Helical Airflow synthesis of Quinoxalines: A Continuous and Efficient Mechanochemical Approach

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Figure S1. Spiral gas-solid two-phase flow device picture

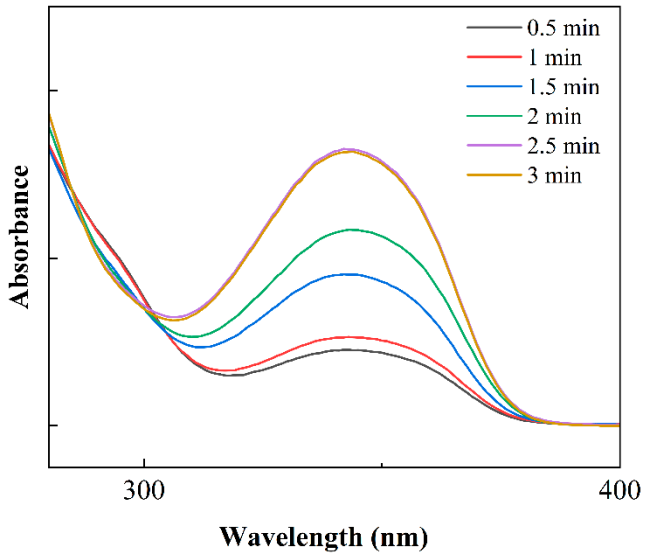


Figure S2. At 0.3 MPa, the UV-Visible absorption spectra of **1** changed with time

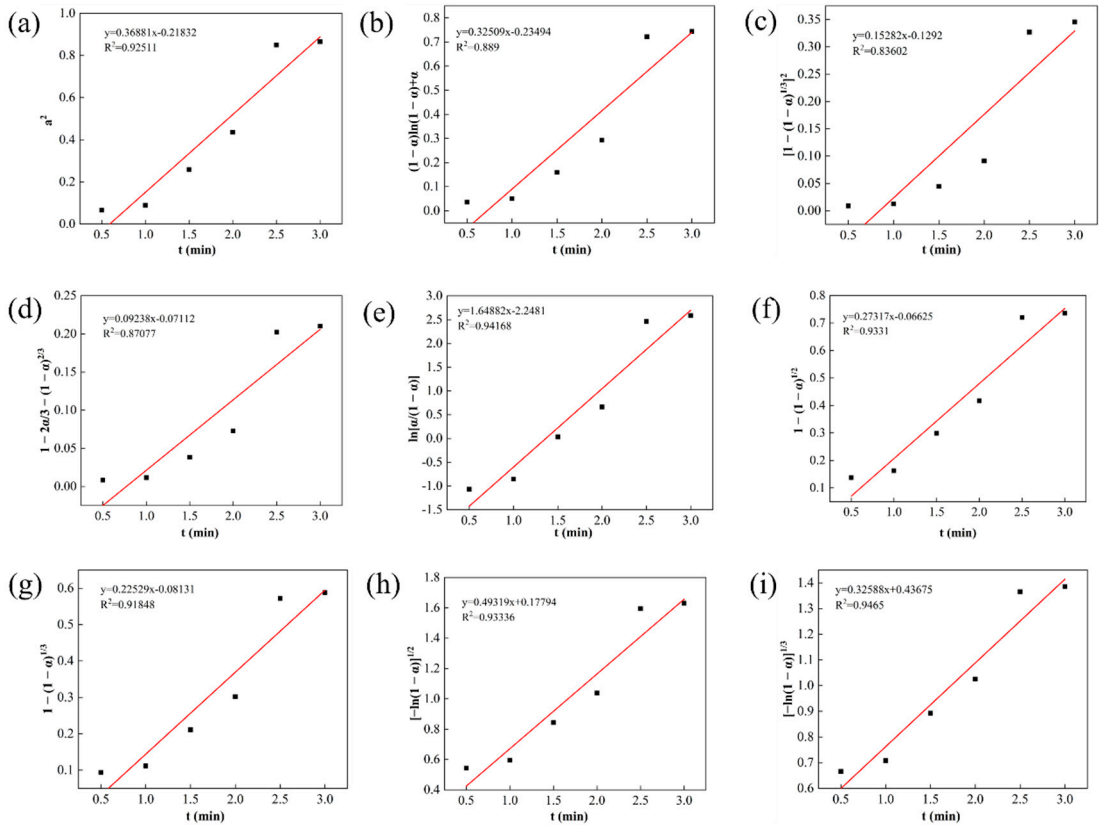


Figure S3. The fitting of It/Imax for the reaction of compound 1 after linearization to nine different models of solidstate reactivity: (a) the D1 model; (b) the D2 model; (c) the D3 model; (d) the D4 model; (e) the B1 model; (f) the R2 model; (g) the R3 model; (h) the A2 model; (i) the A3 model

Standard grinding procedure: At room temperature, a mixture of benzil and *o*-phenylenediamine was ground using an agate mortar. After 0.5 minutes of grinding, the resulting powder was analyzed by XRD.

General Procedure for the Synthesis of Quinoxaline Derivatives via the S-GSF Method： diamine (1.0 equivalent, 6 mmol) and diketone (1.0 equivalent, 6 mmol) were premixed using a mortar. The carrier gas pressure and feed gas pressure were adjusted to 0.8 and 0.84 MPa, respectively, and the premixed raw materials were added to the feeding funnel through the feeder. After the reaction was completed, the product was collected in the collection tank. Following vacuum drying to remove the byproduct water, the product could be used without further purification.

2,3-diphenylquinoxaline (1): Color=White solid（93% yield）; mp=124~126 ℃ (lit. 129~130 ℃)[11]; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.21 (dd, J = 6.4, 3.4 Hz, 2H), 7.79 (dd, J = 6.4, 3.4 Hz, 2H), 7.55 – 7.51 (m, 4H), 7.39 – 7.32 (m, 6H).; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 153.4, 141.2, 139.0, 129.9, 129.8, 129.2, 128.8, 128.2; IR

(KBr):3053, 1601, 1441, 1344, 770 cm^{-1}

6-chloro-2,3-diphenylquinoxaline (2)

Using 0.86 g of 4-chloro-1,2-phenylenediamine and 1.32 g of benzil as starting materials, the reaction was completed within 3 minute with a yield of 92%.

Color= purple solid；mp=119~122 ℃ (lit. 119~121 ℃)[24]; ^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm) 8.18 (d, J = 2.3 Hz, 1H), 8.11 (d, J = 8.8 Hz, 1H), 7.71 (dd, J = 8.9, 2.3 Hz, 1H), 7.53 – 7.49 (m, 4H), 7.41 – 7.32 (m, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ (ppm) 154.3, 153.6, 141.5, 139.7, 138.7, 138.6, 135.6, 130.9, 130.4, 129.8, 129.8, 129.1, 129.0, 128.3, 128.3, 128.1. IR (KBr):3056, 1606, 1551, 1347, 697 cm^{-1}

6,7-dimethyl-2,3-diphenylquinoxaline (3)

Using 0.82 g of 4,5-dimethyl-1,2-phenylenediamine and 1.32 g of benzil as starting materials, the reaction was completed within 1 minute with a yield of 98%.

Color= yellow solid；mp=166~168 ℃; ^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm) 7.93 (s, 2H), 7.54 – 7.47 (m, 4H), 7.37 – 7.29 (m, 6H), 2.52 (s, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ (ppm) 152.5, 140.5, 140.2, 139.4, 134.8, 129.9, 129.8, 129.0, 128.5, 128.2, 128.1, 20.4. IR (KBr):3046, 1628, 1446, 1344, 780 cm^{-1}

Phenanthro[9,10-b]quinoxaline (4)

Using 0.68 g of 1,2-phenylenediamine and 1.25 g of phenanthrenequinone as starting materials, the reaction was completed within 1 minute with a yield of 98%.

Color= brown solid；mp=222~224 ℃ (lit. 300~302 ℃)11; ^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm) 9.40 (dd, J = 7.9, 1.5 Hz, 2H), 8.55 (dd, J = 8.0, 1.2 Hz, 2H), 8.35 – 8.28 (m, 2H), 7.8 – 7.81 (m, 2H), 7.81 – 7.76 (m, 2H), 7.76 – 7.71 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ (ppm) 142.4, 142.1, 132.0, 130.3, 130.2, 129.7, 129.4, 127.8, 126.2, 122.8. IR (KBr):3060, 1605, 1498, 1356, 767 cm^{-1}

acenaphtho[1,2-b]quinoxaline (5)

Using 0.68 g of 1,2-phenylenediamine and 1.09 g of acenaphthenequinone as starting materials, the reaction was completed within 1 minute with a yield of 98%.

Color= yellow solid；mp=241~242 ℃ (lit. 240~242 ℃)[11]; ^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm) 8.44 (d, J = 7.1 Hz, 2H), 8.26 – 8.20 (m, 2H), 8.11 (d, J = 8.2 Hz, 2H), 7.85 (dd, J = 8.2, 6.9 Hz, 2H), 7.80 – 7.74 (m, 2H). ^{13}C NMR (151 MHz,

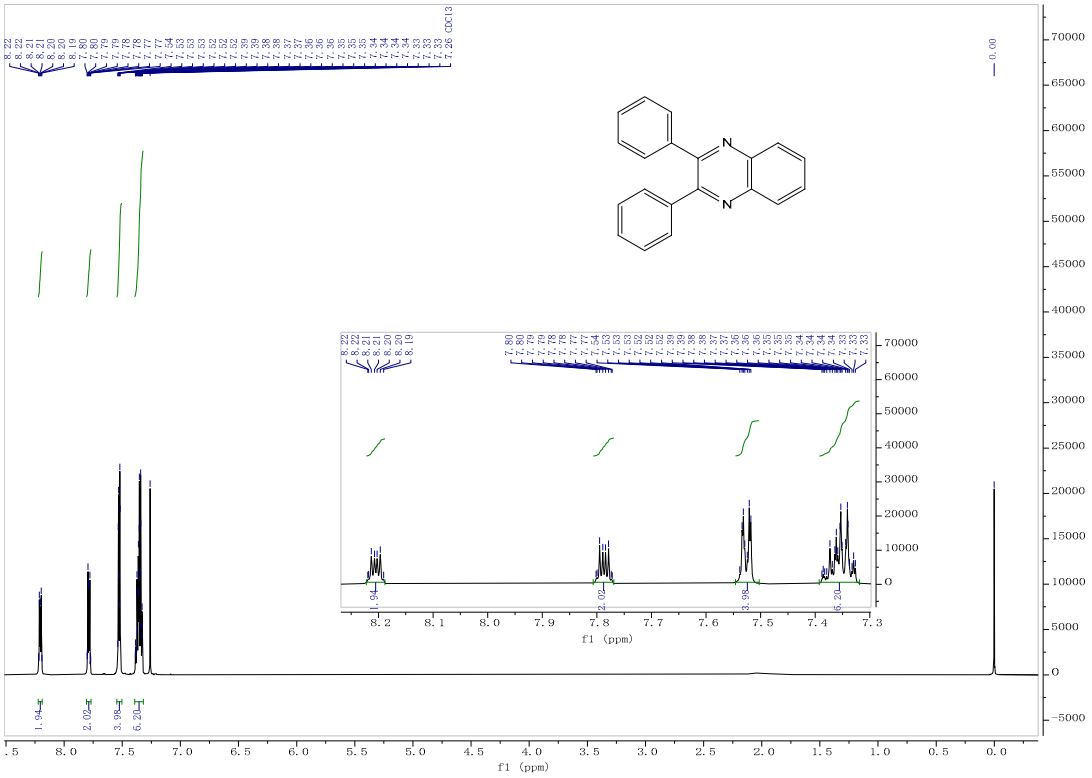
Chloroform-*d*) δ (ppm) 154.0, 141.2, 136.5, 131.8, 130.0, 129.5, 129.5, 129.2, 128.6, 121.9. IR (KBr):3049, 1614, 1571, 1298, 759 cm^{-1}

9-chloroacenaphtho[1,2-b]quinoxaline (6)

Using 0.86 g of 4-chloro-1,2-phenylenediamine and 1.09 g of acenaphthenequinone as starting materials, the reaction was completed within 1 minute with a yield of 98%.

Color= brown solid；mp=228~230 ℃; ^{1}H NMR (600 MHz, Chloroform-*d*) δ (ppm) 8.39 (t, J = 6.5 Hz, 2H), 8.18 (d, J = 2.3 Hz, 1H), 8.14 – 8.09 (m, 3H), 7.87 – 7.81 (m, 2H), 7.68 (dd, J = 8.8, 2.4 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ (ppm) 154.7, 154.1, 141.6, 139.7, 136.6, 134.7, 131.4, 131.4, 130.6, 130.0, 129.8, 129.8, 129.6, 128.7128.6, 122.2, 122.0. IR (KBr):3051, 1615, 1430, 1298, 780 cm^{-1}

Reproduction of ^{1}HNMR and ^{13}CNMR spectra of representative quinoxaline (1-6)



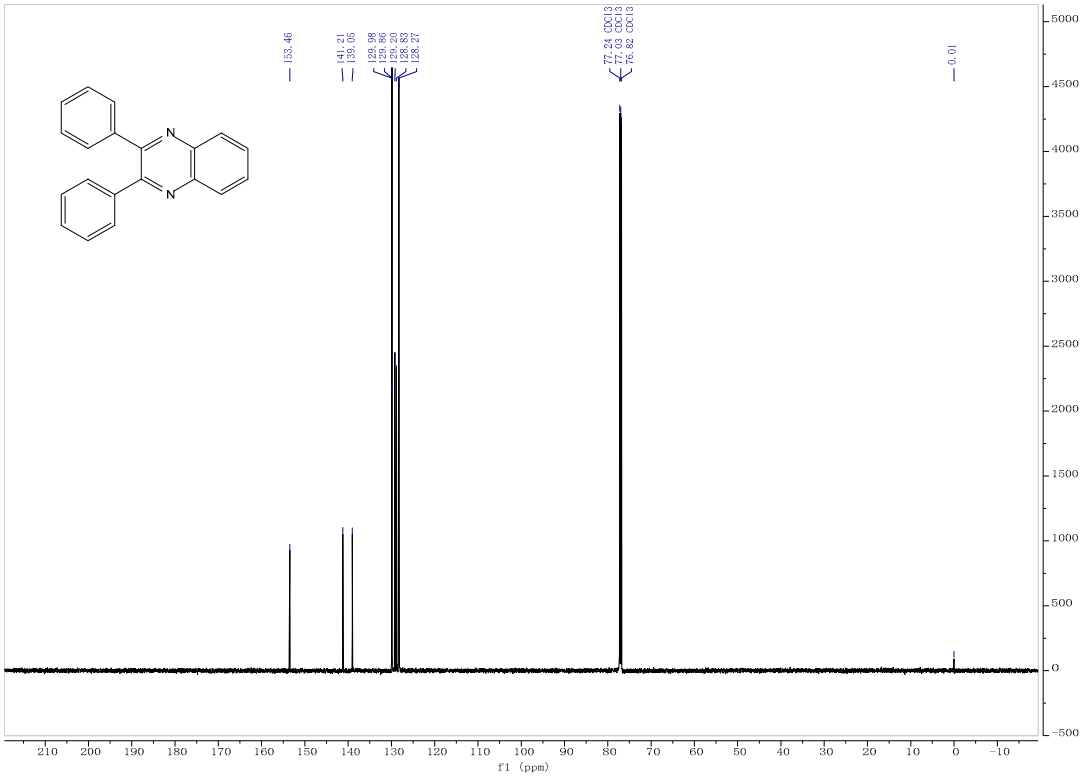


Figure S4. ^{1}HNMR (600 MHz, $CDCl_3$) and ^{13}CNMR (151 MHz, $CDCl_3$) spectral reproduction of 2,3-diphenylquinoxaline (1).

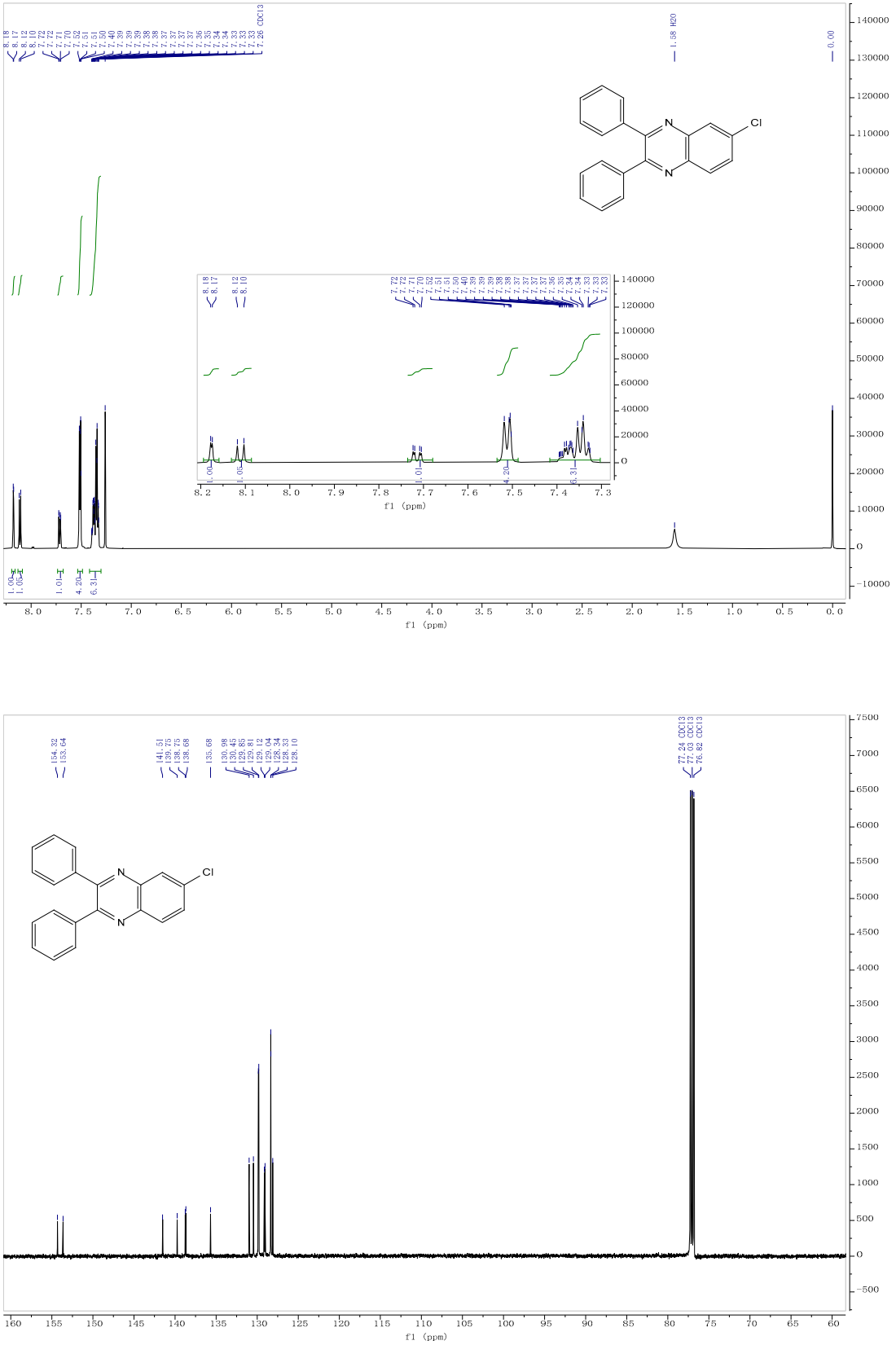
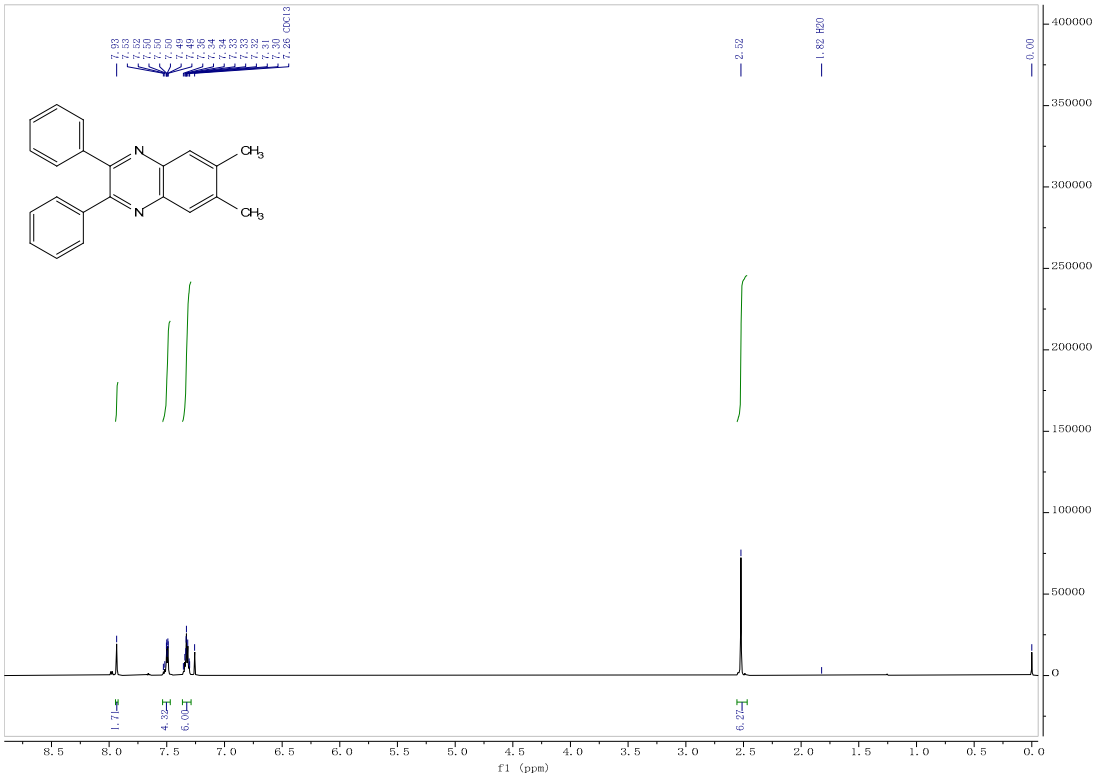


Figure S5. ^{1}HNMR (600 MHz, $CDCl_3$) and ^{13}CNMR (151 MHz, $CDCl_3$) spectral reproduction of 6-chloro-2,3-diphenylquinoxaline (2).



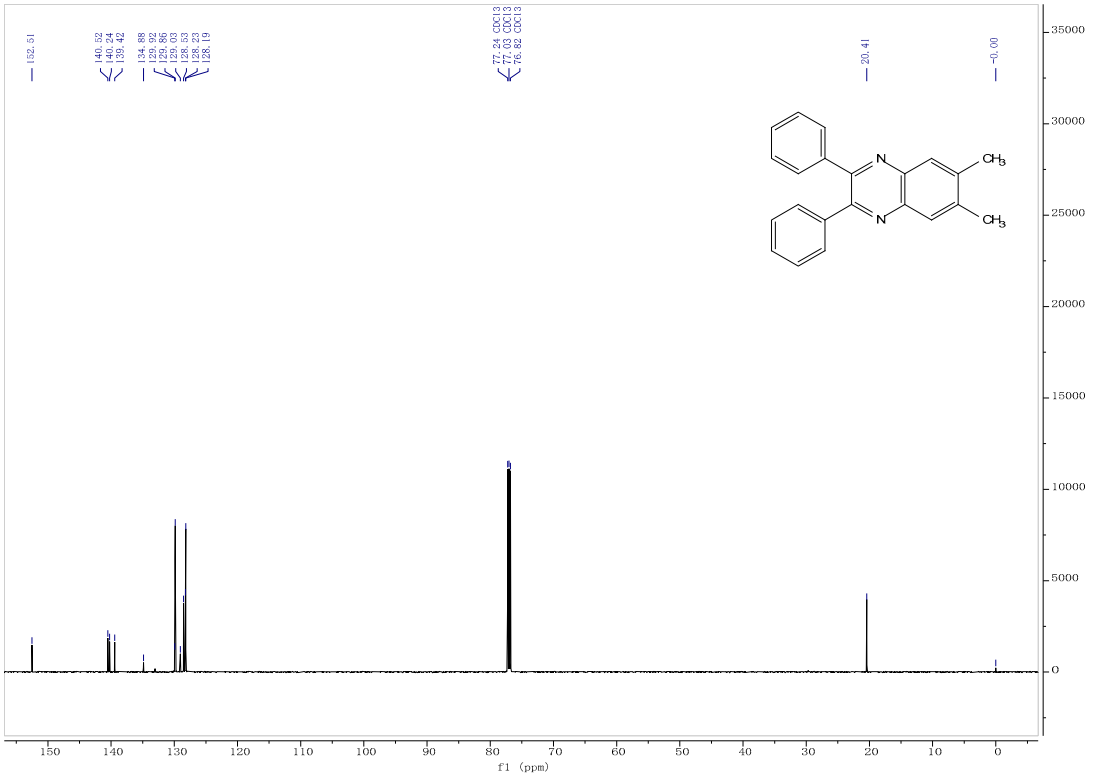
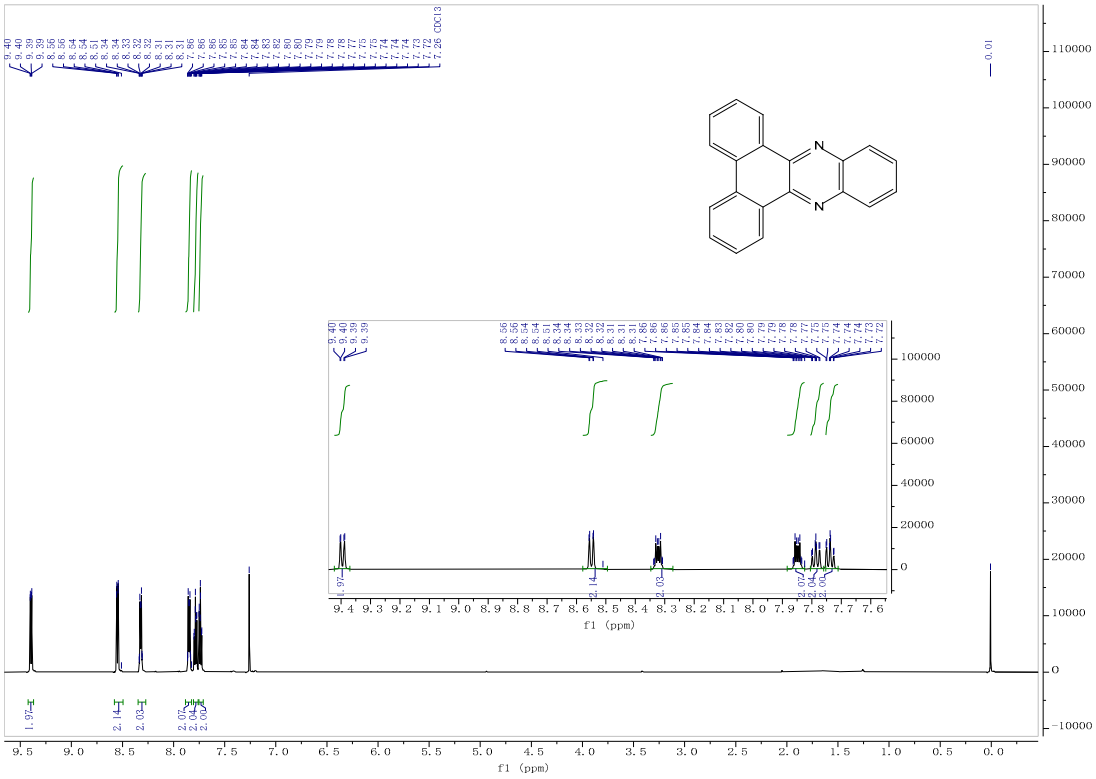


Figure S6. ^{1}HNMR (600 MHz, $CDCl_3$) and ^{13}CNMR (151 MHz, $CDCl_3$) spectral reproduction of 6,7-dimethyl-2,3-diphenylquinoxaline (3).



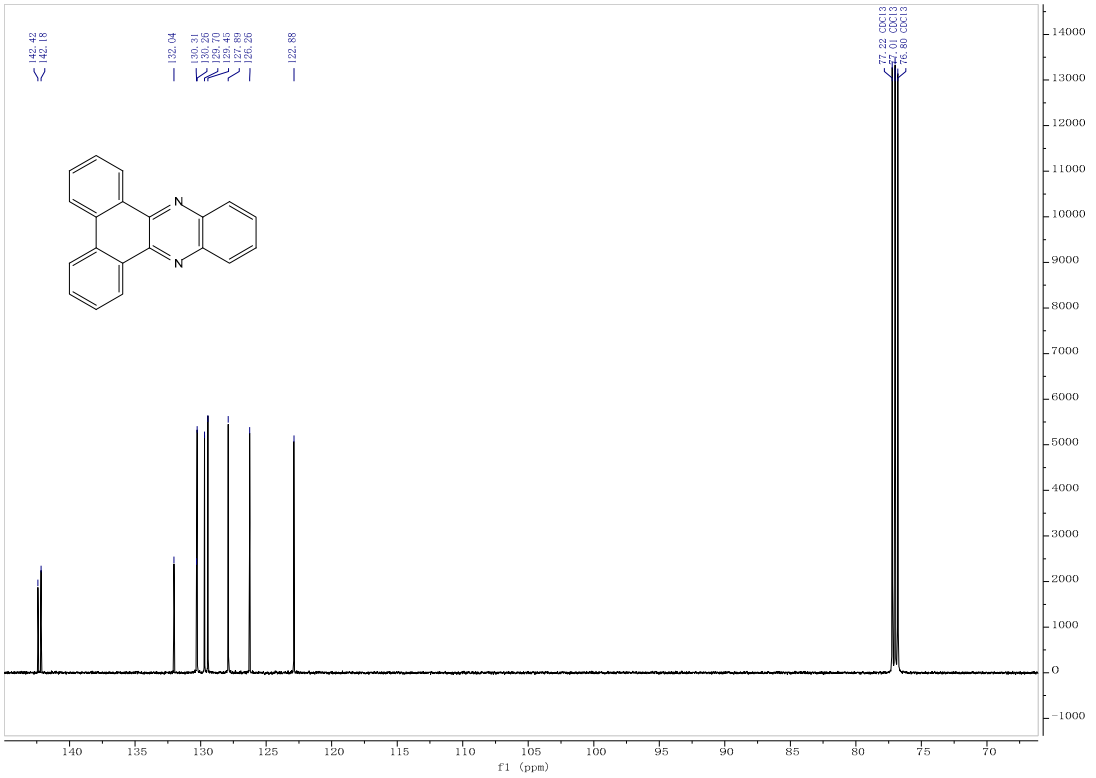
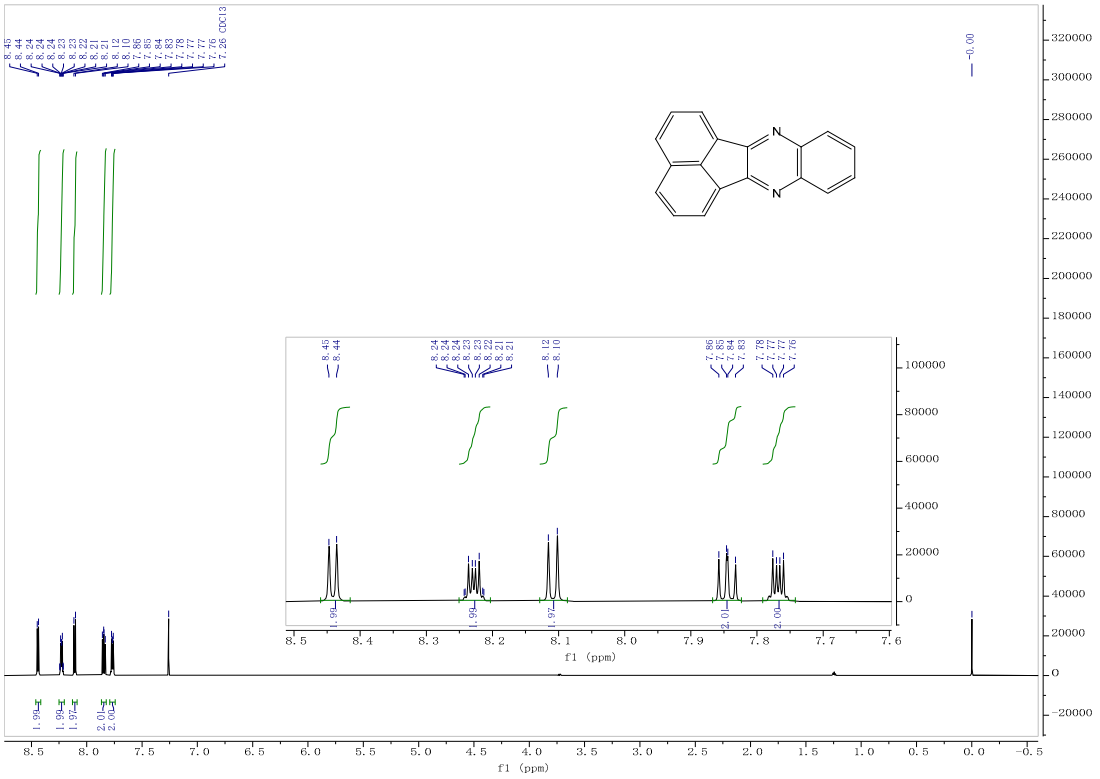


Figure S7. ^{1}HNMR (600 MHz, $CDCl_3$) and ^{13}CNMR (151 MHz, $CDCl_3$) spectral reproduction of Phenanthro[9,10-b]quinoxaline (4).



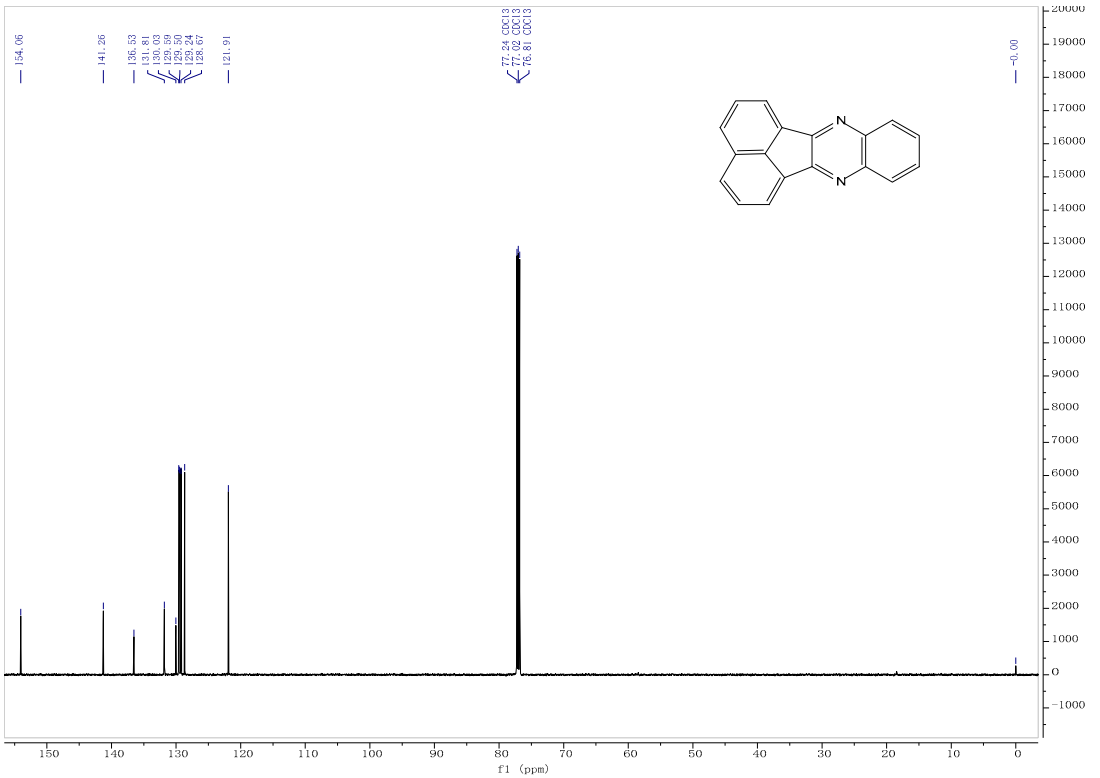


Figure S8. ^{1}HNMR (600 MHz, $CDCl_3$) and ^{13}CNMR (151 MHz, $CDCl_3$) spectral reproduction of acenaphtho[1,2-b]quinoxaline (5).

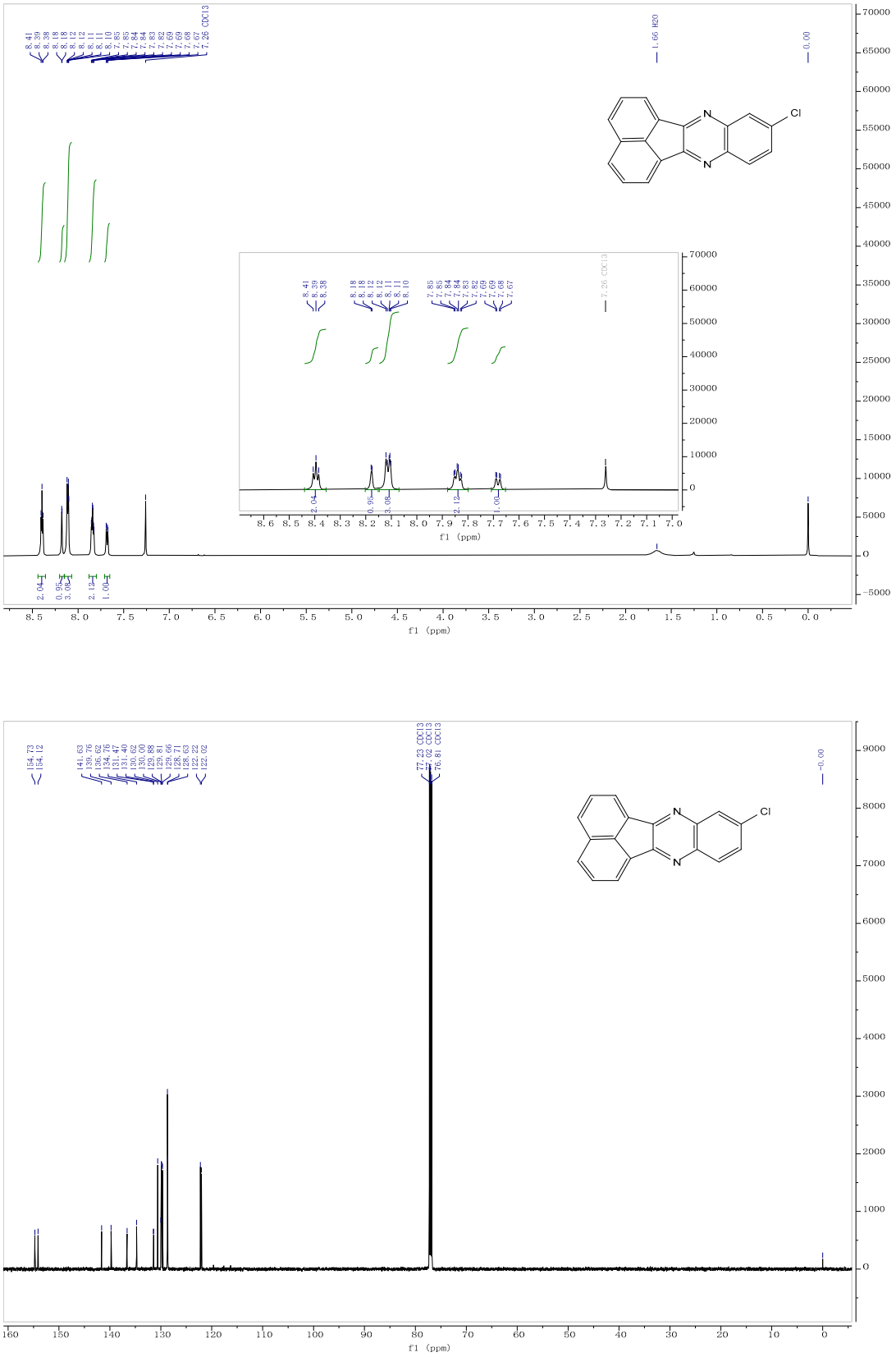


Figure S9. ^{1}HNMR (600 MHz, $CDCl_3$) and ^{13}CNMR (151 MHz, $CDCl_3$) spectral reproduction of 9-chloroacenaphtho[1,2-b]quinoxaline (6)

Reference

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