Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Higher-order [10+2] cycloaddition of 2-alkylidene-1-indanones enables the dearomatization of 3-nitroindoles: an access to polycyclic cyclopenta[*b*]indoline derivatives

Jian-Qiang Zhao,[a,*] Shun Zhou,[a,b] Hui-Ling Qian,[a] Zhen-Hua Wang,[a] Yan-Ping Zhang,[a] Yong You,[a] and Wei-Cheng Yuan[a,*]

[a]Innovation Research Center of Chiral Drugs, Institute for Advanced Study, Chengdu University, Chengdu 610106, China.

[b]National Engineering Research Center of Chiral Drugs, Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, 610041, China.

E-mail: zhaojianqiang@cdu.edu.cn
yuanwc@cioc.ac.cn

Supporting Information

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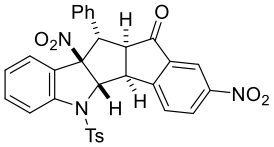
1. General experimental information

Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by TLC. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ and DMSO-d_6. ^{1}H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$ at 7.26 ppm, DMSO-d_6 at 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.20 ppm, DMSO-d_6 at 39.51 ppm). Melting points were recorded on a melting point apparatus.

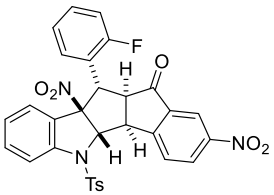
2. General experimental procedures for synthesis of compounds 3

In a dry reaction tube equipped with a magnetic stirring bar, 2-alkylidene-1-indanones **2** (0.12 mmol, 1.2 equiv.), 3-nitroindoles **1** (0.1 mmol), Na_2CO_3 (10.6 mg, 1.0 equiv.) or K_2CO_3 (13.6 mg, 1.0 equiv.) and catalyst TEBA (4.5 mg, 20 mol%, 0.01 mmol) were added successively, and then followed by addition CH_2Cl_2 (1.0 mL). The reaction solution was stirred at room temperature for specified time. After completion, the reaction mixture was directly purified by flash chromatography on silica gel (petroleum ether / dichloromethane 1:3 = 8:1～1:7) to give the corresponding products **3**.



2,9b-dinitro-10-phenyl-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3aa)

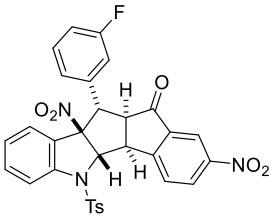
Light yellow solid, 57.0 mg, 98% yield, >20:1 dr; m.p. 222.6-223.2 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.70 (dd, *J* = 8.4, 2.2 Hz, 1H), 8.58 (d, *J* = 2.2 Hz, 1H), 8.48 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.54 – 7.43 (m, 3H), 7.40 – 7.30 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.93 (t, *J* = 7.7 Hz, 1H), 6.10 (d, *J* = 7.9 Hz, 1H), 5.50 (d, *J* = 2.9 Hz, 1H), 4.37 (dd, *J* = 8.0, 2.9 Hz, 1H), 4.21 (d, *J* = 11.7 Hz, 1H), 3.71 (dd, *J* = 11.6, 7.9 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.0, 158.4, 149.1, 145.5, 143.1, 135.7, 133.1, 132.5, 132.2, 130.4, 130.0, 129.9, 129.2, 129.0, 128.7, 128.3, 126.9, 124.7, 122.8, 120.2, 116.6, 105.9, 75.5, 55.9, 54.7, 52.8, 21.6; HRMS (ESI) calcd. for $C_{31}H_{23}N_3O_7S$ $[M + Na]^+$ 604.1149, found: 604.1152.



10-(2-fluorophenyl)-2,9b-dinitro-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3ab)

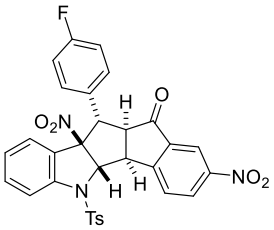
Light yellow solid, 54.7 mg, 91% yield, >20:1 dr; m.p. 224.3-224.9 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.82 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.51 (d, *J* = 8.4 Hz, 1H), 8.40 (d, *J* = 2.2 Hz, 1H), 7.75 (dd, *J* = 17.0, 8.1 Hz, 3H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.49 (q, *J* = 7.1 Hz, 1H), 7.44 – 7.31 (m, 3H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.28 (s, 1H), 5.68 (d, *J* = 2.8 Hz, 1H), 4.57 (d, *J* = 16.9 Hz, 2H), 4.00 (dd, *J* = 10.9, 8.0 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ

200.4, 161.4 (d, *J* = 249.1 Hz), 158.5, 149.2, 145.6, 142.9, 135.7, 132.9, 132.5, 131.0 (d *J* = 8.8 Hz), 130.5, 130.1, 128.5, 127.1, 124.7, 124.3, 123.0, 120.3, 116.4, 116.0 (d, *J* = 22.4 Hz), 105.3, 75.6, 55.7, 53.0, 21.6; ^{19}F NMR (376 MHz, DMSO-d_6) δ -116.4; HRMS (ESI) calcd. for $C_{31}H_{22}FN_3O_7S$ $[M + Na]^+$ 622.1055, found: 622.1075.



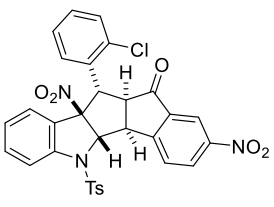
10-(3-fluorophenyl)-2,9b-dinitro-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3ac)

Light yellow solid, 58.2 mg, 97% yield, >20:1 dr; m.p. 224.1-224.7 ºC ; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.78 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.45 (d, *J* = 8.5 Hz, 1H), 8.35 (d, *J* = 2.3 Hz, 1H), 7.73 (dd, *J* = 8.5, 2.1 Hz, 3H), 7.56 – 7.52 (m, 1H), 7.42 – 7.37 (m, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.21 (m, 1H), 7.08 – 7.04 (m, 1H), 7.01 (d, *J* = 7.9 Hz, 1H), 7.00 – 6.96 (m, 1H), 6.08 (dd, *J* = 7.9, 1.3 Hz, 1H), 5.64 (d, *J* = 2.7 Hz, 1H), 4.51 (dd, *J* = 7.9, 2.7 Hz, 1H), 4.43 (d, *J* = 11.2 Hz, 1H), 3.95 (dd, *J* = 11.2, 7.8 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 201.4, 162.1 (d, *J* = 243.7 Hz), 159.2, 149.0, 145.8, 143.1, 137.4 (d, *J* = 7.4 Hz), 136.4, 133.4, 133.2, 130.7, 130.6, 130.5, 130.4, 128.9 (d, *J* = 22.4 Hz), 127.7, 124.6, 123.5, 119.4, 115.9 (d, *J* = 20.5 Hz), 115.7, 106.0, 75.1, 56.2, 53.9, 53.0, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.3; HRMS (ESI) calcd. for $C_{31}H_{22}FN_3O_7S$ $[M + Na]^+$ 622.1055, found: 622.1056.



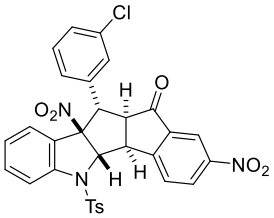
10-(4-fluorophenyl)-2,9b-dinitro-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3ad)

Light yellow solid, 55.1 mg, 92% yield, >20:1 dr; m.p. 224.0-224.9 ºC ; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.77 (dd, *J* = 8.5, 2.3 Hz, 1H), 8.45 (d, *J* = 8.4 Hz, 1H), 8.35 (d, *J* = 2.3 Hz, 1H), 7.72 (dd, *J* = 8.3, 2.4 Hz, 3H), 7.60 – 7.48 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.15 (m, 4H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.06 (d, *J* = 7.8 Hz, 1H), 5.65 (d, *J* = 2.7 Hz, 1H), 4.55 – 4.44 (m, 1H), 4.38 (d, *J* = 11.5 Hz, 1H), 3.89 (dd, *J* = 11.5, 7.8 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 200.9, 162.1 (d, *J* = 244.0 Hz), 158.8, 148.5, 145.3, 142.6, 135.9, 132.8 (d, *J* = 20.3 Hz), 132.3, 132.2, 130.2, 130.1, 128.8, 128.4, 127.2, 124.2, 123.1, 119.0, 115.2 (d, *J* = 9.0 Hz), 114.9, 105.6, 74.5, 55.8, 53.2, 52.6, 21.0; ^{19}F NMR (376 MHz, DMSO-d_6) δ -113.4; HRMS (ESI) calcd. for $C_{31}H_{22}FN_3O_7S$ $[M + Na]^+$ 622.1055, found: 622.1064.



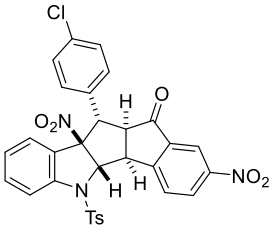
10-(2-chlorophenyl)-2,9b-dinitro-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3ae)

Light yellow solid, 55.6 mg, 90% yield, >20:1 dr; m.p. 219.7-210.6 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.80 (dd, J = 8.4, 2.3 Hz, 1H), 8.50 (d, J = 8.4 Hz, 1H), 8.40 (d, J = 2.2 Hz, 1H), 7.72 (d, J = 8.3 Hz, 1H), 7.70 – 7.65 (m, 2H), 7.55 – 7.50 (m, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.33 – 7.24 (m, 4H), 7.03 – 6.97 (m, 1H), 6.40 (d, J = 7.9 Hz, 1H), 5.59 (d, J = 2.7 Hz, 1H), 4.77 (dd, J = 9.8, 1.9 Hz, 1H), 4.70 (dd, J = 8.0, 2.9 Hz, 1H), 3.96 (dd, J = 9.6, 8.1 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 201.7, 159.3, 149.1, 145.9, 142.8, 136.1, 134.9, 133.1, 133.0, 132.8, 132.2, 131.0, 130.7, 130.6, 129.9, 129.5, 129.0, 127.7, 127.4, 124.7, 123.1, 119.4, 115.8, 106.0, 75.8, 58.5, 53.3, 51.9, 21.5; HRMS (ESI) calcd. for $C_{31}H_{22}{}^{35}ClN_3O_7S$ [M + Na]$^+$ 638.0759, found: 638.0757; calcd. for $C_{31}H_{22}{}^{37}ClN_3O_7S$ [M + Na]$^+$ 640.0744, found: 640.0745.



10-(3-chlorophenyl)-2,9b-dinitro-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3af)

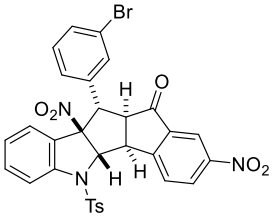
Light yellow solid, 55.8 mg, 91% yield, >20:1 dr; m.p. 229.1-229.8 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.77 (dd, J = 8.4, 2.3 Hz, 1H), 8.46 (d, J = 8.4 Hz, 1H), 8.35 (d, J = 2.3 Hz, 1H), 7.74 (dd, J = 8.4, 2.0 Hz, 3H), 7.57 – 7.52 (m, 1H), 7.49 – 7.45 (m, 1H), 7.38 (t, J = 7.9 Hz, 1H), 7.34 (d, J = 8.1 Hz, 2H), 7.25 – 7.22 (m, 1H), 7.16 (dt, J = 7.9, 1.3 Hz, 1H), 7.03 – 6.94 (m, 1H), 5.66 (d, J = 2.7 Hz, 1H), 4.50 (dd, J = 8.0, 2.7 Hz, 1H), 4.42 (d, J = 11.3 Hz, 1H), 3.94 (dd, J = 11.4, 7.9 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 201.4, 159.2, 148.9, 145.8, 143.1, 137.2, 136.4, 133.4, 133.2, 133.1, 130.7, 130.6, 130.3, 129.4, 129.0, 128.9, 128.8, 127.7, 124.5, 123.5, 119.4, 115.7, 105.9, 75.0, 56.3, 53.7, 53.0, 21.5; HRMS (ESI) calcd. for $C_{31}H_{22}{}^{35}ClN_3O_7S$ [M + Na]$^+$ 638.0759, found: 638.0761; calcd. for $C_{31}H_{22}{}^{37}ClN_3O_7S$ [M + Na]$^+$ 640.0744, found: 640.0747.



10-(4-chlorophenyl)-2,9b-dinitro-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3ag)

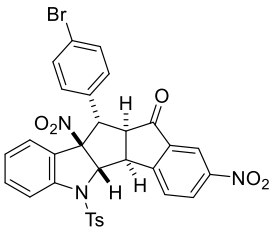
Light yellow solid, 60.2 mg, 98% yield, >20:1 dr; m.p. 218.3-219.2 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.77 (dd, J = 8.4, 2.3 Hz, 1H), 8.46 (d, J = 8.5 Hz, 1H), 8.35 (d, J = 2.3 Hz, 1H), 7.74 (dd, J = 8.5, 2.2 Hz, 3H), 7.58 – 7.51 (m, 1H), 7.46 – 7.40 (m, 2H), 7.34 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 7.05 – 6.96 (m, 1H), 6.12 (dd, J = 7.8, 1.6 Hz, 1H), 5.66 (t, J = 1.9 Hz, 1H), 4.52 – 4.47 (m, 1H), 4.40 (d, J = 11.5 Hz, 1H), 3.94 – 3.82 (m, 1H), 2.31 (s, 3H); ^{13}C NMR (151

MHz, DMSO-d_6) δ 201.3, 159.3, 148.9, 145.8, 143.1, 136.4, 133.8, 133.5, 133.4, 133.2, 132.5, 130.7, 130.6, 129.1, 128.8, 128.6, 127.6, 124.7, 123.5, 119.4, 115.7, 105.9, 74.9, 56.2, 53.6, 53.0, 21.5; HRMS (ESI) calcd. for $C_{31}H_{22}{}^{35}ClN_3O_7S$ [M + Na]$^+$ 638.0759, found: 638.0749; calcd. for $C_{31}H_{22}{}^{37}ClN_3O_7S$ [M + Na]$^+$ 640.0744, found: 640.0734.



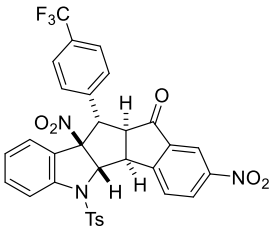
10-(3-bromophenyl)-2,9b-dinitro-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3ah)

Light yellow solid, 59.9 mg, 91% yield, >20:1 dr; m.p. 225.0-225.8 ºC ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 – 8.65 (m, 1H), 8.59 (d, *J* = 2.2 Hz, 1H), 8.48 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.57 – 7.44 (m, 4H), 7.25 – 7.18 (m, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.07 – 6.92 (m, 2H), 6.19 (d, *J* = 7.8 Hz, 1H), 5.50 (d, *J* = 2.8 Hz, 1H), 4.40 (dd, *J* = 7.9, 2.8 Hz, 1H), 4.16 (d, *J* = 11.3 Hz, 1H), 3.65 (dd, *J* = 11.3, 7.9 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 158.3, 149.2, 145.6, 143.2, 135.6, 135.0, 133.1, 132.8, 132.4, 132.3, 130.6, 130.2, 130.1, 129.6, 128.4, 127.9, 127.0, 124.8, 122.8, 122.7, 120.3, 116.6, 105.9, 75.6, 55.2, 52.9, 26.9, 21.6; HRMS (ESI) calcd. for $C_{31}H_{22}{}^{79}BrN_3O_7S$ [M + Na]$^+$ 682.0254, found: 682.0267; calcd. for $C_{31}H_{22}{}^{81}BrN_3O_7S$ [M + Na]$^+$ 684.0238, found: 684.0234.



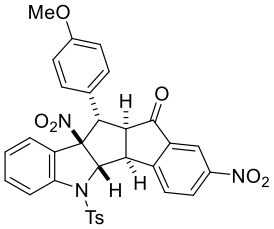
10-(4-bromophenyl)-2,9b-dinitro-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3ai)

Light yellow solid, 59.8 mg, 91% yield, >20:1 dr; m.p. 229.2-229.9 ºC ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, *J* = 8.4, 2.2 Hz, 1H), 8.57 (d, *J* = 2.2 Hz, 1H), 8.48 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.50 (dd, *J* = 16.0, 8.1 Hz, 5H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.97 (dd, *J* = 17.8, 8.0 Hz, 3H), 6.21 (d, *J* = 7.9 Hz, 1H), 5.51 (d, *J* = 2.8 Hz, 1H), 4.38 (dd, *J* = 7.9, 2.8 Hz, 1H), 4.13 (d, *J* = 11.7 Hz, 1H), 3.64 (dd, *J* = 11.6, 7.9 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 158.3, 149.2, 145.6, 143.2, 135.6, 133.2, 132.8, 132.0, 131.5, 130.9, 130.6, 130.1, 129.7, 128.4, 127.0, 124.8, 123.5, 122.6, 120.3, 116.6, 105.7, 75.5, 55.4, 55.0, 52.8, 21.6; HRMS (ESI) calcd. for calcd. for $C_{31}H_{22}{}^{79}BrN_3O_7S$ [M + Na]$^+$ 682.0254, found: 682.0252; $C_{31}H_{22}{}^{81}BrN_3O_7S$ [M + Na]$^+$ 684.0238, found: 684.0243.



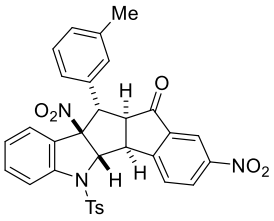
2,9b-dinitro-5-tosyl-10-(4-(trifluoromethyl)phenyl)-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3aj)

Light yellow solid, 60.2 mg, 93% yield, >20:1 dr; m.p. 218.8-219.5 °C ; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.82 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.51 (d, *J* = 8.5 Hz, 1H), 8.39 (d, *J* = 2.3 Hz, 1H), 7.85 – 7.72 (m, 5H), 7.58 (t, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.02 (t, *J* = 7.7 Hz, 1H), 6.11 (d, *J* = 7.8 Hz, 1H), 5.73 (d, *J* = 2.7 Hz, 1H), 4.58 (d, *J* = 10.9 Hz, 2H), 4.00 (dd, *J* = 11.4, 7.9 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 201.3, 159.3, 149.0, 145.8, 143.1, 139.5, 136.4, 133.5, 133.3, 131.7, 130.7, 130.6, 129.3, 129.0, 128.9, 128.8, 127.7, 126.4 (q, *J* = 273.2 Hz), 125.4, 125.3, 124.6, 123.5, 119.4, 115.7, 105.8, 75.0, 56.4, 53.6, 53.0, 21.5; ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.0; HRMS (ESI) calcd. for $C_{32}H_{22}F_3N_3O_7S$ $[M + Na]^+$ 672.1023, found: 672.1034.



10-(4-methoxyphenyl)-2,9b-dinitro-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3ak)

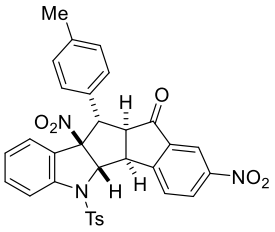
Light yellow solid, 47.5 mg, 85% yield, >20:1 dr; m.p. 208.5-209.2 °C ; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.77 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.43 (d, *J* = 8.4 Hz, 1H), 8.34 (d, *J* = 2.3 Hz, 1H), 7.71 (dd, *J* = 9.9, 8.1 Hz, 3H), 7.60 – 7.48 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.12 – 6.96 (m, 3H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.12 – 6.01 (m, 1H), 5.61 (d, *J* = 2.7 Hz, 1H), 4.44 (d, *J* = 7.8 Hz, 1H), 4.24 (d, *J* = 11.9 Hz, 1H), 3.87 – 3.79 (m, 1H), 3.77 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 200.8, 159.4, 158.8, 148.5, 145.3, 142.6, 135.9, 133.0, 132.6, 131.1, 130.2, 130.1, 129.2, 128.3, 127.1, 125.2, 124.2, 123.1, 119.0, 115.3, 113.5, 105.7, 74.5, 55.3, 55.2, 53.7, 52.5, 21.0; HRMS (ESI) calcd. for $C_{32}H_{25}N_3O_8S$ $[M + Na]^+$ 634.1255, found: 634.1264.



2,9b-dinitro-10-(m-tolyl)-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3al)

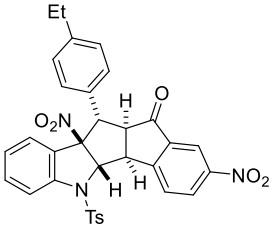
Light yellow solid, 58.9 mg, 99% yield, >20:1 dr; m.p. 214.6-215.3 °C ; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.69 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.36 (d, *J* = 8.5 Hz, 1H), 8.26 (d, *J* = 2.3 Hz, 1H), 7.64

(d, *J* = 8.3 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.47 – 7.43 (m, 1H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.18 – 7.10 (m, 2H), 6.90 – 6.81 (m, 3H), 5.92 (dd, *J* = 7.9, 1.3 Hz, 1H), 5.53 (d, *J* = 2.8 Hz, 1H), 4.39 (dd, *J* = 7.9, 2.8 Hz, 1H), 4.19 (d, *J* = 11.6 Hz, 1H), 3.80 (dd, *J* = 11.6, 7.8 Hz, 1H), 2.22 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6)δ 201.3, 159.2, 149.0, 145.7, 143.1, 137.7, 136.3, 134.0, 133.4, 133.1, 132.0, 130.7, 130.6, 129.7, 129.6, 129.1, 128.8, 128.5, 127.5, 124.5, 123.5, 119.5, 115.8, 106.2, 75.2, 65.5, 55.8, 54.7, 53.1, 30.5, 21.5, 21.4; HRMS (ESI) calcd. for $C_{32}H_{25}N_3O_7S$ $[M + Na]^+$ 618.1305, found: 618.1305.



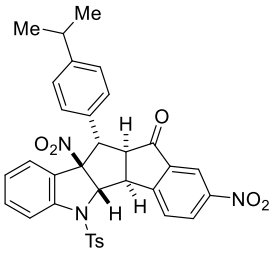
2,9b-dinitro-10-(p-tolyl)-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3am)

Light yellow solid, 51.3 mg, 86% yield, >20:1 dr; m.p. 221.1-221.9 ºC ; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.76 (dd, *J* = 8.5, 2.2 Hz, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 8.32 (t, *J* = 1.4 Hz, 1H), 7.69 (dd, *J* = 11.1, 8.1 Hz, 3H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.97 (dd, *J* = 15.4, 7.7 Hz, 3H), 6.02 (d, *J* = 7.9 Hz, 1H), 5.64 – 5.53 (m, 1H), 4.43 (d, *J* = 7.9 Hz, 1H), 4.25 (d, *J* = 11.7 Hz, 1H), 3.92 – 3.76 (m, 1H), 2.31 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 200.8, 158.8, 148.5, 145.3, 142.6, 138.0, 135.8, 133.0, 132.7, 130.5, 130.3, 130.2, 129.8, 129.1, 128.8, 128.3, 127.1, 124.2, 123.1, 119.0, 115.4, 105.6, 74.6, 55.2, 53.9, 52.5, 21.1, 20.8; HRMS (ESI) calcd. for $C_{32}H_{25}N_3O_7S$ $[M + Na]^+$ 618.1305, found: 618.1314.



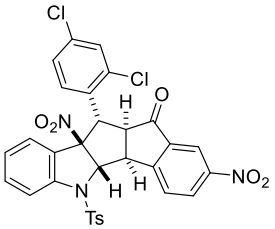
10-(4-ethylphenyl)-2,9b-dinitro-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3an)

Light yellow solid, 60.5 mg, 99% yield, >20:1 dr; m.p. 220.6-221.3 ºC ; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.70 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 8.27 (d, *J* = 2.3 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.64 – 7.59 (m, 2H), 7.49 – 7.43 (m, 1H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.97 (d, *J* = 7.9 Hz, 2H), 6.92 – 6.86 (m, 1H), 5.94 (dd, *J* = 7.9, 1.3 Hz, 1H), 5.54 (d, *J* = 2.8 Hz, 1H), 4.39 (dd, *J* = 8.0, 2.7 Hz, 1H), 4.21 (d, *J* = 11.8 Hz, 1H), 3.80 (dd, *J* = 11.8, 7.8 Hz, 1H), 2.56 (q, *J* = 7.6 Hz, 2H), 2.23 (s, 3H), 1.13 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 201.2, 159.2, 149.0, 145.7, 144.7, 143.1, 136.3, 133.4, 133.1, 131.2, 130.7, 130.6, 130.3, 129.5, 128.7, 128.0, 127.5, 124.6, 123.5, 119.5, 115.8, 106.2, 75.0, 55.6, 54.4, 53.0, 28.3, 21.5, 15.9; HRMS (ESI) calcd. for $C_{33}H_{27}N_3O_7S$ $[M + Na]^+$ 632.1462, found: 632.1443.



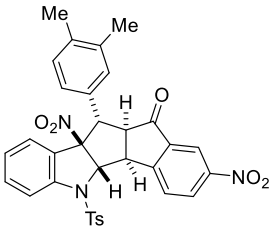
10-(4-isopropylphenyl)-2,9b-dinitro-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3ao)

Light yellow solid, 60.1 mg, 96% yield, >20:1 dr; m.p. 233.9-324.5 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.78 (dd, J = 8.4, 2.3 Hz, 1H), 8.44 (d, J = 8.4 Hz, 1H), 8.35 (d, J = 2.3 Hz, 1H), 7.72 (d, J = 8.2 Hz, 1H), 7.71 – 7.67 (m, 2H), 7.55 – 7.50 (m, 1H), 7.31 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 7.9 Hz, 2H), 6.97 – 6.91 (m, 1H), 5.97 (dd, J = 7.9, 1.3 Hz, 1H), 5.62 (d, J = 2.8 Hz, 1H), 4.47 (dd, J = 8.0, 2.7 Hz, 1H), 4.29 (d, J = 11.7 Hz, 1H), 3.88 (dd, J = 11.7, 7.8 Hz, 1H), 2.92 (p, J = 6.9 Hz, 1H), 2.31 (s, 3H), 1.22 (d, J = 6.9 Hz, 6H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 201.3, 159.2, 149.4, 149.0, 145.7, 143.1, 136.3, 133.4, 133.1, 131.4, 130.7, 130.6, 130.2, 129.5, 128.8, 127.5, 126.5, 124.6, 123.5, 119.5, 115.8, 106.2, 75.1, 55.7, 54.5, 53.1, 33.6, 24.3, 24.2, 21.5; HRMS (ESI) calcd. for $C_{34}H_{29}N_3O_7S$ [M + Na]$^+$ 646.1618, found: 646.1629.



10-(2,4-dichlorophenyl)-2,9b-dinitro-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3ap)

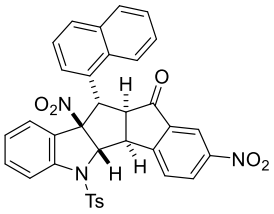
Light yellow solid, 63.5 mg, 97% yield, >20:1 dr; m.p. 216.4-217.1 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.79 (dd, J = 8.4, 2.3 Hz, 1H), 8.49 (d, J = 8.5 Hz, 1H), 8.39 (d, J = 2.3 Hz, 1H), 7.75 – 7.66 (m, 4H), 7.58 – 7.52 (m, 1H), 7.40 (dd, J = 8.5, 2.3 Hz, 1H), 7.31 (dd, J = 14.3, 8.4 Hz, 3H), 7.09 – 7.03 (m, 1H), 6.48 (dd, J = 7.9, 1.3 Hz, 1H), 5.62 (d, J = 3.0 Hz, 1H), 4.75 (d, J = 9.9 Hz, 1H), 4.66 (dd, J = 8.2, 2.9 Hz, 1H), 3.92 (dd, J = 9.9, 8.1 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 201.6, 159.3, 149.1, 145.9, 142.9, 136.1, 136.0, 134.4, 133.6, 133.3, 132.9, 132.3, 131.0, 130.6, 129.4, 129.2, 129.0, 127.7, 127.5, 124.8, 123.1, 119.4, 115.8, 105.7, 75.5, 58.5, 53.1, 51.0, 21.5; HRMS (ESI) calcd. for $C_{31}H_{21}{}^{35}Cl_2N_3O_7S$ [M + Na]$^+$ 672.0369, found: 672.0364; calcd. for $C_{31}H_{21}{}^{35}Cl^{37}ClN_3O_7S$ [M + Na]$^+$ 674.0348, found: 674.0341; calcd. for $C_{31}H_{21}{}^{37}Cl_2N_3O_7S$ [M + Na]$^+$ 676.0335, found: 676.0330.



10-(3,4-dimethylphenyl)-2,9b-dinitro-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3aq)

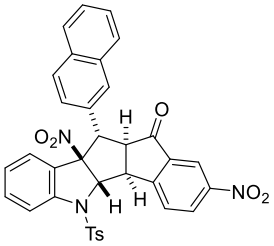
Light yellow solid, 58.1 mg, 95% yield, >20:1 dr; m.p. 219.4-220.1 ºC; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 8.68 (dd, *J* = 8.4, 2.2 Hz, 1H), 8.56 (d, *J* = 2.2 Hz, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.55 – 7.41 (m, 3H), 7.12 (dd, *J* = 17.2, 7.9 Hz, 3H), 6.99 – 6.93 (m, 1H), 6.84 – 6.72 (m, 2H), 6.20 (d, *J* = 7.9 Hz, 1H), 5.51 (d, *J* = 2.9 Hz, 1H), 4.33 (dd, *J* = 7.8, 2.8 Hz, 1H), 4.12 (d, *J* = 11.9 Hz, 1H), 3.68 (dd, *J* = 11.9, 7.8 Hz, 1H), 2.33 (s, 3H), 2.27 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.5, 158.9, 149.5, 145.8, 143.5, 138.2, 137.4, 136.2, 133.7, 132.8, 130.8, 130.7, 130.4, 130.3, 129.7, 128.7, 127.3, 126.7, 125.0, 123.3, 120.6, 116.9, 106.4, 75.9, 56.2, 55.1, 53.2, 22.0, 20.2, 19.9; HRMS (ESI) calcd. for $C_{33}H_{27}N_3O_7S$ $[M + Na]^+$ 632.1462, found: 632.1459.



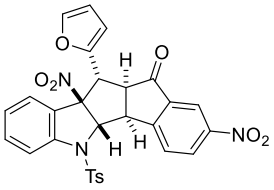
10-(naphthalen-1-yl)-2,9b-dinitro-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3ar)

Light yellow solid, 51.0 mg, 88% yield, >20:1 dr; m.p. 221.0-221.7 °C; ^{1}H NMR (600 MHz, DMSO-d_6) ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.82 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.54 (d, *J* = 8.4 Hz, 1H), 8.35 (d, *J* = 2.3 Hz, 1H), 7.98 – 7.93 (m, 2H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.71 – 7.68 (m, 2H), 7.52 – 7.46 (m, 3H), 7.44 – 7.41 (m, 1H), 7.39 (d, *J* = 7.3 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.92 – 6.86 (m, 1H), 6.05 (dd, *J* = 7.9, 1.3 Hz, 1H), 5.72 (d, *J* = 3.0 Hz, 1H), 5.30 (d, *J* = 10.6 Hz, 1H), 4.64 (dd, *J* = 8.1, 2.9 Hz, 1H), 4.06 (dd, *J* = 10.6, 8.0 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 201.7, 159.6, 149.0, 145.8, 142.9, 136.6, 133.7, 133.3, 133.1, 133.0, 131.2, 130.8, 130.6, 129.7, 129.5, 129.2, 129.1, 128.8, 127.6, 127.0, 126.3, 125.0, 124.3, 123.6, 123.1, 119.5, 115.7, 106.2, 75.4, 58.4, 52.9, 49.0, 21.5; HRMS (ESI) calcd. for $C_{35}H_{25}N_3O_7S$ $[M + Na]^+$ 654.1305, found: 654.1310.



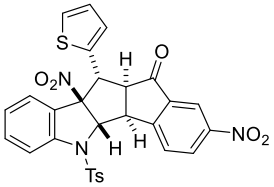
10-(naphthalen-2-yl)-2,9b-dinitro-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3as)

Light yellow solid, 54.4 mg, 94% yield, >20:1 dr; m.p. 219.9-220.5 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.80 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.49 (d, *J* = 8.4 Hz, 1H), 8.36 (d, *J* = 2.3 Hz, 1H), 7.98 – 7.92 (m, 1H), 7.87 (dd, *J* = 12.1, 7.8 Hz, 2H), 7.79 – 7.71 (m, 4H), 7.59 – 7.49 (m, 3H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.28 – 7.22 (m, 1H), 6.86 (t, *J* = 7.6 Hz, 1H), 5.99 (d, *J* = 7.8 Hz, 1H), 5.70 (d, *J* = 2.8 Hz, 1H), 4.61 – 4.48 (m, 2H), 4.05 (dd, *J* = 11.5, 7.8 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 201.4, 159.3, 149.0, 145.8, 143.1, 136.4, 133.4, 133.2, 133.1, 132.8, 131.9, 130.7, 130.6, 129.3, 128.8, 128.4, 128.0, 127.9, 127.6, 127.1, 127.0, 124.6, 123.6, 119.5, 115.8, 106.2, 75.2, 56.2, 54.7, 53.1, 21.5; HRMS (ESI) calcd. for $C_{35}H_{25}N_3O_7S$ $[M + Na]^+$ 654.1305, found: 654.1300.



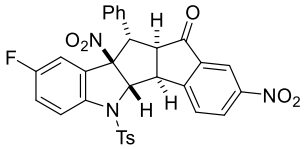
10-(furan-2-yl)-2,9b-dinitro-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3at)

Yellow solid, 37.1 mg, 65% yield, >20:1 dr; m.p. 227.6-228.3 °C ; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.77 (dd, 1H), 8.41 (d, *J* = 8.3 Hz, 1H), 8.36 (d, *J* = 2.3 Hz, 1H), 7.79 – 7.66 (m, 4H), 7.60 – 7.53 (m, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.11 – 7.02 (m, 1H), 6.60 – 6.48 (m, 2H), 6.00 (dd, *J* = 7.9, 1.3 Hz, 1H), 5.56 (d, *J* = 3.0 Hz, 1H), 4.54 (d, *J* = 11.6 Hz, 1H), 4.43 (dd, *J* = 8.3, 2.9 Hz, 1H), 3.74 (dd, *J* = 11.6, 8.1 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 201.0, 159.2, 148.9, 148.5, 145.7, 143.8, 143.0, 136.3, 133.7, 133.3, 130.7, 130.6, 128.8, 127.6, 127.6, 125.2, 123.9, 119.4, 115.9, 111.6, 105.1, 74.9, 54.2, 53.1, 47.6, 40.6, 21.5; HRMS (ESI) calcd. for $C_{29}H_{21}N_3O_8S$ $[M + Na]^+$ 594.0942, found: 594.0959.



2,9b-dinitro-10-(thiophen-2-yl)-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3au)

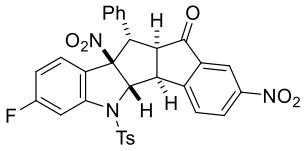
Light yellow solid, 49.1 mg, 92% yield, >20:1 dr; m.p. 234.0-234.8 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, *J* = 8.4, 2.2 Hz, 1H), 8.60 (d, *J* = 2.2 Hz, 1H), 8.46 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.55 – 7.44 (m, 3H), 7.34 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.05 (dd, *J* = 5.2, 3.7 Hz, 1H), 7.01 – 6.90 (m, 2H), 6.15 (d, *J* = 7.8 Hz, 1H), 5.41 (d, *J* = 2.8 Hz, 1H), 4.54 (d, *J* = 11.8 Hz, 1H), 4.32 (dd, *J* = 7.9, 2.8 Hz, 1H), 3.58 (dd, *J* = 11.8, 7.9 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.6, 158.4, 149.6, 145.9, 143.7, 135.9, 135.6, 133.7, 133.1, 130.9, 130.5, 129.6, 128.7, 128.5, 127.8, 127.3, 126.7, 125.4, 123.1, 120.7, 117.0, 106.1, 75.9, 56.6, 53.3, 51.4, 22.0; HRMS (ESI) calcd. for $C_{29}H_{21}N_3O_2S_2$ $[M + Na]^+$ 610.0713, found: 610.0721.



8-fluoro-2,9b-dinitro-10-phenyl-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3ba)

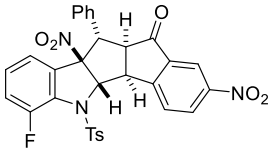
Light yellow solid, 53.1 mg, 89% yield, >20:1 dr; m.p. 243.8-244.7 °C ; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.78 (dd, *J* = 8.5, 2.3 Hz, 1H), 8.44 – 8.39 (m, 1H), 8.36 (d, *J* = 2.3 Hz, 1H), 7.74 (dd, *J* = 9.1, 4.5 Hz, 1H), 7.69 – 7.63 (m, 2H), 7.48 – 7.30 (m, 6H), 7.20 – 7.16 (m, 2H), 5.66 – 5.55 (m, 2H), 4.52 (dd, *J* = 8.0, 2.8 Hz, 1H), 4.36 (d, *J* = 11.2 Hz, 1H), 3.97 (dd, *J* = 11.2, 7.9 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 201.3, 159.1, 158.6 (d, *J* = 242.5 Hz), 149.0, 145.9, 139.5 (d, *J* = 1.9 Hz), 136.4, 134.0, 133.0, 130.8, 130.7, 130.2, 129.3, 128.8, 128.7, 127.6, 125.3 (d, *J* = 9.2 Hz), 120.3 (d, *J* = 24.0 Hz), 119.5, 117.6 (d, *J* = 9.0 Hz), 115.9 (d, *J* = 26.1 Hz), 105.7 (d, *J* = 2.0 Hz), 75.8, 55.6, 54.9, 53.1, 21.5; ^{19}F NMR (376 MHz, DMSO-d_6) δ -117.6;

HRMS (ESI) calcd. for $C_{31}H_{22}FN_3O_7S$ [M + Na]$^+$ 622.1055, found: 622.1069.



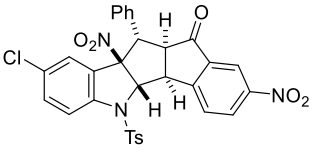
7-fluoro-2,9b-dinitro-10-phenyl-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentalen o[1,2-b]indol-11-one (3ca)

Light yellow solid, 49.2 mg, 82% yield, >20:1 dr; m.p. 213.5-214.3 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.87 (dd, *J* = 8.5, 2.3 Hz, 1H), 8.58 – 8.51 (m, 1H), 8.45 (d, *J* = 2.3 Hz, 1H), 7.94 – 7.81 (m, 2H), 7.55 (dd, *J* = 9.7, 2.5 Hz, 1H), 7.53 – 7.42 (m, 5H), 7.30 – 7.24 (m, 2H), 6.99 – 6.90 (m, 1H), 6.07 (dd, *J* = 8.7, 5.6 Hz, 1H), 5.75 (d, *J* = 2.7 Hz, 1H), 4.66 – 4.55 (m, 1H), 4.43 (d, *J* = 11.5 Hz, 1H), 4.06 (dd, *J* = 11.5, 7.9 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 201.2, 165.0 (d, *J* = 250.4 Hz), 159.0, 149.0, 146.1, 144.8 (d, *J* = 11.9 Hz), 136.4, 134.1, 133.2, 131.2 (d, *J* = 10.5 Hz), 130.8, 130.7, 130.4, 129.2, 128.8, 128.7, 127.7, 119.7, 119.5, 112.0 (d, *J* = 23.1 Hz), 105.6, 103.2 (d, *J* = 28.6 Hz), 75.8, 55.9, 54.5, 53.0, 21.5; ^{19}F NMR (376 MHz, DMSO-d_6) δ -106.4; HRMS (ESI) calcd. for $C_{31}H_{22}FN_3O_7S$ [M + Na]$^+$ 622.1055, found: 622.1059.



6-fluoro-2,9b-dinitro-10-phenyl-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentale no[1,2-b]indol-11-one (3da)

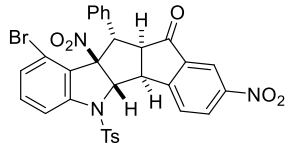
Light yellow solid, 53.2 mg, 89% yield, >20:1 dr; m.p. 222.8-223.3 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.75 (dd, *J* = 8.5, 2.3 Hz, 1H), 8.34 (d, *J* = 2.3 Hz, 1H), 8.19 – 8.12 (m, 1H), 7.72 – 7.63 (m, 2H), 7.46 – 7.42 (m, 1H), 7.41 – 7.35 (m, 4H), 7.18 (dd, *J* = 4.4, 1.1 Hz, 1H), 7.15 – 7.12 (m, 2H), 7.10 – 7.04 (m, 1H), 5.85 (dd, *J* = 7.9, 1.1 Hz, 1H), 5.80 (d, *J* = 3.2 Hz, 1H), 4.47 (dd, *J* = 8.2, 3.2 Hz, 1H), 4.39 (d, *J* = 11.8 Hz, 1H), 3.90 (dd, *J* = 11.7, 8.0 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.6, 158.2, 152.2 (d, *J* = 257.0 Hz), 149.2, 145.7, 135.6, 133.1, 131.7, 130.7, 130.6, 130.1, 129.4, 128.9, 128.3, 127.5, 127.4 (d, *J* = 1.8 Hz), 126.5 (d, *J* = 6.8 Hz), 125.9 (d, *J* = 4.1 Hz), 120.3 (d, *J* = 2.0 Hz), 120.1, 105.2 (d, *J* = 1.8 Hz), 105.2, 76.7, 56.2, 53.8, 52.8, 21.6; ^{19}F NMR (376 MHz, DMSO-d_6) δ -117.4; HRMS (ESI) calcd. for $C_{31}H_{22}FN_3O_7S$ [M + Na]$^+$ 622.1055, found: 622.1069.



8-chloro-2,9b-dinitro-10-phenyl-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentale no[1,2-b]indol-11-one (3ea)

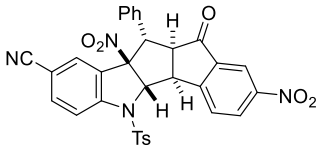
Light yellow solid, 52.8 mg, 86% yield, >20:1 dr; m.p. 256.0-256.7 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.82 – 8.73 (m, 1H), 8.43 (d, *J* = 8.5 Hz, 1H), 8.36 (d, *J* = 2.2 Hz, 1H), 7.75 – 7.69 (m, 3H), 7.62 – 7.57 (m, 1H), 7.46 – 7.40 (m, 1H), 7.40 – 7.33 (m, 4H), 7.18 (d, *J* = 7.5 Hz, 2H), 5.82 (d, *J* = 2.2 Hz, 1H), 5.61 (d, *J* = 2.7 Hz, 1H), 4.56 – 4.47 (m, 1H), 4.38 (d, *J* = 11.2 Hz, 1H), 3.99 (dd, *J* = 11.2, 7.9 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 201.3, 159.0,

149.0, 146.0, 142.0, 136.4, 134.1, 133.1, 133.0, 130.8, 130.7, 130.3, 129.3, 129.1, 128.8, 128.7, 128.4, 127.6, 125.3, 119.5, 117.4, 105.7, 75.6, 55.8, 54.8, 53.1, 21.5; HRMS (ESI) calcd. for $C_{31}H_{22}{}^{35}ClN_3O_7S$ [M + Na]$^+$ 638.0759, found: 638.0758; calcd. for $C_{31}H_{22}{}^{37}ClN_3O_7S$ [M + Na]$^+$ 640.0744, found: 640.0746.



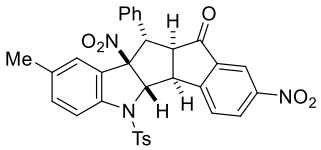
9-bromo-2,9b-dinitro-10-phenyl-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3fa)

Light yellow solid, 36.2 mg, 55% yield, 10:1 dr; m.p. 218.1-218.8 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.74 (dd, J = 8.5, 2.3 Hz, 1H), 8.46 (d, J = 8.5 Hz, 1H), 8.42 (d, J = 2.3 Hz, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.1 Hz, 1H), 7.40 (d, J = 8.2 Hz, 2H), 7.22 (s, 2H), 7.15 (t, J = 8.2 Hz, 1H), 7.12 – 7.06 (m, 3H), 6.96 (d, J = 7.6 Hz, 1H), 5.28 (dd, J = 8.4, 1.7 Hz, 1H), 5.09 (d, J = 2.1 Hz, 1H), 4.89 (d, J = 2.3 Hz, 1H), 3.94 (dd, J = 8.4, 2.4 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 202.9, 159.4, 149.2, 146.5, 144.5, 139.5, 137.2, 133.7, 131.5, 131.1, 130.8, 129.8, 128.7, 128.5, 128.4, 128.2, 126.0, 120.2, 118.8, 118.7, 114.2, 109.1, 81.1, 63.6, 55.8, 53.8, 21.5, 21.4; HRMS (ESI) calcd. for $C_{31}H_{22}{}^{79}BrN_3O_7S$ [M + Na]$^+$ 682.0254, found: 682.0251; calcd. for $C_{31}H_{22}{}^{81}BrN_3O_7S$ [M + Na]$^+$ 684.0238, found: 684.0241.



2,9b-dinitro-11-oxo-10-phenyl-5-tosyl-4b,4c,9b,10,10a,11-hexahydro-5H-benzo[5,6]pentaleno[1,2-b]indole-8-carbonitrile (3ga)

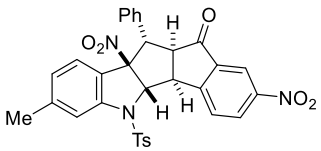
Light yellow solid, 45.3 mg, 75% yield, >20:1 dr; m.p. 277.9-278.7 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.87 (dd, J = 8.4, 2.3 Hz, 1H), 8.56 (d, J = 8.5 Hz, 1H), 8.47 (d, J = 2.3 Hz, 1H), 8.07 (dd, J = 8.6, 1.8 Hz, 1H), 7.99 – 7.86 (m, 3H), 7.57 – 7.45 (m, 5H), 7.37 – 7.27 (m, 2H), 6.28 (d, J = 1.7 Hz, 1H), 5.84 (d, J = 2.5 Hz, 1H), 4.74 – 4.67 (m, 1H), 4.55 (d, J = 10.8 Hz, 1H), 4.12 (dd, J = 10.8, 7.9 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 201.3, 158.8, 149.0, 146.5, 146.4, 137.1, 136.5, 134.5, 133.3, 133.2, 130.9, 130.6, 130.5, 129.3, 128.9, 128.7, 127.8, 124.4, 119.4, 118.2, 116.0, 106.4, 105.4, 75.7, 56.4, 54.8, 53.3, 21.5; HRMS (ESI) calcd. for $C_{32}H_{22}N_4O_7S$ [M + Na]$^+$ 629.1101, found: 629.1077.



8-methyl-2,9b-dinitro-10-phenyl-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3ha)

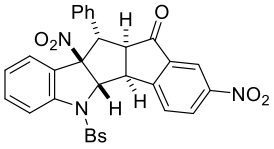
Light yellow solid, 45.2 mg, 76% yield, >20:1 dr; m.p. 230.4-231.2 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.77 (dd, J = 8.4, 2.3 Hz, 1H), 8.43 (d, J = 8.4 Hz, 1H), 8.35 (d, J = 2.2 Hz, 1H), 7.69 – 7.64 (m, 2H), 7.61 (d, J = 8.3 Hz, 1H), 7.43 – 7.39 (m, 1H), 7.38 – 7.33 (m, 3H), 7.32 (d, J = 8.2 Hz, 2H), 7.15 – 7.11 (m, 2H), 5.70 – 5.64 (m, 1H), 5.58 (d, J = 2.8 Hz, 1H), 4.46 (dd, J = 8.1, 2.7 Hz, 1H), 4.32 (d, J = 11.5 Hz, 1H), 3.88 (dd, J = 11.5, 7.9 Hz, 1H), 2.31 (s, 3H), 2.00 (s, 3H); ^{13}C

NMR (151 MHz, DMSO-d_6) δ 201.4, 159.3, 149.0, 145.6, 140.8, 136.3, 134.3, 133.7, 133.6, 133.4, 130.7, 130.6, 130.4, 129.7, 129.1, 128.7, 128.5, 127.6, 123.7, 119.5, 115.6, 106.2, 75.3, 55.7, 54.6, 53.1, 21.5, 20.8; HRMS (ESI) calcd. for $C_{32}H_{24}N_3O_7S$ [M + Na]$^+$ 618.1305, found: 618.1315.



7-methyl-2,9b-dinitro-10-phenyl-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3ia)

Light yellow solid, 45.1 mg, 76% yield, >20:1 dr; m.p. 213.9-214.8 ºC ; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.78 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.43 (d, *J* = 8.4 Hz, 1H), 8.34 (d, *J* = 2.2 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.55 (s, 1H), 7.42 – 7.38 (m, 1H), 7.38 – 7.30 (m, 4H), 7.17 – 7.10 (m, 2H), 6.81 – 6.75 (m, 1H), 5.84 (d, *J* = 8.0 Hz, 1H), 5.59 (d, *J* = 2.8 Hz, 1H), 4.43 (dd, *J* = 7.9, 2.8 Hz, 1H), 4.28 (d, *J* = 11.8 Hz, 1H), 3.89 (dd, *J* = 11.8, 7.8 Hz, 1H), 2.37 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 201.3, 159.3, 149.0, 145.7, 143.5, 143.3, 136.3, 134.0, 133.5, 130.7, 130.6, 130.3, 129.1, 129.0, 128.7, 128.6, 127.5, 125.6, 120.7, 119.5, 116.1, 106.0, 75.3, 55.5, 54.4, 53.0, 21.9, 21.5; HRMS (ESI) calcd. for $C_{32}H_{24}N_3O_7S$ [M + Na]$^+$ 618.1305, found: 618.1308.



2,9b-dinitro-10-phenyl-5-(phenylsulfonyl)-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (3ja)

Light yellow solid, 52.1 mg, 92% yield, >20:1 dr; m.p. 227.9-228.5 ºC ; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.78 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.50 – 8.42 (m, 1H), 8.35 (d, *J* = 2.3 Hz, 1H), 7.84 – 7.79 (m, 2H), 7.78 – 7.74 (m, 1H), 7.71 – 7.65 (m, 1H), 7.58 – 7.49 (m, 3H), 7.41 – 7.32 (m, 3H), 7.15 (dt, *J* = 6.8, 1.5 Hz, 2H), 7.01 – 6.90 (m, 1H), 6.03 – 5.92 (m, 1H), 5.62 (d, *J* = 2.8 Hz, 1H), 4.54 – 4.45 (m, 1H), 4.34 (d, *J* = 11.6 Hz, 1H), 3.91 (dd, *J* = 11.6, 7.9 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 201.3, 159.2, 149.0, 143.0, 136.3, 136.3, 135.0, 134.1, 133.2, 130.7, 130.4, 130.2, 129.4, 129.1, 128.8, 128.6, 127.5, 124.7, 123.6, 119.5, 115.9, 106.2, 75.1, 55.7, 54.5, 53.0; HRMS (ESI) calcd. for $C_{30}H_{21}N_3O_7S$ [M + Na]$^+$ 590.0992, found: 590.1002.

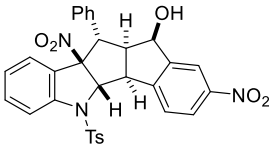
3. Gram-scale reaction for synthesis of 3aa

In a dry reaction tube equipped with a magnetic stirring bar, 2-alkylidene-1-indanone **2a** (0.12 mmol, 1.2 equiv.), 3-nitroindole **1a** (0.1 mmol), Na_2CO_3 (10.6 mg, 1.0 equiv.) and catalyst TEBA (4.5 mg, 20 mol%, 0.01 mmol) were added successively, and then followed by addition CH_2Cl_2 (1.0 mL). The reaction solution was stirred at room temperature for 20 h. After completion, the reaction mixture was directly purified by flash chromatography on silica gel (petroleum ether / dichloromethane = 1:4) to give product **3aa** in 95% yield with >20:1 dr.

4. Synthesis of compound 4

To a solution of compound **3aa** (58.1 mg, 0.1 mmol) in MeOH (2.0 mL) at 0 ºC was added $NaBH_4$ (18.9 mg, 5.0 equiv.). The mixture was stirred at room temperature for 24 h. The resulting mixture was then quenched with saturated NaCl solution and extracted with DCM three times.

The combined organic layers were dried over Na_2SO_4. After evaporation of solvent, the resulting crude mixture was purified by silica gel column chromatography (petroleum ether/ ethyl acetate =3:1) to afford compound **4**.

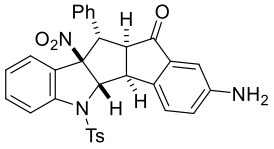


2,9b-dinitro-10-phenyl-5-tosyl-4b,4c,9b,10,10a,11-hexahydro-5H-benzo[5,6]pentaleno[1,2-b]indol-11-ol (4)

Light yellow solid, 43.2 mg, 74% yield, >20:1 dr; m.p. 216.4-216.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 8.3, 2.2 Hz, 1H), 8.27 (d, *J* = 2.1 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.46 – 7.38 (m, 1H), 7.37 – 7.27 (m, 3H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 7.4 Hz, 2H), 6.93 – 6.80 (m, 1H), 5.98 (d, *J* = 7.9 Hz, 1H), 5.55 (d, *J* = 1.9 Hz, 1H), 5.48 (t, *J* = 6.0 Hz, 1H), 4.20 (d, *J* = 12.1 Hz, 1H), 4.11 (d, *J* = 7.9 Hz, 1H), 3.73 – 3.58 (m, 1H), 2.33 (s, 3H), 1.73 (d, *J* = 5.2 Hz, 1H); ^{3}C NMR (101 MHz, $CDCl_3$) δ 149.0, 148.0, 145.4, 144.3, 143.4, 135.5, 133.3, 132.2, 130.2, 130.1, 128.7, 127.1, 126.2, 125.1, 124.2, 123.6, 121.1, 116.0, 104.5, 76.7, 75.3, 55.3, 54.1, 52.2, 21.7; HRMS (ESI) calcd. for $C_{31}H_{25}N_3O_7S$ $[M + Na]^+$ 606.1305, found: 606.1310.

5. Synthesis of compound 4

To a solution of compound **3aa** (58.1 mg, 0.1 mmol) in AcOH (1.0 mL) at 0 °C was added Fe powder (16.8 mg, 3.0 equiv.). The mixture was stirred at room temperature for 12 h. The resulting mixture was then quenched with saturated $NaHCO_3$ solution and extracted with DCM three times. The combined organic layers were dried over Na_2SO_4. After evaporation of solvent, the resulting crude mixture was purified by silica gel column chromatography (petroleum ether/ ethyl acetate =3:1) to afford compound **5**.



2-amino-9b-nitro-10-phenyl-5-tosyl-4b,4c,5,9b,10,10a-hexahydro-11H-benzo[5,6]pentaleno[1,2-b]indol-11-one (5)

Light yellow solid, 32.1 mg, 58% yield, >20:1 dr; m.p. 242.5-246.3 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.80 (d, *J* = 8.1 Hz, 1H), 7.73 – 7.68 (m, 1H), 7.62 – 7.56 (m, 2H), 7.54 – 7.48 (m, 1H), 7.40 – 7.36 (m, 1H), 7.34 (dd, *J* = 8.0, 6.7 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.16 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 2H), 6.94 (td, *J* = 7.7, 1.0 Hz, 1H), 6.77 (d, *J* = 2.2 Hz, 1H), 5.94 (dd, *J* = 7.9, 1.3 Hz, 1H), 5.59 (s, 2H), 5.38 (d, *J* = 2.6 Hz, 1H), 4.14 (d, *J* = 11.4 Hz, 1H), 4.11 (dd, *J* = 7.7, 2.6 Hz, 1H), 3.68 (dd, *J* = 11.3, 7.5 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 203.3, 150.3, 145.6, 143.1, 141.0, 135.6, 134.4, 133.5, 132.9, 130.6, 130.0, 129.6, 129.0, 128.7, 127.4, 127.1, 124.6, 123.7, 123.3, 116.2, 106.6, 106.7, 75.9, 55.8, 55.3, 52.1, 21.5; HRMS (ESI) calcd. for $C_{31}H_{25}N_3O_7S$ $[M + Na]^+$ 574.1407, found: 574.1423.

6. X-ray crystal structure of compound 3aa

Single crystal of compound **3aa** was prepared from the mixture solvent of CH_2Cl_2/ EtOH (*V* : *V* = 1/10) at room temperature by slow evaporation of solvent. A suitable crystal was selected for structure determination on a Xcalibur, Eos, Gemini diffractometer. The crystal was kept at 293(2)

K during data collection. Using Olex2[1], the structure was solved with the ShelXS[2] structure solution program using Direct Methods and refined with the ShelXL[3] refinement package using Least Squares minimisation.

[1] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J, Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.

[2] Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112-122.

[3] Sheldrick, G. M. *Acta Cryst.* **2015**, C71, 3-8.

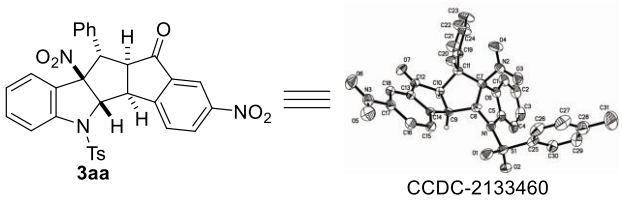
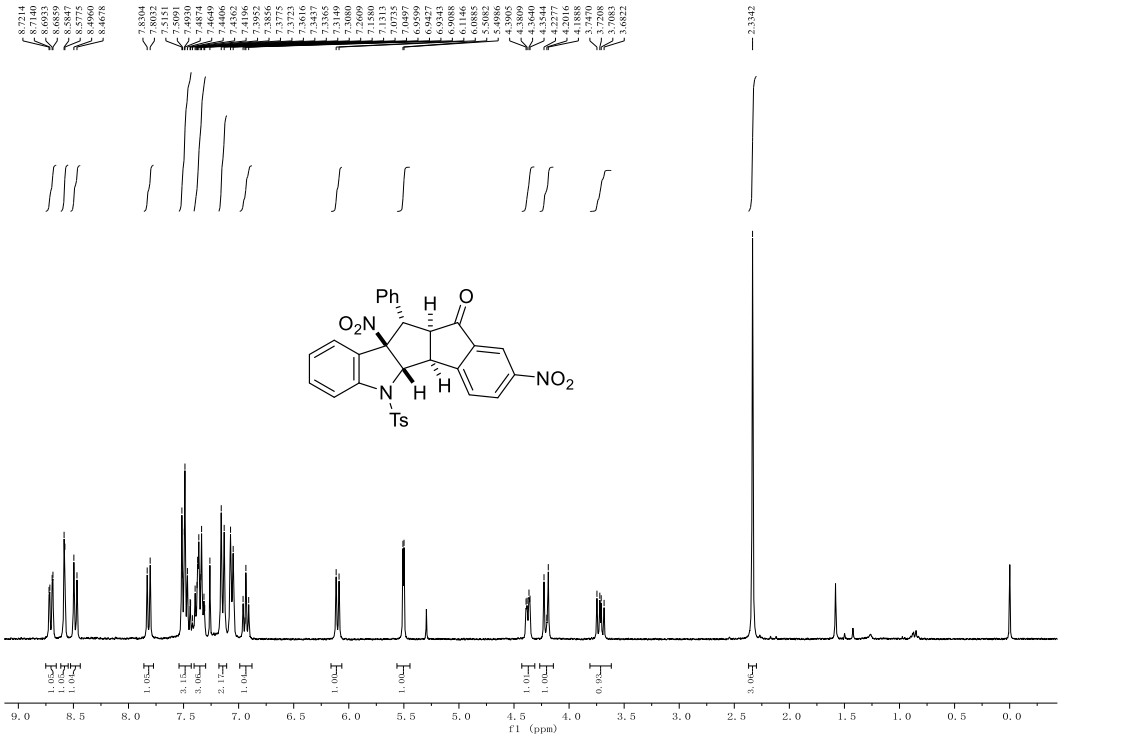


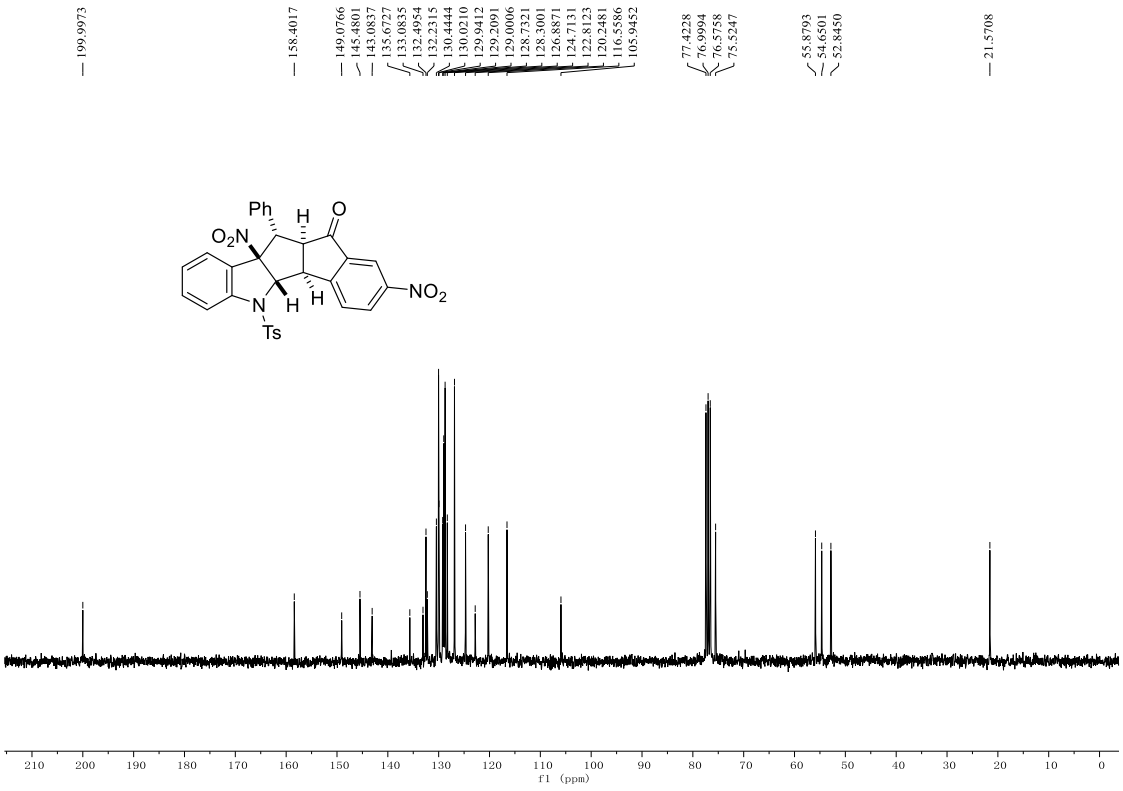
Table 1 Crystal data and structure refinement for 3aa.

Identification code	**3aa**
Empirical formula	$C_{31}H_{23}N_3O_7S$
Formula weight	581.58
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.8236(4)
b/Å	9.8932(3)
c/Å	23.4568(8)
α/°	90
β/°	93.095(3)
γ/°	90
Volume/Å^3	2739.82(17)
Z	4
ρ_{calc}g/cm^3	1.410
μ/mm^{-1}	1.521
F(000)	1208.0
Crystal size/mm^3	0.18 × 0.12 × 0.09
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.488 to 134.15
Index ranges	$-14 \le h \le 14$, $-11 \le k \le 9$, $-27 \le l \le 14$
Reflections collected	10716
Independent reflections	4892 [R_{int} = 0.0315, R_{sigma} = 0.0403]
Data/restraints/parameters	4892/0/381
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0508, wR_2 = 0.1305
Final R indexes [all data]	R_1 = 0.0688, wR_2 = 0.1478
Largest diff. peak/hole / e Å^{-3}	0.23/-0.33

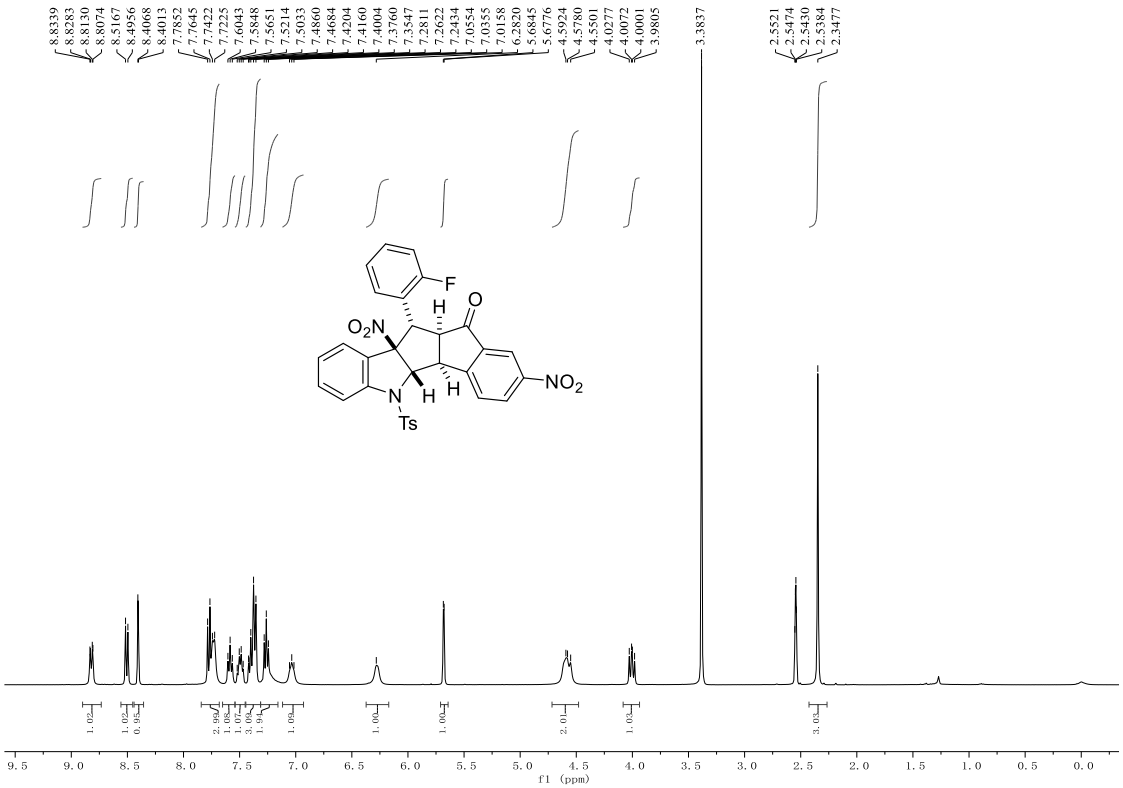
7. The copies of ^{1}H NMR and ^{13}C NMR for compounds 3, 4 and 5

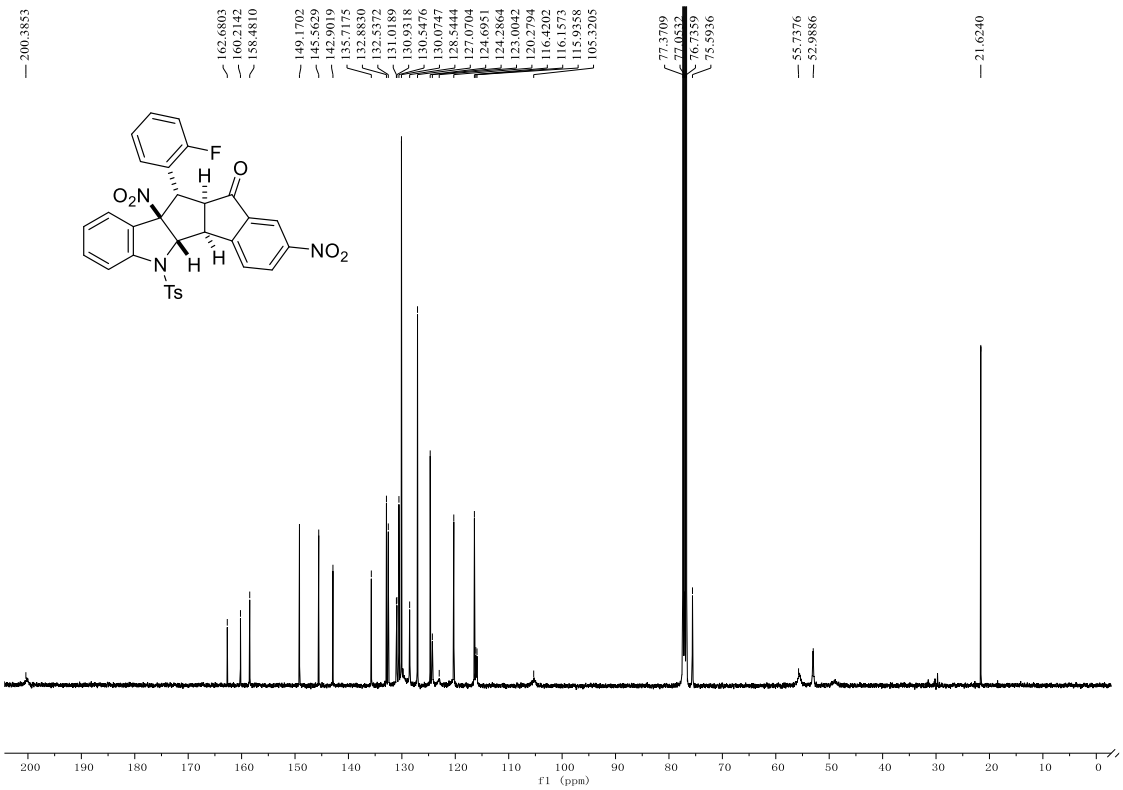
^{1}H and ^{13}C NMR of **3aa**

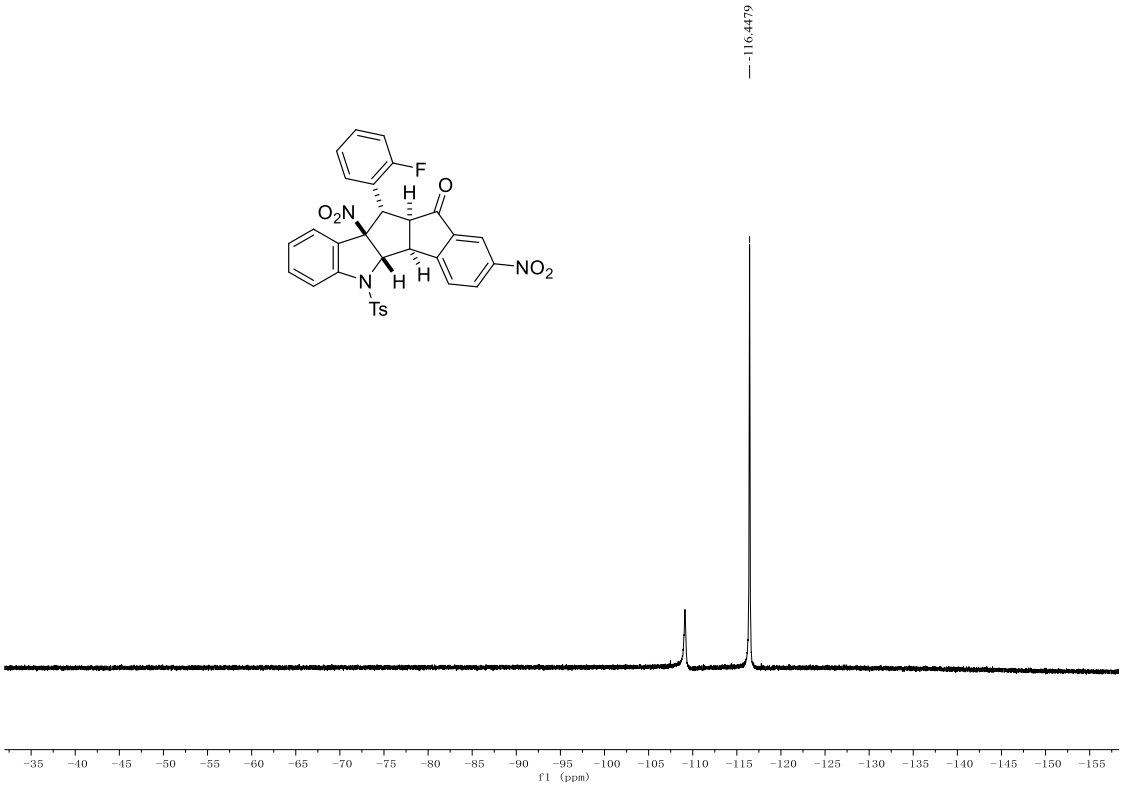




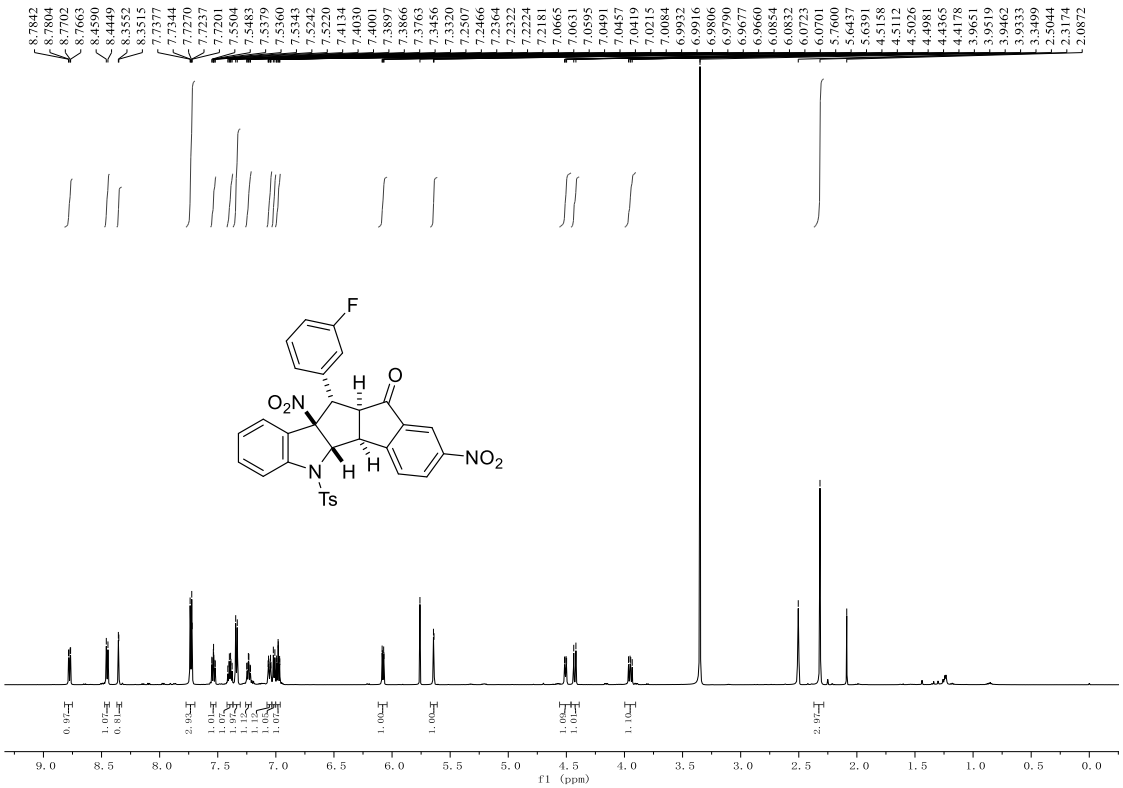
^{1}H and ^{13}C NMR of **3ab**

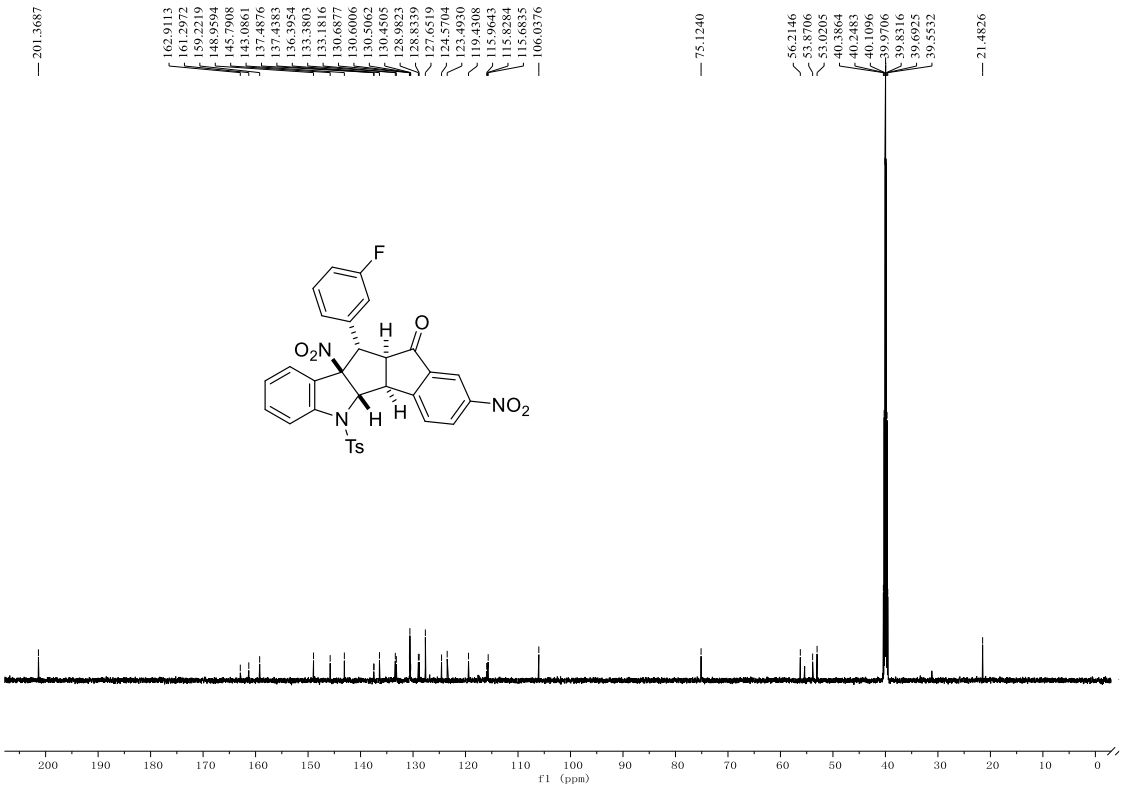


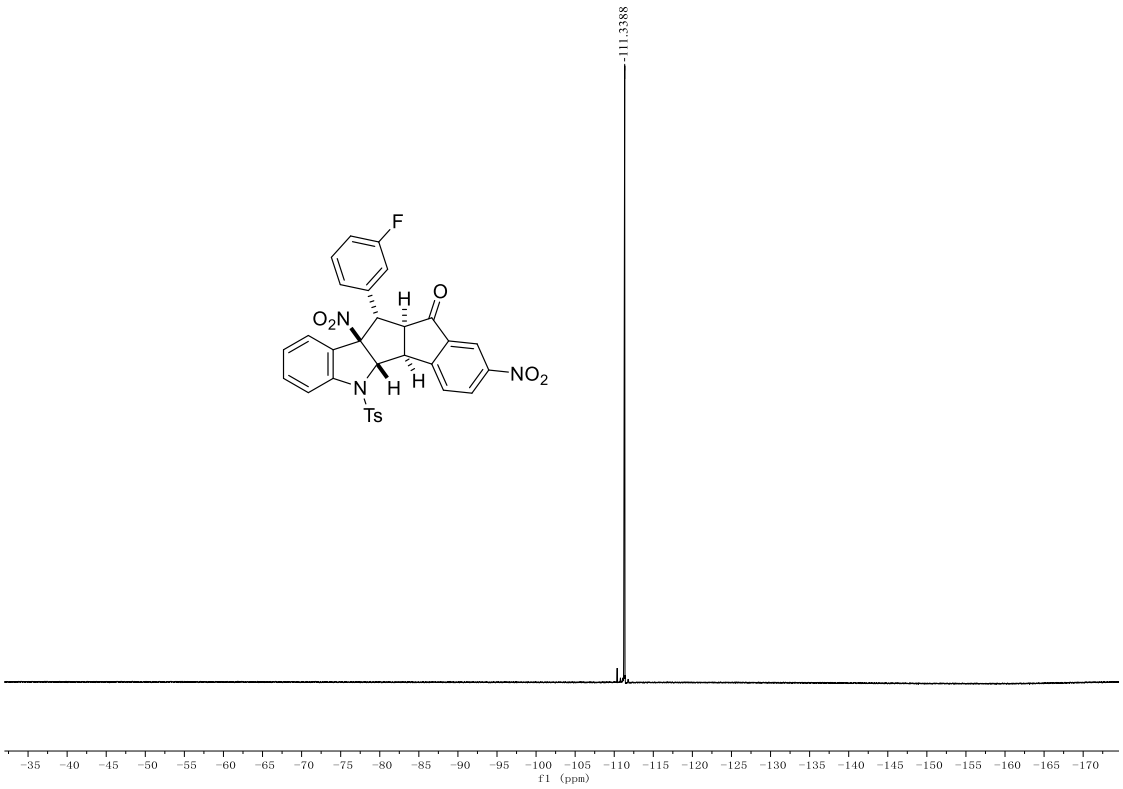



-116.4479
F
H
O
O2N
NO2
N
H
H
Ts
-35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155
f1 (ppm)

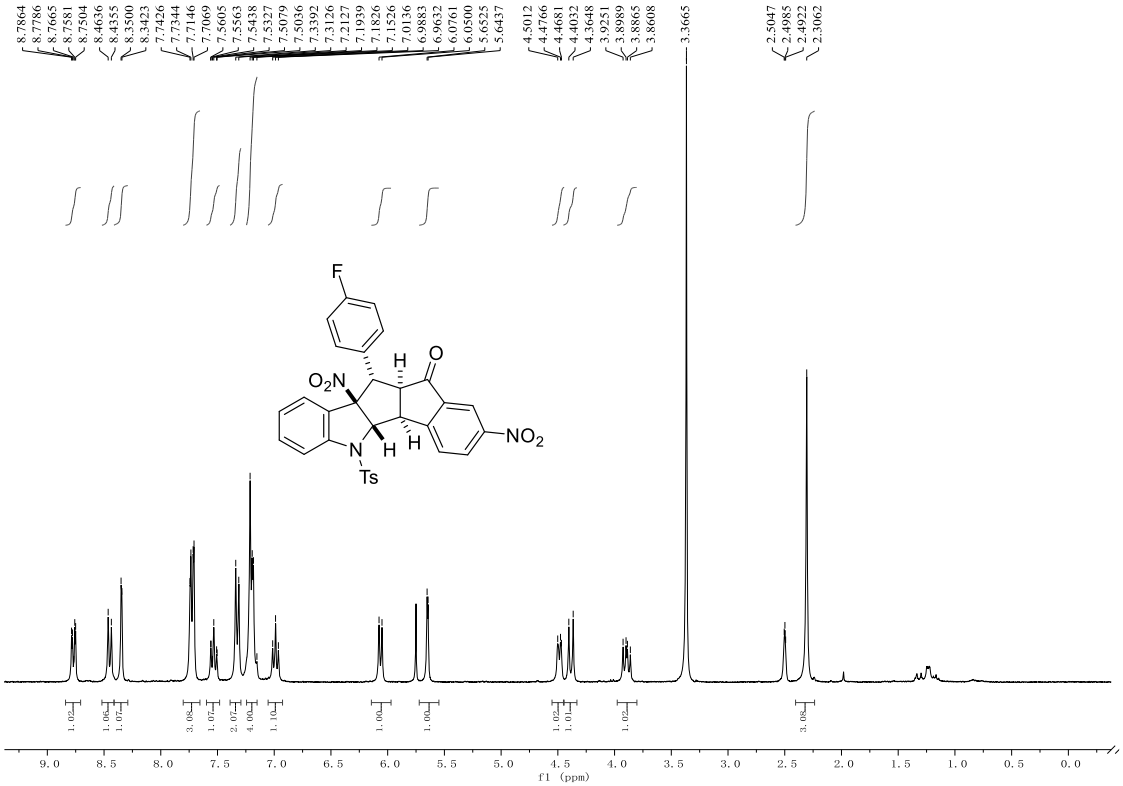
^{1}H and ^{13}C NMR of **3ac**

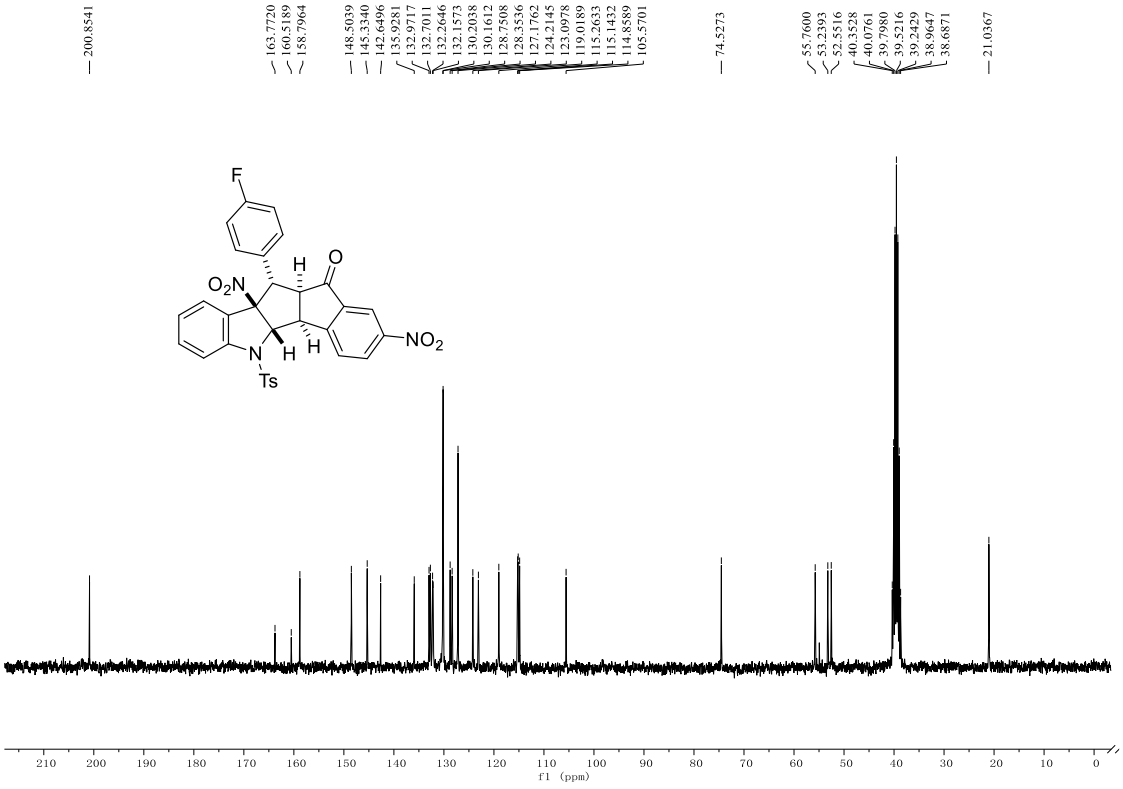


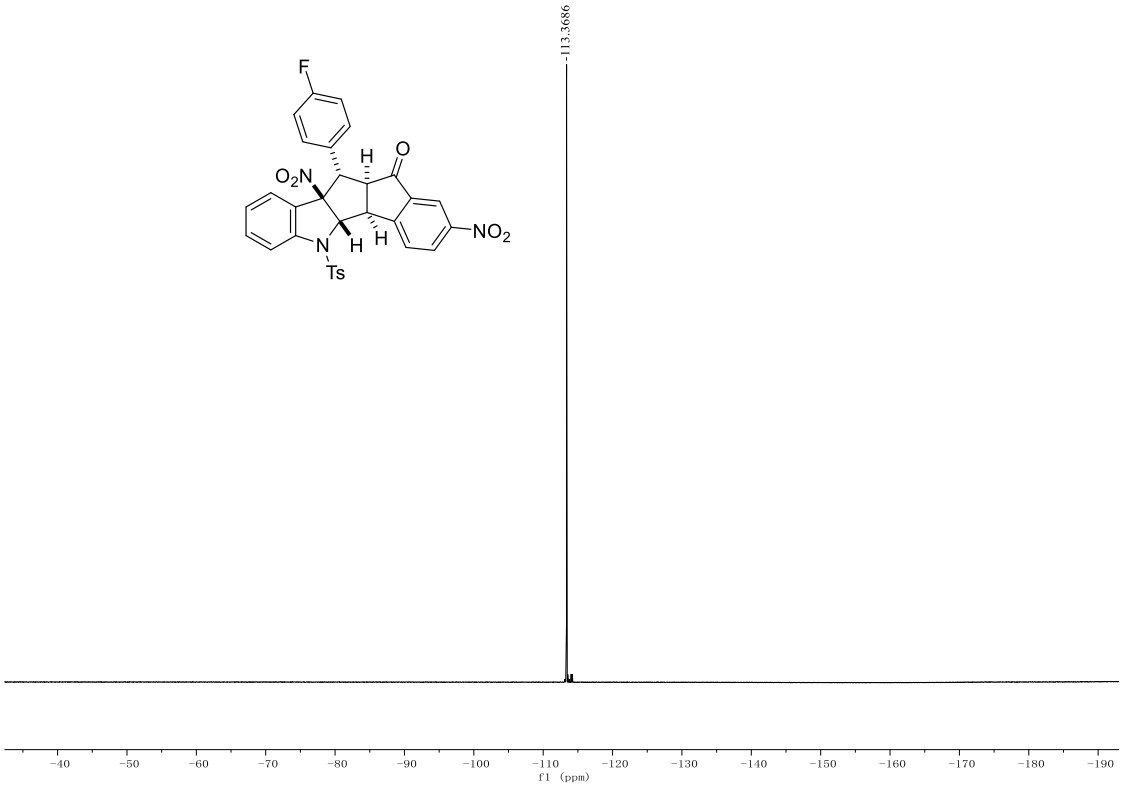



-111.3388
F
H
O
O2N
NO2
N
H
H
Ts
−35 −40 −45 −50 −55 −60 −65 −70 −75 −80 −85 −90 −95 −100 −105 −110 −115 −120 −125 −130 −135 −140 −145 −150 −155 −160 −165 −170
f1 (ppm)

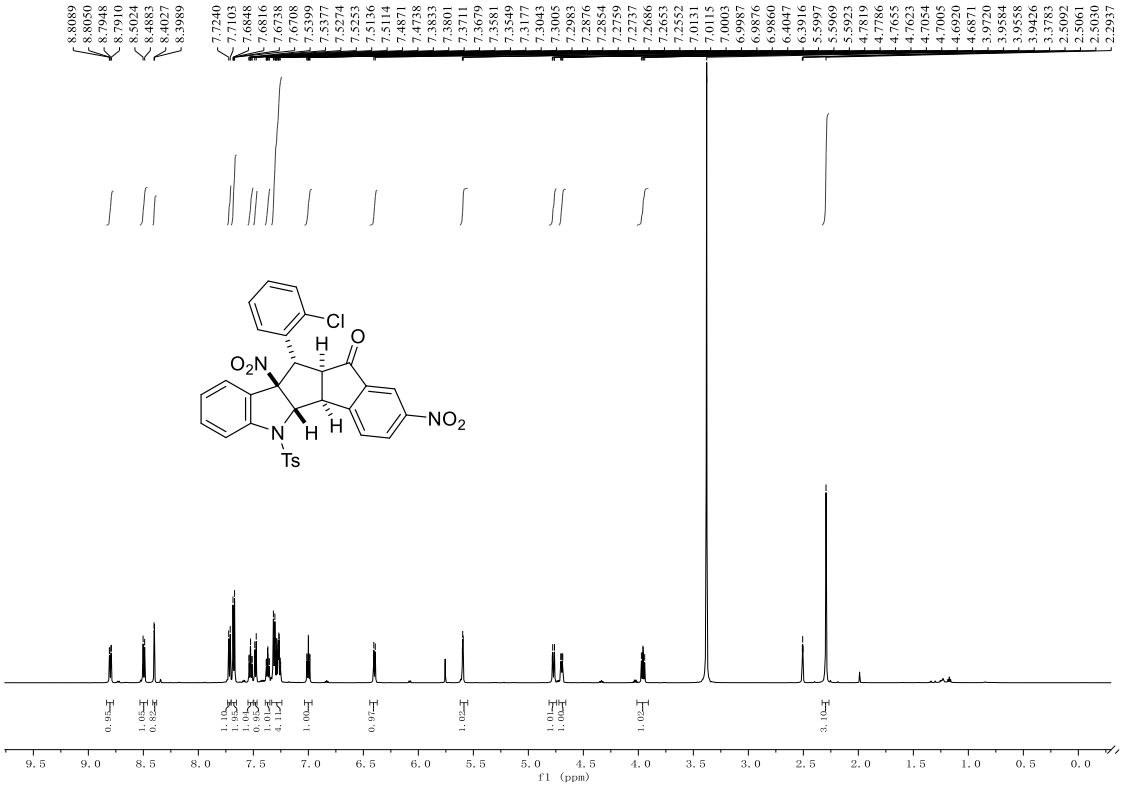
^{1}H, ^{13}C and ^{19}F NMR of **3ad**

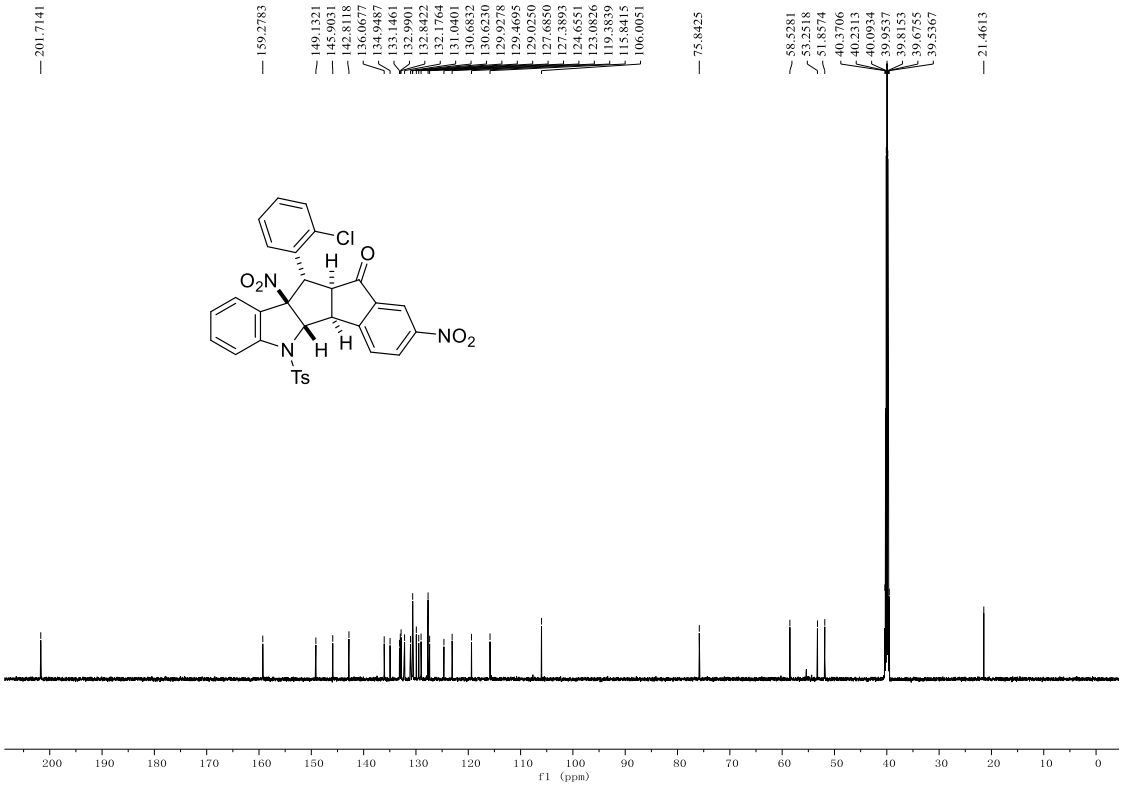




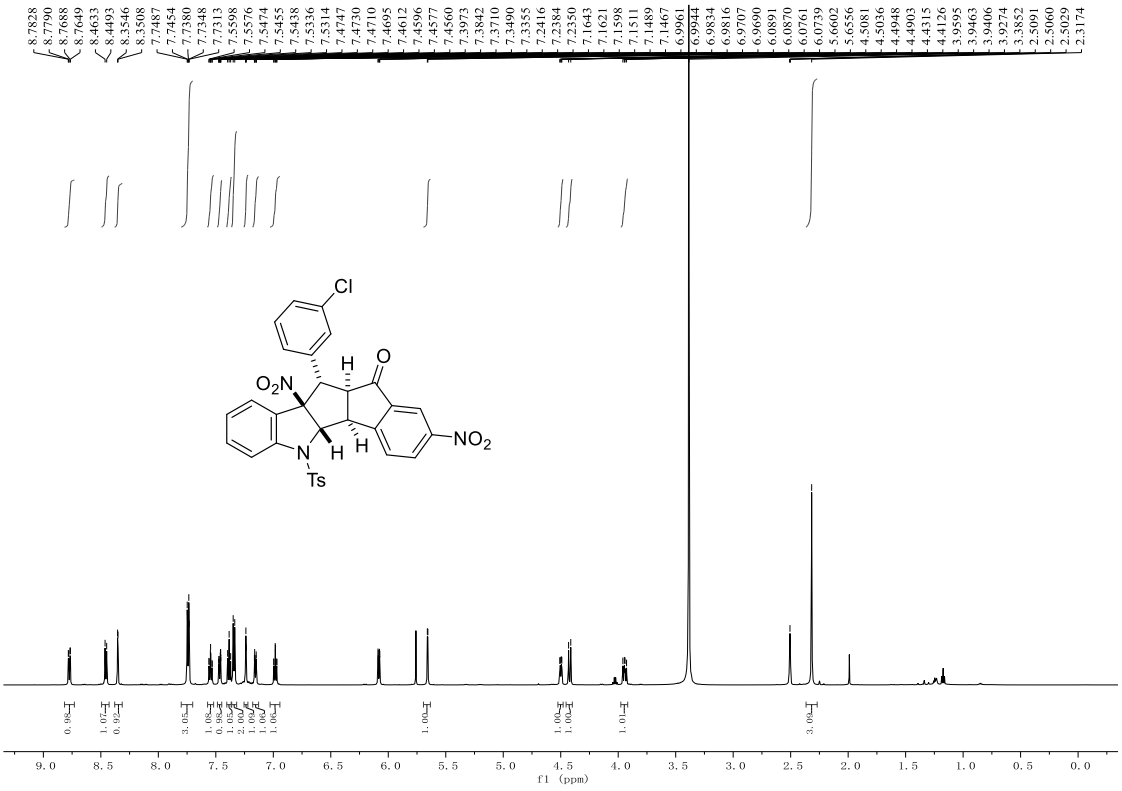

-113.3686
F
O
H
O_2N
NO_2
N
H
H
Ts
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
f1 (ppm)

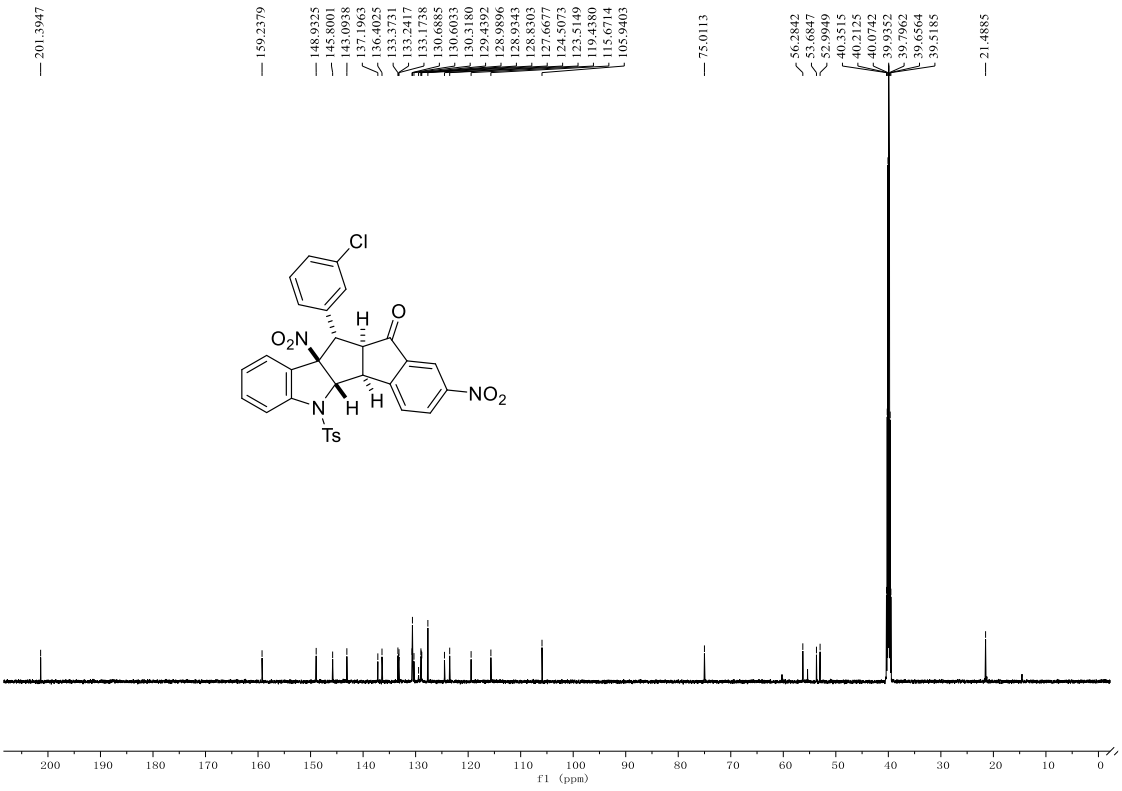
^{1}H and ^{13}C NMR of **3ae**



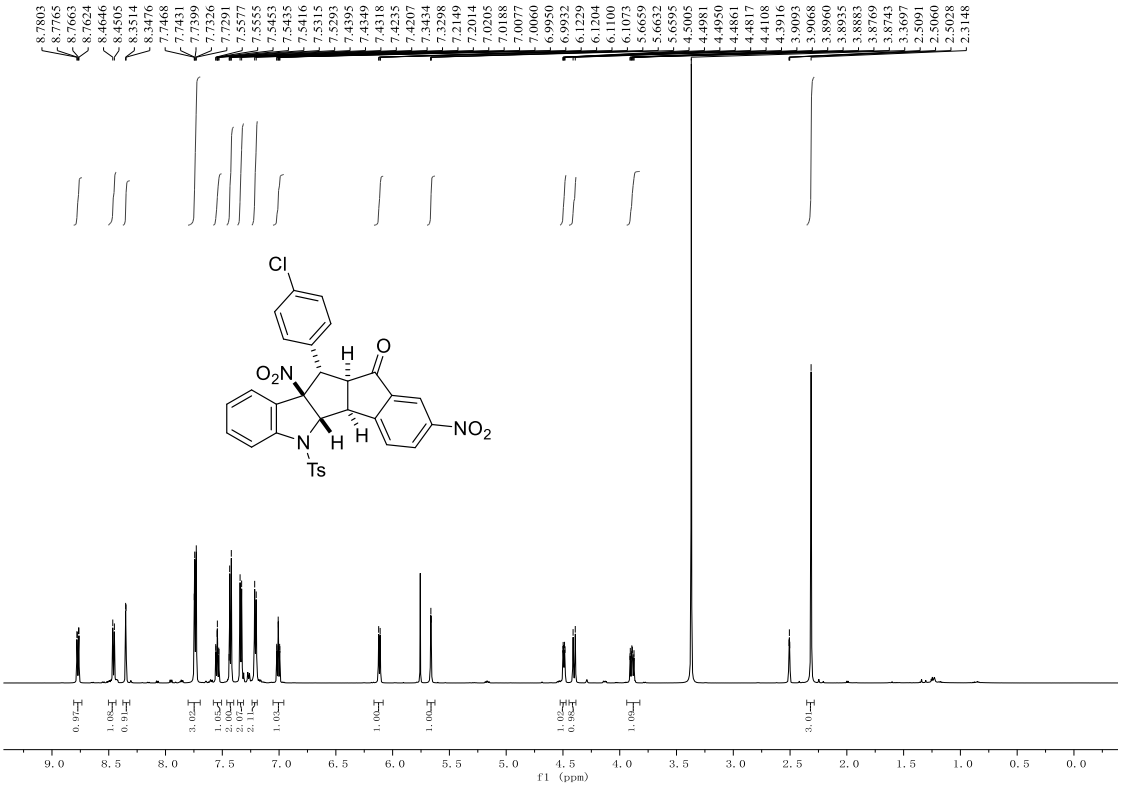


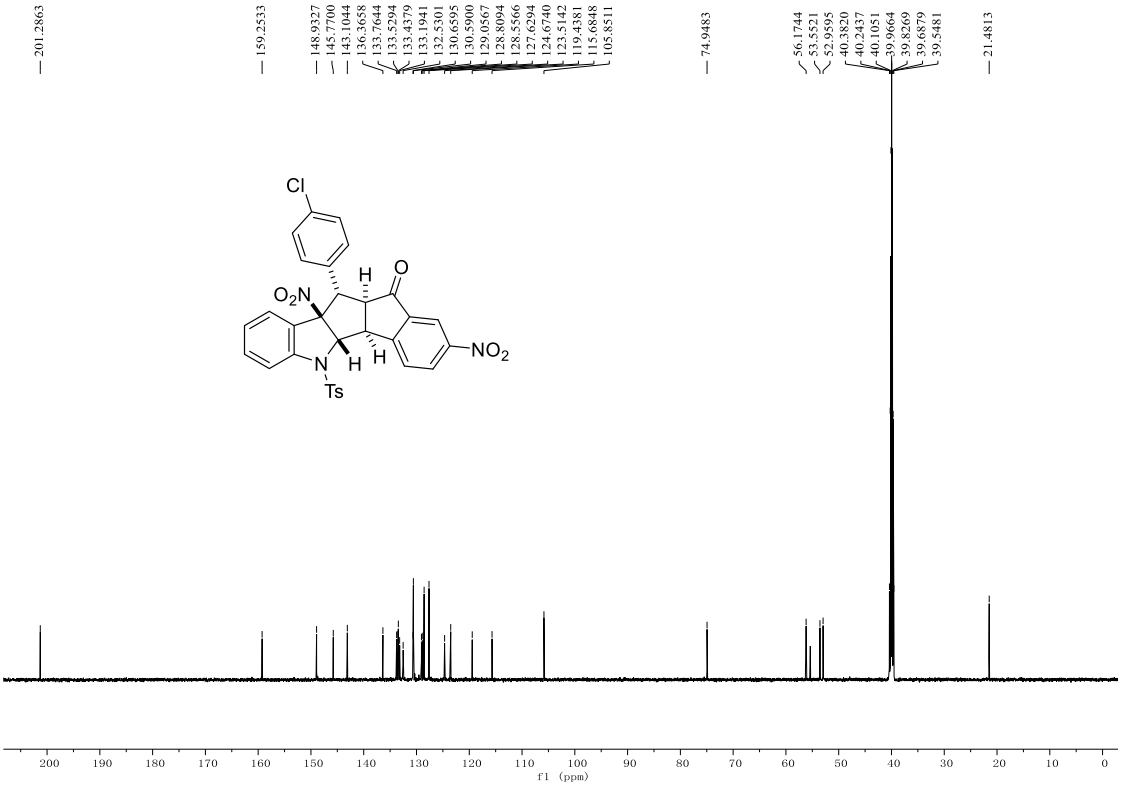
^{1}H and ^{13}C NMR of **3af**



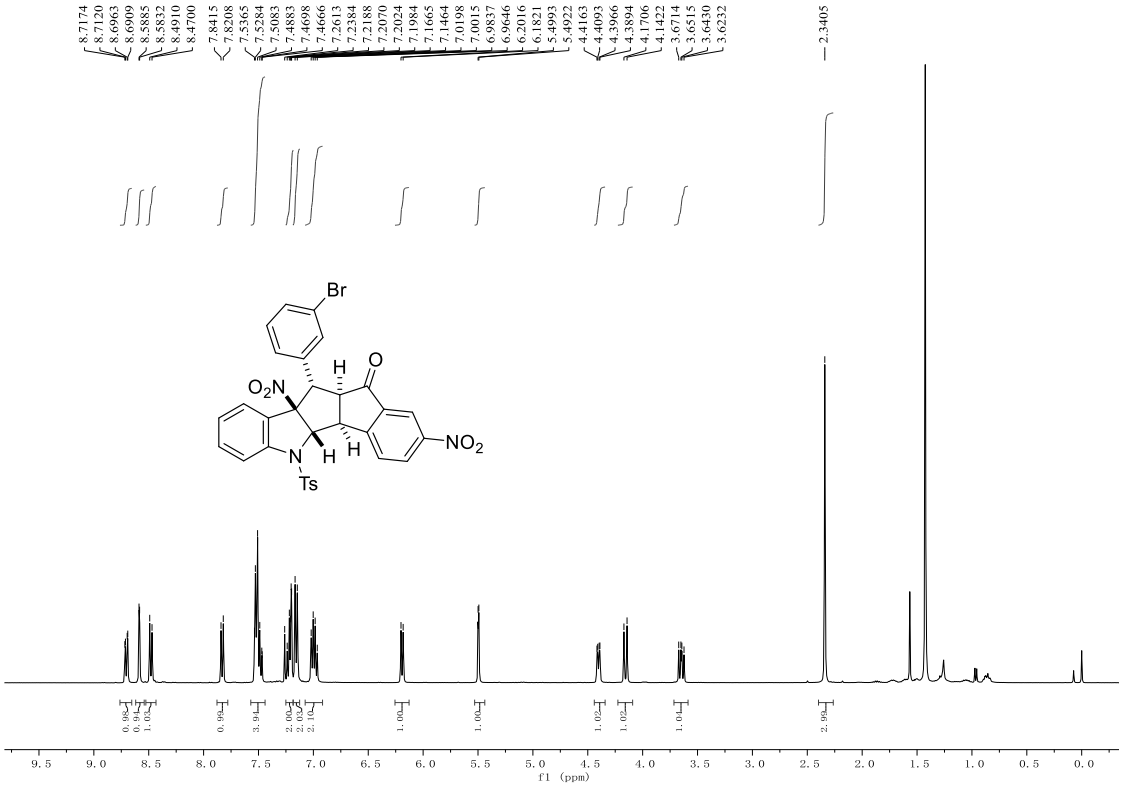


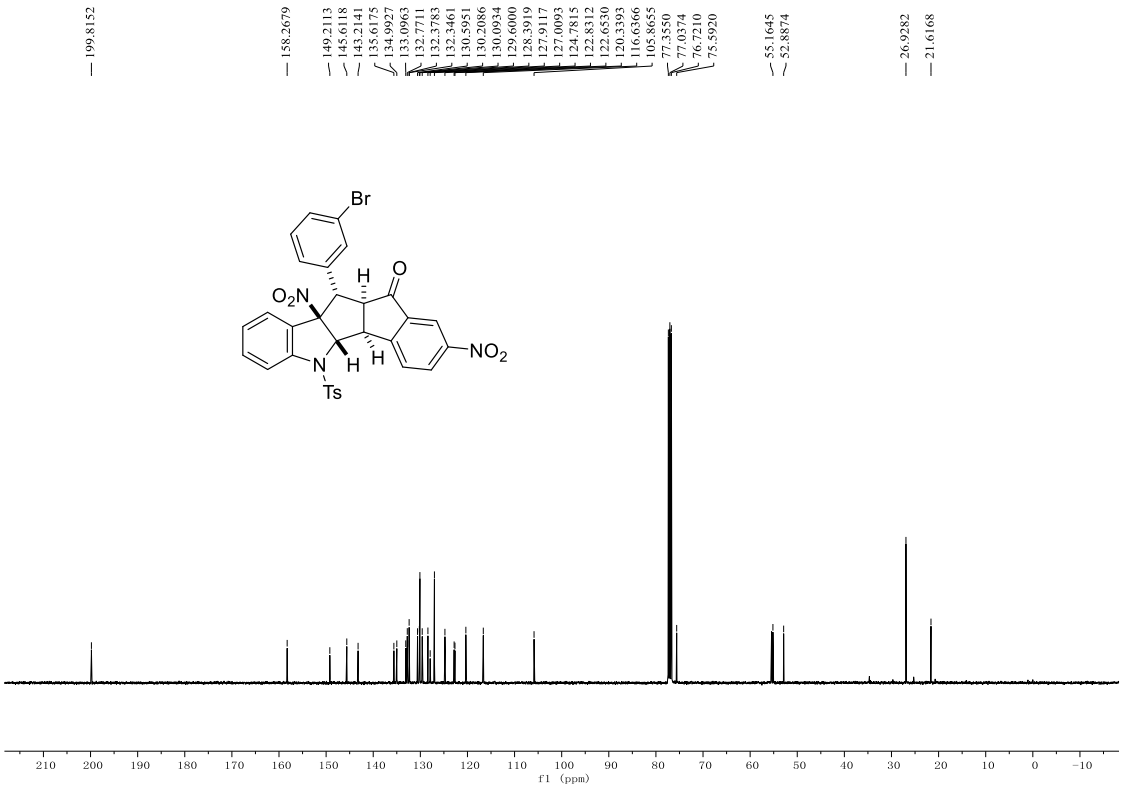
^{1}H and ^{13}C NMR of **3ag**



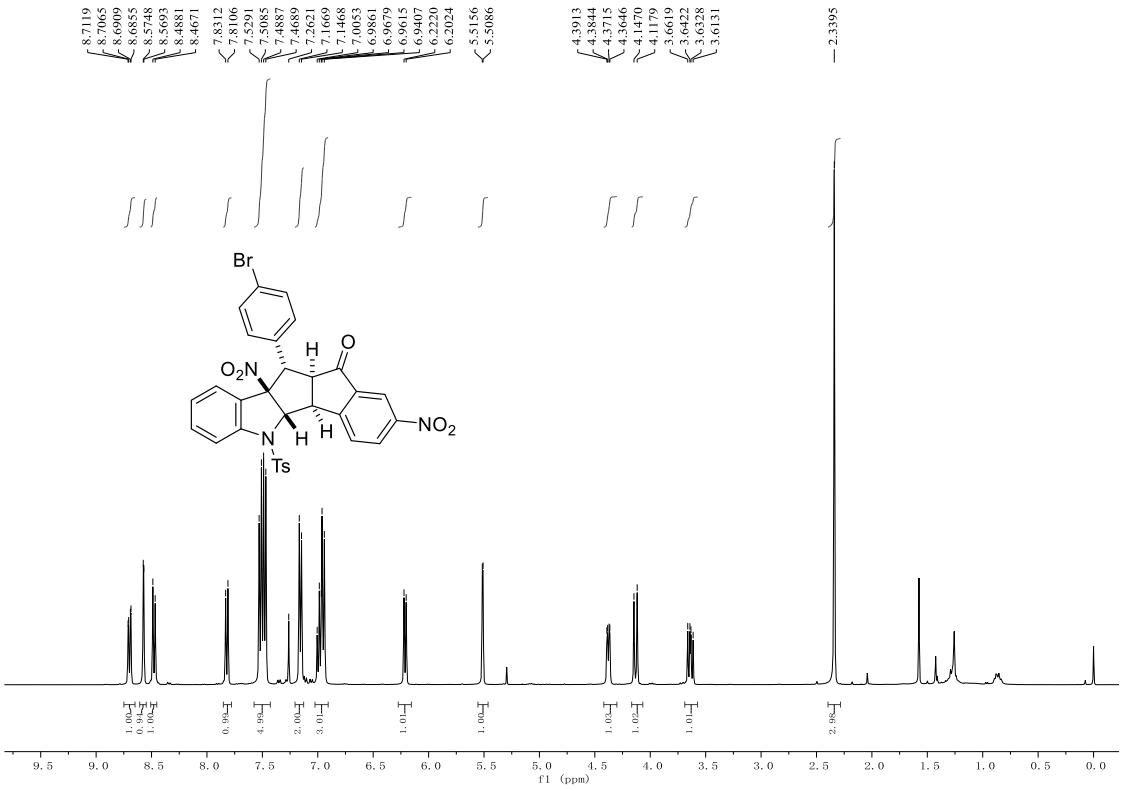


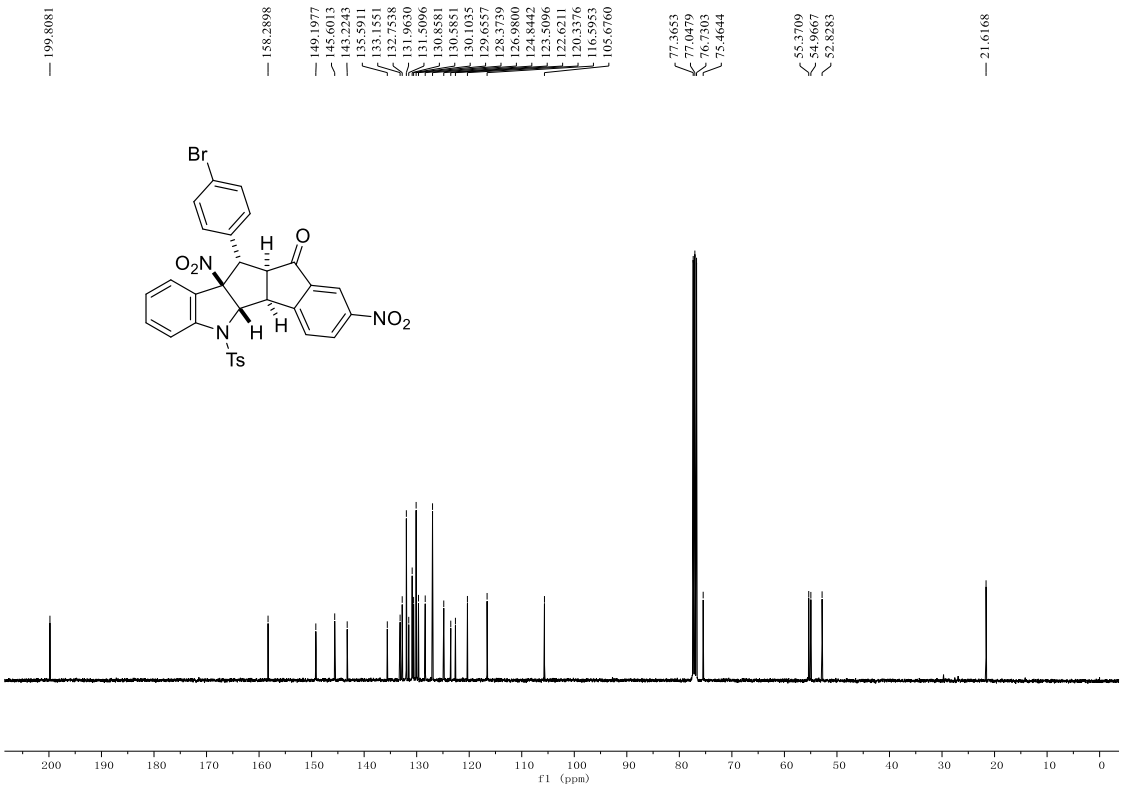
^{1}H and ^{13}C NMR of **3ah**



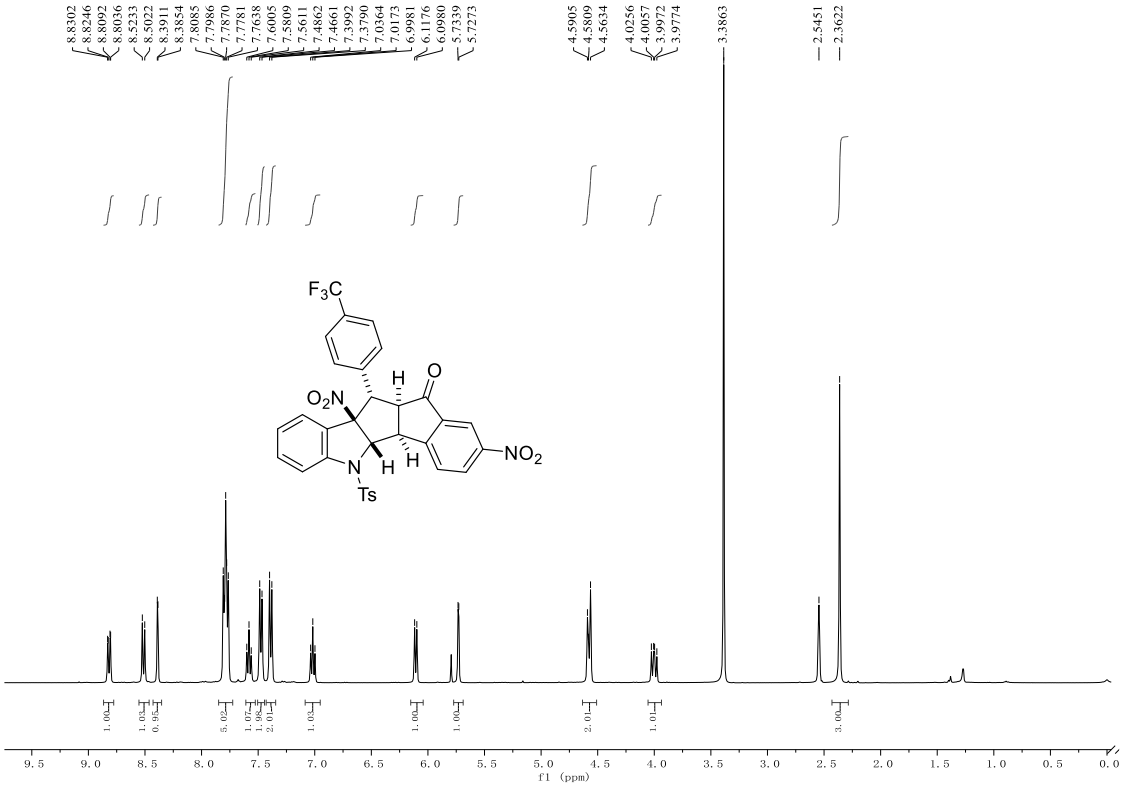


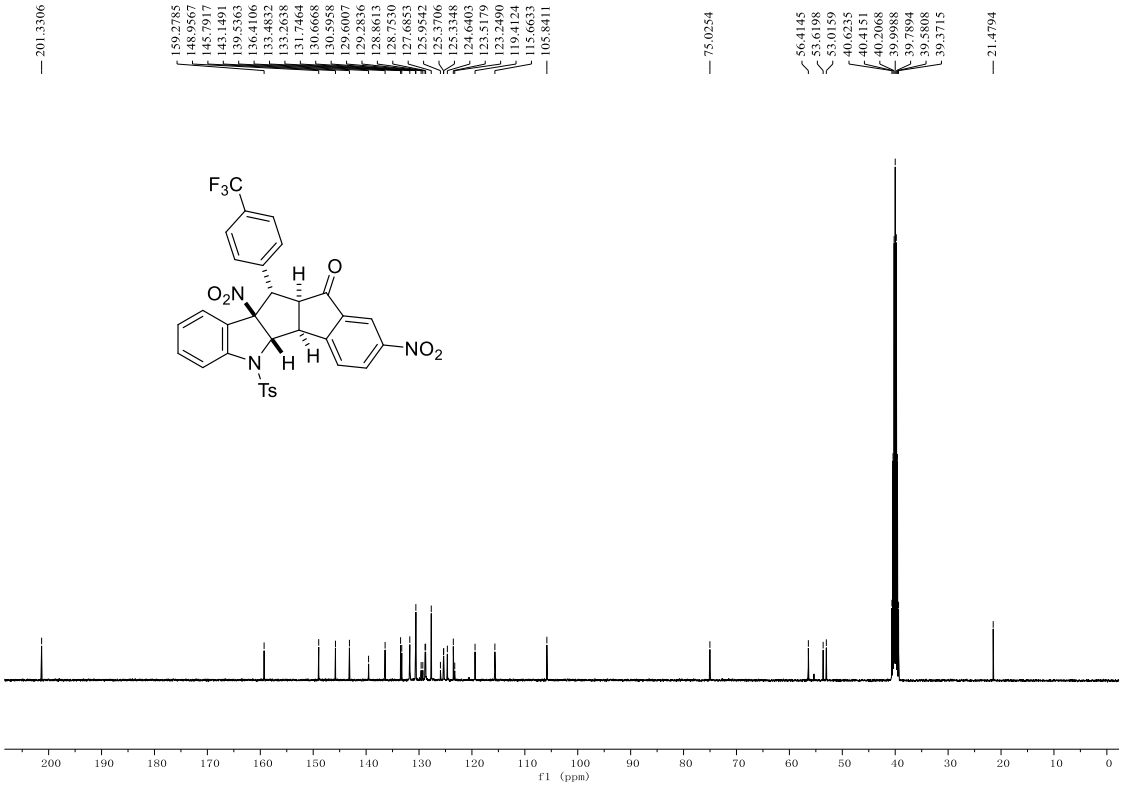
^{1}H and ^{13}C NMR of **3ai**

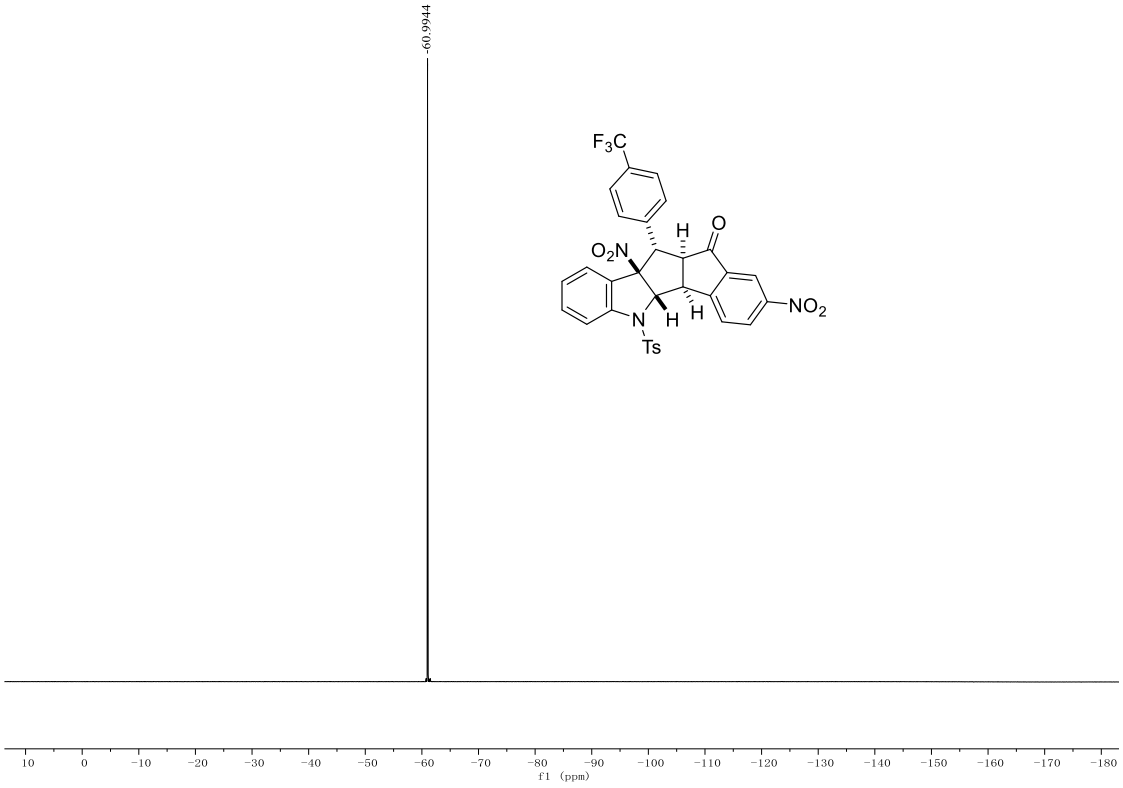




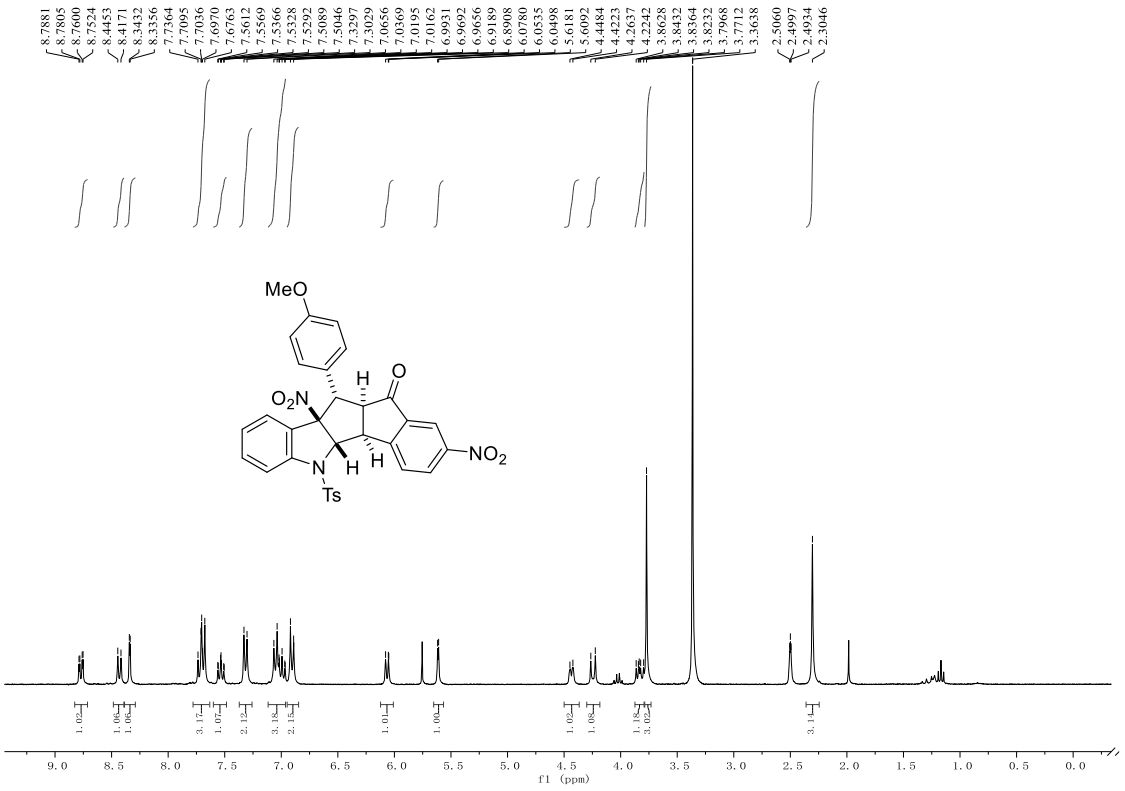
^{1}H, ^{13}C and ^{19}F NMR of **3aj**

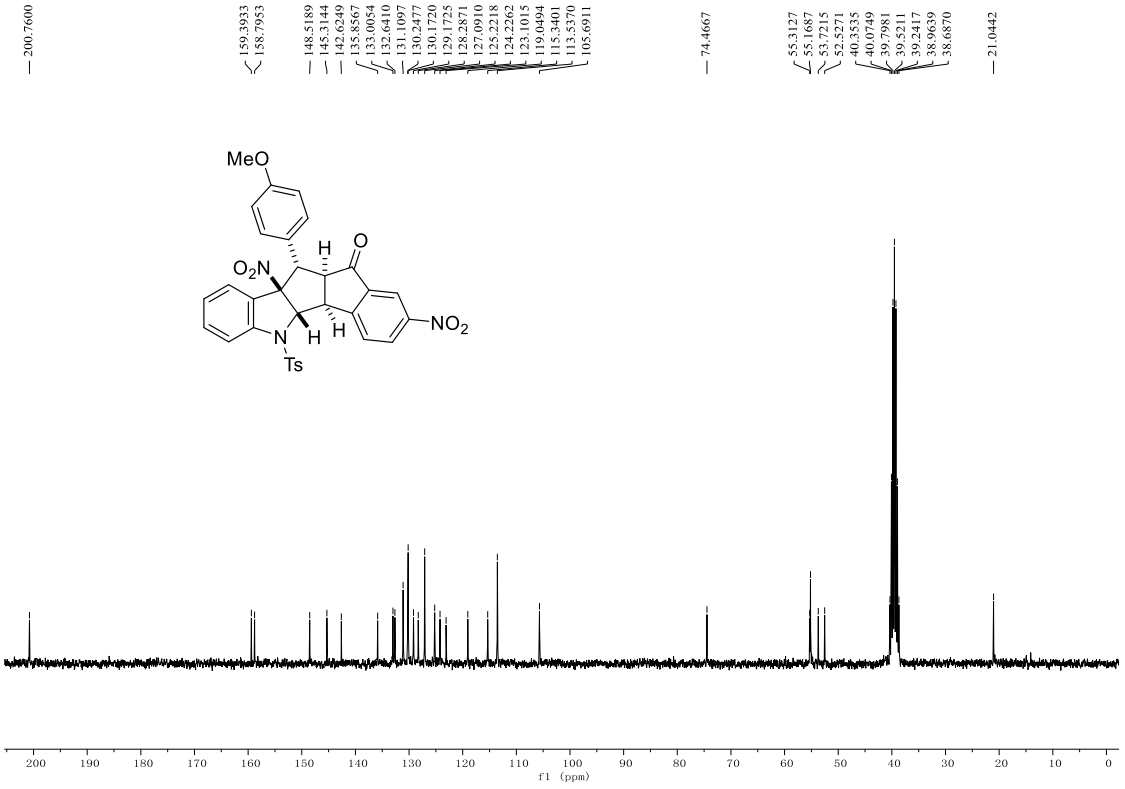




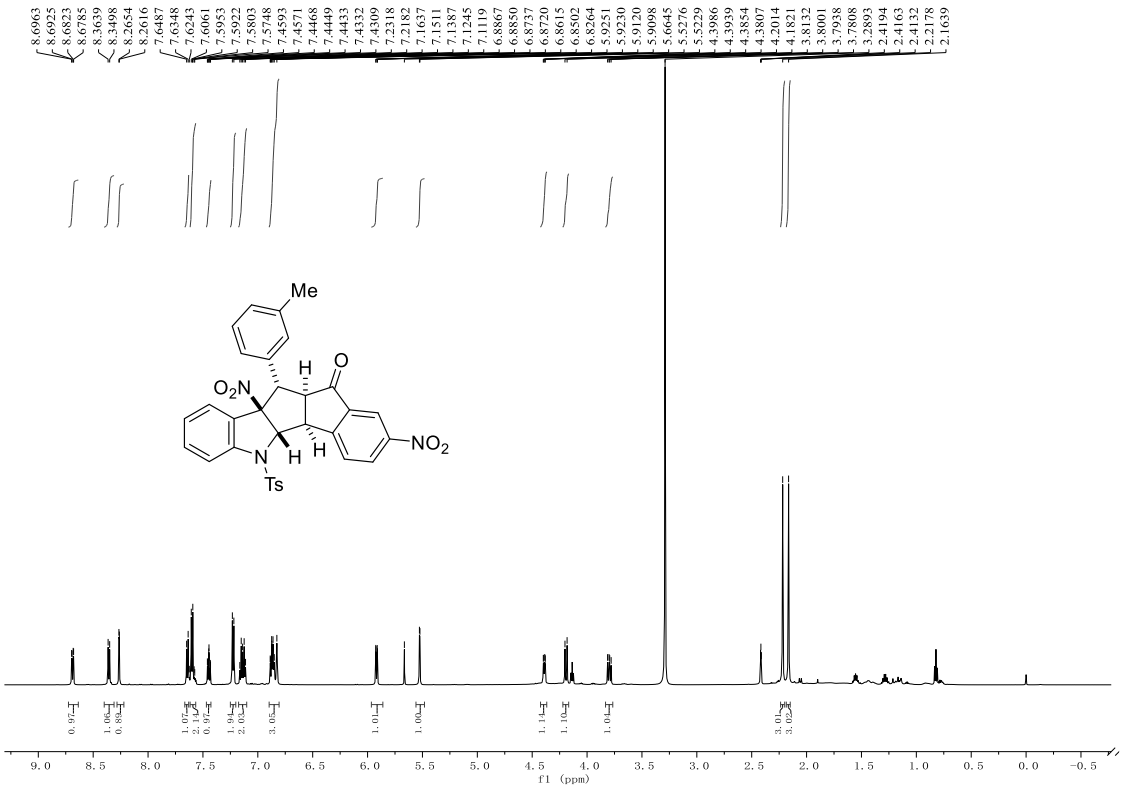

-60.9944
F3C
O
H
O2N
NO2
H
H
N
Ts
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
f1 (ppm)

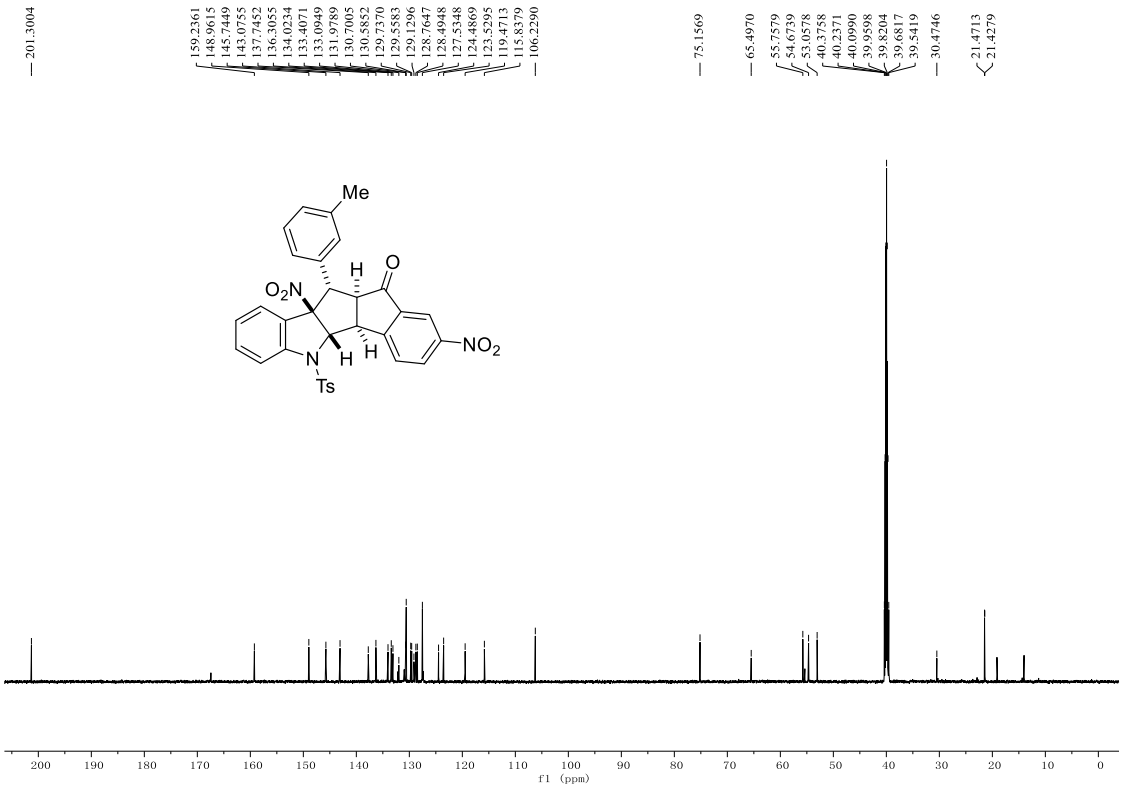
^{1}H and ^{13}C NMR of **3ak**



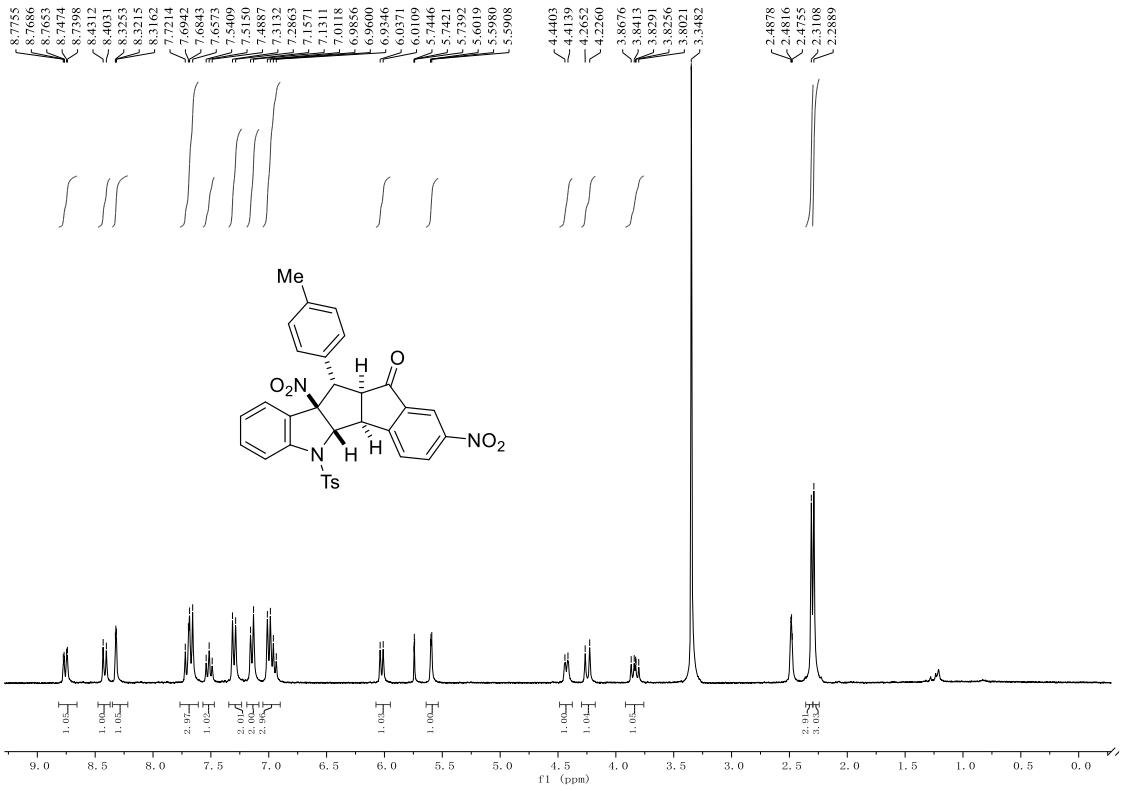


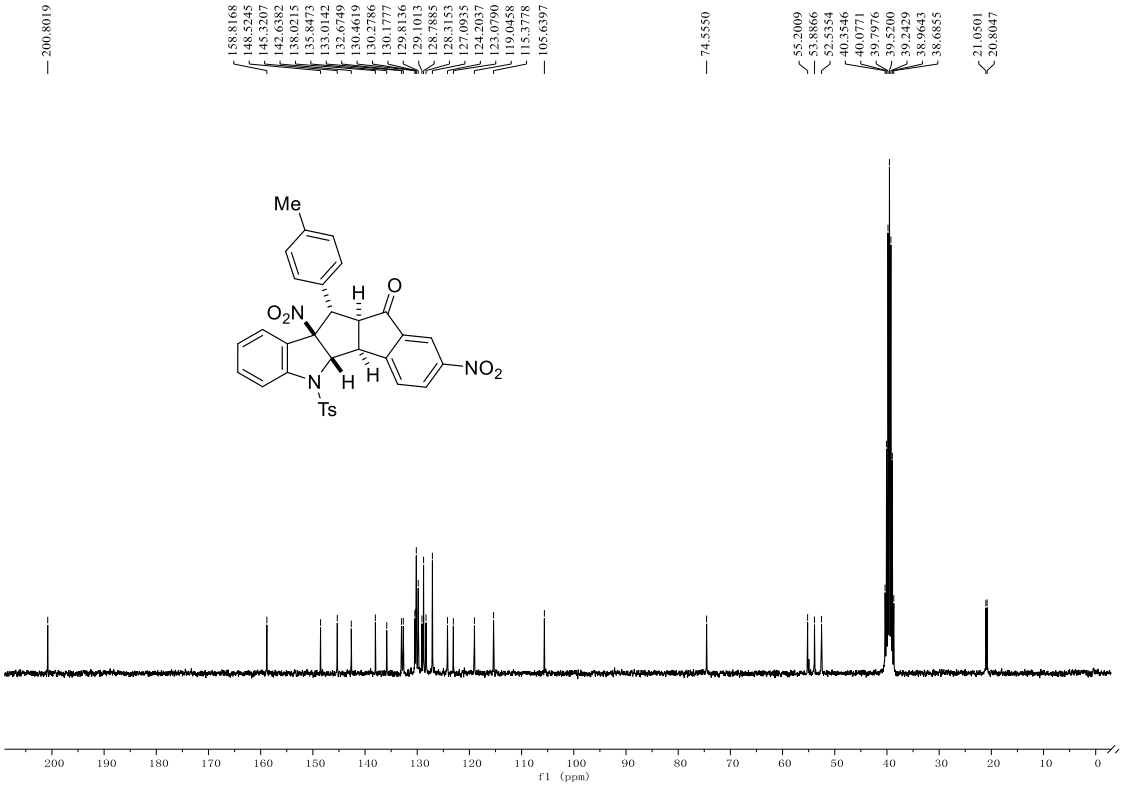
^{1}H and ^{13}C NMR of **3al**



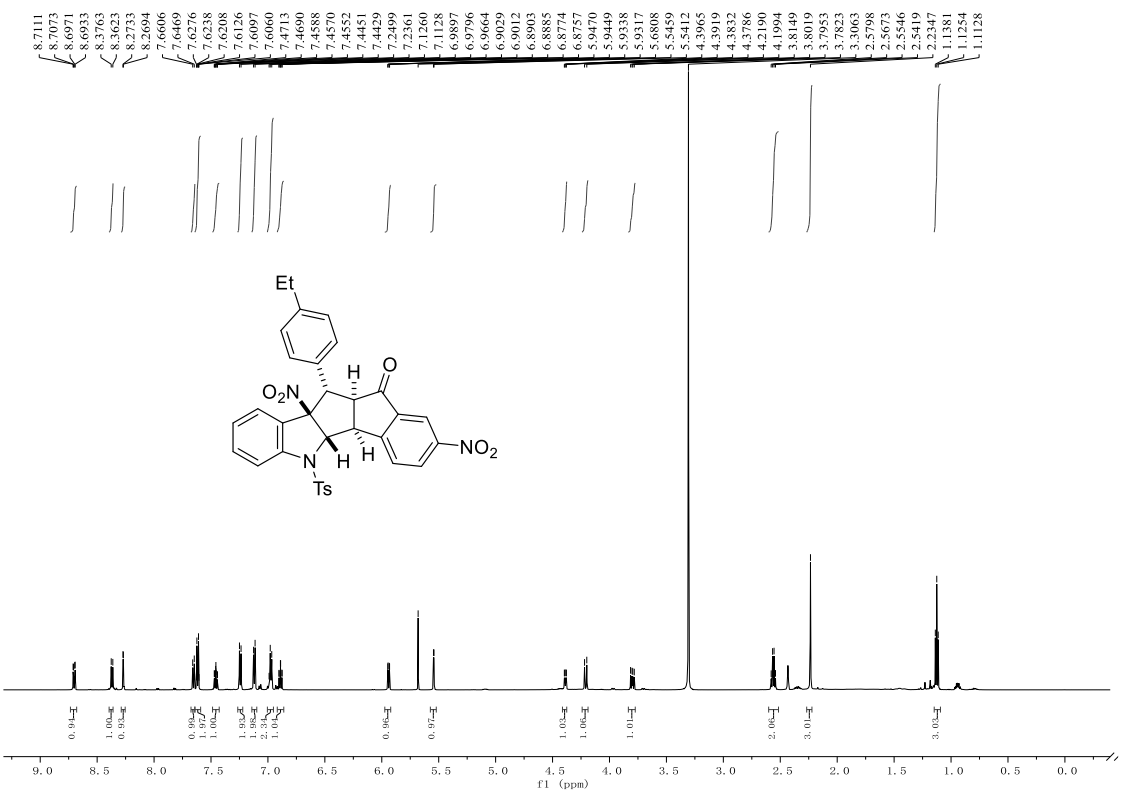


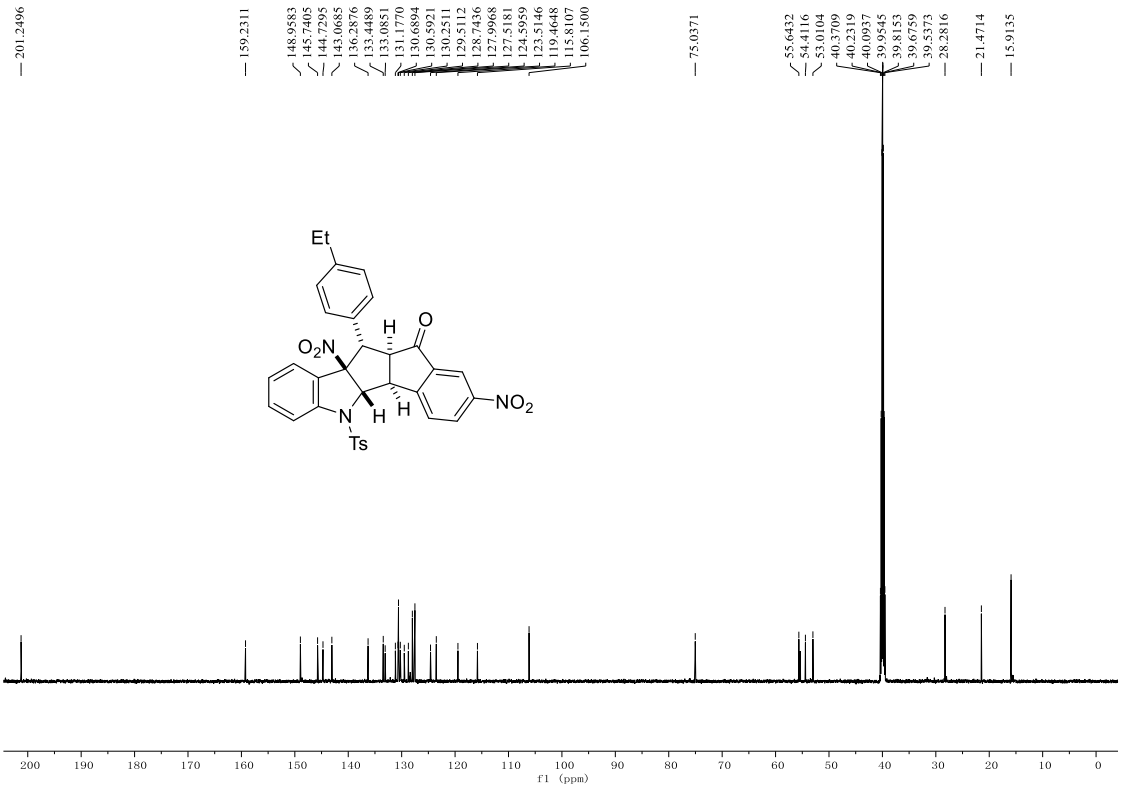
^{1}H and ^{13}C NMR of **3am**



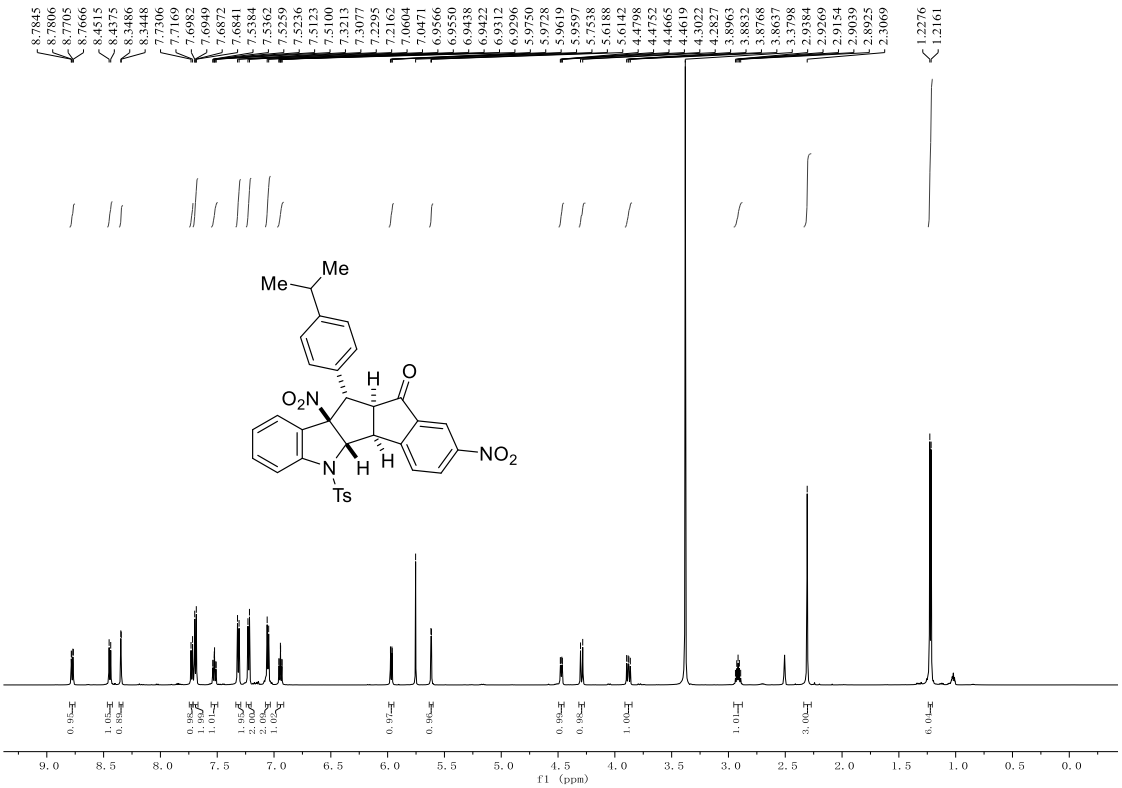


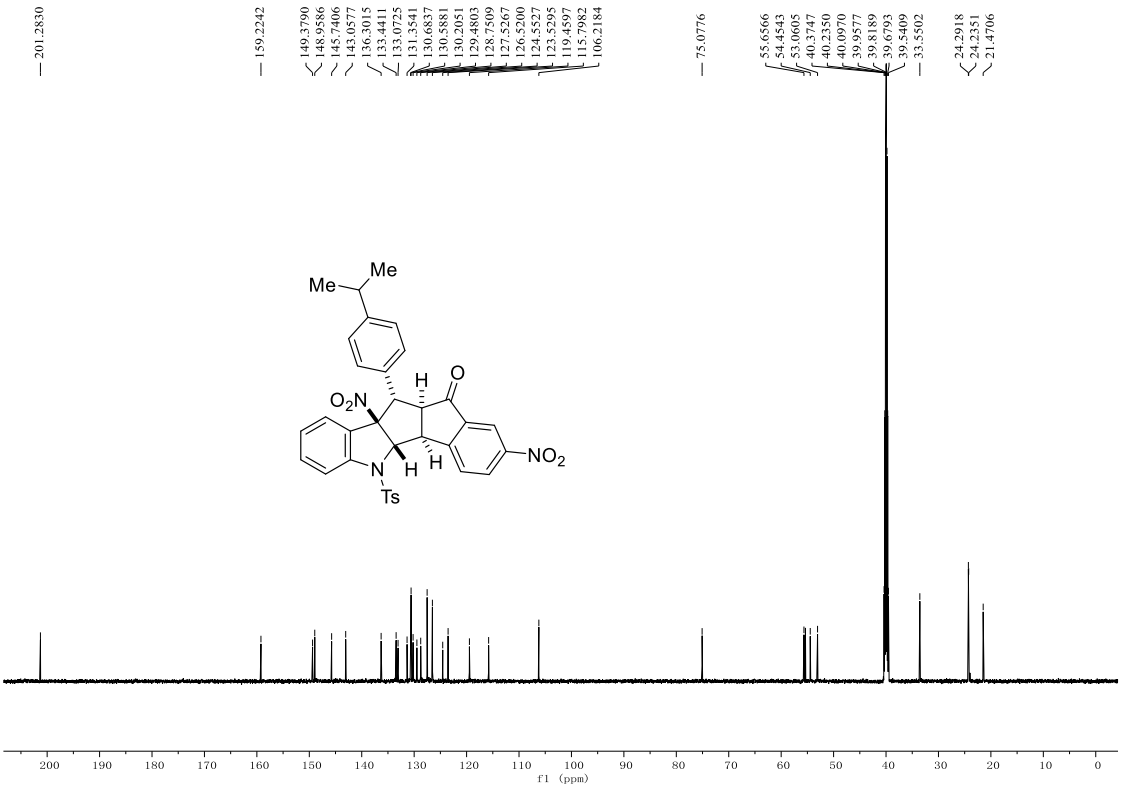
^{1}H and ^{13}C NMR of **3an**



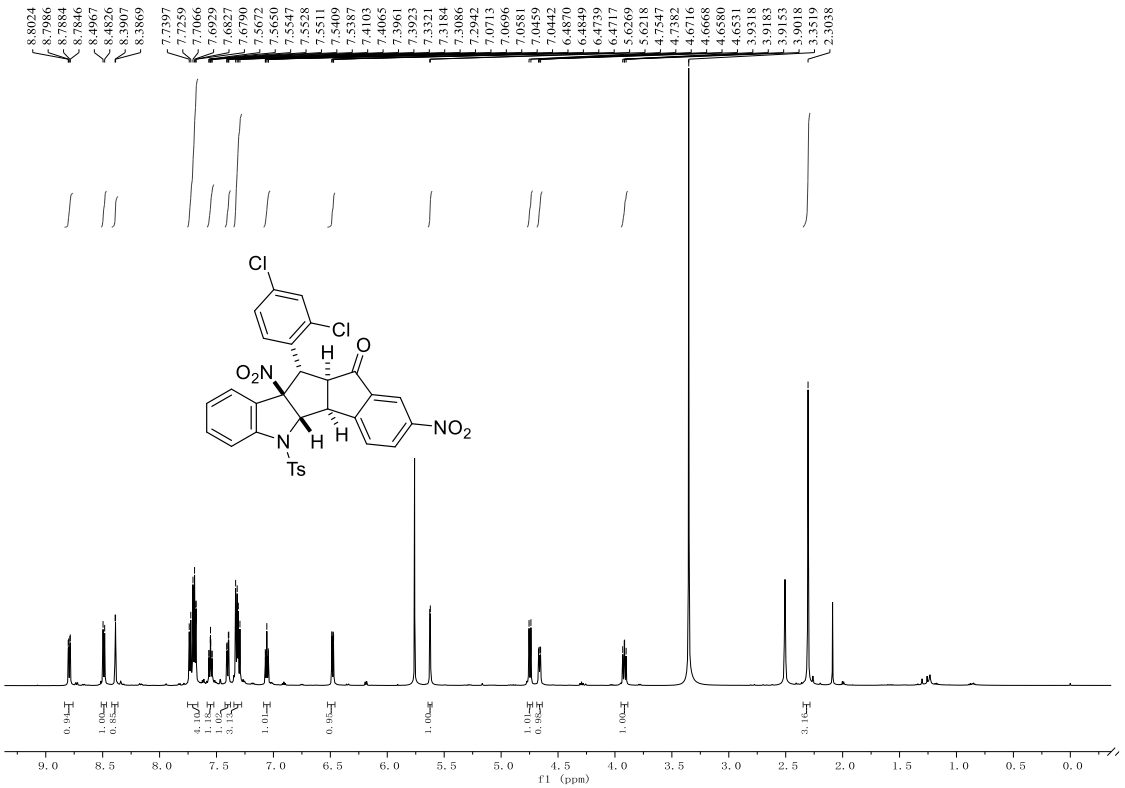


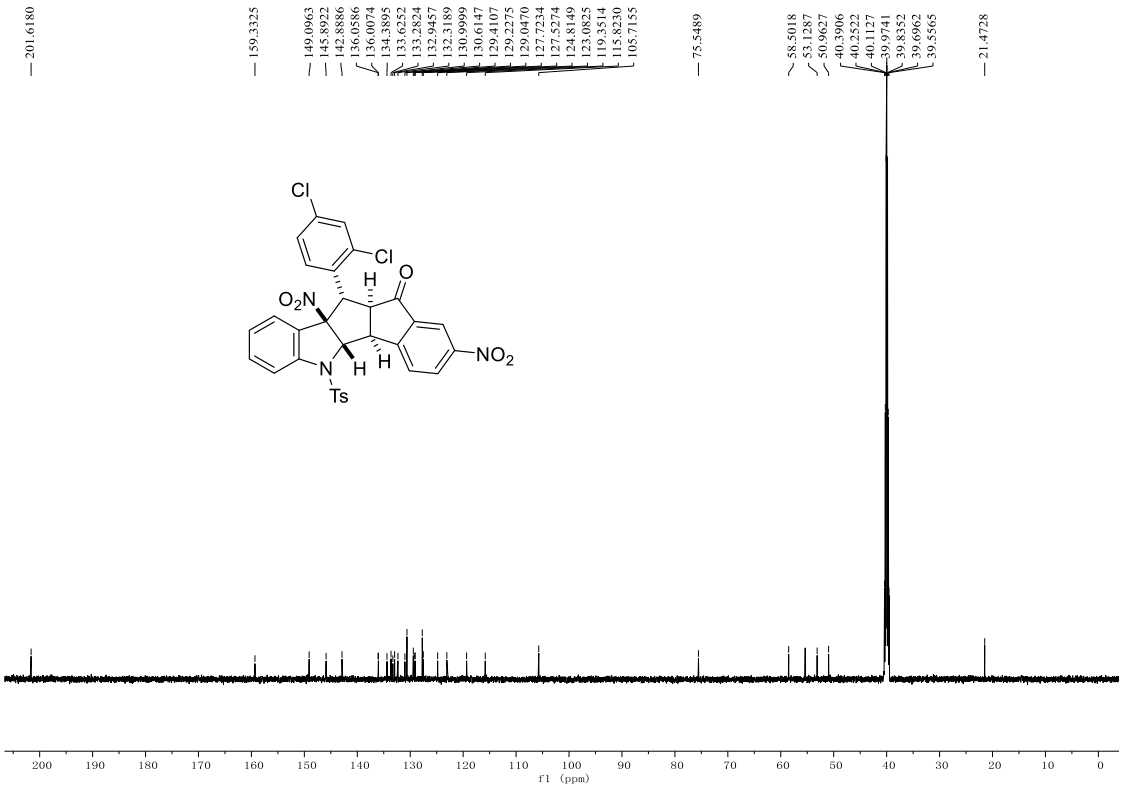
^{1}H and ^{13}C NMR of **3ao**



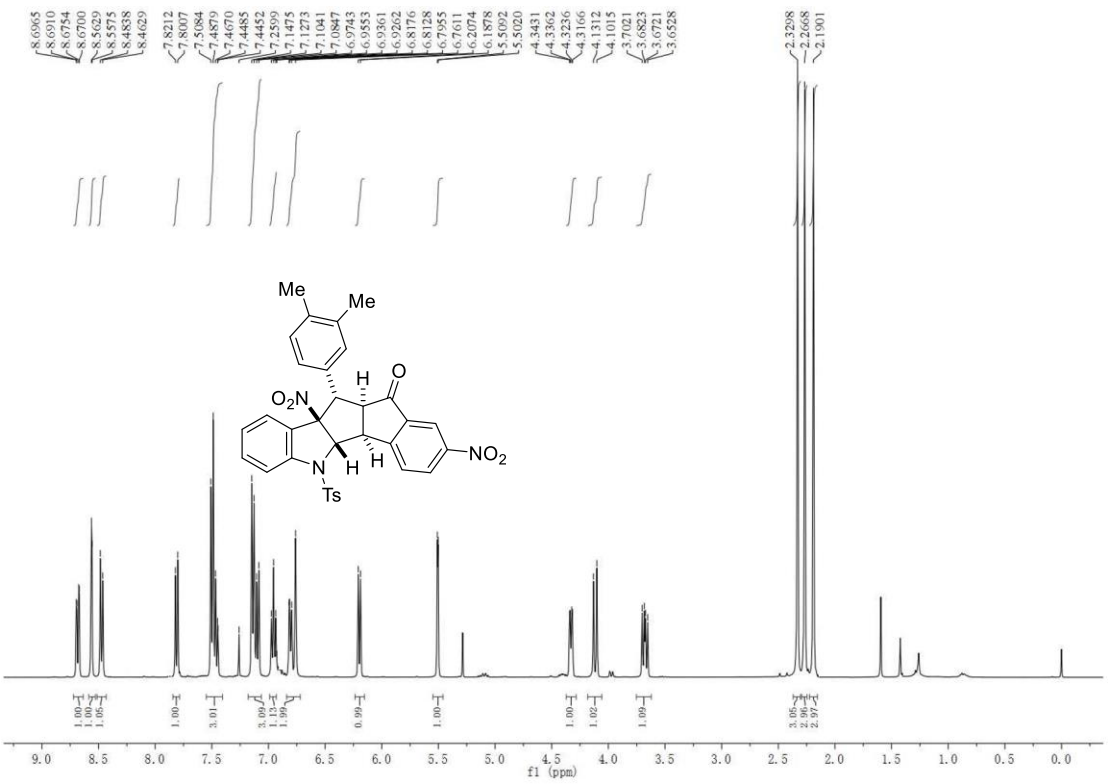


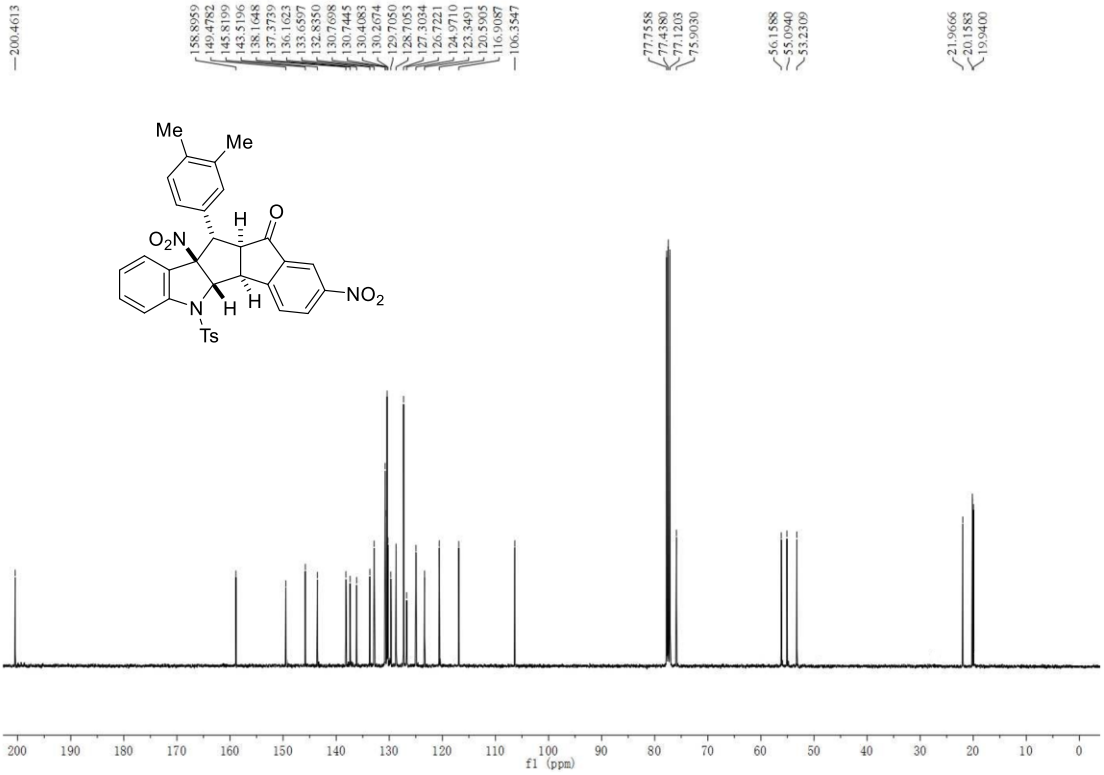
^{1}H and ^{13}C NMR of **3ap**



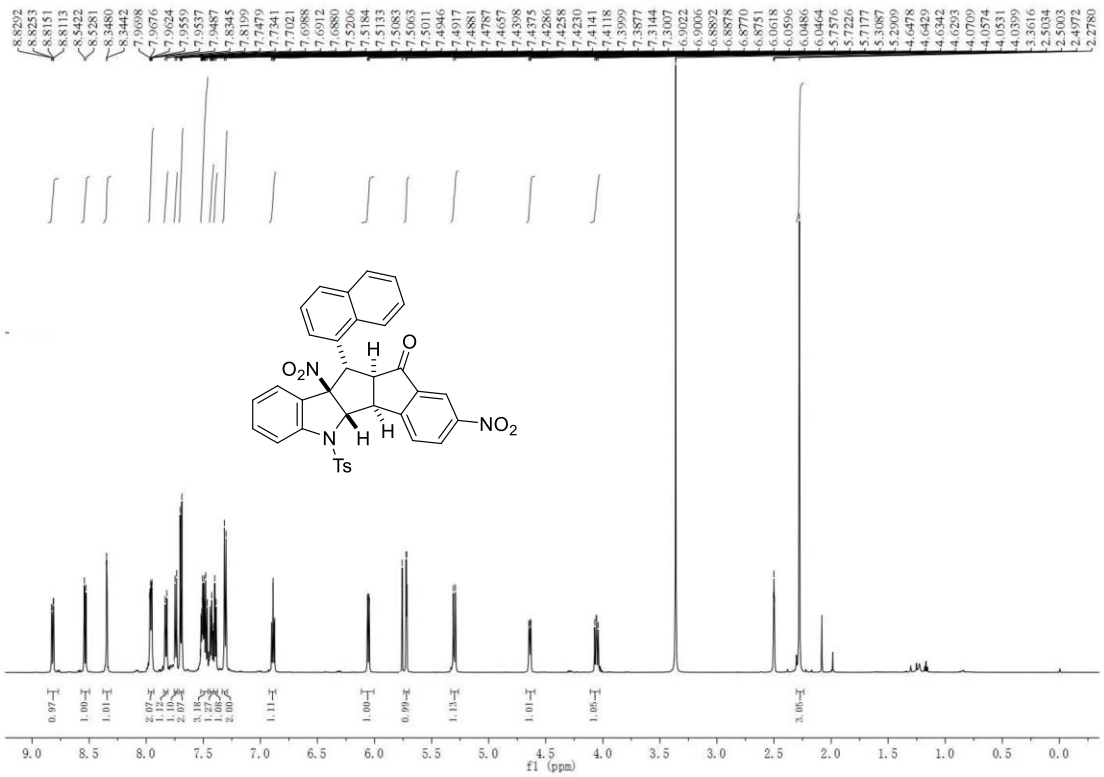


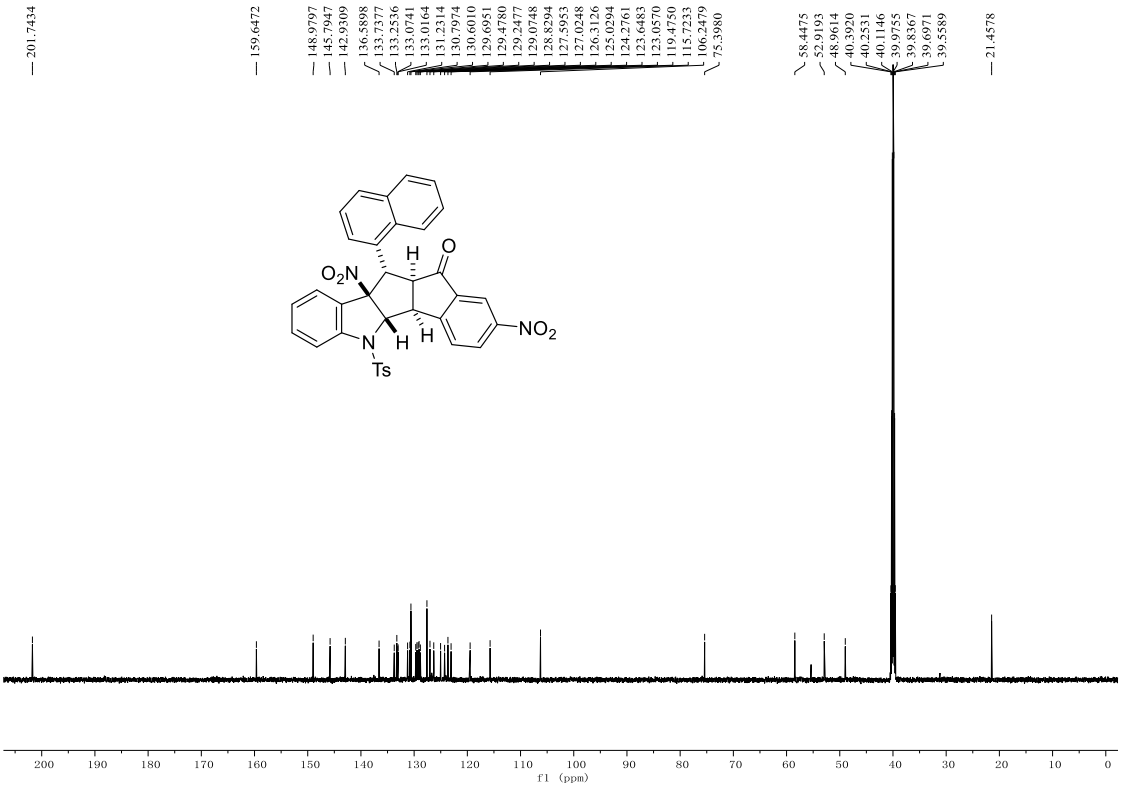
^{1}H and ^{13}C NMR of **3aq**



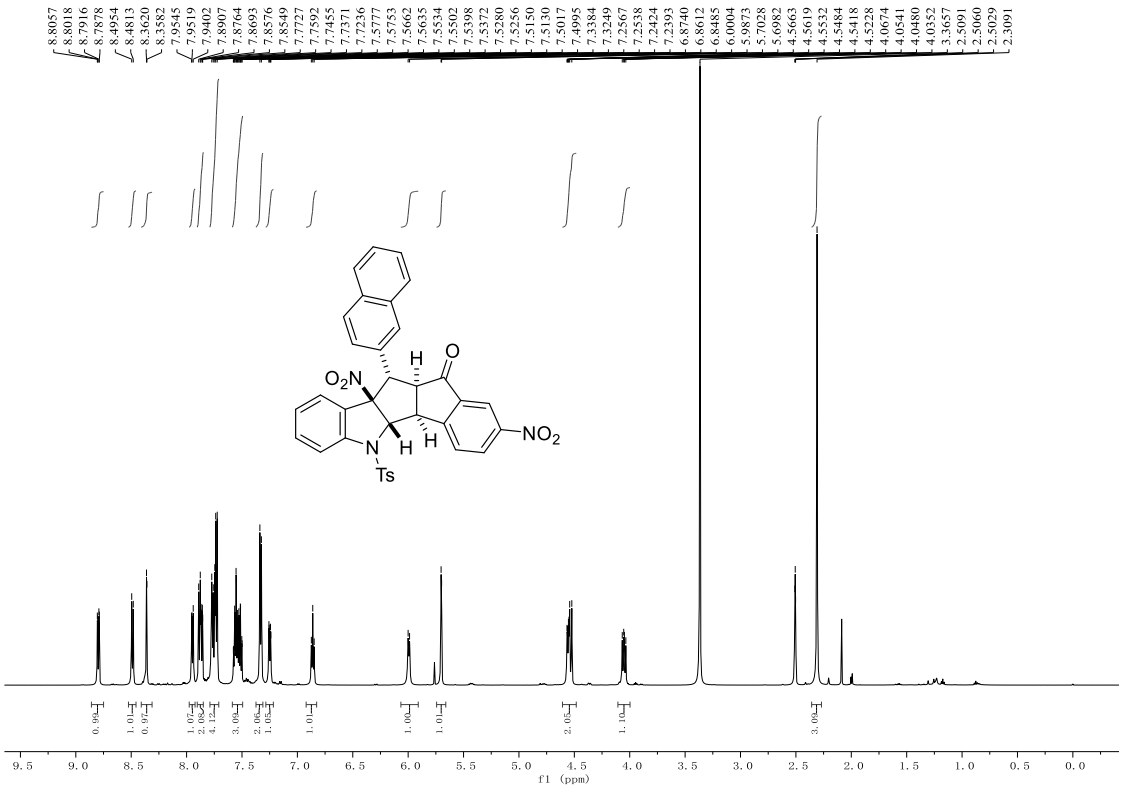


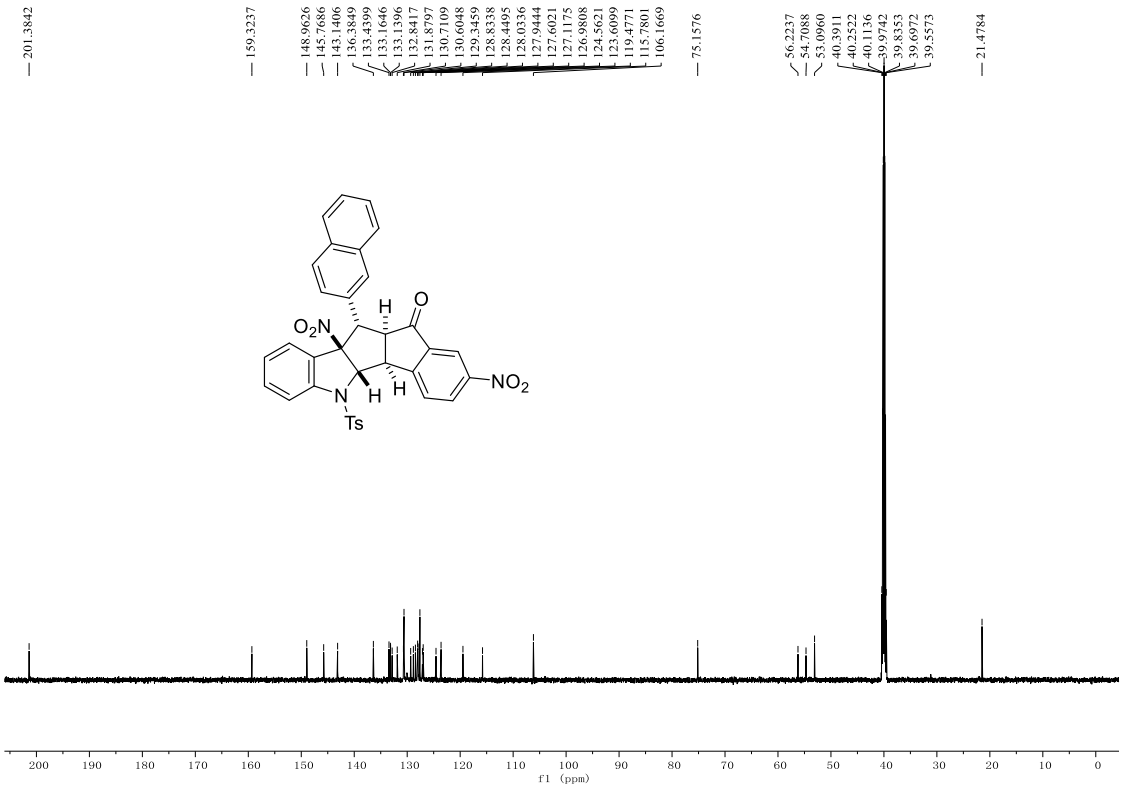
^{1}H and ^{13}C NMR of **3ar**



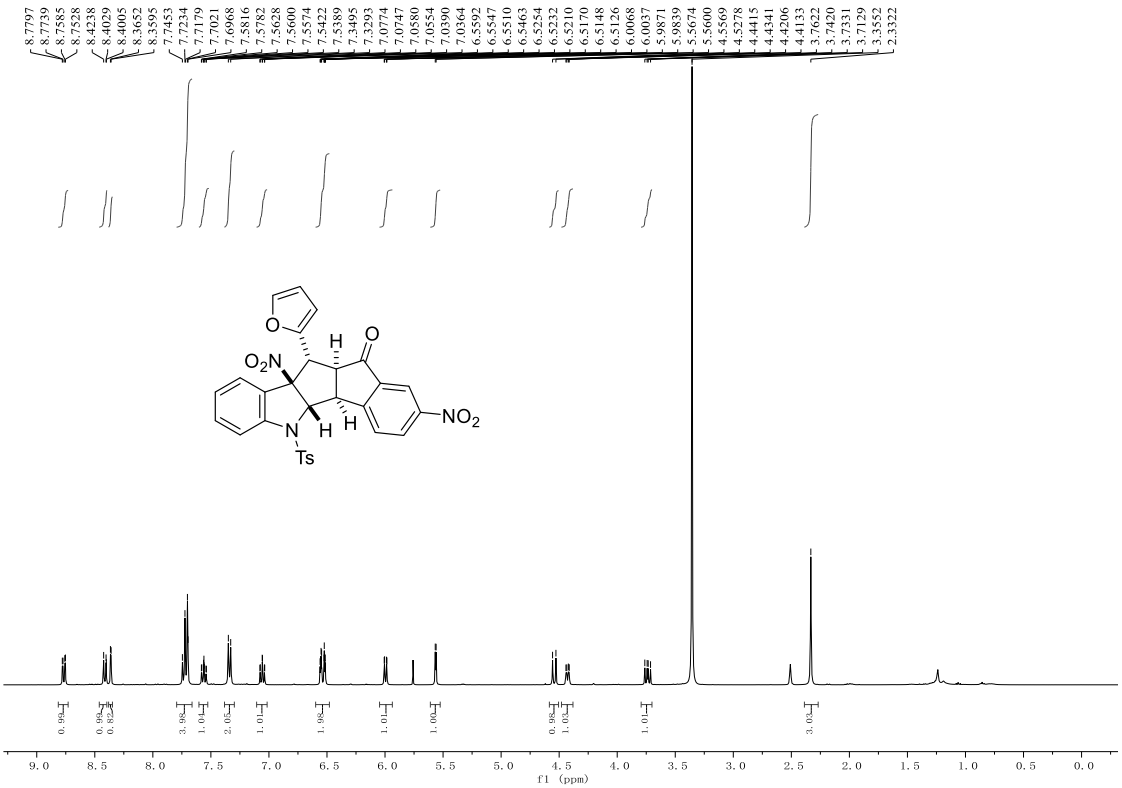


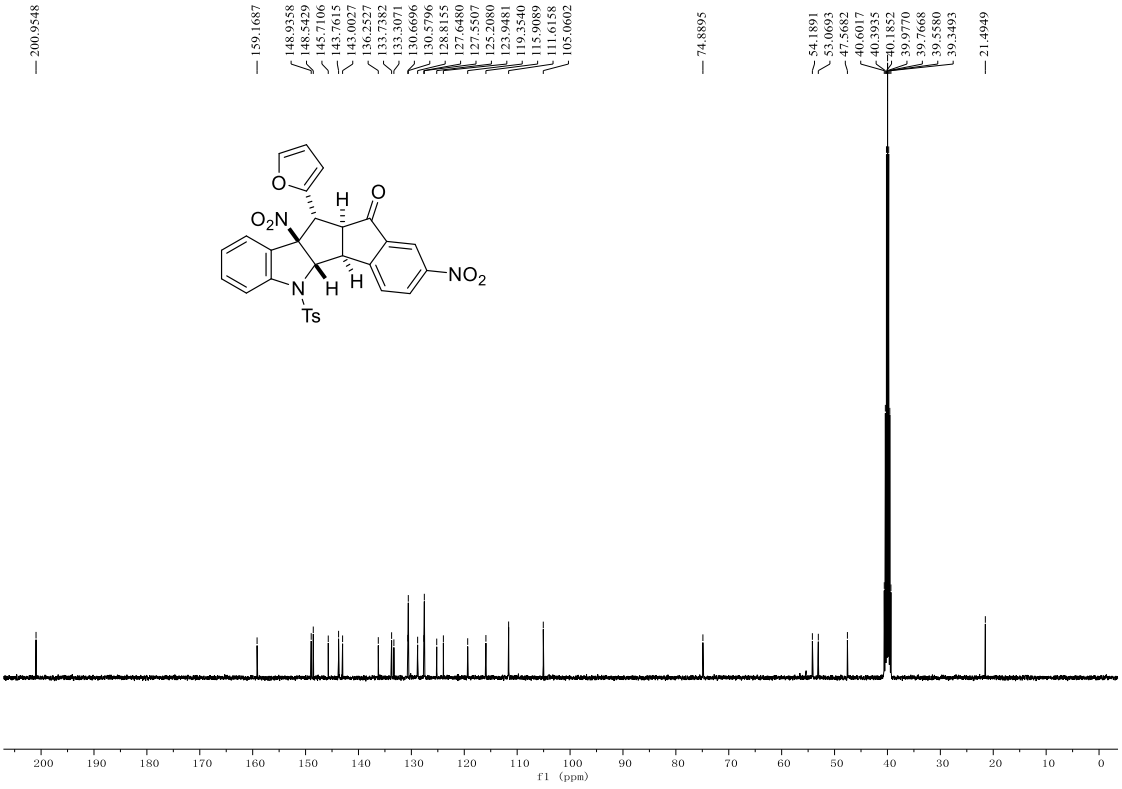
^{1}H and ^{13}C NMR of **3as**



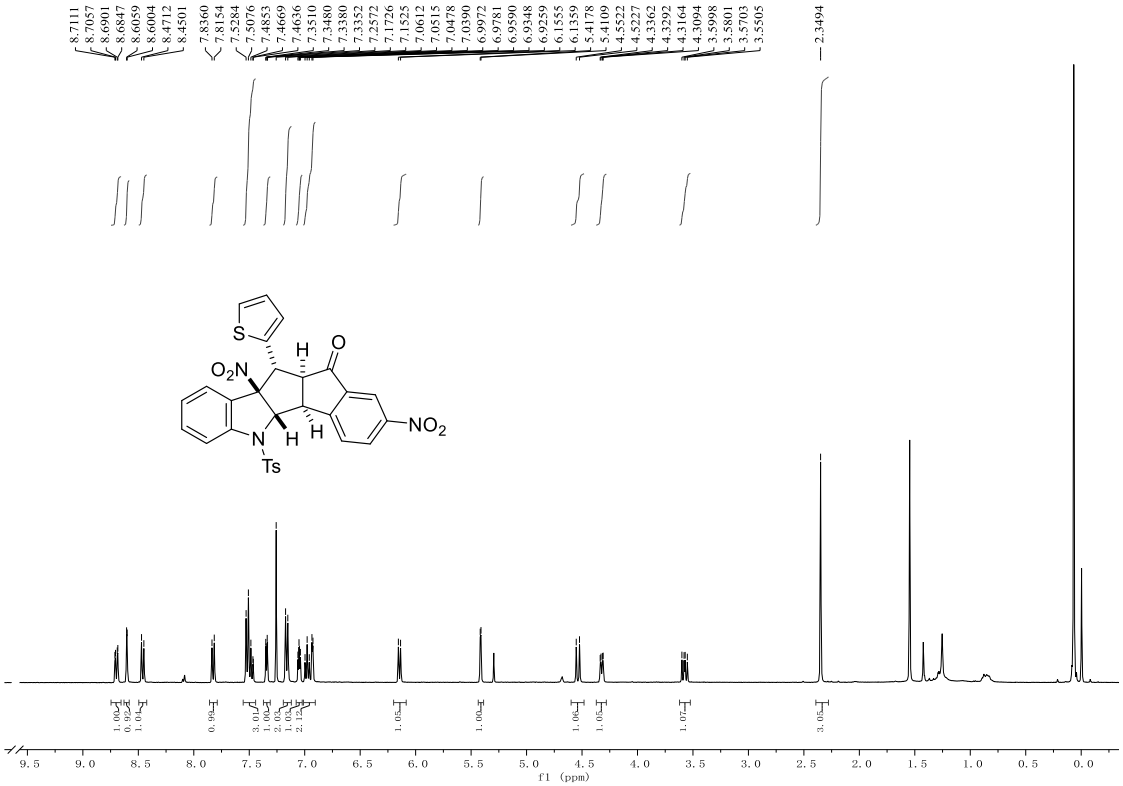


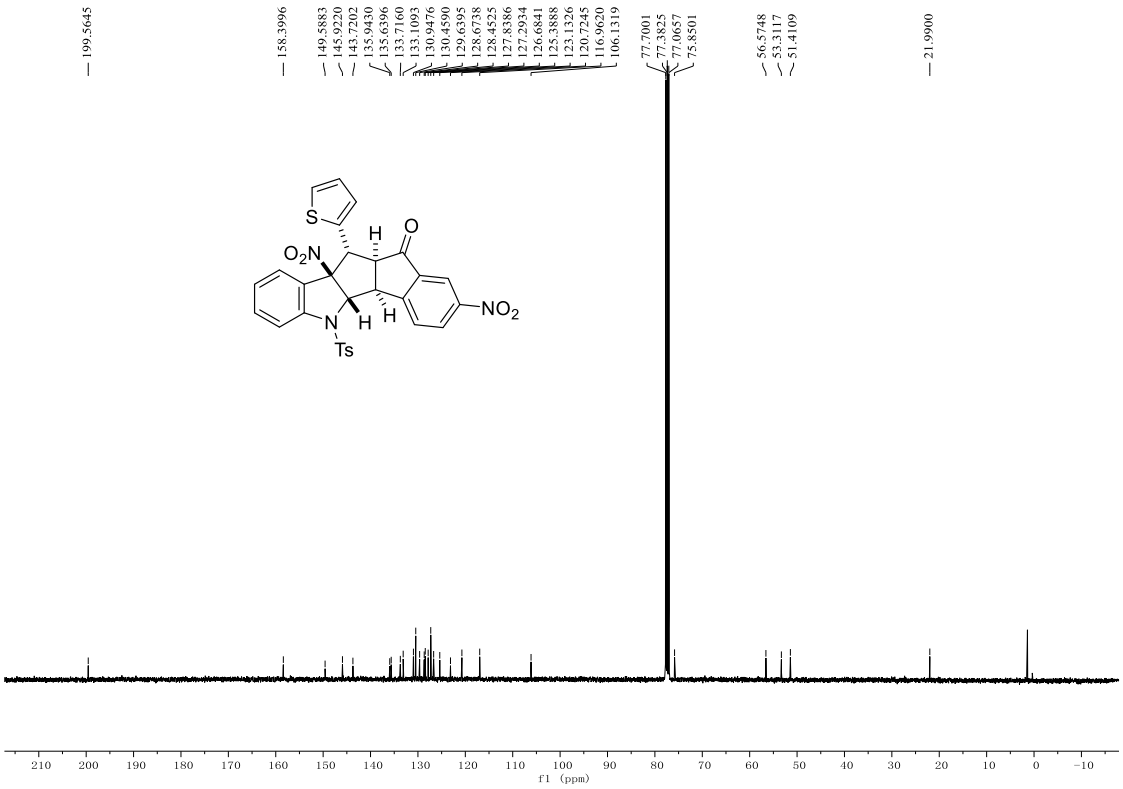
^{1}H and ^{13}C NMR of **3at**



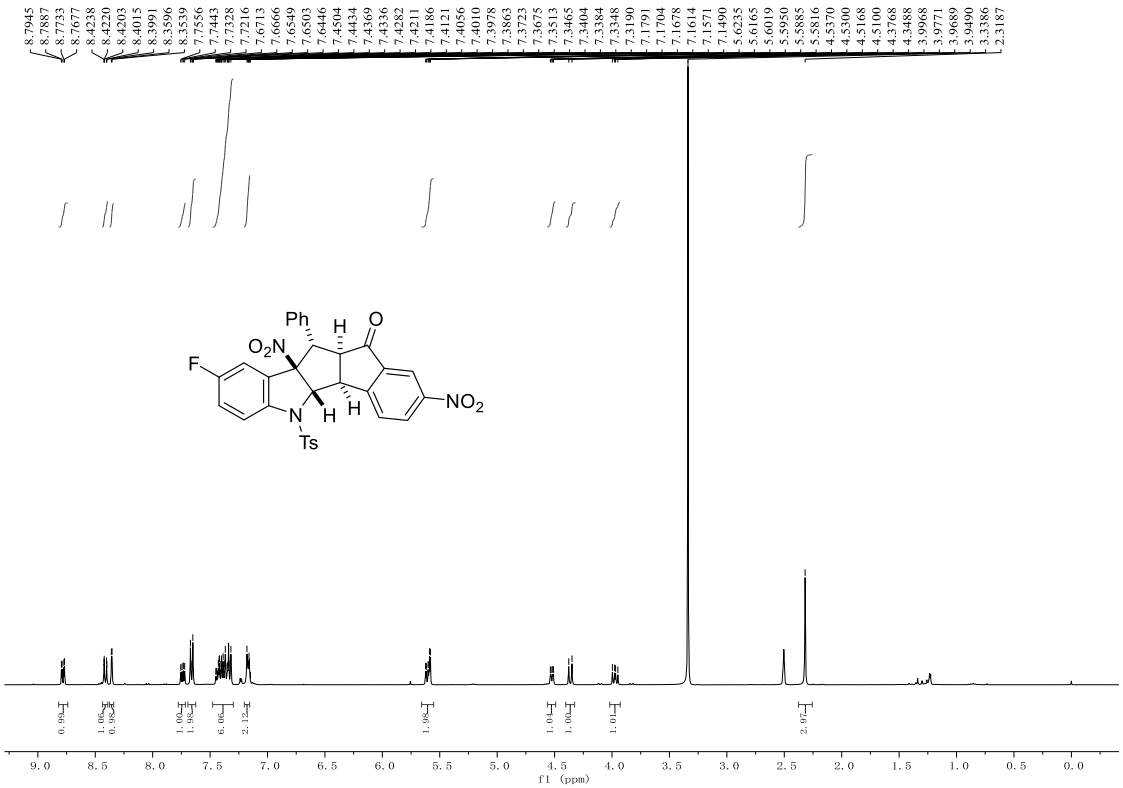


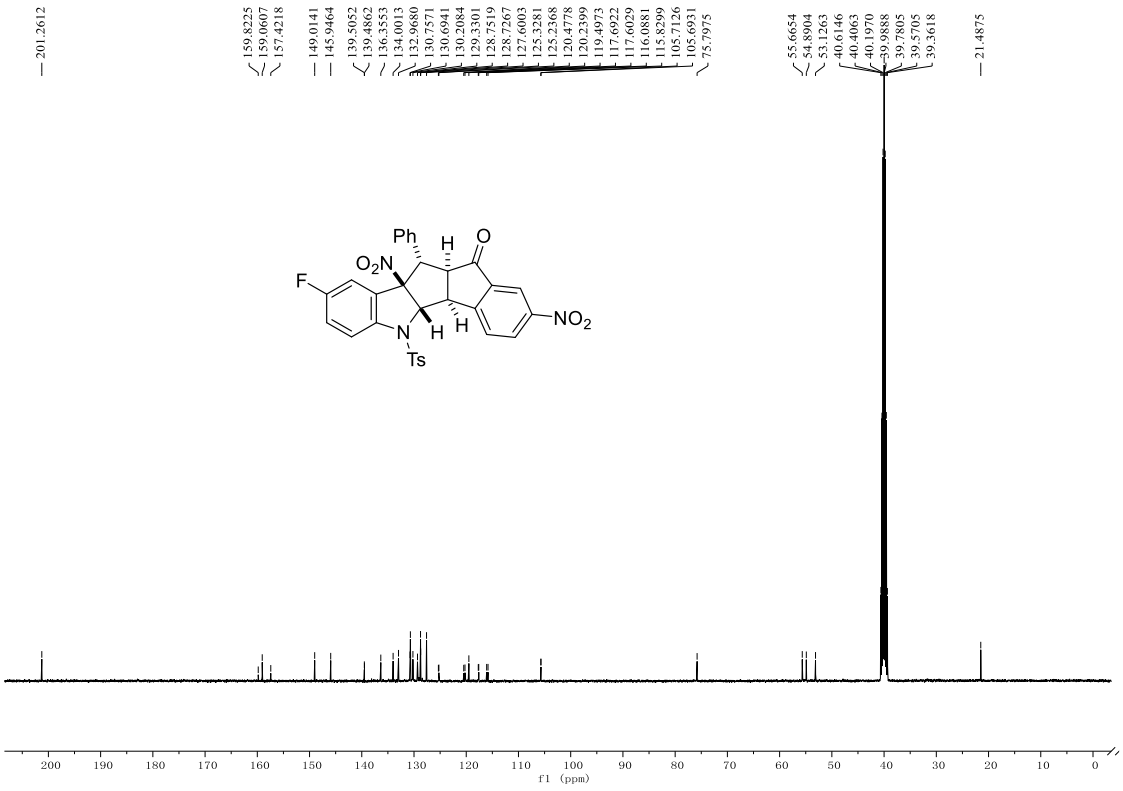
^{1}H and ^{13}C NMR of **3au**

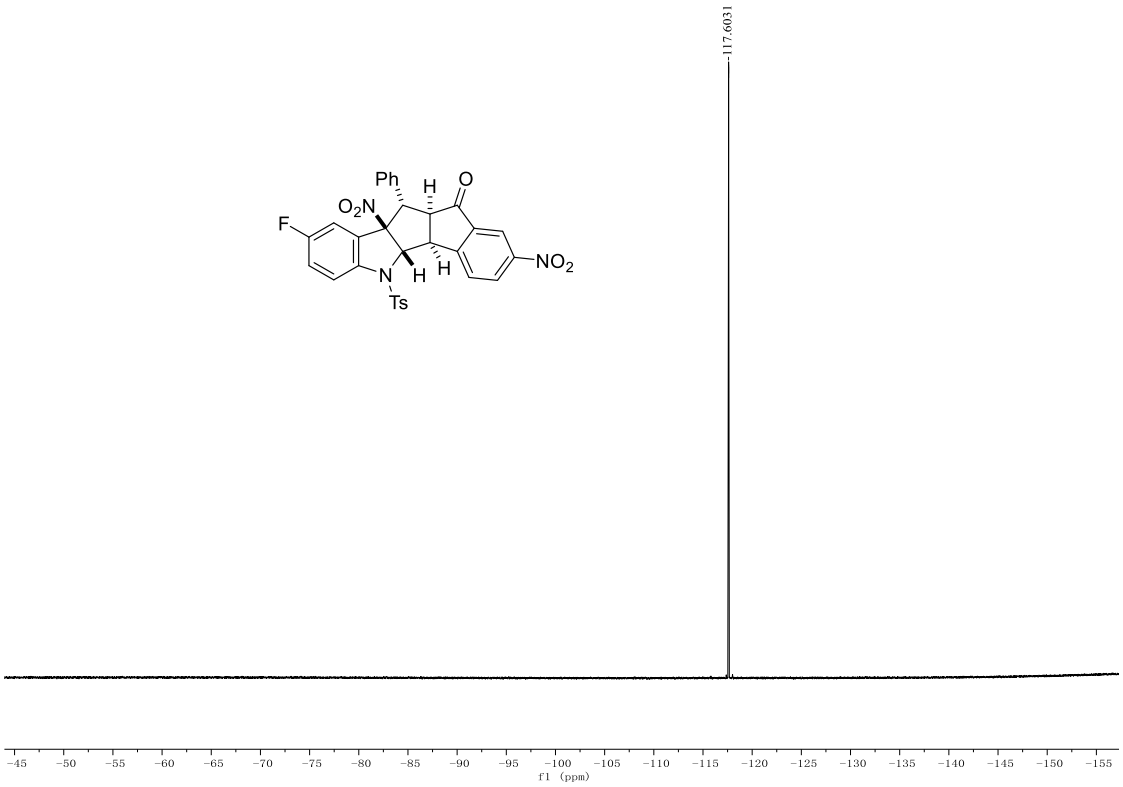




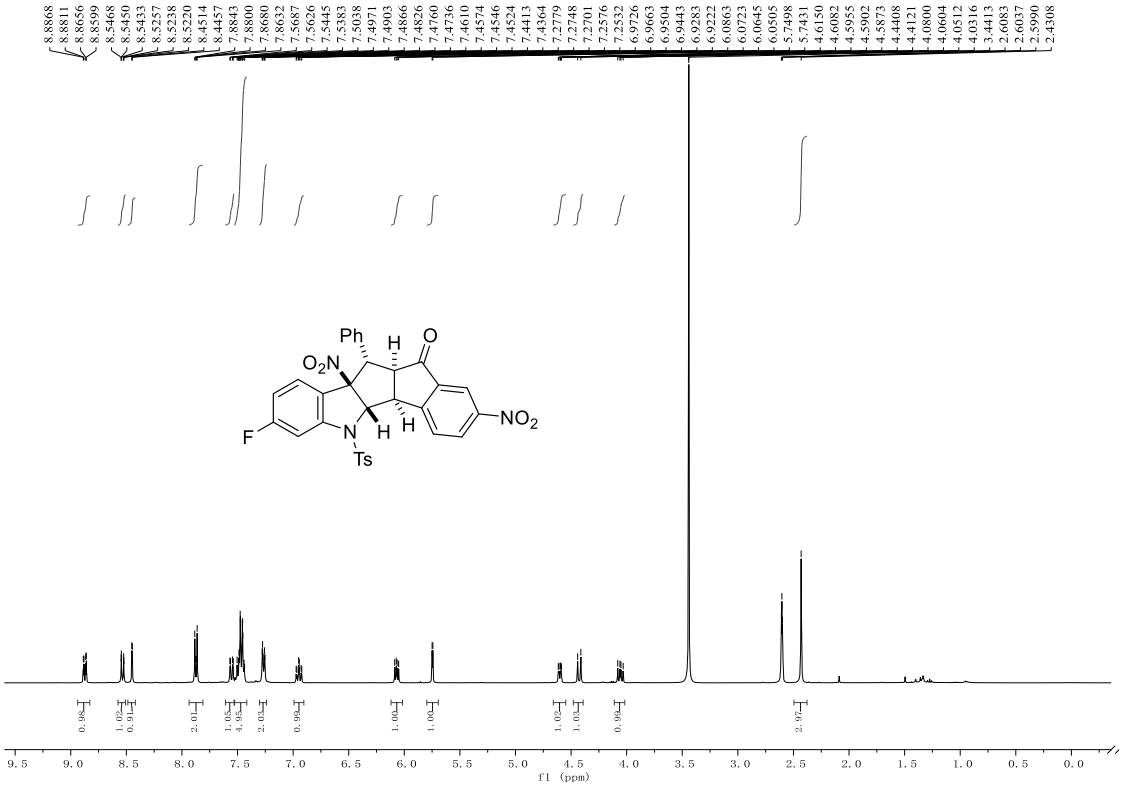
^{1}H, ^{13}C NMR and ^{19}F of **3ba**

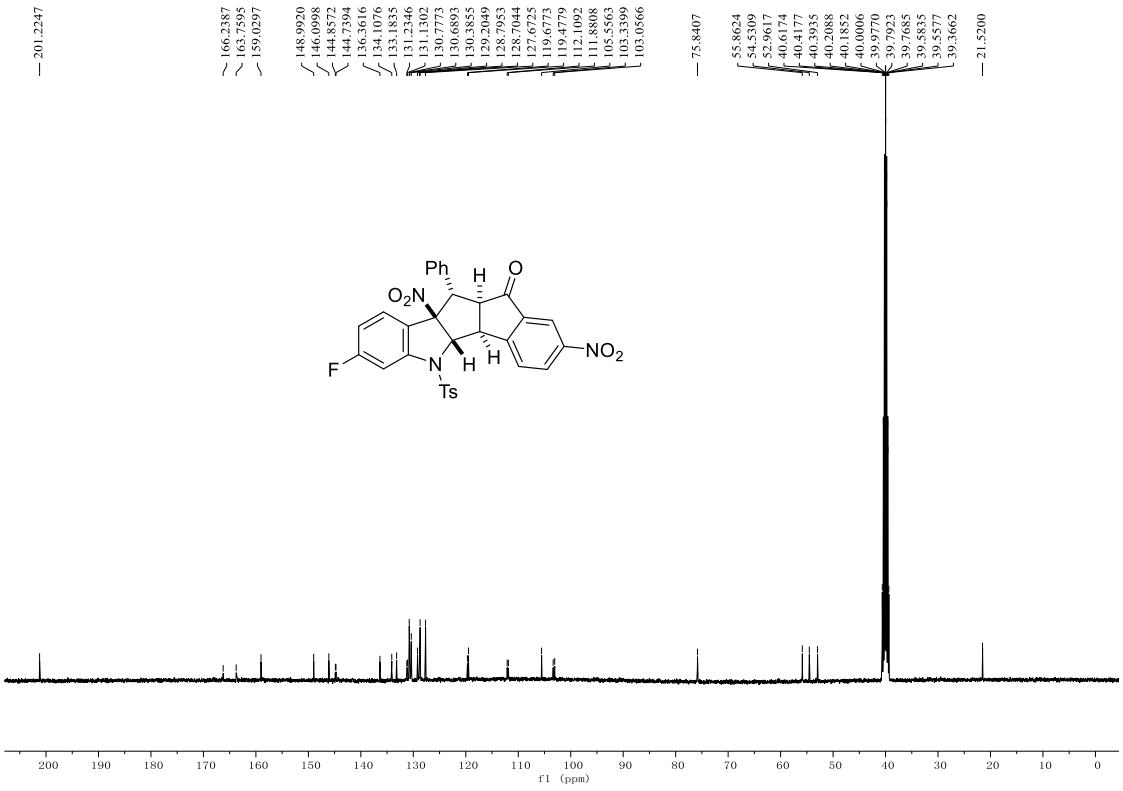


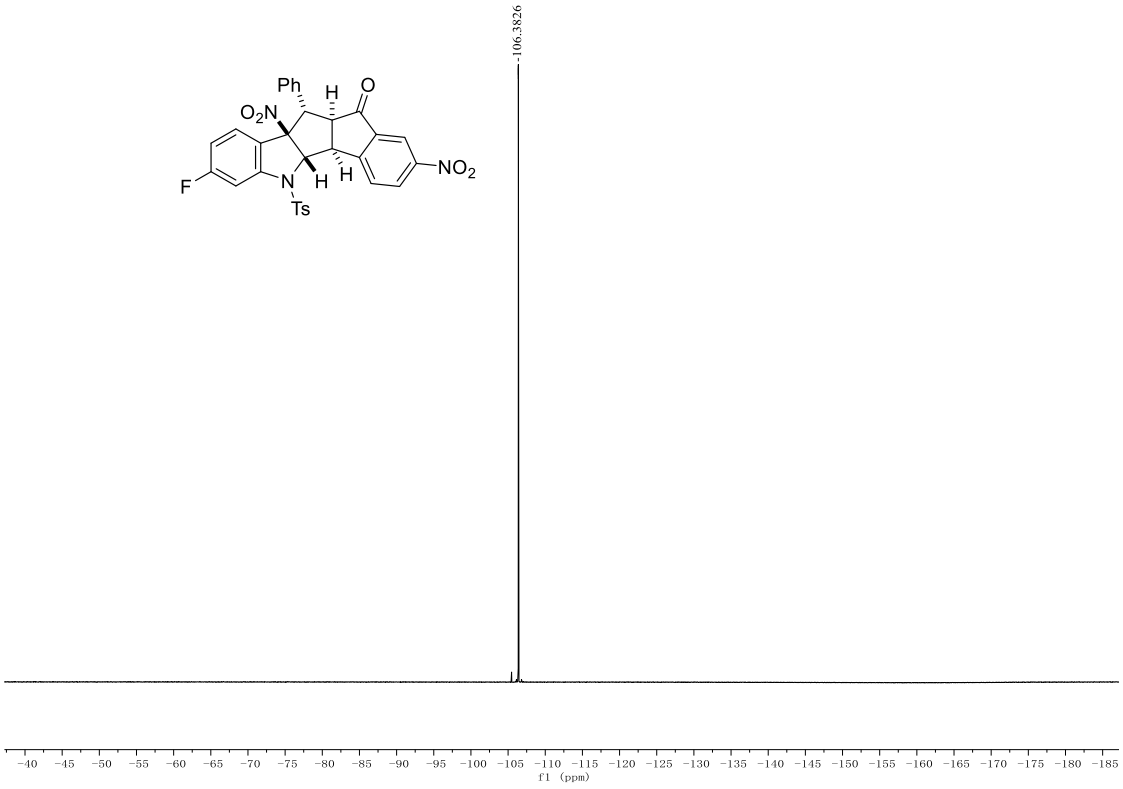



-117.6031
Ph
H
O
O2N
F
NO2
N
H
H
Ts
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
f1 (ppm)

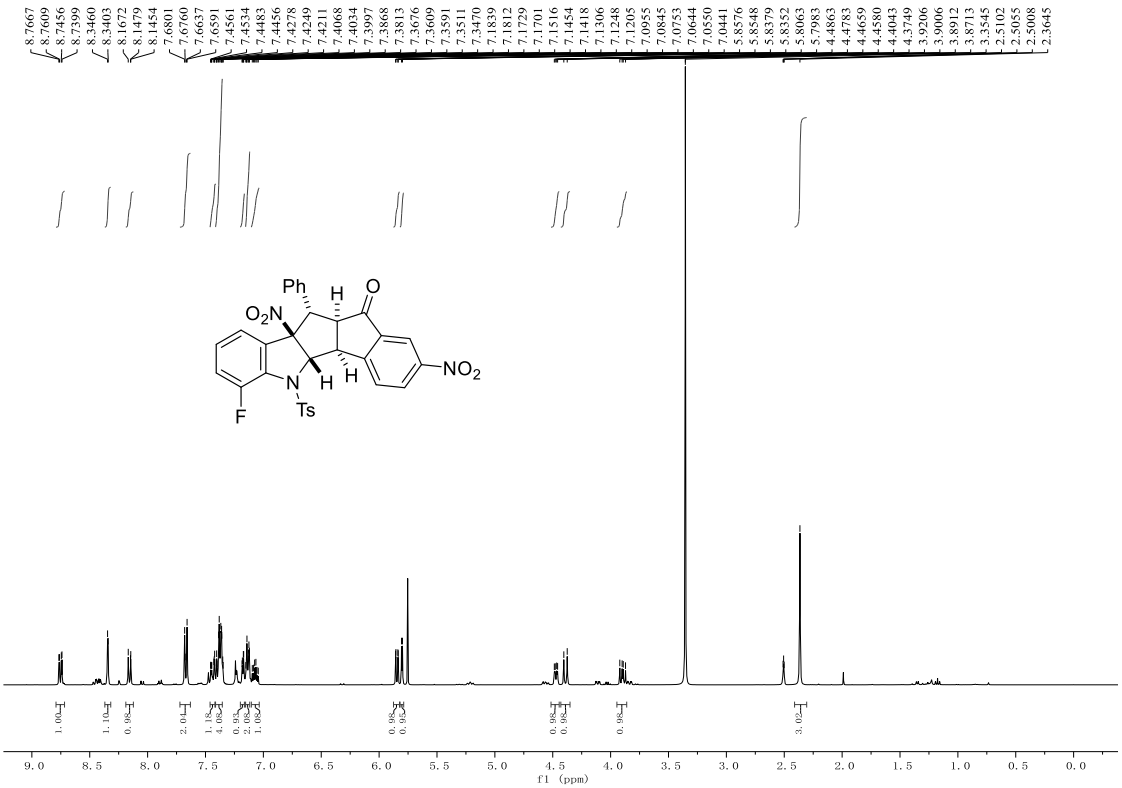
^{1}H, ^{13}C and ^{19}F NMR of **3ca**

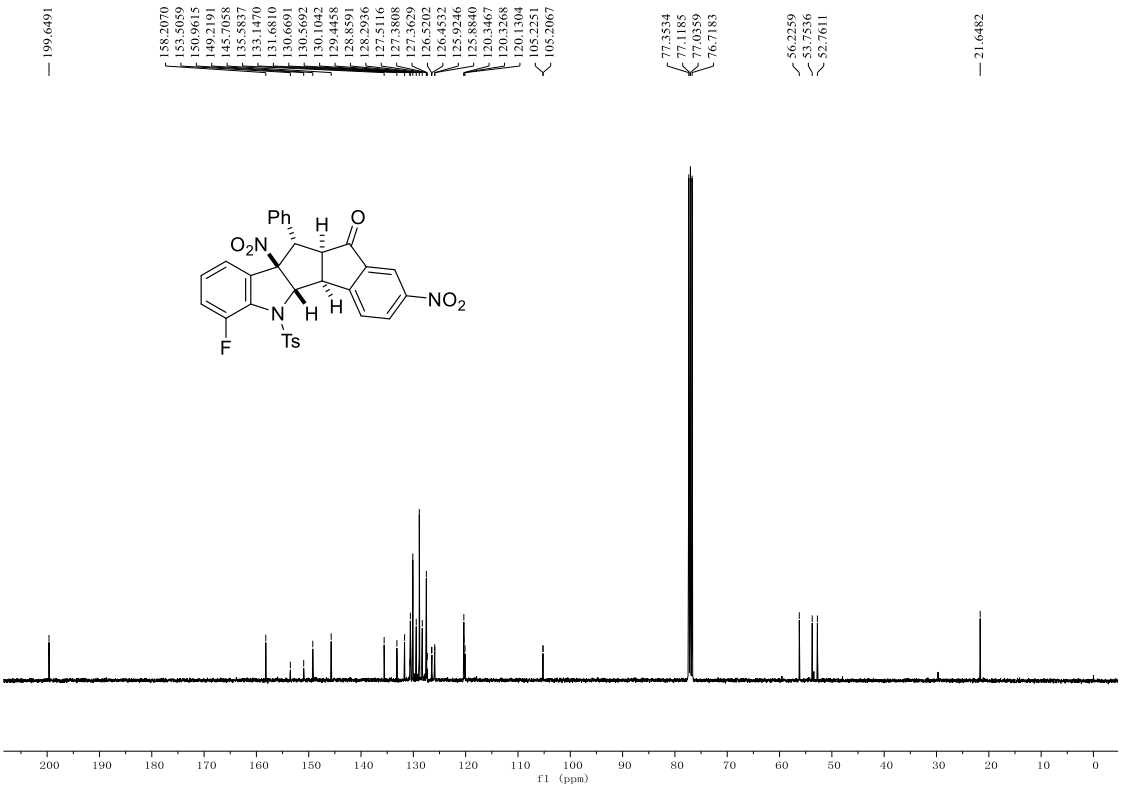


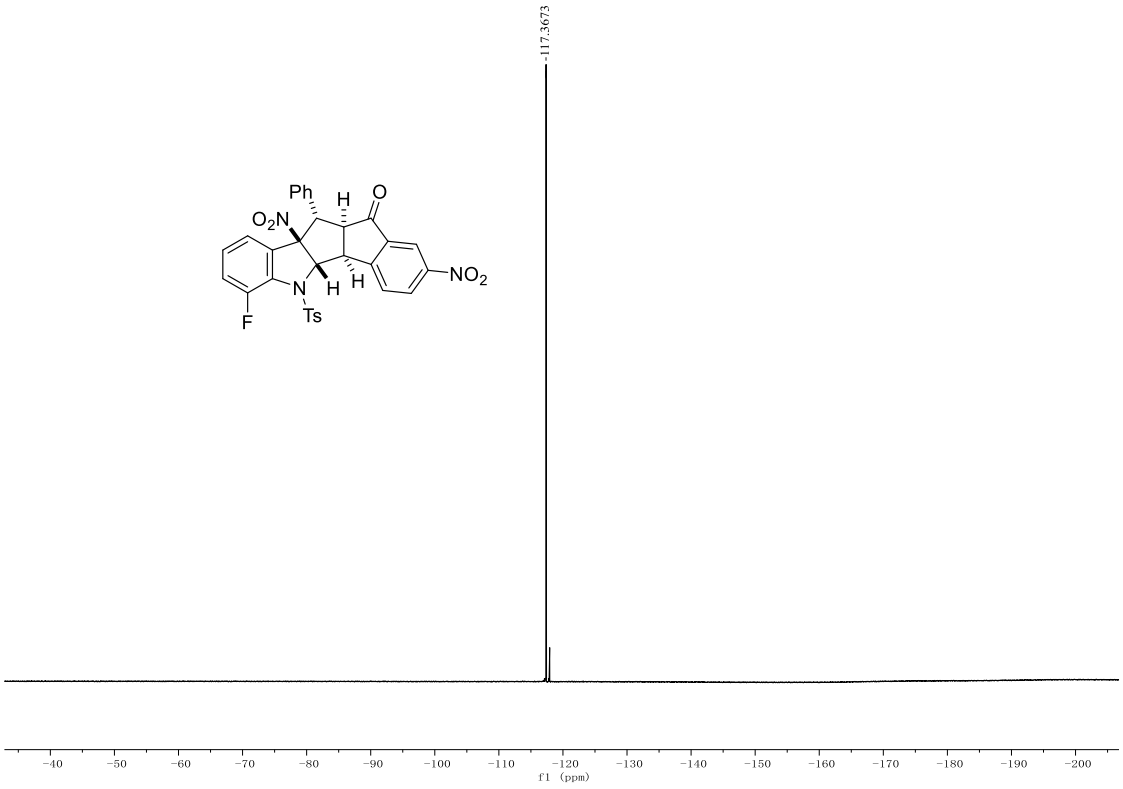



-106.3826
Ph
H
O
O2N
F
N
H
H
NO2
Ts
−40 −45 −50 −55 −60 −65 −70 −75 −80 −85 −90 −95 −100 −105 −110 −115 −120 −125 −130 −135 −140 −145 −150 −155 −160 −165 −170 −175 −180 −185
f1 (ppm)

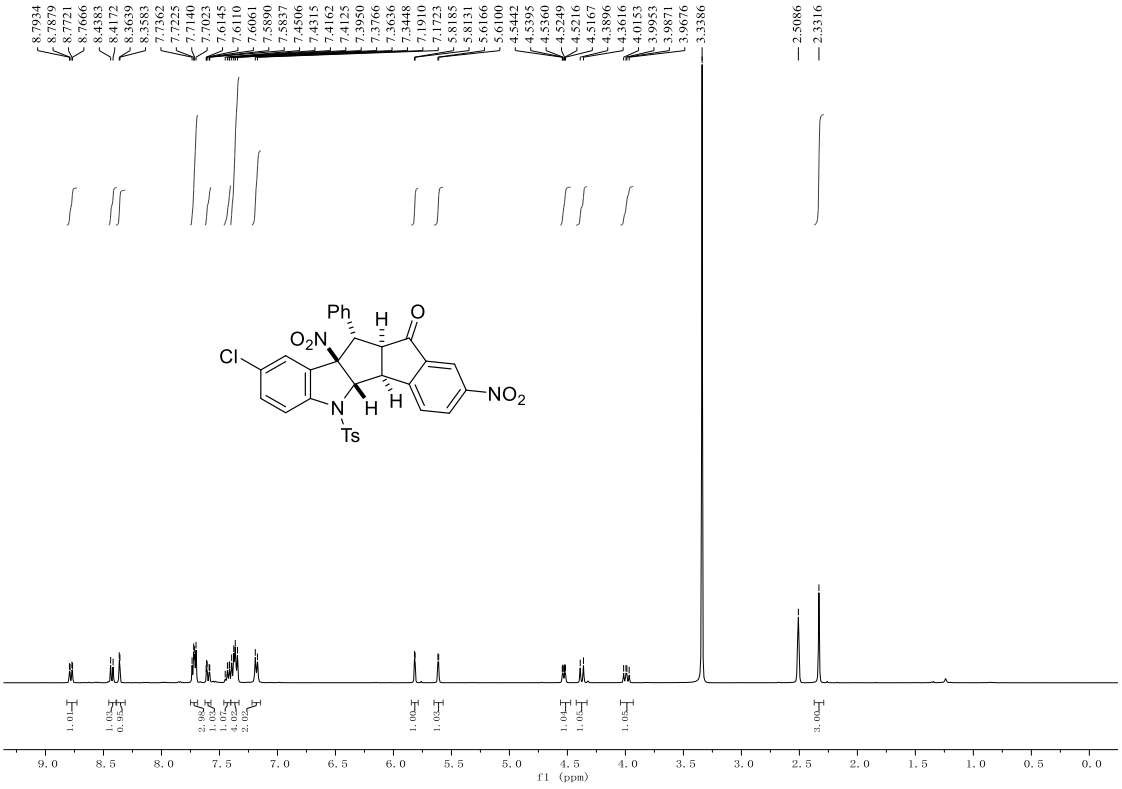
^{1}H, ^{13}C and ^{19}F NMR of **3da**

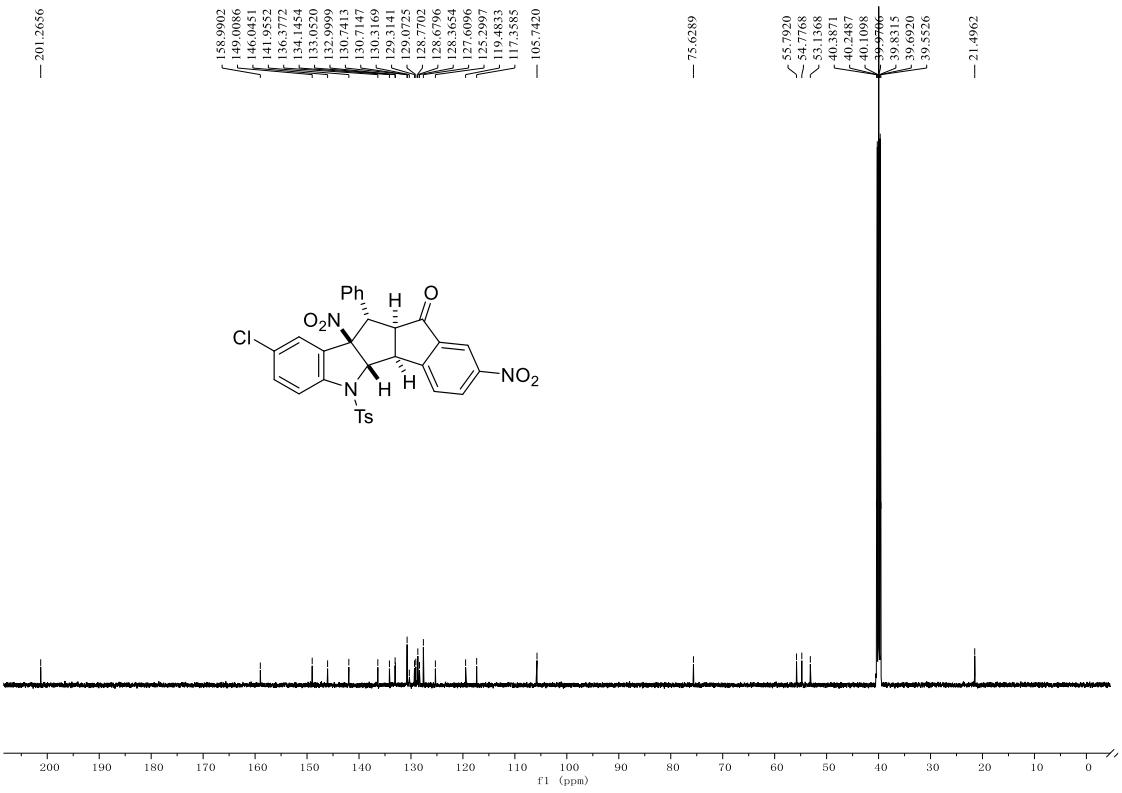




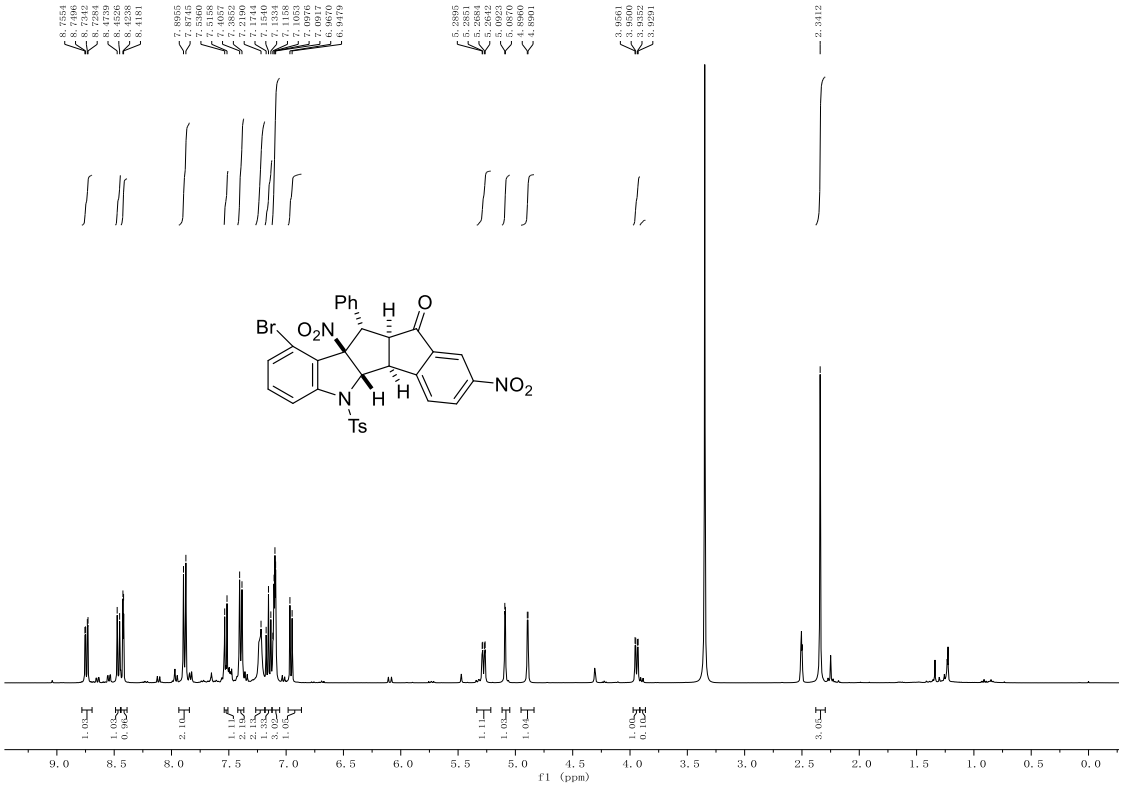

-117.3673
Ph
H
O
O2N
NO2
N
H
H
Ts
F
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

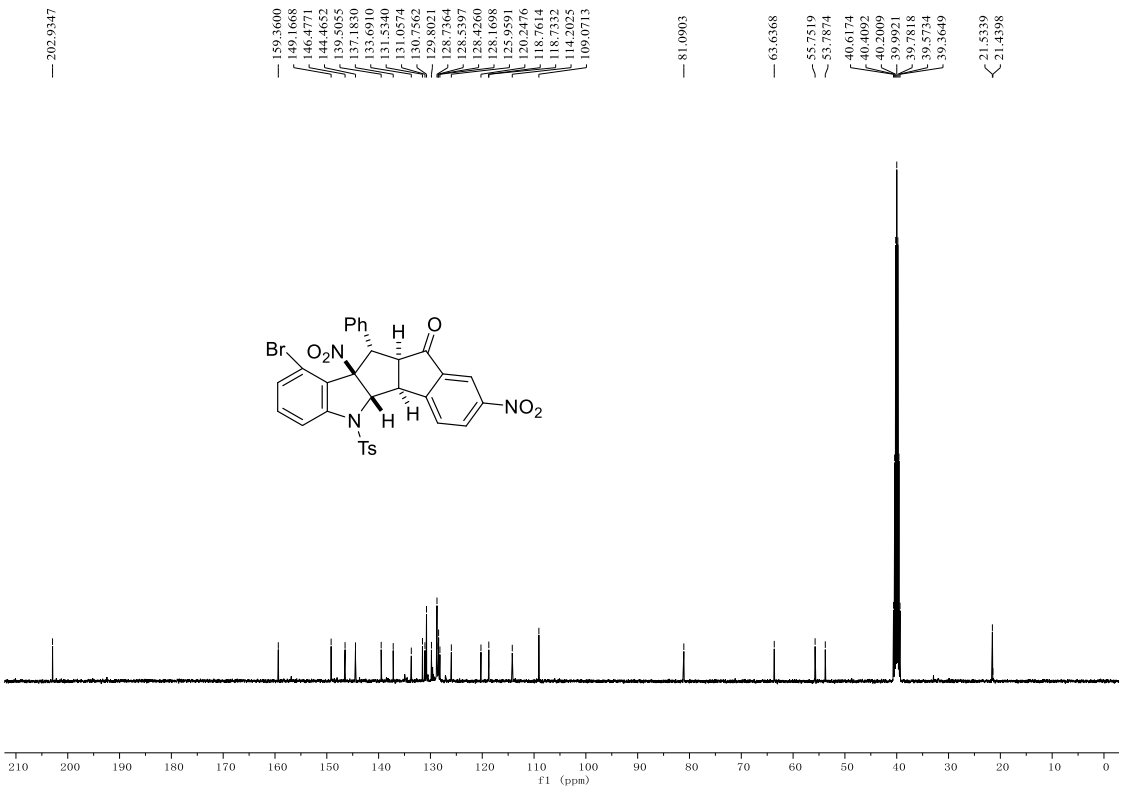
^{1}H and ^{13}C NMR of **3ea**



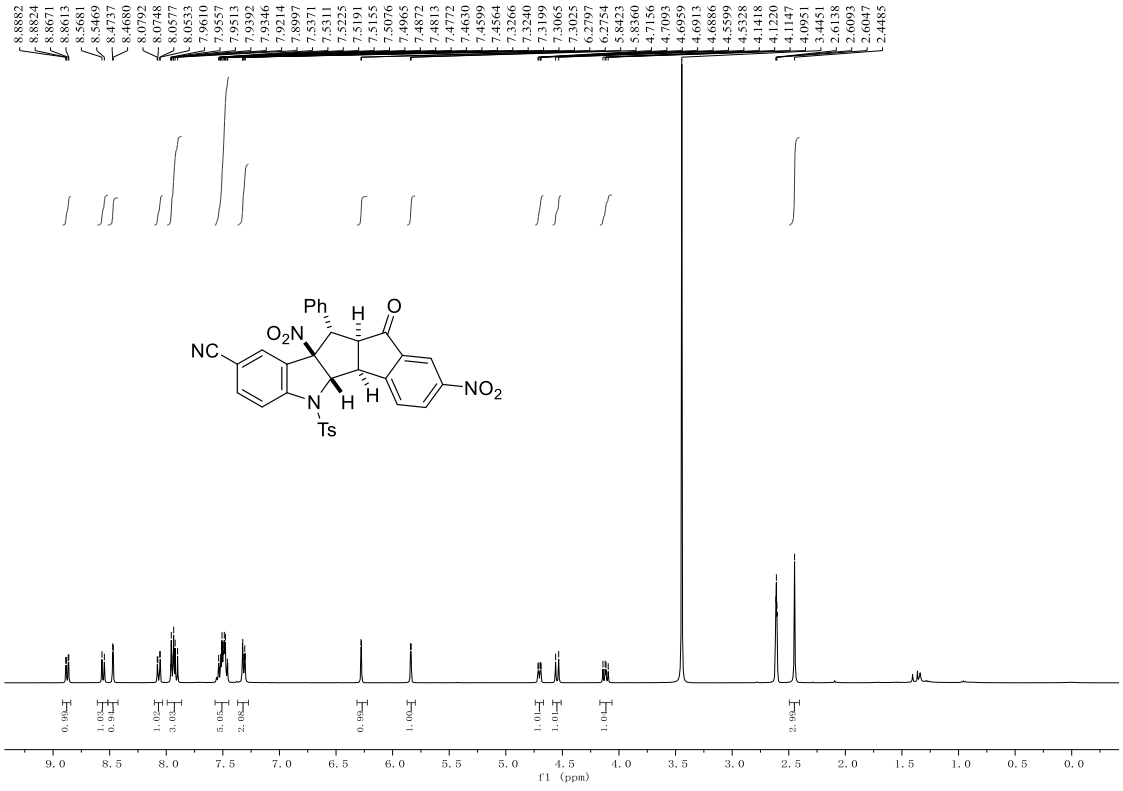


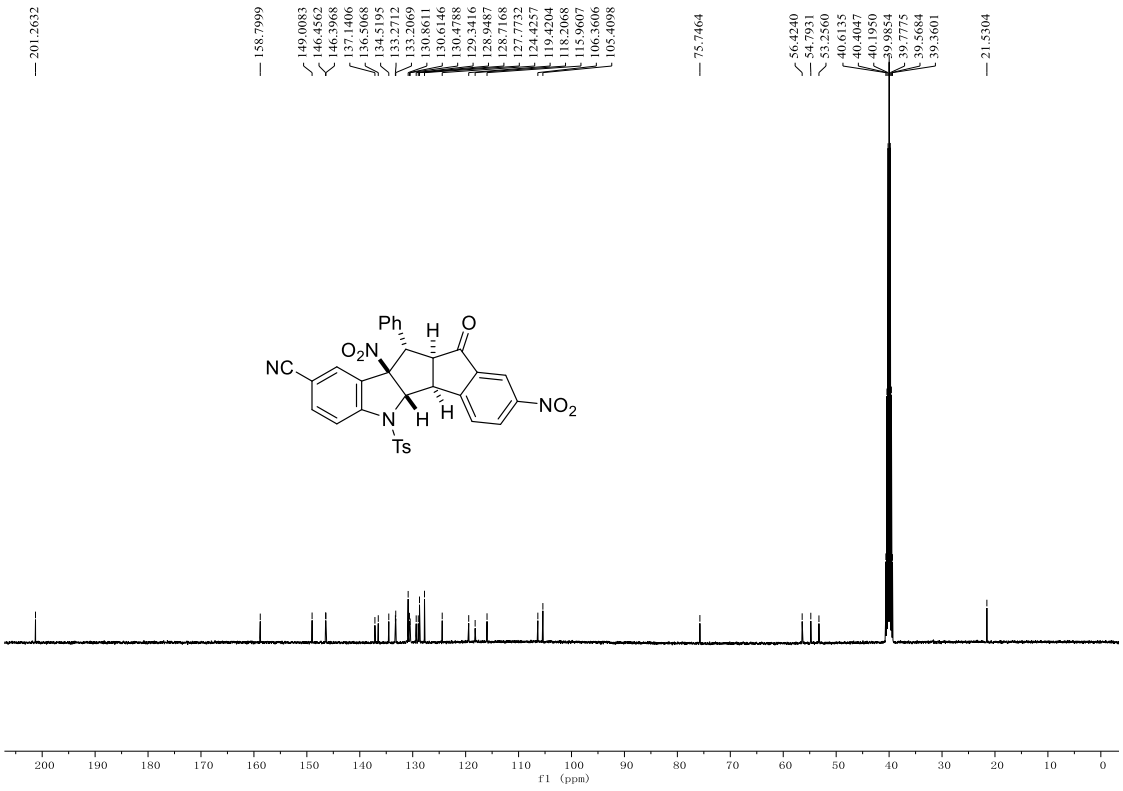
^{1}H and ^{13}C NMR of **3fa**



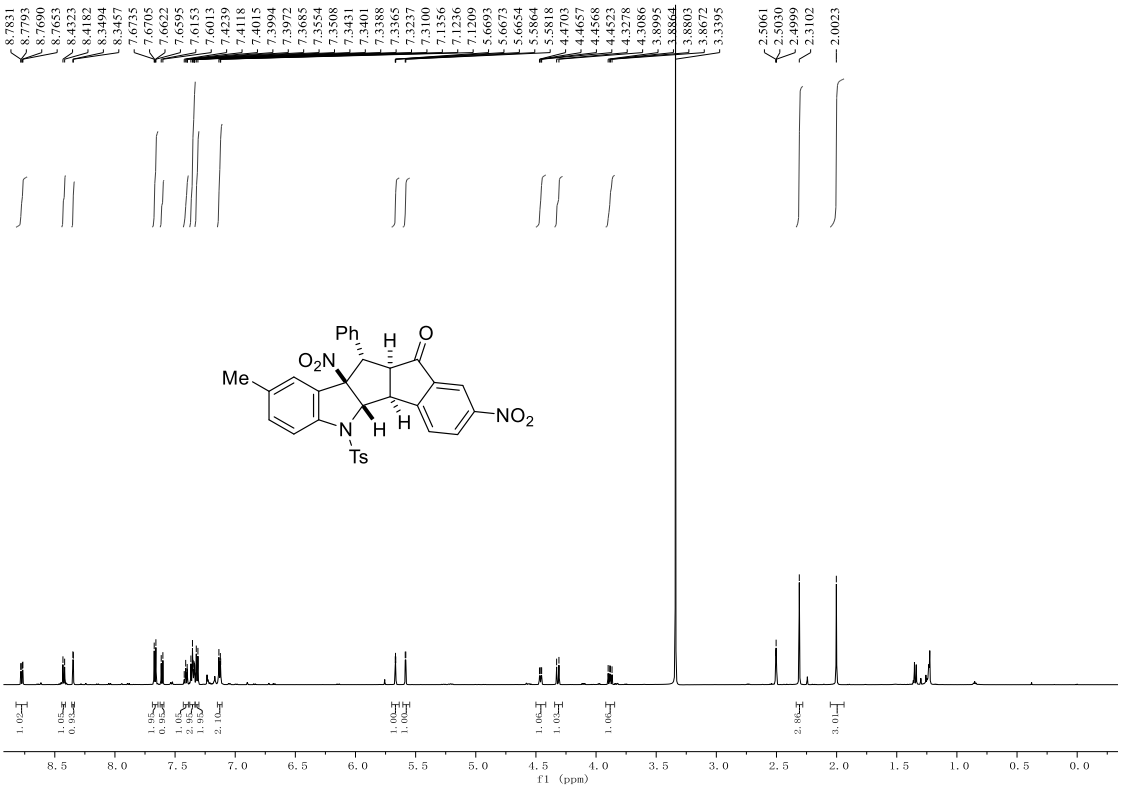


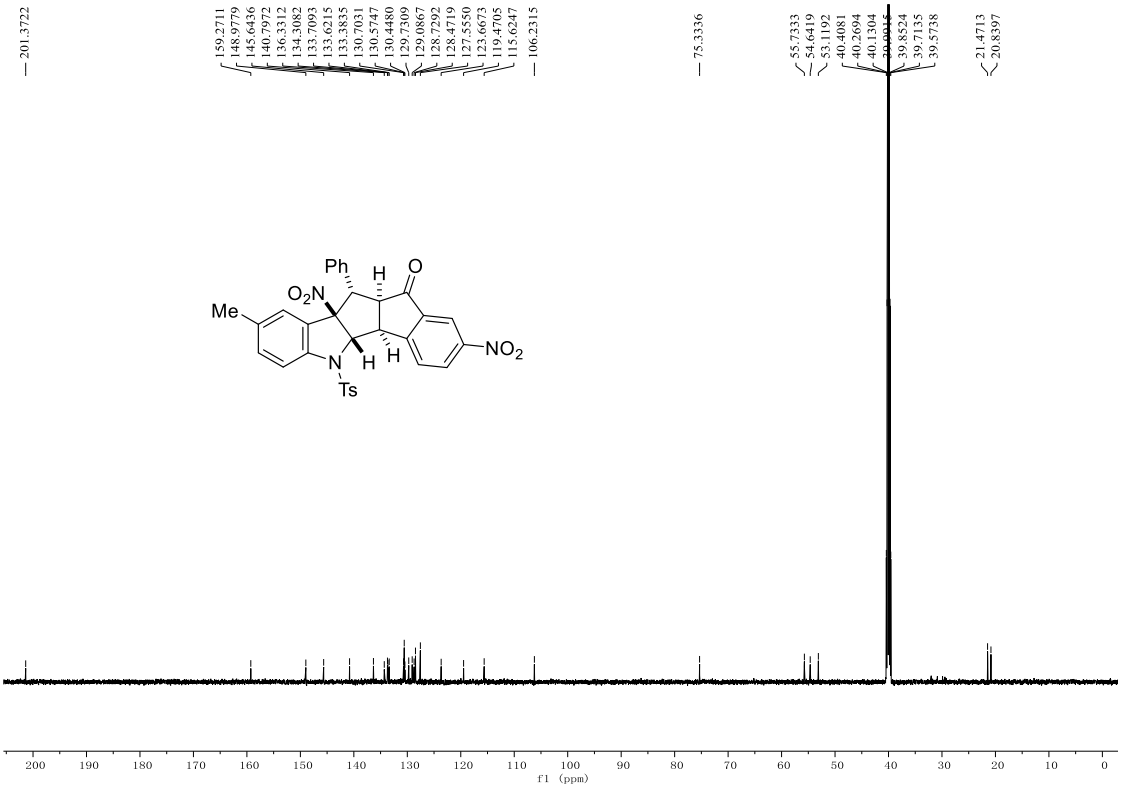
^{1}H and ^{13}C NMR of **3ga**



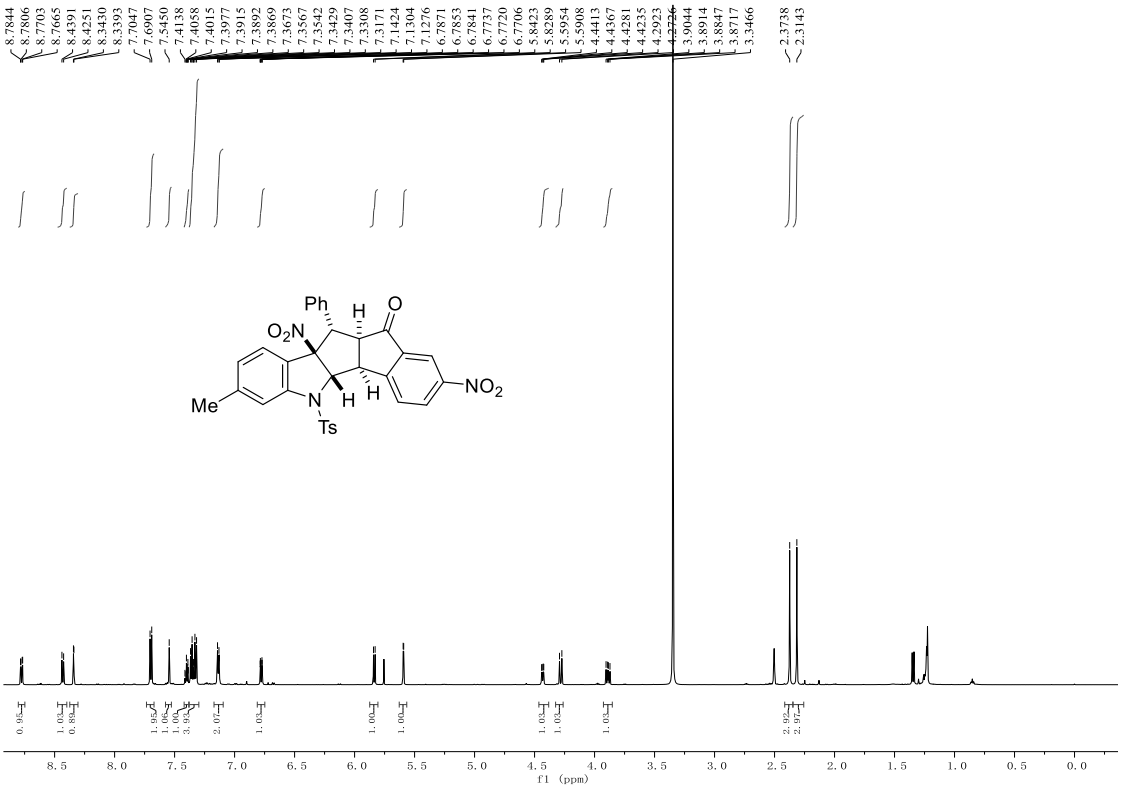


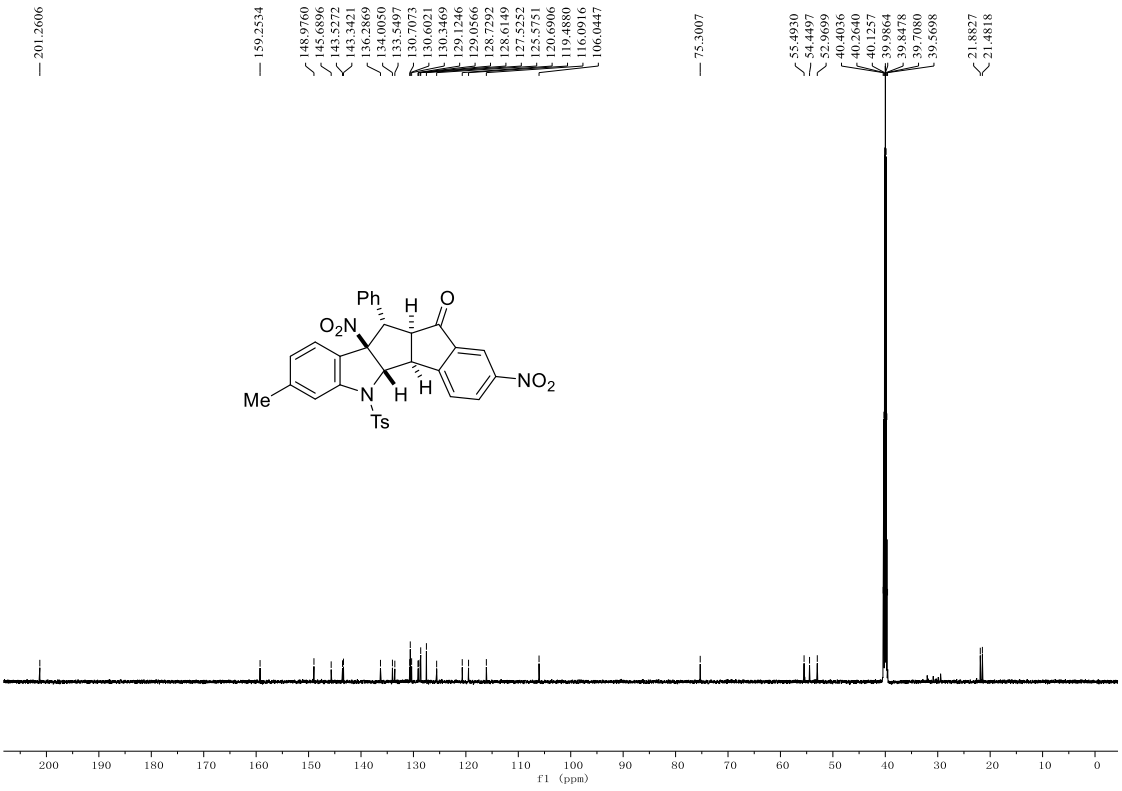
^{1}H and ^{13}C NMR of **3ha**



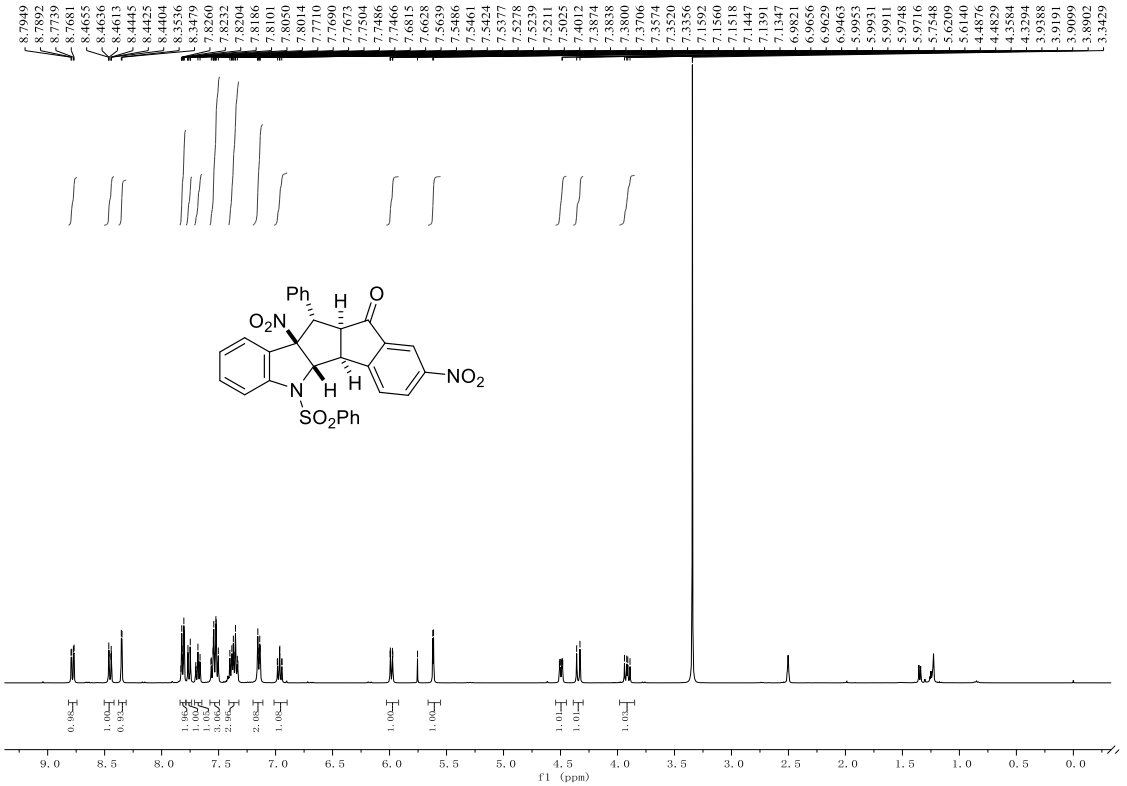


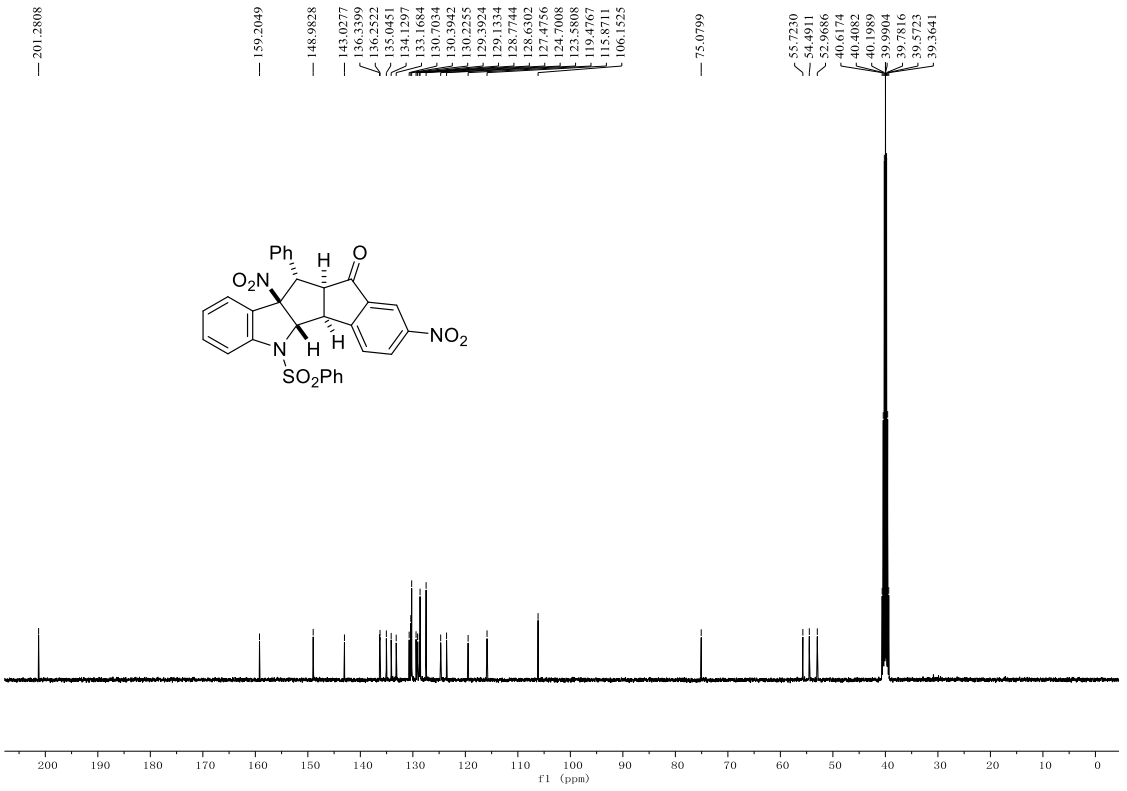
^{1}H and ^{13}C NMR of **3ia**



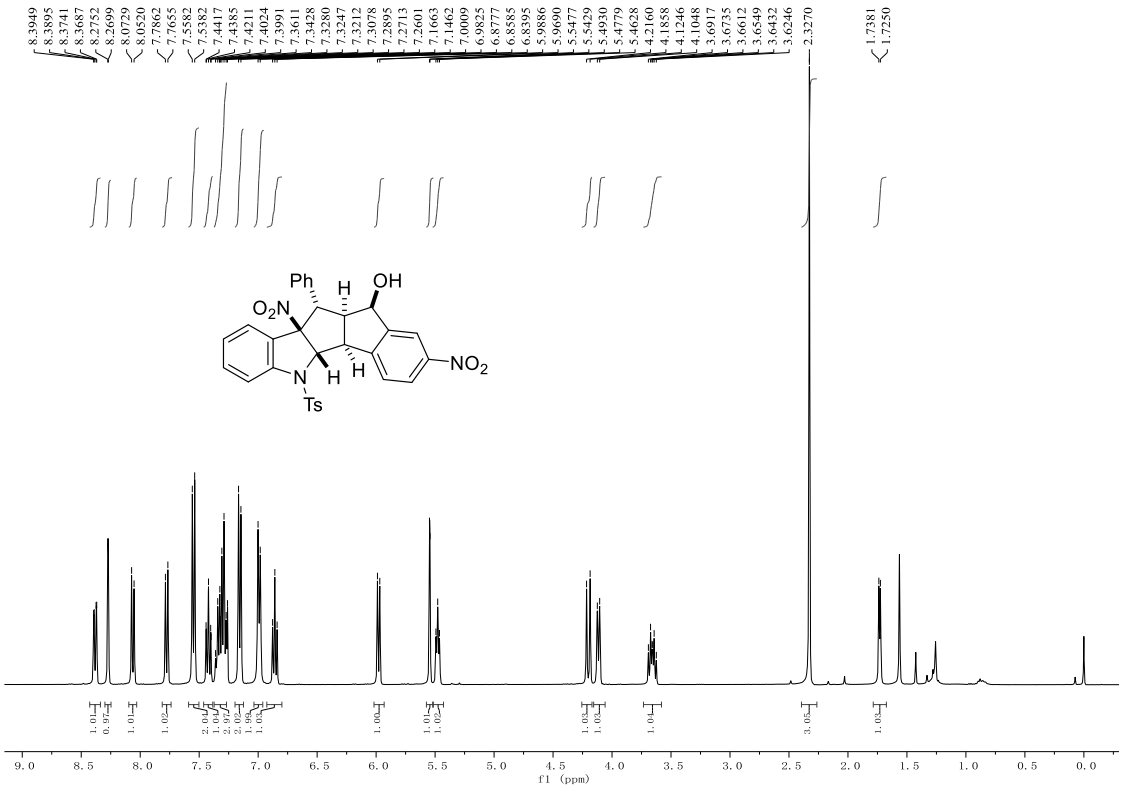


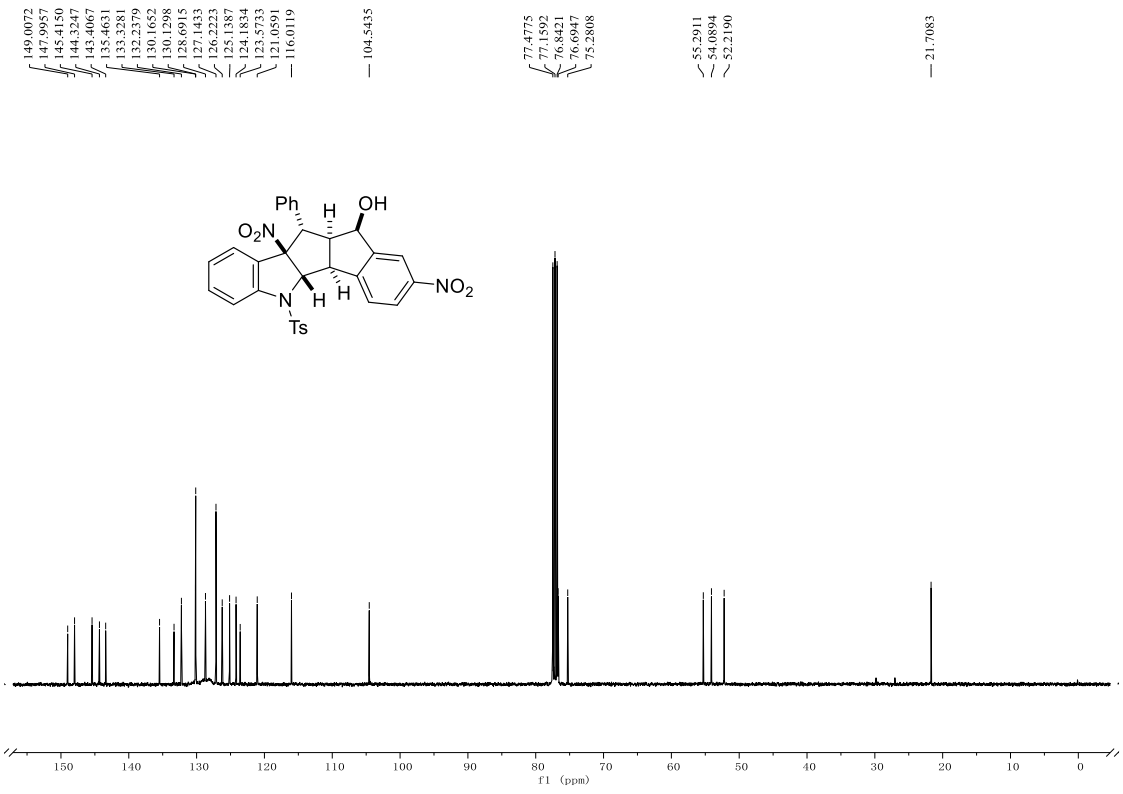
^{1}H and ^{13}C NMR of **3ja**

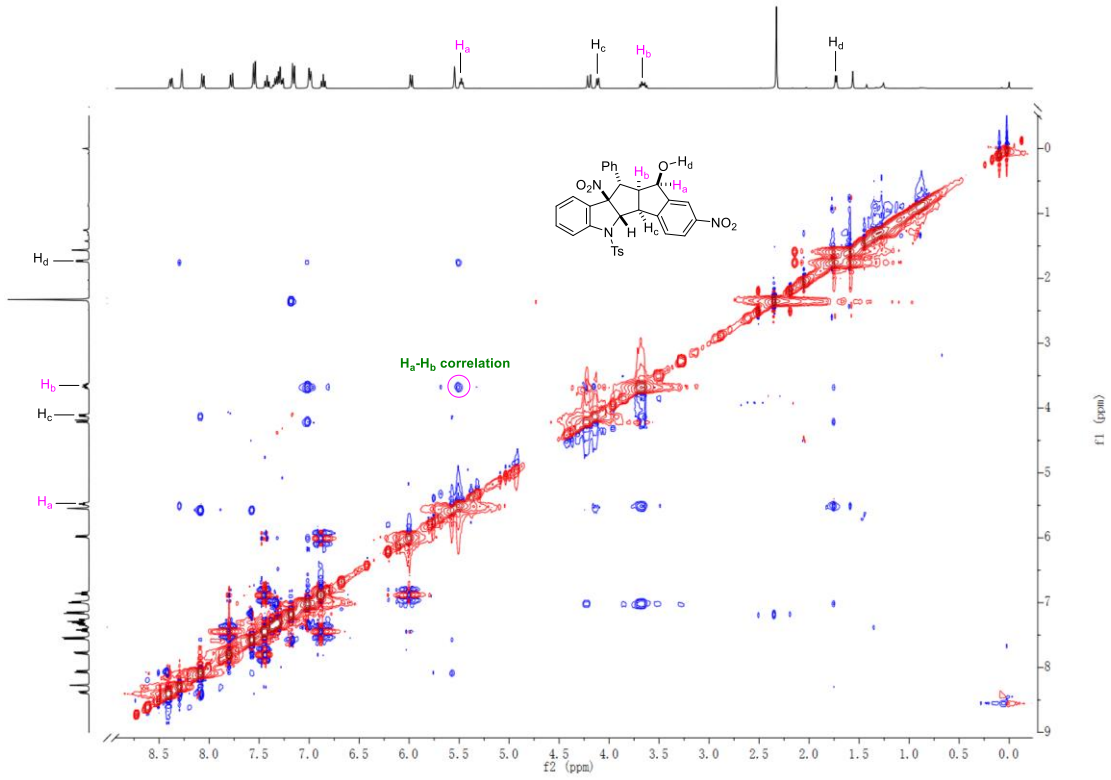




^{1}H, ^{13}C and NOESY (H-H) NMR of **4**






Ha
Hc
Hb
Hd
Ph
O2N
O
Hd
Hb
Ha
NO2
N
H
Hc
Ts
Ha-Hb correlation
f2 (ppm)
f1 (ppm)

^{1}H and ^{13}C NMR of **5**