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Article

A Facile Regioselective Synthesis of Novel Spiroacenaphthene Pyrroloisoquinolines Through 1,3-Dipolar Cycloaddition Reactions

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Se descreve um procedimento eficiente de três componentes em uma única operação para a síntese de novas espiroacenafteno pirroloisoquinolinas com alta regiosseletividade. Estes compostos foram preparados pela cicloadição 1,3-dipolar de uma ilida azometínica gerada a partir da acenaftenoquinona e 1,2,3,4-tetraidroisoquinolina, via deslocamento [1,5]-*H*, com derivados de chalcona e nitroestireno como dipolarófilos. A estrutura e estereoquímica dos cicloadutos foram estabelecidas por difração de raios-X em monocristais e por técnicas espectroscópicas.

An efficient one-pot three-component procedure for the synthesis of novel spiroacenaphthene pyrroloisoquinolines with high regioselectivity is described. These compounds were prepared from 1,3-dipolar cycloaddition of an azomethine ylide generated from acenaphthenequinone and 1,2,3,4-tetrahydroisoquinoline via [1,5]-*H* shift, with chalcone and nitrostyrene derivatives as dipolarophiles. The structure and stereochemistry of the cycloadducts have been established by single crystal X-ray structure and spectroscopic techniques.

Keywords: 1,3-dipolar cycloaddition, azomethine ylide, [1,5]-*H* shift, spiroacenaphthene pyrroloisoquinolines

Introduction

1,3-Dipolar cycloaddition reactions are efficient approaches for the construction of five-membered heterocyclic units in a highly regio- and stereoselective manner.[1-5] These strategies permit the construction of complex molecules from easily available starting materials in a single synthetic step. In particular, 1,3-dipolar cycloaddition reaction of azomethine ylides with various dipolarophiles represents an efficient method for the construction of pyrrolidine and pyrrolizidine structural units.[6-13] Among various nitrogen containing heterocycles, spiropyrrolidine and spiropyrrolizidine derivatives have been attracted much interest as they constitute the central skeletons of many alkaloids and pharmacological active compounds.[14-19] Pyrroloisoquinoline and isoquinoline structural units possess important pharmocological properties such as antimicrobial, antitumor and antibiotic.[20,21] The fact that acenaphthenequinone derivatives have strong antioxidant properties,[22-25] including free radical scavenging activity and can reduce lipid peroxidation, motivated us to investigate cycloaddition reactions of azomethine ylides derived from acenaphthenequinone and pharmacologically active isoquinoline moities.

One of the most useful methods to generate a nonstabilized azomethine ylide is the reaction of an amine with a bifunctional carbonyl compound which involved the [1,5]-prototropic shift.[26-32] As part of our ongoing research program directed toward the synthesis of novel spiropyrrolidinyl derivatives,[33-35] we report herein the regio- and stereoselctive synthesis of spiro[acenaphthylene-1,3'-pyrrolo[2,1-*a*]isoquinolin derivatives through 1,3-dipolar cycloaddition reaction of an azomethine ylide generated by reaction of acenaphthenequinone **1** and 1,2,3,4-tetrahydroisoquinoline **2** via [1,5]-*H* shift, with chalcone and nitrostyrene derivatives.

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Experimental

Equipments

All chalcones and nitrostyrenes were prepared according to literature procedures.[36,37] All other reagents and solvents were purchased from commercial suppliers and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) on silica gel. Melting points were measured on an Electrothermal 9100 apparatus. Infrared spectra were recorded on a Shimadzu IR-8300 series FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400-MHz instrument in $CDCl_3$ solvent with TMS as a standard. Mass spectra were recorded on a JEOL DX303 HF mass spectrometer. Elemental analyses were carried out using a Perkin-Elmer CHN 2400 instrument.

X-ray crystallographic analysis

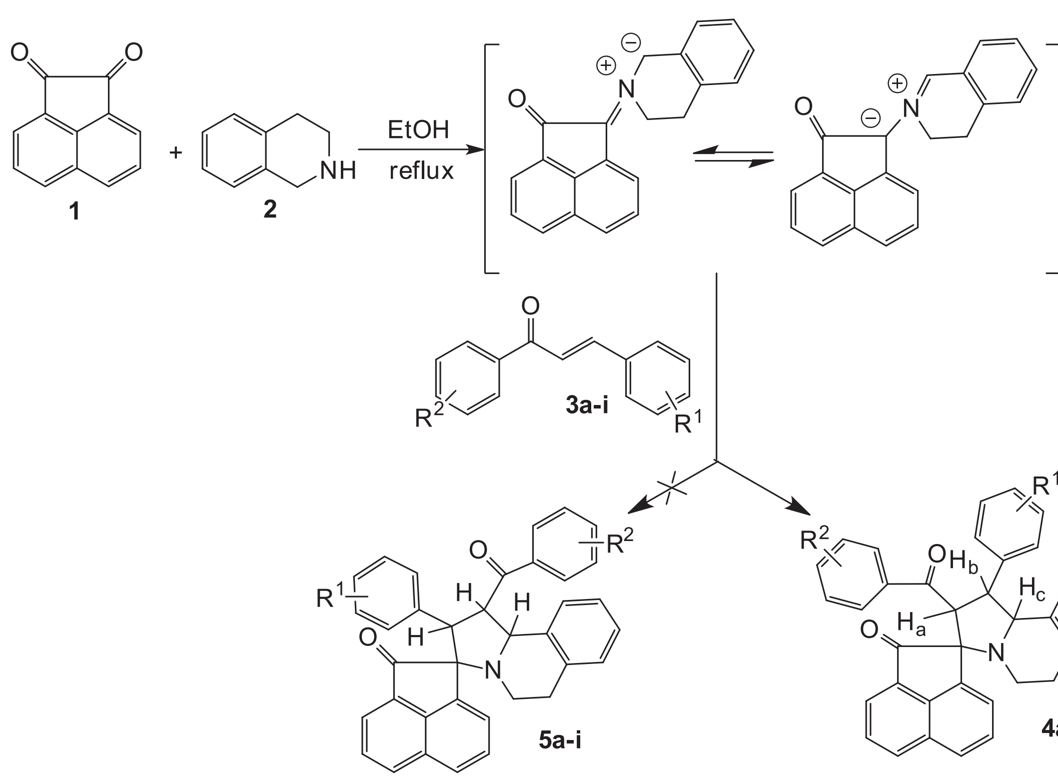
Suitable single crystals of the compounds **4i** and **7f** were selected and the diffraction data were collected using a STOE IPDS II diffractometer with graphite monochromated Mo-K_a radiation (λ = 0.71073 Å), in the rotation method, at room temperature. The structures were solved by using SHELXS.[38] The structure refinement and data reduction were carried out with SHELXL of the X-Step32 suite of programs.[39] The nonhydrogen atoms were refined anisotropically by full matrix least-squares on F^2 values. Hydrogen atoms were located from expected geometry and were not refined. The crystal data are deposited at the Cambridge Crystallographic Data Centre, CCDC 949978 and 949977, for compounds **4i** and **7f**, respectively.

Typical procedure for preparation of spiroacenaphthene pyrroloisoquinoline **4a-l** and **7a-l**

A mixture of acenaphthenequinone (0.182 g, 1 mmol), 1,2,3,4-tetrahydroisoquinoline (0.133 g, 1 mmol) and chalcone (0.208 g, 1 mmol)/nitrostyrene (0.149 g, 1 mmol) in ethanol (8 mL) was stirred at reflux for 4h. After completion of the reaction, as indicated by TLC, the resulting precipitate was filtered and recrystallized from EtOH to afford the pure product in good yield.

Results and discussion

In our initial studies, acenaphthenequinone **1**, 1,2,3,4-tetrahydroisoquinoline **2** and chalcone **3a** were treated at reflux in ethanol to afford the corresponding spiroacenaphthene pyrroloisoquinoline **4a** as sole product in good yield (Scheme 1). After completion of the reaction, as indicated by TLC, the pure cycloadduct was obtained by recrystallization from ethanol.



Scheme 1. Regioselective synthesis of spiropyrroloisoquinolines **4a**-**i**.

We applied this protocol to a series of chalcone derivatives **3a-i** in order to obtain the corresponding spiropyrroloisoquinoline adducts **4a-i** in moderate to good yields. As shown in Table 1, the [3 + 2] cycloaddition of several chalcones having electron-donating substituent and electron-withdrawing groups with non-stabilized azomethine ylide, which were generated through [1,5]-*H* shift, afforded the corresponding cycloadducts with regio- and stereoselective manner.

Table 1. 1,3-Dipolar cycloaddition of chalcones **3a–l** to the *in situ* generated azomethine ylide

entry	Product	R^1	R^2	Yield[a] / %
1	**4a**	H	H	82
2	**4b**	*p*-F	H	78
3	**4c**	*p*-Cl	H	86
4	**4d**	*p*-Br	H	76
5	**4e**	*p*-Me	H	79
6	**4f**	*p*-OMe	H	82
7	**4g**	*p*-NO_2	H	80
8	**4h**	H	*p*-OMe	82
9	**4i**	H	*p*-Cl	83
10	**4j**	H	*m*-Cl	78
11	**4k**	*p*-OMe	*p*-OMe	86
12	**4l**	*p*-Cl	*m*-Cl	76

[a]Isolated yield.

The structure and regiochemistry of the cycloadducts were confirmed by spectroscopic data and X-ray crystal structure analysis (Figure 1).

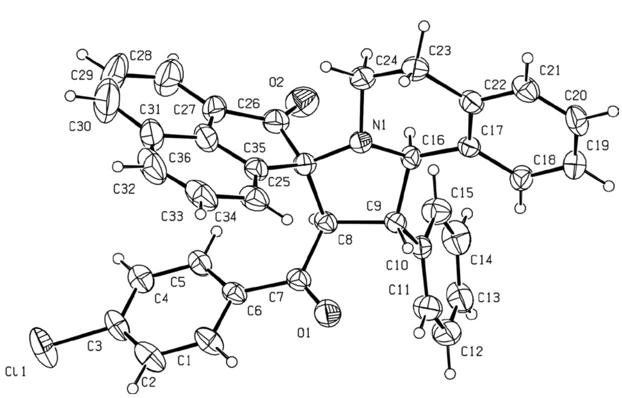


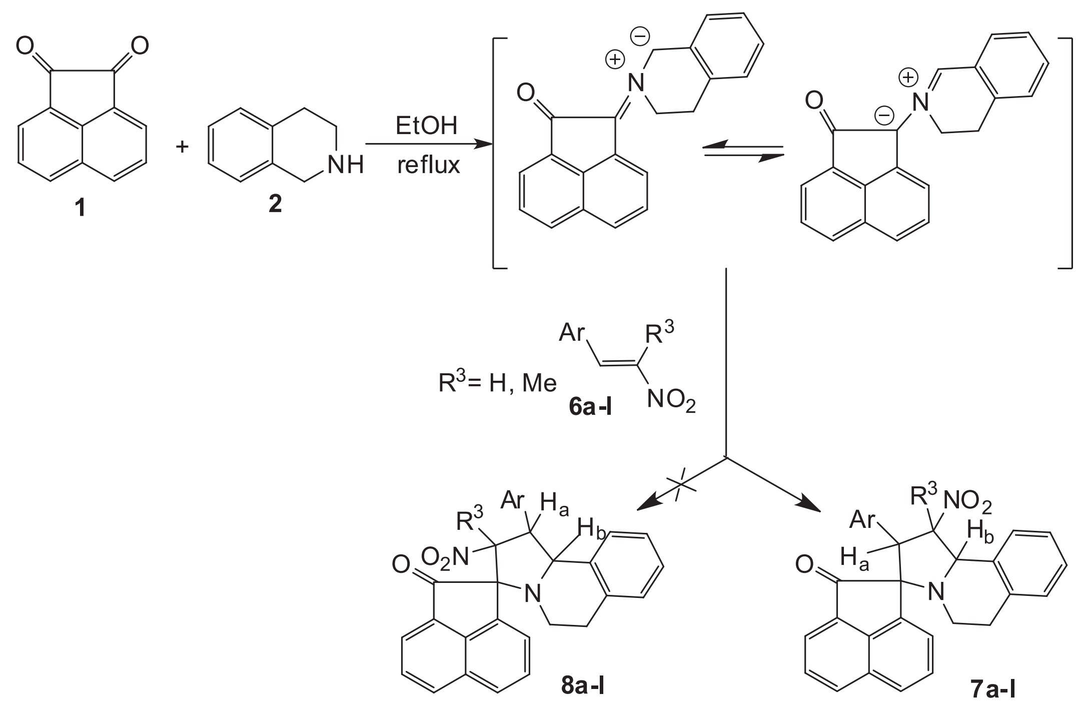
Figure 1. ORTEP diagram of **4i**.

Information concerning to the crystallographic data collection and refinement of the structures are given in Table 2.

The ^1H NMR spectrum of **4b** exhibited two doublets at δ 5.43 (*J* 9.6 Hz) and 4.62 (*J* 9.6 Hz) for the H_c and H_a protons, respectively, and a triplet at 4.55 ppm (*J* 10.8 Hz) for H_b. The ^{13}C NMR of **4b** showed two signals at δ 209.3 and 196.7 ppm for carbonyl groups and a signal at 74.7 ppm for the spiro carbon. The IR spectrum of **4b** showed two sharp peaks at 1708 cm^{-1} and 1681 cm^{-1} for the carbonyl groups and in addition, the appearance of a molecular ion peak at *m/z* 523 (M+) confirmed the formation of the

Table 2. Crystal data and structure refinement of compounds **4i** and **7f**

	4i	**7f**
Empirical formula	$C_{36}H_{26}ClNO_2$	$C_{30}H_{24}N_2O_4$
Formula weight	540.03	476.51
Color	Yellow plate	Yellow plate
Temperature / K	298(2)	298(2)
Wavelength / Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*P*i	*P21/c*
Unit cell dimensions		
a / Å	9.296(4)	15.6575(17)
b / Å	17.754(7)	14.2478(13)
c / Å	16.988(7)	11.3666(11)
α / degree	89.54(3)	90.00
β / degree	99.64(3)	109.676(8)
γ / degree	90.25(3)	90.00
Volume / $Å^3$	2764.1(19)	2387.7(4)
Z	4	4
Density (calc.) / (mg m^{-3})	1.298	1.326
μ / mm^{-1}	0.173	0.089
F(000)	1128	1000
Crystal size / mm^3	0.5 × 0.3 × 0.09	0.38 × 0.20 × 0.12
Theta range / degree	2.43 to 29.32	29.24 to 0.991
Index ranges	–10≤ h ≤ 12, –24≤ k ≤ 21, –23≤ l ≤ 23	–21≤ h ≤ 21, –19≤ k ≤ 19, –15≤ l ≤ 15
Reflections collected	29325	54018
Independent reflections	7467	6445
Refinement method	Full matrix least-squares on F^2	Full matrix least-squares on F^2
Data / restraints / parameters	3322 / 0 / 361	3741 / 0 / 325
Goodness-of-fit on F	1.139	1.114
Final R indices [I > 2sigma(I)]	R_1 = 0.1502, wR_2 = 0.2203	R_1 = 0.0874, wR_2 = 0.1379
R indices (all data)	R_1 = 0.2640, wR_2 = 0.2656	R_1 = 0.1534, wR_2 = 0.1589
Extinction coefficient	None	None
Largest diff. peak and hole / (e $Å^{-3}$)	0.301 and –0.348	0.186 and –0.188



Scheme 2. Regioselective synthesis of spiropyrroloisoquinolines **7a-l**.

cycloadduct. The stereochemistry of compound **4i** was established by X-ray single crystal analysis (Figure 1).

In order to further expand the scope of this protocol for spiro-heterocyclic synthesis, we investigated reactions involving acenaphthenequinone **1**, 1,2,3,4-tetrahydroisoquinoline **2** and nitrostyrene derivatives **6a-l** and a new series of spiropyrroloisoquinoline adducts **7a-l** were obtained in good yields (Scheme 2, Table 3).

From Table 3, it is evident that the rate of the reaction and the yields of the cycloadducts are similar when nitrostyrene derivatives were employed as dipolarophiles instead of acenaphthenequinones. The structure of the final products was elucidated through X-ray crystal structure analysis in addition to standard IR, ^{1}H and ^{13}C NMR techniques. The IR spectrum of **7a** showed a sharp peak at 1708 cm^{-1} for the carbonyl group and two peaks corresponding to NO_2 at 1553 and 1366 cm^{-1}. The ^{1}H NMR spectrum of **7a** exhibited two doublets at δ 5.99 (*J* 7.0 Hz) and 4.78 (*J* 4.8 Hz) for the H_b and H_a protons, respectively, and a doublet of doublet at 6.27 ppm (*J* 7.0, 4.8 Hz) for H (R^3). The ^{13}C NMR spectrum of **7a** showed a peak at δ 79 ppm reflecting the presence of the spiro carbon and the acenaphthenequinone carbonyl carbon exhibited a peak at δ 206.3. The mass spectrum of the compound confirmed the formation of cycloadduct. Finally, the regio- and stereochemical outcome of the cycloaddition reaction was obviously confirmed through the X-ray diffraction analysis of **7f** (Figure 2).

The proposed mechanism of the cycloaddition reactions is shown in Scheme 3. For this 1,3-dipolar cycloaddition reaction, four reactive channels are possible. They are related to two regioisomeric and two stereoisomeric approaches. The stereochemistry of the observed products is consistent with expected preference of an *S*-shaped ylide and subsequent cycloaddition through an *endo* transition state.

The endo-control is presumably determined by stabilizing secondary orbital interactions.

There is no evidence in spectroscopic data for the formation of the other regioisomer arising from the reactions.

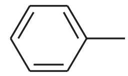
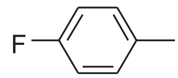
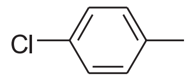
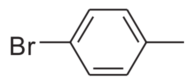
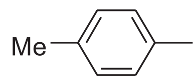
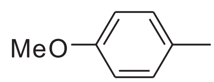
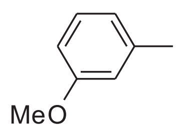
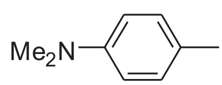
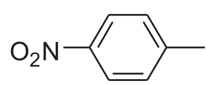
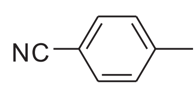
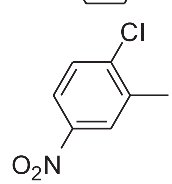
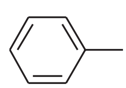
Conclusions

In summary, we have demonstrated a multicomponent 1,3-dipolar cycloaddition which gives an array of containing spiroacenaphthene pyrroloisoquinolines using chalcone and nitrostyrene derivatives as dipolarophiles. The products were isolated by recrystallization without involving further purification process like column chromatography.

Supplementary Information

Crystallographic data (**4i** and **7f**) for the structures in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication

Table 3. 1,3-Dipolar cycloaddition of nitrostyrenes **6a–l** to the *in situ* generated azomethine ylide

entry	Product	Ar	R^3	Yield[a] / %
1	**7a**		H	83
2	**7b**		H	81
3	**7c**		H	76
4	**7d**		H	78
5	**7e**		H	78
6	**7f**		H	81
7	**7g**		H	78
8	**7h**		H	81
9	**7i**		H	78
10	**7j**		H	82
11	**7k**		H	80
12	**7l**		Me	80

[a]Isolated yield.

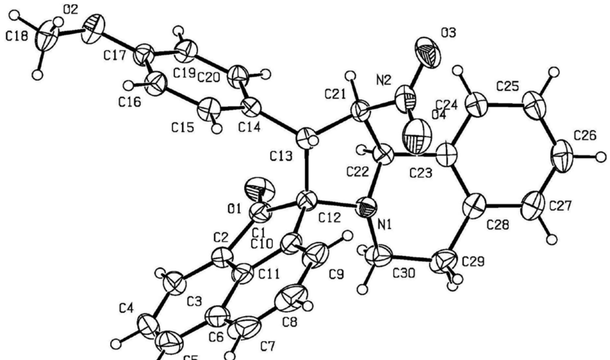


Figure 2. ORTEP diagram of **7f**.

number CCDC 949978 and 949977 respectively. Copies of the data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. E-mail: deposit@ccdc.cam.ac.uk. Supplementary information (Table S1-S10, Figure S1-S85) is available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgment

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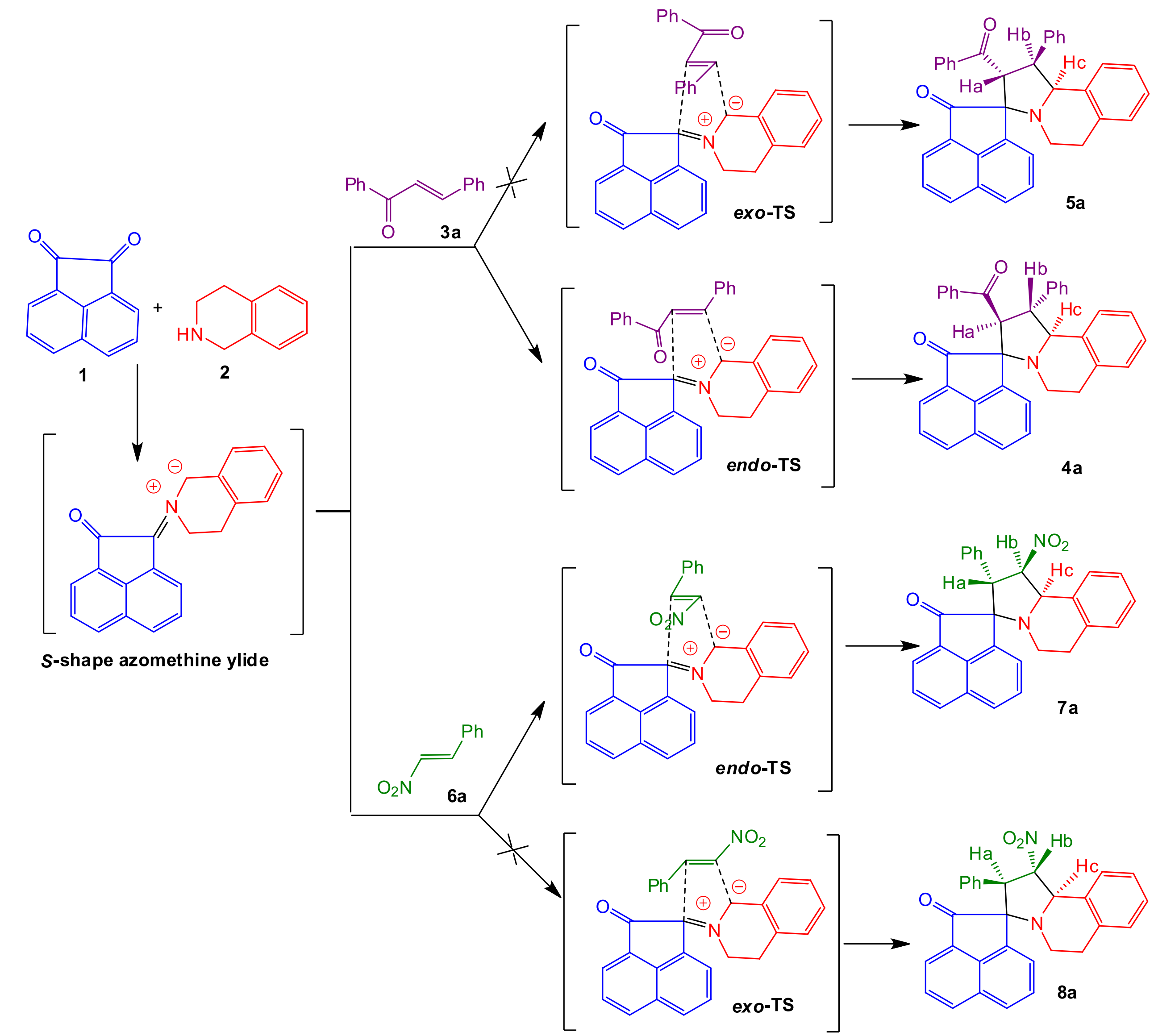

Scheme 3. Proposed mechanism of the cycloaddition of the azomethine ylide with chalcone and nitrostyrene.

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Supplementary Information

A Facile Regioselective Synthesis of Novel Spiroacenaphthene Pyrroloisoquinolines Through 1,3-Dipolar Cycloaddition Reactions

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Characterization data for representative compounds

2'-Benzoyl-1'-phenyl-2',5',6',10b'-tetrahydro-1'H,2H-spiro[acenaphthylene-1,3'-pyrrolo[2,1-a]isoquinolin]-2-one (**4a**)

Yellow solid (0.366 g, 82%); m.p. 183-185 °C; IR (KBr) ν_{max}/cm^{-1} 1713, 1681; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-6.72 (m, 20H, Ar-H), 5.37 (d, 1H, *J* 9.6 Hz, H_c), 4.62 (d, 1H, *J* 9.2 Hz, H_a), 4.48 (t, 1H, *J* 9.6 Hz, H_b), 2.98-2.89 (m, 2H), 2.66-2.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 197.3, 142.5, 140.3, 138.2, 137.2, 136.9, 134.7, 132.0, 131.9, 131.7, 129.8, 129.1, 129.1, 128.8, 128.7, 127.8, 127.4, 127.2, 126.9, 126.3, 125.5, 125.1, 124.7, 123.5, 120.7, 74.7 (C-Spiro), 64.3, 63.8, 50.9, 42.5, 30.4; anal. calcd. for $C_{36}H_{27}NO_2$: C, 85.52; H, 5.38; N, 2.77; found: C, 85.1; H, 5.05; N, 2.35; MS (*m/z*): 505.

2'-Benzoyl-1'-(4-fluorophenyl)-2',5',6',10b'-tetrahydro-1'H,2H-spiro[acenaphthylene-1,3'-pyrrolo[2,1-a]isoquinolin]-2-one (**4b**)

Orange solid (0.408 g, 78%); m.p. 230-232 °C; FT-IR (KBr) ν_{max}/cm^{-1} 1708, 1681; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.132-6.61 (m, 19H, Ar-H), 5.43 (d, 1H, *J* 9.6 Hz, H_c), 4.62 (d, 1H, *J* 9.6 Hz, H_a), 4.55 (t, 1H, *J* 10.8 Hz, H_b), 2.96-2.89 (m, 2H), 2.67-2.62 (m, 1H), 2.56-2.48 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 196.7, 150.4, 147.1, 142.6, 137.4, 136.6, 136.5, 134.8, 132.3, 132.2, 131.4, 130.0, 129.8, 129.1, 128.7, 127.9, 127.5, 127.1, 126.7, 125.6, 125.0, 124.7, 124.4, 123.4, 121.1, 74.7 (C-Spiro), 64.4, 63.6, 50.8, 42.5, 30.4; anal. calcd. for $C_{36}H_{26}FNO_2$: C, 82.58; H, 5.01; N, 2.68; found: C, 82.15; H, 4.85; N, 2.35; MS (*m/z*): 523.

2'-Benzoyl-1'-(4-chlorophenyl)-2',5',6',10b'-tetrahydro-1'H,2H-spiro[acenaphthylene-1,3'-pyrrolo[2,1-a]isoquinolin]-2-one (**4c**)

Yellow solid (0.463 g, 86%); m.p. 199-201°C; FT-IR (KBr) ν_{max}/cm^{-1} 1708, 1682; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-6.76 (m, 19H, Ar-H), 5.98 (d, 1H, *J* 8.8 Hz, H_c), 5.33 (dd, 1H, *J* 7.2, 8.4 Hz, H_b), 4.42 (d, 1H, *J* 7.2 Hz, H_a), 3.20-3.12 (m, 1H), 2.81-2.72 (m, 2H), 2.64-2.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.2, 202.3, 142.7, 138.8, 138.4, 136.0, 135.0, 134.9, 133.0, 132.9, 132.3, 131.5, 130.3, 130.2, 129.2, 129.0, 128.6, 128.4, 128.3, 128.2, 127.4, 127.1, 125.9, 125.2, 121.1, 120.4, 80.0 (C-Spiro), 64.5, 59.9, 52.9, 43.1, 30.3; anal. calcd. for $C_{36}H_{26}ClNO_2$: C, 80.06; H, 4.85; N, 2.59; found: C, 80.56; H, 5.24; N, 2.14; MS (*m/z*): 540.

2'-Benzoyl-1'-(4-bromophenyl)-2',5',6',10b'-tetrahydro-1'H,2H-spiro[acenaphthylene-1,3'-pyrrolo[2,1-a]isoquinolin]-2-one (**4d**)

Yellow solid (0.443 g, 76%); m.p. 194-196 °C; FT-IR (KBr) ν_{max}/cm^{-1} 1705, 1684. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.06-6.74 (m, 19H, Ar-H), 5.96 (d, 1H, *J* 8.4 Hz, H_c), 5.32 (dd, 1H, *J* 7.2, 7.2 Hz, H_b), 4.38 (d, 1H, *J* 7.2 Hz, H_a), 3.19-3.11 (m, 1H), 2.78-2.71 (m, 2H), 2.64-2.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.2, 202.3, 142.7, 138.8, 138.4, 136.0, 135.6, 135.4, 135.0, 132.9, 132.3, 131.5, 131.3, 130.5, 130.2, 129.2, 129.0, 128.6, 128.3, 128.2, 127.8, 125.9, 125.2, 121.2, 121.1, 120.5, 79.9 (C-Spiro), 64.5, 59.9, 52.8, 43.0, 30.3. anal. calcd. for $C_{36}H_{26}BrNO_2$: C, 73.98; H, 4.48; N, 2.40; found: C, 73.62; H, 4.73; N, 2.05; MS (*m/z*): 583.

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2’-Benzoyl-1’-(4-methylphenyl)-2’,5’,6’,10b’-tetrahydro-1’H,2H-spiro[acenaphthylene -1,3’-pyrrolo[2,1-a] isoquinolin]-2-one (**4e**)

Yellow solid (0.410 g, 79%); m.p. 191-193 °C; FT-IR (KBr) ν_{max}/cm^{-1} 1700, 1682; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 8.12-6.65 (m, 19H, Ar-H), 5.16 (d, 1H, *J* 8.0 Hz, H$_c$), 4.51 (d, 1H, *J* 8.0 H$_a$), 4.21 (t, 1H, *J* 10 Hz, H$_b$), 2.75-2.69 (m, 2H), 2.61-2.58 (m, 1H), 2.35-2.33 (m, 1H), 2.31 (s, 3H, Me); ^{13}C NMR (100 MHz, CDCl$_3$) δ 208.8, 197.3, 142.4, 139.3, 138.2, 136.7, 136.6, 136.6, 135.9, 133.1, 132.9, 131.2, 130.3, 129.9, 129.4, 129.1, 128.8, 128.3, 127.24, 126.9, 125.8, 125.6, 124.8, 123.4, 121.6, 74.4 (C-Spiro), 64.3, 63.2, 50.9, 42.7, 30.2, 21.2; anal. calcd. for $C_{37}H_{29}NO_2$: C, 85.52; H, 5.63; N, 2.70; found: C, 85.24; H, 5.23; N, 2.35; MS (*m/z*): 519.

2’-Benzoyl-1’-(4-methoxyphenyl)-2’,5’,6’,10b’-tetrahydro-1’H,2H-spiro[acenaphthylene-1,3’-pyrrolo[2,1-a] isoquinolin]-2-one (**4f**)

Yellow solid (0.439 g, 82%); m.p. 192-194 °C; FT-IR (KBr) ν_{max}/cm^{-1} 1708, 1686; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.03-6.52 (m, 19H, Ar-H), 5.97 (d, 1H, *J* 8.4 Hz, H$_c$), 5.32 (dd, 1H, *J* 7.2, 8.4 Hz, H$_b$), 4.38 (d, 1H, *J* 6.8 Hz, H$_a$), 3.63 (s, 3H, OMe), 3.21-3.13 (m, 1H), 2.82-2.71 (m, 2H), 2.64-2.60 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 207.7, 202.6, 158.5, 142.7, 139.0, 136.4, 135.0, 132.7, 132.5, 131.2, 130.2, 129.9, 129.2, 129.0, 128.5, 128.4, 128.2, 128.1, 125.9, 125.8, 125.2, 125.0, 121.0, 120.2, 113.5, 80.1(C-Spiro), 64.4, 60.2, 55.0, 53.2, 43.1, 30.3; anal. calcd. for $C_{37}H_{29}NO_3$: C, 82.97; H, 5.46; N, 2.61; found: C, 82.63; H, 4.67; N, 2.85; MS (*m/z*): 536.

2’-Benzoyl-1’-(4-nitrophenyl)-2’,5’,6’,10b’-tetrahydro-1’H,2H-spiro[acenaphthylene-1,3’-pyrrolo[2,1-a] isoquinolin]-2-one (**4g**)

Yellow solid (0.440 g, 80%); m.p. 201-202 °C; FT-IR (KBr) ν_{max}/cm^{-1} 1707, 1681, 1510 and 1374; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.93-6.73 (m, 19H, Ar-H), 5.32 (d, 1H, *J* 10 Hz, H$_c$), 4.55 (d, 1H, *J* 9.6 Hz, H$_a$), 4.46 (t, 1H, *J* 9.6 Hz, H$_b$), 2.97-2.88 (m, 2H), 2.66-2.61 (m, 1H), 2.52-2.48 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 209.2, 197.2, 163.2, 160.7, 142.5, 136.8, 134.7, 132.1, 132.0, 131.6, 130.6, 130.5, 129.8, 128.9, 128.7, 127.8, 127.4, 127.1, 126.4, 125.5, 124.9, 124.8, 123.5, 120.8, 116.1, 115.8, 74.7 (C-Spiro), 64.4, 63.8, 50.2, 42.5, 30.4; anal. calcd. for $C_{36}H_{26}N_2O_4$: C, 78.53; H, 4.76; N, 5.09; found: C, 78.77; H, 4.35; N, 4.86; MS (*m/z*): 550.

2'-(4-Methoxybenzoyl)-1'-phenyl-2',5',6',10b'-tetrahydro-1'H,2H-spiro[acenaphthylene-1,3'-pyrrolo[2,1-a]isoquinolin]-2-one (**4h**)

Yellow solid (0.439 g, 82%); m.p. 197-199 °C; FT-IR (KBr) ν_{max}/cm^{-1} 1713, 1670; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.95-6.22 (m, 19H, Ar-H), 5.36 (d, 1H, *J* 10 Hz, H$_c$), 4.57 (d, 1H, *J* 9.2 Hz, H$_a$), 4.48 (t, 1H, *J* 9.6 Hz, H$_b$), 3.56 (s, 3H, OMe), 2.98-2.88 (m, 2H), 2.65-2.52 (m, 1H), 2.50-2.47 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 209.7, 195.6, 162.5, 142.6, 142.5, 138.3, 137.3, 134.8, 131.9, 131.7, 130.2, 129.8, 129.5, 129.1, 129.0, 128.8, 128.7, 128.7, 126.9, 126.3, 125.5, 125.1, 124.7, 123.6, 120.7, 112.6, 75.0 (C-Spiro), 64.3, 63.4, 55.2, 51.1, 42.6, 30.9; anal. calcd. for $C_{37}H_{29}NO_3$: C, 82.97; H, 5.46; N, 2.61; found: C, 82.66; H, 5.01; N, 2.43; MS (*m/z*): 535.

2'-(4-Chlorobenzoyl)-1'-phenyl-2',5',6',10b'-tetrahydro-1'H,2H-spiro[acenaphthylene-1,3'-pyrrolo[2,1-a]isoquinolin]-2-one (**4i**)

Cream solid (0.447 g, 83%); m.p. 214-216 °C; FT-IR (KBr) ν_{max}/cm^{-1} 1713, 1670; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.92-6.70 (m, 19H, Ar-H), 5.37 (d, 1H, *J* 9.6 Hz, H$_c$), 4.55 (d, 1H, *J* 9.6 Hz, H$_a$), 4.45 (t, 1H, *J* 9.8 Hz, H$_b$), 2.97-2.90 (m, 2H), 2.69-2.62 (m, 1H), 2.53-2.50 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 209.4, 196.2 (C=O, chalcone), 142.5, 142.1, 138.3, 138.1, 137.0, 135.3, 134.7, 132.1, 131.5, 129.9, 129.1, 129.1, 128.8, 128.7, 128.5, 128.0, 127.6, 127.0, 126.3, 125.5, 125.1, 124.9, 123.5, 120.9, 74.8 (C-Spiro), 64.3, 64.0, 51.0, 42.5, 30.4; anal. calcd. for $C_{36}H_{26}ClNO_2$: C, 80.06; H, 4.85; N, 2.59; found: C, 79.65; H, 4.56; N, 2.74; MS (*m/z*): 540.

2’-(3-Chlorobenzoyl)-1’-phenyl-2’,5’,6’,10b’-tetrahydro-1’H,2H-spiro[acenaphthylene-1,3’-pyrrolo[2,1-a] isoquinolin]-2-one (**4j**)

Orange solid (0.420 g, 78%); m.p. 212-214 °C; FT-IR (KBr) ν_{max}/cm^{-1} 1704, 1687; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.97-6.63 (m, 19H, Ar-H), 5.39 (d, 1H, *J* 10 Hz, H$_c$), 4.52 (d, 1H, *J* 9.2 Hz, H$_a$), 4.45 (t, 1H, *J* 9.6 Hz, H$_b$), 2.99-2.91 (m, 2H), 2.68-2.58 (m, 1H), 2.55-2.50 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 209.4, 196.2, 142.4, 142.1, 138.4, 138.1, 137.0, 134.7, 133.8, 132.0, 131.8, 131.6, 129.8, 129.1, 129.1, 128.9, 128.7, 128.6, 128.0, 127.3, 127.1, 126.4, 125.5, 125.2, 125.1, 125.0, 123.4, 121.1, 74.7 (C-Spiro), 64.4, 63.6, 50.8, 42.5, 30.5; anal. calcd. for $C_{36}H_{26}ClNO_2$: C, 80.06; H, 4.85; N, 2.59; found: C, 79.76; H, 4.50; N, 2.33; MS (*m/z*): 540

2'-(4-Methoxybenzoyl)-1'-(4-methoxyphenyl)-2',5',6',10b'-tetrahydro-1'H,2H-spiro[acenaphthylene-1,3'-pyrrolo[2,1-a] isoquinolin]-2-one (**4k**)

Orange solid (0.486 g, 86%); m.p. 163-165 °C; FT-IR (KBr) ν_{max}/cm^{-1} 1713, 1676; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-6.23(m, 18H, Ar-H), 5.30 (d, 1H, *J* 10 Hz, H_c), 4.53 (d, 1H, *J* 9.6 Hz, H_a), 4,432 (t, 1H, *J* 9.6 Hz, H_b), 3.84 (s, 3H, OMe), 3.56 (s, 3H, OMe), 2.97-2.88 (m, 2H), 2.65-2.60 (m, 1H), 2.53-2.47 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 195.8, 162.5, 158.5, 142.6, 138.4, 137.3, 134.8, 134.4, 131.9, 131.7, 130.3, 130.0, 129.8, 129.5, 128.8, 128.7, 127.7, 126.2, 125.5, 125.1, 124.7, 123.6, 120.7, 114.5, 112.6, 74.9 (C-Spiro), 64.2, 63.3, 55.3, 55.2, 50.4, 42.6, 30.5; anal. calcd. for $C_{38}H_{31}NO_4$: C, 80.69; H, 5.52; N, 2.48; found: C, 80.84; H, 5.74; N, 2.83; MS (*m/z*): 565.

2'-(3-Chlorobenzoyl)-1'-(4-chlorophenyl)-2',5',6',10b'-tetrahydro-1'H,2H-spiro[acenaphthylene-1,3'-pyrrolo[2,1-a] isoquinolin]-2-one (**4l**)

Yellow solid (0.435 g, 76%); m.p. 205-207 °C; FT-IR (KBr) ν_{max}/cm^{-1} 1708, 1686; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.12-6.58 (m, 18H, Ar-H), 5.18 (d, 1H, *J* 10 Hz, H_c), 4.54 (d, 1H, *J* 9.2 Hz, H_a), 4.92 (t, 1H, *J* 9.6 Hz, H_b), 2.78-2.71 (m, 2H), 2.61-2.58 (m, 1H), 2.39-2.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 196.0, 142.5, 140.7, 138.2, 137.8, 136.8, 134.7, 133.9, 132.9, 132.1, 131.9, 131.5, 130.4, 129.8, 129.3, 129.0, 128.7, 128.6, 128.1, 127.2, 126.5, 125.6, 125.1, 125.1, 124.9, 123.4, 121.1, 74.6 (C-Spiro), 64.3, 64.2, 50.2, 42.5, 30.4; anal. calcd. for $C_{36}H_{25}Cl_2NO_2$: C, 75.26; H, 4.39; N, 2.44; found: C, 75.65; H, 4.69; N, 2.80; MS (*m/z*): 573.

1'-Nitro-2'-phenyl-2',5',6',10b'-tetrahydro-1'H,2H-spiro[acenaphthylene-1,3'-pyrrolo[2,1-a]isoquinolin]-2-one (**7a**)

Yellow solid (0.370 g, 83%); m.p. 196-198 °C; FT-IR (KBr) ν_{max}/cm^{-1} 1708, 1553, 1366; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-7.13 (m, 15H, Ar-H), 6.27 (dd, 1H, *J* 4.8, 7 Hz, H_b), 5.99 (d, 1H, *J* 7 Hz, H_c), 4.78 (d, 1H, *J* 4.8 Hz, H_a), 3.15-3.06 (m, 1H), 2.80-2.67 (m, 2H), 2.64-2.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.3, 142.8, 137.7, 135.3, 134.1, 132.7, 132.0, 131.7, 130.3, 129.3, 129.2, 128.5, 128.4, 128.3, 127.8, 127.1, 126.1, 125.6, 124.7, 121.1, 120.7, 92.6 (CH-NO_2), 79.0 (C-Spiro), 64.3, 60.4, 42.5, 30.0; anal. calcd. for $C_{29}H_{22}N_2O_3$: C, 78.01; H, 4.97; N, 6.27; found: C, 77.74; H, 4.69; N, 6.67; MS (*m/z*): 447.

2'-(4-Fluorophenyl)-1'-nitro-2',5',6',10b'-tetrahydro-1'H,2H-spiro[acenaphthylene-1,3'-pyrrolo[2,1-a]isoquinolin]-2-one (**7b**)

Brown solid (0.376 g, 81%); m.p. 183-185 °C, FT-IR (KBr) ν_{max}/cm^{-1} 1704, 1551, 1305; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-6.73 (m, 14H, Ar-H), 6.20 (dd, 1H, *J* 4.8, 7.2 Hz, H_b), 5.96 (d, 1H, *J* 7.2 Hz, H_c), 4.73 (d, 1H, *J* 4.8 Hz, H_a), 3.14-3.06 (m, 1H), 2.79-2.67 (m, 2H), 2.64-2.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.5, 162.2, 160.9, 142.8, 137.4, 135.2, 132.6, 131.8, 130.3, 130.2, 129.3, 129.2, 128.4, 127.1, 126.1, 125.7, 124.6, 121.1, 120.8, 115.3, 92.8 (CH-NO_2), 79.0 (C-Spiro), 64.2, 59.74, 42.5, 30.0; anal. calcd. for $C_{29}H_{21}FN_2O_3$: C, 74.99; H, 4.56; N, 6.03; found: C, 74.54; H, 4.14; N, 6.43; MS (*m/z*): 464.

2'-(4-Cholorophenyl)-1'-nitro-2',5',6',10b'-tetrahydro-1'H,2H-spiro[acenaphthylene-1,3'-pyrrolo[2,1-a] isoquinolin]-2-one (**7c**)

Cream solid (0.365 g, 76%); m.p. 190-192 °C; FT-IR (KBr) ν_{max}/cm^{-1} 1711, 1547, 1362; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-6.88 (m, 14H, Ar-H), 6.2 (dd, 1H, *J* 4.8, 7.2 Hz, H_b), 5.95 (d, 1H, *J* 7.2 Hz, H_c), 4.73 (d, 1H, *J* 4.8 Hz, H_a), 3.10-3.05 (m, 1H), 2.78-2.65 (m, 2H), 2.64-2.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 142.8, 137.2, 135.2, 133.8, 132.6, 132.5, 131.9, 131.8, 130.3, 129.9, 129.3, 129.2, 128.7, 128.4, 127.2, 126.1, 125.8, 124.6, 121.1, 120.9, 92.5, 78.9 (C-Spiro), 64.2, 59.7, 42.5, 30.0; anal. calcd. for $C_{29}H_{21}ClN_2O_3$: C, 72.42; H, 4.40; N, 5.82; found: C, 72.76; H, 4.03; N, 5.53; MS (*m/z*): 480.

2'-(4-Boromophenyl)-1'-nitro-2',5',6',10b'-tetrahydro-1'H,2H-spiro[acenaphthylene-O3'-pyrrolo[2,1-a]isoquinolin]-2-one (**7d**)

Cream solid (0.409 g, 78%); m.p. 186-188 °C; FT-IR (KBr) ν_{max}/cm^{-1} 1711, 1557, 1362; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12-6.82 (m, 14H, Ar-H), 6.19 (dd, 1H, *J* 4.8, 7.2 Hz, H_b), 5.94 (d, 1H, *J* 7.2 Hz, H_c), 4.72 (d, 1H, *J* 4.8 Hz, H_a), 3.12-3.05 (m, 1H), 2.76-2.64 (m, 2H), 2.63-2.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 142.8, 137.2, 135.2, 133.1, 132.5, 131.9, 131.8, 131.6, 130.3, 129.3, 129.2, 128.4, 127.2, 126.1, 125.8, 125.7, 124.6, 122.0, 121.1, 121.0, 92.5 (CH-NO_2), 78.8 (C-Spiro), 64.2, 59.7, 42.5, 30.0; anal. calcd. for $C_{29}H_{21}BrN_2O_3$: C, 66.30; H, 4.03; N, 5.33; found: C, 66.53; H, 3.81; N, 5.64; MS (*m/z*): 524.

2›-(4-Methylophenyl)-1›-nitro-2›,5›,6›,10b›-tetrahydro-1›H,2H-spiro[acenaphthylene-1,3›-pyrrolo[2,1-a] isoquinolin]-2-one (**7e**)

Yellow solid (0.359 g, 78%); m.p. 195-197 °C; FT-IR (KBr) ν_{max}/cm^{-1} 1712, 1549, 1360; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-6.82 (m, 14H, Ar-H), 6.25 (dd, 1H, *J* 5.2, 7.2 Hz, H_b), 5.96 (d, 1H, *J* 7.2 Hz, H_c), 4.75 (d, 1H, *J* 4.8 Hz, H_a), 3.13-3.05 (m, 1H), 2.78-2.59 (m, 3H), 2.16 (s, 3H, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4 (C=O), 142.8, 137.8, 137.5, 135.3, 132.8, 132.0, 131.6, 131.0, 130.3, 129.3, 129.1, 128.4, 128.2, 127.1, 126.1, 125.5, 124.7, 121.1, 120.7, 92.8 (CH-NO_2), 78.9 (C-Spiro), 64.3, 60.1, 42.5, 30.0, 20.9; anal. calcd. for $C_{30}H_{24}N_2O_3$: C, 78.24; H, 5.25; N, 6.06; found: C, 77.91; H, 5.62; N, 5.73; MS (*m/z*): 460.

2'-(4-Methoxyphenyl)-1'-nitro-2',5',6',10b'-tetrahydro-1'H,2H-spiro[acenaphthylene-1,3'-pyrrolo[2,1-a]isoquinolin]-2-one (**7f**)

Yellow solid (0.385 g, 81%); m.p. 194-196 °C, FT-IR (KBr) ν_{max}/cm^{-1} 1705, 1569, 1367; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-6.57 (m, 14H, Ar-H), 6.22 (dd, 1H, *J* 5.2, 7.2 Hz, H_b), 5.97(d, 1H, *J* 7.2 Hz, H_c), 4.72 (d, 1H, *J* 4.8 Hz, H_a), 3.65 (s, 3H, OMe), 3.12-3.06 (m, 1H), 2.79-2.67 (m, 2H), 2.66-2.63 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.6 (C=O), 159.0, 142.8, 137.8, 135.3, 132.8, 132.0, 131.7, 130.3, 129.7, 129.3, 129.1, 128.3, 127.1, 126.1, 126.0, 125.5, 124.6, 121.1, 120.7, 113.8, 93.0 (CH-NO_2), 79.0 (C-Spiro), 64.2, 59.9, 55.1, 42.5, 30.0; anal. calcd. for $C_{30}H_{24}N_2O_4$: C, 75.61; H, 5.08; N, 5.88; found: C, 75.11; H, 4.73; N, 5.42; MS (*m/z*): 476.

2'-(3-Methoxyphenyl)-1'-nitro-2',5',6',10b'-tetrahydro-1'H,2H-spiro[acenaphthylene-1,3'-pyrrolo[2,1-a]isoquinolin]-2-one (**7g**)

Brown solid (0.371 g, 78%); m.p. 180-182 °C; FT-IR (KBr) ν_{max}/cm^{-1} 1711, 1558, 1366; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-6.39 (m, 14H, Ar-H), 6.25 (dd, 1H, *J* 4.8, 7.2 Hz, H_b), 5.95 (d, 1H, *J* 6.8 Hz, H_c), 4.73 (d, 1H, *J* 4.8 Hz, H_a), 3.51 (s, 3H, OMe), 3.14-3.05 (m, 1H), 2.75-2.68 (m, 2H), 2.63-2.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2 (C=O), 159.2, 142.8, 137.8, 135.5, 135.2, 132.7, 132.0, 131.6, 130.3, 129.5, 129.3, 129.2, 128.3, 127.1, 126.1, 125.6, 124.7, 121.1, 120.7, 120.7, 114.1, 113.4, 92.4 (CH-NO_2), 78.9 (C-Spiro), 64.2, 60.3, 55.0, 42.4, 30.0; anal. calcd. for $C_{30}H_{24}N_2O_4$: C, 75.61; H, 5.08; N, 5.88; found: C, 75.92; H, 5.43; N, 5.51; MS (*m/z*): 476.

2'-(4-(Dimethylamino)phenyl)-1'-nitro-2',5',6',10b'-tetrahydro-1'H,2H-spiro[acenaphthylene-1,3'-pyrrolo[2,1-a]isoquinolin]-2-one (**7h**)

Yellow solid (0.396 g, 81%); m.p. 114-116°C; FT-IR (KBr) ν_{max}/cm^{-1} 1708, 1547, 1360; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-6.38 (m, 14H, Ar-H), 6.19 (dd, 1H, *J* 4.8, 6.8 Hz, H_b), 5.95 (d, 1H, *J* 7.2 Hz, H_c), 4.67 (d, 1H, *J* 4.8 Hz, H_a), 3.13-3.05 (m, 1H), 2.8 (s, 6H, NMe_2), 2.78-2.72 (m, 1H), 2.69-2.66 (m, 1H), 2.62-2.58 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.8 (C=O), 149.7, 142.8, 138.1, 135.3, 133.0, 132.2, 131.5, 130.2, 129.4, 129.3, 129.1, 128.2, 127.0, 126.0, 125.3, 124.6, 121.3, 121.0, 120.6, 112.2, 93.2 (CH-NO_2), 79.0 (C-Spiro), 64.2, 60.0, 42.5, 40.3, 30.0; anal. calcd. for $C_{31}H_{27}N_3O_3$: C, 76.05; H, 5.56; N, 8.58; found: C, 75.74; H, 5.87; N 8.84; MS (*m/z*): 489.

2'-(4-Nitrophenyl)-1'-nitro-2',5',6',10b'-tetrahydro-1'H,2H-spiro[acenaphthylene-1,3'-pyrrolo[2,1-a]isoquinolin]-2-one (**7i**)

Yellow solid (0.383 g, 78%); m.p. 185-187 °C; FT-IR (KBr) ν_{max}/cm^{-1} 1705, 1552, 1515, 1346, 1330; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-7.13 (m, 14H, Ar-H), 6.26 (dd, 1H, *J* 4.8, 7.2 Hz, H_b), 5.98 (d, 1H, *J* 7.2 Hz, H_c), 4.88 (d, 1H, *J* 4.8 Hz, H_a), 3.12-3.05 (m, 1H), 2.78-2.67 (m, 2H), 2.65-2.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.7, 147.3, 142.7, 141.5, 136.6, 135.1, 132.2, 132.1, 131.4, 130.3, 129.5, 129.4, 129.2, 128.6, 127.3, 126.2, 126.1, 124.7, 123.6, 121.3, 121.2, 92.0 (CH-NO_2), 79.0 (C-Spiro), 64.2, 59.6, 42.4, 29.9; anal. calcd. for $C_{29}H_{21}N_3O_5$: C, 70.87; H, 4.31; N, 8.55; found: C, 71.11; H, 4.73; N, 8.93; MS (*m/z*): 492.

2'-(4-Cyanophenyl)-1'-nitro-2',5',6',10b'-tetrahydro-1'H,2H-spiro[acenaphthylene-1,3'-pyrrolo[2,1-a]isoquinolin]-2-one (**7j**)

Yellow solid (0.386 g, 82%); m.p. 114-116 °C; FT-IR (KBr) ν_{max}/cm^{-1} 2228 (C≡N, str.), 1708 (C=O, str.), 1552 and 1343 (NO_2, str.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-7.06 (m, 14H, Ar-H), 6.24 (dd, 1H, *J* 4.8, 7.2 Hz, H_b), 5.61 (d, 1H, *J* 6.8 Hz, H_c), 4.81 (d, 1H, *J* 5.2 Hz, H_a), 3.13-3.05 (m, 1H), 2.78-2.66 (m, 2H), 2.64-2.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.9, 142.7, 139.5, 136.8, 135.2, 132.2, 132.2, 131.5, 130.3, 129.4, 129.3, 129.2, 128.6, 127.3, 126.2, 126.1, 124.7, 121.3, 121.1, 118.2, 111.9, 91.9 (CH-NO_2), 79.0 (C-Spiro), 64.2, 59.9, 42.4, 30.0; anal. calcd. for $C_{30}H_{21}N_3O_3$: C, 76.42; H, 4.49; N, 8.91; found: C, 76.81; H, 4.79; N, 9.22; MS (*m/z*): 471.

2'-(2-Chloro-5-nitrophenyl)-1'-nitro-2',5',6',10b'-tetrahydro-1'H,2H-spiro[acenaphthylene-1,3'-pyrrolo[2,1-a]isoquinolin]-2-one (**7k**)

Brown solid (0.420 g, 80%); m.p. 186-188 °C, FT-IR (KBr) ν_{max}/cm^{-1} 1704, 1555, 1528, 1370, 1353; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.57-7.14 (m, 13H, Ar-H), 6.35 (dd, 1H, *J* 4, 8 Hz, H_b), 5.91 (d, 1H, *J* 4 Hz, H_c), 5.37 (d, 1H, *J* 4 Hz, H_a), 2.88-2.85 (m, 1H), 2.62-2.54 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 206.0, 146.7, 142.5, 140.7, 137.8, 135.7, 135.5, 133.0, 132.4, 131.2, 130.7, 130.3, 130.0, 129.4, 129.1, 127.5, 127.2, 126.9, 126.2, 126.0, 124.5, 122.0, 121.3, 92.5 (CH-NO_2), 78.1 (C-Spiro), 65.3, 55.0, 42.3, 30.0; anal. calcd. for $C_{29}H_{20}ClN_3O_5$: C, 66.23; H, 3.83; N, 7.99; found: C, 66.84; H, 4.11; N, 7.53; MS (*m/z*): 525.

1›-Methyl-1›-nitro-2›-phenyl-2›,5›,6›,10b›-tetrahydro-1›H,2H-spiro[acenaphthylene-1,3›-pyrrolo[2,1-a] isoquinolin]-2-one (**7l**)

Brown solid (0.368 g, 80%); m.p. 190-192 °C, FT-IR (KBr) ν_{max}/cm^{-1} 1708, 1537, 1340; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60-7.00 (m, 15H, Ar-H), 5.52 (s, 1H, H_b), 5.15 (s, 1H, H_a), 3.12-3.05 (m, 1H), 2.72-2.56 (m, 3H), 2.06 (s, 3H, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.1, 142.9, 137.5, 134.9, 134.3, 132.7, 132.4, 132.0, 130.4, 129.5, 129.1, 128.7, 128.4, 128.3, 128.0, 126.6, 126.0, 125.5, 122.5, 120.9, 120.8, 98.0 (CH-NO_2), 77.3 (C-Spiro), 70.0, 65.9, 42.1, 30.1, 24.2; anal. calcd. for $C_{30}H_{24}N_2O_3$: C, 78.24; H, 5.25; N, 6.08; found: C, 78.63; H, 5.76; N, 6.51; MS (*m/z*): 460.

Table S1. Bond lengths (Å) for compound **4i**

C(1)-C(2)	1.390(8)	C(18)-H(18)	0.9300
C(1)-H(1)	0.9300	C(19)-C(20)	1.365(9)
C(2)-C(3)	1.370(9)	C(19)-H(19)	0.9300
C(2)-H(2)	0.9300	C(20)-C(21)	1.383(8)
C(3)-C(4)	1.375(8)	C(20)-H(20)	0.9300
C(3)-Cl1	1.749(6)	C(21)-C(22)	1.382(7)
C(4)-C(5)	1.389(7)	C(21)-H(21)	0.9300
C(4)-H(4)	0.9300	C(22)-C(23)	1.532(8)
C(5)-C(6)	1.371(8)	C(23)-C(24)	1.505(8)
C(5)-H(5)	0.9300	C(23)-H(23A)	0.9700
C(6)-C(7)	1.502(7)	C(23)-H(23B)	0.9700
C(7)-O(1)	1.209(7)	C(24)-N(1)	1.473(7)
C(7)-C(8)	1.531(7)	C(24)-H(24A)	0.9700
C(8)-C(25)	1.553(7)	C(24)-H(24B)	0.9700
C(8)-C(9)	1.563(6)	C(25)-N(1)	1.483(7)
C(8)-H(8)	0.9800	C(25)-C(35)	1.512(7)
C(9)-C(10)	1.510(7)	C(25)-C(26)	1.580(8)
C(9)-C(16)	1.534(7)	C(26)-O(2)	1.205(7)
C(9)-H(9)	0.9800	C(26)-C(27)	1.463(8)
C(10)-C(11)	1.369(8)	C(27)-C(28)	1.367(10)
C(10)-C(15)	1.401(8)	C(27)-C(36)	1.4(15)-(10)
C(11)-C(12)	1.392(9)	C(28)-C(29)	1.412(13)
C(11)-H(11)	0.9300	C(28)-H(28)	0.9300
C(12)-C(13)	1.349(9)	C(29)-C(30)	1.355((15)-)
C(12)-H(12)	0.9300	C(29)-H(29)	0.9300
C(13)-C(14)	1.345(10)	C(30)-C(31)	1.426((15)-)
C(13)-H(13)	0.9300	C(30)-H(30)	0.9300
C(14)-C(15)	1.396(8)	C(31)-C(32)	1.423(12)
C(14)-H(14)	0.9300	C(31)-C(36)	1.434(9)
C(15)-H(15)	0.9300	C(32)-C(33)	1.354(12)
C(16)-N(1)	1.463(6)	C(32)-H(32)	0.9300
C(16)-C(17)	1.524(7)	C(33)-C(34)	1.416(8)
C(16)-H(16)	0.9800	C(33)-H(33)	0.9300
C(17)-C(22)	1.384(7)	C(34)-C(35)	1.368(8)
C(17)-C(18)	1.398(7)	C(34)-H(34)	0.9300
C(18)-C(19)	1.376(8)	C(35)-C(36)	1.400(9)

Table S2. Bond angles (degree) for **4i**

C(2)-C(1)-C(6)	120.0(6)	C(16)-N(1)-C(24)	110.6(4)	C(11)-C(10)-C(15)	117.0(5)	C(27)-C(26)-C(25)	107.3(5)
C(2)-C(1)-H(1)	120.0	C(16)-N(1)-C(25)	109.2(4)	C(11)-C(10)-C(9)	120.2(5)	C(28)-C(27)-C(36)	119.9(7)
C(6)-C(1)-H(1)	120.0	C(24)-N(1)-C(25)	116.6(4)	C(15)-C(10)-C(9)	122.6(5)	C(28)-C(27)-C(26)	133.0(8)
C(3)-C(2)-C(1)	119.1(6)	C(18)-C(19)-H(19	119.8	C(10)-C(11)-C(12)	121.6(6)	C(36)-C(27)-C(26)	107.2(6)
C(3)-C(2)-H(2)	120.4	C(19)-C(20)-C(21)	119.1(5)	C(10)-C(11)-H(11)	119.2	C(27)-C(28)-C(29)	117.8(9)
C(1)-C(2)-H(2)	120.4	C(19)-C(20)-H(20)	120.4	C(12)-C(11)-H(11)	119.2	C(27)-C(28)-H(28)	121.1
C(2)-C(3)-C(4)	122.4(5)	C(21)-C(20)-H(20)	120.4	C(13)-C(12)-C(11)	120.7(7)	C(29)-C(28)-H(28)	121.1
C(2)-C(3)-C(11)	118.3(5)	C(22)-C(21)-C(20)	121.6(6)	C(13)-C(12)-H(12)	119.7	C(30)-C(29)-C(28)	122.3(10)
C(4)-C(3)-C(11)	119.3(5)	C(22)-C(21)-H(21)	119.2	C(11)-C(12)-H(12)	119.7	C(30)-C(29)-H(29)	118.8
C(3)-C(4)-C(5)	117.8(6)	C(20)-C(21)-H(21)	119.2	C(14)-C(13)-C(12)	119.2(6)	C(28)-C(29)-H(29)	118.8
C(3)-C(4)-H(4)	121.1	C(21)-C(22)-C(17)	119.1(5)	C(14)-C(13)-H(13)	120.4	C(29)-C(30)-C(31)	123.5(10)
C(5)-C(4)-H(4)	121.1	C(21)-C(22)-C(23)	119.7(5)	C(12)-C(13)-H(13)	120.4	C(29)-C(30)-H(30)	118.2
C(6)-C(5)-C(4)	122.1(5)	C(17)-C(22)-C(23)	121.1(5)	C(13)-C(14)-C(15)	121.7(7)	C(31)-C(30)-H(30)	118.2
C(6)-C(5)-H(5)	119.0	C(24)-C(23)-C(22)	113.8(5)	C(13)-C(14)-H(14)	119.2	C(32)-C(31)-C(30)	131.7(9)
C(4)-C(5)-H(5)	119.0	C(24)-C(23)-H(23A)	108.8	C(15)-C(14)-H(14)	119.2	C(32)-C(31)-C(36)	1(15)-.9(8)
C(5)-C(6)-C(1)	118.7(5)	C(22)-C(23)-H(23A)	108.8	C(14)-C(15)-C(10)	119.7(6)	C(30)-C(31)-C(36)	112.4(10)
C(5)-C(6)-C(7)	125.3(5)	C(24)-C(23)-H(23B)	108.8	C(14)-C(15)-H(15)	120.1	C(33)-C(32)-C(31)	121.4(7)
C(1)-C(6)-C(7)	116.0(5)	C(22)-C(23)-H(23B)	108.8	C(10)-C(15)-H(15)	120.1	C(33)-C(32)-H(32)	119.3
O(1)-C(7)-C(6)	120.2(5)	H(23A)-C(23)-(23B)	107.7	N(1)-C(16)-C(17)	109.0(4)	C(31)-C(32)-H(32)	119.3
O(1)-C(7)-C(8)	121.7(5)	N(1)-C(24)-C(23)	107.7(5)	N(1)-C(16)-C(9)	101.0(4)	C(32)-C(33)-C(34)	121.7(8)
C(6)-C(7)-C(8)	118.1(5)	N(1)-C(24)-H(24A)	110.2	C(17)-C(16)-C(9)	117.1(4)	C(32)-C(33)-H(33)	119.2
C(7)-C(8)-C(25)	114.3(4)	C(23)-C(24)-H(24A)	110.2	N(1)-C(16)-H(16)	109.8	C(34)-C(33)-H(33)	119.2
C(7)-C(8)-C(9)	111.8(4)	N(1)-C(24)-H(24B)	110.2	C(17)-C(16)-H(16)	109.8	C(35)-C(34)-C(33)	119.2(7)
C(25)-C(8)-C(9)	106.4(4)	C(23)-C(24)-H(24B)	110.2	C(9)-C(16)-H(16)	109.8	C(35)-C(34)-H(34)	120.4
C(7)-C(8)-H(8)	108.0	H(24A)-C24-H(24B)	108.5	C(22)-C(17)-C(18)	118.9(5)	C(33)-C(34)-H(34)	120.4
C(25)-C(8)-H(8)	108.0	N(1)-C(25)-C(35)	110.5(4)	C(22)-C(17)-C(16)	119.2(4)	C(34)-C(35)-C(36)	120.0(6)
C(9)-C(8)-H(8)	108.0	N(1)-C(25)-C(8)	101.9(4)	C(18)-C(17)-C(16)	121.8(5)	C(34)-C(35)-C(25)	132.0(6)
C(10)-C(9)-C(16)	117.3(4)	C(35)-C(25)-C(8)	118.4(4)	C(19)-C(18)-C(17)	120.9(6)	C(36)-C(35)-C(25)	108.0(6)
C(10)-C(9)-C(8)	110.0(4)	N(1)-C(25)-C(26)	114.7(4)	C(19)-C(18)-H(18)	119.6	C(35)-C(36)-C(27)	114.2(5)
C(16)-C(9)-C(8)	103.6(4)	C(35)-C(25)-C(26)	103.2(4)	C(17)-C(18)-H(18)	119.6	C(35)-C(36)-C(31)	121.8(8)
C(10)-C(9)-H(9)	108.6	C(8)-C(25)-C(26)	108.7(5)	C(20)-C(19)-C(18)	120.3(6)	C(27)-C(36)-C(31)	124.0(8)
C(16)-C(9)-H(9)	108.6	O(2)-C(26)-C(27)	128.5(7)	C(20)-C(19)-H(19)	119.8		
C(8)-C(9)-H(9)	108.6	O(2)-C(26)-C(25)	124.2(5)				

Table S3. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for compound **4i**

	x	y	z	U(eq)
C(1)	0.3108(6)	0.1219(4)	–0.0957(4)	0.0666(17)
H(1)	0.3471	0.1068	–0.1408	0.080
C(2)	0.3857(6)	0.1038(4)	–0.0201(4)	0.074(2)
H(2)	0.4722	0.0766	–0.0143	0.089
C(3)	0.3306(6)	0.1265(4)	0.0457(4)	0.0642(17)
C(4)	0.2023(6)	0.1661(4)	0.0398(4)	0.0640(17)
H(4)	0.1657	0.1802	0.0852	0.077
C(5)	0.1294(6)	0.1842(3)	–0.0361(3)	0.0530(14)
H(5)	0.0433	0.2117	–0.0412	0.064
C(6)	0.1802(5)	0.1629(3)	–0.1038(3)	0.0467(13)
C(7)	0.1068(5)	0.1792(3)	–0.1878(3)	0.0480(13)
C(8)	–0.0216(5)	0.2342(3)	–0.2002(3)	0.0433(12)
H(8)	–0.0867	0.2206	–0.1626	0.052
C(9)	–0.1109(5)	0.2296(3)	–0.2866(3)	0.0420(12)
H(9)	–0.0460	0.2122	–0.3226	0.050
C(10)	–0.2341(6)	0.1736(3)	–0.2887(3)	0.0459(13)
C(11)	–0.2099(6)	0.0984(4)	–0.2982(4)	0.0683(18)
H(11)	–0.1193	0.0830	–0.3083	0.082
C(12)	–0.3175(8)	0.0447(4)	–0.2932(4)	0.078(2)
H(12)	–0.2975	–0.0060	–0.2995	0.093
C(13)	–0.4504(8)	0.0653(4)	–0.2793(4)	0.074(2)
H(13)	–0.5211	0.0290	–0.2746	0.089
C(14)	–0.4794(7)	0.1388(4)	–0.2723(4)	0.075(2)
H(14)	–0.5723	0.1531	–0.2650	0.090
C(15)	–0.3735(6)	0.1942(4)	–0.2756(4)	0.0674(17)
H(15)	–0.3953	0.2447	–0.2692	0.081
C(16)	–0.(15)-22(5)	0.3118(3)	–0.3075(3)	0.0420(12)
H(16)	–0.2367	0.3259	–0.2832	0.050
C(17)	–0.1787(5)	0.3336(3)	–0.3956(3)	0.0425(12)
C(18)	–0.2530(6)	0.2861(3)	–0.4541(3)	0.0521(14)
H(18)	–0.2814	0.2383	–0.4397	0.063
C(19)	–0.2847(6)	0.3090(4)	–0.5326(4)	0.0641(17)
H(19)	–0.3338	0.2767	–0.5708	0.077
C(20)	–0.2443(6)	0.3790(4)	–0.5547(3)	0.0645(17)
H(20)	–0.2655	0.3946	–0.6077	0.077
C(21)	–0.1714(6)	0.4265(4)	–0.4971(4)	0.0621(16)
H(21)	–0.1454	0.4746	–0.5119	0.075
C(22)	–0.1361(6)	0.4043(3)	–0.4181(3)	0.0522(14)
C(23)	–0.0475(7)	0.4572(3)	–0.3574(3)	0.0673(18)
H(23A)	0.0517	0.4599	–0.3681	0.081
H(23B)	–0.0887	0.5073	–0.3648	0.081
C(24)	–0.0436(7)	0.4332(3)	–0.2719(4)	0.0650(18)
H(24A)	0.0357	0.4585	–0.2376	0.078
H(24B)	–0.1345	0.4463	–0.2545	0.078
C(25)	0.0228(5)	0.3181(3)	–0.1865(3)	0.0464(13)
C(26)	–0.0598(7)	0.3511(3)	–0.1204(4)	0.0606(16)
C(27)	0.0512(9)	0.3788(4)	–0.0557(3)	0.0734(19)
C(28)	0.0438(11)	0.4093(5)	0.0172(4)	0.112(3)
H(28)	–0.0452	0.4155	0.0344	0.134
C(29)	0.1760(16)	0.4310(8)	0.0655(6)	0.148(5)
H(29)	0.1731	0.4508	0.1157	0.178
C(30)	0.3068(16)	0.4239(8)	0.0413(7)	0.154(5)
H(30)	0.3896	0.4410	0.0749	0.185

Table S3. continuation

	x	y	z	U(eq)
C(31)	0.3246(11)	0.3916(5)	–0.0331(5)	0.097(3)
C(32)	0.4511(9)	0.3779(5)	–0.0677(6)	0.106(3)
H(32)	0.5424	0.3902	–0.0392	0.127
H(32)	0.5424	0.3902	–0.0392	0.127
C(33)	0.4414(7)	0.3473(4)	–0.1412(6)	0.089(3)
H(33)	0.5259	0.3411	–0.1629	0.107
C(34)	0.3058(6)	0.3247(4)	–0.1857(4)	0.0675(18)
H(34)	0.3017	0.3022	–0.2353	0.081
C(35)	0.1809(6)	0.3364(3)	–0.1550(3)	0.0531(14)
C(36)	0.1883(8)	0.3690(4)	–0.0797(4)	0.074(2)
N(1)	–0.0219(5)	0.3510(2)	–0.2673(3)	0.0504(11)
O(1)	0.1498(4)	0.1498(3)	–0.2434(3)	0.0731(13)
O(2)	–0.1907(5)	0.3535(3)	–0.1261(3)	0.0834(14)
Cl(1)	0.4243(2)	0.10107(15)	0.14009(11)	0.1071(8)

Table S4. Anisotropic displacement parameters (Å^2× 10^3) for **4i**.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	0.063(4)	0.070(4)	0.067(4)	0.026(3)	0.015(3)	0.015(3)
C(2)	0.082(5)	0.049(3)	0.090(5)	0.032(4)	0.009(3)	0.014(3)
C(3)	0.053(3)	0.076(5)	0.059(4)	0.029(3)	–0.001(3)	0.002(3)
C(4)	0.062(4)	0.067(4)	0.061(4)	0.010(3)	0.005(3)	0.002(3)
C(5)	0.045(3)	0.054(4)	0.056(3)	0.010(3)	–0.001(3)	0.001(3)
C(6)	0.042(3)	0.037(3)	0.059(3)	0.011(3)	0.003(2)	–0.002(2)
C(7)	0.048(3)	0.039(3)	0.056(3)	0.005(3)	0.004(3)	–0.001(2)
C(8)	0.042(3)	0.038(3)	0.049(3)	0.008(2)	0.004(2)	–0.002(2)
C(9)	0.044(3)	0.040(3)	0.042(3)	0.003(2)	0.006(2)	0.006(2)
C(10)	0.054(3)	0.042(3)	0.038(3)	–0.002(2)	0.003(2)	–0.003(2)
C(11)	0.053(3)	0.054(4)	0.093(5)	–0.002(4)	–0.001(3)	–0.001(3)
C(12)	0.082(5)	0.046(4)	0.097(5)	0.001(4)	–0.010(4)	–0.010(3)
C(13)	0.072(5)	0.059(4)	0.082(5)	0.021(4)	–0.013(4)	–0.021(3)
C(14)	0.046(3)	0.094(6)	0.084(5)	0.010(4)	0.009(3)	–0.021(4)
C(15)	0.062(4)	0.059(4)	0.082(4)	–0.001(3)	0.014(3)	–0.003(3)
C(16)	0.033(2)	0.045(3)	0.045(3)	–0.001(2)	–0.001(2)	–0.006(2)
C(17)	0.040(3)	0.038(3)	0.048(3)	0.001(2)	0.005(2)	0.003(2)
C(18)	0.057(3)	0.049(3)	0.049(3)	–0.001(3)	0.003(3)	–0.007(3)
C(19)	0.063(4)	0.071(5)	0.054(4)	–0.006(3)	–0.004(3)	–0.002(3)
C(20)	0.062(4)	0.089(5)	0.041(3)	0.011(3)	0.003(3)	0.013(3)
C(21)	0.063(4)	0.056(4)	0.066(4)	0.018(3)	0.008(3)	0.001(3)
C(22)	0.050(3)	0.050(4)	0.055(3)	0.005(3)	0.004(2)	0.007(3)
C(23)	0.093(5)	0.039(3)	0.066(4)	0.007(3)	0.003(3)	–0.006(3)
C(24)	0.071(4)	0.039(3)	0.077(4)	–0.004(3)	–0.010(3)	–0.005(3)
C(25)	0.043(3)	0.044(3)	0.051(3)	–0.003(2)	0.003(2)	0.001(2)
C(26)	0.062(4)	0.049(4)	0.069(4)	–0.001(3)	0.004(3)	0.002(3)
C(27)	0.114(6)	0.060(4)	0.042(3)	0.001(3)	–0.002(3)	0.008(4)
C(28)	0.153(8)	0.116(8)	0.062(5)	–0.014(5)	0.007(5)	–0.004(6)
C(29)	0.229(14)	0.149(10)	0.055(5)	–0.038(6)	–0.010(8)	–0.011(11)
C(30)	0.194(13)	0.143(11)	0.096(9)	–0.009(8)	–0.059(9)	–0.030(11)
C(31)	0.121(7)	0.074(5)	0.076(5)	0.007(4)	–0.039(5)	–0.006(5)
C(32)	0.071(5)	0.095(6)	0.129(8)	0.026(6)	–0.048(5)	–0.014(5)

Table S4. continuation

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(33)	0.052(4)	0.068(5)	0.135(7)	0.030(5)	–0.019(4)	–0.007(3)
C(34)	0.057(4)	0.048(4)	0.093(5)	0.013(3)	0.001(3)	–0.002(3)
C(35)	0.057(3)	0.040(3)	0.057(3)	0.007(3)	–0.003(3)	–0.003(3)
C(36)	0.079(5)	0.058(4)	0.073(4)	0.012(3)	–0.024(4)	–0.003(3)
N(1)	0.059(3)	0.038(3)	0.050(3)	–0.001(2)	–0.002(2)	–0.002(2)
O(1)	0.073(3)	0.085(3)	0.060(3)	–0.010(2)	0.006(2)	0.027(2)
O(2)	0.067(3)	0.087(4)	0.099(4)	–0.014(3)	0.024(3)	0.003(3)
C(l1)	0.0880(13)	0.152(2)	0.0724(12)	0.0388(13)	–0.0110(10)	0.0253(13)

Table S5. Torsion angles (degree) for compound **4i**

C(9)-C(8)-C(25)-N(1)	–8.6(5)	C(26)-C(25)-C(35)-C(34)	–177.8(6)
C(7)-C(8)-C(25)-C(35)	–6.0(7)	N(1)-C(25)-C(35)-C(36)	127.2(5)
C(9)-C(8)-C(25)-C(35)	–130.0(5)	C(8)-C(25)-C(35)-C(36)	–116.0(6)
C(7)-C(8)-C(25)-C(26)	–123.2(5)	C(26)-C(25)-C(35)-C(36)	4.1(6)
C(9)-C(8)-C(25)-C(26)	112.8(5)	C(34)-C(35)-C(36)-C(27)	179.2(6)
N(1)-C(25)-C(26)-O(2)	53.5(8)	C(25)-C(35)-C(36)-C(27)	–2.5(7)
C(35)-C(25)-C(26)-O(2)	173.8(6)	C(34)-C(35)-C(36)-C(31)	0.5(9)
C(8)-C(25)-C(26)-O(2)	–59.7(7)	C(25)-C(35)-C(36)-C(31)	178.9(6)
N(1)-C(25)-C(26)-C(27)	–124.7(5)	C(28)-C(27)-C(36)-C(35)	179.1(7)
C(35)-C(25)-C(26)-C(27)	–4.5(6)	C(26)-C(27)-C(36)-C(35)	–0.5(8)
C(8)-C(25)-C(26)-C(27)	122.0(5)	C(28)-C(27)-C(36)-C(31)	–2.3(11)
O(2)-C(26)-C(27)-C(28)	5.5(13)	C(26)-C(27)-C(36)-C(31)	178.1(6)
C(25)-C(26)-C(27)-C(28)	–176.4(8)	C(32)-C(31)-C(36)-C(35)	–0.8(10)
O(2)-C(26)-C(27)-C(36)	–174.9(7)	C(30)-C(31)-C(36)-C(35)	179.7(8)
C(25)-C(26)-C(27)-C(36)	3.2(7)	C(32)-C(31)-C(36)-C(27)	–179.3(7)
C(36)-C(27)-C(28)-C(29)	1.0(13)	C(30)-C(31)-C(36)-C(27)	1.2(11)
C(26)-C(27)-C(28)-C(29)	–179.5(9)	C(17)-C(16)-N(1)-C(24)	62.4(6)
C(27)-C(28)-C(29)-C(30)	1.3(19)	C(9)-C(16)-N(1)-C(24)	–173.7(5)
C(28)-C(29)-C(30)-C(31)	–2(2)	C(17)-C(16)-N(1)-C(25)	–168.0(4)
C(29)-C(30)-C(31)-C(32)	–178.3(12)	C(9)-C(16)-N(1)-C(25)	–44.1(5)
C(29)-C(30)-C(31)-C(36)	1.1(17)	C(23)-C(24)-N(1)-C(16)	–69.6(6)
C(30)-C(31)-C(32)-C(33)	–178.7(10)	C(23)-C(24)-N(1)-C(25)	164.8(5)
C(36)-C(31)-C(32)-C(33)	1.9(12)	C(35)-C(25)-N(1)-C(16)	159.9(4)
C(31)-C(32)-C(33)-C(34)	–2.7(12)	C(8)-C(25)-N(1)-C(16)	33.2(5)
C(32)-C(33)-C(34)-C(35)	2.3(10)	C(26)-C(25)-N(1)-C(16)	–84.1(5)
C(33)-C(34)-C(35)-C(36)	–1.2(9)	C(35)-C(25)-N(1)-C(24)	–73.9(6)
C(33)-C(34)-C(35)-C(25)	–179.1(6)	C(8)-C(25)-N(1)-C(24)	159.5(5)
N(1)-C(25)-C(35)-C(34)	–54.8(8)	C(26)-C(25)-N(1)-C(24)	42.2(7)
C(8)-C(25)-C(35)-C(34)	62.1(8)		

Table S6. Bond lengths (Å) for compound **7f**

C(1)-O(1)	1.210(3)	C(17)-C(19)	1.381(4)
C(1)-C(2)	1.478(4)	C(18)-O(2)	1.410(3)
C(1)-C(12)	1.579(3)	C(18)-H(18A)	0.9600
C(2)-C(3)	1.372(4)	C(18)-H(18B)	0.9600
C(2)-C(11)	1.405(4)	C(18)-H(18C)	0.9600
C(3)-C(4)	1.416(5)	C(19)-C(20)	1.370(4)
C(3)-H(3)	0.9300	C(19)-H(19)	0.9300
C(4)-C(5)	1.370(6)	C(20)-H(20)	0.9300
C(4)-H(4)	0.9300	C(21)-N(2)	1.513(3)
C(5)-C(6)	1.409(6)	C(21)-C(22)	1.533(3)
C(5)-H(5)	0.9300	C(21)-H(21)	0.9800
C(6)-C(11)	1.410(4)	C(22)-N(1)	1.457(3)
C(6)-C(7)	1.416(5)	C(22)-C(23)	1.509(3)
C(7)-C(8)	1.361(5)	C(22)-H(22)	0.9800
C(7)-H(7)	0.9300	C(23)-C(28)	1.389(4)
C(8)-C(9)	1.408(4)	C(23)-C(24)	1.395(4)
C(8)-H(8)	0.9300	C(24)-C(25)	1.382(4)
C(9)-C(10)	1.362(4)	C(24)-H(24)	0.9300
C(9)-H(9)	0.9300	C(25)-C(26)	1.374(5)
C(10)-C(11)	1.401(4)	C(25)-H(25)	0.9300
C(10)-C(12)	1.513(3)	C(26)-C(27)	1.368(5)
C(12)-N(1)	1.466(3)	C(26)-H(26)	0.9300
C(12)-C(13)	1.566(3)	C(27)-C(28)	1.396(4)
C(13)-C(14)	1.509(3)	C(27)-H(27)	0.9300
C(13)-C(21)	1.548(3)	C(28)-C(29)	1.508(4)
C(13)-H(13)	0.9800	C(29)-C(30)	1.511(4)
C(14)-C(15)	1.386(3)	C(29)-H(29A)	0.9700
C(14)-C(20)	1.389(3)	C(29)-H(29B)	0.9700
C(15)-C(16)	1.390(4)	C(30)-(N1)	1.457(3)
C(15)-H(15)	0.9300	C(30)-H(30A)	0.9700
C(16)-C(17)	1.378(3)	C(30)-H(30B)	0.9700
C(16)-H(16)	0.9300	N(2)-O(4)	1.213(3)
C(17)-O(2)	1.363(3)	N(2)-O(3)	1.223(3)

Table S7. Bond angles (degree) for compound **7f**

O(1)-C(1)-C(2)	127.7(3)	H(18A)-C(18)-H(18B)	109.5
O(1)-C(1)-C(12)	124.8(2)	O(2)-C(18)-H(18C)	109.5
C(2)-C(1)-C(12)	107.3(2)	H(18A)-C(18)-H(18C)	109.5
C(3)-C(2)-C(11)	119.5(3)	H(18B)-C(18)-H(18C)	109.5
C(3)-C(2)-C(1)	132.9(3)	C(20)-C(19)-C(17)	120.8(2)
C(11)-C(2)-C(1)	107.6(2)	C(20)-C(19)-H(19)	119.6
C(2)-C(3)-C(4)	117.6(4)	C(17)-C(19)-H(19)	119.6
C(2)-C(3)-H(3)	121.2	C(19)-C(20)-C(14)	121.3(2)
C(4)-C(3)-H(3)	121.2	C(19)-C(20)-H(20)	119.4
C(5)-C(4)-C(3)	122.5(4)	C(14)-C(20)-H(20)	119.4
C(5)-C(4)-H(4)	118.7	N(2)-C(21)-C(22)	110.5(2)
C(3)-C(4)-H(4)	118.7	N(2)-C(21)-C(13)	110.6(2)
C(4)-C(5)-C(6)	121.5(4)	C(22)-C(21)-C(13)	104.7(2)
C(4)-C(5)-H(5)	119.2	N(2)-C(21)-H(21)	110.3
C(6)-C(5)-H(5)	119.2	C(22)-C(21)-H(21)	110.3
C(5)-C(6)-C(11)	114.8(4)	C(13)-C(21)-H(21)	110.3
C(5)-C(6)-C(7)	128.7(4)	N(1)-C(22)-C(23)	110.9(2)
C(11)-C(6)-C(7)	116.5(3)	N(1)-C(22)-C(21)	102.31(19)
C(8)-C(7)-C(6)	120.1(3)	C(23)-C(22)-C(21)	119.3(2)
C(8)-C(7)-H(7)	119.9	N(1)-C(22)-H(22)	107.9
C(6)-C(7)-H(7)	119.9	C(23)-C(22)-H(22)	107.9
C(7)-C(8)-C(9)	122.4(4)	C(21)-C(22)-H(22)	107.9
C(7)-C(8)-H(8)	118.8	C(28)-C(23)-C(24)	119.8(2)
C(9)-C(8)-H(8)	118.8	C(28)-C(23)-C(22)	119.3(2)
C(10)-C(9)-C(8)	119.0(3)	C(24)-C(23)-C(22)	120.9(2)
C(10)-C(9)-H(9)	120.5	C(25)-C(24)-C(23)	120.5(3)
C(8)-C(9)-H(9)	120.5	C(25)-C(24)-H(24)	119.8
C(9)-C(10)-C(11)	119.3(3)	C(23)-C(24)-H(24)	119.8
C(9)-C(10)-C(12)	131.4(3)	C(26)-C(25)-C(24)	119.7(3)
C(11)-C(10)-C(12)	109.4(2)	C(26)-C(25)-H(25)	120.1
C(10)-C(11)-C(2)	113.3(2)	C(24)-C(25)-H(25)	120.1
C(10)-C(11)-C(6)	122.7(3)	C(27)-C(26)-C(25)	120.1(3)
C(2)-C(11)-C(6)	124.0(3)	C(27)-C(26)-H(26)	119.9
N(1)-C(12)-C(10)	112.48(19)	C(25)-C(26)-H(26)	119.9
N(1)-C(12)-C(13)	102.57(19)	C(26)-C(27)-C(28)	121.5(3)
C(10)-C(12)-C(13)	113.3(2)	C(26)-C(27)-H(27)	119.3
N(1)-C(12)-C(1)	112.6(2)	C(28)-C(27)-H(27)	119.3
C(10)-C(12)-C(1)	102.4(2)	C(23)-C(28)-C(27)	118.4(3)
C(13)-C(12)-C(1)	113.91(19)	C(23)-C(28)-C(29)	121.7(2)
C(14)-C(13)-C(21)	115.7(2)	C(27)-C(28)-C(29)	119.8(3)
C(14)-C(13)-C(12)	115.14(19)	C(28)-C(29)-C(30)	113.7(2)
C(21)-C(13)-C(12)	105.21(19)	C(28)-C(29)-H(29A)	108.8
C(14)-C(13)-H(13)	106.7	C(30)-C(29)-H(29A)	108.8
C(21)-C(13)-H(13)	106.7	C(28)-C(29)-H(29B)	108.8
C(12)-C(13)-H(13)	106.7	C(30)-C(29)-H(29B)	108.8
C(15)-C(14)-C(20)	117.3(2)	H(29A)-C(29)-H(29B)	107.7
C(15)-C(14)-C(13)	119.3(2)	N(1)-C(30)-C(29)	108.1(2)
C(20)-C(14)-C(13)	123.3(2)	N(1)-C(30)-H(30A)	110.1
C(14)-C(15)-C(16)	121.9(2)	C(29)-C(30)-H(30A)	110.1
C(14)-C(15)-H(15)	119.1	N(1)-C(30)-H(30B)	110.1
C(16)-C(15)-H(15)	119.1	C(29)-C(30)-H(30B)	110.1
C(17)-C(16)-C(15)	119.4(2)	H(30A)-C(30)-H(30B)	108.4
C(17)-C(16)-H(16)	120.3	C(30)-N(1)-C(22)	112.3(2)
C(15)-C(16)-H(16)	120.3	C(30)-N(1)-C(12)	118.0(2)
O(2)-C(17)-C(16)	124.9(2)	C(22)-N(1)-C(12)	107.51(19)
O(2)-C(17)-C(19)	115.7(2)	O(4)-N(2)-O(3)	124.3(3)
C(16)-C(17)-C(19)	119.3(2)	O(4)-N(2)-C(21)	118.7(3)
O(2)-C(18)-H(18A)	109.5	O(3)-N(2)-C(21)	116.9(3)
O(2)-C(18)-H(18B)	109.5	C(17)-O(2)-C(18)	118.1(2)

Table S8. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for compound **7f**

	x	y	z	U(eq)
C(1)	0.82986(18)	0.47015(19)	0.9203(2)	0.0488(6)
C(2)	0.8255(2)	0.37850(19)	0.9789(3)	0.0560(7)
C(3)	0.8623(2)	0.2922(2)	0.9717(3)	0.0759(10)
H(3)	0.8977	0.2826	0.9215	0.091
C(4)	0.8445(3)	0.2184(2)	1.0436(4)	0.0985(15)
H(4)	0.8684	0.1592	1.0392	0.118
C(5)	0.7932(3)	0.2307(3)	1.1192(4)	0.0963(14)
H(5)	0.7846	0.1803	1.1660	0.116
C(6)	0.7533(2)	0.3179(2)	1.1278(3)	0.0731(10)
C(7)	0.6991(3)	0.3423(3)	1.2008(3)	0.0891(13)
H(7)	0.6858	0.2975	1.2516	0.107
C(8)	0.6664(3)	0.4312(3)	1.1968(3)	0.0834(11)
H(8)	0.6302	0.4456	1.2445	0.100
C(9)	0.6854(2)	0.5022(2)	1.1231(3)	0.0641(8)
H(9)	0.6623	0.5624	1.1224	0.077
C(10)	0.73825(19)	0.48147(19)	1.0528(2)	0.0493(6)
C(11)	0.7718(2)	0.39013(19)	1.0551(3)	0.0547(7)
C(12)	0.76971(17)	0.54115(17)	0.9651(2)	0.0426(6)
C(13)	0.68977(16)	0.58509(17)	0.8560(2)	0.0411(6)
H(13)	0.6377	0.5889	0.8853	0.049
C(14)	0.65943(16)	0.52870(16)	0.7367(2)	0.0391(5)
C(15)	0.59195(18)	0.46183(19)	0.7190(2)	0.0485(6)
H(15)	0.5643	0.4551	0.7792	0.058
C(16)	0.56451(18)	0.40457(19)	0.6139(3)	0.0495(6)
H(16)	0.5190	0.3603	0.6040	0.059
C(17)	0.60534(17)	0.41409(18)	0.5244(2)	0.0450(6)
C(18)	0.5253(2)	0.2852(2)	0.4043(3)	0.0751(9)
H(18A)	0.4680	0.3081	0.4055	0.090
H(18B)	0.5497	0.2414	0.4714	0.090
H(18C)	0.5171	0.2545	0.3261	0.090
C(19)	0.67109(18)	0.48204(18)	0.5394(2)	0.0485(6)
H(19)	0.6975	0.4900	0.4780	0.058
C(20)	0.69786(17)	0.53789(18)	0.6436(2)	0.0457(6)
H(20)	0.7426	0.5828	0.6521	0.055
C(21)	0.71952(17)	0.68721(17)	0.8439(2)	0.0436(6)
H(21)	0.7150	0.7004	0.7574	0.052
C(22)	0.81870(16)	0.69174(17)	0.9300(2)	0.0408(6)
H(22)	0.8565	0.6671	0.8837	0.049
C(23)	0.85818(16)	0.78463(17)	0.9864(2)	0.0431(6)
C(24)	0.83907(18)	0.86683(18)	0.9156(3)	0.0509(7)
H(24)	0.8007	0.8648	0.8329	0.061
C(25)	0.8768(2)	0.9513(2)	0.9674(3)	0.0635(8)
H(25)	0.8638	1.0059	0.9198	0.076
C(26)	0.9334(2)	0.9543(2)	1.0896(4)	0.0718(9)
H(26)	0.9581	1.0113	1.1252	0.086
C(27)	0.9537(2)	0.8738(2)	1.1590(3)	0.0663(8)
H(27)	0.9928	0.8766	1.2412	0.080
C(28)	0.91694(18)	0.7874(2)	1.1091(3)	0.0513(7)
C(29)	0.9412(2)	0.7001(2)	1.1886(3)	0.0654(8)
H(29A)	0.9132	0.7036	1.2527	0.079
H(29B)	1.0064	0.6984	1.2300	0.079
C(30)	0.91163(19)	0.6102(2)	1.1158(3)	0.0584(7)
H(30A)	0.9531	0.5945	1.0718	0.070

Table S8. continuation

	x	y	z	U(eq)
H(30B)	0.9117	0.5591	1.1722	0.070
N(1)	0.82057(14)	0.62414(14)	1.02699(19)	0.0429(5)
N(2)	0.66230(16)	0.75600(17)	0.8864(3)	0.0593(6)
O(1)	0.87438(15)	0.49068(15)	0.8554(2)	0.0671(6)
O(2)	0.58586(14)	0.36100(15)	0.41888(19)	0.0657(6)
O(3)	0.63236(15)	0.82365(15)	0.8189(3)	0.0842(7)
O(4)	0.64971(17)	0.74155(18)	0.9845(3)	0.0889(8)

Table S9. Anisotropic displacement parameters (Å^2 × 10^3) for **7f**

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	0.0507(15)	0.0498(16)	0.0432(15)	–0.0010(12)	0.0124(13)	0.0095(12)
C(2)	0.0614(18)	0.0434(16)	0.0479(16)	–0.0014(13)	–0.0015(14)	0.0050(13)
C(3)	0.086(2)	0.0497(18)	0.068(2)	–0.0051(16)	–0.0059(18)	0.0119(16)
C(4)	0.115(4)	0.0370(19)	0.096(3)	–0.001(2)	–0.027(3)	0.0048(19)
C(5)	0.110(3)	0.058(2)	0.080(3)	0.019(2)	–0.022(2)	–0.031(2)
C(6)	0.086(2)	0.052(2)	0.0552(19)	0.0114(15)	–0.0102(18)	–0.0279(17)
C(7)	0.097(3)	0.104(3)	0.052(2)	0.022(2)	0.006(2)	–0.047(2)
C(8)	0.088(3)	0.113(3)	0.053(2)	0.005(2)	0.0278(19)	–0.037(2)
C(9)	0.074(2)	0.078(2)	0.0452(17)	–0.0052(15)	0.0265(16)	–0.0208(17)
C(10)	0.0599(17)	0.0483(16)	0.0381(14)	–0.0024(12)	0.0144(12)	–0.0133(13)
C(11)	0.0630(18)	0.0470(17)	0.0420(15)	0.0015(12)	0.0017(13)	–0.0136(13)
C(12)	0.0478(14)	0.0410(14)	0.0399(14)	–0.0006(11)	0.0159(12)	–0.0002(11)
C(13)	0.0383(13)	0.0427(14)	0.0453(14)	–0.0013(11)	0.0181(12)	0.0013(10)
C(14)	0.0399(13)	0.0355(13)	0.0422(13)	0.0022(11)	0.0141(11)	0.0031(10)
C(15)	0.0492(15)	0.0528(16)	0.0500(15)	–0.0006(13)	0.0252(13)	–0.0059(12)
C(16)	0.0434(14)	0.0504(16)	0.0554(16)	–0.0032(13)	0.0176(13)	–0.0141(12)
C(17)	0.0421(14)	0.0451(14)	0.0457(15)	–0.0044(12)	0.0119(12)	–0.0005(11)
C(18)	0.066(2)	0.077(2)	0.073(2)	–0.0281(18)	0.0126(17)	–0.0207(17)
C(19)	0.0525(16)	0.0554(17)	0.0444(15)	–0.0017(13)	0.0251(13)	–0.0062(12)
C(20)	0.0467(14)	0.0424(14)	0.0517(15)	–0.0008(12)	0.0212(13)	–0.0079(11)
C(21)	0.0459(14)	0.0379(14)	0.0457(14)	–0.0050(11)	0.0135(12)	0.0047(11)
C(22)	0.0404(13)	0.0402(14)	0.0456(14)	0.0010(11)	0.0194(11)	0.0022(10)
C(23)	0.0380(13)	0.0453(14)	0.0518(16)	–0.0045(12)	0.0226(12)	–0.0029(11)
C(24)	0.0451(15)	0.0453(15)	0.0640(18)	–0.0026(13)	0.0205(13)	–0.0005(12)
C(25)	0.0572(19)	0.0452(17)	0.090(2)	–0.0028(16)	0.0271(18)	–0.0033(14)
C(26)	0.062(2)	0.055(2)	0.100(3)	–0.0221(19)	0.028(2)	–0.0154(16)
C(27)	0.0598(19)	0.071(2)	0.067(2)	–0.0182(17)	0.0194(16)	–0.0172(16)
C(28)	0.0471(15)	0.0596(17)	0.0521(17)	–0.0084(14)	0.0233(13)	–0.0112(13)
C(29)	0.0584(18)	0.079(2)	0.0514(17)	0.0010(16)	0.0084(14)	–0.0163(16)
C(30)	0.0495(16)	0.0656(19)	0.0545(17)	0.0089(14)	0.0100(14)	–0.0010(14)
C(31)	0.0402(11)	0.0439(12)	0.0432(12)	0.0015(10)	0.0121(9)	–0.0016(9)
C(32)	0.0416(13)	0.0472(14)	0.0818(19)	–0.0175(13)	0.0109(13)	0.0011(11)
C(33)	0.0694(14)	0.0739(14)	0.0694(14)	0.0114(11)	0.0383(12)	0.0246(11)
C(34)	0.0662(13)	0.0744(14)	0.0585(12)	–0.0248(11)	0.0236(11)	–0.0211(11)
C(35)	0.0609(14)	0.0505(13)	0.123(2)	–0.0066(14)	0.0074(14)	0.0184(11)
C(36)	0.0887(18)	0.0922(18)	0.104(2)	–0.0220(15)	0.0563(17)	0.0118(14)

Table S10. Torsion angles (degree) for compound **7f**

O(1)-C(1)-C(2)-C(3)	–5.2(5)	C(14)-C(15)-C(16)-C(17)	0.1(4)
C(12)-C(1)-C(2)-C(3)	178.5(3)	C(15)-C(16)-C(17)-O(2)	178.5(3)
O(1)-C(1)-C(2)-C(11)	174.5(3)	C(15)-C(16)-C(17)-C(19)	–1.7(4)
C(12)-C(1)-C(2)-C(11)	–1.8(3)	O(2)-C(17)-C(19)-C(20)	–178.3(2)
C(11)-C(2)-C(3)-C(4)	–0.4(4)	C(16)-C(17)-C(19)-C(20)	1.9(4)
C(1)-C(2)-C(3)-C(4)	179.2(3)	C(17)-C(19)-C(20)-C(14)	–0.6(4)
C(2)-C(3)-C(4)-C(5)	–0.6(5)	C(15)-C(14)-C(20)-C(19)	–1.0(4)
C(3)-C(4)-C(5)-C(6)	1.4(6)	C(13)-C(14)-C(20)-C(19)	176.8(2)
C(4)-C(5)-C(6)-C(11)	–1.2(5)	C(14)-C(13)-C(21)-N(2)	121.3(2)
C(4)-C(5)-C(6)-C(7)	–179.9(4)	C(12)-C(13)-C(21)-N(2)	–110.4(2)
C(5)-C(6)-C(7)-C(8)	179.9(4)	C(14)-C(13)-C(21)-C(22)	–119.6(2)
C(11)-C(6)-C(7)-C(8)	1.2(5)	C(12)-C(13)-C(21)-C(22)	8.6(2)
C(6)-C(7)-C(8)-C(9)	–1.0(5)	N(2)-C(21)-C(22)-N(1)	88.4(2)
C(7)-C(8)-C(9)-C(10)	0.2(5)	C(13)-C(21)-C(22)-N(1)	–30.7(2)
C(8)-C(9)-C(10)-C(11)	0.3(4)	N(2)-C(21)-C(22)-C(23)	–34.4(3)
C(8)-C(9)-C(10)-C(12)	179.6(3)	C(13)-C(21)-C(22)-C(23)	–153.5(2)
C(9)-C(10)-C(11)-C(2)	–179.8(3)	N(1)-C(22)-C(23)-C(28)	22.3(3)
C(12)-C(10)-C(11)-C(2)	0.8(3)	C(21)-C(22)-C(23)-C(28)	140.7(2)
C(9)-C(10)-C(11)-C(6)	0.0(4)	N(1)-C(22)-C(23)-C(24)	–160.1(2)
C(12)-C(10)-C(11)-C(6)	–179.5(2)	C(21)-C(22)-C(23)-C(24)	–41.7(3)
C(3)-C(2)-C(11)-C(10)	–179.6(3)	C(28)-C(23)-C(24)-C(25)	–1.3(4)
C(1)-C(2)-C(11)-C(10)	0.7(3)	C(22)-C(23)-C(24)-C(25)	–178.9(2)
C(3)-C(2)-C(11)-C(6)	0.7(4)	C(23)-C(24)-C(25)-C(26)	0.0(4)
C(1)-C(2)-C(11)-C(6)	–179.1(3)	C(24)-C(25)-C(26)-C(27)	1.1(5)
C(5)-C(6)-C(11)-C(10)	–179.6(3)	C(25)-C(26)-C(27)-C(28)	–0.9(5)
C(7)-C(6)-C(11)-C(10)	–0.7(4)	C(24)-C(23)-C(28)-C(27)	1.5(4)
C(5)-C(6)-C(11)-C(2)	0.1(4)	C(22)-C(23)-C(28)-C(27)	179.1(2)
C(7)-C(6)-C(11)-C(2)	179.0(3)	C(24)-C(23)-C(28)-C(29)	–178.8(2)
C(9)-C(10)-C(12)-N(1)	57.7(4)	C(22)-C(23)-C(28)-C(29)	–1.1(4)
C(11)-C(10)-C(12)-N(1)	–122.9(2)	C(26)-C(27)-C(28)-C(23)	–0.4(4)
C(9)-C(10)-C(12)-C(13)	–58.0(4)	C(26)-C(27)-C(28)-C(29)	179.8(3)
C(11)-C(10)-C(12)-C(13)	121.3(2)	C(23)-C(28)-C(29)-C(30)	11.6(4)
C(9)-C(10)-C(12)-C(1)	178.9(3)	C(27)-C(28)-C(29)-C(30)	–168.6(3)
C(11)-C(10)-C(12)-C(1)	–1.8(3)	C(28)-C(29)-C(30)-N(1)	–42.4(3)
O(1)-C(1)-C(12)-N(1)	–53.2(3)	C(29)-C(30)-N(1)-C(22)	67.2(3)
C(2)-C(1)-C(12)-N(1)	123.2(2)	C(29)-C(30)-N(1)-C(12)	–166.8(2)
O(1)-C(1)-C(12)-C(10)	–174.3(3)	C(23)-C(22)-N(1)-C(30)	–56.6(3)
C(2)-C(1)-C(12)-C(10)	2.2(3)	C(21)-C(22)-N(1)-C(30)	175.1(2)
O(1)-C(1)-C(12)-C(13)	63.1(3)	C(23)-C(22)-N(1)-C(12)	172.00(19)
C(2)-C(1)-C(12)-C(13)	–120.5(2)	C(21)-C(22)-N(1)-C(12)	43.7(2)
N(1)-C(12)-C(13)-C(14)	145.0(2)	C(10)-C(12)-N(1)-C(30)	72.0(3)
C(10)-C(12)-C(13)-C(14)	–93.5(2)	C(13)-C(12)-N(1)-C(30)	–166.0(2)
C(1)-C(12)-C(13)-C(14)	23.0(3)	C(1)-C(12)-N(1)-C(30)	–43.1(3)
N(1)-C(12)-C(13)-C(21)	16.4(2)	C(10)-C(12)-N(1)-C(22)	–159.8(2)
C(10)-C(12)-C(13)-C(21)	137.9(2)	C(13)-C(12)-N(1)-C(22)	–37.7(2)
C(1)-C(12)-C(13)-C(21)	–105.6(2)	C(1)-C(12)-N(1)-C(22)	85.2(2)
C(21)-C(13)-C(14)-C(15)	–146.9(2)	C(22)-C(21)-N(2)-O(4)	–68.2(3)
C(12)-C(13)-C(14)-C(15)	89.9(3)	C(13)-C(21)-N(2)-O(4)	47.2(3)
C(21)-C(13)-C(14)-C(20)	35.3(3)	C(22)-C(21)-N(2)-O(3)	111.1(3)
C(12)-C(13)-C(14)-C(20)	–87.9(3)	C(13)-C(21)-N(2)-O(3)	–133.5(2)
C(20)-C(14)-C(15)-C(16)	1.2(4)	C(16)-C(17)-O(2)-C(18)	–5.8(4)
C(13)-C(14)-C(15)-C(16)	–176.7(2)	C(19)-C(17)-O(2)-C(18)	174.4(3)

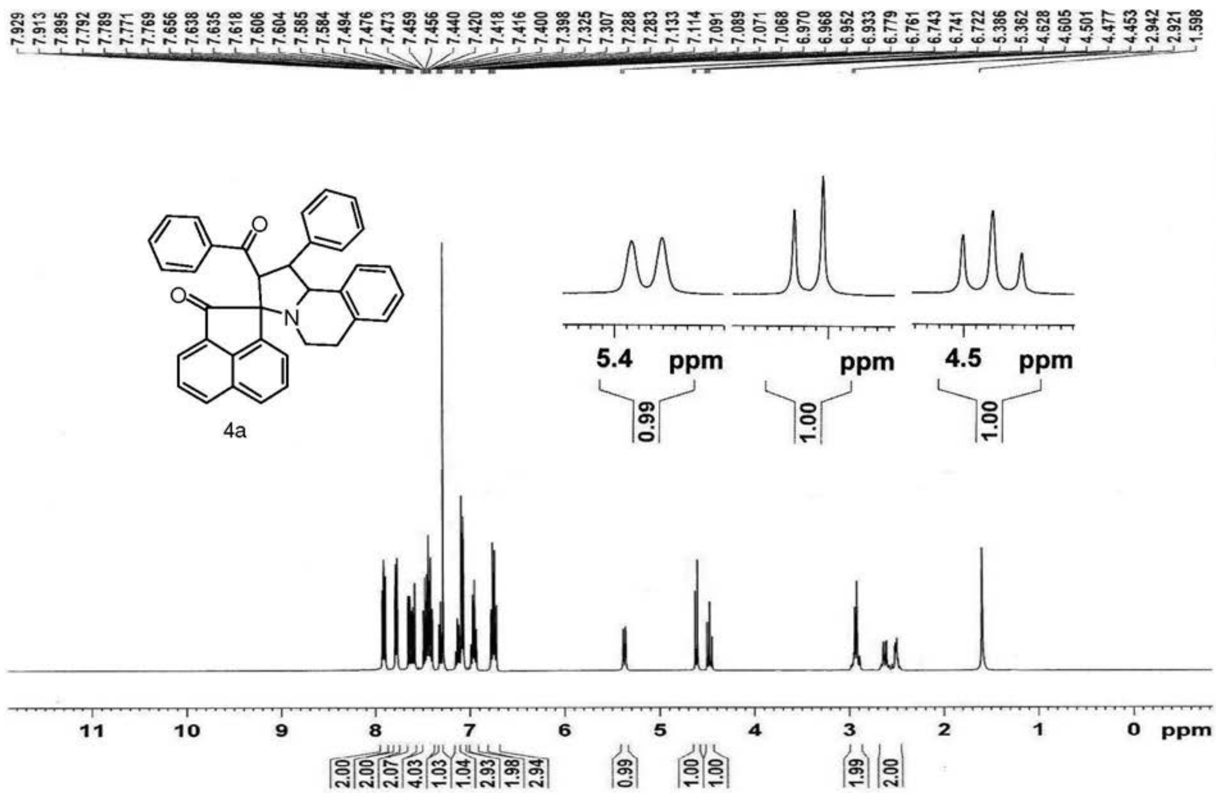

Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) of (**4a**).

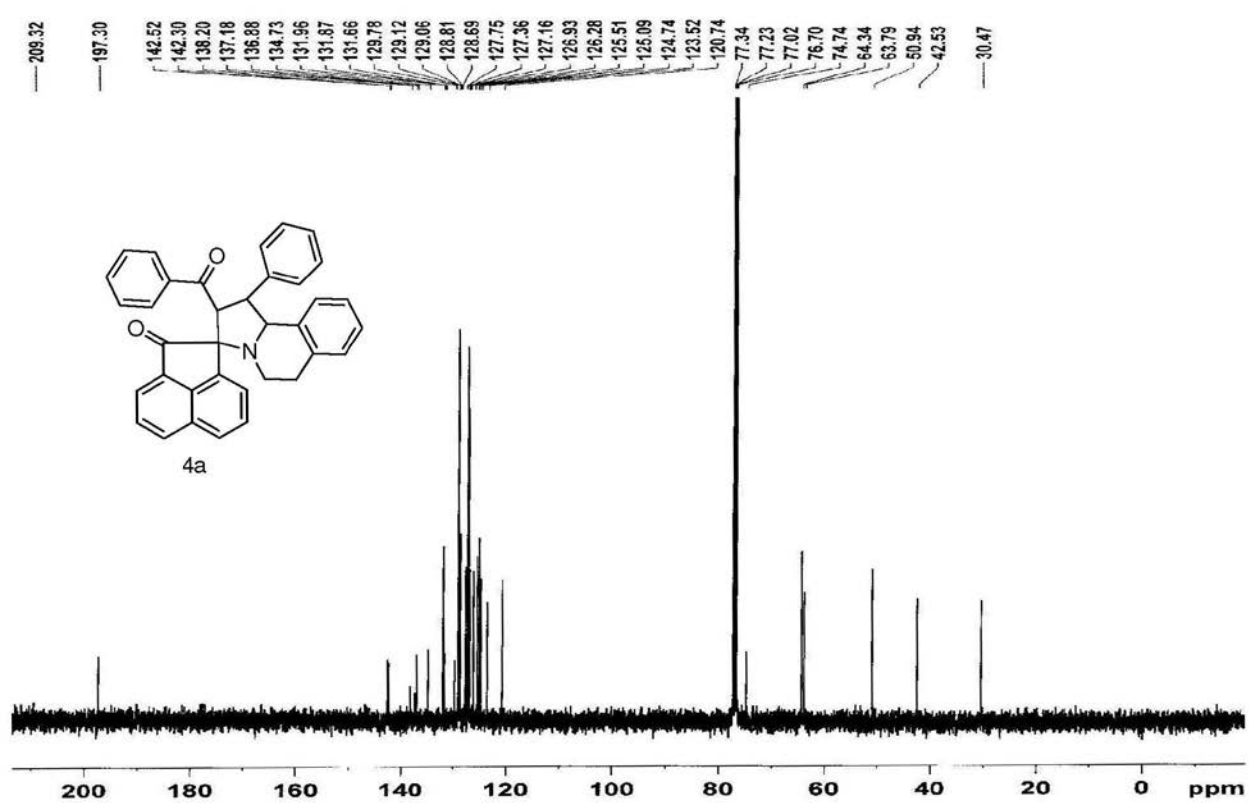

Figure S2. ^{13}C NMR (100 MHz, $CDCl_3$) of (**4a**).

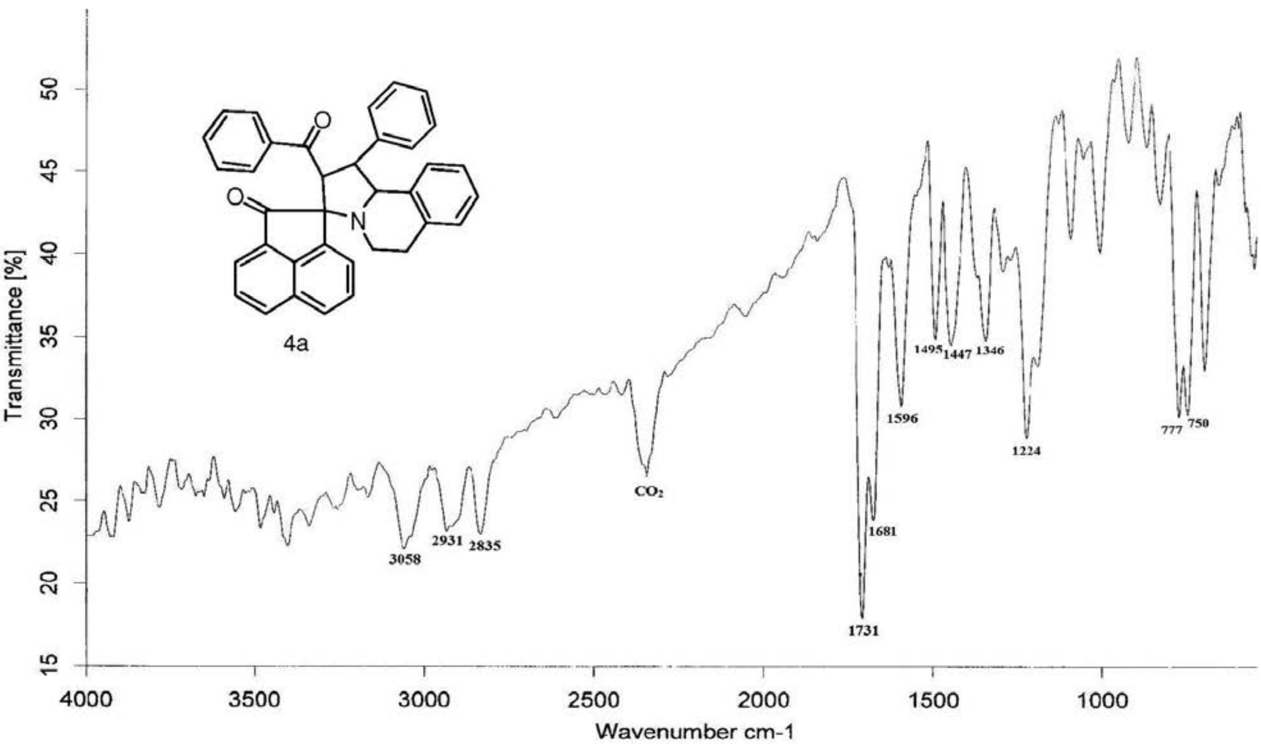

Figure S3. IR (KBr) of (**4a**).

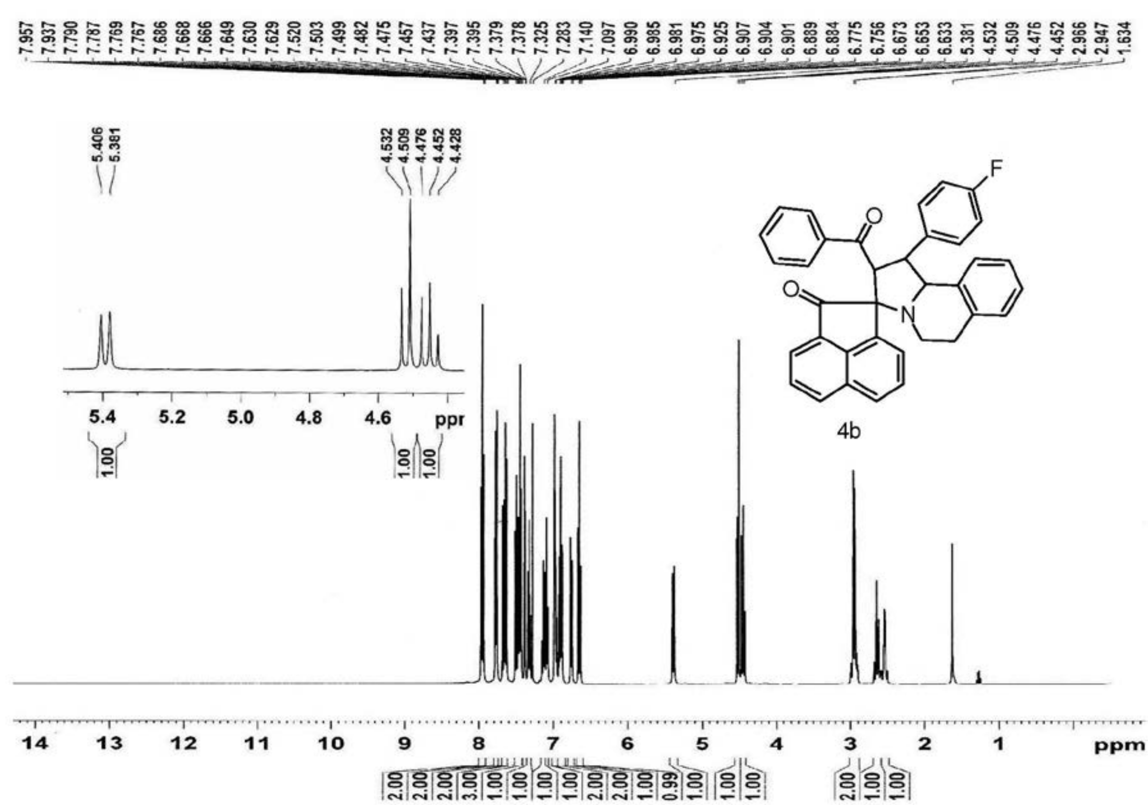

Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$) of (**4b**).

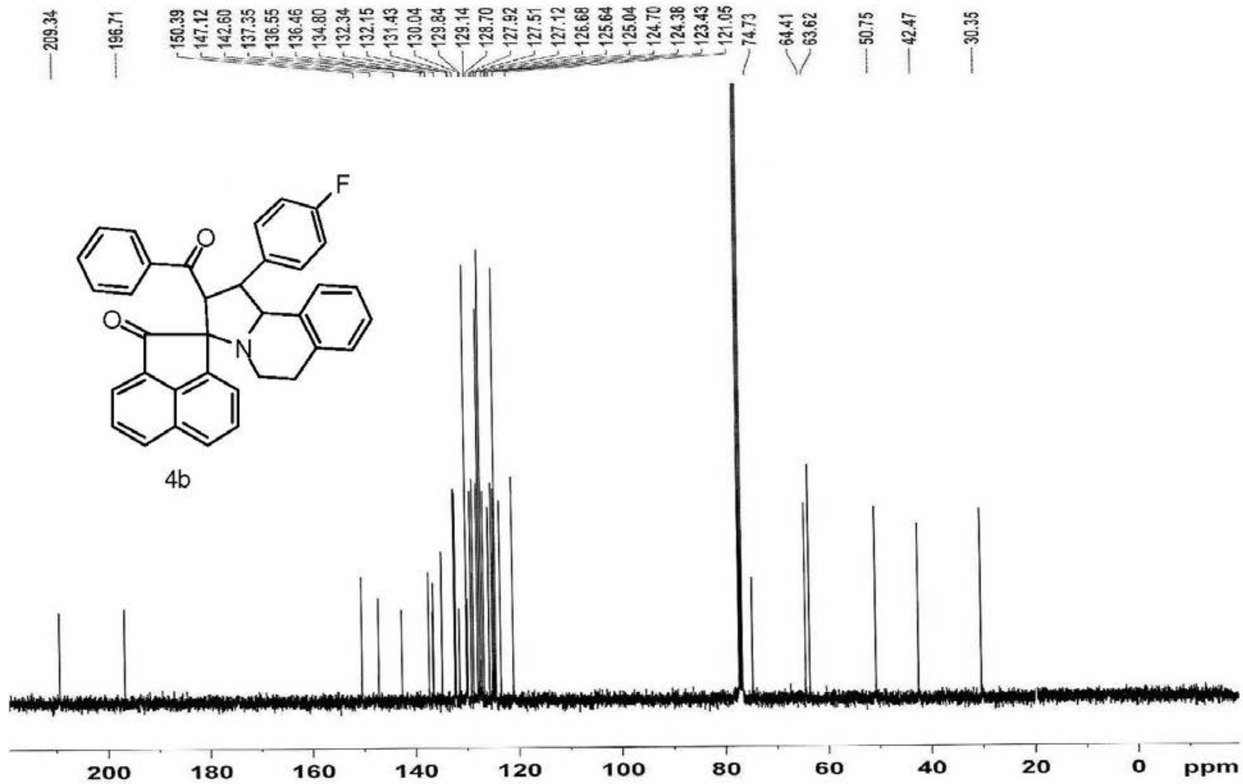

Figure S5. ^{13}C NMR (100 MHz, $CDCl_3$) of (**4b**).

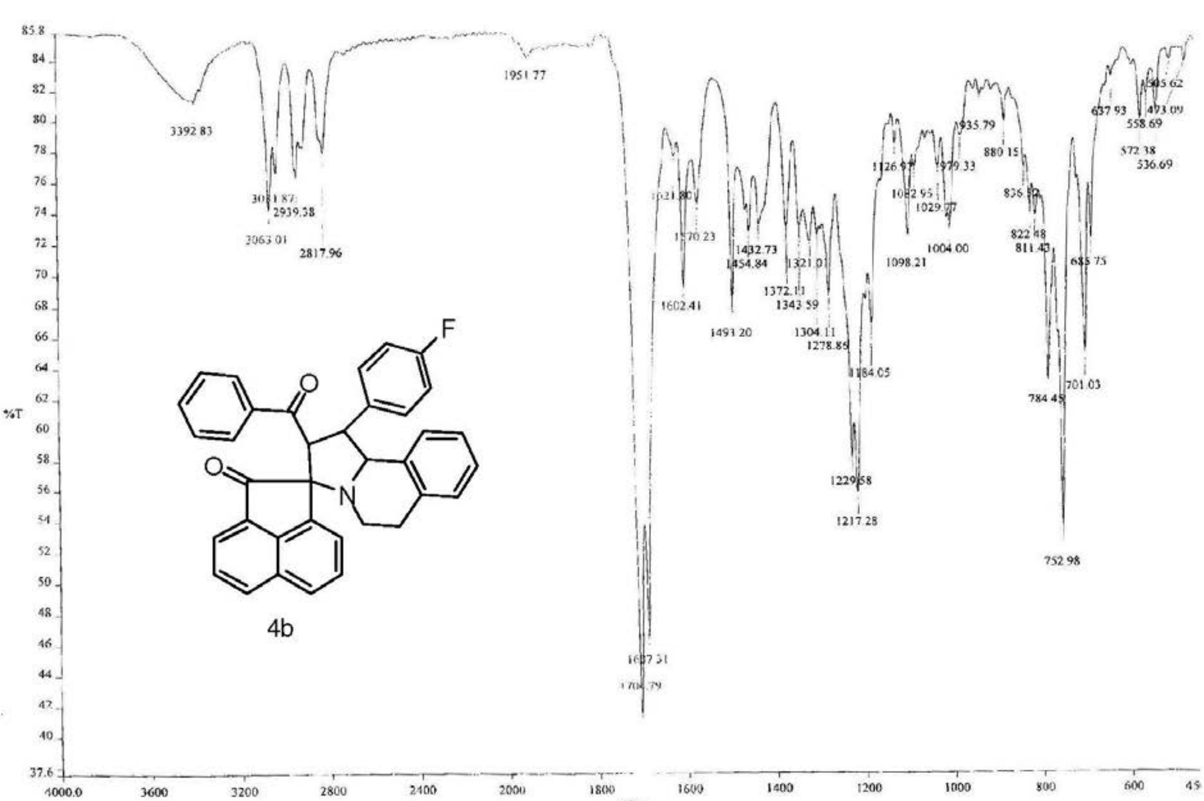

Figure S6. IR (film) of (**4b**).

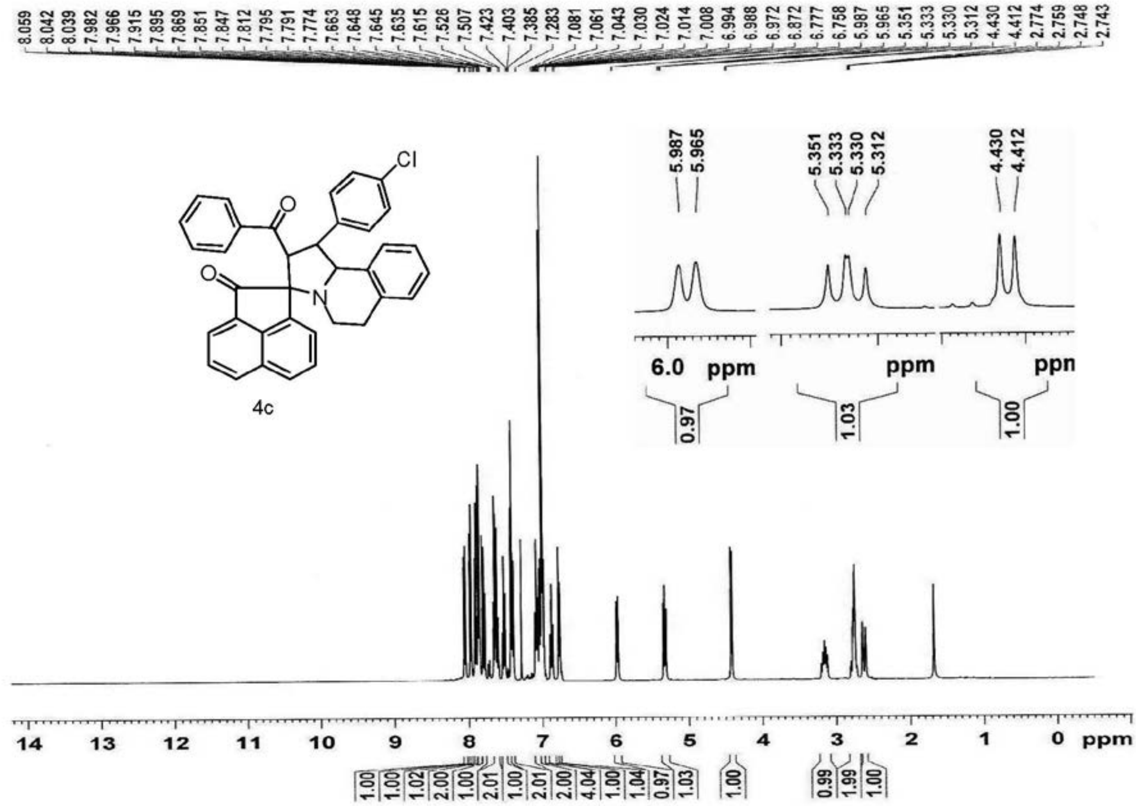

Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) of (**4c**).

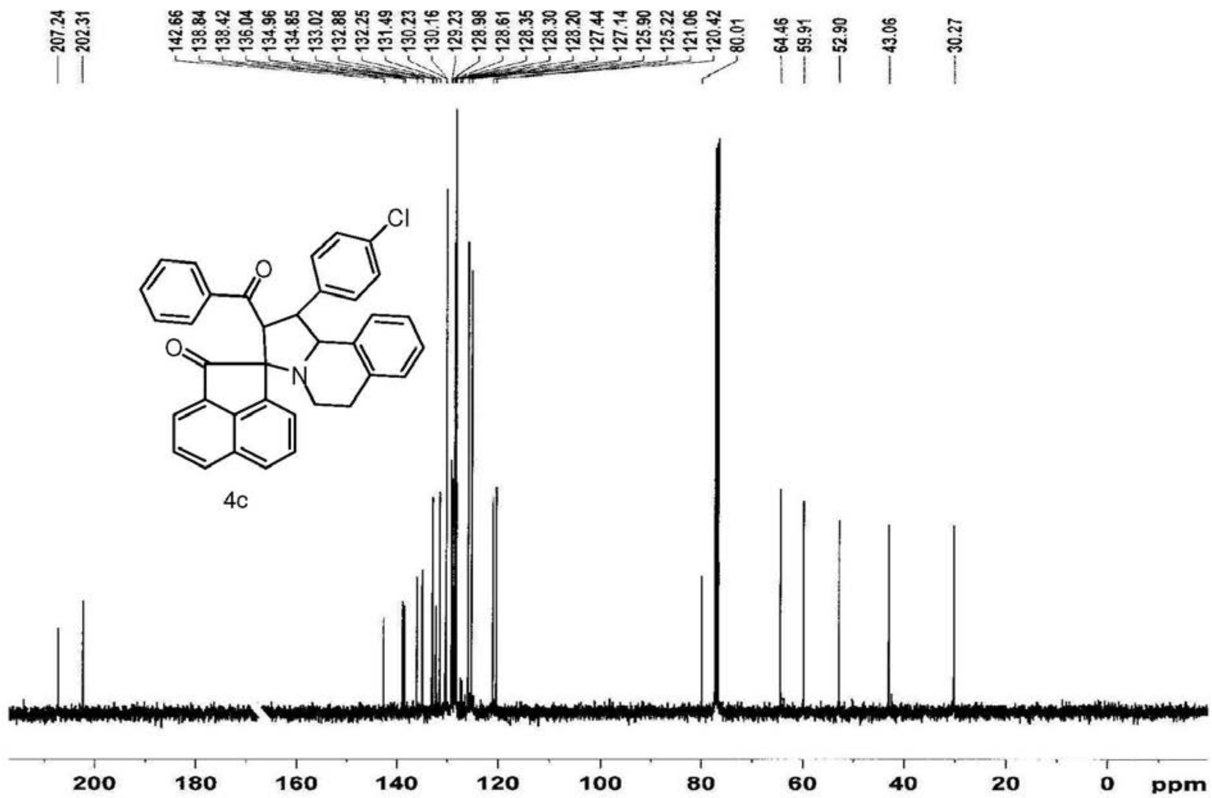

Figure S8. ^{13}C NMR (100 MHz, $CDCl_3$) of (**4c**).

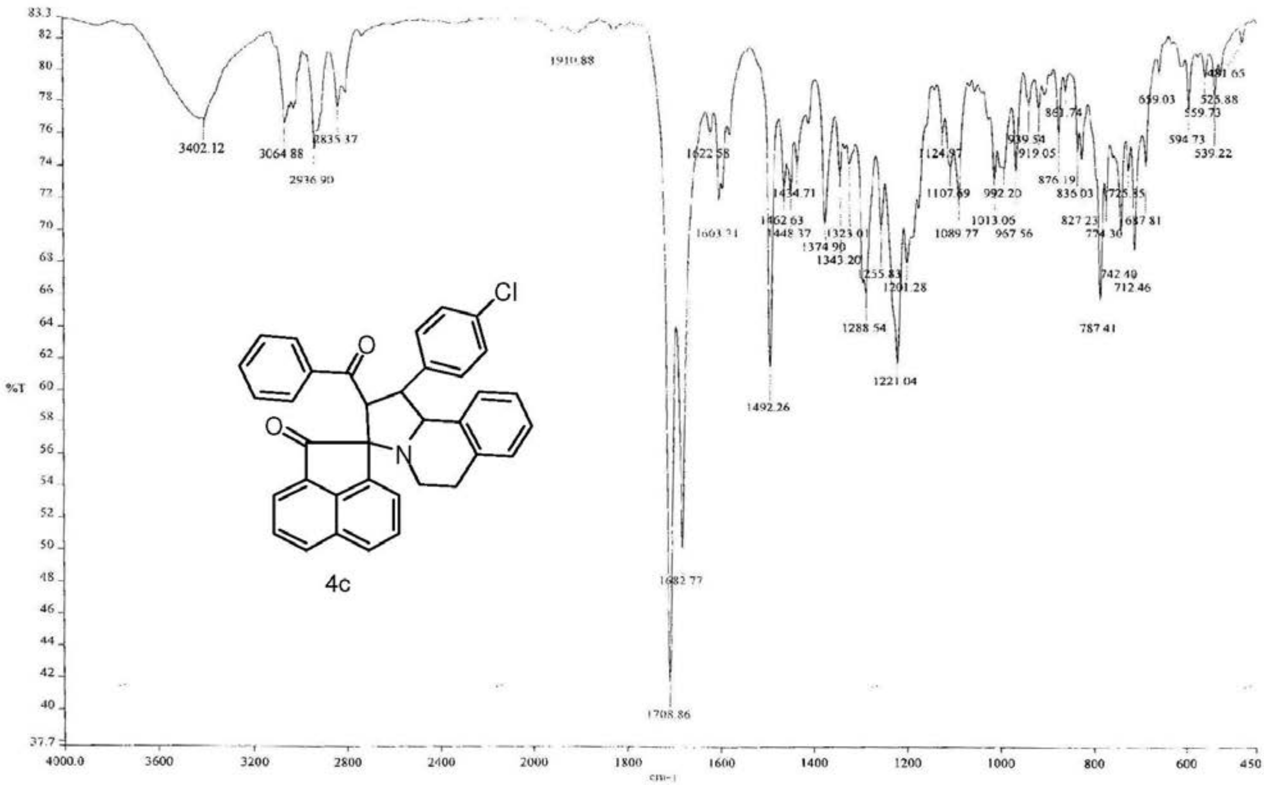

Figure S9. IR (KBr) of (**4c**).

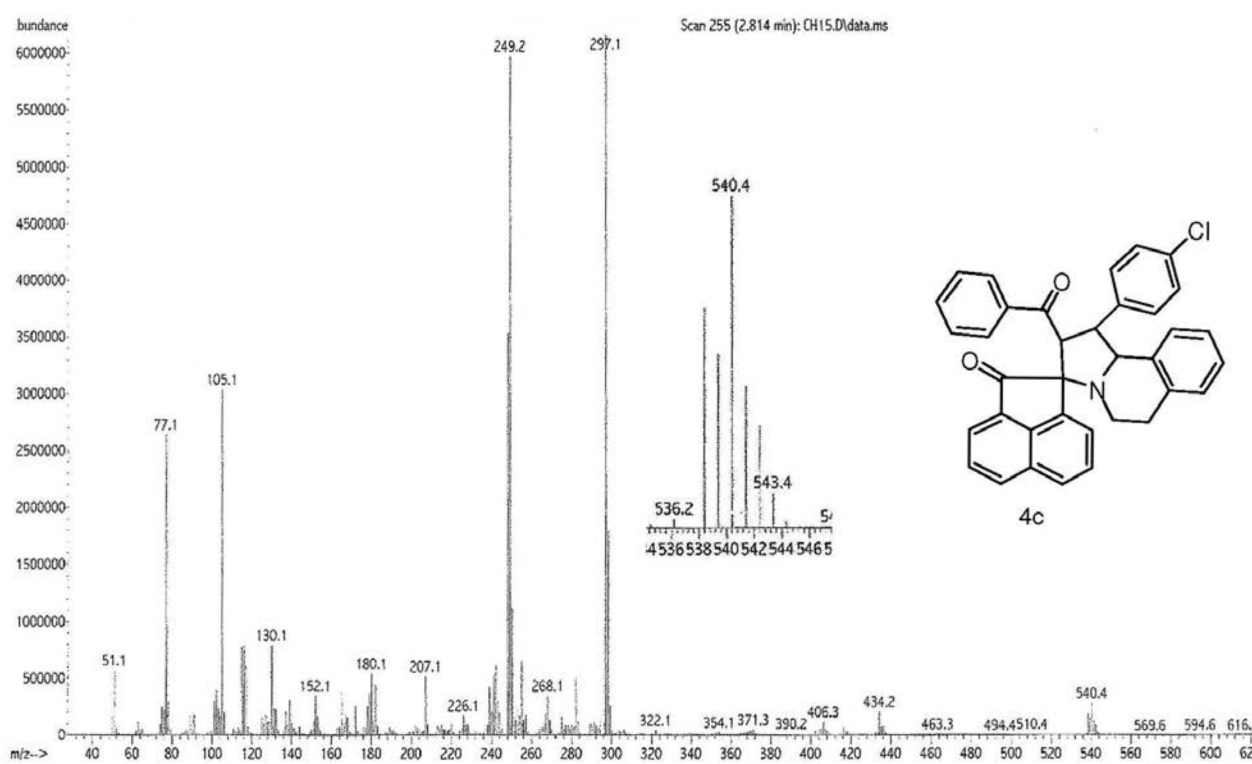

Figure S10. MS (70 eV) of (**4c**).

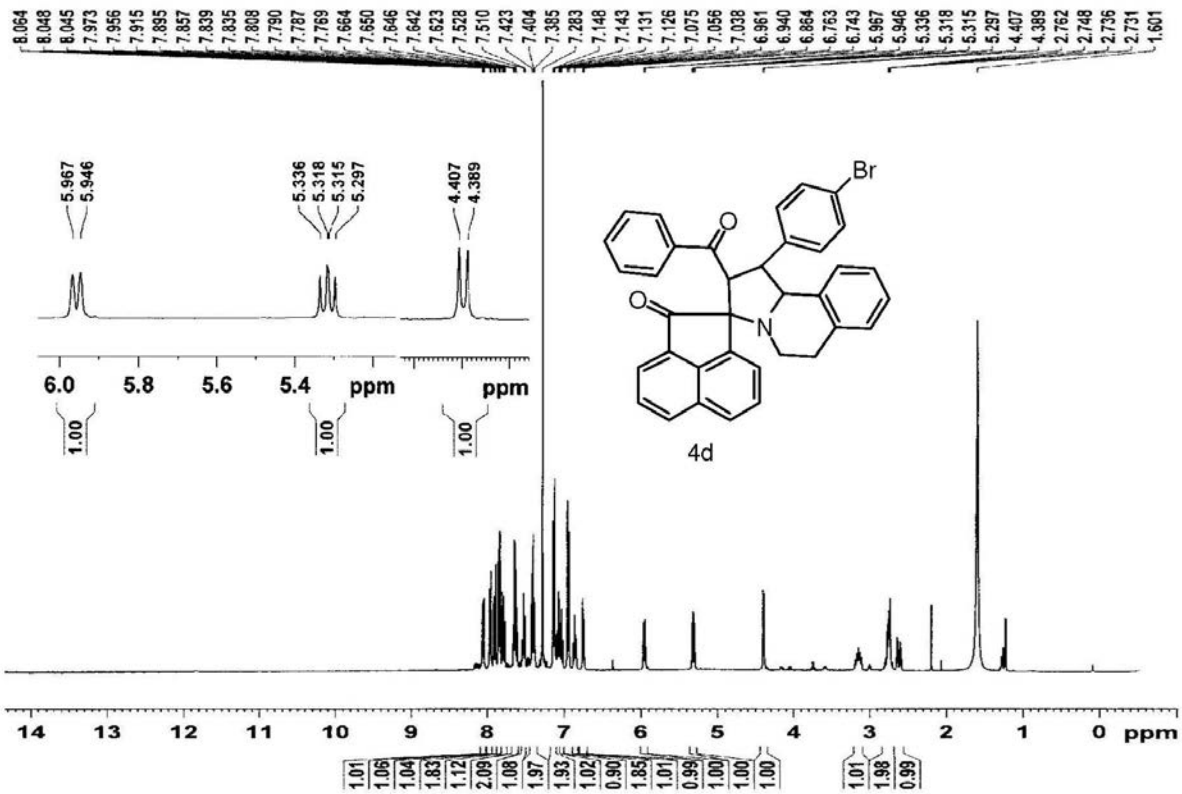

Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) of (**4d**).

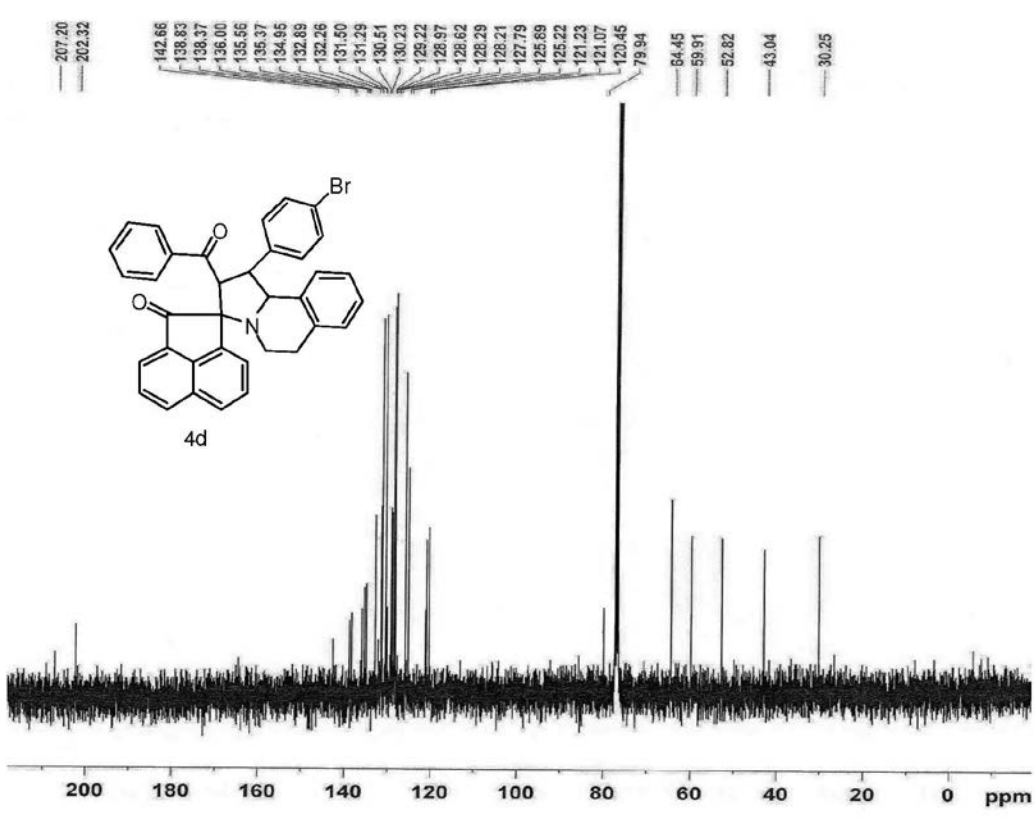

Figure S12. ^{13}C NMR (100 MHz, $CDCl_3$) of (**4d**).

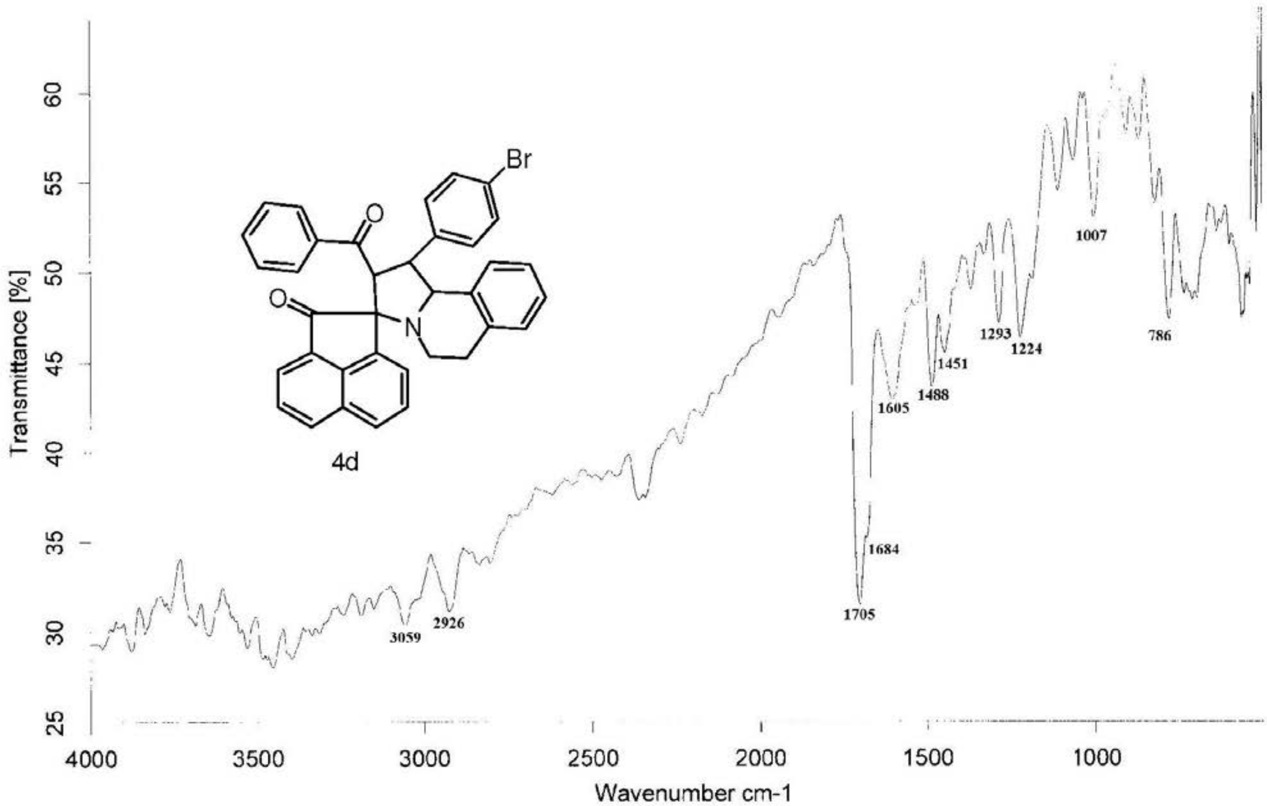

Figure S13. IR (KBr) of (**4d**).

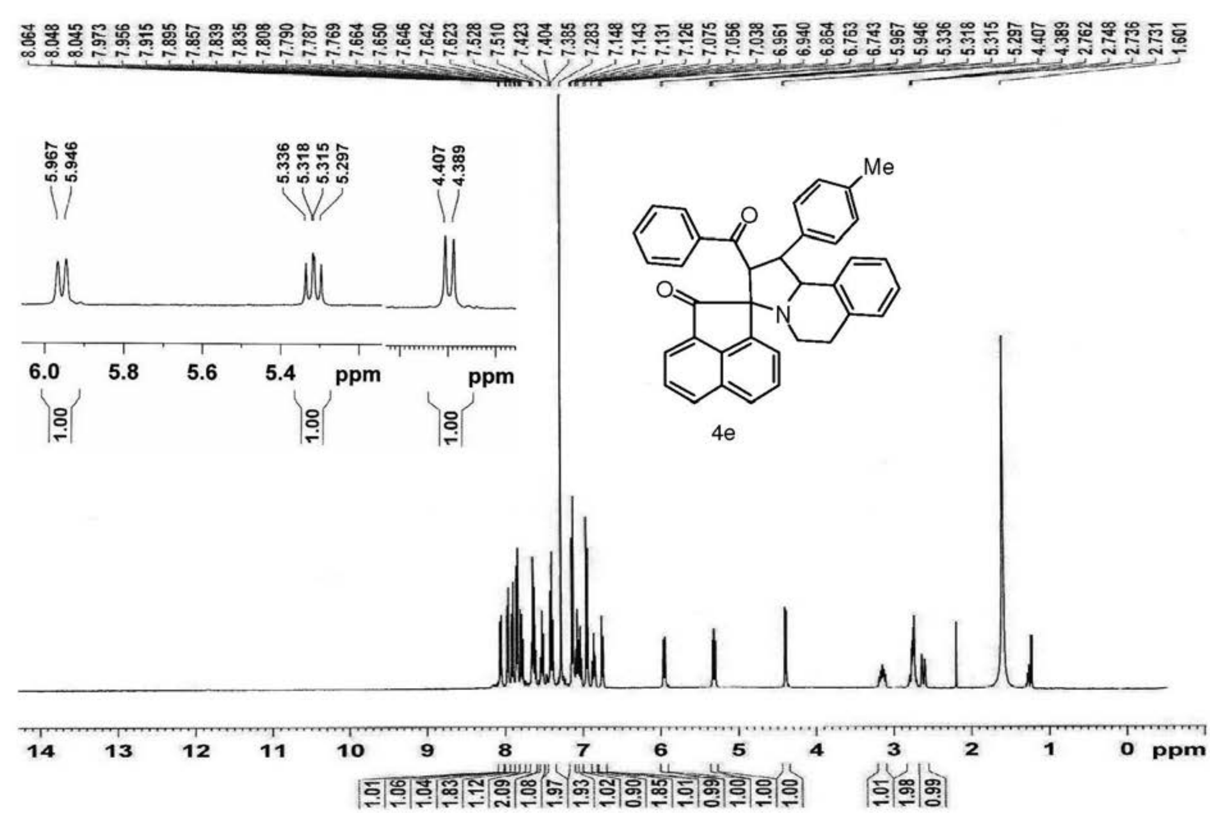

Figure S14. ^{1}H NMR (400 MHz, $CDCl_3$) of (**4e**).

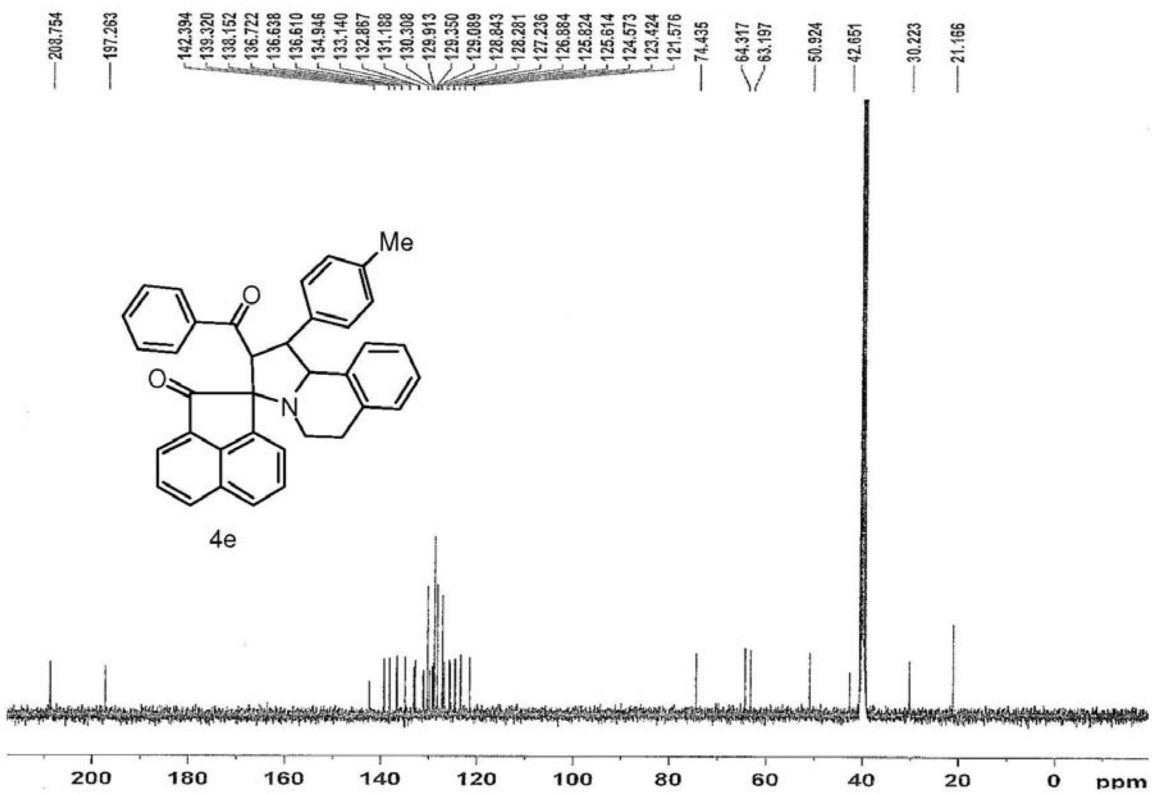

Figure S15. ^{13}C NMR (100 MHz, $CDCl_3$) of (**4e**).

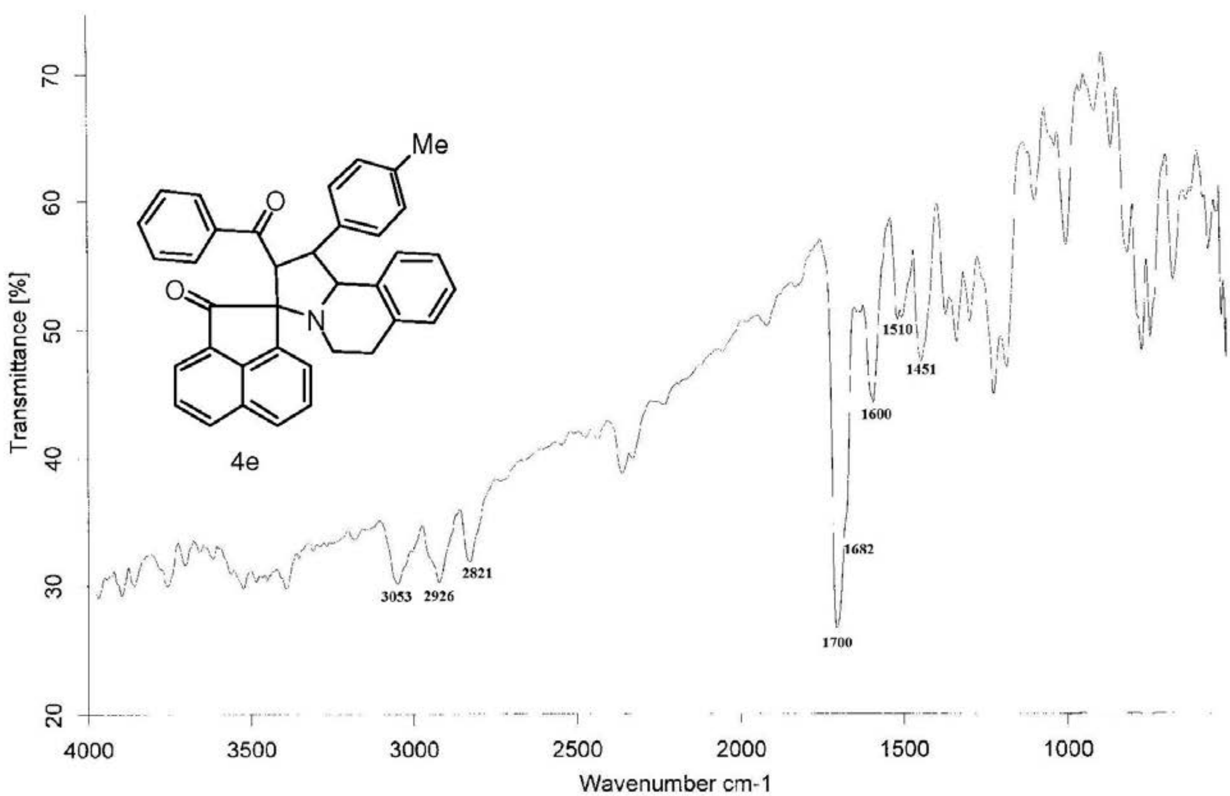

Figure S16. IR (KBr) of (**4e**).

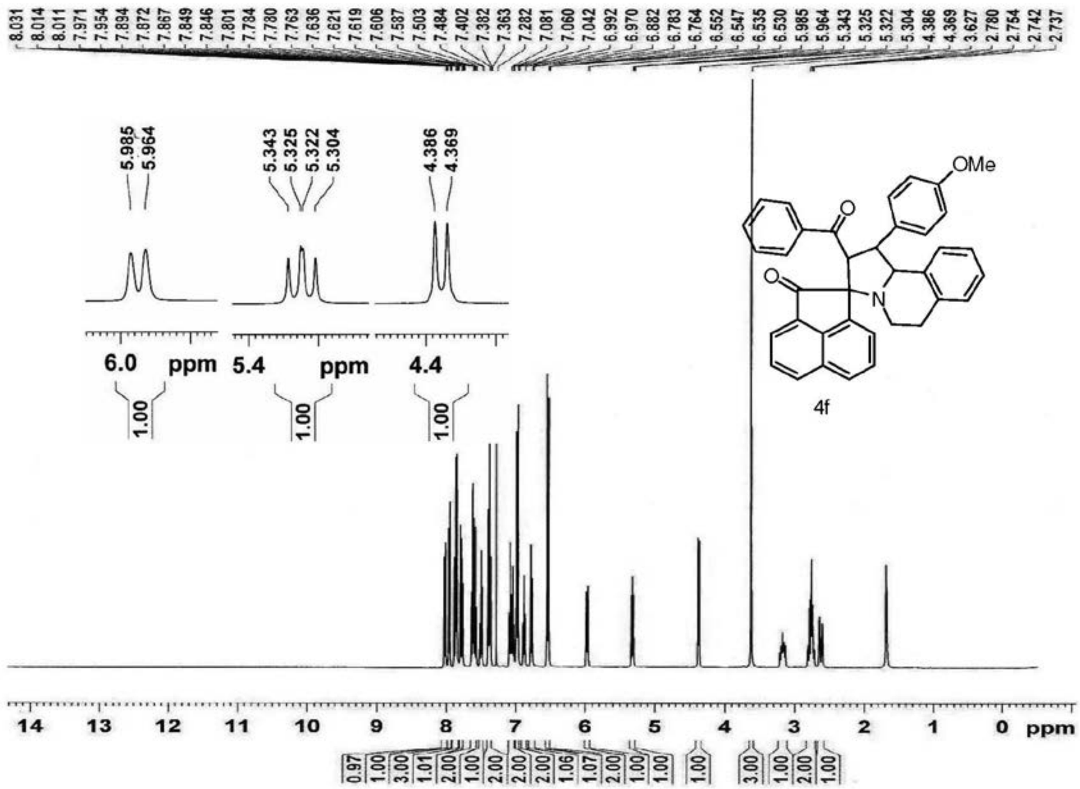

Figure S17. [1]H NMR (400 MHz, $CDCl_3$) of (**4f**).

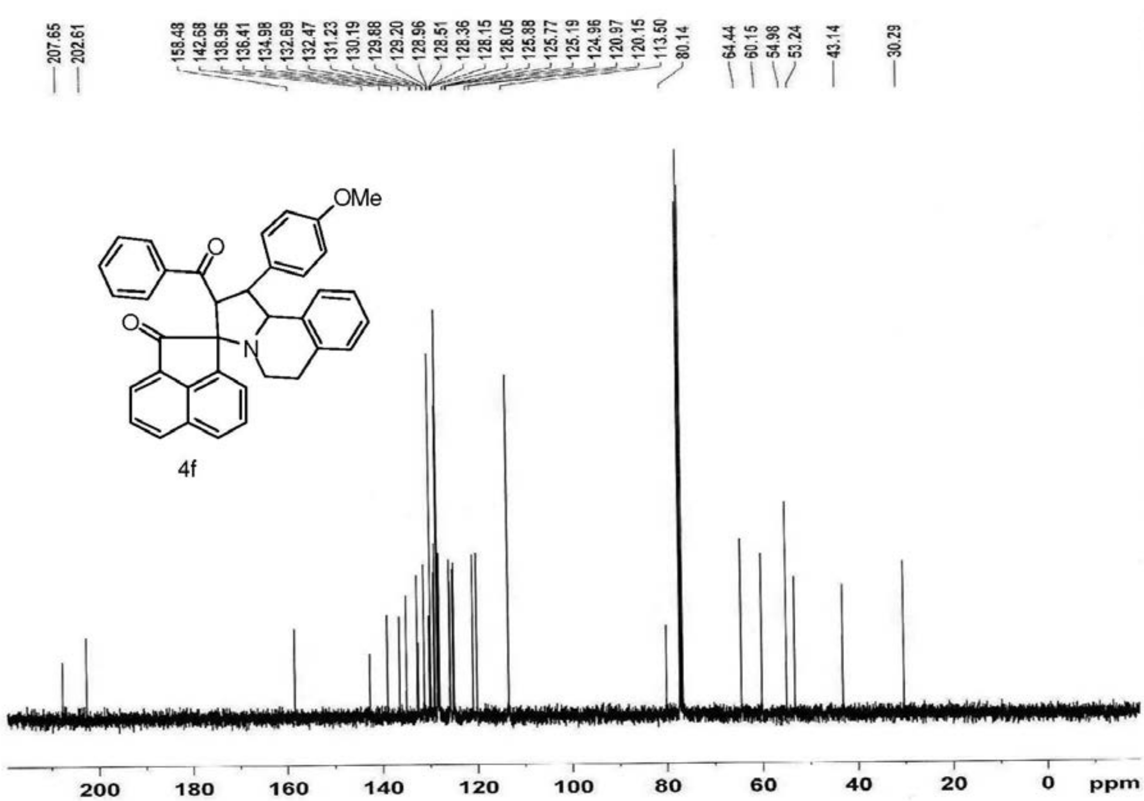

Figure S18. [13]C NMR (100 MHz, $CDCl_3$) of (**4f**).

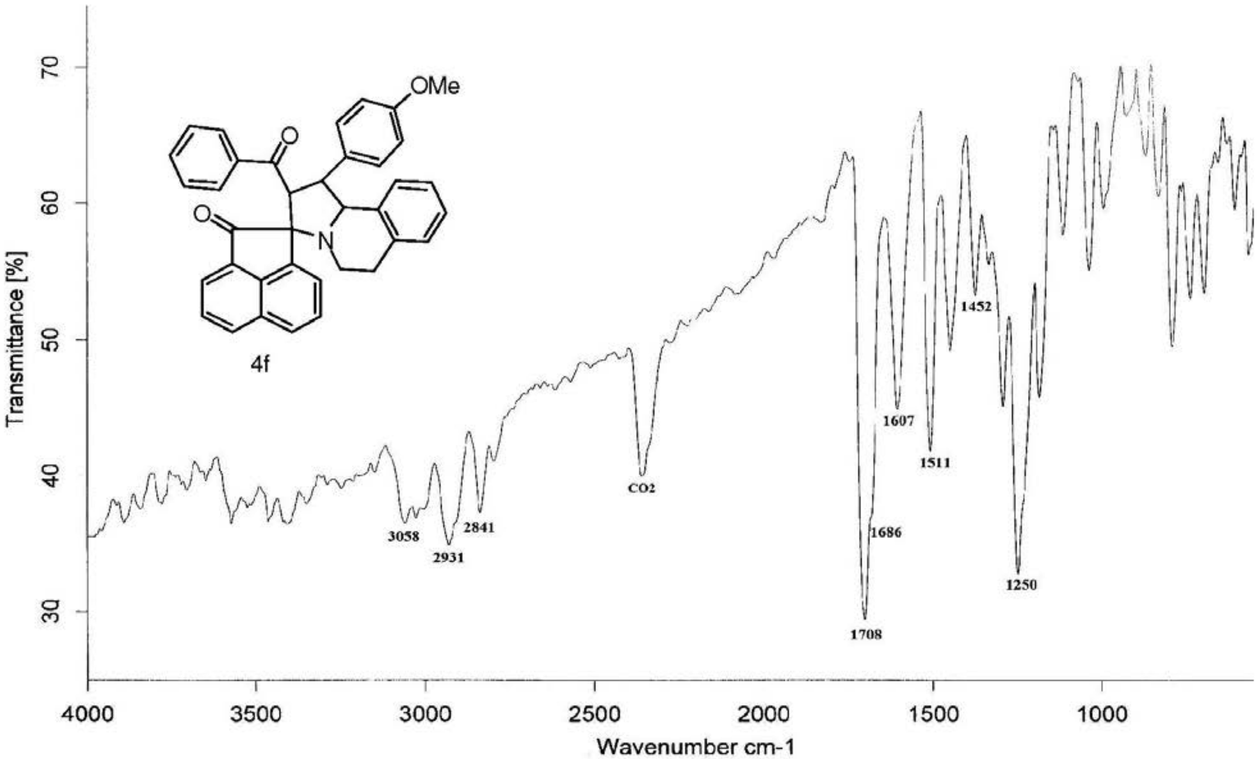

Figure S19. IR (KBr) of (**4f**).

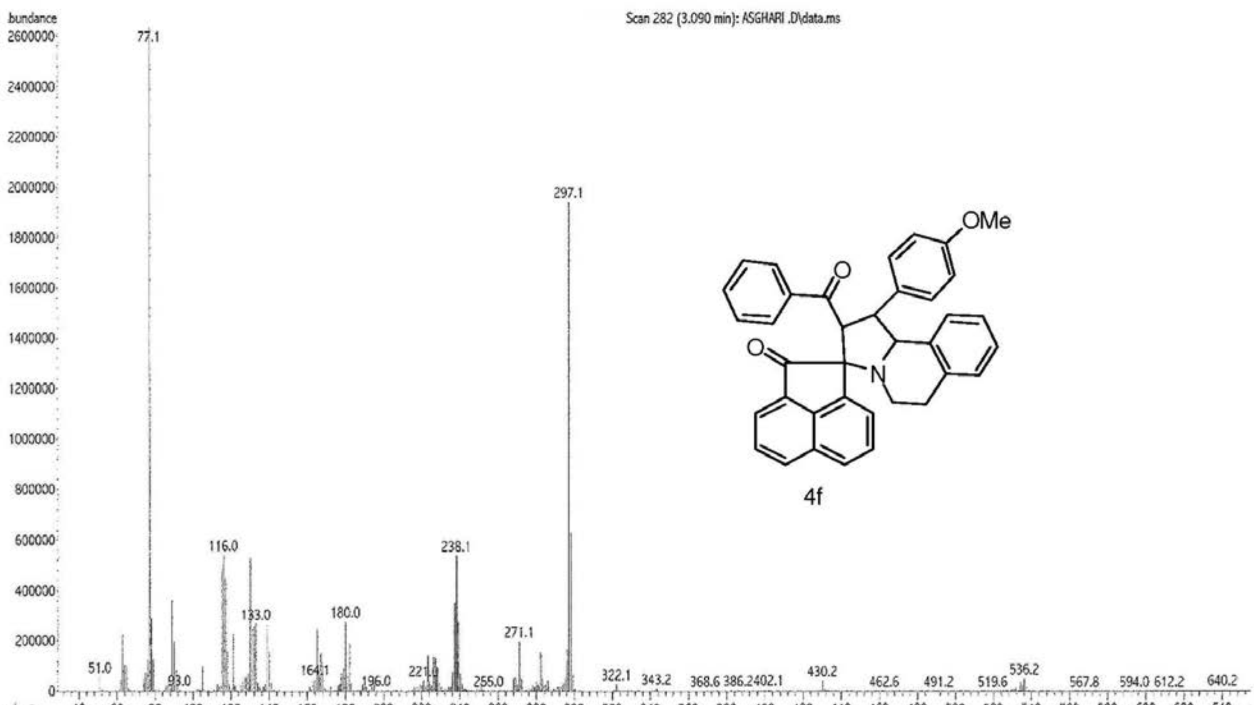

Figure S20. MS (70 eV) of (**4f**).

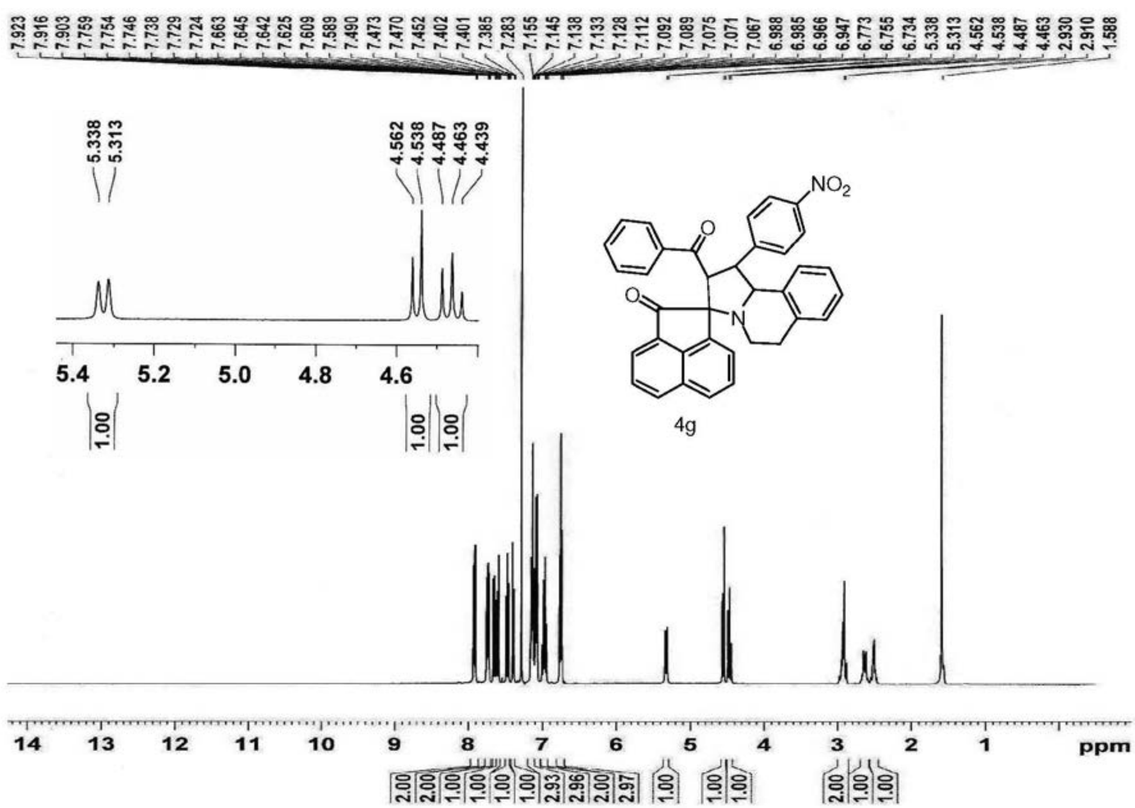

Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$) of (**4g**).

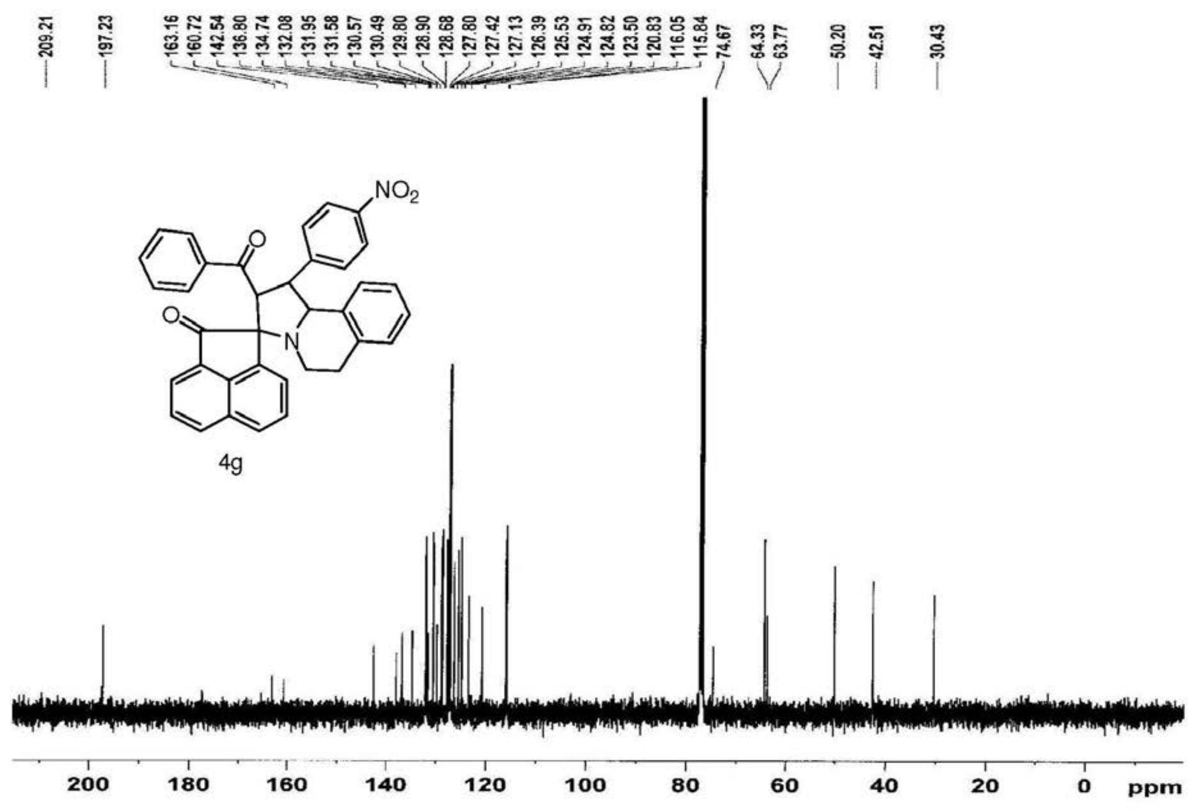

Figure S22. ^{13}C NMR (100 MHz, $CDCl_3$) of (**4g**).

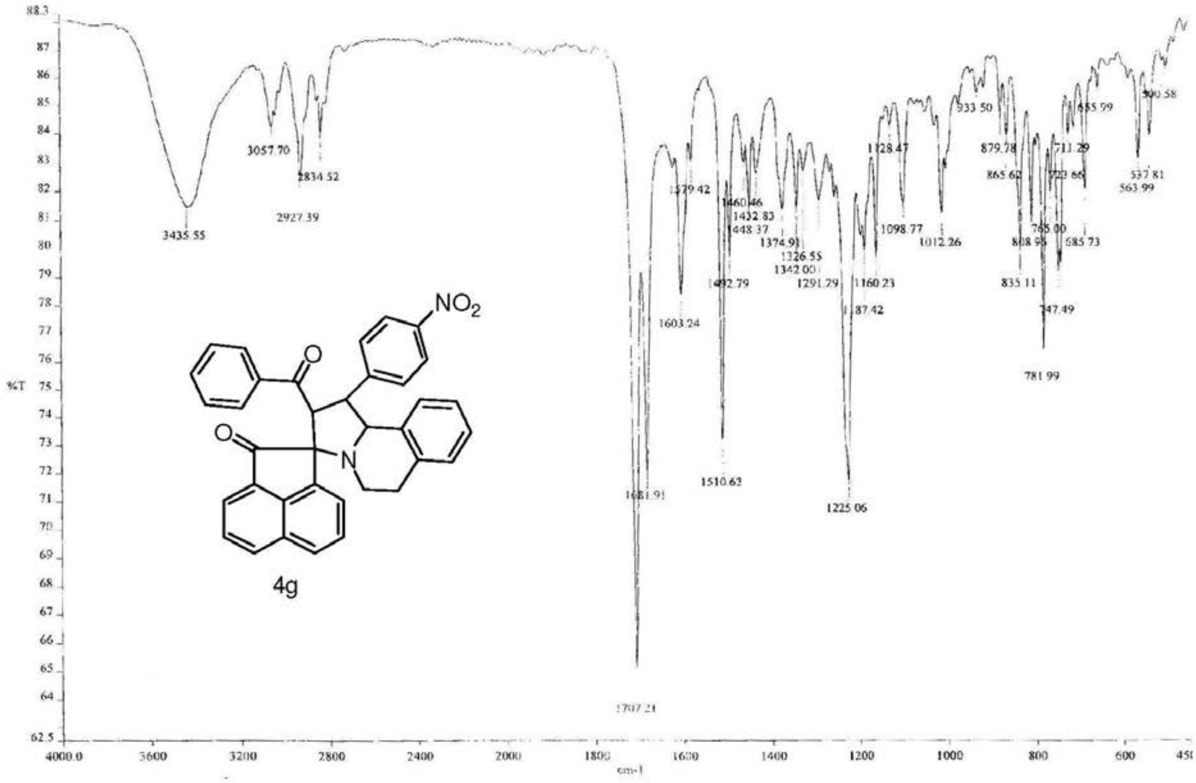

Figure S23. IR (KBr) of (**4g**).

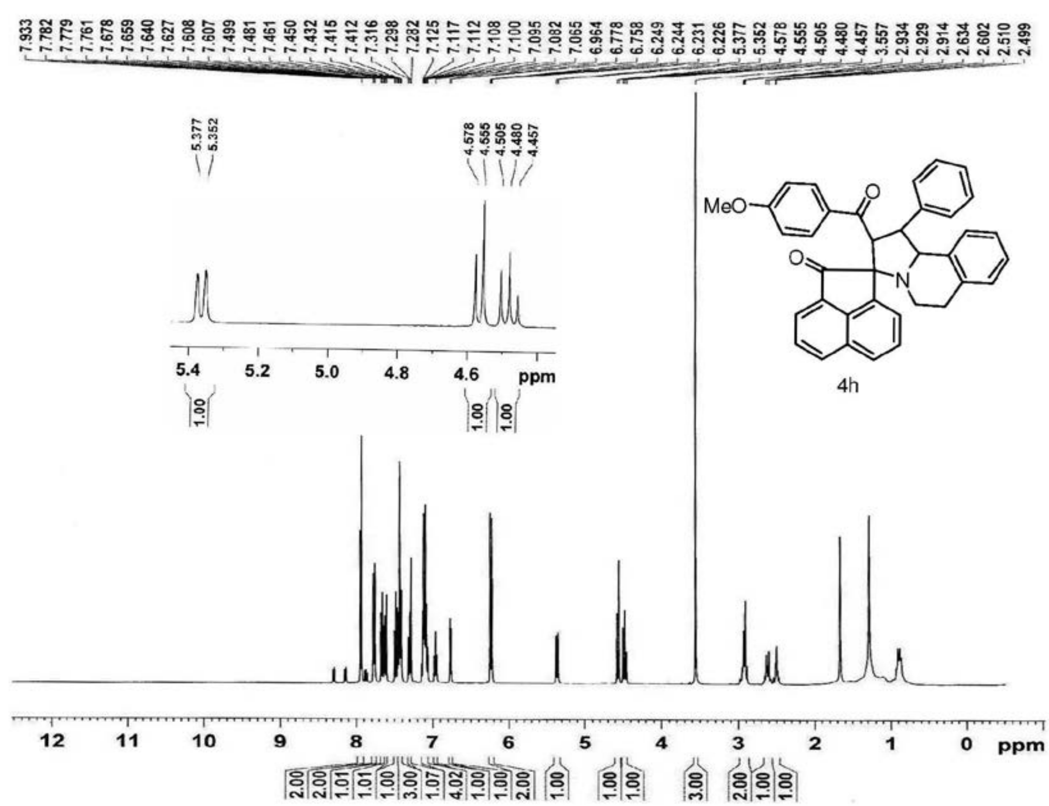

Figure S24. ^{1}H NMR (400 MHz, $CDCl_3$) of (**4h**).

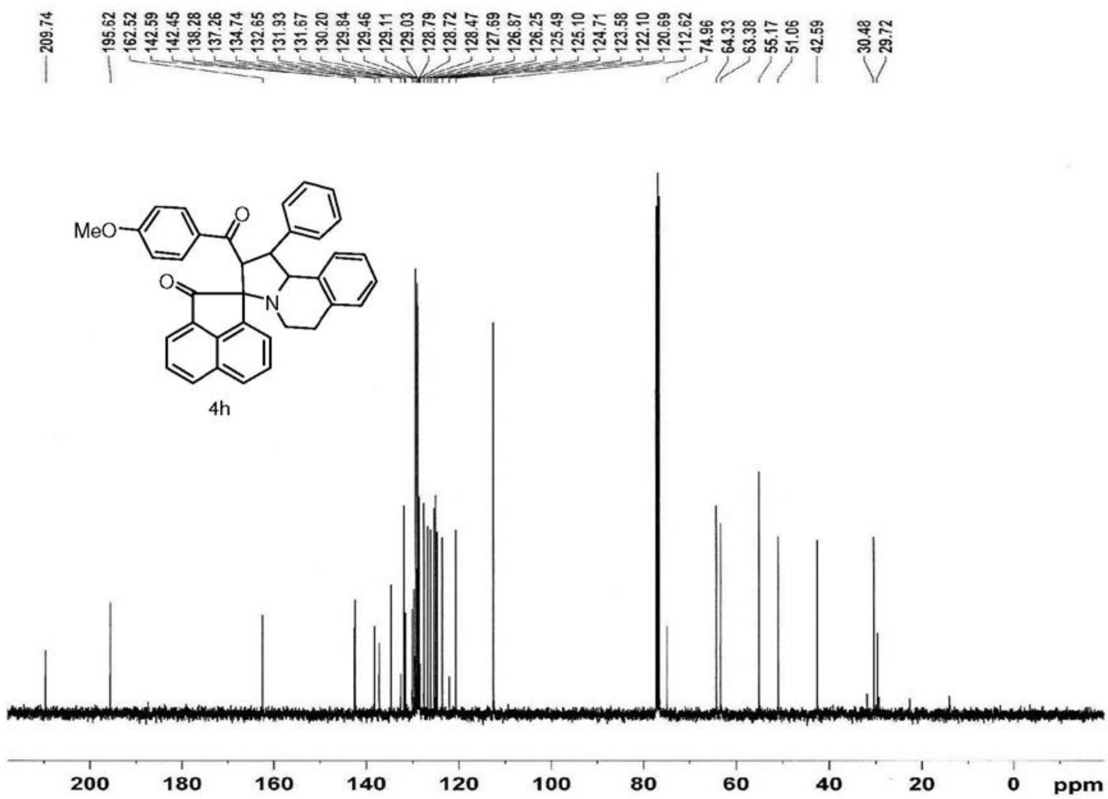

Figure S25. ^{13}C NMR (100 MHz, $CDCl_3$) of (**4h**).

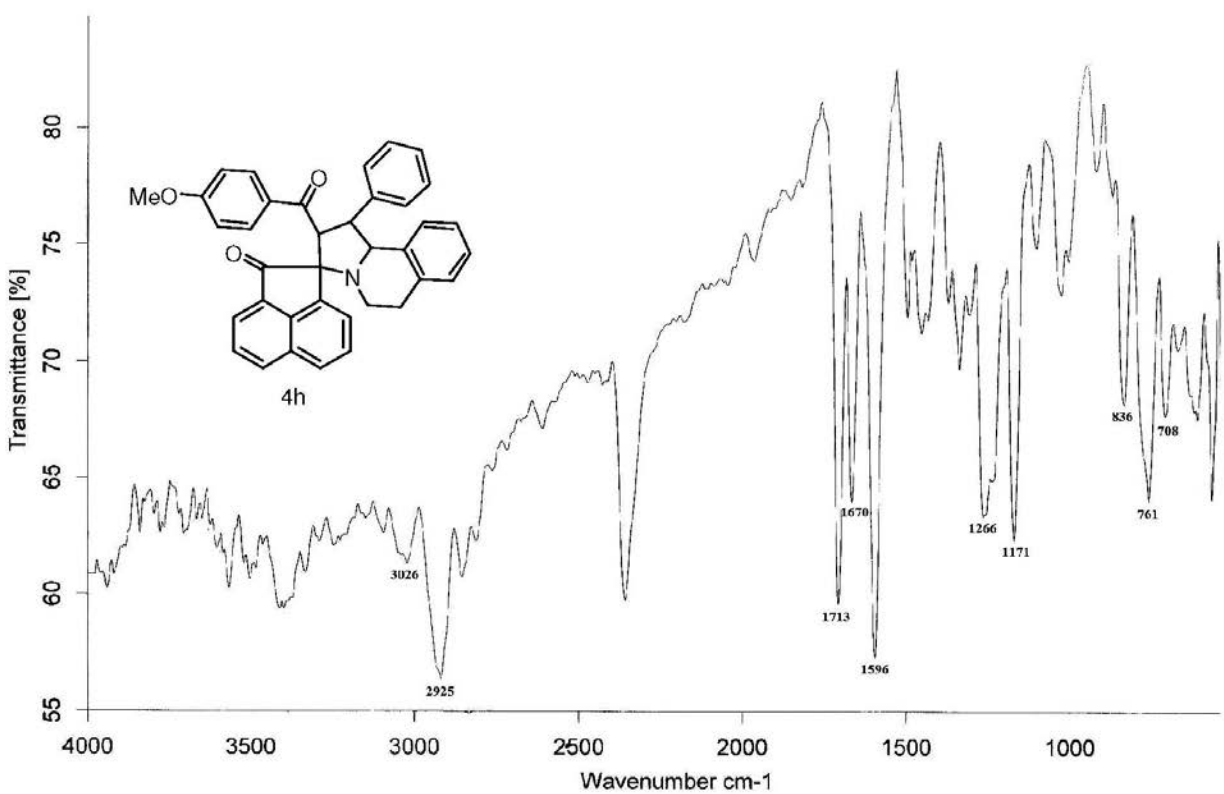

Figure S26. IR (KBr) of (**4h**).

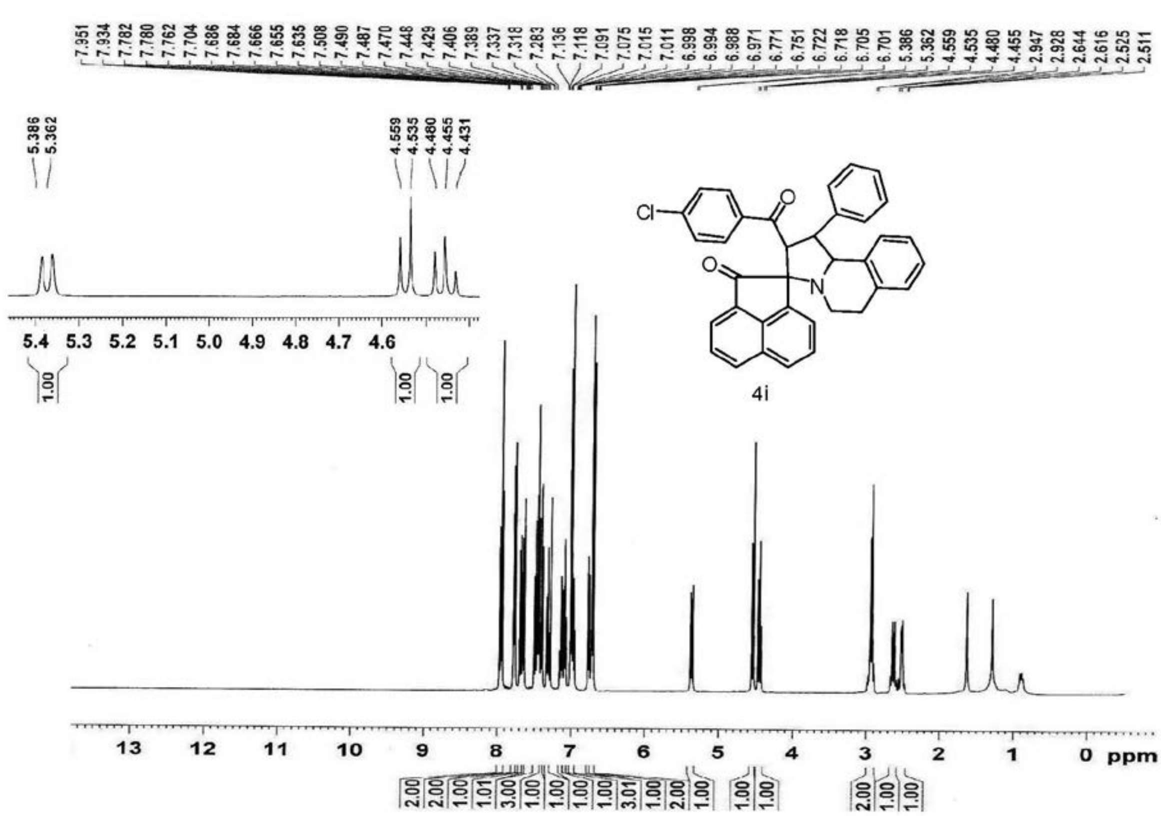

Figure S27. [1]H NMR (400 MHz, $CDCl_3$) of (**4i**).

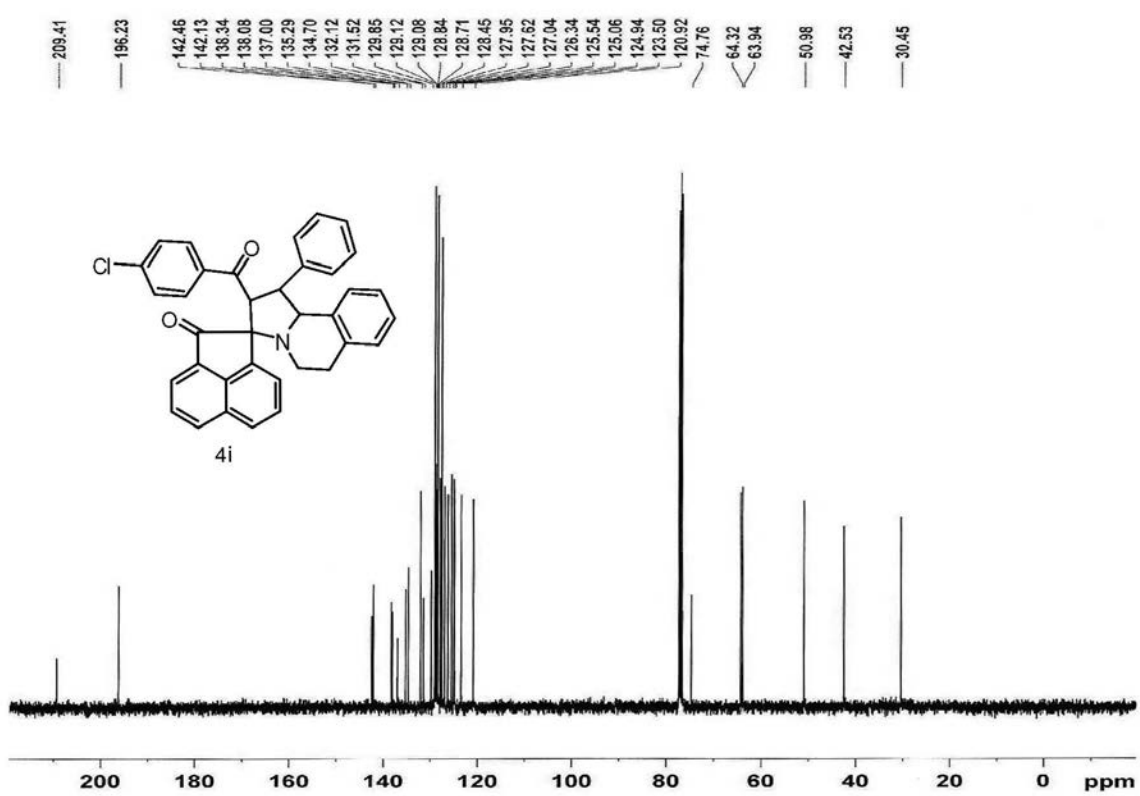

Figure S28. [13]C NMR (100 MHz, $CDCl_3$) of (**4i**).

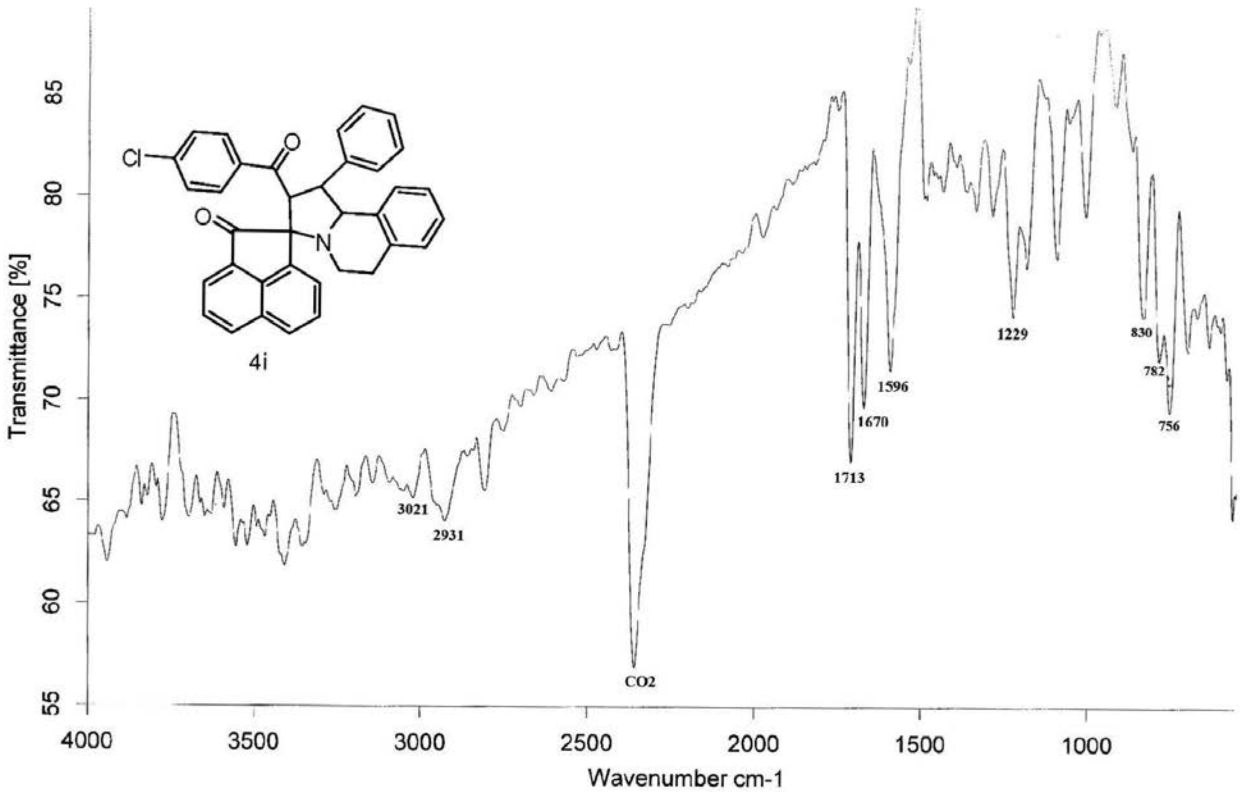

Figure S29. IR (KBr) of (**4i**).

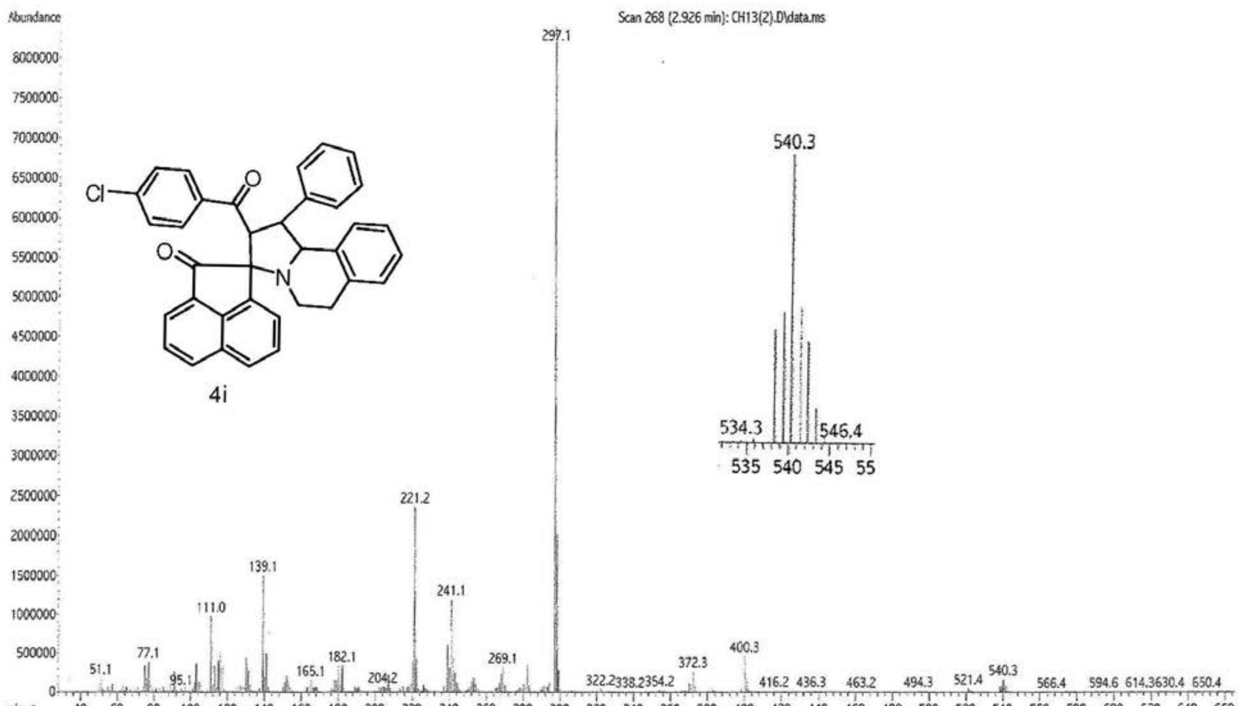

Figure S30. MS (70 eV) of (**4i**).

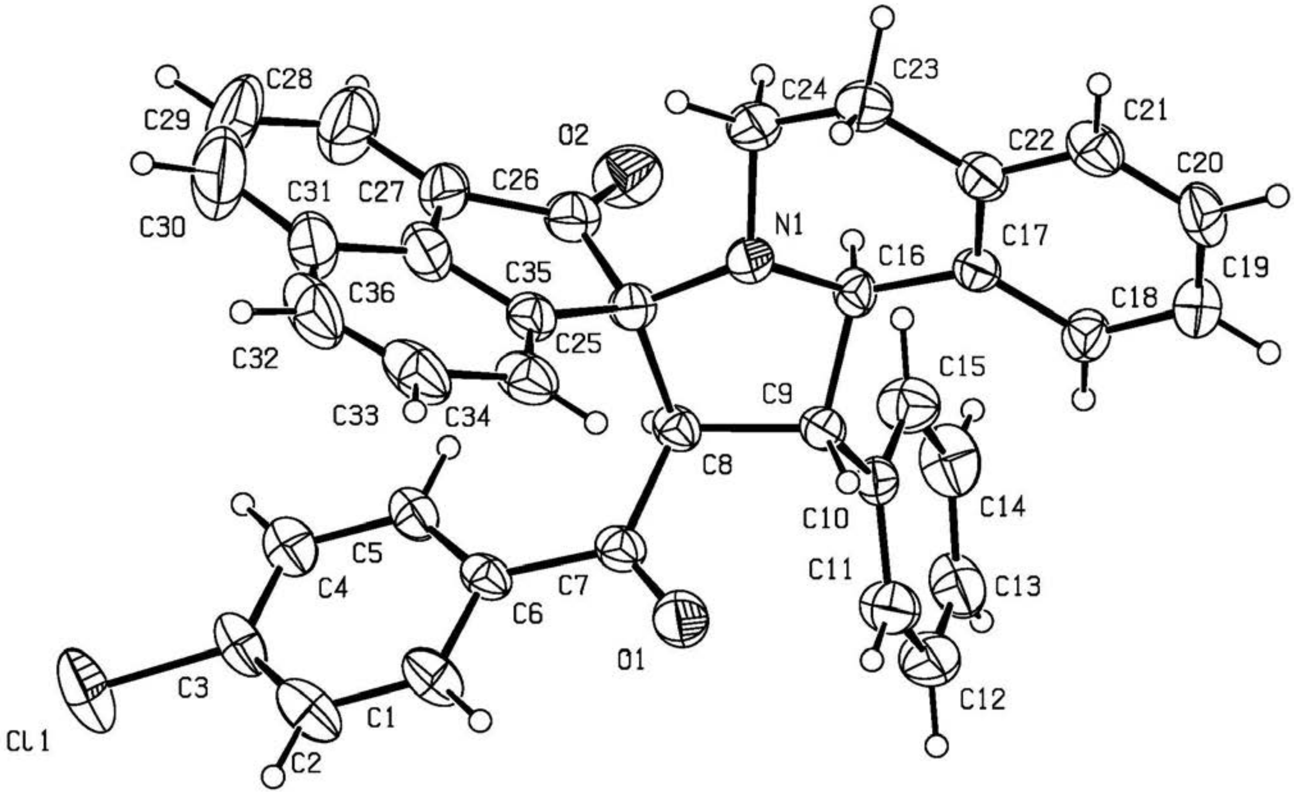

Figure S31. ORTEP diagram of (**4i**).

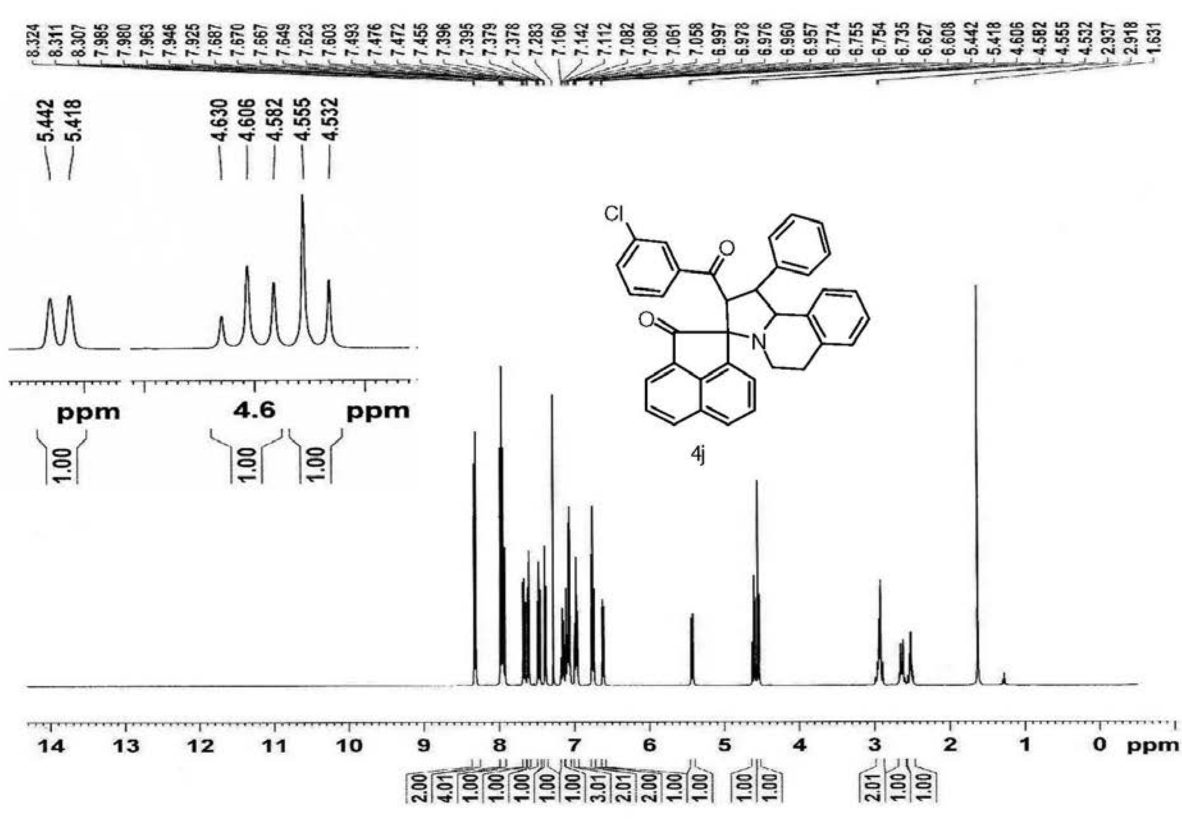

Figure S32. ^{1}H NMR (400 MHz, $CDCl_3$) of (**4j**).

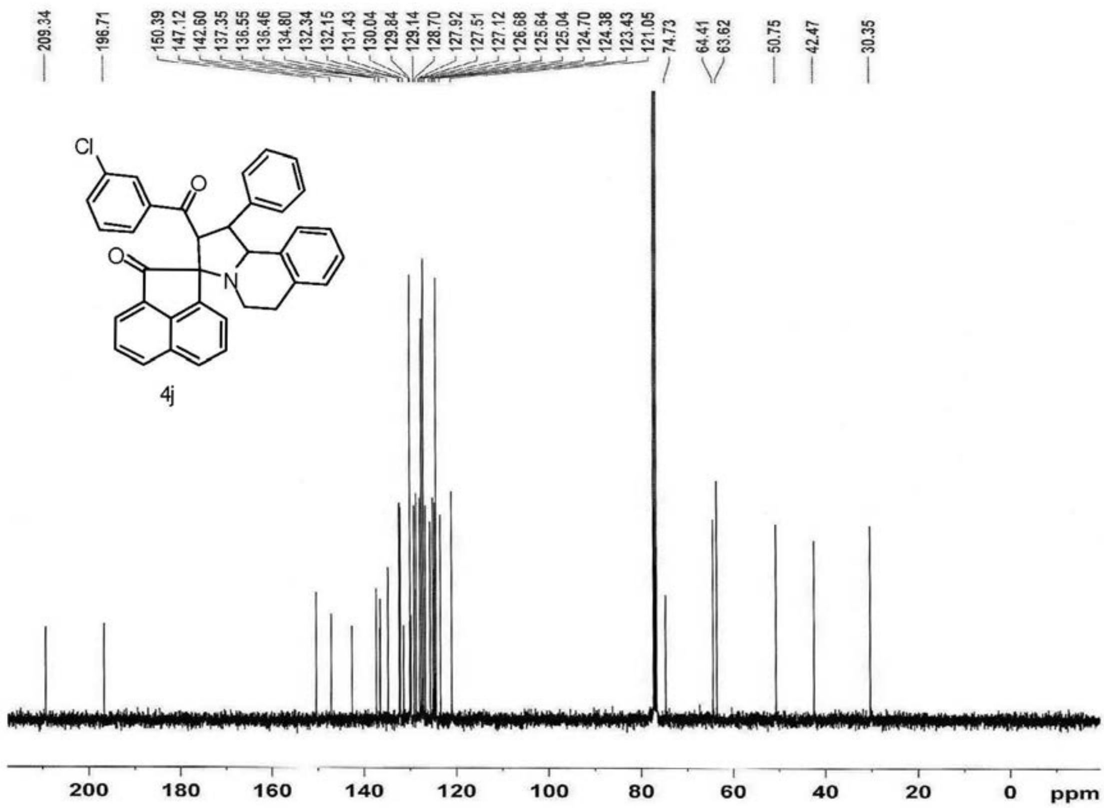

Figure S33. ^{13}C NMR (100 MHz, $CDCl_3$) of (**4j**).

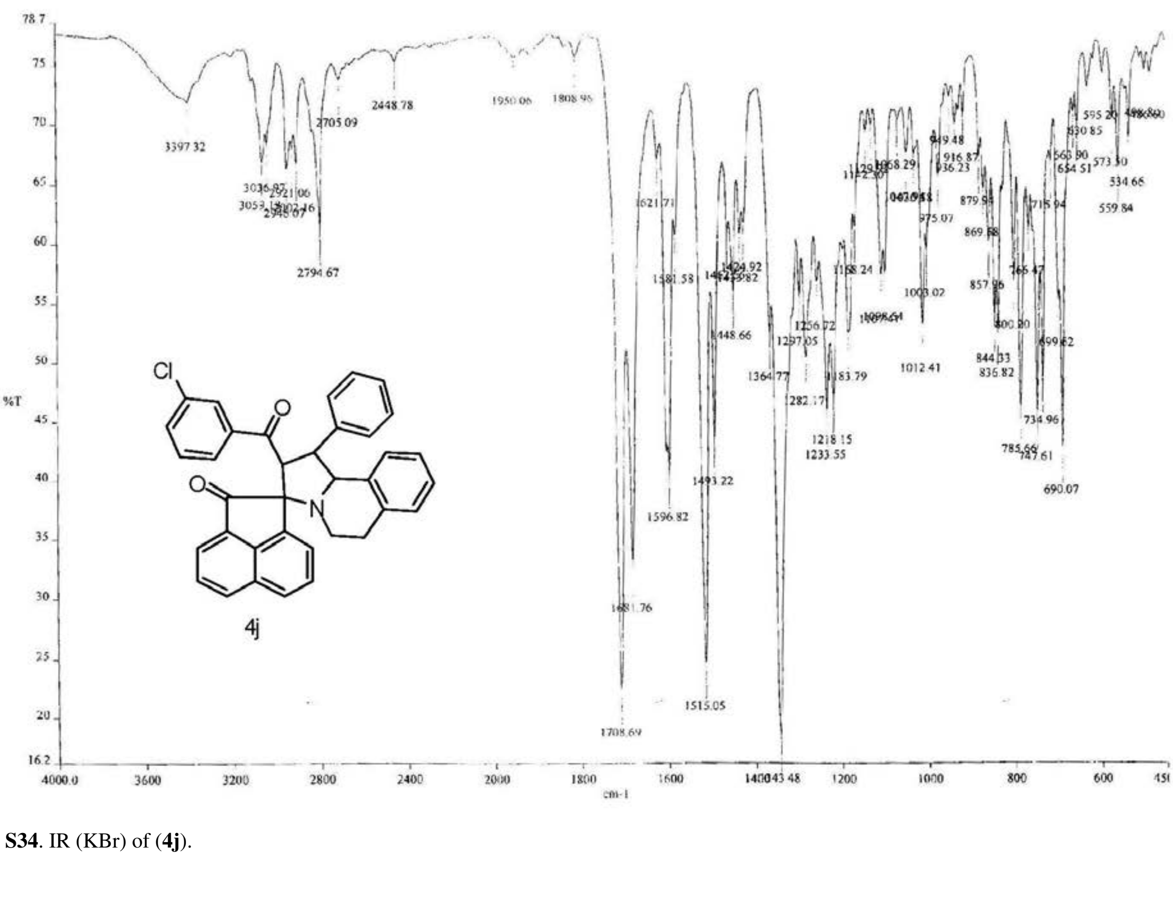

Figure S34. IR (KBr) of (**4j**).

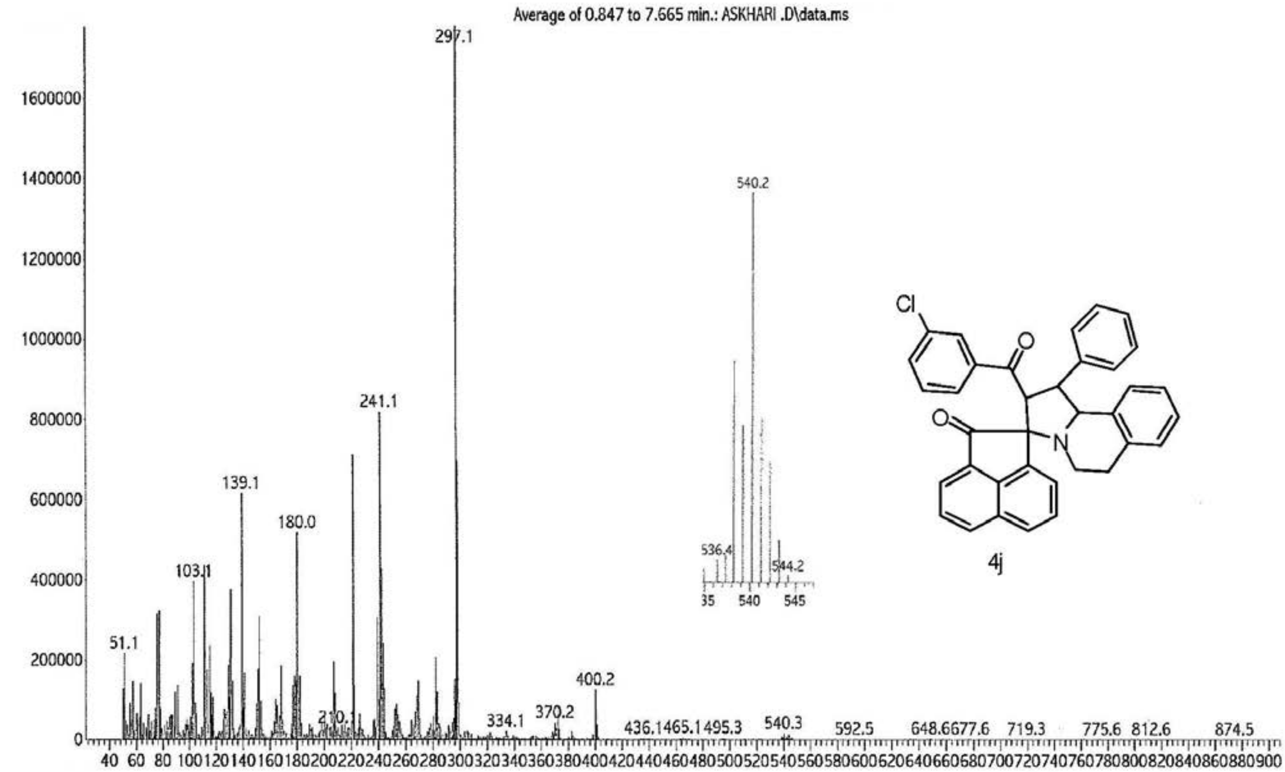

Figure S35. MS (70 eV) of (**4j**).

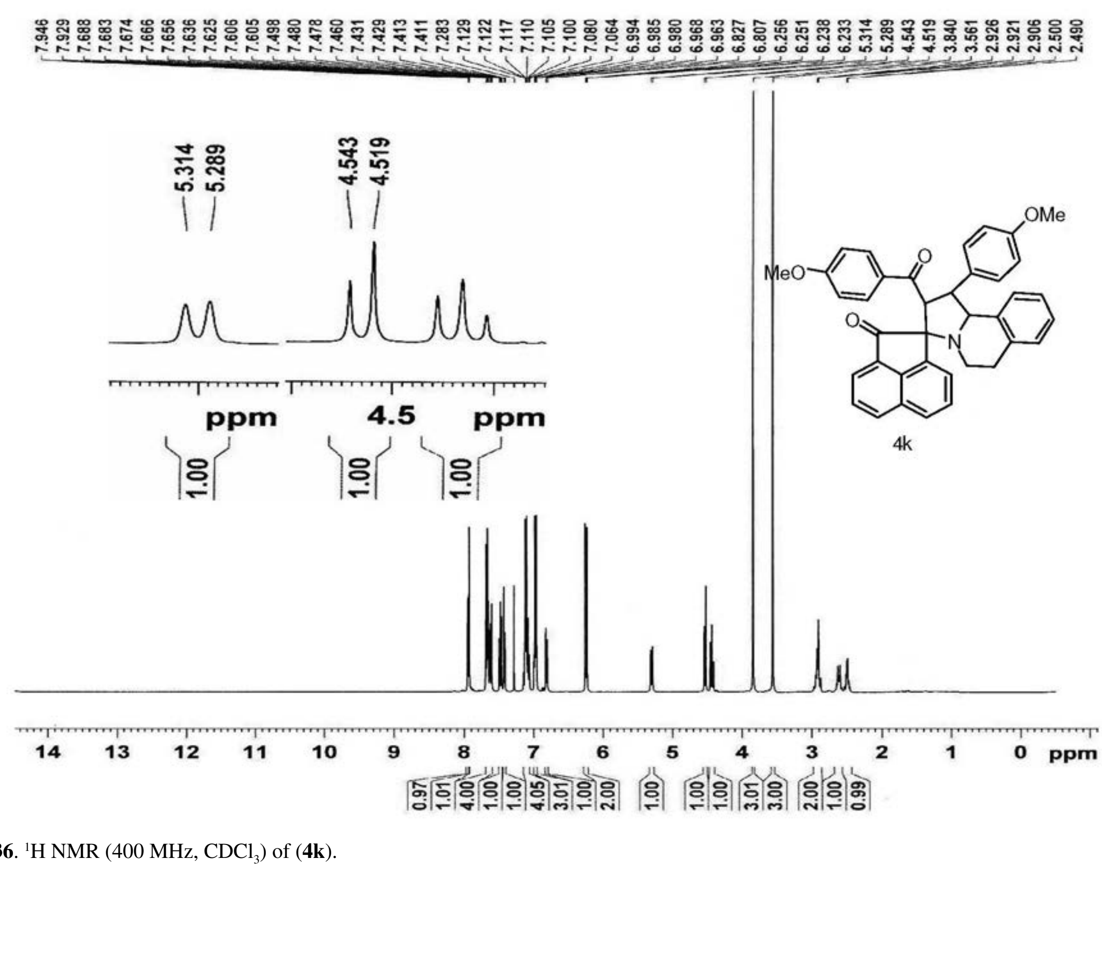

Figure S36. ^{1}H NMR (400 MHz, $CDCl_3$) of (**4k**).

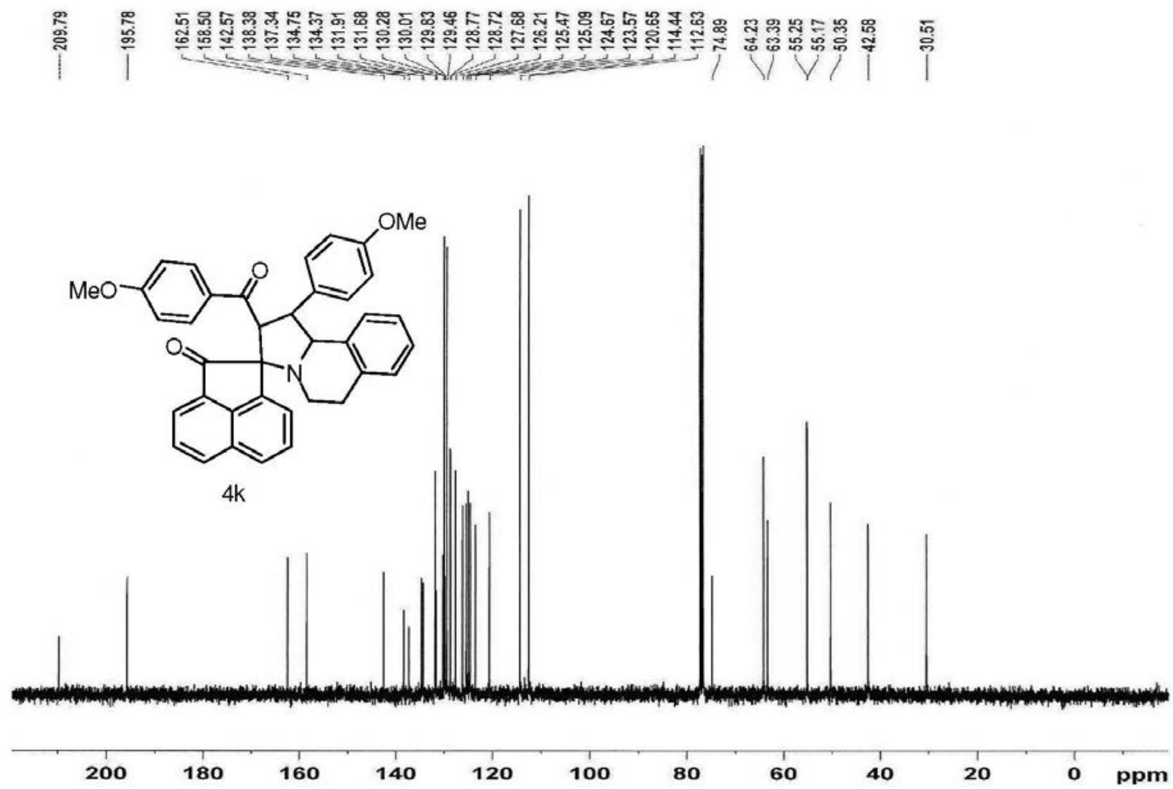

Figure S37. ^{13}C NMR (100 MHz, $CDCl_3$) of (**4k**).

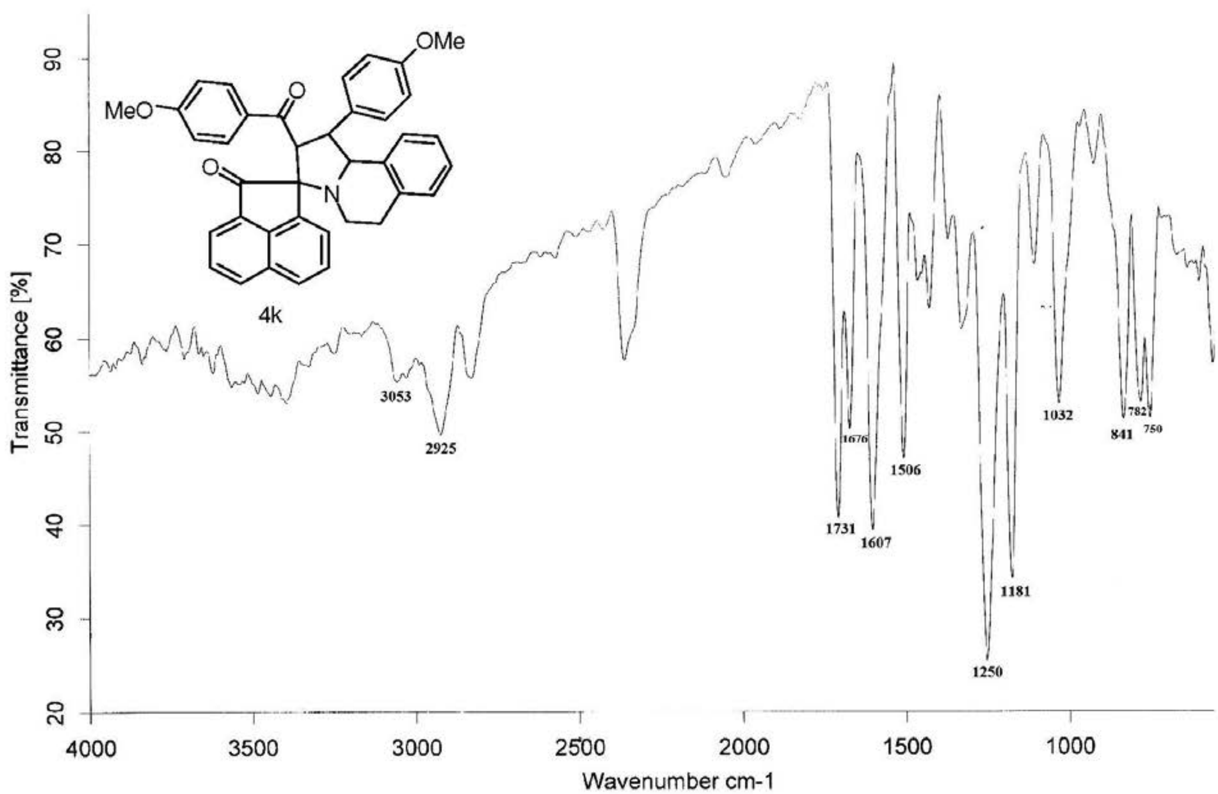

Figure S38. IR (KBr) of (**4k**).

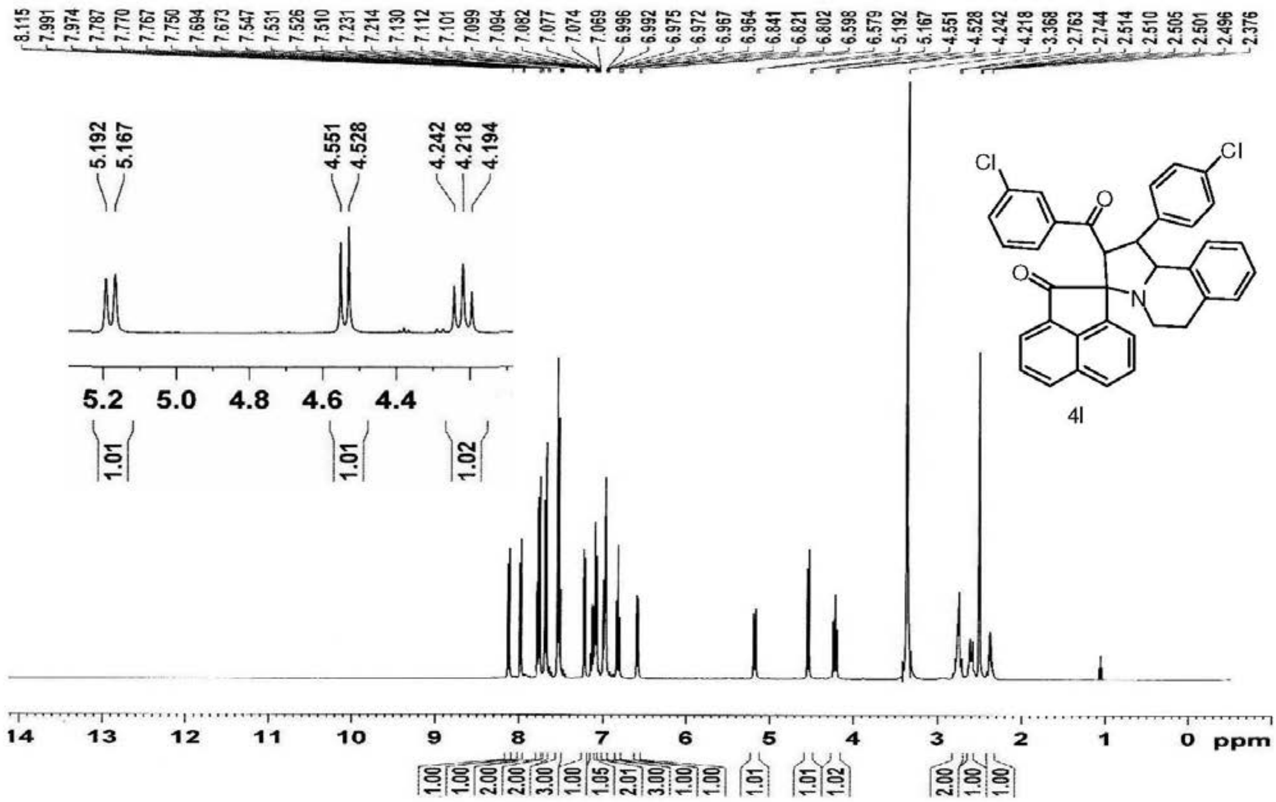

Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) of (**4l**).

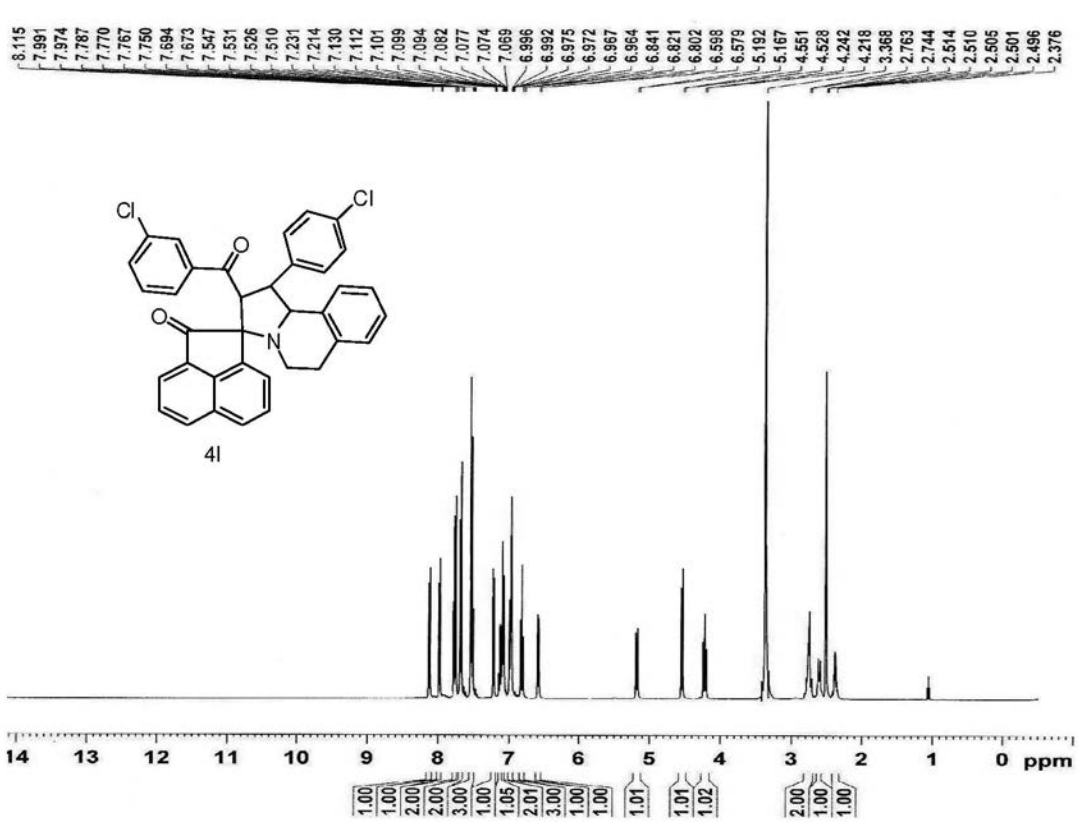

Figure S40. ^{13}C NMR (100 MHz, $CDCl_3$) of (**4l**).

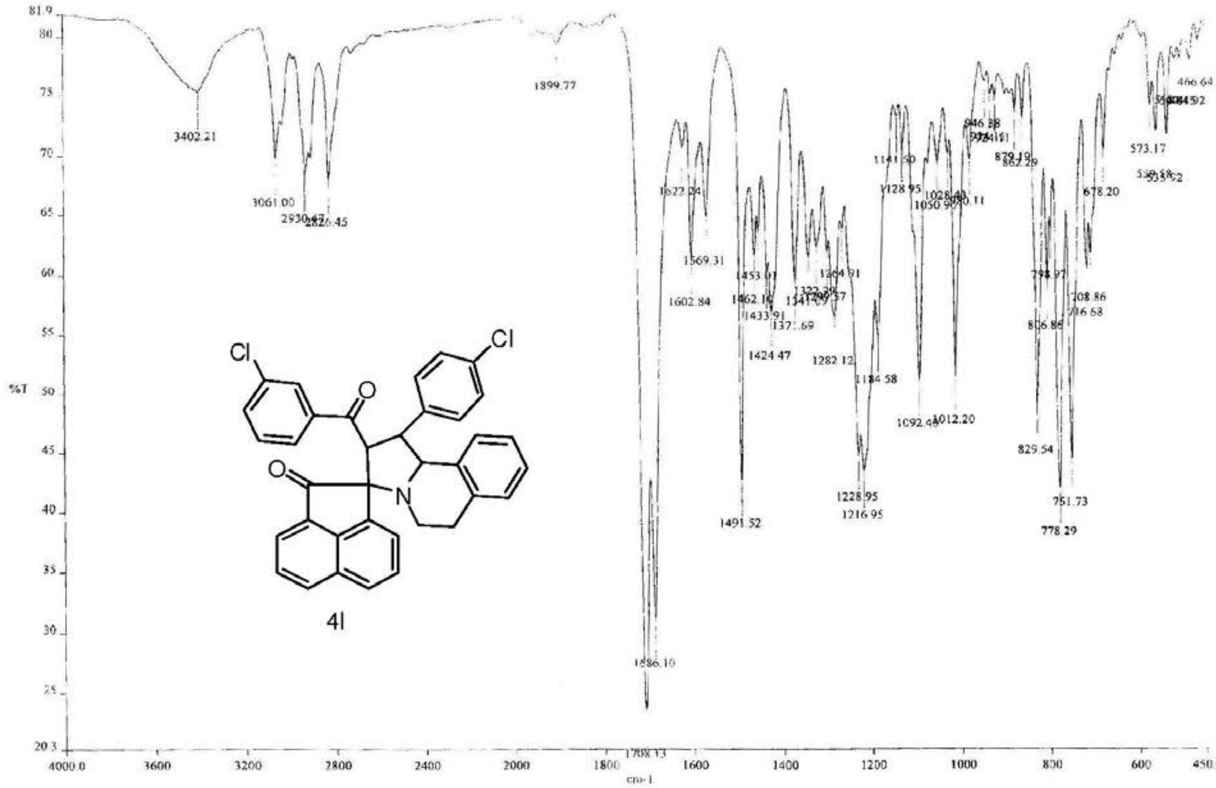

Figure S41. IR (KBr) of (**4l**).

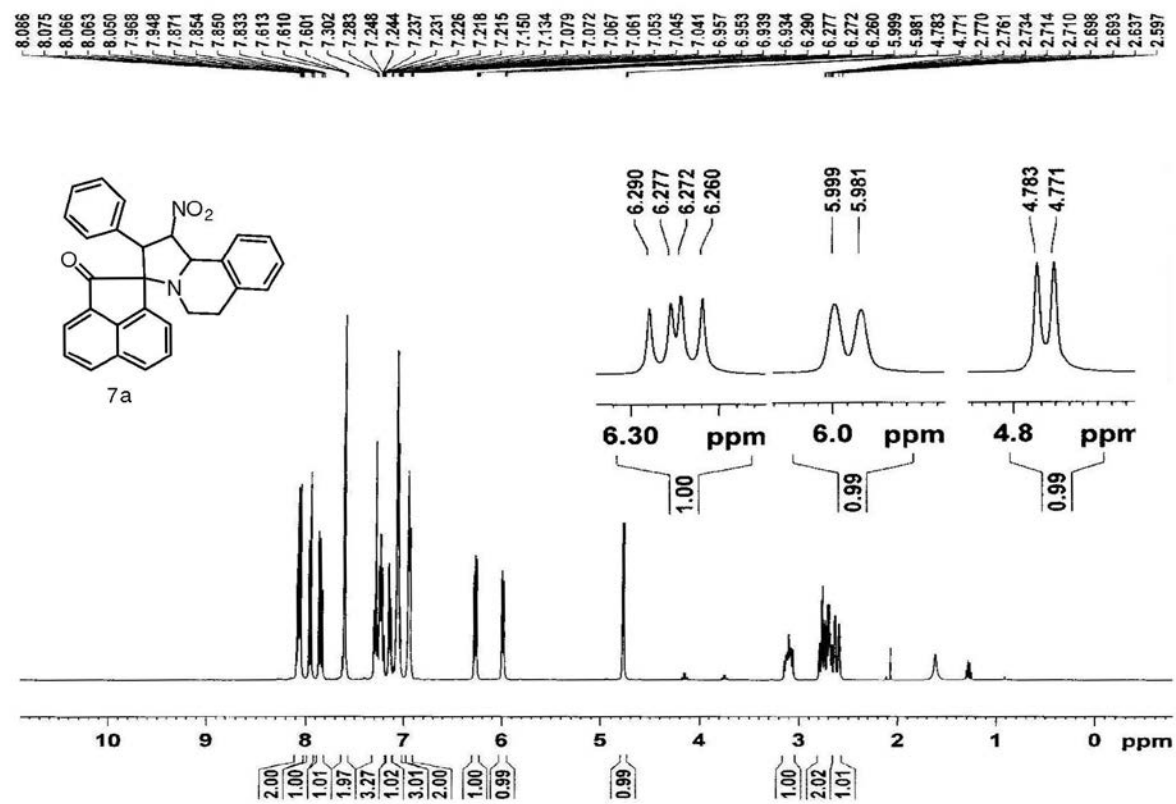

Figure S42. ^{1}H NMR (400 MHz, $CDCl_3$) of (**7a**).

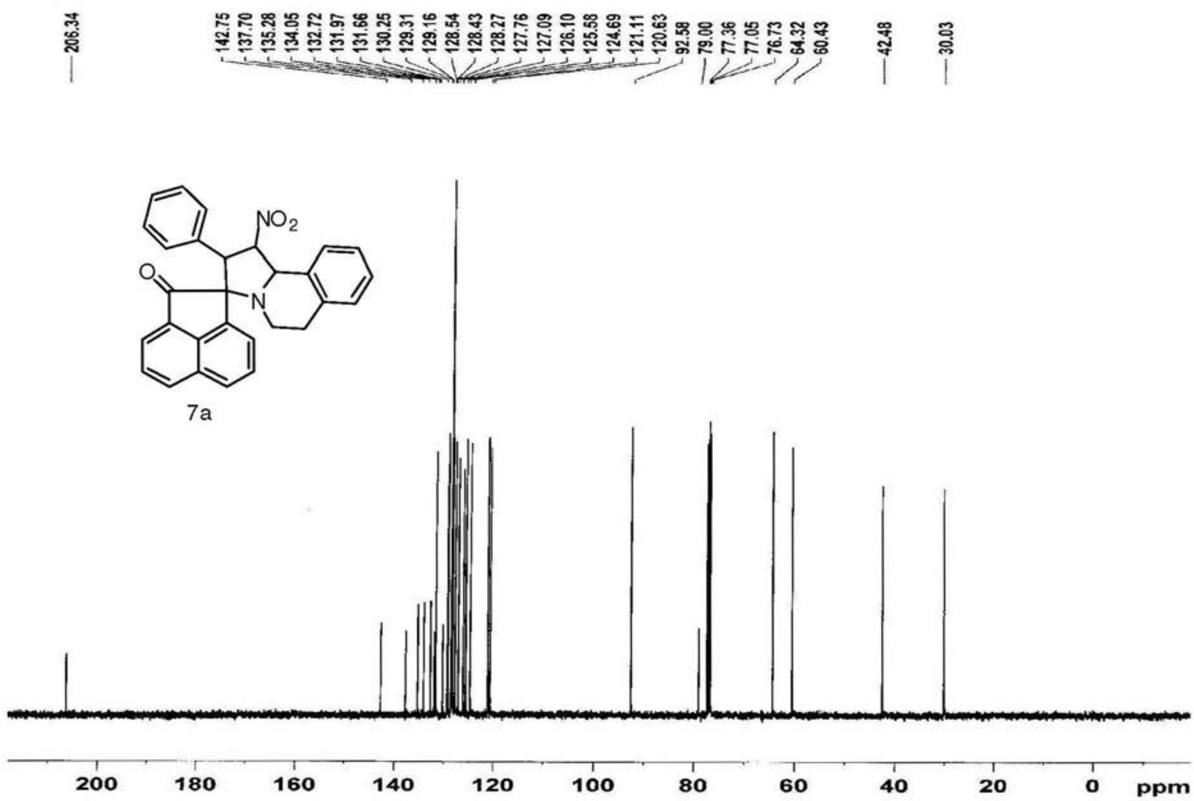

Figure S43. ^{13}C NMR (100 MHz, $CDCl_3$) of (**7a**).

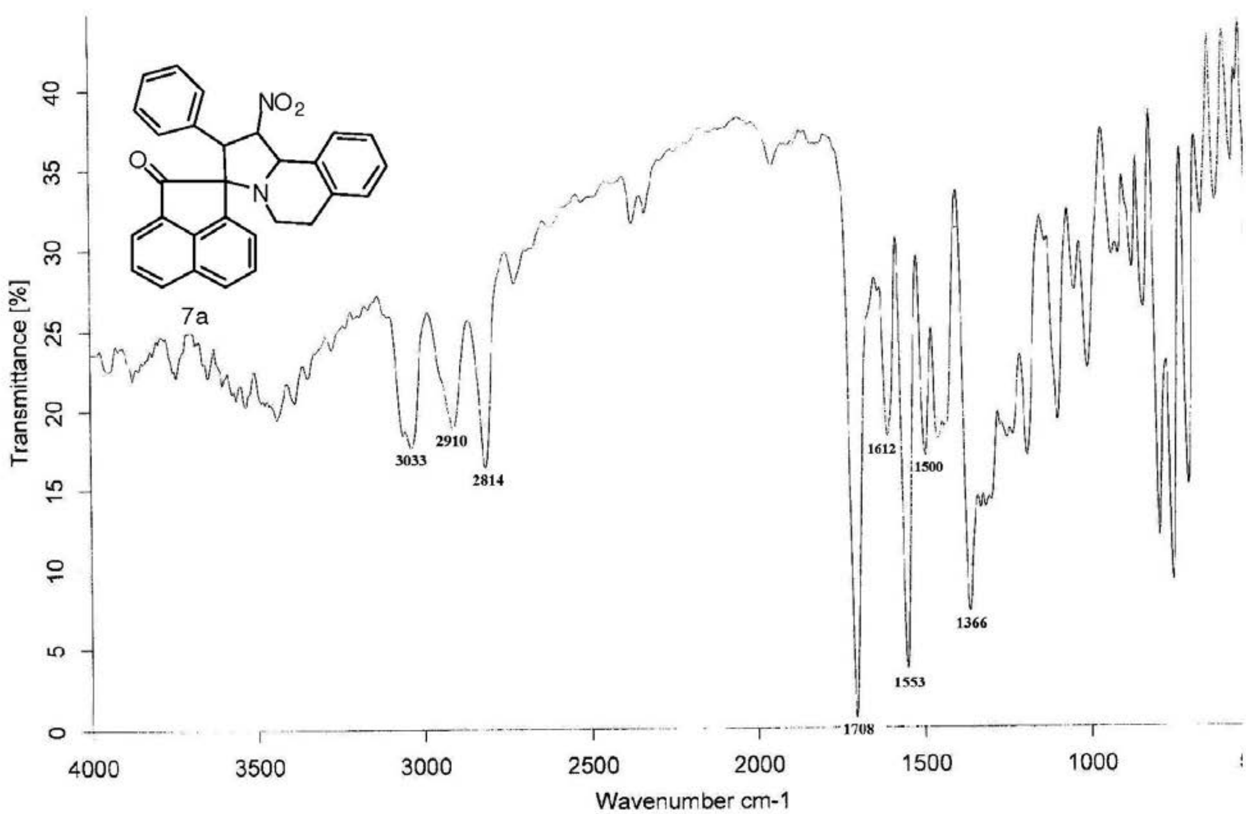

Figure S44. IR (KBr) of (**7a**).

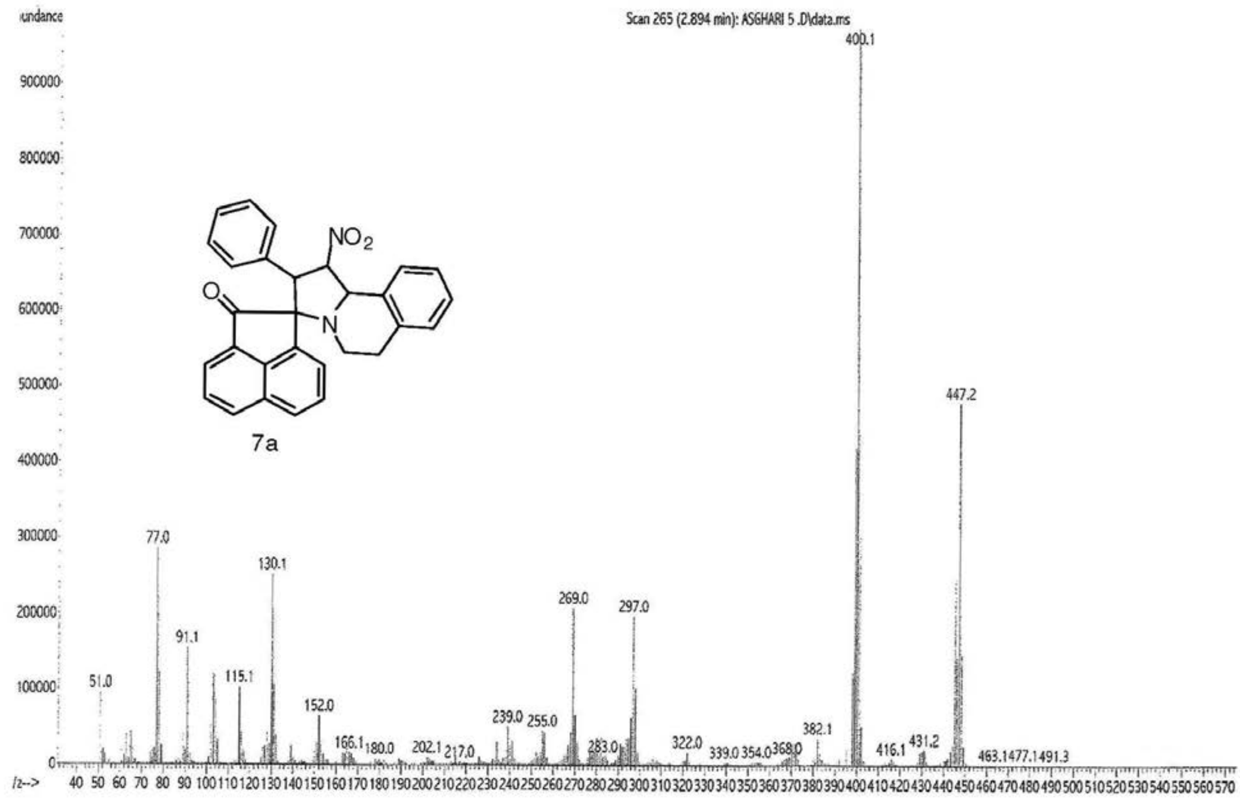

Figure S45. MS (70 eV) of (**7a**).

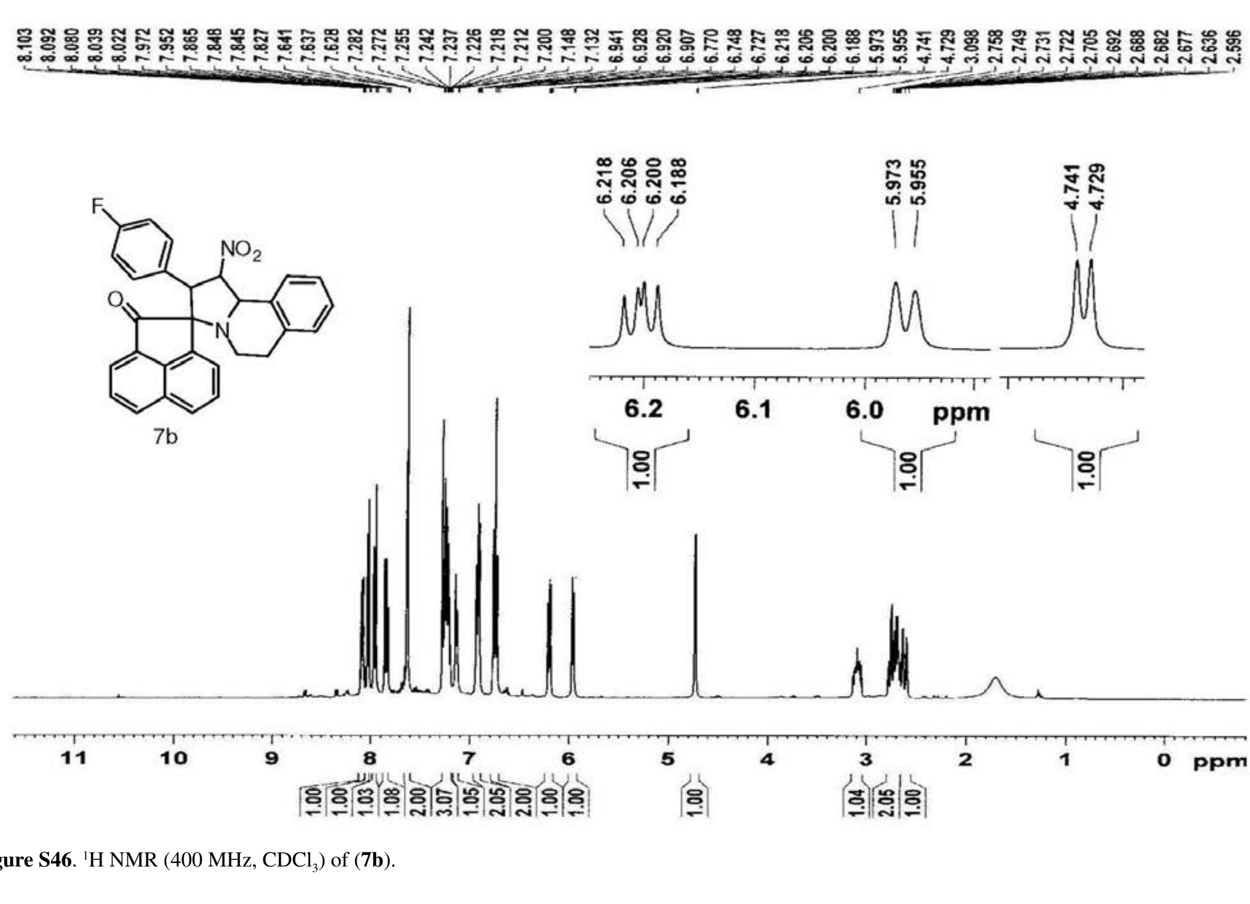

Figure S46. ^{1}H NMR (400 MHz, $CDCl_3$) of (**7b**).

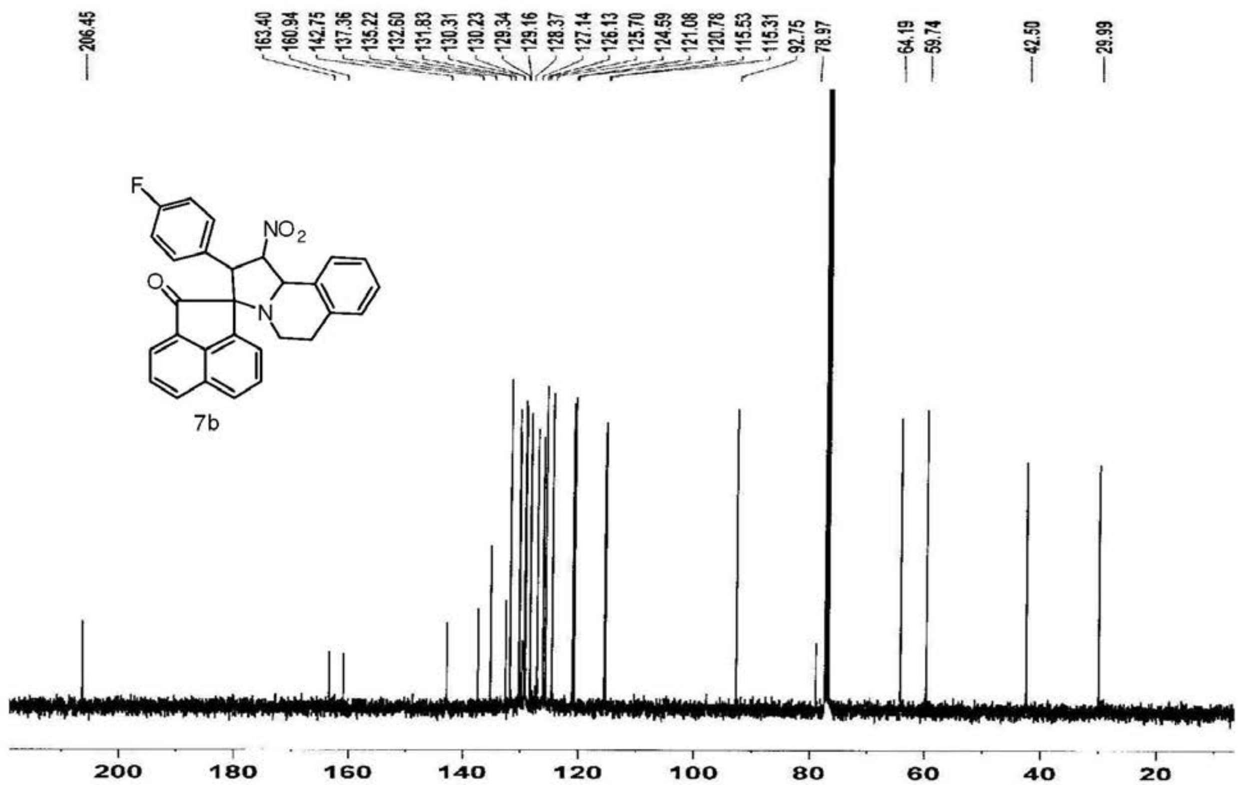

Figure S47. ^{13}C NMR (100 MHz, $CDCl_3$) of (**7b**).

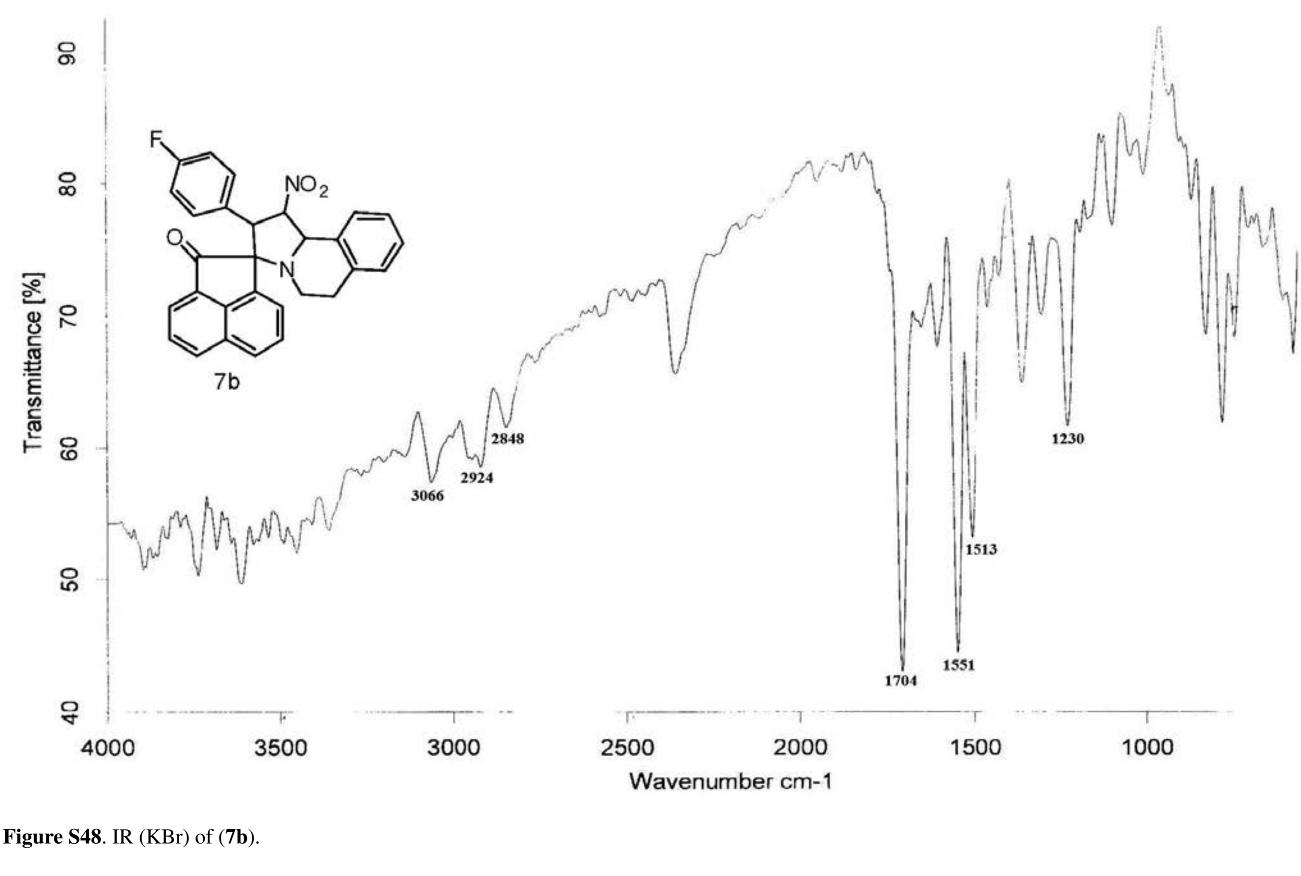

Figure S48. IR (KBr) of (**7b**).

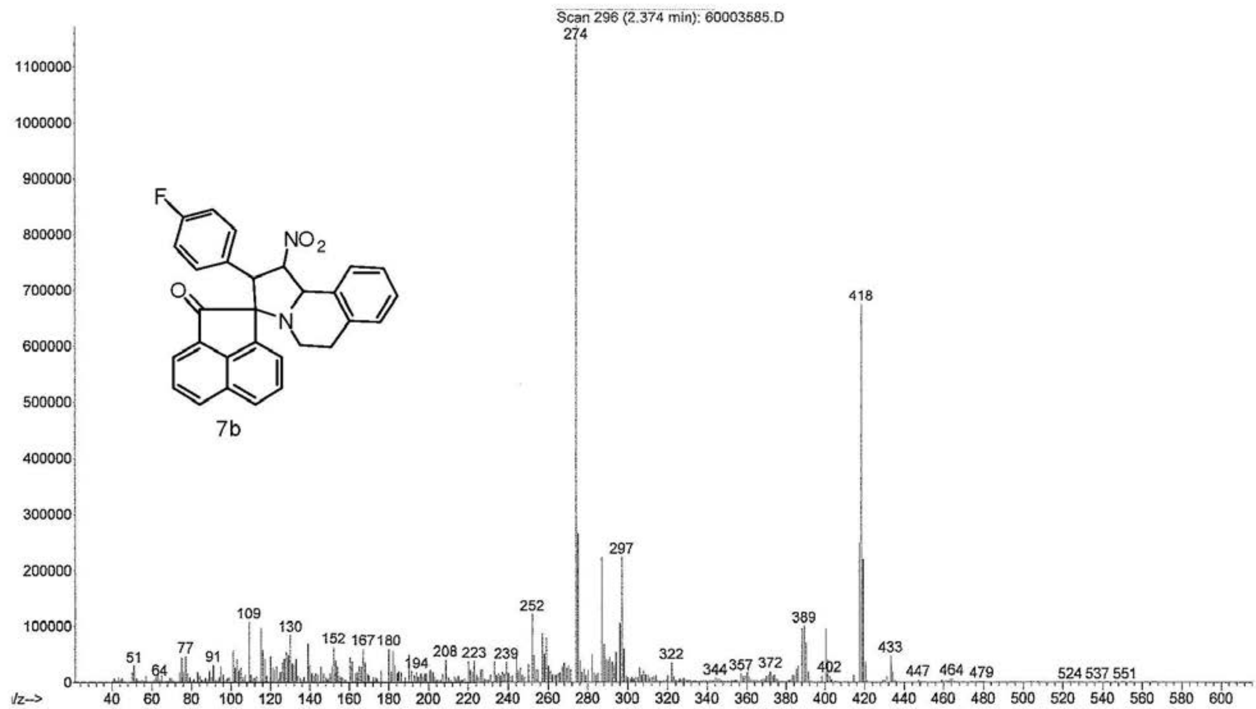

Figure S49. MS (70 eV) of (**7b**).

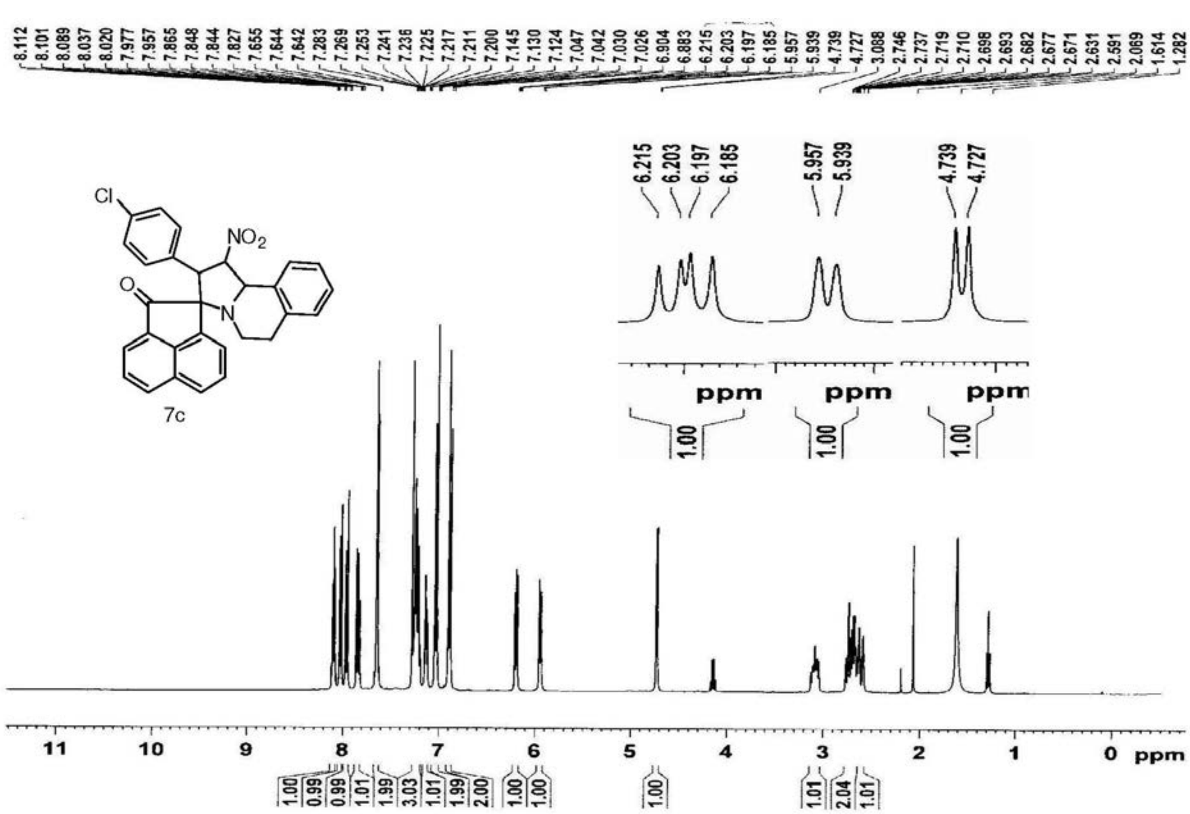

Figure S50. ^{1}H NMR (400 MHz, $CDCl_3$) of (**7c**).

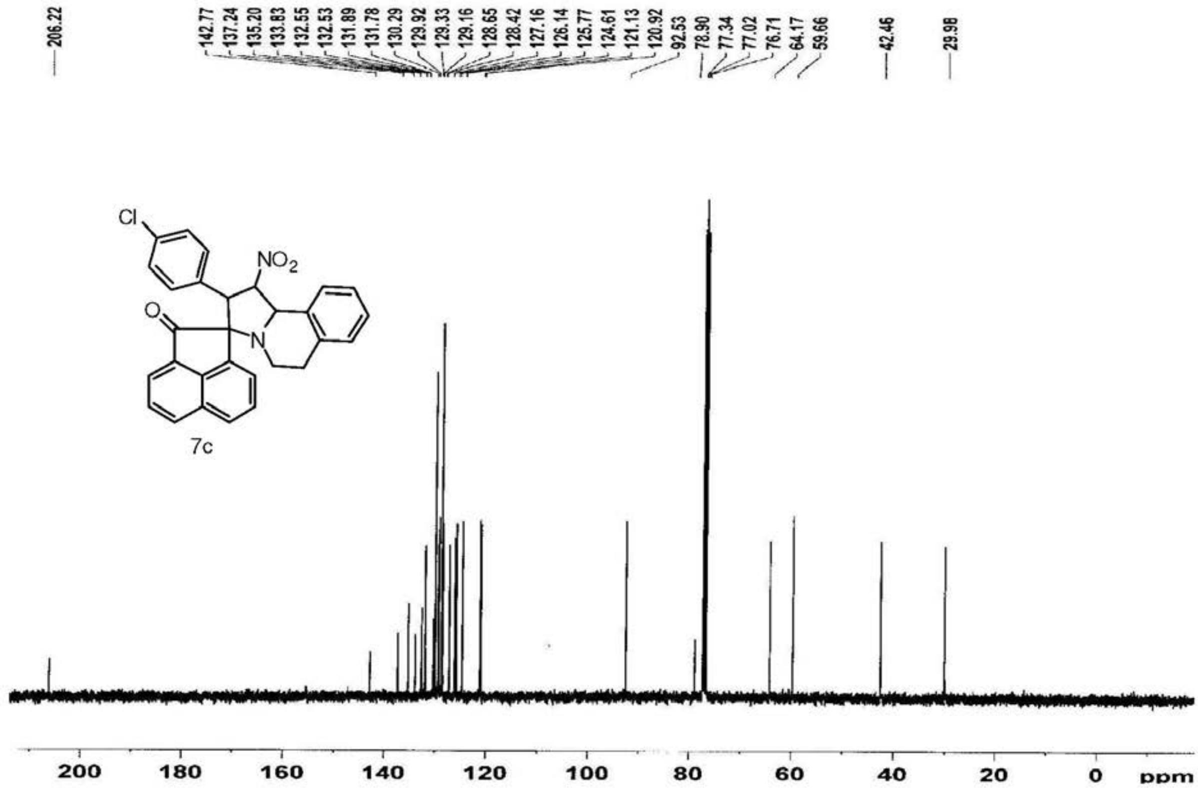

Figure S51. ^{13}C NMR (100 MHz, $CDCl_3$) of (**7c**).

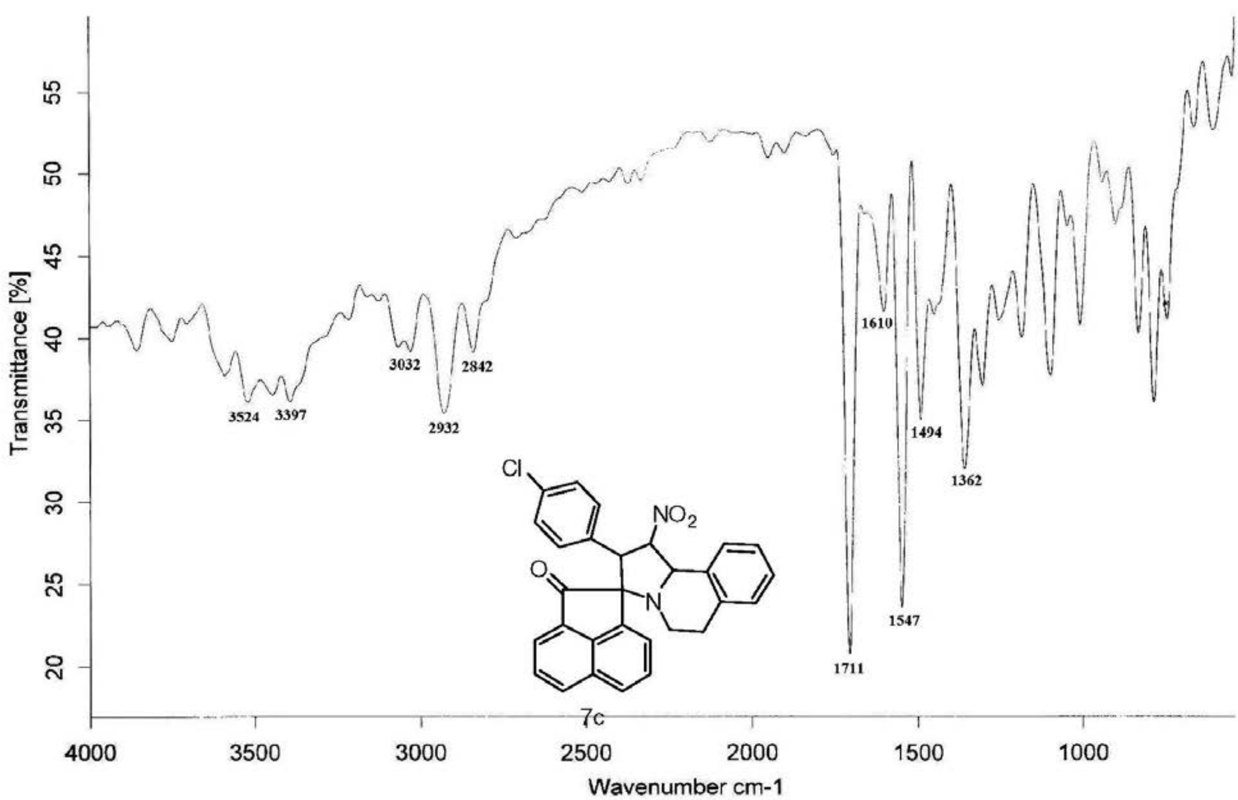

Figure S52. IR (KBr) of (**7c**).

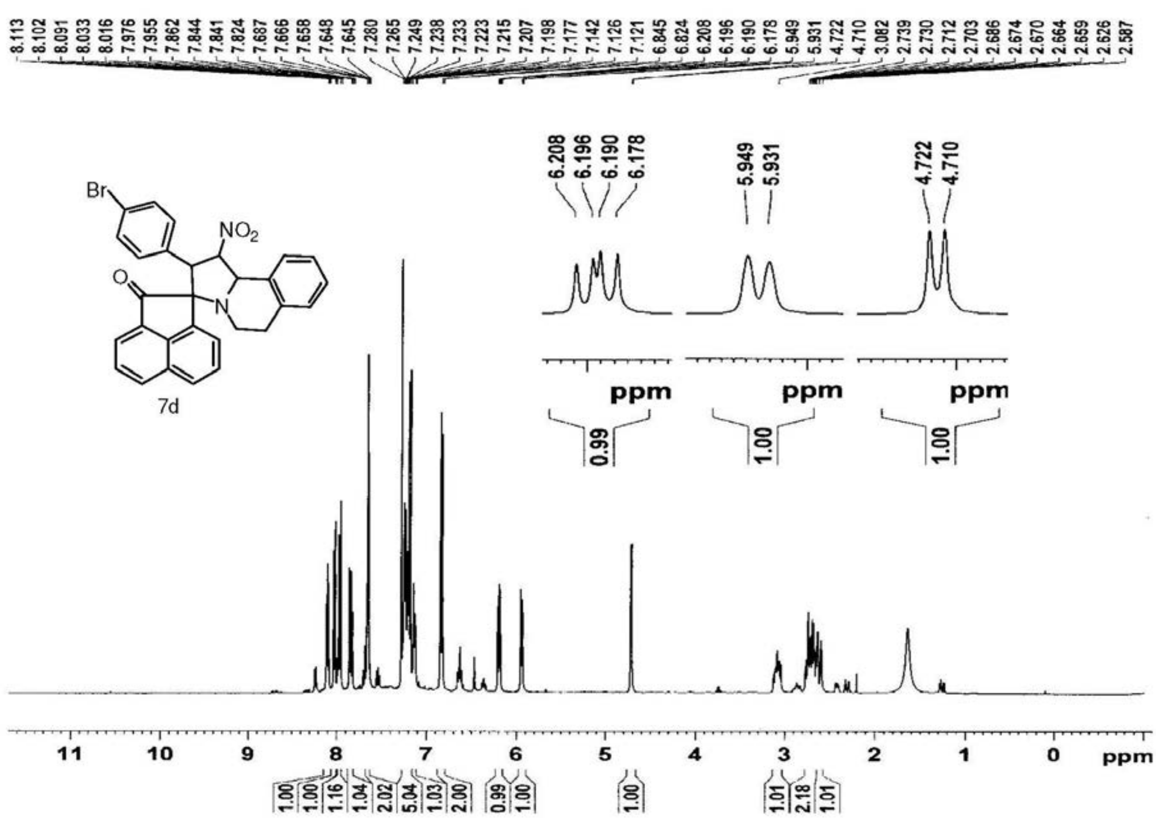

Figure S53. ^{1}H NMR (400 MHz, $CDCl_3$) of (**7d**).

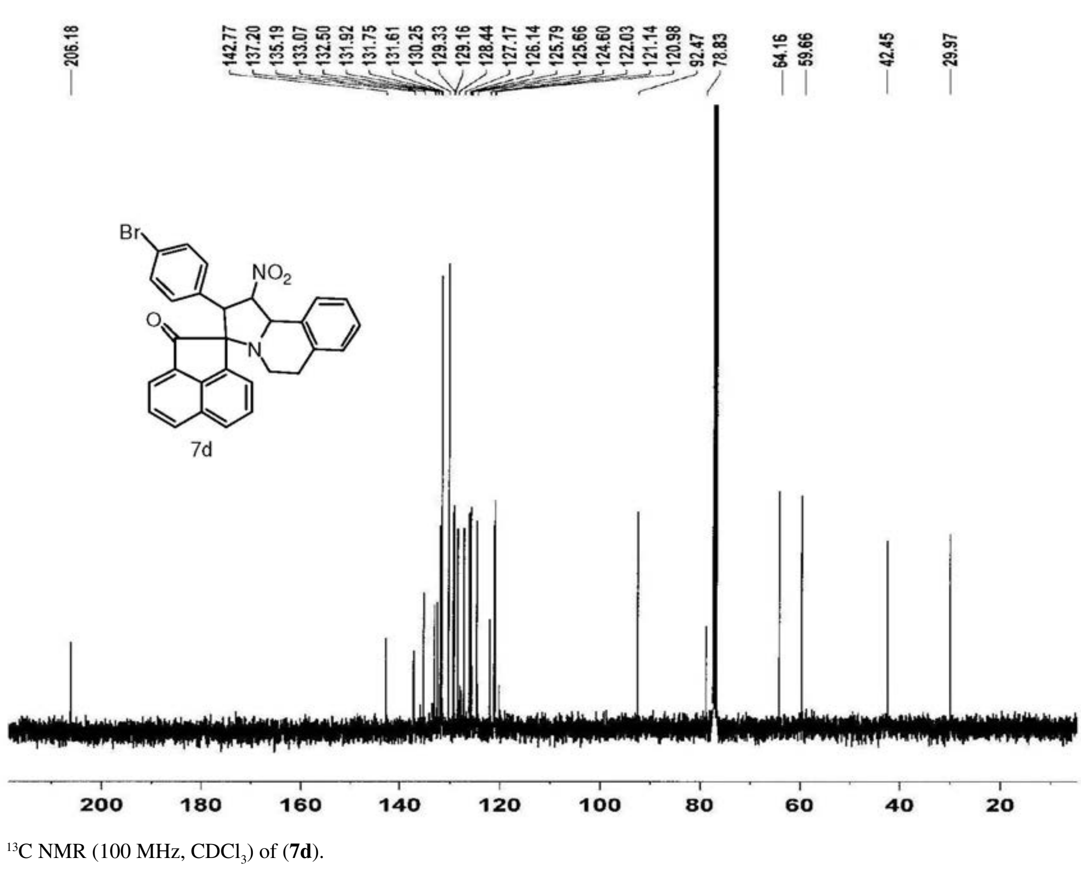

Figure S54. ^{13}C NMR (100 MHz, $CDCl_3$) of (**7d**).

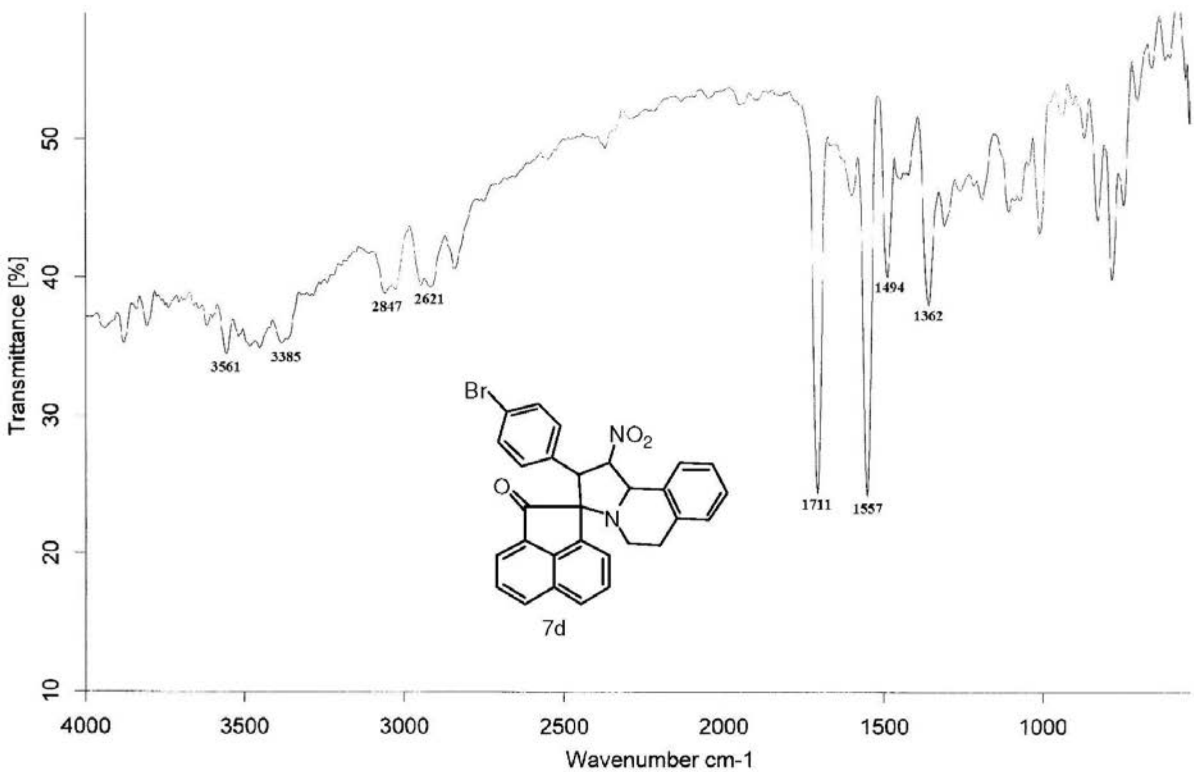

Figure S55. IR (KBr) of (**7d**).

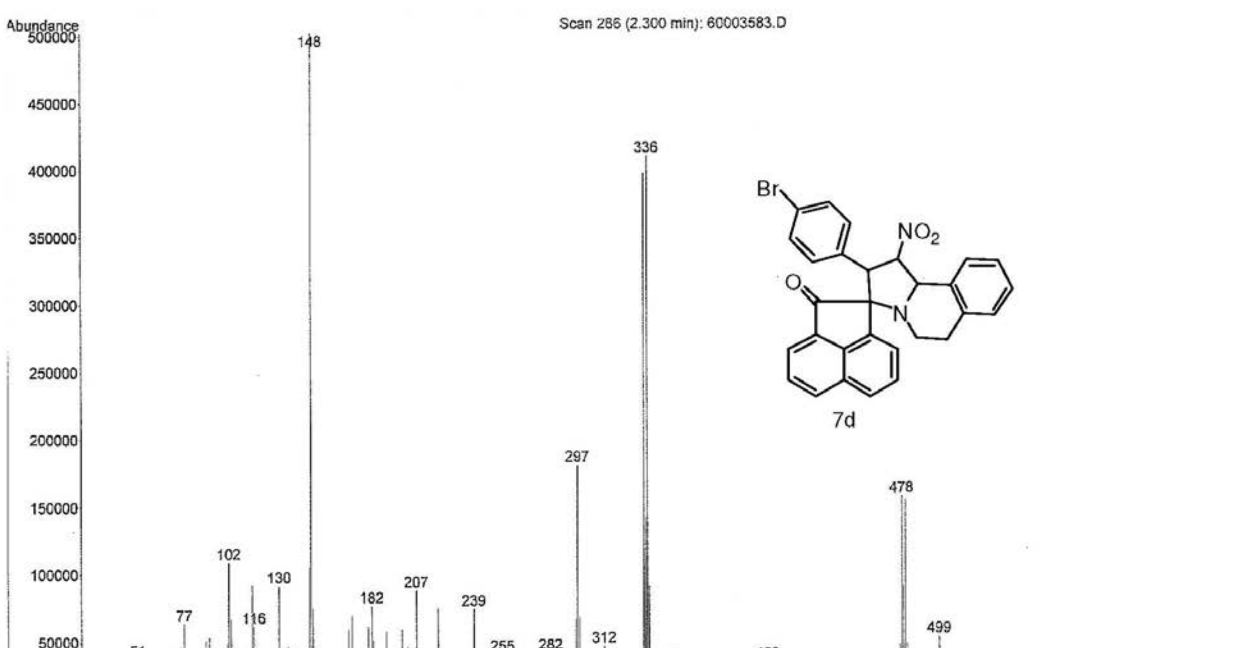

Figure S56. MS (70 eV) of (**7d**).

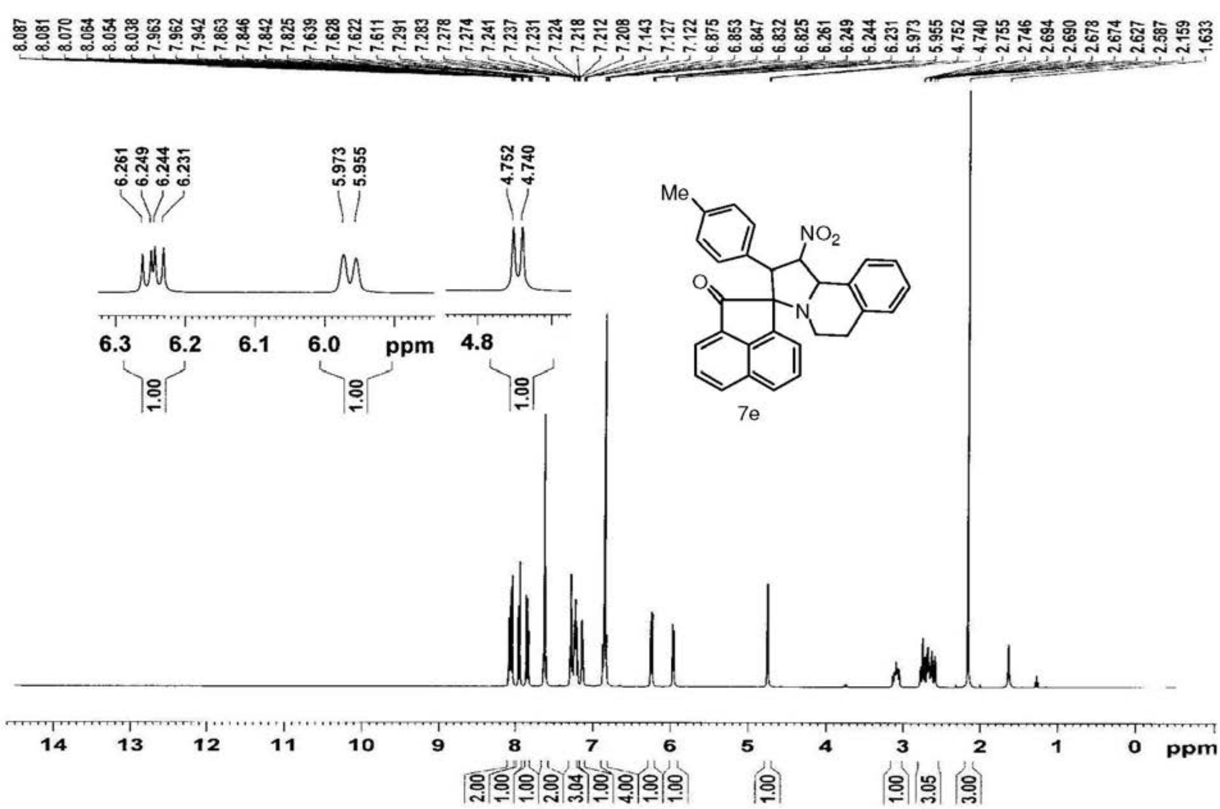

Figure S57. [1]H NMR (400 MHz, $CDCl_3$) of (**7e**).

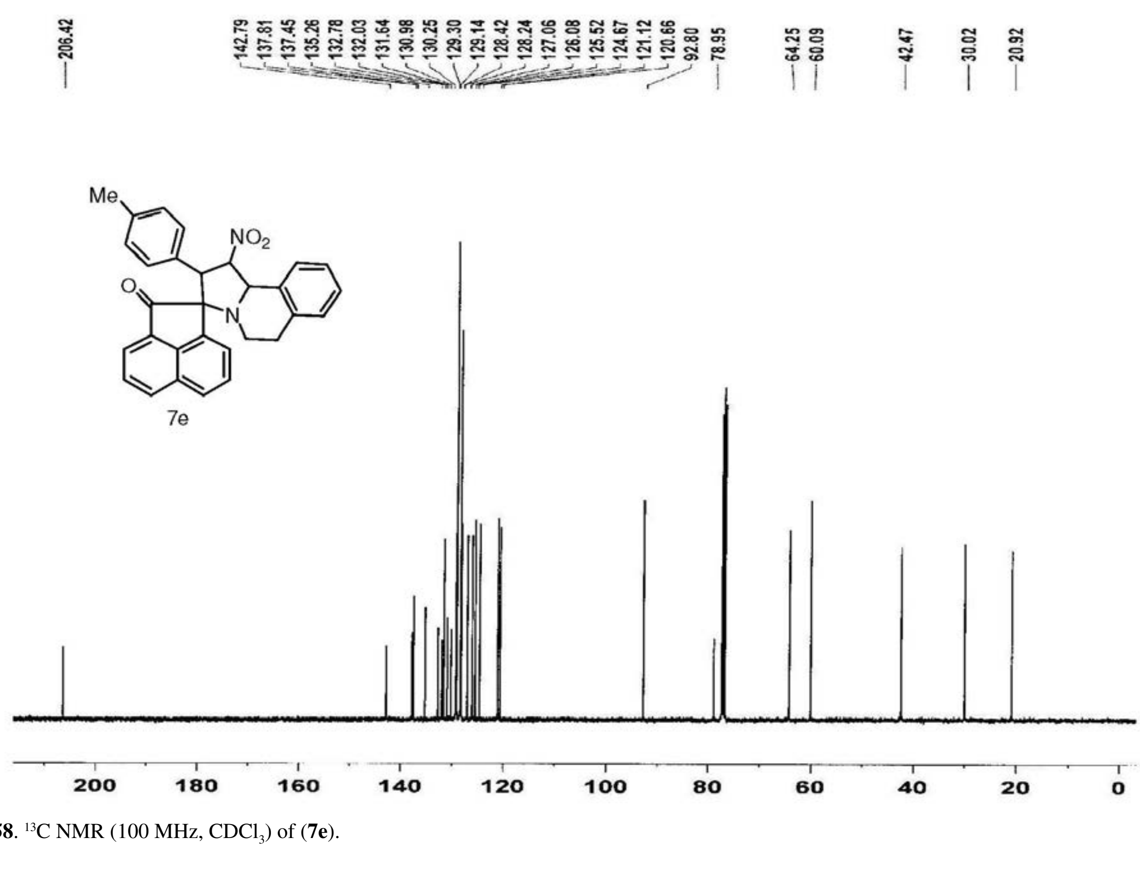

Figure S58. [13]C NMR (100 MHz, $CDCl_3$) of (**7e**).

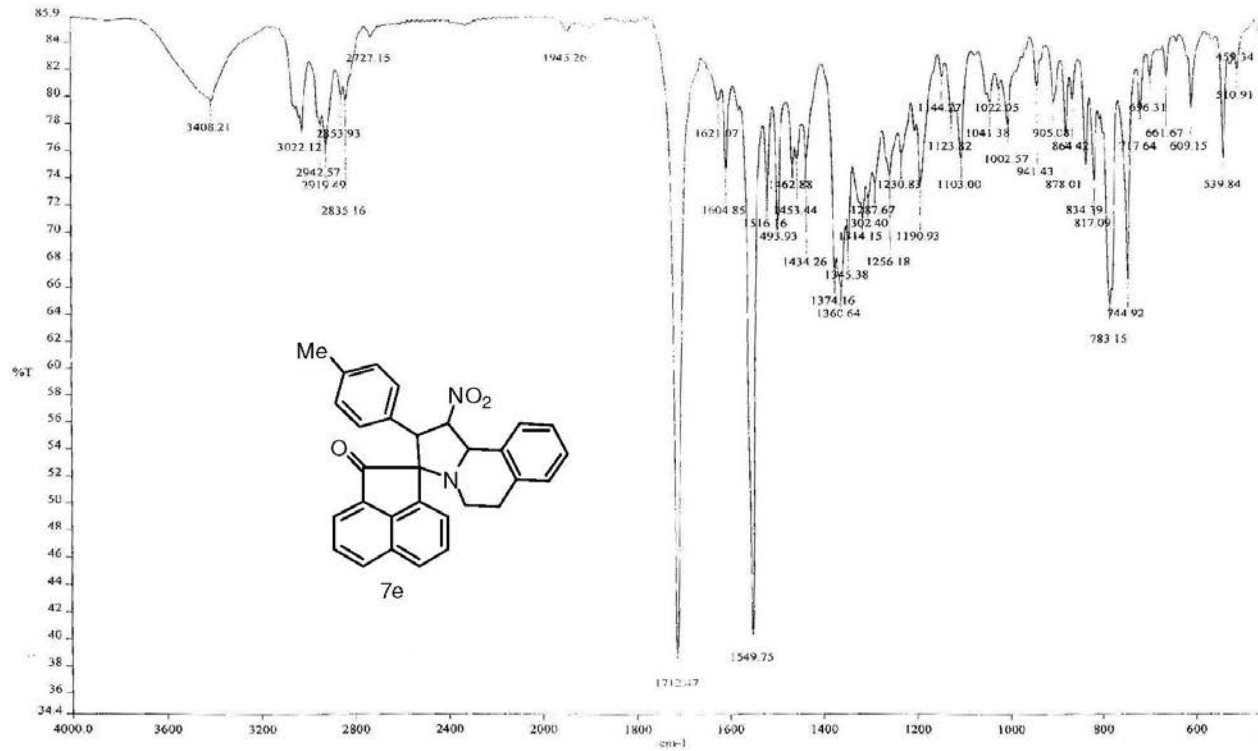

Figure S59. IR (KBr) of (**7e**).

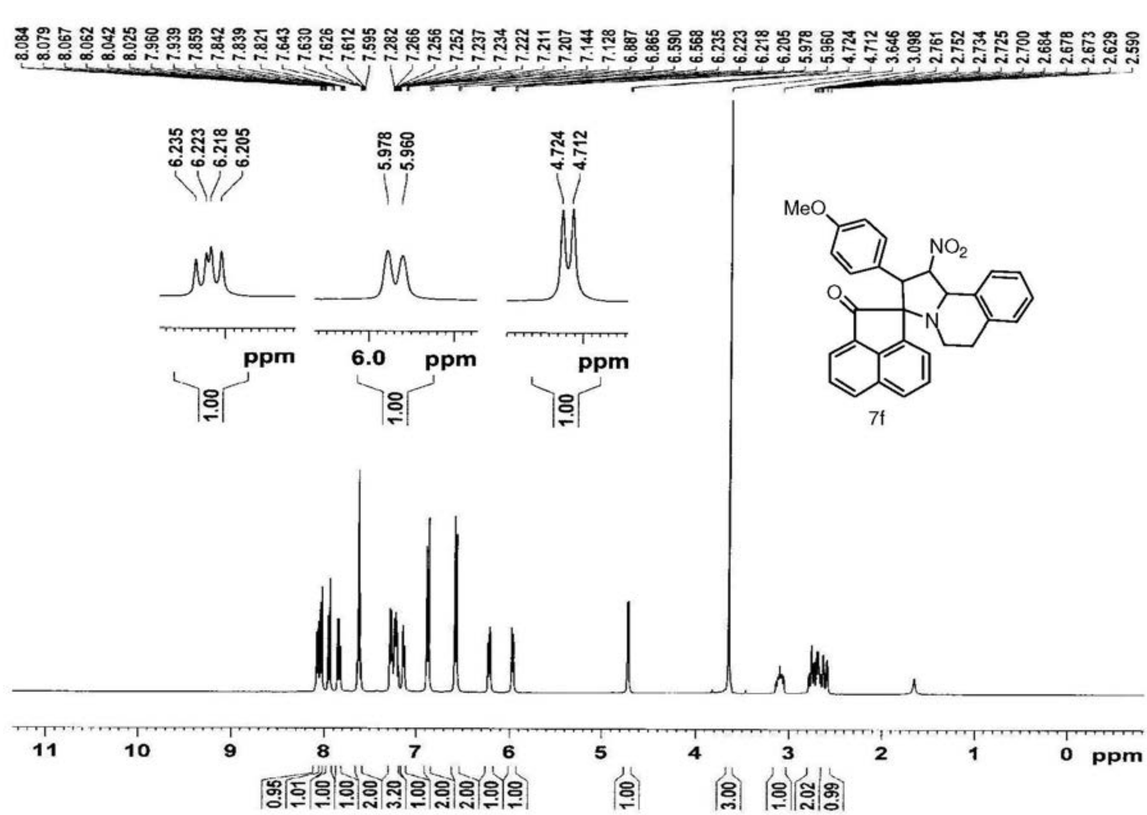

Figure S60. ^{1}H NMR (400 MHz, $CDCl_3$) of (**7f**).

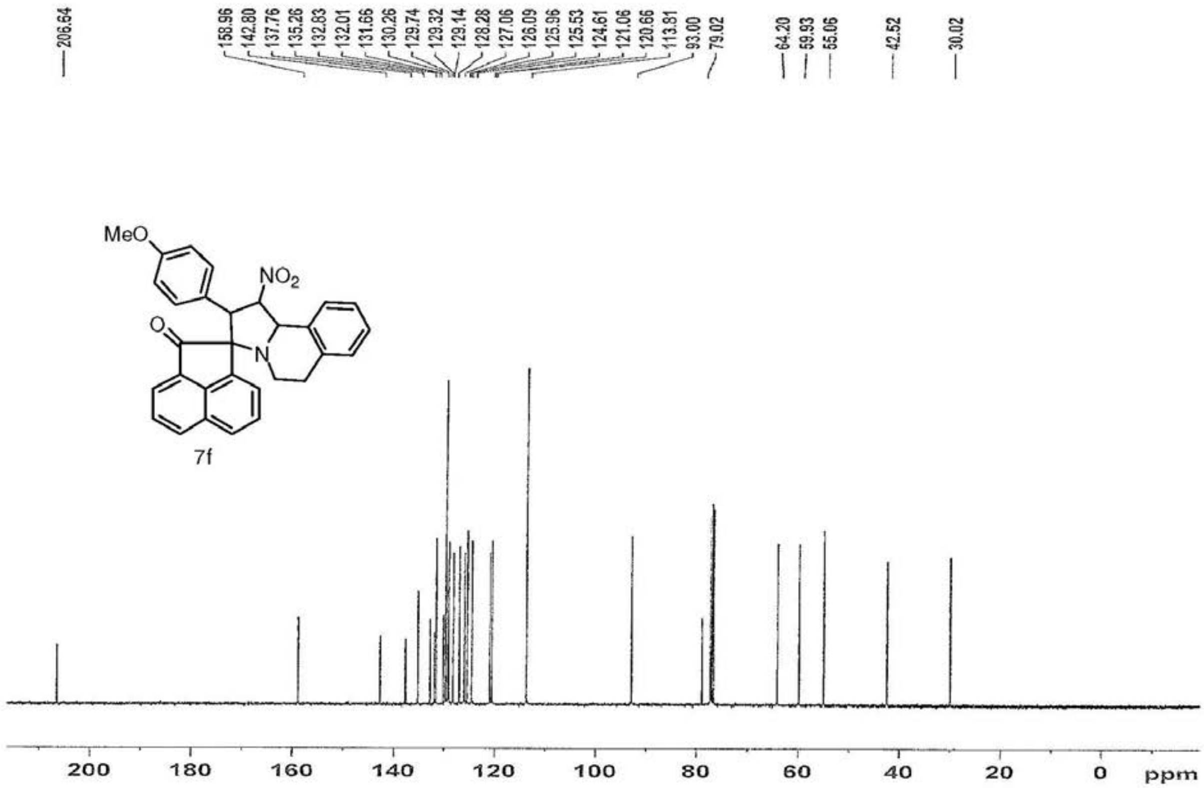

Figure S61. ^{13}C NMR (100 MHz, $CDCl_3$) of (**7f**).

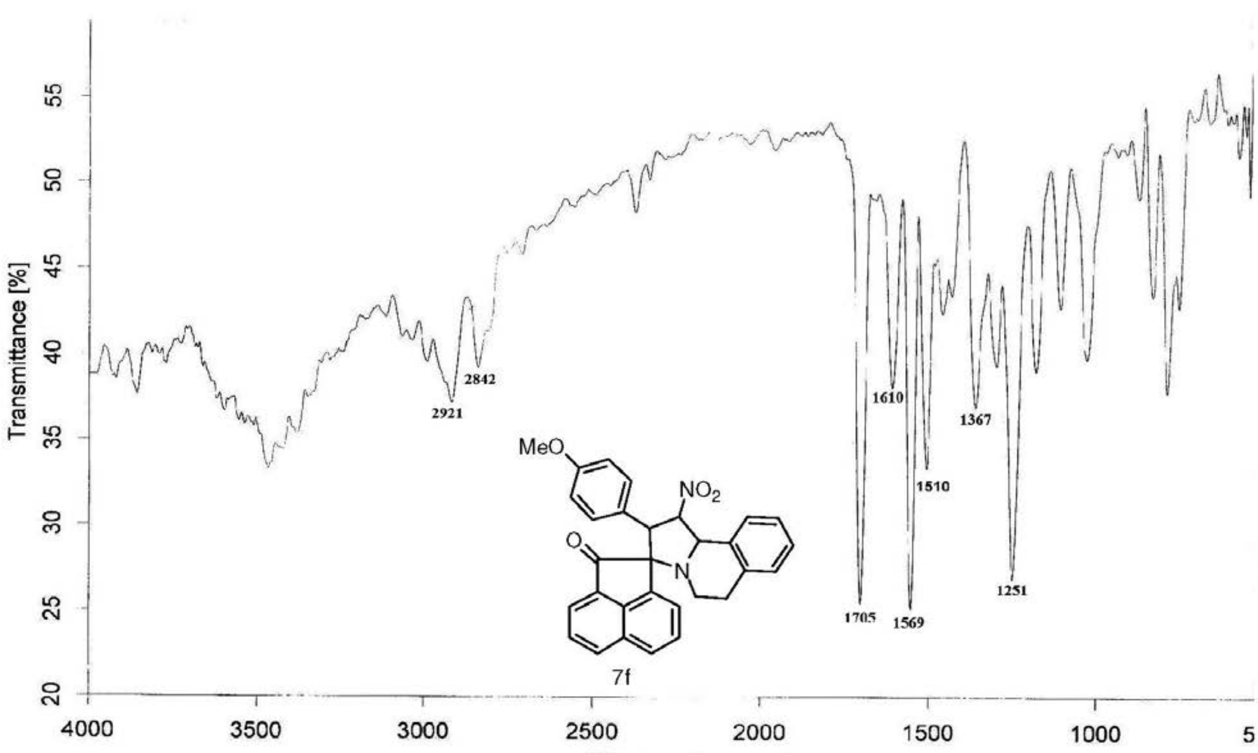

Figure S62. IR (KBr) of (**7f**).

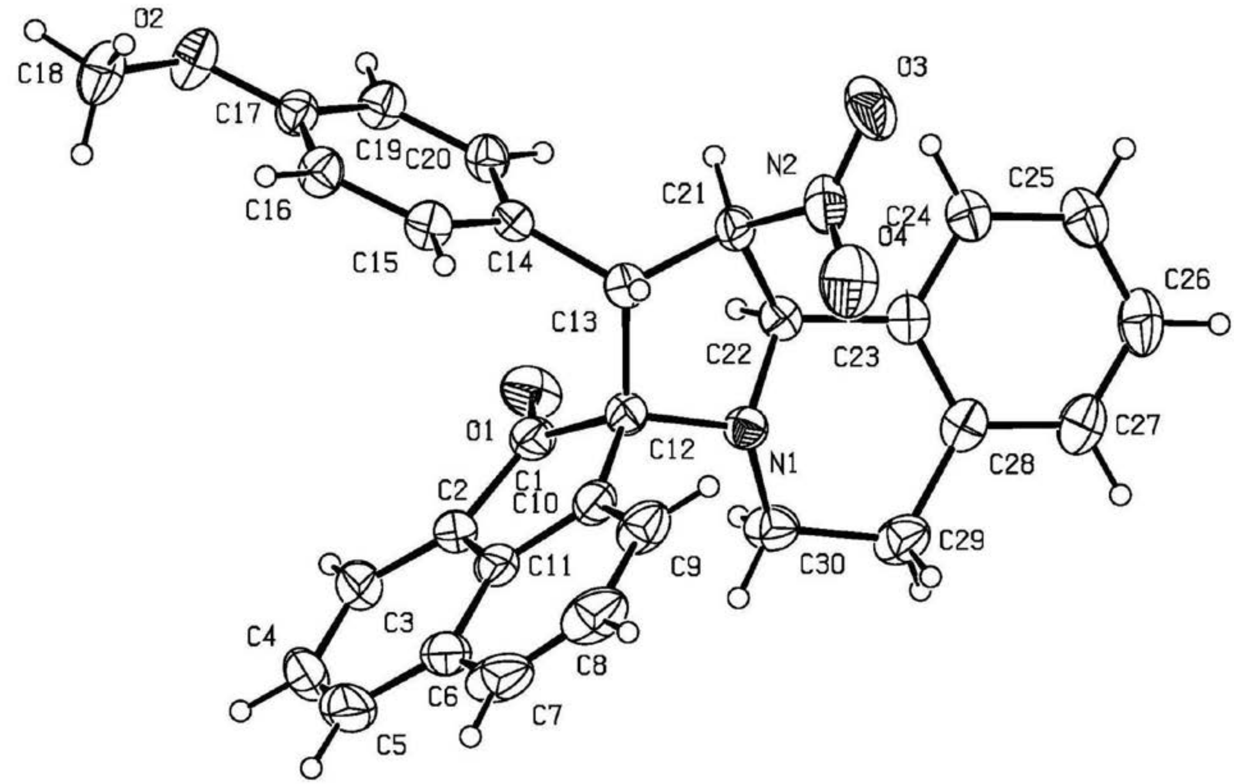

Figure S63. ORTEP diagram of (**7f**).

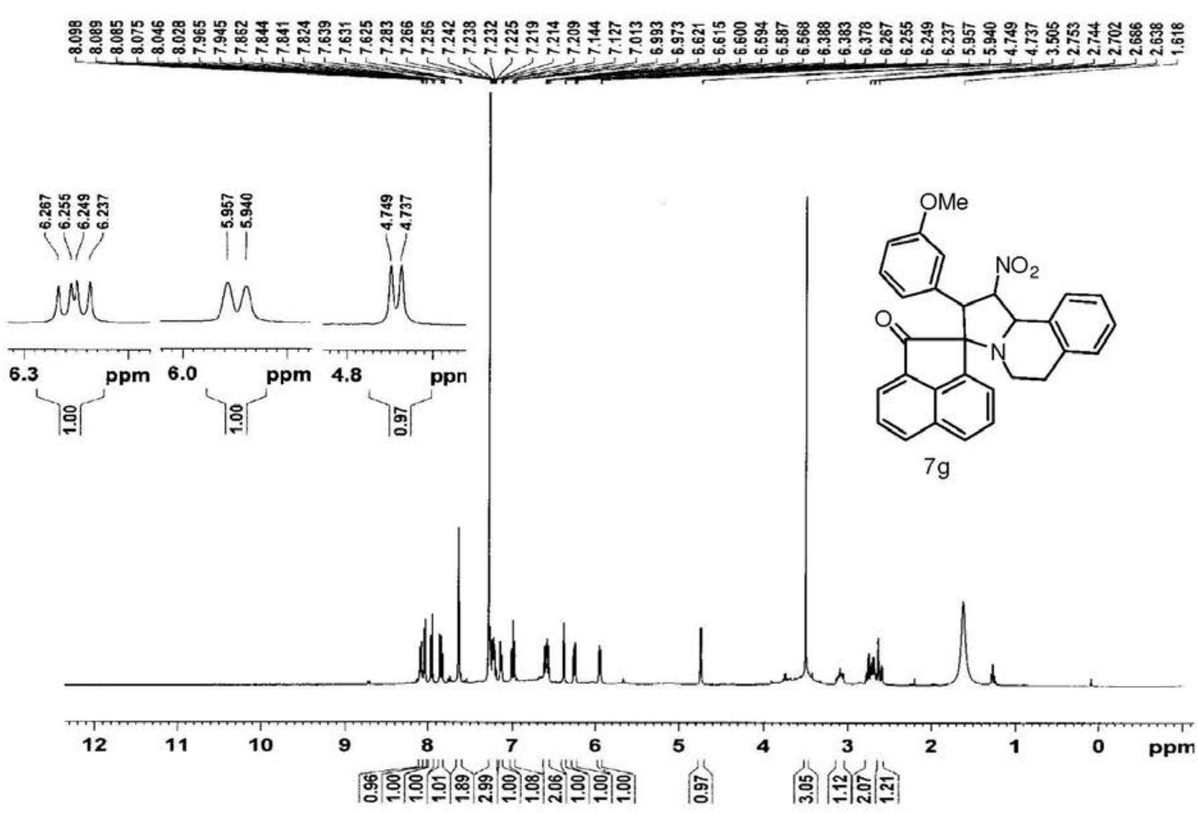

Figure S64. [1]H NMR (400 MHz, $CDCl_3$) of (**7g**).

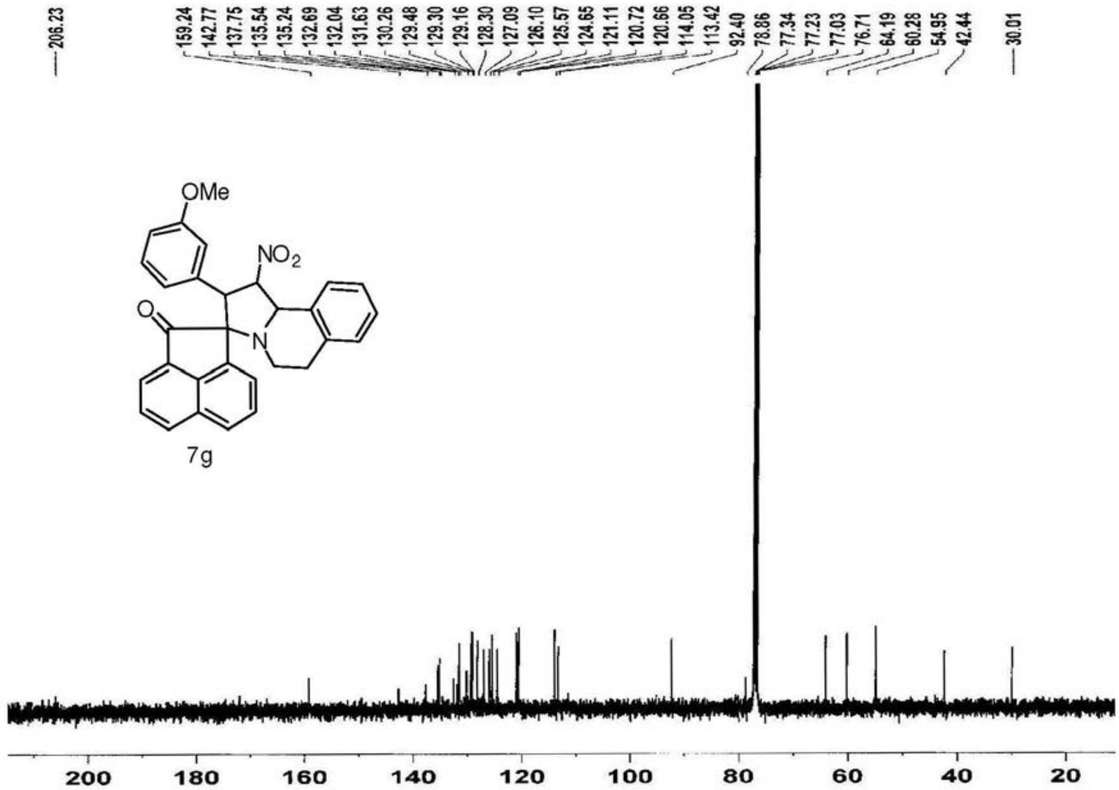

Figure S65. ^{13}C NMR (100 MHz, $CDCl_3$) of (**7g**).

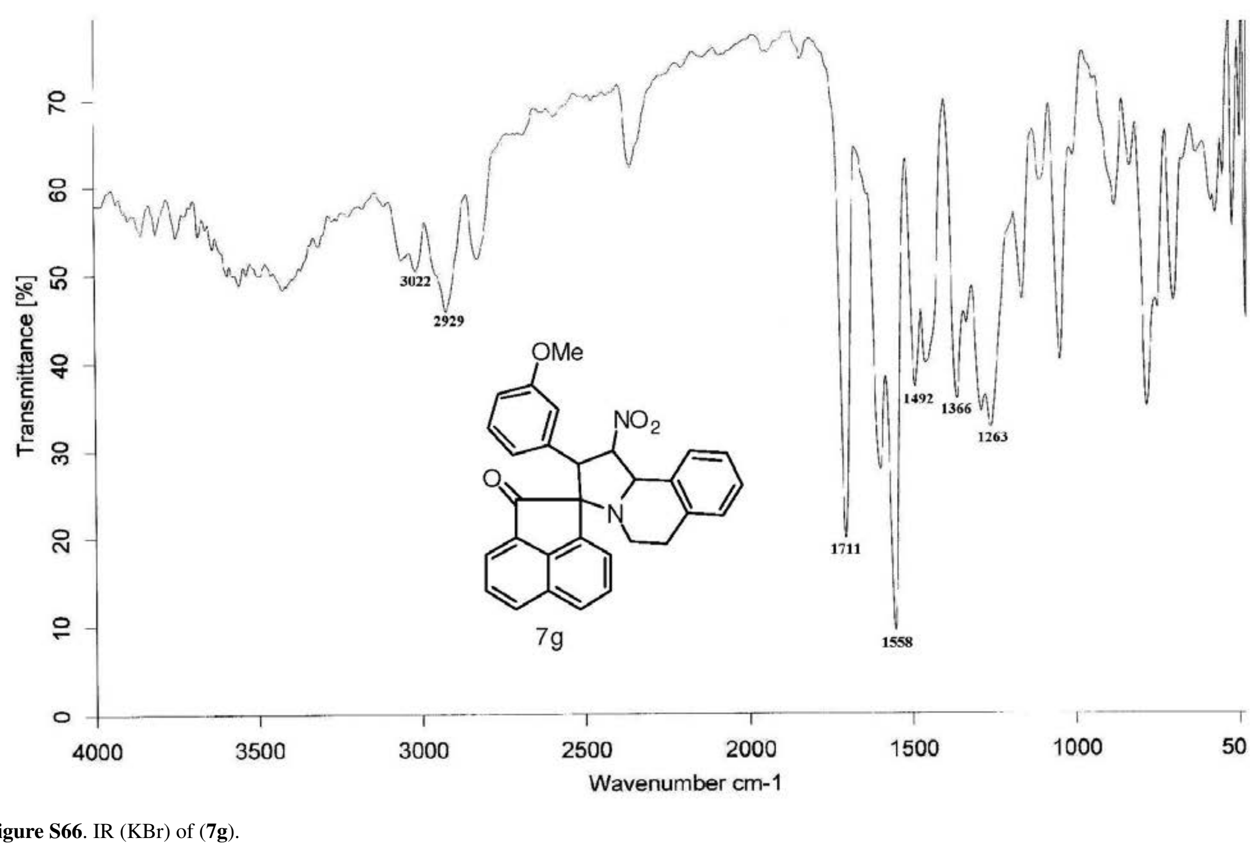

Figure S66. IR (KBr) of (**7g**).

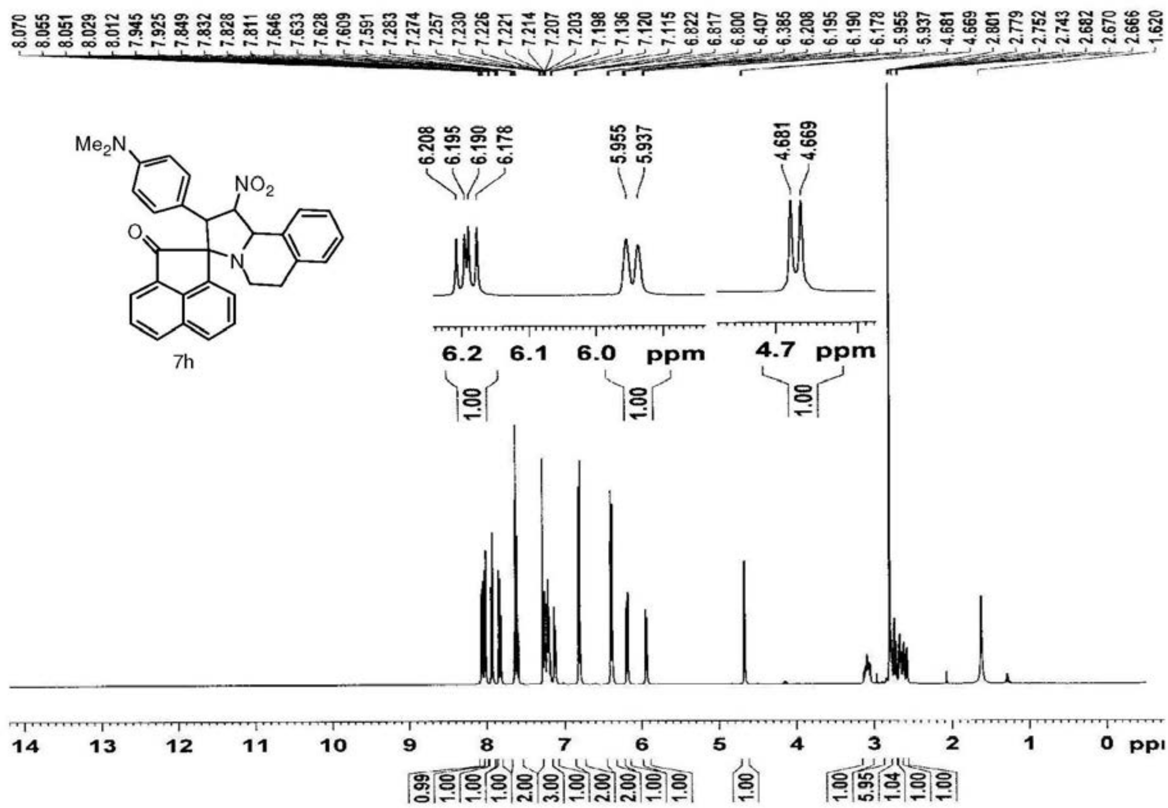

Figure S67. ^{1}H NMR (400 MHz, $CDCl_3$) of (**7h**).

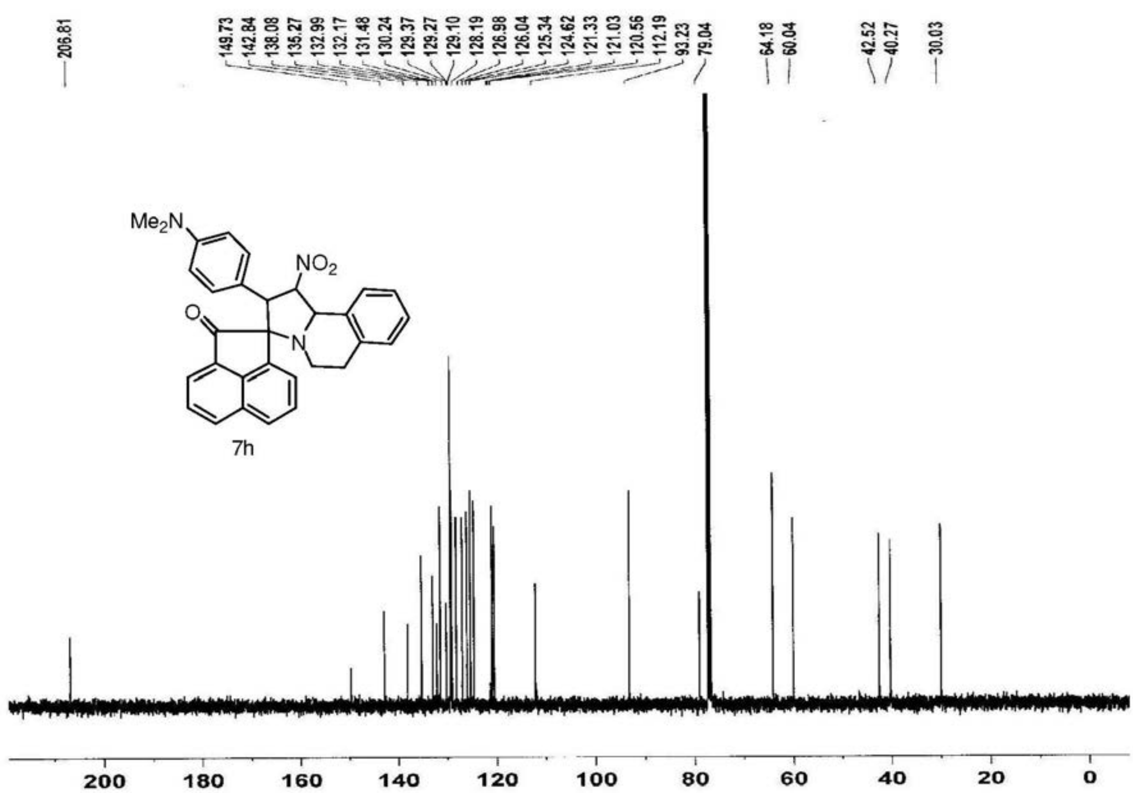

Figure S68. ^{13}C NMR (100 MHz, $CDCl_3$) of (**7h**).

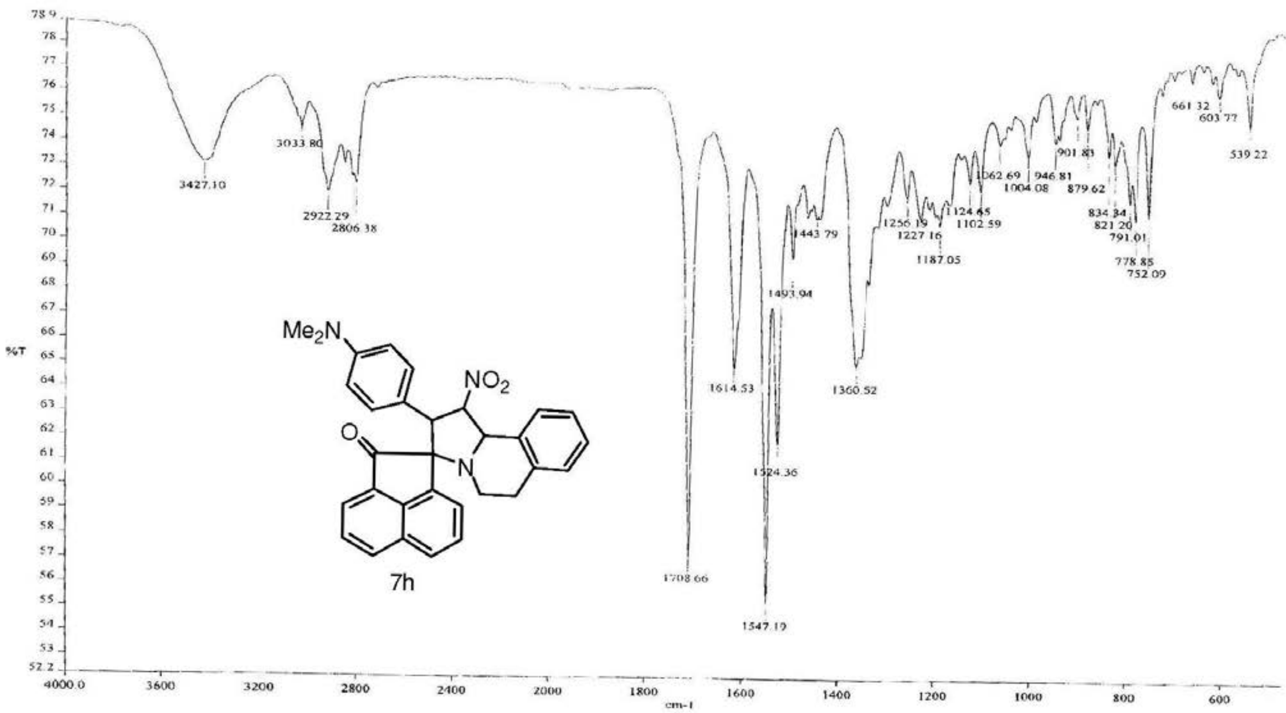

Figure S69. IR (KBr) of (**7h**).

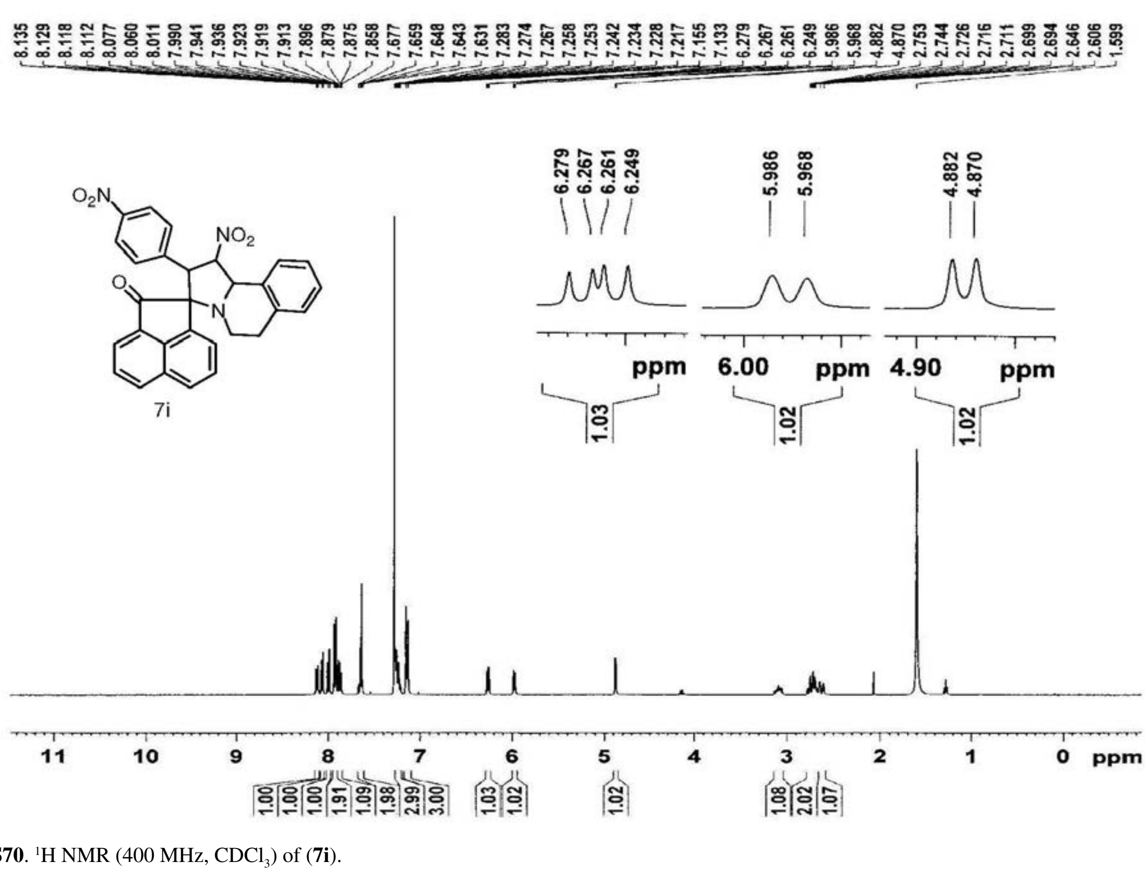

Figure S70. ^{1}H NMR (400 MHz, $CDCl_3$) of (**7i**).

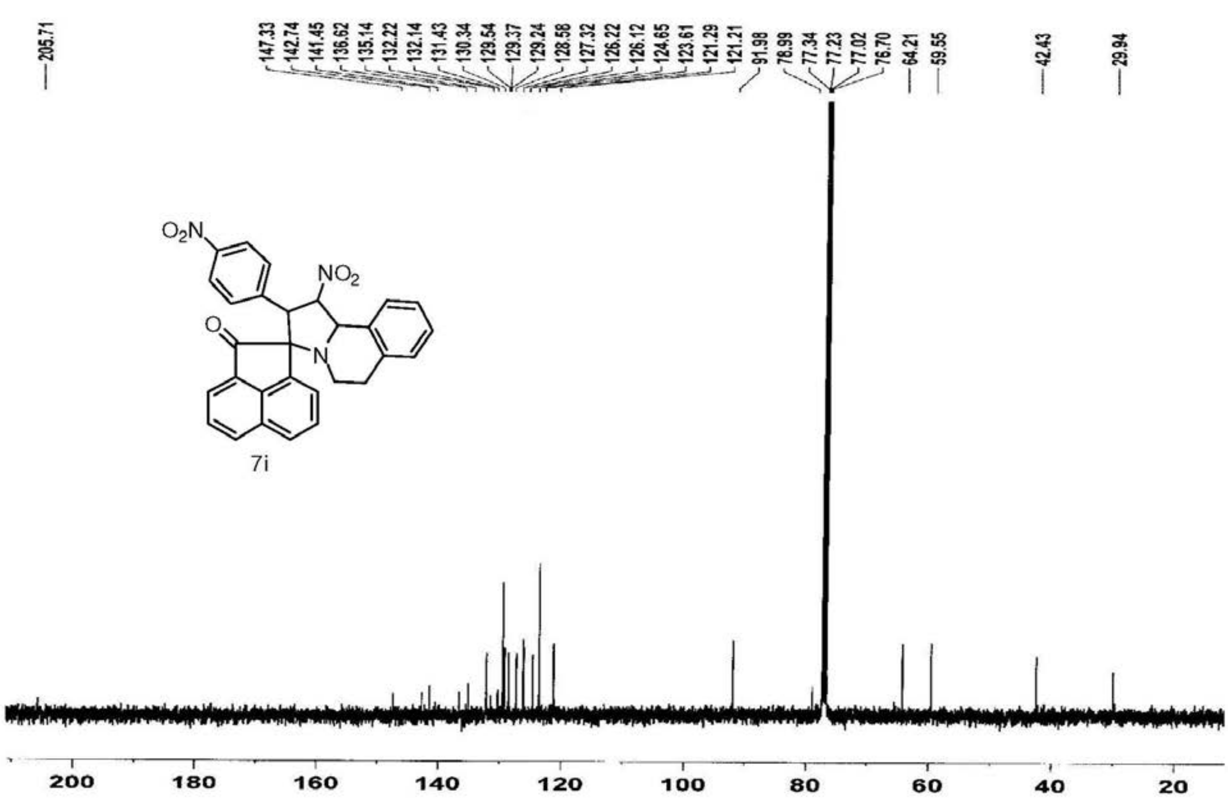

Figure S71. ^{13}C NMR (100 MHz, $CDCl_3$) of (**7i**).

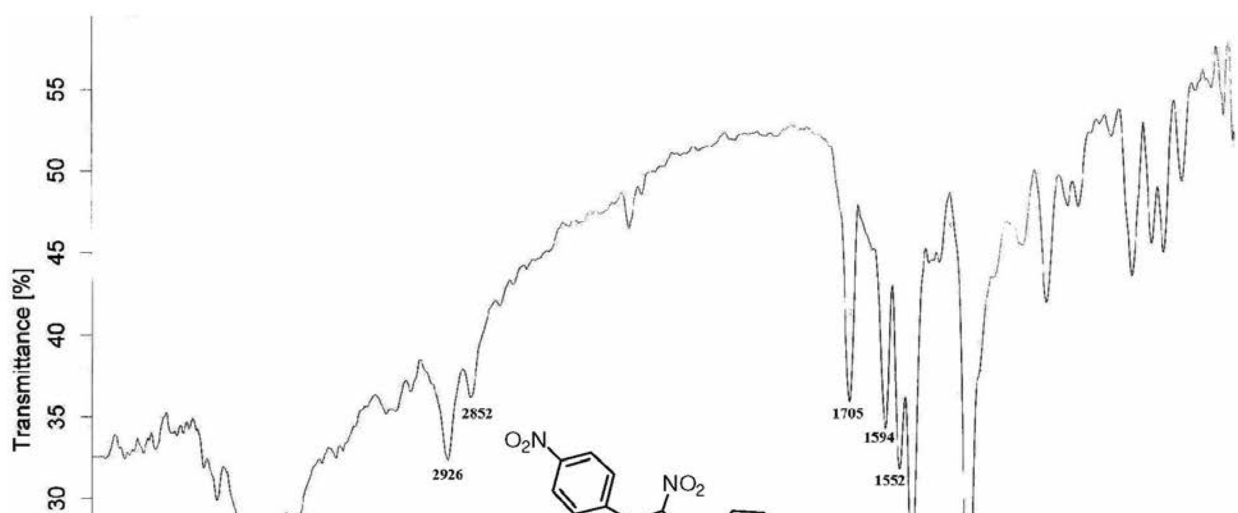

Figure S72. IR (KBr) of (**7i**).

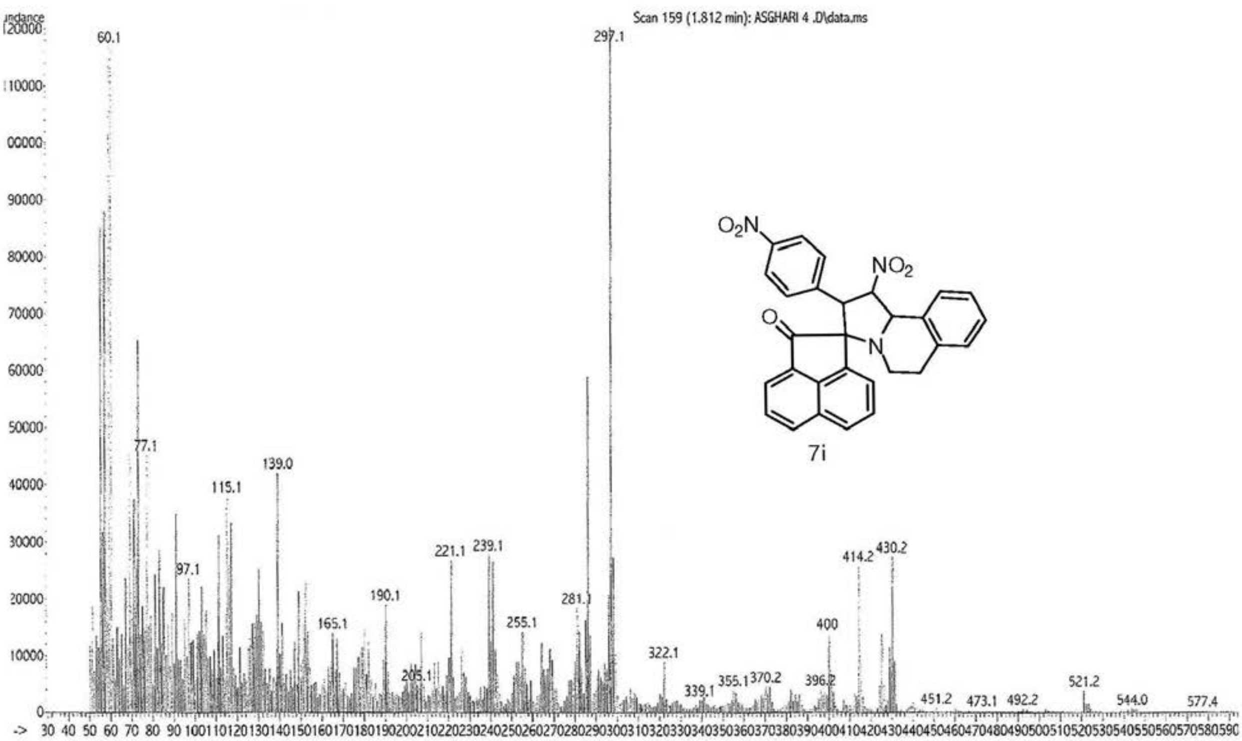

Figure S73. MS (70 eV) of (**7i**).

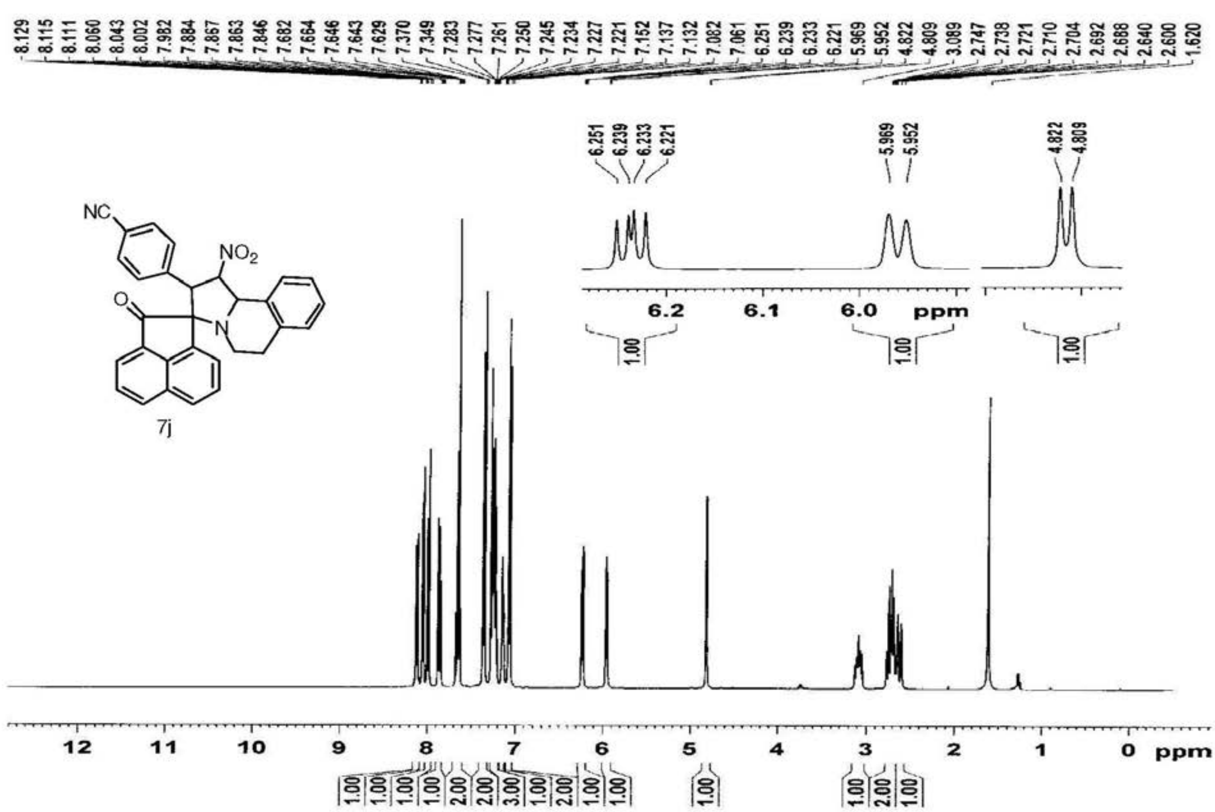

Figure S74. [1]H NMR (400 MHz, $CDCl_3$) of (**7j**).

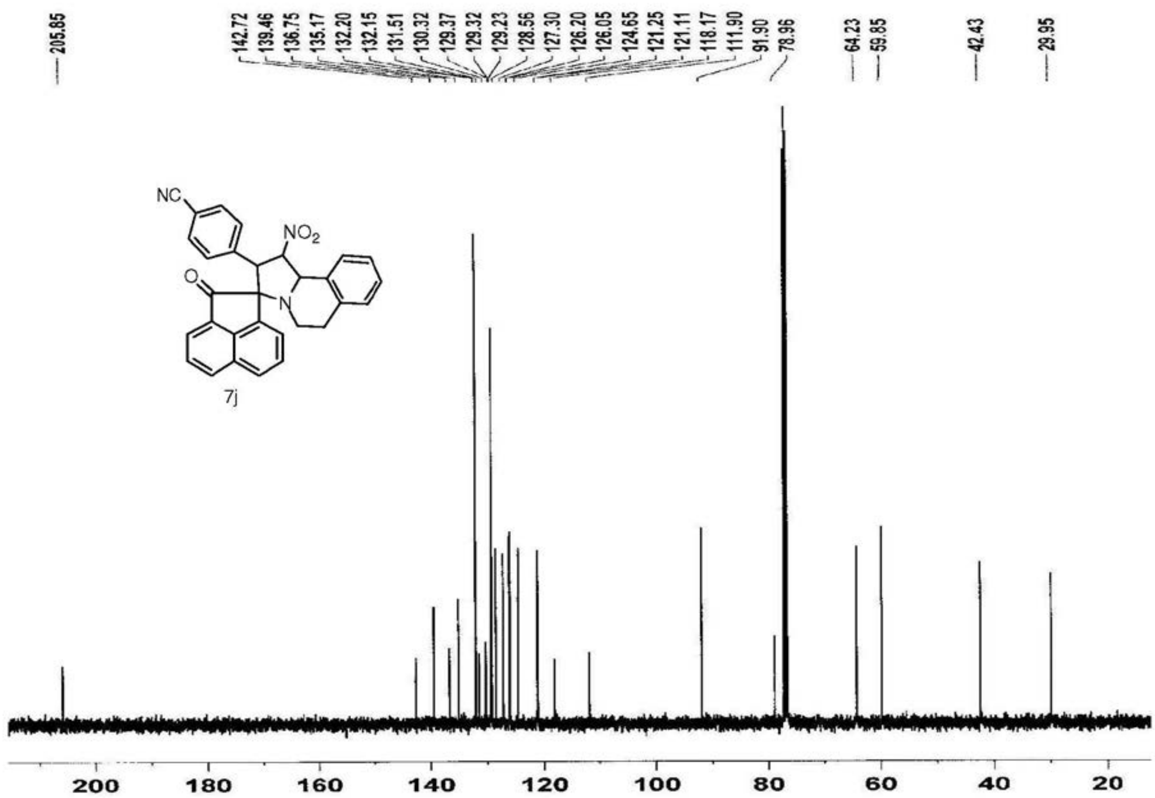

Figure S75. ^{13}C NMR (100 MHz, $CDCl_3$) of (**7j**).

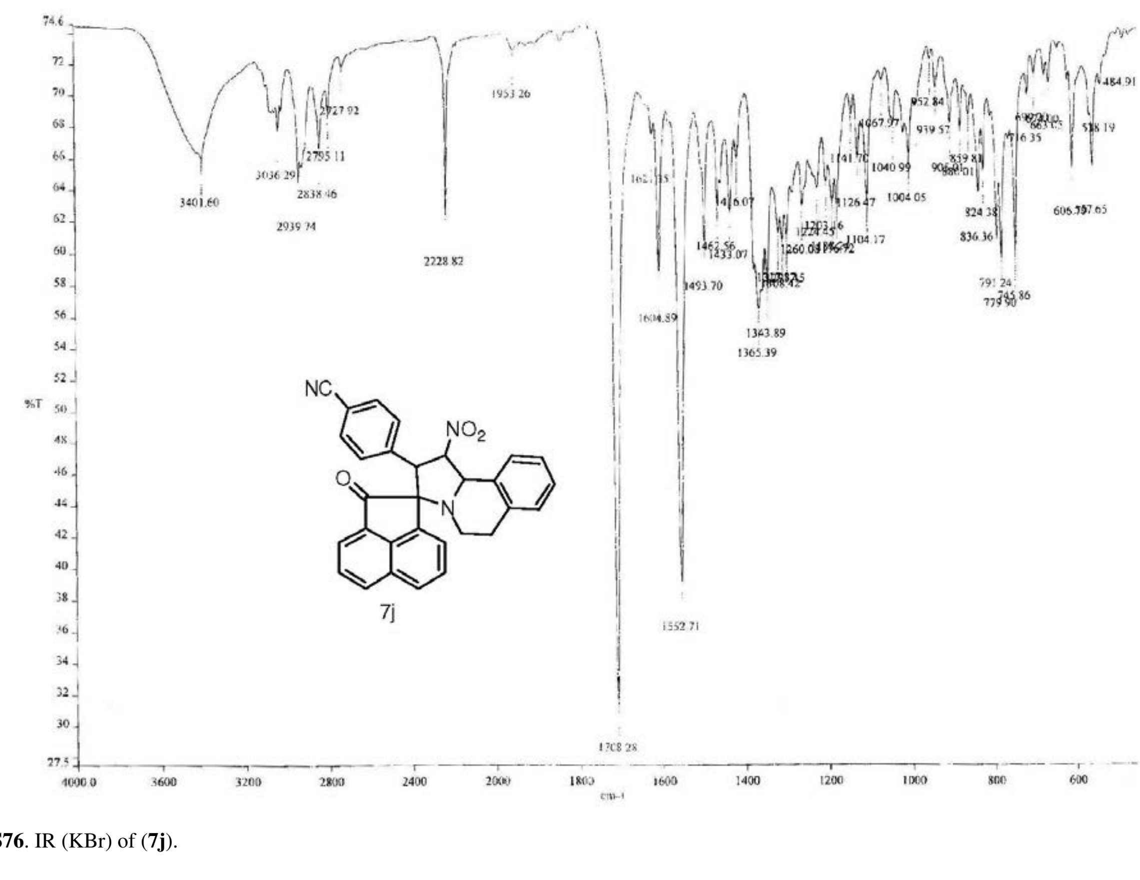

Figure S76. IR (KBr) of (**7j**).

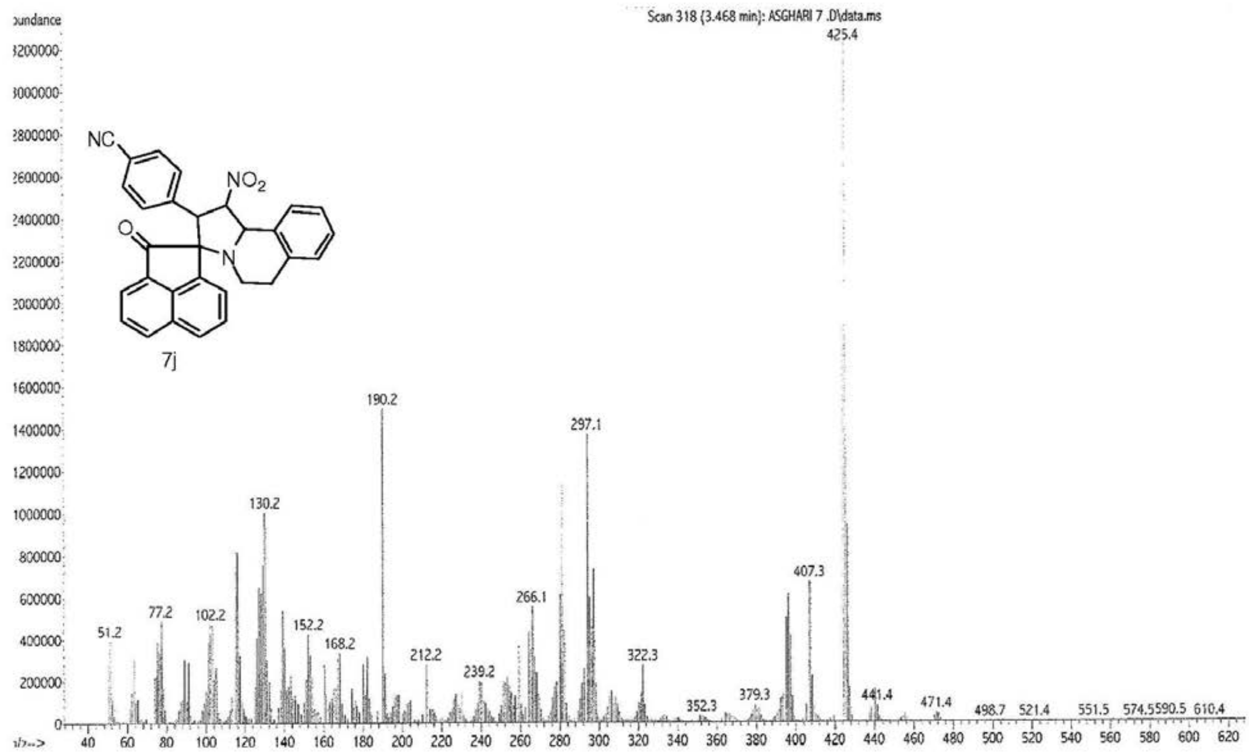

Figure S77. MS (70 eV) of (**7j**).

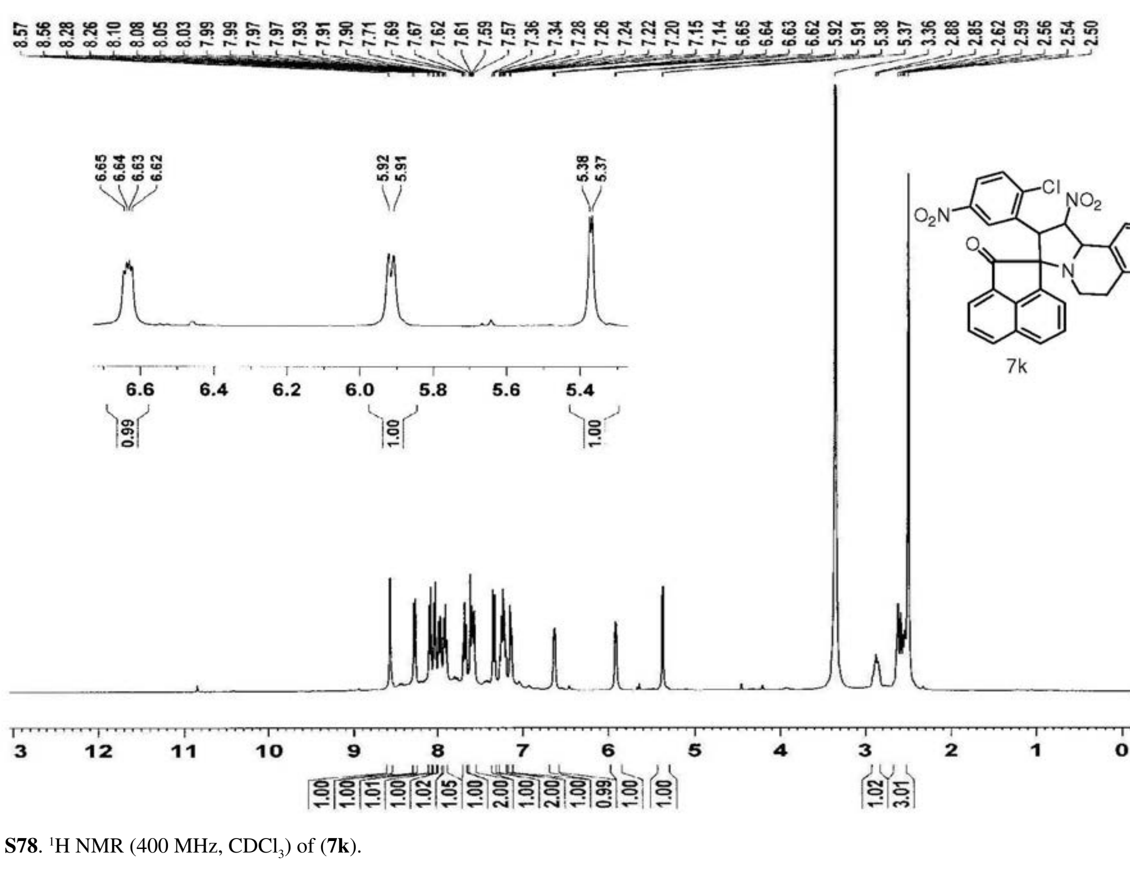

Figure S78. ^{1}H NMR (400 MHz, $CDCl_3$) of (**7k**).

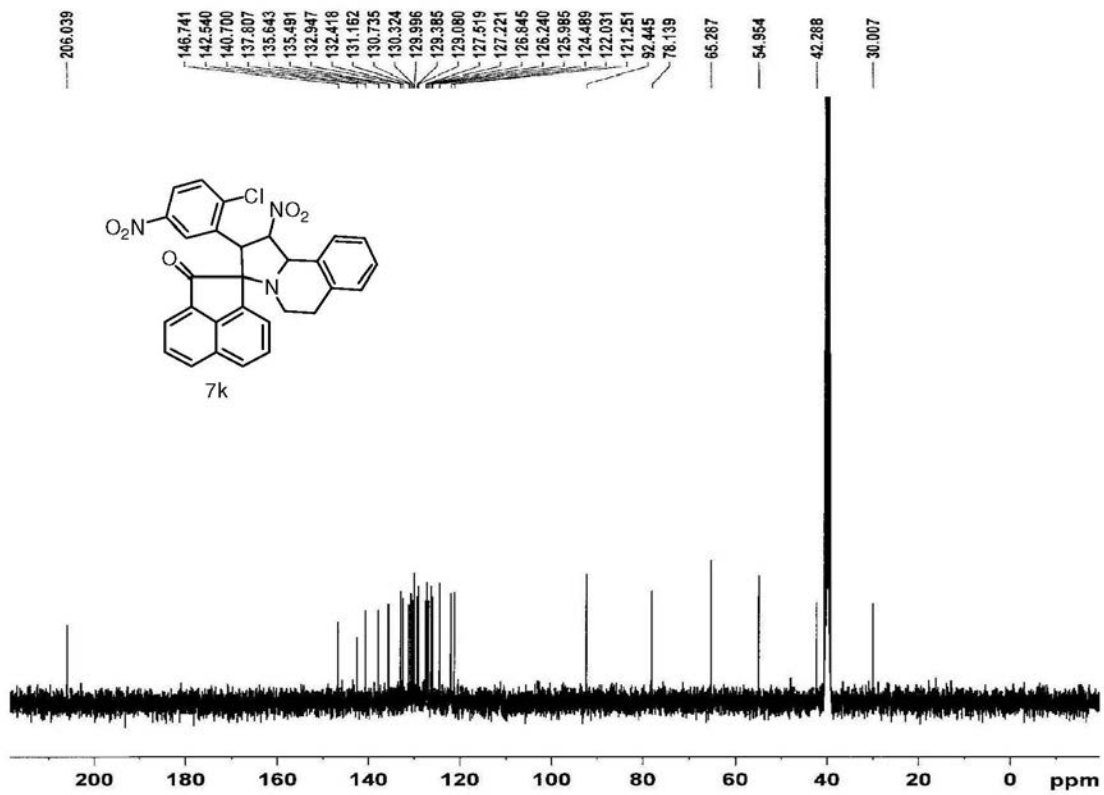

Figure S79. ^{13}C NMR (100 MHz, $CDCl_3$) of (**7k**).

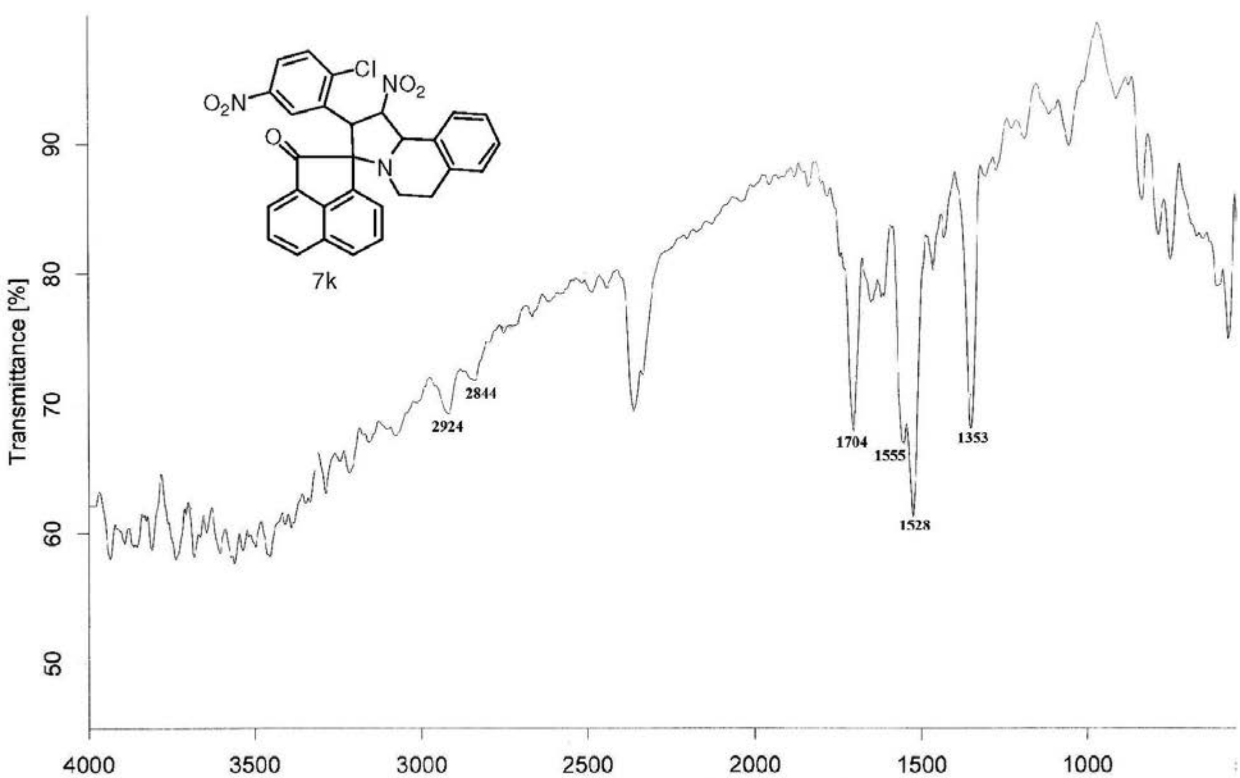

Figure S80. IR (KBr) of (**7k**).

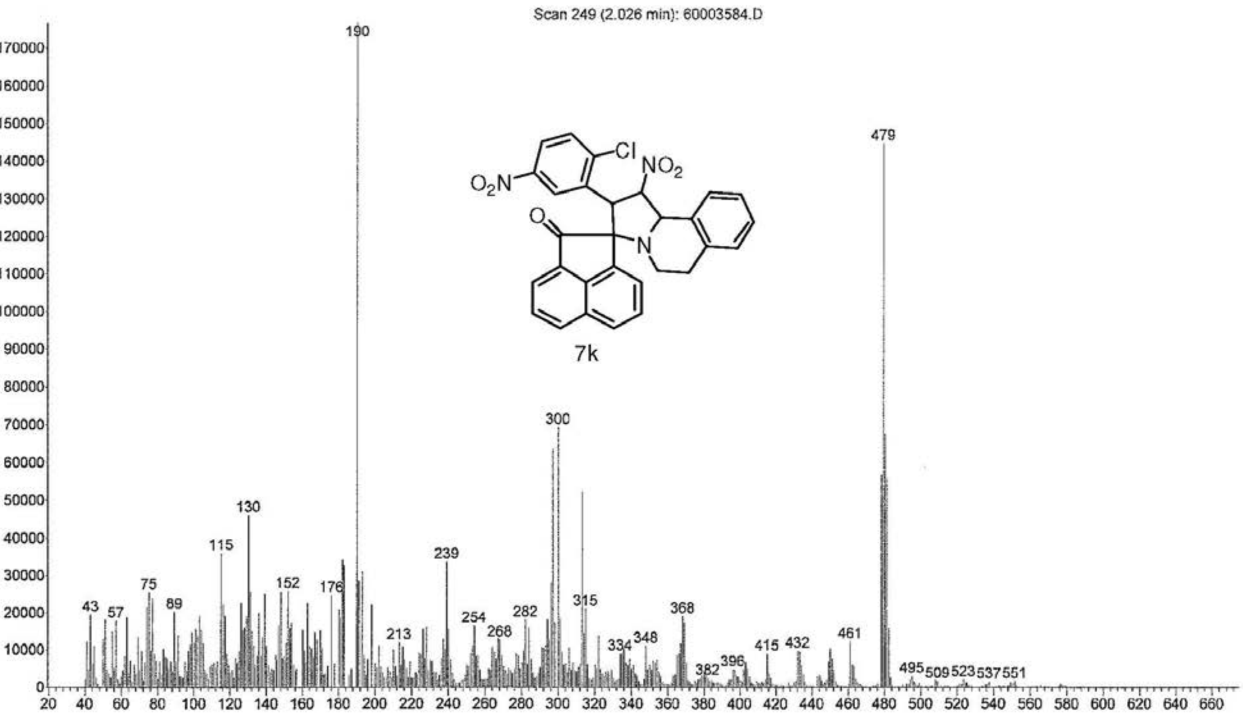

Figure S81. MS (70 eV) of (**7k**).

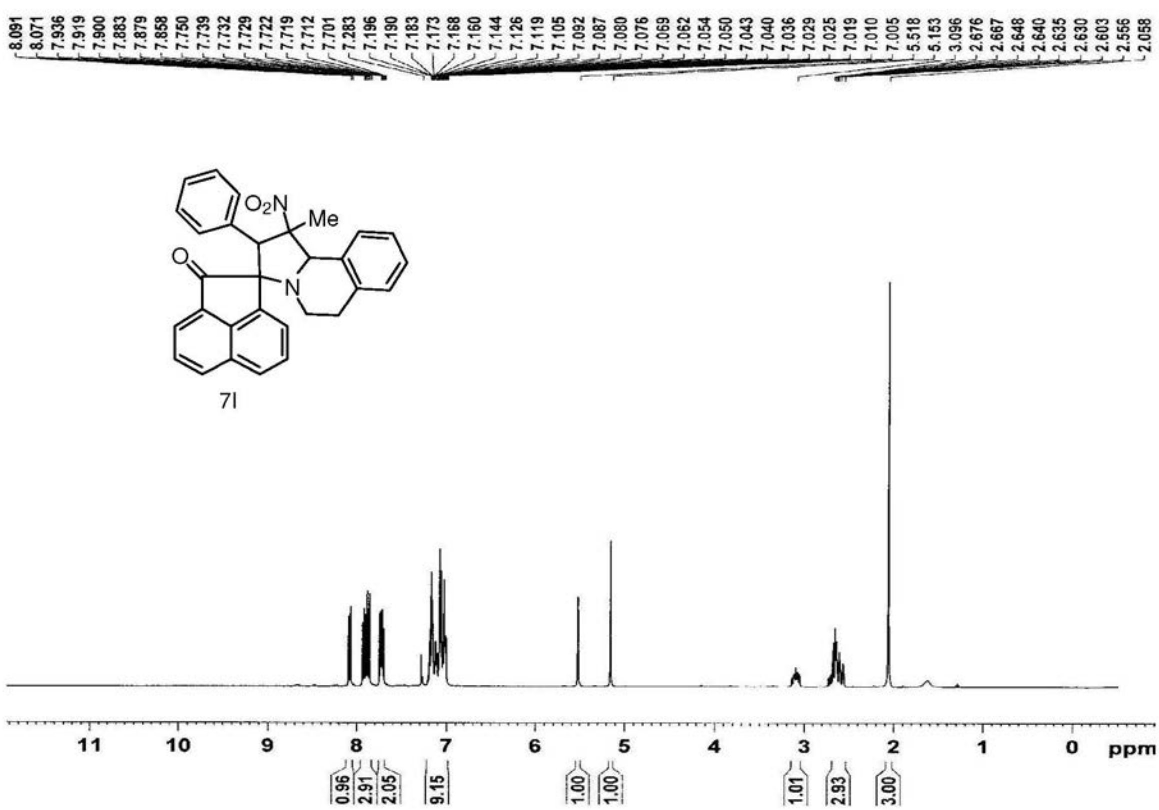

Figure S82. ^{1}H NMR (400 MHz, $CDCl_3$) of (**7l**).

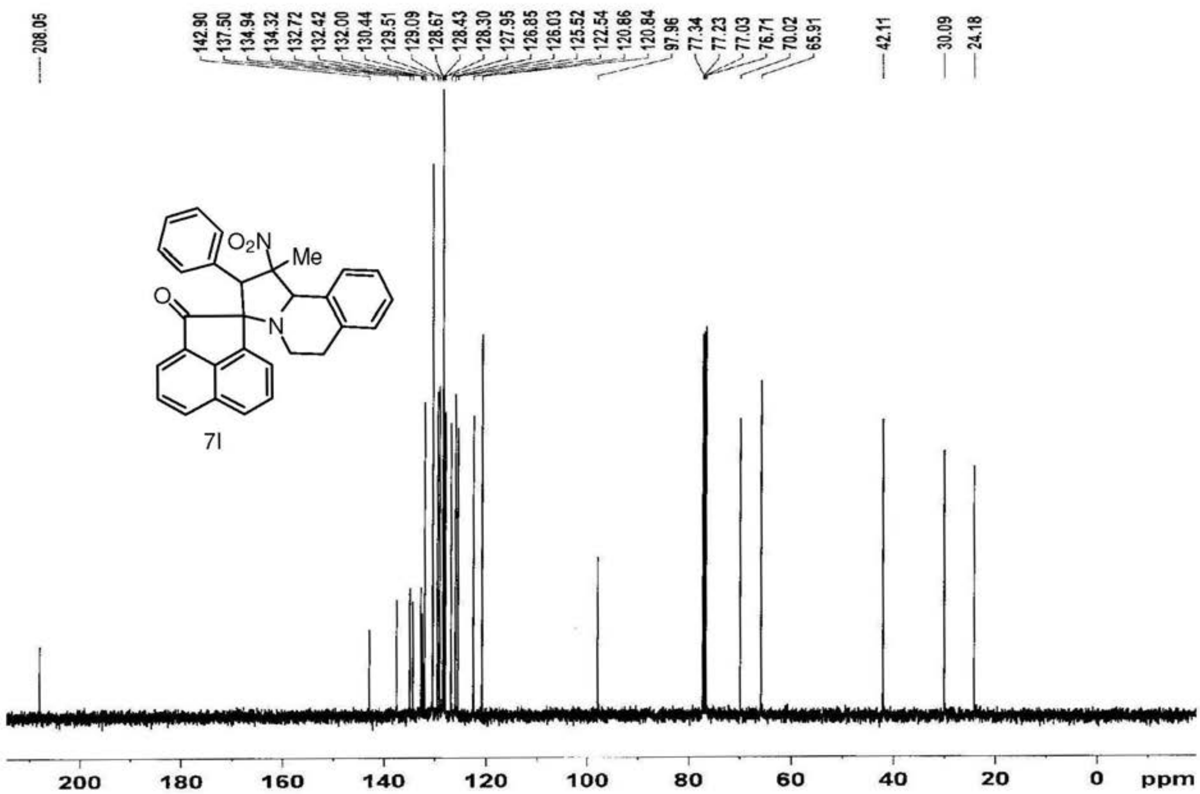

Figure S83. ^{13}C NMR (100 MHz, $CDCl_3$) of (**7l**).

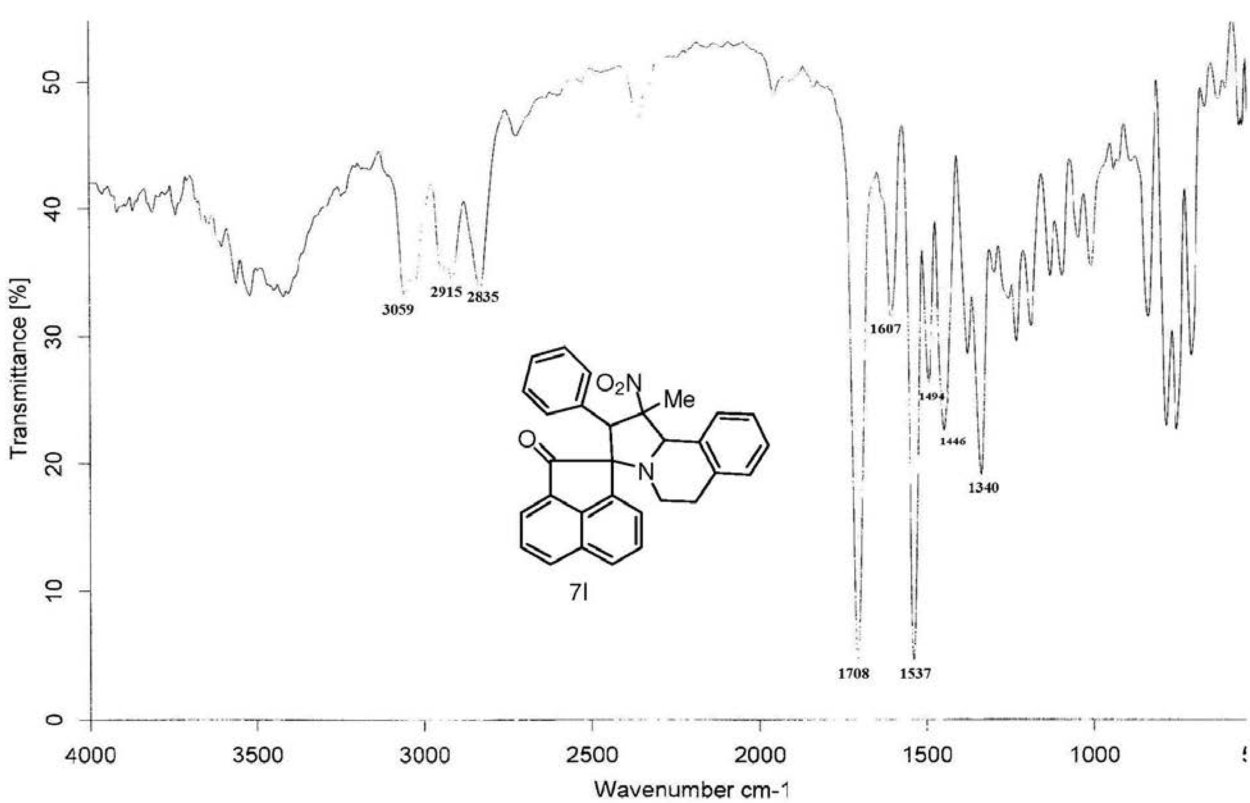

Figure S84. IR (KBr) of (**7l**).

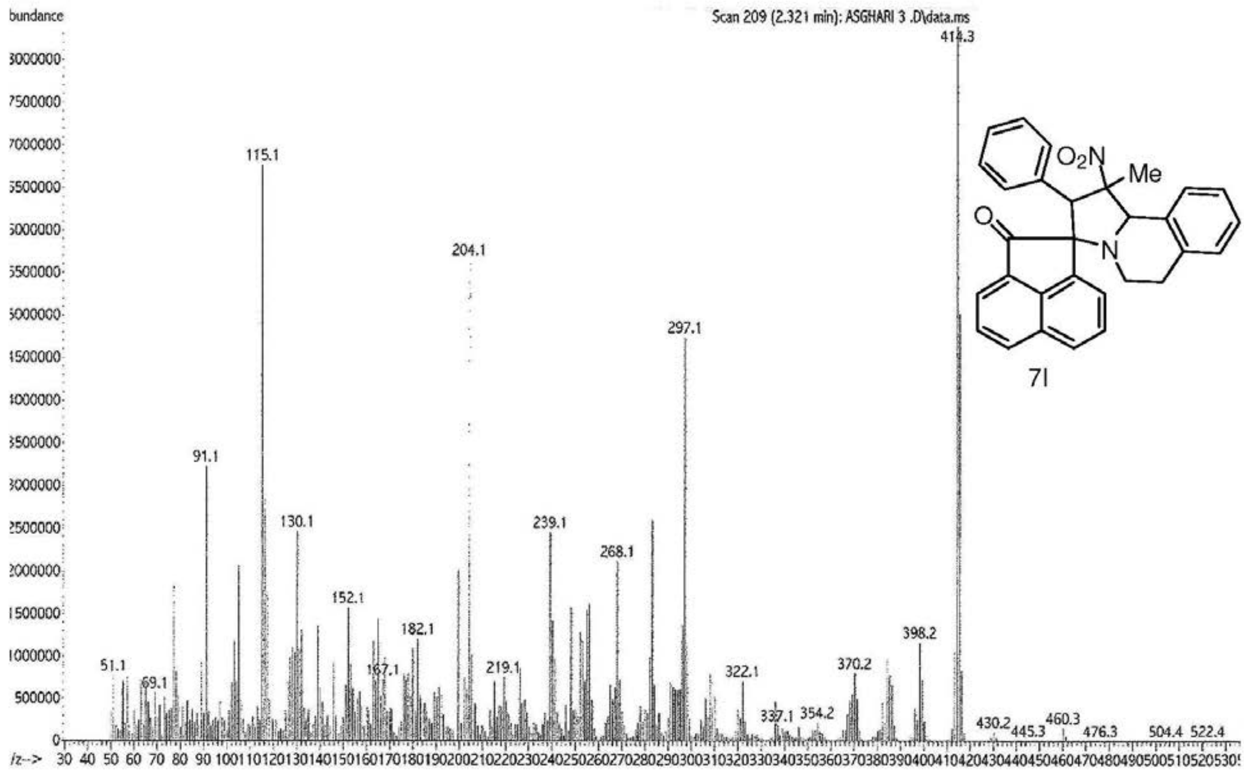

Figure S85. MS (70 eV) of (**7l**).