Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Visible-Light-Induced, Catalyst and Additive-Free Cycloaddition of Vinylcyclopropanes: Access to Sulfur-Containing Seven-Membered Heterocycles

Xiaozhou Huang,[a,c] Rui Wang,[a,c] Cen Zhou,*[b] Rong Gao,[a] Haowen Zhang,[a] Ying Zheng,*[a] and Xiao Zhang*[a]

[a] Fujian Key Laboratory of Polymer Science, Fujian Provincial Key Laboratory of Advanced Materials Oriented Chemical Engineering, College of Chemistry and Materials Science, Fujian Normal University, 8 Shangsan Lu, Fuzhou 350007, China. E-mail: zyingth@sina.com; zhangxiao@fjnu.edu.cn

[b] Fujian Engineering and Research Center of New Chinese Lacquer Materials, Ocean College, Minjiang University, Fuzhou 350108, China. E-mail: zhoucen@mju.edu.cn

[c] These authors contributed equally.

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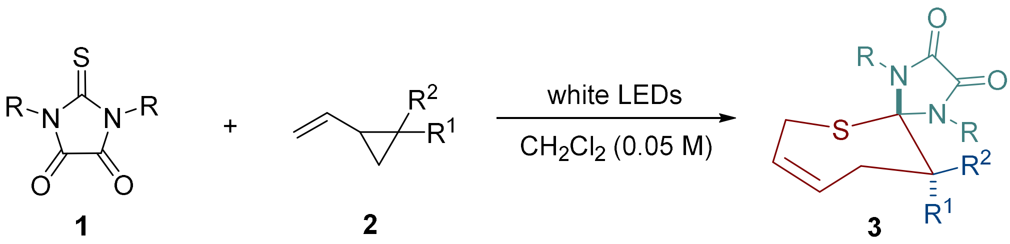
1. General methods

Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use.

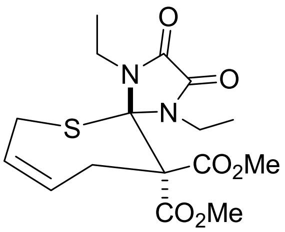
^{1}H and ^{13}C NMR spectra were recorded on a Bruker instrument (400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). HRMS were obtained on an Exactive Plus LC-MS (ESI) mass spectrometer with the use of quadrupole analyzer. Fourier Transform Infrared spectra were recorded on a Nicolet iS50 FT-IR spectrophotometer. Melting points (M.p.) were determined in open capillaries without further correction.

Substrates **1** and **2** were synthesized according to the literature procedures.[1,2] Solvents were purchased from Aladdin, and used without further purification.

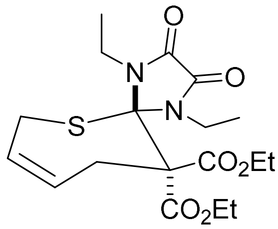
2. General Procedure for Visible-Light-Induced Cycloaddition of Vinylcyclopropanes



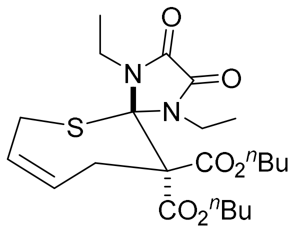
To a flame-dried sealed tube were added **1** (0.3 mmol, 1.0 equiv), **2** (0.6 mmol, 2 equiv), and CH_2Cl_2 (6 mL). The reaction mixture was degassed via freeze-pump-thaw for 3 cycles. After the reaction mixture was thoroughly degassed, the vial was sealed and positioned approximately 2~3 cm from 50 W white LEDs. Then the reaction mixture was stirred at room temperature for the indicated time (monitored by TLC) under nitrogen atmosphere. Afterwards, the reaction mixture was concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 3/1) to afford the desired products **3**. The analytical data of the products **3a**-**3v** are summarized below.



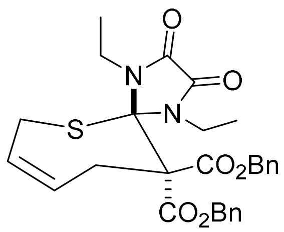
3a, yellow solid, 29.0 mg, 79% yield. m.p. = 125.9-127.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91-5.85 (m, 1H), 5.64-5.58 (m, 1H), 4.02-3.91 (m, 4H), 3.78-3.75 (m, 2H), 3.67 (s, 6H), 3.26-3.23 (m, 2H), 1.35 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 158.7, 128.2, 126.2, 89.0, 72.8, 53.1, 41.0, 33.1, 31.5, 13.5. IR (thin film): νmax (cm^{-1}) = 1732, 1417, 1350, 1275, 1222, 1191, 1118, 1015, 962, 920, 886, 753, 630, 562, 523. HRMS (ESI) calcd for $C_{16}H_{23}N_2O_6S$ [M+H]$^+$: 371.1277. Found: 371.1260.



3b, yellow solid, 64.8 mg, 54% yield. m.p. = 102.8-106.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90-5.84 (m, 1H), 5.64-5.58 (m, 1H), 4.18-4.06 (m, 4H), 3.97 (q, *J* = 7.2 Hz, 4H), 3.79-3.76 (m, 2H), 3.26-3.23 (m, 2H), 1.35 (t, *J* = 7.2 Hz, 6H), 1.21 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 158.8, 128.3, 126.4, 89.1, 73.0, 62.5, 41.2, 33.1, 31.6, 13.7, 13.5. IR (thin film): νmax (cm^{-1}) = 1732, 1441, 1412, 1348, 1294, 1224, 1182, 1089, 1021, 883, 858, 753, 665, 642, 579, 528. HRMS (ESI) calcd for $C_{18}H_{27}N_2O_6S$ $[M+H]^+$: 399.1590 . Found: 399.1576.

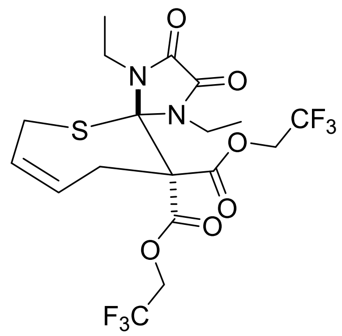


3c, yellow oil, 68 mg, 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89-5.84 (m, 1H), 5.63-5.57 (m, 1H), 4.13-4.07 (m, 2H), 4.01-3.94 (m, 6H), 3.78-3.76 (m, 2H), 3.26-3.24 (m, 2H), 1.59-1.51 (m, 4H), 1.37-1.25 (m, 10H), 0.90 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 158.8, 128.3, 126.3, 89.1, 73.1, 66.2, 41.1, 33.1, 31.6, 29.9, 18.8, 13.5, 13.4. IR (thin film): νmax (cm^{-1}) = 2960, 1736, 1412, 1276, 1218, 1179, 1067, 932, 731, 642, 523. HRMS (ESI) calcd for $C_{22}H_{35}N_2O_6S$ $[M+H]^+$: 455.2216. Found: 455.2211.

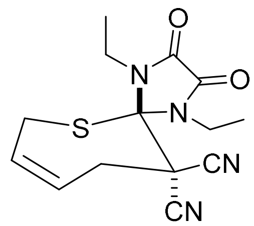


3d, yellow solid, 101.7 mg, 65% yield. m.p. = 142.0-144.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.25 (m, 6H), 7.16-7.14 (m, 4H), 5.79-5.73 (m, 1H), 5.46-5.40 (m, 1H), 5.13 (d, *J* = 12.0 Hz, 2H), 4.79 (d, *J* = 12.8 Hz, 2H), 3.94 (q, *J* = 7.2 Hz, 4H), 3.71-3.69 (m, 2H), 3.24-3.21 (m, 2H), 1.29 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

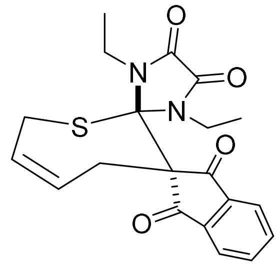
166.2, 158.8, 134.0, 128.64, 128.59, 128.4, 128.3, 126.3, 89.1, 72.9, 68.2, 41.2, 33.1, 31.5, 13.4. IR (thin film): νmax (cm^{-1}) = 1735, 1417, 1274, 1186, 1082, 940, 905, 865, 749, 732, 696, 649, 588, 526, 494, 422. HRMS (ESI) calcd for $C_{28}H_{31}N_2O_6S$ $[M+H]^+$: 523.1903. Found: 523.1891.



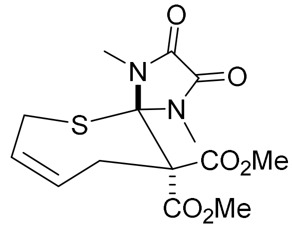
3e, yellow solid, 125.8 mg, 83% yield. m.p. = 121.4-123.2 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 5.94-5.88 (m, 1H), 5.66-5.60 (m, 1H), 4.73-4.64 (m, 2H), 4.26-4.17 (m, 2H), 3.98-3.92 (m, 4H), 3.79-3.76 (m, 2H), 3.34-3.32 (m, 2H), 1.36 (t, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 158.5, 128.9, 125.4, 123.4, 120.7, 88.8, 73.1, 62.0, 61.6, 61.3, 60.9, 41.4, 32.8, 31.7, 13.4. IR (thin film): νmax (cm^{-1}) = 1745, 1717, 1415, 1282, 1149, 1078, 1025, 962, 846, 756, 661, 550, 456. HRMS (ESI) calcd for $C_{18}H_{21}F_6N_2O_6S$ $[M+H]^+$: 507.1025. Found: 507.1008.



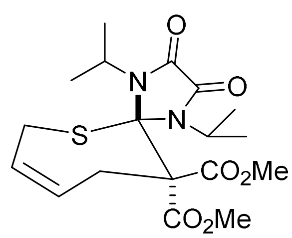
3f, brown solid, 39.7 mg, 43% yield. m.p. = 146.2-148.8 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 6.32-6.25 (m, 1H), 5.79-5.73 (m, 1H), 4.04-3.95 (m, 2H), 3.92-3.83 (m, 4H), 3.30-3.28 (m, 2H), 1.49 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 129.9, 124.8, 112.4, 86.2, 50.3, 40.3, 35.2, 28.8, 13.3. IR (thin film): νmax (cm^{-1}) = 2919, 1744, 1411, 1351, 1297, 1196, 1079, 899, 820, 567, 519. HRMS (ESI) calcd for $C_{14}H_{17}N_4O_2S$ $[M+H]^+$: 305.1072. Found: 305.1060.



3g, brown solid, 22.4 mg, 20% yield. m.p. = 125.1-128.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.87 (m, 4H), 6.25-6.19 (m, 1H), 5.63-5.57 (m, 1H), 4.10-4.07 (m, 2H), 3.69-3.50 (m, 4H), 2.73-2.71 (m, 2H), 1.29 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 157.6, 140.2, 136.9, 128.7, 127.3, 124.1, 88.5, 65.5, 40.0, 31.8, 29.1, 13.1. IR (thin film): νmax (cm^{-1}) = 2976, 1733, 1700, 1586, 1416, 1310, 1249, 1071, 900, 791, 750, 684, 637, 609, 521. HRMS (ESI) calcd for $C_{20}H_{21}N_2O_4S$ $[M+H]^+$: 385.1222. Found: 385.1208.

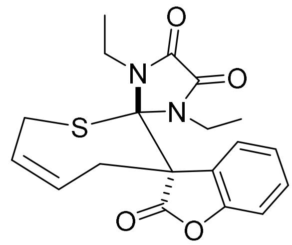


3i, ivory solid, 58.5 mg, 57% yield. m.p. = 185.8-188.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84-5.79 (m, 1H), 5.65-5.59 (m, 1H), 3.82-3.80 (m, 2H), 3.66 (s, 6H), 3.43 (s, 6H), 3.29-3.26 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 158.4, 128.3, 126.0, 88.9, 72.5, 53.2, 32.1, 31.7, 30.9. IR (thin film): νmax (cm^{-1}) = 2988, 1736, 1431, 1394, 1281, 1199, 1074, 999, 966, 895, 766, 666, 644, 562, 528. HRMS (ESI) calcd for $C_{14}H_{19}N_2O_6S$ $[M+H]^+$: 343.0964. Found: 343.0951.

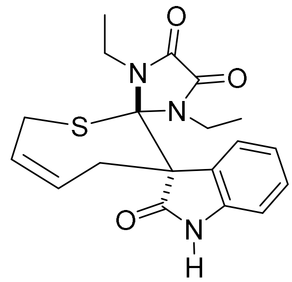


3j, yellow solid, 50.1 mg, 42% yield. m.p. = 133.3-134.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96-5.90 (m, 1H), 5.63-5.57 (m, 1H), 4.65 (s, 2H), 3.87-3.50 (m, 8H), 3.20 (s, 2H), 1.55 (d, *J* = 6.8 Hz, 6H), 1.45 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$)

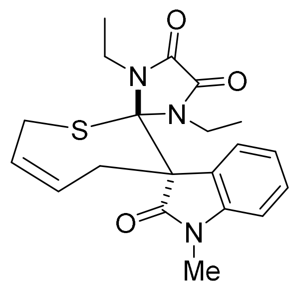
δ 167.1, 158.8, 128.8, 126.5, 90.2, 72.4, 53.3, 51.8, 32.6, 31.8, 20.7, 19.0. IR (thin film): νmax (cm^{-1}) = 2988, 1732, 1423, 1340, 1274, 1219, 1132, 1058, 866, 760, 643, 561. HRMS (ESI) calcd for $C_{18}H_{27}N_2O_6S$ $[M+H]^+$: 399.1590. Found: 399.1576.



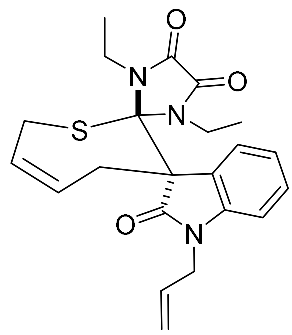
3k, brown solid, 62.6 mg, 56% yield. m.p. = 142.8-144.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.50 (m, 1H), 7.43-7.39 (m, 1H), 7.20-7.12 (m, 2H), 6.39-6.33 (m, 1H), 5.73-5.67 (m, 1H), 4.52-4.45 (m, 1H), 4.02-3.93 (m, 1H), 3.86-3.77 (m, 1H), 3.51-3.40 (m, 2H), 3.27-3.19 (m, 1H), 3.00-2.94 (m, 1H), 2.73-2.66 (m, 1H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 158.3, 157.2, 152.3, 130.8, 129.9, 127.6, 127.0, 126.7, 124.3, 111.1, 87.6, 59.3, 39.9, 39.9, 34.1, 28.8, 13.2, 12.9. IR (thin film): νmax (cm^{-1}) = 2988, 1797, 1736, 1461, 1412, 1285, 1231, 1131, 1072, 886, 757, 663, 603, 534, 490. HRMS (ESI) calcd for $C_{19}H_{21}N_2O_4S$ $[M+H]^+$: 373.1222. Found: 373.1208.



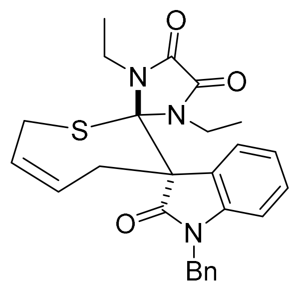
3l, yellow solid, 85.4 mg, 77% yield. m.p. = 168.7-169.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.32-7.27 (m, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.02-6.98 (m, 1H), 6.35-6.28 (m, 1H), 5.77-5.71 (m, 1H), 4.46-4.39 (m, 1H), 4.20-4.11 (m, 1H), 3.96-3.87 (m, 1H), 3.48-3.42 (m, 1H), 3.27-3.19 (m, 1H), 3.04-2.97 (m, 1H), 2.39-2.33 (m, 1H), 2.39-2.33 (m, 1H), 1.47 (t, *J* = 6.8 Hz, 3H), 1.01 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 158.4, 157.8, 140.6, 129.7, 129.2, 128.3, 127.5, 121.7, 111.2, 87.6, 59.4, 40.3, 39.1, 33.0, 28.8, 13.2, 13.0. IR (thin film): νmax (cm^{-1}) = 3675, 2988, 1737, 1701, 1616, 1448, 1413, 1349, 1302, 1211, 1077, 879, 758, 599, 521. HRMS (ESI) calcd for $C_{19}H_{22}N_3O_3S$ $[M+H]^+$: 372.1382. Found: 372.1368.



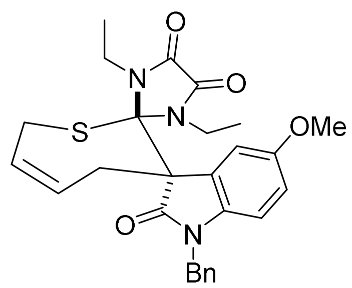
3m, yellow solid, 66.0 mg, 57% yield. 165.7-167.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.55 (m, 1H), 7.38-7.34 (m, 1H), 7.09-7.04 (m, 1H), 6.86-6.84 (m, 1H), 6.36-6.29 (m, 1H), 5.73-5.66 (m, 1H), 4.64-4.57 (m, 1H), 3.99-3.90 (m, 1H), 3.87-3.78 (m, 1H), 3.45-3.39 (m, 1H), 3.36-3.28 (m, 1H), 3.21-3.12 (m, 4H), 2.93-2.86 (m, 1H), 2.52-2.46 (m, 1H), 1.40 (t, *J* = 6.8 Hz, 3H), 1.11 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 158.4, 157.4, 142.7, 129.9, 129.3, 128.6, 128.0, 127.0, 122.4, 108.5, 87.8, 59.6, 39.8, 39.5, 33.5, 28.9, 26.4, 13.3, 13.1.IR (thin film): νmax (cm^{-1}) = 2986, 1704, 1608, 1414, 1349, 1301, 1081, 888, 780, 746, 697, 638, 575, 541, 523, 500. HRMS (ESI) calcd for $C_{20}H_{24}N_3O_3S$ $[M+H]^+$: 386.1538. Found: 386.1522.



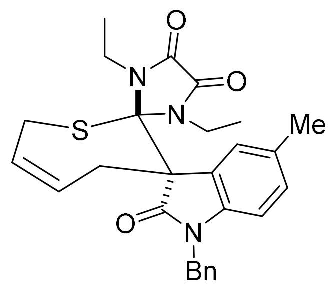
3n, yellow solid, 85.1 mg, 69% yield. 163.1-164.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.66 (m, 1H), 7.35-7.31 (m, 1H), 7.08-7.04 (m, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.36-6.30 (m, 1H), 5.77-5.67 (m, 2H), 5.27-5.22 (m, 2H), 4.55-4.49 (m, 1H), 4.40-4.34 (m, 1H), 4.19-4.14 (m, 1H), 4.13-4.02 (m, 1H), 3.90-3.82 (m, 1H), 3.46-3.40 (m, 1H), 3.25-3.16 (m, 1H), 3.02-2.91 (m, 2H), 2.42-2.36 (m, 1H), 1.44 (t, *J* = 7.2 Hz, 3H), 1.05 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 158.3, 157.5, 142.1, 130.6, 129.7, 129.5, 129.0, 128.1, 127.5, 122.3, 118.9, 109.4, 87.6, 59.2, 42.6, 40.2, 39.4, 33.4, 28.9, 13.4, 13.1. IR (thin film): νmax (cm^{-1}) = 2973, 1732, 1701, 1608, 1488, 1418, 1361, 1298, 1206, 1079, 881, 748, 633, 578, 521, 503. HRMS (ESI) calcd for $C_{22}H_{26}N_3O_3S$ $[M+H]^+$: 412.1695. Found: 412.1687.



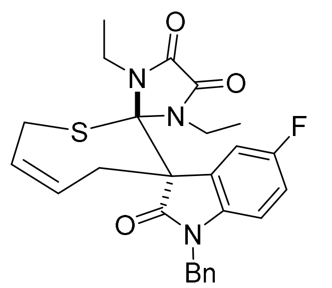
3o, yellow solid, 121.7 mg, 88% yield. 154.8-155.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.71 (m, 1H), 7.35-7.31 (m, 2H), 7.28-7.22 (m, 4H), 7.04-7.00 (m, 1H), 6.81-6.79 (m, 1H), 6.38-6.31 (m, 1H), 5.75-5.68 (m, 1H), 4.91 (d, *J* = 15.2 Hz, 1H), 4.72 (d, *J* = 15.2 Hz, 1H), 4.52-4.45 (m, 1H), 4.10-4.01 (m, 1H), 3.92-3.83 (m, 1H), 3.49-3.43 (m, 1H), 3.14 -3.03 (m, 2H), 2.93-2.85 (m, 1H), 2.39-2.32 (m, 1H), 1.45 (t, *J* = 6.8 Hz, 3H), 0.94 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 158.4, 157.4, 141.9, 134.9, 129.6, 129.5, 128.9, 128.8, 128.0, 127.8, 127.6, 122.2, 109.4, 87.5, 58.9, 44.0, 40.2, 39.4, 33.6, 28.8, 13.1, 13.0. IR (thin film): νmax (cm^{-1}) = 2988, 1739, 1702, 1608, 1413, 1347, 1296, 1078, 879, 749, 697, 551, 520, 457. HRMS (ESI) calcd for $C_{26}H_{27}N_3O_3SNa$ $[M+Na]^+$: 484.1671. Found: 484.1655.



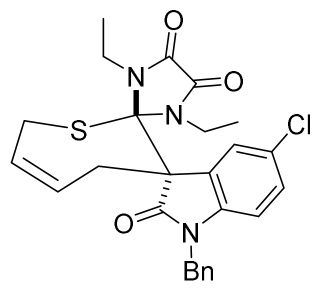
3p, orange solid, 53.7 mg, 36% yield. 176.7-177.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.22 (m, 6H), 6.78-6.75 (m, 1H), 6.69 (d, *J* = 8.4 Hz, 1H), 6.37-6.30 (m, 1H), 5.76-5.69 (m, 1H), 4.87 (d, *J* = 15.2 Hz, 1H), 4.74-4.70 (m, 1H), 4.50 (d, *J* = 16.0 Hz, 1H), 4.06-3.98 (m, 1H), 3.89-3.80 (m, 1H), 3.75 (s, 3H), 3.46-3.40 (m, 1H), 3.19-3.14 (m, 1H), 3.07-2.95 (m, 2H), 2.40-2.33 (m, 1H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.01-0.97 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 158.6, 157.5, 155.2, 135.4, 135.1, 129.6, 129.4, 128.9, 127.9, 127.7, 115.4, 113.5, 109.8, 87.6, 59.3, 55.8, 44.2, 40.2, 39.5, 33.9, 28.9, 13.2, 13.1.IR (thin film): νmax (cm^{-1}) = 2988, 1737, 1701, 1596, 1425, 1342, 1230, 1184, 1080, 971, 873, 812, 746, 699, 613, 519, 466. HRMS (ESI) calcd for $C_{27}H_{29}N_3O_4SNa$ $[M+Na]^+$: 514.1776. Found: 514.1758.



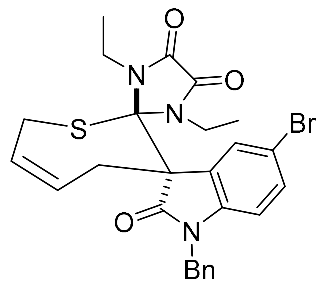
3q, orange solid, 94.7 mg, 66% yield. 158.8-161.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.35-7.31 (m, 2H), 7.25-7.22 (m, 3H), 7.05-7.03 (m, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.36-6.30 (m, 1H), 5.74-5.67 (m, 1H), 4.86-4.74 (m, 2H), 4.56 (d, *J* = 16.0 Hz, 1H), 3.98-3.89 (m, 1H), 3.85-3.77 (m, 1H), 3.46-3.40 (m, 1H), 3.27-3.19 (m, 1H), 3.10-2.94 (m, 2H), 2.45-2.39 (m, 1H), 2.30 (s, 3H), 1.40 (t, *J* = 6.8 Hz, 3H), 1.02 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 158.5, 157.5, 139.5, 135.1, 132.0, 129.9, 129.4, 128.9, 128.2, 128.0, 127.9, 127.7, 109.2, 87.7, 59.5, 44.1, 40.0, 39.6, 34.0, 28.9, 21.3, 13.2, 13.1. IR (thin film): νmax (cm^{-1}) = 2988, 1737, 1703, 1495, 1414, 1342, 1193, 1079, 879, 819, 743, 701, 579, 554, 521, 499, 419. HRMS (ESI) calcd for $C_{27}H_{29}N_3O_3SNa$ $[M+Na]^+$: 498.1827. Found: 498.1812.



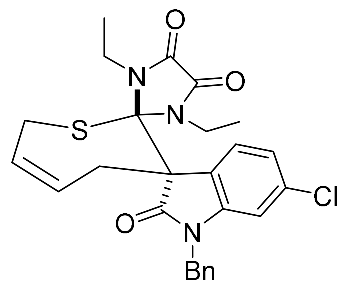
3r, yellow solid, 118.5 mg, 82% yield. 160.7-163.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.60 (m, 1H), 7.36-7.32 (m, 2H), 7.30-7.24 (m, 1H), 7.22-7.20 (m, 2H), 7.00-6.95 (m, 1H), 6.74-6.71 (m, 1H), 6.41-6.35 (m, 1H), 5.78-5.71 (m, 1H), 4.94 (d, *J* = 15.6 Hz, 1H), 4.66 (d, *J* = 15.2 Hz, 1H), 4.41-4.34 (m, 1H), 4.24-4.15 (m, 1H), 3.96-3.87 (m, 1H), 3.53-3.45 (m, 1H), 3.19-3.13 (m, 1H), 3.03-2.94 (m, 1H), 2.77-2.69 (m, 1H), 2.28-2.21 (m, 1H), 1.50 (t, *J* = 6.8 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 159.3, 158.3, 157.5, 156.9, 138.1, 134.7, 130.0, 129.5, 129.4, 129.0, 128.9, 128.0, 127.6, 116.3, 116.1, 116.0, 115.9, 110.0, 110.0, 87.0, 58.7, 44.2, 40.5, 39.3, 33.2, 28.7, 13.2, 13.0. IR (thin film): νmax (cm^{-1}) = 2988, 1737, 1703, 1489, 1414, 1341, 1271, 1177, 1075, 970, 866, 820, 750, 701, 557, 522. HRMS (ESI) calcd for $C_{26}H_{27}FN_3O_3S$ $[M+H]^+$: 480.1757. Found: 480.1739.



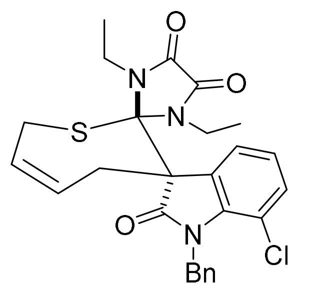
3s, yellow solid, 37.0 mg, 25% yield. 155.3-158.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 2.0 Hz, 1H), 7.36-7.31 (m, 2H), 7.30-7.24 (m, 1H), 7.23-7.18 (m, 2H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.42-6.36 (m, 1H), 5.78-5.71 (m, 1H), 4.92 (d, *J* = 15.2 Hz, 1H), 4.68 (d, *J* = 15.2 Hz, 1H), 4.40-4.34 (m, 1H), 4.24-4.15 (m, 1H), 3.95-3.86 (m, 1H), 3.52-3.46 (m, 1H), 3.19-3.12 (m, 1H), 3.03-2.95 (m, 1H), 2.79-2.70 (m, 1H), 2.27-2.21 (m, 1H), 1.70 (s, 1H), 1.50 (t, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 158.3, 157.5, 140.8, 134.6, 130.2, 129.7, 129.6, 129.1, 128.9, 128.2, 128.1, 127.6, 110.5, 87.1, 58.8, 44.3, 40.6, 39.6, 33.3, 28.8, 13.3, 13.1. IR (thin film): νmax (cm^{-1}) = 2988, 1737, 1706, 1608, 1425, 1337, 1078, 872, 822, 744, 701, 665, 550, 520, 465. HRMS (ESI) calcd for $C_{26}H_{27}ClN_3O_3S$ $[M+H]^+$: 496.1462. Found: 496.1446.



3t, orange solid, 47.4 mg, 29% yield. 154.5-158.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 2.0 Hz, 1H), 7.40-7.32 (m, 3H), 7.20-7.18 (m, 2H), 6.67 (d, *J* = 8.4 Hz, 1H), 6.42-6.35 (m, 1H), 5.78-5.72 (m, 1H), 4.91 (d, *J* = 15.6 Hz, 1H), 4.67 (d, *J* = 15.6 Hz, 1H), 4.37 (d, *J* = 18.0 Hz, 1H), 4.24-4.15 (m, 1H), 3.95-3.86 (m, 1H), 3.53-3.46 (m, 1H), 3.18-3.12 (m, 1H), 3.03-2.95 (m, 1H), 2.80-2.71 (m, 1H), 2.27-2.21 (m, 1H), 1.70 (s, 1H), 1.50 (t, *J* = 6.8 Hz, 3H), 0.92 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 158.3, 157.5, 141.2, 134.5, 132.5, 130.9, 130.2, 129.1, 128.9, 128.1, 127.6, 114.9, 111.0, 87.1, 58.8, 44.2, 40.6, 39.6, 33.3, 28.7, 13.3, 13.1. IR (thin film): νmax (cm^{-1}) = 2988, 1736, 1705, 1603, 1415, 1334, 1077, 962, 871, 803, 746, 706, 664, 557, 535, 495. HRMS (ESI) calcd for $C_{26}H_{26}{}^{81}BrN_3O_3SNa$ $[M+Na]^+$: 564.0755. Found: 564.0737.



3u, yellow solid, 141.0 mg, 95% yield. 166.8-168.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.38-7.33 (m, 2H), 7.30-7.26 (m, 1H), 7.23-7.21 (m, 2H), 7.02-6.99 (m, 1H), 6.79 (d, *J* = 2.0 Hz, 1H), 6.39-6.32 (m, 1H), 5.74-5.67 (m, 1H), 4.92 (d, *J* = 15.6 Hz, 1H), 4.65 (d, *J* = 15.2 Hz, 1H), 4.43-4.39 (m, 1H), 4.14-4.05 (m, 1H), 3.91-3.87 (m, 1H), 3.52-3.45 (m, 1H), 3.11-3.02 (m, 2H), 2.87-2.79 (m, 1H), 2.31-2.25 (m, 1H), 1.46 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 158.2, 157.4, 143.1, 135.5, 134.3, 129.8, 129.0, 128.7, 128.6, 128.0, 127.5, 126.4, 122.1, 109.9, 87.1, 58.5, 44.1, 40.3, 39.4, 33.4, 28.7, 13.1, 12.9. IR (thin film): νmax (cm^{-1}) = 3675, 2988, 1740, 1713, 1602, 1412, 1338, 1251, 1077, 881, 703, 561, 523, 457. HRMS (ESI) calcd for $C_{26}H_{27}ClN_3O_3S$ $[M+H]^+$: 496.1462. Found: 496.1443.



3v, yellow oil, 132.8 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.2 Hz, 1H), 7.32-7.22 (m, 4H), 7.16 (d, *J* = 7.2 Hz, 2H), 6.99 (t, *J* = 8.0 Hz, 1H), 6.37-6.30 (m, 1H), 5.73-5.67 (m, 1H), 5.33-5.25 (m, 2H), 4.50 (d, *J* = 16.8 Hz, 1H), 4.03-3.94 (m, 1H), 3.82-3.74 (m, 1H), 3.48-3.42 (m, 1H), 3.35-3.27 (m, 1H), 3.10-2.97 (m, 2H), 2.45-2.39 (m, 1H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.06 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 158.4, 157.2, 138.2, 136.5, 132.3, 130.7, 129.7, 128.6, 128.4, 127.3, 126.6, 125.9, 123.0, 115.6, 87.6, 58.3, 45.1, 40.2, 39.7, 34.0, 28.9, 13.2, 13.0. IR (thin film): νmax (cm^{-1}) = 2988, 1739, 1712, 1597, 1451, 1413, 1346, 1134, 1077, 879, 728, 702, 667, 561, 519, 459. HRMS (ESI) calcd for $C_{26}H_{26}ClN_3O_3SNa$ $[M+Na]^+$: 518.1281. Found: 518.1262.

3. Mechanistic studies

UV/Vis absorption spectra

UV/vis absorption spectra based on **1a** (0.01 M in CH_2Cl_2), **2a** (0.01 M in CH_2Cl_2) and the mixture of **1a** and **2a** (**1a**:**2a** = 1:1, 0.01 M in CH_2Cl_2) were recorded respectively in 1 cm path quartz cuvettes using Shimadzu UV-1750 UV/Vis spectrometer.

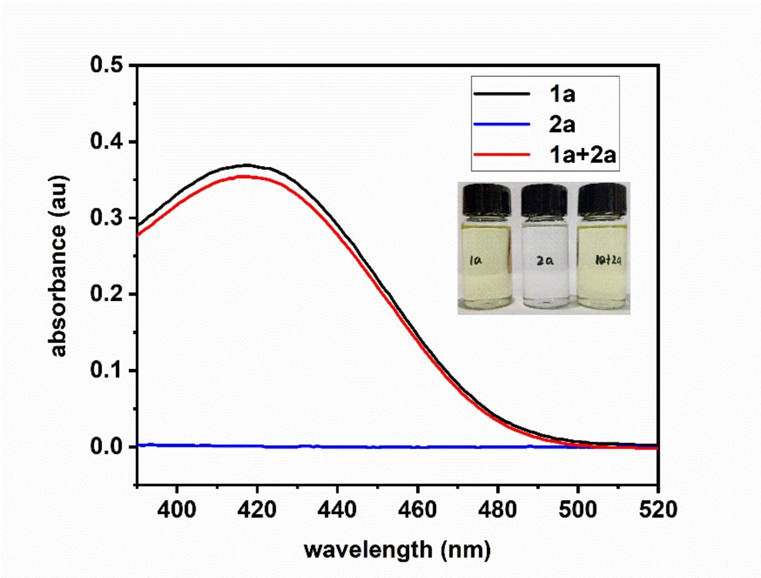


Figure S1. UV/vis spectra of **1a**, **2a** and the mixture of **1a** and **2a**.

Luminescence quenching experiments

The concentration of diethylthioparabanate **1a** was 1×10^{-2} M in DCM. The concentration of the quencher (**2a**, dimethyl vinylcyclopropanedicarboxylate) was 0.1 M in DCM. For each quenching experiment, the quencher was titrated to a solution (5 mL) of the diethylthioparabanate **1a** in a quartz glass bottle. The addition of the quencher refers to an increase of the quencher concentration of 1×10^{-3} M, 3×10^{-3} M, 5×10^{-3} M, 8×10^{-3} M, 1.5×10^{-2} M, 2×10^{-2} M. Then the emission intensity of diethylthioparabanate **1a** was collected respectively.

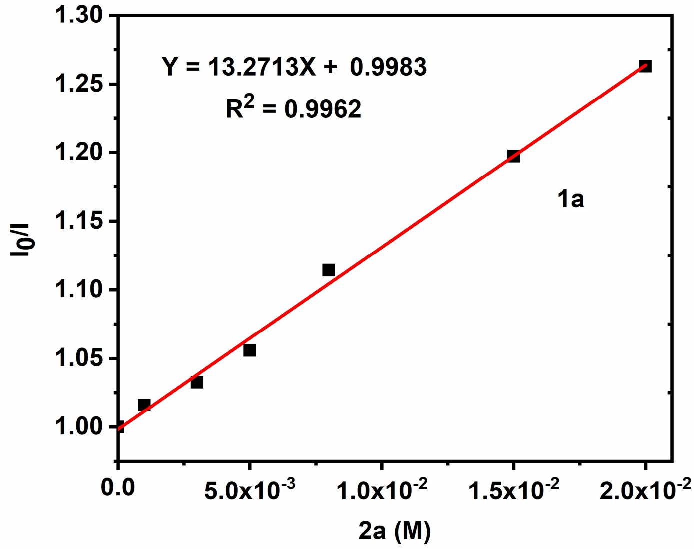


Figure S2. Stern-Volmer luminescence quenching experiments.

Emission spectra of the LED lamps

The following spectra were recorded on EVERFINE Corporation HAAS-2000_VIS_V2 High-precision fast spectroradiometer. The forward current of the LEDs is 25 mA. Electroluminescence (EL) measurements of the LED lamps were carried out at room temperature using Everfine HAAS-2000. For the light collection, the LEDs were placed inside a 30 cm-diameter integrating sphere coupled to a high accuracy array spectroradiometer (wavelength accuracy <0.3 nm) and a programmable test power LED300E.

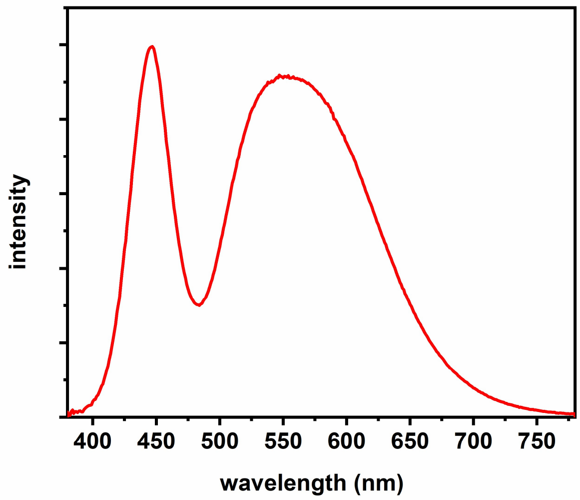


Figure S3. Emission spectra of the white LEDs lamp.

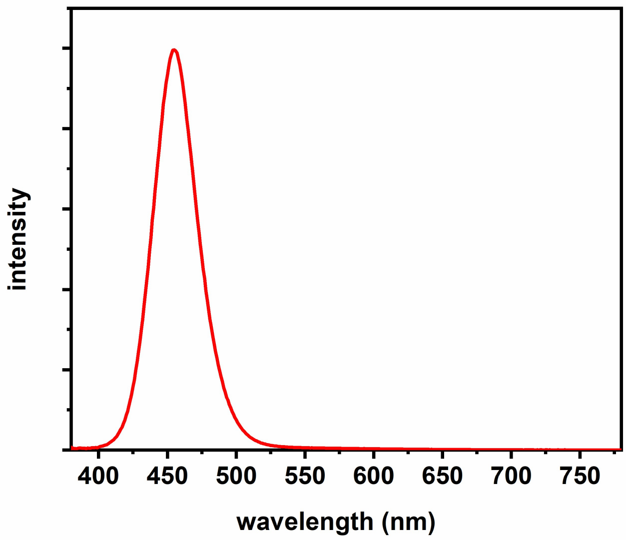


Figure S4. Emission spectra of the blue LEDs lamp.

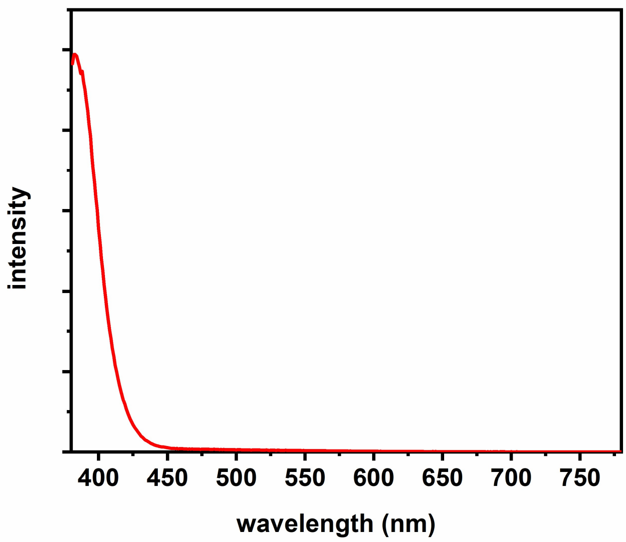


Figure S5. Emission spectra of the purple LEDs lamp.

4. X-Ray crystal data

Figure S6. X-Ray crystal structure of **3a** (The crystal was obtained by slow evaporation of the solution of DCM and PE) (CCDC: 2090931):

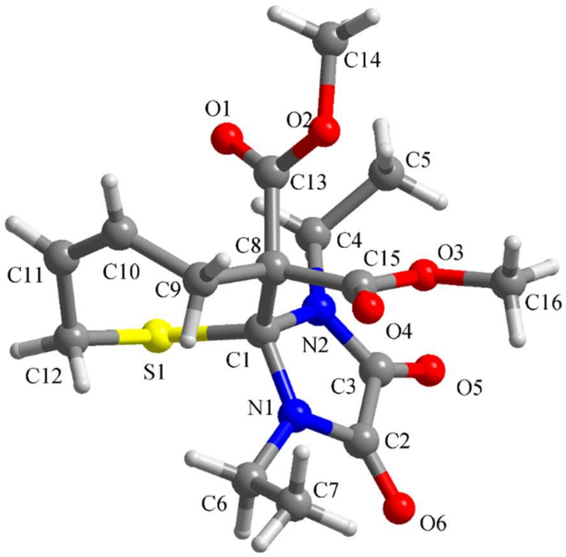


Table 1 Crystal data and structure refinement for 1.

Identification code	1
Empirical formula	$C_{16}H_{22}N_2O_6S$
Formula weight	370.429
Temperature/K	162(17)
Crystal system	monoclinic
Space group	P21/c
a/Å	11.0035(10)
b/Å	12.9016(10)
c/Å	12.5654(10)
α/°	90
β/°	101.836(8)
γ/°	90
Volume/Å3	1745.9(3)
Z	4
ρcalcg/cm3	1.409
μ/mm-1	0.221
F(000)	784.9
Crystal size/mm3	0.05 × 0.05 × 0.05
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	7.14 to 52.04

Index ranges	$-13 \le h \le 14, -17 \le k \le 14, -17 \le l \le 17$
Reflections collected	11808
Independent reflections	3436 [Rint = 0.0585, Rsigma = 0.0804]
Data/restraints/parameters	3436/0/230
Goodness-of-fit on F2	1.043
Final R indexes [I>=2σ (I)]	R1 = 0.0422, wR2 = 0.0913
Final R indexes [all data]	R1 = 0.0617, wR2 = 0.1028
Largest diff. peak/hole / e Å-3	0.51/-0.37

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 1. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	8663.5(5)	1078.6(4)	9656.3(4)	22.59(16)
O6	10019.7(14)	-1727.1(11)	7852.8(11)	27.0(4)
O5	8194.0(13)	-2384.1(11)	9123.1(11)	26.6(4)
N1	9078.4(15)	-146.6(13)	7959.6(12)	18.7(4)
N2	7664.8(15)	-662.7(12)	8943.6(12)	18.0(4)
C1	8069.2(18)	273.0(15)	8450.2(14)	18.3(4)
C2	9239.6(19)	-1177.7(16)	8124.7(14)	19.1(4)
C4	6760.4(19)	-740.9(16)	9661.2(14)	22.2(5)
C3	8306.3(19)	-1515.7(16)	8777.0(15)	20.3(4)
C7	10077(2)	375.6(19)	6426.7(16)	31.7(5)
C5	5583(2)	-1293.8(17)	9110.3(16)	26.2(5)
C6	10071(2)	454.0(17)	7627.2(16)	25.8(5)
C8	7030.3(18)	751.9(15)	7505.3(14)	17.6(4)
C12	8920(2)	2406.6(16)	9266.7(16)	26.9(5)
C9	7370(2)	1857.4(15)	7138.8(15)	22.0(5)
C10	7075(2)	2727.6(16)	7838.2(16)	26.3(5)
C11	7753(2)	2974.0(16)	8791.4(16)	26.7(5)
O3	6530.5(13)	-925.3(10)	6754.6(9)	21.4(3)
O4	6998.3(14)	276.3(11)	5623.0(10)	26.1(4)
C13	5756.3(19)	873.4(15)	7790.4(15)	19.3(4)
C15	6871.7(18)	22.6(16)	6508.3(14)	18.4(4)
O1	5545.1(14)	1145.1(11)	8647.4(10)	26.3(4)
O2	4867.7(13)	708.1(12)	6903.2(10)	25.5(3)
C16	6220(2)	-1630.2(17)	5837.8(16)	32.1(6)
C14	3596(2)	800.3(19)	7031.5(17)	30.5(5)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for 1. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+2hka*b*U$_{12}$+…].

Atom	U11	U22	U33	U12	U13	U23
S1	31.0(3)	15.2(3)	18.5(3)	0.7(2)	-2.1(2)	-3.12(19)
O6	29.9(8)	21.8(8)	29.4(8)	6.1(7)	6.4(6)	-3.1(6)
O5	32.1(9)	13.2(8)	33.3(8)	-0.3(7)	4.1(7)	3.0(6)
N1	22.1(9)	13.4(9)	20.7(8)	1.2(8)	4.8(7)	-1.2(7)
N2	24.7(9)	11.1(8)	17.9(8)	0.5(8)	4.0(7)	0.7(6)
C1	23.5(11)	12.0(10)	18.7(9)	0.7(9)	2.8(8)	-0.3(8)
C2	21.6(11)	15.9(10)	18.1(9)	0.3(9)	0.0(8)	-1.2(8)
C4	30.8(12)	19.0(11)	18.2(10)	2.9(10)	8.3(9)	2.5(8)
C3	22.5(11)	16.1(11)	19.2(10)	2.6(10)	-2.8(8)	-1.7(8)
C7	34.6(13)	29.9(13)	34.1(12)	1.9(11)	15.3(10)	6.5(10)
C5	29.5(12)	23.4(12)	26.9(11)	0.1(10)	8.8(9)	2.5(9)
C6	23.1(11)	21.5(12)	33.4(11)	-2.2(10)	7.4(9)	0.7(9)
C8	24.2(11)	12.5(10)	15.2(9)	-1.1(9)	1.8(8)	-1.4(8)
C12	37.3(13)	14.7(11)	26.0(11)	-2.1(10)	0.4(9)	-4.5(9)
C9	29.0(12)	13.9(10)	21.1(10)	-1.8(10)	0.7(8)	2.6(8)
C10	30.2(12)	12.8(11)	33.3(12)	1.7(10)	0.2(10)	2.2(9)
C11	36.1(13)	12.5(11)	31.4(11)	3.1(10)	6.6(10)	-2.8(9)
O3	33.4(8)	14.2(7)	16.1(6)	-1.9(7)	3.3(6)	-3.0(6)
O4	39.1(9)	22.6(8)	16.9(7)	-5.7(7)	6.5(6)	-0.5(6)
C13	23.8(11)	11.2(10)	22.1(10)	2.1(9)	2.5(8)	1.8(8)
C15	20.6(10)	15.0(10)	18.9(10)	1.6(9)	2.4(8)	-0.3(8)
O1	30.7(9)	27.2(9)	21.8(7)	6.8(7)	7.1(6)	-2.5(6)
O2	21.9(8)	30.7(9)	22.0(7)	2.7(7)	-0.1(6)	-2.5(6)
C16	53.0(16)	16.8(11)	26.3(11)	-5.4(11)	7.4(10)	-8.3(9)
C14	23.3(12)	34.0(14)	33.3(12)	3.9(11)	3.7(9)	1.1(10)

Table 4 Bond Lengths for 1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C1	1.8434(18)	C7	C6	1.513(3)
S1	C12	1.820(2)	C8	C9	1.567(3)
O6	C2	1.215(2)	C8	C13	1.525(3)
O5	C3	1.217(2)	C8	C15	1.548(3)
N1	C1	1.479(2)	C12	C11	1.493(3)
N1	C2	1.352(2)	C9	C10	1.501(3)
N1	C6	1.468(3)	C10	C11	1.313(3)

N2	C1	1.467(2)	O3	C15	1.334(2)
N2	C4	1.477(2)	O3	C16	1.452(2)
N2	C3	1.347(3)	O4	C15	1.195(2)
C1	C8	1.594(3)	C13	O1	1.200(2)
C2	C3	1.504(3)	C13	O2	1.341(2)
C4	C5	1.516(3)	O2	C14	1.446(2)

Table 5 Bond Angles for 1.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C12	S1	C1	110.99(9)	C7	C6	N1	113.81(17)
C2	N1	C1	112.47(16)	C9	C8	C1	113.19(16)
C6	N1	C1	126.27(16)	C13	C8	C1	114.72(14)
C6	N1	C2	118.75(17)	C13	C8	C9	105.16(16)
C4	N2	C1	127.94(16)	C15	C8	C1	108.17(15)
C3	N2	C1	113.11(16)	C15	C8	C9	108.03(14)
C3	N2	C4	118.64(16)	C15	C8	C13	107.23(15)
N1	C1	S1	112.27(13)	C11	C12	S1	113.65(16)
N2	C1	S1	101.75(11)	C10	C9	C8	114.55(16)
N2	C1	N1	101.17(15)	C11	C10	C9	124.4(2)
C8	C1	S1	118.23(13)	C10	C11	C12	121.81(19)
C8	C1	N1	108.45(14)	C16	O3	C15	114.93(14)
C8	C1	N2	113.60(15)	O1	C13	C8	126.71(18)
N1	C2	O6	127.49(19)	O2	C13	C8	109.70(15)
C3	C2	O6	125.79(18)	O2	C13	O1	123.40(19)
C3	C2	N1	106.63(17)	O3	C15	C8	111.09(14)
C5	C4	N2	111.90(15)	O4	C15	C8	124.87(18)
N2	C3	O5	126.99(19)	O4	C15	O3	124.00(17)
C2	C3	O5	126.32(19)	C14	O2	C13	116.85(15)
C2	C3	N2	106.62(17)				

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 1.

Atom	x	y	z	U(eq)
H4a	7135.7(19)	-1113.7(16)	10316.7(14)	26.6(6)
H4b	6552.4(19)	-50.1(16)	9871.2(14)	26.6(6)
H7a	9291(5)	604(11)	6011.9(16)	47.6(8)

H7b	10727(9)	804(9)	6261(3)	47.6(8)
H7c	10216(14)	-331(3)	6246(3)	47.6(8)
H5a	5193(7)	-913(6)	8475(6)	39.3(7)
H5b	5785(2)	-1978(4)	8902(10)	39.3(7)
H5c	5026(5)	-1340(9)	9605(4)	39.3(7)
H6a	9982(2)	1176.5(17)	7810.5(16)	30.9(6)
H6b	10865(2)	214.5(17)	8038.4(16)	30.9(6)
H12a	9353(2)	2779.8(16)	9902.6(16)	32.3(6)
H12b	9453(2)	2398.9(16)	8740.0(16)	32.3(6)
H9a	8251(2)	1874.4(15)	7137.9(15)	26.3(6)
H9b	6926(2)	1973.8(15)	6398.0(15)	26.3(6)
H10	6366(2)	3118.2(16)	7579.1(16)	31.6(6)
H11	7498(2)	3516.9(16)	9180.9(16)	32.1(6)
H16a	5593(10)	-1323(5)	5284(5)	48.2(8)
H16b	6949(4)	-1765(9)	5550(8)	48.2(8)
H16c	5915(13)	-2269(5)	6073(3)	48.2(8)
H14a	3045(2)	632(11)	6357(4)	45.8(8)
H14b	3456(4)	332(8)	7587(8)	45.8(8)
H14c	3443(4)	1498(3)	7235(11)	45.8(8)

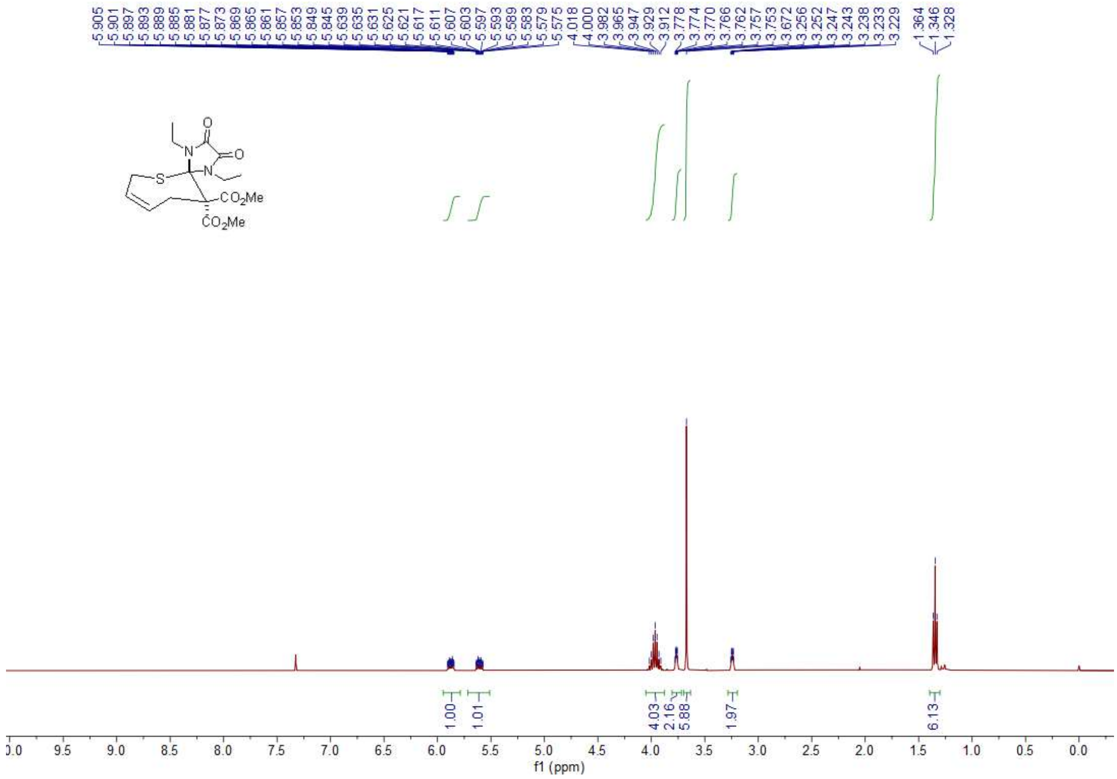
5. References

[1] (a) J. Wang, Z. Dai, C. Xiong, J. Zhu, J. Lu, Q. Zhou, Palladium-Catalyzed Allylic Alkylation of Aldimine Esters with Vinyl-Cyclopropanes to Yield α,α-Disubstituted α-Amino Acid Derivatives, *Adv. Synth. Catal.*, 2019, **361**, 5105-5111; (b) J. Xiao, X. Cheng, Y. Li, Y. He, J. Li, Z. Liu, P. Xia, W. Su, H. Yang, Palladium-catalysed ring-opening [3 + 2]-annulation of spirovinylcyclopropyl oxindole to diastereoselectively access spirooxindoles, *Org. Biomol. Chem.,* 2019, **17**, 103-107.

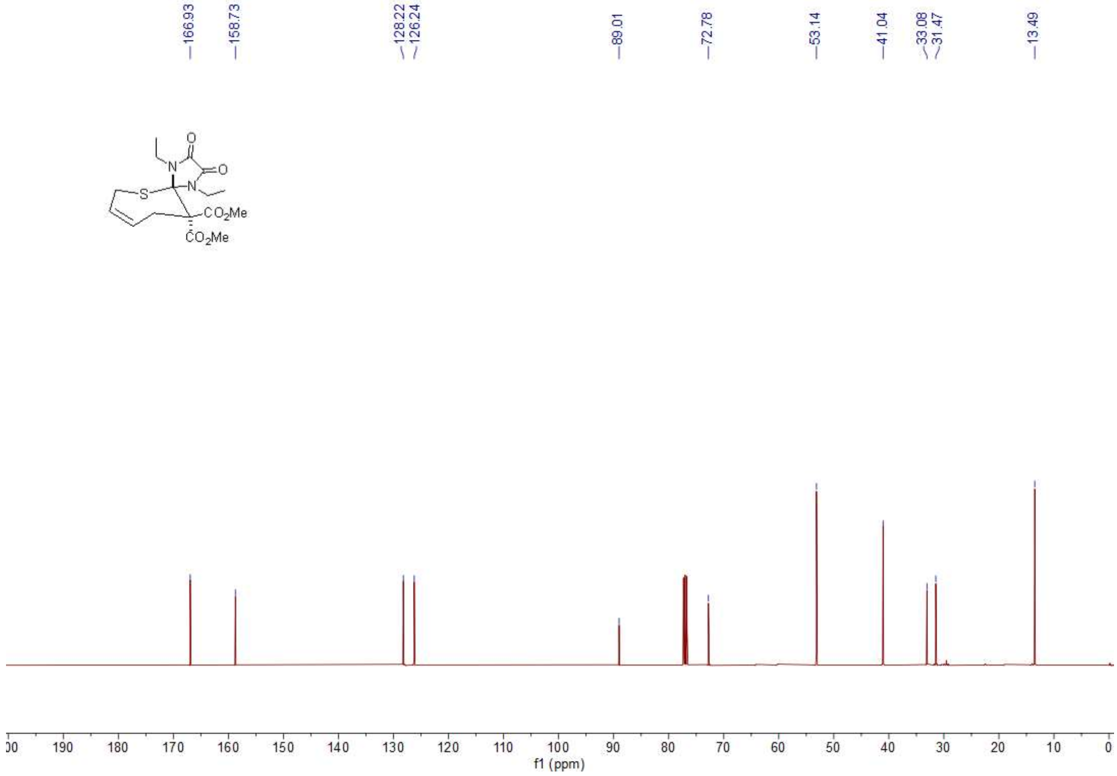
[2] Ş.H. Üngören, İ. Kani, A. Günay, A facile protocol for the preparation of 5-alkylidene and 5-imino substituted hydantoins from N,N′-disubstituted parabanic acids, *Tetrahedron Lett.,* 2012, **53**, 4758-4762.

6. Copies of NMR spectra

[1]H NMR Spectrum of **3a**



[13]C NMR Spectrum of **3a**



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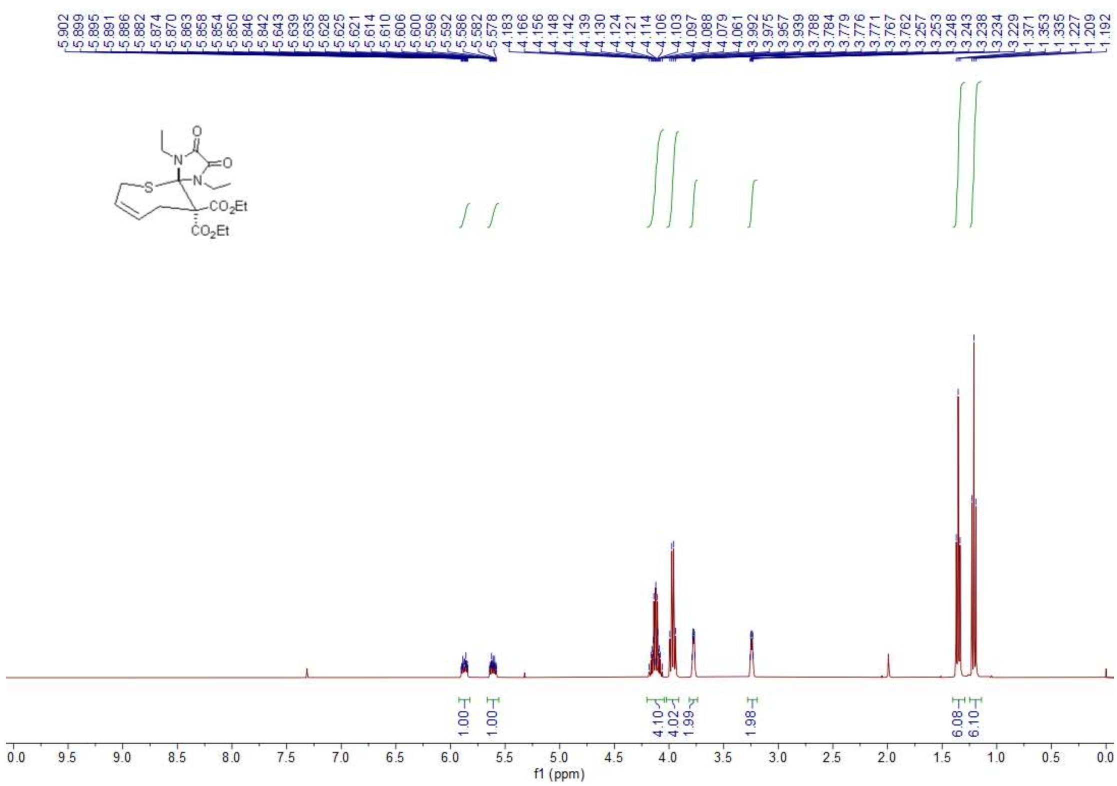

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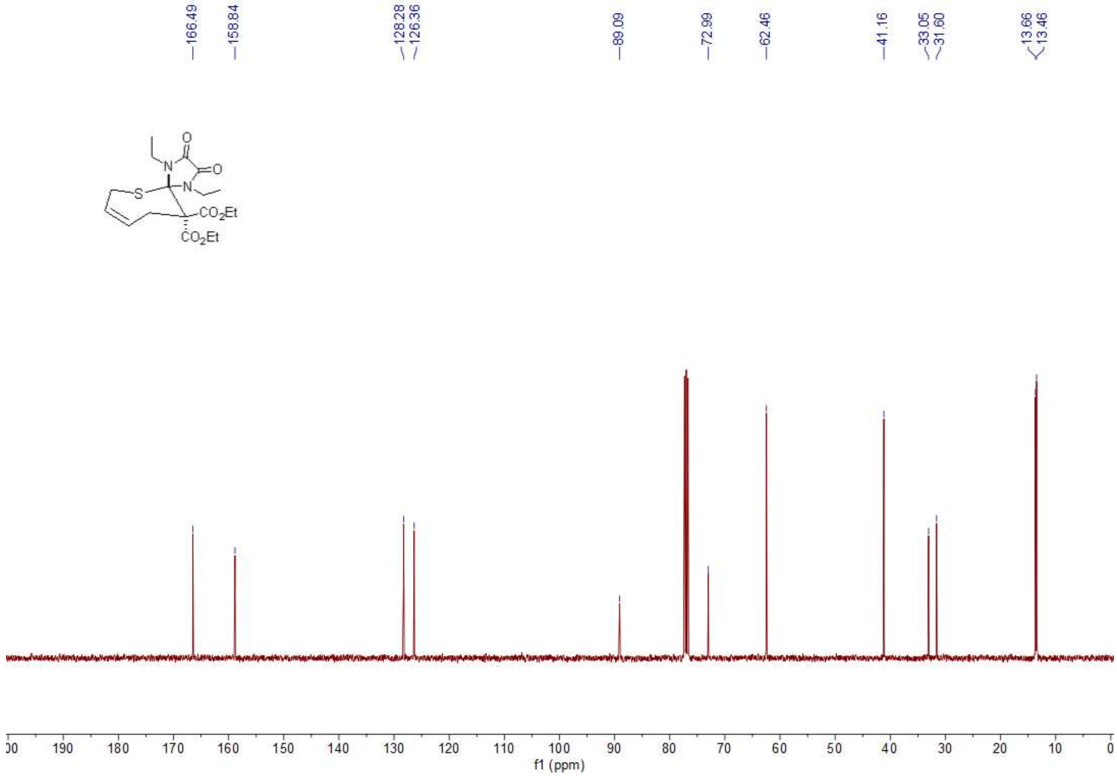
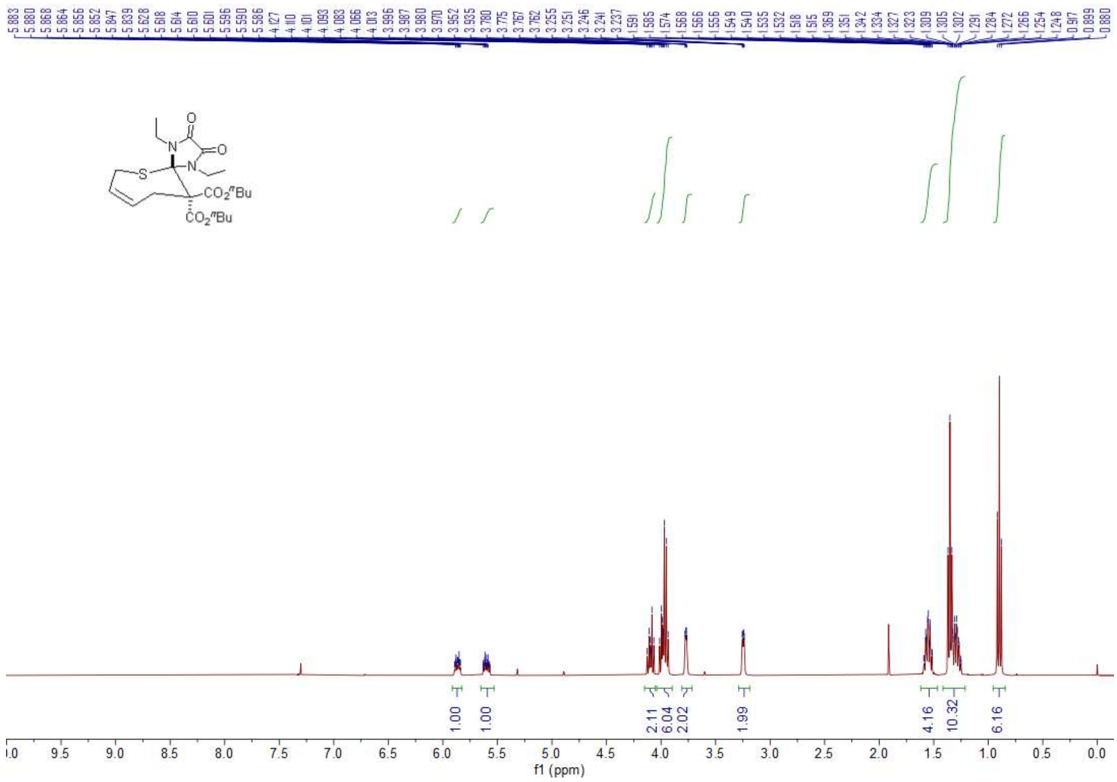
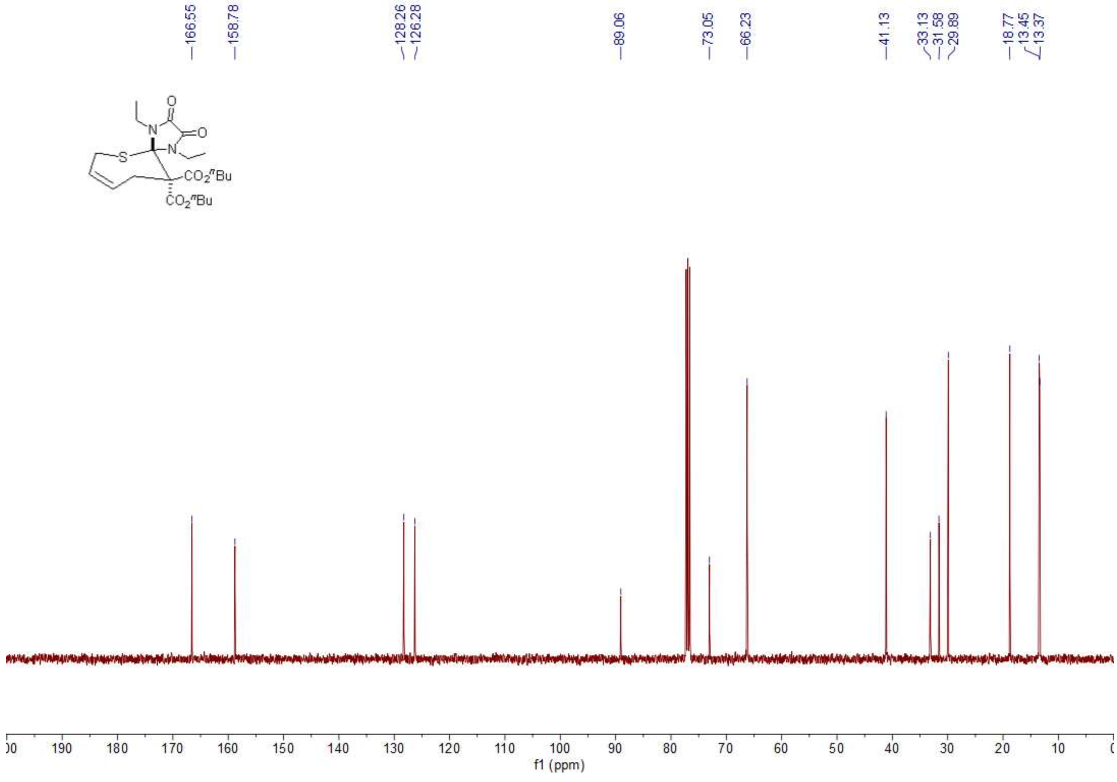


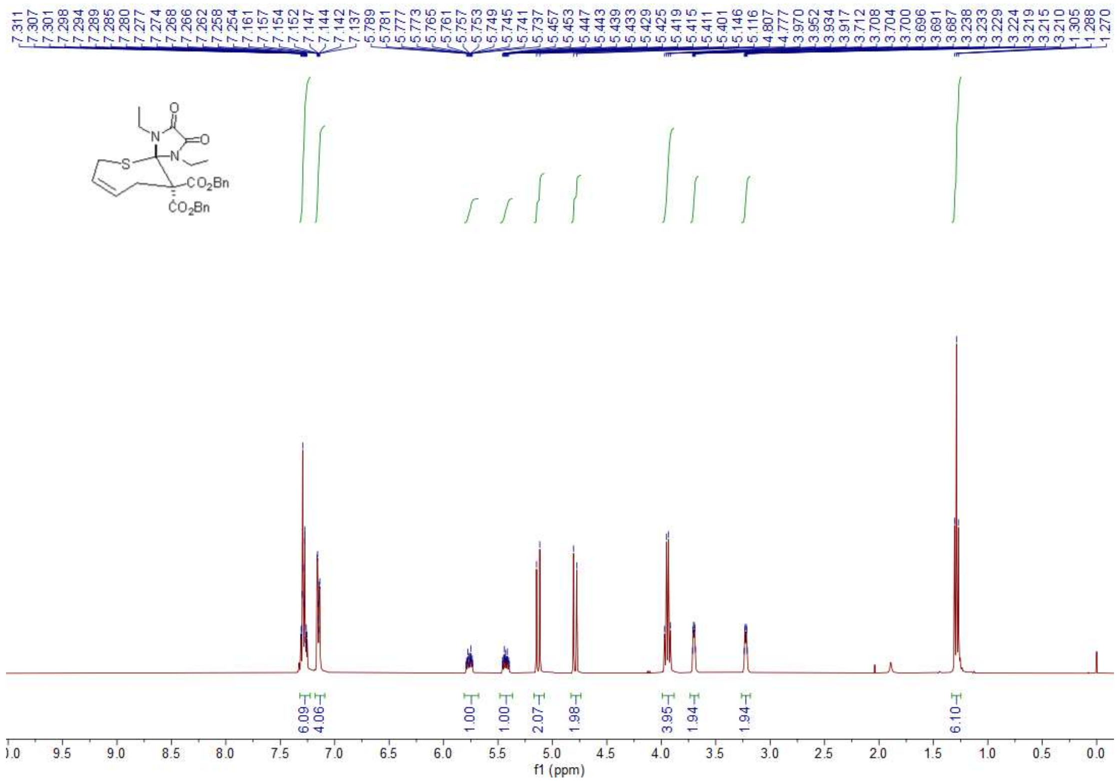
[1]H NMR Spectrum of **3c**



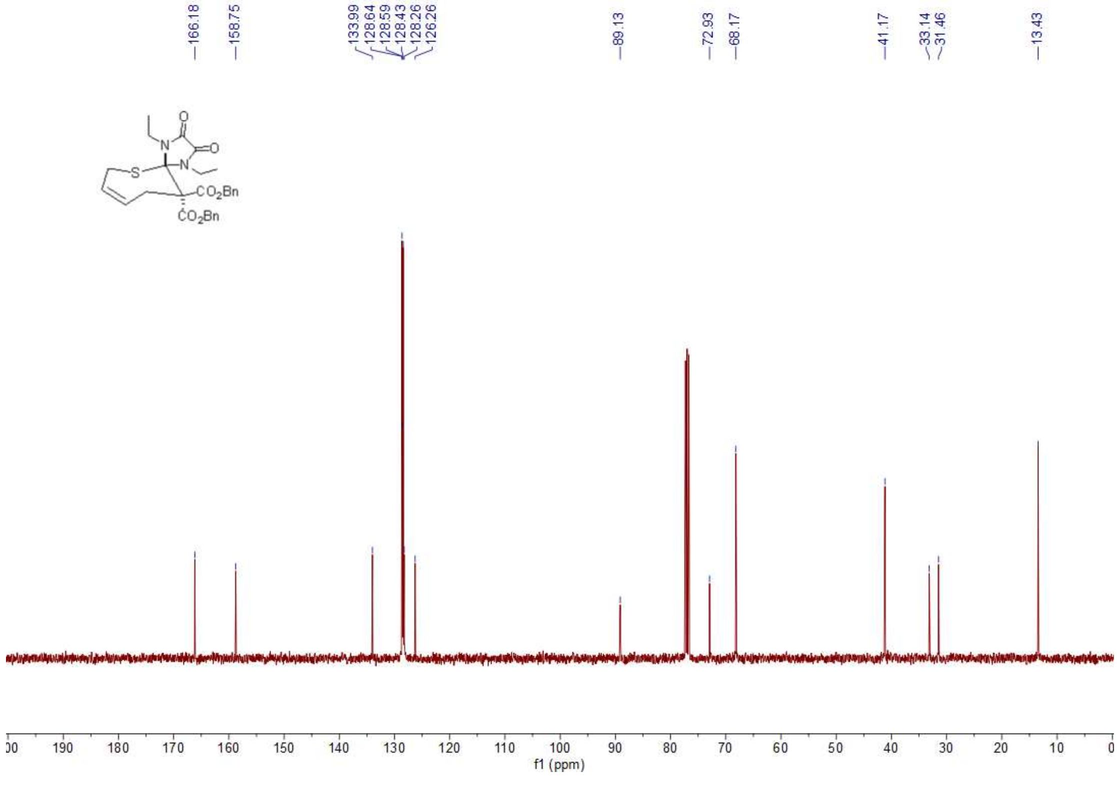
[13]C NMR Spectrum of **3c**



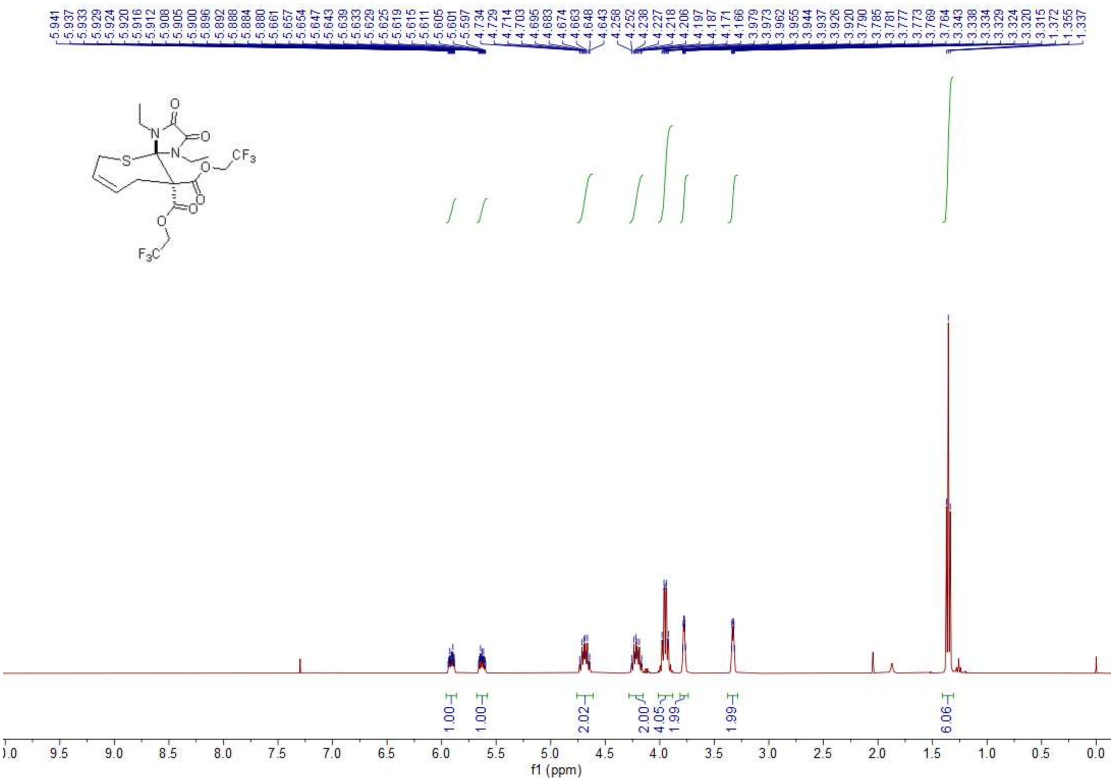
^{1}H NMR Spectrum of **3d**



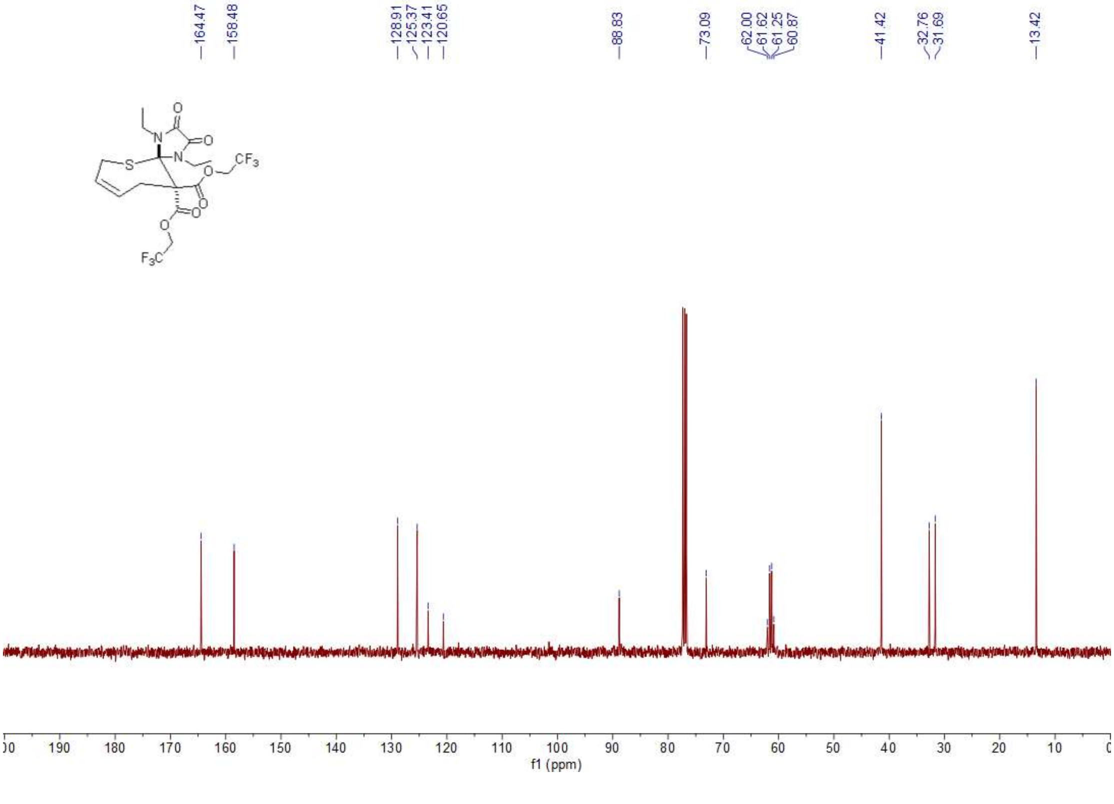
^{13}C NMR Spectrum of **3d**



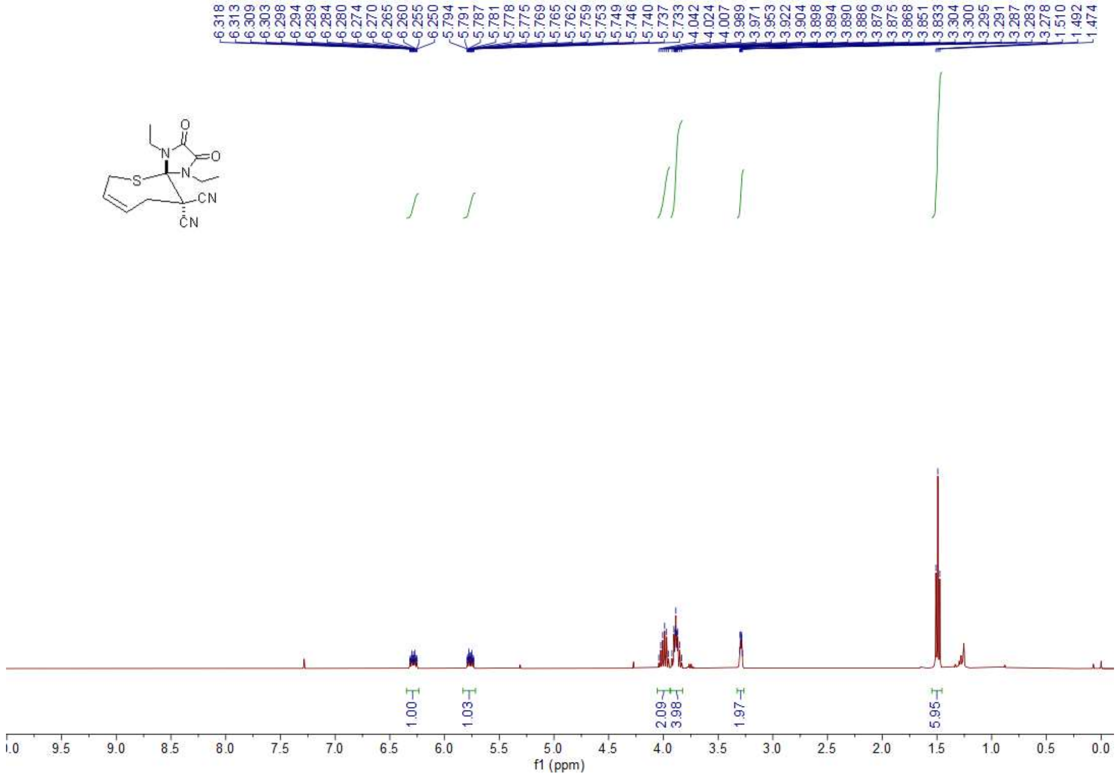
[1]H NMR Spectrum of **3e**



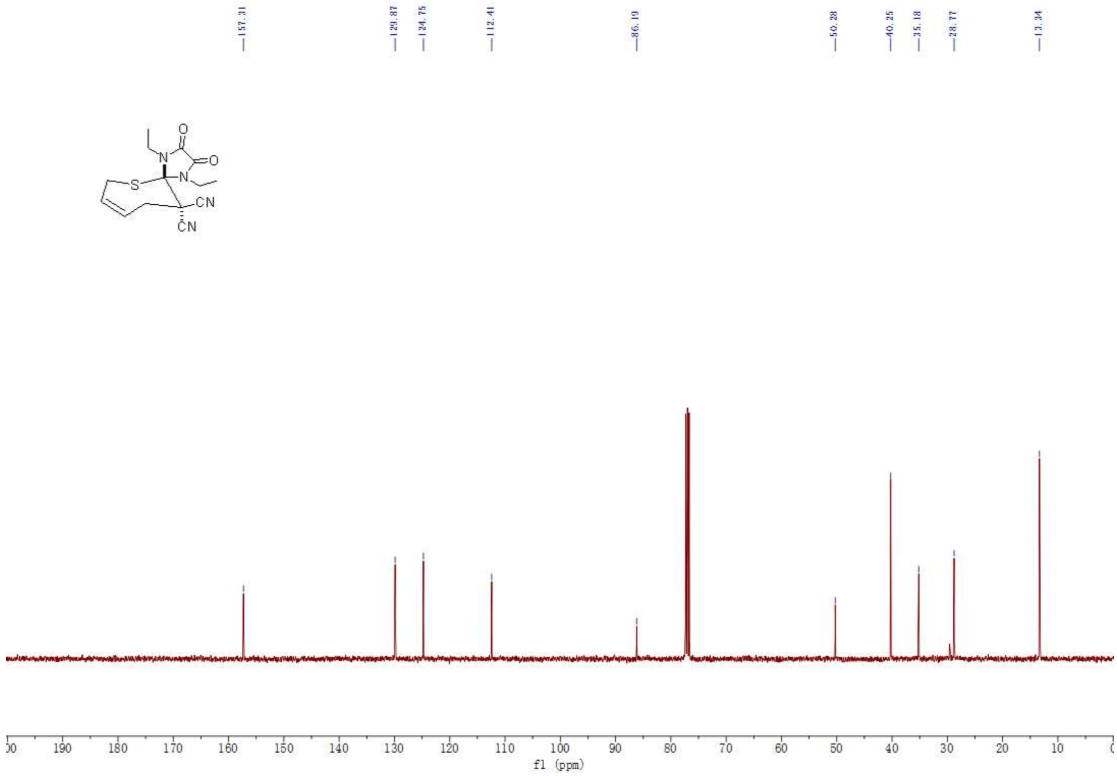
[13]C NMR Spectrum of **3e**



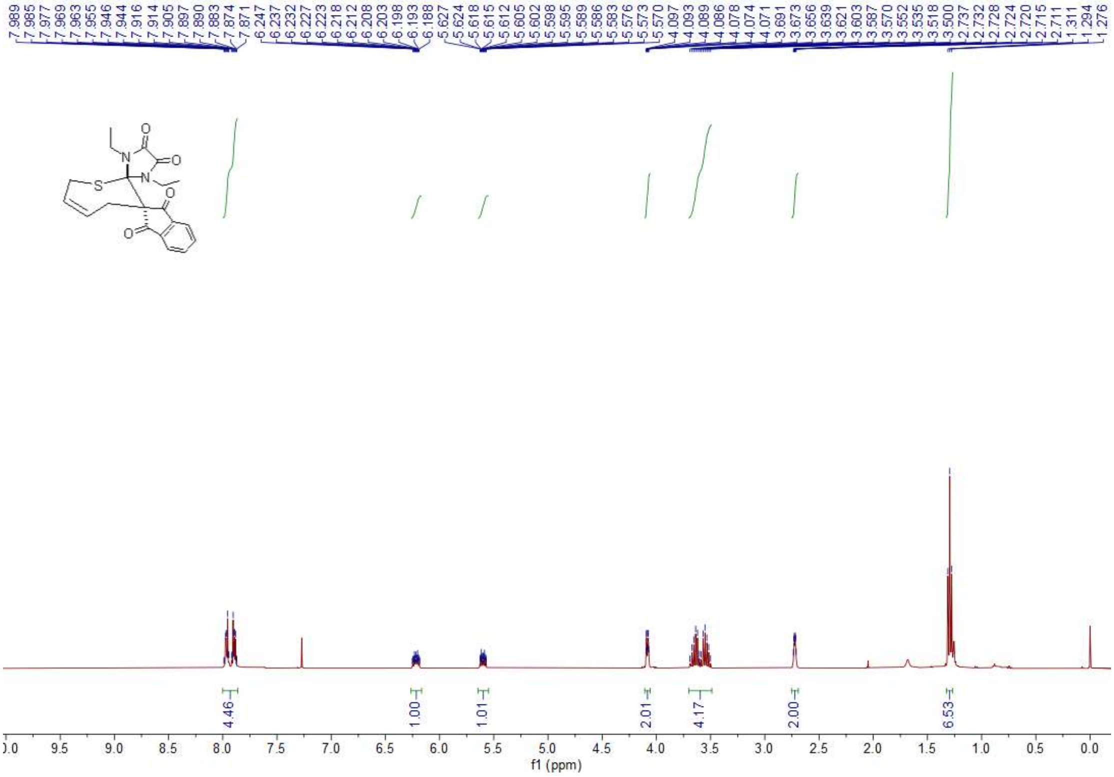
^{1}H NMR Spectrum of **3f**



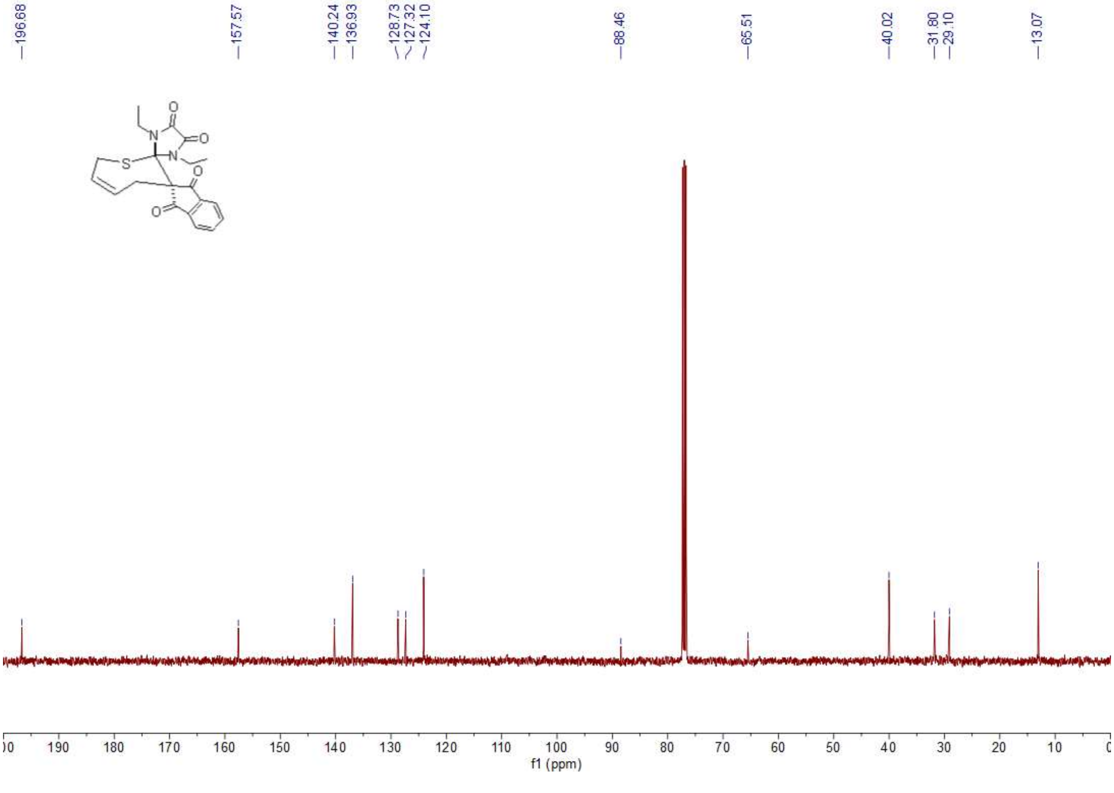
^{13}C NMR Spectrum of **3f**



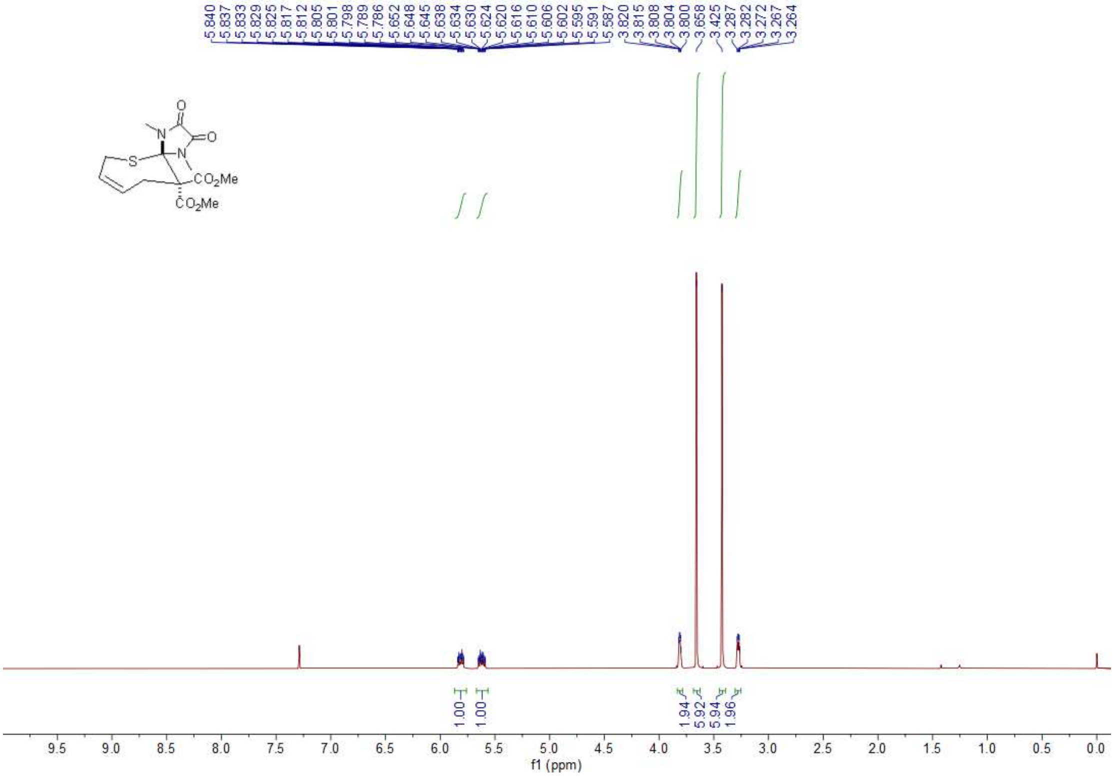
[1]H NMR Spectrum of **3g**



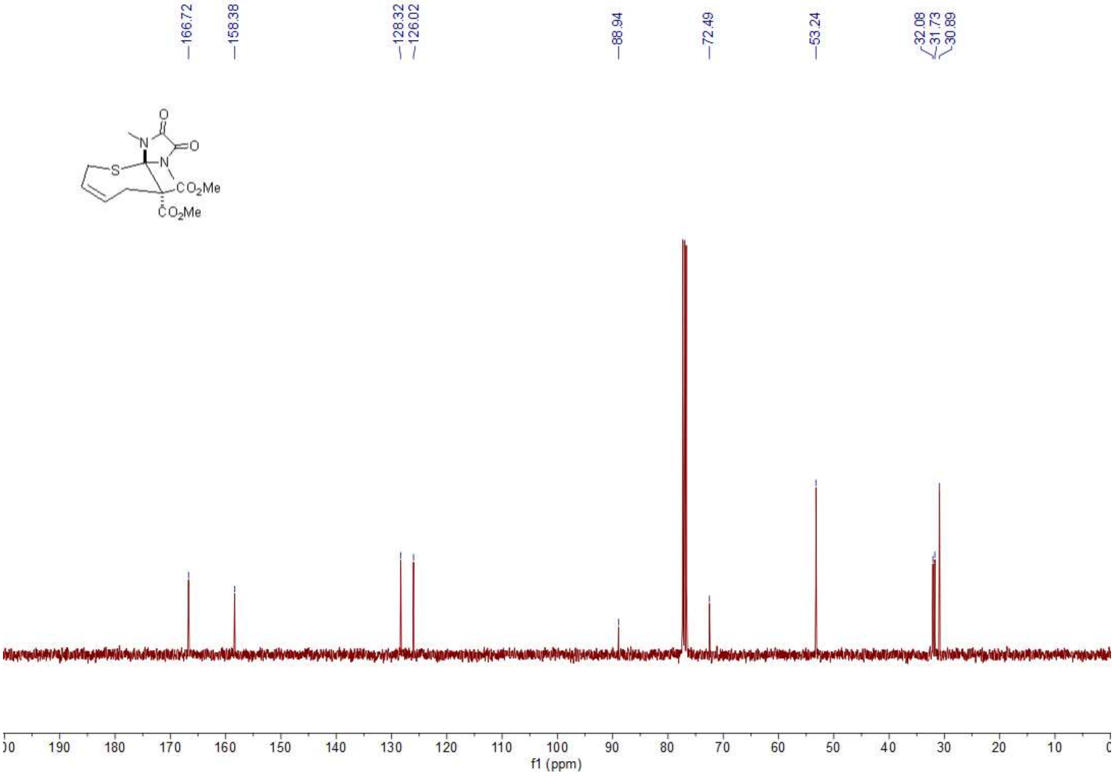
[13]C NMR Spectrum of **3g**



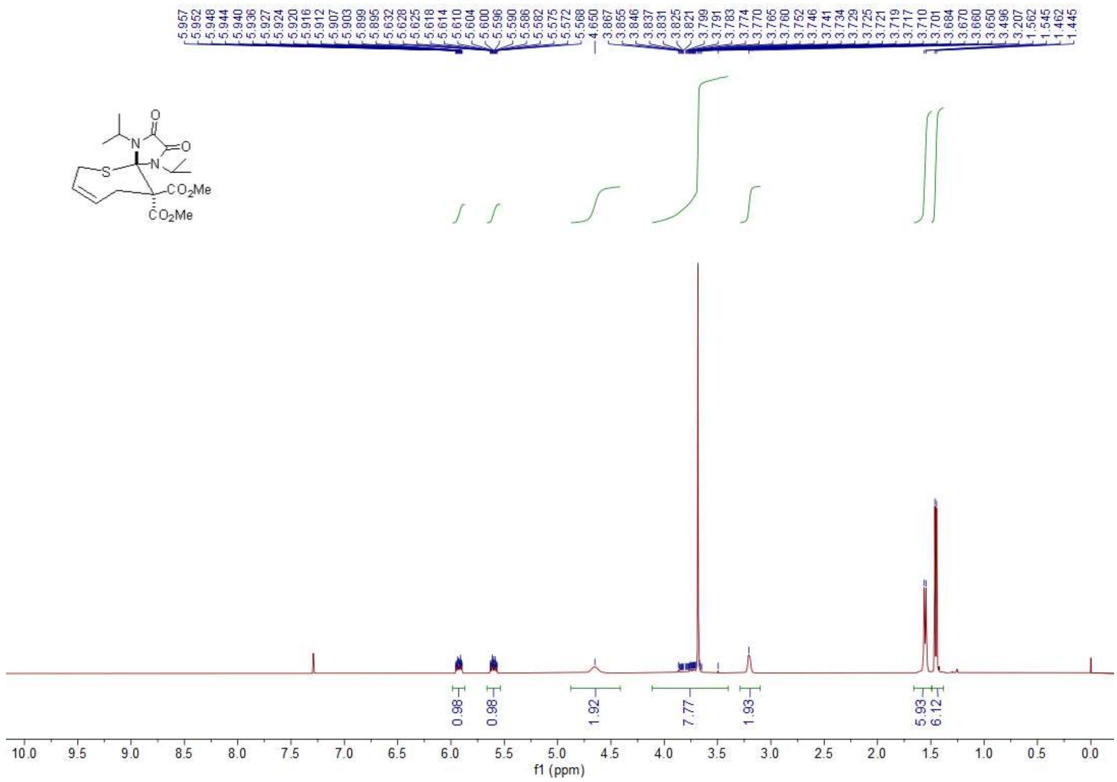
[1]H NMR Spectrum of **3i**



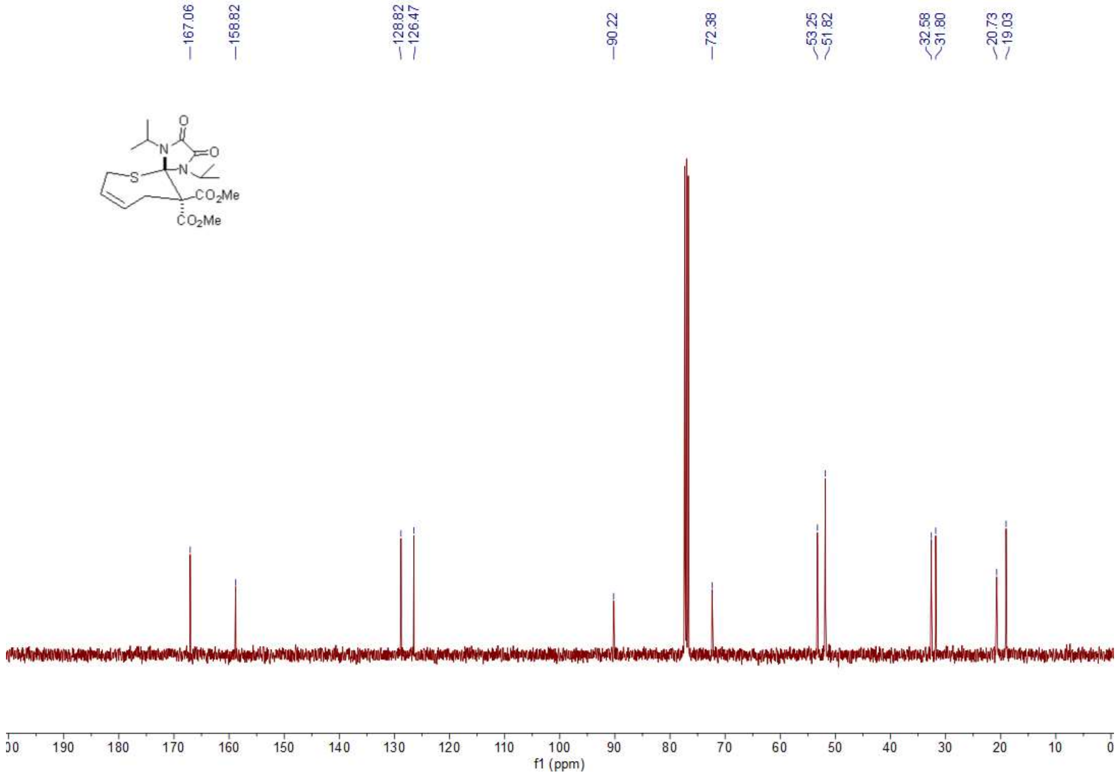
[13]C NMR Spectrum of **3i**



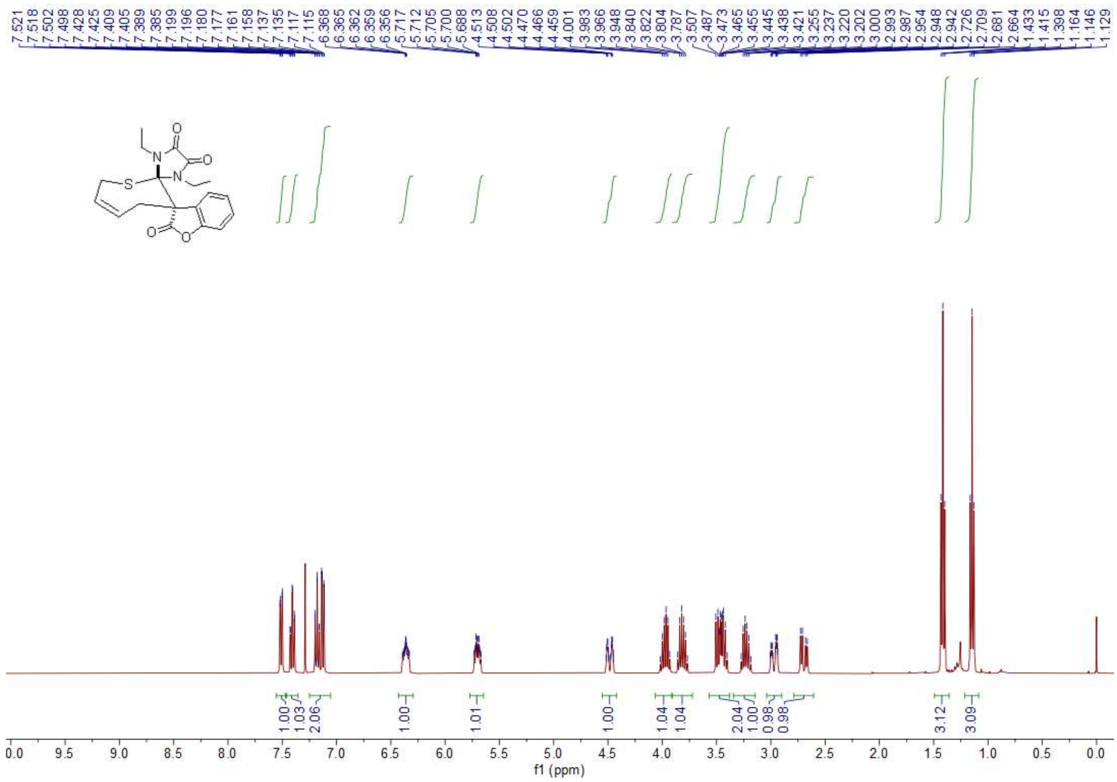
[1]H NMR Spectrum of **3j**



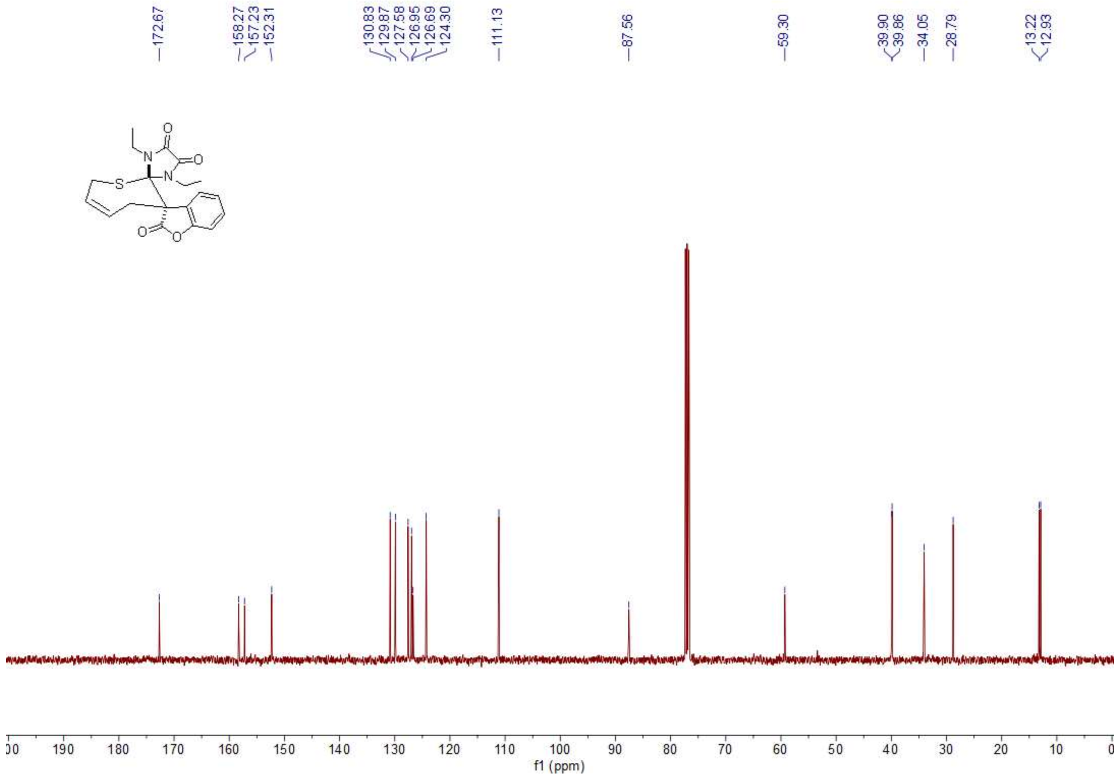
[13]C NMR Spectrum of **3j**



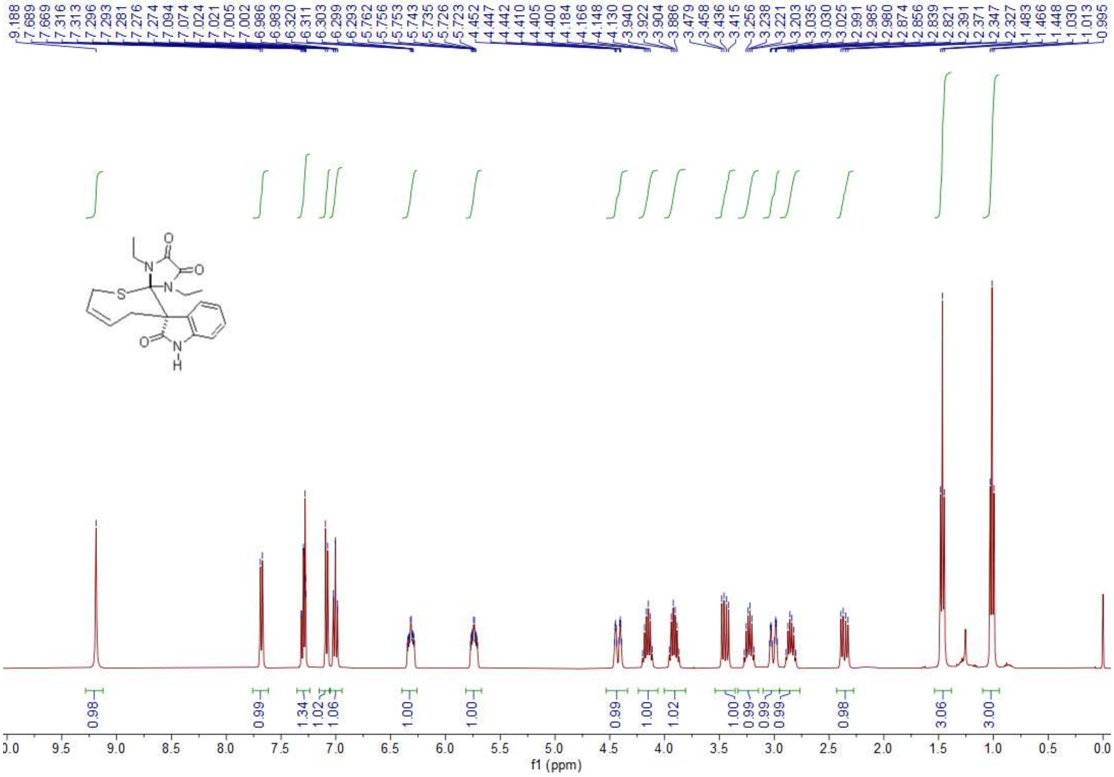
^{1}H NMR Spectrum of **3k**



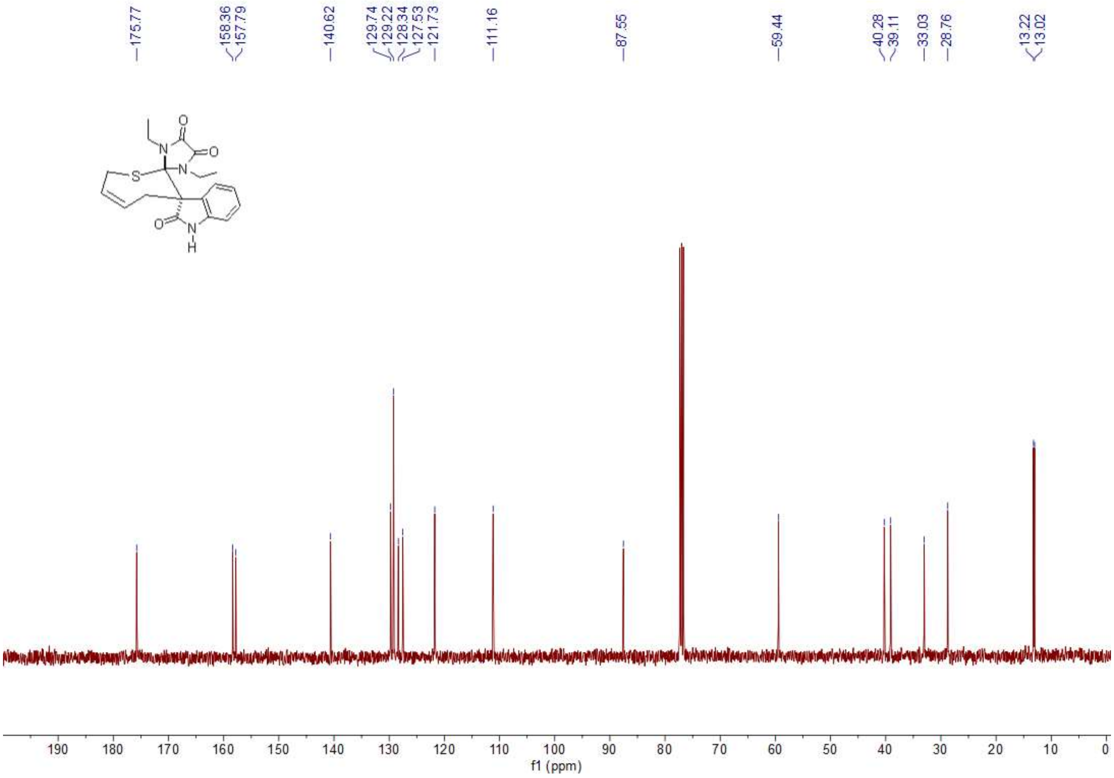
^{13}C NMR Spectrum of **3k**



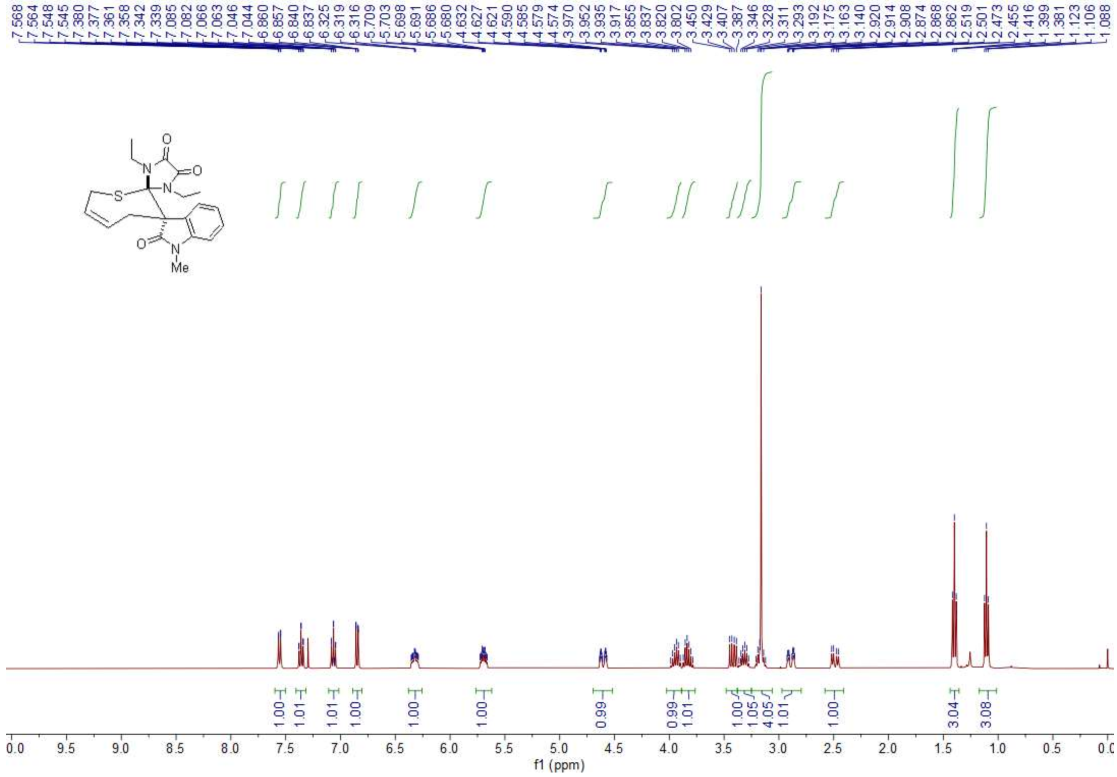
^{1}H NMR Spectrum of **3l**



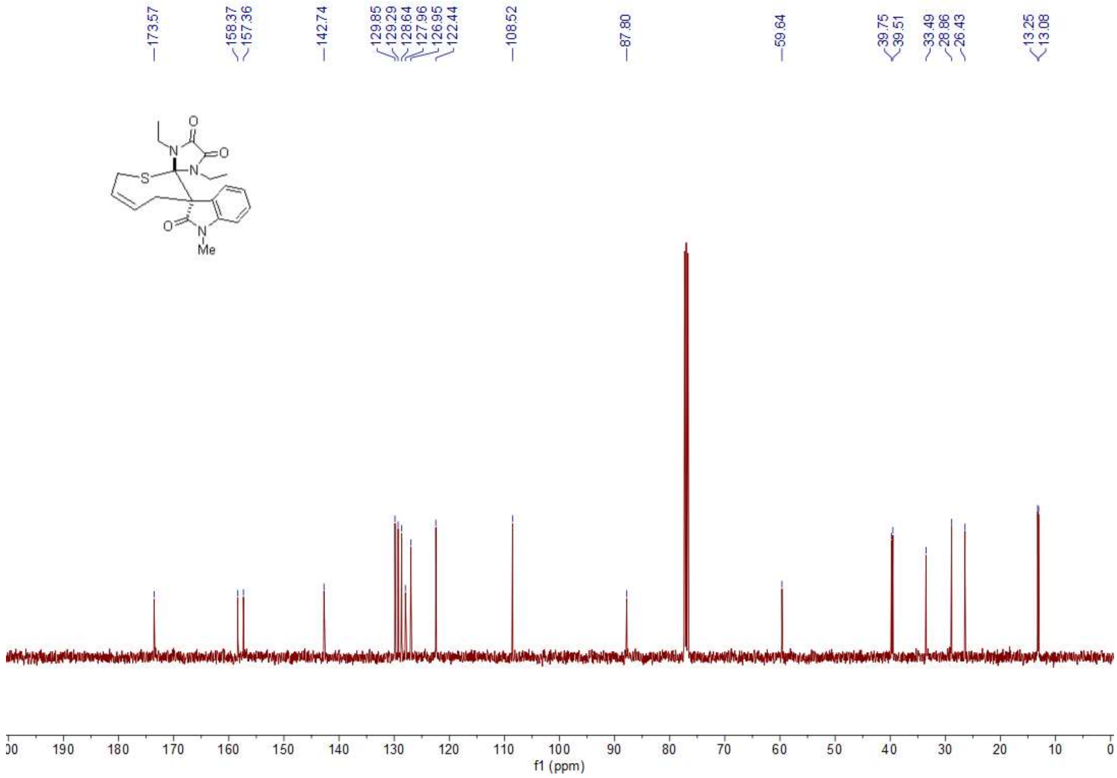
^{13}C NMR Spectrum of **3l**



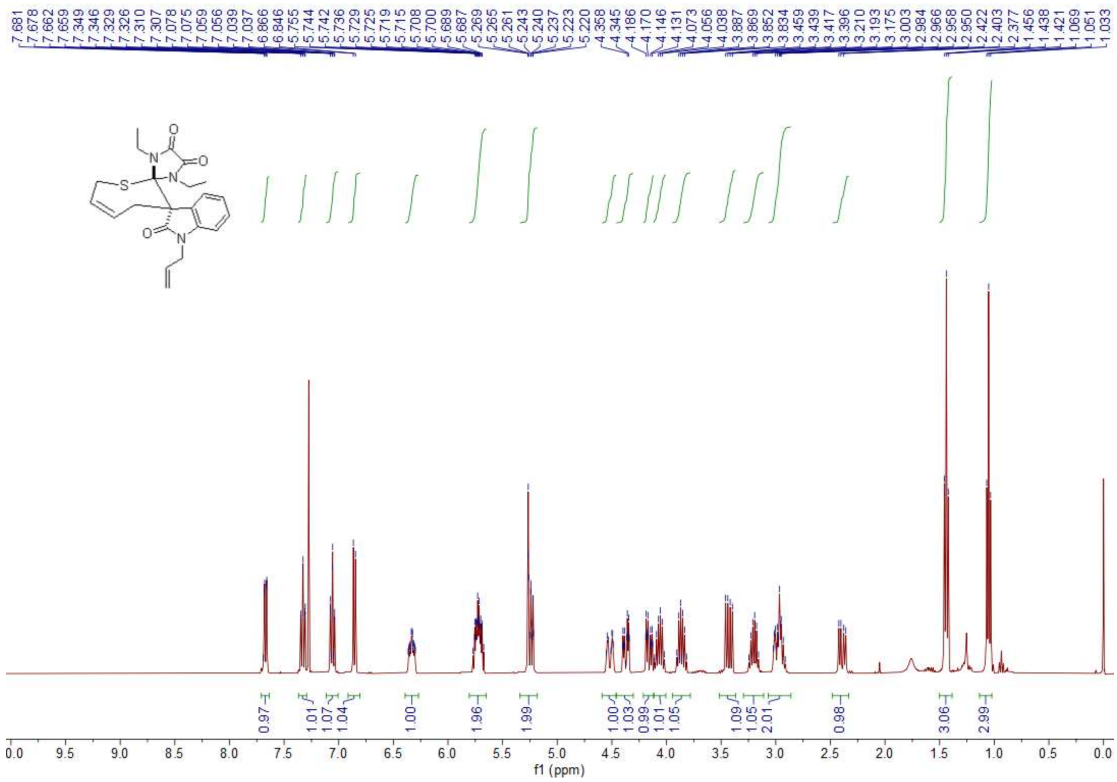
^{1}H NMR Spectrum of **3m**



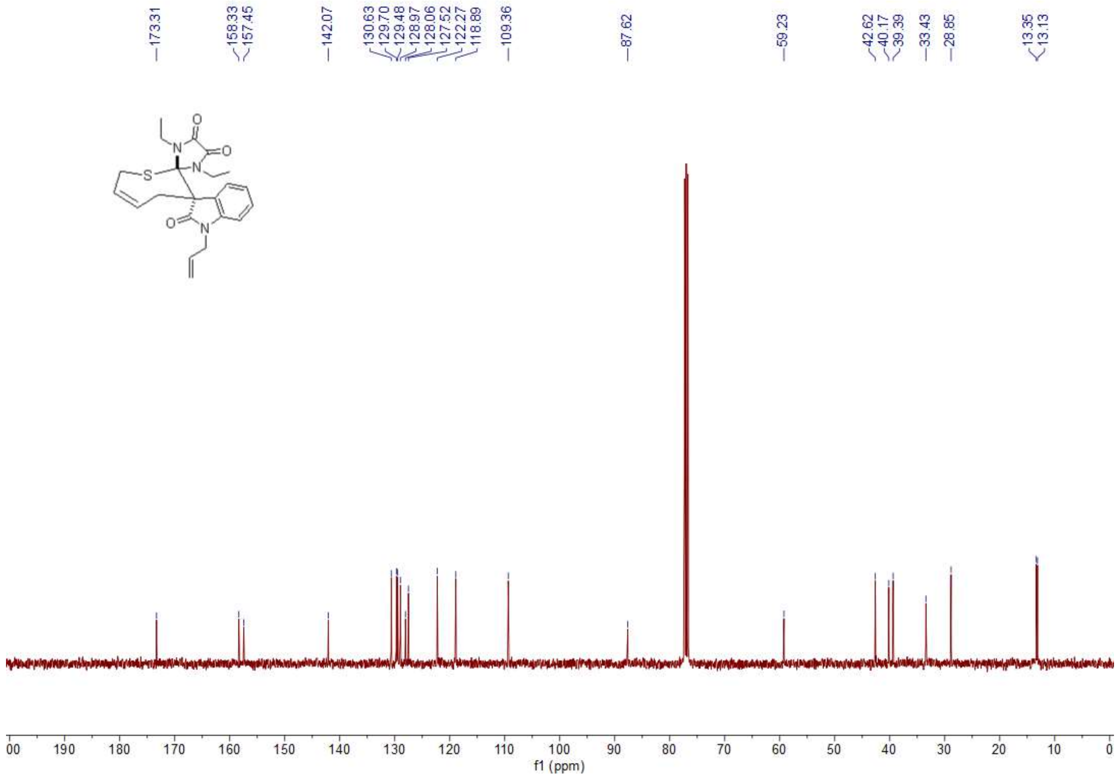
^{13}C NMR Spectrum of **3m**



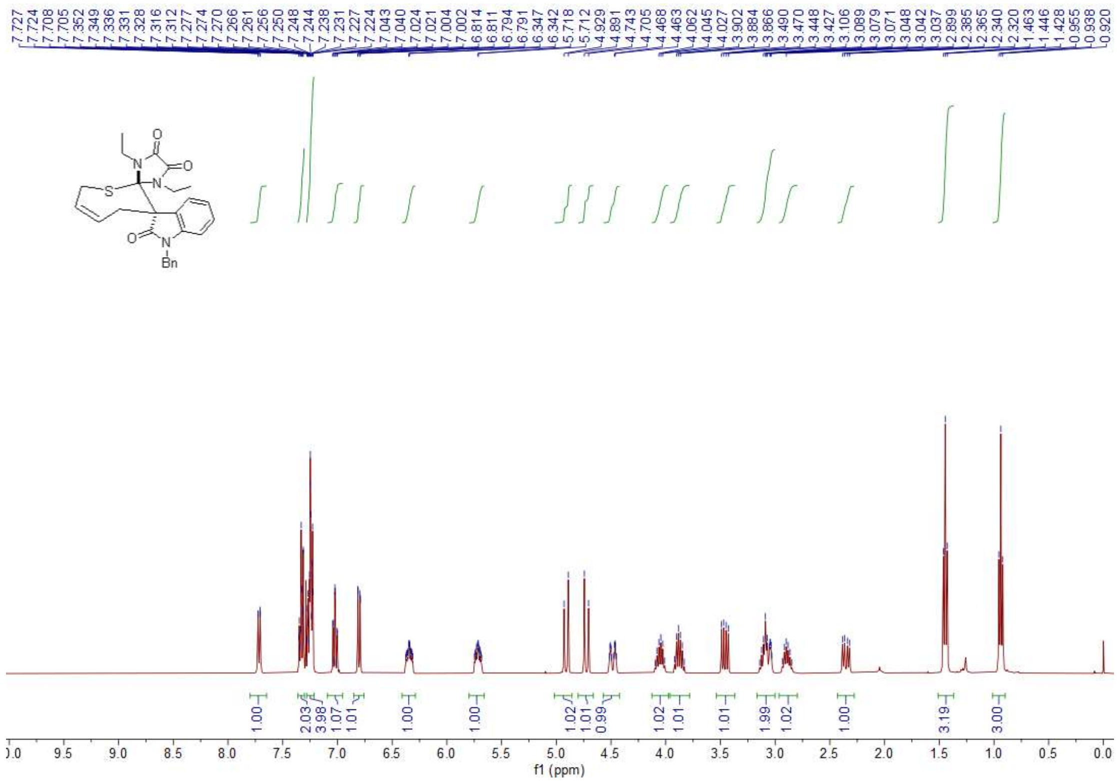
^{1}H NMR Spectrum of **3n**



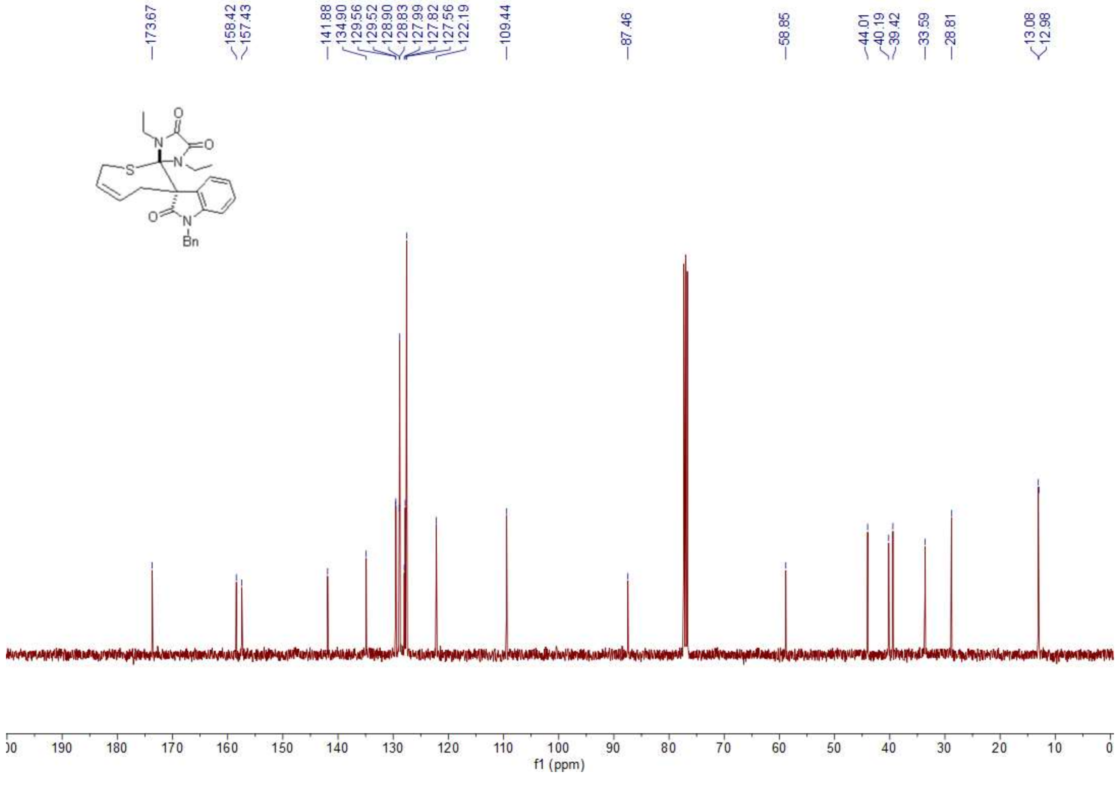
^{13}C NMR Spectrum of **3n**



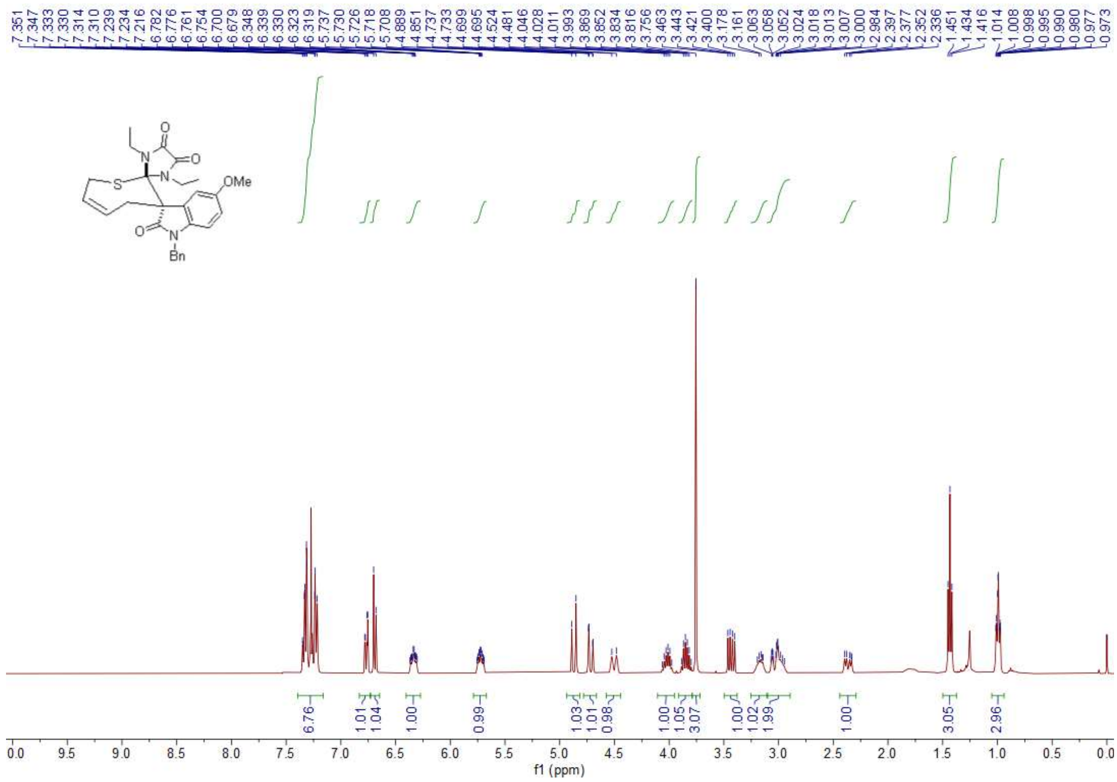
[1]H NMR Spectrum of **3o**



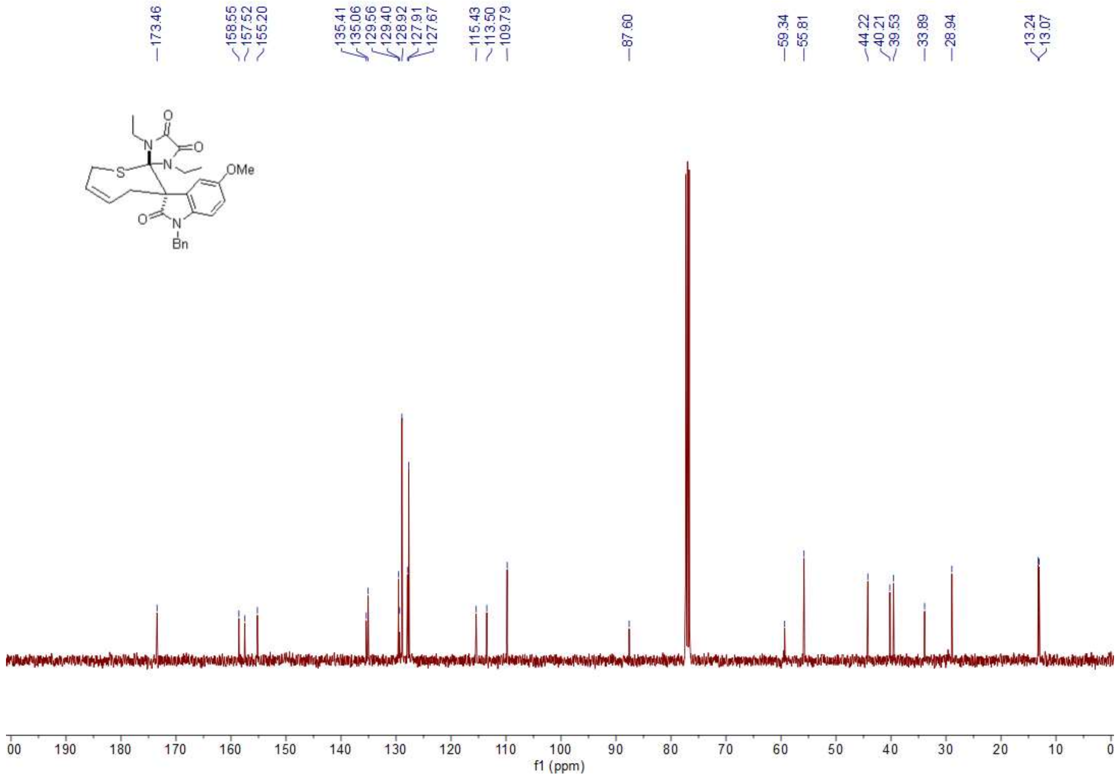
[13]C NMR Spectrum of **3o**



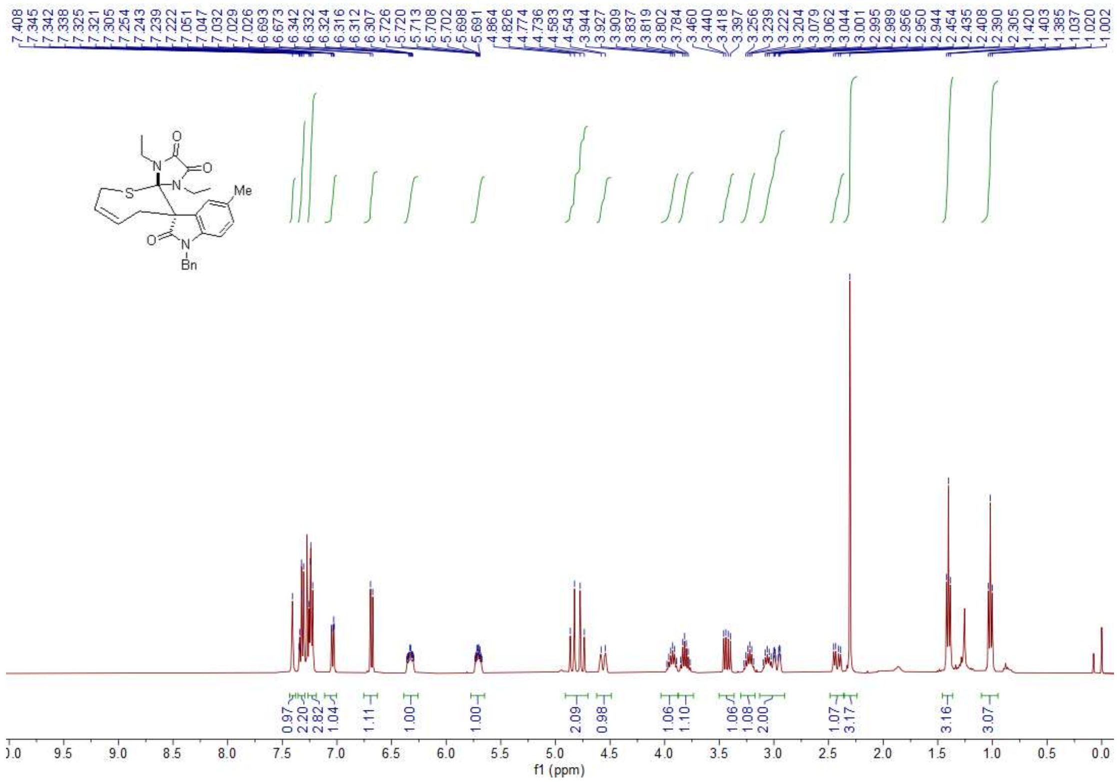
[1]H NMR Spectrum of **3p**



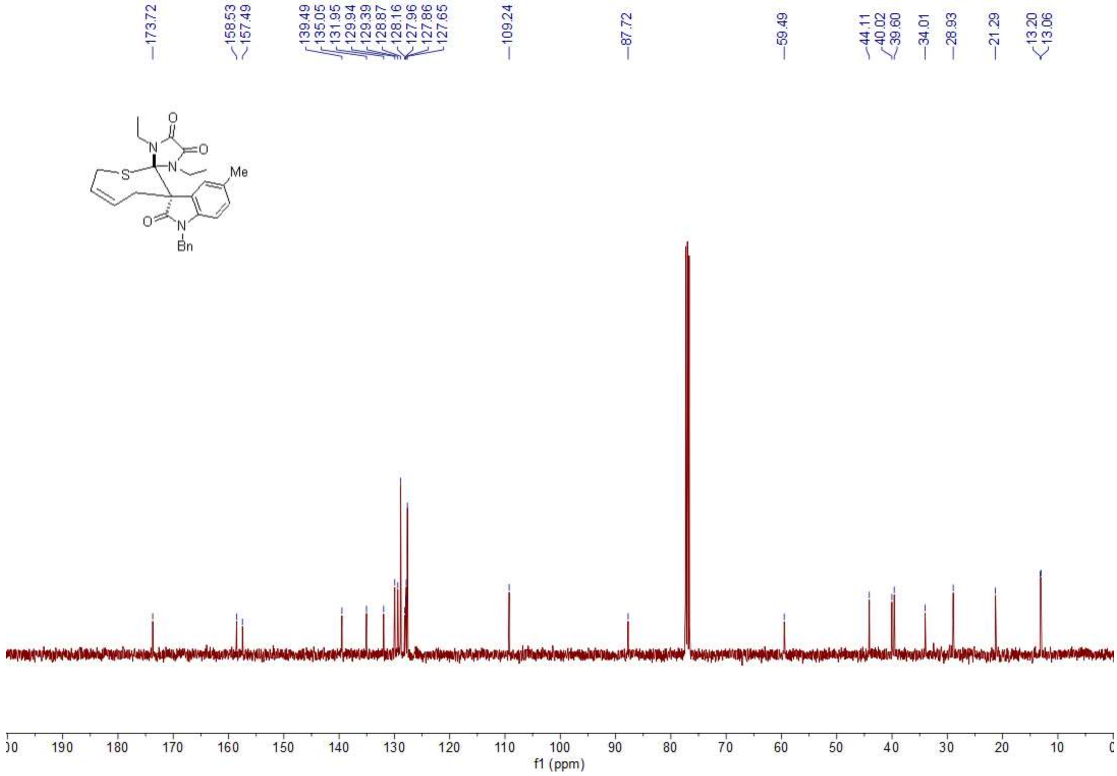
[13]C NMR Spectrum of **3p**



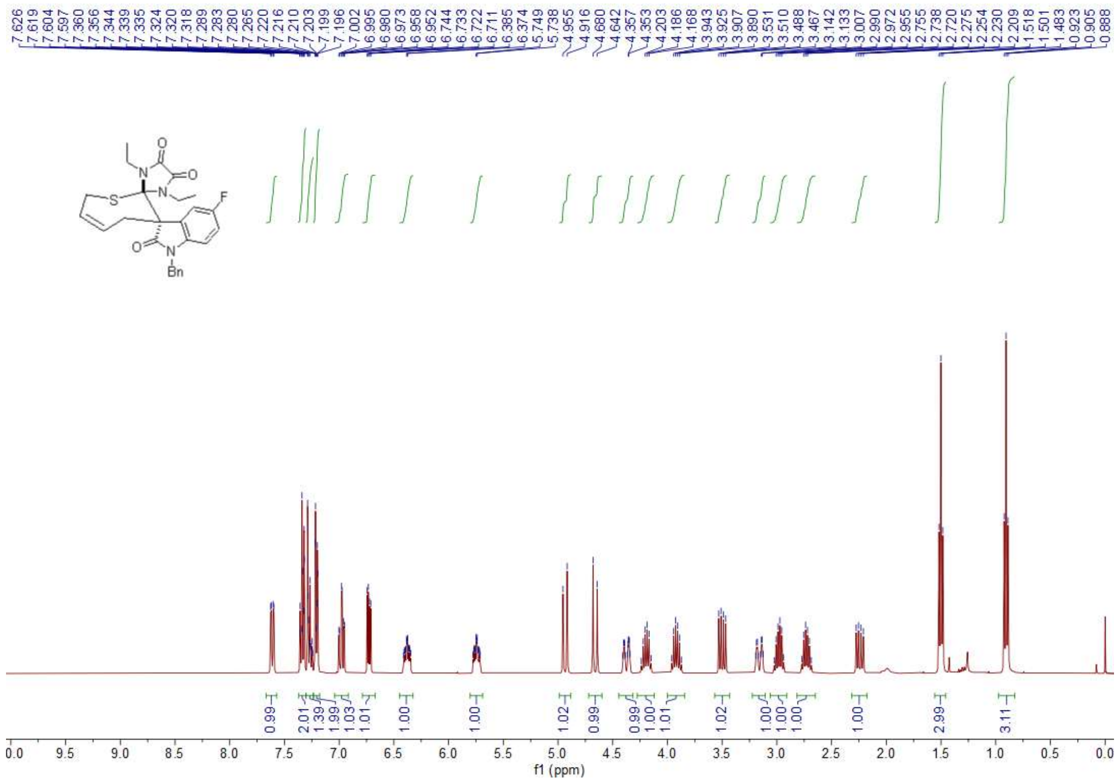
[1]H NMR Spectrum of **3q**



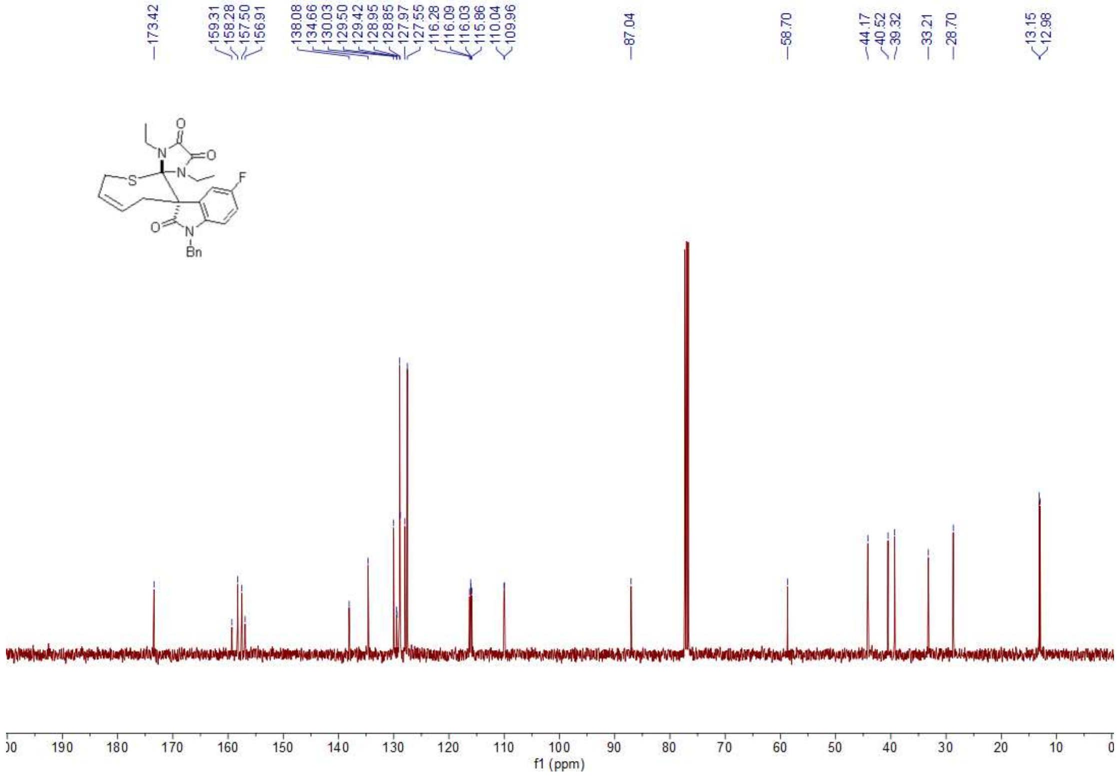
[13]C NMR Spectrum of **3q**



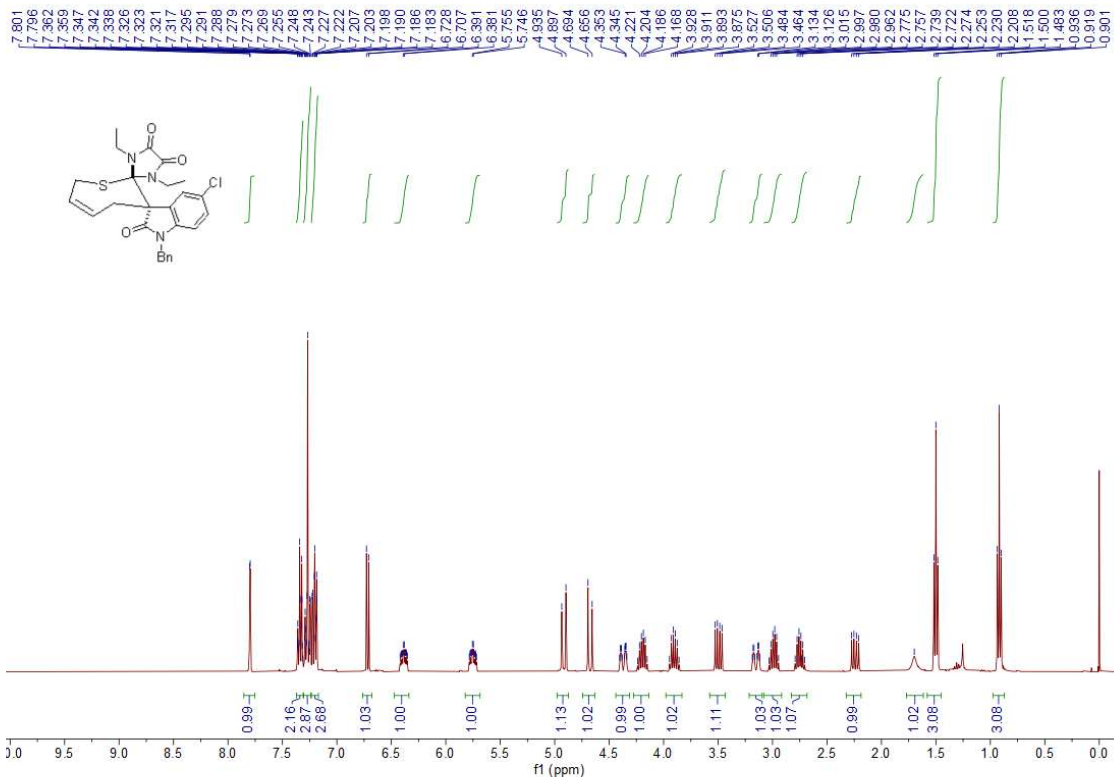
^{1}H NMR Spectrum of **3r**



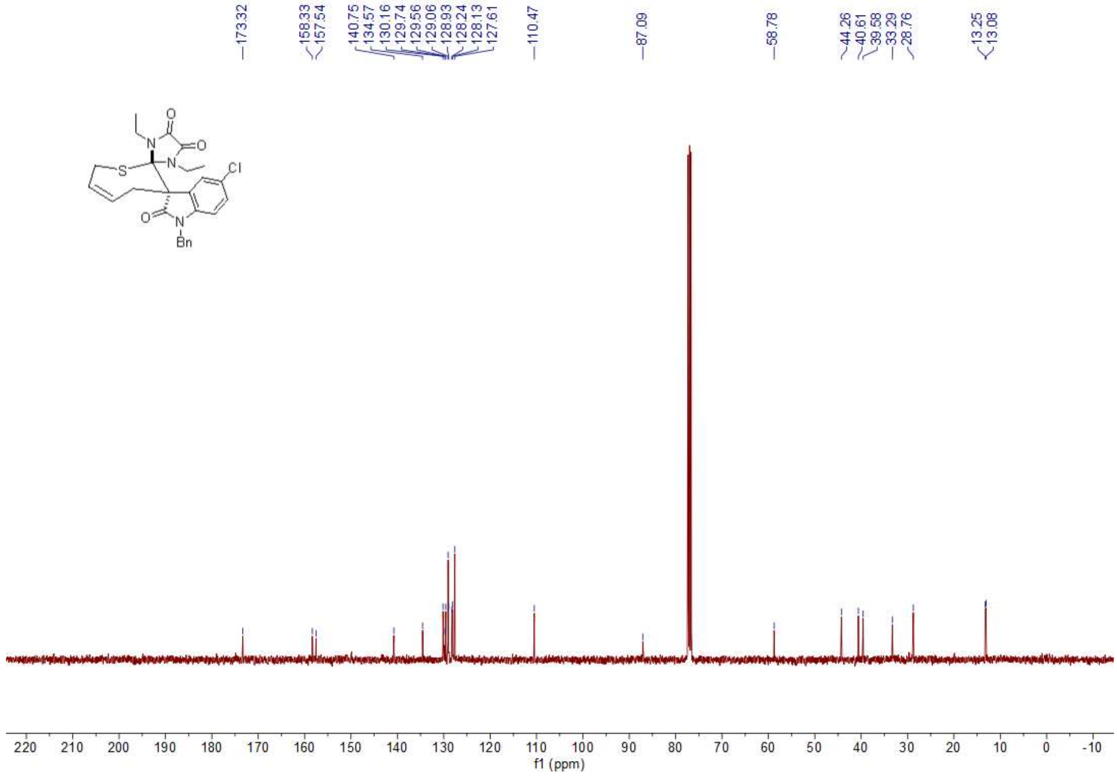
^{13}C NMR Spectrum of **3r**



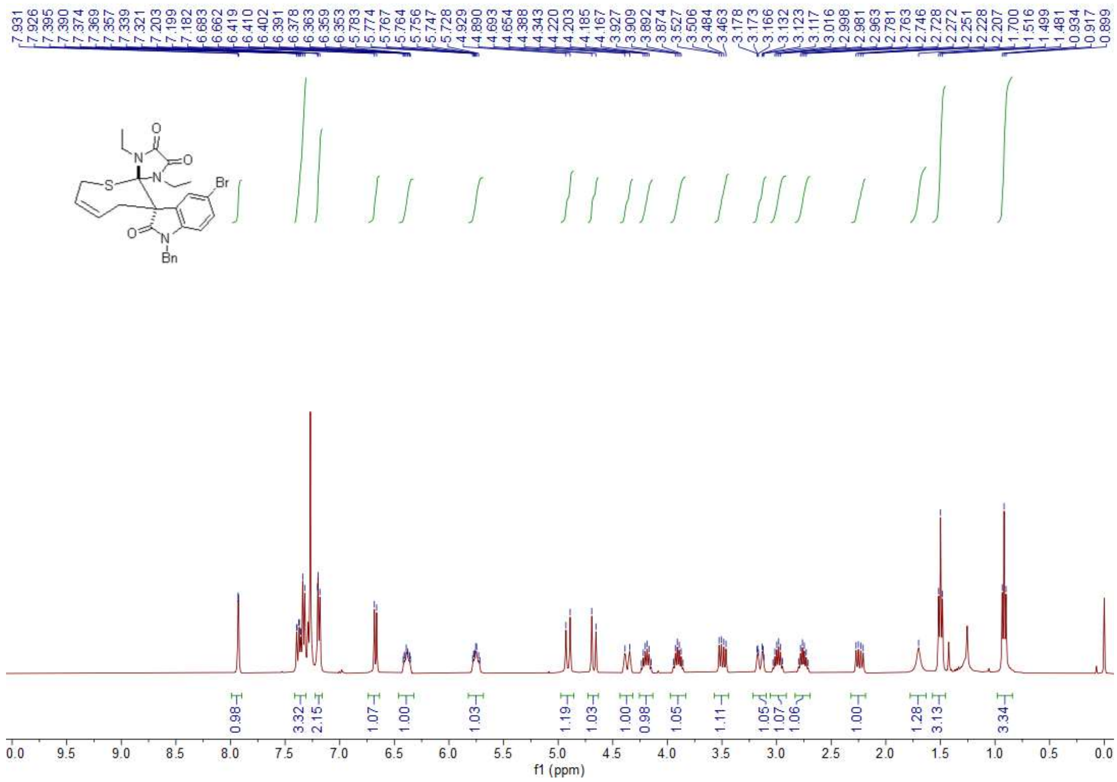
[1]H NMR Spectrum of **3s**



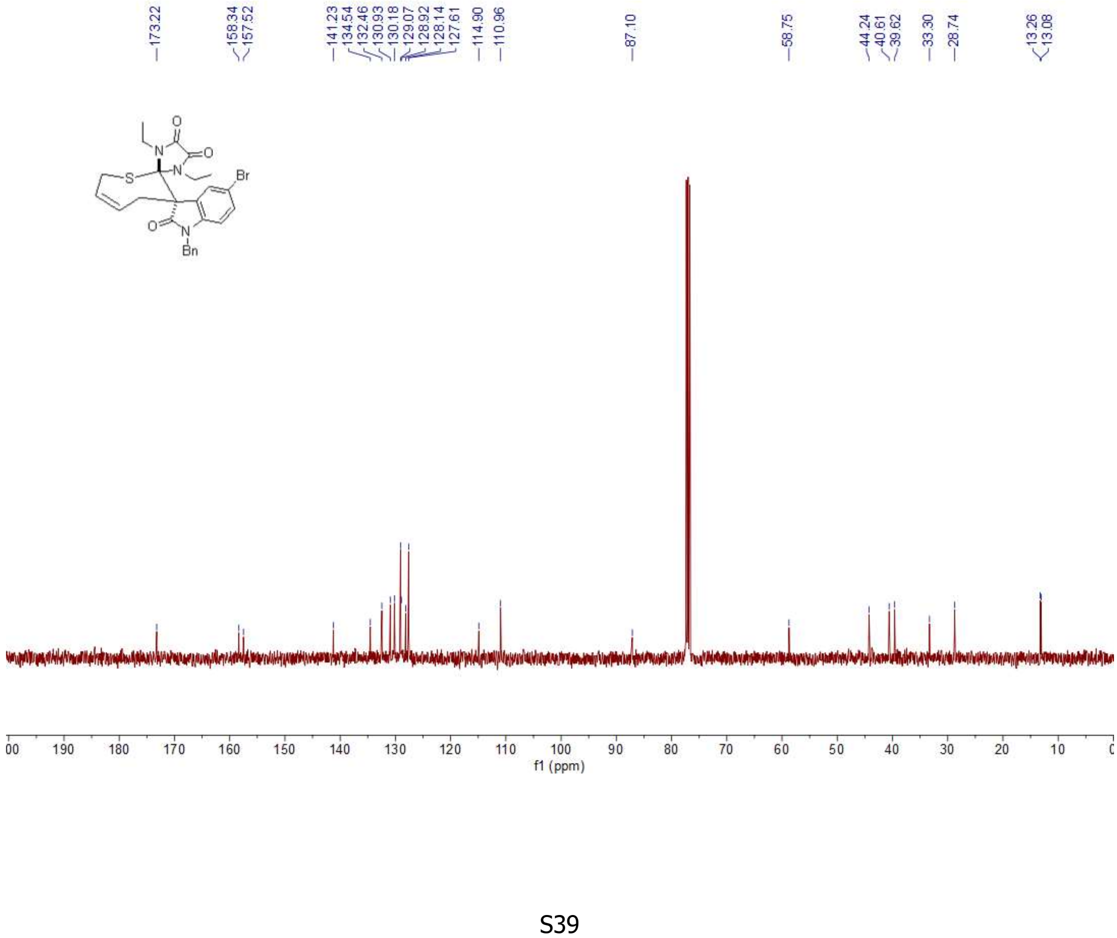
[13]C NMR Spectrum of **3s**



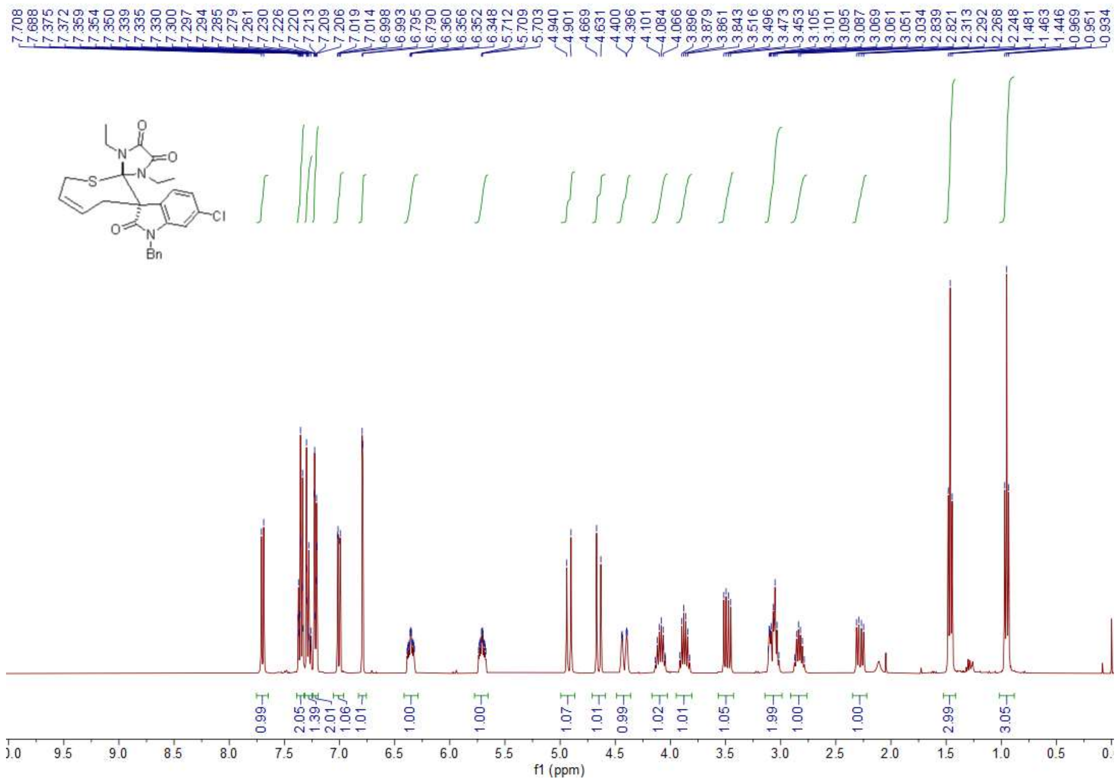
[1]H NMR Spectrum of **3t**



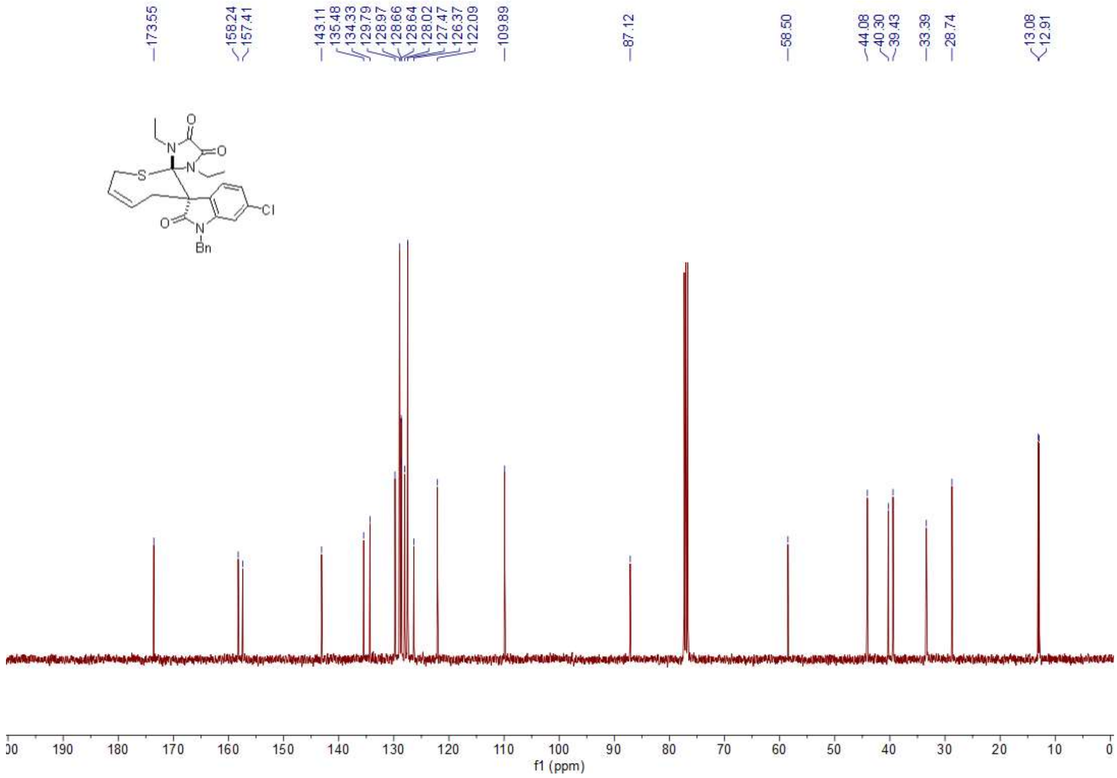
[13]C NMR Spectrum of **3t**



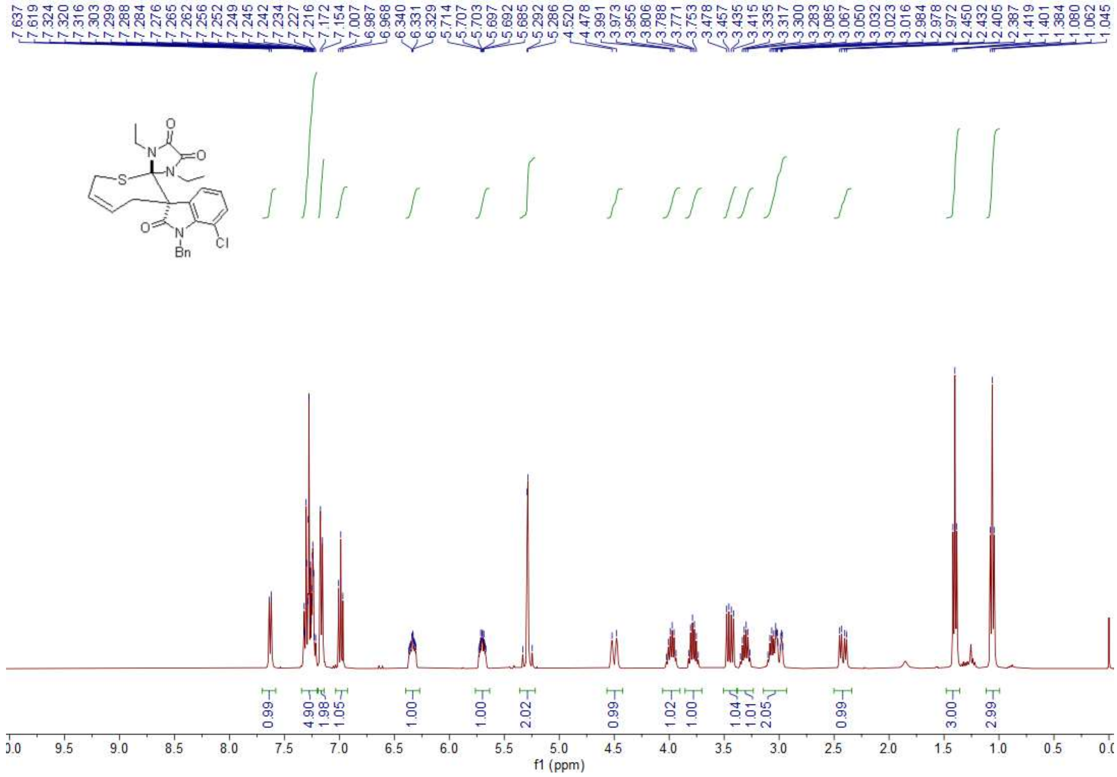
^{1}H NMR Spectrum of **3u**



^{13}C NMR Spectrum of **3u**



^{1}H NMR Spectrum of **3v**



^{13}C NMR Spectrum of **3v**