Supporting Information

Visible light-induced g-C₃N₄ Catalyzed C-H acylation and trifluoromethylation of quinoxalinones: an efficient and recyclable approach

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1. General information

1.1 Materials and instruments

All glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Thin-layer chromatography plates were visualized by exposure to ultraviolet light and/or staining with phosphomolybdic acid followed by heating on a hot plate. Flash chromatography was carried out using silica gel (200-300 mesh). Transmission electron microscope (TEM) images were gained with a JEM-100SX (Japan Electronics, Japan) transmission electron microscope under an acceleration voltage of 200kV. Powder X-ray diffraction measurements were recorded by a PAN analytical X'Pert Pro X-ray diffractometer. Scanning electron microscope (SEM) images were recorded on Field Emission Scanning Electron Microscopy (Hitachi SU8010). ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were recorded on a Bruker AM-400 (500 MHz). The spectra were recorded in CDCl₃ as solvent at room temperature, ¹H NMR, ¹³C NMR and ¹⁹F NMR chemical shifts are reported in ppm relative to the residual solvent peak. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale (CDCl₃: $\delta_{\rm H} = 7.27$ ppm, $\delta_{\rm C} = 77.00$ ppm). Data for ¹H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet), integration, coupling constant (Hz) and assignment. HRMS were performed on a Bruker Apex II mass instrument (ESI). The quinoxalin-2(1H)ones¹ were prepared according to the references.

1. (a) Messaoudi, S.; Alami, M. Org. Lett., **2013**, 15, 5606-5609; (b) Chen, D.; Bao, W. Adv. Synth. Catal., **2010**, 352, 955-960.

1.2 Devices for the photocatalytic reactions.

The Photocatalytic reaction was carried out in a custom-fabricated reactor under 6W blue LEDs irradiation. The reaction temperature was adjusted by regulating the flow rate of circulating water. The maximum emission wavelength and half-peak breadth of the blue LED's is 450 nm and 40 nm, respectively.



Figure S1. Devices for the reactions and the emission spectrum of blue LEDs.

2. General procedure for the synthesis of g-C₃N₄ and C-H

functionalization of quinoxalin-2(1H)-ones

2.1 General procedure for the synthesis of g-C₃N₄.

The g-C₃N₄ was synthesized by thermal polymerization of melamine. Specifically, melamine (10.0 g) was added into a crucible, which was capped with a cover. Gradually heated the crucible to the temperature of 550 °C at a heating rate of 2°C/min and maintained at this temperature for 4 hours. Once the heating process is complete, allow the crucible to cool down naturally to room temperature to obtain the g-C₃N₄ catalyst as yellow powder.

2.2 C-H functionalization of quinoxalin-2(1H)-ones



Under N₂ atmosphere, a reaction tube (10 mL) equipped with a magnetic stirrer bar was charged with quinoxalin-2(1*H*)-ones (**1a**, 0.2 mmol), benzaldehyde (**2a**, 0.4 mmol), g-C₃N₄ (10 mg), (NH₄)₂S₂O₈ (0.4 mmol), CH₃CN (1.0 mL). The reaction mixture was stirred with a 6 W blue LEDs irradiation at room temperature for 48 h. After completion of the reaction, the crude mixture was concentrated, further purified by chromatography on silica gel (elute: PE/EA = 5:1) to give the desired product **3a**.



Under N₂ atmosphere, a reaction tube (10 mL) equipped with a magnetic stirrer bar was charged with quinoxalin-2(1*H*)-ones (**1a**, 0.3 mmol), CF₃SO₂Na (**4a**, 0.36 mmol), g-C₃N₄ (10 mg), (NH₄)₂S₂O₈ (0.6 mmol), DMSO (1.0 mL). The reaction mixture was stirred with a 6 W blue LEDs irradiation at room temperature for 12 h. After disappearance of quinoxalin-2(1H)-ones, the resulting mixture was added with water, and extracted with ethyl acetate for three times. The combined organic layers were dried over Na₂SO₄, filtered and evaporated under reduced pressure. The residue was purified by chromatography on silica gel (elute: PE/EA = 5:1) to give the desired product **5a**.



Two region isomers were obtained in the reaction between 4-methyl-*o*-phenylene diamine and ethyl glycolate, and the two isomers cannot be separated by column chromatography.

3. Control experiments

Two equivalents of TEMPO (2,2,6,6-tetramethylpiperidinoxy) or BHT (Butylated Hydroxytoluene) were added to the reaction of 1a with 4 under the standard conditions. The reaction mixture was then stirred under the irradiation with 6 W blue LEDs for 24 h. The desired product 5a was not detected in the reaction system. Note that, the radical trapping product can be found through LC-MS analysis. The results were shown in Figures S3 and S4.





Figure S3. LC-MS analysis of the adduct of TEMPO and trifluoromethyl radical.



Figure S4. LC-MS analysis of the adduct of BHT and trifluoromethyl radical.

4. Light on/off experiments



Figure S5. Light on/off experiments.

5. Control experiments and mechanism study of acylation reaction of



quinoline-2(1H)-one

Figure S6. Control experiments and mechanism study of acylation reaction.

The acylation reaction was significantly suppressed by adding 2.0 equivalents of either TEMPO or BHT as radical scavengers under standard conditions, suggesting that the reaction likely proceeds through a radical-mediated pathway. Additionally, when potassium iodide (KI) and silver nitrate (AgNO₃) were introduced into the reaction system as hole and electron scavengers, respectively, the photocatalytic activity was completely suppressed. This observation indicates that both photo-generated holes and electrons play a critical role in facilitating the C-H acylation process. Based on the control experiments, a plausible photocatalytic reaction mechanism for the C-H acylation is proposed. Under visible light irradiation, g-C₃N₄ absorbs photons, generating electron-hole pairs. The persulfate anion (S₂O₈²⁻) is reduced by the electrons (e⁻) in the CB to produce the sulfate radicals (SO₄⁻). These radicals abstract a hydrogen

atom from benzaldehyde, forming an acyl radical. The acyl radical adds to the C-3 position of **1a**, forming a nitrogen-centered radical intermediate **A**. Subsequently, intermediate **A** quenches the photogenerated holes (h^+) via a single electron transfer (SET) process, generating a nitrogen cation intermediate **B**. Finally, intermediate **B** undergoes deprotonation to afford the final product 3a.



Figure S7 The analysis of benzoic acid by HPLC (mobile phase: MeOH/H₂O = 0.5/0.5, 1mL/min, $\lambda = 230$ nm).

6. Natural sunlight irradiation experiments

To a 10 mL reaction tube was added quinoxalin-2(1*H*)-ones (0.3 mmol), CF₃SO₂Na (0.36 mmol), g-C₃N₄ (10 mg), (NH₄)₂S₂O₈ (0.6 mmol), DMSO (1.0 mL) and degassed with N₂. The reaction mixture was exposed to natural sunlight for 1 day at ambient temperature (about 26 ° C). After the completion of the reaction as indicated by TLC, the solution was concentrated in vacuo. Then the residue was purified by silica gel flash column chromatography (PE/EA = 5/1) to afford product **5a** (65%).





BeginningFinishedFigure S8. Natural sunlight irradiation experiments.

7. Characterization of the products



3-benzoyl-1-methylquinoxalin-2(1*H*)-one (**3a**): yellow solid, 45 mg, 85% yield, m.p. = 157-159 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.98 (d, J = 5.0 Hz, 2H), 7.92 (d, J = 10.0 Hz, 1H), 7.69-7.65 (m, 1H), 7.63-7.60 (m, 1H), 7.49-7.46 (m, 2H), 7.42-7.39 (m, 2H), 3.74 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 191.77, 154.71, 153.37, 134.86, 134.26, 133.92, 133.71, 132.25, 132.08, 131.06, 130.19, 130.05, 128.71, 124.25, 114.00, 29.10; HRMS (ESI-TOF) *m/z* [M+H]⁺ calcd for C₁₆H₁₃N₂O₂ 265.0899, found 265.0896.



1-methyl-3-(2-methylbenzoyl)quinoxalin-2(1*H*)-one (**3b**): yellow solid, 48 mg, 86% yield, m.p. = 164-165 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.93-7.91 (m, 1H), 7.68-7.65 (m, 1H), 7.61-7.60 (m, 1H), 7.45-7.39 (m, 3H), 7.33 (d, *J* = 10.0 Hz, 1H), 7.24-7.21 (m, 1H), 3.74 (s, 3H), 2.69 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 194.02, 155.72, 153.35, 140.79, 134.24, 133.87, 132.93, 132.27, 132.01, 131.89, 131.02, 125.63, 124.18, 113.93, 29.10, 21.76; HRMS (ESI-TOF) *m*/*z* [M+H]⁺ calcd for C₁₇H₁₅N₂O₂ 279.1055, found 279.1057.



3-(2-methoxybenzoyl)-1-methylquinoxalin-2(1*H*)-one (**3c**): yellow solid, 52 mg, 88% yield, m.p. = 160-161 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.07 (d, *J* = 10.0 Hz, 1H), 7.89 (d, *J* = 5.0 Hz, 1H), 7.63-7.60 (m, 1H), 7.56-7.53 (m, 1H), 7.39-7.37 (m, 2H), 7.10-7.09 (m, 1H), 6.91 (d, *J* = 10.0 Hz, 1H), 3.73 (s, 3H), 3.56 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 191.19, 160.09, 157.39, 153.43, 135.66, 133.60, 132.51, 131.13, 130.96, 130.73, 123.92, 121.30, 113.77, 112.15, 109.49, 107.59, 56.09, 28.73; HRMS (ESI-TOF) *m*/*z* [M+H]⁺ calcd for C₁₇H₁₅N₂O₃ 295.1004, found 295.1001.



3-(2-bromobenzoyl)-1-methylquinoxalin-2(1*H*)-one (**3d**): yellow solid, 43 mg, 63% yield, m.p. = 119-120 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.89 (d, *J* = 10.0 Hz, 1H), 7.83 (d, *J* = 10.0 Hz, 1H), 7.69-7.65 (m, 1H), 7.59 (d, *J* = 5.0 Hz, 1H), 7.48-7.45 (m, 1H), 7.42-7.37 (m, 3H), 3.73 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 192.22, 153.30, 153.16, 138.37, 134.21, 133.55, 133.34, 132.53, 132.34, 131.78, 131.40, 127.66, 114.00, 29.04; HRMS (ESI-TOF) *m*/*z* [M + H]⁺ calcd for C₁₆H₁₂BrN₂O₂ 343.0007, found 343.0006.



3-(2-fluorobenzoyl)-1-methylquinoxalin-2(1*H*)-one (**3e**): yellow solid, 37 mg, 66% yield, m.p. = 113-114 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.09-8.06 (m, 1H),7.90 (d, *J* = 5.0 Hz, 1H), 7.66-7.57 (m, 2H), 7.39-7.36 (m, 2H), 7.32-7.28 (m, 1H),7.09-7.05 (m, 1H), 3.72 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 189.03, 163.64, 161.60, 155.34, 153.32, 153.29, 136.05, 135.98, 133.92, 132.42, 132.05, 130.99, 130.97, 124.79, 124.76, 124.25, 124.19, 116.55, 116.37, 114.07, 28.94; HRMS (ESI-TOF) *m/z* [M+H]⁺ calcd for C₁₆H₁₂FN₂O₂ 283.0805, found 283.0806.



3-(3-bromobenzoyl)-1-methylquinoxalin-2(1*H*)-one (**3f**): yellow solid, 50 mg, 74% yield, m.p. = 138-139 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.10 (s, 1H), 7.91 (t, *J* = 20.0 Hz, 2H), 7.73-7.67 (m, 2H), 7.43-7.40 (m, 2H), 7.37-7.33 (m, 1H), 3.75 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 190.37, 153.65, 153.29, 137.01, 136.69, 136.49, 133.95, 133.08, 132.70, 132.49, 132.14, 131.10, 130.30, 130.06, 128.69, 128.62, 124.41, 122.96, 114.14, 29.18; HRMS (ESI-TOF) *m*/*z* [M+H]⁺ calcd for C₁₆H₁₂BrN₂O₂ 343.0004, found 343.0006.



3-(3-fluorobenzoyl)-1-methylquinoxalin-2(1*H*)-one (**3g**): yellow solid, 43 mg, 78% yield, m.p. = 134-135 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.93 (d, *J* = 5.0 Hz, 1H), 7.75 (d, *J* = 5.0 Hz, 1H), 7.71-7.68 (m, 2H), 7.46-7.42 (m, 3H), 7.32-7.29 (m, 1H), 3.76 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 190.47, 190.45, 163.73, 161.76, 153.82, 153.30, 133.94, 132.43, 132.14, 131.09, 130.47, 130.40, 125.99, 125.96, 124.39, 121.37, 121.20, 116.51, 116.33, 114.12, 29.15; HRMS (ESI-TOF) *m/z* [M+H]⁺ calcd for

 $C_{16}H_{12}FN_2O_2$ 283.0805, found 283.0806.



3-(4-methoxybenzoyl)-1-methylquinoxalin-2(1*H*)-one (**3h**): yellow solid, 39 mg, 67% yield, m.p. = 204-205 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.89-7.92 (m, 3H), 7.65 (t, *J* = 10.0 Hz, 1H), 7.42-7.39 (m, 2H), 6.95 (d, *J* = 10.0 Hz, 2H), 3.88 (s, 3H), 3.75 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 189.21, 163.48, 157.39, 153.97, 152.33, 132.82, 131.46, 131.17, 130.83, 129.90, 126.89, 123.10, 112.98, 112.89, 54.54, 28.02; HRMS (ESI-TOF) *m*/*z* [M+H]⁺ calcd for C₁₇H₁₅N₂O₃ 295.1004, found 295.1007.



3-(4-isopropylbenzoyl)-1-methylquinoxalin-2(1*H*)-one (**3i**): yellow solid, 51 mg, 69% yield, m.p. = 200-202 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.94-7.91 (m, 3H), 7.69-7.66 (m, 1H), 7.43-7.40 (m, 2H), 7.33 (d, *J* = 5.0 Hz, 2H), 3.76 (s, 3H), 3.00-2.95 (m, 1H), 1.26 (d, J = 5.0 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 191.43, 156.05, 155.04, 153.38, 133.90, 132.69, 132.27, 131.95, 131.01, 130.34, 126.91, 124.19, 113.97, 34.48, 29.07, 23.62; HRMS (ESI-TOF) *m/z* [M+H]⁺ calcd for C₁₉H₁₉N₂O₂ 307.1368, found 307.1366.



3-benzoyl-1,5-dimethylquinoxalin-2(1*H*)-one (**3j**): yellow solid, 43 mg, 77% yield, m.p. = 157-158 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.05 (d, *J* = 10.0 Hz, 2H), 7.56-7.53 (m, 2H), 7.42-7.39 (m, 3H), 7.20-7.16 (m, 1H), 3,67 (s, 3H), 2.56 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 194.02, 155.72, 153.35, 140.79, 134.24, 133.87, 132.93, 132.27, 132.01, 131.89, 131.02, 125.63, 124.18, 113.93, 29.10, 21.76; HRMS (ESI-TOF) *m/z* [M+H]⁺ calcd for C₁₇H₁₅N₂O₂ 279.1055, found 279.1056.



3-benzoyl-5,6-dichloro-1-methylquinoxalin-2(1*H*)-one (**3**k): yellow solid, 50 mg, 48% yield, m.p. = 244-246 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.07-7.96 (m, 2H), 7.66-7.63 (m, 1H), 7.55-7.48 (m, 3H), 7.15-7.12 (m, 1H), 3.73 (s, 3H); ¹³C NMR (100 MHz,

CDCl₃): δ 190.00, 155.82, 152.77, 147.71, 147.46, 145.75, 145.28, 134.59, 134.41, 131.26, 130.02, 128.81, 123.25, 120.14, 120.66, 108.83, 108.78, 108.73, 29.51; HRMS (ESI-TOF) *m*/*z* [M+H]⁺ calcd for C₁₆H₁₁Cl₂N₂O₂ 332.0119, found 332.0117.



3-benzoyl-7-bromo-1-methylquinoxalin-2(1*H*)-one (**3l**): yellow solid, 49 mg, 71% yield, m.p. = 199-200 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.07 (d, *J* = 5.0 Hz, 1H), 7.97 (d, *J* = 10.0 Hz, 2H), 7.76 (d, *J* = 10.0 Hz, 1H), 7.66-7.63 (m, 1H), 7.51-7.48 (m, 2H), 7.30-7.28 (m, 1H), 3.73 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 191.21, 155.75, 152.96, 134.76, 134.55, 134.43, 133.27, 133.01, 132.92, 130.00, 128.75, 116.81, 115.43, 29.24; HRMS (ESI-TOF) *m/z* [M+H]⁺ calcd for C₁₆H₁₂BrN₂O₂ 343.0077, found 343.0079.



3-benzoyl-5-chloro-1-methylquinoxalin-2(1*H*)-one (**3m**): yellow solid, 44 mg, 74% yield, m.p. = 199-200 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.11-8.02 (m, 2H), 7.65-7.57 (m, 2H), 7.51-7.48 (m, 3H), 7.33-7.31 (m, 1H), 3.75 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 191.06, 154.50, 152.98, 136.08, 135.46, 134.73, 134.33, 133.73, 132.01, 130.18, 129.05, 128.70, 128.50, 125.16, 112.83, 29.55; HRMS (ESI-TOF) *m/z* [M+H]⁺ calcd for C₁₆H₁₂ClN₂O₂ 299.0509, found 299.0509.



3-benzoyl-5-bromo-1-methylquinoxalin-2(1*H*)-one (**3n**): yellow solid, 50 mg, 73% yield, m.p. = 241-242 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.11 (d, J = 10.0 Hz, 1H), 8.04 (d, J = 10.0 Hz, 1H), 7.70-7.68 (m, 1H), 7.63-7.62 (m, 1H), 7.51-7.48 (m, 3H), 7.37-7.35 (m, 1H), 3.74 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 190.89, 171.53, 154.50, 152.99, 135.32, 134.74, 134.31, 133.76, 132.33, 130.22, 129.97, 128.69, 128.48, 126.69, 113.62, 29.54; HRMS (ESI-TOF) m/z [M+H]⁺ calcd for C₁₆H₁₂BrN₂O₂ 343.0047, found 343.0049.



1-allyl-3-benzoylquinoxalin-2(1*H*)-one (**30**): yellow solid, 45 mg, 77% yield, m.p. = 168-169 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.10 (d, *J* = 5.0 Hz, 1H), 7.99 (d, *J* = 5.0 Hz, 2H), 7.95-7.93 (m, 1H), 7.64-7.59 (m, 2H), 7.50-7.47 (m, 2H), 7.41-7.39 (m, 2H), 5.99-5.92 (m, 1H), 5.33-5.24 (m, 2H), 4.95 (d, *J* = 5.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 191.73, 154.72, 152.95, 134.90, 134.26, 133.68, 133.19, 132.41, 131.98, 131.18, 131.13, 130.33, 130.18, 130.02, 128.72, 128.48, 124.22, 118.82, 114.59, 44.53; HRMS (ESI-TOF) *m*/*z* [M+H]⁺ calcd for C₁₈H₁₅N₂O₂ 291.1055, found 291.1057.



ethyl 2-(3-benzoyl-2-oxoquinoxalin-1(2*H*)-yl)acetate (**3p**): yellow solid, 53 mg, 79% yield, m.p. = 188-189 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.10-8.08 (m, 1H), 7.99-7.93 (m, 2H), 7.65-7.59 (m, 2H), 7.49-7.46 (m, 2H), 7.42-7.39 (m, 1H), 7.18 (d, *J* = 5.0 Hz, 1H), 5.06 (s, 2H), 4.25 (q, *J* = 5.0 Hz, 2H), 1.27 (t, *J* = 5.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 191.62, 166.98, 154.64, 153.19, 135.05, 134.57, 133.92, 133.61, 133.34, 133.27, 132.55, 131.57, 130.40, 130.29, 129.68, 129.02, 128.98, 128.72, 128.33, 124.78, 113.82, 62.53, 43.60, 14.34; HRMS (ESI-TOF) *m/z* [M+H]⁺ calcd for C₁₉H₁₇N₂O₄ 337.1110, found 337.1113.



3-benzoyl-1-benzylquinoxalin-2(1H)-one (**3q**): yellow solid, 56 mg, 82% yield, m.p. = 128-129 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.11 (d, *J* = 10.0 Hz, 2H), 8.02 (d, *J* = 10.0 Hz, 2H), 7.92 (d, *J* = 10.0 Hz, 1H), 7.64-7.58 (m, 2H), 7.53-7.45 (m, 4H), 7.37-7.32 (m, 3H), 5.52 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 191.77, 172.04, 154.78, 153.55, 134.92, 134.88, 134.33, 133.80, 133.27, 132.53, 132.09, 131.15, 130.22, 130.07, 129.42, 129.07, 128.77, 128.51, 127.98, 127.17, 124.32, 114.87, 45.94.; HRMS (ESI-TOF) *m*/*z* [M+H]⁺ calcd for C₂₂H₁₇N₂O₂ 341.1212, found 341.1213.



3-benzoyl-1-(4-bromobenzyl)quinoxalin-2(1*H*)-one (**3r**): yellow solid, 55 mg, 66% yield, m.p. = 196-199 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.09 (d, *J* = 5.0 Hz, 2H), 8.02-

8.00 (m, 1H), 7.95-7.87 (m, 1H), 7.65-7.62 (m, 1H), 7.58-7.50 (m, 4H), 7.48-7.44 (m, 1H), 7.39-7.30 (m, 1H), 7.19 (d, J = 5.0 Hz, 2H), 5.47 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 191.54, 170.97, 154.67, 153.39, 134.81, 134.37, 133.90, 133.68, 133.04, 132.48, 132.20, 132.14, 132.13, 131.45, 131.38, 131.31, 131.31, 130.17, 130.05, 128.96, 128.77, 128.48, 124.45, 121.98, 114.59, 114.54, 45.37; HRMS (ESI-TOF) *m*/*z* [M+H]⁺ calcd for C₂₂H₁₆BrN₂O₂ 419.0371, found 419.0370.



3-benzoyl-1-(4-chlorobenzyl)quinoxalin-2(1*H*)-one (**3s**): yellow solid, 44 mg, 59% yield, m.p. = 208-209 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.02-7.93 (m, 3H), 7.65-7.62 (m, 1H), 7.58-7.55 (m, 1H), 7.52-7.48 (m, 2H), 7.39-7.36 (m, 1H), 7.33-7.31 (m, 3H), 7.30-7.24 (m, 2H), 5.49 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 177.43, 140.58, 139.28, 120.70, 120.23, 119.80, 119.54, 119.25, 118.94, 118.37, 118.00, 117.27, 117.25, 116.05, 115.92, 115.15, 115.13, 115.02, 114.64, 114.53, 114.35, 110.31, 100.54, 100.41, 31.19; HRMS (ESI-TOF) *m/z* [M+H]⁺ calcd for C₂₂H₁₆ClN₂O₂ 375.0822, found 375.0824.



1-methyl-3-(trifluoromethyl)quinoxalin-2(1*H*)-one (**5a**): white solid, 57 mg, 82% yield, m.p. = 134-135 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.01 (, *J* = 5.0 Hz, 1H), 7.76-7.72 (m, 1H), 7.47-7.40 (m, 2H), 3.77 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 150.59, 143.01, 142.74, 133.56, 132.51, 130.76, 129.88, 123.49, 112.99, 28.15; ¹⁹F NMR (376 MHz, CDCl₃): δ -70.13; HRMS (ESI-TOF) *m*/*z* [M+H]⁺ calcd for C₁₀H₈F₃N₂O 229.0510, found 229.0511.



1-ethyl-3-(trifluoromethyl)quinoxalin-2(1*H*)-one (**5b**): pale yellow solid, 57 mg, 78% yield, m.p. = 100-101 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.01 (d, *J* = 5.0 Hz, 1H), 7.75-7.72 (m, 1H), 7.46-7.42 (m, 2H), 4.38 (q, *J* = 5.0 Hz, 2H), 1.43 (t, *J* = 10.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 151.17, 144.42, 144.05, 143.79, 143.52, 133.66, 133.48, 132.03, 131.23, 124.30, 123.26, 121.06, 118.86, 116.66, 113.85, 37.66, 12.35; HRMS (ESI-TOF) m/z [M+H]⁺ calcd for C₁₁H₁₀F₃N₂O 243.0667, found 243.0667.



ethyl 2-(2-oxo-3-(trifluoromethyl)quinoxalin-1(2*H*)-yl)acetate (**5**c): pale yellow solid, 67 mg, 74% yield, m.p. = 152-154 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.02 (d, *J* = 10.0 Hz, 1H), 7.72-7.68 (m, 1H), 7.45 (t, *J* = 15.0 Hz, 1H), 7.16 (d, *J* = 10.0 Hz, 1H), 5.06 (s, 2H), 4.27 (q, *J* = 5.0 Hz, 2H), 1.29 (t, *J* = 5.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.37, 151.18, 144.26, 143.99, 143.44, 133.83, 133.69, 132.09, 131.02, 123.05, 120.86, 118.66, 116.46, 113.56, 62.42, 43.42, 14.08; HRMS (ESI-TOF) m/z [M+H]⁺ calcd for C₁₃H₁₂F₃N₂O₃ 301.0726, found 301.0727.



1-(2-oxo-2-phenylethyl)-3-(trifluoromethyl)quinoxalin-2(1*H*)-one (**5d**): white solid, 68 mg, 68% yield, m.p. = 149-150 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.07 (d, *J* = 10.0 Hz, 2H), 8.03 (d, *J* = 10.0 Hz, 1H), 7.71-7.68 (m, 1H), 7.63-7.55 (m, 3H), 7.44-7.41 (m, 1H), 7.04 (d, *J* = 10.0 Hz, 1H), 5.78 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 190.28, 151.40, 144.12, 143.85, 143.31, 134.62, 134.28, 134.16, 133.56, 132.01, 129.18, 128.21, 124.64, 123.15, 120.95, 118.75, 116.55, 114.00, 48.33; HRMS (ESI-TOF) *m/z* [M+H]⁺ calcd for C₁₇H₁₂F₃N₂O₂ 333.0773, found 333.0775.



1-benzyl-3-(trifluoromethyl)quinoxalin-2(1*H*)-one (**5e**): yellow solid, 57 mg, 62% yield, m.p. = 100-101 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.92 (d, *J* = 10.0 Hz, 1H), 7.54-7.51 (m, 1H), 7.33-7.29 (m, 1H), 7.28-7.24 (m, 3H),7.22-7.18 (m, 3H), 5.45 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 150.71, 143.4, 142.87, 142.60, 133.39, 132.95, 132.45, 130.83, 130.14, 128.05, 127.03, 126.00, 123.50, 113.77, 44.99; ¹⁹F NMR (376 MHz, CDCl₃): δ -70.21; HRMS (ESI-TOF) *m*/*z* [M+H]⁺ calcd for C₁₆H₁₂F₃N₂O 305.0823, found 305.0826.



1-(3-methylbenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (**5f**): pale yellow solid, 68 mg, 71% yield, m.p. = 154-155 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.99 (d, J = 5.0 Hz,1H), 7.62-7.59 (m, 1H), 7.41-7.36 (m, 2H), 7.26-7.20 (m, 1H), 7.10-7.04 (m, 3H),

5.49 (s, 2H), 2.31 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 151.79, 144.50, 144.23, 143.96, 138.97, 134.41, 134.10, 133.48, 131.86, 131.22, 128.96, 128.87, 127.64, 124.51, 124.07, 123.25, 121.06, 118.86, 114.90; HRMS (ESI-TOF) *m/z* [M+H]⁺ calcd for C₁₇H₁₄F₃N₂O 319.0980, found 319.0981.



1-(3-bromobenzyl)-3-(trifluoromethyl)quinoxalin-2(1*H*)-one (**5**g): pale yellow solid, 84 mg, 73% yield, m.p. = 92-93 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.02 (d, *J* = 10.0 Hz, 1H), 7.65-7.62 (m, 1H), 7.44-7.41 (m, 3H), 7.31-7.29 (m, 1H), 7.22-7.17 (m, 2H), 5.49 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 151.67, 144.46, 144.18, 143.91, 143.64, 136.71, 133.80, 133.70, 132.07, 131.38, 131.21, 130.71, 130.04, 125.66, 124.79, 123.18, 114.54, 45.50; HRMS (ESI-TOF) *m*/*z* [M+H]⁺ calcd for C₁₆H₁₁BrF₃N₂O 382.9929, found 382.9930.



1-(3-nitrobenzyl)-3-(trifluoromethyl)quinoxalin-2(1*H*)-one (**5h**): pale yellow solid, 61 mg, 58% yield, m.p. = 132-133 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.18 (d, *J* = 10.0 Hz, 2H), 8.06 (d, *J* = 10.0 Hz, 1H), 7.68-7.65 (m, 1H), 7.61-7.60 (m, 1H), 7.56-7.53 (m, 1H), 7.48-7.45 (m, 1H), 7.31-7.29 (m, 1H), 5.62 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 151.62, 148.64, 136.57, 133.86, 133.61, 132.35, 131.25, 130.38, 125.03, 123.33, 122.18, 114.12, 45.43; HRMS (ESI-TOF) *m*/*z* [M+H]⁺ calcd for C₁₆H₁₁F₃N₃O₃ 350.0674, found 350.0673.



1-(4-chlorobenzyl)-3-(trifluoromethyl)quinoxalin-2(1*H*)-one (**5i**): pale yellow solid, 65 mg, 64% yield, m.p. = 135-137 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.01 (d, *J* = 10.0 Hz, 1H), 7.64-7.61 (m, 1H), 7.44-7.41 (m, 1H), 7.32-7.30 (m, 3H), 7.23-7.22 (m, 2H), 5.49 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 151.68, 144.50, 144.23, 143.69, 134.08, 133.82, 133.58, 132.97, 132.06, 131.22, 129.32, 128.56, 124.71, 123.17, 120.97, 118.7, 116.57, 45.46; HRMS (ESI-TOF) *m*/*z* [M+H]⁺ calcd for C₁₆H₁₁ClF₃N₂O 339.0434, found 339.0434.



1-(4-bromobenzyl)-3-(trifluoromethyl)quinoxalin-2(1*H*)-one (**5j**): pale yellow solid, 80 mg, 70% yield, m.p. = 138-140 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.01 (d, *J* = 10.0 Hz, 1H), 7.64-7.61 (m, 1H), 7.47-7.41 (m, 3H), 7.32-7.30 (m, 1H), 7.16 (d, *J* = 10.0 Hz, 2H), 5.47 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 151.68, 144.4, 144.20,143.93, 143.65, 133.80, 133.62, 133.49, 132.28, 132.06, 131.21, 128.86, 124.75, 122.13, 120.97, 118.77, 114.54, 45.52; HRMS (ESI-TOF) *m*/*z* [M+H]⁺ calcd for C₁₆H₁₁BrF₃N₂O 382.9929, found 382.9930.



1,5-dimethyl-3-(trifluoromethyl)quinoxalin-2(1*H*)-one (**5**k): pale yellow solid, 59 mg, 81% yield, m.p. = 167-168 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.62-7.59 (m, 1H), 7.30-7.27 (m, 1H), 7.23-7.21 (m, 1H), 3.74 (s, 3H), 2.71 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 151.62, 142.33, 142.06, 141.79, 141.52, 141.22, 134.09, 133.34, 129.71, 125.69, 121.17, 118.97, 111.79, 29.30, 17.30; HRMS (ESI-TOF) *m/z* [M+H]⁺ calcd for C₁₁H₁₀F₃N₂O 243.0667, found 243.0667.



5-chloro-1-methyl-3-(trifluoromethyl)quinoxalin-2(1*H*)-one (**5**I): pale yellow solid, 62 mg, 79% yield, m.p. = 112-114 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.00 (s, 1H), 7.69 (d, *J* = 10.0 Hz, 1H), 7.36 (d, *J* = 10.0 Hz, 1H), 3.75 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 151.24, 145.56, 145.29, 145.02, 144.75, 133.59, 133.28, 131.30, 130.89, 130.02, 122.95, 120.75, 118.55, 116.35, 115.25, 29.41; HRMS (ESI-TOF) *m*/*z* [M+H]⁺ calcd for C₁₀H₇ClF₃N₂O 263.0121, found 263.0120.



1,6-dimethyl-3-(trifluoromethyl)quinoxalin-2(1*H*)-one and 1,7-dimethyl-3-(trifluoromethyl)quinoxalin-2(1*H*)-one (**5m**+**5m**'): pale yellow solid, 57 mg, 78% yield; ¹H NMR (500 MHz, CDCl₃): δ 7.87-7.86 (d, *J* = 5.0 Hz, 0.54H), 7.80-7.79 (d, *J* = 5.0 Hz, 0.45H), 7.56-7.54 (m, 0.47H), 7.30-7.29 (m, 1.32H), 7.18 (s, 0.53H); ¹³C NMR (100 MHz, CDCl₃): *δ* 151.83, 151.61, 145.06, 134.85, 134.59, 132.47, 131.46, 131.40, 130.90, 129.24, 125.98, 114.02, 113.73, 29.15, 29.07, 22.45, 20.57.



6-chloro-1-methyl-3-(trifluoromethyl)quinoxalin-2(1*H*)-one (**5n**): pale yellow solid, 60 mg, 76% yield, m.p. = 116-118 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.64 (t, *J* = 10.0 Hz, 1H), 7.53 (d, *J* = 10.0 Hz, 1H), 7.31 (d, *J* = 10.0 Hz, 1H), 3.76 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 151.26, 144.14, 137.02, 136.22, 133.48, 127.91, 125.43, 120.81, 118.61, 112.80, 29.65; HRMS (ESI-TOF) *m*/*z* [M+H]⁺ calcd for C₁₀H₇ClF₃N₂O 263.0121, found 263.0122.



7-fluoro-1-methyl-3-(trifluoromethyl)quinoxalin-2(1*H*)-one (**50**): pale yellow solid, 50 mg, 67% yield, m.p. = 168-170 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.70 (d, *J* = 10.0 Hz, 1H), 7.53-7.49 (m, 1H), 7.41-7.38 (m, 1H), 3.77 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 159.86, 157.90, 151.24, 145.73, 145.46, 144.92, 131.39, 121.75, 121.56, 120.80, 118.60, 117.00, 116.82, 115.38, 29.48; HRMS (ESI-TOF) *m*/*z* [M+H]⁺ calcd for C₁₀H₇F₄N₂O 247.0416, found 247.0417.



7-bromo-1-methyl-3-(trifluoromethyl)quinoxalin-2(1*H*)-one (**5p**): pale yellow solid, 61 mg, 66% yield, m.p. = 150-152 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.15 (d, *J* = 5.0 Hz, 1H), 7.81(d, *J* = 5.0 Hz, 1H), 7.30-7.27 (m, 1H), 3.74 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 151.21, 145.48, 145.20, 144.93, 144.66, 136.28, 133.98, 133.71, 131.58, 117.12, 115.47, 29.37; HRMS (ESI-TOF) *m*/*z* [M+H]⁺ calcd for C₁₀H₇BrF₃N₂O 306.9616, found 306.9614.



7-iodo-1-methyl-3-(trifluoromethyl)quinoxalin-2(1*H*)-one (**5q**): pale yellow solid, 70 mg, 66% yield, m.p. = 180-183 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.36 (s, 1H), 7.98-7.96(m, 1H), 7.15 (d, *J* = 10.0 Hz, 1H), 3.73 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 141.81, 140.17, 134.35, 131.82, 115.63, 86.94, 29.28; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd for C₁₀H₇FI₃N₂O 354.9477, found 354.9478.



7-methoxy-1-methyl-3-(trifluoromethyl)quinoxalin-2(1*H*)-one (**5r**): white solid, 62 mg, 80% yield, m.p. = 85-87 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.90 (d, *J* = 10.0 Hz, 1H), 7.01-7.03 (m, 1H), 6.75-6.74 (m, 1H), 3.98 (s, 3H), 3.71 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 163.87, 152.05, 136.61,133.36, 125.93, 121.37, 119.18, 112.31, 97.72, 56.05, 29.17; HRMS (ESI-TOF) *m*/*z* [M+H]⁺ calcd for C₁₁H₁₀F₃N₂O₂ 259.0616, found 259.0617.



6,7-dichloro-1-methyl-3-(trifluoromethyl)quinoxalin-2(1*H*)-one (**5s**): pale yellow solid, 64 mg, 72% yield, m.p. = 138-140 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.29 (s, 1H), 8.05 (s, 1H), 3.64 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 151.41, 144.90, 144.64, 144.38, 144.12, 136.65, 135.25, 131.79, 130.13, 126.83, 121.36, 119.16, 117.68, 40.47, 40.31, 40.14, 39.97, 39.80, 39.64, 39.47, 30.11; HRMS (ESI-TOF) *m*/*z* [M+H]⁺ calcd for C₁₀H₆Cl₂F₃N₂O 296.9731, found 296.9733.



6-chloro-7-fluoro-1-methyl-3-(trifluoromethyl)quinoxalin-2(1*H*)-one and 7-chloro-6-fluoro-1-methyl-3-(trifluoromethyl)quinoxalin-2(1*H*)-one (5t+5t'): white solid, 64 mg, 72% yield. ¹H NMR (500 MHz, CDCl₃): δ 8.08 (d, J = 10.0 Hz, 0.57H), 7.77 (d, J = 5.0 Hz, 0.91H), 7.47 (d, J = 10.0 Hz, 0.96H), 7.19 (d, J = 10.0 Hz, 0.62H), 3.74 (s, 3H), 3.71 (s, 1.78H); ¹³C NMR (100 MHz, CDCl₃): δ 161.57, 159.52, 155.41, 153.43, 151.07, 150.97, 145.39, 145.12, 134.91, 133.36, 133.34, 131.82, 129.81, 129.73, 128.03, 127.87, 127.72, 117.89, 117.72, 115.71, 102.21, 101.99, 29.65, 29.60.



5,6-difluoro-1-methyl-3-(trifluoromethyl)quinoxalin-2(1*H*)-one (**5u**): pale yellow solid, 51 mg, 64% yield, m.p. = 145-147 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.64-7.59 (m, 1H), 7.17-7.14 (m, 1H), 3.76 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 150.94, 147.75, 147.68, 147.65, 145.64, 145.54, 145.42, 131.98, 122.52, 120.60, 118.40, 116.20, 108.83, 29.64; HRMS (ESI-TOF) *m*/*z* [M+H]⁺ calcd for C₁₀H₆F₅N₂O 265.0322, found 265.0322.



1,5,7-trimethyl-3-(trifluoromethyl)quinoxalin-2(1*H*)-one (**5v**): pale yellow solid, 52 mg, 68% yield, m.p. = 145-147 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.10 (s, 1H), 6.98 (s, 1H), 3.71 (s, 3H), 2.64 (s, 3H), 2.51 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 151.78, 144.78, 140.65, 134.86, 128.01, 127.17, 121.34, 119.15, 115.03, 111.83, 29.16, 22.40, 17.14; HRMS (ESI-TOF) *m/z* [M+H]⁺ calcd for C₁₂H₁₂F₃N₂O 257.0823, found 257.0824.

8. Copies of ¹H, ¹³C and ¹⁹F NMR spectra



¹³C NMR spectrum of compound 3a







¹H NMR spectrum of compound 3b



¹³C NMR spectrum of compound 3b



¹³C NMR spectrum of compound 3c



-3.73

¹³C NMR spectrum of compound 3d



¹³C NMR spectrum of compound 3e



-0.00



¹³C NMR spectrum of compound 3f



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¹³C NMR spectrum of compound 3g



¹H NMR spectrum of compound 3h



¹³C NMR spectrum of compound 3h



¹H NMR spectrum of compound 3i



¹³C NMR spectrum of compound 3i





¹³C NMR spectrum of compound 3j



-3.73

¹H NMR spectrum of compound 3k



¹³C NMR spectrum of compound 3k



-3.73

¹H NMR spectrum of compound 31





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¹H NMR spectrum of compound 3m



¹³C NMR spectrum of compound 3m

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10.0 9.5 9.0



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3.00-I

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1.5 1.0 0.5

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4.5





¹³C NMR spectrum of compound 3n

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¹³C NMR spectrum of compound 30





¹³C NMR spectrum of compound 3p

8.12 8.10 8.10 7.1.92 7.7.92 7.7.53 7.7.735 7.7.53 7.7.53 7.7.53 7.7.53 7.7.53 7.7.53 7.7.53 7.7.53 7.7.53 7.7.53 7.7.53 7.7.53 7.7.53 7.7.735 7.7.755 7.7555 7.7555 7.7555 7.7555 7





¹³C NMR spectrum of compound 3q

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¹H NMR spectrum of compound 3r





¹³C NMR spectrum of compound 3r





¹H NMR spectrum of compound 3s



¹³C NMR spectrum of compound 3s



-3.77

¹H NMR spectrum of compound 5a



¹³C NMR spectrum of compound 5a



¹⁹F NMR spectrum of compound 5a



¹³C NMR spectrum of compound 5b



¹³C NMR spectrum of compound 5c





¹H NMR spectrum of compound 5d



¹³C NMR spectrum of compound 5d



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¹³C NMR spectrum of compound 5e

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20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22

¹⁹F NMR spectrum of compound 5e



¹H NMR spectrum of compound 5f



¹³C NMR spectrum of compound 5f

00:0



¹H NMR spectrum of compound 5g



¹³C NMR spectrum of compound 5g



¹H NMR spectrum of compound 5h



¹³C NMR spectrum of compound 5h



¹H NMR spectrum of compound 5i



¹³C NMR spectrum of compound 5i



¹H NMR spectrum of compound 5j



¹³C NMR spectrum of compound 5j

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¹H NMR spectrum of compound 5k



¹³C NMR spectrum of compound 5k



¹H NMR spectrum of compound 5l



¹³C NMR spectrum of compound 5l



¹H NMR spectrum of compound 5m and 5m'





¹³C NMR spectrum of compound 5m and 5m'





-3.76



¹H NMR spectrum of compound 5n



¹³C NMR spectrum of compound 5n





-3.77

¹H NMR spectrum of compound 50



¹³C NMR spectrum of compound 50







¹³C NMR spectrum of compound 5p

00:0---







-3.73

¹H NMR spectrum of compound 5q



¹³C NMR spectrum of compound 5q

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¹³C NMR spectrum of compound 5r

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¹H NMR spectrum of compound 5s



¹³C NMR spectrum of compound 5s



¹H NMR spectrum of compound 5t and 5t'



¹³C NMR spectrum of compound 5t and 5t'





¹³C NMR spectrum of compound 5u





¹H NMR spectrum of compound 5v





¹³C NMR spectrum of compound 5v