Supporting Information

For

Metal-free C-H methylation and acetylation of Heteroarenes with PEG-400.

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(1) General Information

$^1$H, $^{13}$C and DEPT NMR spectra were recorded on a 400 MHz Varian Unity Plus or Varian Mercury plus spectrometer. The chemical shift ($\delta$) values are reported in parts per million (ppm), and the coupling constants (J) are given in Hz. The spectra were recorded using CDCl$_3$ as a solvent. $^1$H NMR chemical shifts are referenced to tetramethylsilane (TMS) (0 ppm). $^{13}$C NMR was referenced to CDCl$_3$ (77.0 ppm) or DMSO-d$_6$ (39.51 ppm). The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublet; ddd, doublet of doublet of doublet; dt, doublet of triplets; td, triplet of doublet; m, multiplet. Mass spectra and high resolution mass spectra (HRMS) were measured using the ESI (FT-MS solariX) at National Sun Yat-Sen University, Kaohsiung, Taiwan. Melting points were determined on an EZ-Melt (Automated melting point apparatus). All products reported showed $^1$H NMR spectra in agreement with the assigned structures. Reaction progress and product mixtures were routinely monitored by TLC using Merck TLC aluminum sheets (silica gel 60 F254). Column chromatography was carried out with 230–400 mesh silica gel 60 (Merck) and a mixture of hexane/ethyl acetate or hexane as an eluent. Preparative TLC was run on a Merck TLC aluminum sheets (silica gel 60 F254).

(2) Mechanistic studies:

**Fig S1:** GC-MS with different retention time generated from PEG-400 in presence of oxidant & radical scavenger.
Fig S2: GC-MS observed fragments acetaldehyde, 2-oxopropanal, 2-oxopropanoic acid from PEG-400.
Scheme S1 Control Experiments:

(a) \[ \text{1a, 0.25 mmol} \rightarrow \text{2a, 0\%} \]

(b) \[ \text{1a, 0.25 mmol} \rightarrow \text{2a, 0\%} \]

(c) \[ \text{1a, 0.25 mmol} \rightarrow \text{2a, 0\%} \]

(d) \[ \text{3a, 0.25 mmol} \rightarrow \text{4a, 37\%} \]

(e) \[ \text{3a, 0.25 mmol} \rightarrow \text{4a, 43\%} \]

(f) \[ \text{3a, 0.25 mmol} \rightarrow \text{4a, 49\%} \]

(g) \[ \text{3a (0.25 mmol)} \rightarrow \text{2a, 63\%} \]

Parallel experiment

\[ \text{1a (0.25 mmol)} \rightarrow \text{2a, 46\%} \]

(3) Experimental Procedures

(i) General Experimental Procedure for the synthesis of quinazolinone.¹
To an oven dried sealed tube was charged with 1a'-y' (0.5 mmol), ethylene glycol (EG): H₂O (9:1) (0.25 M) and TsOH. H₂O (0.5 mmol) and allowed to stir at 110º C until the completion of reaction (4 ~ 36 h) by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 20 mL of water. The water layer was extracted with (3X20 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X20 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from hexane to 20% ethyl acetate/hexane to afford pure quinazolin-4(3H)-ones 1a-1y in 75%-90% yields.

(ii) General Experimental Procedure (B) and Spectral Characterization for the Synthesis of 2-methyl-3-phenylquinazolin-4(3H)-one with PEG-400 as “–CH₃-” Source

To an oven dried sealed tube was charged with 1a-1w (0.25 mmol), PEG-400 (0.10 M) and TsOH. H₂O (0.25 mmol) and allowed to stir at 110º C until the completion of reaction (4 ~ 36 h) by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X20 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X20 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from hexane to 15-25% ethyl acetate/hexane to afford pure 2-methyl-3-arylquinazolin-4(3H)-one 2a-2w in 66%-82% yields.

(iii) General Experimental Procedure (A) and Spectral Characterization for the Synthesis of 2-methyl-3-phenylquinazolin-4(3H)-one with PEG-400 as “-CH- & –CH₃-” Source

To an oven dried sealed tube was charged with 1a',b',d',e',i',k',n',o' (0.25 mmol), PEG-400 (0.10 M) and TsOH. H₂O (0.15 mmol) and allowed to stir at 110º C until the completion of reaction (4 ~ 36 h) by TLC.
After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X20 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X20 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from hexane to 15-25% ethyl acetate/hexane to afford pure 2-methyl-3-arylquinazolin-4(3H)-one 2a,b,d,e,i,k,n,o in 67%-81% yields.

(iv) General Experimental Procedure (C) and Spectral Characterization for the Synthesis of heteroaryl acetylation with PEG-400 as “CH₃CO” Source

To an oven dried sealed tube was charged with 3a-3za (0.25 mmol), PEG-400 (0.10 M) and TsOH. H₂O (0.25 mmol) and allowed to stir at 110° C until the completion of reaction (4 ~ 24 h) by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 5.0 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from hexane to 10- 20% ethyl acetate/hexane to afford pure heteroaryl acetylation 4a-4za in 48%-85% yields.

(4) Spectral Characterization

2-methyl-3-phenylquinazolin-4(3H)-one (2a): The title compound was prepared according to the general procedure B on a 0.25 mmol scale to obtain as a white solid (46 mg, yield = 80%); Mp.144-146 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.27 (ddd, J = 8.0, 1.6, 0.4 Hz, 1H), 7.79-7.75 (m, 1H), 7.69 (dd, J = 8.4, 0.8, 1H), 7.58-7.54 (m, 2H), 7.53-7.51 (m, 1H), 7.47 (ddd, J = 9.2, 2.0, 0.8 Hz, 1H), 7.28-7.26 (m, 2H), 2.25 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 162.22, 154.16, 147.41, 137.70, 134.54, 129.95, 129.24, 127.97, 127.00, 126.71, 126.59, 120.72, 77.31, 76.99, 76.67, 24.35.

2-methyl-3-(o-tolyl)quinazolin-4(3H)-one (2b): The title compound was prepared according to the general procedure B on a 0.25 mmol scale to obtain as a white solid (44 mg, yield = 71%); Mp.
117-119 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.29 (dd, $J = 8.0$, 1.2 Hz, 1H), 7.78 (ddd, $J = 8.4$, 7.2, 1.6 Hz, 1H), 7.70 (d, $J = 8.8$, 1H), 7.50 - 7.46 (m, 1H), 7.42-7.36 (m, 3H), 7.17 (d, 7.2 Hz, 1H), 2.19 (s, 3H), 2.13 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 161.63, 154.30, 147.61, 136.76, 135.32, 134.57, 131.51, 129.56, 127.88, 127.62, 127.09, 126.74, 126.57, 120.70, 23.85, 17.37.

2-methyl-3-(m-toly)quinazolin-4(3H)-one (2c): The title compound was prepared according to the general procedure B on a 0.25 mmol scale to obtain as a white solid (41 mg, yield = 66 %); Mp. 126-128 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.29 (ddd, $J = 8.0$, 1.6, 0.4 Hz, 1H), 7.79-7.74 (m, 1H), 7.68 (ddd, $J = 8.0$, 1.2, 0.4, 1H), 7.48-7.41 (m, 2H), 7.32-7.29 (m, 1H), 7.08-7.04 (m, 2H), 2.42 (s, 3H), 2.25 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 161.63, 154.30, 147.61, 136.76, 135.32, 134.57, 131.51, 129.56, 127.88, 127.62, 127.09, 126.74, 126.57, 120.70, 23.85, 17.37.

3-(2,4-dimethylphenyl)-2-methylquinazolin-4(3H)-one (2d): The title compound was prepared according to the general procedure B on a 0.25 mmol scale to obtain as a white solid (48 mg, yield = 73 %); Mp. 133-135 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.29 (ddd, $J = 8.0$, 1.6, 0.4 Hz, 1H), 7.79-7.75 (m, 1H), 7.69 (ddd, $J = 7.6$, 0.8 Hz, 1H), 7.47 (ddd, $J = 8.0$, 3.2, 1.2 Hz, 1H), 7.18 (ddd, $J = 7.6$, 1.2, 0.4 Hz, 2H), 7.03 (d, $J = 8.0$ Hz, 1H), 2.40 (s, 3H), 2.19 (s, 3H), 2.08 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 161.76, 154.62, 147.58, 139.52, 134.83, 134.51, 134.09, 132.22, 128.30, 127.54, 127.12, 126.68, 126.51, 120.71, 77.31, 76.99, 76.68, 23.84, 21.16, 17.29.

3-(2-ethylphenyl)-2-methylquinazolin-4(3H)-one (2e): The title compound was prepared according to the general procedure B on a 0.25 mmol scale to obtain as a white solid (45 mg, yield = 69 %); Mp. 88-90 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.29 (ddd, $J = 8.0$, 1.2, 0.4 Hz, 1H), 7.80-7.76 (m, 1H), 7.71-7.68 (m, 1H), 7.49-7.45 (m, 3H), 7.40-7.35 (m, 1H), 7.15-7.13 (m, 1H), 2.46-2.39 (m, 2H), 2.19 (s, 3H), 1.18 (t, $J = 7.6$, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 161.89, 154.50, 147.59, 140.69, 136.18, 134.54, 129.72, 129.46, 128.00, 127.46, 127.11, 126.73, 126.56, 120.71, 77.31, 76.99, 76.67, 24.01, 23.56, 13.59.

3-(4-ethylphenyl)-2-methylquinazolin-4(3H)-one (2f): The title compound was prepared according to the general procedure B on a 0.25 mmol scale to obtain as a white solid (45 mg, yield = 68 %); Mp. 145-147 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.27 (ddd, $J = 8.0$, 1.6, 0.4 Hz, 1H), 7.78-7.73 (m, 1H), 7.67 (ddd, $J = 8.4$, 0.8, 1H), 7.46 (ddd, $J = 8.4$, 7.2, 1.2, 1H), 7.39-7.35 (m, 2H), 7.18-7.15 (m, 2H), 2.75 (q, $J = 8.4$, 2H), 2.25 (s, 3H), 1.30
(t, J = 8.4, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 162.33, 154.50, 147.41, 145.40, 135.15, 134.46, 129.37, 127.66, 127.03, 126.66, 126.51, 120, 28.51, 24.37, 15.23.

3-(2-methoxyphenyl)-2-methylquinazolin-4(3H)-one (2g):$^3$ The title compound was prepared according to the general procedure B on a 0.25 mmol scale to obtain as a white solid (47 mg, yield = 70 %); Mp. 126-128 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.28 (ddd, J = 8.0, 1.6, 0.4 Hz 1H), 7.76 (ddd, J = 8.0, 6.8, 1.2 Hz 1H), 7.68 (ddd, J = 8.4, 1.2, 0.8 Hz 1H), 7.50-7.43 (m, 2H), 7.21 (dd, J = 7.6, 1.6 Hz 1H), 7.11 (ddd, J = 8.8, 7.6, 1.2 Hz 2H), 3.79 (s, 3H), 2.28 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 161.92, 154.98, 154.50, 147.59, 134.37, 130.82, 129.23, 127.05, 126.60, 126.32, 126.12, 120.78, 112.17, 55.69, 23.45.

3-(3-methoxyphenyl)-2-methylquinazolin-4(3H)-one (2h):$^7$ The title compound was prepared according to the general procedure B on a 0.25 mmol scale to obtain as a white solid (48 mg, yield = 71 %); Mp. 152-154 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.28 (dd, J = 8.0, 1.2 Hz 1H), 7.77 (ddd, J = 8.4, 7.2, 1.6 Hz 1H), 7.68 (dd, J = 8.0, 0.4 Hz 1H), 7.48-7.43 (m, 2H), 7.05 (ddd, J = 8.4, 2.4, 0.8 Hz 1H), 6.86 (ddd, J = 7.6, 1.6, 0.8 Hz 1H), 6.80 (t, J = 2.0 Hz 1H), 3.84 (s, 3H), 2.28 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 162.16, 160.78, 154.19, 147.42, 138.74, 134.57, 130.68, 127.12, 126.72, 126.61, 120.74, 115.04, 113.70, 55.47, 24.14.

3-(4-methoxyphenyl)-2-methylquinazolin-4(3H)-one (2i):$^2$ The title compound was prepared according to the general procedure B on a 0.25 mmol scale to obtain as a white solid (49 mg, yield = 73 %); Mp. 167-169 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.27 (ddd, J = 8.0, 1.2, 0.8 Hz 1H), 7.47 (dd, J = 8.4, 7.2, 1.2 Hz 1H), 7.24 (s, 2H), 2.26 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 162.49, 159.90, 154.75, 147.39, 134.49, 130.20, 128.94, 127.04, 126.67, 126.54, 120.73, 115.17, 55.51, 24.37.

3-(4-fluorophenyl)-2-methylquinazolin-4(3H)-one (2j):$^2$ The title compound was prepared according to the general procedure B on a 0.25 mmol scale to obtain as a white solid (39 mg, yield = 62 %); Mp. 132-134°C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.26 (ddd, J = 8.0, 1.6, 0.4 Hz 1H), 7.79-7.75 (m, 1H), 7.68-7.63 (m, 1H), 7.47 (dd, J = 8.4, 7.2, 1.2 Hz 1H), 7.26 (d, J = 0.8, 2H), 2.24 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 13C NMR (101 MHz, cdcl3) δ 163.95, 161.47 (d, J$_F$=280 Hz), 153.97, 147.36, 145.80, 134.47, 129.90 (d, J$_F$=22.9 Hz), 129.82, 127.02, 126.81, 126.76 (d, J$_F$=9 Hz), 120.62, 117.18 (d, J$_F$=5.5 Hz), 116.95, 24.39.
The title compound was prepared according to the general procedure B on a 0.25 mmol scale to obtain as a white solid (50 mg, yield = 74 %); Mp. 124-126 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.29-8.27 (m, 1H), 7.79 (dd, J = 8.8, 7.2, 1.6 Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.63-7.61 (m, 1H), 7.50-7.45 (m, 3H), 7.36-7.33 (m, 1H), 2.23 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 161.45, 153.66, 147.49, 135.41, 132.55, 130.78, 130.73, 129.81, 128.35, 127.11, 126.85, 126.70, 120.54, 23.51.

3-(3-chlorophenyl)-2-methylquinazolin-4(3H)-one (2l):² The title compound was prepared according to the general procedure B on a 0.25 mmol scale to obtain as a white solid (46 mg, yield = 68 %); Mp. 129-131 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.27 (dd, J = 8.0, 1.6 Hz, 1H), 7.79 (dd, J = 8.4, 7.2, 1.6 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.51-7.46 (m, 3H), 7.31 (s, 1H), 7.20-7.17 (m, 1H), 2.27 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 162.07, 153.51, 147.35, 138.79, 135.61, 134.79, 130.93, 129.70, 128.55, 127.04, 126.87, 126.47, 120.59, 24.33.

3-(4-chlorophenyl)-2-methylquinazolin-4(3H)-one (2n):² The title compound was prepared according to the general procedure B on a 0.25 mmol scale to obtain as a white solid (51 mg, yield = 76 %); Mp. 153-155 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.26 (ddd, J = 8.0, 1.6, 0.4 Hz, 1H), 7.80-7.75 (m, 1H), 7.68 (dd, J = 8.4, 0.8, 1H), 7.55-7.52 (m, 2H), 7.48 (ddd, J = 8.0, 7.2, 1.2, 1H), 7.23-7.22 (m, 1H), 7.21-7.20 (m, 1H), 2.25 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 161.42, 153.66, 147.34, 136.15, 135.38, 134.74, 130.27, 129.45, 127.02, 126.83, 126.79, 120.56, 24.36.

3-(2-bromophenyl)-2-methylquinazolin-4(3H)-one (2o):² The title compound was prepared according to the general procedure B on a 0.25 mmol scale to obtain as a white solid (53 mg, yield = 67 %); Mp. 149-151 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.29 (ddd, J = 8.0, 1.6, 0.8 Hz, 1H), 7.79 (ddd, J = 8.4, 2.0, 0.8 Hz, 2H), 7.70 (m, ddd, J = 7.6, 1.2, 0.8 Hz, 1H), 7.54-7.46 (m, 2H), 7.42-7.34 (m, 2H), 2.22 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 161.42, 153.60, 147.50, 137.10, 134.76, 133.95, 130.92, 129.82, 129.08, 127.16, 126.88, 126.72, 122.87, 120.61, 23.70.

3-(4-bromophenyl)-2-methylquinazolin-4(3H)-one (2p):² The title compound was prepared according to the general procedure B on a 0.25 mmol scale to obtain as a white solid (59 mg, yield = 75 %); Mp. 166-168 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.26 (ddd, J = 8.0, 1.6, 0.4 Hz 1H), 7.78 (ddd, J = 8.0, 6.8, 1.6 Hz 1H), 7.71-7.67 (m, 3H), 7.48 (ddd, J =
8.4, 7.2, 1.2  Hz 1H), 7.17-7.14 (m, 2H), 2.25(s, 3H); $^1$C NMR (CDCl$_3$, 100 MHz) δ 162.09, 153.58, 147.32, 136.68, 134.76, 133.26, 129.76, 127.02, 126.81, 123.45, 120.54, 77.31, 76.99, 76.67, 24.36.

2-methyl-3-(4-(trifluoromethyl)phenyl)quinazolin-4(3H)-one (2q):$^9$ The title compound was prepared according to the general procedure B on a 0.25 mmol scale to obtain as a white solid (55 mg, yield = 72%); Mp. 147-149 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.26 (ddd, $J$ = 8.0, 1.6, 0.4 Hz, 1H), 7.85-7.83 (m, 2H), 7.79 (ddd, $J$ = 8.4, 7.2, 1.6, 1H), 7.69 (ddd, $J$ = 8.4, 1.2, 0.4, 1H), 7.49 (ddd, $J$ = 8.0, 7.2, 1.2, 1H), 7.44-7.42 (m, 2H), 2.24 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 162.09, 153.58, 147.32, 136.68, 134.76, 133.26, 129.76, 127.02, 126.81, 123.45, 120.54, 77.31, 76.99, 76.67, 24.36.

2-methylquinazolin-4(3H)-one (2s):$^8$ The title compound was prepared according to the general procedure B on a 0.25 mmol scale to obtain as a white solid (30 mg, yield = 75%); Mp. 230-232 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 12.15 (bs, 1H), 8.31-8.28 (m, 1H), 7.78 (ddd, $J$ = 8.4, 2.8, 1.2 Hz 1H), 7.71-7.68 (m, 1H), 7.49 (ddd, $J$ = 8.0, 6.8, 0.8 Hz 1H), 2.62 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 164.31, 153.35, 149.34, 134.89, 126.94, 126.40, 126.17, 120.19, 77.31, 76.99, 76.68, 22.03.

2,8-dimethyl-3-phenylquinazolin-4(3H)-one (2t): The title compound was prepared according to the general procedure B on a 0.25 mmol scale to obtain as a white solid (52 mg, yield = 83%); Mp. 146-148 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.12 (ddd, $J$ = 8.0, 1.6, 0.8 Hz, 1H), 7.61 (ddd, $J$ = 7.6, 1.6, 0.8 Hz, 1H), 7.57-7.53 (m, 2H), 7.51-7.49 (m, 1H), 7.34 (t, $J$ = 7.6, 1H), 7.27-7.24 (m, 2H), 2.63 (s, 3H), 2.25 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 162.72, 152.71, 146.07, 137.99, 135.33, 135.10, 129.93, 129.13, 128.02, 126.08, 124.67, 120.72, 24.61, 17.33. HRMS (ESI) calcd for C$_{16}$H$_{14}$N$_2$O [M+H]$^+$: 250.1106; found: 250.1109.

7-chloro-2-methyl-3-phenylquinazolin-4(3H)-one (2u):$^{10}$ The title compound was prepared according to the general procedure B on a 0.25 mmol scale to obtain as a white solid (46 mg, yield = 68%); Mp. 173-175 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.27 (ddd, $J$ = 8.0, 1.2, 0.4 Hz 1H), 7.80-7.76 (m, 1H), 7.69 (dd, $J$ = 7.6, 0.8 Hz 1H), 7.51-7.50 (m, 2H), 7.48-7.46 (m, 1H), 7.31 (td, $J$ = 2.8, 1.2 Hz, 1H), 7.20-7.17 (m, 1H), 2.27 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 162.04, 153.48, 147.32, 138.76, 135.57, 134.77, 130.91, 129.67, 128.53, 127.01, 126.85, 126.82, 126.45, 120.56, 24.31.
6-bromo-2-methyl-3-phenylquinazolin-4(3H)-one (2v): The title compound was prepared according to the general procedure B on a 0.25 mmol scale to obtain as a white solid (60 mg, yield = 76%); Mp. 178-180 °C; 1H NMR (CDCl₃, 400 MHz) δ 8.25 (d, J = 8.0, 1.2, 0.4 Hz, 1H), 7.79-7.74 (m, 1H), 7.70-7.65 (m, 3H), 7.47 (ddd, J = 8.0, 3.2, 1.2 Hz, 1H), 7.19-7.14 (m, 2H), 2.24 (s, 3H); 13C NMR (CDCl₃, 100 MHz) δ 162.06, 153.54, 147.31, 134.73, 133.24, 129.75, 126.99, 126.80, 126.78, 123.42, 120.53, 24.35.

2-methyl-3,6-diphenylquinazolin-4(3H)-one (2w): The title compound was prepared according to the general procedure B on a 0.25 mmol scale to obtain as a white solid (61 mg, yield = 79%); Mp. 173-175 °C; 1H NMR (CDCl₃, 400 MHz) δ 8.49 (d, J = 2.4 Hz, 1H), 8.02 (dd, J = 8.4, 2.0 Hz, 1H), 7.75 (d, J = 8.4, 1H), 7.70-7.67 (m, 2H), 7.59-7.45 (m, 5H), 7.40-7.35 (m, 1H), 7.30-7.27 (m, 2H), 2.26 (s, 3H); 13C NMR (CDCl₃, 100 MHz) δ 162.30, 154.12, 146.64, 139.59, 139.52, 137.74, 133.48, 129.99, 129.29, 128.93, 128.00, 127.76, 127.27, 127.13, 124.88, 120.98, 24.40. HRMS (ESI) calcd for C₂₁H₁₆N₂O [M+H]⁺: 312.1263; found: 312.1257.

1-(quinolin-2-yl)ethan-1-one (4a): The title compound was prepared according to the general procedure C on a 0.25 mmol scale to obtain as a white solid (28 mg, yield = 66%) Mp. 51-53 °C; 1H NMR (CDCl₃, 400 MHz) δ 8.26 (d, J = 8.8 Hz, 1H), 8.20 (d, J = 8.8 Hz, 1H), 8.13 (d, J = 8.8 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.80-7.76 (m, 1H), 7.66-64- (m, 1H), 2.87 (s, 3H); 13C NMR (CDCl₃, 100 MHz) δ 200.64, 153.20, 147.20, 136.82, 130.53, 129.94, 129.54, 128.51, 127.60, 117.92, 25.53.

1-(4-methylquinolin-2-yl)ethan-1-one (4b): The title compound was prepared according to the general procedure C on a 0.15 mmol scale to obtain as a white solid (30 mg, yield = 65%) Mp. 66-68 °C; 1H NMR (CDCl₃, 400 MHz) δ 8.19 (ddd, J = 8.4, 0.8, 0.4 Hz, 1H), 8.03(ddd, J = 8.0, 0.8, 0.4 Hz, 1H), 7.96 (d, J = 1.2 Hz, 1H), 7.76 (ddd, J = 8.4, 6.8, 1.6 Hz, 1H), 7.66 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 2.85 (s, 3H), 2.75 (d, J = 0.8 Hz, 3H); 13C NMR (CDCl₃, 100 MHz) δ 201.03, 152.81, 147.07, 145.24, 131.13, 129.55, 128.25, 123.74, 118.43, 25.47, 18.84.

1-(6-bromoquinolin-2-yl)ethan-1-one (4c): The title compound was prepared according to the general procedure C on a 0.15 mmol scale to obtain as a white solid (38 mg, yield = 60%) Mp. 62-64 °C; 1H NMR (CDCl₃, 400 MHz) δ 8.18 (dd, J = 8.4, 0.4 Hz, 1H), 8.14 (d, J = 8.8 Hz, 1H), 8.08-8.05 (m, 1H), 7.05 (d, J = 2.4 Hz, 1H), 7.85 (dd, J = 9.2, 2.4 Hz, 1H).
Hz, 1H), 2.85 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 200.20, 153.41, 145.76, 135.85, 133.57, 132.14, 130.52, 129.73, 122.81, 118.84, 25.49.

1-(4-phenylquinolin-2-yl)ethan-1-one (4d):$^{17}$ The title compound was prepared according to the general procedure C on a 0.15 mmol scale to obtain as a white solid (31 mg, yield = 61 %)

Mp. 68-70 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.18-8.12 (m, 3H), 7.85 (d, $J$ = 2.4 Hz, 1H), 7.71 (dd, $J$ = 8.8, 2.0 Hz, 1H), 2.85 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 200.16, 153.30, 145.53, 135.91, 134.47, 132.07, 131.00, 130.05, 126.32, 118.83, 25.48.

1-(4-phenylquinolin-2-yl)ethan-1-one (4e):$^{11}$ The title compound was prepared according to the general procedure C on a 0.15 mmol scale to obtain as a white solid (36 mg, yield = 58 %)

Mp. 58-60 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.27 (dd, $J$ = 8.8, 0.8 Hz, 1H), 8.08 (s, 1H), 7.98 (dd, $J$ = 8.4, 0.8 Hz, 1H), 7.78 (ddd, $J$ = 8.4, 6.8, 0.4 Hz, 1H), 7.59 (ddd, $J$ = 8.4, 6.8, 1.2 Hz, 1H), 7.53-7.49 (m, 5H), 2.90 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 200.79, 152.69, 149.34, 147.81, 137.70, 130.92, 129.74, 129.52, 128.58, 128.57, 128.54, 128.01, 125.80, 118.12, 25.57.

1-(6-methyl-4-(p-tolyl)quinolin-2-yl)ethan-1-one (4f): The title compound was prepared according to the general procedure C on a 0.15 mmol scale to obtain as a white solid (40 mg, yield = 59 %)

Mp. 176-178 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.17 (d, $J$ = 9.2 Hz, 1H), 8.04 (s, 1H), 7.54-7.49 (m, 5H), 7.44 (dd, $J$ = 8.2, 2.8 Hz, 1H), 7.24 (d, $J$ = 2.8 Hz, 1H), 3.81 (s, 3H), 2.87 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 200.65, 159.60, 150.78, 147.69, 143.80, 138.08, 132.47, 129.43, 129.31, 128.72, 128.53, 122.50, 118.72, 103.57, 55.54, 25.52. HRMS (ESI) calcd for C$_8$H$_6$ON$_2$ [M+H]$^+$: 277.1702 found: 277.1105.

1-(6-methyl-4-(p-tolyl)quinolin-2-yl)ethan-1-one (4g): The title compound was prepared according to the general procedure C on a 0.15 mmol scale to obtain as a white solid (39 mg, yield = 56 %)

Mp. 185-187 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.14 (d, $J$ = 8.8 Hz, 1H), 8.02 (s, 1H), 7.747-7.743 (m, 1H), 7.60 (dd, $J$ = 8.8, 2.0 Hz, 1H), 7.41-7.39 (m, 2H), 7.34 (d, $J$ = 8.0 Hz, 1H), 2.88 (s, 3H), 2.49 (s, 3H), 2.47 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) 13C NMR (101 MHz, cdc13) δ 200.88, 152.00, 148.55, 146.40, 138.81, 138.37, 134.99, 131.98, 130.60, 129.42, 129.28, 128.13, 124.63, 118.22, 25.54, 22.01, 21.29. HRMS (ESI) calcd for C$_8$H$_6$ON$_2$ [M+H]$^+$: 275.1310 found: 275.1312.

1,1'-(pyridine-2,3-diyl)bis(ethan-1-one) (4h):$^{13}$ The title compound was prepared according to the general procedure C on a 0.15 mmol scale to obtain as a white solid (29 mg, yield = 70 %); Mp. 77-
78 °C; ¹H NMR (CDCl₃, 400 MHz) δ 9.21 (dd, J = 2.4, 1.2, 1H), 8.34 (dd, J = 8.4, 2.4, 1H), 8.13 (dd, J = 8.4, 1.2, 1H), 2.76 (s, 3H), 2.69 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 199.31, 196.18, 155.78, 149.17, 136.48, 134.22, 121.48, 27.02, 25.99.

2-acetylnicotinonitrile (4i): The title compound was prepared according to the general procedure C on a 0.15 mmol scale to obtain as a white solid (20 mg, yield = 55%); Mp. 112-114 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.95 (dd, J = 1.6, 1.2, 1H), 8.16-8.10 (m, 2H), 2.75 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 198.51, 167.70, 155.05, 151.75, 140.35, 121.21, 116.01, 112.88, 25.81. HRMS (ESI) calcd for C₈H₈O₂ [M+H]⁺: 146.0480; found: 146.0485.

3-acetylnicotinonitrile (4j):¹⁴ The title compound was prepared according to the general procedure C on a 0.15 mmol scale to obtain as a white solid (26 mg, yield = 72%); Mp. 88-90 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.88 (dd, J = 4.8, 0.8, 1H), 8.26 (dd, J = 1.6, 1.2, 1H), 7.70 (dd, J = 3.2, 1.6, 1H), 2.74 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 198.14, 150.01, 128.06, 126.20, 123.40, 121.64, 115.86, 25.62.

1-(quinoxalin-2-yl)ethan-1-one (4k):¹¹ The title compound was prepared according to the general procedure C on a 0.15 mmol scale to obtain as a white solid (34 mg, yield = 81%); Mp. 77-79 °C; ¹H NMR (CDCl₃, 400 MHz) δ 9.50 (s, 1H), 8.22-8.16 (m, 2H), 7.92-7.84 (m, 2H), 2.86 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 199.77, 146.54, 143.84, 143.02, 141.04, 132.17, 130.69, 130.45, 129.39, 25.52.

1-(3-phenylquinoxalin-2-yl)ethan-1-one (4l):¹⁵ The title compound was prepared according to the general procedure C on a 0.25 mmol scale to obtain as a white solid (47 mg, yield = 77%); Mp. 107-109 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.19-8.16 (m, 2H), 7.89-7.80 (m, 2H), 7.65-7.63 (m, 2H), 7.52-7.48 (m, 3H), 2.76 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 201.17, 152.44, 150.03, 142.32, 139.72, 137.97, 131.82, 130.41, 129.57, 129.39, 129.32, 128.90, 128.62, 28.48.

1-(3-(p-tolyl)quinoxalin-2-yl)ethan-1-one (4m): The title compound was prepared according to the general procedure C on a 0.25 mmol scale to obtain as a white solid (48 mg, yield = 74%); Mp. 114-116 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.17-8.15 (m, 2H), 7.88-7.85 (m, 2H), 7.56-7.35 (m, 2H), 7.32 (d, J = 8.0, 2H), 2.74 (s, 3H), 2.43 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 201.42, 152.33, 150.23, 142.37, 139.60, 135.03, 132.61, 132.02, 131.68, 130.60, 130.21, 129.53, 129.40, 129.27, 128.86, 28.58, 21.40. HRMS (ESI) calcd for C₁₇H₁₄O₂ [M+H]⁺: 262.1106; found: 262.1107.
1-(3-(naphthalen-2-yl)quinoxalin-2-yl)ethan-1-one (4n): The title compound was prepared according to the general procedure C on a 0.25 mmol scale to obtain as a white solid (57 mg, yield = 70%); Mp. 182-184 °C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 8.17 (dddd, $J = 8.5, 7.0, 1.6, 0.6$ Hz, 2H), 7.86 (dddd, $J = 16.8, 8.0, 6.9, 1.6$ Hz, 2H), 7.65-7.61 (m, 2H), 7.52-7.48 (m, 2H), 2.81 (s, 3H), 2.81 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 200.83, 151.49, 149.19, 142.29, 139.75, 137.01, 132.09, 131.71, 130.65, 130.53, 129.63, 129.27, 123.97, 28.28. HRMS (ESI) calcd for C$_{16}$H$_{11}$BrON$_2$ [M+H]$^+$: 326.0055; found: 326.0056.

1-(3-(4-chlorophenyl)quinoxalin-2-yl)ethan-1-one (4o): The title compound was prepared according to the general procedure C on a 0.25 mmol scale to obtain as a white solid (59 mg, yield = 85%); Mp. 167-169 °C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 8.19-8.14 (m, 2H), 7.85 (dddd, $J = 16.7, 8.0, 6.9, 1.6$ Hz, 2H), 7.60-7.56 (m, 2H), 7.49-7.45 (m, 2H), 2.81 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 200.84, 151.39, 149.23, 142.26, 139.72, 136.52, 135.61, 132.06, 130.62, 129.60, 129.25, 128.76, 28.28. HRMS (ESI) calcd for C$_{16}$H$_{11}$ClON$_2$ [M+H]$^+$: 282.0560; found: 282.0562.

1-(3-(naphthalen-2-yl)quinoxalin-2-yl)ethan-1-one (4p): The title compound was prepared according to the general procedure C on a 0.25 mmol scale to obtain as a white solid (54 mg, yield = 73%); Mp. 160-162 °C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 8.22-8.16 (m, 3H), 7.96-7.80 (m, 5H), 7.71 (dd, $J = 8.4, 2.0$ Hz, 1H), 7.56-7.51 (m, 2H), 2.78 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 201.20, 152.34, 150.12, 142.38, 139.70, 135.35, 133.53, 133.14, 131.85, 130.42, 129.59, 129.29, 128.82, 128.66, 128.26, 127.73, 126.98, 126.48, 126.11, 28.47. HRMS (ESI) calcd for C$_{20}$H$_{14}$O$_2$ [M+H]$^+$: 298.1106; found: 298.1112.

1-(6,7-dimethyl-3-phenylquinoxalin-2-yl)ethan-1-one (4q): The title compound was prepared according to the general procedure C on a 0.25 mmol scale to obtain as a white solid (49 mg, yield = 71%); Mp.102-104 °C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.92 (d, $J = 0.8$ Hz, 2H), 7.62-7.59 (m, 2H), 7.48-7.47 (m, 3H), 2.74 (s, 3H), 2.53 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 201.36, 151.65, 149.03, 142.88, 141.33, 141.19, 138.69, 138.35, 129.08, 128.86, 128.50, 128.45, 128.28, 28.44, 20.61, 20.38. HRMS (ESI) calcd for C$_{18}$H$_{16}$ON$_2$ [M+H]$^+$: 276.1263; found: 276.1265.

1-(7-chloro-3-phenylquinoxalin-2-yl)ethan-1-one (4r): The title compound was prepared according to the general procedure C on a 0.25 mmol scale to obtain as a white solid (51 mg, yield = 73%); Mp. 137-139 °C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 8.17 (d, $J = 2.0$ Hz, 1H), 8.11 (d, $J = 9.2$ Hz, 1H), 7.76 (dd, $J = 8.8, 2.4$ Hz, 1H), 7.64 -7.61 (m, 2H), 7.52 -
7.49 (m, 3H), 2.75 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 200.78, 153.34, 150.03, 142.57, 138.17, 137.84, 137.50, 131.51, 130.74, 129.69, 128.92, 128.65, 128.21, 28.41. HRMS (ESI) calcd for C$_{17}$H$_{14}$ON$_2$ [M+H]$^+$: 282.0560; found: 282.0556.

1-(4-phenylquinazolin-2-yl)ethan-1-one (4s):$^{15}$ The title compound was prepared according to the general procedure C on a 0.25 mmol scale to obtain as a white solid (43 mg, yield = 69%); Mp. 106-108 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.31 (ddd, $J$ = 8.4, 0.8, 0.4 Hz, 1H), 8.21 (ddd, $J$ = 8.4, 1.2, 0.8 Hz, 1H), 8.00 (ddd, $J$ = 8.4, 7.2, 1.6 Hz, 1H), 7.85-7.82 (m, 2H), 7.73 (ddd, $J$ = 8.4, 7.2, 1.2 Hz, 1H), 7.60-7.59 (m, 3H), 2.94 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 198.77, 169.27, 155.87, 151.12, 136.79, 134.20, 130.30, 130.25, 130.21, 129.50, 128.65, 127.12, 123.22, 27.20.

1-(4,6-diphenylquinazolin-2-yl)ethan-1-one (4t):$^{16}$ The title compound was prepared according to the general procedure C on a 0.25 mmol scale to obtain as a white solid (34 mg, yield = 42%); Mp. 106-108 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.39-8.35 (m, 2H), 8.26 (ddd, $J$ = 8.8, 2.0 Hz, 1H), 7.89-7.87 (m, 2H), 7.65-7.60 (m, 5H), 7.51-7.47 (m, 2H), 7.44-7.43 (m, 1H), 2.96 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 198.69, 169.22, 155.69, 150.47, 142.44, 139.40, 136.84, 133.94, 130.70, 130.36, 130.20, 129.16, 128.76, 128.47, 127.50, 124.48, 123.46, 27.20.

1-(6-bromo-4-phenylquinazolin-2-yl)ethan-1-one (4u): The title compound was prepared according to the general procedure C on a 0.25 mmol scale to obtain as a white solid (47 mg, yield = 42%) Mp. 127-29 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.35 (dd, $J$ = 2.0, 0.4 Hz, 1H), 8.18 (dd, $J$ = 8.8, 0.4 Hz, 1H), 8.06 (dd, $J$ = 9.2, 2.4 Hz, 1H), 7.83-7.80 (m, 2H), 7.63-7.16 (m, 3H), 2.92 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 198.31, 168.41, 155.89, 149.82, 137.87, 136.17, 131.87, 130.64, 130.09, 130.04, 129.97, 129.24, 128.88, 124.14, 123.80, 27.15. HRMS (ESI) calcd for C$_{16}$H$_{11}$BrON$_2$ [M+H]$^+$: 326.0055; found: 326.0056.

1-(6-chloro-4-phenylquinazolin-2-yl)ethan-1-one (4v):$^{16}$ The title compound was prepared according to the general procedure C on a 0.25 mmol scale to obtain as a white solid (42 mg, yield = 59%) Mp. 102-104 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.25 (d, $J$ = 9.2 Hz, 1H), 8.17 (d, $J$ = 2.0 Hz, 1H), 7.93 (dd, $J$ = 9.2, 2.4 Hz, 1H), 7.82 (dd, $J$ = 6.0, 2.0 Hz, 2H), 7.62 (dd, $J$ = 5.6, 2.4 Hz, 1H), 2.92 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) 198.32, 168.53, 155.92, 149.64, 136.22, 135.57, 135.31, 131.89, 130.64, 130.09, 128.89, 125.92, 123.77, 102.92, 27.16.
1-(benzothiazol-2-yl)ethan-1-one (4w): The title compound was prepared according to the general procedure C on a 0.25 mmol scale to obtain as a white solid (31 mg, yield = 70 %) Mp. 105-107 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.19 (ddd, J = 7.6, 1.2, 0.4, 1H), 7.98 (ddd, J = 8.0, 1.6, 0.8, 1H), 7.60-7.55 (m, 1H), 7.55-7.50 (m, 1H), 2.83 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 198.51, 167.70, 155.05, 151.75, 140.35, 121.21, 116.01, 112.88, 25.81.

1-(quinolin-2-yl)ethan-1-one (4x): The title compound was prepared according to the general procedure C on a 0.25 mmol scale to obtain as a white solid (22 mg, yield = 42 %) Mp. 94-96 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.14-8.07 (m, 3H), 8.43 (dd, J = 9.2, 2.8 Hz, 1H), 7.11 (d, J = 2.8 Hz, 1H), 2.96 (s, 3H), 2.84 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 200.49, 159.44, 151.23, 143.19, 135.27, 132.02, 131.00, 123.06, 118.46, 104.86.

1,1’-(quinoline-2,4-diyl)bis(ethan-1-one) (4a’): The title compound was prepared according to the general procedure C on a 0.25 mmol scale to obtain as a white solid (14 mg, yield = 26%) Mp. 67-69 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.57-8.54 (m, 1H), 8.37 (s, 1H), 8.25 (ddd, J = 8.4 1.5, 0.8 Hz, 1H), 7.83 (ddd, J = 8.4, 6.8, 2.4 Hz, 1H), 7.76-7.72 (m, 1H), 2.89 (s, 3H), 2.79 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 200.99, 199.99, 152.64, 148.31, 142.94, 131.01, 130.38, 130.31, 125.64, 124.99, 116.97, 29.94, 25.38.

1,1’-(6-bromoquinoline-2,4-diyl)bis(ethan-1-one) (4c’): The title compound was prepared according to the general procedure C on a 0.25 mmol scale to obtain as a white solid (15 mg, yield = 21%) Mp. 68-70 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.85 (d, J = 2.0 Hz, 1H), 8.24 (s, 1H), 8.11 (d, J = 6.8 Hz, 1H), 7.91 (dd, J = 7.2,2.0 Hz, 1H), 2.87 (s, 3H), 2.79 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 200.27, 199.60, 152.86, 146.98, 141.39, 134.07, 132.37, 128.28, 125.97, 125.59, 118.10, 29.71, 25.35. HRMS (ESI) calcd for C₁₃H₁₀BrNO₂ [M+H]+: 290.9895; found: 290.9893
(5) X-ray Analysis

Table S1. Crystal data and structure refinement for 2k.

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<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0459, wR2 = 0.1444</td>
</tr>
</tbody>
</table>
R indices (all data) R1 = 0.0501, wR2 = 0.1508
Extinction coefficient n/a
Largest diff. peak and hole 0.728 and -0.682 eÅ^-3

Table S1. Crystal data and structure refinement for 2v.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>2v</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C21 H16 N2 O</td>
</tr>
<tr>
<td>Formula weight</td>
<td>312.36</td>
</tr>
<tr>
<td>Temperature</td>
<td>301(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P21/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 14.5419(6) Å</td>
</tr>
<tr>
<td></td>
<td>b = 15.7313(6) Å</td>
</tr>
<tr>
<td></td>
<td>c = 7.0669(3) Å</td>
</tr>
<tr>
<td></td>
<td>a= 90°.</td>
</tr>
<tr>
<td></td>
<td>b= 91.8219(17)°.</td>
</tr>
<tr>
<td></td>
<td>g = 90°.</td>
</tr>
<tr>
<td>Volume</td>
<td>1615.83(11) Å</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.284 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.080 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>656</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.520 x 0.410 x 0.130 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.945 to 27.093°.</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-18&lt;=h&lt;=18, -20&lt;=k&lt;=20, -9&lt;=l&lt;=9</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>29530</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>3531 [R(int) = 0.0482]</td>
</tr>
<tr>
<td>Completeness to theta = 25.242°</td>
<td>99.0 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
</tbody>
</table>
Max. and min. transmission: 0.9281 and 0.8374
Refinement method: Full-matrix least-squares on $F^2$
Data / restraints / parameters: 3531 / 0 / 217
Goodness-of-fit on $F^2$: 1.052
Final R indices [$I>2\sigma(I)$]: $R1 = 0.0703$, $wR2 = 0.2011$
R indices (all data): $R1 = 0.0964$, $wR2 = 0.2456$
Extinction coefficient: n/a
Largest diff. peak and hole: 0.522 and -0.423 e.$\text{Å}^{-3}$

Table S1. Crystal data and structure refinement for 4w.

<table>
<thead>
<tr>
<th>Identification code</th>
<th>4x</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>$C_9H_7NO_S$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>177.22</td>
</tr>
<tr>
<td>Temperature</td>
<td>285(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P2_1/n$</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>$a = 5.7146(8)$ Å, $a = 90^\circ$</td>
</tr>
<tr>
<td>Volume</td>
<td>$828.4(2)$ Å$^3$</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.421 Mg/m$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.334 mm$^{-1}$</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>368</td>
</tr>
</tbody>
</table>
Crystal size: 0.600 x 0.320 x 0.160 mm\(^3\)
Theta range for data collection: 3.528 to 26.721°.
Index ranges: -7 \(\leq\) h \(\leq\) 7, -13 \(\leq\) k \(\leq\) 13, -17 \(\leq\) l \(\leq\) 17
Reflections collected: 11618
Independent reflections: 1644 [R (int) = 0.0463]
Completeness to theta = 25.242°: 96.9 %
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 0.9268 and 0.7078
Refinement method: Full-matrix least-squares on F\(^2\)
Data / restraints / parameters: 1644 / 0 / 109
Goodness-of-fit on F\(^2\): 1.102
Final R indices [I>2sigma(I)]: R1 = 0.0616, wR2 = 0.1553
R indices (all data): R1 = 0.0853, wR2 = 0.1754
Extinction coefficient: n/a
Largest diff. peak and hole: 0.314 and -0.394 e.Å\(^{-3}\)
(6) References:
Solvent: CDCl₃
Spectrometer Frequency: 400 MHz

Solvent: CDCl₃
Spectrometer Frequency: 100 MHz
Solvent: CDCl$_3$
Spectrometer Frequency: 400.13 MHz
Solvent: CDCl₃
Spectrometer Frequency: 400.40 MHz

Solvent: CDCl₃
Spectrometer Frequency: 100.69 MHz

[Chemical Structures]

[Graphs and Spectra]
Solvent: CDCl₃
Spectrometer Frequency: 400.10

Solvent: CDCl₃
Spectrometer Frequency: 100.69
Solvent: CDCl₃
Spectrometer Frequency: 400.19 MHz

- 7.27 ppm
- 7.19 ppm
- 6.85 ppm
- 5.11 ppm
- 4.56 ppm

Solvent: CDCl₃
Spectrometer Frequency: 100.69 MHz

- 19.14 ppm
- 18.46 ppm
- 16.85 ppm
- 15.79 ppm
- 15.48 ppm

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