Supporting Information for

Designing and Accurate Developing [6+2] Dipolar Cycloaddition for Synthesis of Benzodiazocines

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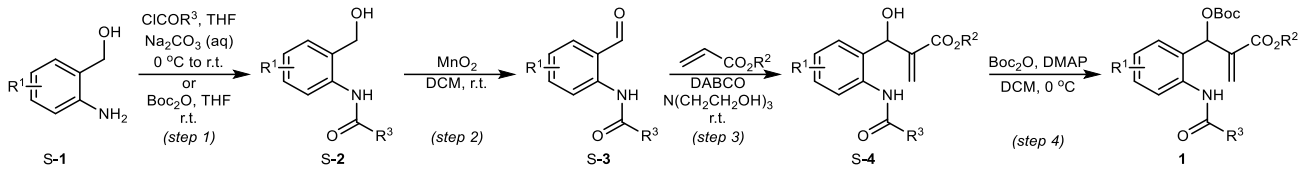
CONTENTS

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 $CDCl_3$ or DMSO-d_6 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, DMSO-d_6: δ 2.50 ppm), carbon ($CDCl_3$: δ 77.07 ppm, DMSO-d_6: δ 39.50 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



2.1 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** (R^1 = H, 5-Me, 5-Cl, 5-NO_2, R^3 = H, Me, Et, Ph) have been reported earlier[2]. Here we broaden the scope of their substituents and made some changes in reaction conditions.

Step 1: When R^3 refers to OMe, OEt, OAllyl, OMenthyl or Ph. To a 500 mL round-bottomed flask, S-**1** (40 mmol, 1 eq.) was dissolved in THF (100 mL) was added saturated aqueous solution of sodium carbonate (150 mL), the resulting mixture was stirred at 0 ℃. Then $ClCOR^3$ (50 mmol, 1.25 eq.) in THF (50 mL) was added to the above solution slowly. After addition was complete, the reaction solution was allowed to gradually warm to room temperature and was stirred for 1 h. The reaction mixture was extracted with ethyl acetate (100 mL × 3). The combined organic layers were washed with a saturated aqueous solution of NaCl and dried over anhydrous Na_2SO_4. After filtration and evaporation, the crude product S-**2** was sufficiently pure to be employed in the subsequent step.

When R^3 refers to O^{t}Bu. To a 250 mL round-bottomed flask S-**1** (40 mmol) was dissolved in THF (80 mL) was added Boc_2O (44 mmol) in THF (20 mL). The reaction mixture was stirred at room temperature for 24 h. The resulting was evaporated directly to obtain corresponding S-**2.**

Step 2: To a 500 mL round-bottomed flask the crude mixture from step 1 (40 mmol, 1 eq.) was dissolved in DCM (250 mL) and MnO_2 (400 mmol, 10 eq.) was added. The reaction was stirred at ambient temperature for 4 h. Upon full conversion, the reaction mixture was filtered through a plug of Celite and purified by column chromatography on silica gel (petroleum ether/ethyl acetate 7:1) to yield the desired product S-**3**.

Step 3: To a 50 mL round-bottomed flask a mixture of S-**3** (20 mmol), acrylate (60-100 mmol, 3-5 eq., When the solubility of S-**3** is poor, add more acrylate), DABCO (20 mmol, 1 eq.), and triethanolamine (16 mmol, 0.8 eq.) was stirred at room temperature until the complete consumption of the starting materials (12-24 h) monitored by TLC. The resulting mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 4:1) to afford the desired product S-**4**.

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[1] Leth, L. A. *et al.* Decarboxylative [4+2] Cycloaddition by Synergistic Palladium and Organocatalysis. *Angew. Chem. Int. Ed.* **55**, 15272-15276 (2016). [2] Lee, K.-J., Lim, H. & Song, Y. Synthesis of Methyl 2-Amino-3H-1-benzazepine-4-carboxylates and 2-(Cyanomethyl)-2,3-dihydro-1H-indole-2-carboxylates from Morita-Baylis-Hillman Acetates of 2-(Acylamino)benzaldehydes. *Synthesis* **2007**, 3376-3384 (2007).

Step 4: To a 250 mL round-bottomed flask S-**4** (20 mmol, 1 eq.) was dissolved in DCM (120 mL) and Boc_2O (22 mmol, 1.1 eq.) was added, the resulting mixture was stirred at 0 ℃. Then DMAP (2 mmol, 0.1 eq.) in DCM (10 mL) was added to the above solution in one portion. The reaction was monitored by TLC until completion (10-60 min). the reaction mixture was neutralized by addition of HCl (0.5 M, 50 mL) and extracted with DCM (50 mL × 3). The combined organic layers were washed with a saturated aqueous solution of NaCl and dried over anhydrous Na_2SO_4. After filtration and evaporation, the resulting mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 6:1) to afford the desired product **1**.

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

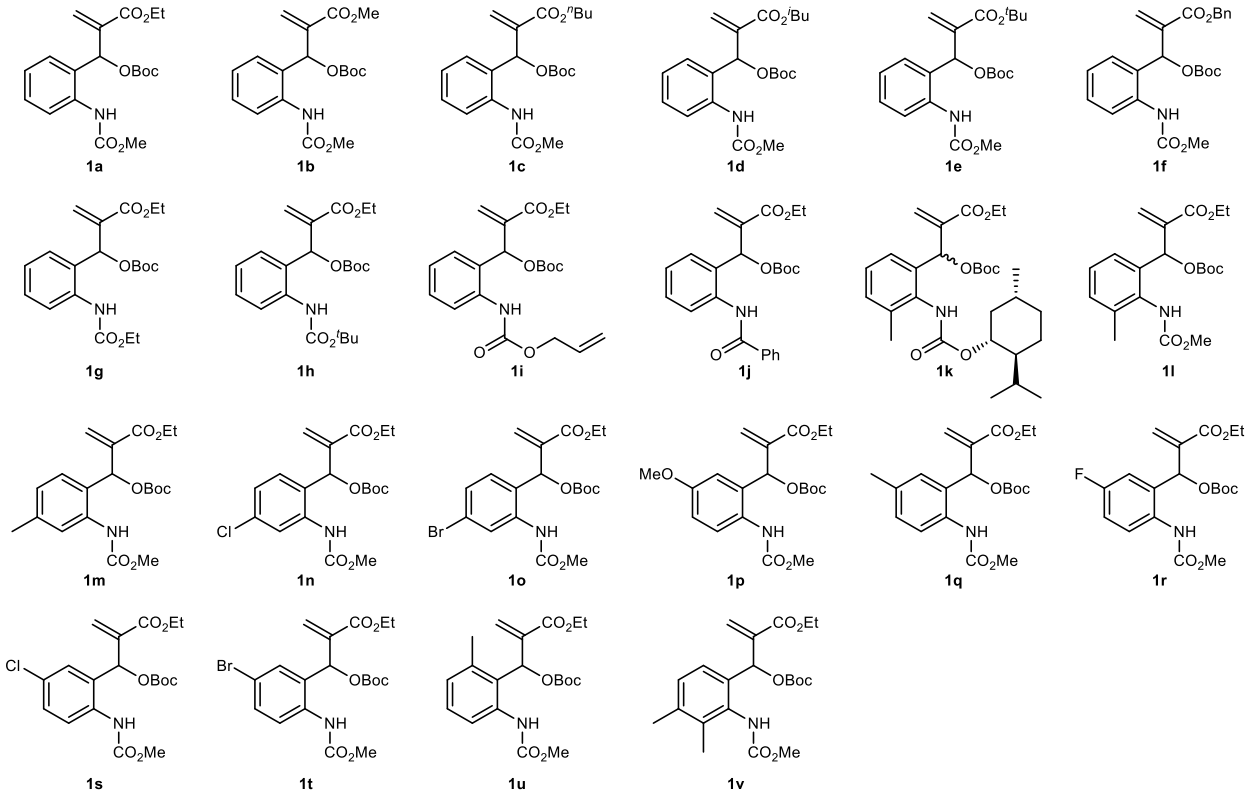
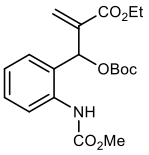


Figure S1. Scopes of *o*-amino-acylation aryl MBH carbonates.

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

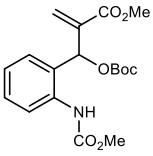
ethyl 2-(((tert-butoxycarbonyl)oxy)(2-((methoxycarbonyl)amino)phenyl)methyl)acrylate (1a)



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.

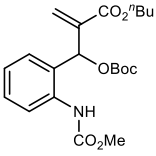
methyl 2-(((tert-butoxycarbonyl)oxy)(2-((methoxycarbonyl)amino)phenyl)methyl)acrylate (1b)



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.

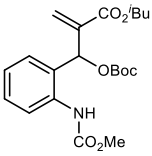
butyl 2-(((tert-butoxycarbonyl)oxy)(2-((methoxycarbonyl)amino)phenyl)methyl)acrylate (1c)



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.

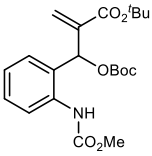
isobutyl 2-(((tert-butoxycarbonyl)oxy)(2-((methoxycarbonyl)amino)phenyl)methyl)acrylate (1d)



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.

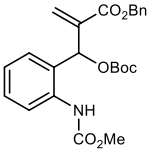
tert-butyl 2-(((tert-butoxycarbonyl)oxy)(2-((methoxycarbonyl)amino)phenyl)methyl)acrylate (1e)



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.

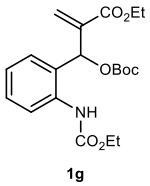
benzyl 2-(((tert-butoxycarbonyl)oxy)(2-((methoxycarbonyl)amino)phenyl)methyl)acrylate (1f)



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.

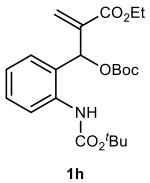
ethyl 2-(((tert-butoxycarbonyl)oxy)(2-((ethoxycarbonyl)amino)phenyl)methyl)acrylate (1g)



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.

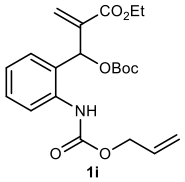
ethyl 2-((2-((tert-butoxycarbonyl)amino)phenyl)((tert-butoxycarbonyl)oxy)methyl)acrylate (1h)



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.

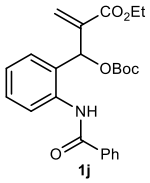
ethyl 2-((2-(((allyloxy)carbonyl)amino)phenyl)((tert-butoxycarbonyl)oxy)methyl)acrylate (1i)



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.

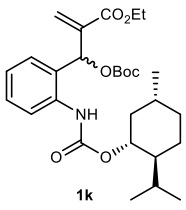
ethyl 2-((2-benzamidophenyl)((tert-butoxycarbonyl)oxy)methyl)acrylate (1j)



1j

3.2 g, 19% yield (4 steps). White solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.80 (s, 1H), 8.12 (d, *J* = 7.6 Hz, 2H), 8.04 (d, *J* = 7.5 Hz, 1H), 7.62 – 7.50 (m, 3H), 7.44 – 7.37 (m, 2H), 7.24 – 7.16 (m, 1H), 6.68 (s, 1H), 6.45 (s, 1H), 6.16 (s, 1H), 4.14 (dtt, *J* = 13.5, 7.0, 3.6 Hz, 2H), 1.47 (d, *J* = 2.6 Hz, 9H), 1.18 (td, *J* = 7.1, 2.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 165.5, 152.8, 139.0, 135.8, 134.7, 131.8, 129.3, 129.0, 128.7, 128.3, 127.5, 125.3, 125.0, 125.0, 83.5, 71.4, 61.5, 27.7, 13.9. **HRMS(ESI)** m/z: $[M + Na]^+$ calcd for $C_{24}H_{27}NNaO_6^+$ 448.1730; Found: 448.1726.

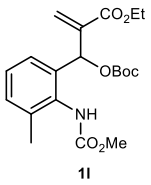
ethyl 2-(((tert-butoxycarbonyl)oxy)(2-(((((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)amino)-3-methylphenyl)methyl)acrylate (1k)



1k

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.

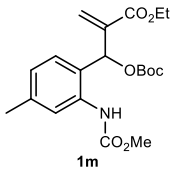
ethyl 2-(((tert-butoxycarbonyl)oxy)(2-((methoxycarbonyl)amino)-3-methylphenyl)methyl)acrylate (1l)



1l

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.

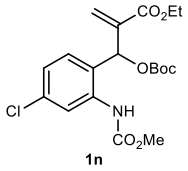
ethyl 2-(((tert-butoxycarbonyl)oxy)(2-((methoxycarbonyl)amino)-4-methylphenyl)methyl)acrylate (1m)



1m

7.2 g, 46% yield (4 steps). White solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 7.60 (s, 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.

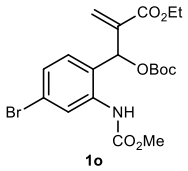
ethyl 2-(((tert-butoxycarbonyl)oxy)(4-chloro-2-((methoxycarbonyl)amino)phenyl)methyl)acrylate (1n)



1n

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.

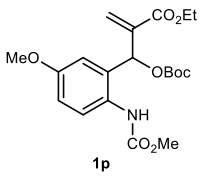
ethyl 2-((4-bromo-2-((methoxycarbonyl)amino)phenyl)((tert-butoxycarbonyl)oxy)methyl)acrylate (1o)



1o

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.

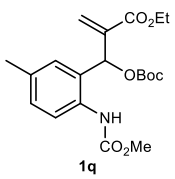
ethyl 2-(((tert-butoxycarbonyl)oxy)(5-methoxy-2-((methoxycarbonyl)amino)phenyl)methyl)acrylate (1p)



1p

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.

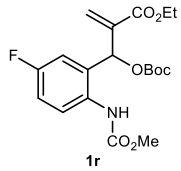
ethyl 2-(((tert-butoxycarbonyl)oxy)(2-((methoxycarbonyl)amino)-5-methylphenyl)methyl)acrylate (1q)



1q

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.

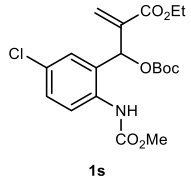
ethyl 2-(((tert-butoxycarbonyl)oxy)(5-fluoro-2-((methoxycarbonyl)amino)phenyl)methyl)acrylate (1r)



1r

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.

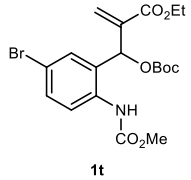
ethyl 2-(((tert-butoxycarbonyl)oxy)(5-chloro-2-((methoxycarbonyl)amino)phenyl)methyl)acrylate (1s)



1s

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.

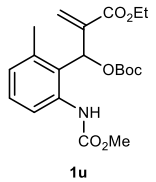
ethyl 2-((5-bromo-2-((methoxycarbonyl)amino)phenyl)((tert-butoxycarbonyl)oxy)methyl)acrylate (1t)



1t

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.

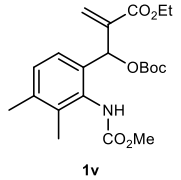
ethyl 2-(((tert-butoxycarbonyl)oxy)(2-((methoxycarbonyl)amino)-6-methylphenyl)methyl)acrylate (1u)



1u

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 (1v)

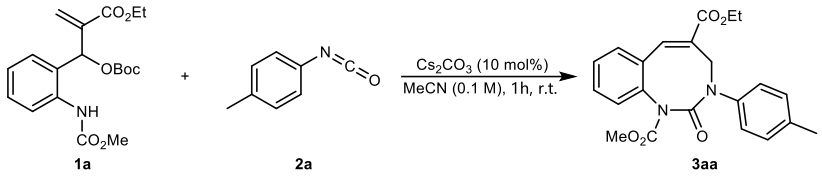


1v

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), 3.83 – 3.63 (m, 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.

3. General Procedure of Optimization and Substrate Scope

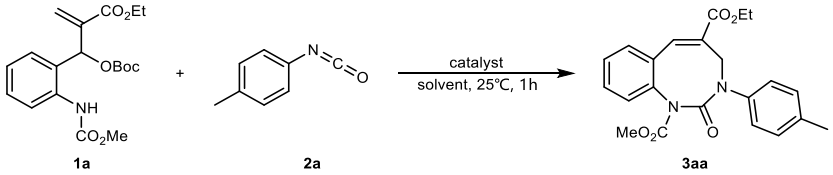
3.1. General procedure 1 (GP1) for the synthesis of benzodiazocine



o-amino-acylation aryl MBH carbonate **1a** (0.1 mmol, 1.0 eq.) and isocyanate **2a** (0.2 mmol, 2.0 eq.) and MeCN (0.5 mL) were added to a dry flask at room temperature, then Cs_2CO_3 (0.01 mmol, 0.1 eq.) in MeCN (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.**

3.2. Optimization of intermolecular cycloaddition reaction conditions

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



Entry	1a (mmol)	2a (mmol)	Solvent[a]	Catalyst[b]	Yield of 3aa (%)[c]
1	0.1	0.1	MeCN	—	no reaction
2	0.1	0.1	MeCN	Cs_2CO_3	62
3	0.1	0.12	MeCN	Cs_2CO_3	73
4	0.1	0.15	MeCN	Cs_2CO_3	79
5	0.1	0.2	MeCN	Cs_2CO_3	**91**
6	0.1	0.2	toluene	Cs_2CO_3	no reaction
7	0.1	0.2	$CHCl_3$	Cs_2CO_3	no reaction
8	0.1	0.2	EtOAc	Cs_2CO_3	no reaction
9	0.1	0.2	THF	Cs_2CO_3	no reaction
10	0.1	0.2	MeCN	NaOAc	43
11	0.1	0.2	MeCN	Na_2CO_3	67
12	0.1	0.2	MeCN	K_2CO_3	86
13	0.1	0.2	MeCN	Ru_2CO_3	90
14	0.1	0.2	MeCN	$K_3PO_4·3H_2O$	75
15	0.1	0.2	MeCN	Et_3N	mess
16	0.1	0.2	$CHCl_3$	quinine	no reaction

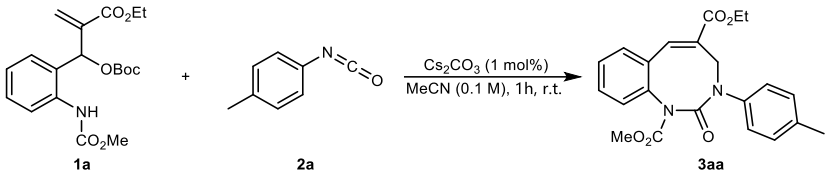
17	0.1	0.2	$CHCl_3$	PPh_3	no reaction

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

4. Gram scale reactions and synthetic transformations

4.1. Gram scale reactions

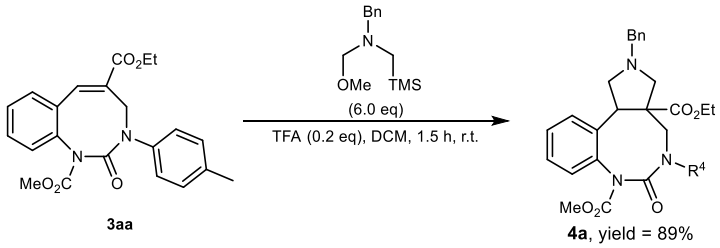
Synthesis of benzodiazocine 3aa



o-amino-acylation aryl MBH carbonate **1a** (1.52g, 4 mmol, 1.0 eq.) and isocyanate **2a** (1.01 mL, 8 mmol, 2.0 eq.) and MeCN (35 mL) were added to a 100 mL dry flask at room temperature, then Cs_2CO_3 (13.0 mg, 0.04 mmol, 0.01 eq.) in MeCN (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 3:1) to provide the desired product **3aa** as a white solid (1.43 g, 91% yield). The analytical data of the gram scale reaction of **3aa** are consistent with those of the 0.1 mmol scale experiment.

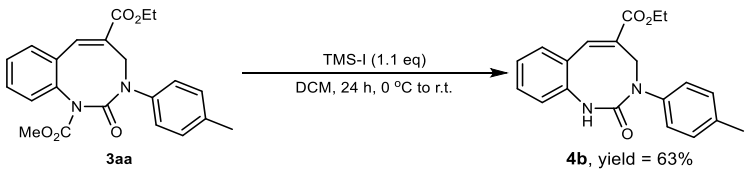
4.2. Synthetic transformations

3aa to 4a (3+2 cycloaddition)



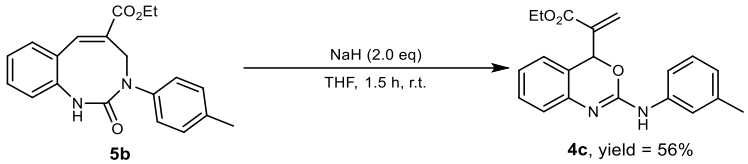
To a stirred solution of **3aa** (39.4 mg, 0.1 mmol, 1.0 eq.) and N-(Methoxymethyl)-N-(trimethylsilylmethyl)benzylamine (142.4 mg, 0.6 mmol, 6.0 eq.) in 1 mL DCM was added TFA (1.5 μL, 0.02 mmol, 0.2 eq.). The resulting solution of the reaction mixture was stirred at room temperature for 1.5 h then evaporated to give the crude product, which was purified by flash chromatography (petroleum ether/ethyl acetate 2:1) to provide the desired product **4a** (38.8 mg, 89% yield).

3aa to 4b (Removal of CO_2Me)



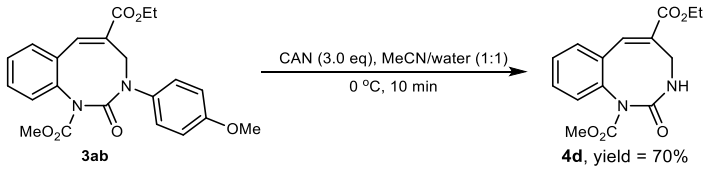
To a stirred solution of **3aa** (39.4 mg, 0.1 mmol, 1.0 eq.) in 1 mL DCM was added TMS-I (22.0 mg, 0.11 mmol, 1.1 eq.) in one portion at 0 ℃. Then the reaction was allowed to warm up to ambient temperature slowly. The resulting solution of the reaction mixture was stirred at room temperature for 24 h then evaporated to give the crude product, which was purified by flash chromatography (petroleum ether/ethyl acetate 2:1) to provide the desired product **4b** (23.6 mg, 63% yield).

4b to 4c (Rearrangement)



4b (33.6 mg, 0.1 mmol, 1.0 eq.) and NaH (4.8 mg, 0.2 mmol, 2.0 eq.) were added to 1 mL dry THF and stirred at room temperature for 1.5 h. NH_4Cl (aq) was added in small portions. Then, extracted with ethyl acetate, and dried with Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 2:1) to provide the desired product **4c** (18.8 mg, 56% yield).

3ab to 4d (Removal of *p*-methoxyphenyl)



To a stirred solution of **3ab** (41.0 mg, 0.1 mmol, 1.0 eq.) in 1 mL MeCN was added solution of CAN (164.5 mg, 0.3 mmol, 3.0 eq.) in 1mL H_2O dropwise at 0 ℃. The reaction mixture was stirred for 10 min then extracted with ethyl acetate (1 mL × 3). The combined organic layers were washed with 5% $NaHSO_3$ (2 mL), brine (2 mL), dried over with Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 2:1) to provide the desired product **4d** (21.3 mg, 70% yield).

5. Density Functional Theory (DFT) Calculations

5.1. Computational Methods

Density functional theory (DFT) investigations were performed to delineate the detailed mechanism of Cs_2CO_3 catalyzed [6+2] dipolar cycloaddition of *o*-amino-acylation aryl MBH carbonate with isocyanate. All DFT calculations were carried out with the Gaussian 09 programs[3]. The geometry optimizations of the reactants, transition states, and products were performed with the M06-2X/6-31G(d) level[4]. 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 (MeCN) effects were considered by single point energy calculations on the gas-phase stationary points using M06-2X functional with the def2-TZVP[5] basis set in a SMD continuum solvation model. The energies given in this work are M06-2X calculated Gibbs free energies in MeCN noted on figures[6]. 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 [6+2] cycloaddition.

Geometry	$E_{(elec)}$[1]	$E_{(solv)}$[2]	$G_{(corr)}$[3]	$H_{(corr)}$[4]	IF[5]
1b	-1280.262547	-1281.14422411	0.344924	0.431572	
PhNCO	-399.491110	-399.731413128	0.072798	0.113236	
CO_3^{2-}	-263.508618	-264.033491015	-0.011079	0.018582	
HCO_3^-	-264.327898	-264.567531234	0.001345	0.031491	
CO_2	-188.517761	-188.596837844	-0.008735	0.015525	
tBuO-	-232.826769	-233.129924515	0.093301	0.129250	
INT1	-1279.705195	-1280.64216088	0.330169	0.416820	
TS2	-1679.193850	-1680.37711268	0.427045	0.530680	-121.22
INT2	-1679.215516	-1680.40583457	0.436806	0.533552	
TS3	-1679.203402	-1680.38797052	0.434589	0.533171	-216.35
INT3	-1679.213894	-1680.40228020	0.435867	0.535133	
TS4	-1679.201305	-1680.38459495	0.433478	0.533486	-223.33
3	-1257.803355	-1258.62428491	0.304189	0.382901	

[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.

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

[4] (a) Zhao, Y. & Truhlar, D. G. Density functionals with broad applicability in chemistry. *Acc. Chem. Res.* **41**, 157-167 (2008). (b) Zhao, Y. & Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: Two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **120**, 215-241 (2008). (c) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **98**, 5648-5652 (1993). (d) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **37**, 785-789 (1988).

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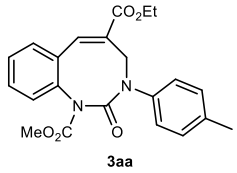
[6] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G., Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. J. Phys. Chem. B. 2009, 113, 6378-6396.

6. Analytical Data

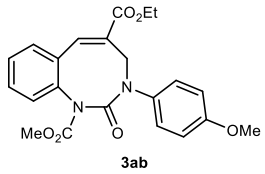
6.1. Cs_2CO_3 catalyzed [6+2] cycloadducts 3

5-ethyl 1-methyl (E)-2-oxo-3-(p-tolyl)-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3aa)



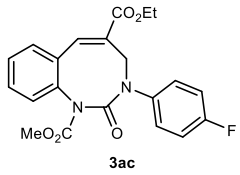
The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3aa** as white solid (35.9 mg, 91% yield, mp: 53-55 ℃). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.55 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.52 – 7.40 (m, 3H), 7.21 – 7.11 (m, 4H), 4.87 (s, 1H), 4.52 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 2.32 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.8, 153.8, 153.8, 140.7, 139.9, 137.2, 136.3, 134.2, 132.7, 131.8, 130.9, 129.8, 129.6, 129.0, 125.5, 61.7, 53.8, 50.7, 21.1, 14.3. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{23}N_2O_5^+$ 395.1602; Found: 395.1604.

5-ethyl 1-methyl (E)-3-(4-methoxyphenyl)-2-oxo-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3ab)



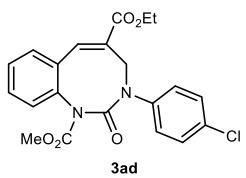
The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3ab** as white solid (34.9 mg, 85% yield, mp: 75-77 ℃). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.58 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.56 – 7.42 (m, 3H), 7.27 – 7.19 (m, 2H), 6.93 – 6.86 (m, 2H), 4.89 (s, 1H), 4.51 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 3.81 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.9, 158.6, 154.0, 153.9, 140.8, 136.4, 135.4, 134.3, 132.8, 131.9, 131.0, 129.7, 129.1, 127.1, 114.5, 61.9, 55.6, 53.9, 51.0, 14.4. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{23}N_2O_6^+$ 411.1551; Found: 411.1553.

5-ethyl 1-methyl (E)-3-(4-fluorophenyl)-2-oxo-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3ac)



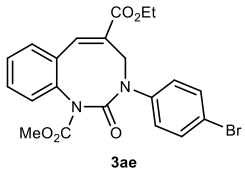
The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3ac** as white solid (31.9 mg, 80% yield, mp: 124-126 ℃). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.50 (ddd, *J* = 29.4, 13.3, 7.4 Hz, 4H), 7.28 (dt, *J* = 8.0, 4.0 Hz, 2H), 7.04 (t, *J* = 8.4 Hz, 2H), 4.84 (s, 1H), 4.46 (s, 1H), 4.28 (q, *J* = 7.0 Hz, 2H), 3.83 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.7, 162.6, 160.2, 153.8, 141.0, 138.6, 136.2, 134.0, 133.0, 131.9, 131.0, 129.5, 129.3, 127.8, 127.7, 116.3, 116.1, 61.9, 54.0, 50.8, 14.4. **^{19}F NMR** (377 MHz, Chloroform-d) δ -114.08 (tt, *J* = 8.7, 4.8 Hz). **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{21}H_{20}FN_2O_5^+$ 399.1351; Found: 399.1351.

5-ethyl 1-methyl (E)-3-(4-chlorophenyl)-2-oxo-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3ad)



The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3ad** as white solid (28.2 mg, 68% yield, mp: 80-82 ℃). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.61 – 7.53 (m, 2H), 7.52 – 7.43 (m, 2H), 7.38 (q, *J* = 2.1 Hz, 1H), 7.34 – 7.22 (m, 3H), 4.86 (s, 1H), 4.52 (s, 1H), 4.33 (q, *J* = 7.3 Hz, 2H), 3.86 (d, *J* = 1.8 Hz, 3H), 1.37 (t, *J* = 7.2 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.5, 153.7, 153.5, 143.5, 141.1, 136.0, 134.6, 133.9, 133.0, 131.8, 130.8, 130.2, 129.3, 129.2, 127.5, 126.1, 124.0, 61.9, 53.9, 50.5, 14.3. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{21}H_{20}ClN_2O_5^+$ 415.1055; Found: 415.1055.

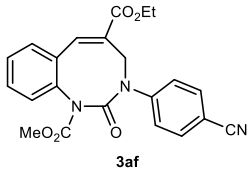
5-ethyl 1-methyl (E)-3-(4-bromophenyl)-2-oxo-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3ae)



3ae

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3ae** as white solid (33.9 mg, 74% yield, mp: 57-59 ℃). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.59 – 7.38 (m, 6H), 7.22 (dd, *J* = 8.7, 1.6 Hz, 2H), 4.84 (s, 1H), 4.49 (s, 1H), 4.29 (q, *J* = 7.3 Hz, 2H), 3.83 (s, 3H), 1.34 (td, *J* = 7.2, 1.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6, 153.7, 153.5, 141.5, 141.0, 136.0, 134.0, 132.9, 132.3, 131.9, 130.9, 129.3, 129.2, 127.4, 120.8, 61.9, 53.9, 50.5, 14.3. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{21}H_{20}BrN_2O_5^+$ 459.0550; Found: 459.0545.

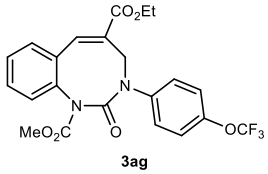
5-ethyl 1-methyl (E)-3-(4-cyanophenyl)-2-oxo-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3af)



3af

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3af** as white solid (16.2 mg, 40% yield, mp: 92-94 ℃). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.71 – 7.63 (m, 2H), 7.55 (dt, *J* = 6.6, 2.8 Hz, 4H), 7.51 – 7.44 (m, 2H), 4.89 (s, 1H), 4.60 (s, 1H), 4.34 (q, *J* = 7.0 Hz, 2H), 3.85 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6, 153.7, 153.5, 146.4, 141.4, 135.8, 134.0, 133.2, 133.0, 132.1, 131.0, 129.5, 129.0, 126.0, 118.4, 110.5, 62.1, 54.1, 50.2, 14.4. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{20}N_3O_5^+$ 406.1398; Found: 406.1400.

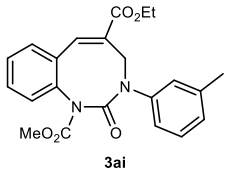
5-ethyl 1-methyl (E)-2-oxo-3-(4-(trifluoromethoxy)phenyl)-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3ag)



3ag

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3ag** as white solid (33.9 mg, 73% yield, mp: 53-55 ℃). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.59 – 7.41 (m, 4H), 7.41 – 7.31 (m, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 4.85 (s, 1H), 4.49 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.5, 153.7, 153.6, 147.7 – 147.6 (m), 141.0, 141.0, 136.0, 133.8, 132.9, 131.8, 130.9, 129.3, 129.2, 127.2, 121.7, 119.1, 61.8, 53.9, 50.5, 14.2. **^{19}F NMR** (377 MHz, Chloroform-*d*) δ -57.96. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{20}F_3N_2O_6^+$ 465.1268; Found: 465.1269.

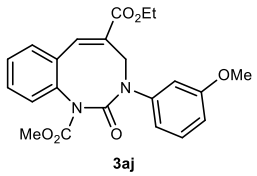
5-ethyl 1-methyl (E)-2-oxo-3-(m-tolyl)-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3ai)



3ai

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3ai** as white solid (34.3 mg, 87% yield, mp: 99-101 ℃). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.56 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.50 (ddd, *J* = 12.8, 6.0, 2.1 Hz, 2H), 7.46 – 7.41 (m, 1H), 7.27 – 7.23 (m, 1H), 7.12 (t, *J* = 2.1 Hz, 1H), 7.10 – 7.05 (m, 2H), 4.87 (s, 1H), 4.53 (s, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 2.33 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.8, 153.8, 153.7, 142.3, 140.7, 139.2, 136.3, 134.1, 132.8, 131.8, 130.9, 129.6, 129.1, 128.2, 126.4, 122.7, 61.7, 53.8, 50.7, 21.4, 14.3. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{23}N_2O_5^+$ 395.1602; Found: 395.1604.

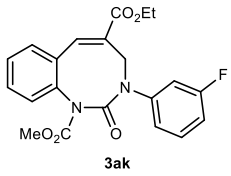
5-ethyl 1-methyl (E)-3-(3-methoxyphenyl)-2-oxo-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3aj)



3aj

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3aj** as white solid (28.3 mg, 69% yield, mp: 68-70 °C). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.53 – 7.40 (m, 3H), 7.32 – 7.22 (m, 2H), 7.01 – 6.85 (m, 2H), 4.72 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 3H), 3.84 (s, 3H), 3.68 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.8, 154.5, 154.0, 153.8, 140.1, 136.2, 133.7, 133.0, 131.4, 131.2, 130.8, 130.1, 129.2, 128.9, 128.4, 121.0, 112.2, 61.5, 55.6, 53.7, 50.2, 14.2. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{23}N_2O_6^+$ 411.1551; Found: 411.1550.

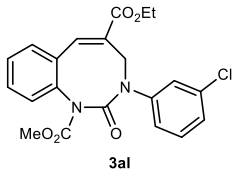
5-ethyl 1-methyl (E)-3-(3-fluorophenyl)-2-oxo-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3ak)



3ak

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3ak** as white solid (36.6 mg, 92% yield, mp: 71-73 °C). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.52 (dddd, *J* = 28.9, 11.6, 7.0, 1.7 Hz, 4H), 7.34 (td, *J* = 8.4, 6.3 Hz, 1H), 7.18 – 7.11 (m, 2H), 6.98 (td, *J* = 8.3, 2.0 Hz, 1H), 4.89 (s, 1H), 4.56 (s, 1H), 4.32 (p, *J* = 6.4, 5.6 Hz, 2H), 3.86 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6, 162.7 (d, J = 246.9 Hz), 153.7, 153.5, 143.8 (d, J = 10.6 Hz), 136.0, 134.0, 132.8, 131.9, 130.9, 130.4, 130.3, 129.3, 129.2, 121.2 (d, J = 3.1 Hz), 114.3 (d, J = 20.5 Hz), 113.3 (d, J = 23.6 Hz), 61.9, 53.9, 50.5, 14.3. **^{19}F NMR** (377 MHz, Chloroform-*d*) δ -111.20 (dd, *J* = 7.8, 6.9 Hz). **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{21}H_{20}FN_2O_5^+$ 399.1351; Found: 399.1356.

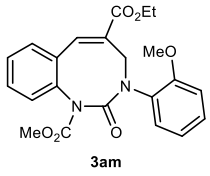
5-ethyl 1-methyl (E)-3-(3-chlorophenyl)-2-oxo-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3al)



3al

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3al** as white solid (21.1 mg, 51% yield, mp: 58-60 °C). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.61 – 7.42 (m, 4H), 7.38 – 7.25 (m, 4H), 4.86 (s, 1H), 4.50 (s, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6, 153.7, 153.6, 141.0, 141.0, 136.0, 133.9, 132.9, 132.9, 131.9, 130.9, 129.8, 129.7, 129.4, 129.3, 129.3, 129.2, 127.1, 61.9, 53.9, 50.5, 14.3. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{21}H_{20}ClN_2O_5^+$ 415.1055; Found: 415.1055.

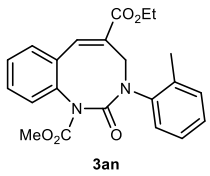
5-ethyl 1-methyl (E)-3-(2-methoxyphenyl)-2-oxo-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3am)



3am

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3am** as white solid (36.1 mg, 88% yield, mp: 99-101 °C). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.50 (ddt, *J* = 29.7, 14.5, 7.4 Hz, 4H), 7.26 (t, *J* = 8.3 Hz, 1H), 6.89 (d, *J* = 6.6 Hz, 2H), 6.82 (d, *J* = 7.4 Hz, 1H), 4.89 (s, 1H), 4.56 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 3.79 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.7, 160.1, 153.7, 153.6, 143.5, 140.7, 136.2, 134.2, 132.7, 131.7, 130.9, 129.9, 129.6, 129.1, 117.8, 113.1, 111.6, 61.7, 55.4, 53.8, 50.6, 14.2. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{23}N_2O_6^+$ 411.1551; Found: 411.1553.

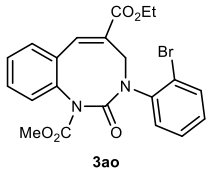
5-ethyl 1-methyl (E)-2-oxo-3-(o-tolyl)-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3an)



3an

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3an** as white solid (34.7 mg, 88% yield, mp: 164-166 ℃). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.64 (dd, J = 7.5, 1.7 Hz, 1H), 7.59 – 7.48 (m, 2H), 7.46 (dd, J = 7.7, 1.4 Hz, 1H), 7.29 – 7.17 (m, 3H), 7.08 (s, 1H), 4.48 (s, 2H), 4.21 (q, J = 7.1 Hz, 2H), 3.74 (s, 3H), 2.09 (s, 3H), 1.23 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 166.6, 153.6, 152.8, 142.1, 140.1, 136.4, 135.5, 134.2, 133.5, 131.9, 131.3, 130.9, 130.5, 129.6, 128.5, 127.4, 127.1, 61.7, 53.8, 50.5, 17.2, 14.3. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{23}N_2O_5^+$ 395.1602; Found: 395.1609.

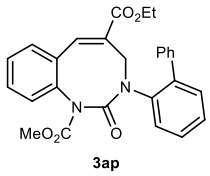
5-ethyl 1-methyl (E)-3-(2-bromophenyl)-2-oxo-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3ao)



3ao

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3ao** as white solid (34.4 mg, 75% yield, mp: 119-121 ℃). R_f = 0.3 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.84 (s, 1H), 7.67 (dd, J = 8.0, 1.2 Hz, 1H), 7.61 (dd, J = 7.4, 1.8 Hz, 1H), 7.58 (d, J = 1.8 Hz, 2H), 7.45 (ddd, J = 12.8, 7.6, 1.4 Hz, 2H), 7.36 – 7.26 (m, 2H), 4.38 (s, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.72 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 166.3, 153.6, 152.5, 142.3, 140.7, 135.9, 134.5, 133.8, 133.1, 131.6, 131.0, 130.3, 130.1, 130.0, 129.6, 129.5, 122.0, 61.7, 53.8, 50.3, 14.4. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{21}H_{20}BrN_2O_5^+$ 459.0550; Found: 459.0554.

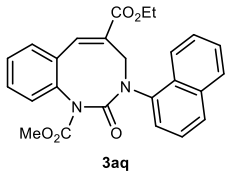
5-ethyl 1-methyl (E)-3-([1,1'-biphenyl]-2-yl)-2-oxo-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3ap)



3ap

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3ap** as white solid (41.5 mg, 91% yield, mp: 132-134 ℃). R_f = 0.3 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.55 – 7.47 (m, 2H), 7.46 (d, J = 4.1 Hz, 2H), 7.43 – 7.39 (m, 2H), 7.35 (dt, J = 5.1, 3.1 Hz, 1H), 7.28 (d, J = 7.3 Hz, 2H), 7.25 – 7.16 (m, 4H), 4.13 (q, J = 7.1 Hz, 4H), 3.68 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 166.3, 153.8, 153.5, 140.9, 139.8, 138.8, 135.9, 134.0, 133.4, 131.7, 131.2, 130.9, 129.7, 129.3, 129.0, 128.8, 128.7, 128.7, 127.8, 127.8, 61.5, 53.8, 50.6, 14.3. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{27}H_{25}N_2O_5^+$ 457.1758; Found: 457.1763.

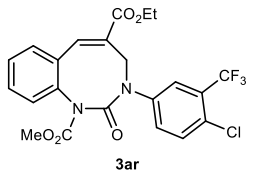
5-ethyl 1-methyl (E)-3-(naphthalen-1-yl)-2-oxo-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3aq)



3aq

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3aq** as white solid (42.6 mg, 99% yield, mp: 178-180 ℃). R_f = 0.3 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.01 – 7.96 (m, 1H), 7.93 (d, J = 8.3 Hz, 1H), 7.88 (s, 1H), 7.85 – 7.74 (m, 1H), 7.74 – 7.68 (m, 1H), 7.64 – 7.47 (m, 6H), 7.32 (d, J = 6.4 Hz, 1H), 4.65 (s, 2H), 4.14 (q, J = 7.1 Hz, 2H), 3.83 (s, 3H), 1.14 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 166.6, 153.6, 153.5, 140.1, 139.6, 137.7, 136.5, 134.7, 133.2, 132.1, 131.0, 130.6, 129.7, 129.6, 128.9, 128.8, 127.4, 126.9, 126.2, 124.9, 122.7, 61.7, 54.0, 51.1, 14.3. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{25}H_{23}N_2O_5^+$ 431.1602; Found: 431.1607.

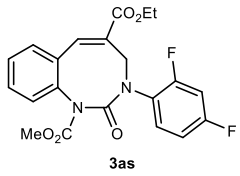
5-ethyl 1-methyl (E)-3-(4-chloro-3-(trifluoromethyl)phenyl)-2-oxo-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3ar)



3ar

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3ar** as white solid (14.9 mg, 31% yield, mp: 104-106 ℃). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.70 (s, 1H), 7.59 – 7.41 (m, 6H), 4.81 (s, 1H), 4.47 (s, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.3, 153.6, 153.5, 141.4, 141.3, 135.7, 133.6, 133.2, 132.2, 131.9, 130.8, 130.1, 129.4, 129.1, 129.0, 124.9 (q, J = 5.3 Hz), 123.7, 121.0, 62.0, 53.9, 50.2, 14.2. **^{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: 483.0924.

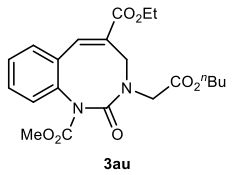
5-ethyl 1-methyl (E)-3-(2,6-difluorophenyl)-2-oxo-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3as)



3as

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3as** as white solid (31.6 mg, 76% yield, mp: 50-52 ℃). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.58 – 7.43 (m, 4H), 7.39 (td, *J* = 8.6, 6.1 Hz, 1H), 6.94 – 6.82 (m, 2H), 4.67 (s, 1H), 4.28 (q, *J* = 7.1 Hz, 3H), 3.81 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.3, 163.4 – 156.3 (m), 153.8, 153.3, 141.0, 135.7, 133.9, 132.5, 131.6, 130.6, 129.8 (dd, J = 9.9, 1.9 Hz), 129.4, 129.2, 126.8 (d, J = 4.3 Hz), 126.6 (d, J = 3.7 Hz), 111.9 (d, J = 18.7 Hz), 106.4 – 103.9 (m), 61.7, 53.9, 50.4, 14.2. **^{19}F NMR** (377 MHz, Chloroform-*d*) δ -109.07 – -109.20 (m), -115.58 (q, *J* = 8.5 Hz). **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{21}H_{19}F_2N_2O_5^+$ 417.1257; Found: 417.1257.

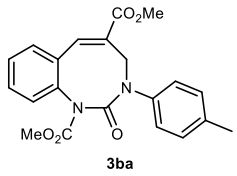
5-ethyl 1-methyl (E)-3-(2-butoxy-2-oxoethyl)-2-oxo-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3au)



3au

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3au** as colorless oil (28.4 mg, 68% yield). R_f = 0.5 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.75 (s, 1H), 7.41 (d, *J* = 13.0 Hz, 2H), 7.35 (s, 2H), 4.55 – 4.27 (m, 2H), 4.22 (q, *J* = 7.0 Hz, 2H), 4.08 – 3.83 (m, 4H), 3.70 (s, 3H), 1.47 (dt, *J* = 14.4, 6.7 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.21 (dd, *J* = 14.2, 6.6 Hz, 2H), 0.82 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.3, 166.5, 154.3, 153.8, 140.7, 135.6, 134.0, 132.5, 131.4, 130.7, 129.3, 129.1, 65.3, 61.7, 53.8, 51.8, 48.3, 30.4, 19.0, 14.2, 13.6. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{21}H_{27}N_2O_7^+$ 419.1813; Found: 419.1811.

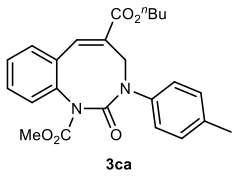
dimethyl (E)-2-oxo-3-(p-tolyl)-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3ba)



3ba

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3ba** as white solid (34.2 mg, 90% yield, mp: 165-167 ℃). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.70 – 7.47 (m, 4H), 7.26 (s, 4H), 4.99 (s, 1H), 4.64 (s, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.3, 153.8, 153.7, 140.9, 139.8, 137.3, 136.4, 134.4, 132.5, 131.9, 131.0, 129.9, 129.3, 129.1, 125.5, 53.8, 52.7, 50.8, 21.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{21}H_{21}N_2O_5^+$ 381.1445; Found: 381.1450.

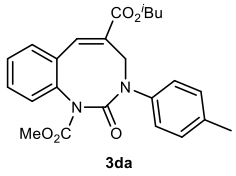
5-butyl 1-methyl (E)-2-oxo-3-(p-tolyl)-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3ca)



3ca

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3ca** as white solid (41.8 mg, 99% yield, mp: 220-222 °C). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.53 – 7.38 (m, 3H), 7.21 – 7.11 (m, 4H), 4.87 (s, 1H), 4.52 (s, 1H), 4.28 – 4.11 (m, 2H), 3.84 (s, 3H), 2.32 (s, 3H), 1.66 (p, *J* = 6.7 Hz, 2H), 1.38 (h, *J* = 7.3, 6.7 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.8, 153.8, 153.7, 140.8, 139.8, 137.2, 136.2, 134.2, 132.7, 131.8, 130.9, 129.8, 129.6, 129.1, 125.5, 65.6, 53.8, 50.7, 30.6, 21.1, 19.2, 13.7. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{24}H_{27}N_2O_5^+$ 423.1915; Found: 423.1918.

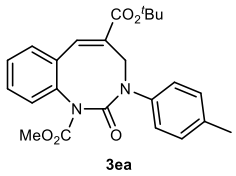
5-isobutyl 1-methyl (E)-2-oxo-3-(p-tolyl)-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3da)



3da

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3da** as white solid (41 mg, 97% yield, mp: 91-93 °C). R_f = 0.5 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.56 (dt, *J* = 7.7, 1.8 Hz, 1H), 7.46 (dddd, *J* = 16.6, 14.7, 8.3, 4.8 Hz, 3H), 7.16 (qd, *J* = 8.6, 2.1 Hz, 4H), 4.90 (d, *J* = 15.3 Hz, 1H), 4.52 (d, *J* = 13.3 Hz, 1H), 4.00 (s, 2H), 3.84 (d, *J* = 2.1 Hz, 3H), 2.32 (d, *J* = 2.1 Hz, 3H), 1.99 (ttd, *J* = 13.4, 6.5, 2.1 Hz, 1H), 0.95 (d, *J* = 2.1 Hz, 3H), 0.93 (d, *J* = 2.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.8, 153.8, 153.7, 140.9, 139.8, 137.2, 136.3, 134.3, 132.7, 131.8, 130.9, 129.8, 129.6, 129.1, 125.5, 71.8, 53.8, 50.7, 27.8, 21.1, 19.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{24}H_{27}N_2O_5^+$ 423.1915; Found: 423.1919.

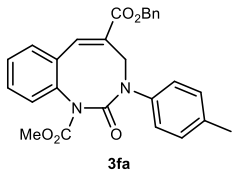
5-(tert-butyl) 1-methyl (E)-2-oxo-3-(p-tolyl)-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3ea)



3ea

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3ea** as colorless viscous oil (37.6 mg, 89% yield). R_f = 0.5 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 (s, 1H), 7.57 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.53 – 7.40 (m, 3H), 7.24 – 7.15 (m, 4H), 3.86 (s, 3H), 2.35 (s, 3H), 1.52 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8, 153.8, 153.7, 140.0, 140.0, 137.1, 136.1, 133.9, 133.1, 131.5, 131.1, 130.8, 129.8, 129.0, 125.5, 82.0, 53.8, 50.7, 28.1, 21.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{24}H_{27}N_2O_5^+$ 423.1915; Found: 423.1922.

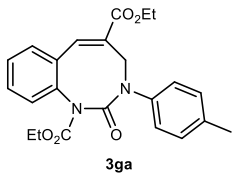
5-benzyl 1-methyl (E)-2-oxo-3-(p-tolyl)-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3fa)



3fa

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3fa** as white solid (41.5 mg, 91% yield, mp: 153-155 °C). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7 7.96 (s, 1H), 7.59 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.56 – 7.43 (m, 3H), 7.38 (tq, *J* = 5.3, 3.2, 2.4 Hz, 5H), 7.21 – 7.13 (m, 4H), 5.36 – 5.19 (m, 2H), 4.94 (d, *J* = 16.6 Hz, 1H), 4.55 (d, *J* = 16.4 Hz, 1H), 3.85 (s, 3H), 2.35 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6, 153.8, 153.7, 141.4, 139.8, 137.2, 136.3, 135.6, 134.3, 132.7, 131.9, 131.0, 129.9, 129.3, 129.1, 128.7, 128.5, 128.3, 125.5, 67.5, 53.9, 50.7, 21.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{27}H_{25}N_2O_5^+$ 457.1758; Found: 457.1762.

diethyl (E)-2-oxo-3-(p-tolyl)-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3ga)

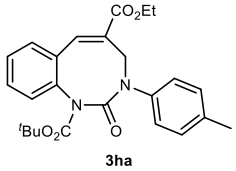


3ga

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3ga** as white solid (40.4 mg, 99% yield, mp: 111-113 °C). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.48 – 7.41 (m, 1H), 7.24 – 7.14 (m, 4H), 4.89

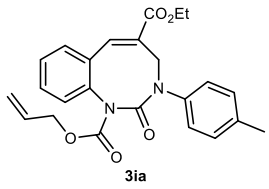
(s, 1H), 4.55 (s, 1H), 4.31 (q, *J* = 7.2 Hz, 4H), 2.35 (s, 3H), 1.35 (td, *J* = 7.1, 3.7 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.8, 153.8, 153.3, 140.9, 139.9, 137.2, 136.3, 134.2, 132.8, 131.7, 130.9, 129.9, 129.6, 129.0, 125.5, 62.9, 61.7, 50.6, 21.1, 14.5, 14.3. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{23}H_{25}N_2O_5^+$ 409.1758; Found: 409.1760.

1-(tert-butyl) 5-ethyl (E)-2-oxo-3-(p-tolyl)-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3ha)



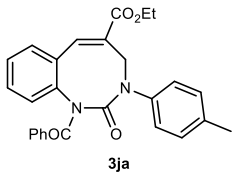
The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3ha** as white solid (31.8 mg, 73% yield, mp: 132-134 °C). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.60 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.55 – 7.46 (m, 2H), 7.45 – 7.38 (m, 1H), 7.19 (s, 4H), 4.90 (s, 1H), 4.56 (s, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 1.56 (s, 9H), 1.36 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.0, 153.9, 152.0, 141.1, 140.1, 137.1, 136.5, 134.4, 132.7, 131.7, 131.1, 129.8, 129.5, 128.7, 125.5, 82.6, 61.7, 50.3, 28.3, 21.1, 14.3. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{25}H_{29}N_2O_5^+$ 437.2071; Found: 437.2063.

1-allyl 5-ethyl (E)-2-oxo-3-(p-tolyl)-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3ia)



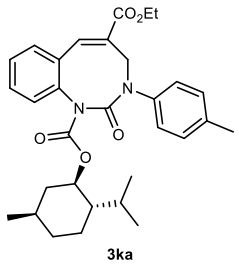
The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3ia** as white solid (35.7 mg, 85% yield, mp: 105-107 °C). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.53 – 7.35 (m, 3H), 7.27 (d, *J* = 11.7 Hz, 2H), 7.17 (t, *J* = 6.3 Hz, 4H), 5.92 (tt, *J* = 10.8, 5.3 Hz, 1H), 5.33 (d, *J* = 17.1 Hz, 1H), 5.24 (d, *J* = 10.5 Hz, 1H), 4.89 (d, *J* = 15.2 Hz, 1H), 4.73 (s, 2H), 4.50 (d, *J* = 15.4 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 2.32 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.8, 153.6, 153.0, 140.8, 139.9, 137.2, 136.2, 134.2, 132.8, 131.8, 131.8, 130.9, 129.9, 129.6, 129.0, 125.5, 118.3, 67.1, 61.7, 50.6, 21.1, 14.3. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{24}H_{25}N_2O_5^+$ 421.1758; Found: 421.1762.

ethyl (E)-1-benzoyl-2-oxo-3-(p-tolyl)-1,2,3,4-tetrahydrobenzo[d][1,3]diazocine-5-carboxylate (3ja)



The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3ja** as white solid (30.8 mg, 70% yield, mp: 141-143 °C). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.02 (s, 1H), 7.52 (t, *J* = 7.7 Hz, 3H), 7.48 – 7.36 (m, 4H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.21 – 7.11 (m, 4H), 4.81 (d, *J* = 14.2 Hz, 1H), 4.34 (q, *J* = 7.0 Hz, 3H), 2.31 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.9, 166.5, 154.6, 141.5, 140.5, 137.2, 136.7, 134.3, 134.0, 132.3, 131.6, 131.4, 131.3, 130.4, 129.9, 129.2, 128.2, 128.1, 125.7, 61.9, 50.6, 21.0, 14.3. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{27}H_{25}N_2O_4^+$ 441.1809; Found: 441.1809.

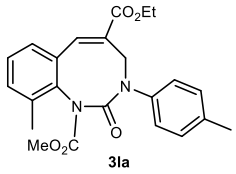
5-ethyl 1-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl) (E)-2-oxo-3-(p-tolyl)-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3ka)



The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3ka** as colorless viscous oil (49.8 mg, 96% yield). R_f = 0.4 (petroleum ether/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.47 (dd, *J* = 15.2, 7.4 Hz, 2H), 7.43 – 7.27 (m, 2H), 7.16 (s, 4H), 4.85 (d, *J* = 15.1 Hz, 1H), 4.68 (s, 1H), 4.47 (d, *J* = 15.4 Hz, 1H), 4.27 (q, *J* = 6.8 Hz, 2H), 2.32 (s, 3H), 2.20 (d, *J* = 26.5 Hz, 1H), 2.01 (d, *J* = 22.5 Hz, 1H), 1.68 (d, *J* = 10.3 Hz, 2H), 1.43 – 1.23 (m, 5H), 1.06 (q, *J* = 12.4 Hz, 2H), 0.95 – 0.87 (m, 6H), 0.81 (d, *J* = 6.1 Hz, 3H). **^{13}C NMR**

(101 MHz, $CDCl_3$) δ 166.8, 153.7, 153.6, 140.1, 137.1, 136.4, 134.8, 134.1, 132.9, 131.6, 131.1, 129.8, 129.6, 129.5, 129.5, 128.8, 125.5, 120.7, 61.7, 50.4, 34.2, 31.4, 23.4, 22.0, 21.0, 20.8, 16.3, 14.2. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{31}H_{39}N_2O_5^+$ 519.2854; Found: 519.2850.

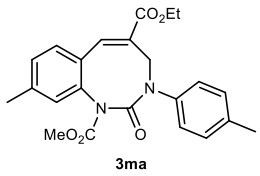
5-ethyl 1-methyl (E)-10-methyl-2-oxo-3-(p-tolyl)-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3la)



3la

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3la** as white solid (23.7 mg, 58% yield, mp: 118-120 ℃). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.46 – 7.33 (m, 2H), 7.32 – 7.28 (m, 1H), 7.25 – 7.15 (m, 4H), 4.66 (dd, *J* = 15.8, 1.0 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 4.15 (d, *J* = 15.8 Hz, 1H), 3.81 (s, 3H), 2.50 (s, 3H), 2.35 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.2, 153.6, 153.3, 141.9, 141.0, 139.8, 137.1, 135.3, 134.4, 133.2, 129.9, 129.4, 129.1, 128.9, 125.9, 61.6, 53.8, 50.4, 21.1, 18.3, 14.3. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{23}H_{25}N_2O_5^+$ 409.1758; Found: 409.1761.

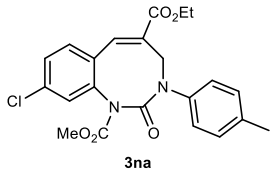
5-ethyl 1-methyl (E)-9-methyl-2-oxo-3-(p-tolyl)-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3ma)



3ma

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3ma** as white solid (40.4 mg, 99% yield, mp: 117-119 ℃). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.37 (dd, *J* = 4.8, 3.1 Hz, 2H), 7.29 – 7.20 (m, 2H), 7.15 (dd, *J* = 8.4, 5.5 Hz, 4H), 4.92 (d, *J* = 16.0 Hz, 1H), 4.60 (d, *J* = 15.3 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 2.41 (s, 3H), 2.32 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.0, 153.9, 153.7, 142.9, 140.7, 139.6, 137.1, 136.2, 134.9, 131.6, 129.9, 129.8, 129.4, 128.4, 125.4, 61.6, 53.8, 50.7, 21.3, 21.1, 14.3. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{23}H_{25}N_2O_5^+$ 409.1758; Found: 409.1764.

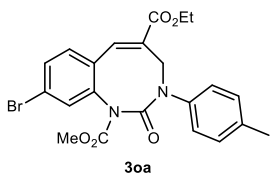
5-ethyl 1-methyl (E)-9-chloro-2-oxo-3-(p-tolyl)-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3na)



3na

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3na** as white solid (36.8 mg, 86% yield, mp: 120-122 ℃). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.64 (d, *J* = 2.0 Hz, 1H), 7.54 – 7.41 (m, 2H), 7.24 (s, 4H), 4.97 (s, 1H), 4.68 (s, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 3.94 (s, 3H), 2.40 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.7, 153.4, 153.4, 139.5, 139.3, 137.4, 137.2, 137.2, 135.5, 131.2, 130.9, 130.0, 129.9, 129.3, 125.4, 125.4, 61.9, 54.0, 50.7, 21.1, 14.2. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{22}ClN_2O_5^+$ 429.1212; Found: 429.1213.

5-ethyl 1-methyl (E)-9-bromo-2-oxo-3-(p-tolyl)-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3oa)

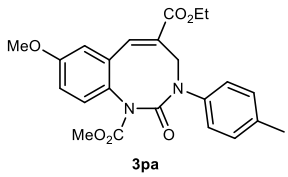


3oa

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3oa** as white solid (34.9 mg, 74% yield, mp: 73-75 ℃). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (s, 1H), 7.71 (d, *J* = 2.1 Hz, 1H), 7.55 (dt, *J* = 8.3, 1.5 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.19 – 7.12 (m, 4H), 4.88 (s, 1H), 4.58 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 2.32 (s,

3H), 1.31 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.7, 153.4, 153.4, 139.5, 139.4, 137.4, 137.2, 135.5, 134.1, 132.3, 131.3, 130.1, 129.9, 125.4, 125.3, 61.9, 54.0, 50.8, 21.1, 14.2. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{22}BrN_2O_5^+$ 473.0707; Found: 473.0700.

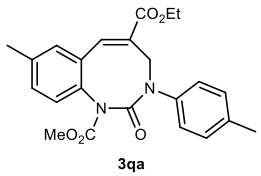
5-ethyl 1-methyl (E)-8-methoxy-2-oxo-3-(p-tolyl)-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3pa)



3pa

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3pa** as white solid (40.3 mg, 95% yield, mp: 140-142 °C). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.82 (s, 1H), 7.46 (d, *J* = 8.7 Hz, 1H), 7.22 – 7.09 (m, 4H), 7.01 (dd, *J* = 8.7, 2.9 Hz, 1H), 6.95 (d, *J* = 2.9 Hz, 1H), 4.81 (d, *J* = 16.6 Hz, 1H), 4.41 (d, *J* = 16.5 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 3.81 (s, 3H), 2.32 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6, 159.5, 154.1, 153.9, 140.8, 140.2, 137.2, 134.3, 131.8, 129.9, 129.8, 128.8, 125.6, 118.2, 116.8, 61.7, 55.7, 53.8, 50.7, 21.1, 14.3. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{23}H_{25}N_2O_6^+$ 425.1707; Found: 425.1710.

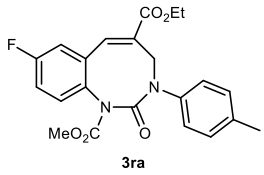
5-ethyl 1-methyl (E)-8-methyl-2-oxo-3-(p-tolyl)-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3qa)



3qa

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3qa** as white solid (37.1 mg, 91% yield, mp: 119-121 °C). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 (s, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.20 – 7.11 (m, 4H), 4.86 (d, *J* = 15.5 Hz, 1H), 4.49 (d, *J* = 15.9 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 2.39 (s, 3H), 2.32 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.8, 153.9, 153.9, 141.0, 139.9, 139.1, 137.2, 134.6, 133.7, 132.5, 132.5, 130.6, 129.8, 129.4, 125.5, 61.7, 53.8, 50.7, 21.1, 21.0, 14.3. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{23}H_{25}N_2O_5^+$ 409.1758; Found: 409.1759.

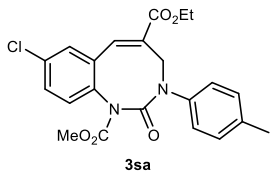
5-ethyl 1-methyl (E)-8-fluoro-2-oxo-3-(p-tolyl)-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3ra)



3ra

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3ra** as white solid (35 mg, 85% yield, mp: 139-141 °C). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 (s, 1H), 7.58 (dd, *J* = 8.7, 5.2 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 6H), 4.90 (d, *J* = 17.4 Hz, 1H), 4.50 (d, *J* = 16.9 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 2.37 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.3, 162.1 (d, J = 250.1 Hz), 153.8, 153.6, 139.9, 139.3, 137.4, 135.0 (d, J = 8.7 Hz), 132.7 (d, J = 8.7 Hz), 132.2 (d), 130.9, 129.9, 125.5, 119.8 (d, J = 23.4 Hz), 118.5 (d, J = 22.3 Hz), 61.9, 53.9, 50.8, 21.1, 14.2. **^{19}F NMR** (377 MHz, Chloroform-*d*) δ -111.90 (td, *J* = 8.7, 5.2 Hz). **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{22}FN_2O_5^+$ 413.1507; Found: 413.1510.

5-ethyl 1-methyl (E)-8-chloro-2-oxo-3-(p-tolyl)-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3sa)

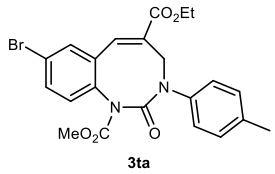


3sa

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3sa** as white solid (36.8 mg, 86% yield, mp: 151-153 °C). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.76 (s, 1H), 7.55 – 7.41 (m, 3H), 7.16 (s, 4H), 4.86 (s, 1H), 4.52 (s, 1H), 4.28 (q, *J* = 7.1 Hz, 2H),

3.84 (s, 3H), 2.32 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.4, 153.6, 153.5, 139.7, 139.1, 137.4, 134.8, 134.3, 133.5, 132.2, 131.5, 131.0, 129.9, 129.4, 125.4, 61.9, 53.9, 50.7, 21.1, 14.2. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{22}ClN_2O_5^+$ 429.1212; Found: 429.1215.

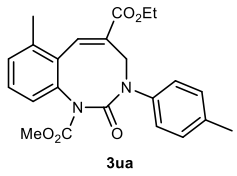
5-ethyl 1-methyl (E)-8-bromo-2-oxo-3-(p-tolyl)-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3ta)



3ta

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3ta** as white solid (34.5 mg, 73% yield, mp: 178-180 °C). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.76 (s, 1H), 7.68 – 7.55 (m, 2H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.16 (s, 4H), 4.86 (s, 1H), 4.53 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 2.32 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.4, 153.5, 153.4, 139.7, 139.0, 137.4, 136.5, 135.3, 134.6, 134.5, 132.4, 131.1, 129.9, 125.4, 122.7, 61.9, 53.9, 50.7, 21.1, 14.2. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{22}H_{22}BrN_2O_5^+$ 473.0707; Found: 473.0708.

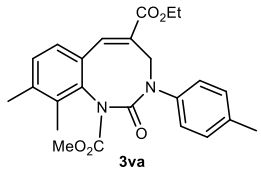
5-ethyl 1-methyl (E)-7-methyl-2-oxo-3-(p-tolyl)-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3ua)



3ua

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3ua** as white solid (18 mg, 44% yield, mp: 146-148 °C). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.46 – 7.35 (m, 2H), 7.31 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.20 (q, *J* = 8.5 Hz, 4H), 4.43 (d, *J* = 14.3 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.79 – 3.63 (m, 4H), 2.36 (s, 3H), 2.33 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 154.3, 152.6, 141.9, 141.2, 137.5, 137.1, 136.2, 135.1, 130.8, 130.5, 129.9, 129.6, 126.8, 126.2, 61.5, 53.7, 50.6, 21.1, 19.9, 14.3. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{23}H_{25}N_2O_5^+$ 409.1758; Found: 409.1759.

5-ethyl 1-methyl (E)-9,10-dimethyl-2-oxo-3-(p-tolyl)-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (3va)

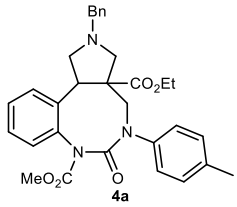


3va

The reaction was conducted on a 0.1 mmol scale according to the GP1 and afforded benzodiazocine **3va** as white solid (24.5 mg, 58% yield, mp: 114-116 °C). R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.28 – 7.12 (m, 7H), 4.67 (d, *J* = 16.1 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.21 (d, *J* = 16.0 Hz, 1H), 3.79 (s, 3H), 2.36 (d, *J* = 2.7 Hz, 6H), 2.32 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.5, 153.8, 153.6, 142.2, 141.3, 140.8, 138.5, 137.0, 134.4, 132.5, 130.4, 129.8, 129.0, 128.5, 125.8, 61.6, 53.8, 50.4, 21.1, 20.9, 14.8, 14.3. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{24}H_{27}N_2O_5^+$ 423.1915; Found: 423.1915.

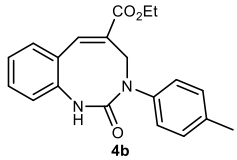
6.2. Products of derivatization

3a-ethyl 7-methyl 2-benzyl-6-oxo-5-(p-tolyl)-1,2,3,5,6,11b-hexahydro-7H-benzo[d]pyrrolo[3,4-f][1,3]diazocine-3a,7(4H)-dicarboxylate (4a)



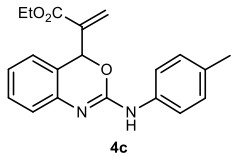
The reaction was conducted on a 0.1 mmol scale according to the corresponding procedure in section 5.2 and afforded **4a** as yellow solid (46.9 mg, 89% yield, mp: 130-132 ℃). R_f = 0.4 (petroleum ether/ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.40 (s, 4H), 7.31 (s, 4H), 7.25 (s, 1H), 7.09 (s, 2H), 6.97 (s, 2H), 4.52 (s, 1H), 4.38 (s, 2H), 3.81 (d, *J* = 3.3 Hz, 3H), 3.67 (d, *J* = 12.9 Hz, 1H), 3.51 (d, *J* = 12.9 Hz, 1H), 3.41 (d, *J* = 14.5 Hz, 1H), 3.32 (s, 1H), 3.09 (d, *J* = 9.0 Hz, 1H), 2.96 (d, *J* = 14.3 Hz, 1H), 2.84 (s, 1H), 2.29 (s, 3H), 2.16 – 2.01 (m, 1H), 1.44 – 1.30 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.0, 153.9, 153.3, 142.0, 141.0, 138.2, 137.1, 135.5, 129.8, 129.3, 128.7, 128.4, 128.4, 127.9, 127.3, 126.7, 126.2, 66.3, 62.0, 59.3, 59.1, 57.3, 56.6, 53.7, 42.7, 21.1, 14.3. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{31}H_{34}N_3O_5^+$ 528.2493; Found: 528.2494.

ethyl (E)-2-oxo-3-(p-tolyl)-1,2,3,4-tetrahydrobenzo[d][1,3]diazocine-5-carboxylate (4b)



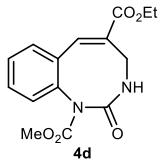
The reaction was conducted on a 0.1 mmol scale according to the corresponding procedure in section 5.2 and afforded **4b** as white solid (21.2 mg, 63% yield, mp: 163-165 ℃). R_f = 0.4 (petroleum ether/ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 9.4 Hz, 5H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.66 (s, 1H), 4.36 (s, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.33 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.9, 156.8, 142.8, 142.2, 137.4, 136.2, 133.1, 131.7, 130.5, 129.6, 129.3, 127.1, 126.8, 126.2, 61.3, 48.1, 21.1, 14.1. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{20}H_{21}N_2O_3^+$ 337.1547; Found: 337.1543.

ethyl 2-(2-(p-tolylamino)-4H-benzo[d][1,3]oxazin-4-yl)acrylate (4c)



The reaction was conducted on a 0.1 mmol scale according to the corresponding procedure in section 5.2 and afforded **4c** as colorless viscous oil (18.8 mg, 56% yield). R_f = 0.5 (petroleum ether/ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.21 (dd, *J* = 21.9, 6.9 Hz, 6H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 6.28 (s, 1H), 5.87 (s, 1H), 5.82 (s, 1H), 4.25 – 4.06 (m, 2H), 2.34 (s, 3H), 1.23 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.4, 153.8, 139.9, 138.6, 136.4, 136.0, 129.6, 128.6, 126.4, 126.3, 125.6, 122.2, 120.0, 114.1, 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: 337.1543.

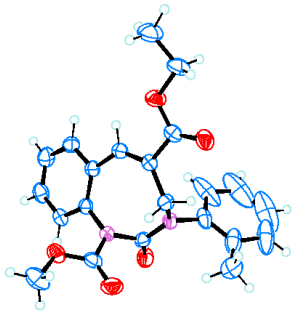
5-ethyl 1-methyl (E)-2-oxo-3,4-dihydrobenzo[d][1,3]diazocine-1,5(2H)-dicarboxylate (4d)



The reaction was conducted on a 0.1 mmol scale according to the corresponding procedure in section 5.2 and afforded **4d** as white solid (21.3 mg, 70% yield, mp: 135-137 ℃). R_f = 0.4 (petroleum ether/ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.46 (d, *J* = 12.3 Hz, 3H), 7.38 (d, *J* = 6.8 Hz, 1H), 6.38 (s, 1H), 4.29 (q, *J* = 6.8 Hz, 2H), 3.74 (s, 5H), 1.35 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8, 154.7, 153.9, 140.9, 135.4, 135.1, 130.9, 130.6, 130.5, 130.2, 129.1, 61.6, 53.8, 40.3, 14.3. **HRMS(ESI)** m/z: $[M + H]^+$ calcd for $C_{15}H_{17}N_2O_5^+$ 305.1132; Found: 305.1128.

7. X-ray Crystallographic Analysis

Cs_2CO_3 catalyzed [6+2] cycloadduct - 3an

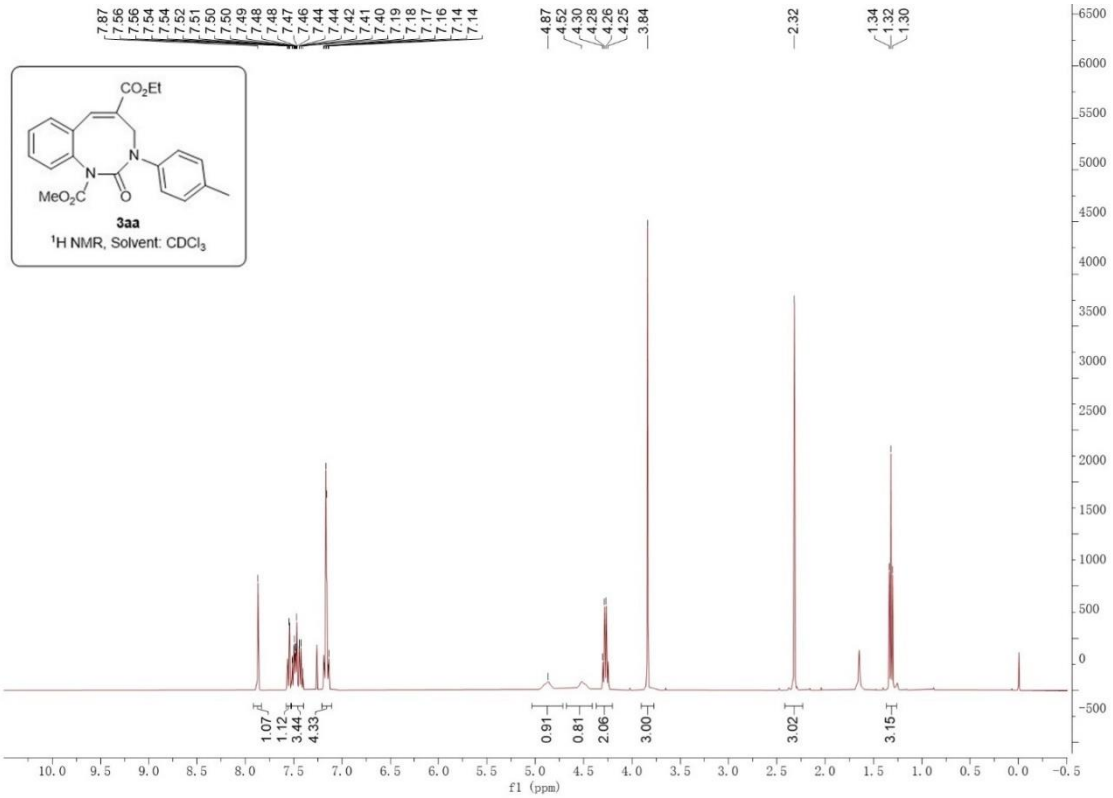


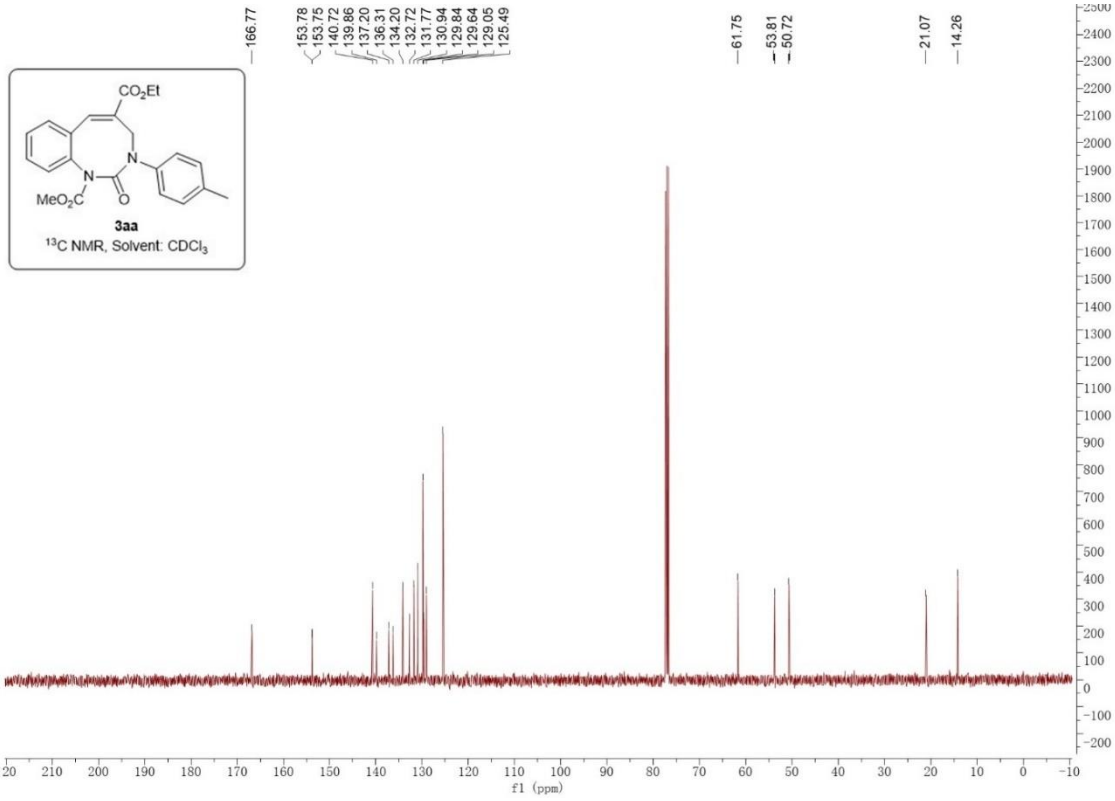
ORTEP diagram of **3an**. Thermal ellipsoids are shown at the 50% probability level. A colorless stick-shaped crystal of **3an** for X-ray diffraction was obtained by slowly volatilizing a saturated solution of 3fa in hexane/ethyl acetate (5:1). The X-ray intensity data was measured on a Rigaku 007 Saturn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

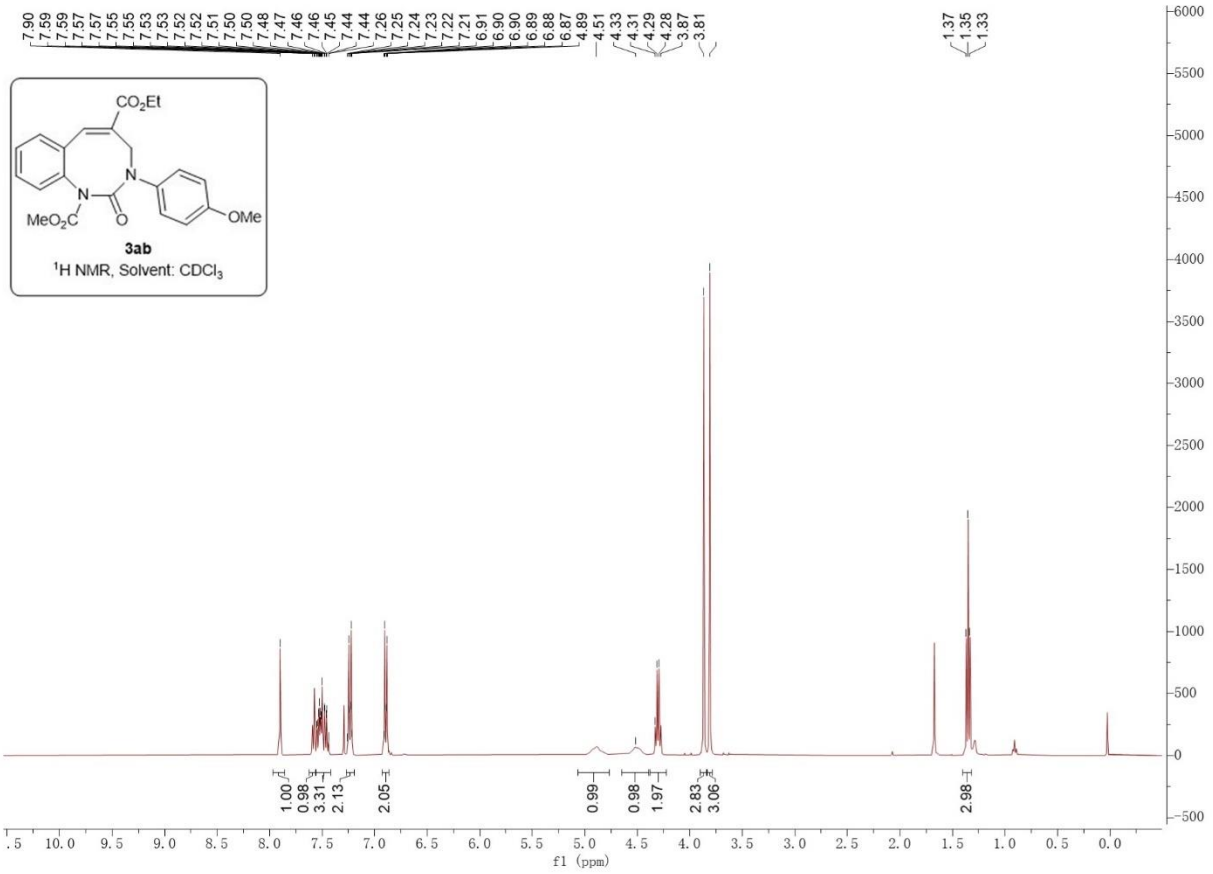
CCDC number	2023952
Identification code	**3an**
Empirical formula	$C_{22}H_{22}N_2O_5$
Formula weight	394.41
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.4099(4)
b/Å	15.0829(6)
c/Å	9.8724(3)
α/°	90
β/°	100.837(3)
γ/°	90
Volume/Å^3	1961.18(12)
Z	4
ρ_{calc}g/cm^3	1.336
μ/mm^{-1}	0.096
F(000)	832.0
Crystal size/mm^3	0.200 × 0.180 × 0.120
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.186 to 58.598
Index ranges	$-18 \le h \le 17$, $-20 \le k \le 11$, $-12 \le l \le 12$
Reflections collected	9042
Independent reflections	4514 [R_{int} = 0.0368, R_{sigma} = 0.0649]
Data/restraints/parameters	4514/0/265
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0755, wR_2 = 0.1737
Final R indexes [all data]	R_1 = 0.1208, wR_2 = 0.2089
Largest diff. peak/hole / e Å^{-3}	0.86/-0.54

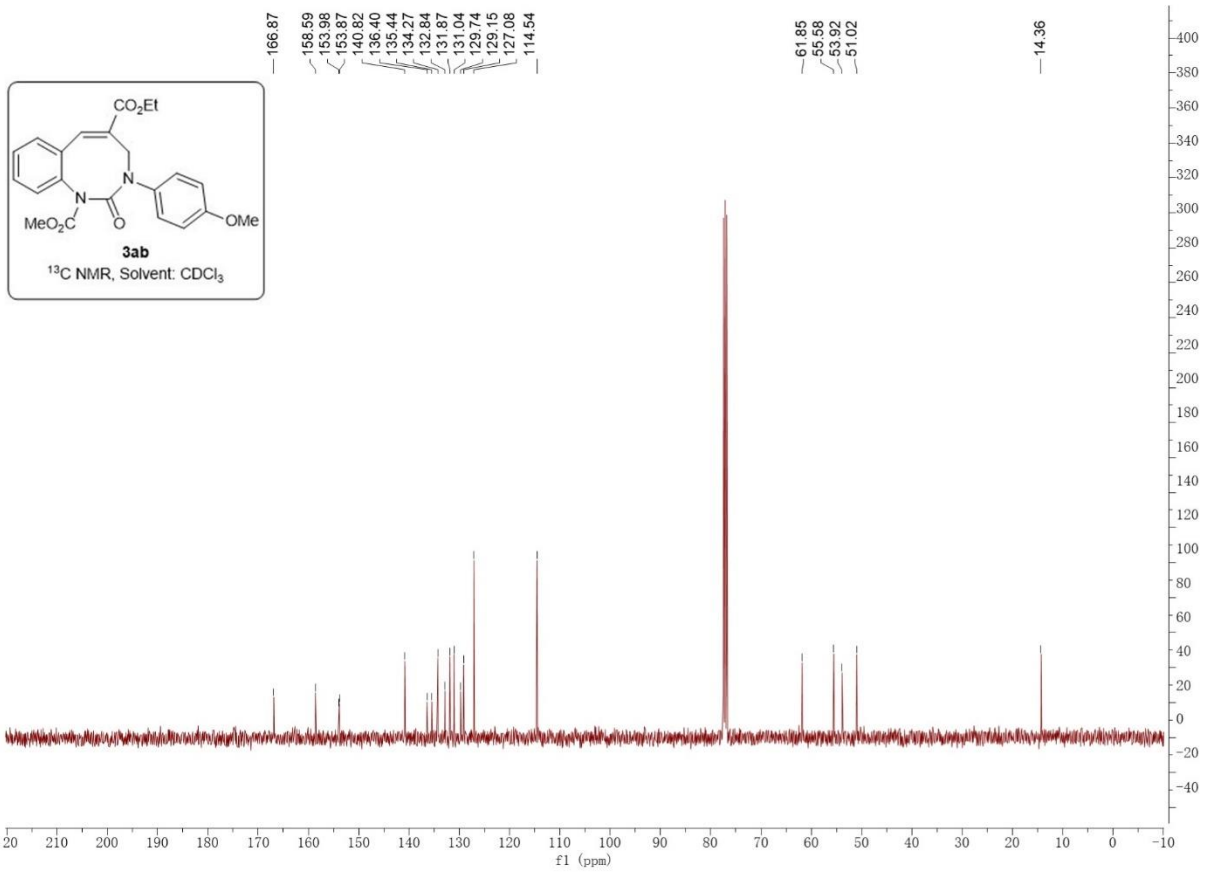
8. NMR Spectra

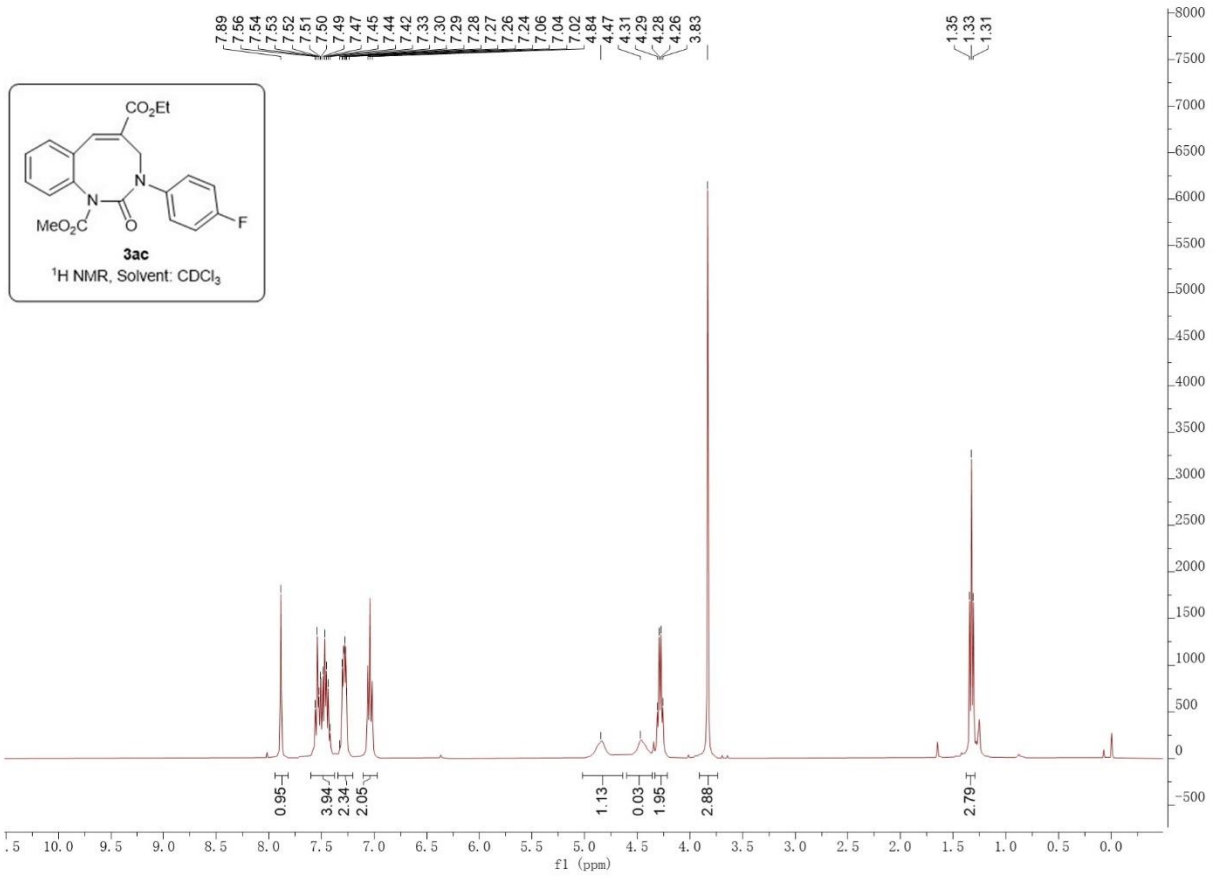
8.1. Cs_2CO_3 catalyzed [6+2] cycloadducts 3






7.90 7.59 7.59 7.57 7.57 7.55 7.55 7.53 7.53 7.52 7.52 7.51 7.50 7.50 7.48 7.47 7.46 7.46 7.45 7.44 7.44 7.26 7.25 7.24 7.23 7.22 7.21 6.91 6.90 6.90 6.89 6.88 6.87 4.89 4.51 4.33 4.31 4.29 4.28 3.87 3.81 1.37 1.35 1.33
CO2Et
N
N
MeO2C
O
OMe
3ab
1H NMR, Solvent: CDCl3
1.00 0.98 3.31 2.13 2.05 0.99 0.98 1.97 2.83 3.06 2.98
f1 (ppm)


166.87 158.59 153.98 153.87 140.82 136.40 135.44 134.27 132.84 131.87 131.04 129.74 129.15 127.08 114.54 61.85 55.58 53.92 51.02 14.36
CO2Et
N
N
MeO2C
O
OMe
3ab
13C NMR, Solvent: CDCl3
f1 (ppm)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7.44
7.42
7.33
7.30
7.29
7.28
7.27
7.26
7.24
7.06
7.04
7.02
4.84
4.47
4.31
4.29
4.28
4.26
3.83
1.35
1.33
1.31
CO2Et
N
N
MeO2C
O
F
3ac
1H NMR, Solvent: CDCl3
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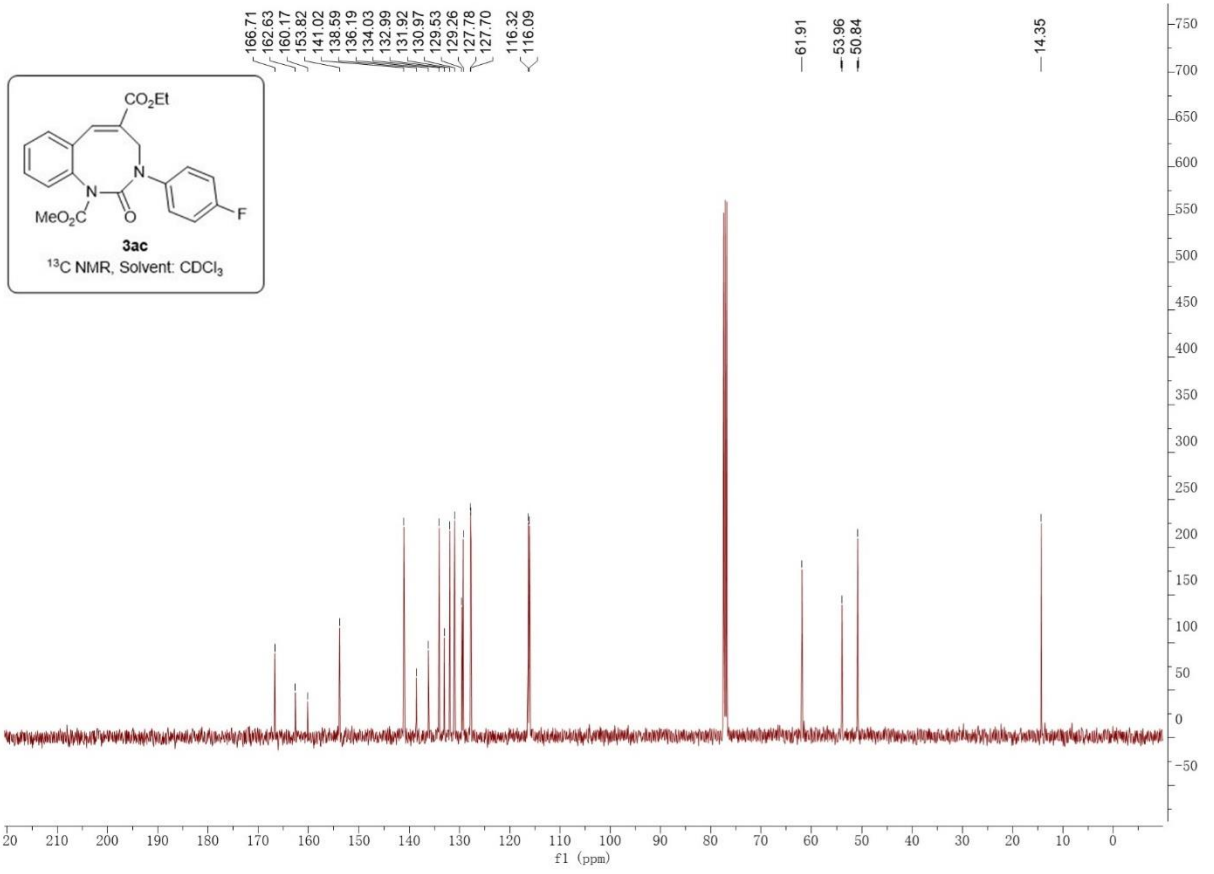
3.94
2.34
2.05
1.13
0.03
1.95
2.88
2.79
f1 (ppm)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153.82
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138.59
136.19
134.03
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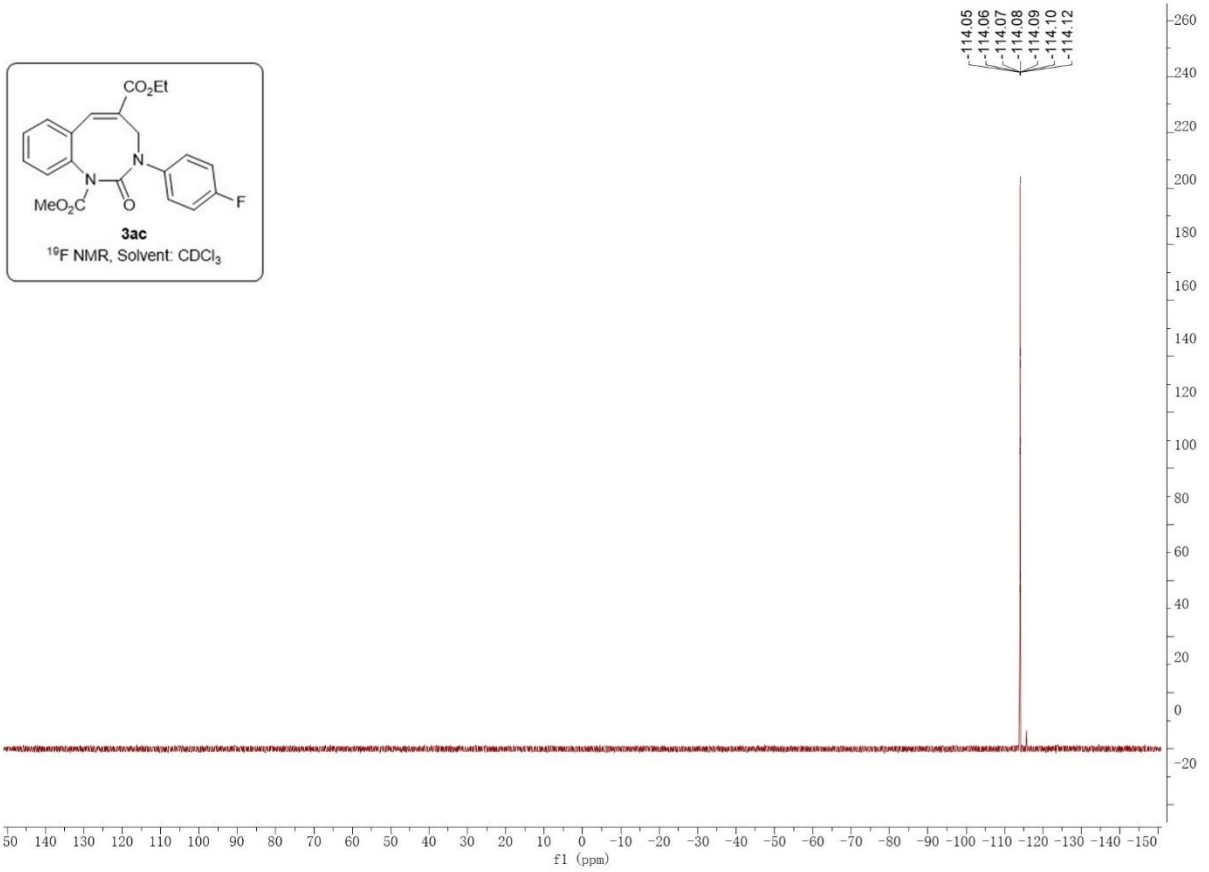
131.92
130.97
129.53
129.26
127.78
127.70
116.32
116.09
61.91
53.96
50.84
14.35
CO2Et
N
N
MeO2C
O
F
3ac
13C NMR, Solvent: CDCl3
f1 (ppm)


CO2Et
N
N
MeO2C
O
F
3ac
19F NMR, Solvent: CDCl3
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-114.06
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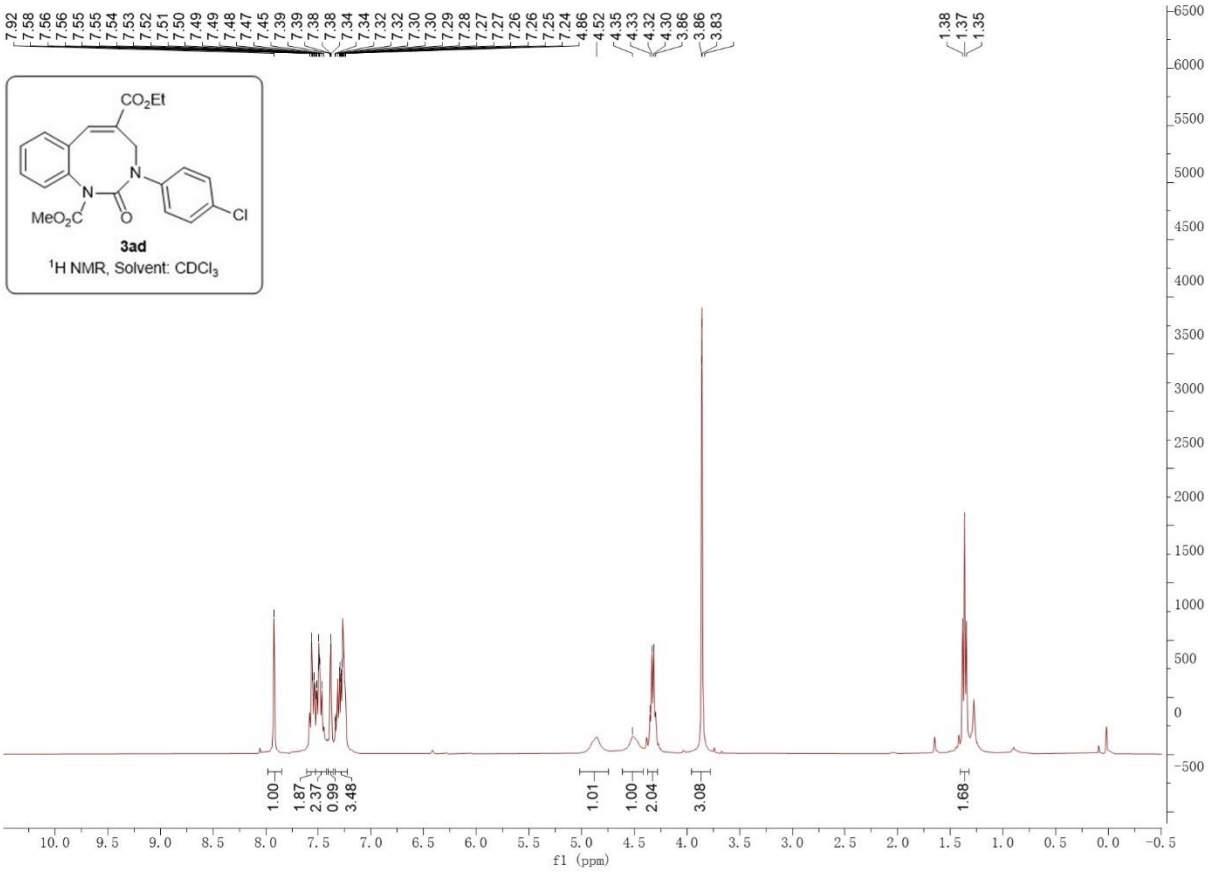
-114.09
-114.10
-114.12
f1 (ppm)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N
N
MeO2C
O
Cl
3ad
1H NMR, Solvent: CDCl3
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7.48
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4.33
4.32
4.30
3.86
3.86
3.83
1.38
1.37
1.35
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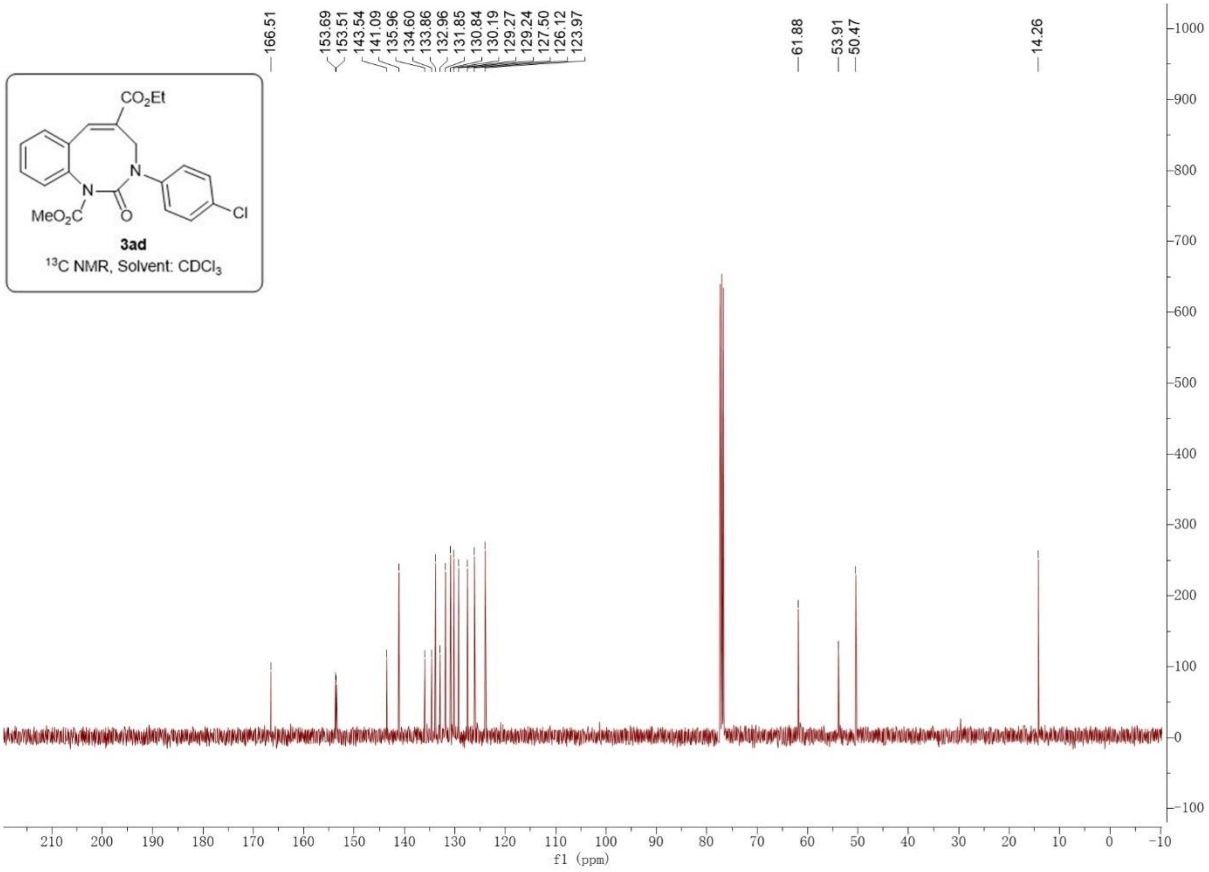
1.01
1.00
2.04
3.08
1.68
f1 (ppm)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129.27
129.24
127.50
126.12
123.97
61.88
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CO2Et
N
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MeO2C
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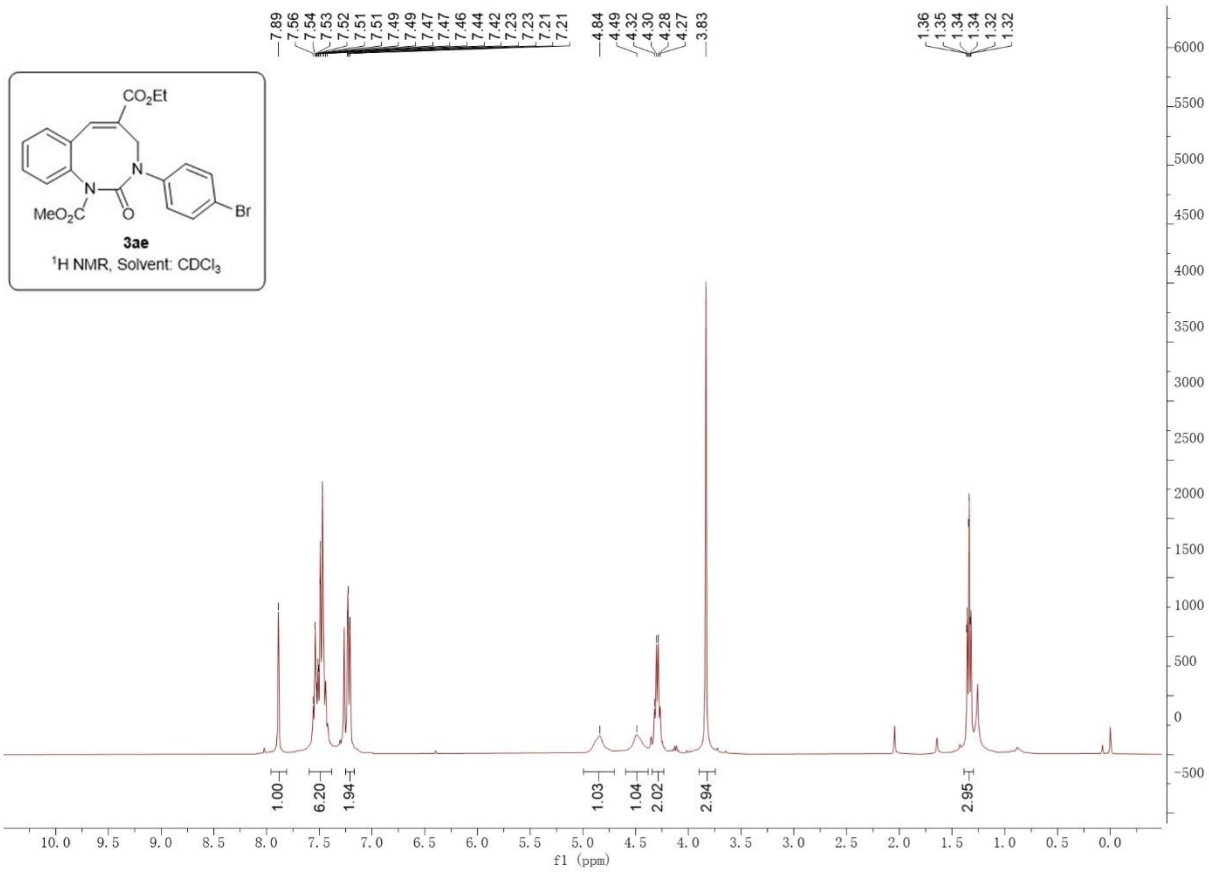
Cl
3ad
13C NMR, Solvent: CDCl3
f1 (ppm)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4.30
4.28
4.27
3.83
1.36
1.35
1.34
1.34
1.32
1.32
CO2Et
N
N
MeO2C
O
Br
3ae
1H NMR, Solvent: CDCl3
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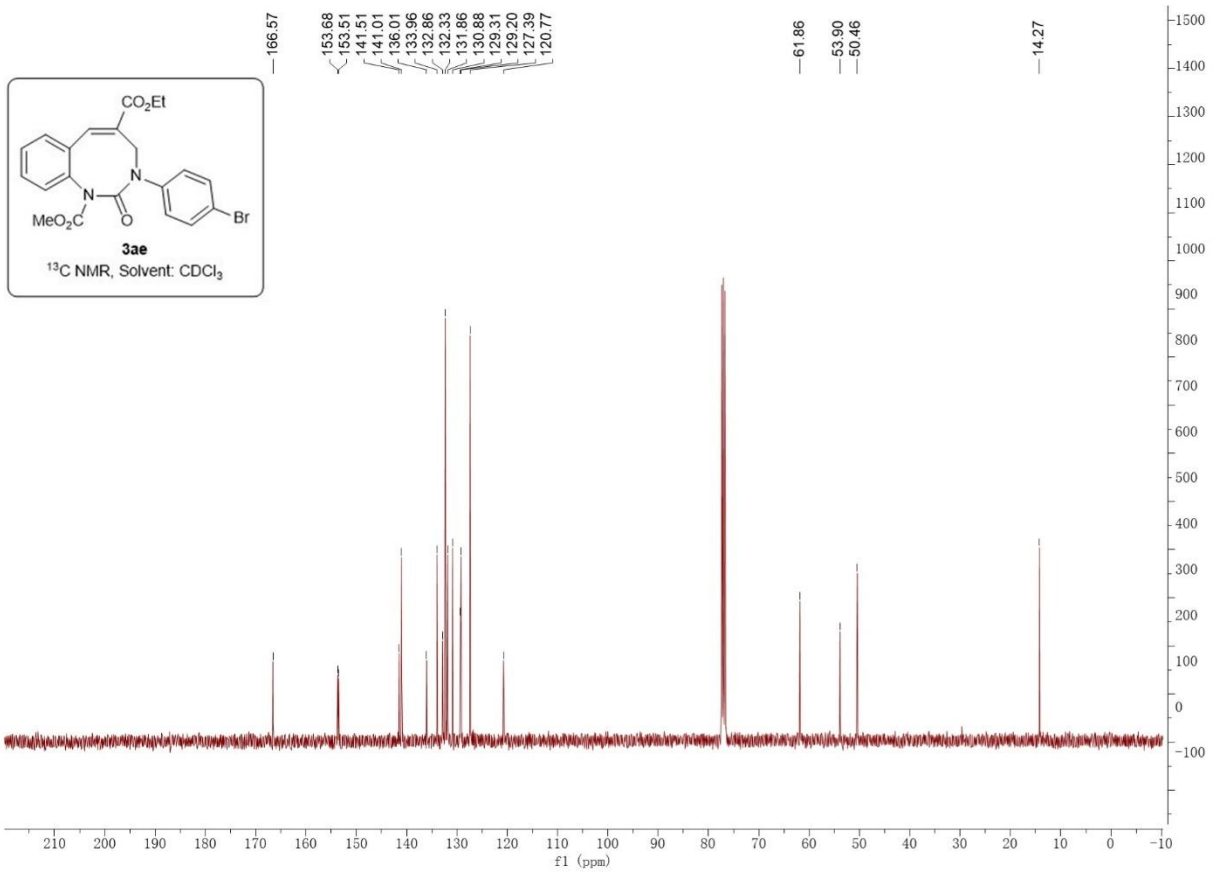
1.03
1.04
2.02
2.94
2.95
f1 (ppm)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136.01
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132.86
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131.86
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129.20
127.39
120.77
61.86
53.90
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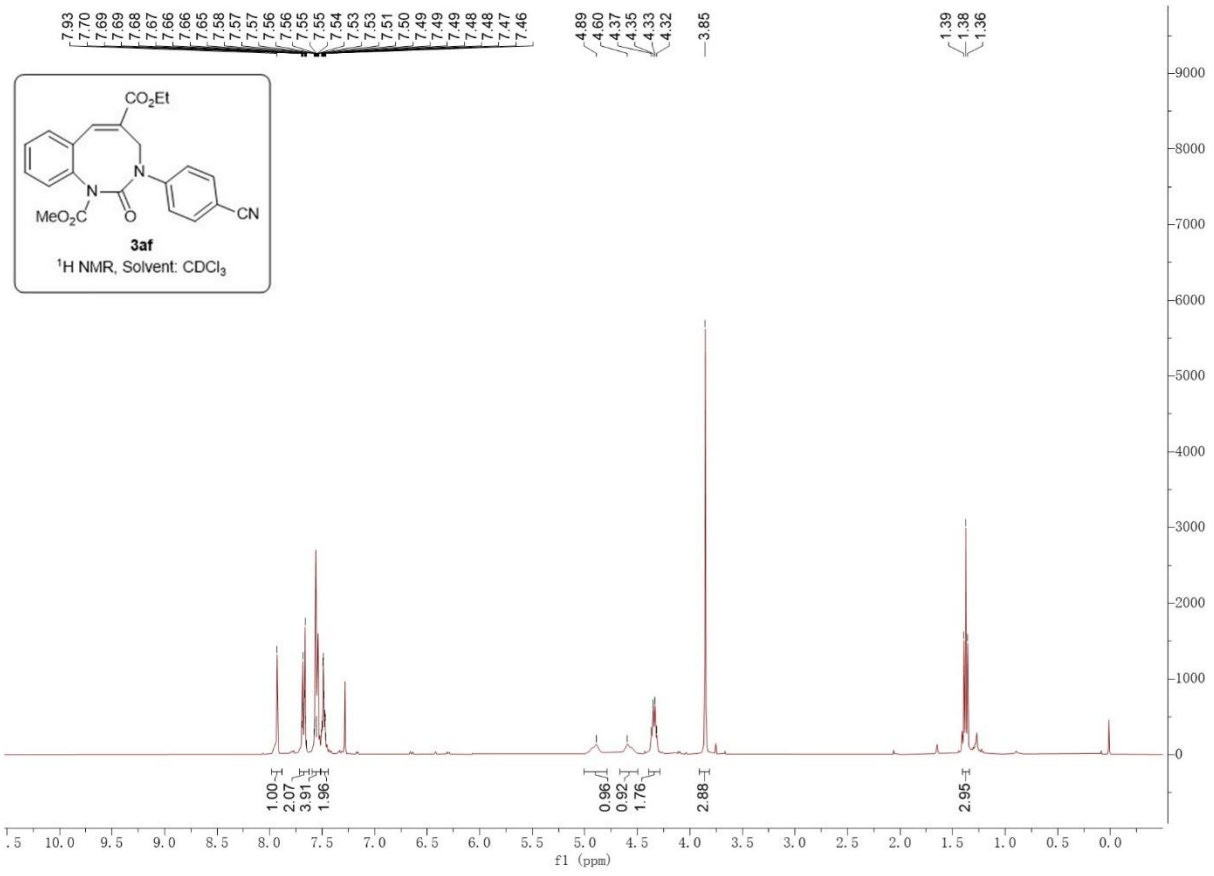
14.27
CO2Et
N
N
MeO2C
O
Br
3ae
13C NMR, Solvent: CDCl3
f1 (ppm)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N
N
MeO2C
O
CN
3af
1H NMR, Solvent: CDCl3
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0.96
0.92
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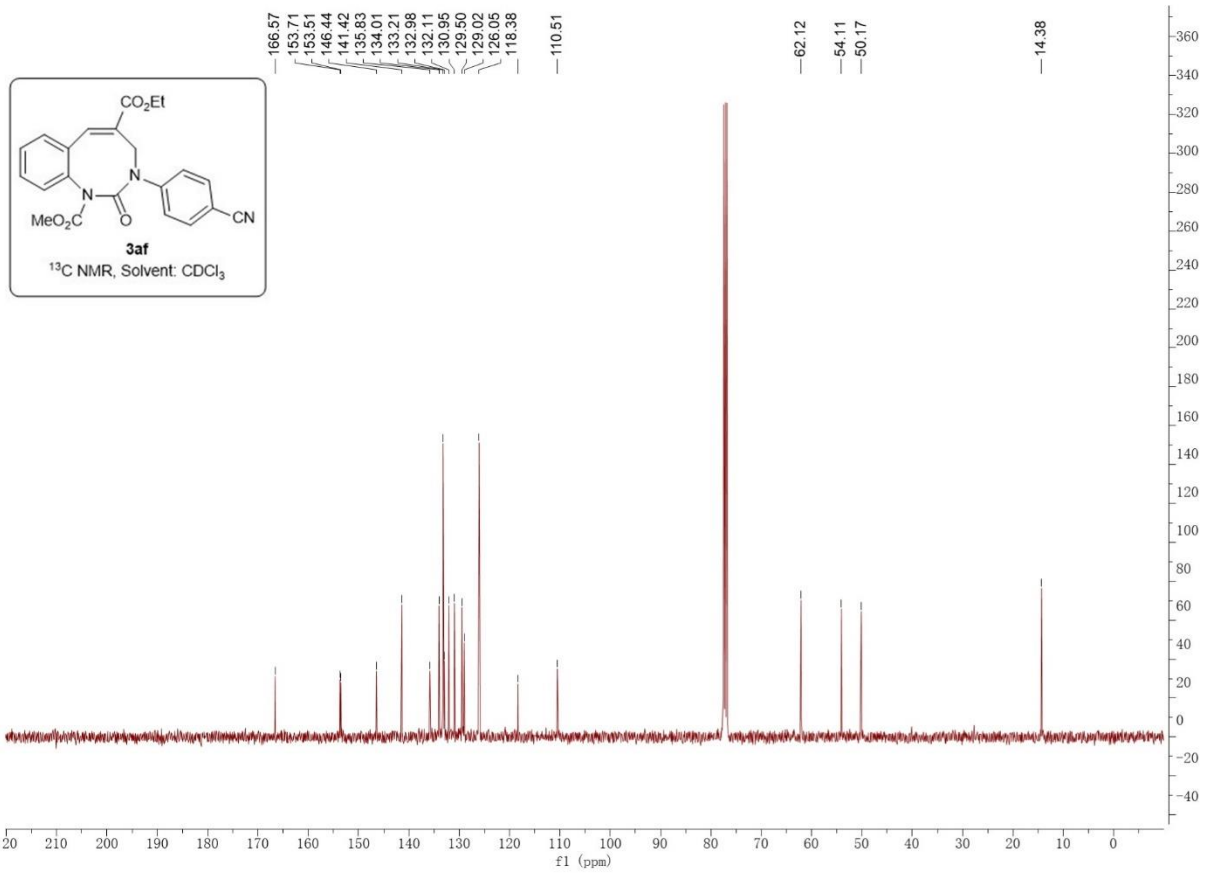
2.95
f1 (ppm)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141.42
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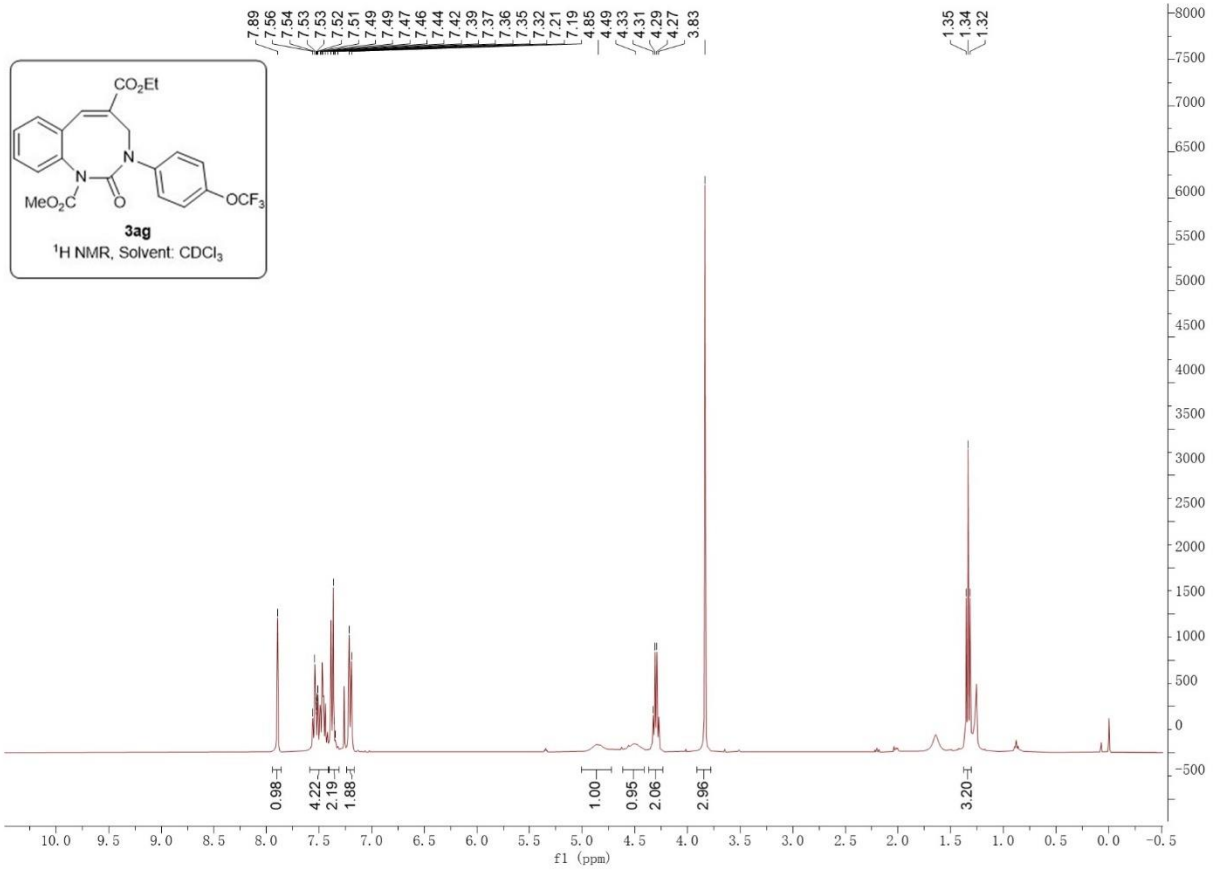
133.21
132.98
132.11
130.95
129.50
129.02
126.05
118.38
110.51
62.12
54.11
50.17
14.38
CO2Et
MeO2C
CN
3af
13C NMR, Solvent: CDCl3
f1 (ppm)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7.36
7.35
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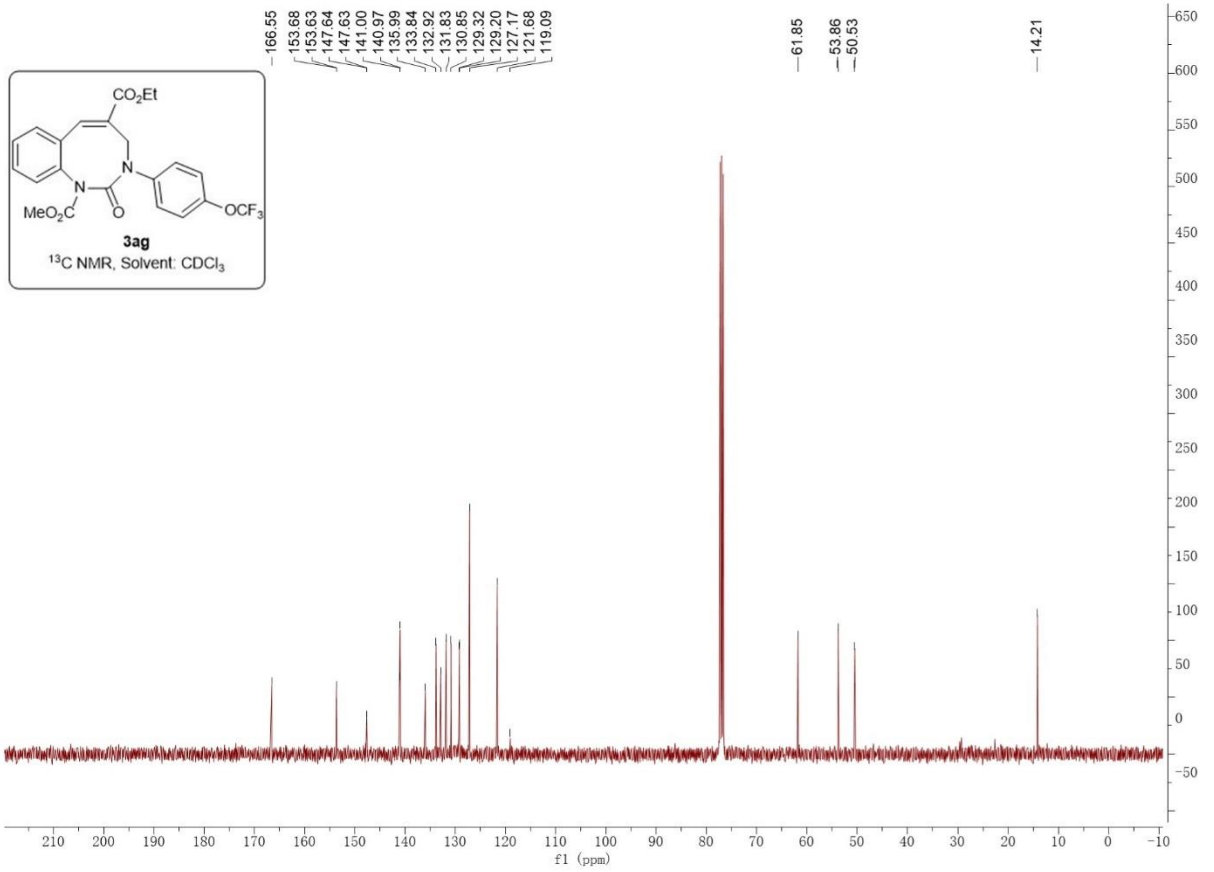
7.21
7.19
4.85
4.49
4.33
4.31
4.29
4.27
3.83
1.35
1.34
1.32
CO2Et
MeO2C
OCF3
3ag
1H NMR, Solvent: CDCl3
0.98
4.22
2.19
1.88
1.00
0.95
2.06
2.96
3.20
f1 (ppm)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153.63
147.64
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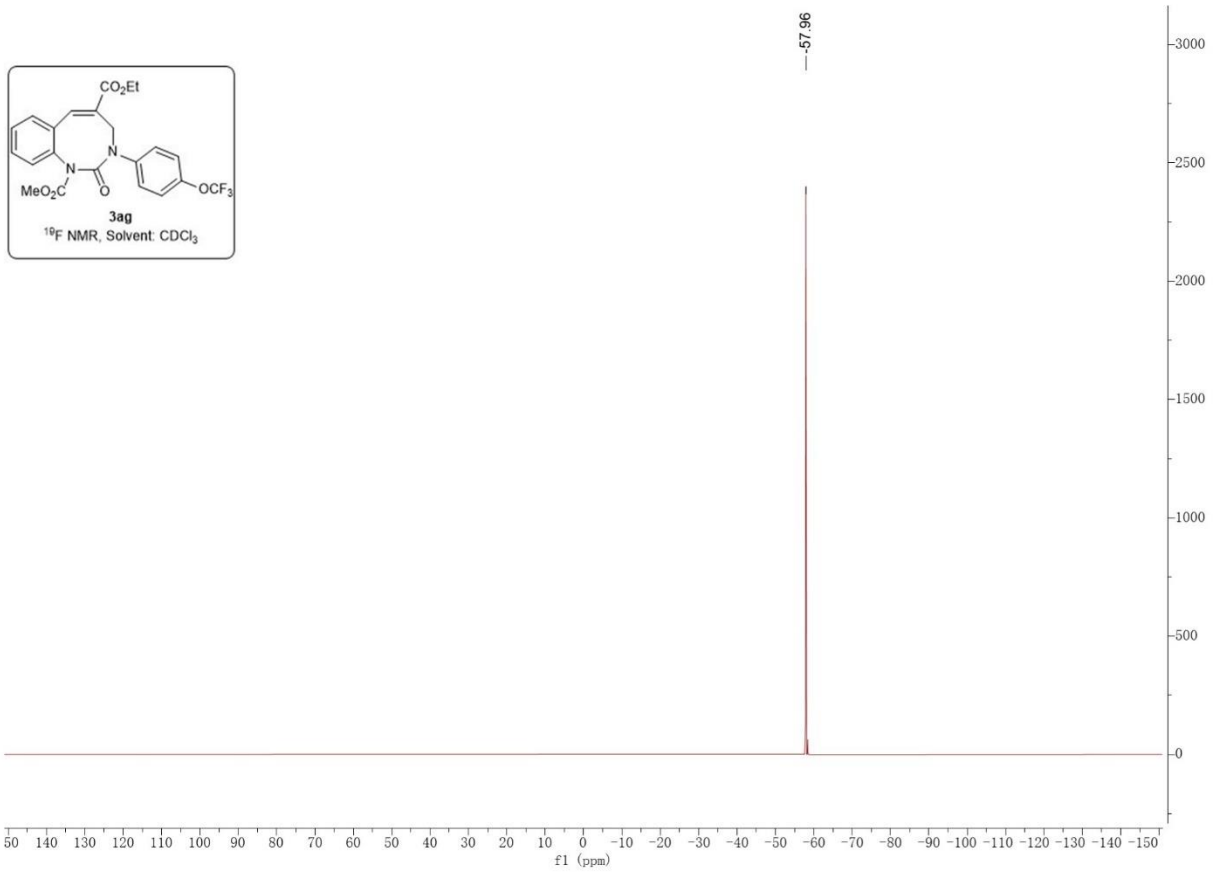
141.00
140.97
135.99
133.84
132.92
131.83
130.85
129.32
129.20
127.17
121.68
119.09
61.85
53.86
50.53
14.21
CO2Et
MeO2C
OCF3
3ag
13C NMR, Solvent: CDCl3
f1 (ppm)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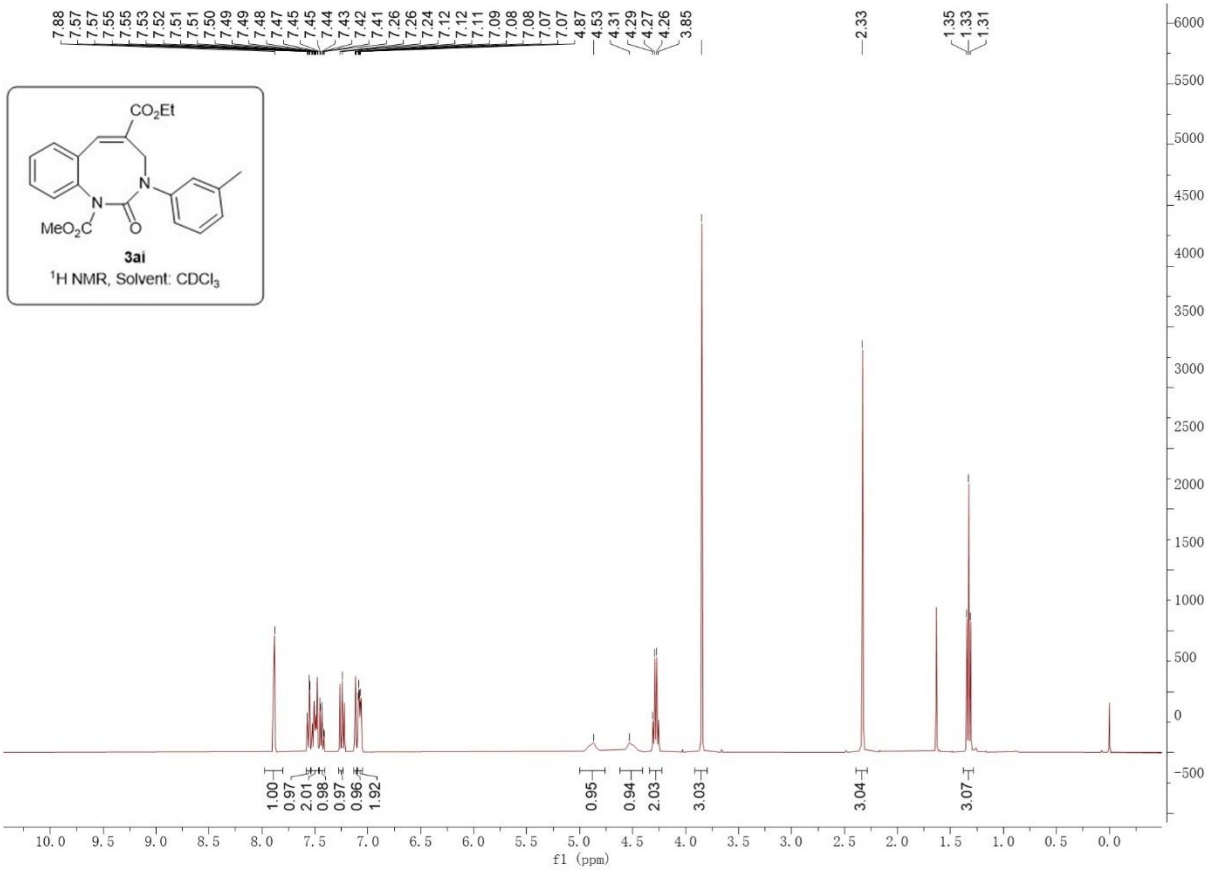
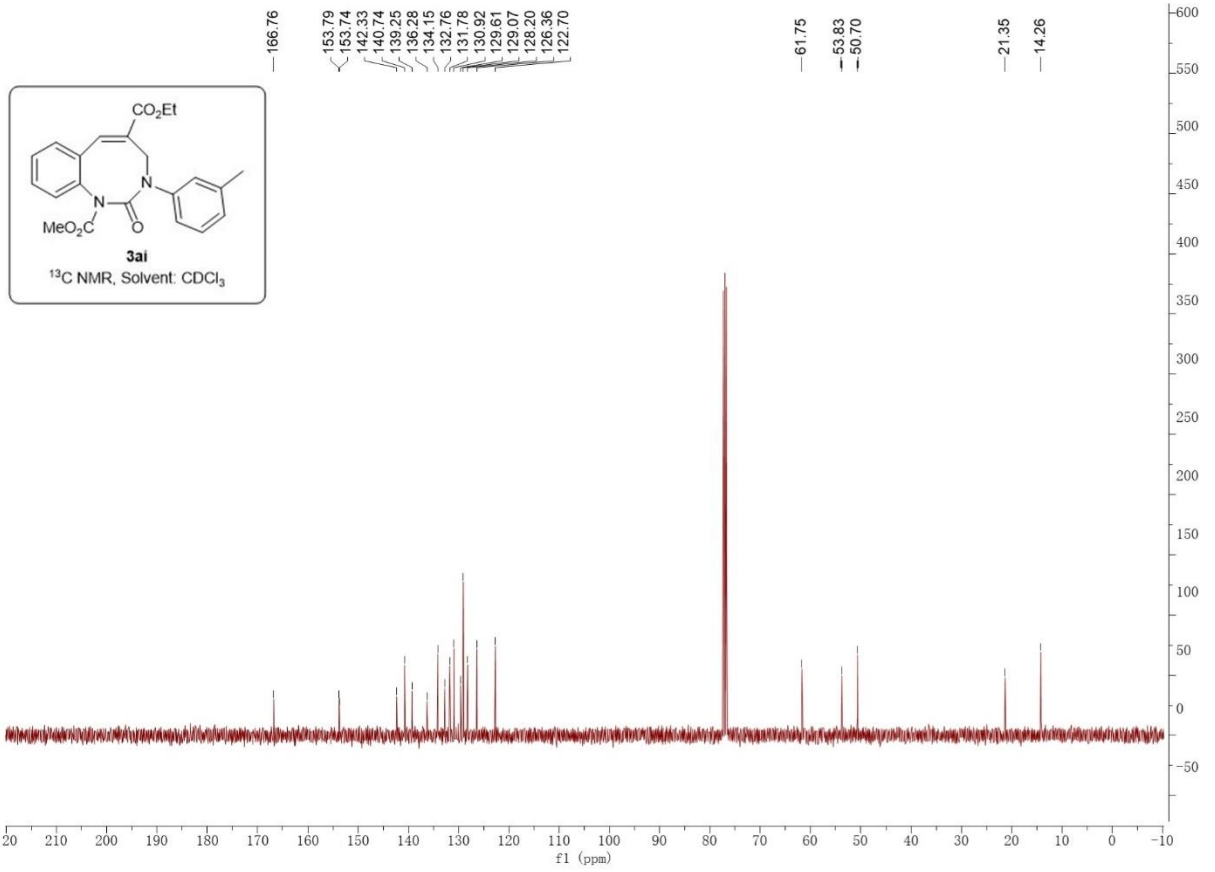
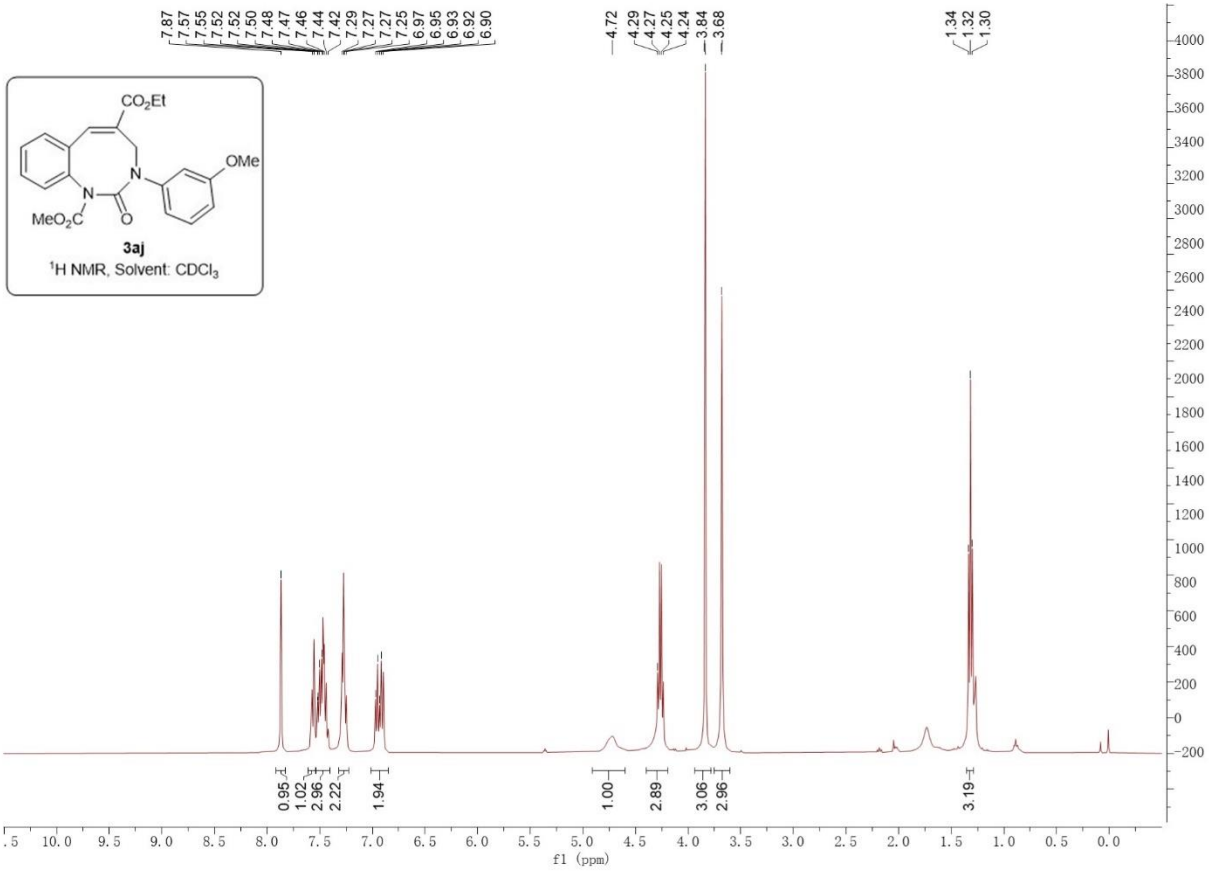
MeO2C
OCF3
3ag
19F NMR, Solvent: CDCl3
f1 (ppm)


CO2Et
MeO2C
3ai
1H NMR, Solvent: CDCl3
f1 (ppm)


CO2Et
MeO2C
3ai
13C NMR, Solvent: CDCl3
f1 (ppm)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7.47
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7.44
7.42
7.29
7.27
7.27
7.25
6.97
6.95
6.93
6.92
6.90
4.72
4.29
4.27
4.25
4.24
3.84
3.68
1.34
1.32
1.30
CO2Et
OMe
N
N
MeO2C
O
3aj
1H NMR, Solvent: CDCl3
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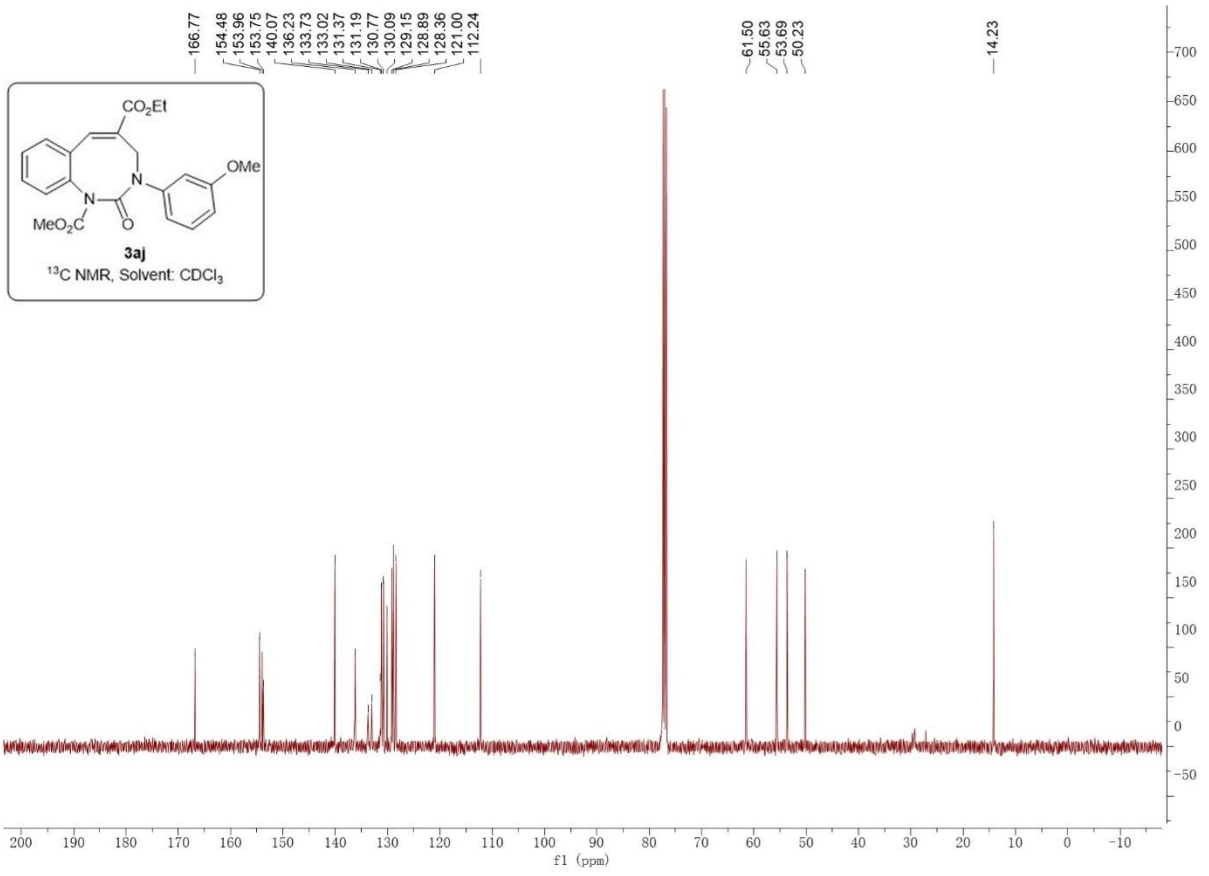
2.96
2.22
1.94
1.00
2.89
3.06
2.96
3.19
f1 (ppm)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133.02
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131.19
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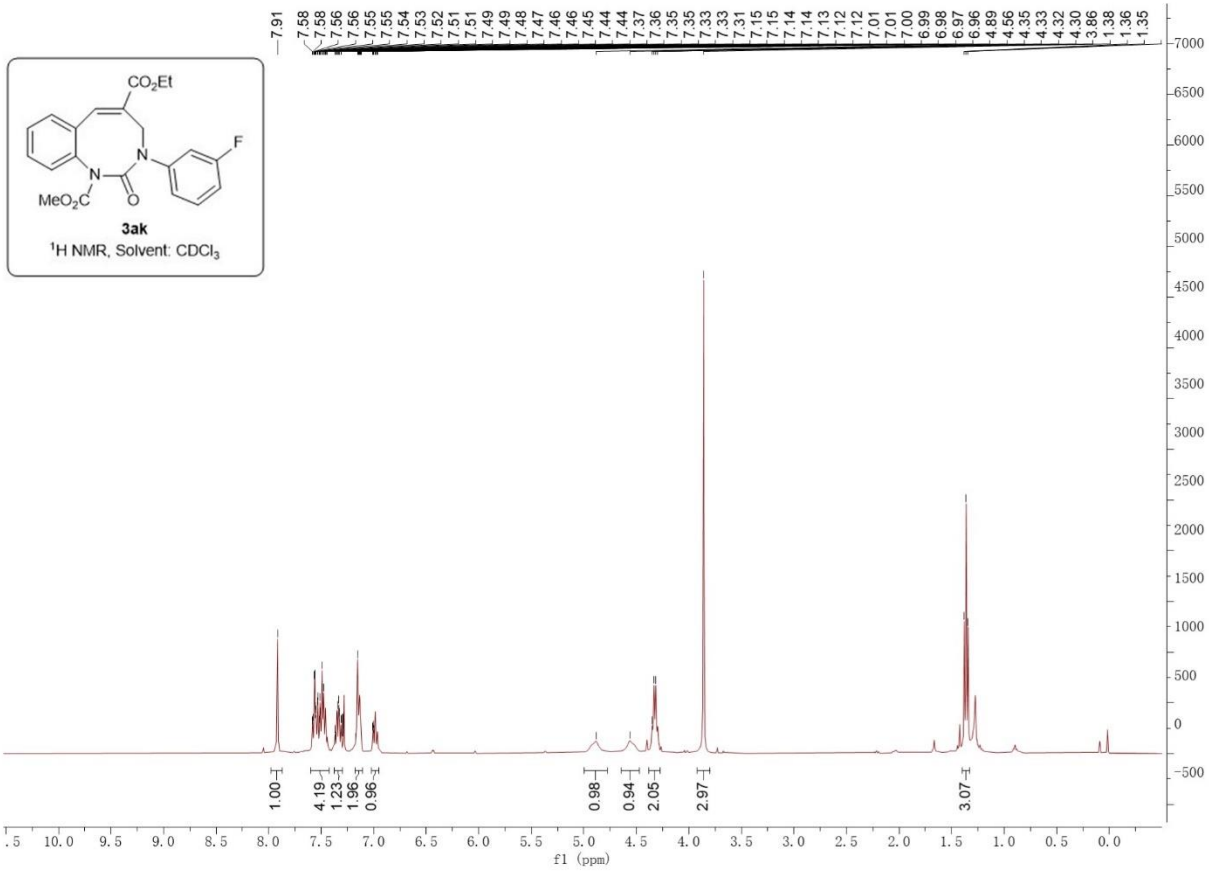
129.15
128.89
128.36
121.00
112.24
61.50
55.63
53.69
50.23
14.23
CO2Et
OMe
N
N
MeO2C
O
3aj
13C NMR, Solvent: CDCl3
f1 (ppm)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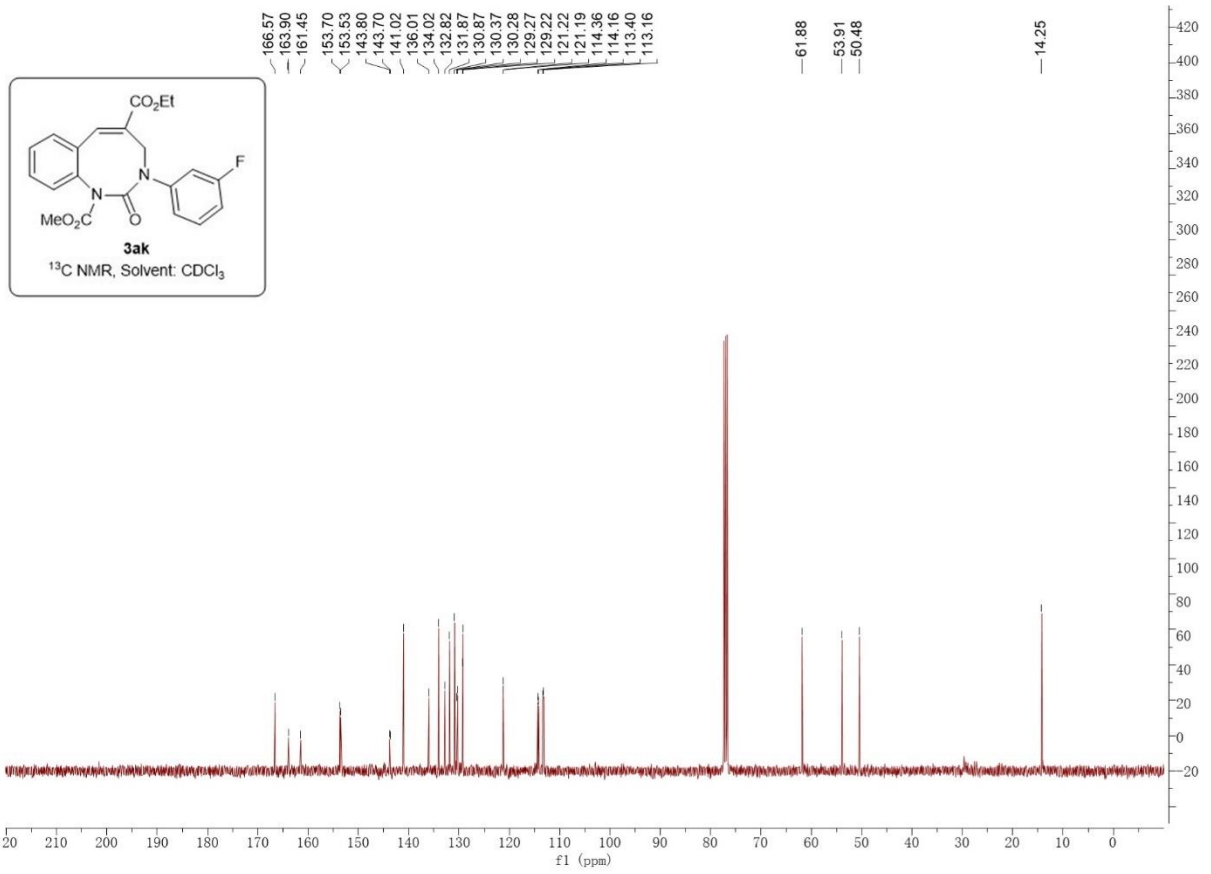
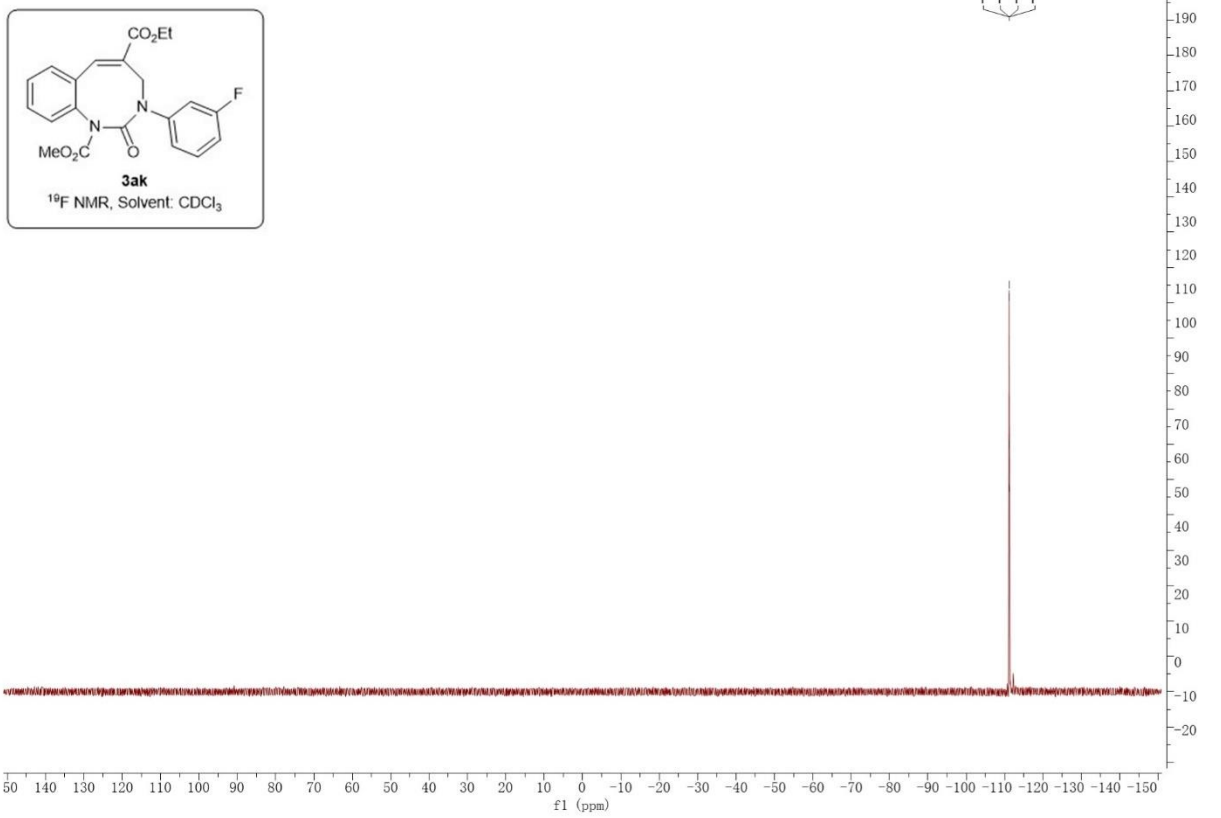
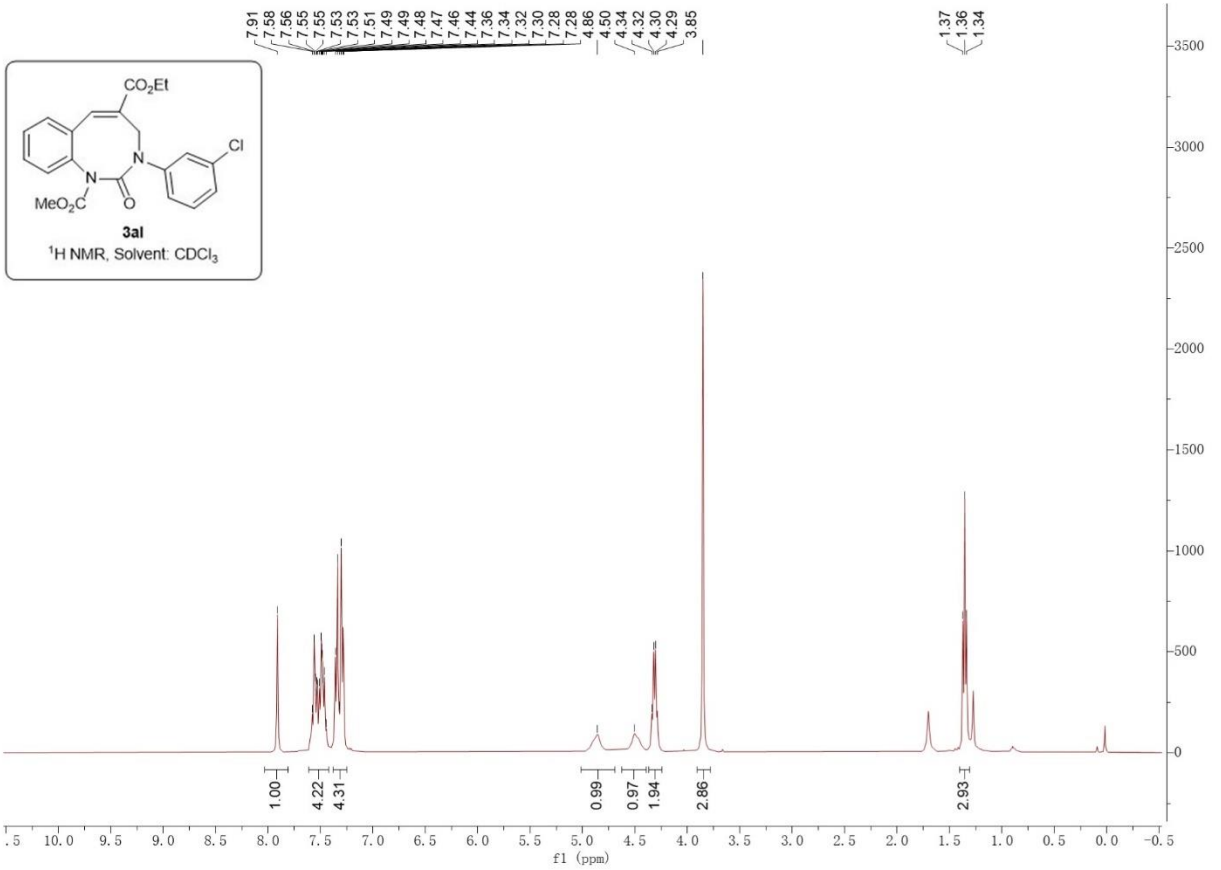
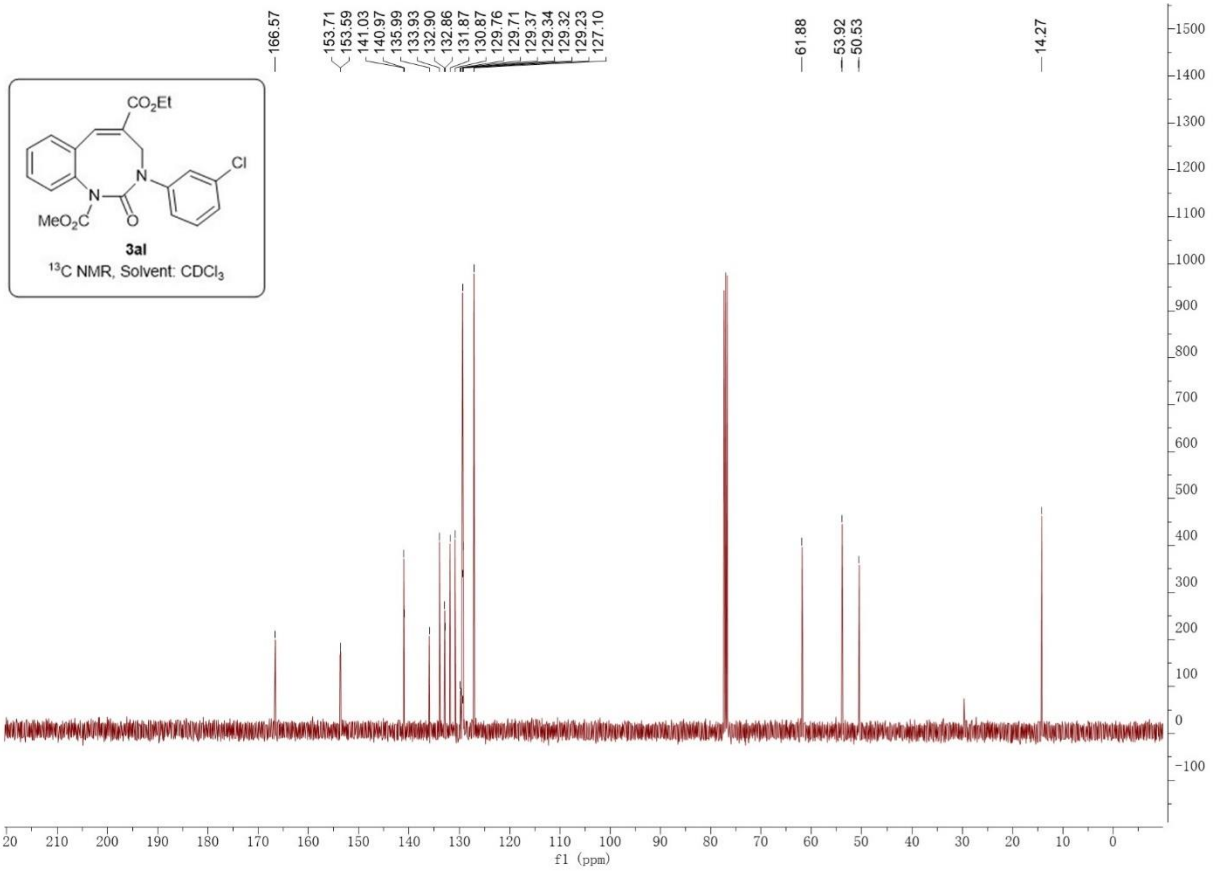
N
F
N
MeO2C
O
3ak
1H NMR, Solvent: CDCl3
f1 (ppm)


CO2Et
N
F
N
MeO2C
O
3ak
13C NMR, Solvent: CDCl3
f1 (ppm)


CO2Et
F
N
N
MeO2C
O
3ak
19F NMR, Solvent: CDCl3
-111.16
-111.19
-111.21
-111.23
f1 (ppm)


CO2Et
Cl
N
N
MeO2C
O
3al
1H NMR, Solvent: CDCl3
7.91
7.58
7.56
7.55
7.55
7.53
7.53
7.51
7.49
7.49
7.48
7.47
7.46
7.44
7.36
7.34
7.32
7.30
7.28
7.28
4.86
4.50
4.34
4.32
4.30
4.29
3.85
1.37
1.36
1.34
1.00
4.22
4.31
0.99
0.97
1.94
2.86
2.93
f1 (ppm)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140.97
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132.90
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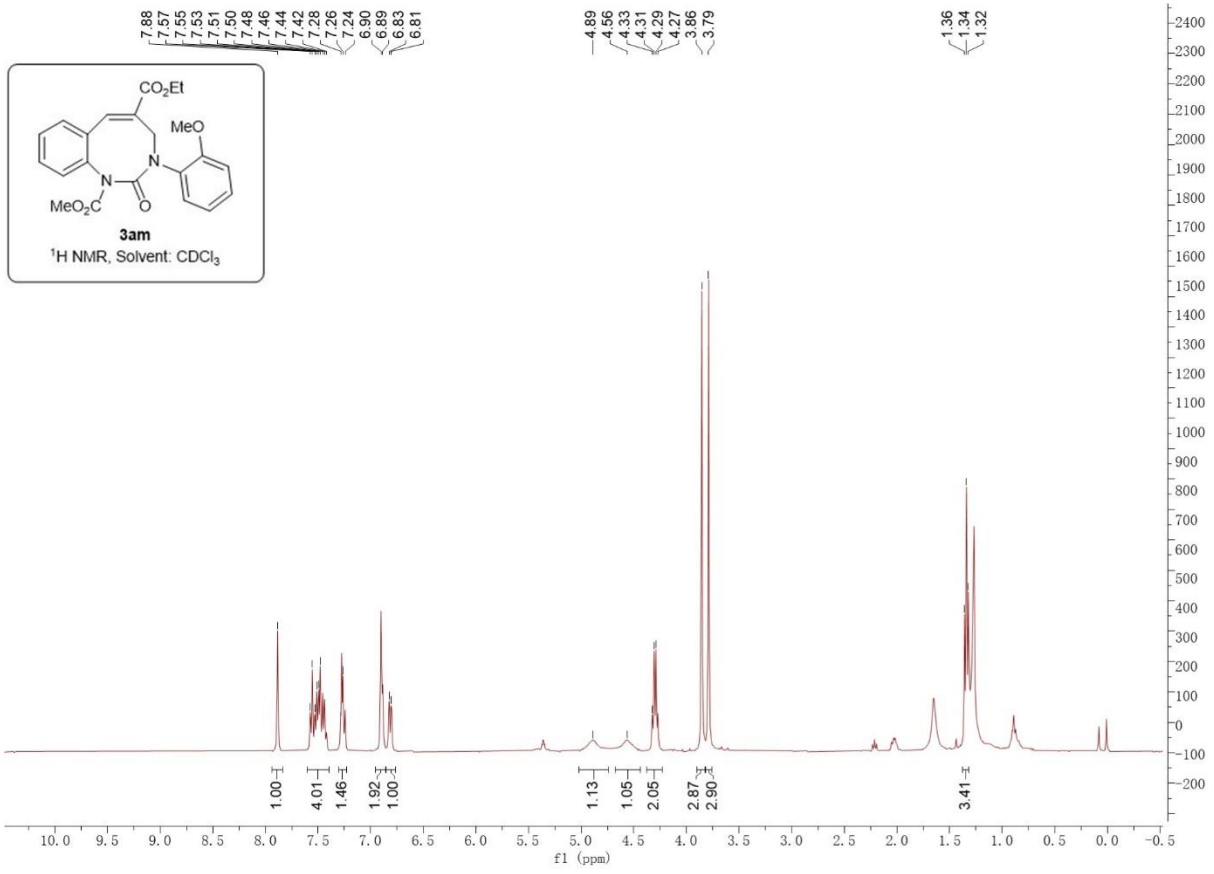
130.87
129.76
129.71
129.37
129.34
129.32
129.23
127.10
61.88
53.92
50.53
14.27
CO2Et
Cl
N
N
MeO2C
O
3al
13C NMR, Solvent: CDCl3
f1 (ppm)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7.53
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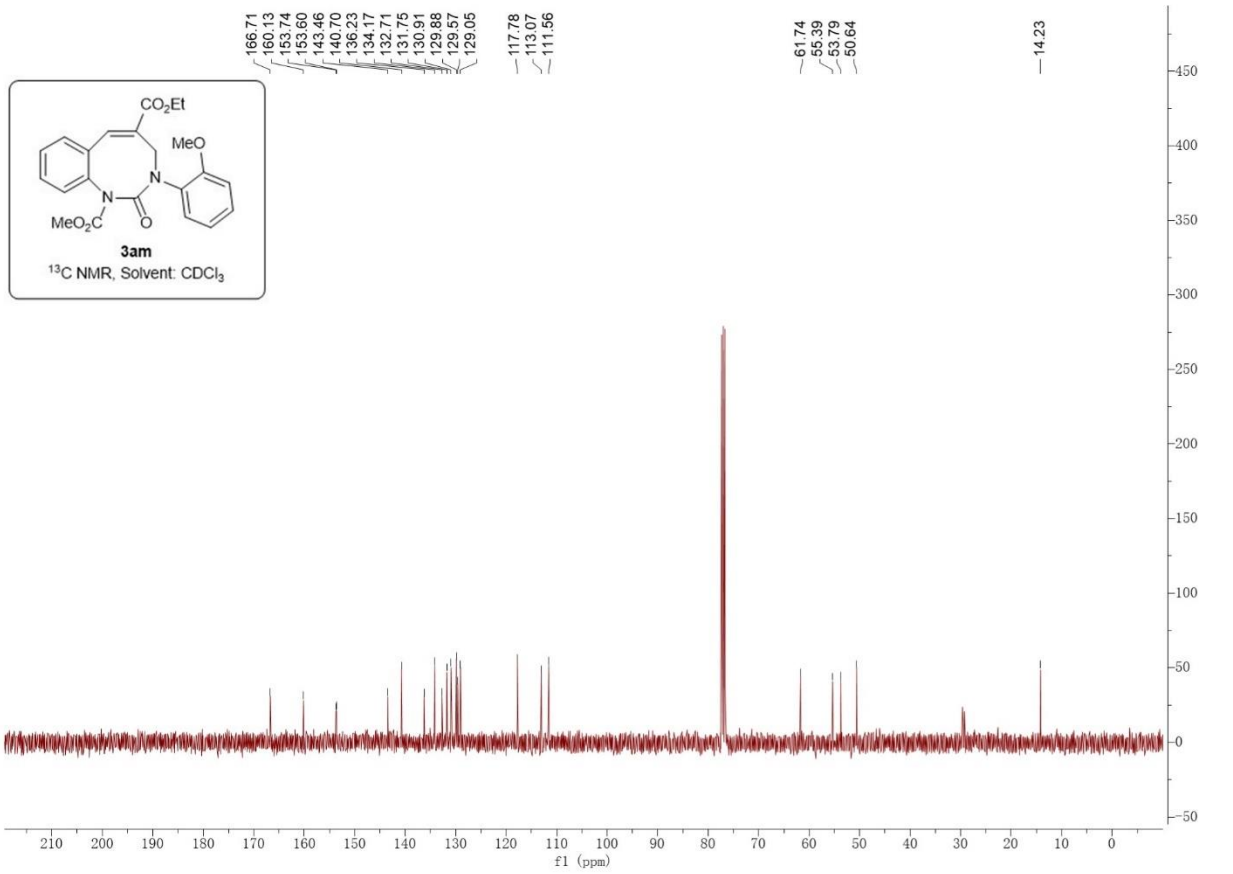
7.50
7.48
7.46
7.44
7.42
7.28
7.26
7.24
6.90
6.89
6.83
6.81
4.89
4.56
4.33
4.31
4.29
4.27
3.86
3.79
1.36
1.34
1.32
CO2Et
MeO
N
N
MeO2C
O
3am
1H NMR, Solvent: CDCl3
1.00
4.01
1.46
1.92
1.00
1.13
1.05
2.05
2.87
2.90
3.41
f1 (ppm)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153.74
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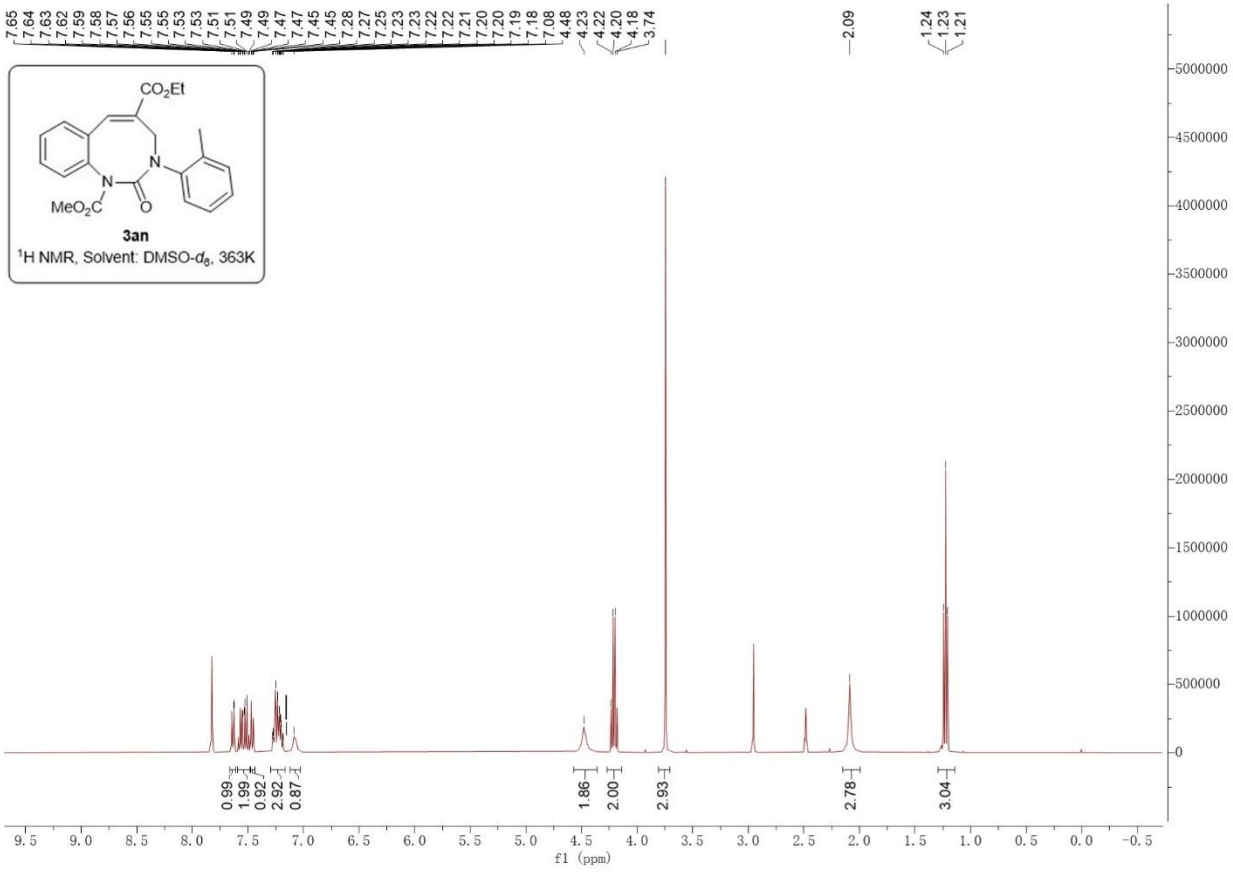
136.23
134.17
132.71
131.75
130.91
129.88
129.57
129.05
117.78
113.07
111.56
61.74
55.39
53.79
50.64
14.23
CO2Et
MeO
N
N
MeO2C
O
3am
13C NMR, Solvent: CDCl3
f1 (ppm)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7.63
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7.58
7.57
7.56
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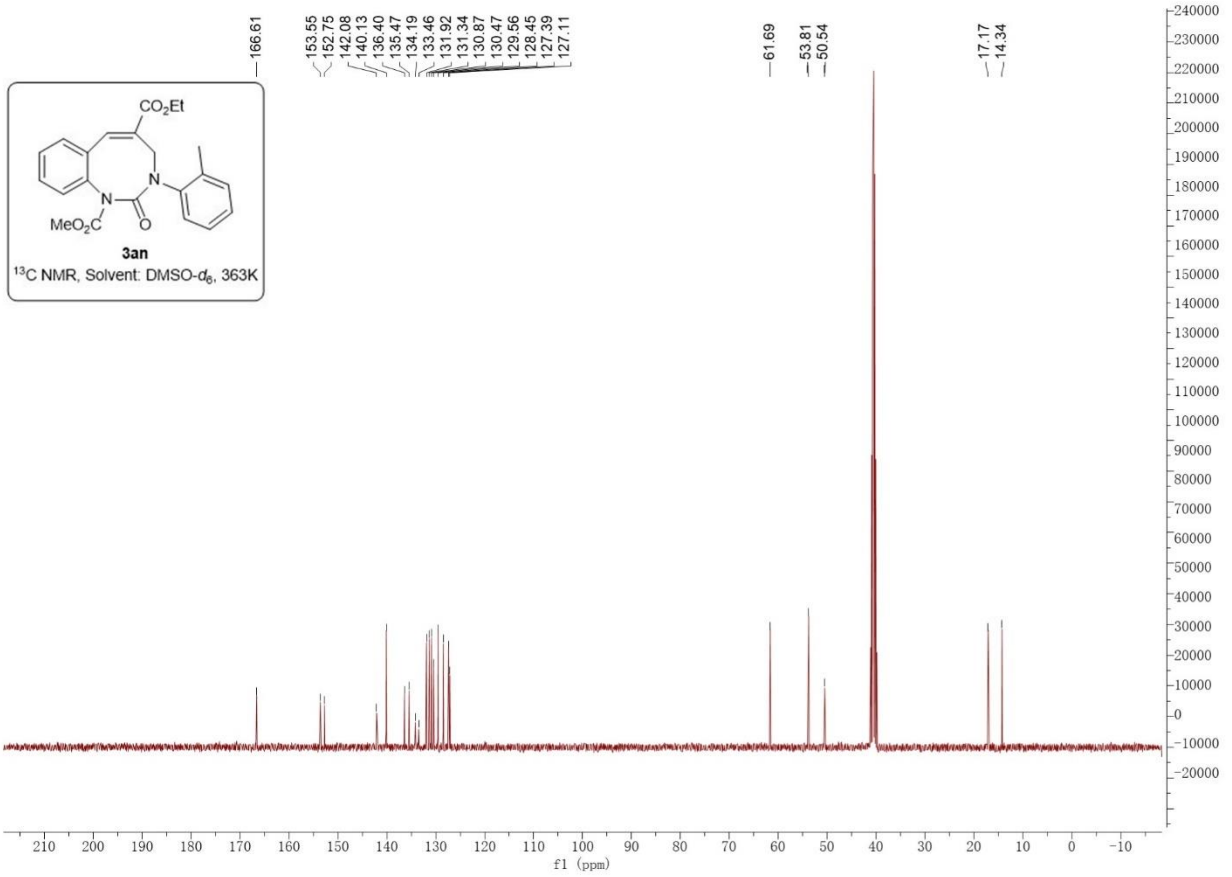
7.55
7.53
7.53
7.51
7.51
7.49
7.49
7.47
7.47
7.45
7.45
7.28
7.27
7.25
7.23
7.23
7.22
7.22
7.21
7.20
7.20
7.19
7.18
7.08
4.48
4.23
4.22
4.20
4.18
3.74
2.09
1.24
1.23
1.21
CO2Et
N
N
MeO2C
O
3an
1H NMR, Solvent: DMSO-d6, 363K
0.99
1.99
0.92
2.92
0.87
1.86
2.00
2.93
2.78
3.04
f1 (ppm)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153.55
152.75
142.08
140.13
136.40
135.47
134.19
133.46
131.92
131.34
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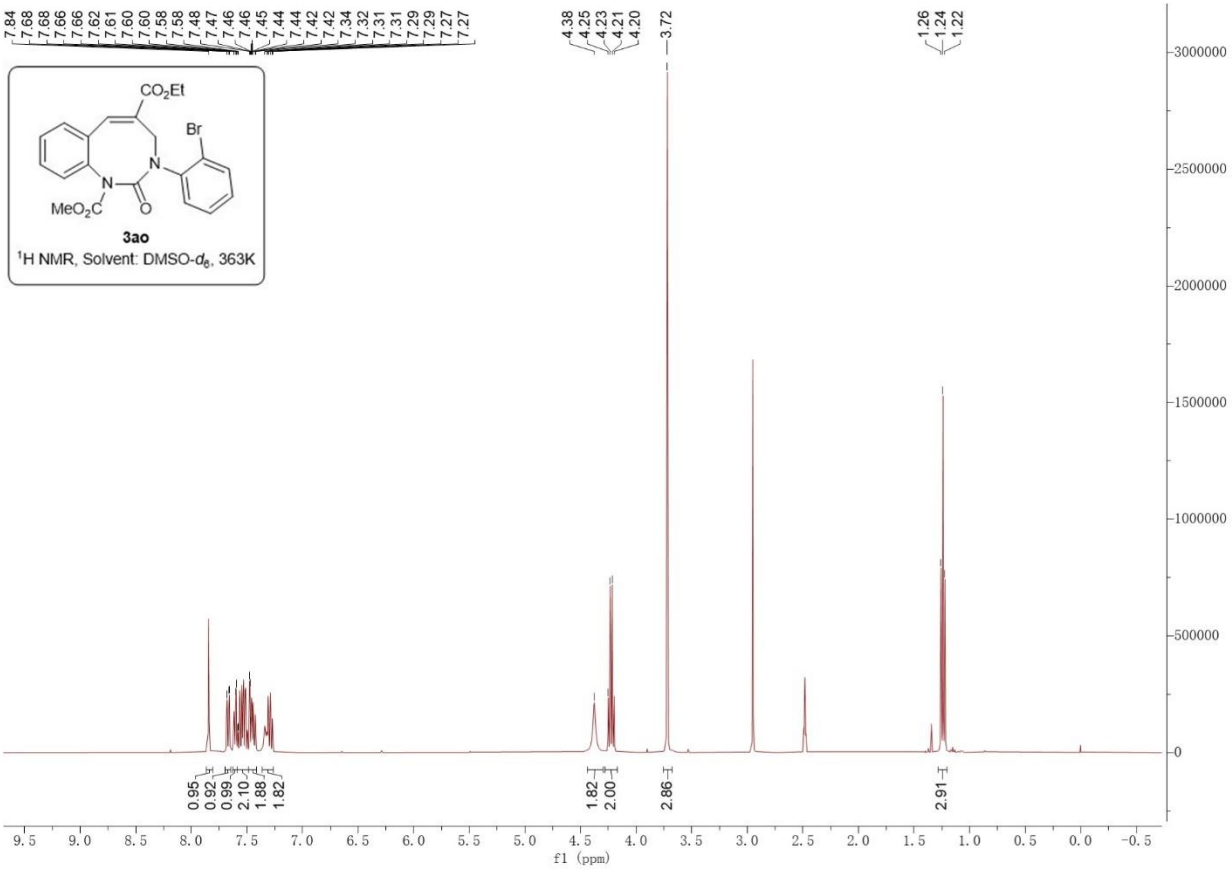
130.47
129.56
128.45
127.39
127.11
61.69
53.81
50.54
17.17
14.34
CO2Et
MeO2C
3an
13C NMR, Solvent: DMSO-d6, 363K
f1 (ppm)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7.58
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7.47
7.46
7.46
7.45
7.44
7.44
7.42
7.42
7.34
7.32
7.31
7.31
7.29
7.29
7.27
7.27
4.38
4.25
4.23
4.21
4.20
3.72
1.26
1.24
1.22
CO2Et
Br
MeO2C
3ao
1H NMR, Solvent: DMSO-d6, 363K
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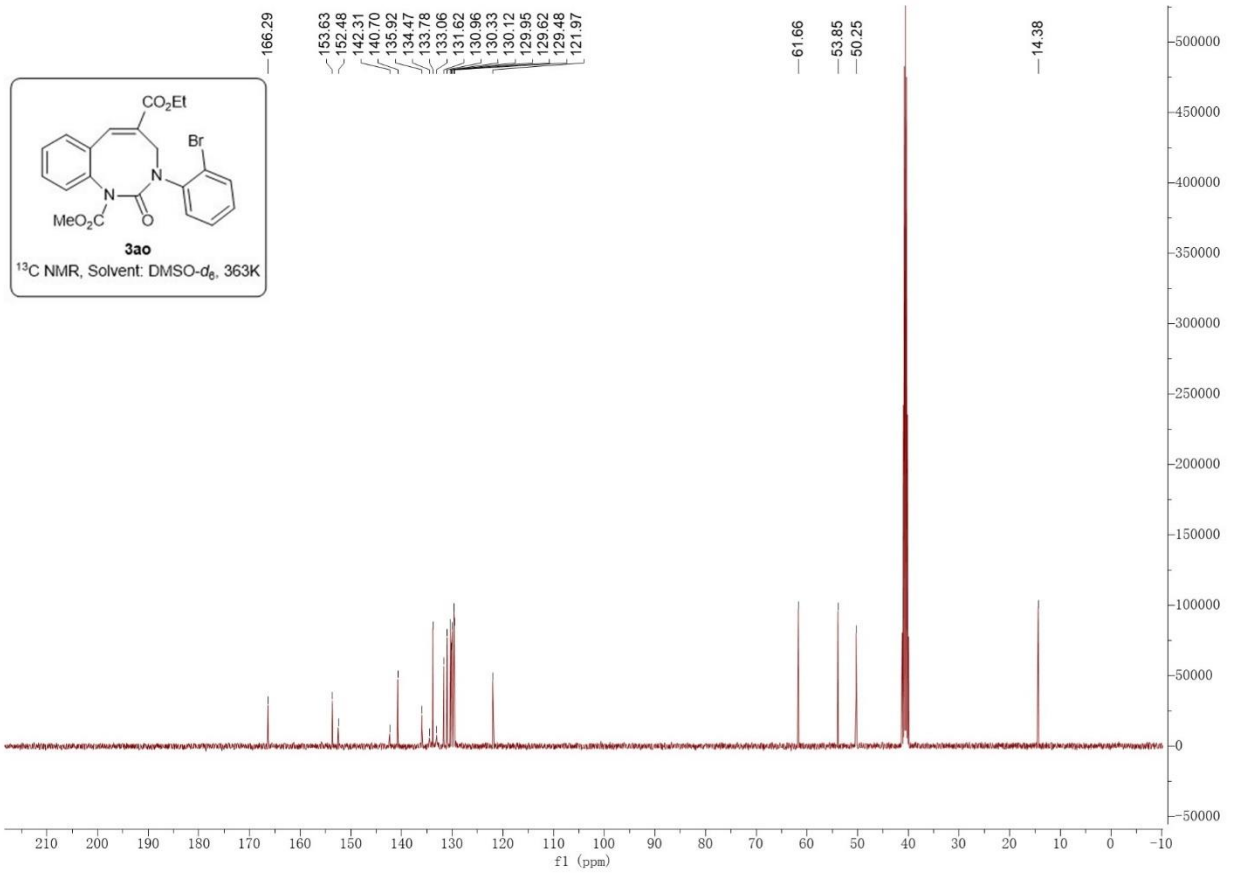
0.92
0.99
2.10
1.88
1.82
1.82
2.00
2.86
2.91
f1 (ppm)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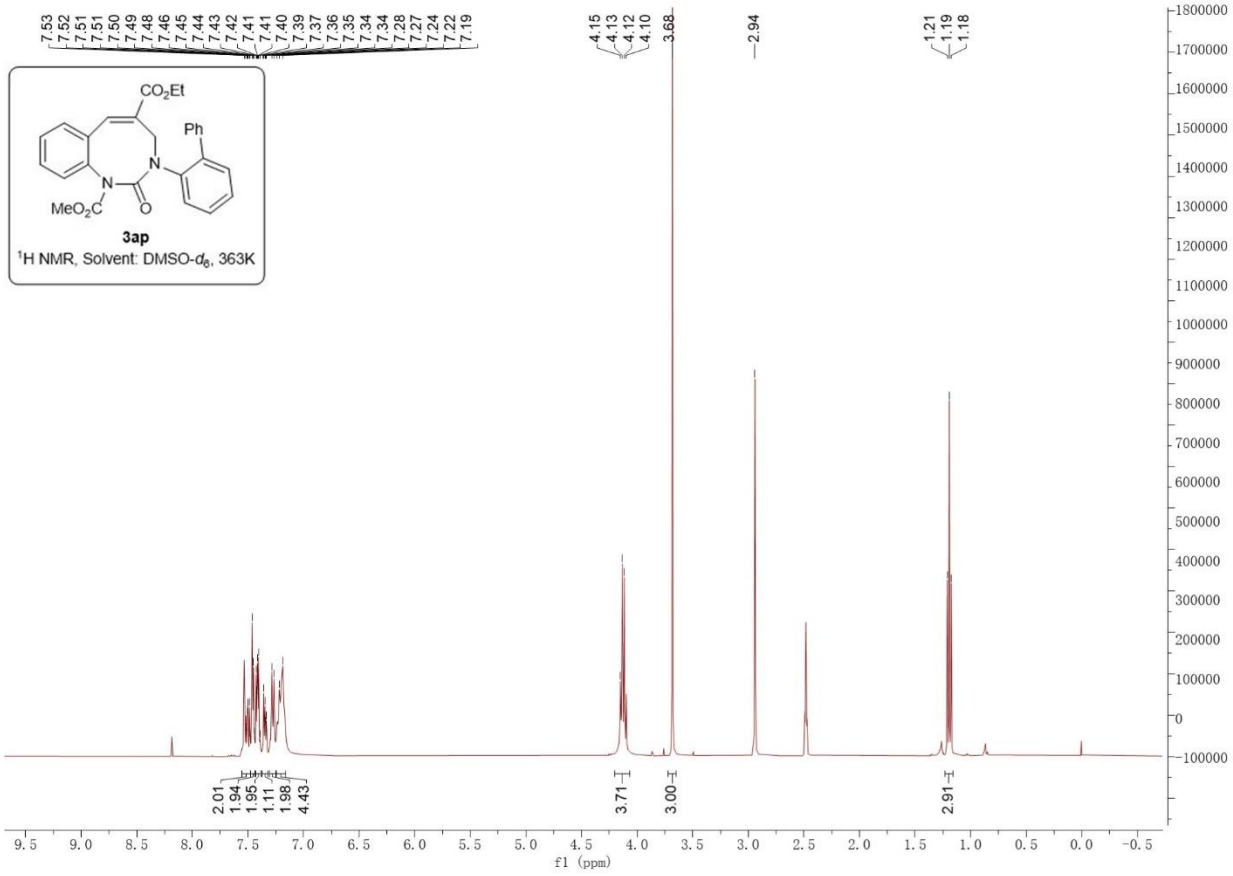
135.92
134.47
133.78
133.06
131.62
130.96
130.33
130.12
129.95
129.62
129.48
121.97
61.66
53.85
50.25
14.38
CO2Et
Br
N
N
MeO2C
O
3ao
13C NMR, Solvent: DMSO-d6, 363K
f1 (ppm)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7.41
7.41
7.40
7.39
7.37
7.36
7.35
7.34
7.34
7.28
7.27
7.24
7.22
7.19
4.15
4.13
4.12
4.10
3.68
2.94
1.21
1.19
1.18
CO2Et
Ph
N
N
MeO2C
O
3ap
1H NMR, Solvent: DMSO-d6, 363K
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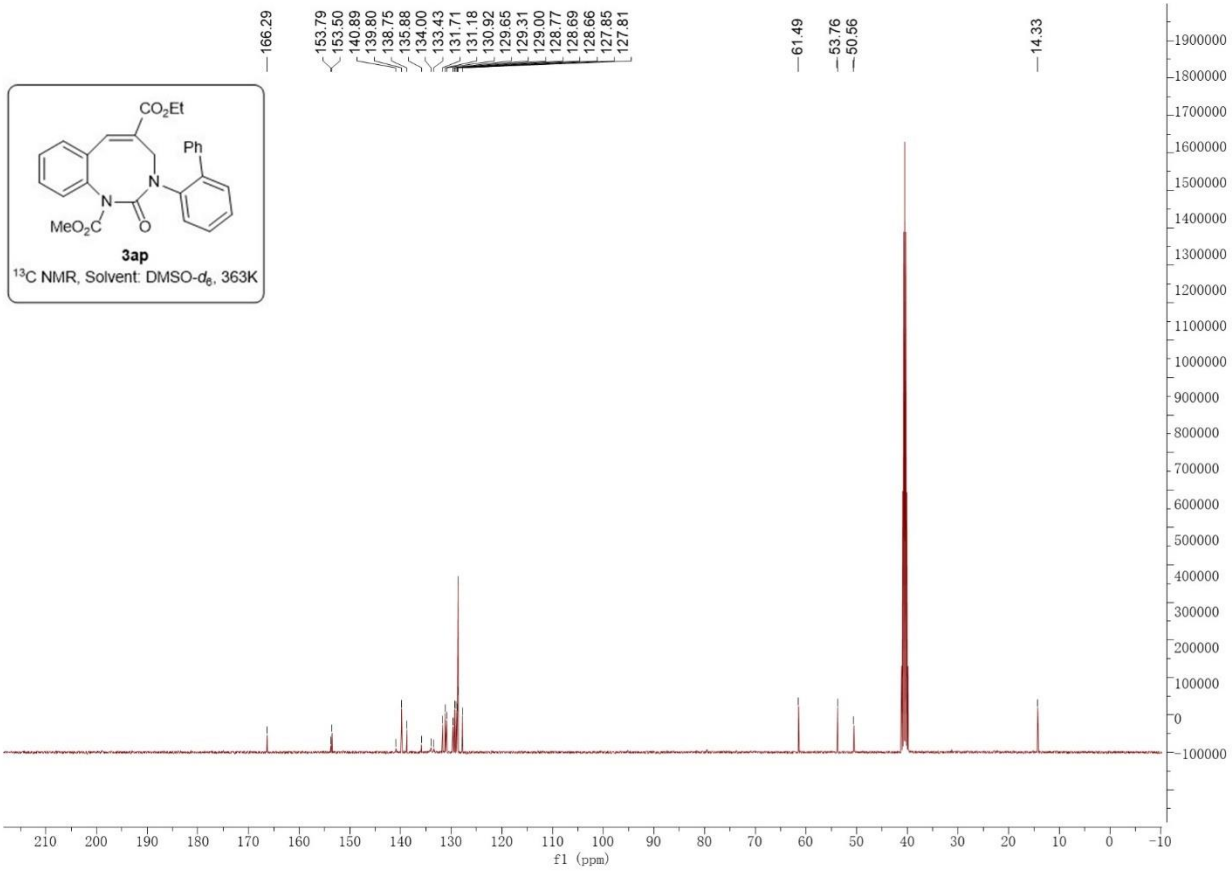
1.94
1.95
1.11
1.98
4.43
3.71
3.00
2.91
f1 (ppm)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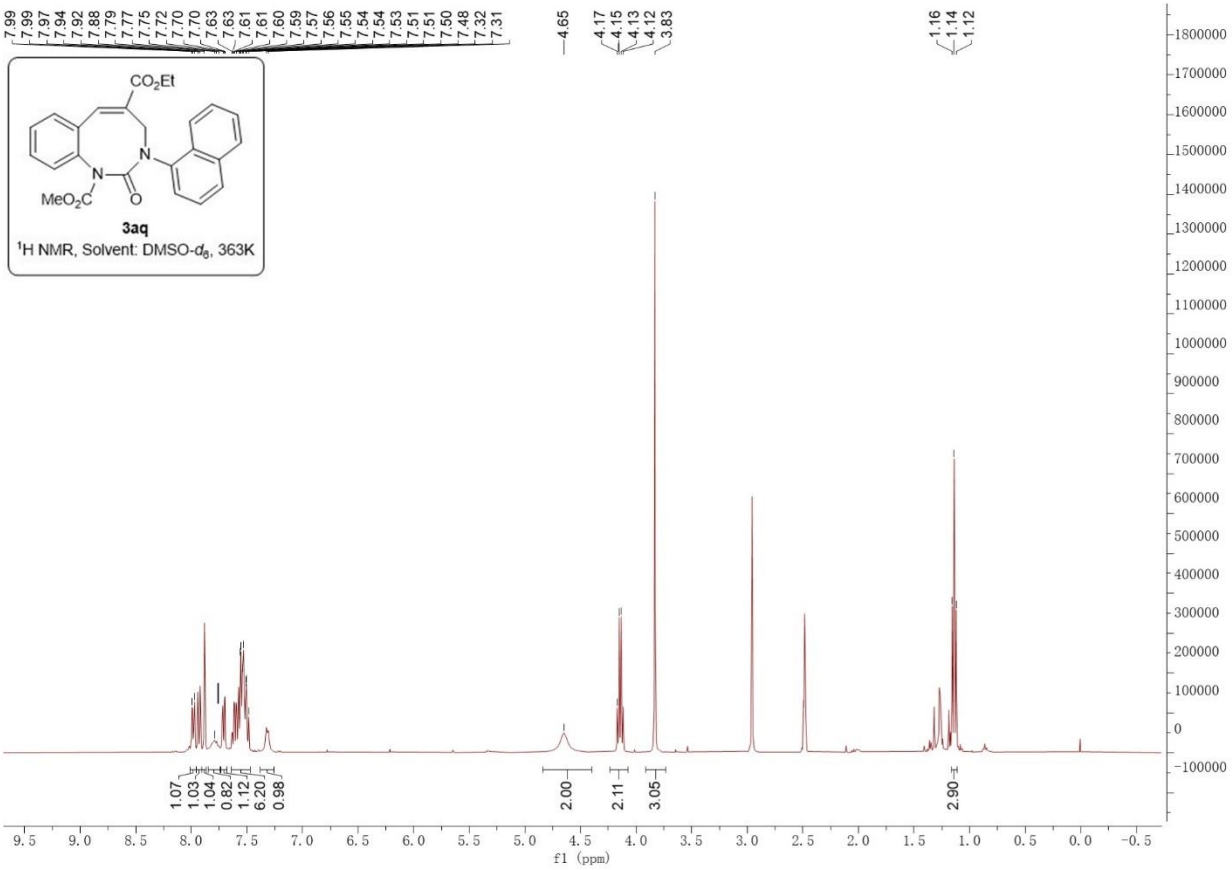
131.18
130.92
129.65
129.31
129.00
128.77
128.69
128.66
127.85
127.81
61.49
53.76
50.56
14.33
CO2Et
Ph
N
N
MeO2C
O
3ap
13C NMR, Solvent: DMSO-d6, 363K
f1 (ppm)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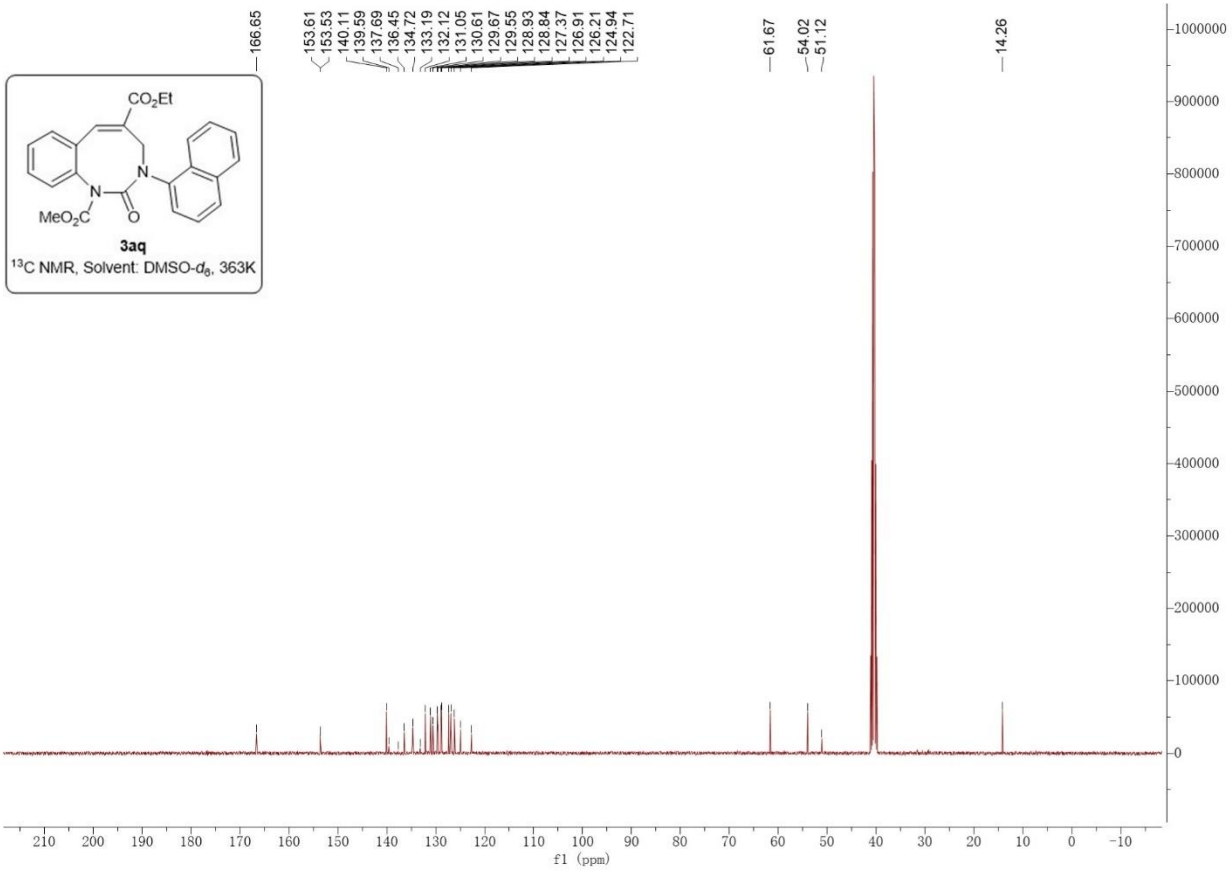
7.88
7.79
7.77
7.75
7.72
7.70
7.70
7.63
7.61
7.61
7.60
7.59
7.57
7.56
7.55
7.54
7.54
7.53
7.51
7.51
7.50
7.48
7.32
7.31
4.65
4.17
4.15
4.13
4.12
3.83
1.16
1.14
1.12
CO2Et
N
N
MeO2C
O
3aq
1H NMR, Solvent: DMSO-d6, 363K
1.07
1.03
1.04
0.82
1.12
6.20
0.98
2.00
2.11
3.05
2.90
f1 (ppm)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153.53
140.11
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137.69
136.45
134.72
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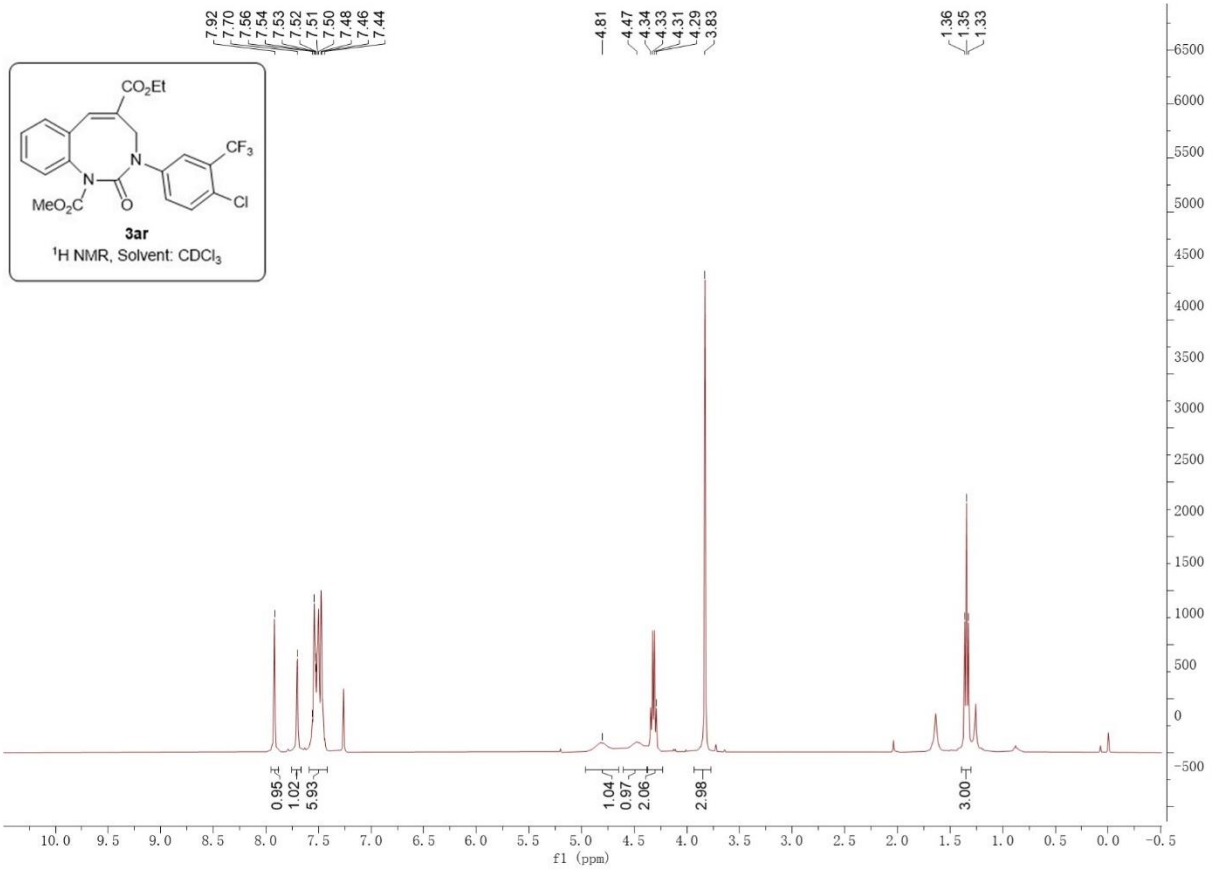
132.12
131.05
130.61
129.67
129.55
128.93
128.84
127.37
126.91
126.21
124.94
122.71
61.67
54.02
51.12
14.26
CO2Et
MeO2C
3aq
13C NMR, Solvent: DMSO-d6, 363K
f1 (ppm)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7.46
7.44
4.81
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4.34
4.33
4.31
4.29
3.83
1.36
1.35
1.33
CO2Et
CF3
Cl
MeO2C
3ar
1H NMR, Solvent: CDCl3
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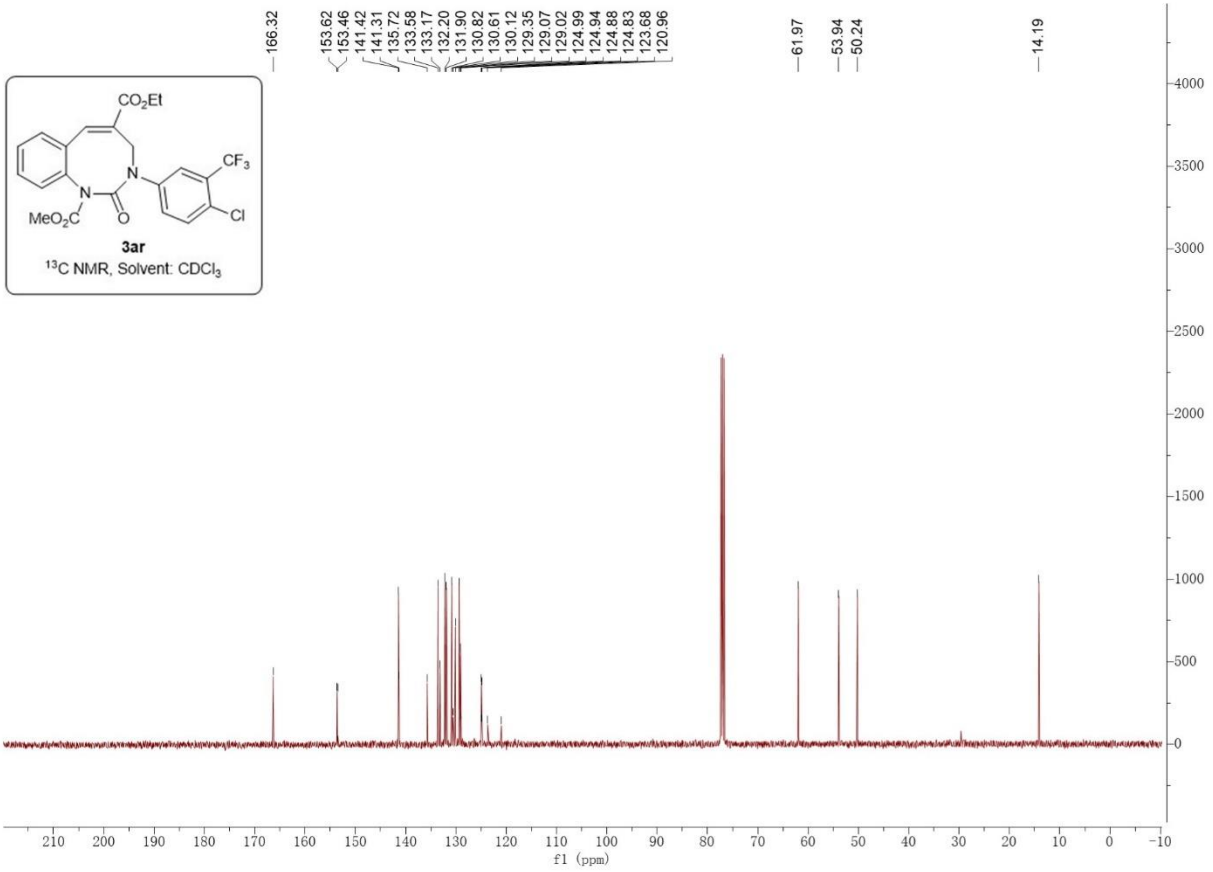
1.02
5.93
1.04
0.97
2.06
2.98
3.00
f1 (ppm)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133.58
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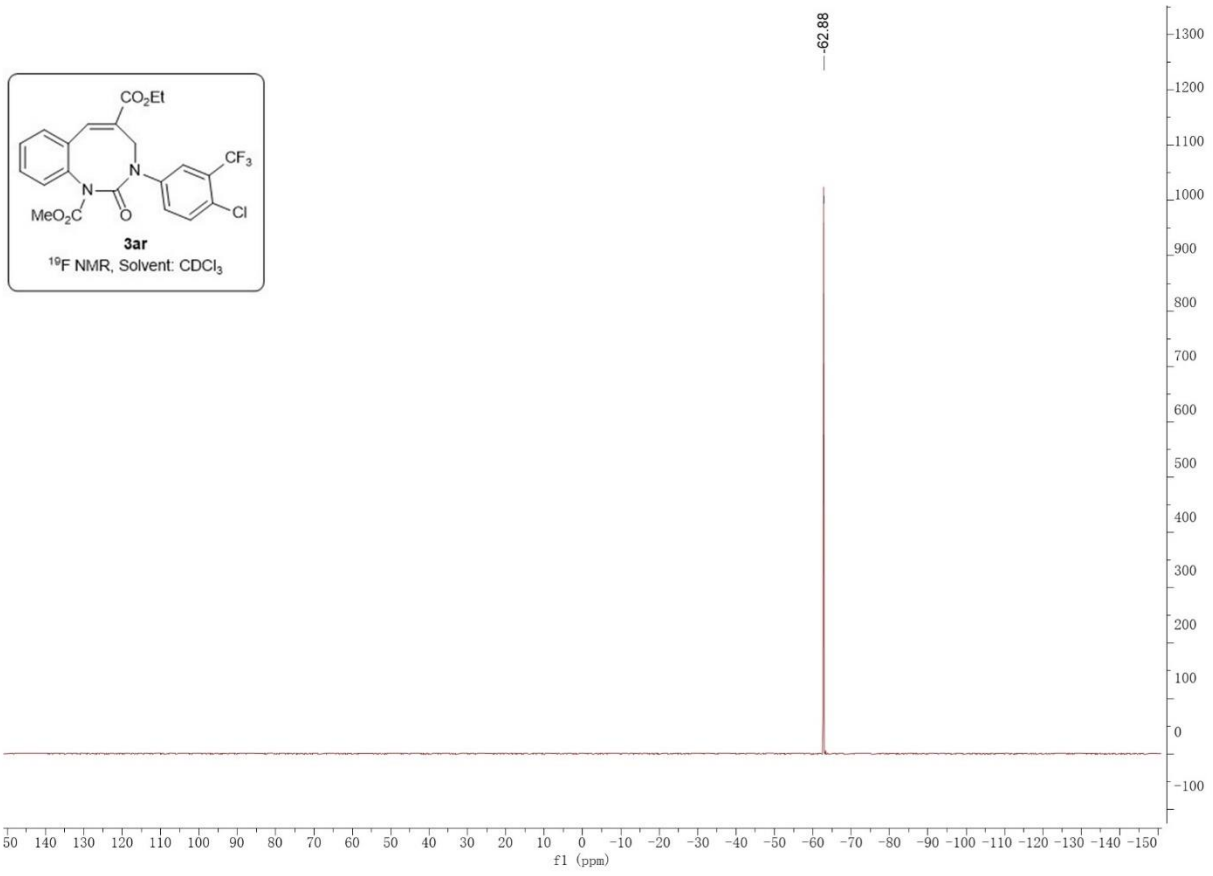
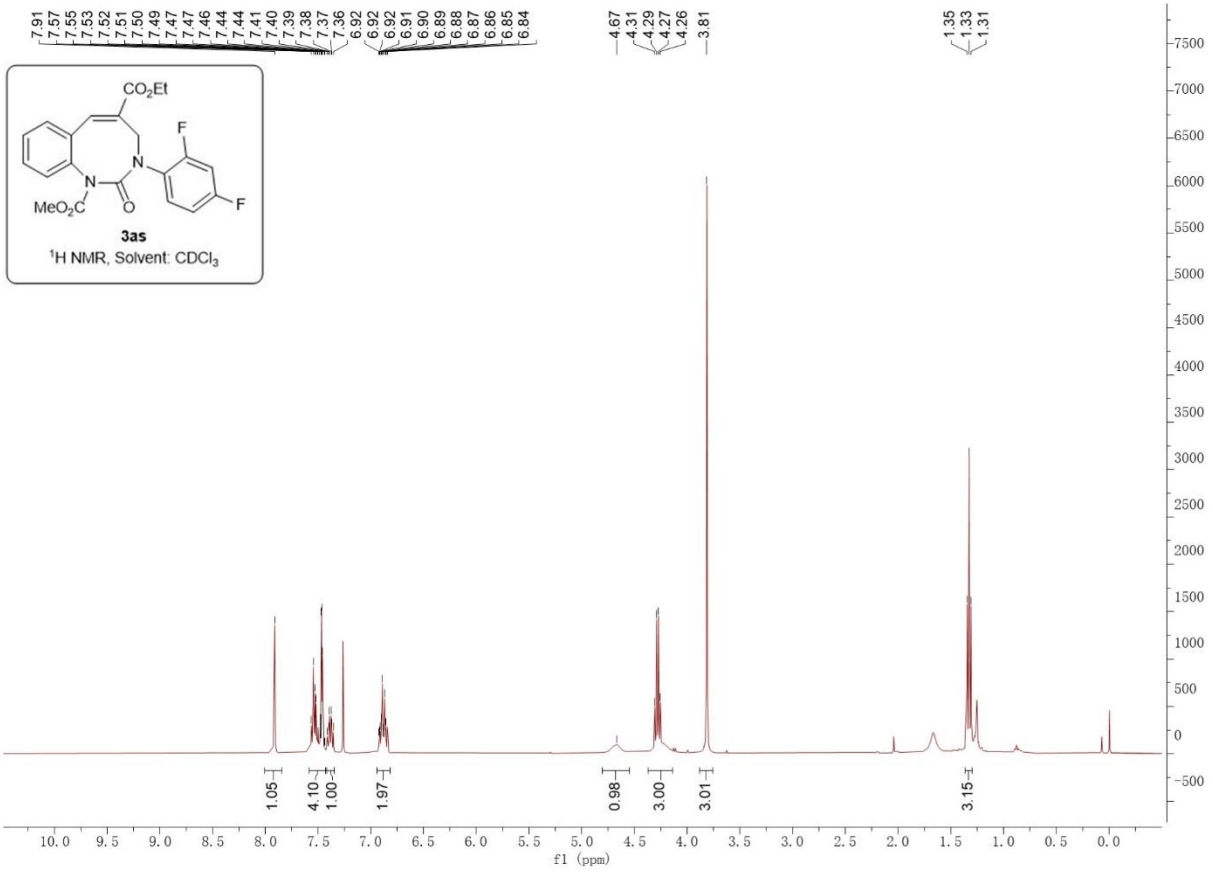
131.90
130.82
130.61
130.12
129.35
129.07
129.02
124.99
124.94
124.88
124.83
123.68
120.96
61.97
53.94
50.24
14.19
CO2Et
CF3
N
N
MeO2C
O
Cl
3ar
13C NMR, Solvent: CDCl3
f1 (ppm)


-62.88
CO2Et
CF3
N
N
MeO2C
O
Cl
3ar
19F NMR, Solvent: CDCl3
f1 (ppm)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7.57
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7.53
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7.50
7.49
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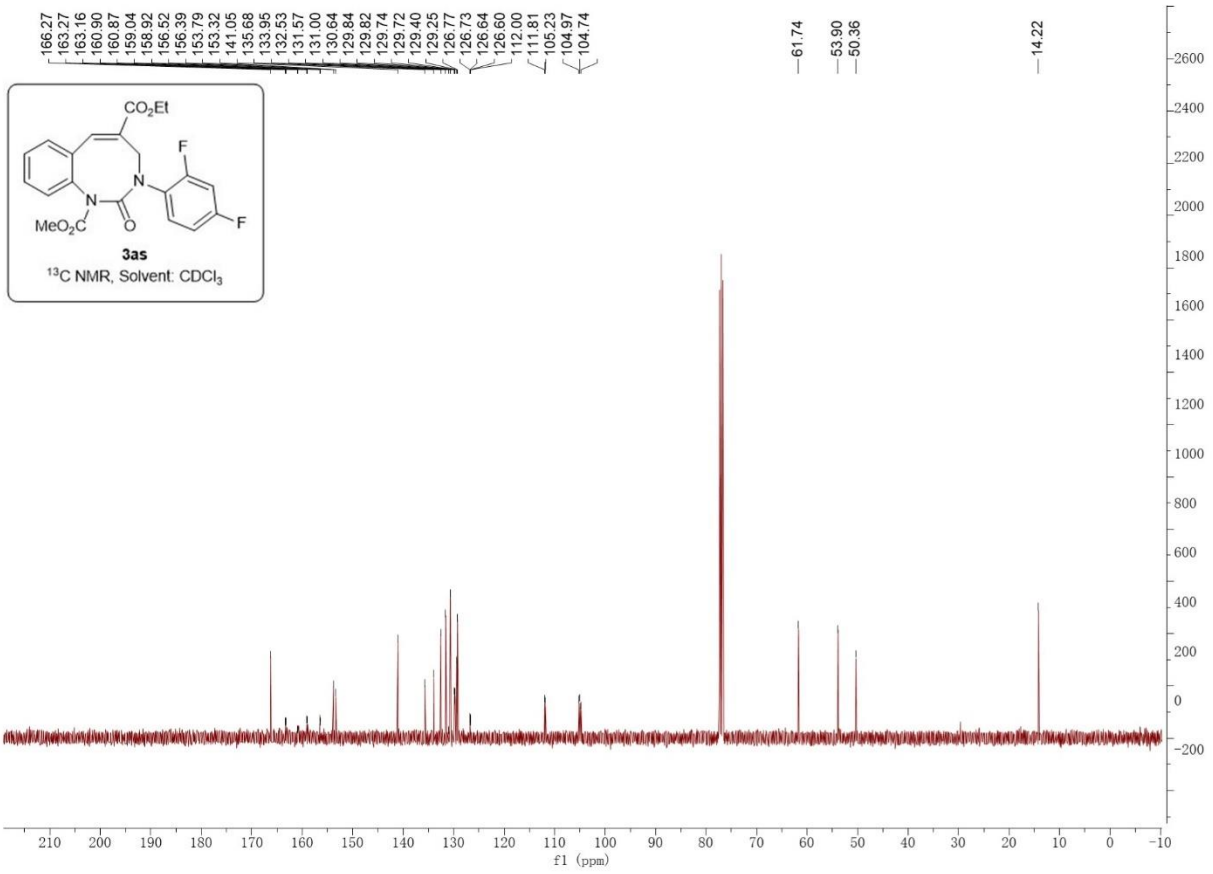
7.46
7.44
7.44
7.41
7.40
7.39
7.38
7.37
7.36
6.92
6.92
6.92
6.91
6.90
6.89
6.88
6.87
6.86
6.85
6.84
4.67
4.31
4.29
4.27
4.26
3.81
1.35
1.33
1.31
CO2Et
F
N
N
MeO2C
O
F
3as
1H NMR, Solvent: CDCl3
1.05
4.10
1.00
1.97
0.98
3.00
3.01
3.15
f1 (ppm)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156.52
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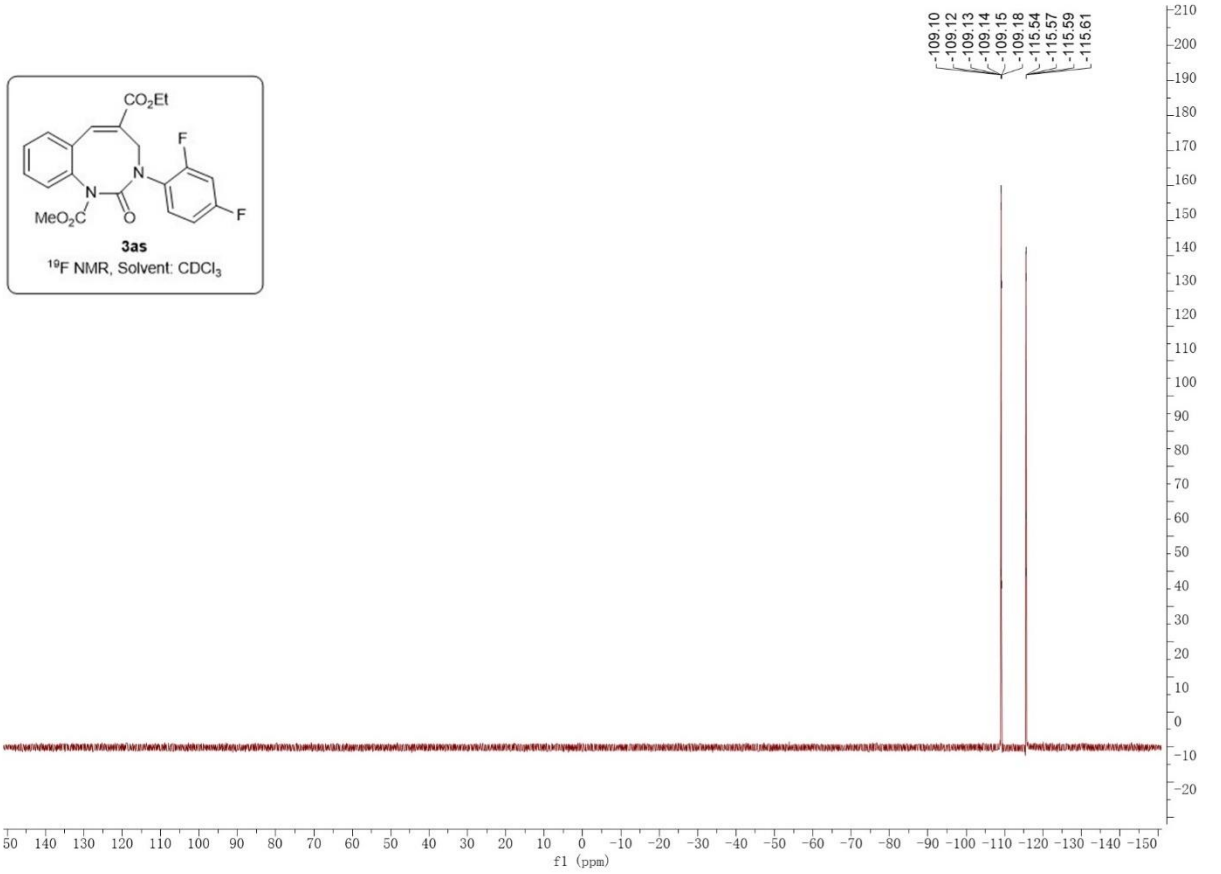
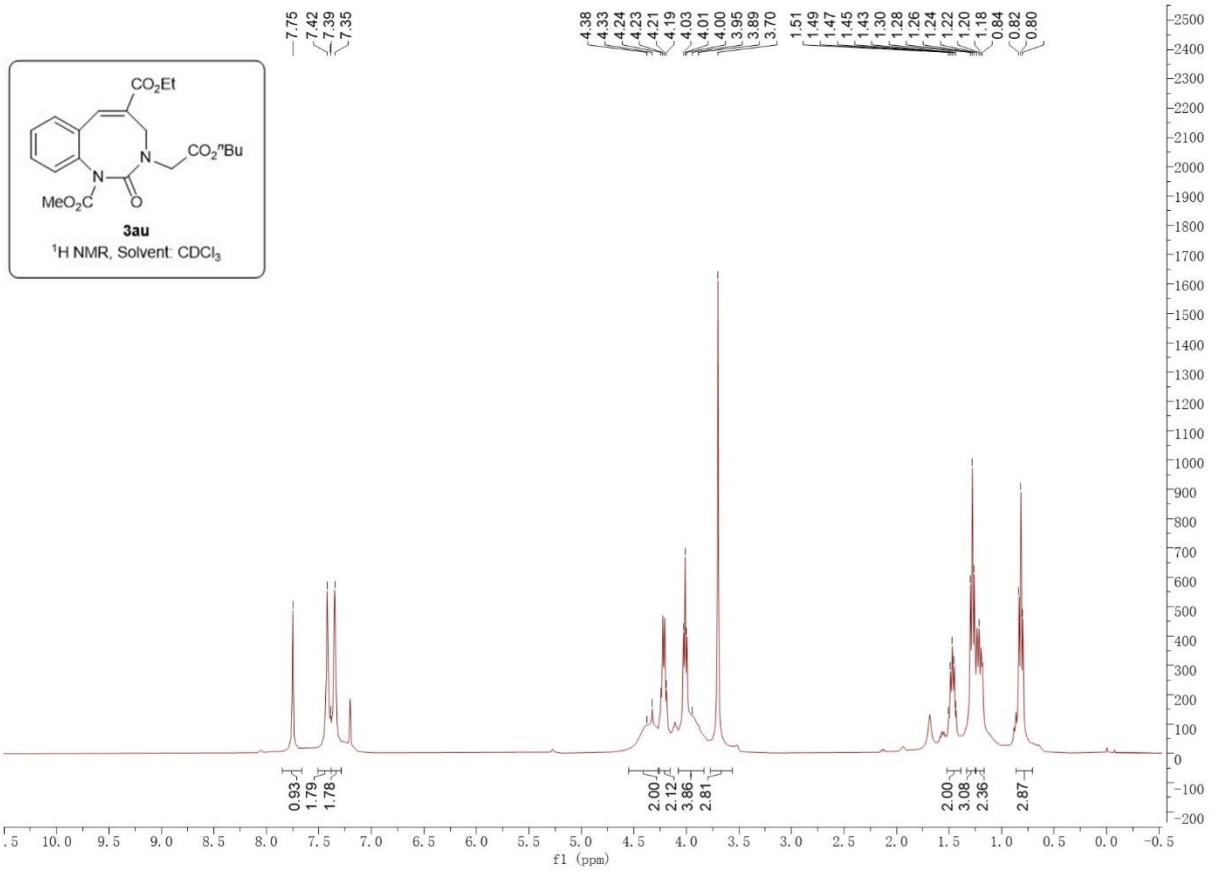
135.68
133.95
132.53
131.57
131.00
130.64
129.84
129.82
129.74
129.72
129.40
129.25
126.77
126.73
126.64
126.60
112.00
111.81
105.23
104.97
104.74
61.74
53.90
50.36
14.22
CO2Et
F
N
N
MeO2C
O
F
3as
13C NMR, Solvent: CDCl3
f1 (ppm)


CO2Et
F
N
N
MeO2C
O
F
3as
19F NMR, Solvent: CDCl3
-109.10
-109.12
-109.13
-109.14
-109.15
-109.18
-115.54
-115.57
-115.59
-115.61
f1 (ppm)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CO2nBu
N
N
MeO2C
O
3au
1H NMR, Solvent: CDCl3
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4.38
4.33
4.24
4.23
4.21
4.19
4.03
4.01
4.00
3.95
3.89
3.70
1.51
1.49
1.47
1.45
1.43
1.30
1.28
1.26
1.24
1.22
1.20
1.18
0.84
0.82
0.80
0.93
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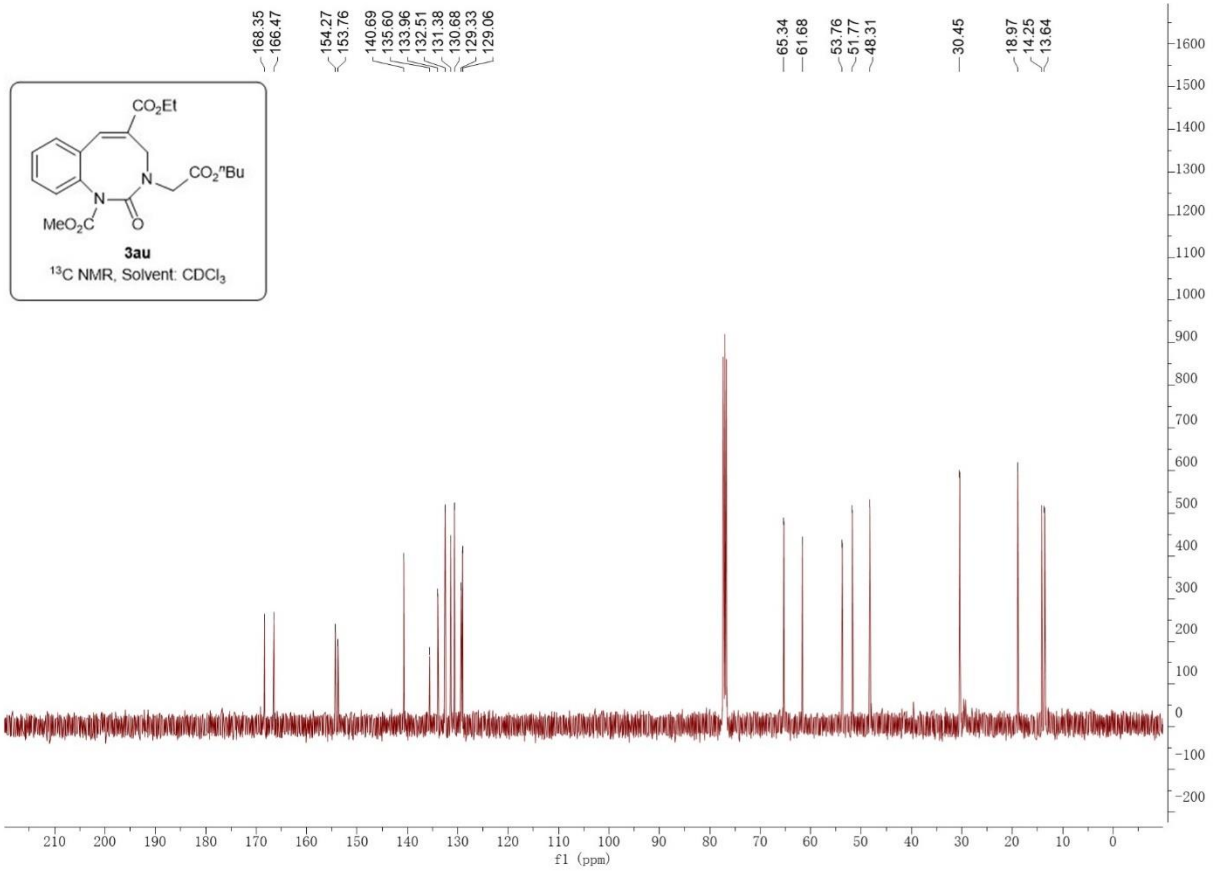
2.12
3.86
2.81
2.00
3.08
2.36
2.87
f1 (ppm)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129.33
129.06
65.34
61.68
53.76
51.77
48.31
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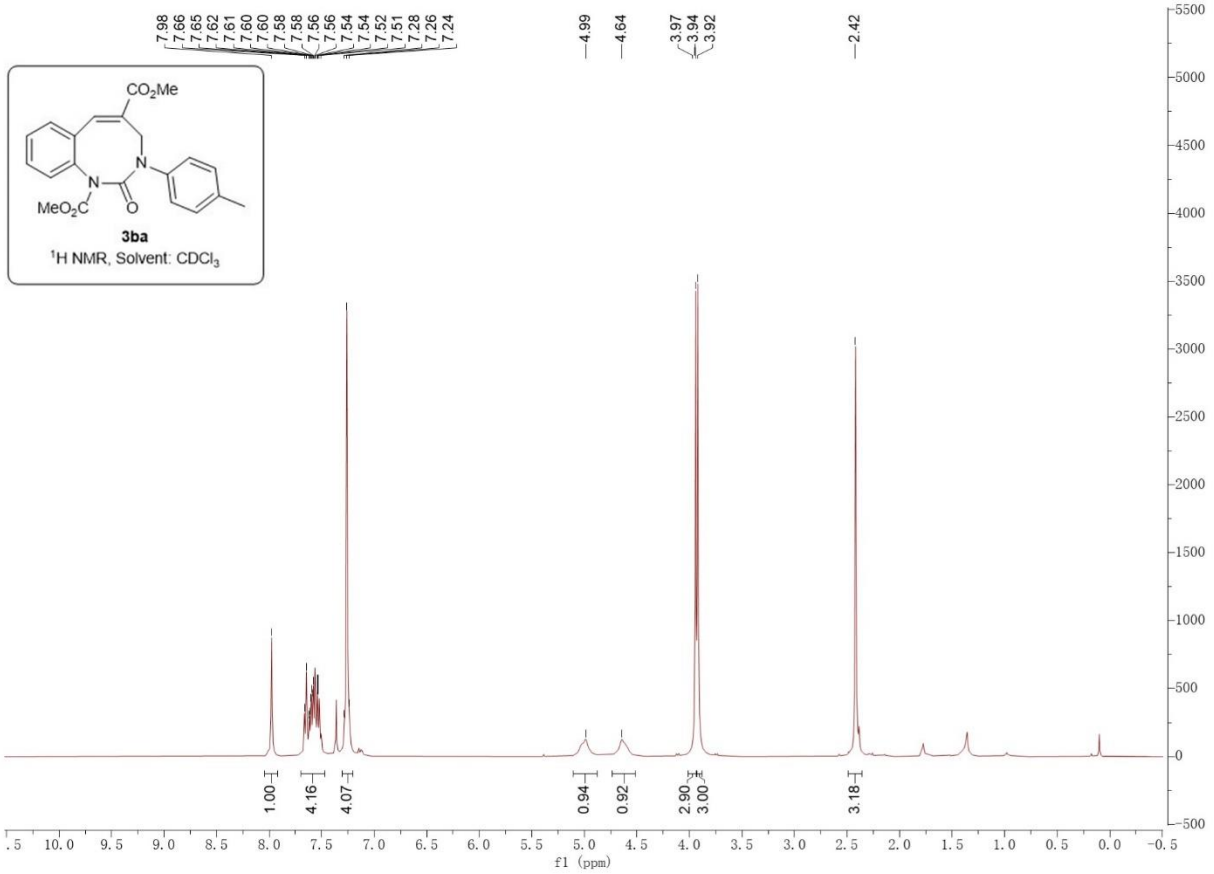
14.25
13.64
CO2Et
CO2nBu
MeO2C
3au
13C NMR, Solvent: CDCl3
f1 (ppm)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7.52
7.51
7.28
7.26
7.24
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4.64
3.97
3.94
3.92
2.42
CO2Me
MeO2C
3ba
1H NMR, Solvent: CDCl3
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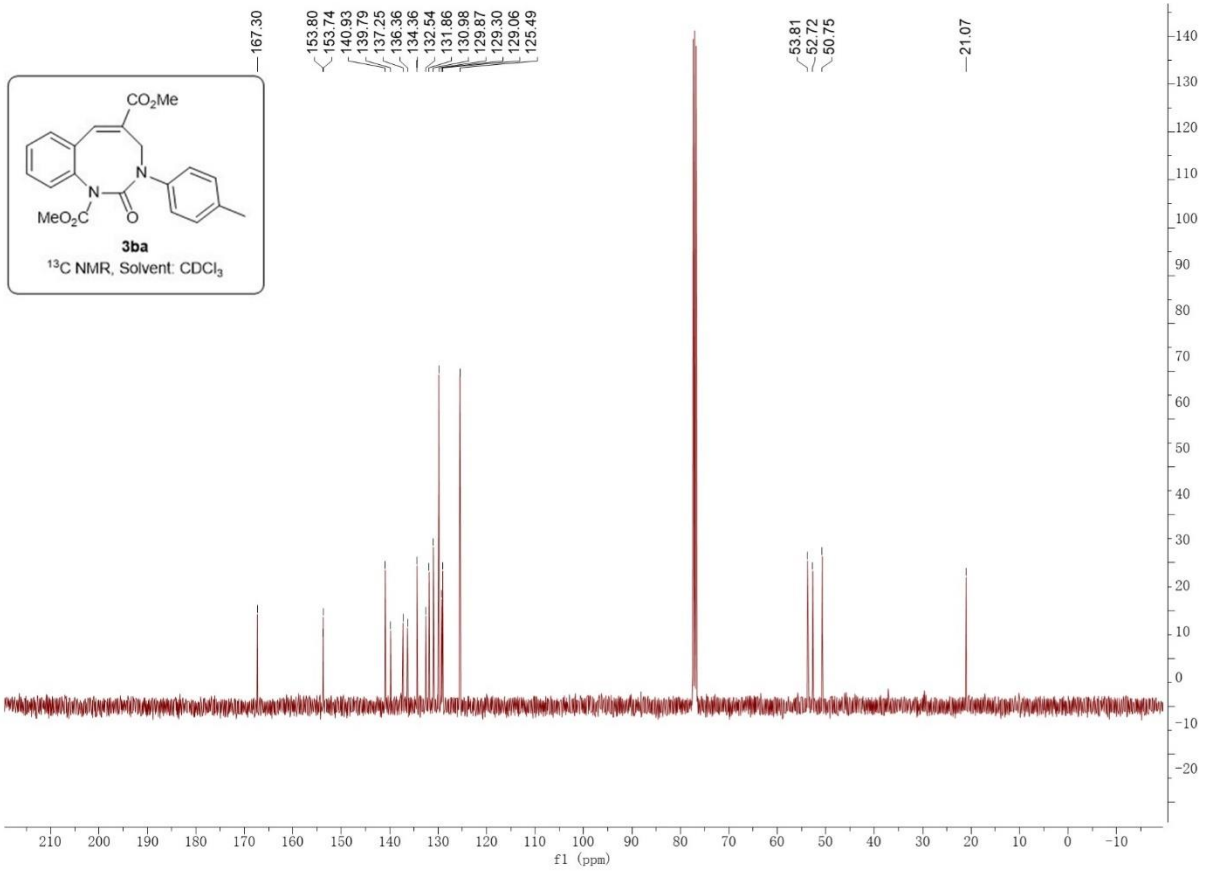
4.16
4.07
0.94
0.92
2.90
3.00
3.18
f1 (ppm)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129.30
129.06
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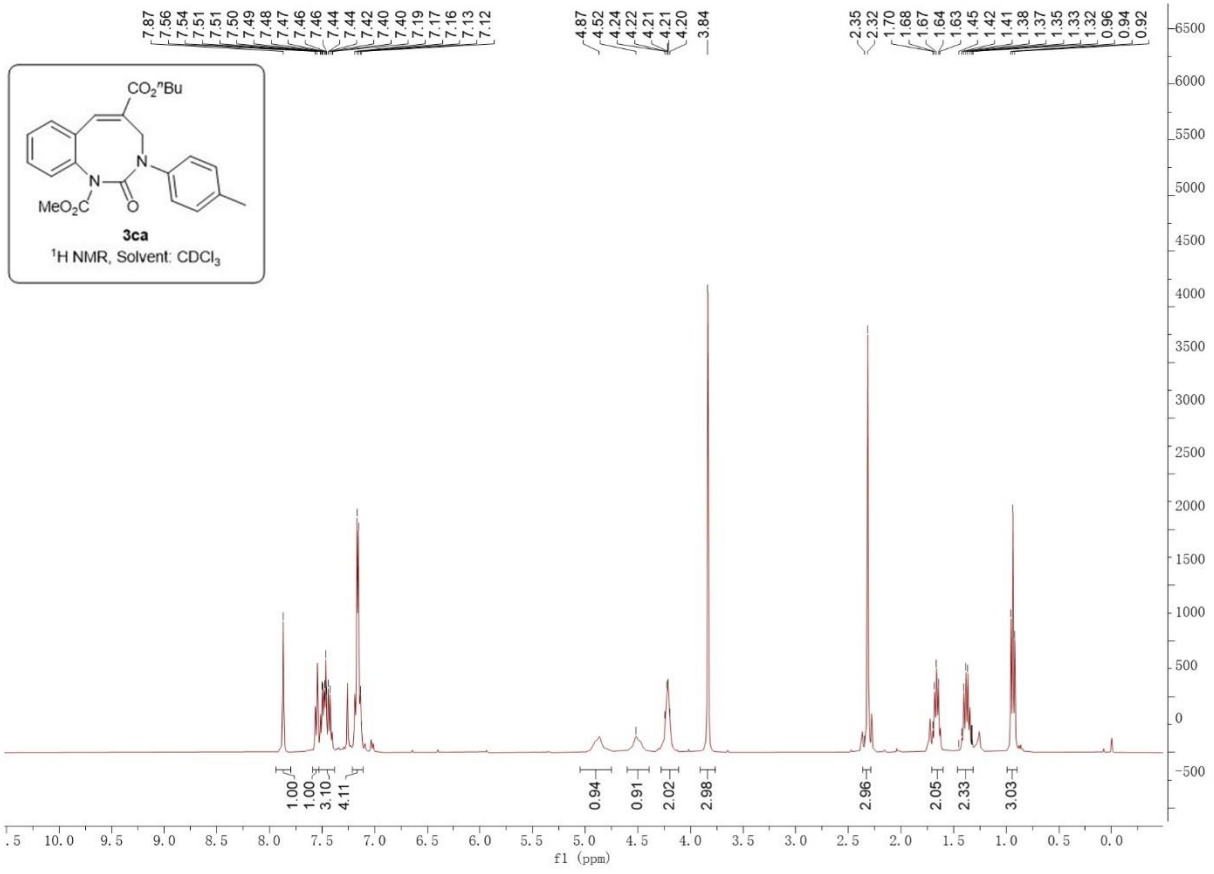
52.72
50.75
21.07
CO2Me
MeO2C
3ba
13C NMR, Solvent: CDCl3
f1 (ppm)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7.40
7.19
7.17
7.16
7.13
7.12
4.87
4.52
4.24
4.22
4.21
4.21
4.20
3.84
2.35
2.32
1.70
1.68
1.67
1.64
1.63
1.45
1.42
1.41
1.38
1.37
1.35
1.33
1.32
0.96
0.94
0.92
CO2nBu
MeO2C
3ca
1H NMR, Solvent: CDCl3
1.00
1.00
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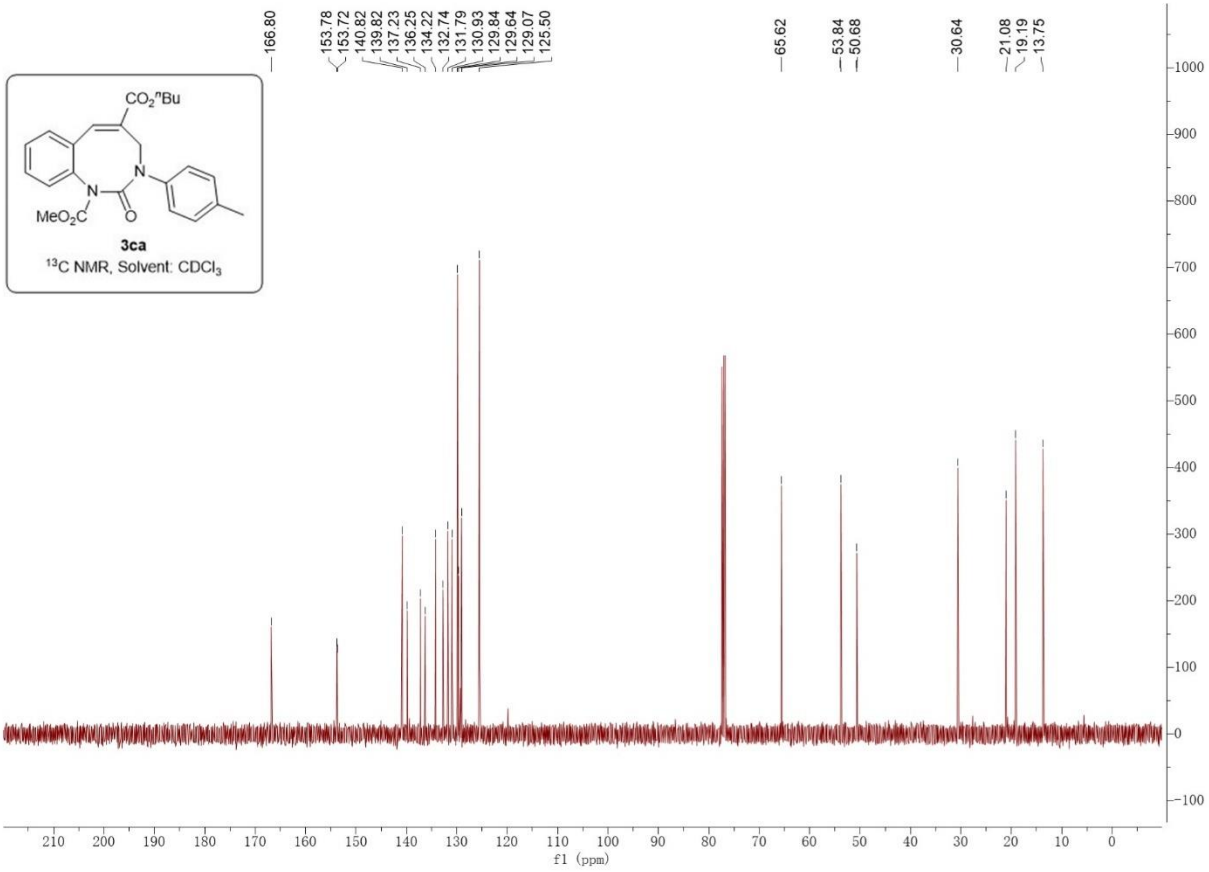
0.94
0.91
2.02
2.98
2.96
2.05
2.33
3.03
f1 (ppm)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134.22
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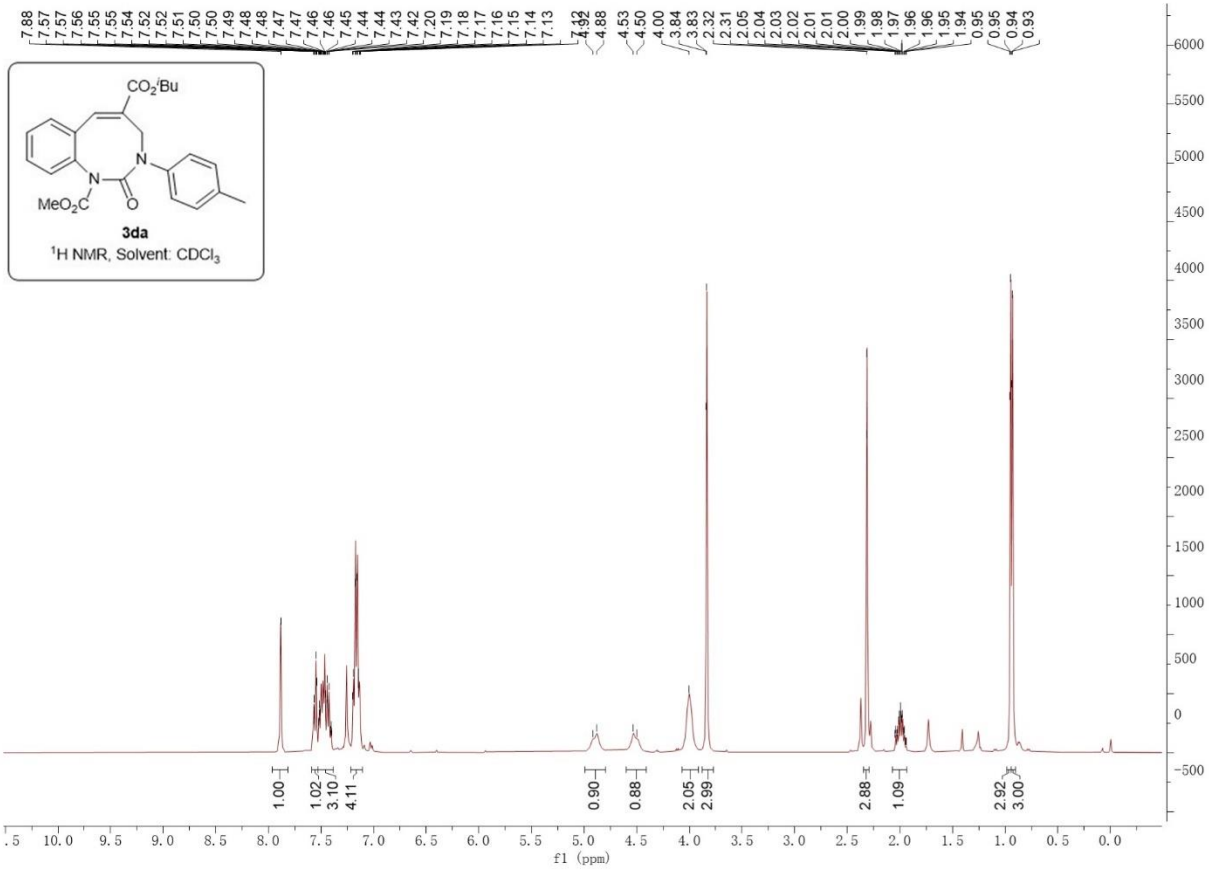
131.79
130.93
129.84
129.64
129.07
125.50
65.62
53.84
50.68
30.64
21.08
19.19
13.75
CO2nBu
MeO2C
3ca
13C NMR, Solvent: CDCl3
f1 (ppm)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MeO2C
3da
1H NMR, Solvent: CDCl3
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3.10
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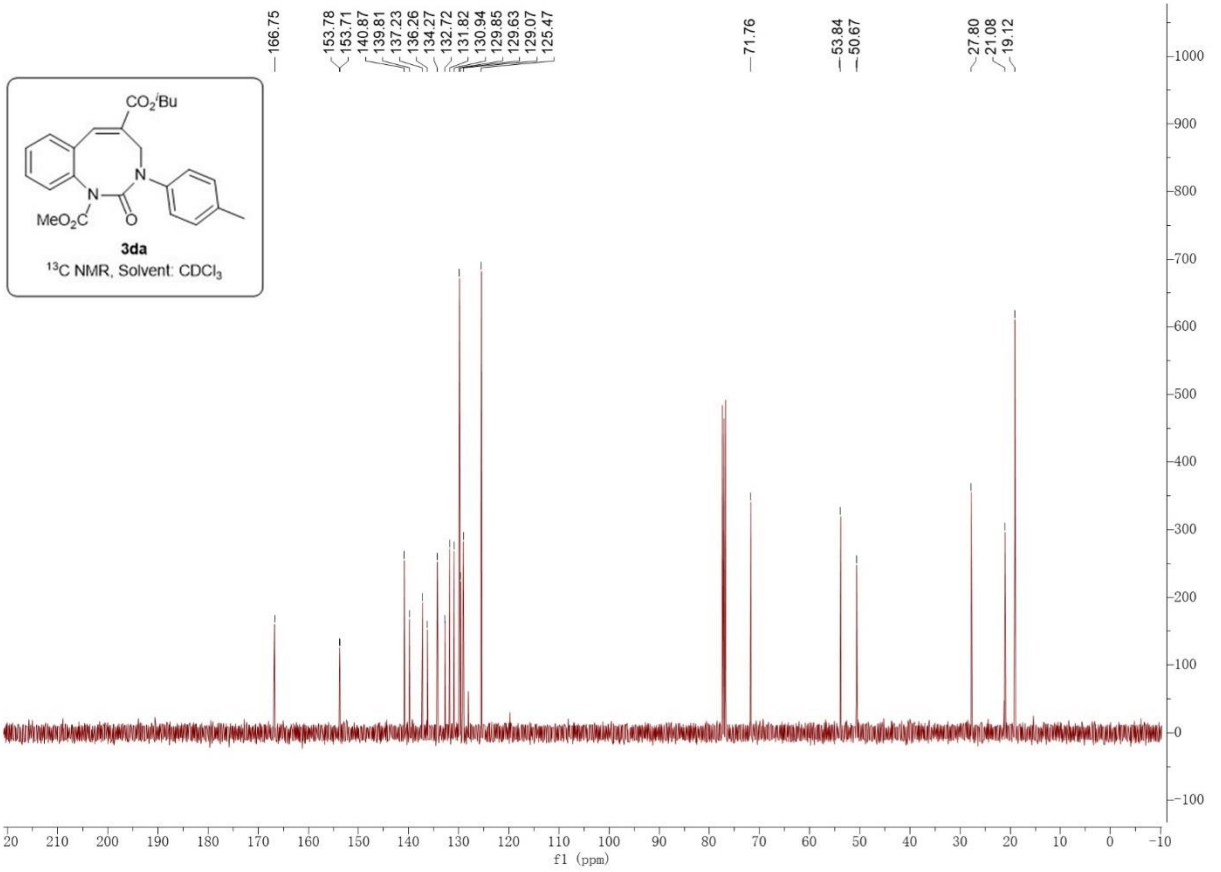
0.90
0.88
2.05
2.99
2.88
1.09
2.92
3.00
f1 (ppm)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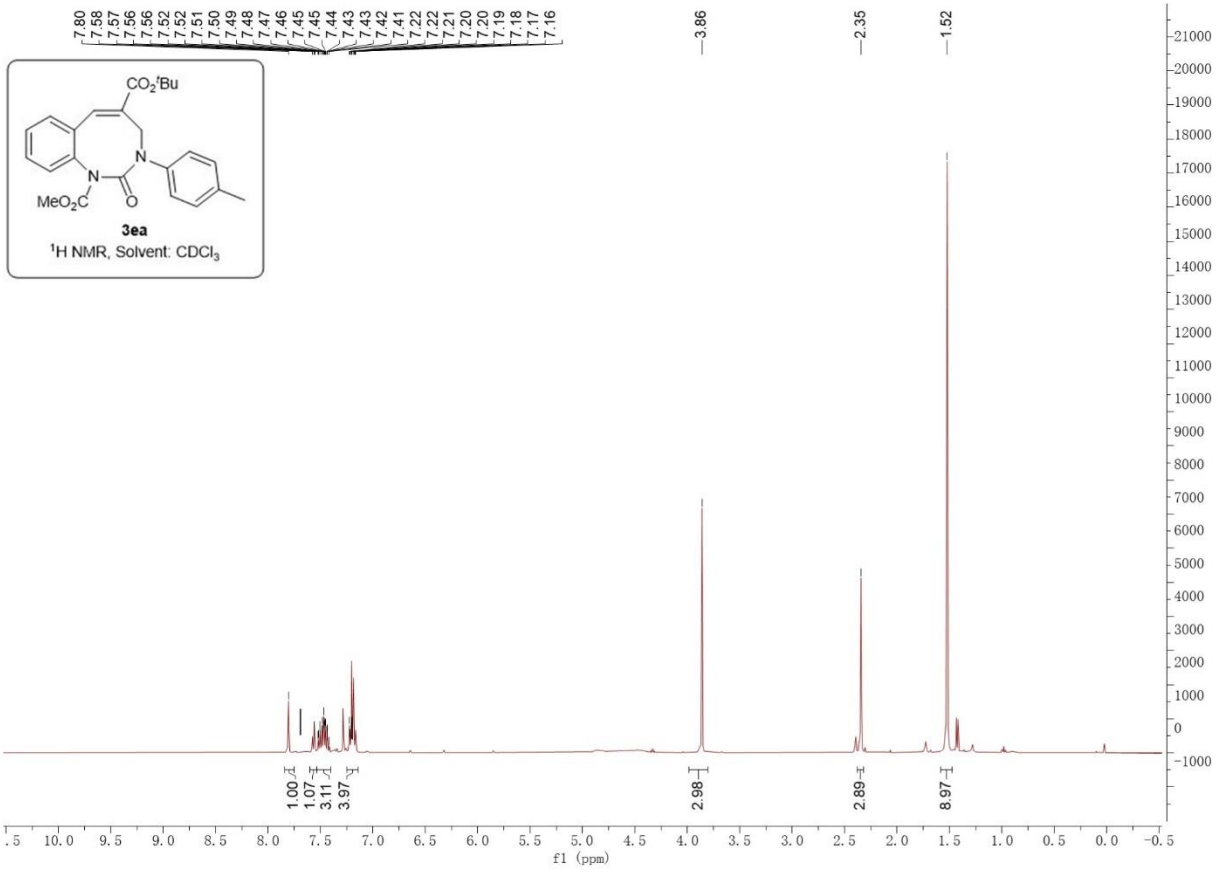
137.23
136.26
134.27
132.72
131.82
130.94
129.85
129.63
129.07
125.47
71.76
53.84
50.67
27.80
21.08
19.12
CO2tBu
MeO2C
3da
13C NMR, Solvent: CDCl3
f1 (ppm)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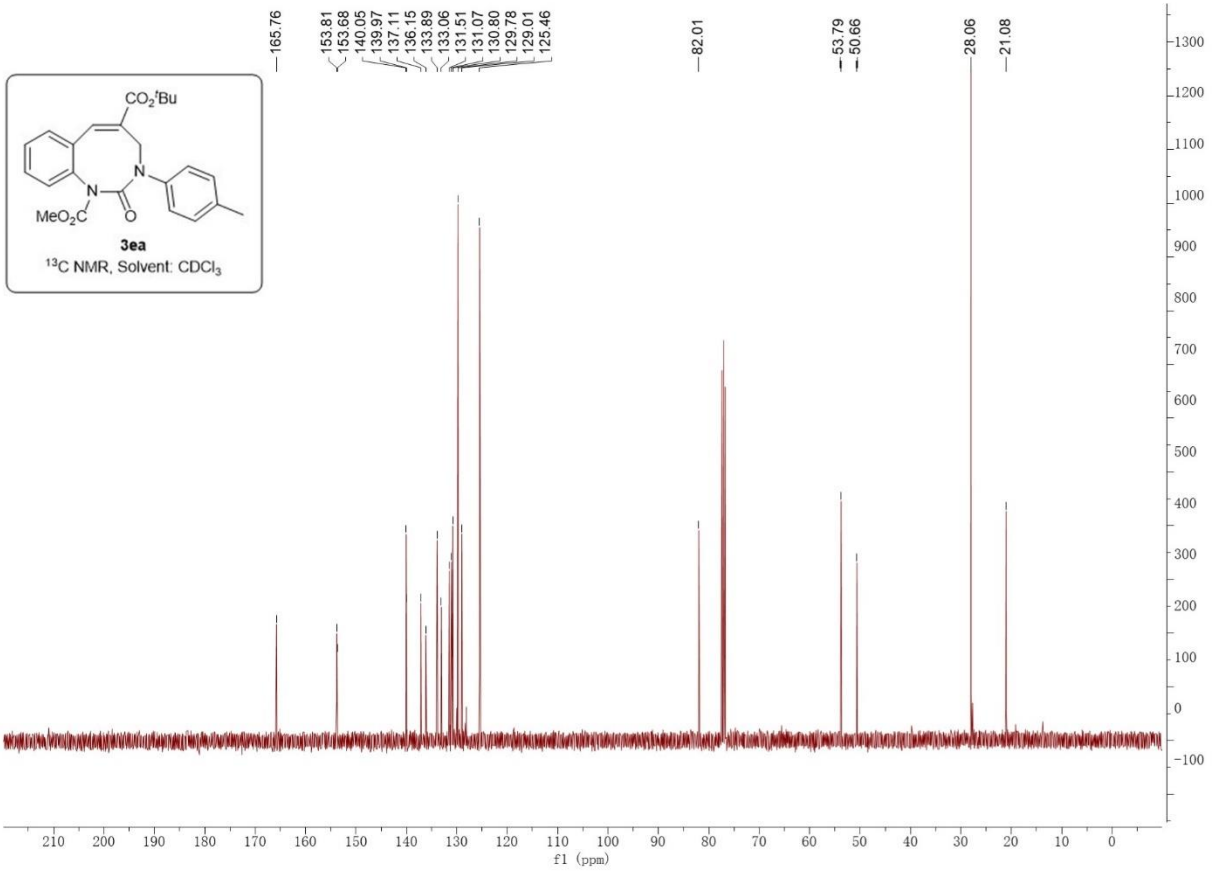
7.56
7.52
7.52
7.51
7.50
7.49
7.48
7.47
7.46
7.45
7.45
7.44
7.43
7.43
7.42
7.41
7.22
7.22
7.21
7.20
7.20
7.19
7.18
7.17
7.16
3.86
2.35
1.52
1.00
1.07
3.11
3.97
2.98
2.89
8.97
CO2tBu
MeO2C
3ea
1H NMR, Solvent: CDCl3
f1 (ppm)


CO2tBu
N
N
MeO2C
O
3ea
13C NMR, Solvent: CDCl3
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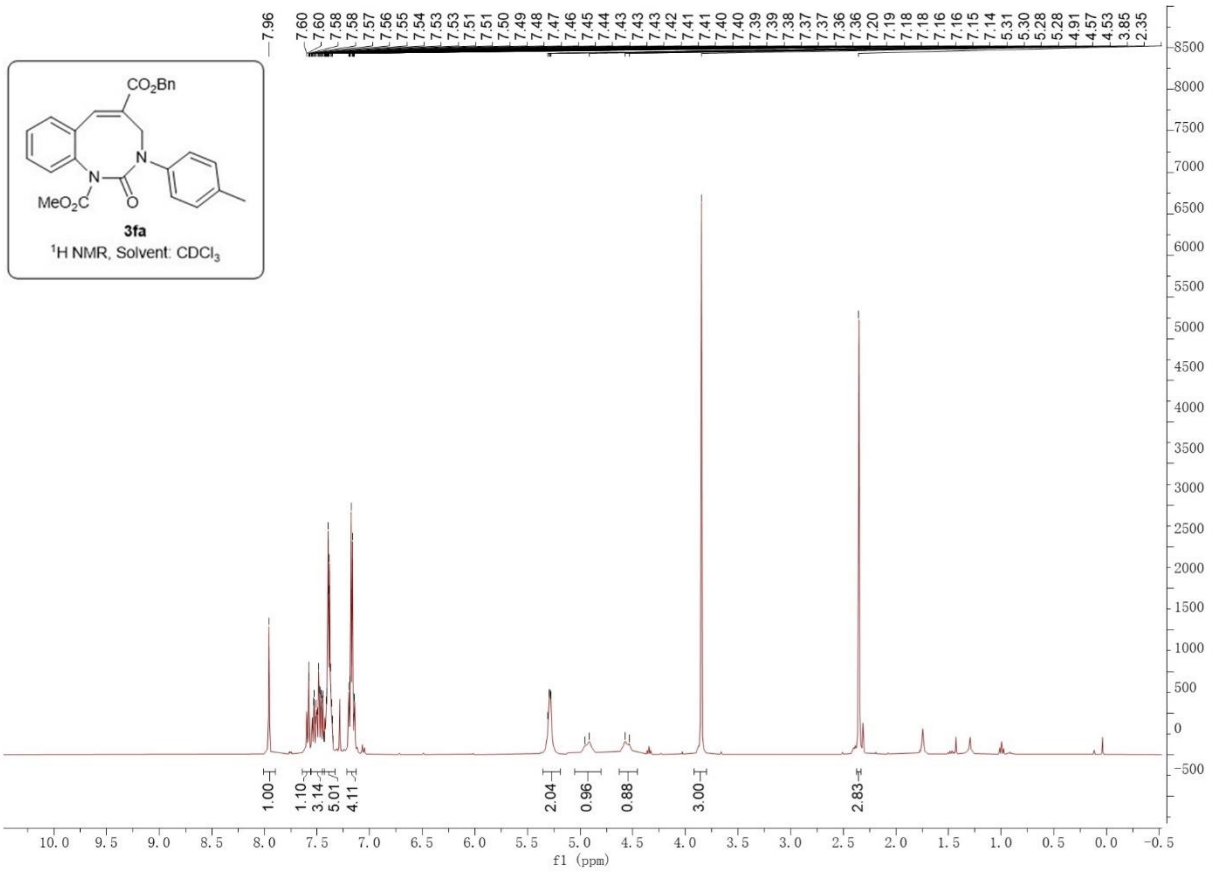
153.81
153.68
140.05
139.97
137.11
136.15
133.89
133.06
131.51
131.07
130.80
129.78
129.01
125.46
82.01
53.79
50.66
28.06
21.08
f1 (ppm)


CO2Bn
N
N
MeO2C
O
3fa
1H NMR, Solvent: CDCl3
7.96
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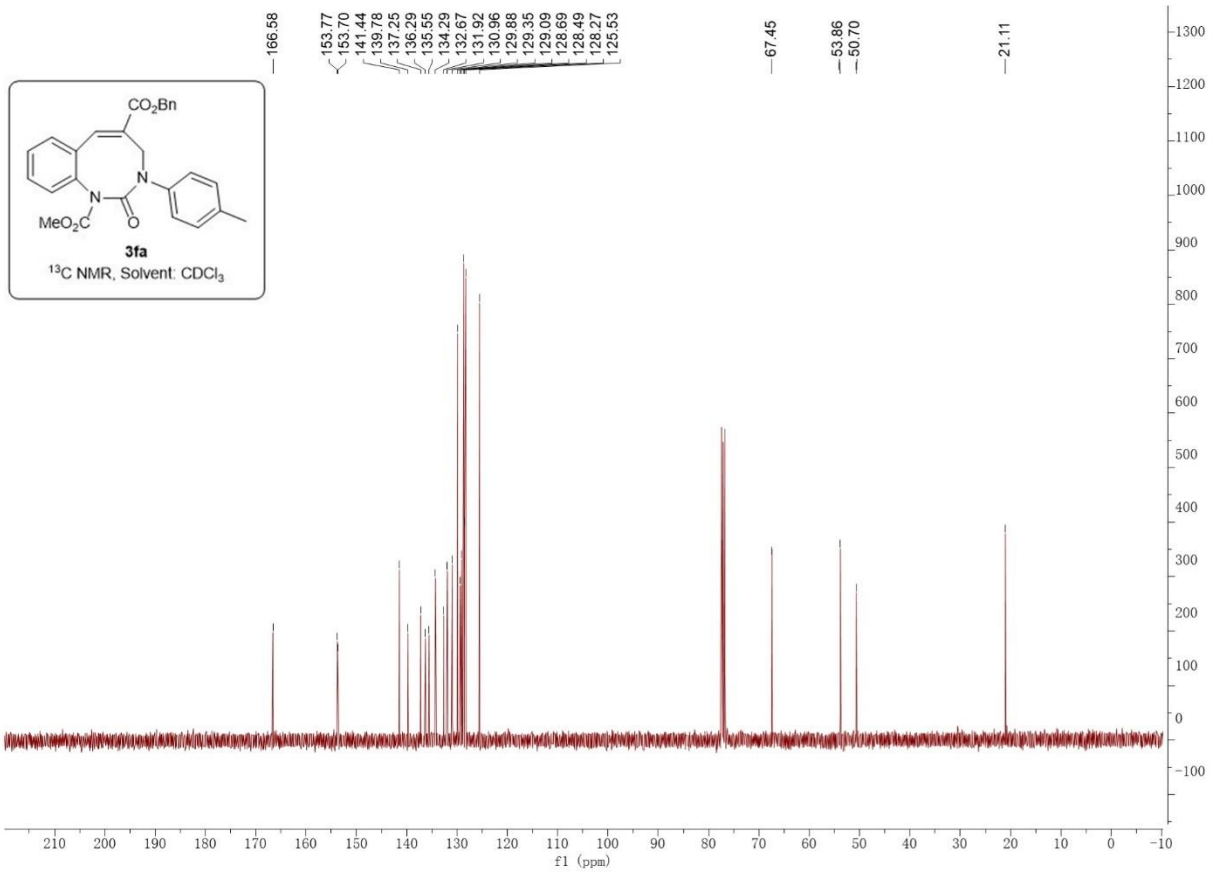
7.58
7.57
7.56
7.55
7.54
7.53
7.51
7.50
7.49
7.48
7.47
7.46
7.45
7.44
7.43
7.42
7.41
7.40
7.39
7.38
7.37
7.36
7.20
7.19
7.18
7.16
7.15
7.14
5.31
5.30
5.28
4.91
4.57
4.53
3.85
2.35
1.00
1.10
3.14
5.01
4.11
2.04
0.96
0.88
3.00
2.83
f1 (ppm)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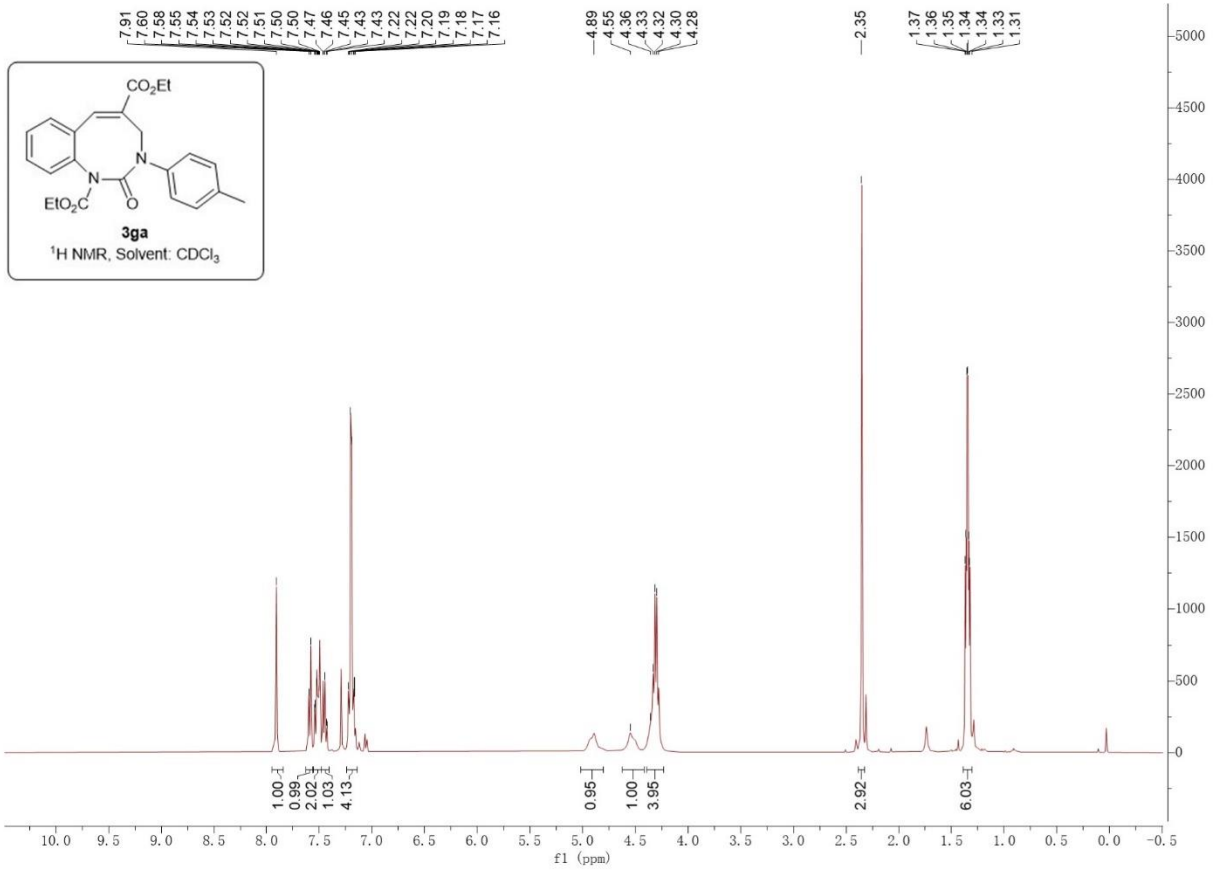
132.67
131.92
130.96
129.88
129.35
129.09
128.89
128.49
128.27
125.53
67.45
53.86
50.70
21.11
CO2Bn
MeO2C
3fa
13C NMR, Solvent: CDCl3
f1 (ppm)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7.50
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7.46
7.45
7.43
7.43
7.22
7.22
7.20
7.19
7.18
7.17
7.16
4.89
4.55
4.36
4.33
4.32
4.30
4.28
2.35
1.37
1.36
1.35
1.34
1.34
1.33
1.31
CO2Et
EtO2C
3ga
1H NMR, Solvent: CDCl3
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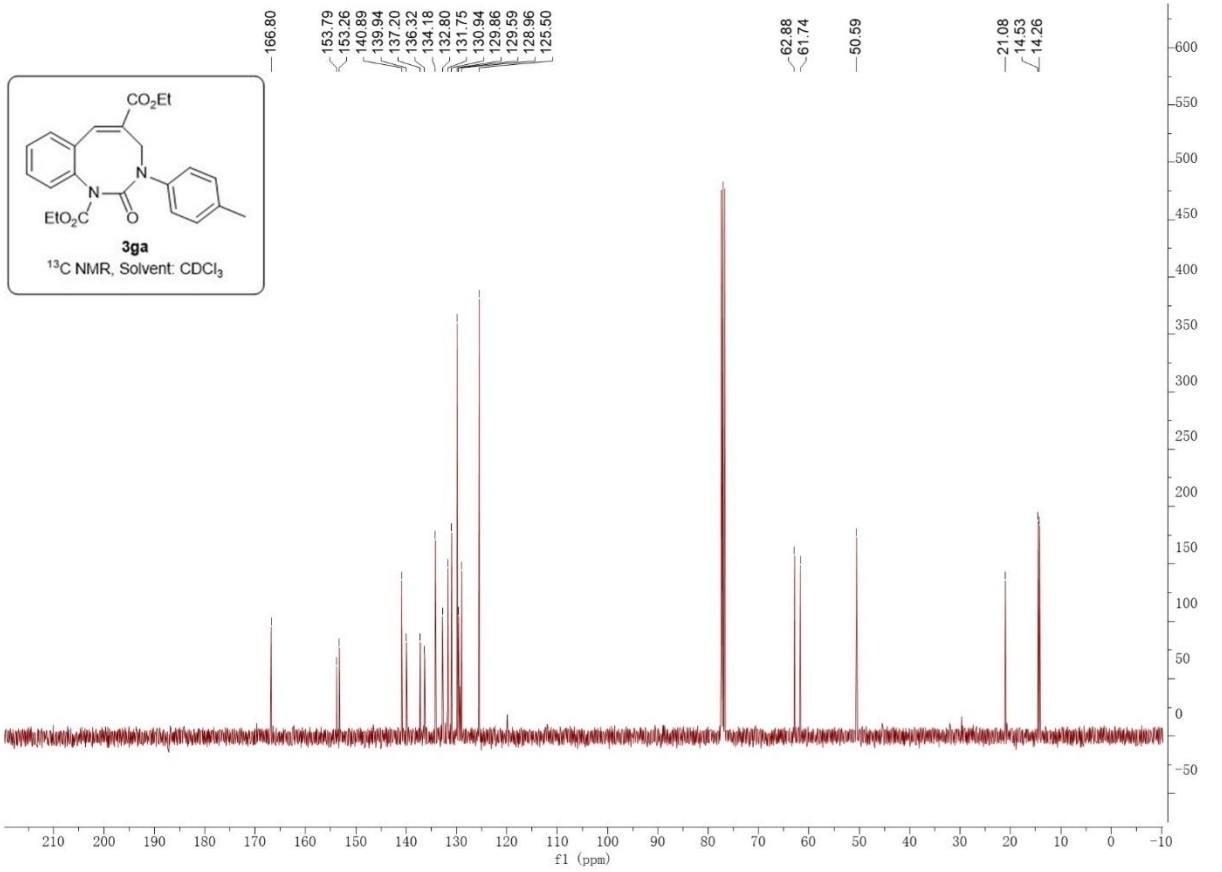
2.02
1.03
4.13
0.95
1.00
3.95
2.92
6.03
f1 (ppm)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129.59
128.96
125.50
62.88
61.74
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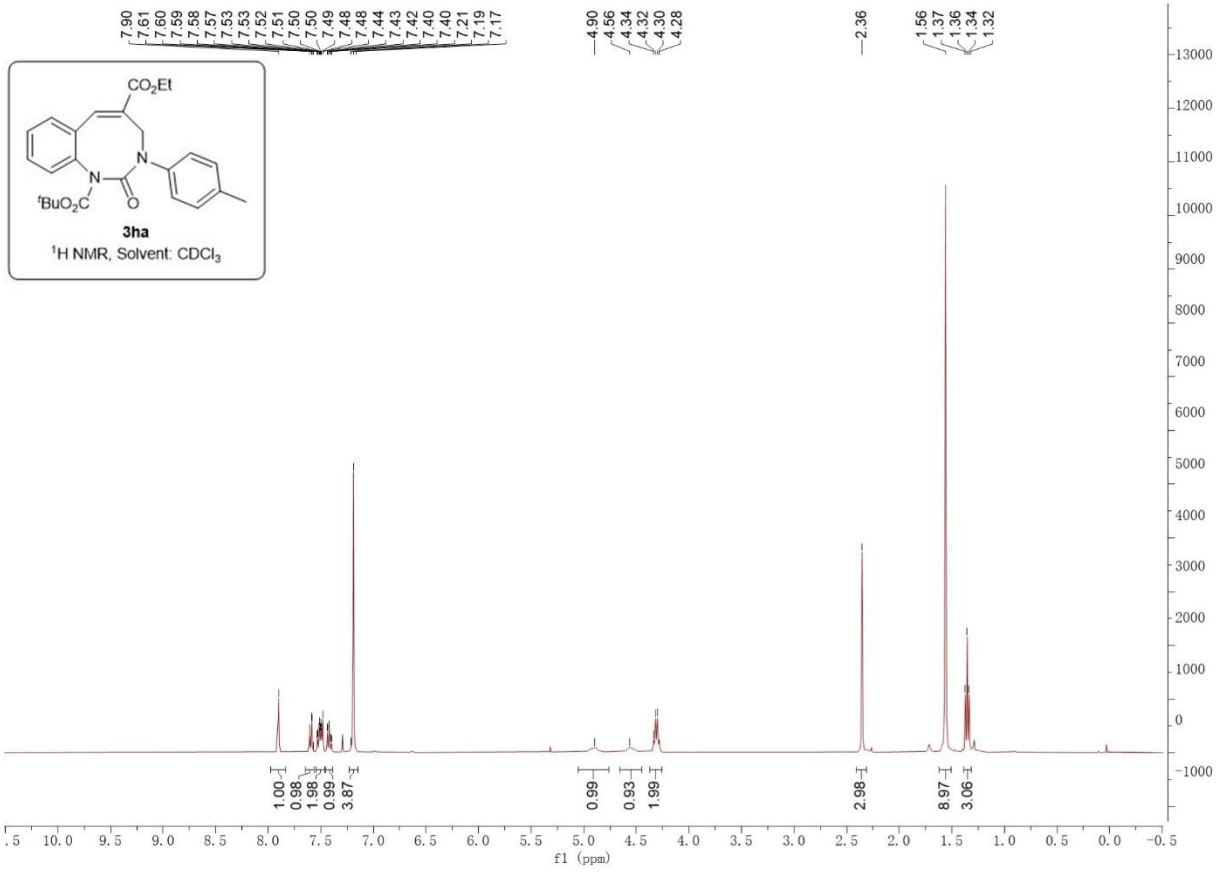
21.08
14.53
14.26
CO2Et
EtO2C
3ga
13C NMR, Solvent: CDCl3
f1 (ppm)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7.49
7.48
7.48
7.44
7.43
7.42
7.40
7.40
7.21
7.19
7.17
4.90
4.56
4.34
4.32
4.30
4.28
2.36
1.56
1.37
1.36
1.34
1.32
CO2Et
tBuO2C
3ha
1H NMR, Solvent: CDCl3
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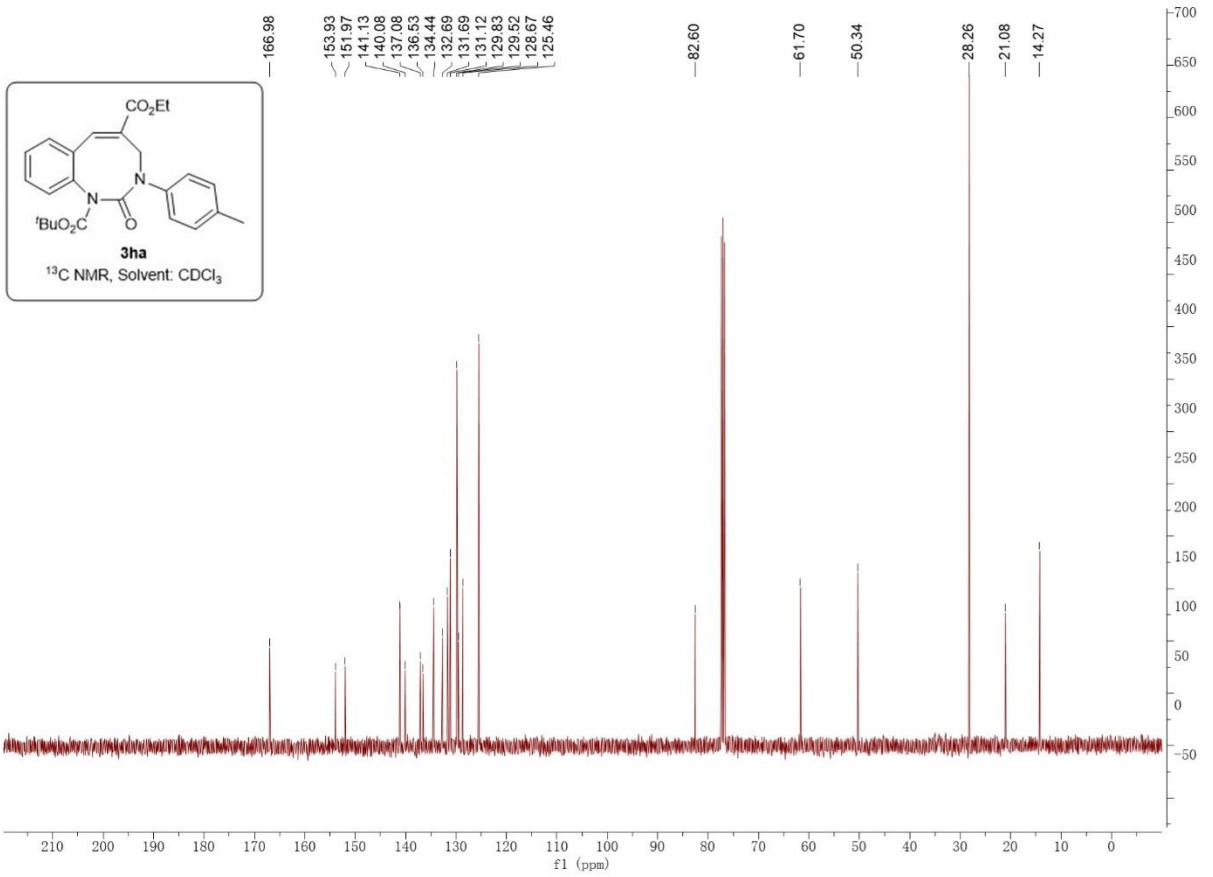
1.98
0.99
3.87
0.99
0.93
1.99
2.98
8.97
3.06
f1 (ppm)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129.52
128.67
125.46
82.60
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21.08
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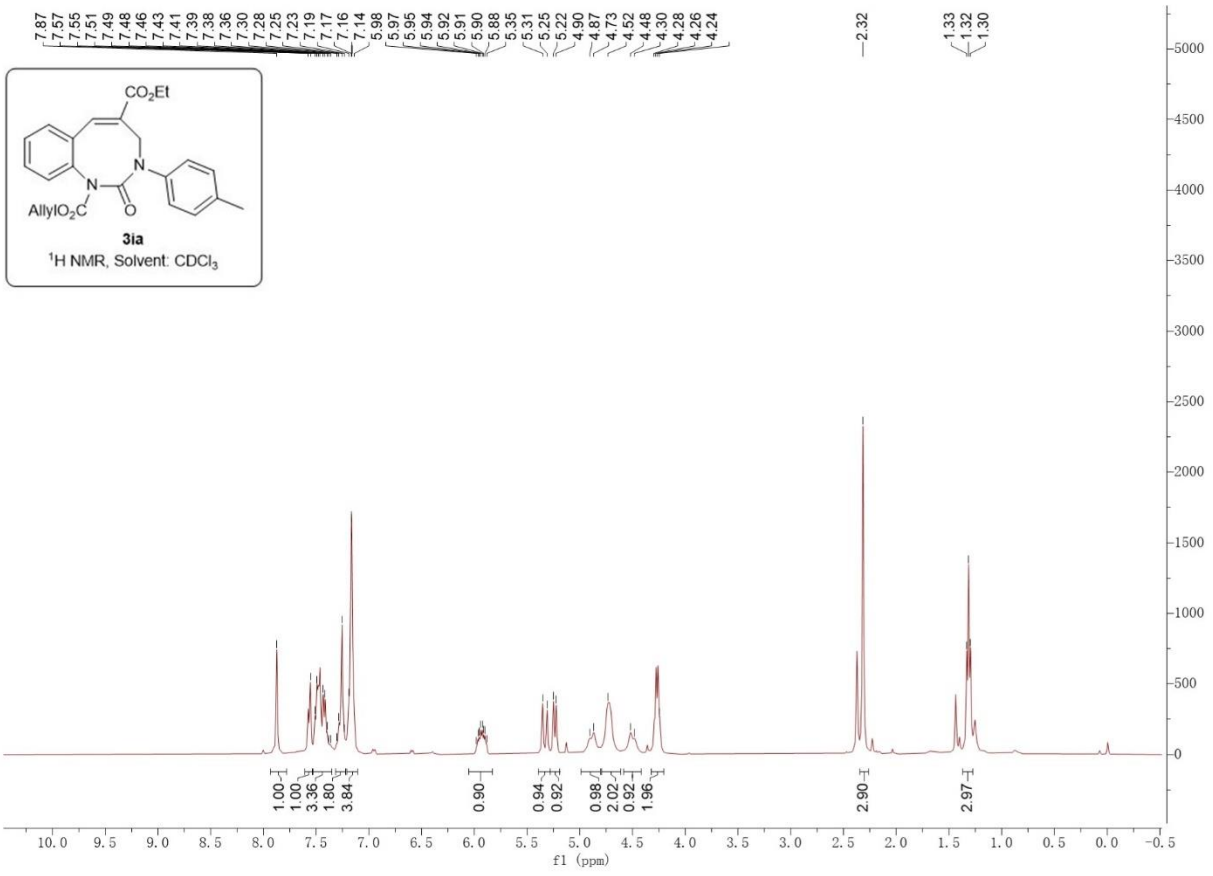
tBuO2C
3ha
13C NMR, Solvent: CDCl3
f1 (ppm)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7.30
7.28
7.25
7.23
7.19
7.17
7.16
7.14
5.98
5.97
5.95
5.94
5.92
5.91
5.90
5.88
5.35
5.31
5.25
5.22
4.90
4.87
4.73
4.52
4.48
4.30
4.28
4.26
4.24
2.32
1.33
1.32
1.30
CO2Et
AllylO2C
3ia
1H NMR, Solvent: CDCl3
1.00
1.00
3.36
1.80
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0.94
0.92
0.98
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0.92
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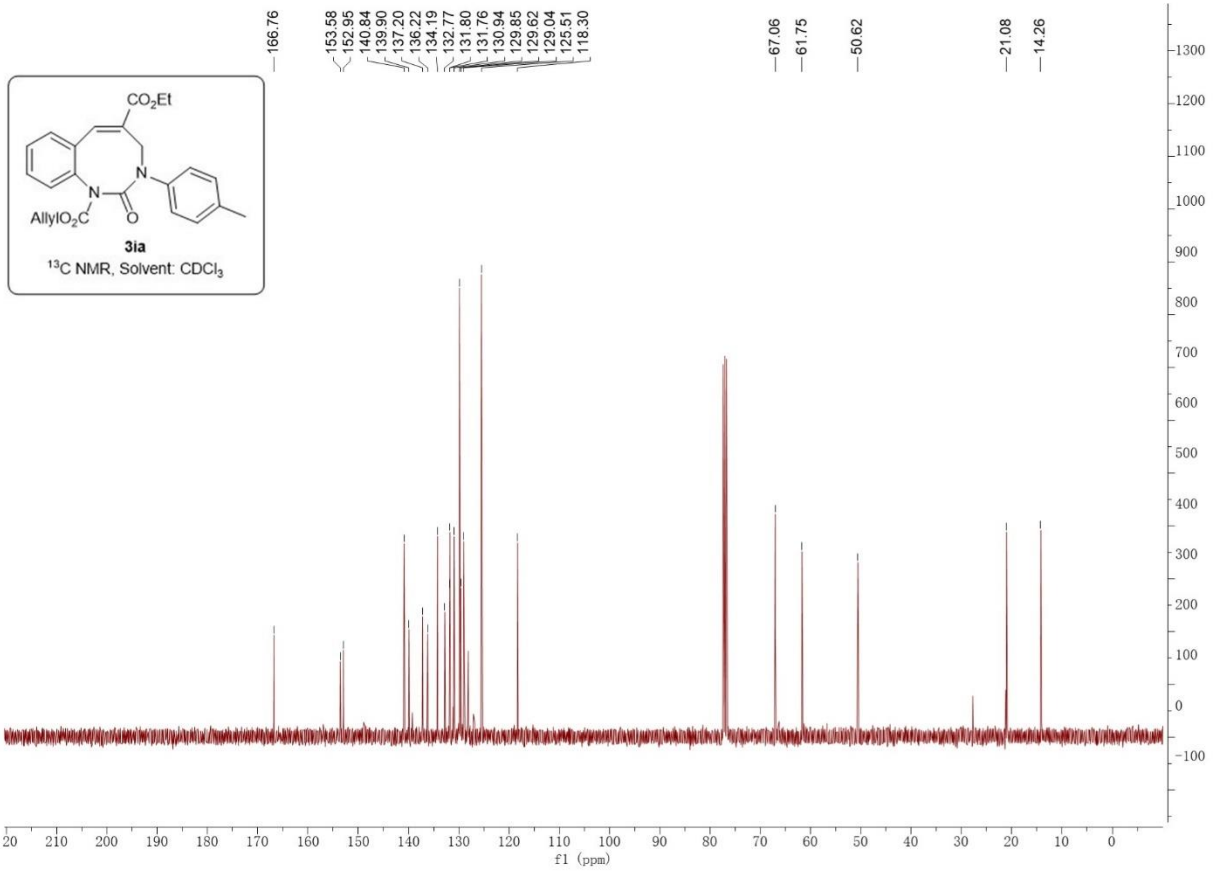
2.90
2.97
f1 (ppm)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129.62
129.04
125.51
118.30
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21.08
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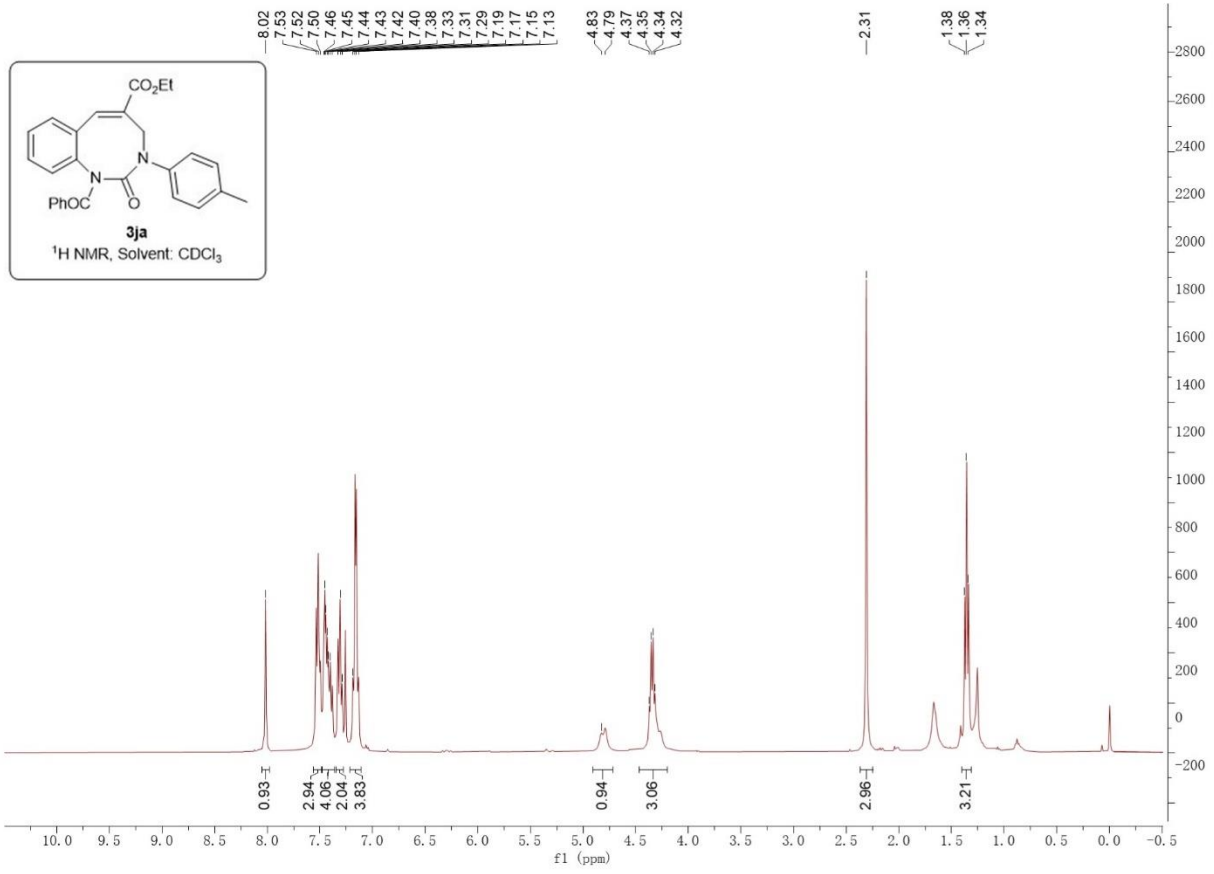
AllylO2C
3ia
13C NMR, Solvent: CDCl3
f1 (ppm)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7.33
7.31
7.29
7.19
7.17
7.15
7.13
4.83
4.79
4.37
4.35
4.34
4.32
2.31
1.38
1.36
1.34
CO2Et
PhOC
3ja
1H NMR, Solvent: CDCl3
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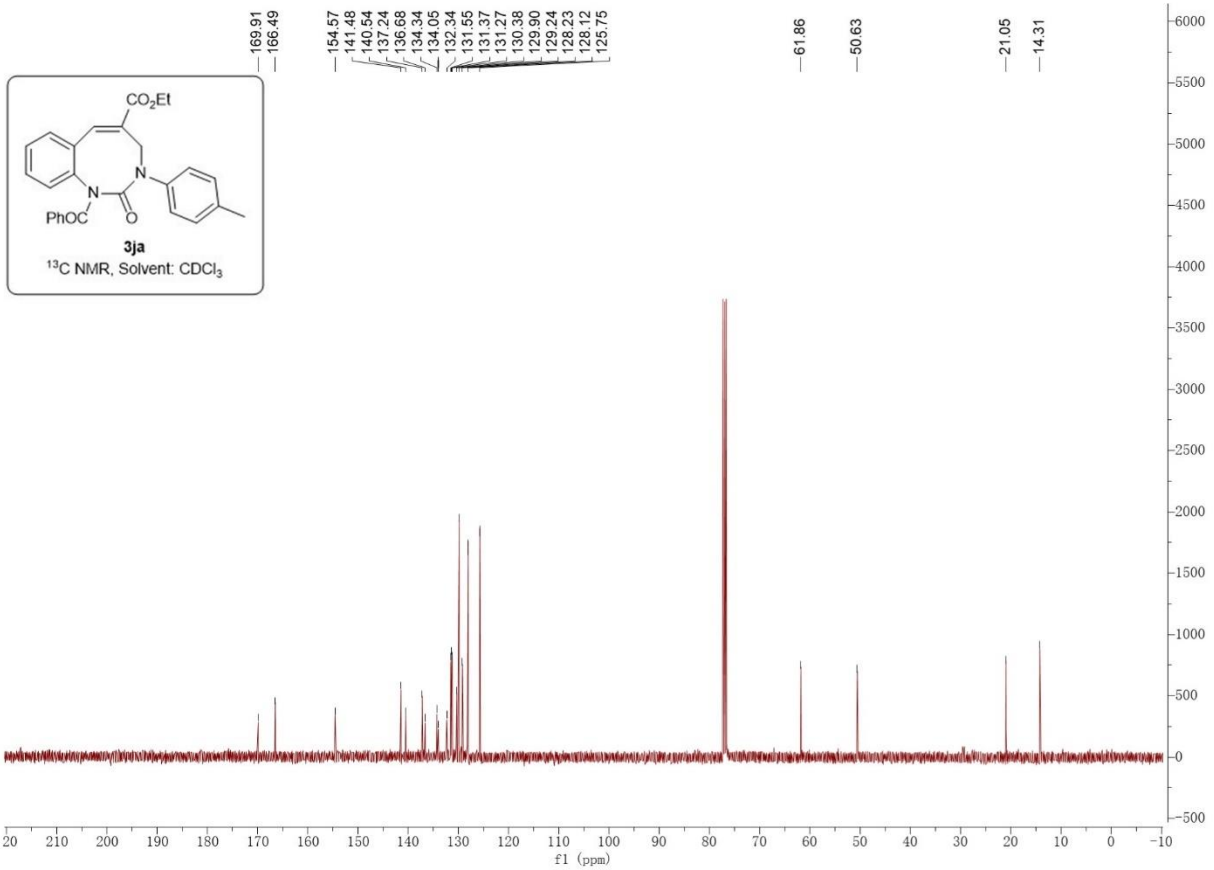
2.94
4.06
2.04
3.83
0.94
3.06
2.96
3.21
f1 (ppm)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131.37
131.27
130.38
129.90
129.24
128.23
128.12
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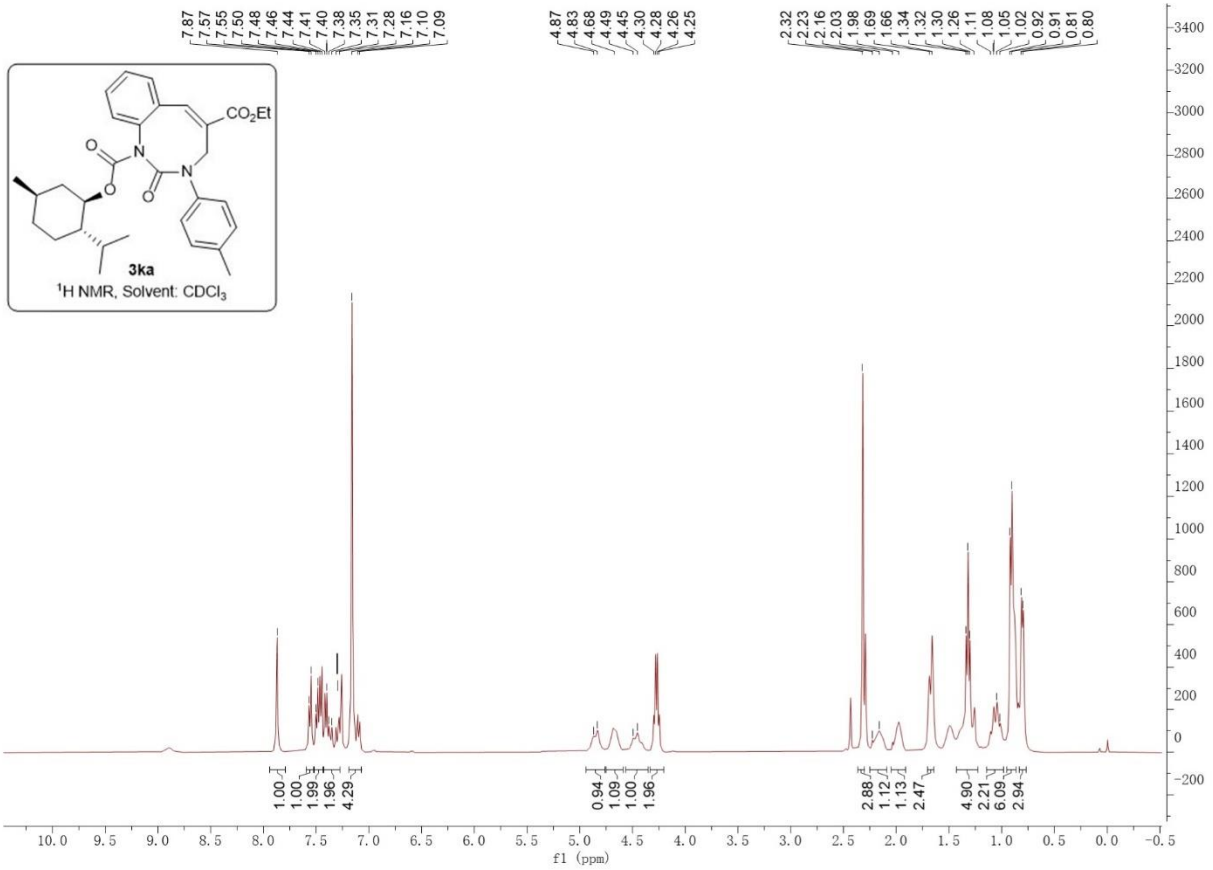
61.86
50.63
21.05
14.31
CO2Et
PhOC
3ja
13C NMR, Solvent: CDCl3
f1 (ppm)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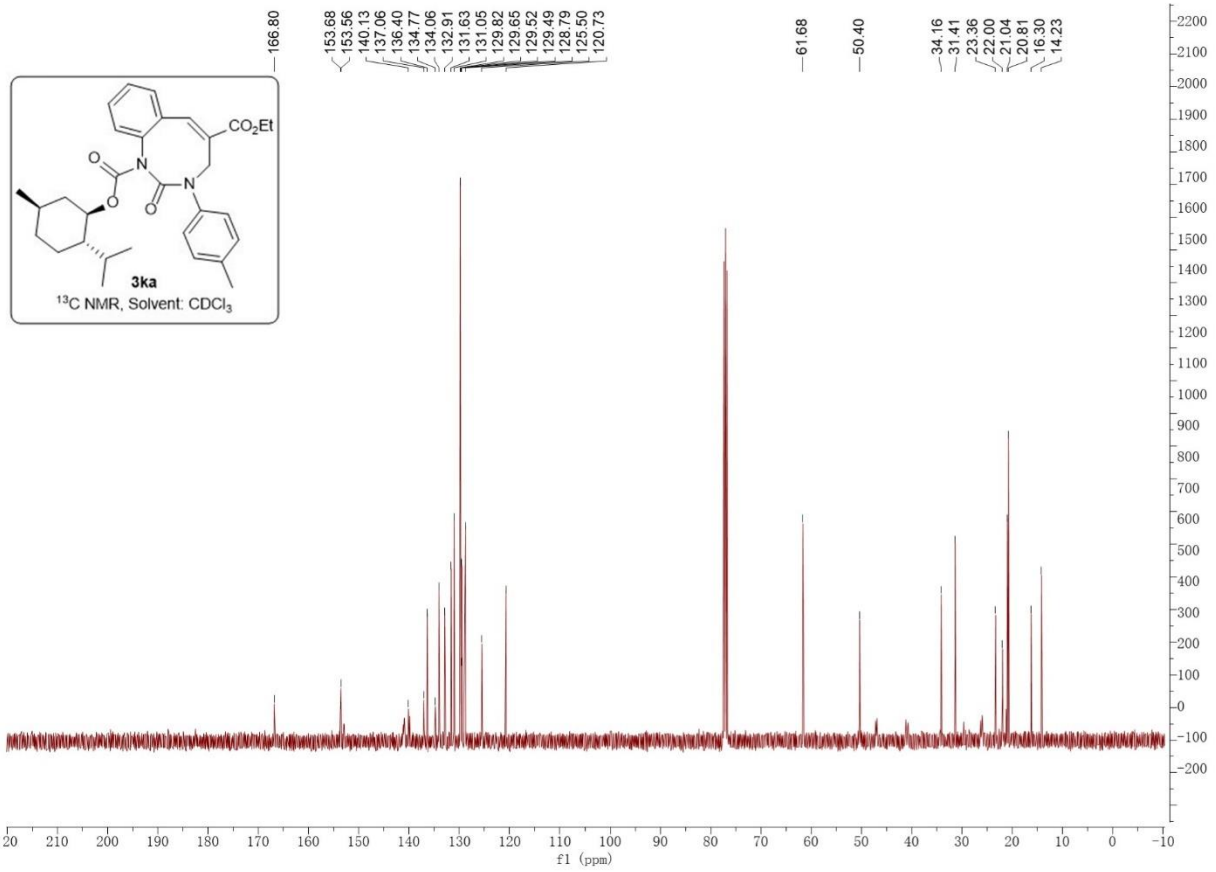
7.28
7.16
7.10
7.09
4.87
4.83
4.68
4.49
4.45
4.30
4.28
4.26
4.25
2.32
2.23
2.16
2.03
1.98
1.69
1.66
1.34
1.32
1.30
1.26
1.11
1.08
1.05
1.02
0.92
0.91
0.81
0.80
CO2Et
3ka
1H NMR, Solvent: CDCl3
1.00
1.00
1.99
1.96
4.29
0.94
1.09
1.00
1.96
2.88
1.12
1.13
2.47
4.90
2.21
6.09
2.94
f1 (ppm)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131.05
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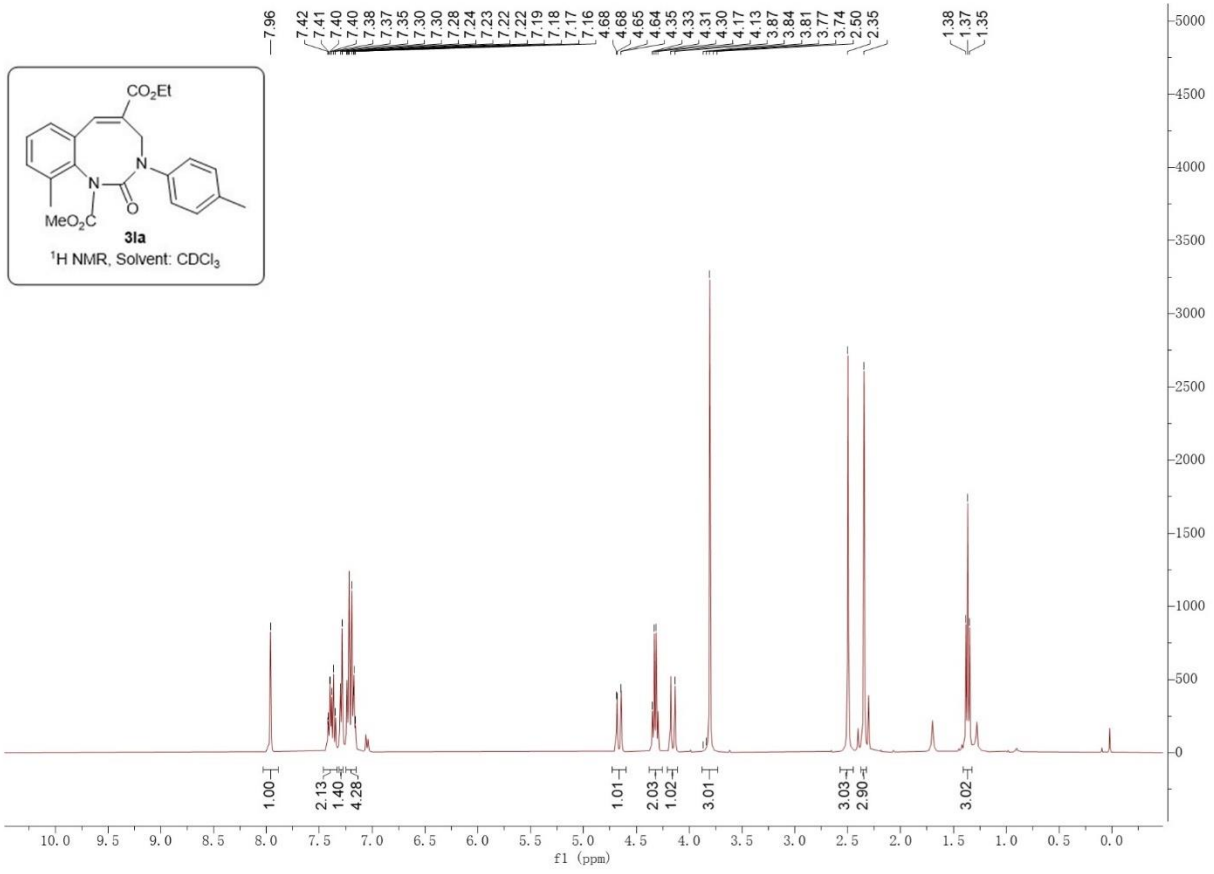
129.65
129.52
129.49
128.79
125.50
120.73
61.68
50.40
34.16
31.41
23.36
22.00
21.04
20.81
16.30
14.23
CO2Et
3ka
13C NMR, Solvent: CDCl3
f1 (ppm)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7.23
7.22
7.22
7.19
7.18
7.17
7.16
4.68
4.65
4.64
4.35
4.33
4.31
4.30
4.17
4.13
3.87
3.84
3.81
3.77
3.74
2.50
2.35
1.38
1.37
1.35
CO2Et
MeO2C
3la
1H NMR, Solvent: CDCl3
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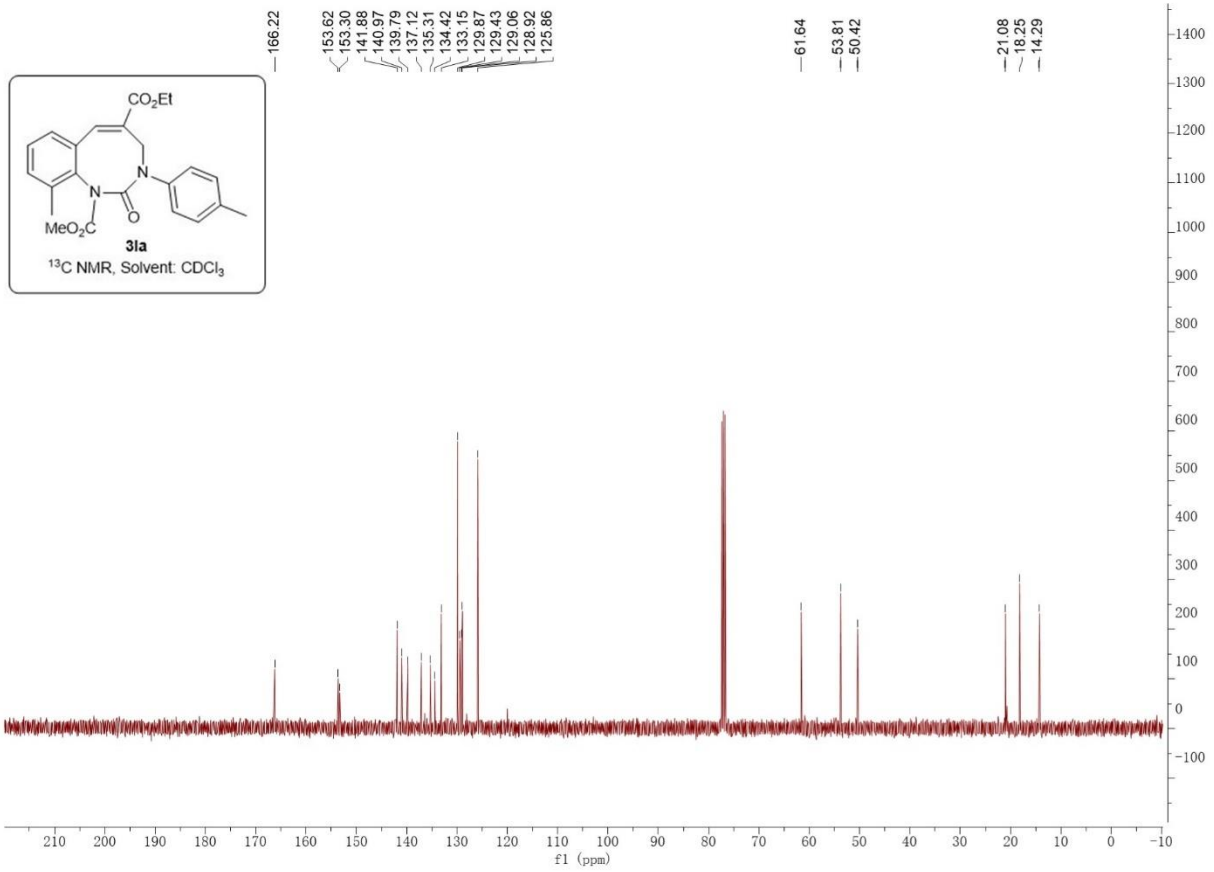
2.13
1.40
4.28
1.01
2.03
1.02
3.01
3.03
2.90
3.02
f1 (ppm)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129.06
128.92
125.86
61.64
53.81
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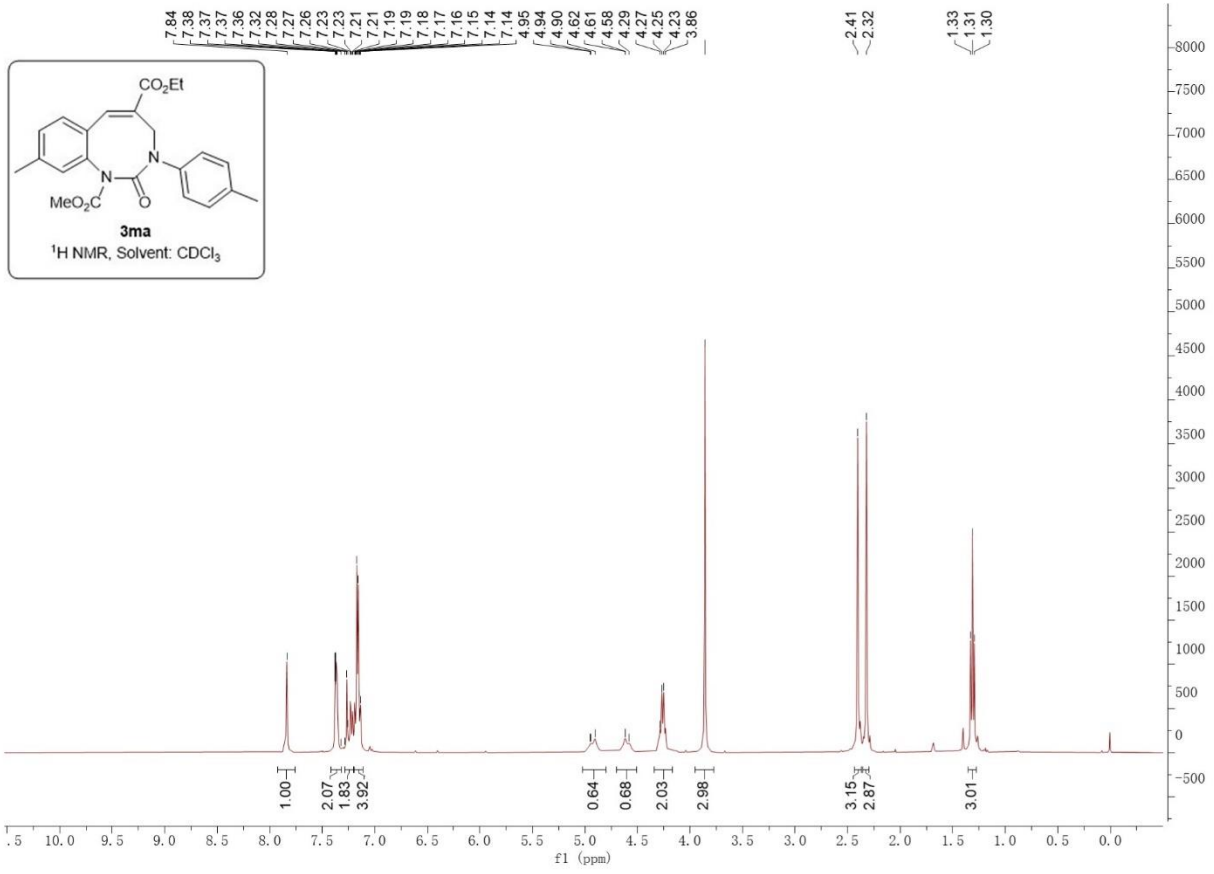
21.08
18.25
14.29
CO2Et
MeO2C
3la
13C NMR, Solvent: CDCl3
f1 (ppm)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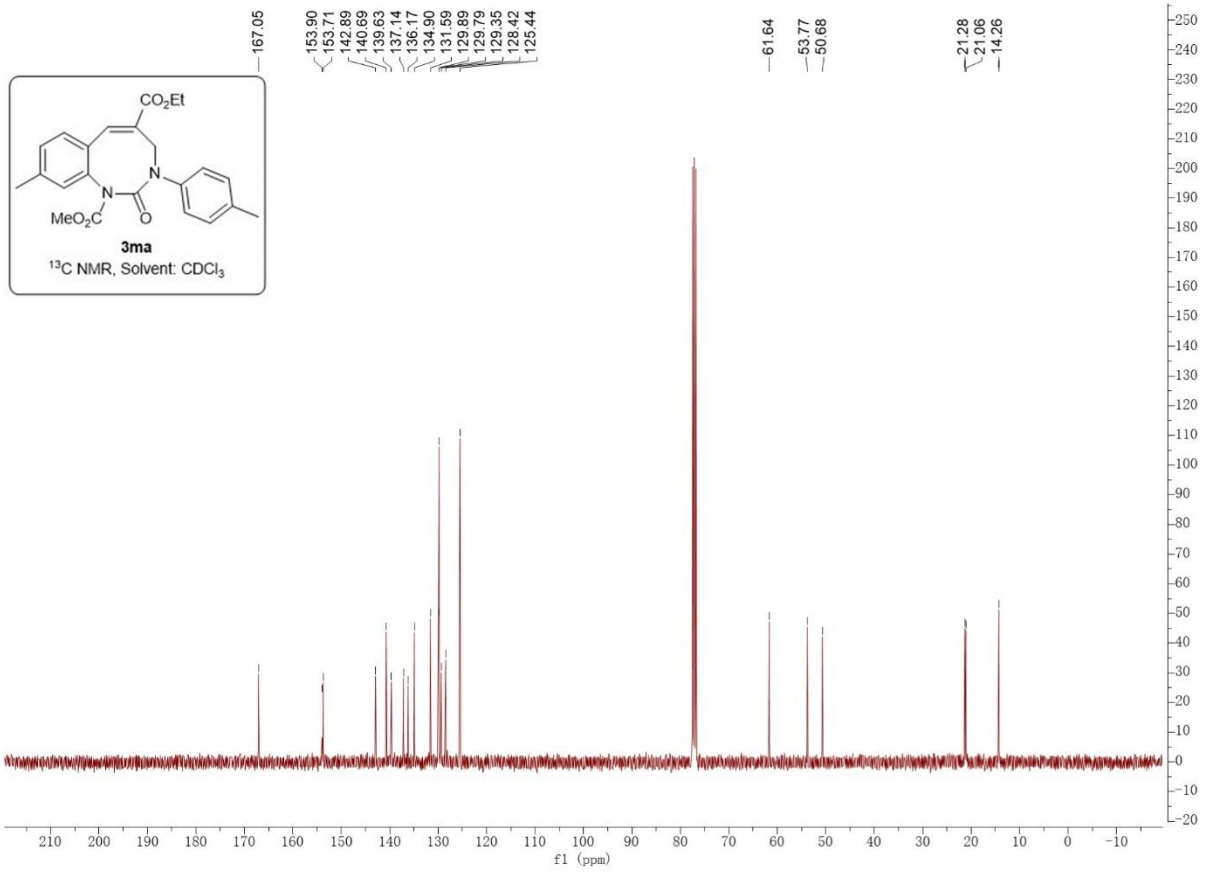
7.28
7.27
7.26
7.23
7.23
7.21
7.21
7.19
7.19
7.18
7.17
7.16
7.15
7.14
7.14
4.95
4.94
4.90
4.62
4.61
4.58
4.29
4.27
4.25
4.23
3.86
2.41
2.32
1.33
1.31
1.30
CO2Et
MeO2C
3ma
1H NMR, Solvent: CDCl3
1.00
2.07
1.83
3.92
0.64
0.68
2.03
2.98
3.15
2.87
3.01
f1 (ppm)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153.71
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136.17
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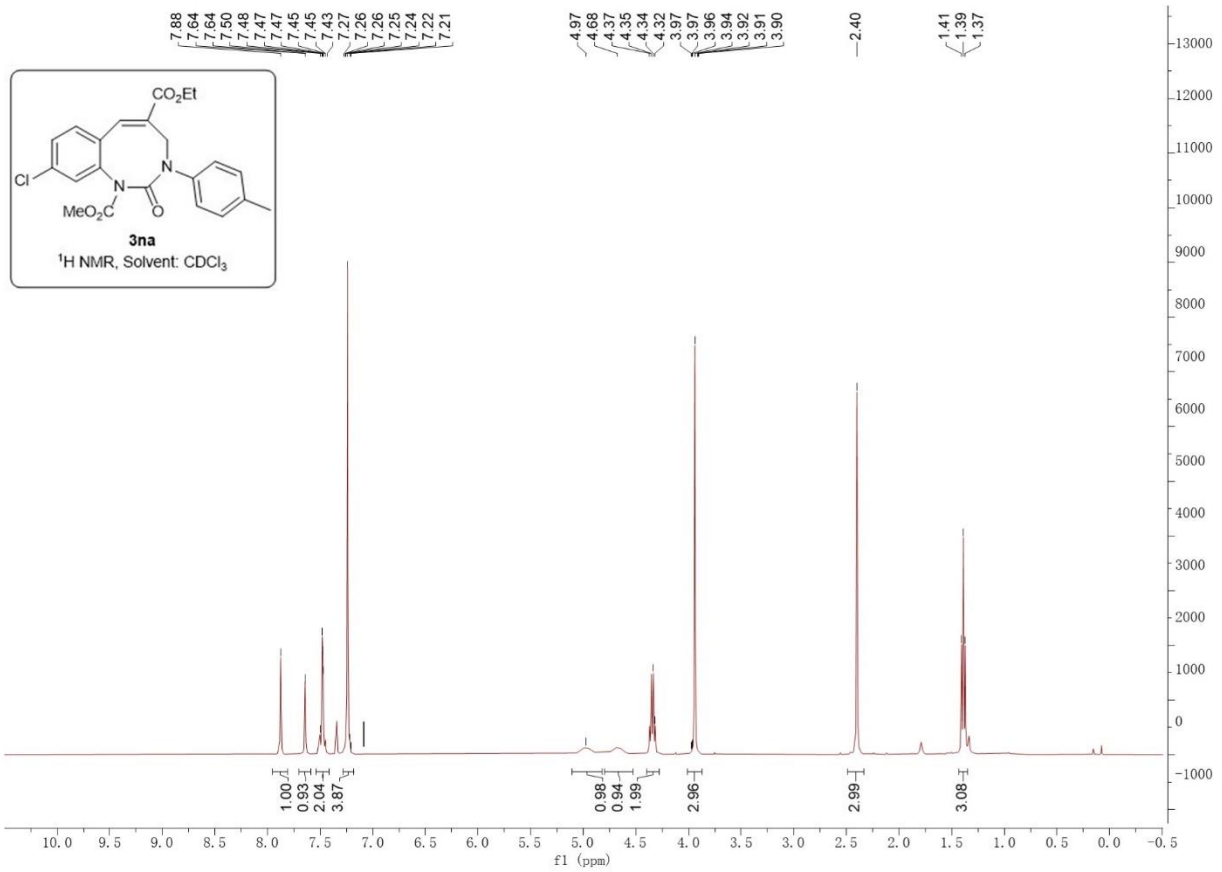
131.59
129.89
129.79
129.35
128.42
125.44
61.64
53.77
50.68
21.28
21.06
14.26
CO2Et
MeO2C
3ma
13C NMR, Solvent: CDCl3
f1 (ppm)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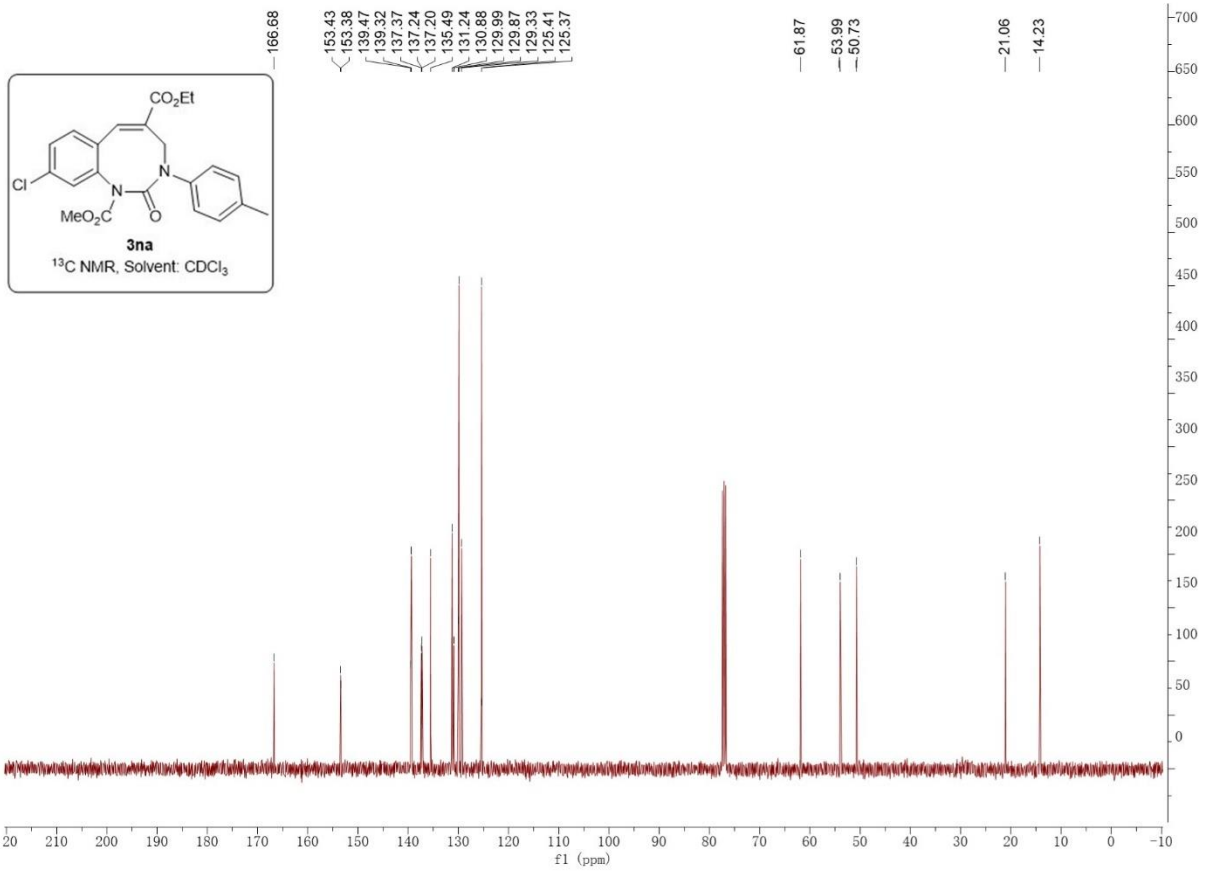
7.26
7.26
7.25
7.24
7.22
7.21
4.97
4.68
4.37
4.35
4.34
4.32
3.97
3.97
3.96
3.94
3.92
3.91
3.90
2.40
1.41
1.39
1.37
CO2Et
Cl
MeO2C
3na
1H NMR, Solvent: CDCl3
1.00
0.93
2.04
3.87
0.98
0.94
1.99
2.96
2.99
3.08
f1 (ppm)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137.20
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131.24
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129.99
129.87
129.33
125.41
125.37
61.87
53.99
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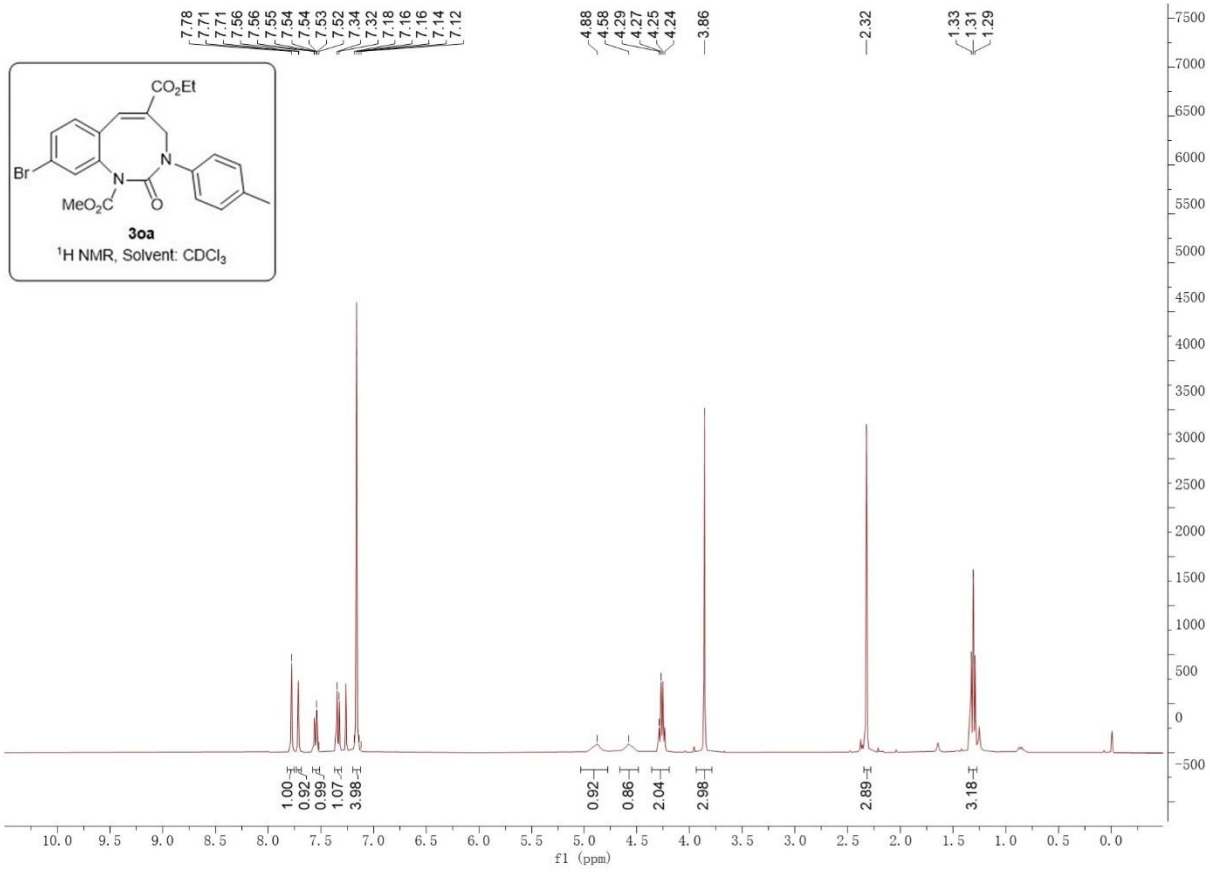
14.23
CO2Et
Cl
N
N
MeO2C
O
3na
13C NMR, Solvent: CDCl3
f1 (ppm)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7.54
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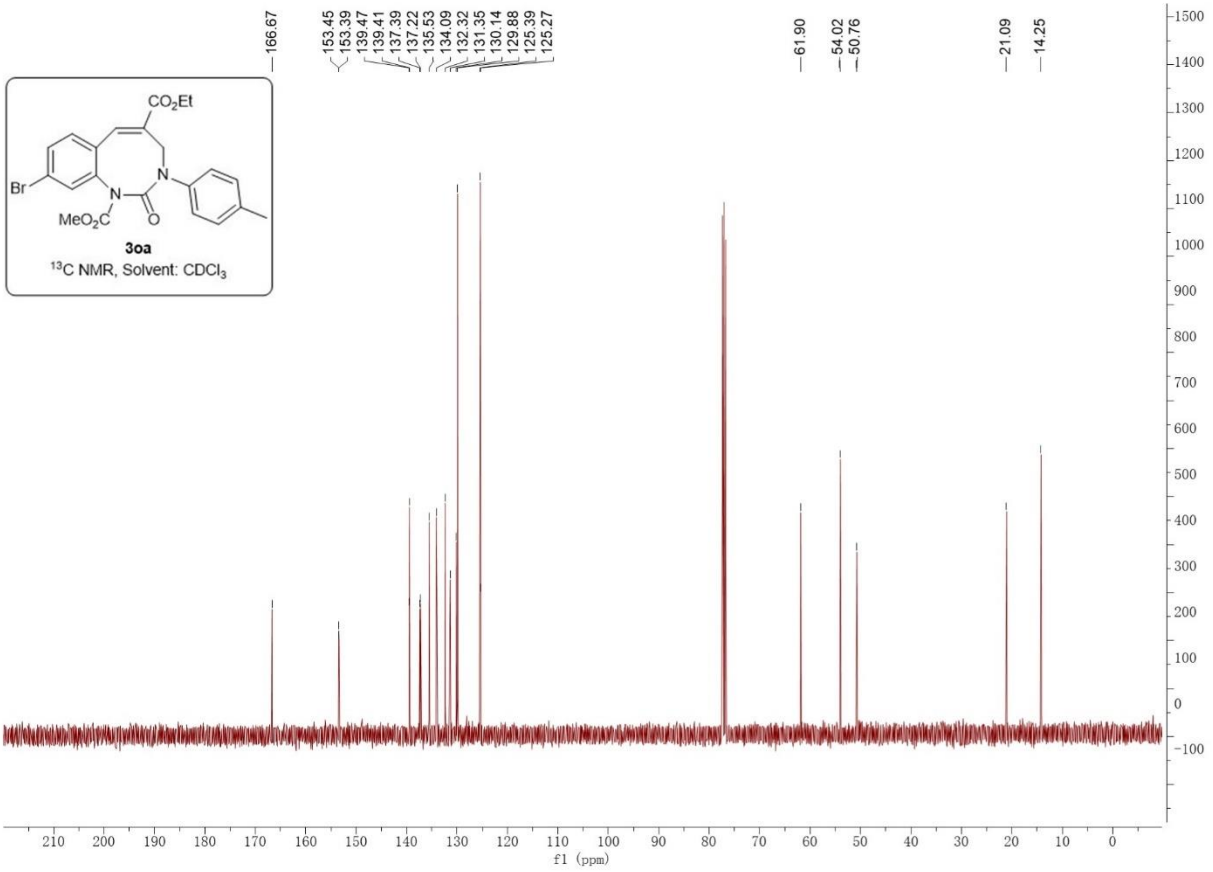
7.34
7.32
7.18
7.16
7.16
7.14
7.12
4.88
4.58
4.29
4.27
4.25
4.24
3.86
2.32
1.33
1.31
1.29
CO2Et
Br
N
N
MeO2C
O
3oa
1H NMR, Solvent: CDCl3
1.00
0.92
0.99
1.07
3.98
0.92
0.86
2.04
2.98
2.89
3.18
f1 (ppm)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135.53
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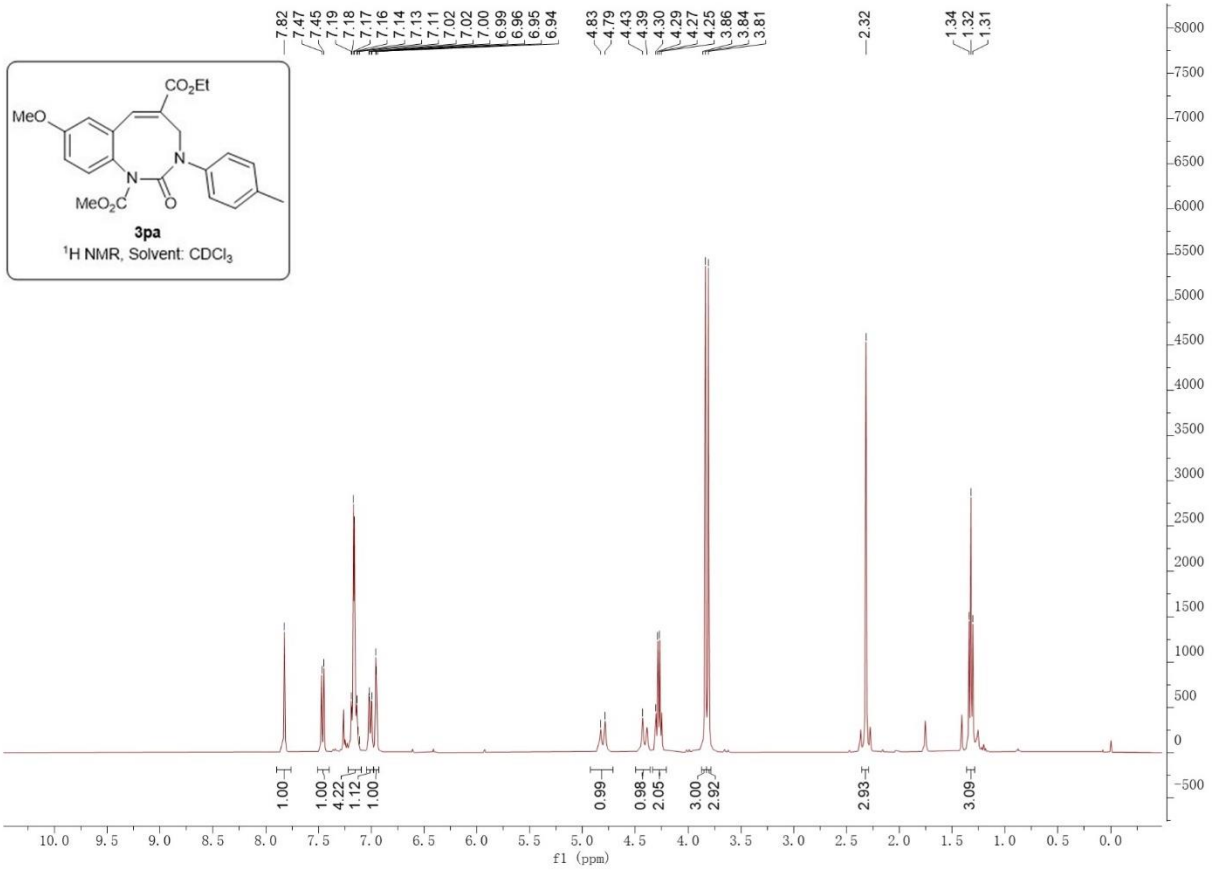
132.32
131.35
130.14
129.88
125.39
125.27
61.90
54.02
50.76
21.09
14.25
CO2Et
Br
N
N
MeO2C
O
3oa
13C NMR, Solvent: CDCl3
f1 (ppm)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7.18
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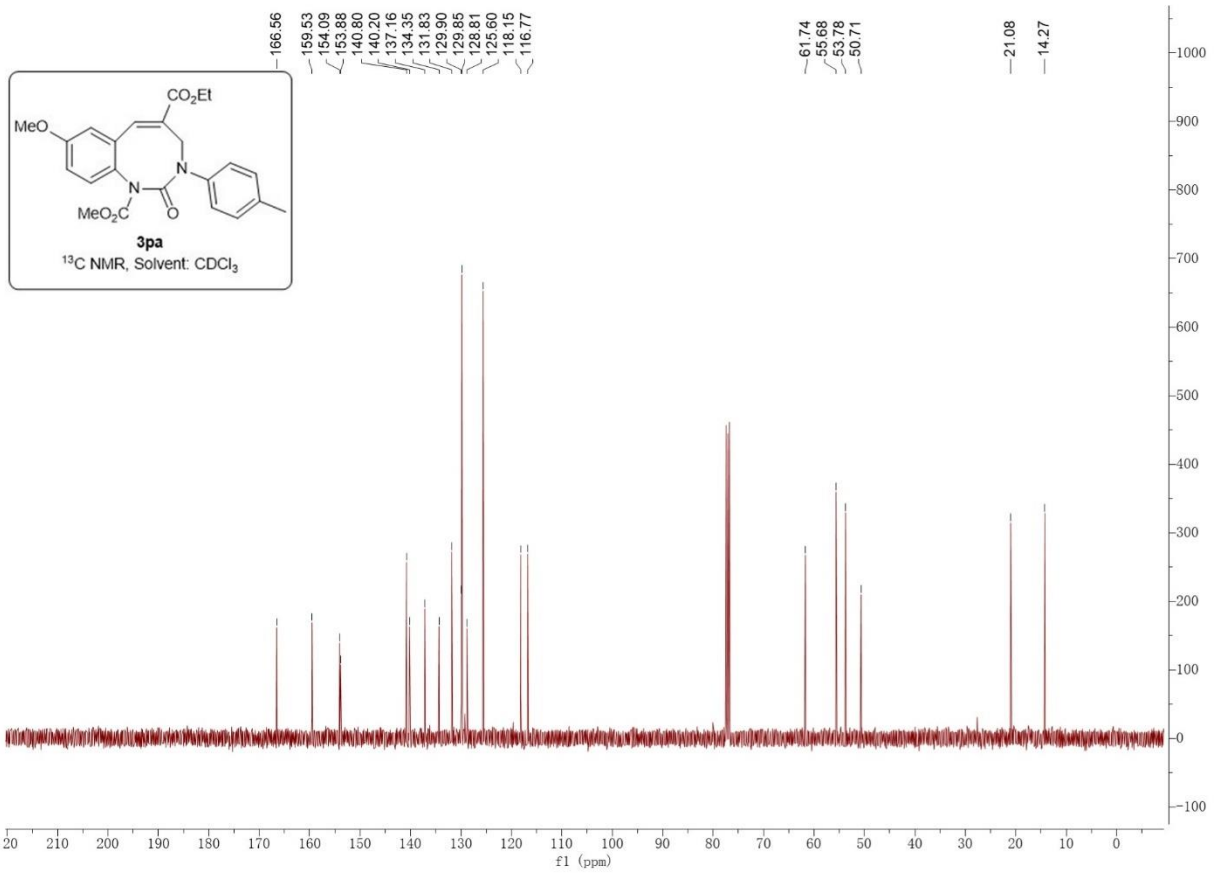
7.16
7.14
7.13
7.11
7.02
7.02
7.00
6.99
6.96
6.95
6.94
4.83
4.79
4.43
4.39
4.30
4.29
4.27
4.25
3.86
3.84
3.81
2.32
1.34
1.32
1.31
CO2Et
MeO
N
N
MeO2C
O
3pa
1H NMR, Solvent: CDCl3
1.00
1.00
4.22
1.12
1.00
0.99
0.98
2.05
3.00
2.92
2.93
3.09
f1 (ppm)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154.09
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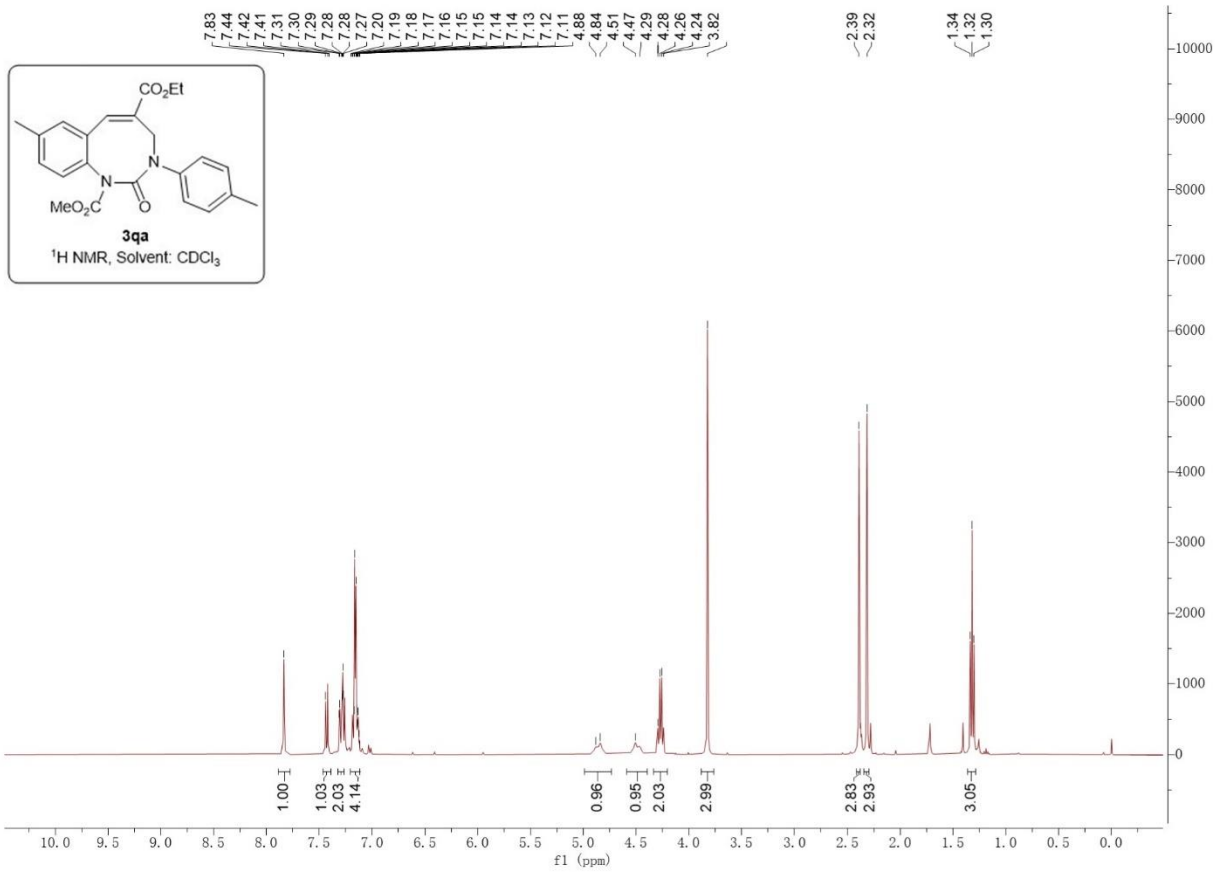
140.80
140.20
137.16
134.35
131.83
129.90
129.85
128.81
125.60
118.15
116.77
61.74
55.68
53.78
50.71
21.08
14.27
CO2Et
MeO
N
N
MeO2C
O
3pa
13C NMR, Solvent: CDCl3
f1 (ppm)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7.20
7.19
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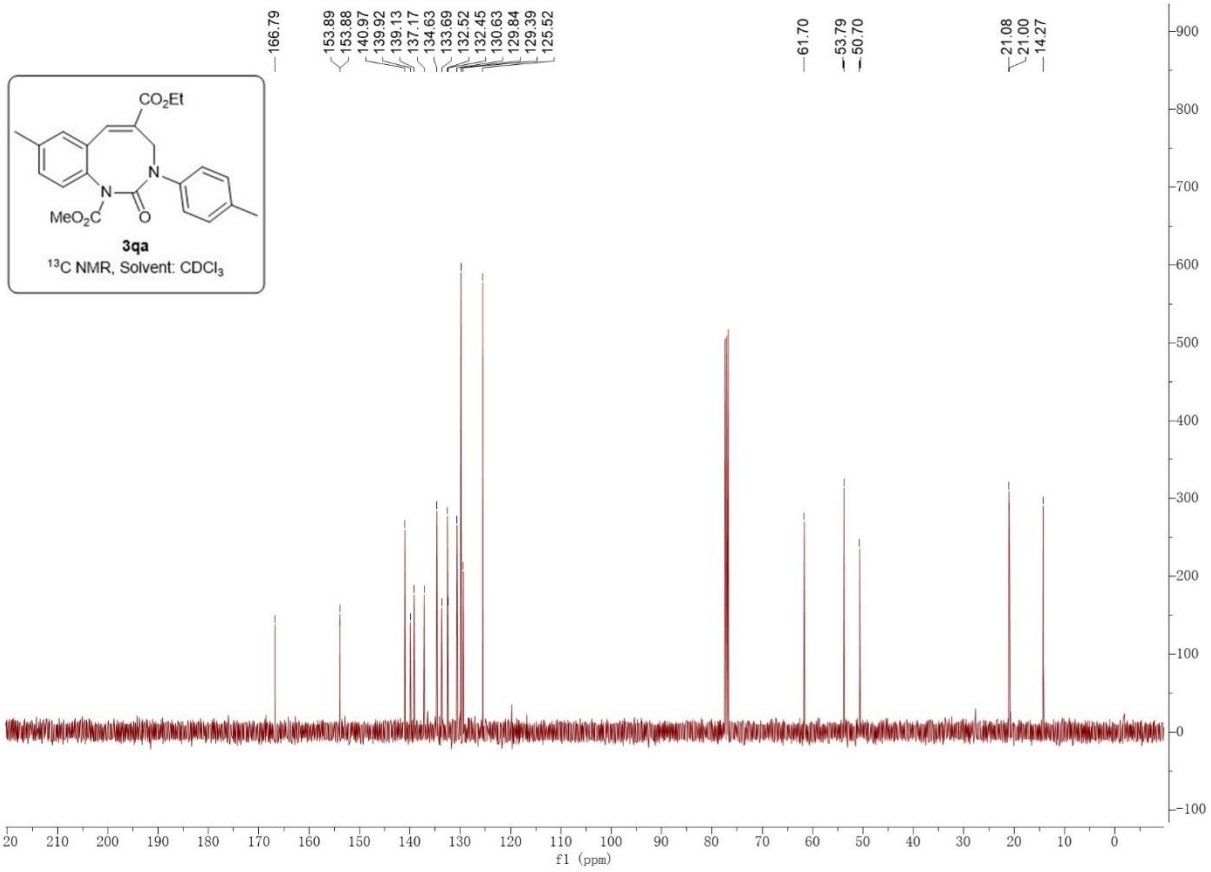
7.17
7.16
7.15
7.15
7.14
7.14
7.13
7.12
7.11
4.88
4.84
4.51
4.47
4.29
4.28
4.26
4.24
3.82
2.39
2.32
1.34
1.32
1.30
CO2Et
N
N
MeO2C
O
3qa
1H NMR, Solvent: CDCl3
1.00
1.03
2.03
4.14
0.96
0.95
2.03
2.99
2.83
2.93
3.05
f1 (ppm)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140.97
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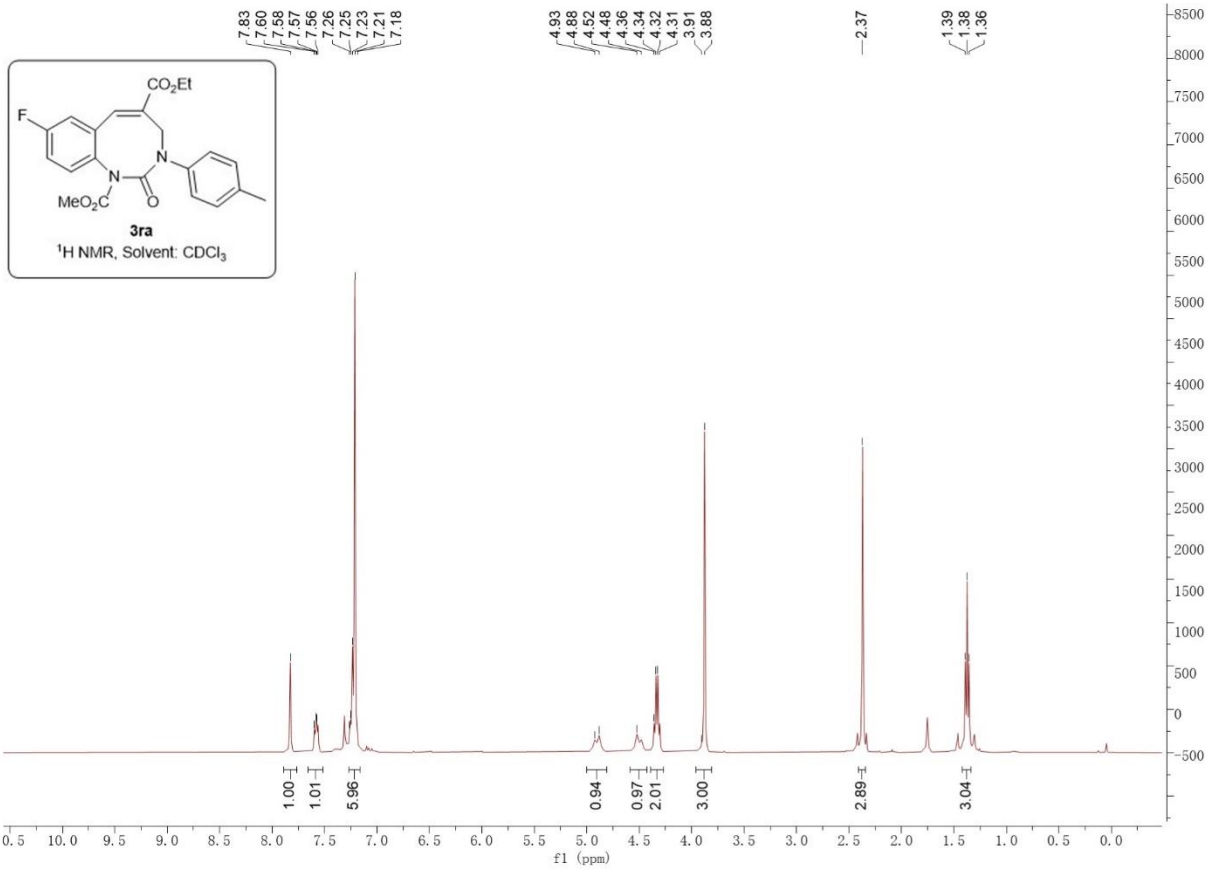
139.13
137.17
134.63
133.69
132.52
132.45
130.63
129.84
129.39
125.52
61.70
53.79
50.70
21.08
21.00
14.27
CO2Et
MeO2C
3qa
13C NMR, Solvent: CDCl3
f1 (ppm)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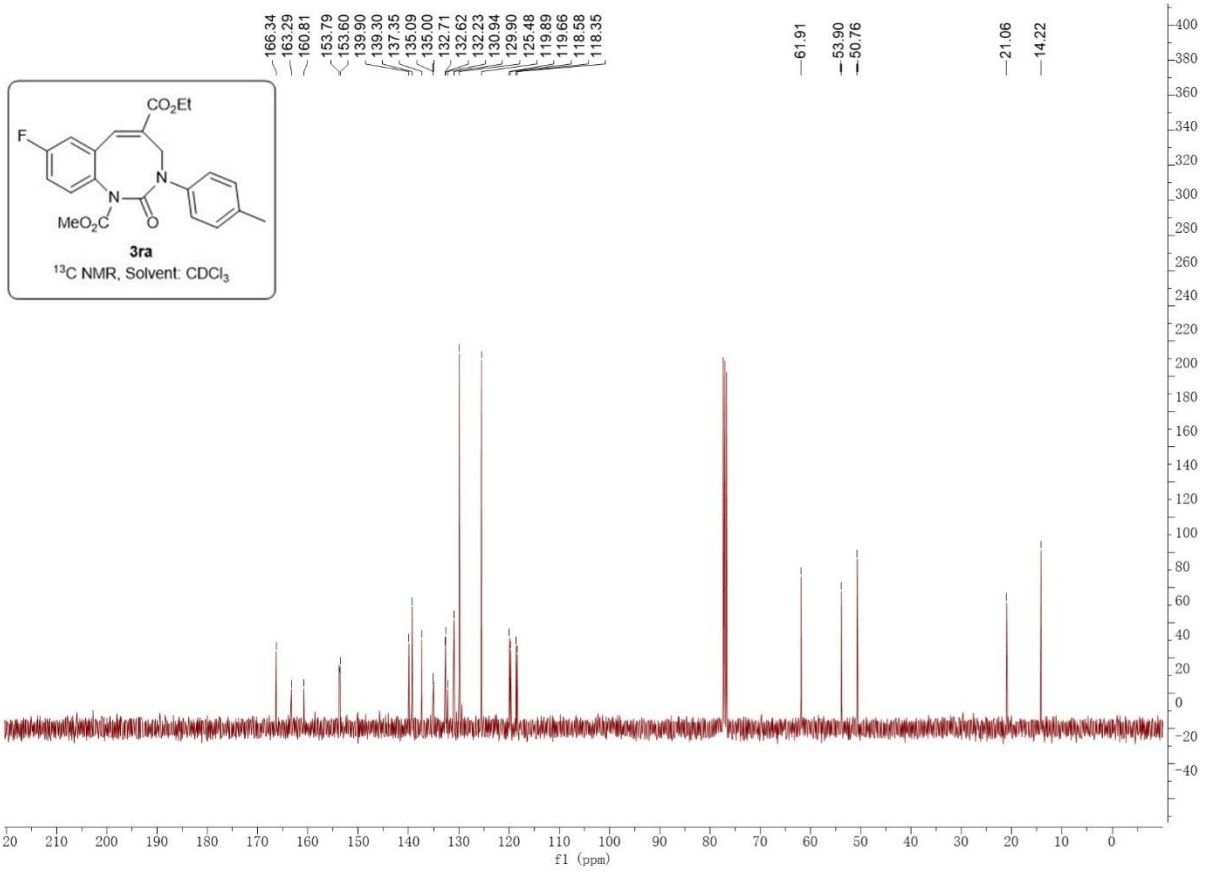
7.60
7.58
7.57
7.56
7.26
7.25
7.23
7.21
7.18
4.93
4.88
4.52
4.48
4.36
4.34
4.32
4.31
3.91
3.88
2.37
1.39
1.38
1.36
CO2Et
F
MeO2C
3ra
1H NMR, Solvent: CDCl3
1.00
1.01
5.96
0.94
0.97
2.01
3.00
2.89
3.04
f1 (ppm)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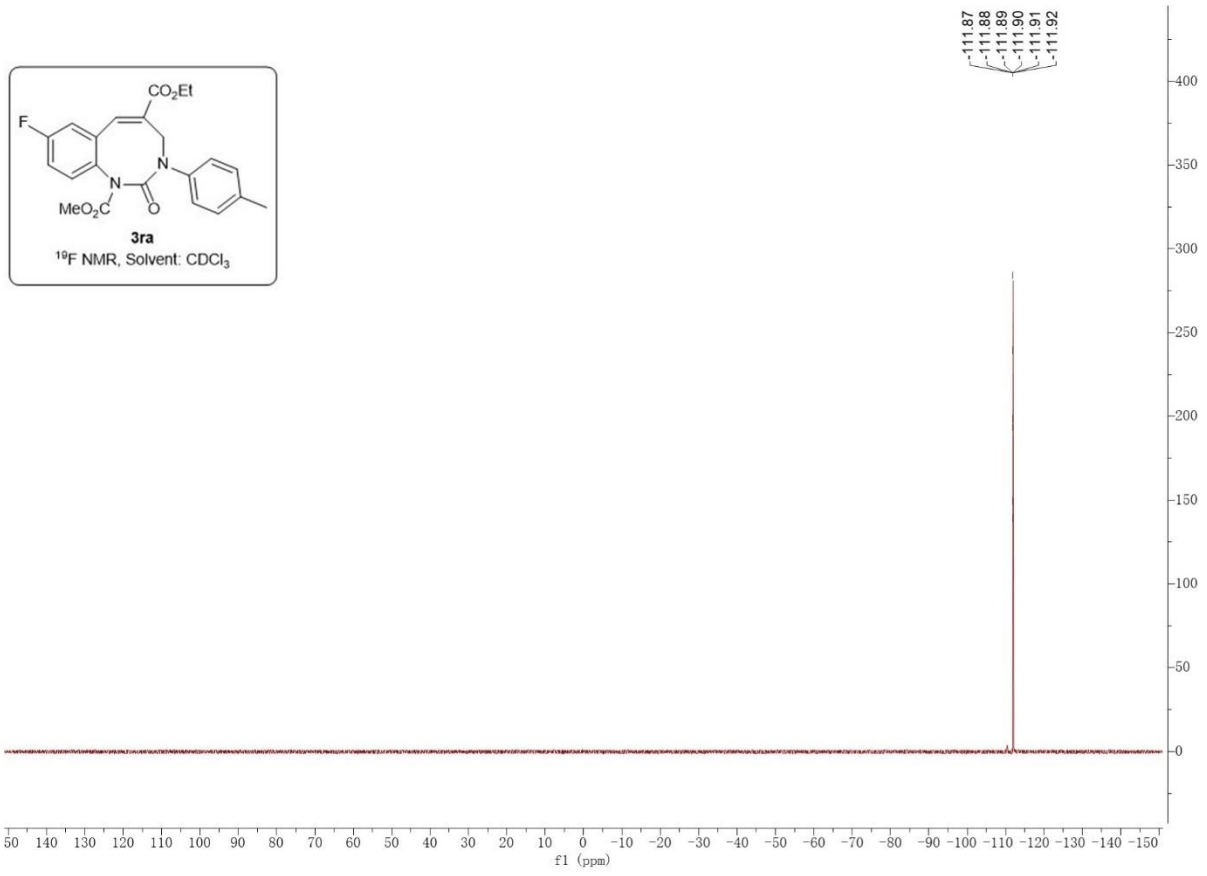
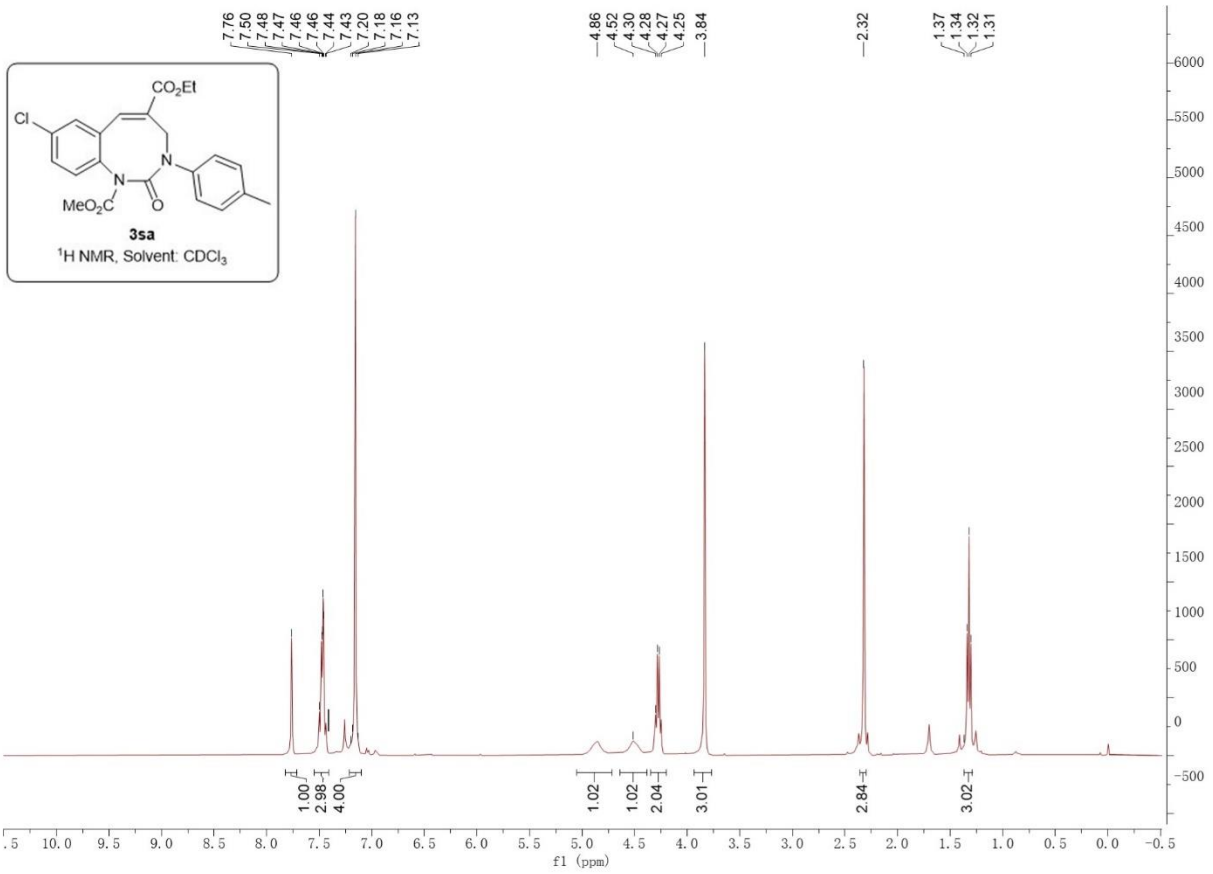
163.29
160.81
153.79
153.60
139.90
139.30
137.35
135.09
135.00
132.71
132.62
132.23
130.94
129.90
125.48
119.89
119.66
118.58
118.35
61.91
53.90
50.76
21.06
14.22
CO2Et
F
N
N
MeO2C
O
3ra
13C NMR, Solvent: CDCl3
f1 (ppm)


-111.87
-111.88
-111.89
-111.90
-111.91
-111.92
CO2Et
F
N
N
MeO2C
O
3ra
19F NMR, Solvent: CDCl3
f1 (ppm)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7.44
7.43
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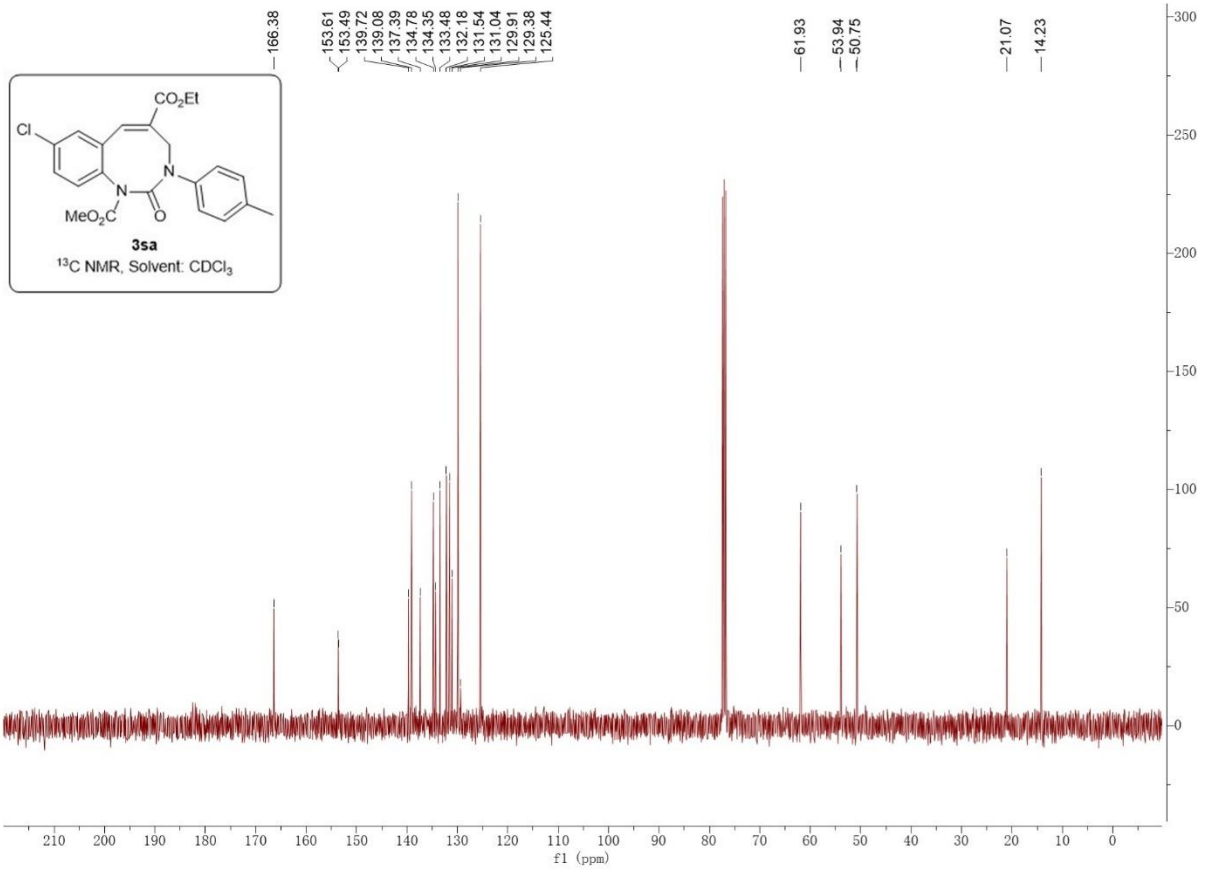
7.18
7.16
7.13
4.86
4.52
4.30
4.28
4.27
4.25
3.84
2.32
1.37
1.34
1.32
1.31
1.00
2.98
4.00
1.02
1.02
2.04
3.01
2.84
3.02
f1 (ppm)
3sa
1H NMR, Solvent: CDCl3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153.61
153.49
139.72
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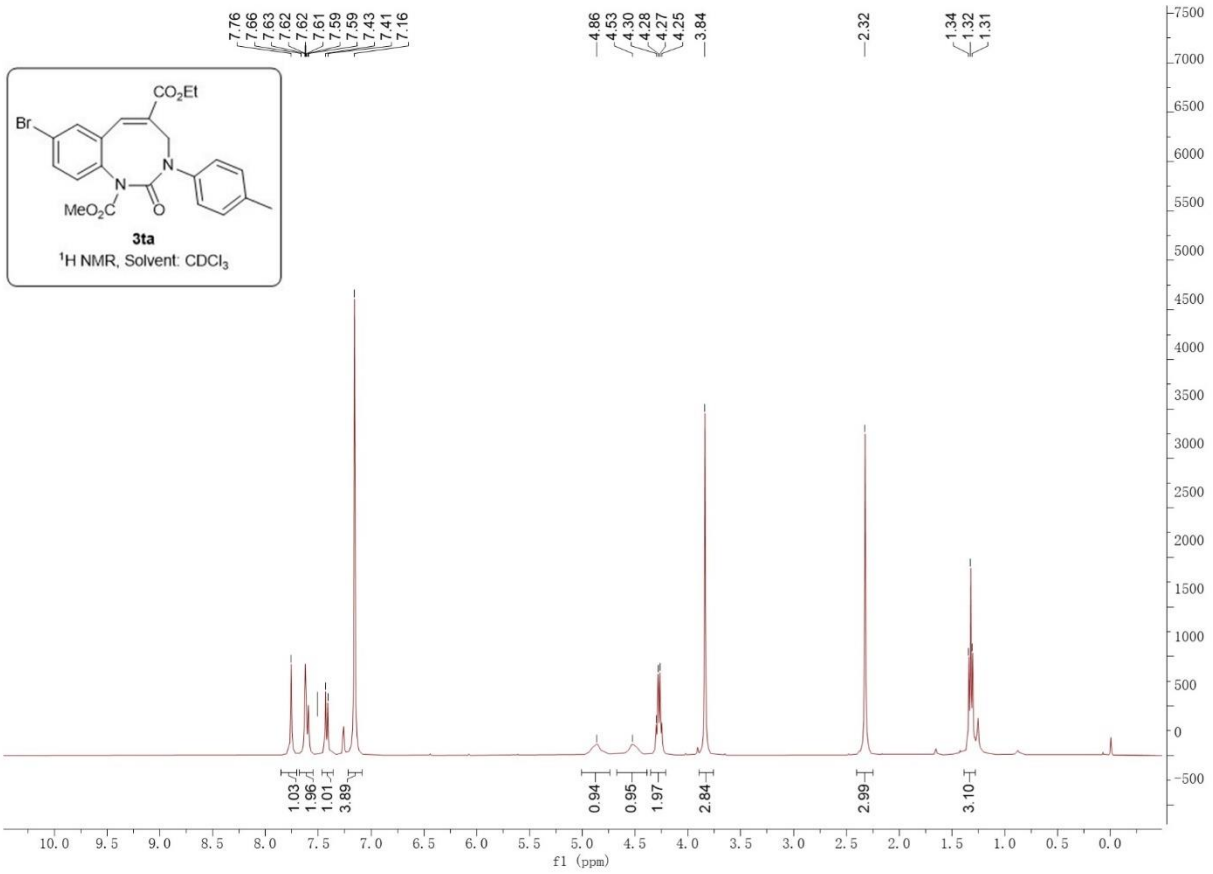
137.39
134.78
134.35
133.48
132.18
131.54
131.04
129.91
129.38
125.44
61.93
53.94
50.75
21.07
14.23
f1 (ppm)
3sa
13C NMR, Solvent: CDCl3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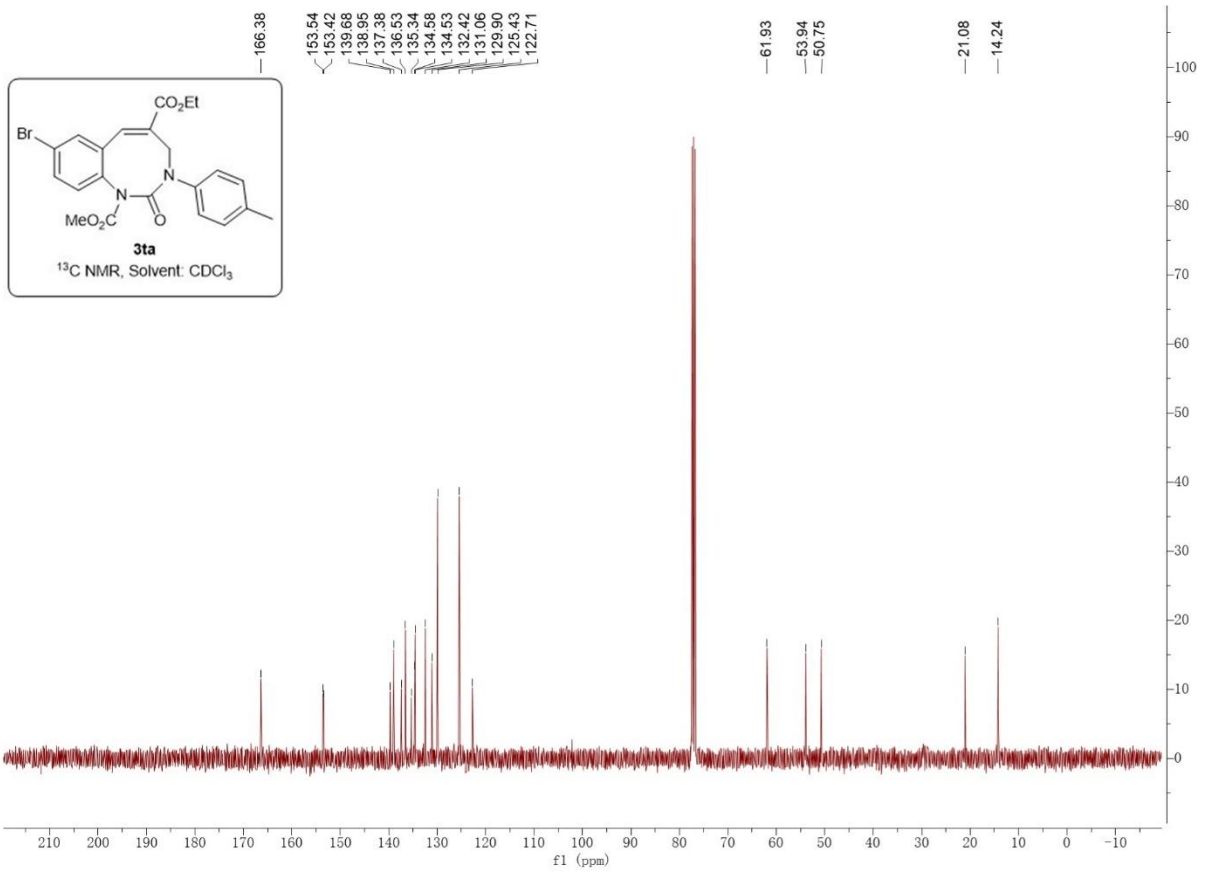
7.63
7.62
7.62
7.61
7.59
7.59
7.43
7.41
7.16
4.86
4.53
4.30
4.28
4.27
4.25
3.84
2.32
1.34
1.32
1.31
CO2Et
Br
N
N
MeO2C
O
3ta
1H NMR, Solvent: CDCl3
1.03
1.96
1.01
3.89
0.94
0.95
1.97
2.84
2.99
3.10
f1 (ppm)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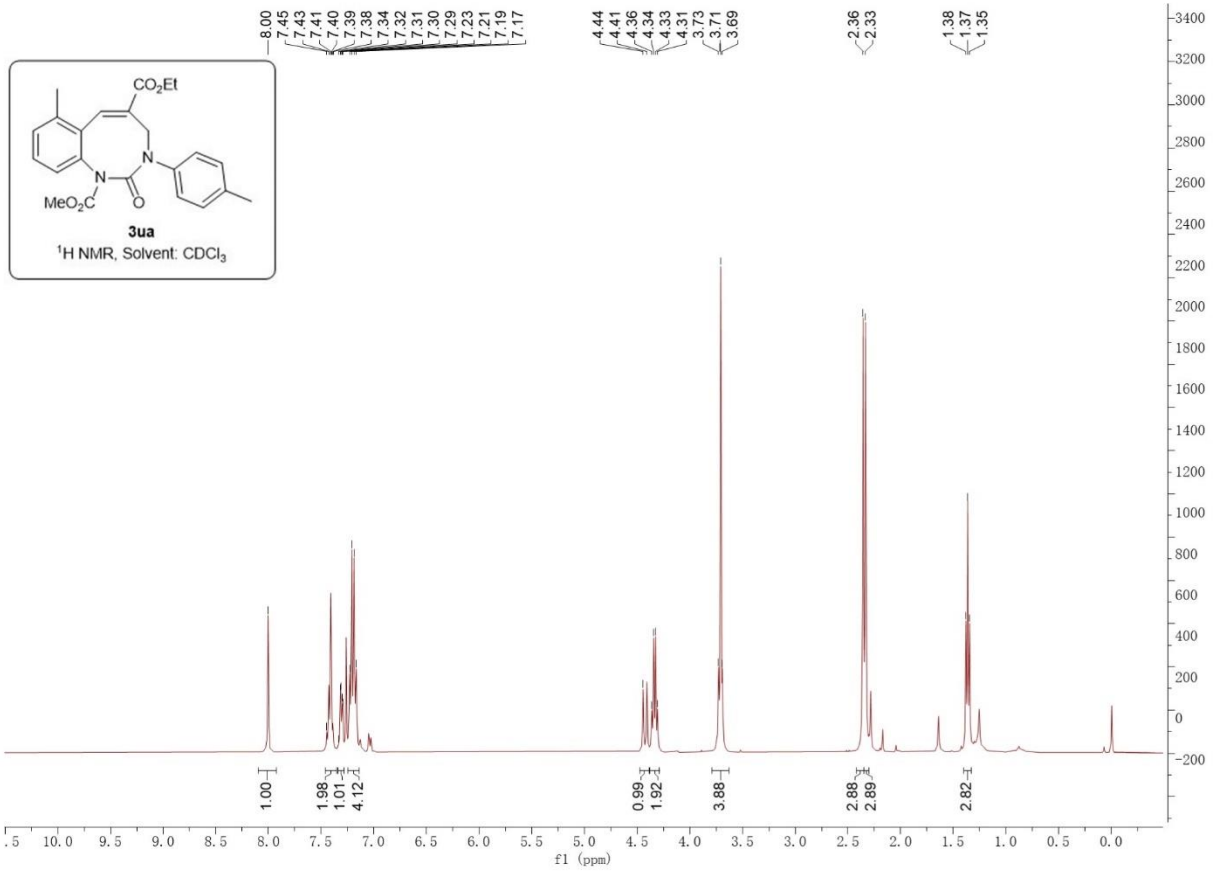
137.38
136.53
135.34
134.58
134.53
132.42
131.06
129.90
125.43
122.71
61.93
53.94
50.75
21.08
14.24
CO2Et
Br
N
N
MeO2C
O
3ta
13C NMR, Solvent: CDCl3
f1 (ppm)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7.34
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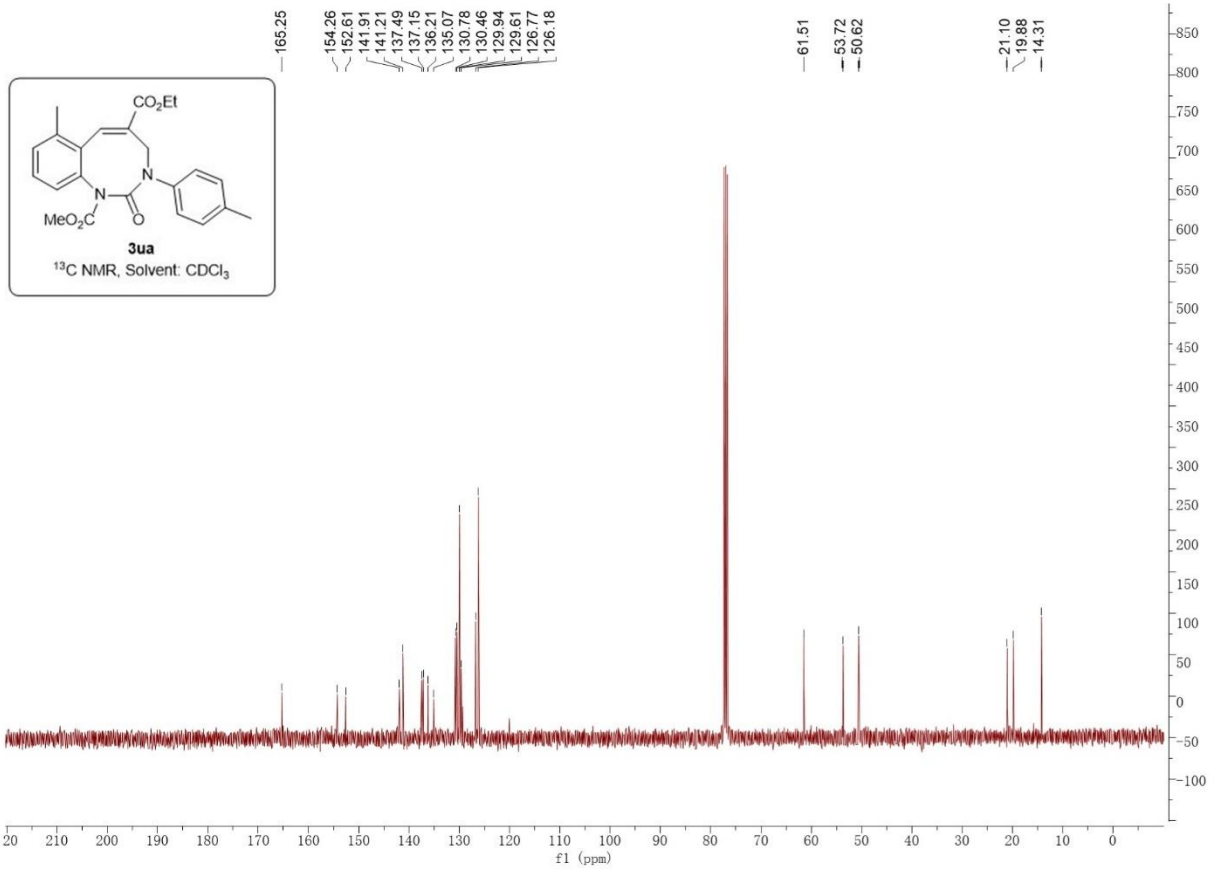
7.30
7.29
7.23
7.21
7.19
7.17
4.44
4.41
4.36
4.34
4.33
4.31
3.73
3.71
3.69
2.36
2.33
1.38
1.37
1.35
1.00
1.98
1.01
4.12
0.99
1.92
3.88
2.88
2.89
2.82
f1 (ppm)
3ua
1H NMR, Solvent: CDCl3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141.21
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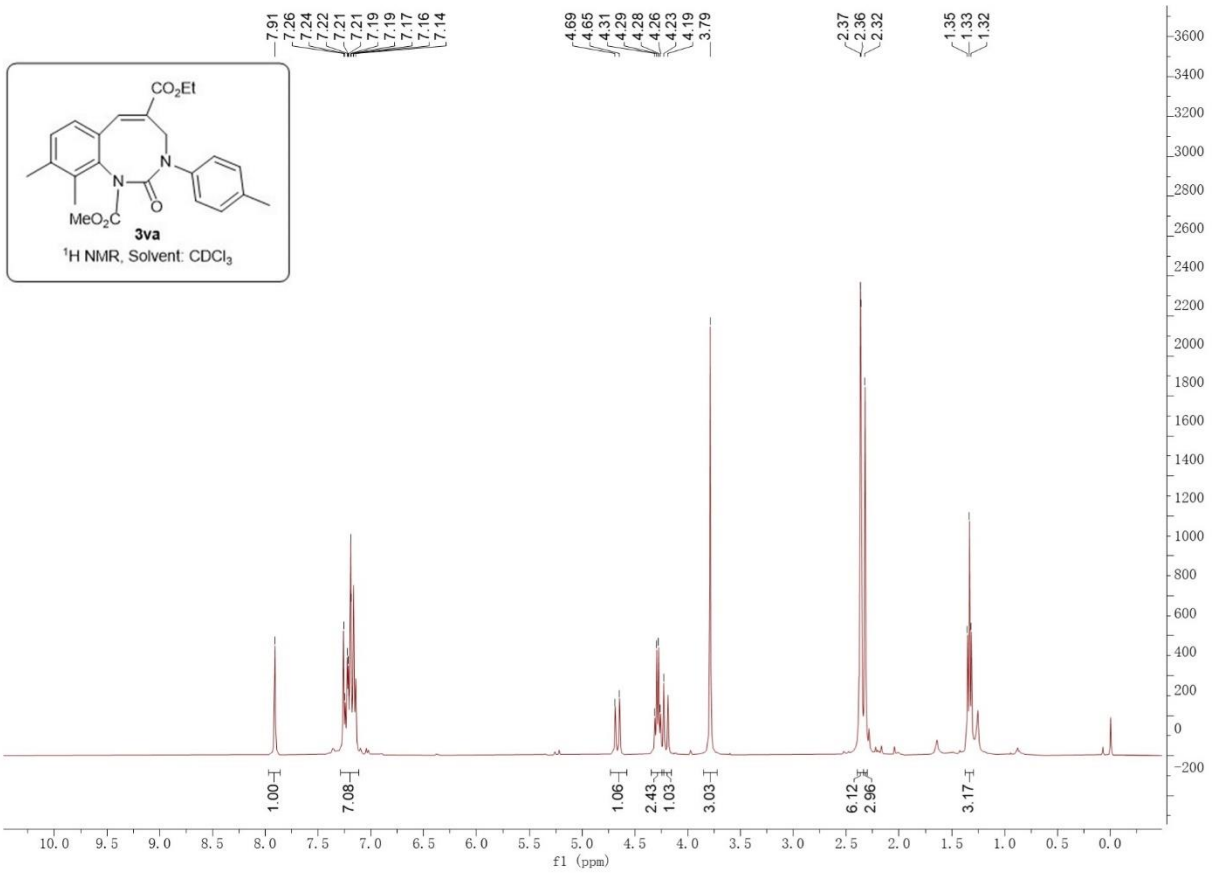
137.15
136.21
135.07
130.78
130.46
129.94
129.61
126.77
126.18
61.51
53.72
50.62
21.10
19.88
14.31
f1 (ppm)
3ua
13C NMR, Solvent: CDCl3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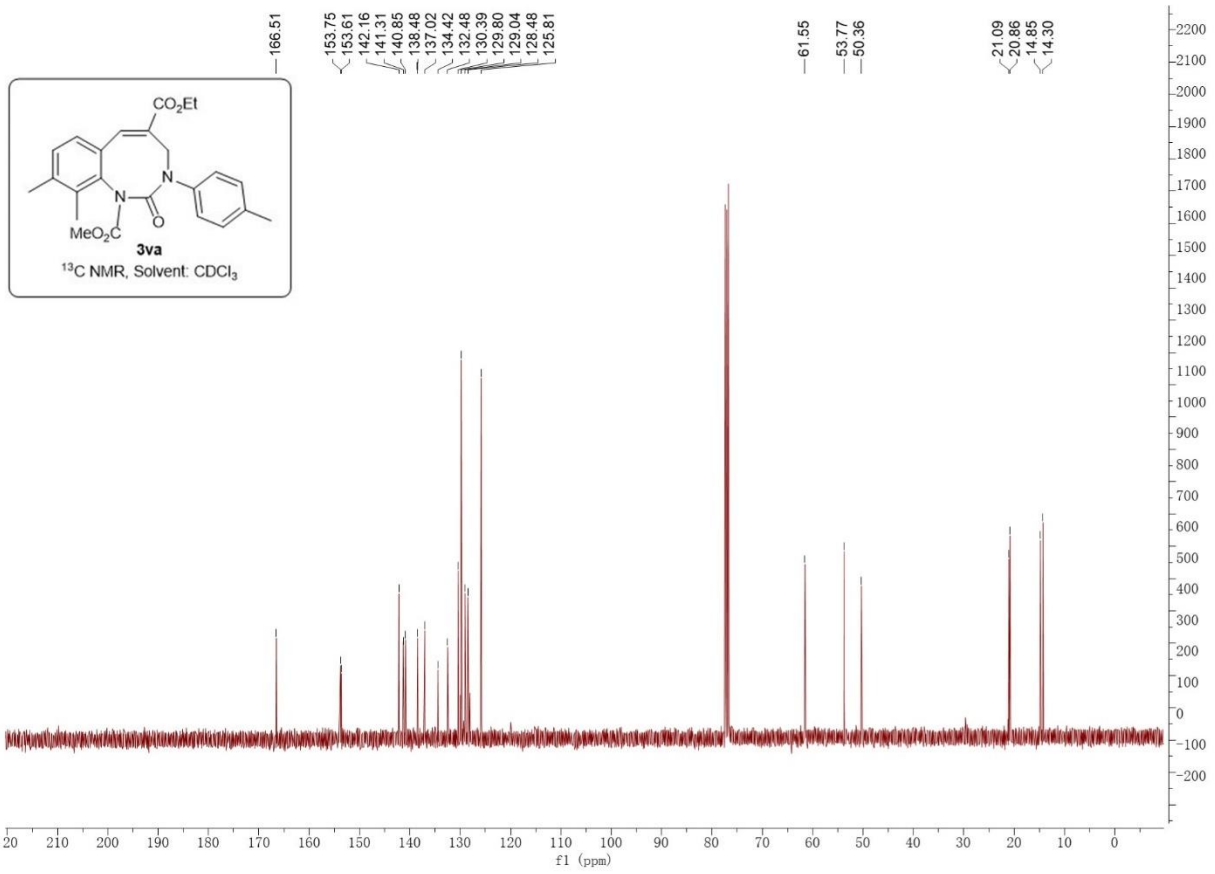
7.26
7.24
7.22
7.21
7.21
7.19
7.19
7.17
7.16
7.14
4.69
4.65
4.31
4.29
4.28
4.26
4.23
4.19
3.79
2.37
2.36
2.32
1.35
1.33
1.32
CO2Et
MeO2C
3va
1H NMR, Solvent: CDCl3
1.00
7.08
1.06
2.43
1.03
3.03
6.12
2.96
3.17
f1 (ppm)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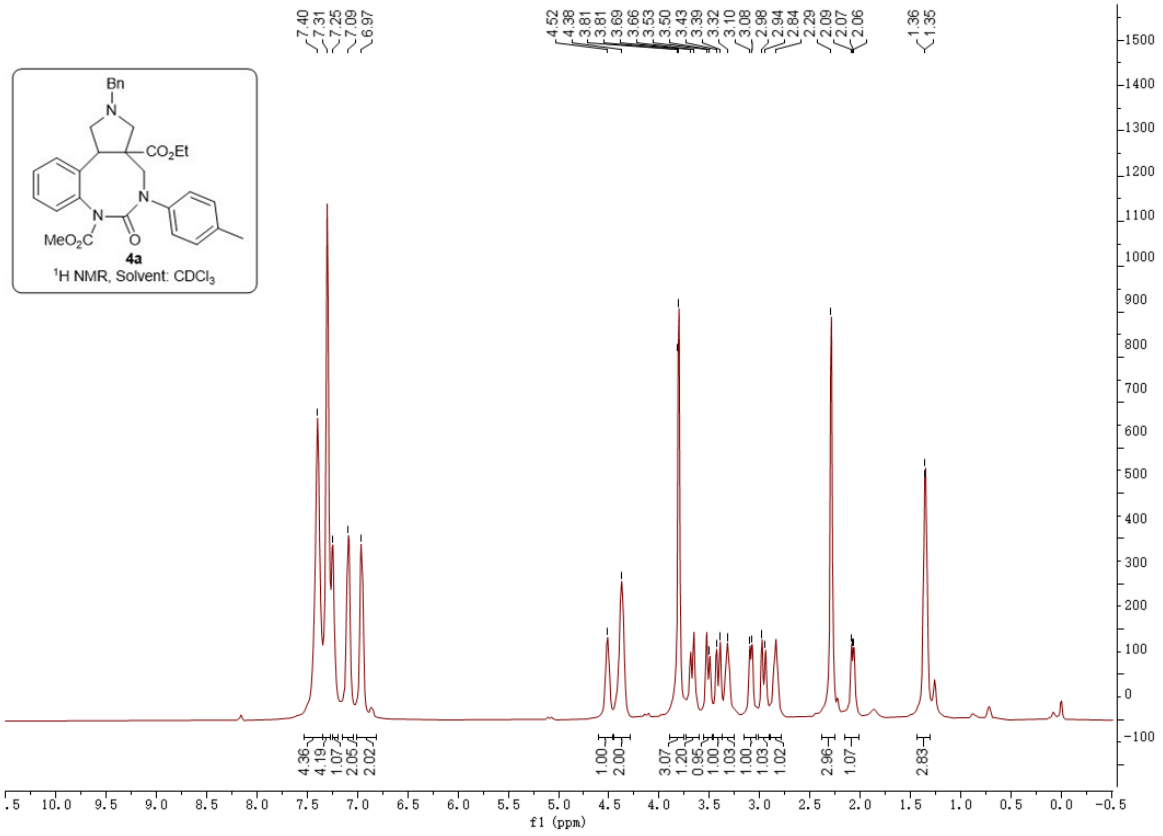
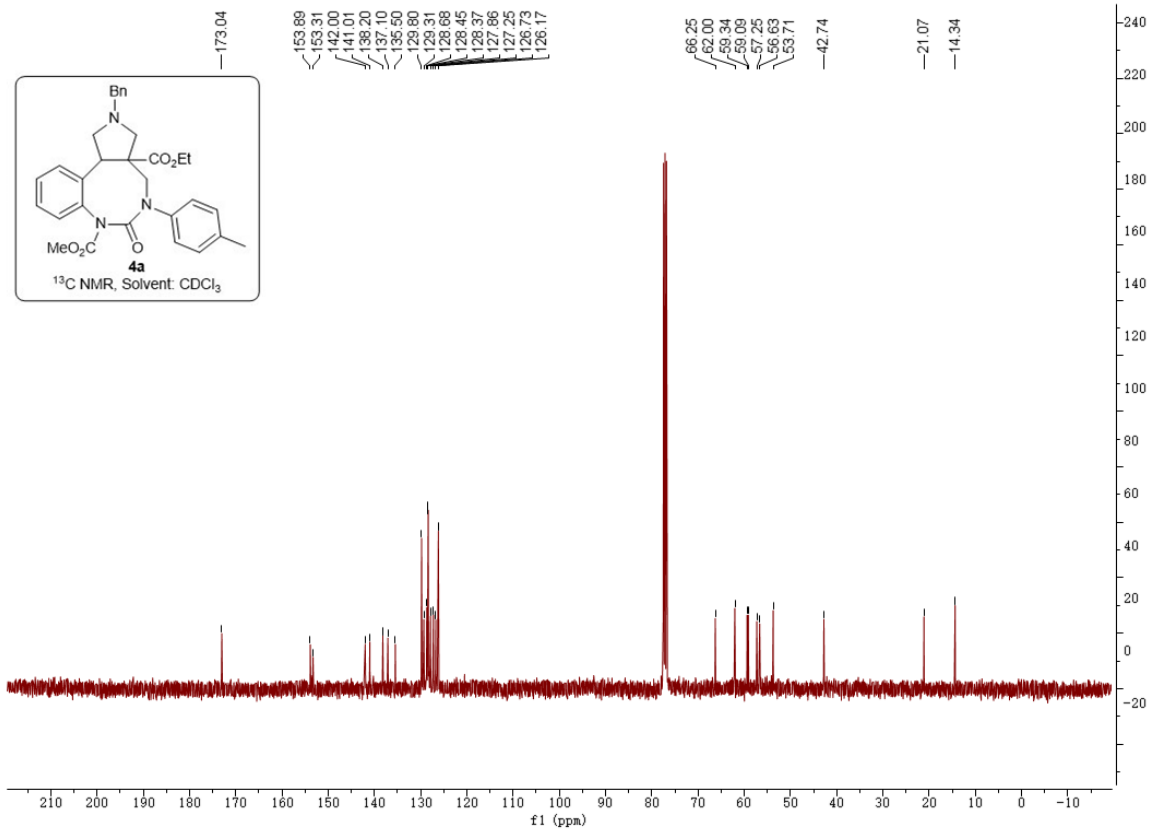
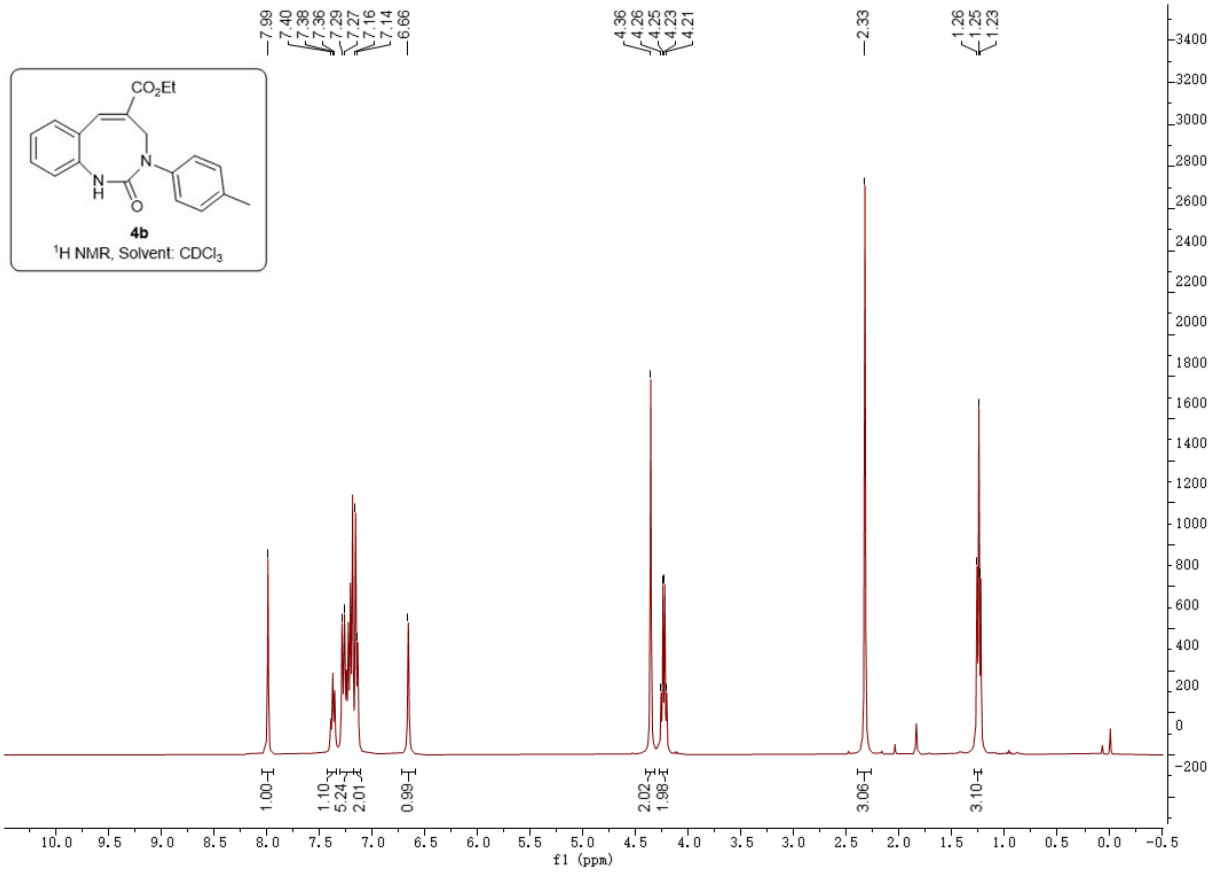
140.85
138.48
137.02
134.42
132.48
130.39
129.80
129.04
128.48
125.81
61.55
53.77
50.36
21.09
20.86
14.85
14.30
CO2Et
MeO2C
3va
13C NMR, Solvent: CDCl3
f1 (ppm)

8.2. Products of Derivatization



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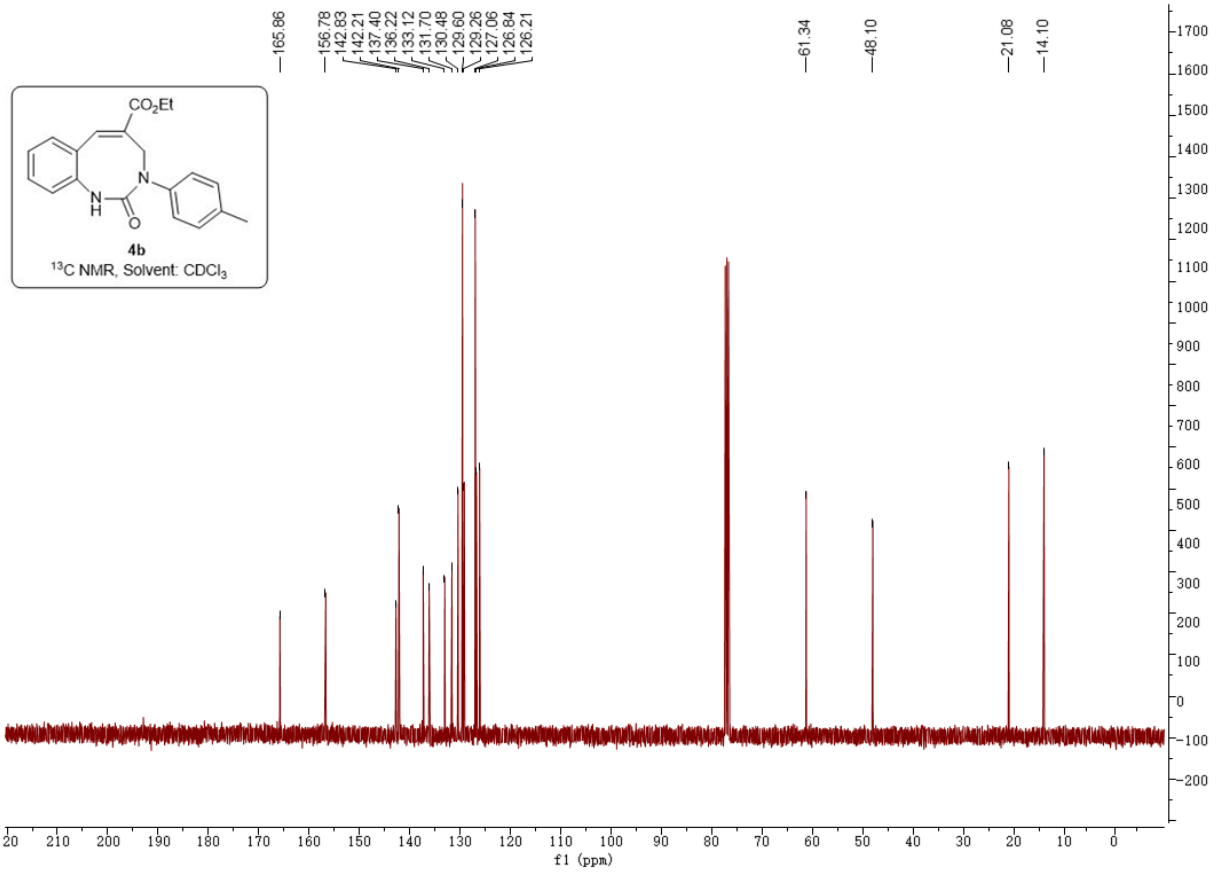
7.27
7.16
7.14
6.66
4.36
4.26
4.25
4.23
4.21
2.33
1.26
1.25
1.23
CO2Et
N
H
O
4b
1H NMR, Solvent: CDCl3
1.00
1.10
5.24
2.01
0.99
2.02
1.98
3.06
3.10
f1 (ppm)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142.21
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136.22
133.12
131.70
130.48
129.60
129.26
127.06
126.84
126.21
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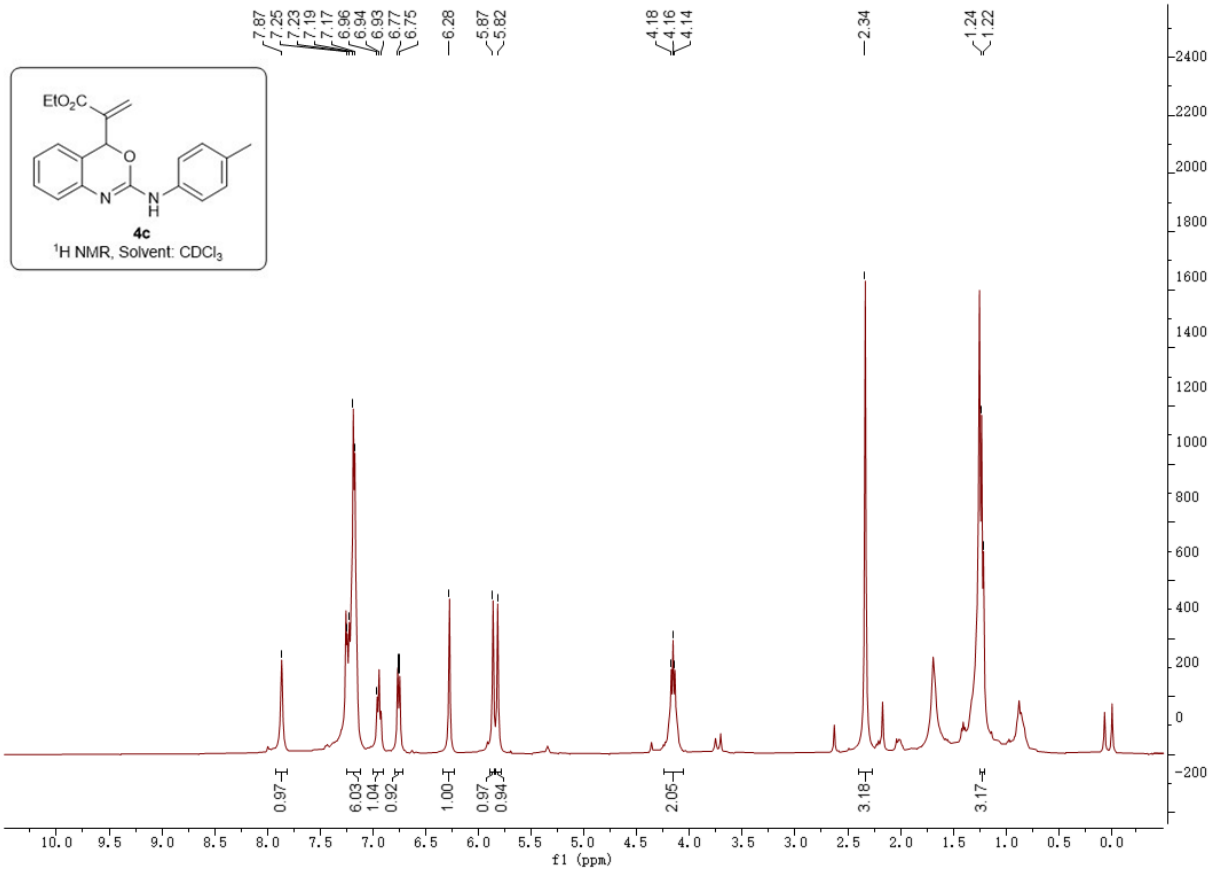
21.08
14.10
CO2Et
N
H
O
4b
13C NMR, Solvent: CDCl3
f1 (ppm)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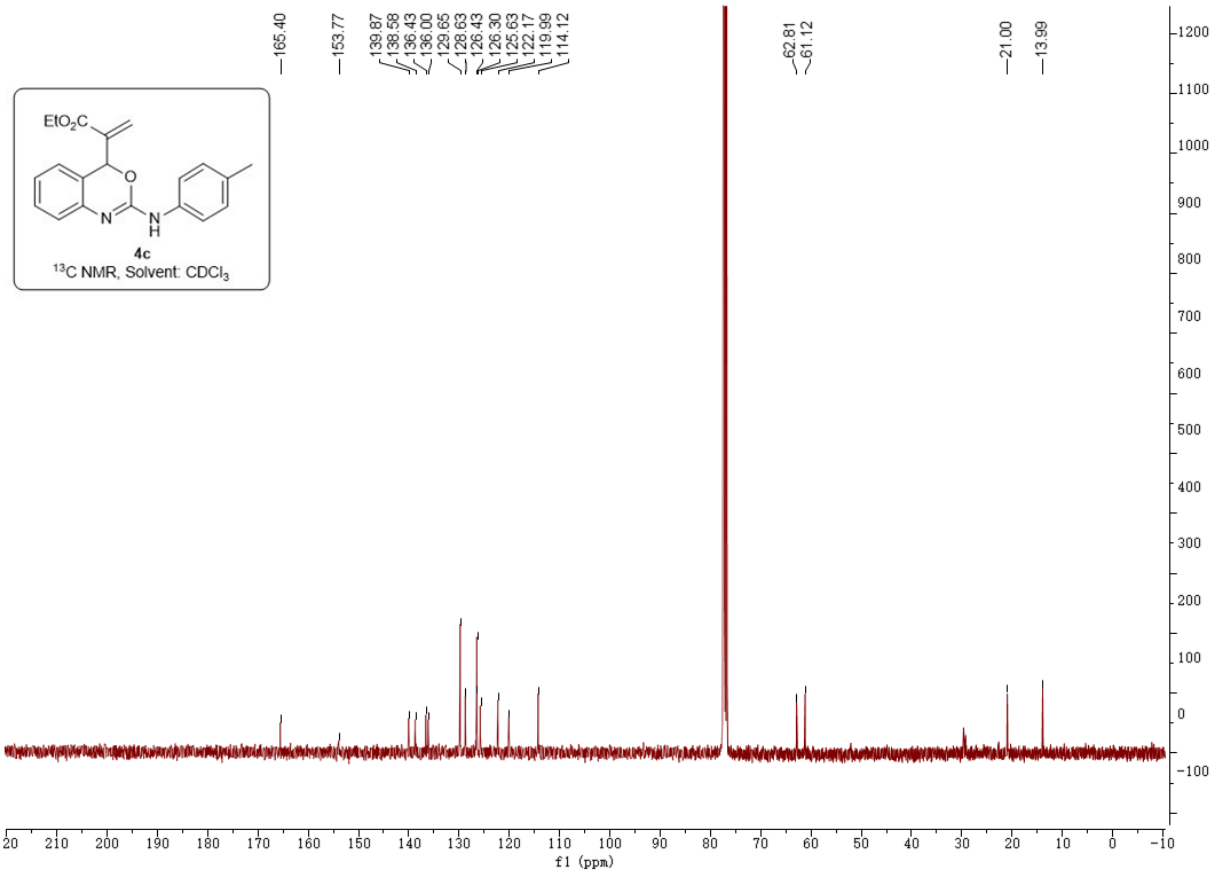
6.96
6.94
6.93
6.77
6.75
6.28
5.87
5.82
4.18
4.16
4.14
2.34
1.24
1.22
EtO2C
O
N
H
4c
1H NMR, Solvent: CDCl3
0.97
6.03
1.04
0.92
1.00
0.97
0.94
2.05
3.18
3.17
f1 (ppm)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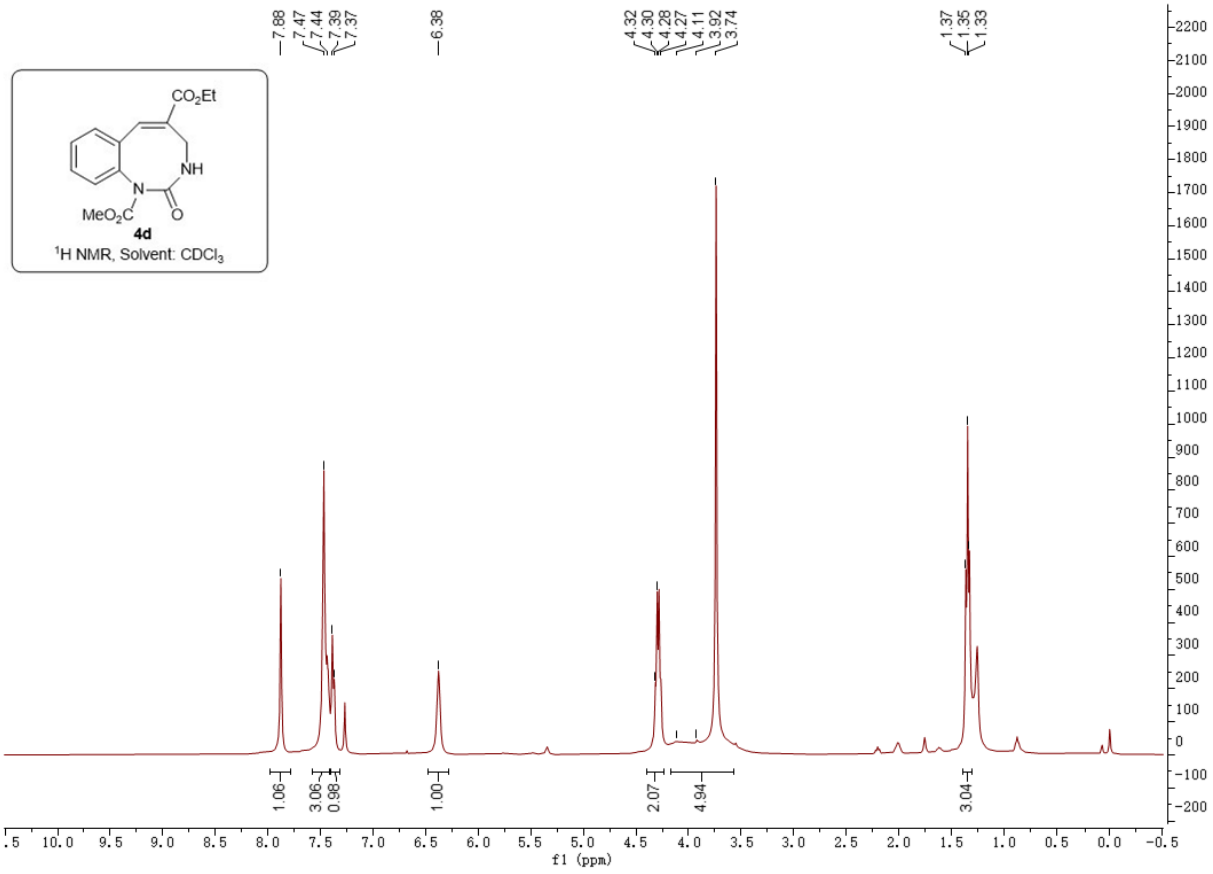
129.65
128.63
126.43
126.30
125.63
122.17
119.99
114.12
62.81
61.12
21.00
13.99
EtO2C
O
N
H
4c
13C NMR, Solvent: CDCl3
f1 (ppm)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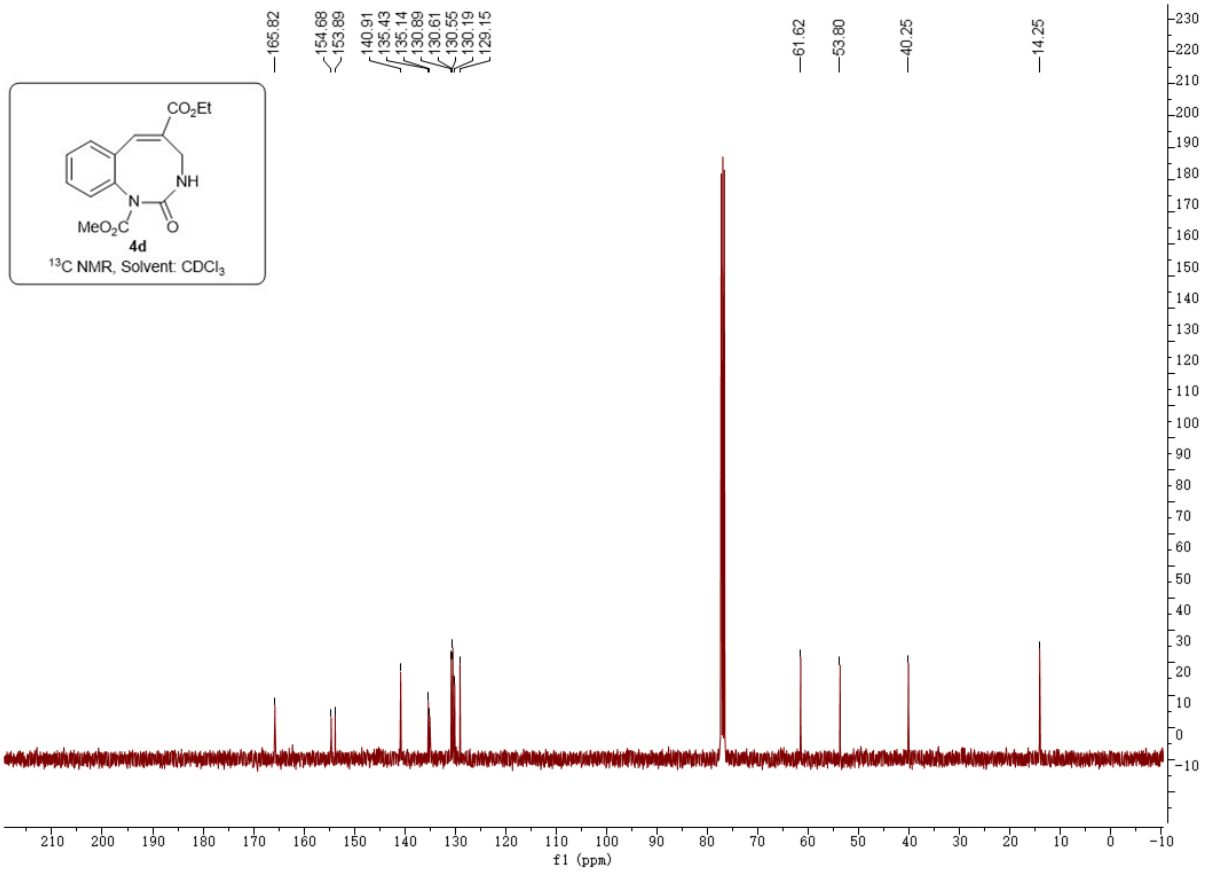
7.47
7.44
7.39
7.37
6.38
4.32
4.30
4.28
4.27
4.11
3.92
3.74
1.37
1.35
1.33
CO2Et
NH
N
O
MeO2C
4d
1H NMR, Solvent: CDCl3
1.06
3.06
0.98
1.00
2.07
4.94
3.04
f1 (ppm)


165.82
154.68
153.89
140.91
135.43
135.14
130.89
130.61
130.55
130.19
129.15
61.62
53.80
40.25
14.25
CO2Et
NH
N
O
MeO2C
4d
13C NMR, Solvent: CDCl3
f1 (ppm)