

Electronic Supplementary Information (ESI)

**Iron-based Metal-Organic Framework, Fe(BTC): An Effective Two-
Function Catalyst for Oxidative Cyclization of Bisnaphthols and Tandem
Synthesis of Quinazolin-4(3*H*)-ones**

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S1. General information.

Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku XDS 2000 diffractometer using nickel-filtered Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) over a range of $2^\circ < 2\theta < 42^\circ$ (time step = 15 s). Samples for scanning electron microscopy (SEM) were sputtered with a layer of Os (5-nm thickness) prior to taking images on a Hitachi S-4800 SEM. NMR spectra were recorded on Jeol 90 MHz and 500 MHz Agilent DD MR-400 system equipped with Agilent 7600 96-sample auto-sampler. ^1H NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale) using the residual solvent resonances as internal standards. Atomic analysis was performed by Varian SpectrAA-600 Atomic Absorption Spectrometer. Fourier-transformed infrared (FTIR) spectroscopy spectra were recorded using a Perkin Elmer Spectrum-FTIR Version 10.01.00. Melting points were determined on a Stuart Scientific SMP3 apparatus and are uncorrected. Chromatographic separations were performed on silica gel 60 (230–400 mesh).

S2. General procedures and materials.

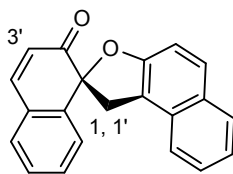
Bis(2-hydroxy-1-naphthyl)methanes [(methylenebisanthol) and arylbisanthols] were synthesized following Mironov and Hewitt's methods.¹ Fe(BTC) (Basolite®F300, Sigma-Aldrich), formaldehyde solution (Sigma-Aldrich, 37 wt% in H₂O), 2-Naphthol (Sigma-Aldrich, 99%), sodium acetate (Sigma-Aldrich, 99%), hydrogen peroxide (Sigma-Aldrich, 30% in H₂O), *tert*-butyl hydroperoxide (Sigma-Aldrich, 70% in H₂O), *o*-aminobenzamide (Sigma-Aldrich, $\geq 98\%$), benzyl alcohols (Merck, for synthesis), and solvents were purchased from commercial sources and were used without further purification. It should be noted that Fe(BTC) was activated at 150 °C for 3 h prior to performing the reactions. The products were identified by comparison of their physical and spectral data with those of known compounds.^{1,2}

S3. A typical procedure for the oxidative cyclization of bis(2-hydroxy-1-naphthyl)methane using Fe(BTC) as a heterogonous catalyst

To a sealed tube, bis(2-hydroxy-1-naphthyl)methane (0.5 mmol), Fe(BTC) (15 mg, equivalent to 3.75 mg of iron, 0.067 mmol of Fe), acetonitrile (5 ml) and then H₂O₂ (30% in water, 1.6 mmol, 3.2 eq.) was added and stirred at 40 °C for 8 hours (monitored by TLC). The reaction proceeded for 8 hours, as observed by TLC. After separation of the catalyst (Fe-BTC) by centrifugation, the remaining solution was evaporated to dryness under reduced pressure. The resulting crude product was then purified by column chromatography (ethyl acetate/n-hexane; 2:10 v/v) to afford the pure product.

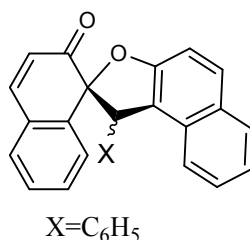
All of the known products were identified by comparison of their physical and spectroscopic data with those reported in the literature.¹ Melting points shown in Table 2.

Spiro{naphthalene-1(2H),2'(1'H)-naphtho[2,1-b]furan}-2-one (Table 2, Entry 1):



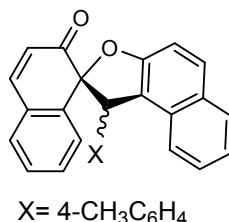
Yellow solid; R_f value: 0.55 (EtOAc/n-hexane, 2:10); IR (ν_{max} , cm⁻¹): 1726 (C=O); ¹H NMR (500 MHz, CDCl₃): δ 3.52 (d, J = 15.6 Hz, 1H), 4.05 (d, J = 15.6 Hz, 1H), 6.25 (d, J = 9.9 Hz, 1H), 7.33-7.52 (m, 9H), 7.80 (d, J = 8.7 Hz, 1 H), 7.84 (d, J = 8.5 Hz, 1H).

1'-Phenyl-spiro{naphthalene-1(2H),2'(1'H)-naphtho[2,1-b]furan}-2-one (Table 2, Entry 2, isomer 1 and isomer 2):



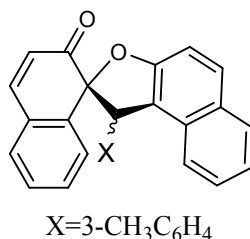
Yellow solid; IR (ν_{max} , cm^{-1}): 1729 ($\text{C}=\text{O}$); ^1H NMR (90 MHz, CDCl_3): δ 5.21 and 5.40 (s, hydrogen number 1, 1H), 5.53 and 6.28 ($J = 10$ Hz and $J = 9.9$ Hz due to hydrogen number 3', 1H), 6.95–7.99 (Ar and hydrogen number 4', 16H).

1'-(4-Methylphenyl)-spiro{naphthalene-1(2H),2'-(1'H)-naphtho[2,1-b]furan}-2-one (Table 2, Entry 3, isomer 1 and isomer 2):



Yellow solid; IR (ν_{max} , cm^{-1}): 1680 ($\text{C}=\text{O}$); ^1H NMR (500 MHz, CDCl_3): δ 2.12 and 2.27 (s, 3H), 5.18 and 5.37 (s, 1H), 5.55 and 6.28 (d, $J = 9.99$ and 9.92 Hz, 1H), 6.66–7.89 (15H).

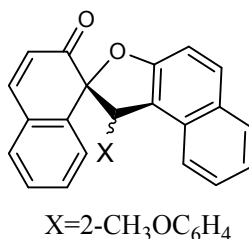
1'-(3-Methylphenyl)-spiro{naphthalene-1(2H),2'-(1'H)-naphtho[2,1-b]furan}-2-one (Table 2, Entry 4, isomer 1 and isomer 2):



Yellow solid; IR (ν_{max} , cm^{-1}): 1687 ($\text{C}=\text{O}$); ^1H NMR (90 MHz, CDCl_3): δ 2.14 and 2.29 (s, 3H); 5.19 and 5.38 (s, hydrogen number 1, 1H), 5.56 and 6.27 (d, $J = 9.9$ Hz and $J = 10$ Hz due to

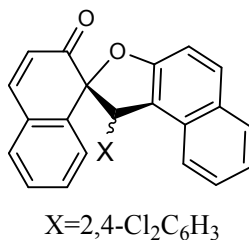
hydrogen number 3', 1H), 6.47–7.97 (Ar and hydrogen number 4', 15H).

1'-(2-Methoxyphenyl)-spiro{naphthalene-1(2H),2'(1'H)-naphtho[2,1-b]furan}-2-one (Table 2, Entry 5, isomer 1 and isomer 2):



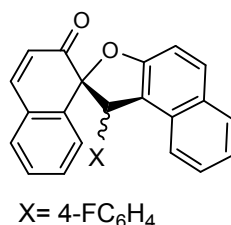
Yellow solid; IR (ν_{max} , cm^{-1}): 1681 (C=O); ^1H NMR (90 MHz, CDCl_3): δ 3.55 and 3.66 (s, 3H); 5.44 and 5.55 (s, hydrogen number 1, 1H), 5.35 and 6.23 (d, $J = 9.9$ Hz and $J = 10$ Hz due to hydrogen number 3', 1H), 6.63–7.96 (Ar and hydrogen number 4', 15H).

1'-(2,4-dichlorophenyl)-spiro{naphthalene-1(2H),2'(1'H)-naphtho[2,1-b]furan}-2-one (Table 2, Entry 6, isomer 1 and isomer 2):



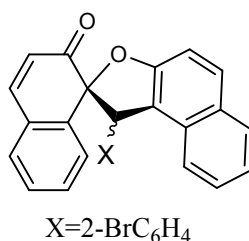
Yellow solid; IR (ν_{max} , cm^{-1}): 1686 (C=O); ^1H NMR (90 MHz, CDCl_3): δ 5.52 and 5.63 (s, hydrogen number 1, 1H), 5.58 and 6.23 (d, both $J = 10$ Hz due to hydrogen number 3', 1H), 6.65–8.00 (Ar and hydrogen number 4', 14H).

1'-(4-Fluorophenyl)-spiro[naphthalene-1(2H),2'(1'H)-naphtho[2,1-b]furan]-2-one (Table 2, Entry 7, isomer 1 and isomer 2):



Yellow solid; IR (ν_{max} , cm^{-1}): 1676 (C=O); ^1H NMR (500 MHz, CDCl_3): δ 5.19 and 5.38 (s, 1H), 5.57 and 6.27 (d, $J = 9.98$ Hz and $J = 9.92$ Hz, 1H); 6.26–7.9 (15H).

1'-(2-Bromophenyl)-spiro{naphthalene-1(2H),2'(1'H)-naphtho[2,1-b]furan}-2-one (Table 2, Entry 8, isomer 3 and isomer 4):



Yellow solid; IR (ν_{max} , cm^{-1}): 1687 (C=O); ^1H NMR (90 MHz, CDCl_3): δ 5.48 and 5.59 (s, hydrogen number 1, 1H), 5.53 and 6.26 (d, both $J = 10$ Hz due to hydrogen number 3', 1H), 6.57–7.98 (Ar and hydrogen number 4', 15H).

S4. Reusability of the catalyst and hot-filtration test

After reaction completion, the catalyst was separated and washed with ethyl acetate and acetone followed by drying at 150 °C. The dried catalyst was then reused for the next cycle.

Table S1. Reusability of Fe(BTC) and hot- filtration test for the oxidative cyclization of bis(2-hydroxy-1-naphthyl)methane by H₂O₂

Entry	Time (h)	Yield (%) ^a
1	8	82
2 ^b	8	76
3 ^c	8	68
4 ^d	8	40
^a Yields refer to pure products. ^b Reusability of Fe(BTC) in second run. ^c Reusability of Fe(BTC) in third run. ^d Hot- filtration test: Fe(BTC) catalyst was removed from the reaction mixture after 4 h, while the supernatant ran further under the same conditions, the reaction did not proceed to completion after 12 h.		

S5. Simulated PXRD pattern of MIL(100)-Fe

PXRD pattern of MIL(100)-Fe derived from the crystal structure, [*Chem. Commun.*, 2007, 2820–2822] using Mercury software as shown in Fig. S1 & S2. The three plots are the same with the various peak shapes [could be obtained from setting section in Mercury software, FWHM (2 theta) = 0.1, 0.4 and 0.8], resulting in further information/clarification of the Fe(BTC) structure (as mentioned in the text).

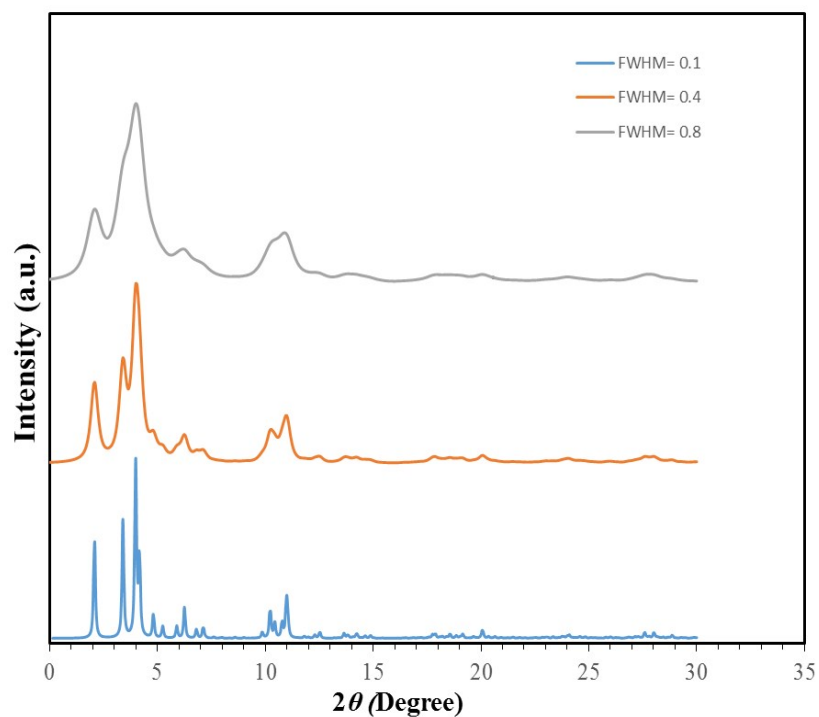


Fig. S1 Simulated PXRD pattern of MIL(100)-Fe derived from the crystal structure [*Chem. Commun.*, 2007, 2820–2822] [The various peak shapes could be obtained from setting section in Mercury software, FWHM (2θ) = 0.1, 0.4 and 0.8].

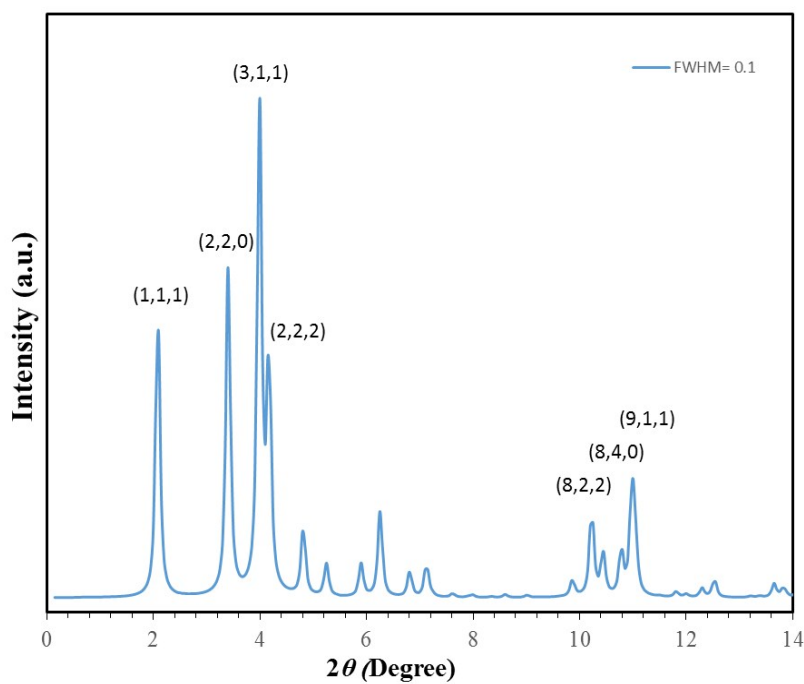


Fig. S2 Simulated PXRD pattern (expanded region, $2\theta = 0\text{--}14^\circ$) of MIL(100)-Fe derived from the crystal structure [*Chem. Commun.*, 2007, 2820–2822] along with the reflections.

S6. FTIR spectra of Fe(BTC)

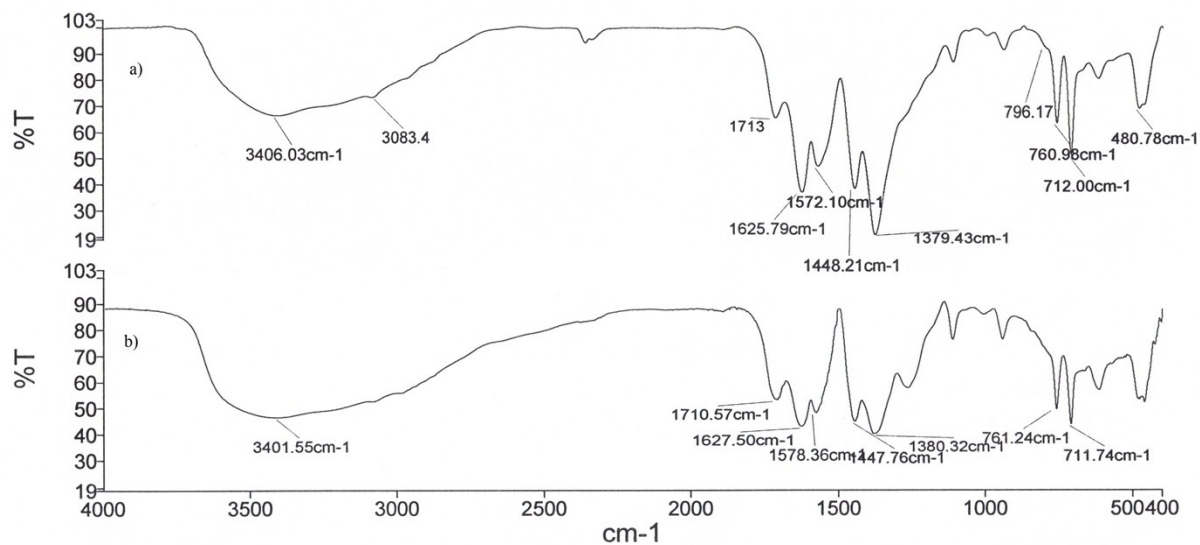


Fig. S3 FTIR spectra of Fe(BTC); a) fresh and b) reused (after the first cycle).

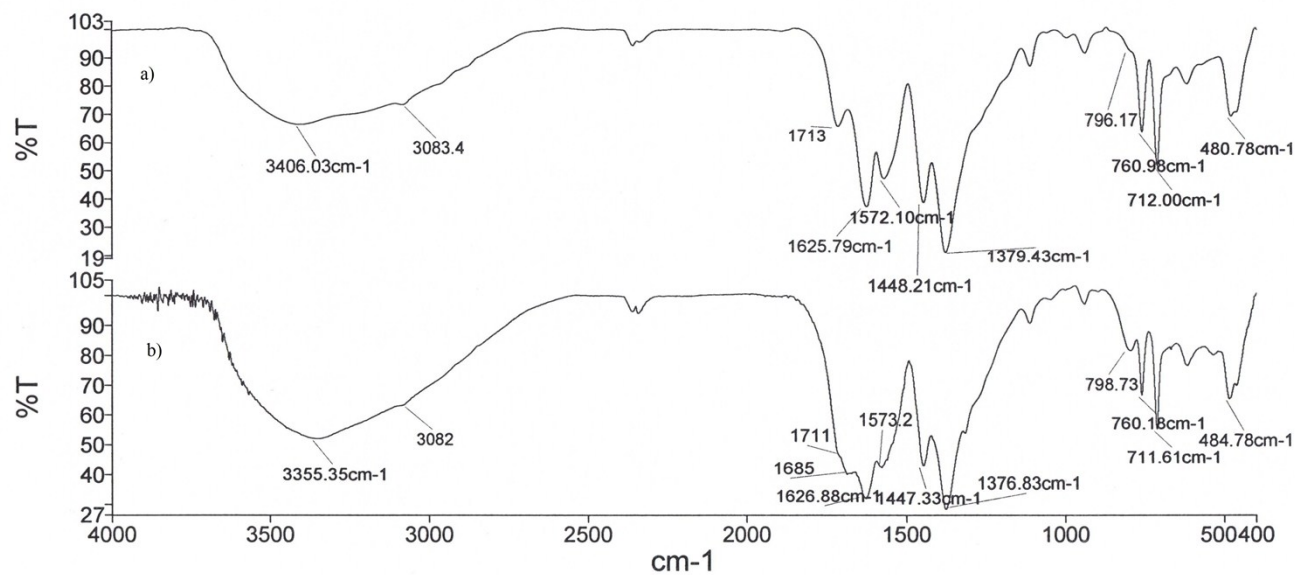
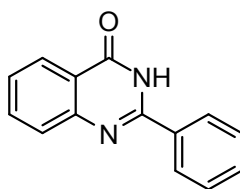


Fig. S4 FTIR spectra of Fe(BTC); a) fresh and b) reused (the last cycle).

S7. Tandem catalytic synthesis of quinazolin-4(3*H*)-ones using Fe(BTC)

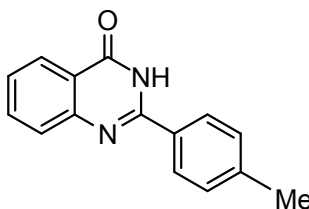
Into a sealed tube equipped with a magnetic stirrer bar were combined primary alcohol (1.5 mmol), *o*-aminobenzamide (0.5 mmol), Fe(BTC) (15 mg), DMSO (3 ml), and TBHP (70% in water, 2 mmol). After stirring for indicated time at 60 °C, EtOAc (5 mL) was added to quench the reaction followed by centrifugal separation of the catalyst. The remaining solution was evaporated to dryness under reduced pressure. The residue was subjected to column chromatography (EtOAc/n-Hexane; 6:4 v/v) or recrystallization (EtOH/H₂O) to afford the solid product. The desired product was characterized by comparison of their physical and NMR data with those of known compounds.²

2-Phenylquinazolin-4(3*H*)-one (Table 4, Entry 1):



White solid, mp: 232–235 °C (lit.² 236-237 °C); IR ($\nu_{\max}$, cm⁻¹): 3196 (N-H), 1668 (C=O); ¹H NMR (90 MHz, DMSO-*d*₆): δ 12.50 (s br, 1H), 8.13-8.16 (m, 3H), 7.50-7.82 (m, 6H); ¹³C NMR (125 MHz, DMSO-*d*₆): δ 163, 153.1, 149.6, 135.4, 133.5, 132.2, 129.4, 128.6, 128.3, 127.4, 126.7, 121.8.

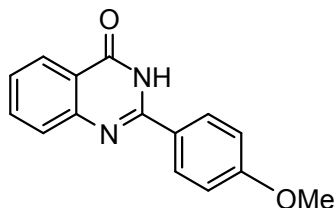
2-(*p*-Tolyl)quinazolin-4(3*H*)-one (Table 4, Entry 2):



White solid, mp: 261–262 °C (lit.² 261-263 °C); IR ($\nu_{\max}$, cm⁻¹): 3176 (N-H), 1659 (C=O);

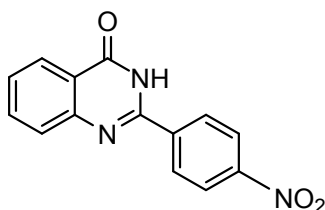
^1H NMR (CDCl_3 , 500 MHz): δ 11.62 (s br, 1H), 8.33 (d, $J = 8.05$ Hz, 1H), 8.16 (d, $J = 8.15$ Hz, 2H), 7.77-7.83 (m, 2H), 7.49-7.50 (m, 1H), 7.36-7.47 (m, 2H), 2.52 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 163.2, 152.2, 150, 142.5, 135.2, 130.4, 130.1, 128.3, 127.7, 126.9, 126.7, 121.2, 21.9.

2-(4-Methoxyphenyl)quinazolin-4(3H)-one (Table 4, Entry 3):



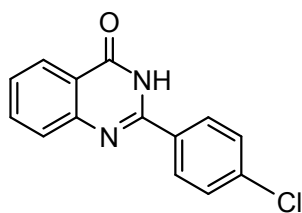
White solid. mp: 245-248 °C (lit.² 247-248 °C); IR (ν_{max} , cm^{-1}): 3171 (N-H), 1664 (C=O); ^1H NMR ($\text{DMSO}-d_6$, 500 MHz): δ 12.3 (s br, 1H), 8.08-8.14 (m, 3H), 7.65-7.75 (m, 2H), 7.43 (s br, 1H), 7.03 (s br, 2H), 3.79 (s, 3H); ^{13}C NMR ($\text{DMSO}-d_6$, 125 MHz): δ 163.1, 162.7, 152.7, 149.8, 135.3, 130.3, 128.1, 126.9, 126.6, 125.6, 121.5, 114.8, 56.3.

2-(4-Nitrophenyl)quinazolin-4(3H)-one (Table 4, Entry 4):



The product was washed with petroleum ether/ethyl acetate (5:1). Yellow solid; mp >300 °C (lit.² >300 °C); IR (ν_{max} , cm^{-1}): 3175 (N-H), 1682 (C=O); ^1H NMR ($\text{DMSO}-d_6$, 500 MHz): δ 12.77 (s br, 1H), 8.28-8.35 (m, 4H), 8.13 (m, 1H), 7.75-7.83 (m, 2H), 7.50-7.54 (m, 1H).

2-(4-Chlorophenyl)quinazolin-4(3H)-one (Table 4, Entry 5):



White solid. mp: 299-301 °C (lit.² 298-300 °C); IR ($\nu_{\max}$, cm^{-1}): 3193 (N-H), 1677 (C=O); ^1H NMR ($\text{DMSO-}d_6$, 500 MHz): δ 12.55 (s br, 1H), 8.10-8.16 (m, 3H), 7.80 (t, $J = 8.0$ Hz, 1H), 7.70 (d, $J = 8.0$ Hz, 1H), 7.57 (d, $J = 8.0$ Hz, 2H), 7.49 (t, $J = 8.0$ Hz, 1H).

S8. Spectroscopic data of the products

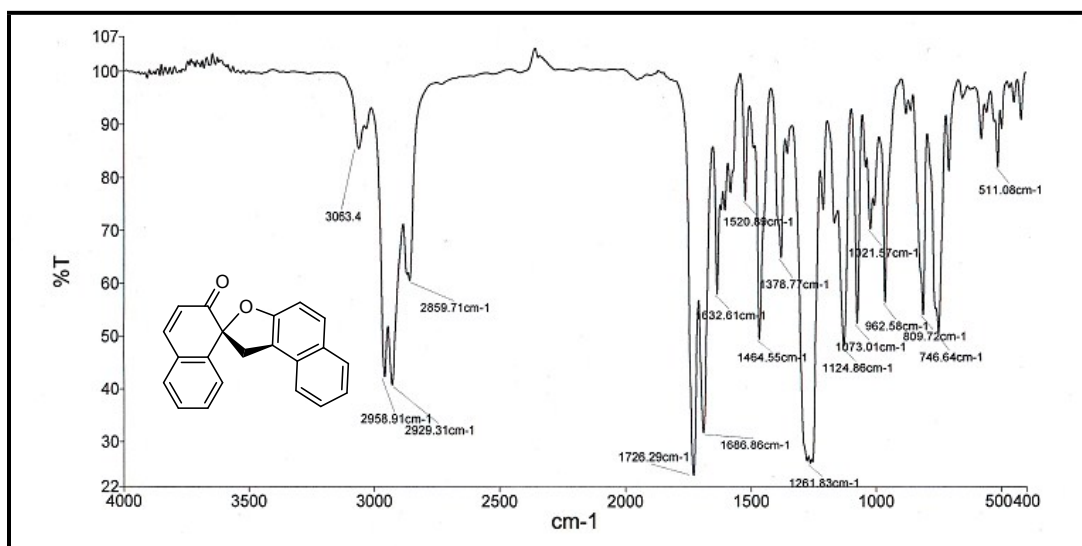


Fig S5. FTIR of spiro{naphthalene-1(2H),2'(1'H)-naphtho[2,1-b]furan}-2-one.

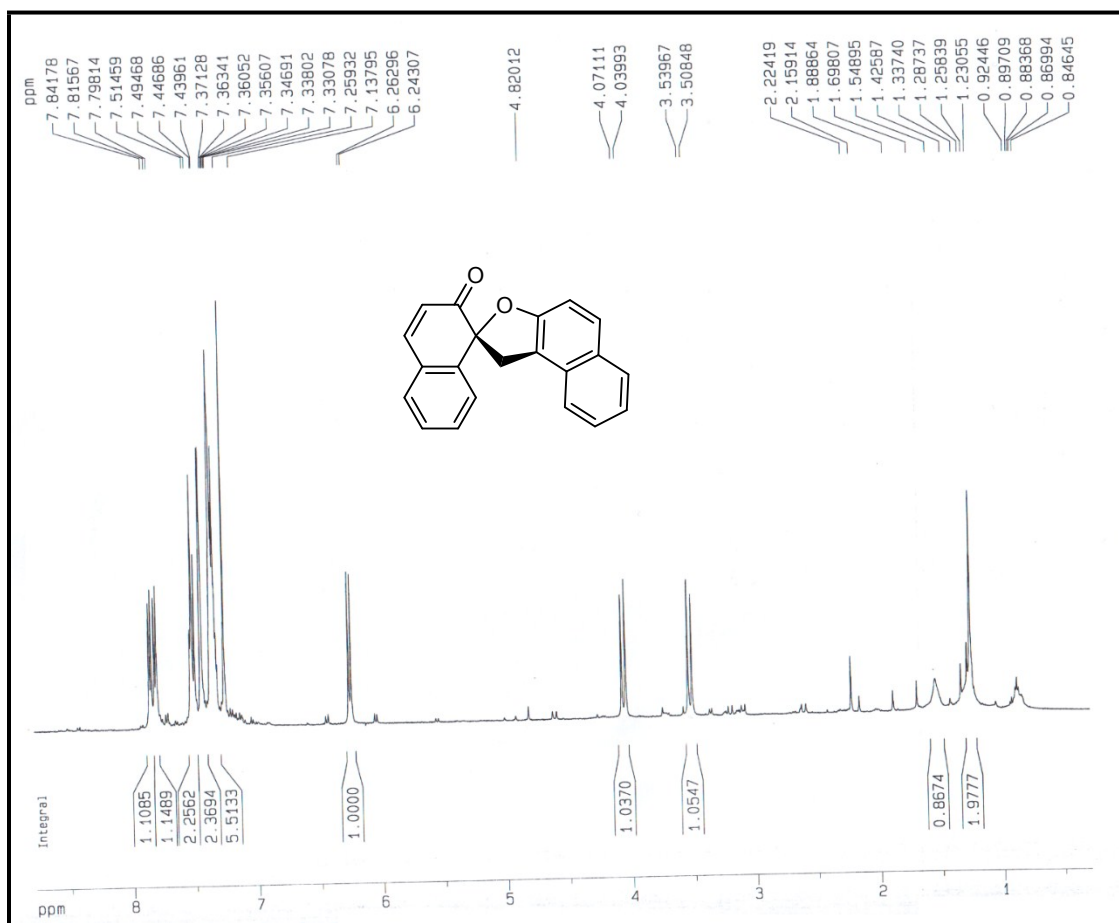


Fig S6. ¹H NMR (500 MHz) of spiro{naphthalene-1(2H),2'(1'H)-naphtho[2,1-b]furan}-2-one.

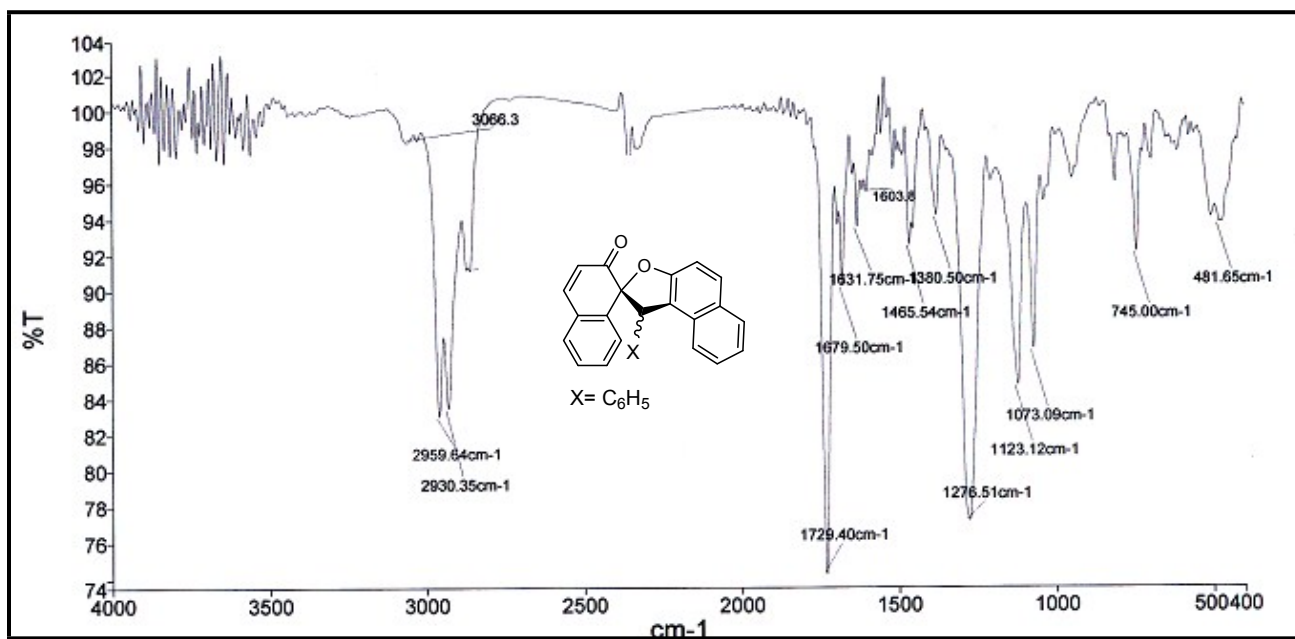


Fig S7. FTIR of 1'-phenyl-spiro{naphthalene-1(2H),2'(1'H)-naphtho[2,1-b]furan}-2-one.

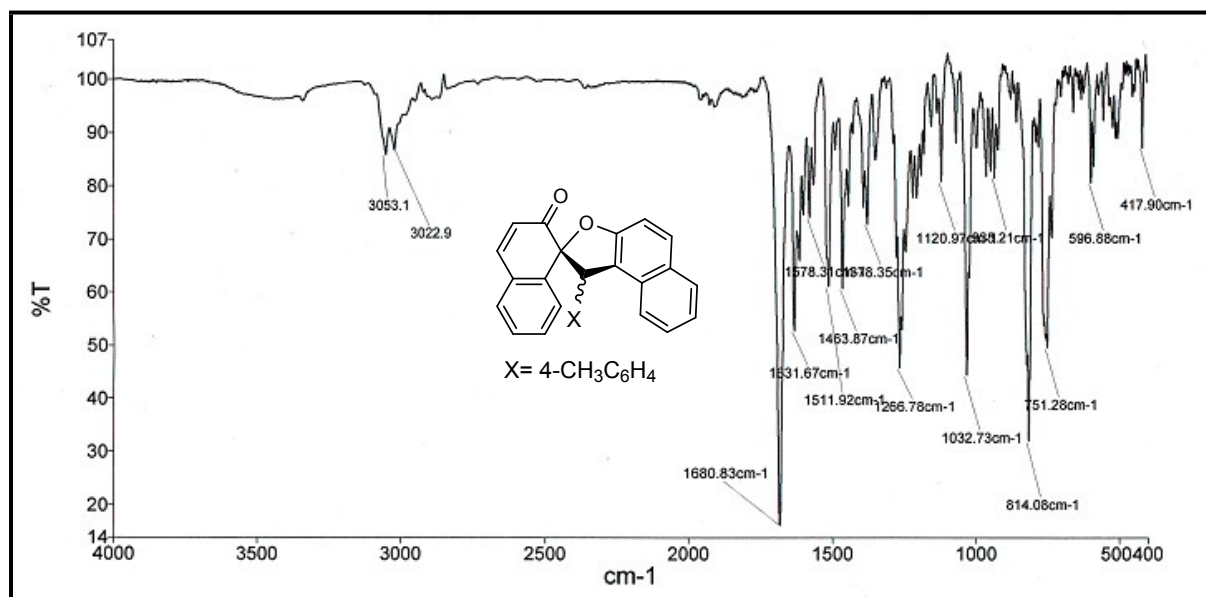


Fig S8. FTIR of 1'-(4-methylphenyl)-spiro{naphthalene-1(2H),2'-(1'H)-naphtho[2,1-b]furan}-2-one.

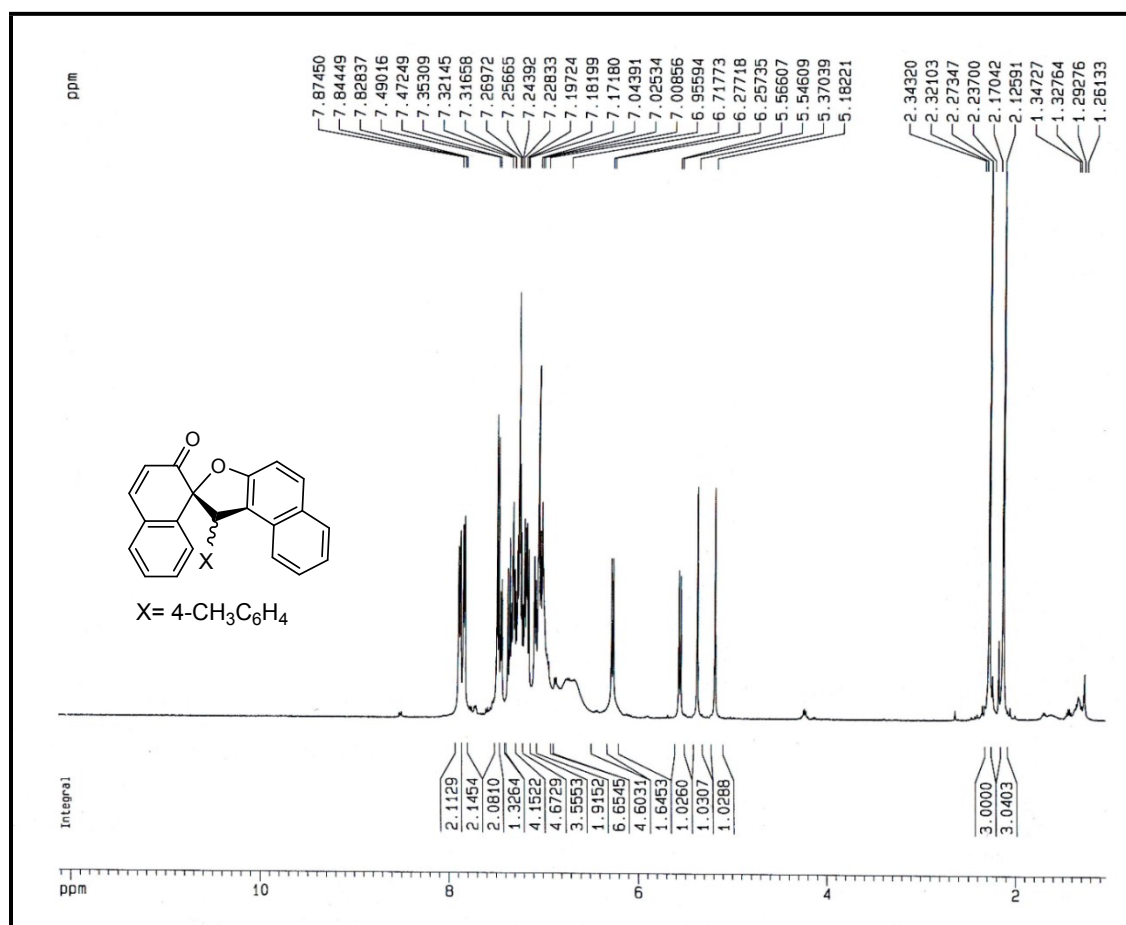


Fig S9. ¹H NMR (500 MHz) of 1'-(4-methylphenyl)-spiro{naphthalene-1(2H),2'-(1'H)-naphtho[2,1-b]furan}-2-one.

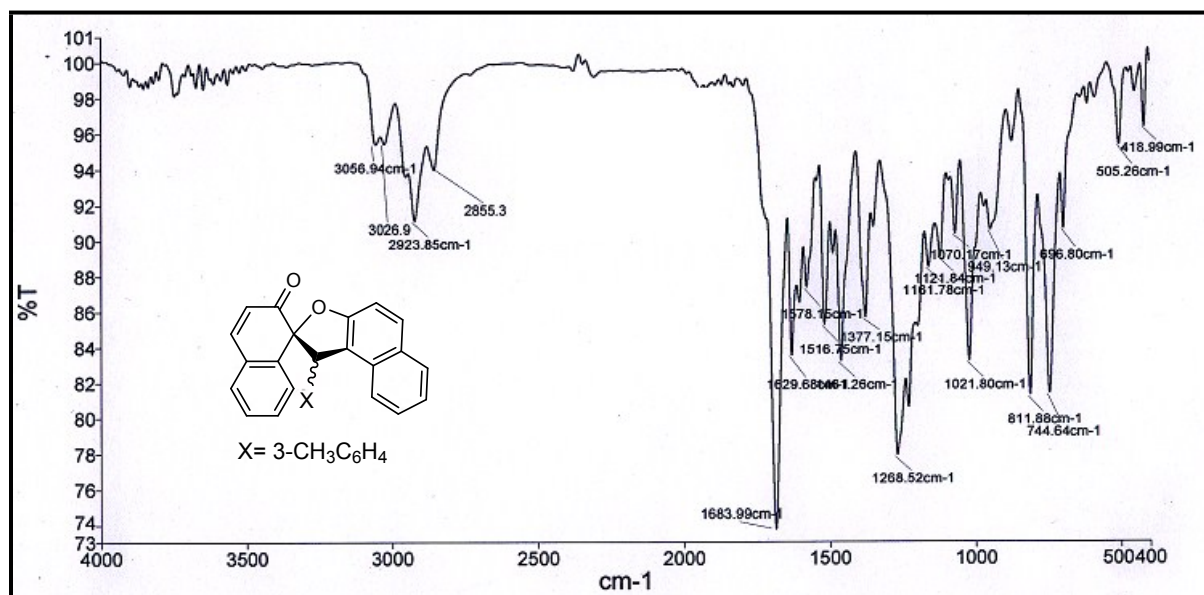


Fig S10. FTIR of 1'-(3-methylphenyl)-spiro{naphthalene-1(2H),2'-(1'H)-naphtho[2,1-b]furan}-2-one.

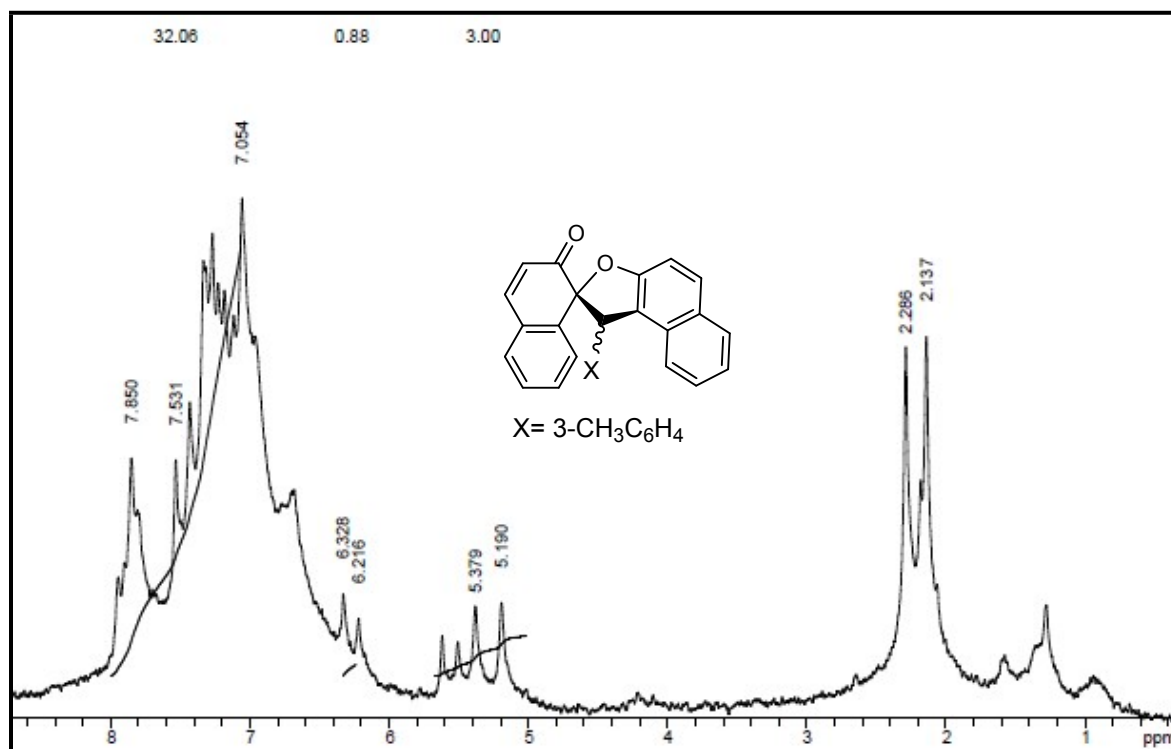


Fig S11. ^1H NMR (90 MHz) of 1'-(3-methylphenyl)-spiro{naphthalene-1(2H),2'-(1'H)-naphtho[2,1-b]furan}-2-one.

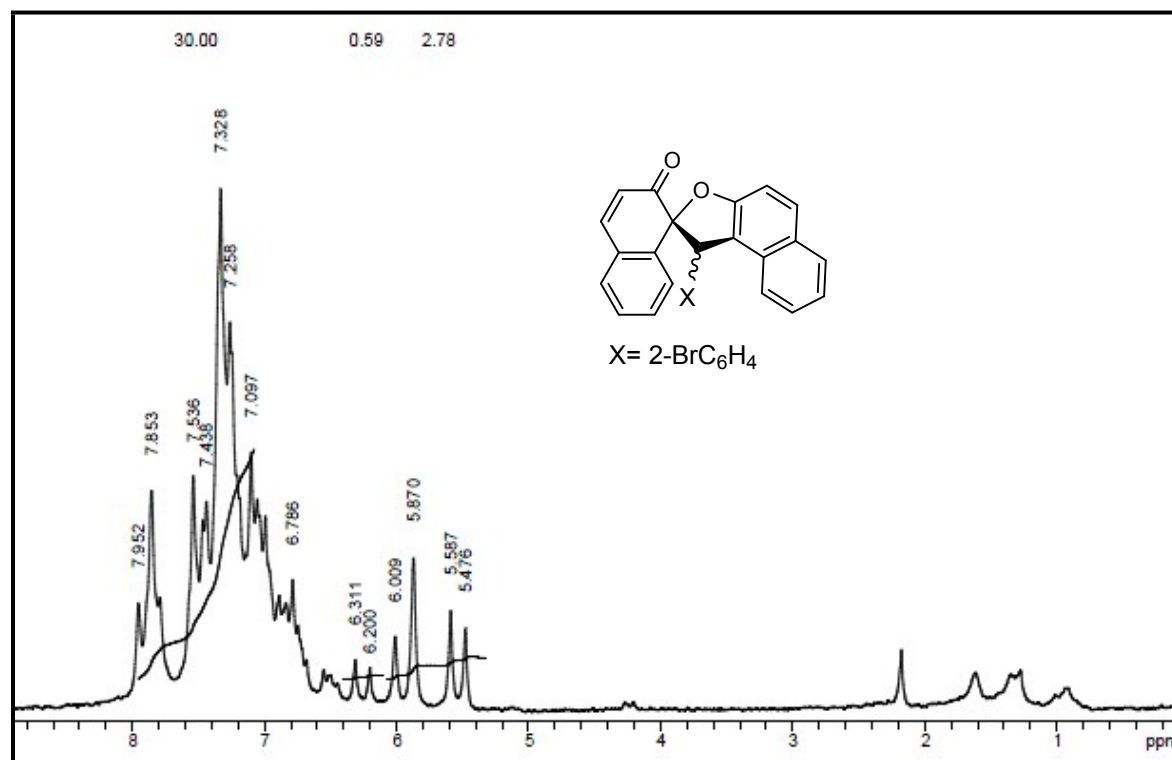


Fig S12. ^1H NMR (90 MHz) of 1'-(2-bromophenyl)-spiro{naphthalene-1(2H),2'(1'H)-naphtho[2,1-b]furan}-2-one.

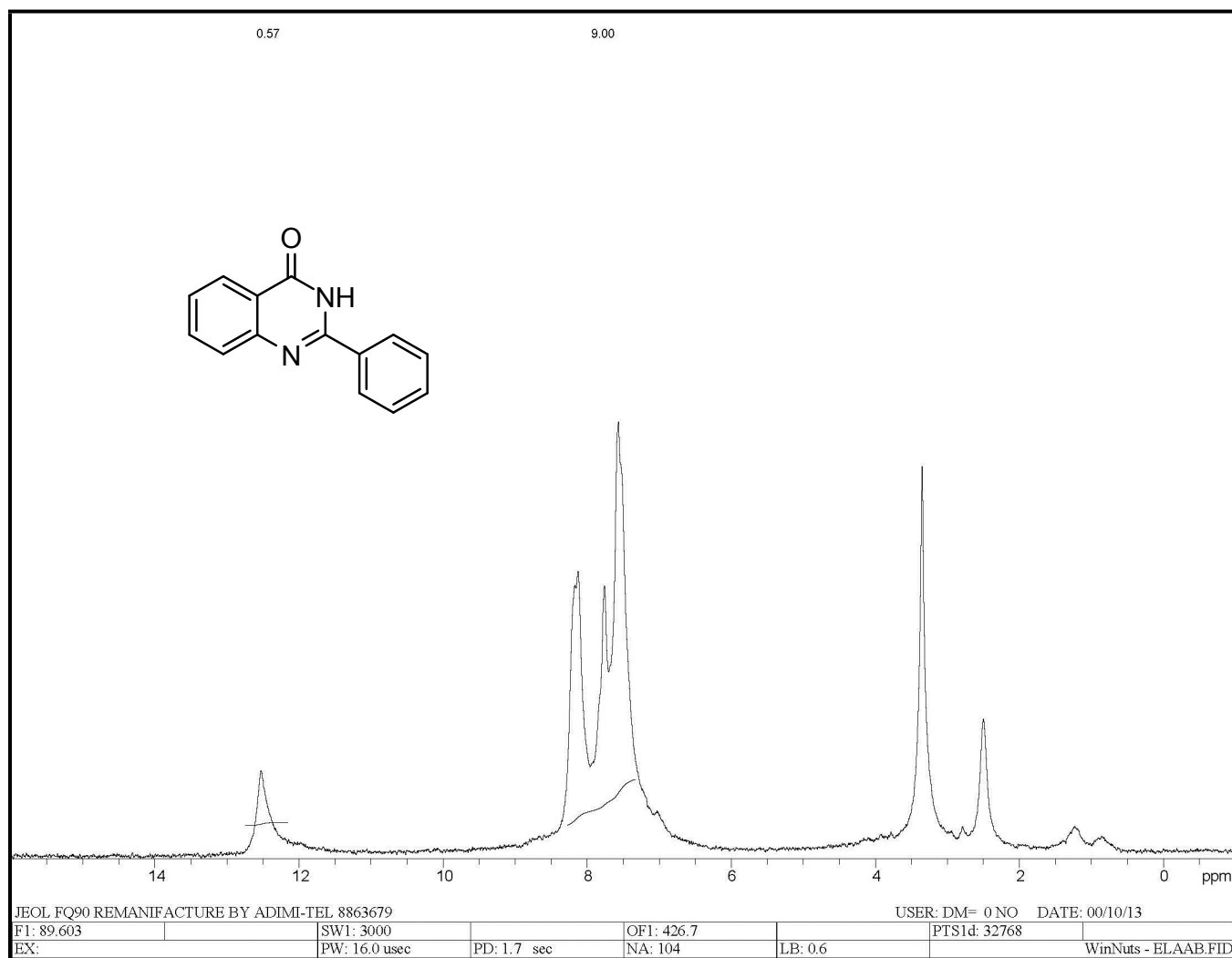


Fig S13. ^1H NMR (90 MHz, CDCl_3) of 2-Phenylquinazolin-4(3H)-one.

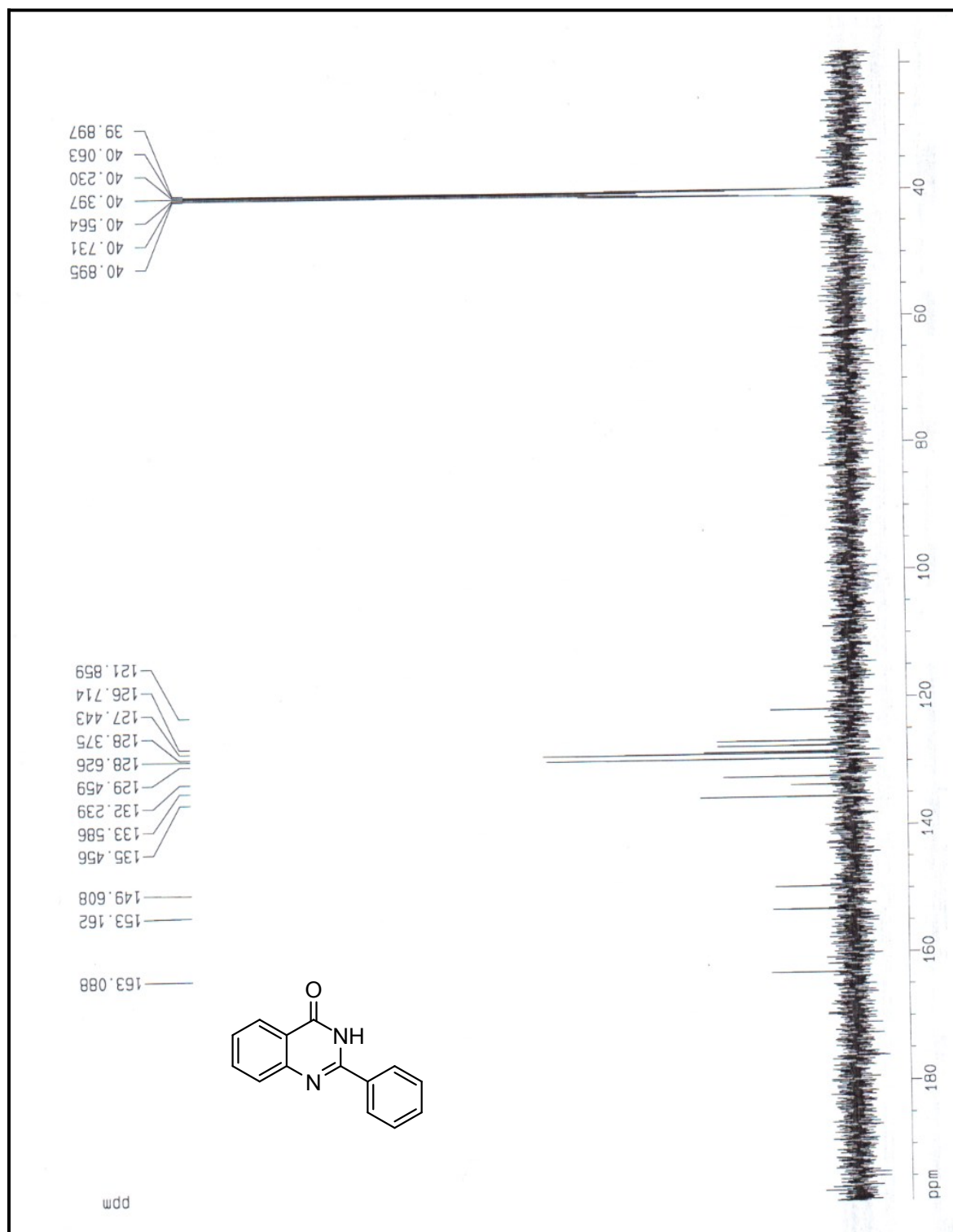


Fig S14. ^{13}C NMR (125 MHz) of 2-phenylquinazolin-4(3H)-one.

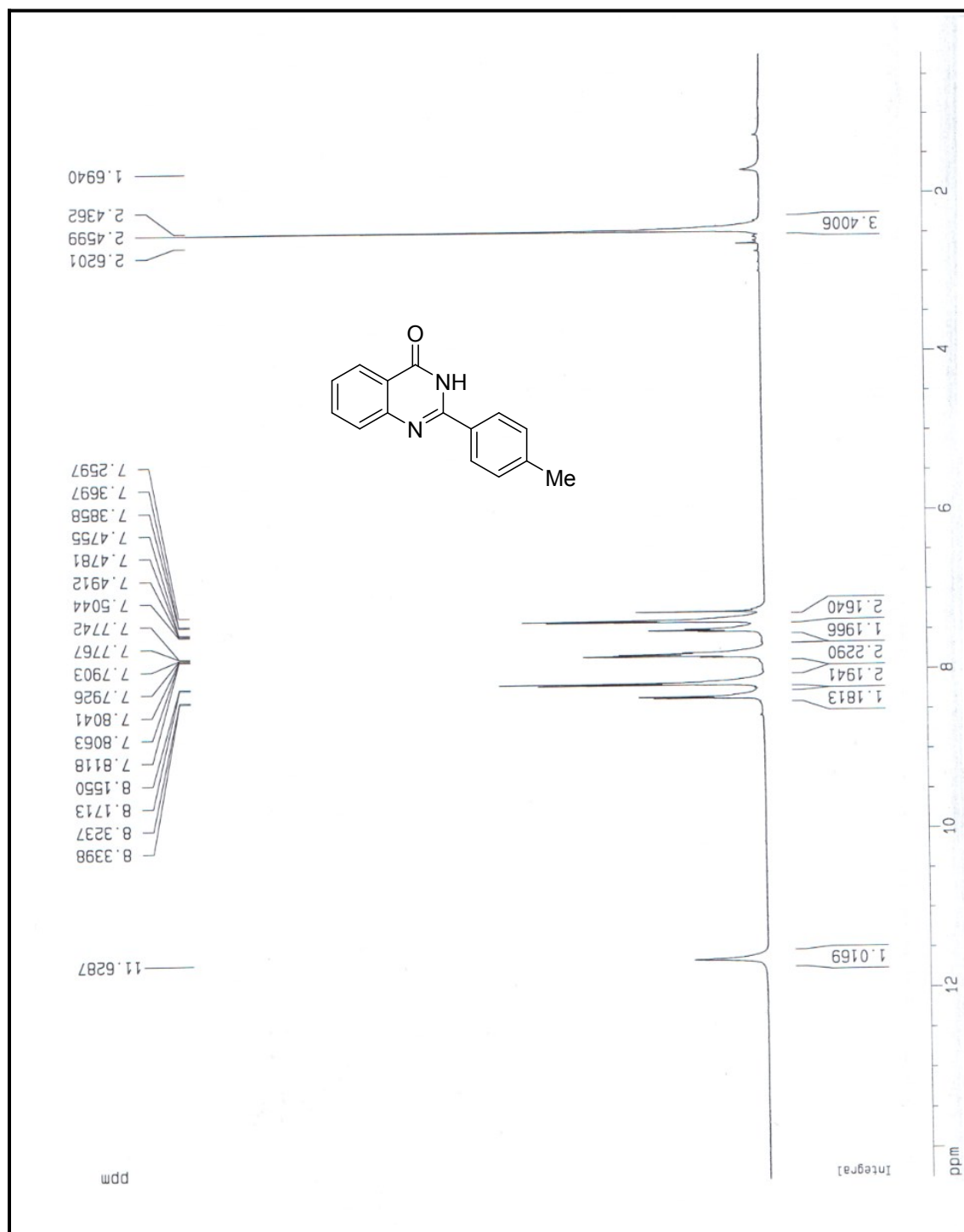


Fig S15. ¹H NMR (500 MHz, CDCl₃) of 2-(p-Tolyl)quinazolin-4(3H)-one.

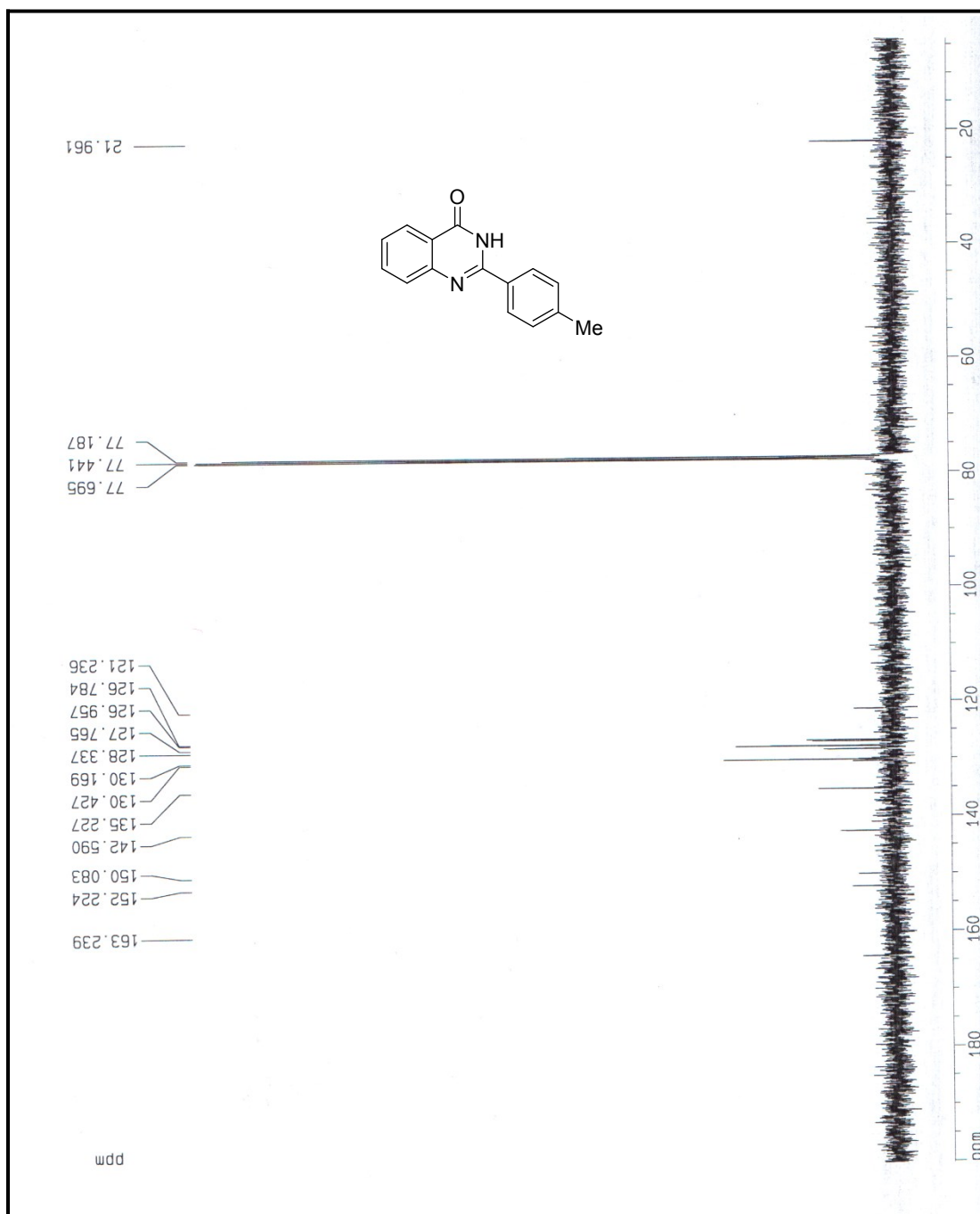


Fig S16. ¹³C NMR (125 MHz, CDCl₃) of 2-(*p*-Tolyl)quinazolin-4(3*H*)-one.

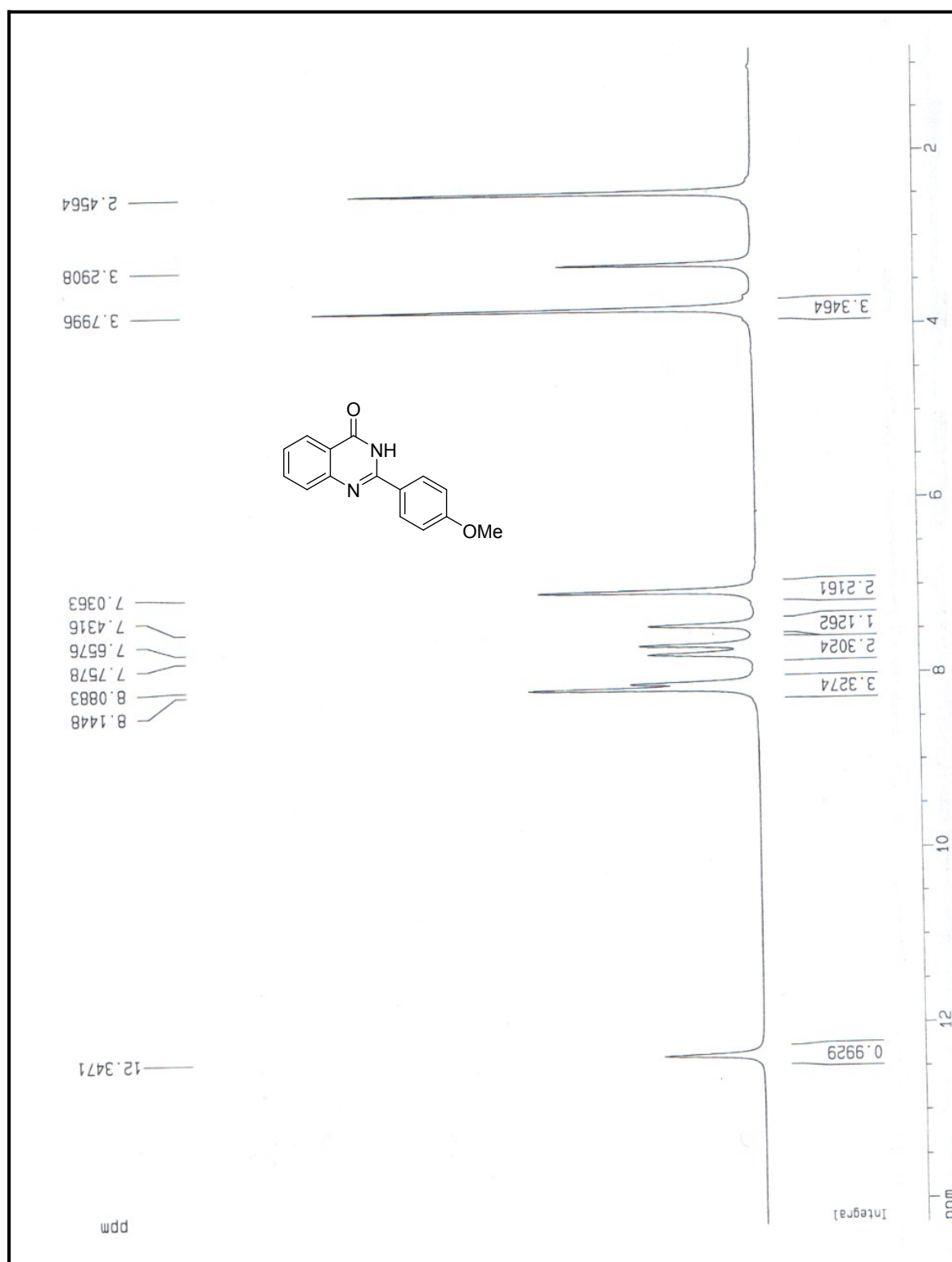


Fig S17. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) of 2-(4-methoxyphenyl)quinazolin-4(3H)-one.

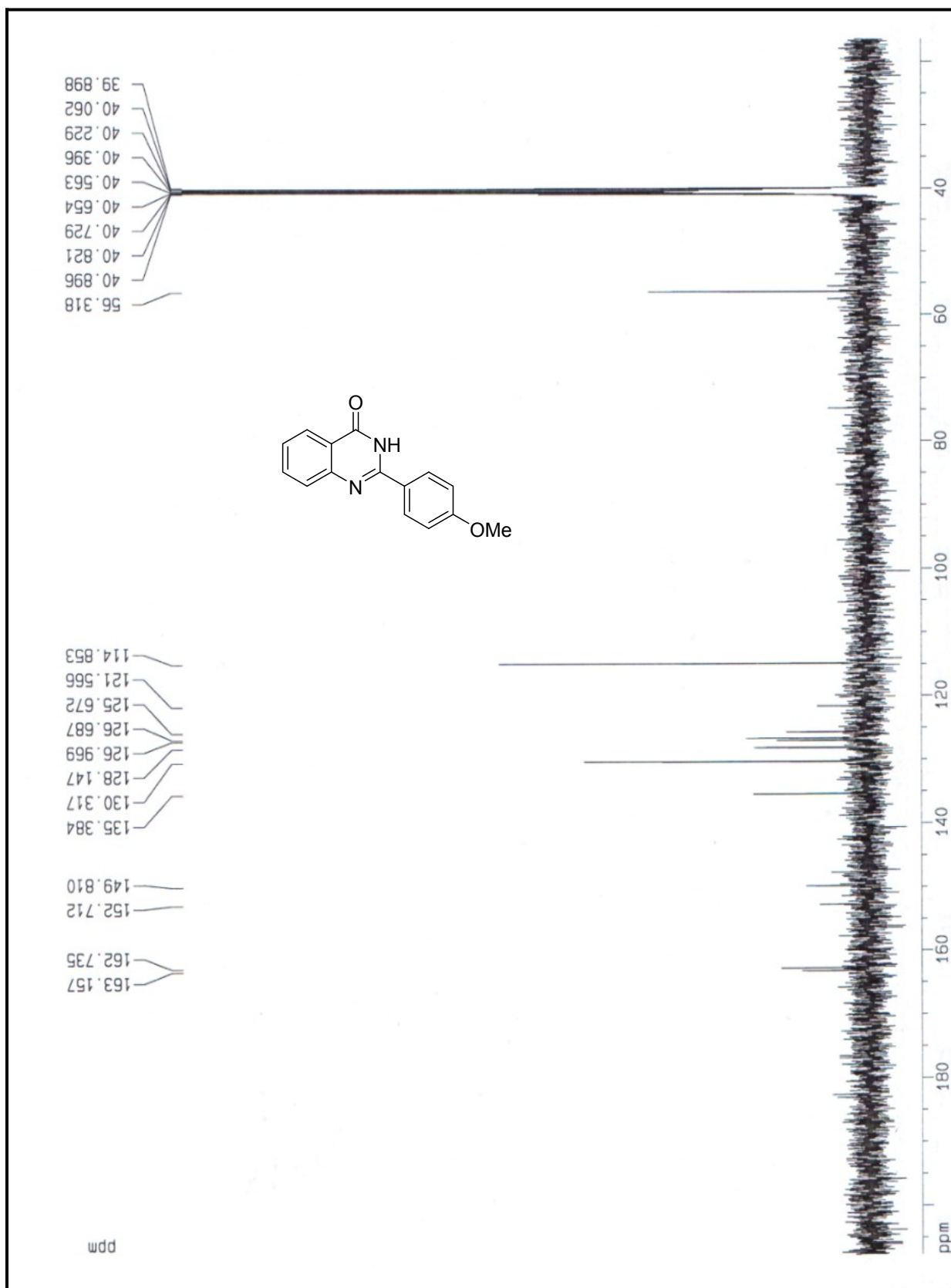


Fig S18. ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) of 2-(4-methoxyphenyl)quinazolin-4(3H)-one.

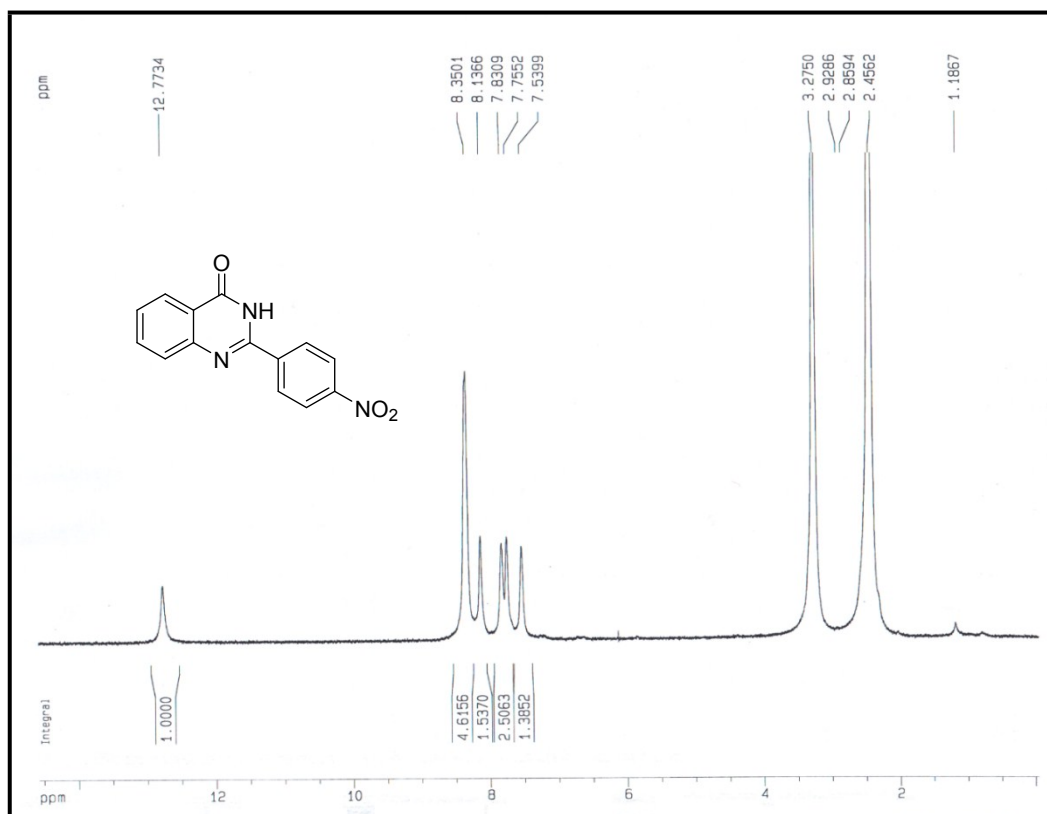


Fig S19. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) of 2-(4-nitrophenyl)quinazolin-4(3H)-one.

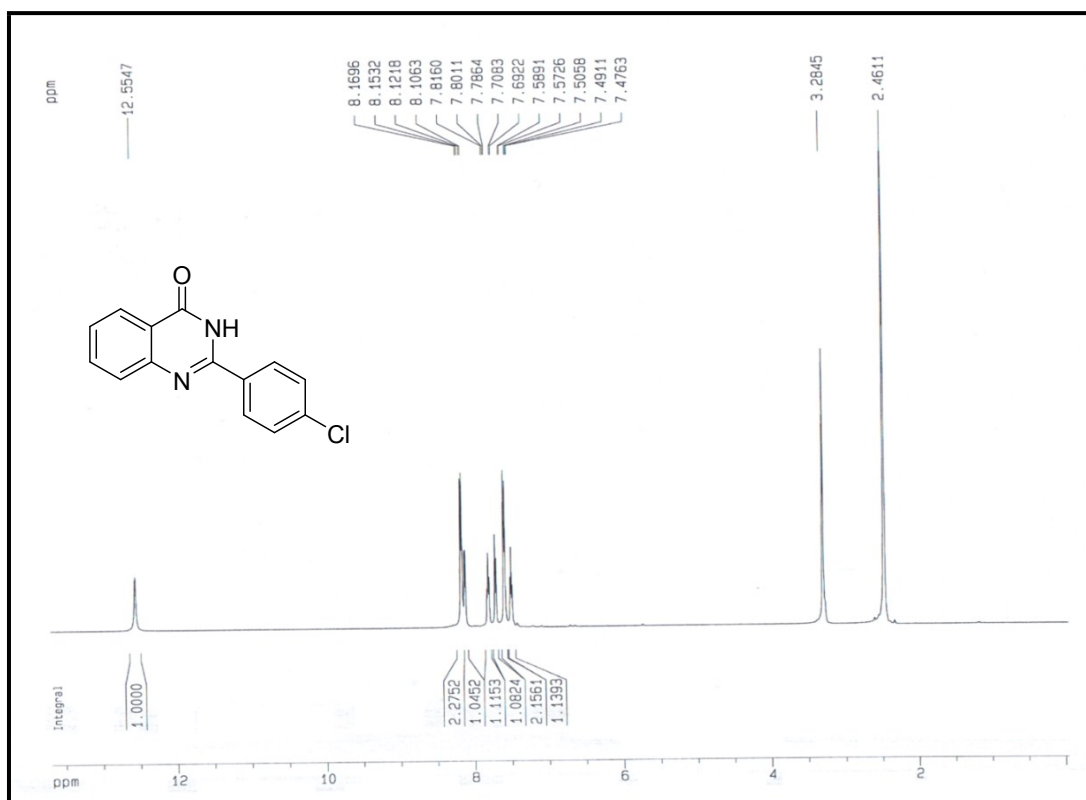


Fig S20. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) of 2-(4-chlorophenyl)quinazolin-4(3H)-one.

S9. Notes and references

1 See these paper and their references: (a) A. Khoramabadi-zad, I. Yavari, A. Shiri and A. Bani, *J. Heterocycl. Chem.*, 2008, **45**, 1351-1358; (b) A. Khoramabadi-zad, A. Shiri, F. Derakhshan-Panah and Z. Salimi, *Mol. Diversity*, 2010, **14**, 829-832; (c) A. Khorramabadi-zad, S. Daliran and A. R. Oveisi, *C. R. Chim.*, 2013, **16**, 972-976.

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