Supplementary Information

Chiral phosphoric acid-catalyzed dual ring formation for enantioselective construction of N–N axially chiral 3,3'-bisquinazolinones

XXX,‡[a] XXX,‡[a] XXX*,[b] and XX*,[a]

[a] *XXXX*

[b] *XXXX*

E-mail: XXX

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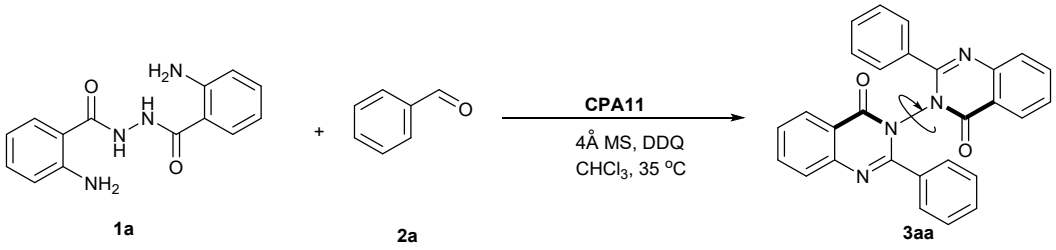
1. General Considerations

All chemicals were used as received without further purification unless stated otherwise. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a 500 MHz spectrometer (125 MHz for ^{13}C). NMR experiments are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 or 77.0 ppm) and $DMSO_{d\text{-}6}$ (δ 2.5 or 36.5 ppm) as the internal standard. The coupling constants *J* are given in Hz. Column chromatography was performed using EM Silica gel 60 (300-400 meshes) or neutral aluminum oxide (200-300 meshes).

2. Experimental Procedures.

2.1 General procedure

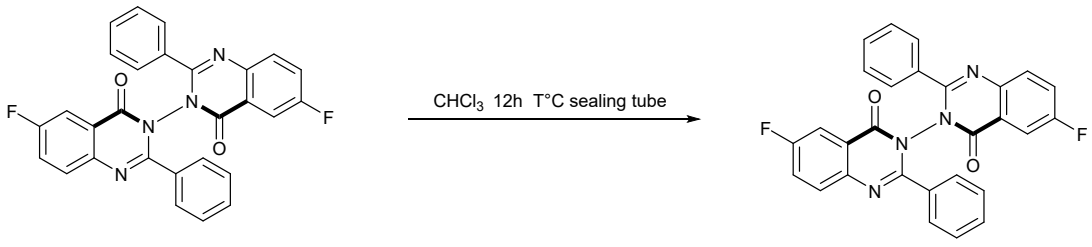


1a 2a 3aa

An oven-dried 25 mL Schlenk tube charged with **1a** (0.1 mmol), CPA (0.01 mmol, 6.1 mg), and DDQ (0.28 mmol, 63.5 mg), 4Å MS (400 mg), 4 mL of $CHCl_3$ added by syringe and benzaldehyde (0.2 mmol, 20 μL) added by pipette. After 24 h, **2a** (0.2 mmol) was added to the reaction mixture. After 36 h, **2a** (0.2 mmol) was added to the reaction mixture. After 48 h, **2a** (0.2 mmol) was added to the reaction mixture. Then, the tube was vacuumed and refilled with Ar for 3 times and was placed in 35 °C oil-bath for 60 h. The crude reaction mixture was concentrated in vacuo and the residue was purified by silica gel flash column chromatography to afford the corresponding products.

2.2 Stability on racemization of product 3ba

We investigated the racemization temperature of this axially chiral 6,6'-difluoro-2,2'-diphenyl-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione scaffold.



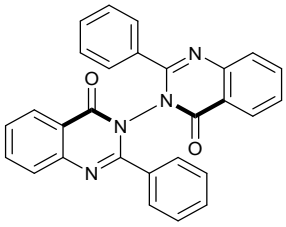
3ba, 92%ee

entry	T / (°C)	Time (h)	ee of recovered **3ba** (%)
1	80	12	92
2	90	12	92
3	100	12	91
4	110	12	92
5	120	12	91

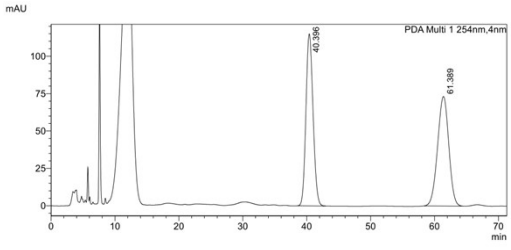
6	130	12	91
7	140	12	92
8	150	24	92

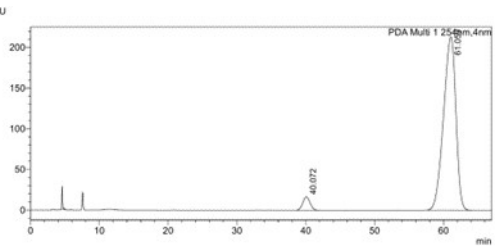
2.3 Characterization Data for the Products

(*S*)-2,2'-diphenyl-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3aa)



Flash column chromatography on silica gel gave the product (40.2 mg, 91% yield) as a white solid: M.p. 187-189 ℃; $[\alpha]_D^{25}$ = + 130.7 (c = 0.12 in $CHCl_3$, 96:4 e.r.); The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, λ = 254 nm, t (major) = 40.1min, t (minor) = 61 min; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.40 (d, *J* = 7.5 Hz, 2H), 7.82 (t, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.26−7.23 (m, 8H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.8, 154.0, 146.6, 135.5, 135.5, 132.2, 130.8, 130.8, 128.3, 128.3, 128.1, 127.8, 127.7, 120.8; HRMS (ESI) m/z calcd for $C_{28}H_{19}N_4O_2^+$ $(M+H)^+$ 443.1503, found 443.1501.





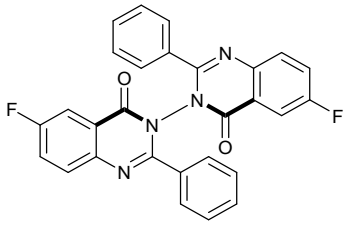
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	40.396	8868863	114966	49.914
2	61.389	8899351	73226	50.086
总计		17768214	188193	100.000

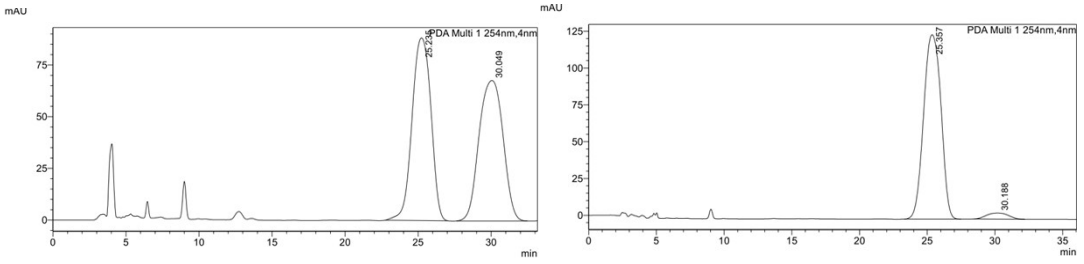
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	40.072	1229897	16514	4.420
2	61.059	26594982	213462	95.580
总计		27824879	229975	100.000

(*S*)-6,6'-difluoro-2,2'-diphenyl-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3ba)



Flash column chromatography on silica gel gave the product (28.7 mg, 60% yield) as a white solid: M.p. 205-206 °C; $[\alpha]_D^{25}$ = + 195.0 (c = 0.12 in $CHCl_3$, 96:4 e.r.); The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 25.4 min, t (minor) = 30.2 min; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.02 (d, *J* = 4.0 Hz, 2H), 7.72 (d, *J* = 4.5 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 5.0 Hz, 4H), 7.20(s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.3 (d, *J* = 250 Hz), 159.1, 159.0, 153.1, 153.1, 143.2, 131.8, 130.9, 130.7 (d, *J* = 8.7 Hz), 128.3, 128.1, 124.1 (d, *J* = 23.7 Hz), 122.1 (d, *J* = 8.7 Hz), 112.7 (d, *J* = 23.7 Hz); ^{19}F NMR (471 MHz $CDCl_3$) δ -110.5; HRMS (ESI) m/z calcd for $C_{28}H_{17}F_2N_4O_2^+$ $(M+H)^+$ 479.1314, found 479.1323.



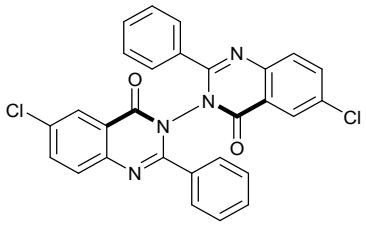
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	25.235	7939779	88324	50.551
2	30.049	7766703	67900	49.449
总计		15706482	156224	100.000

PDA Ch1 254nm

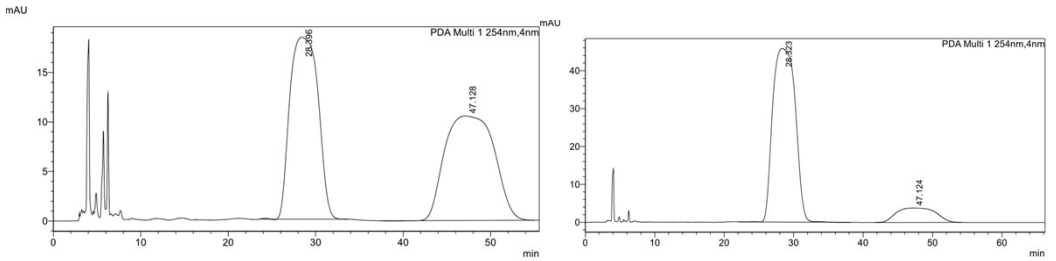
Peak#	Ret. Time	Area	Height	Area%
1	25.357	11165266	125249	96.057
2	30.188	458302	4093	3.943
总计		11623568	129342	100.000

(*S*)-6,6'-dichloro-2,2'-diphenyl-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3ca)



Flash column chromatography on silica gel gave the product (40.8 mg, 80% yield) as a white solid: M.p. 200-202 °C; $[\alpha]_D^{25}$ = + 61.3 (c = 0.14 in $CHCl_3$, 87:13 e.r.); The enantiomeric ratio was

determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 28..3 min, t (minor) = 47.1 min; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.33 (s, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 7.5Hz, 4H), 7.17(d, *J* = 7.5 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 154.0, 145.0, 136.0, 133.9, 131.7, 131.0, 129.8, 129.8, 128.4, 128.0, 126.9, 126.9, 121.7; HRMS (ESI) m/z calcd for $C_{28}H_{17}Cl_2N_4O_2^+$ $(M+H)^+$ 511.0723, found 511.0724.



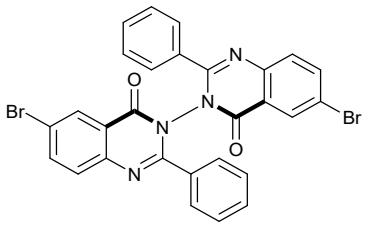
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	28.396	4136295	18380	49.819
2	47.128	4166294	10549	50.181
总计		8302589	28929	100.000

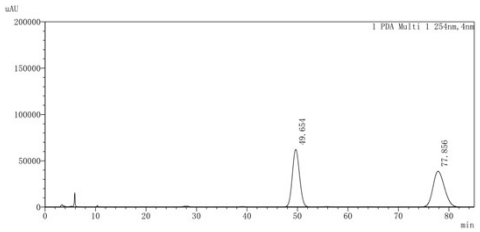
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	28.323	10368618	45829	87.382
2	47.124	1497291	3798	12.618
总计		11865909	49627	100.000

(*S*)-6,6'-dibromo-2,2'-diphenyl-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3da)



Flash column chromatography on silica gel gave the product (47.2 mg, 79% yield) as a white solid: M.p. 189-190 °C; $[\alpha]_D^{25}$ = + 96.3 (c = 0.19 in $CHCl_3$, 97:3 e.r.); The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 35.8 min, t (minor) = 58.9 min; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.50 (s, 2H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 4H), 7.17(d, *J* = 7.5 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.5, 154.1, 145.3, 138.8, 131.7, 131.1, 130.1, 130.0, 130.0, 128.4, 128.0, 128.0, 122.0, 121.6; HRMS (ESI) m/z calcd for $C_{28}H_{17}Br_2N_4O_2^+$ $(M+H)^+$ 598.9713, found 598.9724.



PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
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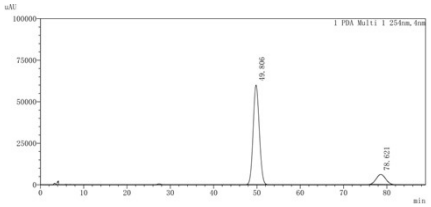
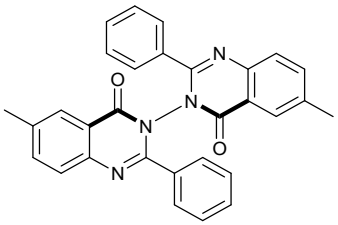
2	77.856	6041150	38504	49.668
总计		12163178	100546	100.000



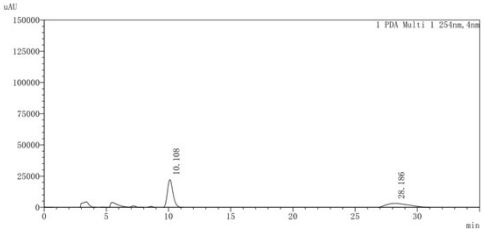
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	49.806	5911252	59908	86.816
2	78.621	897670	6016	13.184
总计		6808922	65924	100.000

(S)-6,6'-dimethyl-2,2'-diphenyl-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3ea)

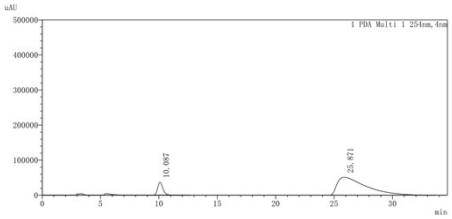


Flash column chromatography on silica gel gave the product (8.5 mg, 18% yield) as a white solid: M.p. 217-219 ^{o}C; $[\alpha]_D^{25}$ = + 52.5 (c = 0.16 in $CHCl_3$, 89:11 e.r.); The enantiomeric ratio was determined by Daicel Chiralcel OD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 25.9 min, t (minor) = 10.1 min; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.12 (s, 2H), 7.62 (s, 4H), 7.35 (s, 2H), 7.21 (s, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 153.2, 144.6, 138.2, 136.9, 136.9, 132.3, 130.6, 128.2, 128.2, 127.9, 127.9, 127.1, 120.6, 21.4; HRMS (ESI) m/z calcd for $C_{30}H_{23}N_4O_2^+$ $(M+H)^+$ 471.1816, found 471.1823.



PDA Ch1 254nm

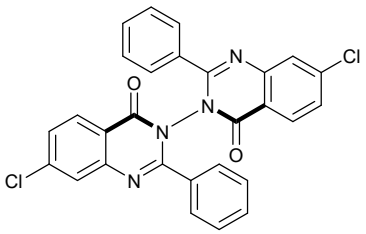
Peak#	Ret. Time	Area	Height	Area%
1	10.108	696603	22312	48.958
2	28.186	726249	4196	51.042
总计		1422852	26508	100.000



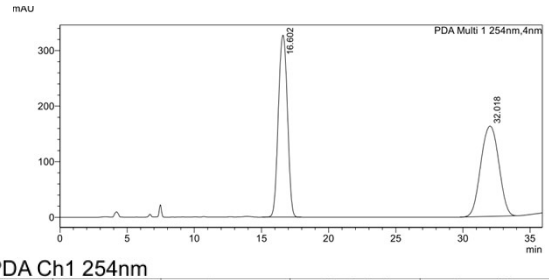
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	10.087	1170069	36862	11.200
2	25.871	9277089	52237	88.800
总计		10447158	89099	100.000

(*S*)-7,7'-dichloro-2,2'-diphenyl-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3fa)

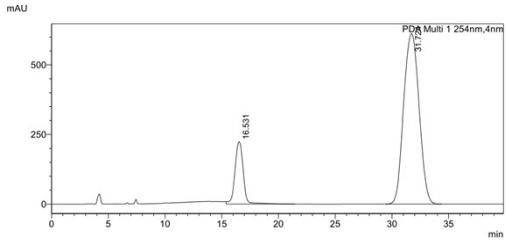


Flash column chromatography on silica gel gave the product (35.7 mg, 70% yield) as a white solid: M.p. 285-286 °C; $[\alpha]_D^{25}$ = + 208.3 (c = 0.14 in $CHCl_3$, 84:16 e.r.); The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 31.7 min, t (minor) = 16.5 min; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.32 (d, *J* = 8.5 Hz, 2H), 7.71 (s, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.25 (s, 4H), 7.18 (d, *J* = 7.5 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 155.1, 147.4, 142.0, 131.7, 131.1, 129.0, 128.5, 128.4, 128.4, 128.0, 127.9, 127.9, 119.1; HRMS (ESI) m/z calcd for $C_{28}H_{17}Cl_2N_4O_2^+$ $(M+H)^+$ 511.0723, found 511.0730.



PDA Ch1 254nm

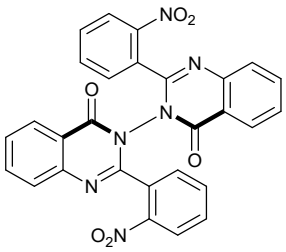
Peak#	Ret. Time	Area	Height	Area%
1	16.602	15383956	327569	50.318
2	32.018	15189670	162603	49.682
总计		30573626	490172	100.000



PDA Ch1 254nm

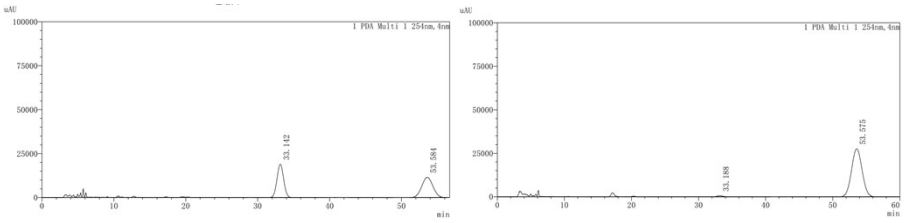
Peak#	Ret. Time	Area	Height	Area%
1	16.531	11400024	223401	16.456
2	31.724	57875472	612961	83.544
总计		69275495	836362	100.000

(*S*)-2-(6-nitrocyclohexa-2,4-dien-1-yl)-2'-(2-nitrophenyl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3ab)



Flash column chromatography on silica gel gave the product (16.2 mg, 30% yield) as a white solid: M.p. 243-245 °C; $[\alpha]_D^{25}$ = + 125.5 (c = 0.15 in $CHCl_3$, 99:1 e.r.); The enantiomeric ratio was

determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 53.6 min, t (minor) = 33.2 min ; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.40 (d, *J* = 8.0 Hz, 2H), 8.03 (d, *J* = 3.0 Hz, 2H), 7.87- 7.81 (m, 4H), 7.63-7.59 (m, 8H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.0, 150.7, 147.9, 146.2, 136.0, 133.5, 131.6, 128.8, 128.3, 128.3, 127.7, 127.6, 125.3, 120.8, HRMS (ESI) m/z calcd for $C_{28}H_{18}N_6O_6^+$ $(M+H)^+$ 535.1361, found 535.1351.



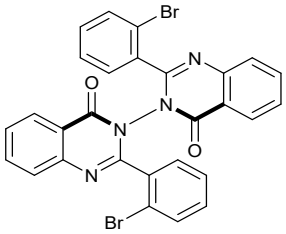
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	33.142	1223982	18953	49.793
2	53.584	1234168	11476	50.207
总计		2458150	30429	100.000

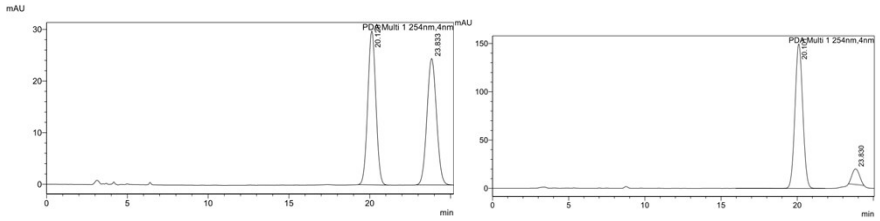
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	33.188	41019	664	1.352
2	53.575	2993412	27542	98.648
总计		3034430	28206	100.000

(*S*)-2,2'-bis(2-bromophenyl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3ac)



Flash column chromatography on silica gel gave the product (47.8 mg, 80% yield) as a white solid: M.p. 280-281 °C; $[\alpha]_D^{25}$ = + 344.3 (c = 0.12 in $CHCl_3$, 91:9 e.r.); The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 20.1 min, t (minor) = 23.8 min; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.41 (s, 2H), 7.86 (s, 2H), 7.79 (s, 2H), 7.66-7.56 (m, 6H), 7.18 (d, *J* = 20 Hz, 4H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 151.9, 146.0, 135.8, 134.9, 132.5, 131.6, 128.5, 128.3, 128.2, 127.7, 127.1, 124.3, 121.0, HRMS (ESI) m/z calcd for $C_{28}H_{17}Br_2N_4O_2^+$ $(M+H)^+$ 598.9713, found 598.9709.



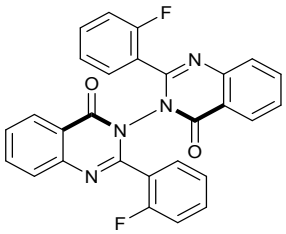
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	20.128	1037574	29781	50.686
2	23.833	1009489	24481	49.314
总计		2047064	54262	100.000

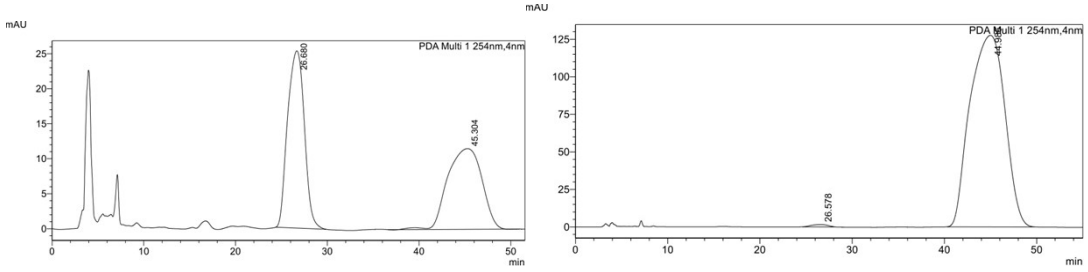
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	20.101	5320236	149591	90.704
2	23.830	545280	16237	9.296
总计		5865516	165829	100.000

(*S*)-2,2'-bis(2-fluorophenyl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3ad)



Flash column chromatography on silica gel gave the product (19.1 mg, 40% yield) as a white solid: M.p. 230-233 °C; $[\alpha]_D^{25}$ = + 94.3 (c = 0.11 in $CHCl_3$, 99:1 e.r.); The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 45.0 min, t (minor) = 26.6 min; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.40 (d, *J* = 8.0 Hz, 2H), 7.83 (t, *J* = 7.5 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 8.0 Hz, 2H), 7.40-7.34 (m, 4H), 7.09 (t, *J* = 9.5Hz, 2H), 6.99 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8 (d, *J* = 252.5 Hz), 159.7, 149.2, 146.2, 135.6, 132.8 (d, *J* = 7.5 Hz), 129.1, 128.3, 128.2, 127.6, 124.0 (d, *J* = 2.5 Hz), 121.0, 120.1 (d, *J* = 13.7 Hz), 116.7 (d, *J* = 22.5 Hz), ^{19}F NMR (471 MHz $CDCl_3$) δ -112.1; HRMS (ESI) m/z calcd for $C_{28}H_{17}F_2N_4O_2^+$ $(M+H)^+$ 479.1314, found 479.1323.



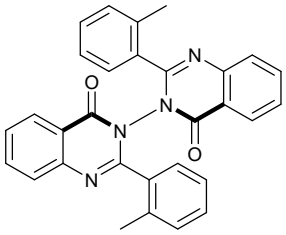
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	26.680	3219169	25325	51.711
2	45.304	3006174	11527	48.289
总计		6225343	36852	100.000

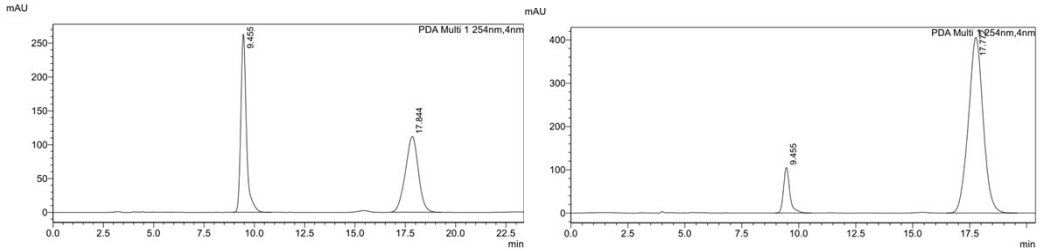
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	26.578	192395	1551	0.567
2	44.986	33712024	127610	99.433
总计		33904419	129161	100.000

(*S*)-2,2'-di-o-tolyl-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3ae)



Flash column chromatography on silica gel gave the product (24.0 mg, 51% yield) as a white solid: M.p. 262-263 °C; $[\alpha]_D^{25}$ = + 249 (c = 0.18 in $CHCl_3$, 90:10 e.r.); The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 17.8 min, t (minor) = 9.5min; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.44 (d, *J* = 8.0 Hz, 2H), 7.84 (t, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.59 (t, *J* = 8.0 Hz, 2H), 7.35 (s, 2H), 7.23-7.19 (m, 4H), 6.99 (t, *J* = 7.5 Hz, 2H), 1.58(s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 146.2, 138.4, 135.5, 131.6, 131.1, 130.3, 128.0, 128.0, 127.8, 127.7, 127.0, 125.6, 120.9, 19.4; HRMS (ESI) m/z calcd for $C_{30}H_{22}N_4O_2^+$ $(M+H)^+$ 471.1816, found 471.1807.



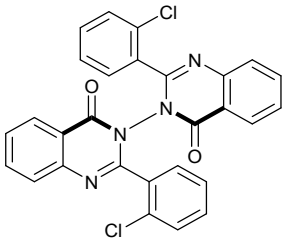
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	9.455	5061146	263043	50.084
2	17.844	5044095	111870	49.916
总计		10105241	374913	100.000

PDA Ch1 254nm

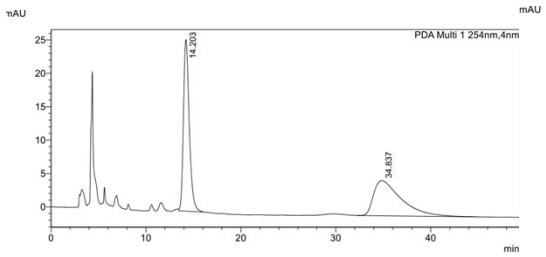
Peak#	Ret. Time	Area	Height	Area%
1	9.455	2028102	105315	9.959
2	17.772	18337161	405999	90.041
总计		20365262	511314	100.000

(*S*)-2,2'-bis(2-chlorophenyl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3af)



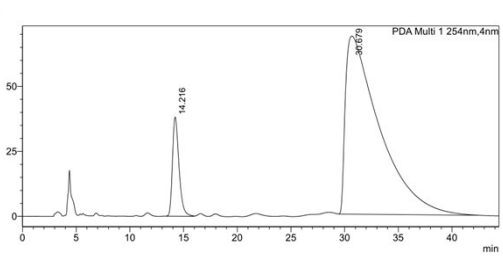
Flash column chromatography on silica gel gave the product (15.8 mg, 31% yield) as a white solid: M.p. 259-261 °C; $[\alpha]_D^{25}$ = + 145.4 (c = 0.15 in $CHCl_3$, 90:10 e.r.); The enantiomeric ratio was

determined by Daicel Chiralcel OD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 30.7 min, t (minor) = 14.2min; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.41 (d, *J* = 8.0 Hz, 2H), 7.86 (t, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 2H), 7.54 (s, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.11(t, *J* = 8.0 Hz 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6, 150.9, 146.1, 135.8, 134.4, 131.5, 131.3, 131.3, 130.6, 128.3, 128.2, 127.7, 126.5, 121.0; HRMS (ESI) m/z calcd for $C_{28}H_{16}Cl_2N_4O_2^+$ $(M+H)^+$ 511.0723, found 511.0714.



PDA Ch1 254nm

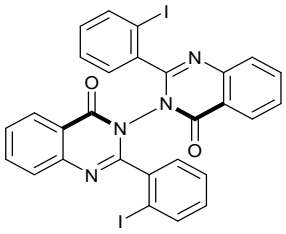
Peak#	Ret. Time	Area	Height	Area%
1	14.203	1094307	25711	50.513
2	34.837	1072100	5269	49.487
总计		2166406	30981	100.000



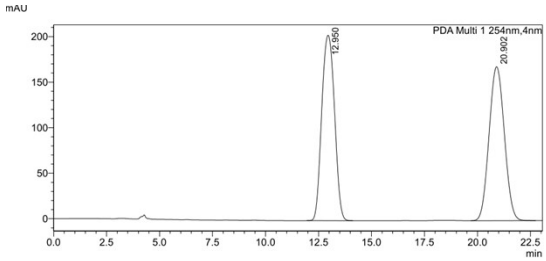
PDA Ch1 254nm

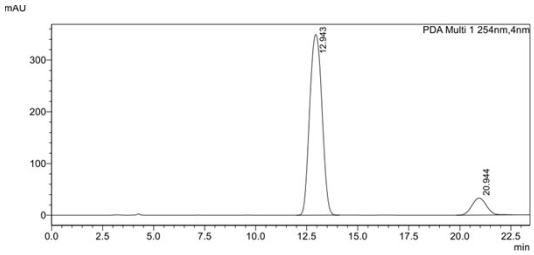
Peak#	Ret. Time	Area	Height	Area%
1	14.216	1612448	38124	9.610
2	30.679	15165811	68510	90.390
总计		16778259	106633	100.000

(*S*)-2,2'-bis(2-iodophenyl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3ag)



Flash column chromatography on silica gel gave the product (34.7 mg, 50% yield) as a white solid: M.p. 270-272 °C; $[\alpha]_D^{25}$ = + 174.1 (c = 0.14 in $CHCl_3$, 90:10 e.r.); The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 12.9 min, t (minor) = 20.9min; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.43 (d, *J* = 6.5 Hz, 2H), 7.99 (d, *J* = 7.5 Hz, 2H), 7.88 (t, *J* = 7.5 Hz, 2H), 7.81 (t, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.5Hz, 2H), 7.56 (s, 2H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.03 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.8, 153.5, 146.0, 142.0, 135.9, 135.9, 131.7, 128.3, 128.2, 128.0, 128.0, 127.7, 121.0, 99.5; HRMS (ESI) m/z calcd for $C_{28}H_{16}I_2N_4O_2^+$ $(M+H)^+$ 694.9435, found 694.9432.





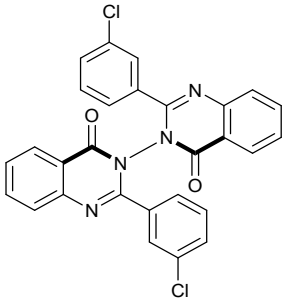
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	12.950	8544109	203607	50.193
2	20.902	8478533	169033	49.807
总计		17022642	372640	100.000

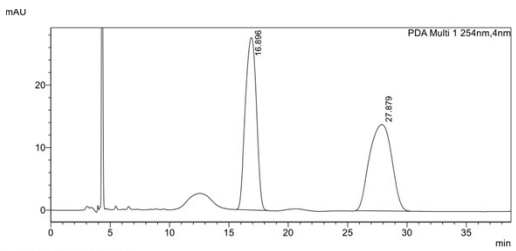
PDA Ch1 254nm

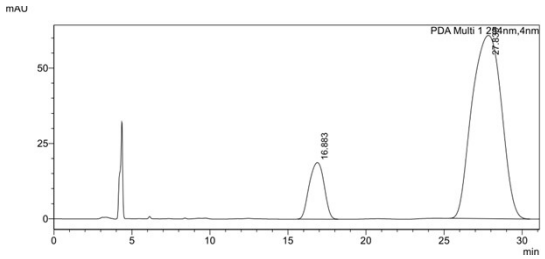
Peak#	Ret. Time	Area	Height	Area%
1	12.943	14662066	349297	89.874
2	20.944	1651944	32922	10.126
总计		16314011	382219	100.000

(*S*)-2,2'-bis(3-chlorophenyl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3ah)



Flash column chromatography on silica gel gave the product (28.1 mg, 55% yield) as a white solid: M.p. 217-220 °C; $[\alpha]_D^{25}$ = + 140.1 (c = 0.13 in $CHCl_3$, 87:13 e.r.); The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 27.8 min, t (minor) = 16.9 min; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.48 (d, *J* = 8.5 Hz, 2H), 7.93 (t, *J* = 8.0 Hz, 2H), 7.80 (t, *J* = 8.0 Hz, 2H), 7.68 (t, *J* = 8.5 Hz, 2H), 7.46 (s, 2H), 7.33 (s, 2H), 7.25 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 152.4, 146.3, 135.8, 134.6, 133.6, 131.1, 129.6, 128.8, 128.3, 128.3, 127.7 125.7, 120.8; HRMS (ESI) m/z calcd for $C_{28}H_{17}Cl_2N_4O_2^+$ $(M+H)^+$ 511.0723, found 511.0717.





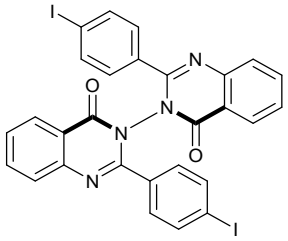
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	16.896	1790954	27589	49.945
2	27.879	1794903	13816	50.055
总计		3585857	41405	100.000

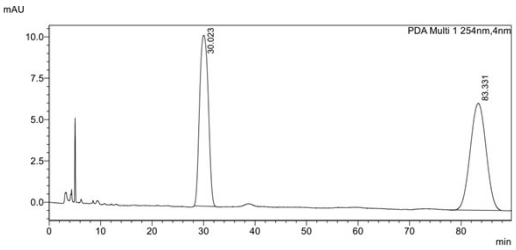
PDA Ch1 254nm

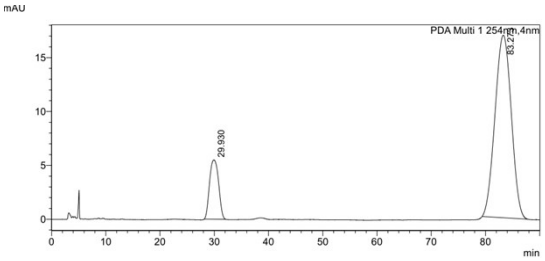
Peak#	Ret. Time	Area	Height	Area%
1	16.883	1240309	18777	13.404
2	27.839	8012917	60797	86.596
总计		9253226	79574	100.000

(*S*)-2,2'-bis(4-iodophenyl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3ai)



Flash column chromatography on silica gel gave the product (43.7 mg, 63% yield) as a white solid: M.p. 277-279 °C; $[\alpha]_D^{25}$ = + 235.9 (c = 0.16 in $CHCl_3$, 85:15 e.r.); The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 83.3 min, t (minor) = 30.0 min; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.38 (d, *J* = 8.0 Hz, 2H), 7.86 (t, *J* = 7.5 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 6H), 6.98 (d, *J* = 8.0 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 152.9, 146.4, 137.6, 137.6, 135.8, 131.7, 129.6, 129.6, 128.4, 128.2, 127.7, 120.7, 97.8; HRMS (ESI) m/z calcd for $C_{28}H_{17}I_2N_4O_2^+$ $(M+H)^+$ 694.9435, found 694.9434.





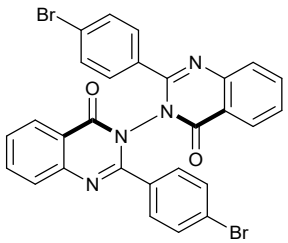
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	30.023	1210802	10342	46.740
2	83.331	1379717	6470	53.260
总计		2590520	16812	100.000

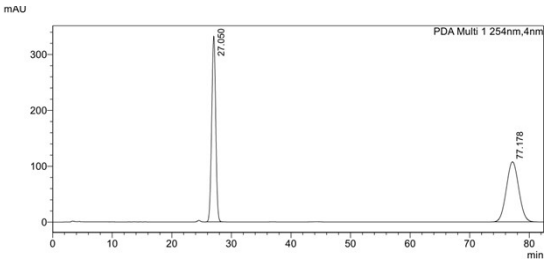
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	29.930	635760	5493	15.248
2	83.273	3533734	16939	84.752
总计		4169494	22432	100.000

(*S*)-2,2'-bis(4-bromophenyl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3aj)

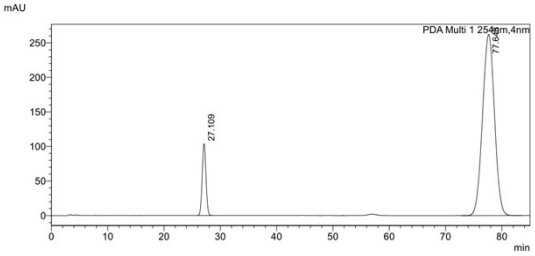


Flash column chromatography on silica gel gave the product (54.4 mg, 91% yield) as a white solid: M.p. 255-258 °C; $[\alpha]_D^{25}$ = + 88.5 (c = 0.14 in $CHCl_3$, 89:11 e.r.); The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 72.0 min, t (minor) = 25.6 min; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.38 (d, *J* = 7.5 Hz, 2H), 7.85 (t, *J* = 7.5 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 2H), 7.40 (d, *J* = 7.5, 4H), 7.13 (d, J = 7.5 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 152.8, 146.4, 135.8, 131.7, 131.7, 131.1, 129.7, 129.7, 128.3, 128.2, 127.7, 125.6, 120.7; HRMS (ESI) m/z calcd for $C_{28}H_{17}Br_2N_4O_2^+$ $(M+H)^+$ 598.9713, found 598.9706.



PDA Ch1 254nm

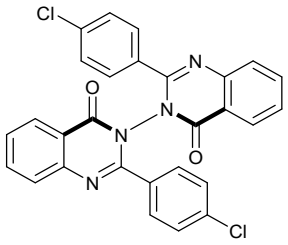
Peak#	Ret. Time	Area	Height	Area%
1	27.050	15571028	332616	50.027
2	77.178	15554513	107591	49.973
总计		31125541	440207	100.000



PDA Ch1 254nm

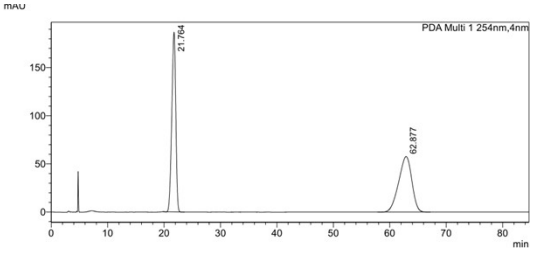
Peak#	Ret. Time	Area	Height	Area%
1	27.109	4867565	103922	11.175
2	77.648	38688408	262148	88.825
总计		43555972	366069	100.000

(*S*)-2,2'-bis(4-chlorophenyl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3ak)



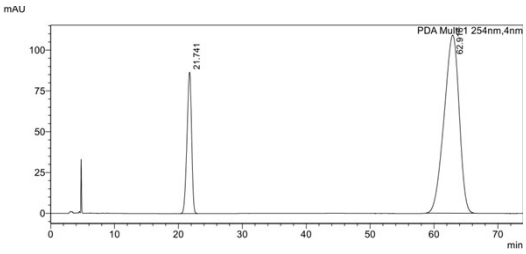
Flash column chromatography on silica gel gave the product (47.9 mg, 94% yield) as a white solid: M.p. 225-226 °C; $[\alpha]_D^{25}$ = + 71.9 (c = 0.16 in $CHCl_3$, 80:20 e.r.); The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 62.9 min, t (minor) = 21.7 min; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.41 (d, *J* = 8.0 Hz, 2H), 7.88 (t, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 4.5 Hz, 4H), 7.22 (d, *J* = 8.0 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 152.7, 146.4, 137.2, 135.8, 130.6, 130.6, 129.5, 129.5, 128.7, 128.3, 128.2, 127.7, 120.7; HRMS (ESI) m/z calcd for

$C_{28}H_{17}Cl_2N_4O_2^+$ $(M+H)^+$ 511.0723, found 511.0728.



PDA Ch1 254nm

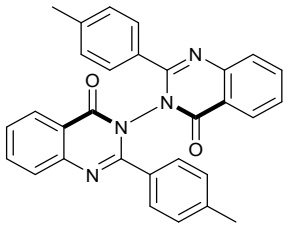
Peak#	Ret. Time	Area	Height	Area%
1	21.764	9203100	186644	49.646
2	62.877	9334511	57751	50.354
总计		18537611	244395	100.000



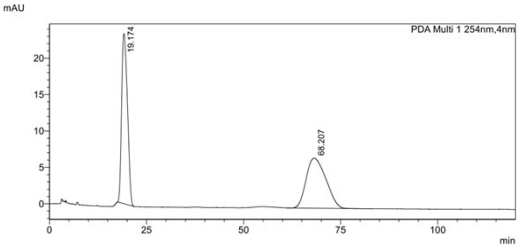
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	21.741	4325471	86634	19.502
2	62.918	17853990	109100	80.498
总计		22179461	195734	100.000

(*S*)-2,2'-di-p-tolyl-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3al)

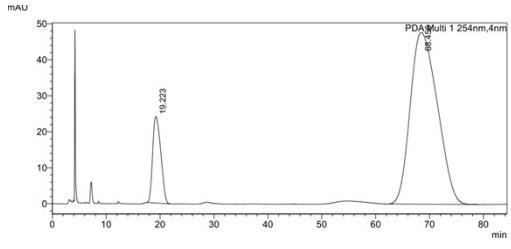


Flash column chromatography on silica gel gave the product (21.2 mg, 45% yield) as a white solid: M.p. 219-220 °C; $[\alpha]_D^{25}$ = + 135.9 (c = 0.20 in $CHCl_3$, 87:13 e.r.); The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 68.5 min, t (minor) = 19.2 min; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.39 (d, *J* = 7.5 Hz, 2H), 7.81 (t, *J* = 7.5 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.56 (t, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 4H), 7.03 (d, *J* = 8.0 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 154.2, 146.7, 141.0, 135.4, 129.4, 128.9, 128.9, 128.1, 128.1, 128.1, 127.7, 127.6, 120.8, 21.4; HRMS (ESI) m/z calcd for $C_{30}H_{23}N_4O_2^+$ $(M+H)^+$ 471.1816, found 471.1824.



PDA Ch1 254nm

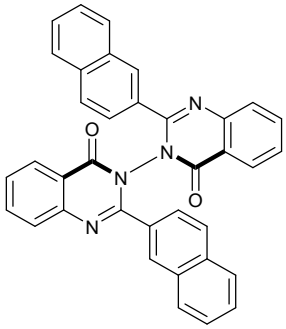
Peak#	Ret. Time	Area	Height	Area%
1	19.174	2435725	23341	50.062
2	68.207	2429677	6885	49.938
总计		4865402	30225	100.000



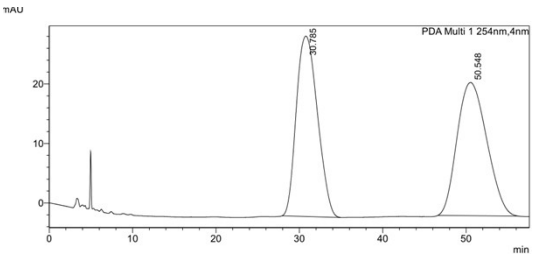
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	19.223	2515860	24027	13.100
2	68.456	16689794	47704	86.900
总计		19205653	71731	100.000

(*S*)-2,2'-di(naphthalen-2-yl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3am)

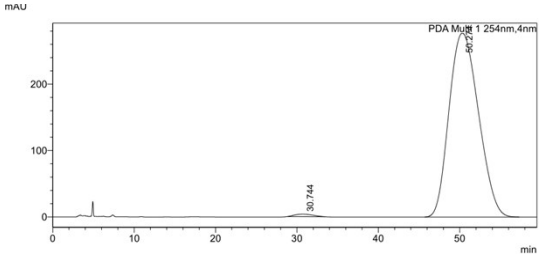


Flash column chromatography on silica gel gave the product (27.1 mg, 50% yield) as a white solid: M.p. 260-263 °C; $[\alpha]_D^{25}$ = + 58.8 (c = 0.15 in $CHCl_3$, 99:1 e.r.); The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 50.3 min, t (minor) = 30.7 min; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.48 (d, *J* = 8.0 Hz, 2H), 7.81 (t, *J* = 8.5 Hz, 4H), 7.67 (t, *J* = 7.5 Hz, 4H), 7.62-7.48 (m, 10H), 7.29 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0, 153.9, 146.6, 135.5, 133.9, 132.3, 129.5, 129.2, 128.6, 128.2, 128.2, 128.0, 127.9, 127.7, 127.7, 126.9, 124.0, 120.9; HRMS (ESI) m/z calcd for $C_{36}H_{23}N_4O_2^+$ $(M+H)^+$ 543.1816, found 543.1819.



PDA Ch1 254nm

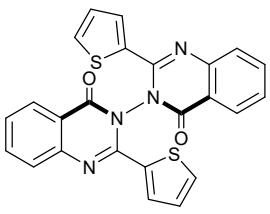
Peak#	Ret. Time	Area	Height	Area%
1	30.785	5371786	30345	49.167
2	50.548	5553837	22393	50.833
总计		10925623	52738	100.000



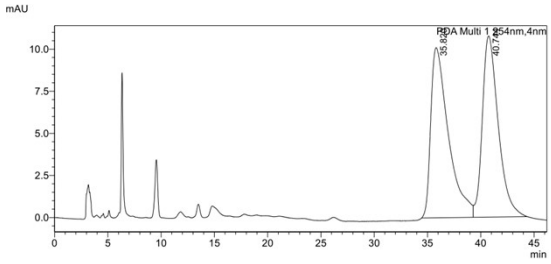
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	30.744	588508	3744	0.837
2	50.274	69693956	276761	99.163
总计		70282464	280505	100.000

(*S*)-2,2'-di(thiophen-2-yl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3an)

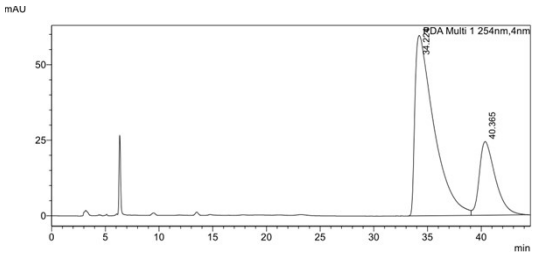


Flash column chromatography on silica gel gave the product (18.2 mg, 40% yield) as a white solid: M.p. 270-272 °C; $[\alpha]_D^{25}$ = + 118.3 (c = 0.18 in $CHCl_3$, 75:25 e.r.); The enantiomeric ratio was determined by Daicel Chiralcel OD-H (0.46 cm × 25 cm), Hexanes/IPA = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 34.2 min, t (minor) = 40.4 min; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.24 (d, *J* = 8.0 Hz, 2H), 7.86 (s, 4H), 7.50 (d, *J* = 17.5 Hz, 4H), 7.42 (s, 2H), 6.94 (t, *J* = 4.5, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 148.4, 147.1, 135.7, 134.1, 131.6, 131.1, 128.2, 128.1, 127.8, 127.4, 120.6; HRMS (ESI) m/z calcd for $C_{24}H_{15}N_4O_2S_2^+$ $(M+H)^+$ 455.0631, found 455.0638.



PDA Ch1 254nm

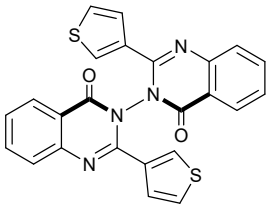
Peak#	Ret. Time	Area	Height	Area%
1	35.820	1162929	10102	50.986
2	40.744	1117956	10752	49.014
总计		2280885	20854	100.000



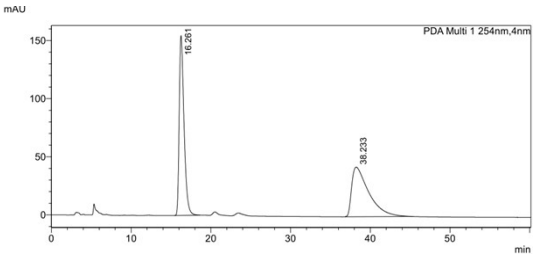
PDA Ch1 254nm

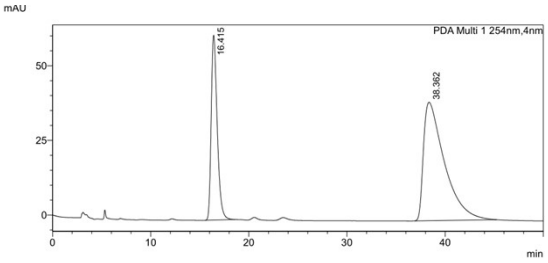
Peak#	Ret. Time	Area	Height	Area%
1	34.224	7405596	59671	74.523
2	40.365	2531763	24384	25.477
总计		9937359	84055	100.000

(S)-2,2'-di(thiophen-3-yl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3ao)



Flash column chromatography on silica gel gave the product (13.6 mg, 30% yield) as a white solid: M.p. 247-249 °C; $[\alpha]_D^{25}$ = + 84.2 (c = 0.16 in $CHCl_3$, 69:31 e.r.); The enantiomeric ratio was determined by Daicel Chiralcel OD-H (0.46 cm × 25 cm), Hexanes/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 38.4 min, t (minor) = 16.4 min; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.30 (d, *J* = 7.5 Hz, 2H), 7.85 (t, *J* = 7.5 Hz, 2H), 7.79 (d, *J* = 9.0 Hz, 2H), 7.55 (t, *J* = 6.5 Hz, 2H), 7.50 (s, 2H), 7.23(s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 149.8, 146.9, 135.6, 132.8, 128.5, 128.2, 127.7, 127.7, 127.6, 126.5, 120.7; HRMS (ESI) m/z calcd for $C_{24}H_{15}N_4O_2S_2^+$ $(M+H)^+$ 455.0631, found 455.0632.





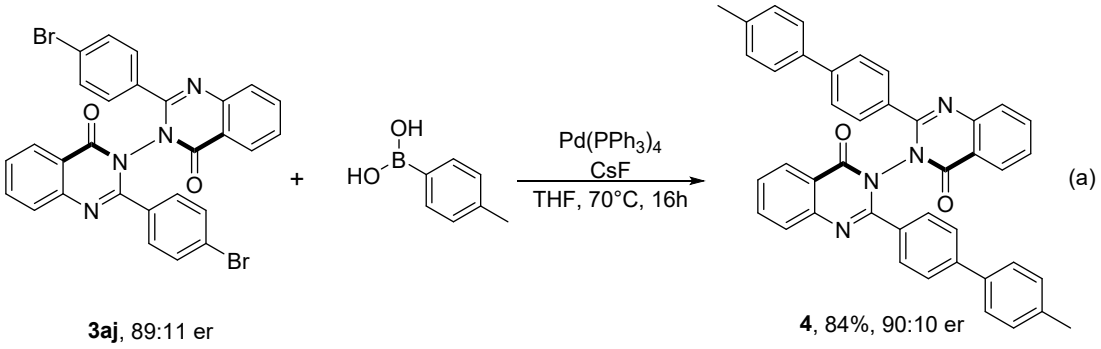
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	16.261	6526259	154708	50.560
2	38.233	6381667	42713	49.440
总计		12907927	197421	100.000

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	16.415	2627731	61877	30.849
2	38.362	5890371	39650	69.151
总计		8518102	101527	100.000

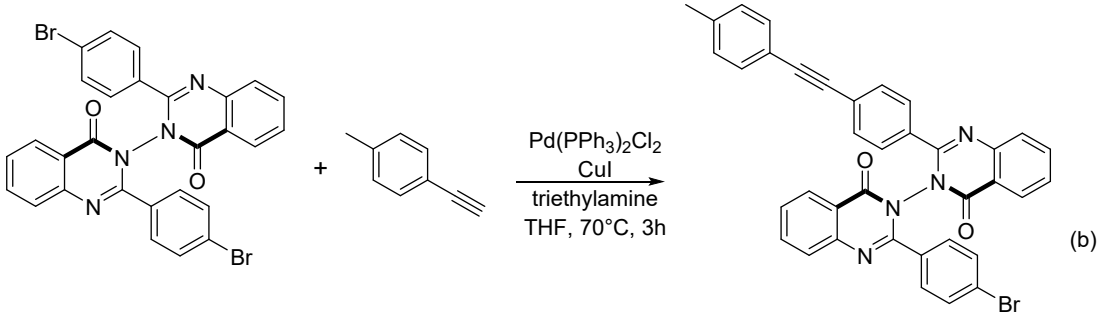
3. Synthetic applications



3aj, 89:11 er

4, 84%, 90:10 er

A dried 25 mL Schlenk tube was charged with **3aj** (0.20 mmol, 119.8 mg), *p*-tolylboronic acid (0.5 mmol, 68 mg) and $Pd(PPh_3)_4$ (0.02 mmol, 23.1 mg), CsF (0.8 mmol, 121.5 mg), 4 mL of THF added by syringe. The reaction tube was vacuumed and refilled with Ar for 3 times, and was placed in 70 ^oC oil-bath for 16 h. The crude reaction mixture was concentrated in vacuo and the residue was purified by silica gel flash column chromatography to afford the corresponding products **4**.

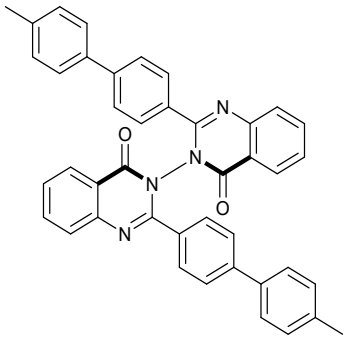


3aj, 89:11 er

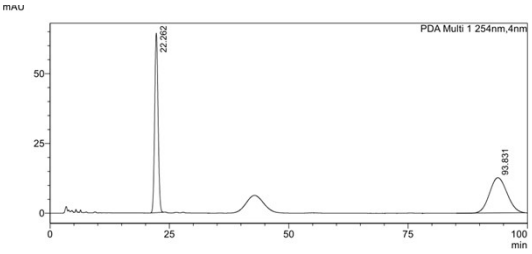
5, 49%, 87:13 er

A dried 25 mL Schlenk tube was charged with **3aj** (0.20 mmol, 119.8mg), 4-methyl phenylacetylene (0.3 mmol, 38 μL), CuI (0.02mmol, 3.8 mg) and $Pd(PPh_3)_2Cl_2$ (0.02 mmol, 14 mg), triethylamine(0.8 mmol, 111 μL), 4 mL of THF added by syringe. The reaction tube was vacuumed and refilled with Ar for 3 times, and was placed in 70 ^oC oil-bath for 3 h. The crude reaction mixture was concentrated in vacuo and the residue was purified by silica gel flash column chromatography to afford the corresponding products **5**.

(*S*)-2,2'-bis(4'-methyl-[1,1'-biphenyl]-4-yl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (4)

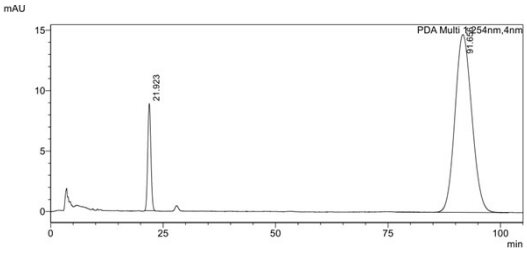


Flash column chromatography on silica gel gave the product (104.5 mg, 84% yield) as a white solid: M.p. 250-251 °C; $[\alpha]_D^{25}$ = + 91.8 (c = 0.13 in $CHCl_3$, 90:10 e.r.); The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 91.7 min, t (minor) = 21.9 min; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.42 (s, 2H), 7.83 (s, 2H), 7.74 (s, 2H), 7.58 (s, 2H), 7.45 (d, *J* = 16.5 Hz, 8H), 7.34 (s, 4H), 7.23 (s, 4H), 2.38 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 153.9, 146.7, 143.4, 138.1, 136.7, 135.5, 130.7, 129.6, 128.7, 128.2, 127.8, 127.7, 126.9, 126.6, 120.8, 21.1; HRMS (ESI) m/z calcd for $C_{42}H_{31}N_4O_2^+$ $(M+H)^+$ 623.2442, found 623.2452.



PDA Ch1 254nm

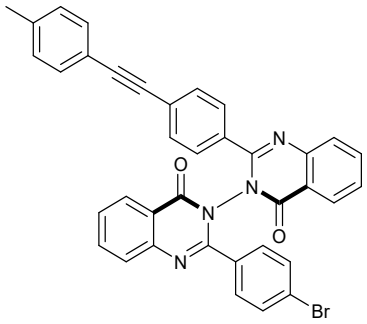
Peak#	Ret. Time	Area	Height	Area%
1	22.262	3165458	64271	49.605
2	93.831	3215903	12599	50.395
总计		6381361	76870	100.000



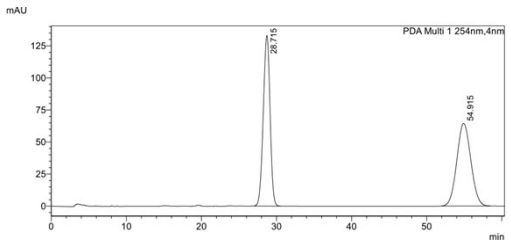
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	21.923	433018	8852	10.172
2	91.656	3823732	14700	89.828
总计		4256750	23552	100.000

(*S*)-2-(4-bromophenyl)-2'-(4-(p-tolylethynyl)phenyl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (5)

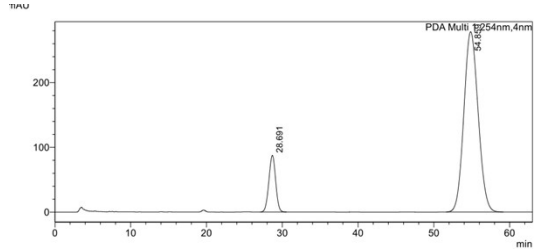


Flash column chromatography on silica gel gave the product (62.1 mg, 49% yield) as a white solid: M.p. 220-223 °C; $[\alpha]_D^{25}$ = + 87.8 (c = 0.15 in $CHCl_3$, 87:13 e.r.); The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 54.9 min, t (minor) = 28.7 min; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.39 (d, *J* = 7.5 Hz, 2H), 7.84 (t, *J* = 7.5 Hz, 2H), 7.76-7.70 (m, 2H), 7.60 (t, *J* = 7.5 Hz, 2H), 7.39 (s, 6H), 7.22 (d, *J* = 7.5 Hz, 2H), 7.13 (t, *J* = 10.5 Hz, 4H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 159.6, 153.1, 152.8, 146.5, 146.4, 139.1, 135.7, 135.7, 131.6, 131.5, 131.3, 131.3, 131.3, 131.1, 129.7, 129.2, 128.3, 128.1, 128.1, 127.7, 126.3, 125.6, 120.7, 120.6, 119.3, 92.4, 87.6, 21.5; HRMS (ESI) m/z calcd for $C_{37}H_{24}BrN_4O_2^+$ $(M+H)^+$ 635.1077, found 635.1082.



PDA Ch1 254nm

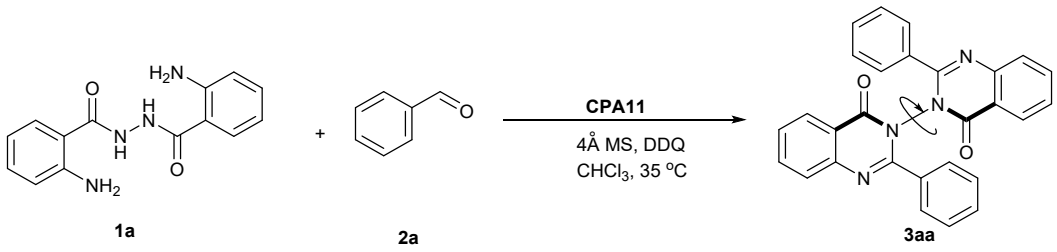
Peak#	Ret. Time	Area	Height	Area%
1	28.715	8329884	133071	49.943
2	54.915	8348803	64464	50.057
总计		16678688	197535	100.000



PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	28.691	5451723	87470	13.000
2	54.859	36483786	278374	87.000
总计		41935509	365845	100.000

4. One-mmol-scale synthesis of compound 3aa

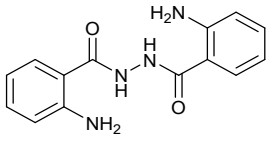


An oven-dried 100 mL Schlenk tube charged with **1a** (1 mmol), **CPA11** (0.1 mmol, 61 mg), and DDQ (2.8 mmol, 635 mg), 4Å MS (1000 mg), 10 mL of $CHCl_3$ added by syringe and benzaldehyde (2 mmol, 200 μL) added by pipette. After 24 h, **2a** (2 mmol) was added to the reaction mixture. After 36 h, **2a** (2 mmol) was added to the reaction mixture. After 48 h, **2a** (2 mmol) was added to the reaction mixture. Then, the tube was vacuumed and refilled with Ar for 3 times and was placed in 35 °C oil-bath for 60 h. The crude reaction mixture was concentrated in vacuo and the residue was purified by silica gel flash column chromatography to afford the corresponding products.

5. Synthesis of Substrates

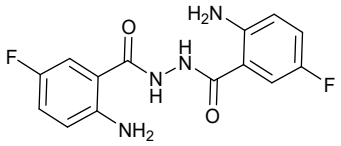
To an efficiently stirred suspension of isatoic anhydride in 1,4-dioxane was added hydrazine monohydrate and the mixture heated at reflux for16 h. The crude reaction mixture was concentrated in vacuo and the residue was purified by silica gel flash column chromatography to afford the corresponding products **1a-1f**.

2-amino-*N*'-(2-aminobenzoyl)benzohydrazide (1a)



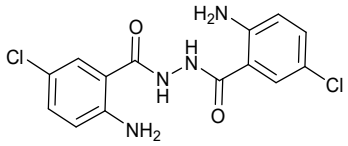
Flash column chromatography on silica gel gave the product (1.08 g, 80% yield) as a white solid: M.p. 210-212 °C; ^{1}H NMR ($DMSO_{d\text{-}6}$, 500 MHz) δ 10.04 (s, 2H), 7.61 (t, J = 5.5 Hz, 2H), 7.19 (t, J = 8.0 Hz, 2H), 6.74 (d, J = 8.0 Hz, 2H), 6.55 (t, J = 7.5 Hz 2H), 6.42 (s, 4H); ^{13}C NMR (125 MHz, $DMSO_{d\text{-}6}$) δ 168.6, 145.0, 132.4, 128.3, 116.5, 114.8, 112.8; HRMS (ESI) m/z calcd for $C_{14}H_{15}N_4O_2^+$ $(M+H)^+$ 271.1190, found 271.1182.

2-amino-N'-(2-amino-5-fluorobenzoyl)-5-fluorobenzohydrazide (1b)



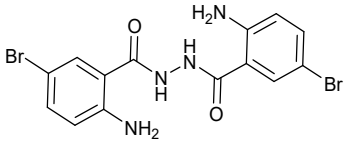
Flash column chromatography on silica gel gave the product (428 mg, 70% yield) as a white solid: M.p. 226-229 °C; ^{1}H NMR ($DMSO_{d-6}$, 500 MHz) δ 10.18 (s, 2H), 7.44 (d, *J* = 9.5 Hz 2H), 7.12 (s, 2H), 6.77 (s, 2H), 6.32 (s, 4H); ^{13}C NMR (125 MHz, $DMSO_{d-6}$) δ 167.5, 152.6 (d, *J* = 230 Hz), 146.8, 120.1 (d, *J* = 22.5 Hz), 117.9 (d, *J* = 7.5 Hz), 113.5 (d, *J* = 22.5 Hz), 112.0 (d, *J* = 5.0 Hz); ^{19}F NMR (471 MHz $DMSO_{d-6}$) δ -129.7; RMS (ESI) m/z calcd for $C_{14}H_{13}F_2N_4O_2^{+}$ $(M+H)^+$ 307.1001, found 307.1009.

2-amino-*N*'-(2-amino-5-chlorobenzoyl)-5-chlorobenzohydrazide (1c)



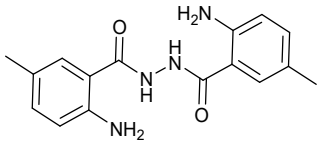
Flash column chromatography on silica gel gave the product (473.2 mg, 70% yield) as a white solid: M.p. 255-258 °C; ^{1}H NMR ($DMSO_{d-6}$, 500 MHz) δ 10.22 (s, 2H), 7.65 (s, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.73 (d, *J* = 9.0 Hz, 2H), 6.55 (s, 4H); ^{13}C NMR (125 MHz, $DMSO_{d-6}$) δ 167.3, 148.8, 132.2, 127.5, 118.2, 117.8, 113.2; HRMS (ESI) m/z calcd for $C_{14}H_{13}Cl_2N_4O_2^{+}$ $(M+H)^+$ 339.0410, found 339.0419.

2-amino-*N*'-(2-amino-5-bromobenzoyl)-5-bromobenzohydrazide (1d)



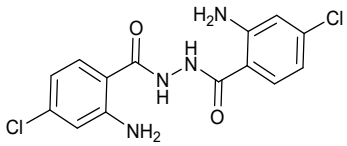
Flash column chromatography on silica gel gave the product (707.0 mg, 83% yield) as a white solid: M.p. 239-240 °C; ^{1}H NMR ($DMSO_{d-6}$, 500 MHz) δ 10.23 (s, 2H), 7.76 (s, 2H), 7.33 (d, *J* = 9.0 Hz, 2H), 6.72 (d, *J* = 9.0 Hz, 2H), 6.57 (s, 4H); ^{13}C NMR (125 MHz, $DMSO_{d-6}$) δ 167.2, 149.1, 134.8, 130.3, 118.6, 113.9, 104.9; HRMS (ESI) m/z calcd for $C_{14}H_{13}Br_2N_4O_2^{+}$ $(M+H)^+$ 426.9400, found 426.9407.

2-amino-*N*'-(2-amino-5-methylbenzoyl)-5-methylbenzohydrazide (1e)



Flash column chromatography on silica gel gave the product (298.1 mg, 50% yield) as a white solid: M.p. 236-239 ^{o}C; ^{1}H NMR ($DMSO_{d-6}$, 500 MHz) δ 9.98 (s, 2H), 7.44 (s, 2H), 7.24 (d, J = 8.5 Hz, 2H), 6.65 (d, J = 8.0 Hz, 2H), 6.18 (s, 4H), 2.18 (s, 6H); ^{13}C NMR (125 MHz, $DMSO_{d-6}$) δ 168.5, 147.6, 133.1, 128.2, 123.0, 116.5, 112.8, 20.0; HRMS (ESI) m/z calcd for $C_{16}H_{19}N_4O_2^+$ $(M+H)^+$ 299.1503, found 299.1495.

2-amino-*N*'-(2-amino-4-chlorobenzoyl)-4-chlorobenzohydrazide (1f)



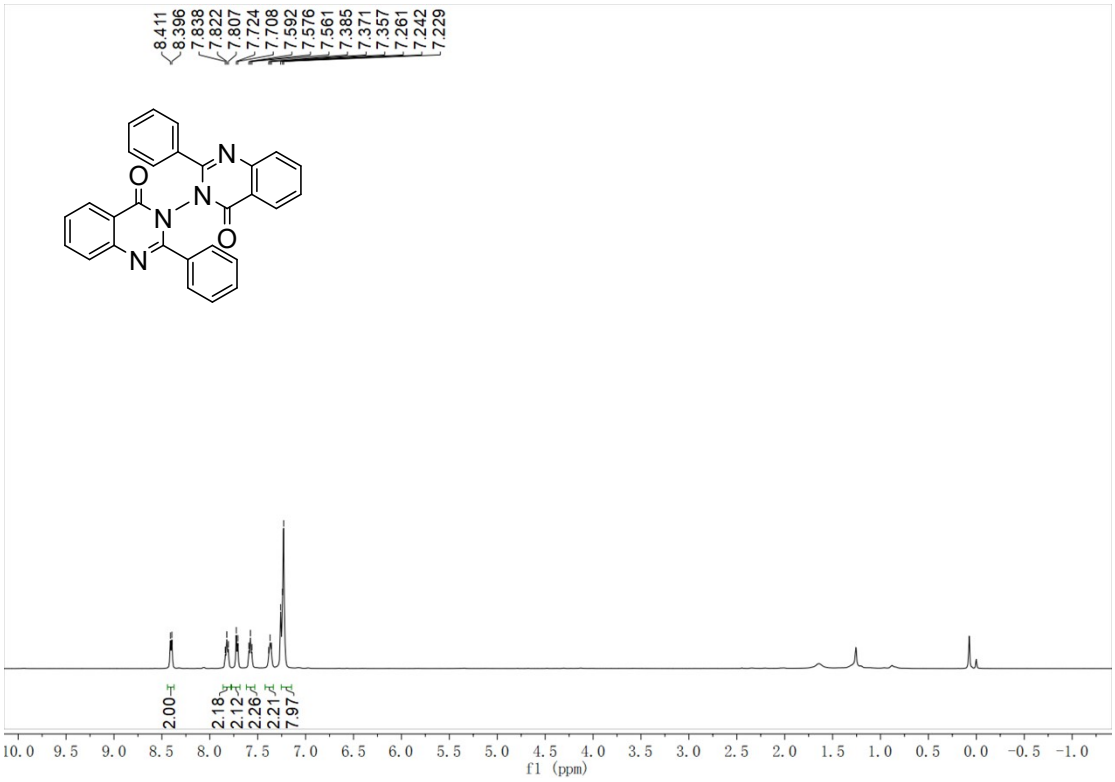
Flash column chromatography on silica gel gave the product (60% yield) as a white solid: mp 274.7-276.1^{o}C; ^{1}H NMR (DMSO, 500 MHz) δ 10.15 (s, 2H), 7.60 (d, J = 8.0 Hz, 2H), 6.81 (s, 2H), 6.68 (s, 4H), 6.57 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.1, 151.6, 137.3, 130.5, 115.6, 114.8, 111.7; HRMS (ESI) m/z calcd for $C_{14}H_{13}Cl_2N_4O_2^+$ $(M+H)^+$ 339.0410, found 339.0401.

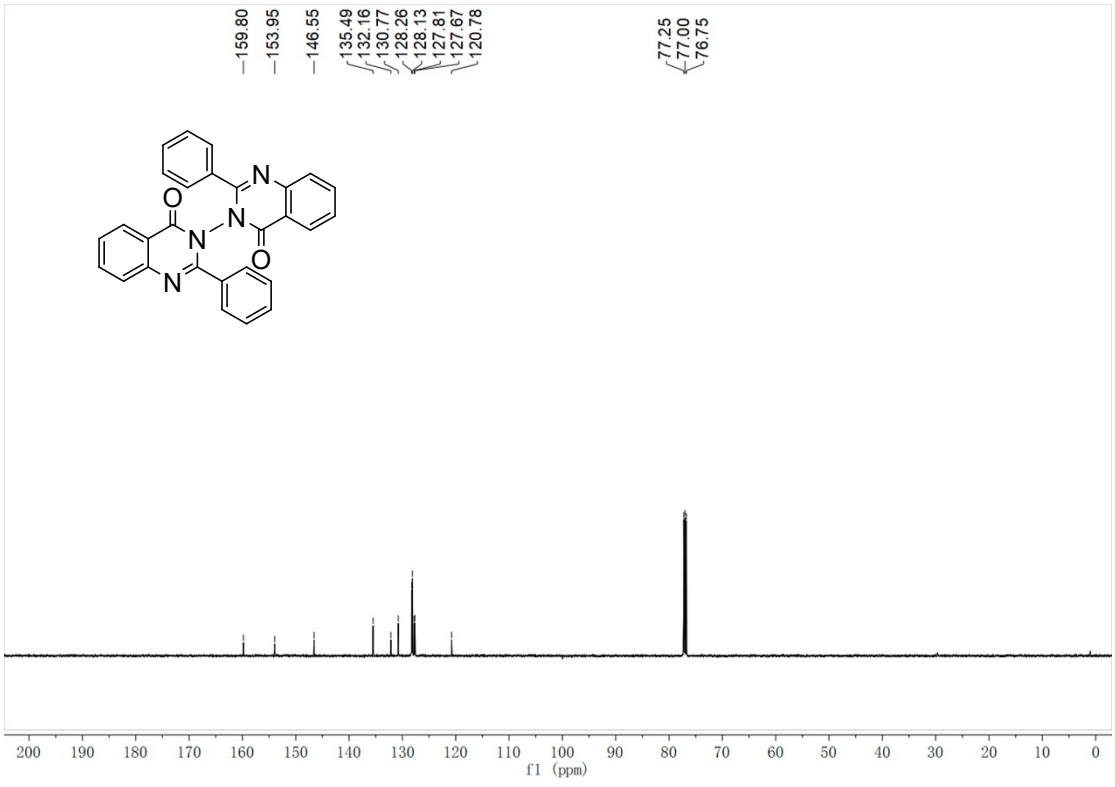
6. References

1 M. P. Coogan and S. C. Passey J. Chem. Soc., Perkin Trans. 2, **2000**, 2060-2066.

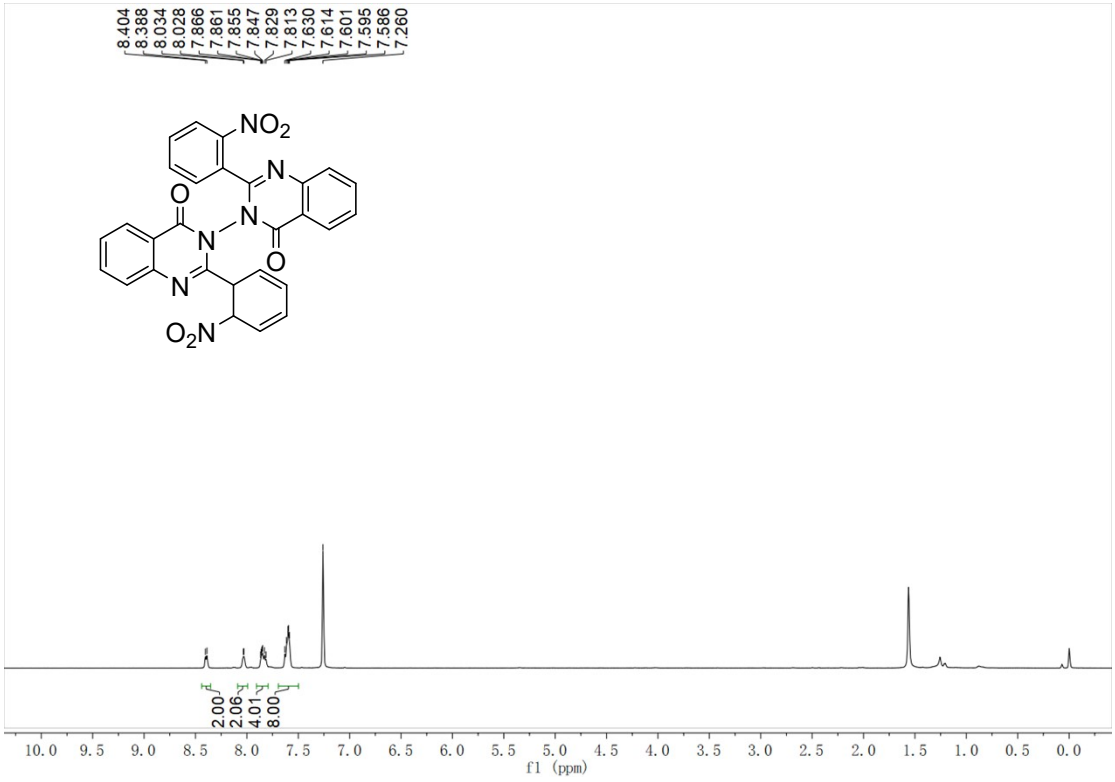
7. Copies of the ^{1}H NMR and ^{13}C NMR Spectra

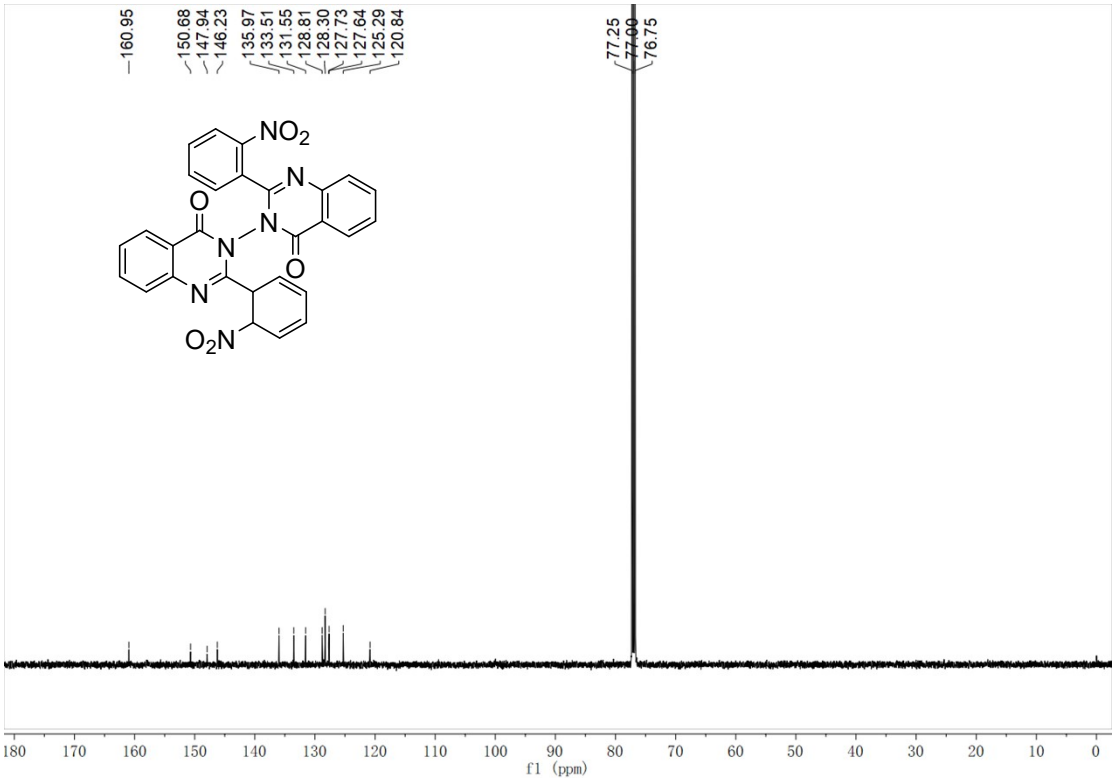
2,2'-diphenyl-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3aa)



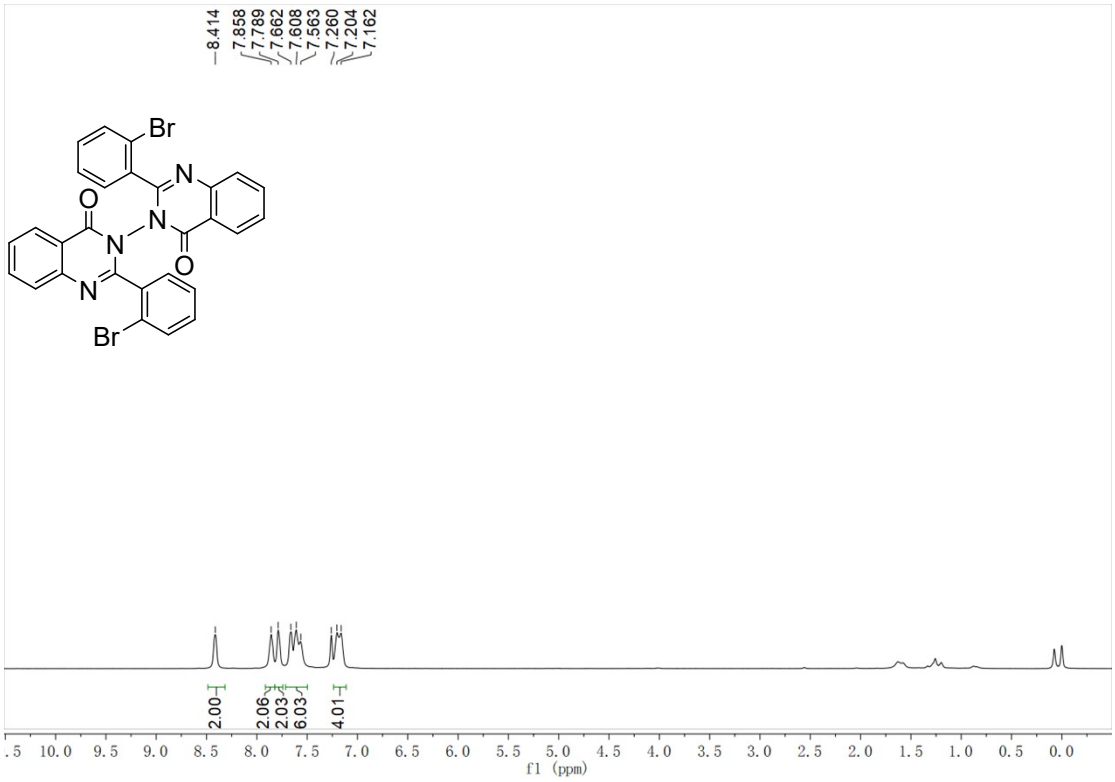


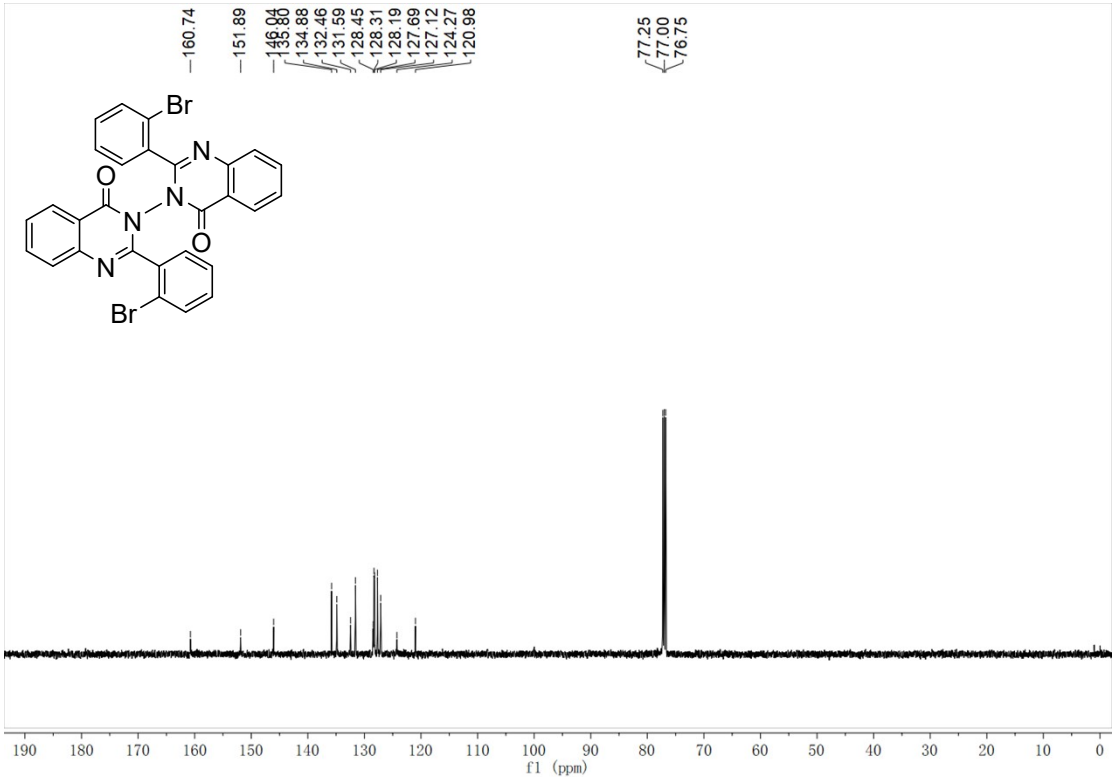
(*S*)-2-(6-nitrocyclohexa-2,4-dien-1-yl)-2'-(2-nitrophenyl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3ab)



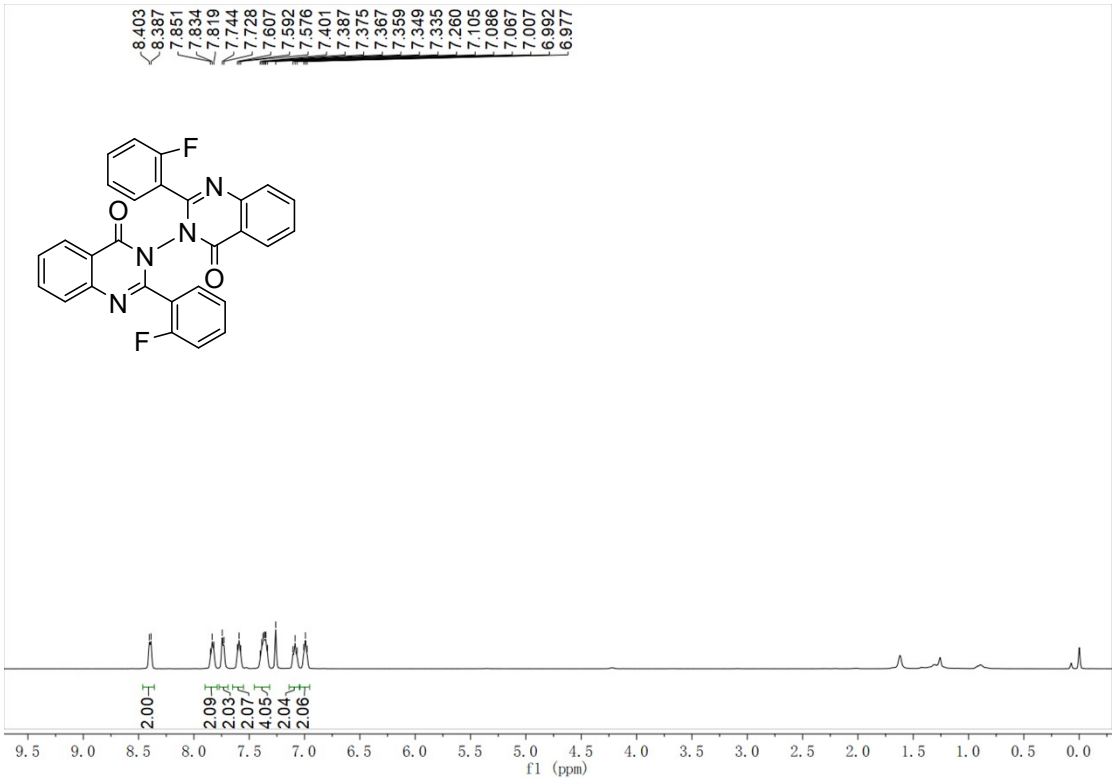


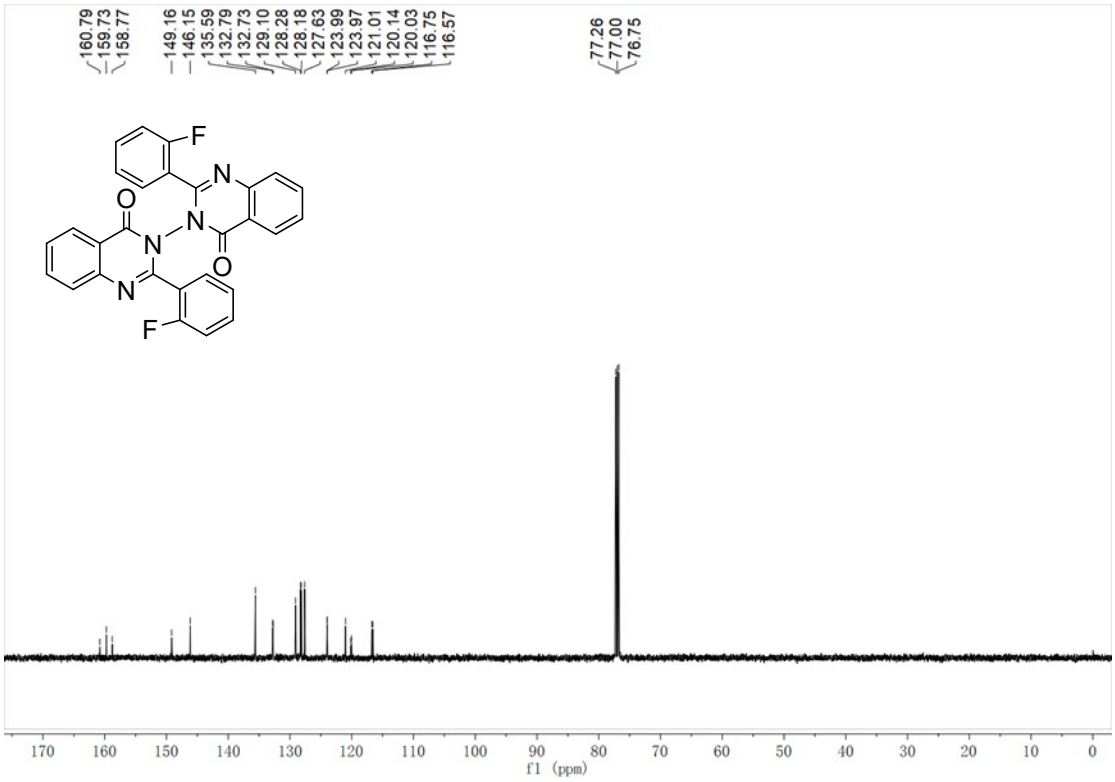
(*S*)-2,2'-bis(2-bromophenyl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3ac)



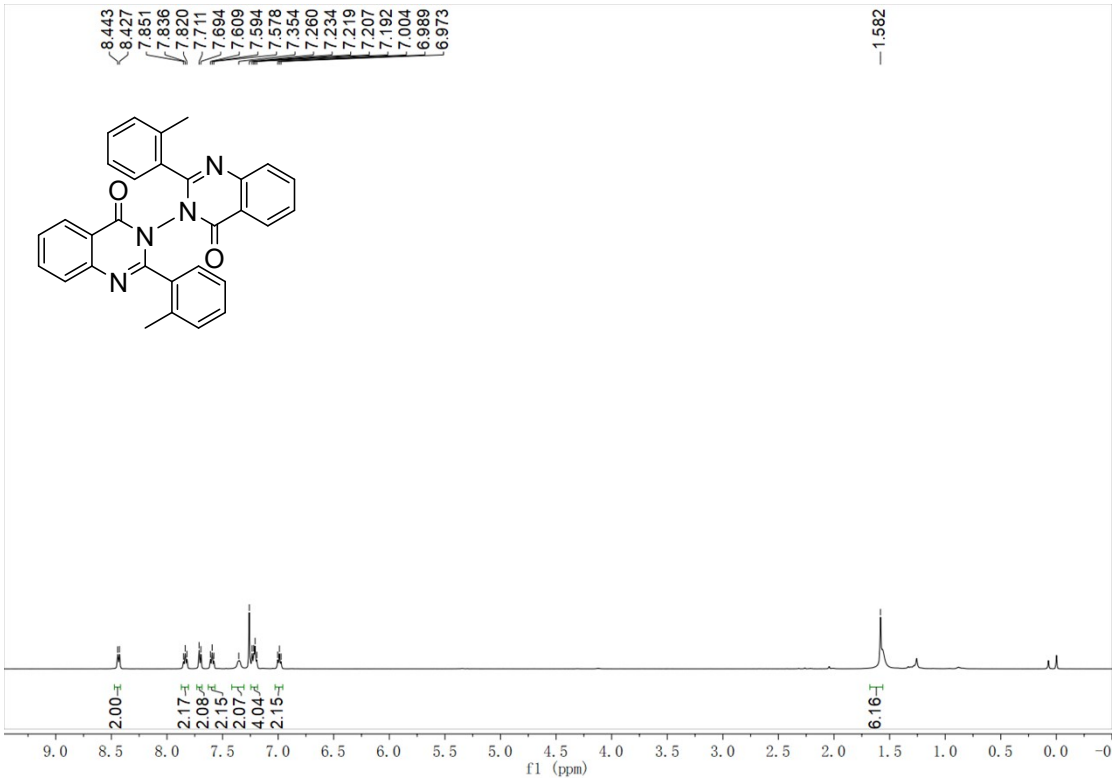


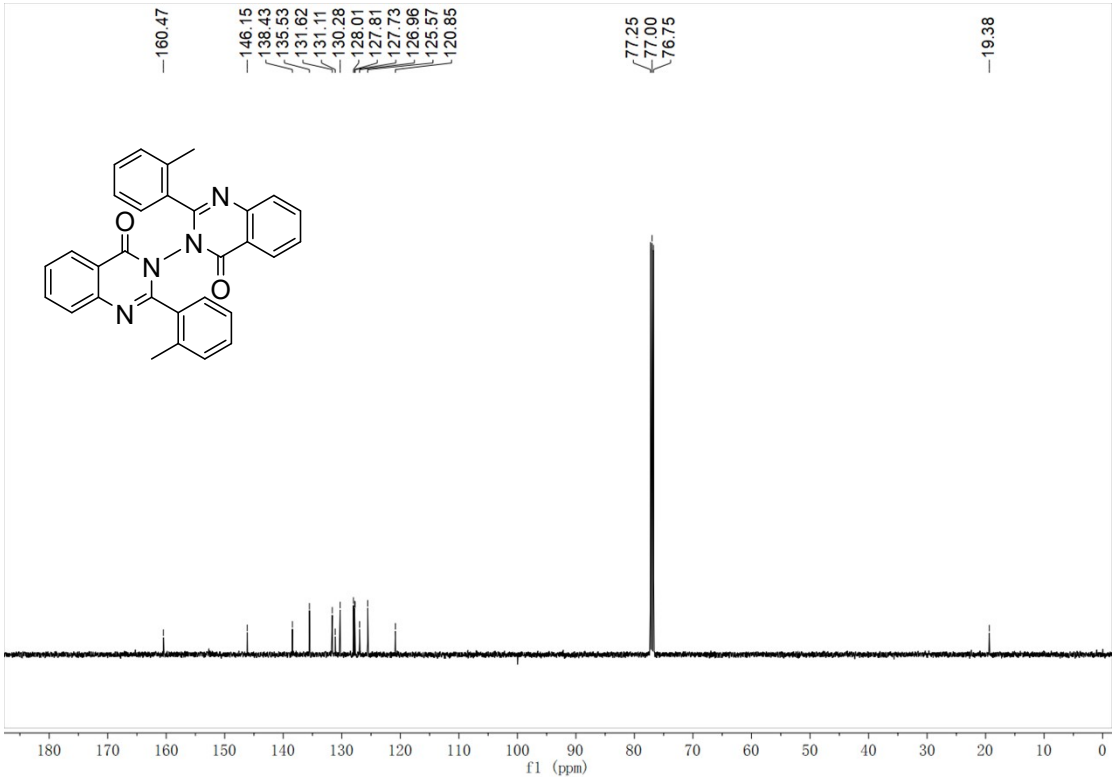
(*S*)-2,2'-bis(2-fluorophenyl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3ad)



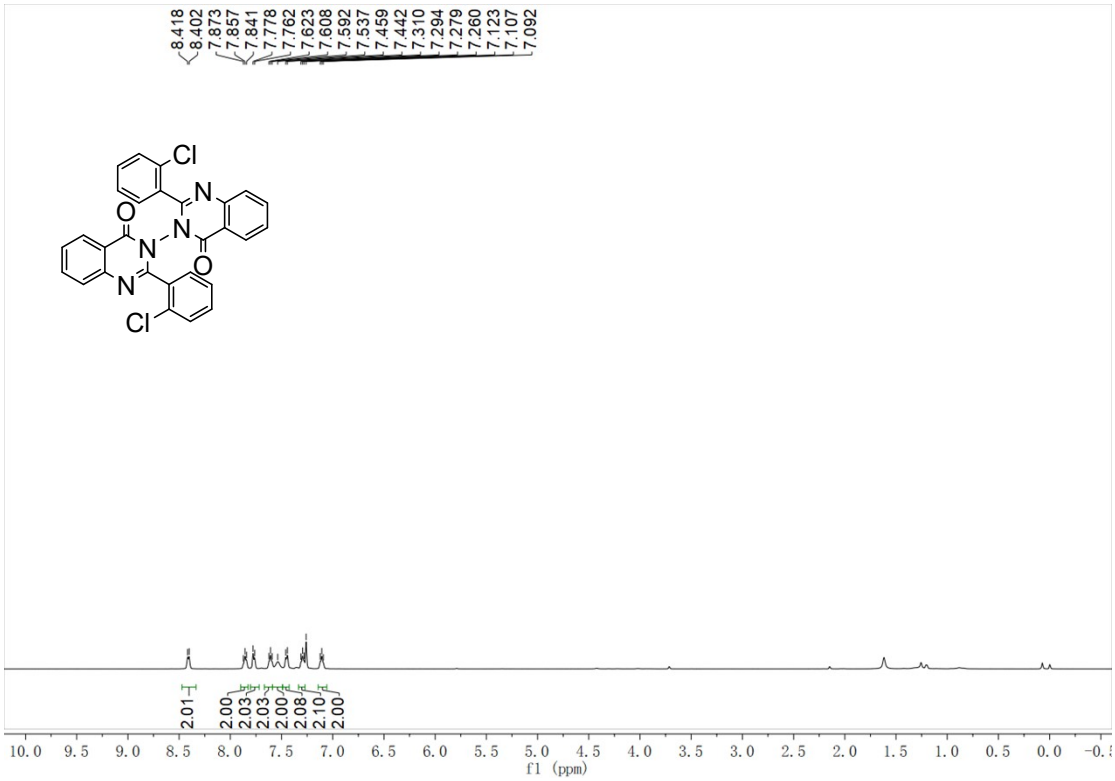


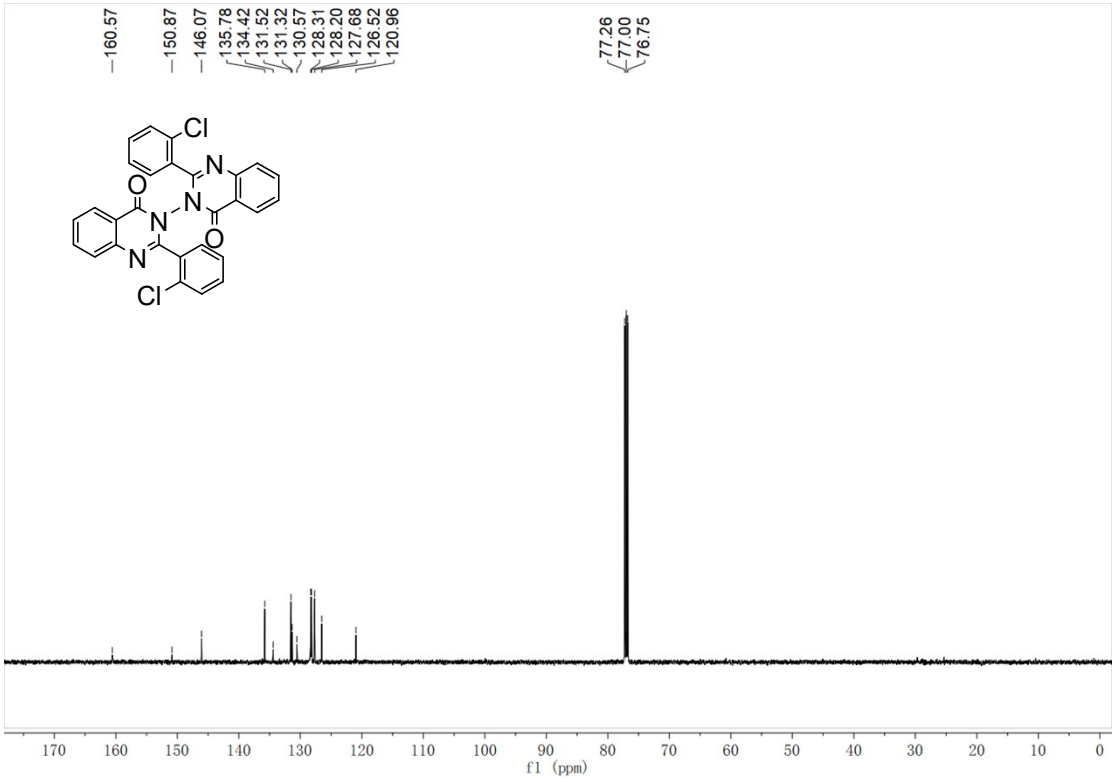
(*S*)-2,2'-di-o-tolyl-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3ae)



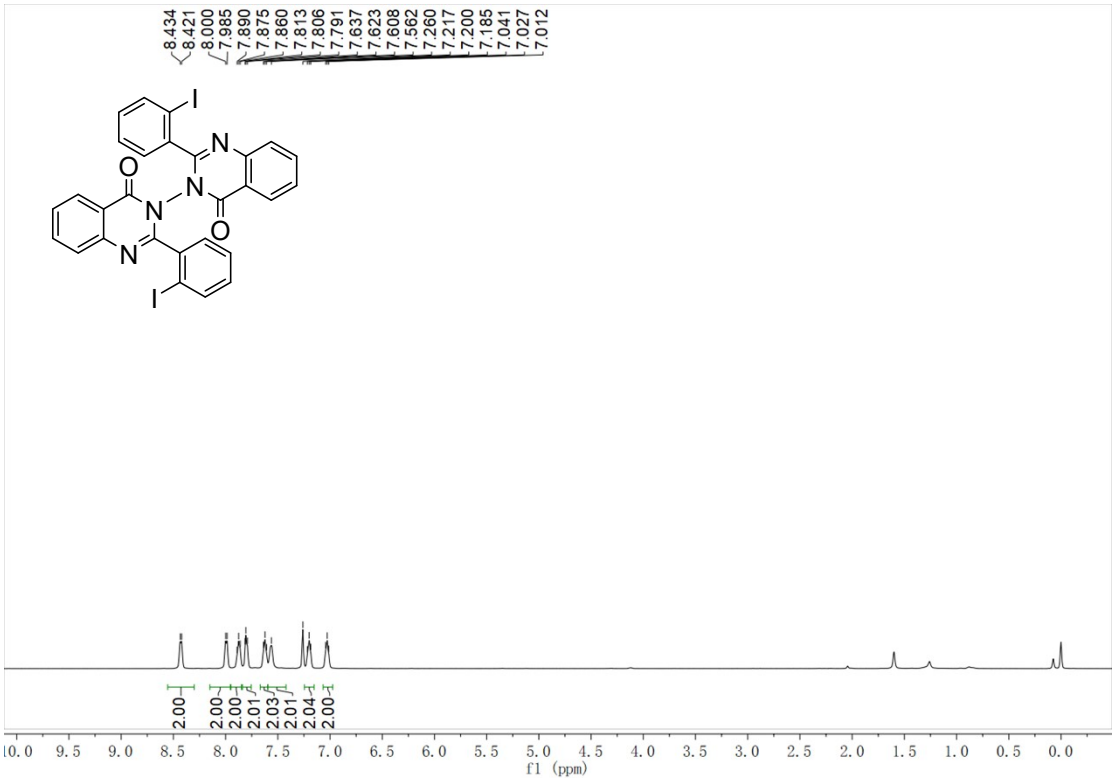


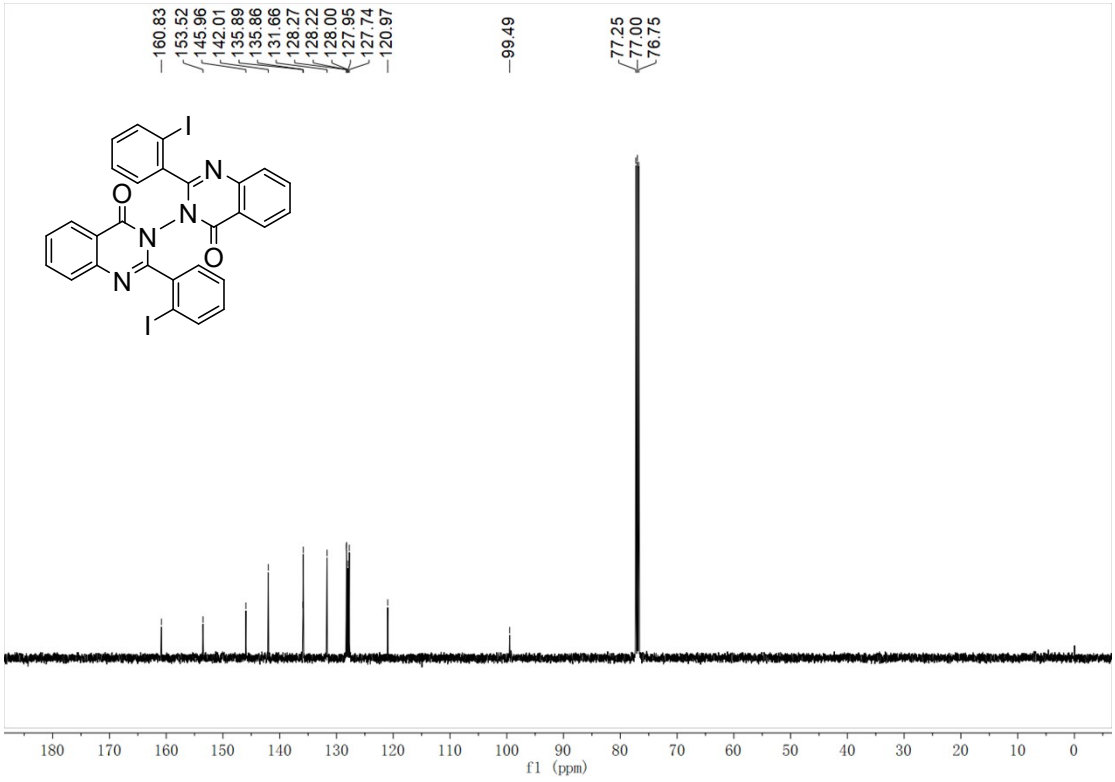
(*S*)-2,2'-bis(2-chlorophenyl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3af)



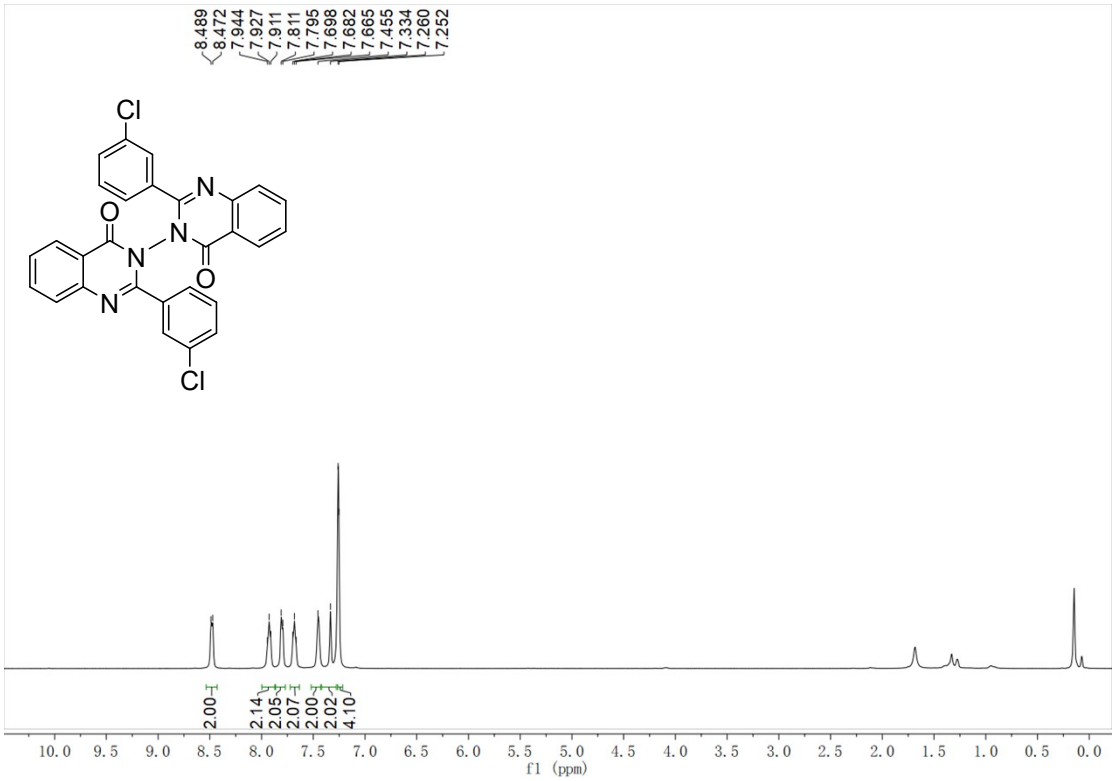


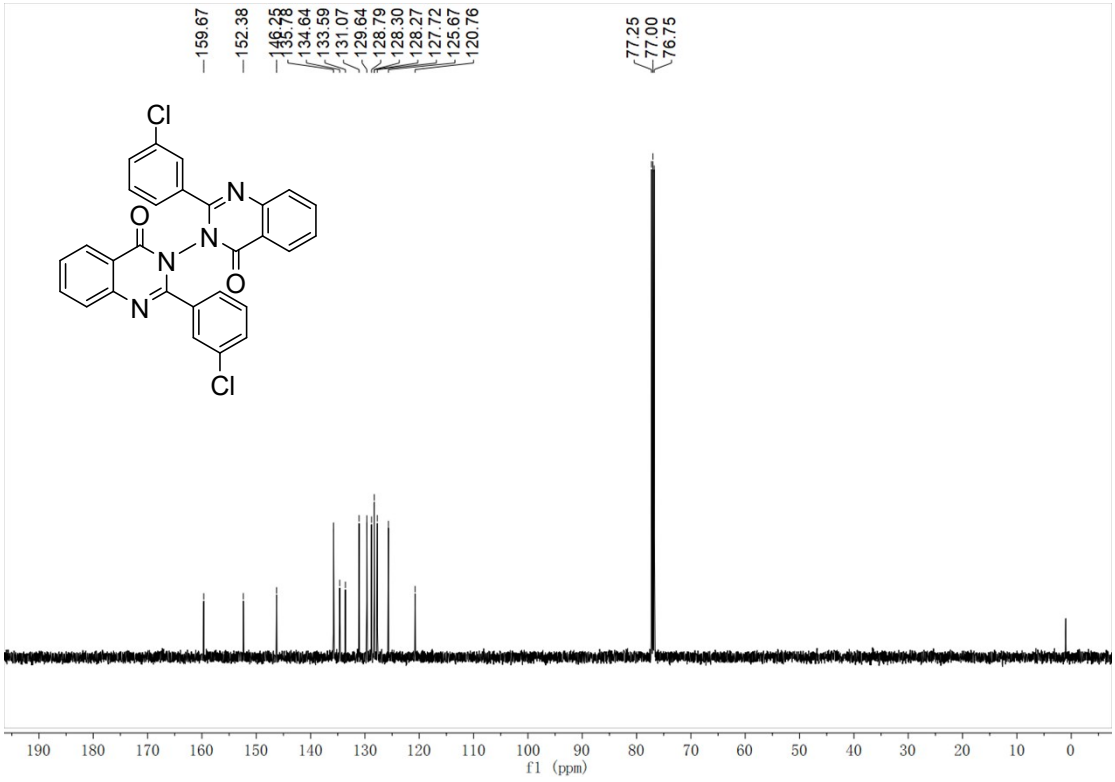
(*S*)-2,2'-bis(2-iodophenyl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3ag)



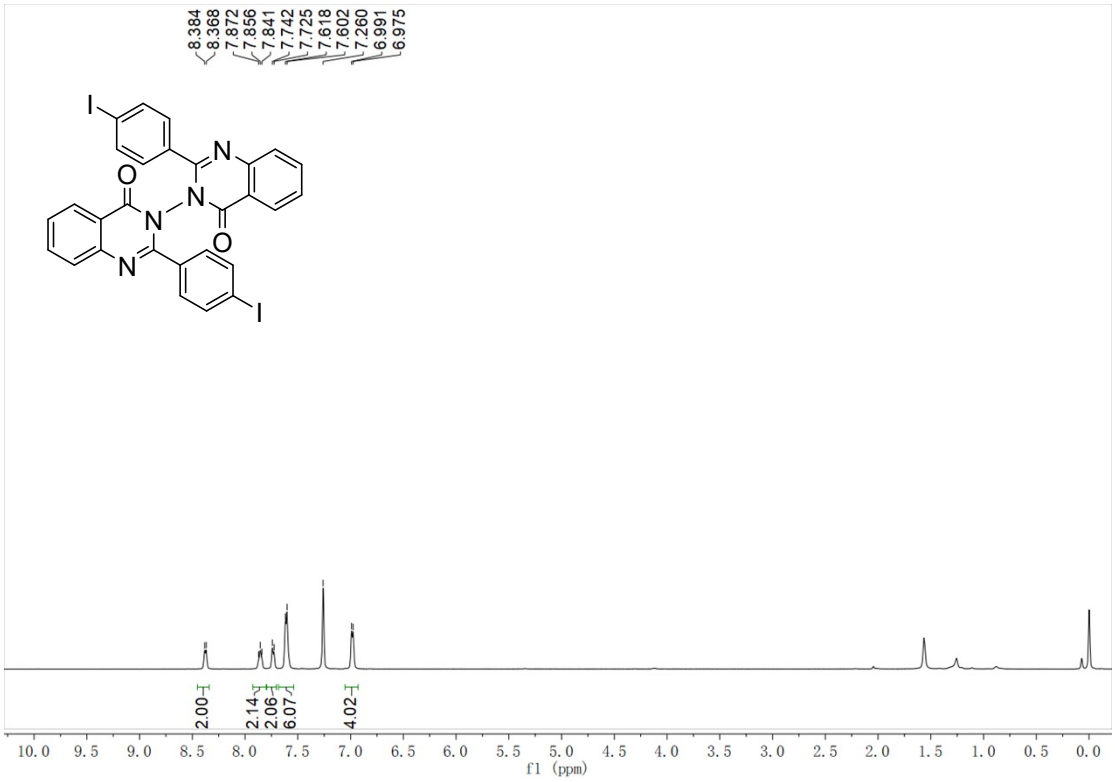


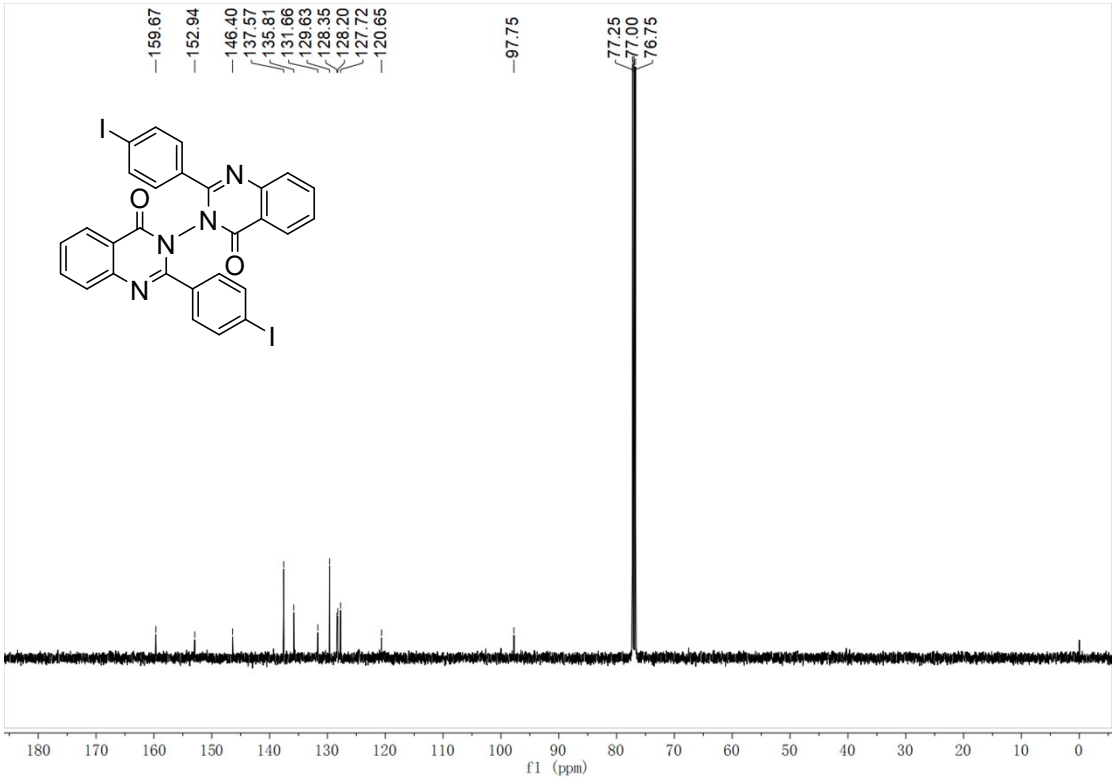
(*S*)-2,2'-bis(3-chlorophenyl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3ah)



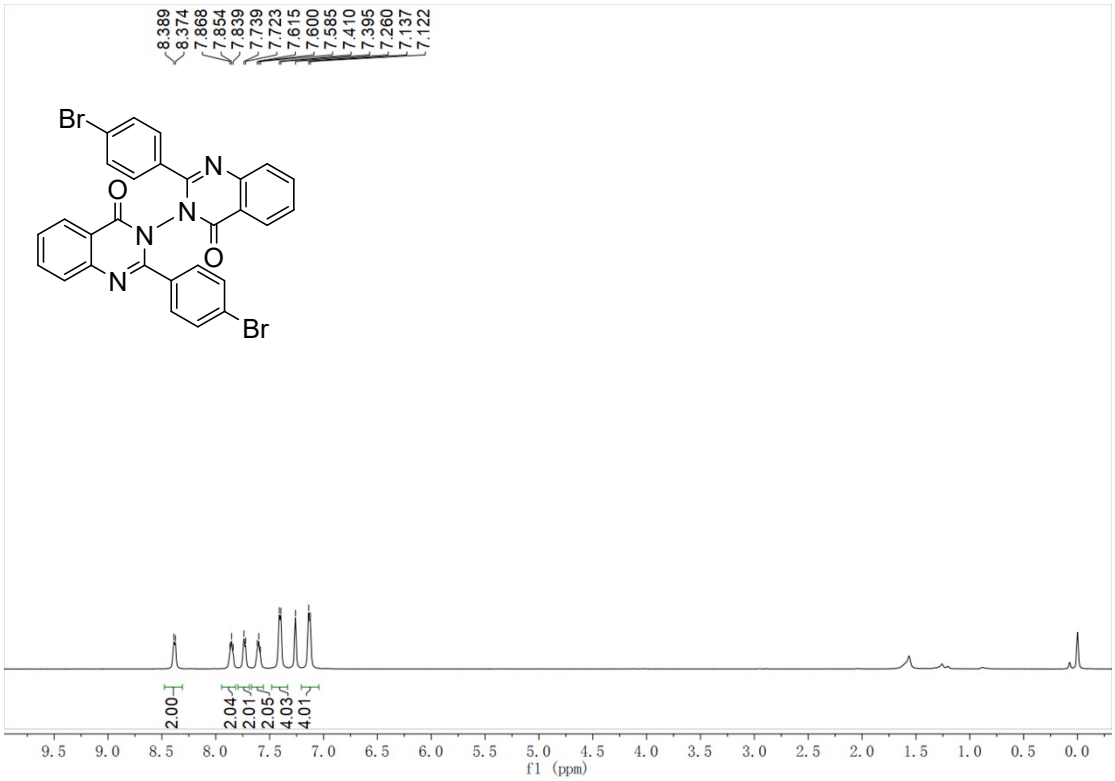


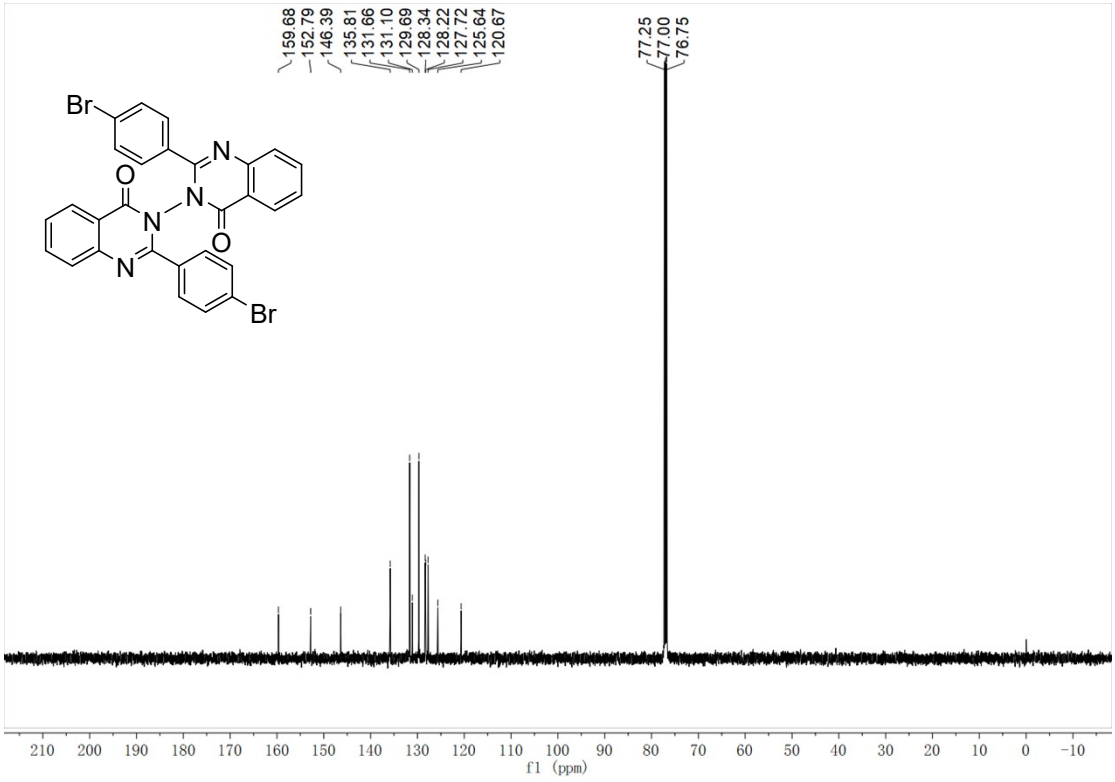
(*S*)-2,2'-bis(4-iodophenyl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3ai)



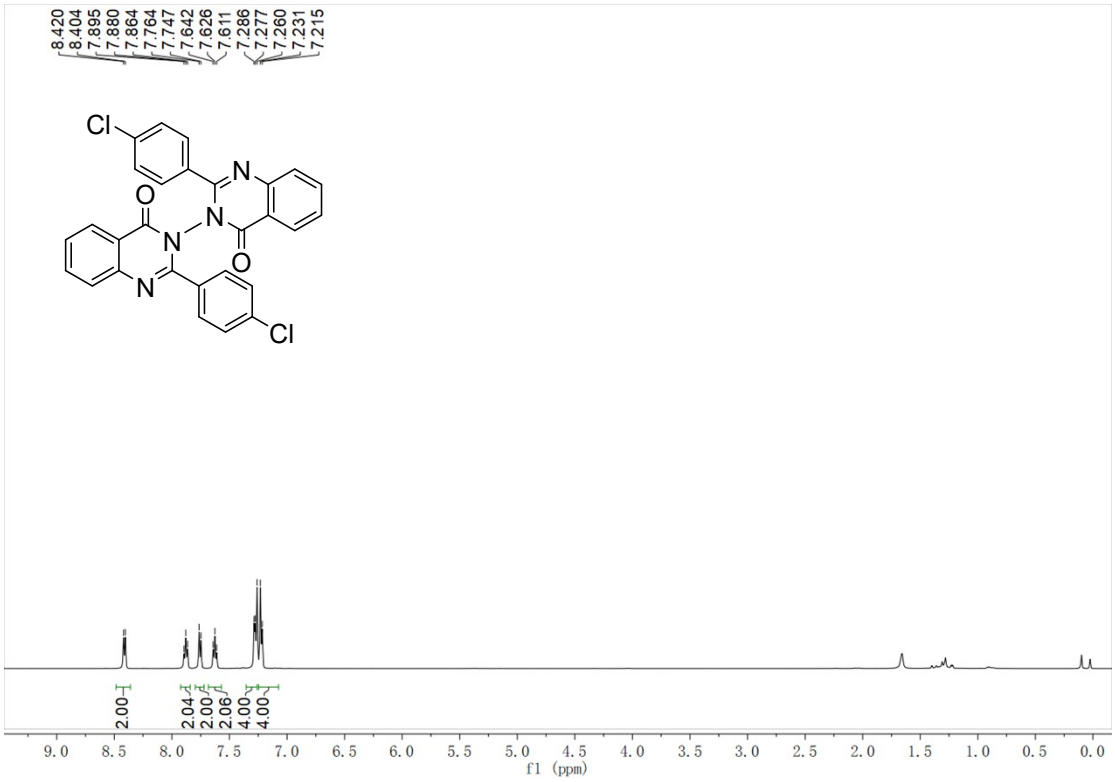


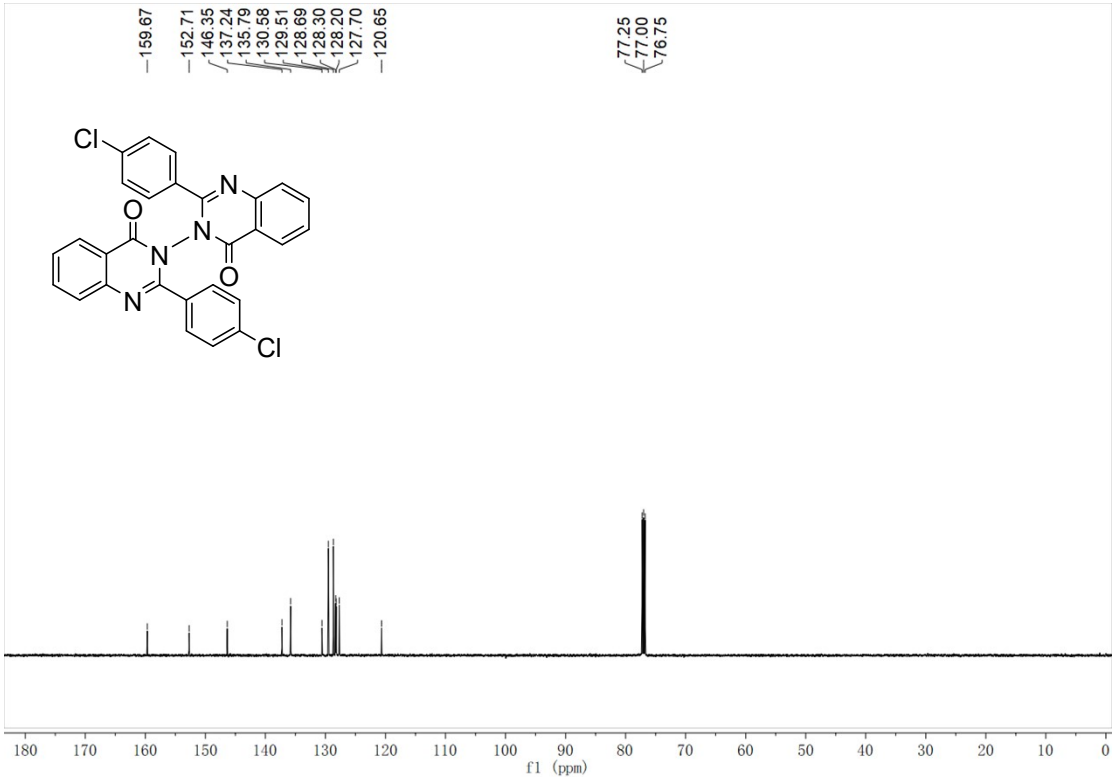
(*S*)-2,2'-bis(4-bromophenyl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3aj)



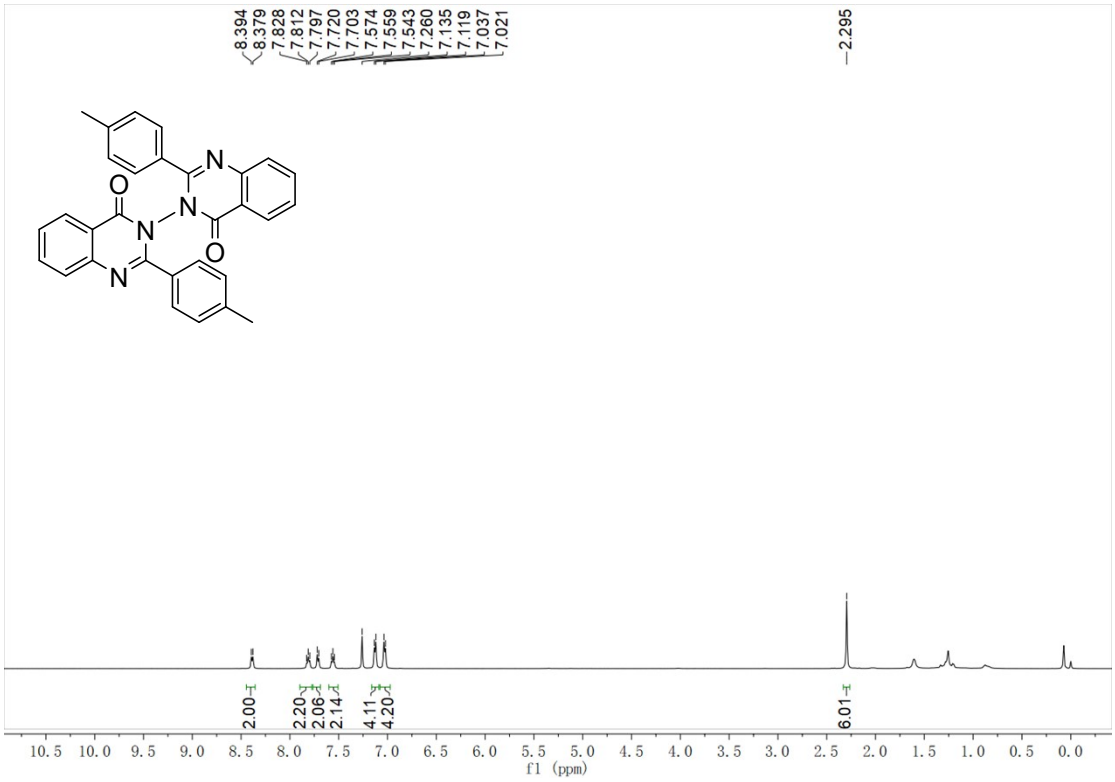


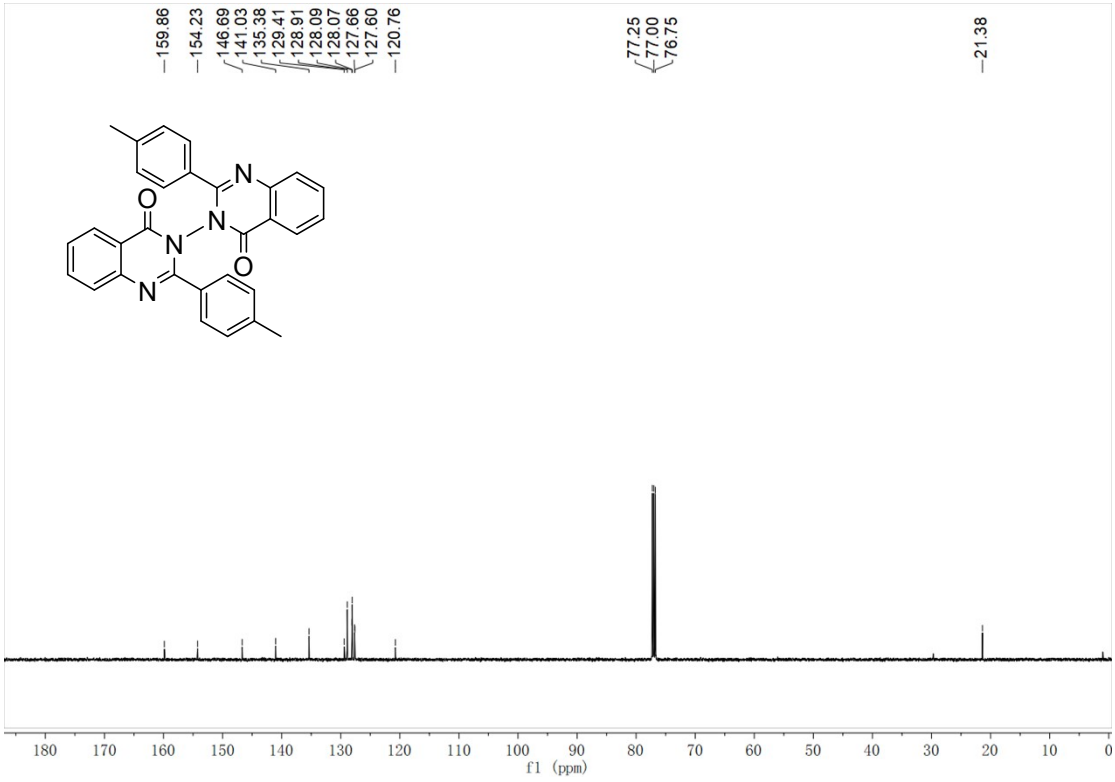
(*S*)-2,2'-bis(4-chlorophenyl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3ak)



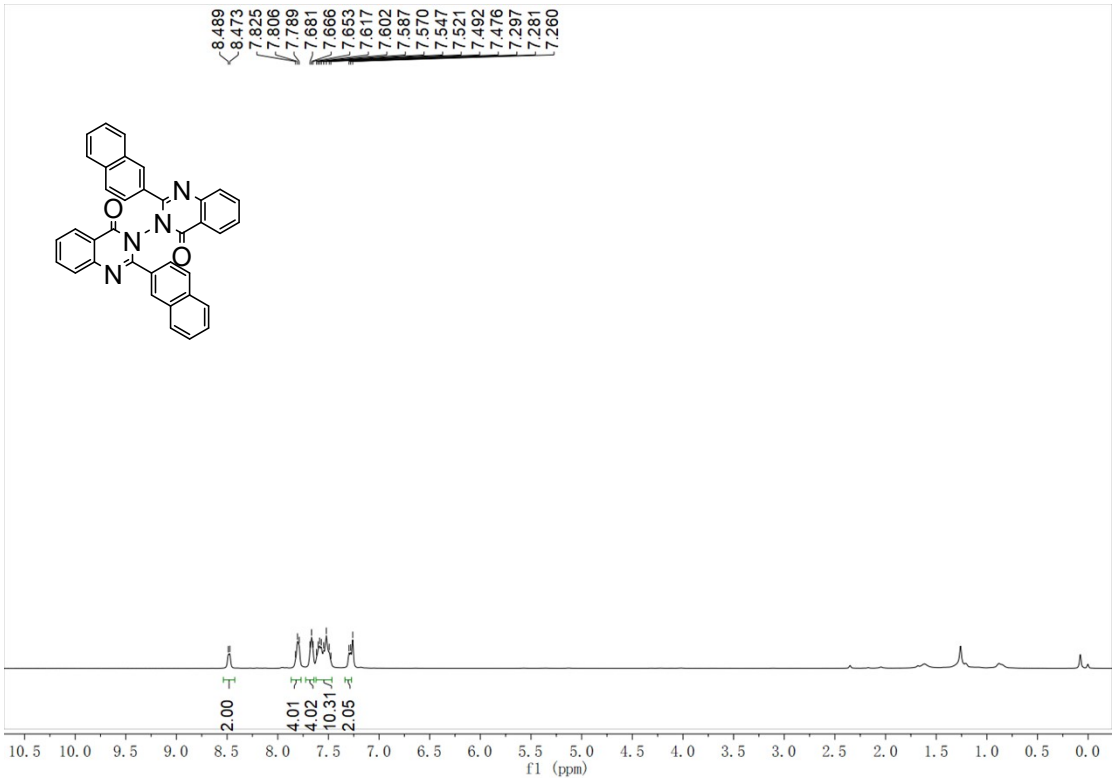


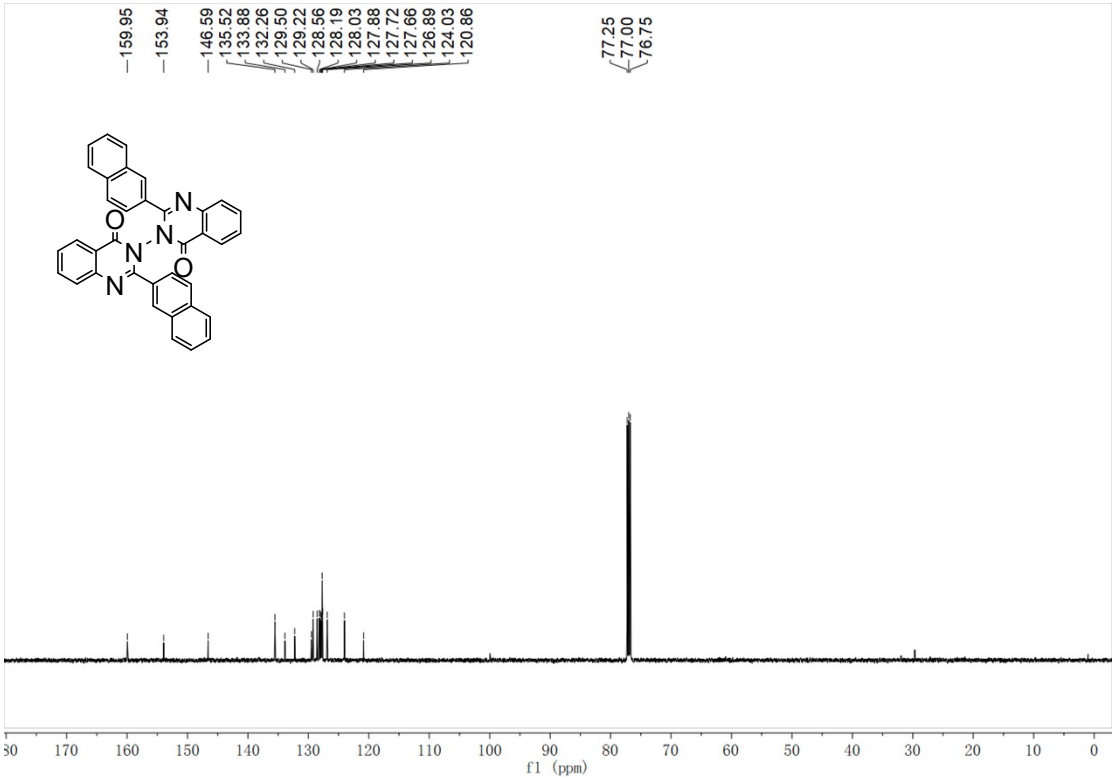
(*S*)-2,2'-di-p-tolyl-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3al)



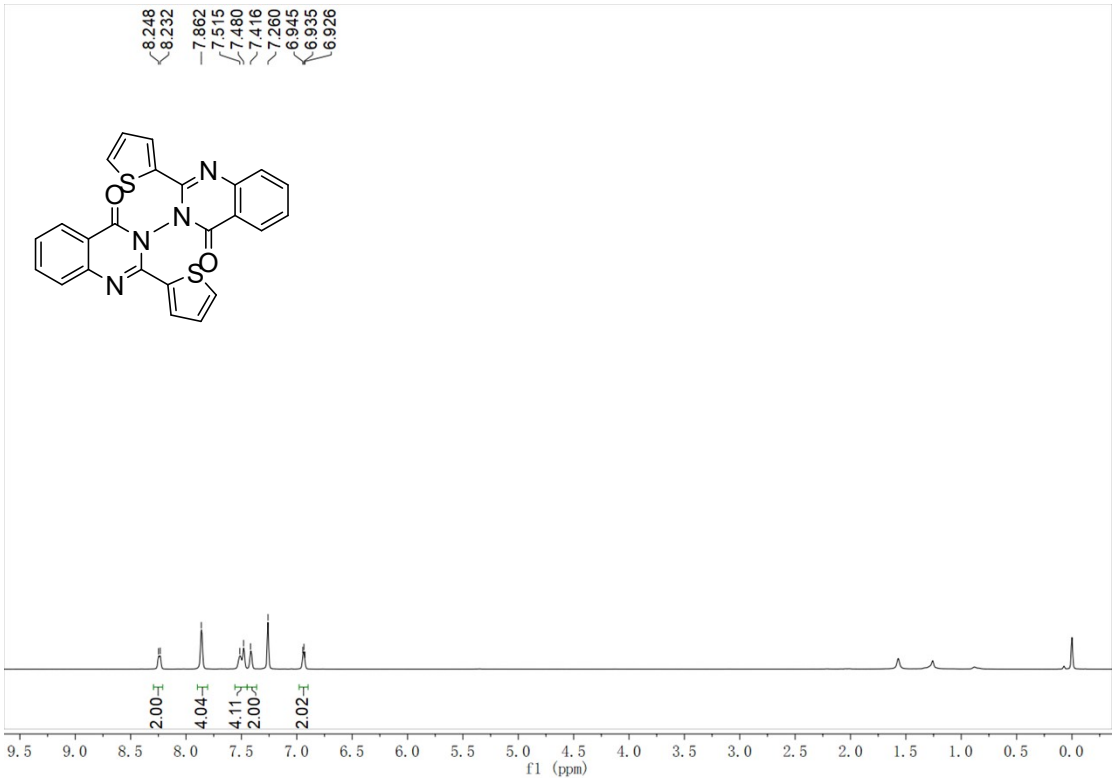


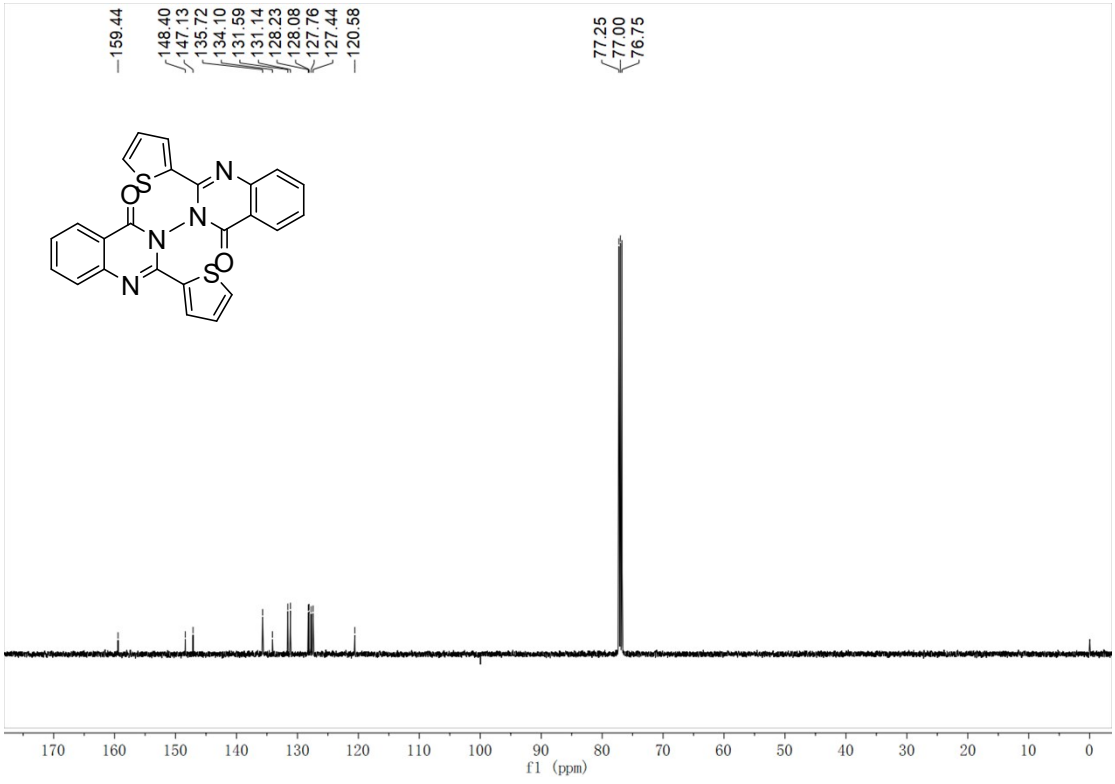
(*S*)-2,2'-di(naphthalen-2-yl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3am)



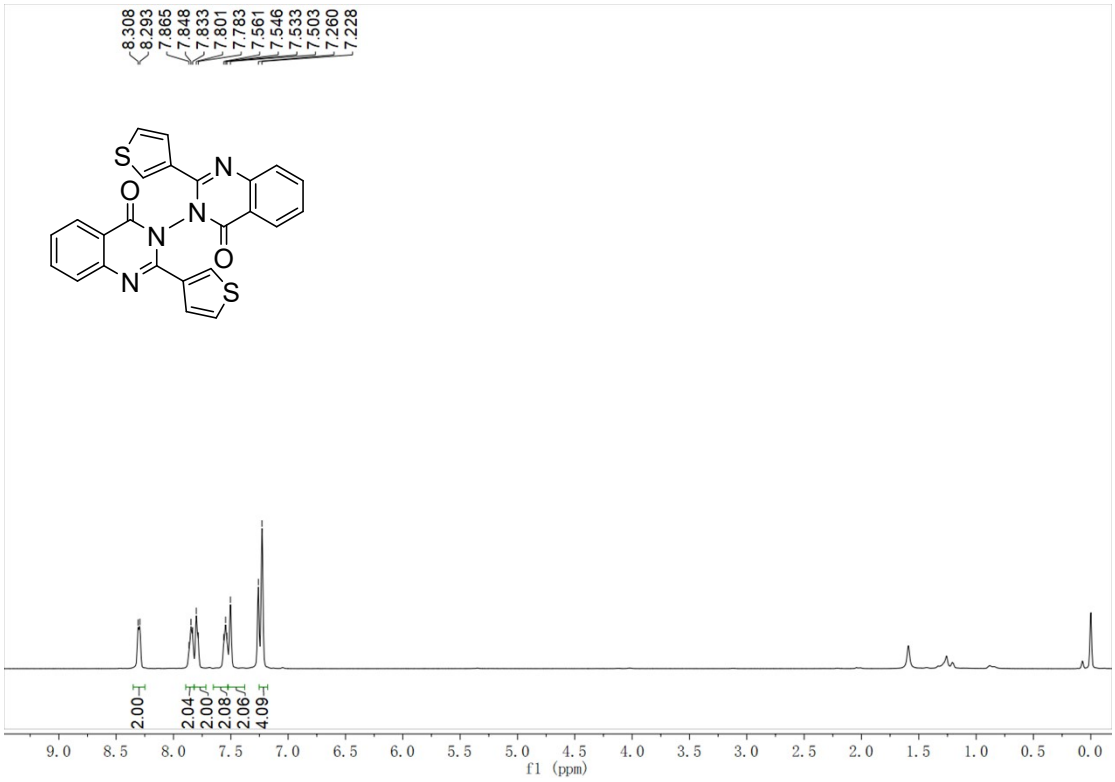


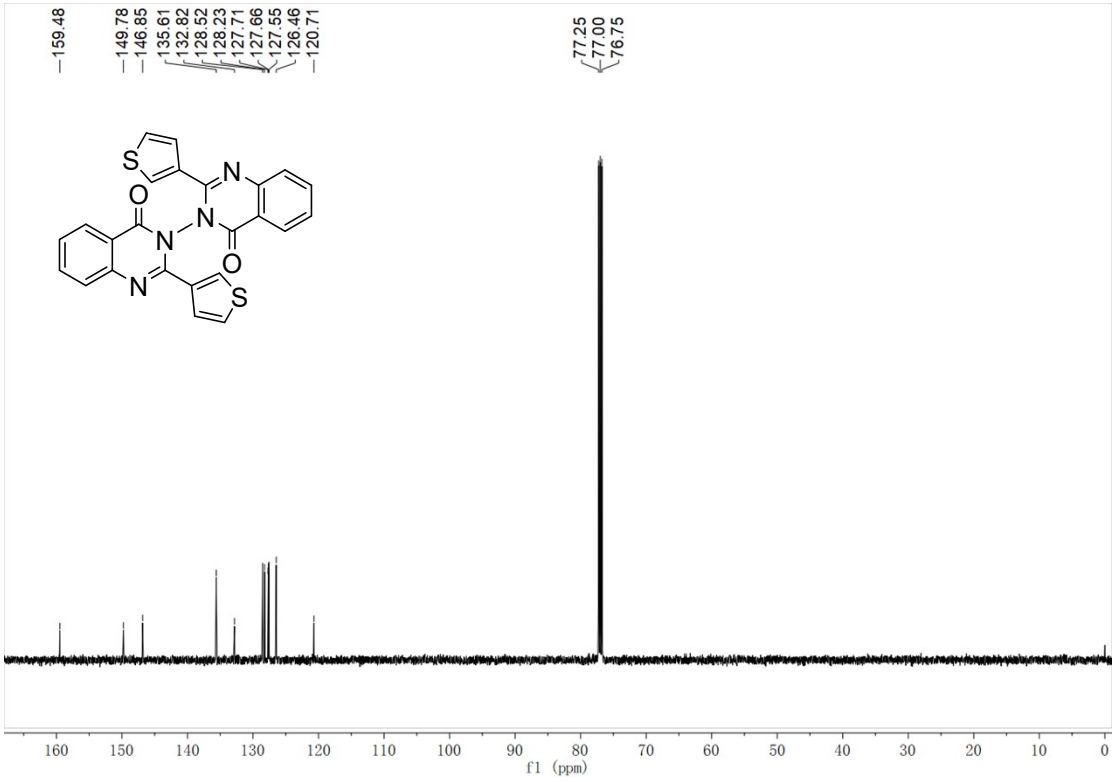
(*S*)-2,2'-di(thiophen-2-yl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3an)



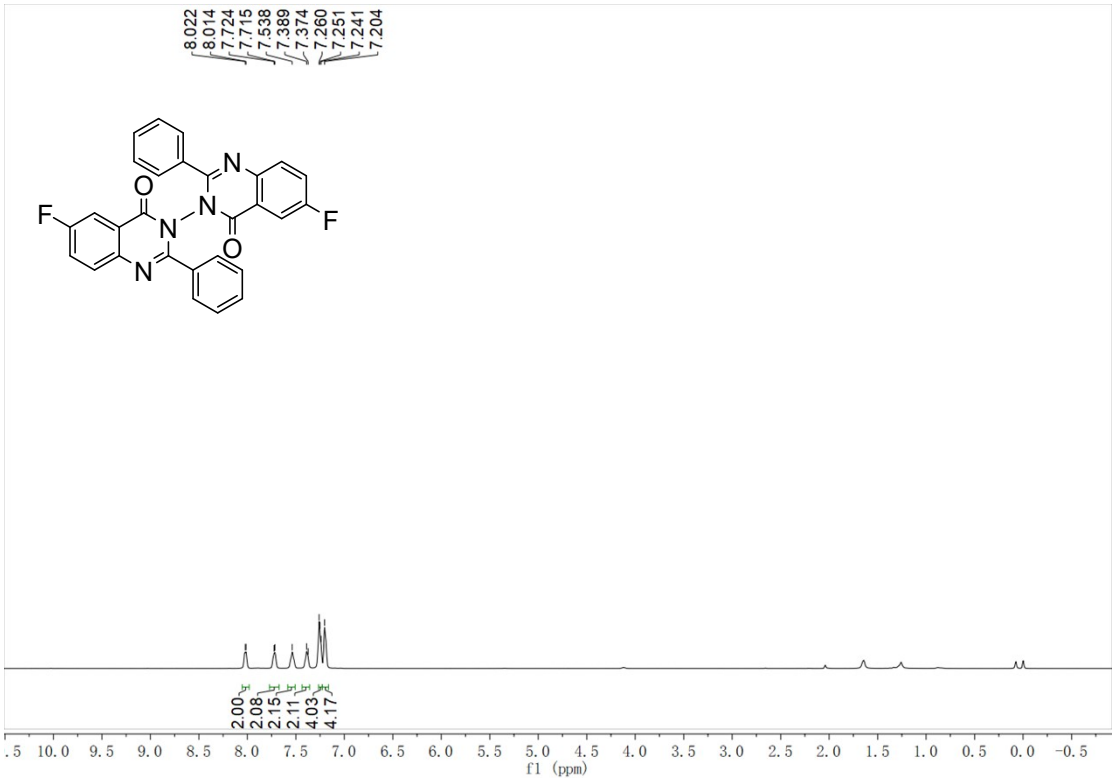


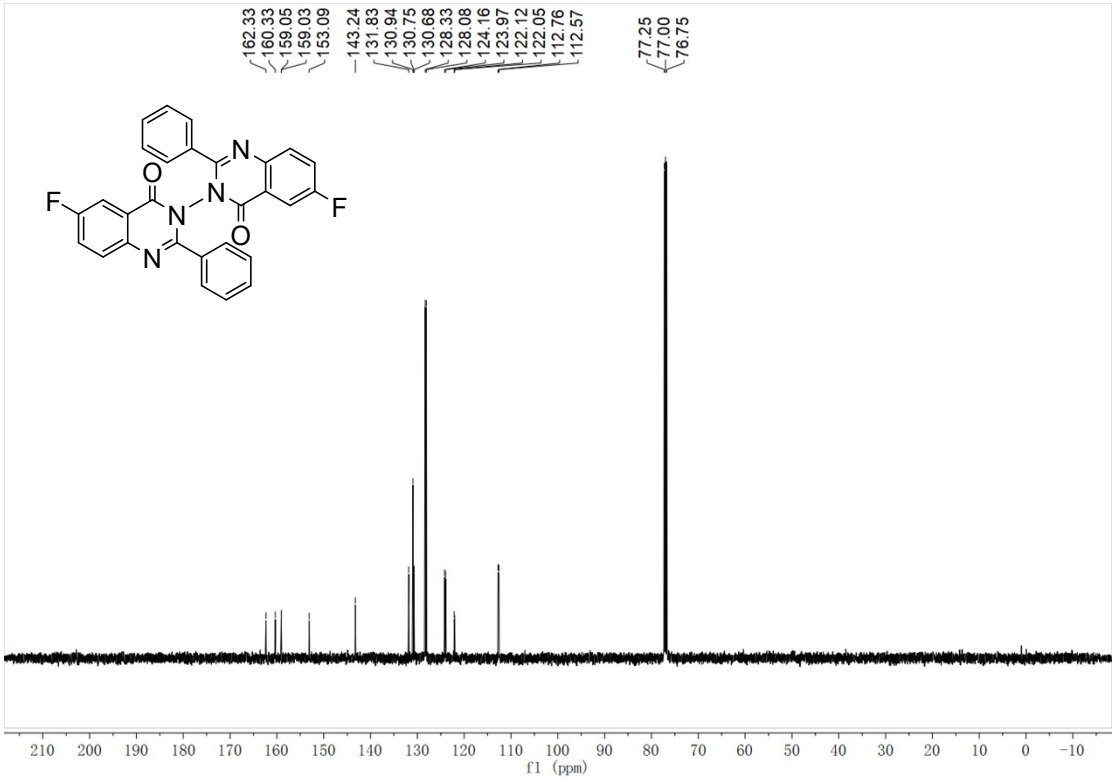
(*S*)-2,2'-di(thiophen-3-yl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3ao)



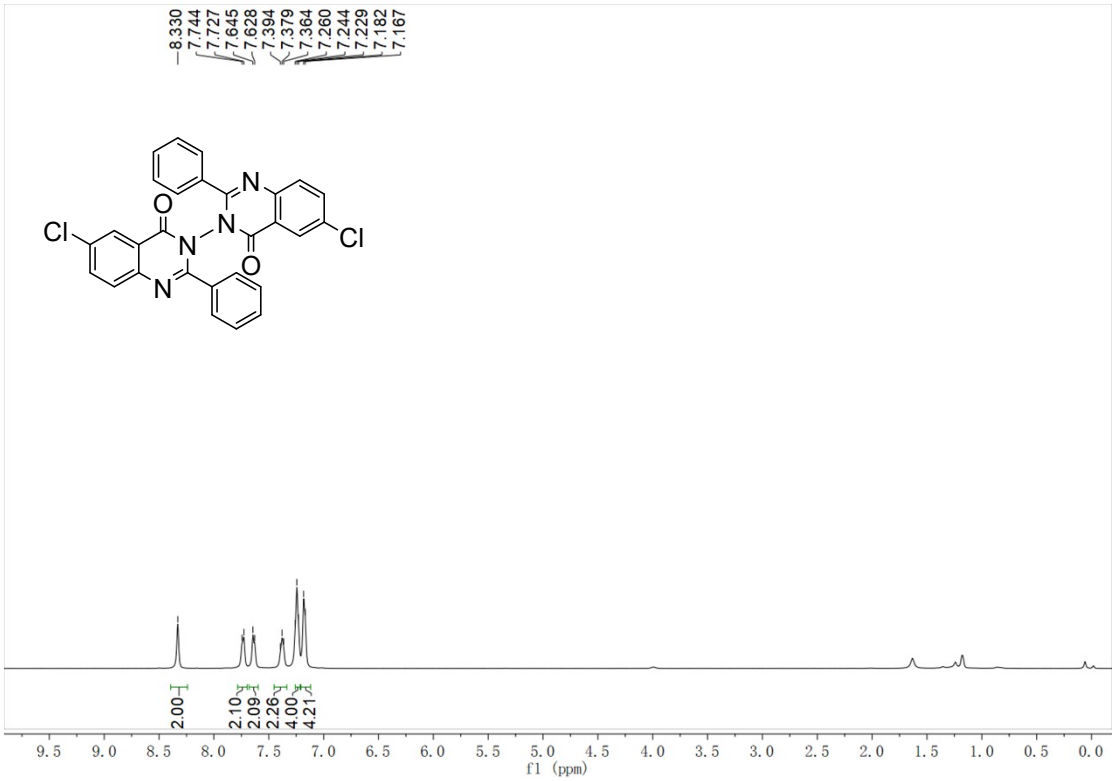


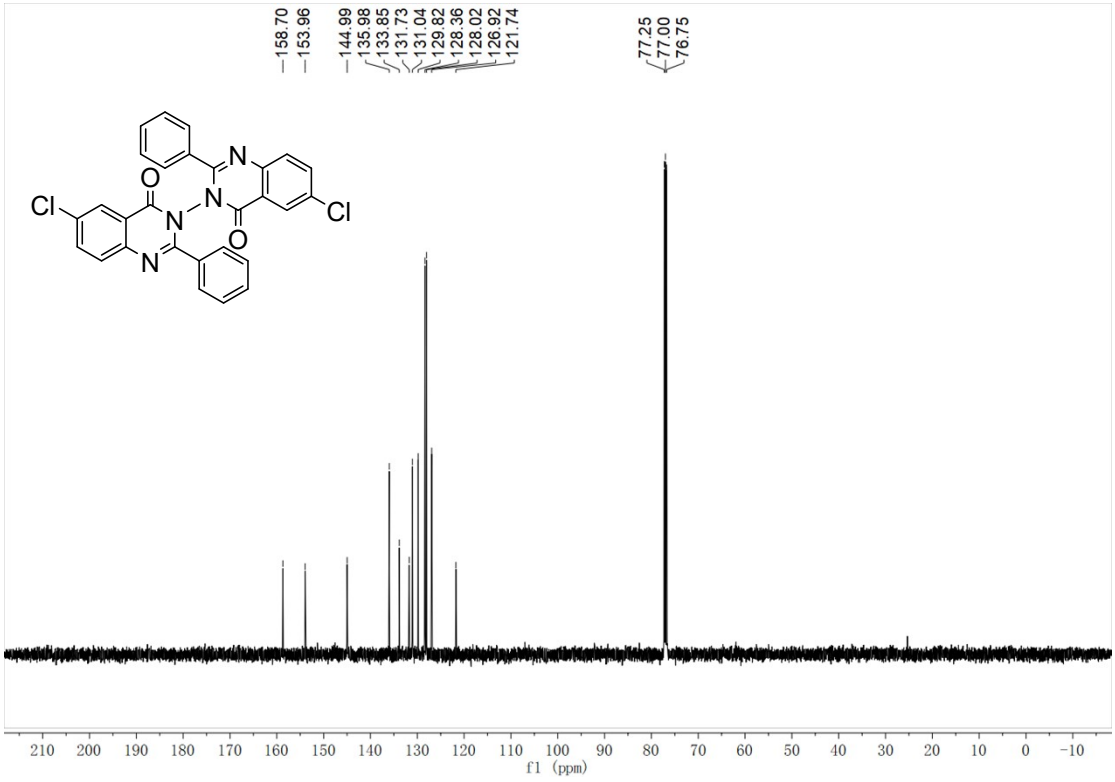
(*S*)-6,6'-difluoro-2,2'-diphenyl-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3ba)



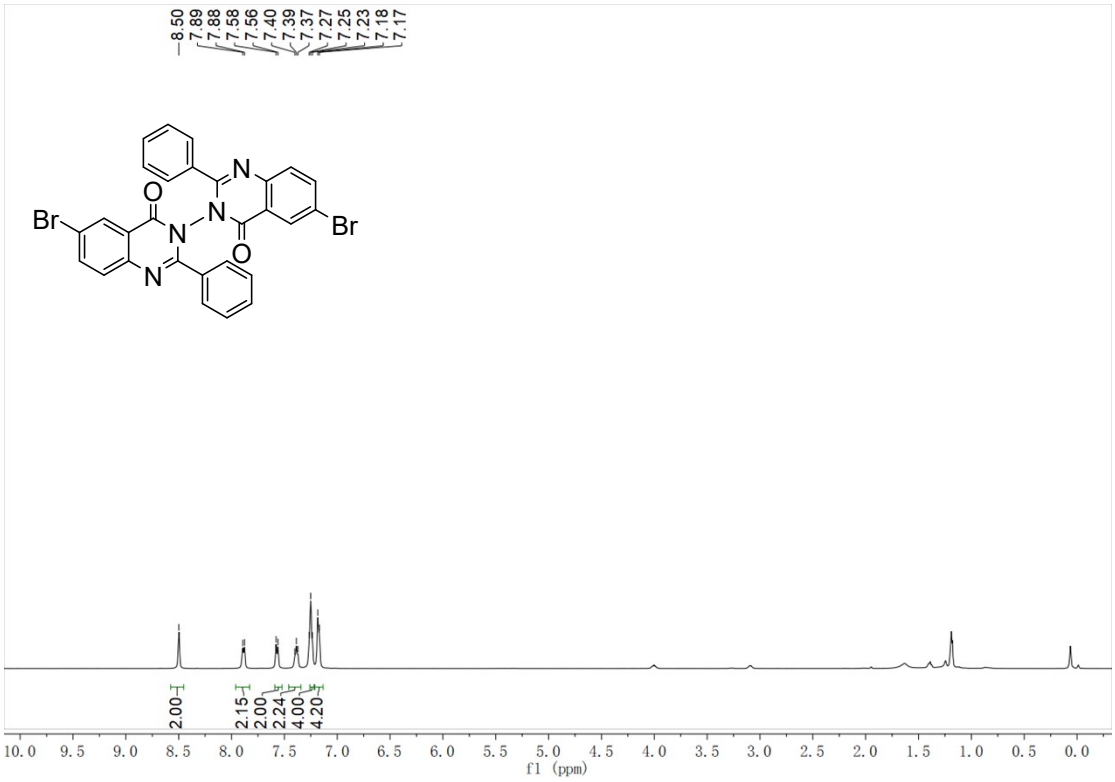


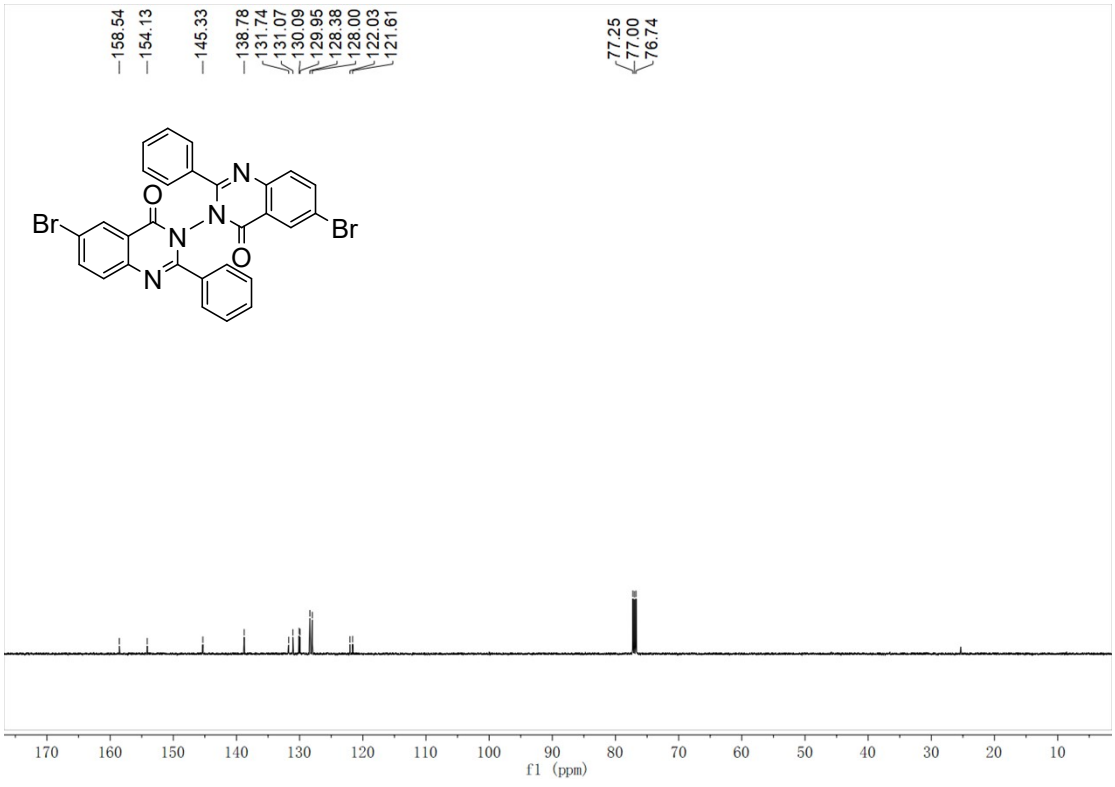
(*S*)-6,6'-dichloro-2,2'-diphenyl-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3ca)



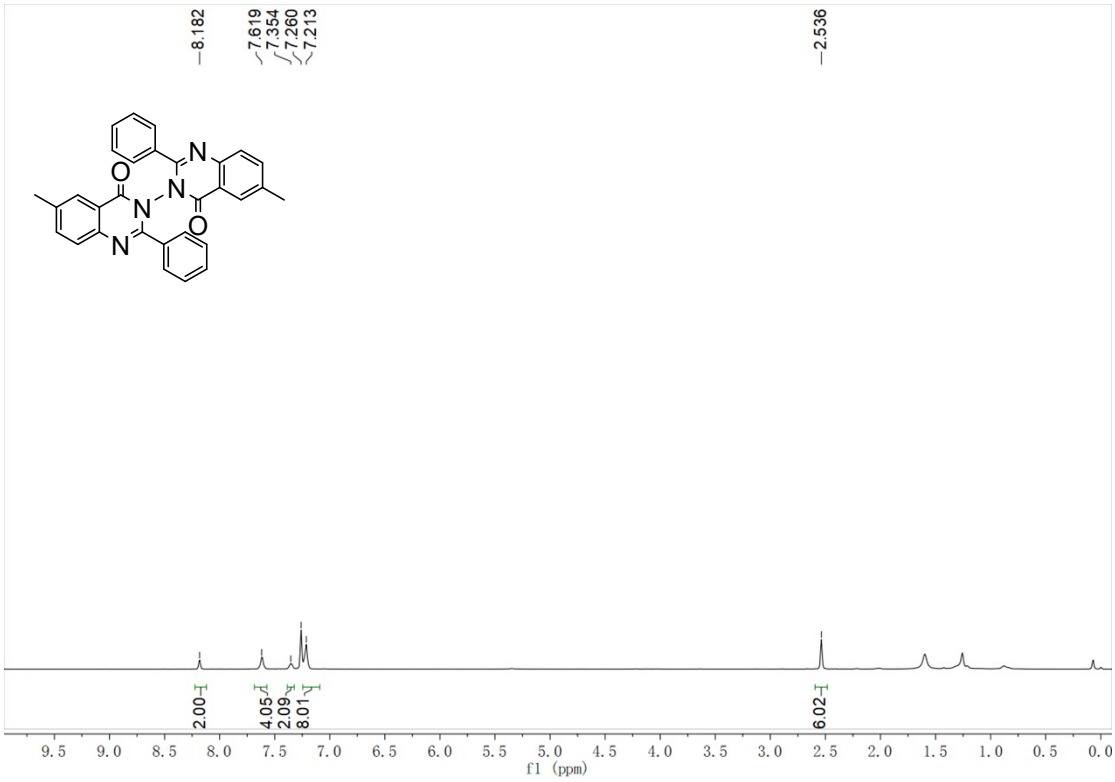


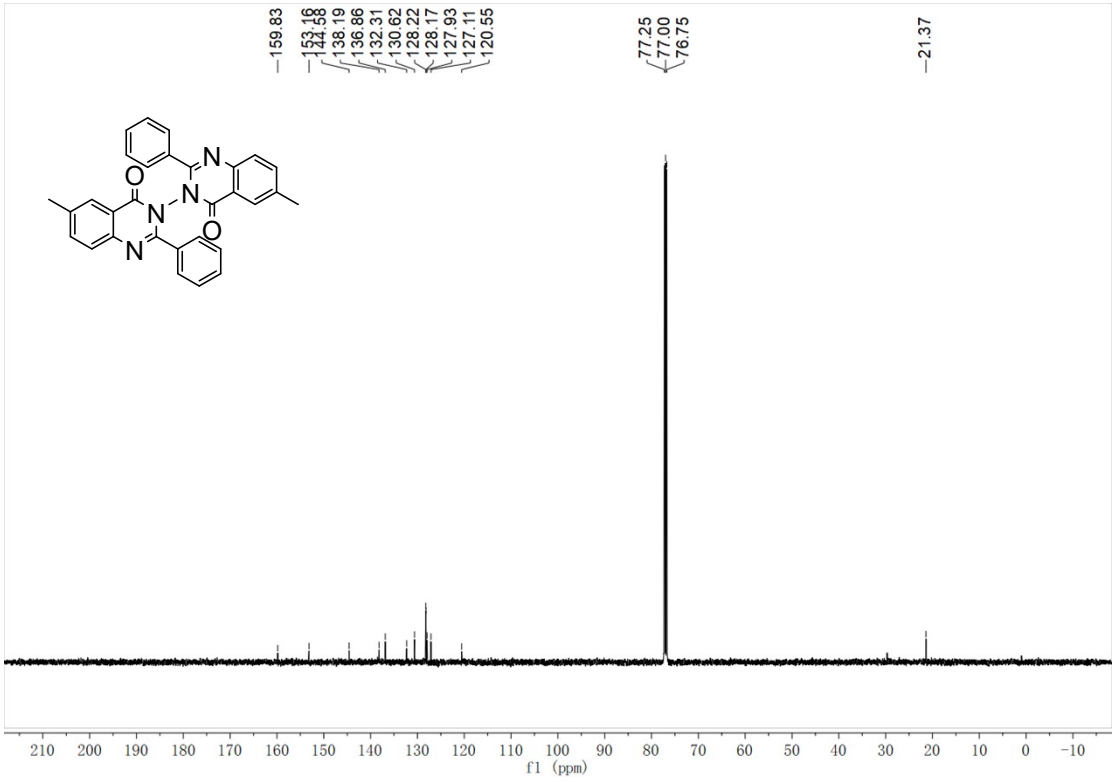
(*S*)-6,6'-dibromo-2,2'-diphenyl-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3da)



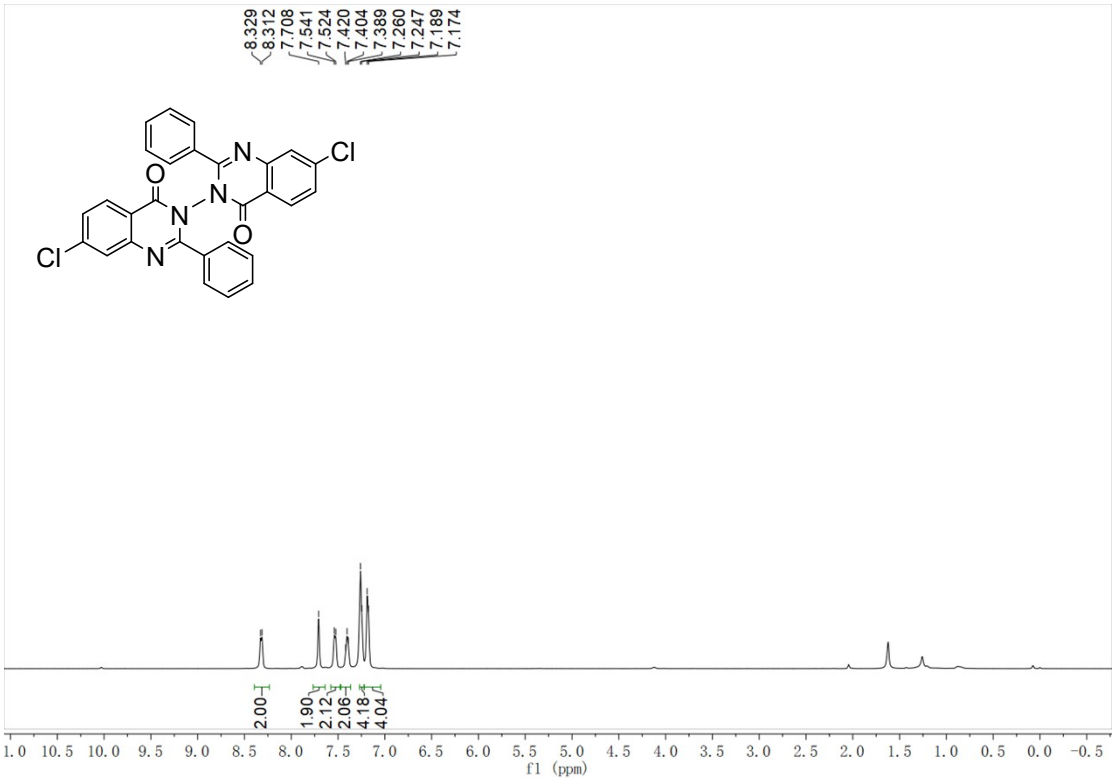


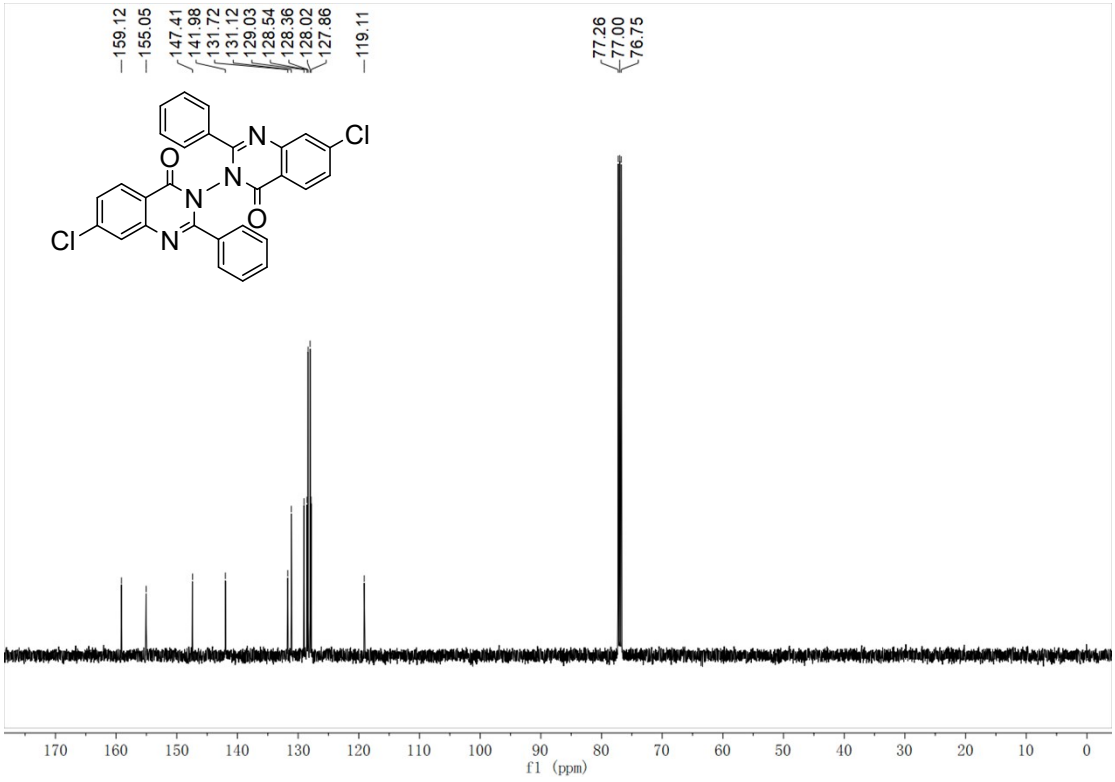
(*S*)-6,6'-dimethyl-2,2'-diphenyl-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3ea)



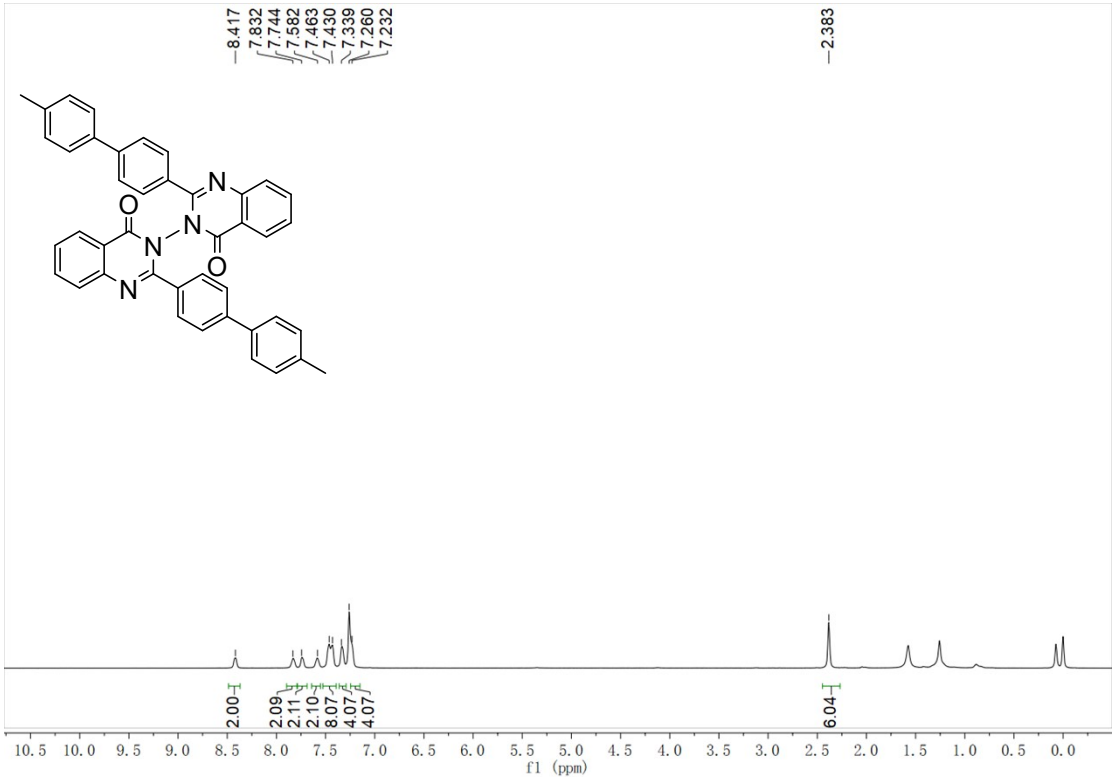


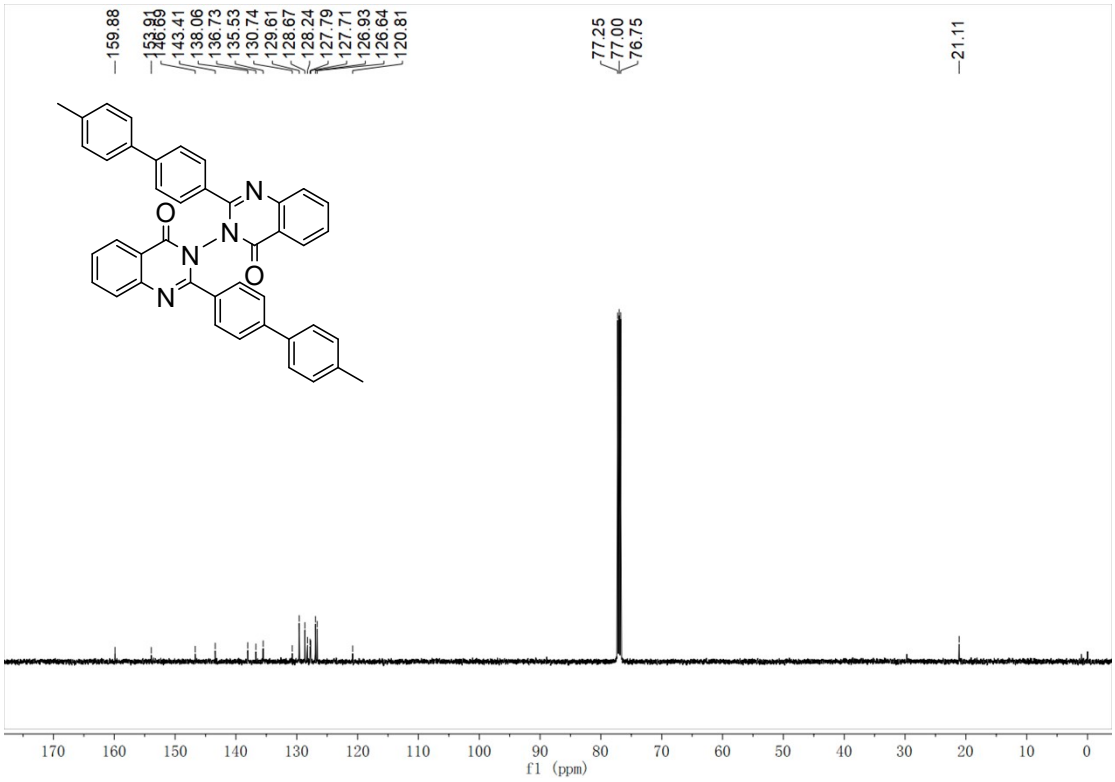
(*S*)-7,7'-dichloro-2,2'-diphenyl-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (3fa)



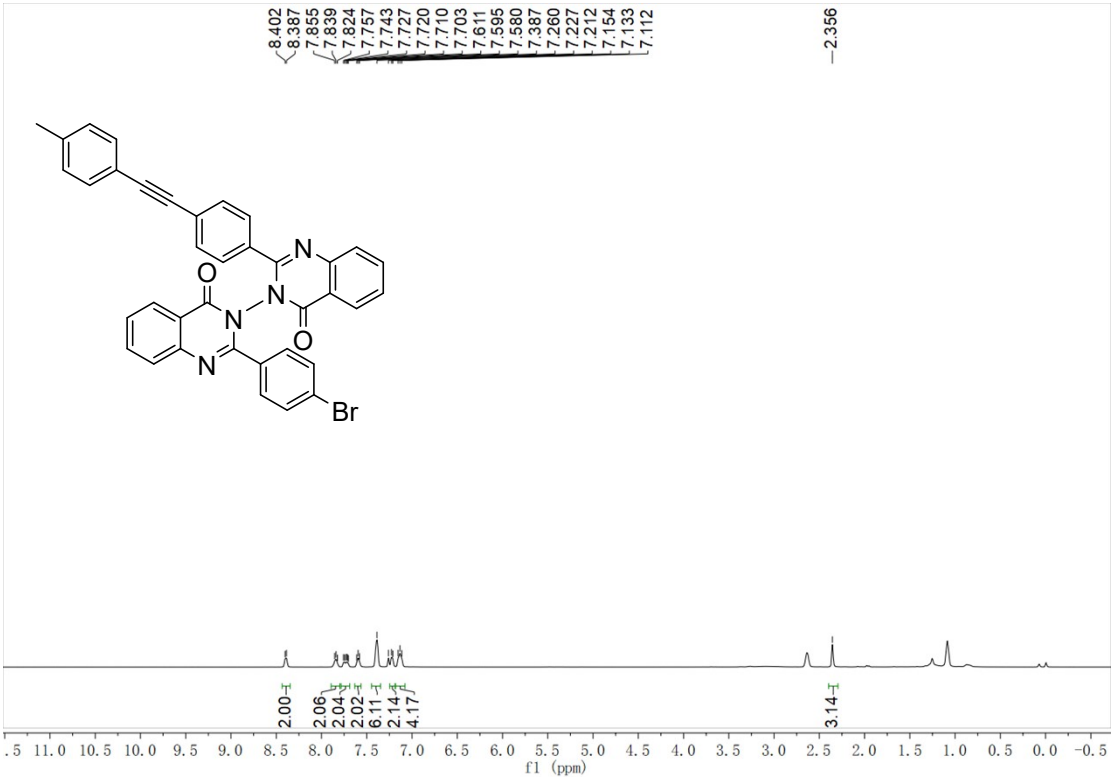


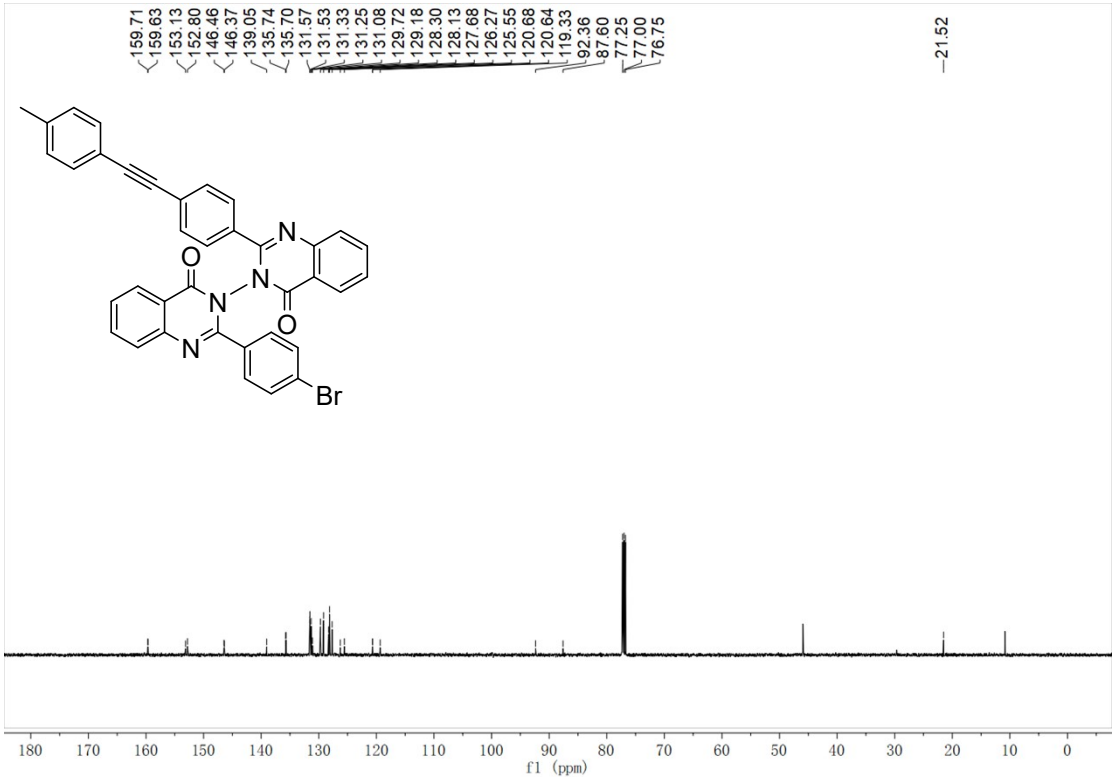
(*S*)-2,2'-bis(4'-methyl-[1,1'-biphenyl]-4-yl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (4)



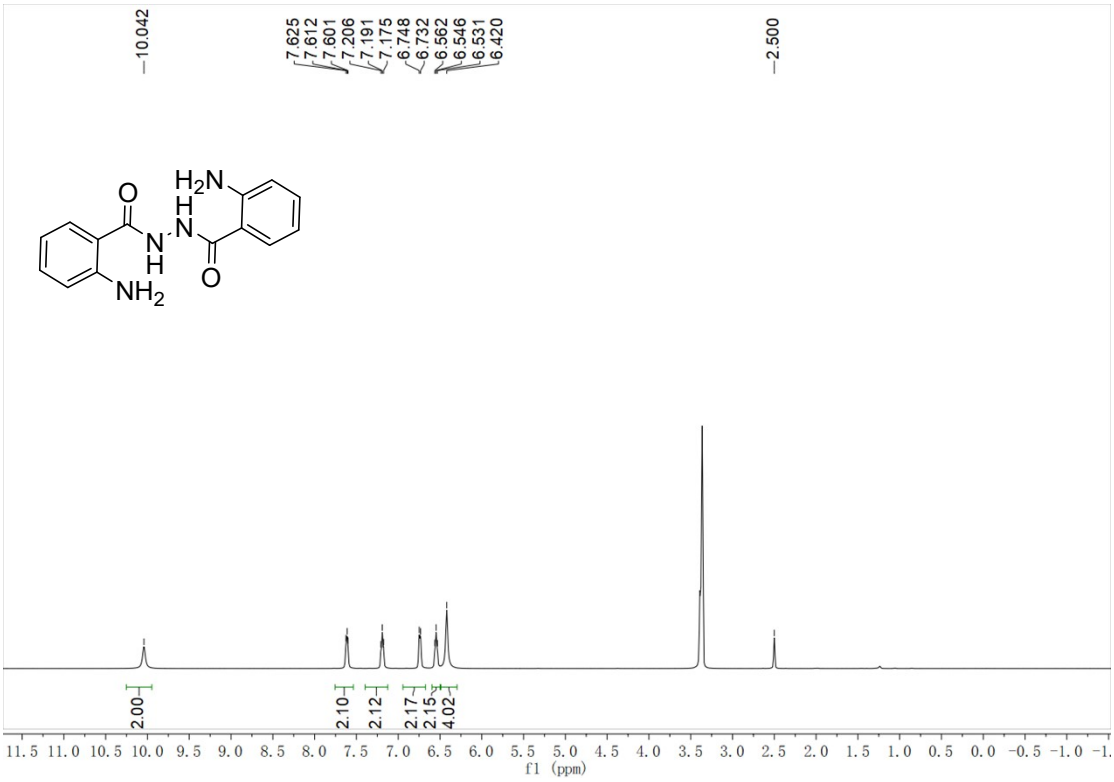


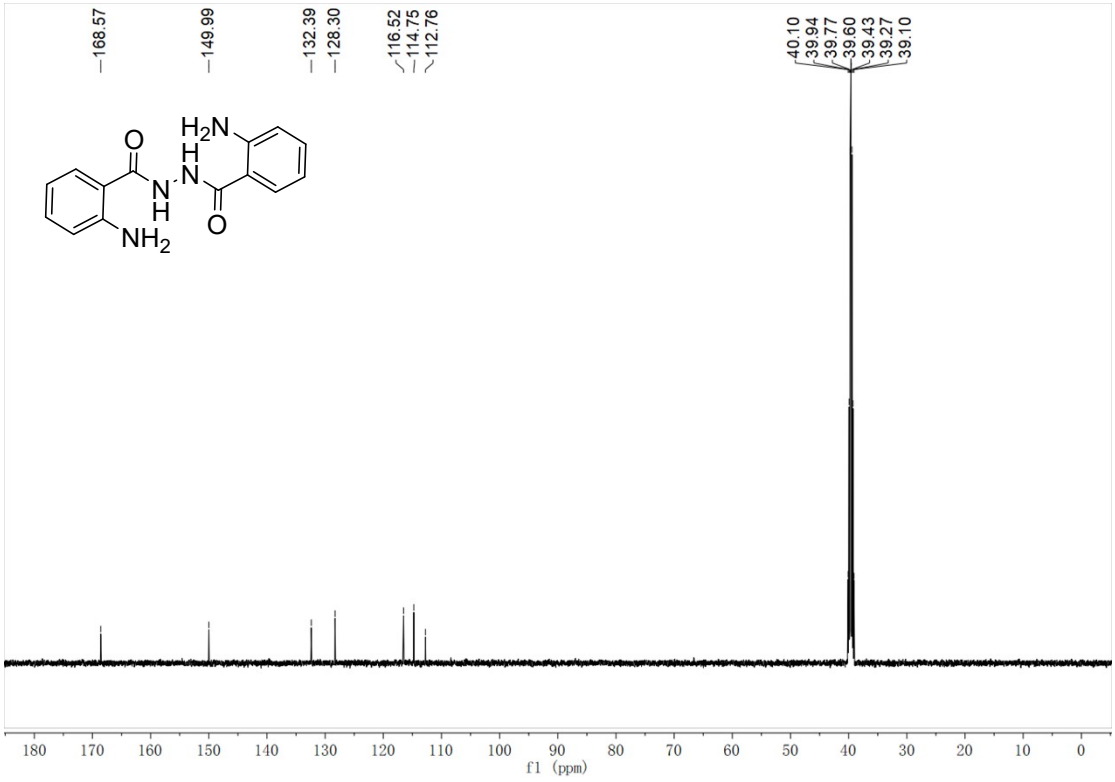
(*S*)-2-(4-bromophenyl)-2'-(4-(p-tolylethynyl)phenyl)-4*H*,4'*H*-[3,3'-biquinazoline]-4,4'-dione (5)



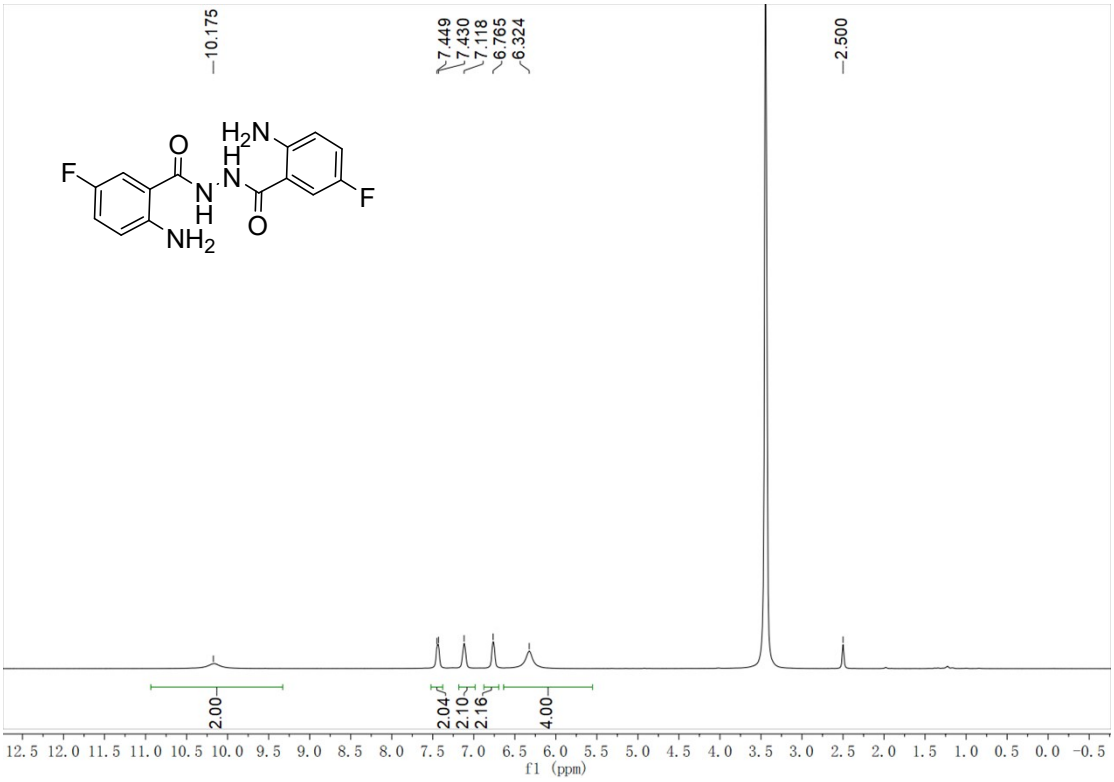


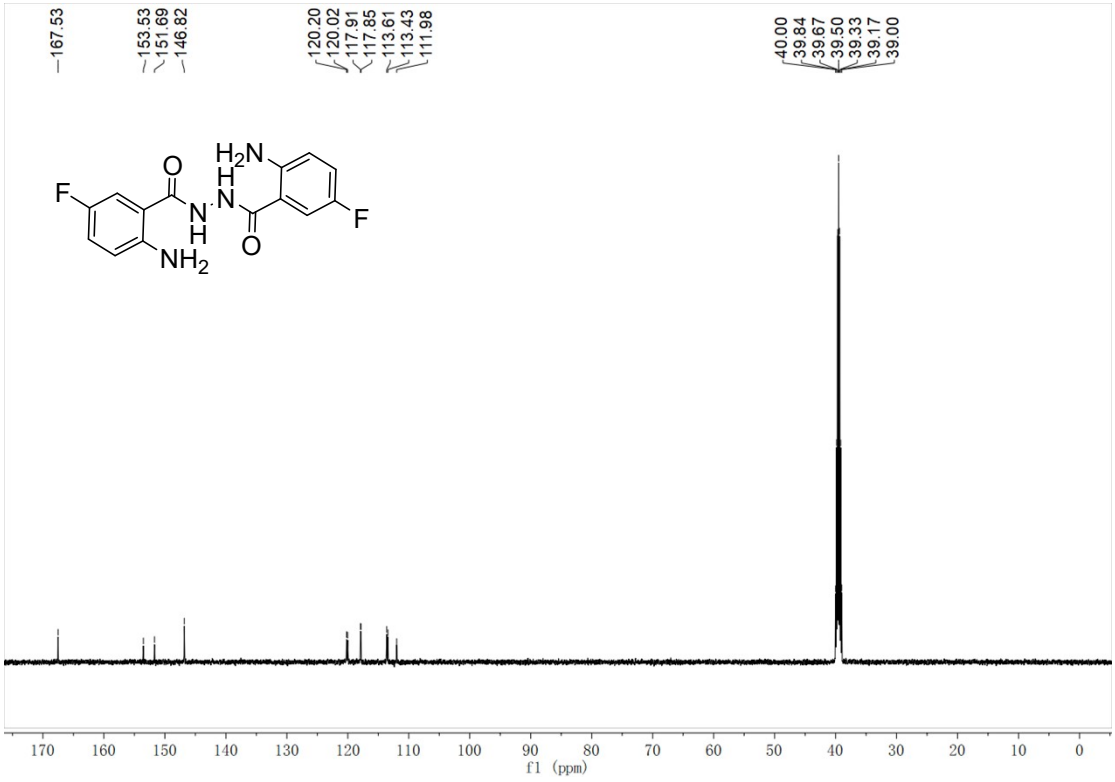
2-amino-*N*'-(2-aminobenzoyl)benzohydrazide (1a)



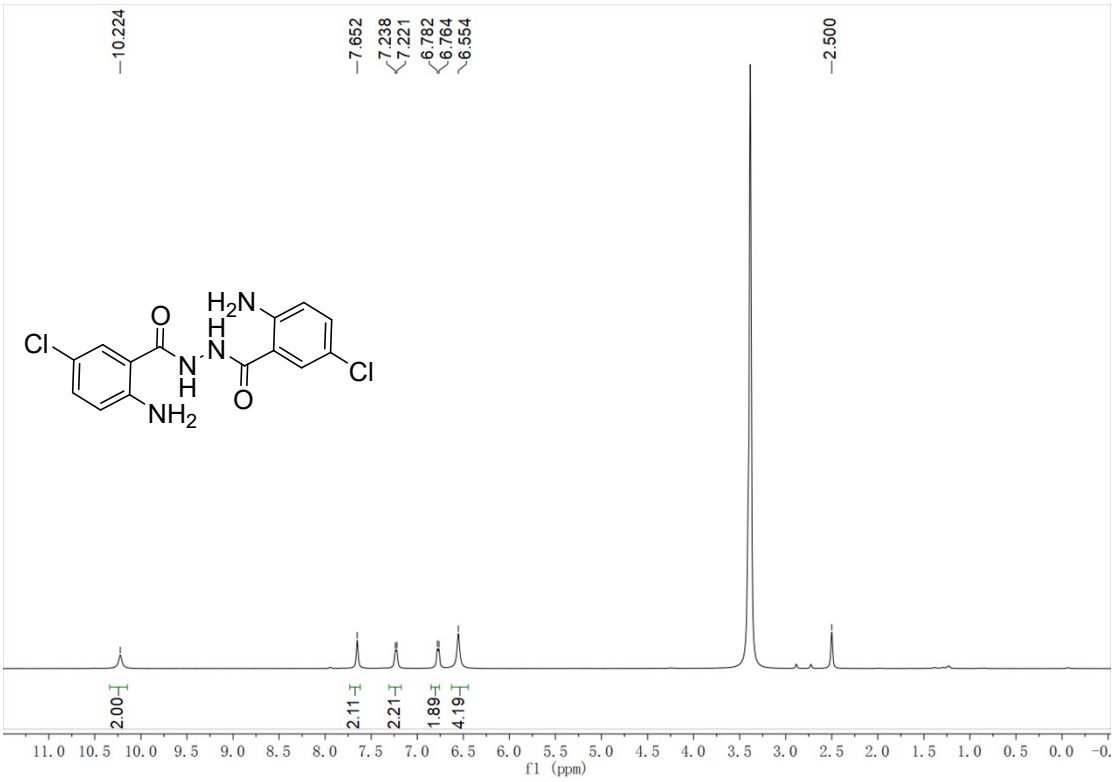


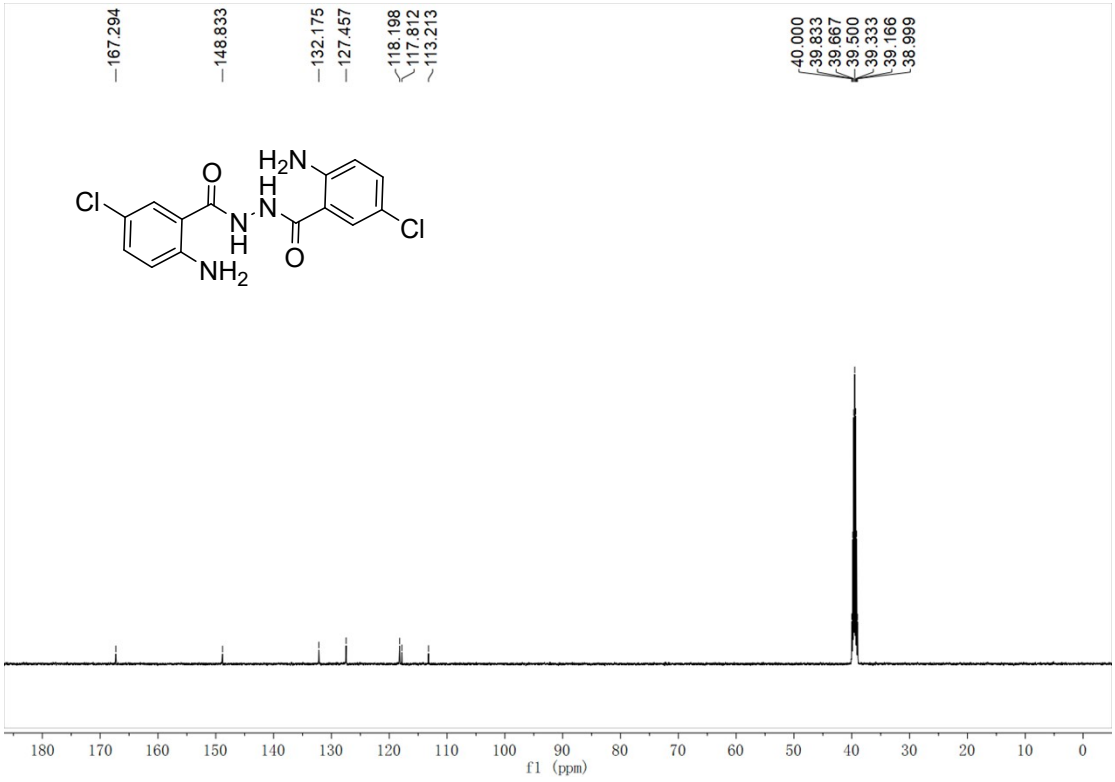
2-amino-*N*'-(2-amino-5-fluorobenzoyl)-5-fluorobenzohydrazide (1b)



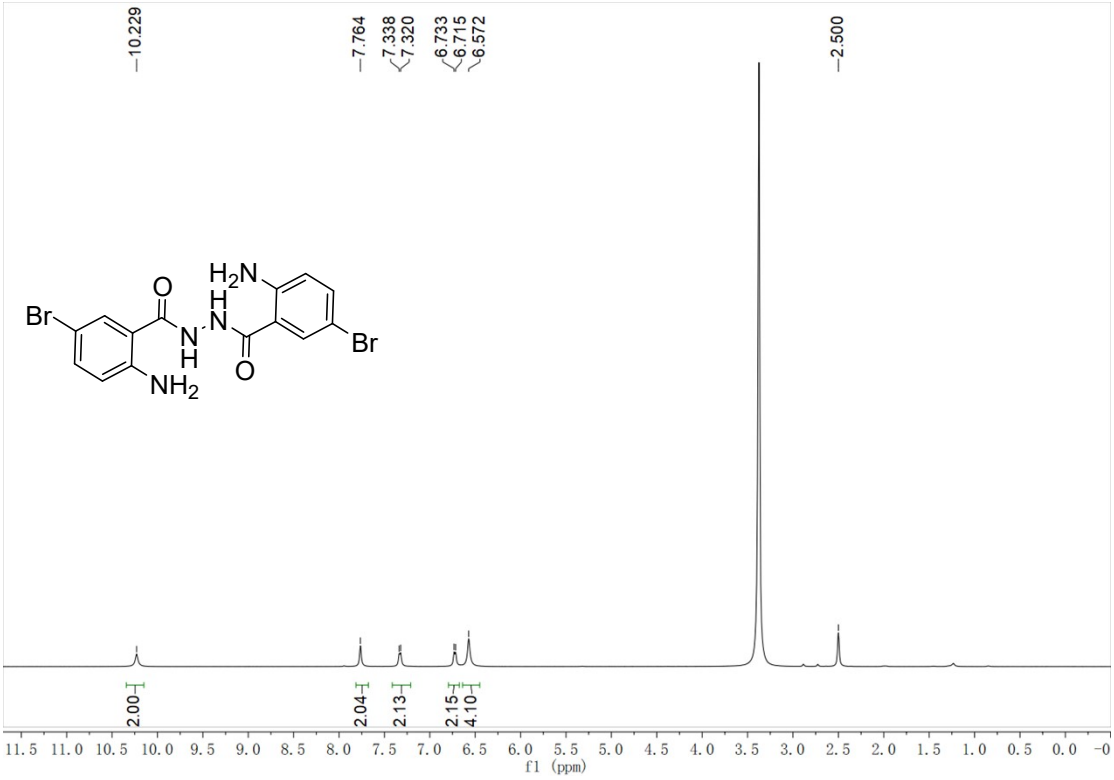


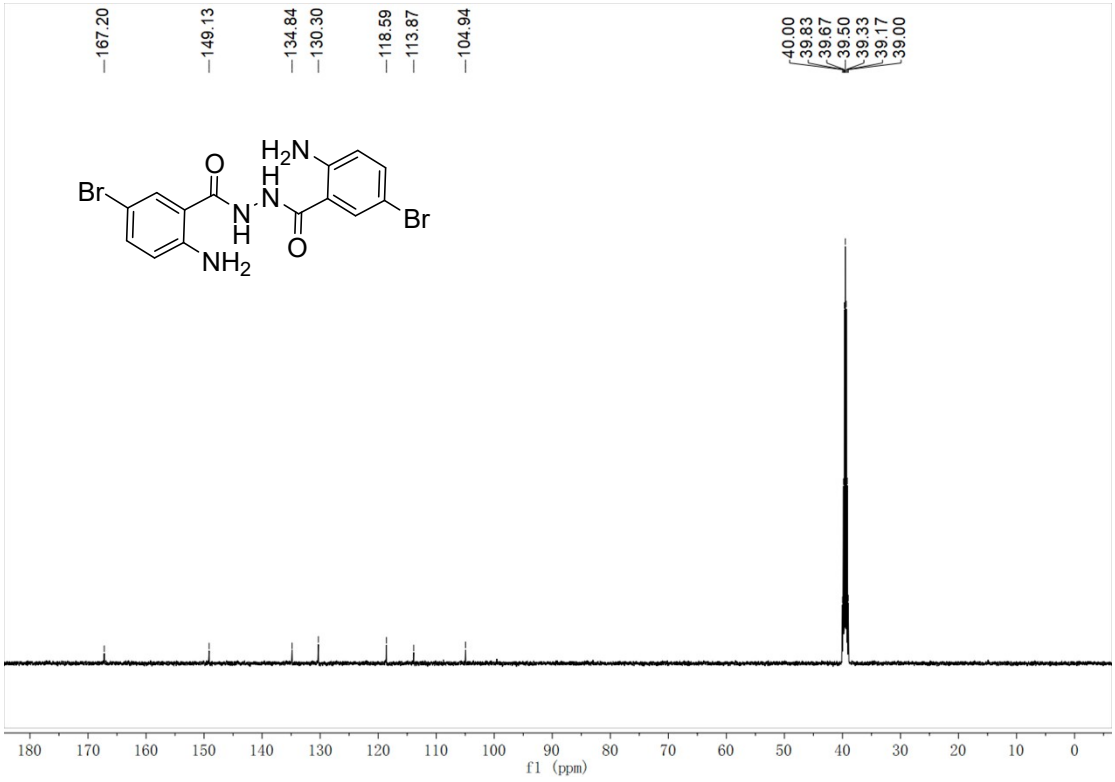
2-amino-*N*'-(2-amino-5-chlorobenzoyl)-5-chlorobenzohydrazide (1c)



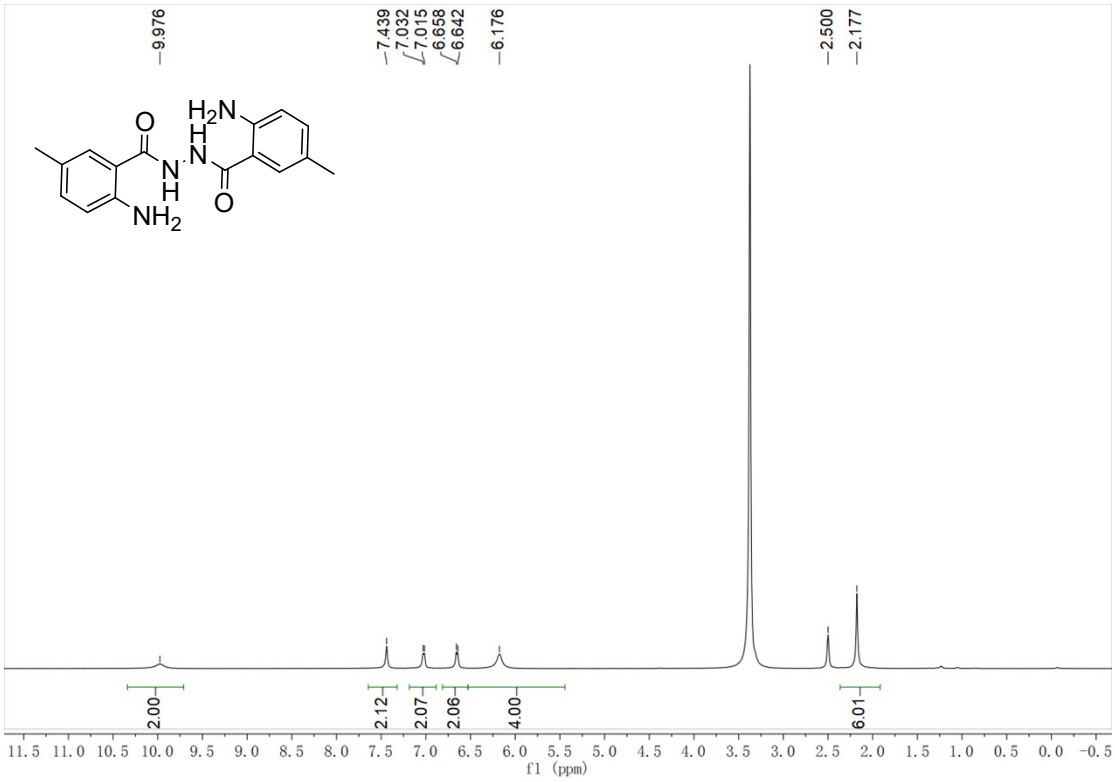


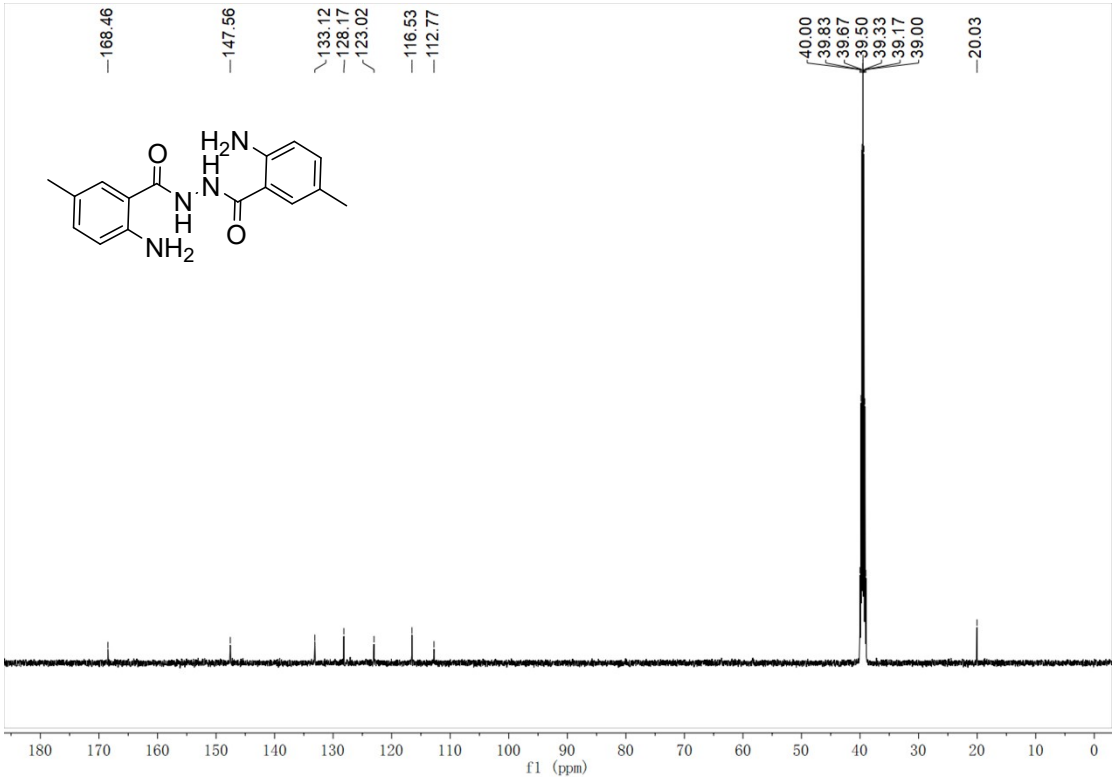
2-amino-*N*'-(2-amino-5-bromobenzoyl)-5-bromobenzohydrazide (1d)





2-amino-*N*'-(2-amino-5-methylbenzoyl)-5-methylbenzohydrazide (1e)





2-amino-*N*'-(2-amino-4-chlorobenzoyl)-4-chlorobenzohydrazide (1f)