Supporting Information

Efficient Synthesis of Quinoline-Enone Esters via Copper-Catalyzed Coupling with Electron-Deficient Alkynes and Exploration of Fluorescence in Difluoroboron Complexes

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1. General information

All reactions were carried out under an atmosphere of N_2 unless otherwise noted. All the reactions were monitored by thin layer chromatography (TLC), carried out on 0.25 mm silica gel plates using UV light as visualizing agent. Column chromatography was carried out on silica gel (particle size 100-200 mesh). Unless otherwise stated, all yields refer to isolated products following purification by flash column chromatography. NMR spectra were acquired on a Bruker Avance III HD 500 spectrometer operating at 500 or 600 MHz. All ^{1}H, ^{13}C, ^{11}B, ^{19}F NMR spectra were recorded using $CDCl_3$ as solvent. Tetramethylsilane (TMS) signals or residual solvent signals were used [TMS δ=0.00 (^{1}H NMR), $CDCl_3$=7.26 ppm (^{1}H NMR), 77.16 ppm (^{13}C NMR) as internal standards. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-resolution mass spectrometry (HRMS) data were acquired on an Agilent 6545 Q-TOF LC/MS instrument.

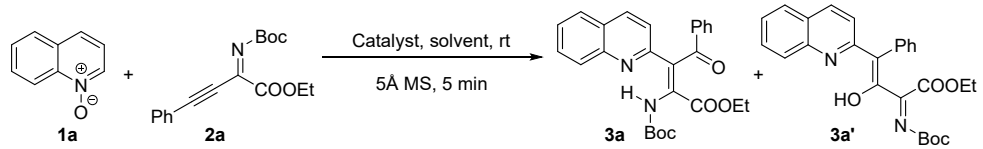
2. Preparation of starting materials

1 was prepared according to reported procedures. [1]

2 and **4** was prepared according to reported procedures. [2]

3. Optimization of reaction conditions

Table S1. Optimization of the coupling reaction between quinoline N-oxides and alkynyl imines. [a]

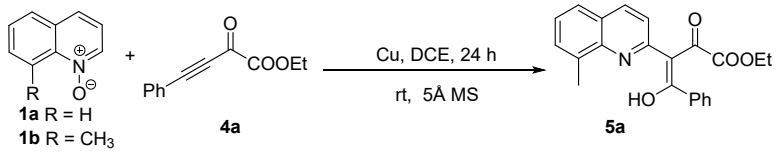


entry	Catalyst	[Cat] %	solvent	Yield (%) [b]	rr (3a/3a') [c]
1	-	-	DCE	55	15/1
2	CuDPP	10	DCE	93	25/1
3	$Cu(CH_3CN)_4BF_4$	10	DCE	87	23/1
4	CuTc	10	DCE	80	24/1
5	$Cu(OTf)_2$	10	DCE	80	23/1
6	$Cu(OAc)_2$	10	DCE	70	19/1
7	$Cu(CH_3CN)_4PF_6$	10	DCE	99	25/1

8	**$Cu(CH_3CN)_4PF_6$**	**5**	**DCE**	**99**	**25/1**
9	$Cu(CH_3CN)_4PF_6$	1	DCE	80	25/1
10	$Cu(CH_3CN)_4PF_6$	5	DCM	73	23/1
11	$Cu(CH_3CN)_4PF_6$	5	$CHCl_3$	76	22/1
12	$Cu(CH_3CN)_4PF_6$	5	MeCN	62	17/1
13	$Cu(CH_3CN)_4PF_6$	5	toluene	71	19/1
14	$Cu(CH_3CN)_4PF_6$	5	THF	73	16/1
15	$Cu(CH_3CN)_4PF_6$	5	MTBE	72	18/1
16	$Cu(CH_3CN)_4PF_6$	5	EtOAc	56	15/1

[a] Reaction conditions: A mixture of 1a (0.24 mmol), 2a (0.2 mmol), [Cat] (x mmol%), solvent (2 mL) and 5Å MS (100 mg) at room temperature for 5 min. [b] Isolated yields. [c] Regioisomeric ratio (rr) was determined by ^1H NMR analysis of the crude reaction mixtures.

Table S2. Optimization of the coupling reaction between quinoline N-oxides and ynones. [a]

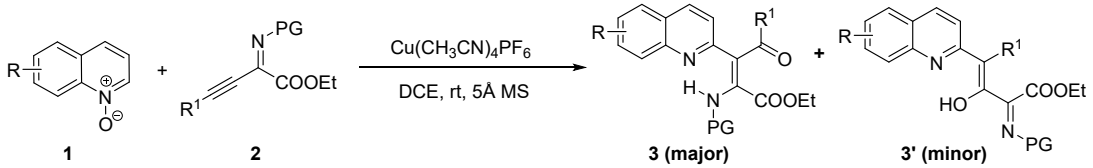


entry	1a or 1b	Catalyst	Yield (%) [b]
1	**1a**	$Cu(CH_3CN)_4PF_6$	n.d.
2	**1b**	$Cu(CH_3CN)_4PF_6$	49
3	**1b**	CuDPP	61
4	**1b**	$CuSO_4$	60
5	**1b**	$Cu(ClO_4)_2$	50
6	**1b**	$Cu(acac)_2$	54
7	**1b**	CuTc	74
8	**1b**	$Cu(OTf)_2$	53
9	**1b**	**$Cu(OAc)_2$**	**96**

[a] Reaction conditions: A mixture of 1a or 1b (0.24 mmol), 4a (0.2 mmol), [Cat] (5 mmol%), DCE (2 mL) and 5Å MS (100 mg) at room temperature. [b] Isolated yields.

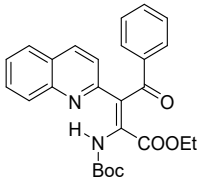
4. Preparation and characterization of compounds 3 and 5

4.1. Preparation and characterization of 3 or 3'



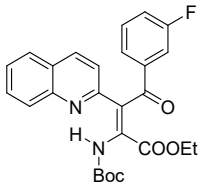
A mixture of quinoline N-oxides **1** (0.24 mmol), alkynyl imines **2** (0.20 mmol),

$Cu(CH_3CN)_4PF_6$ (0.01 mmol, 5 mol%) and 5Å molecular sieves (100 mg) in anhydrous DCE (2 mL) was stirred at room temperature for 5 minutes. Upon completion (as monitored by TLC), the reaction mixture was filtered, concentrated under reduced pressure, and purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1 to 3:1) to afford the desired products **3** or **3'**.



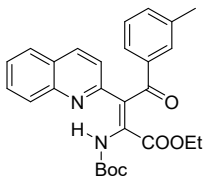
3a

3a, yellow solid, m.p. 104.5-105.5 °C, 99% yield, 25/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 12.95 (s, 1H), 8.00-7.94 (m, 4H), 7.75-7.71 (m, 2H), 7.54-7.50 (m, 2H), 7.40 (t, *J*=7.7Hz, 2H), 7.18 (d, *J*=8.8Hz, 1H), 4.02 (q, *J*=7.2Hz, 2H), 1.55 (s, 9H), 1.07 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 195.24, 163.69, 154.65, 152.20, 146.26, 137.99, 137.61, 136.73, 133.58, 130.39, 129.87, 128.62, 128.28, 127.59, 127.09, 126.38, 121.40, 118.54, 81.69, 61.88, 28.20, 13.44. HRMS (ESI, m/z) calcd for $C_{26}H_{26}N_2O_5$ $[M+H]^+$ 447.1915, found 447.1920.



3b

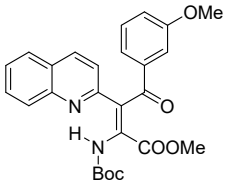
3b, yellow solid, m.p. 99.8-100.8 °C, 78% yield, 25/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 12.92 (s, 1H), 8.01-7.98 (m, 2H), 7.77-7.73 (m, 3H), 7.68 (dt, *J*=9.0Hz, 2.5Hz, 1H), 7.56-7.53 (m, 1H), 7.39-7.35 (m, 1H), 7.24 (td, *J*=8.0Hz, 3.0Hz, 1H), 7.14 (d, *J*=8.5Hz, 1H), 4.07 (q, *J*=7.0Hz, 2H), 1.55 (s, 9H), 1.11 (t, *J*=7.0Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 194.10 (d, *J*=2.3Hz), 163.7230, 162.87 (d, *J*=240.6Hz), 154.43, 152.19, 146.35, 140.21 (d, *J*=6.3Hz), 138.15, 136.89, 130.55, 130.39 (d, *J*=7.7Hz), 128.38, 127.66, 127.24, 126.47, 125.89 (d, *J*=2.9Hz), 121.33, 120.64 (d, *J*=21.5Hz), 118.08, 116.19 (d, *J*=22.4Hz), 81.92, 62.08, 28.25, 13.54. ^{19}F NMR (471 MHz, $CDCl_3$) δ (ppm) -111.66. HRMS (ESI, m/z) calcd for $C_{26}H_{25}FN_2O_5$ $[M+Na]^+$ 487.1640, found 487.1645.



3c

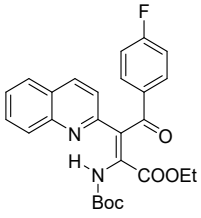
3c, yellow solid, m.p. 114.3-115.3 °C, 98% yield, 30/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$)

δ (ppm) 12.96 (s, 1H), 8.01 (d, *J*=8.5Hz, 1H), 7.98 (d, *J*=8.8Hz, 1H), 7.81 (s, 1H), 7.77-7.73 (m, 3H), 7.54 (t, *J*=8.0Hz, 1H), 7.36-7.34 (m, 1H), 7.30-7.27 (m, 1H), 7.21 (d, *J*=8.8Hz, 1H), 4.02 (q, *J*=7.1Hz, 2H), 2.36 (s, 3H), 1.55 (s, 9H), 1.09 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 195.53, 163.82, 154.84, 152.30, 146.36, 138.55, 138.07, 137.59, 136.77, 134.50, 130.42, 130.22, 128.59, 128.43, 127.64, 127.42, 127.11, 126.49, 121.55, 118.79, 81.75, 61.96, 28.29, 21.39, 13.54. HRMS (ESI, m/z) calcd for $C_{27}H_{28}N_2O_5$ $[M+Na]^+$ 483.1891, found 483.1903.



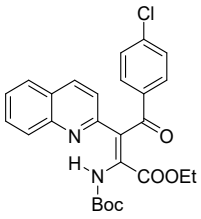
3d

3d, yellow solid, m.p. 122.7-123.7 °C, 75% yield, 25/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 12.97 (s, 1H), 8.00 (d, *J*=8.4Hz, 1H), 7.97 (d, *J*=8.8Hz, 1H), 7.76-7.73 (m, 2H), 7.55-7.52 (m, 2H), 7.49 (d, *J*=7.6Hz, 1H), 7.29-7.26 (m, 1H), 7.18 (d, *J*=8.8Hz, 1H), 7.10-7.07 (m, 1H), 3.82 (s, 3H), 3.59 (s, 3H), 1.55 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 195.07, 164.30, 159.93, 154.79, 152.24, 146.29, 139.28, 137.74, 136.75, 130.44, 129.70, 128.40, 127.63, 127.17, 126.47, 123.09, 121.62, 120.49, 118.49, 113.25, 81.91, 55.57, 52.58, 28.27. HRMS (ESI, m/z) calcd for $C_{26}H_{26}N_2O_6$ $[M+Na]^+$ 485.1684, found 485.1689.



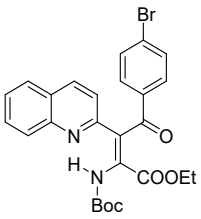
3e

3e, yellow oil, 83% yield, 30/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 12.90 (s, 1H), 8.02-7.98 (m, 4H), 7.77-7.74 (m, 2H), 7.54 (t, *J*=7.6Hz, 1H), 7.16 (d, *J*=8.8Hz), 7.08 (t, *J*=8.5Hz, 2H), 4.06 (q, *J*=7.1Hz, 2H), 1.55 (s, 9H), 1.11 (t, *J*=7.2Hz,3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 193.71, 166.02 (d, *J*=255.8Hz), 163.68, 154.46, 152.15, 146.29, 137.64, 136.78, 134.46 (d, *J*=2.8Hz), 132.50 (d, *J*=9.4Hz), 130.43, 128.31, 127.56, 127.12, 126.37, 121.26, 118.12, 115.77 (d, *J*=21.8Hz), 81.77, 61.96, 28.17, 13.47. ^{19}F NMR (471 MHz, $CDCl_3$) δ (ppm) -104.08. HRMS (ESI, m/z) calcd for $C_{26}H_{25}FN_2O_5$ $[M+Na]^+$ 487.1640, found 487.1655.



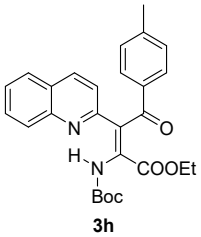
3f

3f, yellow solid, m.p. 117.3-118.3 °C, 70% yield, 25/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 12.90 (s, 1H), 7.99 (t, *J*=7.0Hz, 2H), 7.92 (d, *J*=8.5Hz, 2H), 7.77-7.74 (m, 2H), 7.54 (t, *J*=7.5Hz, 1H), 7.38 (d, *J*=8.6Hz, 2H), 7.13 (d, *J*=8.8Hz, 1H), 4.07 (q, *J*=7.2Hz, 2H), 1.55 (s, 9H), 1.12 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 194.17, 163.75, 154.50, 152.21, 146.39, 140.14, 138.01, 136.90, 136.50, 131.31, 130.55, 129.06, 128.41, 127.67, 127.24, 126.47, 121.37, 118.06, 81.92, 62.11, 28.27, 13.59. HRMS (ESI, m/z) calcd for $C_{26}H_{25}ClN_2O_5$ $[M+Na]^+$ 503.1345, found 503.1364.



3g

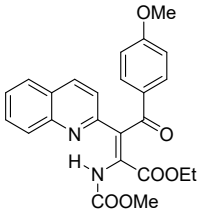
3g, yellow solid, m.p. 120.3-121.3 °C, 73% yield, 30/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 12.90 (s, 1H), 7.99 (t, *J*=6.7Hz, 2H), 7.84 (d, *J*=8.3Hz, 2H), 7.77-7.74 (m, 2H), 7.56-7.53 (m, 3H), 7.12 (d, *J*=8.8Hz, 1H), 4.07 (q, *J*=7.2Hz, 2H), 1.55 (s, 9H), 1.12 (t, *J*=7.2Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.37, 163.75, 154.47, 152.19, 146.36, 138.06, 136.90, 136.88, 132.05, 131.38, 130.56, 128.93, 128.39, 127.67, 127.25, 126.46, 121.37, 117.98, 81.93, 62.12, 28.26, 13.59. HRMS (ESI, m/z) calcd for $C_{26}H_{25}BrN_2O_5$ $[M+H]^+$ 525.1020, found 525.1025.



3h

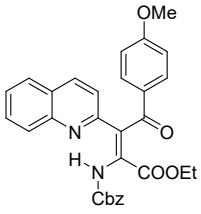
3h, yellow solid, m.p. 123.7-124.5 °C, 97% yield, 22/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 12.93 (s, 1H), 8.00 (d, *J*=8.4Hz, 1H), 7.96 (d, *J*=8.8Hz, 1H), 7.88 (d, *J*=8.2Hz, 2H), 7.76-7.72 (m, 2H), 7.54-7.50 (m, 1H), 7.21-7.18 (m, 3H), 4.03 (q, *J*=7.2Hz, 2H), 2.37 (s, 3H), 1.55 (s, 9H), 1.09 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 194.90, 163.75, 154.81, 152.27, 146.31, 144.63, 137.30, 136.71, 135.57, 130.37, 130.08, 129.38, 128.36, 127.60, 127.07, 126.42, 121.49, 118.76, 81.66, 61.90, 28.25, 21.80, 13.50. HRMS (ESI, m/z) calcd for $C_{27}H_{28}N_2O_5$ $[M+H]^+$ 461.2071, found

461.2082.



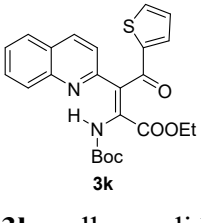
3i

3i, yellow solid, m.p. 143.7-144.7 °C, 65% yield, 75/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 13.18 (s, 1H), 8.06 (d, *J*=9.3Hz, 1H), 8.00-7.95 (m, 3H), 7.77-7.73 (m, 2H), 7.55-7.52 (m, 1H), 7.21 (d, *J*=8.7Hz, 1H), 6.89 (d, *J*=9.0Hz, 1H), 4.06 (q, *J*=7.2Hz, 2H), 3.84(s, 3H), 3.84 (s, 3H), 1.10 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 187.15, 163.65, 154.50, 152.21, 146.35, 145.41, 137.57, 136.87, 135.55, 135.44, 130.43, 128.42, 128.25, 127.65, 127.17, 126.55, 121.31, 118.37, 81.84, 62.14, 28.26, 13.59. HRMS (ESI, m/z) calcd for $C_{24}H_{22}N_2O_6$ $[M+Na]^+$ 457.1371, found 457.1380.



3j

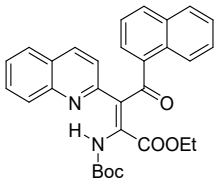
3j, yellow solid, m.p. 149.7-150.7 °C, 71% yield, 50/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 13.24 (s, 1H), 8.01-7.96 (m, 4H), 7.74-7.71 (m, 2H), 7.53 (t, *J*=7.4Hz, 1H), 7.46-7.44 (m, 2H), 7.41-7.33 (m, 3H), 7.22 (d, *J*=8.8Hz, 1H), 6.89 (d, *J*=8.7Hz, 2H), 5.28 (s, 2H), 4.02 (q, *J*=7.2Hz, 2H), 3.83 (s, 3H), 1.08 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 193.50, 164.17, 163.50, 154.60, 153.45, 146.25, 136.93, 136.32, 135.94, 132.34, 130.91, 130.46, 128.65, 128.40, 128.38, 128.19, 127.59, 127.22, 126.51, 121.47, 119.87, 113.97, 67.75, 62.05, 55.59, 13.49. HRMS (ESI, m/z) calcd for $C_{30}H_{26}N_2O_6$ $[M+Na]^+$ 533.1684, found 533.1696.



3k

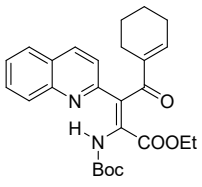
3k, yellow solid, m.p. 106.5-107.5 °C, 70% yield, 20/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 12.93 (s, 1H), 8.04-7.99 (m, 2H), 7.77-7.74 (m, 2H), 7.68 (d, *J*=4.9Hz, 1H), 7.61 (d, *J*=4.1Hz, 1H), 7.54 (t, *J*=7.5Hz, 1H), 7.39 (d, *J*=8.8Hz, 1H), 7.03 (t, *J*=4.5Hz, 1H), 4.08 (q, *J*=7.2Hz, 2H), 1.54 (s, 9H), 1.15 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 187.05, 163.55, 154.40, 152.10, 146.24, 145.31, 137.47, 136.77, 135.45, 135.34, 130.33, 128.31, 128.14, 127.55, 127.06, 126.45, 121.20, 118.27, 81.74, 62.03, 28.16, 13.49. HRMS (ESI, m/z) calcd for $C_{24}H_{24}N_2O_5S$ $[M+H]^+$

453.1479, found 453.1487.



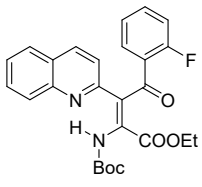
3l

3l, yellow solid, m.p. 122.9-123.8 °C, 94% yield, 36/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 13.07 (s, 1H), 8.44 (s, 1H), 8.12-8.10 (m, 1H), 8.03 (d, *J*=8.5Hz, 1H), 7.94 (d, *J*=8.8Hz, 1H), 7.88-7.83 (m, 3H), 7.77-7.71 (m, 2H), 7.58-7.47 (m, 3H), 7.25 (d, *J*=4.4Hz, 1H), 3.95 (q, *J*=7.2Hz, 2H), 1.57 (s, 9H), 0.97 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 195.25, 163.81, 154.87, 152.28, 146.33, 137.85, 136.81, 135.90, 135.49, 132.4997, 130.44, 129.88, 128.87, 128.70, 128.36, 127.85, 127.64, 127.12, 126.86, 126.46, 124.76, 121.52, 118.59, 81.79, 61.94, 28.27, 13.43. HRMS (ESI, m/z) calcd for $C_{30}H_{28}N_2O_5$ $[M+H]^+$ 497.2071, found 497.2076.



3m

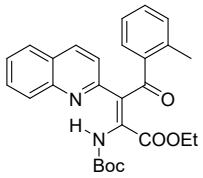
3m, yellow solid, m.p. 93.1-94.1 °C, 58% yield, 50/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 12.82 (s, 1H), 8.06 (d, *J*=8.8Hz, 1H), 7.96 (d, *J*=8.5Hz, 1H), 7.77-7.71 (m, 2H), 7.52 (t, *J*=7.5Hz, 1H), 7.37 (d, *J*=6.6Hz, 1H), 6.87 (t, *J*=4.1Hz, 1H), 4.23 (q, *J*=7.2Hz, 2H), 2.40-2.37 (m, 2H), 2.18-2.14 (m, 2H), 1.69-1.56 (m, 4H), 1.52 (s, 9H), 1.31 (t, *J*=7.1Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 196.08, 164.16, 155.01, 152.37, 146.31, 145.74, 141.15, 136.75, 136.39, 130.26, 128.39, 127.58, 127.01, 126.54, 121.16, 119.21, 81.50, 61.93, 28.25, 26.35, 23.25, 21.96, 21.68, 13.98. HRMS (ESI, m/z) calcd for $C_{26}H_{30}N_2O_5$ $[M+Na]^+$ 473.2047, found 473.2050.



3n

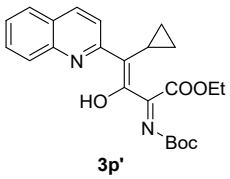
3n, yellow solid, m.p. 115.6-117.1 °C, 96% yield, 5/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 13.03 (s, 1H), 8.00-7.97 (m, 2H), 7,87 (td, *J*=7.9Hz, 0.8Hz, 1H), 7.74-7.71 (m, 2H), 7.53-7.45 (m, 2H), 7.27 (d, *J*=8.9Hz, 1H), 7.18 (t, *J*=7.6Hz, 1H), 7.03 (t, *J*=10.7Hz, 1H), 4.05 (d, *J*=7.2Hz, 2H), 1.53 (s, 9H), 1.14 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 191.85, 163.86, 162.70, 160.64, 154.57, 152.03, 146.26, 138.59, 136.75, 134.98 (d, *J*=35.9Hz), 131.98, 130.36, 128.33, 127.60, 127.05, 126.44,

124.30 (d, *J*=14.5Hz), 121.02, 119.60, 116.80 (d, *J*=88.1Hz), 81.83, 62.03, 28.21, 13.58. ^{19}F NMR (471 MHz, $CDCl_3$) δ (ppm) -110.37. HRMS (ESI, m/z) calcd for $C_{26}H_{25}N_2O_5$ $[M+Na]^+$ 487.1640, found 487.1656.



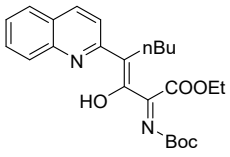
3o

3o, yellow oil, 84% yield, 7/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 13.21 (s, 1H), 8.00 (d, *J*=8.9Hz, 2H), 7.78-7.73 (m, 2H), 7.68 (dd, *J*=7.8Hz, 1.5Hz, 1H), 7.53 (t, *J*=8.4Hz, 1H), 7.35 (td, *J*=7.5Hz, 1.5Hz, 1H), 7.31 (d, *J*=8.9Hz, 1H), 7.26-7.24 (m, 1H), 7.13 (t, *J*=7.5Hz, 1H), 3.95 (q, *J*=7.2Hz, 2H), 2.66 (s, 1H), 1.54 (s, 9H), 1.07 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 196.95, 163.98, 155.30, 152.07, 146.21, 140.26, 138.91, 136.73, 132.22, 132.08, 131.86, 130.33, 128.32, 127.61, 127.03, 126.43, 125.62, 121.48, 119.34, 81.80, 61.90, 28.25, 21.44, 13.57. HRMS (ESI, m/z) calcd for $C_{27}H_{28}N_2O_5$ $[M+Na]^+$ 483.1891, found 483.1904.



3p'

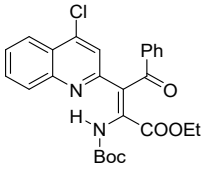
3p', yellow oil, 80% yield, 1/2 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 11.61 (s, 1H), 8.16 (d, *J*=8.16Hz, 1H), 8.09 (d, *J*=8.5Hz, 1H), 7.82 (d, *J*=8.2Hz, 1H), 7.73-7.70 (m, 1H), 7.57-7.48 (m, 3H), 3.92 (q, *J*=7.1Hz, 2H), 1.68-1.63 (m, 1H), 1.46 (s, 9H), 1.15-1.12 (m, 2H), 0.88 (t, *J*=7.2Hz, 3H), 0.77-0.74 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 202.31, 162.97, 155.48, 151.43, 148.00, 144.20, 136.27, 129.97, 129.53, 127.65, 127.10, 127.04, 124.26, 116.54, 82.59, 61.71, 28.09, 23.32, 20.80, 13.63, 12.82. HRMS (ESI, m/z) calcd for $C_{23}H_{26}N_2O_5$ $[M+Na]^+$ 433.1734, found 433.1739.



3q'

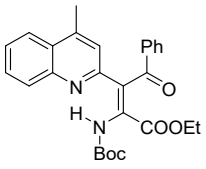
3q', yellow oil, 67% yield, 1/5 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 11.59 (s, 1H), 8.18 (d, *J*=8.4Hz, 1H)， 8.10 (d, *J*=8.5Hz, 1H), 7.85 (dd, *J*=8.3Hz, 1.4Hz, 1H), 7.7-7.73 (m, 1H), 7.60-7.57 (m, 1H), 7.44 (d, *J*=8.4Hz, 1H), 3.44 (s, 3H), 2.32 (t, *J*=7.3Hz, 2H), 1.48 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 203.52, 163.50, 155.14, 151.58, 148.02, 144.15, 136.50, 130.05, 129.58, 127.70, 127.19, 127.01, 123.84, 116.38, 82.82, 52.44, 42.23, 28.12, 26.09, 22.20, 13.91. HRMS (ESI, m/z) calcd for

$C_{23}H_{28}N_2O_5$ $[M+H]^+$ 413.2071, found 413.2080.



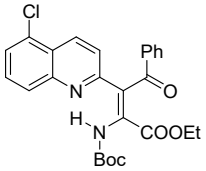
3r

3r, yellow solid, m.p. 145.3-146.3 °C, 99% yield, 25/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 12.71 (s, 1H), 8.13 (d, *J*=8.4Hz, 1H), 8.02-7.96 (m, 2H), 7.80 (t, *J*=7.9Hz, 1H), 7.62 (t, *J*=7.8Hz, 1H), 7.56 (t, *J*=7,5Hz, 1H), 7.43 (t, *J*=7.7Hz, 2H), 7.38 (s, 1H), 3.95 (q, *J*=7.2Hz, 2H), 1.54 (s, 9H), 1.05 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 194.81, 163.50, 154.53, 152.02, 147.03, 143.37, 138.28, 137.81, 133.86, 131.33, 129.95, 128.73, 128.66, 128.03, 124.82, 124.19, 121.18, 117.69, 82.0155, 62.06, 28.22, 13.46. HRMS (ESI, m/z) calcd for $C_{26}H_{25}ClN_2O_5$ $[M+Na]^+$ 503.1345, found 503.1358.



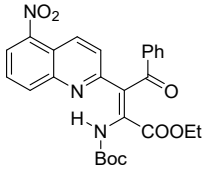
3s

3s, yellow solid, m.p. 122.6-123.6 °C, 90% yield, 50/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 13.01 (s, 1H), 8.00-7.98 (m, 3H), 7.90 (dd, *J*=8.4Hz, 1.4Hz, 1H), 7.75-7.72 (m, 1H), 7.56-7.52 (m, 2H), 7.43-7.40 (m, 2H), 7.07 (s, 1H), 3.98 (q, *J*=7.2Hz, 2H), 2.52 (s, 3H), 1.54 (s, 9H), 1.05 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 195.41, 163.79, 154.33, 152.33, 146.13, 145.35, 138.05, 137.33, 133.61, 130.08, 129.94, 128.97, 128.65, 126.88, 126.68, 123.82, 121.82, 118.81, 81.63, 61.89, 28.26, 18.97, 13.49. HRMS (ESI, m/z) calcd for $C_{27}H_{28}N_2O_5$ $[M+H]^+$ 461.2071, found 461.2082.



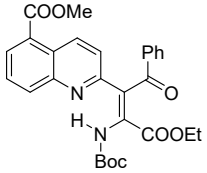
3t

3t, yellow solid, m.p. 150.6-151.6 °C, 89% yield, 35/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 12.75 (s, 1H), 8.37 (d, *J*=9.0Hz, 1H), 7.98-7.91(m, 3H), 7.66(t, *J*=7.7Hz, 1H), 7.61-7.54(m, 2H), 7.42(t, *J*=7.7Hz, 2H), 7.29(d, *J*=9.1Hz, 1H), 4.02(q, *J*=7.2Hz, 2H), 1.55(s, 9H), 1.08(t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 195.13, 163.61, 155.59, 152.07, 147.07, 138.52, 138.00, 133.77, 133.68, 131.57, 130.19, 129.98, 128.78, 127.52, 127.00, 124.55, 122.37, 117.94, 82.06, 62.11, 28.27, 13.52. HRMS (ESI, m/z) calcd for $C_{26}H_{25}ClN_2O_5$ $[M+H]^+$ 481.1525, found 481.1529.



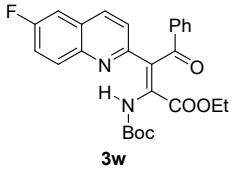
3u

3u, yellow solid, m.p. 188.9-189.9 °C, 94% yield, 60/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 12.55 (s, 1H), 8.77 (d, *J*=9.3Hz, 1H), 8.29 (dd, *J*=32.1Hz, 7.7Hz, 2H), 7.97 (d, *J*=7.8Hz, 2H), 7.84 (t, *J*=8.1Hz, 1H), 7.55 (t, *J*=7.5Hz, 1H), 7.41 (q, *J*=7.6Hz, 3H), 4.01 (q, *J*=7.2Hz, 2H), 1.54 (s, 9H), 1.07 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 194.70, 163.29, 156.18, 151.75, 146.45, 145.39, 139.30, 137.79, 135.02, 133.89, 132.68, 129.89, 128.78, 128.59, 124.70, 124.31, 119.20, 117.17, 82.33, 62.16, 28.17, 13.42. HRMS (ESI, m/z) calcd for $C_{26}H_{25}N_3O_7$ $[M+H]^+$ 492.1766, found 492.1774.



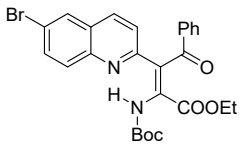
3v

3v, yellow solid, m.p. 175.3-176.3 °C, 82% yield, 25/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 12.82 (s, 1H), 9.12 (d, *J*=9.3Hz, 1H), 8.24 (d, *J*=7.3Hz, 1H), 8.16 (d, *J*=8.4Hz, 1H), 7.96 (d, *J*=7.7Hz, 2H), 7.76 (t, *J*=7.7Hz, 1H), 7.54 (t, *J*=7.4Hz, 1H), 7.42-7.39 (m, 2H), 7.27 (d, *J*=9.5Hz, 1H), 4.02 (q, *J*=7.2Hz, 2H), 3.94 (s, 3H), 1.54 (s, 9H), 1.07 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 195.11, 166.69, 163.59, 154.98, 152.07, 146.42, 138.29, 137.95, 135.18, 133.70, 133.59, 131.06, 129.92, 129.04, 128.72, 126.81, 125.19, 122.90, 117.99, 81.95, 62.03, 52.44, 28.23, 13.47. HRMS (ESI, m/z) calcd for $C_{28}H_{28}N_2O_7$ $[M+Na]^+$ 527.1789, found 527.1816.



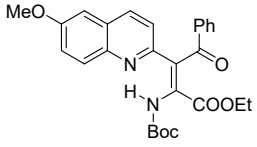
3w

3w, yellow solid, m.p. 130.4-131.4 °C, 88% yield, 30/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 12.66 (s, 1H), 8.00-7.92 (m, 4H), 7.55-7.50 (m, 2H), 7.42-7.35 (m, 3H), 7.23 (d, *J*=8.9Hz, 1H), 4.00 (q, *J*=7.1Hz, 2H), 1.54 (s, 9H), 1.06 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 195.17, 163.67, 160.81 (d, *J*=250.3Hz), 154.14 (d, *J*=2.7Hz), 152.15, 143.43, 137.97, 137.53, 136.17 (d, *J*=5.3Hz), 133.70, 130.85(d, *J*=9.1Hz), 129.93, 128.71, 127.09 (d, *J*=10.1Hz), 122.20, 120.67 (d, *J*=25.9Hz), 118.52, 110.84 (d, *J*=22.0Hz), 81.89, 62.00, 28.24, 13.48. ^{19}F NMR (471 MHz, $CDCl_3$) δ (ppm) -112.04. HRMS (ESI, m/z) calcd for $C_{26}H_{25}FN_2O_5$ $[M+H]^+$ 465.1821, found 465.1833.



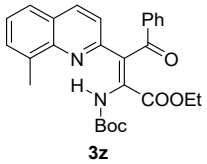
3x

3x, yellow solid, m.p. 143.8-144.8 °C, 89% yield, 27/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 12.70 (s, 1H), 7.97 (d, *J*=7.4Hz, 2H), 7.91-7.86 (m, 3H), 7.82-7.80 (m, 1H), 7.55 (t, *J*=7.4Hz, 1H), 7.42 (t, *J*=7.7Hz, 2H), 7.23 (d, *J*=8.8Hz, 1H), 4.00 (q, *J*=7.2Hz, 2H), 1.54 (s, 9H), 1.07 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 195.15, 163.65, 155.21, 152.11, 145.00, 138.11, 137.99, 135.75, 133.94, 133.77, 130.05, 129.99, 129.72, 128.76, 127.50, 122.38, 120.96, 118.26, 82.04, 62.09, 28.28, 13.52. HRMS (ESI, m/z) calcd for $C_{26}H_{25}BrN_2O_5$ $[M+H]^+$ 525.1020, found 525.1025.



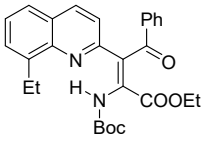
3y

3y, yellow solid, m.p. 117.6-118.6 °C, 98% yield, 25/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 12.72 (s, 1H), 7.99-7.97 (m, 2H), 7.91-7.86 (m, 2H), 7.55-7.52 (m, 1H), 7.42-7.39 (m, 3H), 7.17 (d, *J*=8.8Hz, 1H), 7.00 (d, *J*=2.8Hz, 1H), 4.00 (q, *J*=7.1Hz, 2H), 3.92 (s, 3H), 1.54 (s, 9H), 1.06 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 195.45, 163.90, 158.49, 152.40, 152.17, 142.48, 138.11, 136.43, 135.50, 133.59, 129.97, 128.69, 127.66, 123.31, 121.82, 119.33, 105.15, 81.65, 61.91, 55.77, 28.31, 13.53. HRMS (ESI, m/z) calcd for $C_{27}H_{28}N_2O_6$ $[M+H]^+$ 477.2021, found 477.2033.



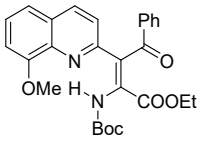
3z

3z, yellow solid, m.p. 141.1-142.1 °C, 93% yield, 100/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 13.17 (s, 1H), 8.00-7.94 (m, 3H), 7.60 (t, *J*=7.1Hz, 2H), 7.54 (t, *J*=7.4Hz, 1H), 7.42 (q, *J*=7.3Hz, 3H), 7.15 (d, *J*=8.8Hz, 1H), 4.05 (q, *J*=7.2Hz, 2H), 2.86 (s, 3H), 1.54 (s, 9H), 1.09 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 195.56, 163.87, 153.70, 152.34, 145.63, 138.11, 137.60, 137.15, 136.05, 133.64, 130.64, 130.01, 128.70, 126.89, 126.40, 125.69, 121.29, 118.67, 81.70, 62.00, 28.25, 19.05, 13.52. HRMS (ESI, m/z) calcd for $C_{27}H_{28}N_2O_5$ $[M+Na]^+$ 483.1891, found 483.1911.



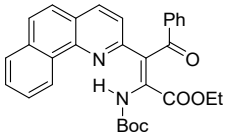
3aa

3aa, yellow solid, m.p. 153.2-154.2 °C, 99% yield, 100/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 12.91 (s, 1H), 8.00 (d, *J*=7.7Hz, 2H), 7.95 (d, *J*=8.9Hz, 1H), 7.62-7.53 (m, 3H), 7.49-7.40 (m, 3H), 7.15 (d, *J*=8.8Hz, 1H), 4.05 (q, *J*=14.3Hz, 2H), 3.33 (q, *J*=7.6Hz, 2H), 1.56 (s, 9H), 1.47 (t, *J*=7.5Hz, 3H), 1.08 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 195.67, 163.94, 153.66, 152.42, 145.07, 141.61, 138.10, 137.29, 137.27, 133.65, 130.01, 128.78, 128.70, 127.02, 126.58, 125.68, 121.30, 118.90, 81.81, 61.99, 28.31, 25.0147, 14.40, 13.52. HRMS (ESI, m/z) calcd for $C_{28}H_{30}N_2O_5$ $[M+Na]^+$ 497.2047, found 497.2084.



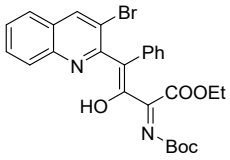
3ab

3ab, yellow solid, m.p. 157.3-158.3 °C, 99% yield, 75/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 13.16 (s, 1H), 7.98 (d, *J*=7.2Hz, 2H), 7.90 (d, *J*=8.8Hz, 1H), 7.54-7.50 (m, 1H), 7.44-7.37 (m, 3H), 7.27 (d, *J*=8.3Hz, 1H), 7.18 (d, *J*=8.8Hz, 1H), 7.06 (d, *J*=7.8Hz, 1H), 4.11 (s, 3H), 3.99 (q, 7.2Hz, 2H), 1,57 (s, 9H), 1.06 (t, *J*=7.1Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 195.50, 164.12, 154.71, 152.98, 152.73, 138.18, 138.06, 137.49, 136.39, 133.54, 129.93, 128.59, 127.23, 127.19, 121.42, 119.03, 118.64, 108.29, 81.45, 61.76, 55.99, 28.36, 13.47. HRMS (ESI, m/z) calcd for $C_{27}H_{28}N_2O_6$ $[M+H]^+$ 477.2021, found 477.2030.



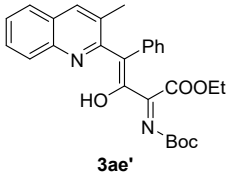
3ac

3ac, yellow solid, m.p. 175.3-176.3 °C, 74% yield, 25/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 13.10 (s, 1H), 9.12-9.11 (m, 1H), 8.03-7.99 (m, 3H), 7.96-7.94 (m, 1H), 7.81 (d, *J*=8.8Hz, 1H), 7.77-7.73 (m, 2H), 7.60 (d, *J*=8.8Hz, 1H), 7.55 (t, *J*=7.4Hz, 1H), 7.42 (t, *J*=7.6Hz, 2H), 7.28 (d, *J*=8.5Hz, 1H), 4.08 (q, *J*=7.2Hz, 2H), 1.64 (s, 9H), 1.11 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 195.56, 163.87, 153.32, 152.31, 145.03, 138.05, 136.87, 136.83, 134.34, 133.67, 130.41, 130.06, 128.73, 128.72, 128.56, 127.57, 125.06, 124.98, 124.14, 122.39, 119.21, 81.85, 62.06, 28.46, 13.56. HRMS (ESI, m/z) calcd for $C_{30}H_{28}N_2O_5$ $[M+H]^+$ 497.2071, found 497.2075



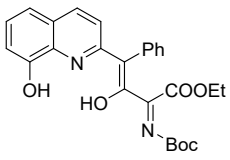
3ad'

3ad', yellow solid, m.p. 139.9-141.4 °C, 99% yield, 1/3 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 11.47 (s, 1H), 8.11-8.09 (m, 2H), 7.75-7.71 (m, 1H), 7.65-7.63 (m, 1H), 7.55-7.52 (m, 1H), 7.36 (d, *J*=7.7Hz, 2H), 7.26-7.20 (m, 2H), 7.04 (t, *J*=7.6Hz, 2H), 3.95 (q, *J*=7.2Hz, 2H), 1.50 (s, 9H), 0.94 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 195.64, 162.44, 155.19, 151.04, 147.02, 146.19, 140.10, 139.02, 131.19, 130.14, 129.28, 128.53, 127.92, 127.57, 126.62, 120.55, 115.30, 82.93, 61.81, 28.02, 13.63. HRMS (ESI, m/z) calcd for $C_{26}H_{25}BrN_2O_5$ $[M+Na]^+$ 547.0840, found 547.0853.



3ae'

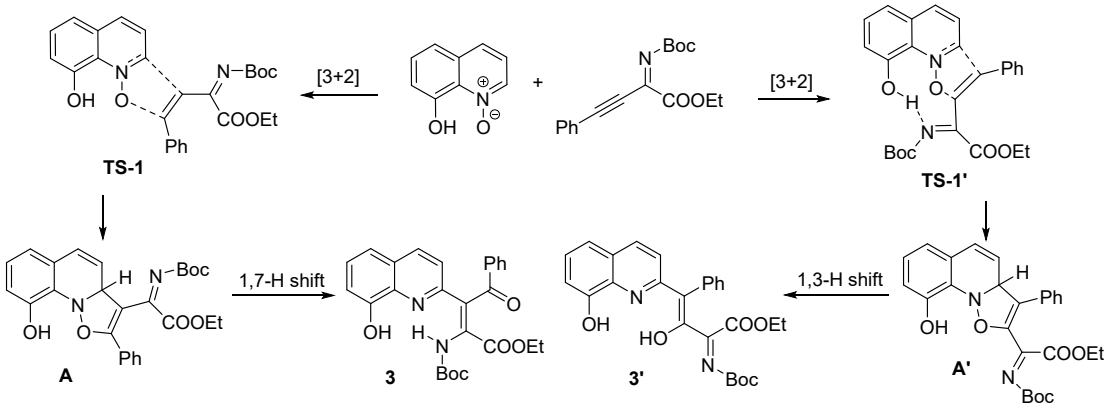
3ae', yellow solid, m.p. 135.1-136.6 °C, 78% yield, 1/2 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 11.58 (s, 1H), 8.10 (d, *J*=8.6Hz, 1H), 7.91 (d, *J*=7.8Hz, 1H), 7.68 (s, 1H), 7.66-7.64 (m, 2H), 7.62-7.59 (m, 1H), 7.49 (t, *J*=7.9Hz, 1H), 7.33-7.30 (m, 2H), 7.21 (t, *J*=7.8Hz, 1H), 7.03 (t, *J*=7.7Hz, 2H), 3.90 (q, *J*=7.2Hz, 2H), 2.10 (s, 3H), 1.50 (s, 9H), 0.90 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 196.00, 162.80, 156.70, 151.31, 147.01, 146.37, 140.10, 136.19, 132.26, 131.33, 129.62, 129.12, 128.85, 128.42, 127.78, 126.95, 126.93, 115.11, 82.89, 61.77, 28.10, 19.47, 13.64. HRMS (ESI, m/z) calcd for $C_{27}H_{28}N_2O_5$ $[M+H]^+$ 461.2071, found 461.2089.



3af'

3af', yellow solid, m.p. 141.3-142.8 °C, 86% yield, 1/2 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 11.03 (s, 0.33H), 10.47 (s, 0.67H), 8.03 (d, *J*=8.7Hz, 0.64H), 7.96 (d, *J*=7.8Hz, 1.30H), 7.84 (d, *J*=8.6Hz, 0.35H), 7.55-7.29 (m, 5.2H), 7.24-7.14 (m, 2.18H), 7.02 (d, *J*=8.6Hz, 0.34H), 4.08 (q, *J*=7.2Hz, 2H), 1.52 (s, 6H), 1.51 (s, 3H), 1.09 (t, *J*=7.2Hz, 2H), 0.98 (t, *J*=7.2Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 196.97, 194.77, 163.54, 163.51, 153.49, 152.92, 152.32, 151.86, 151.56, 151.16, 146.47, 139.80, 137.74, 137.39, 137.09, 135.72, 133.65, 131.85, 129.90, 128.77, 128.70, 128.54, 128.26, 128.17, 127.31, 126.84, 124.61, 122.66, 118.49, 117.70, 112.20, 110.52, 83.18, 82.59, 62.34, 62.26, 28.25, 28.14, 13.58, 13.54. HRMS (ESI,

m/z) calcd for $C_{26}H_{26}N_2O_6$ $[M+H]^+$ 463.1864, found 463.1872.



Scheme S1 Reaction mechanism involving 8-hydroxyquinoline N-oxide

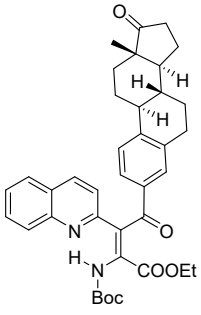
In the reaction of 8-hydroxyquinoline N-oxide with the alkynyl imine, we propose that an intermolecular hydrogen bond is formed between the hydroxyl group of the quinoline N-oxide and the nitrogen atom of the alkynyl imine substrate. This non-covalent interaction pre-organizes the two reactants in a specific orientation that favors the [3+2] cycloaddition pathway leading to intermediate **A′** (the precursor to the minor regioisomer **3af′**), rather than the normally favored intermediate **A**. As a result, the final product **3af′** becomes the major regioisomer, with a observed ratio of 1:2 (rr) and 86% isolated yield.

This hypothesis is supported by several considerations:

(1) The 8-hydroxy group is a good hydrogen bond donor, and the imine nitrogen (or the carbonyl oxygen of the Boc) in the alkyne is a good hydrogen bond acceptor.

(2) Such intermolecular hydrogen bonding interactions are known to influence regio-selectivity in cycloaddition reactions by stabilizing specific transition states.

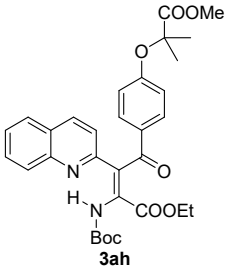
(3) The absence of this effect in 8-substituted quinolines lacking a free OH group (e.g., 8-Me **3z**, 8-Et **3aa**, 8-OMe **3ab**) leads to the normal selectivity (favoring **3**), which further supports the key role of the OH group in directing the selectivity through hydrogen bonding.



3ag

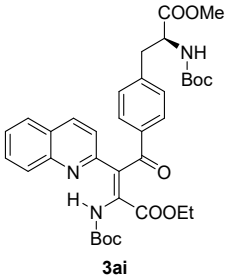
3ag, yellow solid, m.p. 156.1-157.1 °C, 60% yield, 23/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 12.94 (s, 1H), 8.01-7.96 (m, 2H), 7.77-7.72 (m, 4H), 7.53 (t, *J*=7.4Hz, 1H), 7.31 (d, *J*=8.1Hz, 1H), 7.20 (d, *J*=8.8Hz, 1H), 4.05 (q, *J*=7.2Hz, 2H), 2.95-2.88

(m, 2H), 2.52-2.47 (m, 1H), 2.41-2.28 (m, 2H), 2.17-1.95 (m, 4H), 1.67-1.39 (m, 15H), 1.11 (t, *J*=7.2Hz, 3H), 0.89 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 195.22, 163.90, 154.89, 152.32, 146.36, 146.21, 137.30, 137.12, 136.75, 135.68, 130.41, 130.38, 128.43, 127.62, 127.58, 127.10, 126.47, 125.72, 121.58, 118.84, 81.72, 61.93, 50.67, 47.96, 44.91, 37.88, 35.90, 31.64, 28.29, 26.34, 25.61, 21.68, 13.91, 13.61. HRMS (ESI, m/z) calcd for $C_{38}H_{42}N_2O_6$ $[M+Na]^+$ 623.3116, found 623.3122.



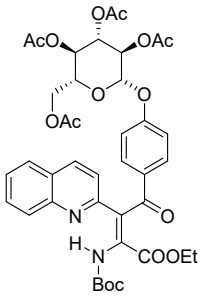
3ah

3ah, yellow solid, m.p. 123.5-124.5 °C, 75% yield, 34/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 12.90 (s, 1H), 7.99-7.96 (m, 2H), 7.89 (d, *J*=8.6Hz, 2H), 7.75-7.72 (m, 2H), 7.52 (t, *J*=8.35Hz, 1H), 7.22 (d, *J*=8.7Hz, 1H), 6.75 (d, *J*=8.5Hz, 2H), 4.03 (q, *J*=7.1Hz, 2H), 3.71 (s, 3H), 1.61 (s, 6H), 1.53 (s, 9H), 1.07 (t, *J*=7.1Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 193.76, 174.12, 163.79, 160.28, 154.77, 152.29, 146.32, 137.06, 136.74, 131.95, 131.66, 130.36, 128.36, 127.60, 127.07, 126.44, 121.47, 118.67, 117.44, 81.65, 79.43, 61.87, 52.71, 28.24, 25.44, 13.51. HRMS (ESI, m/z) calcd for $C_{31}H_{34}N_2O_8$ $[M+H]^+$ 563.2338, found 563.2393.



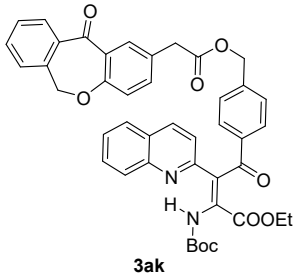
3ai

3ai, yellow solid, m.p. 95.5-96.5 °C, 66% yield, 27/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 12.91 (s, 1H), 7.98 (t, *J*=8.5Hz, 2H), 7.90 (d, *J*=7.9Hz, 2H), 7.75-7.72 (m, 2H), 7.52 (t, *J*=7.5Hz, 1H), 7.19-7.16 (m, 3H), 5.00 (d, *J*=8.2Hz, 1H), 4.57 (q, *J*=6.7Hz, 1H), 4.00 (q, *J*=7.2Hz, 2H), 3.67 (s, 3H), 3.18-3.04 (m, 2H), 1.53 (s, 9H), 1.38 (s, 9H), 1.07 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 194.78, 171.91, 163.71, 155.03, 154.64, 152.22, 146.31, 142.49, 137.55, 136.8357, 136.76, 130.41, 130.12, 129.66, 128.34, 127.60, 127.11, 126.43, 121.43, 118.54, 81.73, 80.15, 61.93, 54.25, 52.38, 38.40, 28.32, 28.22, 13.51. HRMS (ESI, m/z) calcd for $C_{35}H_{41}N_3O_9$ $[M+Na]^+$ 670.2735, found 670.2756.



3aj

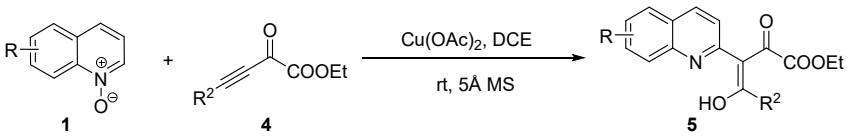
3aj, yellow solid, m.p. 151.9-152.9 °C, 68% yield, 30/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 12.83 (s, 1H), 7.93 (t, *J*=9.1Hz, 4H), 7.72-7.69 (m, 2H), 7.49 (t, *J*=7.6Hz, 1H), 7.10 (t, *J*=8.8Hz, 1H), 6.95 (d, *J*=8.9Hz, 2H), 5.29-5.22 (m, 2H), 5.17-5.10 (m, 2H), 4.25-4.21 (m, 1H), 4.11-4.08 (m, 1H), 4.02 (q, *J*=7.2Hz, 2H), 3.89-3.86 (m, 1H), 1.99-1.96 (m, 12H), 1.50 (s, 9H), 1.07 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 193.68, 170.37, 170.03, 169.31, 169.14, 163.66, 160.60, 154.52, 152.11, 146.19, 137.23, 136.72, 133.10, 132.05, 130.37, 128.20, 127.53, 127.05, 126.29, 121.28, 118.31, 116.25, 97.97, 81.62, 77.36, 72.52, 72.19, 70.97, 68.09, 61.83, 61.80, 28.11, 20.55, 20.51, 20.48, 13.45. HRMS (ESI, m/z) calcd for $C_{40}H_{44}N_2O_{15}$ $[M+Na]^+$ 815.2634, found 815.2662.



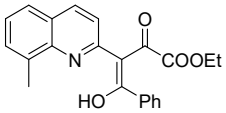
3ak

3ak, yellow solid, m.p. 123.7-124.7 °C,55% yield, 30/1 rr, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 12.93 (s, 1H), 7.93 (t, *J*=9.1Hz, 4H), 8.12 (d, *J*=2.4Hz, 1H), 8.01-7.95 (m, 4H), 7.86 (d, *J*=7.7Hz, 1H), 7.77-7.72 (m, 2H), 7.55-7.51 (m, 2H), 7.46-7.43 (m, 1H), 7.40 (dd, *J*=8.5Hz, 2.5Hz, 1H), 7.36-7.33 (m, 3H), 7.15 (d, *J*=8.8Hz, 1H), 7.01 (d, *J*=8.5Hz, 1H), 5.16 (d, *J*=6.0Hz, 4H), 4.03 (q, *J*=7.2Hz, 2H), 3.69 (s, 2H), 1.55 (s, 9H), 1.08 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 194.80, 190.79, 171.05, 163.73, 160.63, 154.63, 152.20, 146.32, 141.53, 140.45, 137.77, 136.82, 136.33, 135.60, 132.88, 132.56, 130.44, 130.20, 129.54, 129.35, 128.37, 127.91, 127.84, 127.63, 127.47, 127.12, 126.43, 125.25, 121.46, 121.22, 118.40, 81.79, 73.69, 65.89, 61.99, 40.20, 28.25, 13.53. HRMS (ESI, m/z) calcd for $C_{43}H_{38}N_2O_9$ $[M+H]^+$ 727.2651, found 727.2662.

4.2. Preparation and characterization of 5

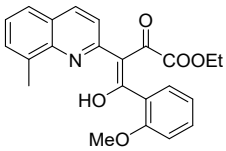


A mixture of quinoline N-oxides **1** (0.24 mmol), ynones **4** (0.20 mmol), $Cu(OAc)_2$ (0.01 mmol, 5 mol%) and 5Å molecular sieves (100 mg) in anhydrous DCE (2 mL) was stirred at room temperature. Upon completion (monitored by TLC), the reaction mixture was filtered, concentrated under reduced pressure, and purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1 to 1:1) to afford product **5**.



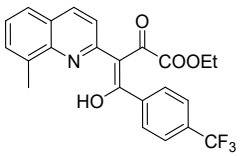
5a

5a, yellow oil, 96% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.00 (d, *J*=9.4Hz, 1H), 7.87 (d, *J*=7.6Hz, 2H), 7.63-7.58 (m, 3H), 7.51 (t, *J*=7.6Hz, 1H), 7.43-7.40 (m, 3H), 3.88 (q, *J*=7.3Hz, 2H), 2.76 (s, 3H), 1.11 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 194.99, 179.89, 165.13, 154.51, 141.02, 139.69, 135.54, 132.91, 132.51, 129.49, 128.59, 127.47, 125.89, 125.84, 124.28, 119.78, 105.29, 61.83, 17.24, 13.81. HRMS (ESI, m/z) calcd for $C_{22}H_{19}NO_4$ $[M+Na]^+$ 384.1207, found 384.1222.



5b

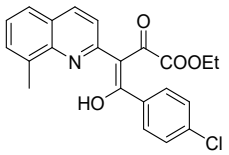
5b, yellow oil, 78% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.67-8.01 (m, 2H), 7.58-7.36 (m, 5H), 6.96 (t, *J*=7.5Hz, 1H), 6.89 (d, *J*=8.4Hz, 1H), 3.81-3.57 (m, 5H), 2.70 (s, 3H), 1.11 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 192.63, 186.98, 183.41, 165.66, 154.54, 139.97, 135.20, 132.63, 132.14, 131.32, 130.69, 127.30, 125.72, 125.64, 124.23, 120.39, 119.89, 111.40, 61.48, 55.83, 17.15, 13.77. HRMS (ESI, m/z) calcd for $C_{23}H_{21}NO_5$ $[M+Na]^+$ 414.1312, found 414.1318.



5c

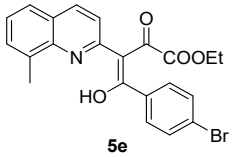
5c, yellow oil, 70% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.06-7.94 (m, 3H), 7.67-7.58 (m, 5H), 7.42 (t, *J*=7.6Hz, 3H), 3.86 (q, *J*=6.5Hz, 2H), 2.74 (s, 3H), 1.07 (t, *J*=7.3Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 193.66, 180.29, 165.01, 154.32, 144.14, 140.18, 135.35, 133.08, 129.68, 127.43, 127.05, 126.00 (d, *J*=31.5Hz), 125.48, 124.35, 123.80 (d, *J*=272.2Hz), 120.55, 119.45, 104.66, 61.96, 17.13, 13.66. ^{19}F NMR

(471 MHz, $CDCl_3$) δ (ppm) -62.98. HRMS (ESI, m/z) calcd for $C_{23}H_{18}F_3NO_4$ $[M+Na]^+$ 452.1081, found 452.1083.



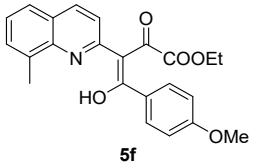
5d

5d, yellow oil, 73% yield, ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.99 (d, *J*=9.4Hz, 1H), 7.78 (d, *J*=8.1Hz, 2H), 7.57-7.54 (m, 4H), 7.41-7.35 (m, 3H), 3.92 (q, *J*=7.4Hz, 2H), 2.71 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 193.57, 179.60, 164.99, 154.22, 139.8561, 139.36, 138.73, 135.38, 132.96, 130.77, 128.77, 127.35, 125.97, 125.83, 124.22, 119.48, 104.86, 61.89, 17.11, 13.76. HRMS (ESI, m/z) calcd for $C_{22}H_{18}ClNO_4$ $[M+Na]^+$ 418.0817, found 418.0824.



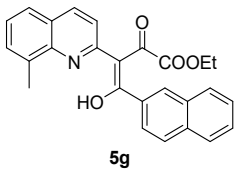
5e

5e, yellow oil, 55% yield, ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.01 (d, *J*=9.4Hz, 1H), 7.73 (d, *J*=8.1Hz, 2H), 7.61-7.54 (m, 5H), 7.42 (t, *J*=7.6Hz, 1H), 3.94 (q, *J*=7.3Hz, 2H), 2.76 (s, 3H), 1.14 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 193.84, 179.69, 165.03, 154.32, 139.94, 139.85, 135.51, 133.04, 131.84, 130.98, 127.50, 126.04, 125.89, 124.33, 119.60, 104.91, 62.01, 17.22, 13.83. HRMS (ESI, m/z) calcd for $C_{22}H_{18}BrNO_4$ $[M+Na]^+$ 462.0312, found 462.0317.



5f

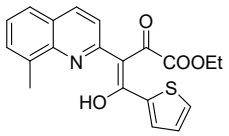
5f, yellow oil, 80% yield, ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.94 (d, *J*=9.4Hz, 1H), 7.85 (d, *J*=8.4Hz, 2H), 7.55 (d, *J*=7.6Hz, 2H), 7.47 (d, *J*=9.3Hz, 1H), 7.37 (t, *J*=7.6Hz, 1H), 6.88 (d, *J*=8.8Hz, 2H), 3.94 (q, *J*=7.2Hz, 2H), 3.82 (s, 3H), 2.71 (s, 3H), 1.12 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 193.62, 178.70, 165.07, 163.29, 154.29, 139.38, 135.56, 133.68, 132.78, 131.66, 127.34, 125.77, 125.72, 124.14, 119.73, 113.76, 105.55, 61.72, 55.53, 17.15, 13.81. HRMS (ESI, m/z) calcd for $C_{23}H_{21}NO_5$ $[M+Na]^+$ 414.1312, found 414.1312.



5g

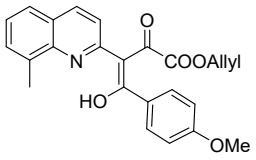
5g, yellow oil, 77% yield, ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.26 (s, 1H), 8.01-

7.95 (m, 2H), 7.87-7.82 (m, 3H), 7.69 (d, *J*=9.5Hz, 1H), 7.56-7.46 (m, 4H), 7.37 (t, *J*=7.1Hz, 1H), 3.68 (q, *J*=7.3Hz, 2H), 2.73 (s, 3H), 0.85 (t, *J*=7.3Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 194.76, 180.07, 165.09, 154.43, 139.72, 138.47, 135.33, 135.25, 132.83, 132.34, 130.75, 129.41, 128.61, 128.20, 127.74, 127.25, 126.74, 125.83, 125.77, 125.31, 124.18, 119.64, 105.24, 61.66, 17.11, 13.44. HRMS (ESI, m/z) calcd for $C_{26}H_{21}NO_4$ $[M+Na]^+$ 434.1363, found 434.1371.



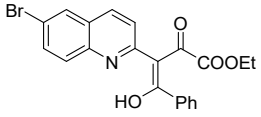
5h

5h, yellow oil, 90% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.12 (d, *J*=9.4Hz, 1H), 7.68-7.54 (m, 5H), 7.39 (t, *J*=7.6Hz, 1H), 7.02 (t. *J*=4.4Hz, 1H), 3.98 (q, *J*=7.2Hz, 2H), 2.73 (s, 3H), 1.14 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 186.67, 178.23, 164.88, 153.96, 148.05, 139.76, 135.43, 133.86, 133.04, 132.90, 127.74, 127.37, 125.90, 125.83, 124.28, 119.44, 105.71, 61.98, 17.16, 13.83. HRMS (ESI, m/z) calcd for $C_{20}H_{17}NO_4S$ $[M+Na]^+$ 390.0771, found 390.0778.



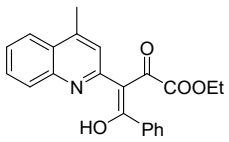
5i

5i, yellow oil, 83% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.95 (d, *J*=9.4Hz, 1H), 7.83 (d, *J*=8.4Hz, 2H), 7.56-7.48 (m, 3H), 7.37 (t, *J*=7.6Hz, 1H), 6.87 (d, *J*=8.7Hz, 2H), 5.77-5.69 (m, 1H), 5.24-5.14 (m, 2H), 4.34 (d, *J*=6.1Hz, 2H), 3.82 (s, 3H), 2.71 (S, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 193.59, 178.58, 164.75, 163.25, 154.26, 139.46, 135.46, 133.61, 132.80, 131.67, 131.28, 127.30, 125.77, 124.14, 119.71, 119.18, 113.76, 105.51, 66.33, 55.51, 17.14. HRMS (ESI, m/z) calcd for $C_{24}H_{21}NO_5$ $[M+Na]^+$ 426.1312, found 426.1335.



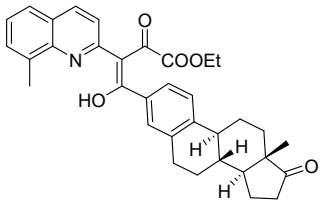
5j

5j, yellow oil, 94% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.87-7.87 (m, 5H), 7.57-7.50 (m, 3H), 7.41 (t, *J*=7.6Hz, 2H), 3.84 (s, 2H), 1.09 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 196.70, 181.26, 164.73, 154.96, 140.74, 137.82, 135.37, 135.19, 132.62, 130.21, 129.44, 128.64, 125.37, 121.34, 120.73, 119.39, 106.12, 61.85, 13.76. HRMS (ESI, m/z) calcd for $C_{21}H_{16}BrNO_4$ $[M+Na]^+$ 448.0155, found 448.0166.



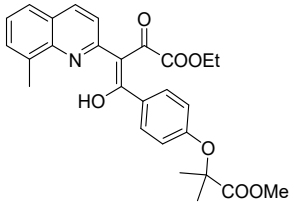
5k

5k, yellow oil, 96% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.00 (d, *J*=9.4Hz, 1H), 7.87 (d, *J*=7.6Hz, 2H), 7.63-7.49 (m, 4H), 7.41 (t, *J*=7.5Hz, 3H), 3.88 (q, *J*=7.2Hz, 2H), 2.76 (s, 3H), 1.11 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 195.33, 165.12, 154.37, 148.84, 141.24, 135.80, 132.25, 132.00, 129.45, 128.48, 125.98, 124.51, 124.49, 119.73, 119.42, 104.04, 61.62, 19.77, 13.74. HRMS (ESI, m/z) calcd for $C_{22}H_{19}NO_4$ $[M+Na]^+$ 384.1207, found 384.1215.



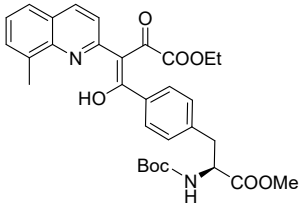
5l

5l, yellow oil, 60% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.97 (d, *J*=9.4Hz, 1H), 7.64-7.53 (m, 5H), 7.38 (t, *J*=7.6Hz, 1H), 7.31 (d, *J*=8.1Hz, 1H), 3.92 (q, *J*=7.1Hz, 2H), 2.92-2.89 (m, 2H), 2.73 (s, 3H), 2.52-2.46 (m, 1H), 2.44-2.40 (m, 1H), 2.33-2.28 (m, 1H), 2.17-2.09 (m, 1H), 2.07-2.00 (m, 2H), 1.97-1.94 (m, 1H), 1.66-1.40 (m, 6H), 1.10 (t, *J*=7.2Hz, 3H), 0.89 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 194.51, 179.11, 164.96, 154.16, 144.70, 139.41, 138.25, 136.71, 135.28, 132.70, 129.91, 127.12, 126.77, 125.68, 125.47, 124.01, 119.53, 105.32, 77.36, 61.56, 50.45, 47.79, 44.62, 37.83, 35.74, 31.49, 29.19, 26.24, 25.56, 21.52, 17.00, 13.76, 13.67. HRMS (ESI, m/z) calcd for $C_{34}H_{35}NO_5$ $[M+Na]^+$ 560.2408, found 560.2418.



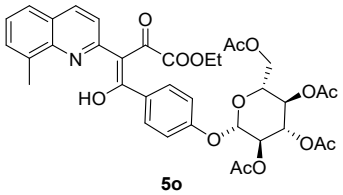
5m

5m, yellow oil, 80% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.95 (d, *J*=9.4Hz, 1H), 7.78 (d, *J*=8.4Hz, 2H), 7.56-7.49 (m, 3H), 7.73 (t, *J*=7.6Hz, 1H), 6.77 (d, *J*=8.8Hz, 2H), 3.93 (q, *J*=7.1Hz, 2H), 3.73 (s, 3H), 2.71 (s, 3H), 1.61 (s, 6H), 1.11 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 193.64, 179.01, 174.28, 165.06, 159.37, 154.27, 139.47, 135.49, 134.47, 132.81, 131.26, 127.33, 125.77, 124.15, 119.69, 117.62, 105.35, 79.36, 61.73, 52.68, 25.44, 17.15, 13.80. HRMS (ESI, m/z) calcd for $C_{27}H_{27}NO_7$ $[M+Na]^+$ 500.1680, found 500.1695.



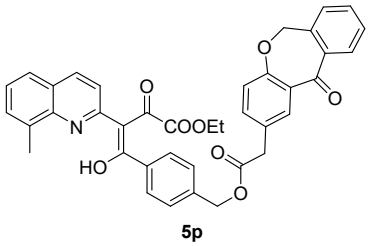
5n

5n, yellow oil, 75% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.97 (d, *J*=9.4Hz, 1H), 7.78 (d, *J*=7.8Hz, 2H), 7.57-7.52 (m, 3H), 7.38 (t, *J*=7.6Hz, 1H), 7.16 (d, *J*=7.9Hz, 2H), 5.00 (d, *J*=8.2Hz, 1H), 4.56 (q, *J*=6.0Hz, 1H), 3.87 (q, *J*=7.3Hz, 2H), 3.69 (s, 3H), 3.17-3.05 (m, 2H), 2.72 (s, 3H), 1.40 (s, 9H), 1.11 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 194.38, 179.66, 171.99, 165.04, 155.08, 154.38, 141.13, 139.74, 139.62, 135.43, 132.86, 129.64, 129.50, 127.34, 125.85, 125.78, 124.20, 119.67, 105.20, 80.14, 61.75, 54.37, 52.38, 38.28, 28.35, 17.13, 13.78. HRMS (ESI, m/z) calcd for $C_{31}H_{34}N_2O_8$ $[M+Na]^+$ 585.2208, found 585.2222.



5o

5o, yellow oil, 78% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.95 (d, *J*=9.4Hz, 1H), 7.83 (d, *J*=8.3Hz, 2H), 7.56-7.35 (m, 4H), 6.96 (d, *J*=8.5Hz, 2H), 5.30-5.23 (m, 2H), 5.15-5.11 (m, 2H), 4.27-4.23 (m, 1H), 4.14-4.11 (m, 1H), 3.95-3.86 (m, 3H), 2.70 (s, 3H), 2.03-2.00 (m, 12H), 1.10 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 193.43, 178.84, 170.49, 170.15, 169.39, 169.23, 164.98, 159.95, 154.14, 139.59, 135.93, 135.45, 132.86, 131.45, 127.32, 125.82, 125.78, 124.13, 119.54, 116.30, 105.23, 98.33, 72.63, 72.30, 71.12, 68.23, 61.94, 61.76, 20.70, 20.61, 20.59, 20.58, 17.10, 13.77. HRMS (ESI, m/z) calcd for $C_{36}H_{37}NO_{14}$ $[M+Na]^+$ 730.2107, found 730.2121.



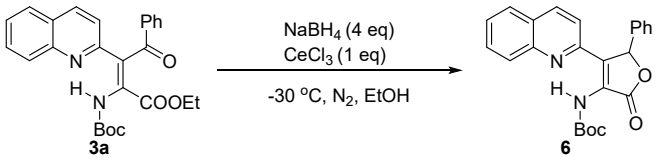
5p

5p, yellow oil, 87% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.12 (d, *J*=2.4Hz, 1H), 7.98 (d, *J*=9.4Hz, 1H), 7.88-7.84 (m, 3H), 7.59-7.52 (m, 4H), 7.46-7.33 (m, 6H), 7.02 (d, *J*=8.4Hz, 1H), 5.17 (s, 4H), 3.89 (q, *J*=7.3Hz, 2H), 3.70 (s, 2H), 2.75 (s, 3H), 1.10 (t, *J*=7.3Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 194.36, 190.82, 179.65, 171.12, 165.07, 160.66, 154.37, 140.72, 140.50, 140.33, 139.74, 136.36, 135.66, 135.52, 132.93, 132.89, 132.60, 129.72, 129.59, 129.37, 127.92, 127.88, 127.57, 127.44, 125.90, 125.84, 125.31, 124.27, 121.25, 119.70, 105.25, 73.75, 66.07, 61.85,

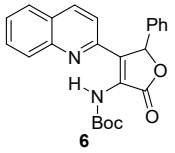
40.28, 17.20, 13.81. HRMS (ESI, m/z) calcd for $C_{39}H_{31}NO_8$ $[M+Na]^+$ 664.1942, found 664.1962.

5. Synthetic applications

5.1. Synthesis of 6

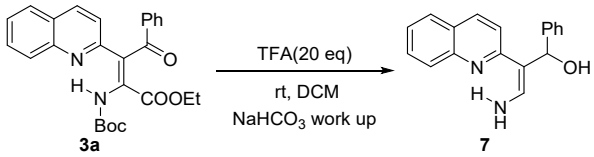


A solution of compound **3a** (0.20 mmol) in anhydrous EtOH (2 mL) was cooled to –30 °C. To this solution were slowly added $NaBH_4$ (0.80 mmol) and $CeCl_3$ (0.20 mmol). The resulting mixture was stirred at this temperature for 4 h. The reaction was then quenched by the addition of water. The mixture was extracted with DCM (3 × 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1) afforded the desired product **6**.

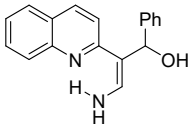


6, yellow solid, m.p. 197.3-198.5 °C, 72% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.77 (s, 1H), 8.03 (t, *J*=11.3Hz, 2H), 7.75-7.71 (m, 2H), 7.54 (t, *J*=7.6Hz, 1H), 7.40-7.38 (m, 2H), 7.31-7.30 (m, 3H), 7.21 (d, *J*=8.6Hz, 1H), 6.48 (s, 1H), 1.48 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 168.23, 151.78, 150.69, 147.40, 138.21, 136.34, 135.57, 130.39, 129.64, 129.53, 129.07, 128.19, 127.76, 127.68, 127.36, 127.28, 120.60, 82.21, 82.06, 28.20. HRMS (ESI, m/z) calcd for $C_{24}H_{22}N_2O_4$ $[M+Na]^+$ 425.1472, found 425.1483.

5.2. Synthesis of 7



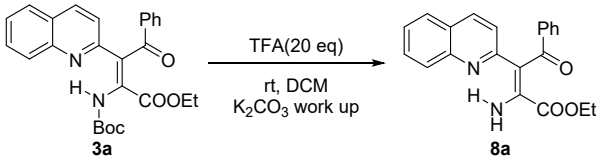
To a solution of compound **3a** (0.20 mmol) in DCM (2 mL) was slowly added trifluoroacetic acid (TFA, 4.0 mmol, 20 equiv) at room temperature. The mixture was stirred for 2 h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution. The mixture was extracted with DCM (3 × 5 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by silica gel column chromatography (petroleum ether/ethyl acetate = 1:1) afforded the desired product **7**.



7

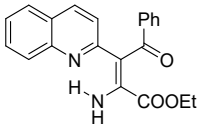
7, yellow solid, m.p. 127.8-128.5 °C, 94% yield, ^{1}H NMR (500 MHz, DMSO) δ (ppm) 8.46 (s, 0.7Hz), 8.31 (s, 0.3Hz), 8.12-8.10 (m, 2H), 7.79 (dd, *J*=8.0Hz, 1.4Hz, 1H), 7.72-7.69 (m, 1H), 7.59-7.58 (m, 2H), 7.50-7.47 (m, 2H), 7.39-7.32 (m, 3H), 7.21 (d, *J*=8.8Hz, 1H), 3.41 (s, 1H). ^{13}C NMR (126 MHz, DMSO) δ (ppm) 167.77, 153.33, 147.26, 139.86, 135.83, 129.93, 128.91, 128.56, 128.20, 127.71, 126.07, 125.81, 125.47, 119.57, 79.26. HRMS (ESI, m/z) calcd for $C_{18}H_{16}N_2O$ $[M+Na]^+$ 299.1155, found 299.1155.

5.3. Synthesis of 8a



3a **8a**

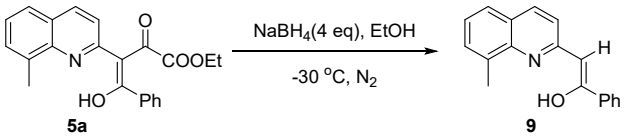
A solution of compound **3a** (0.20 mmol) in DCM (2 mL) was treated slowly with trifluoroacetic acid (TFA, 4.0 mmol, 20 equiv) at room temperature. After stirring for 2 h, the reaction was quenched with saturated aqueous K_2CO_3 solution. The mixture was extracted with DCM (3 × 5 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by silica gel column chromatography (petroleum ether/ethyl acetate = 3:1) afforded the desired product **8a**.



8a

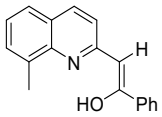
8a, yellow solid, m.p. 110.8-111.3 °C, 91% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.03-7.98 (m, 3H), 7.88-7.87 (m, 1H), 7.69-7.66 (m, 2H), 7.53-7.50 (m, 1H), 7.47-7.40 (m, 3H), 7.10 (d, *J*=8.9Hz, 1H), 4.07 (q, *J*=7.2Hz, 2H), 1.03 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 197.42, 164.46, 156.66, 146.75, 140.01, 139.35, 135.71, 132.83, 129.22, 128.59, 128.07, 127.44, 125.94, 125.61, 121.13, 111.29, 62.41, 13.43. HRMS (ESI, m/z) calcd for $C_{21}H_{18}N_2O_3$ $[M+Na]^+$ 369.1210, found 369.1197.

5.4. Synthesis of 9



5a **9**

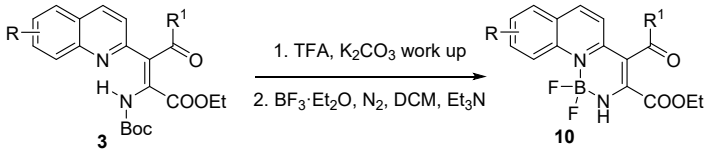
At –30 °C under a nitrogen atmosphere, $NaBH_4$ (0.40 mmol) was slowly added to a solution of **5a** (0.10 mmol) in EtOH (1 mL). The mixture was stirred at this temperature for 2 h. The reaction was quenched by adding water. The mixture was extracted with DCM (3 × 5 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) afforded product **9**.



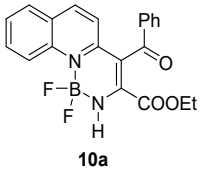
9

9, yellow oil, 83% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 19.97 (s, 1H), 7.99-7.97 (m, 2H), 7.69 (d, *J*=9.1Hz, 1H), 7.45-7.41 (m, 5H), 7.20 (t, *J*=7.6Hz, 1H), 6.90 (d, *J*=9.1Hz, 1H), 6.15 (s, 1H), 2.70 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 184.19, 154.18, 140.10, 137.04, 136.88, 131.82, 130.45, 128.41, 126.87, 126.38, 125.57, 123.54, 123.38, 121.93, 90.22, 17.41. HRMS (ESI, m/z) calcd for $C_{18}H_{15}NO$ $[M+H]^+$ 262.1227, found 262.1252.

5.5. Synthesis of 10



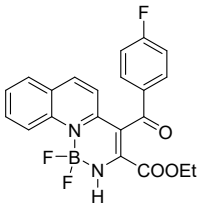
10 was prepared from quinoline-enamine **3** (0.10 mmol) using a one-pot procedure. The crude **8** was used directly in the next step without purification. A solution of crude **8** in DCM (1.25 mL) was placed under a nitrogen atmosphere at room temperature. To this solution, $BF_3{\cdot}Et_2O$ (1.03 mmol) and Et_3N (1.05 mmol) were added dropwise sequentially. The mixture was stirred for 0.5 h, then quenched with water. The mixture was extracted with DCM (3 × 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by silica gel column chromatography (petroleum ether/DCM = 1:4) afforded the desired product **10**.



10a

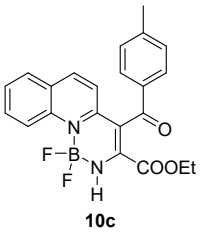
10a, yellow solid, m.p. 122.8-123.8 °C, 48% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.85 (d, *J*=8.9Hz, 1H), 7.97-7.93 (m, 3H), 7.76-7.68 (m, 2H), 7.56-7.50 (m, 2H), 7.43 (t, *J*=7.6Hz, 2H), 7.24 (d, *J*=4.6Hz, 1H), 6.84 (s, 1H), 4.06 (q, *J*=6.9Hz, 2H), 1.01 (t, *J*=7.0Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 194.63, 162.20, 151.93, 144.93, 140.22, 139.16, 133.66, 132.23, 129.34, 129.04, 128.58, 126.96, 126.37,

123.65 (t, *J*=9.5Hz), 119.90, 105.12, 63.52, 13.49. HRMS (ESI, m/z) calcd for $C_{21}H_{17}BF_2N_2O_3$ $[M+Na]^+$ 417.1193, found 417.1207.



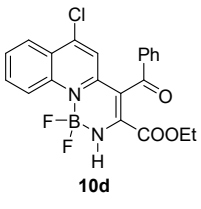
10b

10b, yellow oil, 46% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.87 (d, *J*=8.7Hz, 1H), 8.01-7.98 (m, 3H), 7.80-7.72 (m, 2H), 7.55 (t, *J*=7.5Hz, 1H), 7.23 (d, *J*=9.1Hz, 1H), 7.13 (t, *J*=8.4Hz, 2H), 6.86 (s, 1H), 4.13 (q, *J*=7.1Hz, 2H), 1.09 (t, *J*=7.4Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 193.16, 166.15 (d, *J*=256.5Hz), 162.03, 151.72, 144.69, 140.37, 140.16, 135.61 (d, *J*=2.9Hz), 132.35, 131.97 (d, *J*=9.5Hz) 128.62, 127.06, 126.37, 123.64 (t, *J*=8.8Hz), 119.72, 116.21 (d, *J*=22.0Hz), 104.89, 63.60, 13.60. HRMS (ESI, m/z) calcd for $C_{21}H_{16}BF_3N_2O_3$ $[M+Na]^+$ 435.1099, found 435.1093.



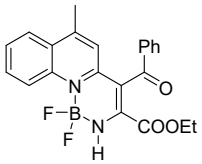
10c

10c, yellow solid, m.p. 131.5-132.5 °C, 28% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.87 (d, *J*=9.1Hz, 1H), 7.97 (d, *J*=9.1Hz, 1H), 7.86 (d, *J*=8.1Hz, 2H), 7.79-7.76 (m, 1H), 7.72-7.70 (m, 1H), 7.54 (t, *J*=7.6Hz, 1H), 7.25 (d, *J*=7.1Hz, 3H), 6.85 (s, 1H), 4.10 (q, *J*=7.2Hz, 2H), 2.41 (s, 3H), 1.06 (t, *J*=7.1Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 194.34, 162.22, 151.96, 144.71, 144.63, 140.13, 136.67, 132.20, 129.75, 129.51, 128.57, 126.92, 126.35, 123.62(t, *J*=9.4Hz), 120.00, 105.39, 63.49, 21.86, 13.54. HRMS (ESI, m/z) calcd for $C_{22}H_{19}BF_2N_2O_3$ $[M+Na]^+$ 431.1349, found 431.1358.



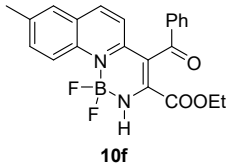
10d

10d, yellow solid, m.p. 150.8-151.8 °C, 40% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.90 (d, *J*=9.3Hz, 1H), 8.17 (d, *J*=8.1Hz, 1H), 7.95 (d, *J*=7.2Hz, 2H), 7.83 (t, *J*=8.0Hz, 1H), 7.64-7.58 (m, 2H), 7.49-7.46 (m, 3H), 6.94 (s, 1H), 4.06 (q, *J*=7.2Hz, 2H), 1.03 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 194.15, 162.00, 151.53, 146.65, 146.00, 140.92, 139.16, 133.81, 133.04, 129.31, 129.11, 127.53, 125.21, 124.50, 123.86(t, *J*=9.7Hz), 119.55, 104.25, 63.70, 13.47. HRMS (ESI, m/z) calcd for $C_{21}H_{16}BClF_2N_2O_3$ $[M+Na]^+$ 451.0803, found 451.0809.



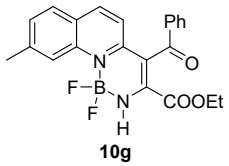
10e

10e, yellow solid, m.p. 133.3-134.3 °C, 56% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.91 (d, *J*=9.0Hz, 1H), 7.98-7.96 (m, 2H), 7.89 (dd, *J*=8.3Hz, 1.6Hz, 1H), 7.79-7.75 (m, 1H), 7.59-7.55 (m, 2H), 7.46 (t, *J*=7.6Hz, 2H), 7.14 (s, 1H), 6.76 (s, 1H), 4.07 (q, *J*=7.2Hz, 2H), 2.58 (s, 3H), 1.04 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 194.93, 162.28, 151.31, 149.19, 144.61, 139.89, 139.33, 133.60, 131.80, 129.18 (d, *J*=40.4Hz), 126.78, 126.60, 124.48, 124.05 (t, *J*=9.6Hz), 120.03, 104.78, 63.43, 19.89, 13.53. ^{11}B NMR (160 MHz, $CDCl_3$) δ (ppm) 2.73 (t, *J*=32.6Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ (ppm) -120.67 (dd, *J*=65.52Hz, 30.5Hz). HRMS (ESI, m/z) calcd for $C_{22}H_{19}BF_2N_2O_3$ $[M+Na]^+$ 431.1349, found 431.1363.



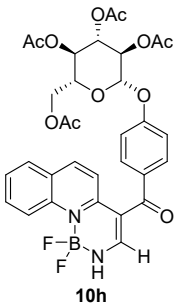
10f

10f, yellow oil, 46% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.76 (d, *J*=9.3Hz, 1H), 7.96 (d, *J*=7.3Hz, 2H), 7.92 (d, *J*=9.1Hz, 1H), 7.61-7.56 (m, 2H), 7.49-7.45 (m, 3H), 7.24 (d, *J*=9.3Hz, 1H), 6.78 (s, 1H), 4.08 (q, *J*=7.1Hz, 2H), 2.50 (s, 3H), 1.03 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 194.76, 162.29, 151.17, 144.29, 139.84, 139.17, 138.43, 137.23, 134.13, 133.61, 129.34, 129.01, 127.67, 126.56, 123.39 (t, *J*=9.3Hz), 119.83, 105.14, 63.43, 21.14, 13.50. HRMS (ESI, m/z) calcd for $C_{22}H_{19}BF_2N_2O_3$ $[M+Na]^+$ 431.1349, found 431.1354.



10g

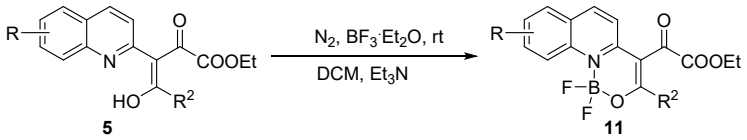
10g, yellow solid, m.p. 148.3-149.3 °C, 34% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.66 (s, 1H), 7.97-7.93 (m, 3H), 7.62-7.55 (m, 2H), 7.45 (t, *J*=7.6Hz, 2H), 7.37 (d, *J*=8.1Hz, 1H), 7.19 (d, *J*=9.1Hz, 1H), 6.79 (s, 1H), 4.09 (q, *J*=7.2Hz, 2H), 2.61 (s, 3H), 1.04 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 194.80, 162.28, 151.75, 144.40, 143.42, 140.37, 140.02, 139.14, 133.62, 129.34, 129.01, 128.94, 128.29, 124.56, 123.04(t, *J*=9.16Hz), 118.92, 105.17, 63.45, 22.87, 13.50. HRMS (ESI, m/z) calcd for $C_{22}H_{19}BF_2N_2O_3$ $[M+Na]^+$ 431.1349, found 431.1350.



10h

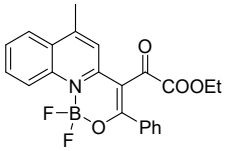
10h, yellow solid, m.p. 176.4-177.4 °C, 48% yield, ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.70 (d, *J*=8.9Hz, 1H), 8.10 (d, *J*=8.8Hz, 1H), 7.93 (d, *J*=8.9Hz, 2H), 7.79-7.76 (m, 1H), 7.72 (d, *J*=7.3Hz, 1H), 7.52 (t, *J*=7.7Hz, 1H), 7.19 (d, *J*=8.7Hz, 1H), 7.02 (d, *J*=8.9Hz, 2H), 6.31 (s, 1H), 5.34-5.28 (m, 2H), 5.18 (t, *J*=9.8Hz, 2H), 4.31-4.28 (m, 2H), 4.20-4.17 (m, 1H), 3.94-3.91 (m, 1H), 2.09-2.04 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 170.70, 170.32, 169.55, 169.43, 164.33, 159.36, 154.06, 141.28, 139.62, 132.51, 128.76, 128.62, 128.57, 126.70, 126.54, 122.95 (t, *J*=7.9Hz), 121.25, 116.67, 98.51, 93.54, 72.76, 72.36 71.22, 68.32, 62.05, 20.87, 20.77, 20.73, 20.71. HRMS (ESI, m/z) calcd for $C_{32}H_{31}BF_2N_2O_{11}$ $[M+H]^+$ 669.2062, found 669.2076.

5.6. Synthesis of 11



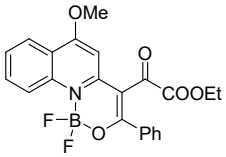
5 **11**

To a solution of compound **5** (0.10 mmol) in DCM (1.25 mL) under a nitrogen atmosphere at room temperature were slowly added $BF_3{\cdot}Et_2O$ (1.03 mmol) and Et_3N (1.05 mmol). The mixture was stirred for 0.5 h. The reaction was quenched with water and extracted with DCM (3 × 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by silica gel column chromatography (petroleum ether/DCM = 1:4) afforded the desired product **11**.



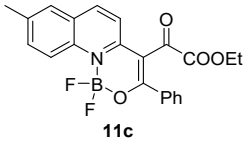
11a

11a, yellow oil, 83% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.91 (d, *J*=8.7Hz, 1H), 8.03-8.00 (m, 3H), 7.89 (t, *J*=8.6Hz, 1H), 7.70 (t, *J*=7.7Hz, 1H), 7.61 (t, *J*=7.5Hz, 1H), 7.48 (t, *J*=9.6Hz, 2H), 7.14 (s, 1H), 4.16 (q, *J*=7.1Hz, 2H), 2.69 (s, 3H), 1.71 (t, *J*=7.1Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 192.53, 161.93, 153.36, 150.76, 149.92, 139.77, 137.87, 134.13, 133.14, 129.23, 129.16, 128.30, 127.95, 124.68, 124.56 (t, *J*=8.74Hz), 119.77, 114.14, 62.91, 20.10, 13.84. ^{11}B NMR (160 MHz, $CDCl_3$) δ (ppm) 1.94 (t, *J*=17.7Hz).^{19}F NMR (471 MHz, $CDCl_3$) δ (ppm) -127.69 (dd, *J*=33.7Hz, 14.3Hz). HRMS (ESI, m/z) calcd for $C_{22}H_{18}BF_2N_2O_4$ $[M+Na]^+$ 432.1190, found 432.1205.



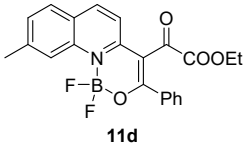
11b

11b, yellow oil, 85% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.80 (d, *J*=8.9Hz, 1H), 8.20 (d, *J*=8.3Hz, 1H), 8.00 (d, *J*=7.8Hz, 2H), 7.86 (t, *J*=7.9Hz, 1H), 7.60 (q, *J*=7.8Hz, 2H), 7.47 (t, *J*=7.6Hz, 2H), 7.47 (t, *J*=7.6Hz, 2H), 6.60 (s, 1H), 4.15 (q, *J*=7.1Hz, 2H), 3.95 (s, 3H), 1.17 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 192.89, 166.08, 162.09, 152.26, 150.93, 141.32, 138.00, 134.06, 133.47, 129.17, 129.14, 127.53, 123.82 (t, *J*=8.6Hz), 122.55, 120.87, 114.08, 97.56, 62.88, 56.99, 13.84. HRMS (ESI, m/z) calcd for $C_{22}H_{18}BF_2N_2O_5$ $[M+Na]^+$ 448.1139, found 448.1158.



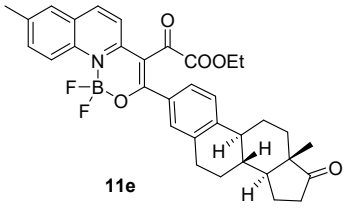
11c

11c, yellow oil, 75% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.76 (d, *J*=9.4Hz, 1H), 8.23 (d, *J*=8.9Hz, 1H), 7.98 (d, *J*=7.4Hz, 2H), 7.72 (d, *J*=9.1Hz, 1H), 7.63-7.58 (m, 2H), 7.46 (t, *J*=7.7Hz, 2H), 7.23 (d, *J*=8.9Hz, 1H), 4.16 (q, *J*=7.2Hz, 2H), 2.54 (s, 3H), 1.16 (t, *J*=7.1Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.35, 161.89, 150.29, 149.70, 142.77, 139.19, 138.53, 137.69, 135.76, 134.13, 129.19, 129.13, 128.25, 127.68, 123.68(t, *J*=8.5Hz), 119.23, 114.39, 62.86, 21.31, 13.78. HRMS (ESI, m/z) calcd for $C_{22}H_{18}BF_2NO_4$ $[M+Na]^+$ 432.1190, found 432.1200.



11d

11d, yellow oil, 73% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.66 (s, 1H), 8.26 (d, *J*=8.8Hz, 1H), 7.99 (d, *J*=8.2Hz, 2H), 7.75 (d, *J*=8.3Hz, 1H), 7.59 (t, *J*=7.4Hz, 1H), 7.52 (d, *J*=8.2Hz, 1H), 7.46 (t, *J*=7.7Hz, 2H), 7.20 (d, *J*=8.8Hz, 1H), 4.17 (q, *J*=7.1Hz, 2H), 2.64 (s, 3H), 1.17 (t, *J*=7.2Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 192.41, 161.92, 150.48, 150.44, 145.35, 143.03, 140.47, 137.72, 134.14, 130.73, 129.23, 129.16, 128.50, 126.39, 123.18 (t, *J*=8.4Hz), 118.37, 114.45, 62.92, 22.9519, 13.82. HRMS (ESI, m/z) calcd for $C_{22}H_{18}BF_2NO_4$ $[M+Na]^+$ 432.1190, found 432.1202.

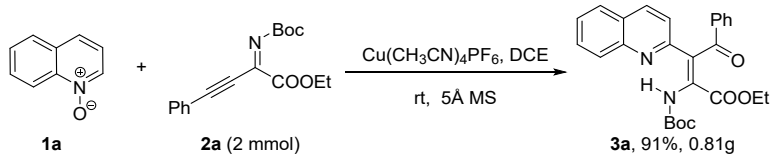


11e

11e, yellow solid, m.p. 168.4-169.4 °C, 63% yield, ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.80 (d, *J*=9.3Hz, 1H), 8.21 (d, *J*=8.9Hz, 1H), 7.76-7.74 (m, 3H), 7.63 (s, 1H), 7.38 (d, *J*=8.3Hz, 1H), 7.24 (d, *J*=8.9Hz, 1H), 4.22 (q, *J*=7.1Hz, 2H), 2.94-2.91 (m,

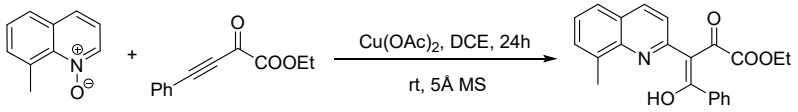
2H), 2.56(s, 3H), 2.53-2.49 (m, 1H), 2.44-2.41 (m, 1H), 2.35-2.30 (m, 1H), 2.18-2.12 (m, 1H), 2.09-2.02 (m, 2H), 1.99-1.96 (m, 1H), 1.65-1.48 (m, 6H), 1.23 (t, *J*=7.14Hz, 3H), 0.90 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 192.28, 162.12, 149.96, 146.89, 142.64, 139.21, 138.65, 137.74, 135.83, 135.37, 129.70, 128.31, 127.65, 126.80, 126.28, 123.88 (t, *J*=8.7Hz), 119.46, 114.76, 62.94, 50.66, 47.98, 45.01, 37.84, 35.93, 31.65, 29.44, 26.33, 25.62, 21.71, 21.41, 13.98, 13.93. HRMS (ESI, m/z) calcd for $C_{34}H_{34}BF_2NO_5$ $[M+H]^+$ 586.2571, found 586.2575.

6. Gram scale experiments



1a **2a** (2 mmol) **3a**, 91%, 0.81g

A mixture of quinoline N-oxides **1a** (2.4 mmol), alkynyl imines **2a** (2.0 mmol), $Cu(CH_3CN)_4PF_6$ (0.10 mmol, 5 mol%), and 5Å molecular sieves (1.0 g) in anhydrous DCE (20 mL) was stirred under a nitrogen atmosphere at room temperature for 5 min. After the reaction was complete, the mixture was filtered, and the filtrate was concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1 to 4:1) afforded the desired product **3a** (0.81 g, 91% yield).



1b **4a** (2 mmol) **5a**, 88%, 0.63g

A mixture of quinoline N-oxides **1b** (2.4 mmol), ynones **4a** (2.0 mmol), $Cu(OAc)_2$ (0.10 mmol, 5 mol%), and 5Å molecular sieves (1.0 g) in anhydrous DCE (20 mL) was stirred under a nitrogen atmosphere at room temperature. After the reaction was complete, the mixture was filtered, and the filtrate was concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1 to 1:1) afforded the desired product **5a** (0.63 g, 88% yield).

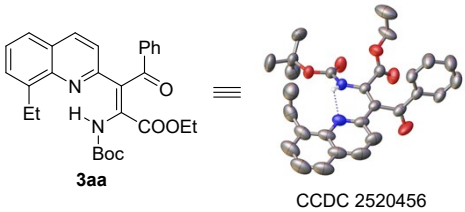
7. Reference

[1] J. Wu and Z. Xia, *Adv. Synth. Catal*. 2023, **365**, 3335– 3341

[2] J. Yang, Z. Wang, Z. He, G. Li, L. Hong, W. Sun and R. Wang, *Angew. Chem. Int. Ed.* 2020, **59**, 642 – 647.

8. X-ray crystallography

The crystal of **3aa** suitable for XRD analysis was prepared by recrystallization from a mixed solvent of DCM and n-hexane. CCDC 2520456 (**3aa**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

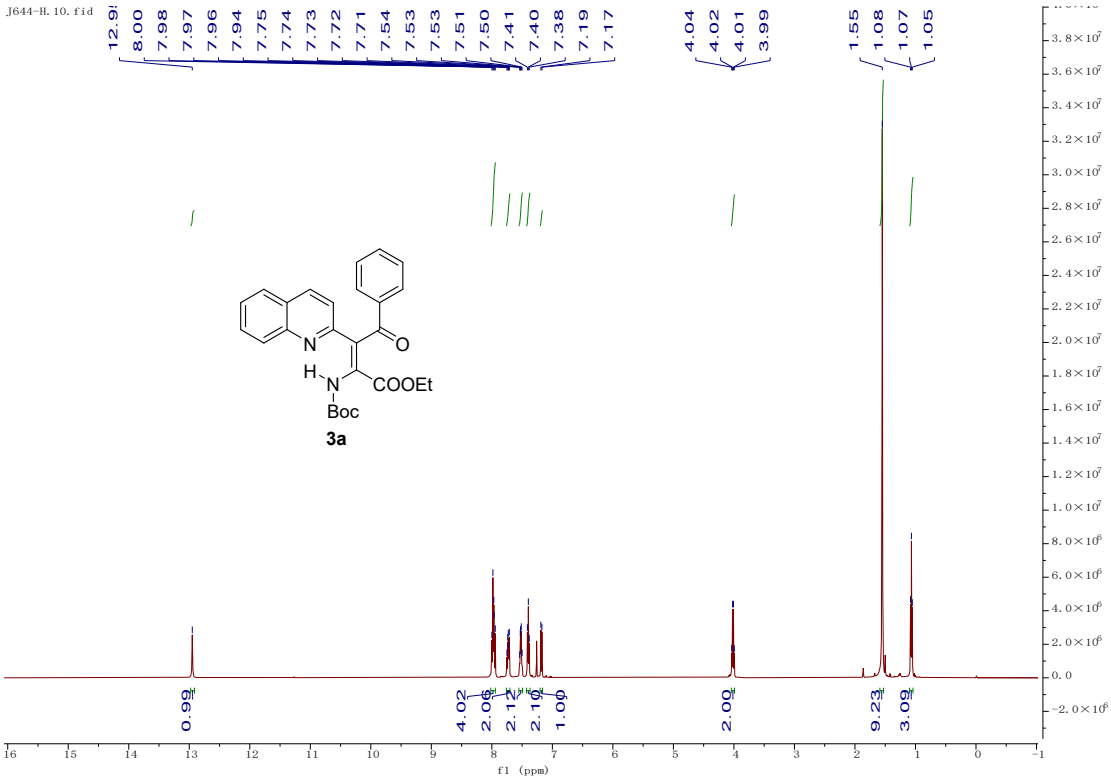


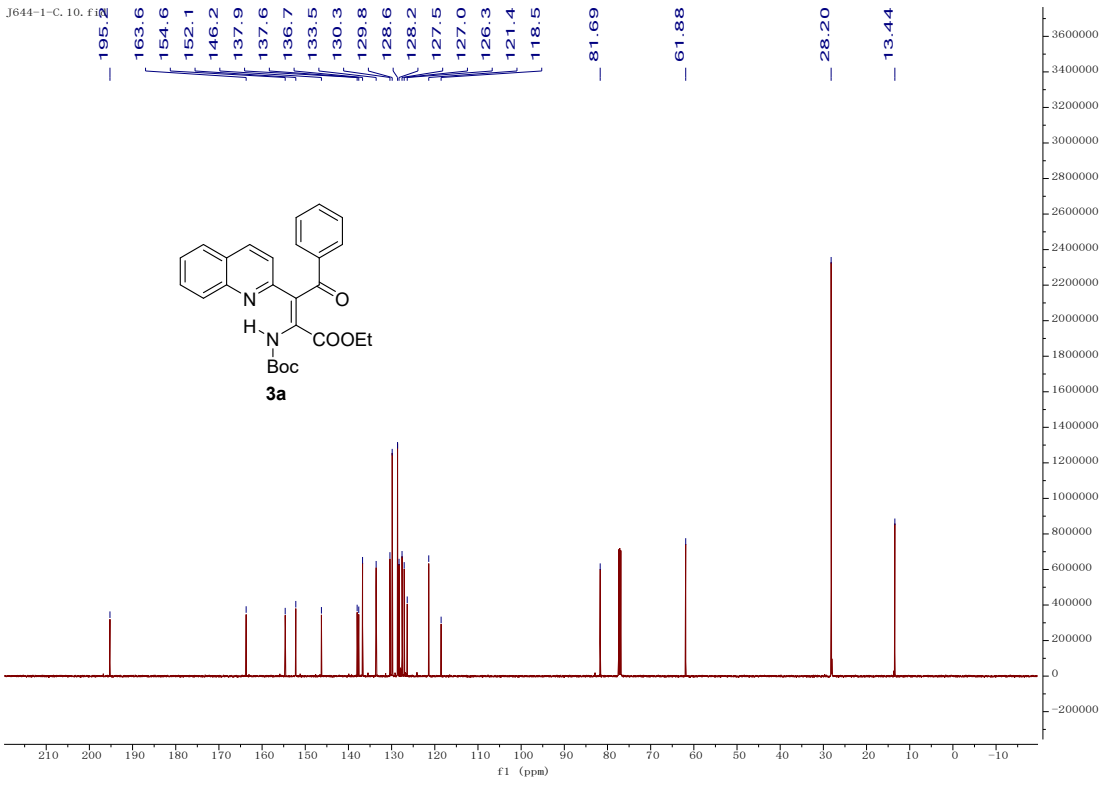
3aa

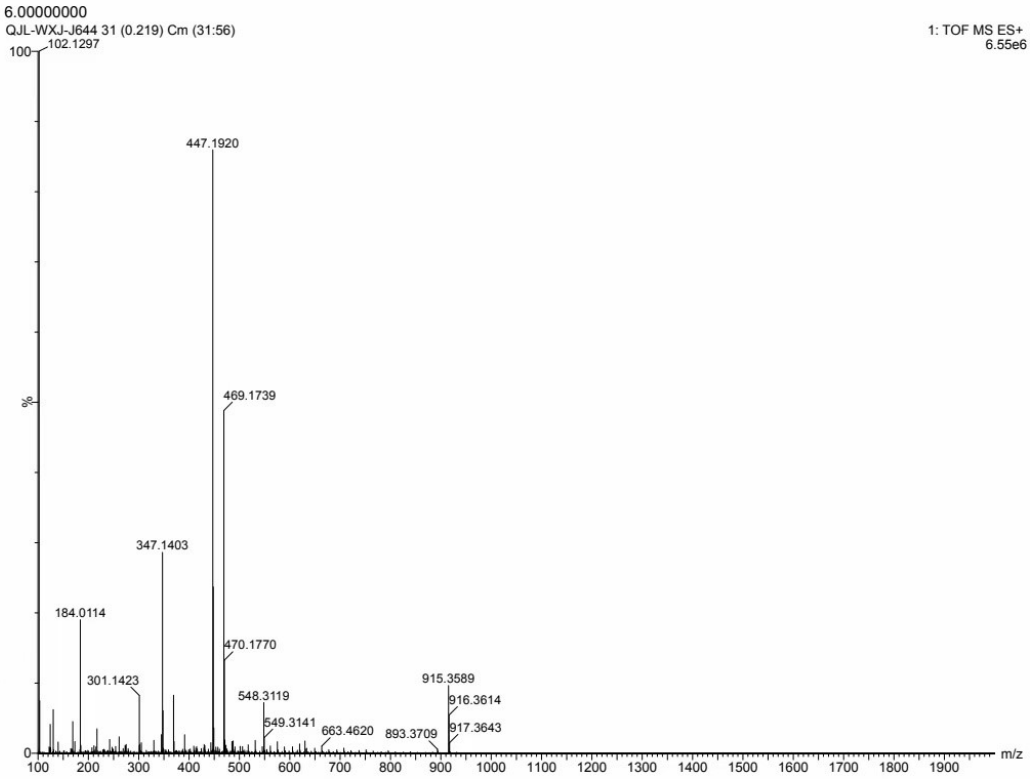
CCDC 2520456

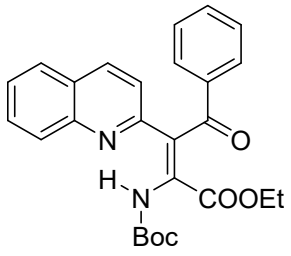
9. NMR and HRMS spectra of all compounds

3a









3a

Chemical Formula: $C_{26}H_{26}N_2O_5$

Exact Mass: 446.1842

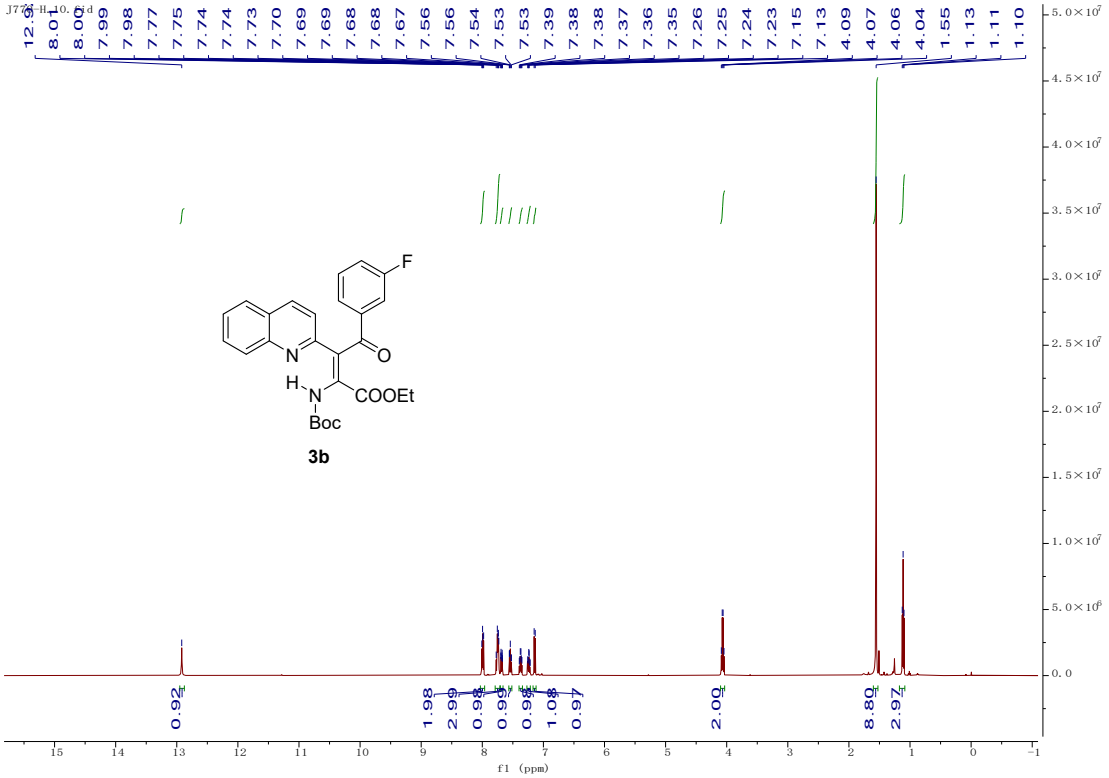
Molecular Weight: 446.5030

m/z: 446.1842 (100.0%), 447.1875 (28.1%), 448.1909 (3.8%), 448.1884 (1.0%)

Elemental Analysis: C, 69.94; H, 5.87; N, 6.27; O, 17.92

HRMS (ESI, m/z) calcd for $C_{26}H_{26}N_2O_5$ $[M+H]^+$ 447.1915, found 447.1920.

3b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7.68
7.68
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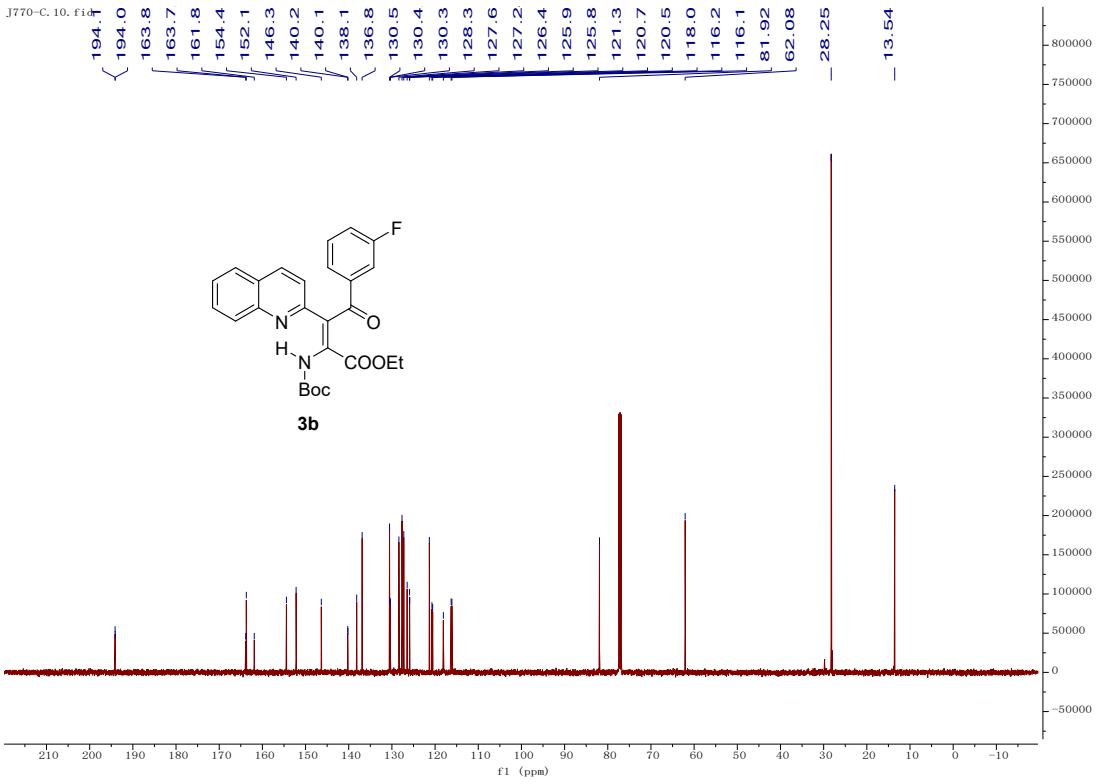
7.56
7.56
7.54
7.53
7.53
7.39
7.38
7.38
7.37
7.36
7.35
7.26
7.25
7.24
7.23
7.15
7.13
4.09
4.07
4.06
4.04
1.55
1.13
1.11
1.10
F
O
N
H
N
COOEt
Boc
3b
0.92
1.98
2.99
0.98
0.99
0.98
1.08
0.97
2.00
8.80
2.97
f1 (ppm)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152.1
146.3
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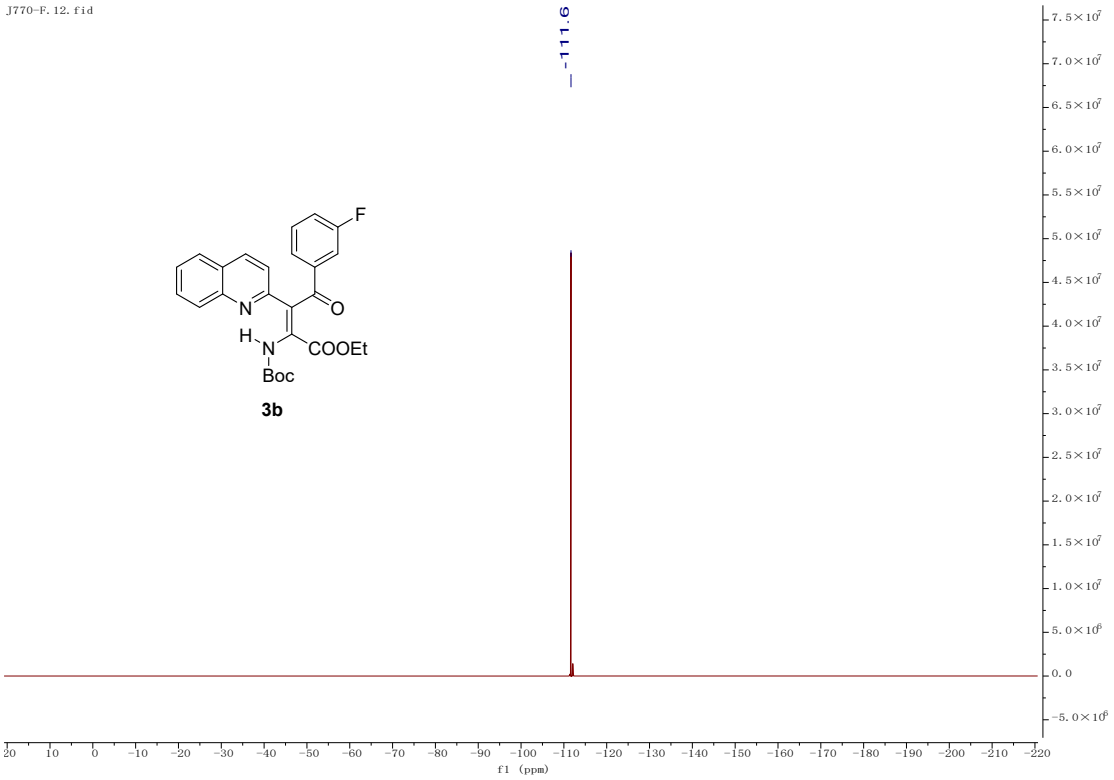
140.1
138.1
136.8
130.5
130.4
130.3
128.3
127.6
127.2
126.4
125.9
125.8
121.3
120.7
120.5
118.0
116.2
116.1
81.92
62.08
28.25
13.54
F
O
N
H
N
COOEt
Boc
3b
f1 (ppm)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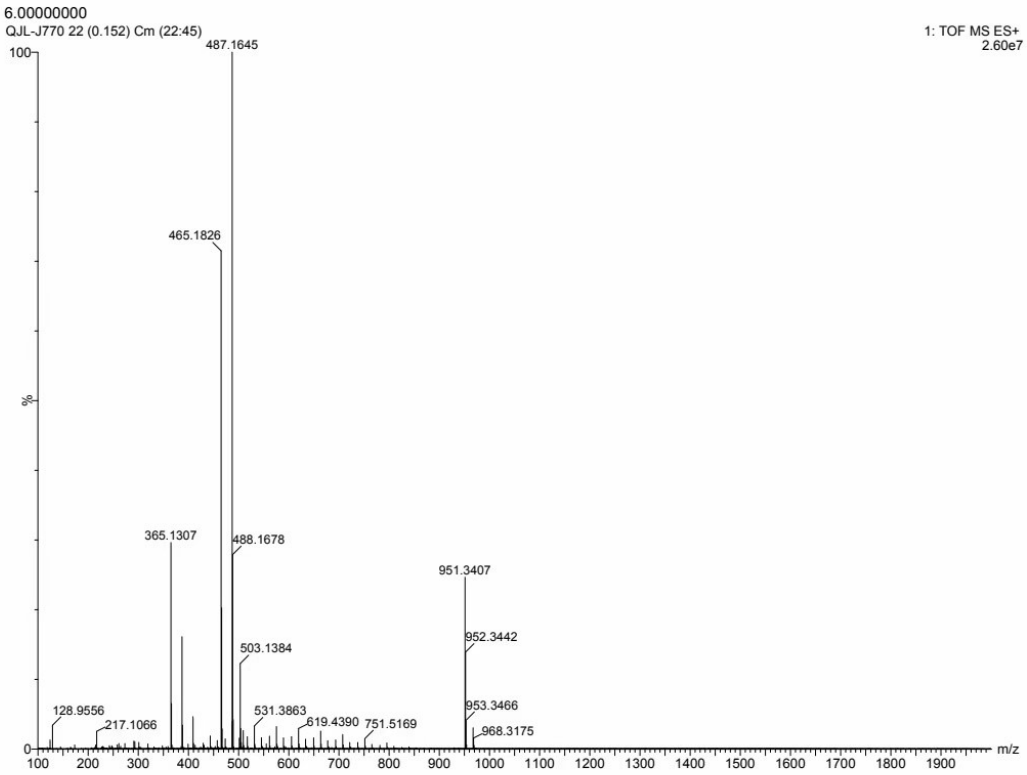
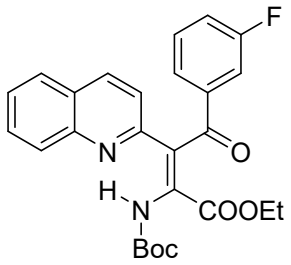
F
O
N
H
N
COOEt
Boc
3b
7.5×10^7
7.0×10^7
6.5×10^7
6.0×10^7
5.5×10^7
5.0×10^7
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
-5.0×10^6
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)





3b

Chemical Formula: $C_{26}H_{25}FN_2O_5$

Exact Mass: 464.1748

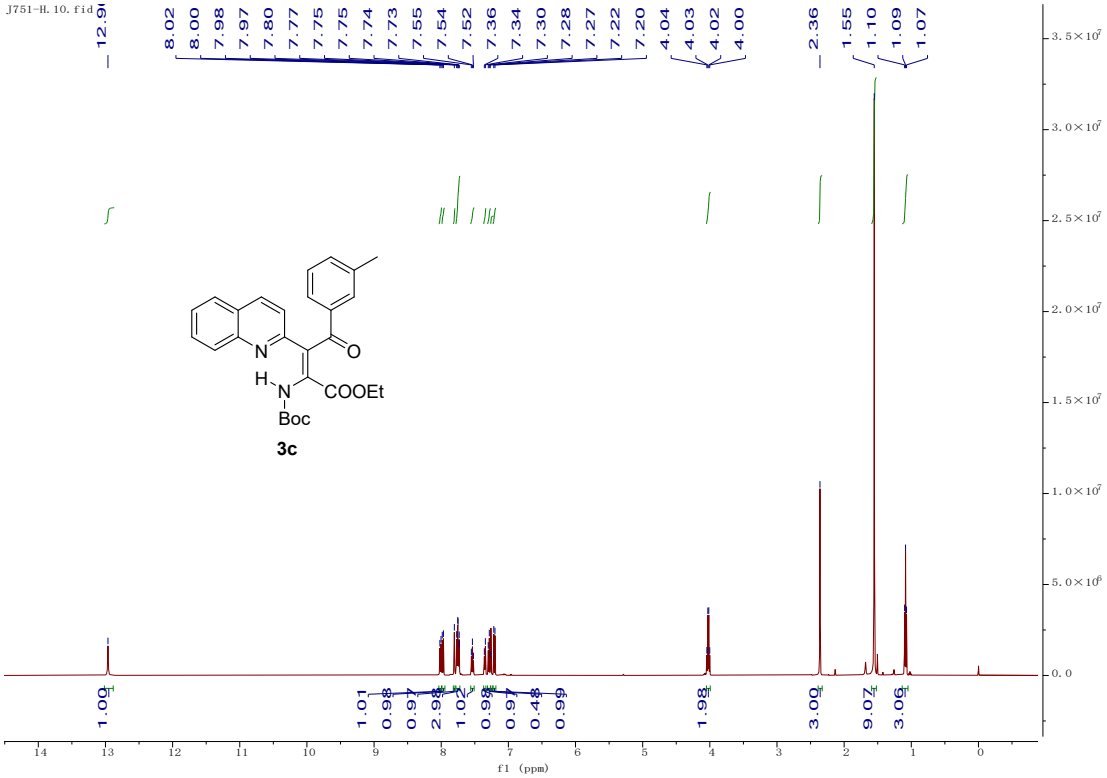
Molecular Weight: 464.4934

m/z: 464.1748 (100.0%), 465.1781 (28.1%), 466.1815 (3.8%), 466.1790 (1.0%)

Elemental Analysis: C, 67.23; H, 5.43; F, 4.09; N, 6.03; O, 17.22

HRMS (ESI, m/z) calcd for $C_{26}H_{25}FN_2O_5$ $[M+Na]^+$ 487.1640, found 487.1645.

3c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7.73
7.55
7.54
7.52
7.36
7.34
7.30
7.28
7.27
7.22
7.20
4.04
4.03
4.02
4.00
2.36
1.55
1.10
1.09
1.07
1.00
1.01
0.98
0.97
2.99
1.02
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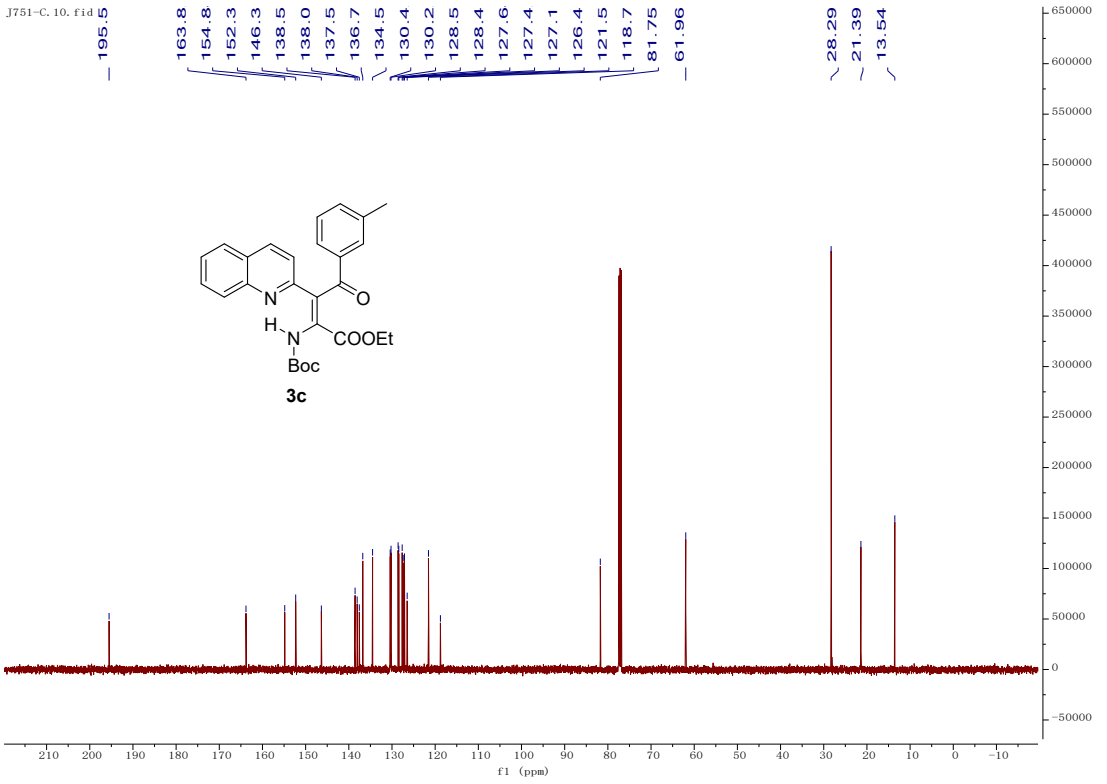
0.97
0.48
0.99
1.98
3.00
9.07
3.06
f1 (ppm)
3c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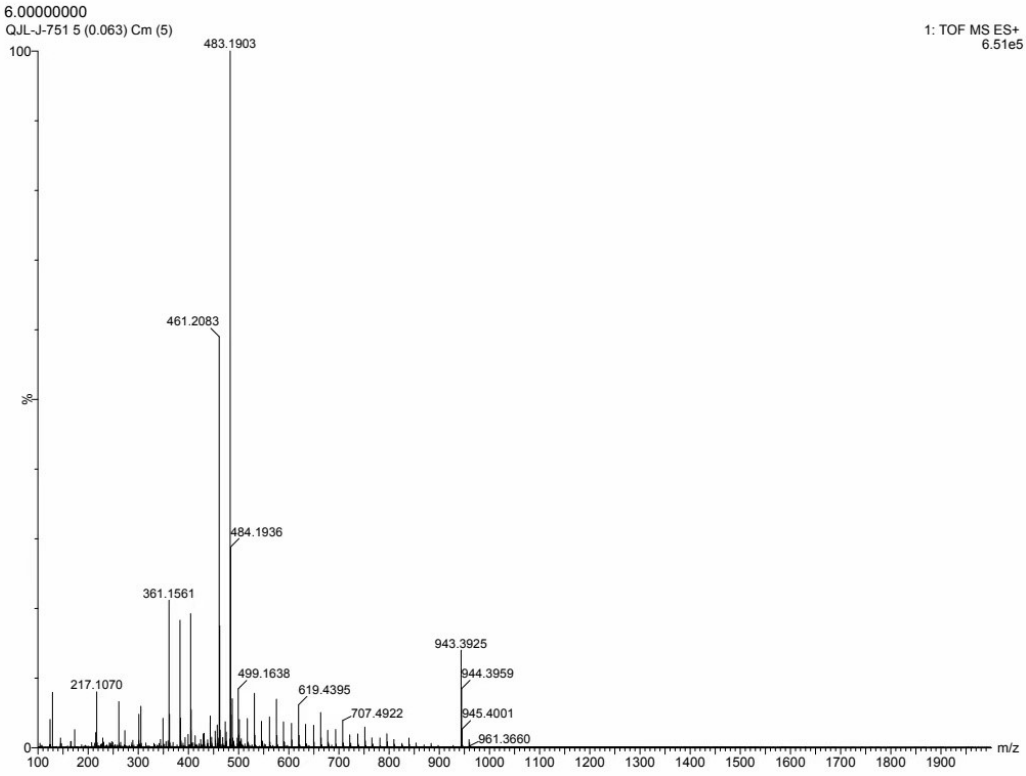
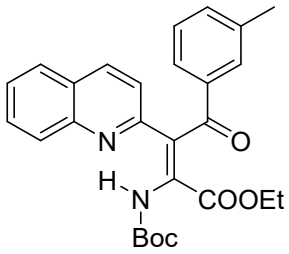
136.7
134.5
130.4
130.2
128.5
128.4
127.6
127.4
127.1
126.4
121.5
118.7
81.75
61.96
28.29
21.39
13.54
f1 (ppm)
3c



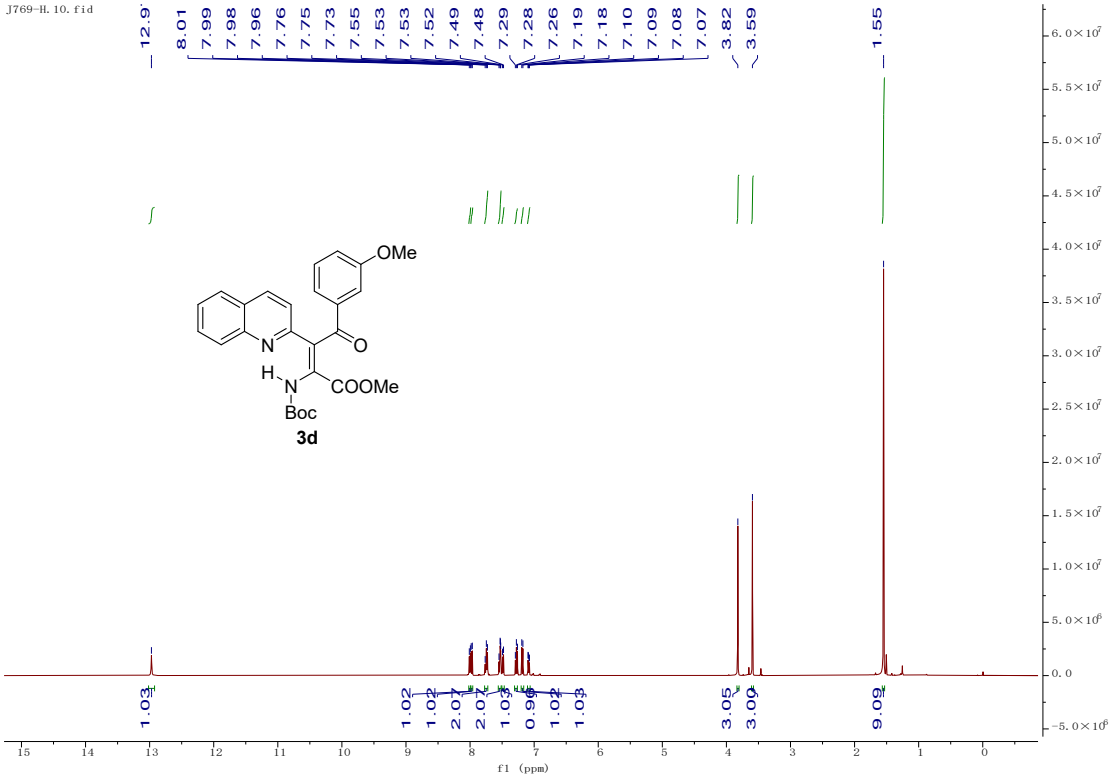


3c

Chemical Formula: $C_{27}H_{28}N_2O_5$
Exact Mass: 460.1998
Molecular Weight: 460.5300
m/z: 460.1998 (100.0%), 461.2032 (29.2%), 462.2065 (4.1%), 462.2041 (1.0%)
Elemental Analysis: C, 70.42; H, 6.13; N, 6.08; O, 17.37

HRMS (ESI, m/z) calcd for $C_{27}H_{28}N_2O_5$ $[M+Na]^+$ 483.1891, found 483.1903.

3d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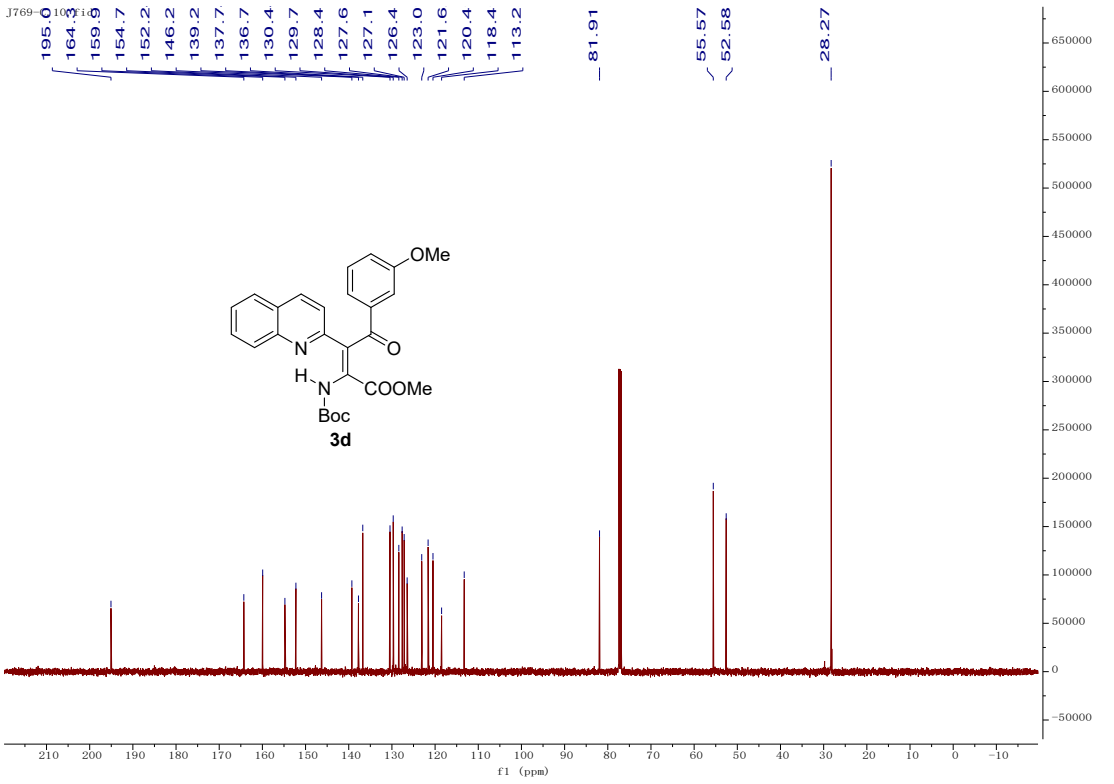
7.52
7.49
7.48
7.29
7.28
7.26
7.19
7.18
7.10
7.09
7.08
7.07
3.82
3.59
1.55
OMe
O
N
H
N
COOMe
Boc
3d
1.03
1.02
1.02
2.07
2.07
1.03
0.96
1.02
1.03
3.05
3.00
9.09
f1 (ppm)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159.5
154.7
152.2
146.2
139.2
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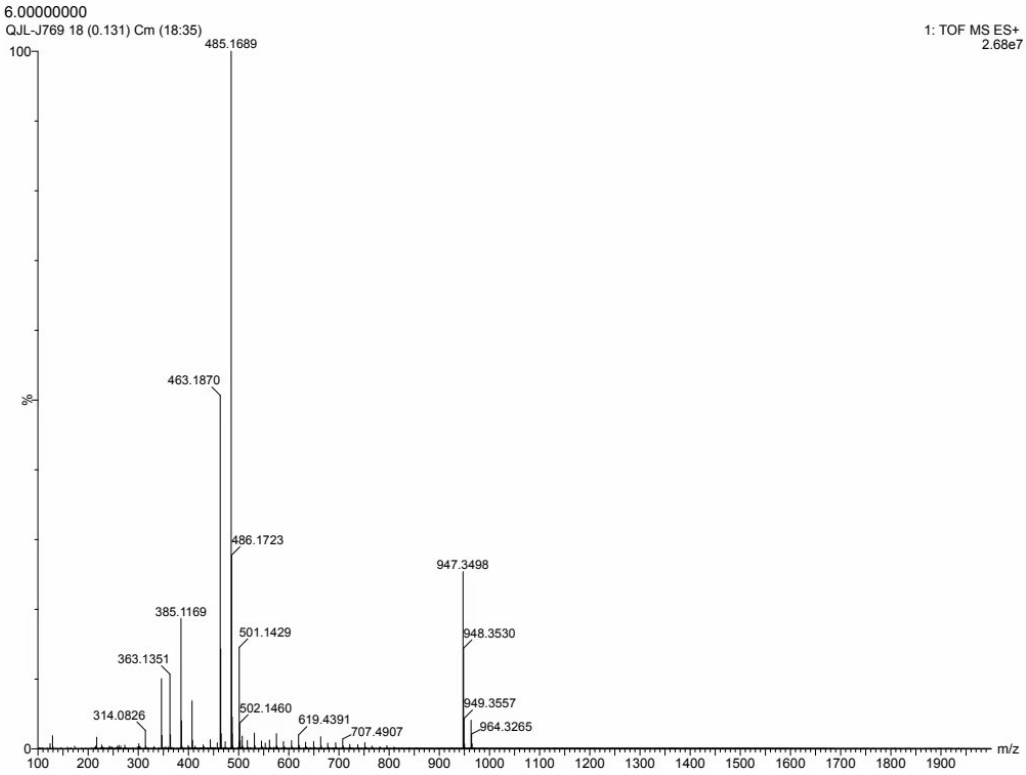
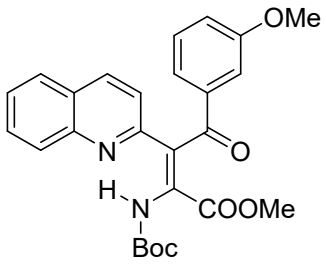
130.4
129.7
128.4
127.6
127.1
126.4
123.0
121.6
120.4
118.4
113.2
81.91
55.57
52.58
28.27
OMe
O
N
H
N
COOMe
Boc
3d
f1 (ppm)



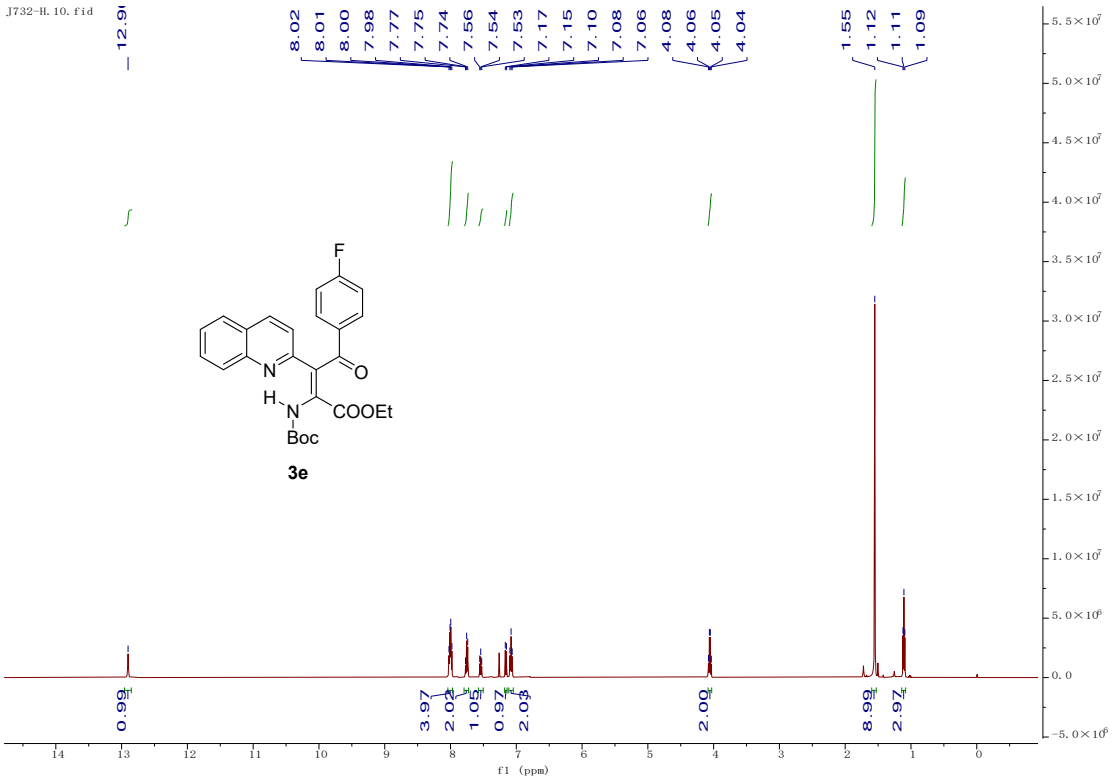


3d

Chemical Formula: $C_{26}H_{26}N_2O_6$
Exact Mass: 462.1791
Molecular Weight: 462.5020
m/z: 462.1791 (100.0%), 463.1824 (28.1%), 464.1858 (3.8%), 464.1833 (1.2%)
Elemental Analysis: C, 67.52; H, 5.67; N, 6.06; O, 20.76

HRMS (ESI, m/z) calcd for $C_{26}H_{26}N_2O_6$ $[M+Na]^+$ 485.1684, found 485.1689.

3e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8.01
8.00
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7.53
7.17
7.15
7.10
7.08
7.06
4.08
4.06
4.05
4.04
1.55
1.12
1.11
1.09
F
O
N
H
N
COOEt
Boc
3e
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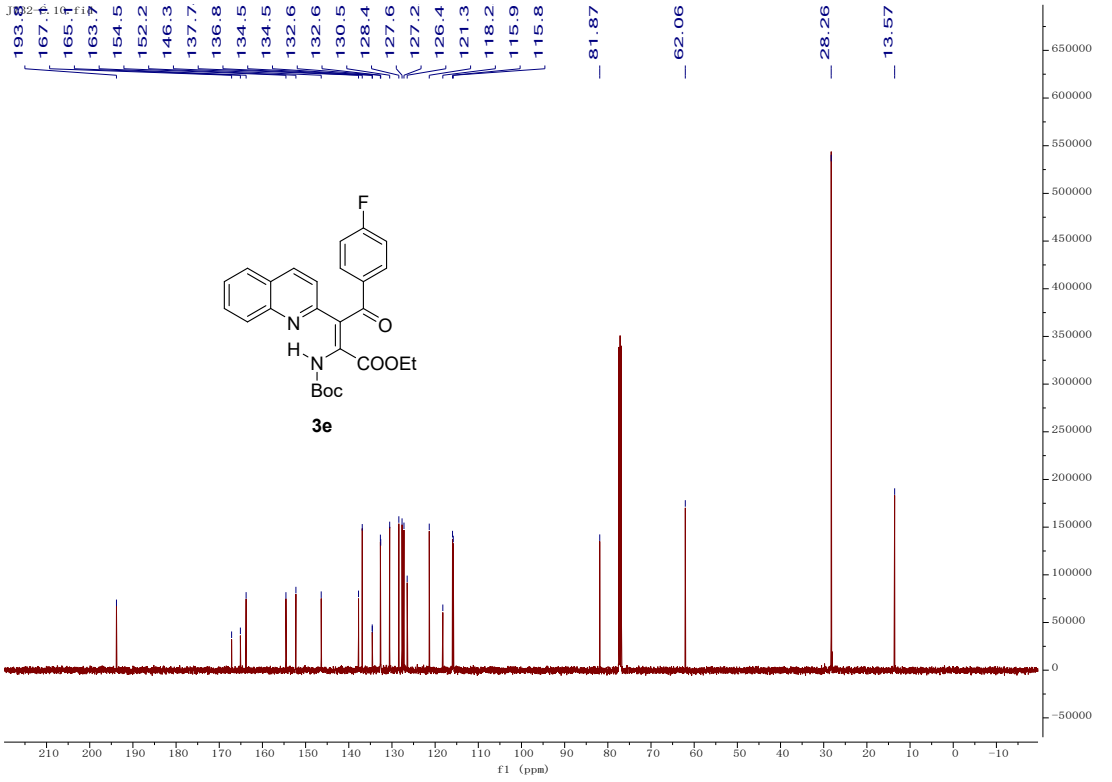
3.97
2.02
1.05
0.97
2.03
2.00
8.99
2.97
f1 (ppm)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137.7
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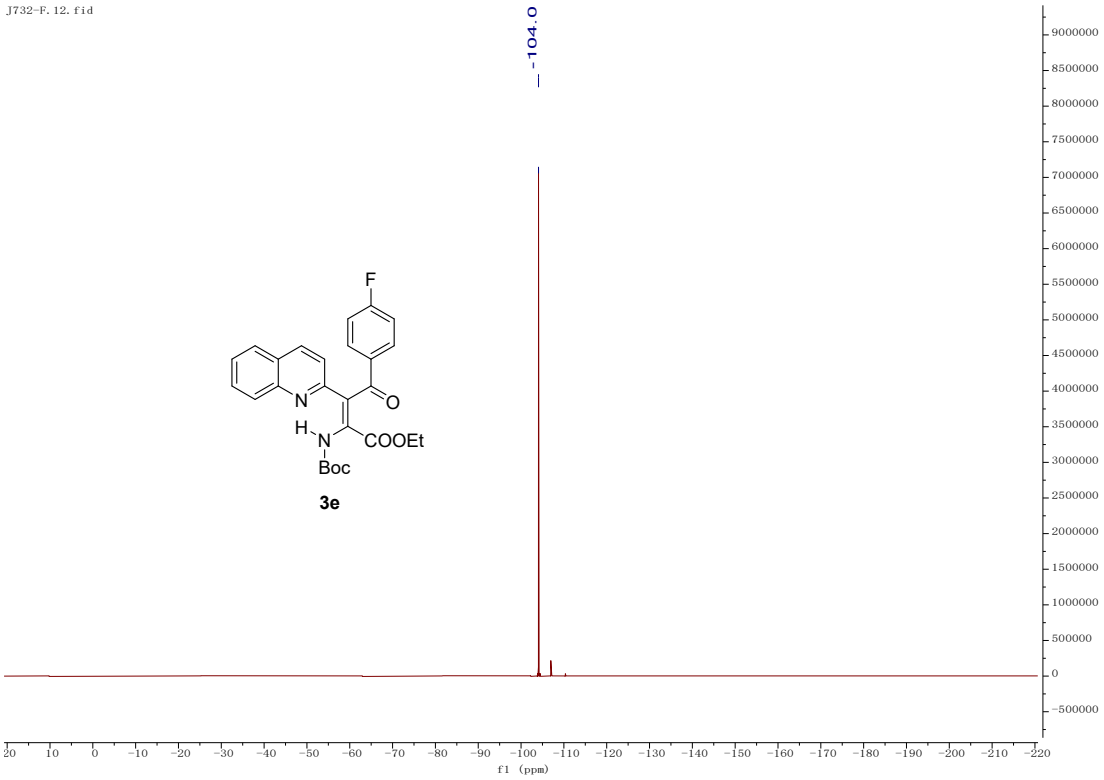
134.5
132.6
132.6
130.5
128.4
127.6
127.2
126.4
121.3
118.2
115.9
115.8
81.87
62.06
28.26
13.57
F
O
N
H
N
COOEt
Boc
3e
f1 (ppm)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6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
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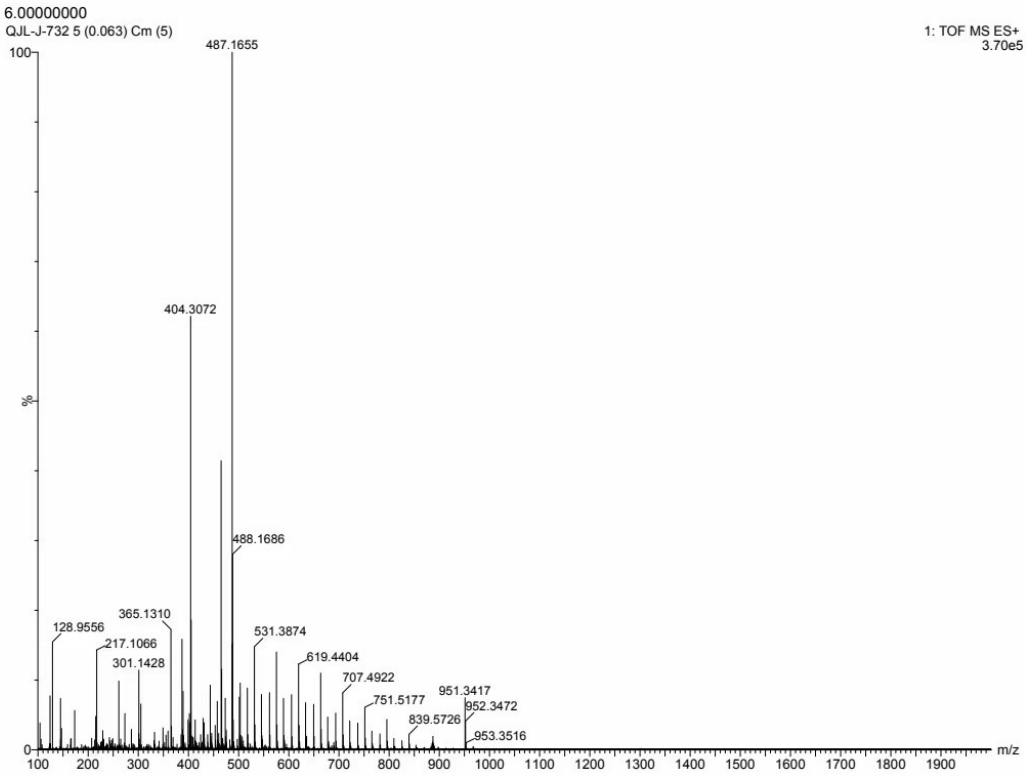
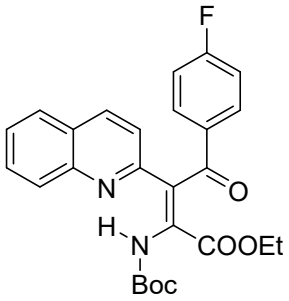
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)





3e

Chemical Formula: $C_{26}H_{25}FN_2O_5$

Exact Mass: 464.1748

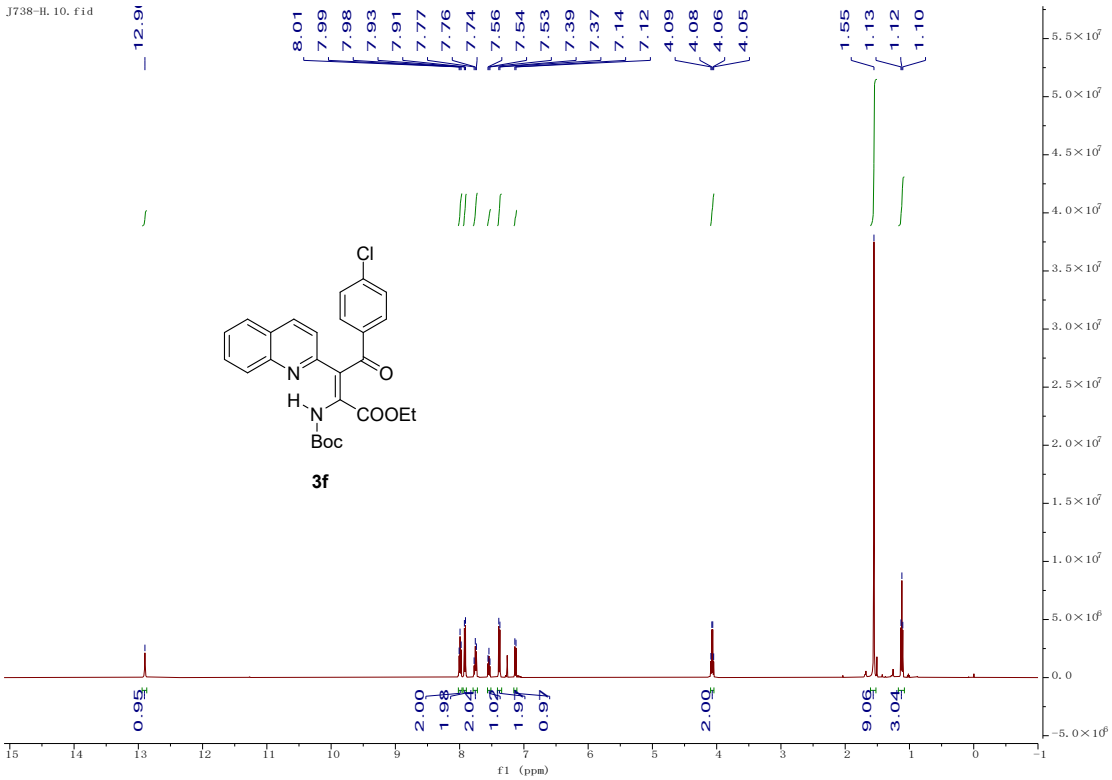
Molecular Weight: 464.4934

m/z: 464.1748 (100.0%), 465.1781 (28.1%), 466.1815 (3.8%), 466.1790 (1.0%)

Elemental Analysis: C, 67.23; H, 5.43; F, 4.09; N, 6.03; O, 17.22

HRMS (ESI, m/z) calcd for $C_{26}H_{25}FN_2O_5$ $[M+Na]^+$ 487.1640, found 487.1655.

3f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7.37
7.14
7.12
4.09
4.08
4.06
4.05
1.55
1.13
1.12
1.10
Cl
O
N
H
N
COOEt
Boc
3f
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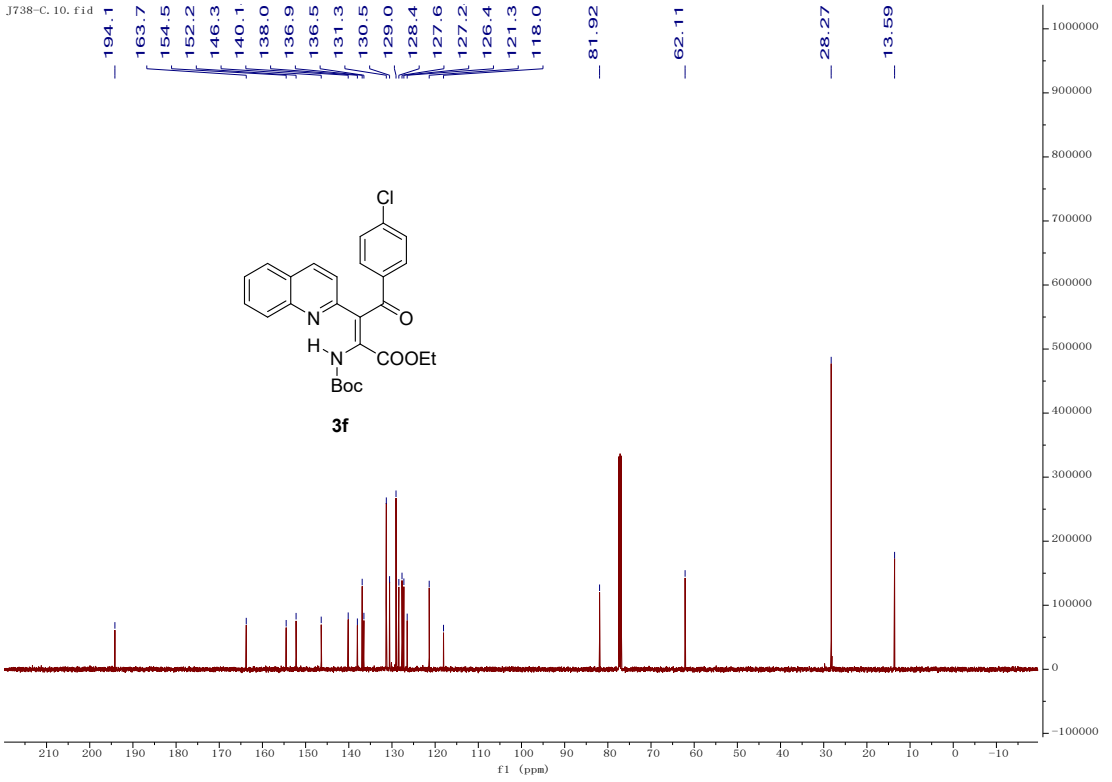
2.00
1.98
2.04
1.07
1.97
0.97
2.00
9.06
3.04
f1 (ppm)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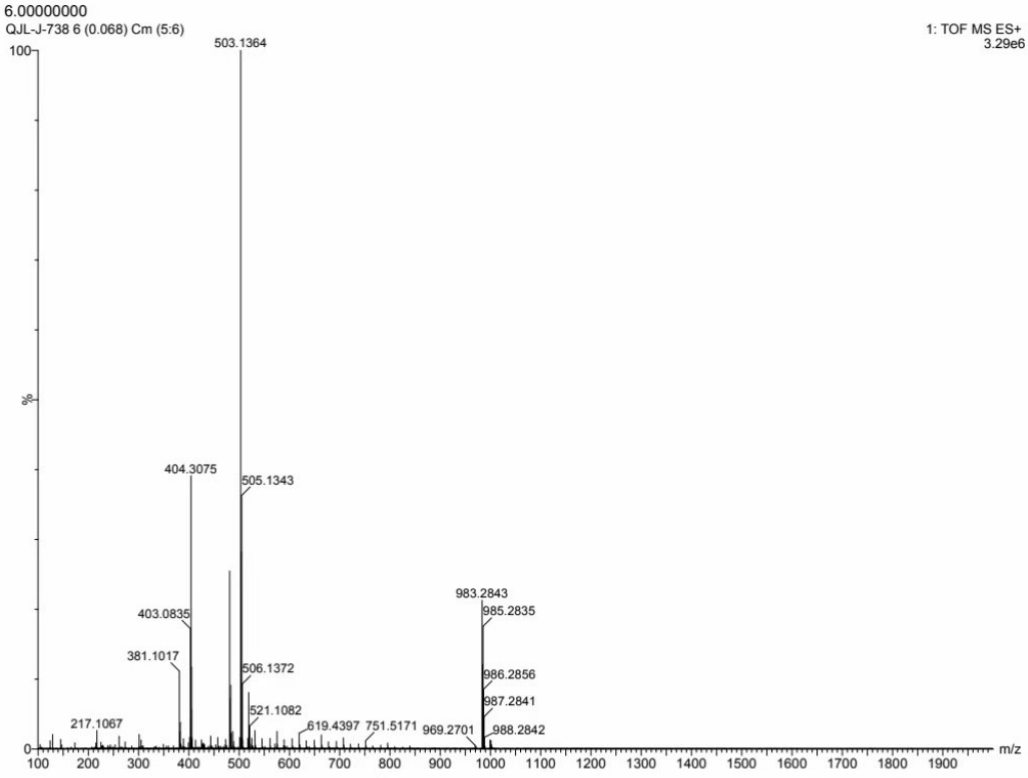
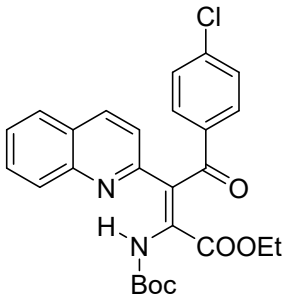
130.5
129.0
128.4
127.6
127.2
126.4
121.3
118.0
81.92
62.11
28.27
13.59
Cl
O
N
H
N
COOEt
Boc
3f
f1 (ppm)



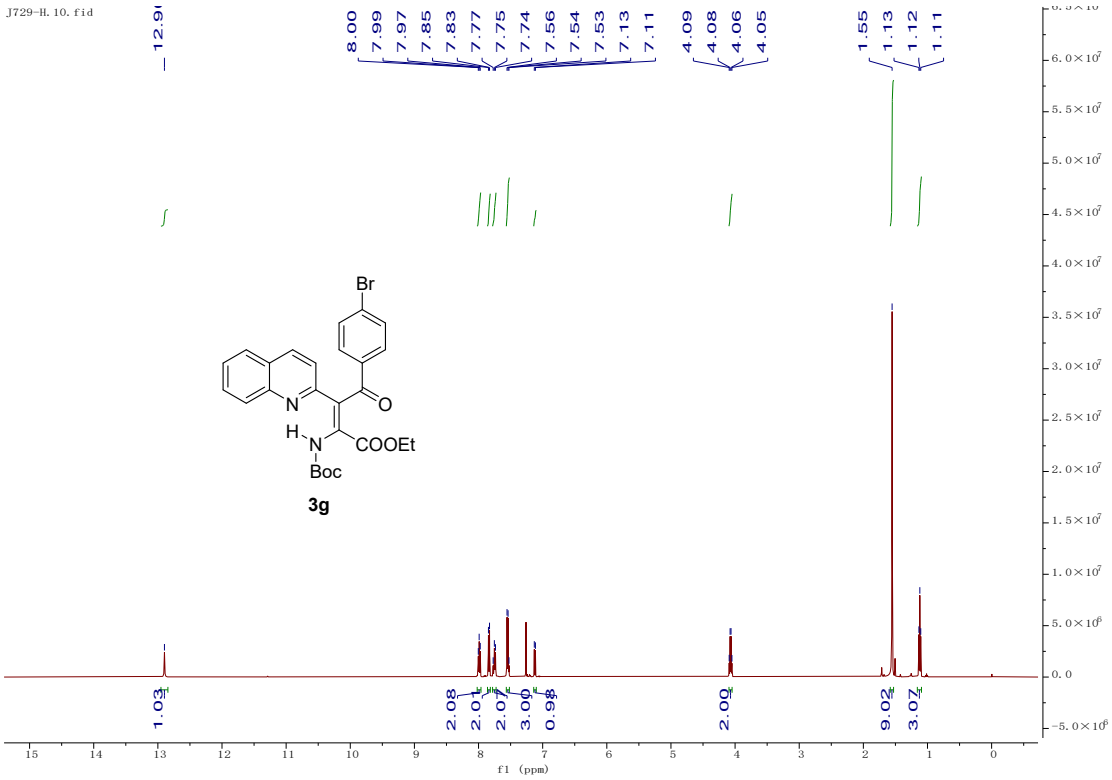


3f

Chemical Formula: $C_{26}H_{25}ClN_2O_5$
Exact Mass: 480.1452
Molecular Weight: 480.9450
m/z: 480.1452 (100.0%), 482.1422 (32.0%), 481.1486 (28.1%),
483.1456 (9.0%), 482.1519 (3.8%), 484.1490 (1.2%), 482.1494 (1.0%)
Elemental Analysis: C, 64.93; H, 5.24; Cl, 7.37; N, 5.82; O, 16.63

HRMS (ESI, m/z) calcd for $C_{26}H_{25}ClN_2O_5$ $[M+Na]^+$ 503.1345, found 503.1364.

3g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7.97
7.85
7.83
7.77
7.75
7.74
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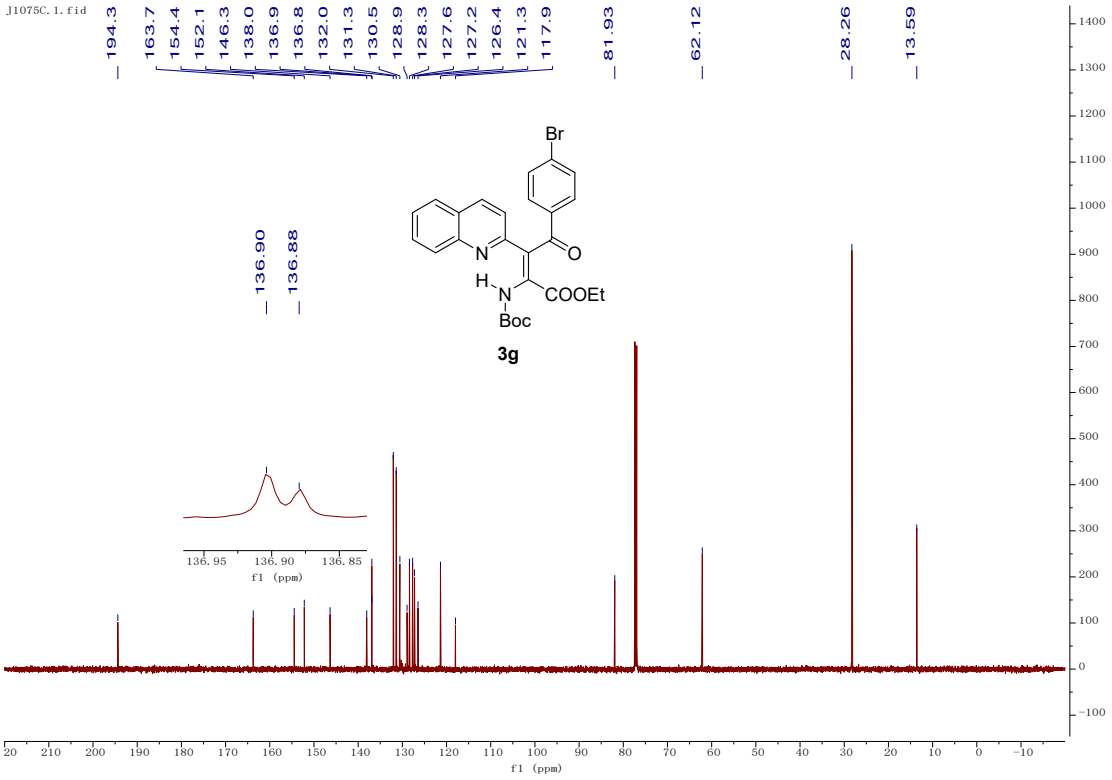
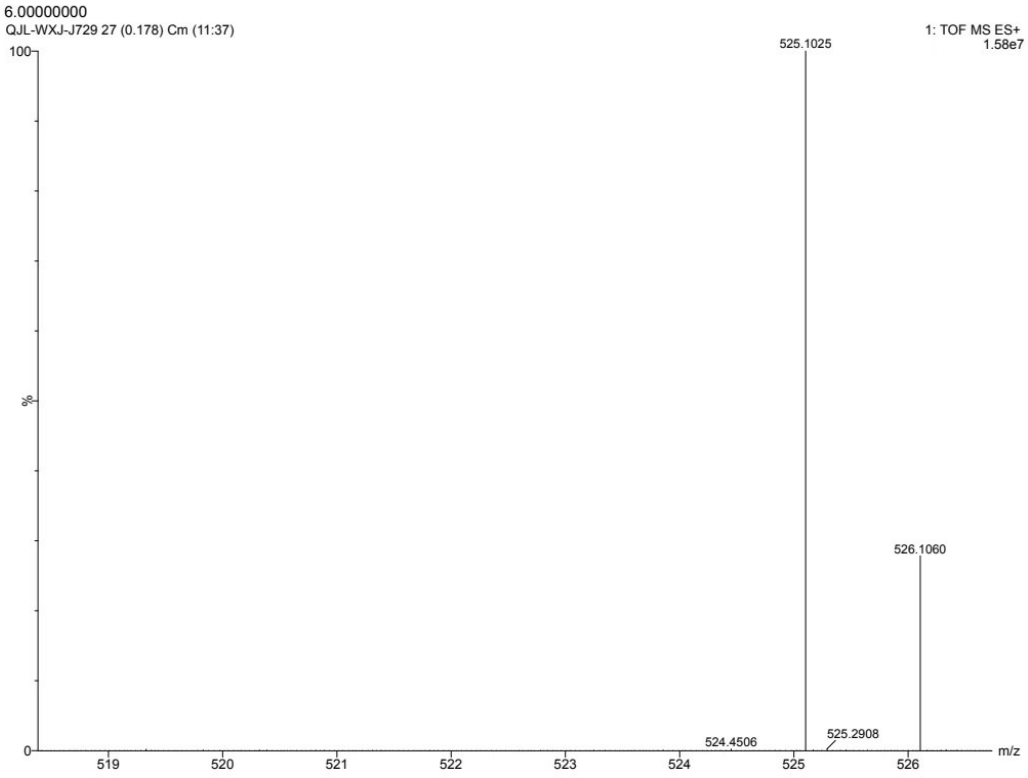
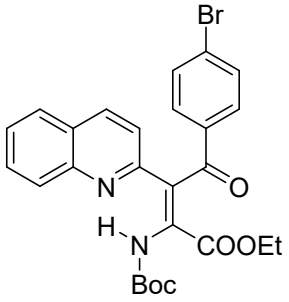
7.13
7.11
4.09
4.08
4.06
4.05
1.55
1.13
1.12
1.11
Br
O
N
H
N
COOEt
Boc
3g
1.03
2.08
2.01
2.07
3.00
0.98
2.00
9.02
3.07
f1 (ppm)


J1075C.1.fid
194.3
163.7
154.4
152.1
146.3
138.0
136.9
136.8
132.0
131.3
130.5
128.9
128.3
127.6
127.2
126.4
121.3
117.9
81.93
62.12
28.26
13.59
136.90
136.88
Br
O
N
H
N
COOEt
Boc
3g
136.95
136.90
136.85
f1 (ppm)
f1 (ppm)





3g

Chemical Formula: $C_{26}H_{25}BrN_2O_5$

Exact Mass: 524.0947

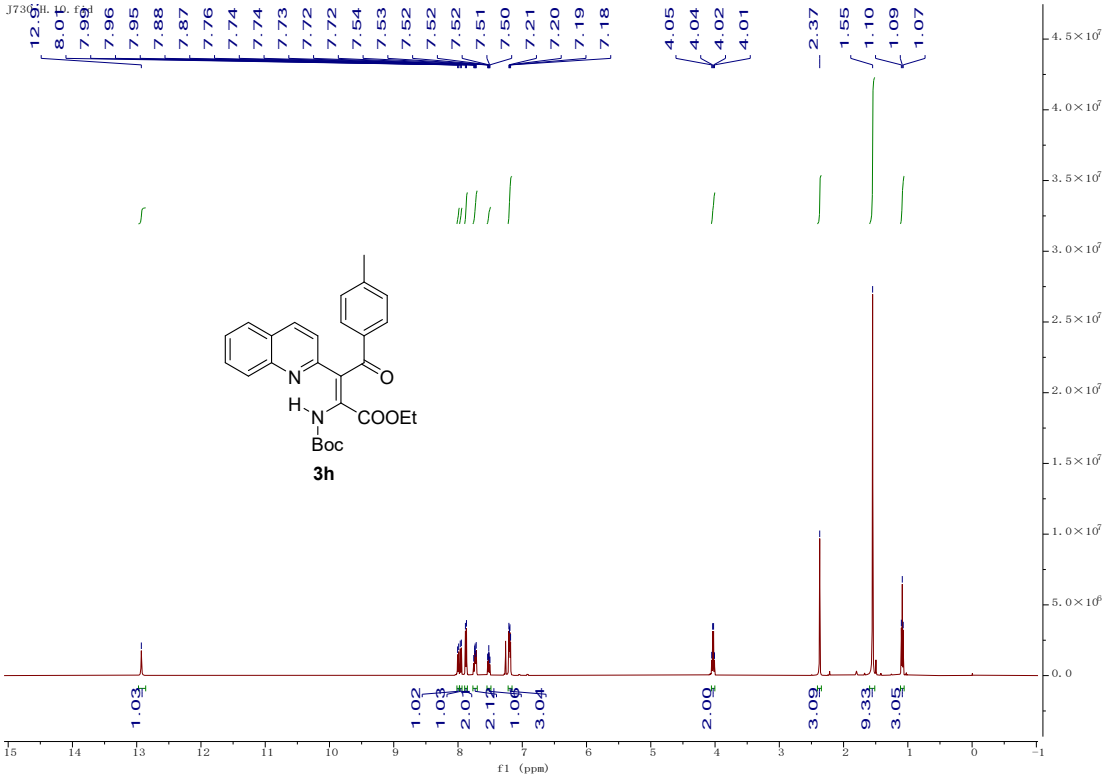
Molecular Weight: 525.3990

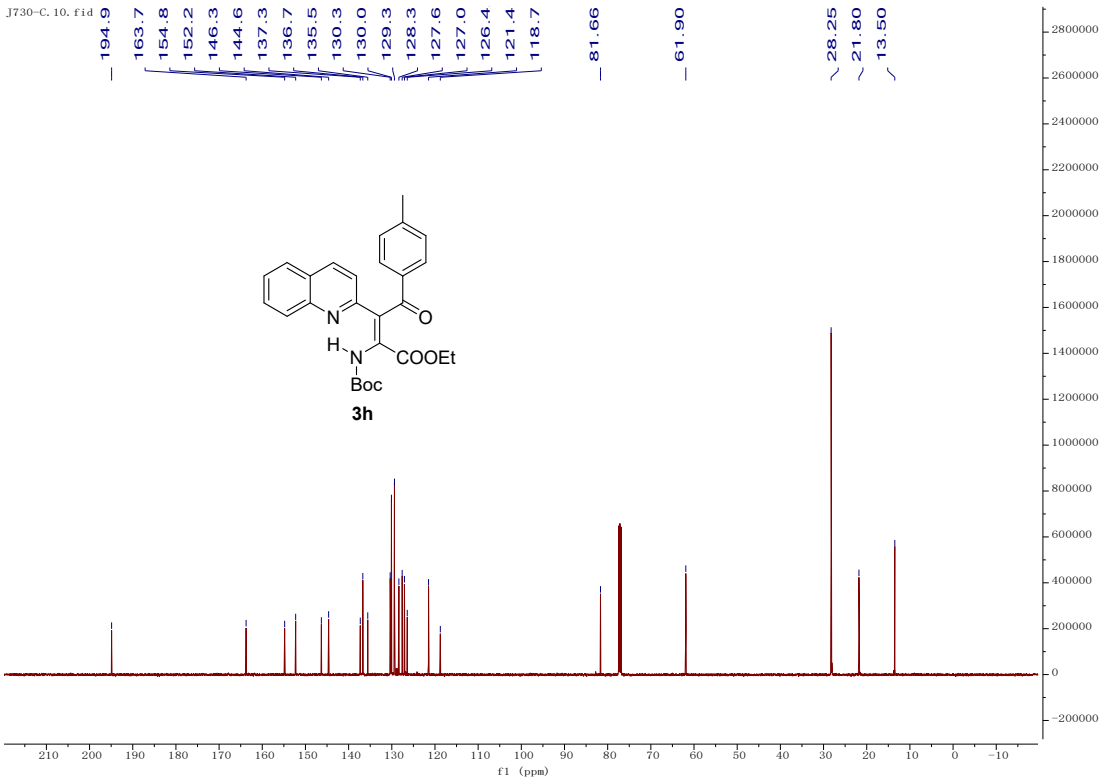
m/z: 524.0947 (100.0%), 526.0926 (97.3%), 525.0980 (28.1%),
527.0960 (27.4%), 526.1014 (3.8%), 528.0993 (3.7%), 526.0989 (1.0%), 528.0969 (1.0%)

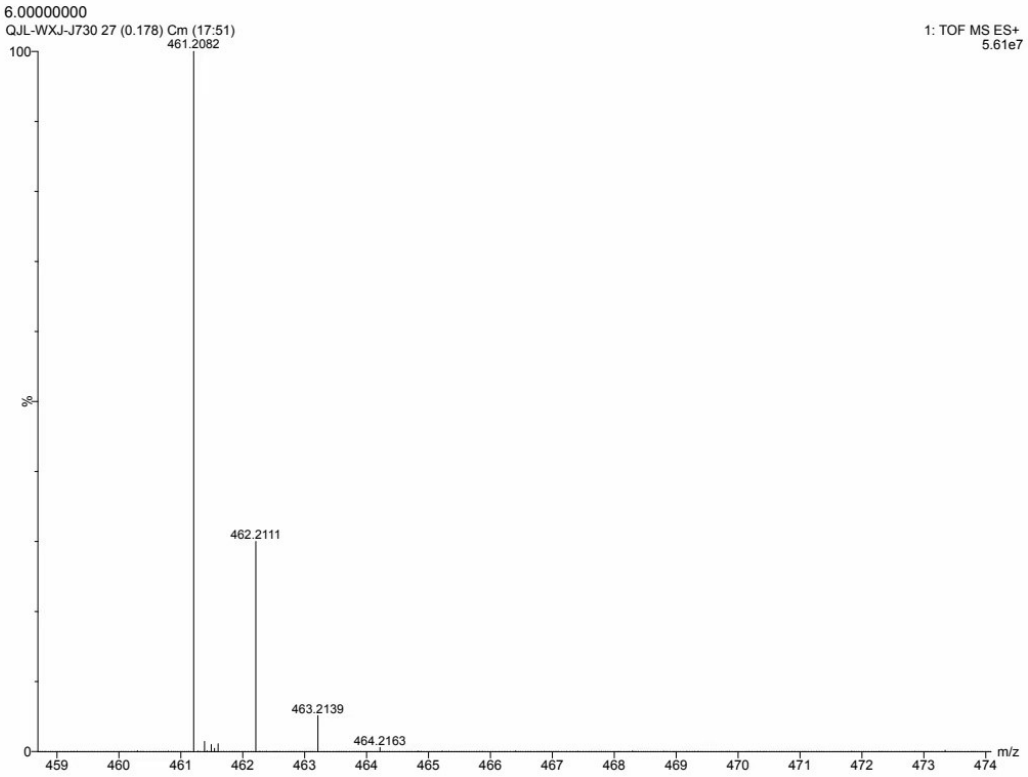
Elemental Analysis: C, 59.44; H, 4.80; Br, 15.21; N, 5.33; O, 15.23

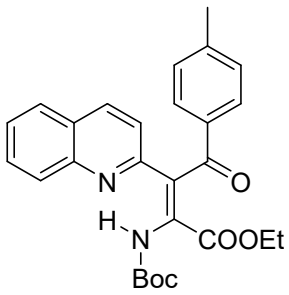
HRMS (ESI, m/z) calcd for $C_{26}H_{25}BrN_2O_5$ $[M+H]^+$ 525.1020, found 525.1025.

3h


J730-H. 10. fid
12.99
8.01
7.99
7.96
7.95
7.88
7.87
7.76
7.74
7.74
7.73
7.72
7.72
7.54
7.53
7.52
7.52
7.52
7.51
7.50
7.21
7.20
7.19
7.18
4.05
4.04
4.02
4.01
2.37
1.55
1.10
1.09
1.07
1.03
1.02
1.03
2.07
2.11
1.06
3.04
2.00
3.09
9.33
3.05
f1 (ppm)


J730-C. 10. fid
194.9
163.7
154.8
152.2
146.3
144.6
137.3
136.7
135.5
130.3
130.0
129.3
128.3
127.6
127.0
126.4
121.4
118.7
81.66
61.90
28.25
21.80
13.50
f1 (ppm)





3h

Chemical Formula: $C_{27}H_{28}N_2O_5$

Exact Mass: 460.1998

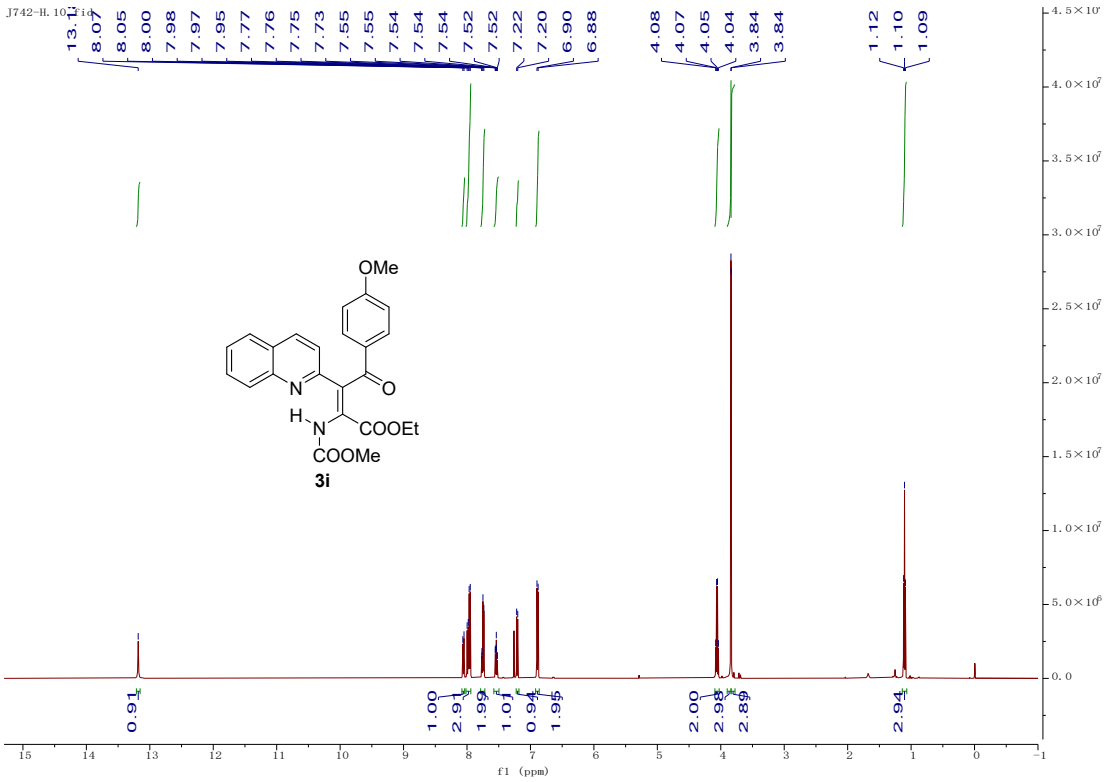
Molecular Weight: 460.5300

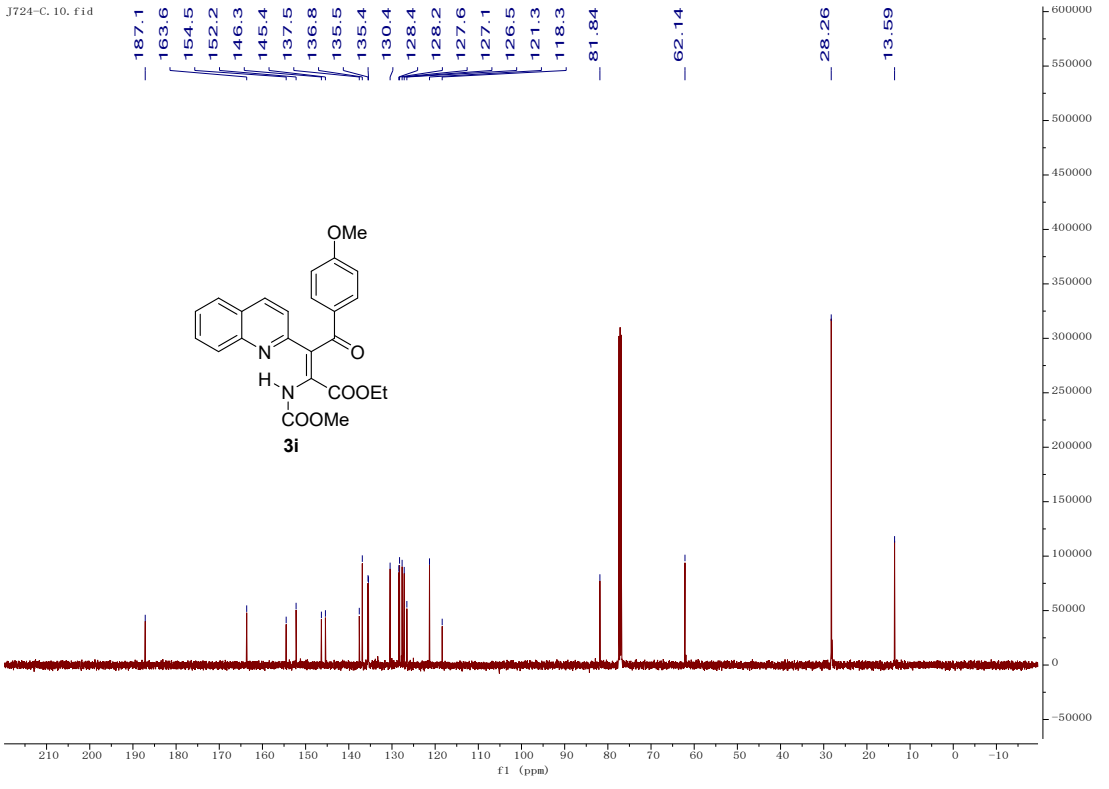
m/z: 460.1998 (100.0%), 461.2032 (29.2%), 462.2065 (4.1%), 462.2041 (1.0%)

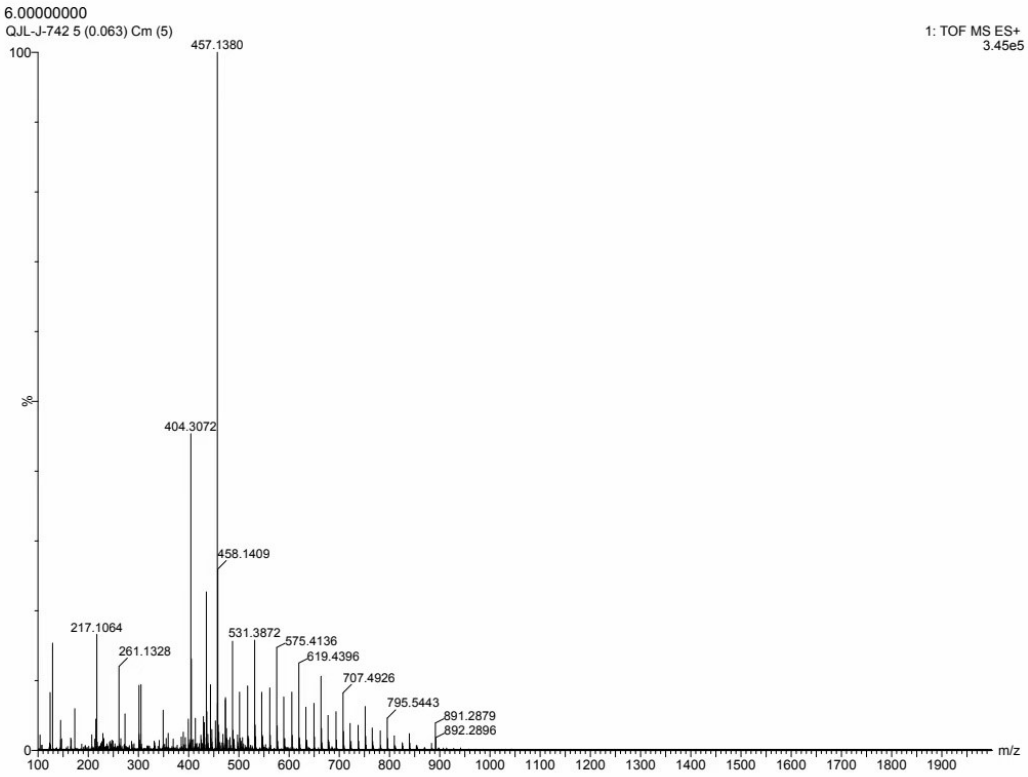
Elemental Analysis: C, 70.42; H, 6.13; N, 6.08; O, 17.37

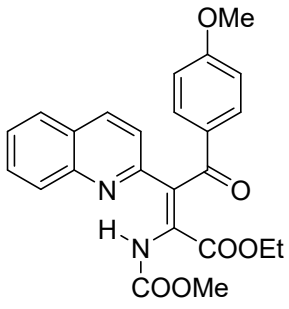
HRMS (ESI, m/z) calcd for $C_{27}H_{28}N_2O_5$ $[M+H]^+$ 461.2071, found 461.2082.

3i


J742-H. 10. fid
13.11
8.07
8.05
8.00
7.98
7.97
7.95
7.77
7.76
7.75
7.73
7.55
7.55
7.54
7.54
7.54
7.52
7.52
7.22
7.20
6.90
6.88
4.08
4.07
4.05
4.04
3.84
3.84
1.12
1.10
1.09
OMe
O
N
H
N
COOEt
COOMe
3i
0.91
1.00
2.91
1.99
1.01
0.94
1.95
2.00
2.98
2.89
2.94
f1 (ppm)


J724-C. 10. fid
187.1
163.6
154.5
152.2
146.3
145.4
137.5
136.8
135.5
135.4
130.4
128.4
128.2
127.6
127.1
126.5
121.3
118.3
81.84
62.14
28.26
13.59
OMe
O
N
H
N
COOEt
COOMe
3i
f1 (ppm)





3i

Chemical Formula: $C_{24}H_{22}N_2O_6$

Exact Mass: 434.1478

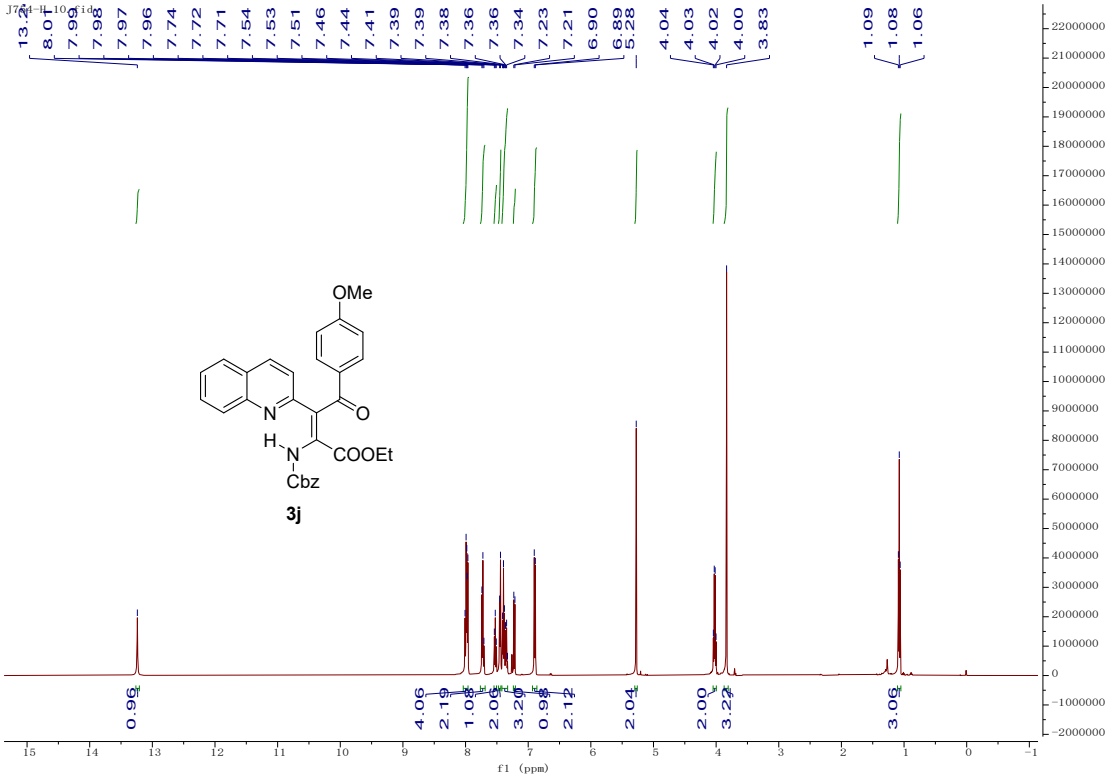
Molecular Weight: 434.4480

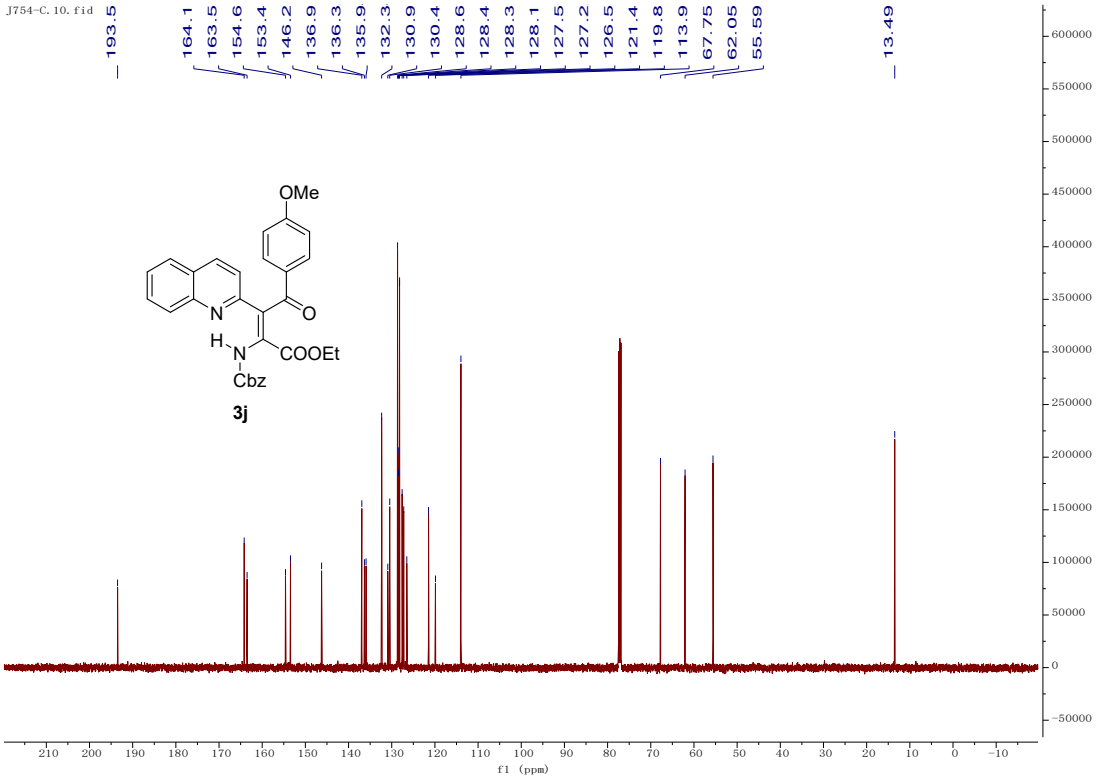
m/z: 434.1478 (100.0%), 435.1511 (26.0%), 436.1545 (3.2%), 436.1520 (1.2%)

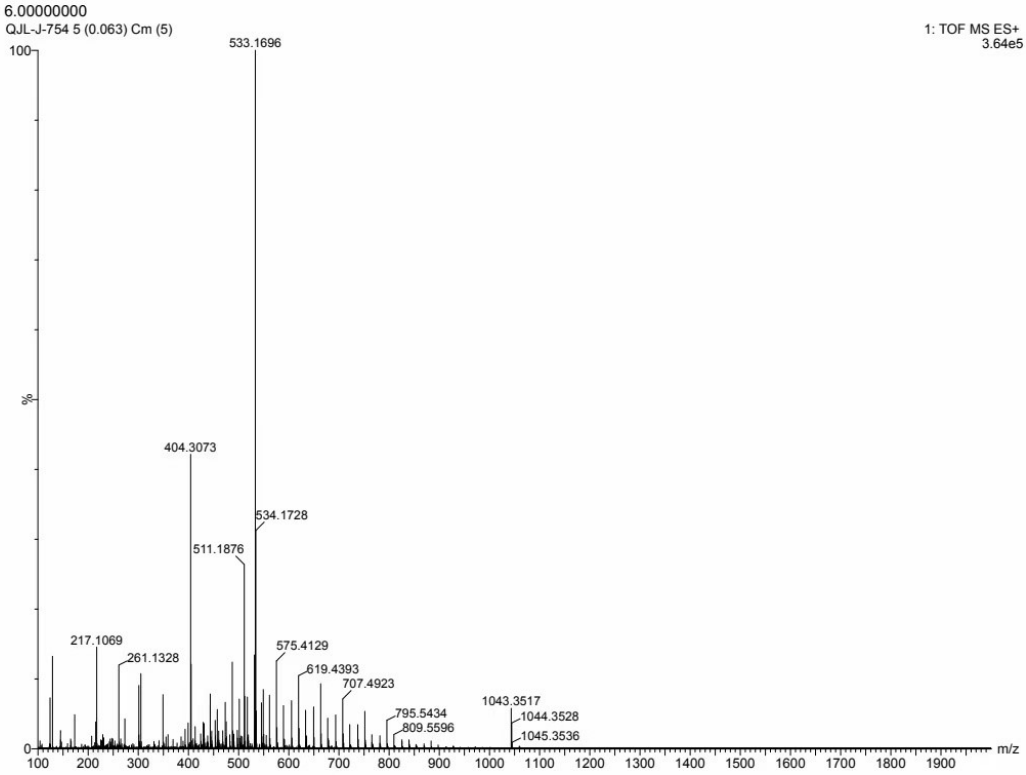
Elemental Analysis: C, 66.35; H, 5.10; N, 6.45; O, 22.10

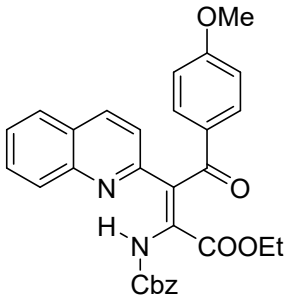
HRMS (ESI, m/z) calcd for $C_{24}H_{22}N_2O_6$ $[M+Na]^+$ 457.1371, found 457.1380.

3j


J754-H.10.fid
13.21
8.01
7.99
7.98
7.97
7.96
7.74
7.72
7.71
7.54
7.53
7.51
7.46
7.44
7.41
7.39
7.39
7.38
7.36
7.36
7.34
7.23
7.21
6.90
6.89
5.28
4.04
4.03
4.02
4.00
3.83
1.09
1.08
1.06
OMe
O
N
H
N
COOEt
Cbz
3j
0.96
4.06
2.19
1.08
2.05
3.20
0.98
2.12
2.04
2.00
3.22
3.06
f1 (ppm)


J754-C.10.fid
193.5
164.1
163.5
154.6
153.4
146.2
136.9
136.3
135.9
132.3
130.9
130.4
128.6
128.4
128.3
128.1
127.5
127.2
126.5
121.4
119.8
113.9
67.75
62.05
55.59
13.49
OMe
O
N
H
N
COOEt
Cbz
3j
f1 (ppm)





3j

Chemical Formula: $C_{30}H_{26}N_2O_6$

Exact Mass: 510.1791

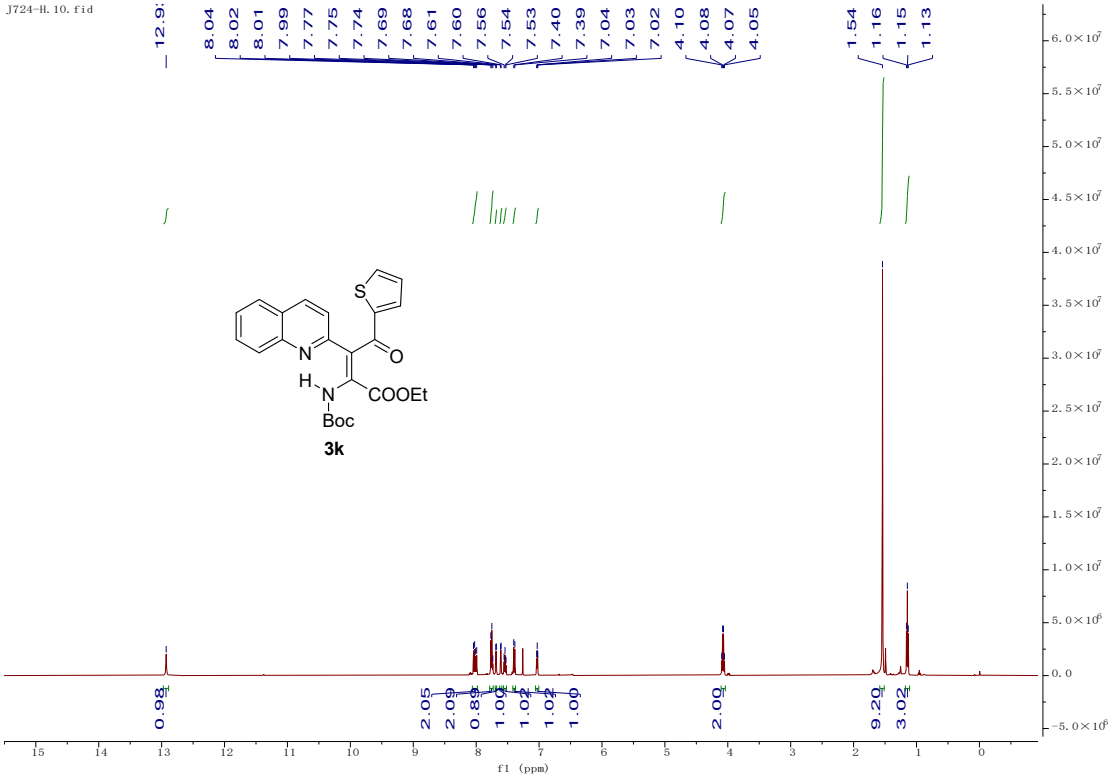
Molecular Weight: 510.5460

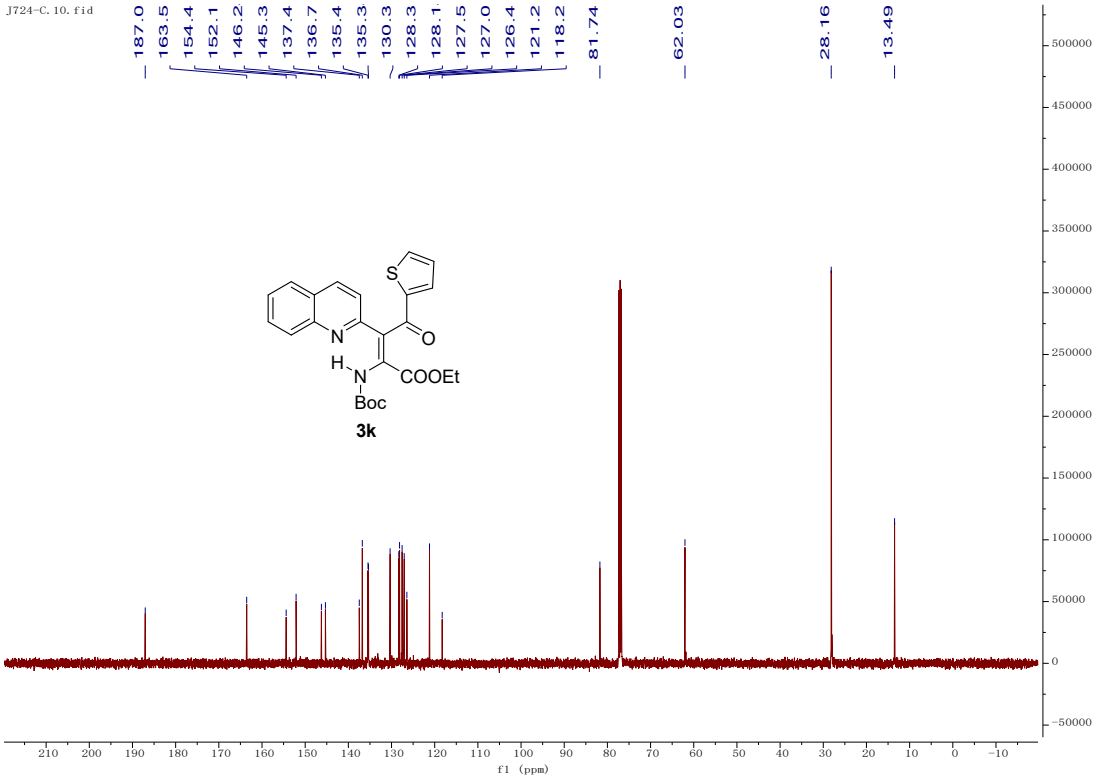
m/z: 510.1791 (100.0%), 511.1824 (32.4%), 512.1858 (5.1%), 512.1833 (1.2%)

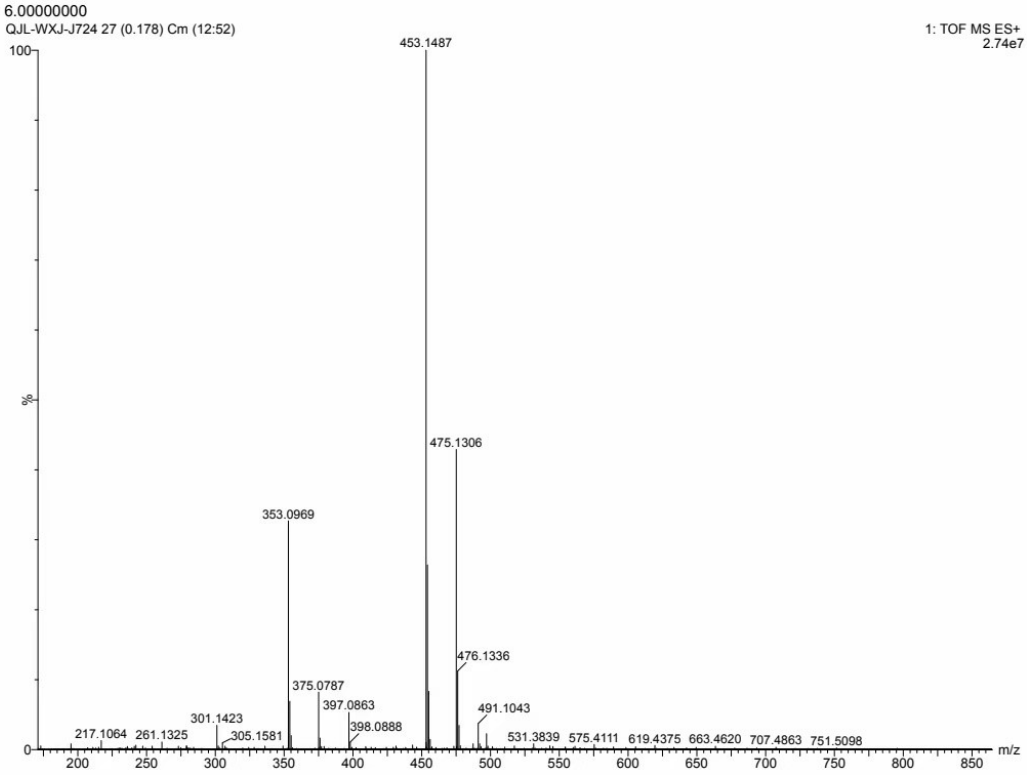
Elemental Analysis: C, 70.58; H, 5.13; N, 5.49; O, 18.80

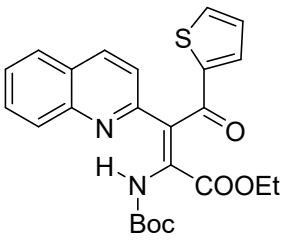
HRMS (ESI, m/z) calcd for $C_{30}H_{26}N_2O_6$ $[M+Na]^+$ 533.1684, found 533.1696.

3k


J724-H.10.fid
12.9
8.04
8.02
8.01
7.99
7.77
7.75
7.74
7.69
7.68
7.61
7.60
7.56
7.54
7.53
7.40
7.39
7.04
7.03
7.02
4.10
4.08
4.07
4.05
1.54
1.16
1.15
1.13
S
O
N
H
N
COOEt
Boc
3k
0.98
2.05
2.09
0.89
1.00
1.02
1.02
1.00
2.00
9.20
3.02
f1 (ppm)


J724-C.10.fid
187.0
163.5
154.4
152.1
146.2
145.3
137.4
136.7
135.4
135.3
130.3
128.3
128.1
127.5
127.0
126.4
121.2
118.2
81.74
62.03
28.16
13.49
S
O
N
H
N
COOEt
Boc
3k
f1 (ppm)





3k

Chemical Formula: $C_{24}H_{24}N_2O_5S$

Exact Mass: 452.1406

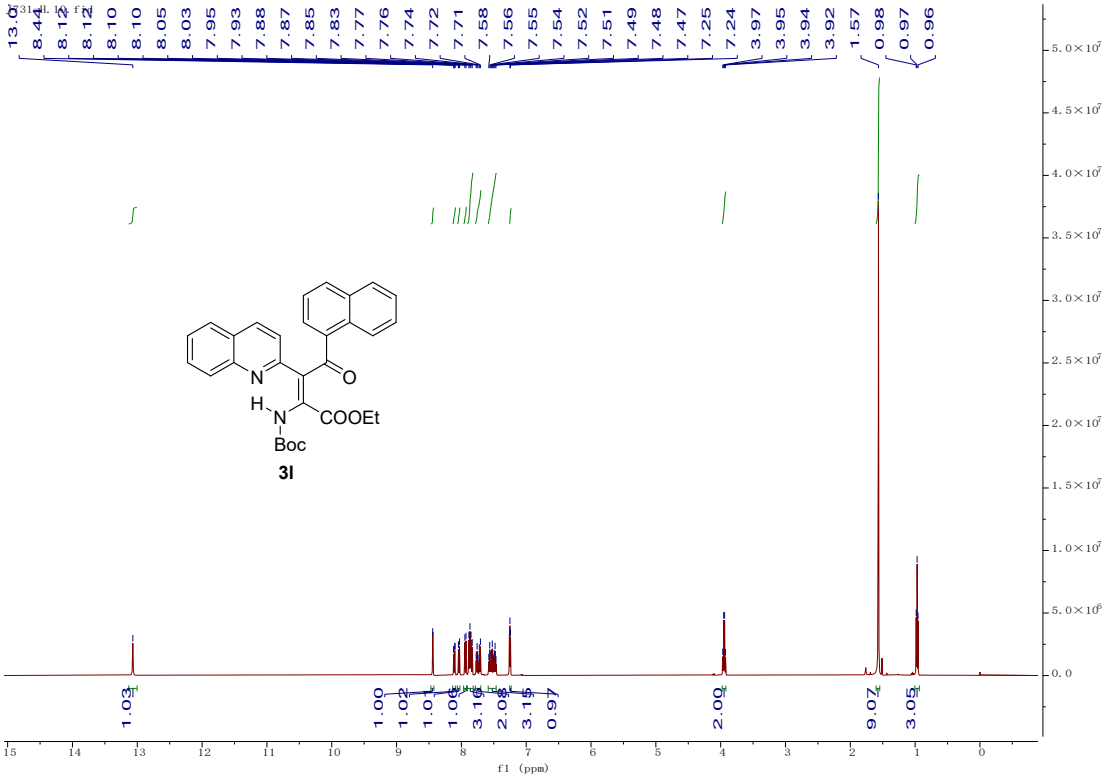
Molecular Weight: 452.5250

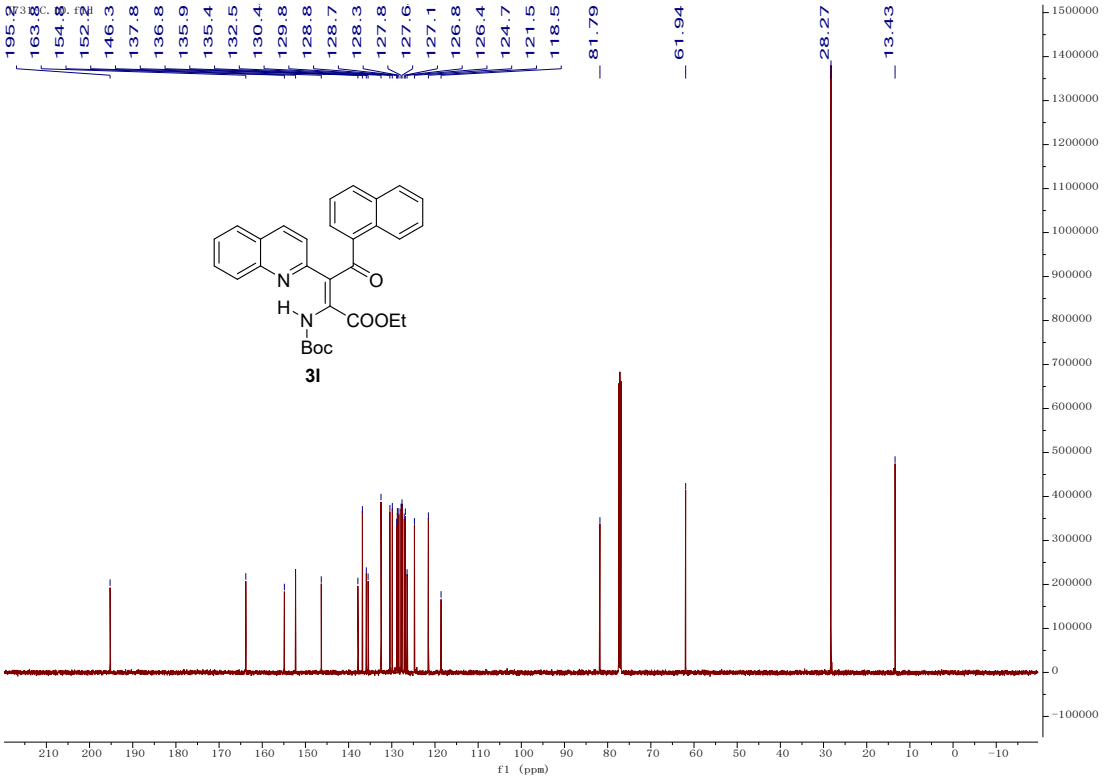
m/z: 452.1406 (100.0%), 453.1439 (26.0%), 454.1364 (4.5%),
454.1473 (3.2%), 455.1397 (1.2%), 454.1448 (1.0%)

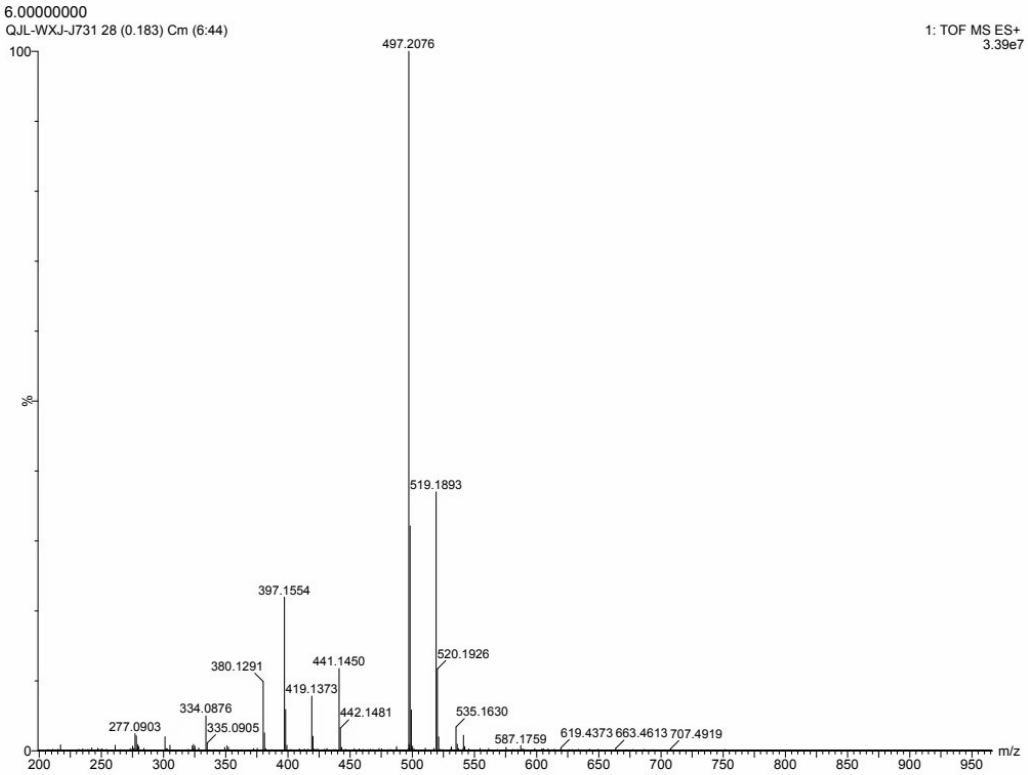
Elemental Analysis: C, 63.70; H, 5.35; N, 6.19; O, 17.68; S, 7.08

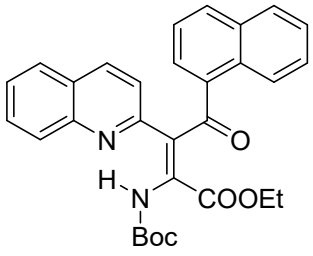
HRMS (ESI, m/z) calcd for $C_{24}H_{24}N_2O_5S$ $[M+H]^+$ 453.1479, found 453.1487.

3l


13.03
8.44
8.12
8.12
8.10
8.10
8.05
8.03
7.95
7.93
7.88
7.87
7.85
7.83
7.77
7.76
7.74
7.72
7.71
7.58
7.56
7.55
7.54
7.52
7.51
7.49
7.48
7.47
7.25
7.24
3.97
3.95
3.94
3.92
1.57
0.98
0.97
0.96
1.03
1.00
1.02
1.01
1.00
3.16
2.08
3.15
0.97
2.00
9.07
3.05
f1 (ppm)
N
H
N
Boc
COOEt
O
3l


195.2
163.8
154.8
152.1
146.3
137.8
136.8
135.9
135.4
132.5
130.4
129.8
128.8
128.7
128.3
127.8
127.6
127.1
126.8
126.4
124.7
121.5
118.5
81.79
61.94
28.27
13.43
f1 (ppm)
N
H
N
Boc
COOEt
O
3l





3l

Chemical Formula: $C_{30}H_{28}N_2O_5$

Exact Mass: 496.1998

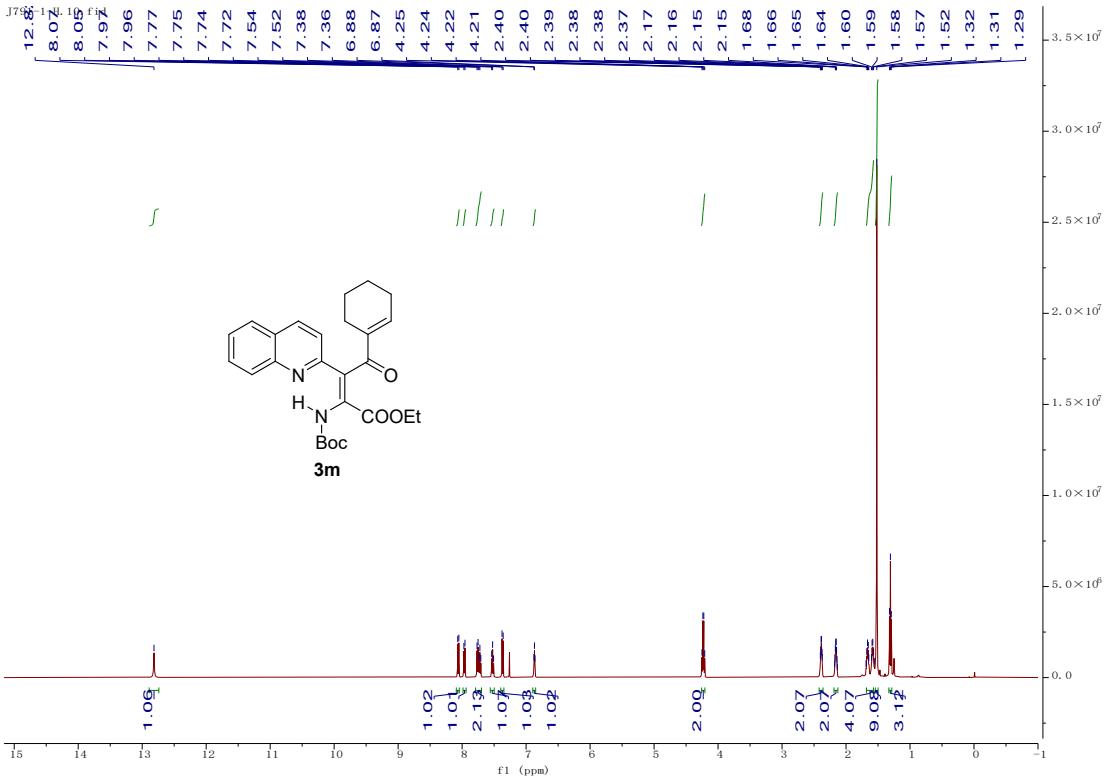
Molecular Weight: 496.5630

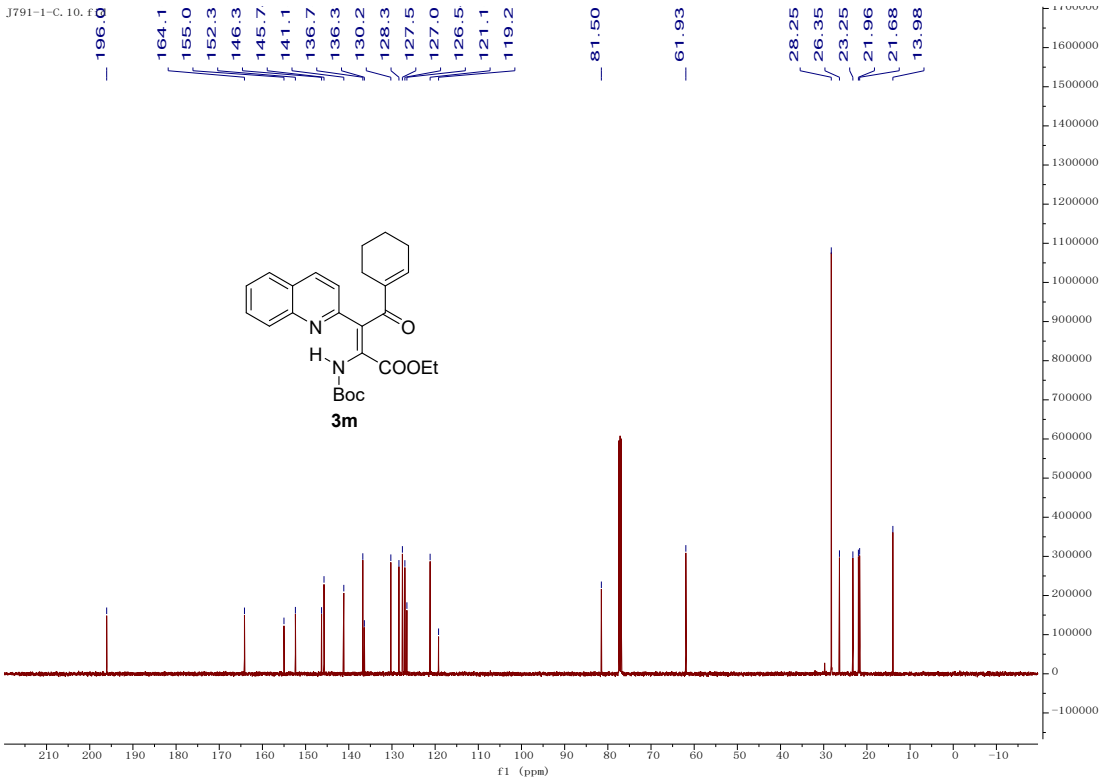
m/z: 496.1998 (100.0%), 497.2032 (32.4%), 498.2065 (5.1%), 498.2041 (1.0%)

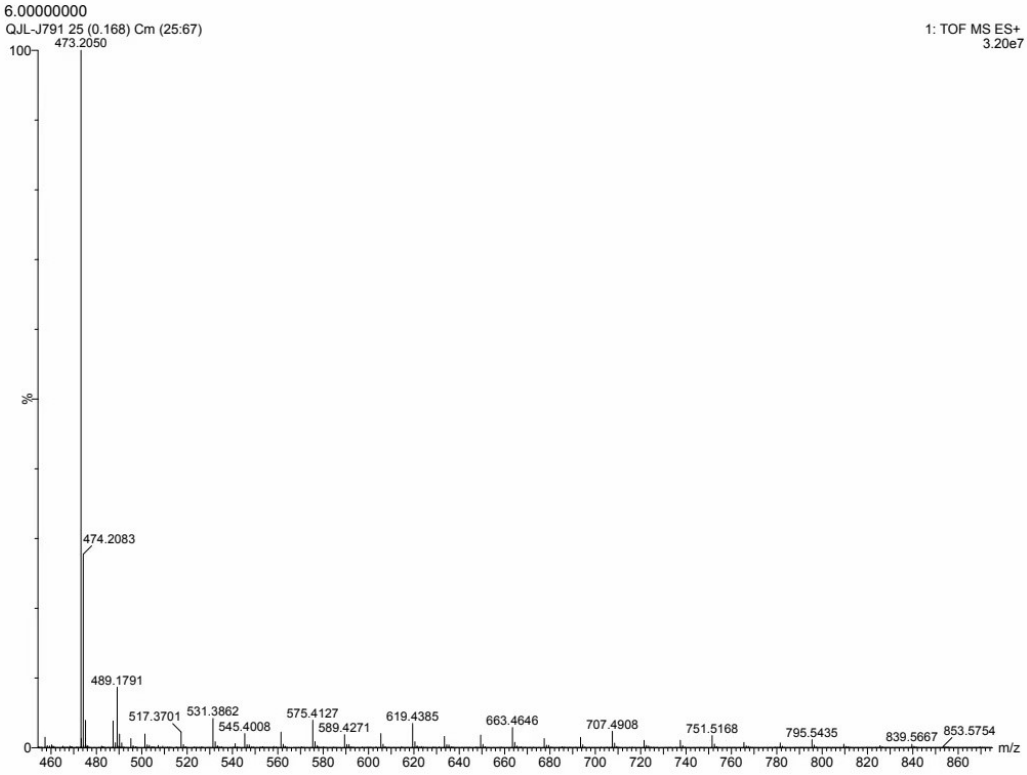
Elemental Analysis: C, 72.56; H, 5.68; N, 5.64; O, 16.11

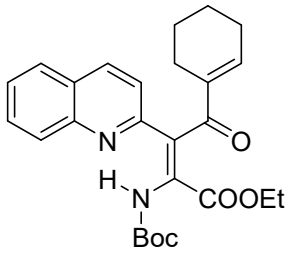
HRMS (ESI, m/z) calcd for $C_{30}H_{28}N_2O_5$ $[M+H]^+$ 497.2071, found 497.2076.

3m


12.83
8.07
8.05
7.97
7.96
7.77
7.75
7.74
7.72
7.54
7.52
7.38
7.36
6.88
6.87
4.25
4.24
4.22
4.21
2.40
2.40
2.39
2.38
2.38
2.37
2.17
2.16
2.15
2.15
1.68
1.66
1.65
1.64
1.60
1.59
1.58
1.57
1.52
1.32
1.31
1.29
1.06
1.02
1.01
2.13
1.07
1.03
1.02
2.00
2.07
2.07
4.07
9.05
3.12
f1 (ppm)
3m


196.0
164.1
155.0
152.3
146.3
145.7
141.1
136.7
136.3
130.2
128.3
127.5
127.0
126.5
121.1
119.2
81.50
61.93
28.25
26.35
23.25
21.96
21.68
13.98
f1 (ppm)
3m





3m

Chemical Formula: $C_{26}H_{30}N_2O_5$

Exact Mass: 450.2155

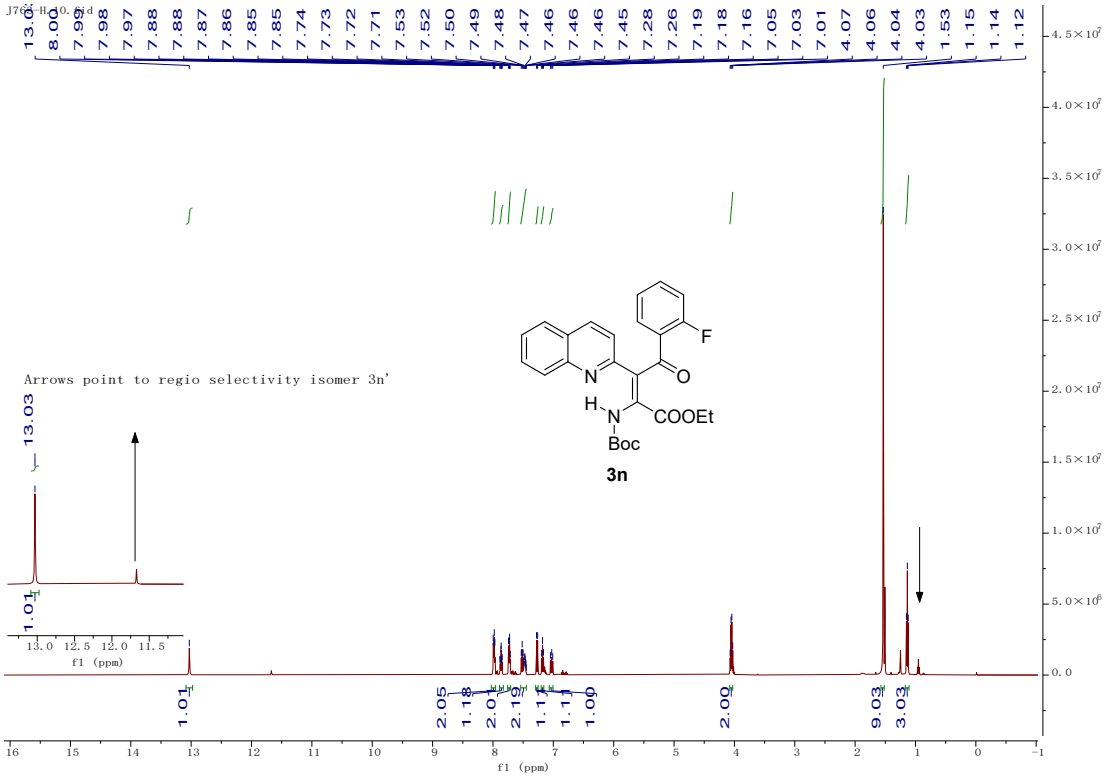
Molecular Weight: 450.5350

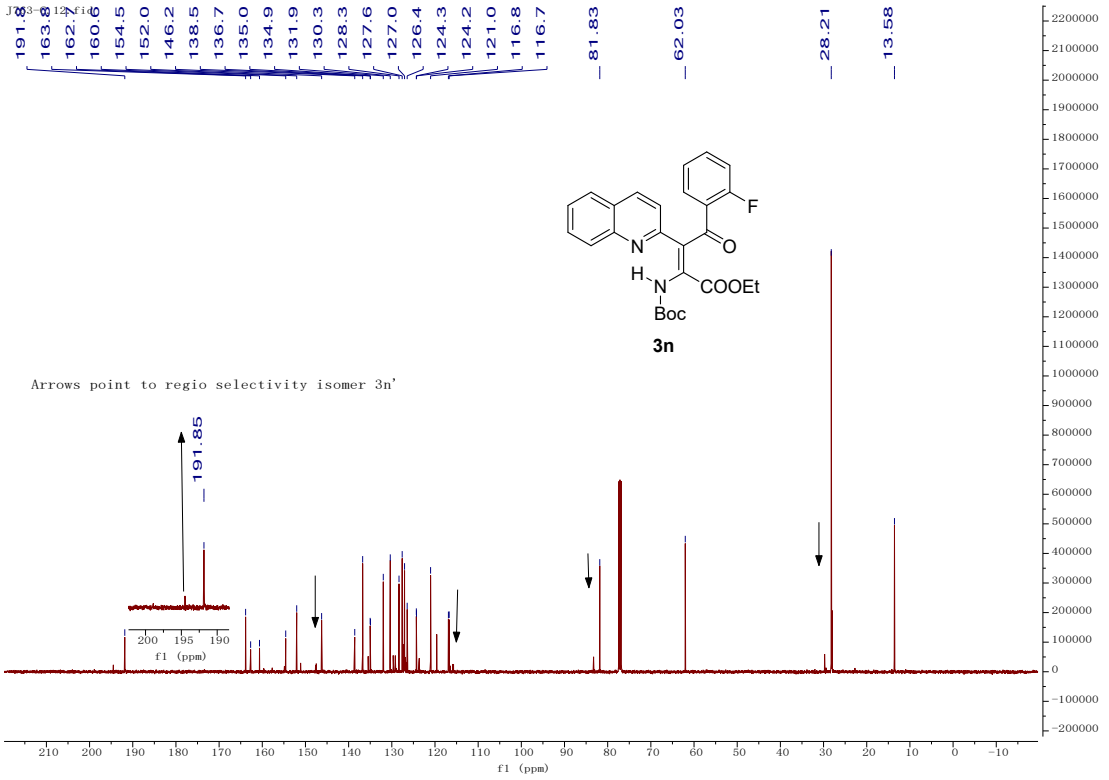
m/z: 450.2155 (100.0%), 451.2188 (28.1%), 452.2222 (3.8%), 452.2197 (1.0%)

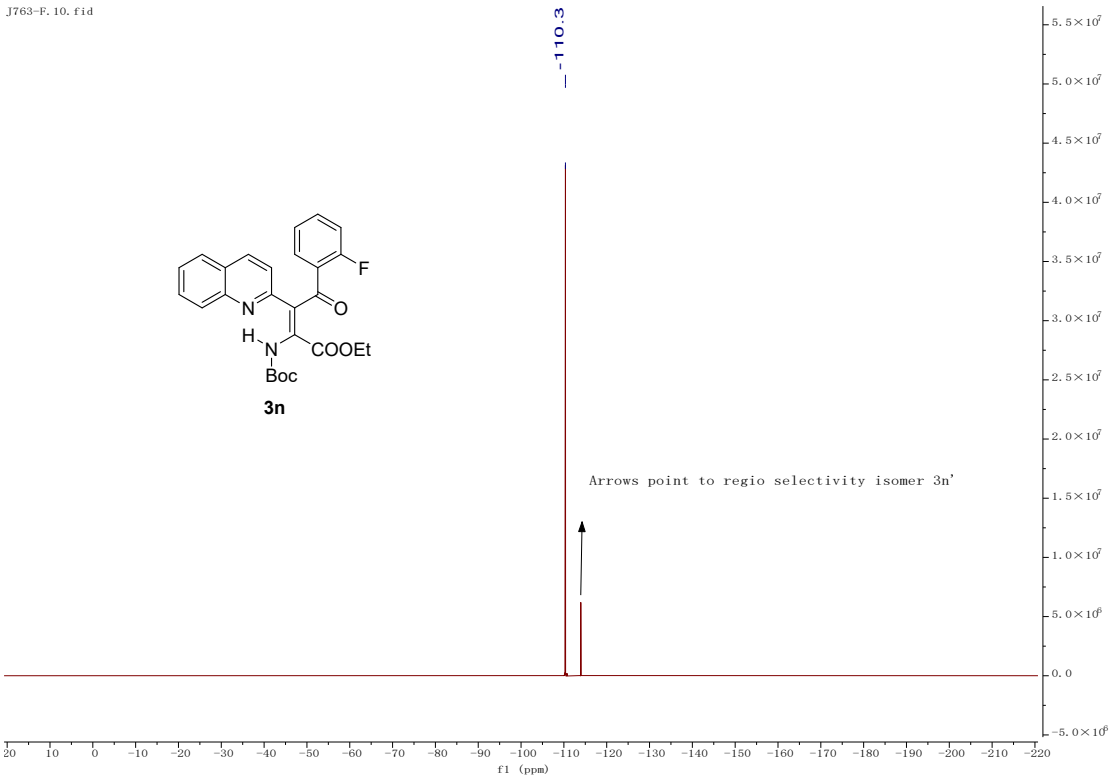
Elemental Analysis: C, 69.31; H, 6.71; N, 6.22; O, 17.76

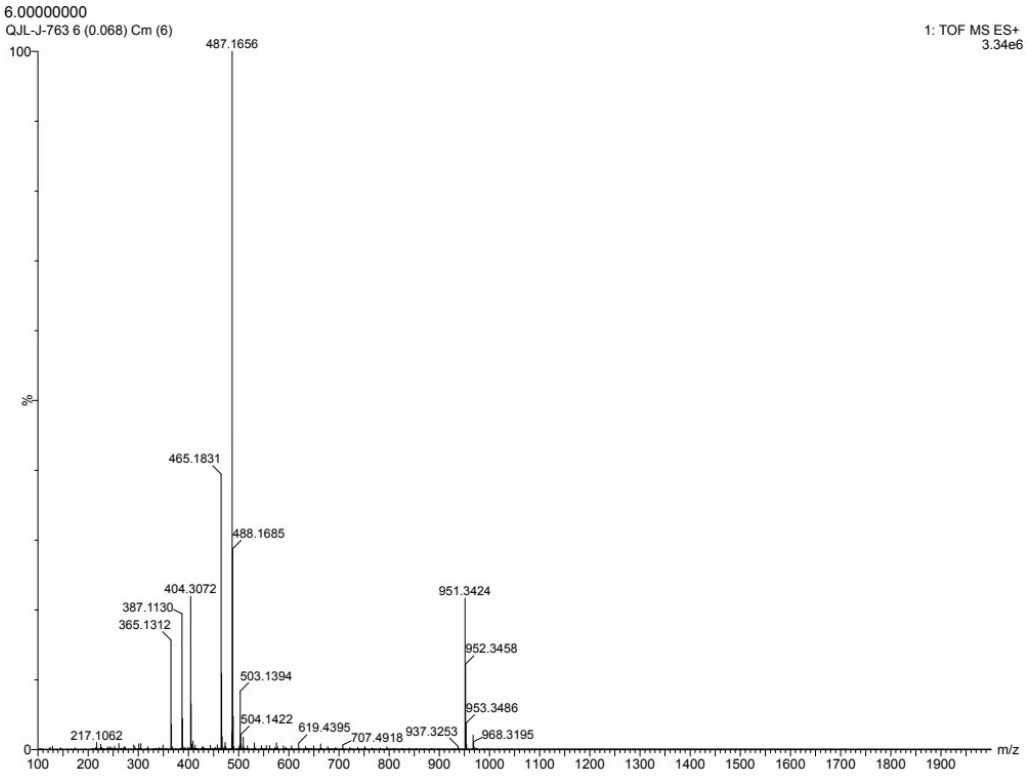
HRMS (ESI, m/z) calcd for $C_{26}H_{30}N_2O_5$ $[M+Na]^+$ 473.2047, found 473.2050.

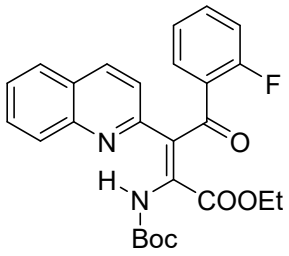
3n


Arrows point to regio selectivity isomer 3n'
F
O
N
H
N
COOEt
Boc
3n
f1 (ppm)


191.85
81.83
62.03
28.21
13.58
Arrows point to regio selectivity isomer 3n'
F
O
N
H
N
COOEt
Boc
3n
f1 (ppm)


J763-F.10.fid
-110.3
F
O
N
H
N
COOEt
Boc
3n
Arrows point to regio selectivity isomer 3n'
f1 (ppm)





3n

Chemical Formula: $C_{26}H_{25}FN_2O_5$

Exact Mass: 464.1748

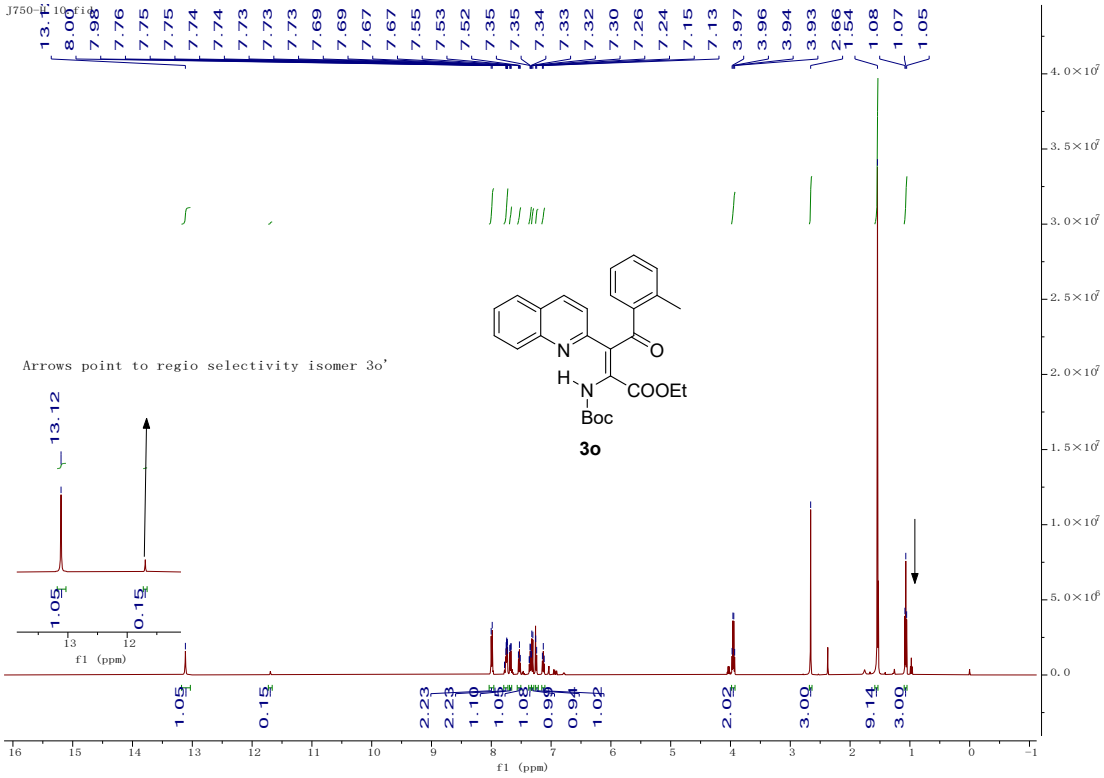
Molecular Weight: 464.4934

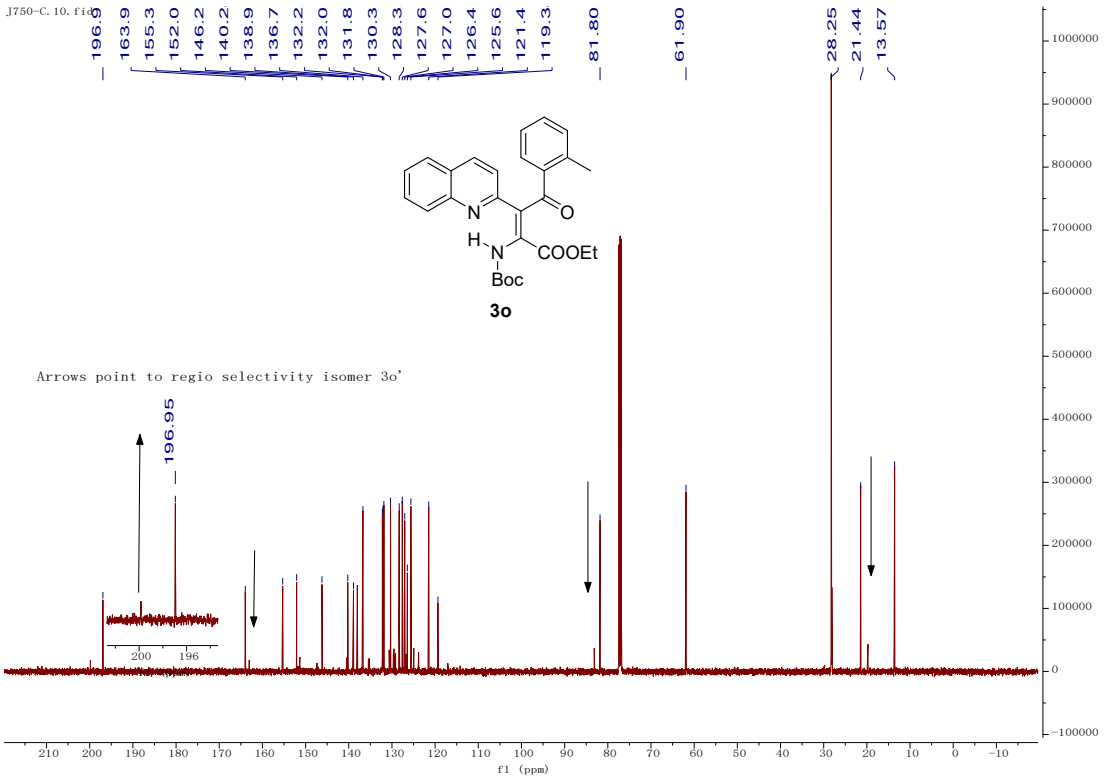
m/z: 464.1748 (100.0%), 465.1781 (28.1%), 466.1815 (3.8%), 466.1790 (1.0%)

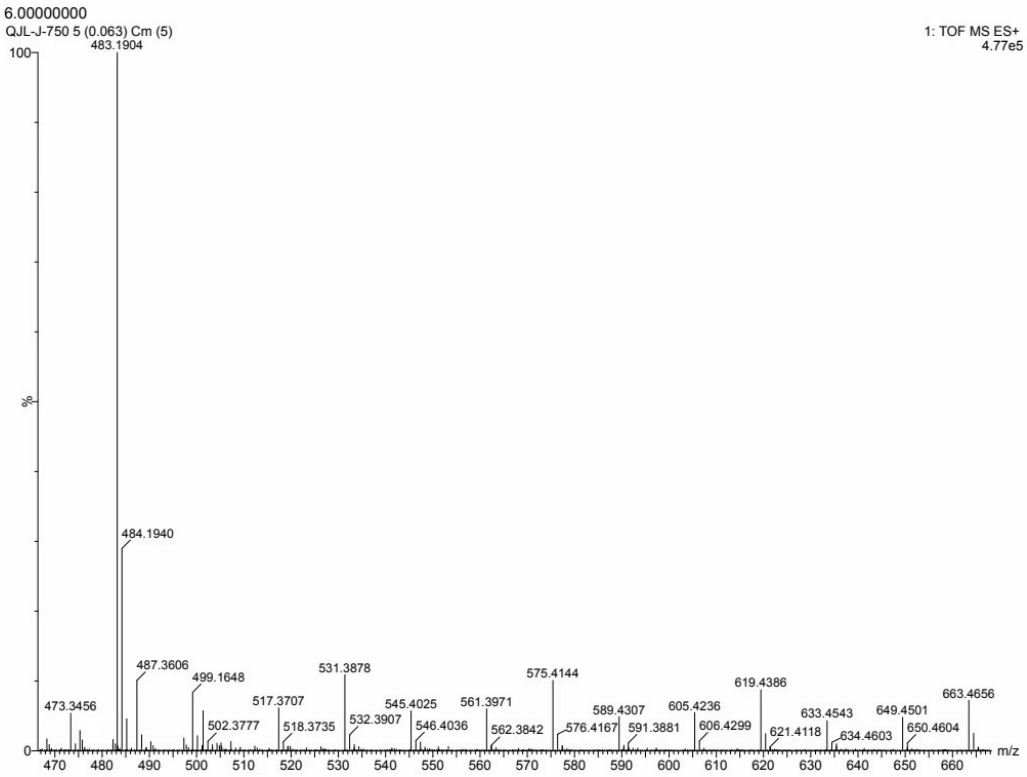
Elemental Analysis: C, 67.23; H, 5.43; F, 4.09; N, 6.03; O, 17.22

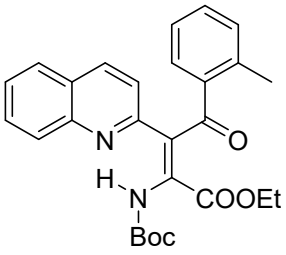
HRMS (ESI, m/z) calcd for $C_{26}H_{25}N_2O_5$ $[M+Na]^+$ 487.1640, found 487.1656.

3o


Arrows point to regio selectivity isomer 3o'
3o
f1 (ppm)


Arrows point to regio selectivity isomer 3o'
3o
f1 (ppm)





3o

Chemical Formula: $C_{27}H_{28}N_2O_5$

Exact Mass: 460.1998

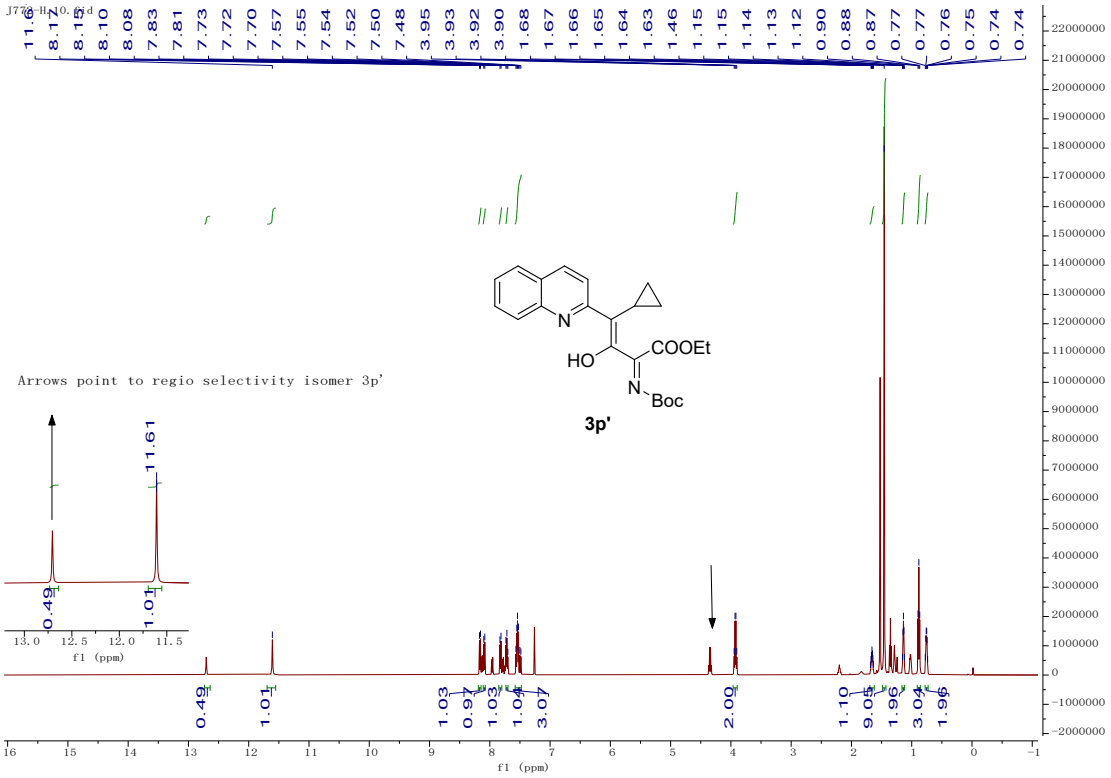
Molecular Weight: 460.5300

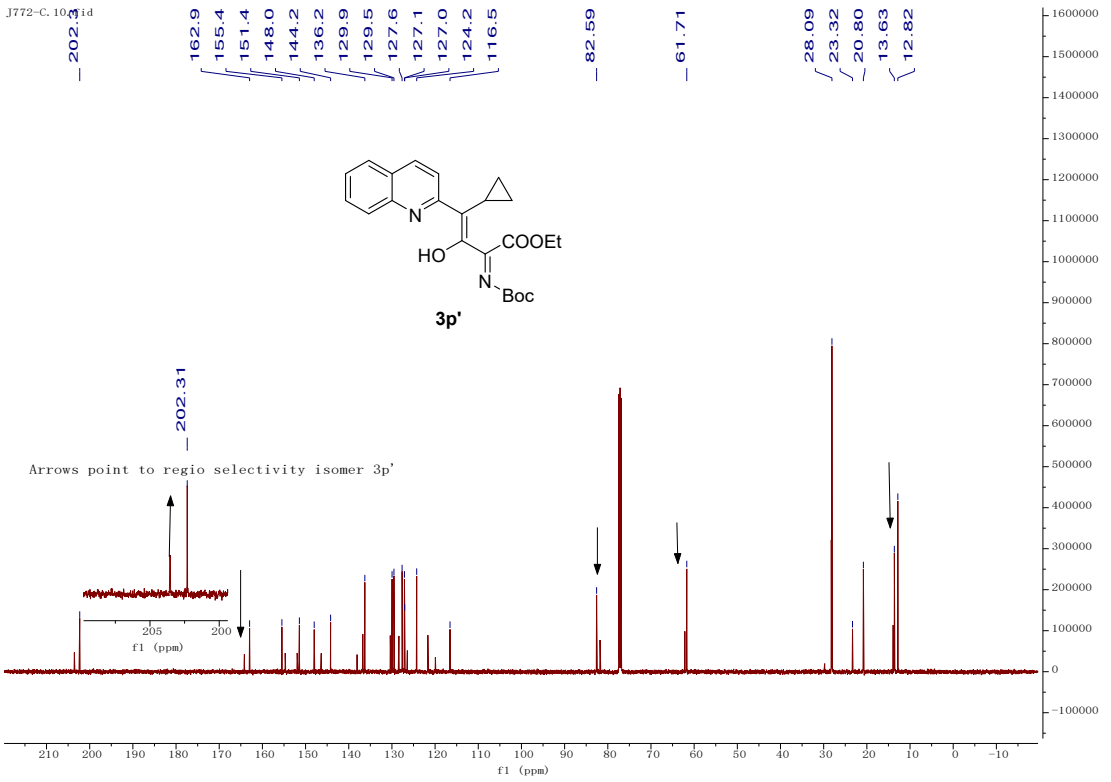
m/z: 460.1998 (100.0%), 461.2032 (29.2%), 462.2065 (4.1%), 462.2041 (1.0%)

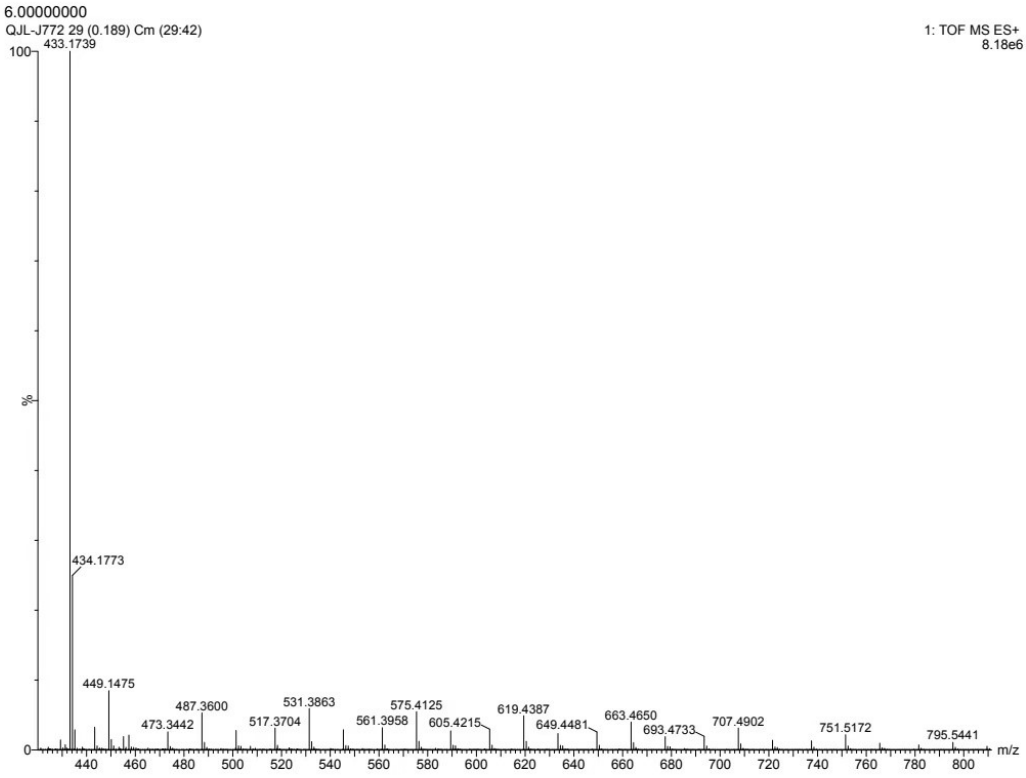
Elemental Analysis: C, 70.42; H, 6.13; N, 6.08; O, 17.37

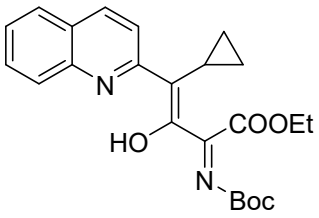
HRMS (ESI, m/z) calcd for $C_{27}H_{28}N_2O_5$ $[M+Na]^+$ 483.1891, found 483.1904.

3p’


Arrows point to regio selectivity isomer 3p’
HO
COOEt
N
Boc
3p'


Arrows point to regio selectivity isomer 3p’
HO
COOEt
N
Boc
3p'





3p'

Chemical Formula: $C_{23}H_{26}N_2O_5$

Exact Mass: 410.1842

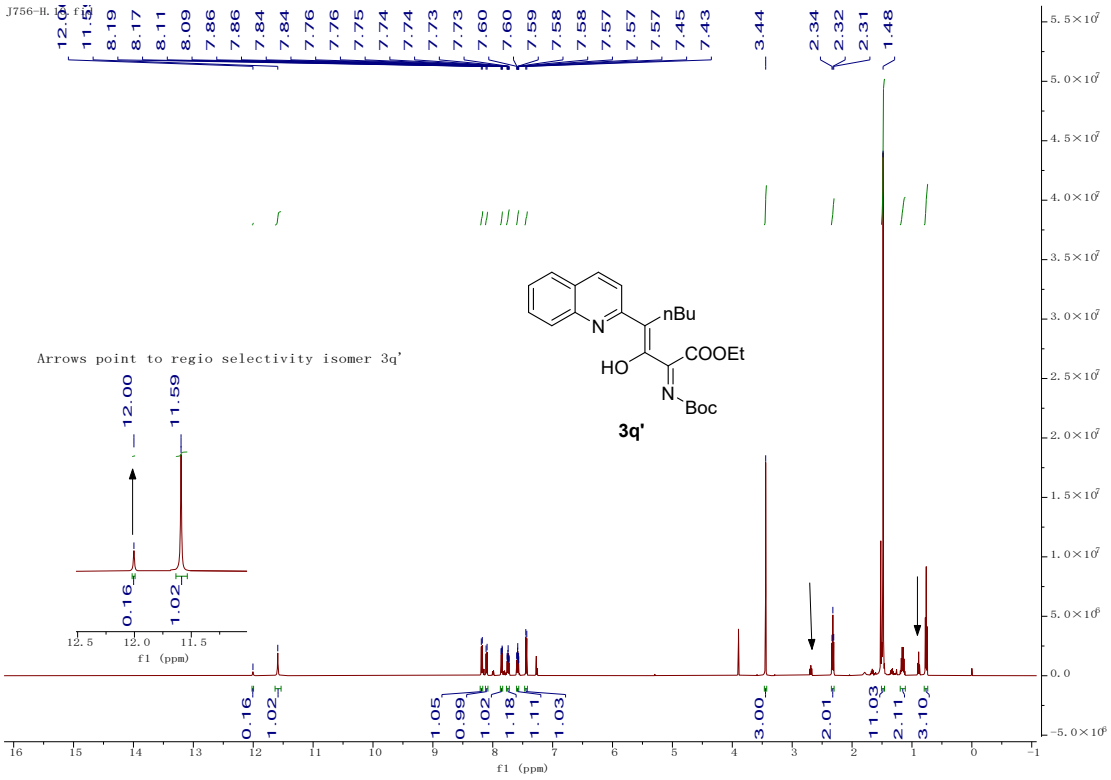
Molecular Weight: 410.4700

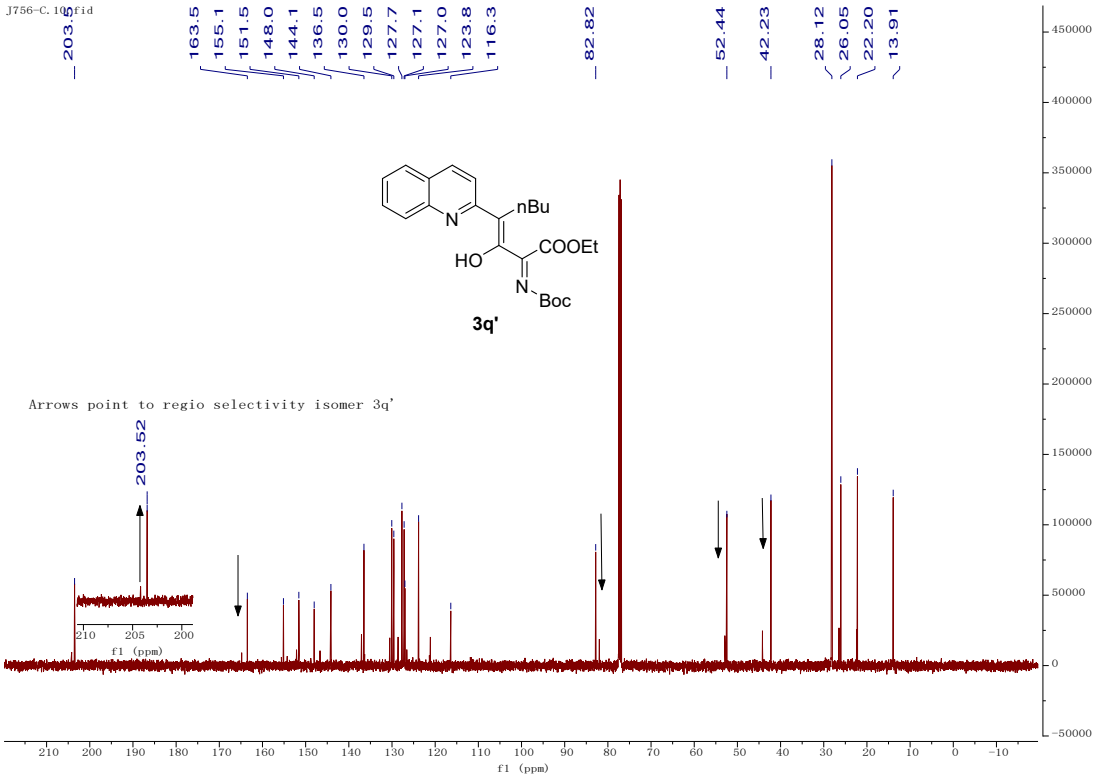
m/z: 410.1842 (100.0%), 411.1875 (24.9%), 412.1909 (3.0%), 412.1884 (1.0%)

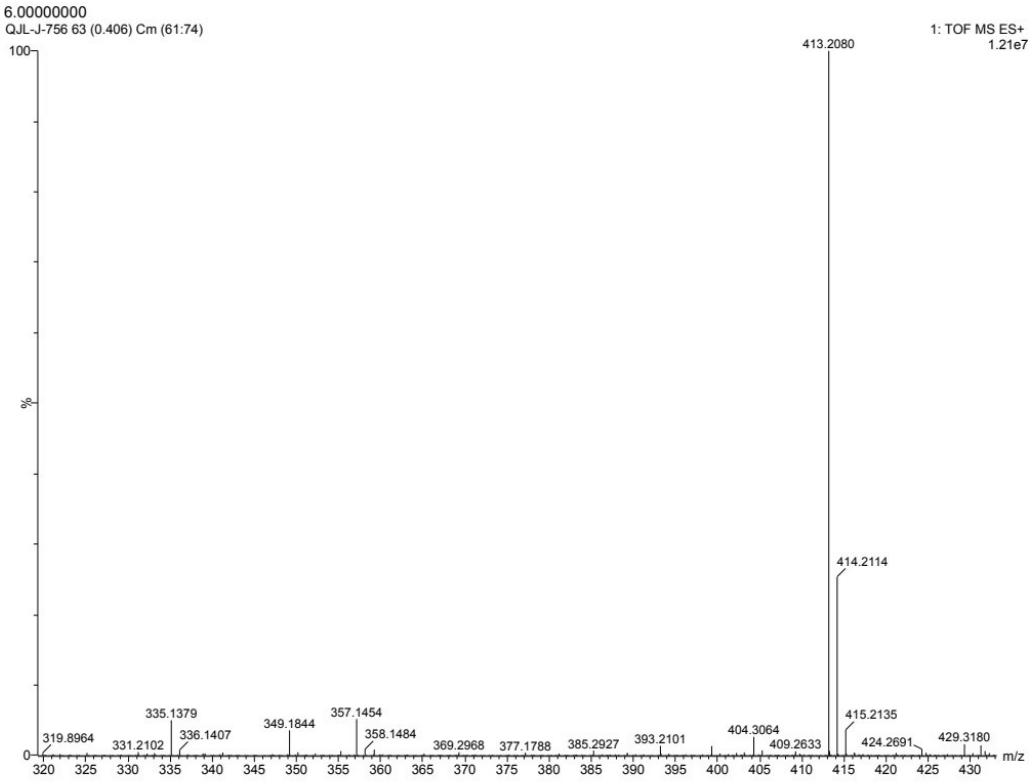
Elemental Analysis: C, 67.30; H, 6.38; N, 6.82; O, 19.49

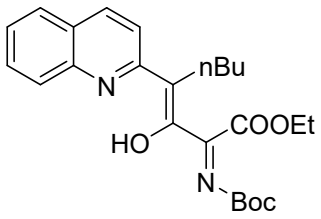
HRMS (ESI, m/z) calcd for $C_{23}H_{26}N_2O_5$ $[M+Na]^+$ 433.1734, found 433.1739.

3q’


Arrows point to regio selectivity isomer 3q’
nBu
COOEt
HO
N
Boc
3q'
f1 (ppm)


Arrows point to regio selectivity isomer 3q’
nBu
COOEt
HO
N
Boc
3q'
f1 (ppm)





3q'

Chemical Formula: $C_{23}H_{28}N_2O_5$

Exact Mass: 412.1998

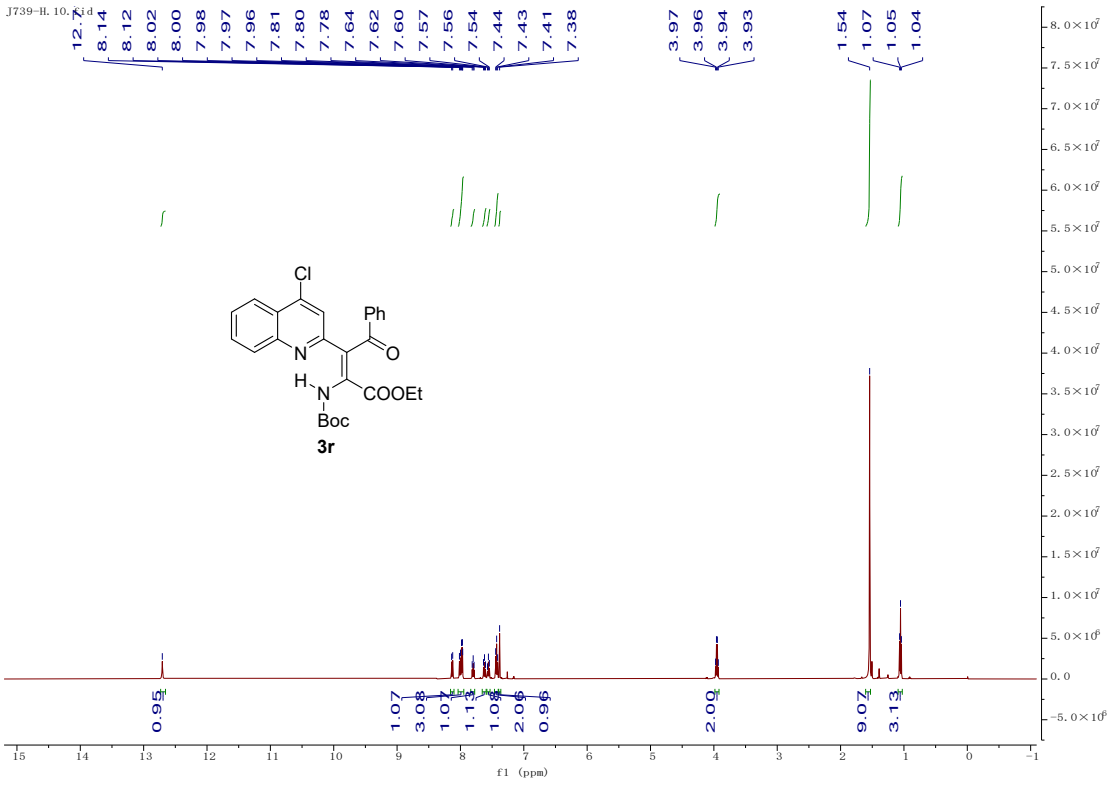
Molecular Weight: 412.4860

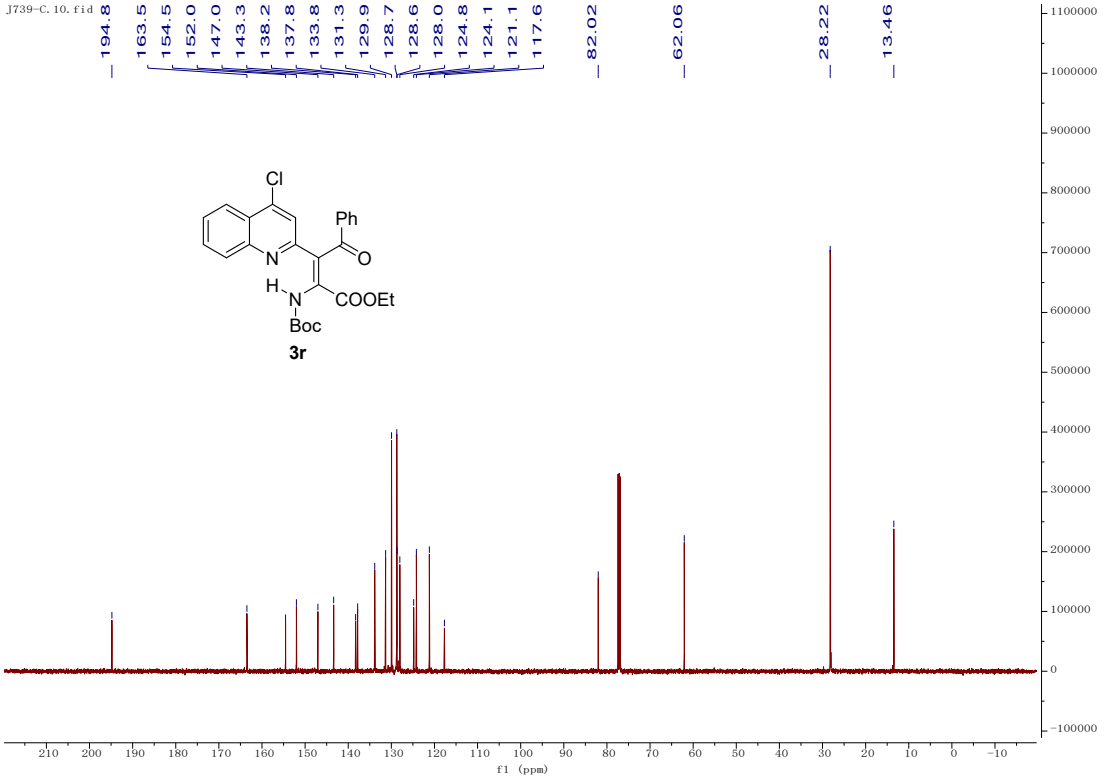
m/z: 412.1998 (100.0%), 413.2032 (24.9%), 414.2065 (3.0%), 414.2041 (1.0%)

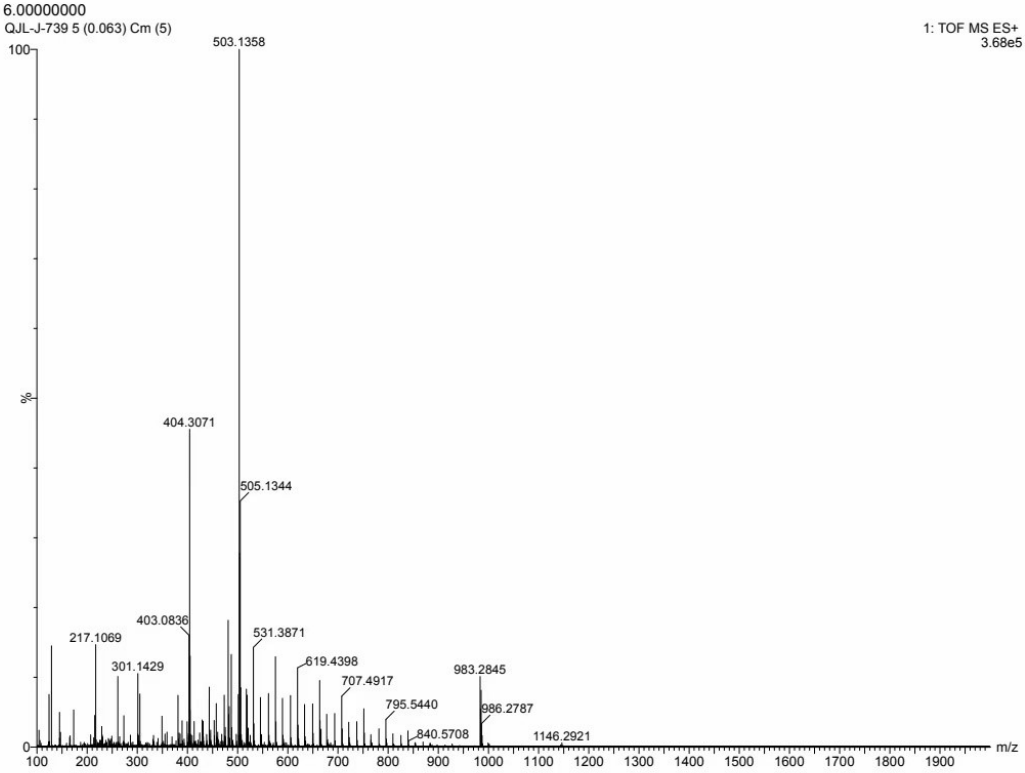
Elemental Analysis: C, 66.97; H, 6.84; N, 6.79; O, 19.39

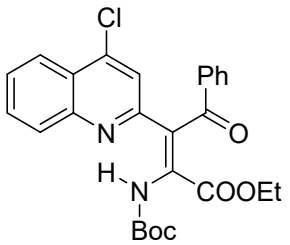
HRMS (ESI, m/z) calcd for $C_{23}H_{28}N_2O_5$ $[M+H]^+$ 413.2071, found 413.2080.

3r


J739-H.10.fid
12.71
8.14
8.12
8.02
8.00
7.98
7.97
7.96
7.81
7.80
7.78
7.64
7.62
7.60
7.57
7.56
7.54
7.44
7.43
7.41
7.38
3.97
3.96
3.94
3.93
1.54
1.07
1.05
1.04
Cl
Ph
O
N
H
N
COOEt
Boc
3r
0.95
1.07
3.08
1.01
1.17
1.08
2.06
0.96
2.00
9.07
3.13
f1 (ppm)


J739-C.10.fid
194.8
163.5
154.5
152.0
147.0
143.3
138.2
137.8
133.8
131.3
129.9
128.7
128.6
128.0
124.8
124.1
121.1
117.6
82.02
62.06
28.22
13.46
Cl
Ph
O
N
H
N
COOEt
Boc
3r
f1 (ppm)



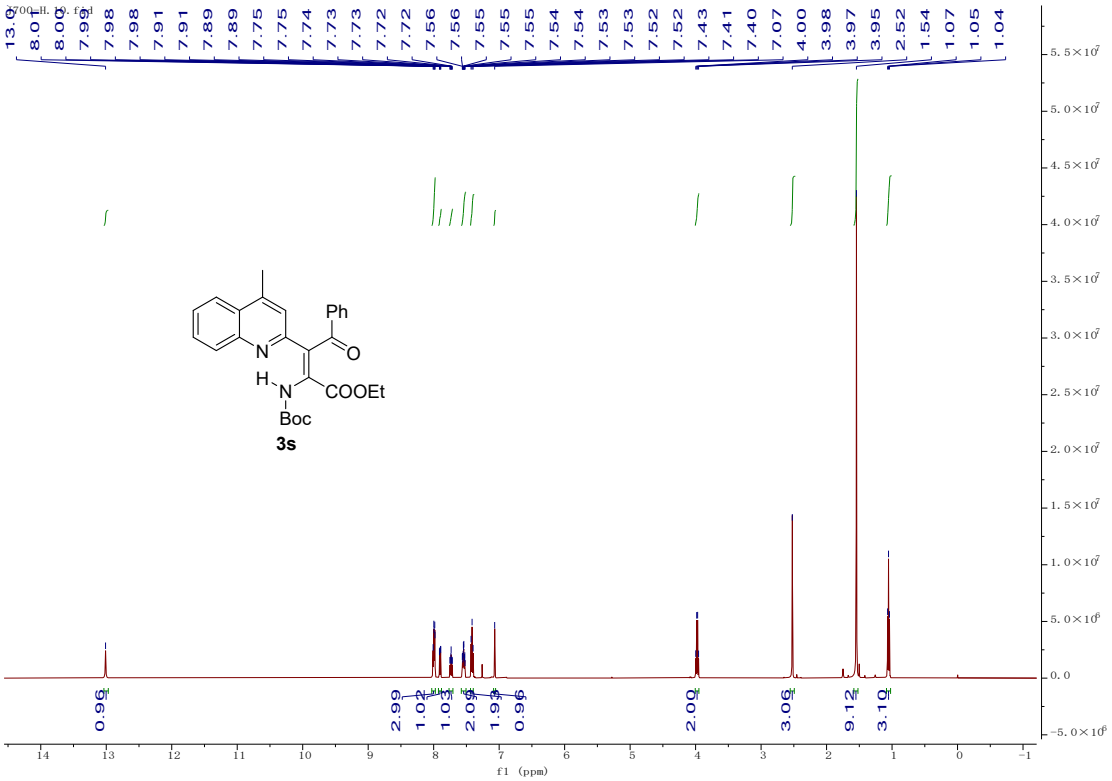


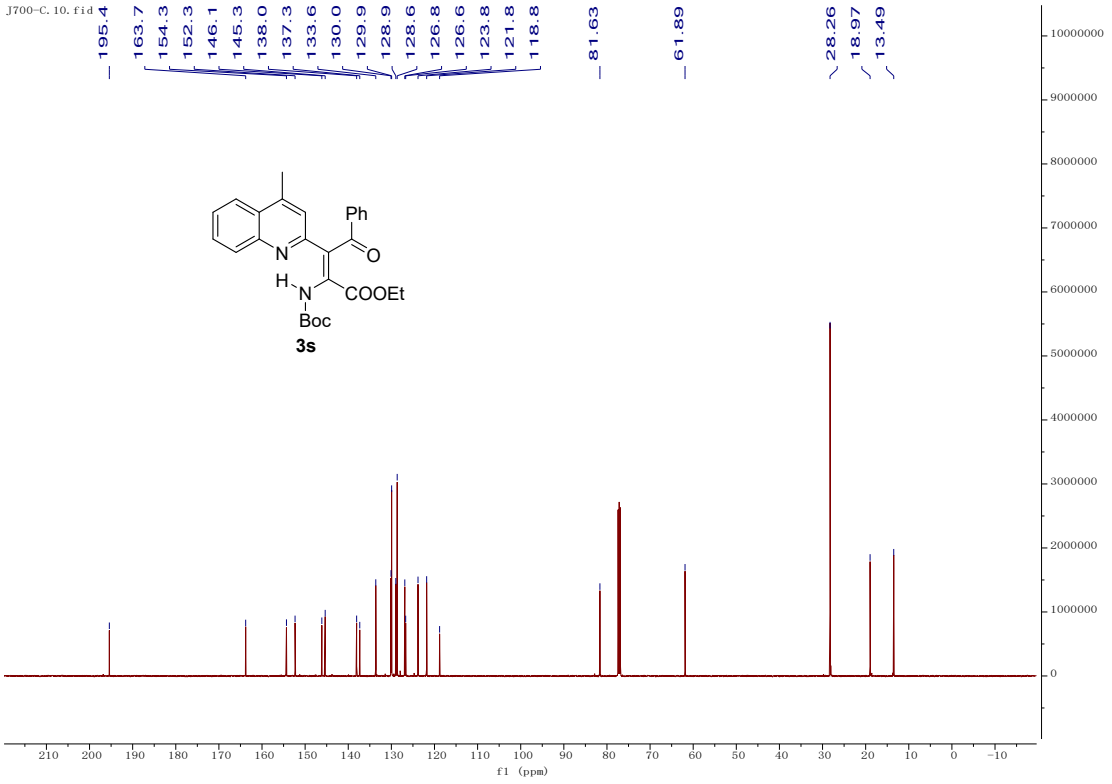
3r

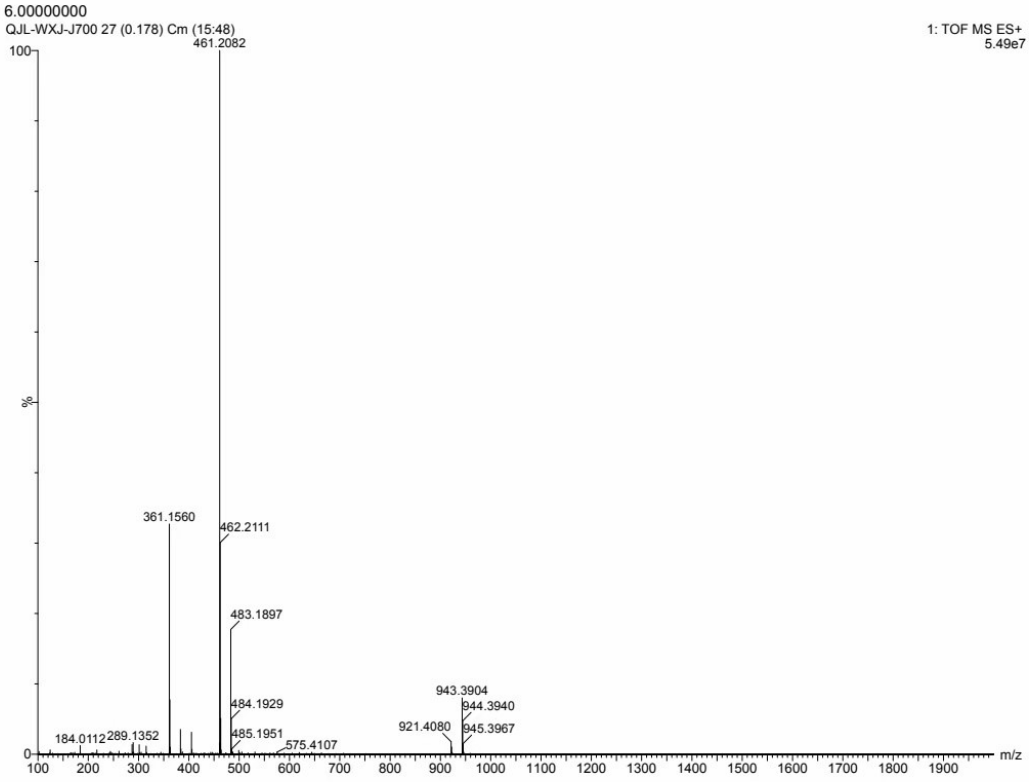
Chemical Formula: $C_{26}H_{25}ClN_2O_5$
Exact Mass: 480.1452
Molecular Weight: 480.9450
m/z: 480.1452 (100.0%), 482.1422 (32.0%), 481.1486 (28.1%),
483.1456 (9.0%), 482.1519 (3.8%), 484.1490 (1.2%), 482.1494 (1.0%)
Elemental Analysis: C, 64.93; H, 5.24; Cl, 7.37; N, 5.82; O, 16.63

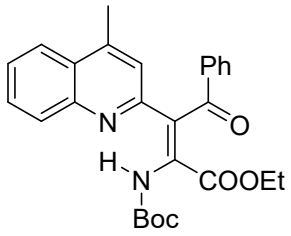
HRMS (ESI, m/z) calcd for $C_{26}H_{25}ClN_2O_5$ $[M+Na]^+$ 503.1345, found 503.1358.

3s


J700-H. 10. fid
13.04
8.01
8.00
7.99
7.98
7.98
7.91
7.91
7.89
7.89
7.75
7.75
7.74
7.73
7.73
7.72
7.72
7.56
7.56
7.55
7.55
7.55
7.54
7.54
7.53
7.53
7.52
7.52
7.43
7.41
7.40
7.07
4.00
3.98
3.97
3.95
2.52
1.54
1.07
1.05
1.04
Ph
O
N
H
N
COOEt
Boc
3s
0.96
2.99
1.02
1.03
2.09
1.94
0.96
2.00
3.06
9.12
3.10
f1 (ppm)


J700-C. 10. fid
195.4
163.7
154.3
152.3
146.1
145.3
138.0
137.3
133.6
130.0
129.9
128.9
128.6
126.8
126.6
123.8
121.8
118.8
81.63
61.89
28.26
18.97
13.49
Ph
O
N
H
N
COOEt
Boc
3s
f1 (ppm)



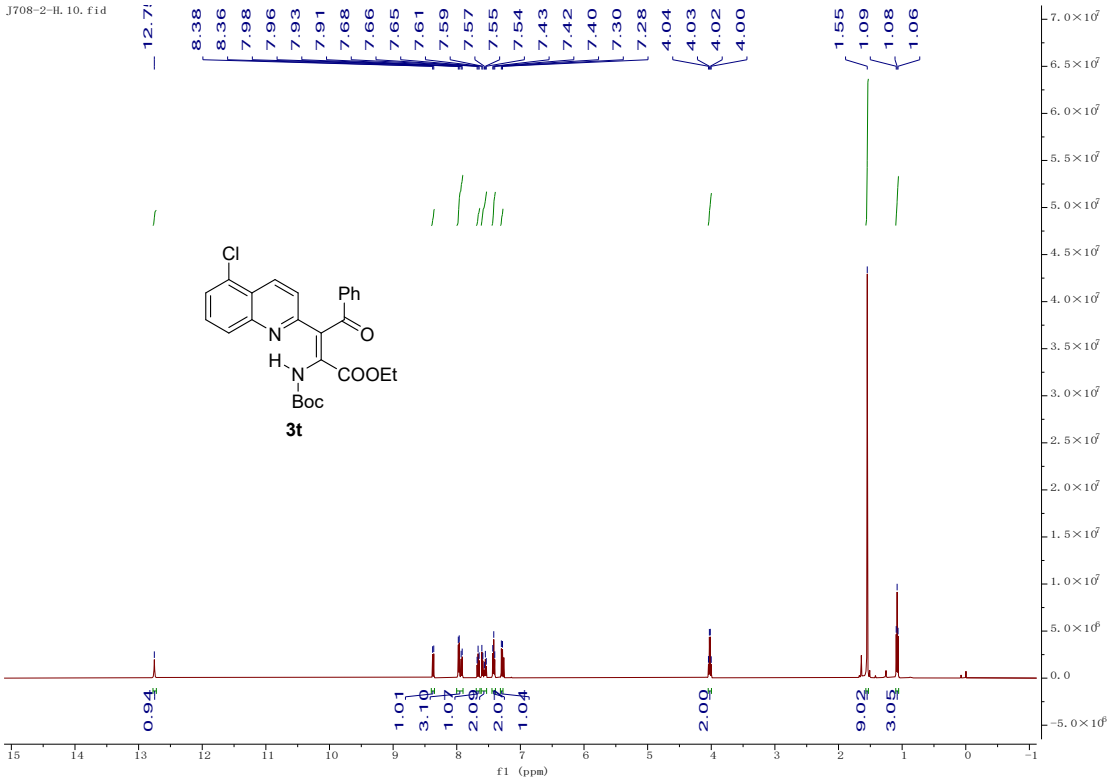


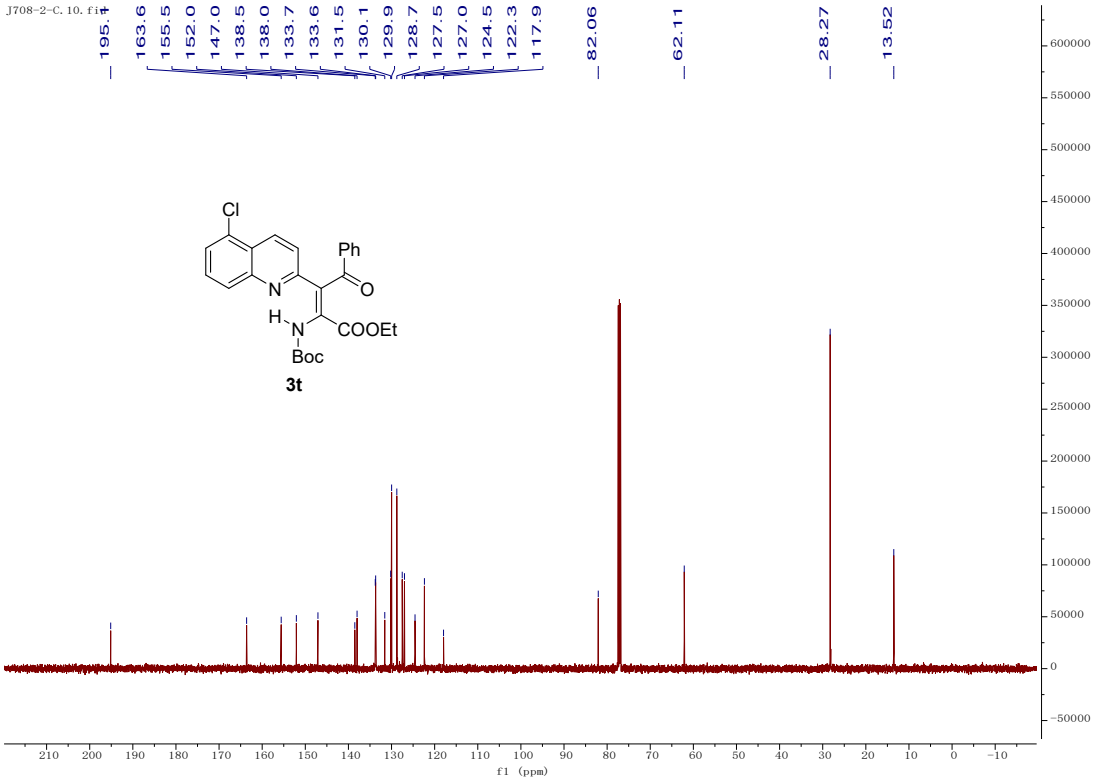
3s

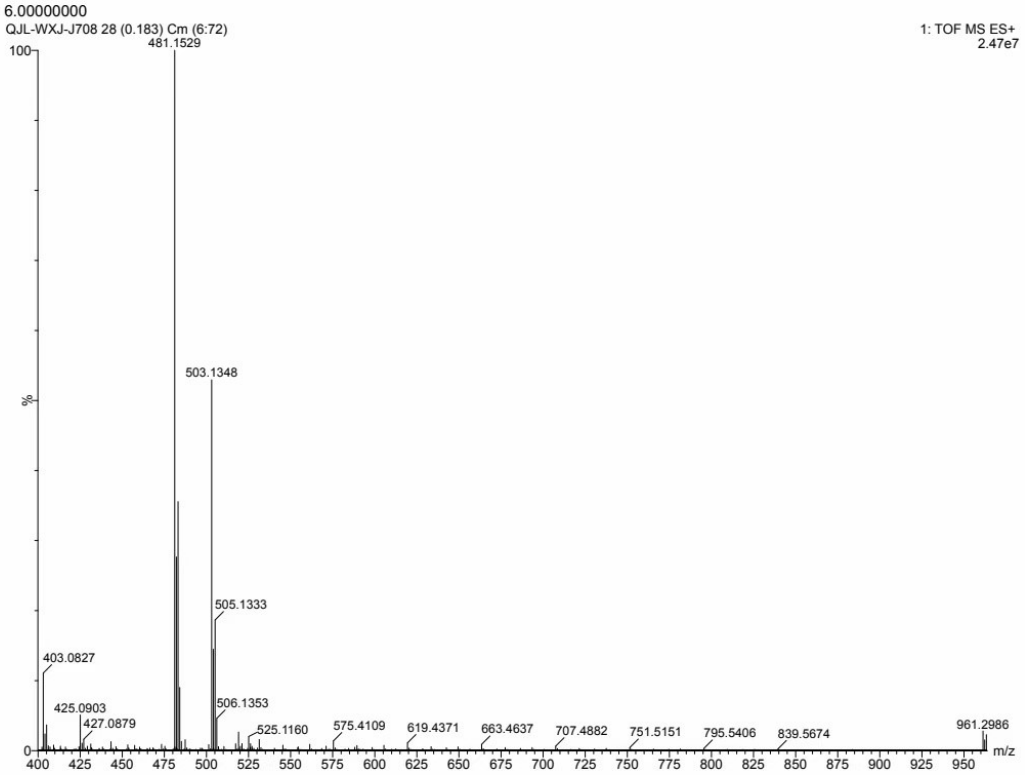
Chemical Formula: $C_{27}H_{28}N_2O_5$
Exact Mass: 460.1998
Molecular Weight: 460.5300
m/z: 460.1998 (100.0%), 461.2032 (29.2%), 462.2065 (4.1%), 462.2041 (1.0%)
Elemental Analysis: C, 70.42; H, 6.13; N, 6.08; O, 17.37

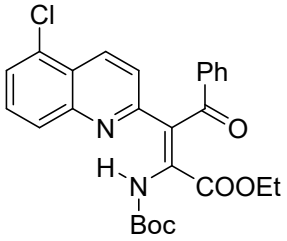
HRMS (ESI, m/z) calcd for $C_{27}H_{28}N_2O_5$ $[M+H]^+$ 461.2071, found 461.2082.

3t


J708-2-H.10.fid
12.71
8.38
8.36
7.98
7.96
7.93
7.91
7.68
7.66
7.65
7.61
7.59
7.57
7.55
7.54
7.43
7.42
7.40
7.30
7.28
4.04
4.03
4.02
4.00
1.55
1.09
1.08
1.06
0.94
1.01
3.11
1.07
2.09
2.07
1.04
2.00
9.02
3.05
Cl
Ph
O
N
H
N
COOEt
Boc
3t
f1 (ppm)


J708-2-C.10.fid
195.4
163.6
155.5
152.0
147.0
138.5
138.0
133.7
133.6
131.5
130.1
129.9
128.7
127.5
127.0
124.5
122.3
117.9
82.06
62.11
28.27
13.52
Cl
Ph
O
N
H
N
COOEt
Boc
3t
f1 (ppm)



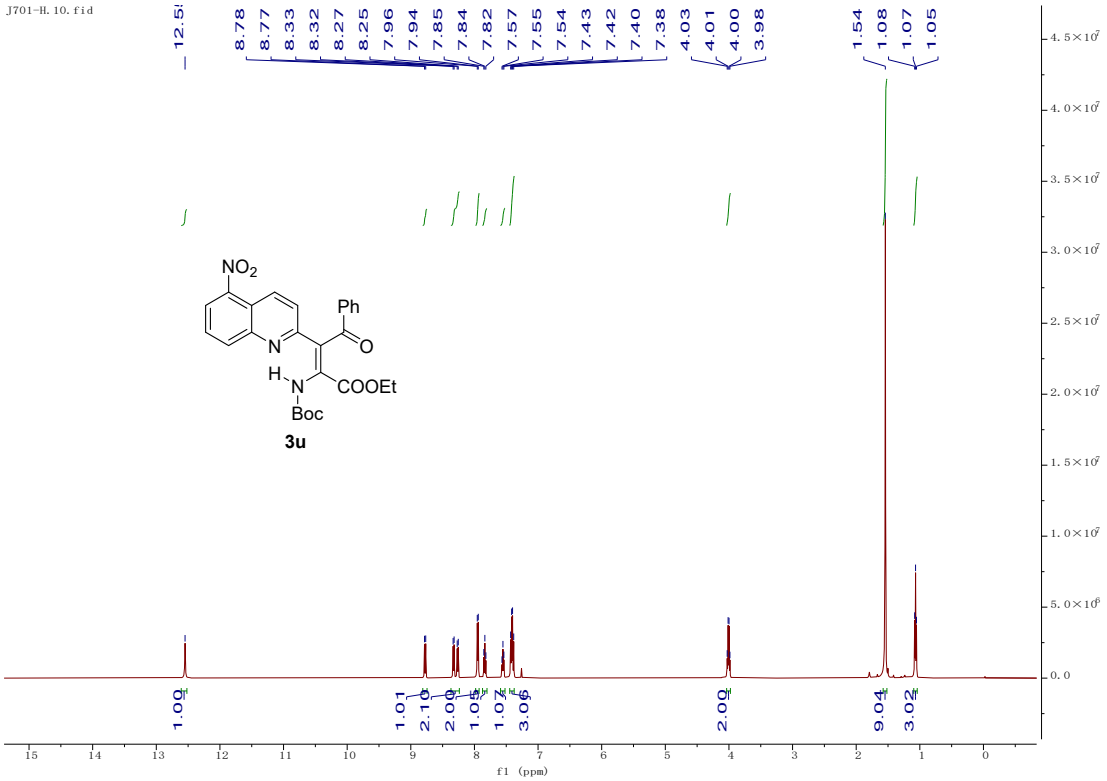


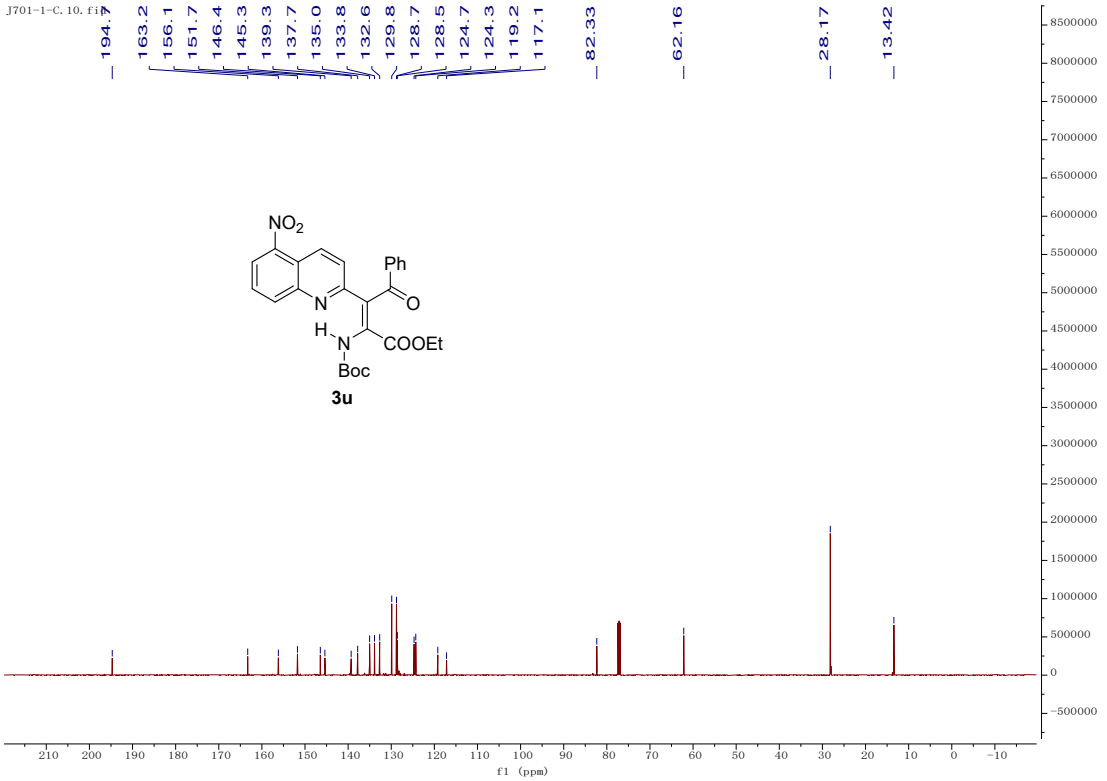
3t

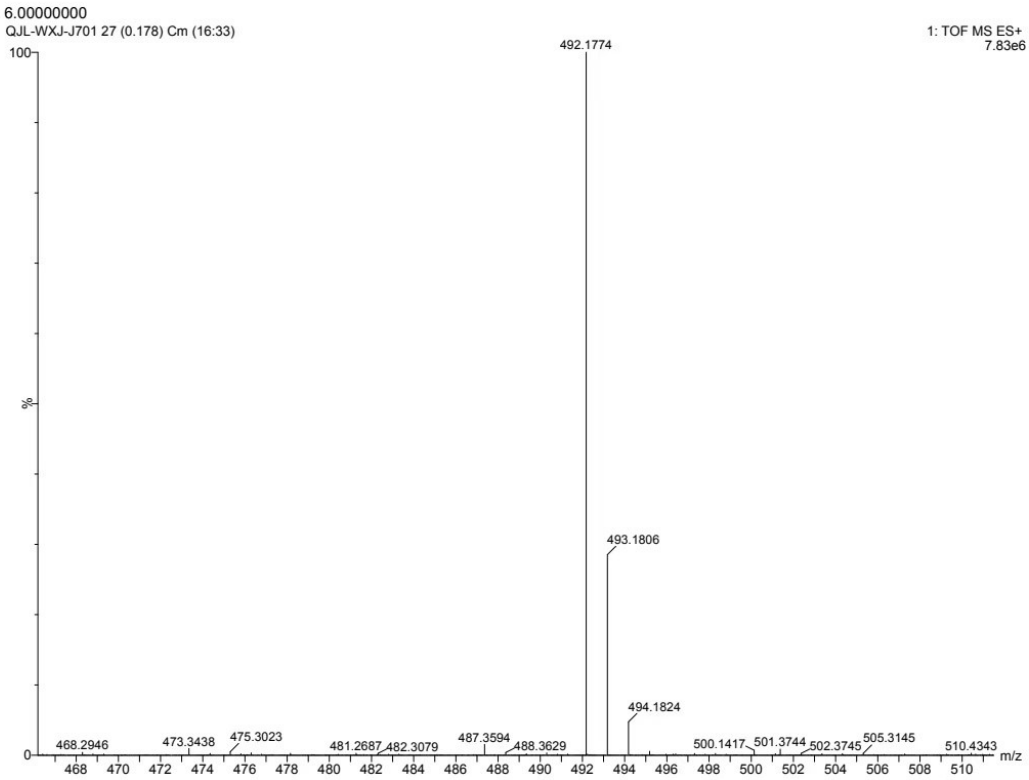
Chemical Formula: $C_{26}H_{25}ClN_2O_5$
Exact Mass: 480.1452
Molecular Weight: 480.9450
m/z: 480.1452 (100.0%), 482.1422 (32.0%), 481.1486 (28.1%),
483.1456 (9.0%), 482.1519 (3.8%), 484.1490 (1.2%), 482.1494 (1.0%)
Elemental Analysis: C, 64.93; H, 5.24; Cl, 7.37; N, 5.82; O, 16.63

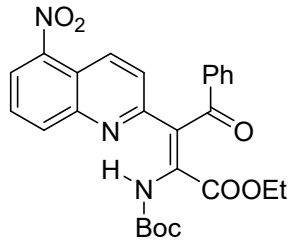
HRMS (ESI, m/z) calcd for $C_{26}H_{25}ClN_2O_5$ $[M+H]^+$481.1525, found 481.1529.

3u


J701-H. 10. fid
12.51
8.78
8.77
8.33
8.32
8.27
8.25
7.96
7.94
7.85
7.84
7.82
7.57
7.55
7.54
7.43
7.42
7.40
7.38
4.03
4.01
4.00
3.98
1.54
1.08
1.07
1.05
NO2
Ph
O
N
H
N
COOEt
Boc
3u
1.00
1.01
2.10
2.00
1.05
1.02
3.06
2.00
9.04
3.02
f1 (ppm)


J701-1-C. 10. fi
194.7
163.2
156.1
151.7
146.4
145.3
139.3
137.7
135.0
133.8
132.6
129.8
128.7
128.5
124.7
124.3
119.2
117.1
82.33
62.16
28.17
13.42
NO2
Ph
O
N
H
N
COOEt
Boc
3u
f1 (ppm)





3u

Chemical Formula: $C_{26}H_{25}N_3O_7$

Exact Mass: 491.1693

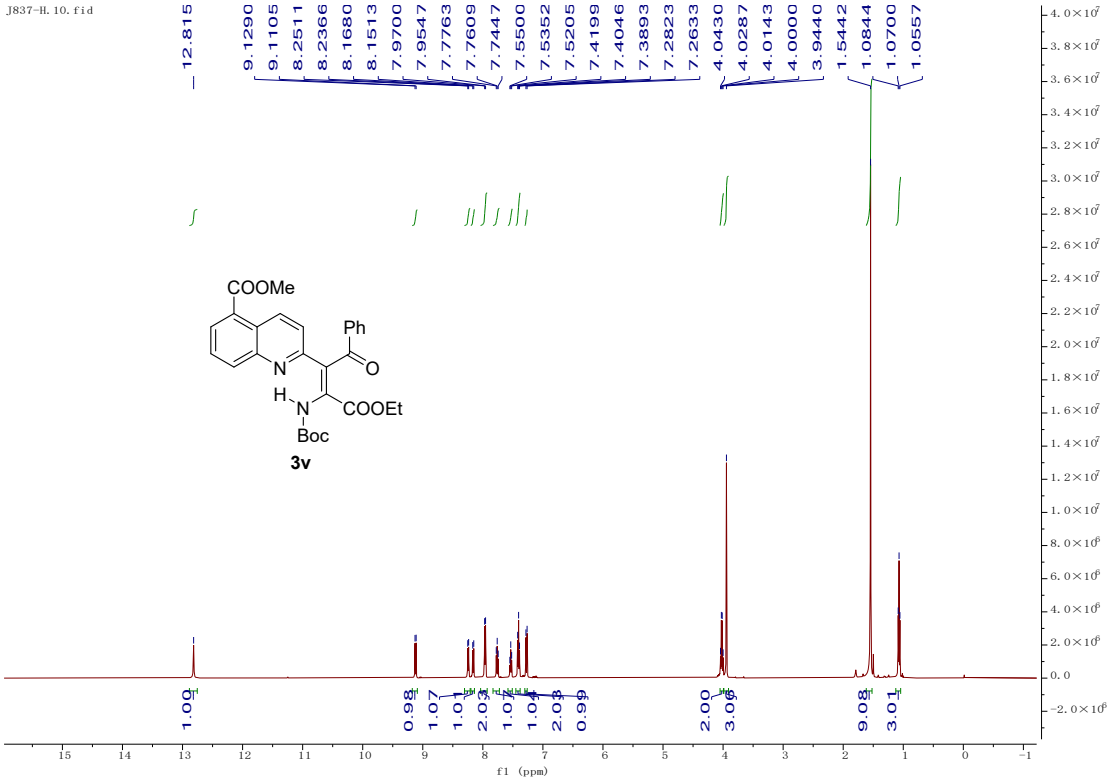
Molecular Weight: 491.5000

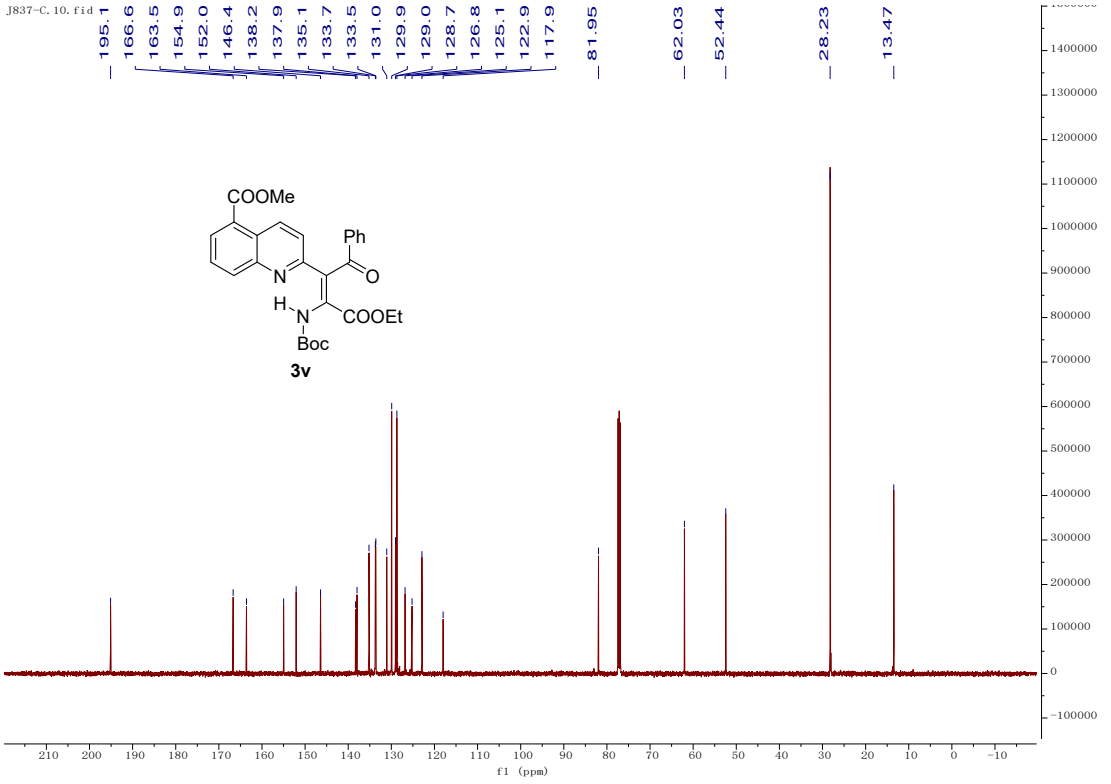
m/z: 491.1693 (100.0%), 492.1726 (28.1%), 493.1760 (3.8%), 493.1735 (1.4%), 492.1663 (1.1%)

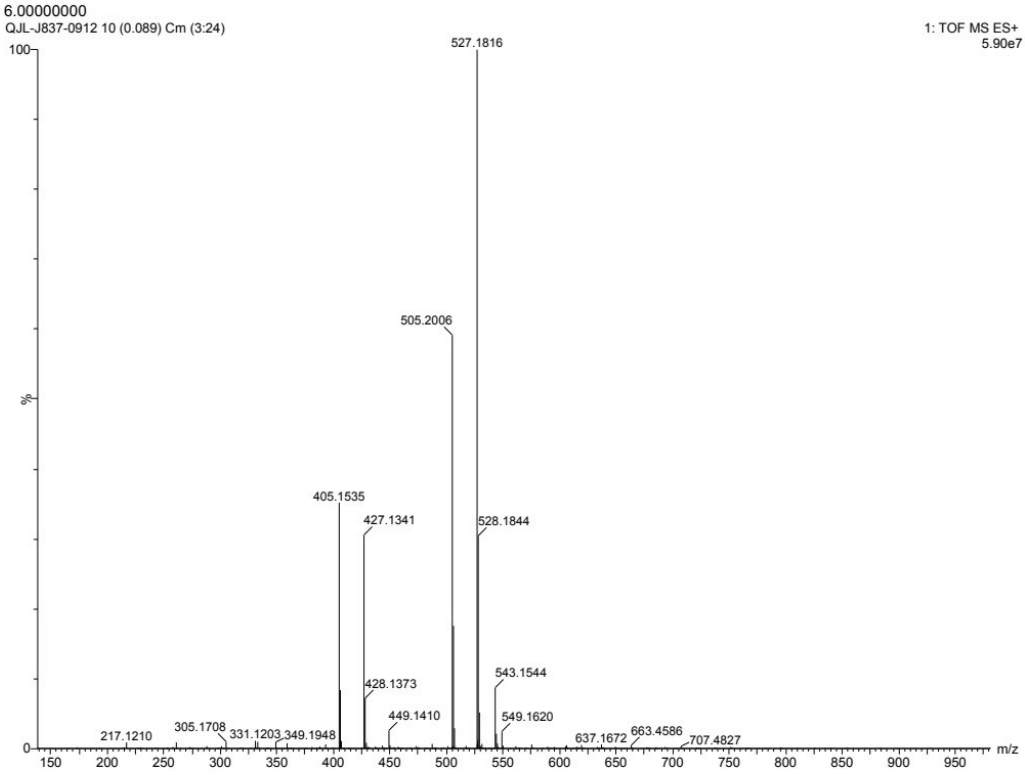
Elemental Analysis: C, 63.54; H, 5.13; N, 8.55; O, 22.79

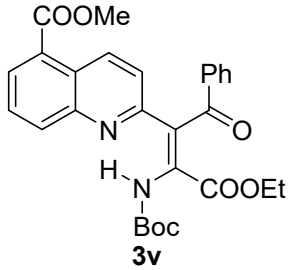
HR MS (ESI, m/z) calcd for $C_{26}H_{25}N_3O_7$ $[M+H]^+$ 492.1766, found 492.1774.

3v


J837-H.10.fid
12.815
9.1290
9.1105
8.2511
8.2366
8.1680
8.1513
7.9700
7.9547
7.7763
7.7609
7.7447
7.5500
7.5352
7.5205
7.4199
7.4046
7.3893
7.2823
7.2633
4.0430
4.0287
4.0143
4.0000
3.9440
1.5442
1.0844
1.0700
1.0557
1.00
0.98
1.07
1.01
2.02
1.07
1.04
2.08
0.99
2.00
3.06
9.08
3.01
COOMe
Ph
O
N
H
N
COOEt
Boc
3v
f1 (ppm)


J837-C.10.fid
195.1
166.6
163.5
154.9
152.0
146.4
138.2
137.9
135.1
133.7
133.5
131.0
129.9
129.0
128.7
126.8
125.1
122.9
117.9
81.95
62.03
52.44
28.23
13.47
COOMe
Ph
O
N
H
N
COOEt
Boc
3v
f1 (ppm)





3v

Chemical Formula: $C_{28}H_{28}N_2O_7$

Exact Mass: 504.1897

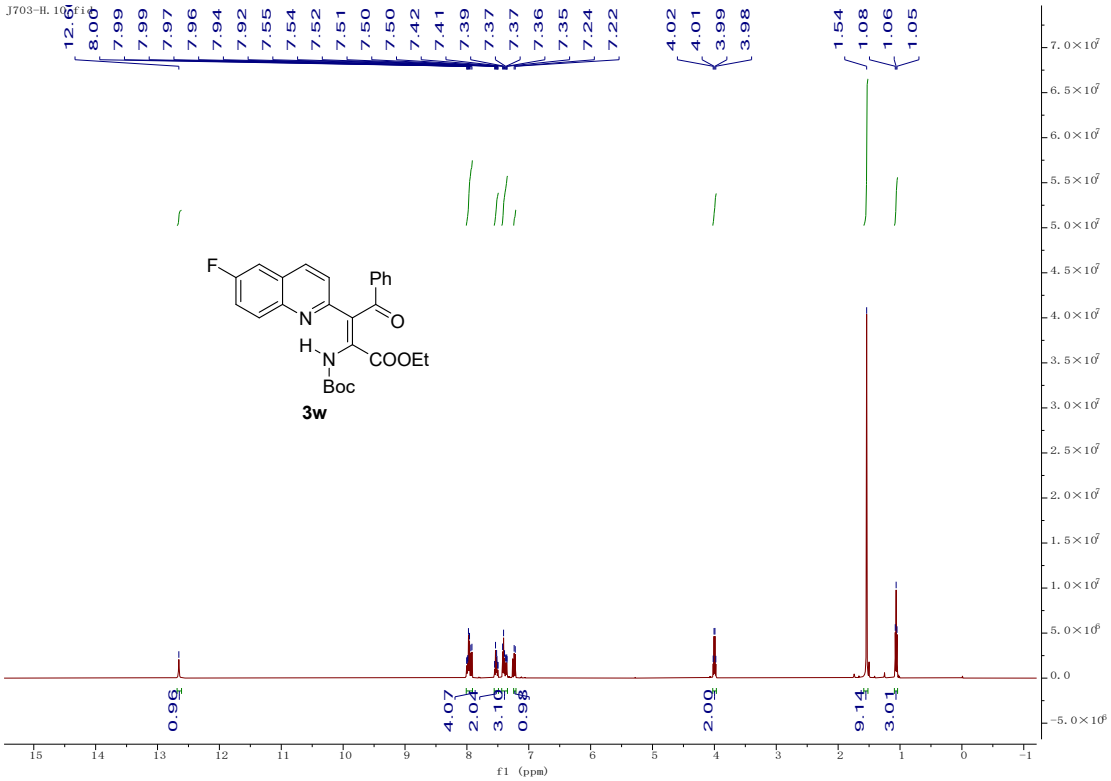
Molecular Weight: 504.5390

m/z: 504.1897 (100.0%), 505.1930 (30.3%), 506.1964 (4.4%), 506.1939 (1.4%)

Elemental Analysis: C, 66.66; H, 5.59; N, 5.55; O, 22.20

HRMS (ESI, m/z) calcd for $C_{28}H_{28}N_2O_7$ $[M+Na]^+$ 527.1789, found 527.1816.

3w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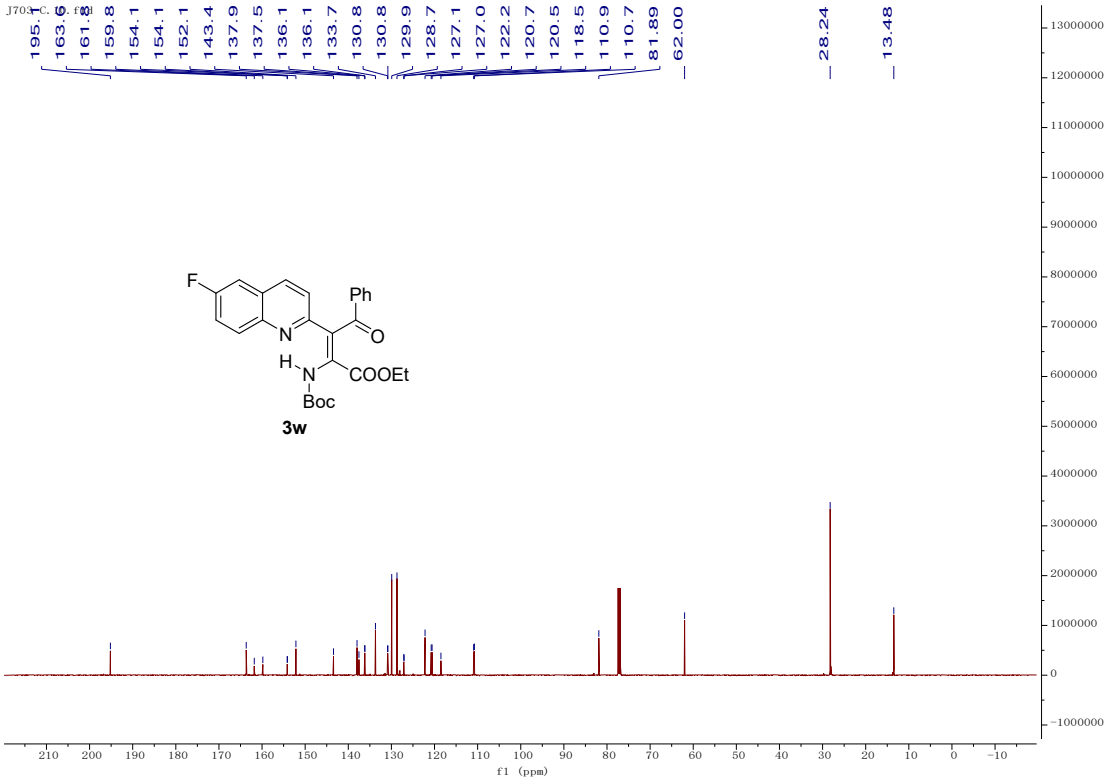
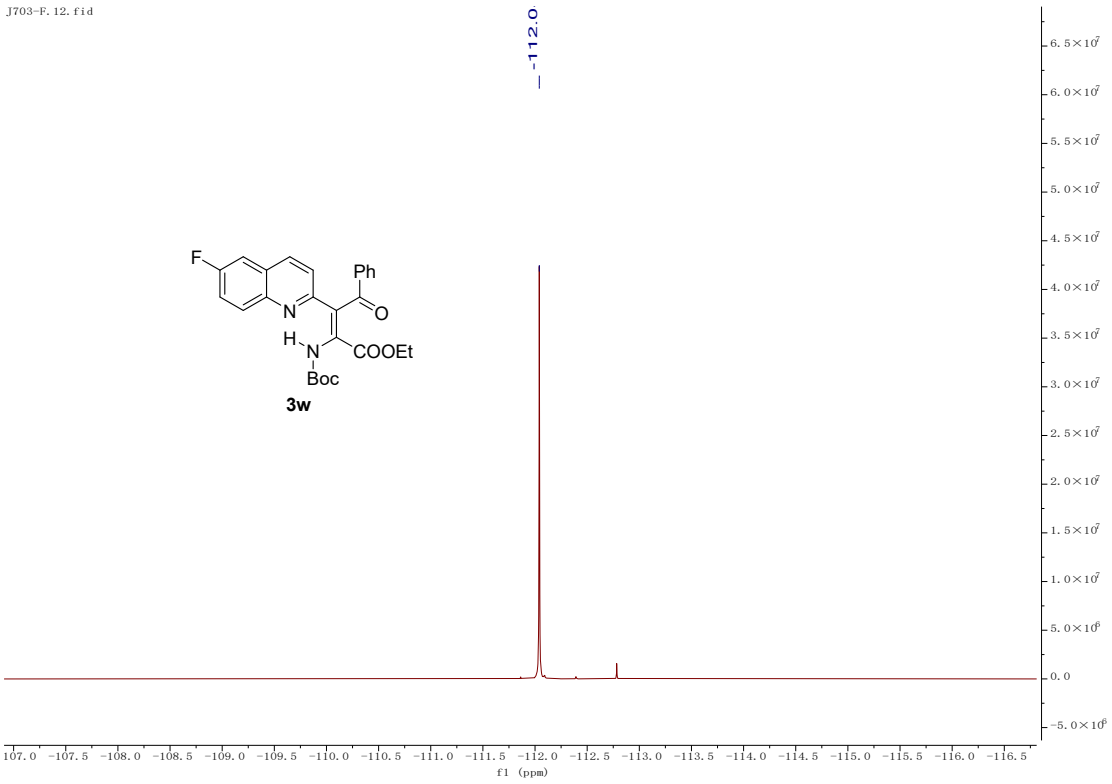
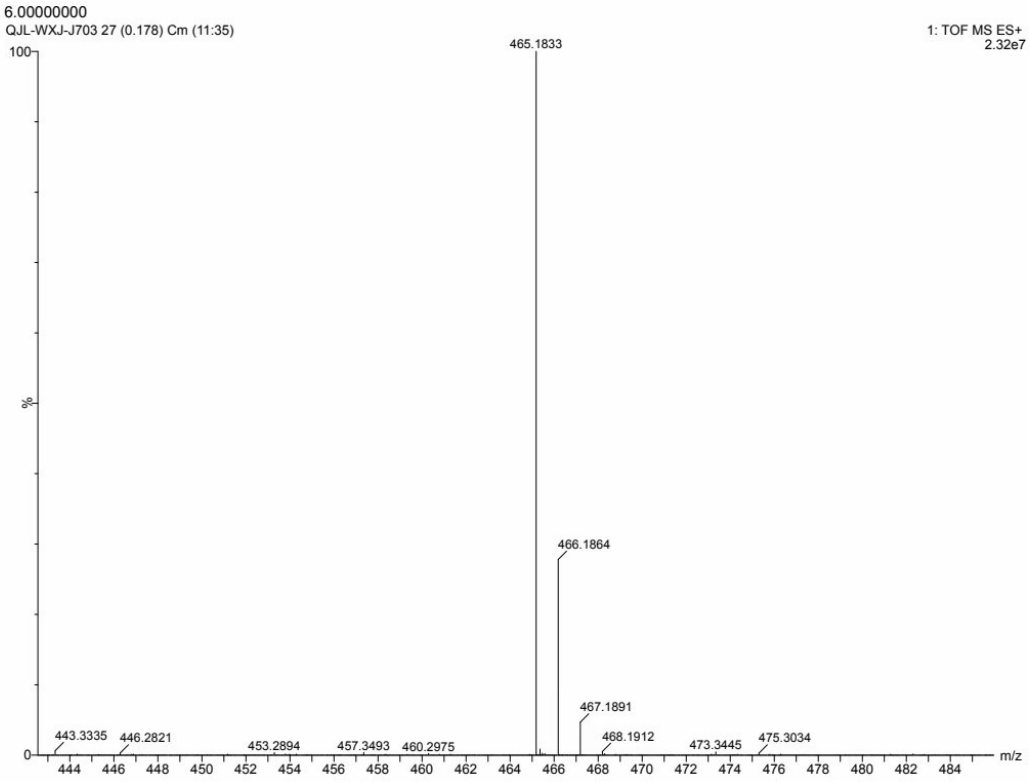
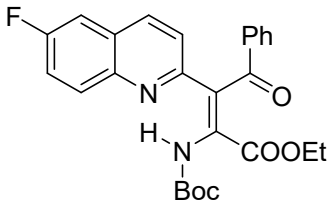
8.00
7.99
7.99
7.97
7.96
7.94
7.92
7.55
7.54
7.52
7.51
7.50
7.50
7.42
7.41
7.39
7.37
7.37
7.36
7.35
7.24
7.22
4.02
4.01
3.99
3.98
1.54
1.08
1.06
1.05
F
Ph
O
N
H
N
COOEt
Boc
3w
0.96
4.07
2.04
3.10
0.98
2.00
9.14
3.01
f1 (ppm)


195.1
163.6
161.8
159.8
154.1
154.1
152.1
143.4
137.9
137.5
136.1
136.1
133.7
130.8
130.8
129.9
128.7
127.1
127.0
122.2
120.7
120.5
118.5
110.9
110.7
81.89
62.00
28.24
13.48
F
Ph
O
N
H
N
COOEt
Boc
3w
f1 (ppm)


J703-F. 12. fid
-112.0
F
Ph
O
N
H
N
COOEt
Boc
3w
6. 5×10⁷
6. 0×10⁷
5. 5×10⁷
5. 0×10⁷
4. 5×10⁷
4. 0×10⁷
3. 5×10⁷
3. 0×10⁷
2. 5×10⁷
2. 0×10⁷
1. 5×10⁷
1. 0×10⁷
5. 0×10⁶
0. 0
-5. 0×10⁶
107. 0 -107. 5 -108. 0 -108. 5 -109. 0 -109. 5 -110. 0 -110. 5 -111. 0 -111. 5 -112. 0 -112. 5 -113. 0 -113. 5 -114. 0 -114. 5 -115. 0 -115. 5 -116. 0 -116. 5
f1 (ppm)



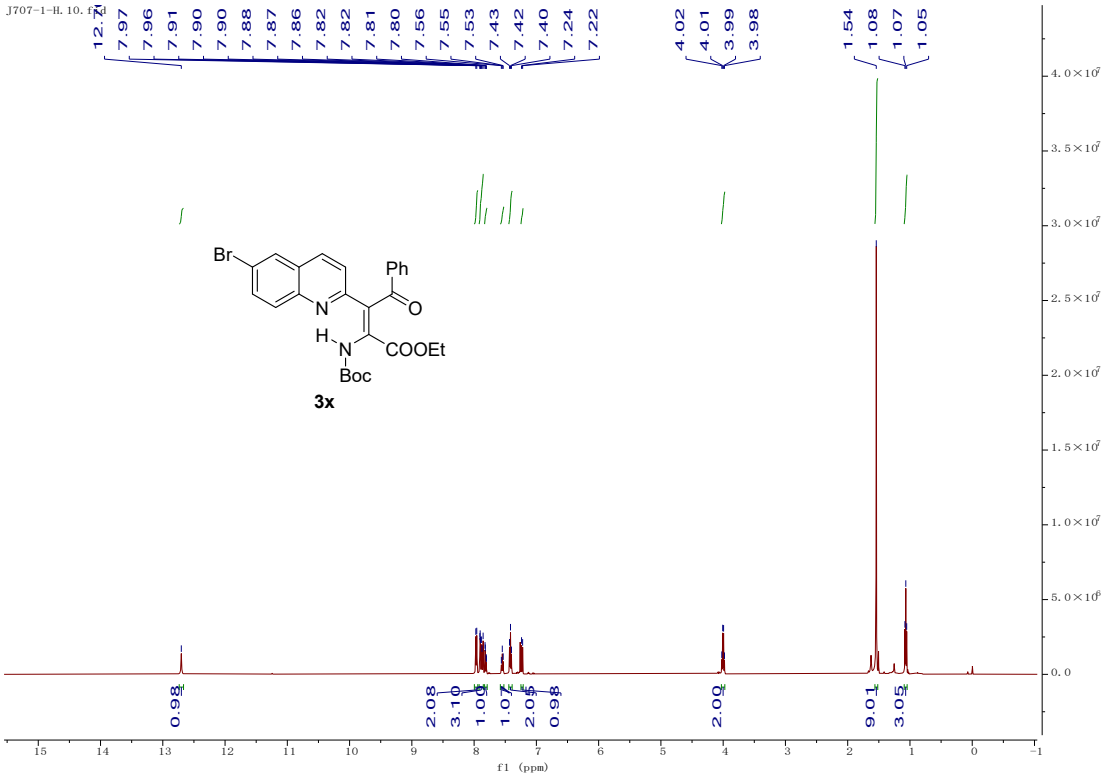


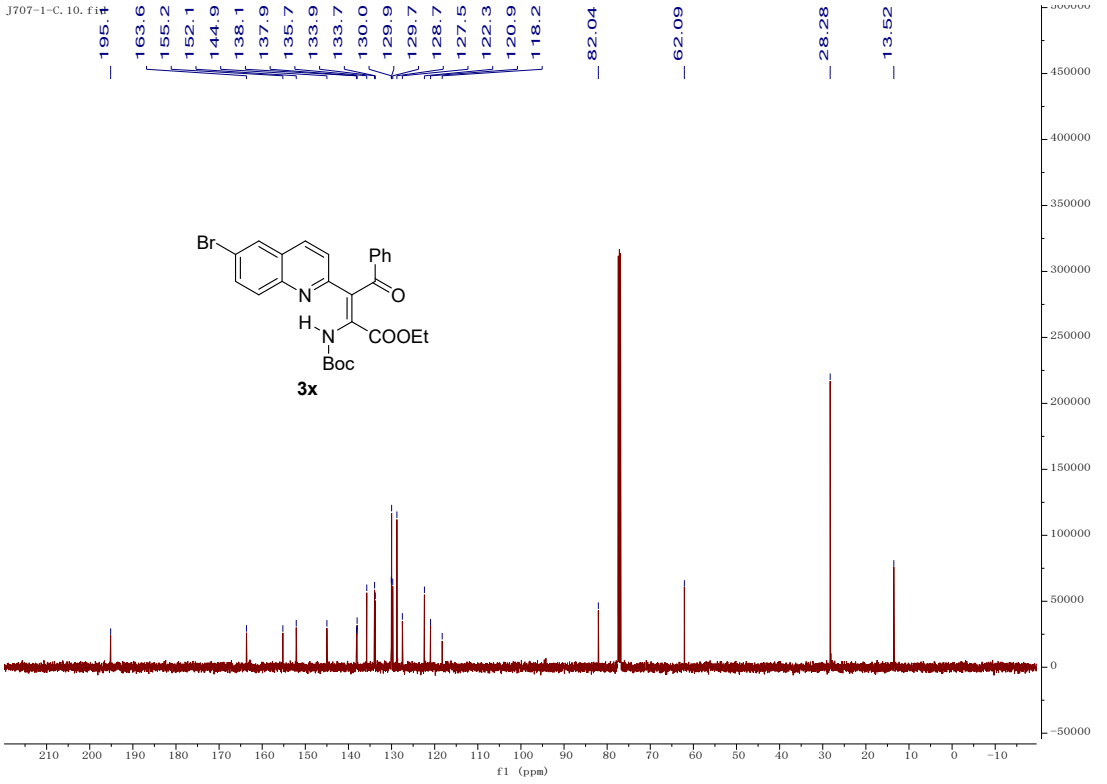
3w

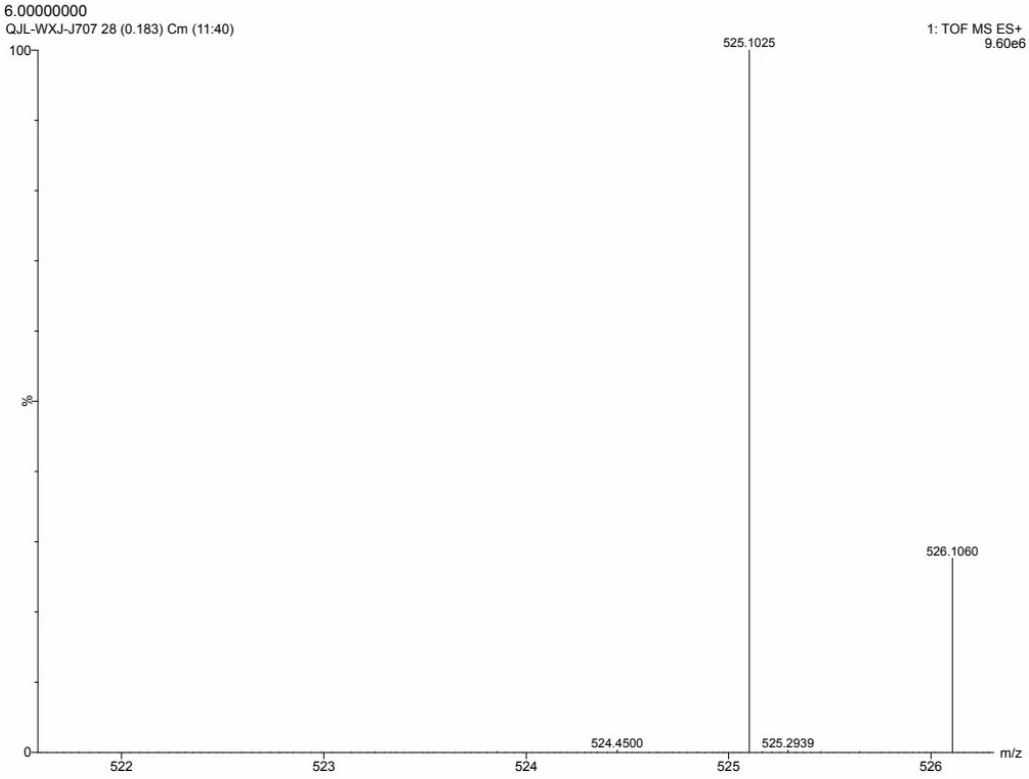
Chemical Formula: $C_{26}H_{25}FN_2O_5$
Exact Mass: 464.1748
Molecular Weight: 464.4934
m/z: 464.1748 (100.0%), 465.1781 (28.1%), 466.1815 (3.8%), 466.1790 (1.0%)
Elemental Analysis: C, 67.23; H, 5.43; F, 4.09; N, 6.03; O, 17.22

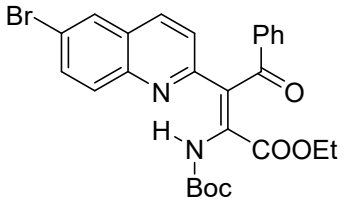
HRMS (ESI, m/z) calcd for $C_{26}H_{25}FN_2O_5$ $[M+H]^+$ 465.1821, found 465.1833.

3x


12.24
7.97
7.96
7.91
7.90
7.90
7.88
7.87
7.86
7.82
7.82
7.81
7.80
7.56
7.55
7.53
7.43
7.42
7.40
7.24
7.22
4.02
4.01
3.99
3.98
1.54
1.08
1.07
1.05
Br
Ph
O
N
H
N
COOEt
Boc
3x
0.92
2.08
3.10
1.00
1.07
2.09
0.98
2.00
9.01
3.05
f1 (ppm)


195.4
163.6
155.2
152.1
144.9
138.1
137.9
135.7
133.9
133.7
130.0
129.9
129.7
128.7
127.5
122.3
120.9
118.2
82.04
62.09
28.28
13.52
Br
Ph
O
N
H
N
COOEt
Boc
3x
f1 (ppm)



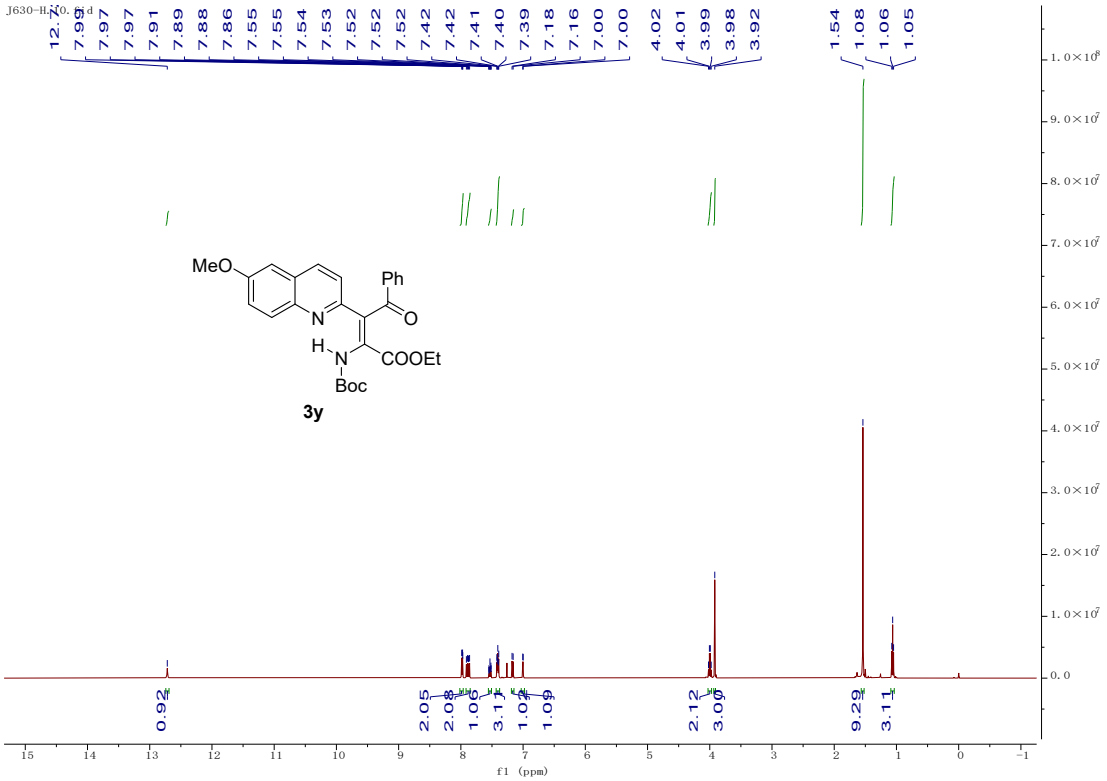


3x

Chemical Formula: $C_{26}H_{25}BrN_2O_5$
Exact Mass: 524.0947
Molecular Weight: 525.3990
m/z: 524.0947 (100.0%), 526.0926 (97.3%), 525.0980 (28.1%),
527.0960 (27.4%), 526.1014 (3.8%), 528.0993 (3.7%), 526.0989 (1.0%), 528.0969 (1.0%)
Elemental Analysis: C, 59.44; H, 4.80; Br, 15.21; N, 5.33; O, 15.23

HRMS (ESI, m/z) calcd for $C_{26}H_{25}BrN_2O_5$ $[M+H]^+$ 525.1020, found 525.1025.

3y


12.77
7.99
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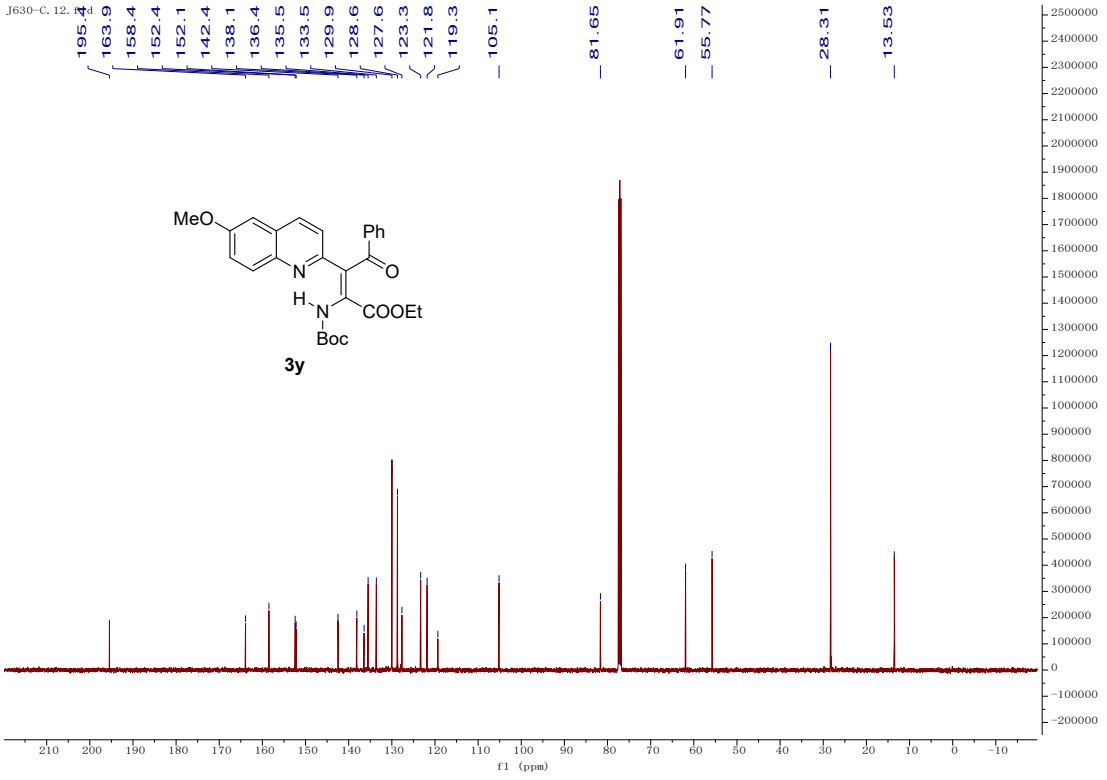
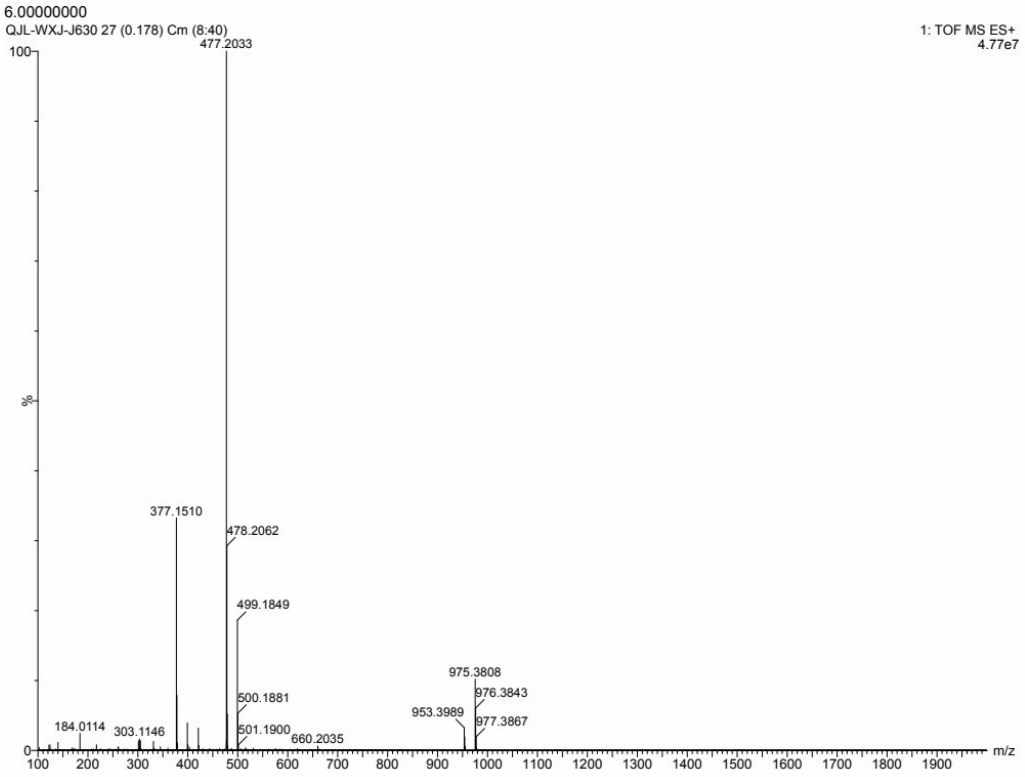
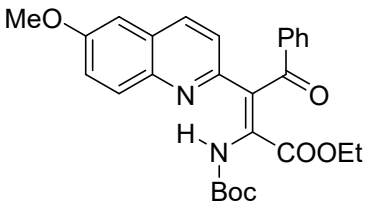
7.97
7.91
7.89
7.88
7.86
7.55
7.55
7.54
7.53
7.52
7.52
7.52
7.42
7.42
7.41
7.40
7.39
7.18
7.16
7.00
7.00
4.02
4.01
3.99
3.98
3.92
1.54
1.08
1.06
1.05
MeO
Ph
O
N
H
N
COOEt
Boc
3y
0.92
2.05
2.08
1.00
3.11
1.04
1.09
2.12
3.00
9.29
3.11
f1 (ppm)


195.4
163.9
158.4
152.4
152.1
142.4
138.1
136.4
135.5
133.5
129.9
128.6
127.6
123.3
121.8
119.3
105.1
81.65
61.91
55.77
28.31
13.53
MeO
Ph
O
N
H
N
COOEt
Boc
3y
f1 (ppm)





3y

Chemical Formula: $C_{27}H_{28}N_2O_6$

Exact Mass: 476.1947

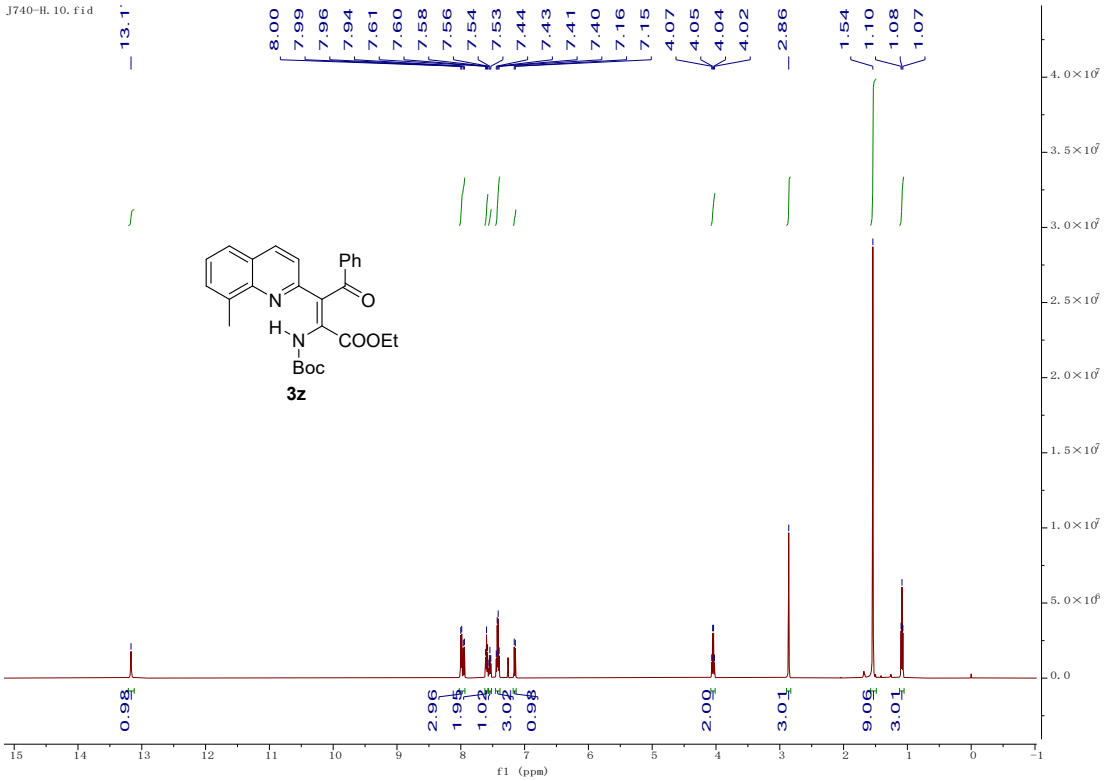
Molecular Weight: 476.5290

m/z: 476.1947 (100.0%), 477.1981 (29.2%), 478.2014 (4.1%), 478.1990 (1.2%)

Elemental Analysis: C, 68.05; H, 5.92; N, 5.88; O, 20.14

HRMS (ESI, m/z) calcd for $C_{27}H_{28}N_2O_6$ $[M+H]^+$ 477.2021, found 477.2033

3z


J740-H.10.fid
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7.96
7.94
7.61
7.60
7.58
7.56
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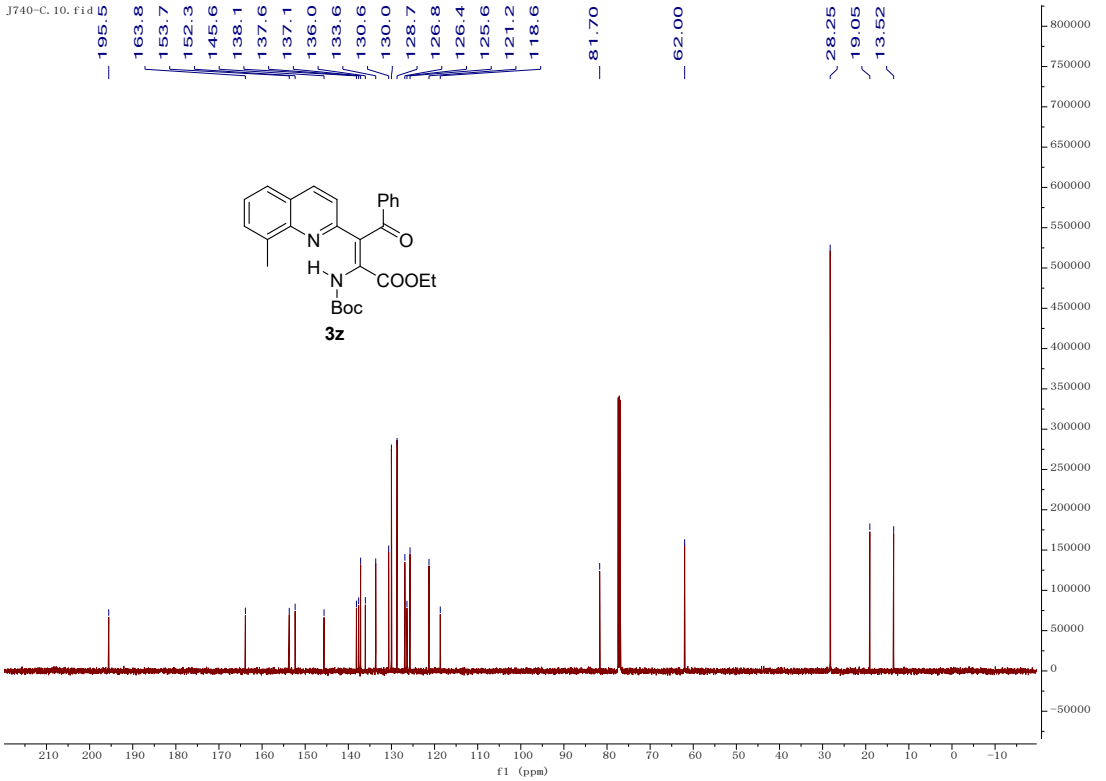
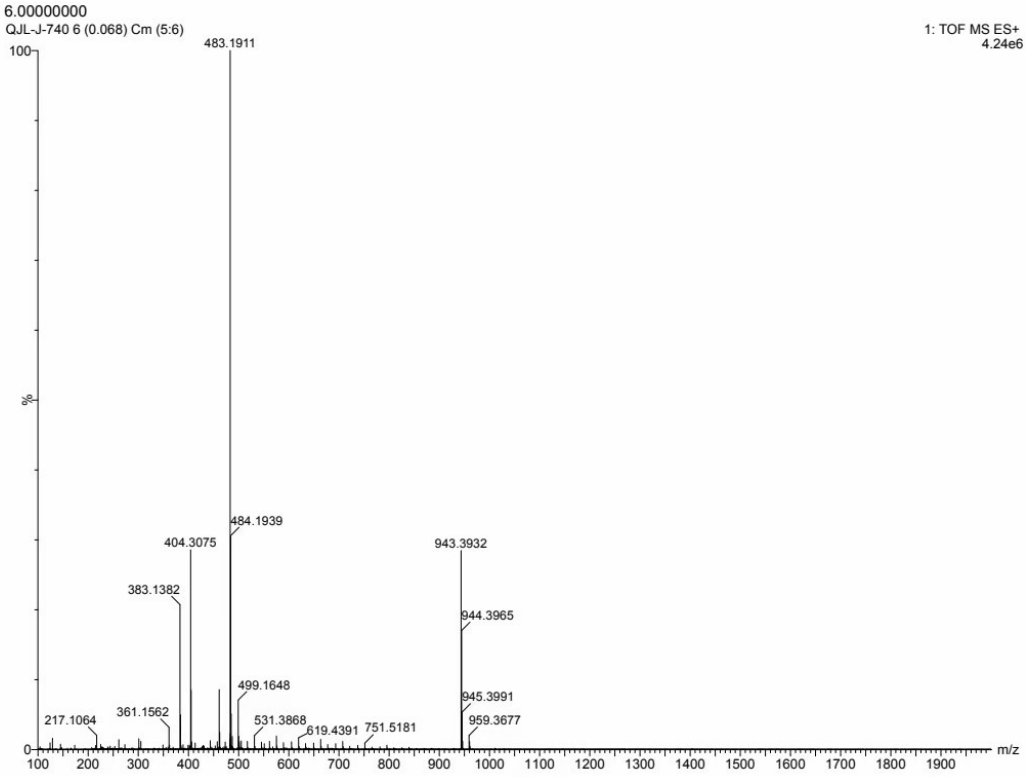
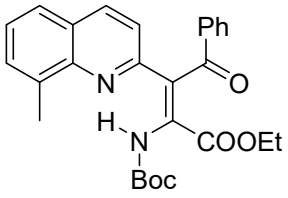
7.53
7.44
7.43
7.41
7.40
7.16
7.15
4.07
4.05
4.04
4.02
2.86
1.54
1.10
1.08
1.07
Ph
O
N
H
N
COOEt
Boc
3z
0.98
2.96
1.93
1.02
3.02
0.98
2.00
3.01
9.06
3.01
f1 (ppm)


J740-C.10.fid
195.5
163.8
153.7
152.3
145.6
138.1
137.6
137.1
136.0
133.6
130.6
130.0
128.7
126.8
126.4
125.6
121.2
118.6
81.70
62.00
28.25
19.05
13.52
Ph
O
N
H
N
COOEt
Boc
3z
f1 (ppm)





3z

Chemical Formula: $C_{27}H_{28}N_2O_5$

Exact Mass: 460.1998

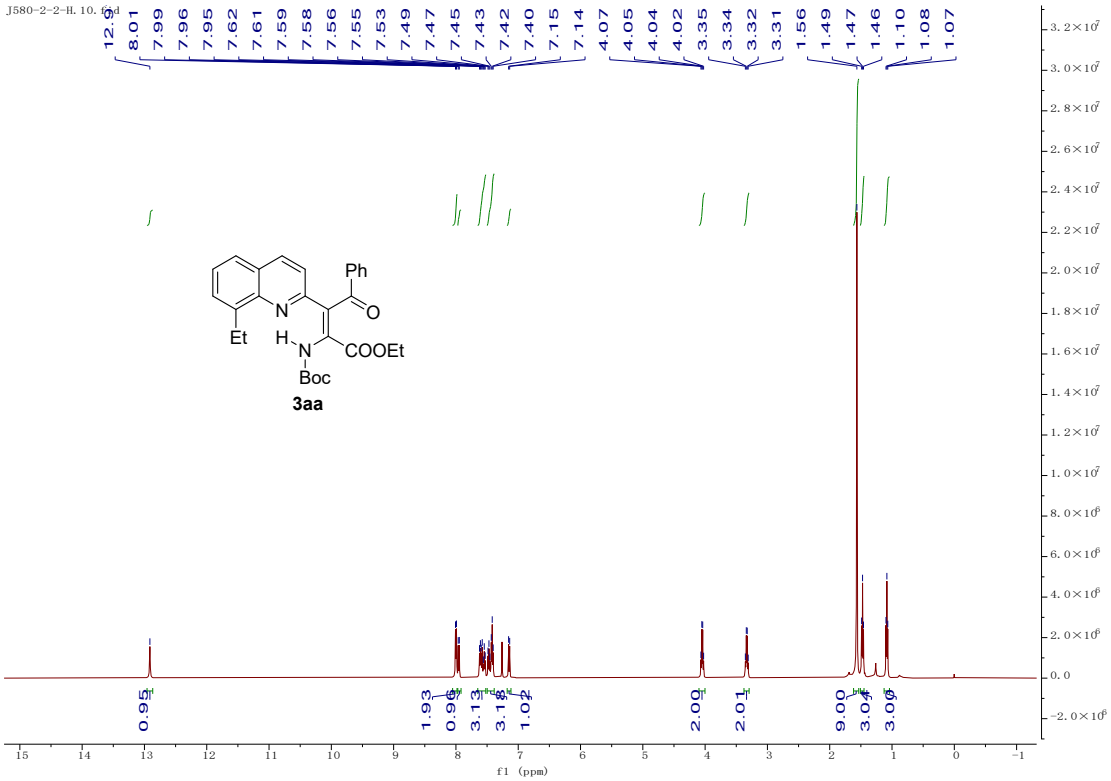
Molecular Weight: 460.5300

m/z: 460.1998 (100.0%), 461.2032 (29.2%), 462.2065 (4.1%), 462.2041 (1.0%)

Elemental Analysis: C, 70.42; H, 6.13; N, 6.08; O, 17.37

HRMS (ESI, m/z) calcd for $C_{27}H_{28}N_2O_6$ $[M+Na]^+$ 483.1891, found 483.1911

3aa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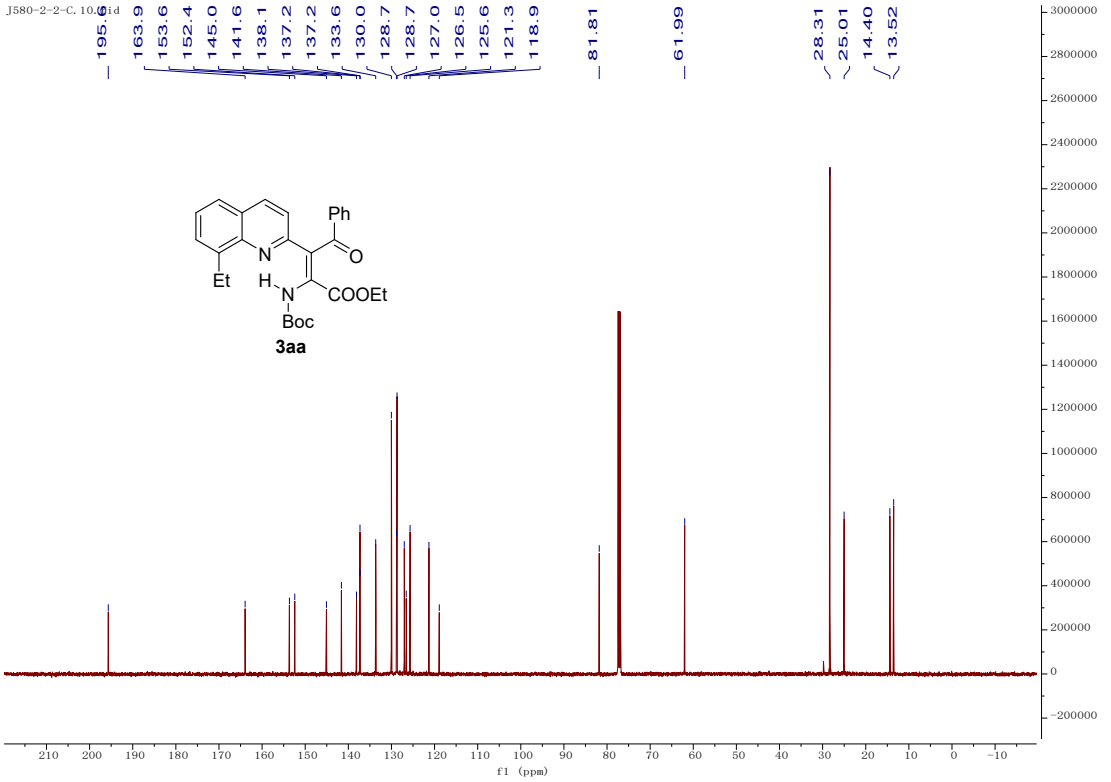
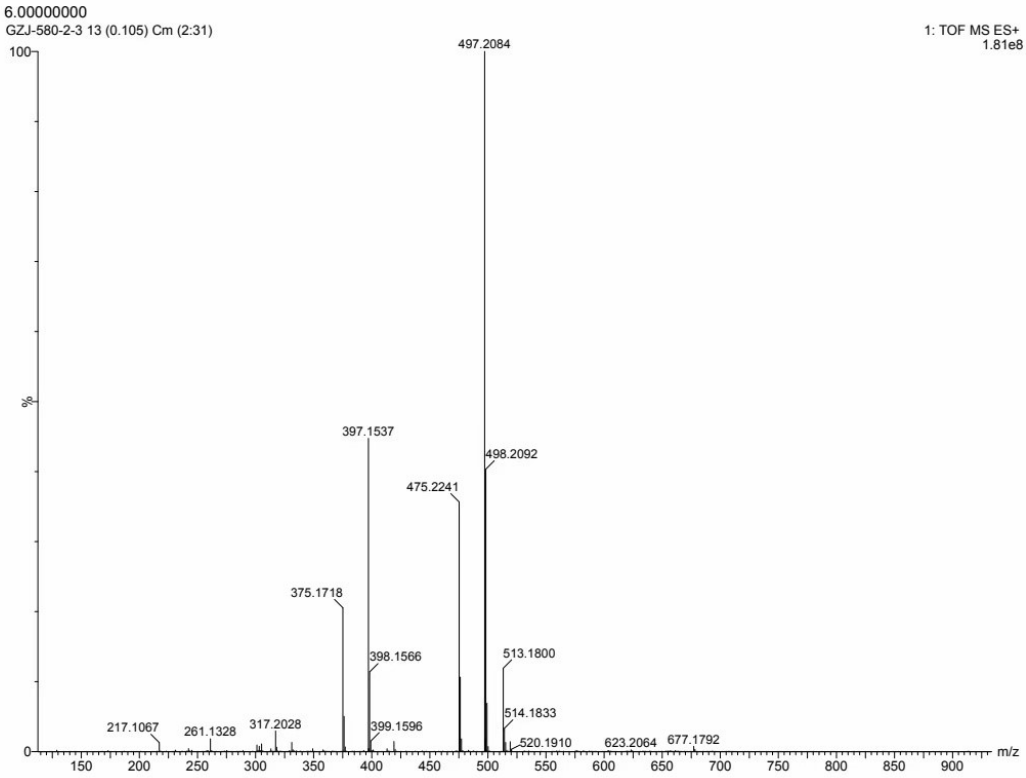
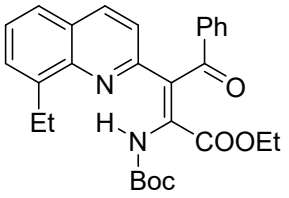
7.99
7.96
7.95
7.62
7.61
7.59
7.58
7.56
7.55
7.53
7.49
7.47
7.45
7.43
7.42
7.40
7.15
7.14
4.07
4.05
4.04
4.02
3.35
3.34
3.32
3.31
1.56
1.49
1.47
1.46
1.10
1.08
1.07
Ph
O
N
Et
H
N
COOEt
Boc
3aa
0.95
1.93
0.96
3.13
3.16
1.02
2.00
2.01
9.00
3.04
3.00
f1 (ppm)


195.6
163.9
153.6
152.4
145.0
141.6
138.1
137.2
137.2
133.6
130.0
128.7
128.7
127.0
126.5
125.6
121.3
118.9
81.81
61.99
28.31
25.01
14.40
13.52
Ph
O
N
Et
H
N
COOEt
Boc
3aa
f1 (ppm)



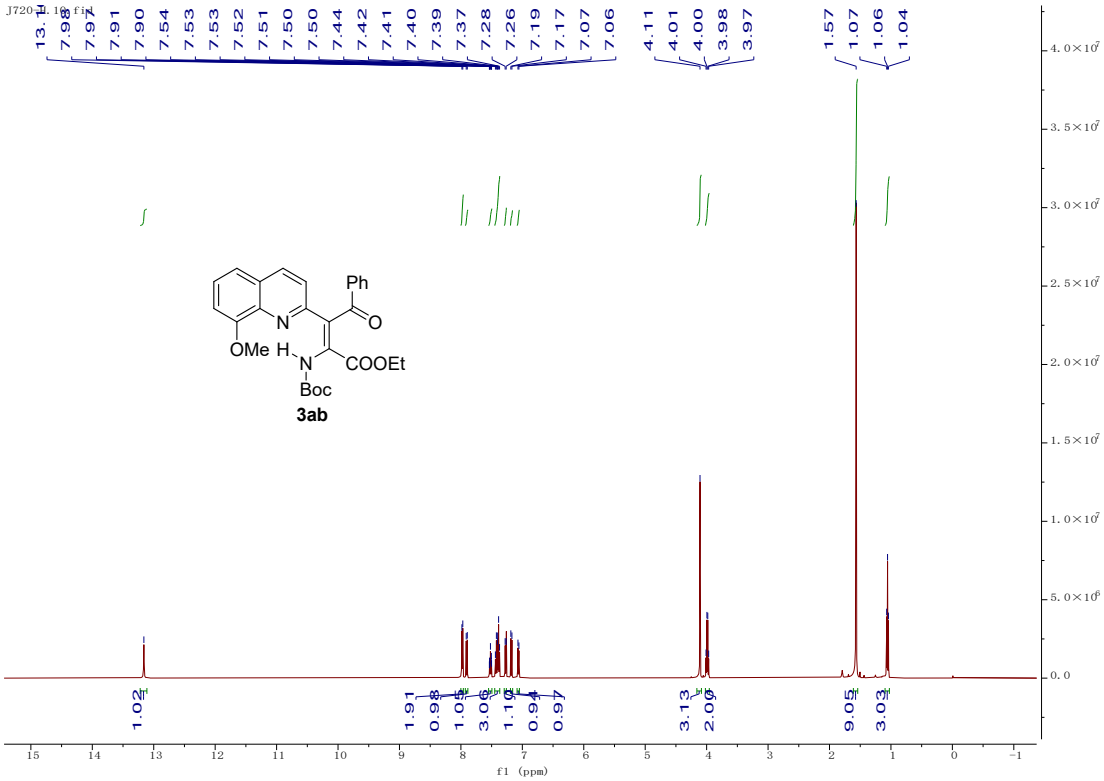


3aa

Chemical Formula: $C_{28}H_{30}N_2O_5$
Exact Mass: 474.2155
Molecular Weight: 474.5570
m/z: 474.2155 (100.0%), 475.2188 (30.3%), 476.2222 (4.4%), 476.2197 (1.0%)
Elemental Analysis: C, 70.87; H, 6.37; N, 5.90; O, 16.86

HRMS (ESI, m/z) calcd for $C_{28}H_{30}N_2O_5$ $[M+Na]^+$ 497.2047, found 497.2084.

3ab


J720-H. 10. fid
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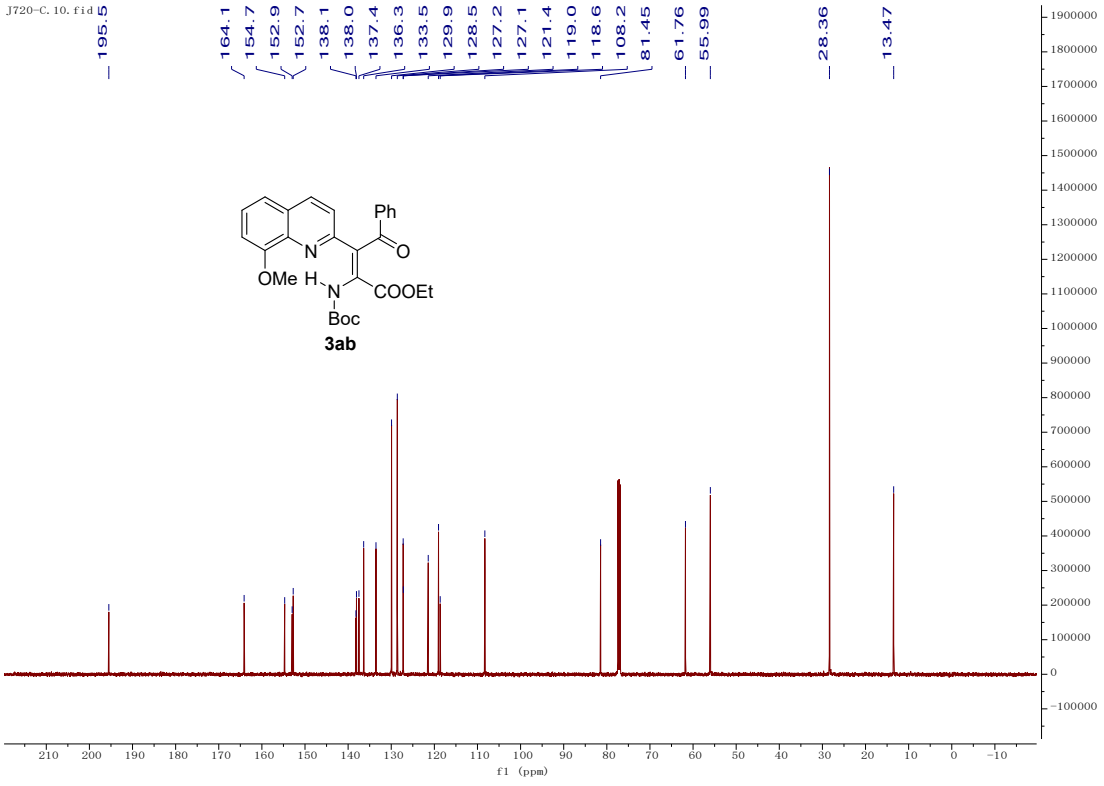
7.98
7.97
7.91
7.90
7.54
7.53
7.53
7.52
7.51
7.50
7.50
7.44
7.42
7.41
7.40
7.39
7.37
7.28
7.26
7.19
7.17
7.07
7.06
4.11
4.01
4.00
3.98
3.97
1.57
1.07
1.06
1.04
Ph
O
N
OMe H
N
COOEt
Boc
3ab
1.02
1.91
0.98
1.05
3.00
1.10
0.94
0.97
3.13
2.00
9.05
3.03
f1 (ppm)


J720-C. 10. fid
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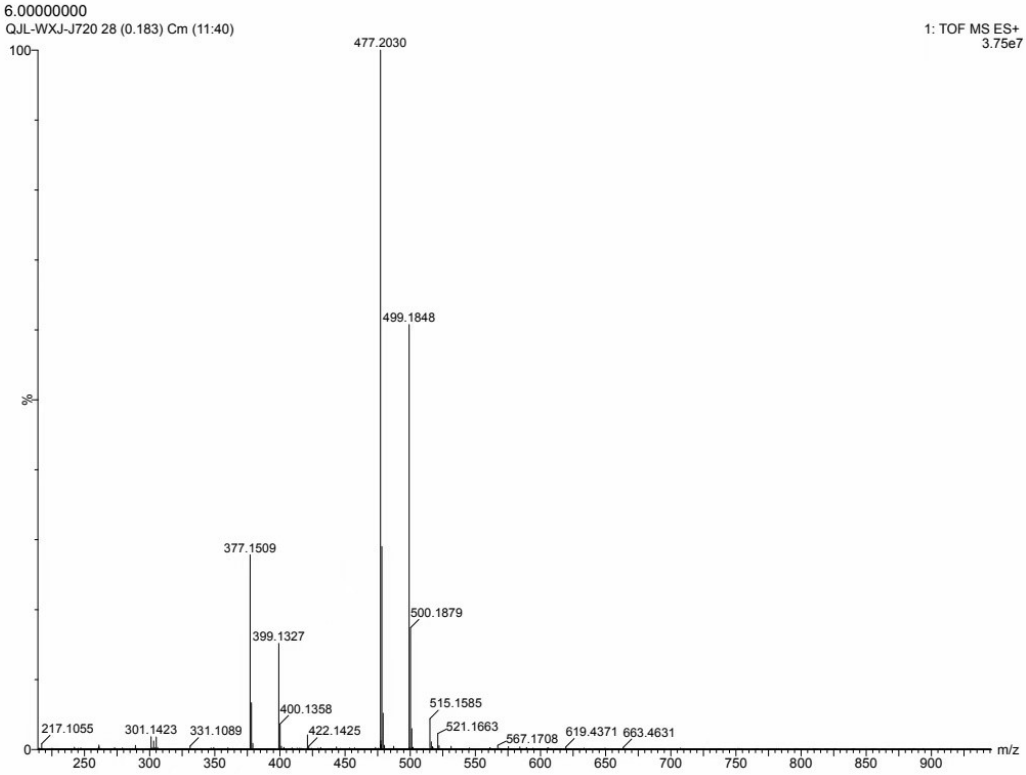
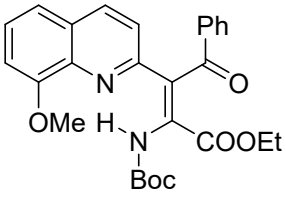
164.1
154.7
152.9
152.7
138.1
138.0
137.4
136.3
133.5
129.9
128.5
127.2
127.1
121.4
119.0
118.6
108.2
81.45
61.76
55.99
28.36
13.47
Ph
O
N
OMe H
N
COOEt
Boc
3ab
f1 (ppm)





3ab

Chemical Formula: $C_{27}H_{28}N_2O_6$

Exact Mass: 476.1947

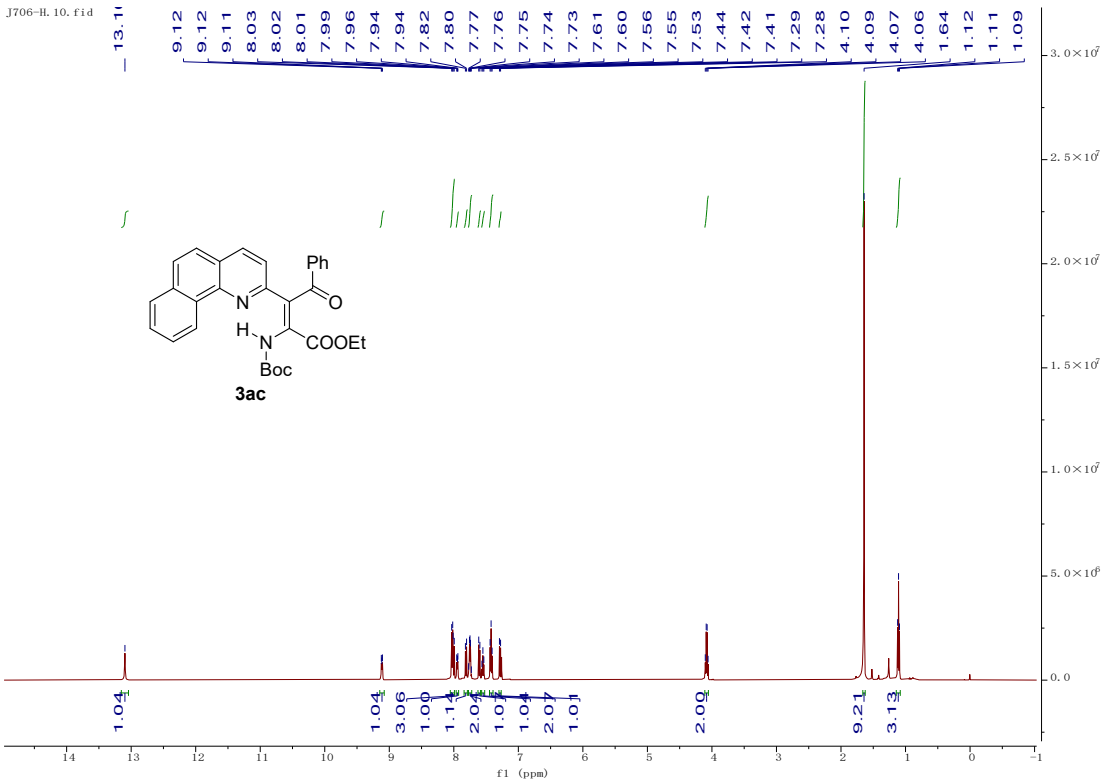
Molecular Weight: 476.5290

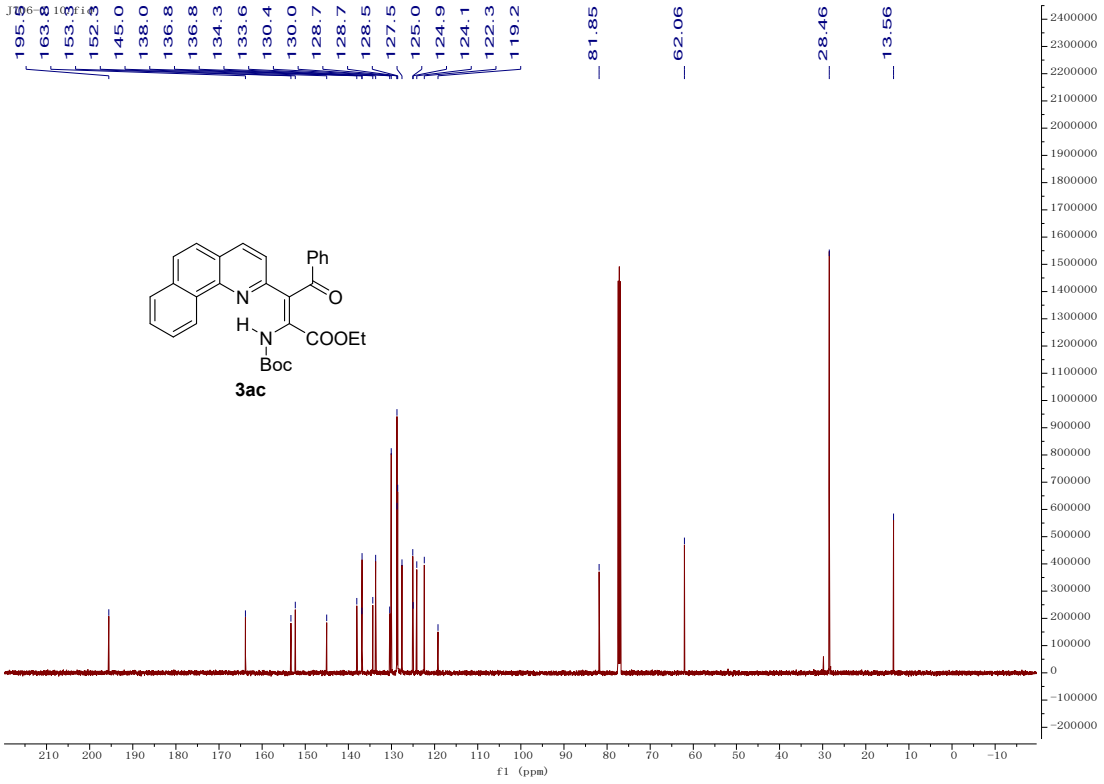
m/z: 476.1947 (100.0%), 477.1981 (29.2%), 478.2014 (4.1%), 478.1990 (1.2%)

Elemental Analysis: C, 68.05; H, 5.92; N, 5.88; O, 20.14

HRMS (ESI, m/z) calcd for $C_{27}H_{28}N_2O_6$ $[M+H]^+$ 477.2021, found 477.2030.

3ac


J706-H.10.fid
13.11
9.12
9.12
9.11
8.03
8.02
8.01
7.99
7.96
7.94
7.94
7.82
7.80
7.77
7.76
7.75
7.74
7.73
7.61
7.60
7.56
7.55
7.53
7.44
7.42
7.41
7.29
7.28
4.10
4.09
4.07
4.06
1.64
1.12
1.11
1.09
Ph
O
N
H
N
COOEt
Boc
3ac
1.04
1.04
3.06
1.00
1.11
2.04
1.07
1.04
2.07
1.01
2.09
9.21
3.13
f1 (ppm)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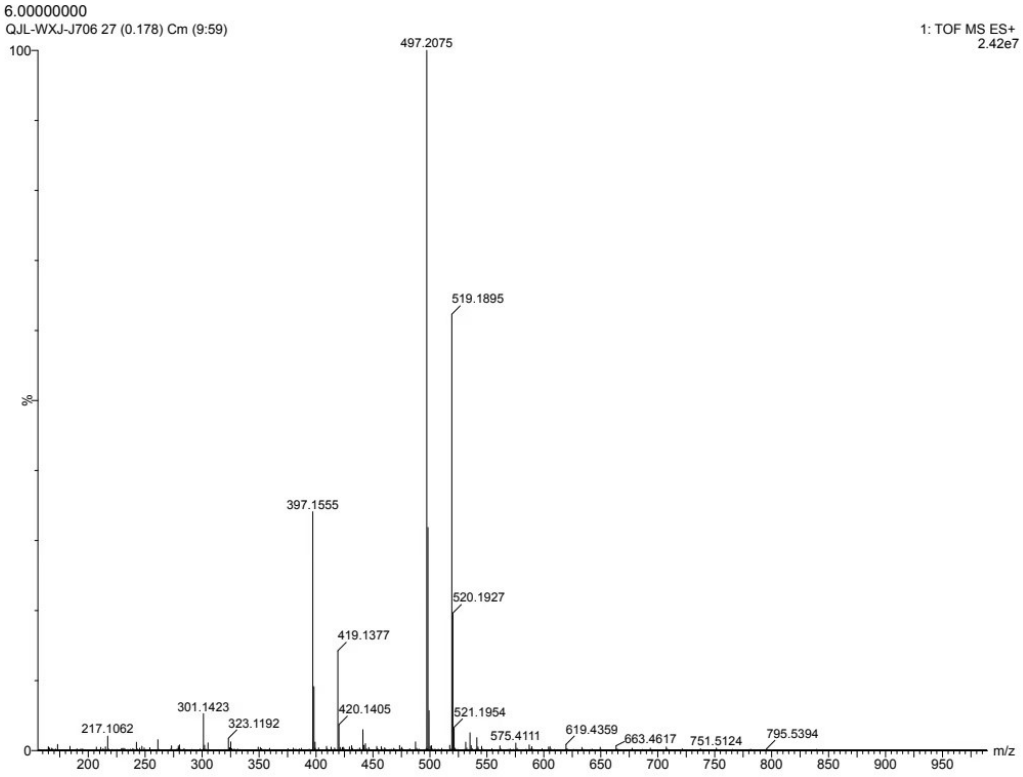
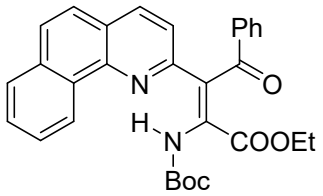
153.3
152.3
145.0
138.0
136.8
136.8
134.3
133.6
130.4
130.0
128.7
128.7
128.5
127.5
125.0
124.9
124.1
122.3
119.2
81.85
62.06
28.46
13.56
Ph
O
N
H
N
COOEt
Boc
3ac
f1 (ppm)





3ac

Chemical Formula: $C_{30}H_{28}N_2O_5$

Exact Mass: 496.1998

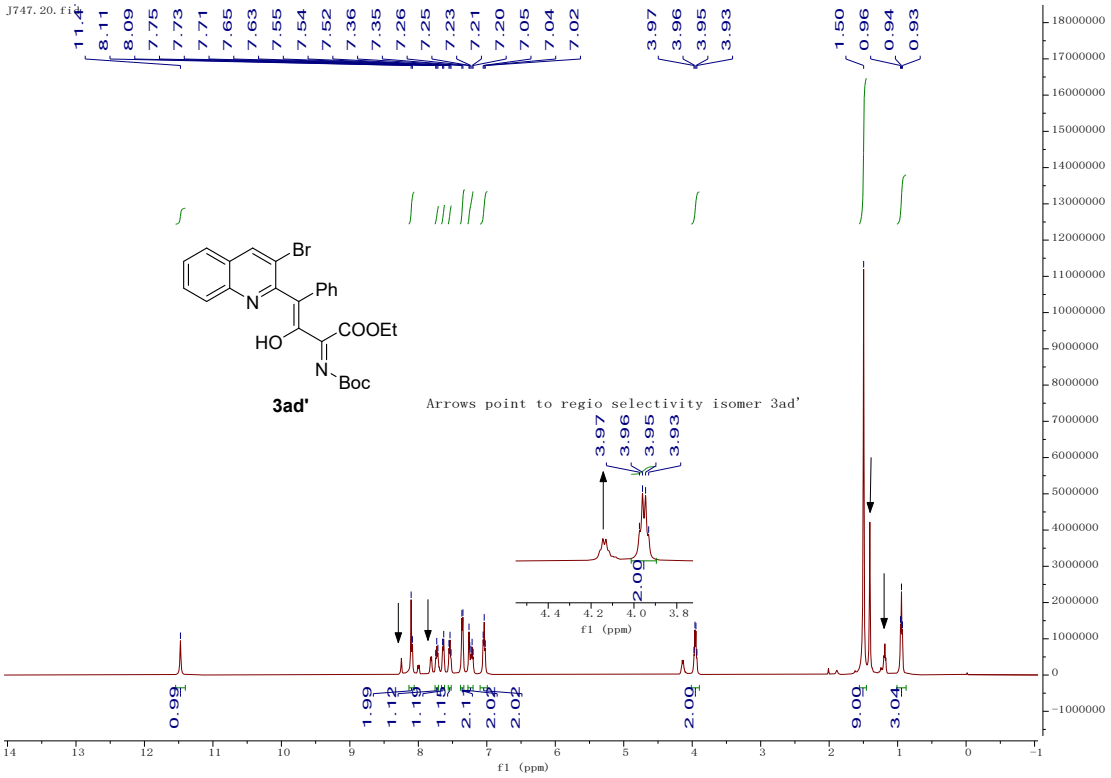
Molecular Weight: 496.5630

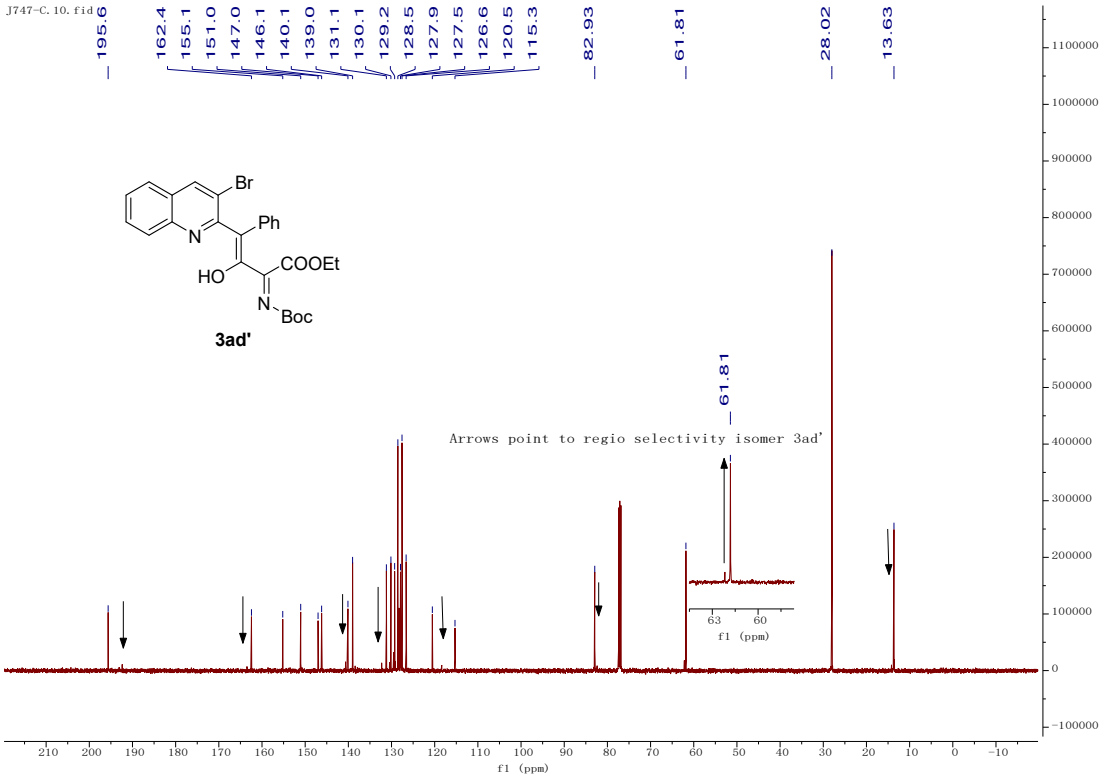
m/z: 496.1998 (100.0%), 497.2032 (32.4%), 498.2065 (5.1%), 498.2041 (1.0%)

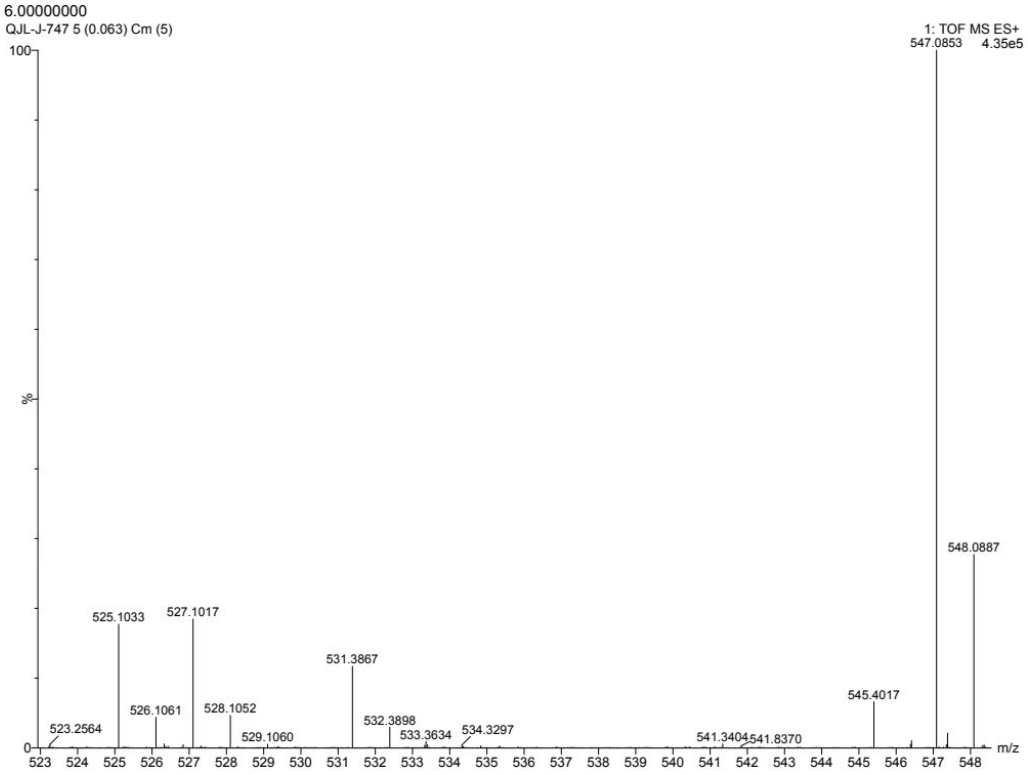
Elemental Analysis: C, 72.56; H, 5.68; N, 5.64; O, 16.11

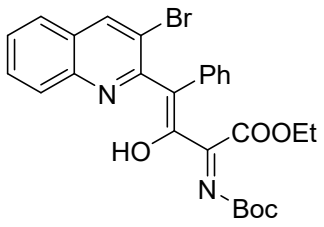
HRMS (ESI, m/z) calcd for $C_{30}H_{28}N_2O_5$ $[M+H]^+$ 497.2071, found 497.2075

3ad’


J747.20.fid
11.4
8.11
8.09
7.75
7.73
7.71
7.65
7.63
7.55
7.54
7.52
7.36
7.35
7.26
7.25
7.23
7.21
7.20
7.05
7.04
7.02
3.97
3.96
3.95
3.93
1.50
0.96
0.94
0.93
Br
N
Ph
HO
COOEt
N
Boc
3ad'
Arrows point to regio selectivity isomer 3ad’
f1 (ppm)


J747-C.10.fid
195.6
162.4
155.1
151.0
147.0
146.1
140.1
139.0
131.1
130.1
129.2
128.5
127.9
127.5
126.6
120.5
115.3
82.93
61.81
28.02
13.63
Br
N
Ph
HO
COOEt
N
Boc
3ad'
Arrows point to regio selectivity isomer 3ad’
f1 (ppm)





3ad'

Chemical Formula: $C_{26}H_{25}BrN_2O_5$

Exact Mass: 524.0947

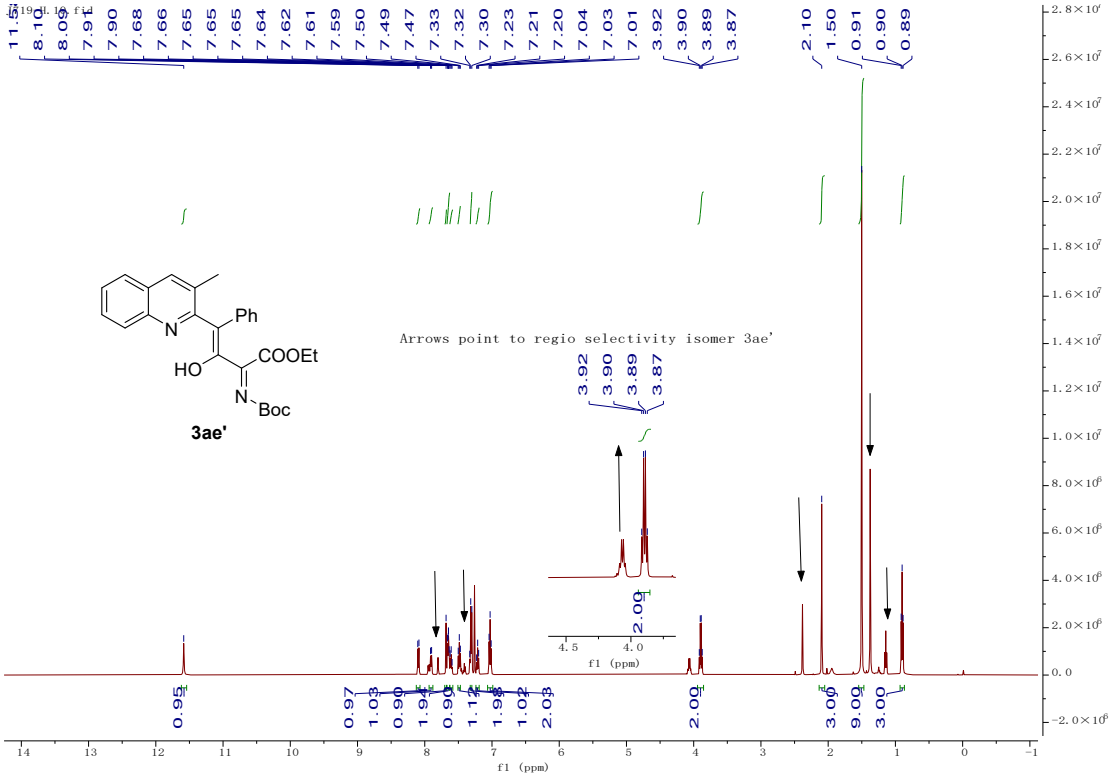
Molecular Weight: 525.3990

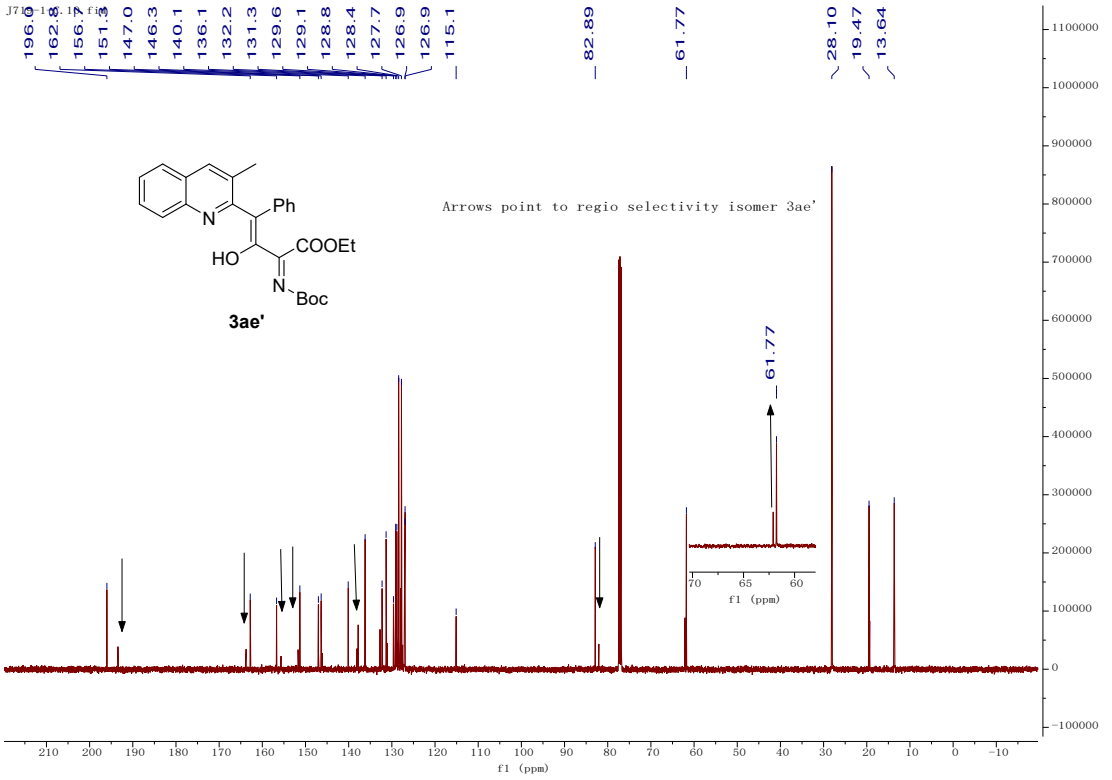
m/z: 524.0947 (100.0%), 526.0926 (97.3%), 525.0980 (28.1%),527.0960 (27.4%), 526.1014(3.8%), 528.0993 (3.7%), 526.0989 (1.0%), 528.0969 (1.0%)

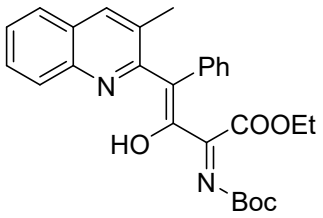
Elemental Analysis: C, 59.44; H, 4.80; Br, 15.21; N, 5.33; O, 15.23

HRMS (ESI, m/z) calcd for $C_{26}H_{25}BrN_2O_5$ $[M+Na]^+$ 547.0840, found 547.0853.

3ae'


Arrows point to regio selectivity isomer 3ae'
3ae'
f1 (ppm)


Arrows point to regio selectivity isomer 3ae'
3ae'
f1 (ppm)

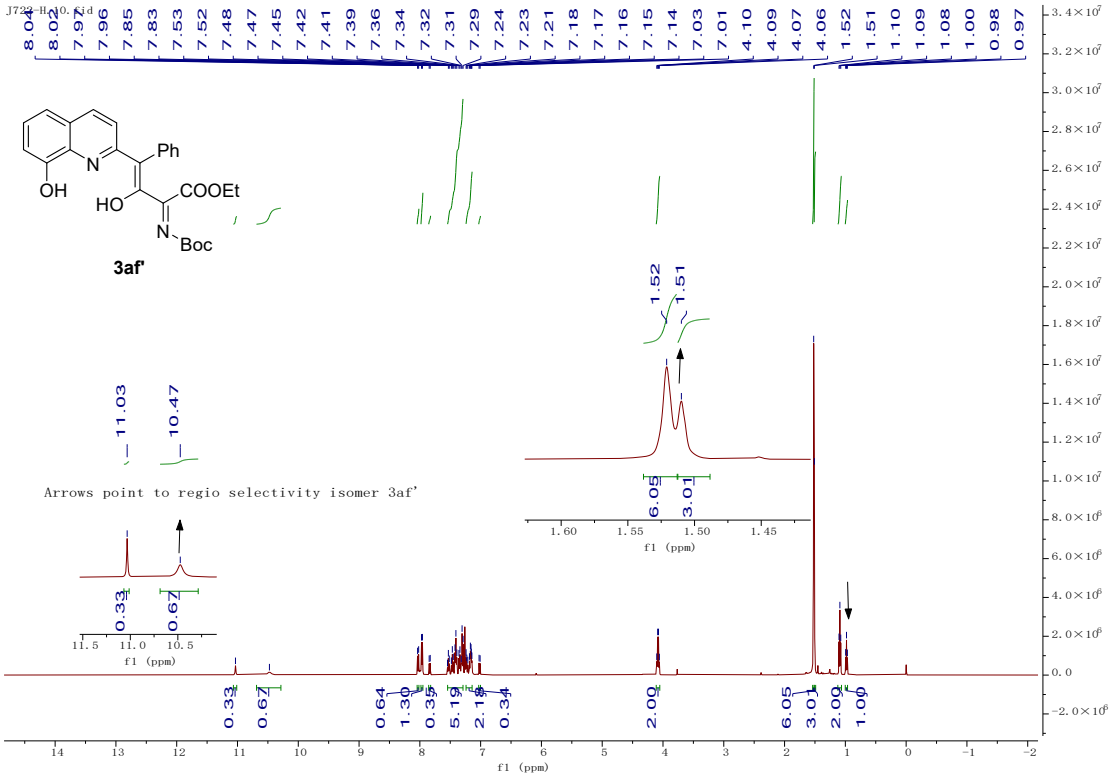


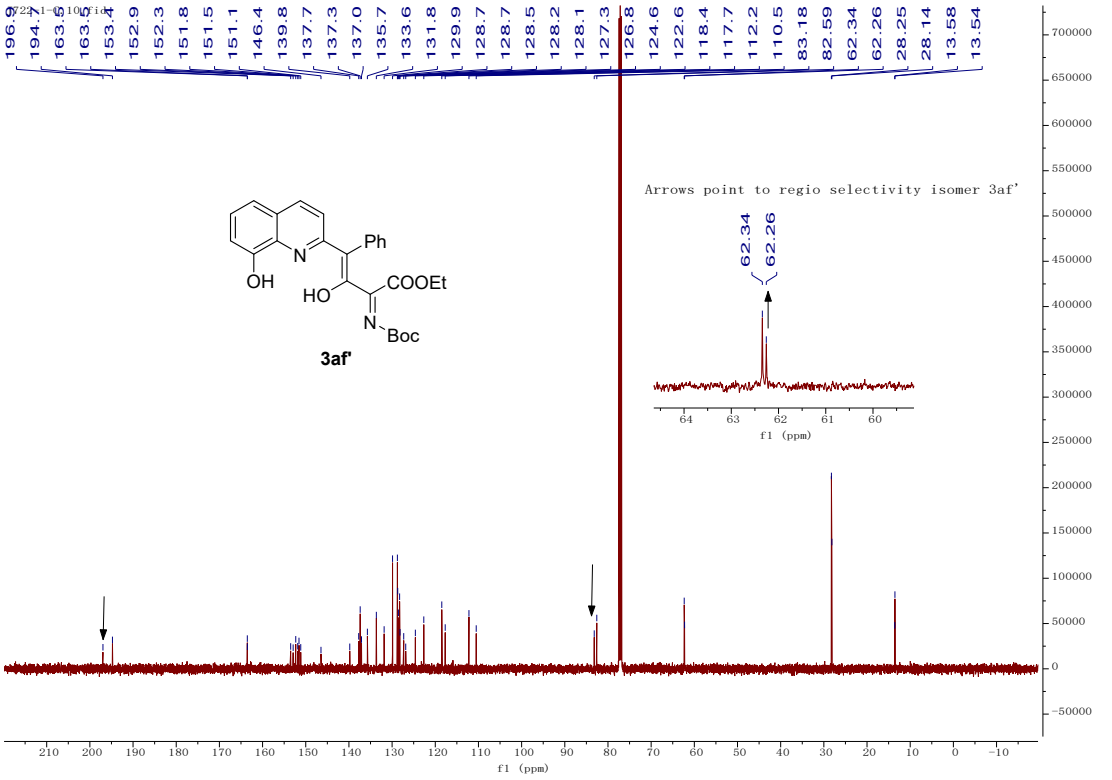
3ae'

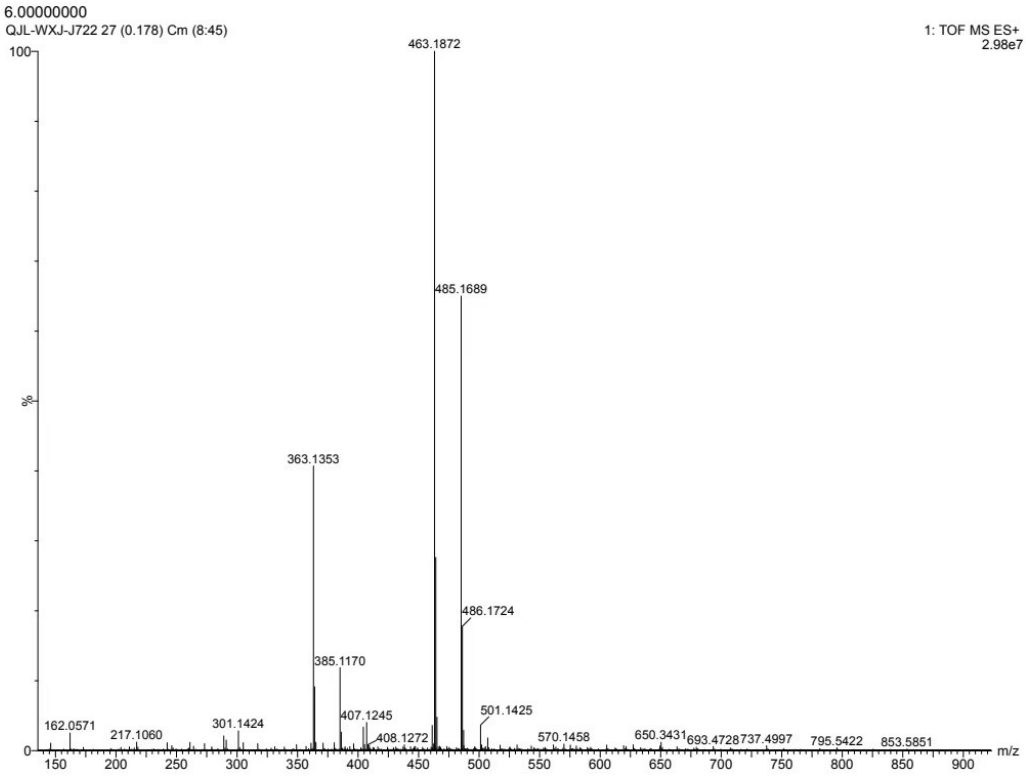
Chemical Formula: $C_{27}H_{28}N_2O_5$
Exact Mass: 460.1998
Molecular Weight: 460.5300
m/z: 460.1998 (100.0%), 461.2032 (29.2%), 462.2065 (4.1%), 462.2041 (1.0%)
Elemental Analysis: C, 70.42; H, 6.13; N, 6.08; O, 17.37

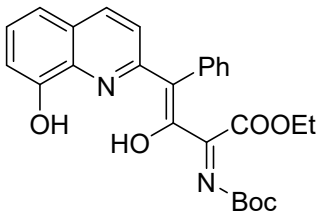
HRMS (ESI, m/z) calcd for $C_{27}H_{28}N_2O_5$ $[M+H]^+$ 461.2071, found 461.2089.

3af’


Ph
OH
HO
COOEt
N
Boc
3af'
Arrows point to regio selectivity isomer 3af’
f1 (ppm)


Ph
OH
HO
COOEt
N
Boc
3af'
Arrows point to regio selectivity isomer 3af’
f1 (ppm)





3af'

Chemical Formula: $C_{26}H_{26}N_2O_6$

Exact Mass: 462.1791

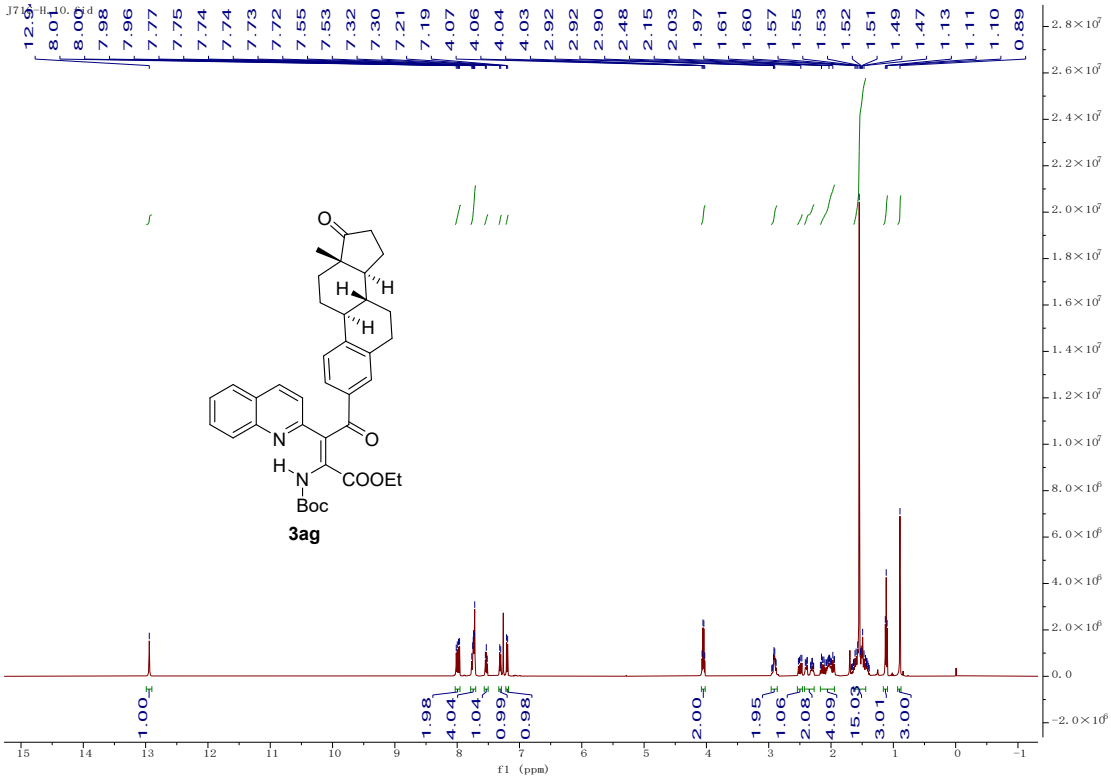
Molecular Weight: 462.5020

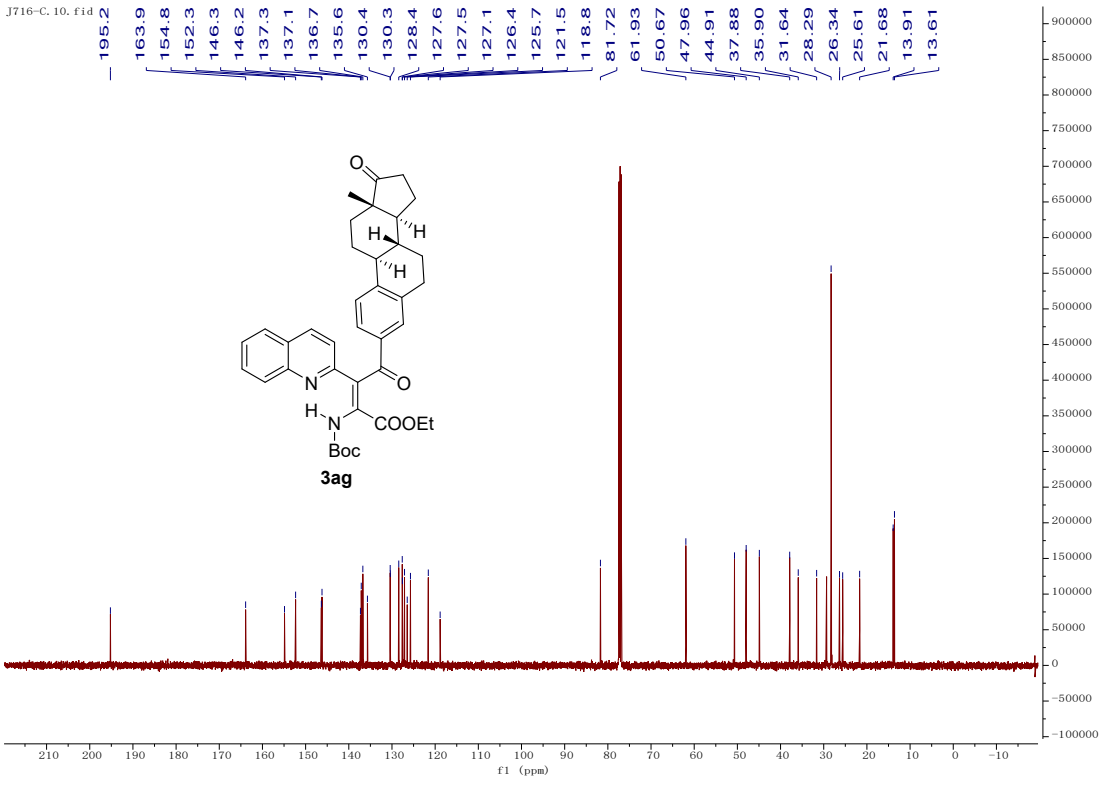
m/z: 462.1791 (100.0%), 463.1824 (28.1%), 464.1858 (3.8%), 464.1833 (1.2%)

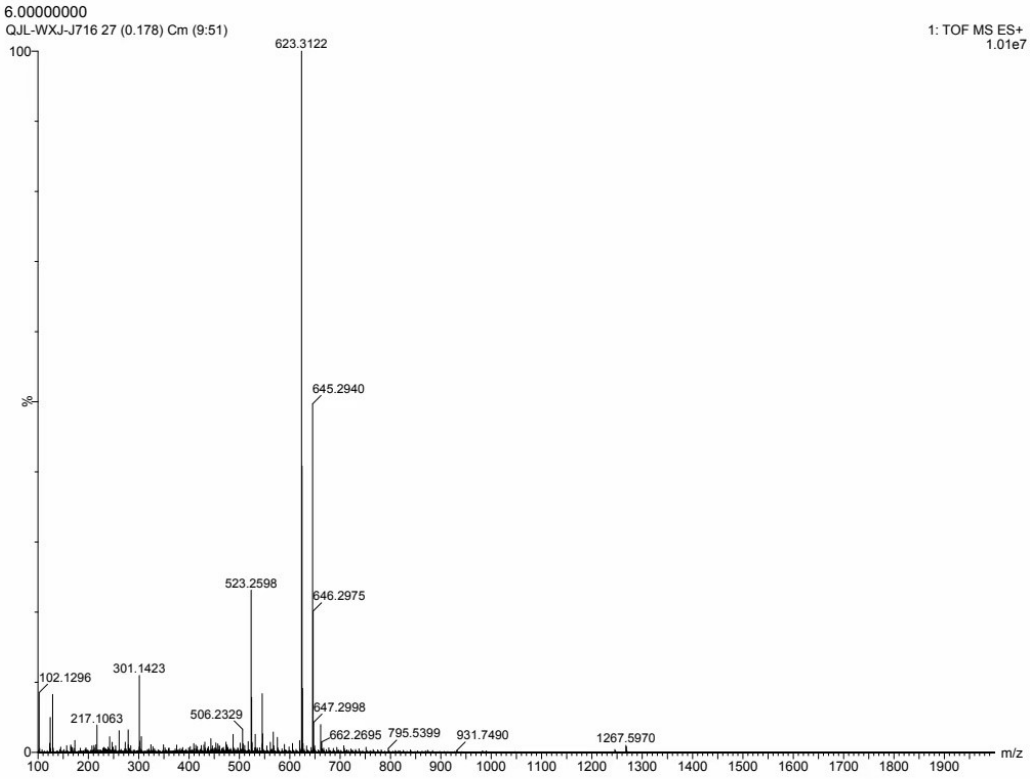
Elemental Analysis: C, 67.52; H, 5.67; N, 6.06; O, 20.76

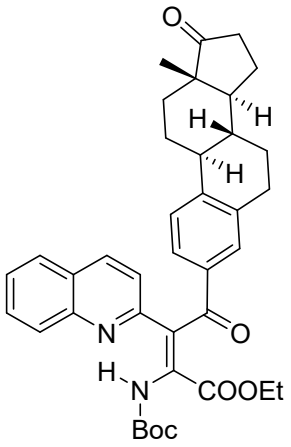
HRMS (ESI, m/z) calcd for $C_{26}H_{26}N_2O_6$ $[M+H]^+$ 463.1864, found 463.1872.

3ag


J716-H.10.fid
12.61 8.01 8.00 7.98 7.96 7.77 7.75 7.74 7.74 7.73 7.72 7.55 7.53 7.32 7.30 7.21 7.19 4.07 4.06 4.04 4.03 2.92 2.92 2.90 2.48 2.15 2.03 1.97 1.61 1.60 1.57 1.55 1.53 1.52 1.51 1.49 1.47 1.13 1.11 1.10 0.89
1.00 1.98 4.04 1.04 0.99 0.98 2.00 1.95 1.06 2.08 4.09 15.03 3.01 3.00
f1 (ppm)
3ag


J716-C.10.fid
195.2 163.9 154.8 152.3 146.3 146.2 137.3 137.1 136.7 135.6 130.4 130.3 128.4 127.6 127.5 127.1 126.4 125.7 121.5 118.8 81.72 61.93 50.67 47.96 44.91 37.88 35.90 31.64 28.29 26.34 25.61 21.68 13.91 13.61
f1 (ppm)
3ag





3ag

Chemical Formula: $C_{38}H_{42}N_2O_6$

Exact Mass: 622.3043

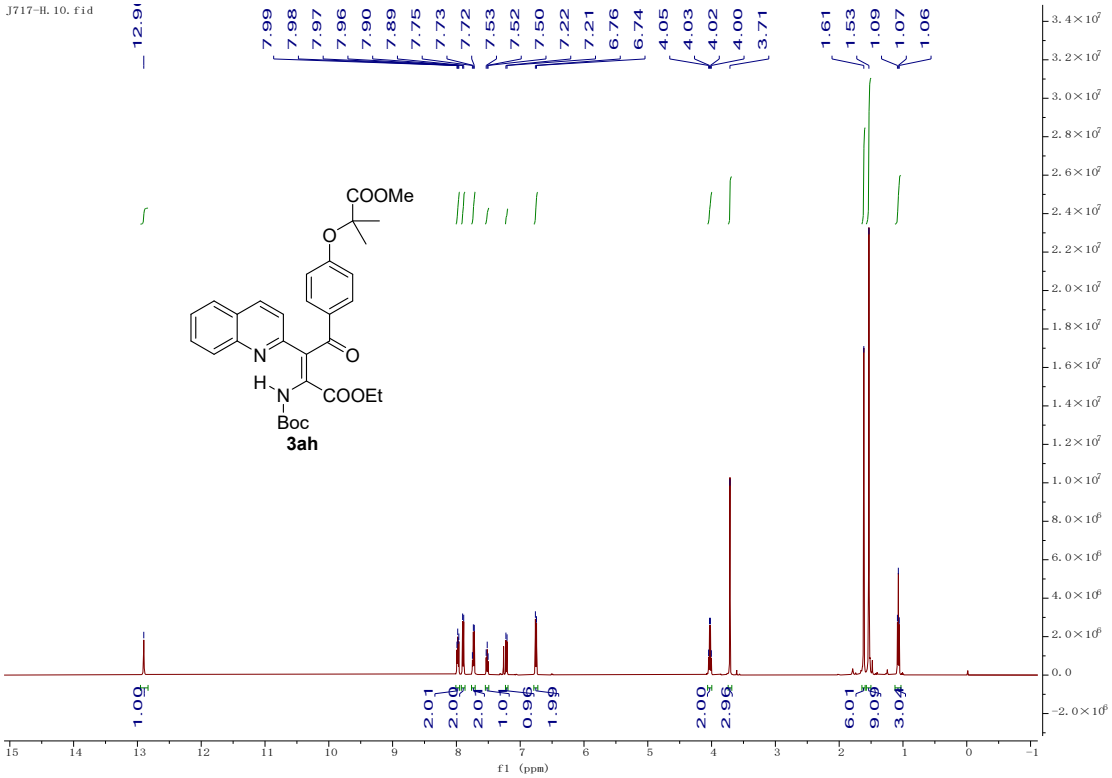
Molecular Weight: 622.7620

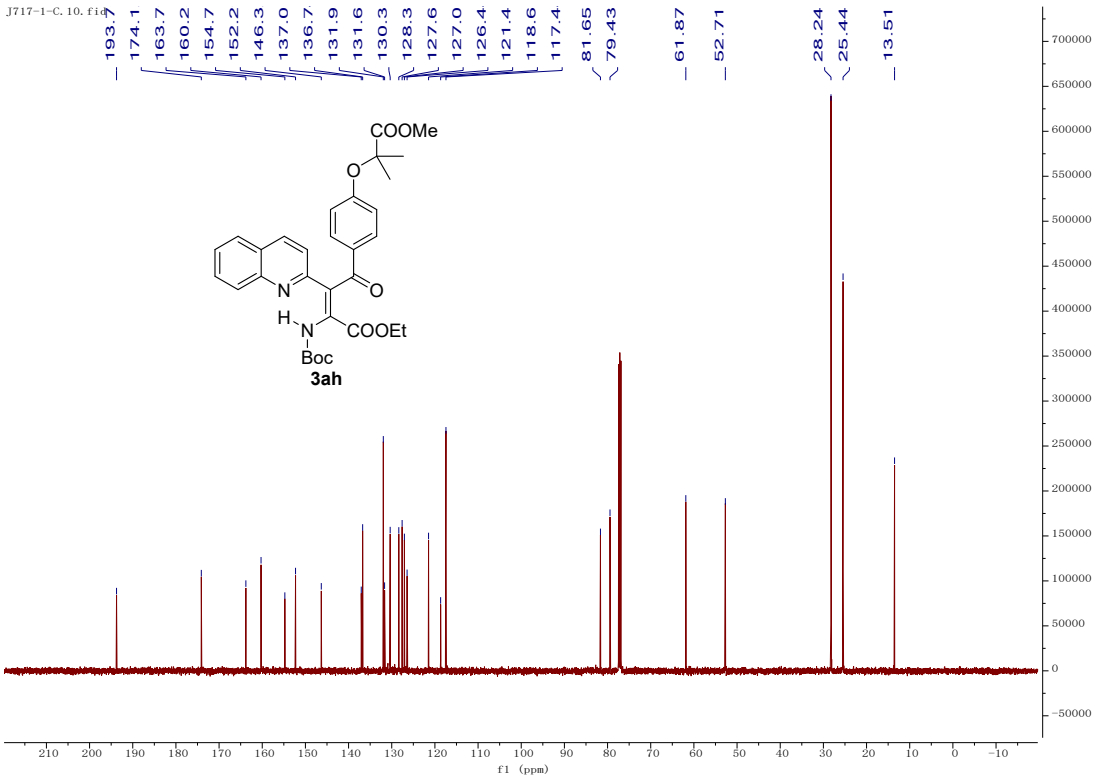
m/z: 622.3043 (100.0%), 623.3076 (41.1%), 624.3110 (8.2%), 624.3085 (1.2%), 625.3144 (1.1%)

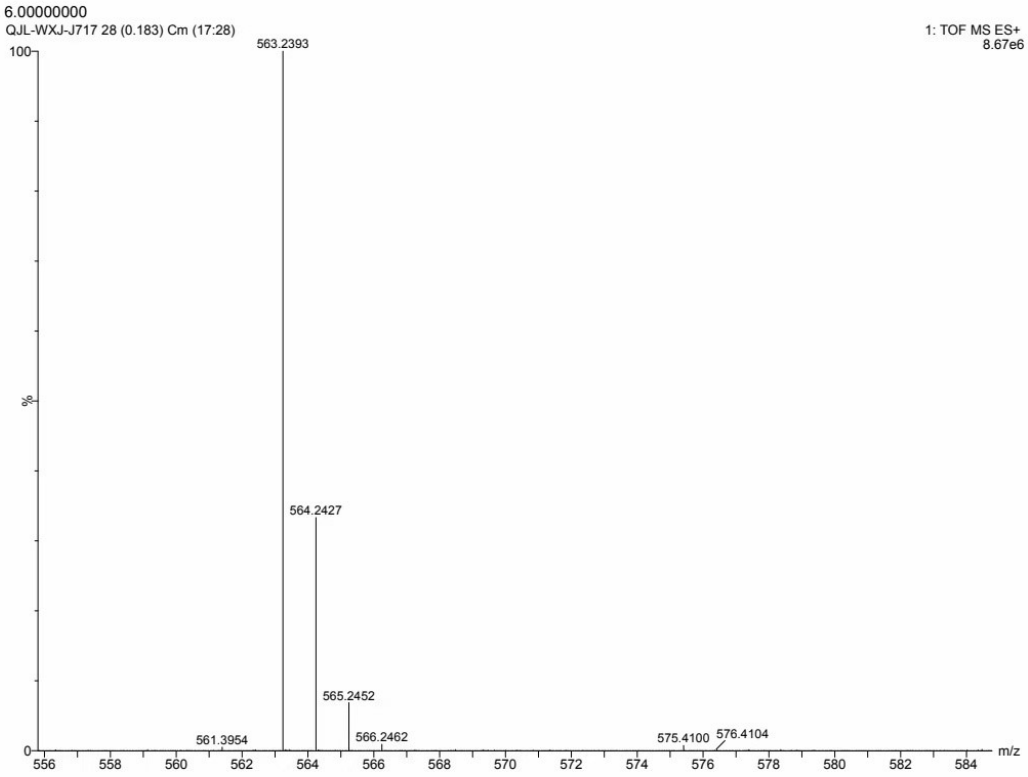
Elemental Analysis: C, 73.29; H, 6.80; N, 4.50; O, 15.41

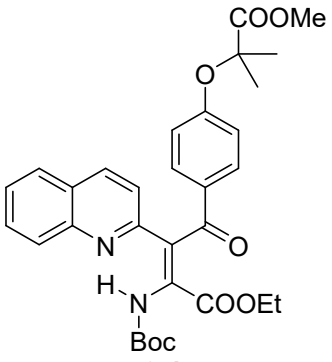
HRMS (ESI, m/z) calcd for $C_{38}H_{42}N_2O_6$ $[M+H]^+$ 623.3116, found 623.3122.

3ah


J717-H. 10. fid
12.91
7.99
7.98
7.97
7.96
7.90
7.89
7.75
7.73
7.72
7.53
7.52
7.50
7.22
7.21
6.76
6.74
4.05
4.03
4.02
4.00
3.71
1.61
1.53
1.09
1.07
1.06
COOMe
O
N
O
H
N
COOEt
Boc
3ah
1.00
2.01
2.00
2.01
1.01
0.96
1.99
2.00
2.96
6.01
9.05
3.04
f1 (ppm)


J717-1-C. 10. fid
193.7
174.1
163.7
160.2
154.7
152.2
146.3
137.0
136.7
131.9
131.6
130.3
128.3
127.6
127.0
126.4
121.4
118.6
117.4
81.65
79.43
61.87
52.71
28.24
25.44
13.51
COOMe
O
N
O
H
N
COOEt
Boc
3ah
f1 (ppm)





3ah

Chemical Formula: $C_{31}H_{34}N_2O_8$

Exact Mass: 562.2315

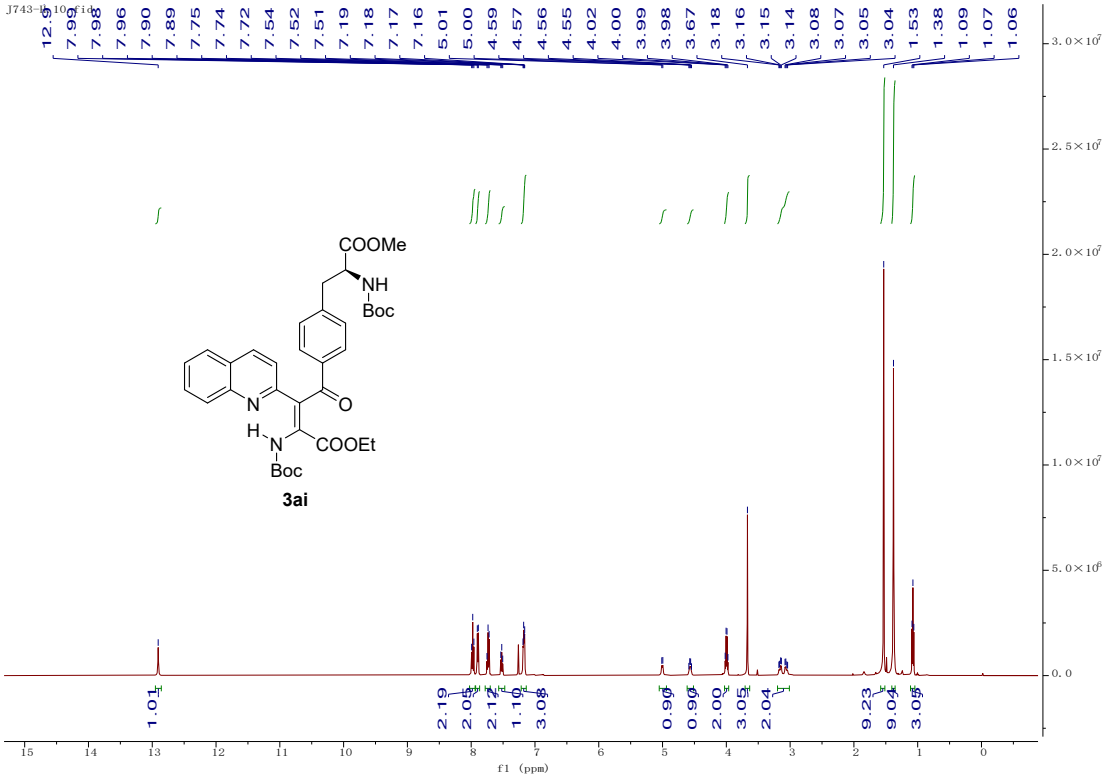
Molecular Weight: 562.6190

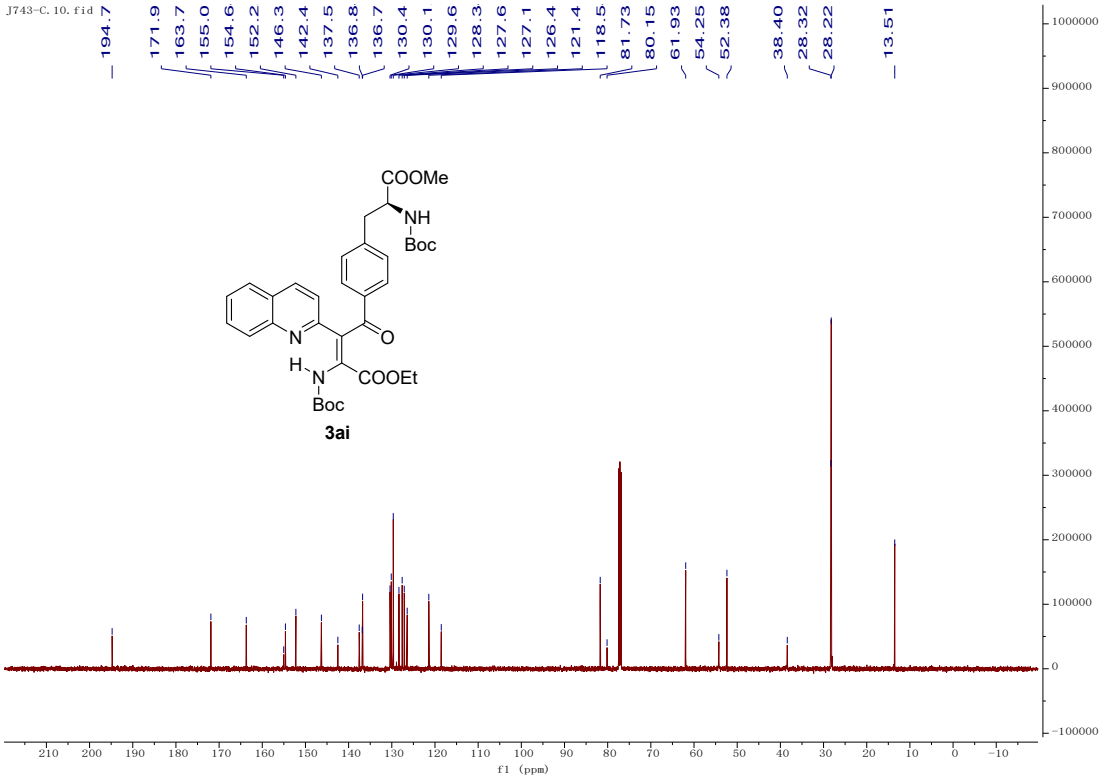
m/z: 562.2315 (100.0%), 563.2349 (33.5%), 564.2382 (5.4%), 564.2358 (1.6%)

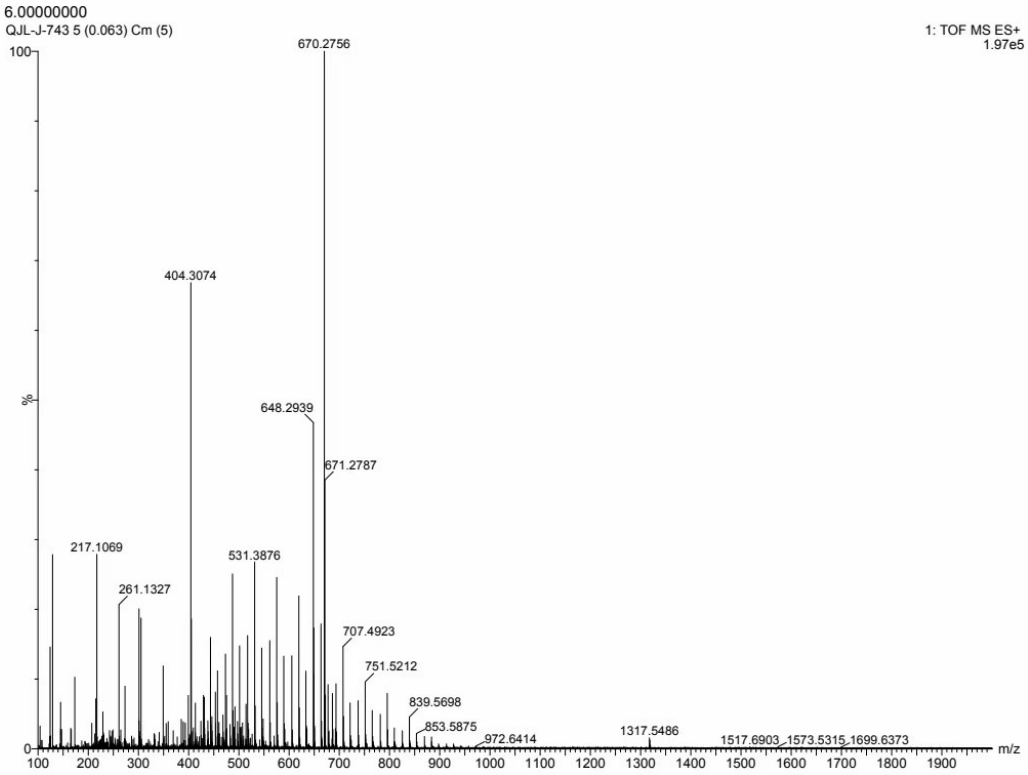
Elemental Analysis: C, 66.18; H, 6.09; N, 4.98; O, 22.75

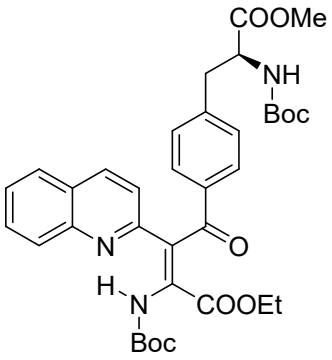
HRMS (ESI, m/z) calcd for $C_{31}H_{34}N_2O_8$ $[M+H]^+$ 563.2338, found 563.2393.

3ai


COOMe
NH
Boc
O
N
H
N
COOEt
Boc
3ai
f1 (ppm)


COOMe
NH
Boc
O
N
H
N
COOEt
Boc
3ai
f1 (ppm)



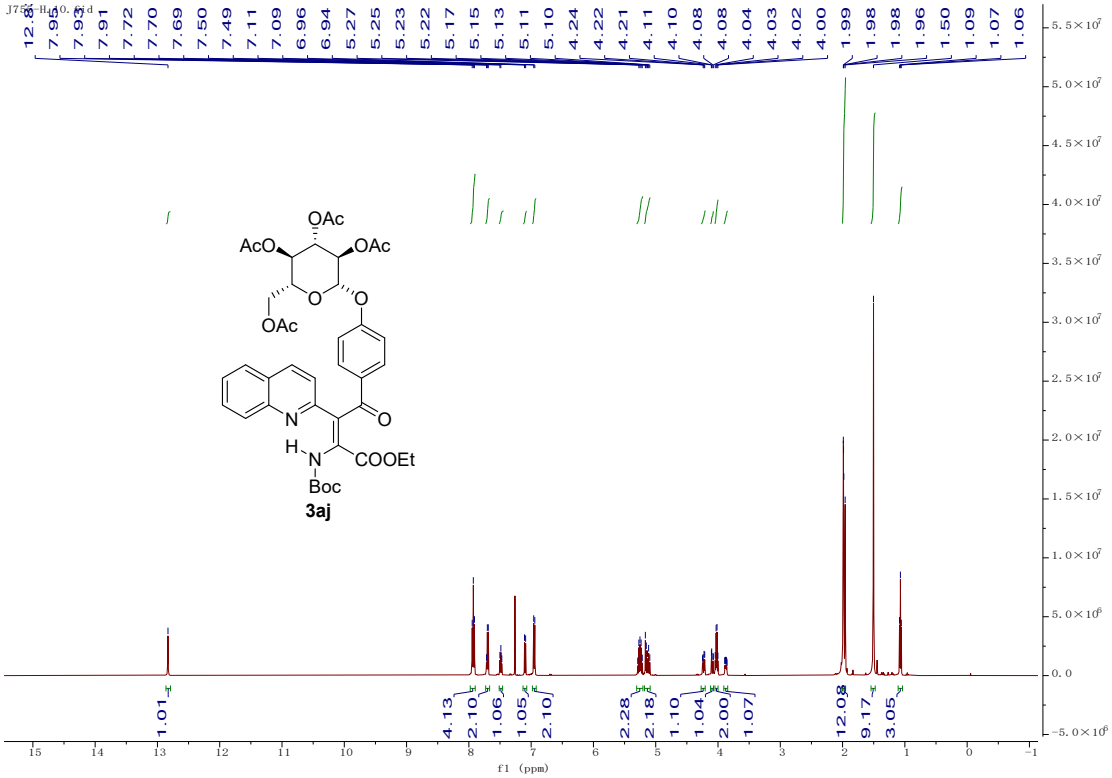


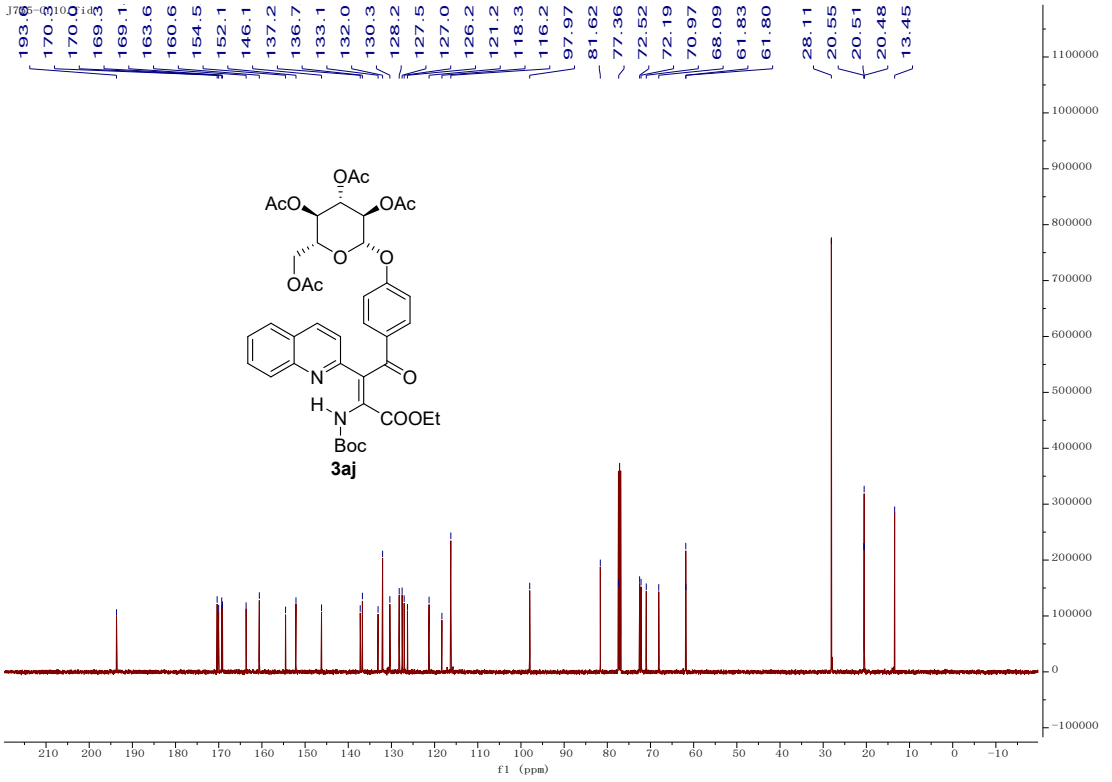
3ai

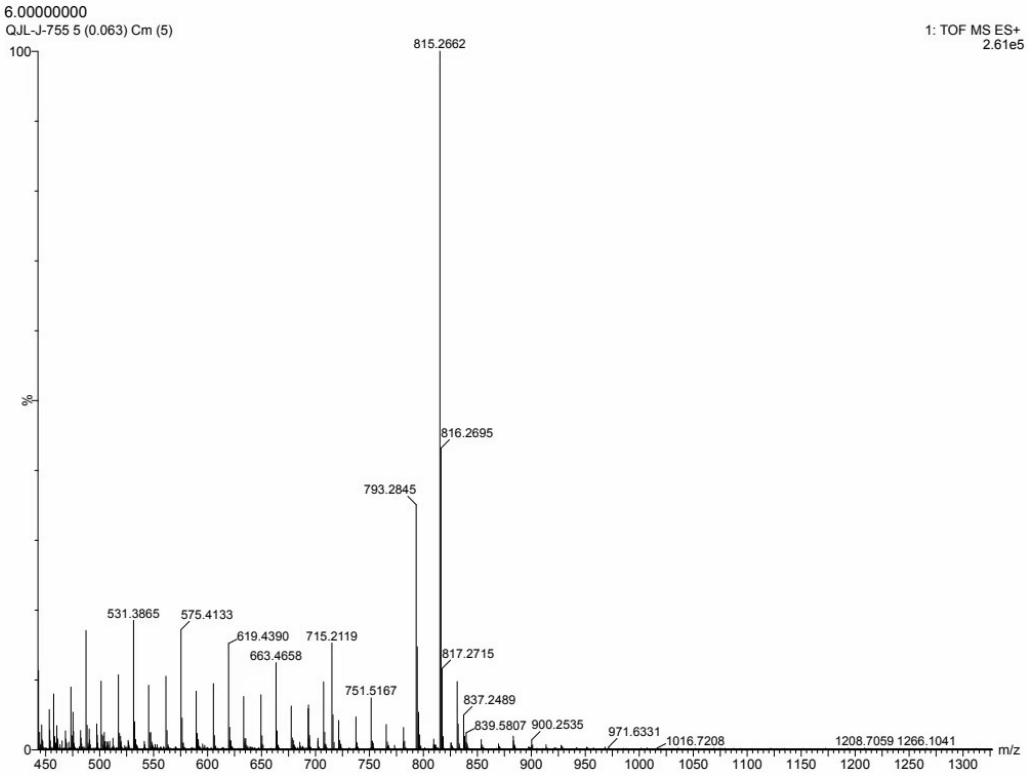
Chemical Formula: $C_{35}H_{41}N_3O_9$
Exact Mass: 647.2843
Molecular Weight: 647.7250
m/z: 647.2843 (100.0%), 648.2876 (37.9%), 649.2910 (7.0%), 649.2885 (1.8%), 648.2813 (1.1%)
Elemental Analysis: C, 64.90; H, 6.38; N, 6.49; O, 22.23

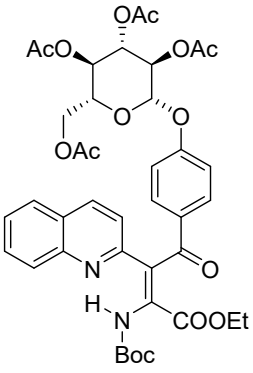
HRMS (ESI, m/z) calcd for $C_{35}H_{41}N_3O_9$ $[M+Na]^+$ 670.2735, found 670.2756.

3aj


12.81
7.95
7.93
7.91
7.72
7.70
7.69
7.50
7.49
7.11
7.09
6.96
6.94
5.27
5.25
5.23
5.22
5.17
5.15
5.13
5.11
5.10
4.24
4.22
4.21
4.11
4.10
4.08
4.08
4.04
4.03
4.02
4.00
1.99
1.98
1.98
1.96
1.50
1.09
1.07
1.06
OAc
AcO
OAc
O
O
OAc
N
O
H
N
COOEt
Boc
3aj
1.01
4.13
2.10
1.06
1.05
2.10
2.28
2.18
1.10
1.04
2.00
1.07
12.08
9.17
3.05
f1 (ppm)


193.6
170.3
170.0
169.3
169.1
163.6
160.6
154.5
152.1
146.1
137.2
136.7
133.1
132.0
130.3
128.2
127.5
127.0
126.2
121.2
118.3
116.2
97.97
81.62
77.36
72.52
72.19
70.97
68.09
61.83
61.80
28.11
20.55
20.51
20.48
13.45
OAc
AcO
OAc
O
O
OAc
N
O
H
N
COOEt
Boc
3aj
f1 (ppm)





3aj

Chemical Formula: $C_{40}H_{44}N_2O_{15}$

Exact Mass: 792.2742

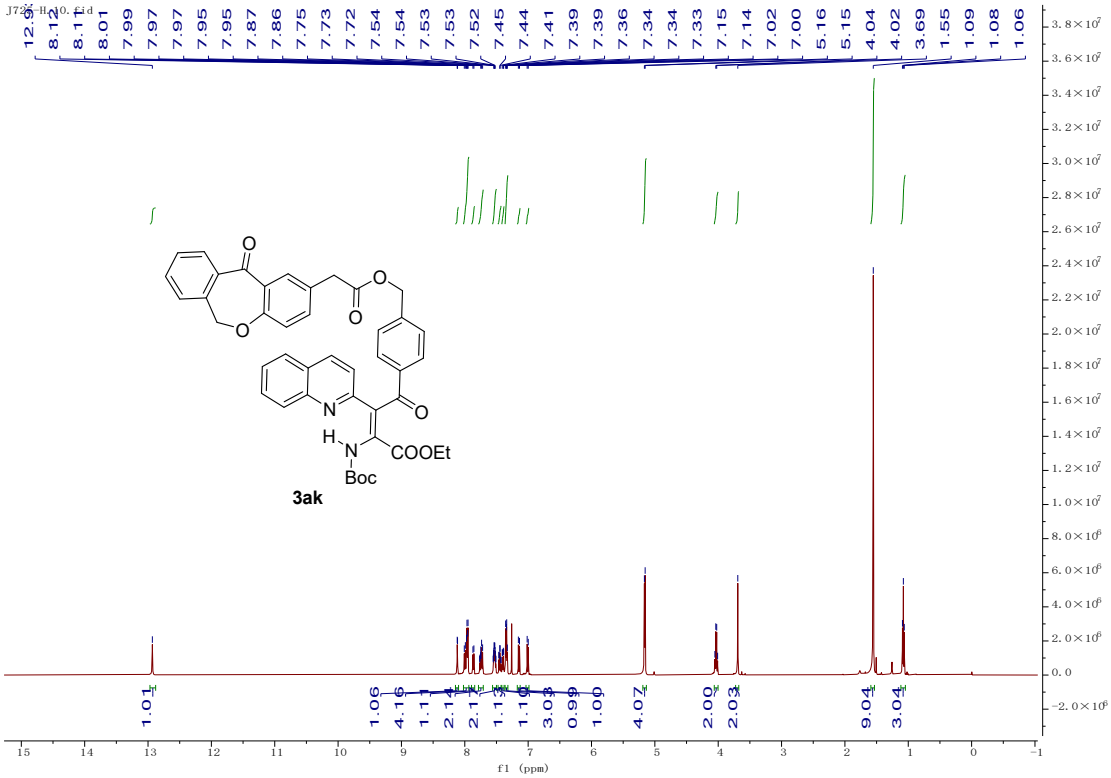
Molecular Weight: 792.7910

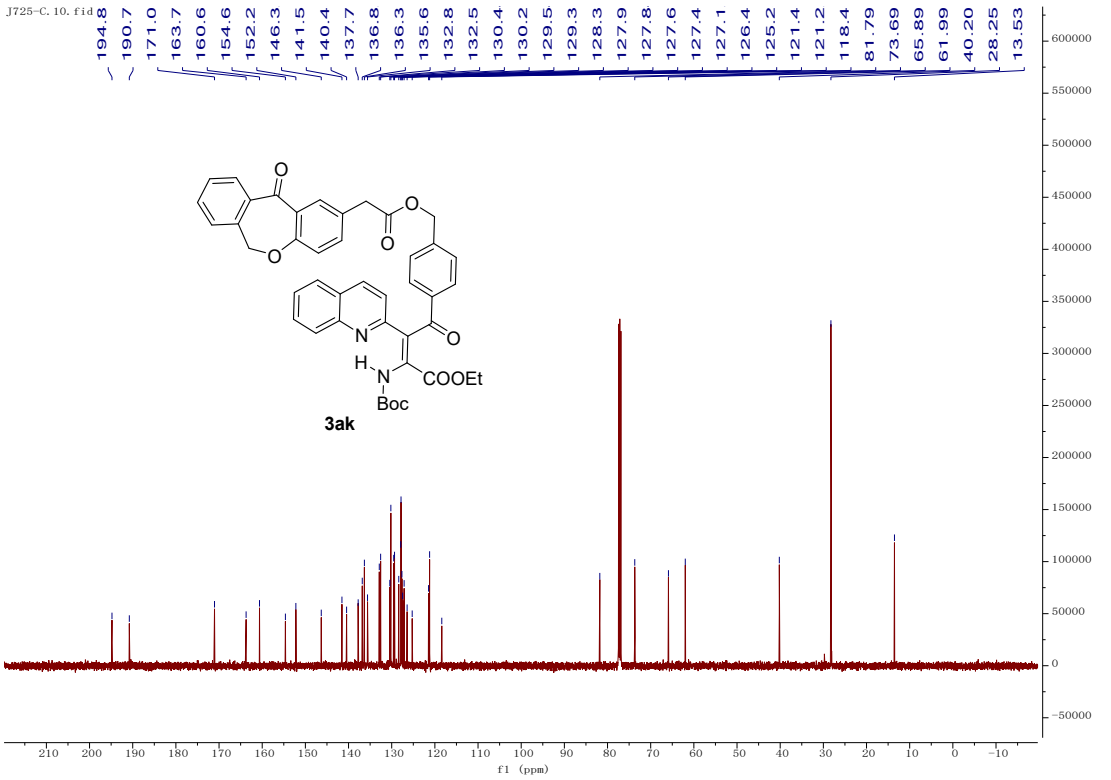
m/z: 792.2742 (100.0%), 793.2775 (43.3%), 794.2809 (9.1%),794.2784 (3.1%), 795.2818 (1.3%), 795.2842 (1.3%)

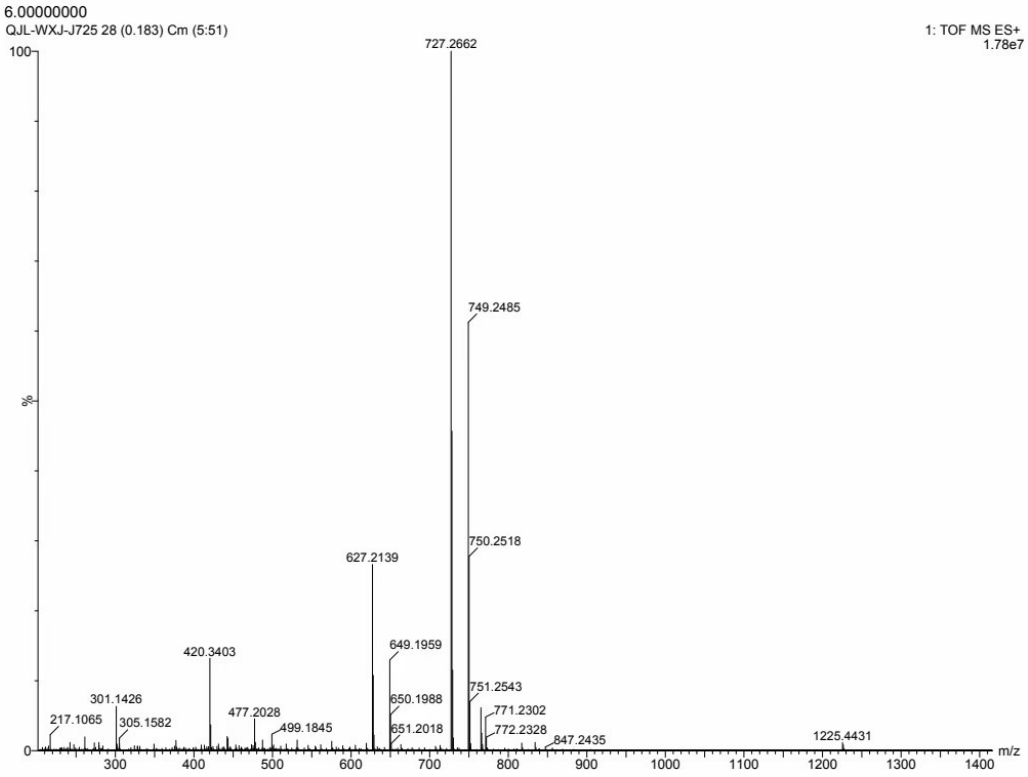
Elemental Analysis: C, 60.60; H, 5.59; N, 3.53; O, 30.27

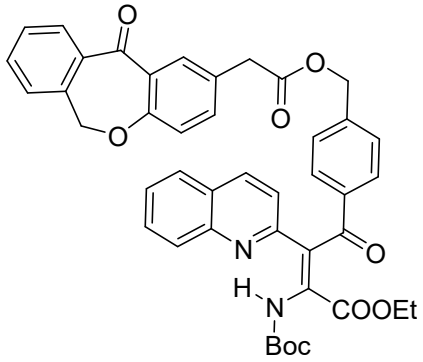
HRMS (ESI, m/z) calcd for $C_{40}H_{44}N_2O_{15}$ $[M+Na]^+$ 815.2634, found 815.2662.

3ak









3ak

Chemical Formula: $C_{43}H_{38}N_2O_9$

Exact Mass: 726.2577

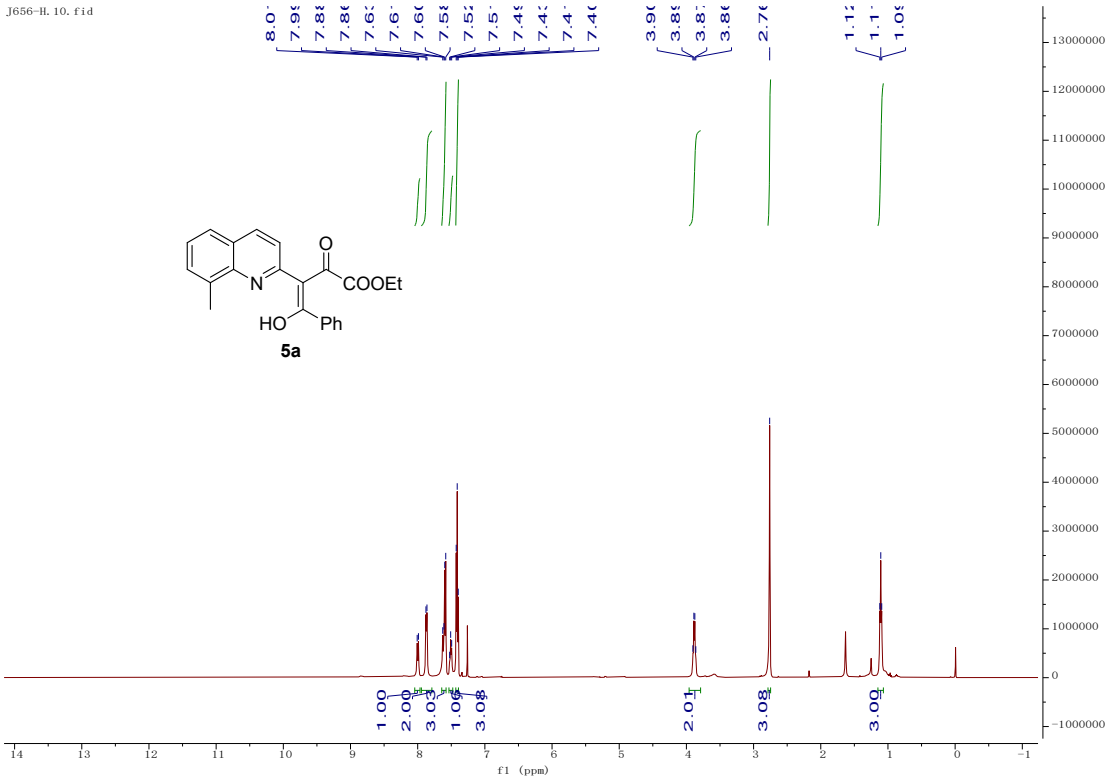
Molecular Weight: 726.7820

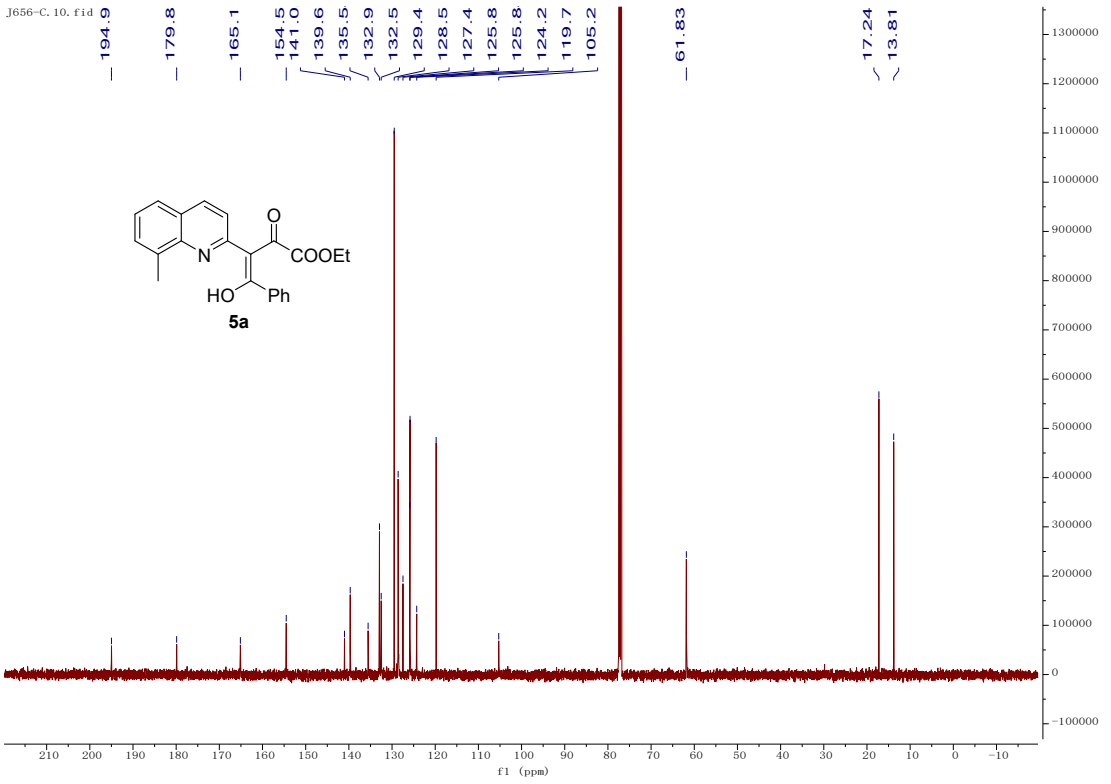
m/z: 726.2577 (100.0%), 727.2611 (46.5%), 728.2644 (10.6%), 728.2620 (1.8%), 729.2678 (1.6%)

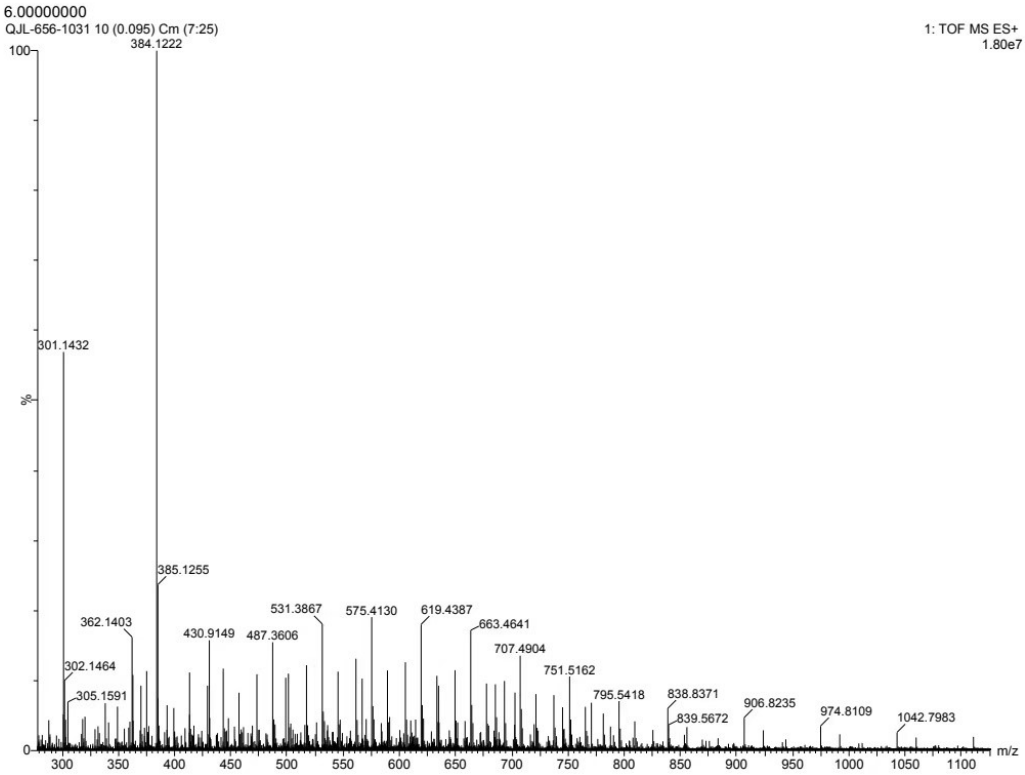
Elemental Analysis: C, 71.06; H, 5.27; N, 3.85; O, 19.81

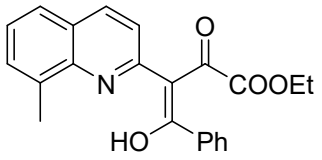
HRMS (ESI, m/z) calcd for $C_{43}H_{38}N_2O_9$ $[M+H]^+$ 727.2651, found 727.2662.

5a


J656-H. 10. fid
8.0
7.9
7.8
7.8
7.8
7.6
7.6
7.6
7.5
7.5
7.5
7.4
7.4
7.4
7.4
3.9
3.8
3.8
3.8
2.7
1.1
1.1
1.0
O
N
COOEt
HO
Ph
5a
1.00
2.00
3.03
1.06
3.08
2.01
3.08
3.00
f1 (ppm)


J656-C. 10. fid
194.9
179.8
165.1
154.5
141.0
139.6
135.5
132.9
132.5
129.4
128.5
127.4
125.8
125.8
124.2
119.7
105.2
61.83
17.24
13.81
O
N
COOEt
HO
Ph
5a
f1 (ppm)





5a

Chemical Formula: $C_{22}H_{19}NO_4$

Exact Mass: 361.1314

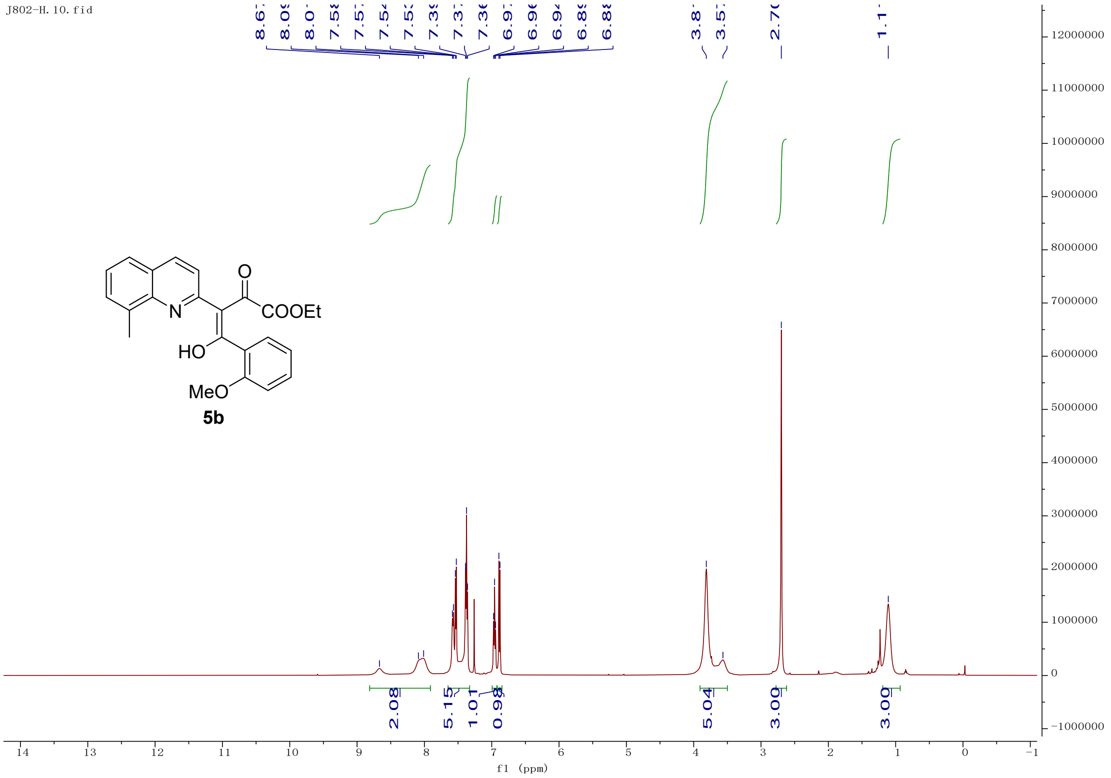
Molecular Weight: 361.3970

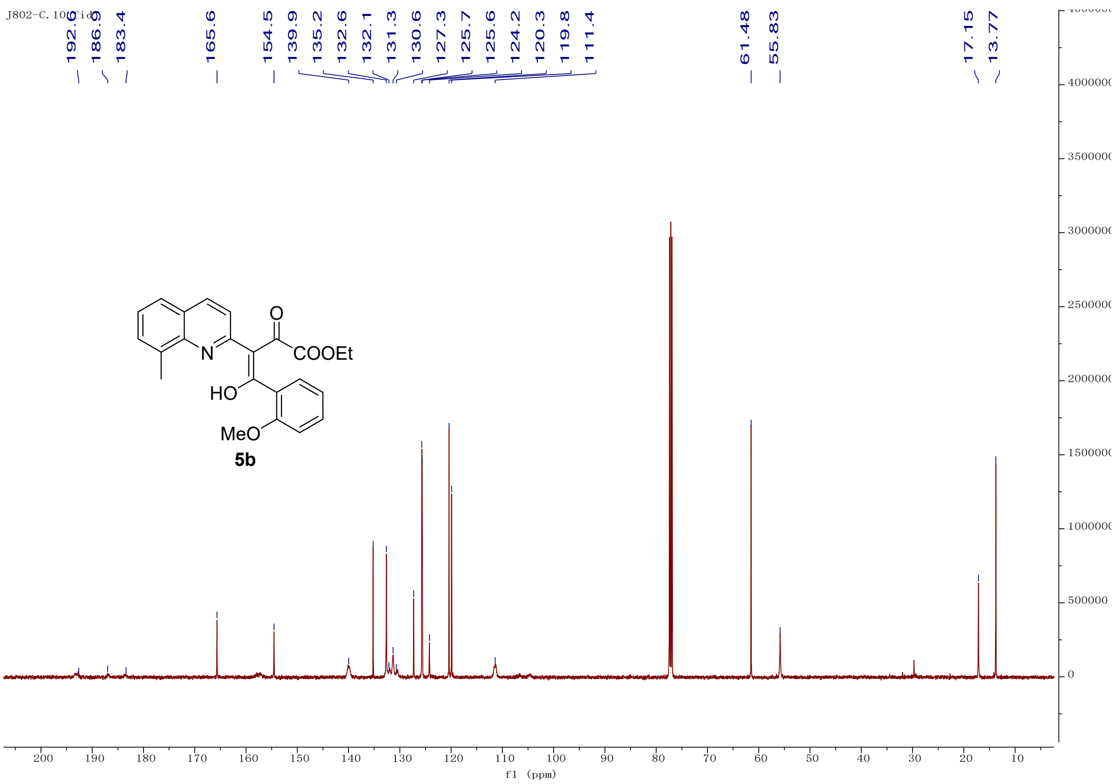
m/z: 361.1314 (100.0%), 362.1348 (23.8%), 363.1381 (2.7%)

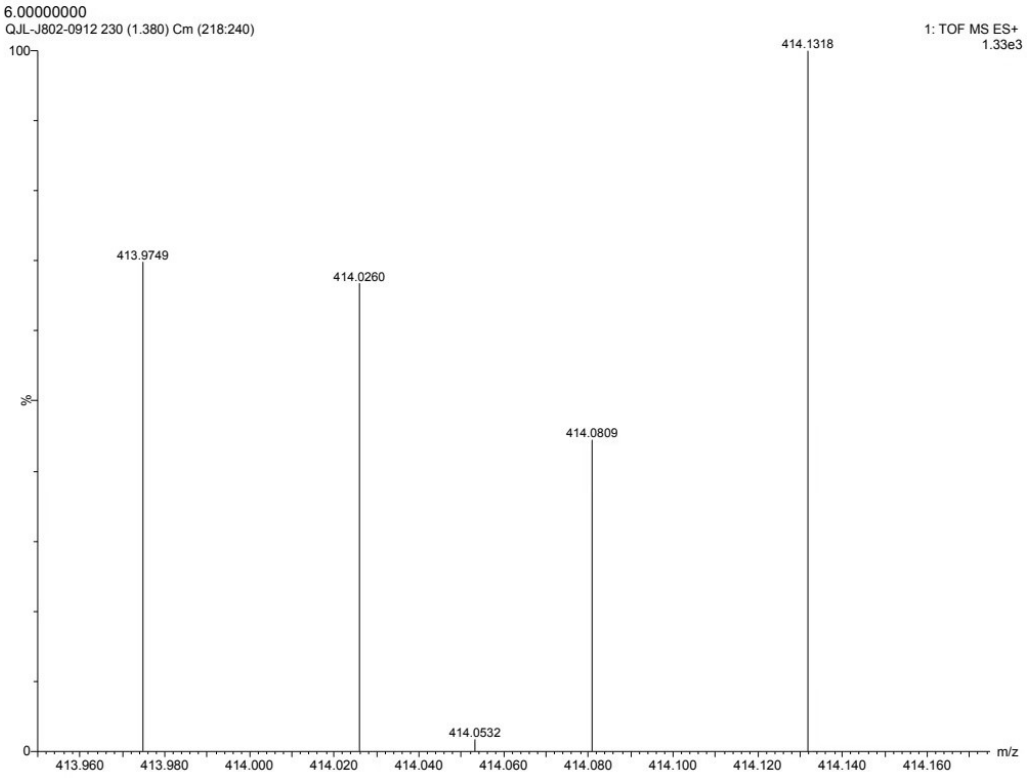
Elemental Analysis: C, 73.12; H, 5.30; N, 3.88; O, 17.71

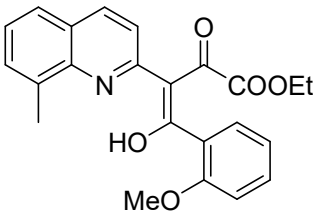
HRMS (ESI, m/z) calcd for $C_{22}H_{19}NO_4$ $[M+Na]^+$ 384.1207, found 384.1222.

5b


J802-H.10.fid
3.8
3.5
2.70
1.1
COOEt
HO
MeO
N
O
5b
2.08
5.15
1.01
0.98
5.04
3.00
3.00
f1 (ppm)


J802-C.10.fid
192.6
186.9
183.4
165.6
154.5
139.9
135.2
132.6
132.1
131.3
130.6
127.3
125.7
125.6
124.2
120.3
119.8
111.4
61.48
55.83
17.15
13.77
COOEt
HO
MeO
N
O
5b
f1 (ppm)





5b

Chemical Formula: $C_{23}H_{21}NO_5$

Exact Mass: 391.1420

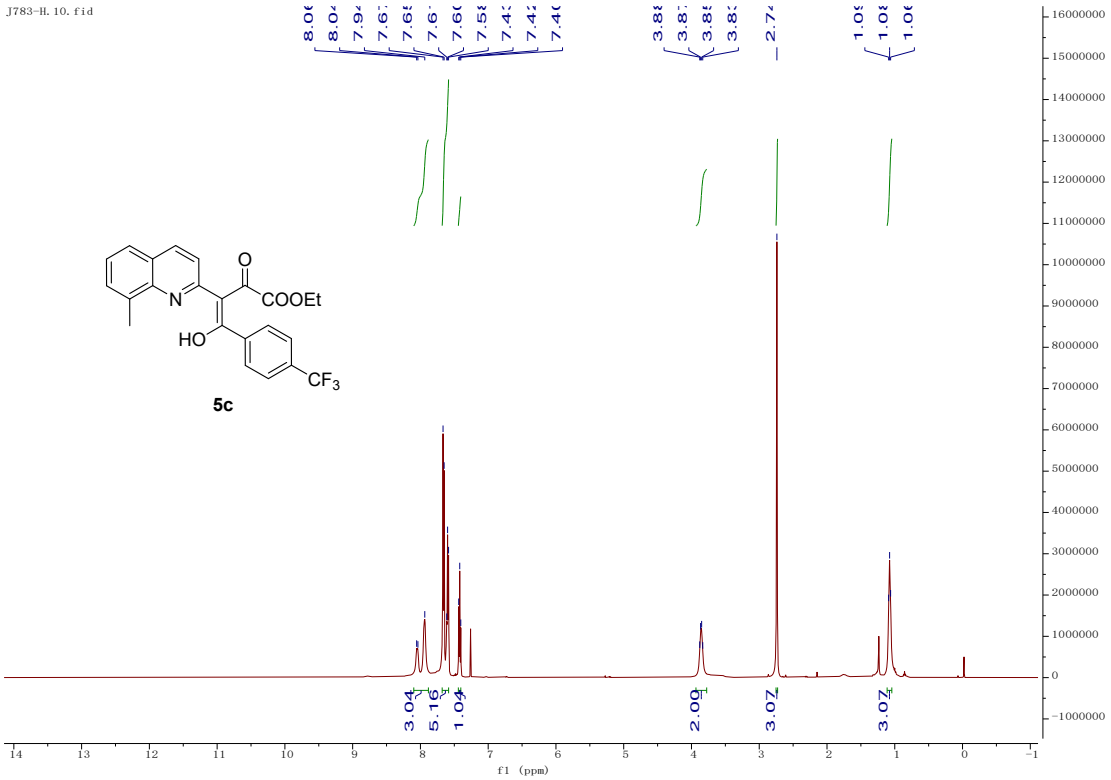
Molecular Weight: 391.4230

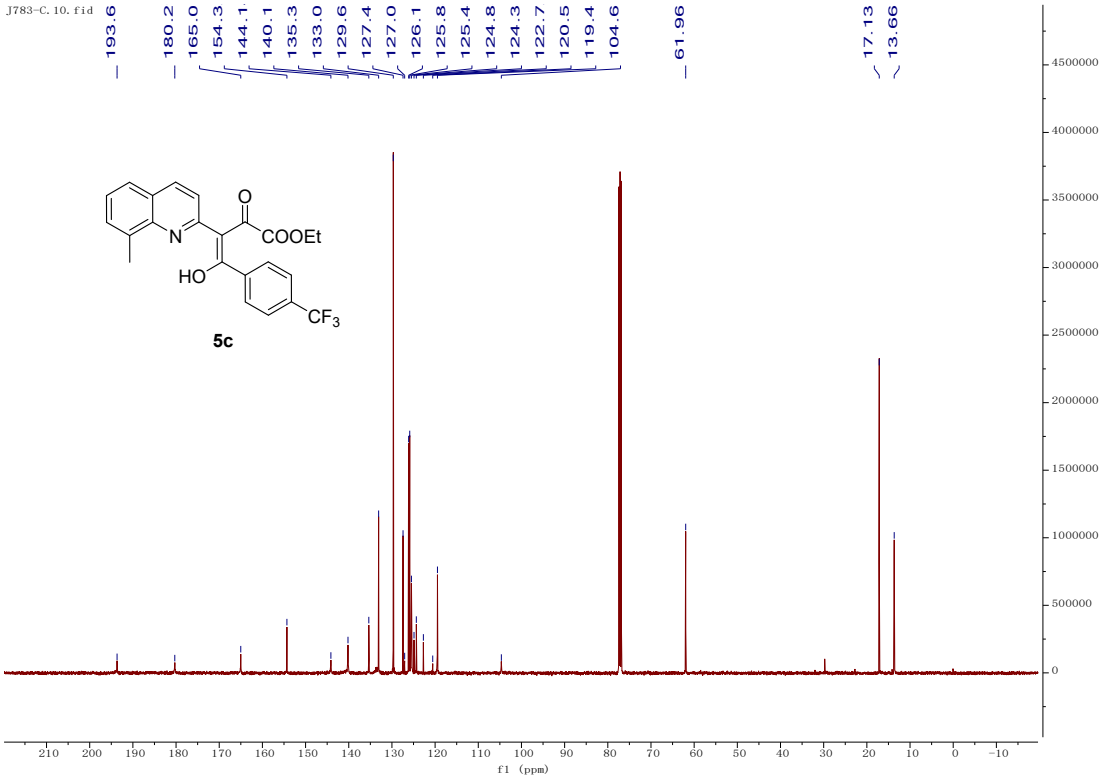
m/z: 391.1420 (100.0%), 392.1453 (24.9%), 393.1487 (3.0%), 393.1462 (1.0%)

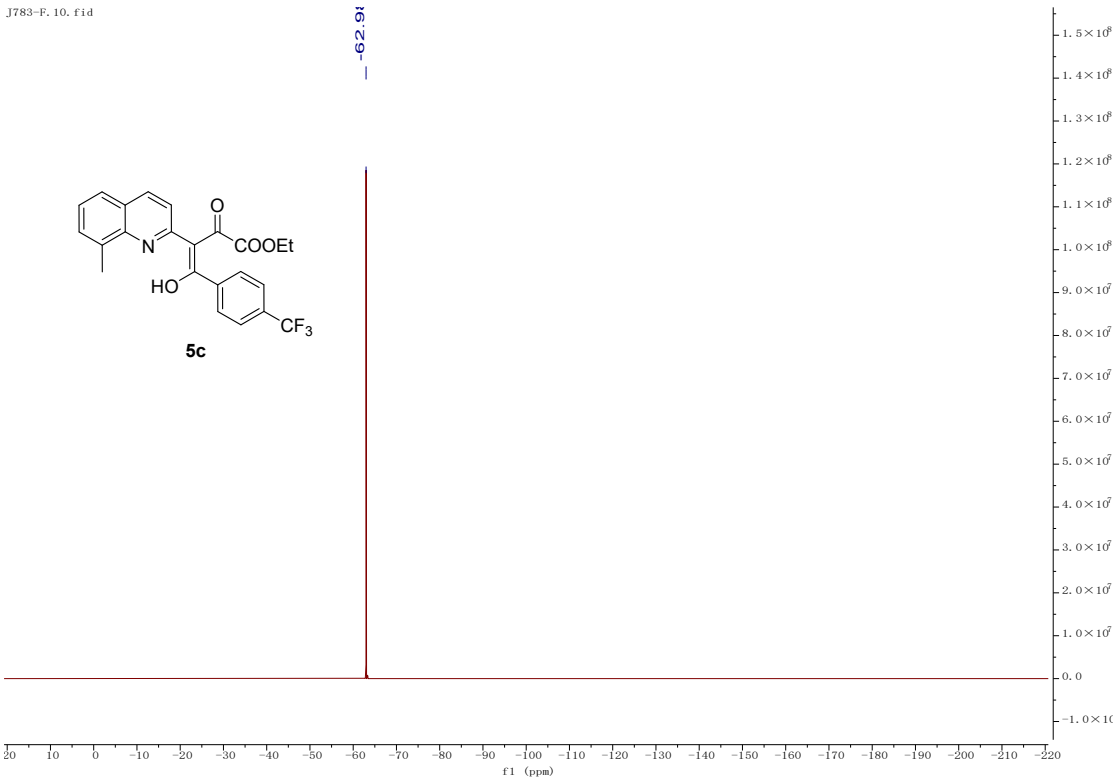
Elemental Analysis: C, 70.58; H, 5.41; N, 3.58; O, 20.44

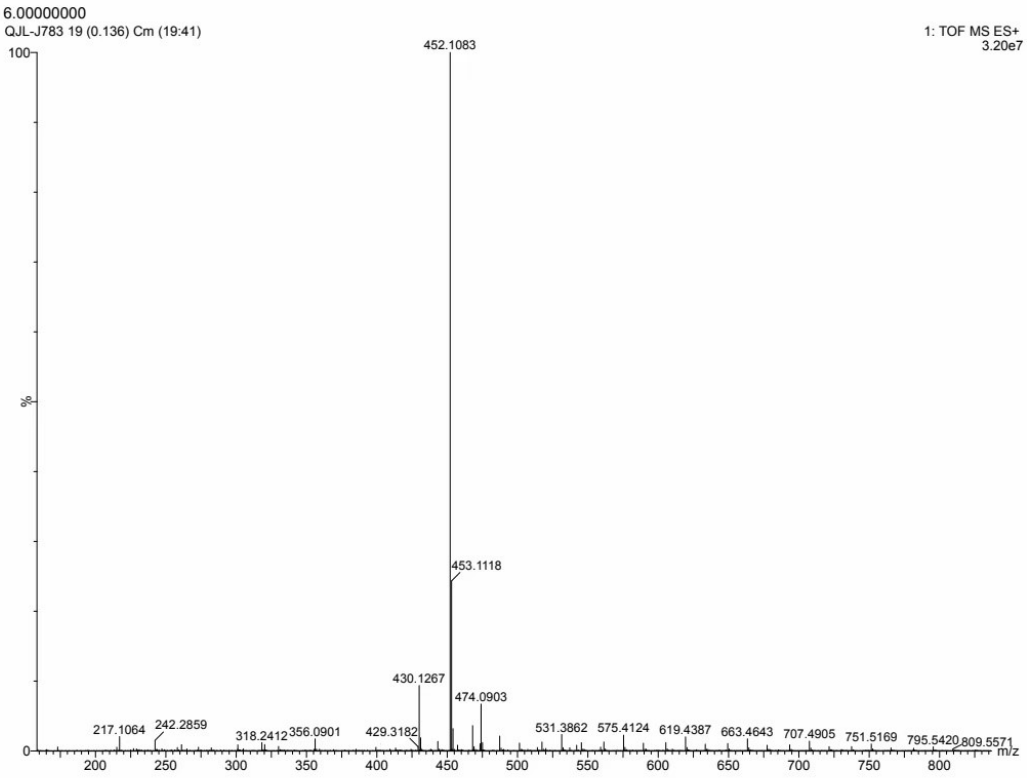
HRMS (ESI, m/z) calcd for $C_{23}H_{21}NO_5$ $[M+Na]^+$ 414.1312, found 414.1318.

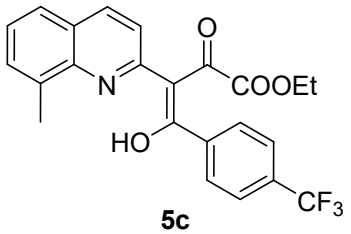
5c


J783-H. 10. fid
8.04
8.04
7.94
7.67
7.65
7.61
7.60
7.58
7.43
7.42
7.40
3.84
3.83
3.81
3.80
2.74
1.05
1.01
1.01
3.04
5.16
1.04
2.00
3.07
3.07
O
N
COOEt
HO
CF3
5c
f1 (ppm)


J783-C. 10. fid
193.6
180.2
165.0
154.3
144.1
140.1
135.3
133.0
129.6
127.4
127.0
126.1
125.8
125.4
124.8
124.3
122.7
120.5
119.4
104.6
61.96
17.13
13.66
O
N
COOEt
HO
CF3
5c
f1 (ppm)


J783-F.10.fid
-62.91
O
COOEt
N
HO
CF3
5c
1.5×10^8
1.4×10^8
1.3×10^8
1.2×10^8
1.1×10^8
1.0×10^8
9.0×10^7
8.0×10^7
7.0×10^7
6.0×10^7
5.0×10^7
4.0×10^7
3.0×10^7
2.0×10^7
1.0×10^7
0.0
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



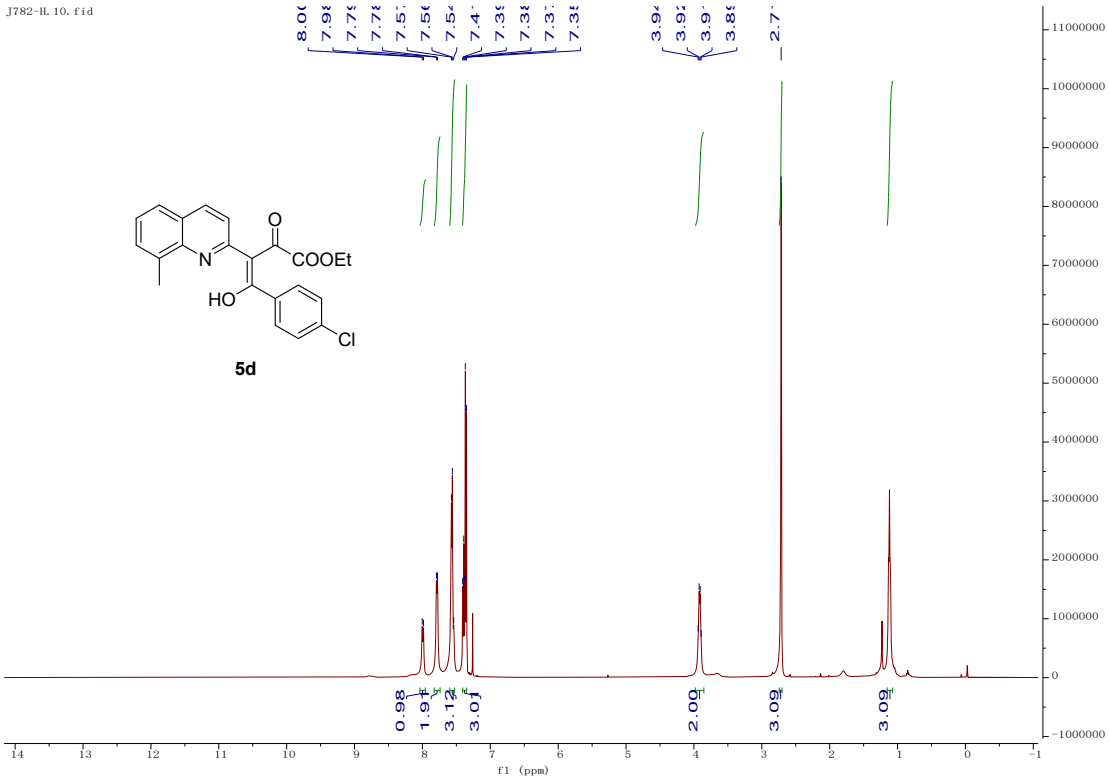


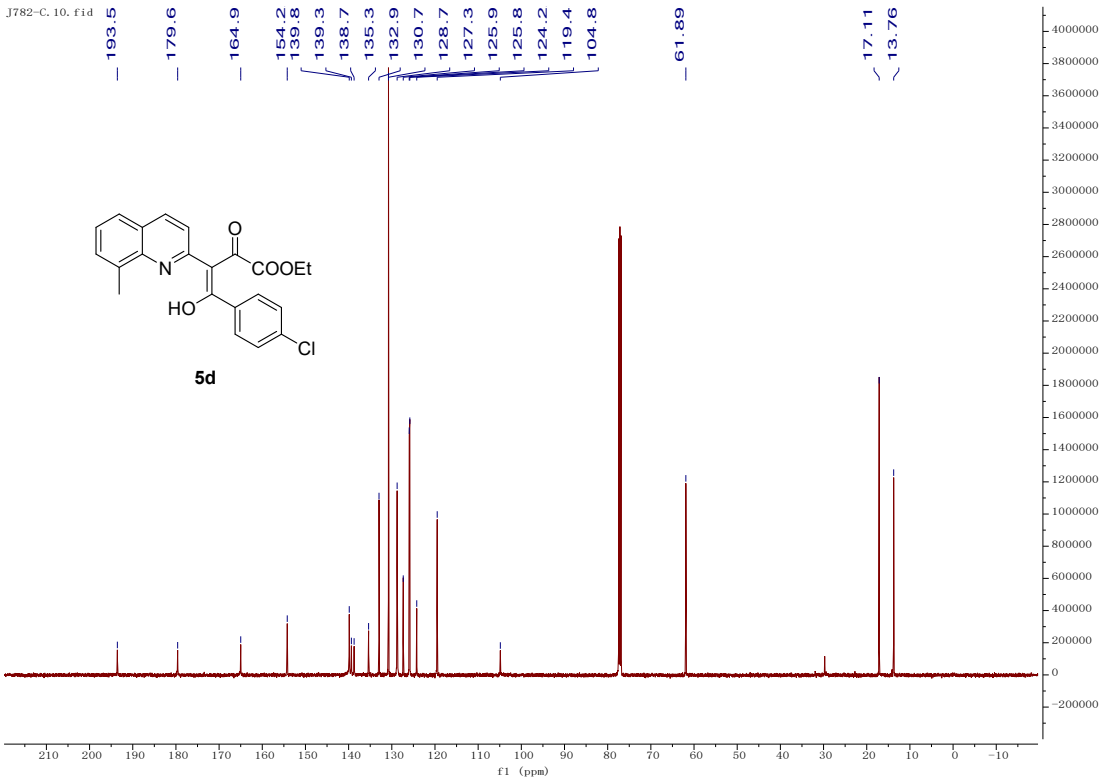
5c

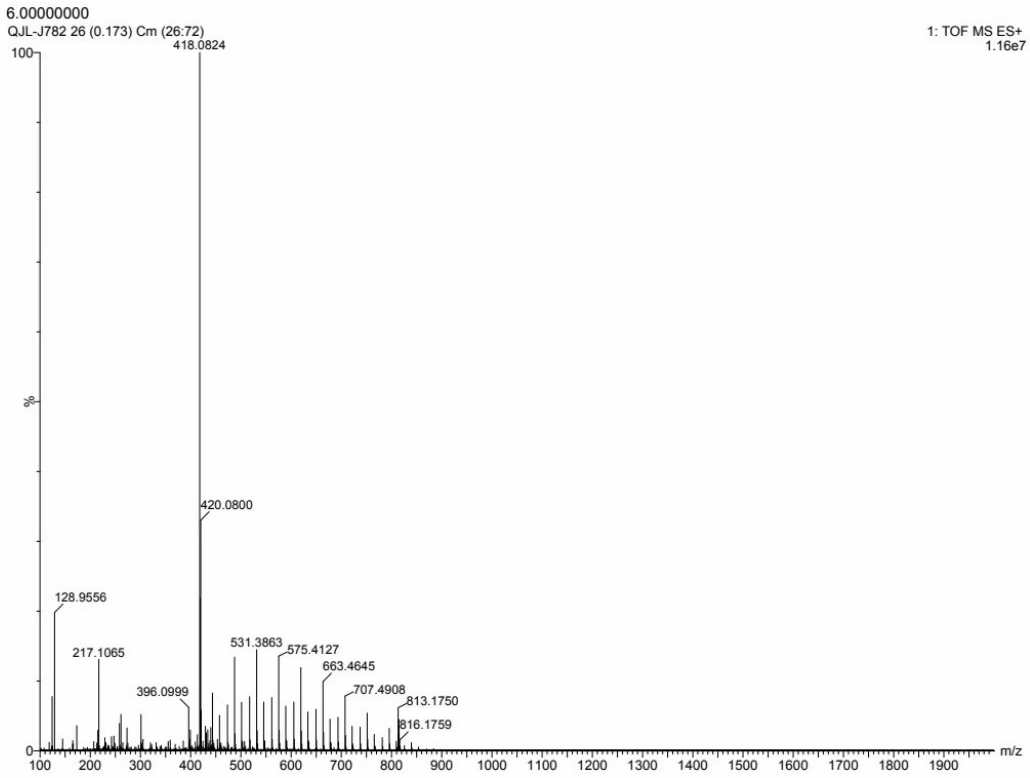
Chemical Formula: $C_{23}H_{18}F_3NO_4$
Exact Mass: 429.1188
Molecular Weight: 429.3952
m/z: 429.1188 (100.0%), 430.1221 (24.9%), 431.1255 (3.0%)
Elemental Analysis: C, 64.34; H, 4.23; F, 13.27; N, 3.26; O, 14.90

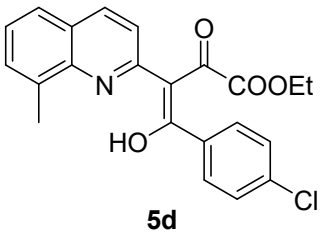
HRMS (ESI, m/z) calcd for $C_{23}H_{18}F_3NO_4$ $[M+Na]^+$ 452.1081, found 452.1083.

5d


J782-H.10.fid
8.00
7.98
7.79
7.78
7.55
7.56
7.54
7.41
7.39
7.38
7.37
7.35
3.94
3.92
3.90
3.85
2.77
0.98
1.93
3.12
3.01
2.00
3.09
3.09
f1 (ppm)
O
N
COOEt
HO
Cl
5d


J782-C.10.fid
193.5
179.6
164.9
154.2
139.8
139.3
138.7
135.3
132.9
130.7
128.7
127.3
125.9
125.8
124.2
119.4
104.8
61.89
17.11
13.76
f1 (ppm)
O
N
COOEt
HO
Cl
5d





5d

Chemical Formula: $C_{22}H_{18}ClNO_4$

Exact Mass: 395.0924

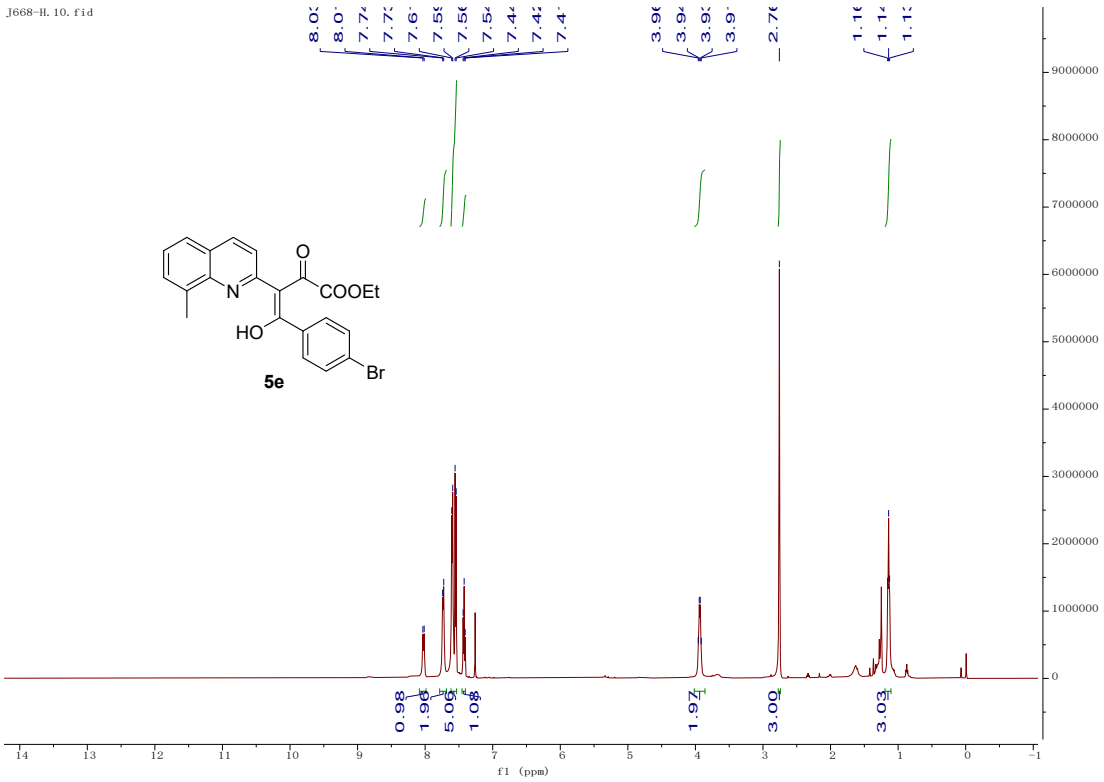
Molecular Weight: 395.8390

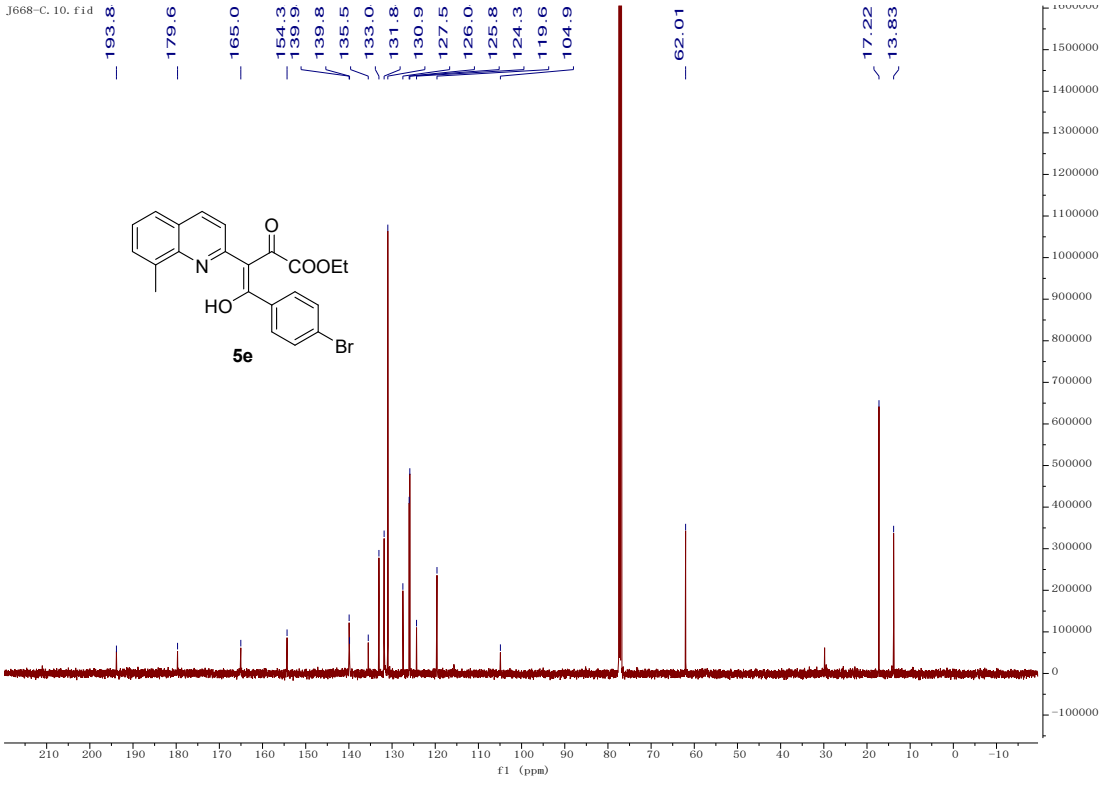
m/z: 395.0924 (100.0%), 397.0895 (32.0%), 396.0958 (23.8%), 398.0928 (7.6%), 397.0991 (2.7%)

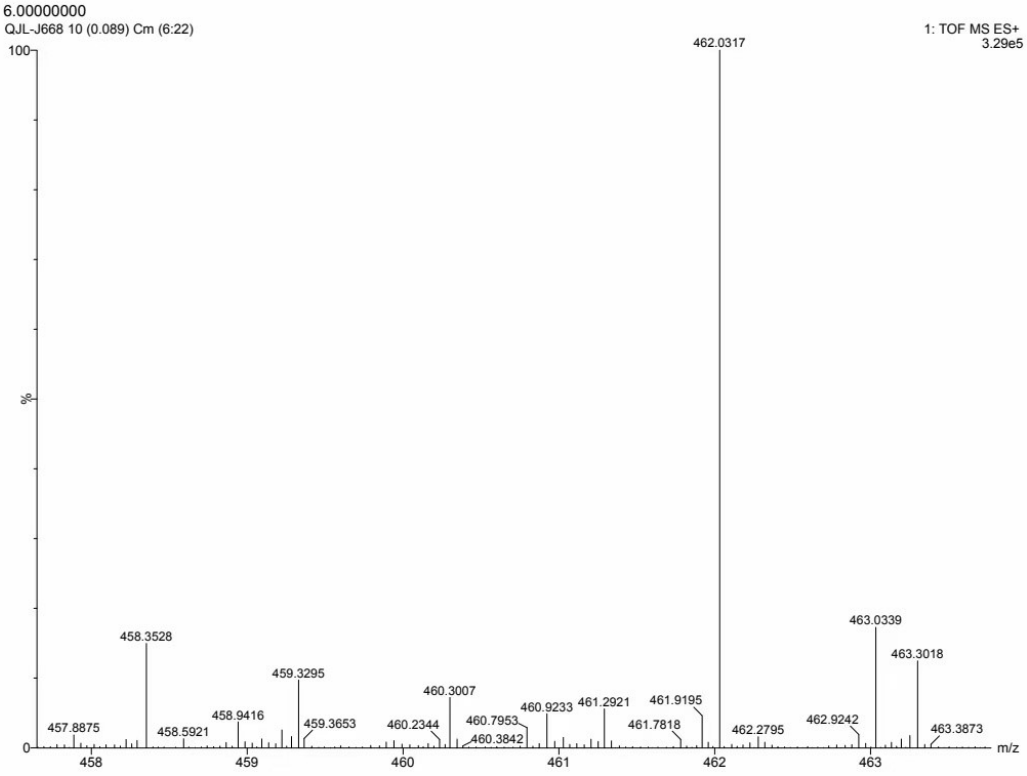
Elemental Analysis: C, 66.75; H, 4.58; Cl, 8.96; N, 3.54; O, 16.17

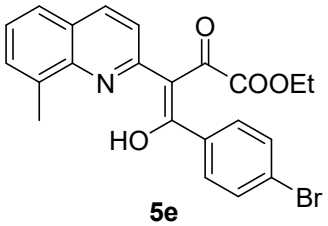
HRMS (ESI, m/z) calcd for $C_{22}H_{18}ClNO_4$ $[M+Na]^+$ 418.0817, found 418.0824.

5e


J668-H. 10. fid
8.0
8.0
7.7
7.7
7.6
7.5
7.5
7.5
7.4
7.4
7.4
3.9
3.9
3.9
3.9
2.7
1.1
1.1
1.1
O
N
COOEt
HO
Br
5e
0.98
1.96
5.05
1.08
1.97
3.00
3.03
f1 (ppm)


J668-C. 10. fid
193.8
179.6
165.0
154.3
139.9
139.8
135.5
133.0
131.8
130.9
127.5
126.0
125.8
124.3
119.6
104.9
62.01
17.22
13.83
O
N
COOEt
HO
Br
5e
f1 (ppm)





5e

Chemical Formula: $C_{22}H_{18}BrNO_4$

Exact Mass: 439.0419

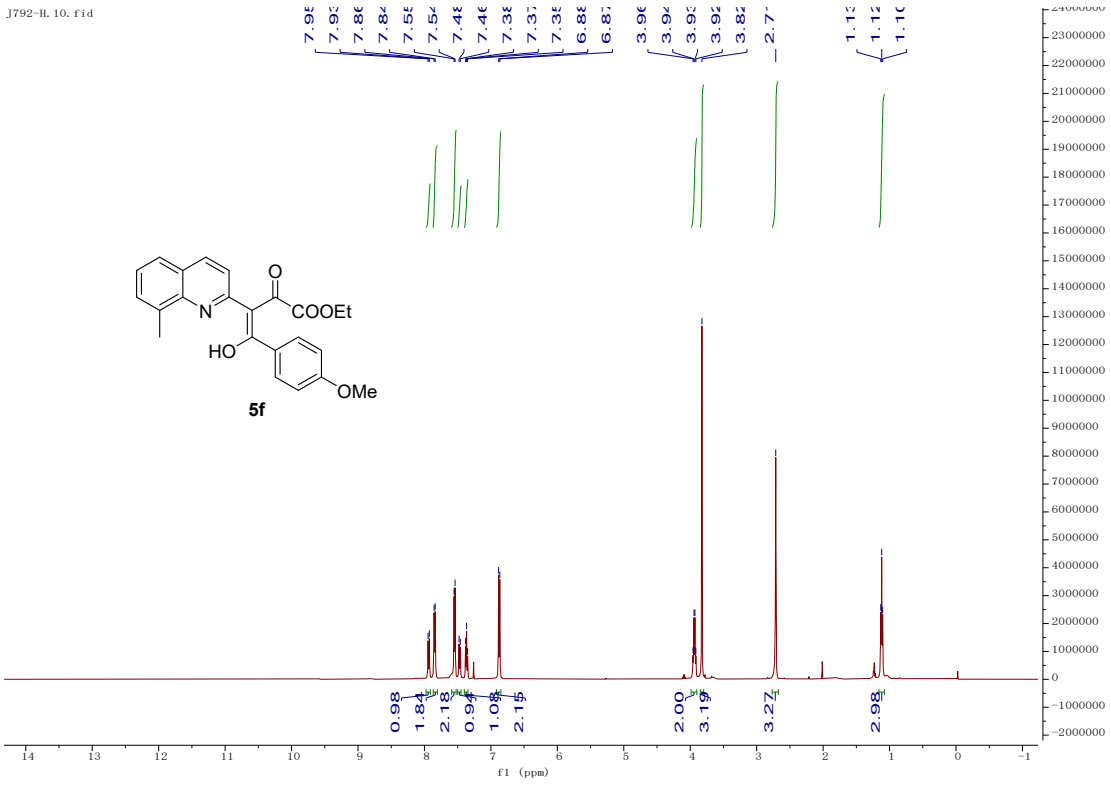
Molecular Weight: 440.2930

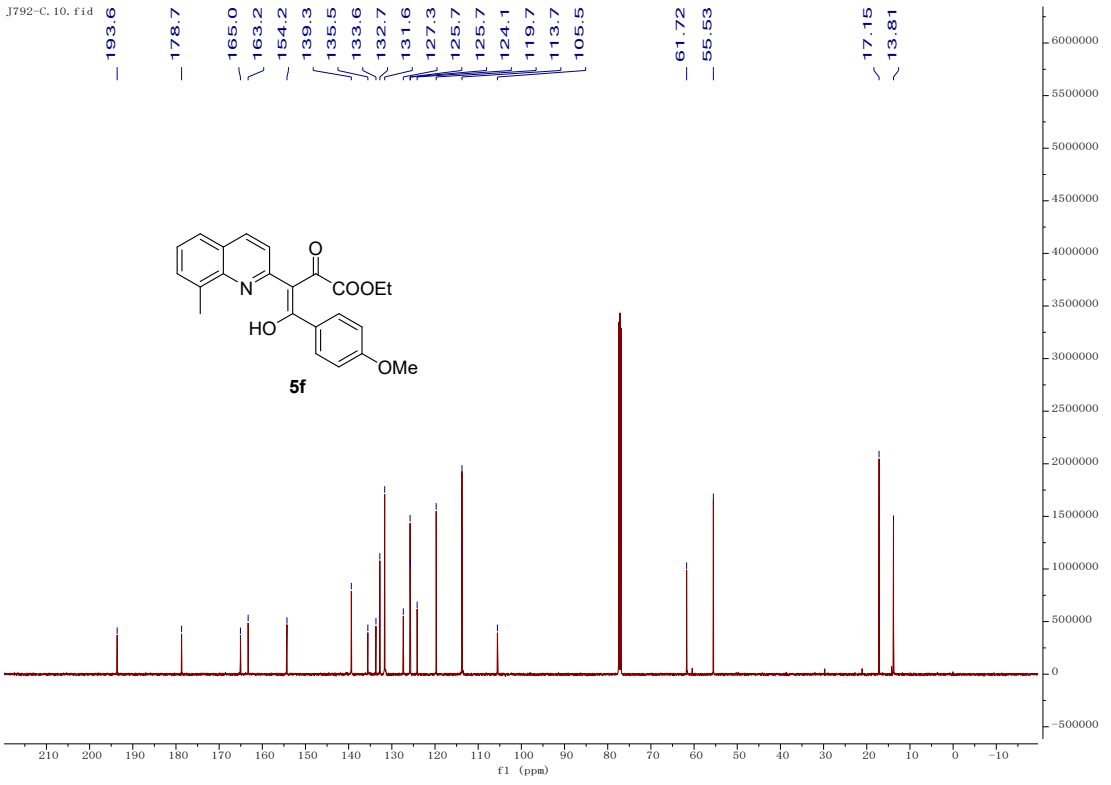
m/z: 439.0419 (100.0%), 441.0399 (97.3%), 440.0453 (23.8%), 442.0432 (23.1%), 441.0486 (2.7%), 443.0466 (2.6%)

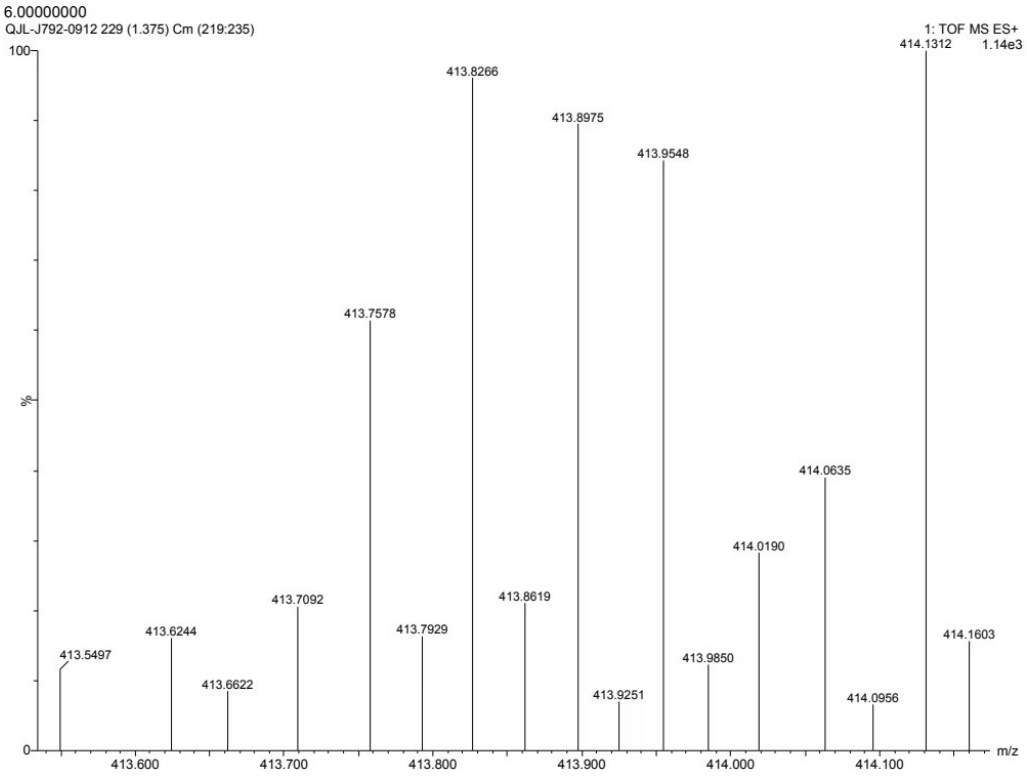
Elemental Analysis: C, 60.02; H, 4.12; Br, 18.15; N, 3.18; O, 14.53

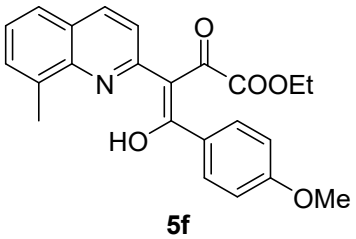
HRMS (ESI, m/z) calcd for $C_{22}H_{18}BrNO_4$ $[M+Na]^+$ 462.0312, found 462.0317.

5f


J792-H.10.fid
7.95
7.93
7.86
7.84
7.55
7.54
7.48
7.46
7.38
7.37
7.35
6.88
6.87
3.96
3.94
3.93
3.92
3.82
2.71
1.13
1.12
1.10
O
N
COOEt
HO
OMe
5f
0.98
1.84
2.18
0.94
1.09
2.15
2.00
3.19
3.27
2.98
f1 (ppm)


J792-C.10.fid
193.6
178.7
165.0
163.2
154.2
139.3
135.5
133.6
132.7
131.6
127.3
125.7
125.7
124.1
119.7
113.7
105.5
61.72
55.53
17.15
13.81
O
N
COOEt
HO
OMe
5f
f1 (ppm)



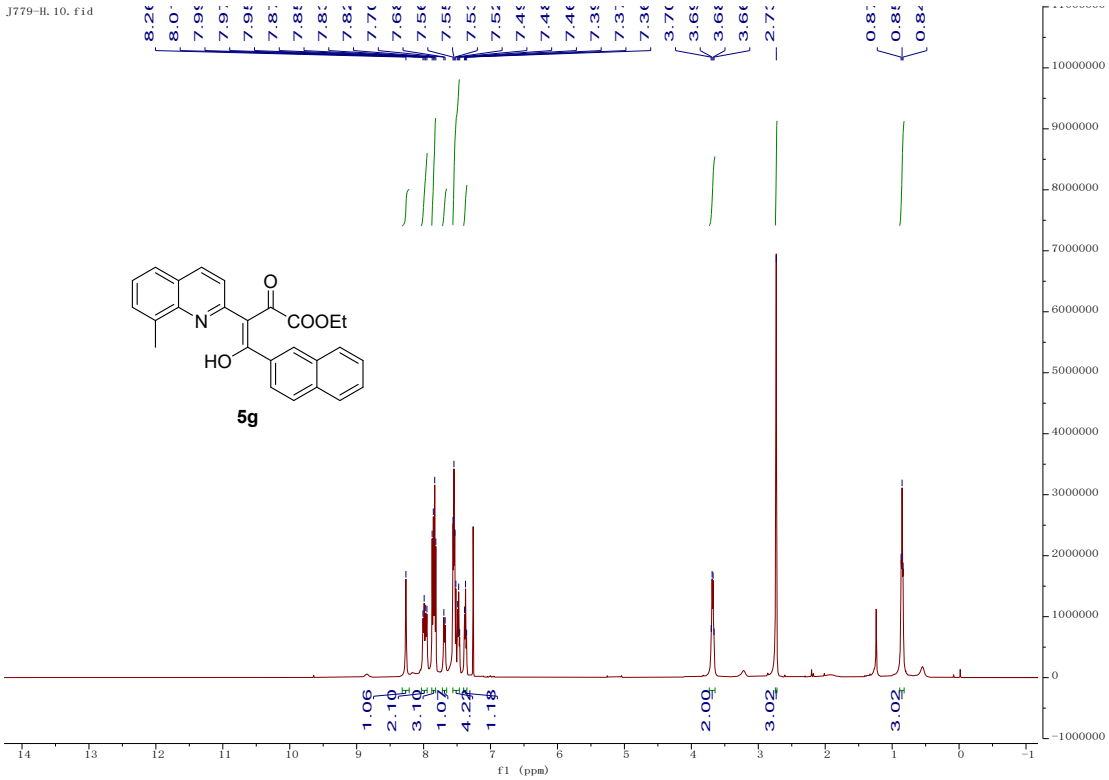


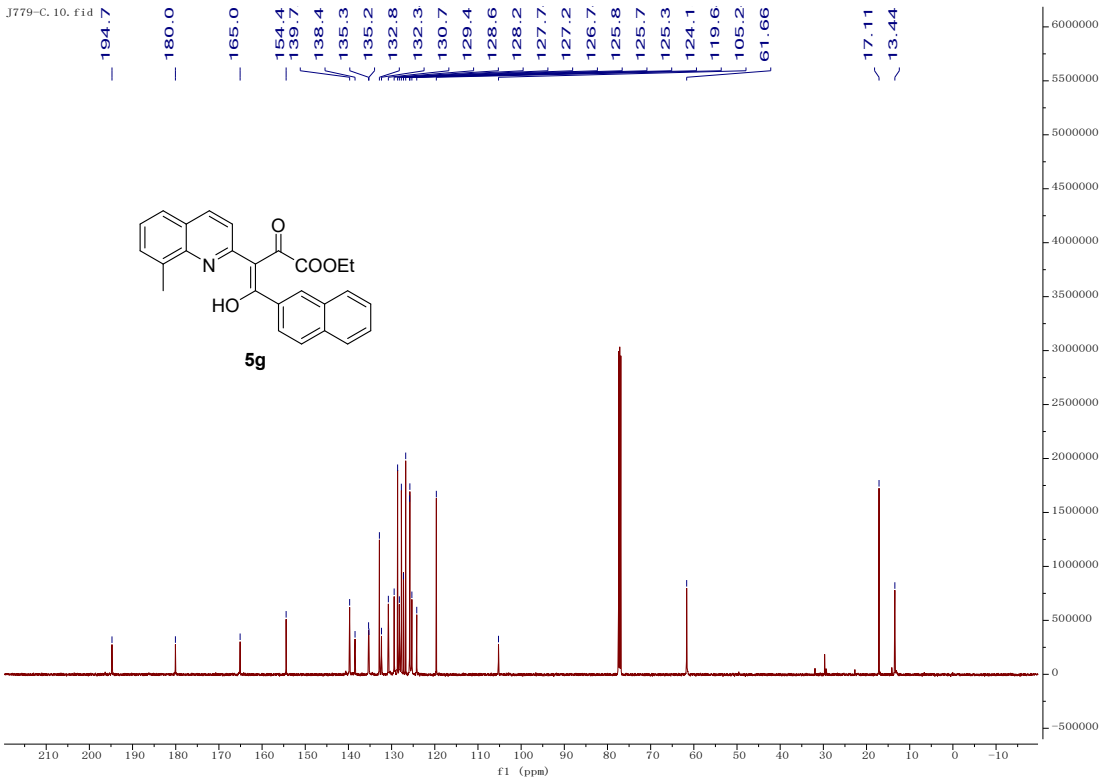
5f

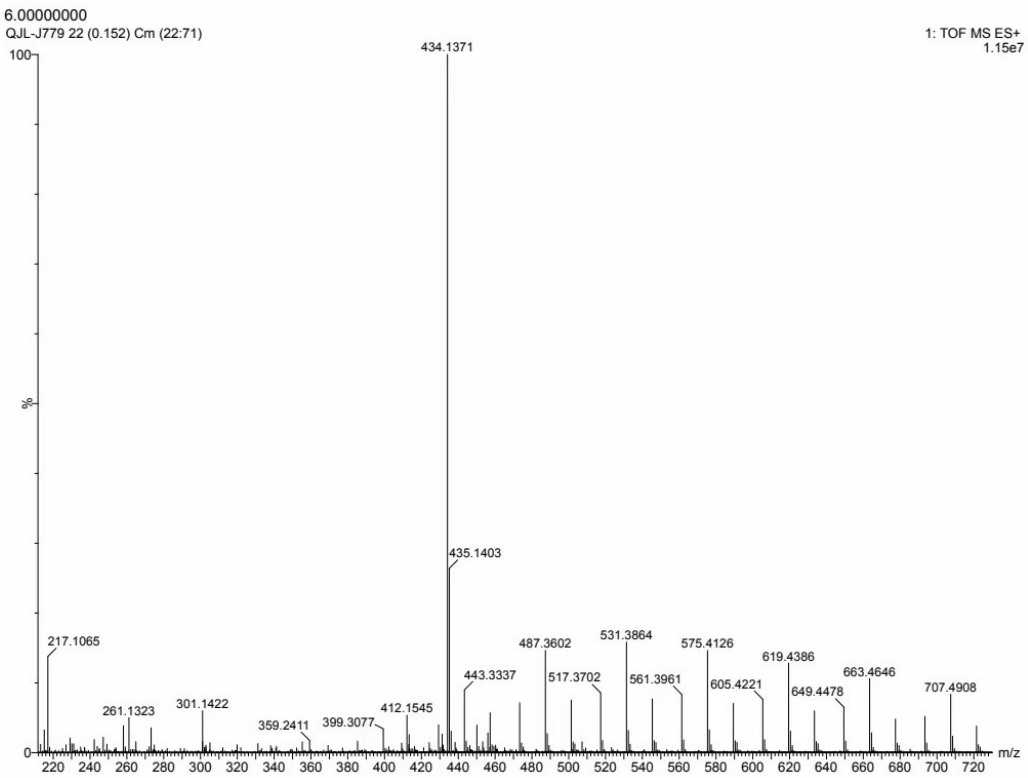
Chemical Formula: $C_{23}H_{21}NO_5$
Exact Mass: 391.1420
Molecular Weight: 391.4230
m/z: 391.1420 (100.0%), 392.1453 (24.9%), 393.1487 (3.0%), 393.1462 (1.0%)
Elemental Analysis: C, 70.58; H, 5.41; N, 3.58; O, 20.44

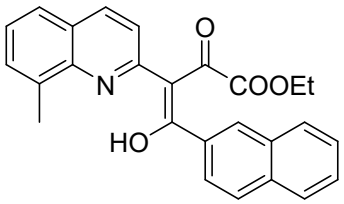
HRMS (ESI, m/z) calcd for $C_{23}H_{21}NO_5$ $[M+Na]^+$ 414.1312, found 414.1312.

5g


J779-H.10.fid
8.26
8.01
7.95
7.93
7.91
7.87
7.85
7.83
7.82
7.81
7.77
7.76
7.68
7.56
7.55
7.54
7.52
7.45
7.43
7.41
7.40
7.35
7.33
7.30
3.70
3.65
3.64
3.60
2.72
0.87
0.85
0.84
O
N
COOEt
HO
5g
1.06
2.10
3.10
1.07
4.22
1.18
2.00
3.02
3.02
f1 (ppm)


J779-C.10.fid
194.7
180.0
165.0
154.4
139.7
138.4
135.3
135.2
132.8
132.3
130.7
129.4
128.6
128.2
127.7
127.2
126.7
125.8
125.7
125.3
124.1
119.6
105.2
61.66
17.11
13.44
O
N
COOEt
HO
5g
f1 (ppm)



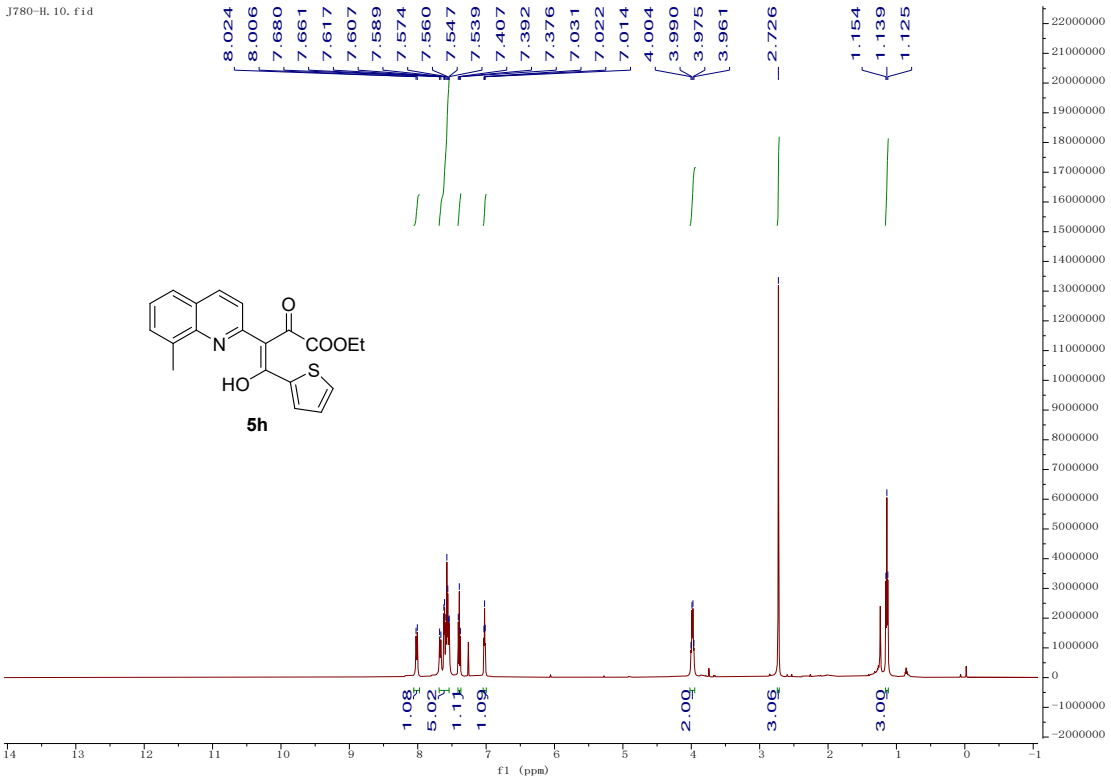


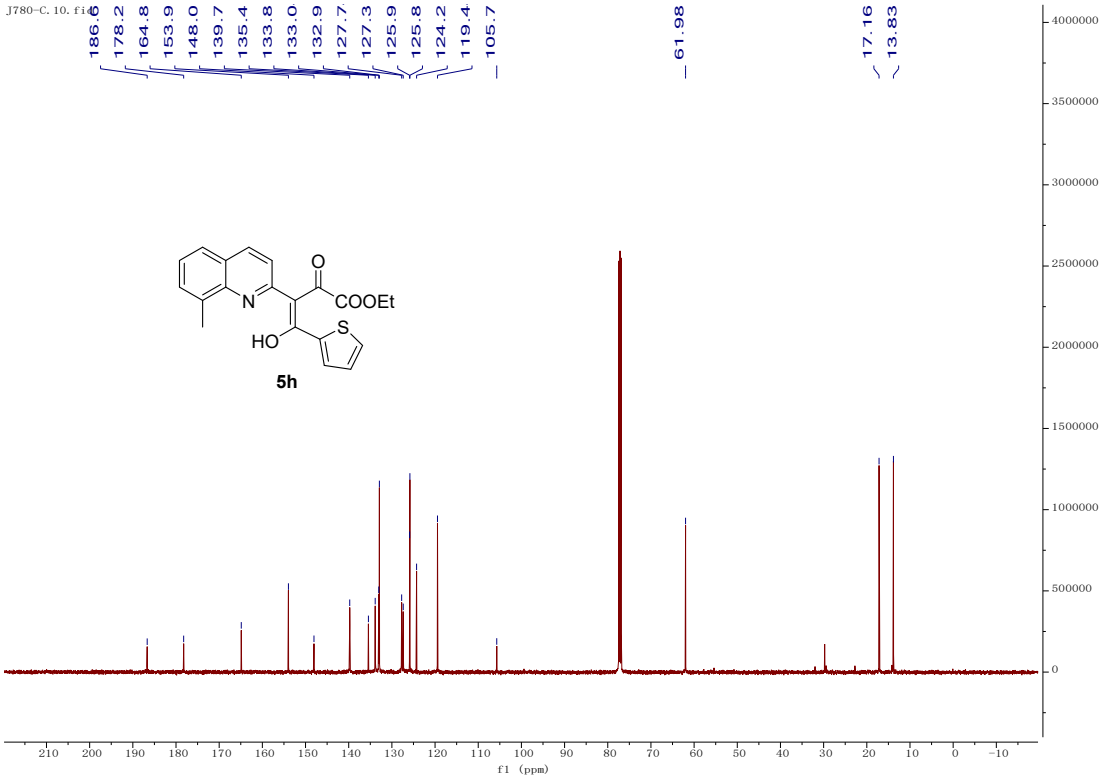
5g

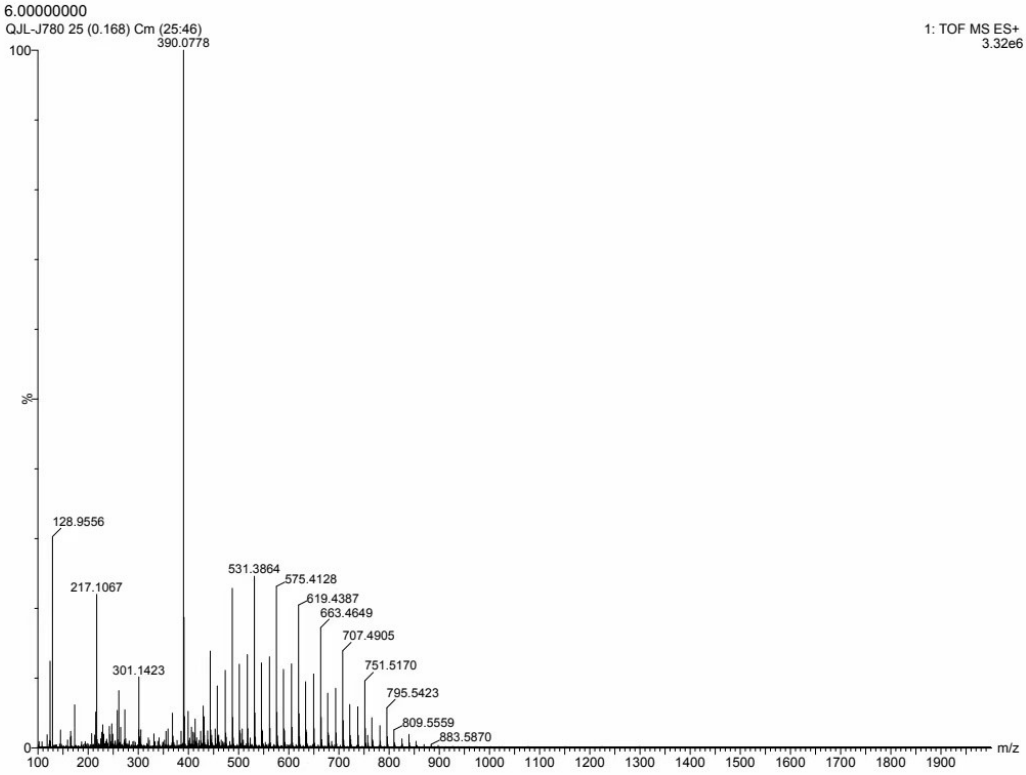
Chemical Formula: $C_{26}H_{21}NO_4$
Exact Mass: 411.1471
Molecular Weight: 411.4570
m/z: 411.1471 (100.0%), 412.1504 (28.1%), 413.1538 (3.8%)
Elemental Analysis: C, 75.90; H, 5.14; N, 3.40; O, 15.55

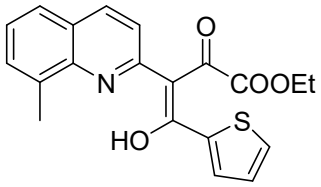
HRMS (ESI, m/z) calcd for $C_{26}H_{21}NO_4$ $[M+Na]^+$ 434.1363, found 434.1371.

5h


J780-H. 10. fid
8.024
8.006
7.680
7.661
7.617
7.607
7.589
7.574
7.560
7.547
7.539
7.407
7.392
7.376
7.031
7.022
7.014
4.004
3.990
3.975
3.961
2.726
1.154
1.139
1.125
O
N
COOEt
HO
S
5h
1.08
5.02
1.11
1.09
2.00
3.06
3.00
f1 (ppm)


J780-C. 10. fid
186.6
178.2
164.8
153.9
148.0
139.7
135.4
133.8
133.0
132.9
127.7
127.3
125.9
125.8
124.2
119.4
105.7
61.98
17.16
13.83
O
N
COOEt
HO
S
5h
f1 (ppm)



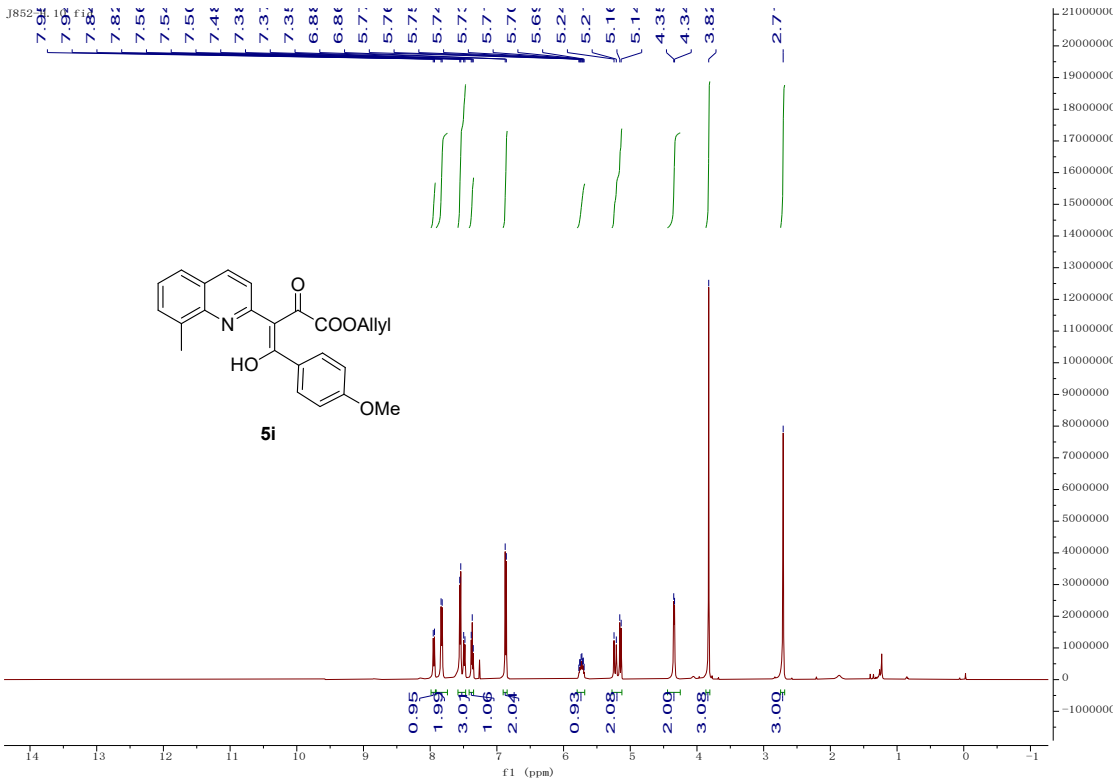


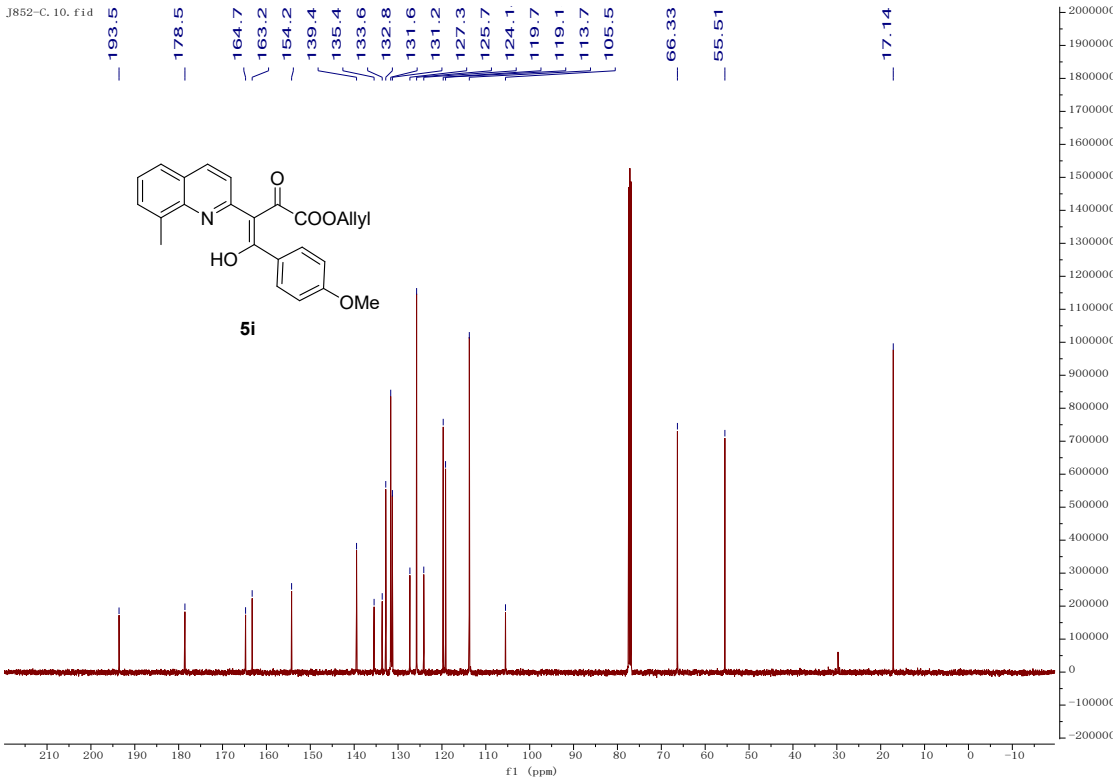
5h

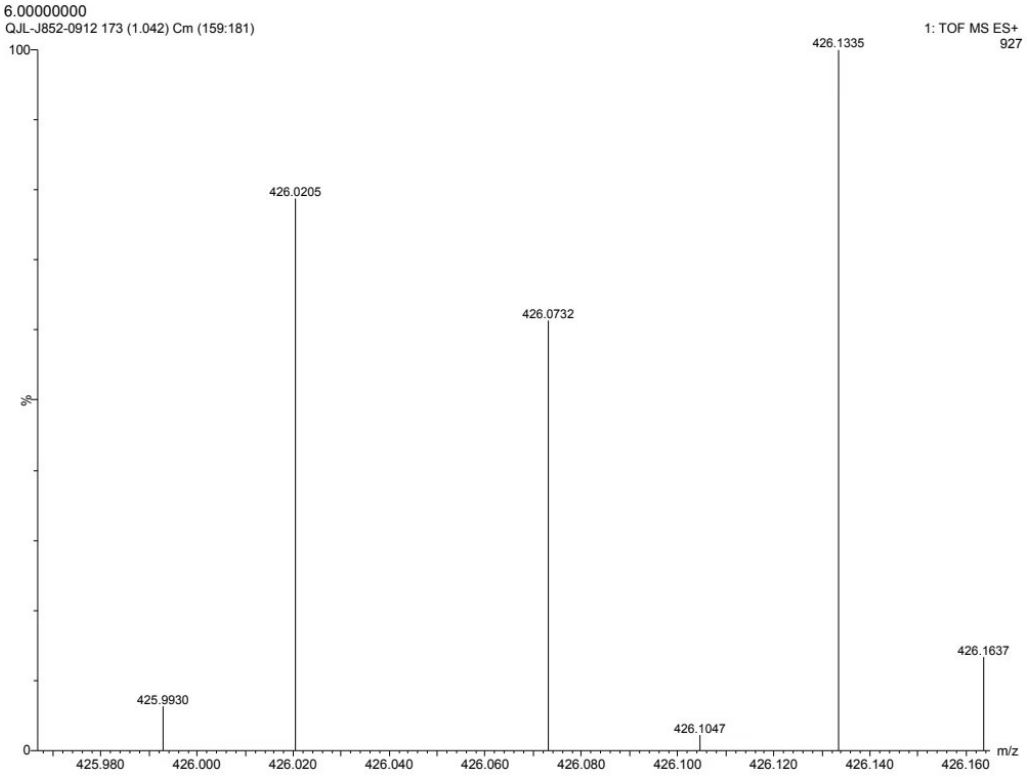
Chemical Formula: $C_{20}H_{17}NO_4S$
Exact Mass: 367.0878
Molecular Weight: 367.4190
m/z: 367.0878 (100.0%), 368.0912 (21.6%),
369.0836 (4.5%), 369.0945 (2.2%), 370.0870 (1.0%)
Elemental Analysis: C, 65.38; H, 4.66; N, 3.81; O, 17.42; S, 8.73

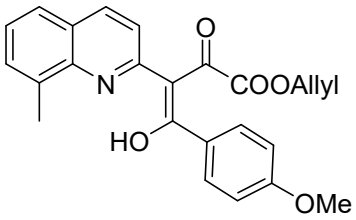
HRMS (ESI, m/z) calcd for $C_{20}H_{17}NO_4S$ $[M+Na]^+$ 390.0771, found 390.0778.

5i







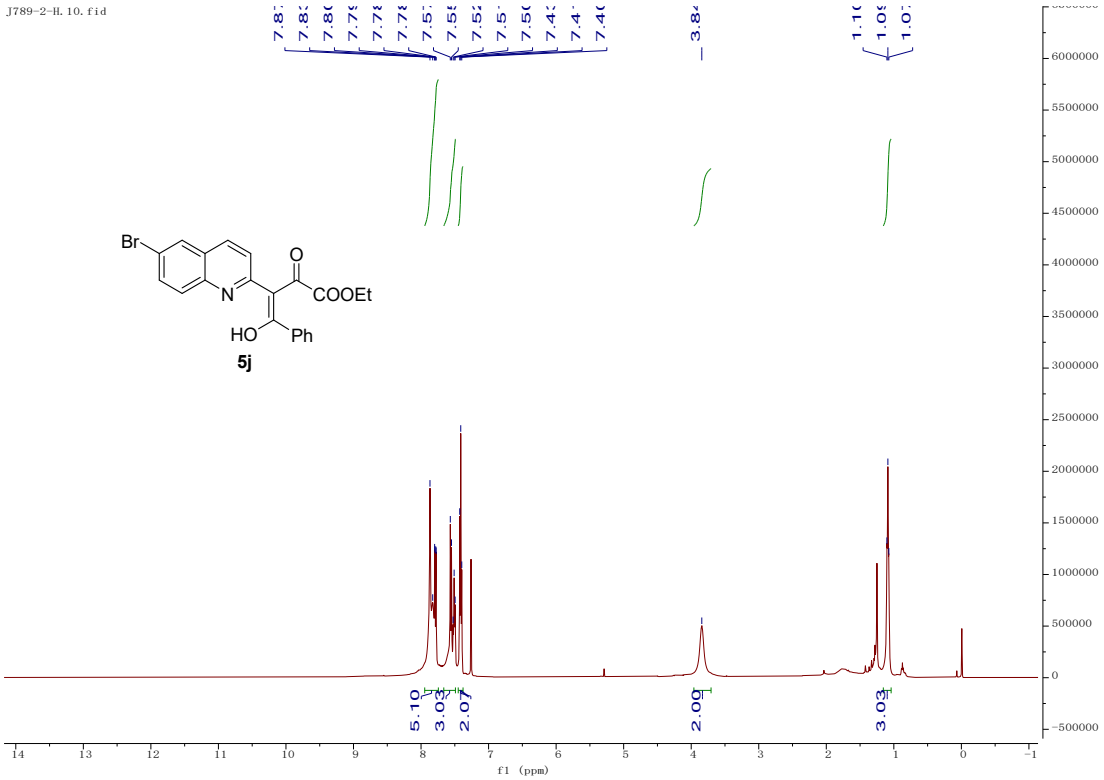


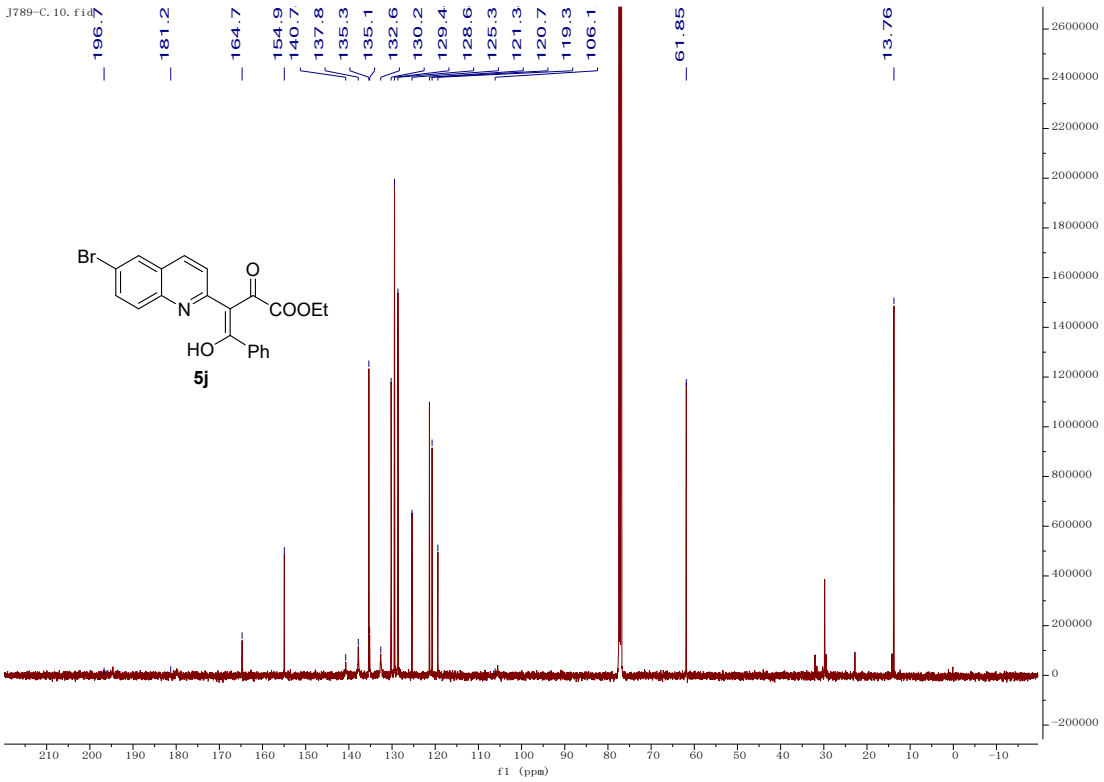
5i

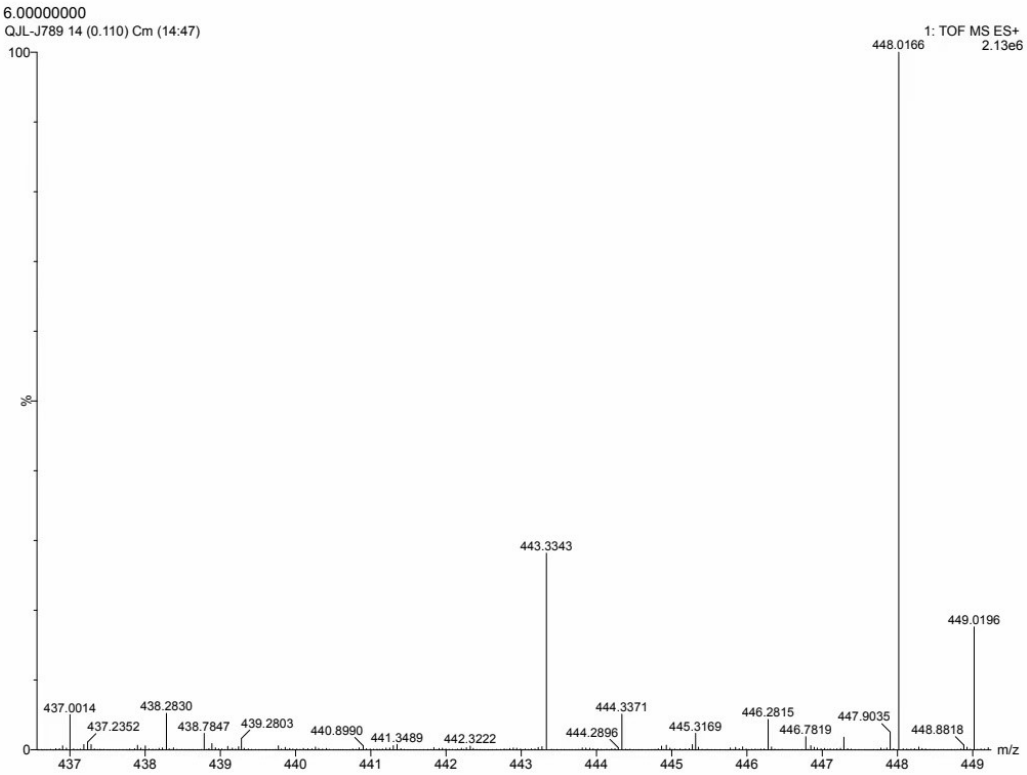
Chemical Formula: $C_{24}H_{21}NO_5$
Exact Mass: 403.1420
Molecular Weight: 403.4340
m/z: 403.1420 (100.0%), 404.1453 (26.0%), 405.1487 (3.2%), 405.1462 (1.0%)
Elemental Analysis: C, 71.45; H, 5.25; N, 3.47; O, 19.83

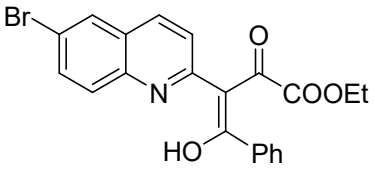
HRMS (ESI, m/z) calcd for $C_{24}H_{21}NO_5$ $[M+Na]^+$ 426.1312, found 426.1335.

5j


J789-2-H.10.fid
Br
O
N
COOEt
HO
Ph
5j
5.10
3.02
2.07
2.00
3.03
f1 (ppm)


J789-C.10.fid
196.7
181.2
164.7
154.9
140.7
137.8
135.3
135.1
132.6
130.2
129.4
128.6
125.3
121.3
120.7
119.3
106.1
61.85
13.76
Br
O
N
COOEt
HO
Ph
5j
f1 (ppm)



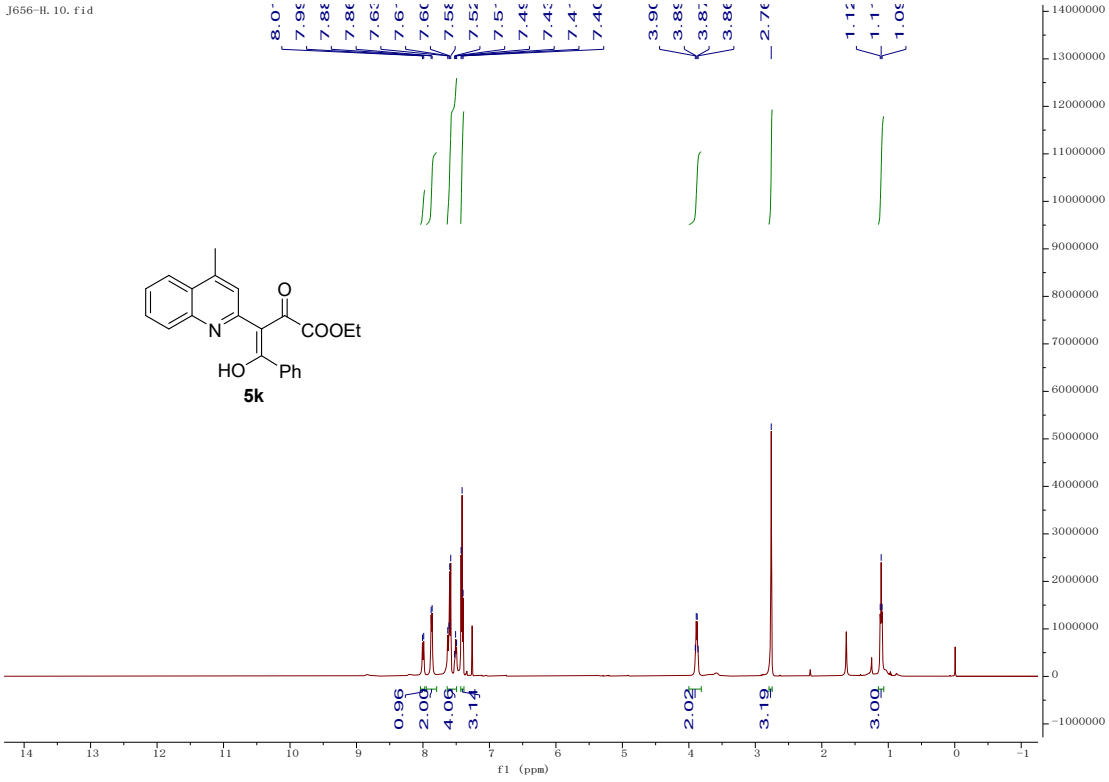


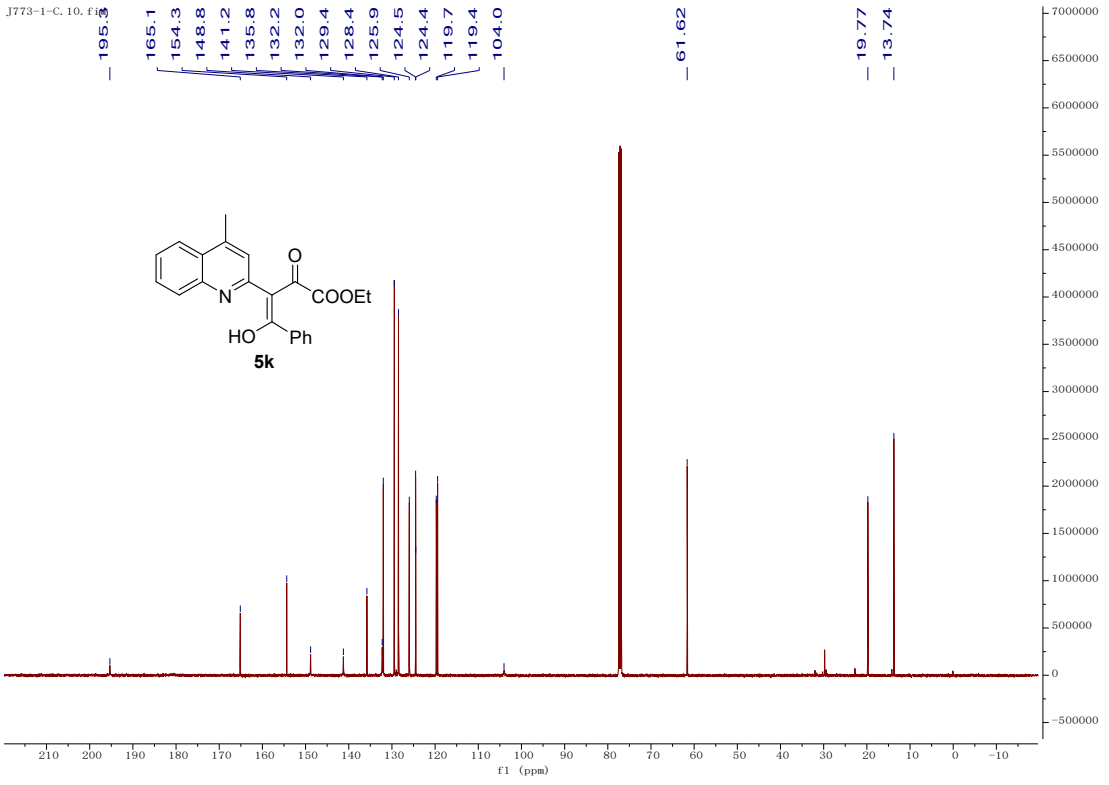
5j

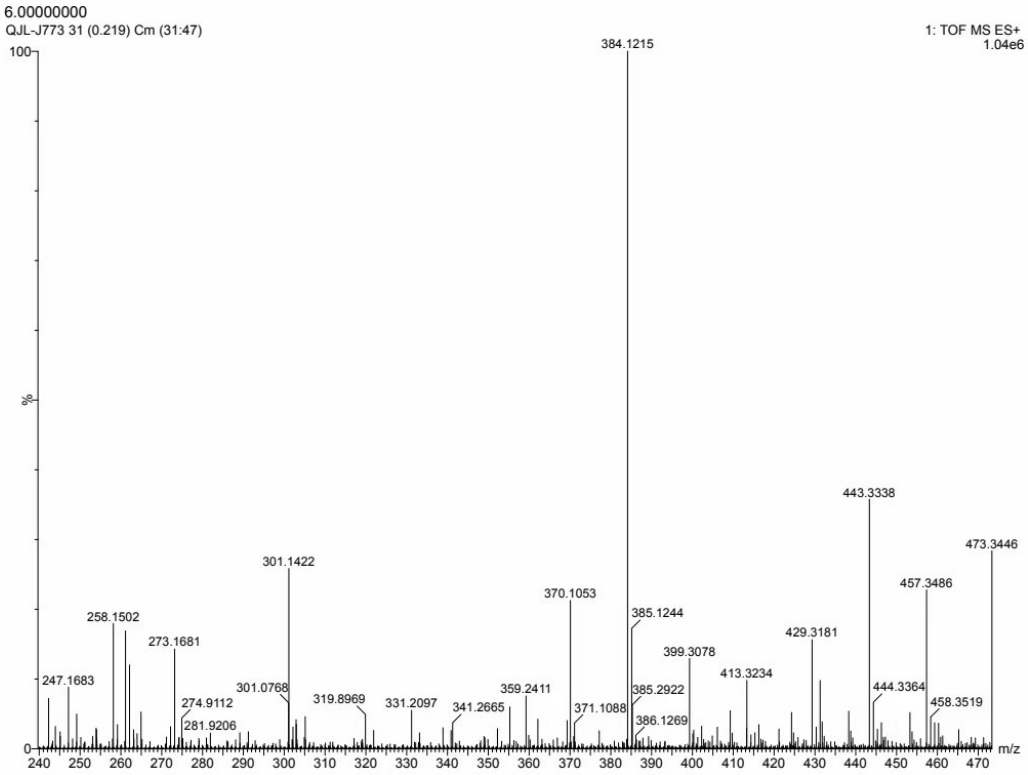
Chemical Formula: $C_{21}H_{16}BrNO_4$
Exact Mass: 425.0263
Molecular Weight: 426.2660
m/z: 425.0263 (100.0%), 427.0242 (97.3%), 426.0296 (22.7%),
428.0276 (22.1%), 427.0330 (2.5%), 429.0309 (2.4%)
Elemental Analysis: C, 59.17; H, 3.78; Br, 18.75; N, 3.29; O, 15.01

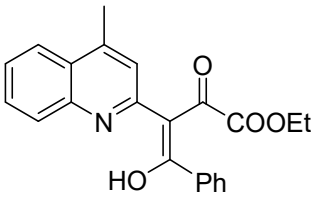
HRMS (ESI, m/z) calcd for $C_{21}H_{16}BrNO_4$ $[M+Na]^+$ 448.0155, found 448.0166.

5k


J656-H. 10. fid
8.0
7.95
7.85
7.86
7.63
7.6
7.60
7.58
7.52
7.5
7.45
7.42
7.4
7.40
3.90
3.85
3.87
3.86
2.76
1.15
1.1
1.05
O
N
COOEt
HO
Ph
5k
0.96
2.00
4.06
3.14
2.02
3.19
3.00
f1 (ppm)


J773-1-C. 10. fid
195.3
165.1
154.3
148.8
141.2
135.8
132.2
132.0
129.4
128.4
125.9
124.5
124.4
119.7
119.4
104.0
61.62
19.77
13.74
O
N
COOEt
HO
Ph
5k
f1 (ppm)



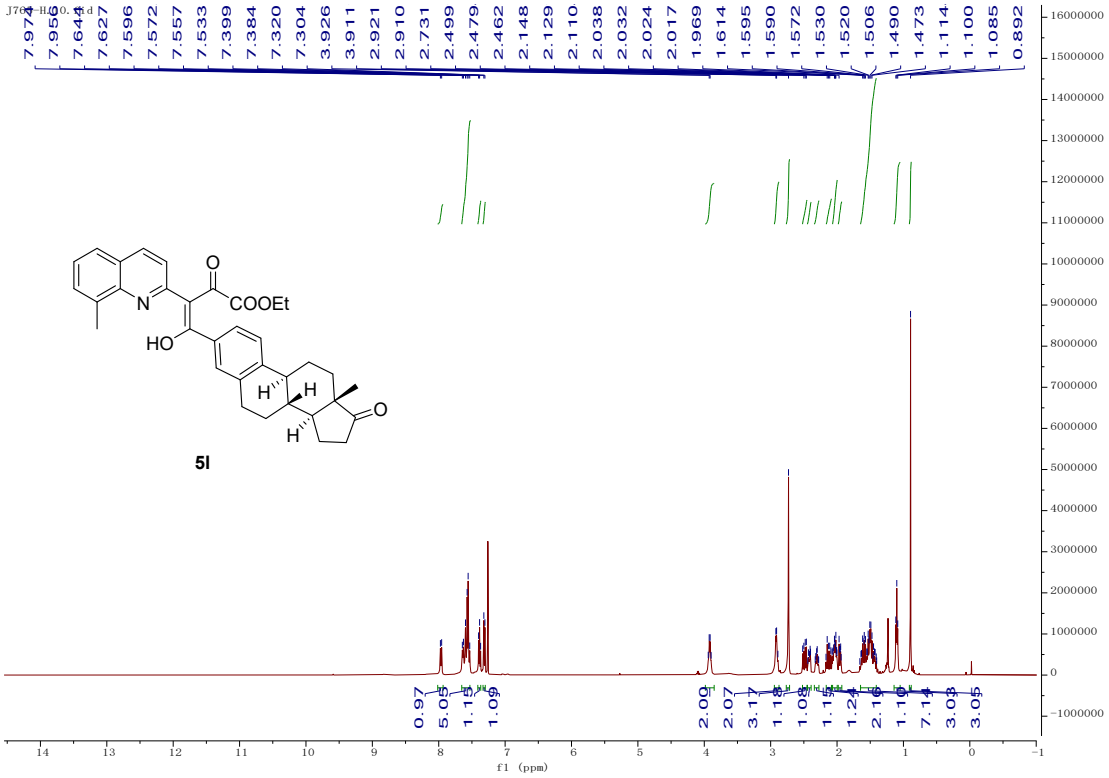


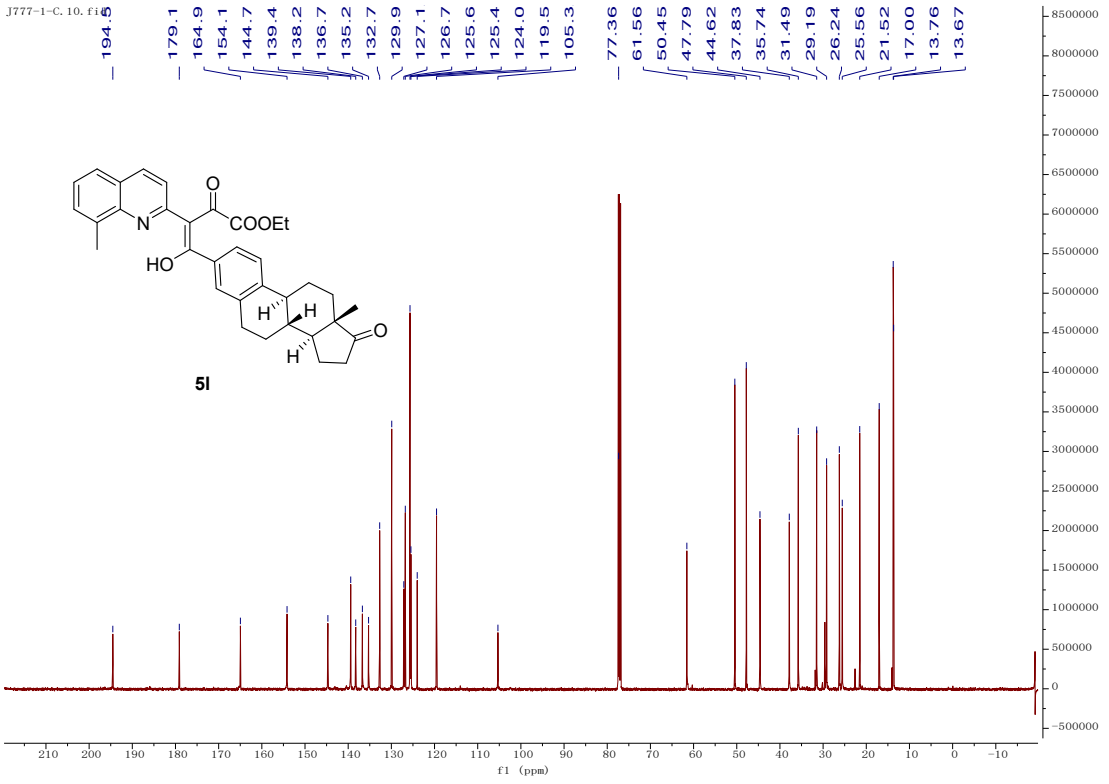
5k

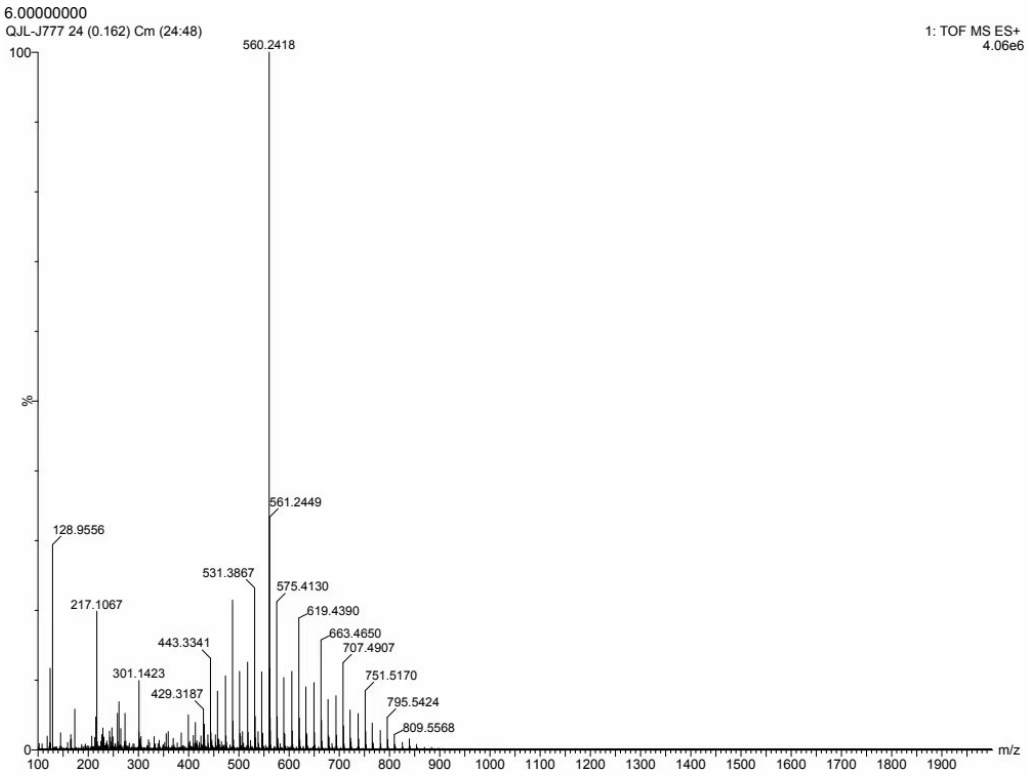
Chemical Formula: $C_{22}H_{19}NO_4$
Exact Mass: 361.1314
Molecular Weight: 361.3970
m/z: 361.1314 (100.0%), 362.1348 (23.8%), 363.1381 (2.7%)
Elemental Analysis: C, 73.12; H, 5.30; N, 3.88; O, 17.71

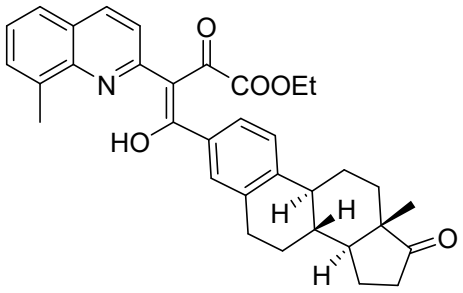
HRMS (ESI, m/z) calcd for $C_{22}H_{19}NO_4$ $[M+Na]^+$ 384.1207, found 384.1215.

5l


7.974
7.956
7.644
7.627
7.596
7.572
7.557
7.533
7.399
7.384
7.320
7.304
3.926
3.911
2.921
2.910
2.731
2.499
2.479
2.462
2.148
2.129
2.110
2.038
2.032
2.024
2.017
1.969
1.614
1.595
1.590
1.572
1.530
1.520
1.506
1.490
1.473
1.114
1.100
1.085
0.892
O
N
COOEt
HO
H
H
H
O
5l
0.97
5.00
1.15
1.09
2.00
2.07
3.17
1.18
1.02
1.15
1.24
2.16
1.19
7.14
3.03
3.05
f1 (ppm)


194.5
179.1
164.9
154.1
144.7
139.4
138.2
136.7
135.2
132.7
129.9
127.1
126.7
125.6
125.4
124.0
119.5
105.3
77.36
61.56
50.45
47.79
44.62
37.83
35.74
31.49
29.19
26.24
25.56
21.52
17.00
13.76
13.67
O
N
COOEt
HO
H
H
H
O
5l
f1 (ppm)



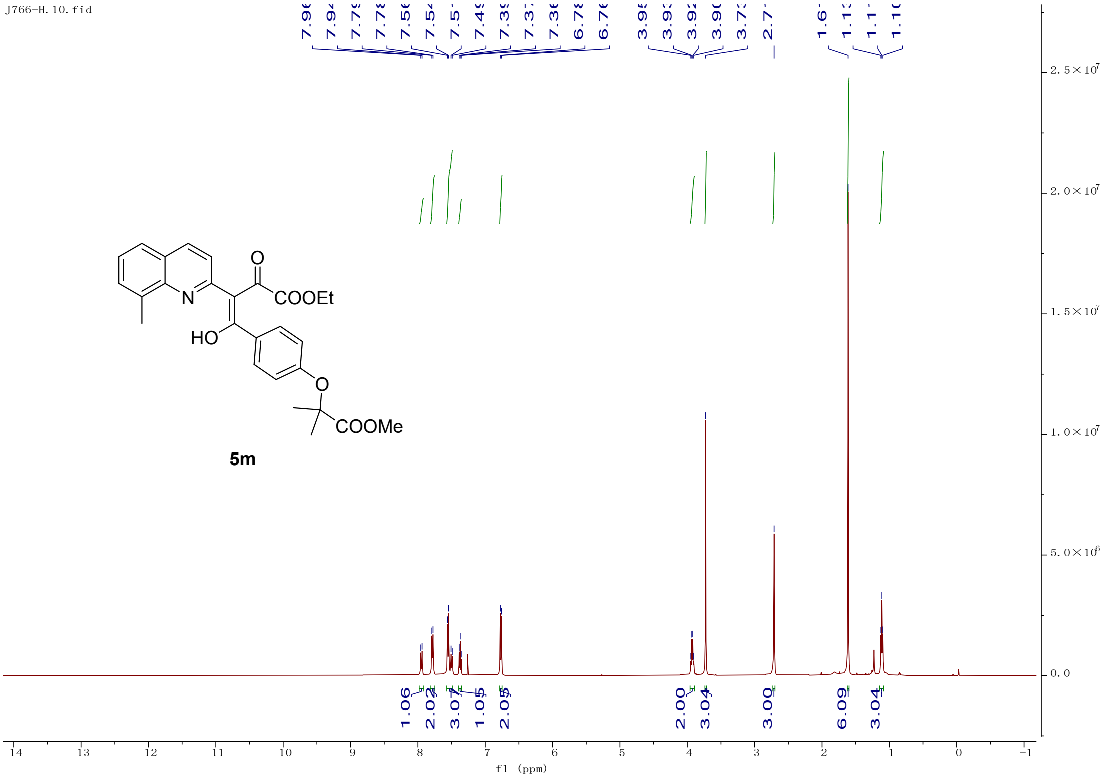


5l

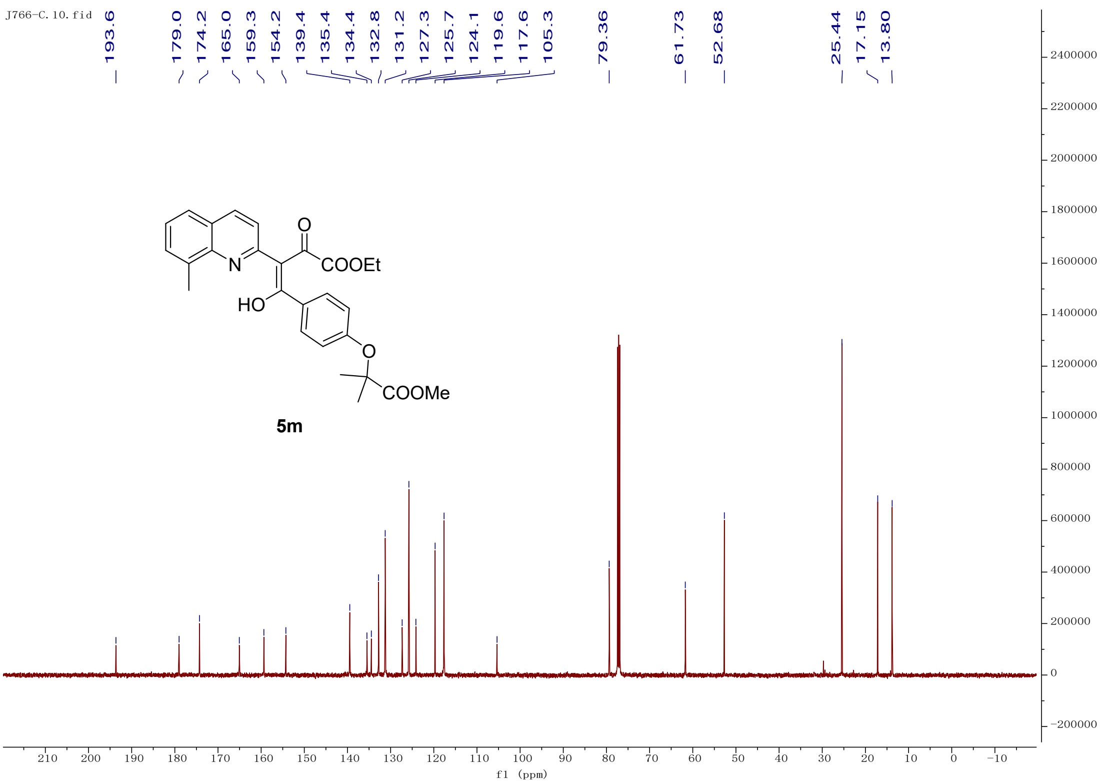
Chemical Formula: $C_{35}H_{37}NO_5$
Exact Mass: 551.2672
Molecular Weight: 551.6830
m/z: 551.2672 (100.0%), 552.2705 (37.9%), 553.2739 (7.0%), 553.2714 (1.0%)
Elemental Analysis: C, 76.20; H, 6.76; N, 2.54; O, 14.50

HRMS (ESI, m/z) calcd for $C_{34}H_{35}NO_5$ $[M+Na]^+$ 560.2408, found 560.2418.

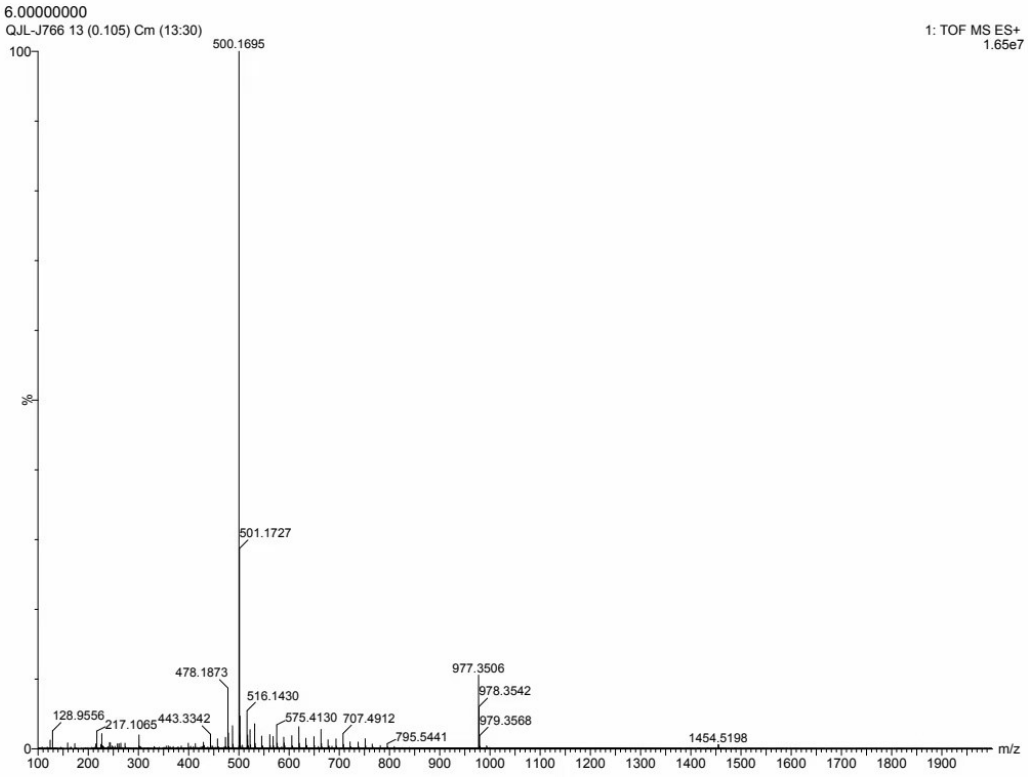
5m

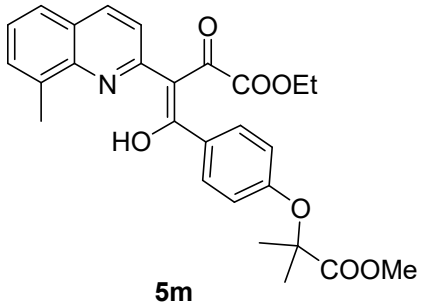


J766-H.10.fid
7.96
7.94
7.79
7.78
7.56
7.54
7.51
7.49
7.39
7.37
7.36
6.78
6.76
3.95
3.93
3.92
3.90
3.73
2.71
1.61
1.13
1.11
1.10
HO
N
O
COOEt
O
COOMe
5m
1.06
2.02
3.07
1.05
2.05
2.00
3.04
3.00
6.09
3.04
f1 (ppm)



J766-C.10.fid
193.6
179.0
174.2
165.0
159.3
154.2
139.4
135.4
134.4
132.8
131.2
127.3
125.7
124.1
119.6
117.6
105.3
79.36
61.73
52.68
25.44
17.15
13.80
HO
N
O
COOEt
O
COOMe
5m
f1 (ppm)





5m

Chemical Formula: $C_{27}H_{27}NO_7$

Exact Mass: 477.1788

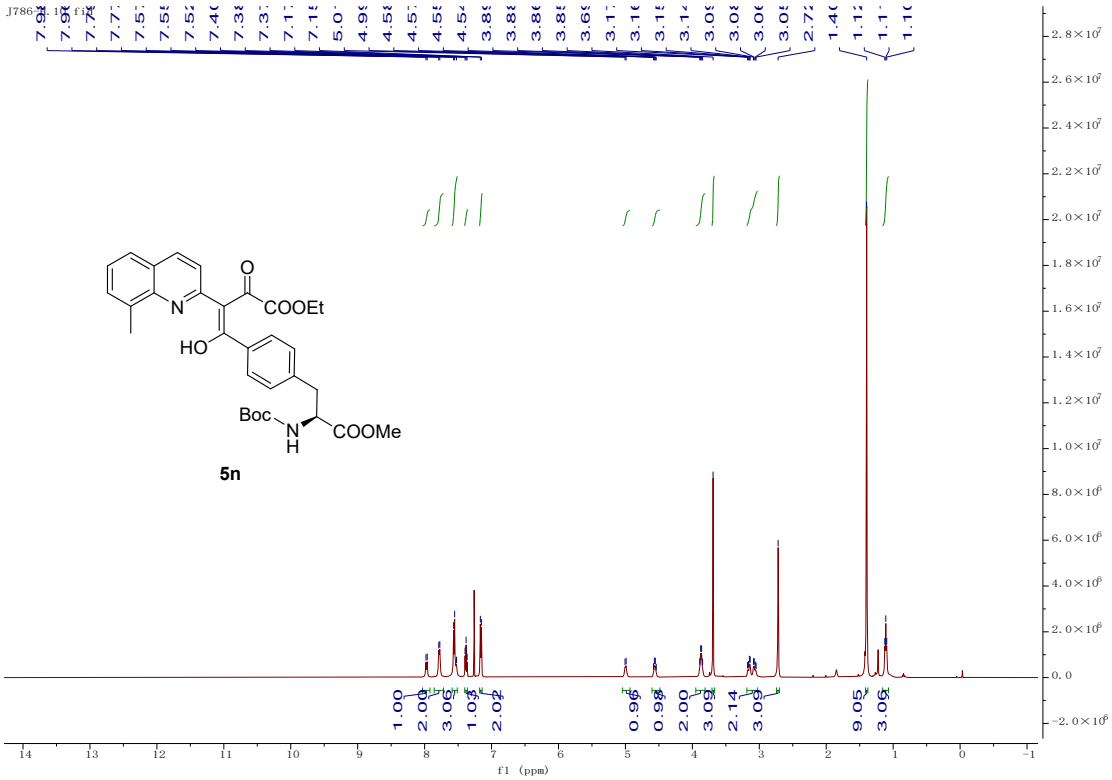
Molecular Weight: 477.5130

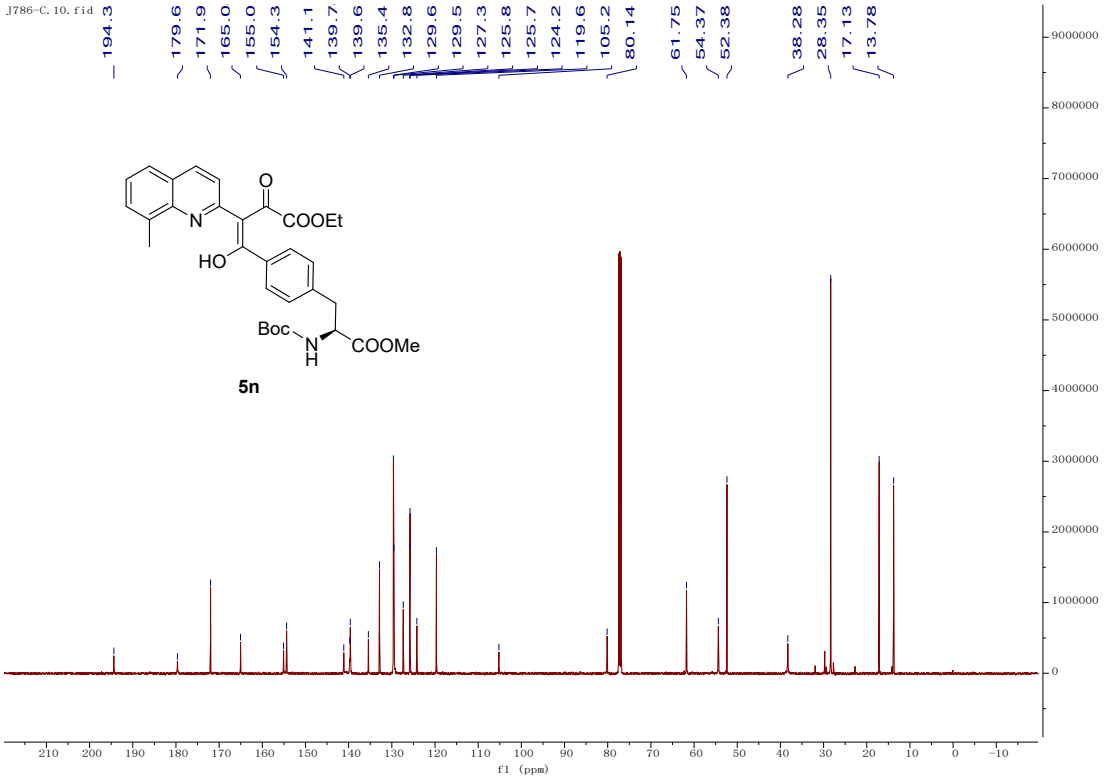
m/z: 477.1788 (100.0%), 478.1821 (29.2%), 479.1855 (4.1%), 479.1830 (1.4%)

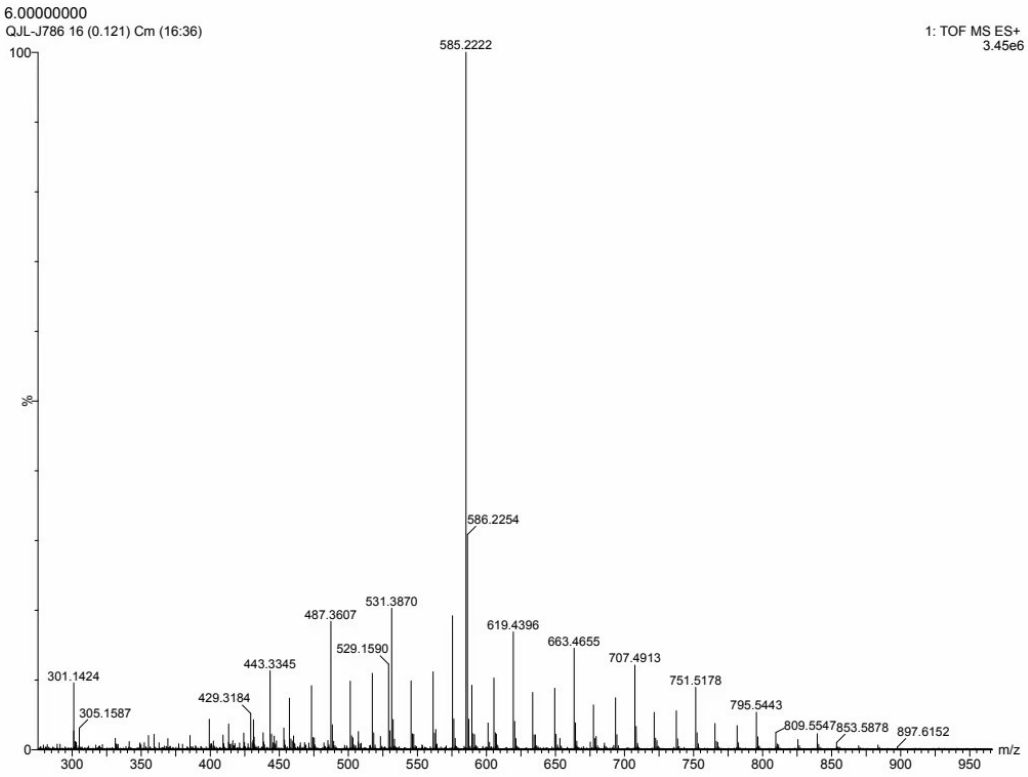
Elemental Analysis: C, 67.91; H, 5.70; N, 2.93; O, 23.45

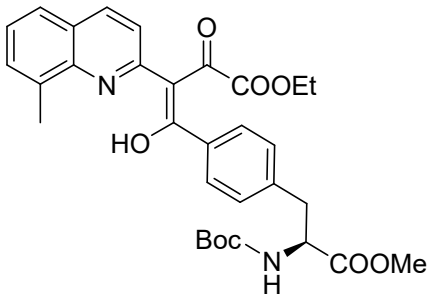
HRMS (ESI, m/z) calcd for $C_{27}H_{27}NO_7$ $[M+Na]^+$ 500.1680, found 500.1695.

5n


J786-H.1.fid
O
N
COOEt
HO
Boc
N
H
COOMe
5n
f1 (ppm)


J786-C.10.fid
O
N
COOEt
HO
Boc
N
H
COOMe
5n
f1 (ppm)





5n

Chemical Formula: $C_{31}H_{34}N_2O_8$

Exact Mass: 562.2315

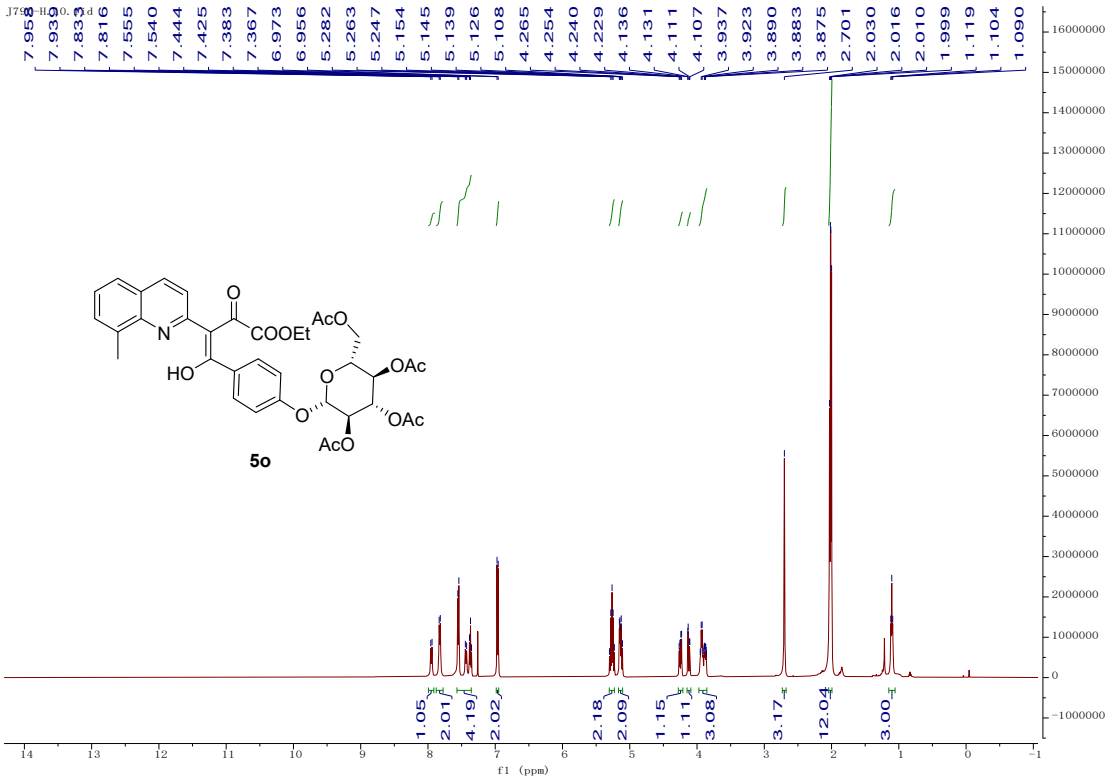
Molecular Weight: 562.6190

m/z: 562.2315 (100.0%), 563.2349 (33.5%), 564.2382 (5.4%), 564.2358 (1.6%)

Elemental Analysis: C, 66.18; H, 6.09; N, 4.98; O, 22.75

HRMS (ESI, m/z) calcd for $C_{31}H_{34}N_2O_8$ $[M+Na]^+$ 585.2208, found 585.2222.

5o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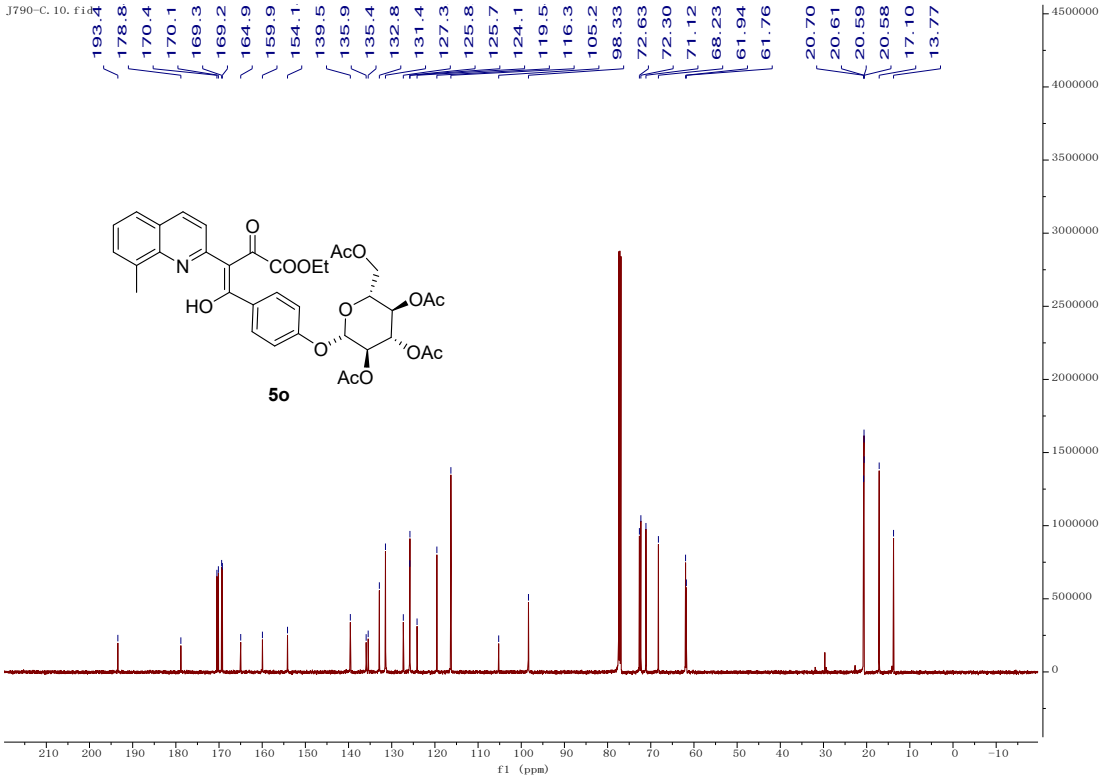
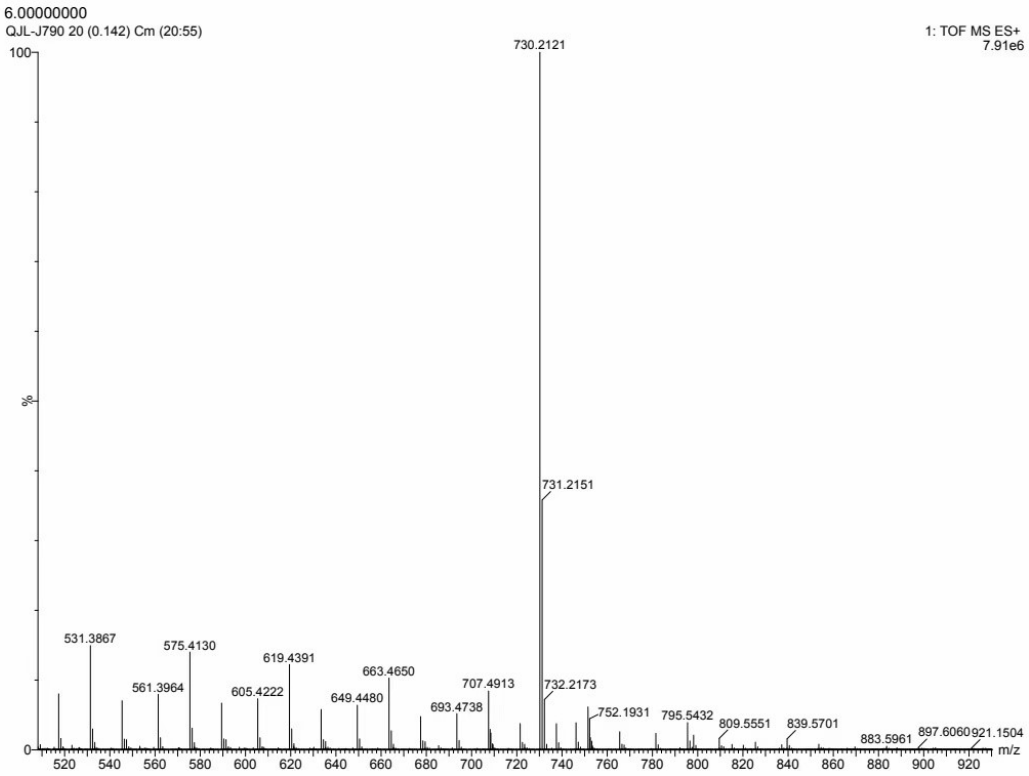
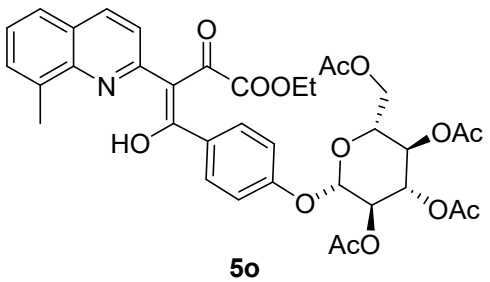
7.939
7.833
7.816
7.555
7.540
7.444
7.425
7.383
7.367
6.973
6.956
5.282
5.263
5.247
5.154
5.145
5.139
5.126
5.108
4.265
4.254
4.240
4.229
4.136
4.131
4.111
4.107
3.937
3.923
3.890
3.883
3.875
2.701
2.030
2.016
2.010
1.999
1.119
1.104
1.090
1.05
2.01
4.19
2.02
2.18
2.09
1.15
1.11
3.08
3.17
12.04
3.00
f1 (ppm)


193.4
178.8
170.4
170.1
169.3
169.2
164.9
159.9
154.1
139.5
135.9
135.4
132.8
131.4
127.3
125.8
125.7
124.1
119.5
116.3
105.2
98.33
72.63
72.30
71.12
68.23
61.94
61.76
20.70
20.61
20.59
20.58
17.10
13.77
f1 (ppm)



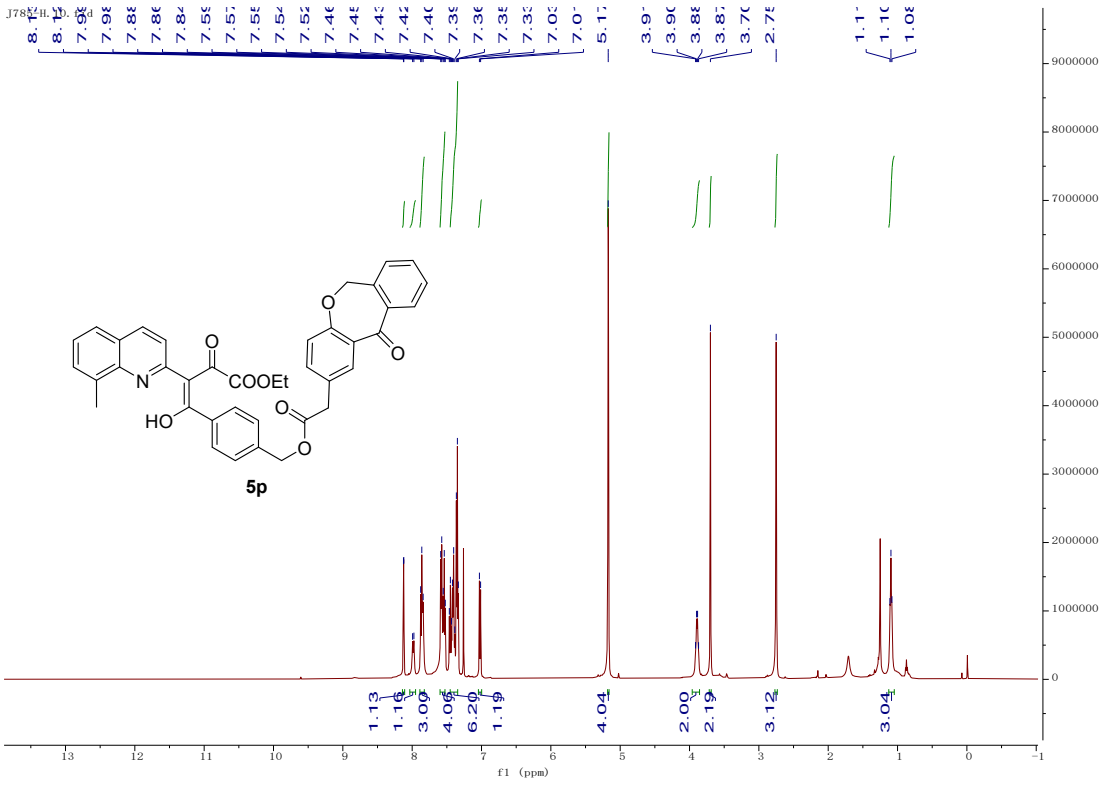


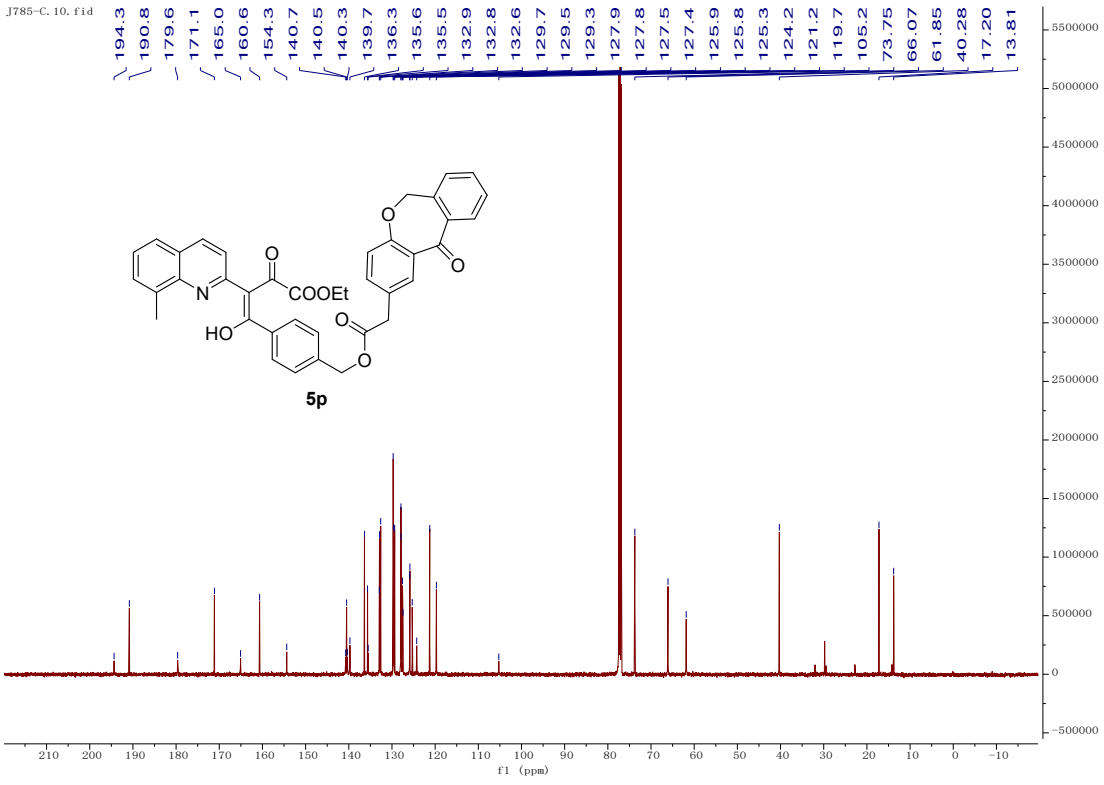
5o

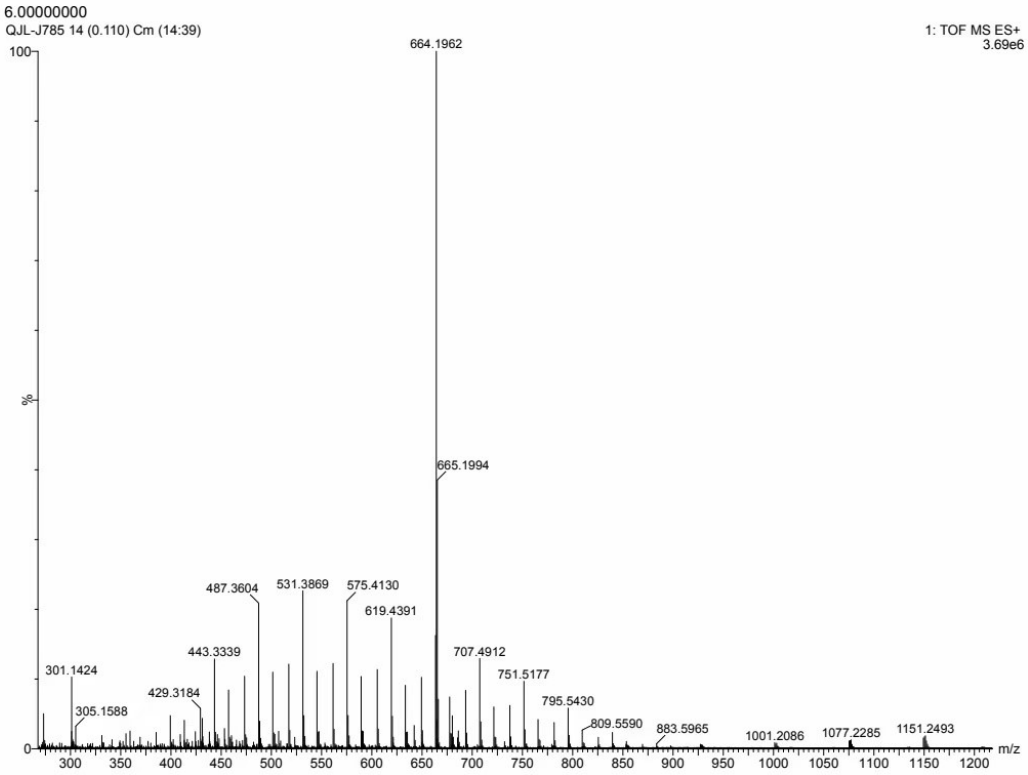
Chemical Formula: $C_{36}H_{37}NO_{14}$
Exact Mass: 707.2214
Molecular Weight: 707.6850
m/z: 707.2214 (100.0%), 708.2248 (38.9%), 709.2281 (7.4%), 709.2257 (2.9%), 710.2290 (1.1%)
Elemental Analysis: C, 61.10; H, 5.27; N, 1.98; O, 31.65

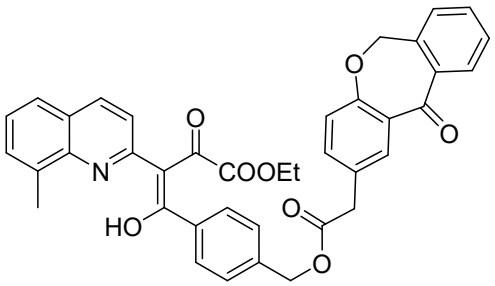
HRMS (ESI, m/z) calcd for $C_{36}H_{37}NO_{14}$ $[M+Na]^+$ 730.2107, found 730.2121.

5p


1.13
1.16
3.05
4.05
6.20
1.19
4.04
2.00
2.19
3.12
3.04
f1 (ppm)


194.3
190.8
179.6
171.1
165.0
160.6
154.3
140.7
140.5
140.3
139.7
136.3
135.6
135.5
132.9
132.8
132.6
129.7
129.5
129.3
127.9
127.8
127.5
127.4
125.9
125.8
125.3
124.2
121.2
119.7
105.2
73.75
66.07
61.85
40.28
17.20
13.81
f1 (ppm)





5p

Chemical Formula: $C_{39}H_{31}NO_8$

Exact Mass: 641.2050

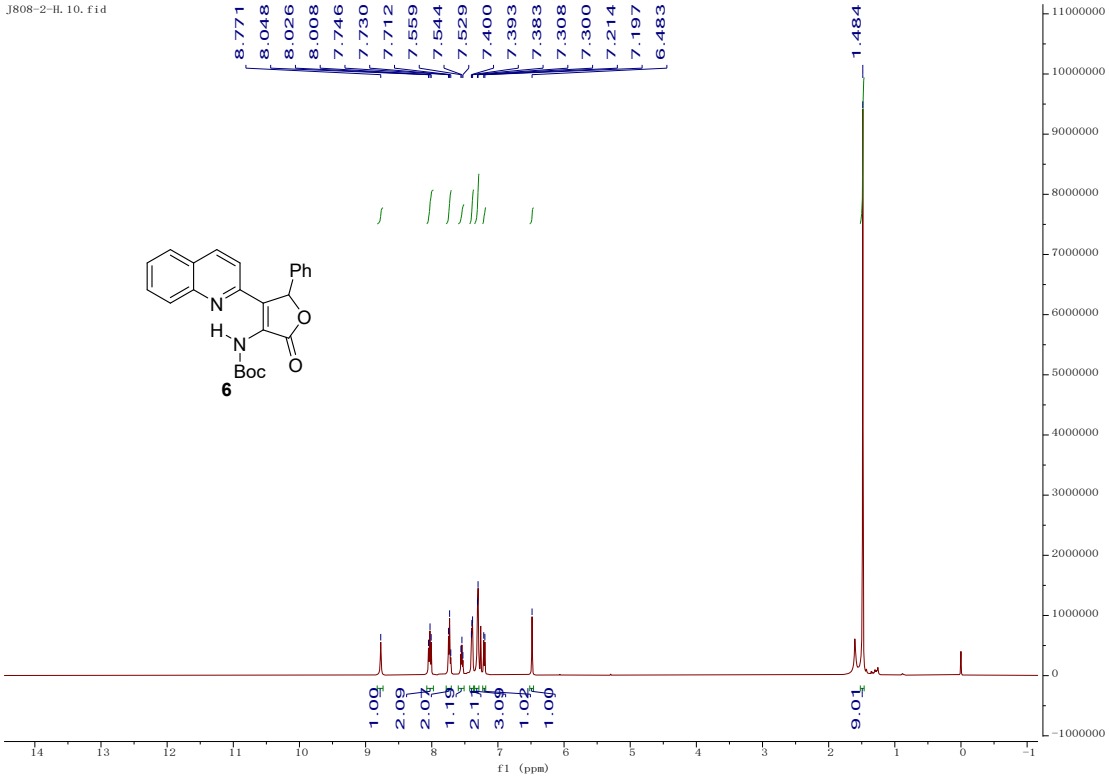
Molecular Weight: 641.6760

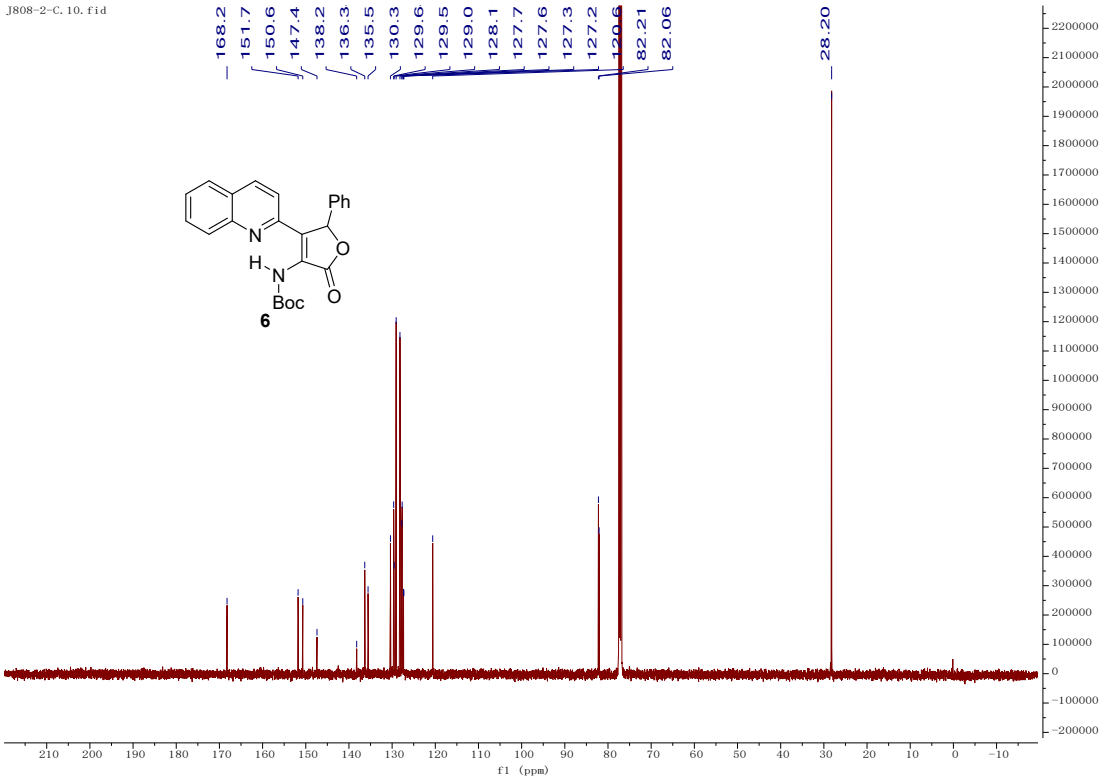
m/z: 641.2050 (100.0%), 642.2083 (42.2%), 643.2117 (8.7%), 643.2092 (1.6%), 644.2150 (1.2%)

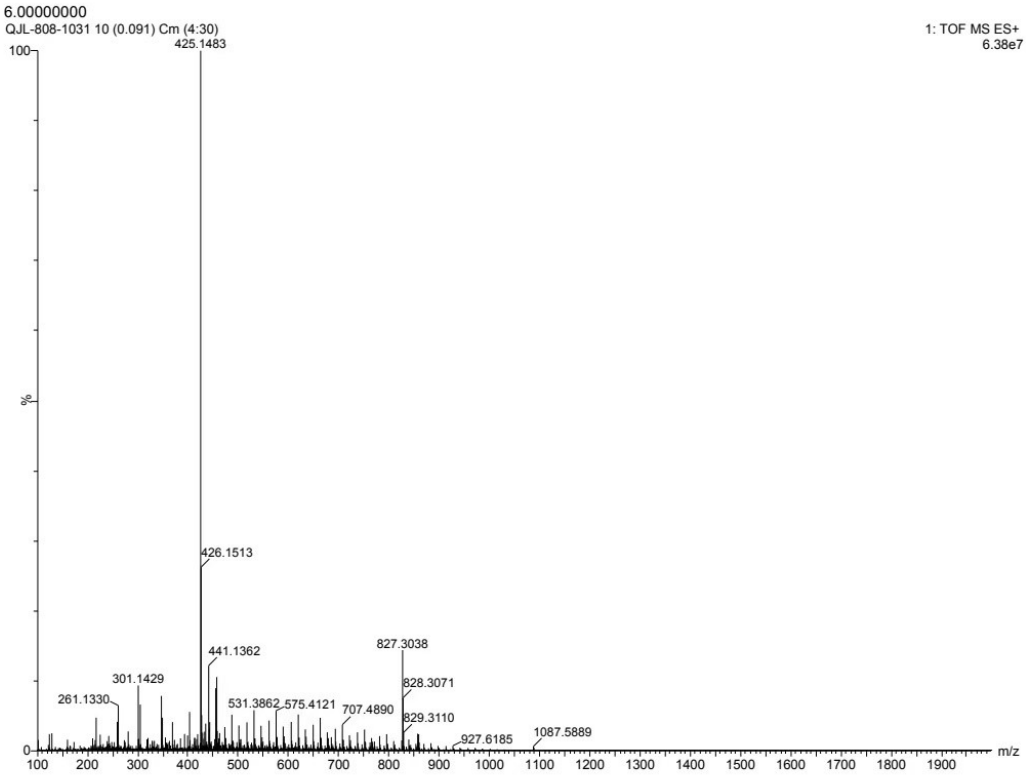
Elemental Analysis: C, 73.00; H, 4.87; N, 2.18; O, 19.95

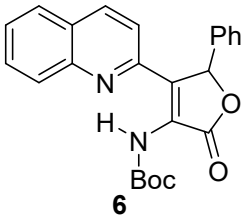
HRMS (ESI, m/z) calcd for $C_{39}H_{31}NO_8$ $[M+Na]^+$ 664.1942, found 664.1962.

6


J808-2-H. 10. fid
8.771
8.048
8.026
8.008
7.746
7.730
7.712
7.559
7.544
7.529
7.400
7.393
7.383
7.308
7.300
7.214
7.197
6.483
1.484
Ph
N
H
N
Boc
O
O
6
1.00
2.09
2.07
1.19
2.11
3.09
1.02
1.00
9.01
f1 (ppm)


J808-2-C. 10. fid
168.2
151.7
150.6
147.4
138.2
136.3
135.5
130.3
129.6
129.5
129.0
128.1
127.7
127.6
127.3
127.2
120.6
82.21
82.06
28.20
Ph
N
H
N
Boc
O
O
6
f1 (ppm)



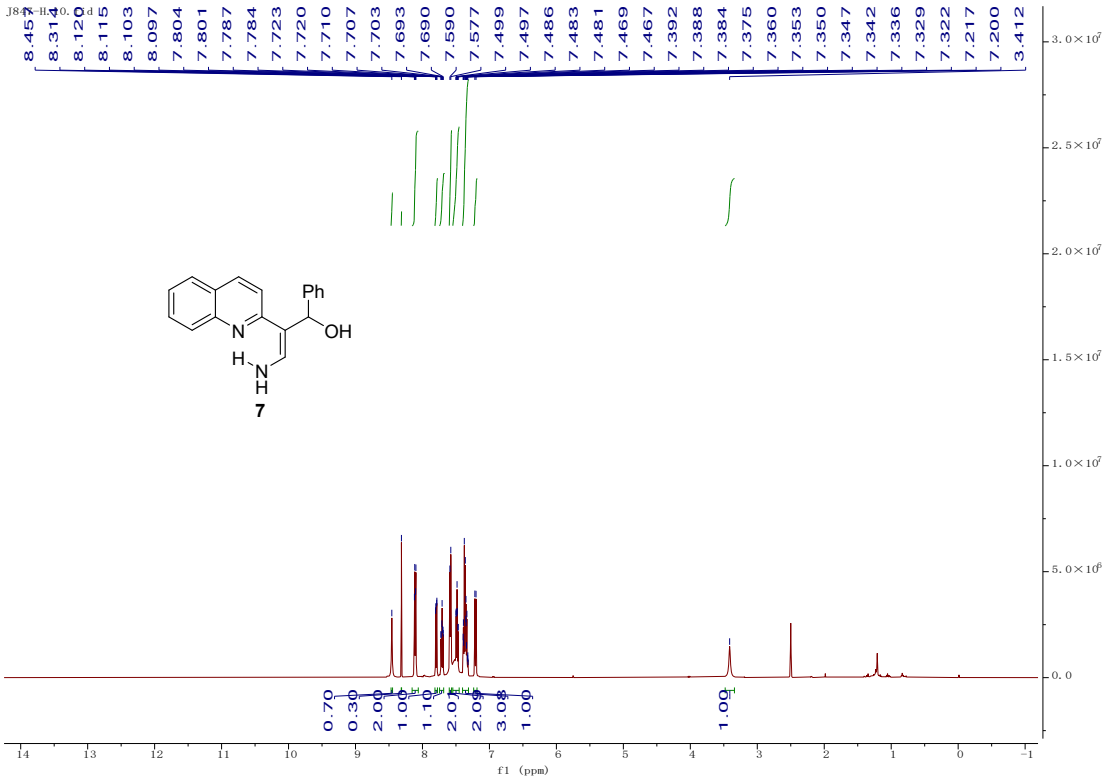


6

Chemical Formula: $C_{24}H_{22}N_2O_4$
Exact Mass: 402.1580
Molecular Weight: 402.4500
m/z: 402.1580 (100.0%), 403.1613 (26.0%), 404.1647 (3.2%)
Elemental Analysis: C, 71.63; H, 5.51; N, 6.96; O, 15.90

HRMS (ESI, m/z) calcd for $C_{24}H_{22}N_2O_4$ $[M+Na]^+$ 425.1472, found 425.1483.

7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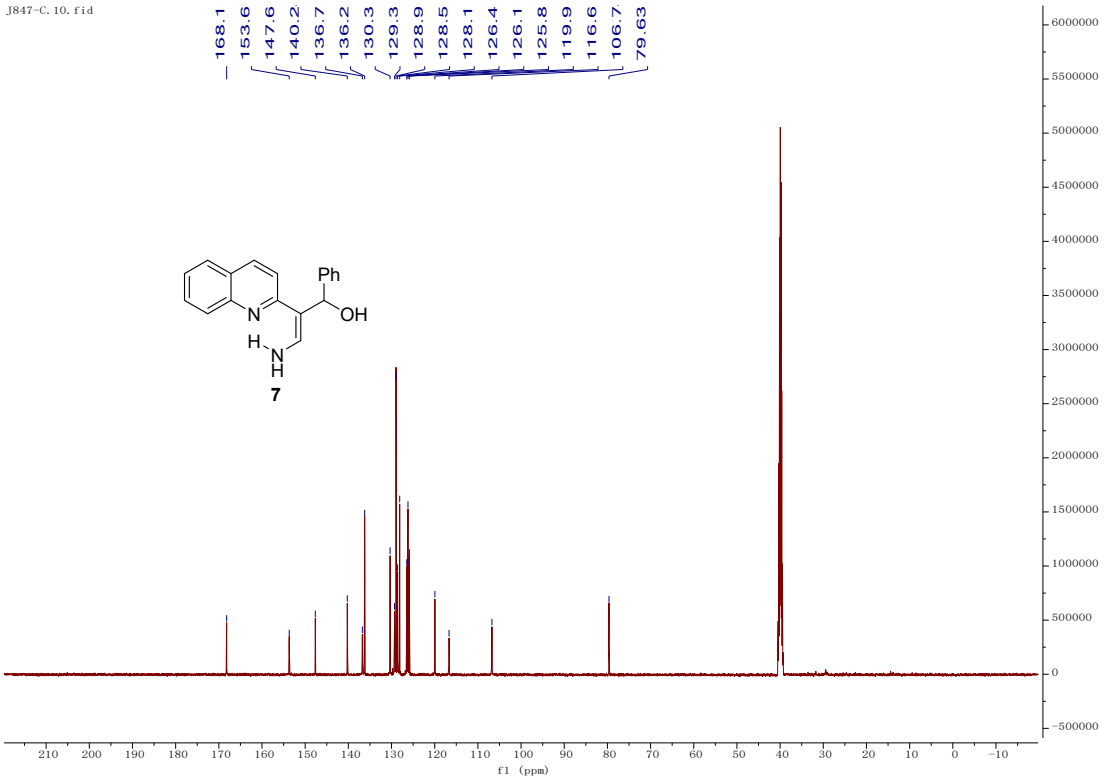
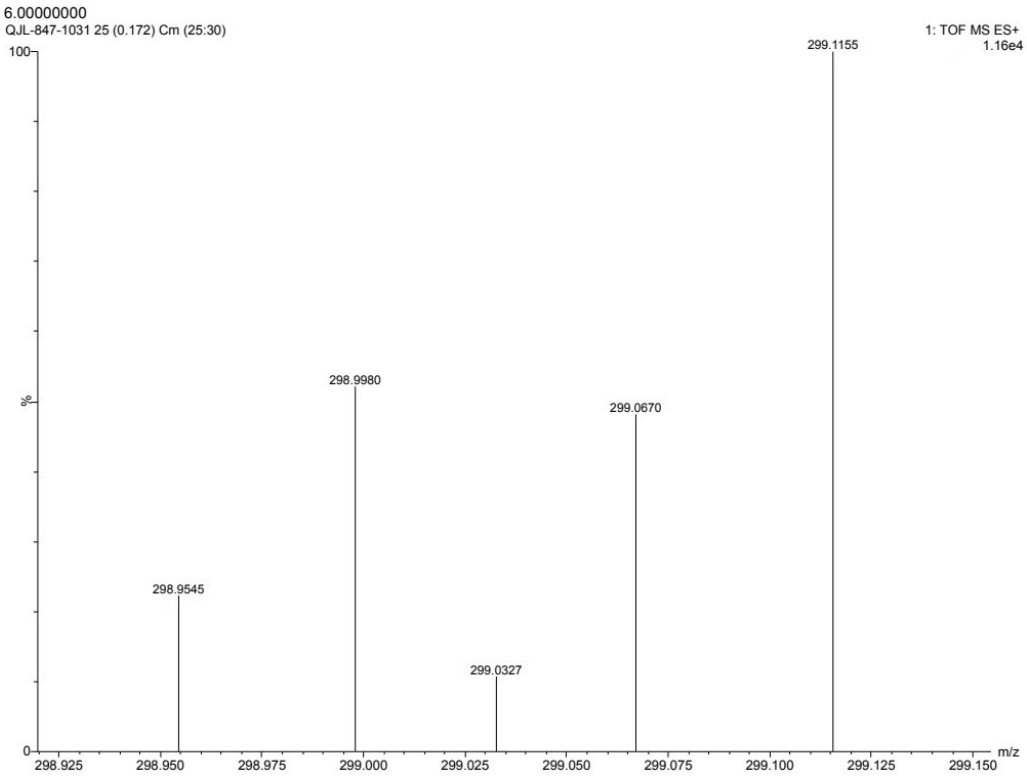
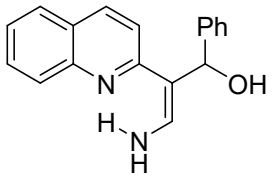
8.120
8.115
8.103
8.097
7.804
7.801
7.787
7.784
7.723
7.720
7.710
7.707
7.703
7.693
7.690
7.590
7.577
7.499
7.497
7.486
7.483
7.481
7.469
7.467
7.392
7.388
7.384
7.375
7.360
7.353
7.350
7.347
7.342
7.336
7.329
7.322
7.217
7.200
3.412
Ph
OH
N
H
N
H
7
0.70
0.30
2.00
1.00
1.10
2.07
2.05
3.08
1.00
1.00
f1 (ppm)


J847-C.10.fid
168.1
153.6
147.6
140.2
136.7
136.2
130.3
129.3
128.9
128.5
128.1
126.4
126.1
125.8
119.9
116.6
106.7
79.63
Ph
OH
N
H
N
H
7
f1 (ppm)



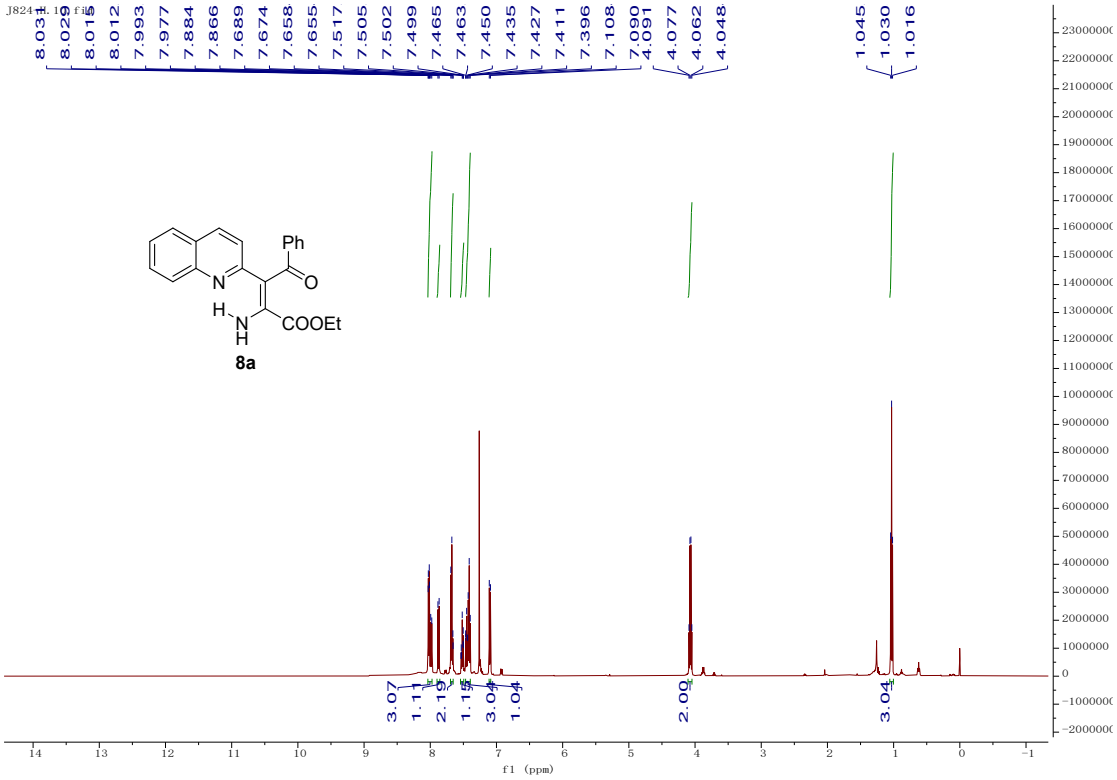


7

Chemical Formula: $C_{18}H_{16}N_2O$
Exact Mass: 276.1263
Molecular Weight: 276.3390
m/z: 276.1263 (100.0%), 277.1296 (19.5%), 278.1330 (1.8%)
Elemental Analysis: C, 78.24; H, 5.84; N, 10.14; O, 5.79

HRMS (ESI, m/z) calcd for $C_{18}H_{16}N_2O$ $[M+Na]^+$ 299.1155, found 299.1155.

8a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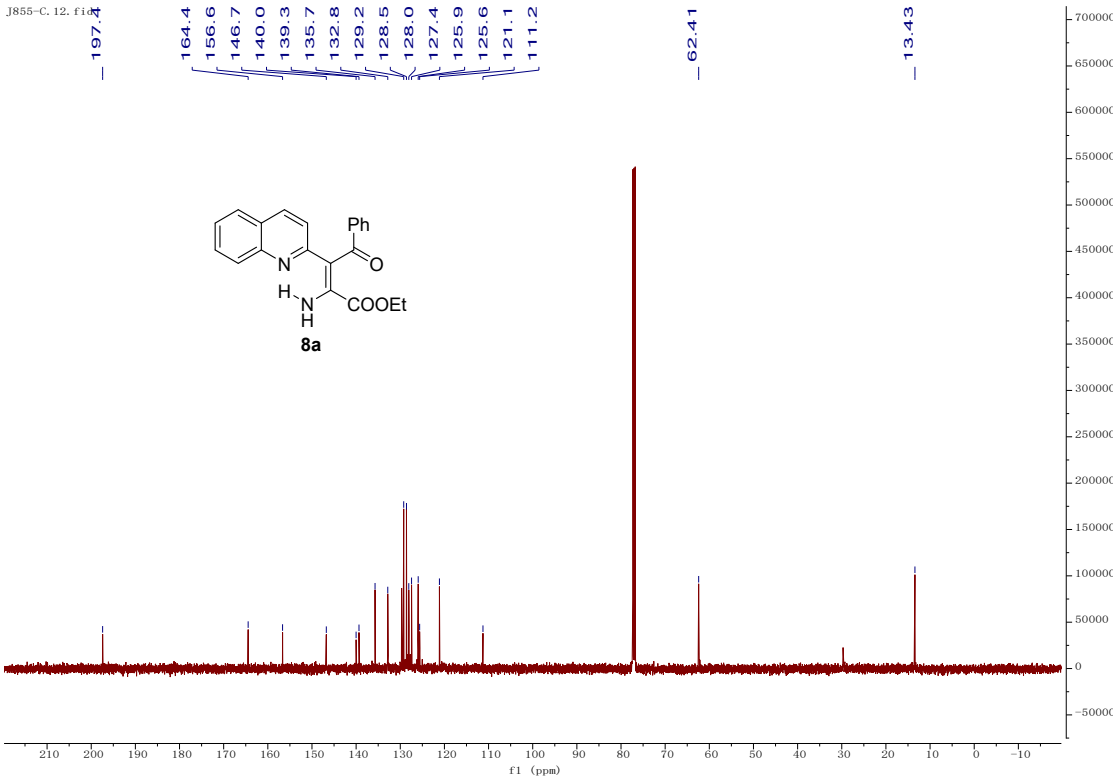
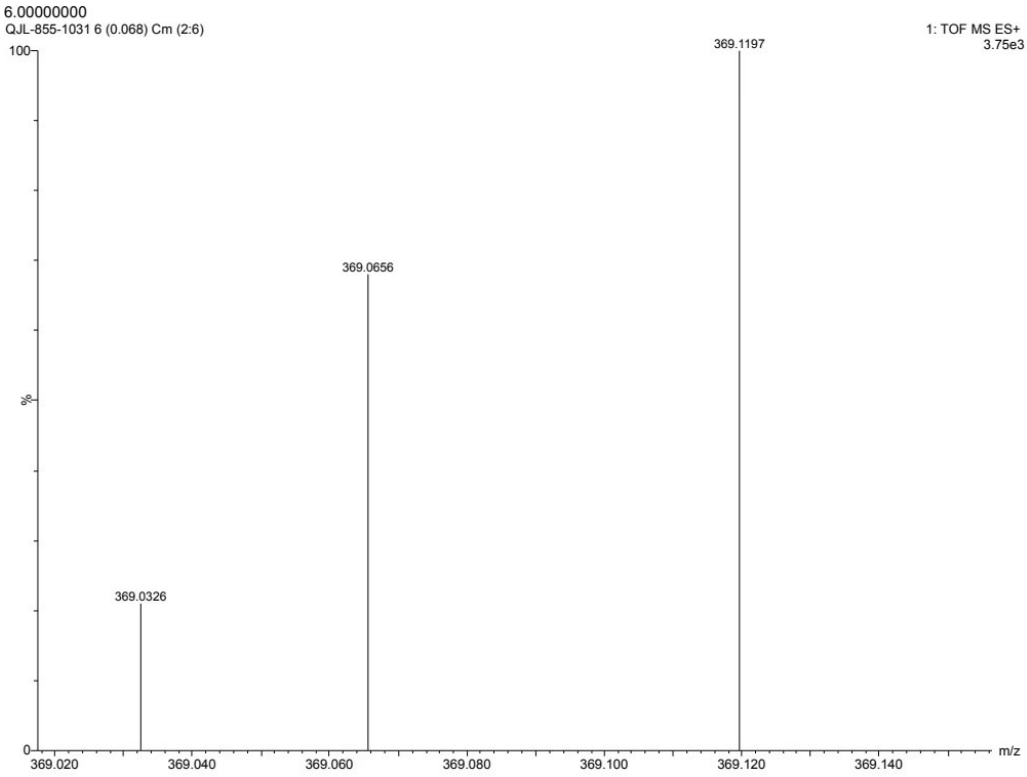
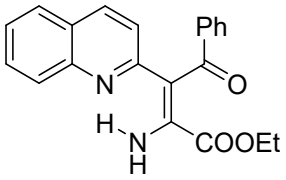
8.029
8.015
8.012
7.993
7.977
7.884
7.866
7.689
7.674
7.658
7.655
7.517
7.505
7.502
7.499
7.465
7.463
7.450
7.435
7.427
7.411
7.396
7.108
7.090
4.091
4.077
4.062
4.048
1.045
1.030
1.016
Ph
O
N
H
N
H
COOEt
8a
3.07
1.11
2.19
1.15
3.04
1.04
2.00
3.04
f1 (ppm)


197.4
164.4
156.6
146.7
140.0
139.3
135.7
132.8
129.2
128.5
128.0
127.4
125.9
125.6
121.1
111.2
62.41
13.43
Ph
O
N
H
N
H
COOEt
8a
f1 (ppm)





8a

Chemical Formula: $C_{21}H_{18}N_2O_3$

Exact Mass: 346.1317

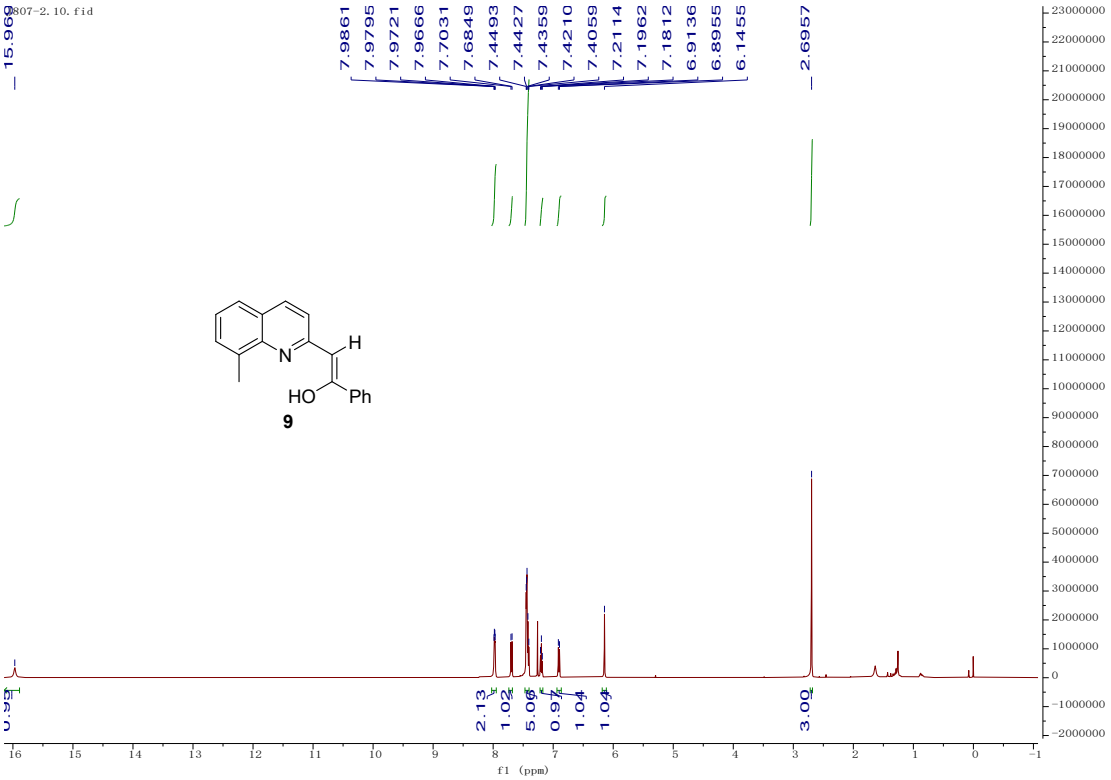
Molecular Weight: 346.3860

m/z: 346.1317 (100.0%), 347.1351 (22.7%), 348.1385 (2.5%)

Elemental Analysis: C, 72.82; H, 5.24; N, 8.09; O, 13.86

HRMS (ESI, m/z) calcd for $C_{21}H_{18}N_2O_3$ $[M+Na]^+$ 369.1210, found 369.1197.

9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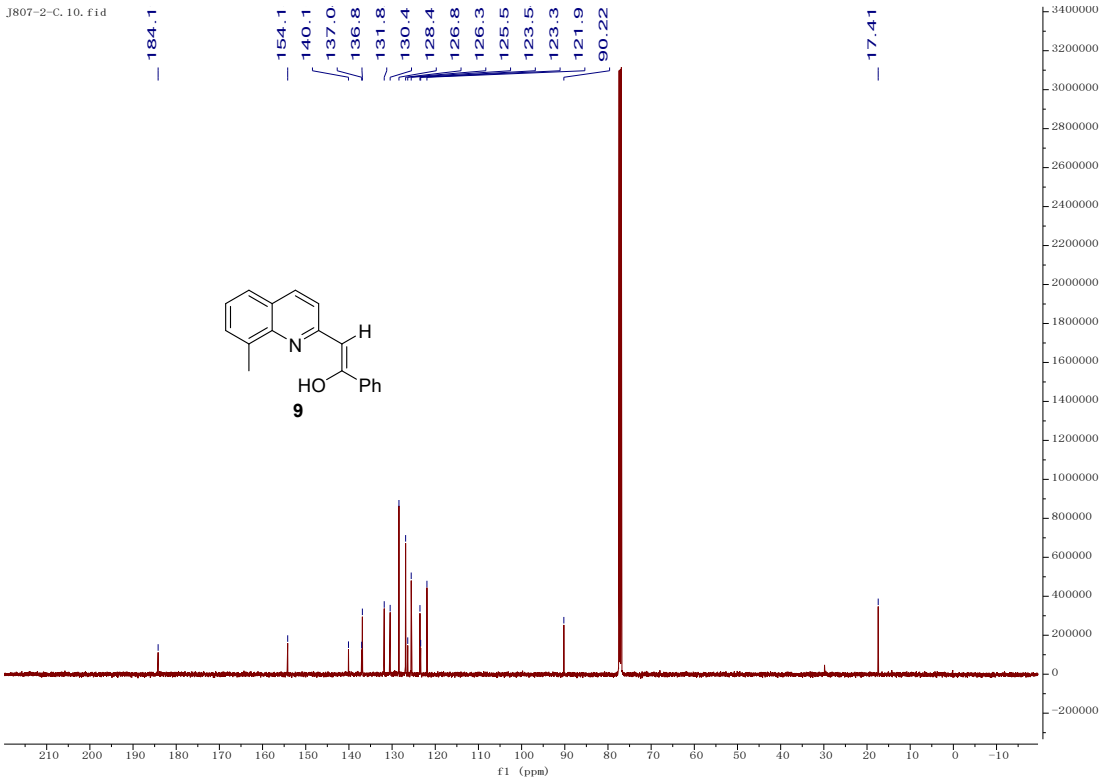
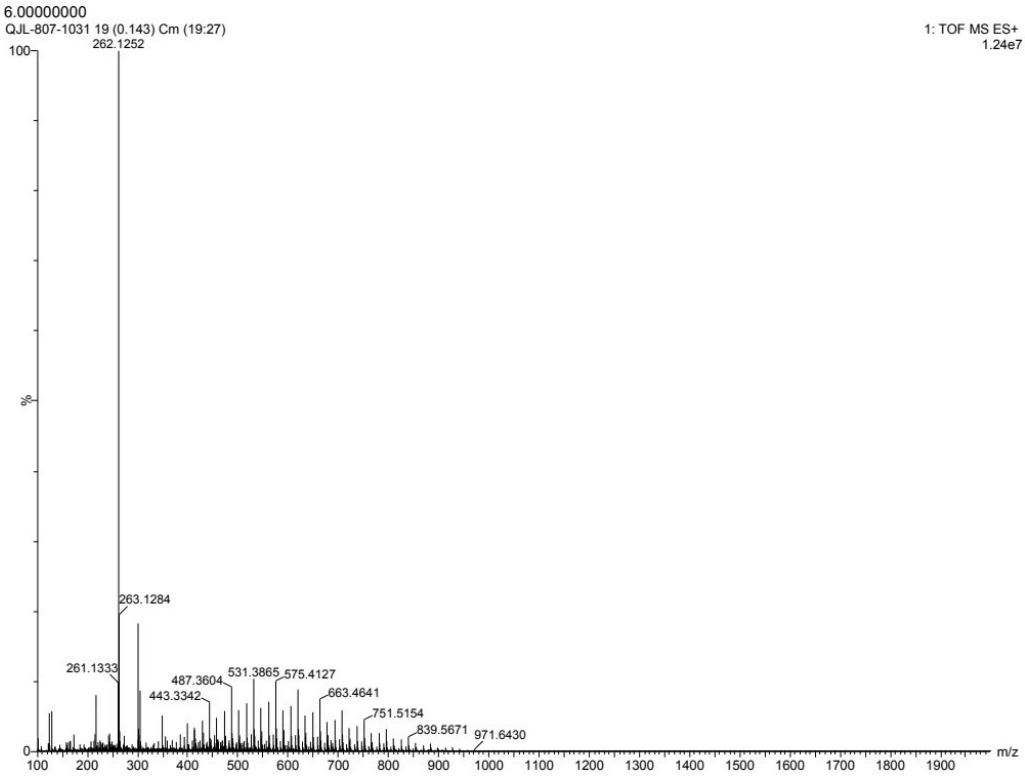
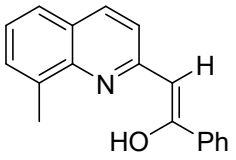
7.9795
7.9721
7.9666
7.7031
7.6849
7.4493
7.4427
7.4359
7.4210
7.4059
7.2114
7.1962
7.1812
6.9136
6.8955
6.1455
2.6957
0.93
2.13
1.02
5.06
0.97
1.04
1.04
3.00
N
H
HO
Ph
9
f1 (ppm)


J807-2-C.10.fid
184.1
154.1
140.1
137.0
136.8
131.8
130.4
128.4
126.8
126.3
125.5
123.5
123.3
121.9
90.22
17.41
N
H
HO
Ph
9
f1 (ppm)



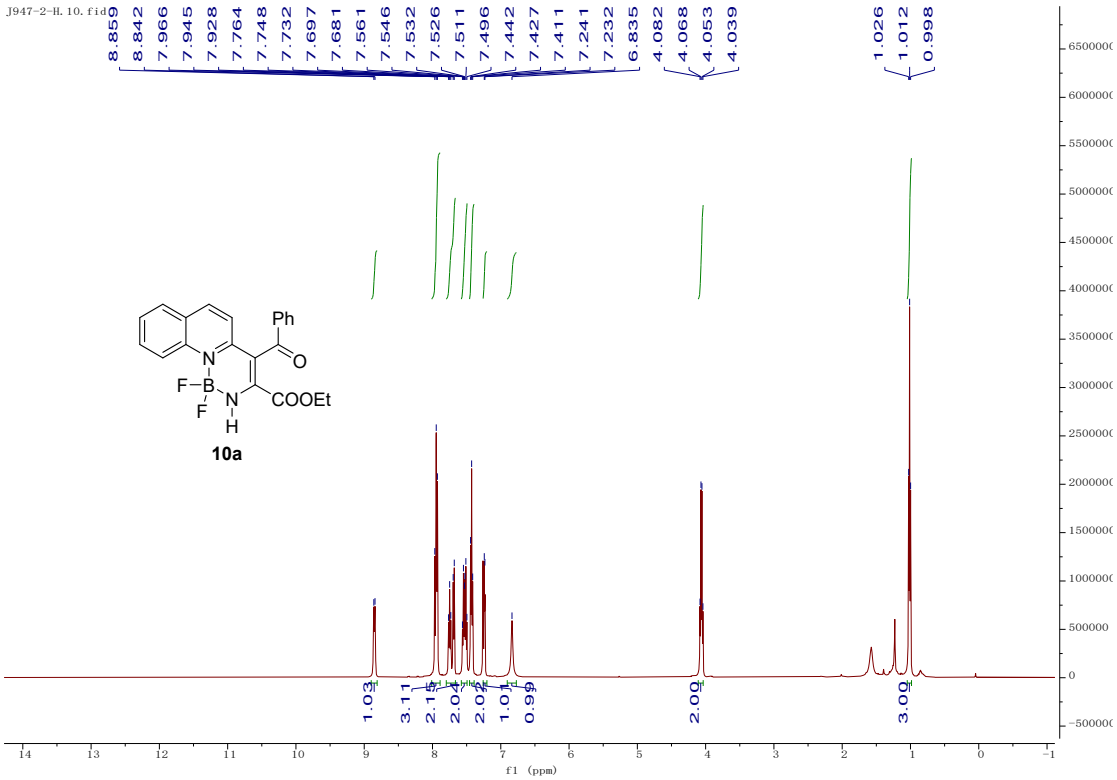


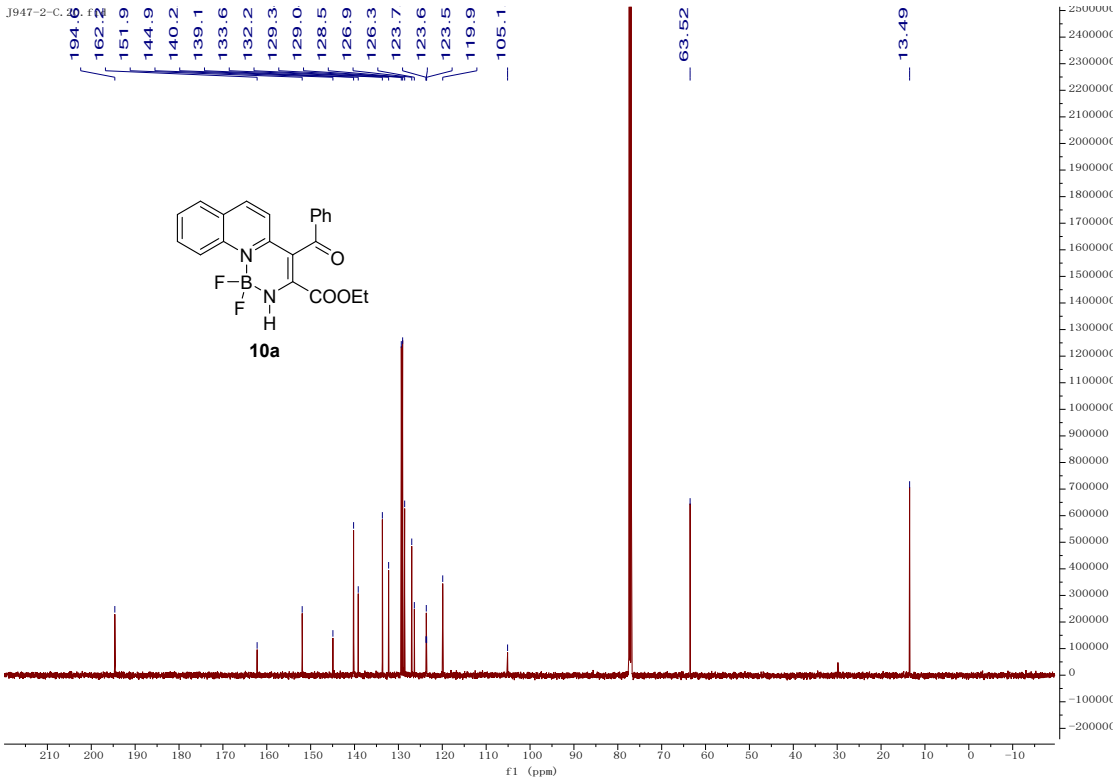
9

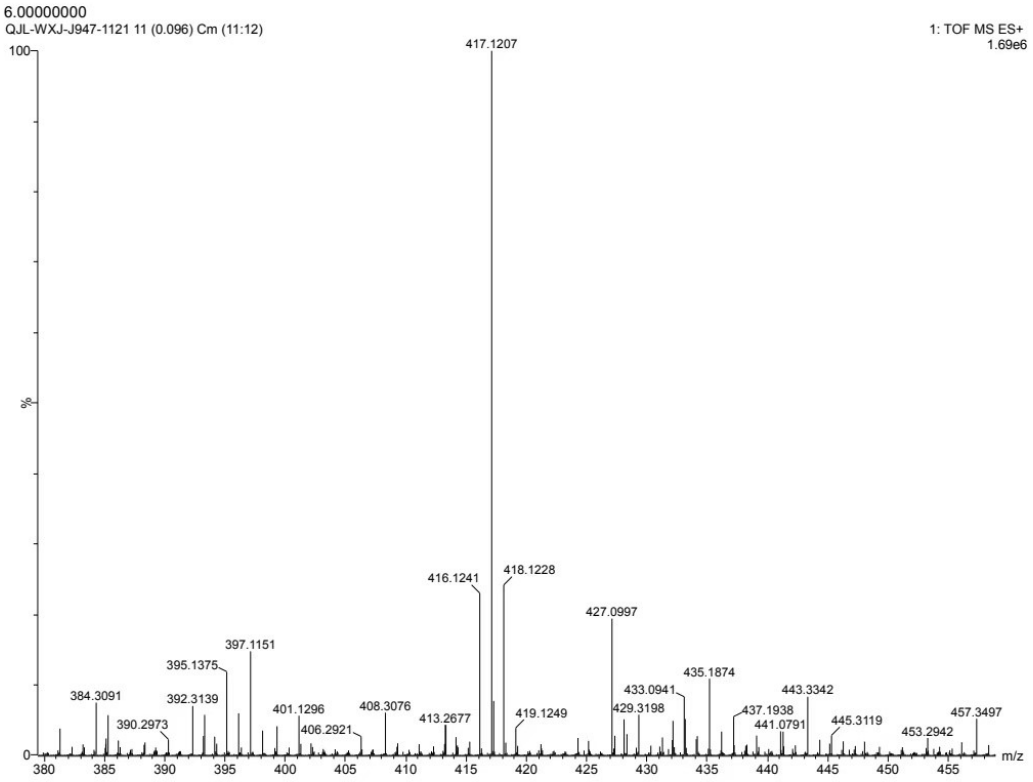
Chemical Formula: $C_{18}H_{15}NO$
Exact Mass: 261.1154
Molecular Weight: 261.3240
m/z: 261.1154 (100.0%), 262.1187 (19.5%), 263.1221 (1.8%)
Elemental Analysis: C, 82.73; H, 5.79; N, 5.36; O, 6.12

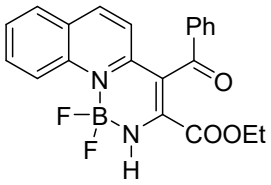
HRMS (ESI, m/z) calcd for $C_{18}H_{15}NO$ $[M+H]^+$ 262.1227, found 262.1252.

10a


J947-2-H. 10. fid
8.859
8.842
7.966
7.945
7.928
7.764
7.748
7.732
7.697
7.681
7.561
7.546
7.532
7.526
7.511
7.496
7.442
7.427
7.411
7.241
7.232
6.835
4.082
4.068
4.053
4.039
1.026
1.012
0.998
1.03
3.11
2.13
2.07
2.05
1.01
0.99
2.00
3.00
Ph
O
N
F
B
F
N
H
COOEt
10a
f1 (ppm)


194.6
162.2
151.9
144.9
140.2
139.1
133.6
132.2
129.3
129.0
128.5
126.9
126.3
123.7
123.6
123.5
119.9
105.1
63.52
13.49
Ph
O
N
F
B
F
N
H
COOEt
10a
f1 (ppm)





10a

Chemical Formula: $C_{21}H_{17}BF_2N_2O_3$

Exact Mass: 394.1300

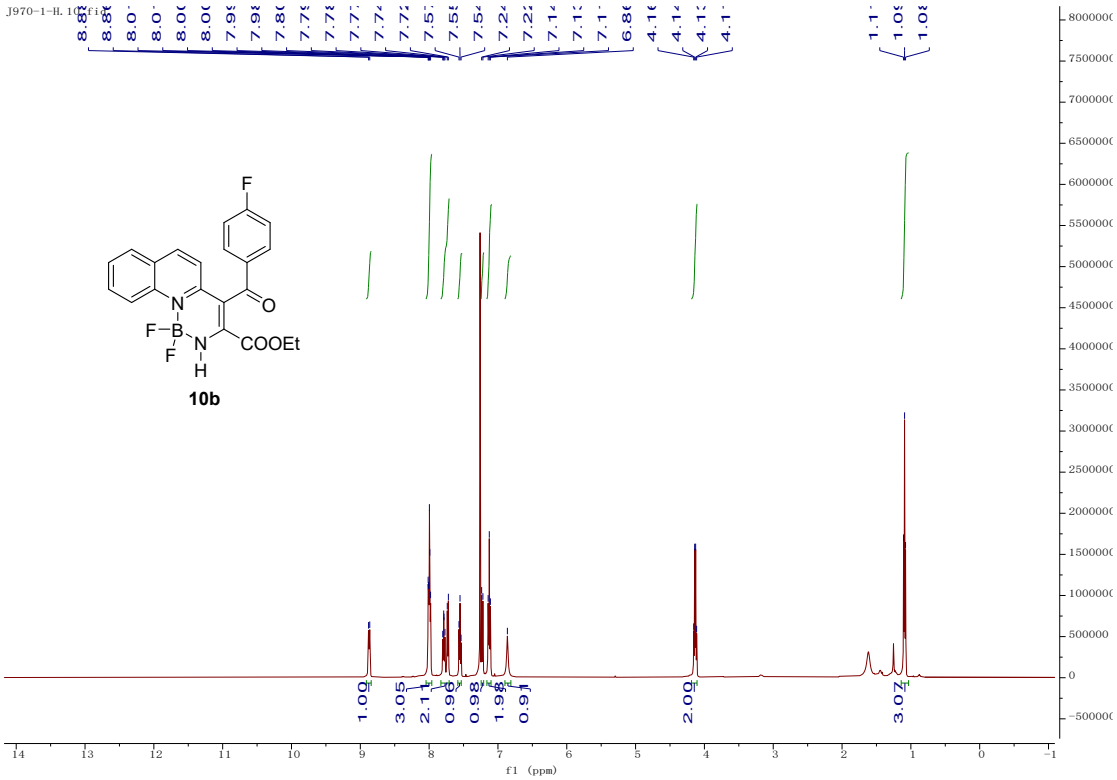
Molecular Weight: 394.1848

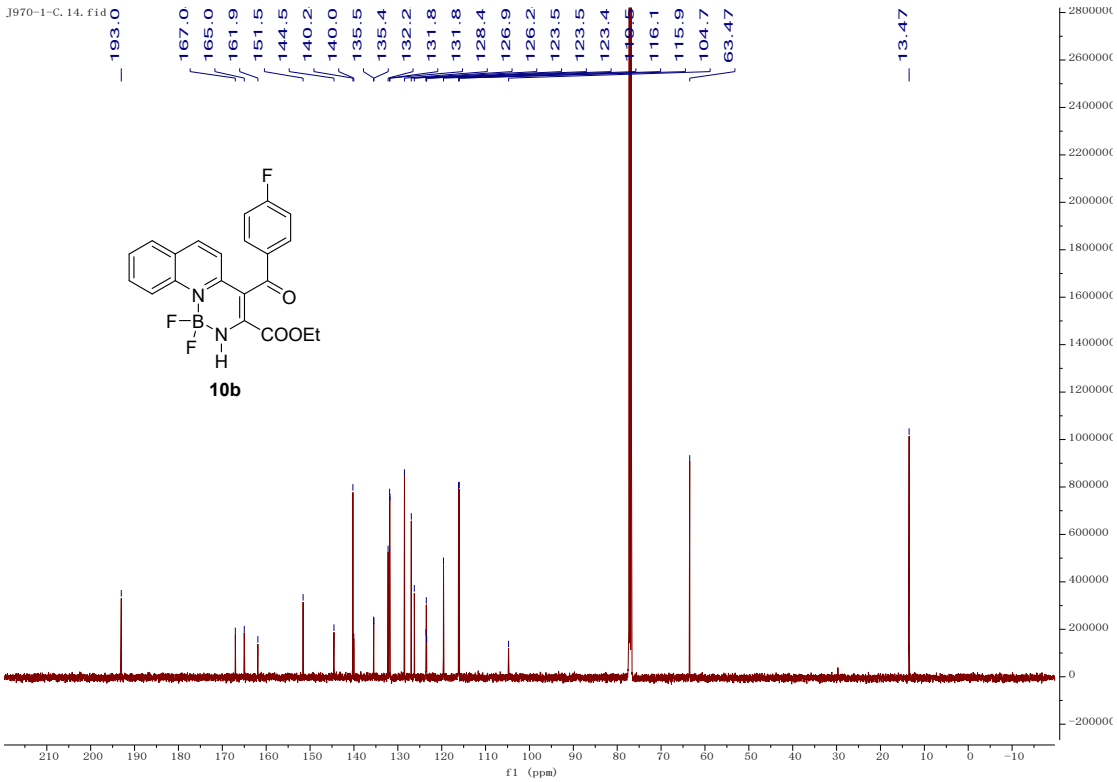
m/z: 394.1300 (100.0%), 393.1337 (24.8%), 395.1334 (22.7%), 394.1370 (5.6%), 396.1367 (2.5%)

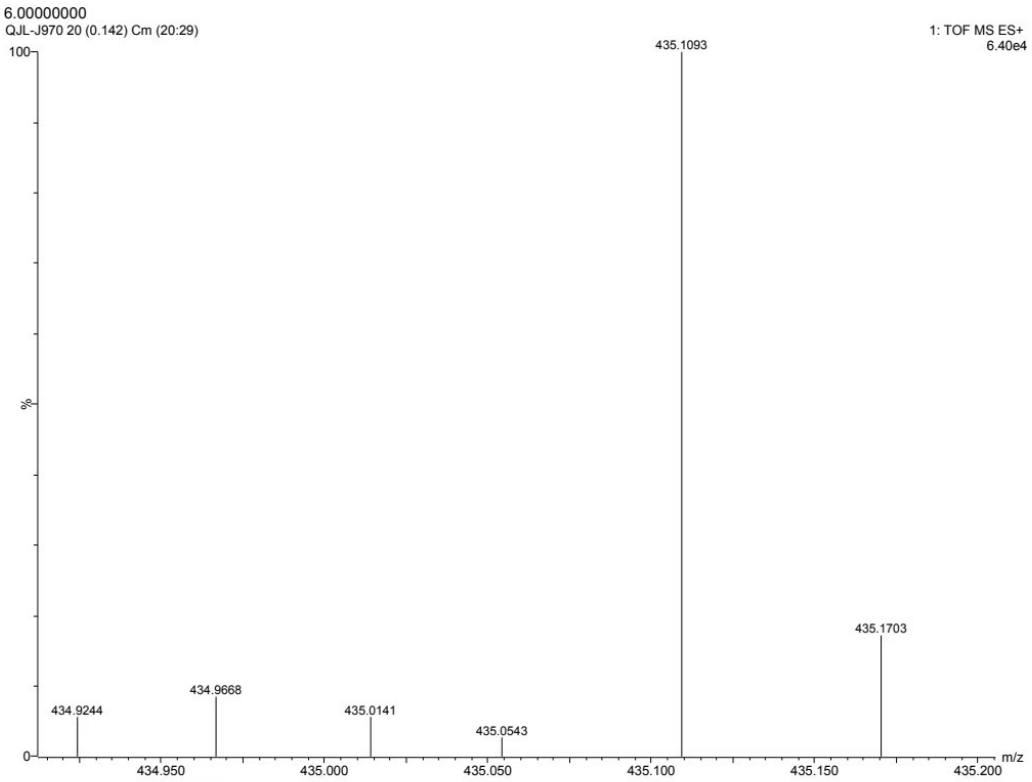
Elemental Analysis: C, 63.99; H, 4.35; B, 2.74; F, 9.64; N, 7.11; O, 12.18

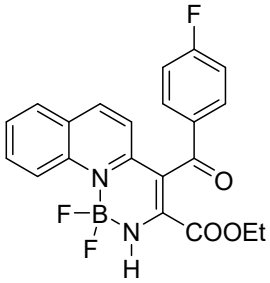
HRMS (ESI, m/z) calcd for $C_{21}H_{17}BF_2N_2O_3$ $[M+Na]^+$ 417.1193, found 417.1207.

10b









10b

Chemical Formula: $C_{21}H_{16}BF_3N_2O_3$

Exact Mass: 412.1206

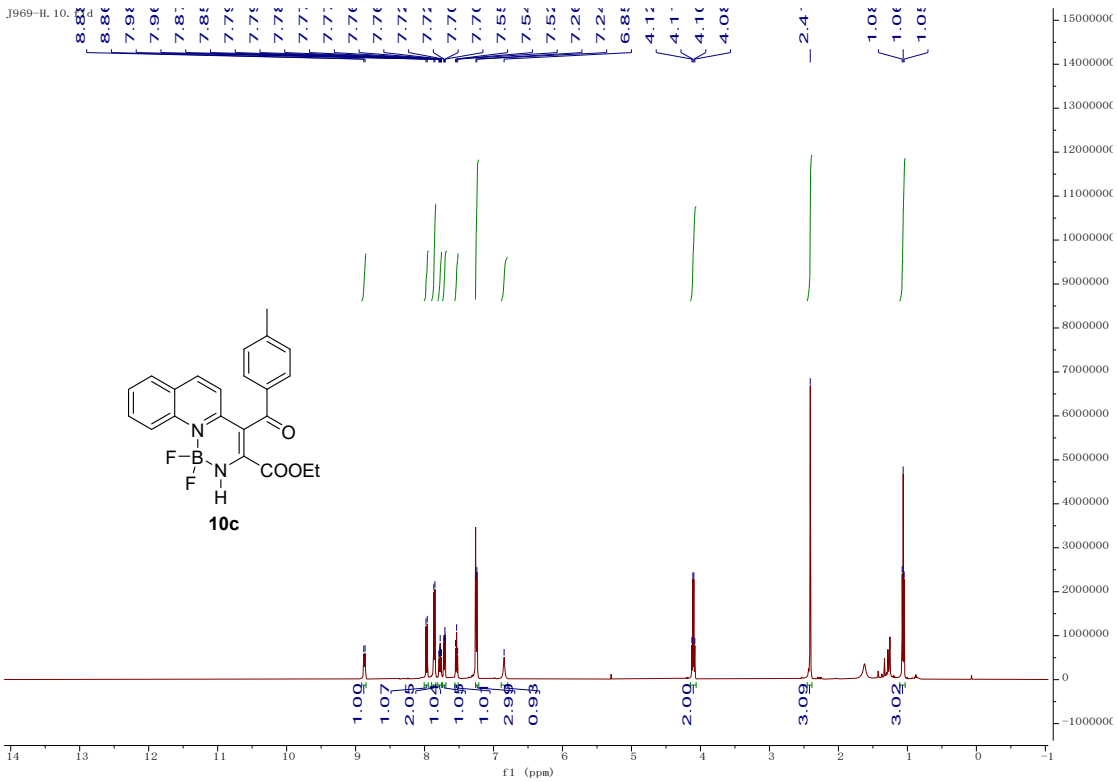
Molecular Weight: 412.1752

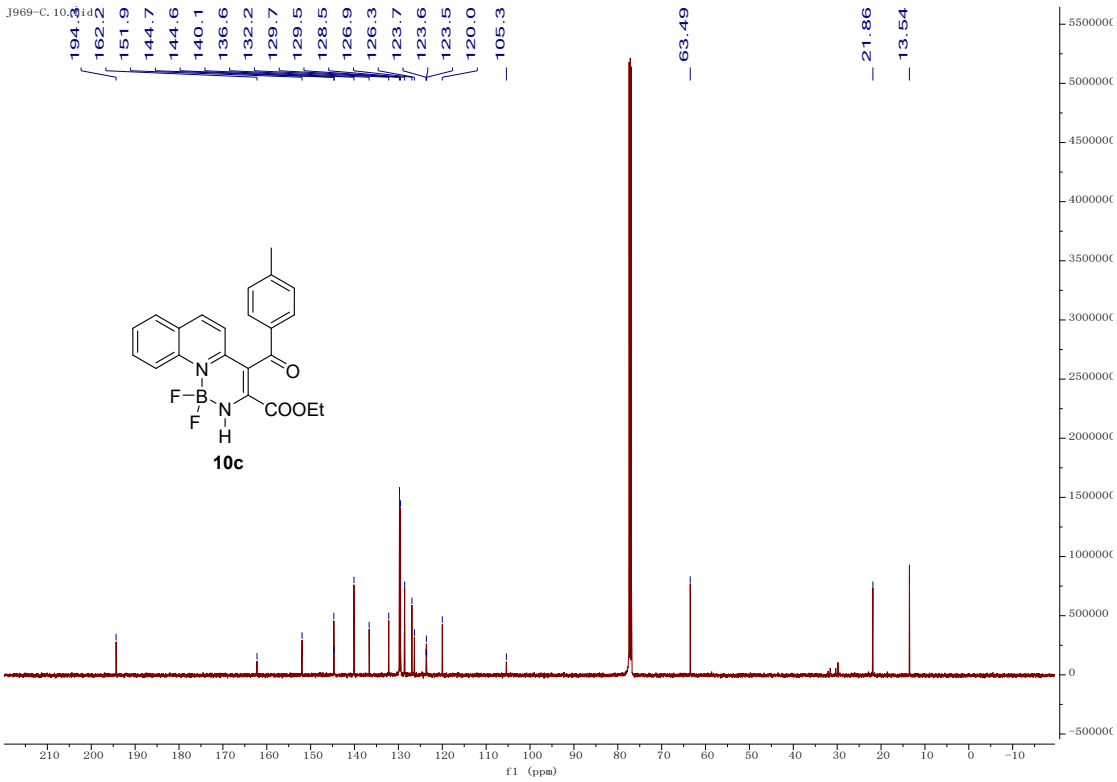
m/z: 412.1206 (100.0%), 411.1242 (24.8%), 413.1240 (22.7%), 412.1276 (5.6%), 414.1273 (2.5%)

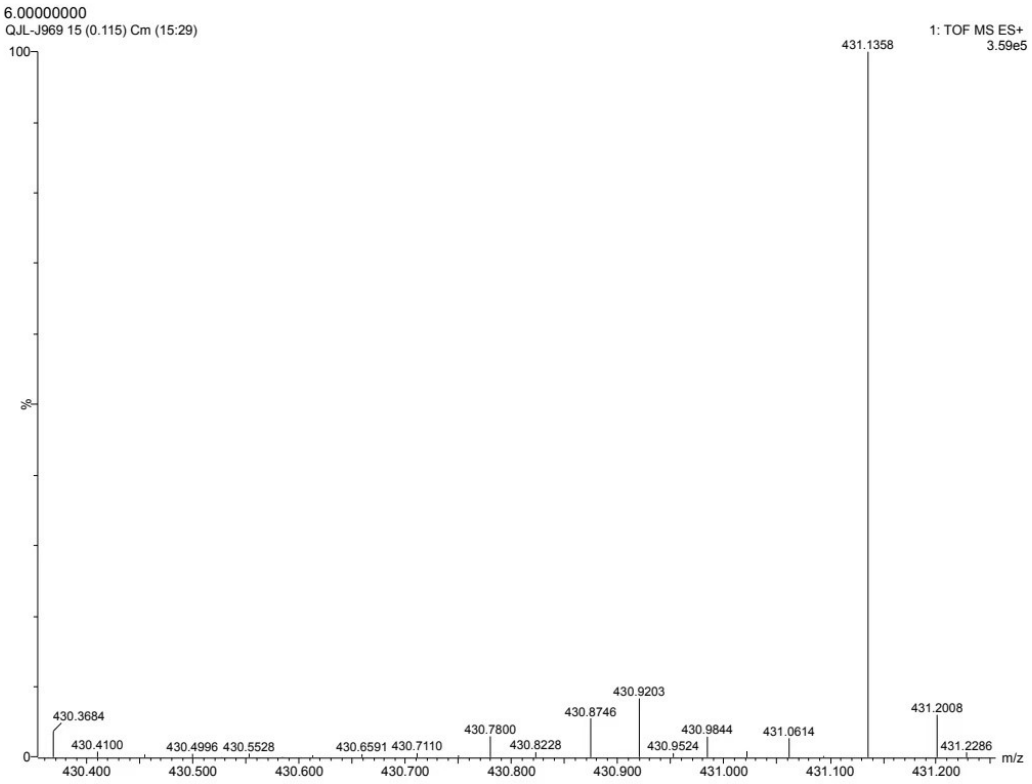
Elemental Analysis: C, 61.20; H, 3.91; B, 2.62; F, 13.83; N, 6.80; O, 11.64

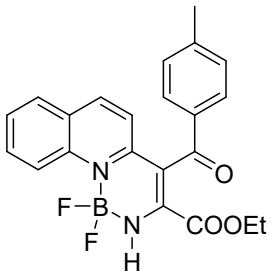
HRMS (ESI, m/z) calcd for $C_{21}H_{16}BF_3N_2O_3$ $[M+Na]^+$ 435.1099, found 435.1093.

10c









10c

Chemical Formula: $C_{22}H_{19}BF_2N_2O_3$

Exact Mass: 408.1457

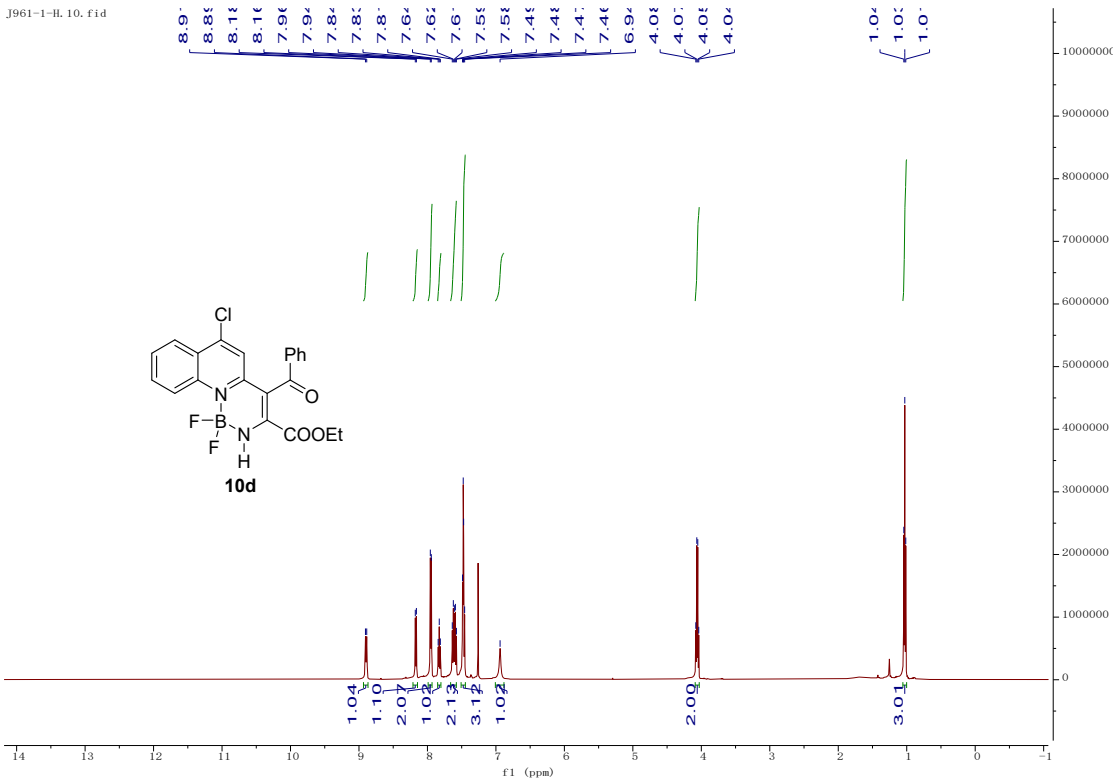
Molecular Weight: 408.2118

m/z: 408.1457 (100.0%), 407.1493 (24.8%), 409.1490 (23.8%), 408.1527 (5.9%), 410.1524 (2.7%)

Elemental Analysis: C, 64.73; H, 4.69; B, 2.65; F, 9.31; N, 6.86; O, 11.76

HRMS (ESI, m/z) calcd for $C_{22}H_{19}BF_2N_2O_3$ $[M+Na]^+$ 431.1349, found 431.1358.

10d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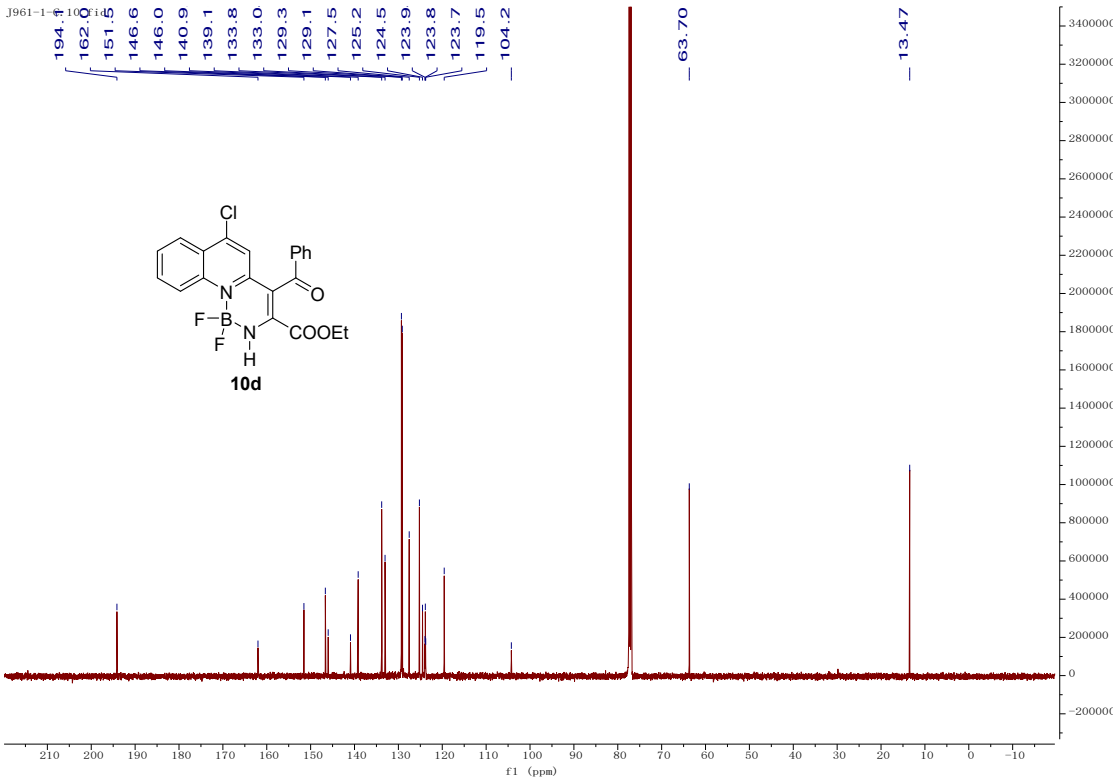
Cl
Ph
O
N
F–B
F
N
H
COOEt
10d
f1 (ppm)


J961-1-C.10.fid
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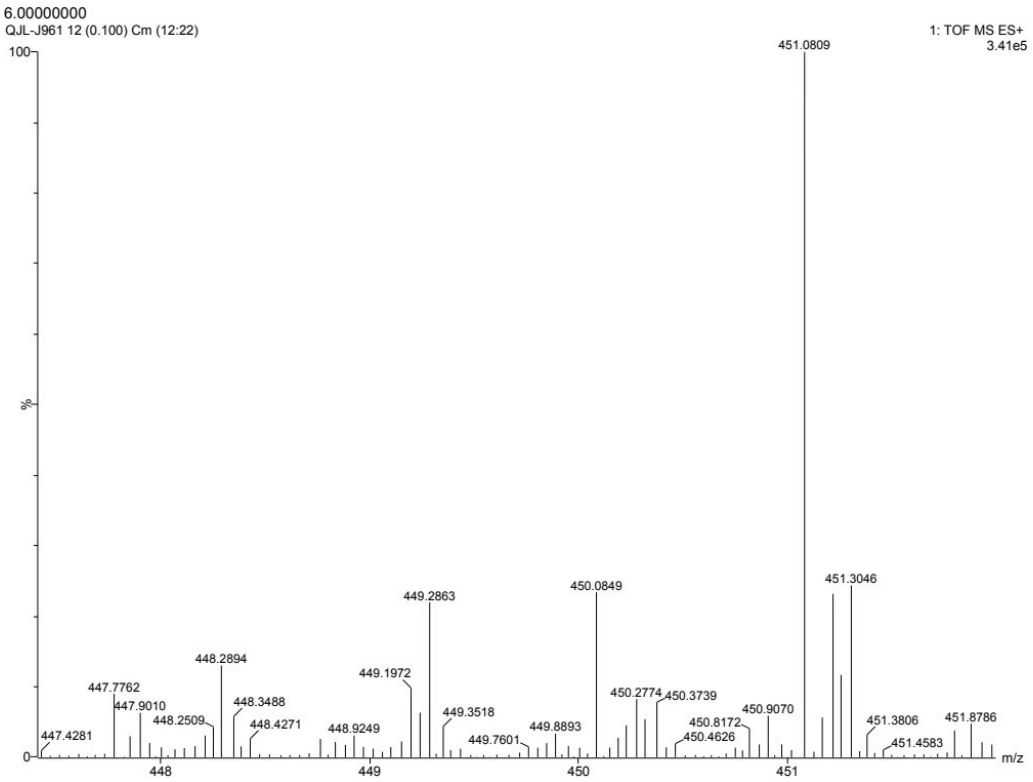
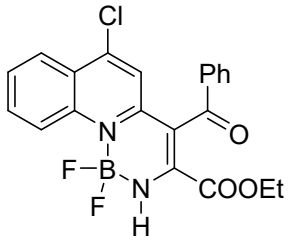
146.0
140.9
139.1
133.8
133.0
129.3
129.1
127.5
125.2
124.5
123.9
123.8
123.7
119.5
104.2
63.70
13.47
Cl
Ph
O
N
F–B
F
N
H
COOEt
10d
f1 (ppm)





10d

Chemical Formula: $C_{21}H_{16}BClF_2N_2O_3$

Exact Mass: 428.0911

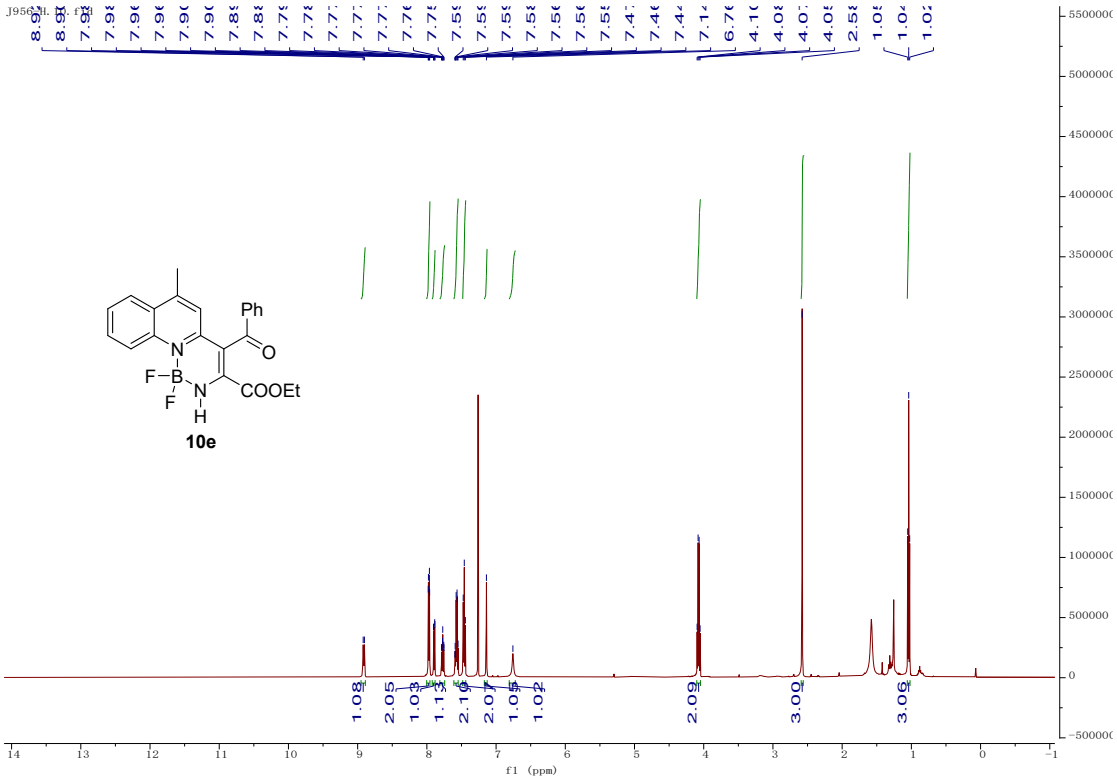
Molecular Weight: 428.6268

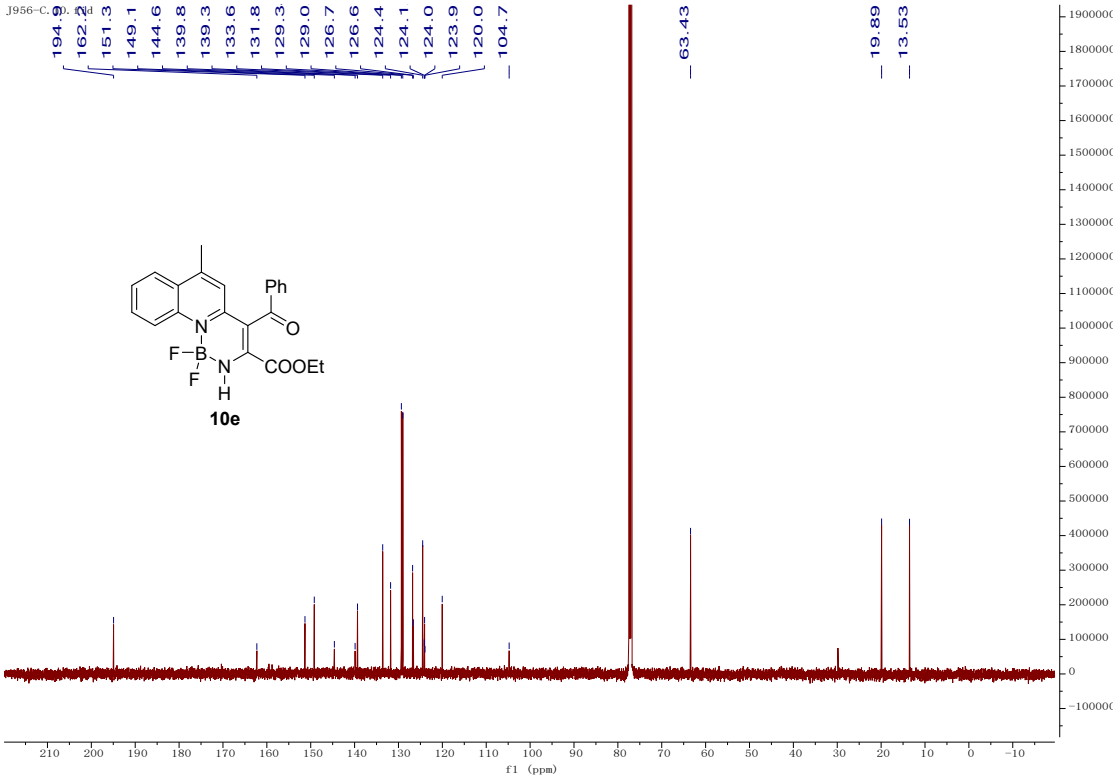
m/z: 428.0911 (100.0%), 430.0881 (32.0%), 427.0947 (24.8%), 429.0944 (22.7%), 429.0917 (7.9%), 431.0915 (7.3%), 428.0980 (5.6%), 430.0978 (2.5%), 430.0951 (1.8%)

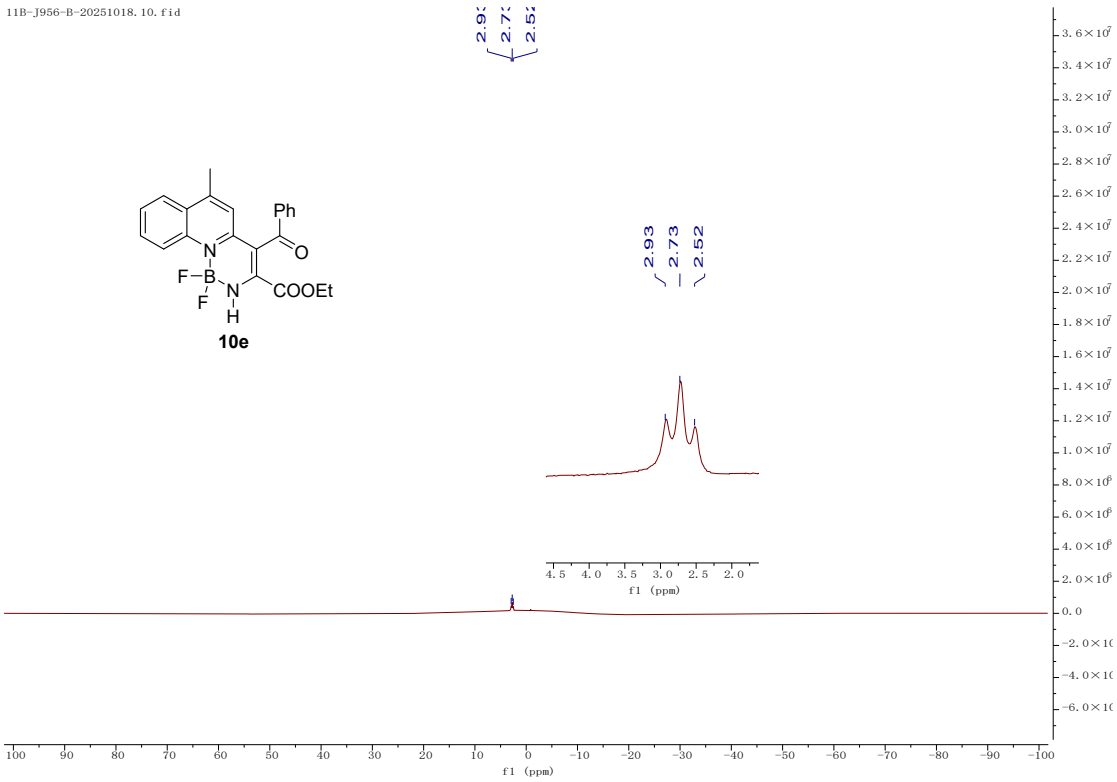
Elemental Analysis: C, 58.85; H, 3.76; B, 2.52; Cl, 8.27; F, 8.86; N, 6.54; O, 11.20

HRMS (ESI, m/z) calcd for $C_{21}H_{16}BClF_2N_2O_3$ $[M+Na]^+$ 451.0803, found 451.0809.

10e


Ph
O
N
F–B
F
N
H
COOEt
10e
f1 (ppm)


194.9
162.2
151.3
149.1
144.6
139.8
139.3
133.6
131.8
129.3
129.0
126.7
126.6
124.4
124.1
124.0
123.9
120.0
104.7
63.43
19.89
13.53
Ph
O
N
F–B
F
N
H
COOEt
10e
f1 (ppm)


11B-J956-B-20251018.10.fid
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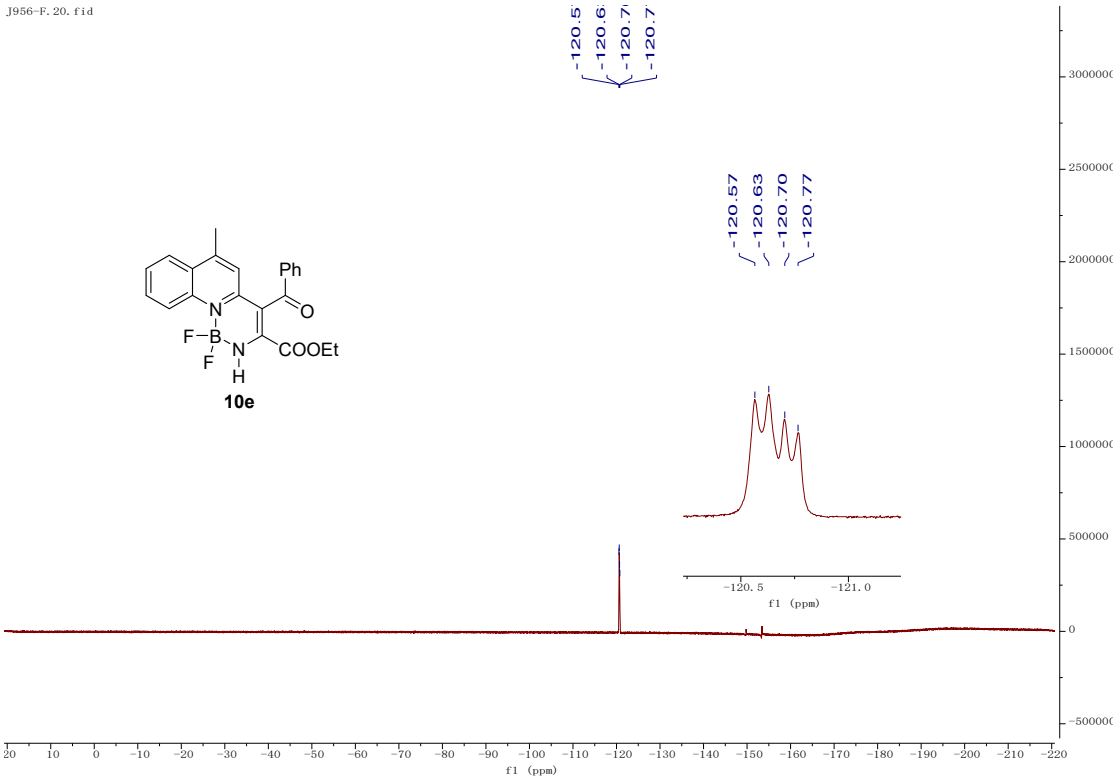
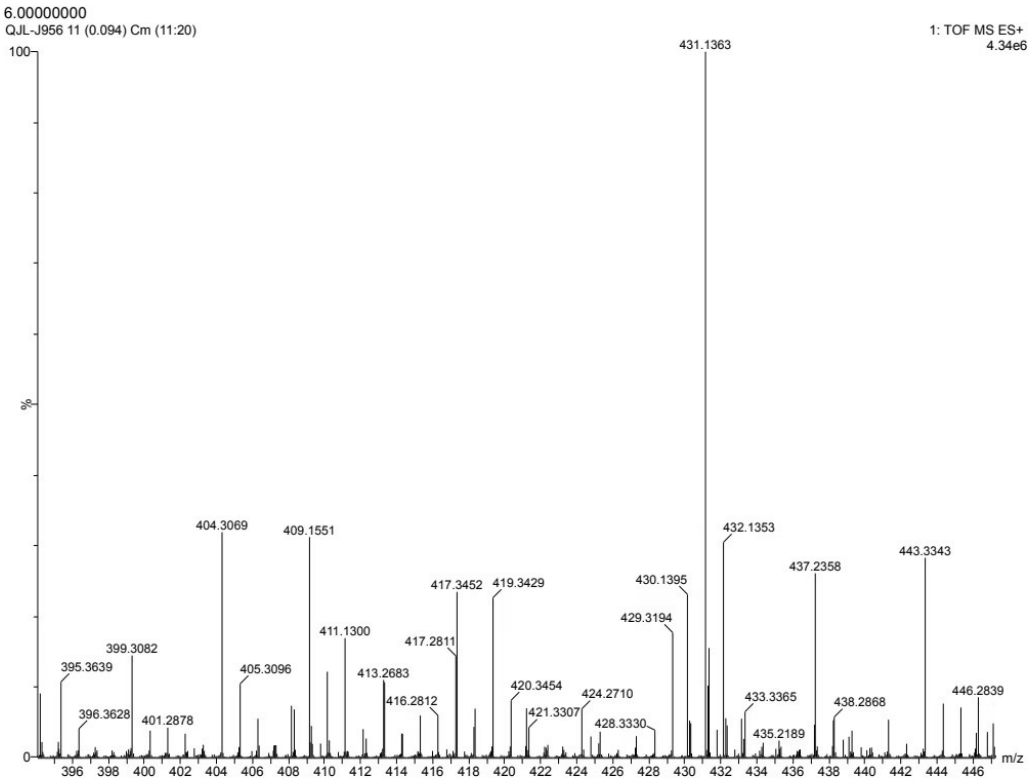
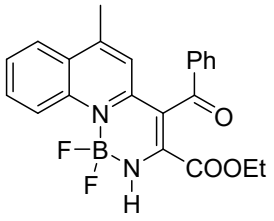
2.73
2.52
Ph
O
N
F–B
F
N
H
COOEt
10e
f1 (ppm)


J956-F.20.fid
-120.57
-120.63
-120.70
-120.77
Ph
O
N
F–B
F
N
H
COOEt
10e
f1 (ppm)





10e

Chemical Formula: $C_{22}H_{19}BF_2N_2O_3$

Exact Mass: 408.1457

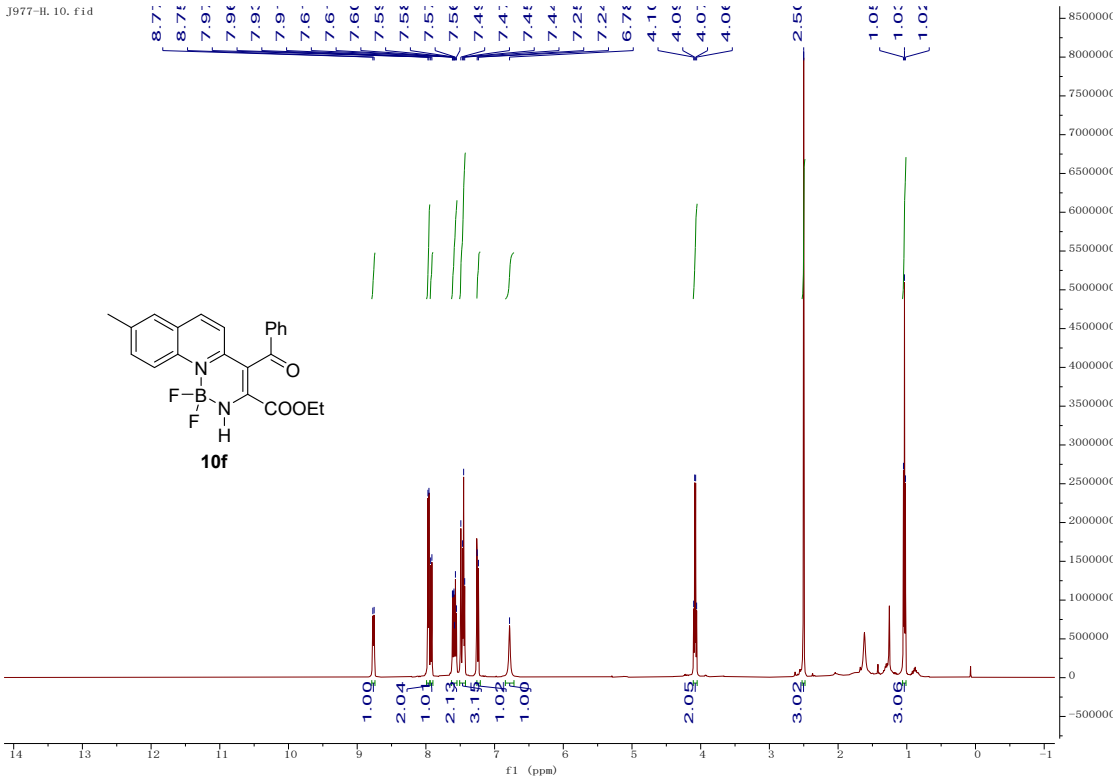
Molecular Weight: 408.2118

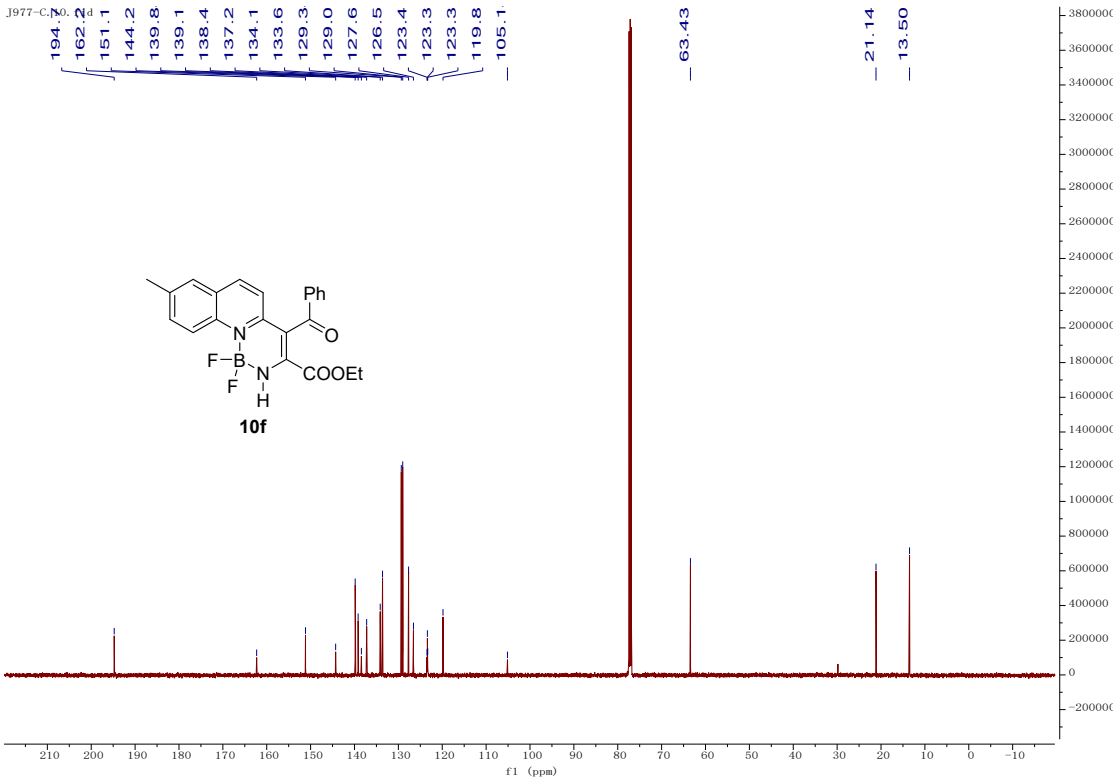
m/z: 408.1457 (100.0%), 407.1493 (24.8%), 409.1490 (23.8%), 408.1527 (5.9%), 410.1524 (2.7%)

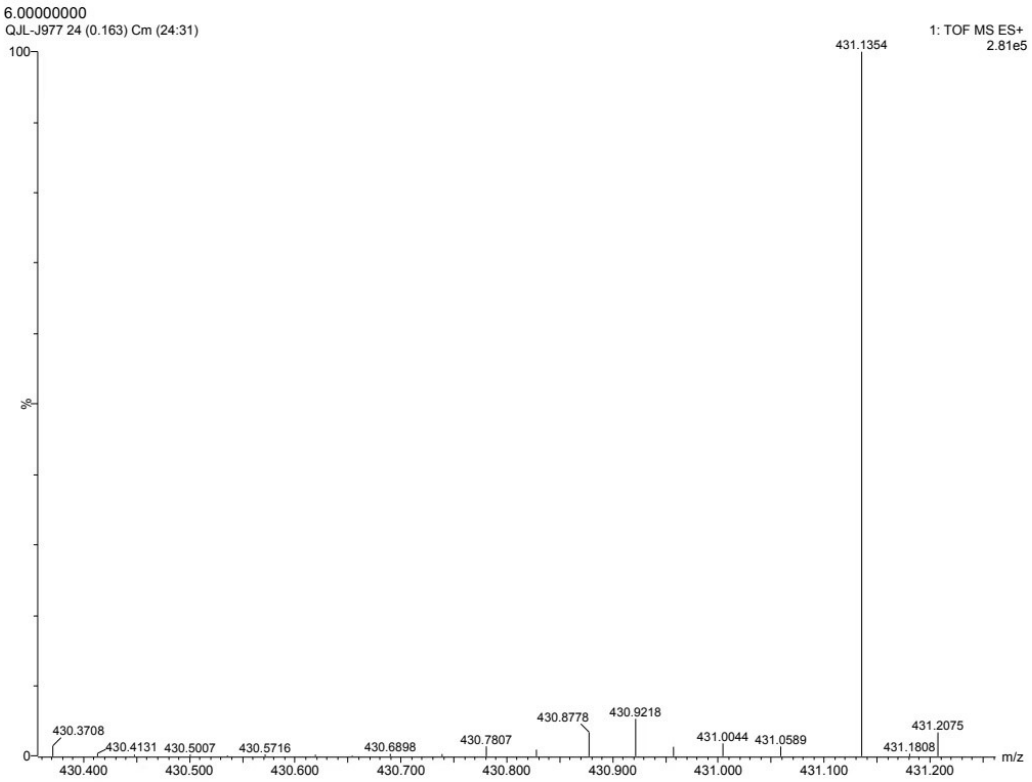
Elemental Analysis: C, 64.73; H, 4.69; B, 2.65; F, 9.31; N, 6.86; O, 11.76

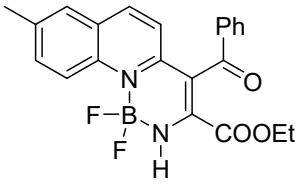
HRMS (ESI, m/z) calcd for $C_{22}H_{19}BF_2N_2O_3$ $[M+Na]^+$ 431.1349, found 431.1363.

10f


J977-H.10.fid
Ph
O
N
F—B
F
N
H
COOEt
10f
f1 (ppm)


J977-C.10.fid
63.43
21.14
13.50
Ph
O
N
F—B
F
N
H
COOEt
10f
f1 (ppm)





10f

Chemical Formula: $C_{22}H_{19}BF_2N_2O_3$

Exact Mass: 408.1457

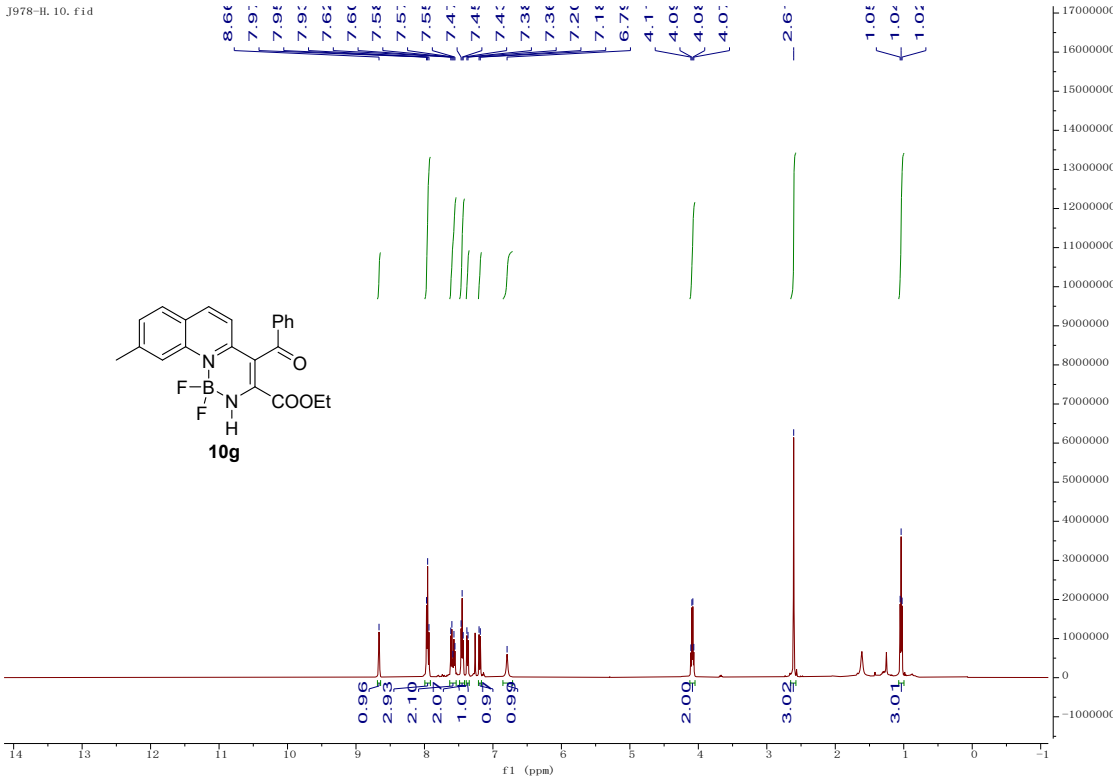
Molecular Weight: 408.2118

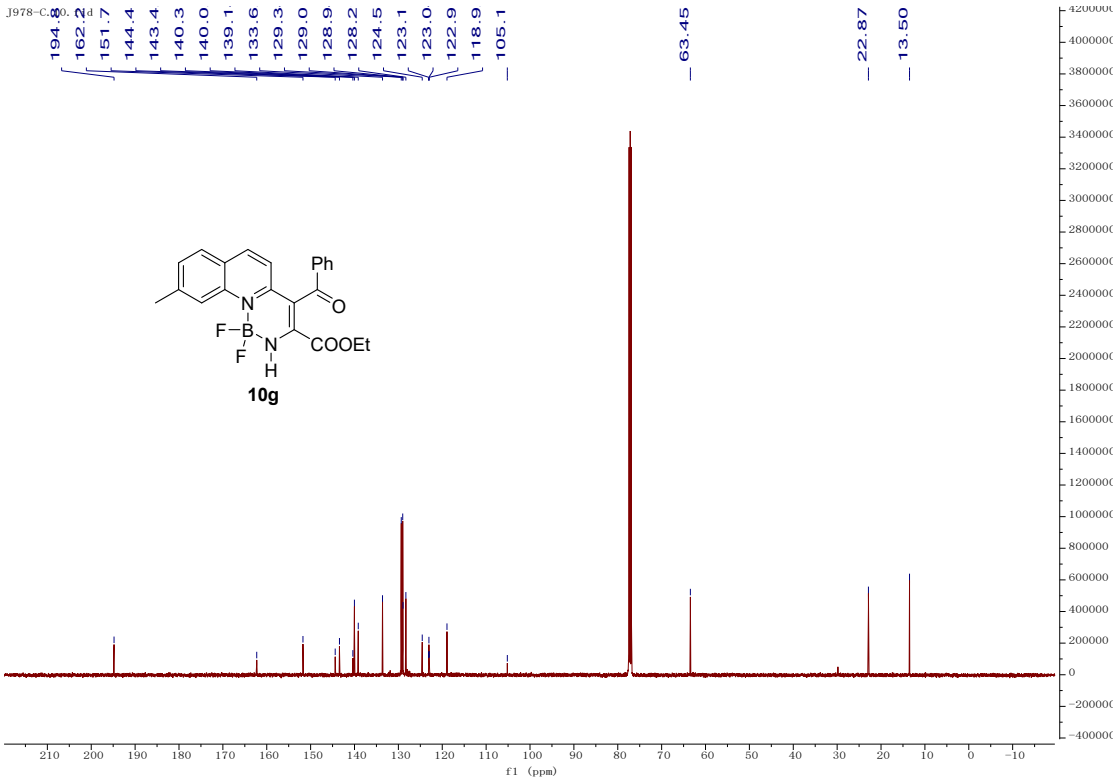
m/z: 408.1457 (100.0%), 407.1493 (24.8%), 409.1490 (23.8%), 408.1527 (5.9%), 410.1524 (2.7%)

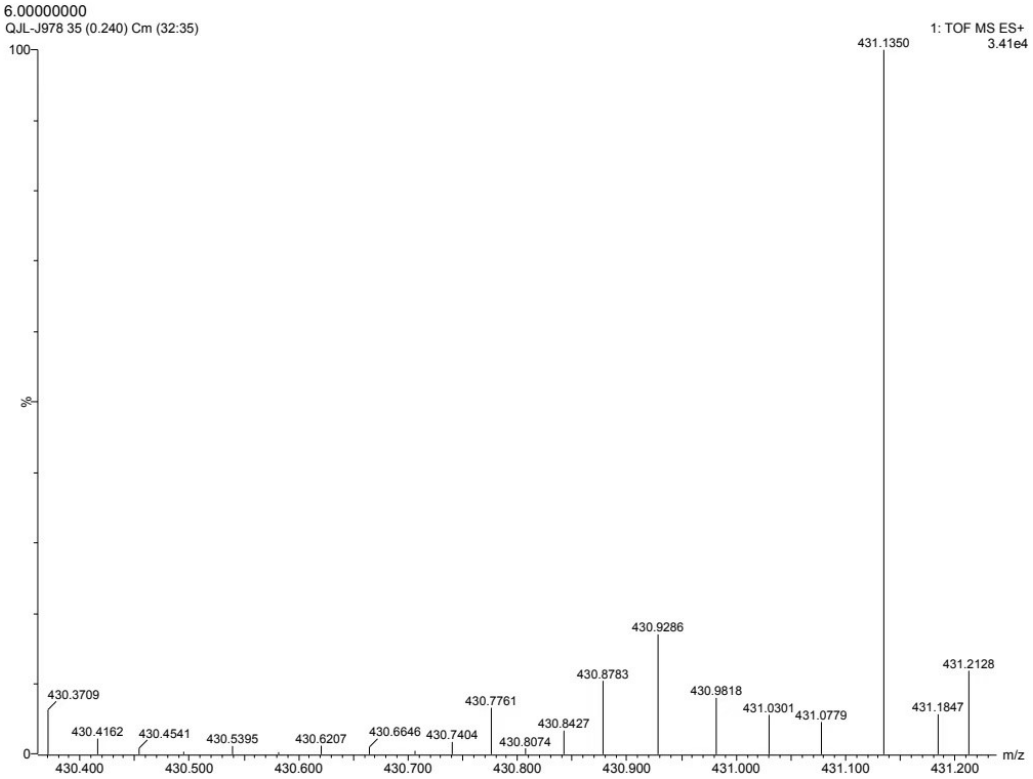
Elemental Analysis: C, 64.73; H, 4.69; B, 2.65; F, 9.31; N, 6.86; O, 11.76

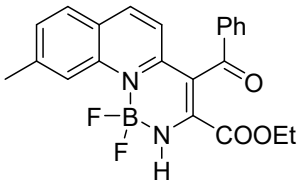
HRMS (ESI, m/z) calcd for $C_{22}H_{19}BF_2N_2O_3$ $[M+Na]^+$ 431.1349, found 431.1354.

10g


J978-H.10.fid
Ph
O
N
F–B
F
N
H
COOEt
10g
f1 (ppm)


J978-C.10.fid
194.8
162.2
151.7
144.4
143.4
140.3
140.0
139.1
133.6
129.3
129.0
128.9
128.2
124.5
123.1
123.0
122.9
118.9
105.1
63.45
22.87
13.50
Ph
O
N
F–B
F
N
H
COOEt
10g
f1 (ppm)





10g

Chemical Formula: $C_{22}H_{19}BF_2N_2O_3$

Exact Mass: 408.1457

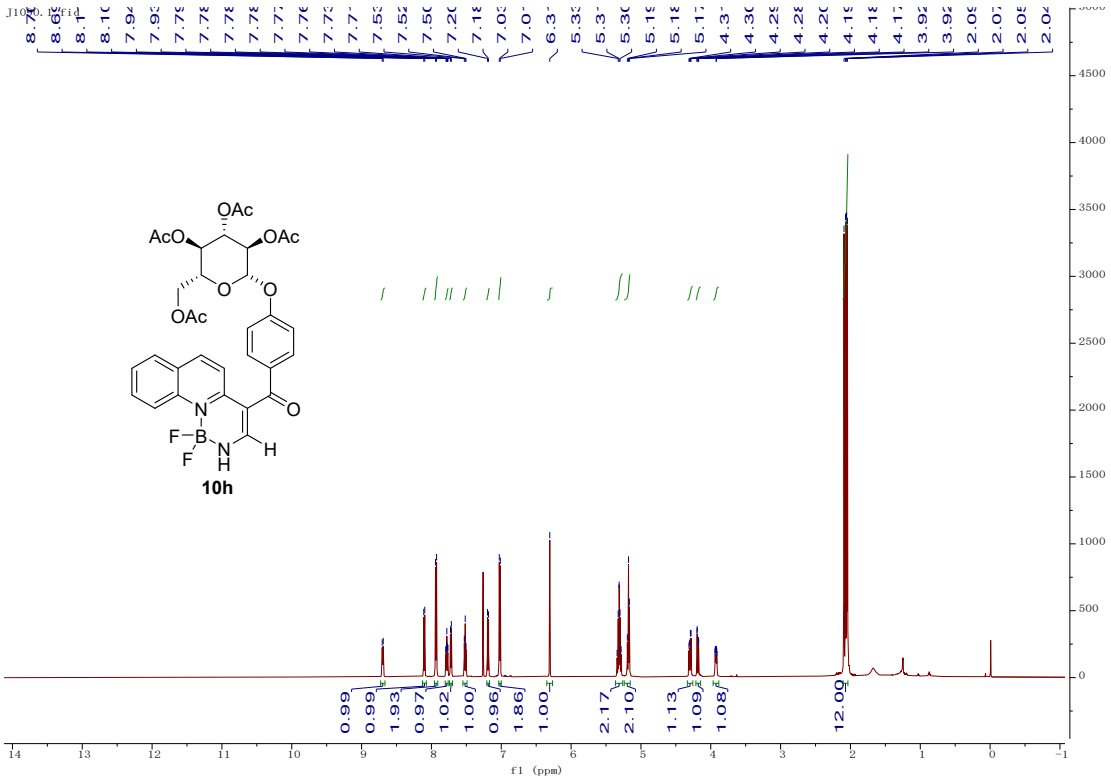
Molecular Weight: 408.2118

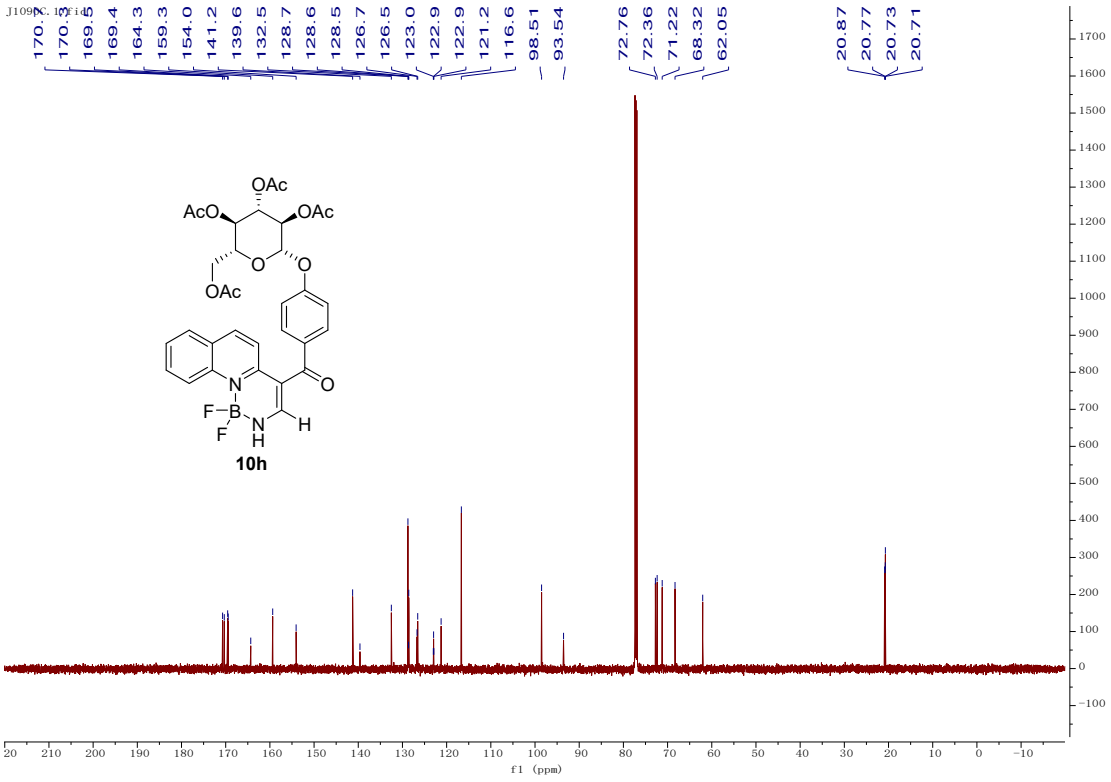
m/z: 408.1457 (100.0%), 407.1493 (24.8%), 409.1490 (23.8%), 408.1527 (5.9%), 410.1524 (2.7%)

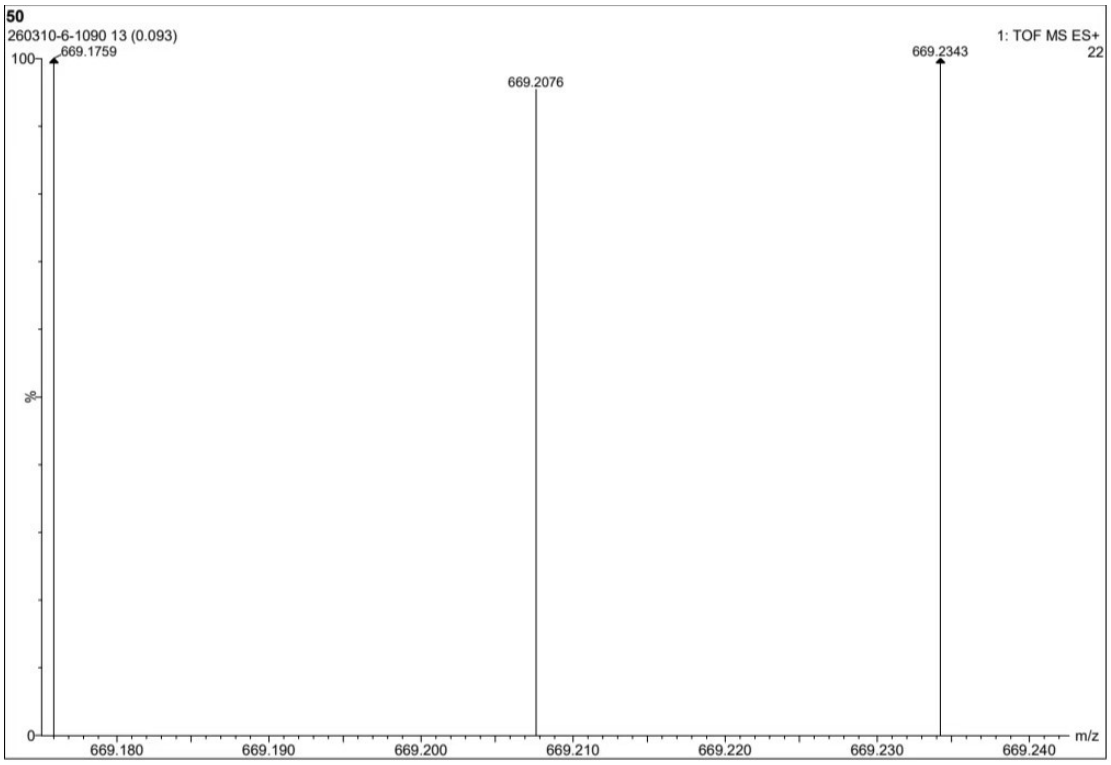
Elemental Analysis: C, 64.73; H, 4.69; B, 2.65; F, 9.31; N, 6.86; O, 11.76

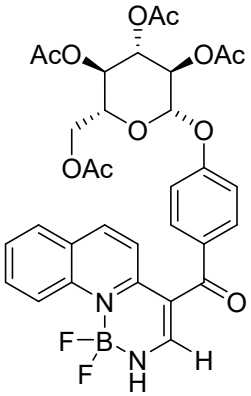
HRMS (ESI, m/z) calcd for $C_{22}H_{19}BF_2N_2O_3$ $[M+Na]^+$ 431.1349, found 431.1350.

10h


OAc
AcO
OAc
OAc
O
O
N
F–B
F
N
H
H
O
10h
f1 (ppm)


OAc
AcO
OAc
OAc
O
O
N
F–B
F
N
H
H
O
10h
f1 (ppm)



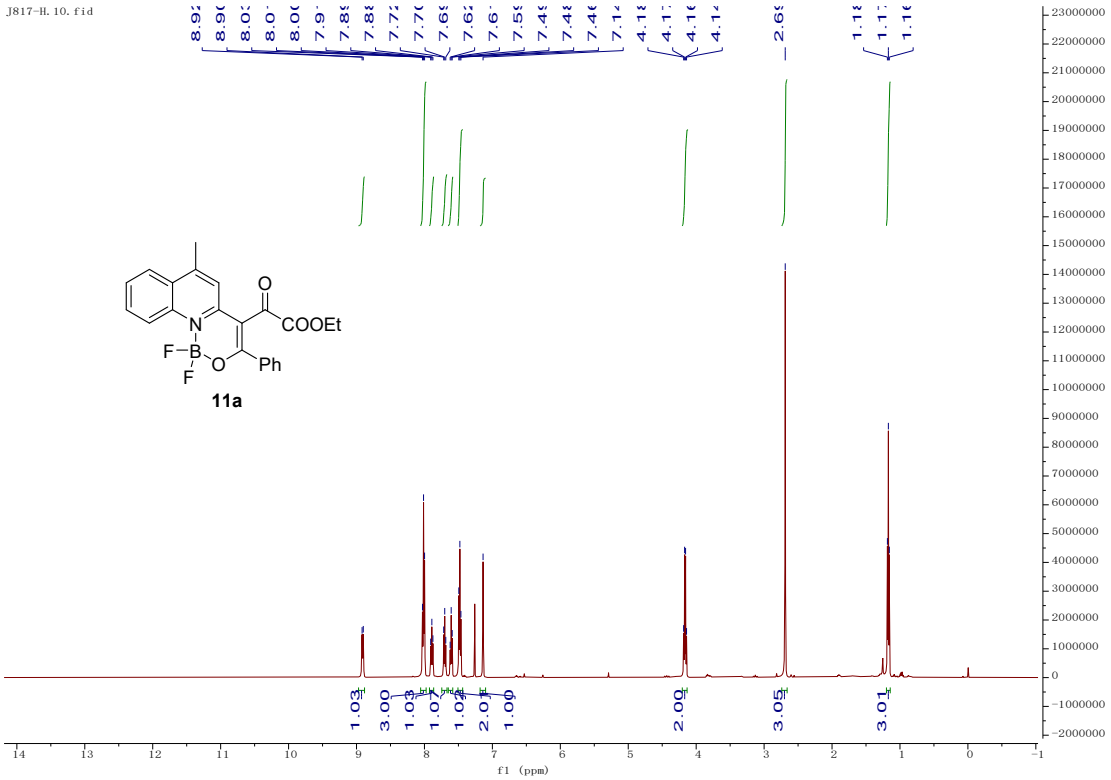


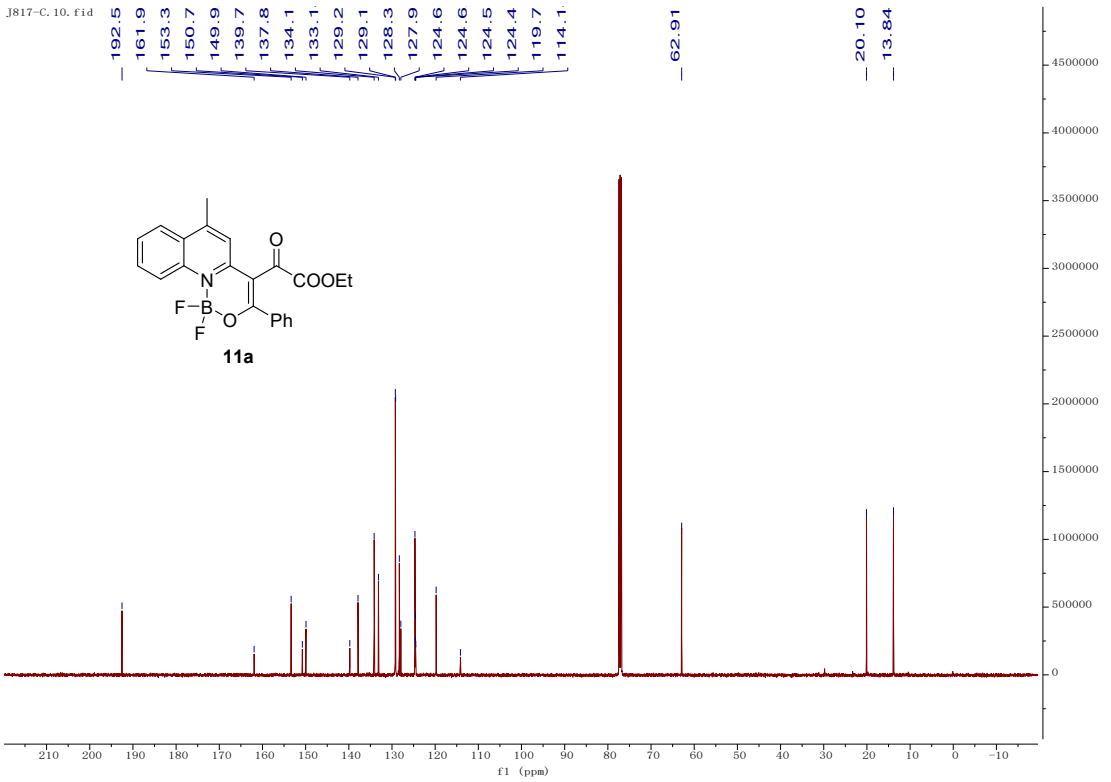
10h

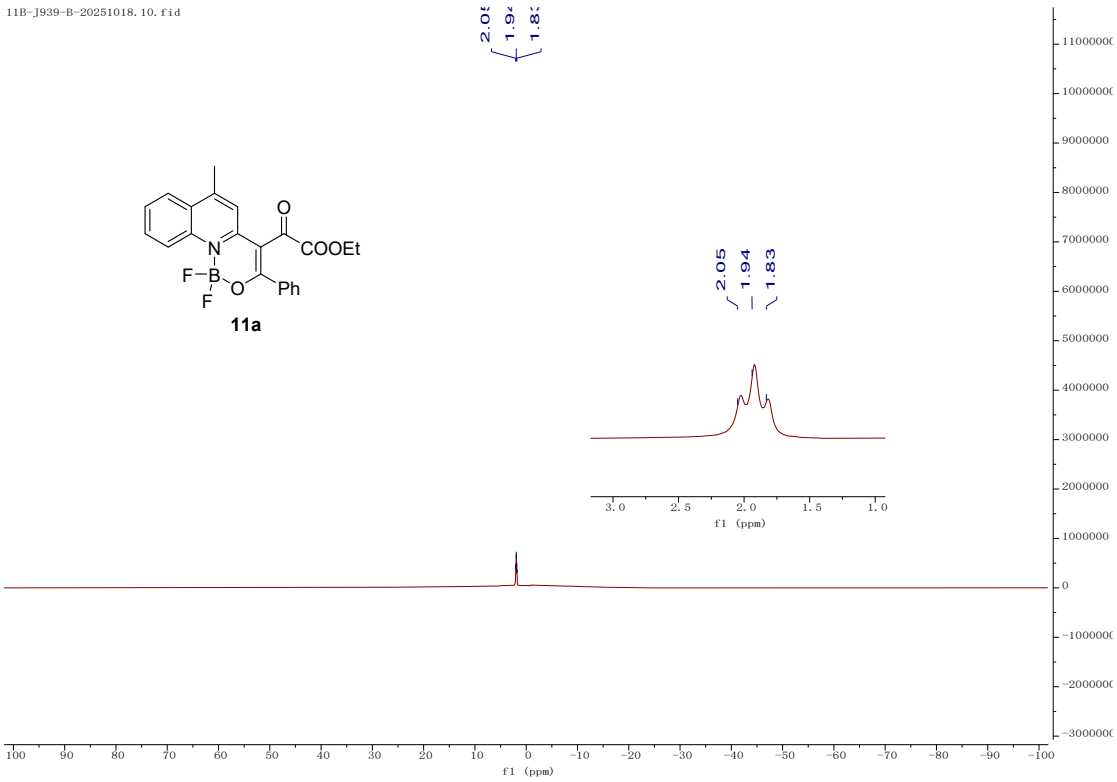
Chemical Formula: $C_{32}H_{31}BF_2N_2O_{11}$
Exact Mass: 668.1989
Molecular Weight: 668.4098
m/z: 668.1989 (100.0%), 669.2023 (34.6%), 667.2025 (24.8%),
668.2059 (8.6%), 670.2056 (5.8%), 670.2031 (2.3%), 669.2092 (1.4%)
Elemental Analysis: C, 57.50; H, 4.67; B, 1.62; F, 5.68; N, 4.19; O, 26.33

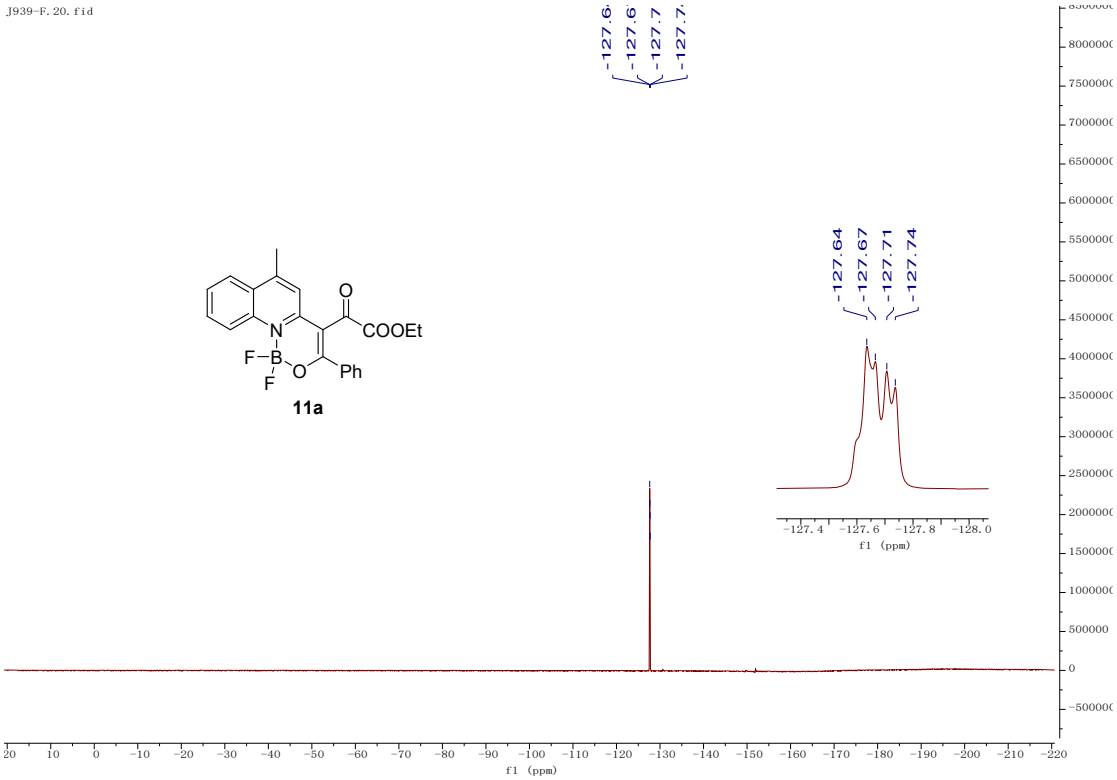
HRMS (ESI, m/z) calcd for $C_{32}H_{31}BF_2N_2O_{11}$ $[M+H]^+$ 669.2062, found 669.2076.

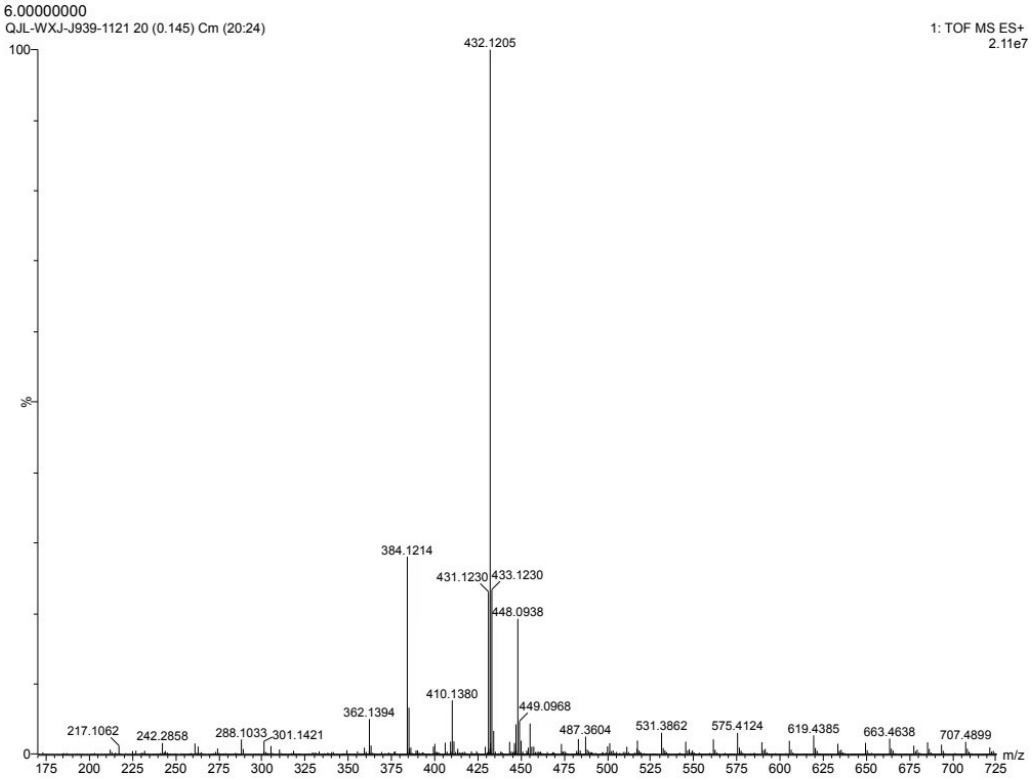
11a

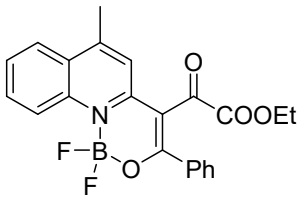

J817-H.10.fid
COOEt
Ph
11a
f1 (ppm)


J817-C.10.fid
COOEt
Ph
11a
f1 (ppm)


11B-J939-B-20251018.10.fid
2.05
1.94
1.83
COOEt
Ph
11a
f1 (ppm)


J939-F.20.fid
-127.64
-127.67
-127.71
-127.74
COOEt
Ph
11a
f1 (ppm)





11a

Chemical Formula: $C_{22}H_{18}BF_2NO_4$

Exact Mass: 409.1297

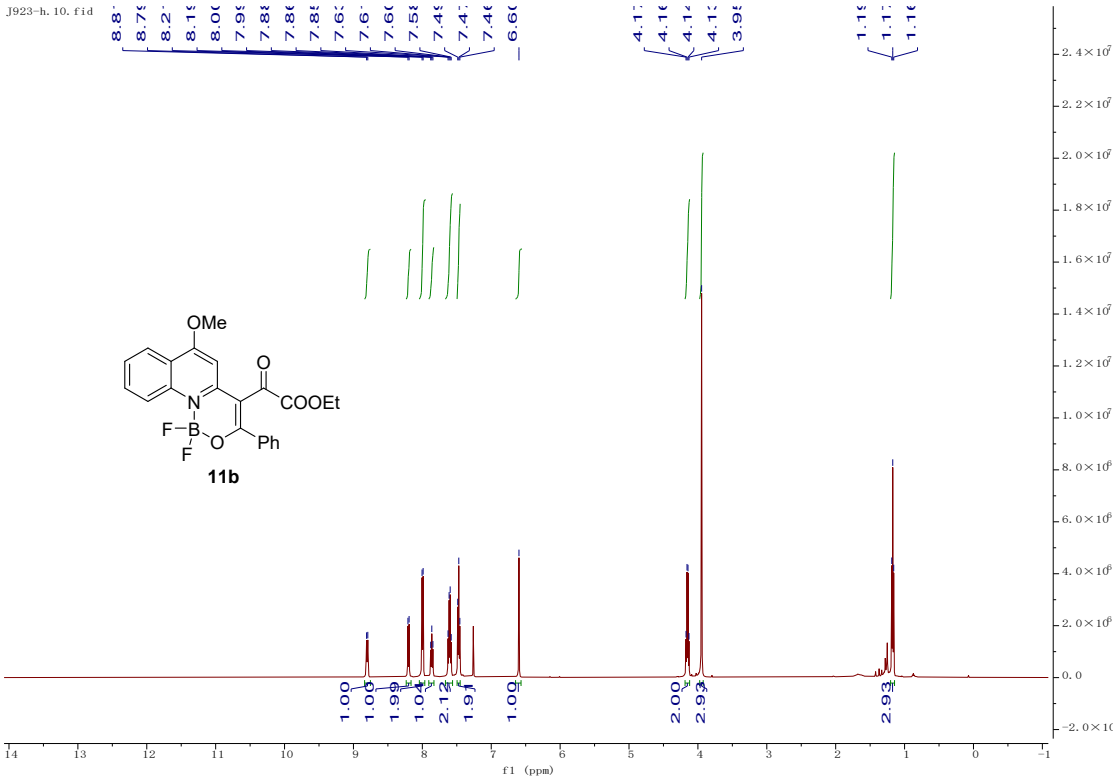
Molecular Weight: 409.1958

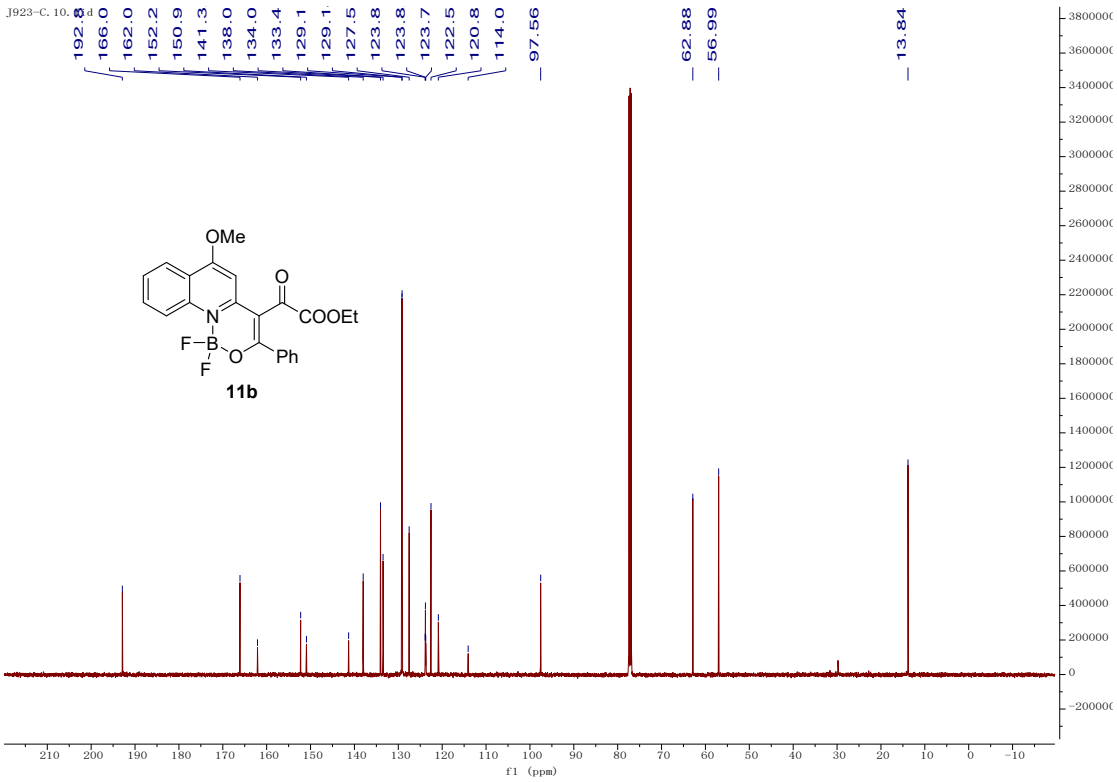
m/z: 409.1297 (100.0%), 408.1333 (24.8%), 410.1330 (23.8%), 409.1367 (5.9%), 411.1364 (2.7%)

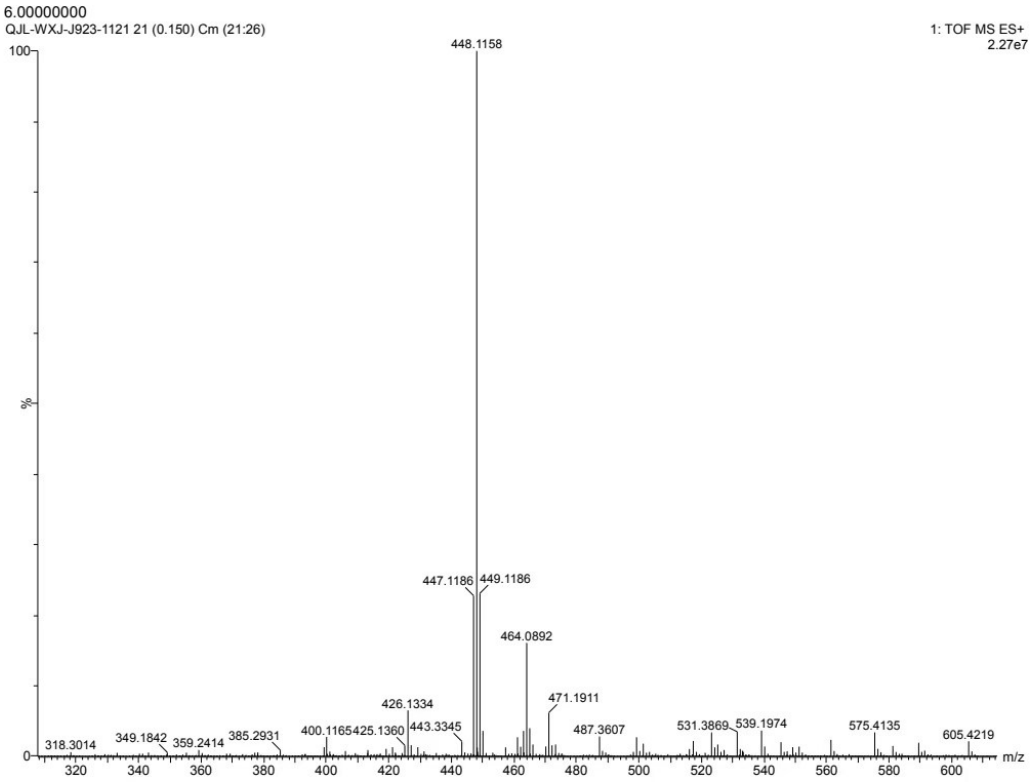
Elemental Analysis: C, 64.58; H, 4.43; B, 2.64; F, 9.29; N, 3.42; O, 15.64

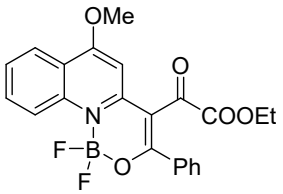
HRMS (ESI, m/z) calcd for $C_{22}H_{18}BF_2N_2O_4$ $[M+Na]^+$ 432.1190, found 432.1205.

11b


J923-h.10.fid
OMe
O
COOEt
N
F–B
O
F
Ph
11b
f1 (ppm)


J923-C.10.fid
192.8
166.0
162.0
152.2
150.9
141.3
138.0
134.0
133.4
129.1
129.1
127.5
123.8
123.8
123.7
122.5
120.8
114.0
97.56
62.88
56.99
13.84
OMe
O
COOEt
N
F–B
O
F
Ph
11b
f1 (ppm)





11b

Chemical Formula: $C_{22}H_{18}BF_2NO_5$

Exact Mass: 425.1246

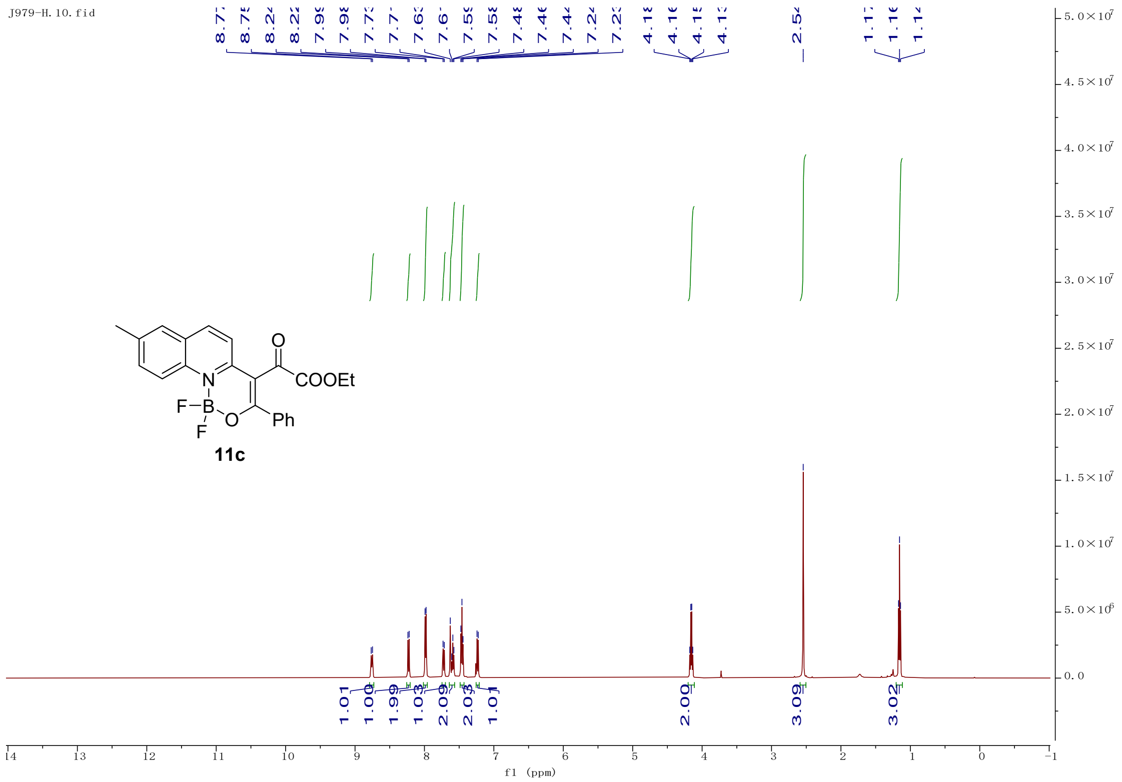
Molecular Weight: 425.1948

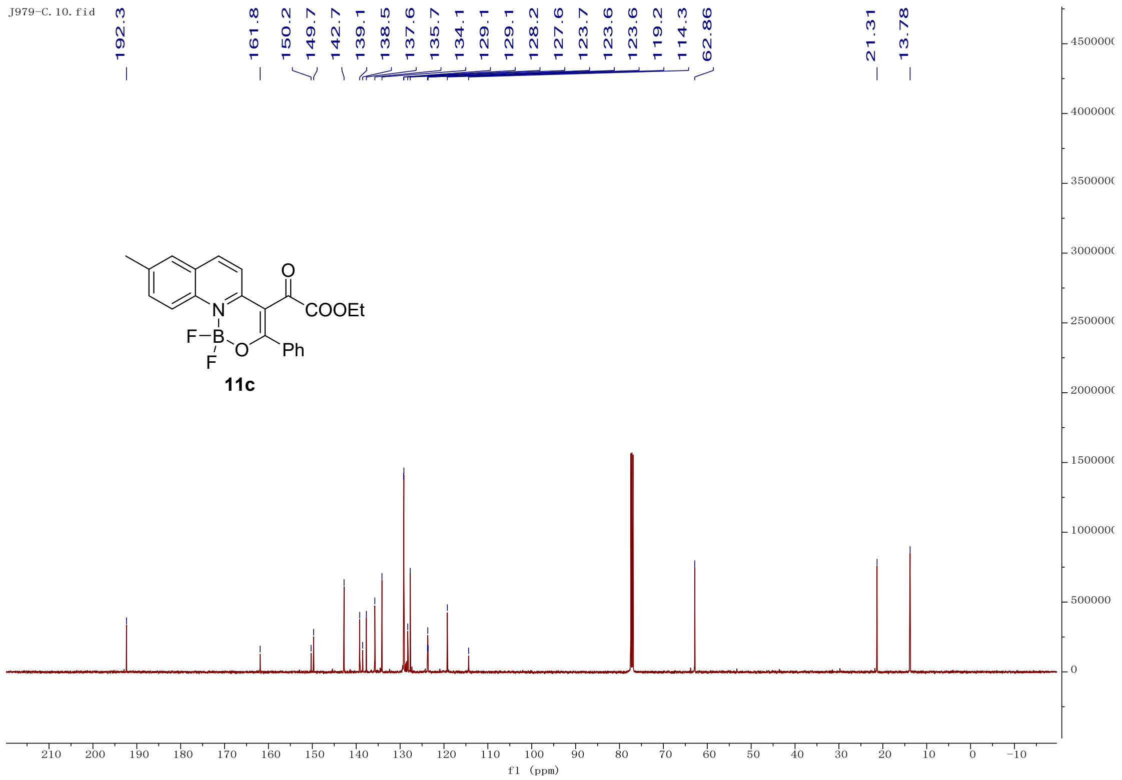
m/z: 425.1246 (100.0%), 424.1282 (24.8%), 426.1280 (23.8%), 425.1316 (5.9%), 427.1313 (2.7%), 427.1289 (1.0%)

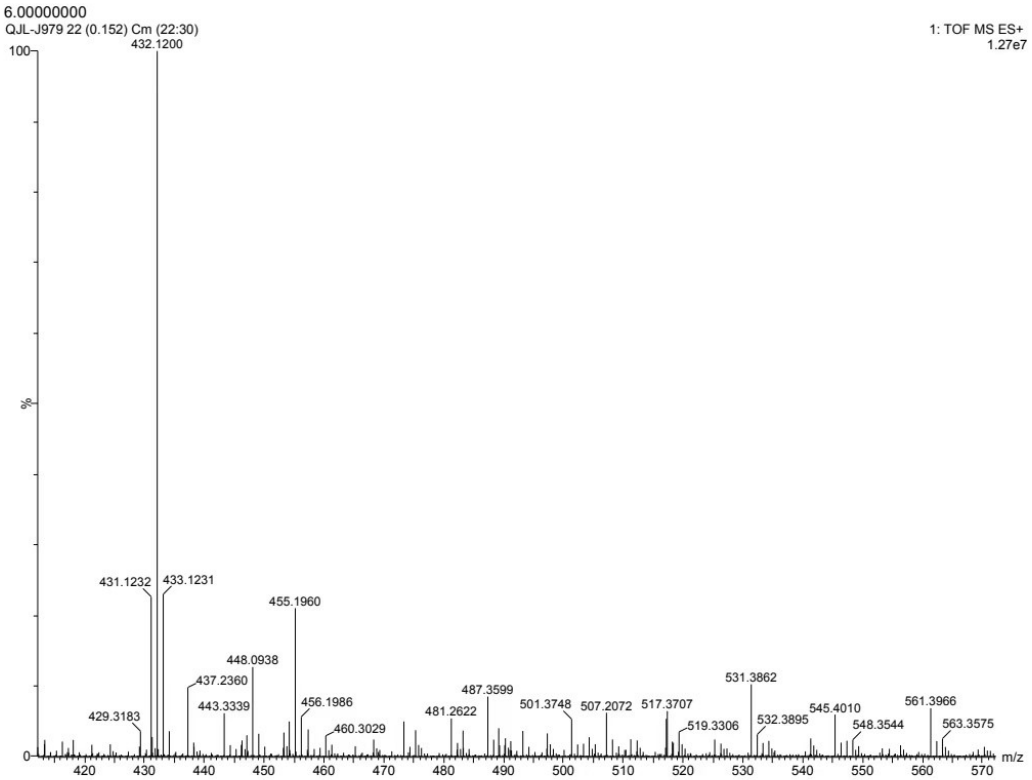
Elemental Analysis: C, 62.15; H, 4.27; B, 2.54; F, 8.94; N, 3.29; O, 18.81

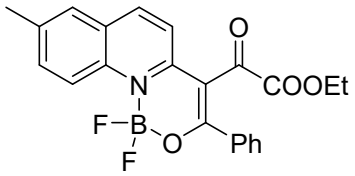
HRMS (ESI, m/z) calcd for $C_{22}H_{18}BF_2N_2O_5$ $[M+Na]^+$ 448.1139, found 448.1158.

11c


J979-H.10.fid
COOEt
Ph
11c
1.01
1.00
1.99
1.03
2.09
2.03
1.01
2.00
3.09
3.02
f1 (ppm)


J979-C.10.fid
192.3
161.8
150.2
149.7
142.7
139.1
138.5
137.6
135.7
134.1
129.1
129.1
128.2
127.6
123.7
123.6
123.6
119.2
114.3
62.86
21.31
13.78
COOEt
Ph
11c
f1 (ppm)





11c

Chemical Formula: $C_{22}H_{18}BF_2NO_4$

Exact Mass: 409.1297

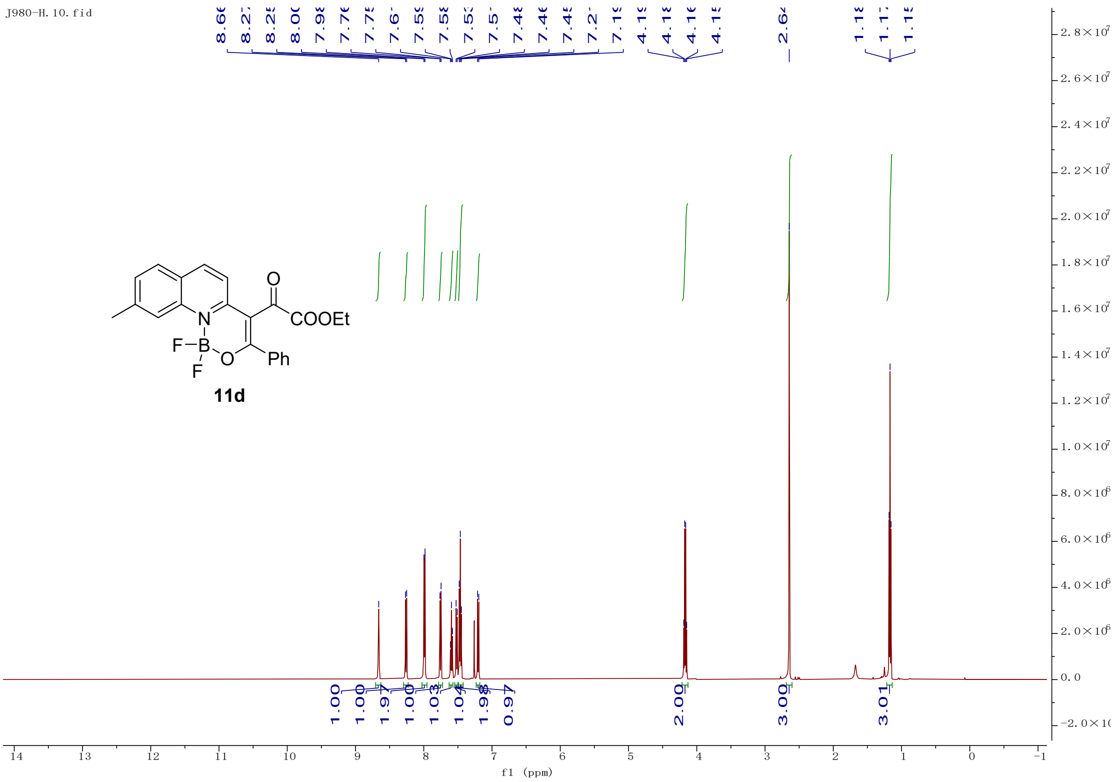
Molecular Weight: 409.1958

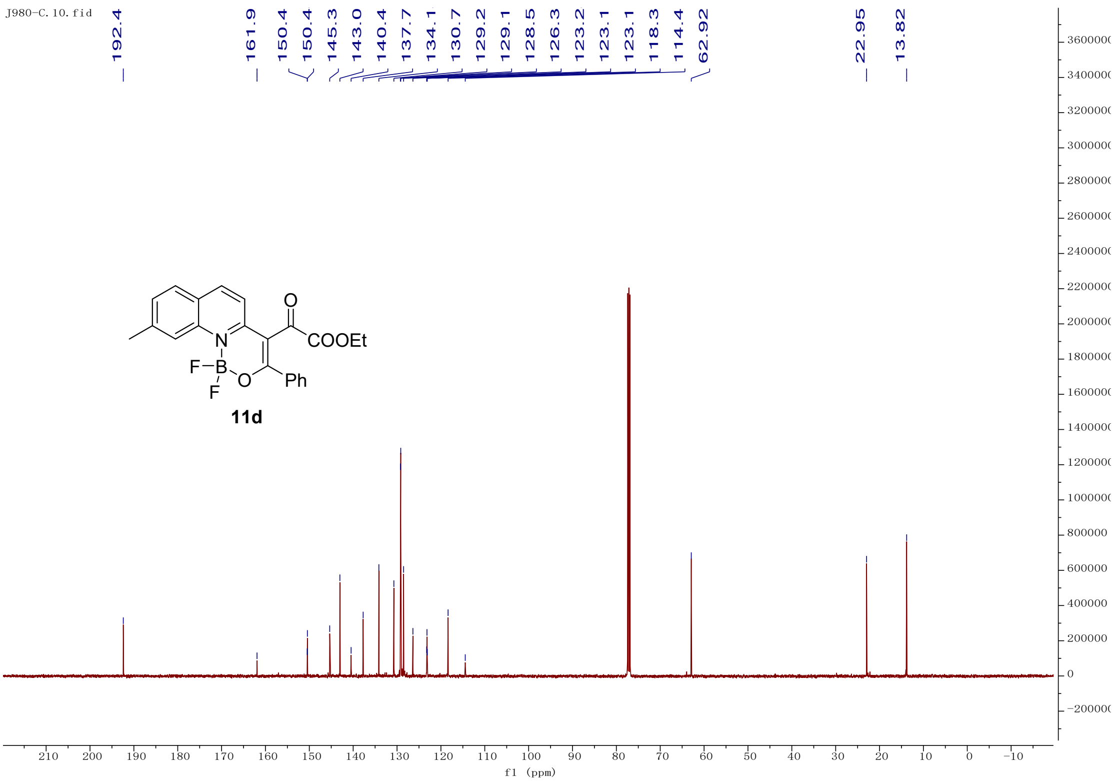
m/z: 409.1297 (100.0%), 408.1333 (24.8%), 410.1330 (23.8%), 409.1367 (5.9%), 411.1364 (2.7%)

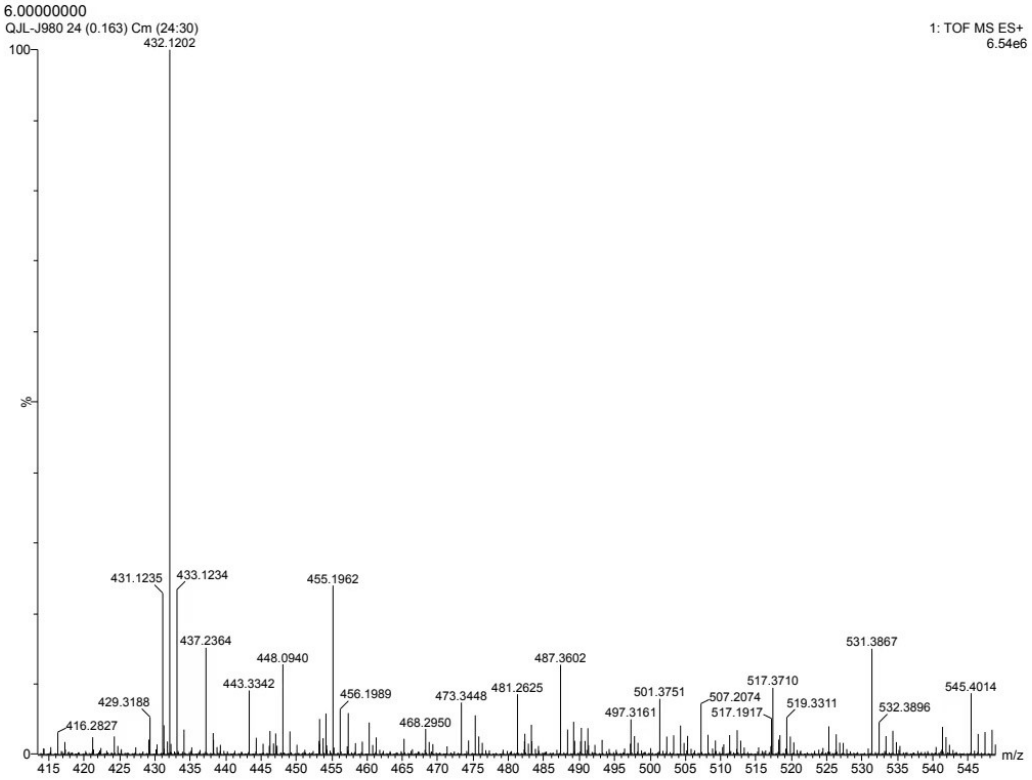
Elemental Analysis: C, 64.58; H, 4.43; B, 2.64; F, 9.29; N, 3.42; O, 15.64

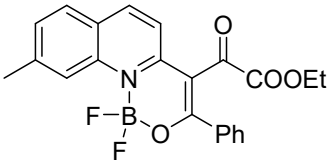
HRMS (ESI, m/z) calcd for $C_{22}H_{18}BF_2NO_4$ $[M+Na]^+$ 432.1190, found 432.1200.

11d


J980-H.10.fid
COOEt
Ph
11d
f1 (ppm)


J980-C.10.fid
192.4
161.9
150.4
150.4
145.3
143.0
140.4
137.7
134.1
130.7
129.2
129.1
128.5
126.3
123.2
123.1
123.1
118.3
114.4
62.92
22.95
13.82
COOEt
Ph
11d
f1 (ppm)





11d

Chemical Formula: $C_{22}H_{18}BF_2NO_4$

Exact Mass: 409.1297

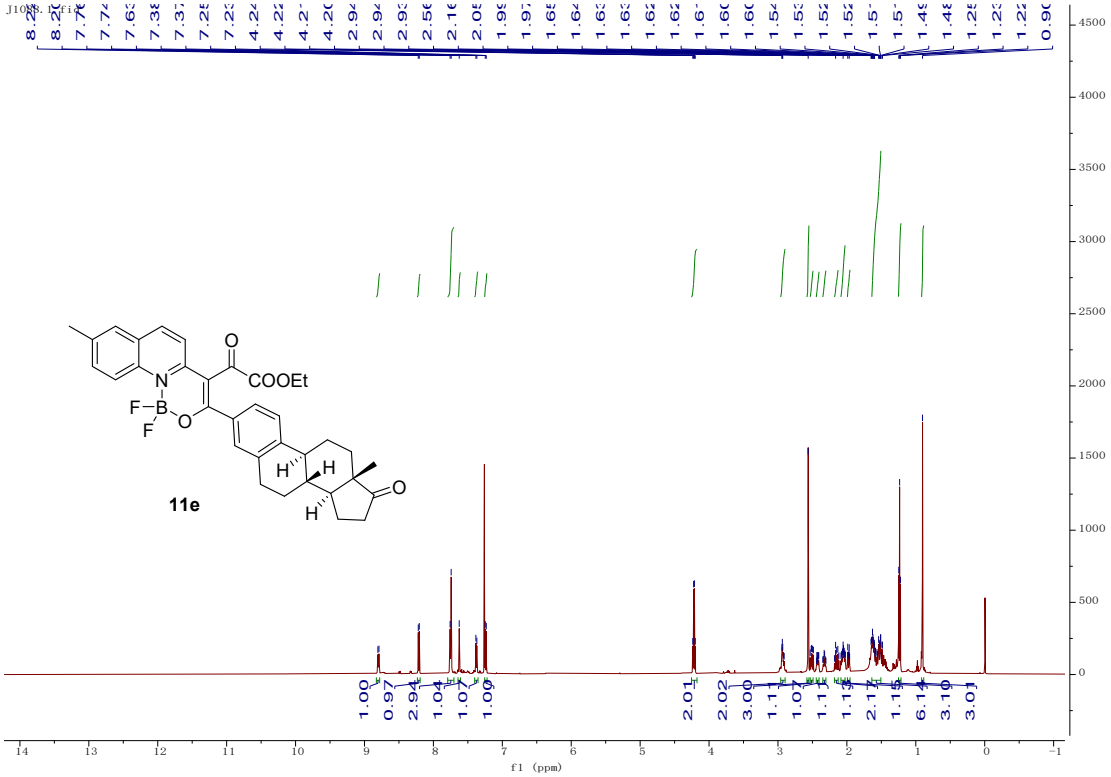
Molecular Weight: 409.1958

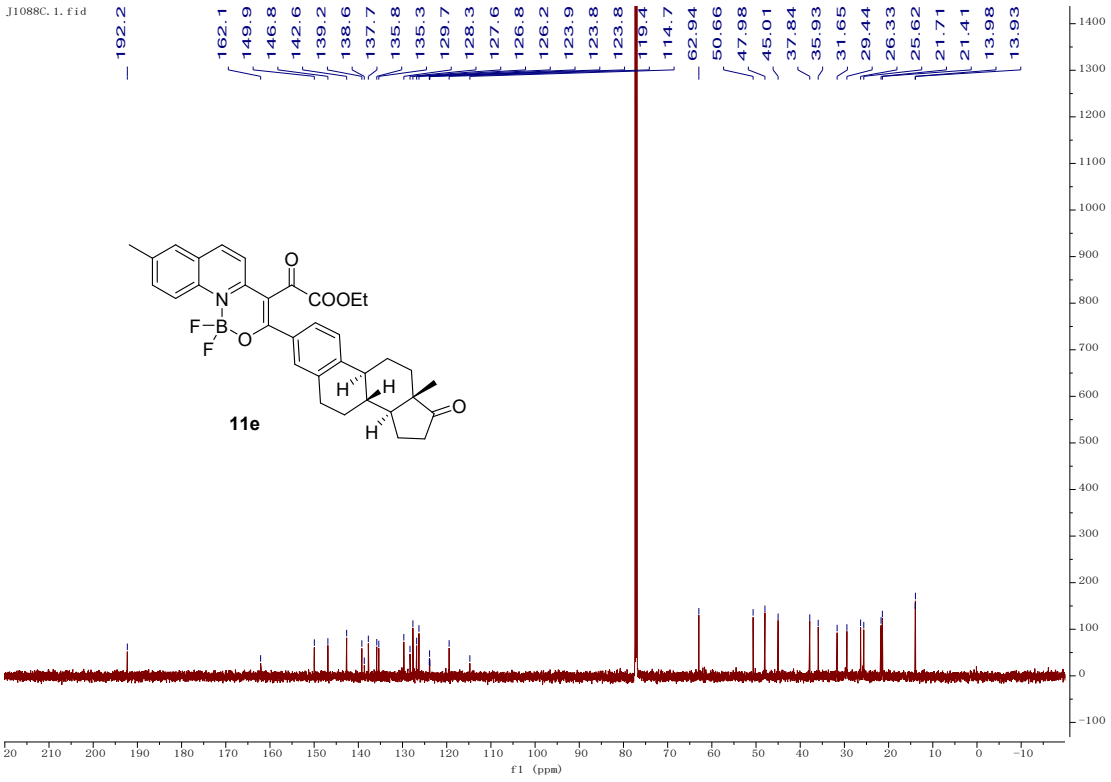
m/z: 409.1297 (100.0%), 408.1333 (24.8%), 410.1330 (23.8%), 409.1367 (5.9%), 411.1364 (2.7%)

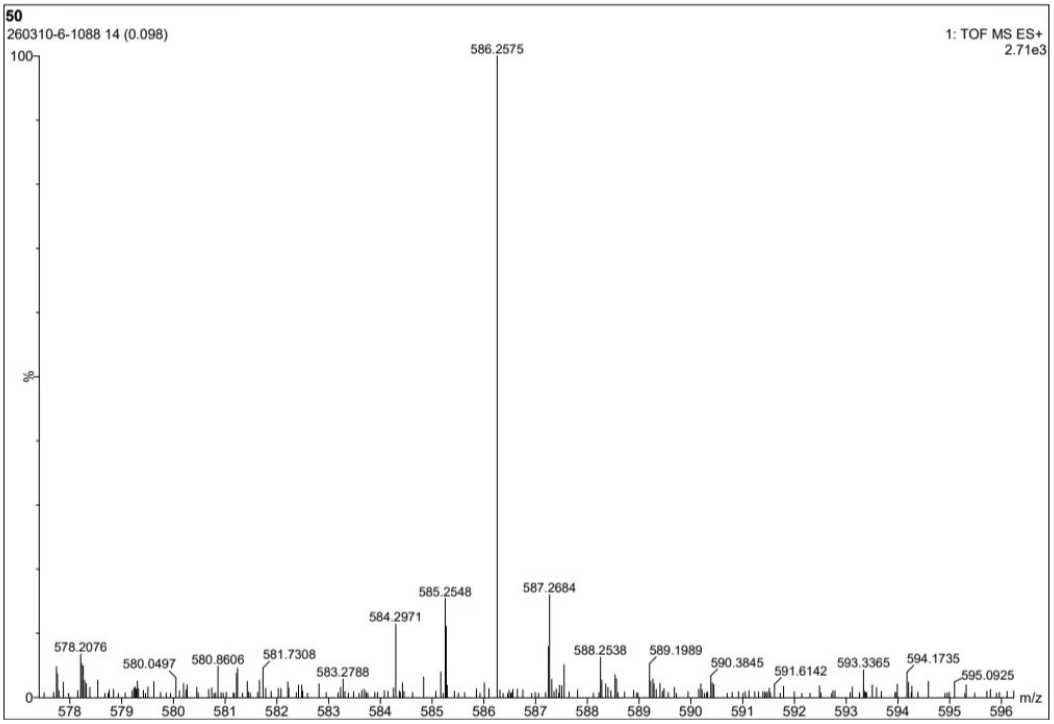
Elemental Analysis: C, 64.58; H, 4.43; B, 2.64; F, 9.29; N, 3.42; O, 15.64

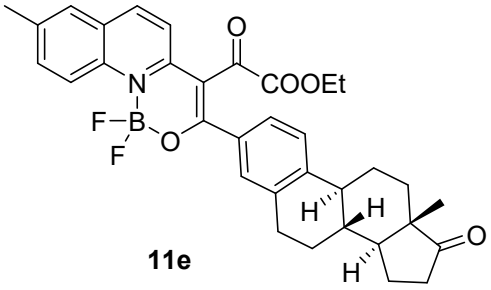
HRMS (ESI, m/z) calcd for $C_{22}H_{18}BF_2NO_4$ $[M+Na]^+$ 432.1190, found 432.1202.

11e









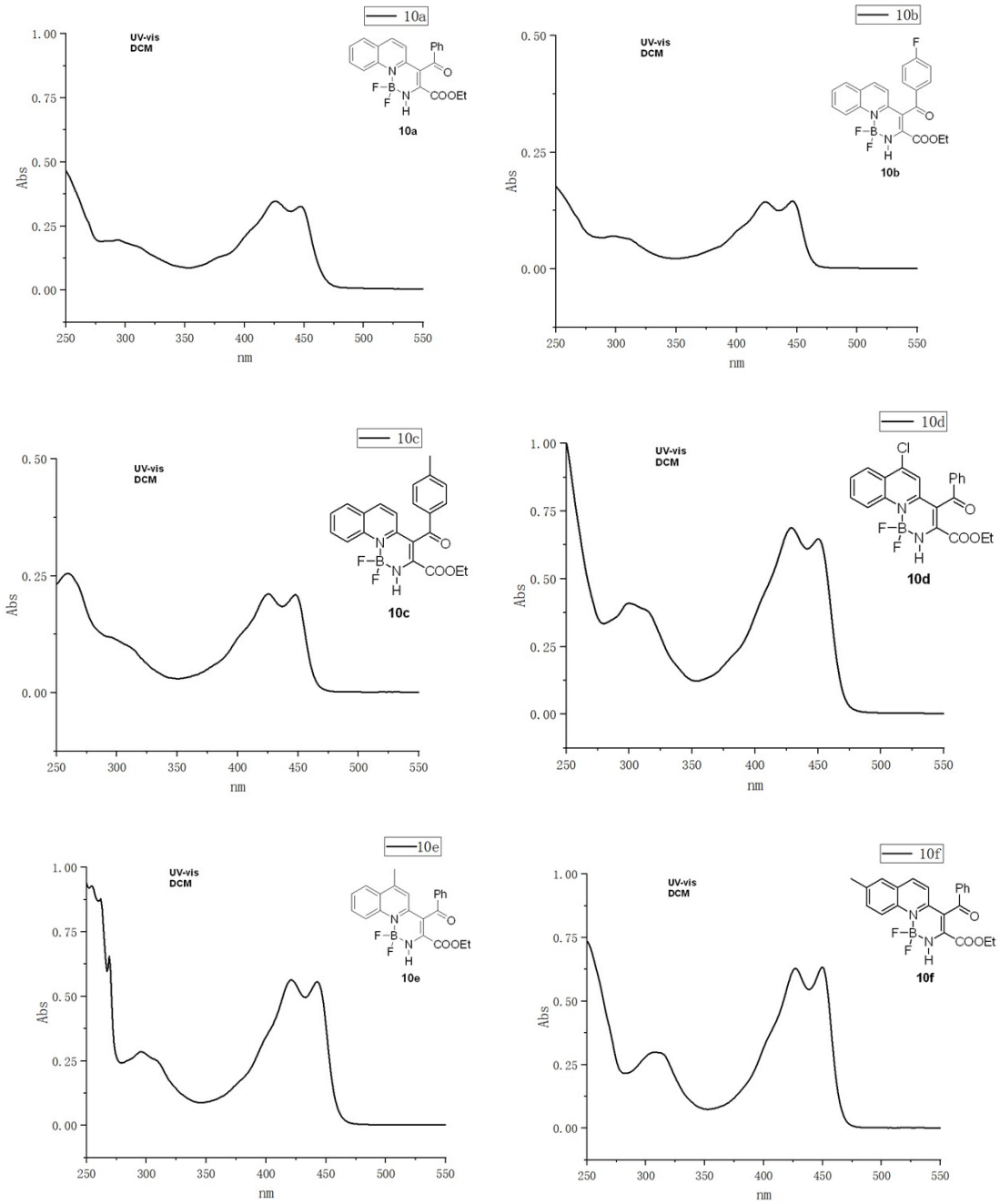
11e

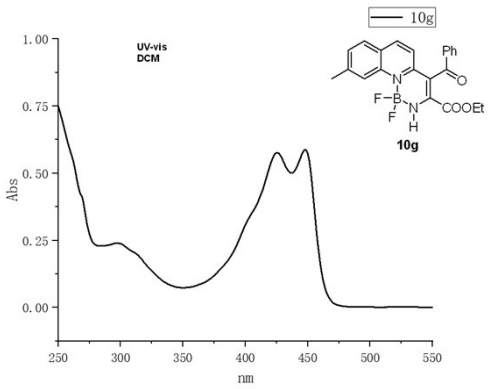
Chemical Formula: $C_{34}H_{34}BF_2NO_5$
Exact Mass: 585.2498
Molecular Weight: 585.4548
m/z: 585.2498 (100.0%), 586.2532 (36.8%), 584.2534 (24.8%),
585.2568 (9.1%), 587.2565 (6.6%), 586.2602 (1.6%), 587.2541 (1.0%)
Elemental Analysis: C, 69.75; H, 5.85; B, 1.85; F, 6.49; N, 2.39; O, 13.66

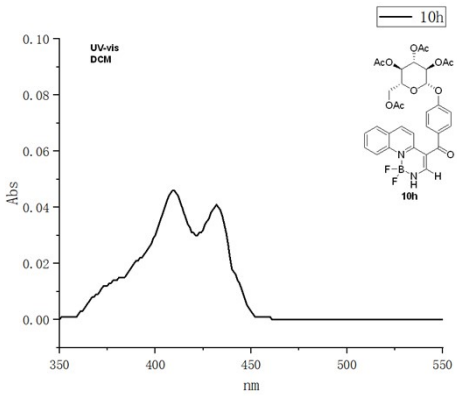
HRMS (ESI, m/z) calcd for $C_{34}H_{34}BF_2NO_5$ $[M+H]^+$ 586.2571, found 586.2575.

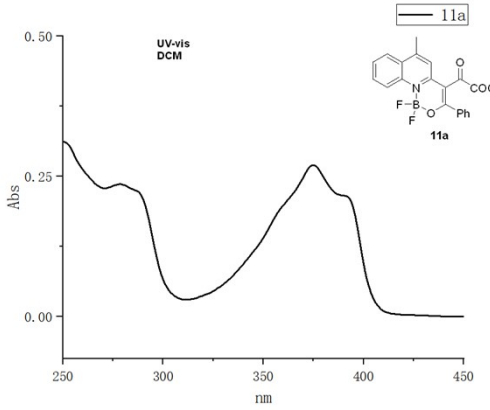
10. UV-Vis absorption and Fluorescence emission spectra and Photophysical Measurements

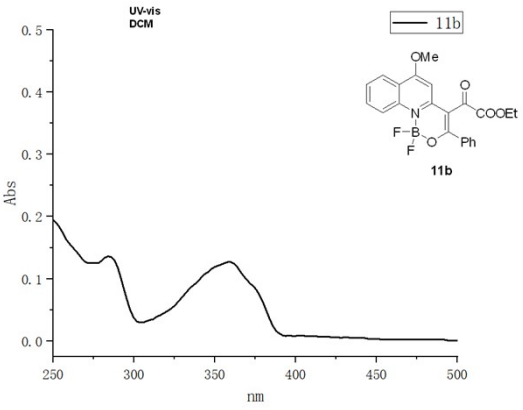
Figure S1. UV-vis absorption spectra

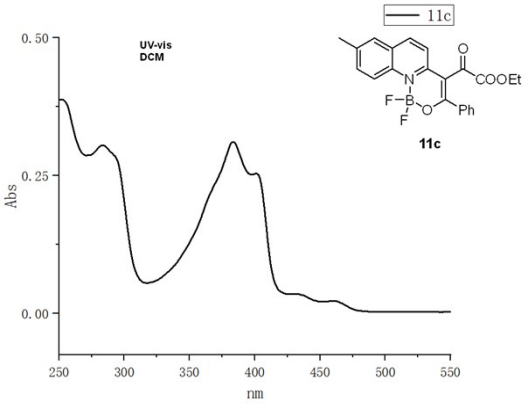


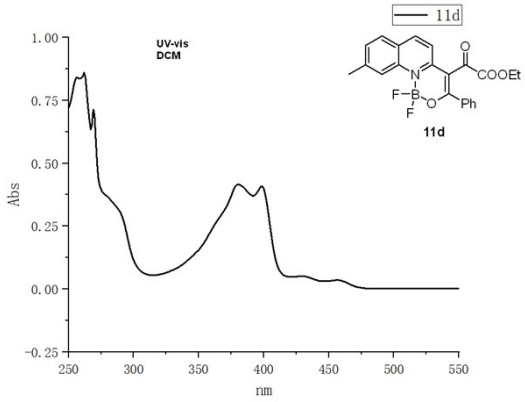

10g
UV-vis
DCM
Abs
nm
10g

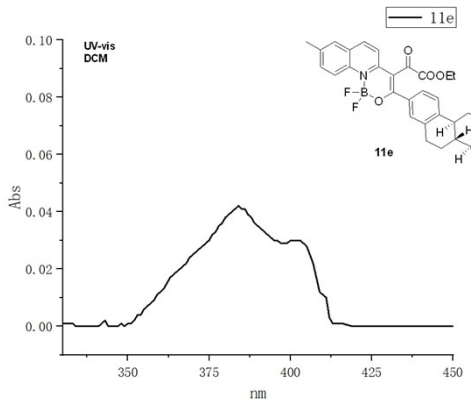

10h
UV-vis
DCM
Abs
nm
10h


11a
UV-vis
DCM
Abs
nm
11a


11b
UV-vis
DCM
Abs
nm
11b


11c
UV-vis
DCM
Abs
nm
11c


11d
UV-vis
DCM
Abs
nm
11d


11e
UV-vis
DCM
Abs
nm
11e

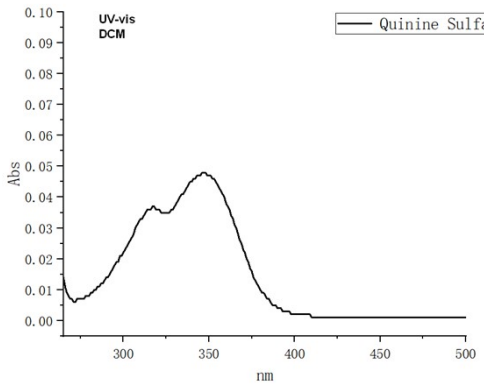
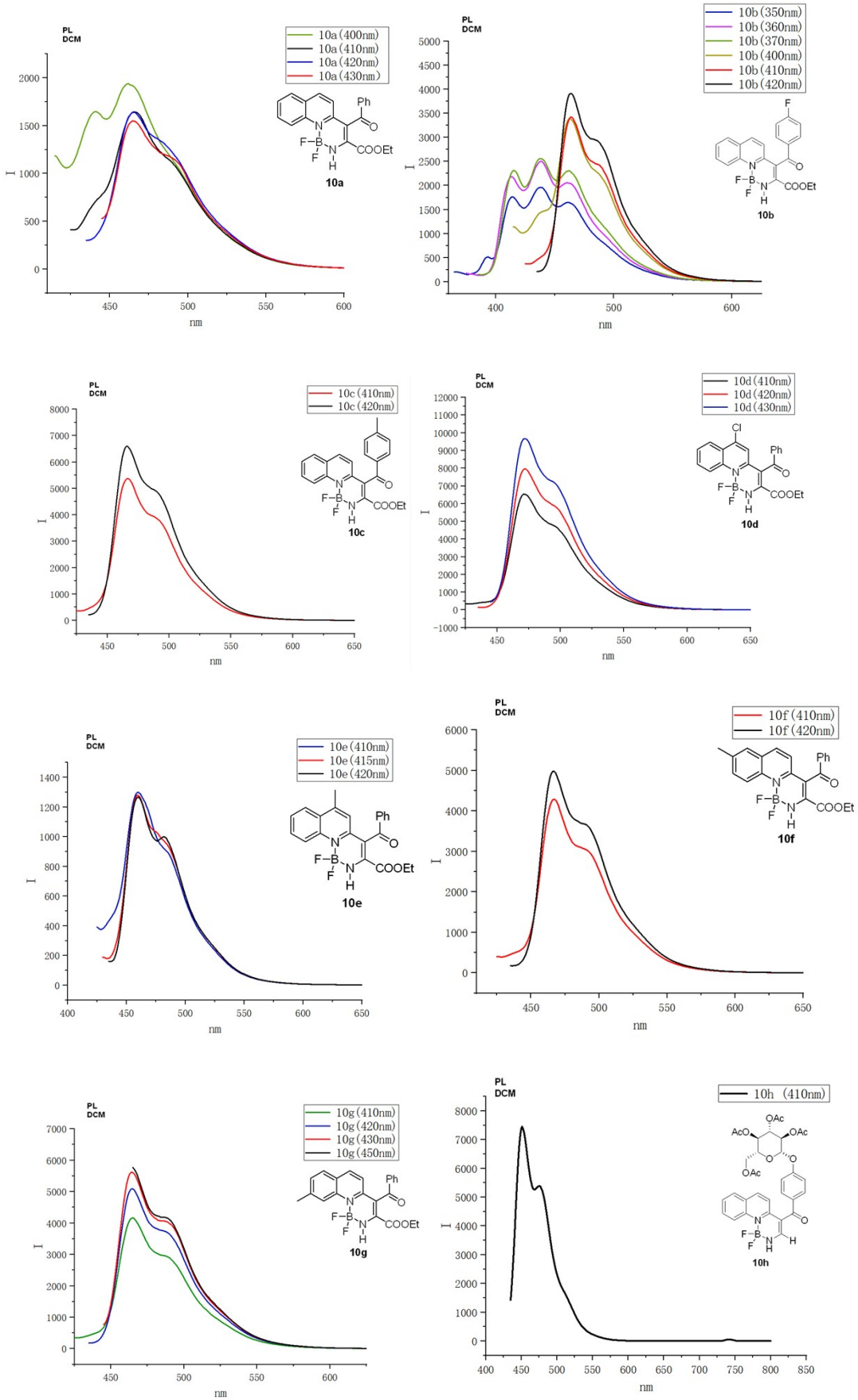
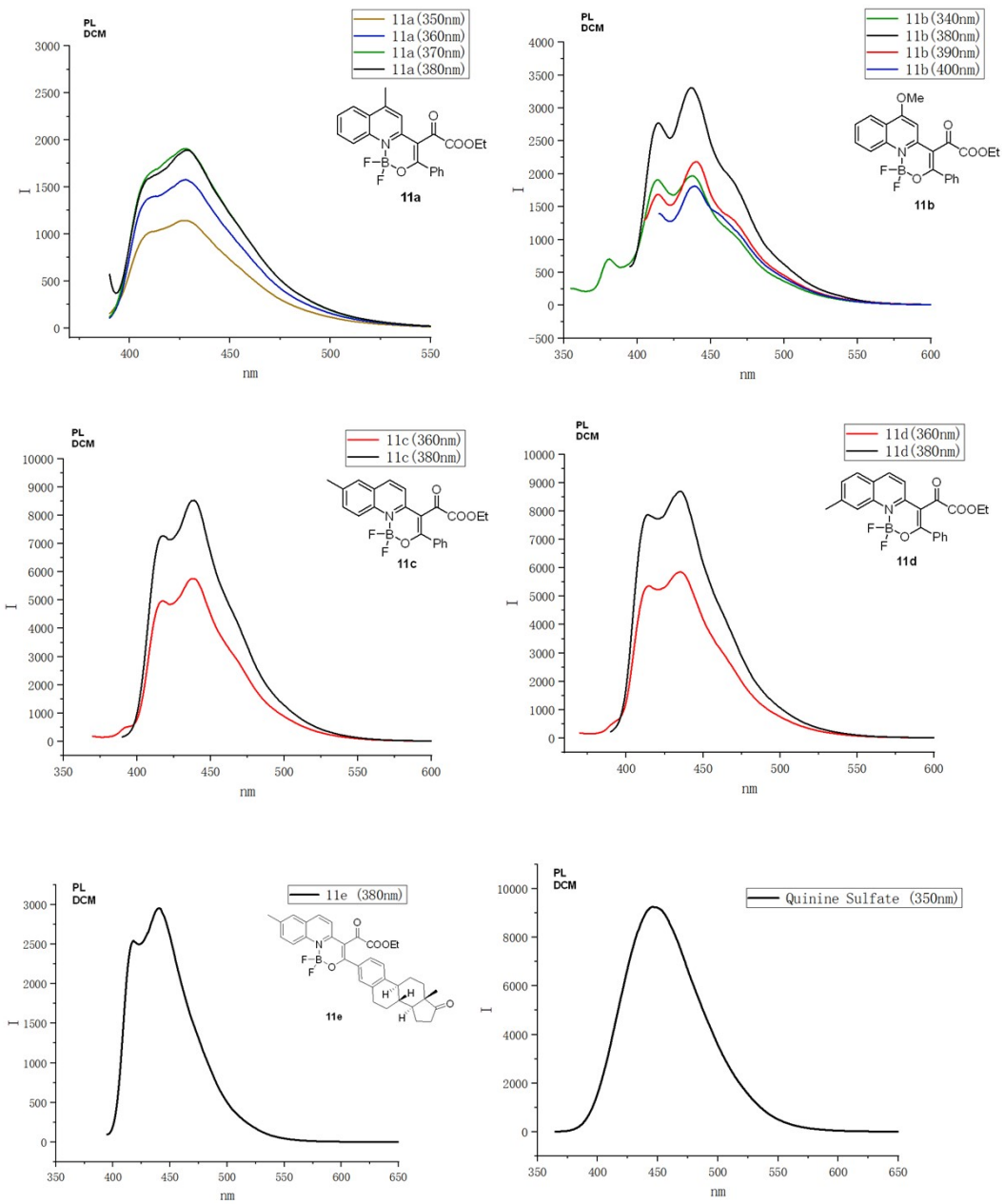

Quinine Sulfate
UV-vis
DCM
Abs
nm

Figure S2. Fluorescence emission spectra [a]





[a] Note: Values in parentheses represent the excitation wavelength (λ_{ex}, unit: nm).

UV–vis absorption spectra were recorded in DCM at 298 K using a 1 cm quartz cuvette. Fluorescence spectra were measured under the same conditions.

The molar extinction coefficient was calculated according to the following equation:

$$\varepsilon = A/(c \cdot l)$$

where A is the absorbance measured at the maximum absorption wavelength λ_{abs} (nm) for a solution with a known concentration c ($mol \cdot L^{-1}$), using a 1 cm quartz cuvette.

The quantum yield was calculated according to the equation:

$$\phi_s = \phi_r \times \frac{A_r}{A_s} \times \frac{F_s}{F_r} \times \left(\frac{n_s}{n_r}\right)^2$$

Where A is the absorbance at the excitation wavelength (maintained below 0.05 to minimize inner filter effects), F is the integrated area under the corrected emission spectrum, and n is the refractive index of the solvent. Subscripts s and r refer to the sample and the reference standard, respectively. Quinine sulfate in 0.05 M H_2SO_4 (Φ_r = 0.546) was used as the standard.

Table S3. Photophysical Data of Compounds 10 and 11 in DCM at 298 K

Compound	λ_{abs} (nm)[a]	$\varepsilon_{abs, max}$ ($L \cdot mol^{-1} \cdot cm^{-1}$)[b]	λ_{em} (nm)[c]	Φ_s[d]	Brightness ($L \cdot mol^{-1} \cdot cm^{-1}$)[e]
10a	424	688	467	0.091	62.61
10b	422	286	462	0.188	53.77
10c	424	622	467	0.352	218.94
10d	429	138	471	0.483	66.46
10e	418	112	462	0.070	7.87
10f	426	1254	468	0.233	292.18
10g	424	1146	465	0.266	304.84
10h	410	9200	452	0.333	3063.60
11a	374	532	428	0.106	56.39
11b	360	254	440	0.198	50.29
11c	382	622	439	0.469	291.72
11d	381	826	436	0.516	426.22
11e	380	840	441	0.050	42.00

[a]Absorption maximum. [b]Molar absorption coefficients (ε, $L \cdot mol^{-1} \cdot cm^{-1}$) calculated at the absorption maximum. [c]Fluorescence emission maxima. [d]Fluorescence quantum yield Φ determined by a standard method using quinine sulfate in 0.05 M H_2SO_4 (Φ_r = 0.546) as the reference. [e]Brightness = ε × Φ.

In dichloromethane, compounds **10h** and **11d** displayed the most favorable photophysical properties within their respective series. Compound **10h** exhibited an exceptionally high molar extinction coefficient (ε = 9200 $L \cdot mol^{-1} \cdot cm^{-1}$) and a

fluorescence quantum yield of 0.333 (relative to quinine sulfate in 0.05 M H_2SO_4, Φr = 0.546), granting it the highest brightness of 3063.60 $L \cdot mol^{-1} \cdot cm^{-1}$ among all the synthesized compounds. Within the 11 series, compound **11d** showed the highest fluorescence quantum yield (0.516), accompanied by a molar extinction coefficient of ε = 826 $L \cdot mol^{-1} \cdot cm^{-1}$ (λ_{abs} = 381 nm) and a brightness of 426.22 $L \cdot mol^{-1} \cdot cm^{-1}$.