

Supporting Information

BPO-Promoted [4 + 2] cyclization of enaminones and *o*-phenylenediamines to 2-acyl quinoxalines via a cascade transamination and C–H amination

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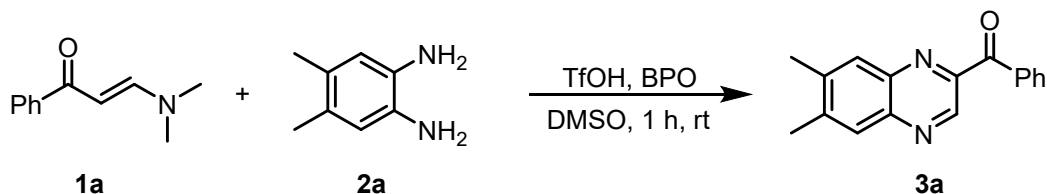
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1. General considerations

All ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometer (400/100/376 MHz). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, J , are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). Crystallographic data of product **3i**, **4d** was collected on Bruker SMART APEX II (Mo target, voltage 50 KV, current 30 mA). The chemicals and solvents were purchased from commercial suppliers either Aldrich (USA), or Shanghai Chemical Company (P. R. China). Products were purified by flash chromatography on 200–300 mesh silica gels, SiO_2 .

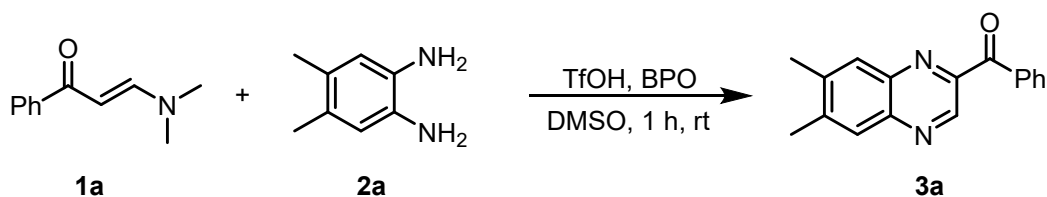
2. General procedures for the synthesis of products

2.1 General procedure for the synthesis 3/4 (3a as example)



Under air atmosphere, a 15 mL pressure-resistant tubes equipped with a magnetic stir bar was charged with enaminone (**1a**, 52.6 mg, 0.30 mmol), 3,4-dimethyl-o-phenylenediamine (**2a**, 27.2 mg, 0.20 mmol), TfOH (30.0 mg, 0.20 mmol), BPO (145.3 mg, 0.60 mmol) and DMSO (2.0 mL). The reaction mixture was stirred at room temperature with stirring for 1 h. After completion of the reaction, the reaction mixture was diluted with ethyl acetate and Sodium bicarbonate saturated solution (1 mL). The resulting mixture was extracted with ethyl acetate, and the combined organic layers were washed with brine, dried over Na₂SO₄, filtered and concentrated. The residue was purified with silica gel chromatography (petroleum ether/ethyl acetate = 10:1, V/V) to give the product **3a** (39.4 mg, 75% yield).

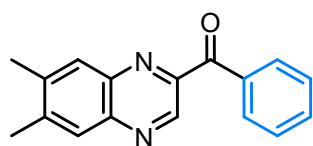
2.2 General procedure for the synthesis 3a in 5.0 mmol scale



Under air atmosphere, a 50 mL round-bottom flask equipped with a magnetic stir bar was charged with enaminone (**1a**, 1.3g, 7.5 mmol), 3,4-dimethyl-o-phenylenediamine (**2a**, 681 mg, 5.0 mmol), TfOH (750 mg, 5.0 mmol), BPO (3.6 g, 15.0 mmol) and DMSO (20.0 mL). The reaction mixture was stirred at room temperature with stirring for 5 h. After completion of the reaction, the reaction mixture was diluted with ethyl acetate and Sodium bicarbonate saturated solution (10

mL). The resulting mixture was extracted with ethyl acetate, and the combined organic layers were washed with brine, dried over Na₂SO₄, filtered and concentrated. The residue was purified with silica gel chromatography (petroleum ether/ethyl acetate = 10:1, V/V) to give the product **3a** (865 mg, 66% yield).

3. Characterization data of products



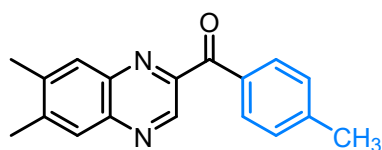
3a

(6,7-Dimethylquinoxalin-2-yl)(phenyl)methanone: 39.4 mg, 75% yield. Yellow solid, melting point: 78.0–79.0 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

¹H NMR (400 MHz, chloroform-*d*) δ 9.38 (s, 1H), 8.23–8.20 (m, 2H), 7.91 (s, 2H), 7.66–7.61 (m, 1H), 7.54–7.50 (m, 2H), 2.53 (s, 3H), 2.50 (s, 3H).

¹³C NMR (100 MHz, chloroform-*d*) δ 192.5, 147.7, 144.4, 143.2, 142.1, 141.5, 139.3, 135.7, 133.35, 131.2, 129.3, 128.3, 128.2, 20.6, 20.3.

HRMS (ESI) *m/z*: Calcd for C₁₇H₁₅N₂O⁺ [M + H]⁺: 263.1179; found: 263.1177.



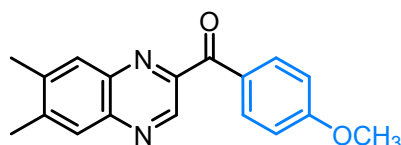
3b

(6,7-Dimethylquinoxalin-2-yl)(*p*-tolyl)methanone: 39.7 mg, 72% yield. Yellow solid, melting point: 98.8–100.2 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

$^1\text{H NMR}$ (400 MHz, chloroform-*d*) δ 9.35 (s, 1H), 8.12 (d, J = 8.0 Hz, 2H), 7.89 (d, J = 2.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 2.51 (s, 3H), 2.48 (s, 3H), 2.43 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, chloroform-*d*) δ 192.1, 148.0, 144.4, 144.3, 142.9, 142.0, 141.4, 139.3, 133.1, 131.3, 129.2, 129.0, 128.2, 21.7, 20.5, 20.3.

HRMS (ESI) m/z : Calcd for $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}^+$ [$\text{M} + \text{H}$] $^+$: 277.1335; found: 277.1333.



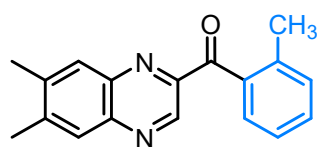
3c

(6,7-Dimethylquinoxalin-2-yl)(4-methoxyphenyl)methanone: 43.4 mg, 74% yield. Yellow solid, melting point: 136.7–138.2 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

$^1\text{H NMR}$ (400 MHz, chloroform-*d*) δ 9.30 (s, 1H), 8.24 (d, J = 8.8 Hz, 2H), 7.85 (d, J = 5.6 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H), 2.47 (s, 3H), 2.45 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, chloroform-*d*) δ 190.6, 163.8, 148.3, 144.4, 142.7, 141.8, 141.3, 139.1, 133.6, 129.1, 128.4, 128.2, 113.5, 55.4, 20.4, 20.2.

HRMS (ESI) m/z : Calcd for $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}^+$ [$\text{M} + \text{H}$] $^+$: 293.1285; found: 293.1281.



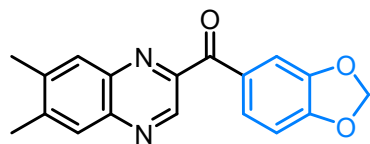
3d

(6,7-Dimethylquinoxalin-2-yl)(o-tolyl)methanone: 30.4 mg, 55% yield. Yellow solid, melting point: 96.6–98.2 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

$^1\text{H NMR}$ (400 MHz, chloroform-*d*) δ 9.44 (s, 1H), 7.92 (s, 1H), 7.86 (s, 1H), 7.60–7.57 (m, 1H), 7.48–7.44 (m, 1H), 7.34–7.32 (m, 1H), 7.30–7.26 (m, 1H), 2.53 (s, 3H), 2.47 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, chloroform-*d*) δ 196.3, 147.8, 144.0, 143.3, 142.2, 141.5, 139.7, 138.7, 136.3, 131.4, 131.3, 131.0, 129.4, 128.2, 125.0, 20.8, 20.6, 20.2.

HRMS (ESI) *m/z*: Calcd for $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}^+$ [$\text{M} + \text{H}$] $^+$: 277.1335; found: 277.1333.



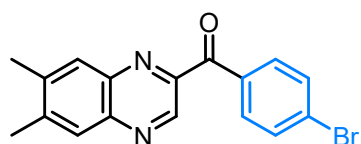
3e

Benzo[*d*][1,3]dioxol-5-yl(6,7-dimethylquinoxalin-2-yl)methanone: 35.5 mg, 58% yield. Yellow solid, melting point: 149.3–151.3 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

^1H NMR (400 MHz, chloroform-*d*) δ 9.28 (s, 1H), 7.89–7.85 (m, 3H), 7.71–7.70 (m, 1H), 6.86 (d, $J = 8.0$ Hz, 1H), 6.04 (s, 2H), 2.48 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, chloroform-*d*) δ 190.2, 152.2, 148.1, 147.7, 144.4, 142.9, 141.9, 141.4, 139.1, 130.1, 129.1, 128.41, 128.2, 110.5, 107.8, 101.8, 20.5, 20.2.

HRMS (ESI) *m/z*: Calcd for $\text{C}_{18}\text{H}_{15}\text{N}_2\text{O}_3^+$ [$\text{M} + \text{H}$] $^+$: 307.1077; found: 307.1074.



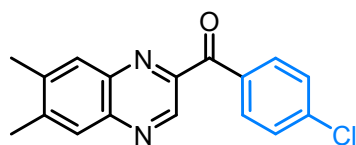
3f

(4-Bromophenyl)(6,7-dimethylquinoxalin-2-yl)methanone: 42.4 mg, 62% yield. Yellow solid, melting point: 124.5–126.2 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

^1H NMR (400 MHz, chloroform-*d*) δ 9.36 (s, 1H), 8.10 (d, $J = 8.8$ Hz, 2H), 7.87 (d, $J = 5.6$ Hz, 2H), 7.62 (d, $J = 8.8$ Hz, 2H), 2.51 (s, 3H), 2.48 (s, 3H).

^{13}C NMR (100 MHz, chloroform-*d*) δ 191.2, 147.1, 144.3, 143.4, 142.1, 141.6, 139.1, 134.4, 132.7, 131.5, 129.2, 128.7, 128.3, 20.6, 20.3.

HRMS (ESI) *m/z*: Calcd for $\text{C}_{17}\text{H}_{14}\text{BrN}_2\text{O}^+$ [$\text{M} + \text{H}$] $^+$: 341.0284; found: 341.0283.



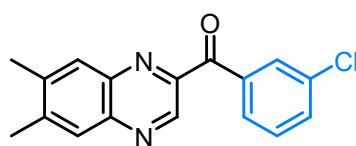
3g

(4-Chlorophenyl)(6,7-dimethylquinoxalin-2-yl)methanone: 38.6 mg, 65% yield. Yellow solid, melting point: 120.7–122.5 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

¹H NMR (400 MHz, chloroform-*d*) δ 9.35 (s, 1H), 8.18 (d, J = 8.8 Hz, 2H), 7.85 (d, J = 4.8 Hz, 2H), 7.44 (d, J = 8.8 Hz, 2H), 2.49 (s, 3H), 2.47 (s, 3H).

¹³C NMR (100 MHz, chloroform-*d*) δ 190.9, 147.1, 144.3, 143.4, 142.1, 141.6, 139.8, 139.1, 134.0, 132.6, 129.1, 128.4, 128.2, 20.5, 20.2.

HRMS (ESI) m/z : Calcd for C₁₇H₁₄ClN₂O⁺ [M + H]⁺: 297.0789; found: 297.0787.



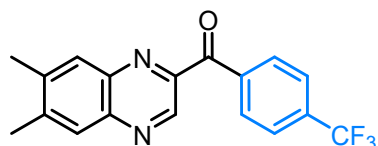
3h

(3-Chlorophenyl)(6,7-dimethylquinoxalin-2-yl)methanone: 27.4 mg, 46% yield. Yellow solid, melting point: 101.4–102.4 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

¹H NMR (400 MHz, chloroform-*d*) δ 9.40 (s, 1H), 8.24–8.23 (m, 1H), 8.13–8.11 (m, 1H), 7.91 (s, 2H), 7.61–7.58 (m, 1H), 7.47–7.43 (m, 1H), 2.54 (s, 3H), 2.51 (s, 3H).

¹³C NMR (100 MHz, chloroform-*d*) δ 191.0, 147.0, 144.3, 143.6, 142.3, 141.8, 139.3, 137.3, 134.4, 133.2, 131.1, 129.5, 129.3, 129.3, 128.3, 20.6, 20.3.

HRMS (ESI) m/z : Calcd for C₁₇H₁₄ClN₂O⁺ [M + H]⁺: 297.0789; found: 297.0788.



3i

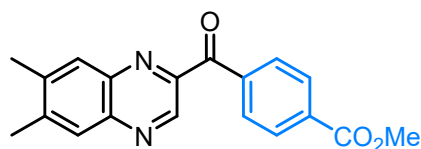
(6,7-Dimethylquinoxalin-2-yl)(4-(trifluoromethyl)phenyl)methanone: 29.8 mg, 45% yield. Yellow solid, melting point: 106.8–108.7 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

¹H NMR (400 MHz, chloroform-*d*) δ 9.42 (s, 1H), 8.32 (d, $J = 8.0$ Hz, 2H), 7.89 (d, $J = 9.2$ Hz, 2H), 7.76 (d, $J = 8.0$ Hz, 2H), 2.52 (s, 3H), 2.50 (s, 3H).

¹³C NMR (100 MHz, chloroform-*d*) δ 191.4, 146.7, 144.3, 143.8, 142.3, 141.8, 139.2, 138.7, 134.22 (q, $J = 32.6$ Hz), 131.4, 129.2, 128.3, 125.09 (q, $J = 3.7$ Hz), 123.63 (q, $J = 272.8$ Hz), 20.6, 20.3.

¹⁹F NMR (376 MHz, chloroform-*d*) δ -63.12 (s, 3F).

HRMS (ESI) m/z : Calcd for C₁₈H₁₄F₃N₂O⁺ [M + H]⁺: 331.1053; found: 331.1050.



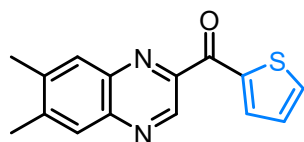
3j

Methyl 4-(6,7-dimethylquinoxaline-2-carbonyl)benzoate: 28.2 mg, 44% yield. Yellow solid, melting point: 149.2–151.3 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

¹H NMR (400 MHz, chloroform-*d*) δ 9.41 (s, 1H), 8.26 (d, $J = 8.4$ Hz, 2H), 8.16 (d, $J = 8.4$ Hz, 2H), 7.89 (d, $J = 8.0$ Hz, 2H), 3.95 (s, 3H), 2.52 (s, 3H), 2.50 (s, 3H).

¹³C NMR (100 MHz, chloroform-*d*) δ 192.0, 166.3, 147.0, 144.3, 143.6, 142.3, 141.7, 139.3, 139.3, 133.7, 131.0, 129.3, 129.3, 128.3, 52.4, 20.6, 20.3.

HRMS (ESI) m/z : Calcd for C₁₉H₁₇N₂O₃⁺ [M + H]⁺: 321.1234; found: 321.1231.



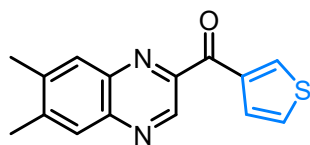
3k

(6,7-Dimethylquinoxalin-2-yl)(thiophen-2-yl)methanone: 27.4 mg, 51% yield. Yellow solid, melting point: 146.3–148.2 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

¹H NMR (400 MHz, chloroform-*d*) δ 9.37 (s, 1H), 8.43–8.42 (m, 1H), 7.80 (s, 1H), 7.75–7.73 (m, 2H), 7.17–7.15 (m, 1H), 2.41 (s, 6H).

¹³C NMR (100 MHz, chloroform-*d*) δ 182.4, 146.0, 143.5, 143.3, 142.2, 141.4, 139.5, 139.0, 136.7, 136.6, 128.9, 128.2, 127.6, 20.5, 20.1.

HRMS (ESI) *m/z*: Calcd for C₁₅H₁₃N₂OS⁺ [M + H]⁺: 269.0743; found: 269.0741.



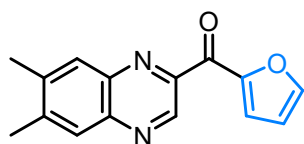
3l

(6,7-Dimethylquinoxalin-2-yl)(thiophen-3-yl)methanone: 34.4 mg, 64% yield. Yellow solid, melting point: 146.1–147.2 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

¹H NMR (400 MHz, chloroform-*d*) δ 9.43 (s, 1H), 9.02–8.99 (m, 1H), 7.95–7.92 (m, 1H), 7.91 (s, 1H), 7.87 (s, 1H), 7.36 (dd, *J* = 5.2, 2.8 Hz, 1H), 2.50 (s, 3H), 2.49 (s, 3H).

¹³C NMR (100 MHz, chloroform-*d*) δ 184.6, 147.5, 144.2, 143.2, 142.2, 141.5, 139.4, 139.3, 137.4, 129.2, 129.1, 128.3, 125.3, 20.6, 20.3.

HRMS (ESI) *m/z*: Calcd for C₁₅H₁₃N₂OS⁺ [M + H]⁺: 269.0743; found: 269.0742.



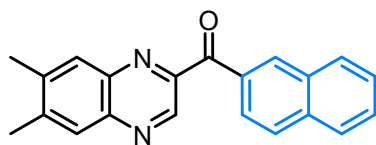
3m

(6,7-Dimethylquinoxalin-2-yl)(furan-2-yl)methanone: 31.4 mg, 62% yield. Yellow solid, melting point: 183.8–185.5 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

¹H NMR (400 MHz, chloroform-*d*) δ 9.49 (s, 1H), 8.21 (d, *J* = 3.5 Hz, 1H), 7.94 (s, 1H), 7.91 (s, 1H), 7.82–7.79 (m, 1H), 6.67 (dd, *J* = 3.6, 1.6 Hz, 1H), 2.53 (s, 6H).

¹³C NMR (100 MHz, chloroform-*d*) δ 178.3, 150.8, 148.2, 146.4, 143.8, 143.5, 142.6, 141.6, 139.6, 129.2, 128.4, 124.7, 112.6, 20.6, 20.3.

HRMS (ESI) *m/z*: Calcd for C₁₅H₁₃N₂O₂⁺ [M + H]⁺: 253.0972; found: 253.0971.



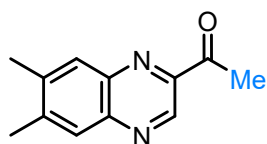
3n

(6,7-Dimethylquinoxalin-2-yl)(naphthalen-2-yl)methanone: 30.8 mg, 49% yield. Yellow solid, melting point: 117.9–120.1 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

¹H NMR (400 MHz, chloroform-*d*) δ 9.42 (s, 1H), 8.80 (s, 1H), 8.26–8.20 (m, 1H), 7.96–7.90 (m, 4H), 7.88–7.84 (m, 1H), 7.62–7.56 (m, 1H), 7.54–7.49 (m, 1H), 2.51 (s, 3H), 2.48 (s, 3H).

¹³C NMR (100 MHz, chloroform-*d*) δ 192.3, 148.0, 144.4, 143.1, 142.0, 141.5, 139.3, 135.6, 134.0, 133.0, 132.2, 129.9, 129.2, 128.7, 128.3, 128.0, 127.7, 126.6, 125.9, 20.5, 20.3.

HRMS (ESI) *m/z*: Calcd for C₂₁H₁₇N₂O⁺ [M + H]⁺: 313.1331; found: 313.1331.



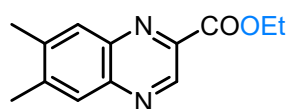
3o

1-(6,7-Dimethylquinoxalin-2-yl)ethan-1-one: 28.6 mg, 71% yield. Yellow solid, melting point: 104.9–106.3 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

¹H NMR (400 MHz, chloroform-*d*) δ 9.38 (s, 1H), 7.91 (s, 1H), 7.88 (s, 1H), 2.82 (s, 3H), 2.52 (s, 3H), 2.51 (s, 3H).

¹³C NMR (100 MHz, chloroform-*d*) δ 199.9, 145.9, 143.4, 142.8, 142.2, 141.4, 140.0, 129.3, 128.4, 25.5, 20.6, 20.3.

HRMS (ESI) *m/z*: Calcd for C₁₂H₁₃N₂O⁺ [M + H]⁺: 201.1022; found: 201.1020.



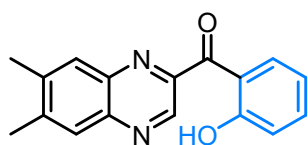
3p

Ethyl 6,7-dimethylquinoxaline-2-carboxylate: 26.8 mg, 58% yield. Brown solid, melting point: 96.1–97.8 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

¹H NMR (400 MHz, chloroform-*d*) δ 9.44 (s, 1H), 8.04 (s, 1H), 7.91 (s, 1H), 4.58 (q, *J* = 7.2 Hz, 2H), 2.53 (s, 3H), 2.52 (s, 3H), 1.50 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, chloroform-*d*) δ 164.5, 144.3, 143.6, 142.7, 141.8, 141.8, 140.5, 129.4, 128.2, 62.4, 20.6, 20.4, 14.3.

HRMS (ESI) *m/z*: Calcd for C₁₃H₁₅N₂O₂⁺ [M + H]⁺: 231.1128; found: 231.1126.



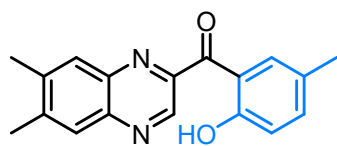
3q

(6,7-Dimethylquinoxalin-2-yl)(2-hydroxyphenyl)methanone: 34.8 mg, 63% yield. Yellow solid, melting point: 115.1–117.2 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

$^1\text{H NMR}$ (400 MHz, chloroform-*d*) δ 12.18 (s, 1H), 9.30 (s, 1H), 8.39–8.29 (m, 1H), 7.95 (d, $J = 7.1$ Hz, 2H), 7.61–7.48 (m, 1H), 7.10 (d, $J = 8.4$ Hz, 1H), 6.94 (t, $J = 7.5$ Hz, 1H), 2.56 (s, 3H), 2.55 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, chloroform-*d*) δ 196.14, 163.99, 148.17, 144.14, 143.43, 142.08, 141.94, 139.09, 137.16, 134.34, 129.13, 128.37, 119.00, 118.81, 118.50, 20.64, 20.39.

HRMS (ESI) m/z : Calcd for $\text{C}_{17}\text{H}_{15}\text{N}_2\text{O}_2^+$ $[\text{M} + \text{H}]^+$: 279.1128; found: 279.1125.



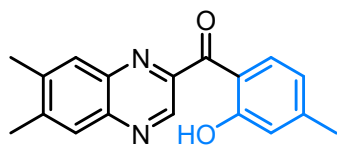
3r

(6,7-Dimethylquinoxalin-2-yl)(2-hydroxy-5-methylphenyl)methanone: 36.2 mg, 62% yield. Yellow solid, melting point: 122.2–124.7 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

$^1\text{H NMR}$ (400 MHz, chloroform-*d*) δ 12.00 (s, 1H), 9.26 (s, 1H), 8.03–8.00 (m, 1H), 7.96 (d, $J = 5.6$ Hz, 2H), 7.40–7.36 (m, 1H), 7.01 (d, $J = 8.5$ Hz, 1H), 2.57 (s, 3H), 2.55 (s, 3H), 2.29 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, chloroform-*d*) δ 196.26, 161.99, 148.45, 144.12, 143.38, 142.09, 141.99, 139.20, 138.44, 133.76, 129.14, 128.41, 128.19, 118.56, 118.35, 20.67, 20.62, 20.45.

HRMS (ESI) m/z : Calcd for $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_2^+$ $[\text{M} + \text{H}]^+$: 293.1285; found: 293.1283.



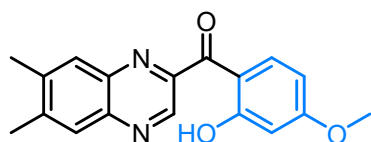
3s

(6,7-Dimethylquinoxalin-2-yl)(2-hydroxy-4-methylphenyl)methanone: 36.2 mg, 62% yield. Yellow solid, melting point: 135.8–137.3 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

¹H NMR (400 MHz, chloroform-*d*) δ 12.23 (s, 1H), 9.28 (s, 1H), 8.20 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 6.7 Hz, 2H), 6.90 (s, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 2.56 (s, 3H), 2.54 (s, 3H), 2.40 (s, 3H).

¹³C NMR (100 MHz, chloroform-*d*) δ 195.58, 164.31, 149.20, 148.48, 144.19, 143.30, 142.07, 141.88, 139.21, 134.16, 129.19, 128.40, 120.51, 118.54, 116.62, 22.17, 20.67, 20.44.

HRMS (ESI) *m/z*: Calcd for C₁₈H₁₇N₂O₂⁺ [M + H]⁺: 293.1285; found: 293.1284.



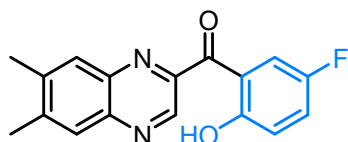
3t

(6,7-Dimethylquinoxalin-2-yl)(2-hydroxy-4-methoxyphenyl)methanone: 38.0 mg, 65% yield. Yellow solid, melting point: 147.2–149.2 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 7/1, V/V).

¹H NMR (400 MHz, chloroform-*d*) δ 12.78 (s, 1H), 9.28 (s, 1H), 8.32 (d, *J* = 9.1 Hz, 1H), 7.95 (d, *J* = 8.7 Hz, 2H), 6.54–6.53 (m, 1H), 6.51–6.48 (m, 1H), 3.89 (s, 3H), 2.56 (s, 3H), 2.54 (s, 3H).

¹³C NMR (100 MHz, chloroform-*d*) δ 194.02, 167.46, 166.96, 148.71, 144.27, 143.15, 141.99, 141.81, 139.22, 135.97, 129.16, 128.40, 112.95, 108.24, 100.93, 55.71, 20.66, 20.43.

HRMS (ESI) *m/z*: Calcd for C₁₈H₁₇N₂O₃⁺ [M + H]⁺: 309.1234; found: 309.1231.



3u

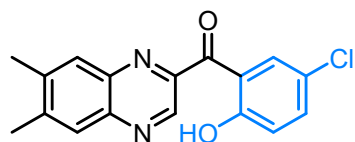
(6,7-Dimethylquinoxalin-2-yl)(5-fluoro-2-hydroxyphenyl)methanone: 26.2 mg, 44% yield. Yellow solid, melting point: 138.1–139.8 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

¹H NMR (400 MHz, chloroform-*d*) δ 12.06 (s, 1H), 9.36 (s, 1H), 8.30 (dd, $J = 9.7, 3.2$ Hz, 1H), 7.97 (d, $J = 12.4$ Hz, 2H), 7.34–7.29 (m, 1H), 7.08–7.04 (m, 1H), 2.57 (s, 3H), 2.56 (s, 3H).

¹³C NMR (100 MHz, chloroform-*d*) δ 194.7 (d, $J = 2.2$ Hz), 160.3, 154.7 (d, $J = 237.6$ Hz), 147.6, 144.3, 144.0, 142.3, 139.0, 129.2, 128.4, 124.9 (d, $J = 23.9$ Hz), 119.8 (d, $J = 7.2$ Hz), 119.1 (d, $J = 24.8$ Hz), 118.4 (d, $J = 7.5$ Hz), 20.7, 20.4.

¹⁹F NMR (376 MHz, chloroform-*d*) δ -123.70–123.78 (m, 1F).

HRMS (ESI) m/z : Calcd for C₁₇H₁₄FN₂O₂⁺ [M + H]⁺: 297.1034; found: 297.1032.



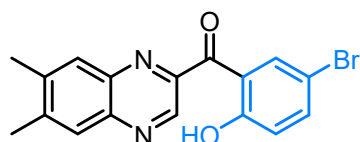
3v

(5-Chloro-2-hydroxyphenyl)(6,7-dimethylquinoxalin-2-yl)methanone: 26.8 mg, 43% yield. Yellow solid, melting point: 161.6–162.8 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

¹H NMR (400 MHz, chloroform-*d*) δ 12.21 (s, 1H), 9.34 (s, 1H), 8.54–8.49 (m, 1H), 7.97 (d, $J = 12.0$ Hz, 2H), 7.50 (dd, $J = 8.9, 2.6$ Hz, 1H), 7.08–7.04 (m, 1H), 2.57 (s, 3H), 2.56 (s, 3H).

¹³C NMR (100 MHz, chloroform-*d*) δ 194.75, 162.44, 147.46, 144.23, 144.02, 142.32, 142.30, 138.94, 136.98, 133.35, 129.21, 128.44, 123.75, 120.18, 119.51, 20.73, 20.43.

HRMS (ESI) m/z : Calcd for C₁₇H₁₄ClN₂O₂⁺ [M + H]⁺: 313.0738; found: 313.0738.



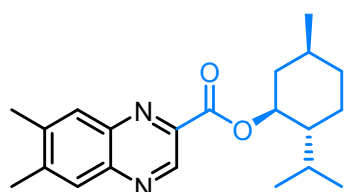
3w

(5-Bromo-2-hydroxyphenyl)(6,7-dimethylquinoxalin-2-yl)methanone: 29.2 mg, 41% yield. Yellow solid, melting point: 155.3–157.6 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

¹H NMR (400 MHz, chloroform-*d*) δ 12.24 (s, 1H), 9.35 (s, 1H), 8.68–8.63 (m, 1H), 7.98 (d, J = 10.8 Hz, 2H), 7.65–7.62 (m, 1H), 7.01 (d, J = 8.9 Hz, 1H), 2.58 (s, 3H), 2.57 (s, 3H).

¹³C NMR (100 MHz, chloroform-*d*) δ 194.68, 162.85, 147.43, 144.23, 144.06, 142.34, 139.72, 138.95, 136.39, 129.21, 128.44, 120.58, 120.16, 110.70, 20.74, 20.45.

HRMS (ESI) m/z : Calcd for C₁₇H₁₄BrN₂O₂⁺ [M + H]⁺: 357.0233; found: 357.0234.



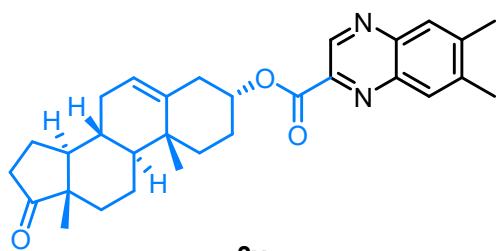
3x

(1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl 6,7-dimethylquinoxaline-2-carboxylate: 50.6 mg, 74.3% yield. Yellow solid, melting point: 102.6–104.7 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

¹H NMR (400 MHz, chloroform-*d*) δ 9.40 (s, 1H), 8.05 (s, 1H), 7.90 (s, 1H), 5.11 (td, J = 8.0, 4.0 Hz, 1H), 2.53 (s, 3H), 2.51 (s, 3H), 2.24–2.16 (m, 1H), 2.05–1.95 (m, 1H), 1.80–1.71 (m, 2H), 1.68–1.54 (m, 2H), 1.23–1.07 (m, 2H), 0.98–0.90 (m, 7H), 0.82 (d, J = 8.0 Hz, 3H).

¹³C NMR (100 MHz, chloroform-*d*) δ 163.8, 144.2, 143.4, 142.6, 142.2, 141.6, 140.8, 129.5, 128.1, 47.0, 40.7, 34.2, 31.5, 26.4, 23.5, 22.0, 20.7, 20.6, 20.4, 16.4.

HRMS (ESI) m/z : Calcd for C₂₁H₂₉N₂O₂⁺ [M + H]⁺: 341.2224; found: 341.2222.



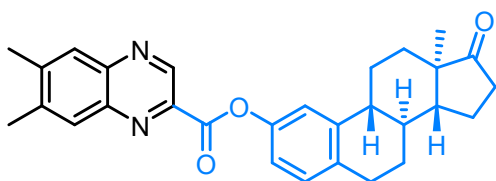
3y

(3R,8R,9S,10R,13S,14S)-10,13-Dimethyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 6,7-dimethylquinoxaline-2-carboxylate: 38.2 mg, 40% yield. Yellow solid, melting point: 207.1–209.2 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

¹H NMR (400 MHz, chloroform-*d*) δ 9.42 (s, 1H), 8.05 (s, 1H), 7.92 (s, 1H), 5.49 (d, *J* = 4.0 Hz, 1H), 5.12–4.95 (m, 1H), 2.65–2.57 (m, 2H), 2.54 (s, 3H), 2.53 (s, 3H), 2.50–2.44 (m, 1H), 2.16–2.08 (m, 3H), 2.01–1.95 (m, 2H), 1.90–1.85 (m, 2H), 1.73–1.68 (m, 3H), 1.58–1.50 (m, 2H), 1.37–1.24 (m, 4H), 1.12 (s, 3H), 0.91 (s, 3H).

¹³C NMR (100 MHz, chloroform-*d*) δ 221.2, 163.9, 144.3, 143.6, 142.7, 142.1, 141.8, 140.7, 139.7, 129.5, 128.2, 122.4, 76.0, 51.7, 50.2, 47.6, 38.0, 37.0, 36.8, 35.9, 31.5, 31.4, 30.8, 27.7, 21.9, 20.7, 20.5, 20.4, 19.5, 13.6.

HRMS (ESI) *m/z*: Calcd for C₃₀H₃₇N₂O₃⁺ [M + H]⁺: 473.2799; found: 473.2799.



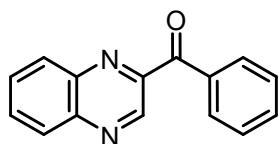
3z

(8S,9R,13R,14R)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-2-yl 6,7-dimethylquinoxaline-2-carboxylate: 39.2 mg, 43% yield. Yellow solid, melting point: 199.7–201.4 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

¹H NMR (400 MHz, chloroform-*d*) δ 9.56 (s, 1H), 8.09 (s, 1H), 7.96 (s, 1H), 7.40–7.34 (m, 1H), 7.11–7.06 (m, 1H), 7.05–7.03 (m, 1H), 3.00–2.94 (m, 2H), 2.57 (s, 3H), 2.55 (s, 3H), 2.53–2.40 (m, 2H), 2.38–2.29 (m, 1H), 2.23–2.13 (m, 1H), 2.13–2.08 (m, 1H), 2.02–1.88 (m, 2H), 1.68–1.50 (m, 6H), 0.94 (s, 3H).

¹³C NMR (100 MHz, chloroform-*d*) δ 220.9, 163.4, 148.6, 144.6, 144.2, 143.0, 142.2, 141.2, 140.7, 138.2, 138.0, 129.5, 128.3, 126.6, 121.6, 118.8, 50.5, 48.0, 44.2, 38.0, 35.9, 31.6, 29.5, 26.4, 25.8, 21.6, 20.8, 20.5, 13.9.

HRMS (ESI) *m/z*: Calcd for C₂₉H₃₁N₂O₃⁺ [M + H]⁺: 455.2329; found: 455.2326.



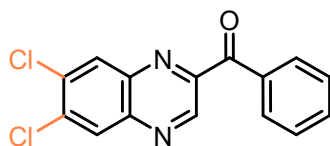
4a

Phenyl(quinoxalin-2-yl)methanone: 21.1 mg, 45% yield. Yellow solid, melting point: 63.9–65.2 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

¹H NMR (400 MHz, chloroform-*d*) δ 9.49 (s, 1H), 8.26–8.18 (m, 4H), 7.93–7.83 (m, 2H), 7.69–7.63 (m, 1H), 7.57–7.51 (m, 2H).

¹³C NMR (100 MHz, chloroform-*d*) δ 192.3, 148.6, 145.3, 143.1, 140.4, 135.4, 133.6, 132.0, 131.2, 130.8, 130.4, 129.4, 128.4.

HRMS (ESI) *m/z*: Calcd for C₁₅H₁₁N₂O⁺ [M + H]⁺: 235.0866; found: 235.0864.



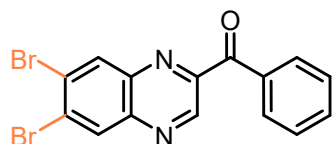
4b

(6,7-Dichloroquinoxalin-2-yl)(phenyl)methanone: 48.0 mg, 79% yield. Yellow solid, melting point: 151.1–153.8 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

$^1\text{H NMR}$ (400 MHz, chloroform-*d*) δ 9.45 (s, 1H), 8.30 (d, $J = 2.8$ Hz, 2H), 8.21–8.17 (m, 2H), 7.69–7.64 (m, 1H), 7.56–7.51 (m, 2H).

$^{13}\text{C NMR}$ (100 MHz, chloroform-*d*) δ 191.5, 149.1, 146.3, 141.7, 139.0, 136.8, 135.7, 135.0, 133.8, 131.1, 130.7, 130.0, 128.4.

HRMS (ESI) m/z : Calcd for $\text{C}_{15}\text{H}_9\text{Cl}_2\text{N}_2\text{O}^+$ [$\text{M} + \text{H}$] $^+$: 303.0086; found: 303.0084.



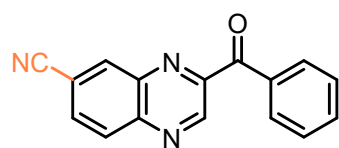
4c

(6,7-Dibromoquinoxalin-2-yl)(phenyl)methanone: 41.6 mg, 53% yield. Yellow solid, melting point: 165.6–167.5 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

$^1\text{H NMR}$ (400 MHz, chloroform-*d*) δ 9.47 (s, 1H), 8.51 (s, 2H), 8.22–8.18 (m, 2H), 7.70–7.64 (m, 1H), 7.57–7.51 (m, 2H).

$^{13}\text{C NMR}$ (100 MHz, chloroform-*d*) δ 191.6, 149.2, 146.4, 142.1, 139.5, 135.0, 134.2, 133.9, 133.4, 131.1, 129.2, 128.4, 127.8.

HRMS (ESI) m/z : Calcd for $\text{C}_{15}\text{H}_9\text{Br}_2\text{N}_2\text{O}^+$ [$\text{M} + \text{H}$] $^+$: 390.9076; found: 390.9076.



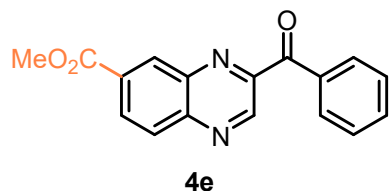
4d

3-Benzoylquinoxaline-6-carbonitrile: 41.6 mg, 80% yield. Yellow solid, melting point: 99.8–101.5 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

$^1\text{H NMR}$ (400 MHz, chloroform-*d*) δ 9.55 (s, 1H), 8.59–8.54 (m, 1H), 8.32–8.27 (m, 1H), 8.21–8.17 (m, 2H), 8.04–7.99 (m, 1H), 7.70–7.64 (m, 1H), 7.55–7.50 (m, 2H).

^{13}C NMR (100 MHz, chloroform-*d*) δ 191.2, 149.9, 147.7, 144.2, 139.3, 136.1, 134.8, 134.0, 132.4, 131.1, 131.0, 128.4, 117.4, 114.4.

HRMS (ESI) *m/z*: Calcd for $\text{C}_{16}\text{H}_{10}\text{N}_3\text{O}^+$ [$\text{M} + \text{H}$] $^+$: 260.0818; found: 260.0817.

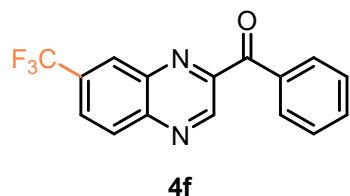


Methyl 3-benzoylquinoxaline-6-carboxylate: 48.2 mg, 82% yield. Yellow solid, melting point: 119.9–121.3 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

^1H NMR (400 MHz, chloroform-*d*) δ 9.51 (s, 1H), 8.85 (s, 1H), 8.45–8.40 (m, 1H), 8.24–8.18 (m, 3H), 7.67–7.61 (m, 1H), 7.54–7.49 (m, 2H), 3.99 (s, 3H).

^{13}C NMR (100 MHz, chloroform-*d*) δ 191.6, 165.7, 149.2, 146.9, 144.8, 139.5, 135.1, 133.7, 132.9, 132.1, 131.3, 131.2, 129.6, 128.3, 52.7.

HRMS (ESI) *m/z*: Calcd for $\text{C}_{17}\text{H}_{13}\text{N}_2\text{O}_3^+$ [$\text{M} + \text{H}$] $^+$: 293.0921; found: 293.0921.



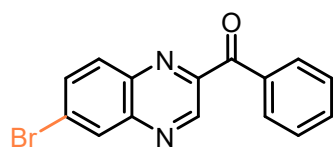
Phenyl(7-(trifluoromethyl)quinoxalin-2-yl)methanone: 41.6 mg, 69% yield. Yellow solid, melting point: 60.6–62.1 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

^1H NMR (400 MHz, chloroform-*d*) δ 9.57 (s, 1H), 8.52 (s, 1H), 8.36–8.30 (m, 1H), 8.26–8.20 (m, 2H), 8.09–8.03 (m, 1H), 7.71–7.64 (m, 1H), 7.58–7.52 (m, 2H).

^{13}C NMR (100 MHz, chloroform-*d*) δ 191.6, 149.6, 147.2, 144.1, 139.4, 135.0, 133.9, 132.5 (q, $J = 33.5$ Hz), 131.5, 130.7, 128.5, 128.3 (q, $J = 4.4$ Hz), 127.5 (q, $J = 2.8$ Hz), 123.3 (q, $J = 272.9$ Hz).

^{19}F NMR (376 MHz, chloroform-*d*) δ -62.76 (s, 3F).

HRMS (ESI) m/z : Calcd for $C_{16}H_{10}F_3N_2O^+$ $[M + H]^+$: 303.0740; found: 303.0736.



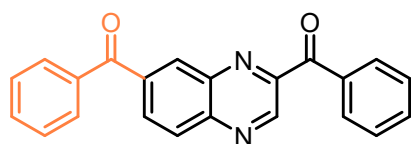
4g

(6-Bromoquinoxalin-2-yl)(phenyl)methanone: 30.8 mg, 49% yield. Orange solid, melting point: 100.8–102.5 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 30/1, V/V).

1H NMR (400 MHz, chloroform-*d*) δ 9.49 (s, 1H), 8.40 (d, $J = 2.0$ Hz, 1H), 8.24–8.21 (m, 2H), 8.10–8.06 (m, 1H), 8.00–7.96 (m, 1H), 7.68 (t, $J = 7.4$ Hz, 1H), 7.55 (t, $J = 7.7$ Hz, 2H).

^{13}C NMR (101 MHz, chloroform-*d*) δ 192.0, 149.2, 145.6, 142.0, 141.0, 135.6, 135.3, 133.9, 132.6, 131.2, 130.7, 128.5, 125.0.

HRMS (ESI) m/z : Calcd for $C_{15}H_{10}BrN_2O^+$ $[M + H]^+$: 312.9971; found: 312.9969.



4h

Quinoxaline-2,7-diylbis(phenyl)methanone: 50.7 mg, 75% yield. Yellow solid, melting point: 144.5–146.2 °C (Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1, V/V).

1H NMR (400 MHz, chloroform-*d*) δ 9.54 (s, 1H), 8.54 (s, 1H), 8.35–8.28 (m, 2H), 8.23–8.18 (m, 2H), 7.89–7.84 (m, 2H), 7.66–7.60 (m, 2H), 7.53–7.48 (m, 4H).

^{13}C NMR (100 MHz, chloroform-*d*) δ 195.1, 191.7, 149.4, 146.9, 144.6, 139.5, 139.3, 136.6, 135.1, 133.8, 133.1, 132.9, 131.8, 131.1, 130.1, 129.8, 128.5, 128.4.

HRMS (ESI) m/z : Calcd for $C_{22}H_{15}N_2O_2^+$ $[M + H]^+$: 339.1128; found: 339.1125.

4. Control experiments

When a radical scavenger BHT (2,6-di-*tert*-butyl-4-methylphenol) in 2.0 equiv. was added to the model reaction, the significantly lower product yield of **3a** was observed, demonstrating a possible radical pathway in this transformation. Meanwhile, a BHT-adduct (**A'**) of the carbon-centered radical intermediate **A** was detected by HRMS analysis (Figure S1).

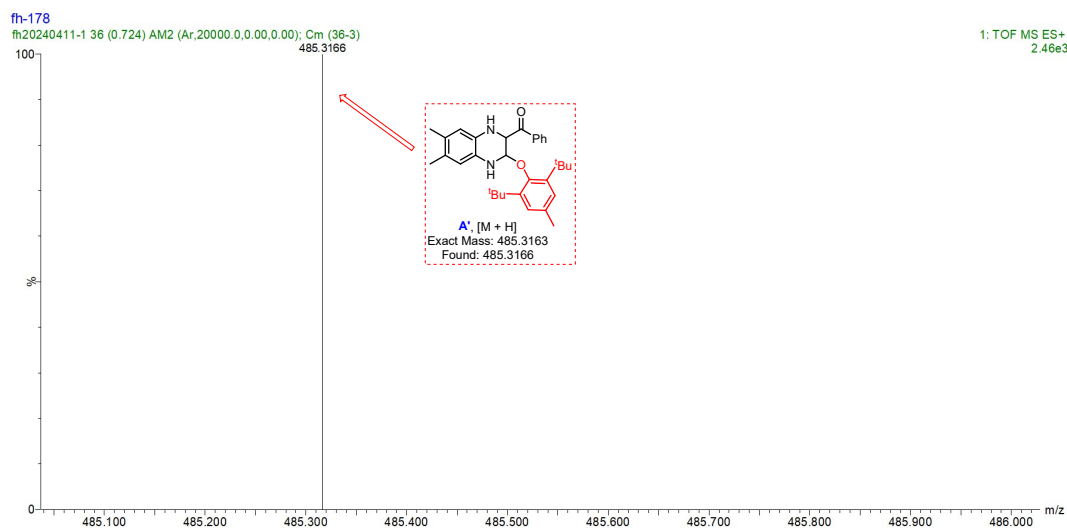
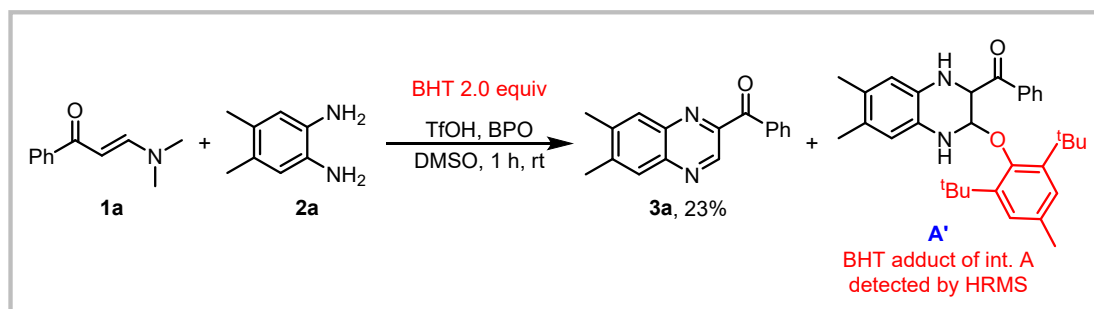
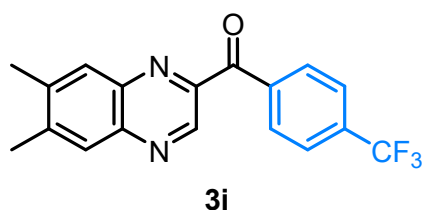


Figure S1 HRMS analysis of a BHT-adduct (**A'**).

5. Crystallographic data and molecular structure of **3i** and **4d**

(CCDC: 2342561, 2342561)



General procedure for crystal culture of **3i**: To a test tube (15 mL) with added **3a** (20 mg), dichloromethane (1.0 mL) was added slowly to make it dissolve completely. After it dissolved, a mixture of petroleum ether (2.0 mL) and EtOAc (3.0 mL) was added. Then, the test tube was sealed with a rubber stopper, and connected to air with a syringe needle. Finally, the tube was put in a dry and ventilated place to make the organic solvent to volatilize slowly. After a few days, the crystal of **3i** was obtained. The X-ray crystal structure of **3i** was shown in Figure S2.

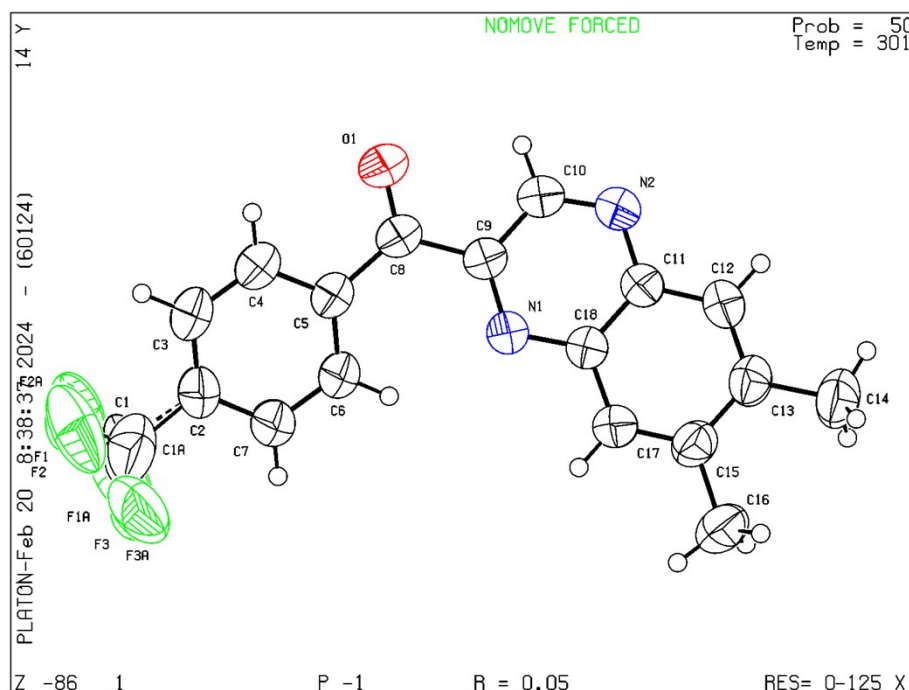
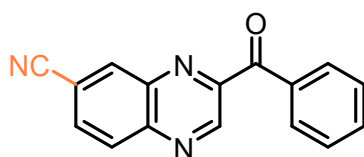


Figure S2 ORTEP diagram of **3i** with thermal displacement parameters drawn at 30% probability.

Datablock: 1

Bond precision:	C-C = 0.0024 Å	Wavelength=1.54178	
Cell:	a=7.2674 (4)	b=9.6649 (6)	c=11.5209 (7)
	alpha=93.372 (3)	beta=95.007 (3)	gamma=97.994 (3)
Temperature:	301 K		
	Calculated	Reported	
Volume	796.22 (8)	796.22 (8)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	C18 H13 F3 N2 O	?	
Sum formula	C18 H13 F3 N2 O	C18 H13 F3 N2 O	
Mr	330.30	330.30	
Dx, g cm ⁻³	1.378	1.378	
Z	2	2	
Mu (mm ⁻¹)	0.947	0.947	
F000	340.0	340.0	
F000'	341.25		
h, k, lmax	8, 11, 13	8, 11, 13	
Nref	2934	2920	
Tmin, Tmax	0.782, 0.812		
Tmin'	0.782		
Correction method= Not given			
Data completeness=	0.995	Theta (max)= 68.383	
R(reflections)=	0.0532 (2254)	wR2 (reflections)=	
		0.1664 (2920)	
S =	1.088	Npar= 257	



4d

General procedure for crystal culture of **4d**: To a test tube (15 mL) with added **4d** (20 mg), dichloromethane (1.0 mL) was added slowly to make it dissolve completely. After it dissolved, a mixture of petroleum ether (2.0 mL) and EtOAc (3.0 mL) was added. Then, the test tube was sealed with a rubber stopper, and connected

to air with a syringe needle. Finally, the tube was put in a dry and ventilated place to make the organic solvent to volatilize slowly. After a few days, the crystal of **4d** was obtained. The X-ray crystal structure of **4d** was shown in Figure S3.

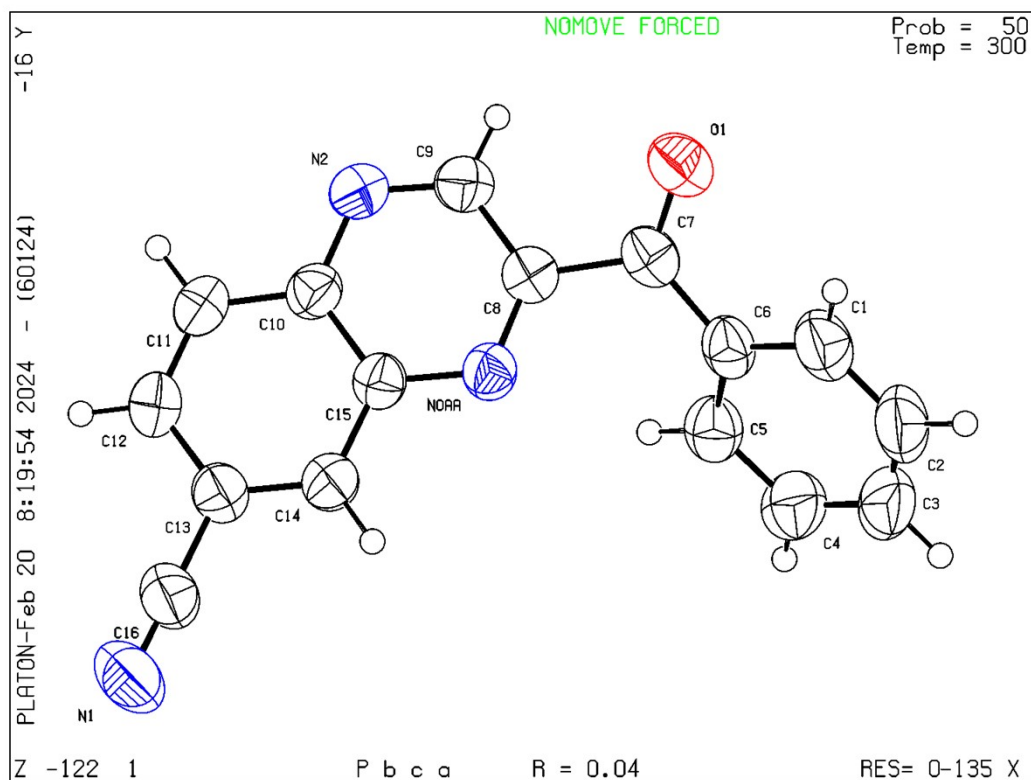


Figure S3 ORTEP diagram of **4d** with thermal displacement parameters drawn at 30% probability.

Datablock: 1

Bond precision: C-C = 0.0019 Å

Wavelength=1.54178

Cell: a=12.5878 (4)
alpha=90

b=9.5702 (3)
beta=90

c=21.3754 (6)
gamma=90

Temperature: 300 K

	Calculated	Reported
Volume	2575.05 (14)	2575.05 (14)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C16 H9 N3 O	?
Sum formula	C16 H9 N3 O	C16 H9 N3 O
Mr	259.26	259.26
Dx, g cm ⁻³	1.337	1.337
Z	8	8
Mu (mm ⁻¹)	0.704	0.704
F000	1072.0	1072.0
F000'	1075.22	
h, k, lmax	15, 11, 25	15, 11, 25
Nref	2351	2340
Tmin, Tmax	0.845, 0.869	
Tmin'	0.845	

Correction method= Not given

Data completeness= 0.995

Theta(max)= 68.293

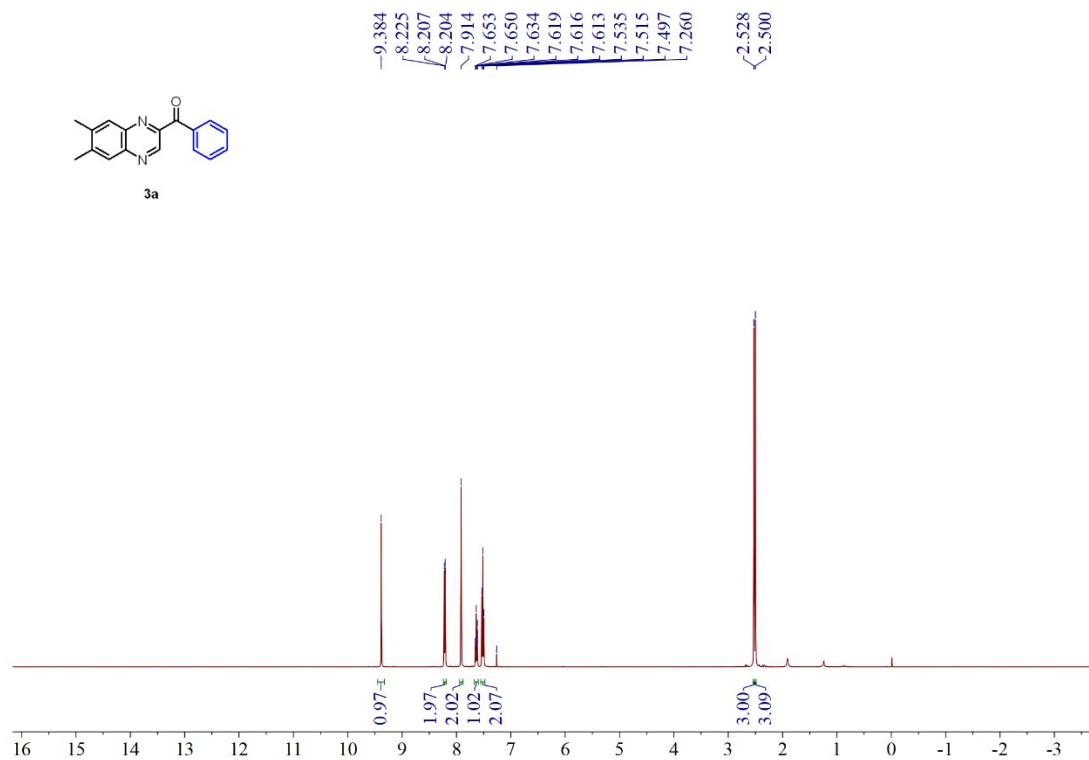
R(reflections)= 0.0350 (2080)

wR2(reflections)=
0.1004 (2340)

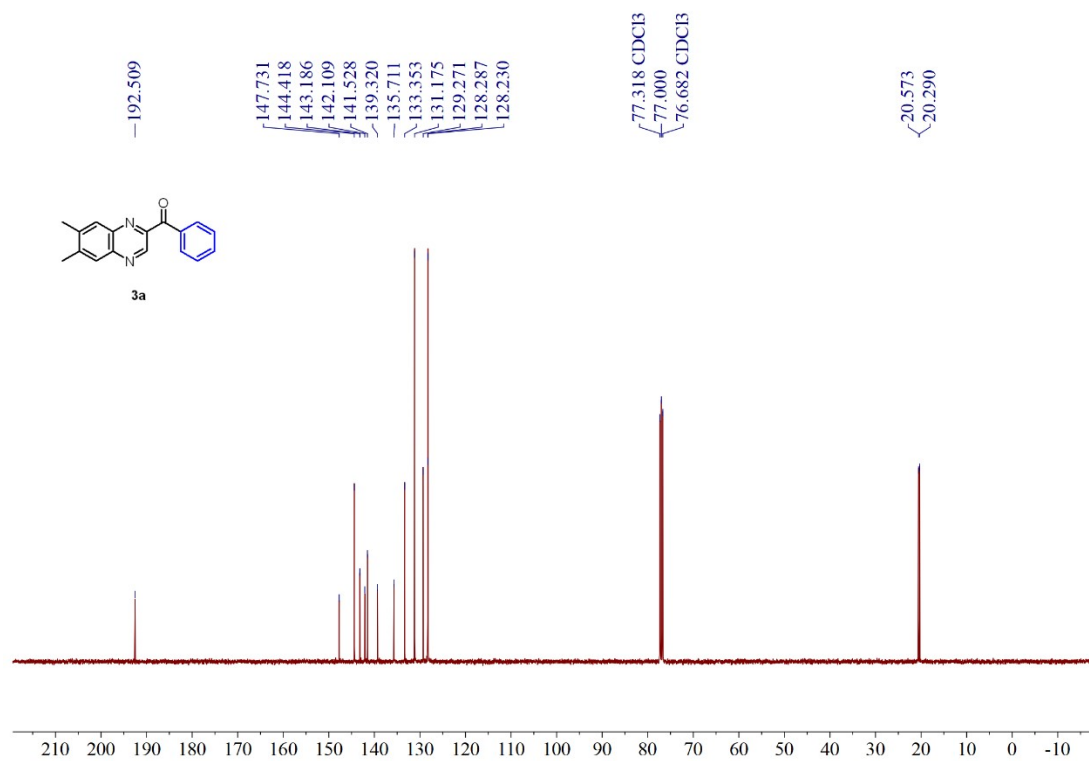
S = 1.069

Npar= 181

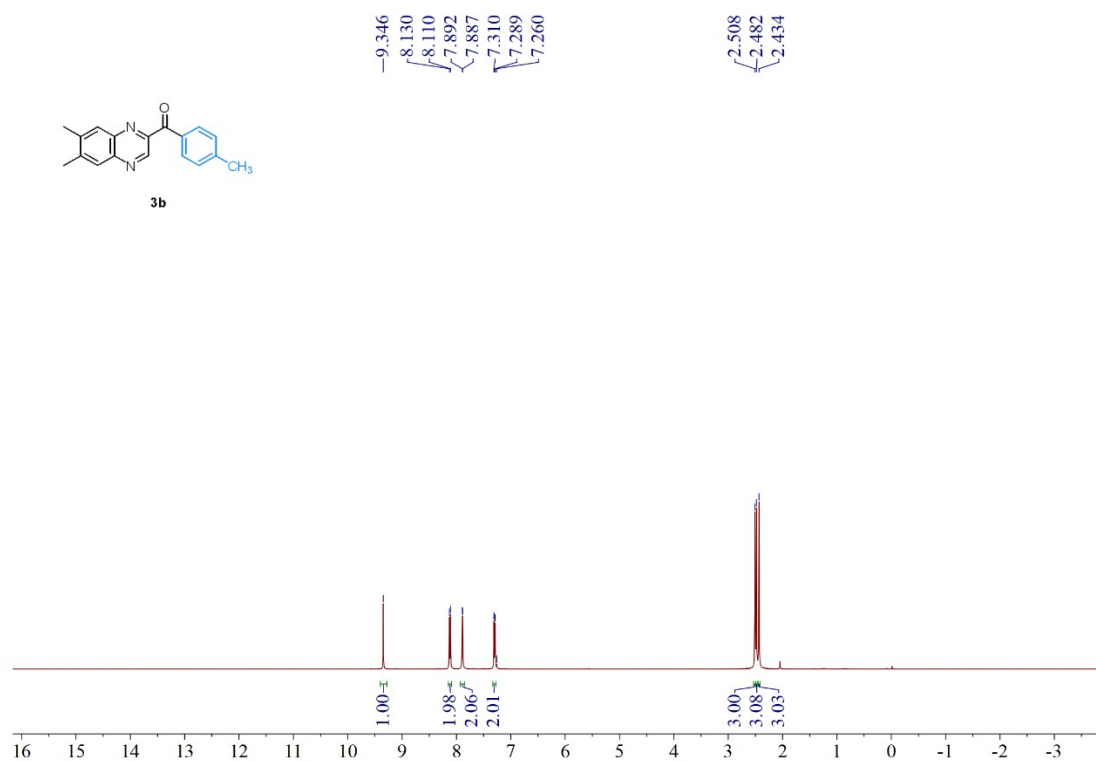
6. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of the products



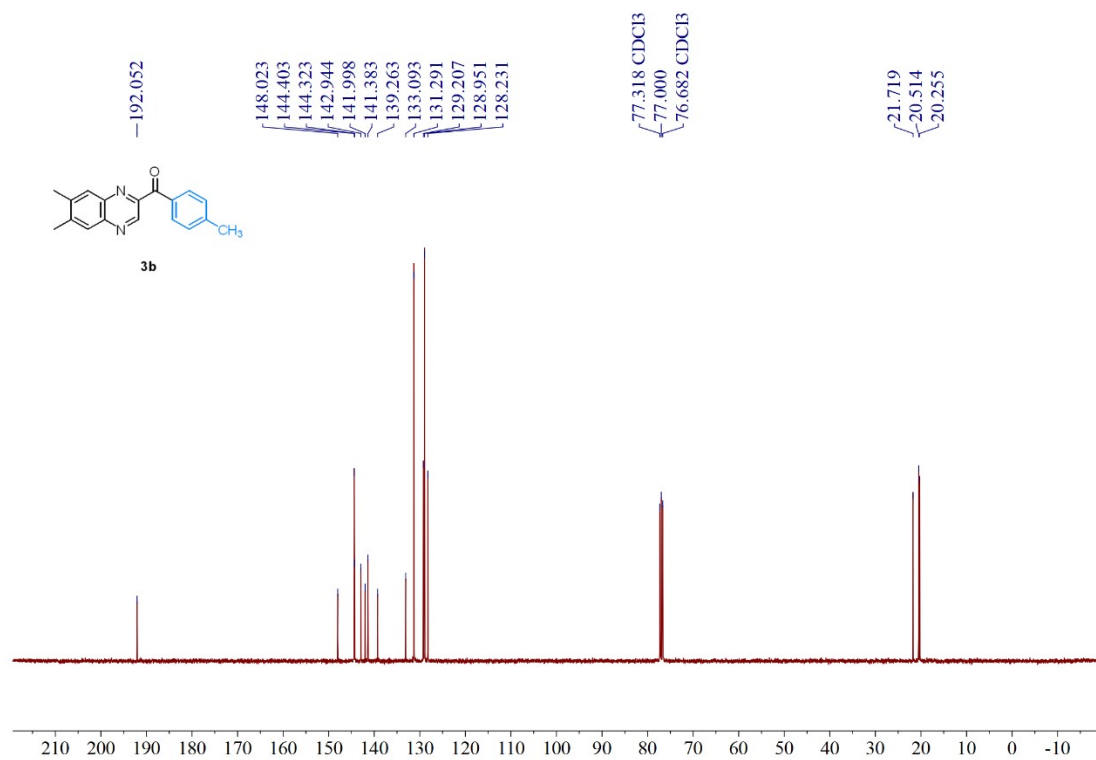
^1H NMR Spectrum of Compound **3a** (400 MHz, CDCl_3)



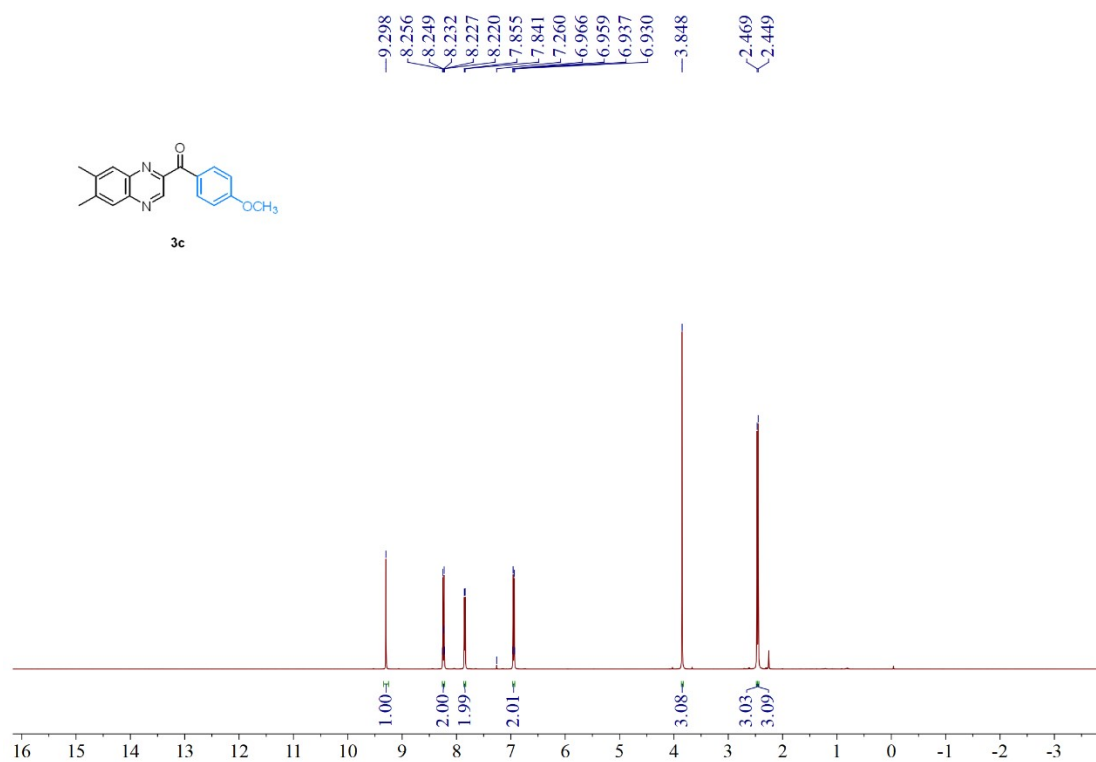
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of Compound **3a** (100 MHz, CDCl_3)



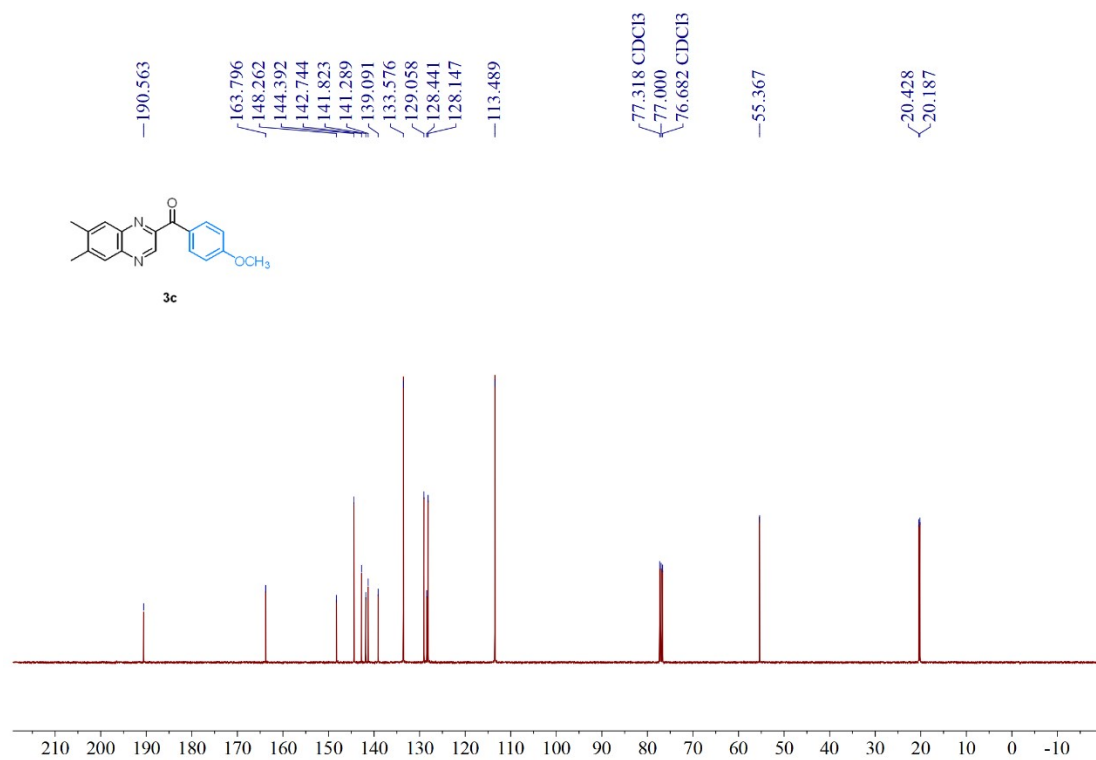
^1H NMR Spectrum of Compound **3b** (400 MHz, CDCl_3)



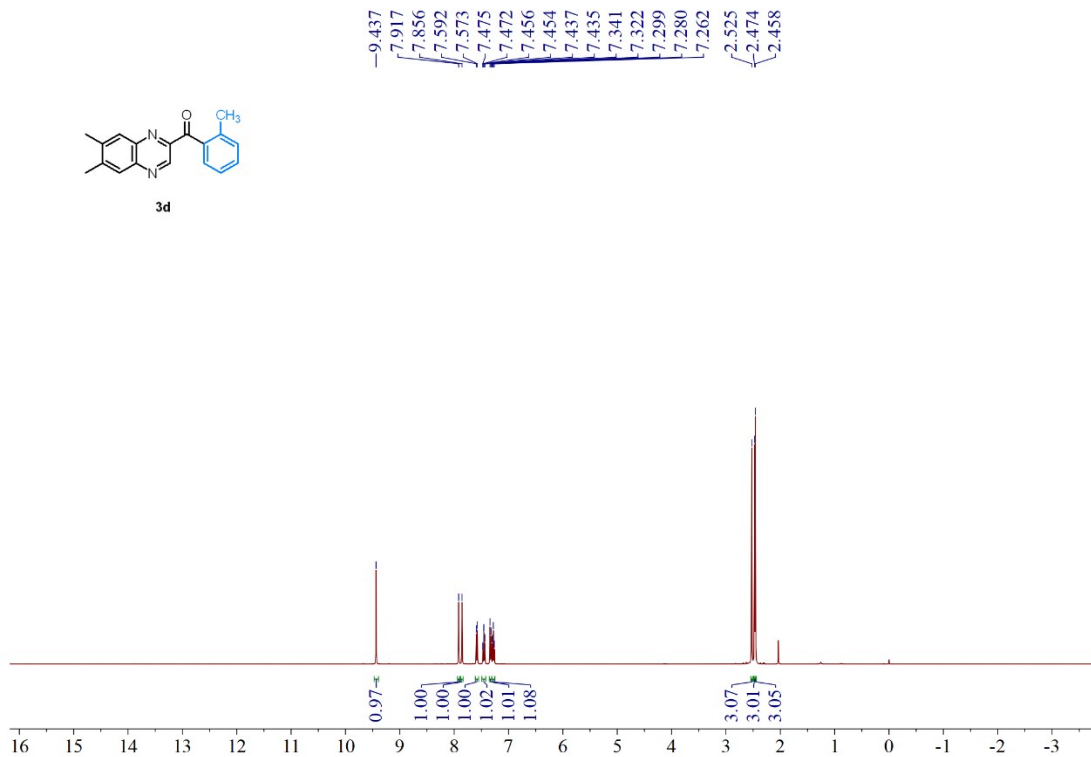
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of Compound **3b** (100 MHz, CDCl_3)



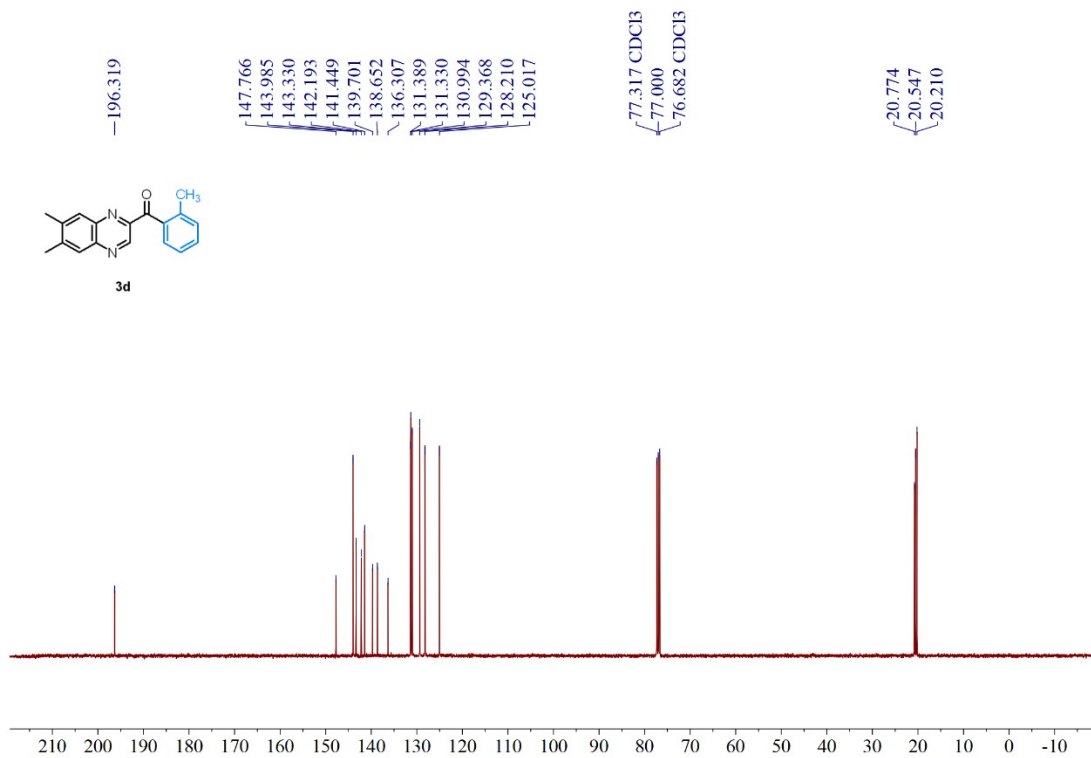
¹H NMR Spectrum of Compound **3c** (400 MHz, CDCl₃)



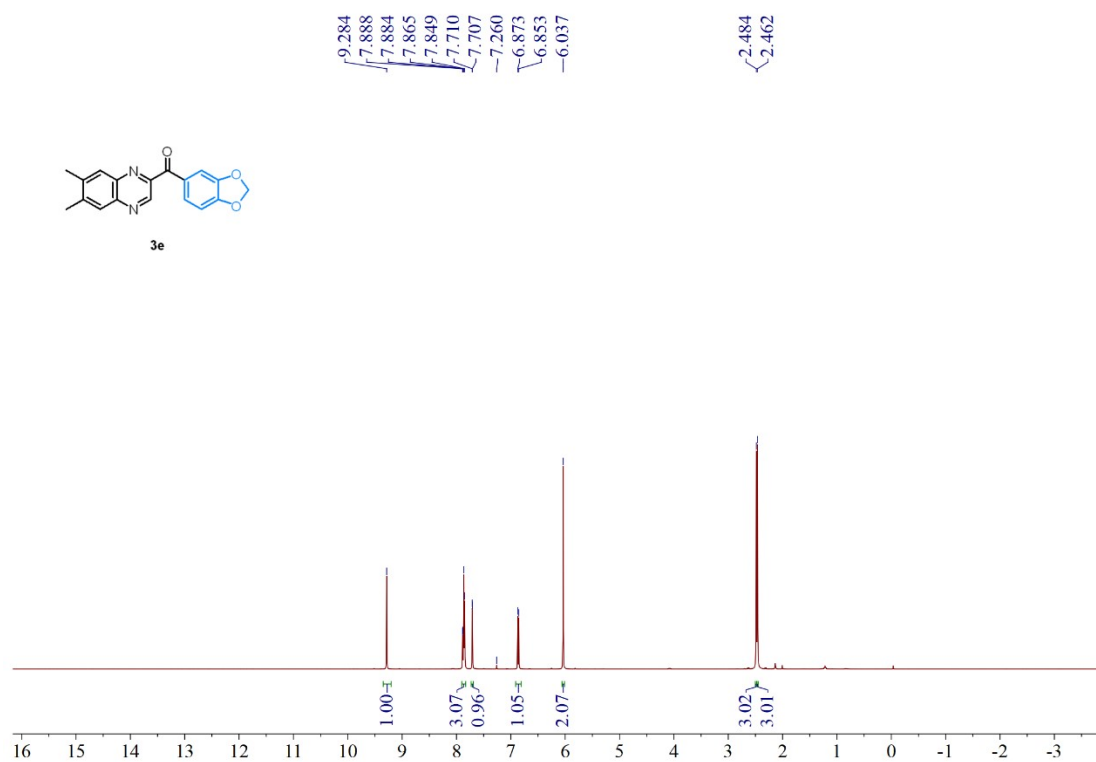
¹³C {¹H} NMR Spectrum of Compound **3c** (100 MHz, CDCl₃)



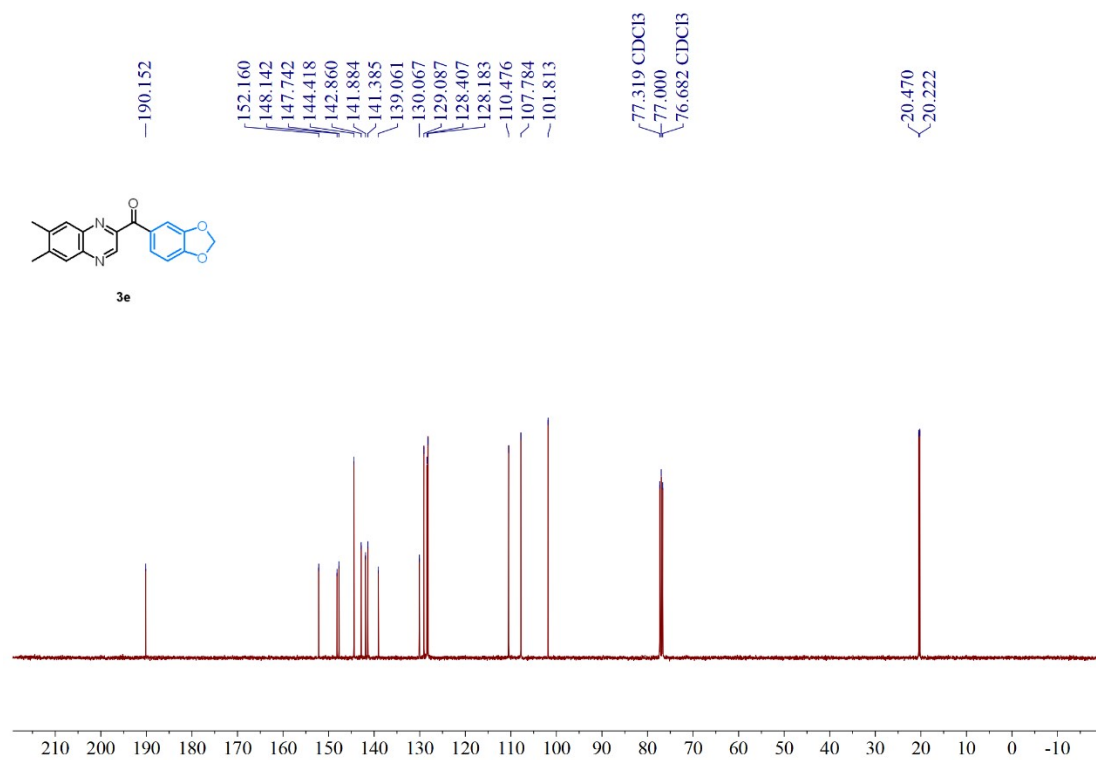
¹H NMR Spectrum of Compound **3d** (400 MHz, CDCl₃)



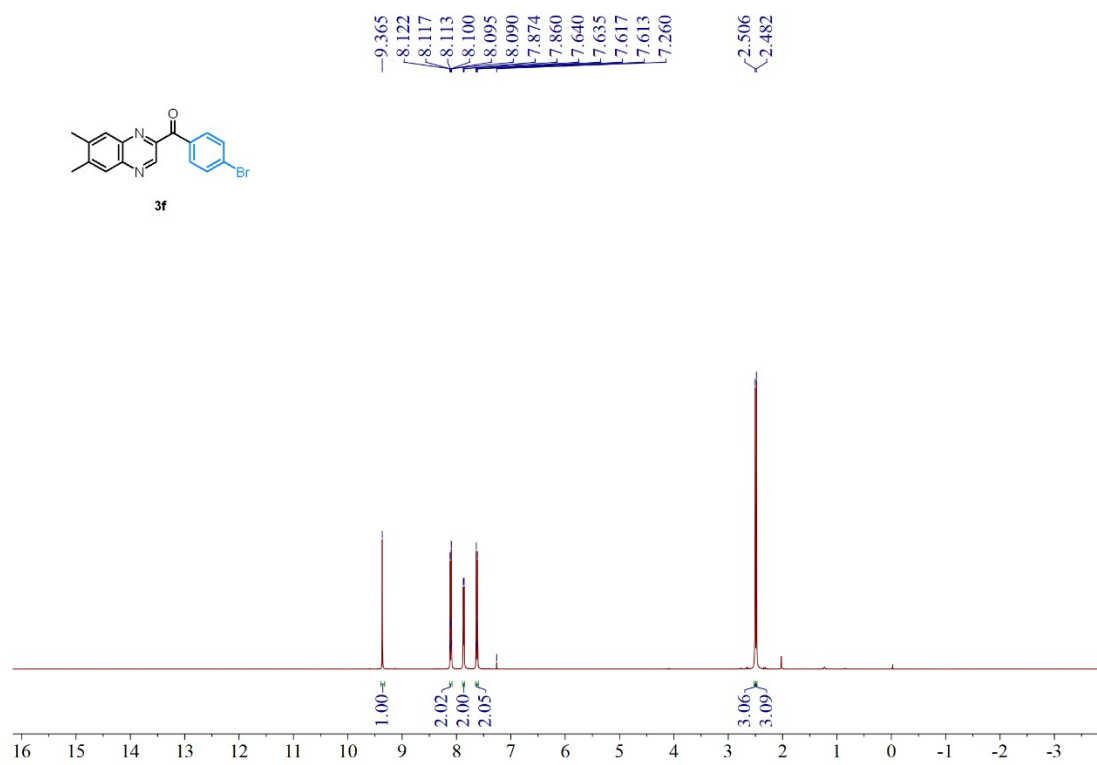
¹³C {¹H} NMR Spectrum of Compound **3d** (100 MHz, CDCl₃)



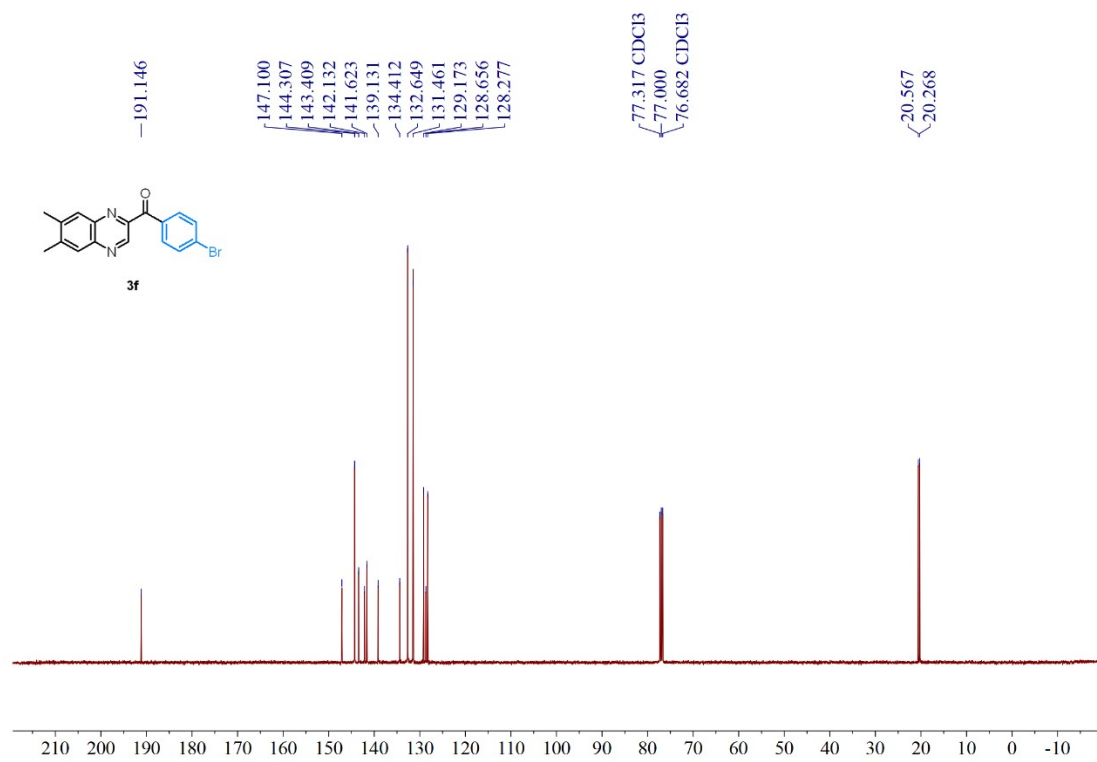
^1H NMR Spectrum of Compound **3e** (400 MHz, CDCl_3)



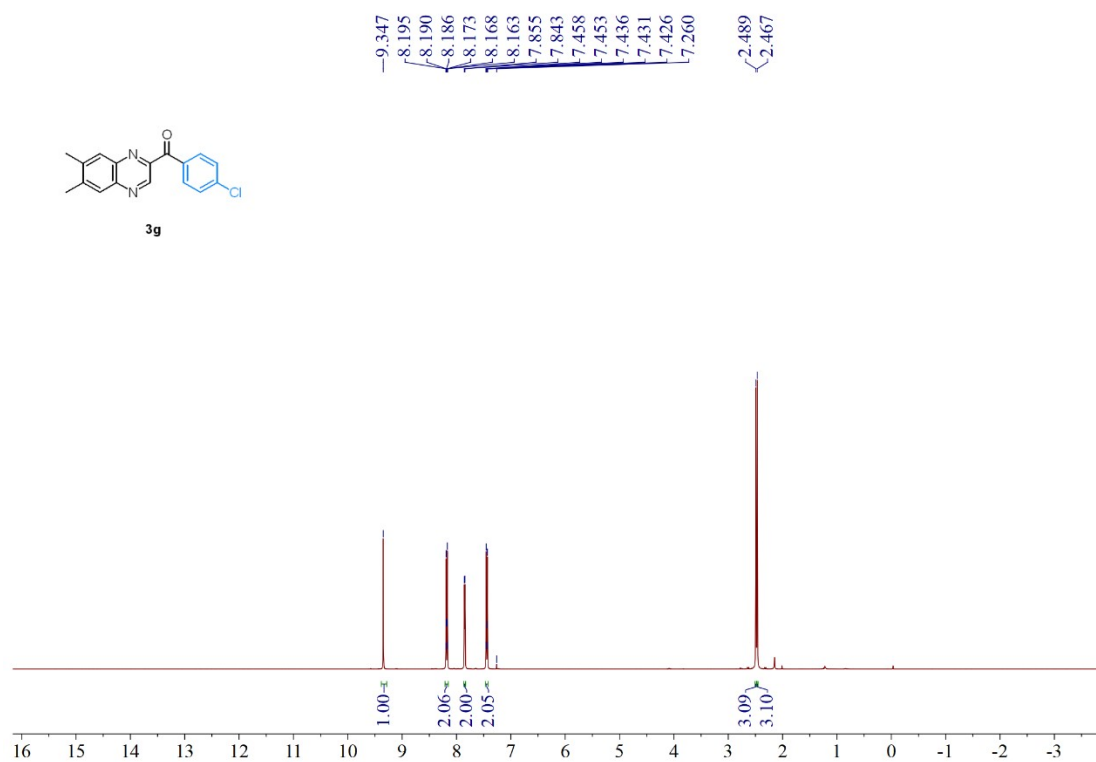
^{13}C NMR Spectrum of Compound **3e** (100 MHz, CDCl_3)



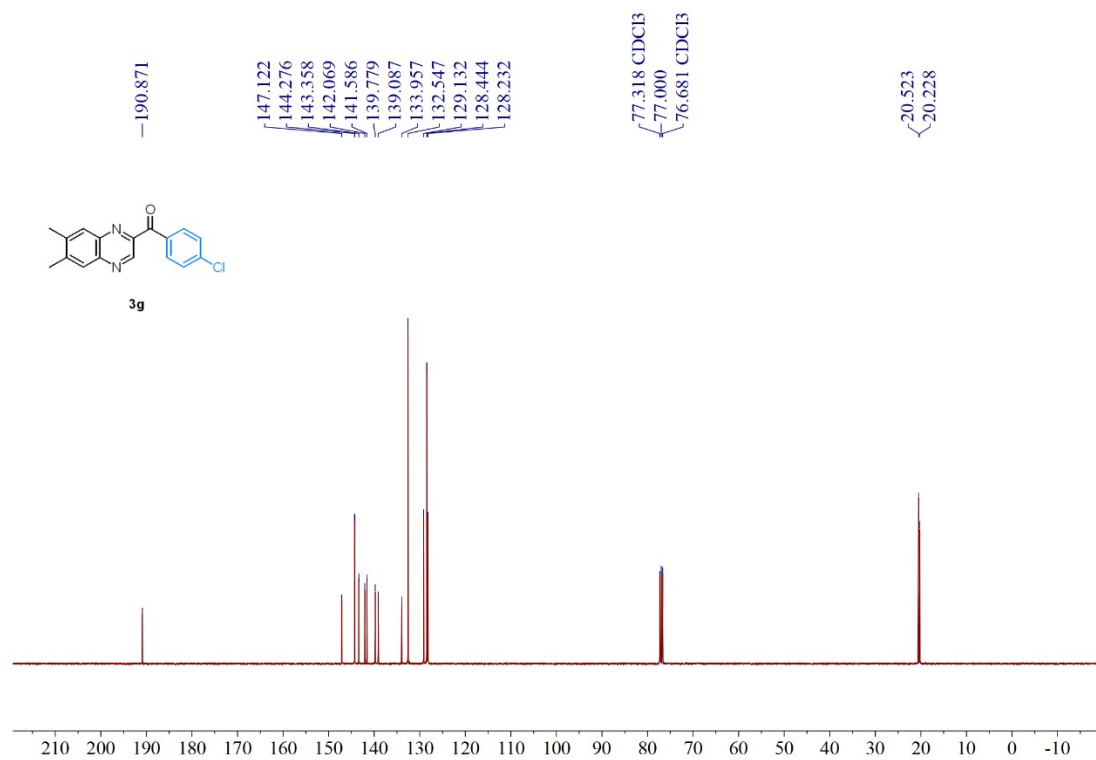
¹H NMR Spectrum of Compound **3f** (400 MHz, CDCl₃)



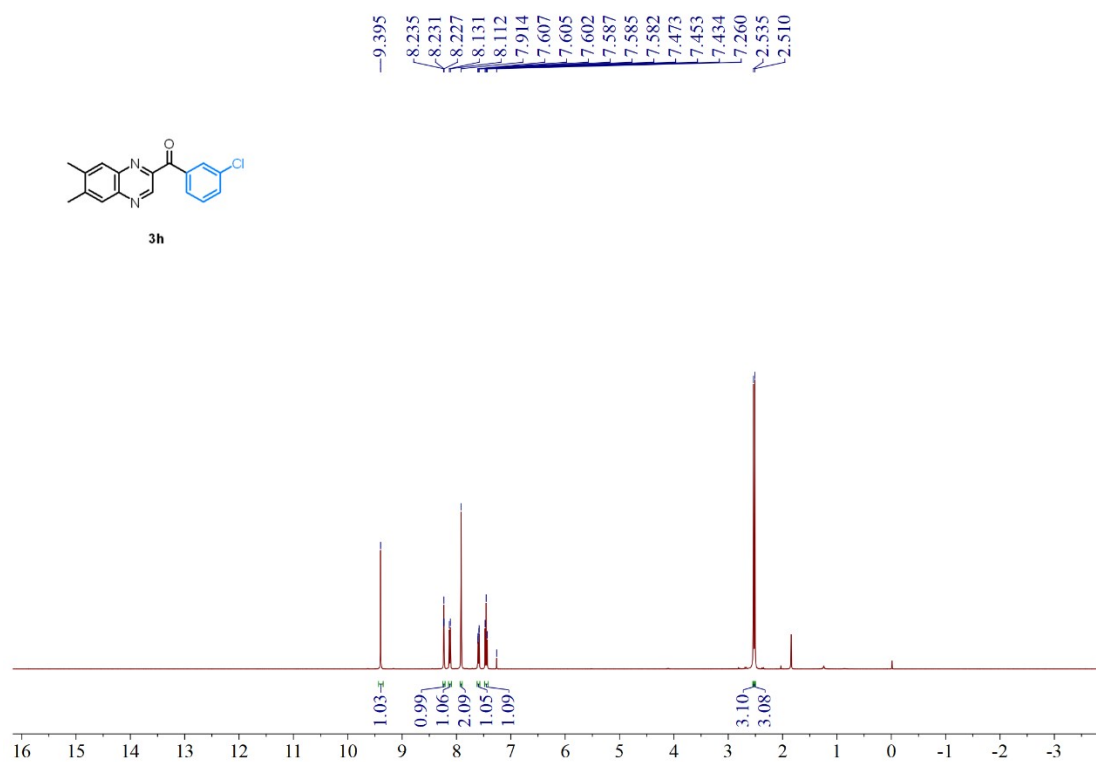
¹³C {¹H} NMR Spectrum of Compound **3f** (100 MHz, CDCl₃)



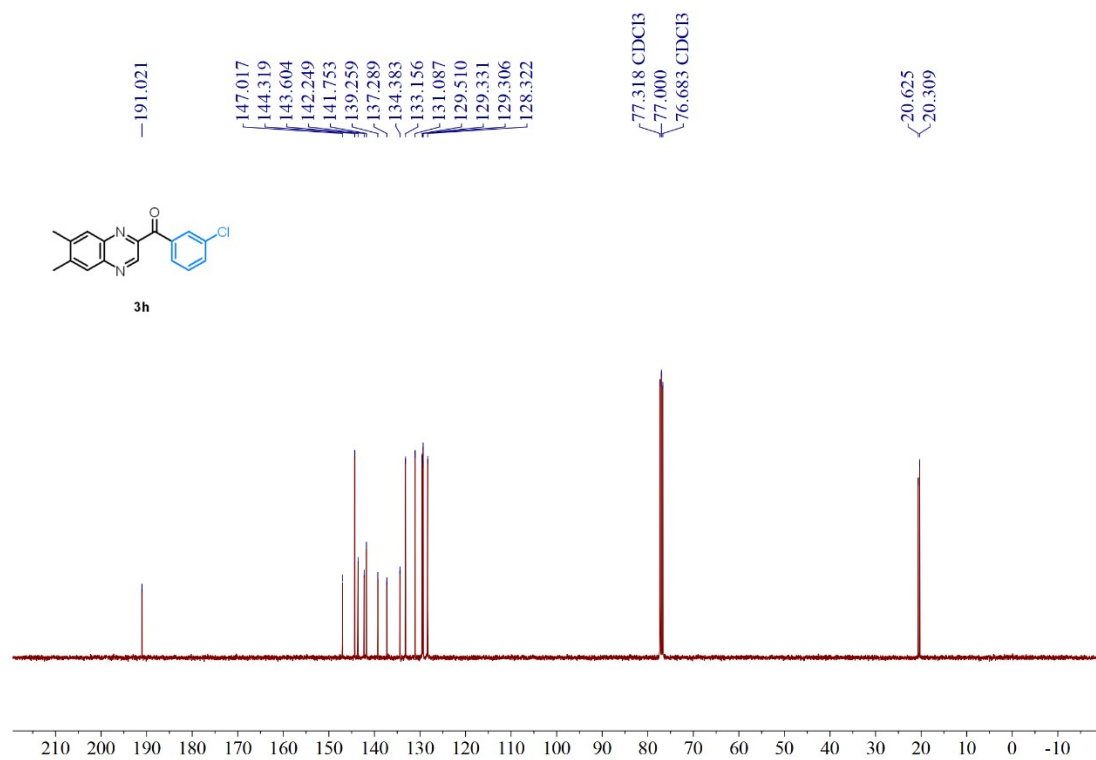
¹H NMR Spectrum of Compound **3g (400 MHz, CDCl₃)**



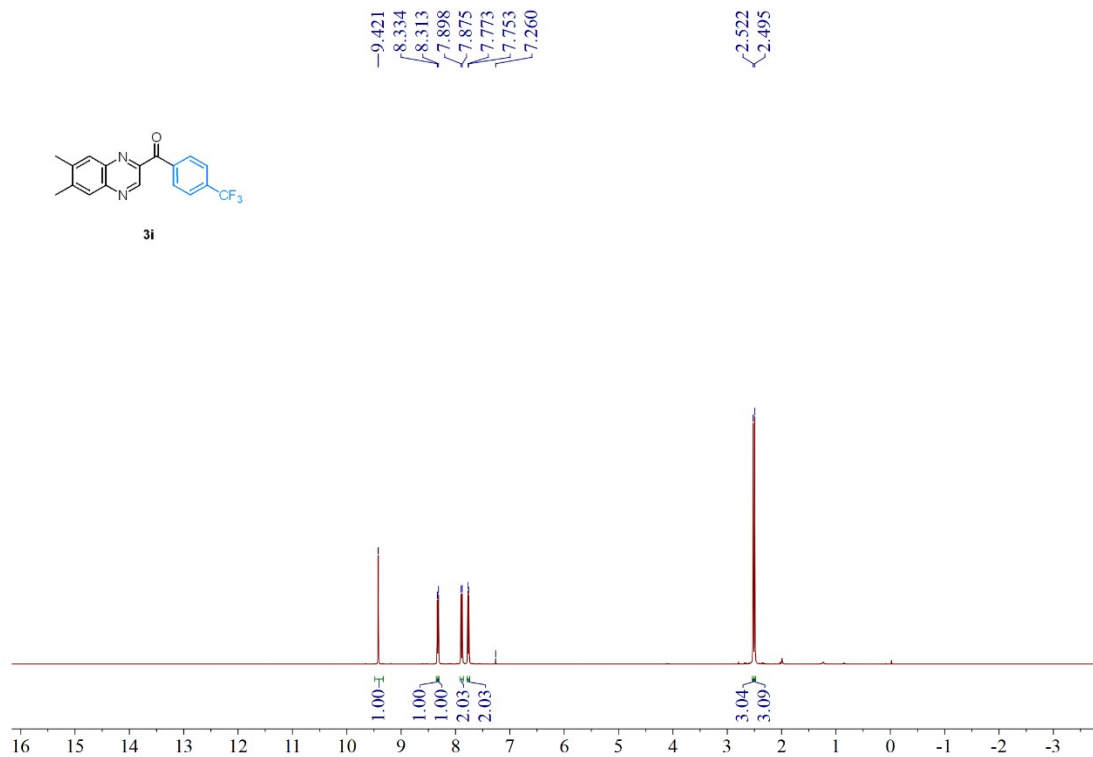
¹³C {¹H} NMR Spectrum of Compound **3g (100 MHz, CDCl₃)**



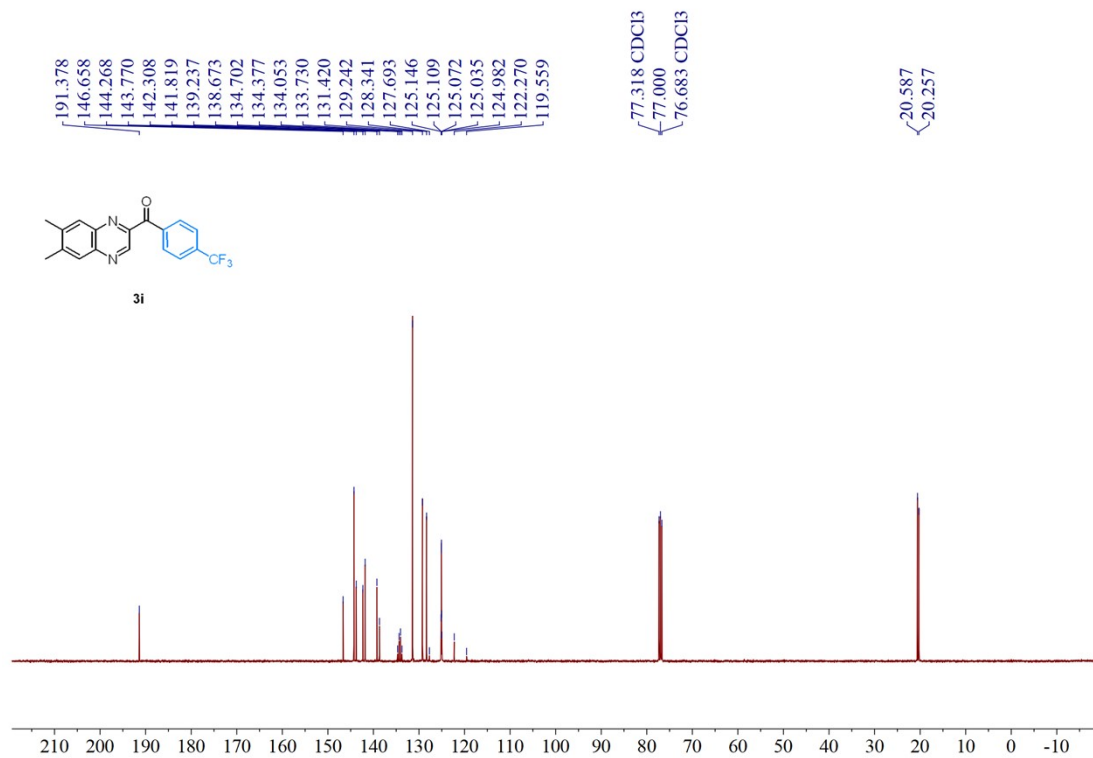
^1H NMR Spectrum of Compound **3h** (400 MHz, CDCl_3)



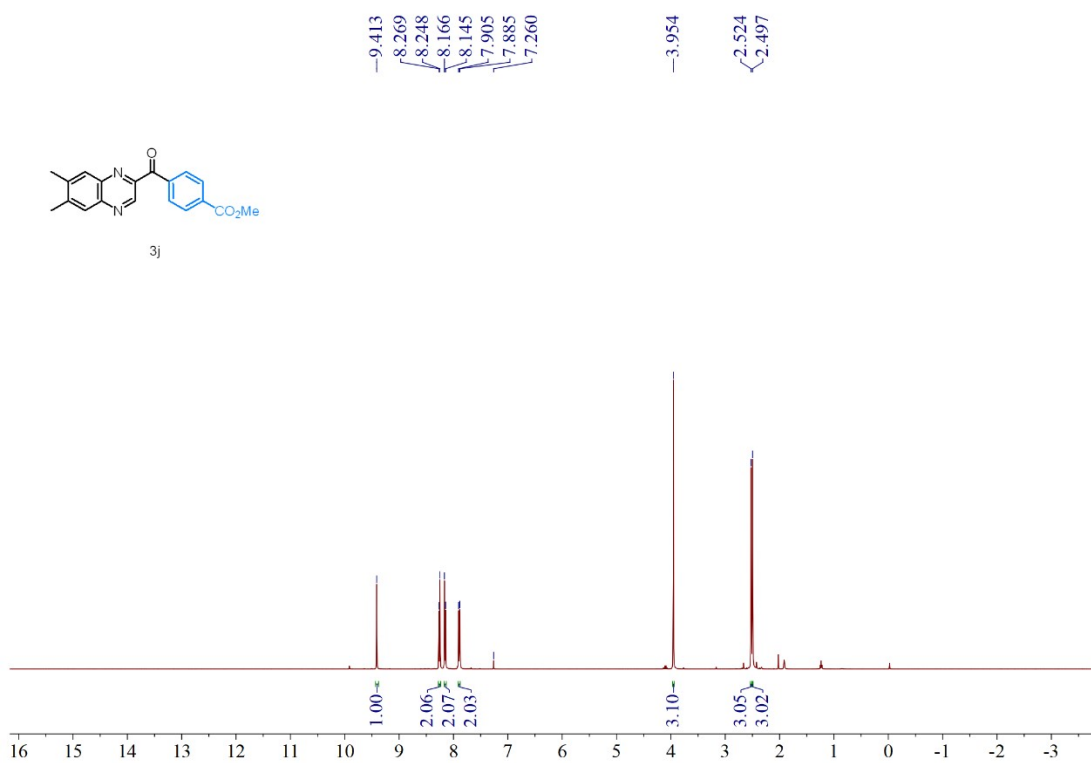
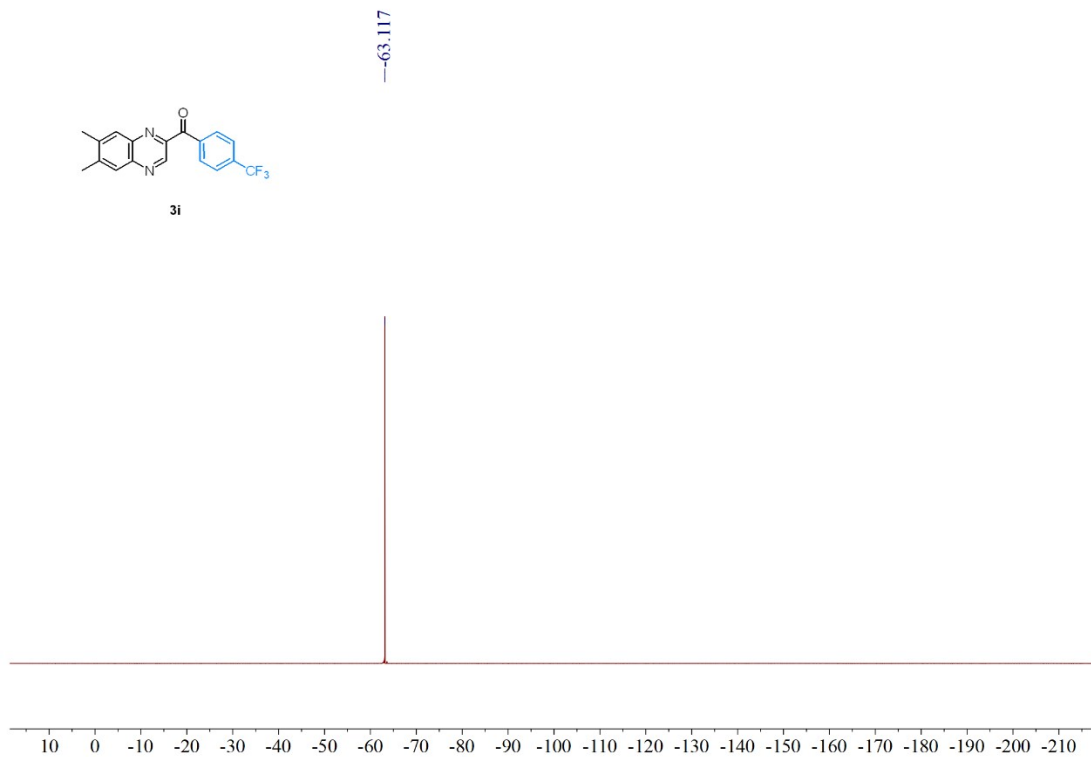
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of Compound **3h** (100 MHz, CDCl_3)

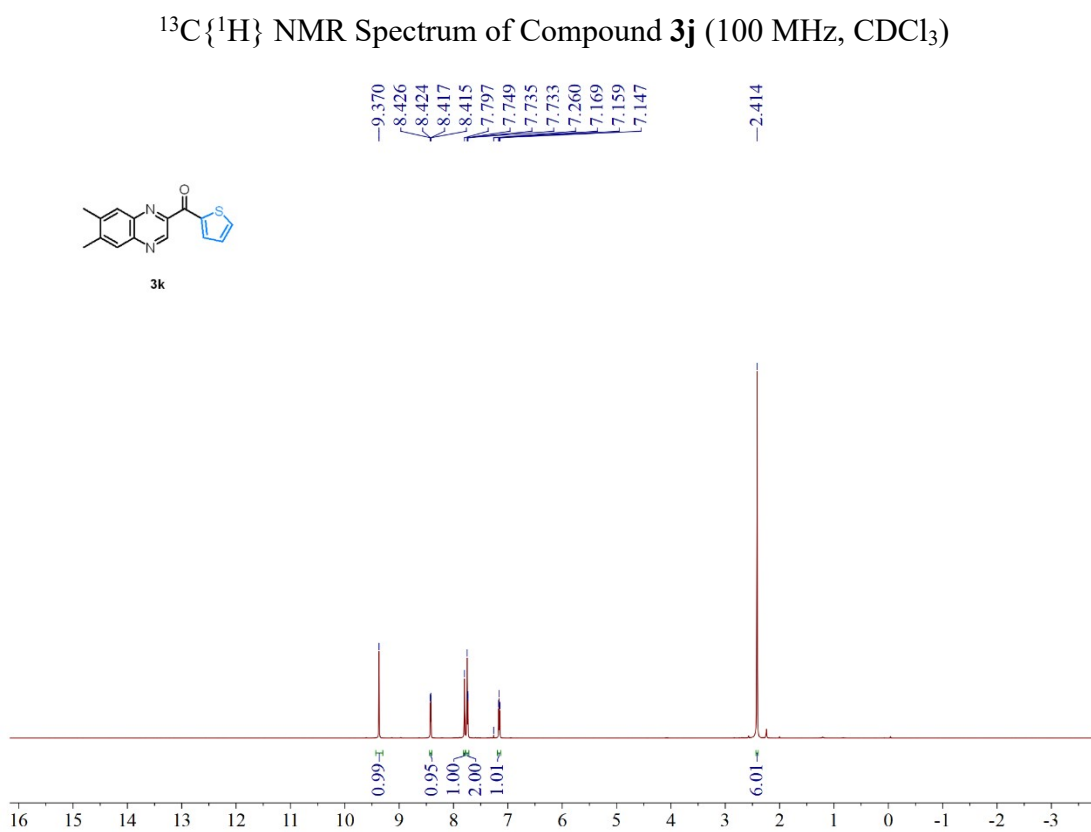
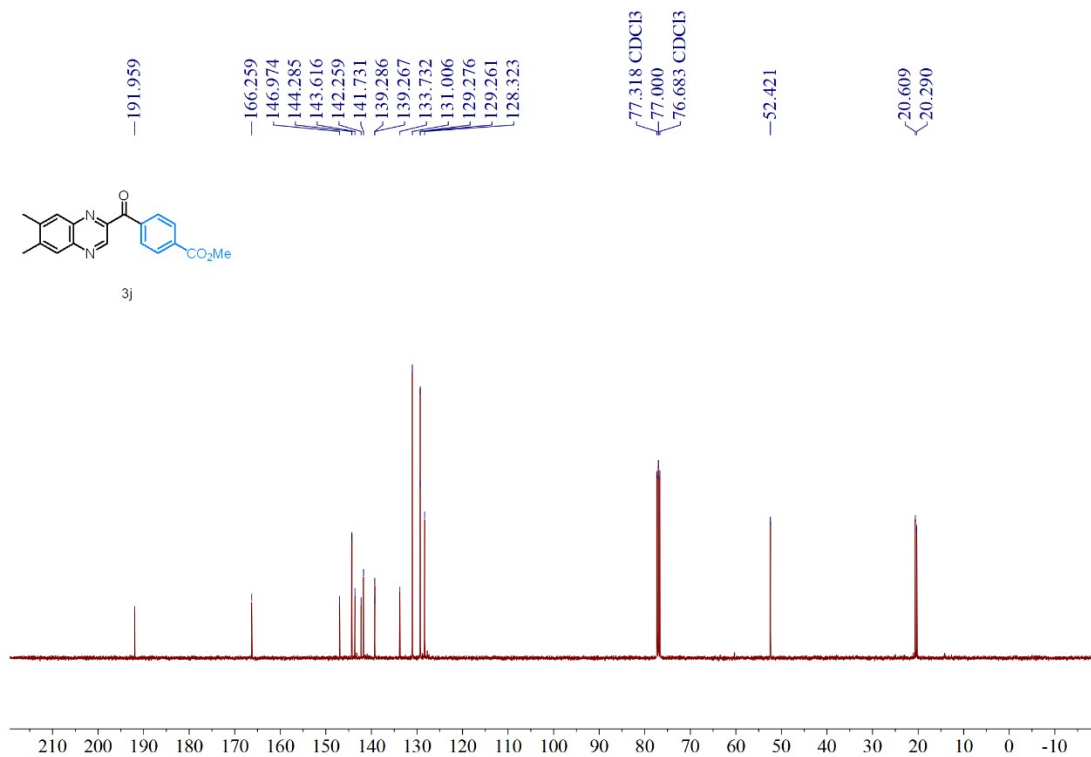


¹H NMR Spectrum of Compound **3i** (400 MHz, CDCl₃)

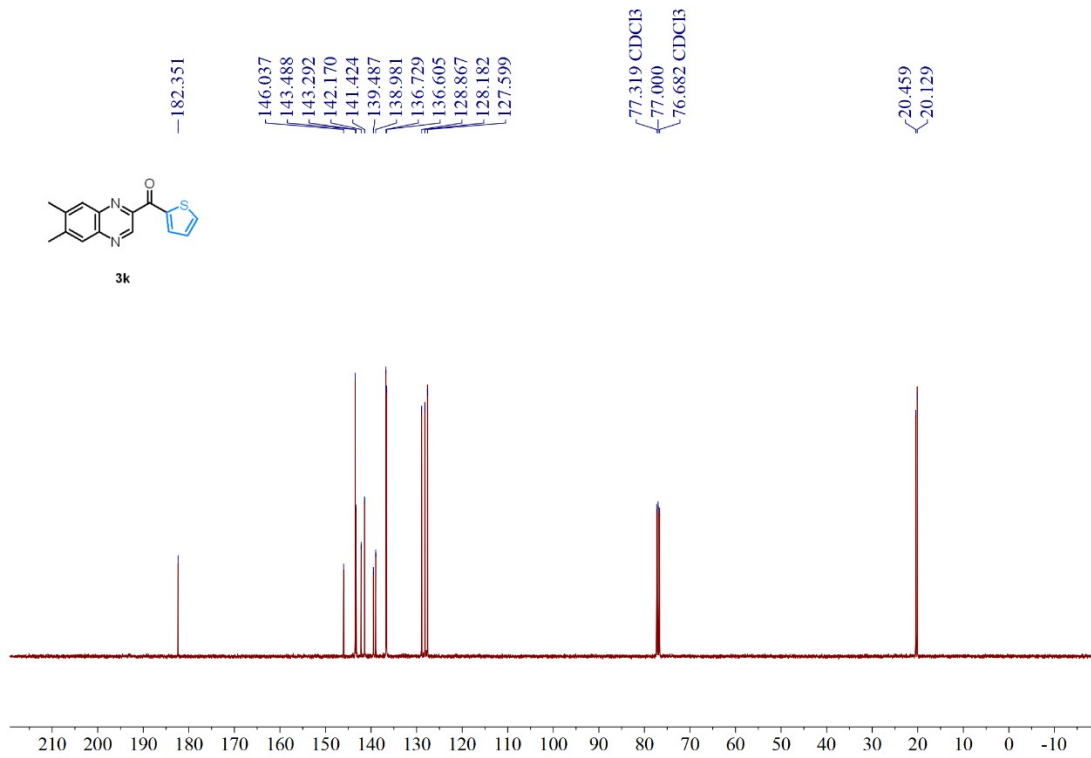


¹³C {¹H} NMR Spectrum of Compound **3i** (100 MHz, CDCl₃)

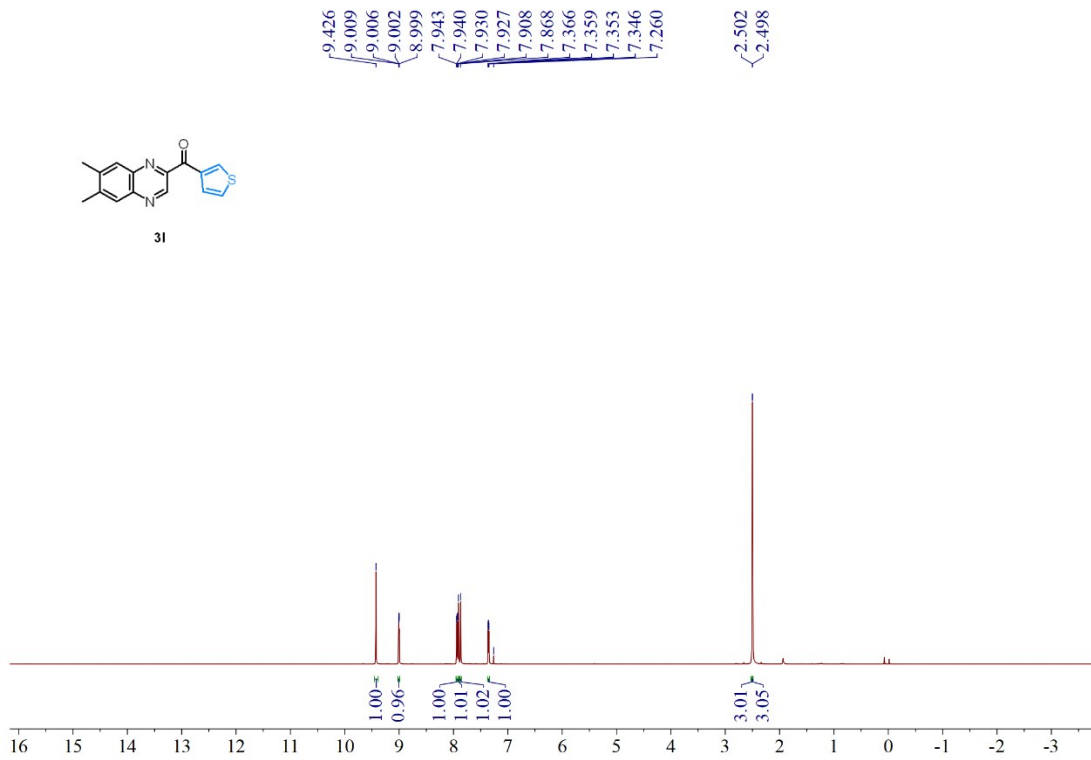




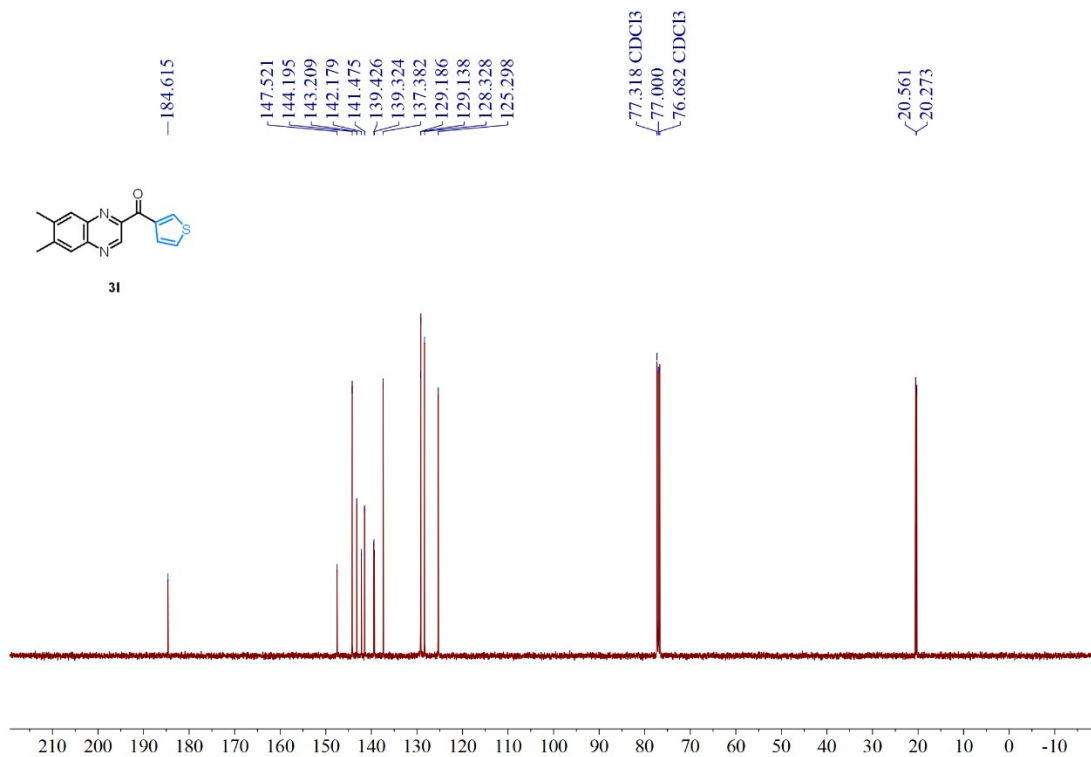
^1H NMR Spectrum of Compound **3k** (400 MHz, CDCl_3)



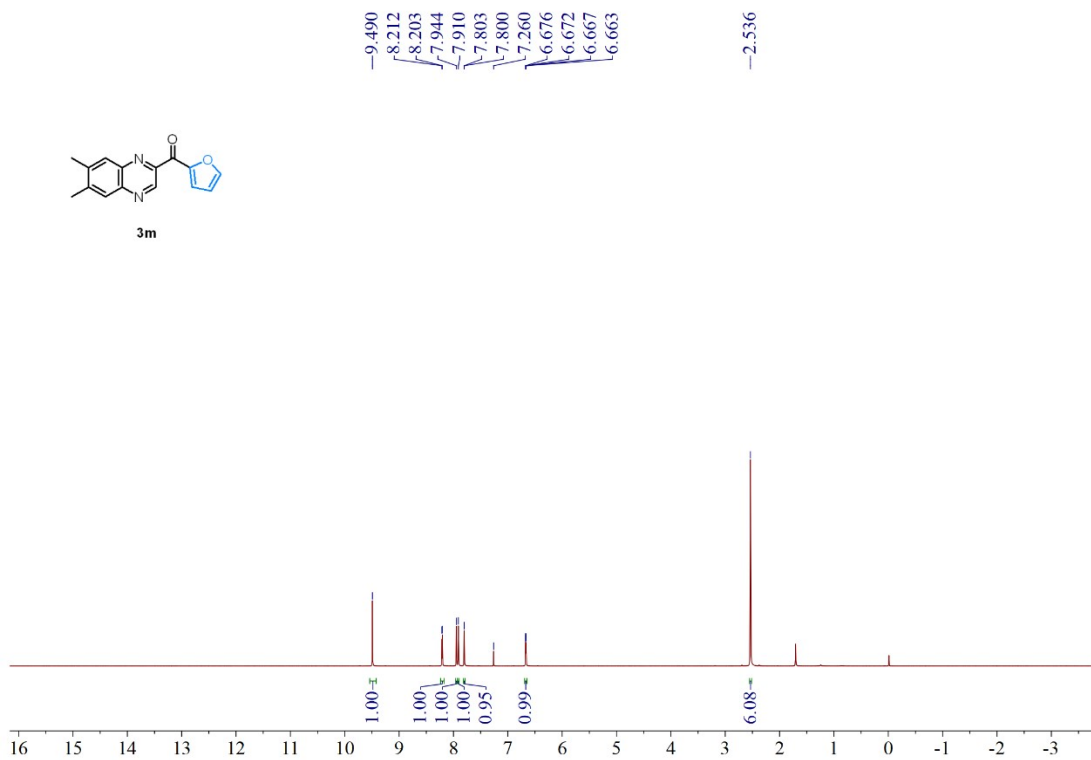
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of Compound **3k** (100 MHz, CDCl_3)



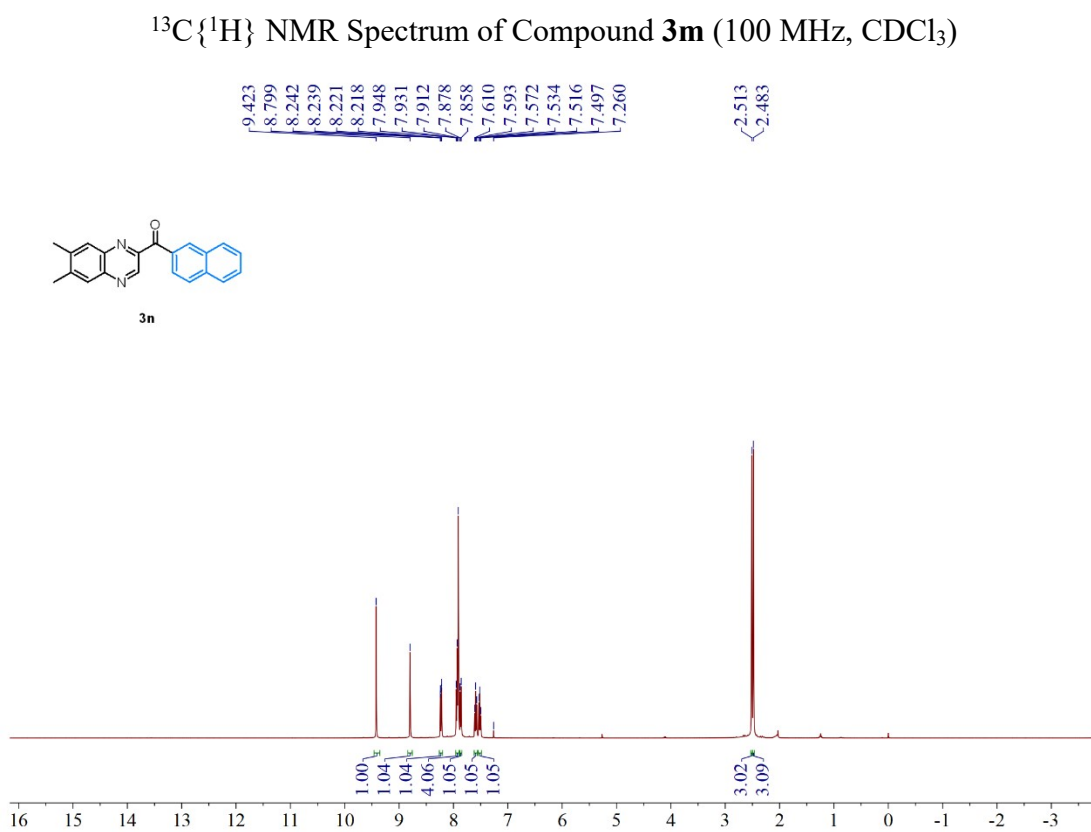
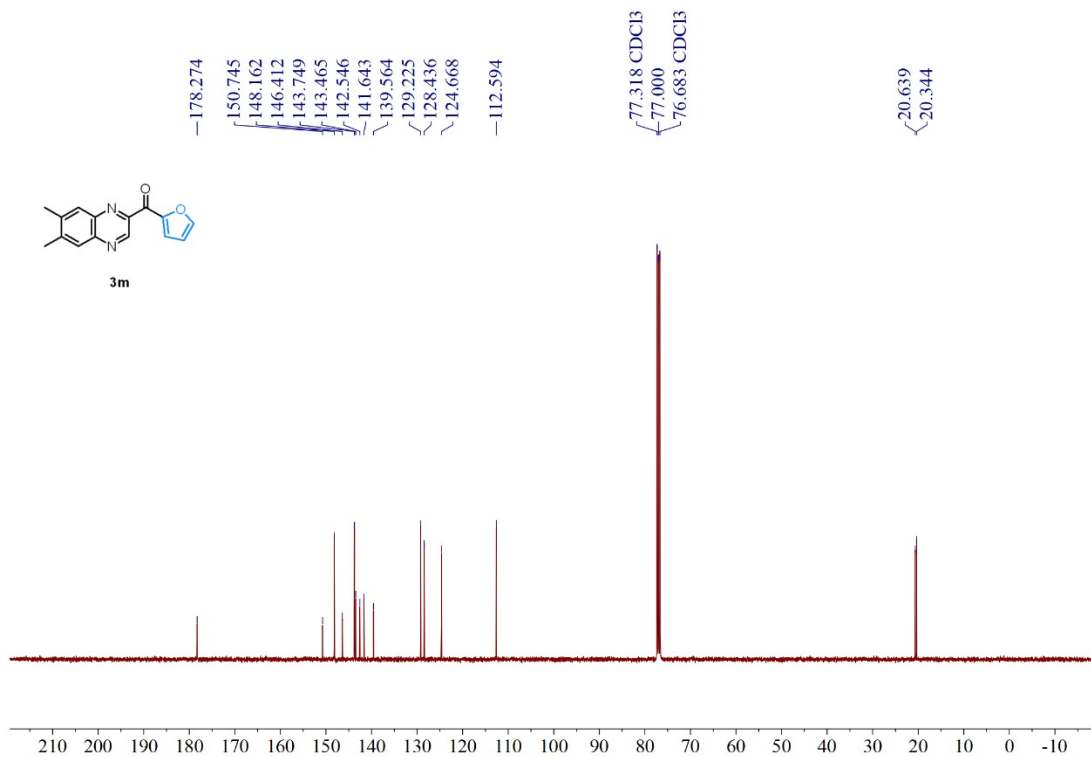
^1H NMR Spectrum of Compound **3l** (400 MHz, CDCl_3)

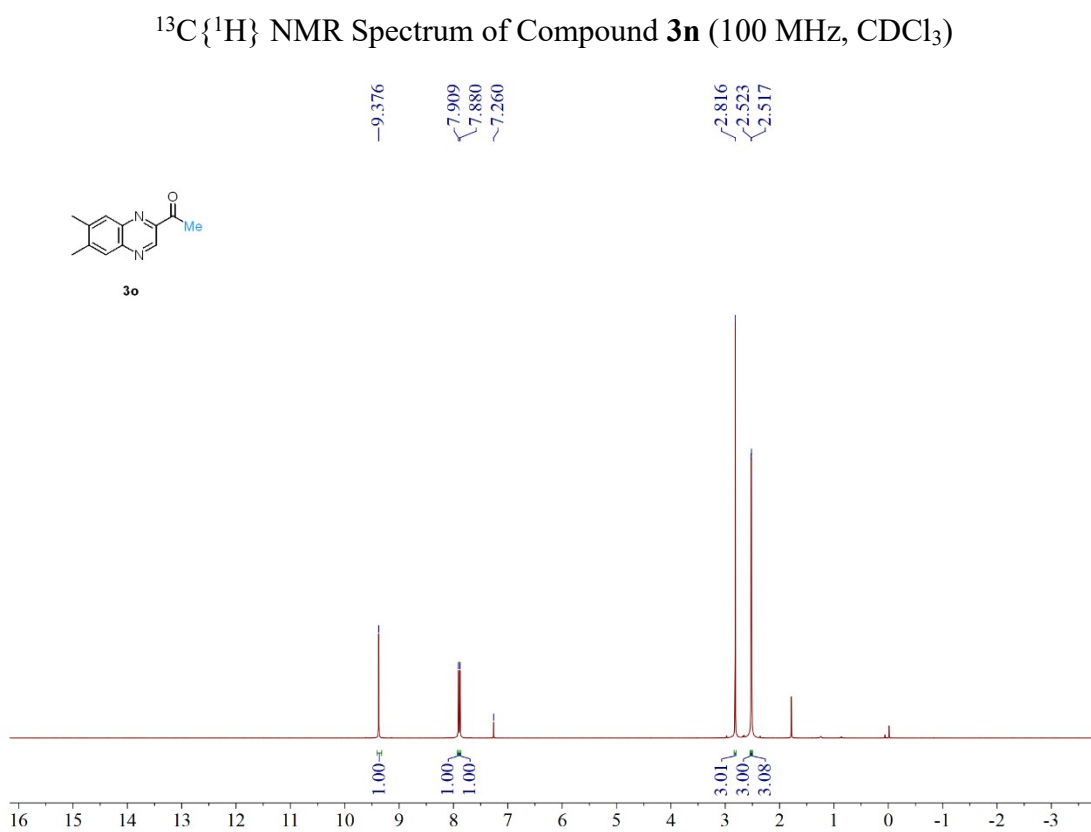
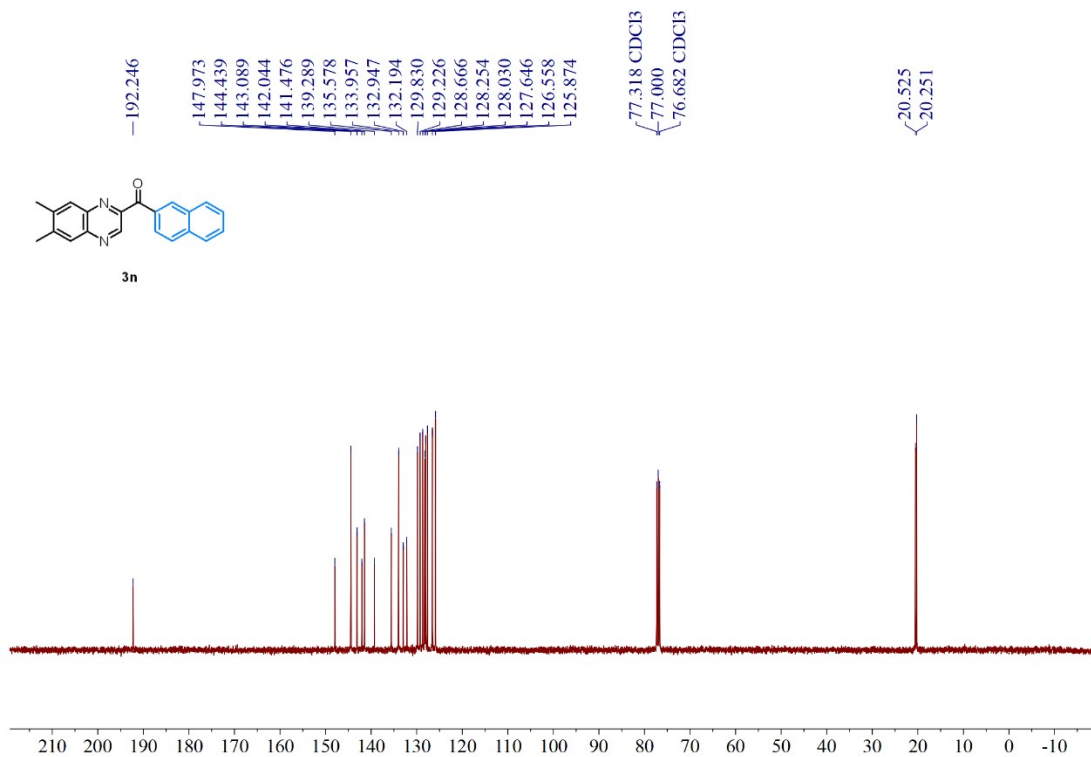


$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of Compound **3l** (100 MHz, CDCl_3)

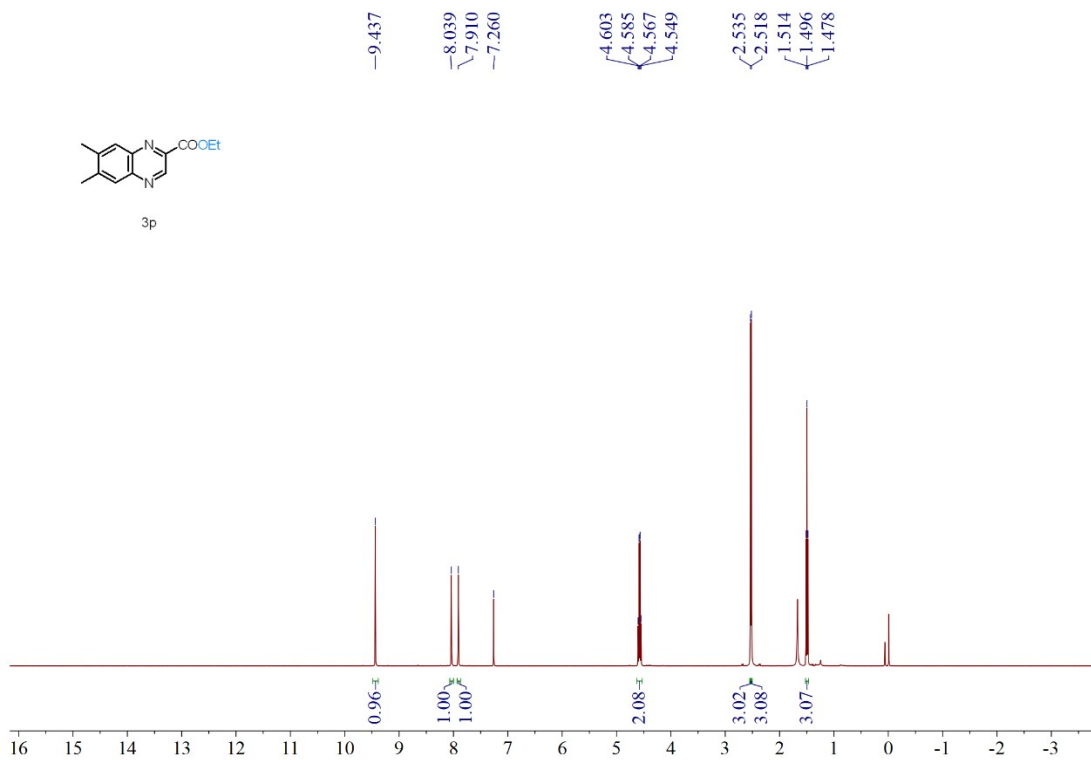
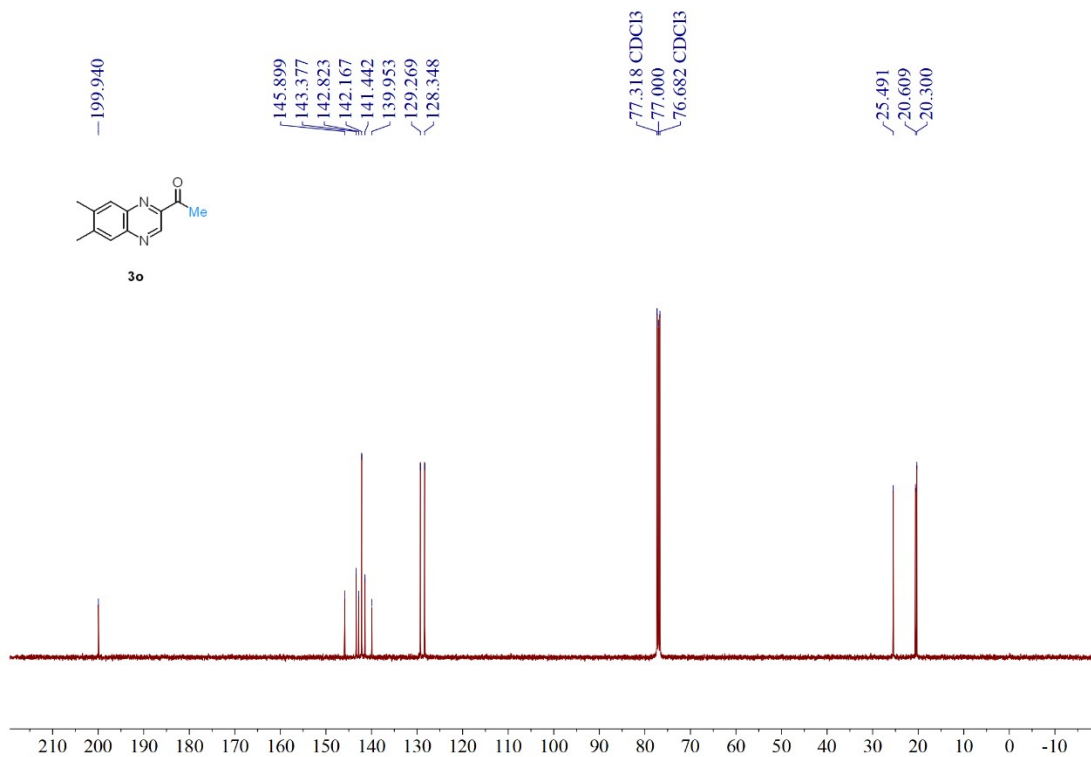


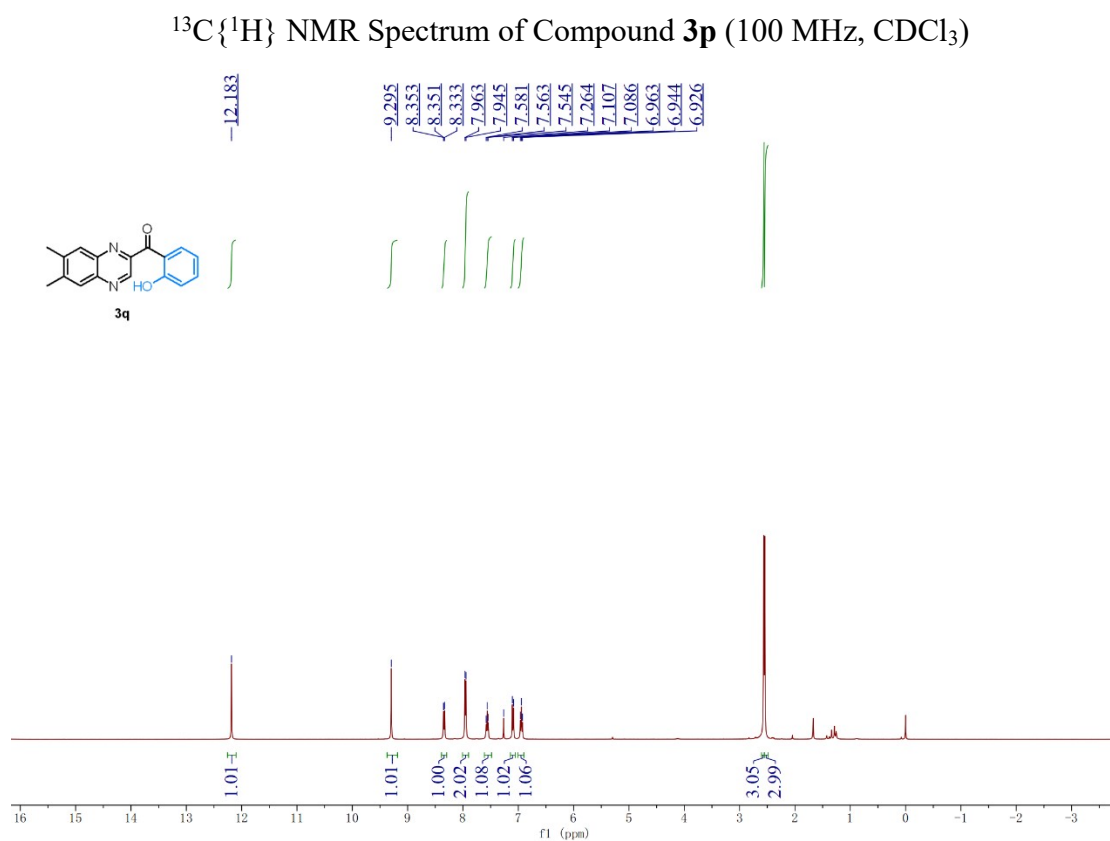
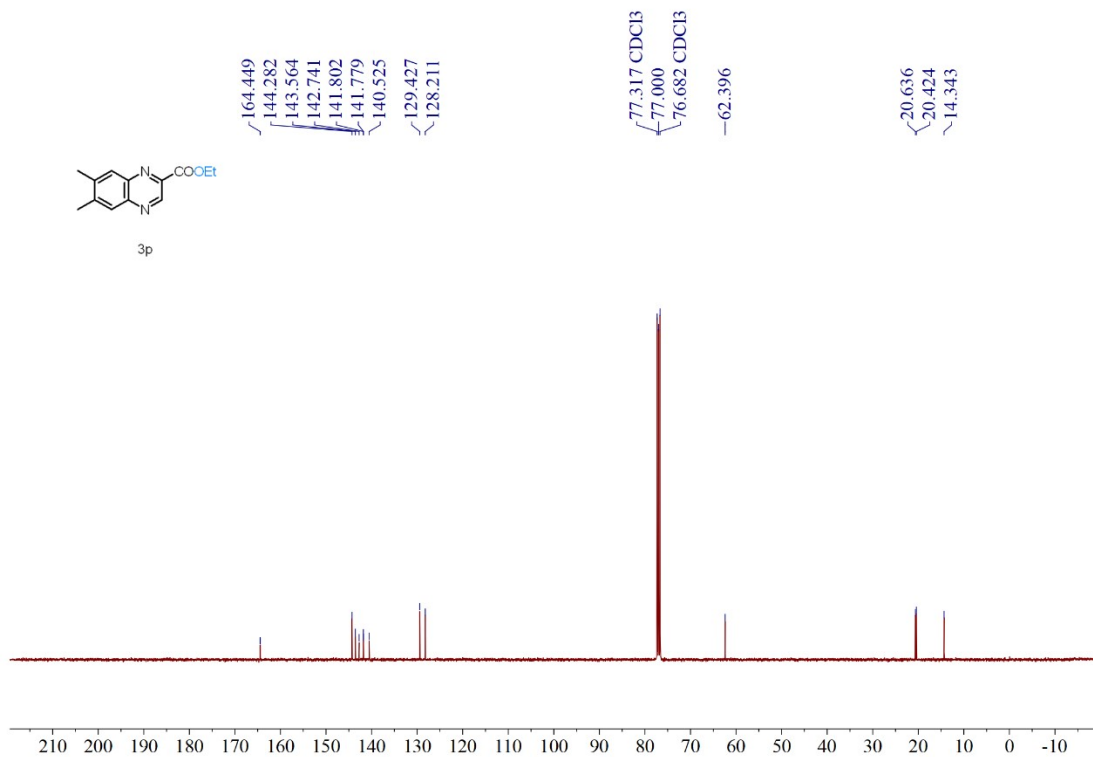
^1H NMR Spectrum of Compound **3m** (400 MHz, CDCl_3)



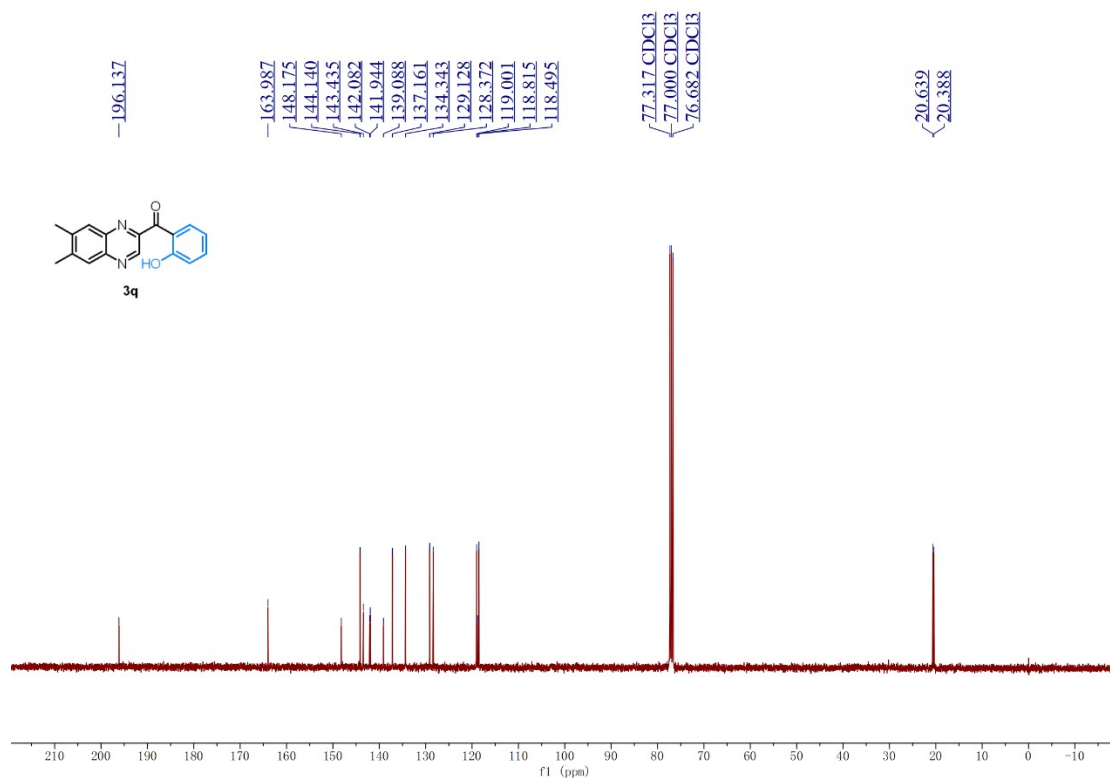


^1H NMR Spectrum of Compound **3o** (400 MHz, CDCl_3)

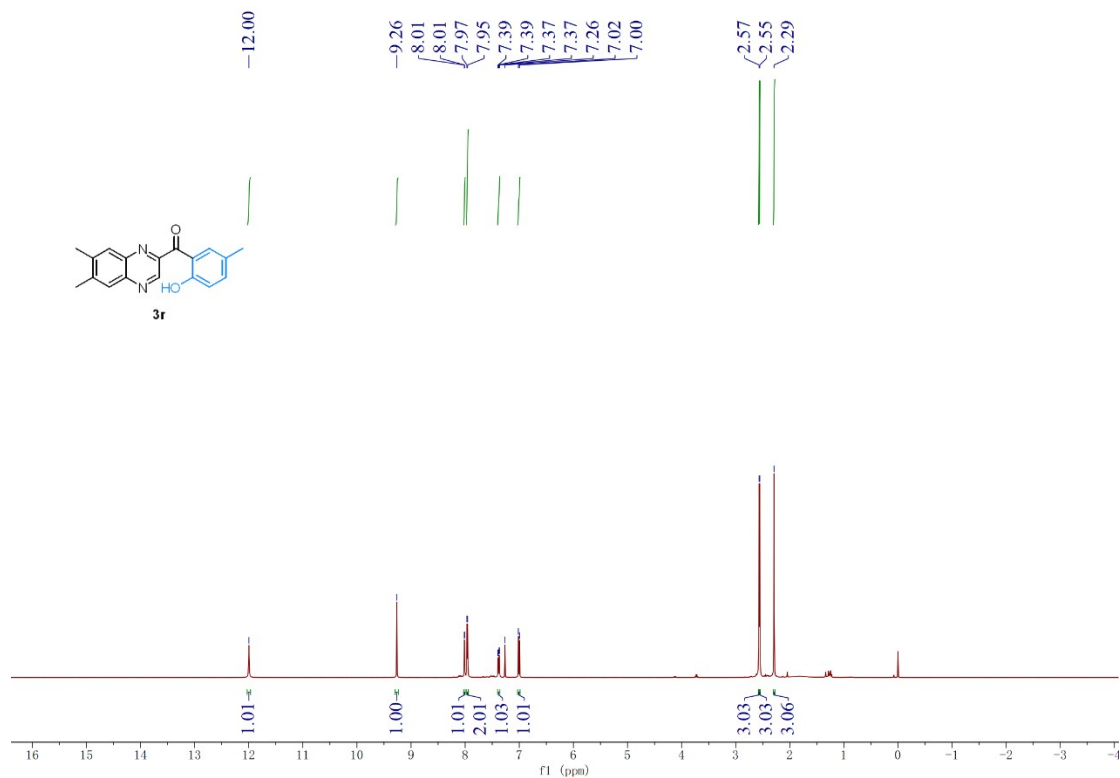




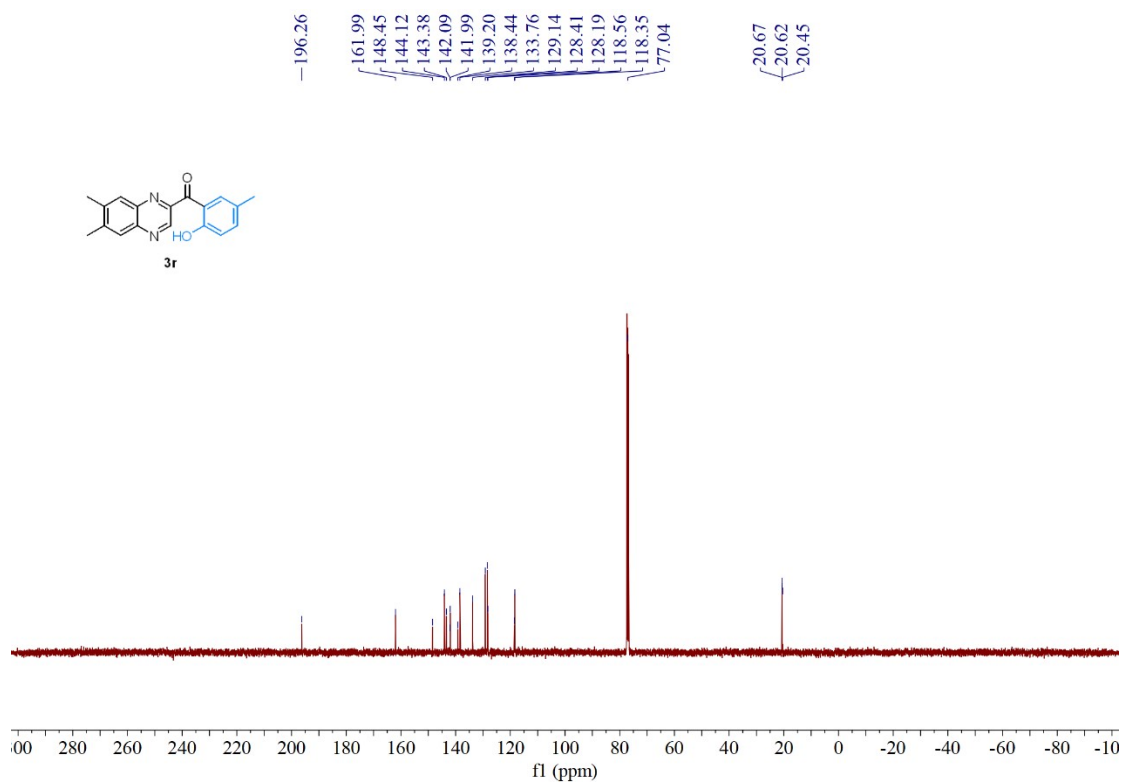
^1H NMR Spectrum of Compound **3q** (400 MHz, CDCl_3)



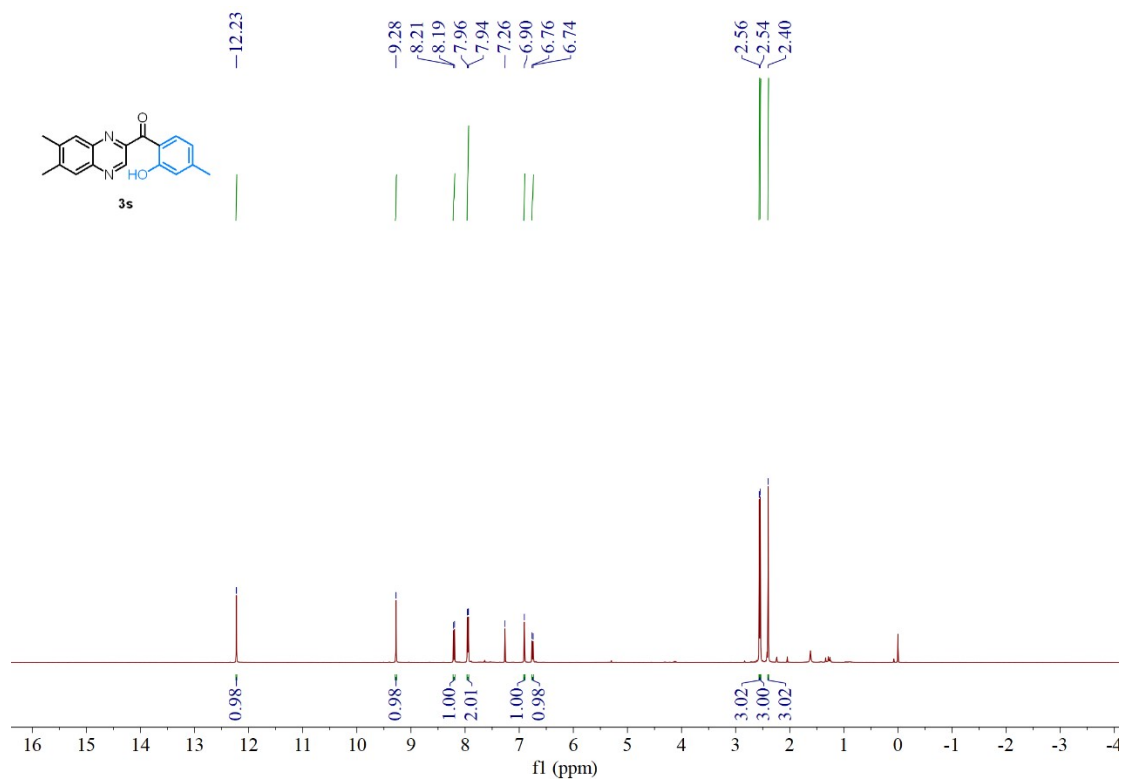
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of Compound **3q** (100 MHz, CDCl₃)



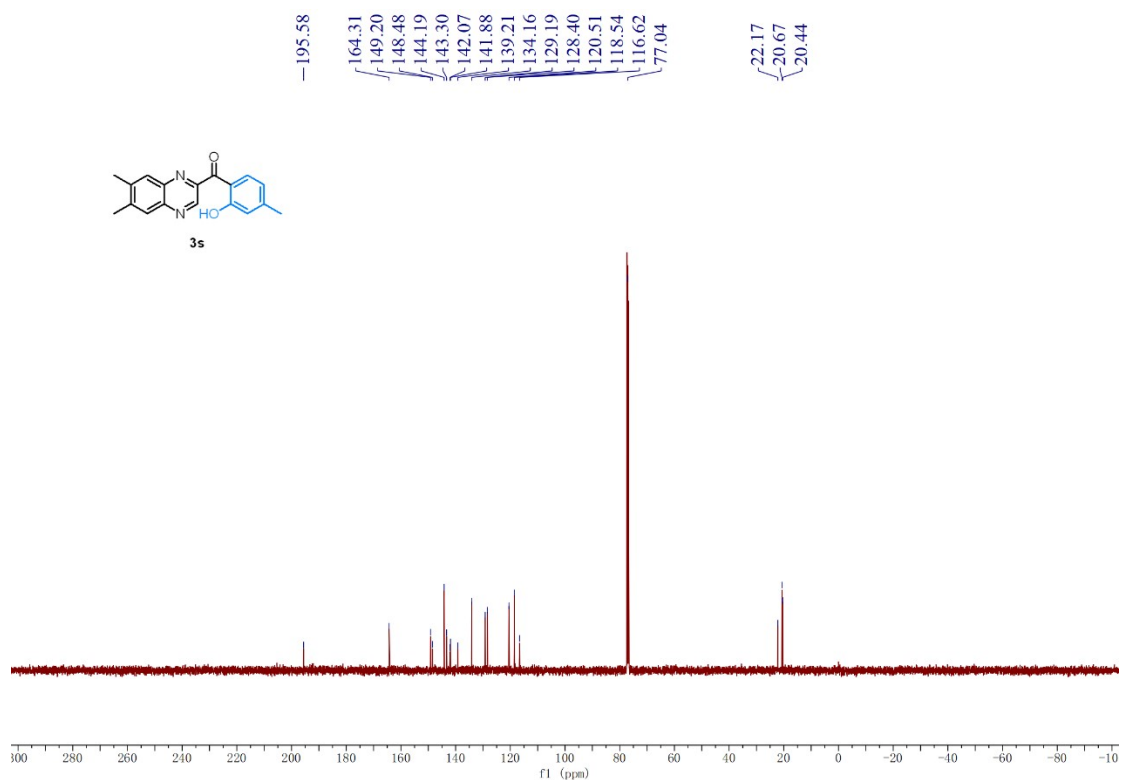
^1H NMR Spectrum of Compound **3r** (400 MHz, CDCl₃)



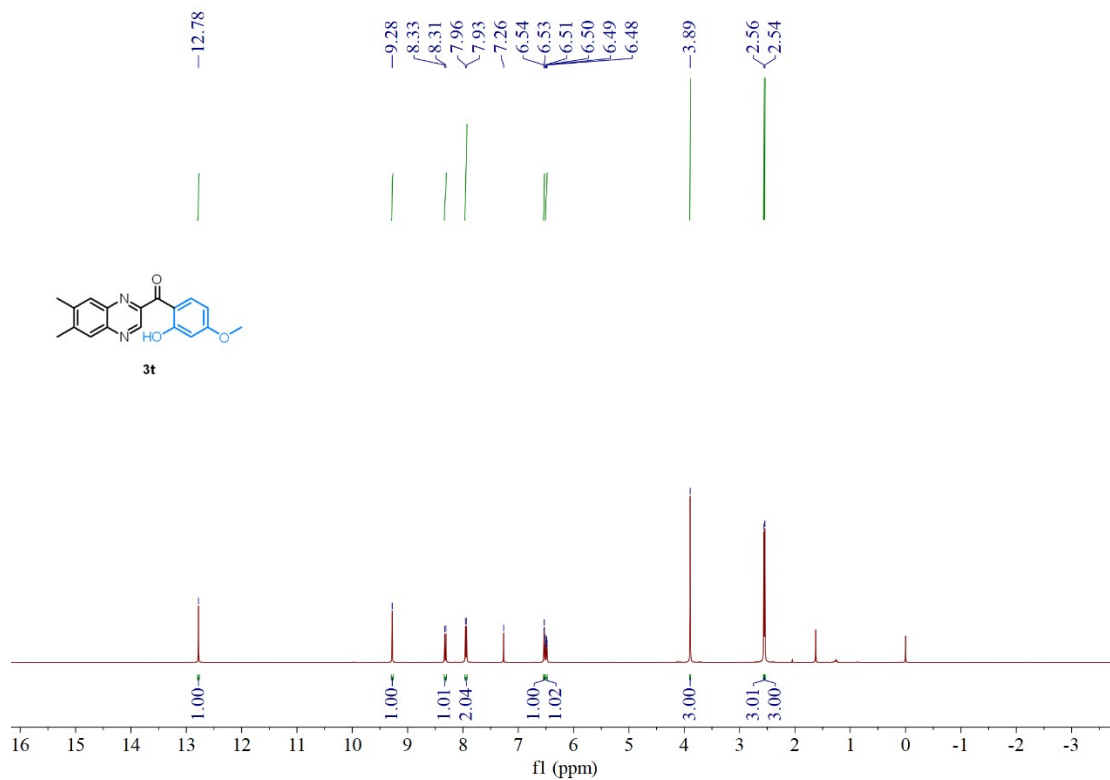
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of Compound **3r** (100 MHz, CDCl_3)



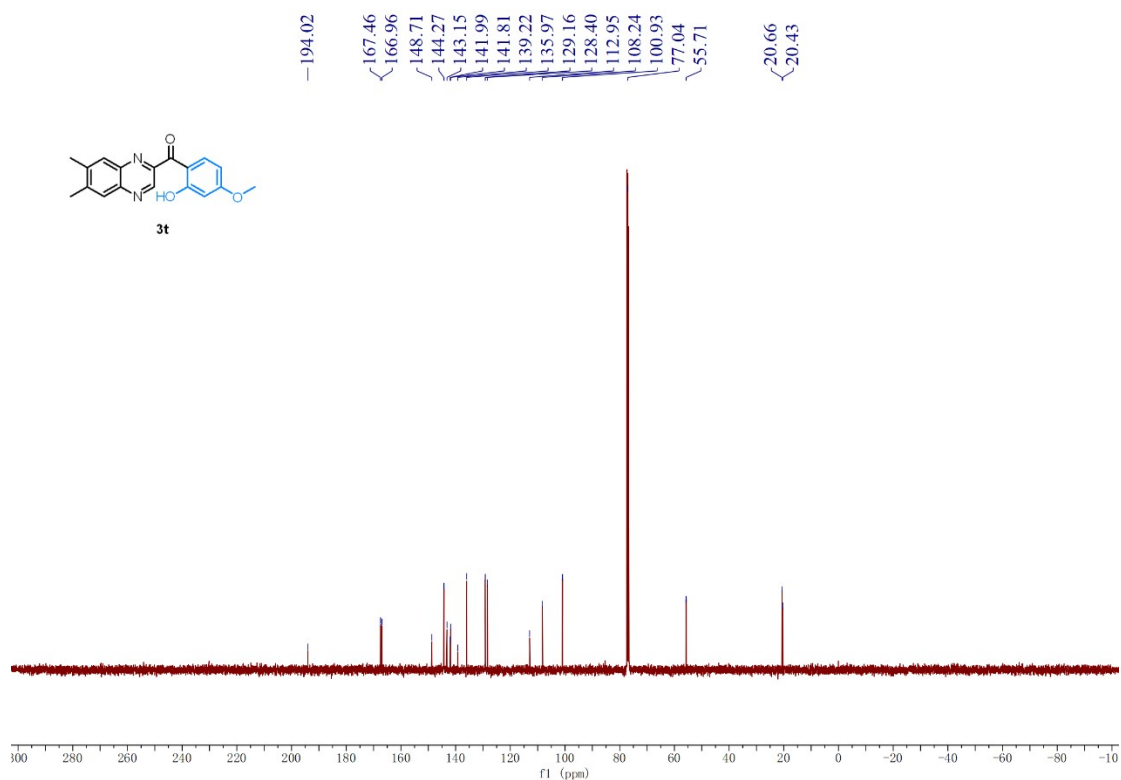
^1H NMR Spectrum of Compound **3s** (400 MHz, CDCl_3)



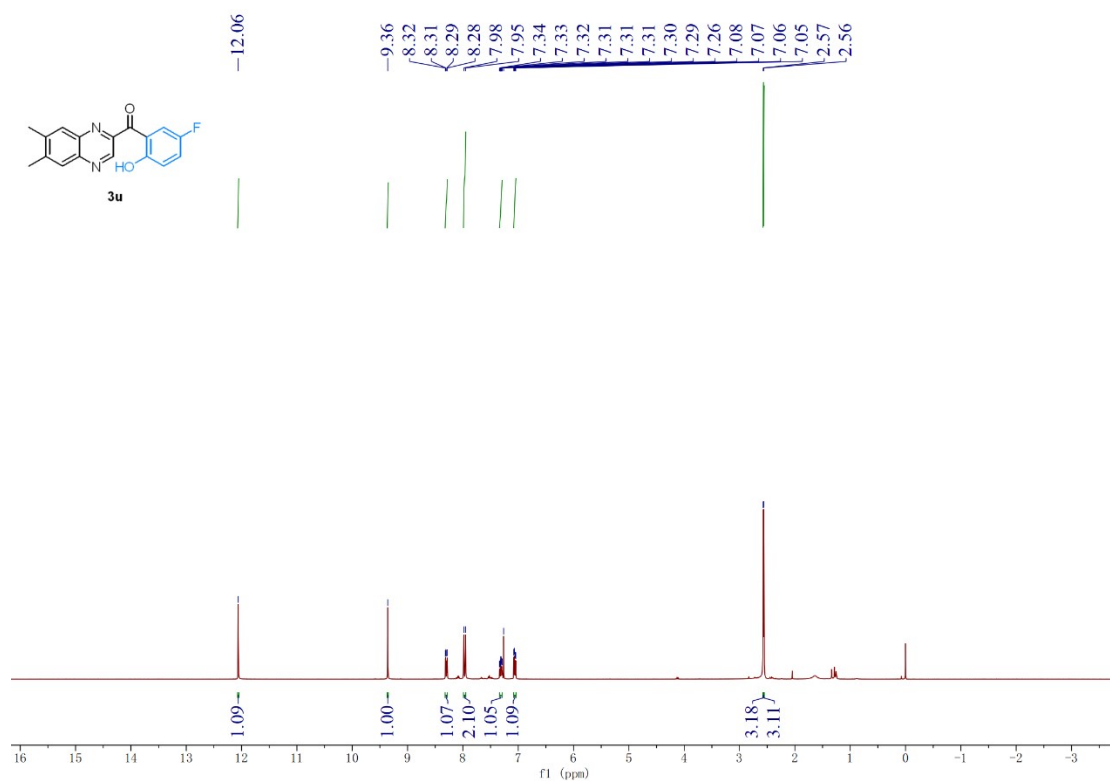
¹³C {¹H} NMR Spectrum of Compound 3s (100 MHz, CDCl₃)



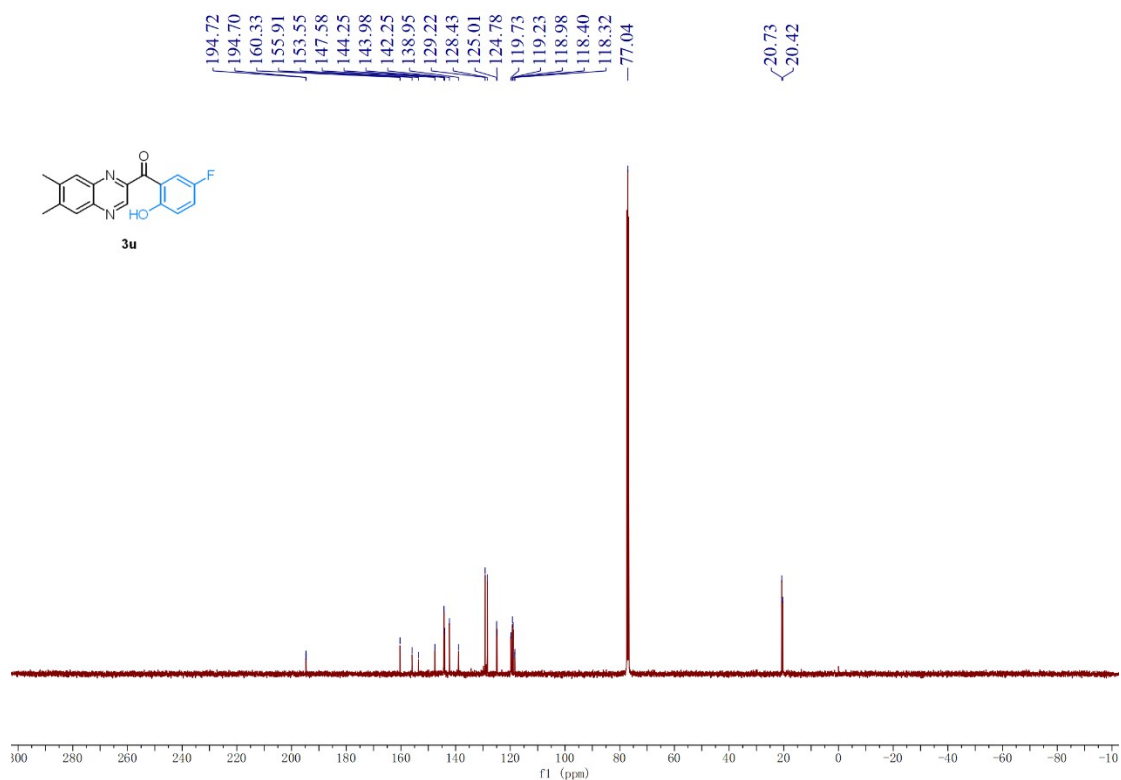
¹H NMR Spectrum of Compound 3t (400 MHz, CDCl₃)



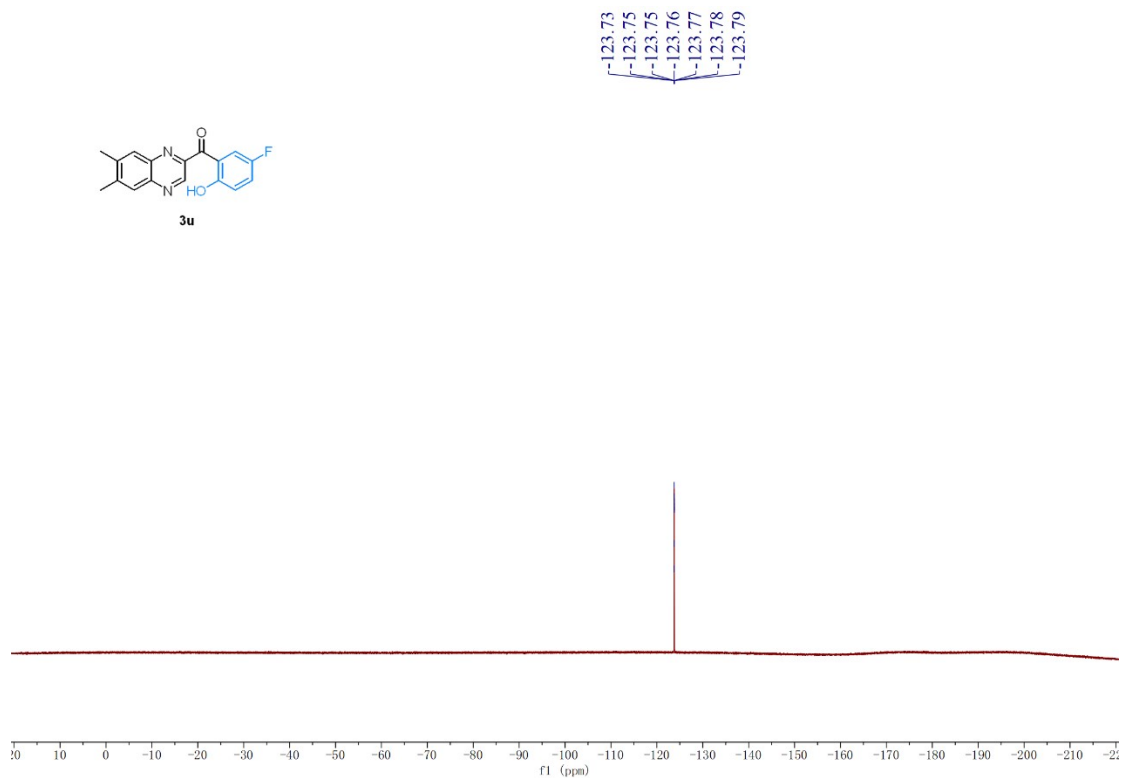
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of Compound **3t** (100 MHz, CDCl_3)



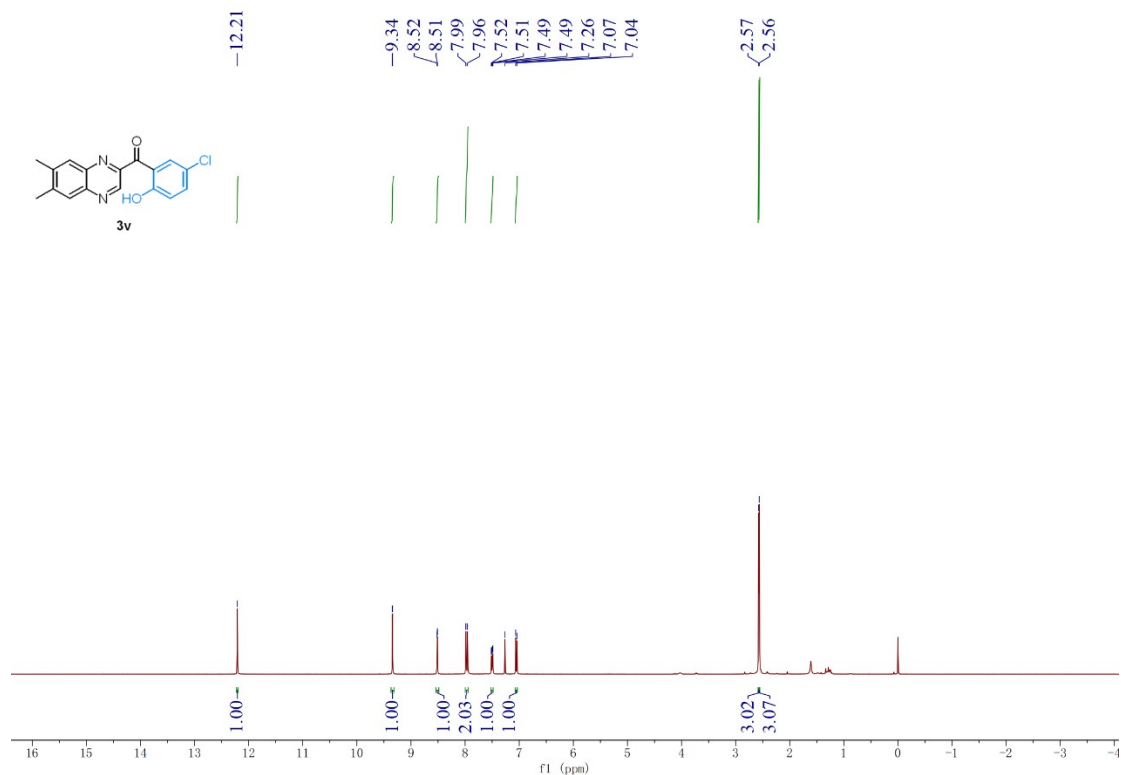
^1H NMR Spectrum of Compound **3u** (400 MHz, CDCl_3)



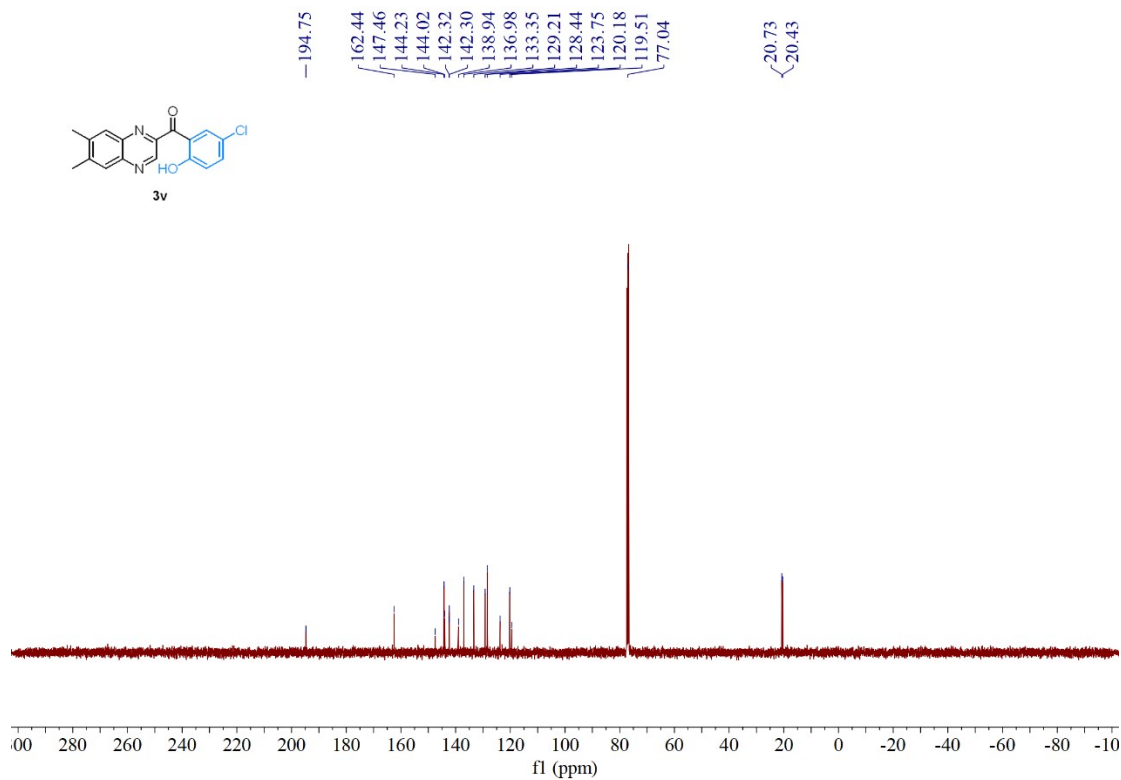
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of Compound **3u** (100 MHz, CDCl_3)



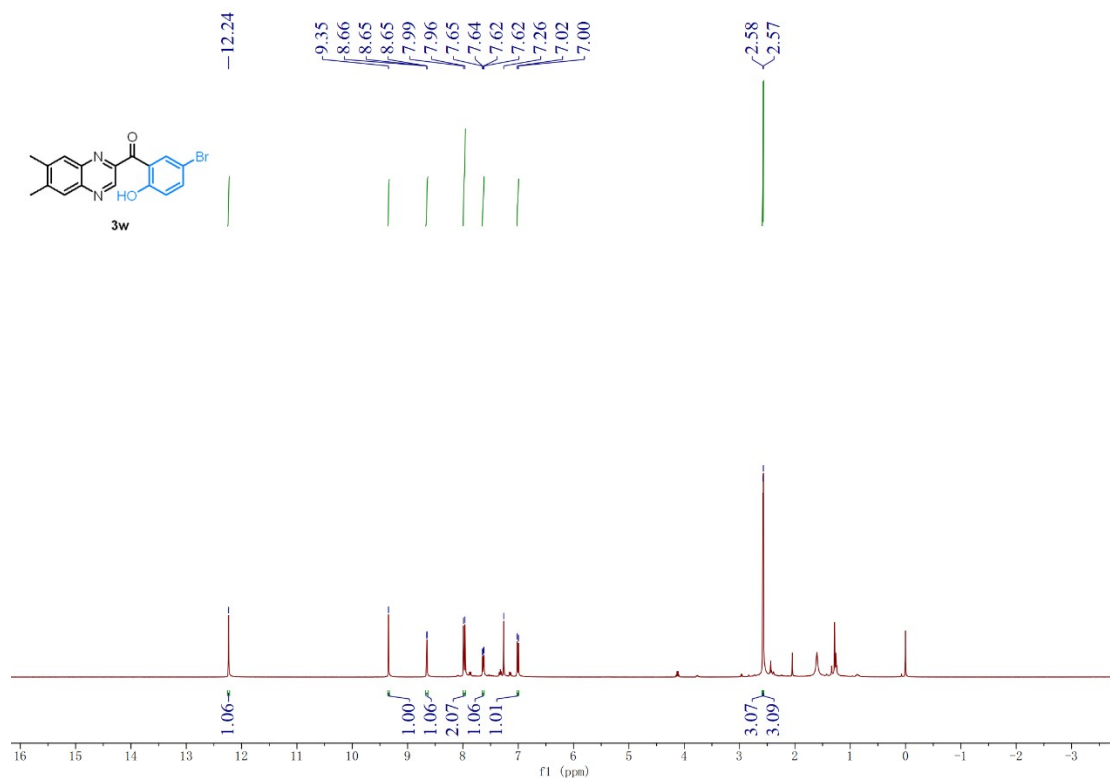
$^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum of Compound **3u** (376 MHz, CDCl_3)



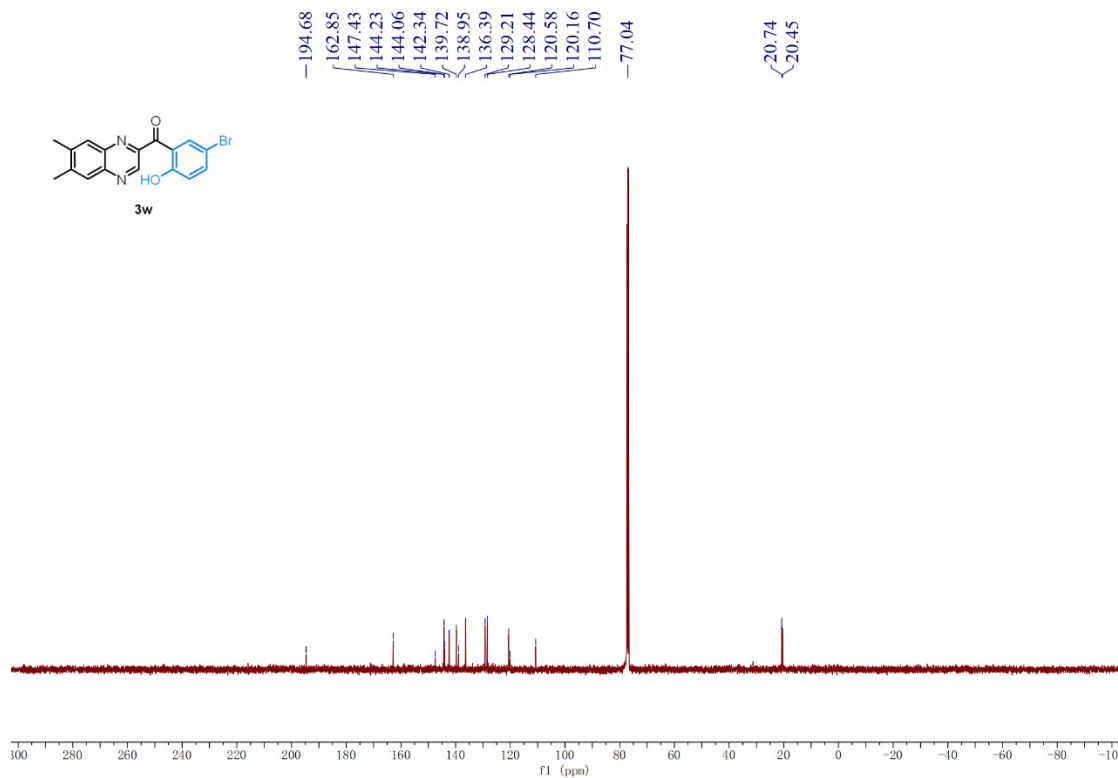
¹H NMR Spectrum of Compound 3v (400 MHz, CDCl₃)



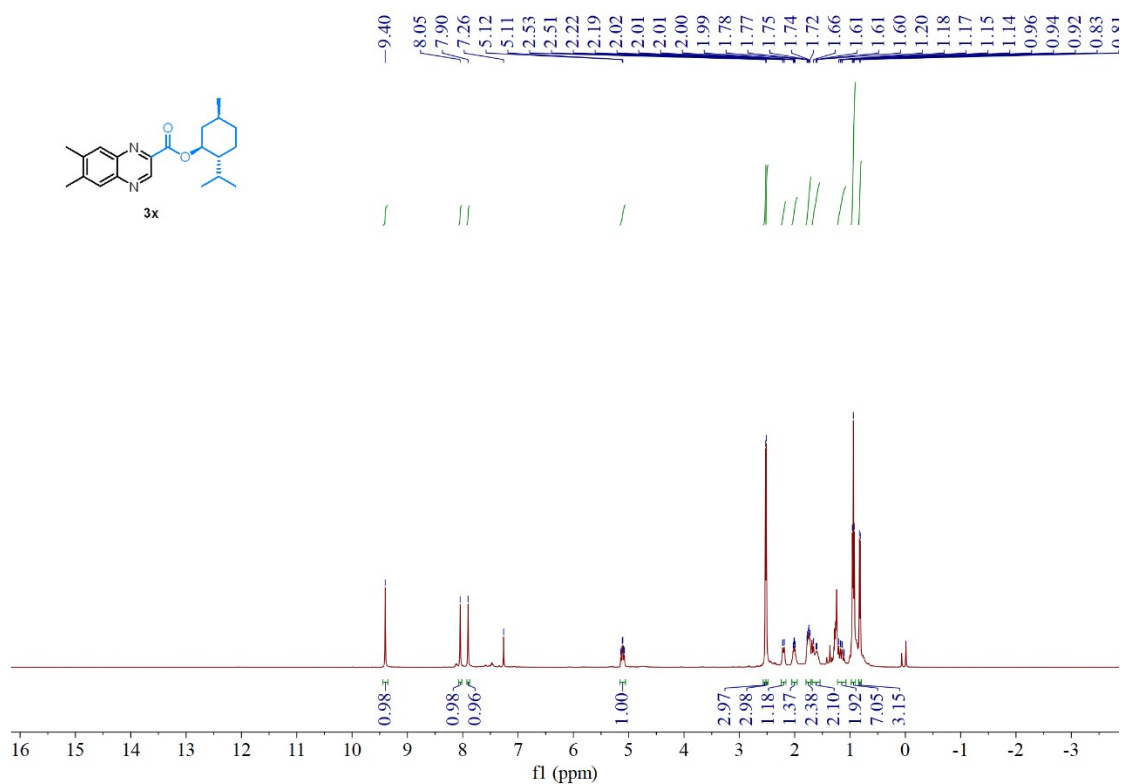
¹³C{¹H} NMR Spectrum of Compound 3v (100 MHz, CDCl₃)



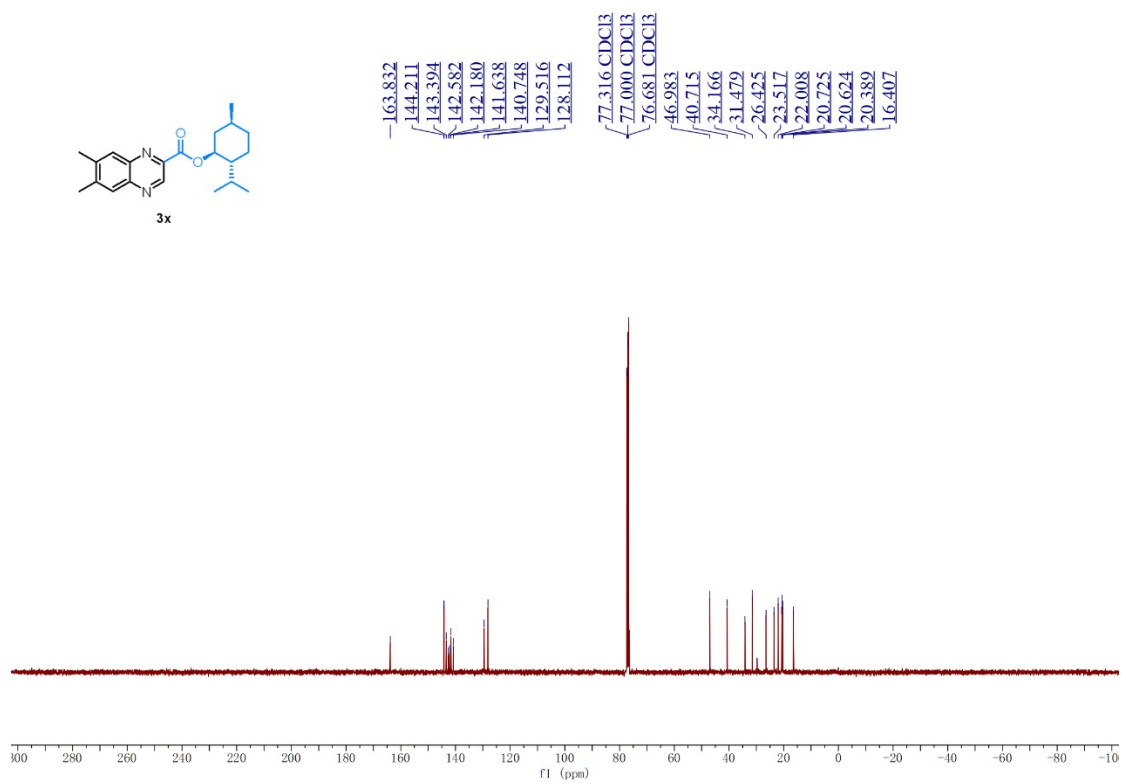
¹H NMR Spectrum of Compound 3w (400 MHz, CDCl₃)



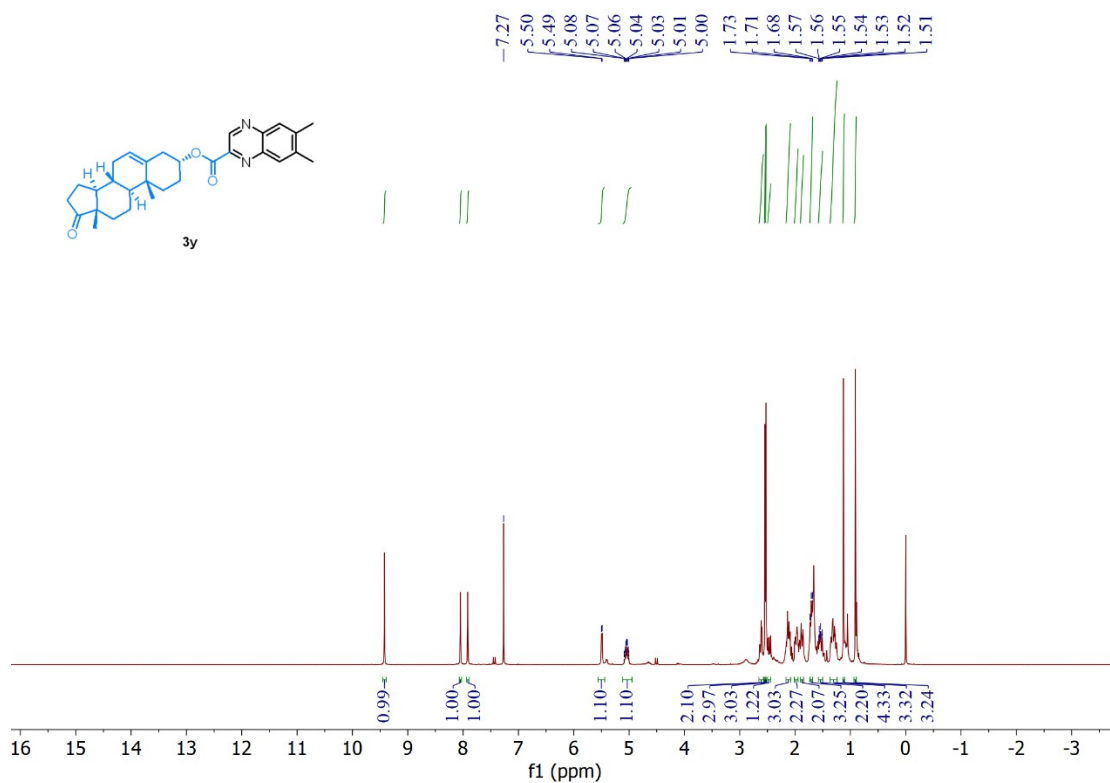
¹³C{¹H} NMR Spectrum of Compound 3w (100 MHz, CDCl₃)



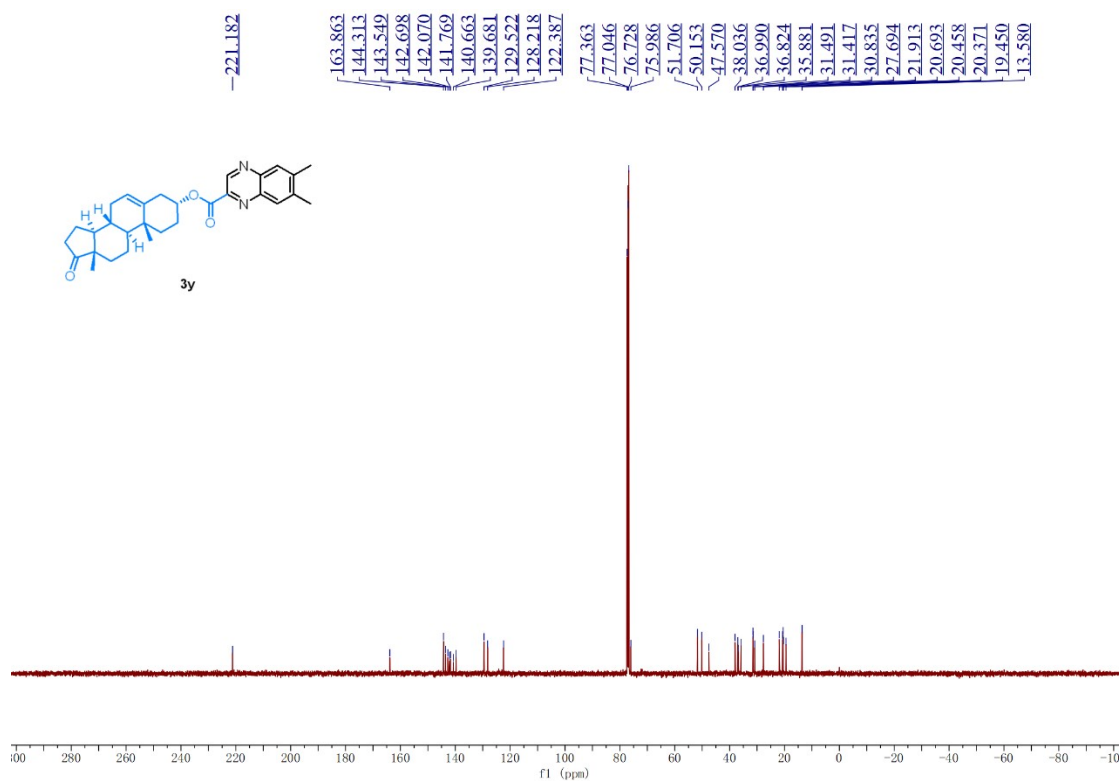
^1H NMR Spectrum of Compound **3x** (400 MHz, CDCl_3)



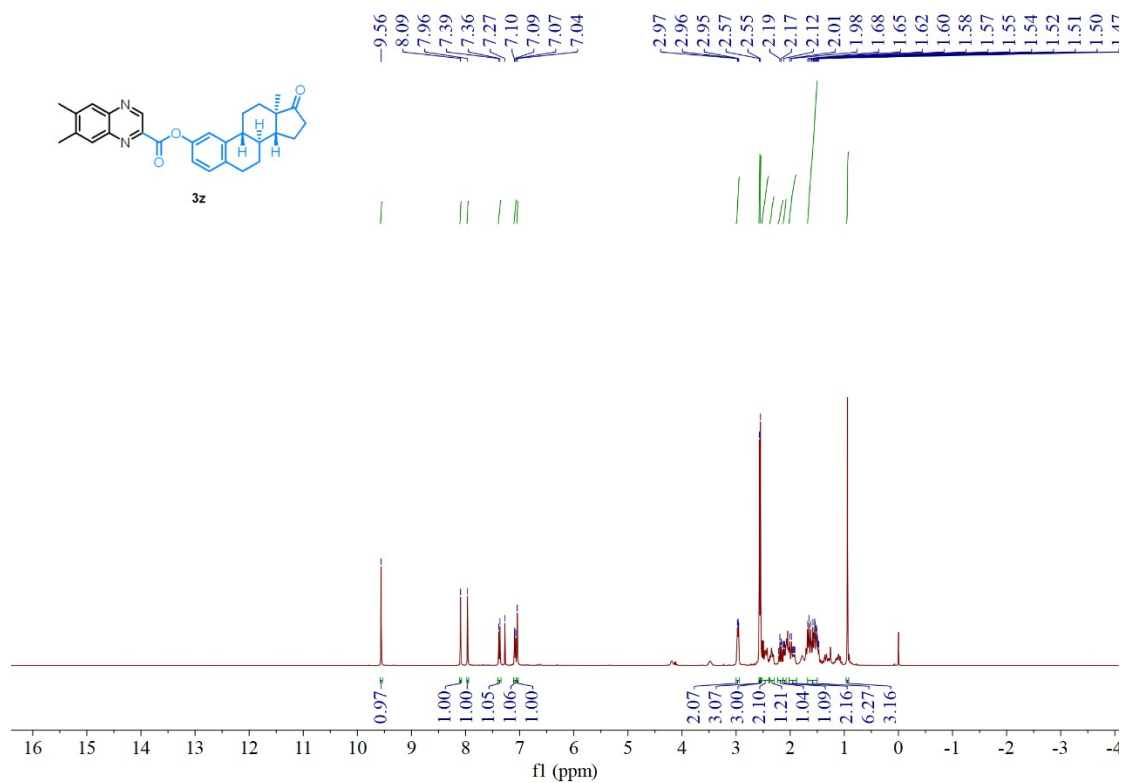
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of Compound **3x** (100 MHz, CDCl_3)



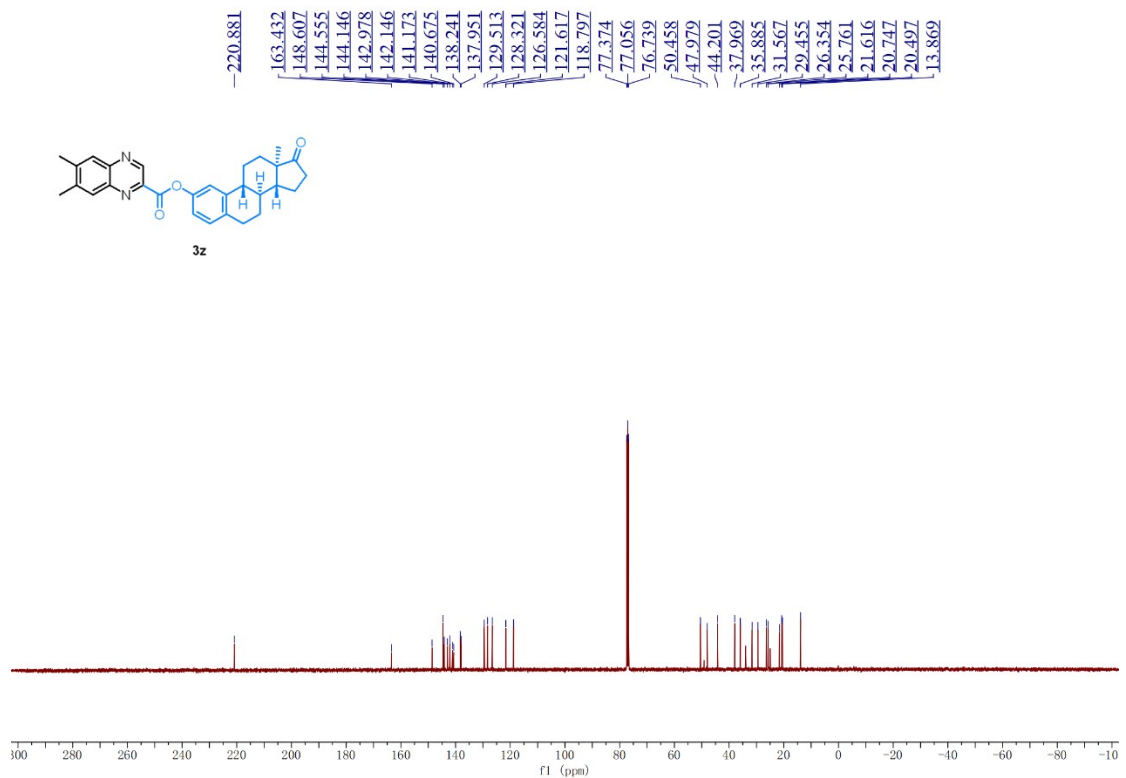
¹H NMR Spectrum of Compound 3y (400 MHz, CDCl₃)



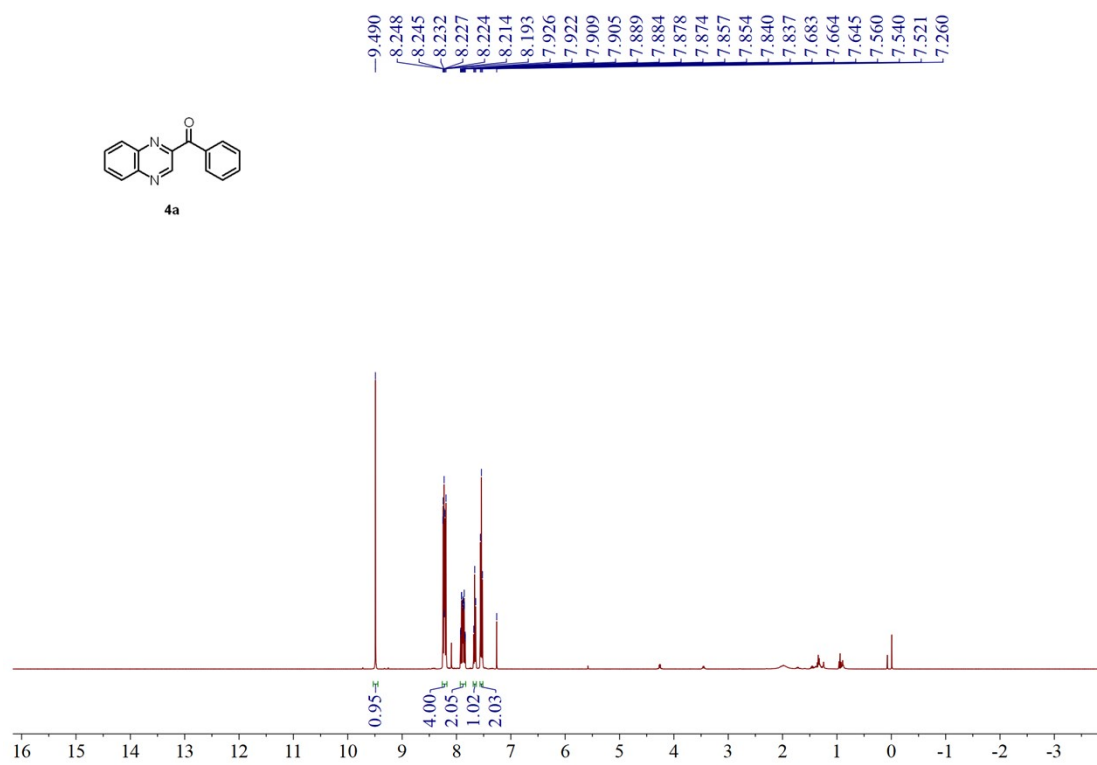
¹³C {¹H} NMR Spectrum of Compound 3y (100 MHz, CDCl₃)



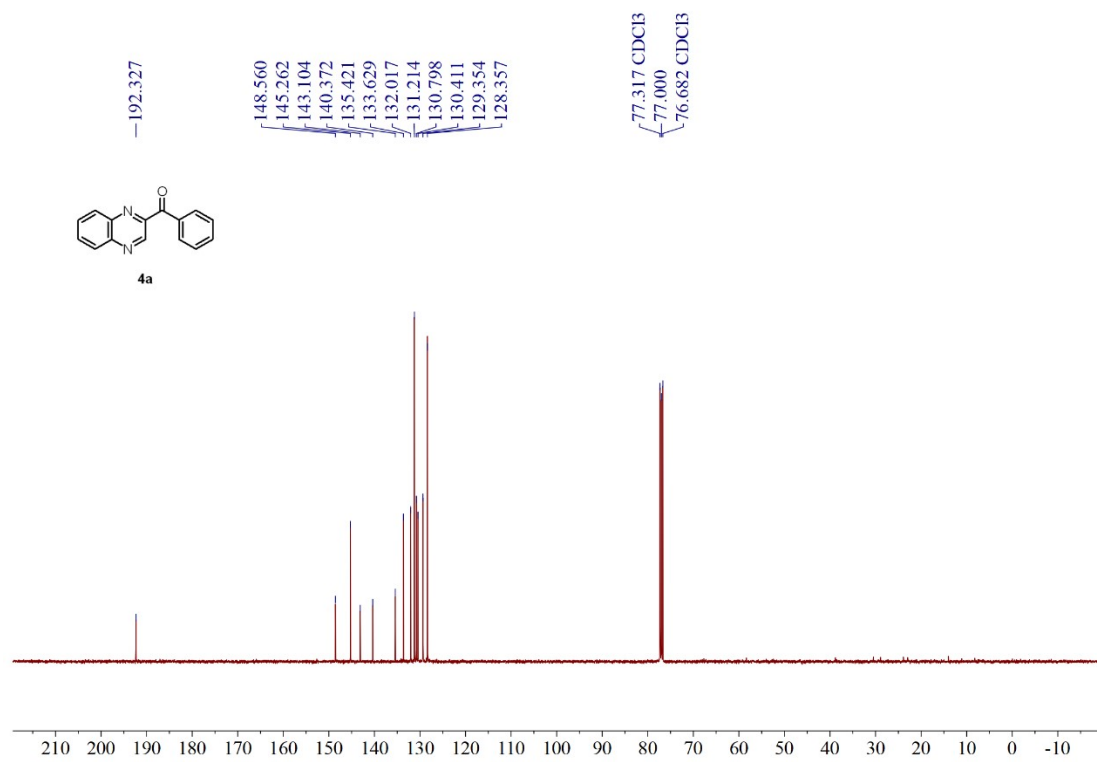
¹H NMR Spectrum of Compound 3z (400 MHz, CDCl₃)



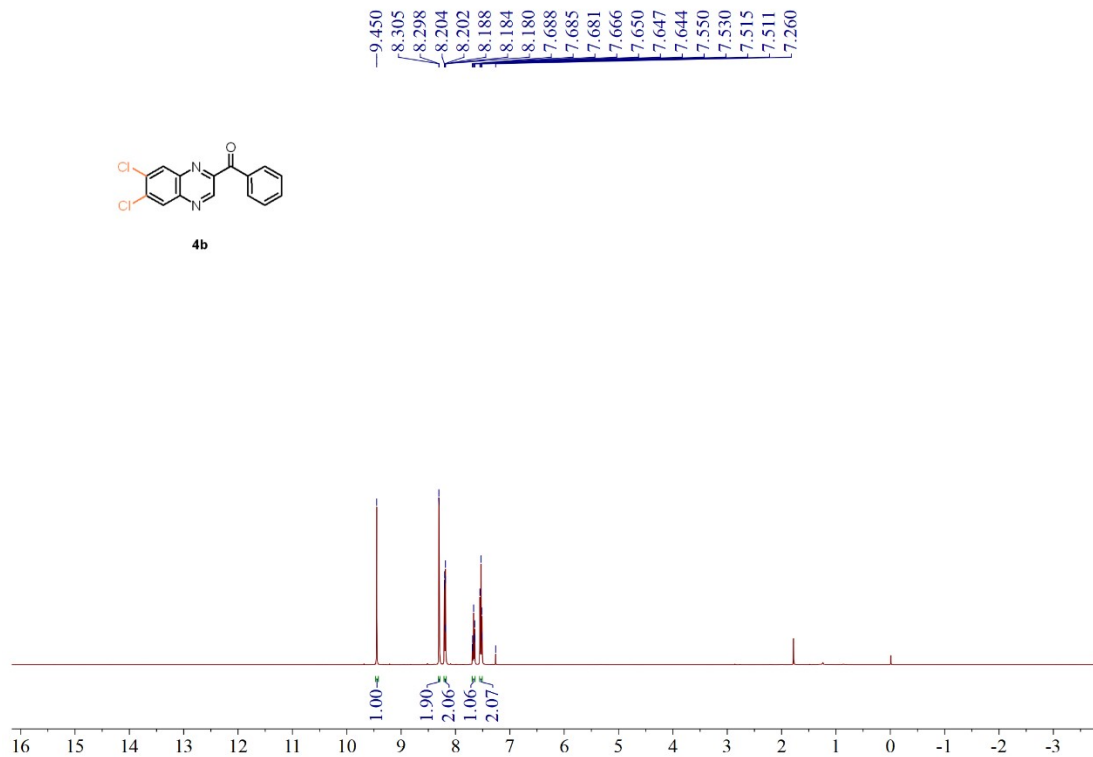
¹³C {¹H} NMR Spectrum of Compound 3z (100 MHz, CDCl₃)



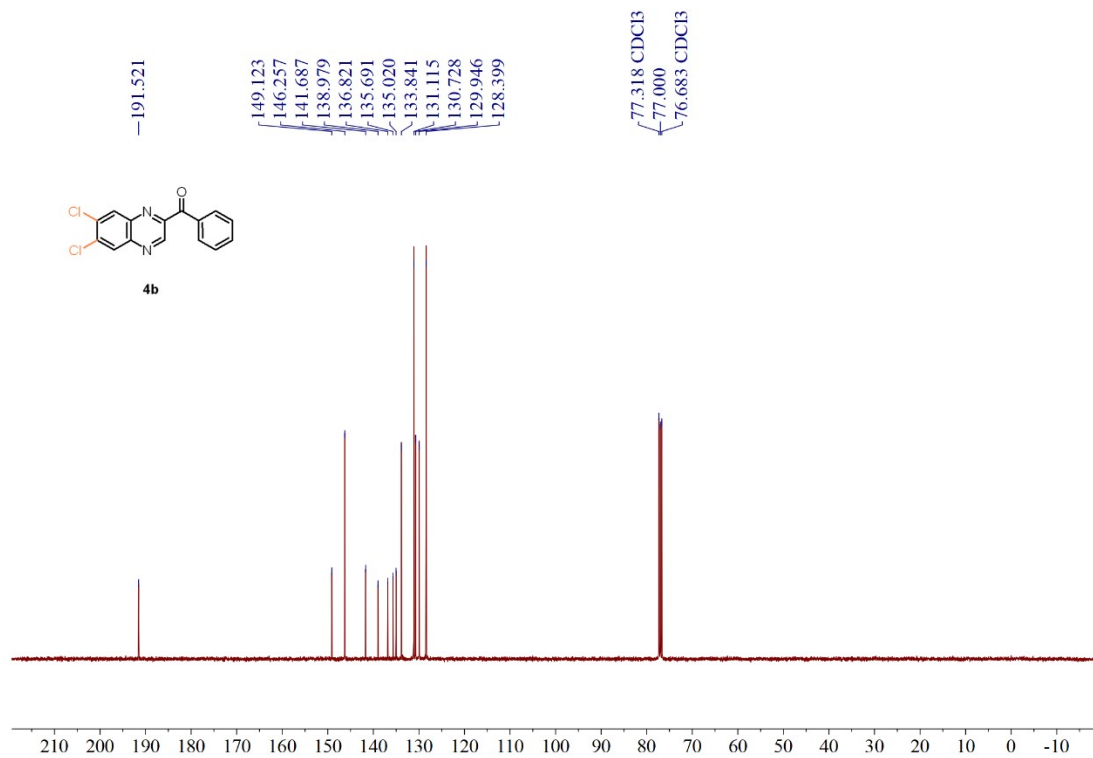
¹H NMR Spectrum of Compound **4a** (400 MHz, CDCl₃)



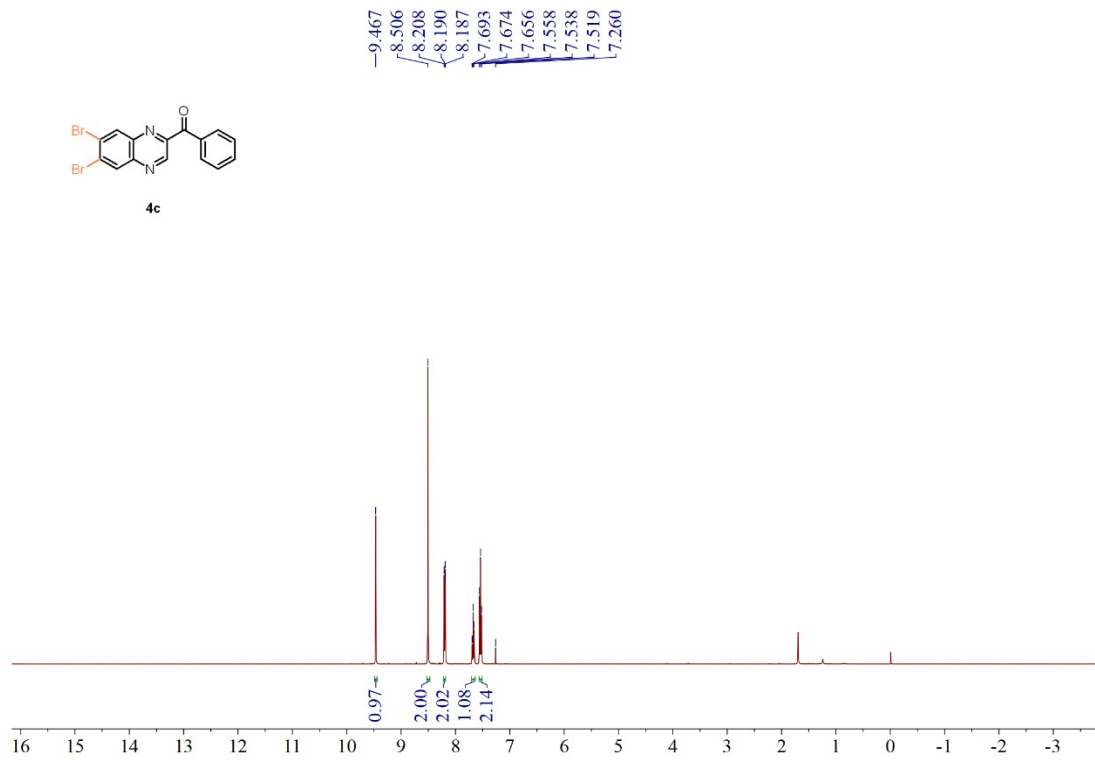
¹³C {¹H} NMR Spectrum of Compound **4a** (100 MHz, CDCl₃)



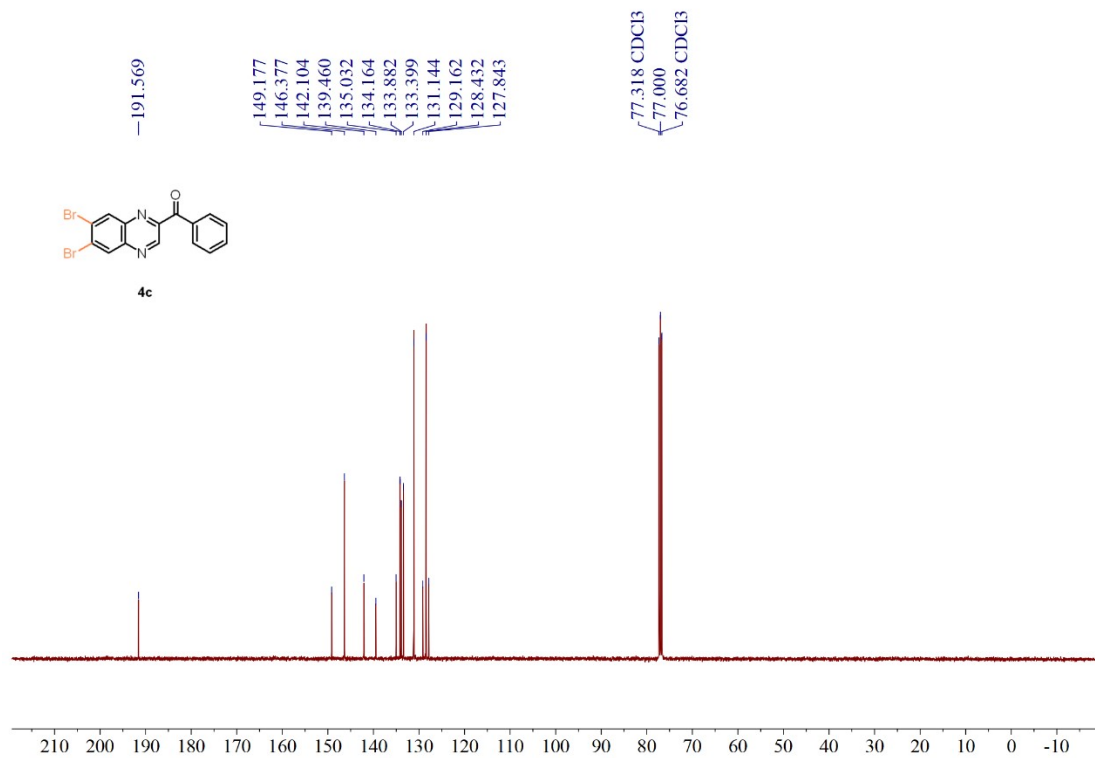
^1H NMR Spectrum of Compound **4b** (400 MHz, CDCl_3)



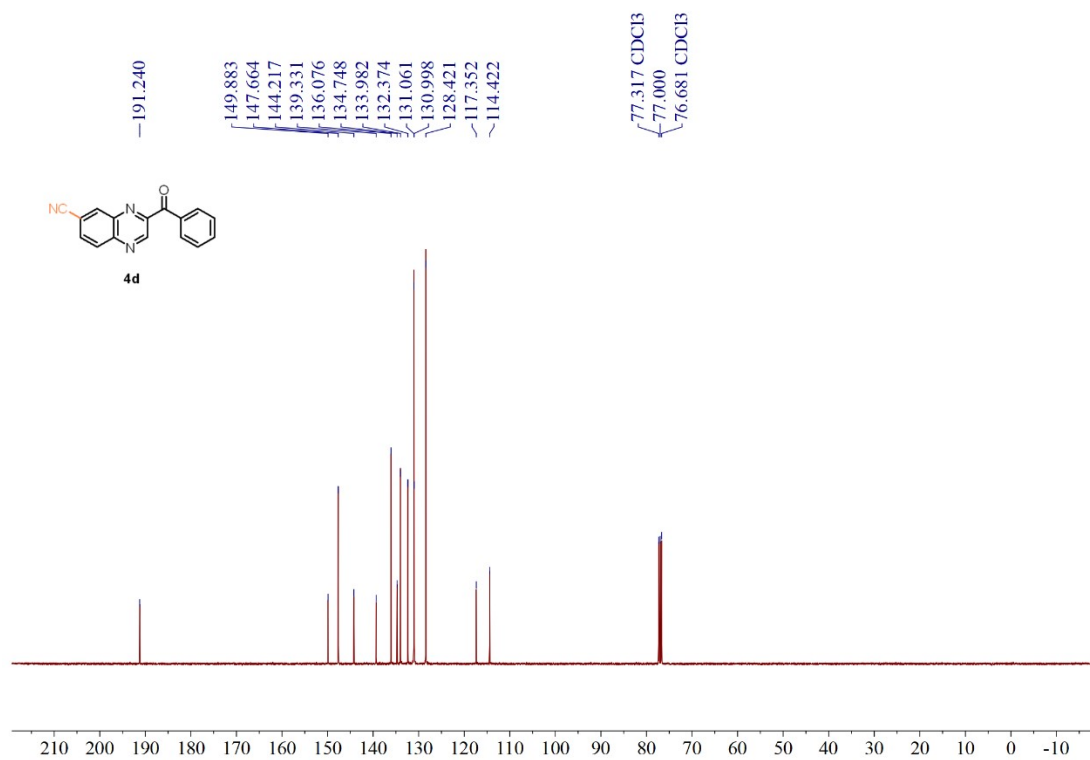
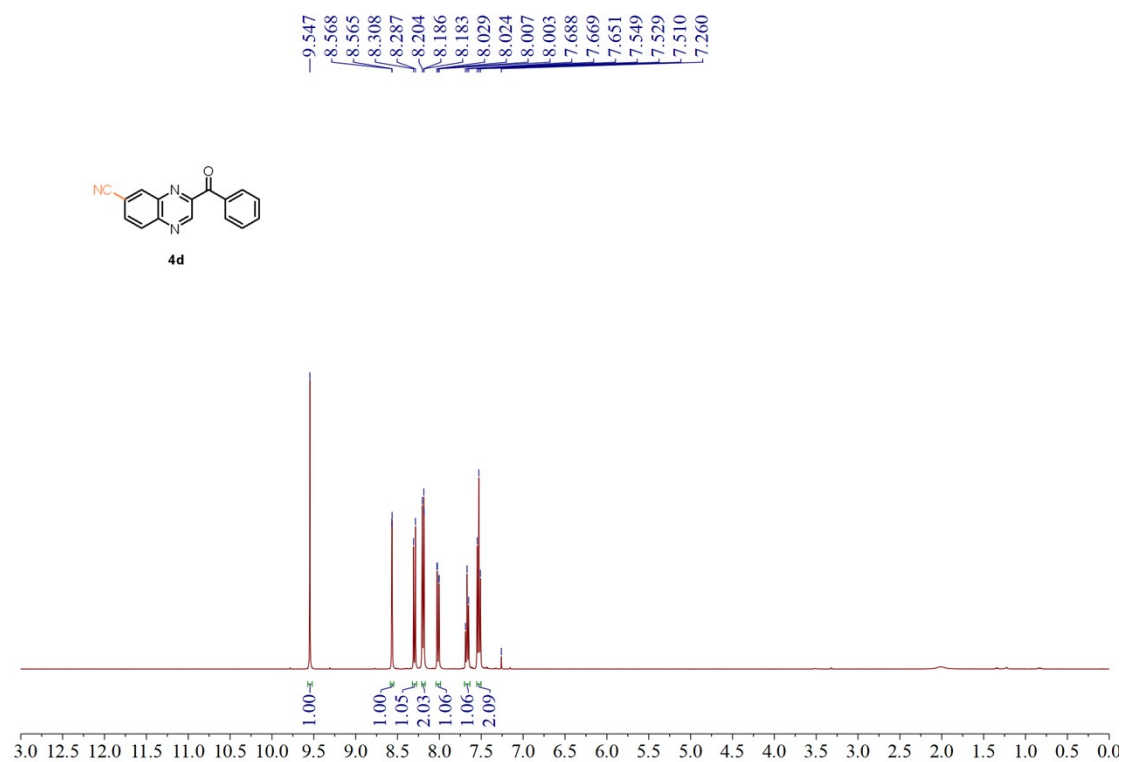
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of Compound **4b** (100 MHz, CDCl_3)

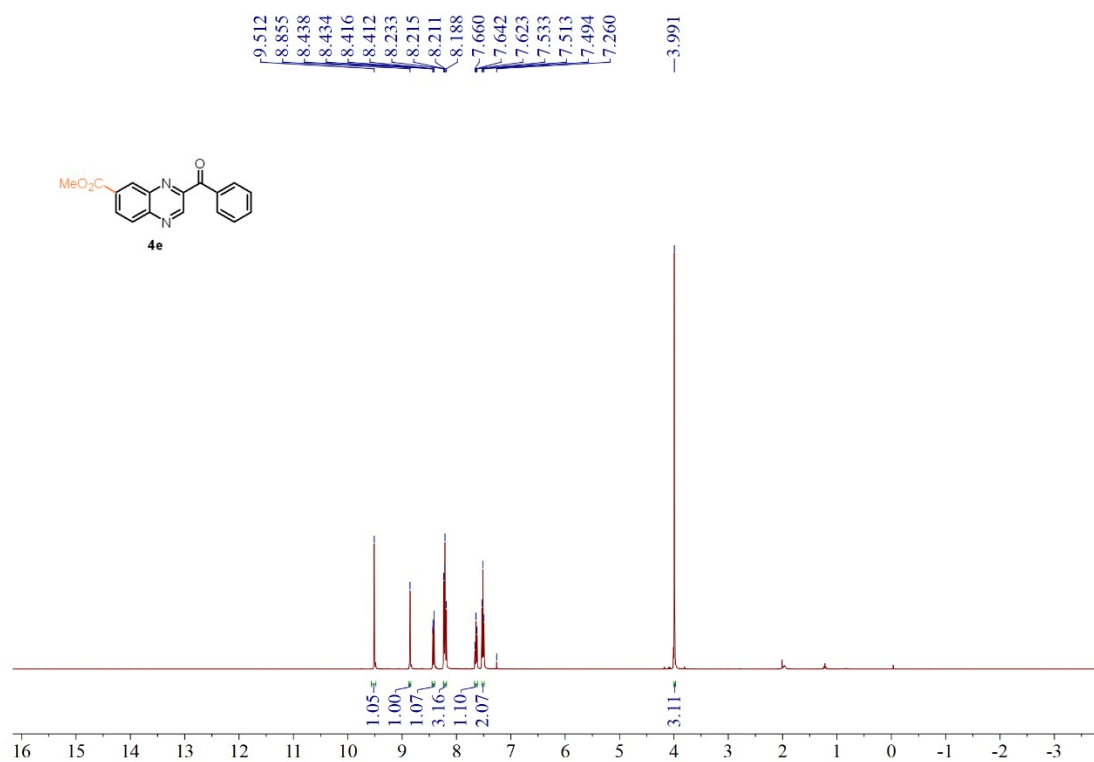


^1H NMR Spectrum of Compound **4c** (400 MHz, CDCl_3)

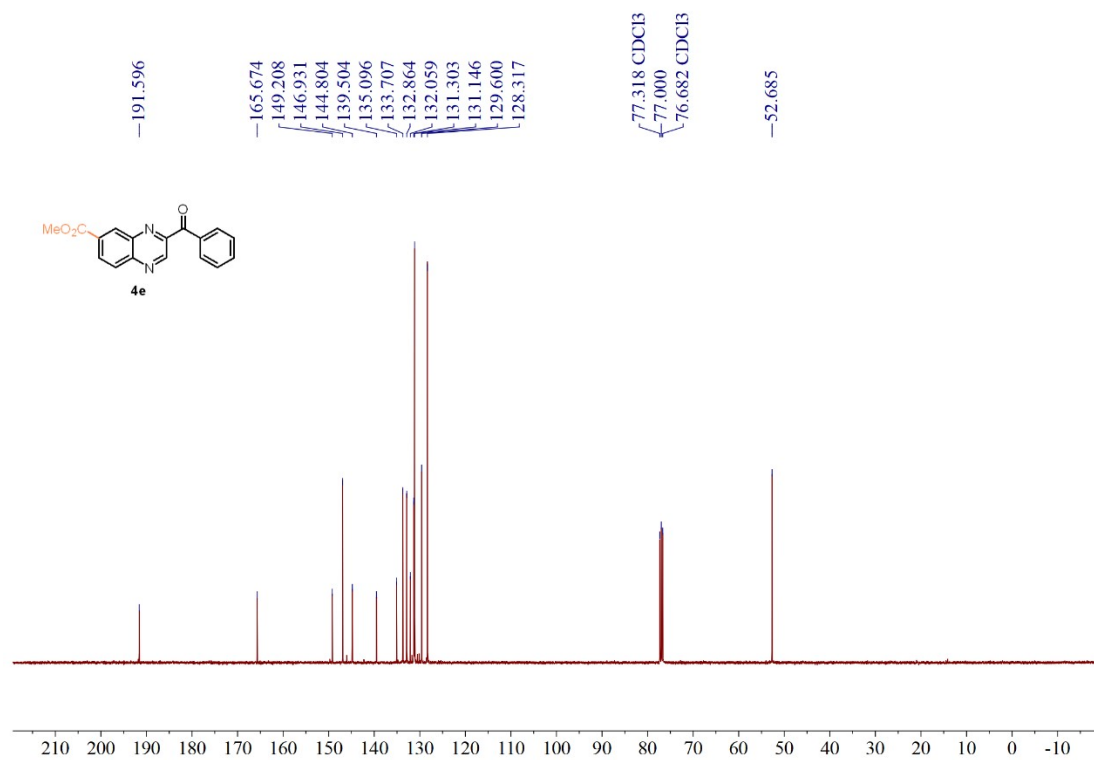


$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of Compound **4c** (100 MHz, CDCl_3)

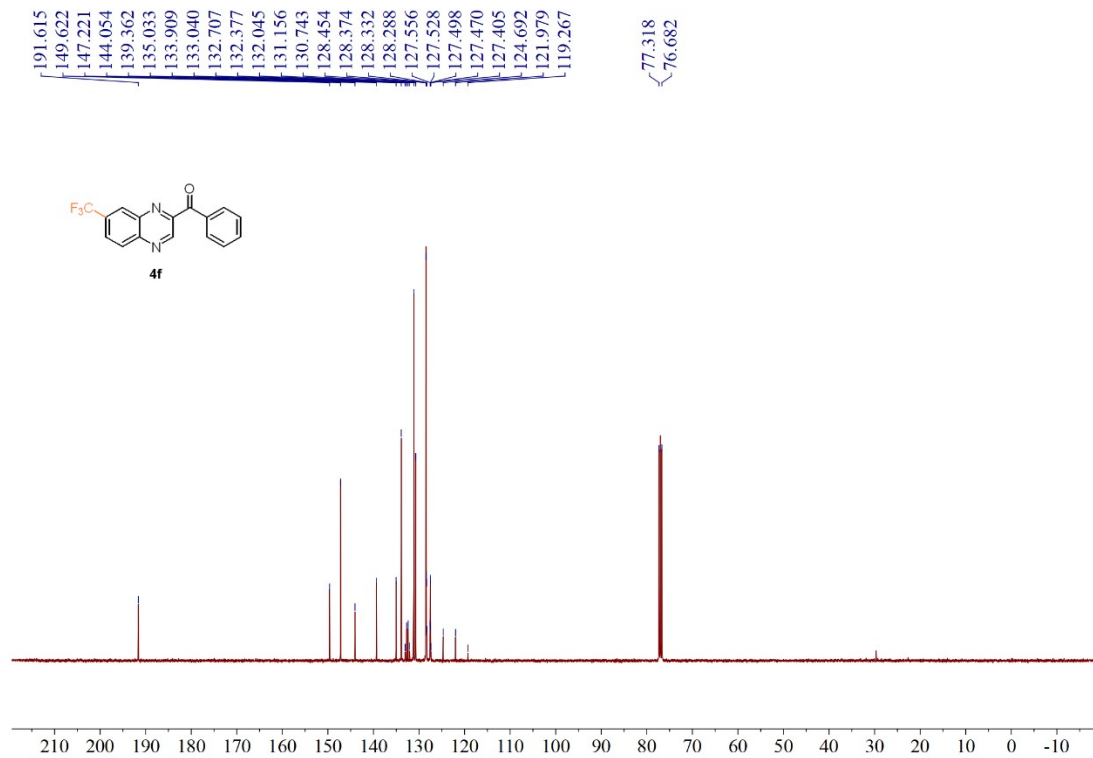
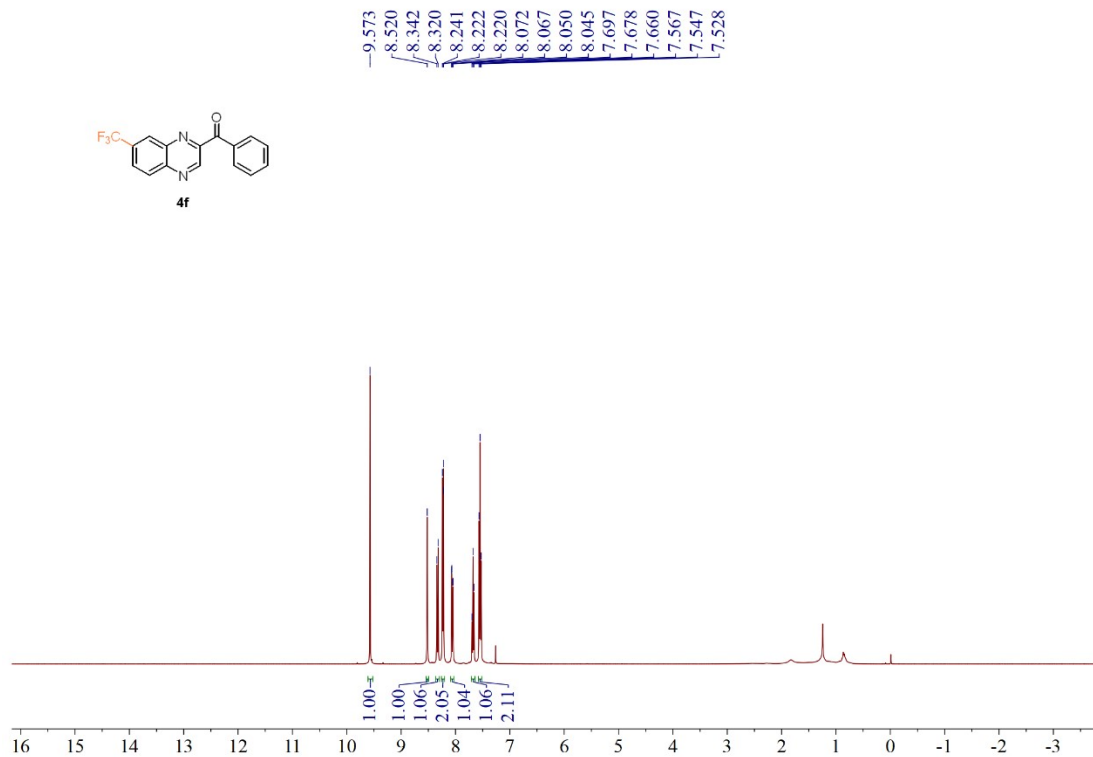


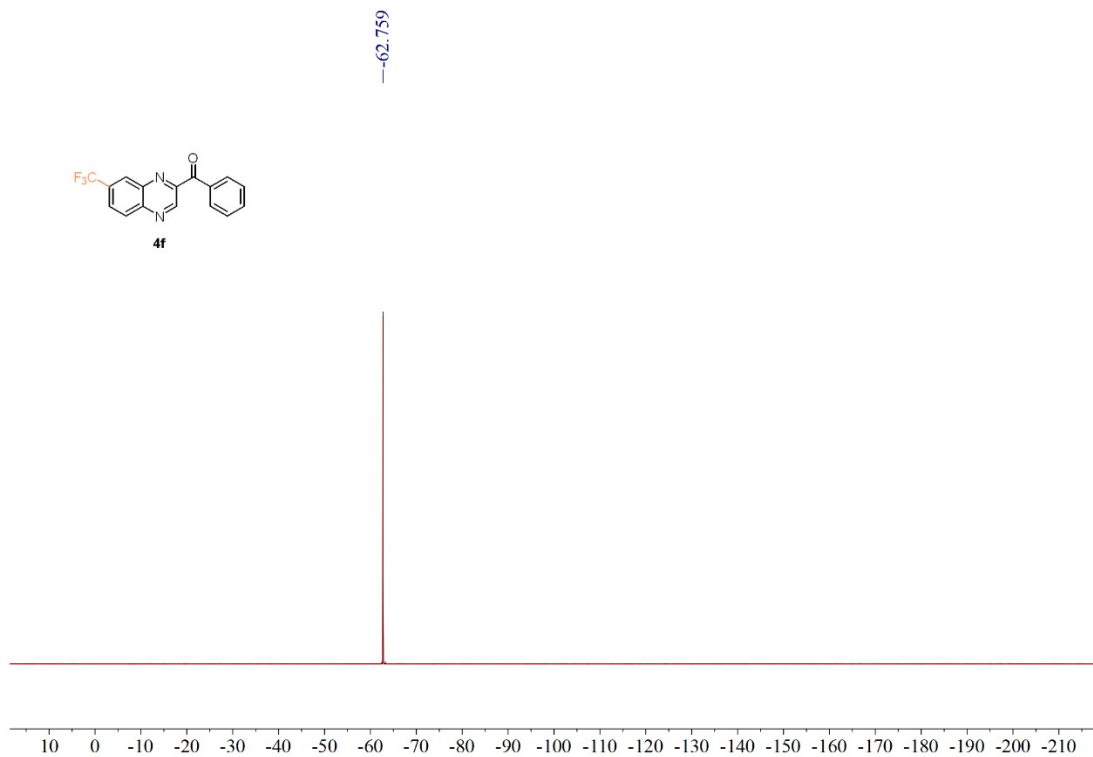


¹H NMR Spectrum of Compound 4e (400 MHz, CDCl₃)

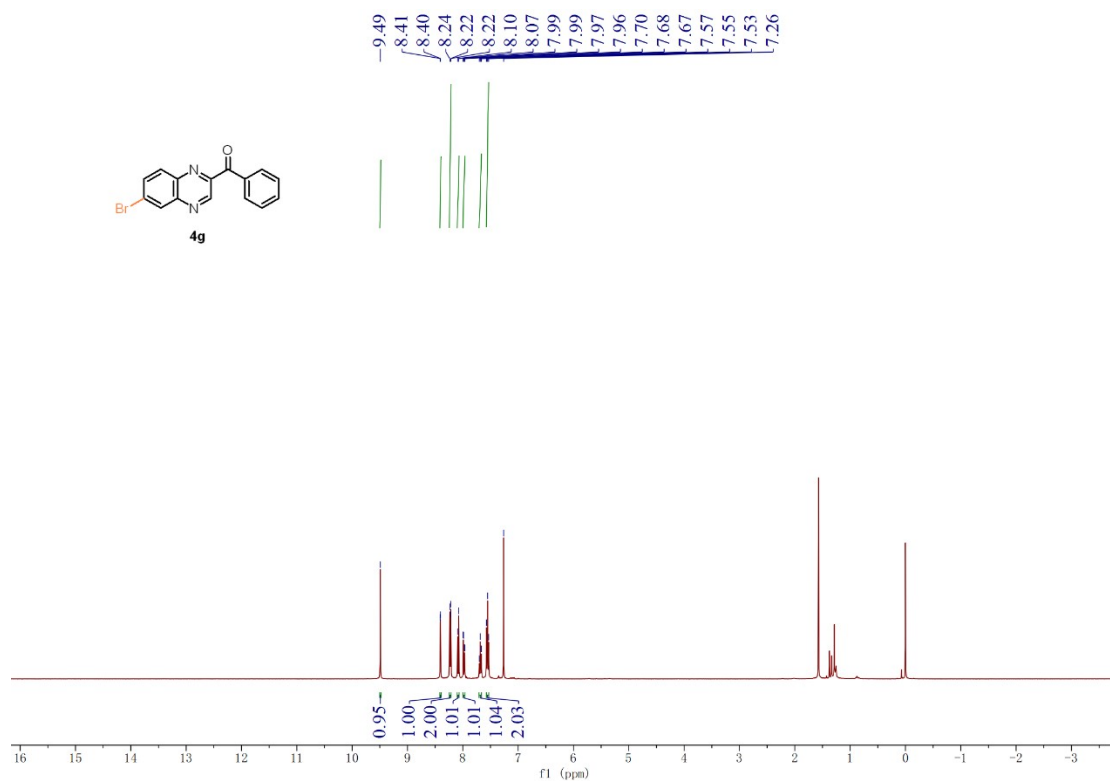


¹³C {¹H} NMR Spectrum of Compound 4e (100 MHz, CDCl₃)

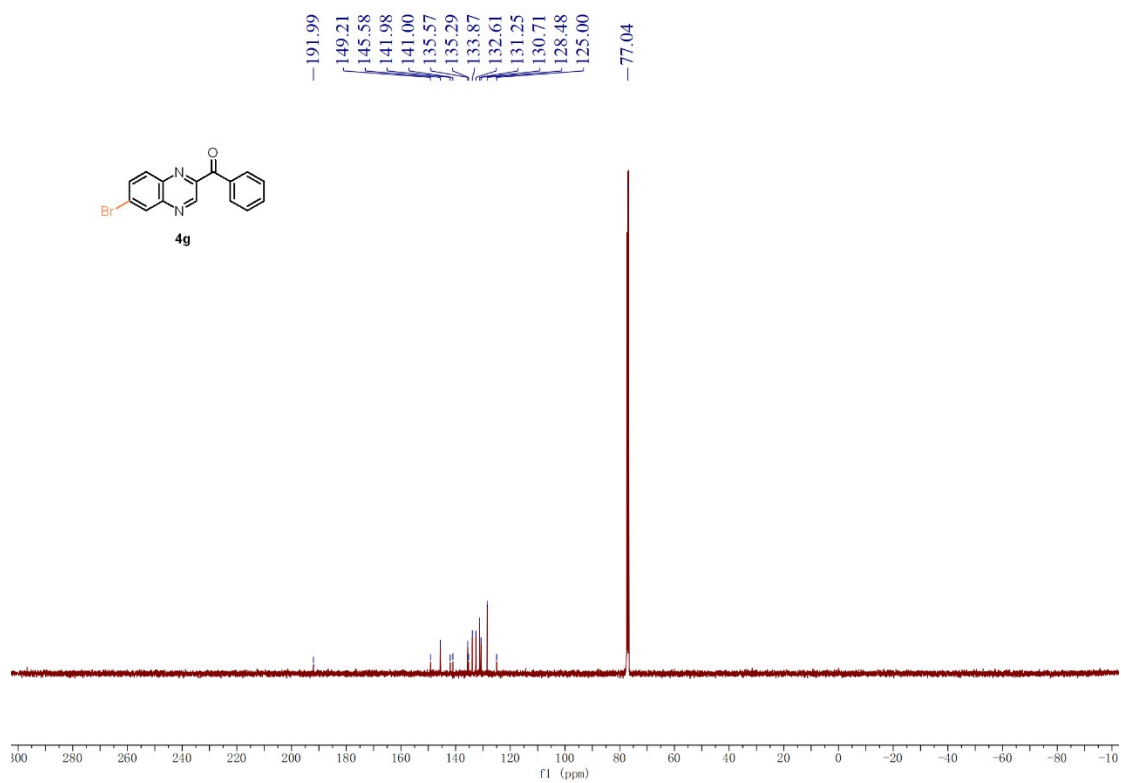




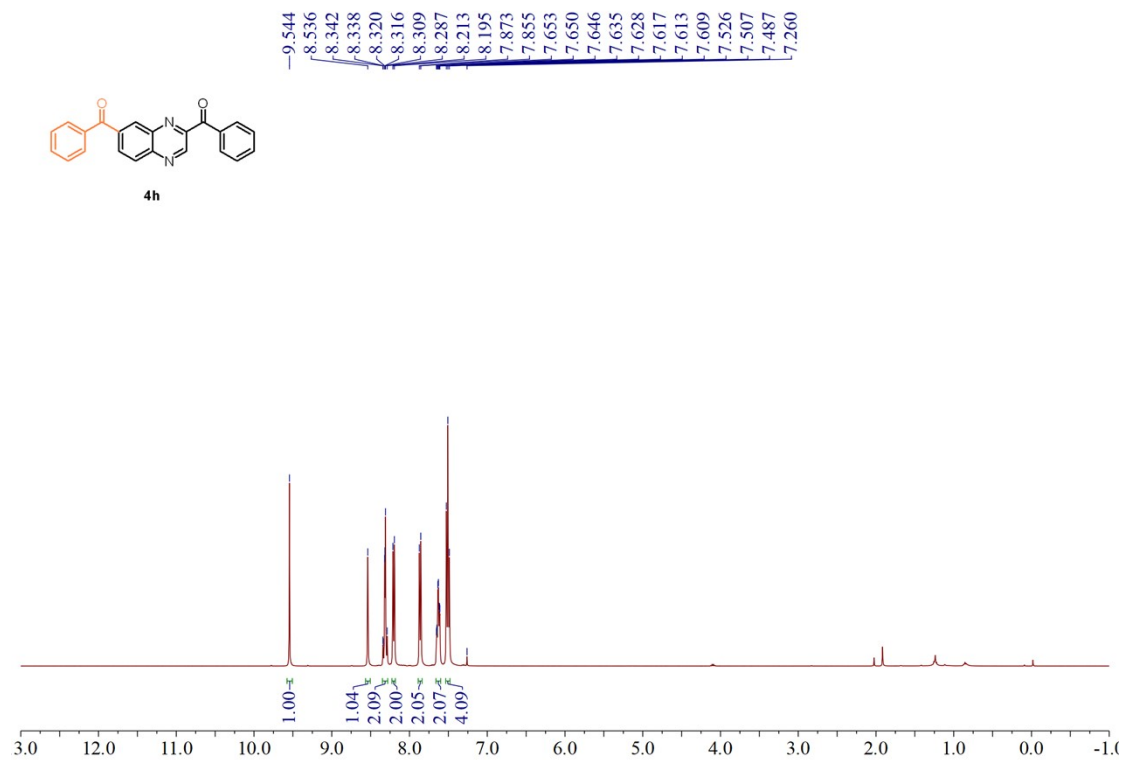
$^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum of Compound **4f** (376 MHz, CDCl_3)



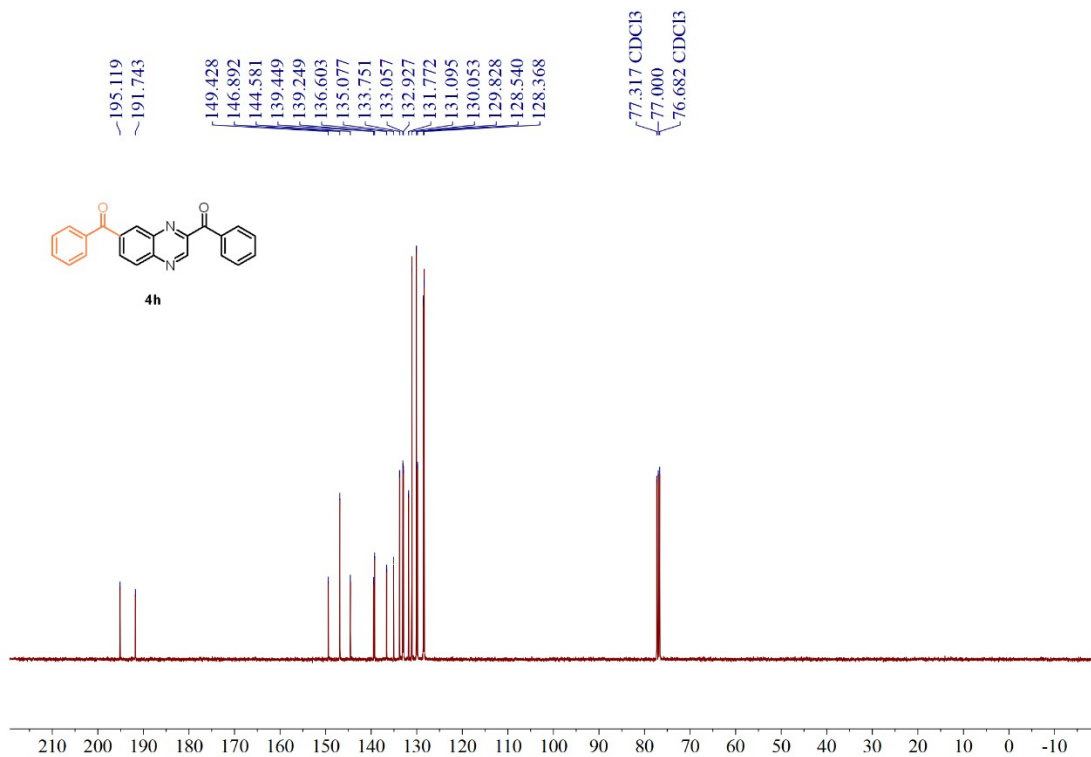
^1H NMR Spectrum of Compound **4g** (400 MHz, CDCl_3)



$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of Compound **4g** (100 MHz, CDCl_3)



^1H NMR Spectrum of Compound **4h** (400 MHz, CDCl_3)



$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of Compound **4h** (100 MHz, CDCl_3)