Supporting Information

Fe/S Cluster Catalyzed Cascade Cyclization of N,S-1,6-Enynes for the Synthesis of Thieno[3,4-*b*]indoles

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Experimental procedures and analytical data

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1. General considerations

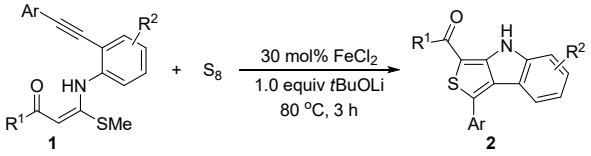
The solvents were dried and distilled prior to use by the literature methods. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a 400 MHz spectrometer and all chemical shift values refer to $CDCl_3$ ($\delta(^{1}H)$, 7.26 ppm; $\delta(^{13}C)$, 77.16 ppm). The HRMS analysis was obtained on a Waters GC-TOF CA156 mass spectrometer. All the melting points were uncorrected. X-Ray Crystallographic analysis was achieved by the Analysis Center, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Analytical TLC plates were viewed by UV light (254 nm). Column chromatographic purifications were performed on silica gel 160. All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. The starting materials α-oxo ketene *S*,*S*-acetals,[1,2] 2-(arylethynyl)anilines,[3] 2-(prop-1-yn-1-yl)anilines,[4,5] *N*,*S*-1,6-enynes **1** and enyne **6**[6] were prepared by the reported procedures.

References

1. X. G. Yang, K. K. Wu, P. Wu, J. P. Chen, C. L. Sun and Z. K. Yu, *Chem. - Eur. J.,* 2015, **21**, 9323-9327.
2. X. G. Yang, Z. Q. Liu, C. L. Sun, J. P. Chen and Z. K. Yu, *Chem. - Eur. J.,* 2015, **21**, 14085-14094.
3. C. M. Le, T. Sperger, R. Fu, X. Hou, Y. H. Lim, F. Schoenebeck, M. Lautens, *J. Am. Chem. Soc.,* 2016, **138**, 14441-14448.
4. F. Nissen and H. Detert, *Eur. J. Org. Chem.,* 2011, **2011**, 2845-2853.
5. C. Maaliki, Y. Chevalier, E. Thiery and J. Thibonnet, *Tetrahedron Lett.,* 2016, **57**, 3358-3362.
6. Z. Q. Liu, R. L. Gao, J. Lou, Y. He, and Z. K. Yu, *Adv. Synth. Catal.,* 2018, **19**, 3660–3663.

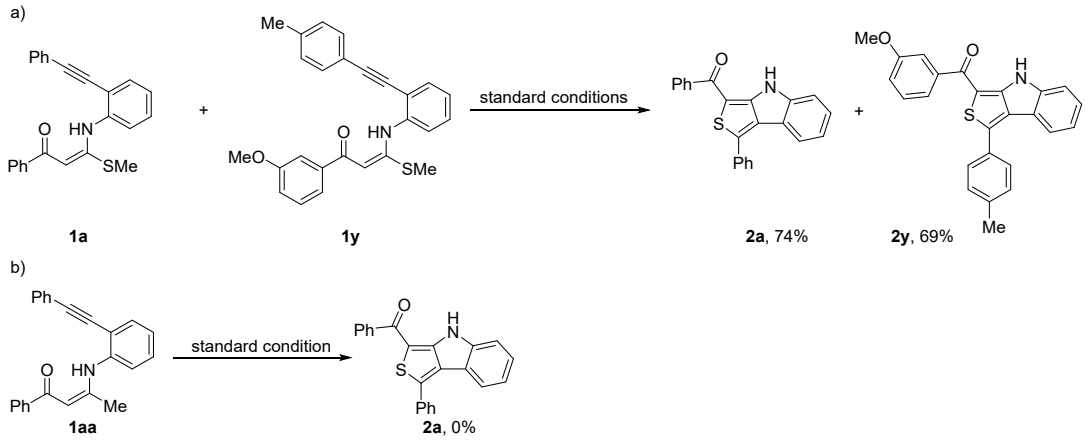
2. Experimental procedures

2.1 Synthesis of 4*H*-thieno[3,4-*b*]indoles (2)



A typical procedure for the synthesis of 2 – *Synthesis of phenyl(1-phenyl-4H-thieno[3,4-b]indol-3-yl)methanone (2a):* A mixture of **1a** (71 mg, 0.2 mmol), $FeCl_2$ (8 mg, 0.06 mmol), S_8 (51 mg, 0.2 mmol), and *t*BuOLi (16 mg, 0.2 mmol) in 2 mL DMF was stirred at 80 °C for 3 h under an argon atmosphere. After cooled to ambient temperature, the mixture was evaporated all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/ethyl acetate = 50:1, v/v) to afford **2a** as a yellow solid (52 mg, 74%).

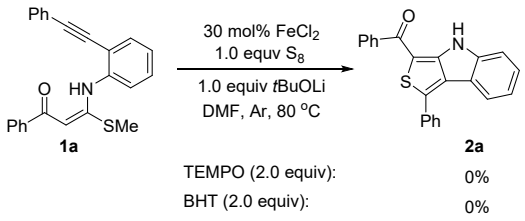
2.2 Control Experiments



Scheme S1. Control Experiments

A mixture of **1a** (37 mg, 0.1 mmol), **1y** (41 mg, 0.1 mmol), $FeCl_2$ (8 mg, 0.06 mmol), S_8 (51 mg, 0.2 mmol), and *t*BuOLi (16 mg, 0.2 mmol) in 2 mL DMF was stirred at 80 °C for 3 h under an argon atmosphere. After cooled to ambient temperature, the mixture was evaporated all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/ethyl acetate = 30:1, v/v) to successively afford products **2a** (26 mg, 74%) and **2y** (27 mg, 69%).

2.2.1 **Radical trapping experiments**

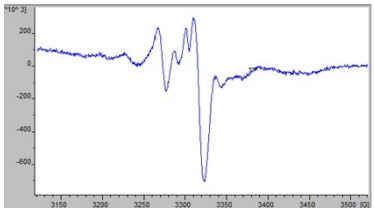


Scheme S2. Radical trapping experiments

A mixture of **1a** (71 mg, 0.2 mmol), $FeCl_2$ (8 mg, 0.06 mmol), S_8 (51 mg, 0.2 mmol), *t*BuOLi (16 mg, 0.2 mmol) and TEMPO (63 mg, 0.4 mmol) or BHT (88 mg, 0.4 mmol) in 3 mL DMF was stirred at 80 °C for 3 h under an argon atmosphere seperately. After compound **1a** was completely consumed by TLC monitoring on silica gel, the yields were carefully checked by ^{1}H NMR analysis of the target product **2a** with 1,3,5-methoxylbenzene as the internal standard.

2.3 EPR studies

A mixture of **1a** (71 mg, 0.2 mmol), $FeCl_2$ (8 mg, 0.06 mmol), S_8 (51 mg, 0.2 mmol), and *t*BuOLi (16 mg, 0.2 mmol) in 2 mL DMF was stirred at 80 °C for 15 min under an argon atmosphere. The resultant mixture was used for the EPR studies at 112 K and an EPR signal was detected at 3320 G.



Scheme S3. EPR studies

3. X-Ray crystallographic studies

Single crystals for the X–ray diffraction studies for compounds **2a** was carried out on a SMART APEX diffractometer with graphite-monochromated Mo radiation (λ = 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined

anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package. The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers CCDC 1857986 for **2a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www. ccdc.cam.ac.uk).

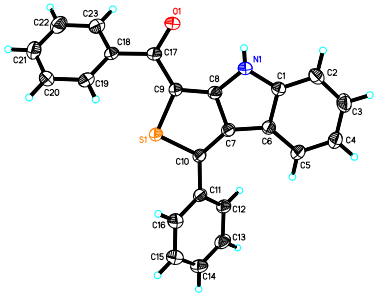


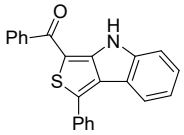
Fig. 1 Molecular structure of compound **2a**.
Perspective view of **2a** with thermal ellipsoids at 30% probability level.

Table 1 Crystal data and structure refinement for compound **2a**

Identification code	LZQE-258	
Empirical formula	C23 H15 N O S	
Formula weight	353.42	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 8.8280(10) Å	α= 90°.
	b = 19.5033(17) Å	β= 102.118(12)°.
	c = 10.3158(12) Å	γ = 90°.
Volume	1736.6(3) $Å^3$	
Z	4	
Density (calculated)	1.352 Mg/m^3	
Absorption coefficient	0.198 mm^{-1}	
F(000)	736	
Crystal size	0.180 x 0.150 x 0.130 mm^3	
Theta range for data collection	2.765 to 25.994°.	

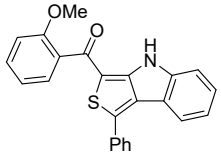
Index ranges	-10<=h<=10, -24<=k<=20, -10<=l<=12
Reflections collected	9958
Independent reflections	5743 [R(int) = 0.0434]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.5402
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5743 / 3 / 474
Goodness-of-fit on F^2	1.060
Final R indices [I>2sigma(I)]	R1 = 0.0491, wR2 = 0.1153
R indices (all data)	R1 = 0.0650, wR2 = 0.1321
Absolute structure parameter	0.39(6)
Largest diff. peak and hole	0.350 and -0.264 e.Å^{-3}

4. Analytical data



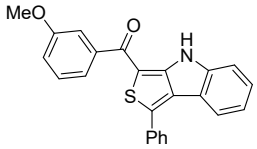
Phenyl(1-phenyl-4*H*-thieno[3,4-*b*]indol-3-yl)methanone (2a)

This compound was prepared according to general procedure and purified by flash chromatography on silica gel (hexane/AcOEt, 10:1) to provide the corresponding product yellow solid, 52 mg, yield 74%, , m.p.: 172-173 °C. ^{1}H NMR (400 MHz, 23 °C, D_6-DMSO) δ 11.70 (br, 1 H, NH), 8.00 and 7.74–7.48 (m each, 2:7 H, aromatic CH), 7.90 (t, J = 6.9 Hz, 3 H, aromatic CH), 7.42 (t, J = 7.4 Hz, 1 H, aromatic CH), 7.14 (t, J = 7.5 Hz, 1 H, aromatic CH). ^{13}C{^{1}H} NMR (100 MHz, 23 °C, D_6-DMSO) δ 185.5 (Cq, CO), 150.2 , 148.7 , 141.1 , 140.1 , 133.2 , 132.3 , 130.2 , 130.1 , 129.3 , 129.1 , 128.6 , 128.5 , 127.9 , 121.3 , 120.8 , 118.6 , 113.3 and 107.4 (aromatic CH). HRMS (EI) calcd for $C_{23}H_{15}NOS$ [M+H]$^+$: 354.0953; Found: 354.0954.



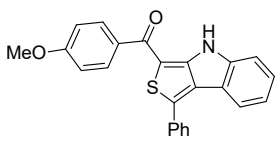
(2-Methoxyphenyl)(1-phenyl-4*H*-thieno[3,4-*b*]indol-3-yl)methanone (2b)

This compound was prepared according to general procedure and purified by flash chromatography on silica gel (hexane/AcOEt, 10:1) to provide the corresponding product yellow solid, 60 mg, yield 78%, m.p.: 201-202 °C. ^{1}H NMR (700 MHz, 23 °C, D_6-DMSO) δ 11.63 (br, 1 H, NH), 7.88 (d, J = 7.8 Hz, 1 H, aromatic CH), 7.81 (m, 2 H, aromatic CH), 7.58 (t, J = 7.6 Hz, 2 H, aromatic CH), 7.54 (d, J = 8.1 Hz, 1 H, aromatic CH), 7.53–7.49 and 7.40 (m each, 2:1 H, aromatic CH), 7.47 (dd, J = 7.4 and 1.6 Hz, 1 H, aromatic CH), 7.19 (d, J = 8.4 Hz, 1 H, aromatic CH), 7.12 (dd, J = 11.1 and 4.0 Hz, 1 H, aromatic CH), 7.07 (dd, J = 10.9 and 4.0 Hz, 1 H, aromatic CH), 3.79 (s, 3 H, OCH_3). ^{13}C{^{1}H} (175 MHz, 23 °C, D_6-DMSO) δ 184.9 (Cq, CO), 156.0 (Cq, *C*-OCH_3), 148.2, 148.1, 140.2, 132.8, 129.9, 128.6, 118.1 and 109.8 (Cq), 131.6, 129.5, 129.4, 128.2, 127.9, 127.2, 120.7, 120.3, 120.2, 112.7 and 112.0 (aromatic CH), 55.5 (OCH_3). HRMS (EI) calcd for $C_{24}H_{17}NO_2S$ $[M+H]^+$: 384.1058; Found: 384.1052.



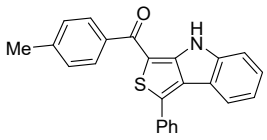
(3-Methoxyphenyl)(1-phenyl-4*H*-thieno[3,4-*b*]indol-3-yl)methanone (2c)

This compound was prepared according to general procedure and purified by flash chromatography on silica gel (hexane/AcOEt, 10:1) to provide the corresponding product yellow solid, 57 mg, yield 75%, m.p.: 200-201 °C. ^{1}H NMR (400 MHz, 23 °C, D_6-DMSO) δ 11.67 (br, 1 H, NH), 7.89 and 7.47 (m each, 3:6 H, aromatic CH), 7.62 (t, J = 7.4 Hz, 2 H, aromatic CH), 7.21 (dd, J = 7.9 and 1.5 Hz, 1 H, aromatic CH), 7.13 (t, J = 7.5 Hz, 1 H, aromatic CH), 3.85 (s, 3 H, OCH_3). ^{13}C{^{1}H} NMR (100 MHz, 23 °C, D_6-DMSO) δ 185.1 (Cq, CO), 159.8 (Cq, *C*-OCH_3), 150.1, 148.7, 141.4, 141.1, 133.1, 129.1, 118.6 and 107.4 (Cq), 130.4, 130.1, 130.0, 128.6, 127.8, 121.2, 120.7, 120.6, 117.9, 113.5 and 113.2 (aromatic CH), 55.8 (OCH_3). HRMS (EI) calcd for $C_{24}H_{17}NO_2S$ $[M+H]^+$: 384.1058; Found: 384.1057.



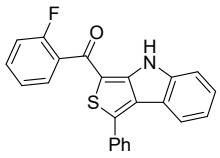
(4-Methoxyphenyl)(1-phenyl-4*H*-thieno[3,4-*b*]indol-3-yl)methanone (2d)

This compound was prepared according to general procedure and purified by flash chromatography on silica gel (hexane/AcOEt, 10:1) to provide the corresponding product yellow solid, 58 mg, yield 76%, m.p.: 201-202 °C. ^{1}H NMR (700 MHz, 23 °C, D_6-DMSO) δ 11.58 (br, 1 H, NH), 8.00 (d, J = 8.7 Hz, 2 H, aromatic CH), 7.96–7.72 (m, 3 H, aromatic CH), 7.62 (t, J = 7.6 Hz, 2 H, aromatic CH), 7.55 (dd, J = 7.5 and 5.6 Hz, 2 H, aromatic CH), 7.40 (t, J = 7.6 Hz, 1 H, aromatic CH), 7.12 (dd, J = 12.1 and 5.0 Hz, 3 H, aromatic CH), 3.87 (s, 3 H, OCH_3). ^{13}C{^{1}H} (175 MHz, 23 °C, D_6-DMSO) δ 183.7 (Cq, CO), 162.2 (Cq, *C*-OCH_3), 149.6, 148.2, 139.6, 118.1 and 106.9 (Cq), 132.8, 131.8, 130.2, 129.5, 128.0, 127.2, 120.7, 120.0, 114.0 and 112.7 (aromatic CH), 55.5 (OCH_3). HRMS (EI) calcd for $C_{24}H_{17}NO_2S$ $[M+H]^+$: 384.1058; Found: 384.1051.



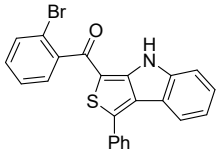
((1-Phenyl-4H-thieno[3,4-*b*]indol-3-yl)(*p*-tolyl)methanone (2e)

This compound was prepared according to general procedure and purified by flash chromatography on silica gel (hexane/AcOEt, 10:1) to provide the corresponding product yellow solid, 51 mg, yield 70%, m.p.: 219-220 °C. ^{1}H NMR (700 MHz, 23 °C, D_6-DMSO) δ 11.65 (s, 1H, aromatic CH), 7.88 (dd, J = 11.6, 7.8 Hz, 3H, aromatic CH), 7.78 – 7.72 (m, 2H, aromatic CH), 7.61 (t, J = 7.6 Hz, 2H, aromatic CH), 7.54 (dd, J = 12.8, 7.6 Hz, 2H, aromatic CH), 7.49-7.43 (m, 2H, aromatic CH), 7.41 (t, J = 7.6 Hz, 1H, aromatic CH), 7.12 (t, J = 7.5 Hz, 1H, aromatic CH), 2.41 (s, 3H, CH_3). ^{13}C{^{1}H} (175 MHz, 23 °C, D_6-DMSO) δ 185.7 (Cq, CO), 150.1 (s), 148.7 (s), 141.0 (s), 140.1 (s), 138.7 (s), 133.2 (s), 132.9 (s), 130.2 (s), 130.1 (s), 129.1 (s), 129.1 (s), 128.9 (s), 128.6 (s), 127.9 (s), 125.7 (s), 121.2 (s), 120.8 (s), 118.6 (s), 113.3 (s), 107.6 (aromatic CH or Cq), 21.5 (CH_3). HRMS (EI) calcd for $C_{24}H_{17}NOS$ $[M+H]^+$: 368.1109; Found: 368.1102.



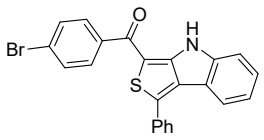
(2-Fluorophenyl)(1-phenyl-4H-thieno[3,4-b]indol-3-yl)methanone (2f)

This compound was prepared according to general procedure and purified by flash chromatography on silica gel (hexane/AcOEt, 10:1) to provide the corresponding product yellow solid, 50 mg, yield 68%, m.p.: 235-236 ^{o}C. ^{1}H NMR (400 MHz, 23 ^{o}C, D_6-DMSO) δ 11.77 (br, 1 H, NH), 7.89 (d, J = 7.9 Hz, 1 H, aromatic CH), 7.86 (d, J = 7.3 Hz, 2 H, aromatic CH), 7.76 (t, J = 7.3 Hz, 1 H, aromatic CH), 7.60 and 7.41 (m each, 5:3 H, aromatic CH), 7.14 (t, J = 7.5 Hz, 1 H, aromatic CH). ^{13}C{^{1}H} (176 MHz, 23 ^{o}C, D_6-DMSO) δ 181.5 (Cq, CO), 158.6 (Cq and d, J = 248.5 Hz, C-F), 148.7, 148.2, 141.5, 132.5, 128.8, 128.2 (d, J = 16.0 Hz) 118.1 and 108.7 (Cq), 132.8 (d, J = 8.3 Hz), 129.8, 129.5, 129.4 (d, J = 2.7 Hz), 128.0, 127.4, 124.7, 120.6 (d, J = 54.6 Hz), 116.4 (d, J = 21.1 Hz) and 112.8 (aromatic CH). HRMS (EI) calcd for $C_{23}H_{14}FNOS$ $[M+H]^{+}$: 372.0858; Found: 372.0859.



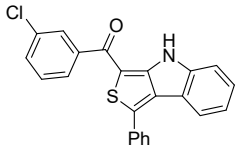
(2-Bromophenyl)(1-phenyl-4*H*-thieno[3,4-*b*]indol-3-yl)methanone (2g)

This compound was prepared according to general procedure and purified by flash chromatography on silica gel (hexane/AcOEt, 10:1) to provide the corresponding product yellow solid, 65 mg, yield 75%, m.p.: 206-207 ^{o}C. ^{1}H NMR (700 MHz, 23 ^{o}C, D_6-DMSO) δ 11.82 (br, 1 H, NH), 7.89 (d, J = 7.8 Hz, 1 H, aromatic CH), 7.83, 7.54, 7.48, 7.42 and 7.14 (m each, 2:3:1:1:1 H, aromatic CH), 7.77 (d, J = 8.1 Hz, 1 H, aromatic CH), 7.67 (dd, J = 7.5 and 1.6 Hz, 1 H, aromatic CH), 7.58 (t, J = 7.6 Hz, 2 H, aromatic CH). ^{13}C{^{1}H} (176 MHz, 23 ^{o}C, D_6-DMSO) δ 184.3 (Cq, CO), 148.5, 148.2, 141.7, 141.3, 132.5, 128.6, 118.1 and 108.2 (Cq), 133.0, 131.6, 129.8, 128.9, 127.7, 127.4, 120.8, 120.4 and 112.8 (aromatic CH). HRMS (EI) calcd for $C_{23}H_{14}BrNOS$ $[M+H]^{+}$: 432.0058; Found: 432.0061.



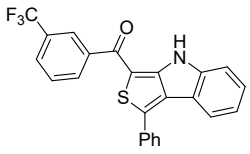
(4-Bromophenyl)(2-phenyl-4*H*-thieno[3,2-*b*]indol-3-yl)methanone (2h)

This compound was prepared according to general procedure and purified by flash chromatography on silica gel (hexane/AcOEt, 10:1) to provide the corresponding product yellow solid, 64 mg, yield 74%, m.p.: 209-210 °C. ^{1}H NMR (700 MHz, 23 °C, D_6-DMSO) δ 11.68 (br, 1 H, NH), 7.83, 7.55, 7.41 and 7.12 (m each, 5:2:1:1 H, aromatic CH), 7.79 (d, J = 8.4 Hz, 2 H, aromatic CH), 7.62 (t, J = 7.6 Hz, 2 H, aromatic CH). ^{13}C{^{1}H} (176 MHz, 23 °C, D_6-DMSO) δ 183.7 (Cq, CO), 149.6, 148.2, 140.8, 138.4, 132.6, 128.6, 125.5 and 106.7 (Cq), 131.8, 130.0, 129.7, 129.5, 128.0, 127.4, 120.7, 120.3 and 112.8 (aromatic CH). HRMS (EI) calcd for $C_{23}H_{14}BrNOS$ $[M+H]^+$: 432.0058; Found: 432.0050.



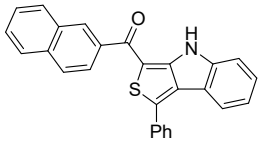
(3-Chlorophenyl)(1-phenyl-4*H*-thieno[3,4-*b*]indol-3-yl)methanone (2i)

This compound was prepared according to general procedure and purified by flash chromatography on silica gel (hexane/AcOEt, 10:1) to provide the corresponding product yellow solid, 57 mg, yield 74%, m.p.: 203-204 °C. ^{1}H NMR (700 MHz, 23 °C, D_6-DMSO) δ 11.73 (br, 1 H, NH), 7.91 and 7.72 (m each, 5:1 H, aromatic CH), 7.61 (t, J = 7.7 Hz, 3 H, aromatic CH), 7.55 (dd, J = 7.7 and 5.4 Hz, 2 H, aromatic CH), 7.41 (t, J = 7.6 Hz, 1 H, aromatic CH), 7.13 (t, J = 7.5 Hz, 1 H, aromatic CH). ^{13}C{^{1}H} (176 MHz, 23 °C, D_6-DMSO) δ 183.2 (Cq, CO), 149.8, 148.2, 141.4, 141.1, 133.6, 132.5, 128.7, 118.1 and 106.6 (Cq), 131.5, 130.7, 129.8, 129.5, 128.1, 127.6, 127.4, 126.6, 120.7, 120.3 and 112.8 (aromatic CH). HRMS (EI) calcd for $C_{23}H_{14}ClNOS$ $[M+H]^+$: 388.0563; Found: 388.0561.



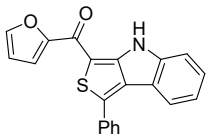
(2-Phenyl-4*H*-thieno[3,2-*b*]indol-3-yl)(4-(trifluoromethyl)phenyl)methanone (2j)

This compound was prepared according to general procedure and purified by flash chromatography on silica gel (hexane/AcOEt, 10:1) to provide the corresponding product yellow solid, 56 mg, yield 66%, m.p.: 243-244 °C. ^{1}H NMR (400 MHz, 23 °C, DMSO) δ 11.74 (br, 1 H, NH), 8.26 (d, J = 7.7 Hz, 1 H, aromatic CH), 8.19 (s, 1 H, aromatic CH), 8.00 (d, J = 7.8 Hz, 1 H, aromatic CH), 7.80 (m, 4 H, aromatic CH), 7.60 (t, J = 7.4 Hz, 2 H, aromatic CH), 7.55 (dd, J = 11.2 and 5.3 Hz, 2 H, aromatic CH), 7.41 (t, J = 7.6 Hz, 1 H, aromatic CH), 7.13 (t, J = 7.5 Hz, 1 H, aromatic CH). ^{13}C{^{1}H} (176 MHz, 23 °C, D_6-DMSO) δ 183.4 (Cq, CO), 149.9, 148.3, 141.4, 140.4, 132.6, 129.7 (Cq and q, J = 32.3 Hz), 128.9, 118.2, 106.7, 132.0, 130.2, 129.9, 129.7, 128.3 (q, J = 3.4 Hz), 128.2, 127.5, 124.5 (q, J = 3.5 Hz), δ 124.0 (Cq and q, J = 272.5 Hz, CF_3), 120.9, 120.5 and 112.9 (aromatic CH). HRMS (EI) calcd for $C_{24}H_{14}F_3NOS$ $[M+H]^+$: 422.0826; Found: 422.0829.



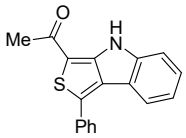
Naphthalen-2-yl(1-phenyl-4*H*-thieno[3,4-*b*]indol-3-yl)methanone (2k)

This compound was prepared according to general procedure and purified by flash chromatography on silica gel (hexane/AcOEt, 10:1) to provide the corresponding product yellow solid, 60 mg, yield 75%, m.p.: 255-256 °C. ^{1}H NMR (400 MHz, 23 °C, D_6-DMSO) δ 11.71 (br, 1 H, NH), 8.64 (s, 1 H, aromatic CH), 8.17 (d, J = 7.7 Hz, 1 H, aromatic CH), 8.11 (d, J = 8.6 Hz, 1 H, aromatic CH), 8.04 (d, J = 7.8 Hz, 1 H, aromatic CH), 8.00 and 7.65 (m each, 1:4 H, aromatic CH), 7.91 (t, J = 7.2 Hz, 3 H, aromatic CH), 7.56 (dd, J = 10.0 and 5.0 Hz, 2 H, aromatic CH), 7.42 (dd, J = 11.3 and 4.1 Hz, 1 H, aromatic CH), 7.14 (t, J = 7.6 Hz, 1 H, aromatic CH). ^{13}C{^{1}H} (176 MHz, 23 °C, D_6-DMSO) δ 184.9 (Cq, CO), 149.5, 148.2, 140.7, 136.8, 134.3, 132.7, 132.1, 128.7, 118.1 and 107.3 (Cq), 129.7, 129.5, 129.2, 128.6, 128.5, 128.1, 127.7, 127.3, 126.9, 124.6, 120.7, 120.2 and 112.7 (aromatic CH). HRMS (EI) calcd for $C_{27}H_{17}NOS$ $[M+H]^+$: 404.1109; Found: 404.1107.



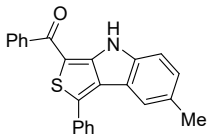
Furan-2-yl(1-phenyl-4*H*-thieno[3,4-*b*]indol-3-yl)methanone (2l)

This compound was prepared according to general procedure and purified by flash chromatography on silica gel (hexane/AcOEt, 10:1) to provide the corresponding product yellow solid, 51 mg, yield 74%, m.p.: 259-260 ^{o}C. ^{1}H NMR (700 MHz, 23 ^{o}C, D_6-DMSO) δ 11.63 (br, 1 H, NH), 8.11 (s, 1 H, aromatic CH), 7.93 (d, J = 7.4 Hz, 2 H, aromatic CH), 7.90 (d, J = 7.8 Hz, 1 H, aromatic CH), 7.65 (t, J = 7.6 Hz, 2 H, aromatic CH), 7.57 (dd, J = 13.1 and 7.6 Hz, 2 H, aromatic CH), 7.48 (d, J = 3.3 Hz, 1 H, aromatic CH), 7.41 (t, J = 7.6 Hz, 1 H, aromatic CH), 7.13 (t, J = 7.4 Hz, 1 H, aromatic CH), 6.82 (d, J = 1.8 Hz, 1 H, aromatic CH). ^{13}C{^{1}H} (176 MHz, 23 ^{o}C, D_6-DMSO) δ 171.1 (Cq, CO), 152.1, 150.4, 148.1, 147.1, 140.8, 132.8, 118.1 and 105.3 (Cq), 129.7, 129.6, 128.1, 127.9, 127.3, 120.7, 120.3, 116.8, 112.9 and 112.8 (aromatic CH). HRMS (EI) calcd for $C_{21}H_{13}NO_2S$ $[M+H]^+$: 344.0745; Found: 344.0746.



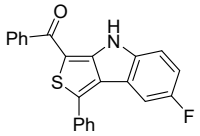
1-(1-Phenyl-4*H*-thieno[3,4-*b*]indol-3-yl)ethanone (2m)

This compound was prepared according to general procedure and purified by flash chromatography on silica gel (hexane/AcOEt, 10:1) to provide the corresponding product yellow solid, 36 mg, yield 61%, m.p.: 110-111 ^{o}C. ^{1}H NMR (700 MHz, 23 ^{o}C, D_6-DMSO) δ 11.37 (br, 1 H, NH), 7.84 (m, 3 H, aromatic CH), 7.61 (t, J = 7.6 Hz, 2 H, aromatic CH), 7.53 (t, J = 7.4 Hz, 1 H, aromatic CH), 7.48 (d, J = 8.0 Hz, 1 H, aromatic CH), 7.38 (t, J = 7.6 Hz, 1 H, aromatic CH), 7.09 (t, J = 7.4 Hz, 1 H, aromatic CH), 2.54 (s, 3 H, CH_3). ^{13}C{^{1}H} (176 MHz, 23 ^{o}C, D_6-DMSO) δ 187.9 (Cq, CO), 148.4, 146.9, 138.4, 129.3, 132.9, 118.5 (Cq), 129.6, 129.5, 128.1, 127.3, 120.7, 120.1 and 112.5 (aromatic CH), 28.3 (CH_3). HRMS (EI) calcd for $C_{18}H_{13}NOS$ $[M+H]^+$: 292.0796; Found: 292.0793.



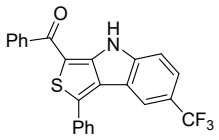
(7-Methyl-1-phenyl-4H-thieno[3,4-b]indol-3-yl)(phenyl)methanone (2n)

This compound was prepared according to general procedure and purified by flash chromatography on silica gel (hexane/AcOEt, 10:1) to provide the corresponding product yellow solid, 51 mg, yield 70%, m.p.:166-167 ^{o}C. ^{1}H NMR (700 MHz, 23 ^{o}C, D_6-DMSO) δ 11.57 (br, 1 H, NH), 7.97, 7.88 and 7.64 (m, 2:2:3 H, aromatic CH), 7.68 (s, 1 H, aromatic CH), 7.59 (t, J = 7.5 Hz, 2 H, aromatic CH), 7.56 (t, J = 7.4 Hz, 1 H, aromatic CH), 7.44 (d, J = 8.2 Hz, 1 H, aromatic CH), 7.24 (d, J = 8.2 Hz, 1 H, aromatic CH), 2.38 (s, 3 H, CH_3). ^{13}C{^{1}H} (176 MHz, 23 ^{o}C, D_6-DMSO) δ 184.9 (Cq, CO), 149.9, 146.3, 140.4, 139.6, 132.7, 131.7, 128.4, 118.2 and 106.6 (Cq), 129.6, 129.5 128.9, 128.7, 128.4, 128.1, 127.9, 120.7, 112.5 (aromatic CH), 21.1 (CH_3). HRMS (EI) calcd for $C_{24}H_{17}NOS$ $[M+H]^+$: 368.1109; Found: 368.1104.



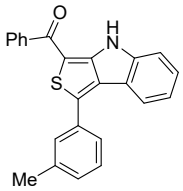
(7-Fluoro-1-phenyl-4*H*-thieno[3,4-*b*]indol-3-yl)(phenyl)methanone (2o)

This compound was prepared according to general procedure and purified by flash chromatography on silica gel (hexane/AcOEt, 10:1) to provide the corresponding product yellow solid, 55 mg, yield 74%, m.p.: 173-174 ^{o}C. ^{1}H NMR (700 MHz, 23 ^{o}C, D_6-DMSO) δ 11.72 (br, 1 H, NH), 7.98, 7.64 and 7.55 (m, 2:3:3 H, aromatic CH), 7.86 (d, J = 7.2 Hz, 2 H, aromatic CH), 7.59 (t, J = 7.6 Hz, 2 H, aromatic CH), 7.29 (td, J = 9.1 and 2.5 Hz, 1 H, aromatic CH). ^{13}C{^{1}H}(176 MHz, 23 ^{o}C, D_6-DMSO) δ 184.8 (Cq, CO), 156.6 (d, J = 234.3 Hz, C-F), 150.3, 144.6, 141.4, 139.4, 132.3, 118.3 (d, J = 9.8 Hz), 107.0, 106.7 (d, J = 25.0 Hz, Cq), 131.8, 129.8, 129.7, 128.7, 128.0, 127.9, 114.6 (d, J = 24.7 Hz) and 113.6 (d, J = 9.0 Hz, aromatic CH). HRMS (EI) calcd for $C_{23}H_{14}FNOS$ $[M+H]^+$: 372.0858; Found: 372.0857.



Phenyl(1-phenyl-7-(trifluoromethyl)-4H-thieno[3,4-b]indol-3-yl)methanone (2p)

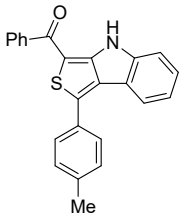
This compound was prepared according to general procedure and purified by flash chromatography on silica gel (hexane/AcOEt, 10:1) to provide the corresponding product yellow solid, 61 mg, yield 72%, m.p.: 133-134 ^{o}C. ^{1}H NMR (700 MHz, 23 ^{o}C, D_6-DMSO) δ 12.10 (br, 1 H, NH), 8.09 (s, 1 H, aromatic CH), 8.00, 7.89 and 7.67 (m each, 2:2:1 H, aromatic CH), 7.77 (dd, J = 8.6 and 1.2 Hz, 1 H, aromatic CH), 7.72 (d, J = 8.5 Hz, 1 H, aromatic CH), 7.65 (d, J = 7.8 Hz, 2 H, aromatic CH), 7.61 (d, J = 7.8 Hz, 2 H, aromatic CH), 7.58 (d, J = 7.4 Hz, 1 H, aromatic CH). ^{13}C{^{1}H}(176 MHz, 23 ^{o}C, D_6-DMSO) δ 185.6 (Cq, CO), 150.7, 150.1, 142.1, 139.7, 132.7, 118.2 and 108.6 (Cq), 132.5, 130.6, 130.2, 129.3, 128.6, 128.5, 128.1, 125.4 (q, J = 271.3 Hz, CF_3), 124.7 (q, J = 3.3 Hz), 120.9 (q, J = 31.6 Hz, *C*-CF_3), 117.7 (q, J = 4.4 Hz), 113.8 (aromatic CH). HRMS (EI) calcd for $C_{24}H_{14}F_3NOS$ $[M+H]^+$: 422.0826; Found: 422.0823.



Phenyl(1-(*m*-tolyl)-4*H*-thieno[3,4-*b*]indol-3-yl)methanone (2r)

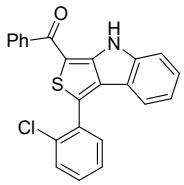
This compound was prepared according to general procedure and purified by flash chromatography on silica gel (hexane/AcOEt, 10:1) to provide the corresponding product yellow liquid, 48 mg, yield 66%, ^{1}H NMR (400 MHz, 23 ^{o}C, D_6-DMSO) δ 11.67 (br, 1 H, NH), 7.98 (m, 2 H, aromatic CH), 7.89 (d, J = 7.8 Hz, 1 H, aromatic CH), 7.70 (m, J = 11.3 Hz, 2 H, aromatic CH), 7.64 (m, 1 H, aromatic CH), 7.59 (dd, J = 11.4 and 4.5 Hz, 2 H, aromatic CH), 7.55 (d, J = 8.1 Hz, 1 H, aromatic CH), 7.51 (t, J = 7.6 Hz, 1 H, aromatic CH), 7.41 (t, J = 7.4 Hz, 1 H, aromatic CH), 7.37 (d, J = 7.6 Hz, 1 H, aromatic CH), 7.14 (t, J = 7.3 Hz, 1 H, aromatic CH), 2.43 (s, 3 H, CH_3). ^{13}C{^{1}H} (100 MHz, 23 ^{o}C, D_6-DMSO) δ 185.1 (Cq, CO), 149.8, 148.3, 140.9, 139.7, 139.1, 132.7, 128.5, 118.3 and 106.9 (Cq), 131.9,

130.5, 129.5, 128.9, 128.6, 128.1, 127.4, 125.3, 120.8, 120.4 and 112.9 (aromatic CH), 21.0 (CH_3). HRMS (EI) calcd for $C_{24}H_{17}NOS$ $[M+H]^+$: 368.1109; Found: 368.1108.



Phenyl(1-(*p*-tolyl)-4*H*-thieno[3,4-*b*]indol-3-yl)methanone (2s)

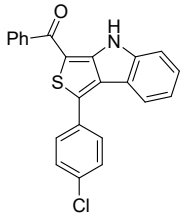
This compound was prepared according to general procedure and purified by flash chromatography on silica gel (hexane/AcOEt, 10:1) to provide the corresponding product yellow solid, 57 mg, yield 78%, m.p.: 160-161 °C. ^{1}H NMR (700 MHz, 23 °C, D_6-DMSO) δ 11.67 (br, 1 H, NH), 7.97 (d, J = 7.1 Hz, 2 H, aromatic CH), 7.90 (d, J = 7.8 Hz, 1 H, aromatic CH), 7.79 (d, J = 8.0 Hz, 2 H, aromatic CH), 7.65 (t, J = 7.4 Hz, 1 H, aromatic CH), 7.59 (t, J = 7.5 Hz, 2 H, aromatic CH), 7.55 (d, J = 8.0 Hz, 1 H, aromatic CH), 7.43 (d, J = 7.9 Hz, 2 H, aromatic CH), 7.40 (d, J = 7.4 Hz, 1 H, aromatic CH), 7.13 (t, J = 7.5 Hz, 1 H, aromatic CH), 2.41 (s, 3 H, CH_3). ^{13}C{^{1}H} (176 MHz, 23 °C, D_6-DMSO) δ 184.9 (Cq, CO), 149.8, 148.2, 141.1, 139.7, 129.9, 118.3 and 106.6, 131.8, 130.2, 128.8, 128.4, 128.1, 128.0, 127.3, 120.8, 120.3 and 112.8 (aromatic CH), 21.1 (CH_3). HRMS (EI) calcd for $C_{24}H_{17}NOS$ $[M+H]^+$: 368.1109; Found: 368.1111.



(1-(2-Chlorophenyl)-4H-thieno[3,4-b]indol-3-yl)(phenyl)methanone (2t)

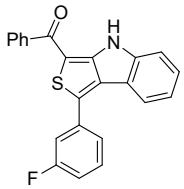
This compound was prepared according to general procedure and purified by flash chromatography on silica gel (hexane/AcOEt, 10:1) to provide the corresponding product yellow liquid, 25 mg, yield 32%. ^{1}H NMR (700 MHz, 23 °C, D_6-DMSO) δ 11.67 (br, 1 H, NH), 7.96, 7.76, 7.65, 7.60, 7.38 and 7.08 (m each, 2:2:1:3:1:1 H, aromatic CH), 7.55 (td, J = 7.6 and 1.2 Hz, 1 H, aromatic CH), 7.53 (d, J = 8.1 Hz, 1 H, aromatic CH), 7.33 (d, J = 7.7 Hz, 1 H, aromatic CH). ^{13}C{^{1}H} (176

MHz, 23 °C, D_6-DMSO) δ 185.2 (Cq, CO), 148.5, 148.2, 139.4, 135.3, 132.5, 131.6, 130.9, 118.1 and 107.8 (Cq), 132.4, 131.9, 131.4, 130.4, 128.8, 127.9, 127.8, 127.3, 121.2, 120.2, 112.6 (aromatic CH). HRMS (EI) calcd for $C_{23}H_{14}ClNOS$ $[M+H]^+$: 388.0563; Found: 388.0558.



(1-(4-Chlorophenyl)-4*H*-thieno[3,4-*b*]indol-3-yl)(phenyl)methanone (2u)

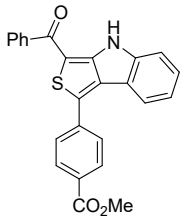
This compound was prepared according to general procedure and purified by flash chromatography on silica gel (hexane/AcOEt, 10:1) to provide the corresponding product yellow solid, 57 mg, yield 73%, m.p.: 169-170 °C. ^{1}H NMR (700 MHz, 23 °C, D_6-DMSO) δ 11.70 (br, 1 H, NH), 7.96 (d, J = 7.3 Hz, 2 H, aromatic CH), 7.88 and 7.66 (m each, 3:3 H, aromatic CH), 7.59 (t, J = 7.5 Hz, 2 H, aromatic CH), 7.55 (d, J = 8.1 Hz, 1 H, aromatic CH), 7.42 (t, J = 7.6 Hz, 1 H, aromatic CH), 7.13 (t, J = 7.4 Hz, 1 H aromatic CH). ^{13}C{^{1}H} (176 MHz, 23 °C, D_6-DMSO) δ 185.0 (Cq, CO), 149.6, 148.3, 139.5, 138.7, 134.3, 131.5, 128.9, 117.9, 107.1 (Cq), 131.8, 129.8, 129.6, 128.8, 127.9, 127.5, 120.8, 120.3, 112.8 (aromatic CH). HRMS (EI) calcd for $C_{23}H_{14}ClNOS$ $[M+H]^+$: 388.0563; Found: 388.0567.



(1-(3-Fluorophenyl)-4*H*-thieno[3,4-*b*]indol-3-yl)(phenyl)methanone (2v)

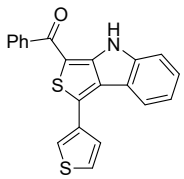
This compound was prepared according to general procedure and purified by flash chromatography on silica gel (hexane/AcOEt, 10:1) to provide the corresponding product yellow solid, 54 mg, yield 73%, m.p.: 166-167 °C. ^{1}H NMR (700 MHz, 23 °C, D_6-DMSO) δ 11.71 (br, 1 H, NH), 7.97 (m, 2 H, aromatic CH), 7.87 (d, J = 7.8 Hz, 1 H, aromatic CH), 7.73 (d, J = 8.0 Hz, 1 H, aromatic CH), 7.66, 7.43 and 7.14 (m each, 3:1:1 H, aromatic CH), 7.59 (dd, J = 10.4 and 4.7 Hz, 2 H,

aromatic CH), 7.56 (d, J = 8.1 Hz, 1 H, aromatic CH), 7.39 (td, J = 8.4 and 2.1 Hz, 1 H, aromatic CH), 7.17-7.11 (m, 1H, aromatic CH). $^{13}C\{^{1}H\}$ (175 MHz, 23 ^{o}C, D_6-DMSO) δ 185.1 (Cq, CO), 162.5 (Cq and d, J = 245.8 Hz, C-F), 149.5, 148.3, 139.4, 138.3 (d, J = 2.3 Hz), 134.8 (d, J = 8.4 Hz), 129.1, 117.9 and 107.3 (Cq), 131.8, 131.7 (d, J = 8.7 Hz), 128.7, 127.9, 127.5, 124.3 (d, J = 2.5 Hz), 120.8, 120.3, 116.4 (d, J = 21.1 Hz), 114.7 (d, J = 22.8 Hz), 112.8, 107.3 (aromatic CH). HRMS (EI) calcd for $C_{23}H_{14}FNOS$ $[M+H]^+$: 372.0858; Found: 372.0855.



Methyl 4-(3-benzoyl-4*H*-thieno[3,4-*b*]indol-1-yl)benzoate (2w)

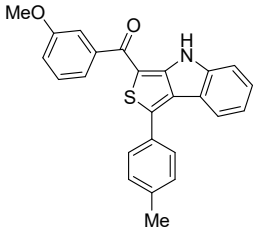
This compound was prepared according to general procedure and purified by flash chromatography on silica gel (hexane/AcOEt, 10:1) to provide the corresponding product yellow solid, 58 mg, yield 70%, m.p.: 176-177 ^{o}C. ^{1}H NMR (700 MHz, 23 ^{o}C, D_6-DMSO) δ 11.72 (br, 1 H, NH), 8.12 (d, J = 7.8 Hz, 2 H, aromatic CH), 7.91 and 7.56 (m each, 4:3 H, aromatic CH), 7.91 (d, J = 7.7 Hz, 1 H, aromatic CH), 7.65 (t, J = 7.1 Hz, 1 H, aromatic CH), 7.42 (t, J = 7.4 Hz, 1 H, aromatic CH), 7.12 (t, J = 7.3 Hz, 1 H, aromatic CH), 3.89 (s, 3 H, OCH_3). $^{13}C\{^{1}H\}$ (176 MHz, 23 ^{o}C, D_6-DMSO) δ 185.0 (Cq, CO), 165.6 (Cq, CO_2), 149.5, 148.4, 139.3, 138.2, 137.2, 130.2, 129.9, 129.3, 128.7, 128.2, 127.9, 117.8 and 107.7 (Cq), 131.8, 127.6, 120.9, 120.2 and 112.8 (aromatic CH), 52.3 (OCH_3). HRMS (EI) calcd for $C_{25}H_{17}NO_3S$ $[M+H]^+$: 412.1007; Found: 412.1009.



Phenyl(1-(thiophen-3-yl)-4*H*-thieno[3,4-*b*]indol-3-yl)methanone (2x)

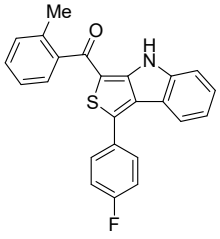
This compound was prepared according to general procedure and purified by flash chromatography on silica gel (hexane/AcOEt, 10:1) to provide the

corresponding product yellow solid, 55 mg, yield 76%, m.p.: 174-175 °C. ^{1}H NMR (700 MHz, 23 °C, D_6-DMSO) δ 11.71 (br, 1 H, NH), 8.08 and 7.88–7.38 (m each, 3:7 H, aromatic CH), 7.23 (d, J = 75.7 Hz, 2 H, aromatic CH). ^{13}C{^{1}H} (176 MHz, 23 °C, D_6-DMSO) δ 184.7 (Cq, CO), 149.7, 148.1, 139.5, 134.1, 132.9, 127.9, 117.8 and 105.6 (Cq), 131.7, 128.9, 128.7, 128.4, 127.8, 127.4, 121.1, 120.3 and 112.7 (aromatic CH). HRMS (EI) calcd for $C_{21}H_{13}NOS_2$ $[M+H]^+$: 360.0517; Found: 360.0512.



(3-Methoxyphenyl)(1-(p-tolyl)-4*H*-thieno[3,4-*b*]indol-3-yl)methanone (2y)

This compound was prepared according to general procedure and purified by flash chromatography on silica gel (hexane/AcOEt, 10:1) to provide the corresponding product yellow solid, 57 mg, yield 72%, m.p.: 143-144 °C. ^{1}H NMR (700 MHz, 23 °C, D_6-DMSO) δ 11.65 (br, 1 H, NH), 7.89 and 7.53 (d each, J = 7.8 Hz, 1:1 H, aromatic CH), 7.76 (d, J = 7.9 Hz, 2 H, aromatic CH), 7.55 (d, J = 8.2 Hz, 1 H, aromatic CH), 7.49 (t, J = 7.8 Hz, 1 H, aromatic CH), 7.45 (s, 1 H, aromatic CH), 7.40 (m, 3 H, aromatic CH), 7.20 (dd, J = 8.0 and 1.7 Hz, 1 H, aromatic CH), 7.12 (t, J = 7.5 Hz, 1 H, aromatic CH), 3.85 (s, 3 H, OCH_3), 2.39 (s, 3 H, C-CH_3). ^{13}C{^{1}H}(176 MHz, 23 °C, D_6-DMSO) δ 184.5 (Cq, CO), 159.3, 149.7, 148.1, 141.1, 141.0, 139.6, 129.8, 128.3, 118.2 and 106.6 (Cq), 130.1, 129.9, 127.9, 127.2, 120.7, 120.2, 120.1, 117.4, 113.0 and 112.7 (aromatic CH), 55.4 (OCH_3), 20.9 (C-CH_3). HRMS (EI) calcd for $C_{25}H_{19}NO_2S$ $[M+H]^+$: 398.1215; Found: 398.1213.



(1-(4-Fluorophenyl)-4*H*-thieno[3,4-*b*]indol-3-yl)(o-tolyl)methanone (2z)

This compound was prepared according to general procedure and purified by flash chromatography on silica gel (hexane/AcOEt, 10:1) to provide the corresponding

product yellow liquid, 59 mg, yield 76%. ^{1}H NMR (700 MHz, 23 ^{o}C, D_6-DMSO) δ 11.72 (br, 1 H, NH), 7.59 (d, J = 7.3 Hz, 1 H, aromatic CH), 7.54 (d, J = 8.1 Hz, 1 H, aromatic CH), 7.46–7.37 and 7.45 (m each, 4:3 H, aromatic CH), 7.35 (d, J = 8.0 Hz, 1 H, aromatic CH), 7.32 (d, J = 7.4 Hz, 1 H, aromatic CH), 7.11 (t, J = 7.4 Hz, 1 H, aromatic CH), 2.36 (s, 3 H, CH_3). ^{13}C{^{1}H}(176 MHz, 23 ^{o}C, D_6-DMSO) δ 187.6 (Cq, CO), 163.2 (d, J = 248.1 Hz, C-F), 148.9, 148.7, 140.3, 140.0, 135.6, 129.6 (d, J = 3.1 Hz), 129.4, 118.5 and 109.3 (Cq), 131.3, 130.8 (d, J = 8.6 Hz), 130.5, 127.8, 127.5, 125.9, 121.1, 120.7, 117.0 (d, J = 22.0 Hz) and 113.2 (aromatic CH), 19.6 (CH_3). HRMS (EI) calcd for $C_{24}H_{16}FNOS$ $[M+H]^{+}$: 386.1015; Found: 386.1013.

5. Copies of NMR spectra for thiophene-fused *N*-heterocycles 2

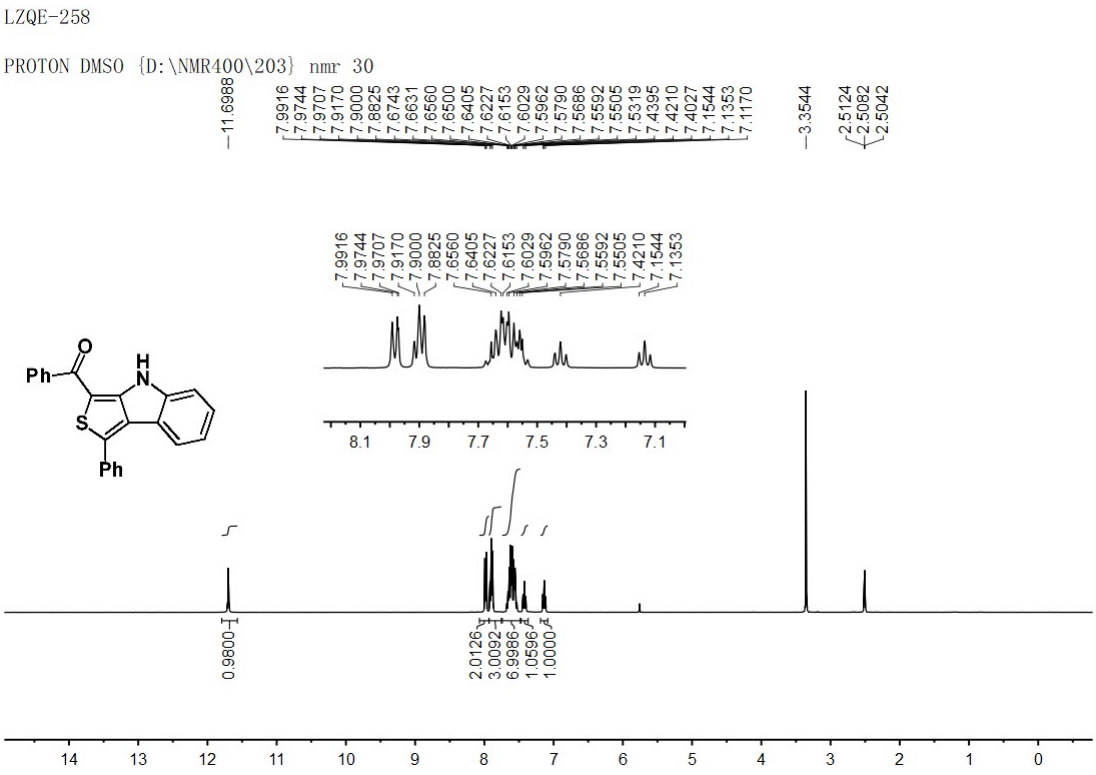


Figure S1. [1]H NMR spectrum of **2a** (d6-DMSO, 400 MHz).

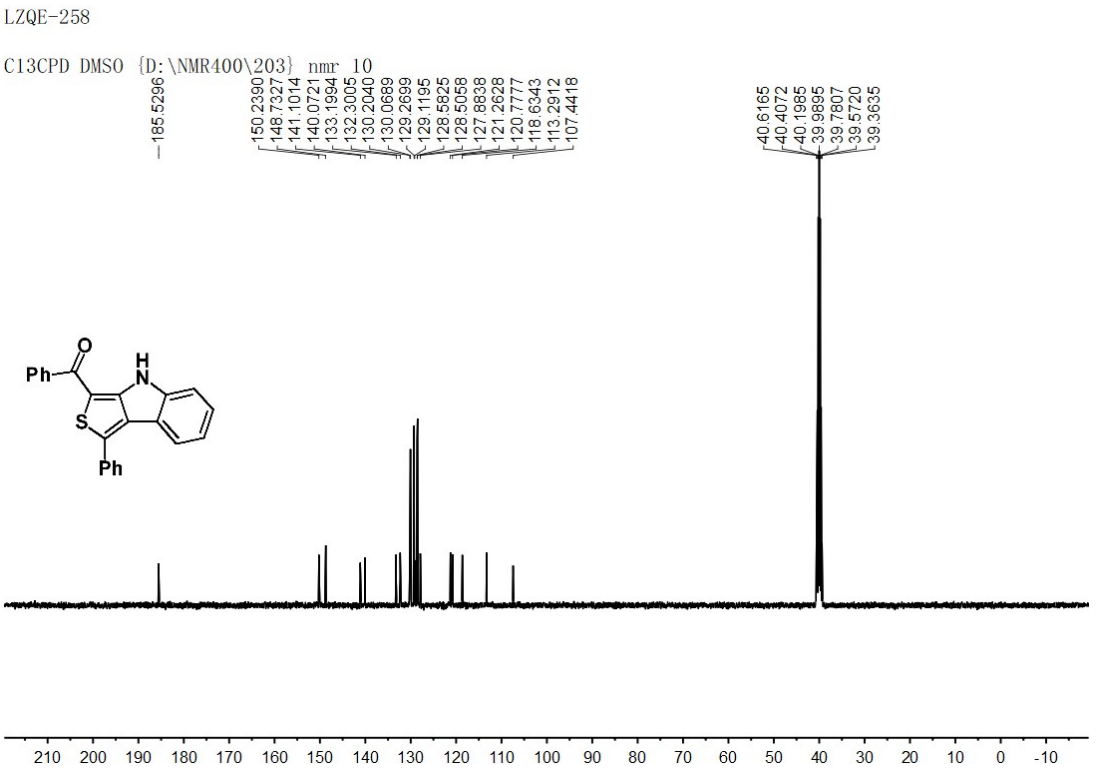


Figure S2. [13]C NMR spectrum of **2a** (d6-DMSO, 100 MHz).

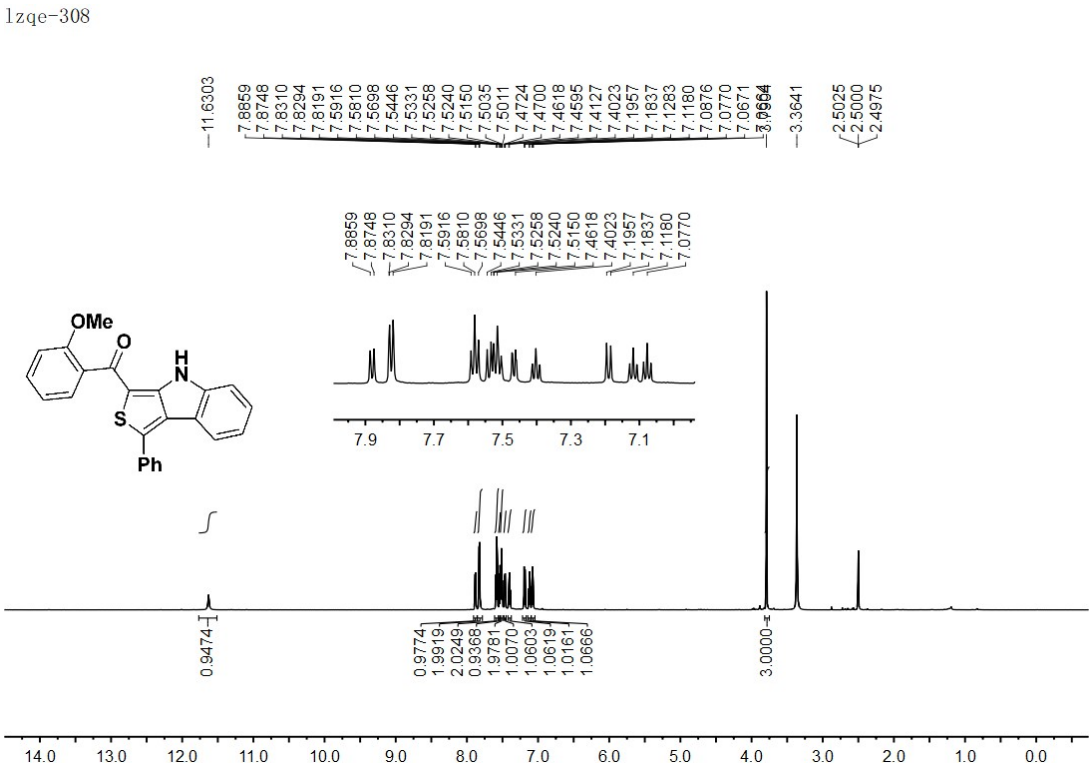


Figure S3. ^{1}H NMR spectrum of **2b** (d6-DMSO, 400 MHz).

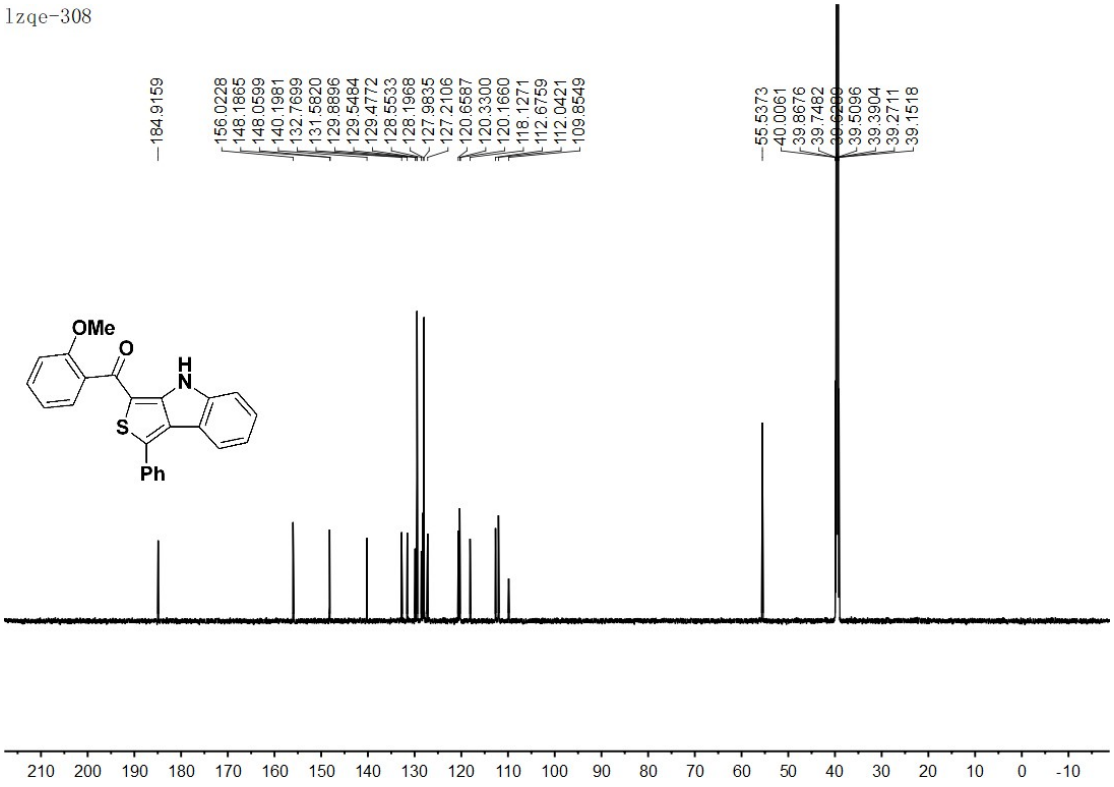


Figure S4. ^{13}C NMR spectrum of **2b** (d6-DMSO, 100 MHz).

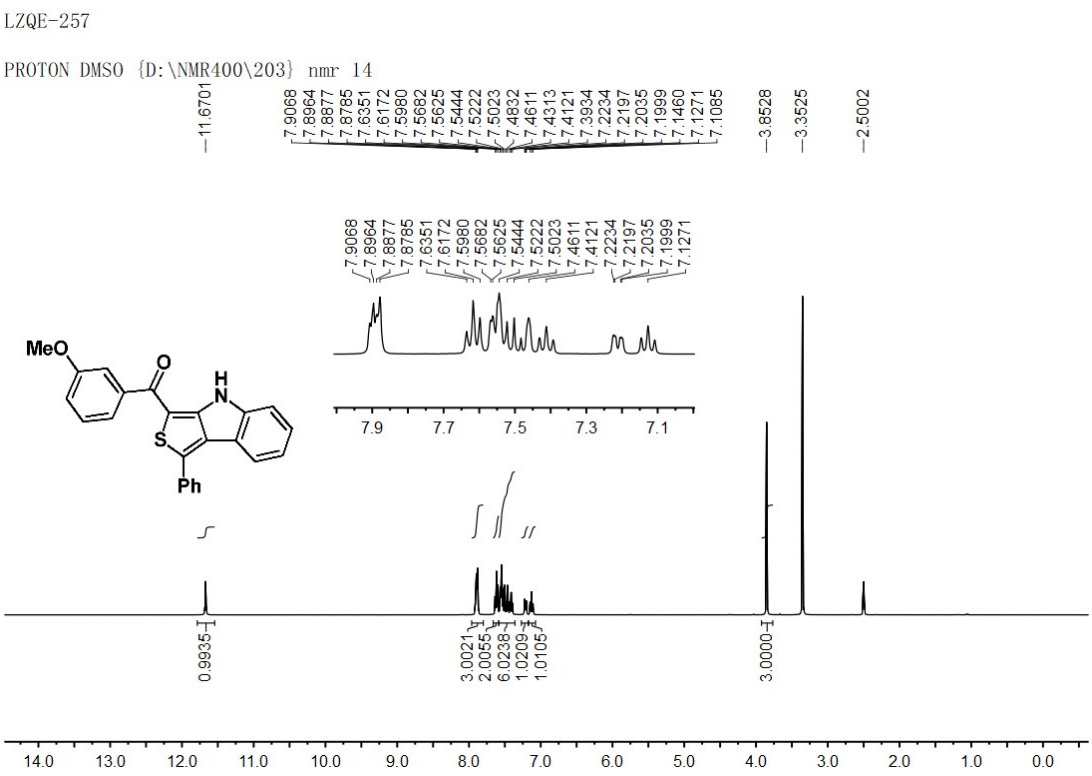


Figure S5. [1]H NMR spectrum of **2c** (d6-DMSO, 400 MHz).

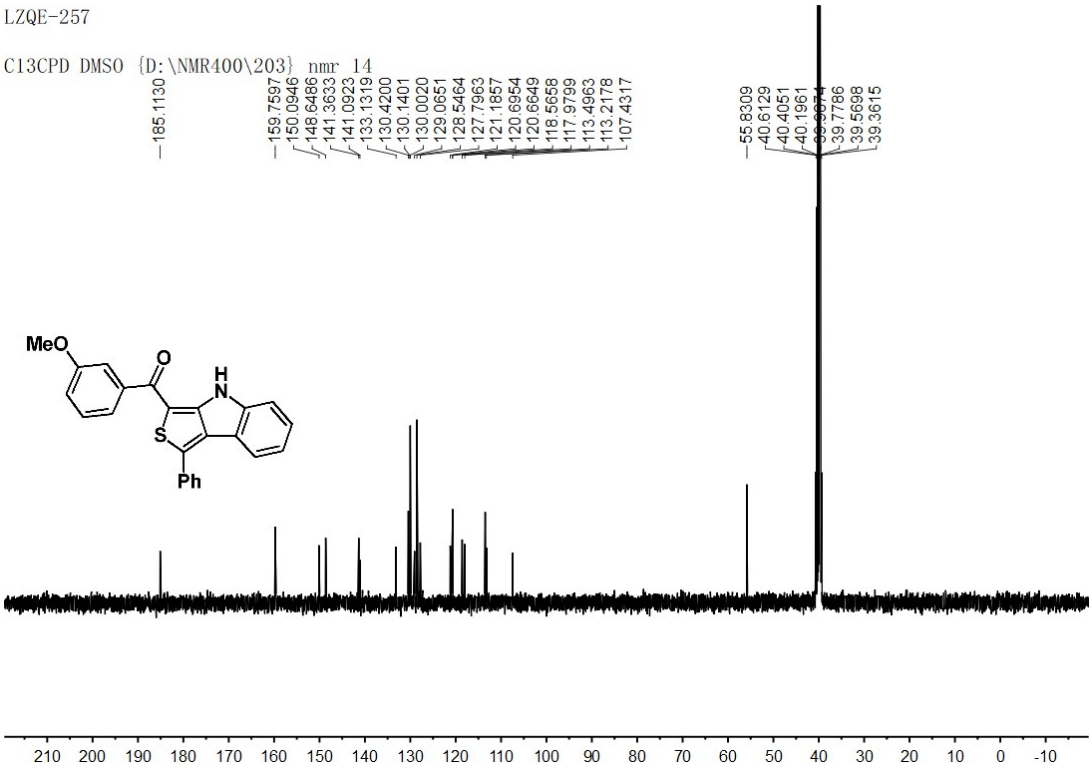


Figure S6. [13]C NMR spectrum of **2c** (d6-DMSO, 100 MHz).

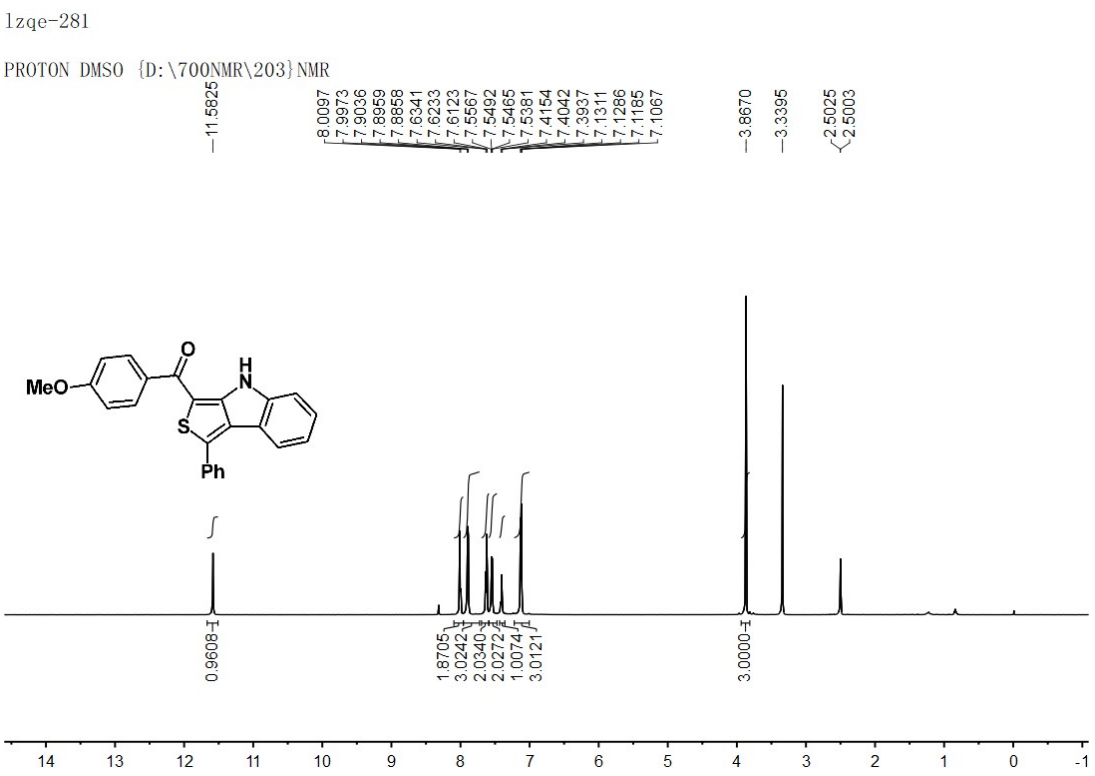


Figure S7. [1]H NMR spectrum of **2d** (d6-DMSO, 400 MHz).

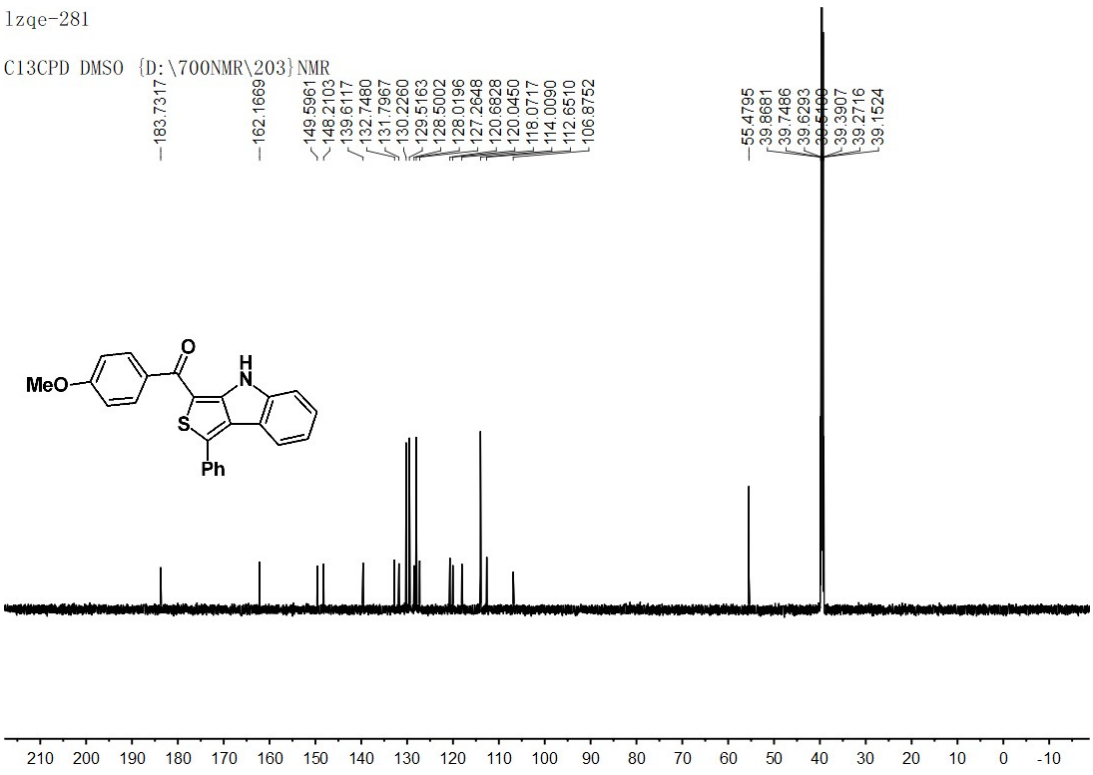


Figure S8. [13]C NMR spectrum of **2d** (d6-DMSO, 100 MHz).

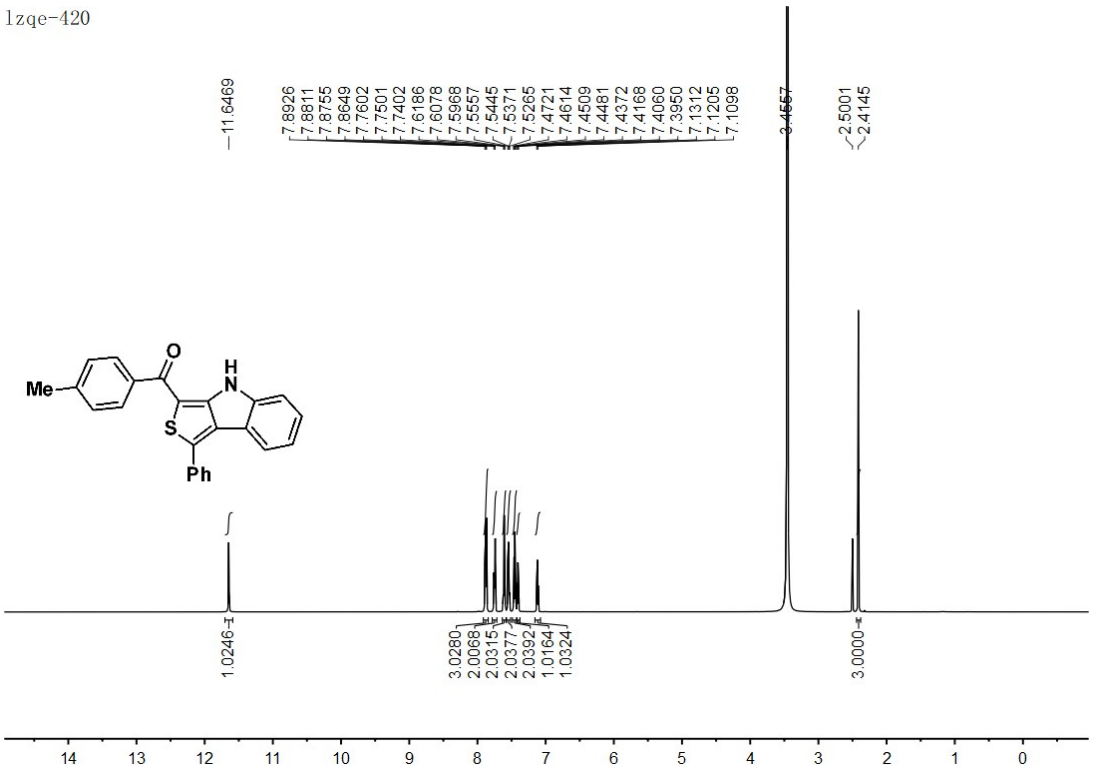


Figure S9. [1]H NMR spectrum of **2e** (d6-DMSO, 400 MHz).

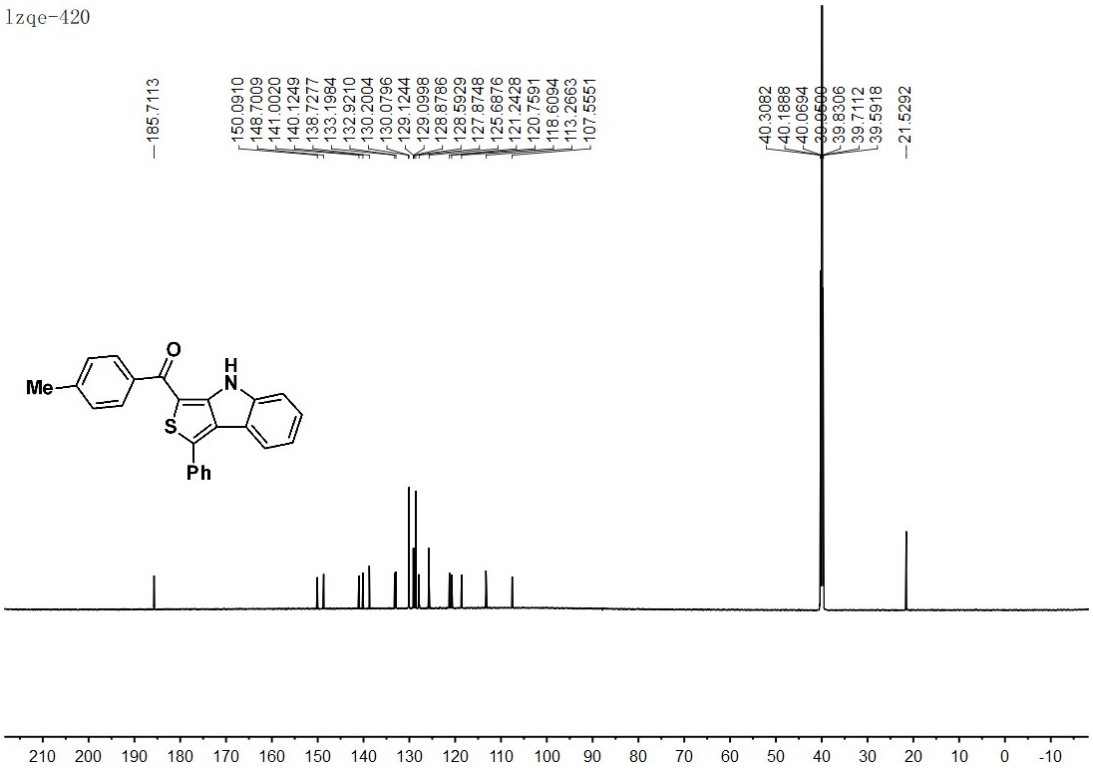


Figure S10. [13]C NMR spectrum of **2e** (d6-DMSO, 100 MHz).

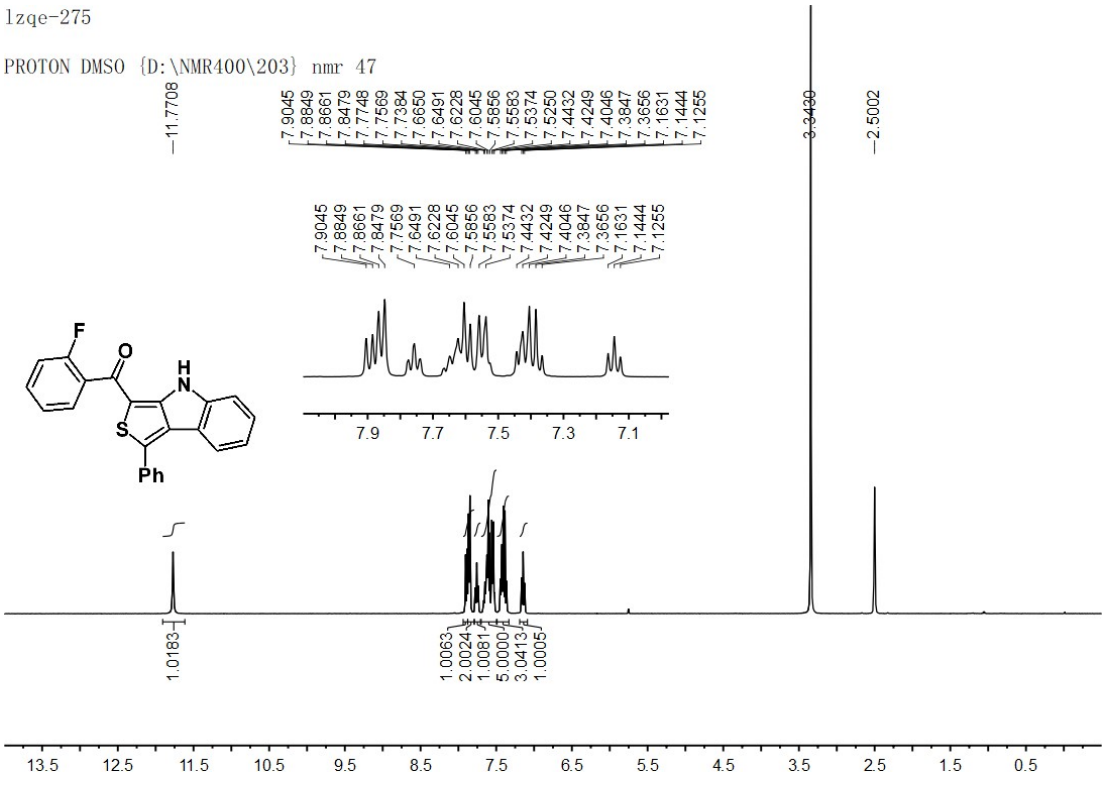


Figure S11. [1]H NMR spectrum of **2f** (d6-DMSO, 400 MHz).

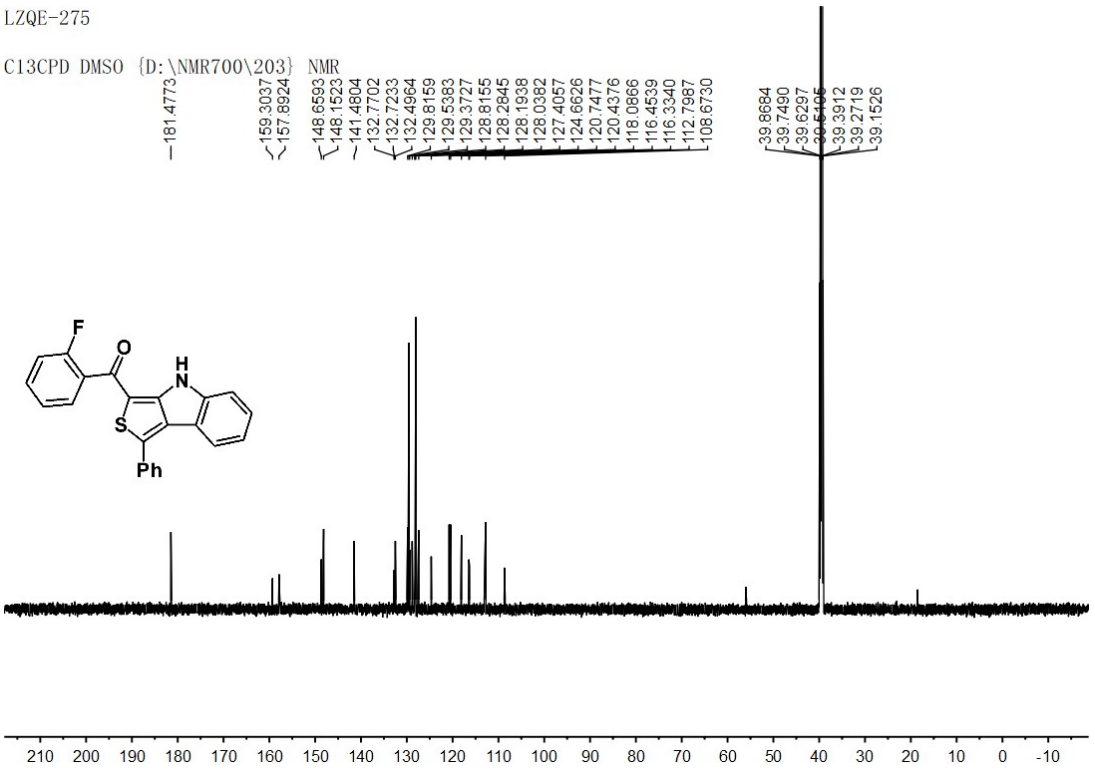


Figure S12. [13]C NMR spectrum of **2f** (d6-DMSO, 100 MHz).

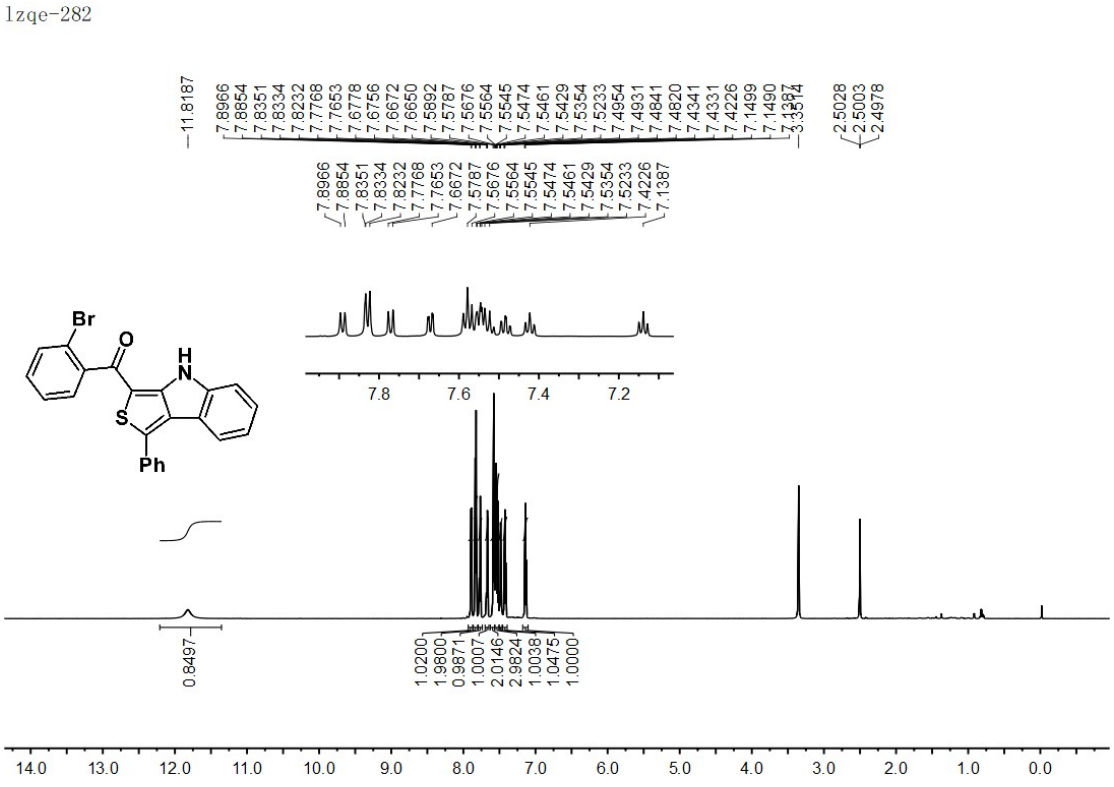


Figure S13. [1]H NMR spectrum of **2g** (d6-DMSO, 400 MHz).

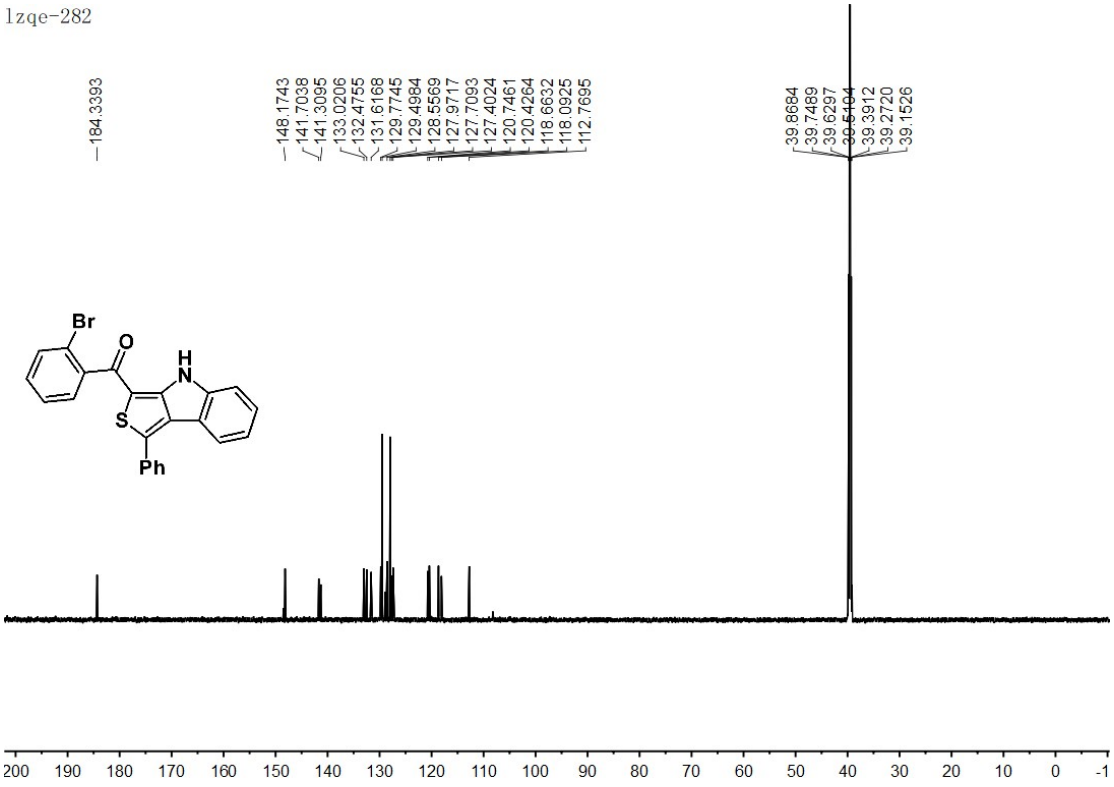


Figure S14. [13]C NMR spectrum of **2g** (d6-DMSO, 100 MHz).

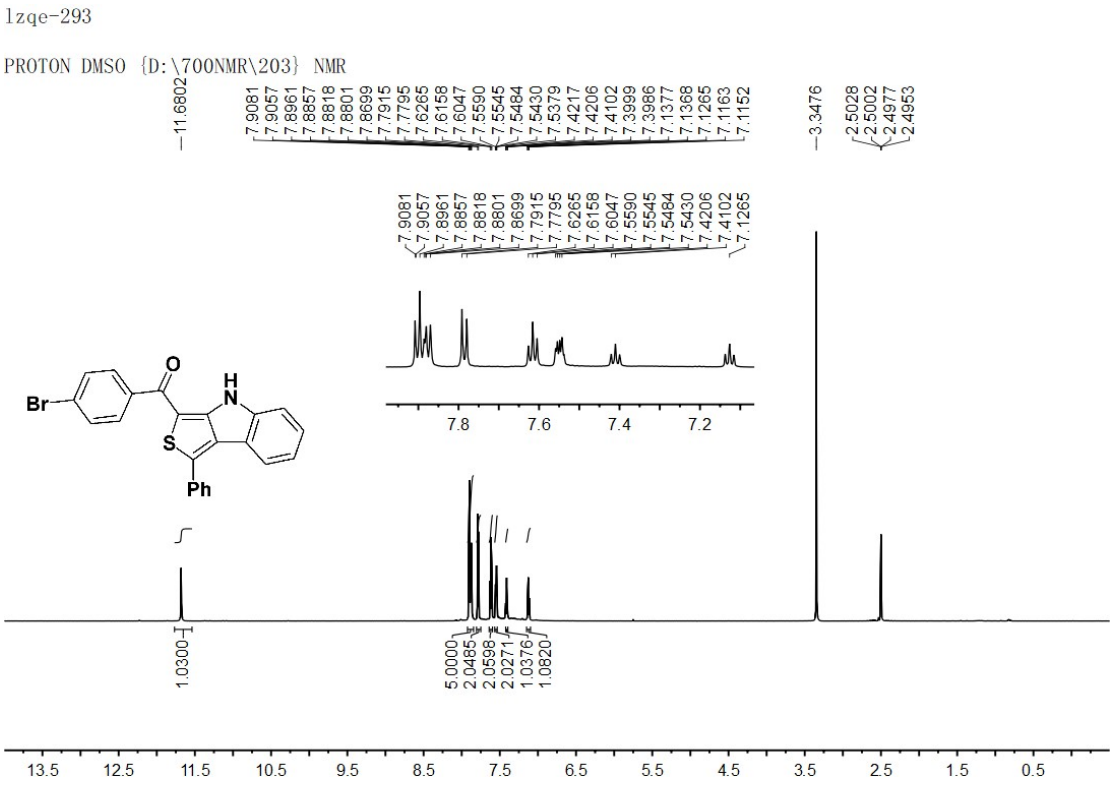


Figure S15. [1]H NMR spectrum of **2h** (d6-DMSO, 400 MHz).

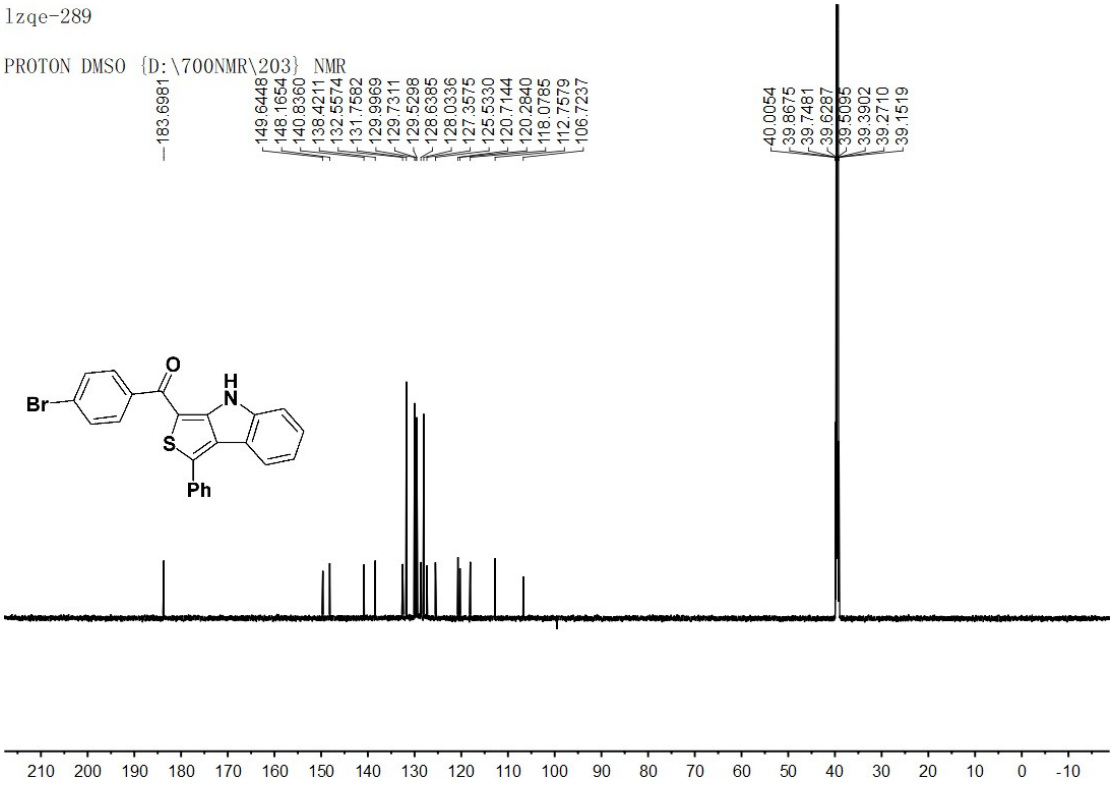


Figure S16. [13]C NMR spectrum of **2h** (d6-DMSO, 100 MHz).

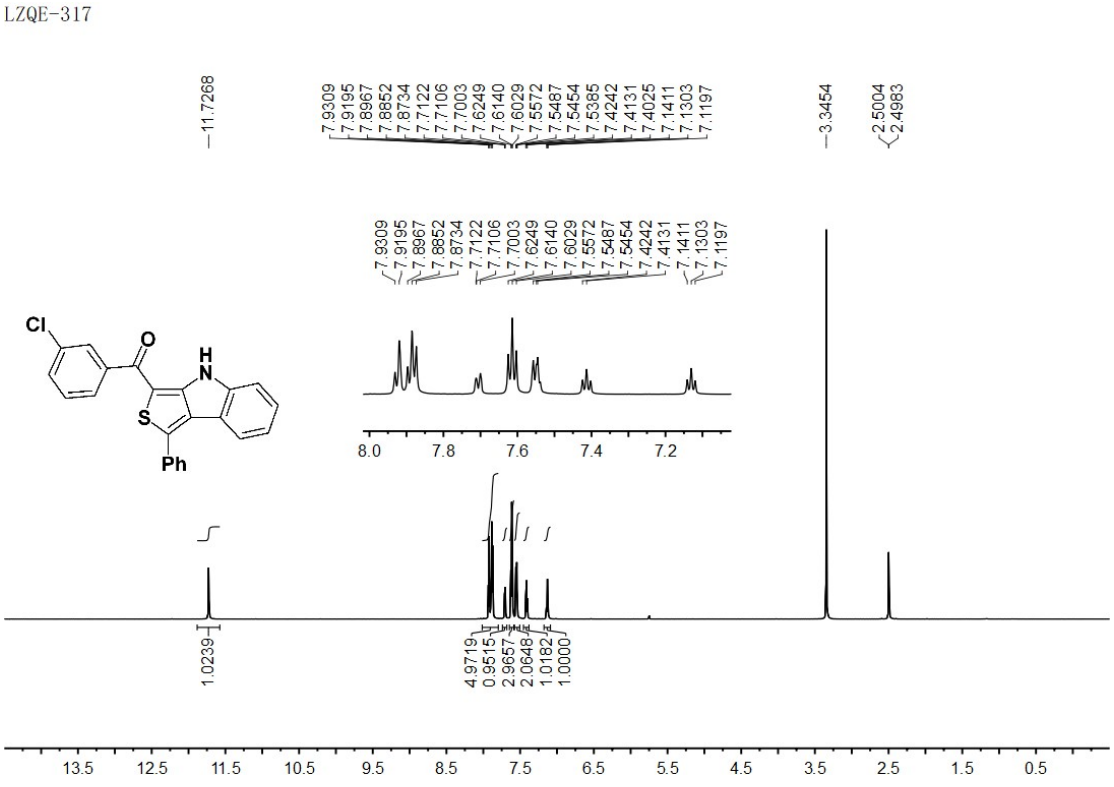


Figure S17. [1]H NMR spectrum of **2i** (d6-DMSO, 400 MHz).

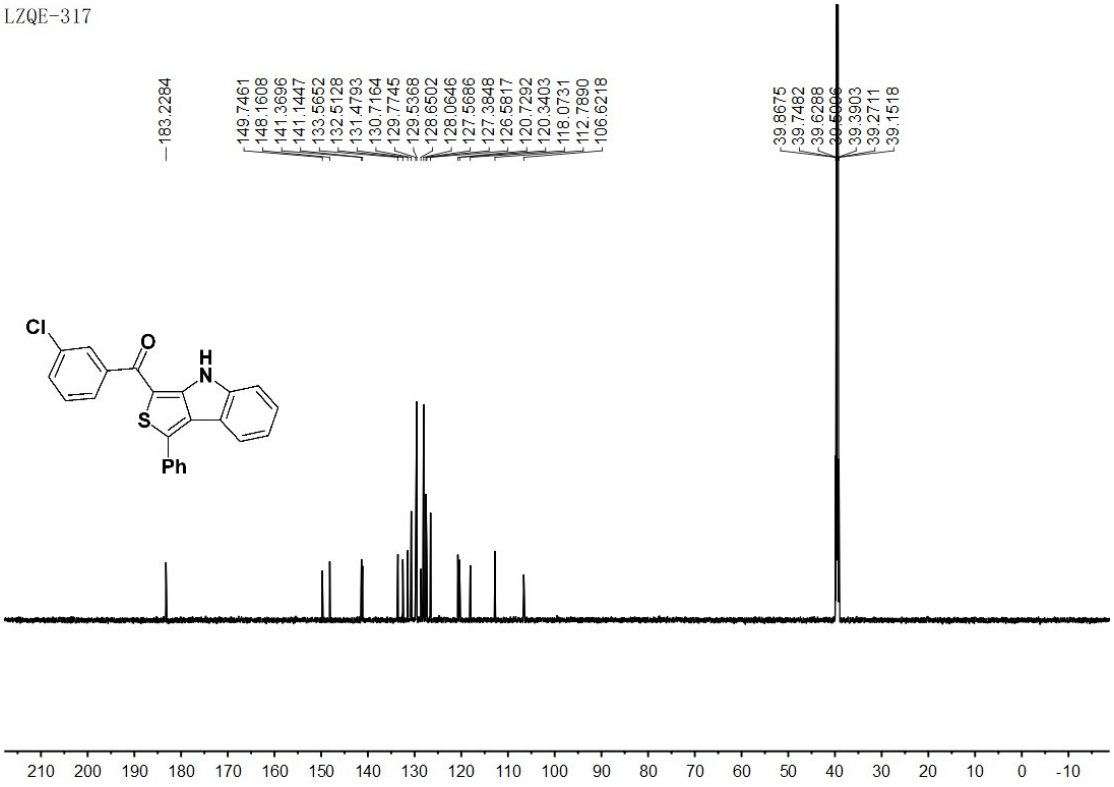


Figure S18. [13]C NMR spectrum of **2i** (d6-DMSO, 100 MHz).

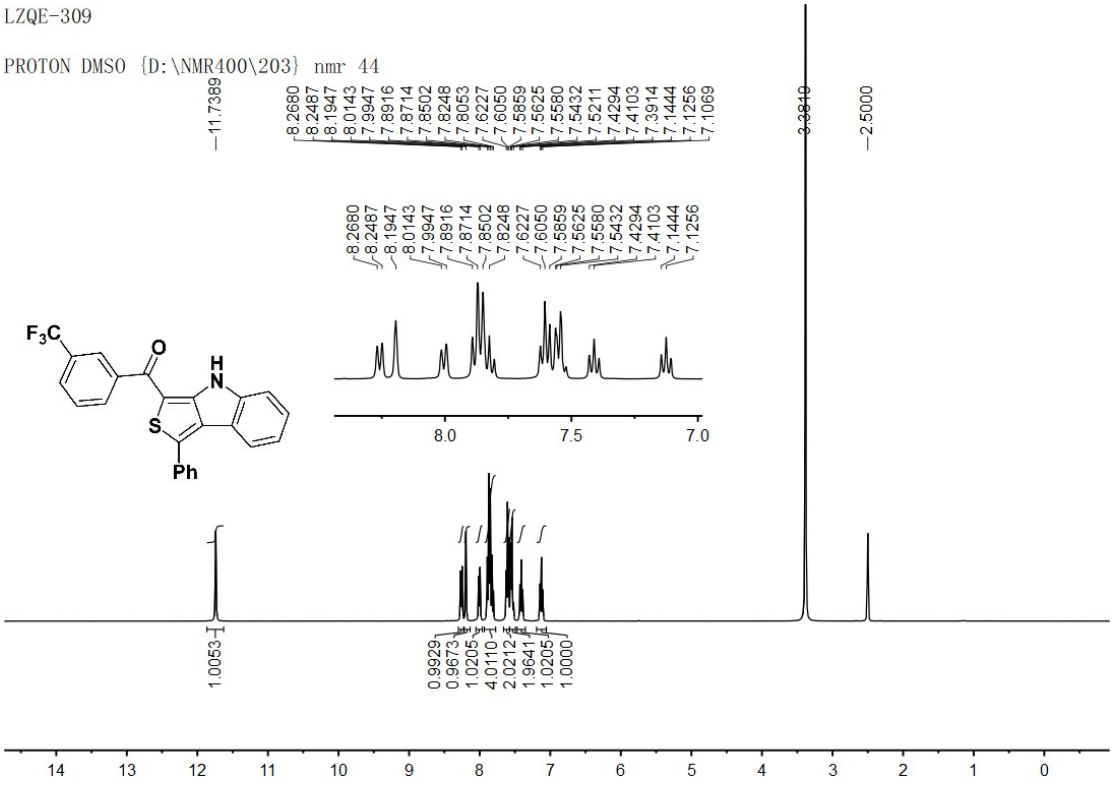


Figure S19. [1]H NMR spectrum of **2j** (d6-DMSO, 400 MHz).

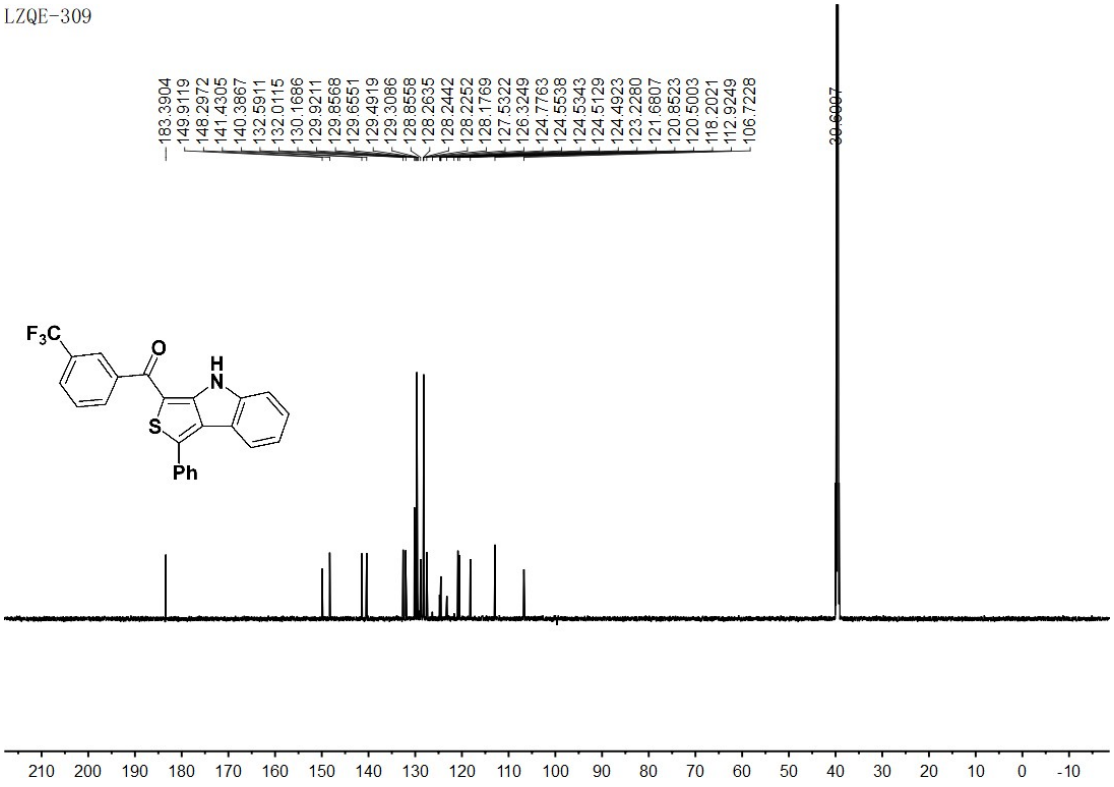


Figure S20. [13]C NMR spectrum of **2j** (d6-DMSO, 100 MHz).

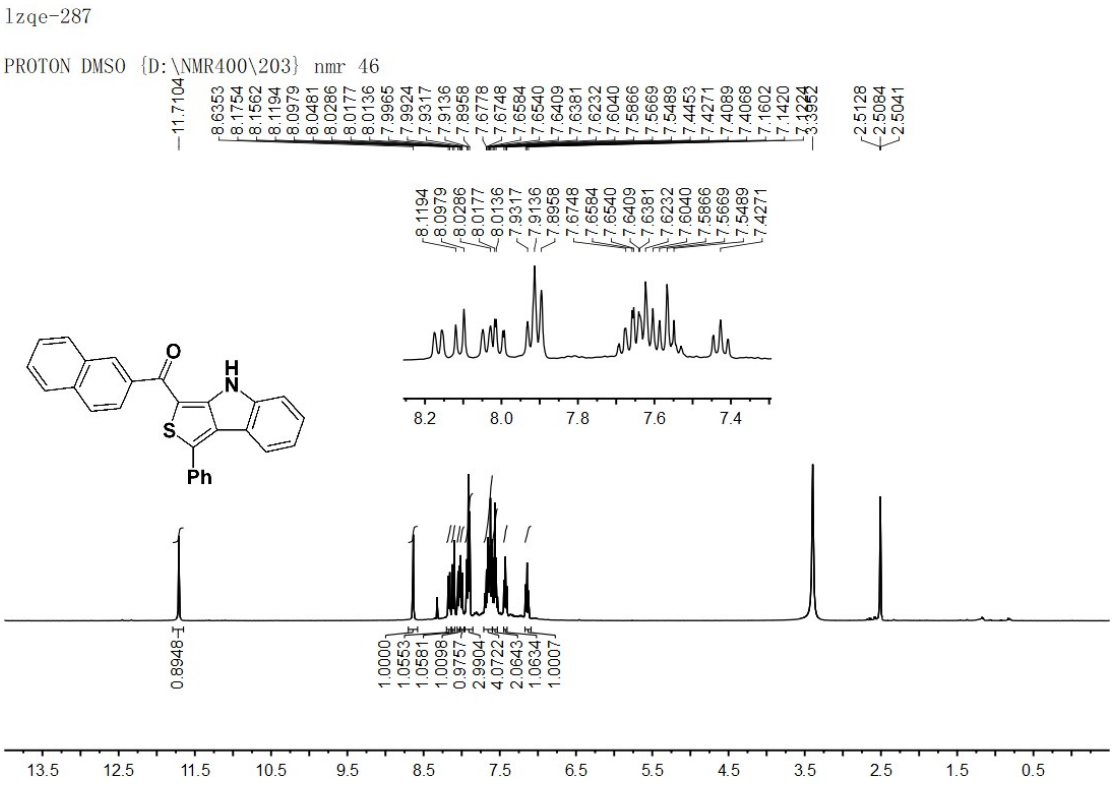


Figure S21. [1]H NMR spectrum of **2k** (d6-DMSO, 400 MHz).

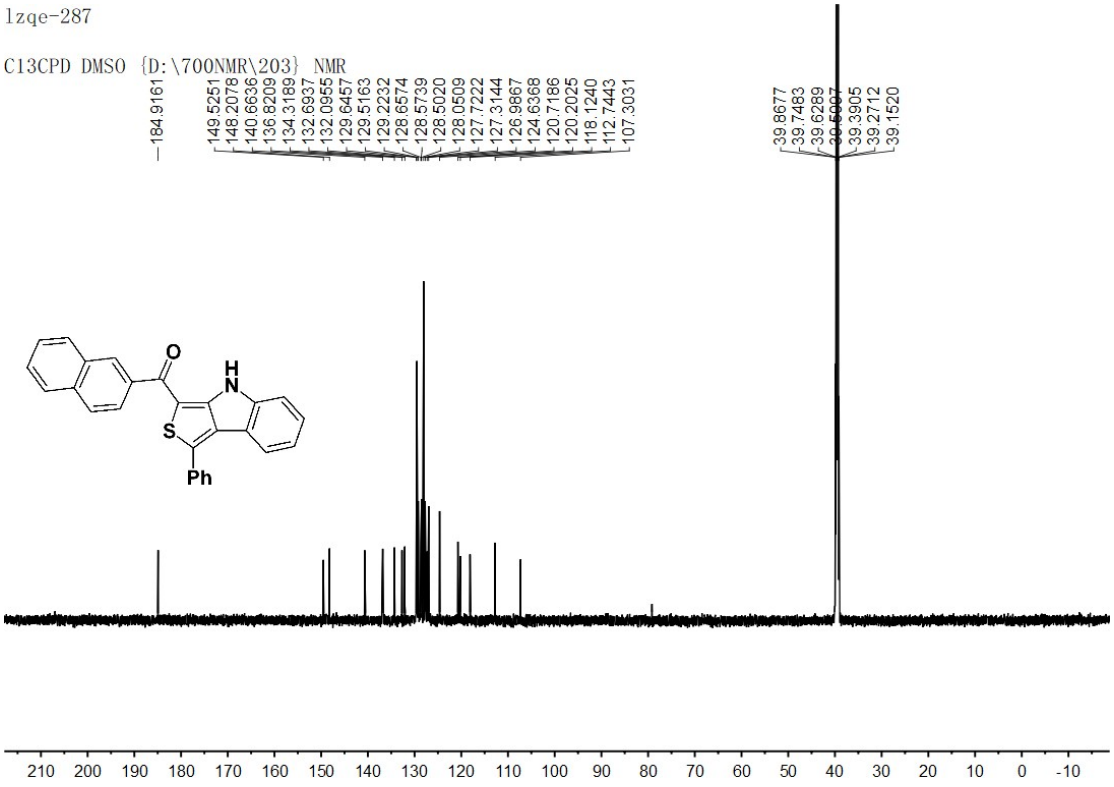


Figure S22. [13]C NMR spectrum of **2k** (d6-DMSO, 100 MHz).

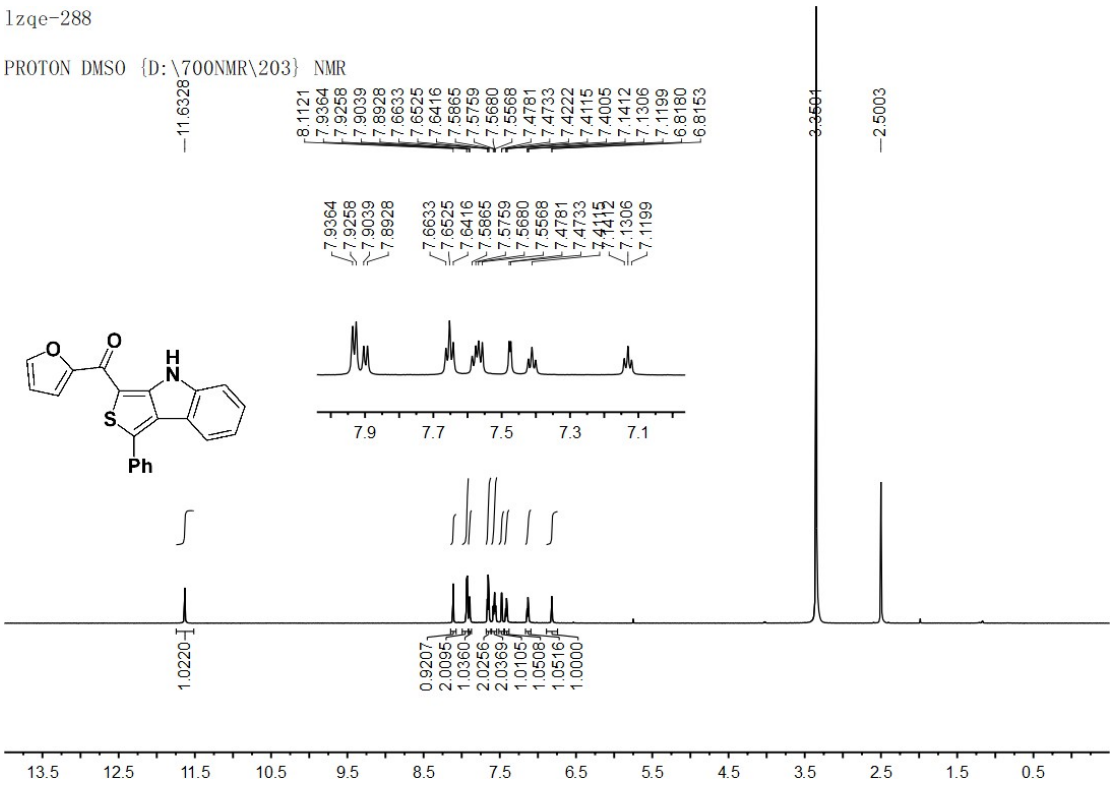


Figure S23. [1]H NMR spectrum of **2l** (d6-DMSO, 400 MHz).

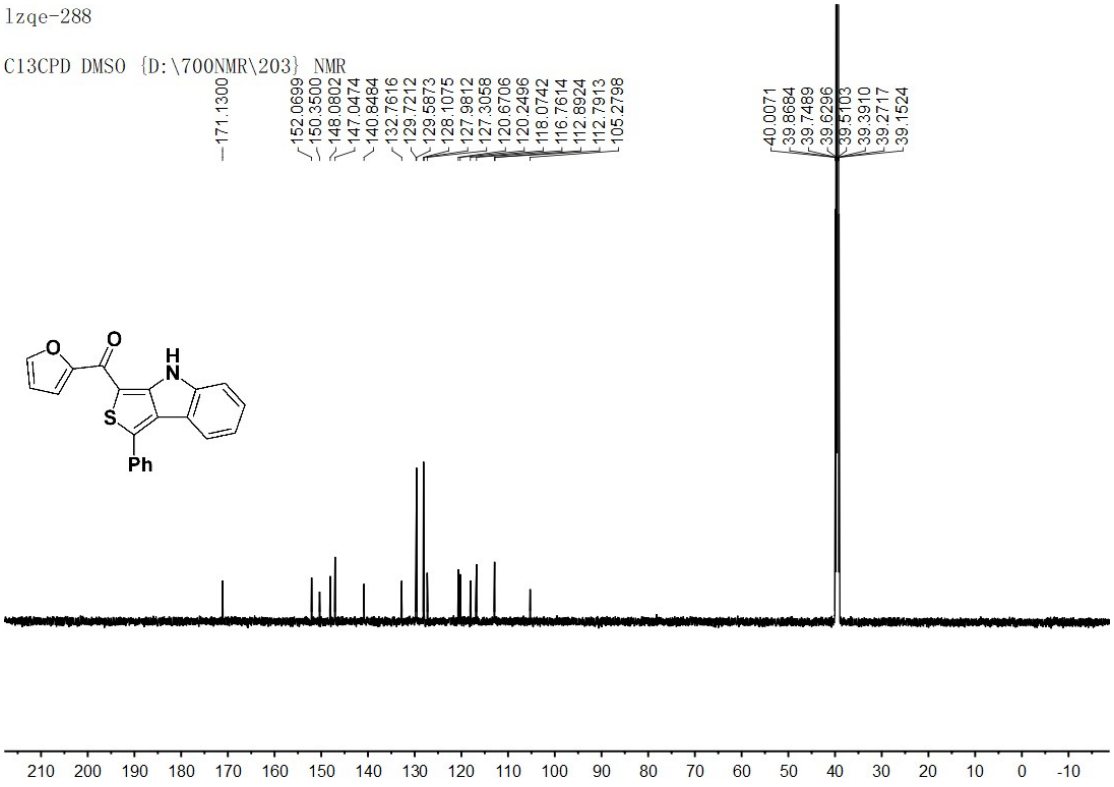


Figure S24. [13]C NMR spectrum of **2l** (d6-DMSO, 100 MHz).

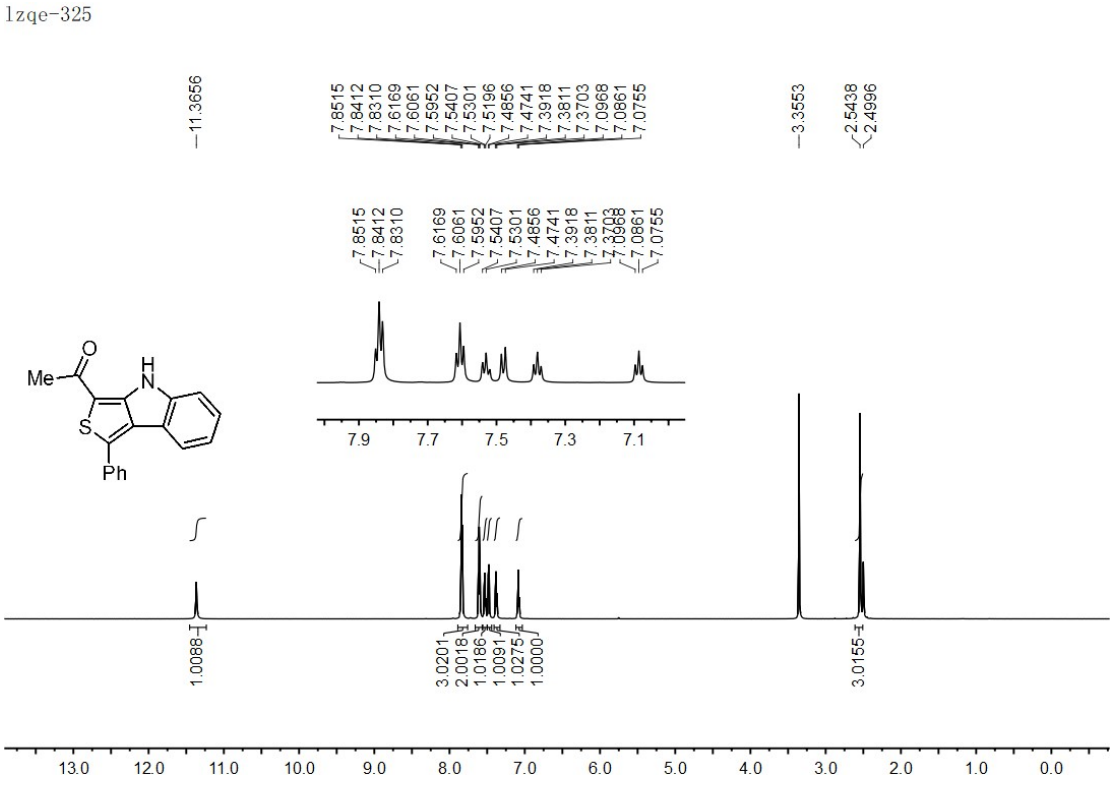


Figure S25. [1]H NMR spectrum of **2m** (d6-DMSO, 400 MHz).

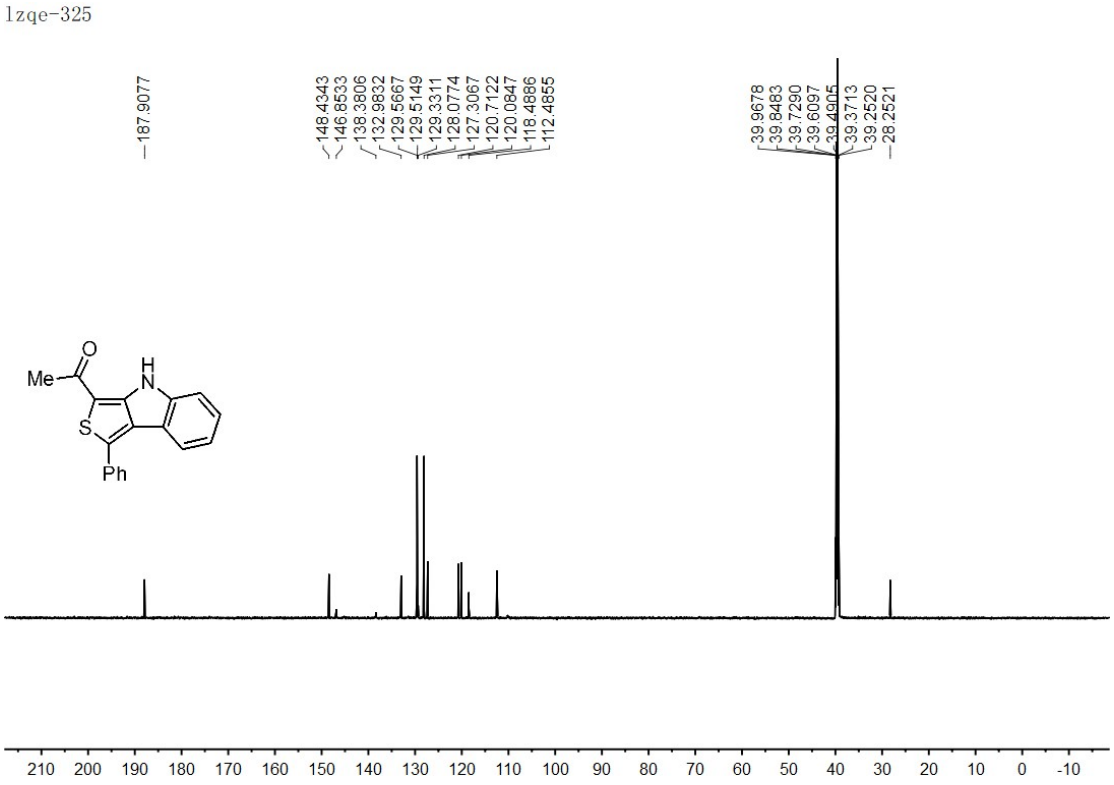


Figure S26. [13]C NMR spectrum of **2m** (d6-DMSO, 100 MHz).

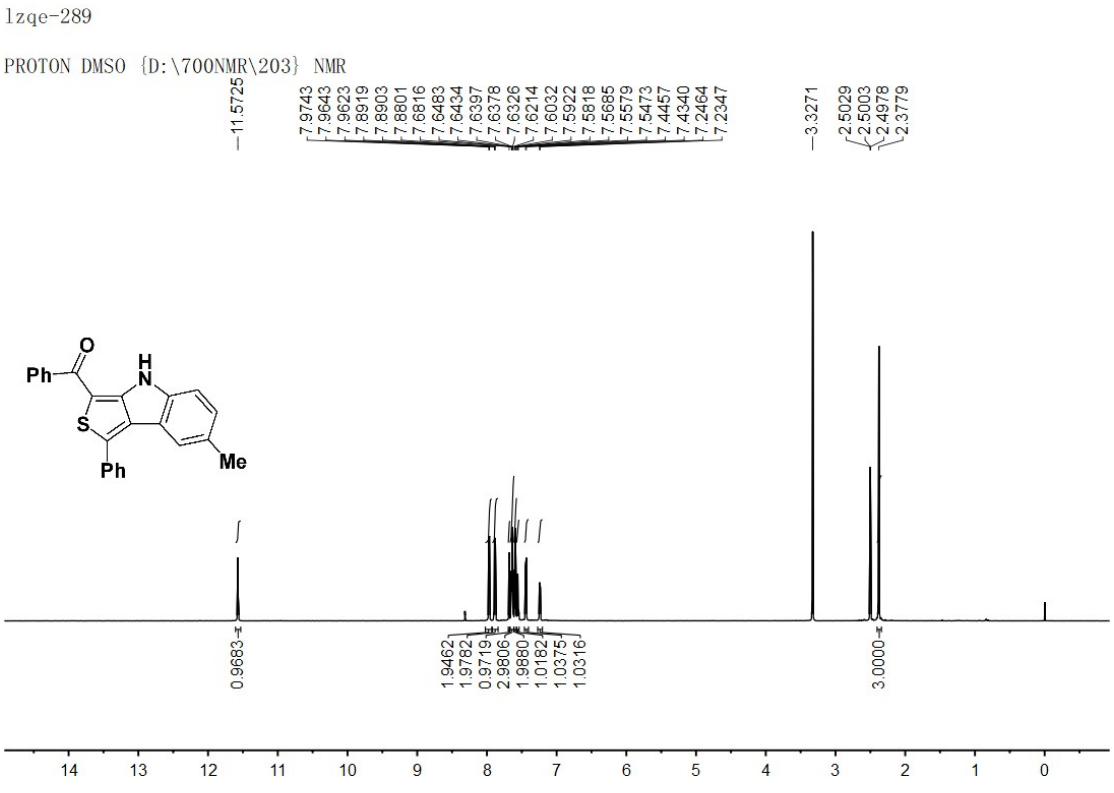


Figure S27. [1]H NMR spectrum of **2n** (d6-DMSO, 400 MHz).

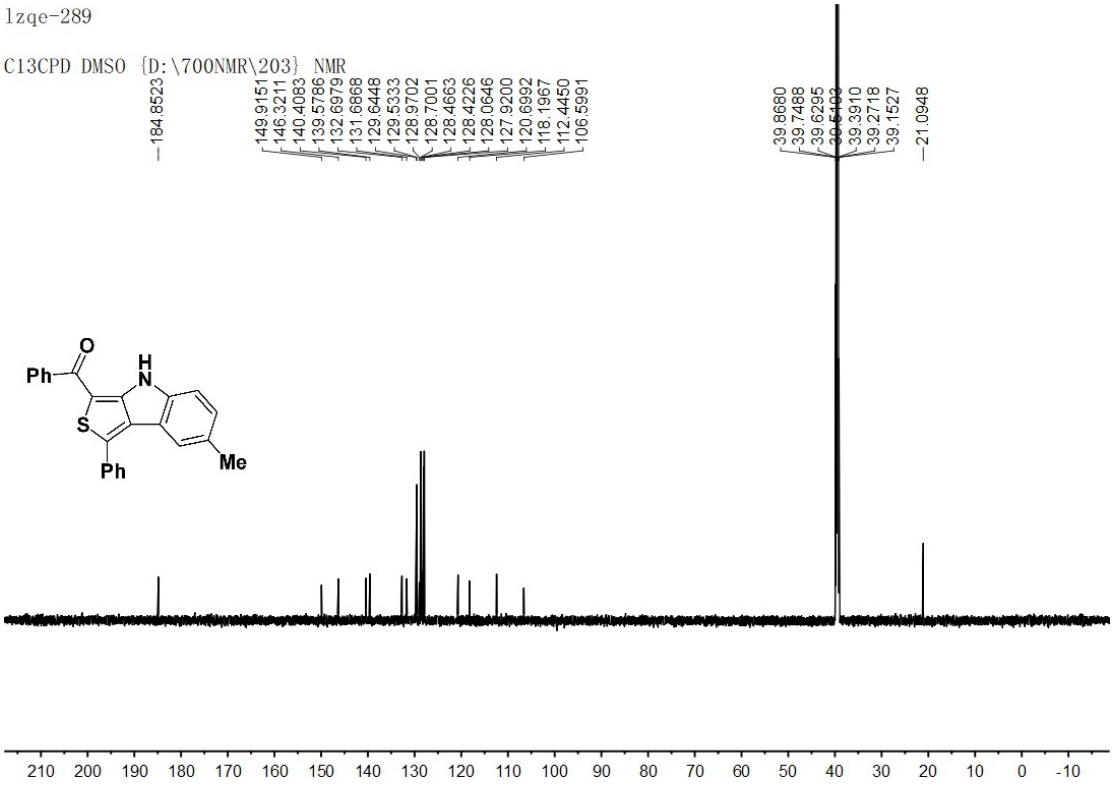


Figure S28. [13]C NMR spectrum of **2n** (d6-DMSO, 100 MHz).

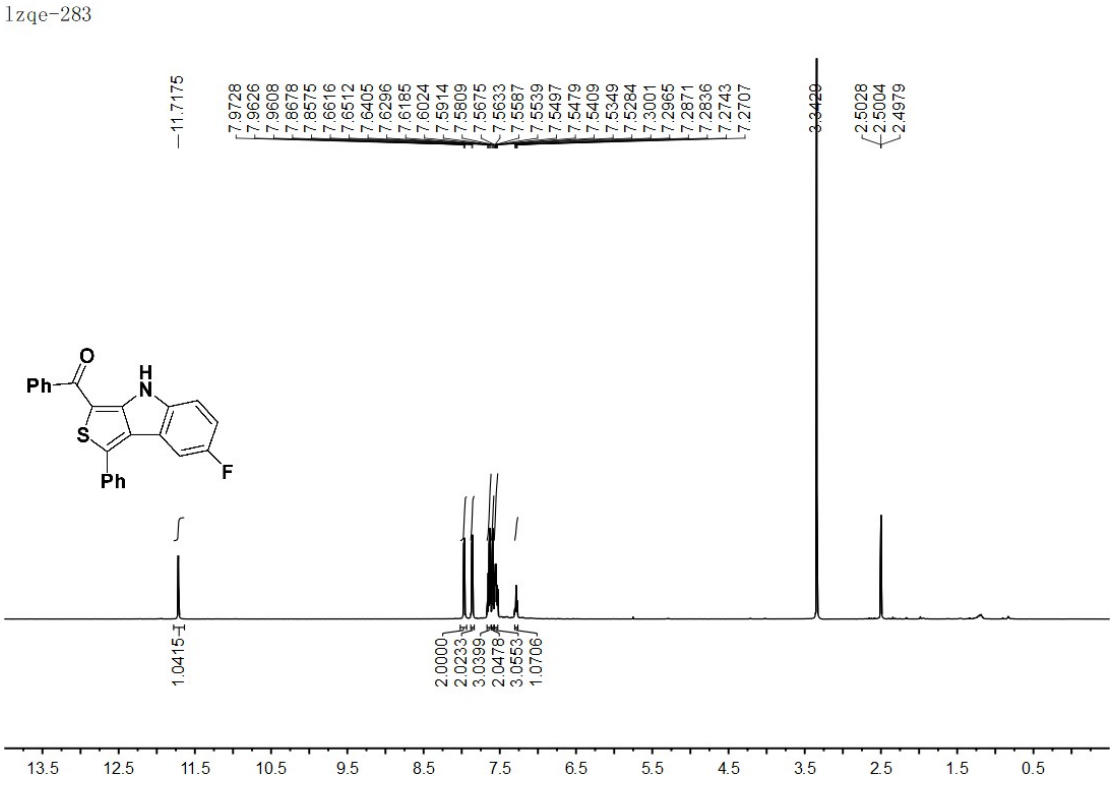


Figure S29. [1]H NMR spectrum of **2o** (d6-DMSO, 400 MHz).

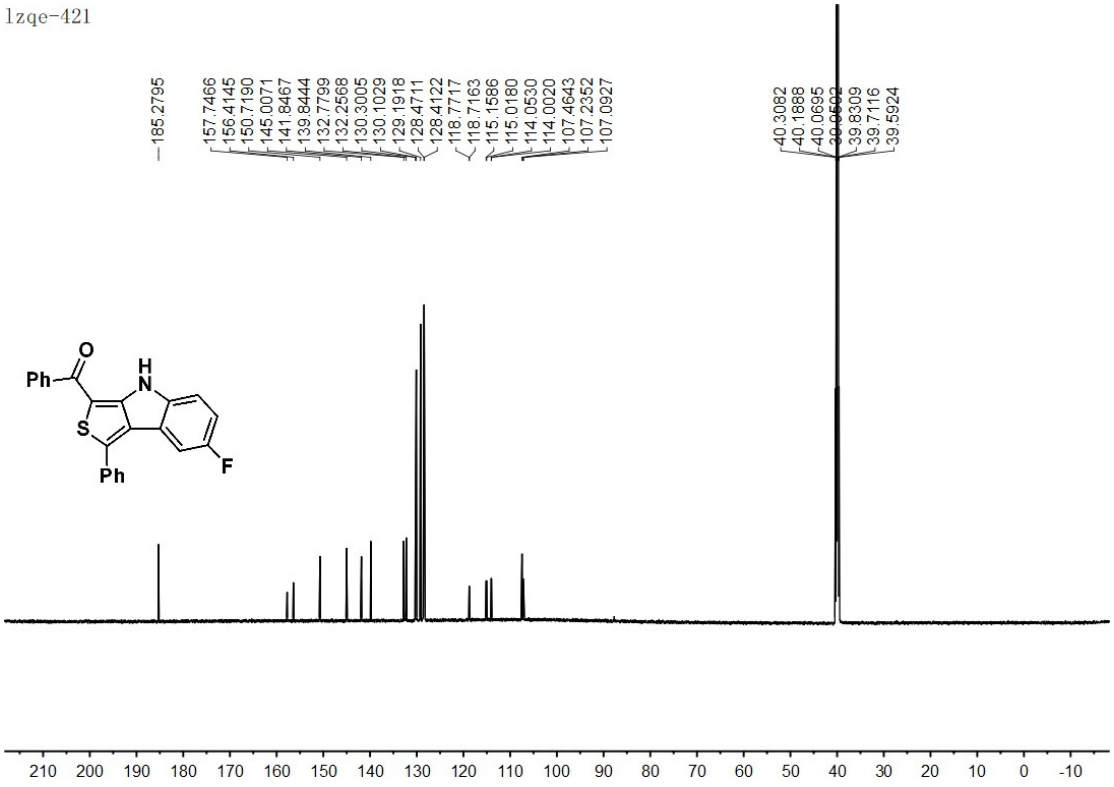


Figure S30. [13]C NMR spectrum of **2o** (d6-DMSO, 100 MHz).

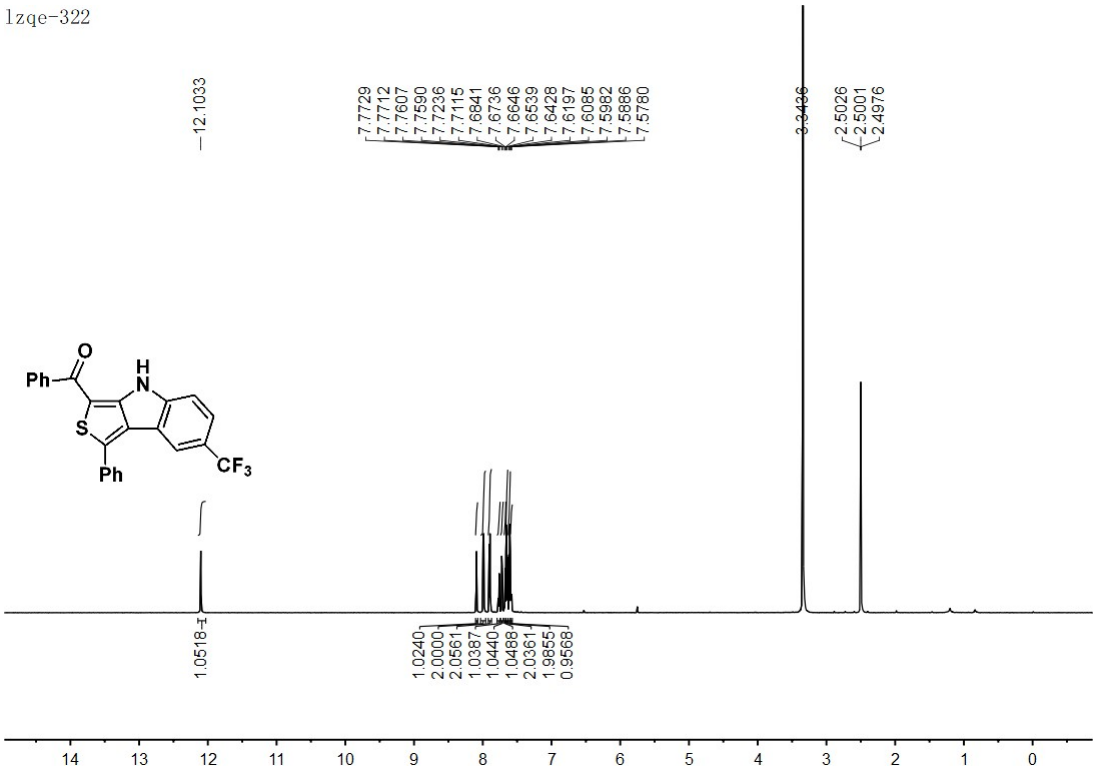


Figure S31. [1]H NMR spectrum of **2p** (d6-DMSO, 400 MHz).

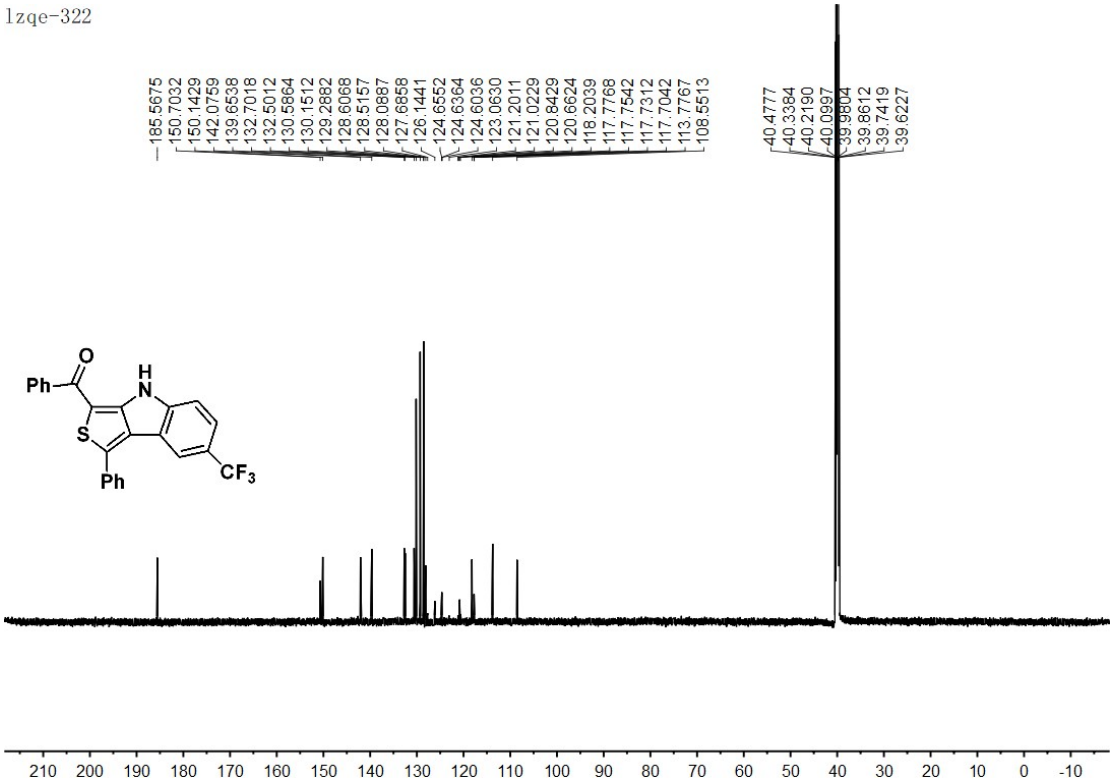


Figure S32. [13]C NMR spectrum of **2p** (d6-DMSO, 100 MHz).

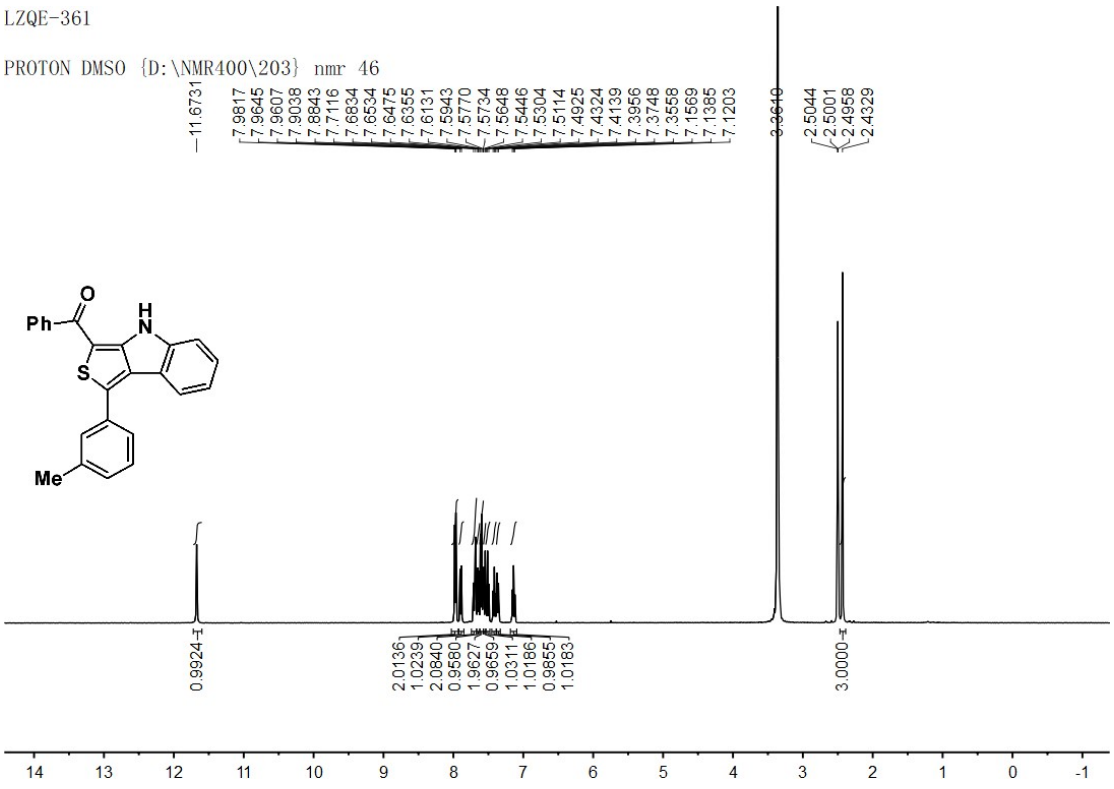


Figure S33. [1]H NMR spectrum of **2r** (d6-DMSO, 400 MHz).

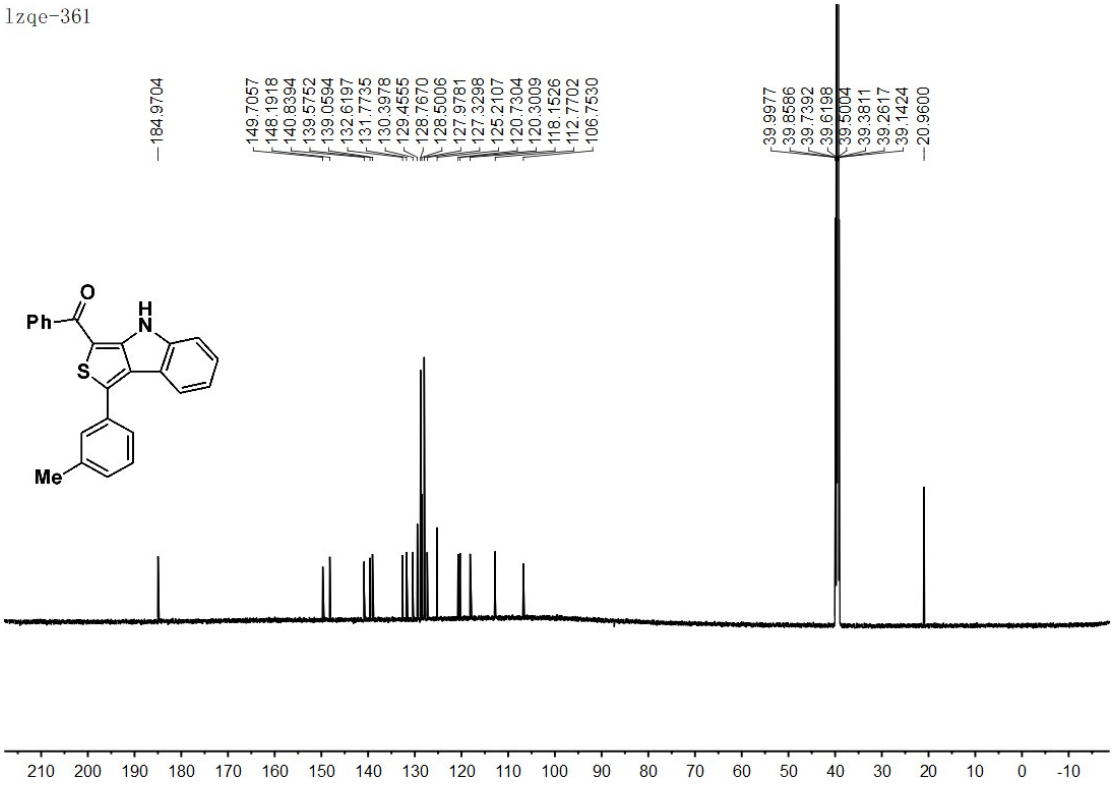


Figure S34. [13]C NMR spectrum of **2r** (d6-DMSO, 100 MHz).

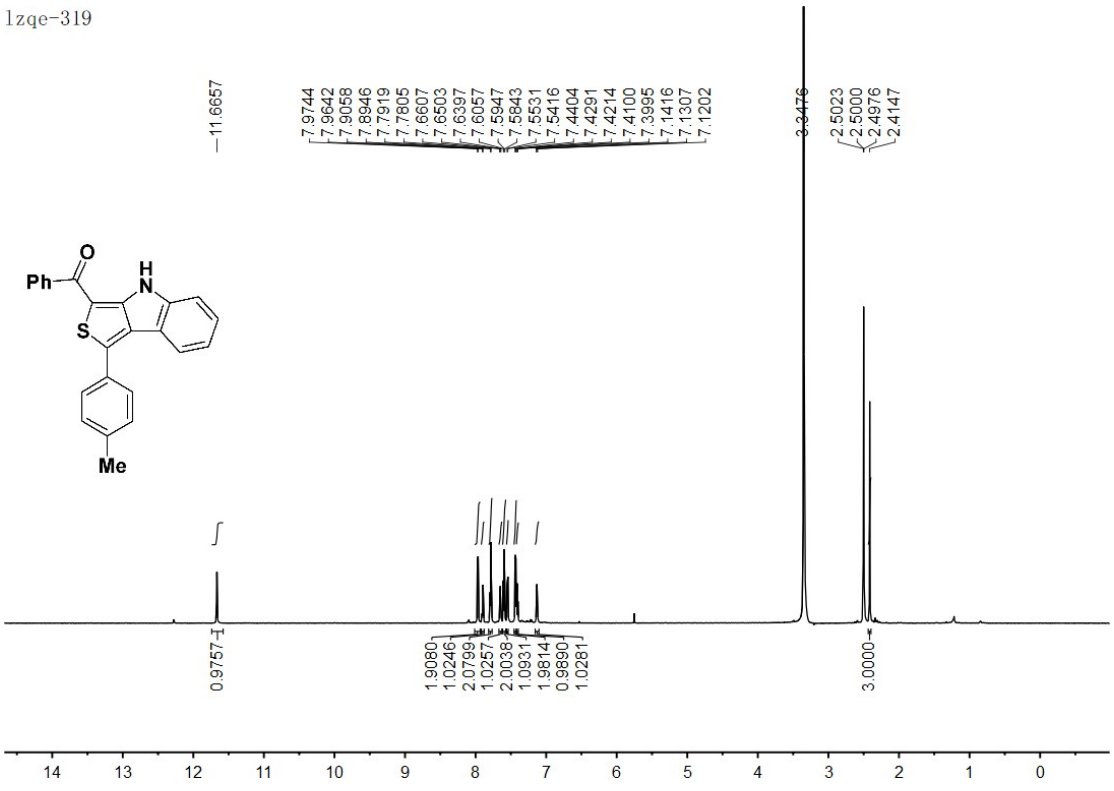


Figure S35. [1]H NMR spectrum of **2s** (d6-DMSO, 400 MHz).

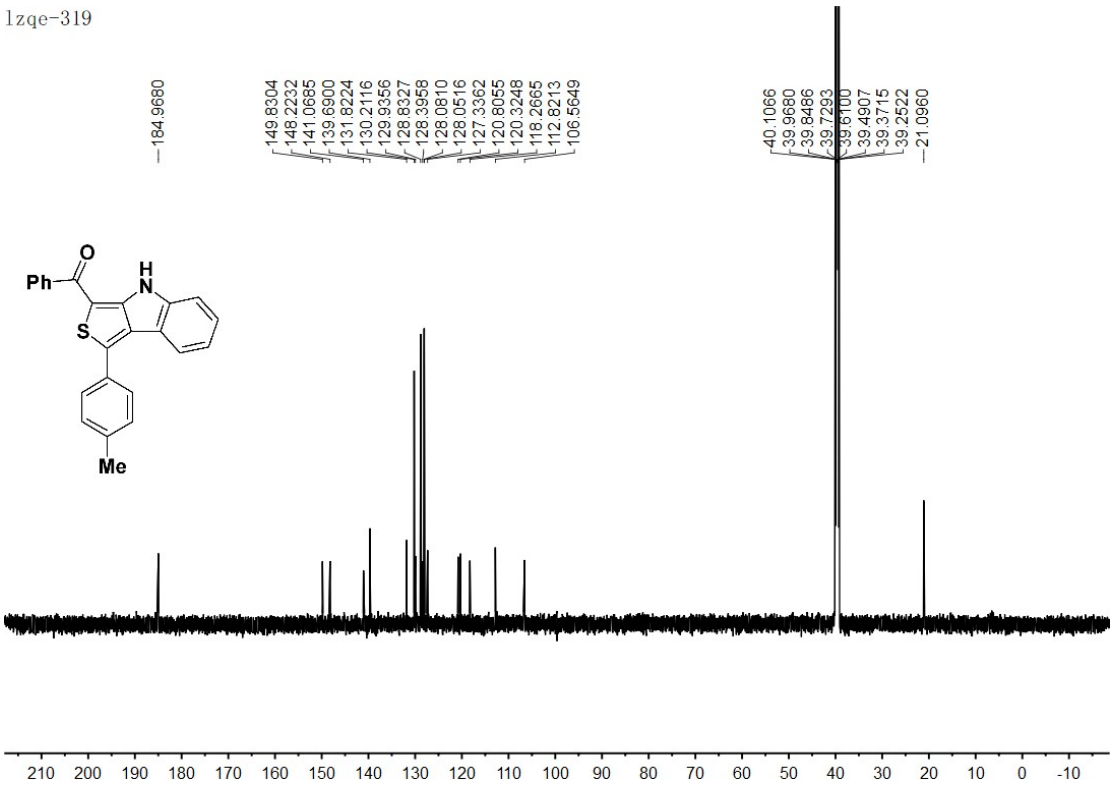


Figure S36. [13]C NMR spectrum of **2s** (d6-DMSO, 100 MHz).

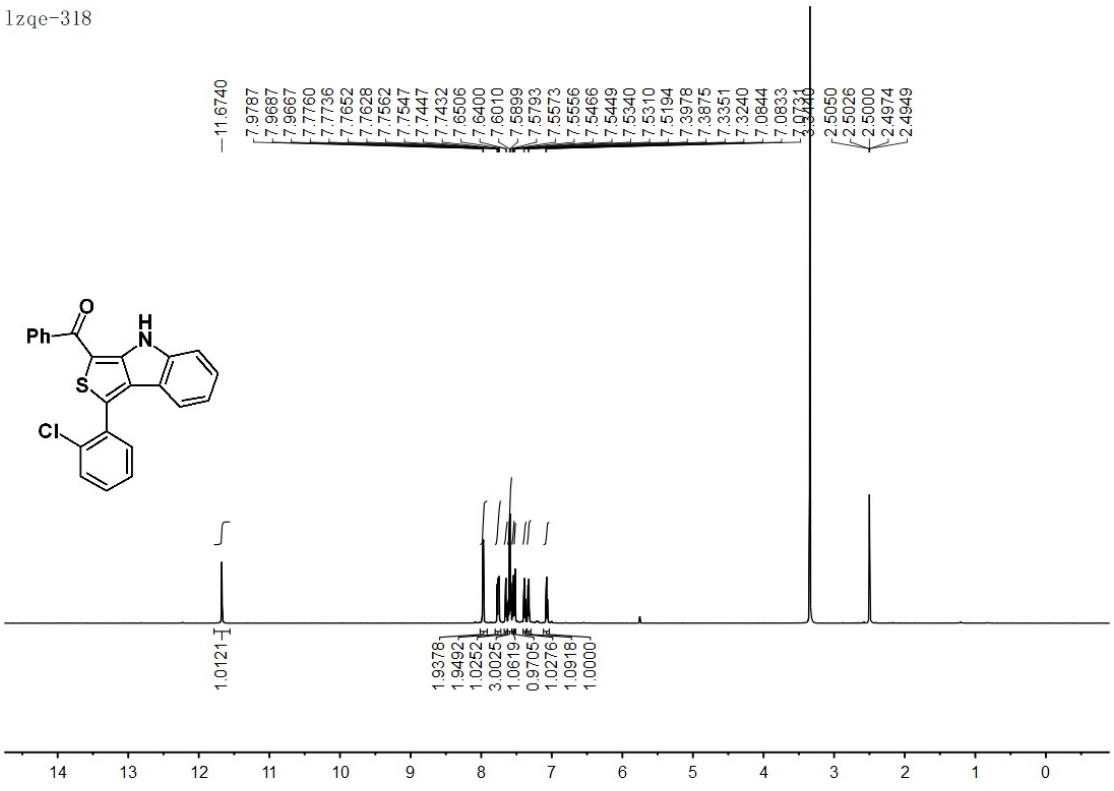


Figure S37. [1]H NMR spectrum of **2t** (d6-DMSO, 400 MHz).

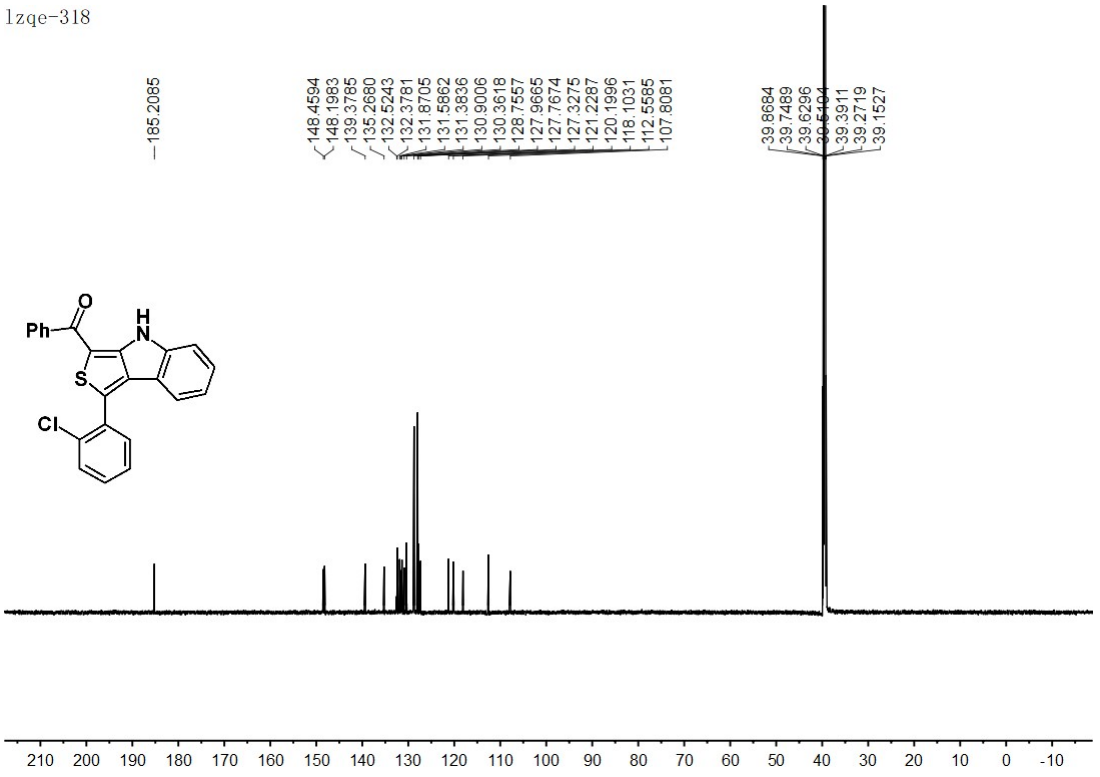


Figure S38. [13]C NMR spectrum of **2t** (d6-DMSO, 100 MHz).

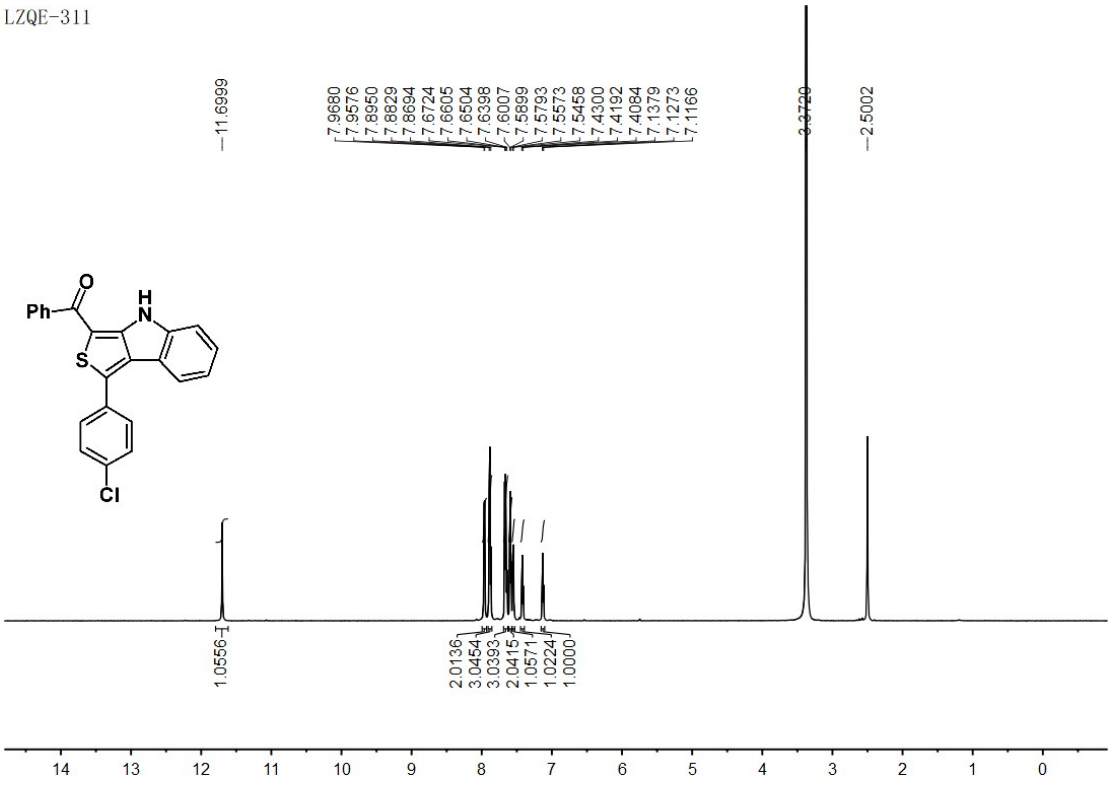


Figure S39. [1]H NMR spectrum of **2u** (d6-DMSO, 400 MHz).

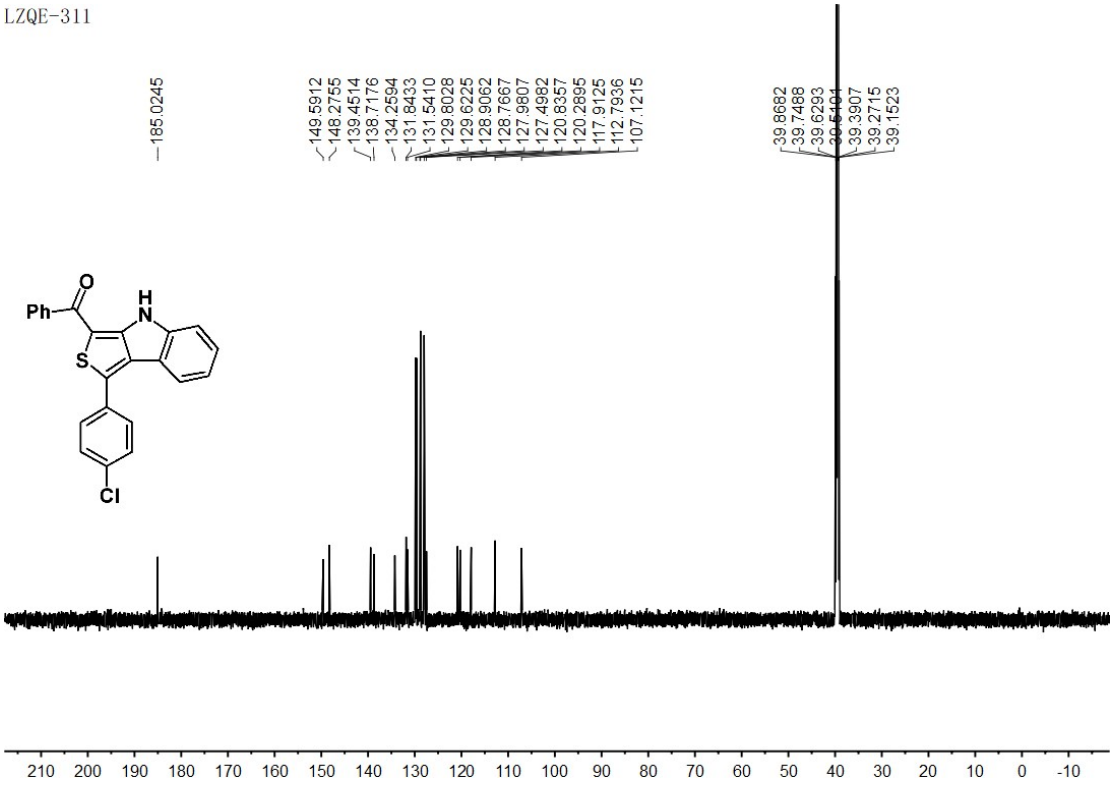


Figure S40. [13]C NMR spectrum of **2u** (d6-DMSO, 100 MHz).

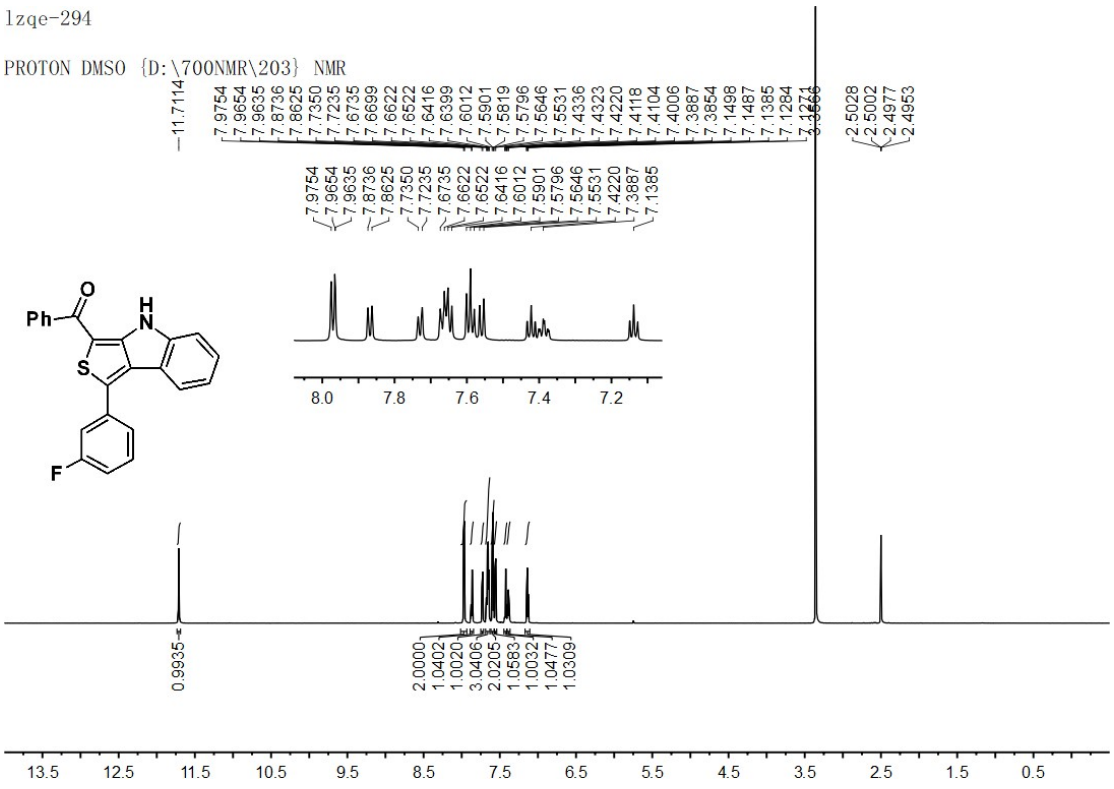


Figure S41. [1]H NMR spectrum of **2v** (d6-DMSO, 400 MHz).

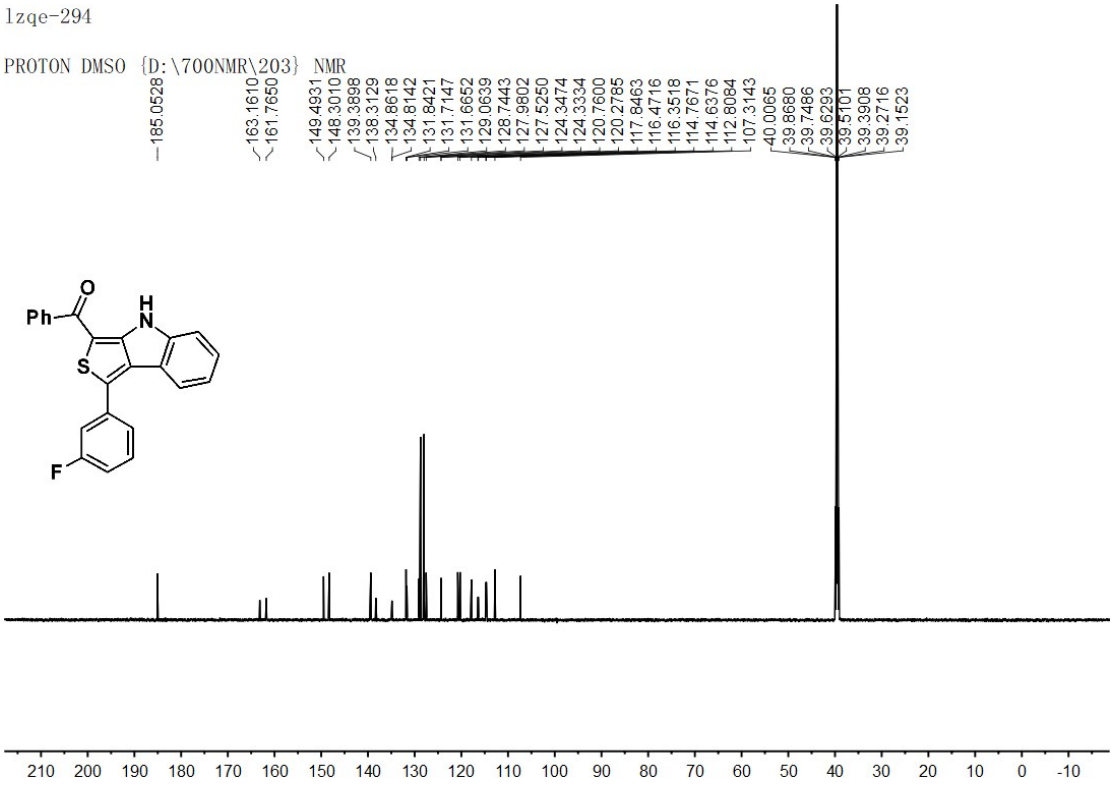


Figure S42. [13]C NMR spectrum of **2v** (d6-DMSO, 100 MHz).

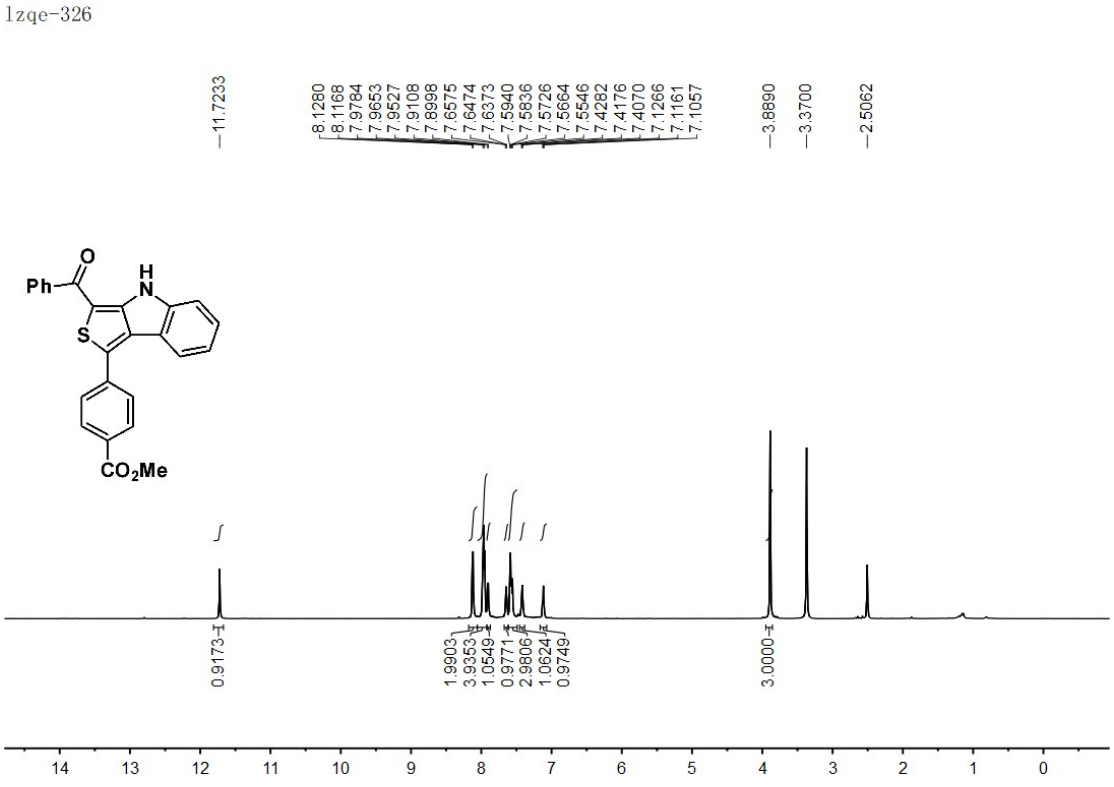


Figure S43. [1]H NMR spectrum of **2w** (d6-DMSO, 400 MHz).

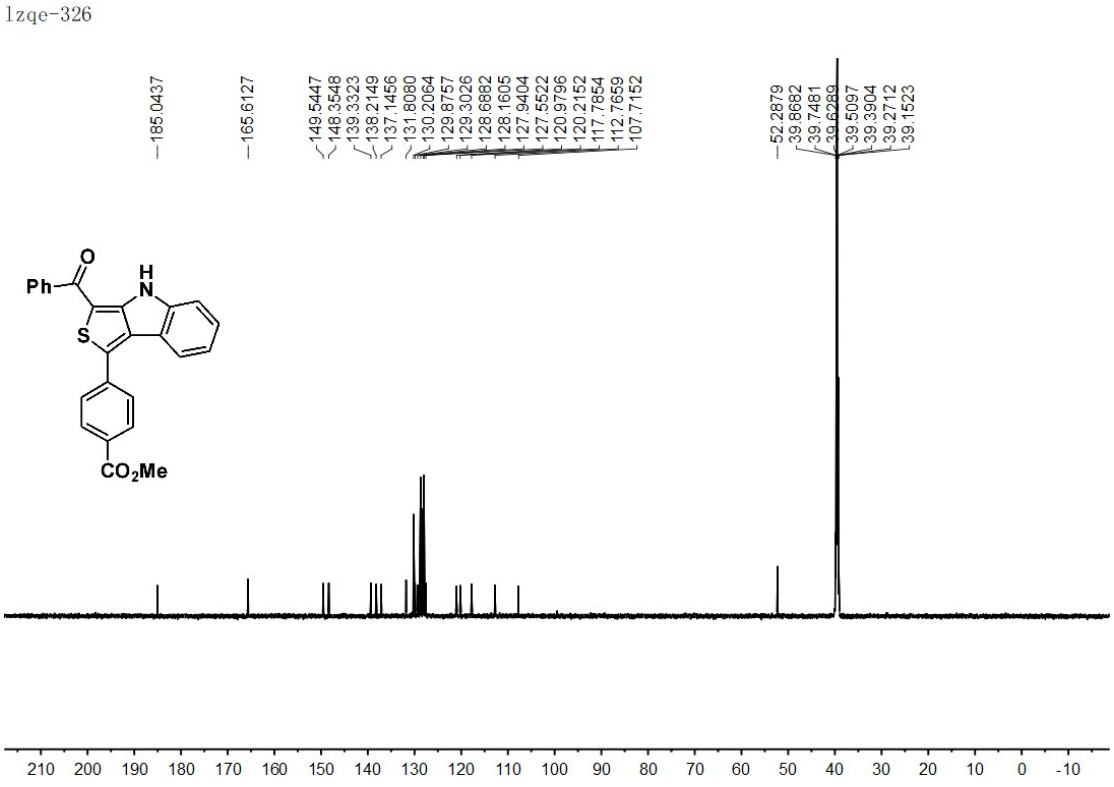


Figure S44. [13]C NMR spectrum of **2w** (d6-DMSO, 100 MHz).

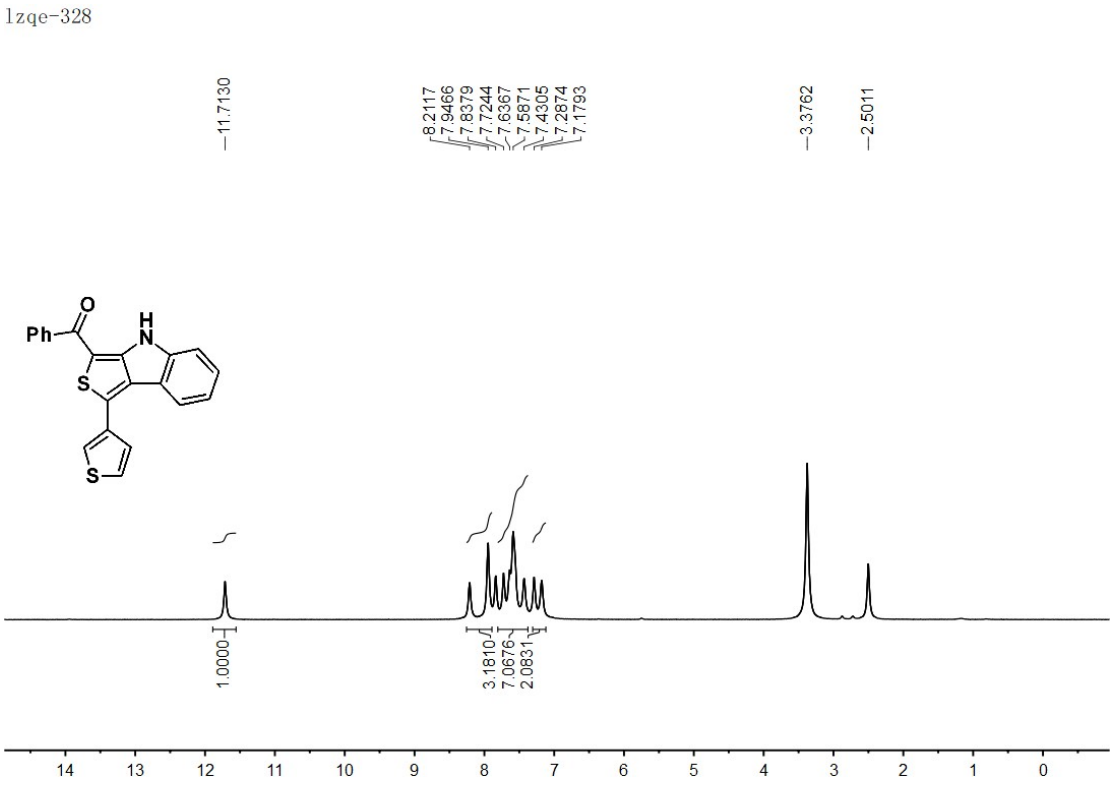


Figure S45. [1]H NMR spectrum of **2x** (d6-DMSO, 400 MHz).

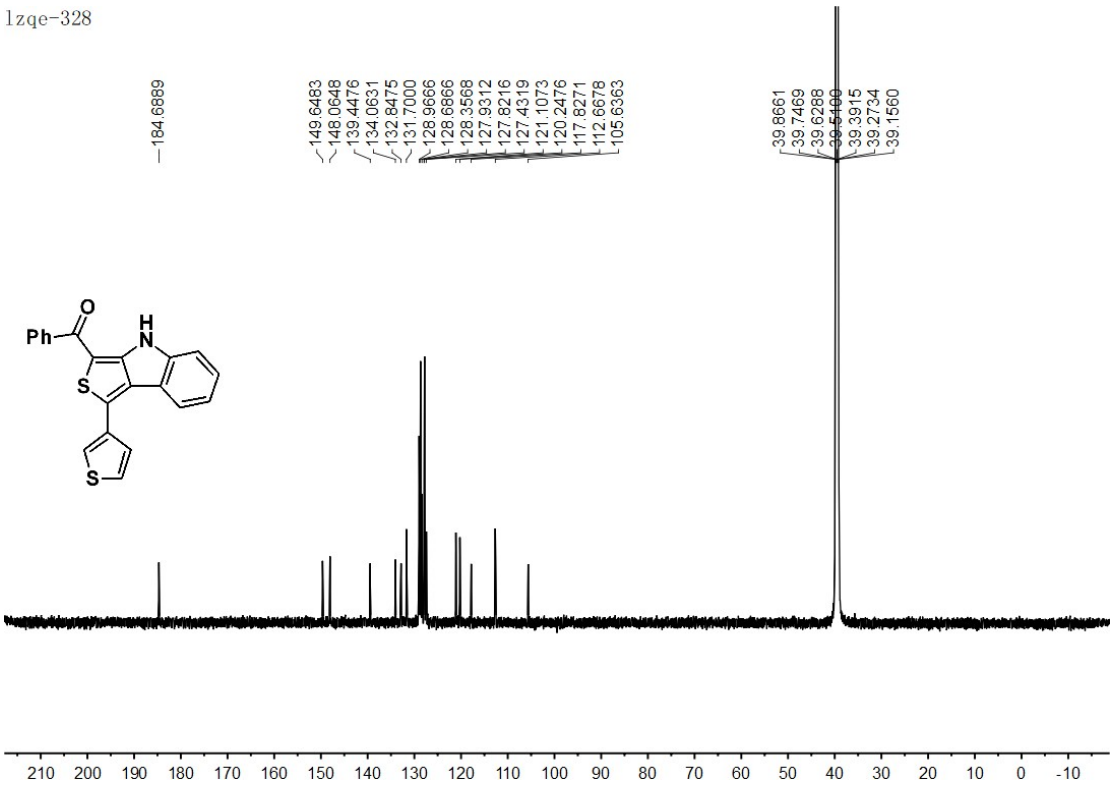


Figure S46. [13]C NMR spectrum of **2x** (d6-DMSO, 100 MHz).

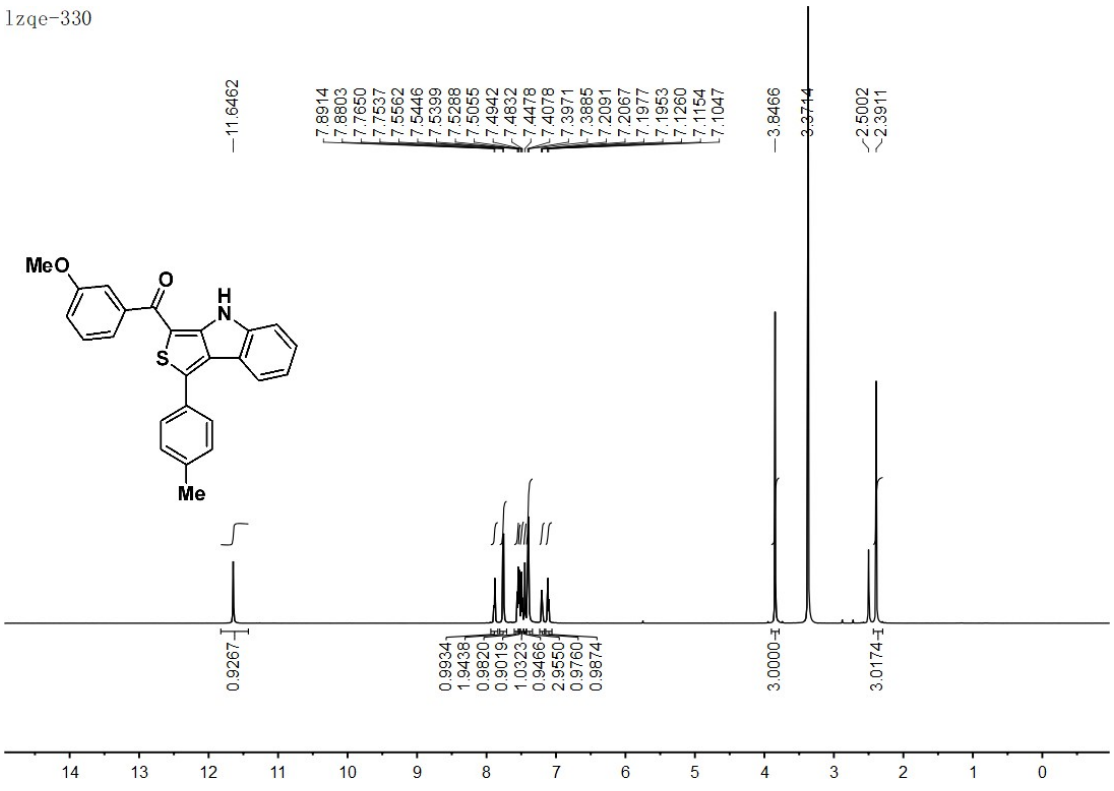


Figure S47. [1]H NMR spectrum of **2y** (d6-DMSO, 400 MHz).

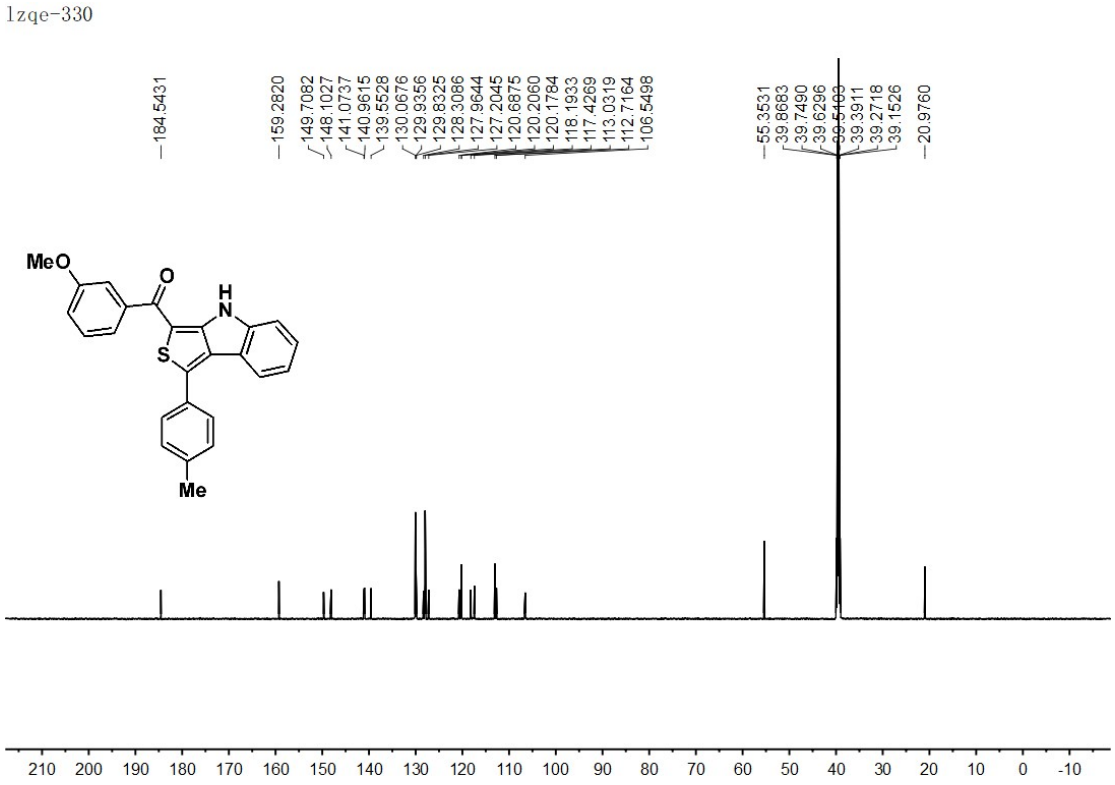


Figure S48. [13]C NMR spectrum of **2y** (d6-DMSO, 100 MHz).

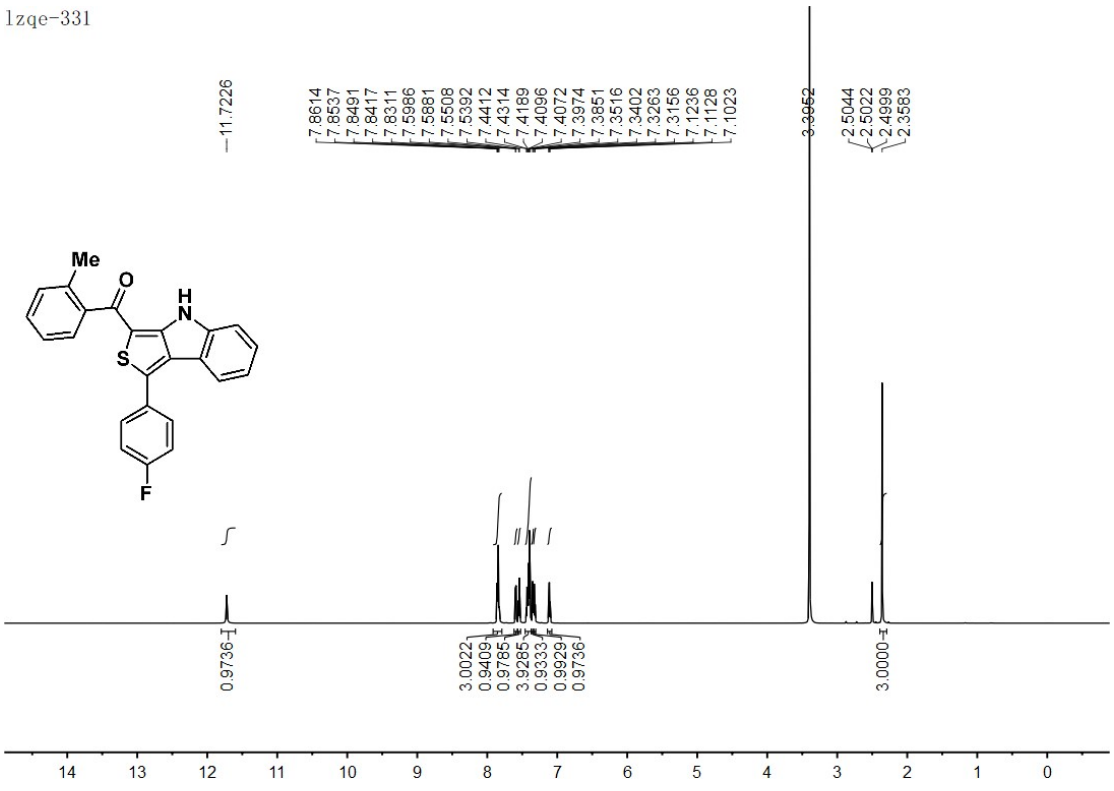


Figure S49. [1]H NMR spectrum of **2z** (d6-DMSO, 400 MHz).

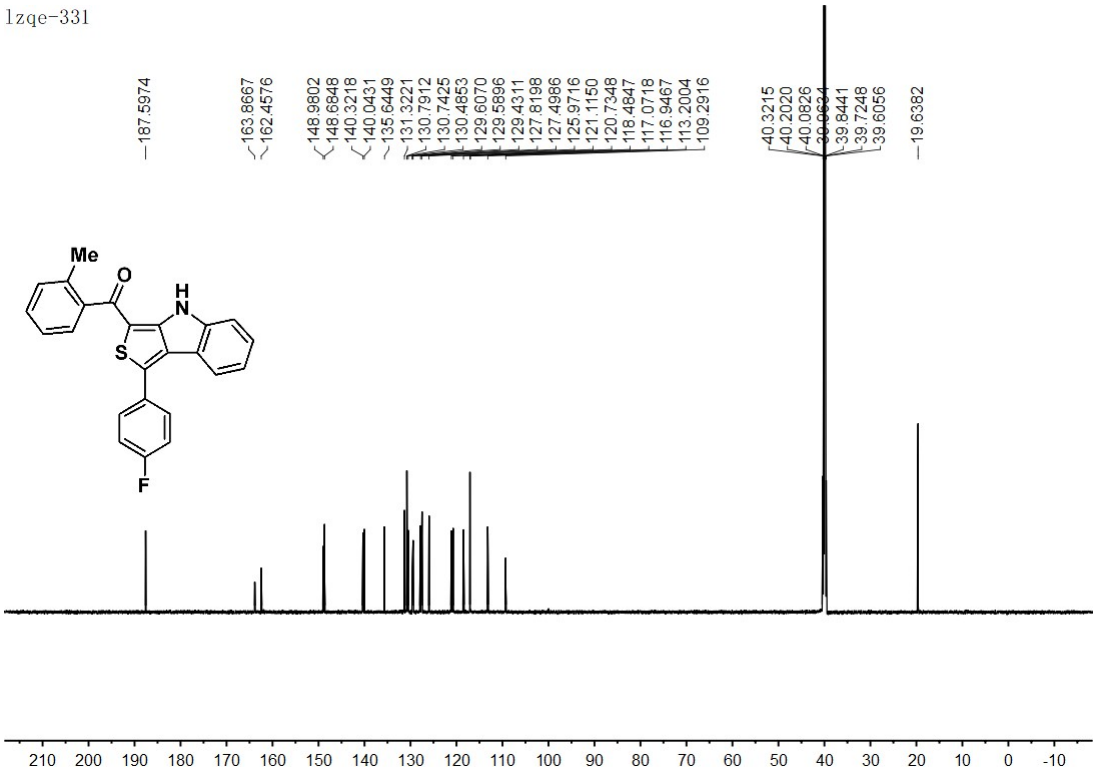


Figure S50. [13]C NMR spectrum of **2z** (d6-DMSO, 100 MHz).