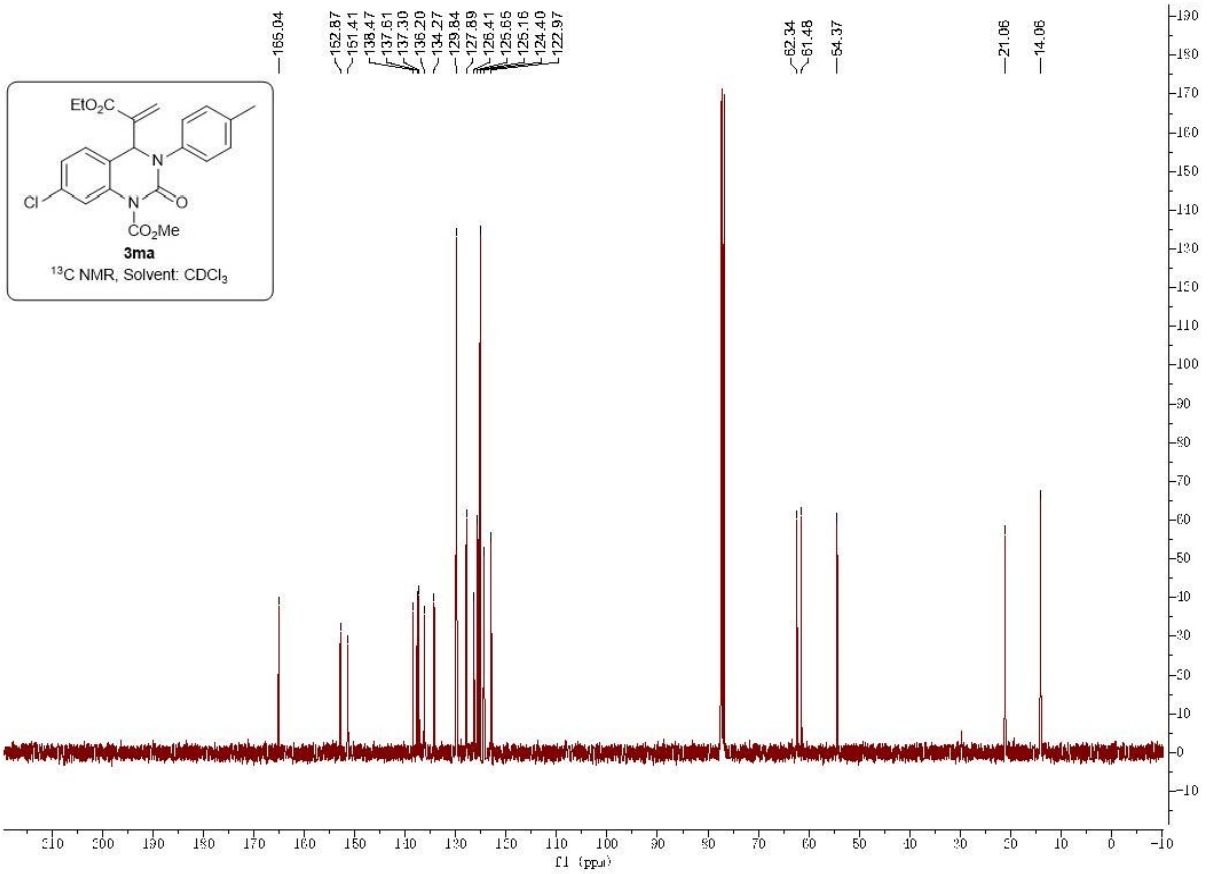

3ka
^{1}H NMR, Solvent: $CDCl_3$
f1 (ppm)

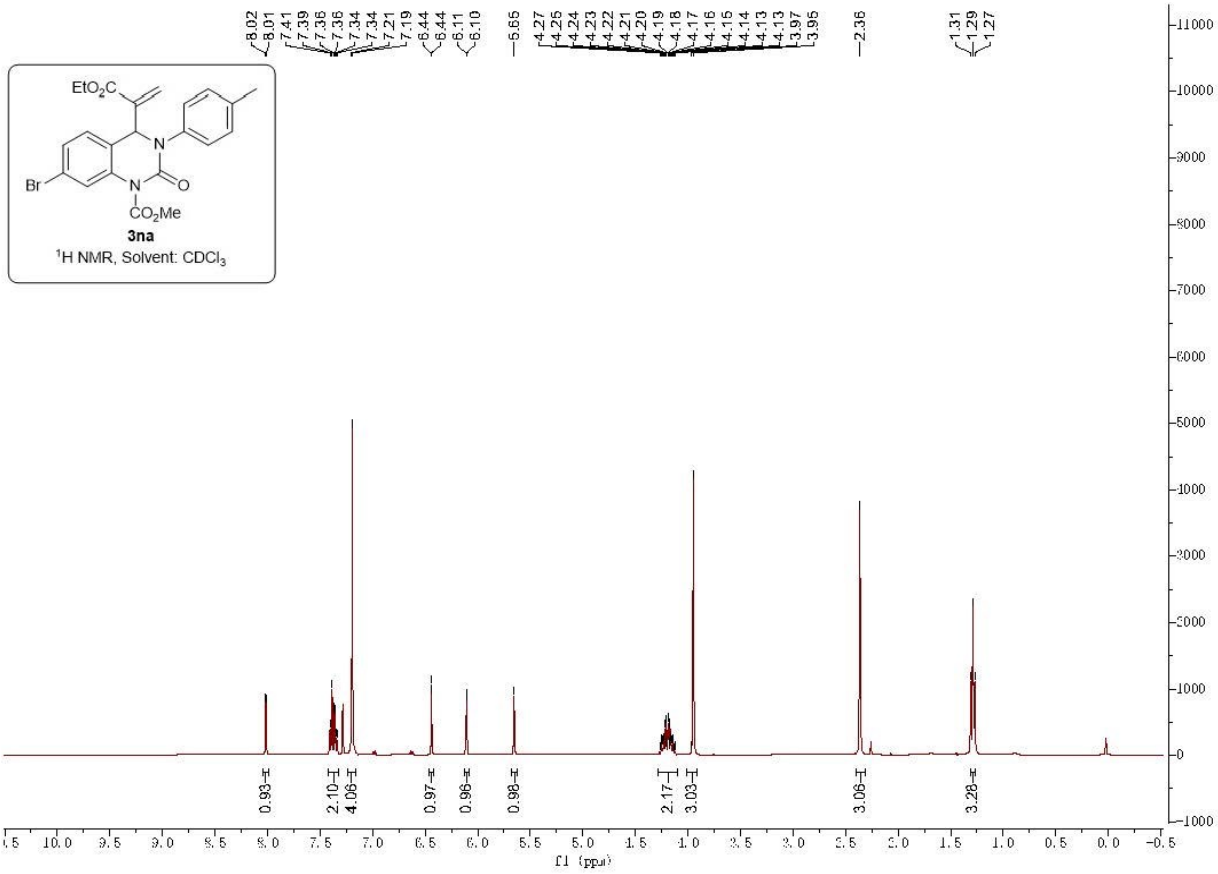

EtO2C
N
N
O
CO2Me
3ka
13C NMR, Solvent: CDCl3
165.21
152.22
151.84
138.58
138.43
137.06
134.48
134.42
131.51
131.09
129.75
126.77
124.98
124.78
123.61
63.71
61.38
53.90
21.06
18.35
14.02
f1 (ppm)

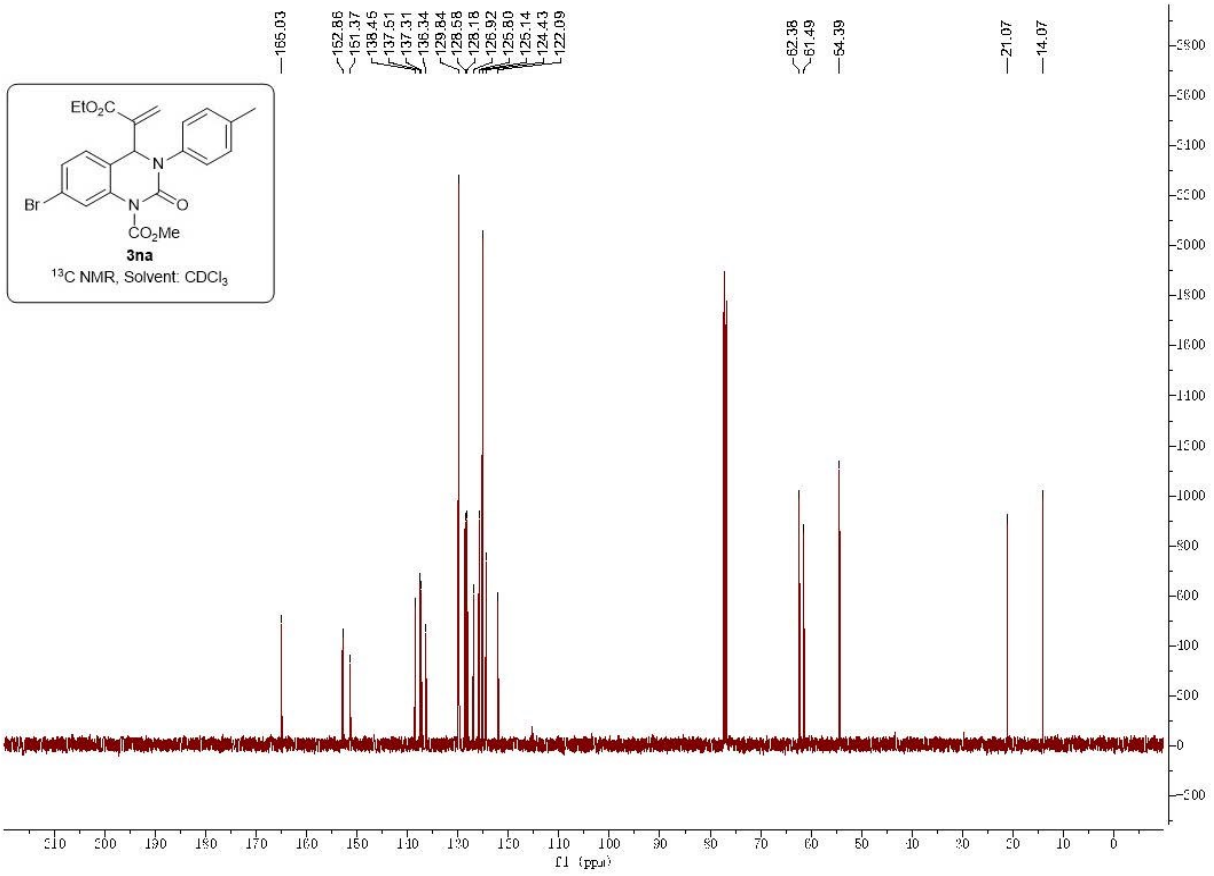

EtO2C
N
N
O
CO2Me
3la
1H NMR, Solvent: CDCl3
7.59
7.36
7.34
7.20
7.17
7.15
7.02
7.00
6.40
6.37
6.08
6.04
5.64
4.24
4.22
4.21
4.20
4.19
4.18
4.17
4.16
4.15
4.13
4.12
4.11
4.10
4.09
4.09
3.91
2.39
2.33
2.30
1.27
1.25
1.24
0.97
1.04
3.94
0.98
1.00
1.00
0.98
2.10
2.97
2.92
3.02
3.34
f1 (ppm)

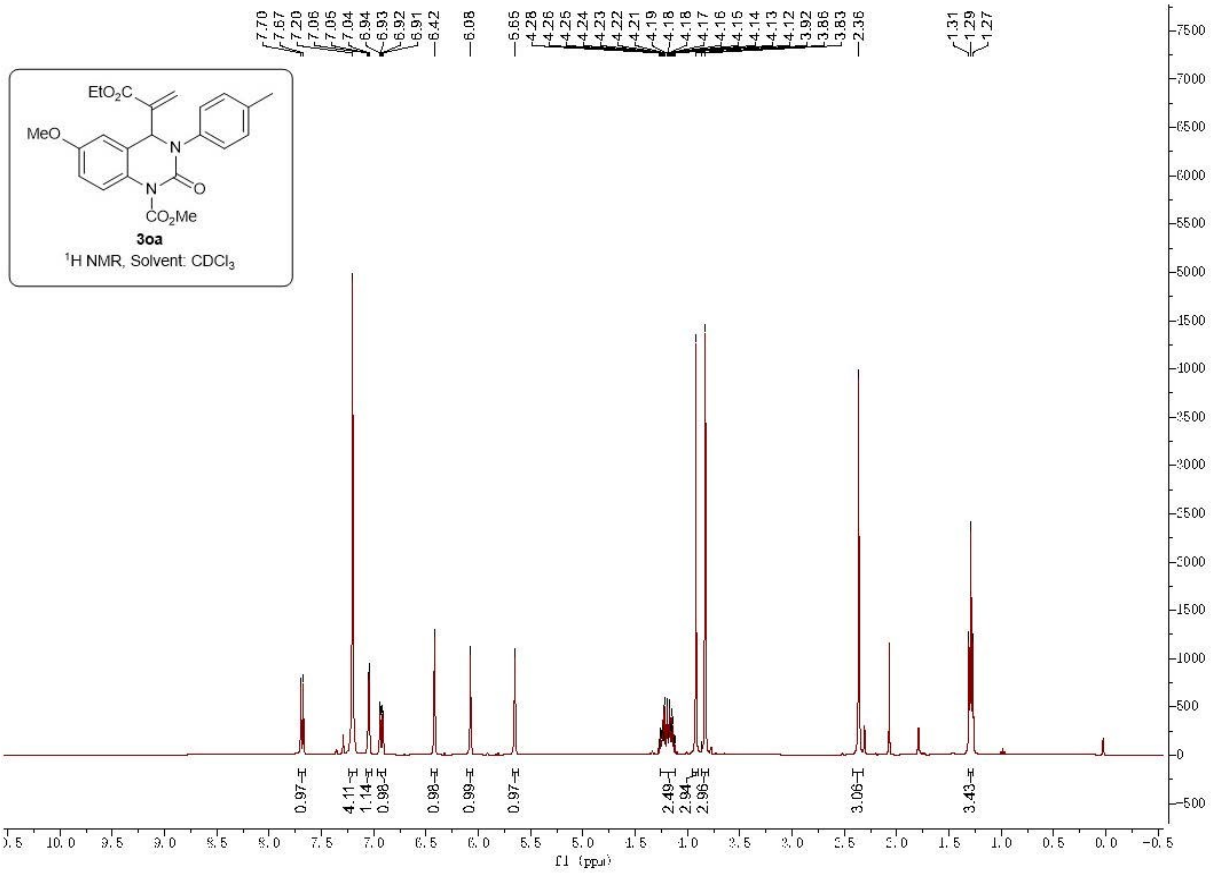

EtO2C
N
N
O
CO2Me
3la
13C NMR, Solvent: CDCl3
165.23
153.18
151.97
138.81
138.58
138.24
137.00
135.20
129.73
126.55
126.32
125.37
125.21
123.86
123.40
62.63
61.31
54.10
21.50
21.04
14.05
f1 (ppm)

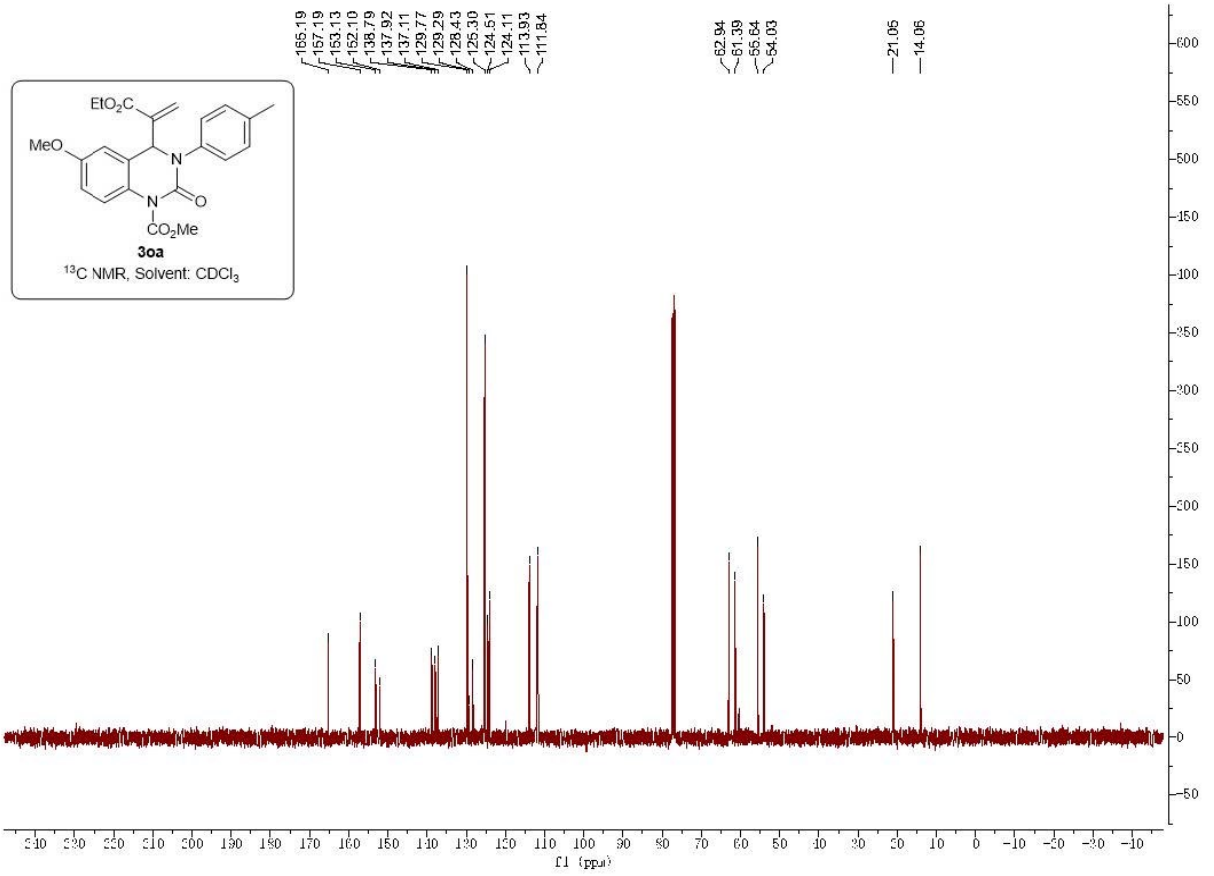

EtO2C
N
Cl
N
O
CO2Me
3ma
1H NMR, Solvent: CDCl3
7.84
7.84
7.44
7.42
7.21
7.19
7.17
7.16
6.42
6.08
5.65
4.25
4.23
4.22
4.21
4.20
4.18
4.17
4.15
4.14
4.13
4.12
4.11
4.10
4.09
3.93
2.34
2.29
1.28
1.27
1.25
0.95
1.03
5.01
1.00
1.00
1.00
2.17
3.02
3.07
3.32
f1 (ppm)

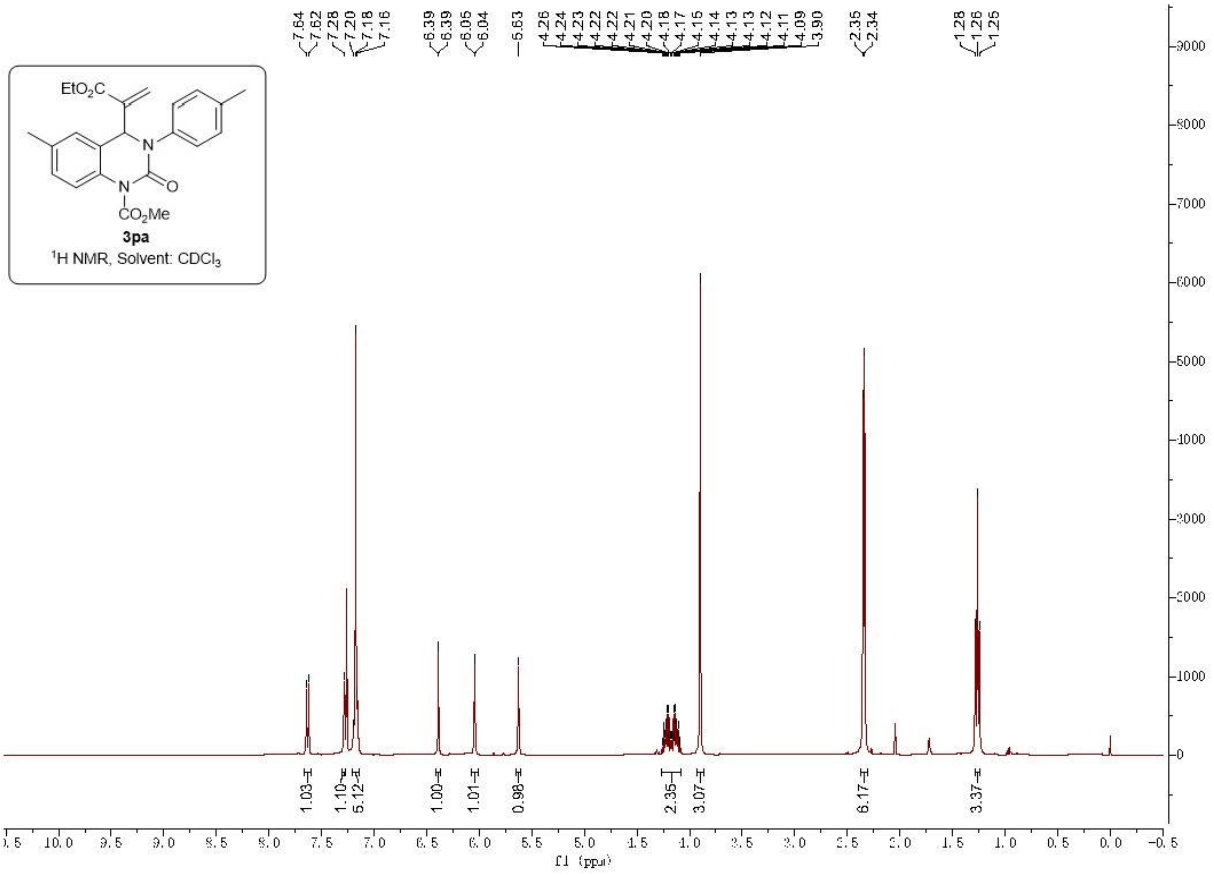

EtO2C
N
Cl
N
O
CO2Me
3ma
13C NMR, Solvent: CDCl3
165.04
152.87
151.41
138.47
137.61
137.30
136.20
134.27
129.84
127.89
126.41
125.55
125.16
124.40
122.97
62.34
61.48
54.37
21.06
14.06
f1 (ppm)

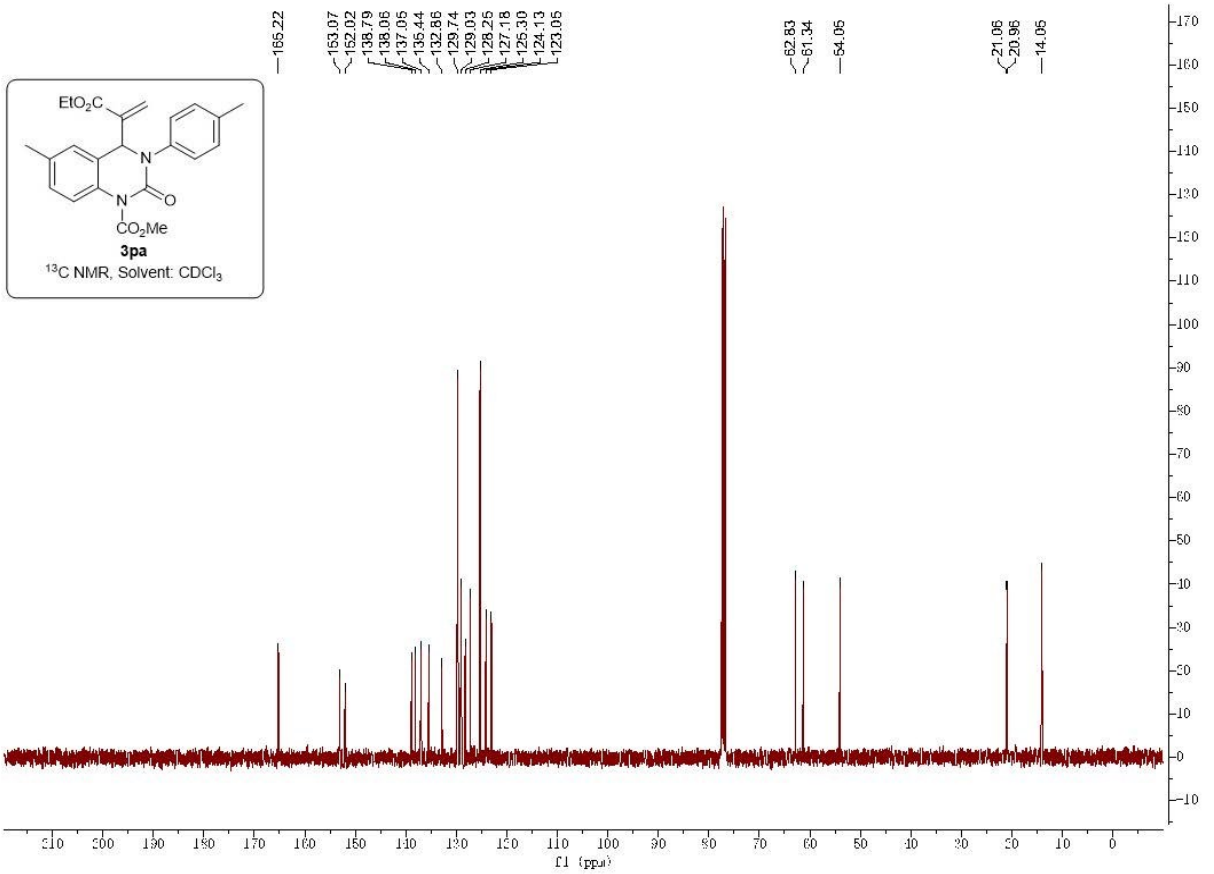

EtO2C
N
Br
N
O
CO2Me
3na
1H NMR, Solvent: CDCl3
8.02
8.01
7.41
7.39
7.36
7.36
7.34
7.34
7.21
7.19
6.44
6.44
6.11
6.10
5.65
4.27
4.25
4.24
4.23
4.22
4.21
4.20
4.19
4.18
4.17
4.16
4.15
4.14
4.13
4.13
3.97
3.95
2.36
1.31
1.29
1.27
0.93
2.10
4.08
0.97
0.96
0.98
2.17
3.03
3.06
3.28
f1 (ppm)

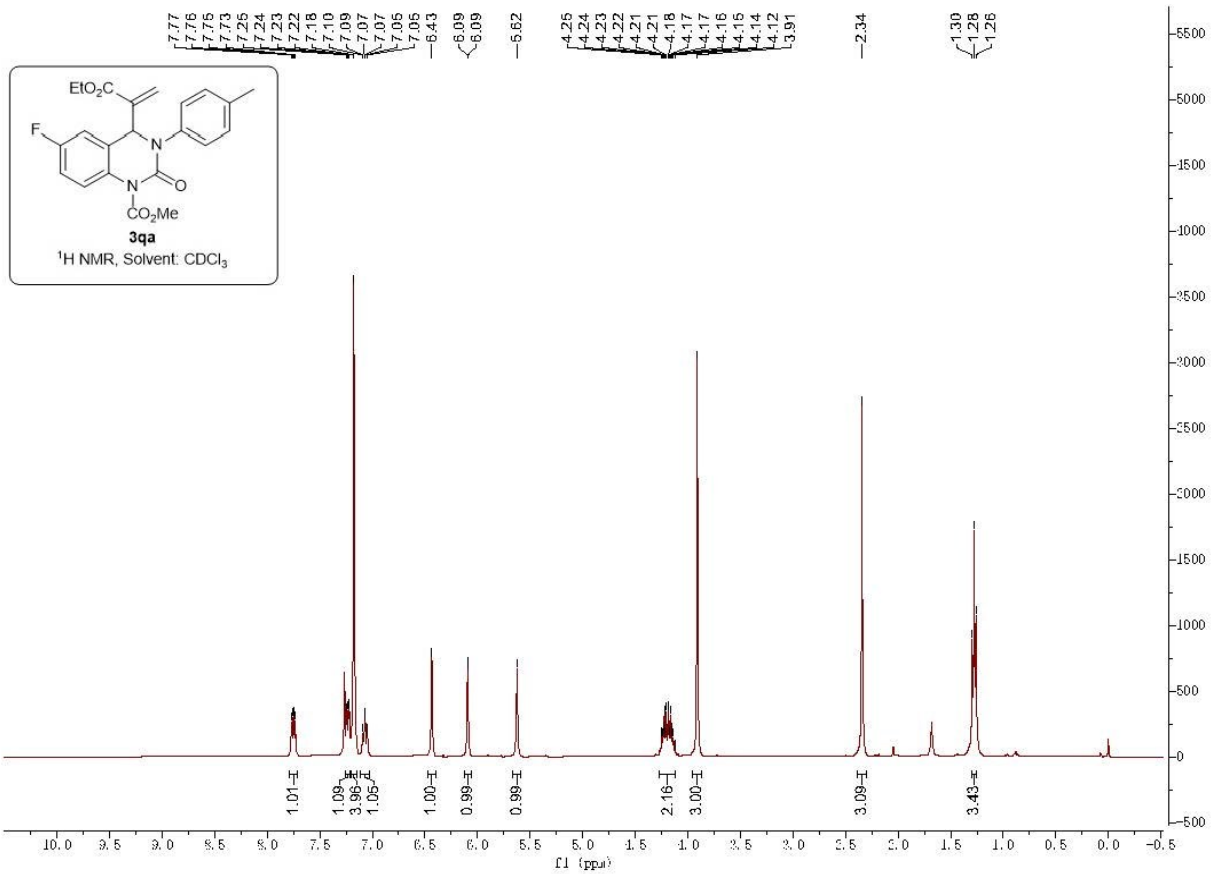

EtO2C
Br
N
O
CO2Me
3na
13C NMR, Solvent: CDCl3
165.03
152.86
151.37
138.45
137.51
137.31
136.34
129.84
128.58
128.18
126.92
125.80
125.14
124.43
122.09
62.38
61.49
54.39
21.07
14.07
f1 (ppm)

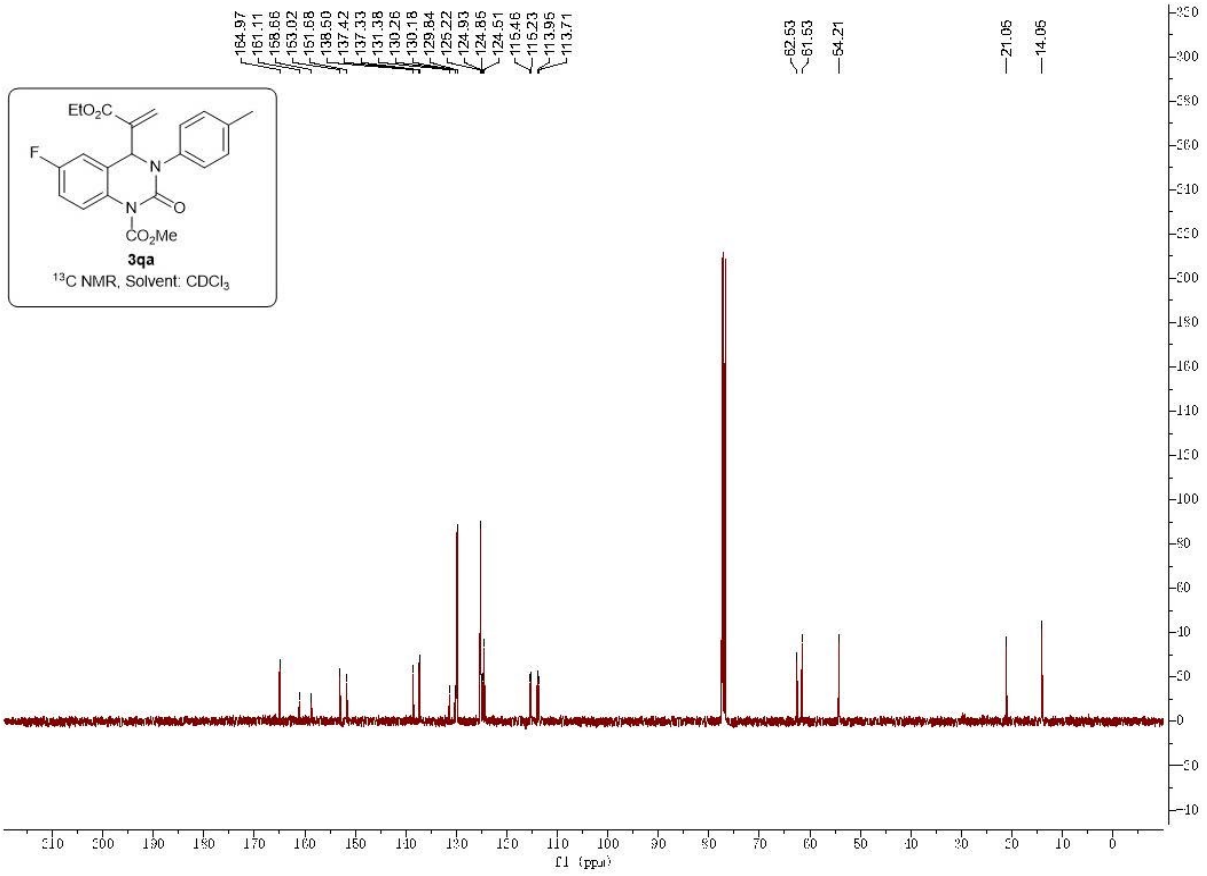

EtO2C
MeO
N
O
CO2Me
3oa
1H NMR, Solvent: CDCl3
7.70
7.67
7.20
7.06
7.05
7.04
6.94
6.93
6.92
6.91
6.42
6.08
5.65
4.28
4.26
4.25
4.24
4.23
4.22
4.21
4.19
4.18
4.18
4.17
4.16
4.15
4.14
4.13
4.12
3.92
3.86
3.83
2.36
1.31
1.29
1.27
0.97
4.11
1.14
0.98
0.98
0.99
0.97
2.49
2.94
2.96
3.06
3.43
f1 (ppm)

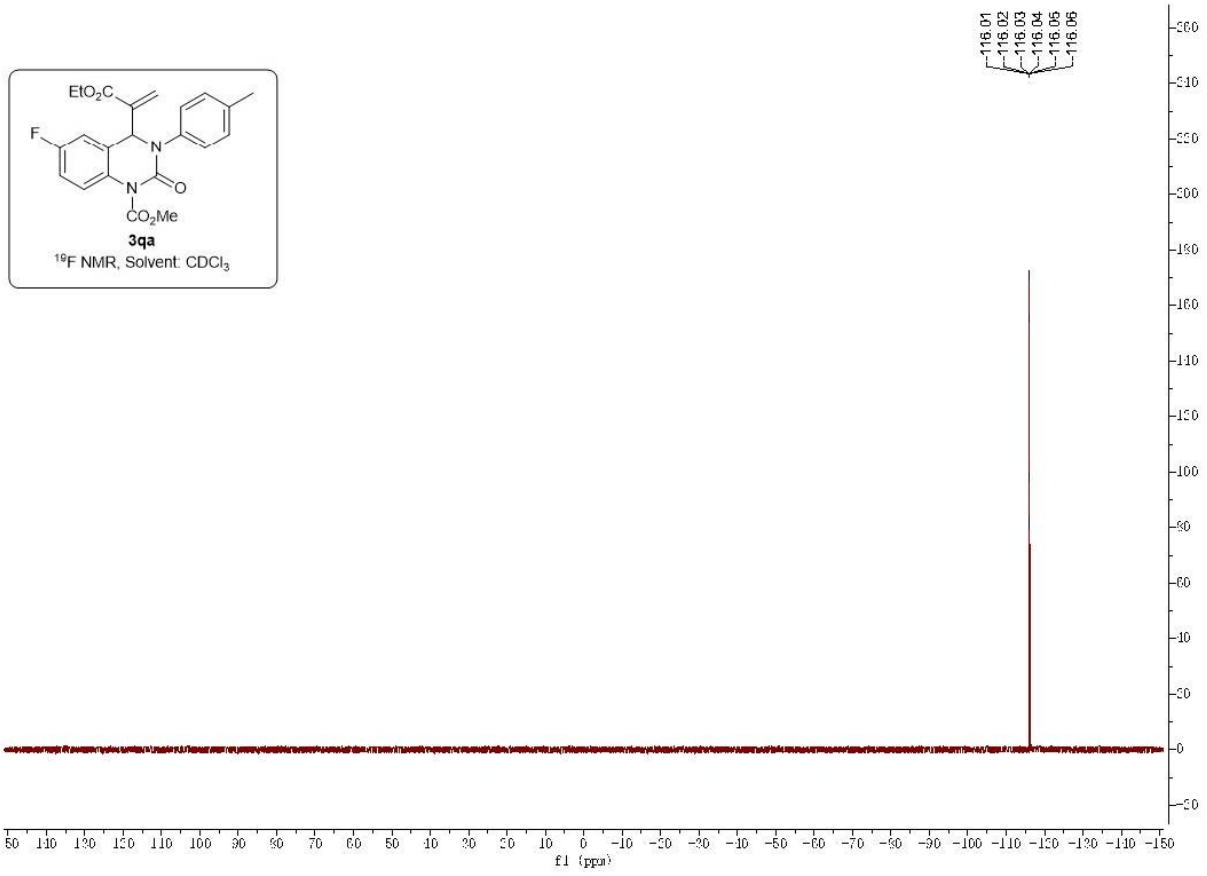

EtO2C
MeO
N
N
O
CO2Me
3oa
13C NMR, Solvent: CDCl3
165.19
157.19
153.13
152.10
138.79
137.92
137.11
129.77
129.29
128.43
125.30
124.51
124.11
113.93
111.84
62.94
61.39
55.64
54.03
21.05
14.06
f1 (ppm)

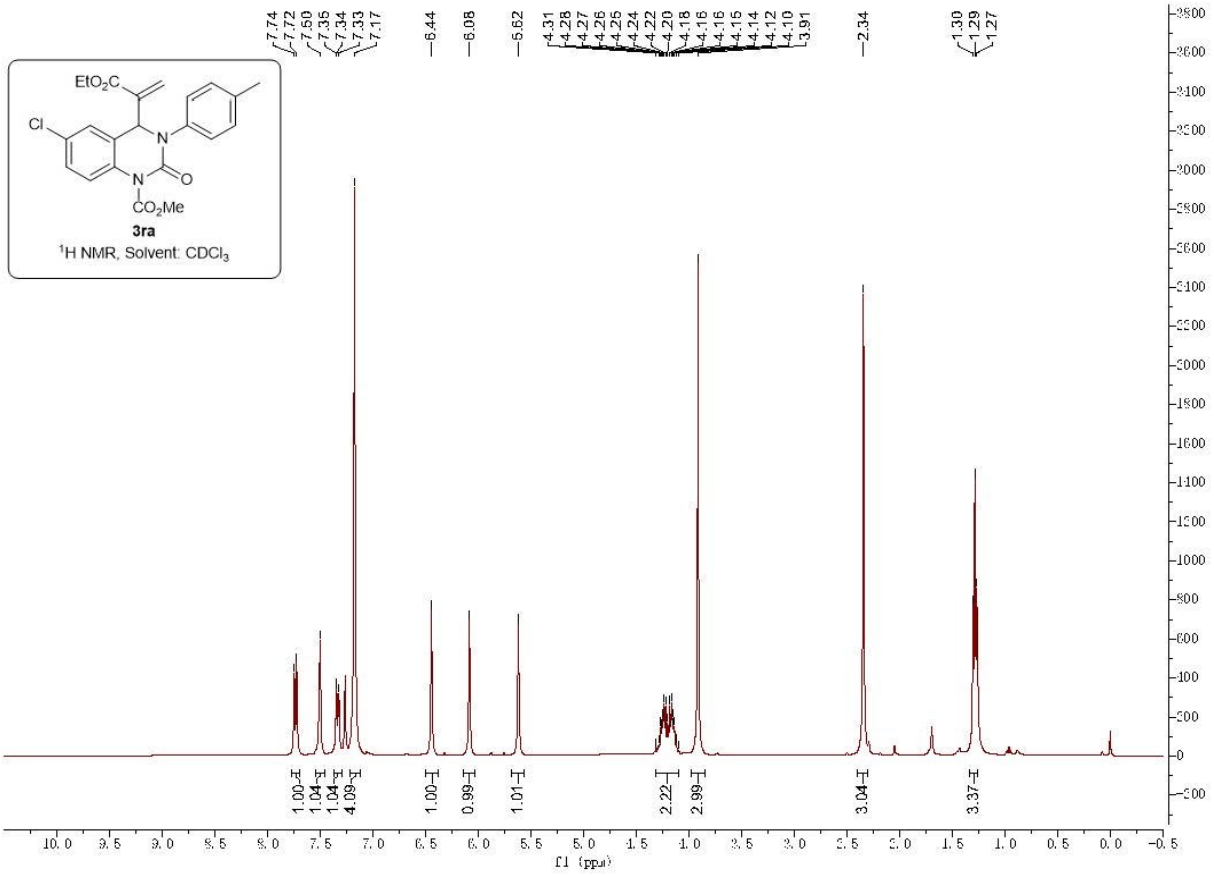

EtO2C
N
N
O
CO2Me
3pa
1H NMR, Solvent: CDCl3
7.64
7.62
7.28
7.20
7.18
7.16
6.39
6.39
6.05
6.04
5.63
4.26
4.24
4.23
4.22
4.22
4.21
4.20
4.18
4.17
4.15
4.14
4.13
4.13
4.12
4.11
4.09
3.90
2.35
2.34
1.28
1.26
1.25
1.03
1.10
5.12
1.00
1.01
0.98
2.35
3.07
6.17
3.37
f1 (ppm)

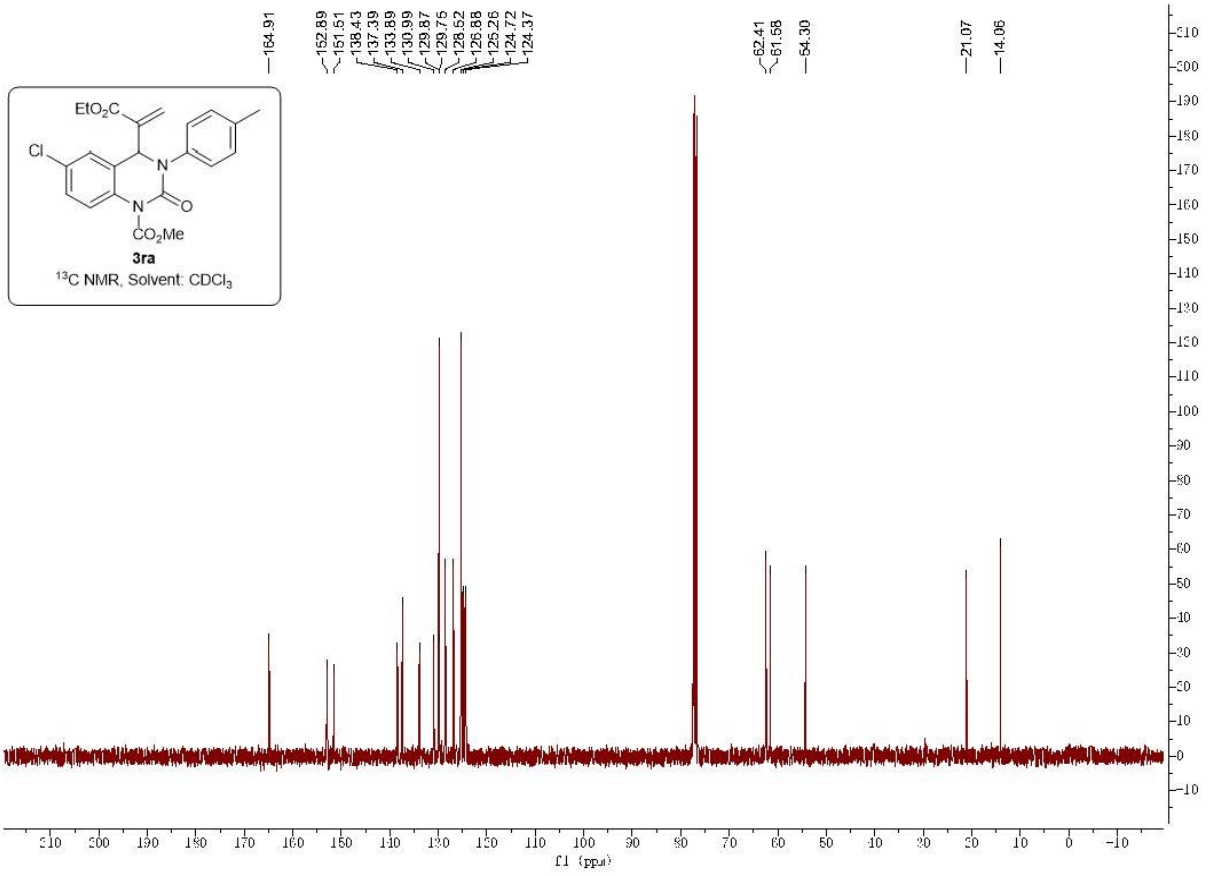

EtO2C
N
N
O
CO2Me
3pa
13C NMR, Solvent: CDCl3
165.22
153.07
152.02
138.79
138.06
137.05
135.44
132.86
129.74
129.03
128.25
127.18
125.30
124.13
123.05
62.83
61.34
54.05
21.06
20.96
14.05
f1 (ppm)

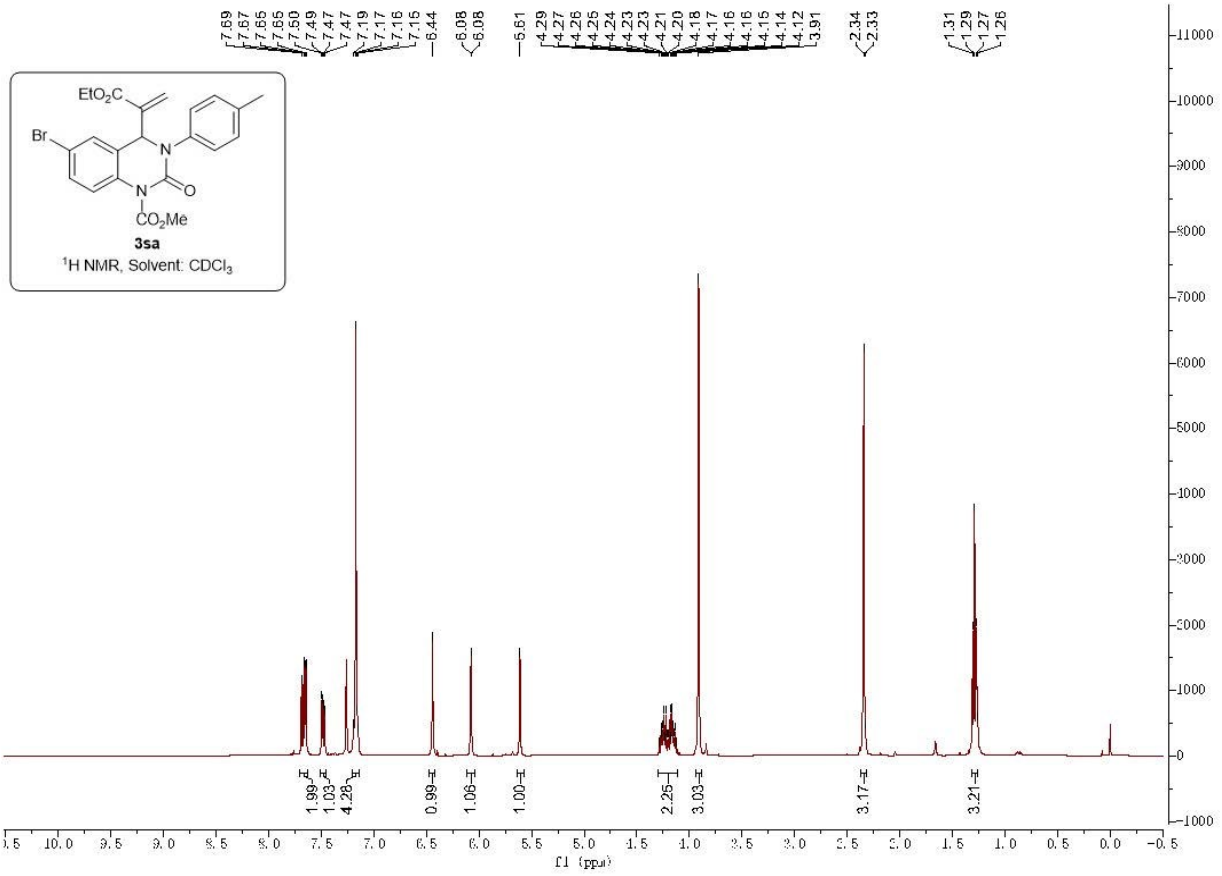

EtO2C
F
N
N
O
CO2Me
3qa
1H NMR, Solvent: CDCl3
7.77
7.76
7.75
7.73
7.25
7.24
7.23
7.22
7.18
7.10
7.09
7.07
7.07
7.05
7.05
6.43
6.09
6.09
5.62
4.25
4.24
4.23
4.22
4.21
4.21
4.18
4.17
4.17
4.16
4.15
4.14
4.12
3.91
2.34
1.30
1.28
1.26
1.01
1.09
3.96
1.05
1.00
0.99
0.99
2.16
3.00
3.09
3.43
f1 (ppm)

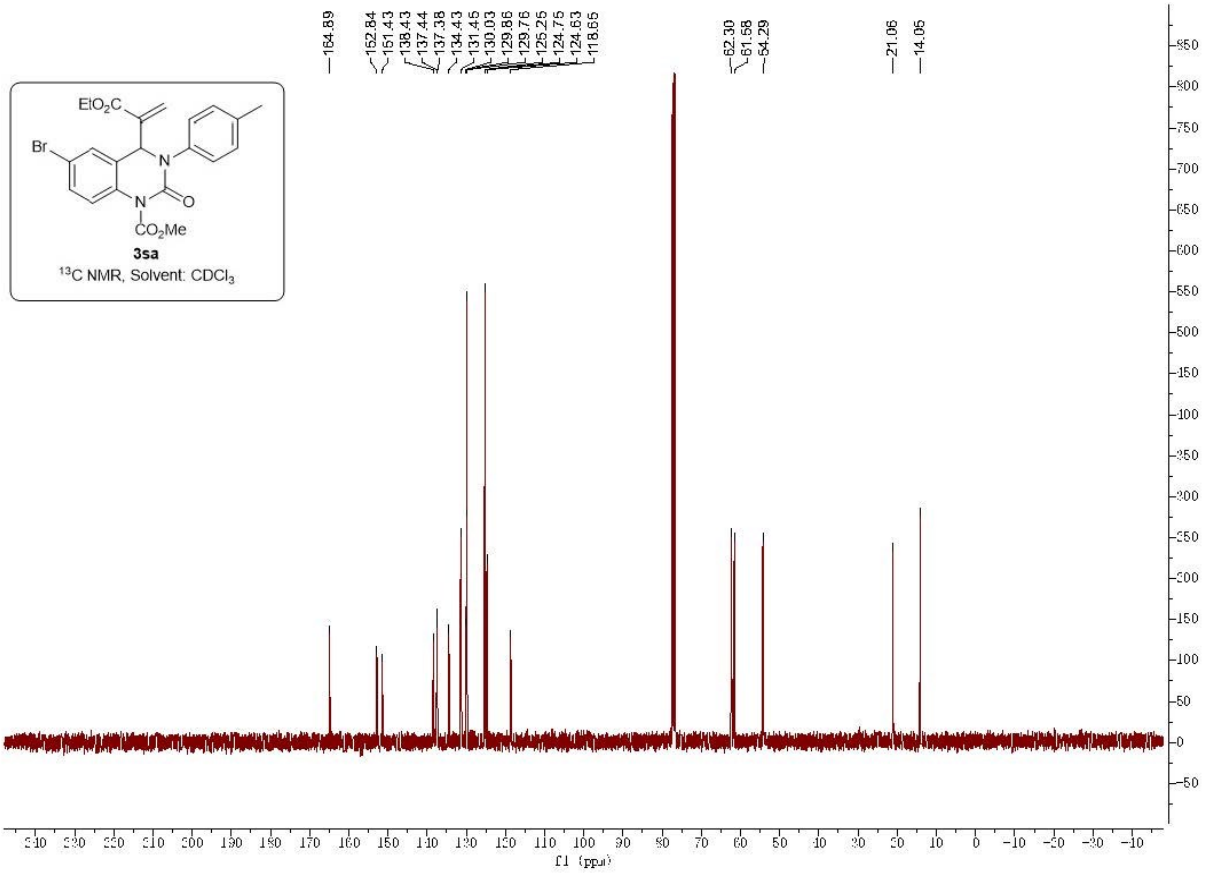

EtO2C
F
N
O
N
CO2Me
3qa
13C NMR, Solvent: CDCl3
164.97
161.11
158.66
153.02
151.88
138.50
137.42
137.33
131.38
130.26
130.18
129.84
125.22
124.93
124.85
124.51
115.46
115.23
113.95
113.71
62.53
61.53
54.21
21.05
14.05
f1 (ppm)

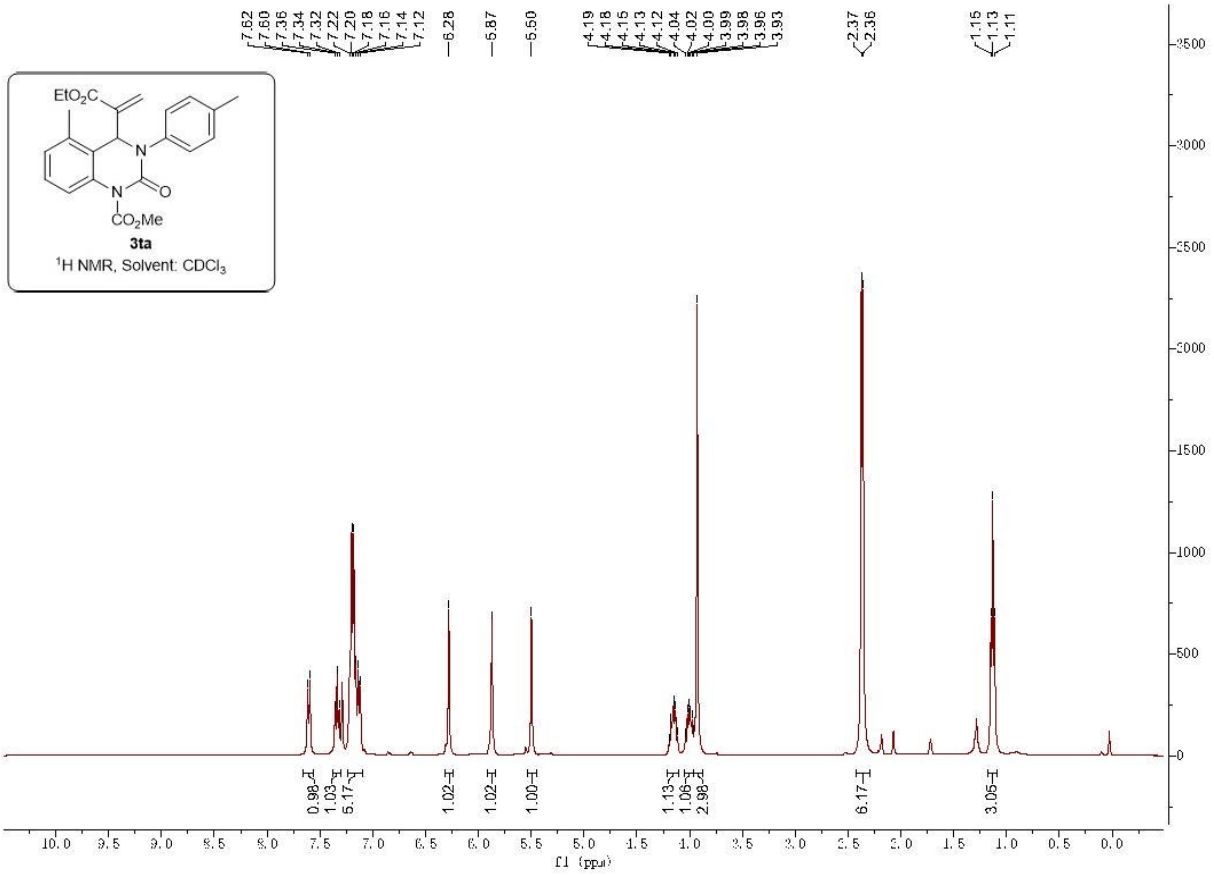

EtO2C
F
N
O
N
CO2Me
3qa
19F NMR, Solvent: CDCl3
116.01
116.02
116.03
116.04
116.05
116.06
f1 (ppm)

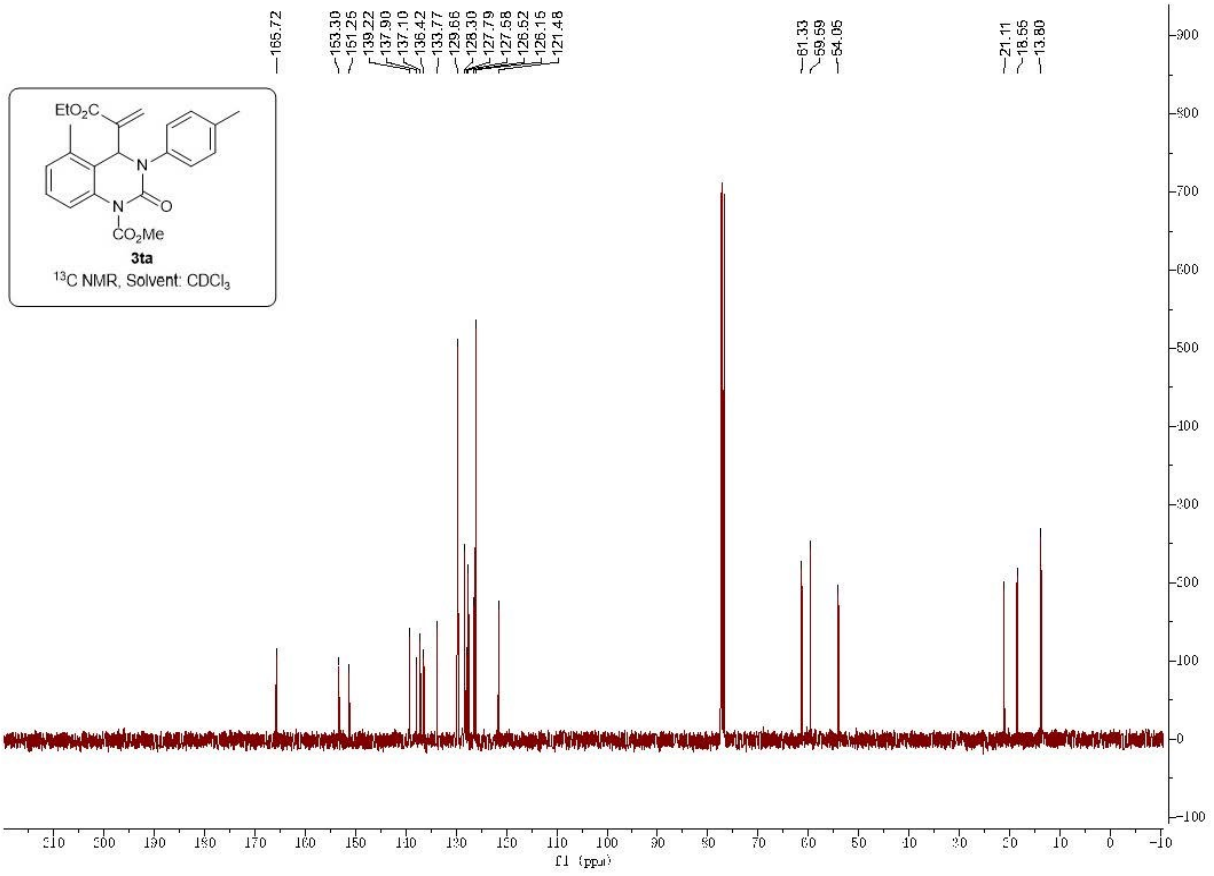

EtO2C
Cl
N
N
O
CO2Me
3ra
1H NMR, Solvent: CDCl3
7.74
7.72
7.50
7.35
7.34
7.33
7.17
6.44
6.08
5.62
4.31
4.28
4.27
4.26
4.25
4.24
4.22
4.20
4.18
4.16
4.16
4.15
4.14
4.12
4.10
3.91
2.34
1.30
1.29
1.27
1.00
1.04
1.04
4.09
1.00
0.99
1.01
2.22
2.99
3.04
3.37
f1 (ppm)

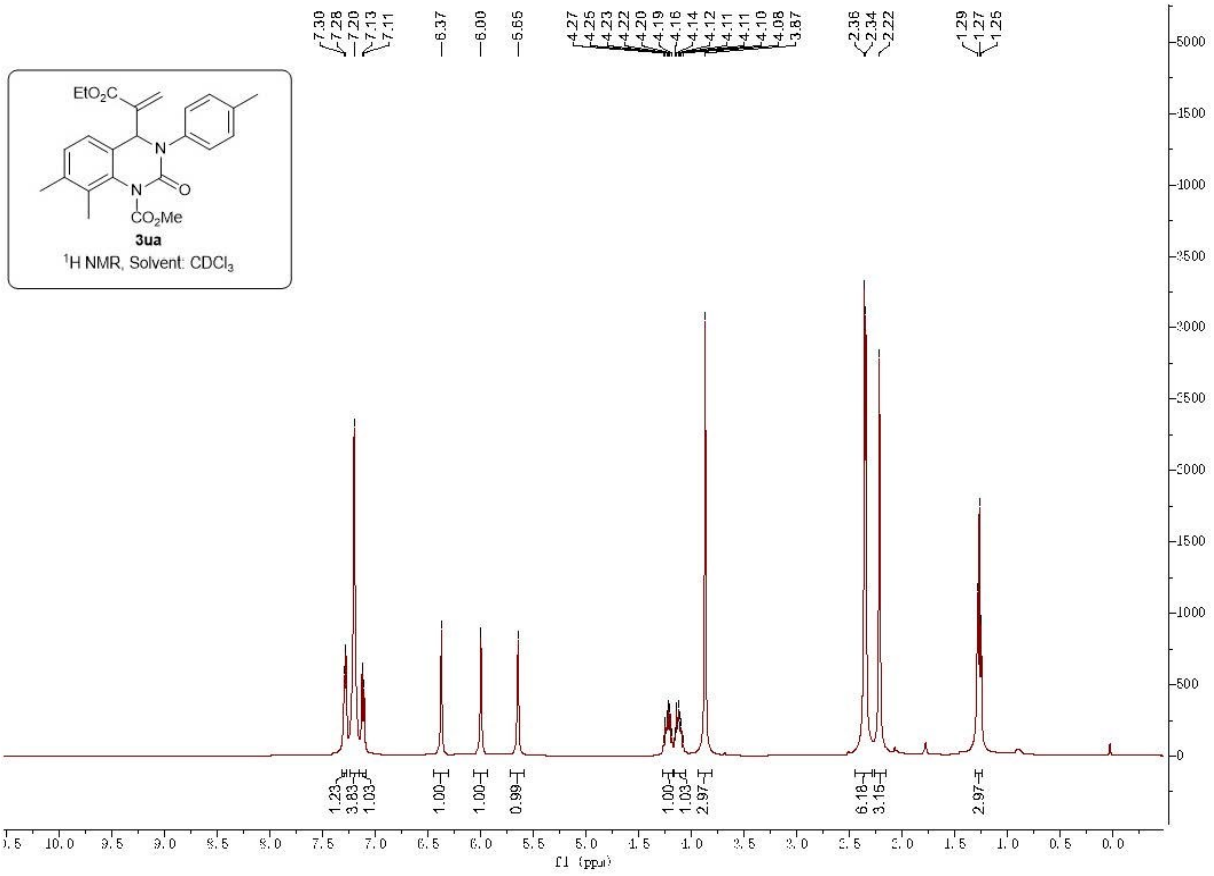

EtO2C
Cl
N
N
O
CO2Me
3ra
13C NMR, Solvent: CDCl3
164.91
152.89
151.51
138.43
137.39
133.89
130.99
129.87
129.75
128.52
126.88
125.26
124.72
124.37
62.41
61.58
54.30
21.07
14.06
f1 (ppm)

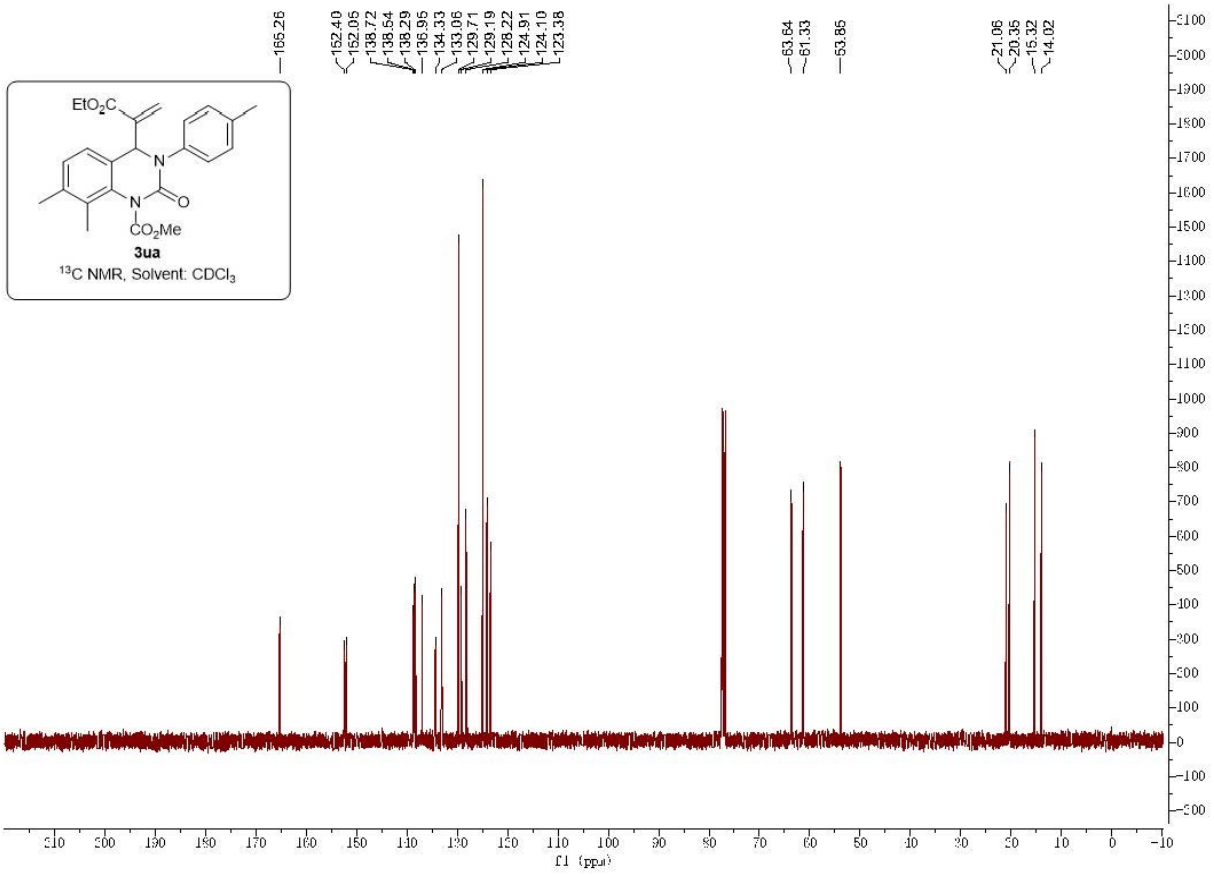

EtO2C
Br
N
N
O
CO2Me
3sa
1H NMR, Solvent: CDCl3
7.69
7.67
7.65
7.65
7.50
7.49
7.47
7.47
7.19
7.17
7.16
7.15
6.44
6.08
6.08
5.61
4.29
4.27
4.26
4.25
4.24
4.23
4.23
4.21
4.20
4.18
4.17
4.16
4.16
4.15
4.14
4.12
3.91
2.34
2.33
1.31
1.29
1.27
1.26
1.99
1.03
4.28
0.99
1.06
1.00
2.25
3.03
3.17
3.21
f1 (ppm)


EtO2C
Br
N
N
O
CO2Me
3sa
13C NMR, Solvent: CDCl3
164.89
152.84
151.43
138.43
137.44
137.38
134.43
131.45
130.03
129.86
129.76
125.25
124.75
124.63
118.65
62.30
61.58
54.29
21.06
14.06
f1 (ppm)

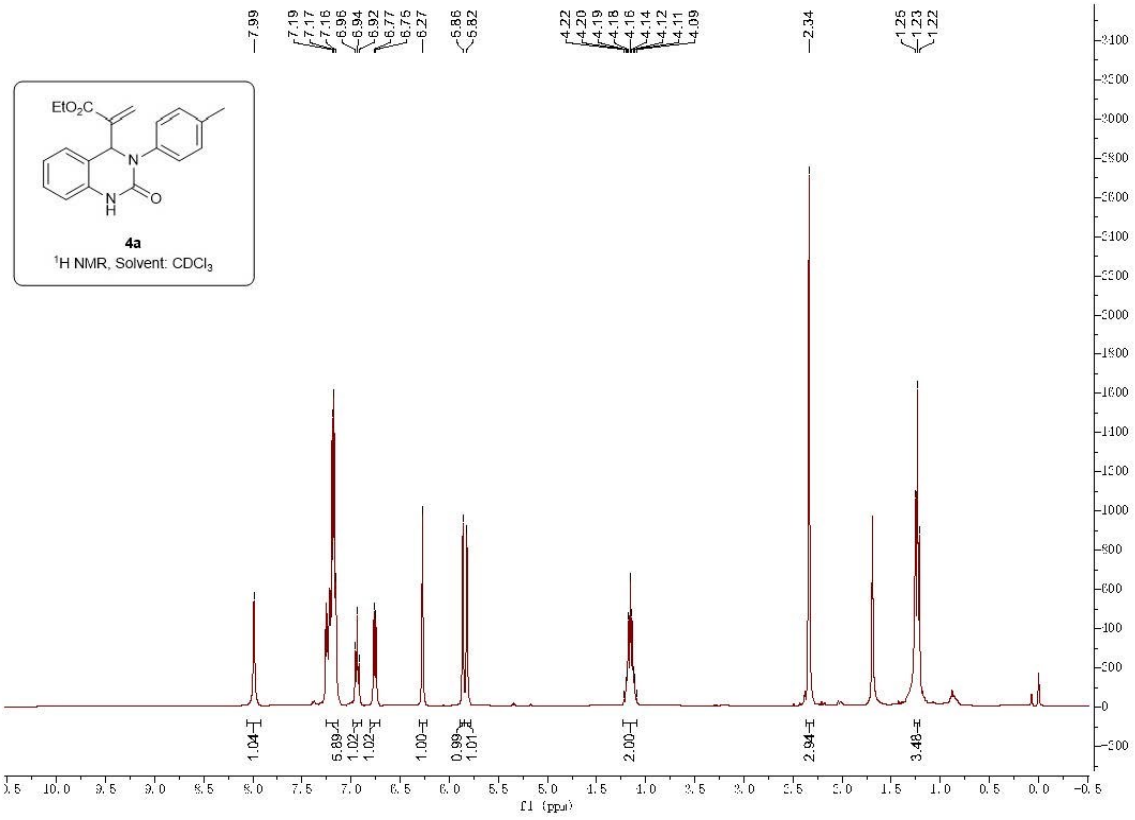

7.62
7.60
7.36
7.34
7.32
7.22
7.20
7.18
7.16
7.14
7.12
6.28
5.87
5.50
4.19
4.18
4.15
4.13
4.12
4.04
4.02
4.00
3.99
3.98
3.96
3.93
2.37
2.36
1.15
1.13
1.11
EtO2C
N
N
O
CO2Me
3ta
1H NMR, Solvent: CDCl3
0.98
1.03
5.17
1.02
1.02
1.00
1.13
1.06
2.98
6.17
3.05
f1 (ppm)

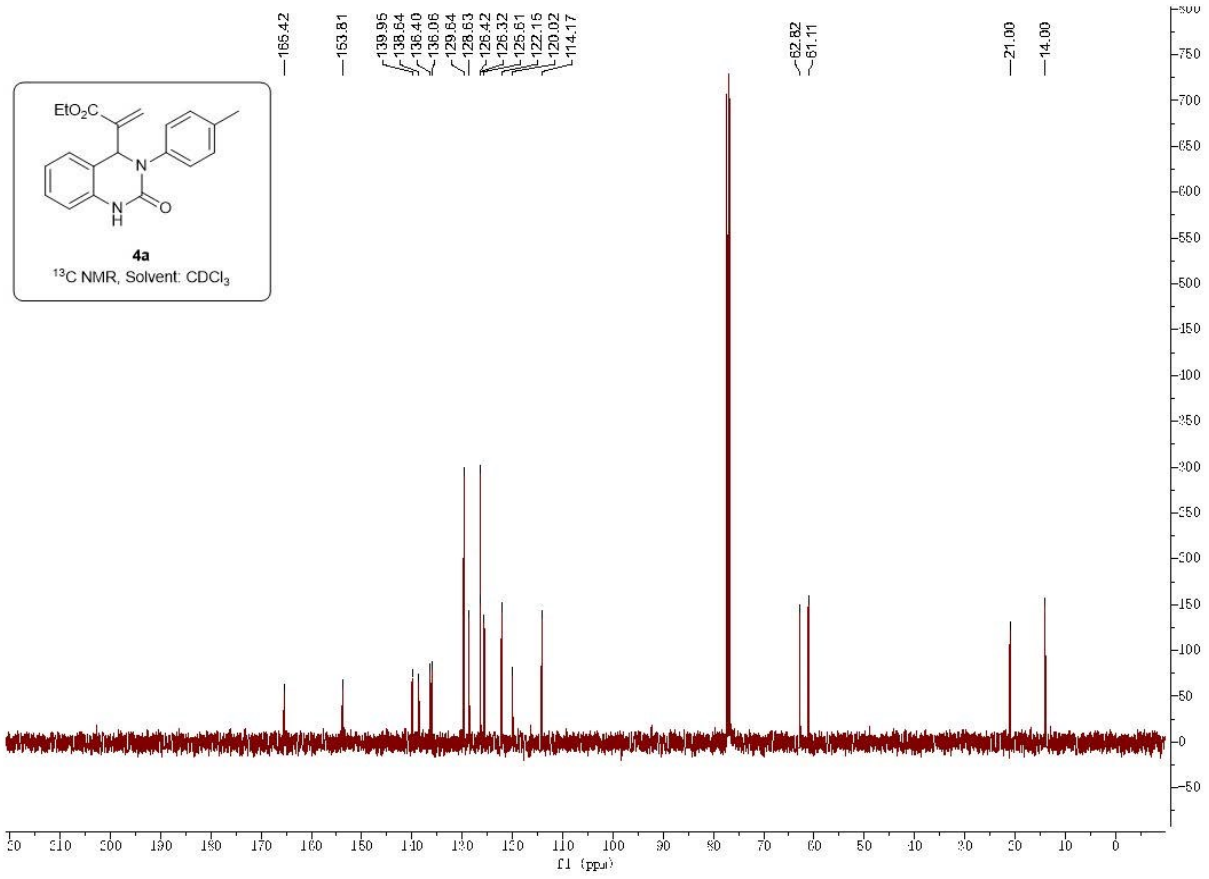

165.72
153.30
151.25
139.22
137.90
137.10
136.42
133.77
129.66
128.30
127.79
127.58
126.52
126.15
121.48
61.33
59.59
54.05
21.11
18.55
13.80
EtO2C
N
N
O
CO2Me
3ta
13C NMR, Solvent: CDCl3
f1 (ppm)

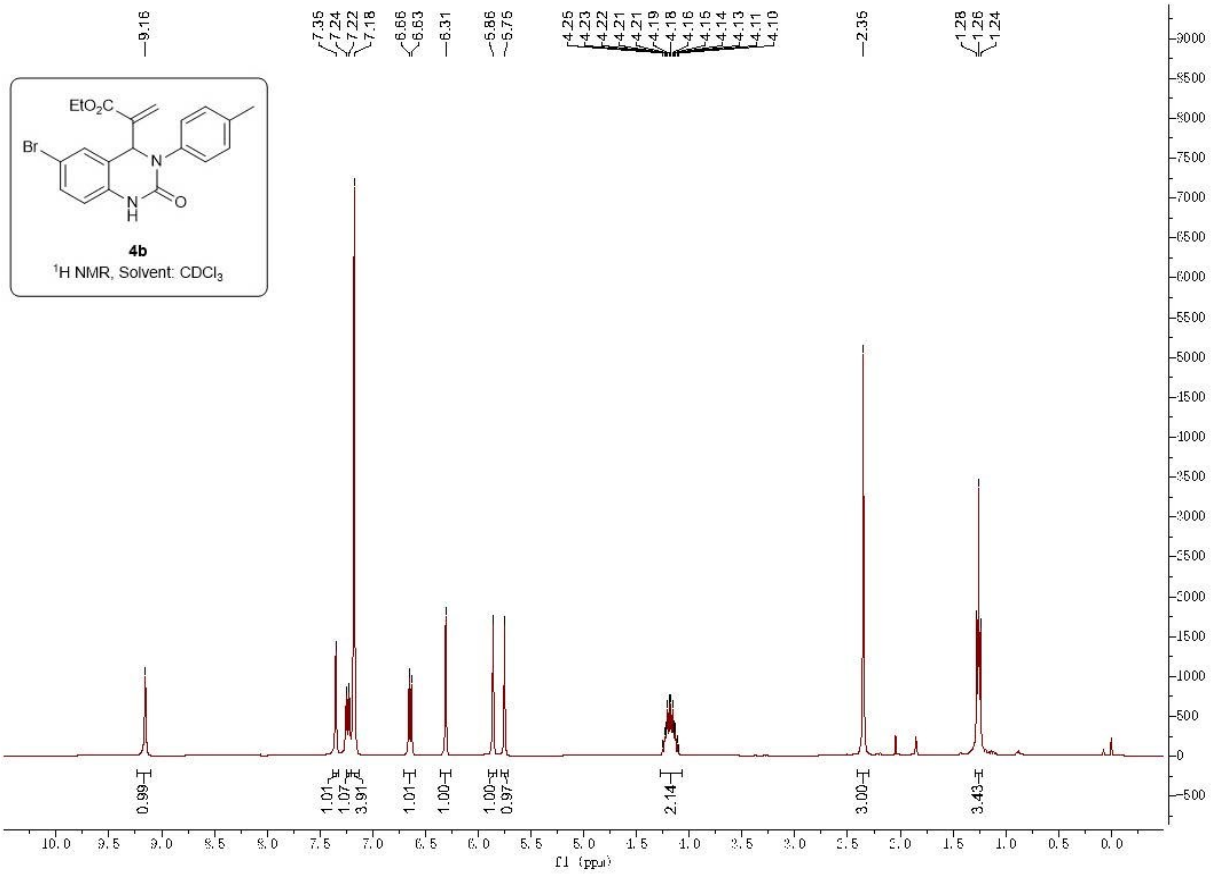

EtO2C
N
N
O
CO2Me
3ua
1H NMR, Solvent: CDCl3
7.30
7.28
7.20
7.13
7.11
6.37
6.00
5.65
4.27
4.25
4.23
4.22
4.20
4.19
4.16
4.14
4.12
4.11
4.11
4.10
4.08
3.87
2.36
2.34
2.22
1.29
1.27
1.25
1.23
3.83
1.03
1.00
1.00
0.99
1.00
1.03
2.97
6.18
3.15
2.97
f1 (ppm)

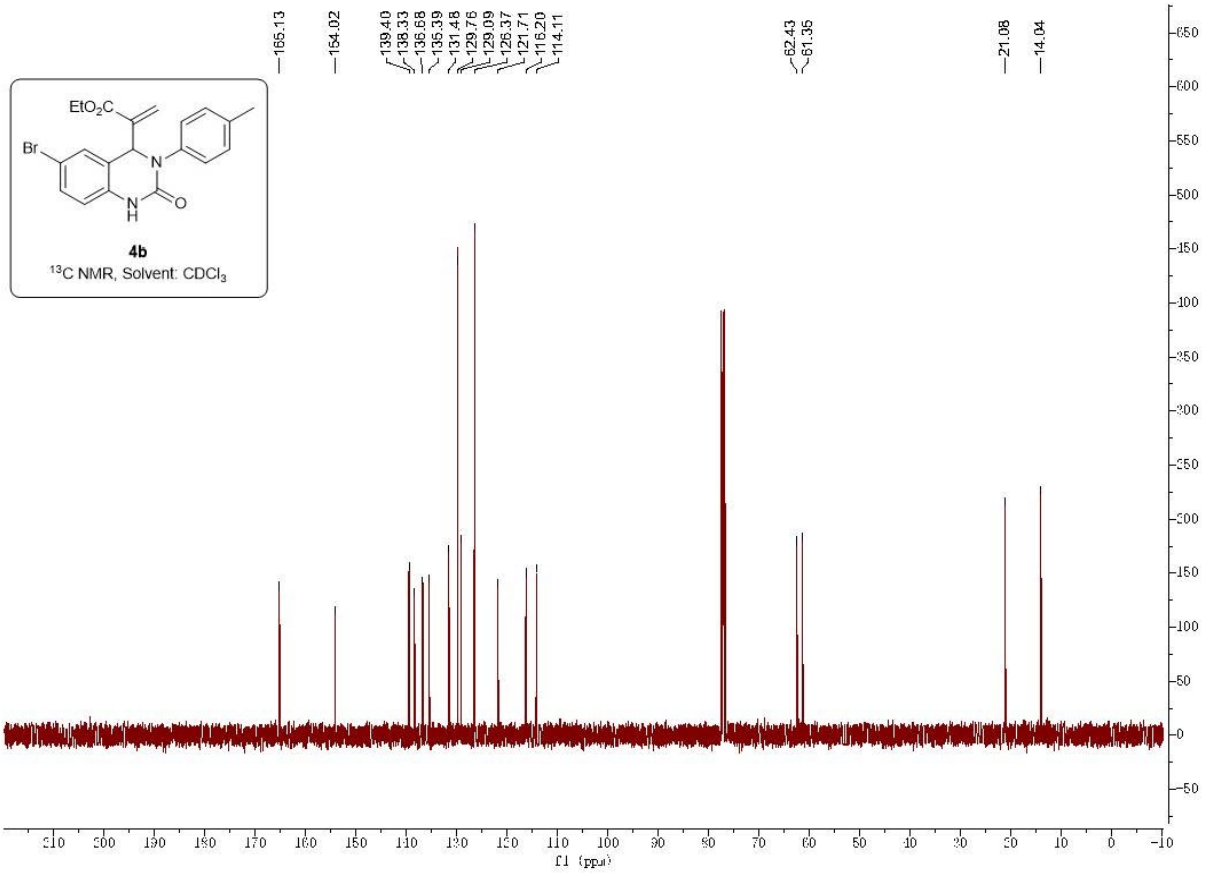

EtO2C
N
N
O
CO2Me
3ua
13C NMR, Solvent: CDCl3
165.26
152.40
152.05
138.72
138.54
138.29
136.95
134.33
133.06
129.71
129.19
128.22
124.91
124.10
123.38
63.64
61.33
53.85
21.06
20.35
15.32
14.02
f1 (ppm)

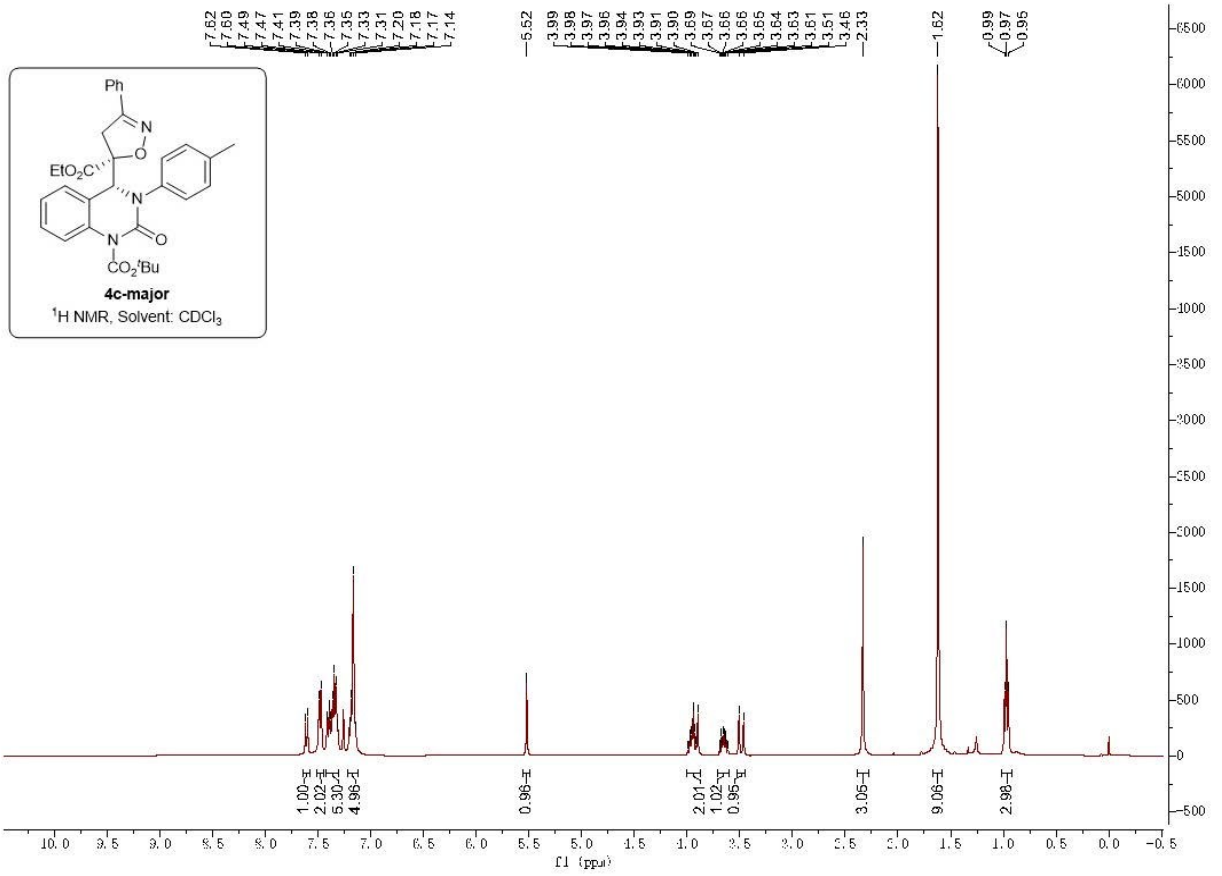
8.3. Products of Derivatization

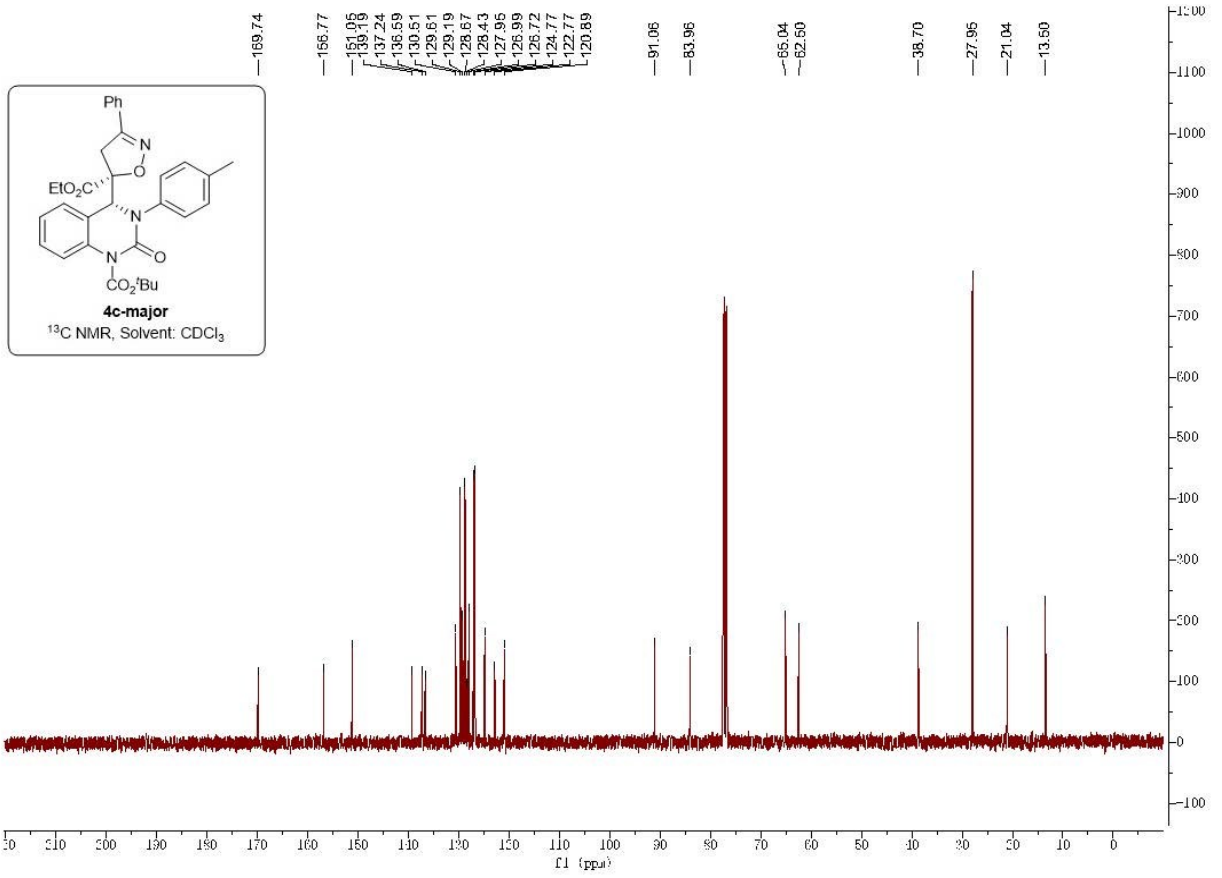


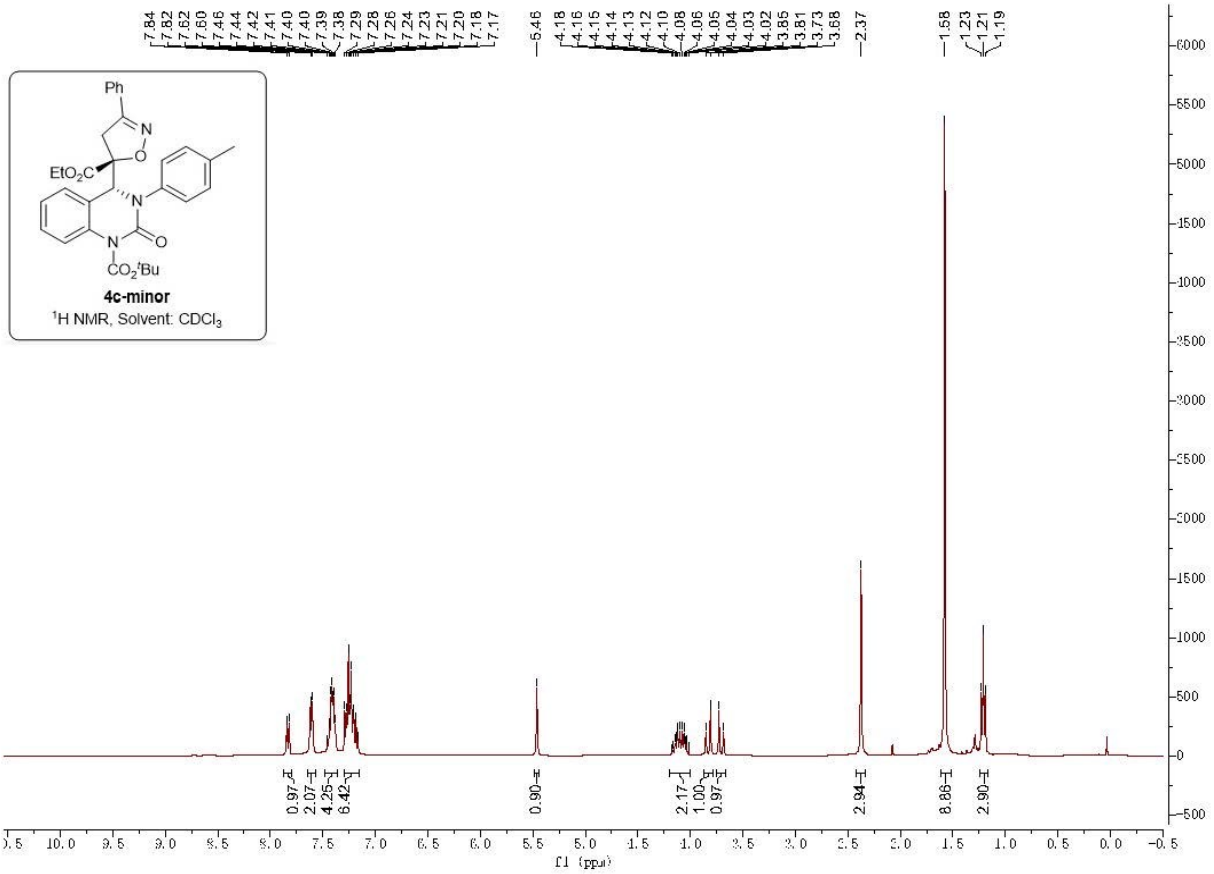


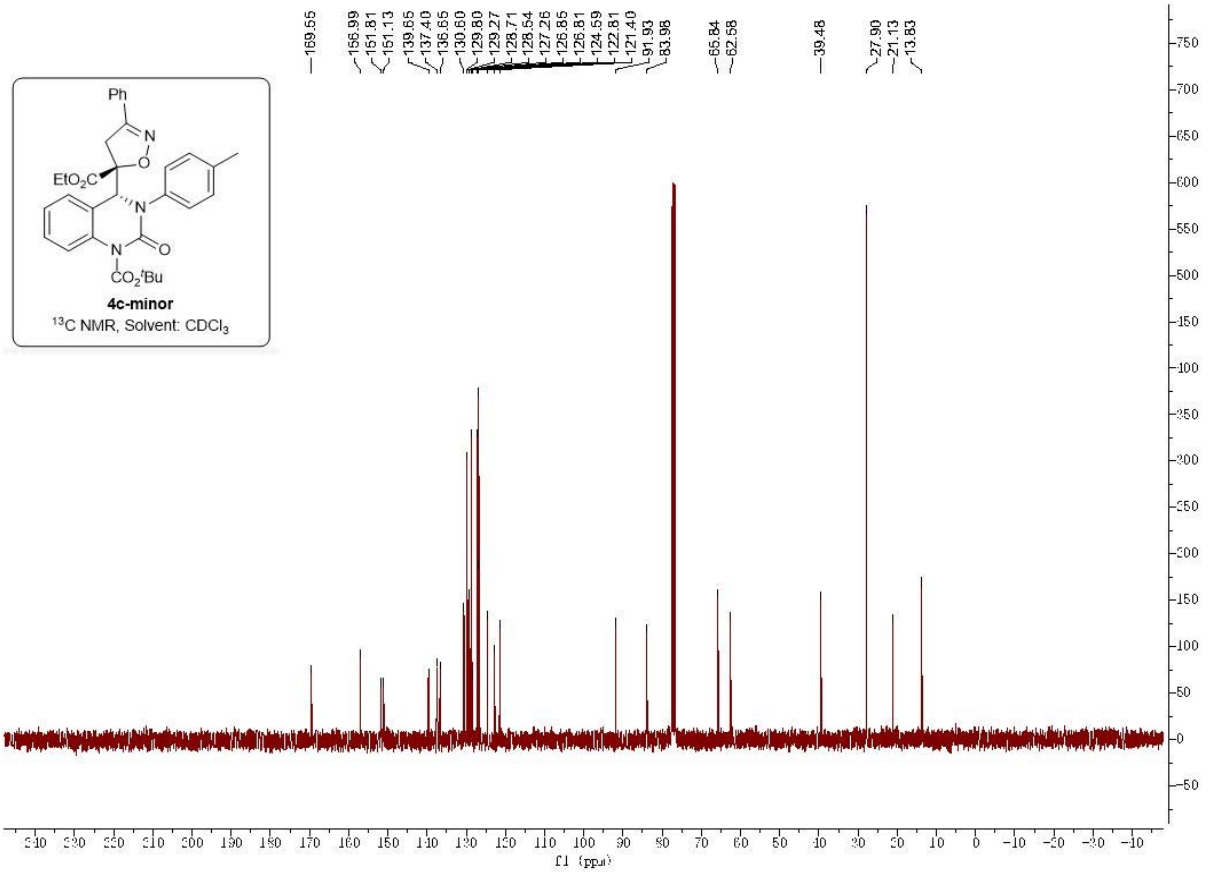

EtO2C
Br
N
N
H
O
4b
1H NMR, Solvent: CDCl3
9.16
7.35
7.24
7.22
7.18
6.66
6.63
6.31
5.86
5.75
4.25
4.23
4.22
4.21
4.21
4.19
4.18
4.16
4.15
4.14
4.13
4.11
4.10
2.35
1.28
1.26
1.24
0.99
1.01
1.07
3.91
1.01
1.00
1.00
0.97
2.14
3.00
3.43
f1 (ppm)


EtO2C
Br
N
N
H
O
4b
13C NMR, Solvent: CDCl3
165.13
154.02
139.40
138.33
136.68
135.39
131.48
129.76
129.09
126.37
121.71
116.20
114.11
62.43
61.35
21.08
14.04
f1 (ppm)


Ph
EtO2C
CO2tBu
4c-major
1H NMR, Solvent: CDCl3
f1 (ppm)


Ph
EtO2C
CO2tBu
4c-major
13C NMR, Solvent: CDCl3
f1 (ppm)


Ph
N
O
EtO2C
N
N
O
CO2tBu
4c-minor
1H NMR, Solvent: CDCl3
f1 (ppm)


Ph
N
O
EtO2C
N
N
O
CO2tBu
4c-minor
13C NMR, Solvent: CDCl3
f1 (ppm)