Supporting Information

Synthesis of the Methylene-Bridged α,β-Unsaturated Ketones: α-C_{sp3}-H Methylenation of Aromatic Ketones Using Selectfluor as a Mild Oxidant

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1. General Information

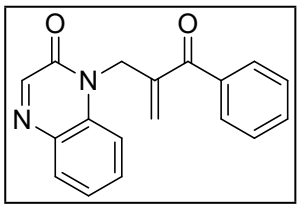
Chemicals. Unless otherwise stated, the reaction was carried out in a Teflon screw-cap sealed tube (50 ml) under Air atmosphere. All commercial-grade chemicals were used without further purification. Dioxane was distilled over sodium under N_2. Volume reduction and drying steps were performed *in vacuo*.

General Physical Measurements. Chromatography was performed on silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance III (400 MHz) and chemical shifts were expressed in δ ppm values with reference to tetramethylsilane (TMS) as internal standard. HR-MS (ESI) spectra were obtained using a Bruker Impact II quardrupole time off light mass spectrometer. The single crystal diffraction data were collected on an Oxford Diffraction Supernova dual diffractometer equipped with an Oxford Cryostream 700 low-temperature apparatus.

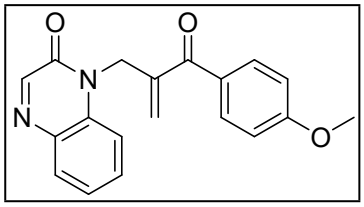
2. General Experimental Procedures

Synthesis of compounds 4 : 2-Hydroxy-quinoxaline **1** (0.20 mmol), acetophenone **2** (0.10 mmol), *tetra*-methylethylenediamine (TMEDA, 0.50 mmol) , Selectfluor (0.50 mmol) and dioxane (1 mL) were mixed in a 50 mL Teflon screw-cap sealed tube. The mixture was vigorously stirred at 120 ^{o}C under air atmosphere for 24 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (20 mL), filtered through a pad of silica gel and concentrated under reduced pressure. The crude product was purified on a silica gel column eluted with petroleum ether/ethyl acetate (3:1 to 2:1 v/v) to afford the products **4**.

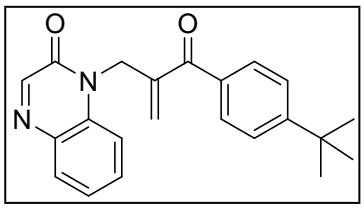
3. Characterization Data for the Products



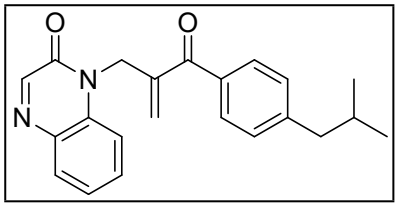
1-(2-Benzoylallyl)quinoxalin-2(1H)-one (4a): yield, 73% (21.1 mg); yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.91 (d, J = 7.9 Hz, 1H), 7.80 (d, J = 8.0 Hz, 2H), 7.58 (dd, J = 13.6, 6.8 Hz, 2H), 7.47 (t, J = 7.7 Hz, 2H), 7.36 (dd, J = 14.1, 8.1 Hz, 2H), 5.80 (s, 1H), 5.57 (s, 1H), 5.31 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4 (s), 155.0 (s), 150.1 (s), 140.3 (s), 136.8 (s), 133.6 (s), 133.0 (s), 132.1 (s), 131.4 (s), 130.7 (s), 129.7 (s), 128.5 (s), 127.0 (s), 124.1 (s), 114.4 (s), 42.5 (s). HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{18}H_{14}N_2NaO_2$, 313.0953; found, 313.0948.



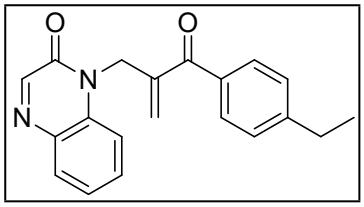
1-(2-(4-Methoxybenzoyl)allyl)quinoxalin-2(1H)-one (4b): yield, 61% (19.5 mg); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.9 Hz, 2H), 7.56 (t, J = 8.6 Hz, 1H), 7.41 – 7.33 (m, 2H), 6.93 (d, J = 8.9 Hz, 2H), 5.70 (s, 1H), 5.45 (s, 1H), 5.28 (s, 2H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.9 (s), 163.7 (s), 155.0 (s), 150.0 (s), 140.4 (s), 133.6 (s), 132.2 (s), 132.1 (s), 131.4 (s), 130.6 (s), 129.2 (s), 124.7 (s), 124.1 (s), 114.6 (s), 113.8 (s), 55.6 (s), 42.9 (s). HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{19}H_{16}N_2NaO_3$, 343.1059; found, 343.1054.



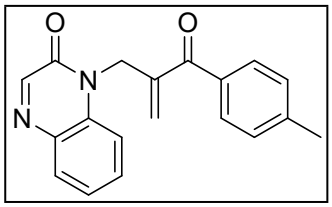
1-(2-(4-(Tert-butyl)benzoyl)allyl)quinoxalin-2(1H)-one (4c): yield, 60% (20.7 mg); yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 8.6 Hz, 2H), 7.57 (t, J = 7.9 Hz, 1H), 7.48 (d, J = 8.6 Hz, 2H), 7.40 – 7.34 (m, 2H), 5.80 (s, 1H), 5.54 (s, 1H), 5.31 (s, 2H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9 (s), 155.1 (s), 150.1 (s), 140.3 (s), 131.4 (s), 130.6 (s), 129.8 (s), 125.5 (s), 124.1 (s), 114.5 (s), 42.7 (s), 35.2 (s), 31.1 (s). HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{22}H_{22}N_2NaO_2$, 369.1579; found, 369.1574.



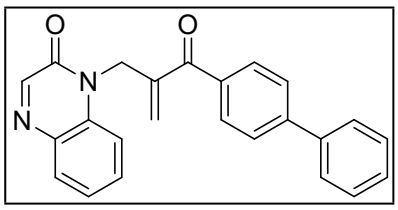
1-(2-(4-Isobutylbenzoyl)allyl)quinoxalin-2(1H)-one (4d): yield, 65% (22.5 mg); yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 8.2 Hz, 2H), 7.56 (t, J = 7.9 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.23 (d, J = 8.2 Hz, 2H), 5.78 (s, 1H), 5.52 (s, 1H), 5.30 (s, 2H), 2.53 (d, J = 7.2 Hz, 2H), 1.98 – 1.81 (m, 1H), 0.91 (d, J = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1 (s), 155.0 (s), 150.1 (s), 147.7 (s), 140.3 (s), 134.3 (s), 133.6 (s), 132.1 (s), 131.4 (s), 130.6 (s), 129.8 (s), 129.3 (s), 126.1 (s), 124.1 (s), 114.5 (s), 45.4 (s), 42.7 (s), 30.1 (s), 22.4 (s). HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{22}H_{22}N_2NaO_2$, 369.1579; found, 369.1574.



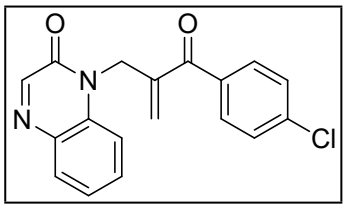
1-(2-(4-ethylbenzoyl)allyl)quinoxalin-2(1H)-one (4e): yield, 75% (23.9 mg); yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.60 (t, *J* = 7.9 Hz, 1H), 7.40 (dd, *J* = 8.1, 5.6 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 5.81 (s, 1H), 5.55 (s, 1H), 5.33 (s, 2H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.9 (s), 155.1 (s), 150.1 (s), 150.1 (s), 140.4 (s), 134.3 (s), 133.6 (s), 132.1 (s), 131.4 (s), 130.6 (s), 130.0 (s), 128.0 (s), 126.1 (s), 124.1 (s), 114.5 (s), 42.7 (s), 29.0 (s), 15.2 (s). HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{20}H_{18}N_2NaO_2$, 341.1266; found, 341.1262.



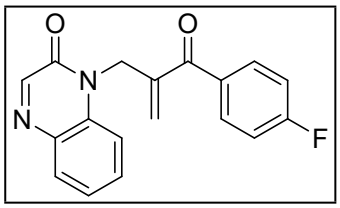
1-(2-(4-Methylbenzoyl)allyl)quinoxalin-2(1H)-one (4f): yield, 80% (24.7 mg); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.91 (d, J = 6.8 Hz, 1H), 7.73 (d, J = 8.2 Hz, 2H), 7.56 (t, J = 7.9 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.26 (d, J = 7.9 Hz, 2H), 5.76 (s, 1H), 5.51 (s, 1H), 5.30 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.0 (s), 155.0 (s), 150.1 (s), 144.0 (s), 140.3 (s), 134.1 (s), 133.6 (s), 132.1 (s), 131.4 (s), 130.6 (s), 129.9 (s), 129.2 (s), 126.1 (s), 124.1 (s), 114.5 (s), 42.7 (s), 21.7 (s). HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{19}H_{16}N_2NaO_2$, 327.1110; found, 327.1105.



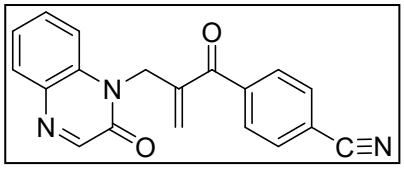
1-(2-([1,1'-Biphenyl]-4-carbonyl)allyl)quinoxalin-2(1H)-one (4g): yield, 74% (27.1 mg); pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.95 – 7.88 (m, 3H), 7.69 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 7.1 Hz, 2H), 7.58 (t, J = 7.9 Hz, 1H), 7.48 (t, J = 7.4 Hz, 2H), 7.44 – 7.35 (m, 3H), 5.85 (s, 1H), 5.58 (s, 1H), 5.33 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.9 (s), 155.0 (s), 150.1 (s), 145.8 (s), 140.4 (s), 139.7 (s), 135.4 (s), 133.6 (s), 132.1 (s), 131.4 (s), 130.7 (s), 130.4 (s), 129.0 (s), 128.6 (s), 127.3 (s), 127.2 (s), 126.5 (s), 124.1 (s), 114.5 (s), 42.7 (s). HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{24}H_{18}N_2NaO_2$, 389.1266; found, 389.1261.



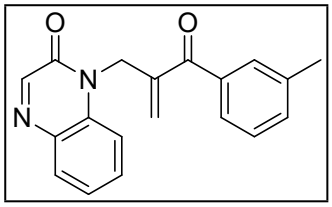
1-(2-(4-Chlorobenzoyl)allyl)quinoxalin-2(1H)-one (4h): yield, 65% (20.0 mg); yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.95 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.79 (d, *J* = 8.6 Hz, 2H), 7.60 (t, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 5.80 (s, 1H), 5.60 (s, 1H), 5.32 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.1 (s), 155.0 (s), 150.0 (s), 140.2 (s), 139.6 (s), 135.0 (s), 133.6 (s), 132.1 (s), 131.4 (s), 131.1 (s), 130.7 (s), 128.9 (s), 126.8 (s), 124.2 (s), 114.3 (s), 42.5 (s). HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{18}H_{13}ClN_2NaO_2$, 347.0563; found, 347.0558.



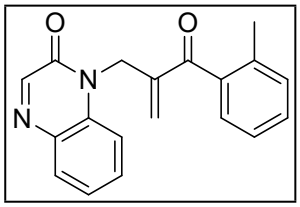
1-(2-(4-Fluorobenzoyl)allyl)quinoxalin-2(1H)-one (4i): yield, 55% (16.9 mg); pale yellow solid; ^{1}H NMR (400 MHz, DMSO) δ 8.32 (s, 1H), 7.92 – 7.79 (m, 3H), 7.66 (t, J = 7.2 Hz, 1H), 7.57 (d, J = 8.2 Hz, 1H), 7.46 – 7.31 (m, 3H), 5.66 (s, 1H), 5.54 (s, 1H), 5.20 (s, 2H). ^{13}C NMR (101 MHz, DMSO) δ 194.9 (s), 154.7 (s), 150.7 (s), 140.8 (s), 133.7 (d, *J* = 3.0 Hz), 133.4 (s), 132.8 (d, *J* = 9.4 Hz), 131.7 (s), 131.5 (d, *J* = 245.7 Hz), 126.4 (s), 124.2 (s), 116.1 (d, *J* = 22.0 Hz), 115.6 (s), 73.0 (s), 63.5 (s), 43.0 (s). HRMS (ESI-TOF) *m/z* [M+Na]$^{+}$ calcd For $C_{18}H_{13}FN_2NaO_2$, 331.0859; found, 331.0854.



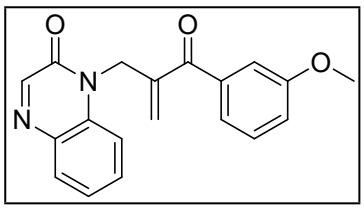
4-(2-((2-oxoquinoxalin-1(2H)-yl)methyl)acryloyl)benzonitrile (4j): yield, 52% (16.4 mg); yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.96 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.61 (t, *J* = 7.9 Hz, 1H), 7.42 (t, *J* = 7.1 Hz, 1H), 7.31 (d, *J* = 8.5 Hz, 1H), 5.82 (s, 1H), 5.70 (s, 1H), 5.32 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.7 (s), 154.9 (s), 150.0 (s), 140.3 (s), 140.1 (s), 133.7 (s), 132.4 (s), 131.5 (s), 130.9 (s), 129.9 (s), 128.4 (s), 127.7 (s), 124.3 (s), 117.8 (s), 116.2 (s), 114.1 (s), 42.2 (s). HRMS (ESI-TOF) *m/z* [M+Na]$^{+}$ calcd For $C_{19}H_{13}N_3NaO_2$, 338.0906; found, 338.0901.



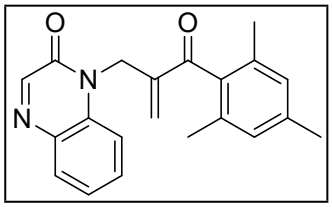
1-(2-(3-Methylbenzoyl)allyl)quinoxalin-2(1H)-one (4k): yield, 66% (23.1 mg); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.92 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.65 – 7.51 (m, 3H), 7.44 – 7.31 (m, 4H), 5.80 (s, 1H), 5.56 (s, 1H), 5.31 (s, 2H), 2.41 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 196.5 (s), 155.0 (s), 150.1 (s), 140.4 (s), 138.4 (s), 136.9 (s), 133.7 (d, *J* = 49.5 Hz), 133.6 (s), 132.1 (s), 131.4 (s), 130.6 (s), 130.1 (s), 128.3 (s), 127.0 (s), 126.8 (s), 124.1 (s), 114.5 (s), 42.6 (s), 21.4 (s). HRMS (ESI-TOF) *m/z* [M+Na]$^{+}$ calcd For $C_{19}H_{16}N_2NaO_2$, 327.1110; found, 327.1105.



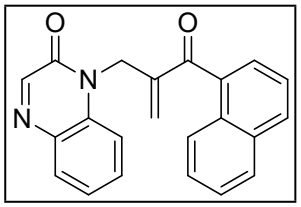
1-(2-(2-Methylbenzoyl)allyl)quinoxalin-2(1H)-one (4l): yield, 69% (20.9 mg); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.58 (dd, *J* = 14.5, 7.4 Hz, 1H), 7.42 – 7.27 (m, 4H), 7.28 – 7.20 (m, 2H), 5.74 (s, 1H), 5.63 (s, 1H), 5.32 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8 (s), 155.0 (s), 150.1 (s), 141.8 (s), 137.6 (s), 136.7 (s), 133.6 (s), 132.1 (s), 131.4 (s), 131.1 (s), 130.7 (s), 130.6 (s), 129.8 (s), 128.5 (s), 125.3 (s), 124.1 (s), 114.3 (s), 41.4 (s), 19.9 (s). HRMS (ESI-TOF) *m/z* [M+Na]$^{+}$ calcd For $C_{19}H_{12}N_2NaO_2$, 327.1110; found, 327.1105.



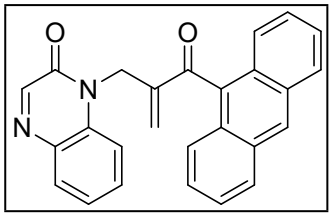
1-(2-(3-Methoxybenzoyl)allyl)quinoxalin-2(1H)-one (4m): yield, 56% (17.9 mg); yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.91 (d, *J* = 8.0 Hz,1H), 7.60 – 7.53 (m, 1H), 7.41 – 7.31 (m, 5H), 7.17 – 7.10 (m, 1H), 5.83 (s, 1H), 5.56 (s, 1H), 5.31 (s, 2H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1 (s), 159.7 (s), 155.0 (s), 150.1 (s) , 140.3 (s), 138.1 (s), 133.6 (s), 132.1 (s), 131.4 (s), 130.7 (s), 129.5 (s), 127.0 (s), 124.1 (s), 122.4 (s), 119.4 (s), 114.4 (s), 114.0 (s), 55.5 (s), 42.5 (s).HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{19}H_{12}N_2NaO_3$, 343.1059; found, 343.1054.



1-(2-(2,4,6-Trimethylbenzoyl)allyl)quinoxalin-2(1H)-one (4n): yield, 63% (20.9 mg); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 7.9 Hz, 1H), 7.37 (t, *J* = 7.1 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 6.85 (s, 2H), 5.76 (s, 1H), 5.61 (s, 1H), 5.32 (s, 2H), 2.28 (s, 3H), 2.16 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.5 (s), 155.0 (s), 150.1 (s), 142.0 (s), 138.9 (s), 135.8 (s), 134.2 (s), 133.6 (s), 132.1 (s), 131.6 (s), 130.7 (s), 130.1 (s), 128.4 (s), 124.1 (s), 114.3 (s), 40.5 (s), 21.1 (s), 19.3 (s). HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{21}H_{20}N_2NaO_2$, 355.1423; found, 355.1418.

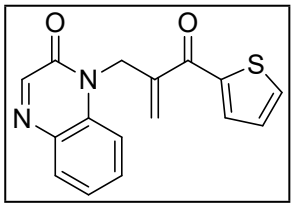


1-(2-(1-naphthoyl)allyl)quinoxalin-2(1H)-one (4o): yield, 72% (24.5 mg); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.36 (s, 1H), 8.03 – 7.83 (m, 5H), 7.71 – 7.52 (m, 3H), 7.49 – 7.37 (m, 2H), 5.89 (s, 1H), 5.63 (s, 1H), 5.41 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3 (s), 155.1 (s), 150.1 (s), 140.5 (s), 135.5 (s), 134.0 (s), 133.6 (s), 132.2 (s), 132.1 (s), 131.7 (s), 131.5 (s), 130.7 (s), 129.5 (s), 128.7 (s), 128.6 (s), 127.8 (s), 127.0 (s), 126.6 (s), 125.2 (s), 124.2 (s), 114.5 (s), 42.7 (s). HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{22}H_{16}N_2NaO_2$, 363.1110; found, 363.1106.

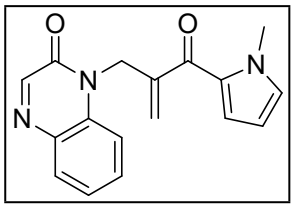


1-(2-(Anthracene-9-carbonyl)allyl)quinoxalin-2(1H)-one (4p): yield, 65% (25.2 mg); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.40 (s, 1H), 8.06 – 8.00 (m, 2H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.83 – 7.74 (m, 2H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.54 – 7.45 (m, 5H), 7.44 – 7.37 (m, 1H), 5.65 (s, 1H), 5.60 (s, 1H), 5.58 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.2 (s), 155.0 (s), 150.3 (s), 150.2

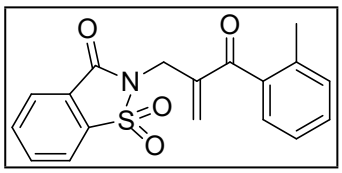
(s), 142.9 (s), 133.7 (s), 132.7 (s), 132.4 (s), 132.3 (s), 131.5 (s), 131.0 (s), 130.9 (s), 128.8 (s), 128.8 (s), 127.0 (s), 125.7 (s), 124.9 (s), 124.3 (s), 114.3 (s), 40.9 (s). HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{26}H_{18}N_2NaO_2$, 413.1266; found, 413.1261.



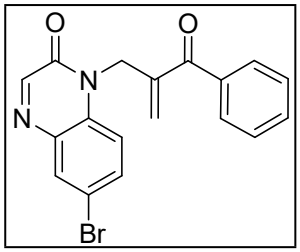
1-(2-(thiophene-2-carbonyl)allyl)quinoxalin-2(1H)-one (4q): yield, 75% (22.2 mg); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.94 (d, *J* = 9.4 Hz, 1H), 7.76 (dt, *J* = 3.6, 1.1 Hz, 2H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.45 – 7.36 (m, 2H), 7.21 – 7.14 (m, 1H), 6.01 (s, 1H), 5.48 (s, 1H), 5.31 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 187.5 (s), 155.0 (s), 150.0 (s), 142.4 (s), 140.6 (s), 135.1 (s), 134.8 (s), 133.6 (s), 132.0 (s), 131.4 (s), 130.6 (s), 128.2 (s), 124.2 (s), 124.2(s), 114.6 (s), 42.7 (s).HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{16}H_{12}N_2NaO_2S$, 319.0517; found, 319.0513.



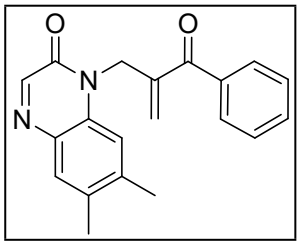
1-(2-(1-methyl-1H-pyrrole-2-carbonyl)allyl)quinoxalin-2(1H)-one (4r): yield, 20% (5.9 mg); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 6.93 (t, *J* = 1.9 Hz, 1H), 6.90 (dd, *J* = 4.1, 1.7 Hz, 1H), 6.14 (dd, *J* = 4.1, 2.5 Hz, 1H), 5.79 (s, 1H), 5.25 (s, 1H), 5.24 (s, 2H), 4.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.2 (s), 155.1 (s), 150.1 (s), 141.4 (s), 133.6 (s), 132.6 (s), 132.2 (s), 131.3 (s), 130.5 (s), 128.7 (s), 124.0 (s), 123.1 (s), 122.0 (s), 114.8 (s), 108.5 (s), 42.9 (s), 37.4 (s). HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{16}H_{15}N_3NaO_2$, 304.1062; found, 304.1057.



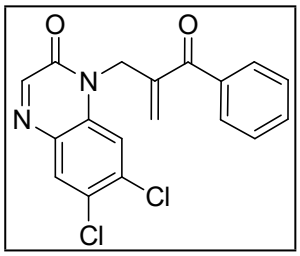
2-(2-(2-methylbenzoyl)allyl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide (4s): yield, 73% (24.9 mg); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 6.9 Hz, 1H), 7.95 (d, *J* = 7.1 Hz, 1H), 7.92 – 7.82 (m, 2H), 7.40 – 7.31 (m, 2H), 7.22 (dd, *J* = 15.1, 7.6 Hz, 2H), 6.25 (t, *J* = 1.4 Hz, 1H), 5.88 (s, 1H), 4.83 (s, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0 (s), 158.7 (s), 142.0 (s), 137.9 (s), 137.5 (s), 136.9 (s), 135.0 (s), 134.5 (s), 131.5 (s), 131.0 (s), 130.4 (s), 128.7 (s), 127.2 (s), 125.4 (s), 125.1 (s), 121.1 (s), 38.7 (s), 19.8 (s). HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{18}H_{15}NNaO_4S$, 364.0620; found, 364.0616.



6-bromo-1-(2-oxo-3-phenylbut-3-enyl)quinoxalin-2(1H)-one (4t): yield, 68% (26.6 mg); yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.07 (s, 1H), 7.82 (d, J = 7.0 Hz, 2H), 7.67 (d, J = 8.9 Hz, 1H), 7.62 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.29 (s, 1H), 5.84 (s, 1H), 5.61 (s, 1H), 5.30 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.20 (s), 154.63 (s), 151.21 (s), 140.11 (s), 136.62 (s), 134.40 (s), 134.16 (s), 133.10 (s), 133.00 (s), 131.27 (s), 129.70 (s), 128.55 (s), 127.14 (s), 116.74 (s), 115.99 (s), 42.65 (s). HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{18}H_{13}BrN_2NaO_2$, 391.0058; found, 391.0054.



6,7-dimethyl-1-(2-oxo-3-phenylbut-3-enyl)quinoxalin-2(1H)-one (4u): yield, 58% (19.8 mg); white solid; 1H NMR (400 MHz, $CDCl_3$) δ 8.31 (s,1H), 7.81 (d, J = 7.0 Hz, 2H), 7.65 (s, 1H), 7.59 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.10 (d, J = 9.0 Hz, 1H), 5.78 (s, 1H), 5.53 (s, 1H), 5.28 (s, 2H), 2.38 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.50 (s), 155.13 (s), 148.82 (s), 141.50 (s), 140.40 (s), 136.89 (s), 133.20 (s), 132.92 (s), 132.09 (s), 130.61 (s), 130.10 (s), 129.69 (s), 128.48 (s), 126.69 (s), 114.81 (s), 42.49 (s), 20.69 (s), 19.19 (s). HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{20}H_{18}N_2NaO_2$, 341.1266; found, 341.1261.



6,7-dichloro-1-(2-oxo-3-phenylbut-3-enyl)quinoxalin-2(1H)-one (4v): yield, 50% (19.0 mg); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.02 (s, 1H), 7.83 (d, *J* = 7.1 Hz, 2H), 7.67 – 7.59 (m, 1H), 7.57 – 7.44 (m, 3H), 5.87 (s, 1H), 5.63 (s, 1H), 5.26 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.08 (s), 154.36 (s), 151.18 (s), 139.85 (s), 136.57 (s), 135.88 (s), 133.14 (s), 132.59 (s), 131.54 (s), 131.40 (s), 129.72 (s), 128.57 (s), 128.11 (s), 127.17 (s), 116.04 (s), 42.92 (s). HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{18}H_{12}Cl_2N_2NaO_2$, 381.0174; found, 381.0170.

4. Experimental procedure for the reactions shown in the Fig. 3.

(a) A solution of **1** (0.20 mmol), tetra-methylethylenediamine (TMEDA, 0.50 mmol) and selectfluor (0.50 mmol) in dried dioxane (1 mL) was added with 1-(4-bromophenyl)ethanone (0.10 mmol) and stirred at 120 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (20 mL), filtered through a pad of silica gel and concentrated under reduced pressure. The residue was purified on a silica gel column eluted with petroleum ether/ethyl acetate (2:1 v/v) to afford the product **3t** in yield 60% (21.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.6 Hz, 2H), 7.64 – 7.54 (m, 3H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 4.75 – 4.61 (m, 2H), 3.48 – 3.34 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.40 (s), 154.93 (s), 149.97 (s), 141.87 (s), 134.82 (s), 133.71 (s), 132.14 (s), 131.39 (s), 130.96 (s), 129.61 (s), 128.99 (s), 123.99 (s), 113.54 (s), 37.67 (s), 35.74 (s). HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{17}H_{13}BrN_2NaO_2$, 379.0058; found, 379.0053.

(b) A solution of **1** (0.20 mmol), tetra-methylethylenediamine (TMEDA, 0.5 mmol) and selectfluor (0.5 mmol) in dried dioxane (1 mL) was added with 1-(3,5-dimethylphenyl)ethanone (0.10 mmol) and stirred at 120 °C for 24 h. AAfter cooling to room temperature, the reaction mixture was diluted with dichloromethane (20 mL), filtered through a pad of silica gel and concentrated under reduced pressure. The residue was purified on a silica gel column eluted with petroleum ether/ethyl acetate (2:1 v/v) to afford the product **3v** in yield 40% (12.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.72 – 7.52 (m, 3H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.22 (s, 1H), 4.79 – 4.61 (m, 2H), 3.53 – 3.34 (m, 2H), 2.35 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 197.77 (s), 167.91 (s), 136.26 (s), 133.60 (s), 132.76 (s), 130.61 (s), 128.72 (s), 128.18 (s), 123.47 (s), 123.04 (s), 110.15 (s), 109.79 (s), 39.52 (s), 36.53 (s). HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{19}H_{18}N_2NaO_2$, 329.1266; found, 329.1261.

(c) A solution of **2** (0.10 mmol), tetra-methylethylenediamine (TMEDA, 0.50 mmol) and selectfluor (0.50 mmol) in dried dioxane (1 mL) was added with 1H-benzo[d]imidazole-2(3H)-thione (0.20 mmol) and stirred at 120 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (20 mL), filtered through a pad of silica gel and concentrated under reduced pressure. The crude product was purified on a silica gel column eluted with petroleum ether/ethyl acetate (1:1 v/v) to afford the product **3u** in yield 45% (12.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.96 (d, *J* = 1.3 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.48 – 7.36 (m, 3H), 7.27 – 7.24 (m, 2H), 7.24 – 7.19 (m, 2H), 4.71 (t, *J* = 7.0 Hz, 2H), 3.64 (t, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.72 (s), 168.31 (s), 147.49 (s), 136.28 (s), 133.59 (s), 130.37 (s), 128.71 (s), 128.19 (s), 123.47 (s), 123.11 (s), 109.87 (s), 100.00 (s), 39.58 (s), 36.47 (s).HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{16}H_{14}N_2NaOS$, 305.0725; found, 305.0720.

(d) A solution of **1** (0.20 mmol), tetra-methylethylenediamine (TMEDA, 0.40 mmol) and selectfluor (0.30 mmol) in dried dioxane (1 mL) was added with acetophenone (0.10 mmol) and stirred at 120 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (20 mL), filtered through a pad of silica gel and concentrated under reduced pressure. The residue was purified on a silica gel column eluted with petroleum ether/ethyl acetate (2:1 v/v) to afford the product **3a** in yield 35% (9.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.98 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.66-7.58 (m,

2H), 7.48 (dd, J = 10.6, 4.8 Hz, 3H), 7.40 (t, J = 7.6 Hz, 1H), 4.84 – 4.63 (m, 2H), 3.54 – 3.39 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.41 (s), 154.96 (s), 150.00 (s), 136.13 (s), 133.74 (s), 133.71 (s), 132.20 (s), 131.37 (s), 130.90 (s), 128.80 (s), 128.13 (s), 123.93 (s), 113.64 (s), 37.79 (s), 35.77 (s). HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{17}H_{14}N_2NaO_2$, 301.0953; found, 301.0948.

(e) A solution of tetra-methylethylenediamine (TMEDA, 0.50 mmol) and selectfluor (0.50 mmol) in dried dioxane (1 mL) was added with **3a** (0.20 mmol), and stirred at 120 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (20 mL), filtered through a pad of silica gel and concentrated under reduced pressure. The residue was purified on a silica gel column eluted with petroleum ether/ethyl acetate (2:1 v/v) to afford the product **4a** in yield 75% (43.5 mg).

(f) A solution of **1** (0.20 mmol), tetra-methylethylenediamine (TMEDA, 0.50 mmol), BHT (0.30 mmol) and selectfluor (0.50 mmol) in dried dioxane (1 mL) was added with acetophenone (0.10 mmol) and stirred at 120 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (20 mL), filtered through a pad of silica gel and concentrated under reduced pressure. The residue was purified on a silica gel column eluted with petroleum ether/ethyl acetate (2:1 v/v) to afford the product **4a** in yield 67% (19.4 mg).

(g) A solution of **1** (0.20 mmol), tetra-methylethylenediamine (TMEDA, 0.50 mmol), TEMPO (0.30 mmol) and selectfluor (0.50 mmol) in dried dioxane (1 mL) was added with acetophenone (0.10 mmol) and stirred at 120 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (20 mL), filtered through a pad of silica gel and concentrated under reduced pressure. The residue was purified on a silica gel column eluted with petroleum ether/ethyl acetate (2:1 v/v) to afford the product **4a** in yield 70% (20.3 mg).

(h) A solution of **1** (0.20 mmol), tetra-methylethylenediamine (TMEDA, 0.50 mmol) and selectfluor (0.50 mmol) in dried dioxane (1 mL) was added with acetophenone (0.10 mmol) and stirred at 120 °C for 24 h in nitrogen atmosphere. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (20 mL), filtered through a pad of silica gel and concentrated under reduced pressure. The residue was purified on a silica gel column eluted with petroleum ether/ethyl acetate (2:1 v/v) to afford the product **4a** in yield 68% (19.7 mg).

(i) A solution of **1** (0.20 mmol), tetra-ethylethylenediamine (TEEDA, 0.50 mmol) and selectfluor (0.50 mmol) in dried dioxane (1 mL) was added with acetophenone (0.10 mmol) and stirred at 120 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (20 mL), filtered through a pad of silica gel and concentrated under reduced pressure. The residue was purified on a silica gel column eluted with petroleum ether/ethyl acetate (2:1 v/v) to afford the product **3a** in yield 43% (11.9 mg).

(j) A solution of **1** (0.20 mmol), triethylamine (TEA, 0.50 mmol) and selectfluor (0.50 mmol) in dried dioxane (1 mL) was added with acetophenone (0.10 mmol) and stirred at 120 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (20 mL), filtered through a pad of silica gel and concentrated under reduced pressure. The residue was purified on a silica gel column eluted with petroleum ether/ethyl acetate (2:1 v/v) to afford

the product **3a** in yield 35% (9.7 mg).

(k) A solution of **1** (0.20 mmol), triethylenediamine (DABCO, 0.30 mmol) and selectfluor (0.50 mmol) in dried dioxane (1 mL) was added with acetophenone (0.10 mmol) and stirred at 120 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (20 mL), filtered through a pad of silica gel and concentrated under reduced pressure. No product could be obtained.

5. X-ray Structure Determinations

Diffraction data were collected on an Oxford Diffraction Supernova dual diffractometer equipped with an Oxford Cryostream 700 low-temperature apparatus. Cu K\a radiation source (λ = 1.54184 Å) was used for the data collection. Single crystals were coated with Paratone-N oil and mounted on a Nylon loop for diffraction. The data reduction and cell refinement were processed using CrysAlisPro software.[1] Structures were solved by direct methods using the SHELXTL program packages.[2] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were added geometrically. Crystal data and refinement details were given in Tables S1. Other refinement details and explanations were included in individual CIF files.

6. Crystallographic data of compounds

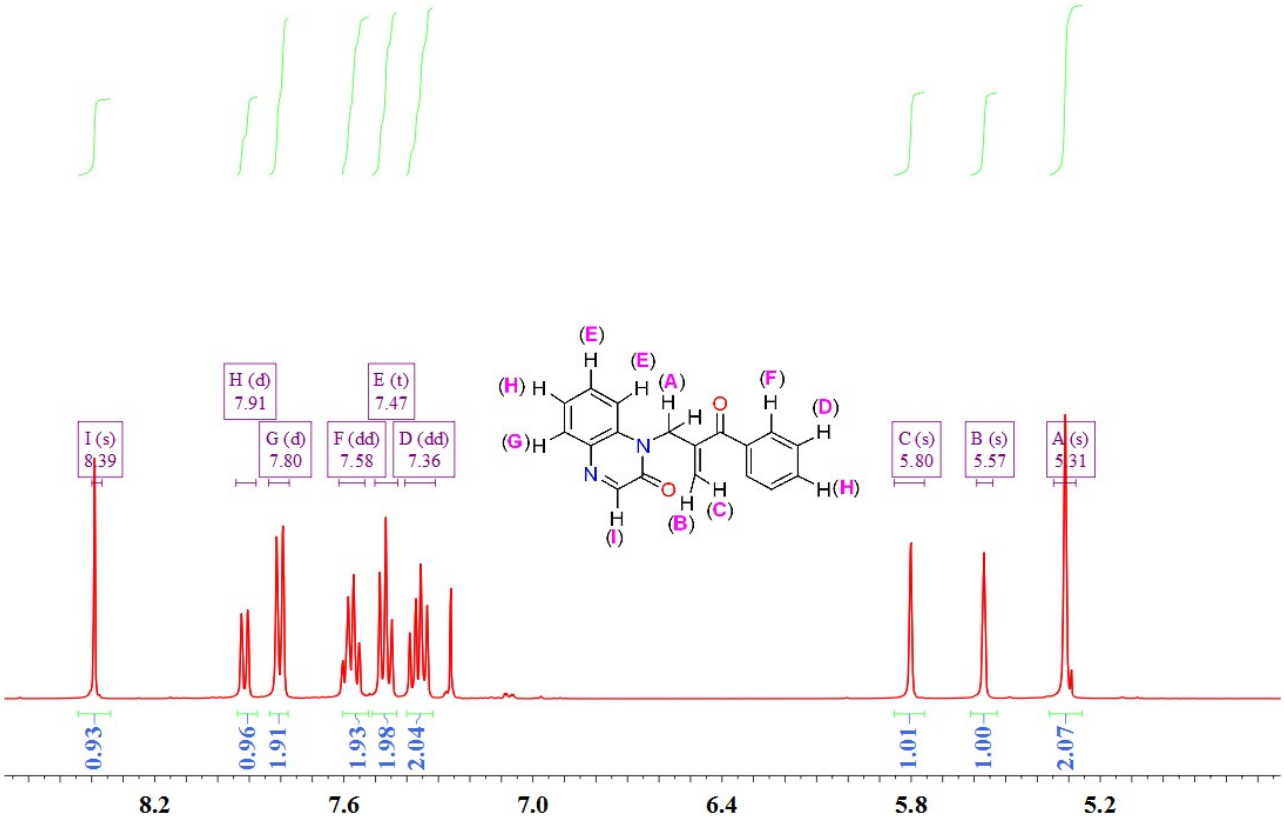
Table S1. Crystallographic data[a] for compounds **4a** and **4b**.

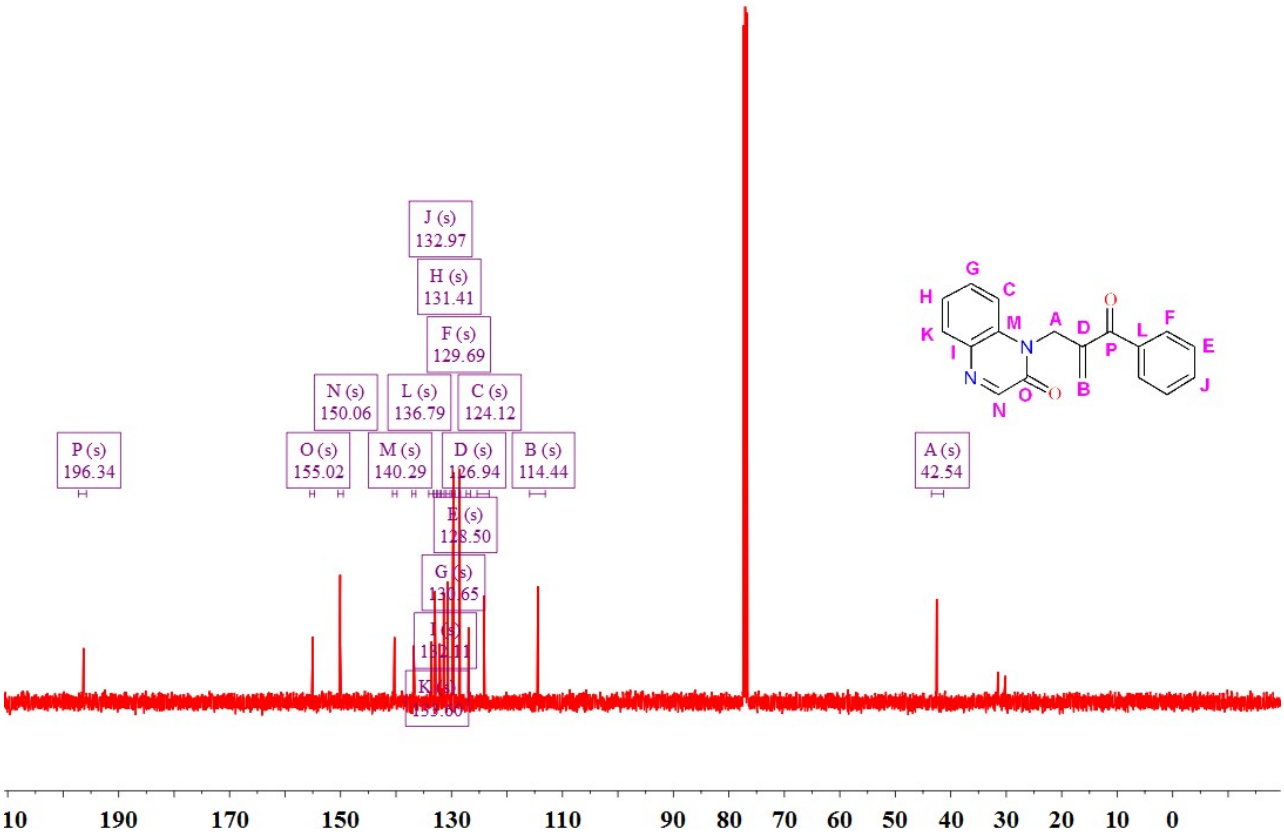
	4a	**4b**
formula	$C_{18}H_{14}N_2O_2$	$C_{19}H_{16}N_2O_3$
M	290.31	320.34
crystal system	monoclinic	monoclinic
space group	C2/c	$P2_1/c$
a, Å	16.6926(3)	9.9698(2)
b, Å	6.67230(10)	14.9389(3)
c, Å	26.1236(7)	21.1714(4)
α, deg	90.00	90.00
β, deg	99.220(2)	91.459(2)
γ, deg	90.00	90.00
V, Å^3	2872.00(10)	3152.20(11)
Z	8	8
μ, mm^{-1}	0.719	0.755
independent data	2703	5911
refined parameters	200	433
R_1[b], wR_2[c]($I>2\sigma(I)$)	0.0340, 0.0902	0.0409, 0.1035
R_1,wR_2 (all data)	0.0368, 0.0921	0.0557, 0.1110

[a]T = 150(2) K, Cu Kα radiation (λ = 1.54178 Å). [b]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c]$wR_2 = \{\Sigma[w(Fo^2 - F_c^2)^2/(F_o^2)^2]\}^{1/2}$.

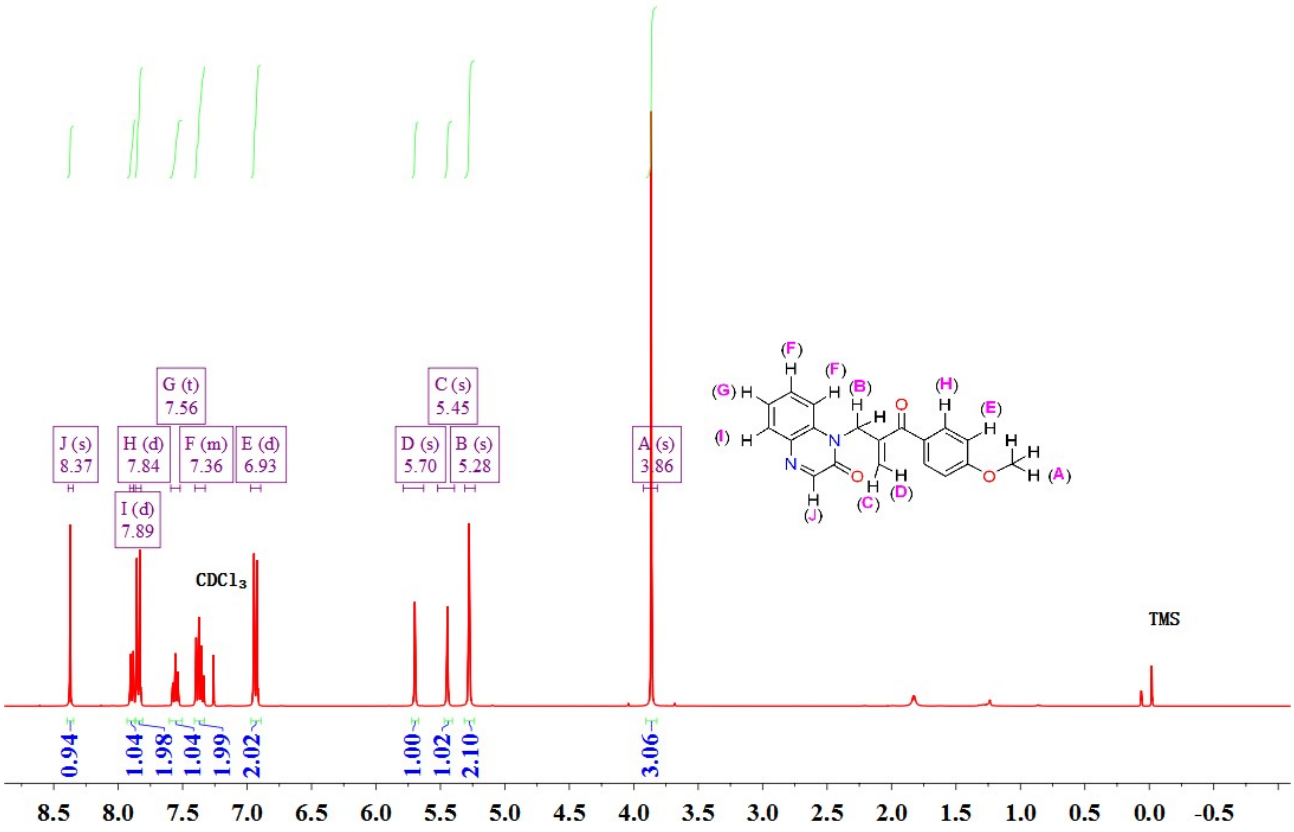
7. ^{1}H NMR and ^{13}C NMR spectra of compounds

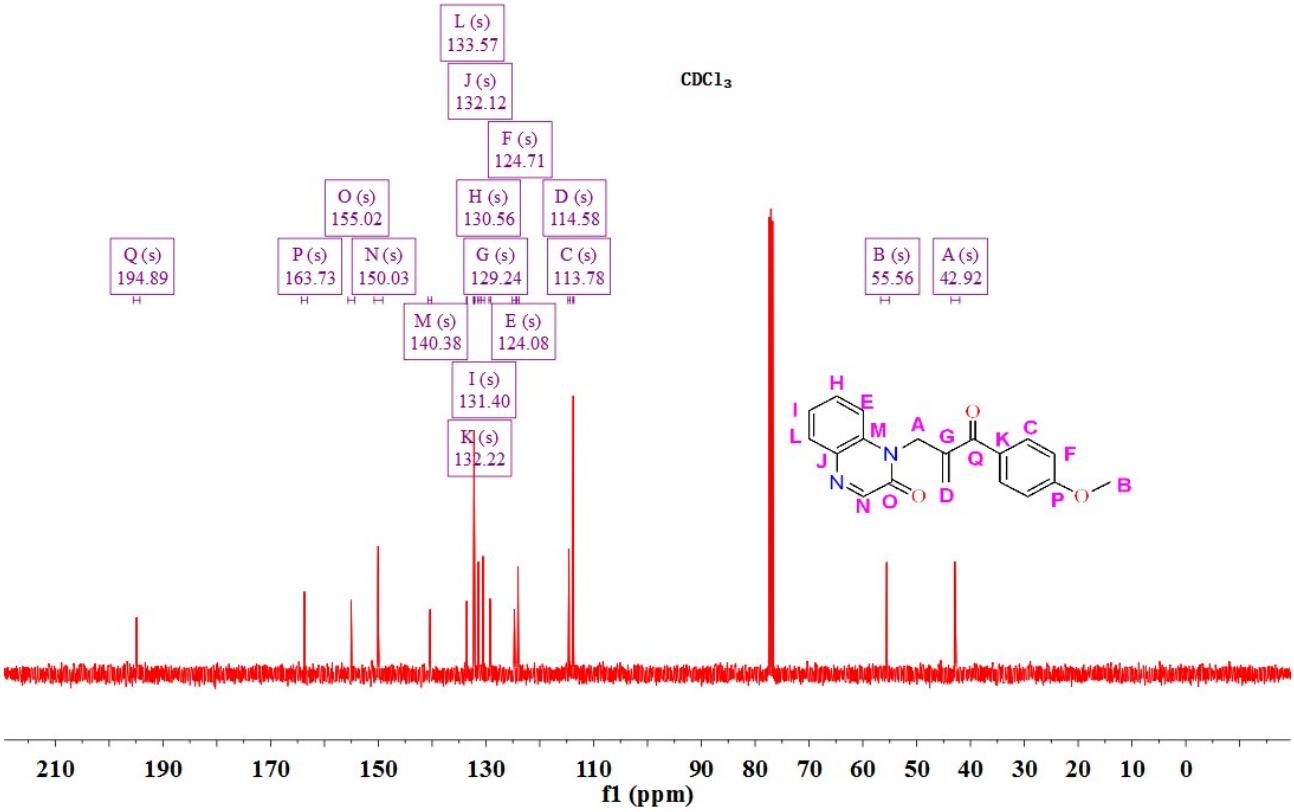
1-(2-Benzoylallyl)quinoxalin-2(1H)-one (4a)



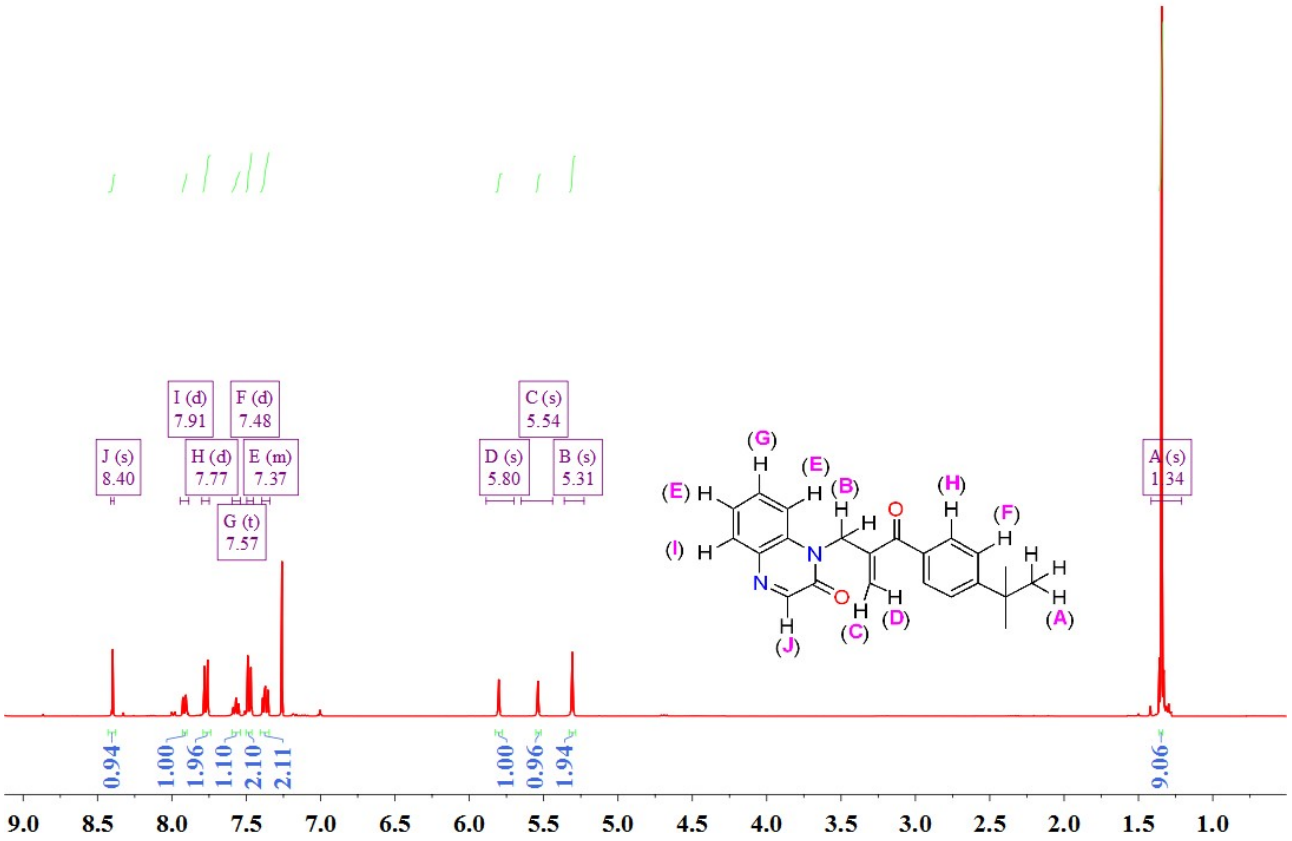


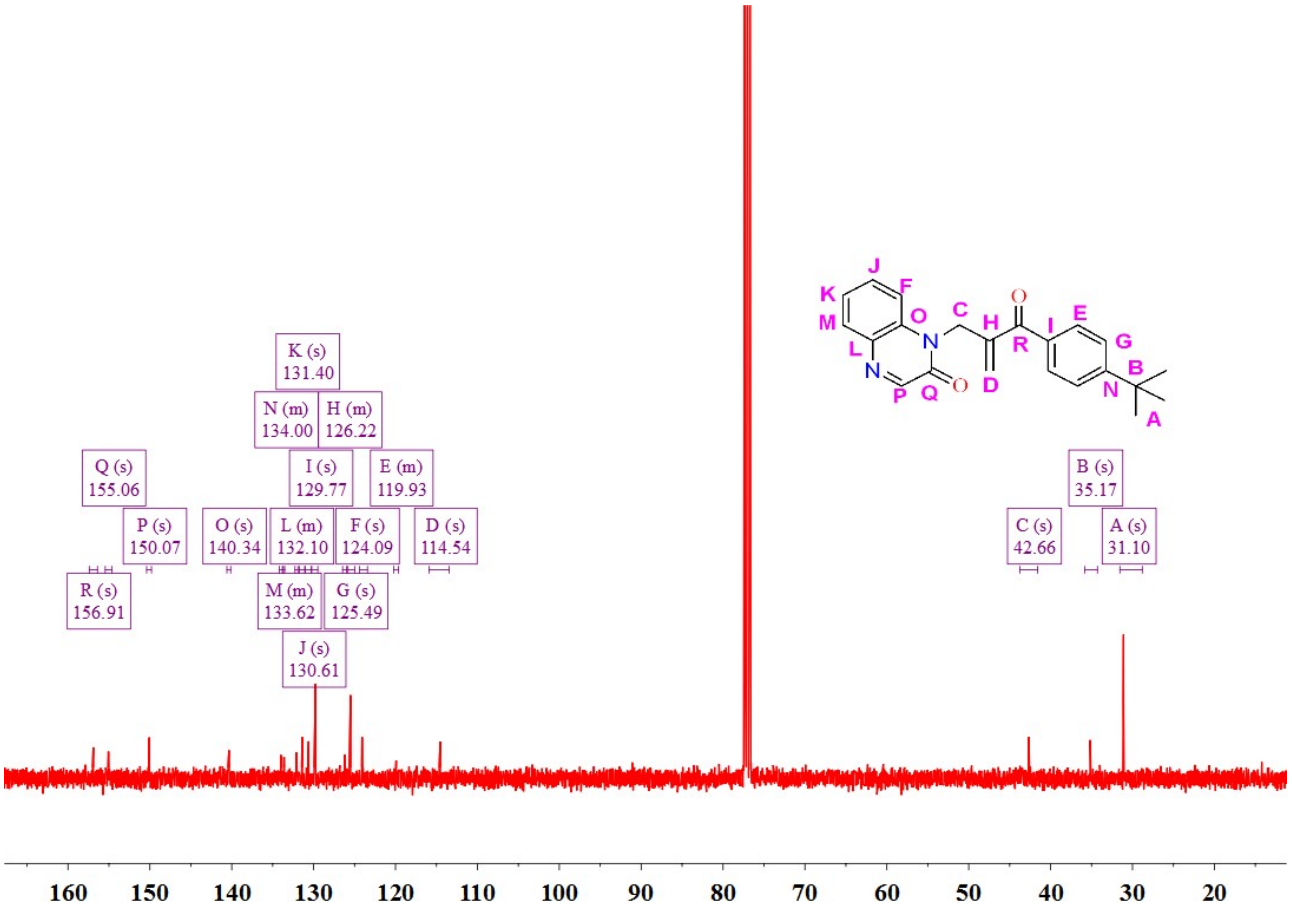
1-(2-(4-Methoxybenzoyl)allyl)quinoxalin-2(1H)-one (4b)



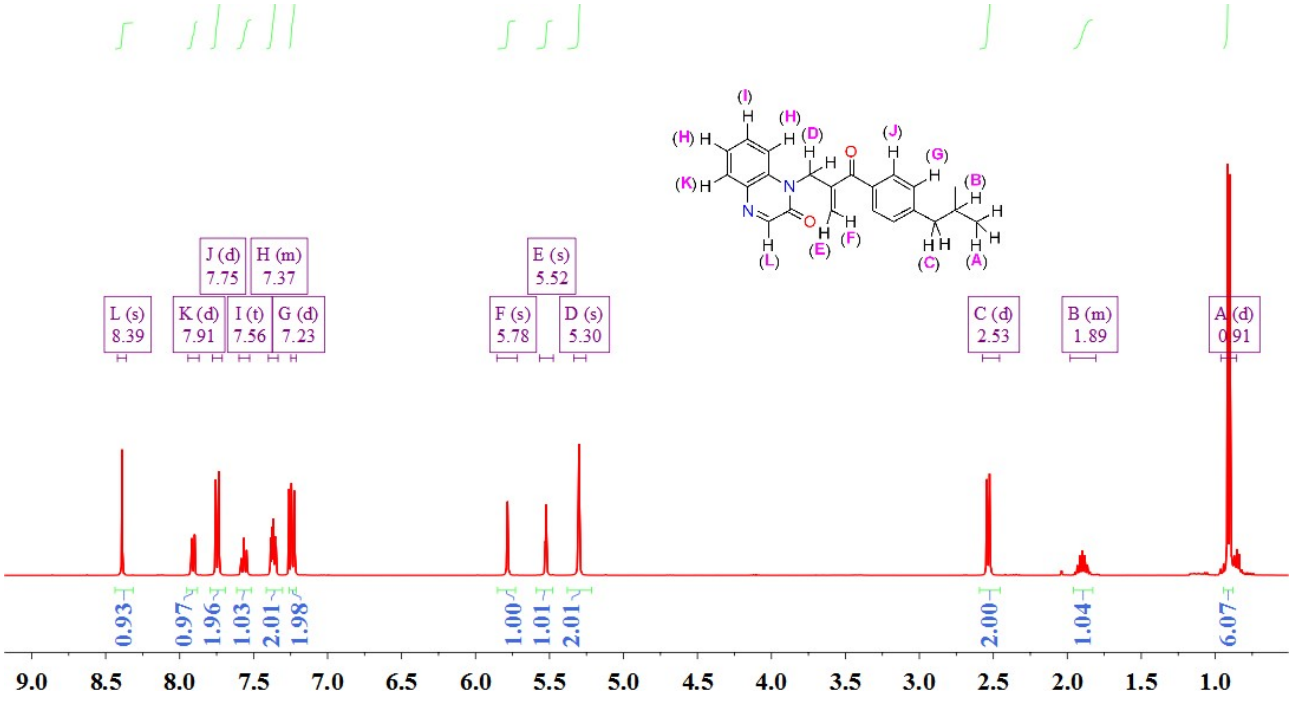


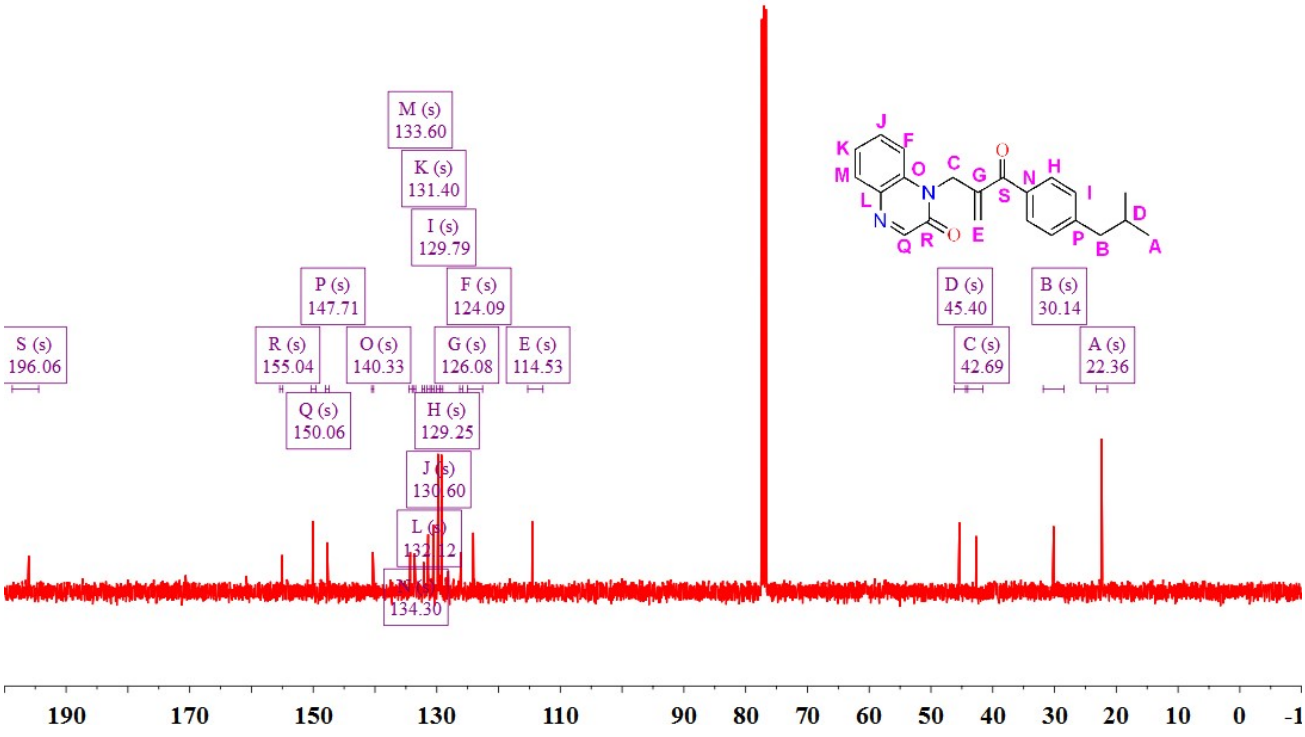
1-(2-(4-(Tert-butyl)benzoyl)allyl)quinoxalin-2(1H)-one (4c)



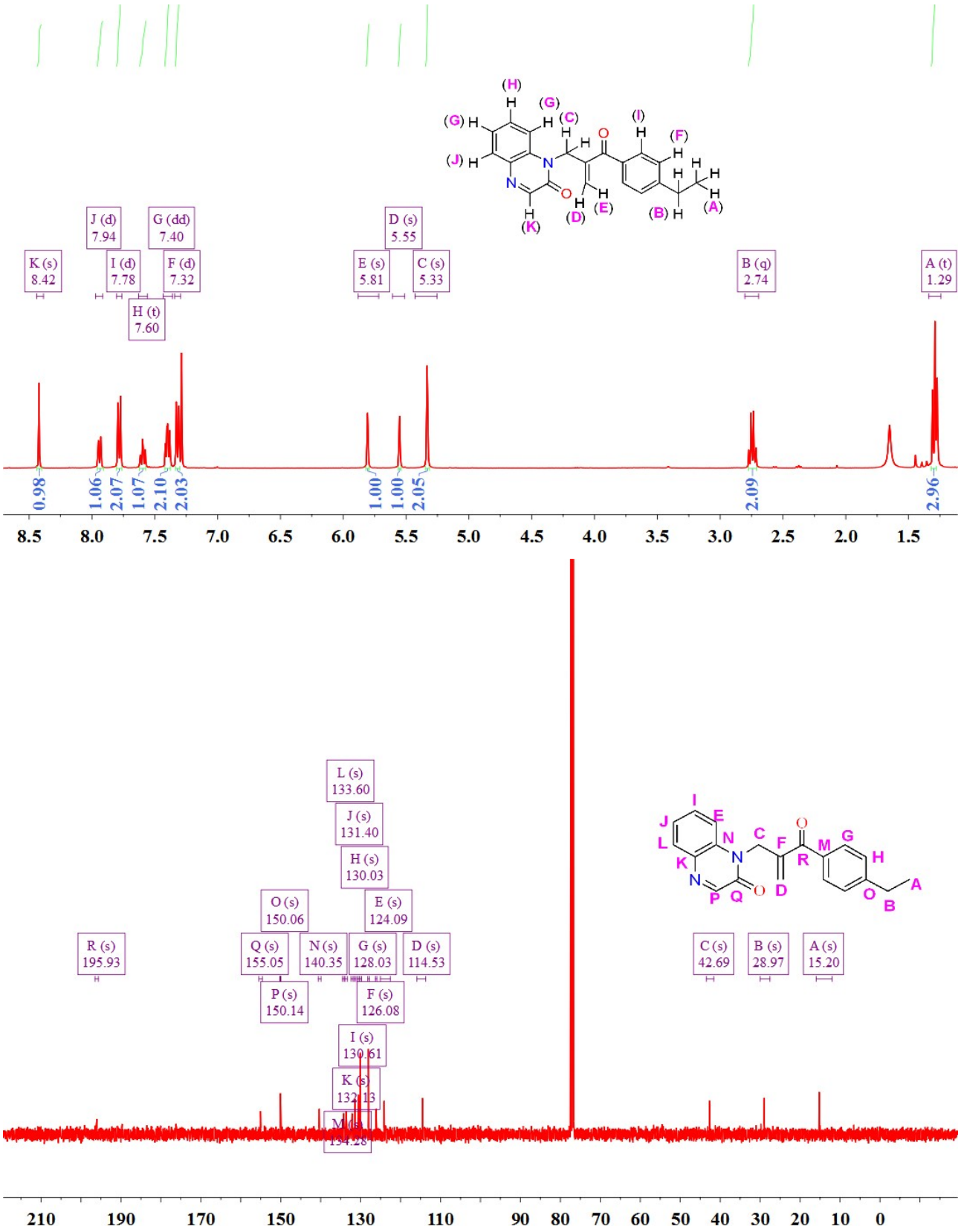


1-(2-(4-Isobutylbenzoyl)allyl)quinoxalin-2(1H)-one (4d)

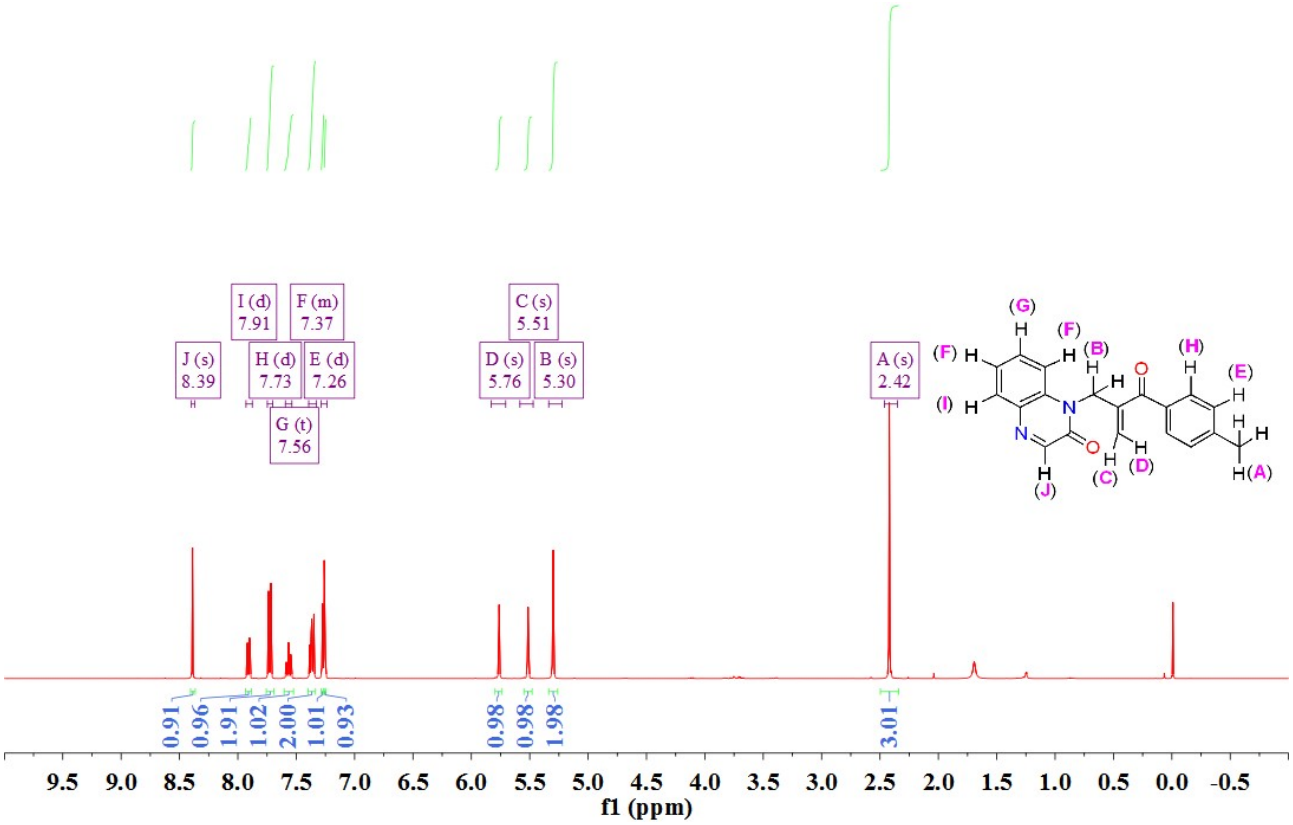


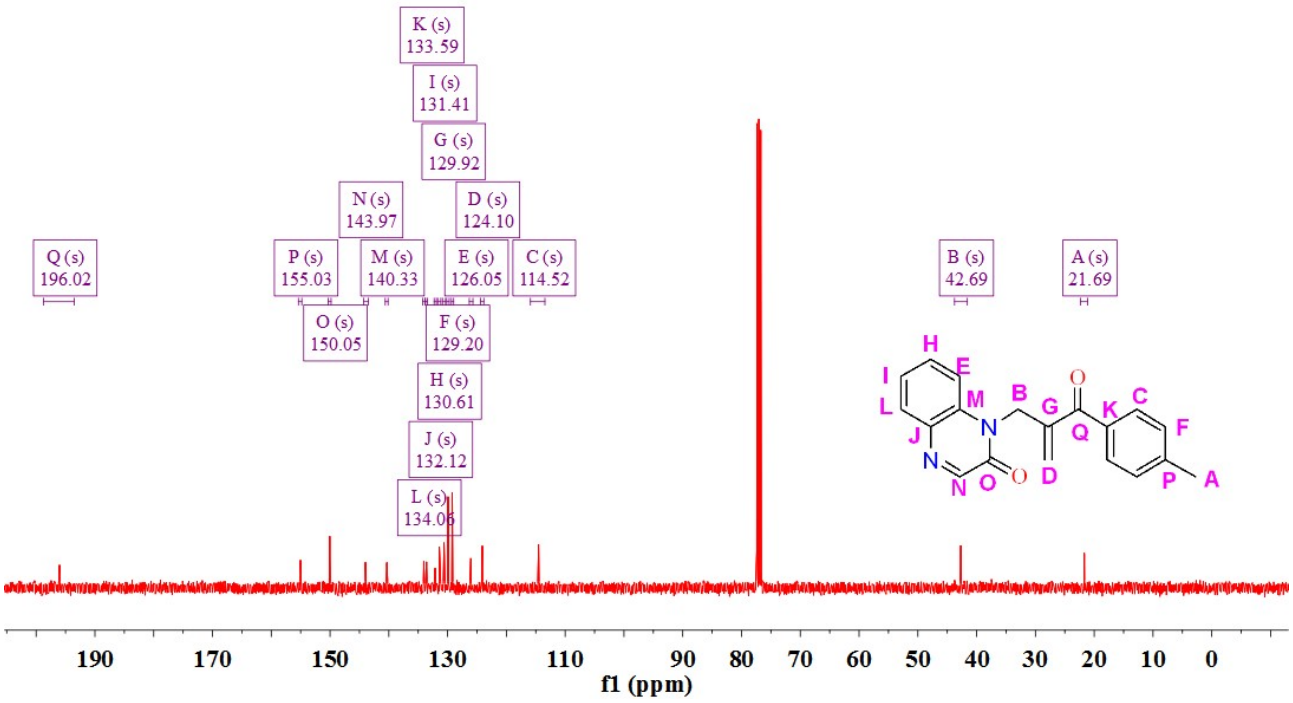


1-(2-(4-ethylbenzoyl)allyl)quinoxalin-2(1H)-one (4e)

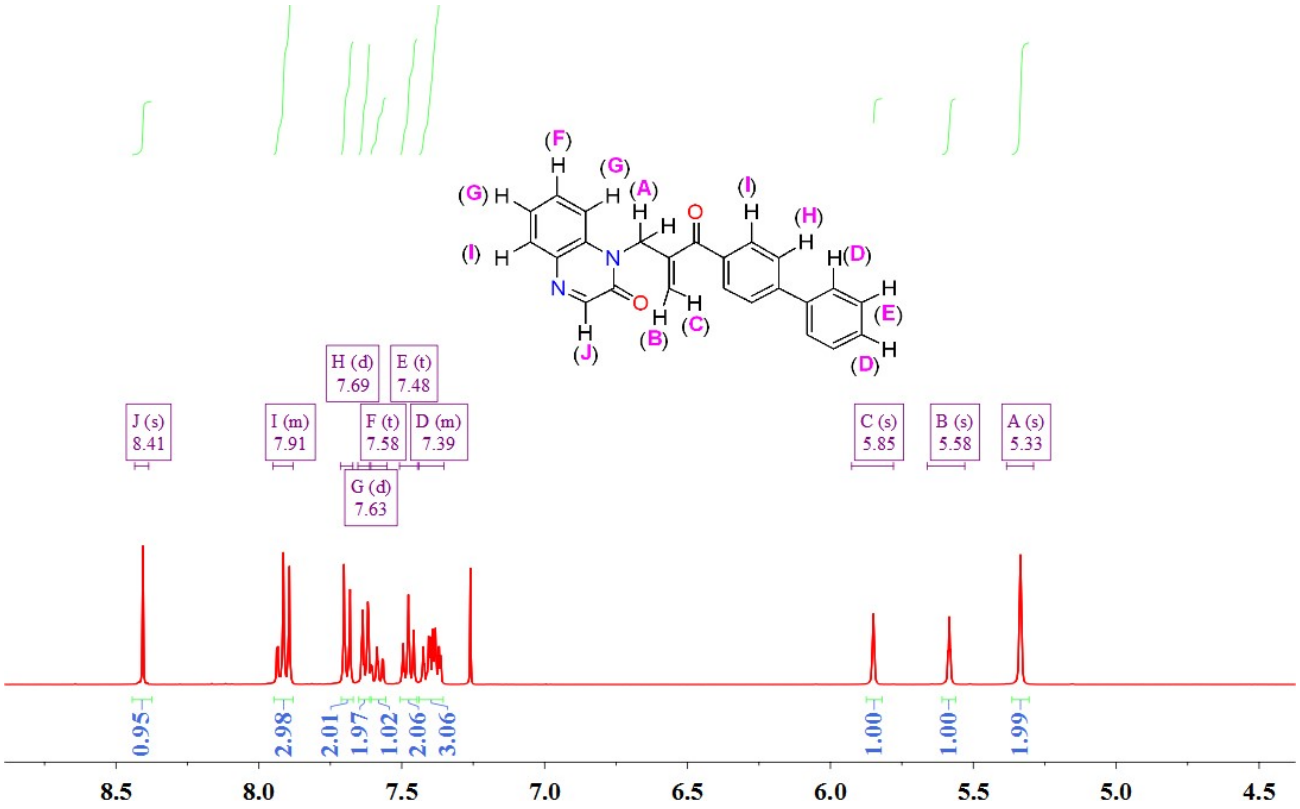


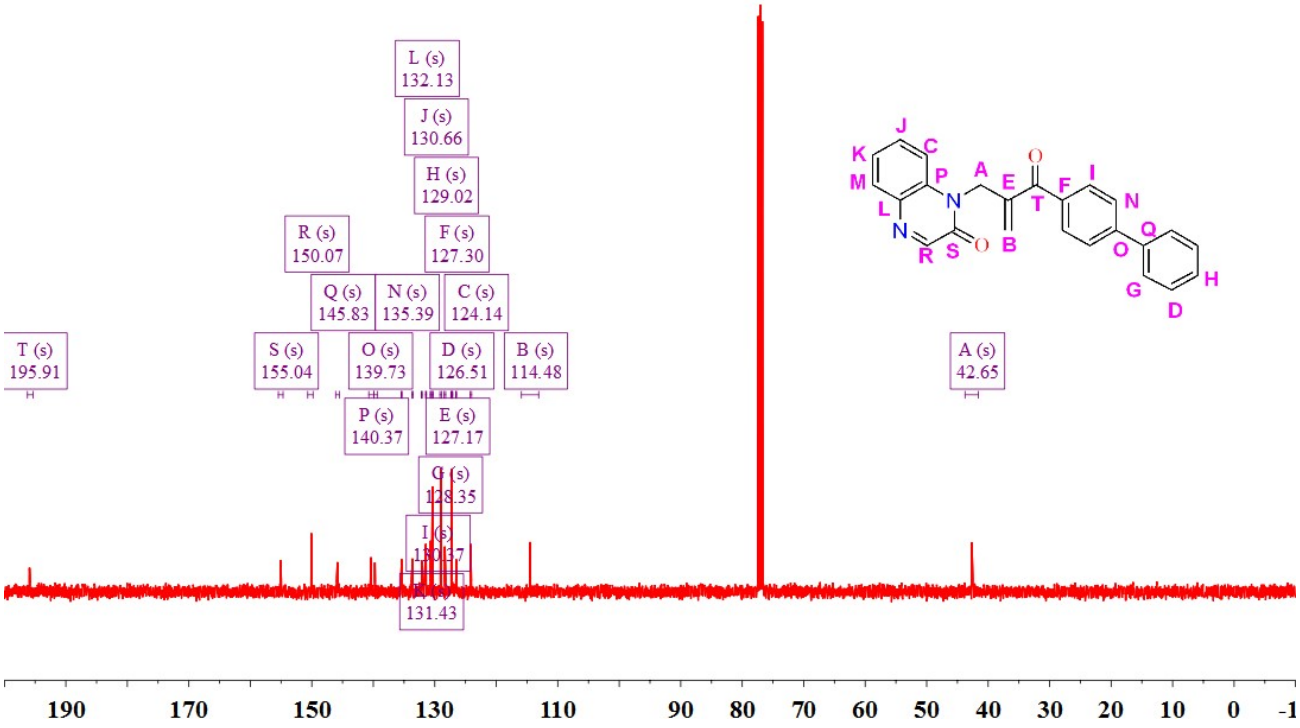
1-(2-(4-Methylbenzoyl)allyl)quinoxalin-2(1H)-one (4f)



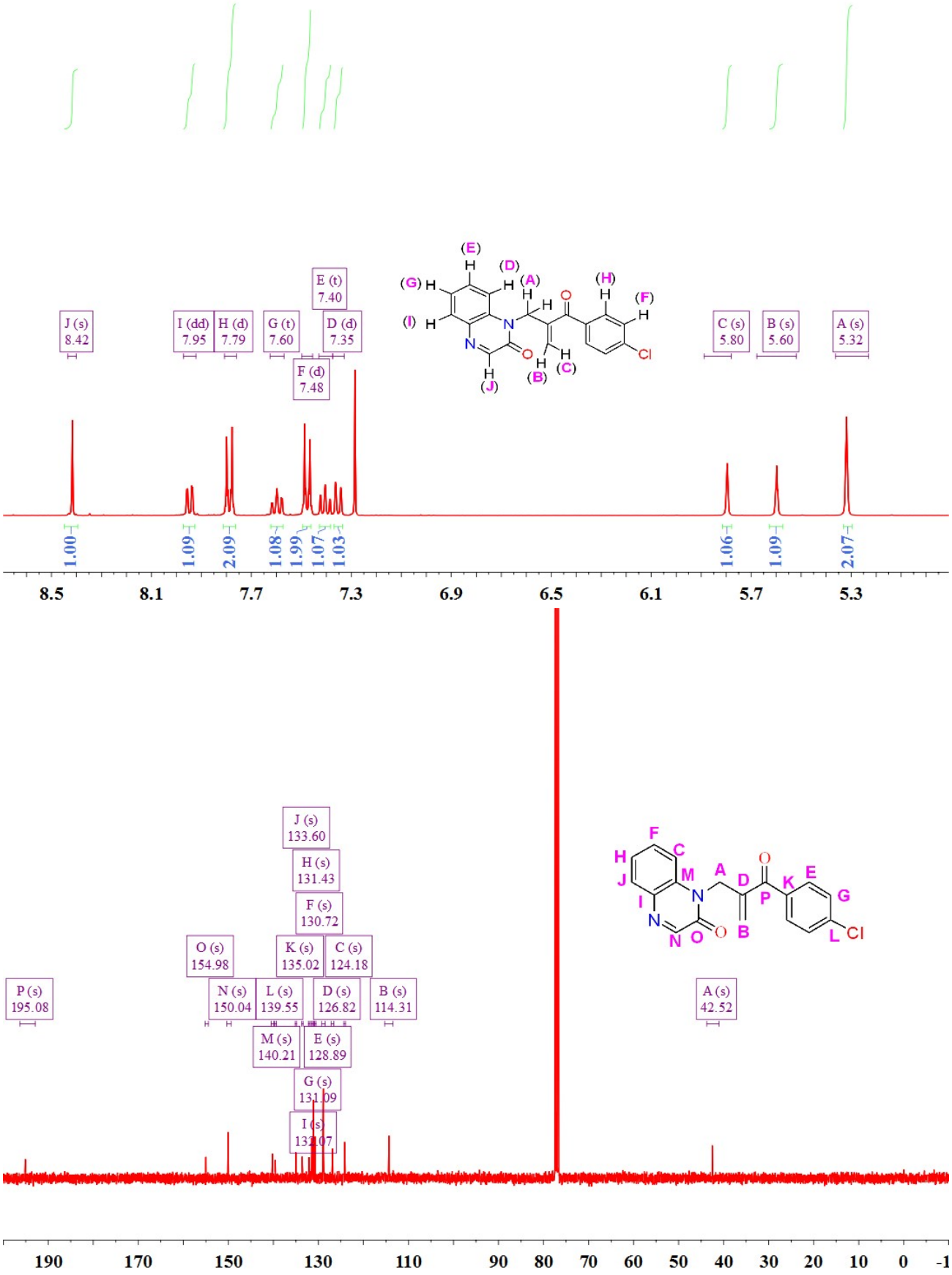


1-(2-([1,1'-Biphenyl]-4-carbonyl)allyl)quinoxalin-2(1H)-one (4g)

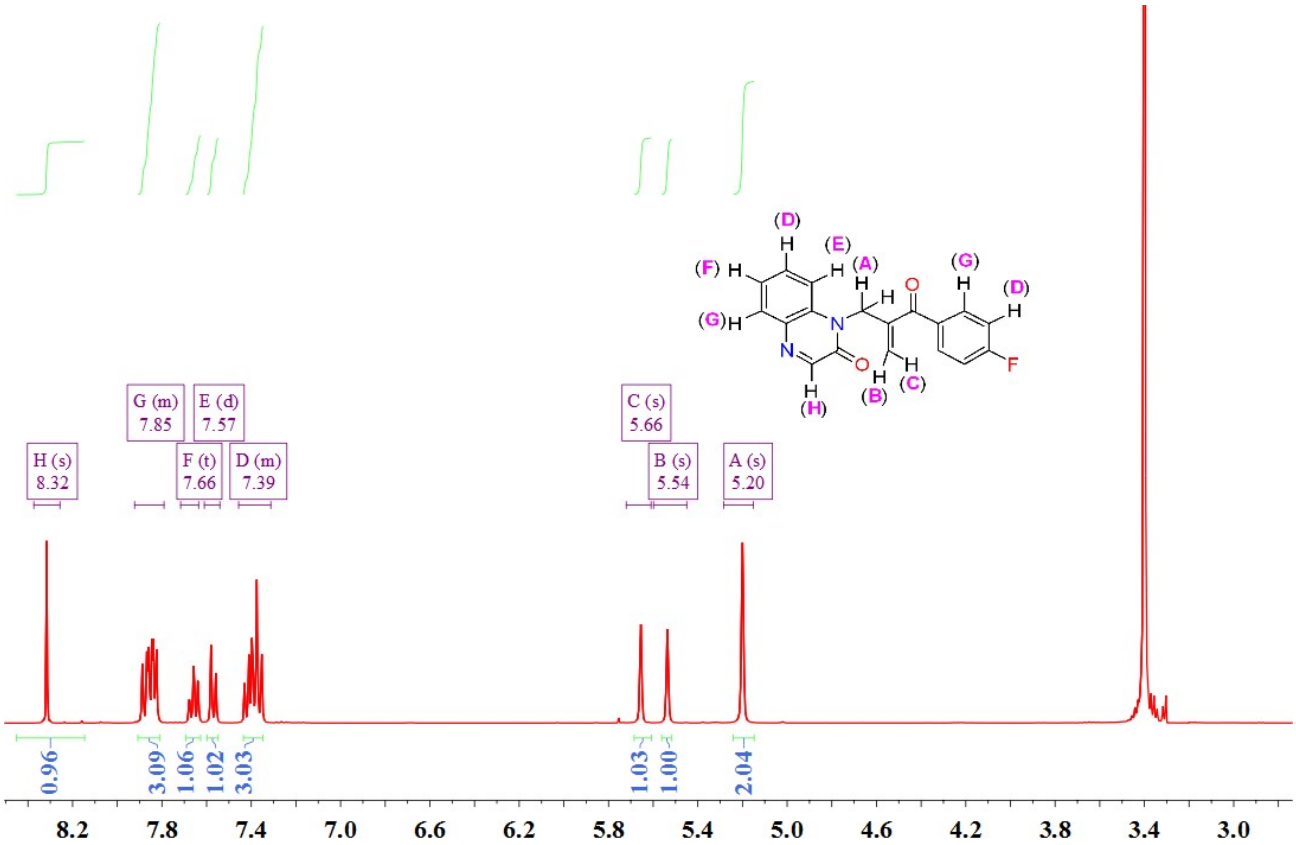


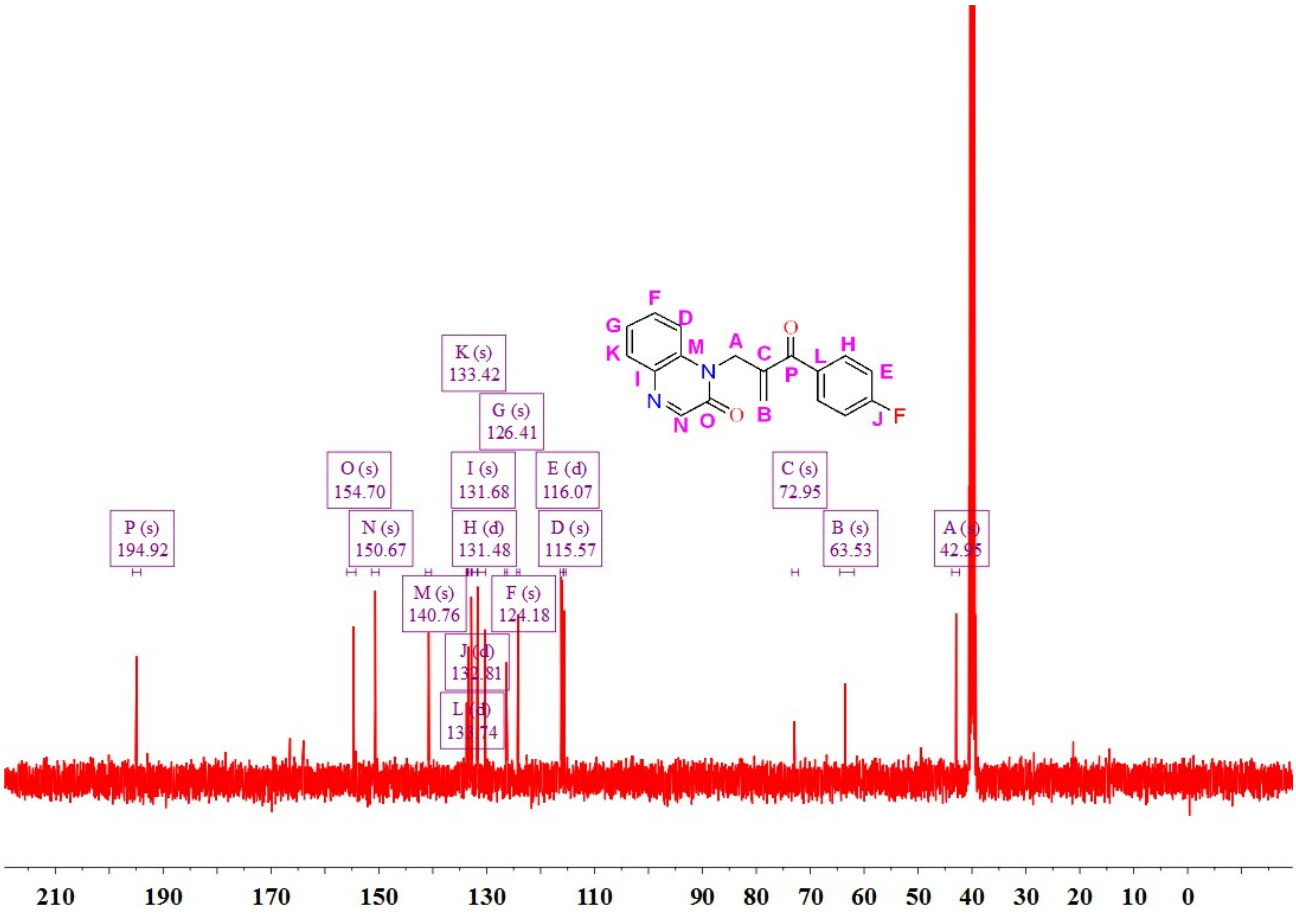


1-(2-(4-Chlorobenzoyl)allyl)quinoxalin-2(1H)-one (4h)

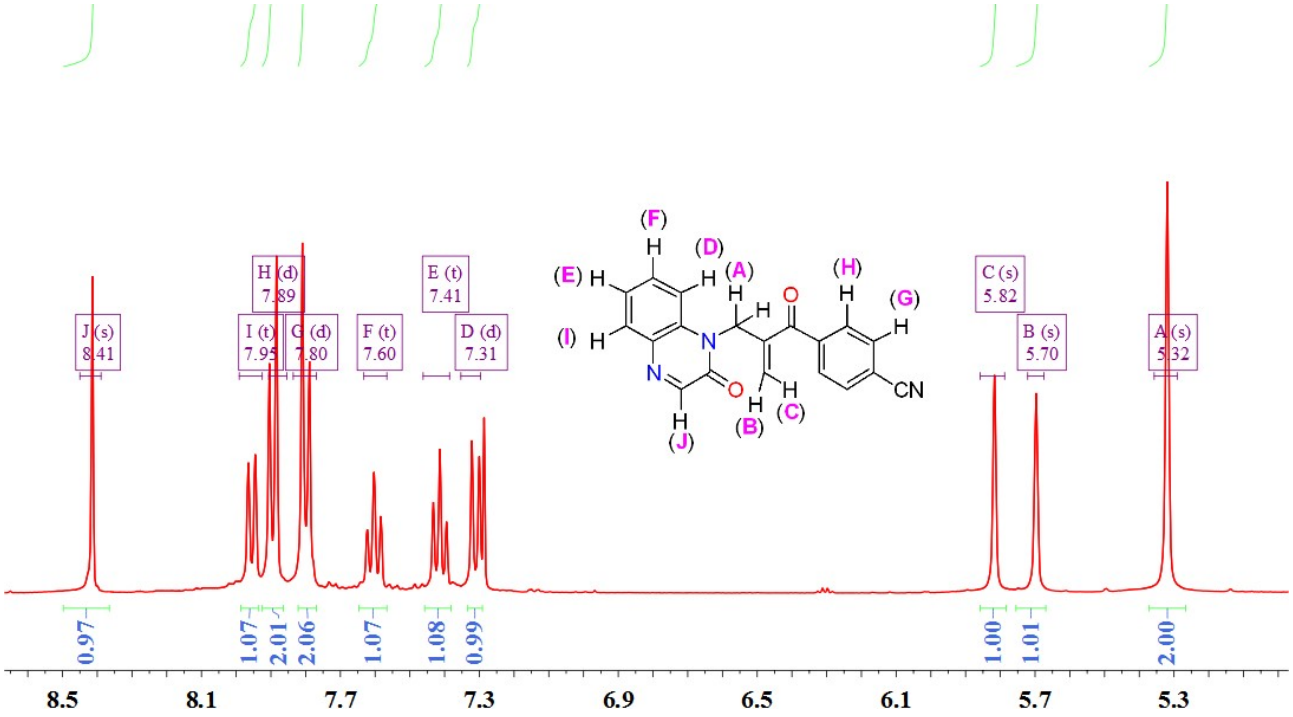


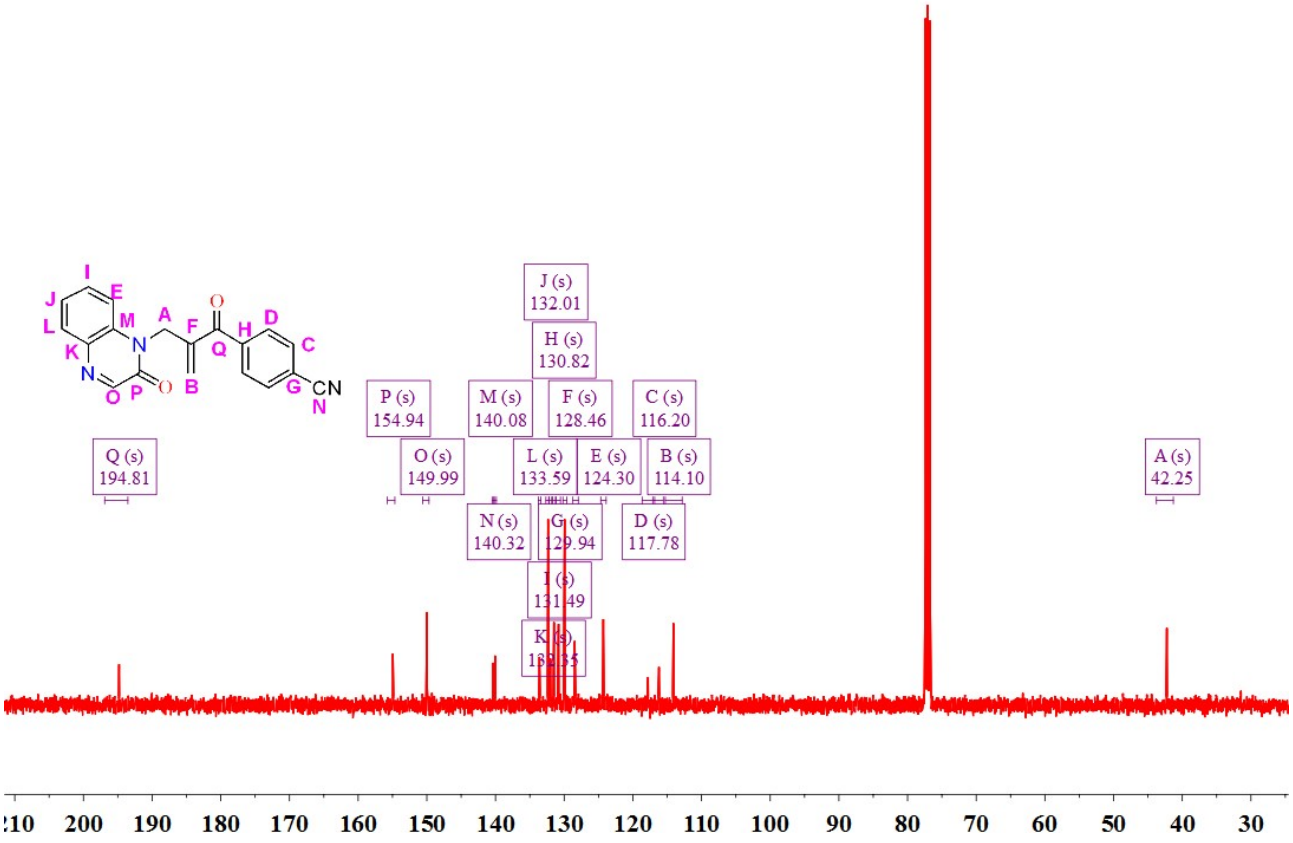
1-(2-(4-Fluorobenzoyl)allyl)quinoxalin-2(1H)-one (4i)



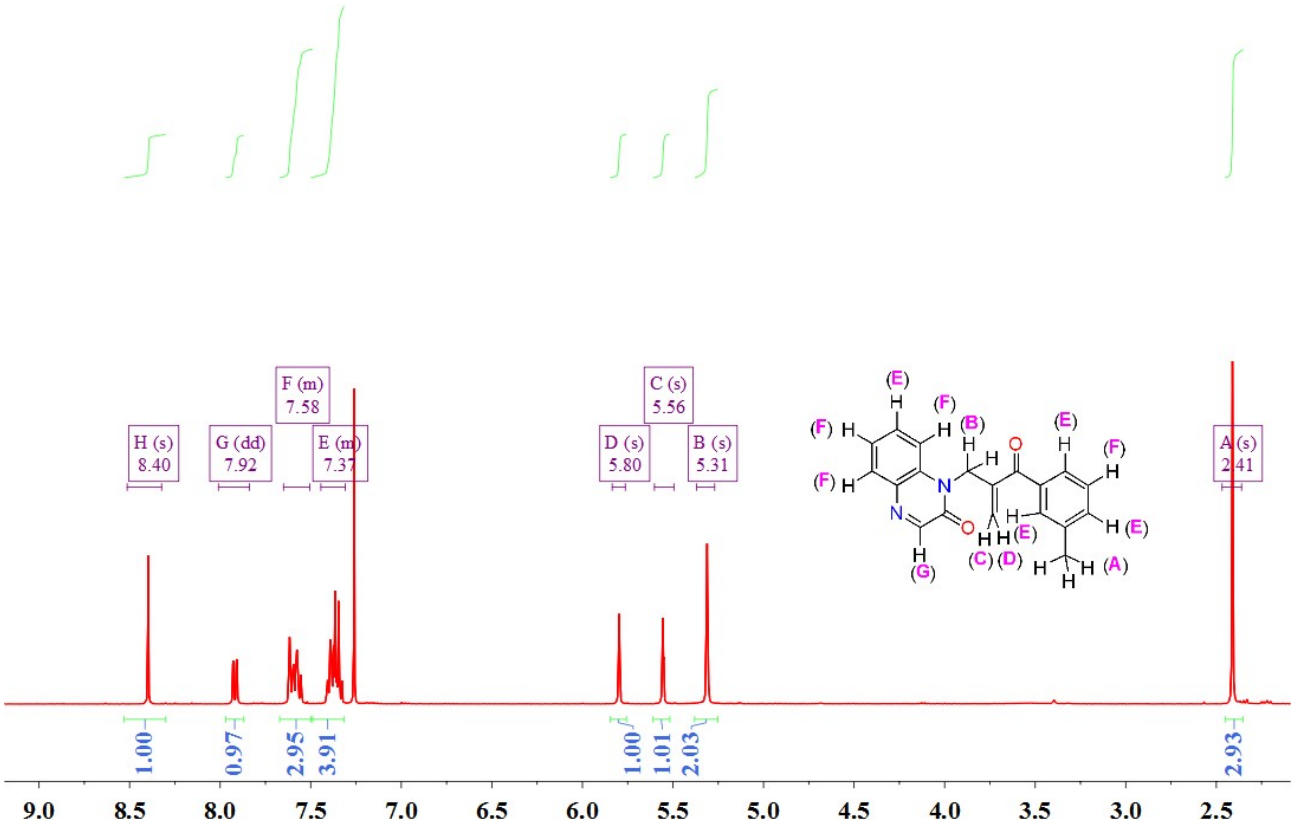


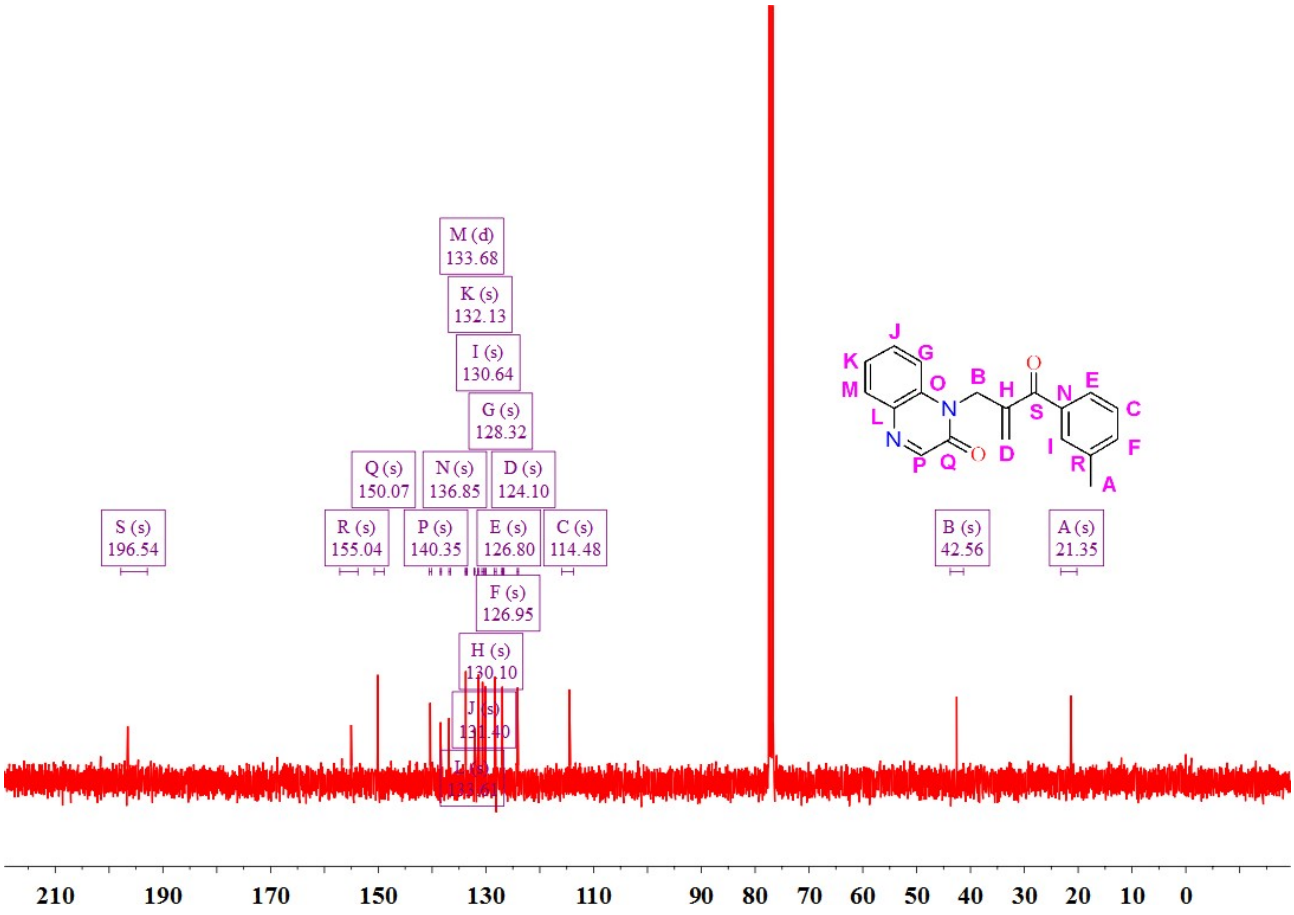
2-(2-((2-oxoquinoxalin-1(2H)-yl)methyl)acryloyl)benzonitrile (4j)



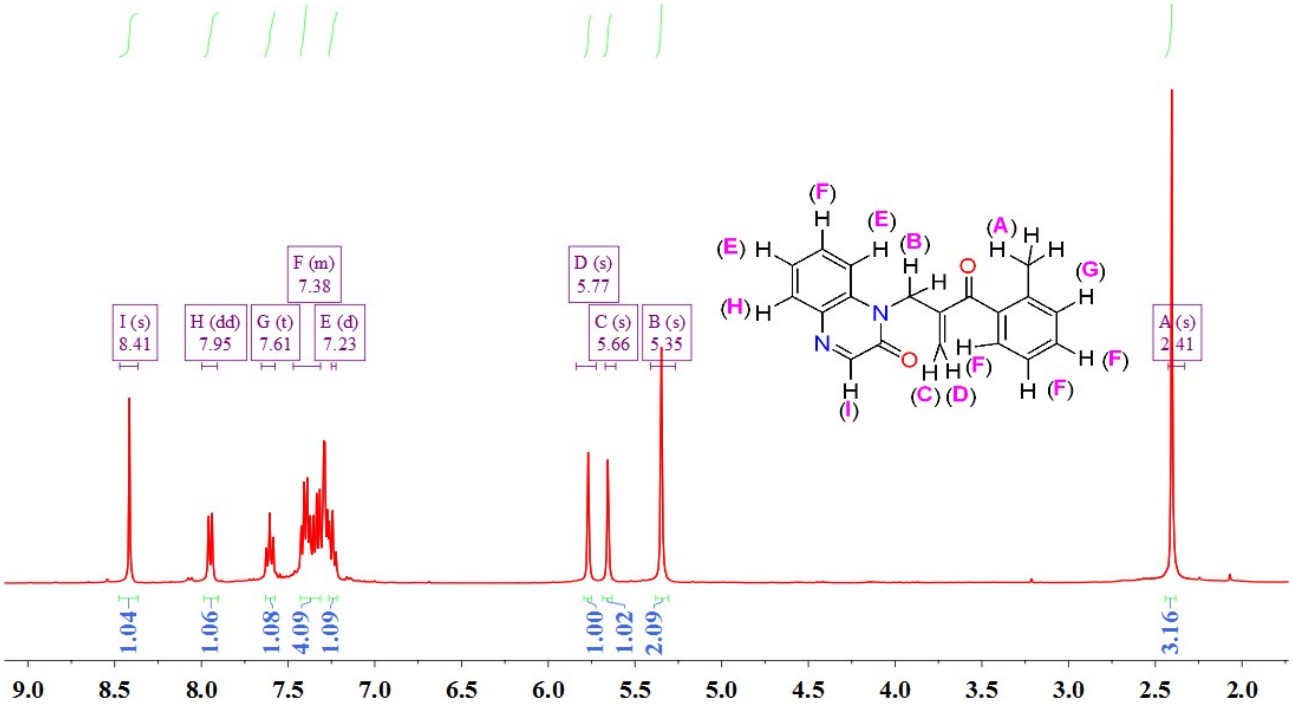


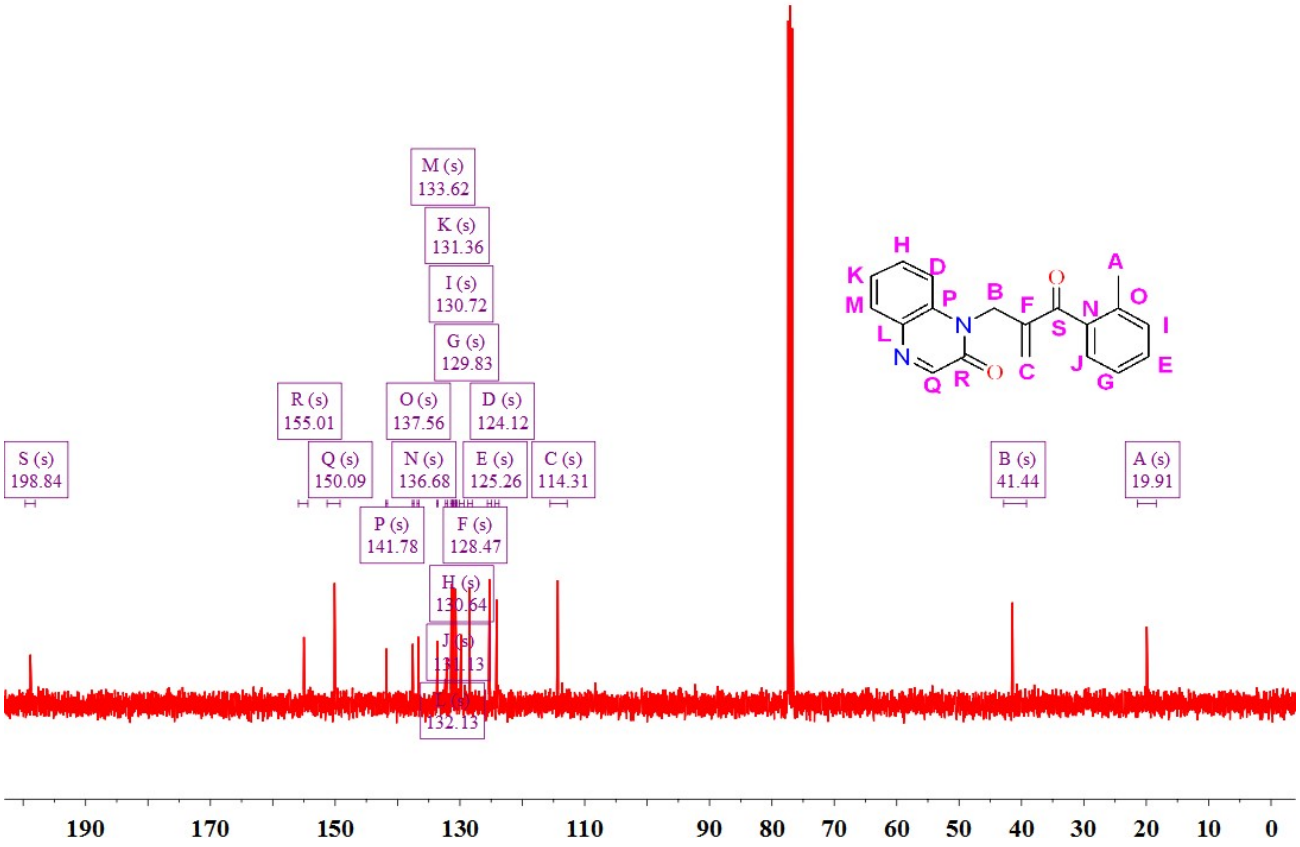
1-(2-(3-Methylbenzoyl)allyl)quinoxalin-2(1H)-one (4k)



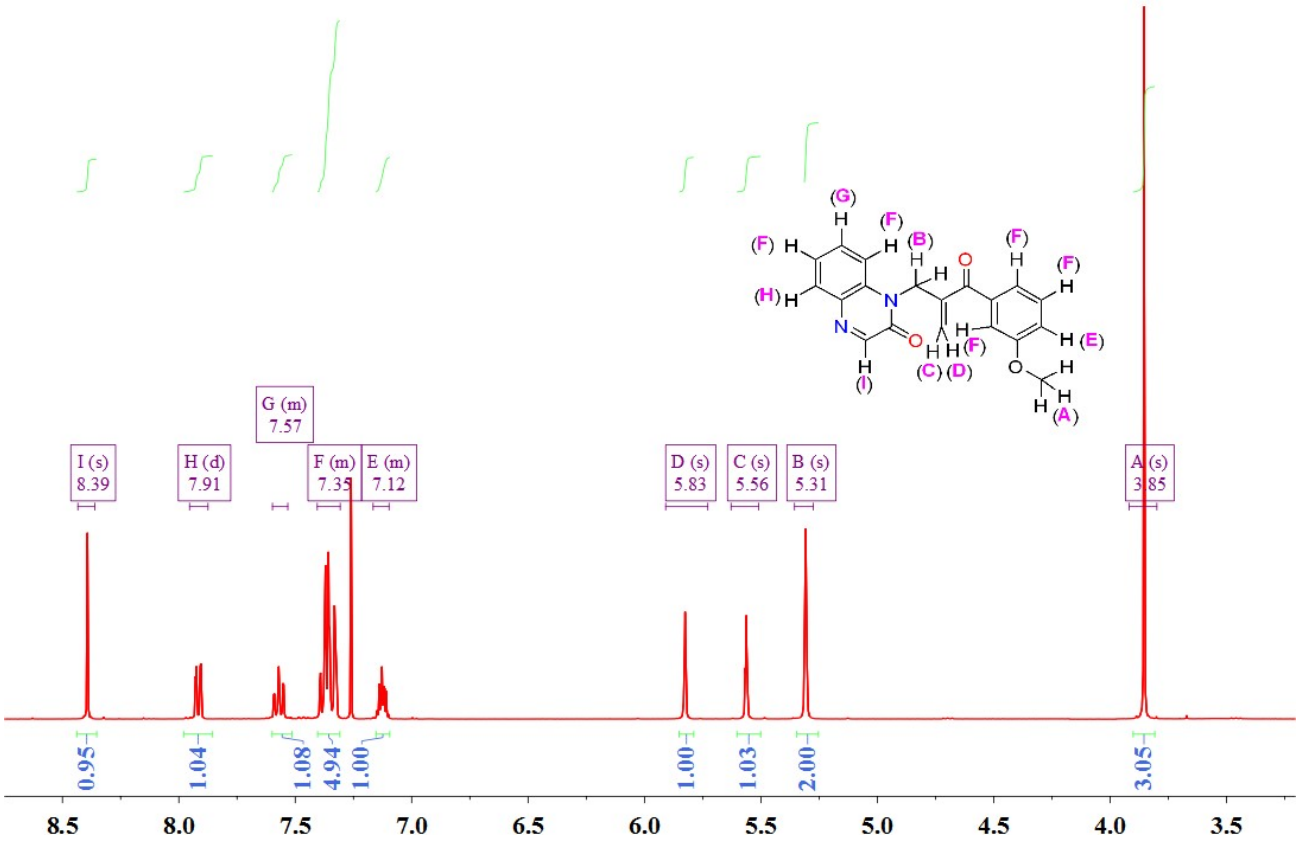


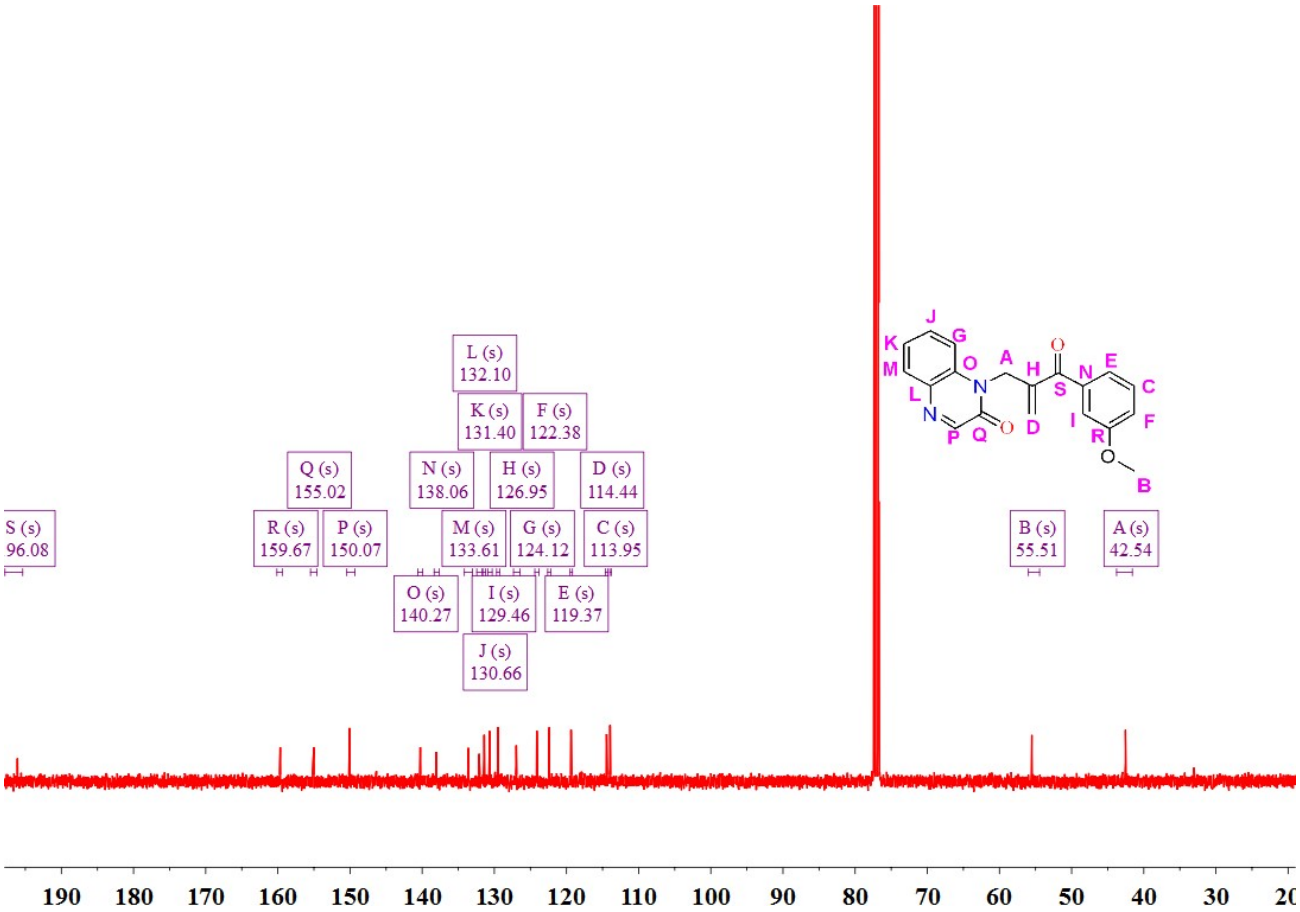
1-(2-(2-Methylbenzoyl)allyl)quinoxalin-2(1H)-one (4l)



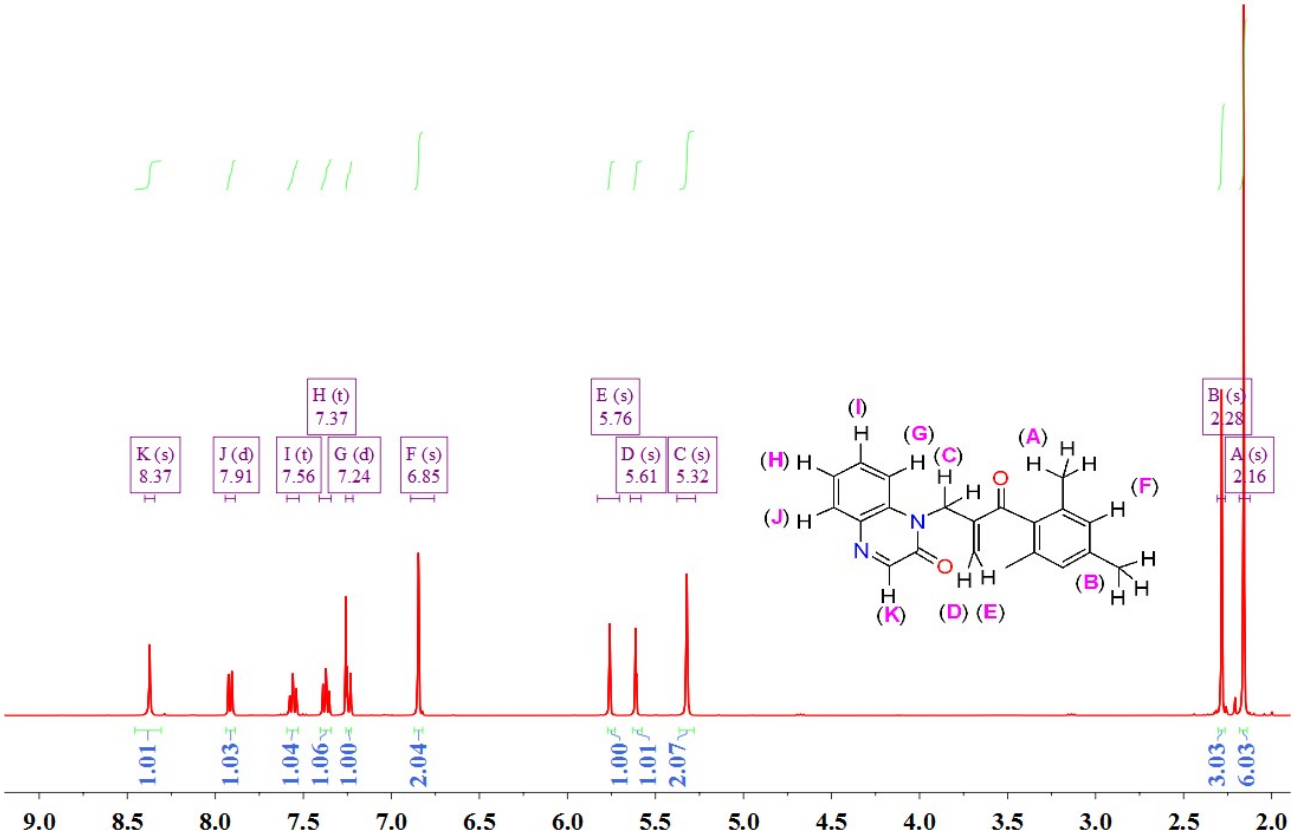


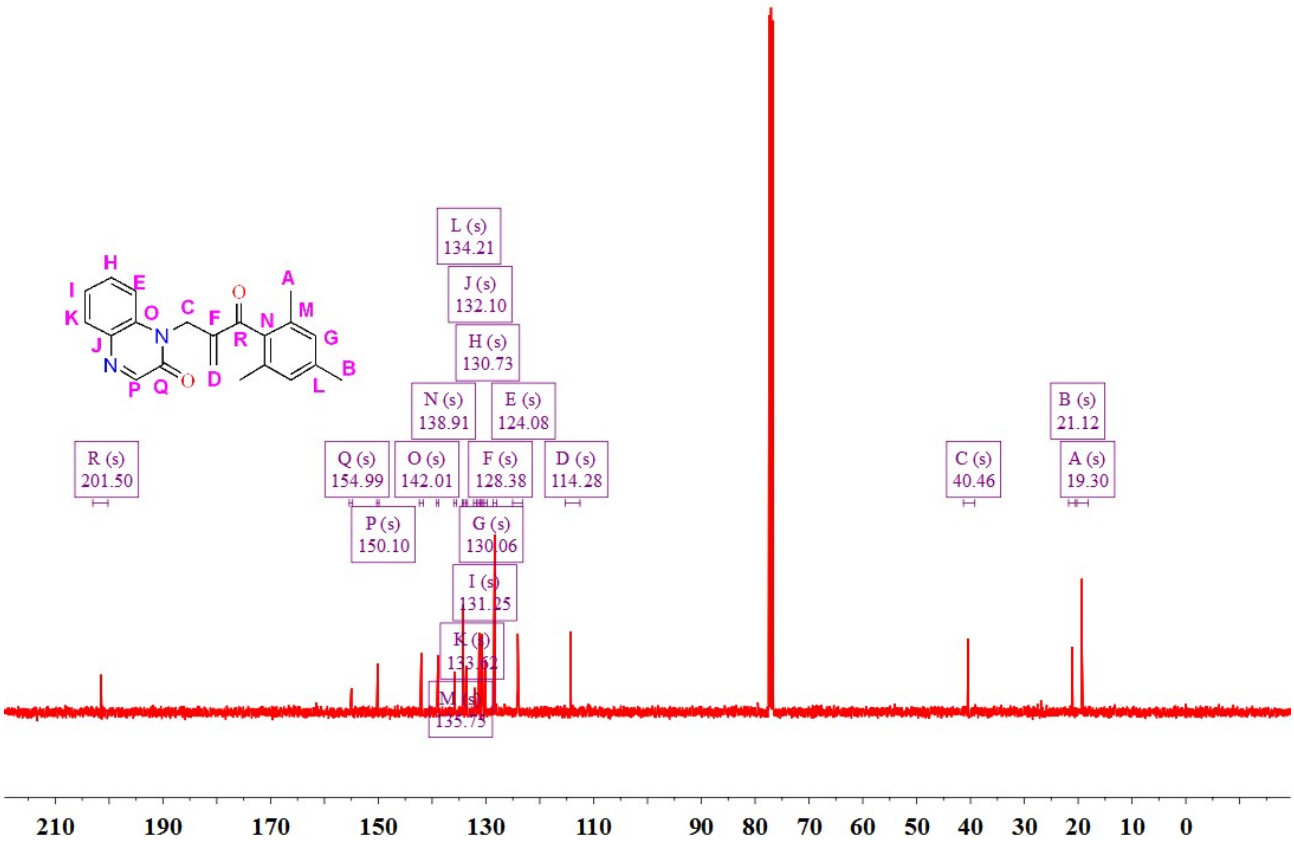
1-(2-(3-Methoxybenzoyl)allyl)quinoxalin-2(1H)-one (4m)



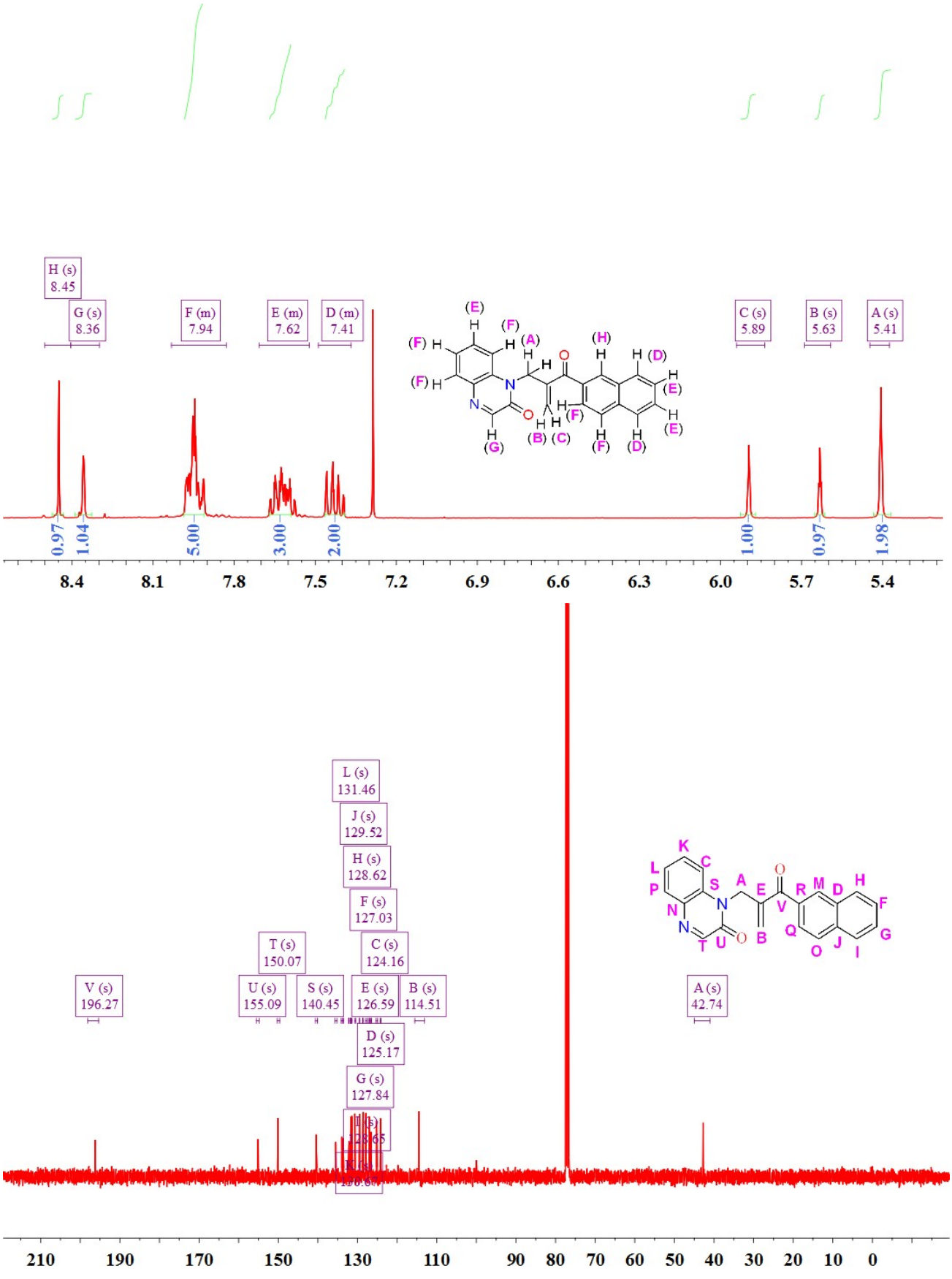


1-(2-(2,4,6-Trimethylbenzoyl)allyl)quinoxalin-2(1H)-one (4n)

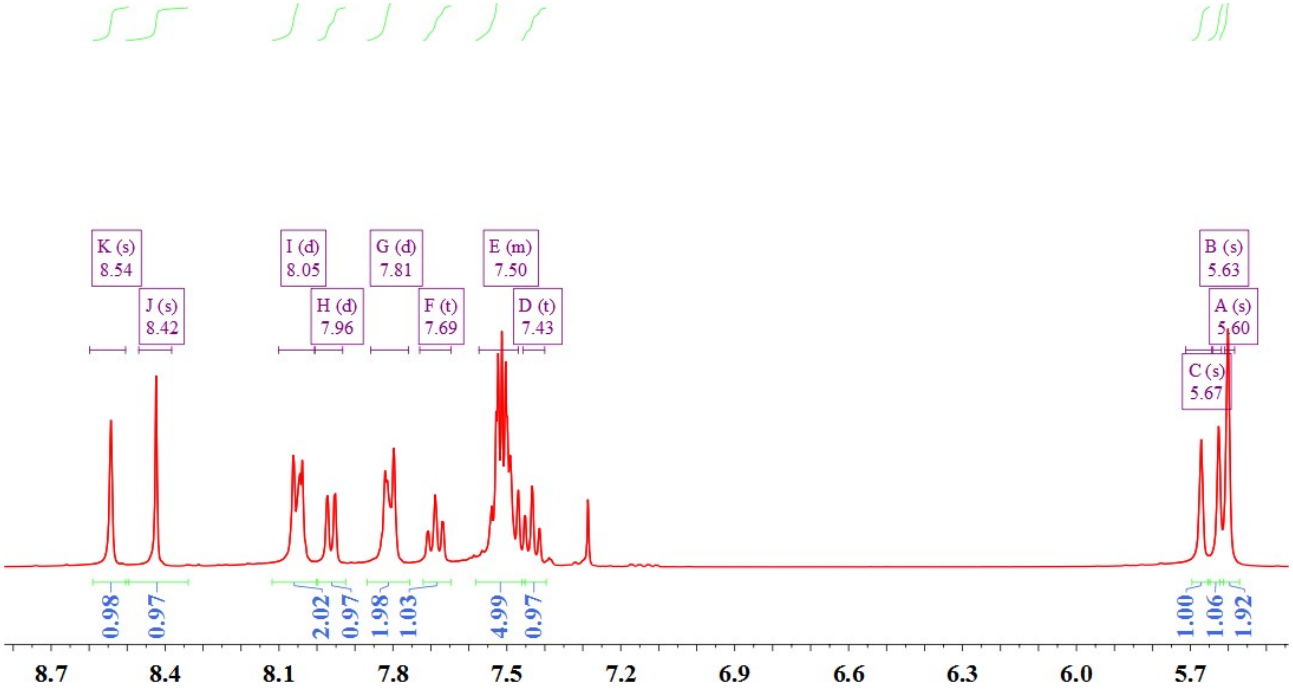


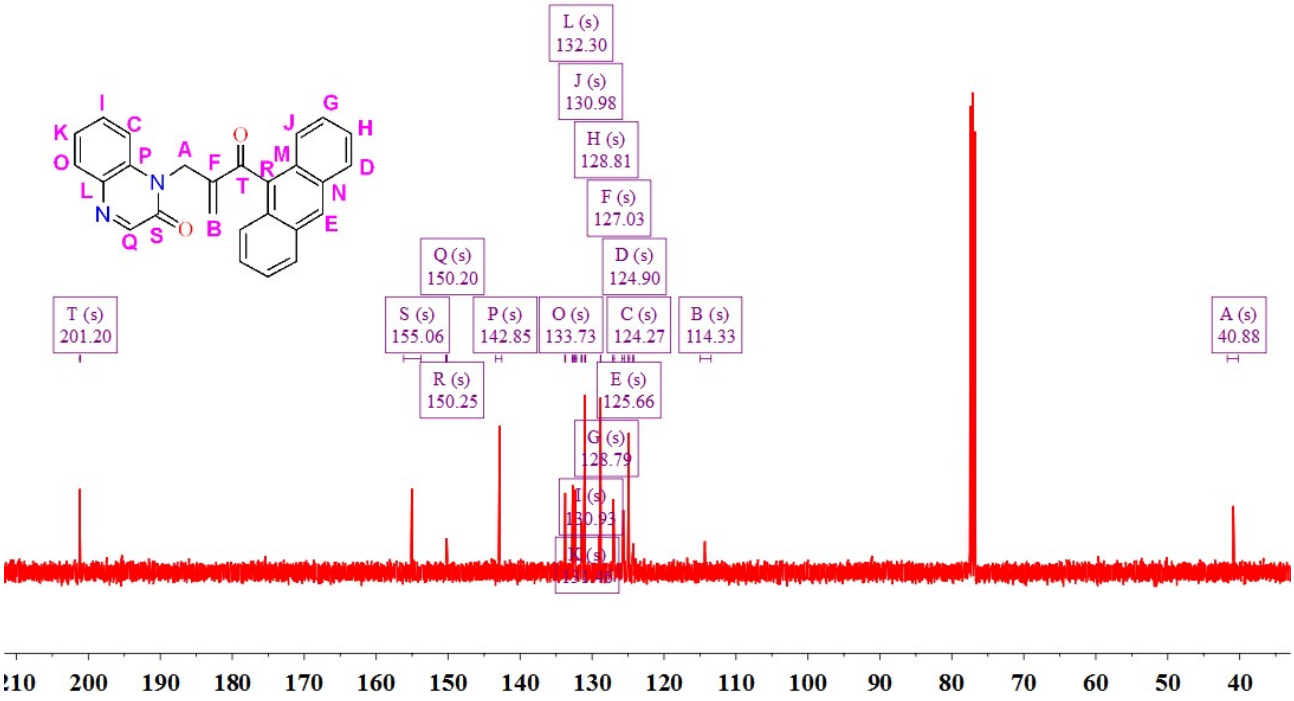


1-(2-(1-naphthoyl)allyl)quinoxalin-2(1H)-one (4o)

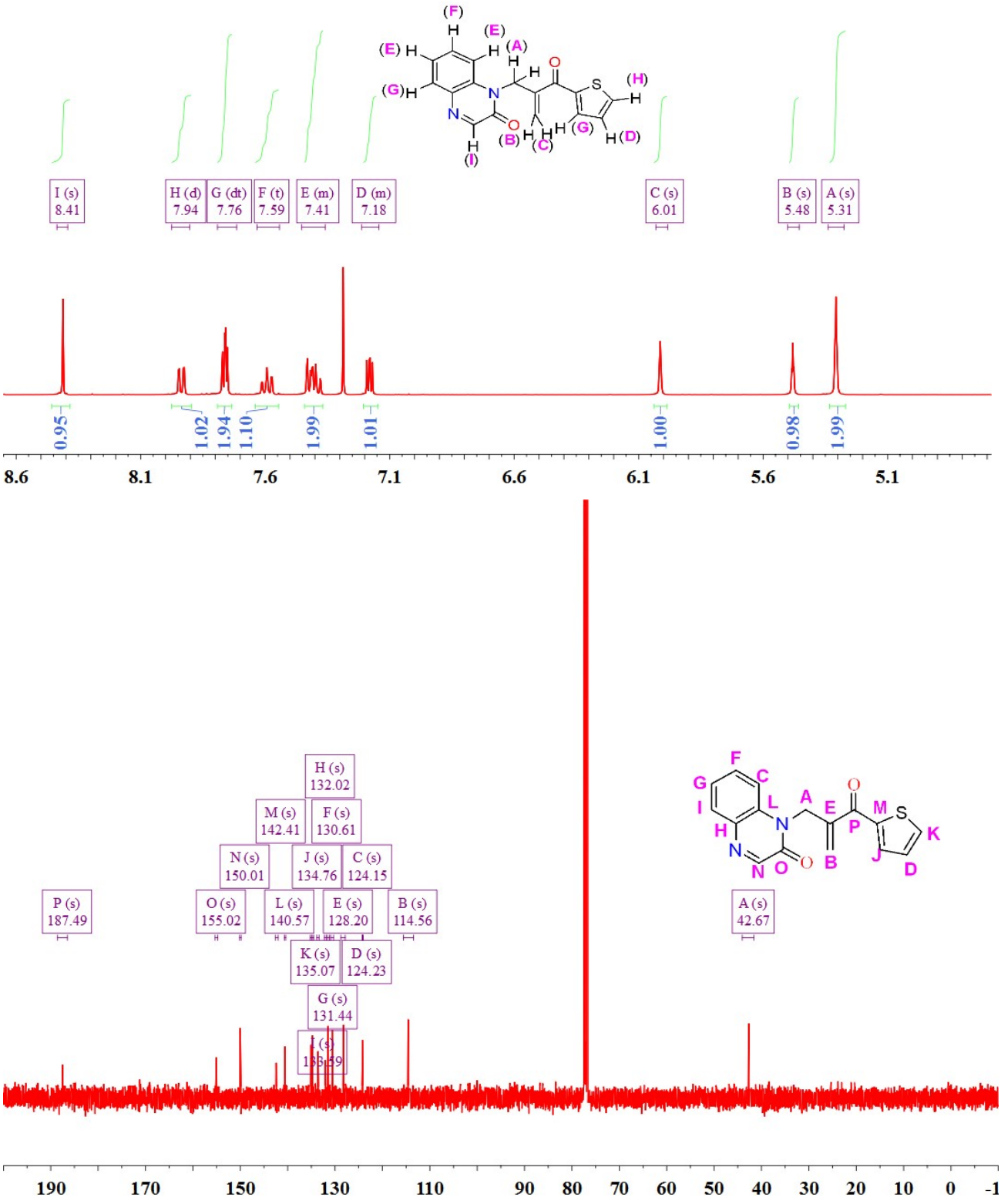


1-(2-(Anthracene-9-carbonyl)allyl)quinoxalin-2(1H)-one (4p)

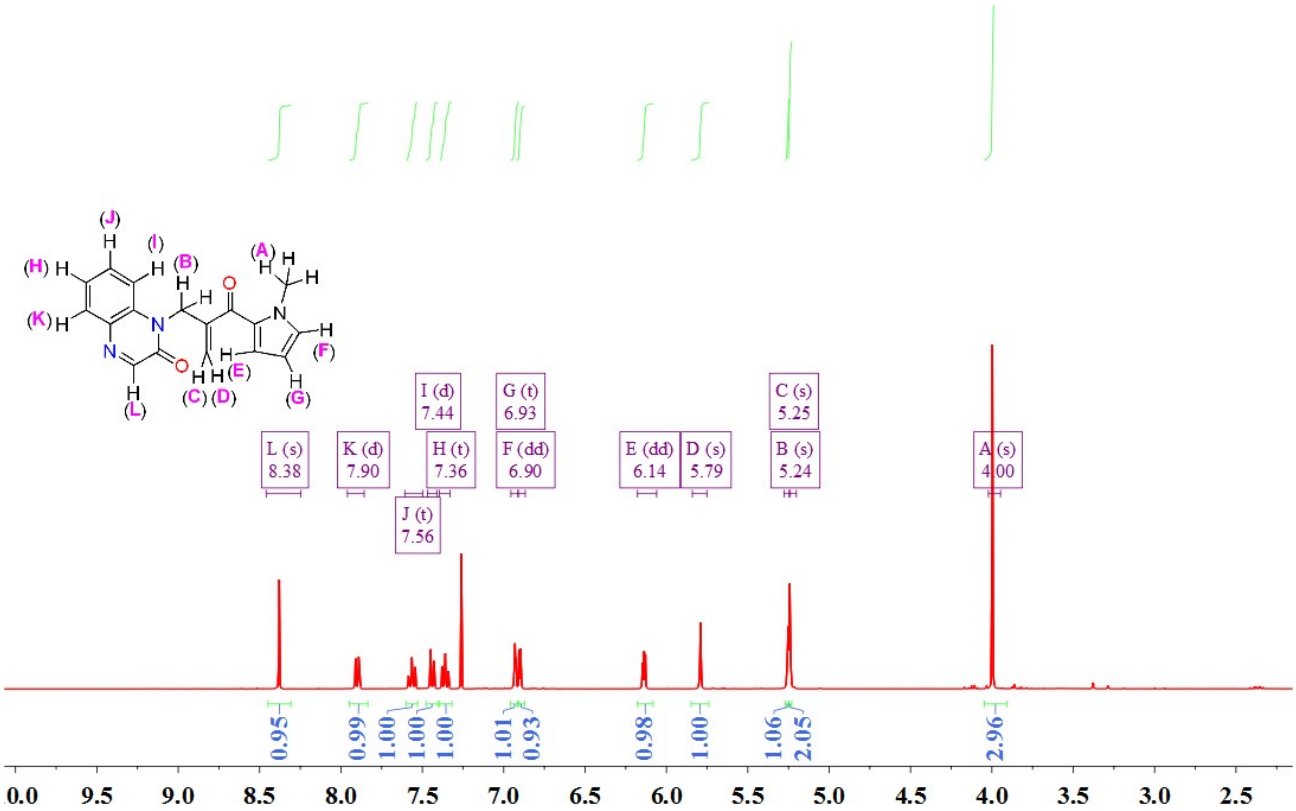


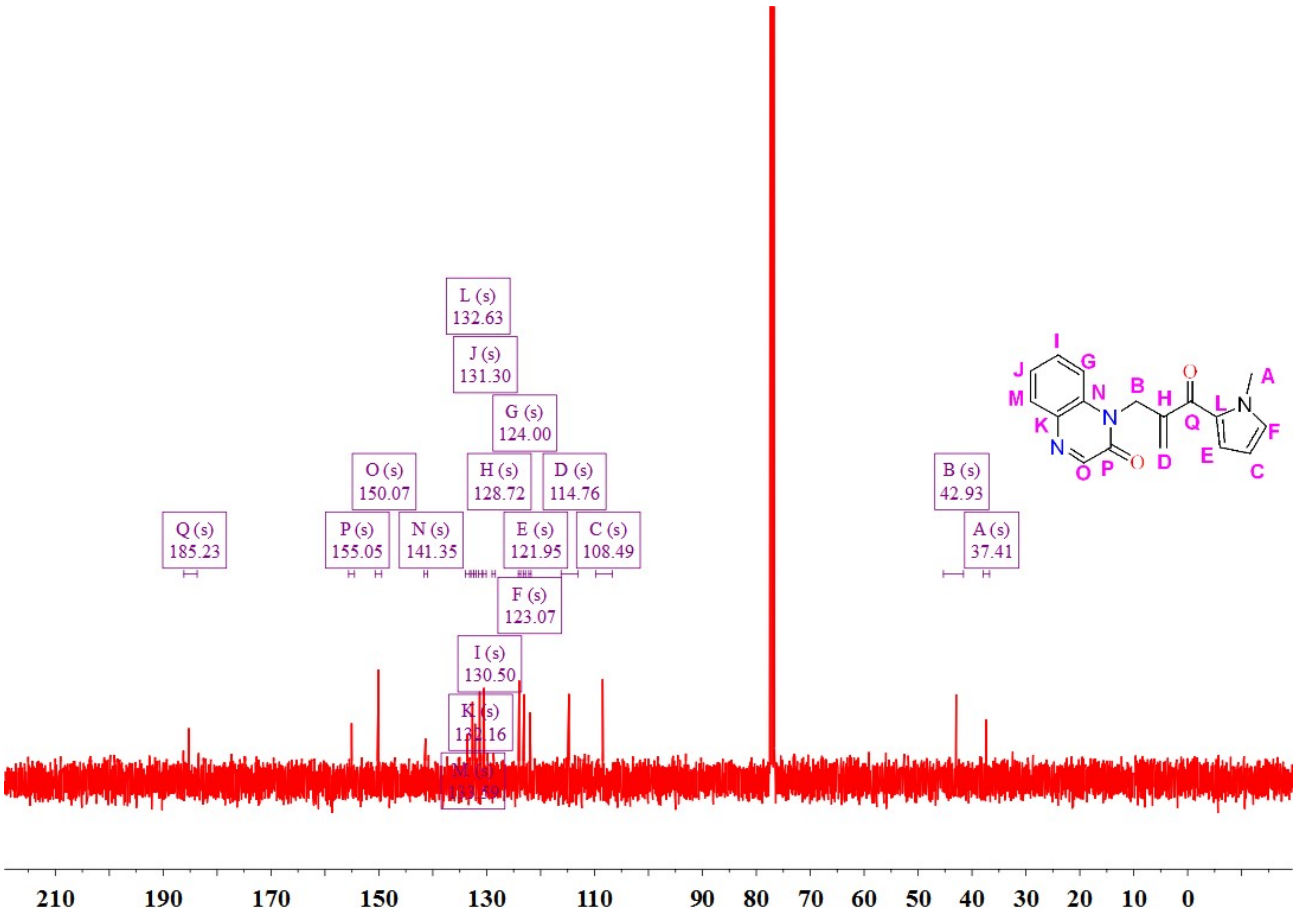


1-(2-(thiophene-2-carbonyl)allyl)quinoxalin-2(1H)-one (4q)

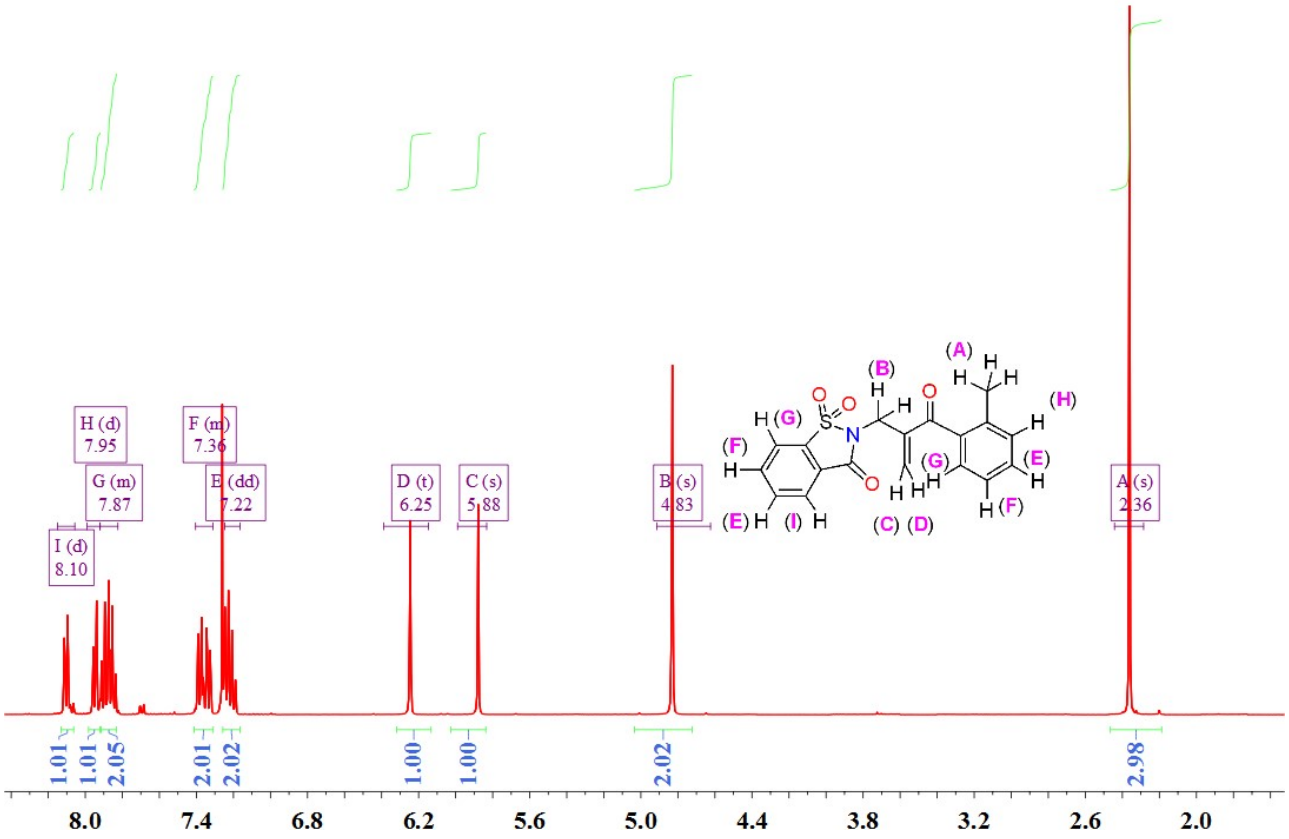


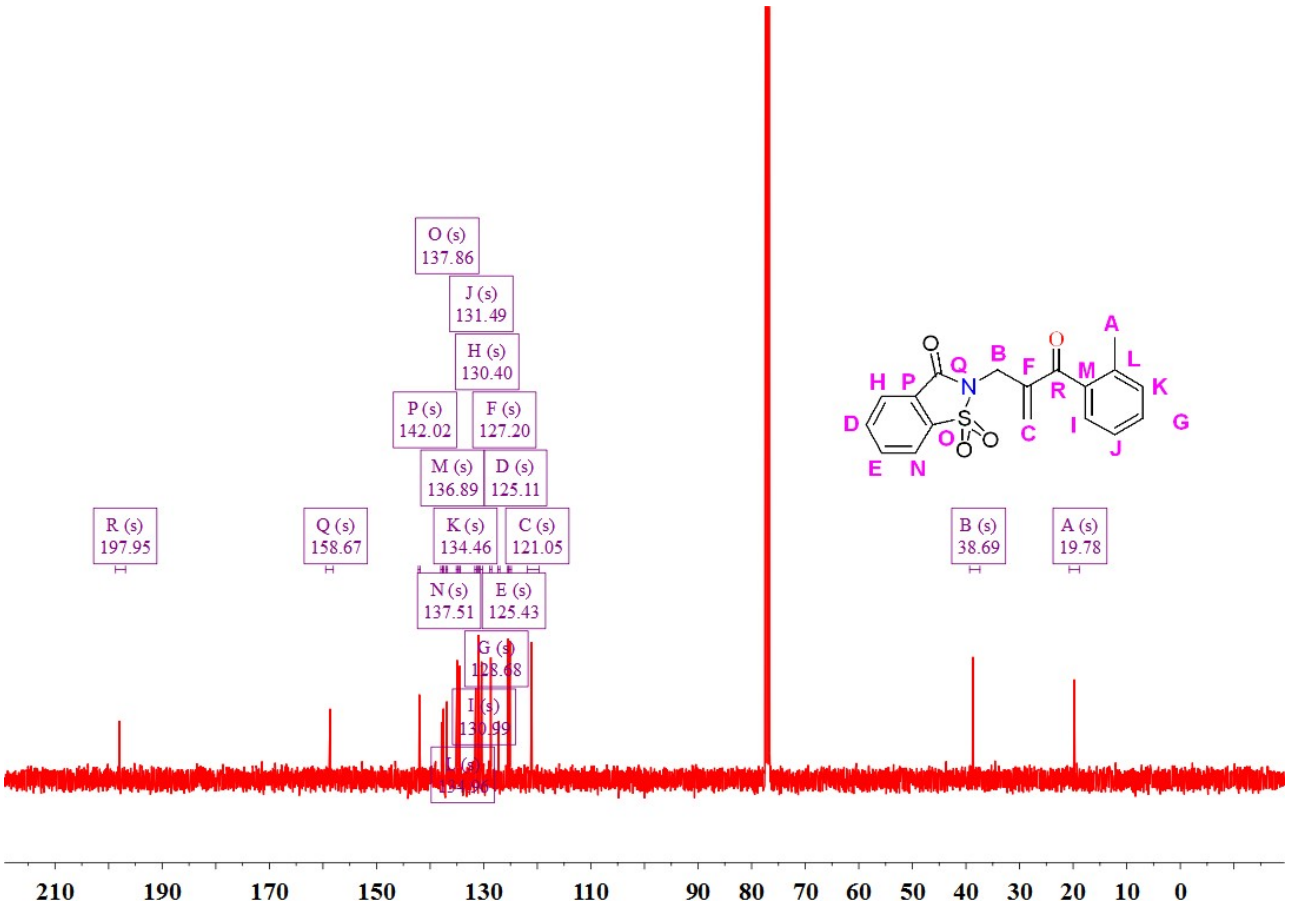
1-(2-(1-methyl-1H-pyrrole-2-carbonyl)allyl)quinoxalin-2(1H)-one (4r)



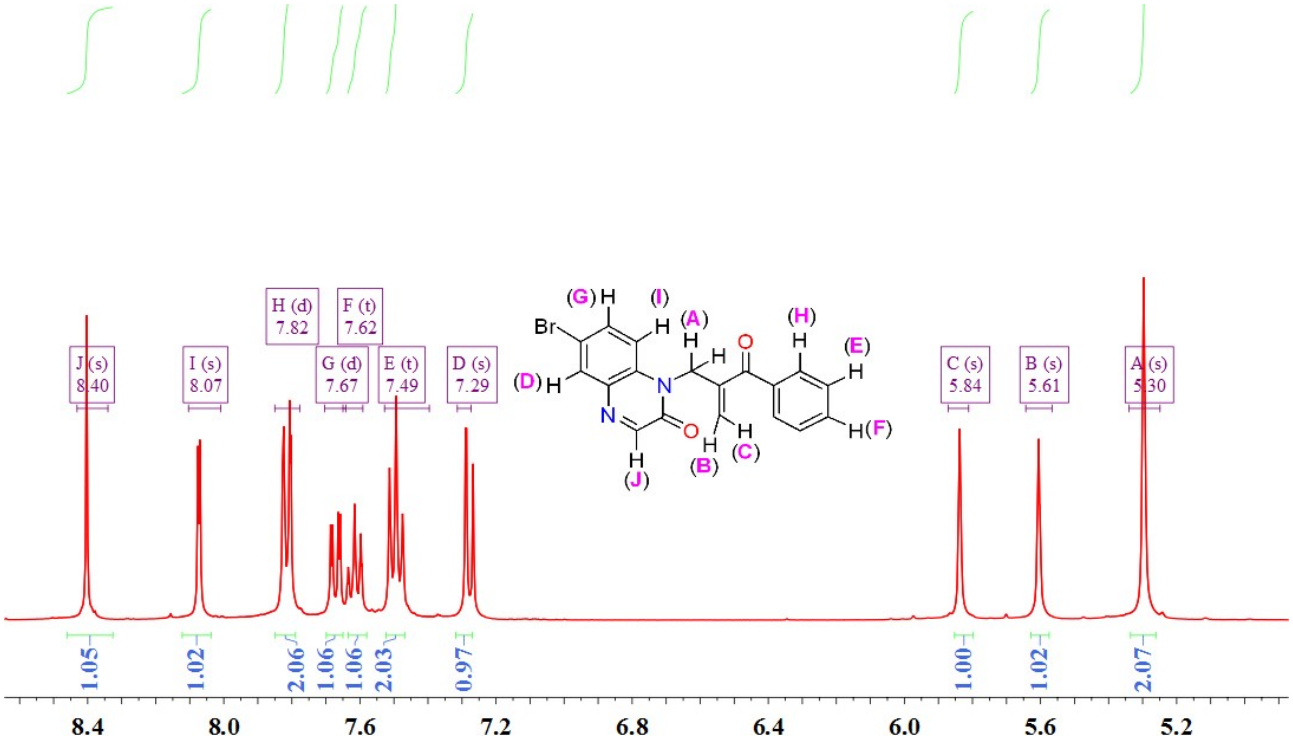


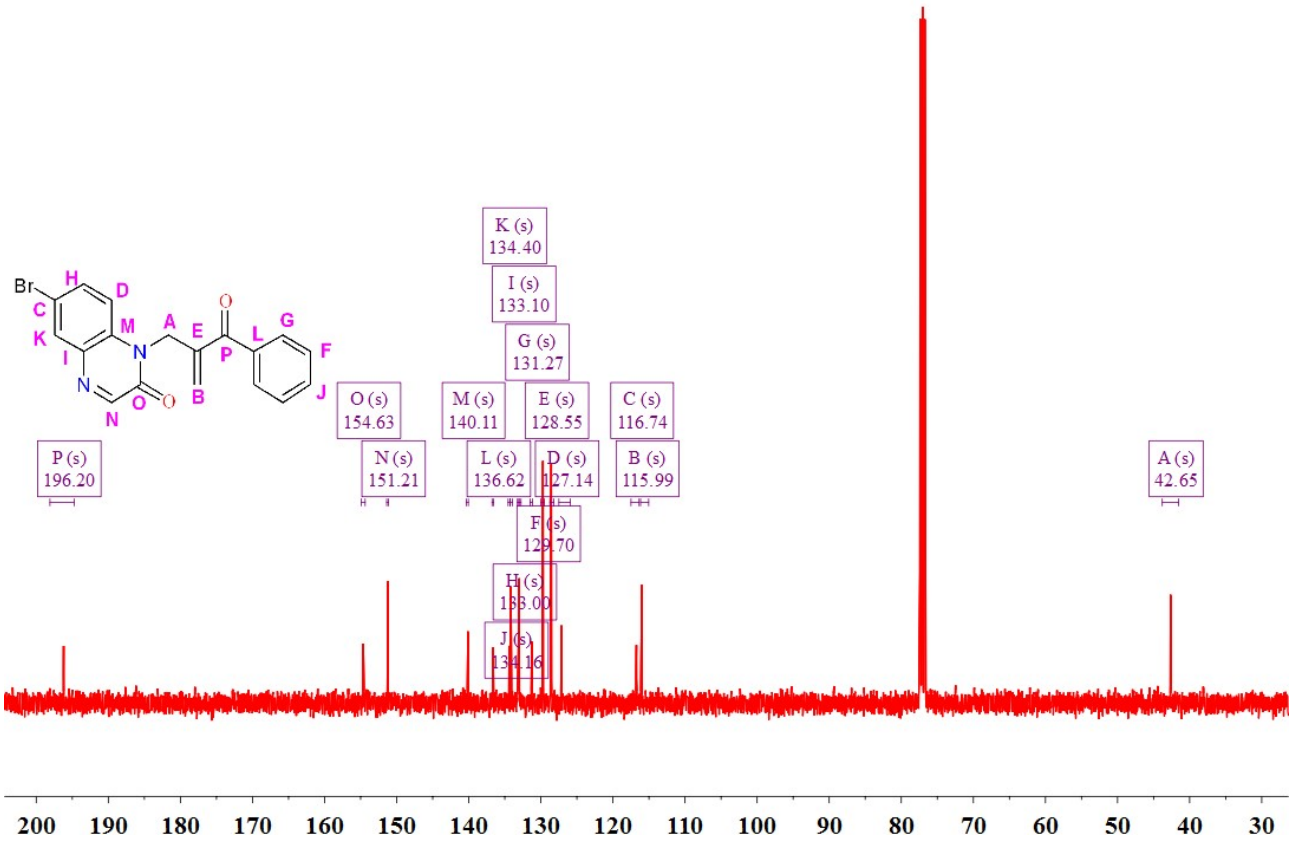
2-(2-(2-methylbenzoyl)allyl)benzo[d]isothiazol-3(2H)-one-1,1-dioxide (4s)



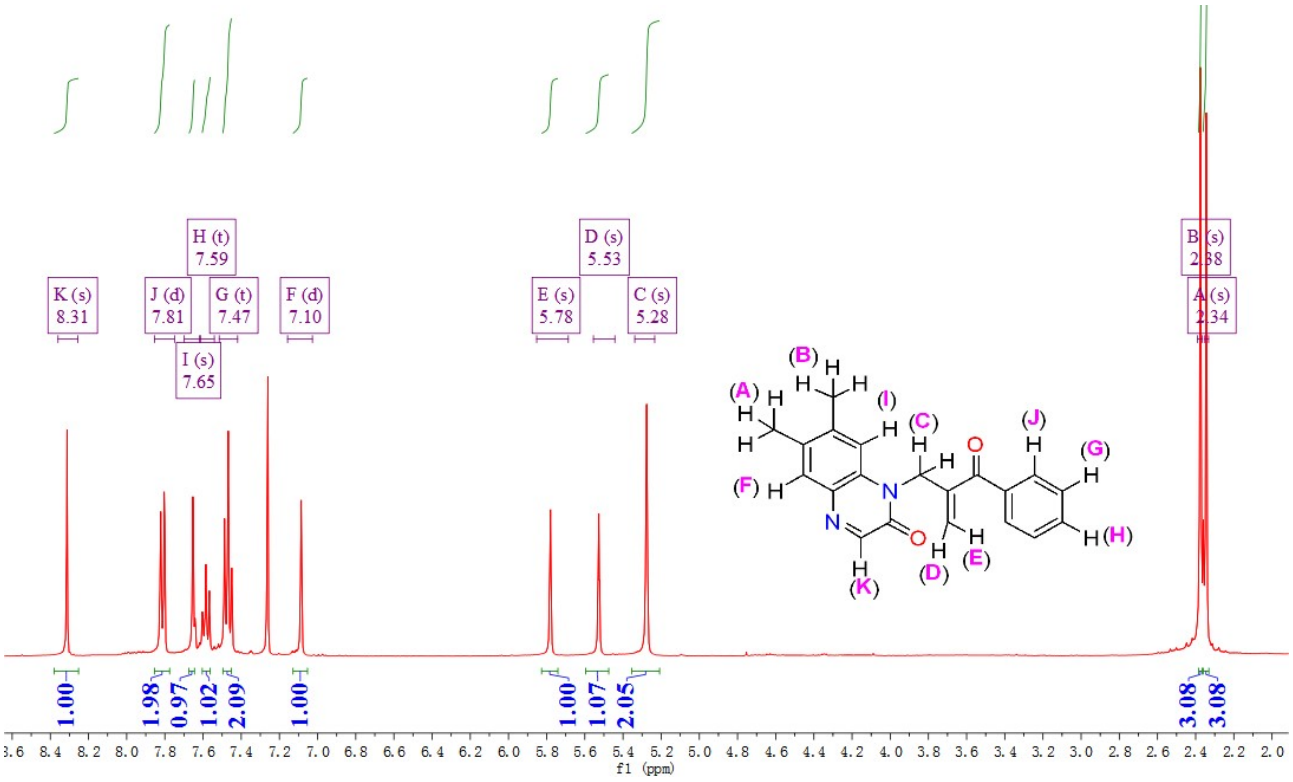


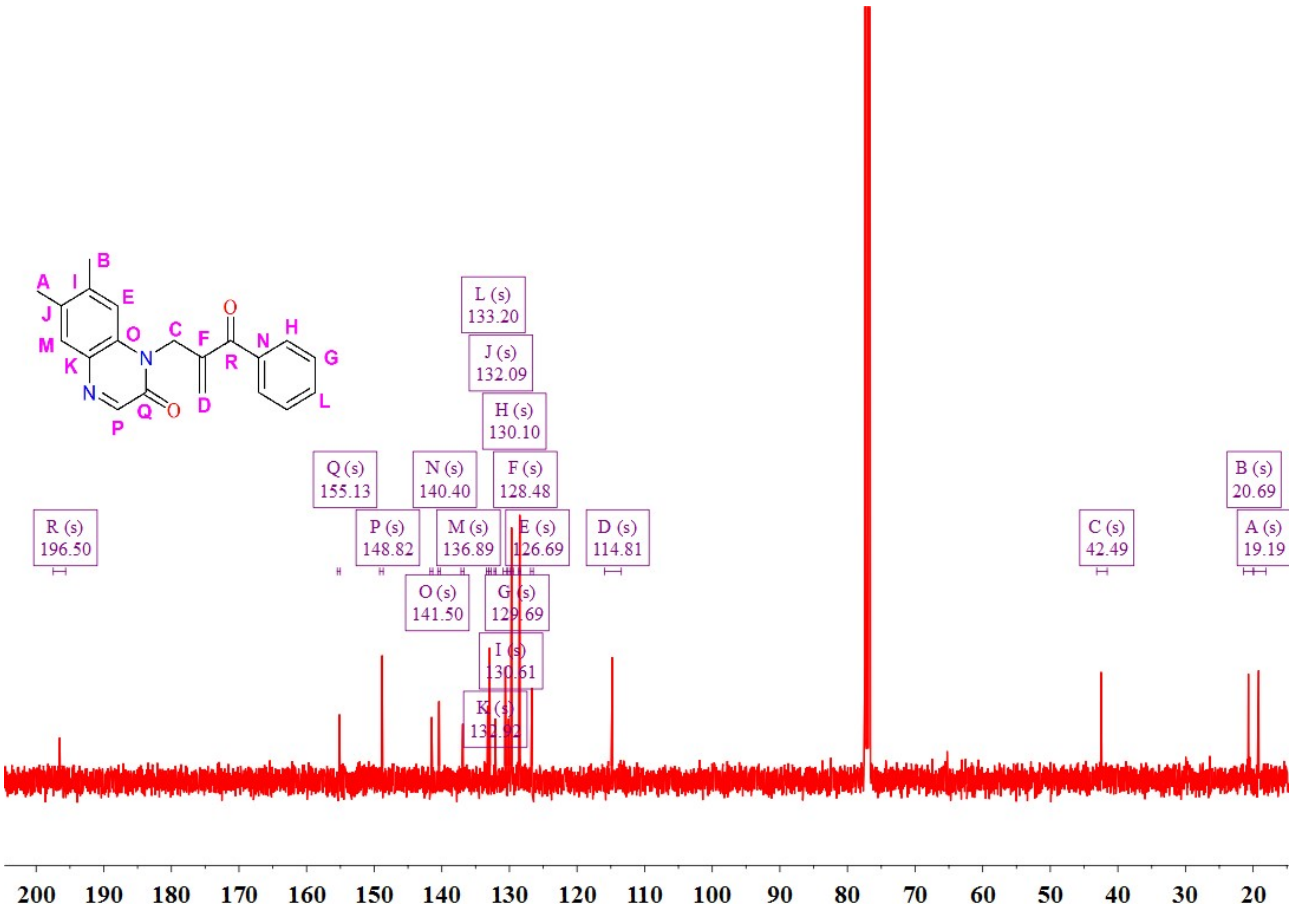
6-bromo-1-(3-methyl-2-oxobut-3-enyl)quinoxalin-2(1H)-one (4t)



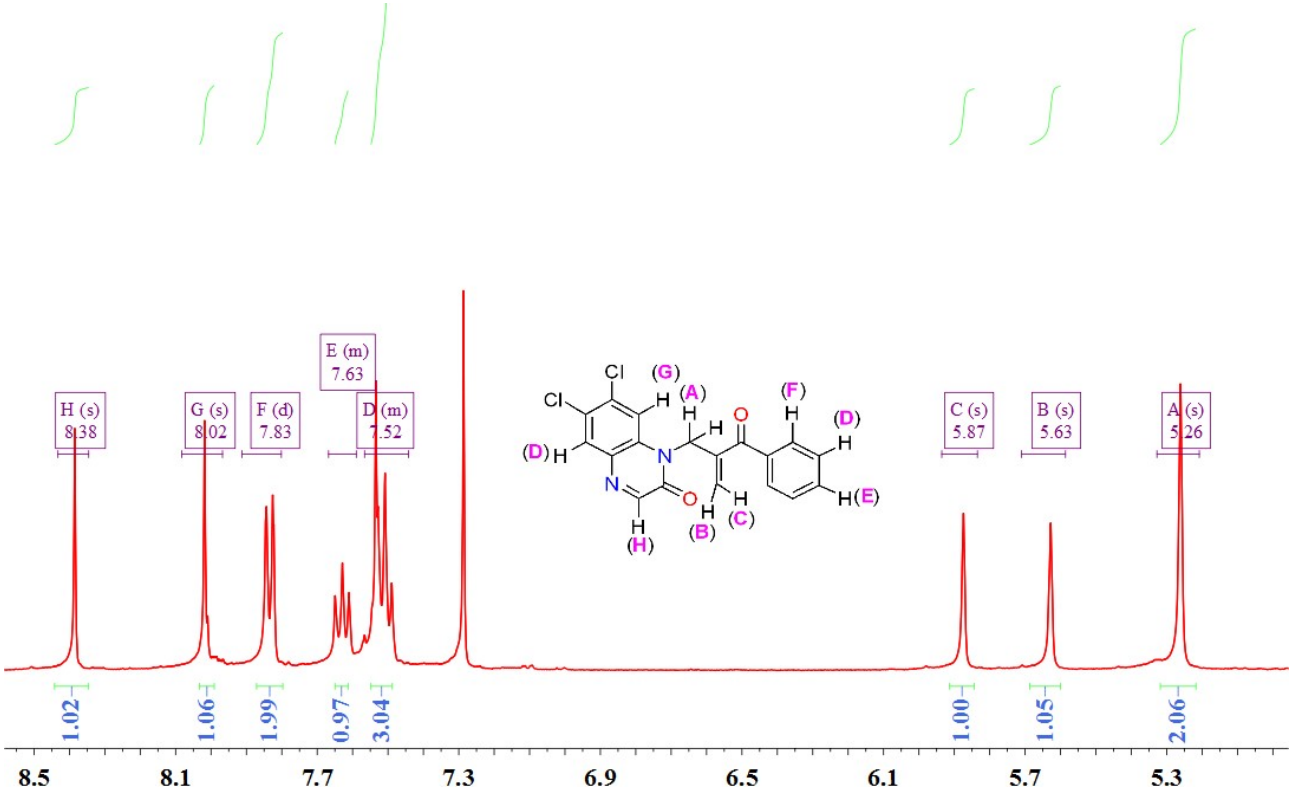


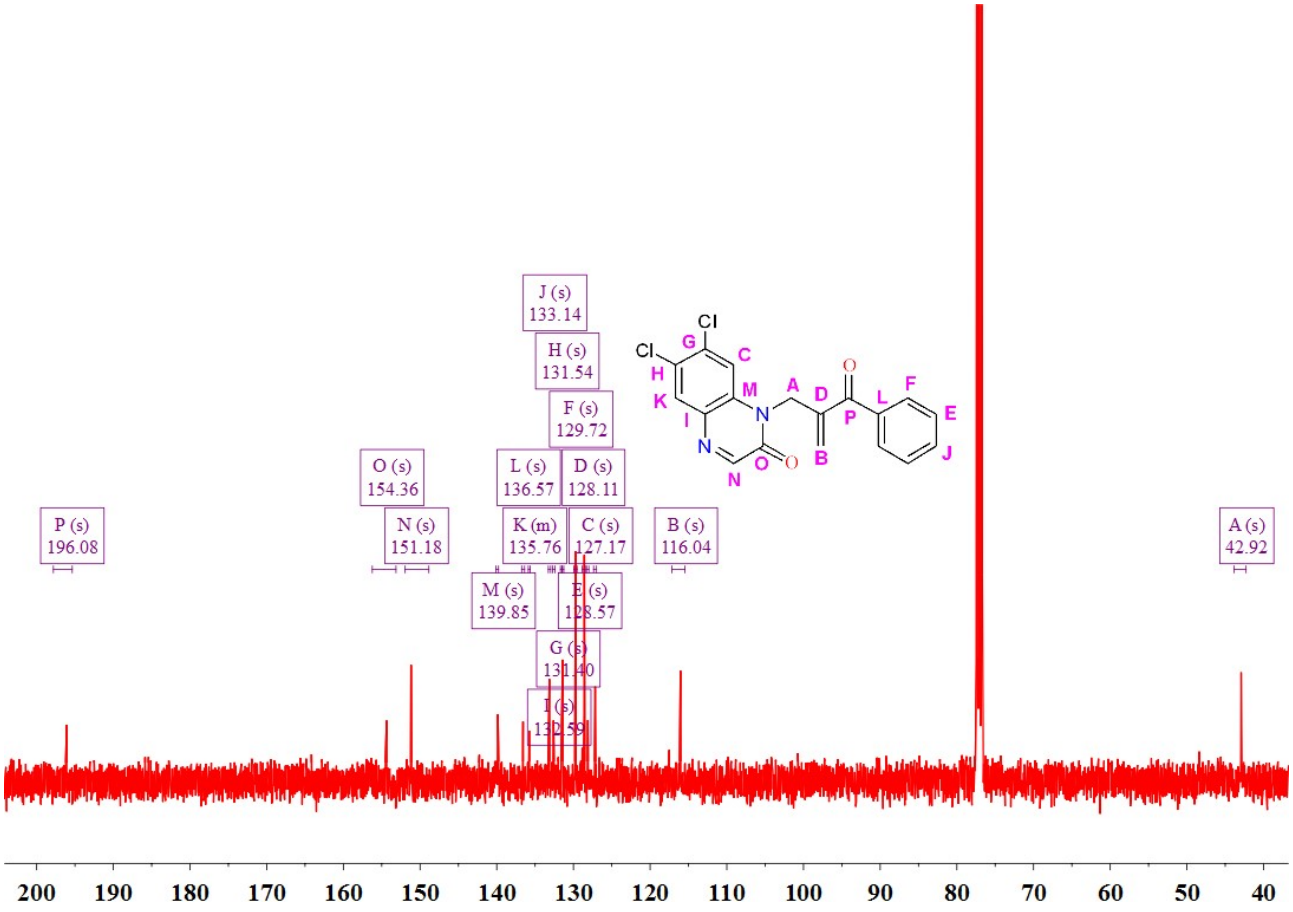
6,7-dimethyl-1-(2-oxo-3-phenylbut-3-enyl)quinoxalin-2(1H)-one (4u)



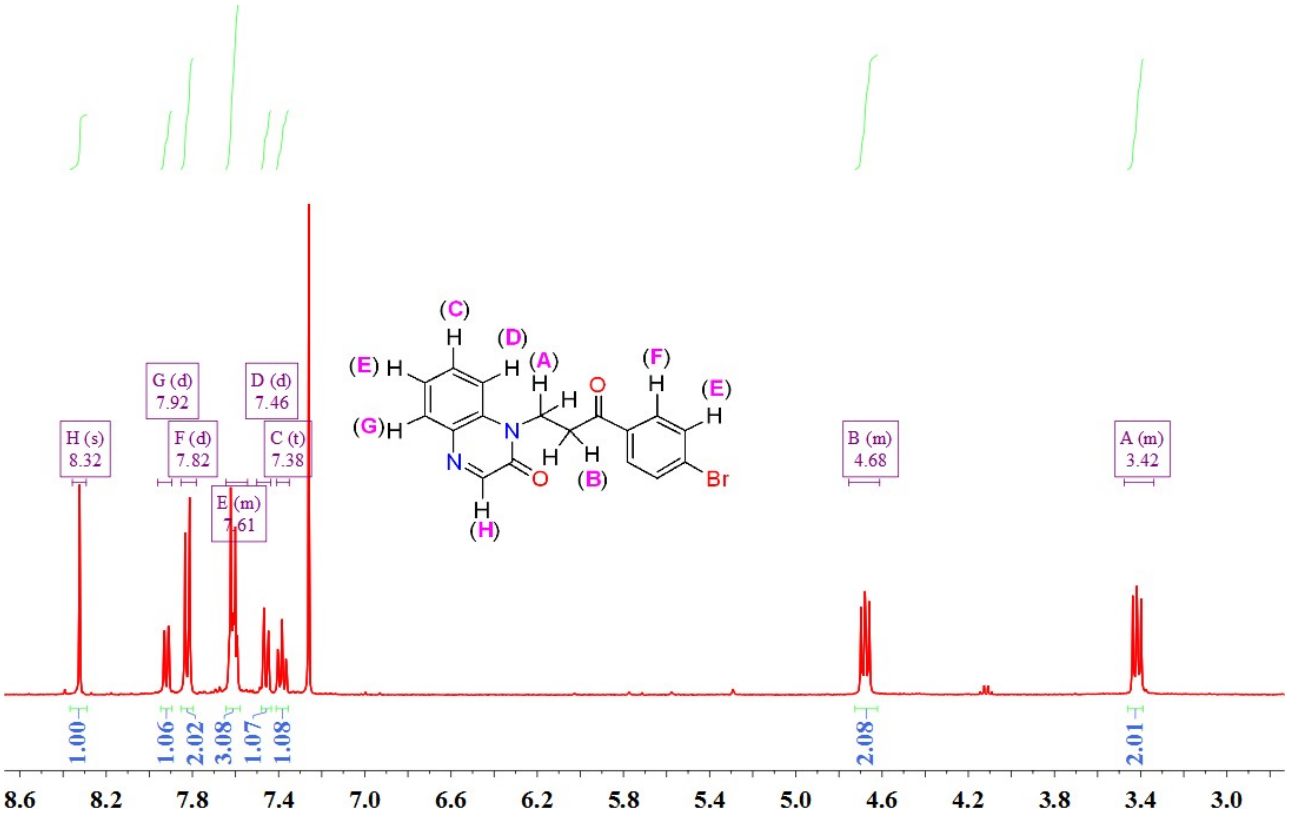


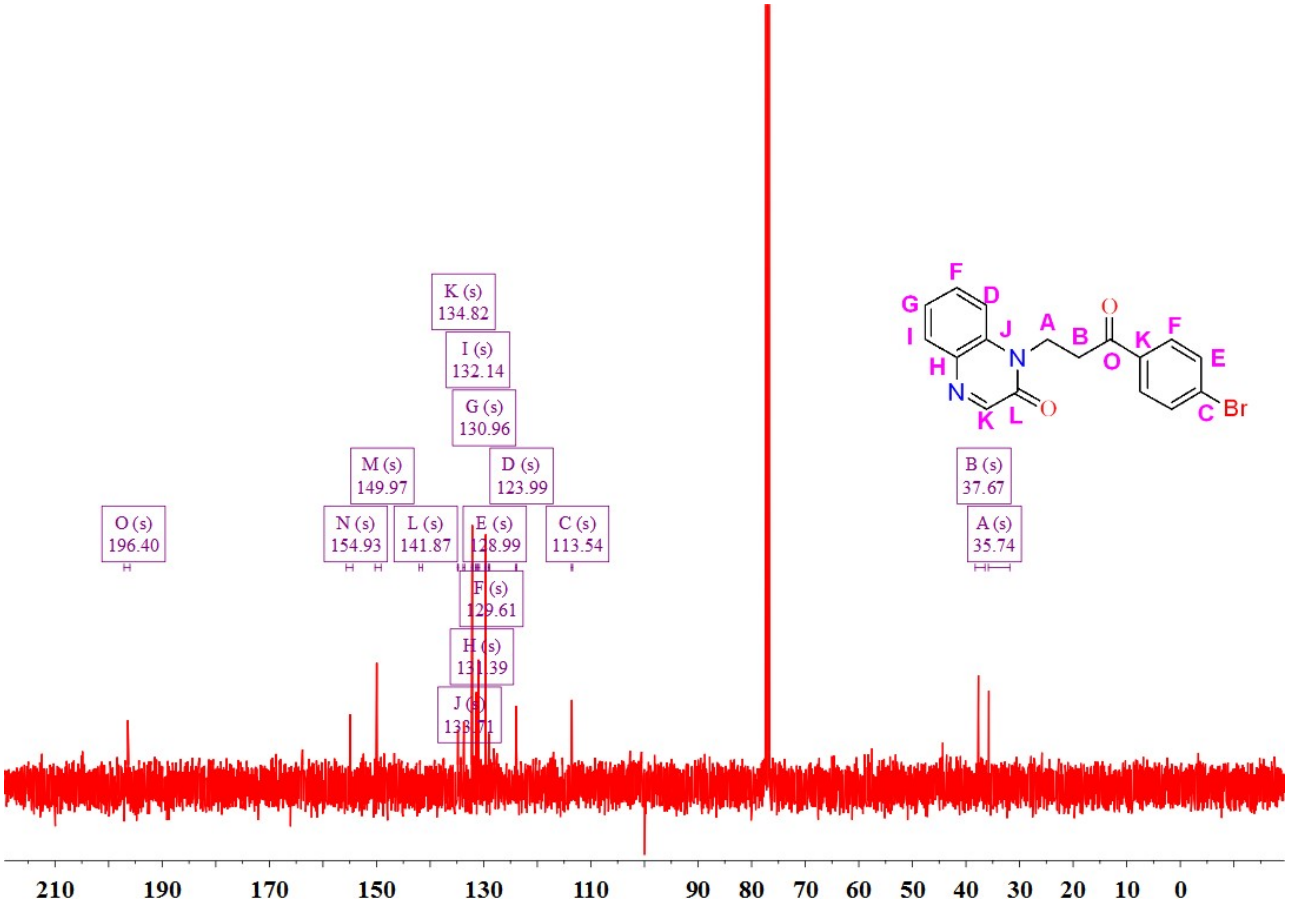
6,7-dichloro-1-(2-oxo-3-phenylbut-3-enyl)quinoxalin-2(1H)-one (4v)



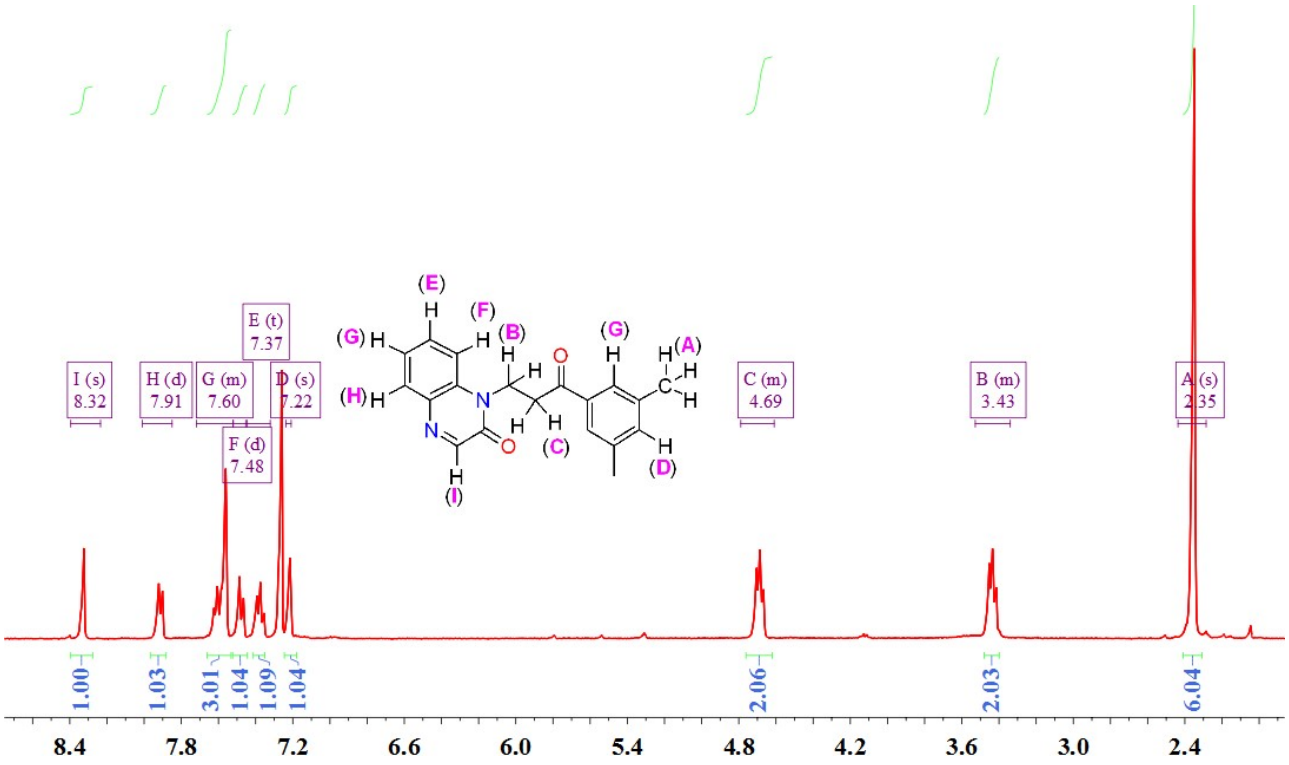


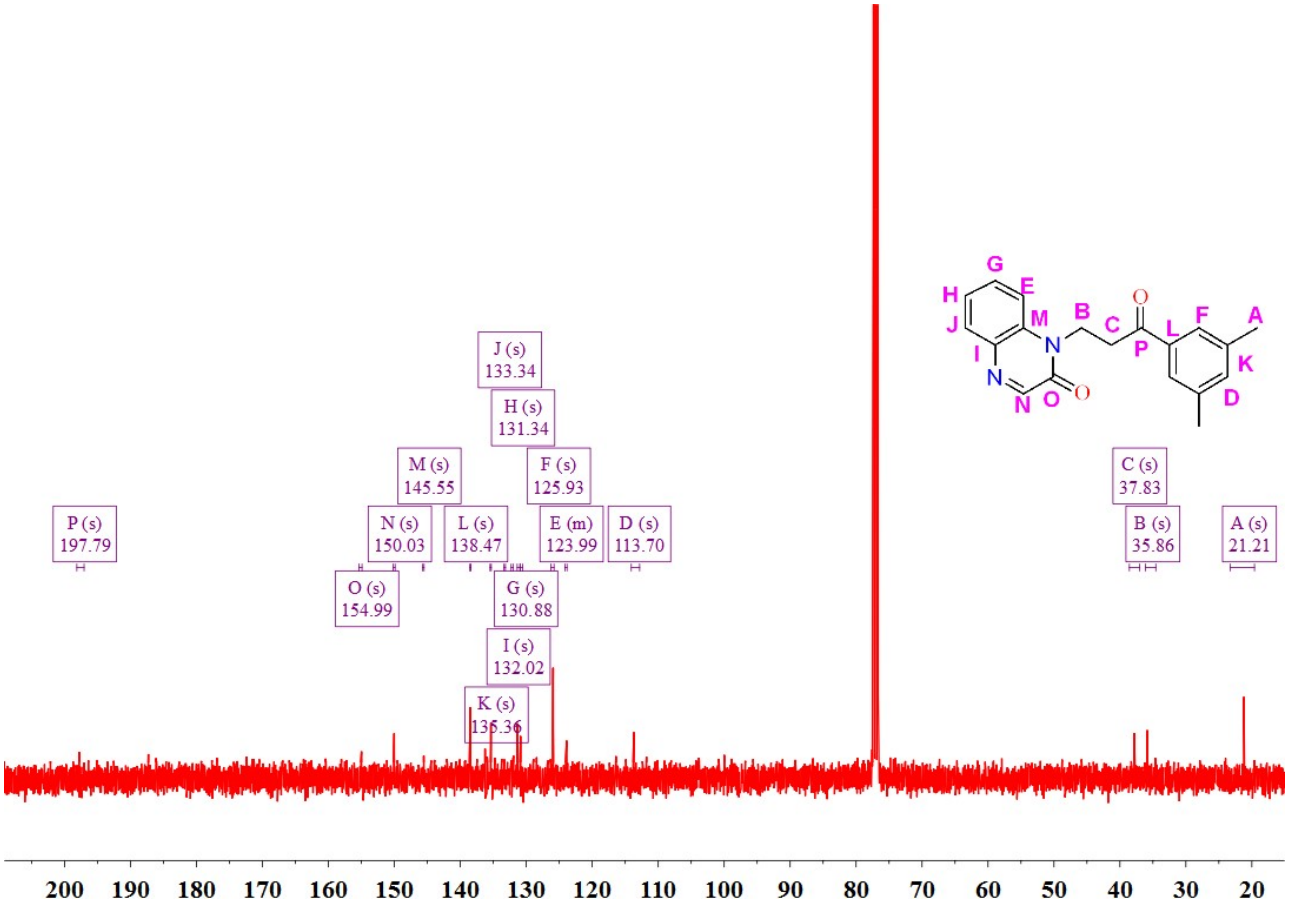
1-(3-(4-bromophenyl)-3-oxopropyl)quinoxalin-2(1H)-one (3t)



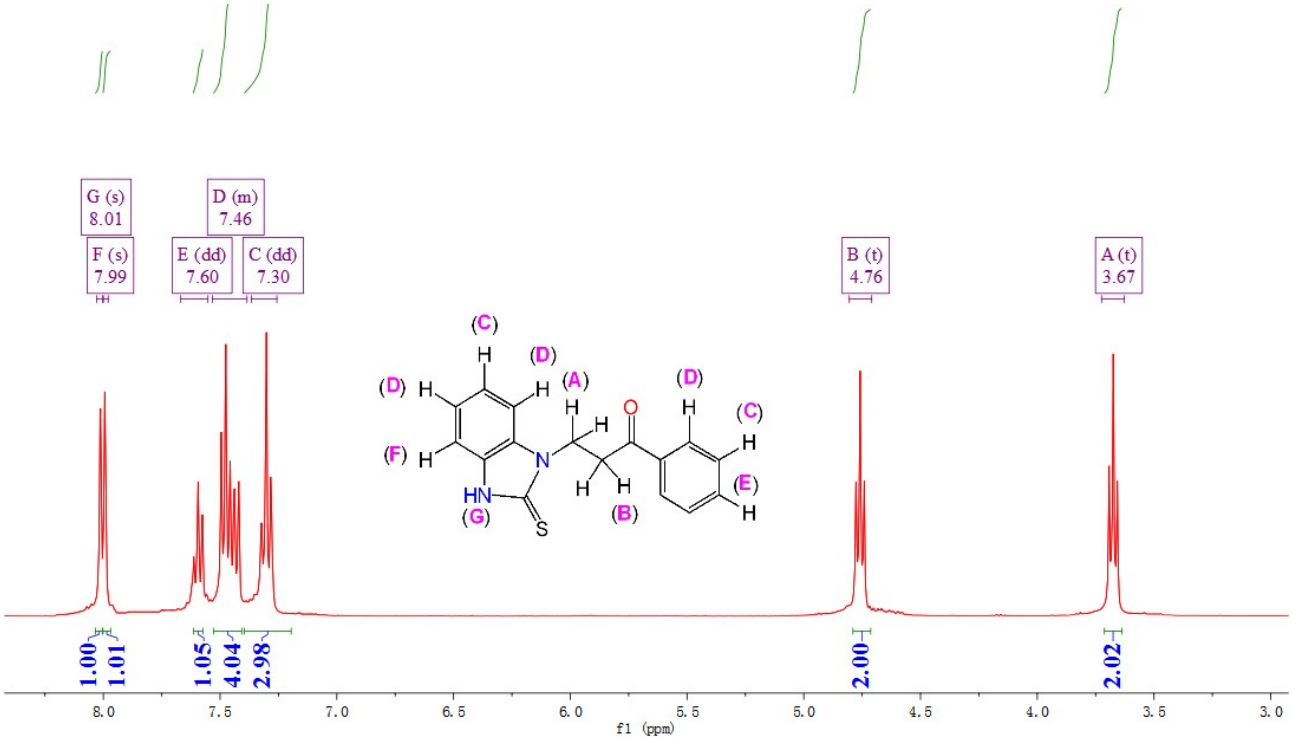


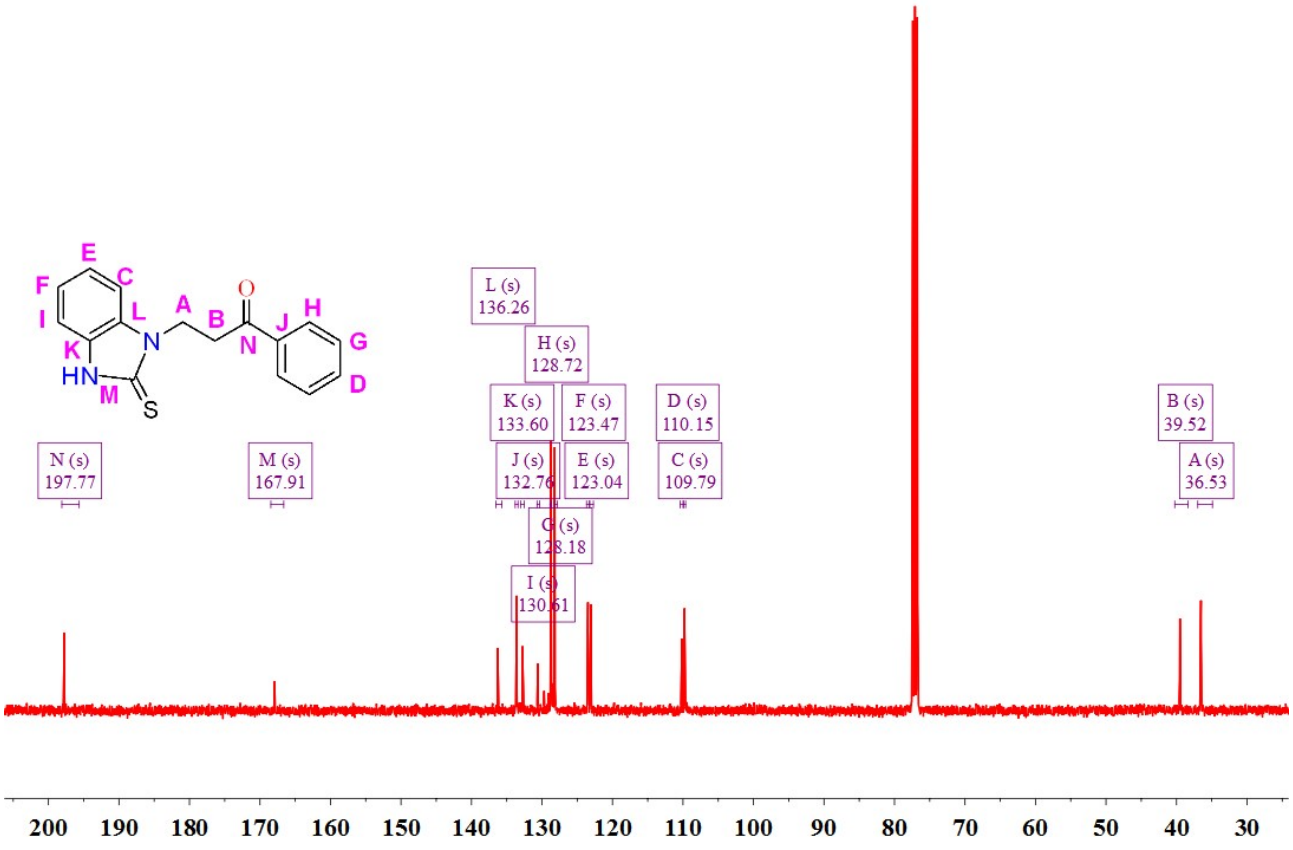
1-(3-(3,5-dimethylphenyl)-3-oxopropyl)quinoxalin-2(1H)-one (3u)



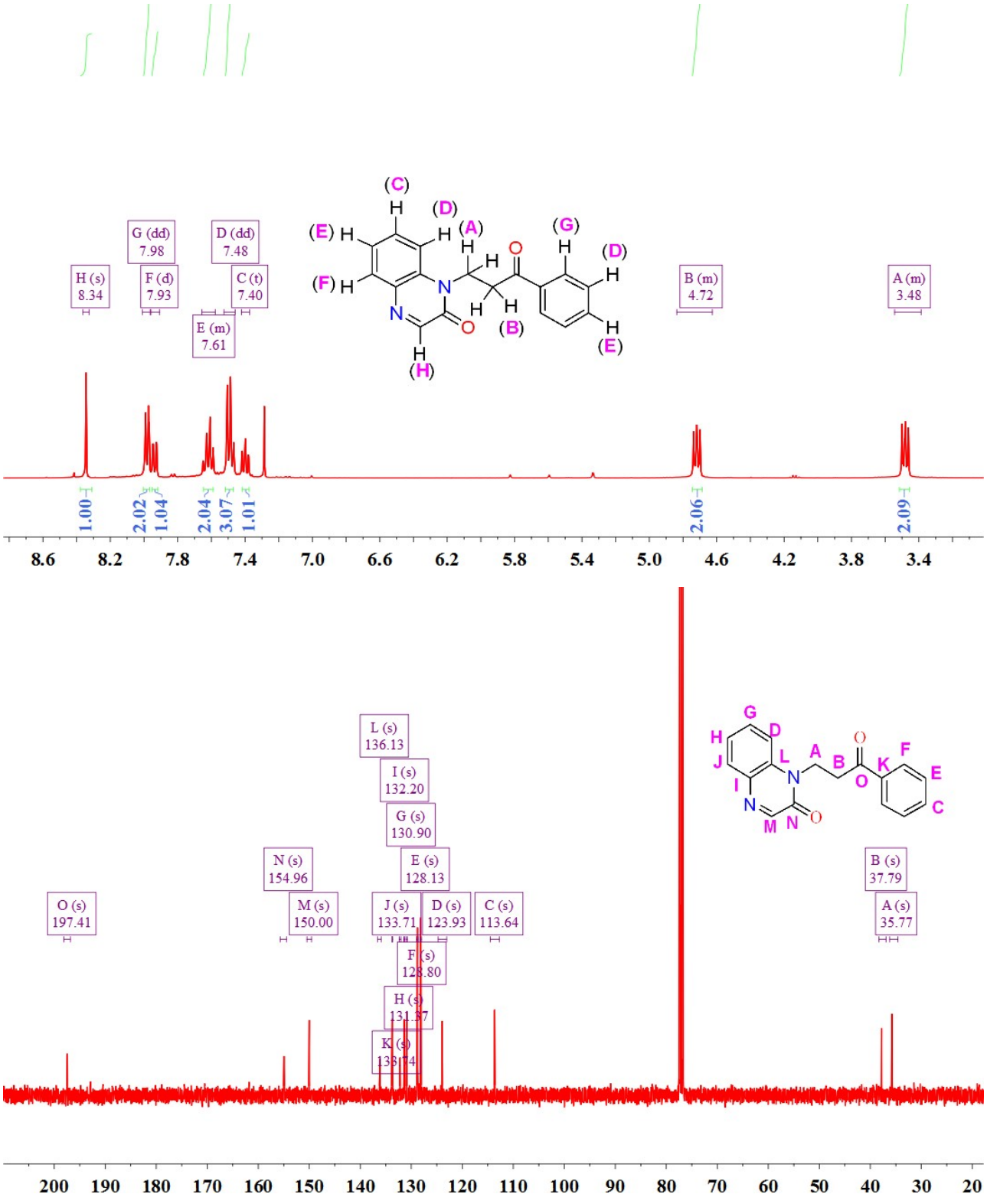


1-phenyl-3-(2-thioxo-2,3-dihydro-1H-benzo[d]imidazol-1-yl)propan-1-one (3v)





1-(3-oxo-3-phenylpropyl)quinoxalin-2(1H)-one (3a)



8. References

1. CrysAlisPro, Oxford Diffraction (Poland), 2010.
2. (a) G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structure. University of Göttingen, Germany 1997. (b) G. M. Sheldrick, *Acta Crystallogr*., 2015, **C71**, 3.