

Supporting information for

Visible-light-photocatalysis driven denitrogenative/radical 1,3-shift of benzotriazole: access to 3-aryl-aminoquinoxalin-2(1*H*)-ones scaffolds

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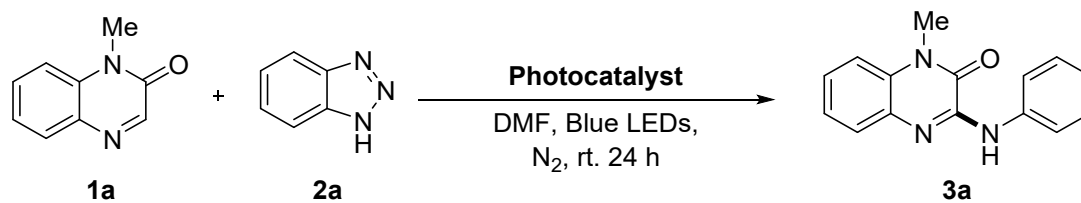
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1. General information

All the starting materials were obtained from commercial sources and used without further purification unless otherwise stated. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 MHz and 100 MHz, respectively) instrument internally referenced to SiMe_4 , chloroform or dimethyl sulfoxide signals. Chemical shifts are referenced to solvent residual peak (2.50 ppm ^1H , 39.50 ppm ^{13}C for DMSO- d_6 , and 0 ppm ^1H for tetramethylsilane, 77.00 ppm ^{13}C for CDCl_3). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br (broad singlet). Coupling constants (J) were reported in Hertz (Hz). All high resolution mass spectra were obtained on a Thermo LTQ mass spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 or 365 nm. Flash chromatographic separations were performed on Merck 60 (200-300) mesh silica gel.

2. Optimization of reaction conditions

Table S1: Optimization of photocatalyst ^a



Entry	Photosensitizer (x mol%)	Yield ^b (%)
1	Eosin B (5 mol%)	45
2	Eosin Y (5 mol%)	trace
3	Rose bengal (5 mol%)	56
4	Eosin Y Disodium Salt (5 mol%)	49
5	TiO ₂ (5 mol%)	N.R.
6	Ru(bpy) ₃ Cl ₂ (5 mol%)	N.R.
7	Co(bpy) ₃ (PF ₆) ₂ (5 mol%)	trace
8	Fe(bpy) ₃ (PF ₆) ₂ (5 mol%)	trace
9	Ni(bpy) ₃ (PF ₆) ₂ (5 mol%)	N.R.
10 ^c	Rose bengal (5 mol%)	29
11 ^d	Rose bengal (5 mol%)	N.R.
12	-	N.R.
13	Rose bengal (10 mol%)	52
14	Rose bengal (20 mol%)	54

^a Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), photocatalyst, in DMF (1.0 mL) under 35 W Blue LEDs irradiation at room temperature for 24 h in N₂ atmosphere. ^b Isolated yield based on **1a**.

^c Air. ^d Dark.

Table S2: Optimization of solvent ^a

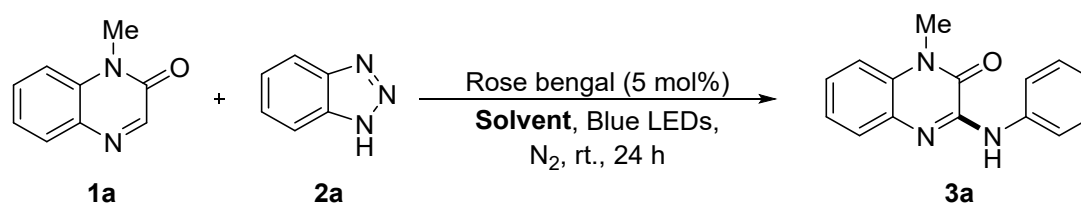
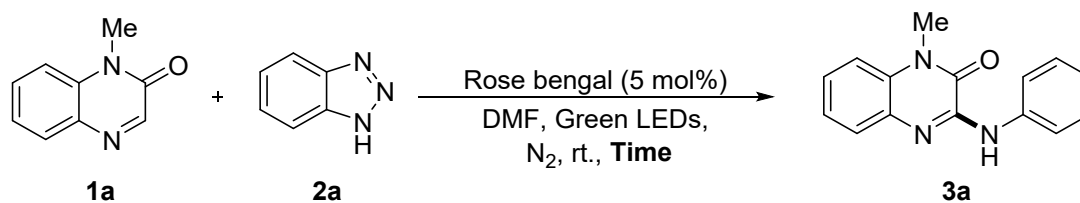
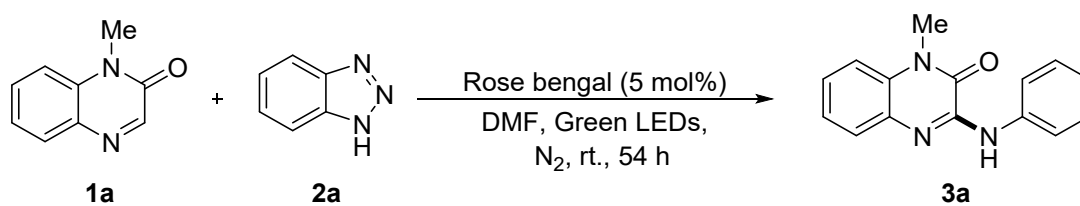


Table S4: Optimization of time ^a

Entry	Time (h)	Yield ^b (%)
1	8	21
2	16	43
3	24	62
4	32	65
5	40	68
6	54	71
7	72	69
8	80	67

^a Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), Rose bengal (5 mol%) in DMF (1.0 mL) under 35 W Green LEDs irradiation at room temperature for indicate time in N₂ atmosphere. ^b Isolated yield based on **1a**.

Table S5: Optimization of others ^a

Entry	1a/2a	DMF (x mL)	Yield ^b (%)
1	1:1.5	1.0	71
2	1:2	1.0	73
3	1:2.5	1.0	72
4	1:3	1.0	78
5	1.5:1	1.0	66
6	2:1	1.0	50

Entry	1a/2a	DMF (x mL)	Yield ^b (%)
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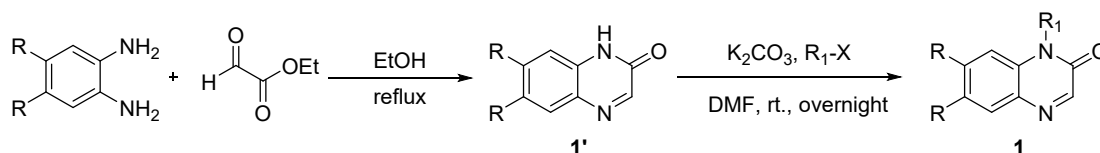
7	1:3	0.5	72
8	1:3	1.1	70
9	1:3	0.9	80
10	1:3	0.8	85
11	1:3	0.7	75

^a Reaction conditions: **1a** (0.1 mmol), **2a**, Rose bengal (5 mol%) in DMF under 35 W Green LEDs irradiation at room temperature for 54 h in N₂ atmosphere. ^b Isolated yield based on the few of **1a** and **2a**.

3. Preparation of Substrates

Substrates **1a-1t**, **1v-1y** were prepared according to the reported literature. [1]

To a suspension of *o*-arylenediamine (5 mmol) in ethanol (10 mL) was added ethyl 2-oxoacetate (50% solution in toluene) (5.5 mmol). The mixture was stirred at 80 °C reflux for 1h, then at room temperature overnight. The precipitated solid was filtered and repeat rinsing a few times until the solids turn white, then dried to give quinoxalinone **1'**. To a suspension of quinoxalinone **1'** (5 mmol) in DMF (8 mL) was added potassium carbonate (6 mmol) and the corresponding halogenoalkane (8 mmol). The mixture was stirred at room temperature overnight. Ethyl acetate and water were added. The aqueous layer was extracted twice with EtOAc. The combined organic layers were over MgSO₄, filtered and evaporated under reduced pressure. The residue is purified by flash chromatography over silica gel to afford the Desired product **1**.

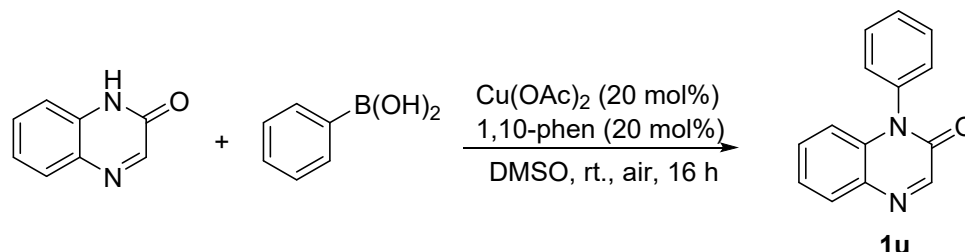


Scheme S1. synthesis of quinoxalinones

Substrates **1u** were prepared according to the reported literature. [2]

In a dry round-bottomed flask were added magneton, quinoxalin-2(1*H*)-one (5 mmol, 1.0 equiv.), phenylboronic acid (7.5 mmol, 1.5 equiv.), copper acetate (1 mmol, 20 mol%), 1, 10-phenanthroline (1 mmol, 20 mol%) and dimethyl sulfoxide (5 mL), the mixture was stirred at room temperature for 16 h. After the reaction was completed, the

mixture was extracted with ethyl acetate and water, and the aqueous layer was extracted twice with ethyl acetate. The combined organic layers were dried over MgSO₄, filtered, evaporated under reduced pressure, and the residue was purified by flash chromatography on silica gel to give the desired product **1u**.



Scheme S2. synthesis of 1-phenylquinoxalin-2(1*H*)-one

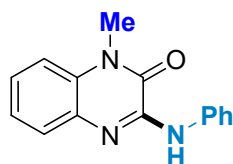
4. Typical procedure for the synthesis of 3-aryl-aminoquinoxalin-2(1*H*)-ones



To an over-dried reaction tube equipped with a magnetic stir bar was charged with quinoxaline-2(1*H*)-ones (**1**, 0.1 mmol), 1*H*-Benzotriazole (**2**, 0.3 mmol), Rose bengal (5.0 mg, 5 mol%), DMF (0.8 mL). The solution was stirred at room temperature with the irradiation of a 35 W Green LEDs for 54 h. After the reaction was completed, the resulting mixture was extracted with ethyl acetate (5.0 mL×3). The combined organic extracts were dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to obtain the desired pure product.

Characterization data for the products

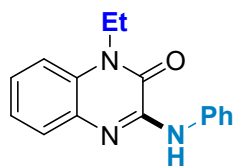
1-Methyl-3-(phenylamino)quinoxalin-2(1*H*)-one (**3a**)



The reaction was conducted with 1-methylquinoxalin-2(1*H*)-one (**1a**, 16.0 mg, 0.1 mmol) and 1*H*-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 5:1) to provide 21.3 mg, 85% yield of **3a** as white solid. m.p.: 175-177 °C.

¹H NMR (400 MHz, CDCl₃, ppm) δ 8.45 (br, 1H, N-H), 7.95 (d, *J* = 7.6 Hz, 2H), 7.69 (m, 1H), 7.39 (t, *J* = 8 Hz, 2H), 7.31 (m, 2H), 7.24 (m, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 3.76 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 152.0, 145.8, 138.9, 133.2, 129.8, 129.0, 127.1, 125.2, 124.3, 123.2, 119.3, 113.6, 29.7. HRMS (ESI) *m/z* calcd for C₁₅H₁₃N₃ONa [M+Na]⁺ 274.0956, found 274.0910.

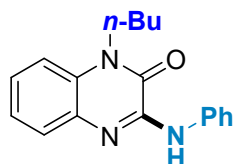
1-Ethyl-3-(phenylamino)quinoxalin-2(1*H*)-one (**3b**)



The reaction was conducted with 1-ethylquinoxalin-2(1*H*)-one (**1b**, 17.4 mg, 0.1 mmol) and 1*H*-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 5:1) to provide 21.1 mg, 80% yield of **3b** as light yellow solid. m.p.: 136-137 °C.

¹H NMR (400 MHz, CDCl₃, ppm) δ 8.48 (br, 1H, N-H), 7.95 (d, *J* = 7.6 Hz, 2H), 7.73-7.71 (m, 1H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.33-7.28 (m, 3H), 7.10 (t, *J* = 7.4 Hz, 1H), 4.41-4.35 (m, 2H), 1.42 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 151.3, 145.8, 138.9, 133.5, 128.9, 128.5, 127.4, 125.2, 124.1, 123.1, 119.2, 113.4, 37.8, 12.4. HRMS (ESI)*m/z* calcd for C₁₆H₁₆N₃O [M+H]⁺ 266.1293, found 266.1252.

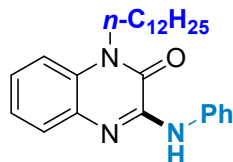
1-Butyl-3-(phenylamino)quinoxalin-2(1*H*)-one (**3c**)



The reaction was conducted with 1-butylquinoxalin-2(1*H*)-one (**1c**, 20.2 mg, 0.1 mmol) and 1*H*-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 10:1) to provide 23.7 mg, 81% yield of **3c** as colorless liquid.

¹H NMR (400 MHz, CDCl₃, ppm) δ 8.45 (br, 1H, N-H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.71-7.69 (m, 1H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.33-7.28 (m, 2H), 7.27-7.25 (m, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 4.31 (t, *J* = 7.8 Hz, 2H), 1.81-1.75 (m, 2H), 1.55-1.45 (m, 2H), 1.01 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 151.6, 145.8, 138.9, 133.5, 129.0, 128.8, 127.4, 125.2, 124.1, 123.8, 119.2, 113.6, 42.7, 29.3, 20.2, 13.8. HRMS (ESI)*m/z* calcd for C₁₈H₂₀N₃O [M+H]⁺ 294.1606, found 294.1572.

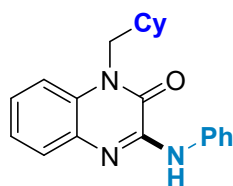
1-Dodecyl-3-(phenylamino)quinoxalin-2(1*H*)-one (**3d**)



The reaction was conducted with 1-dodecylquinoxalin-2(1*H*)-one (**1d**, 31.4 mg, 0.1 mmol) and 1*H*-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 30:1) to provide 27.1 mg, 67% yield of **3d** as white solid. m.p.: 77-78 °C.

¹H NMR (400 MHz, CDCl₃, ppm) δ 8.46 (br, 1H, N-H), 7.95 (d, *J* = 7.6 Hz, 2H), 7.71-7.69 (m, 1H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.31-7.29 (m, 2H), 7.24 (t, *J* = 1.8 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 4.30 (t, *J* = 7.8 Hz, 2H), 1.83-1.76 (m, 2H), 1.50-1.43 (m, 2H), 1.39-1.33 (m, 2H), 1.32-1.26 (m, 14H), 0.88 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 151.6, 145.8, 139.0, 133.5, 129.0, 128.9, 127.4, 125.2, 124.1, 123.1, 119.2, 113.6, 42.9, 31.9, 29.7, 29.6, 29.5, 29.5, 29.3, 29.3, 27.3, 27.0, 22.7, 14.1. HRMS(ESI)*m/z* calcd for C₂₆H₃₆N₃O [M+H]⁺ 406.2858, found 406.2828.

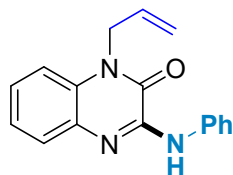
1-(Cyclohexylmethyl)-3-(phenylamino)quinoxalin-2(1H)-one (**3e**)



The reaction was conducted with 1-(cyclohexylmethyl)quinoxalin-2(1H)-one (**1e**, 24.2 mg, 0.1 mmol) and 1H-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 25:1) to provide 22.0 mg, 66% yield of **3e** as white solid. m.p.: 127-128 °C.

¹H NMR (400 MHz, CDCl₃, ppm) δ 8.48 (br, 1H, N-H), 7.95 (d, *J* = 7.6 Hz, 2H), 7.71-7.69 (m, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.30-7.28 (m, 2H), 7.25-7.22 (m, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 4.19 (d, *J* = 7.2 Hz, 2H), 1.75-1.65 (m, 5H), 1.25-1.10 (m, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 152.1, 145.7, 138.9, 133.4, 129.2, 129.0, 127.3, 125.0, 124.1, 123.1, 119.2, 114.0, 48.6, 36.4, 30.8, 26.1, 25.7. HRMS (ESI) *m/z* calcd for C₂₁H₂₄N₃O [M+H]⁺ 334.1919, found 334.1871.

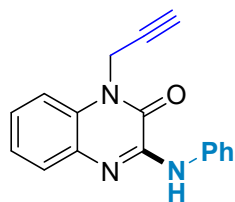
1-Allyl-3-(phenylamino)quinoxalin-2(1H)-one (**3f**)



The reaction was conducted with 1-allylquinoxalin-2(1H)-one (**1f**, 18.6 mg, 0.1 mmol) and 1H-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 5:1) to provide 18.0 mg, 65% yield of **3f** as white solid. m.p.: 153-154 °C.

¹H NMR (400 MHz, CDCl₃, ppm) δ 8.46 (br, 1H, N-H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.70-7.68 (m, 1H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.31-7.27 (m, 2H), 7.22-7.20 (m, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.01-5.92 (m, 1H), 5.28 (d, *J* = 10.4 Hz, 1H), 5.18 (d, *J* = 17.2 Hz, 1H), 4.95 (d, *J* = 4.8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 151.5, 145.7, 138.8, 133.3, 130.4, 128.9, 128.8, 127.2, 125.1, 124.3, 123.1, 119.2, 118.0, 114.1, 45.0. HRMS (ESI) *m/z* calcd for C₁₇H₁₆N₃O [M+H]⁺ 278.1293, found 278.1259.

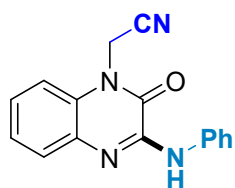
3-(Phenylamino)-1-(prop-2-yn-1-yl)quinoxalin-2(1H)-one (3g)



The reaction was conducted with 1-propargyl-quinoxalin-2(1H)-one (**1g**, 18.4 mg, 0.1 mmol) and 1H-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 3:1) to provide 19.2 mg, 70% yield of **3g** as light brown solid. m.p.: 243-245 °C.

¹H NMR (400 MHz, DMSO-d₆, ppm) δ 9.53 (br, 1H, N-H), 8.13 (d, *J* = 6.8 Hz, 2H), 7.58 (d, *J* = 6.8 Hz, 1H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.38-7.30 (m, 5H), 7.07 (t, *J* = 6.2 Hz, 1H), 5.15 (s, 2H). ¹³C NMR (100 MHz, DMSO-d₆, ppm) δ 150.5, 145.9, 139.4, 132.7, 128.5, 128.3, 126.3, 125.1, 124.2, 122.9, 120.1, 114.7, 78.0, 75.3, 31.8. HRMS (ESI) *m/z* calcd for C₁₇H₁₄N₃O [M+H]⁺ 276.1137, found 276.1088.

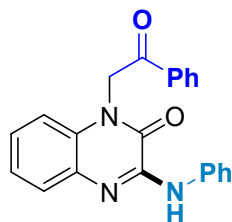
2-(2-Oxo-3-(phenylamino)quinoxalin-1(2H)-yl)acetonitrile (3h)



The reaction was conducted with 1-ethylcyanoquinoxalin-2(1H)-one (**1h**, 18.5 mg, 0.1 mmol) and 1H-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 3:1) to provide 24.6 mg, 89% yield of **3h** as white solid. m.p.: 249-251 °C.

¹H NMR (400 MHz, DMSO-d₆, ppm) δ 9.61 (br, 1H, N-H), 8.14 (d, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 3.6 Hz, 2H), 7.42-7.33 (m, 4H), 7.07 (t, *J* = 7.4 Hz, 1H), 5.50 (s, 2H). ¹³C NMR (100 MHz, DMSO-d₆, ppm) δ 150.9, 145.8, 139.3, 132.8, 128.6, 128.2, 126.5, 125.3, 124.7, 123.0, 120.2, 115.6, 114.1, 30.6. HRMS (ESI) *m/z* calcd for C₁₆H₁₃N₄O [M+H]⁺ 277.1089, found 277.1063.

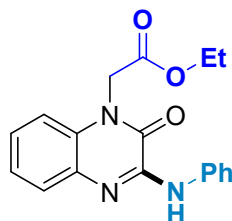
1-(2-Oxo-2-phenylethyl)-3-(phenylamino)quinoxalin-2(1H)-one (3i)



The reaction was conducted with 1-(2-oxo-2-phenethyl)quinoxalin-2(1*H*)-one (**1i**, 26.4 mg, 0.1 mmol) and 1*H*-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 3:1) to provide 20.6 mg, 58% yield of **3i** as light brown solid. m.p.: 220-222 °C.

¹H NMR (400 MHz, CDCl₃, ppm) δ 8.39 (br, 1H, N-H), 8.09 (d, *J* = 7.6 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.73-7.67 (m, 2H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 4.0 Hz, 1H), 5.77 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 190.8, 152.0, 145.5, 138.8, 134.5, 134.3, 133.4, 129.1, 129.1, 129.0, 128.2, 127.4, 125.3, 124.4, 123.2, 119.3, 113.3, 49.1. HRMS (ESI) *m/z* calcd for C₂₂H₁₈N₃O₂ [M+H]⁺ 356.1399, found 356.1322.

Ethyl 2-(2-oxo-3-(phenylamino)quinoxalin-1(2*H*)-yl)acetate (**3j**)

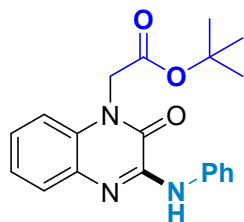


The reaction was conducted with ethyl 2-(2-oxoquinoxalin-1(2*H*)-yl)acetate (**1j**, 23.2mg, 0.1 mmol) and 1*H*-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 5:1) to provide 22.9 mg, 71% yield of **3j** as yellow solid. m.p.: 186-188 °C.

¹H NMR (400 MHz, CDCl₃, ppm) δ 8.38 (br, 1H, N-H), 7.95 (d, *J* = 7.6 Hz, 2H), 7.72-7.70 (m, 1H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.33-7.28 (m, 2H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.04-6.99 (m, 1H), 5.08 (s, 2H), 4.29-4.24 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 167.0, 151.9, 145.5, 138.8, 133.3, 129.0, 128.9, 127.5, 125.4, 124.6, 123.3, 119.3, 113.9, 62.1, 44.1, 14.1. HRMS (ESI) *m/z* calcd for C₁₈H₁₈N₃O₃

[M+H]⁺ 324.1348, found 324.1311.

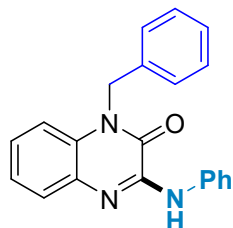
Tert-butyl 2-(2-oxo-3-(phenylamino)quinoxalin-1(2H)-yl)acetate (3k)



The reaction was conducted with ethyl 2-(2-oxoquinoxalin-1(2H)-yl)acetate tert-butyl ester (**1k**, 26.0 mg, 0.1 mmol) and 1H-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 5:1) to provide 23.6 mg, 67% yield of **3k** as white solid. m.p.: 165-166 °C.

¹H NMR (400 MHz, CDCl₃, ppm) δ 8.39 (br, 1H, N-H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.73-7.70 (m, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.32-7.28 (m, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.03-6.99 (m, 1H), 4.98 (s, 2H), 1.47 (s, 9H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 166.0, 151.8, 145.4, 138.8, 133.2, 129.0, 127.4, 125.3, 124.5, 123.2, 119.3, 113.0, 83.2, 44.8, 27.9. HRMS (ESI) *m/z* calcd for C₂₀H₂₂N₃O₃ [M+H]⁺ 352.1662, found 352.1629.

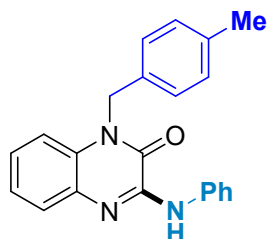
1-Benzyl-3-(phenylamino)quinoxalin-2(1H)-one (3l)



The reaction was conducted with 1-benzylquinoxalin-2(1H)-one (**1l**, 23.6 mg, 0.1 mmol) and 1H-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 10:1) to provide 21.3 mg, 65% yield of **3l** as white solid. m.p.: 194 -196.0 °C.

¹H NMR (400 MHz, CDCl₃, ppm) δ 8.51 (br, 1H, N-H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.34-7.31 (m, 3H), 7.28-7.25 (m, 3H), 7.20-7.19 (m, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 5.55 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 152.1, 145.8, 138.9, 135.1, 133.5, 129.0, 129.0, 128.9, 127.7, 127.2, 126.7, 125.2, 124.3, 123.2, 119.2, 114.4, 46.5. HRMS (ESI) *m/z* calcd for C₂₁H₁₈N₃O [M+H]⁺ 328.1450, found 328.1419.

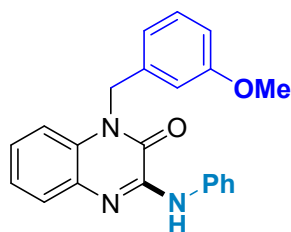
1-(4-Methylbenzyl)-3-(phenylamino)quinoxalin-2(1H)-one (3m)



The reaction was conducted with 1-(4-methylbenzyl)quinoxalin-2(1H)-one (**1m**, 25.0 mg, 0.1 mmol) and 1H-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 10:1) to provide 26.3 mg, 77% yield of **3m** as light yellow solid. m.p.: 160-162 °C.

¹H NMR (400 MHz, CDCl₃, ppm) δ 8.51 (br, 1H, N-H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.23-7.20 (m, 2H), 7.17-7.09 (m, 6H), 5.50 (s, 2H), 2.30 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 152.1, 145.8, 138.9, 137.5, 133.5, 132.0, 129.6, 129.1, 129.0, 127.2, 126.7, 125.2, 124.3, 123.2, 119.2, 114.4, 46.3, 21.1. HRMS (ESI) *m/z* calcd for C₂₂H₂₀N₃O [M+H]⁺ 342.1606, found 342.1565.

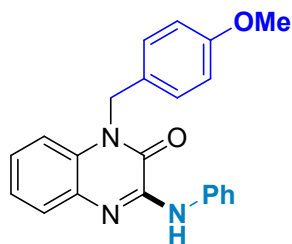
1-(3-Methoxybenzyl)-3-(phenylamino)quinoxalin-2(1H)-one (3n)



The reaction was conducted with 1-(3-methoxybenzyl)quinoxalin-2(1H)-one (**1n**, 26.6 mg, 0.1 mmol) and 1H-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 10:1) to provide 20.3 mg, 57% yield of **3n** as light brown solid. m.p.: 182-183 °C.

¹H NMR (400 MHz, CDCl₃, ppm) δ 8.51 (br, 1H, N-H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.27-7.23 (m, 2H), 7.18-7.17 (m, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.83-6.78 (m, 3H), 5.50 (s, 2H), 3.74 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 160.0, 152.1, 145.7, 138.9, 136.6, 133.4, 130.0, 129.0, 129.0, 127.2, 125.2, 124.3, 123.2, 119.2, 118.9, 114.4, 112.7, 112.7, 55.2, 46.4. HRMS (ESI) *m/z* calcd for C₂₂H₂₀N₃O₂ [M+H]⁺ 358.1556, found 358.1519.

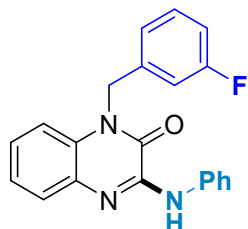
1-(4-Methoxybenzyl)-3-(phenylamino)quinoxalin-2(1H)-one (**3o**)



The reaction was conducted with 1-(4-methoxybenzyl)quinoxalin-2(1H)-one (**1o**, 26.6 mg, 0.1 mmol) and 1H-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 10:1) to provide 21.1 mg, 59% yield of **3o** as white solid. m.p.: 168-169 °C.

¹H NMR (400 MHz, CDCl₃, ppm) δ 8.52 (br, 1H, N-H), 7.96 (d, $J = 7.6$ Hz, 2H), 7.68 (d, $J = 8.0$ Hz, 1H), 7.39 (t, $J = 7.8$ Hz, 2H), 7.27-7.25 (m, 1H), 7.22-7.19 (m, 4H), 7.10 (t, $J = 7.4$ Hz, 1H), 6.84 (d, $J = 8.4$ Hz, 2H), 5.46 (s, 2H), 3.75 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 159.0, 152.1, 145.8, 138.9, 133.4, 129.0, 129.0, 128.2, 127.2, 127.1, 125.2, 124.3, 123.1, 119.2, 114.3, 114.2, 55.2, 45.9. HRMS(ESI)m/z calcd for C₂₂H₂₀N₃O₂ [M+H]⁺ 358.1556, found 358.1517.

1-(3-Fluorobenzyl)-3-(phenylamino)quinoxalin-2(1H)-one (**3p**)

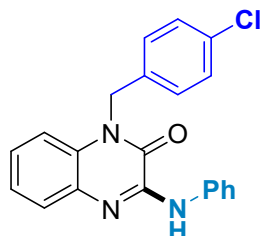


The reaction was conducted with 1-(3-fluorobenzyl)quinoxalin-2(1H)-one (**1p**, 25.4 mg, 0.1 mmol) and 1H-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 10:1) to provide 16.9 mg, 49% yield of **3p** as white solid. m.p.: 155-156 °C.

¹H NMR (400 MHz, CDCl₃, ppm) δ 8.49 (br, 1H, N-H), 7.96 (d, $J = 7.6$ Hz, 2H), 7.69 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 7.39 (t, $J = 8.0$ Hz, 2H), 7.30-7.23 (m, 2H), 7.18 (td, $J_1 = 7.8$ Hz, $J_2 = 1.6$ Hz, 1H), 7.12-7.09 (m, 2H), 7.02 (d, $J = 7.6$ Hz, 1H), 6.95 (t, $J = 8.2$ Hz, 2H), 5.50 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 163.0 (d, $J = 246.0$ Hz), 152.0, 145.6, 138.8, 137.6 (d, $J = 7.0$ Hz), 133.4, 130.5 (d, $J = 8.0$ Hz), 129.0, 128.8,

127.3, 125.2, 124.5, 123.2, 122.3 (d, $J = 3.0$ Hz), 119.2, 114.7 (d, $J = 21.0$ Hz), 114.1, 113.8 (d, $J = 22$ Hz), 46.0. HRMS (ESI) m/z calcd for $C_{21}H_{17}FN_3O$ $[M+H]^+$ 346.1356, found 346.1329.

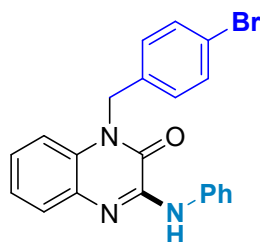
1-(4-Chlorobenzyl)-3-(phenylamino)quinoxalin-2(1H)-one (3q)



The reaction was conducted with 1-(4-chlorobenzyl)quinoxalin-2(1H)-one (**1q**, 27.0 mg, 0.1 mmol) and 1H-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 10:1) to provide 20.2 mg, 56% yield of **3q** as white solid. m.p.: 191-193 °C.

1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.48 (br, 1H, N-H), 7.97 (d, $J = 7.6$ Hz, 2H), 7.72-7.69 (m, 1H), 7.41 (t, $J = 8.0$ Hz, 2H), 7.31-7.28 (m, 3H), 7.23-7.18 (m, 3H), 7.12 (t, $J = 8.2$ Hz, 2H), 5.51 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 152.1, 145.7, 138.8, 133.6, 133.6, 133.5, 129.1, 129.0, 128.8, 128.2, 127.4, 125.3, 124.5, 123.3, 119.3, 114.1, 45.9. HRMS (ESI) m/z calcd for $C_{21}H_{17}ClN_3O$ $[M+H]^+$ 362.1060, found 362.1018.

1-(4-Bromobenzyl)-3-(phenylamino)quinoxalin-2(1H)-one (3r)

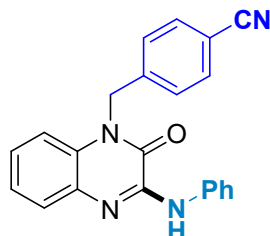


The reaction was conducted with 1-(4-bromobenzyl)quinoxalin-2(1H)-one (**1r**, 23.2 mg, 0.1 mmol) and 1H-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 5:1) to provide 21.9 mg, 54% yield of **3r** as yellow solid. m.p.: 190-192 °C.

1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.48 (br, 1H, N-H), 7.97 (d, $J = 8.0$ Hz, 2H), 7.72-7.69 (m, 1H), 7.46-7.39 (m, 4H), 7.29 (t, $J = 4.2$ Hz, 1H), 7.22-7.18 (m, 1H), 7.15-7.10

(m, 4H), 5.49 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 152.1, 145.7, 138.8, 134.1, 133.5, 132.1, 129.0, 128.8, 128.5, 127.4, 125.3, 124.5, 123.3, 121.7, 119.3, 114.1, 45.9. HRMS (ESI)m/z calcd for C₂₁H₁₇BrN₃O [M+H]⁺ 406.0555, found 406.0516.

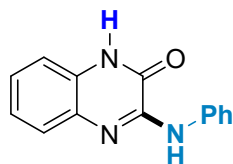
4-((2-Oxo-3-(phenylamino)quinoxalin-1(2H)-yl)methyl)benzonitrile (**3s**)



The reaction was conducted with 1-(4-cyanobenzyl)quinoxalin-2(1H)-one (**1s**, 23.2 mg, 0.1 mmol) and 1H-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 10:1) to provide 25.7 mg, 73% yield of **3s** as White solid. m.p.: 192-193 °C.

¹H NMR (400 MHz, CDCl₃, ppm) δ 8.45 (br, 1H, N-H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.72 (dd, *J*₁ = 8.0 Hz, *J*₂ = 1.2 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.23-7.18 (m, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 5.59 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 152.1, 145.6, 140.5, 138.7, 133.5, 132.8, 129.0, 128.6, 127.5, 127.4, 125.4, 124.7, 123.5, 119.3, 118.4, 113.8, 111.8, 46.1. HRMS (ESI)m/z calcd for C₂₂H₁₇N₄O [M+H]⁺ 353.1402, found 353.1367.

3-(Phenylamino)quinoxalin-2(1H)-one (**3t**)^[3]

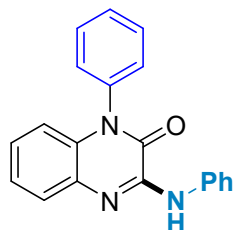


The reaction was conducted with quinoxalin-2(1H)-one (**1t**, 16.0 mg, 0.1 mmol) and 1H-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 5:1) to provide 18.0 mg, 76% yield of **3t** as white solid. m.p.: 251-253 °C.

¹H NMR (400 MHz, DMSO-d₆, ppm) δ 12.48 (br, 1H, N-H), 9.42 (br, 1H, N-H), 8.16 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 6.8 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.25-7.18 (m,

3H), 7.05 (t, $J = 7.2$ Hz, 1H). ^{13}C NMR (100 MHz, DMSO- d_6 , ppm) δ 151.5, 147.2, 139.6, 132.2, 128.6, 128.5, 125.4, 124.9, 123.5, 122.7, 119.7, 115.1. HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{12}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 238.0980, found 238.0934.

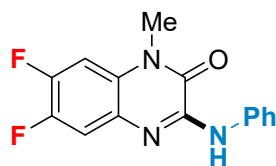
1-Phenyl-3-(phenylamino)quinoxalin-2(1H)-one (3u)



The reaction was conducted with 1-phenylquinoxalin-2(1H)-one (**1u**, 22.2 mg, 0.1 mmol) and 1H-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 10:1) to provide 21.0 mg, 67% yield of **3u** as white solid. m.p.: 181-182 °C.

^1H NMR (400 MHz, CDCl_3 , ppm) δ 8.46 (br, 1H, N-H), 7.97 (d, $J = 7.6$ Hz, 2H), 7.73 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 7.66-7.56 (m, 3H), 7.41 (t, $J = 7.8$ Hz, 2H), 7.35-7.33 (m, 2H), 7.30-7.28 (m, 1H), 7.14-7.09 (m, 2H), 6.61-6.59 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 151.8, 146.1, 138.8, 135.9, 133.1, 130.9, 130.2, 129.5, 129.0, 128.2, 126.8, 124.9, 124.4, 123.3, 119.4, 115.4. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{16}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 314.1293, found 314.1256.

6,7-Difluoro-1-methyl-3-(phenylamino)quinoxalin-2(1H)-one (3v)

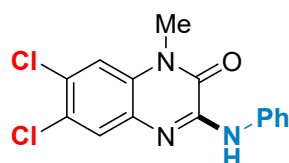


The reaction was conducted with 6,7-difluoro-1-methylquinoxalin-2(1H)-one (**1v**, 19.6 mg, 0.1 mmol) and 1H-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 5:1) to provide 23.0 mg, 80% yield of **3v** as white solid. m.p.: 202-203 °C.

^1H NMR (400 MHz, CDCl_3 , ppm) δ 8.41 (br, 1H, N-H), 7.88 (d, $J = 8.0$ Hz, 2H), 7.48-7.43 (m, 1H), 7.39 (t, $J = 8.0$ Hz, 2H), 7.12 (t, $J = 7.4$ Hz, 1H), 7.05-7.01 (m, 1H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6 , ppm) δ 150.9, 147.5 (dd, $J_1 = 88.0$ Hz, $J_2 =$

14.0 Hz), 146.3 (d, $J = 1.0$ Hz), 145.13 (dd, $J_1 = 87.0$ Hz, $J_2 = 14.0$ Hz), 139.2, 129.2 (dd, $J_1 = 10.0$ Hz, $J_2 = 2$ Hz), 128.5, 126.8 (d, $J = 9$ Hz), 123.0, 120.1, 113.3 (d, $J = 18.0$ Hz), 103.6 (d, $J = 23$ Hz), 30.2. HRMS (ESI) m/z calcd for $C_{15}H_{12}F_2N_3O$ $[M+H]^+$ 288.0948, found 288.0918.

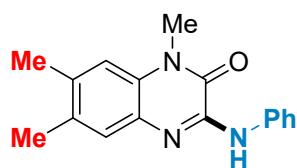
6,7-Dichloro-1-methyl-3-(phenylamino)quinoxalin-2(1H)-one (3w)



The reaction was conducted with 6,7-Dichloro-1-methylquinoxalin-2(1H)-one (**1w**, 22.9 mg, 0.1 mmol) and 1H-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 5:1) to provide 20.7 mg, 65% yield of **3w** as primrose yellow solid. m.p.: 223-224 °C.

1H NMR (400 MHz, DMSO- d_6 , ppm) δ 9.68 (br, 1H, N-H), 8.13 (d, $J = 7.6$ Hz, 2H), 7.73 (d, $J = 8.0$ Hz, 2H), 7.36 (t, $J = 7.8$ Hz, 2H), 7.09 (t, $J = 7.4$ Hz, 1H), 3.66 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6 , ppm) δ 151.4, 147.4, 139.5, 133.1, 130.5, 129.0, 126.9, 126.8, 126.1, 123.7, 120.9, 116.5, 30.4. HRMS (ESI) m/z calcd for $C_{15}H_{12}Cl_2N_3O$ $[M+H]^+$ 320.0357, found 320.0308.

1,6,7-Trimethyl-3-(phenylamino)quinoxalin-2(1H)-one (3x)

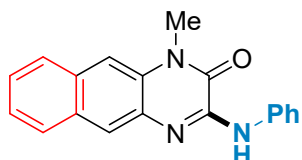


The reaction was conducted with 1,6,7-trimethylquinoxalin-2(1H)-one (**1x**, 18.8 mg, 0.1 mmol) and 1H-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 5:1) to provide 20.1 mg, 72% yield of **3x** as primrose yellow solid. m.p.: 220-221 °C.

1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.39 (br, 1H, N-H), 7.93 (d, $J = 8.0$ Hz, 2H), 7.45 (s, 1H), 7.38 (t, $J = 7.8$ Hz, 2H), 7.08 (t, $J = 7.4$ Hz, 1H), 6.97 (s, 1H), 3.71 (s, 3H), 2.35

(s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 151.8, 145.3, 139.1, 134.3, 133.0, 131.0, 128.9, 127.6, 127.4, 122.8, 119.0, 114.3, 29.6, 20.1, 19.2. HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{18}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 280.1450, found 280.1416.

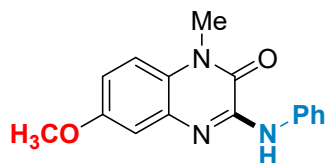
1-Methyl-3-(phenylamino)benzo[g]quinoxalin-2(1H)-one (3y)



The reaction was conducted with 1-methylbenzo[g]quinoxalin-2(1H)-one (**1y**, 21.0 mg, 0.1 mmol) and 1H-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 5:1) to provide 19.3 mg, 64% yield of **3y** as primrose yellow solid. m.p.: 208-209 °C.

^1H NMR (400 MHz, CDCl_3 , ppm) δ 8.49 (br, 1H, N-H), 8.11 (s, 1H), 7.98 (d, $J = 7.6$ Hz, 2H), 7.88 (t, $J = 4.8$ Hz, 1H), 7.84 (t, $J = 4.6$ Hz, 1H), 7.51 (s, 1H), 7.45-7.40 (m, 4H), 7.13 (t, $J = 7.2$ Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 152.3, 145.2, 138.7, 132.4, 130.9, 130.7, 129.8, 129.0, 127.4, 127.1, 125.8, 125.2, 124.2, 123.4, 119.4, 110.3, 29.8. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{16}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 302.1293, found 302.1255.

6-Methoxy-1-methyl-3-(phenylamino)quinoxalin-2(1H)-one (3z)

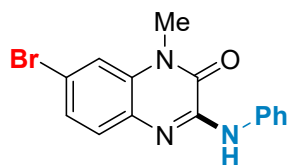


The reaction was conducted with 6-methoxy-1-methylquinoxalin-2(1H)-one (**1z**, 19.0 mg, 0.1 mmol) and 1H-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 5:1) to provide 22.4 mg, 80% yield of **3z** as white solid. m.p.: 216-218 °C.

^1H NMR (400 MHz, CDCl_3 , ppm) δ 8.53 (br, 1H, N-H), 7.92 (d, $J = 8.0$ Hz, 2H), 7.41 (t, $J = 8.0$ Hz, 2H), 7.18-7.11 (m, 3H), 6.94 (dd, $J_1 = 9.0$ Hz, $J_2 = 2.4$ Hz, 1H), 3.89 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 156.8, 151.4, 146.1, 138.5,

136.6, 133.7, 129.1, 123.6, 119.7, 114.4, 113.9, 109.3, 55.7, 29.9. HRMS (ESI) m/z calcd for $C_{16}H_{16}N_3O$ $[M+H]^+$ 282.1276, found 282.1238.

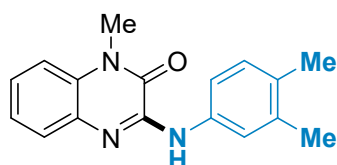
7-Bromo-1-methyl-3-(phenylamino)quinoxalin-2(1H)-one (**3aa**)



The reaction was conducted with 7-bromo-1-methylquinoxalin-2(1H)-one (**1aa**, 23.9 mg, 0.1 mmol) and 1H-benzotriazole (**2a**, 35.7 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 5:1) to provide 25.0 mg, 76% yield of **3aa** as white solid. m.p.: 198-200 °C.

1H NMR (400 MHz, DMSO- d_6 , ppm) δ 9.54 (br, 1H, N-H), 8.12 (d, $J = 7.6$ Hz, 1H), 7.64 (d, $J = 2.0$ Hz, 1H), 7.48-7.46 (m, 1H), 7.43-7.41 (m, 1H), 7.36 (t, $J = 8.0$ Hz, 2H), 7.07 (t, $J = 7.2$ Hz, 1H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6 , ppm) δ 151.0, 146.3, 139.3, 131.7, 131.3, 128.5, 127.5, 126.5, 122.9, 120.1, 117.0, 117.0, 29.7. HRMS (ESI) m/z calcd for $C_{15}H_{13}BrN_3O$ $[M+H]^+$ 330.1176, found 330.1142.

3-((3,4-Dimethylphenyl)amino)-1-methylquinoxalin-2(1H)-one (**4a**)

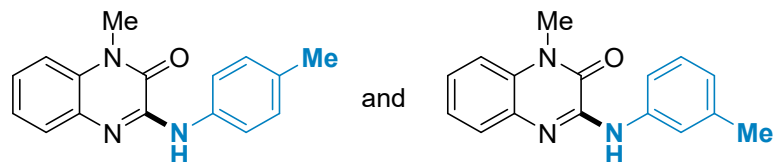


The reaction was conducted with 1-methylquinoxalin-2(1H)-one (**1a**, 16.0 mg, 0.1 mmol) and 5,6-dimethylbenzotriazole (**2b**, 44.1 mg, 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 10:1) to provide 22.9 mg, 82% yield of **4a** as white solid. m.p.: 185-186 °C.

1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.36 (br, 1H, N-H), 7.76-7.73 (m, 1H), 7.70-7.68 (m, 1H), 7.63 (s, 1H), 7.30-7.28 (m, 2H), 7.24-7.21 (m, 1H), 7.15 (d, $J = 8.0$ Hz, 1H), 3.75 (s, 3H), 2.30 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 151.9, 145.7, 137.1, 136.4, 133.2, 131.7, 130.0, 129.6, 126.7, 124.9, 124.3, 120.7, 116.9, 113.5, 29.7, 20.1, 19.2. HRMS (ESI) m/z calcd for $C_{17}H_{18}N_3O$ $[M+H]^+$ 280.1450, found

280.1426.

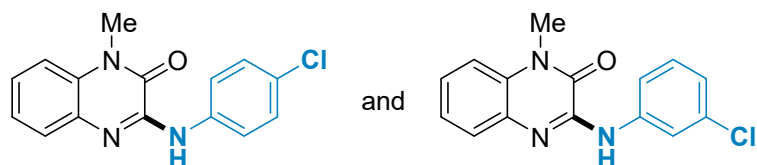
1-Methyl-3-(*p*-tolylamino)quinoxalin-2(1*H*)-one and 1-methyl-3-(*m*-tolylamino)quinoxalin-2(1*H*)-one (4b and 4b')



The reaction was conducted with 1-methylquinoxalin-2(1*H*)-one (**1a**, 16.0 mg. 0.1 mmol) and 5-methylbenzotriazole (**2c**, 39.9 mg. 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 10:1) to provide 21.2 mg, 80% yield of **3b and 3b'** as white solid mixture.

¹H NMR (400 MHz, mixture, CDCl₃, ppm) δ 8.42 (br, 0.5H, N-H), 8.40 (br, 0.5H, N-H), 7.82 (d, $J = 8.0$ Hz, 1.5H), 7.72-7.68 (m, 1.5H), 7.34-7.29 (m, 3H), 7.25-7.23 (m, 0.5H), 7.20 (d, $J = 8.0$ Hz, 1H), 6.92 (d, $J = 8.0$ Hz, 0.5H), 3.76 (s, 3H), 2.40 (s, 1.5H), 2.35 (s, 1.5H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 151.9, 145.7, 138.8, 138.7, 136.2, 133.2, 133.2, 132.8, 129.7, 129.7, 129.5, 128.8, 127.0, 126.9, 125.1, 125.0, 124.3, 124.1, 119.9, 119.4, 116.4, 113.5, 29.7, 21.6, 20.9. HRMS (ESI) m/z calcd for C₁₆H₁₆N₃O [M+H]⁺ 266.1293, found 266.1284.

3-((3-Chlorophenyl)amino)-1-methylquinoxalin-2(1*H*)-one and 3-((4-chlorophenyl)amino)-1-methylquinoxalin-2(1*H*)-one (4c and 4c')

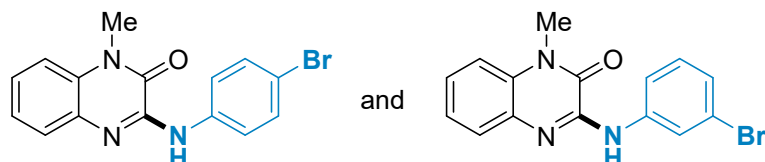


The reaction was conducted with 1-methylquinoxalin-2(1*H*)-one (**1a**, 16.0 mg. 0.1 mmol) and 5-chlorobenzotriazole (**2d**, 45.9 mg. 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 10:1) to provide 22.2 mg, 78% yield of **4c and 4c'** as white solid mixture.

¹H NMR (400 MHz, mixture, CDCl₃, ppm) δ 8.47 (br, 0.5H, N-H), 8.44 (br, 0.5H, N-H), 8.16 (s, 0.5H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.70-7.66 (m, 1.5H), 7.32-7.29 (m, 3H), 7.27 (s, 0.5H), 7.21 (d, $J = 8.0$ Hz, 1H), 7.04 (d, $J = 8.0$ Hz, 0.5H), 3.72 (s, 3H). ¹³C

NMR (100 MHz, CDCl₃, ppm) δ 151.8, 151.7, 145.5, 140.2, 138.0, 133.0, 132.8, 131.9, 130.2, 129.9, 129.8, 127.3, 127.2, 125.9, 125.7, 125.6, 124.4, 122.7, 121.9, 120.7, 117.7, 115.5, 113.6, 29.7. HRMS (ESI) m/z calcd for C₁₅H₁₃ClN₃O [M+H]⁺ 286.0747, found 286.0723.

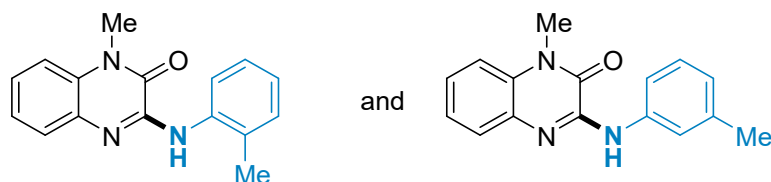
3-((3-Bromophenyl)amino)-1-methylquinoxalin-2(1H)-one and 3-((4-bromophenyl)amino)-1-methylquinoxalin-2(1H)-one (**4d** and **4d'**)



The reaction was conducted with 1-methylquinoxalin-2(1H)-one (**1a**, 16.0 mg. 0.1 mmol) and 5-bromobenzotriazole (**2e**, 59.1 mg. 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 10:1) to provide 27.6 mg, 84% yield of **4d** and **4d'** as white solid mixture.

¹H NMR (400 MHz, mixture, CDCl₃, ppm) δ 8.45 (br, 0.5H, N-H), 8.42 (br, 0.5H, N-H), 8.28 (s, 0.5H), 7.82 (d, J = 8.0 Hz, 1H), 7.76-7.74 (m, 0.5H), 7.67-7.62 (m, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.32-7.28 (m, 2H), 7.20 (d, J = 8.0 Hz, 2H), 3.70 (s, 1.5H), 3.71 (s, 1.5H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ 151.6, 151.6, 145.4, 145.4, 140.1, 137.9, 132.8, 132.7, 131.7, 130.1, 129.7, 129.7, 127.2, 127.1, 125.8, 125.6, 125.5, 124.3, 122.6, 121.8, 120.6, 117.6, 115.3, 113.6, 29.7. HRMS (ESI) m/z calcd for C₁₅H₁₃BrN₃O [M+H]⁺ 330.0242, found 330.0208.

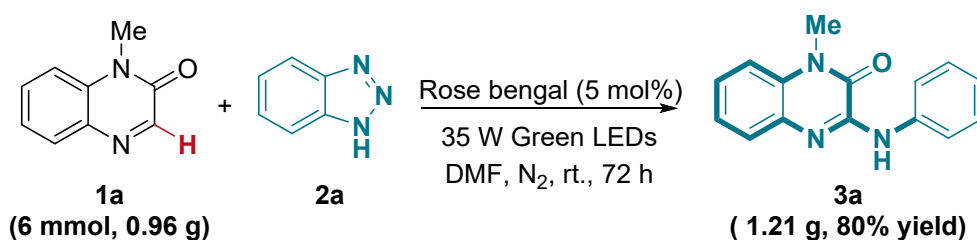
1-Methyl-3-(*o*-tolylamino)quinoxalin-2(1H)-one and 1-methyl-3-(*m*-tolylamino)quinoxalin-2(1H)-one (**4e** and **4e'**)



The reaction was conducted with 1-methylquinoxalin-2(1H)-one (**1a**, 16.0 mg. 0.1 mmol) and 1-methylbenzotriazole (**2f**, 39.9 mg. 0.3 mmol). The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 25:1-10:1) to provide 12.7 mg, 48% yield of **4e** and **4e'** as white solid mixture.

^1H NMR (400 MHz, mixture, CDCl_3 , ppm) δ 8.39 (br, 0.5H, N-H), 8.37 (br, 0.5H, N-H), 7.81 (d, $J = 8.0$ Hz, 1.5H), 7.68-7.64 (m, 1.5H), 7.30-7.28 (m, 1.5H), 7.27-7.24 (m, 1.5H), 7.21-7.17 (m, 1.5H), 6.90 (d, $J = 7.6$ Hz, 0.5H), 3.69 (s, 3H), 2.38 (s, 2H), 2.33 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 151.9, 151.9, 145.7, 138.7, 138.7, 136.3, 133.2, 133.2, 132.7, 129.7, 129.6, 129.4, 128.8, 127.0, 126.9, 125.1, 124.9, 124.2, 124.0, 119.8, 119.3, 116.4, 113.5, 29.6, 29.6, 21.6, 20.9. HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{16}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 266.1293, found 266.1282.

5. Gram-scale synthesis

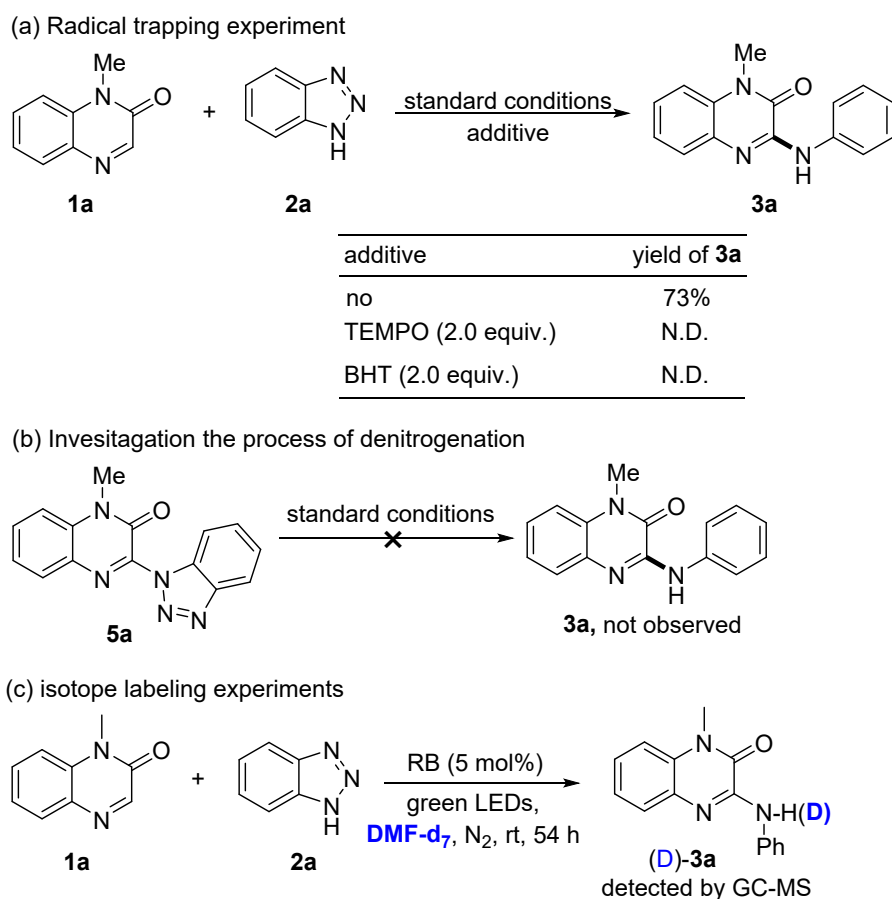


Scheme S3. Scale-up synthesis

To a reaction tube equipped with a magnetic stir bar was charged with 1-methylquinoxalin-2(1H)-one (**1a**, 0.96 g, 6 mmol), 1H-benzotriazole (**2a**, 2.14 g, 18 mmol), Rose Bengal (0.31 g, 5 mol%) and DMF (48 mL). The solution was stirred at room temperature with the irradiation of a 35 W Green LEDs for 72 h. After the reaction was completed, the resulting mixture was extracted with ethyl acetate (30 mL \times 3). The combined organic extracts were dried over MgSO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluant: petroleum ether/ethyl acetate = 25:1 to 5:1, V/V) to obtain the **3a** pure product in 1.21 g, 80% yield.

6. Mechanism studies

a) Control experiments



Scheme S3. Control experiments

In order to gain preliminary insights into the mechanism of this novel visible-light-photocatalysis induced denitrogenative and radical 1,3-shift of benzotriazole, a series of control experiments were carried out as shown in *Scheme S3*. Firstly, the radical trapping experiments were carried out. Addition of the radical quencher neither TEMPO or BHT into the model reaction, the desired product was not detected by in situ GC-MS and NMR technique. This above results suggested that free radical may be involved in this reaction (*Scheme S3a*). Of note, in order to investigate the process of denitrogenation during this reaction, the direct coupled and without denitrogenative product **5a** was prepared *via* the cross-dehydrogenative coupling between quinoxalin-2(1*H*)-ones and 1*H*-benzotriazole. When the intermediate **5a** was used as a starting substrate under the standard reaction for 54 h, the desired target **3a** was not observed by in situ GC-MS in our catalytic system. This result forthrightly indicated that the process of denitrogenation was not generated at this stage and also suggested that the 1*H*-benzotriazole was more easy underwent dehydrogenation in this reaction (*Scheme S3b*).

Furthermore, we also conducted an isotope labelling experiment. As shown in the scheme 3c, when used DMF-d₇ as solvent under the standard conditions, the corresponding deuterium product d-3a was detected by GC-MS (Figure S1). This result supported the proton source may be originated from the solvent (DMF) in this reaction. In addition (Scheme S3c).

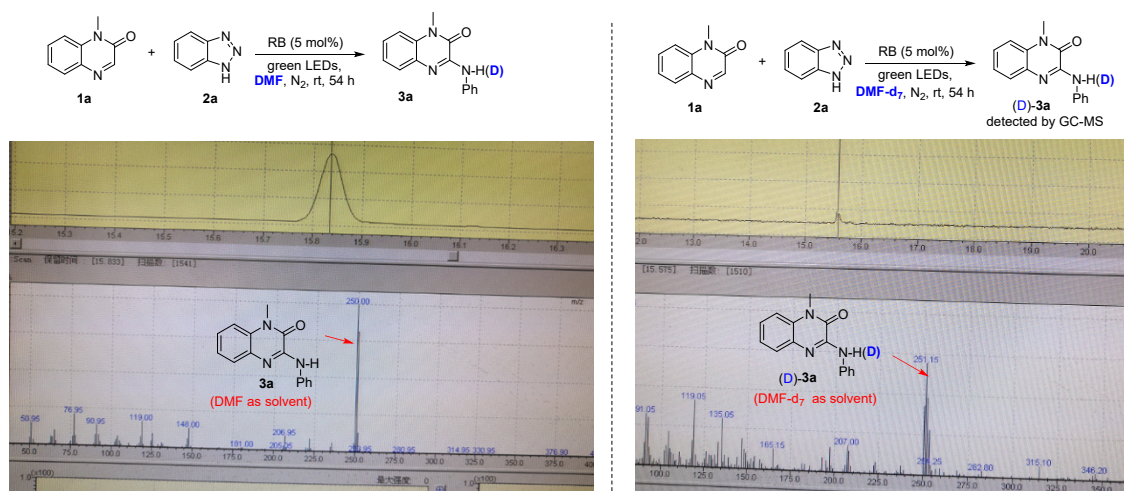


Figure S1. Isotope labelling experiment

In addition, the light on/off visible-light-irradiation experiments was carried out and result was shown in the Figure S2, which clearly supported that continuous visible light is indispensable element for this radical cascade process.

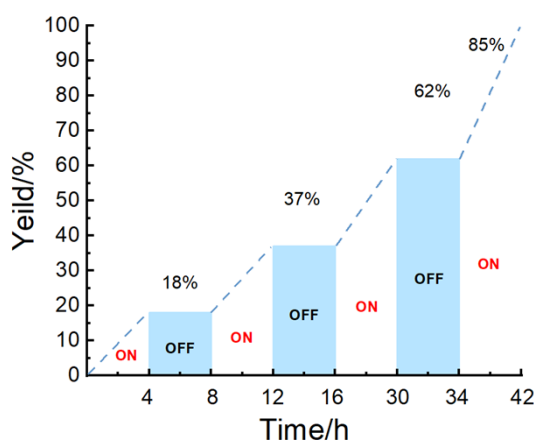
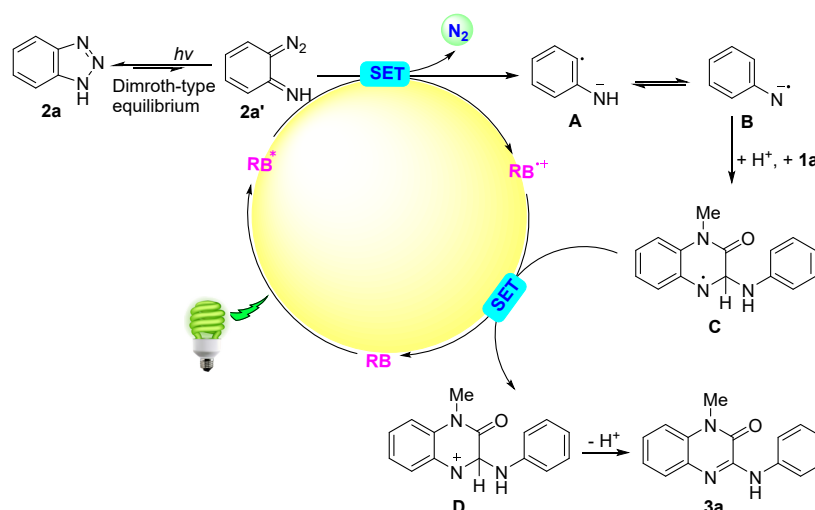


Figure S2. Light on/off experiments

b) Proposed reaction mechanism

According to the observations of the abovementioned mechanism experimental results and previous reports,^[4] a plausible mechanism for this transformation was

depicted in *Scheme S4*. Initially, we speculated that the 1*H*-benzotriazole (**2a**) was easy to translate into its diazo species (**2a'**) with N-N bond fission under the light irradiation *via* a Dimroth-type equilibrium.^[5] Subsequently, the diazo species (**2a'**) was being photoexcited *via* single electron transfer (SET) in the presence of green LEDs light irradiation and organic photosensitizer (Rose Bengals) to release N₂ and generate aryl radical (**A**), which underwent 1,3-shift to produce new arylamine radical anion (**B**) quickly. It was worth mentioned that this novel radical transfer pathway of benzotriazoles is very rare in the previous reports, and our new findings may enrich the function of benzotriazoles and radical chemistry. Next, the arylamine radical anion (**B**) attack another substrate **1a** and then to inform intermediate **C**, which was oxidized to cationic intermediate **D** through single-electron transfer and also regenerated photosensitizer (Rose Bengals) into another catalytic circle. Finally, the desired target **3a** was formed through the deprotonation of the intermediate **D**.



Scheme S4. Proposed reaction mechanism

7. References

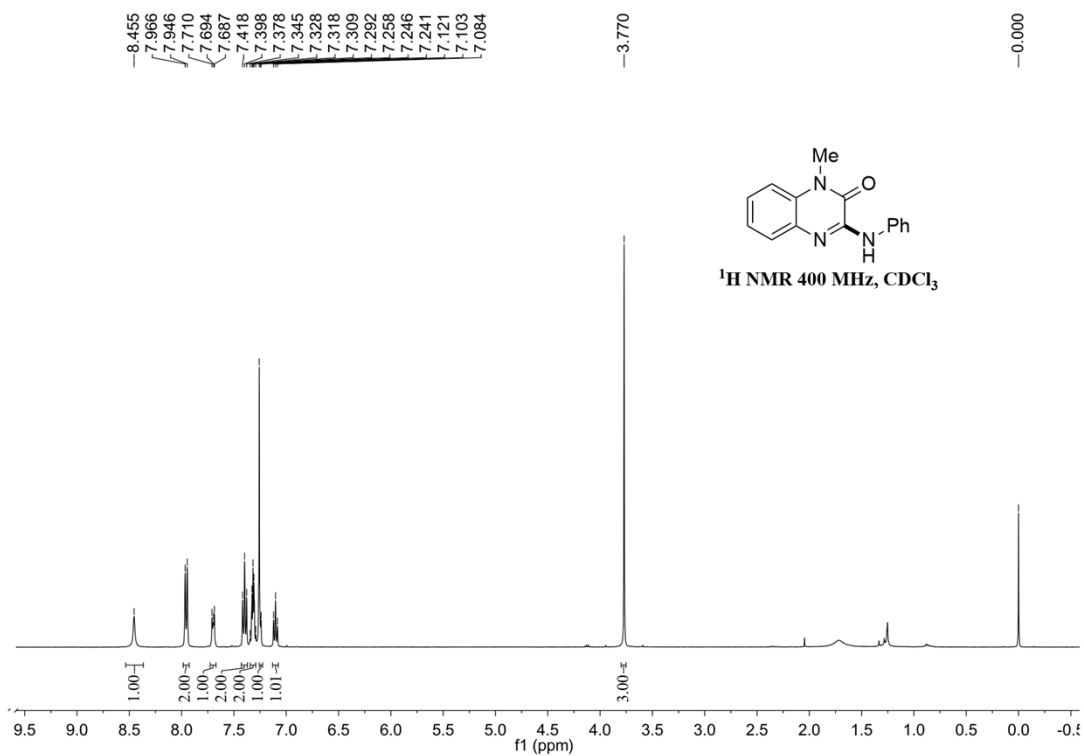
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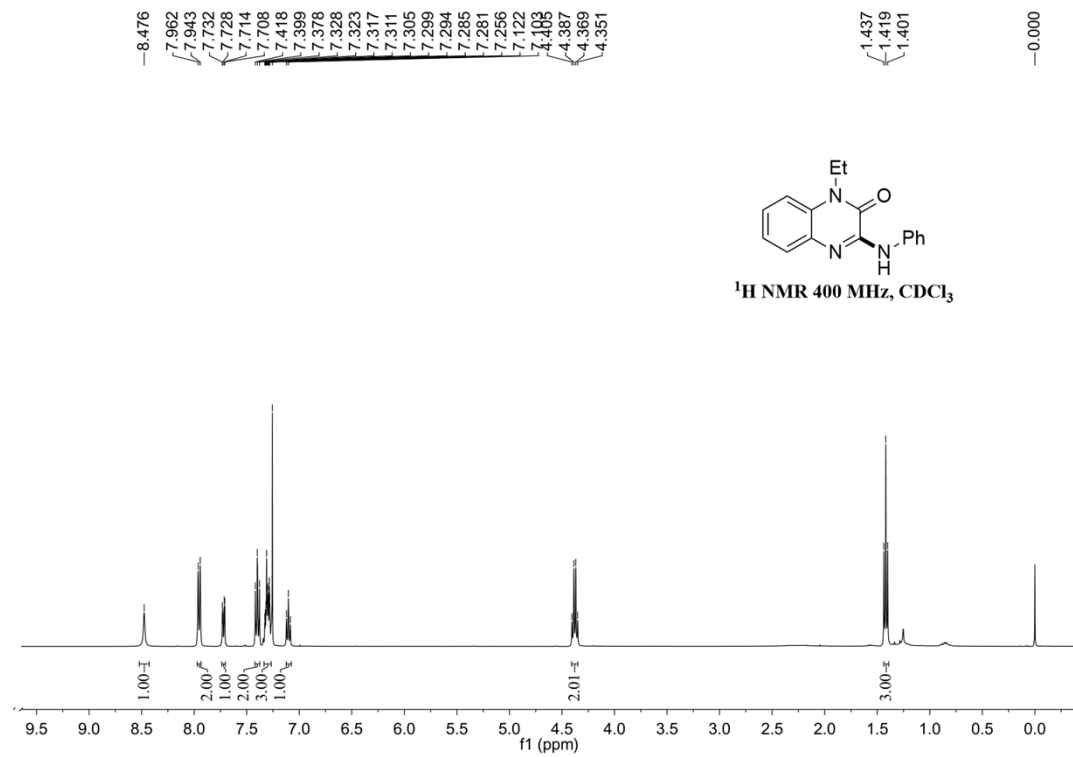
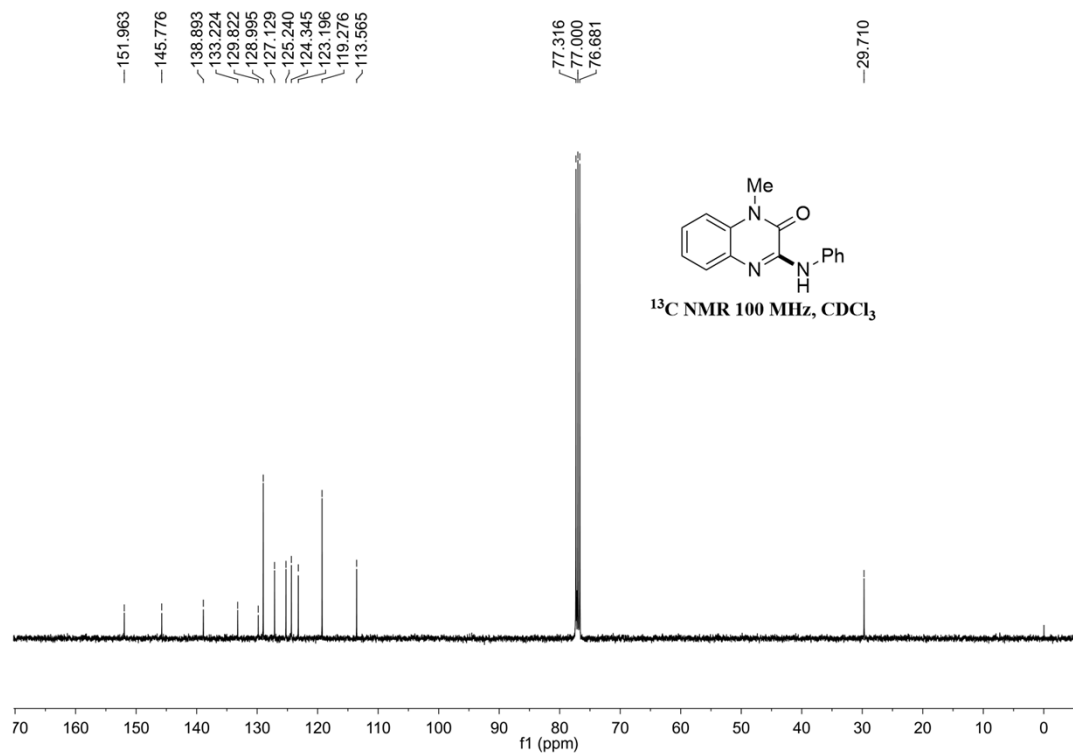
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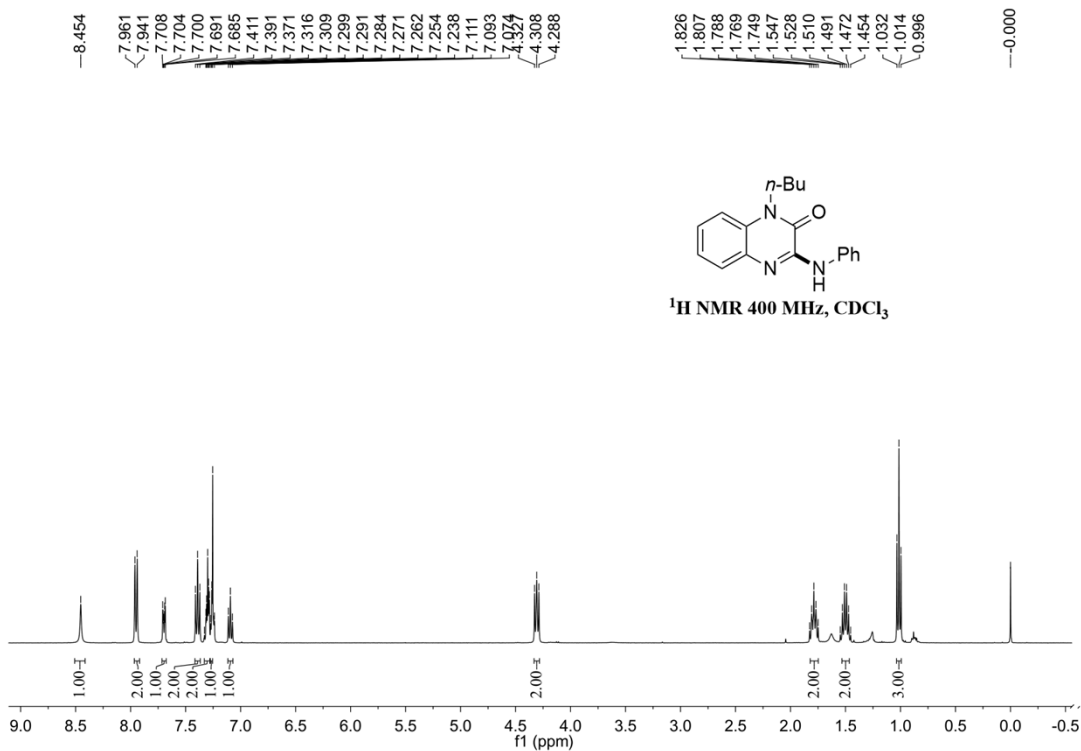
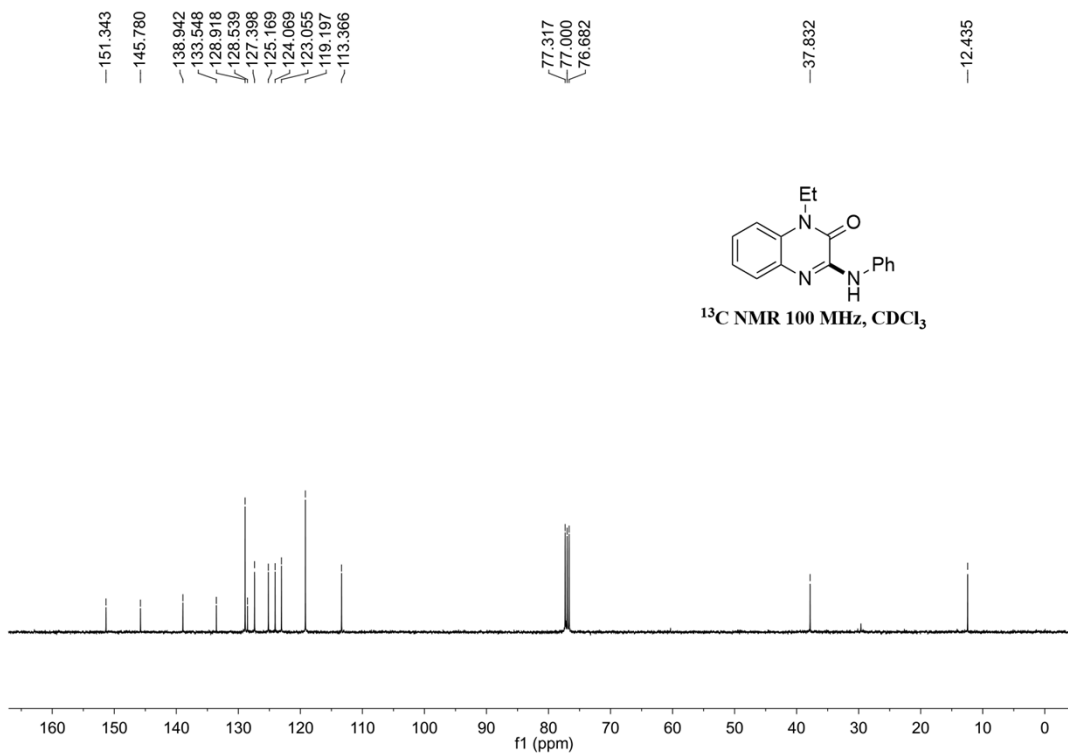
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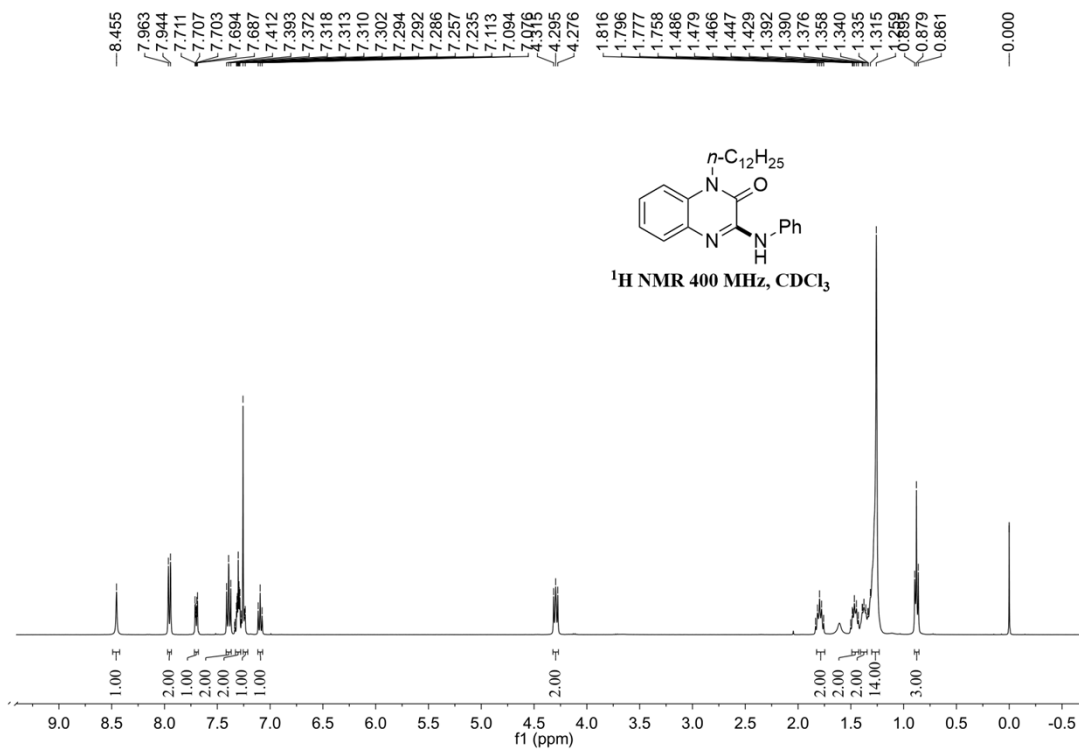
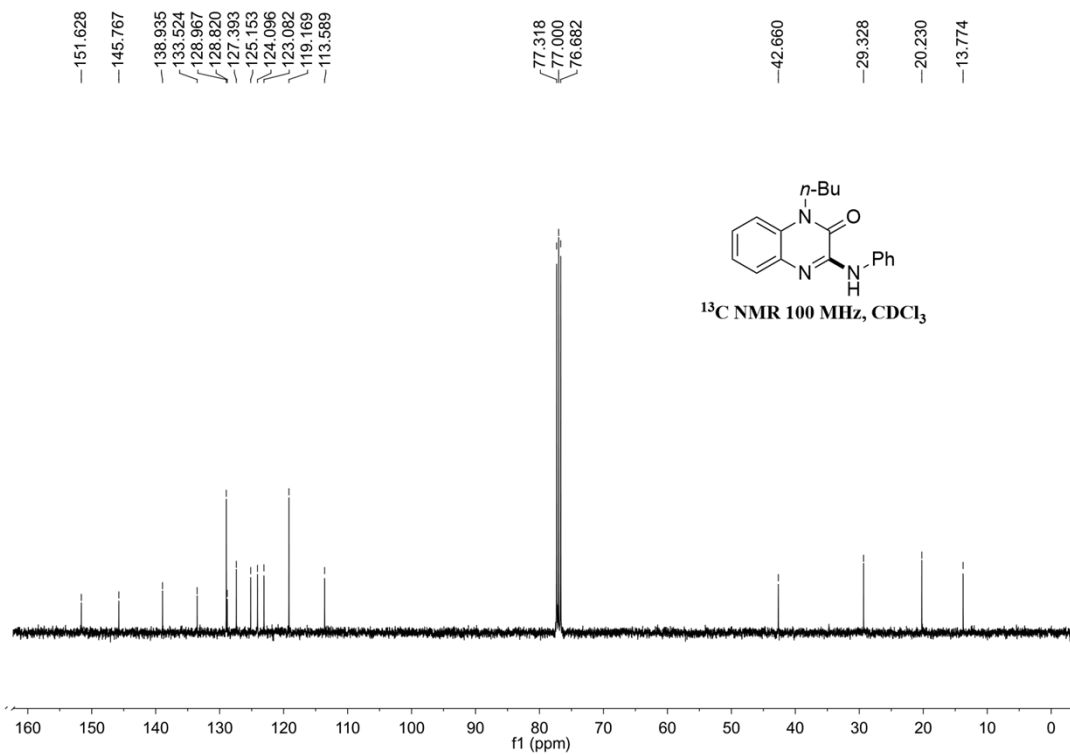
8. NMR spectra

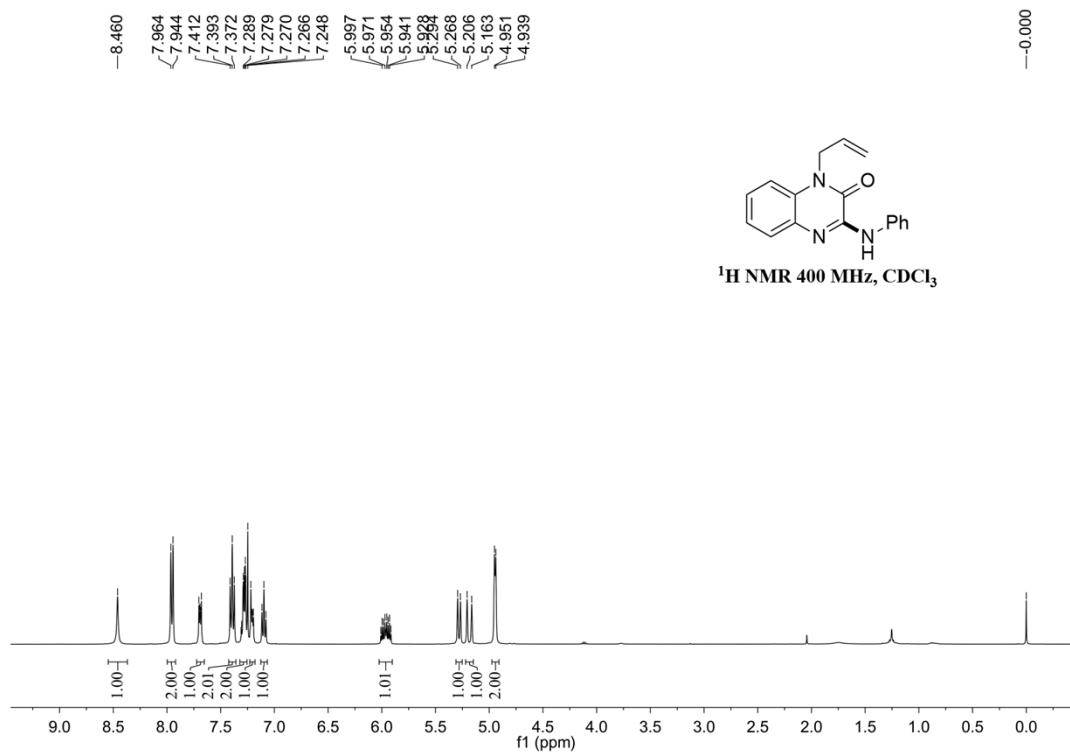
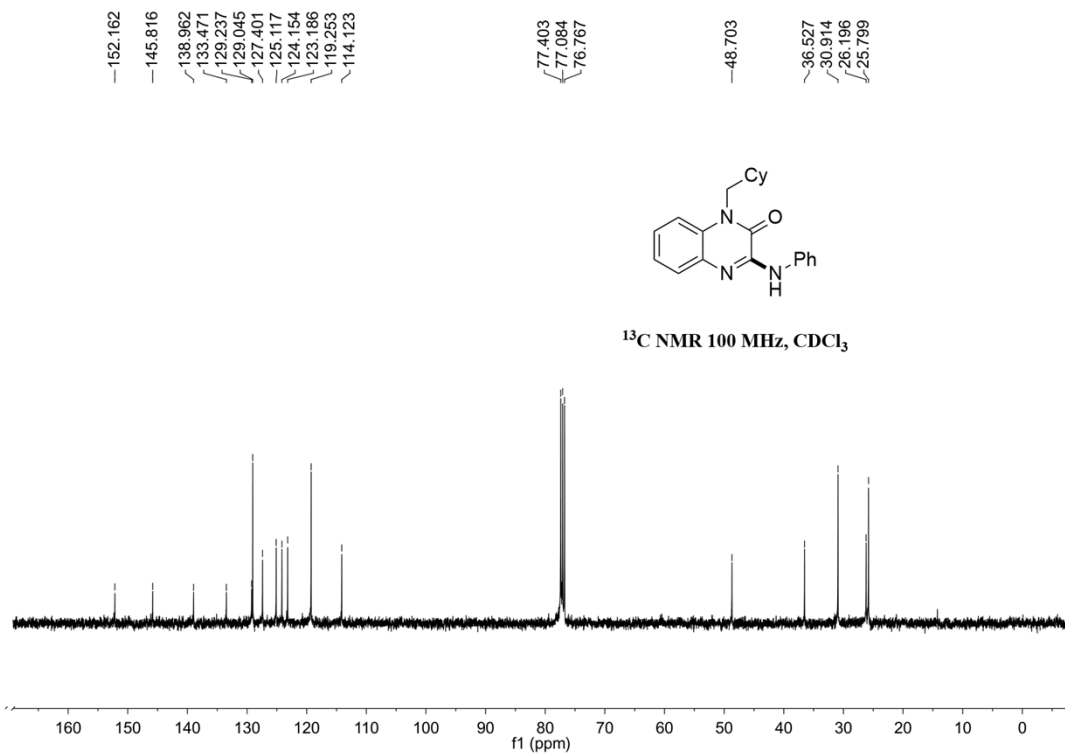
a) Copies of ^1H and ^{13}C NMR spectra of sectional substrates

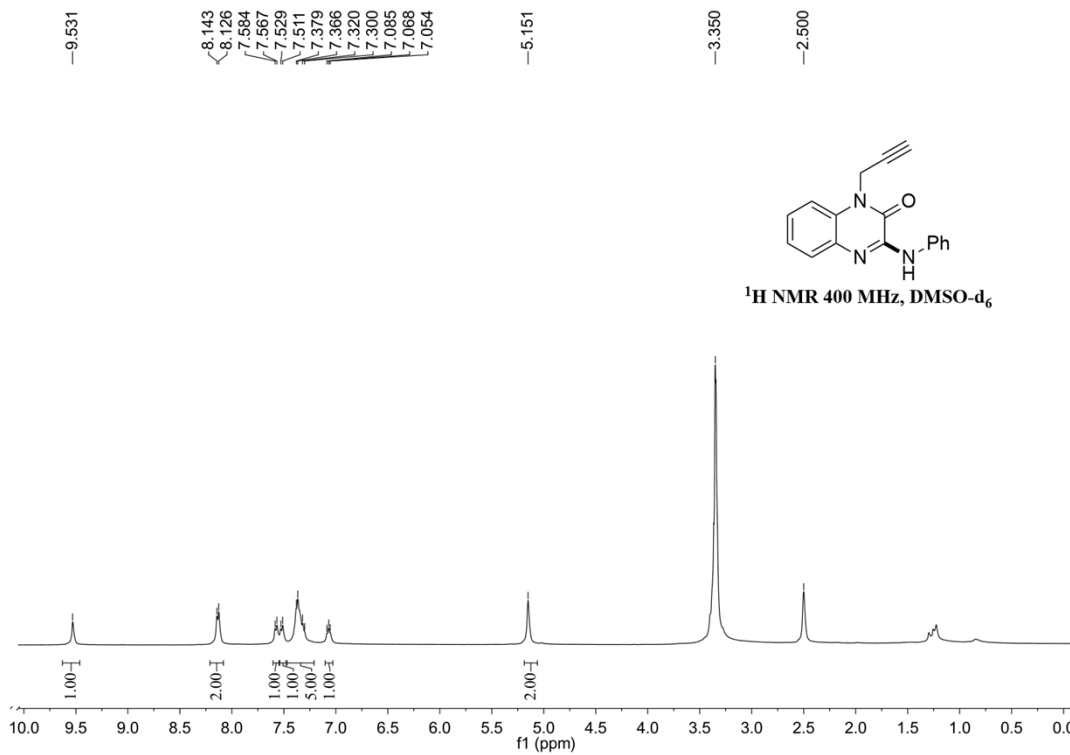
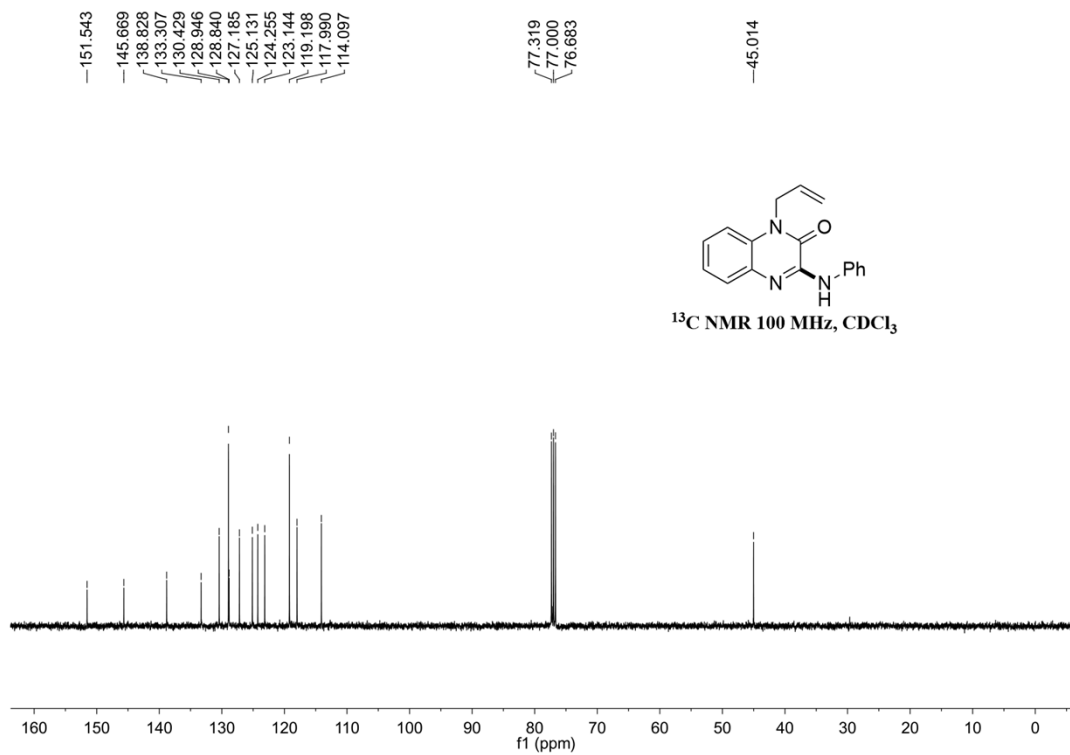


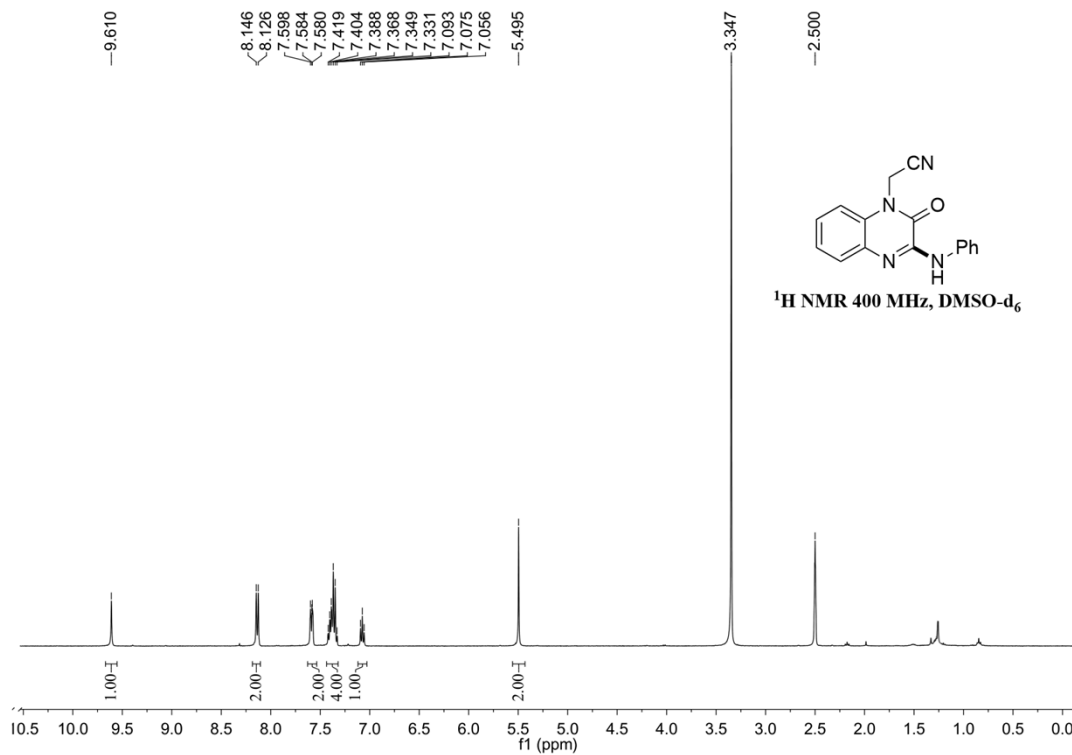
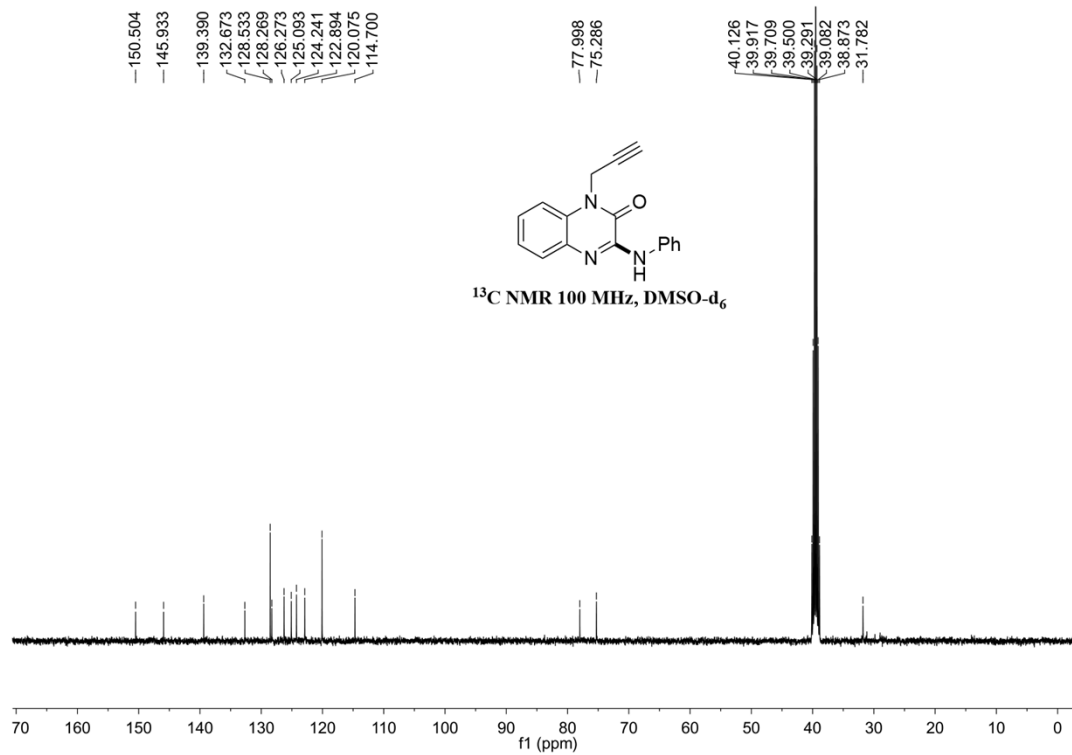


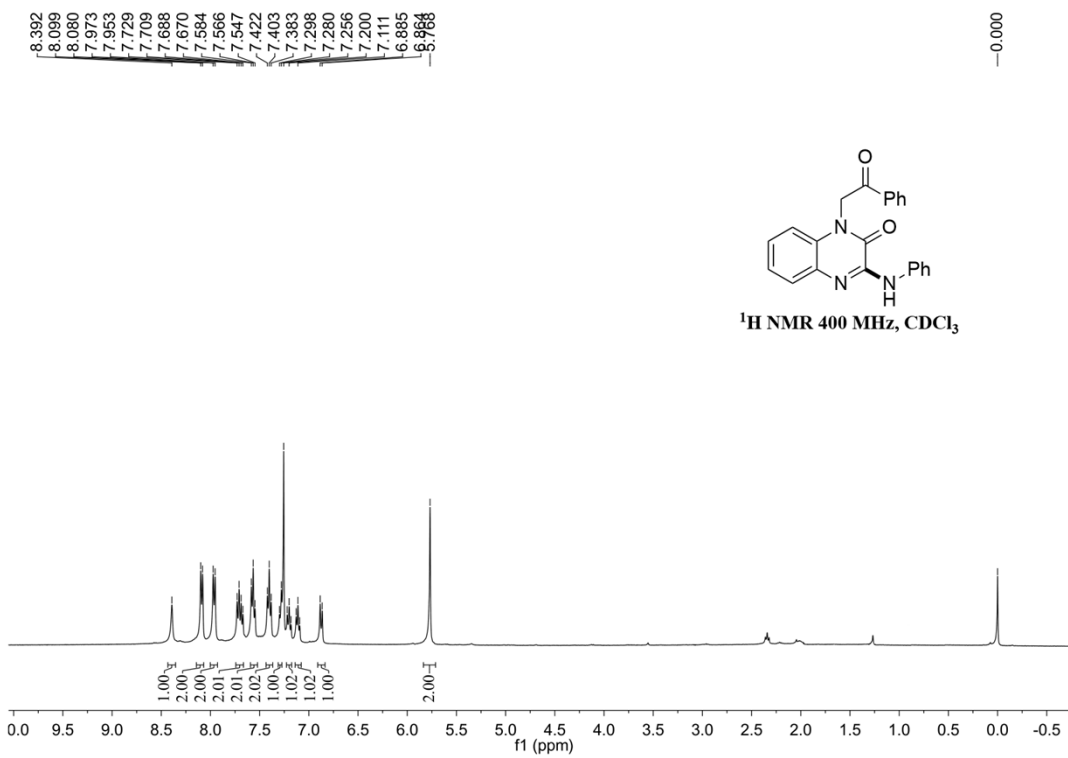
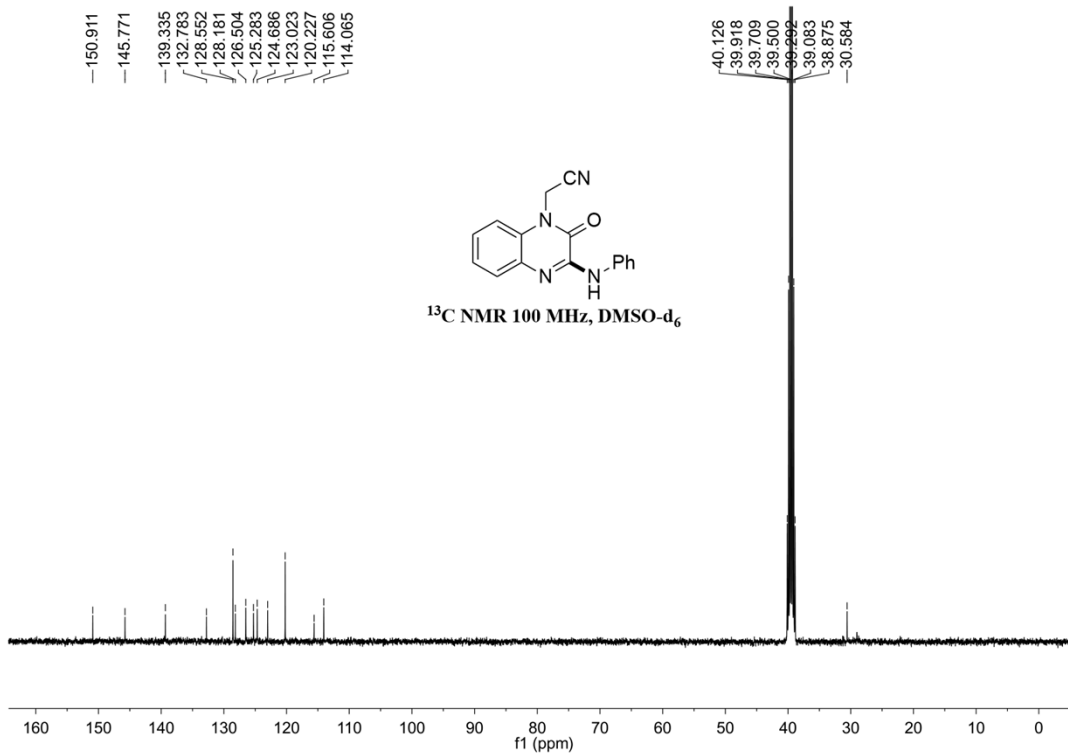


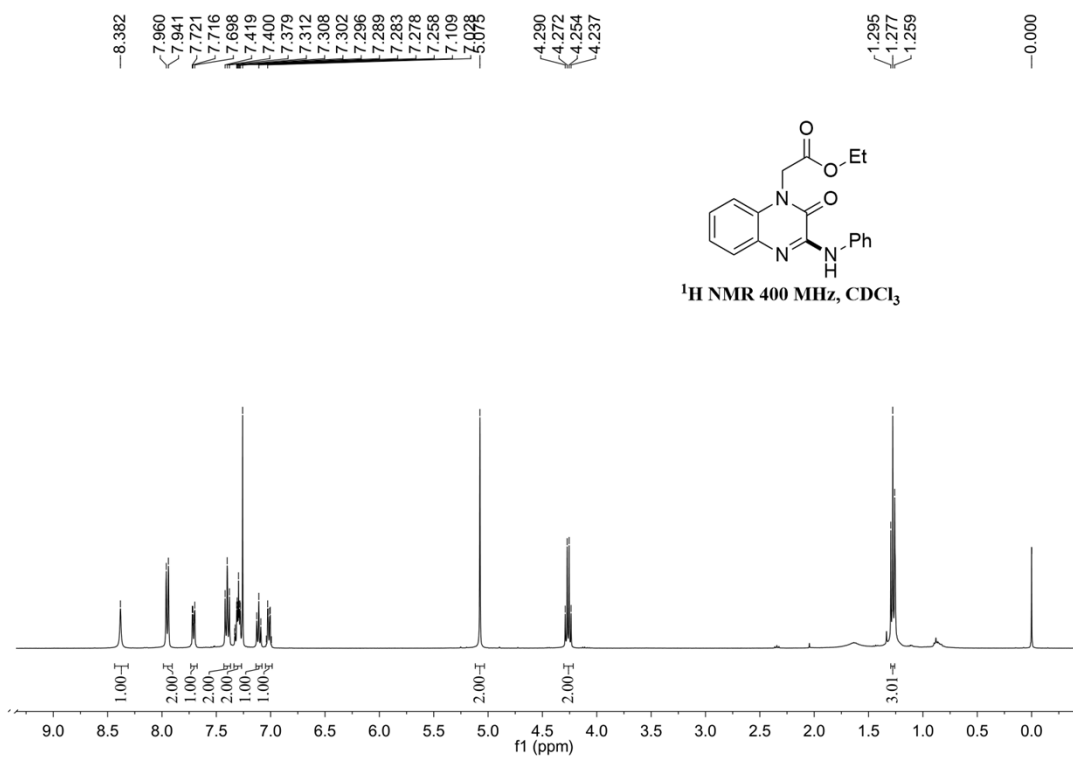
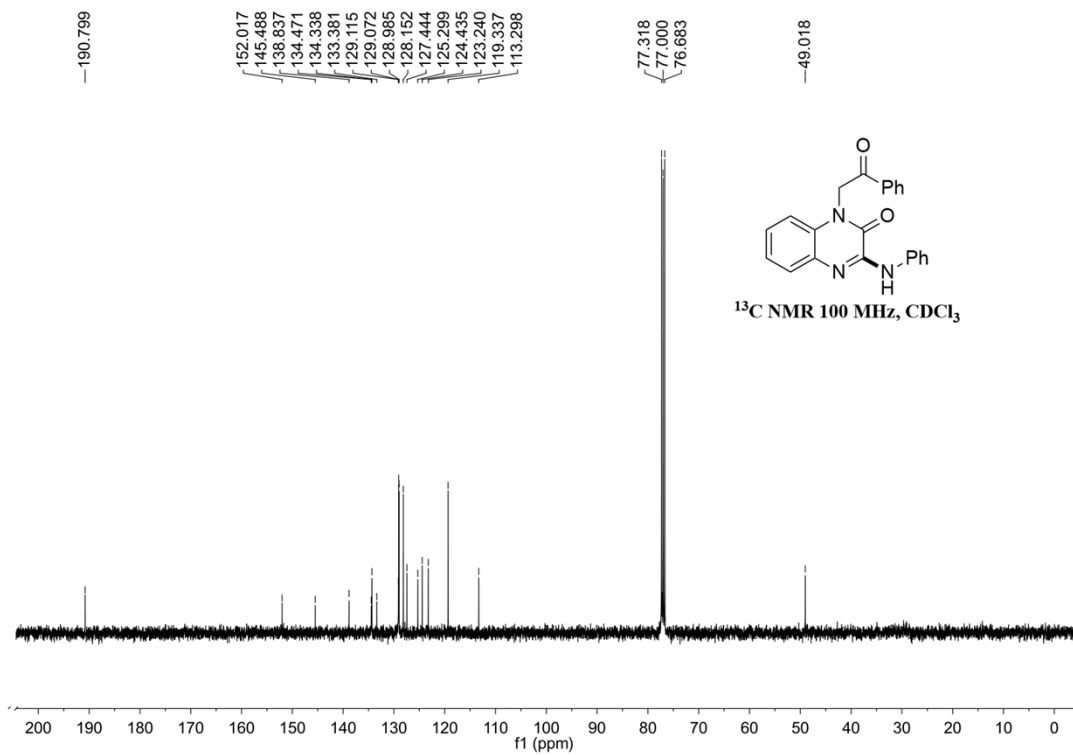


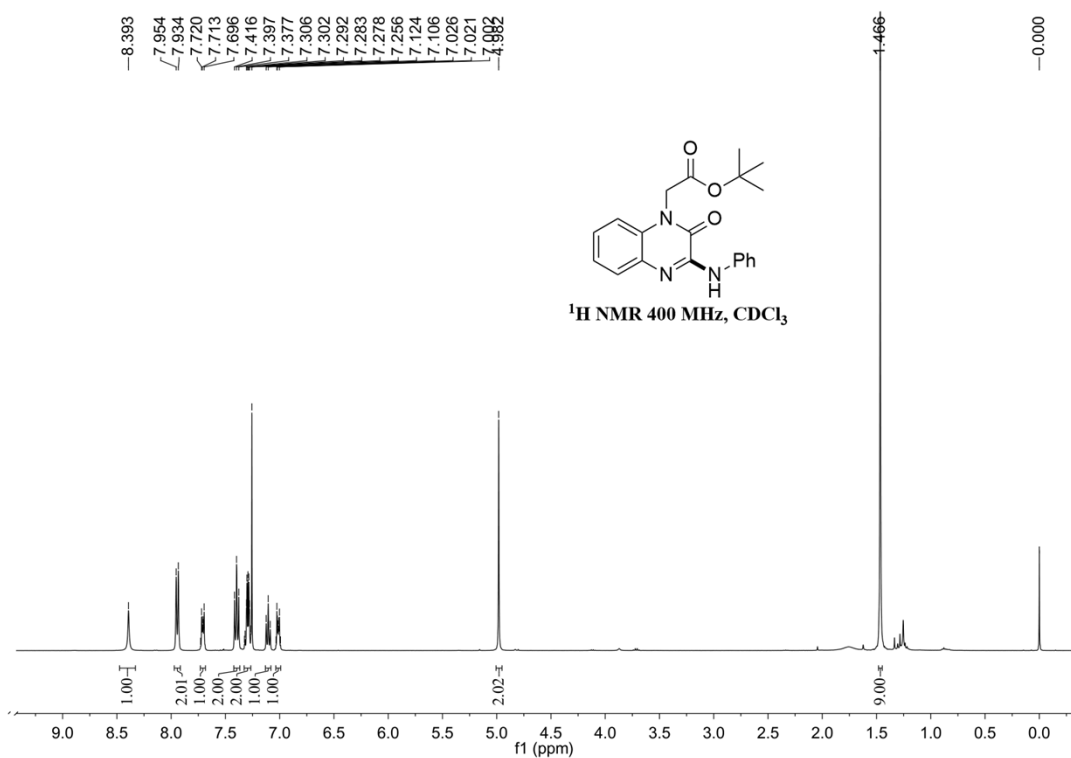
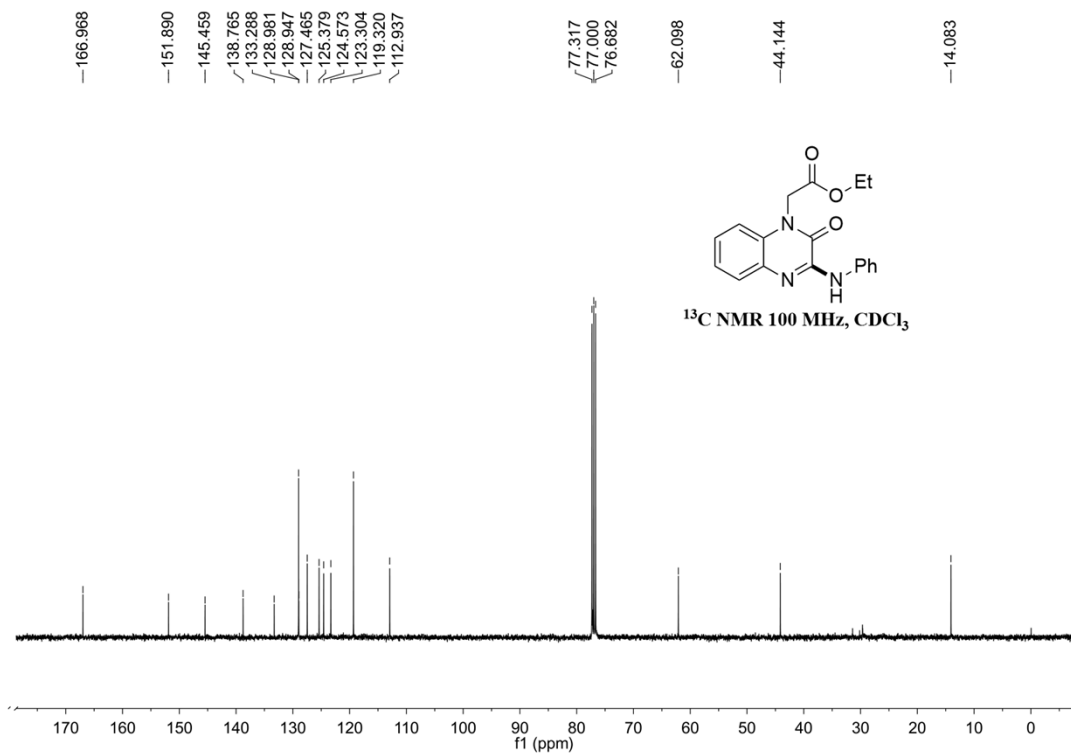


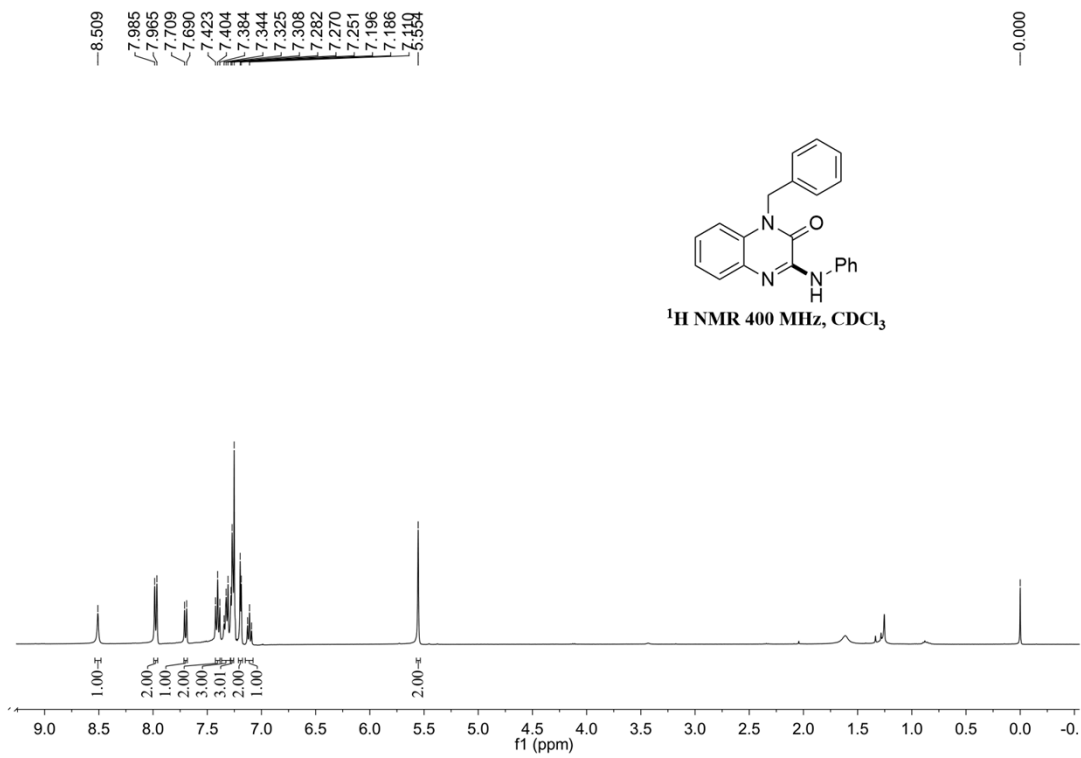
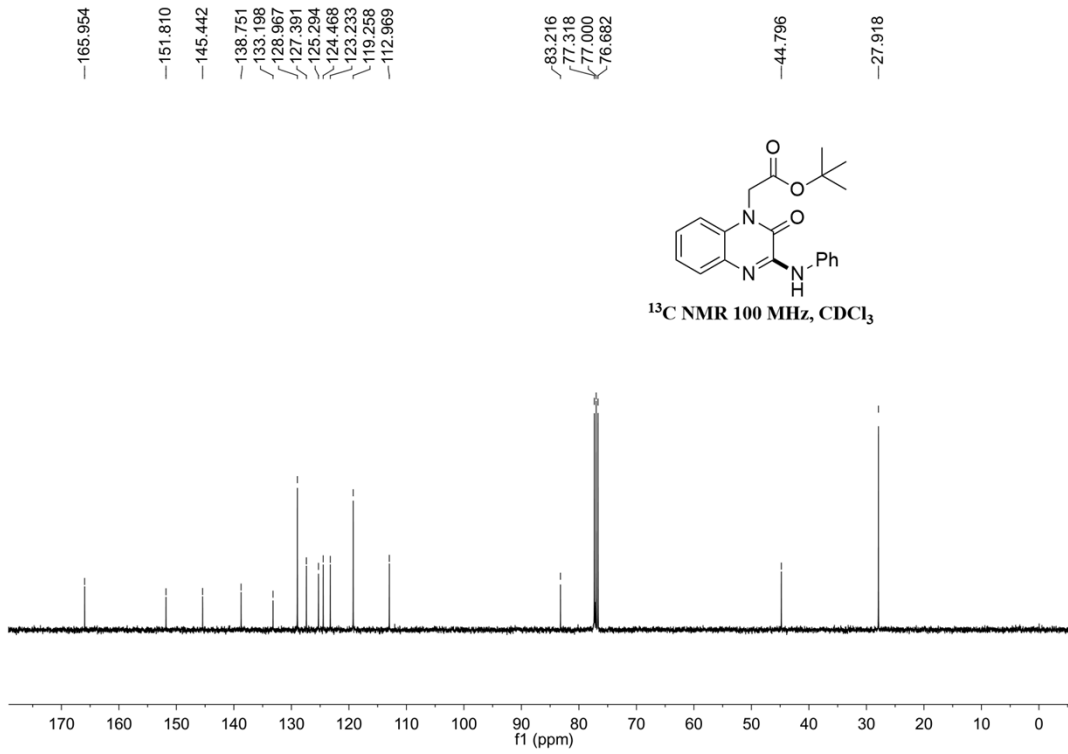


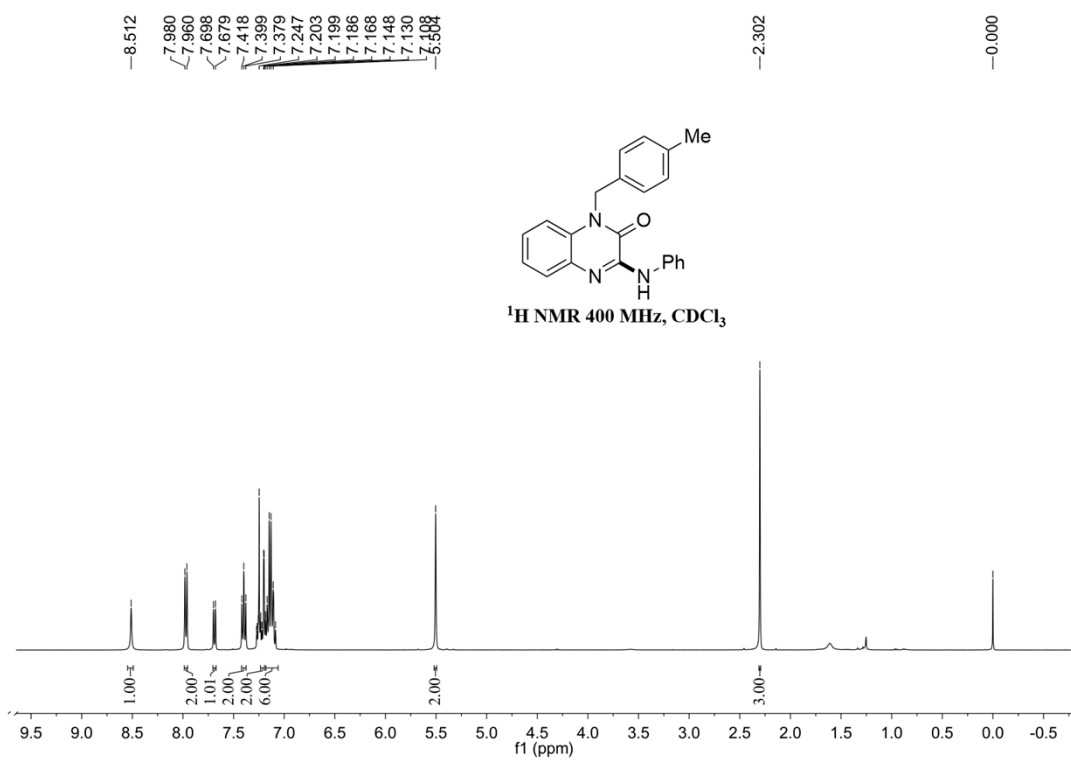
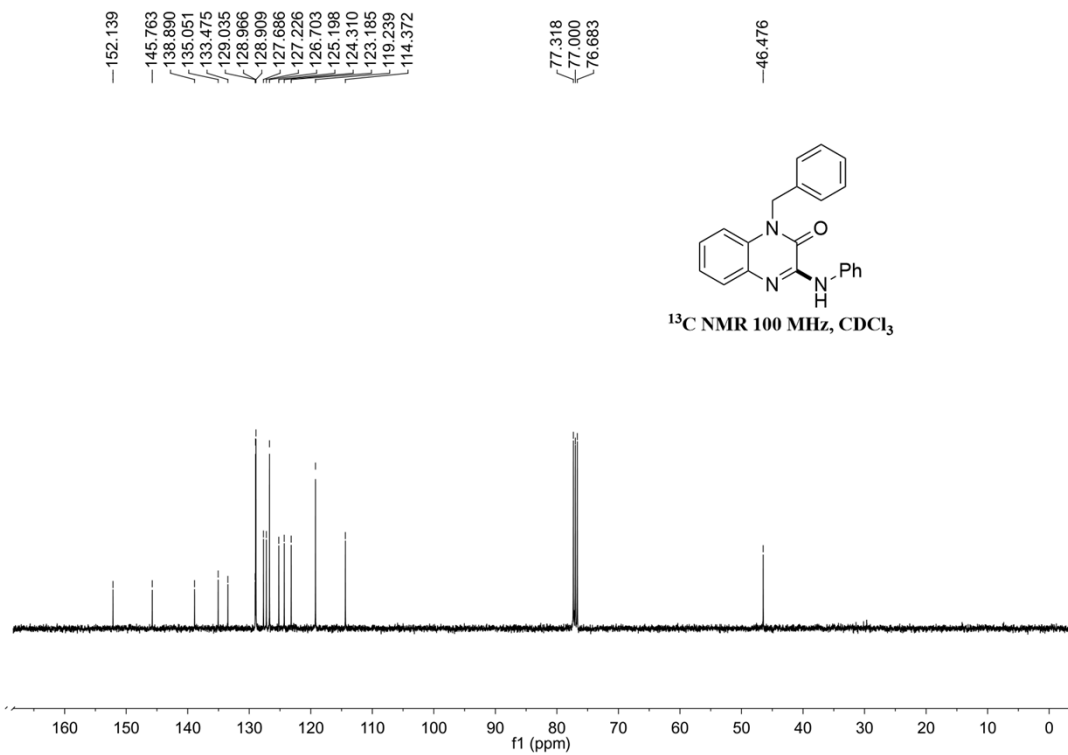


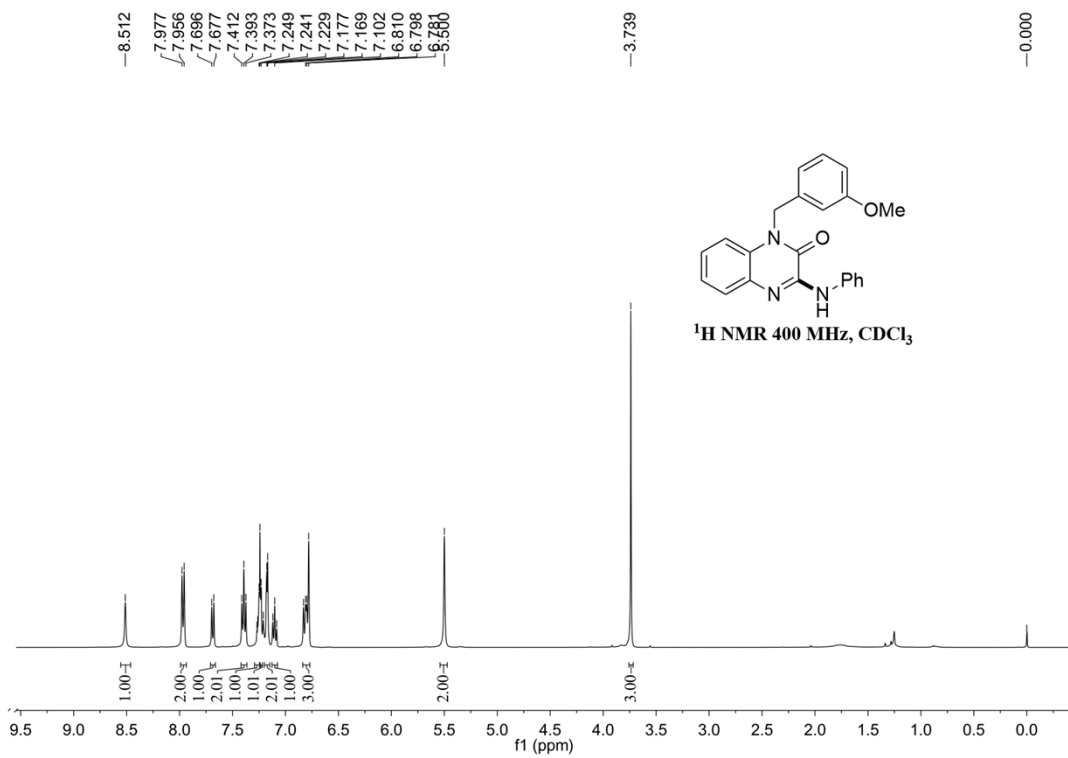
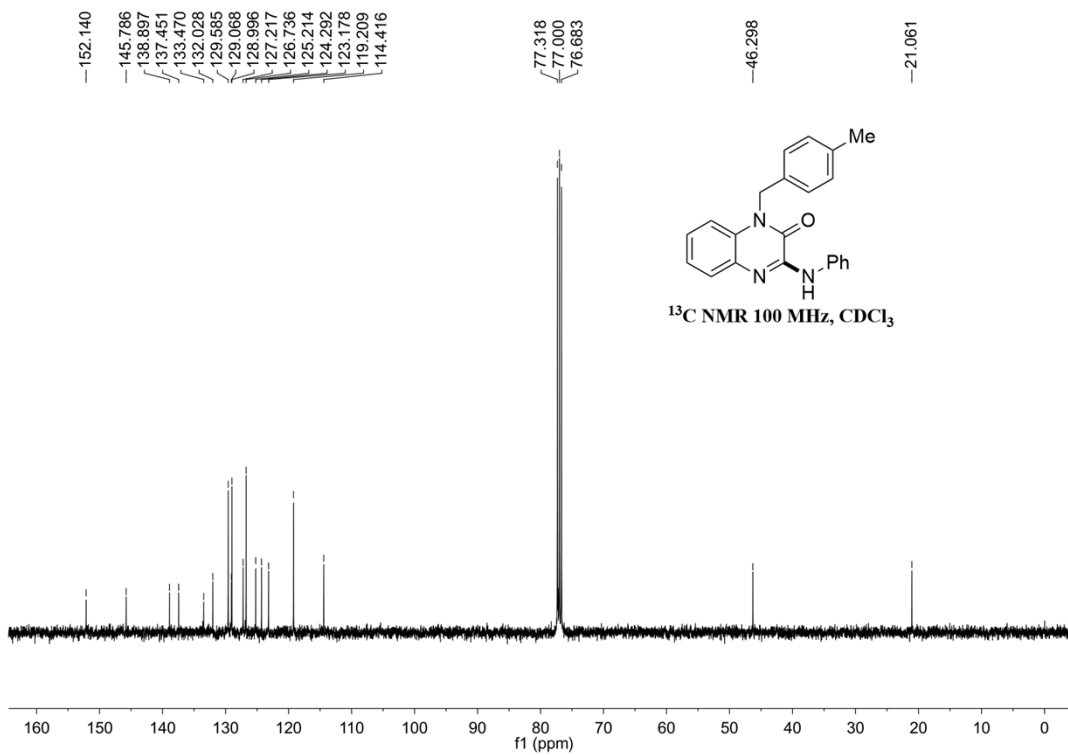


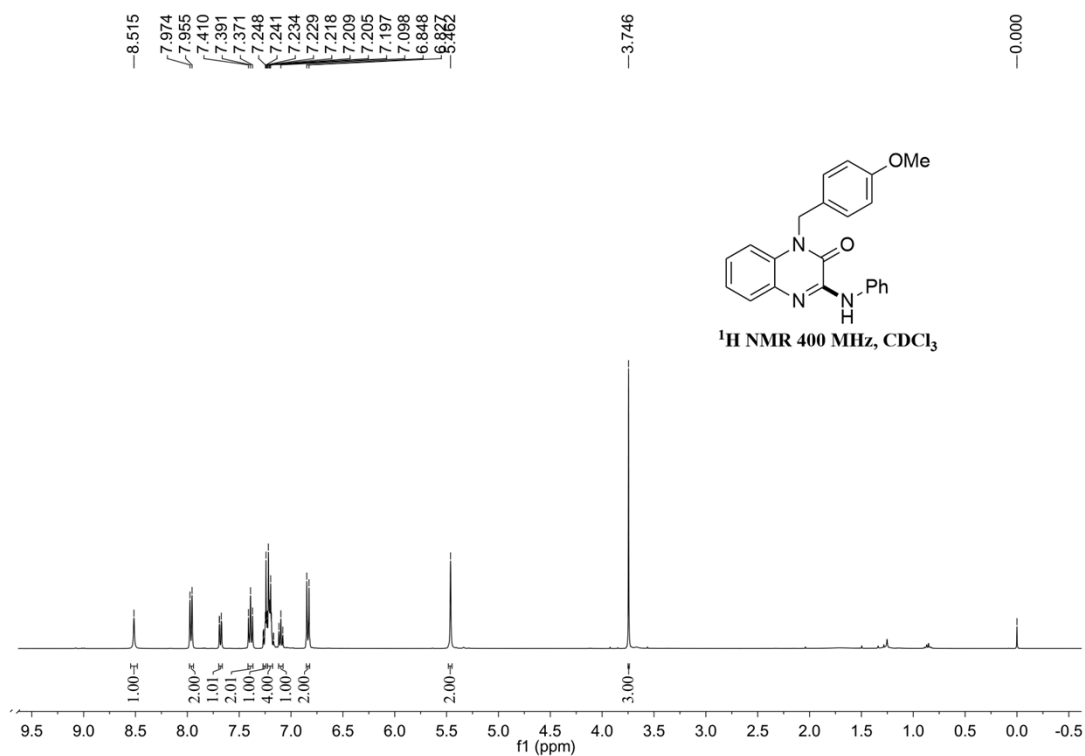
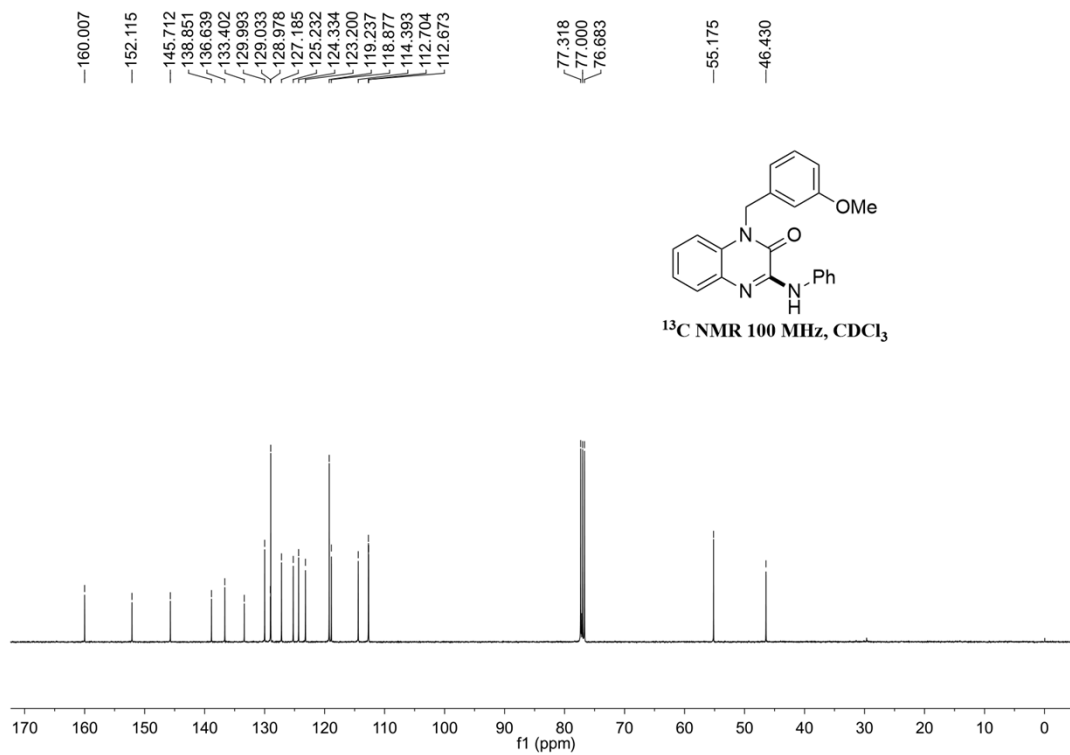


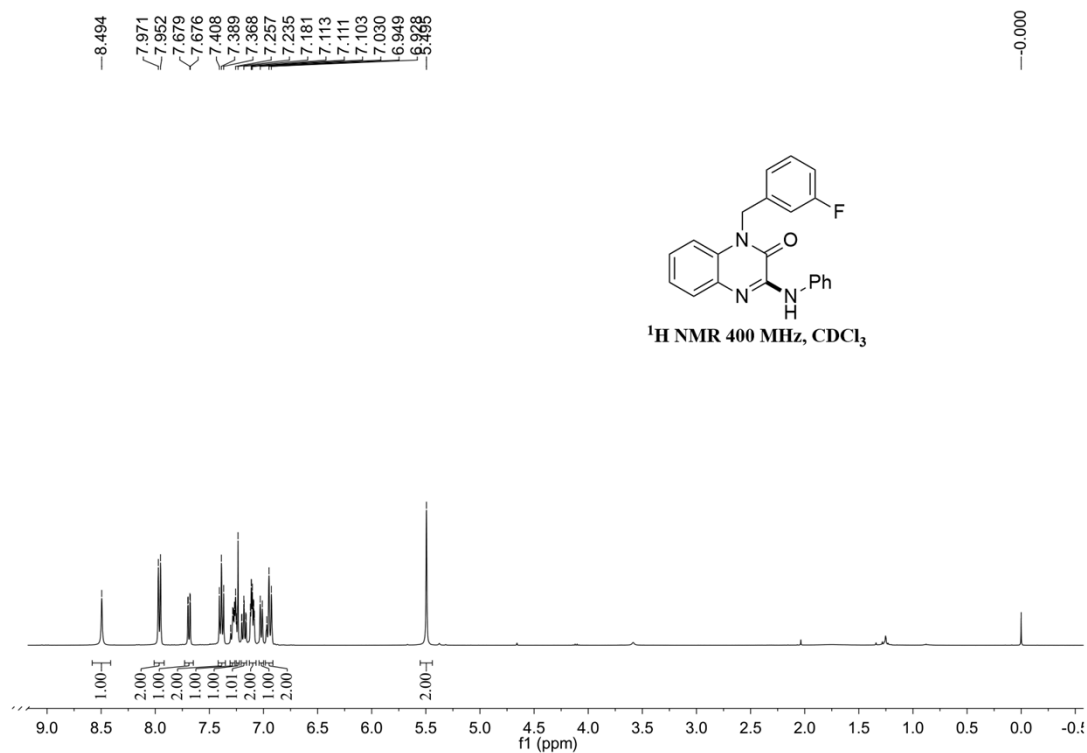
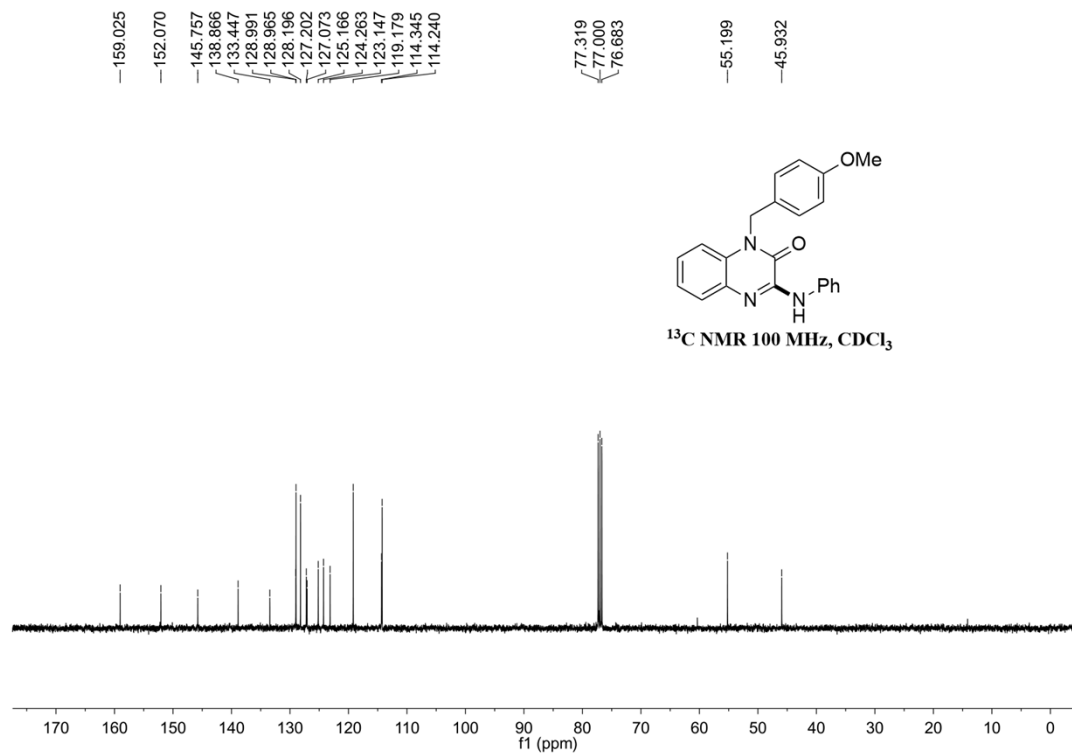


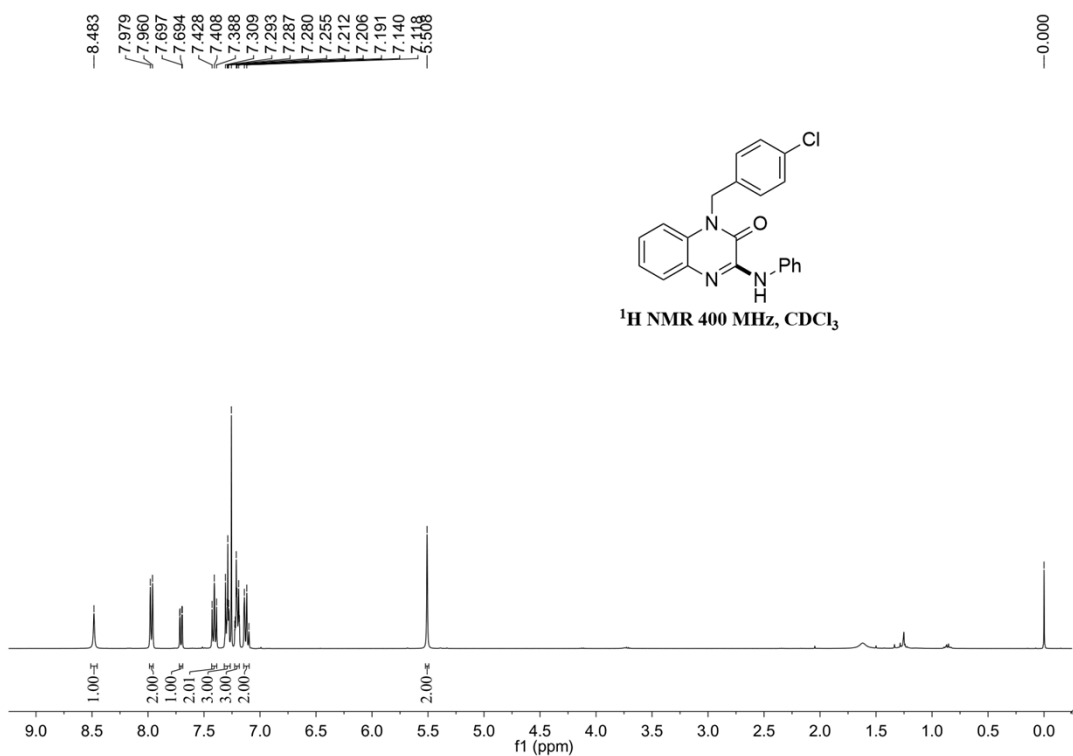
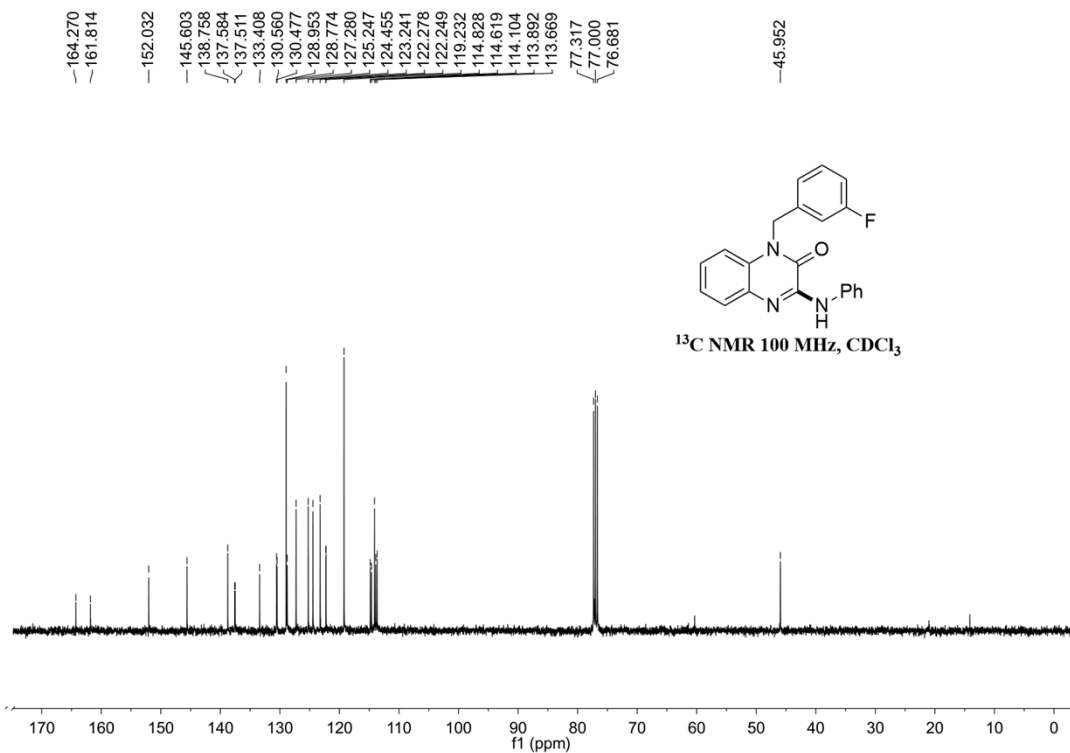


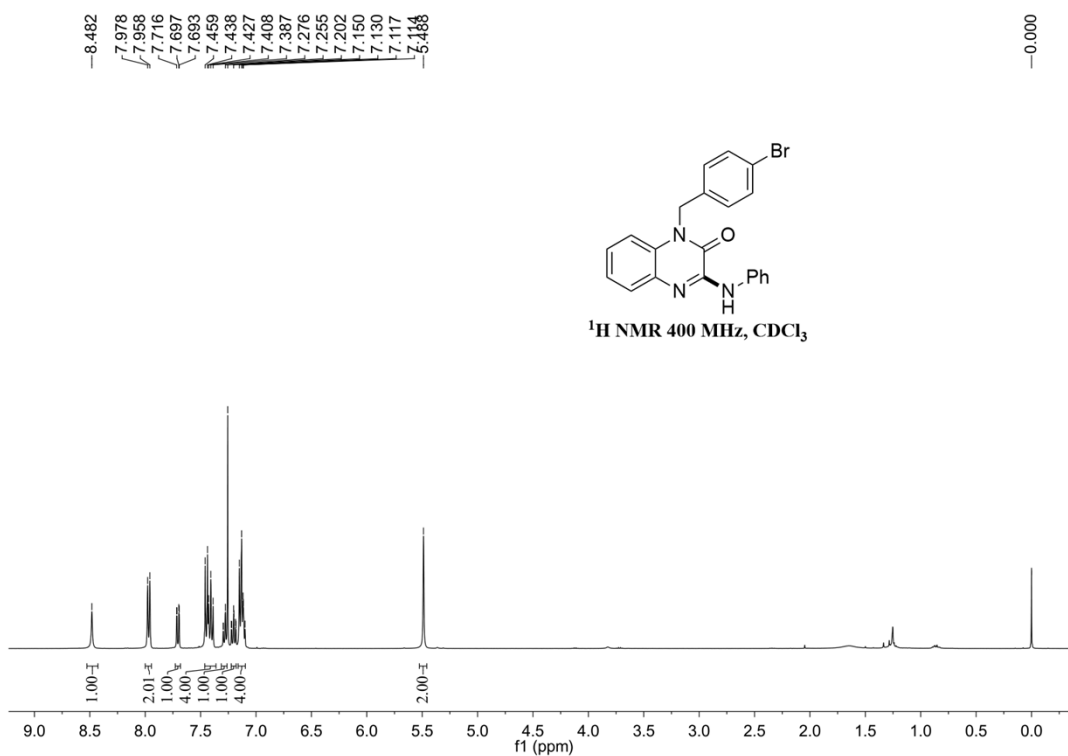
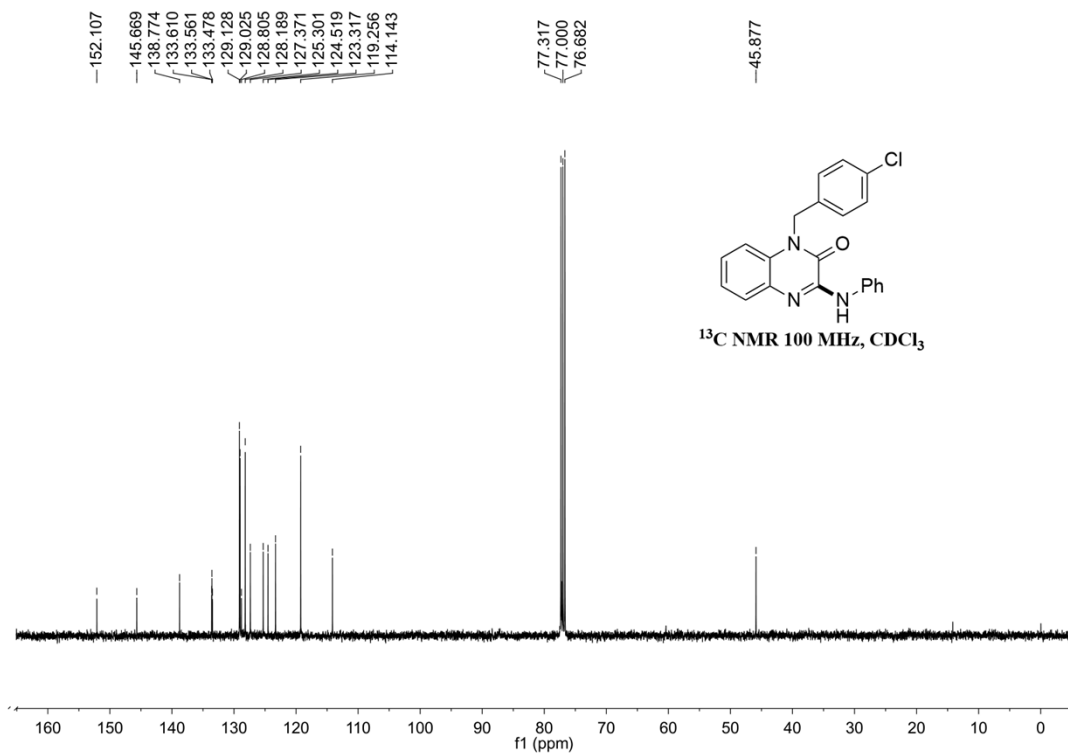


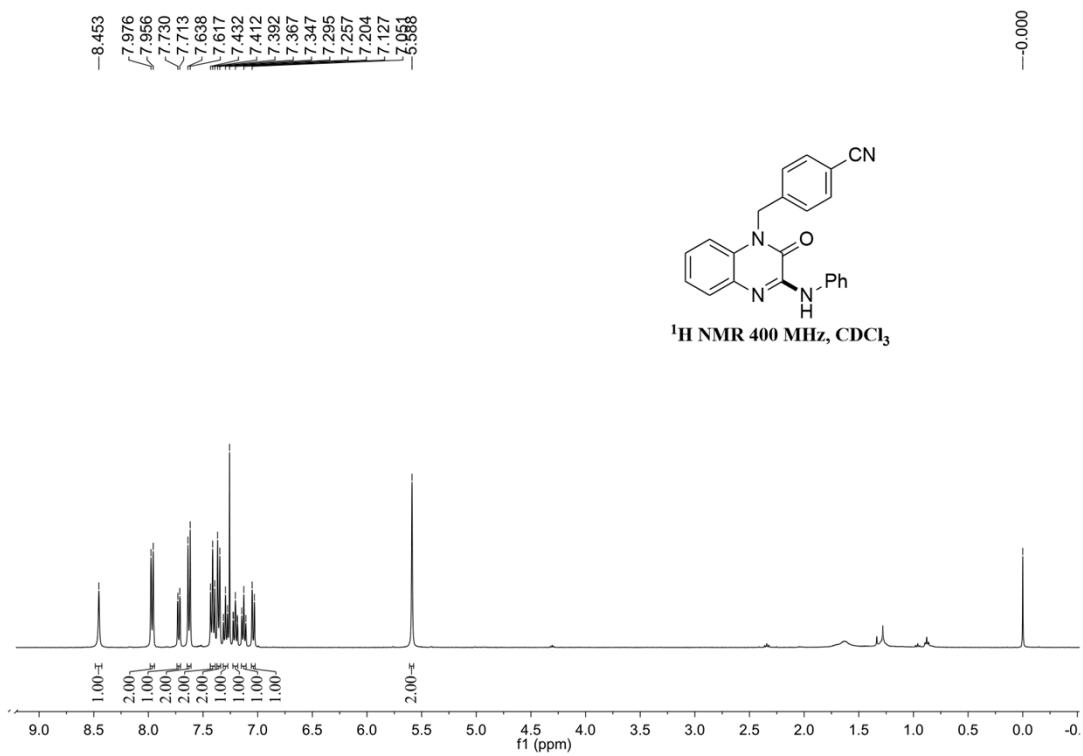
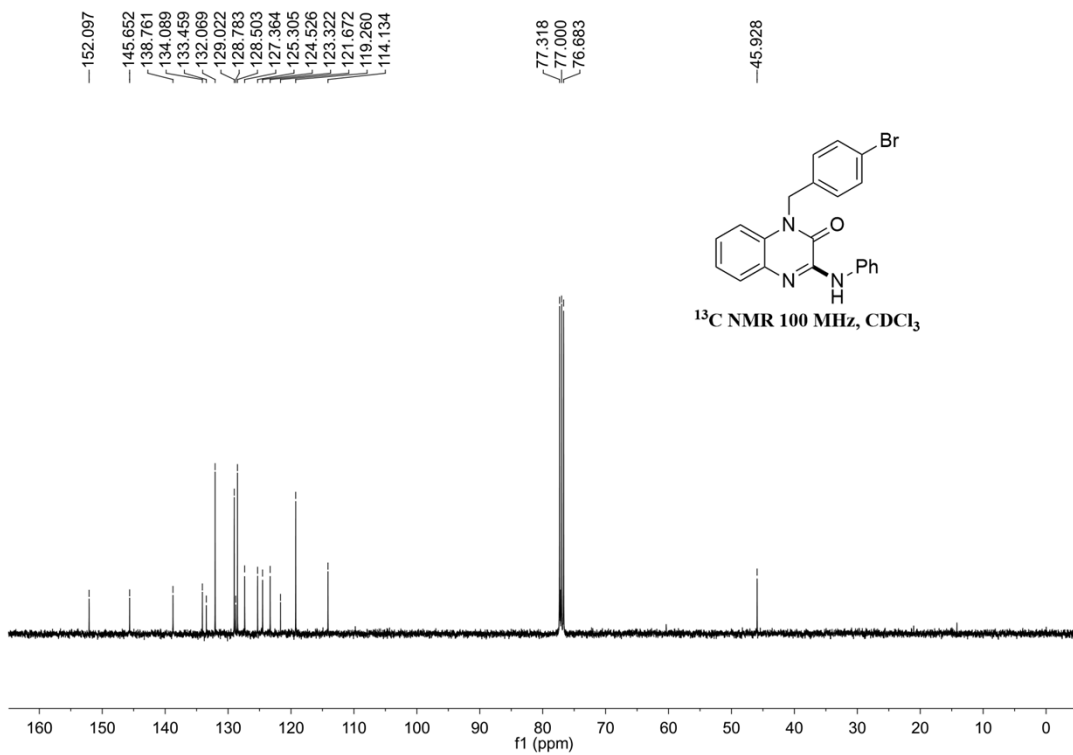


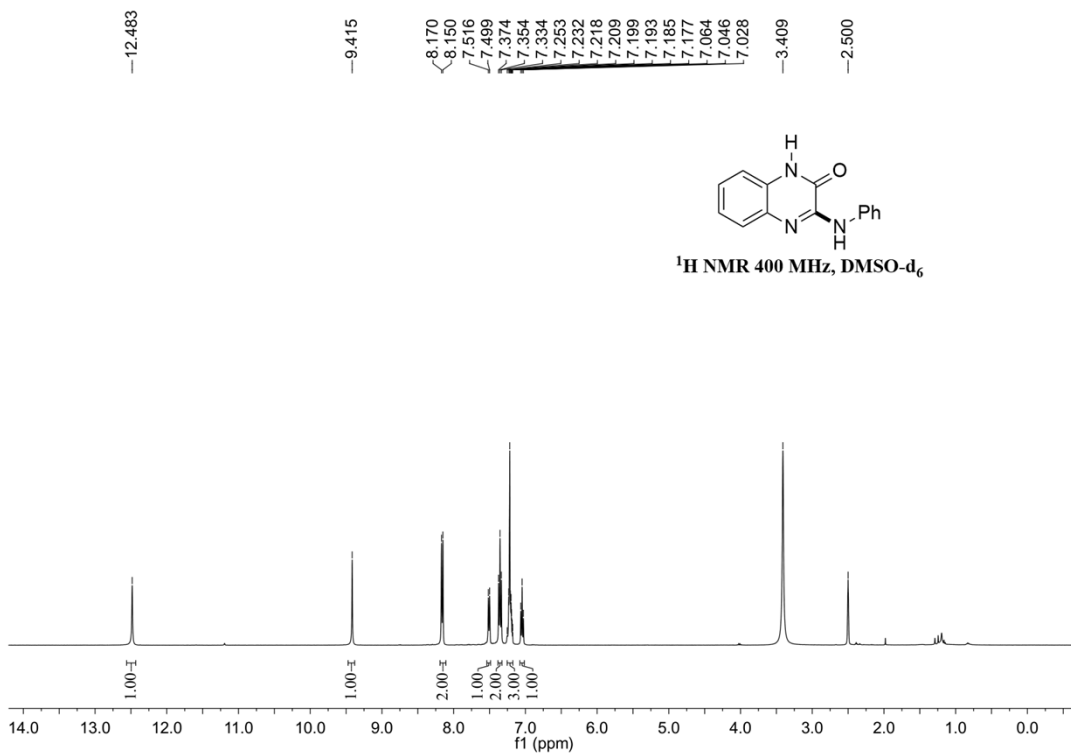
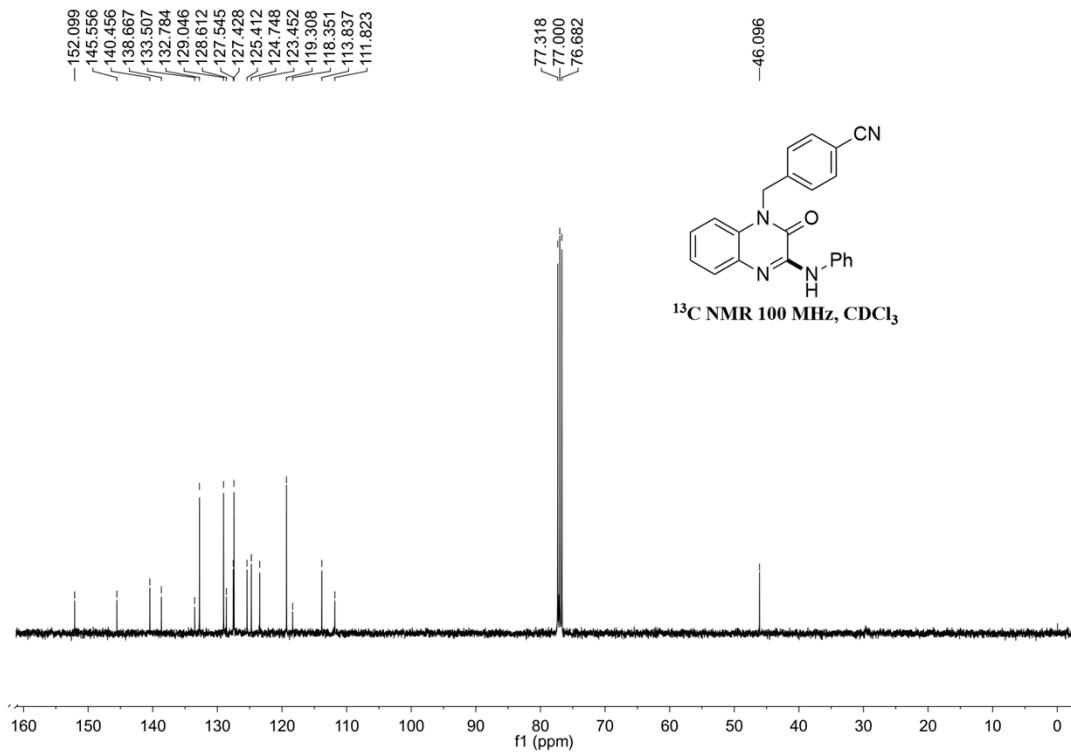


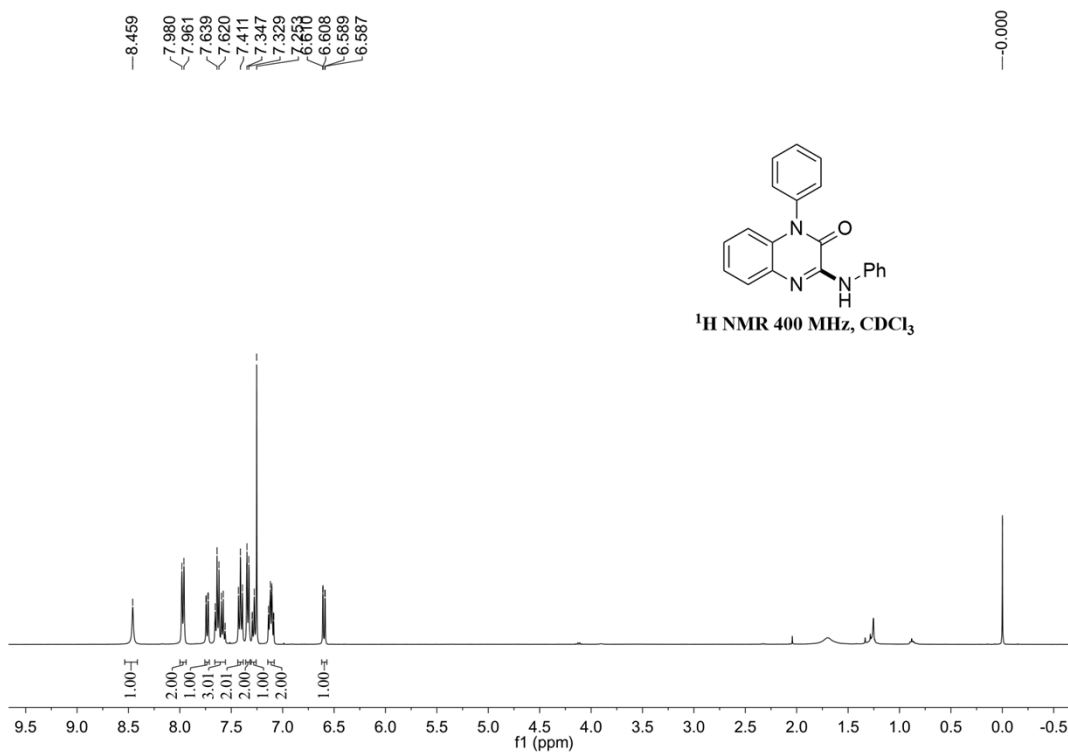
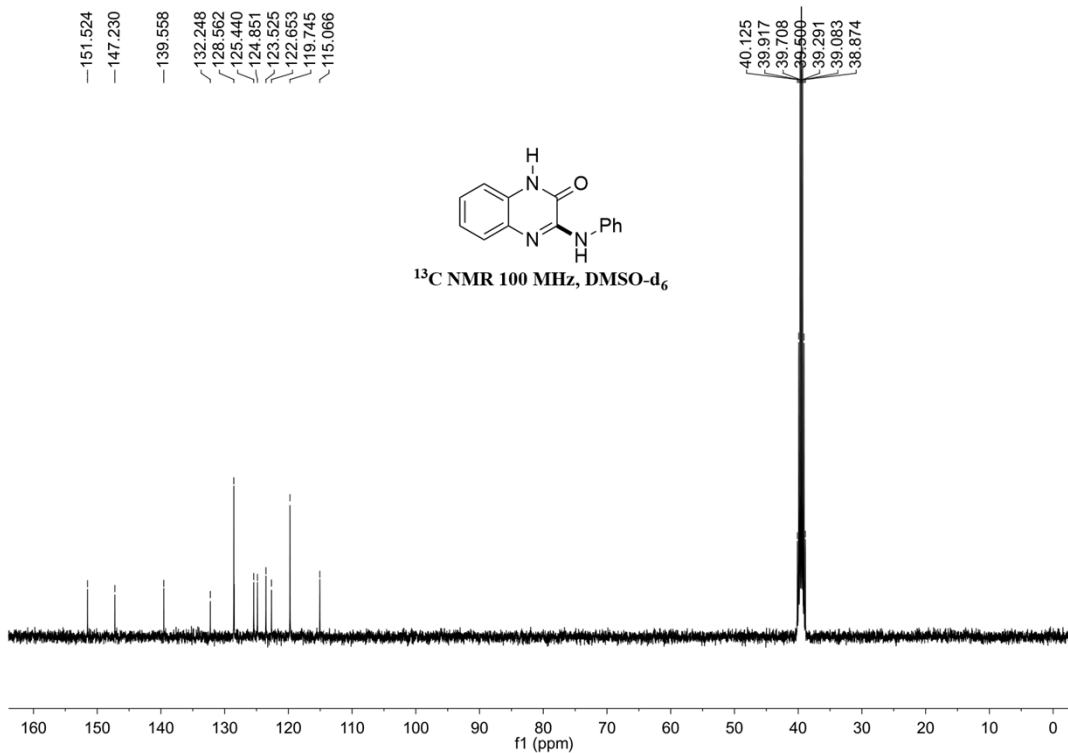


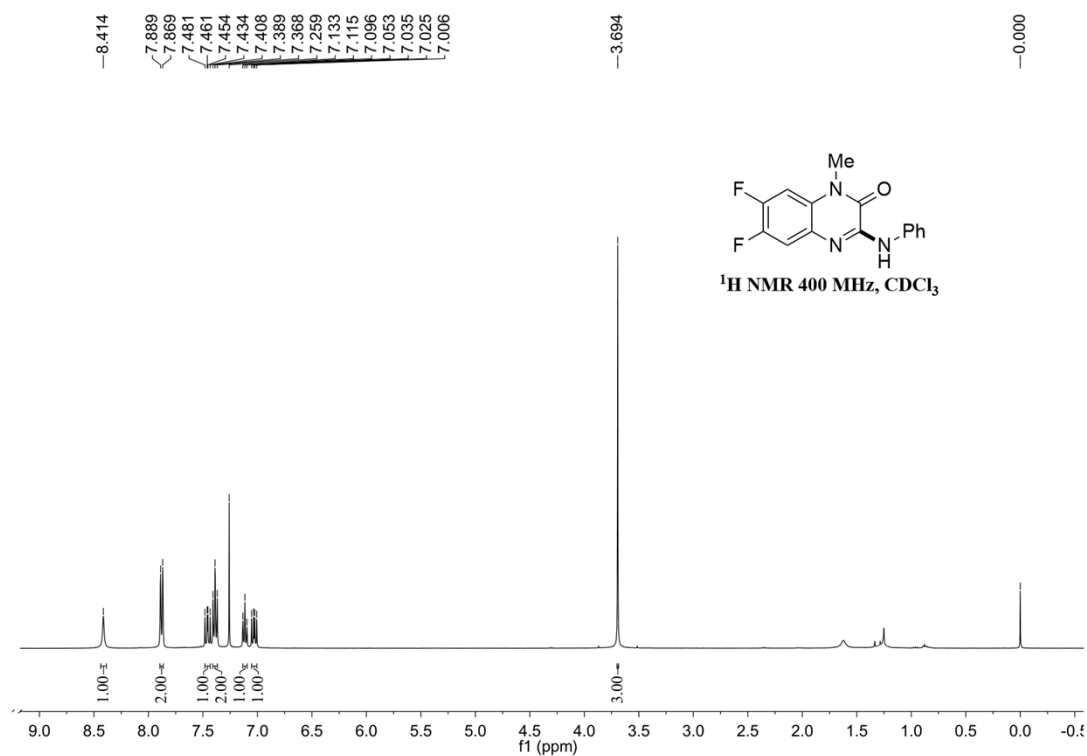
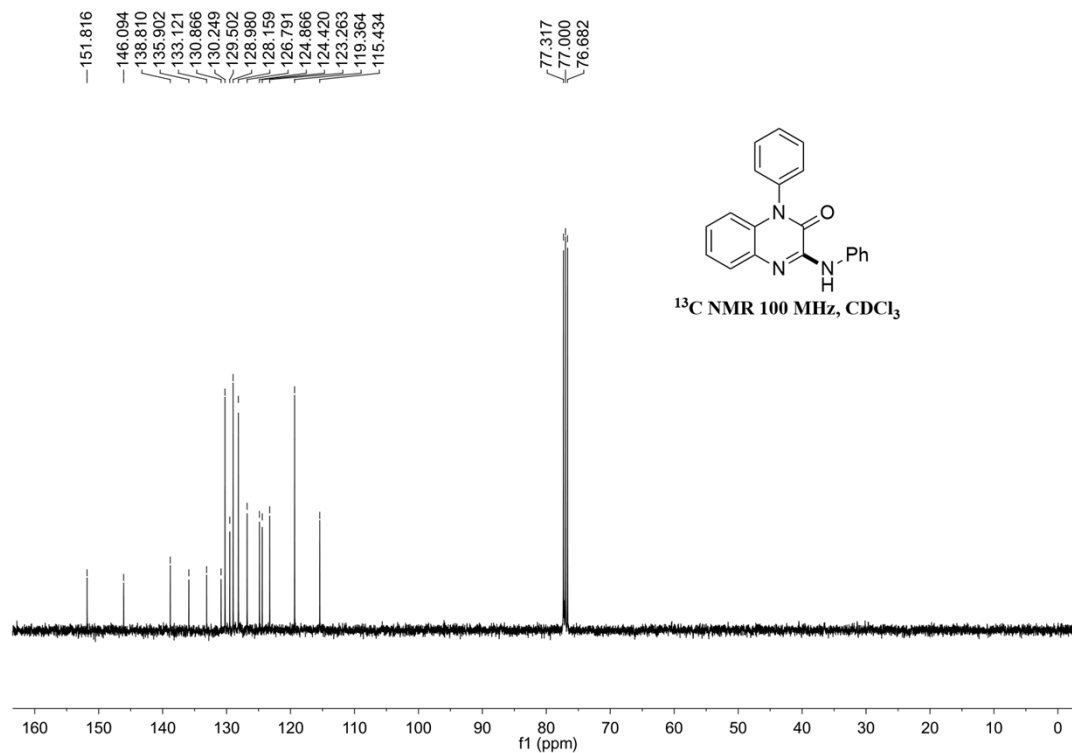


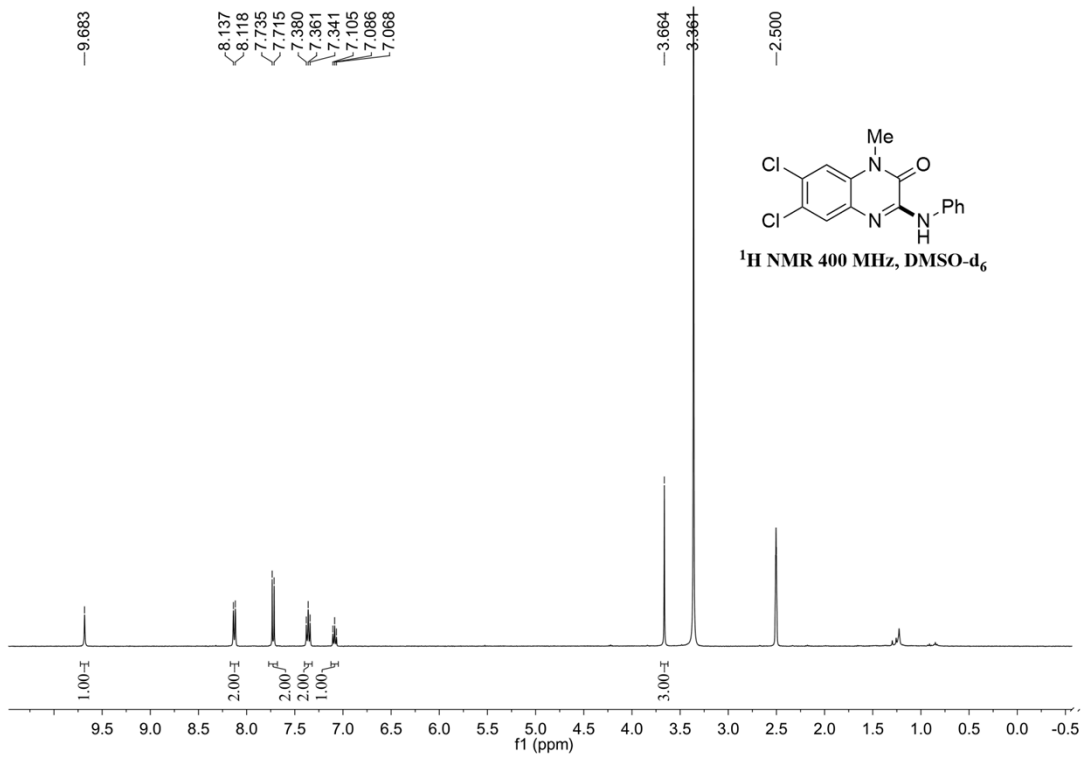
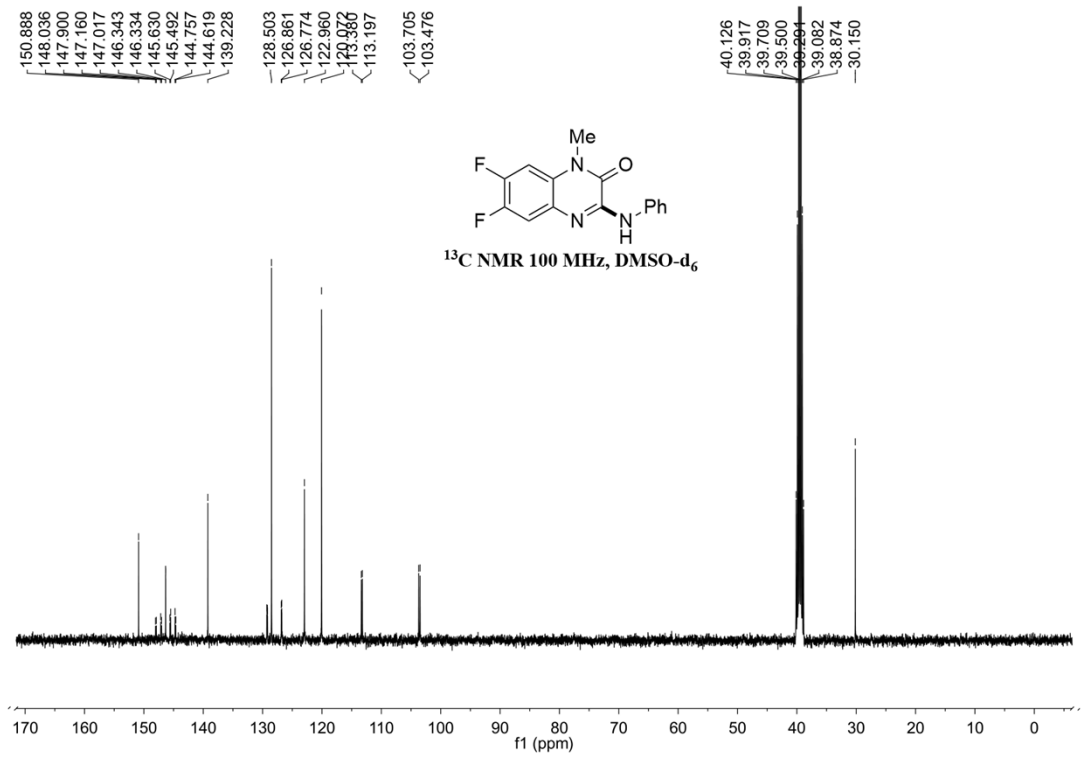


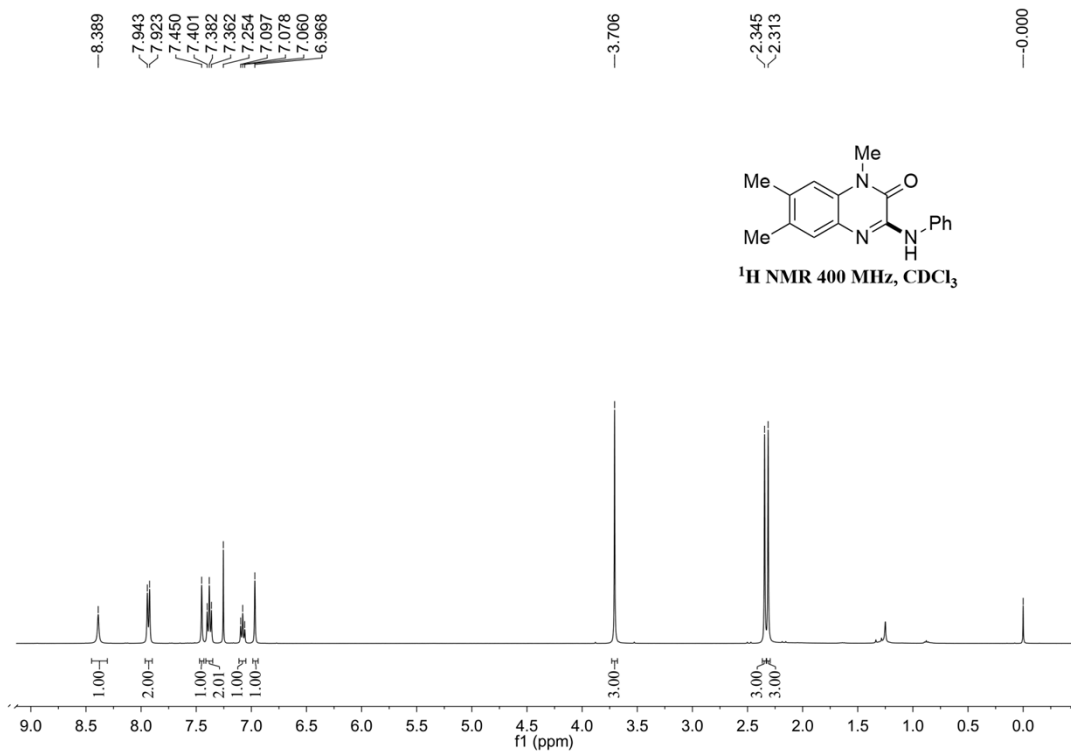
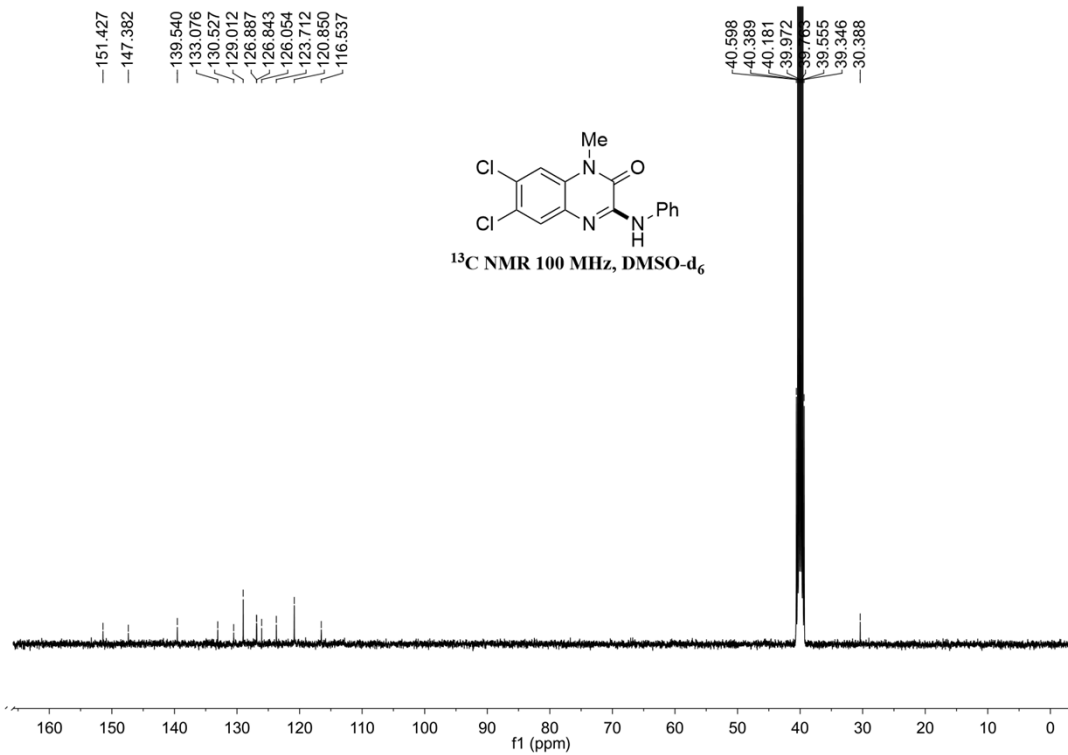


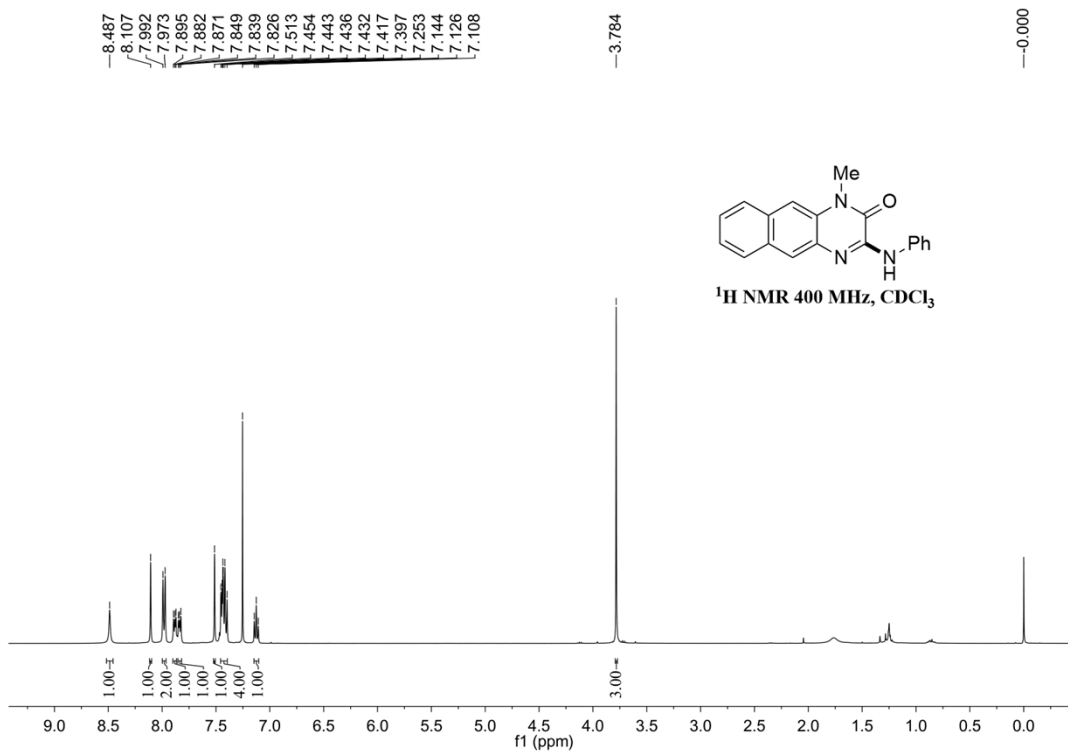
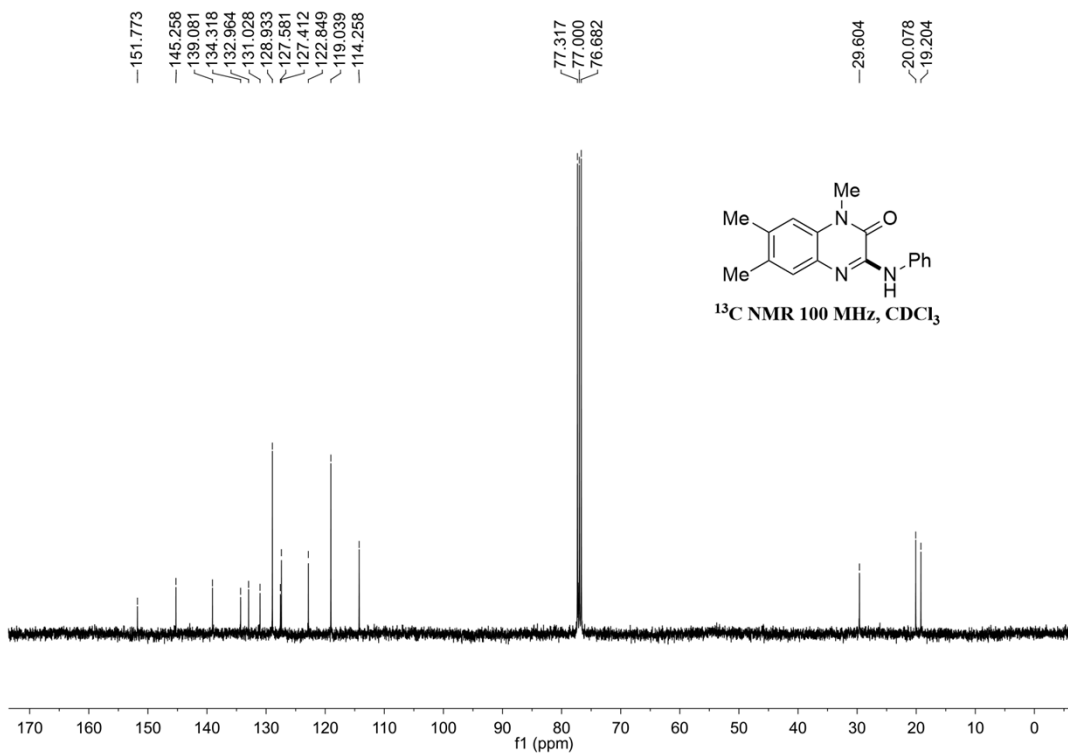


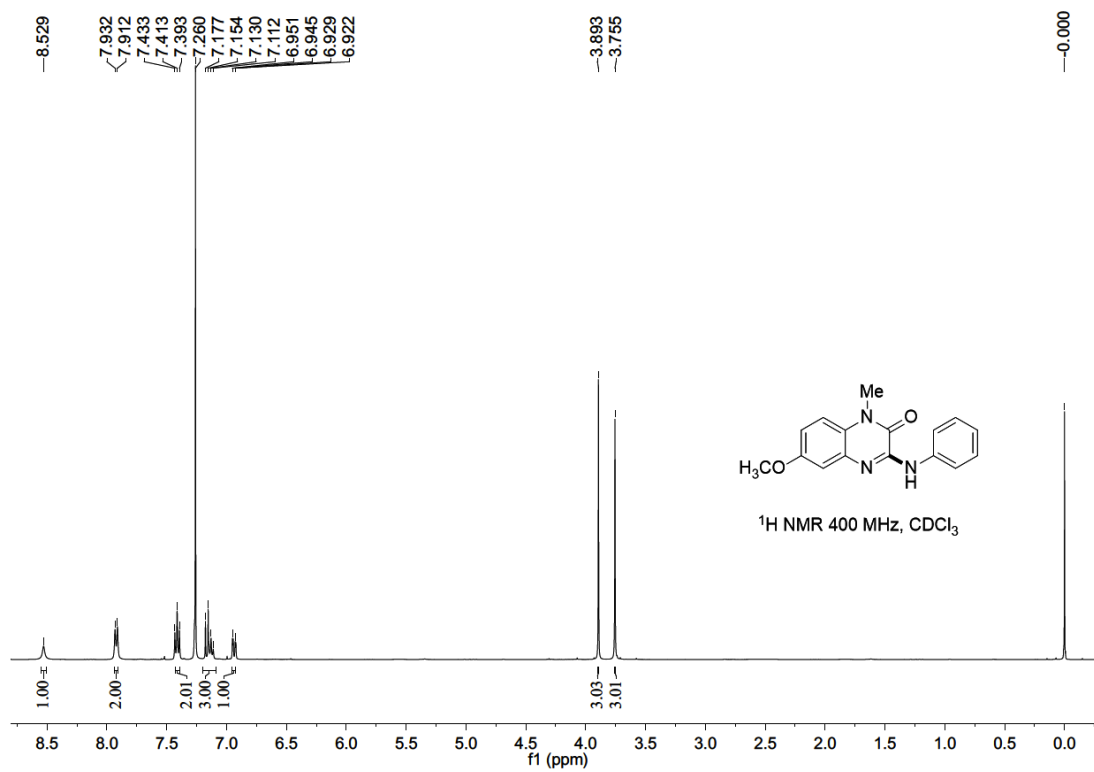
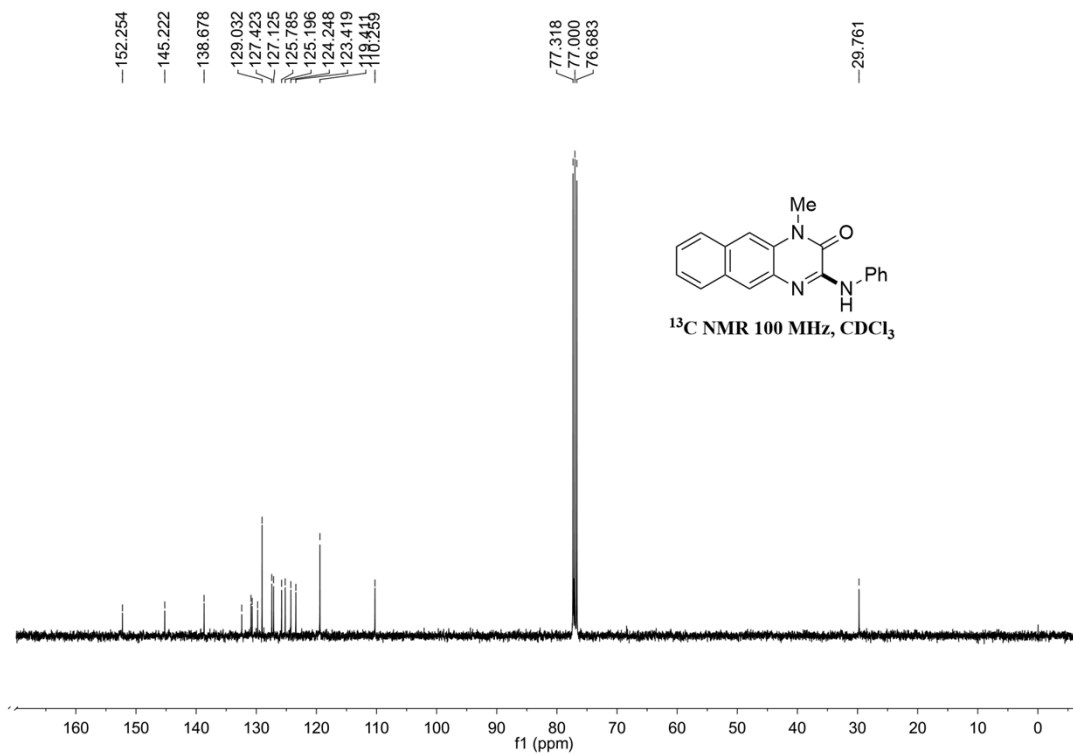


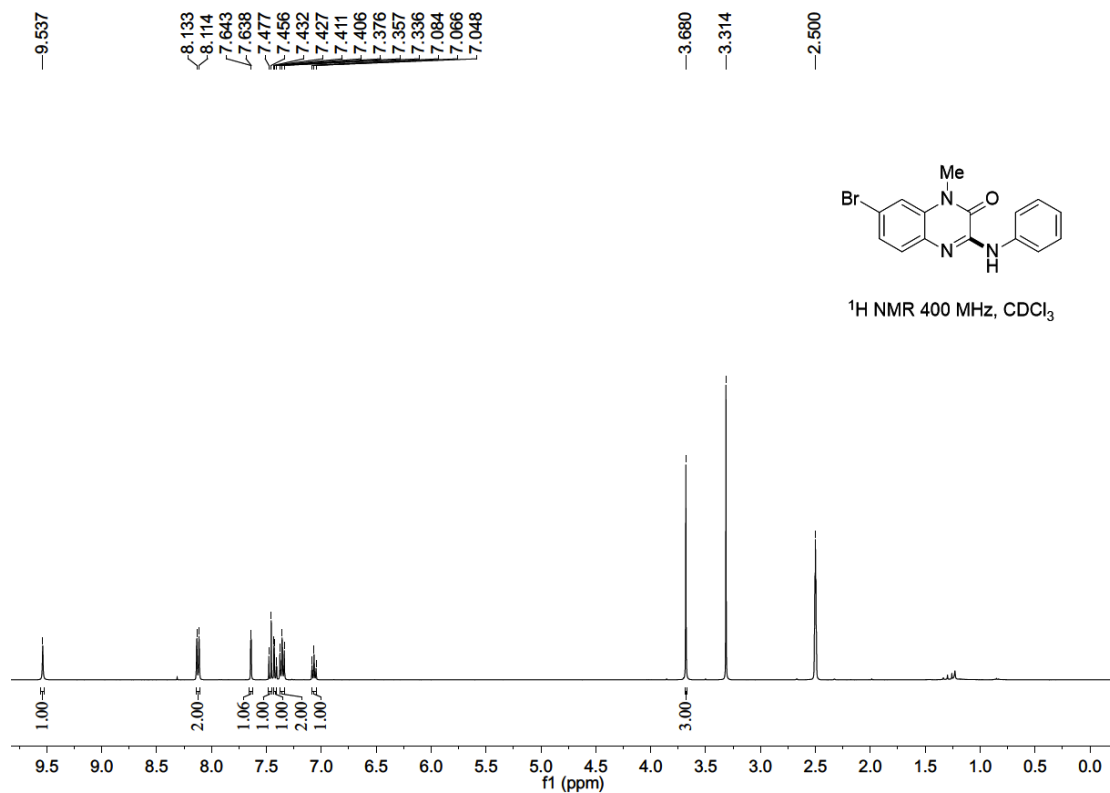
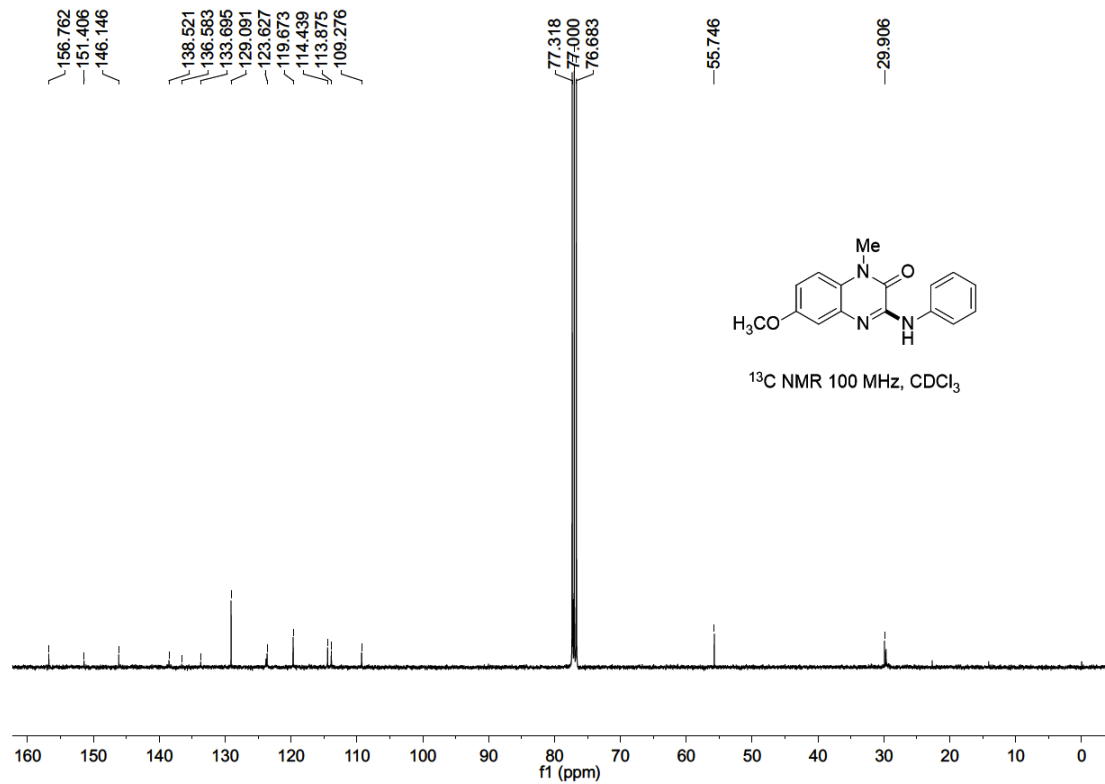


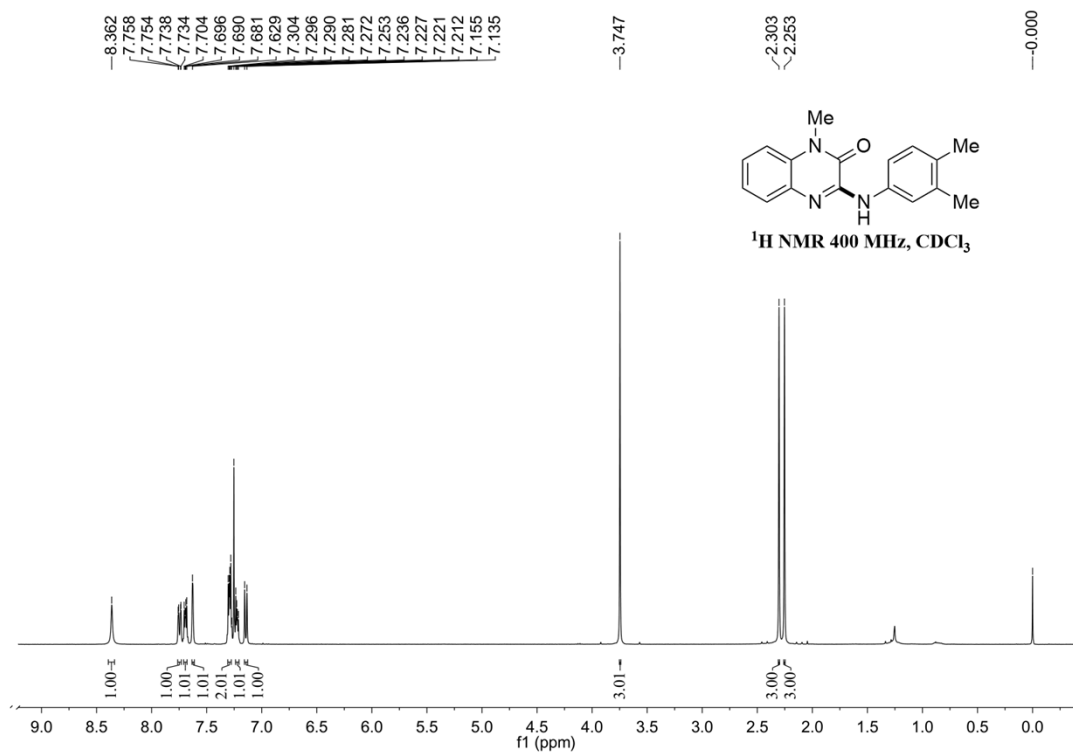
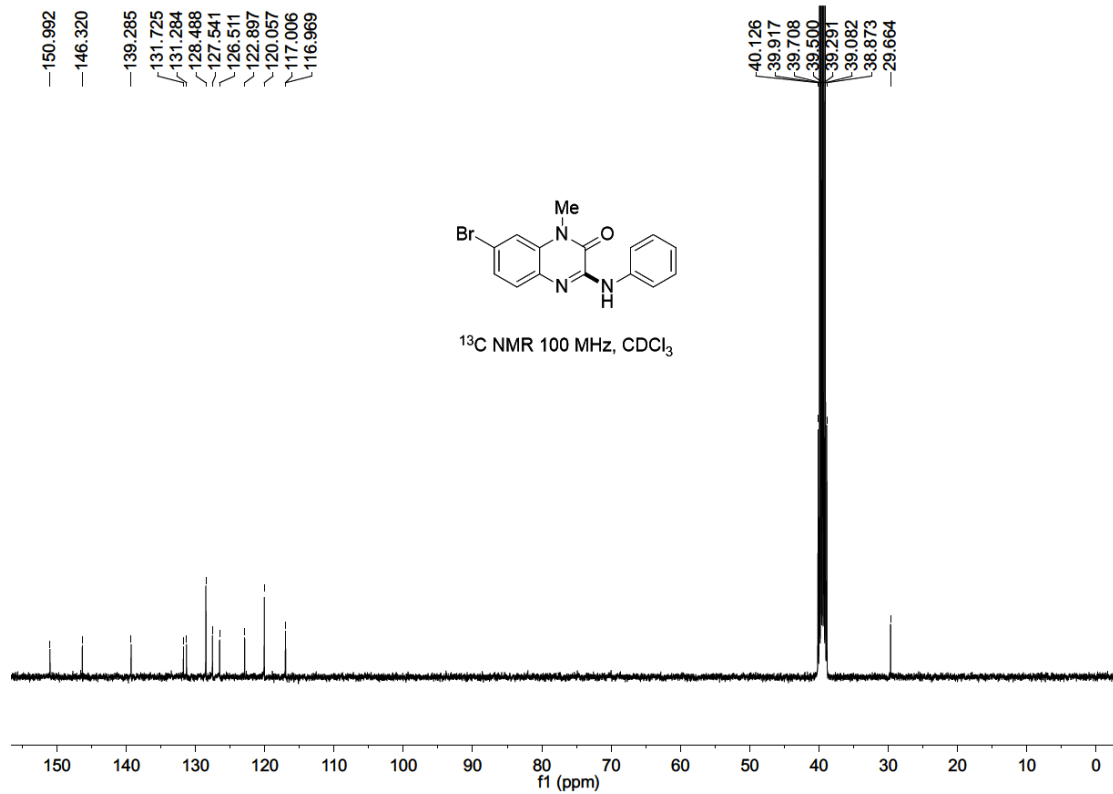


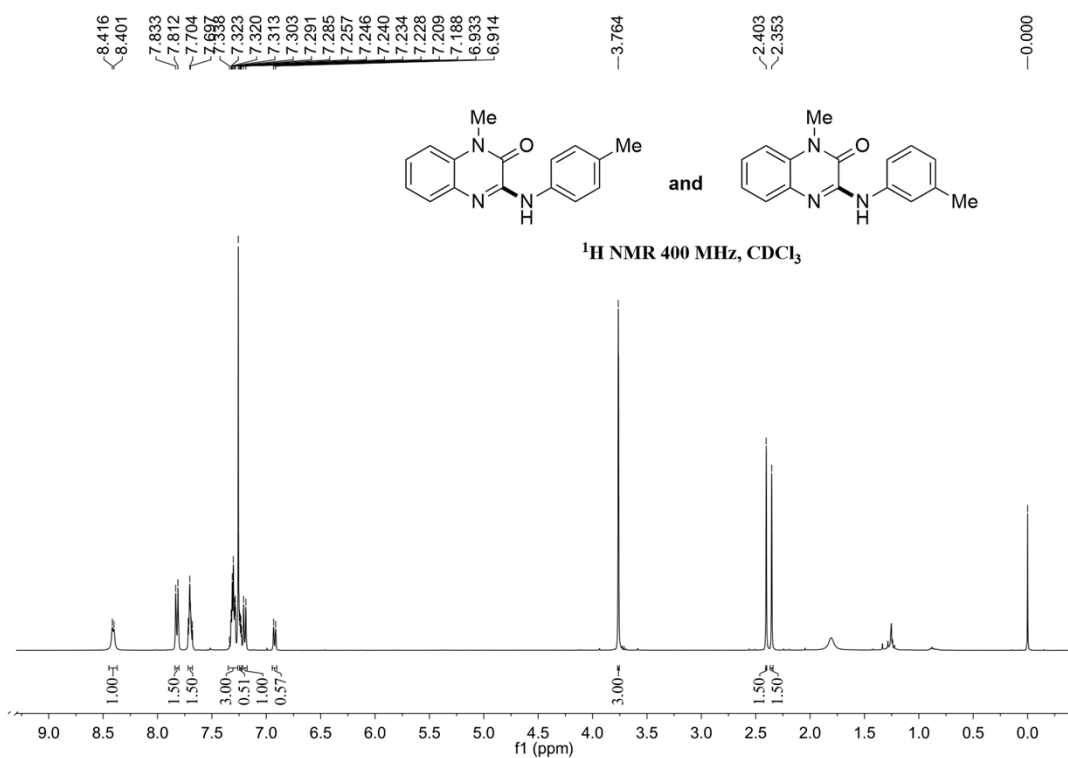
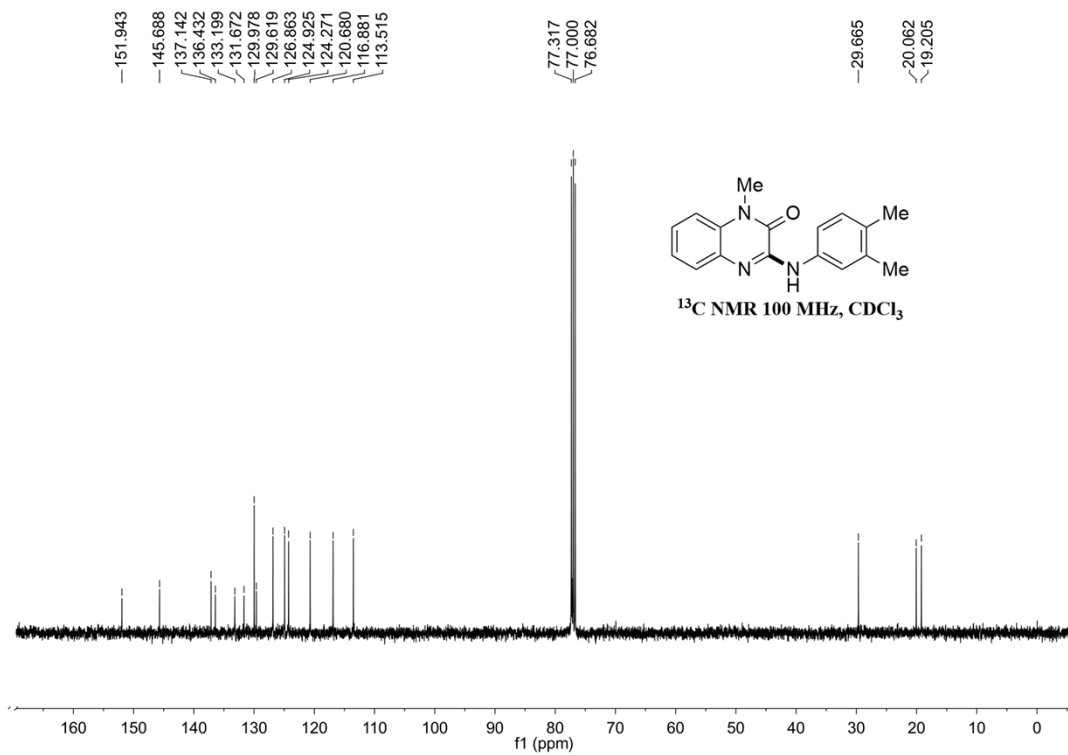


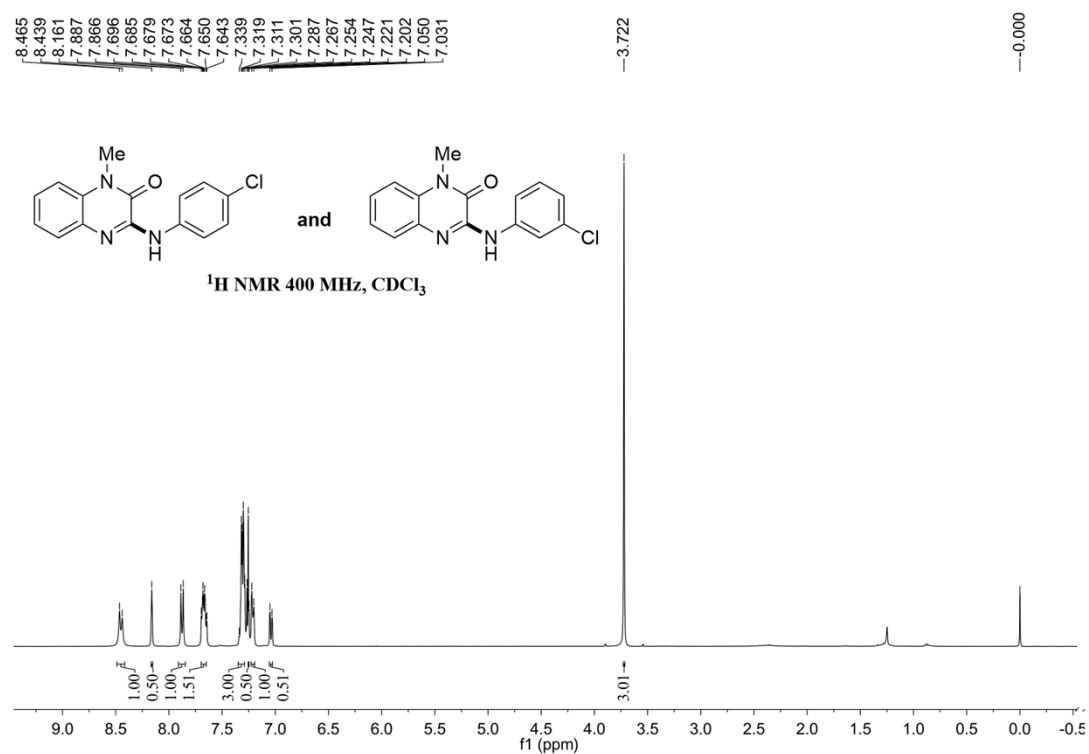
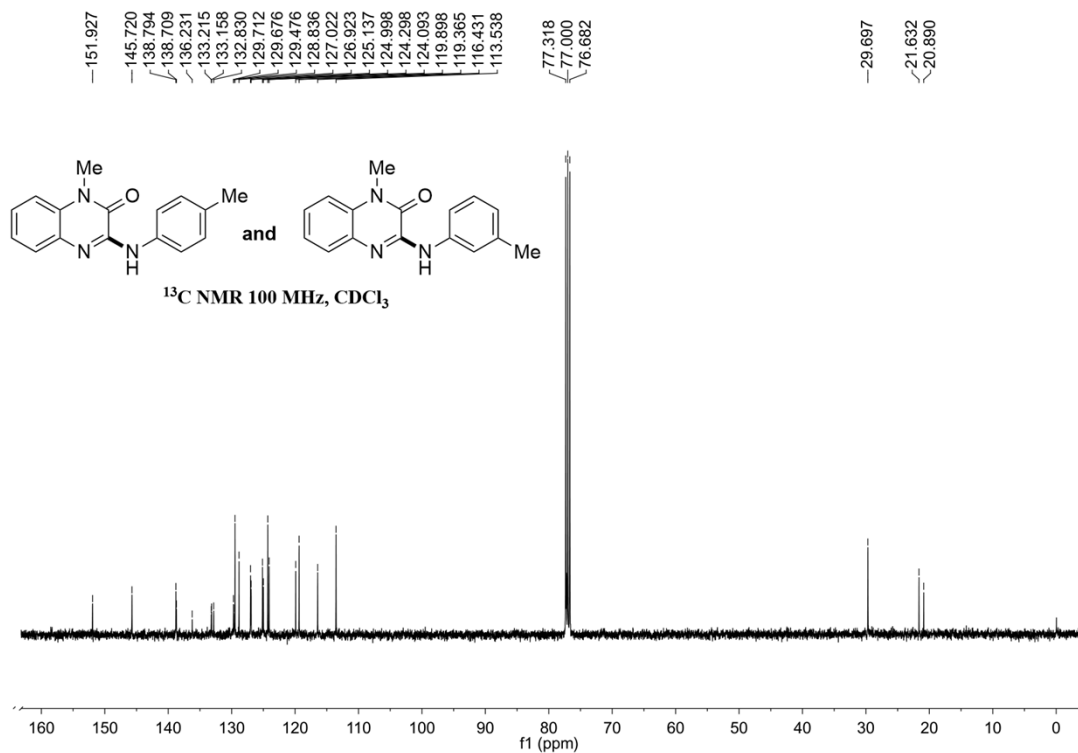


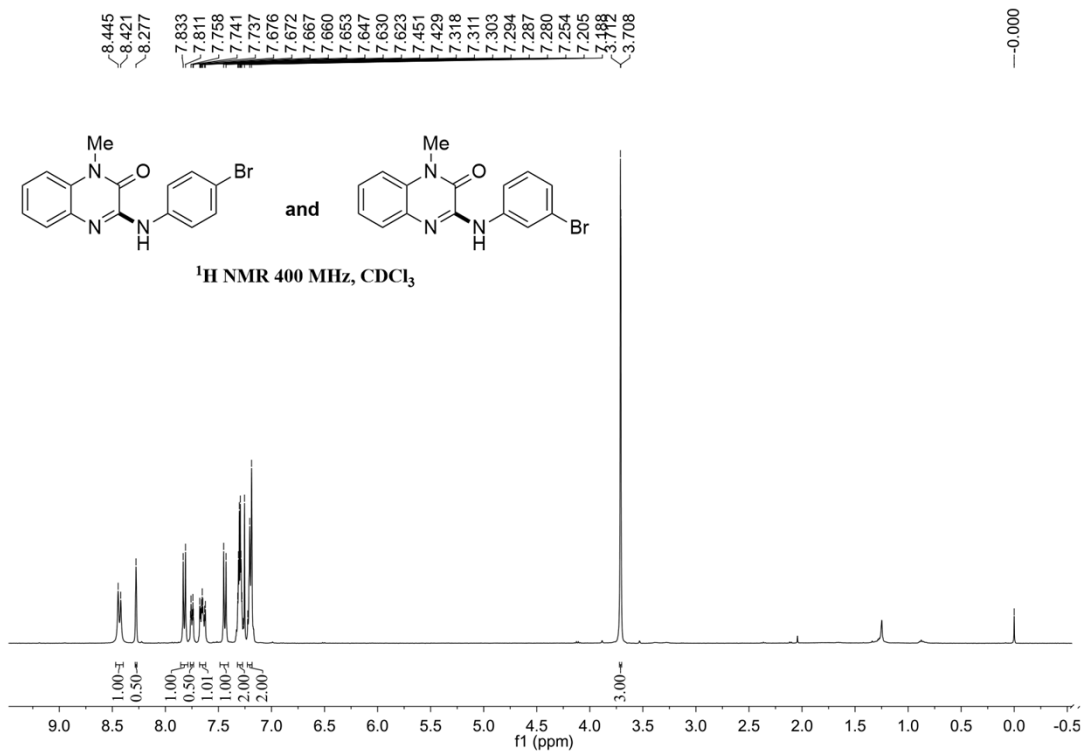
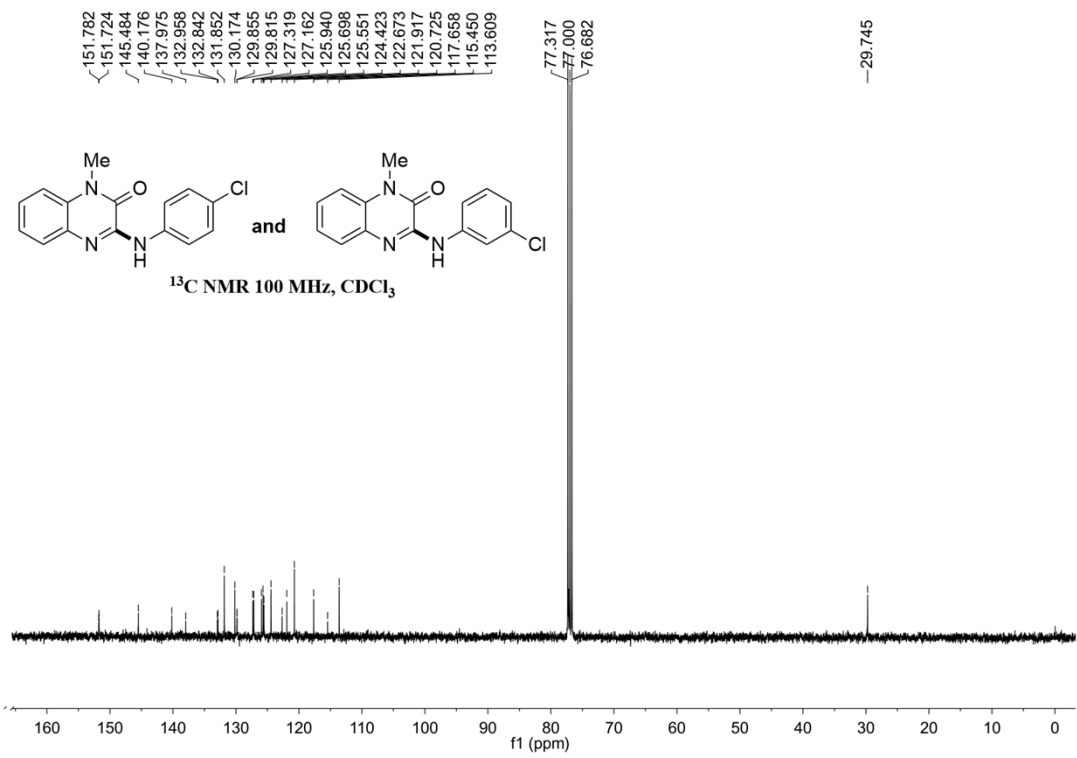


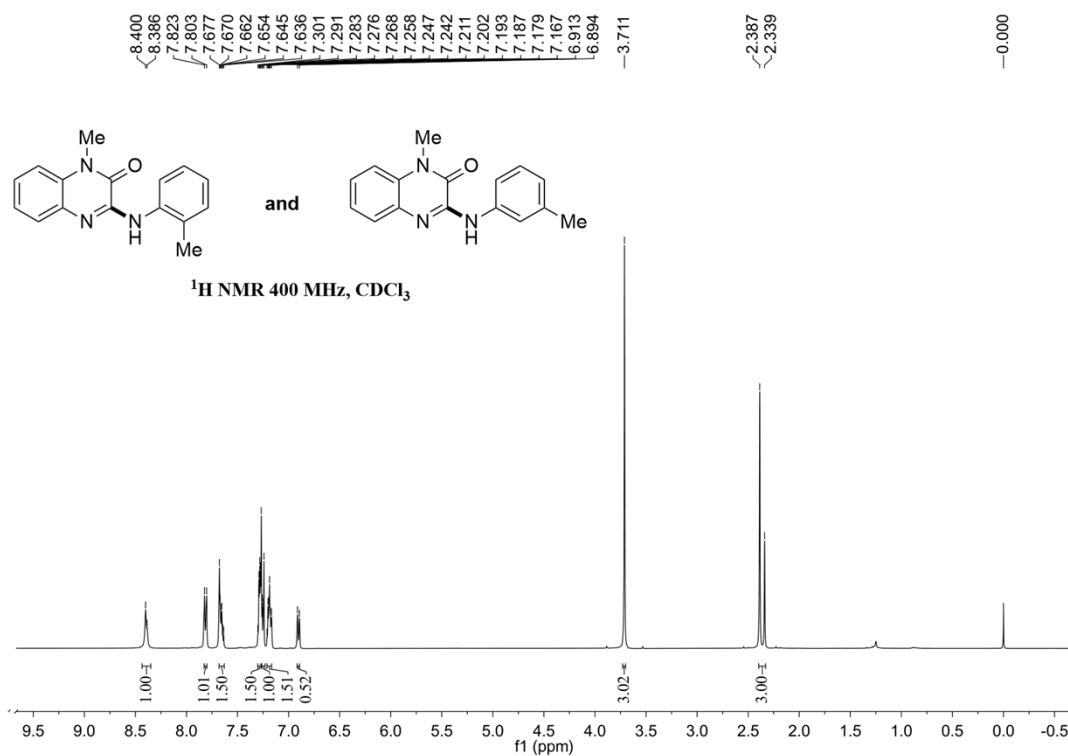
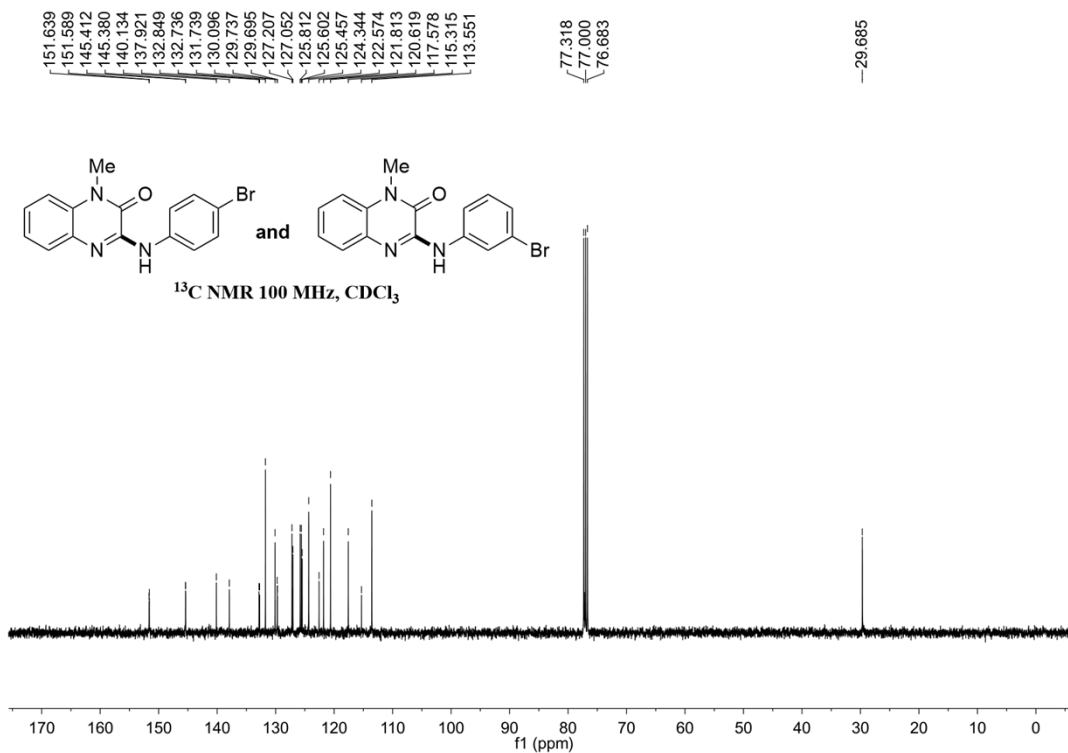




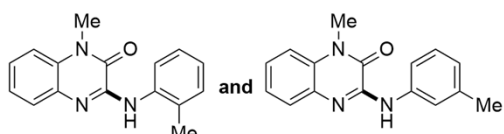








δ 151.887
 δ 151.868
 δ 145.686
 δ 138.740
 δ 138.727
 δ 136.263
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 δ 133.162
 δ 132.726
 δ 129.679
 δ 129.643
 δ 129.427
 δ 128.795
 δ 126.994
 δ 126.901
 δ 125.078
 δ 124.932
 δ 124.240
 δ 124.013
 δ 119.821
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 δ 20.867



^{13}C NMR 100 MHz, CDCl_3

