Supporting Information for

Rhodium-Catalyzed Malonation of 2-Aryllquinazolines with 2-Diazomalonates: Double C-H Functionalization

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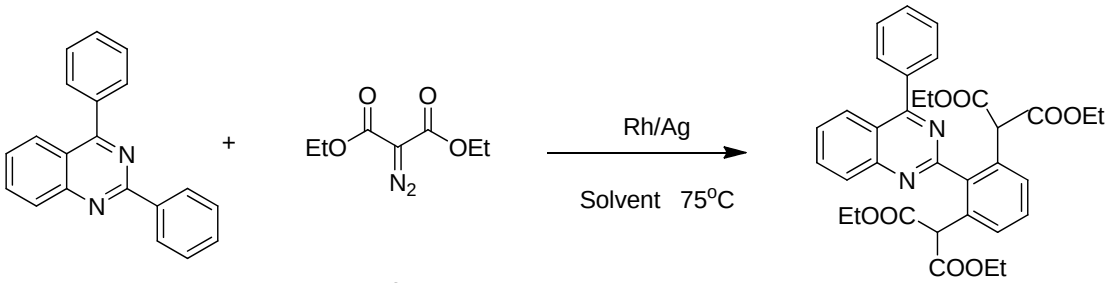
1. General Information

Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32-63μm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr at 25-40 ^{o}C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker DRX - 400 spectromete operating at 400 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF II Instrument.

2. The Optimization of Reaction Conditions



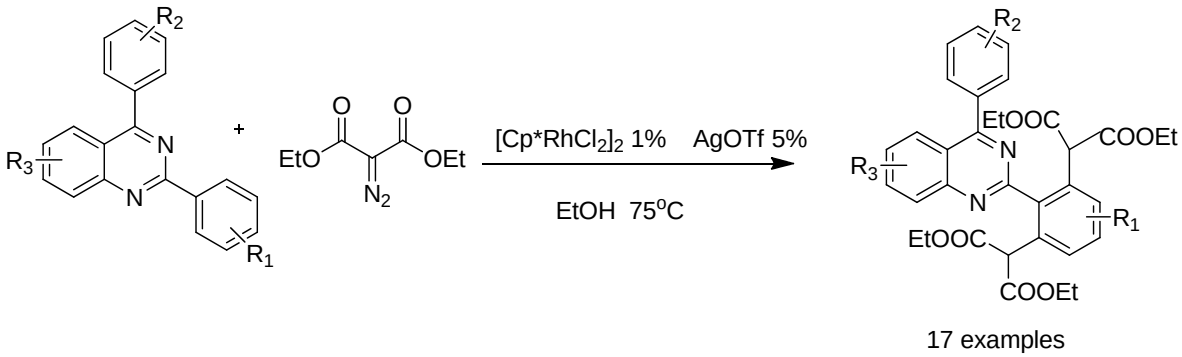
1a 2a 3a

Entry	Catalyst (mol %)	Additive (mol %)	Solvent	t℃	2a (eq)	Yield (%)[c]
1	$[Cod*Rh(BF_4)_2]$(5)	CF_3COOAg(10)	EtOH	75	2	Trace
2	$RhCl_3•H_2O$(5)	CF_3COOAg(10)	EtOH	75	2	Trace
3	$[Cp*RhCl_2]_2$(5)	CF_3COOAg(10)	EtOH	75	2	20
4	$[Cp*RhCl_2]_2$(5)	AgOAc(10)	EtOH	75	3	0
5	$[Cp*RhCl_2]_2$(5)	$AgNO_3$(10)	EtOH	75	3	0
6	$[Cp*RhCl_2]_2$(5)	$AgBF_4$(10)	EtOH	75	3	45
7	$[Cp*RhCl_2]_2$(5)	AgOTf(10)	EtOH	75	3	72
8	**$[Cp*RhCl_2]_2$(1)**	**AgOTf(5)**	**EtOH**	**75**	**3**	**83**
9	$[Cp*RhCl_2]_2$(2)	AgOTf(10)	EtOH	75	3	82
10	$[Cp*RhCl_2]_2$(3)	AgOTf(15)	EtOH	75	3	77
11	$[Cp*RhCl_2]_2$(4)	AgOTf(20)	EtOH	75	3	75
12	$[Cp*RhCl_2]_2$(5)	AgOTf(25)	EtOH	75	3	72
13	$[Cp*RhCl_2]_2$(1)	AgOTf(5)	EtOH	75	1	47
14	$[Cp*RhCl_2]_2$(1)	AgOTf(5)	EtOH	75	2	54
15	$[Cp*RhCl_2]_2$(1)	AgOTf(5)	EtOH	75	3	83

16	[Cp*RhCl$_2$]$_2$(1)	AgOTf(5)	EtOH	75	4	83
17	[Cp*RhCl$_2$]$_2$(1)	AgOTf(5)	EtOH	r.t.	3	NR
18	[Cp*RhCl$_2$]$_2$(1)	AgOTf(5)	EtOH	45	3	39
19	[Cp*RhCl$_2$]$_2$(1)	AgOTf(5)	EtOH	65	3	64
20	[Cp*RhCl$_2$]$_2$(1)	AgOTf(5)	EtOH	75	3	84
21	[Cp*RhCl$_2$]$_2$(1)	AgOTf(5)	MeOH	75	3	56
22	[Cp*RhCl$_2$]$_2$(1)	AgOTf(5)	THF	75	3	20
23	[Cp*RhCl$_2$]$_2$(1)	AgOTf(5)	DCM	75	3	17
24	[Cp*RhCl$_2$]$_2$(1)	AgOTf(5)	DCE	75	3	65
25	[Cp*RhCl$_2$]$_2$(1)	AgOTf(5)	1,4-Dioxane	75	3	14
26[b]	[Cp*RhCl$_2$]$_2$(1)	AgOTf(5)	EtOH	75	3	83

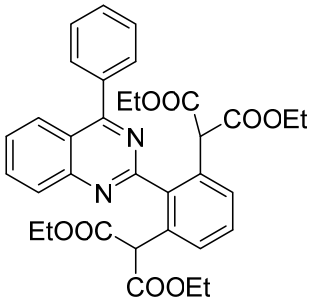
[a] Reaction conditions: all reaction were performed with 2,4-diphenylquinazoline **1a** (0.2 mmol), diethyl 2-diazomalonate **2a**, [Rh], [Ag] , solvent (2.0 mL) for 5 h; [b]at the atmosphere of N_2; [c] Isolated yield based on 2,4-diphenylquinazoline **1a**, NR = no reaction;

3. Typical procedure for Rhodium-Catalyzed Malonation of 2-Phenylquinazolines with 2-Diazomalonates

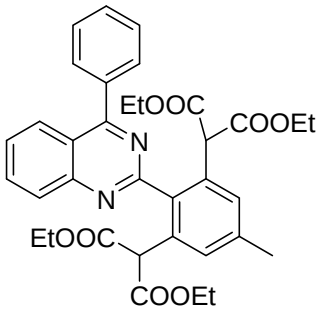


17 examples

A mixture of 2,4-diphenylquinazoline **1** (0.3 mmol) and diethyl 2-diazomalonate **2** (0.6 mmol), [Cp*RhCl$_2$]$_2$ (1 mol%), AgOTf (5 mol%) and EtOH (2.0 mL) were added into a flask . The mixture was stirred at 75 ^{o}C and the reaction was monitored by TLC analysis for about 5 h. After being cooling to room temperature, evaporation of the solvent under reduced pressure followed purification by silica gel chromatography using petroleum ether/ethyl acetate (6:1) as eluent to provide the desired products **3**.



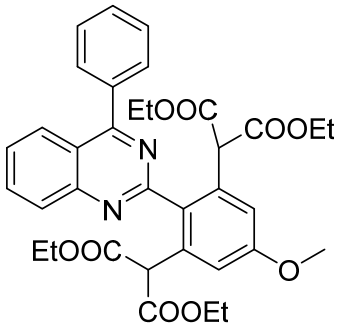
Tetraethyl 2,2'-(2-(4-phenylquinazolin-2-yl)-1,3-phenylene)dimalonate (**3a**)
White solid (103 mg, 86% yield), mp 114.5-116.7℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.96 (t, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 3.6 Hz, 2H), 7.68 (t, *J* = 7.0 Hz, 1H), 7.62 (d, *J* = 7.4 Hz, 2H), 7.57 – 7.55 (m, 3H), 7.52 (d, *J* = 8.6 Hz, 1H), 4.75 (s, 2H), 4.16 (q, *J* = 7.2 Hz, 4H), 4.02 (q, *J* = 7.2 Hz, 4H), 1.13 (t, *J* = 7.2 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 168.2, 160.8, 151.2, 139.5, 137.0, 134.0, 132.3, 130.4, 130.1, 129.2, 129.1, 129.0, 128.5, 128.2, 127.1, 121.1, 61.6, 55.7, 13.9. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{34}H_{33}N_2NaO_8$, 621.2207; found 621.2227.



Tetraethyl 2,2'-(5-methyl-2-(4-phenylquinazolin-2-yl)-1,3-phenylene)dimalonate (**3b**)

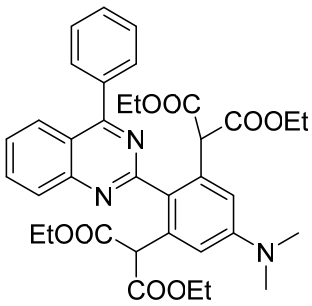
White solid (109 mg, 89% yield), mp 115.2-116.5℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ

8.20 (d, *J* = 8.8 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.94 (t, *J* = 7.6 Hz, 1H), 7.8-7.81 (m, 2H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.58 – 7.53 (m, 3H), 7.41 (s, 2H), 4.78 (s, 2H), 4.16 (q, *J* = 7.2 Hz, 4H), 4.04 (q, *J* = 7.2 Hz, 4H), 2.45 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 168.1, 161.0, 151.2, 138.9, 137.1, 136.8, 133.8, 132.1, 130.4, 130.0, 129.8, 129.0, 128.4, 128.0, 127.1, 61.5, 55.6, 21.6, 13.9. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{35}H_{36}N_2NaO_8$, 635.2364; found: 635.2347.



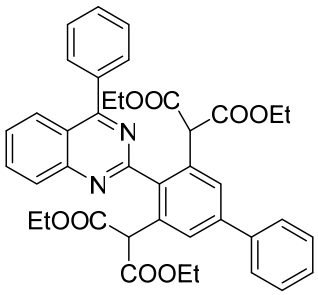
Tetraethyl 2,2'-(5-methoxy-2-(4-phenylquinazolin-2-yl)-1,3-phenylene)dimalonate (**3c**)
White solid (92 mg, 73% yield), mp 96.5-97.9℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19

(d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.94 (t, *J* = 7.6 Hz, 1H), 7.84-7.82 (m, 2H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.57 – 7.56 (m, 3H), 7.18 (s, 2H), 4.85 (s, 2H), 4.16 (q, *J* = 7.2 Hz, 4H), 4.01 (q, *J* = 7.2 Hz, 4H), 3.88 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 168.0, 160.7, 159.6, 151.2, 137.0, 133.9, 133.8, 132.4, 130.4, 130.1, 129.0, 128.5, 128.0, 127.1, 120.9, 61.6, 55.8, 55.5, 13.9. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{35}H_{36}N_2NaO_9$ 651.2313; found: 651.2333.



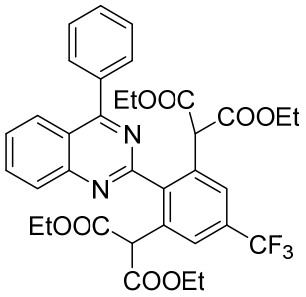
Tetraethyl 2,2'-(5-(dimethylamino)-2-(4-phenylquinazolin-2-yl)-1,3-phenylene) dimalonate (**3d**)

Yellow solid (127 mg, 99% yield), mp 142.6-144.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.86 (t, *J* = 8.0 Hz, 1H), 7.79 (s, 2H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.52 (s, 3H), 6.89 (s, 2H), 4.94 (s, 2H), 4.14 (q, *J* = 7.2 Hz, 4H), 3.98 (q, *J* = 7.2 Hz, 4H), 3.00 (s, 6H), 1.10 (t, *J* = 7.2 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 167.6, 161.3, 151.3, 150.3, 137.3, 133.5, 133.3, 130.3, 129.8, 128.9, 128.3, 127.9, 127.5, 126.9, 120.6, 113.0, 61.3, 56.0, 40.2, 13.9. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{36}H_{39}N_3NaO_8$ 664.2635; found: 664.2607.

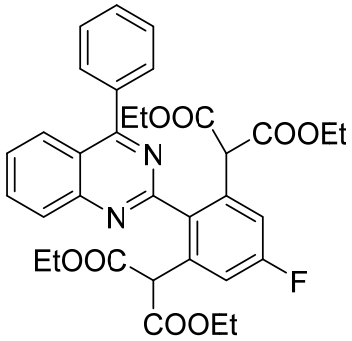


Tetraethyl 2,2'-(4-(4-phenylquinazolin-2-yl)-[1,1'-biphenyl]-3,5-diyl)dimalonate (**3e**)

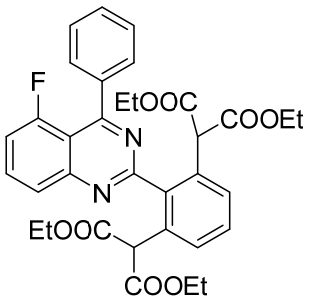
White solid (109 mg, 81% yield), mp 125.2-127.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.96 (t, *J* = 7.8 Hz, 1H), 7.87-7.85 (m, 4H), 7.71 – 7.65 (m, 3H), 7.59 – 7.55 (m, 3H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 6.8 Hz, 1H), 4.86 (s, 2H), 4.16 (q, *J* = 7.2 Hz, 4H), 4.02 (q, *J* = 7.2 Hz, 4H), 1.13 (t, *J* = 7.2 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 168.2, 160.8, 151.3, 141.7, 140.3, 138.5, 137.0, 134.0, 132.7, 130.4, 130.1, 129.1, 128.8, 128.5, 128.2, 128.1, 127.7, 127.4, 127.1, 121.1, 61.6, 55.7, 13.9. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{40}H_{38}N_2NaO_8$ 697.2526; found:697.2545.



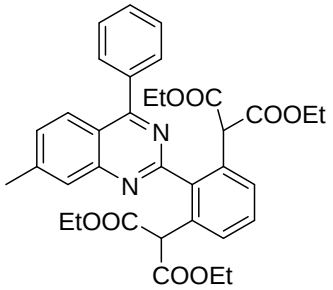
Tetraethyl 2,2'-(2-(4-phenylquinazolin-2-yl)-5-(trifluoromethyl)-1,3-phenylene)dimalonate (**3f**) Light yellow solid (107 mg, 80% yield), mp 142.2-144.5℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.6 Hz, 1H), 8.08 (d, *J* = 7.6 Hz, 1H), 8.00 (t, *J* = 7.6 Hz, 1H), 7.94 (s, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.73 (t, *J* = 7.6 Hz,1H), 7.60 – 7.56 (m, 3H), 4.77 (s, 2H), 4.17 (q, *J* = 7.2 Hz, 4H), 4.06 (q, *J* = 7.2 Hz, 4H), 1.14 (t, *J* = 7.2 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 167.6, 159.8, 151.2, 142.9, 136.8, 134.2, 133.3, 130.9, (q, $^{2}J_{C-F}$ = 33.0 Hz), 130.3, 130.2, 129.1, 128.6, 128.5, 127.2, 126.4 (q, $^{3}J_{C-F}$ = 4.0 Hz), 123.8(q, $^{1}J_{C-F}$ = 271.0 Hz), 121.3, 61.8, 55.5, 13.8. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{35}H_{33}F_3N_2NaO_8$; 689.2081; found: 689.2078.



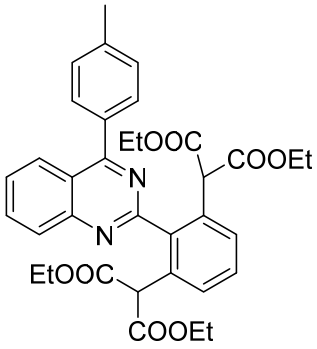
Tetraethyl 2,2'-(5-fluoro-2-(4-phenylquinazolin-2-yl)-1,3-phenylene)dimalonate (**3g**) White solid (92 mg, 75% yield), mp 114.5-116.7℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.96 (t, *J* = 8.4 Hz, 1H), 7.85-7.83 (m, 2H), 7.68 (t, *J* = 8.0 Hz,1H), 7.57-7,56 (m, 3H), 7.41 (d, *J* = 8.4 Hz, 2H), 4.79 (s, 2H), 4.19 (q, *J* = 7.2 Hz, 4H), 4.04 (q, *J* = 7.2 Hz, 4H), 1.02 (t, *J* = 7.2 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 167.9, 162.3 (d, $^{1}J_{C-F}$ = 248.0 Hz), 160.1, 151.2, 136.9, 135.9 (d, $^{3}J_{C-F}$ = 4.0 Hz), 134.7, 134.6, 134.1, 130.3, 129.0, 128.5, 128.4, 127.2, 121.1, 116.6 (d, $^{2}J_{C-F}$ = 23.0 Hz), 61.8, 55.6, 13.9. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{34}H_{33}FN_2NaO_8$; 639.2119; found: 639.2119.



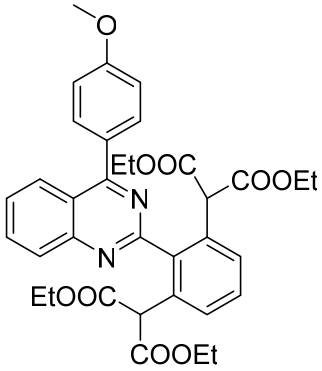
Tetraethyl 2,2'-(2-(5-fluoro-4-phenylquinazolin-2-yl)-1,3-phenylene)dimalonate (**3h**)
White solid (108 mg, 88% yield), mp 99.6-101.2℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 2.0 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.55 –7.48 (m, 4H), 7.35 –7.30 (m, 1H), 4.72 (s, 2H), 4.16 (q, *J* = 7.2 Hz, 4H), 4.02 (q, *J* = 7.2 Hz, 4H), 1.13 (t, *J* = 7.2 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 166.1, 161.1, 157.9 (d, $^1J_{C\text{-}F}$ = 261.0 Hz), 152.5, 139.4, 139.1, 134.1(d, $^3J_{C\text{-}F}$ = 10.0 Hz), 132.3, 129.8, 129.5 (d, $^3J_{C\text{-}F}$ = 4.0 Hz), 129.3, 129.1, 127.7, 125.3, 113.4 (d, $^2J_{C\text{-}F}$ = 21.0 Hz), 112.1 (d, $^2J_{C\text{-}F}$ = 12.0 Hz), 61.6, 55.6, 13.9. HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{34}H_{33}FN_2NaO_8$; 639.2119; found: 639.2126.



Tetraethyl 2,2'-(2-(7-methyl-4-phenylquinazolin-2-yl)-1,3-phenylene)dimalonate (**3i**)
White solid (91 mg, 74% yield), mp 135.6-136.8℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.82 – 7.80 (m, 3H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.53-7.52 (m, 3H), 7.49 (t, *J* = 7.2 Hz, 2H), 4.77 (s, 2H), 4.14 (q, *J* = 7.2 Hz, 4H), 4.02 (q, *J* = 7.2 Hz, 4H), 2.60 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 167.7, 160.9, 151.5, 145.0, 139.8, 137.2, 132.3, 130.4, 130.3, 129.9, 129.2, 128.7, 128.4, 128.0, 126.7, 119.3, 61.5, 55.2, 22.1, 13.8. HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{35}H_{36}N_2NaO_8$, 635.2369; found: 635.2363.

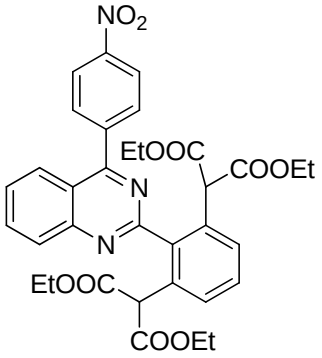


Tetraethyl 2,2'-(2-(4-(*p*-tolyl)quinazolin-2-yl)-1,3-phenylene)dimalonate (**3j**)
White solid (116 mg, 95% yield), mp 101.5-103.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.93 (t, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.77 (s, 2H), 4.16 (q, *J* = 7.2 Hz, 4H), 4.02 (q, *J* = 7.2 Hz, 4H), 2.47 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 168.2, 160.8, 151.2, 140.4, 139.7, 134.2, 133.8, 132.3, 130.4, 129.2, 129.2, 129.0, 128.9, 128.0, 127.2, 121.1 61.6, 55.7, 21.4, 13.9. HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{35}H_{36}N_2NaO_8$; 635.2369; found: 635.2376.

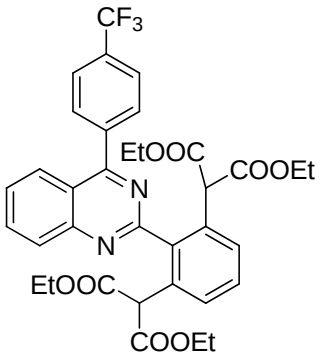


Tetraethyl 2,2'-(2-(4-(4-methoxyphenyl)quinazolin-2-yl)-1,3-phenylene)dimalonate (**3k**)

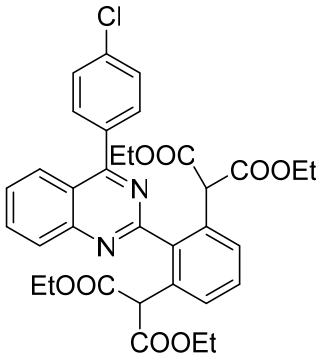
Light yellow solid (124 mg, 99% yield), mp106.7-108.9℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.93 (t, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 4.77 (s, 2H), 4.15 (q, *J* = 7.2 Hz, 4H), 4.04 (q, *J* = 7.2 Hz, 4H), 3.90 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 167.6, 161.5, 160.8, 151.3, 139.8, 133.7, 132.2, 132.1, 129.5, 129.2, 129.1, 128.8, 127.9, 127.1, 121.0, 114.0, 61.5, 55.7, 55.5, 13.9. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{35}H_{36}N_2NaO_9$; 651.2313; found:651.2343.



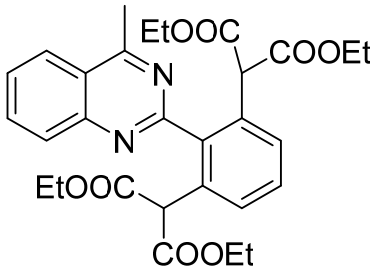
Tetraethyl 2,2'-(2-(4-(4-nitrophenyl)quinazolin-2-yl)-1,3-phenylene)dimalonate (**3l**) Yellow solid (103 mg, 80% yield), mp 102.3-104.5℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.4 Hz, 2H), 8.02 (t, *J* = 7.2 Hz, 2H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 7.2 Hz, 1H), 4.61 (s, 2H), 4.17 (q, *J* = 7.2 Hz, 4H), 4.06 (q, *J* = 7.2 Hz, 4H), 1.15 (t, *J* = 7.2 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 165.9, 160.8, 151.3, 148.8, 142.9, 139.1, 134.6, 132.3, 131.3, 129.4, 129.4, 129.2, 129.0, 126.1, 123.7, 120.7, 61.7, 55.8, 13.9. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{34}H_3N_3NaO_{10}$ 666.2064; found: 666.2079.



Tetraethyl 2,2'-(2-(4-(4-(trifluoromethyl)phenyl)quinazolin-2-yl)-1,3-phenylene)dimalonate (**3m**) White solid (131 mg, 98%yield), mp101.2-103.5℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (t, *J* = 8.0 Hz, 2H), 7.89-7.93 (m, 3H), 7.77-7.75 (m, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 4.65 (s, 2H), 4.08 (q, *J* = 7.2 Hz, 4H), 3.95 (q, *J* = 7.2 Hz, 4H),, 1.05 (t, *J* = 7.2 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 166.7, 160.9, 151.3, 140.5, 139.3, 134.3, 132.3, 132.1（q, $^{2}J_{C\text{-}F}$ = 32.0 Hz）, 130.7, 129.3, 129.2, 129.0, 128.6, 126.4, 125.4 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 123.9 (q, $^{1}J_{C\text{-}F}$ = 271.0 Hz), 120.9, 61.6, 55.8, 13.8. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{35}H_{33}F_3N_2NaO_8$; 689.2087; found: 689.2123.

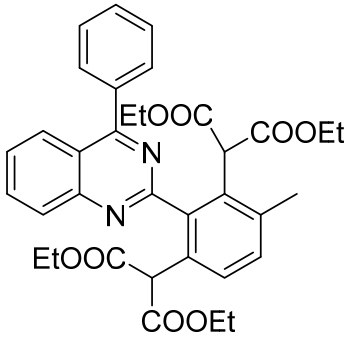


Tetraethyl 2,2'-(2-(4-(4-chlorophenyl)quinazolin-2-yl)-1,3-phenylene)dimalonate (**3n**) White solid (124mg, 98%yield), mp 79.8-82.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.96 (t, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.56-7.35 (m, 3H), 4.73 (s, 2H), 4.14 (q, *J* = 7.6 Hz, 4H), 4.04 (q, *J* = 7.6 Hz, 4H), 1.13 (t, *J* = 7.6 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 166.9, 160.8, 151.3, 139.4, 136.6, 135.4, 134.2, 132.3, 131.7, 129.3, 129.2, 129.0, 128.8, 128.4, 126.7, 120.9, 61.6, 55.7, 13.9. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{34}H_{33}ClN_2NaO_8$; 655.1851; found: 655.1827.

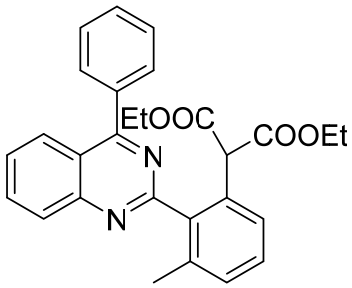


Tetraethyl 2,2'-(2-(4-methylquinazolin-2-yl)-1,3-phenylene)dimalonate (**3o**)

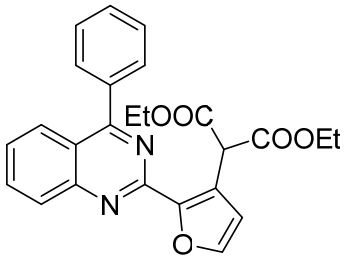
White solid (89 mg, 83% yield), mp 94.2-95.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.92 (t, *J* = 7.6 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 8.0 Hz 1H), 4.69 (s, 2H), 4.20 (q, *J* = 7.6 Hz, 4H), 4.04 (q, *J* = 7.6 Hz, 8H) 2.96 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 168.3, 160.5, 149.6, 139.4, 133.9, 132.3, 129.2, 129.2, 128.9, 128.0, 125.0, 122.4, 61.6, 55.9, 21.5, 14.0. HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{29}H_{32}N_2NaO_8$; 559.2056; found: 559.2035.



Tetraethyl 2,2'-(4-methyl-2-(4-phenylquinazolin-2-yl)-1,3-phenylene)dimalonate (**3p**)
White solid (51mg, 42%yield), mp 112.6-114.5℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.94 (t, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.56 – 7.51 (m, 4H), 7.36 (d, *J* = 8.4 Hz, 1H), 4.69 (s, 1H), 4.61 (s, 1H), 4.17 – 4.10 (m, 4H), 4.03 – 3.94 (m, 4H), 2.43 (s, 3H), 1.12-1.08 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 168.3, 168.1, 161.8, 151.2, 141.3, 138.8, 137.0, 134.0, 132.1, 131.3, 130.4, 130.2, 129.6, 129.1, 128.8, 128.5, 128.2, 127.1, 121.0, 61.5, 61.4, 55.5, 55.4, 20.5, 13.9, 13.9. HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{35}H_{36}N_2NaO_8$; 635.2369; found: 635.2376.

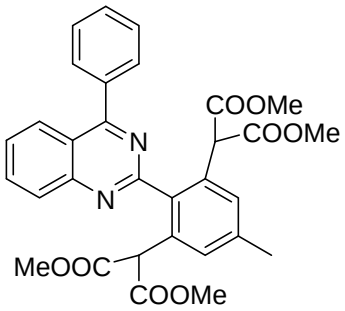


Diethyl 2-(3-methyl-2-(4-phenylquinazolin-2-yl)phenyl)malonate (**3q**)
Colorless oil (70mg, 77% yield) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.93 (t, *J* = 8.4 Hz, 1H), 7.84-7.83 (m, 2H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.56-7.55 (m, 3H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 4.62 (s, 1H), 4.13 (q, *J* = 7.6 Hz, 2H), 4.05 (q, *J* = 7.6 Hz, 2H), 2.30 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 168.4, 162.4, 151.4, 139.6, 137.1, 136.8, 134.0, 131.6, 130.4, 130.2, 130.1, 129.0, 128.7, 128.6, 128.0, 127.1, 126.8, 121.1, 61.5, 55.5, 20.8, 14.0. HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{28}H_{26}N_2NaO_4$; 477.1790; found: 477.1797.



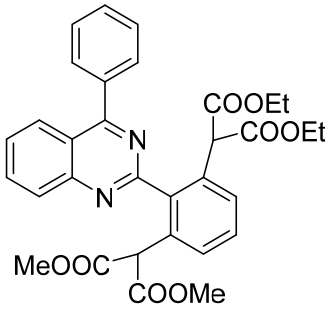
Diethyl 2-(2-(4-phenylquinazolin-2-yl)furan-3-yl)malonate (**3r**)

Brown solid (56mg, 65%yield), mp 86.2-88.5℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.76-7.74 (m, 2H), 7.58 (d, *J* = 1.3 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 3H), 7.44 (t, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 1.5 Hz, 1H), 6.27 (s, 1H), 4.12 (q, *J* = 7.2 Hz, 4H), 1.15 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.39 , 168.30 , 153.92 , 151.58 , 148.17 , 144.04 , 137.08 , 133.98 , 130.19 , 130.08 , 128.99 , 128.56 , 127.27 , 127.15 , 121.92 , 121.37 , 113.79 , 61.70 , 50.22 , 14.04. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{25}H_{22}N_2NaO_5$; 453.1426; found: 453.1438.



Tetramethyl 2,2'-(5-methyl-2-(4-phenylquinazolin-2-yl)-1,3-phenylene)dimalonate (**3s**)

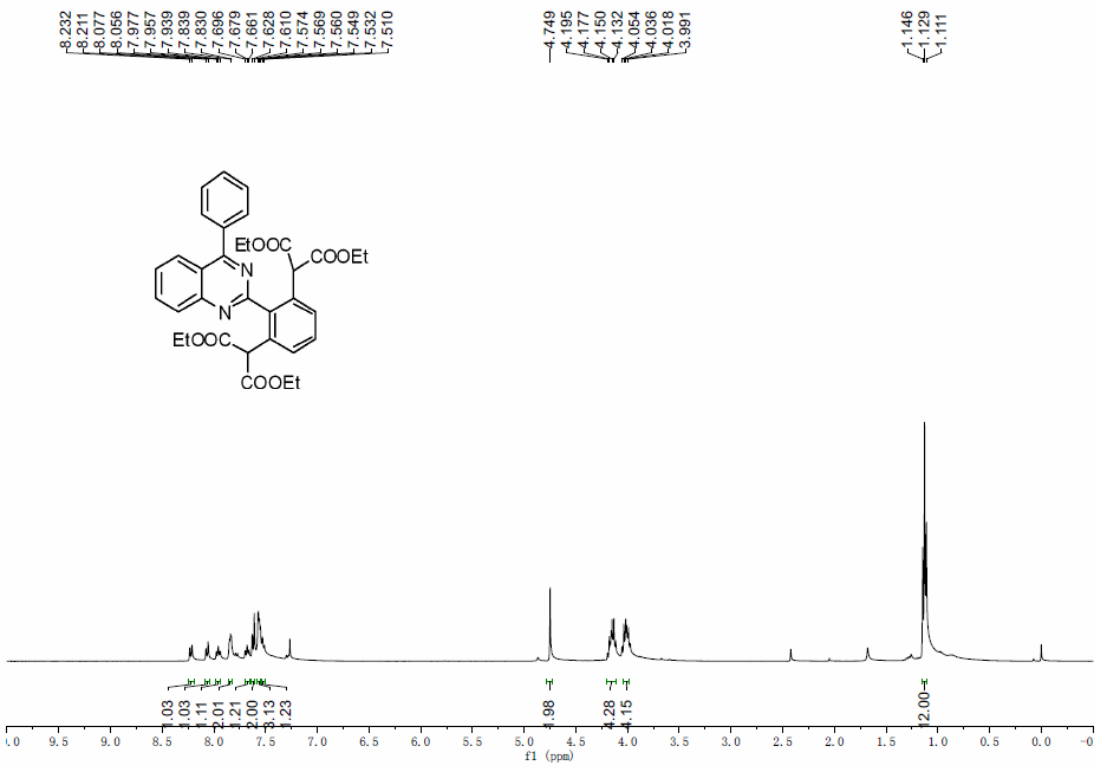
White solid (87 mg, 78% yield)，mp 149.5-151.5℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.87 (dt, *J* = 1.2, 8.4 Hz, 1H), 7.73 – 7.70 (m, 2H), 7.58 (dt, *J* = 0.8, 7.8Hz, 1H), 7.49 – 7.47 (m, 3H), 7.32 (s, 2H), 4.72 (s, 2H), 3.52 (s, 12H), 2.37 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 167.1, 159.5, 149.9, 138.1, 135.6, 135.9, 132.9, 130.9, 129.1, 128.9, 128.8, 127.9, 127.3, 127.0, 126.0, 119.8, 54.2, 51.4, 20.5.

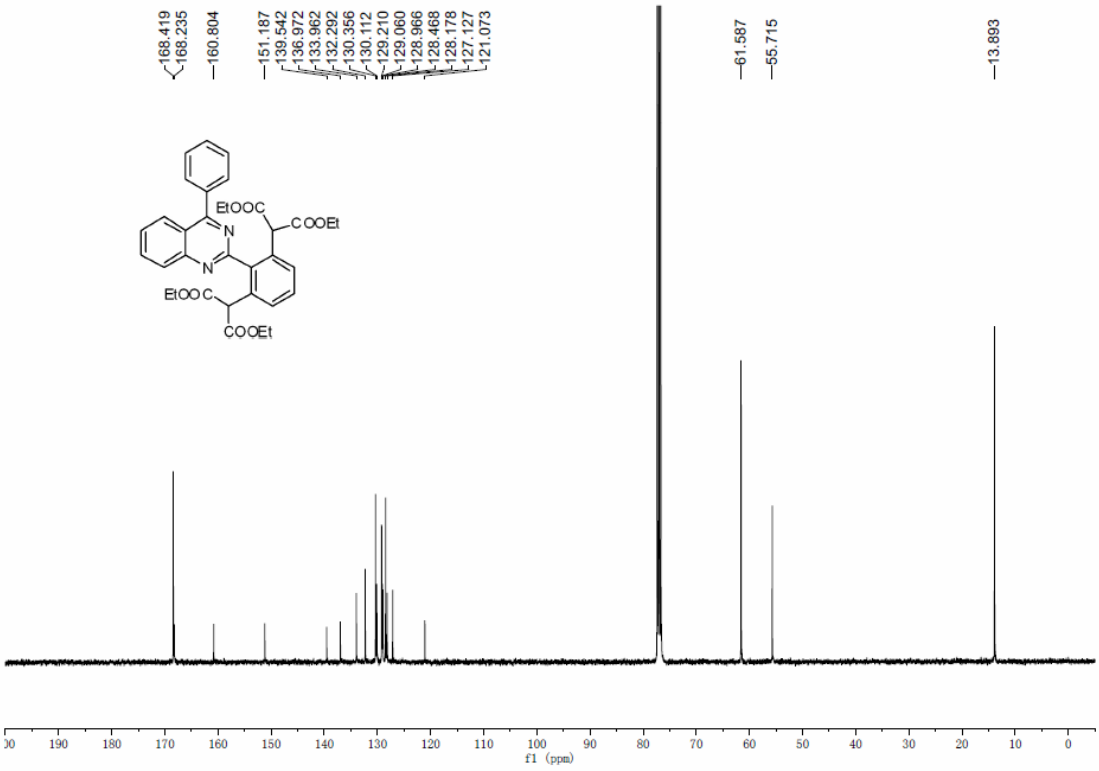


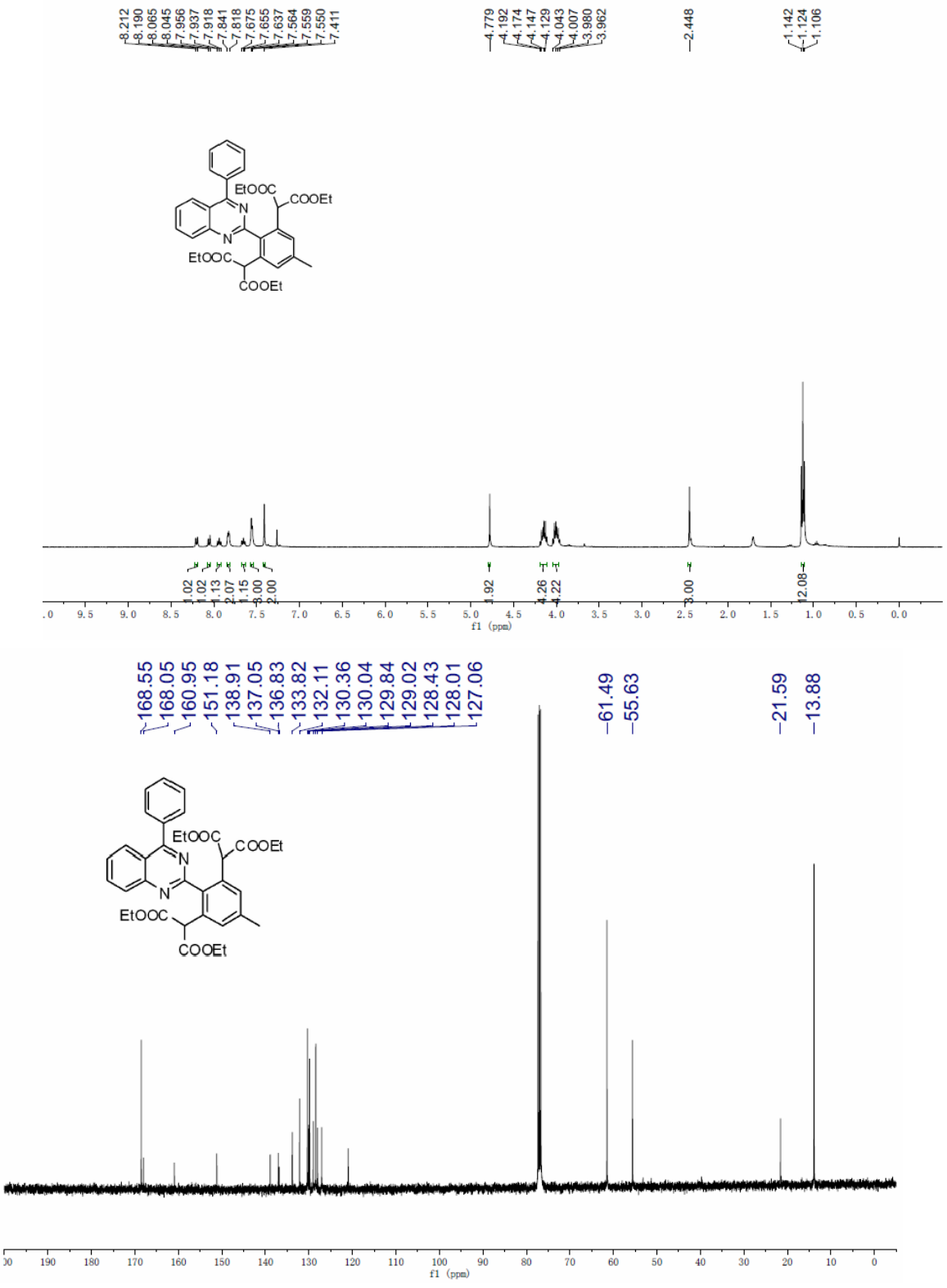
Diethyl 2-(3-(1,3-dimethoxy-1,3-dioxopropan-2-yl)-2-(4-phenylquinazolin-2-yl) phenyl) malonate

White solid (58 mg, 51% yield)，mp 118.5-120.5℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.88 (t, *J* = 7.6 Hz, 1H), 7.79-7.75 (m, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.58 -7.32 (m, 6H), 4.69 (d, *J* = 4.4 Hz, 2H), 4.08 (q, *J* = 7.0 Hz, 2H), 3.95 (q, *J* = 6.8 Hz, 2H), 3.52 (s, 6H), 1.05 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 168.4, 168.3, 160.7, 151.1, 139.5, 137.0, 134.1, 132.4, 132.1, 130.3, 130.1, 129.4, 129.2, 129.0, 128.5, 128.3, 127.1, 121.1, 61.6, 55.7, 55.4, 52.6, 13.9.

4. ^{1}H and ^{13}C NMR spectra of compounds



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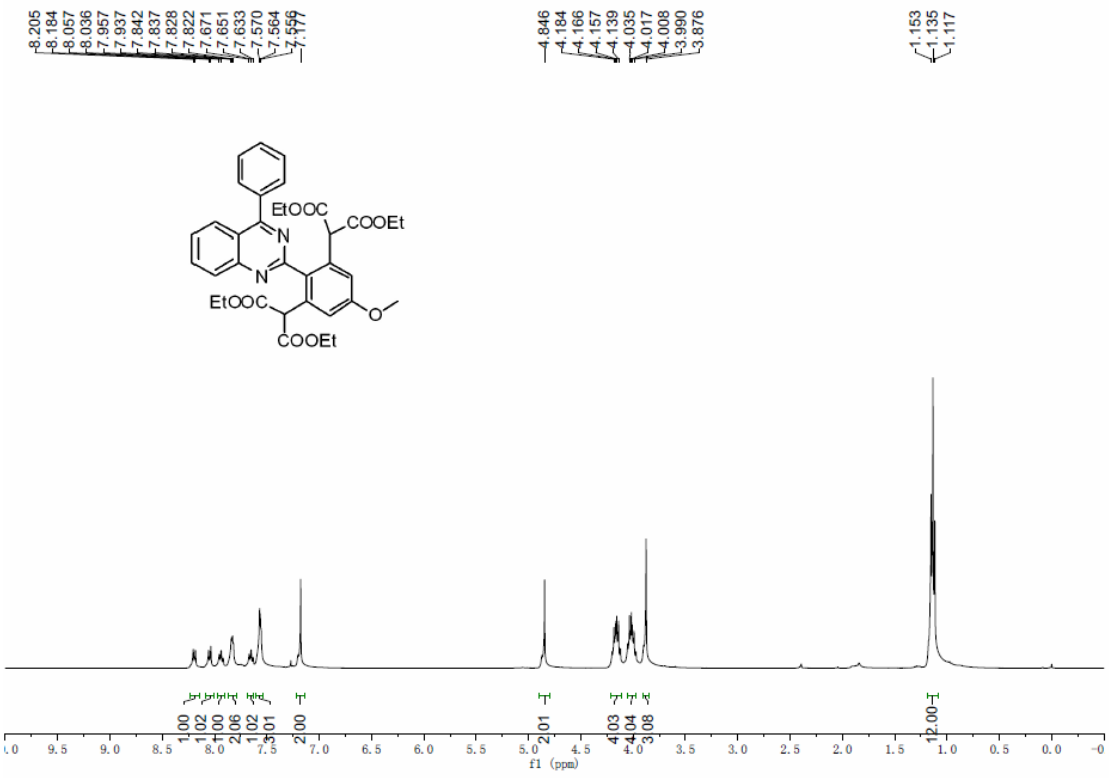
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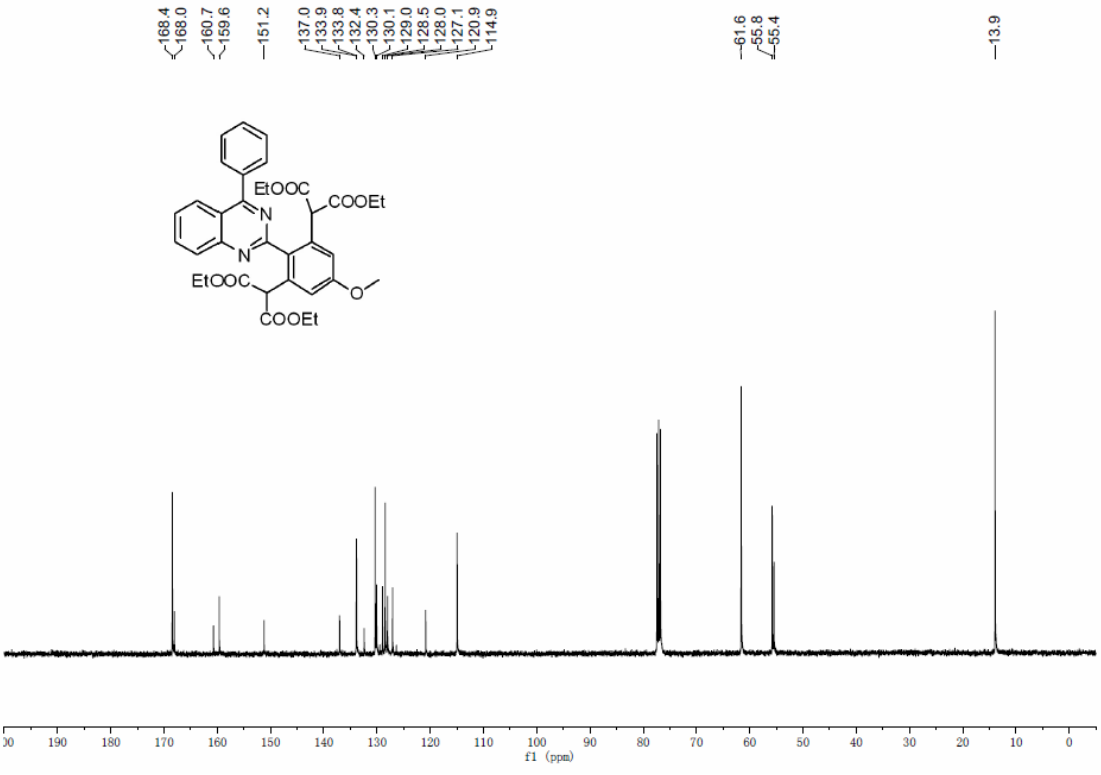
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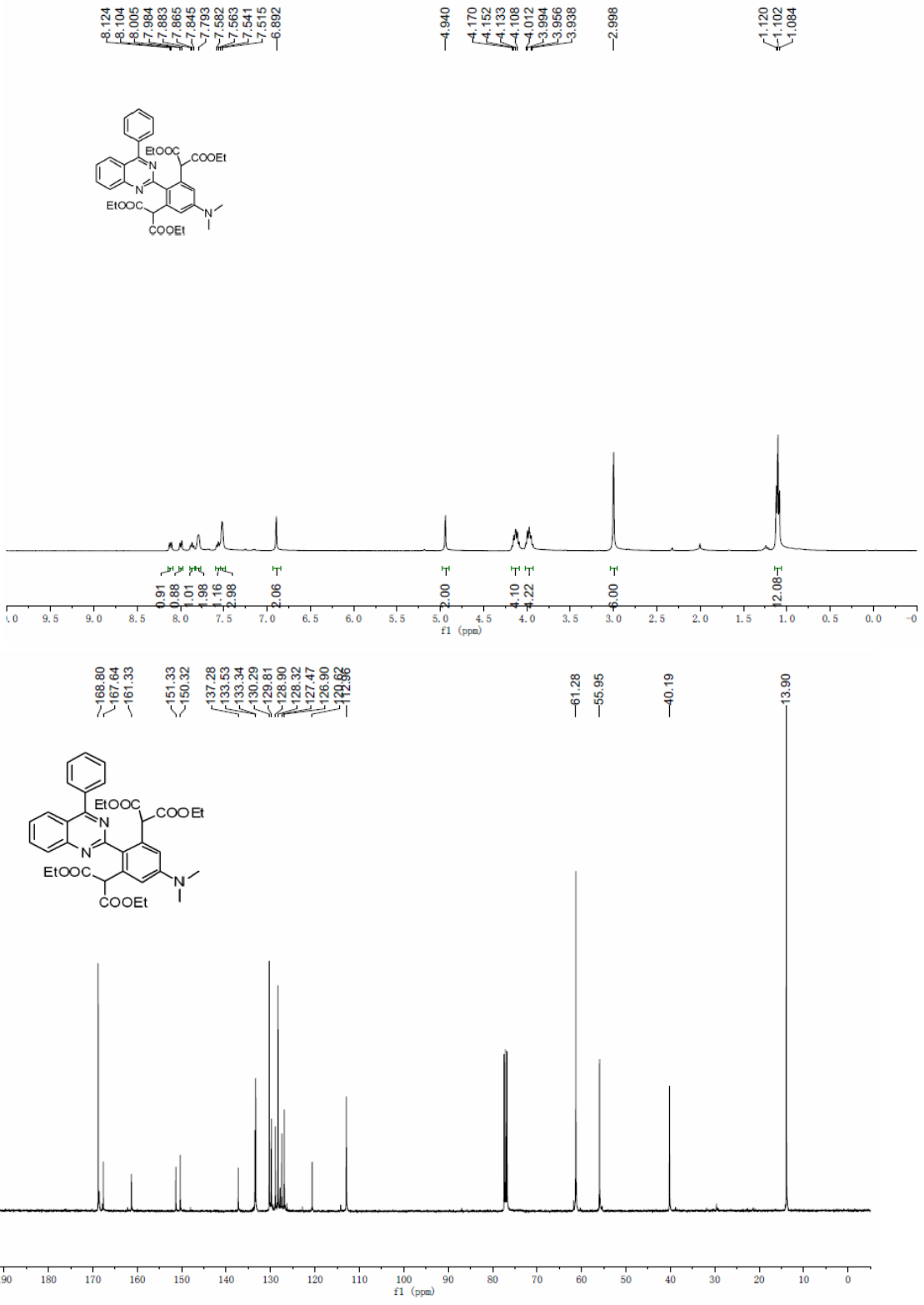
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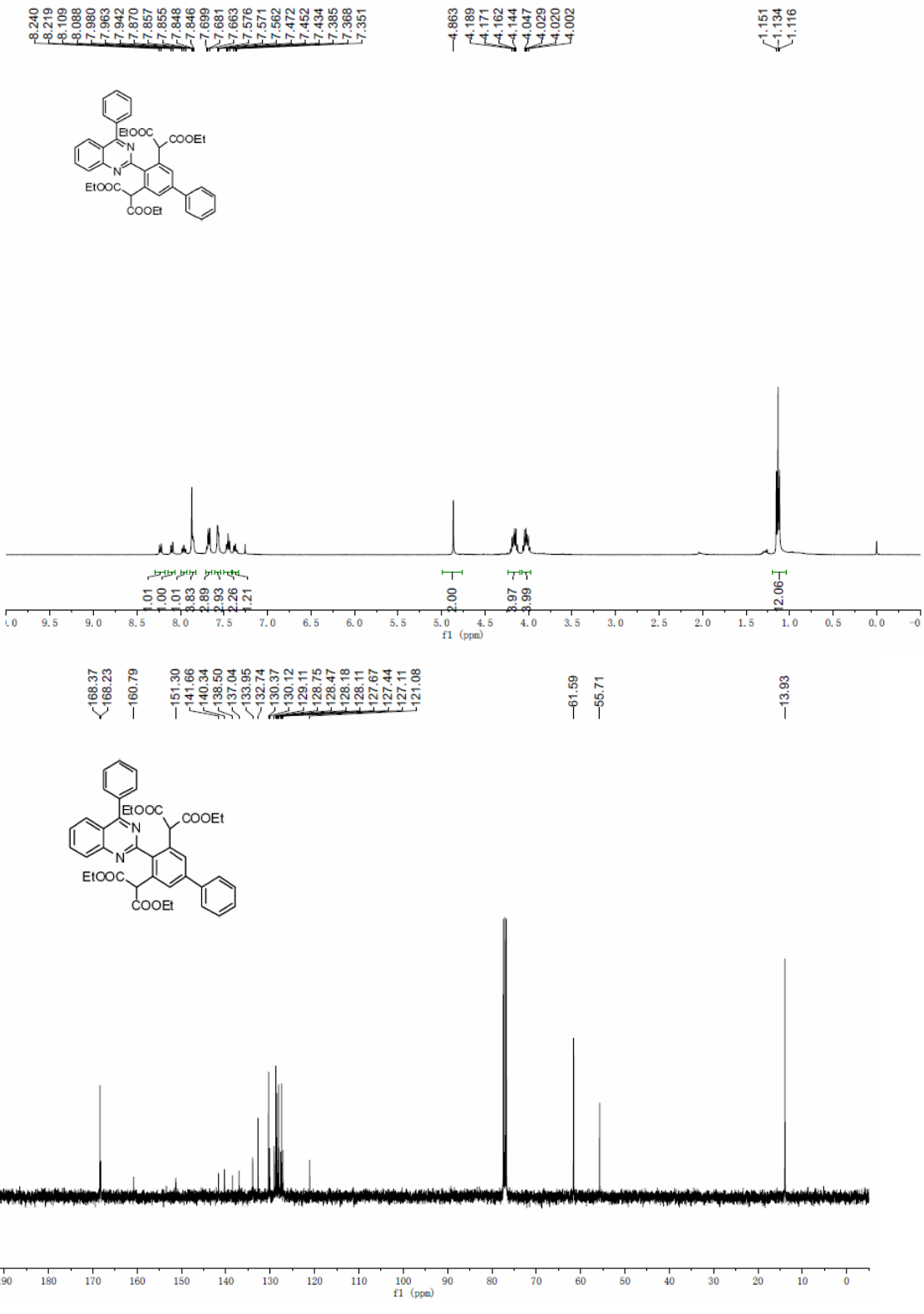
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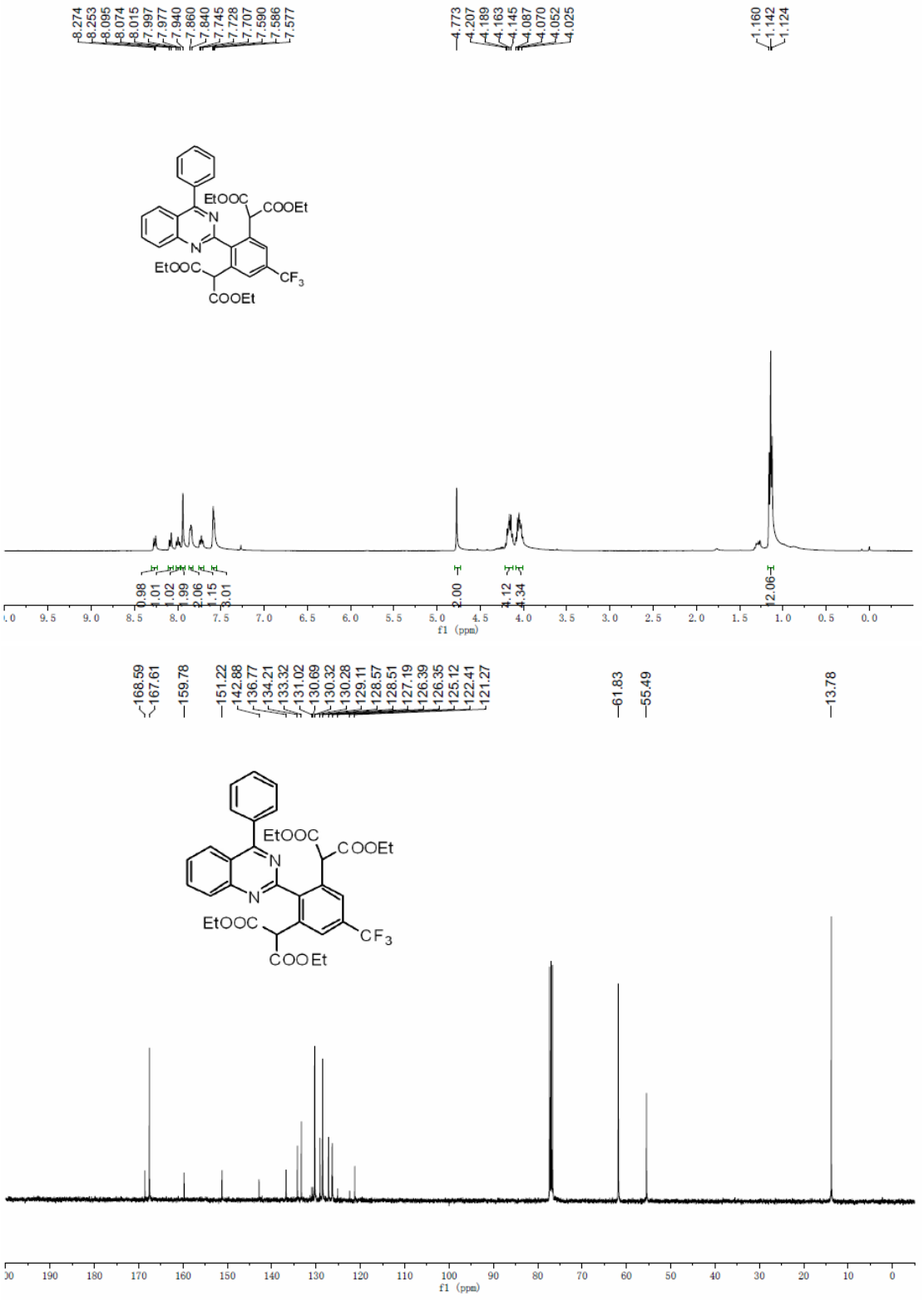
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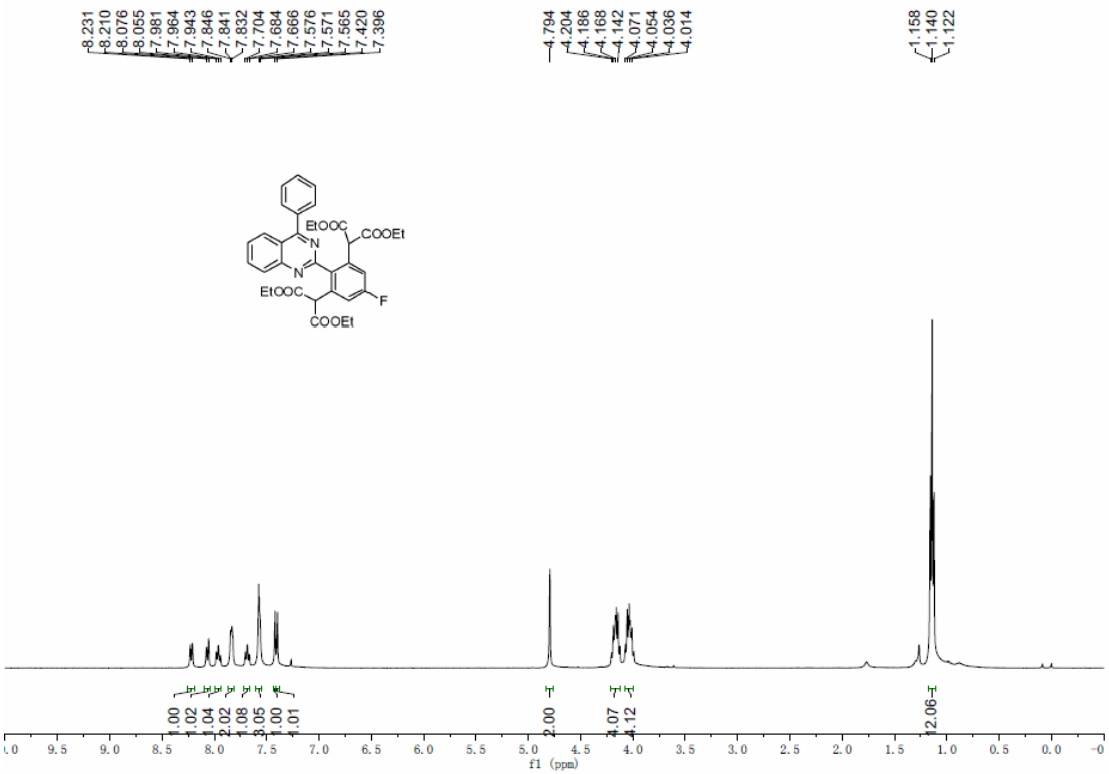
COOEt
f1 (ppm)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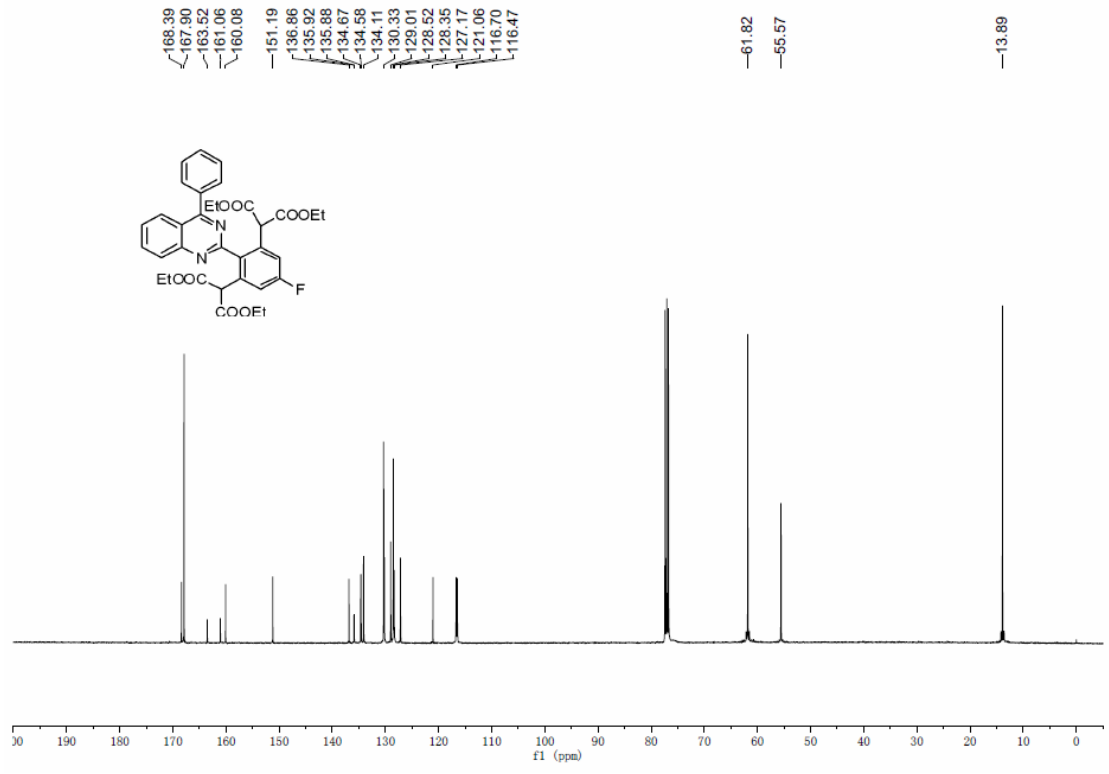
8.210
8.076
8.055
7.981
7.964
7.943
7.846
7.841
7.832
7.704
7.684
7.666
7.576
7.571
7.565
7.420
7.396
4.794
4.204
4.186
4.168
4.142
4.071
4.054
4.036
4.014
1.158
1.140
1.122
EtOOC
COOEt
N
N
EtOOC
F
COOEt
1.00
1.02
1.04
2.02
1.08
3.05
1.00
1.01
2.00
4.07
4.12
12.06
f1 (ppm)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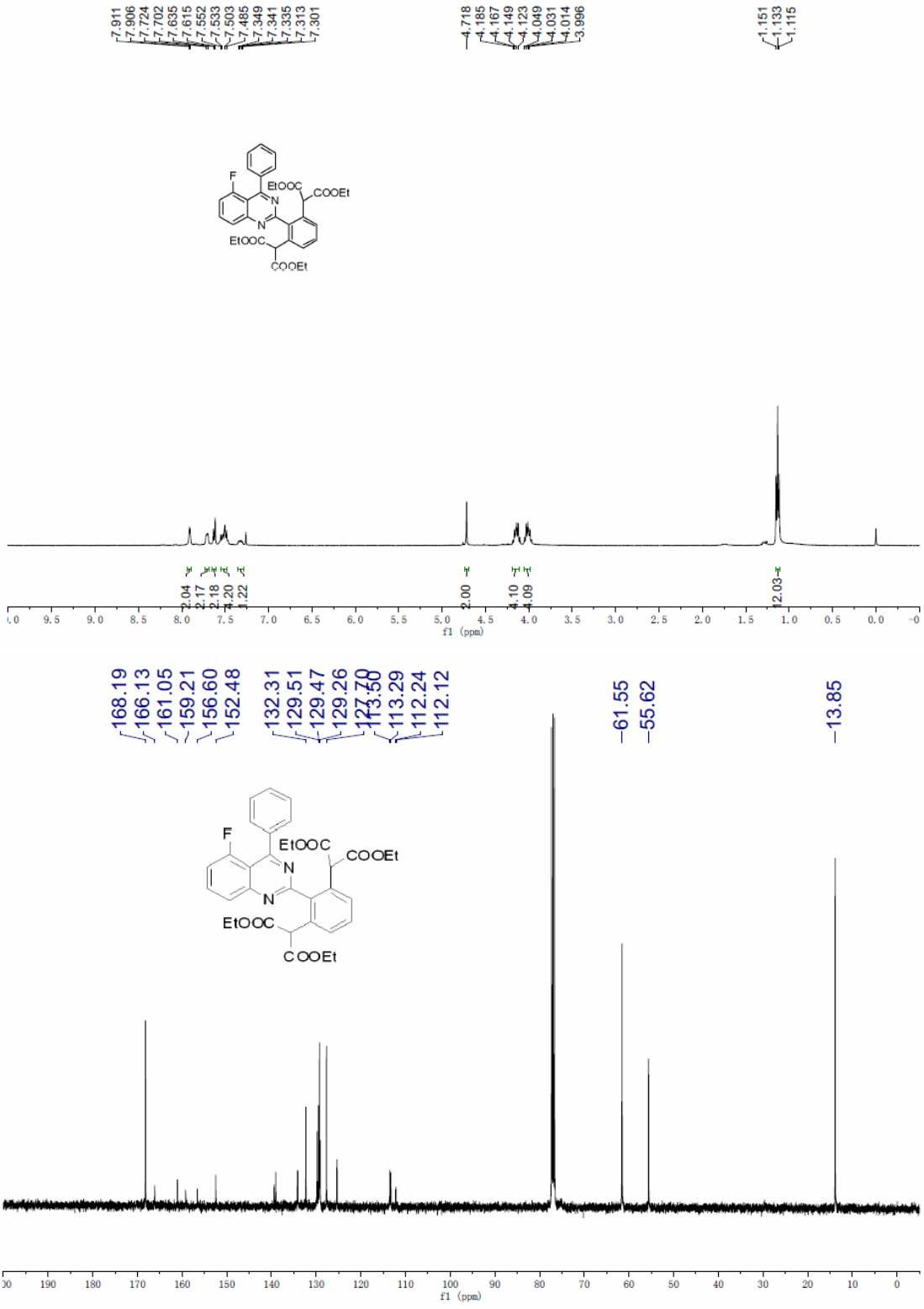
167.90
163.52
161.06
160.08
151.19
136.86
135.92
135.88
134.67
134.58
134.11
130.33
129.01
128.52
128.35
127.17
121.06
116.70
116.47
61.82
55.57
13.89
EtOOC
COOEt
N
N
EtOOC
F
COOEt
f1 (ppm)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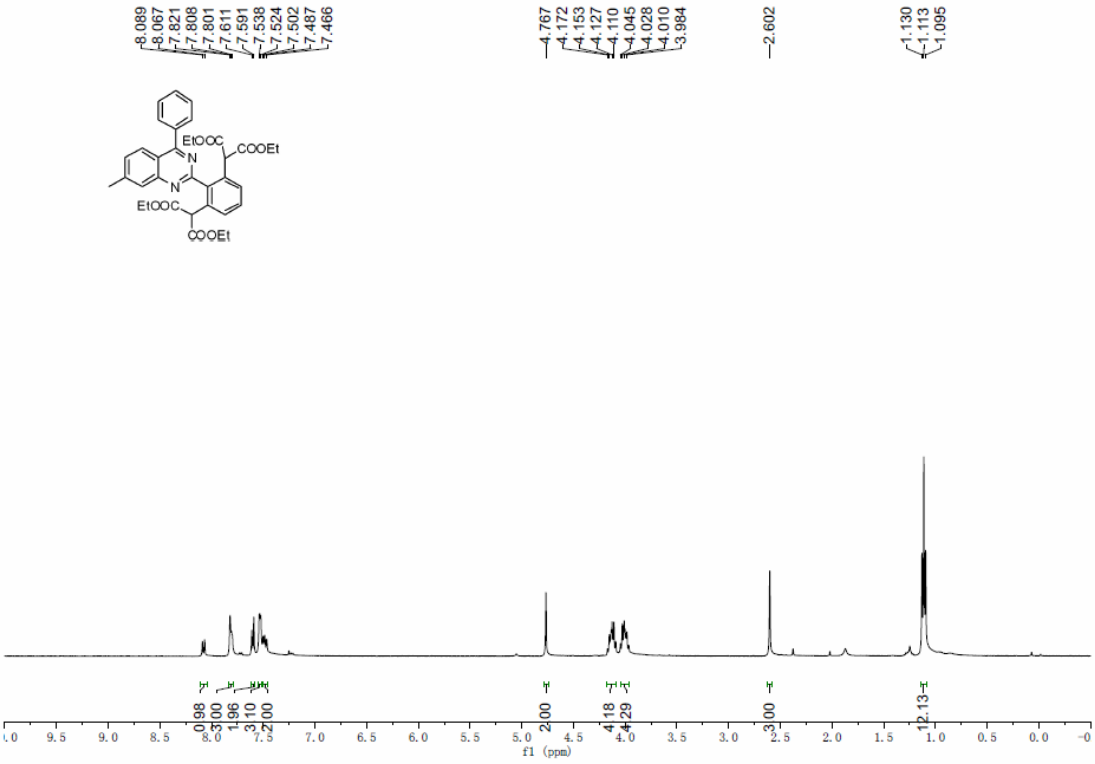
7.906
7.724
7.702
7.635
7.615
7.552
7.533
7.503
7.485
7.349
7.341
7.335
7.313
7.301
4.718
4.185
4.167
4.149
4.123
4.049
4.031
4.014
3.996
1.151
1.133
1.115
F
EtOOC
COOEt
N
N
EtOOC
COOEt
2.04
2.17
2.18
4.20
1.22
2.00
4.10
4.09
12.03
f1 (ppm)
168.19
166.13
161.05
159.21
156.60
152.48
132.31
129.51
129.47
129.26
127.70
113.50
113.29
112.24
112.12
61.55
55.62
13.85
f1 (ppm)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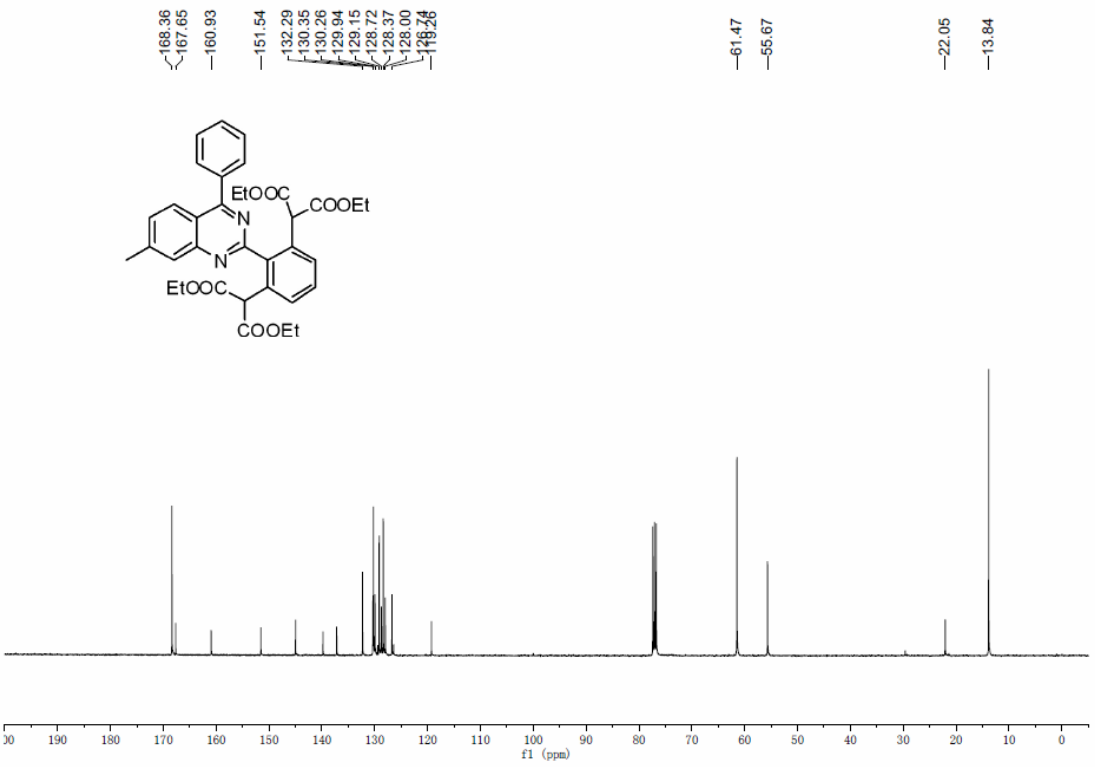
8.067
7.821
7.808
7.801
7.611
7.591
7.538
7.524
7.502
7.487
7.466
4.767
4.172
4.153
4.127
4.110
4.045
4.028
4.010
3.984
2.602
1.130
1.113
1.095
EtOOC
COOEt
N
N
EtOOC
COOEt
0.98
3.00
1.96
3.10
2.00
2.00
4.18
4.29
3.00
12.13
f1 (ppm)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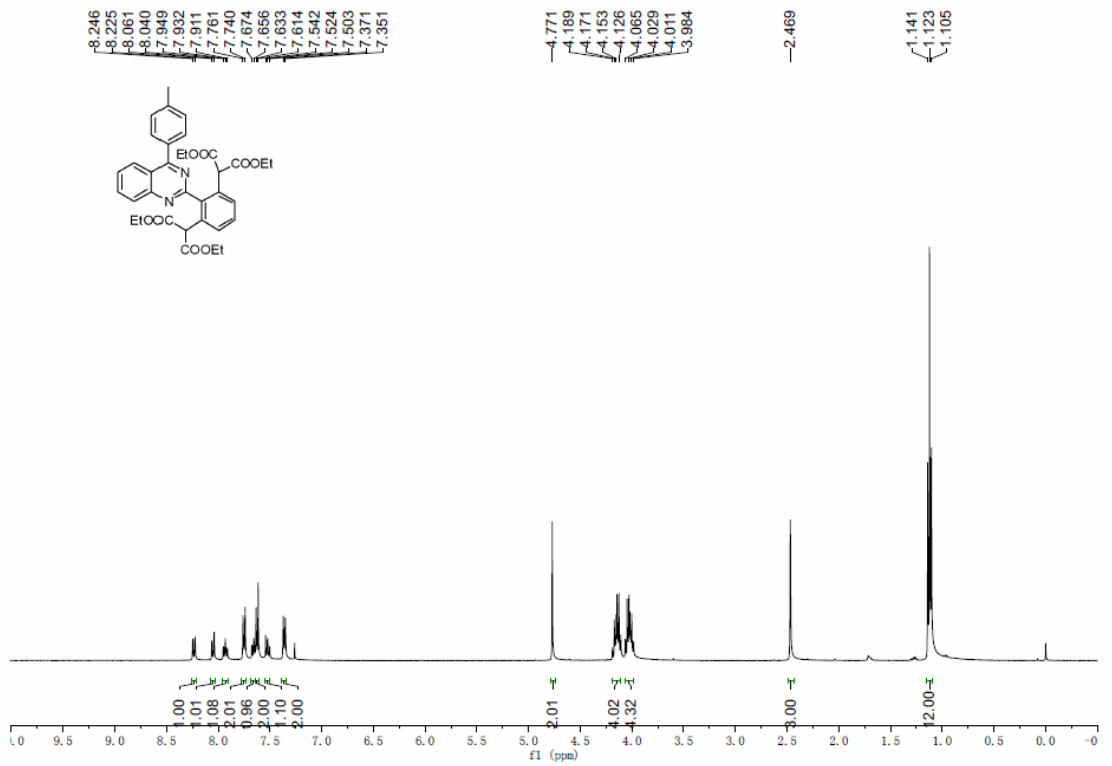
167.65
160.93
151.54
132.29
130.35
130.26
129.94
129.15
128.72
128.37
128.00
61.47
55.67
22.05
13.84
EtOOC
COOEt
N
N
EtOOC
COOEt
f1 (ppm)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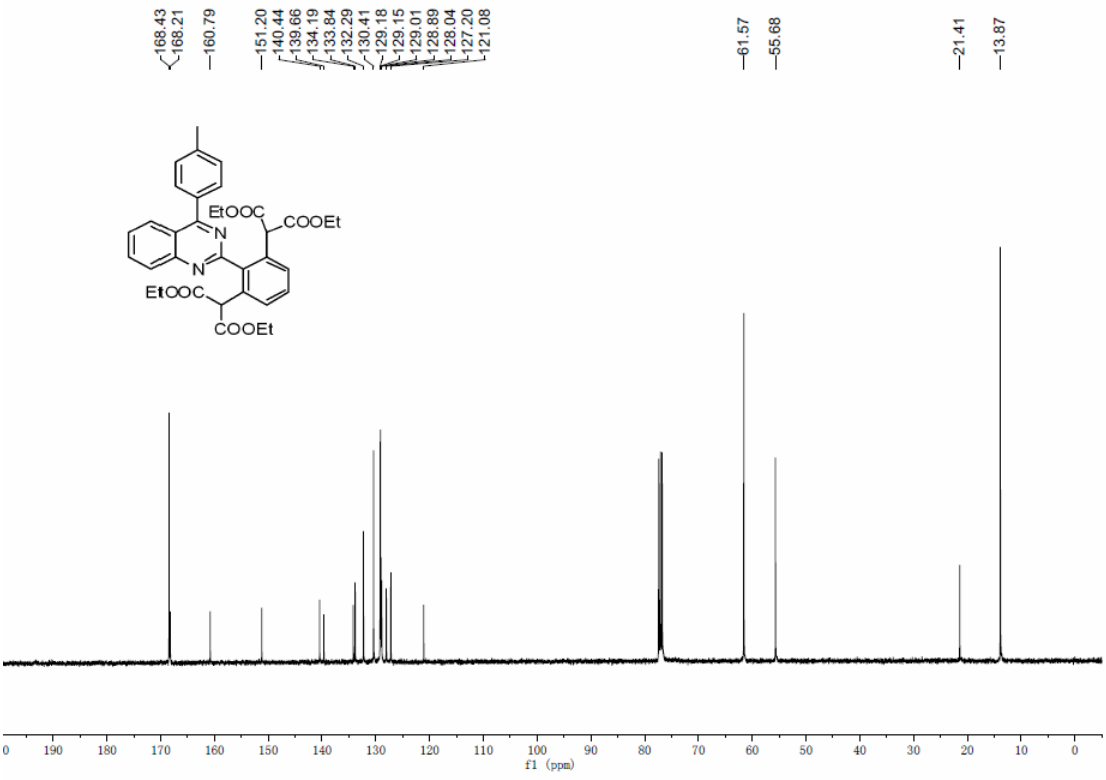
8.225
8.061
8.040
7.949
7.932
7.911
7.761
7.740
7.674
7.656
7.633
7.614
7.542
7.524
7.503
7.371
7.351
4.771
4.189
4.171
4.153
4.126
4.065
4.029
4.011
3.984
2.469
1.141
1.123
1.105
EtOOC
COOEt
EtOOC
COOEt
1.00
1.01
1.08
2.01
0.96
2.00
1.10
2.00
2.01
4.02
4.32
3.00
12.00
f1 (ppm)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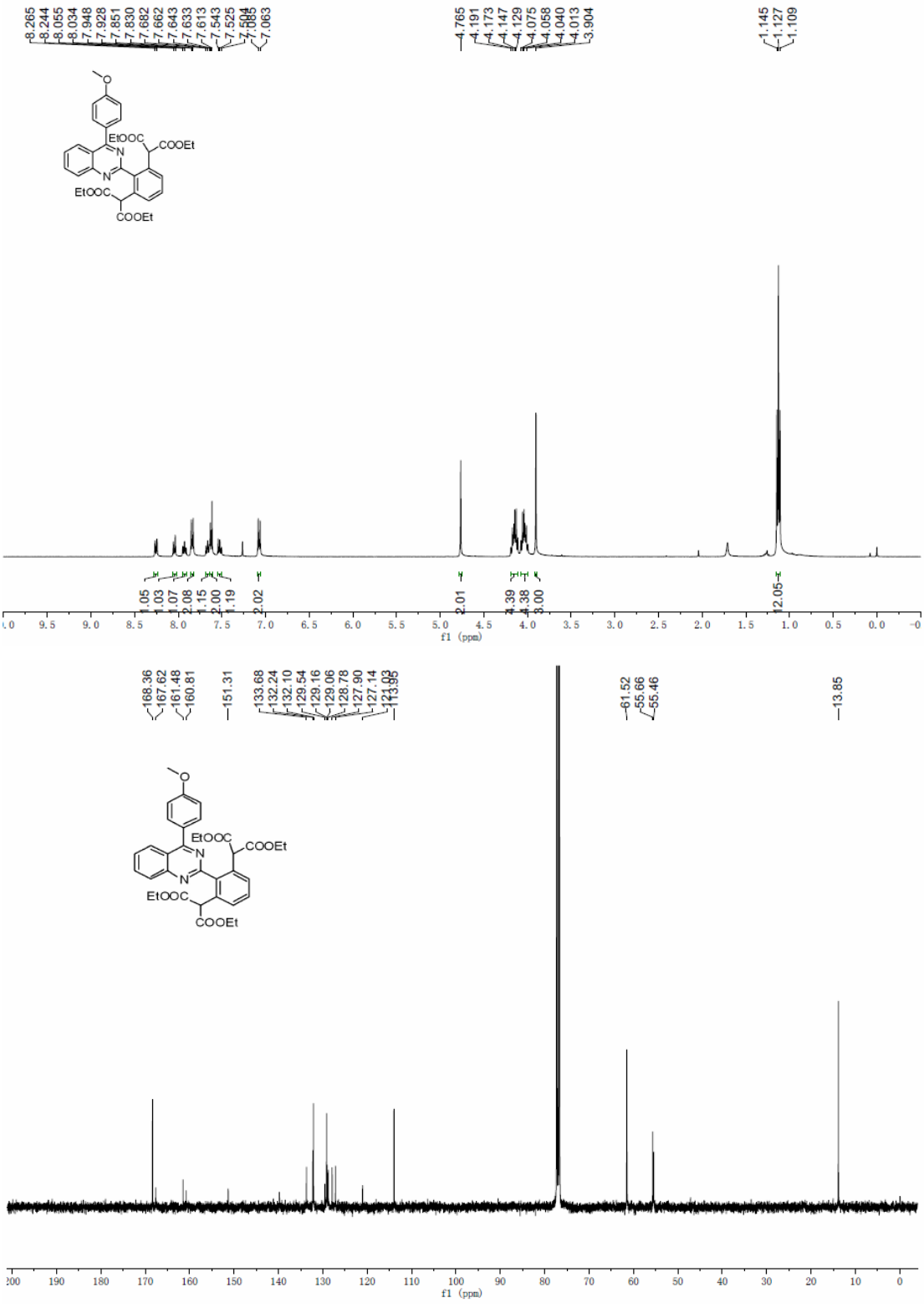
168.21
160.79
151.20
140.44
139.66
134.19
133.84
132.29
130.41
129.18
129.15
129.01
128.89
128.04
127.20
121.08
61.57
55.68
21.41
13.87
EtOOC
COOEt
EtOOC
COOEt
f1 (ppm)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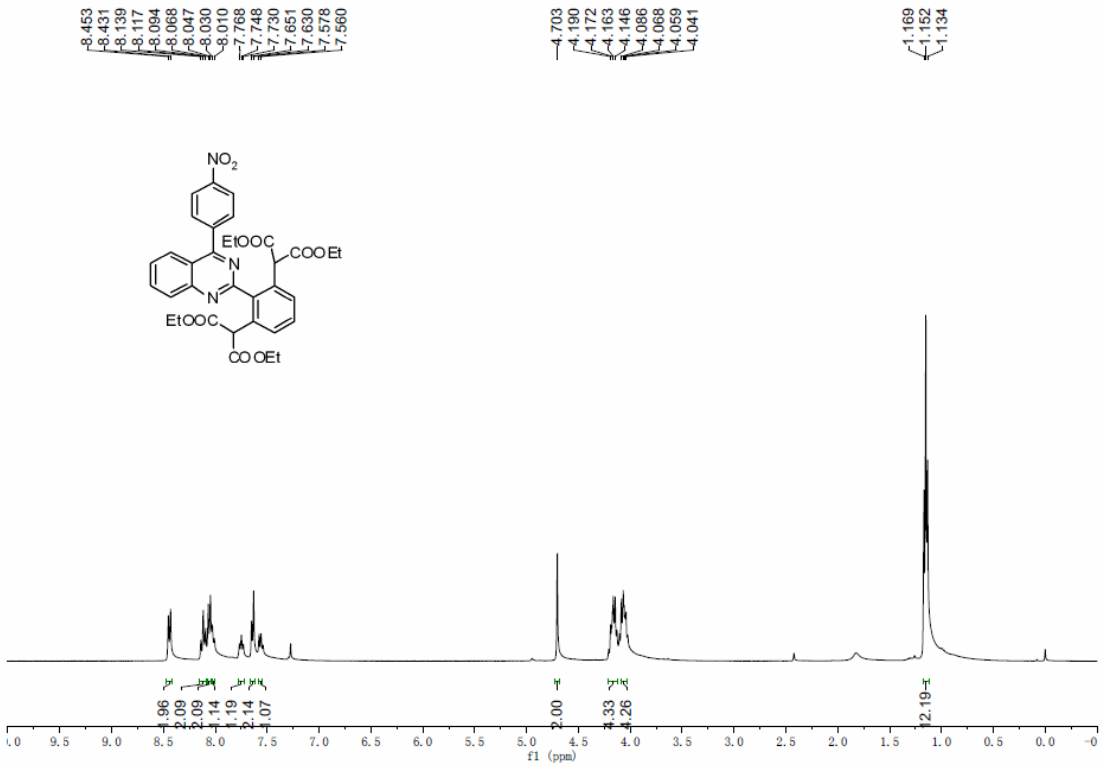
8.244
8.055
8.034
7.948
7.928
7.851
7.830
7.682
7.662
7.643
7.633
7.613
7.543
7.525
7.504
7.085
7.063
4.765
4.191
4.173
4.147
4.129
4.075
4.058
4.040
4.013
3.904
1.145
1.127
1.109
EtOOC
COOEt
EtOOC
COOEt
1.05
1.03
1.07
2.08
1.15
2.00
1.19
2.02
2.01
1.39
1.38
3.00
12.05
f1 (ppm)
168.36
167.62
161.48
160.81
151.31
133.68
132.24
132.10
129.54
129.16
129.06
128.78
127.90
127.14
121.03
113.95
61.52
55.66
55.46
13.85
EtOOC
COOEt
EtOOC
COOEt
f1 (ppm)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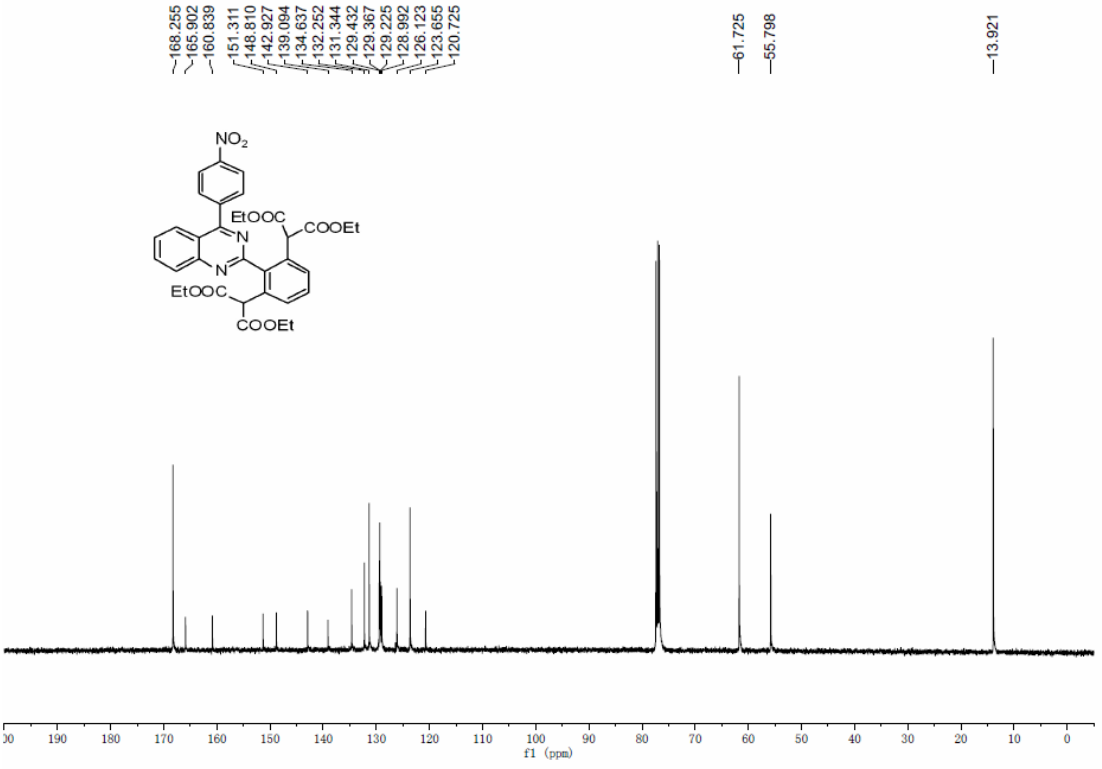
8.139
8.117
8.094
8.068
8.047
8.030
8.010
7.768
7.748
7.730
7.651
7.630
7.578
7.560
4.703
4.190
4.172
4.163
4.146
4.086
4.068
4.059
4.041
1.169
1.152
1.134
NO2
EtOOC
COOEt
N
N
EtOOC
COOEt
1.96
2.09
2.09
1.14
1.19
2.14
1.07
2.00
4.33
4.26
12.19
f1 (ppm)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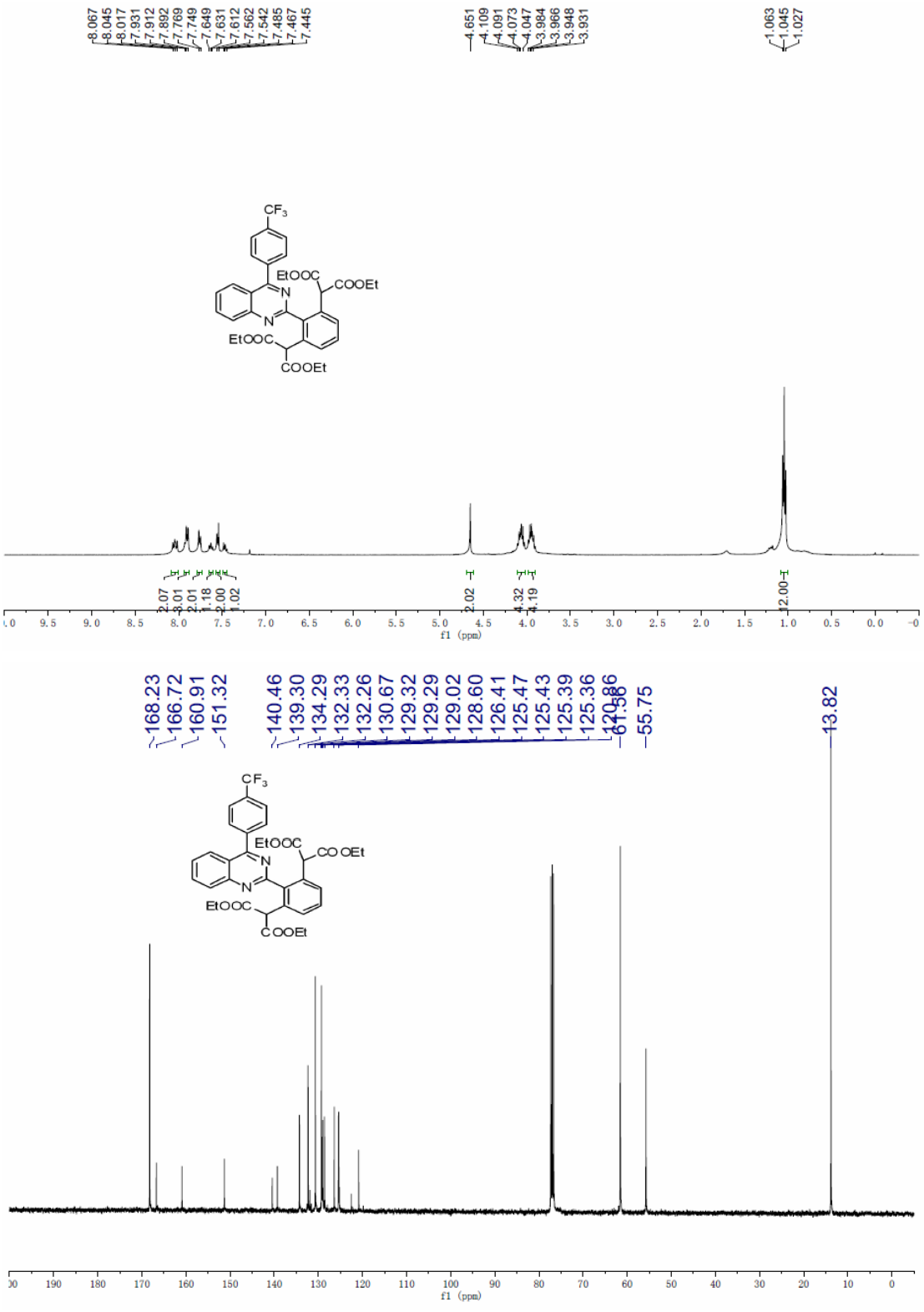
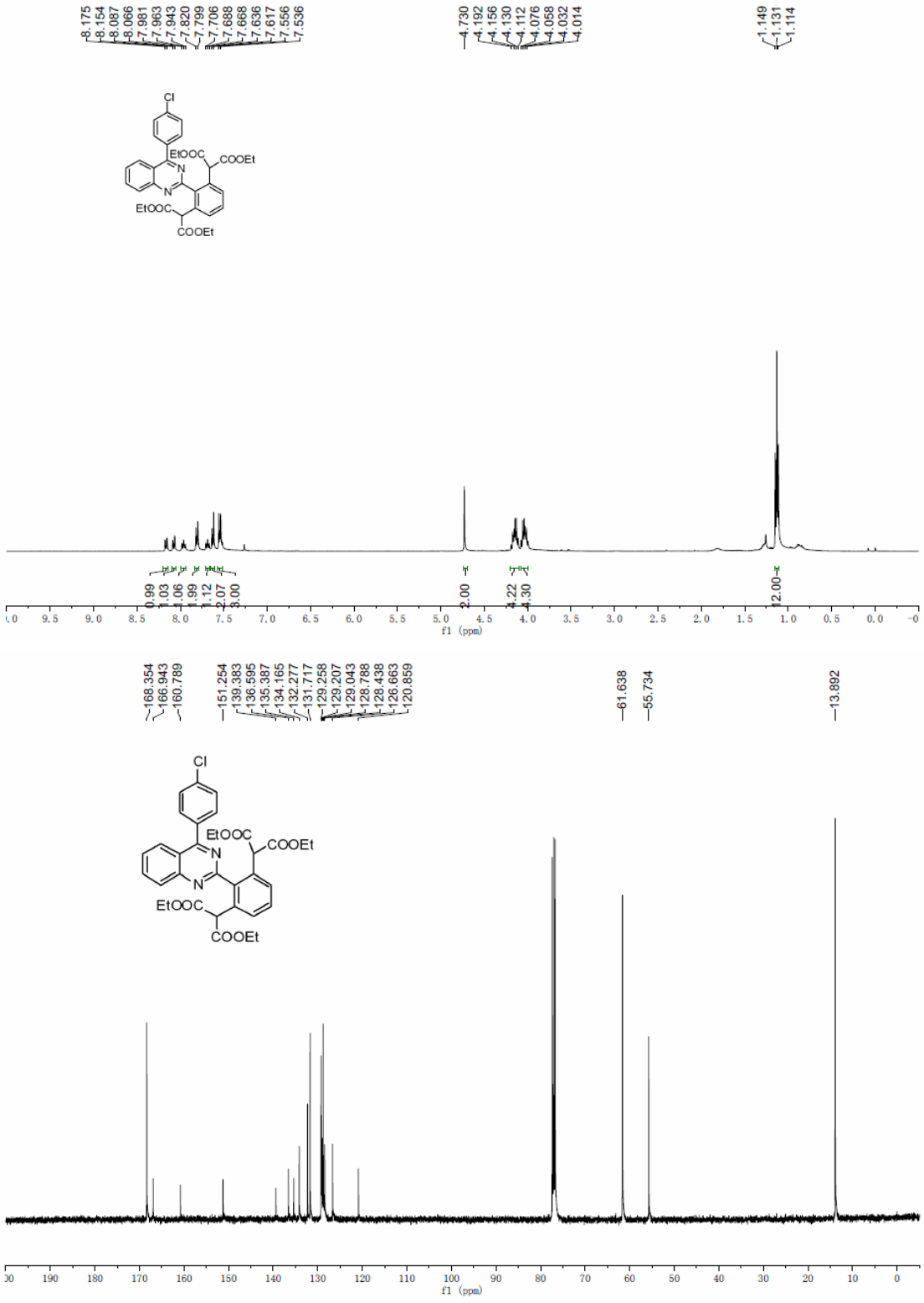
160.839
151.311
148.810
142.927
139.094
134.637
132.252
131.344
129.432
129.367
129.225
128.992
126.123
123.655
120.725
61.725
55.798
13.921
NO2
EtOOC
COOEt
N
N
EtOOC
COOEt
f1 (ppm)


8.067
8.045
8.017
7.931
7.912
7.892
7.769
7.749
7.649
7.631
7.612
7.562
7.542
7.485
7.467
7.445
4.651
4.109
4.091
4.073
4.047
3.984
3.966
3.948
3.931
1.063
1.045
1.027
CF3
EtOOC
COOEt
N
N
EtOOC
COOEt
2.07
3.01
2.01
1.18
2.00
1.02
2.02
4.32
4.19
12.00
f1 (ppm)
168.23
166.72
160.91
151.32
140.46
139.30
134.29
132.33
132.26
130.67
129.32
129.29
129.02
128.60
126.41
125.47
125.43
125.39
125.36
61.58
55.75
13.82
CF3
EtOOC
CO OEt
N
N
EtOOC
COOEt
f1 (ppm)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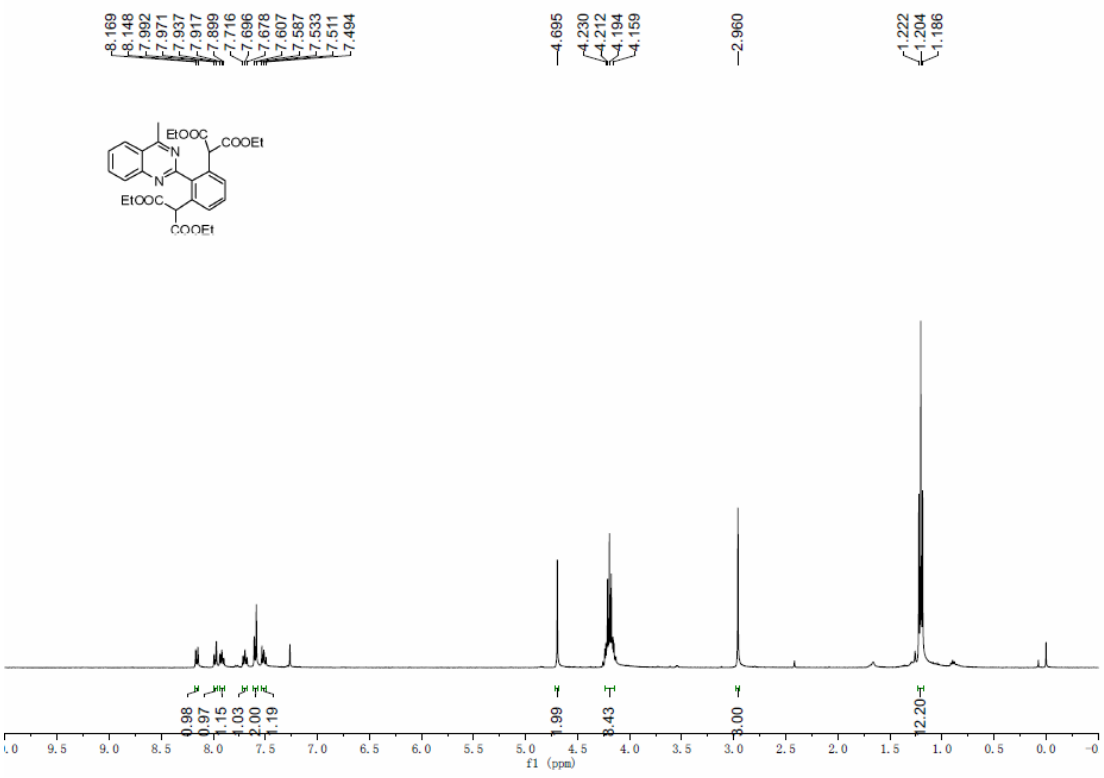
8.154
8.087
8.066
7.981
7.963
7.943
7.820
7.799
7.706
7.688
7.668
7.636
7.617
7.556
7.536
4.730
4.192
4.156
4.130
4.112
4.076
4.058
4.032
4.014
1.149
1.131
1.114
Cl
EtOOC
COOEt
N
N
EtOOC
COOEt
0.99
1.03
1.06
1.99
1.12
2.07
3.00
2.00
4.22
4.30
12.00
f1 (ppm)
168.354
166.943
160.789
151.254
139.383
136.595
135.387
134.165
132.277
131.717
129.258
129.207
129.043
128.788
128.438
126.663
120.859
61.638
55.734
13.892
Cl
EtOOC
COOEt
N
N
EtOOC
COOEt
f1 (ppm)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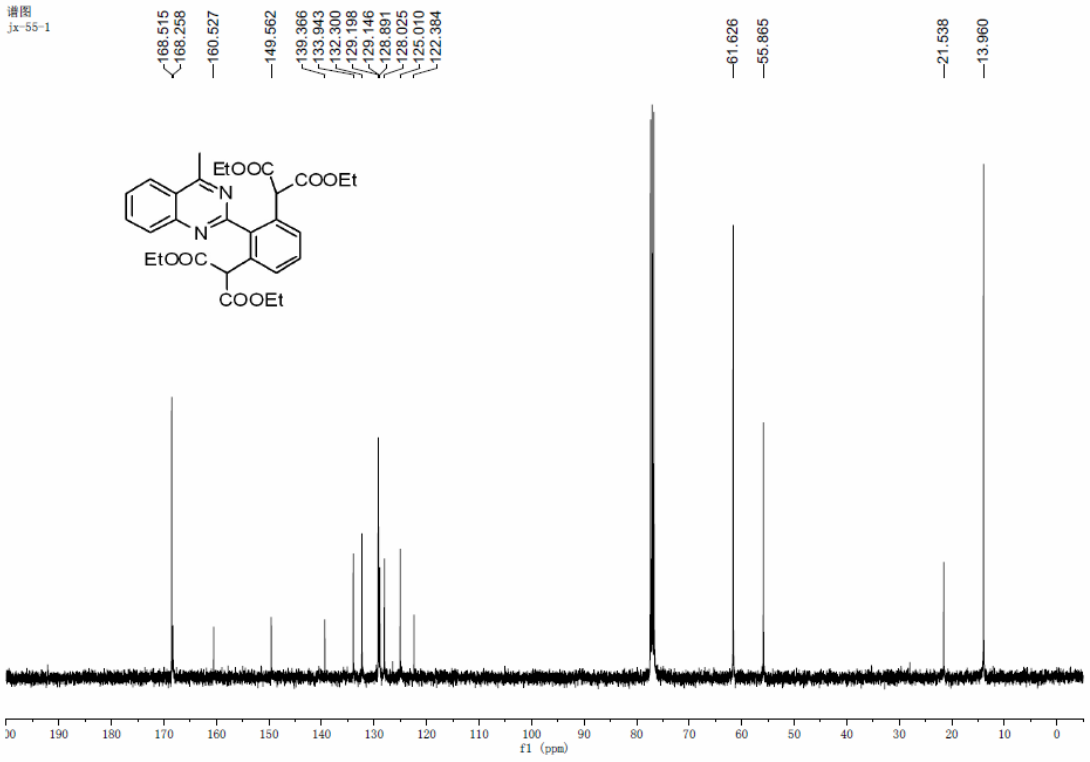
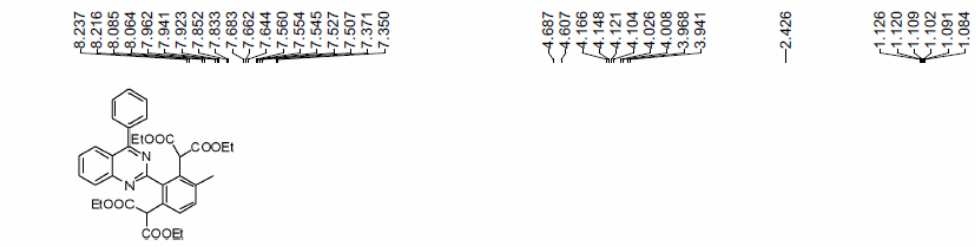
8.148
7.992
7.971
7.937
7.917
7.899
7.716
7.696
7.678
7.607
7.587
7.533
7.511
7.494
4.695
4.230
4.212
4.194
4.159
2.960
1.222
1.204
1.186
EtOOC
COOEt
EtOOC
COOEt
0.98
0.97
1.15
4.03
2.00
1.19
1.99
8.43
3.00
12.20
f1 (ppm)


谱图
jx-55-1
168.515
168.258
160.527
149.562
139.366
133.943
132.300
129.198
129.146
128.891
128.025
125.010
122.384
61.626
55.865
21.538
13.960
EtOOC
COOEt
EtOOC
COOEt
f1 (ppm)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8.216
8.085
8.064
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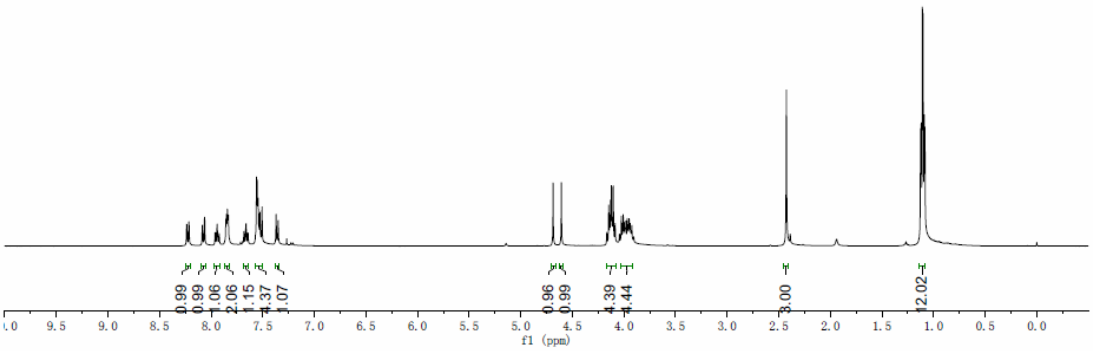
7.941
7.923
7.852
7.833
7.683
7.662
7.644
7.560
7.554
7.545
7.527
7.507
7.371
7.350
4.687
4.607
4.166
4.148
4.121
4.104
4.026
4.008
3.968
3.941
2.426
1.126
1.120
1.109
1.102
1.091
1.084
EtOOC
COOEt
N
N
EtOOC
COOEt


0.99
0.99
1.06
2.06
1.15
4.37
1.07
0.96
0.99
4.39
4.44
3.00
12.02
f1 (ppm)


168.38
168.32
168.14
161.82
151.24
141.27
138.78
137.00
133.98
132.06
131.34
130.40
130.17
129.61
129.06
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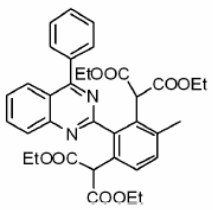
128.46
128.20
127.08
121.04
61.50
61.39
55.50
55.44
20.46
13.91
13.87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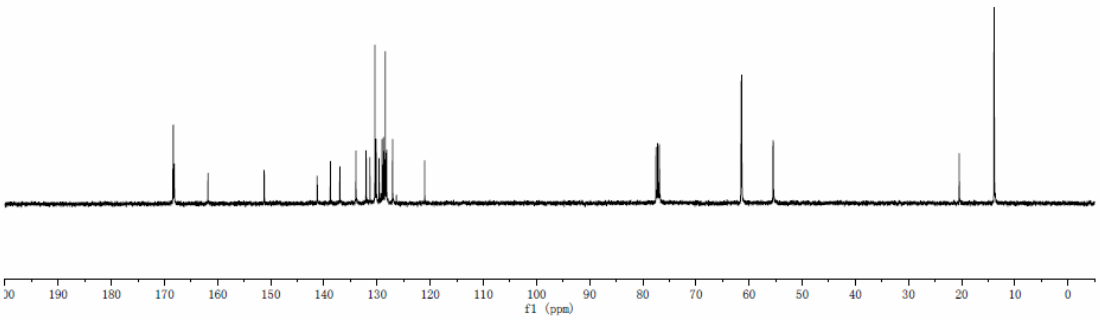
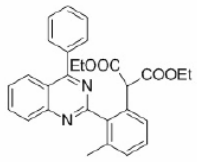
COOEt
N
N
EtOOC
COOEt


f1 (ppm)


8.217
8.197
8.138
8.117
7.955
7.934
7.913
7.847
7.832
7.663
7.642
7.625
7.559
7.551
7.544
7.497
7.478
7.397
7.378
7.359
7.308
7.289
4.625
4.163
4.136
4.118
4.100
4.082
4.064
4.046
4.029
2.302
1.142
1.124
1.106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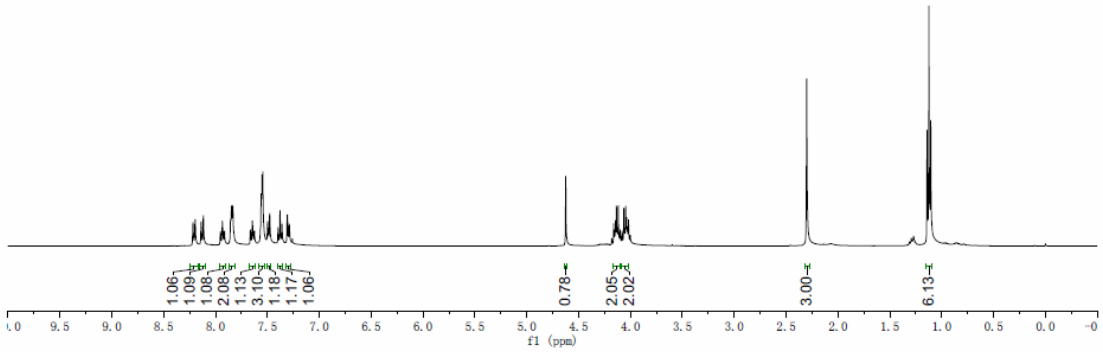
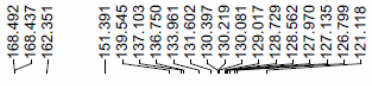
COOEt
N
N


1.06
1.09
1.08
2.08
1.13
3.10
1.18
1.17
1.06
0.78
2.05
2.02
3.00
6.13
f1 (ppm)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139.545
137.103
136.750
133.961
131.602
130.397
130.219
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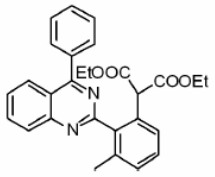
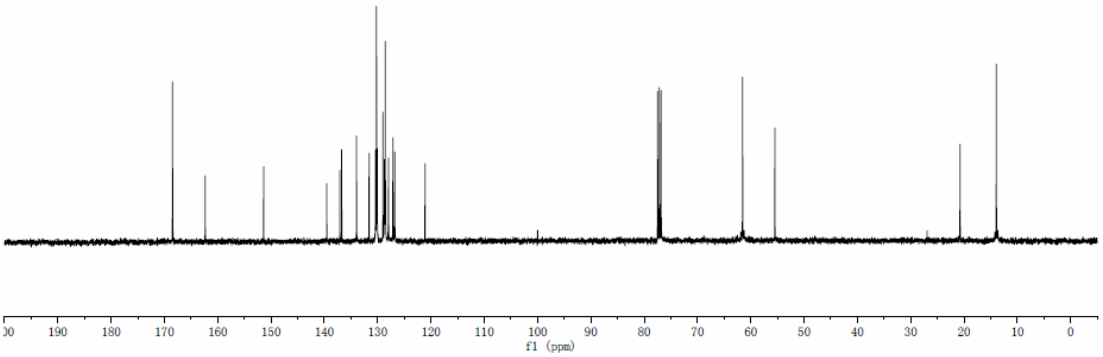
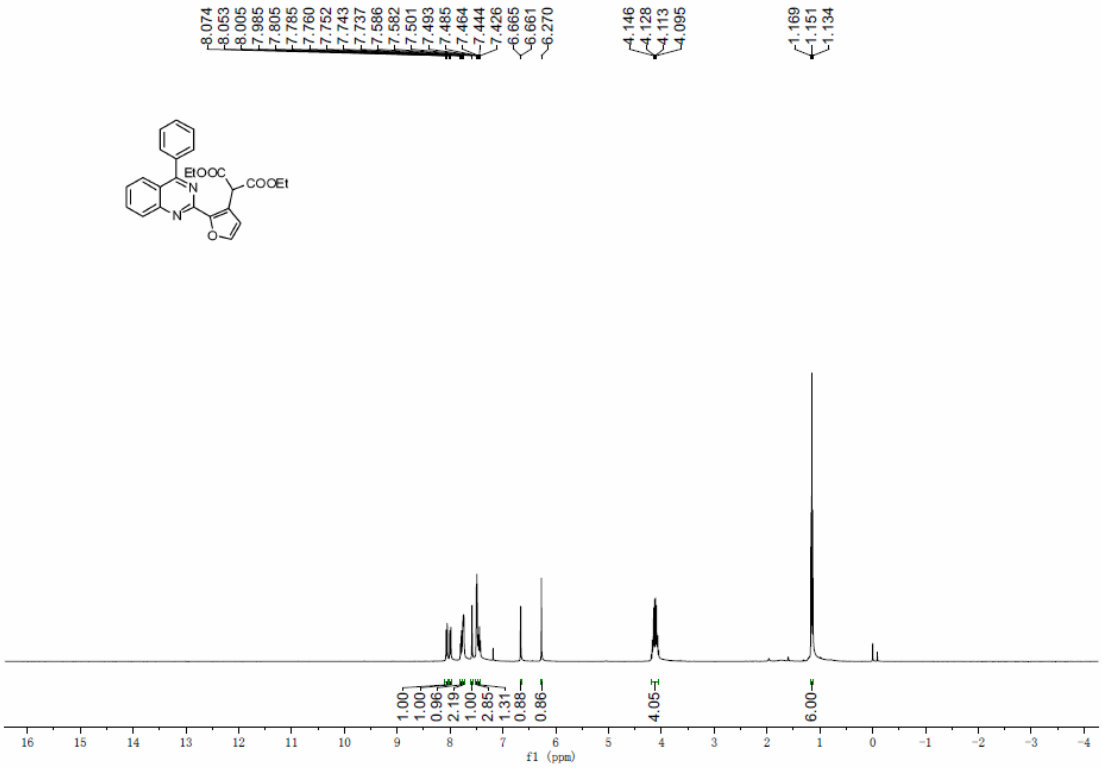
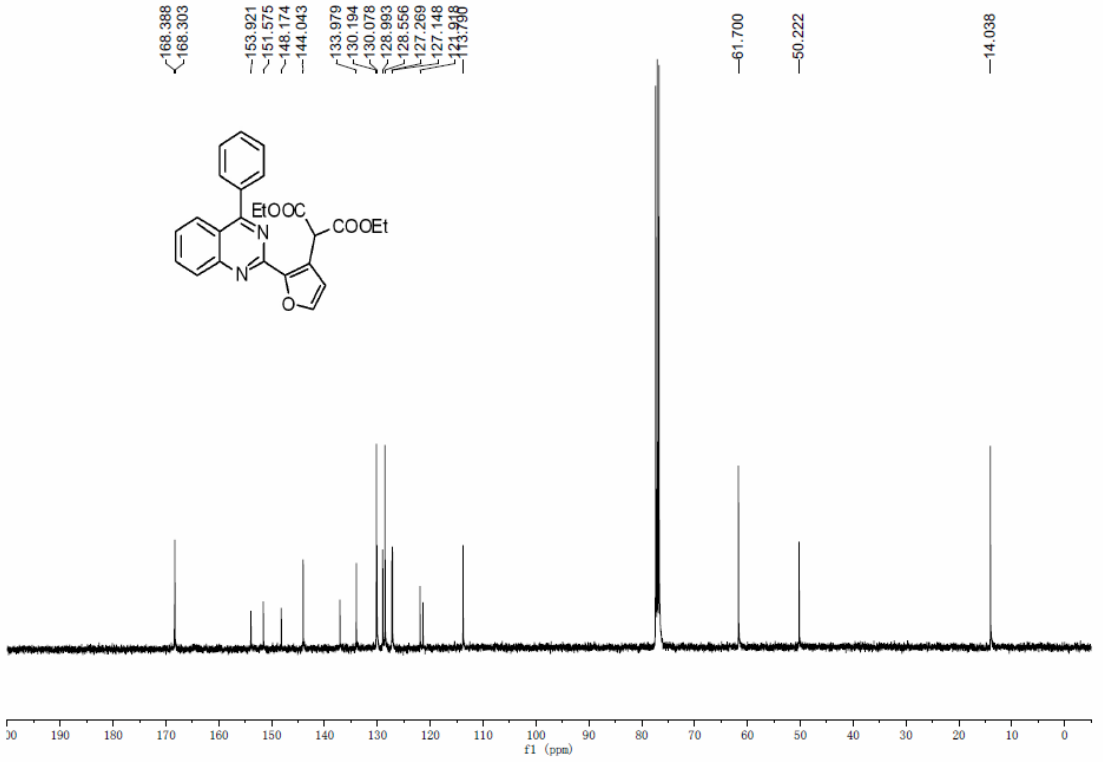
128.562
127.970
127.135
126.799
121.118
61.541
55.495
20.752
13.947


EtOOC
COOEt
N
N


f1 (ppm)


8.074
8.053
8.005
7.985
7.805
7.785
7.760
7.752
7.743
7.737
7.586
7.582
7.501
7.493
7.485
7.464
7.444
7.426
6.665
6.661
6.270
4.146
4.128
4.113
4.095
1.169
1.151
1.134
EtOOC
COOEt
N
N
O
1.00
1.00
0.96
2.19
1.00
2.85
1.31
0.88
0.86
4.05
6.00
f1 (ppm)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148.174
144.043
133.979
130.194
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128.993
128.556
127.269
127.148
121.918
113.790
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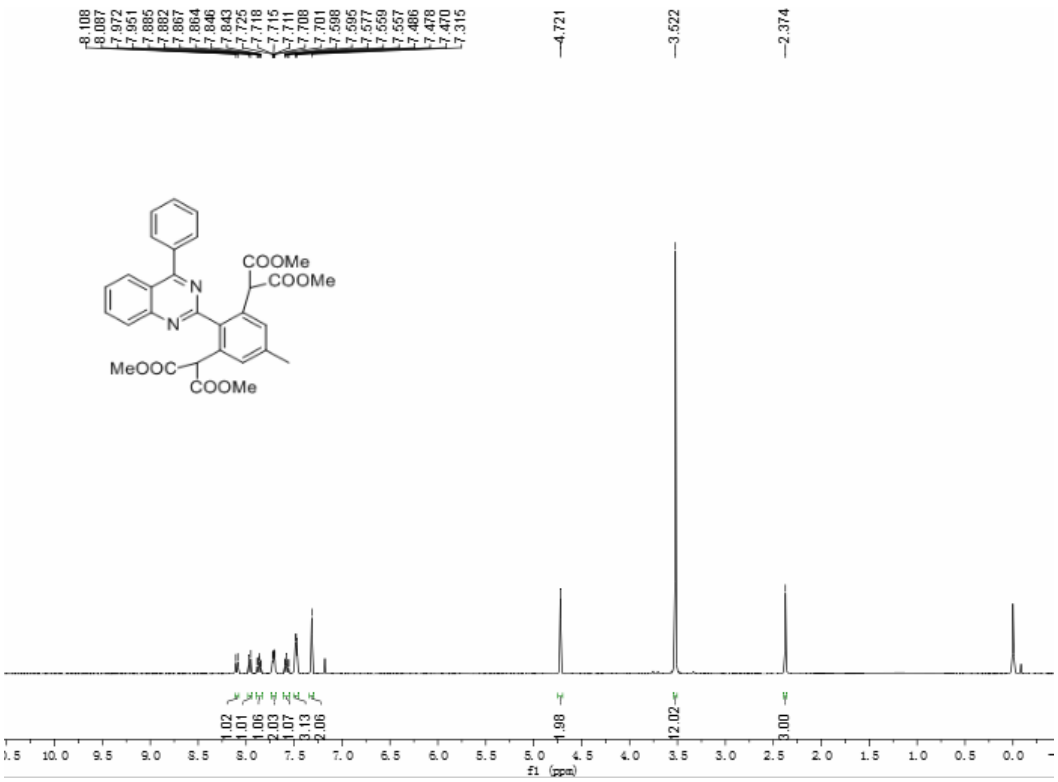
50.222
14.038
EtOOC
COOEt
N
N
O
f1 (ppm)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7.882
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7.864
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7.843
7.725
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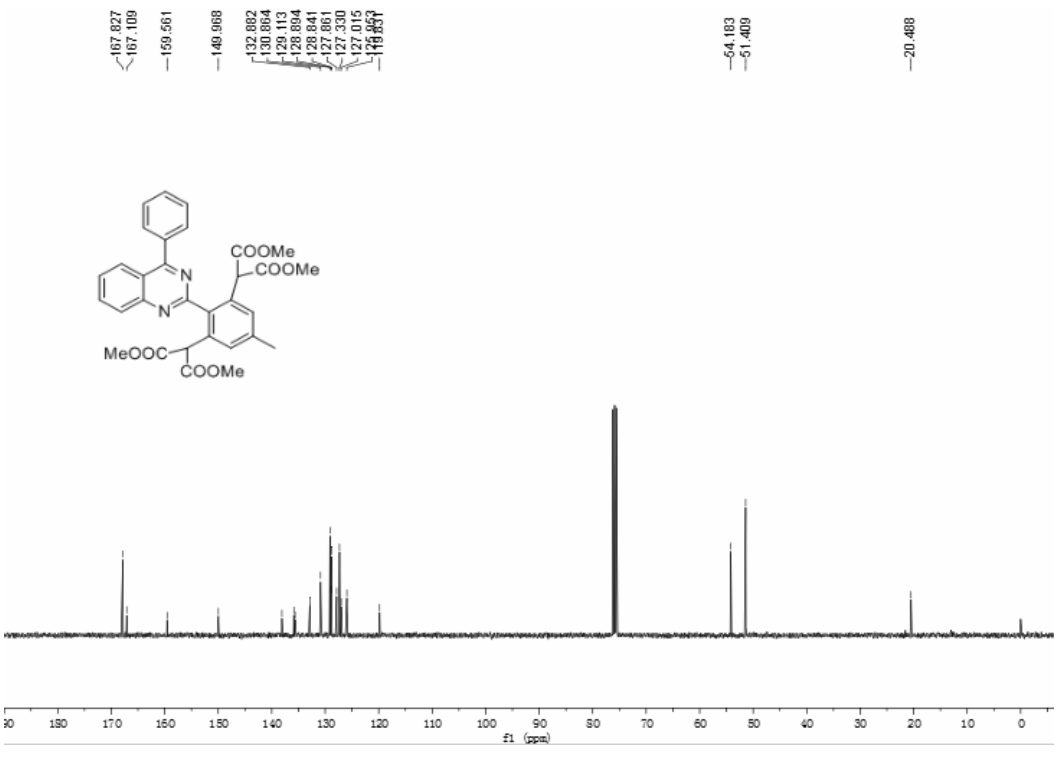
7.715
7.711
7.708
7.701
7.598
7.595
7.577
7.559
7.557
7.486
7.478
7.470
7.315
4.721
3.522
2.374
COOMe
COOMe
N
N
MeOOC
COOMe
1.02
1.01
1.06
2.03
1.07
3.13
2.06
1.98
12.02
3.00
f1 (ppm)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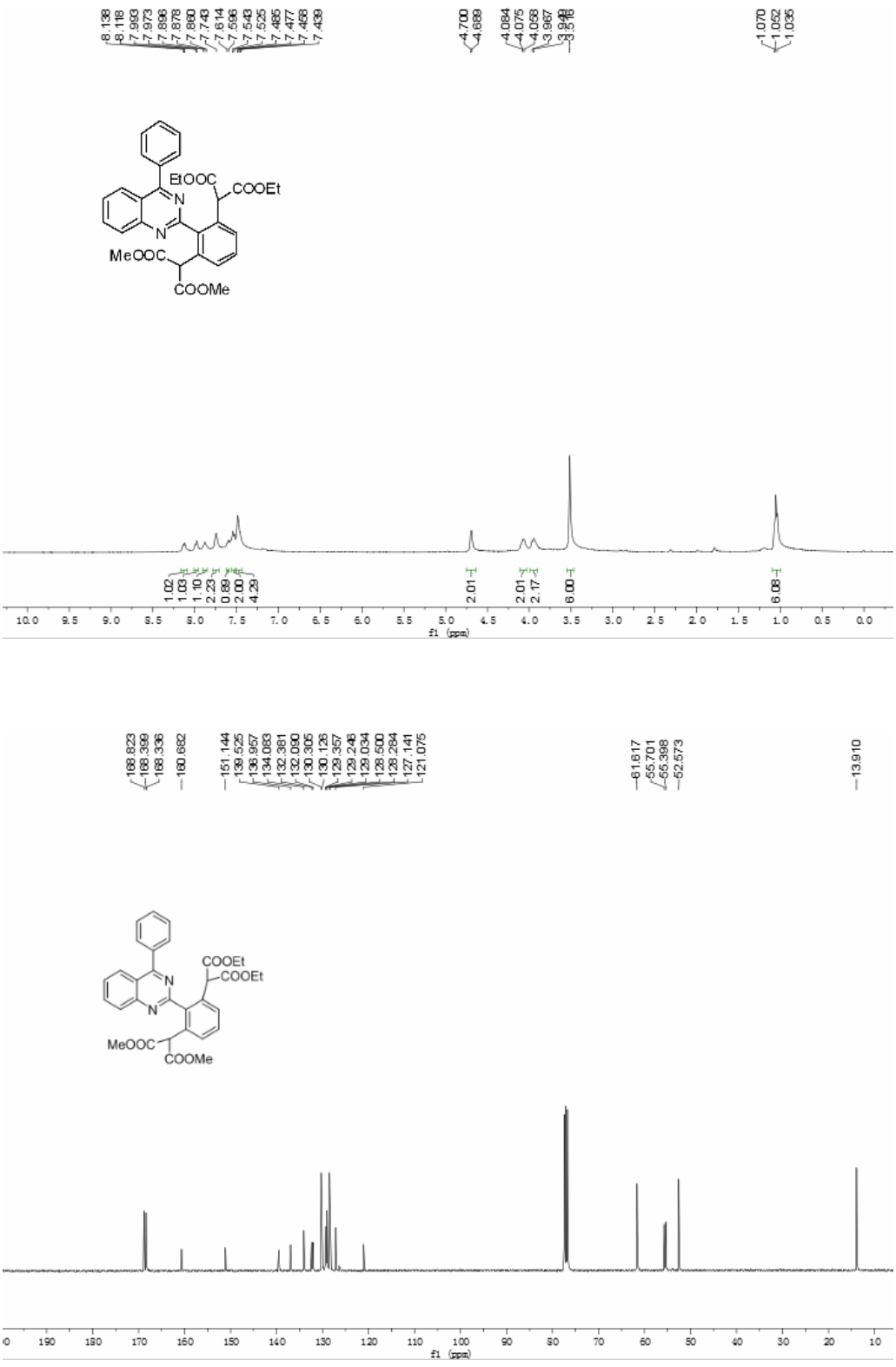
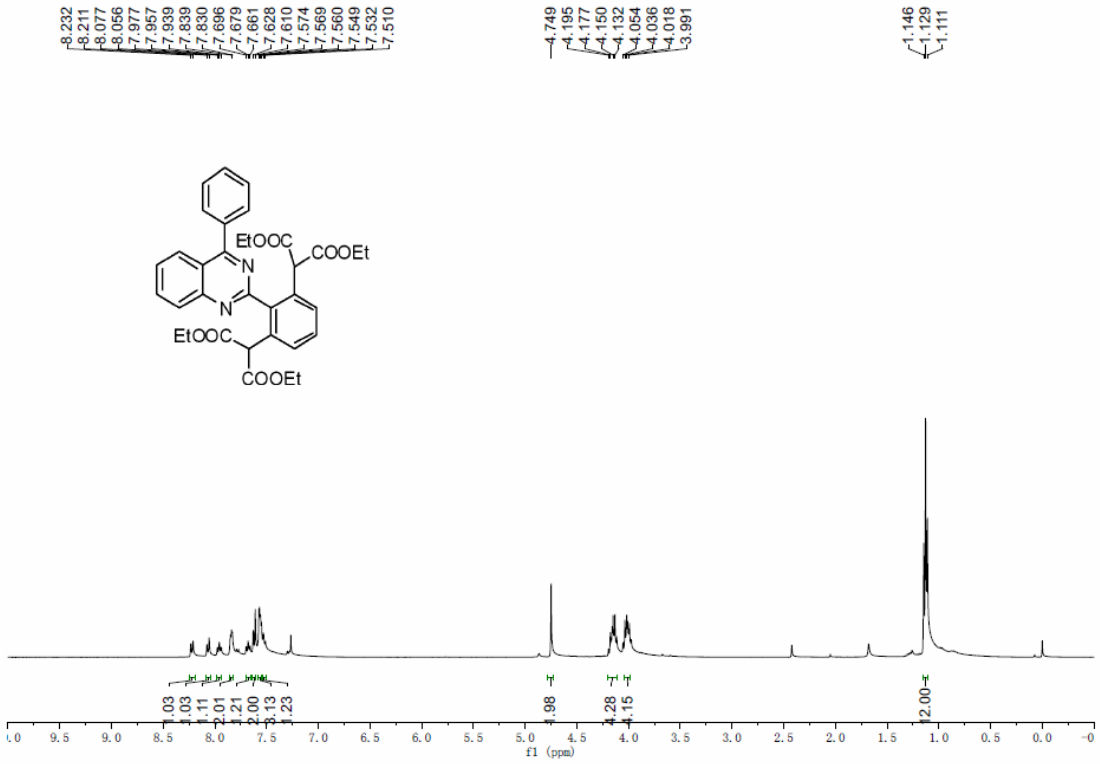
128.841
127.861
127.330
127.015
54.183
51.409
20.488
COOMe
COOMe
N
N
MeOOC
COOMe
f1 (ppm)

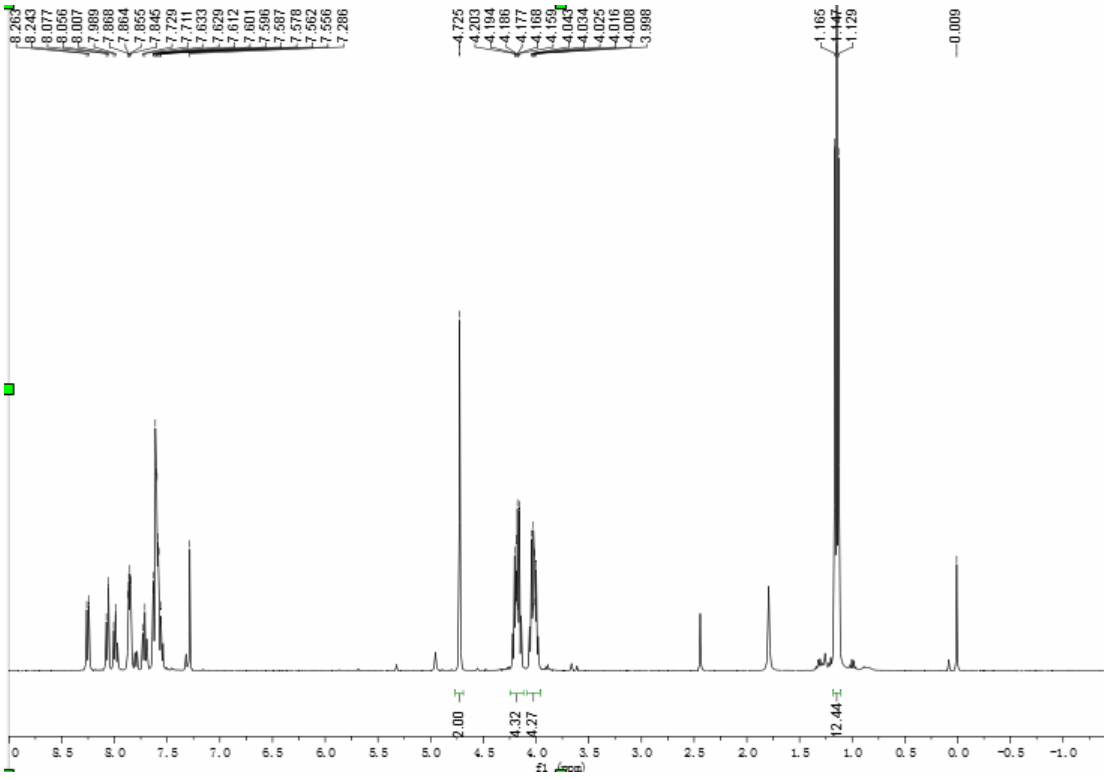

8.138
8.118
7.993
7.973
7.896
7.878
7.860
7.743
7.614
7.596
7.543
7.525
7.485
7.477
7.468
7.439
4.700
4.689
4.084
4.075
4.058
3.967
3.516
1.070
1.052
1.035
EtOOC
COOEt
N
N
MeOOC
COOMe
1.02
1.03
1.10
2.23
0.89
2.00
4.29
2.01
2.01
2.17
6.00
6.08
f1 (ppm)
168.823
168.399
168.336
160.682
151.144
139.525
136.957
134.083
132.381
132.090
130.305
130.126
129.357
129.246
129.034
128.500
128.284
127.141
121.075
61.617
55.701
55.398
52.573
13.910
COOEt
COOEt
N
N
MeOOC
COOMe
f1 (ppm)

5. Track record ^{1}HNMRs spectra at temperature changing from 25℃ to -20℃

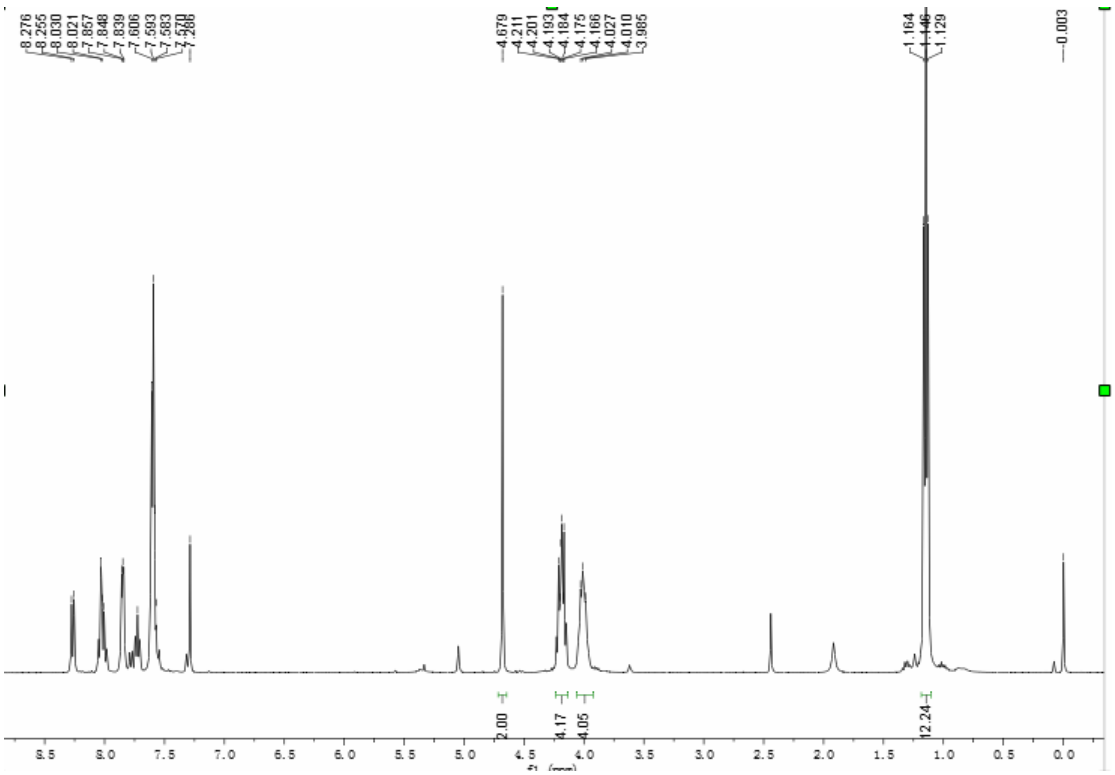
Tx-49-1　25℃



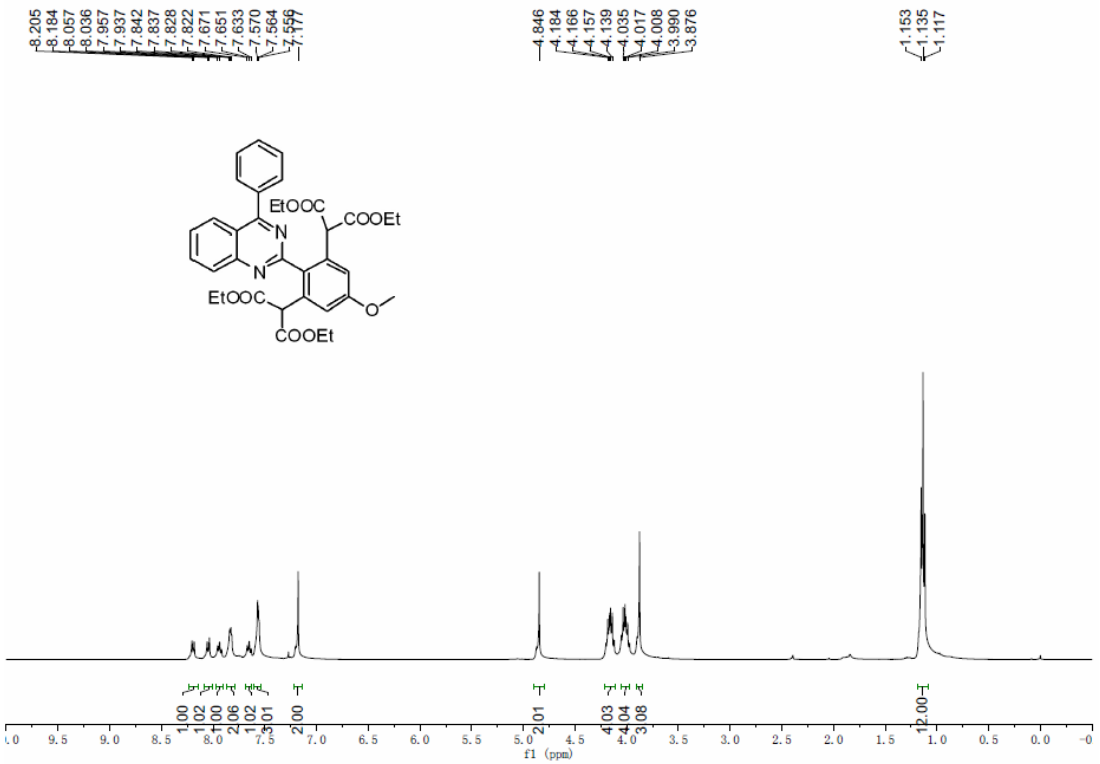
Tx-49-1　0℃



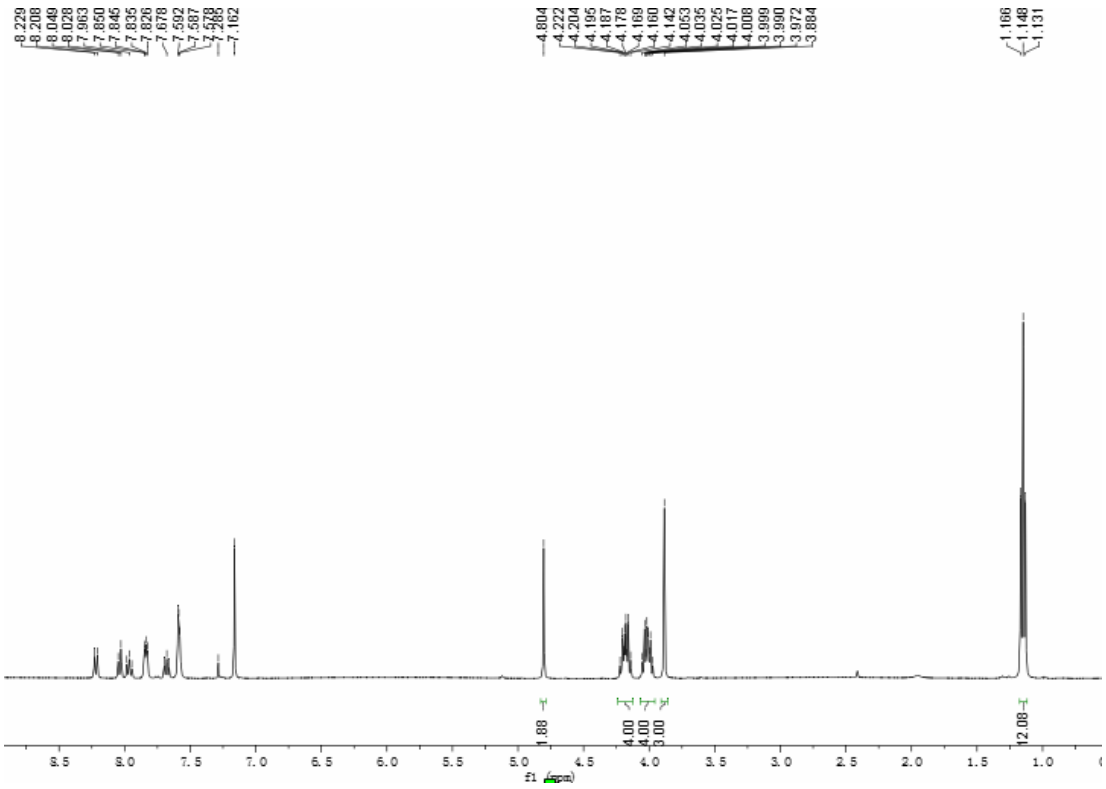
Tx-49-1 -20℃



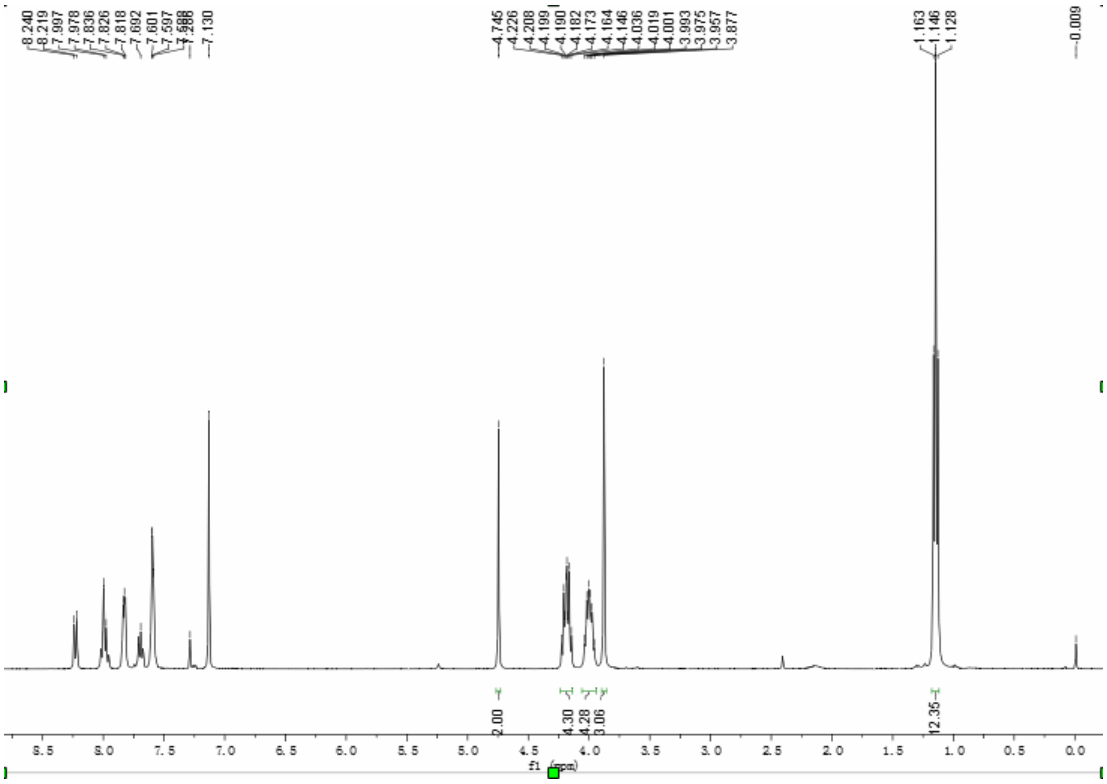
Tx-58-1　25℃



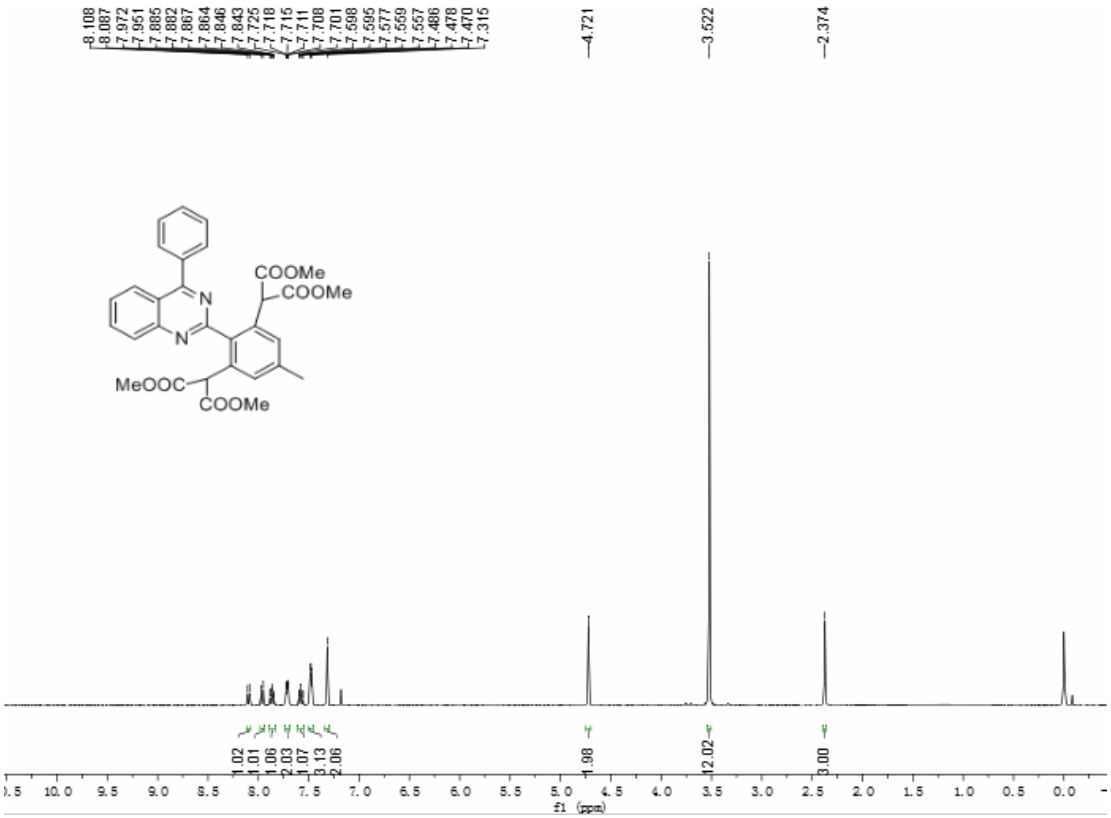
Tx-58-1　0℃



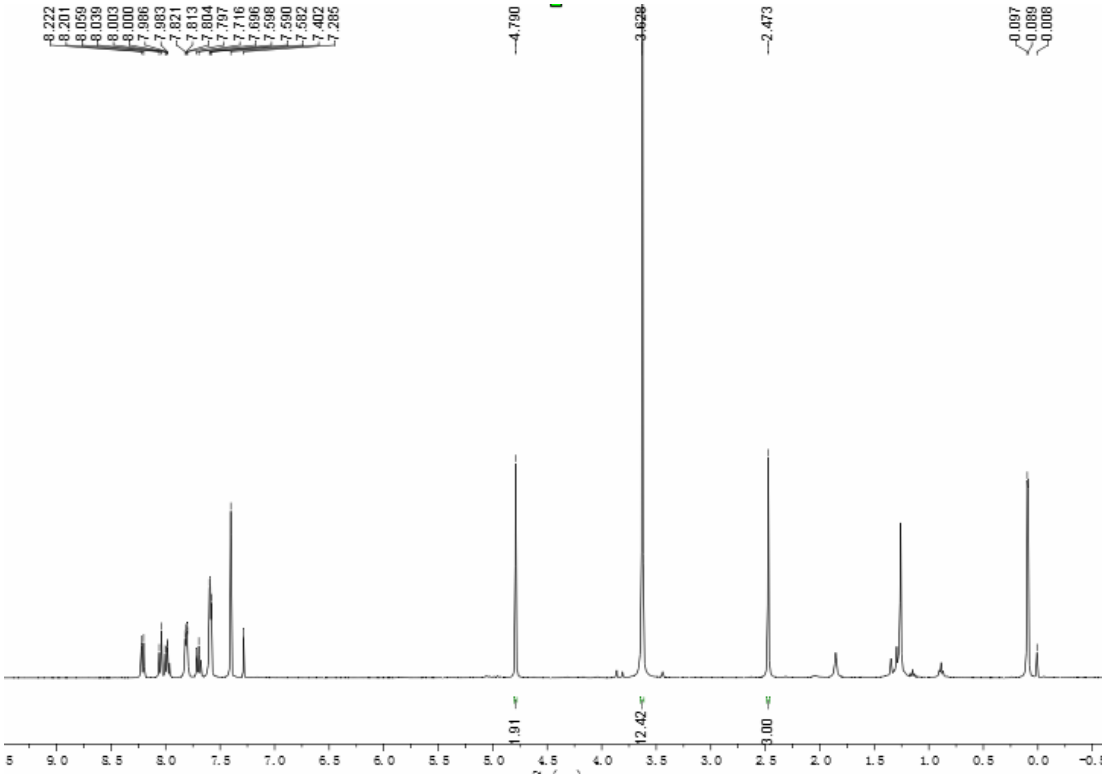
Tx-58-1 -20℃



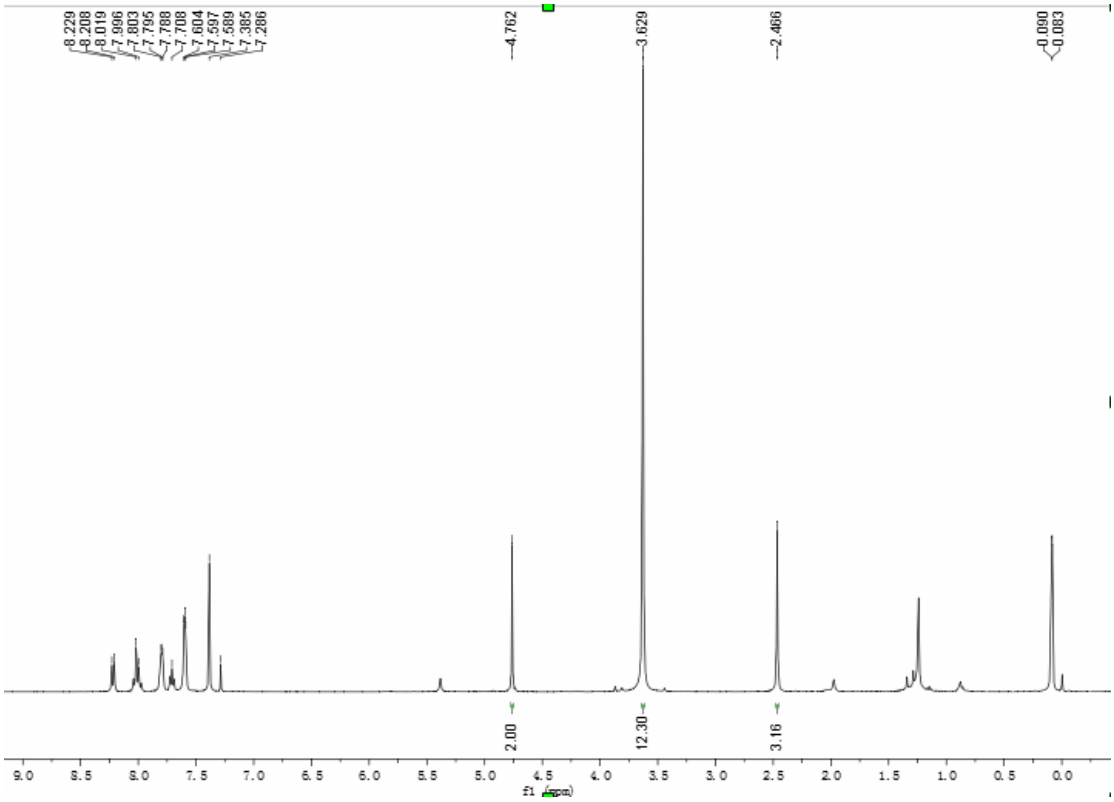
Zzp-2-7　25℃



Zzp-2-7 0℃

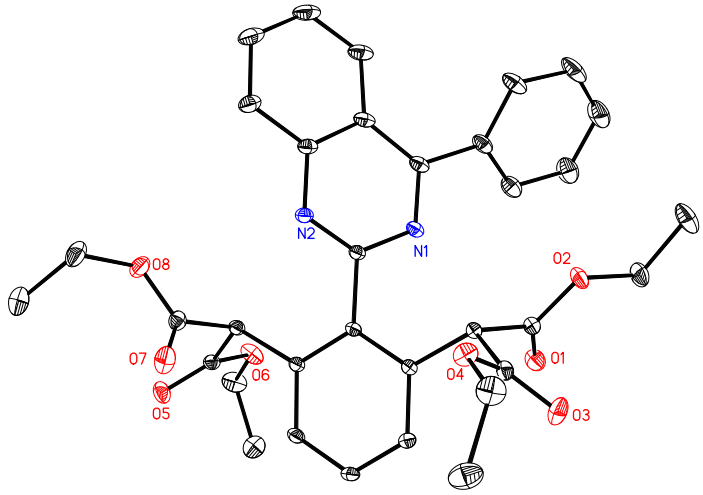


Zzp-2-7 -20℃


8.229
8.208
8.019
7.996
7.803
7.795
7.788
7.708
7.604
7.597
7.589
7.385
7.286
4.762
3.629
2.466
0.090
0.083
2.00
12.30
3.16
f1 (ppm)

6. X-ray illustration of compound 3a and 3k

3a



3k