Supporting Information

Synthesis of Tetracyclic Dibenzo[*b,f*][1,4]oxazepine-Fused β-lactams *via* Visible-Light-Induced Staudinger annulation

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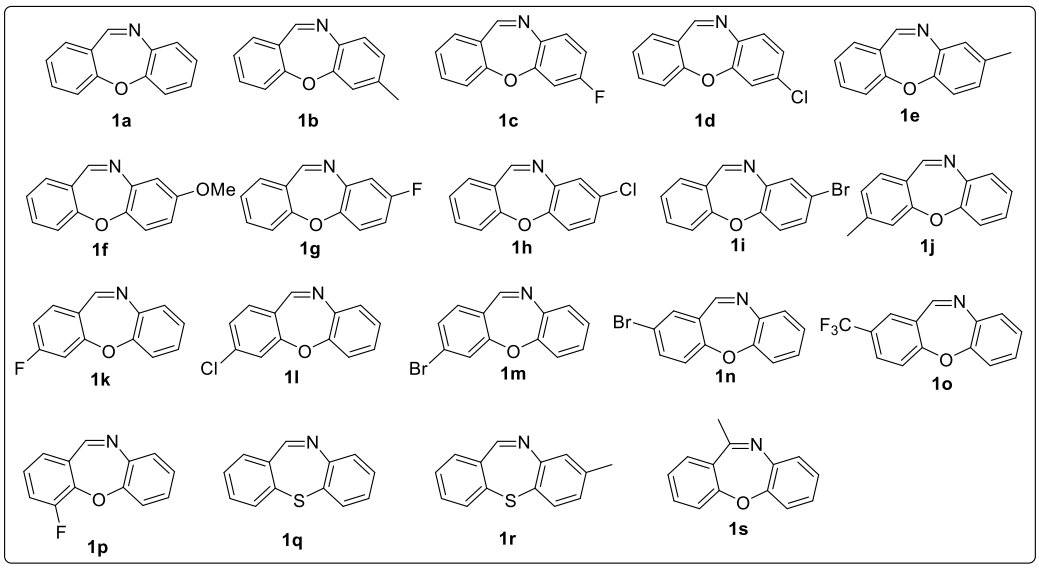
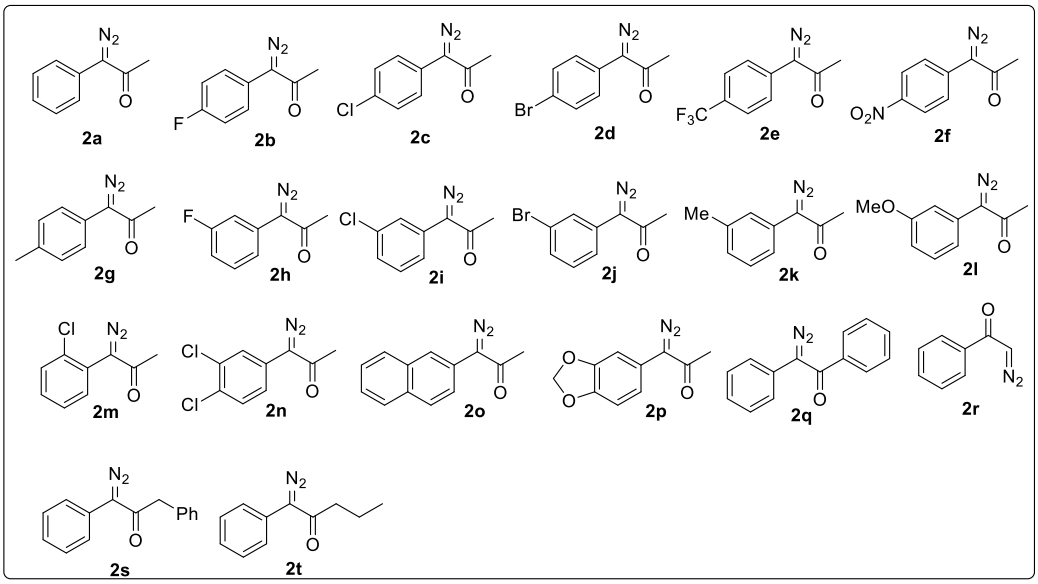
1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to standard methods. Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H NMR spectra were recorded on 400 MHz spectrophotometers. Chemical shifts (δ) are reported in ppm from the resonance of tetramethyl silane as the internal standard (TMS: 0.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on 100 MHz with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). The high resolution mass spectra (HRMS) were measured on a Shimadzu LCMS-IT-TOF mass spectrometer or DIONEX UltiMate 3000 & Bruker Compact TOF mass spectrometer by ESI.

2. Preparation of the Substrates

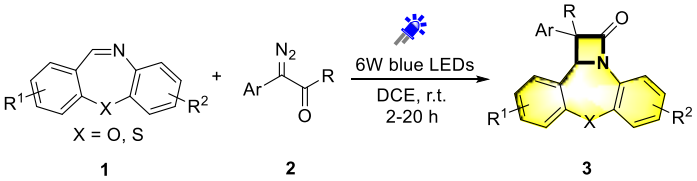
All the solvents were treated according to standard methods and all chemicals were used without purification. The dibenzoxazepine-imines **1**[1] and α-diazo ketones **2**[2] were known compounds or prepared from conventional methods.





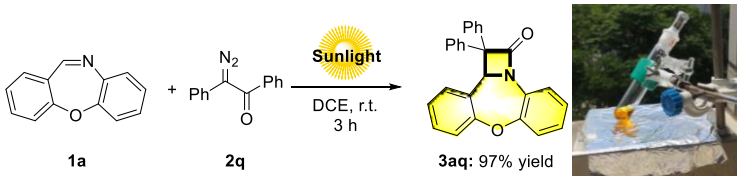
3. General Procedures for the Synthesis of Products

3.1 General procedure for the synthesis of products 3.



Procedure: An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with dibenzoxazepine-imines **1** (0.15 mmol, 1.0 equiv.), α-diazo ketones **2** (0.3 mmol, 2.0 equiv.) and 2 mL of anhydrous DCE under Argon and irradiation of 6W blue LEDs, after 2 h of stirring at room temperature until the reaction was completed, as monitored by TLC analysis. The product was purified by flash column chromatography on silica gel (PE/EA=20/1) to give product **3**. All the products **3** were prepared according to the above procedure.

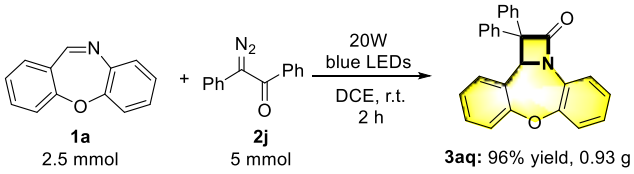
3.2 General procedure of the sunlight reaction.



Procedure: An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was

charged with dibenzoxazepine-imine **1a** (0.15 mmol, 1.0 equiv.), α-diazo ketone **2q** (0.3 mmol, 1.5 equiv.) and 2 mL of anhydrous DCE under Ar and irradiation of sunlight, after 3 h of stirring at ambient temperature until the reaction was completed, as monitored by TLC analysis. The product **3aq** was purified by flash column chromatography on silica gel (PE/EA=20/1).

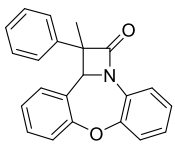
3.3 General procedure of gram-scale reaction.



Procedure: An oven-dried 100 mL Schlenk bottle equipped with a magnetic stir bar was charged with dibenzoxazepine-imine **1a** (2.5 mmol, 1.0 equiv.), α-diazo ketone **2q** (5 mmol, 1.5 equiv.) and 33 mL of anhygrous DCE under Argon and irradiation of 20W blue LEDs, after 4 h of stirring at room temperature until the reaction was completed, as monitored by TLC analysis. The product **3aq** was purified by flash column chromatography on silica gel (PE/EA=20/1).

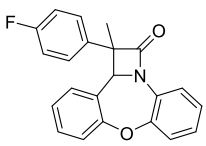
4. Characterization Data of Products

1-methyl-1-phenyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3aa)



White solid, 41.2 mg, 84% yield, >20:1 d.r.; m.p.: 125-126 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.75 (dd, J = 7.3, 2.2 Hz, 1H), 7.60 (d, J = 7.3 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.40-7.31 (m, 4H), 7.27 (dd, J = 7.1, 5.2 Hz, 1H), 7.18 (m, 3H), 5.42 (s, 1H), 1.65 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 169.2, 155.76, 150.3, 140.9, 129.6, 129.1, 129.0, 128.0, 127.5, 127.3, 126.6, 126.0, 125.1, 124.6, 124.5, 122.5, 121.5, 65.0, 64.4, 21.6; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1752; **HRMS** (ESI) for: $C_{22}H_{18}NO_2$ $[M+H]^+$: calcd 328.1332 found 328.1340.

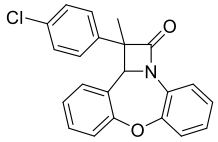
1-(4-fluorophenyl)-1-methyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3ab)



White solid, 45.1 mg, 87% yield, >20:1 d.r.; m.p.: 166-168 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.74 (d, J = 7.4 Hz, 1H), 7.60-7.52 (m, 2H), 7.37-7.24 (m, 4H), 7.21-7.10 (m, 5H), 5.37 (s,

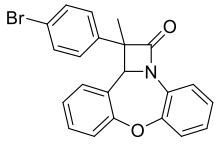
1H), 1.62 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 169.0, 162.1 (d, J = 246.6 Hz), 155.7, 150.3, 136.7 (d, J = 3.3 Hz), 129.7, 129.0, 127.8, 127.7, 127.6, 127.4, 126.4, 125.2, 124.6 (d, J = 2.7 Hz), 122.5, 121.5, 115.8 (d, J = 21.4 Hz), 65.1, 63.8, 21.7; **^{19}F NMR** (400 MHz, $CDCl_3$): δ (ppm) -114.60; **IR** (KBr, $\tilde{v}$, cm^{-1}): 1750; **HRMS** (ESI) for: $C_{22}H_{17}FNO_2$ $[M+H]^+$: calcd 346.1238, found 346.1246.

1-(4-chlorophenyl)-1-methyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3ac)



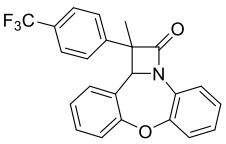
White solid, 45.6 mg, 84% yield, >20:1 d.r.; m.p.: 172-174 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.73 (d, J = 7.5 Hz, 1H), 7.53 (d, J = 8.1 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 7.38-7.28 (m, 4H), 7.23-7.12 (m, 3H), 5.37 (s, 1H), 1.62 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 168.8, 155.7, 150.4, 139.4, 133.4, 129.7, 129.1, 129.0, 127.9, 127.4, 126.3, 125.2, 124.6, 122.5, 121.6, 64.9, 63.9, 21.6; **IR** (KBr, $\tilde{v}$, cm^{-1}): 1748; **HRMS** (ESI) for: $C_{22}H_{17}ClNO_2$ $[M+H]^+$: calcd 362.0942, found 362.0949.

1-(4-bromophenyl)-1-methyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3ad)



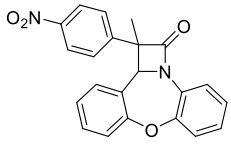
White solid, 53.6 mg, 88% yield, >20:1 d.r.; m.p.: 161-162 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.73 (d, J = 5.7 Hz, 1H), 7.59-7.54 (m, 2H), 7.47 (d, J = 8.1 Hz, 2H), 7.38-7.24 (m, 4H), 7.23-7.11 (m, 3H), 5.36 (s, 1H), 1.61 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 168.7, 155.7, 150.4, 139.9, 132.1, 129.7, 129.0, 127.9, 127.8, 127.4, 126.3, 125.2, 124.6, 122.5, 121.5, 121.5, 64.9, 63.9, 21.5; **IR** (KBr, $\tilde{v}$, cm^{-1}): 1751; **HRMS** (ESI) for: $C_{22}H_{17}BrNO_2$ $[M+H]^+$: calcd 406.0437, found 406.0442.

1-methyl-1-(4-(trifluoromethyl)phenyl)-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3ae)



White solid, 55.2 mg, 93% yield, >20:1 d.r.; m.p.:113-114 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.74-7.69 (m, 5H), 7.41-7.11 (m, 7H), 5.42 (s, 1H), 1.66 (d, J = 1.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 168.4, 155.8, 150.5, 144.9, 130.0 (q, J = 30), 129.9, 128.9, 127.9, 127.6, 126.5, 126.2, 126.0 (q, J = 3.3), 125.2, 124.7, 124.6, 124.0 (q, J = 270), 122.6, 121.6, 64.7, 64.2, 21.6; **^{19}F NMR** (400 MHz, $CDCl_3$): δ (ppm) -62.50; **IR** (KBr, $\tilde{v}$, cm^{-1}): 1755; **HRMS** (ESI) for: $C_{23}H_{17}F_3NO_2$ $[M+H]^+$: calcd 396.1206, found 396.1203.

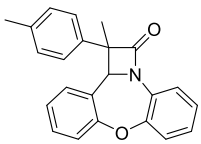
1-methyl-1-(4-nitrophenyl)-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3af)



White solid, 45.2 mg, 81% yield, >20:1 d.r.; m.p.: 150-152 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.31 (d, J = 7.6 Hz, 2H), 7.79 (d, J = 7.6 Hz, 2H), 7.73 (d, J = 7.3 Hz, 1H), 7.43-7.14 (m, 7H),

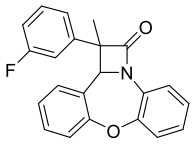
5.44 (s, 1H), 1.68 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 167.9, 155.9, 150.5, 148.1, 147.3, 130.1, 128.8, 127.8, 127.7, 127.1, 125.9, 125.3, 124.8, 124.7, 124.2, 122.7, 121.6, 64.6, 64.2, 21.7; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1757; **HRMS** (ESI) for: $C_{22}H_{17}N_2O_4$ $[M+H]^+$: calcd373.1183, found 373.1177.

1-methyl-1-(p-tolyl)-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3ag)



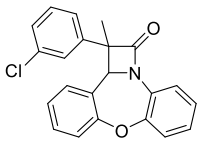
White solid, 43.5 mg, 85% yield, >20:1 d.r.; m.p.: 130-131 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.74 (d, J = 7.4 Hz, 1H), 7.48 (d, J = 7.7 Hz, 2H), 7.38-7.09 (m, 9H), 5.38 (s, 1H), 2.38 (s, 3H), 1.62 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 169.3, 155.7, 150.4, 138.0, 137.2, 129.6, 129.5, 129.1, 128.0, 127.2, 126.6, 125.9, 125.1, 124.6, 124.5, 122.4, 121.5, 65.1, 64.2, 21.5, 21.1; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1749; **HRMS** (ESI) for: $C_{23}H_{19}NNaO_2$ $[M+Na]^+$: calcd 364.1308, found 364.1306.

1-(3-fluorophenyl)-1-methyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3ah)



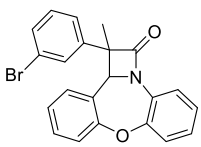
White solid, 50.3 mg, 97% yield, >20:1 d.r.; m.p.: 126-128 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.74 (dd, J = 7.5, 2.0 Hz, 1H), 7.45-7.12 (m, 10H), 7.06-7.02 (m, 1H), 5.38 (s, 1H), 1.63 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 168.6, 163.0 (d, J = 247.0 Hz), 155.7, 150.4, 143.3 (d, J = 7.2 Hz), 130.6 (d, J = 8.4 Hz), 129.7, 128.9, 127.9, 127.5, 126.2, 125.2, 124.7, 124.6, 122.5, 121.7 (d, J = 2.9 Hz), 121.5, 114.5 (d, J = 21.0 Hz), 113.3 (d, J = 22.2 Hz), 65.0, 64.1 (d, J = 1.8 Hz), 21.4; **^{19}F NMR** (400 MHz, $CDCl_3$): δ (ppm) -111.63; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1755; **HRMS** (ESI) for: $C_{22}H_{16}FNNaO_2$ $[M+Na]^+$: calcd 368.1057, found 368.1058.

1-(3-chlorophenyl)-1-methyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3ai)



White solid, 44.5 mg, 82% yield, >20:1 d.r.; m.p.: 117-119 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.74 (d, J = 5.5 Hz, 1H), 7.57 (d, J = 1.9 Hz, 1H), 7.52-7.47 (m, 1H), 7.41-7.11 (m, 9H), 5.38 (s, 1H), 1.63 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 168.6, 155.8, 150.4, 142.8, 134.9, 130.3, 129.8, 128.9, 127.9, 127.8, 127.5, 126.3, 126.3, 125.2, 124.6, 124.2, 122.5, 121.6, 64.9, 64.0, 21.4; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1750; **HRMS** (ESI) for: $C_{22}H_{16}ClNNaO_2$ $[M+Na]^+$: calcd 384.0762, found 384.0764.

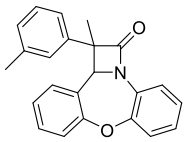
1-(3-bromophenyl)-1-methyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3aj)



White solid, 54.2 mg, 89% yield; >20:1 d.r.; m.p.: 134-136 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.77-7.70 (m, 2H), 7.55-7.47 (m, 2H), 7.39-7.12 (m, 8H), 5.39 (s, 1H), 1.63 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 168.5, 155.8, 150.4, 143.1, 130.7, 130.5,

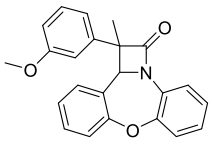
129.8, 129.2, 129.0, 127.9, 127.5, 126.3, 125.2, 124.7, 124.7, 124.6, 123.1, 122.6, 121.6, 64.9, 64.0, 21.5; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1753; **HRMS** (ESI) for: $C_{22}H_{17}BrNO_2$ $[M+H]^+$: calcd 406.0437, found 406.0436.

1-methyl-1-(m-tolyl)-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3ak)



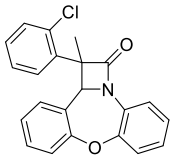
White solid, 46.1 mg, 90% yield, >20:1 d.r.; m.p.: 93-95 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.76 (dd, J = 7.0, 2.3 Hz, 1H), 7.47-7.10 (m, 11H), 5.42 (s, 1H), 2.41 (s, 3H), 1.64 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 169.2, 155.8, 150.1, 140.9, 138.7, 129.5, 129.1, 128.8, 128.2, 127.9, 127.1, 126.7, 126.6, 125.1, 124.5, 124.4, 123.0, 122.4, 121.5, 64.9, 64.3, 21.7, 21.5; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1751; **HRMS** (ESI) for: $C_{23}H_{20}NO_2$ $[M+H]^+$: calcd 342.1489, found 342.1487.

1-(3-methoxyphenyl)-1-methyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3al)



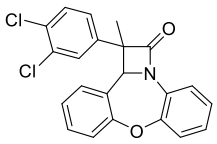
White solid, 50.9 mg, 95% yield, >20:1 d.r.; m.p.: 79-81 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.74 (d, J = 7.4 Hz, 1H), 7.40-7.23 (m, 5H), 7.20-7.11 (m, 5H), 6.90-6.85 (m, 1H), 5.40 (s, 1H), 3.85 (s, 3H), 1.63 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 169.0, 159.9, 155.7, 150.2, 142.5, 130.0, 129.5, 129.0, 127.9, 127.2, 126.5, 125.0, 124.5, 124.5, 122.4, 121.5, 118.2, 112.5, 112.0, 64.9, 64.3, 55.3, 21.6; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1755; **HRMS** (ESI) for: $C_{23}H_{20}NO_3$ $[M+H]^+$: calcd 358.1438, found 358.1439.

1-(2-chlorophenyl)-1-methyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3am)



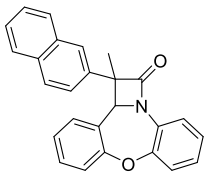
White solid, 47.8 mg, 88% yield, >20:1 d.r.; m.p.: 85-87 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.01 (d, J = 7.8 Hz, 1H), 7.95-7.91 (m, 1H), 7.43-7.38 (m, 1H), 7.31 (t, J = 4.7 Hz, 2H), 7.26-7.01 (m, 5H), 6.85-6.81 (m, 1H), 6.58 (d, J = 7.8 Hz, 1H), 5.76 (s, 1H), 2.18 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 168.1, 157.6, 146.1, 135.4, 134.0, 130.8, 130.0, 129.6, 129.4, 129.4, 127.5, 125.4, 125.2, 125.1, 124.9, 121.3, 121.3, 121.1, 63.8, 62.1, 24.9; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1744; **HRMS** (ESI) for: $C_{22}H_{17}ClNO_2$ $[M+H]^+$: calcd 362.0942, found 362.0945.

1-(3,4-dichlorophenyl)-1-methyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3an)



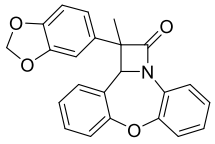
White solid, 55.9 mg, 94% yield; >20:1 d.r.; m.p.: 141-143 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.73 (dd, J = 7.6, 1.9 Hz, 1H), 7.68 (d, J = 2.1 Hz, 1H), 7.53-7.42 (m, 2H), 7.38-7.13 (m, 7H), 5.35 (s, 1H), 1.61 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 168.2, 155.7, 150.4, 141.0, 133.1, 131.7, 130.9, 129.9, 128.8, 128.1, 127.8, 127.6, 126.0, 125.5, 125.2, 124.7, 124.6, 122.6, 121.6, 64.8, 63.5, 21.4; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1765; **HRMS** (ESI) for: $C_{22}H_{16}Cl_2NO_2$ $[M+H]^+$: calcd 396.0553, found 396.0556.

1-methyl-1-(naphthalen-2-yl)-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3ao)



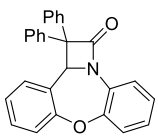
White solid, 47.6 mg, 84% yield; >20:1 d.r.; m.p.: 123-125 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.07 (s, 1H), 7.96-7.84 (m, 3H), 7.79 (dd, J = 7.3, 2.1 Hz, 1H), 7.68 (dd, J = 8.6, 1.9 Hz, 1H), 7.58-7.06 (m, 9H), 5.51 (s, 1H), 1.74 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 169.2, 155.8, 150.3, 138.2, 133.4, 132.6, 129.6, 129.2, 128.9, 128.1, 128.0, 127.7, 127.3, 126.7, 126.5, 126.2, 125.2, 124.7, 124.6, 124.1, 122.5, 121.5, 65.0, 64.6, 21.5; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1749; **HRMS** (ESI) for: $C_{26}H_{20}NO_2$ $[M+H]^+$: calcd 378.1489, found 378.1488.

1-(benzo[d][1,3]dioxol-5-yl)-1-methyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3ap)



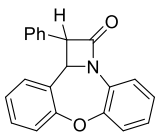
White solid, 50.1 mg, 90% yield; >20:1 d.r.; m.p.: 133-135 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.74 (dd, J = 7.4, 1.9 Hz, 1H), 7.37-7.02 (m, 9H), 6.86 (d, J = 8.0 Hz, 1H), 5.98 (s, 2H), 5.33 (s, 1H), 1.60 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 169.2, 155.6, 150.4, 148.1, 146.9, 134.7, 129.6, 129.1, 127.9, 127.3, 126.5, 125.1, 124.6, 124.5, 122.4, 121.5, 119.1, 108.6, 106.7, 101.2, 65.4, 64.1, 21.5; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1751; **HRMS** (ESI) for: $C_{23}H_{18}NO_4$ $[M+H]^+$: calcd 372.1230, found 372.1236.

1,1-diphenyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3aq)[3]



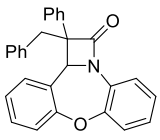
White solid, 57.2 mg, 98% yield; m.p.: 195-197 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.07 (dd, J = 7.6, 2.2 Hz, 1H), 7.70 (d, J = 7.6 Hz, 2H), 7.49 (t, J = 7.5 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 7.31-7.23 (m, 1H), 7.22-7.10 (m, 7H), 7.04 (d, J = 6.3 Hz, 2H), 6.76 (t, J = 7.5 Hz, 1H), 6.38 (d, J = 7.8 Hz, 1H), 6.18 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 166.7, 157.5, 147.0, 138.6, 137.8, 129.4, 129.2, 129.0, 128.8, 128.3, 128.1, 127.9, 127.8, 127.4, 125.9, 125.2, 124.0, 122.1, 121.6, 121.6, 72.2, 64.0; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1758; **HRMS** (ESI) for: $C_{27}H_{20}NO_2$ $[M+H]^+$: calcd 390.1489, found 390.1485.

1-phenyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3ar)



White solid, 42.3 mg, 90% yield; >20:1 d.r.; m.p.: 112-114 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.09 (d, J = 8.0 Hz, 1H), 7.58-7.19 (m, 10H), 7.09 (t, J = 7.7 Hz, 1H), 7.01 (t, J = 7.7 Hz, 1H), 5.68 (d, J = 2.9 Hz, 1H), 4.84 (d, J = 3.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 163.9, 158.3, 144.0, 134.1, 130.4, 130.4, 130.0, 129.1, 128.0, 127.5, 126.2, 125.3, 125.3, 124.4, 121.7, 121.6, 120.1, 60.2, 58.6; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1756; **HRMS** (ESI) for: $C_{21}H_{16}NO_2$ $[M+H]^+$: calcd 314.1176, found 314.1175.

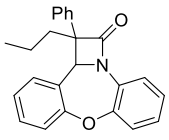
1-benzyl-1-phenyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3as)



White solid, 38.1 mg, 63% yield; 1:1.7 d.r.; m.p.: 101-103 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.58-6.97 (m, 16.45H, major+minor), 6.79-6.75 (m, 0.65H, minor), 6.68 (d, J = 7.4 Hz, 0.71H, minor), 6.46

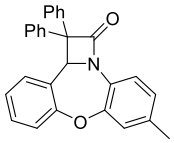
(d, *J* = 7.7 Hz, 0.64H, minor), 5.32 (s, 0.35H, minor), 5.24 (s, 0.61H, major), 3.74-3.63 (m, 1.33H, major), 3.34-2.98 (m, 0.77H, minor); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm, major+minor) 168.3, 168.0, 156.1, 155.3, 153.3, 149.9, 139.1, 136.2, 135.9, 135.3, 130.7, 130.4, 129.7, 129.2, 128.9, 128.8, 128.7, 128.5, 128.4, 128.3, 127.8, 127.7, 127.4, 127.2, 127.0, 126.6, 126.5, 126.3, 125.7, 125.2, 125.0, 124.7, 123.9, 123.8, 122.9, 121.7, 121.5, 121.3, 69.2, 65.4, 61.1, 42.4, 39.8; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1757; **HRMS** (ESI) for: $C_{28}H_{22}NO_2$ $[M+H]^+$: calcd 404.1645, found 404.1646.

1-phenyl-1-propyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3at)



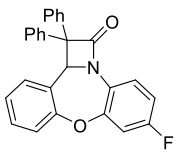
White solid, 34.7 mg, 65% yield; 1:1 d.r.; m.p.: 97-99 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm, major+minor) 8.01-7.91 (m, 0.50H), 7.65-7.60 (m, 1.47H), 7.50-7.01 (m, 10.91H), 6.72 (t, *J* = 7.4 Hz, 0.51H), 6.26 (d, *J* = 7.8 Hz, 0.49H), 5.40 (s, 0.50H), 5.23 (s, 0.49H), 2.58-2.27 (m, 1.05H), 1.96-1.79 (m, l.66H), 1.70-1.46 (m, 1.39H), 1.05 (t, *J* = 7.4 Hz, 1.57H), 0.72 (t, *J* = 7.3 Hz, 1.50H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm, major+minor) 168.7, 168.6, 156.8, 155.4, 151.8, 148.5, 140.0, 136.0, 129.5, 129.0, 128.9, 128.8, 128.4, 128.3, 127.9, 127.8(8), 127.7(7), 127.7(0), 127.6(7), 127.6(1), 127.3, 126.6, 126.3, 126.3, 125.5, 125.2, 125.1, 124.5, 124.0, 123.1, 122.6, 121.5, 121.4(7), 121.4(4), 68.8, 68.4, 65.2, 63.6, 37.8, 37.5, 18.2, 18.0, 14.5, 14.3; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1747; **HRMS** (ESI) for: $C_{24}H_{22}NO_2$ $[M+H]^+$: calcd 356.1645, found 356.1649.

6-methyl-1,1-diphenyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3bq)



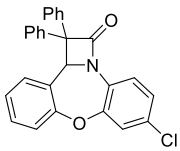
White solid, 53.3 mg, 88% yield; m.p.: 179-181 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.88 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.20-7.00 (m, 8H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.42 (d, *J* = 7.7 Hz, 1H), 6.09 (s, 1H), 2.32 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 166.6, 157.2, 147.5, 138.7, 137.9, 136.5, 129.1, 128.9, 128.8, 128.3(0), 128.2(5), 128.1(9), 127.8, 127.7, 127.1, 126.6, 125.7, 123.9, 122.2, 121.9, 121.7, 72.4, 64.0, 21.0; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1755; **HRMS** (ESI) for: $C_{28}H_{22}NO_2$ $[M+H]^+$: calcd 404.1645, found 404.1640.

6-fluoro-1,1-diphenyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3cq)



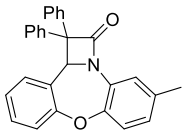
White solid, 60.5 mg, 99% yield; m.p.: 249-252 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.04 (d, *J* = 8.6 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.51-7.40 (m, 3H), 7.28-7.09 (m, 7H), 7.01 (d, *J* = 7.2 Hz, 2H), 6.82-6.70 (m, 1H), 6.34 (d, *J* = 7.8 Hz, 1H), 6.18 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 166.8, 160.0 (d, *J* = 247.1 Hz), 156.6, 148.8 (d, *J* = 11.3 Hz), 138.5, 137.6, 129.3, 128.89, 128.85, 128.5, 128.27, 128.25, 127.9, 127.8, 126.8, 125.6 (d, *J* = 3 Hz), 124.3, 123.6 (d, *J* = 9.5 Hz), 121.7, 112.0 (d, *J* = 22.3 Hz), 109.3 (d, *J* = 24.7 Hz), 72.8, 64.1; **^{19}F NMR** (400 MHz, $CDCl_3$): δ (ppm) -113.61; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1755; **HRMS** (ESI) for: $C_{27}H_{19}FNO_2$ $[M+H]^+$: calcd 408.1394, found 408.1393.

6-chloro-1,1-diphenyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3dq)



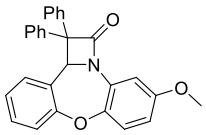
White solid, 63.5 mg, >99% yield; m.p.: 219-221 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.98-7.94 (m, 1H), 7.70 (d, J = 7.5 Hz, 2H), 7.52-7.40 (m, 3H), 7.16 (t, J = 4.0 Hz, 6H), 7.04-6.98 (m, 3H), 6.93-6.74 (m, 3H), 6.47 (d, J = 7.7 Hz, 1H), 6.08 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 166.6, 157.2, 146.9, 138.4, 137.6, 130.1, 129.4, 129.0, 128.9, 128.4, 128.2, 128.1, 128.0, 127.3, 125.2, 124.3, 122.5, 122.0, 121.6, 72.3, 63.8; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1756; **HRMS** (ESI) for: $C_{27}H_{19}ClNO_2$ $[M+H]^+$: calcd 424.1099, found 404.1091.

5-methyl-1,1-diphenyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3eq)



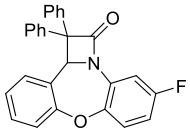
White solid, 54.5 mg, 90% yield; m.p.: 185-187 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.89 (s, 1H), 7.75-7.64 (m, 2H), 7.54-7.37 (m, 3H), 7.23-7.10 (m, 6H), 7.08-7.02 (m, 2H), 6.91 (d, J = 8.2 Hz, 1H), 6.75 (t, J = 7.3 Hz, 1H), 6.37 (d, J = 7.8 Hz, 1H), 6.15 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 166.7, 157.6, 145.0, 138.7, 137.9, 135.1, 129.2, 129.0, 128.9, 128.8, 128.3, 128.1, 127.8, 127.8, 127.4, 126.5, 123.9, 122.3, 121.6, 121.2, 72.1, 64.0, 20.8; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1759; **HRMS** (ESI) for: $C_{28}H_{22}NO_2$ $[M+H]^+$: calcd 404.1645, found 404.1646.

5-methoxy-1,1-diphenyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3fq)



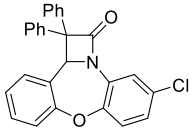
White solid, 52.2 mg, 83% yield; m.p.: 137-140 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.70-7.68 (m, 3H), 7.50-7.39 (m, 3H), 7.25-7.10 (m, 6H), 7.05-7.04 (m, 2H), 6.82-6.71 (m, 1H), 6.64-6.61 (m, 1H), 6.32 (d, J = 7.7 Hz, 1H), 6.21 (s, 1H), 3.79 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 166.8, 158.1, 156.6, 140.5, 138.6, 137.9, 129.7, 129.2, 129.0, 128.9, 128.3, 128.2, 128.0, 127.9, 127.6, 123.9, 122.2, 121.5, 111.8, 105.9, 72.0, 63.9, 55.8; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1748; **HRMS** (ESI) for: $C_{28}H_{22}NO_3$ $[M+H]^+$: calcd 420.1594, found 420.1593.

5-fluoro-1,1-diphenyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3gq)



White solid, 61.1 mg, >99% yield; m.p.: 207-209 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.91 (d, J = 9.0 Hz, 1H), 7.67 (d, J = 7.5 Hz, 1H), 7.51-7.40 (m, 3H), 7.29-7.14 (m, 6H), 7.03 (d, J = 7.3 Hz, 2H), 6.78-6.75 (m, 2H), 6.29-6.26 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 166.8, 159.2 (d, J = 243.8 Hz), 157.9, 142.1, 138.3, 137.6, 130.1 (d, J = 11.7 Hz), 129.4, 129.1, 128.9, 128.4, 128.2, 128.05, 127.99, 127.9, 127.8, 124.3, 122.5 (d, J = 9.5 Hz), 121.49, 111.7 (d, J = 23.4 Hz), 108.3 (d, J = 28.0 Hz), 72.04, 63.82; **^{19}F NMR** (400 MHz, $CDCl_3$): δ (ppm) -115.57; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1751; **HRMS** (ESI) for: $C_{27}H_{19}FNO_2$ $[M+H]^+$: calcd 408.1394, found 408.1399.

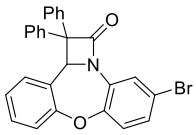
5-chloro-1,1-diphenyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3hq)



White solid, 63.6 mg, >99% yield; m.p.: 190-191 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.17 (d, J = 2.4 Hz, 1H), 7.67 (d, J = 7.6 Hz, 2H), 7.51-7.41 (m, 3H), 7.25-7.15 (m, 6H), 7.06-7.01 (m, 3H), 6.77

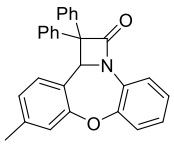
(p, *J* = 3.9 Hz, 1H), 6.30 (d, *J* = 7.8 Hz, 1H), 6.23 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): *δ* (ppm) 166.7, 157.5, 144.7, 138.3, 137.6, 130.2, 130.1, 129.4, 129.0, 128.9, 128.4, 128.2, 128.04, 128.01, 127.96, 127.5, 125.3, 124.3, 122.7, 121.5, 121.2, 72.1, 63.9; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1750; **HRMS** (ESI) for: $C_{27}H_{19}ClNO_2$ $[M+H]^+$: calcd 424.1099, found 404.1106.

5-bromo-1,1-diphenyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3iq)



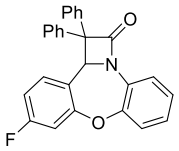
White solid, 70.2 mg, >99% yield; m.p.: 193-194 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 8.31 (d, *J* = 2.2 Hz, 1H), 7.75-7.64 (m, 2H), 7.51-7.40 (m, 3H), 7.29-7.11 (m, 7H), 7.02 (d, *J* = 7.2 Hz, 2H), 6.79-6.75 (m, 1H), 6.31 (d, *J* = 7.8 Hz, 1H), 6.22 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): *δ* (ppm) 166.7, 157.4, 145.3, 138.3, 137.5, 130.5, 129.4, 129.0, 128.9, 128.39, 128.36, 128.2, 128.04, 128.01, 127.96, 127.5, 124.3, 124.1, 123.0, 121.6, 117.5, 72.2, 63.9; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1756; **HRMS** (ESI) for: $C_{27}H_{19}BrNO_2$ $[M+H]^+$: calcd 468.0594, found 468.0597.

10-methyl-1,1-diphenyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3jq)



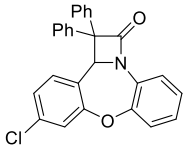
White solid, 57.5 mg, 95% yield; m.p.: 155-157 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 8.08 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.49-7.37 (m, 3H), 7.27 – 7.00 (m, 9H), 6.56 (d, *J* = 7.9 Hz, 1H), 6.20 (d, *J* = 7.9 Hz, 1H), 6.15 (s, 1H), 2.22 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): *δ* (ppm) 166.7, 157.4, 146.7, 139.5, 138.7, 137.9, 129.4, 129.0, 128.8, 128.2, 127.79, 127.76, 127.67, 125.7, 125.1, 124.7, 124.4, 122.1, 121.8, 121.5, 71.9, 63.8, 20.9; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1759; **HRMS** (ESI) for: $C_{28}H_{22}NO_2$ $[M+H]^+$: calcd 404.1645, found 404.1649.

10-fluoro-1,1-diphenyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3kq)



White solid, 59.9 mg, 98% yield; m.p.: 197-199 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 8.06 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.50-7.39 (m, 3H), 7.30-7.09 (m, 6H), 7.02 (d, *J* = 7.0 Hz, 2H), 6.92 (d, *J* = 9.2 Hz, 1H), 6.48 (t, *J* = 8.4 Hz, 1H), 6.32 (t, *J* = 7.5 Hz, 1H), 6.10 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): *δ* (ppm) 166.5, 162.2 (d, *J* = 249.6 Hz), 158.1 (d, *J* = 10.8 Hz), 146.5, 138.4, 137.6, 129.15, 129.07 (d, *J* = 4.7 Hz), 128.9, 128.9, 128.4, 128.2, 128.0, 127.9, 126.0, 125.4, 123.4 (d, *J* = 3.8 Hz), 122.1, 121.5, 111.0 (d, *J* = 21.1 Hz), 109.5 (d, *J* = 23.2 Hz), 72.3, 63.5; **^{19}F NMR** (400 MHz, $CDCl_3$): *δ* (ppm) -130.98; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1750; **HRMS** (ESI) for: $C_{27}H_{19}FNO_2$ $[M+H]^+$: calcd 408.1394, found 408.1393.

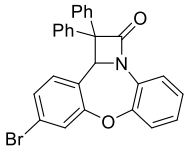
10-chloro-1,1-diphenyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3lq)



White solid, 63.5 mg, >99% yield; m.p.: 192-194 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 8.11-8.03 (m, 1H), 7.67 (d, *J* = 7.7 Hz, 2H), 7.57-7.37 (m, 3H), 7.30-7.10 (m, 6H), 7.02 (d, *J* = 7.3 Hz, 2H), 6.75 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.28 (d, *J* = 8.5 Hz, 1H), 6.11 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): *δ* (ppm) 166.5, 157.7, 146.5, 138.3, 137.5, 134.2, 129.1,

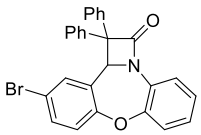
128.9, 128.4, 128.2, 128.1, 128.0, 126.0, 125.5, 124.2, 122.2, 122.1, 121.5, 72.3, 63.5; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1748; **HRMS** (ESI) for: $C_{27}H_{18}ClNNaO_2$ $[M+Na]^+$: calcd 446.0918, found 446.0927.

10-bromo-1,1-diphenyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3mq)



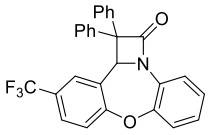
White solid, 70.2 mg, >99% yield; m.p.: 181-183 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.07 (d, J = 7.7 Hz, 1H), 7.66 (d, J = 7.6 Hz, 2H), 7.52-7.33 (m, 4H), 7.28-7.08 (m, 6H), 7.02 (d, J = 7.1 Hz, 2H), 6.89 (dd, J = 8.2, 1.9 Hz, 1H), 6.21 (d, J = 8.3 Hz, 1H), 6.09 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 166.4, 157.7, 146.3, 138.3, 137.5, 129.1, 129.1, 128.9, 128.4, 128.2, 128.1, 128.0, 127.1, 126.6, 126.0, 125.5, 125.1, 122.0, 121.9, 121.5, 72.3, 63.5; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1752; **HRMS** (ESI) for: $C_{27}H_{19}BrNO_2$ $[M+H]^+$: calcd 468.0594, found 468.0599.

11-bromo-1,1-diphenyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3nq)



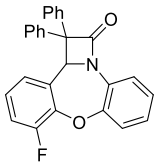
White solid, 66 mg, 94% yield; m.p.: 174-176 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.06 (d, J = 7.7 Hz, 1H), 7.67 (d, J = 7.5 Hz, 2H), 7.54-7.36 (m, 3H), 7.27-7.21 (m, 5H), 7.18-7.01 (m, 5H), 6.38 (s, 1H), 6.12 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 166.4, 156.4, 146.4, 138.2, 137.3, 132.0, 131.1, 129.4, 129.1, 128.91, 128.89, 128.5, 128.22, 128.19, 128.0, 126.0, 125.4, 123.3, 122.1, 121.4, 116.8, 72.4, 63.2; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1756; **HRMS** (ESI) for: $C_{27}H_{19}BrNO_2$ $[M+H]^+$: calcd 468.0594, found 468.0596.

1,1-diphenyl-11-(trifluoromethyl)-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3oq)



White solid, 63.1 mg, 92% yield; m.p.: 134-136 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.08 (d, J = 7.6 Hz, 1H), 7.69 (d, J = 7.6 Hz, 2H), 7.50 (t, J = 7.5 Hz, 2H), 7.44-7.39 (m, 2H), 7.30-7.10 (m, 7H), 7.02 (d, J = 7.3 Hz, 2H), 6.57 (s, 1H), 6.16 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 166.2, 159.6, 146.1, 138.1, 137.1, 129.0, 128.9, 128.8, 128.6, 128.3, 128.2, 128.1, 126.23 (q, J = 3.5), 126.21, 126.1, 125.9, 125.7 (q, J = 3.6), 125.5, 123.3 (q, J = 270), 122.2, 122.1, 121.5, 72.6, 63.2; **^{19}F NMR** (400 MHz, $CDCl_3$): δ (ppm) -62.48; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1754; **HRMS** (ESI) for: $C_{28}H_{19}F_3NO_2$ $[M+H]^+$: calcd 458.1362, found 458.1353.

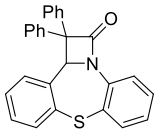
9-fluoro-1,1-diphenyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]oxazepin-2-one (3pq)



White solid, 61.1 mg, >99% yield; m.p.: 116-118 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.09 (d, J = 7.7 Hz, 1H), 7.68 (d, J = 7.5 Hz, 2H), 7.56-7.33 (m, 4H), 7.23-7.11 (m, 5H), 7.04 (d, J = 7.2 Hz, 2H), 6.97 (t, J = 9.1 Hz, 1H), 6.70 (q, J = 7.5 Hz, 1H), 6.21 (s, 1H), 6.11 (d, J = 7.9 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 166.6, 154.4 (d, J = 249.6 Hz), 146.4, 145.2 (d, J = 12.0 Hz), 138.4, 137.7, 130.2, 129.5, 128.94, 128.91, 128.4, 128.2, 128.0, 125.9, 125.7, 124.3 (d, J = 7.5 Hz), 122.9 (d, J = 3.9 Hz), 122.0 (d,

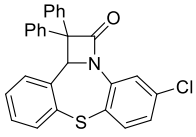
J = 9.1 Hz), 116.2 (d, *J* = 18.8 Hz), 72.3, 63.8; **^{19}F NMR** (400 MHz, $CDCl_3$): δ (ppm) -113.61; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1749; **HRMS** (ESI) for: $C_{27}H_{19}FNO_2$ $[M+H]^+$: calcd 408.1394, found 408.1389.

1,1-diphenyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]thiazepin-2-one (3qq)



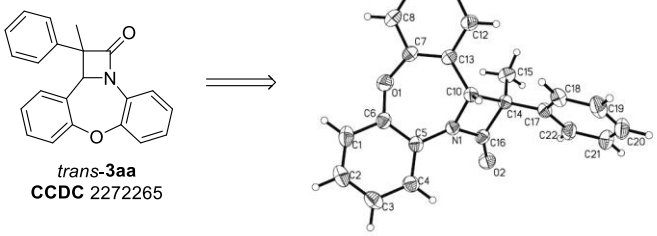
White solid, 60.8 mg, >99% yield; m.p.: 163-165 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.92 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.57-7.36 (m, 5H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.22-7.02 (m, 7H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 7.7 Hz, 1H), 6.34 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 167.6, 139.1, 138.3, 138.1, 136.6, 134.2, 132.5, 132.0, 129.4, 129.3, 128.9, 128.8, 128.2, 128.1, 127.8, 127.7, 127.5, 127.4, 126.6, 124.2, 72.7, 67.1; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1760; **HRMS** (ESI) for: $C_{27}H_{20}NOS$ $[M+H]^+$: calcd 406.1260, found 406.1264.

5-Chloro-1,1-diphenyl-1,12b-dihydro-2*H*-azeto[1,2-*d*]dibenzo[*b,f*][1,4]thiazepin-2-one (3rq)



White solid, 64.7 mg, 98% yield; m.p.: 185-187 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.10 (t, *J* = 2.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.53-7.38 (m, 5H), 7.23-6.90 (m, 8H), 6.59 (d, *J* = 7.8 Hz, 1H), 6.51 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 167.6, 139.0, 138.8, 138.0, 137.0, 135.0, 134.5, 132.9, 132.6, 129.0, 128.96, 128.90, 128.5, 128.3, 128.13, 128.08, 127.9, 127.8, 126.0, 123.6, 123.3, 72.3, 67.2; **IR** (KBr, $\tilde{\nu}$, cm^{-1}): 1770; **HRMS** (ESI) for: $C_{27}H_{19}ClNOS$ $[M+H]^+$: calcd 440.0870, found 440.0874.

5. X-ray cryster structure of 3aa

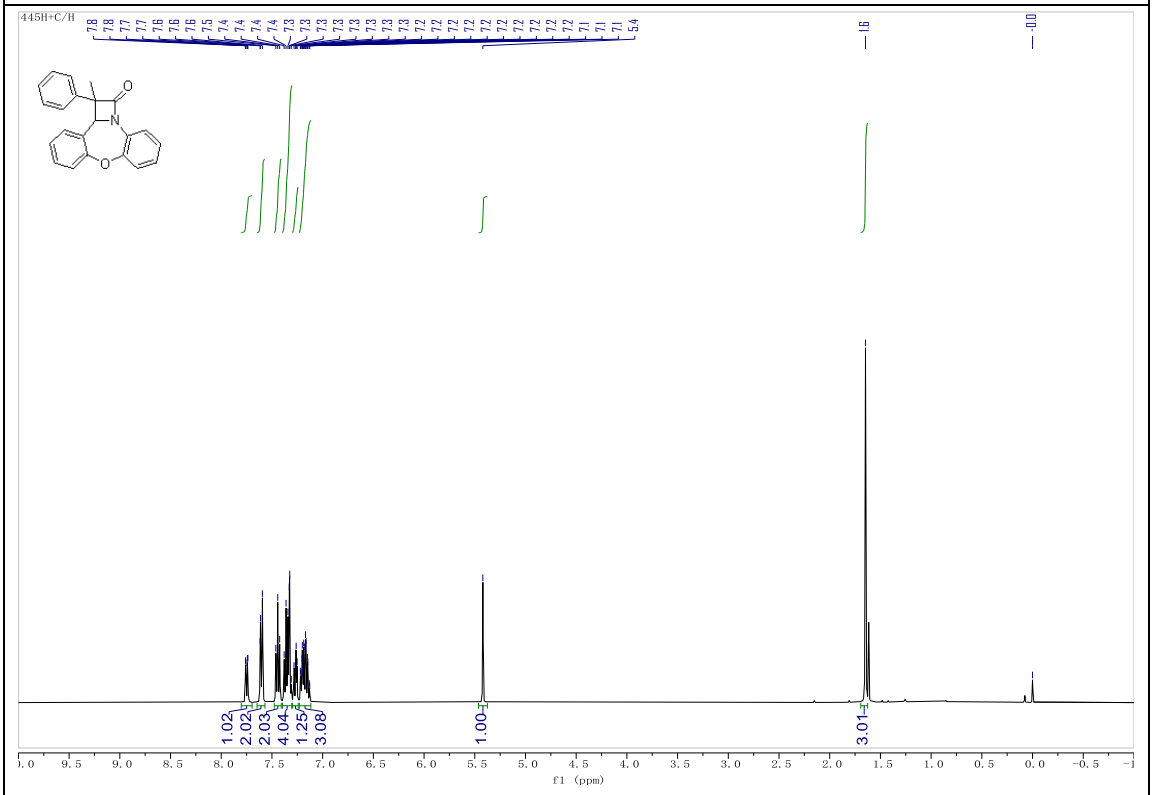


References

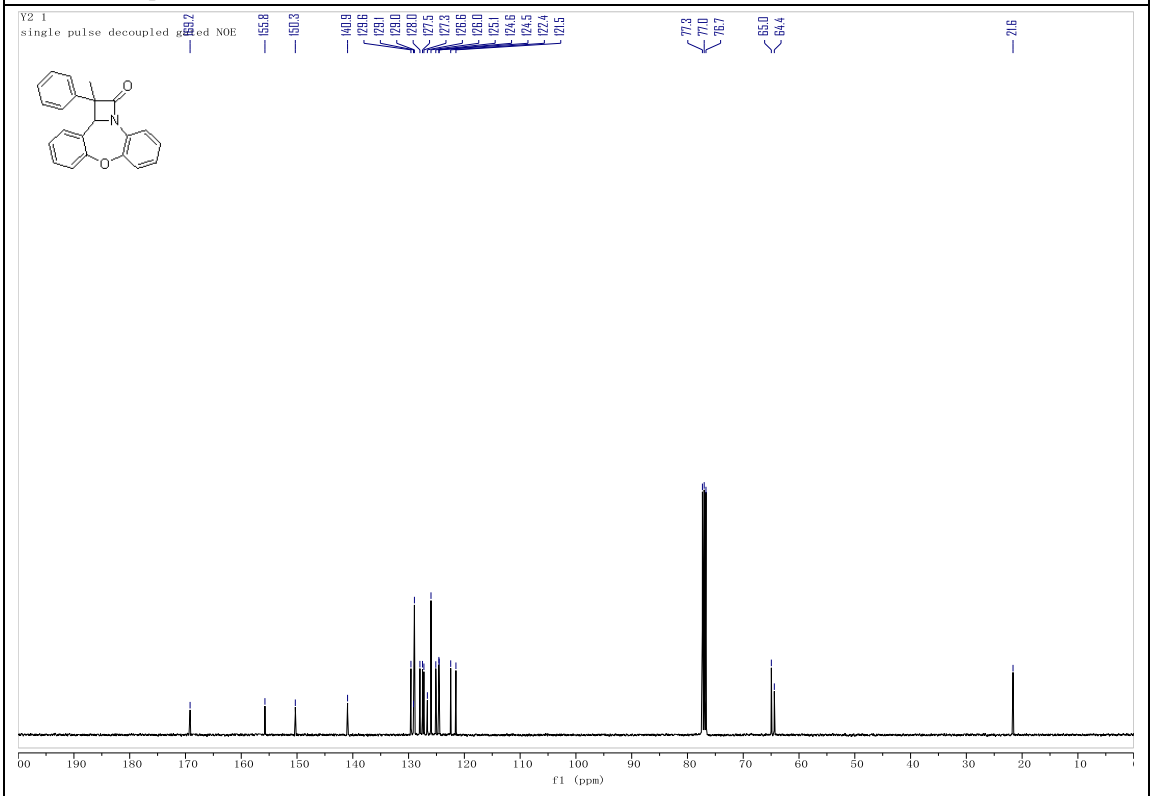
1. (a) G. J. Wang, Z. Q. Fu and W. Huang, *Org. Lett.*, 2017, **19**, 3362-3365; (b) M. Fr ás, A. C. Carrasco, A. *Chem. Eur. J.*, 2018, **24**, 3117-3121.
2. (a) B. Xu, S. F. Zhu, X. D. Zuo, Z. C. Zhang and Q. L. Zhou, *Angew. Chem., Int. Ed.*, 2014, **53**, 3913-3916; (b) J. Yang, C. Q. Ke, X. H. Liu and X. M. Feng, *Org. Lett.*, 2018, **20**, 4536-4539.
3. H. Yang, H.-J. Li, G. Wei and Z.-Y. Jiang, *Angew. Chem. Int. Ed.*, 2021, **60**, 19696-19700.

6. Copies of ^{1}H and ^{13}C NMR Spectra

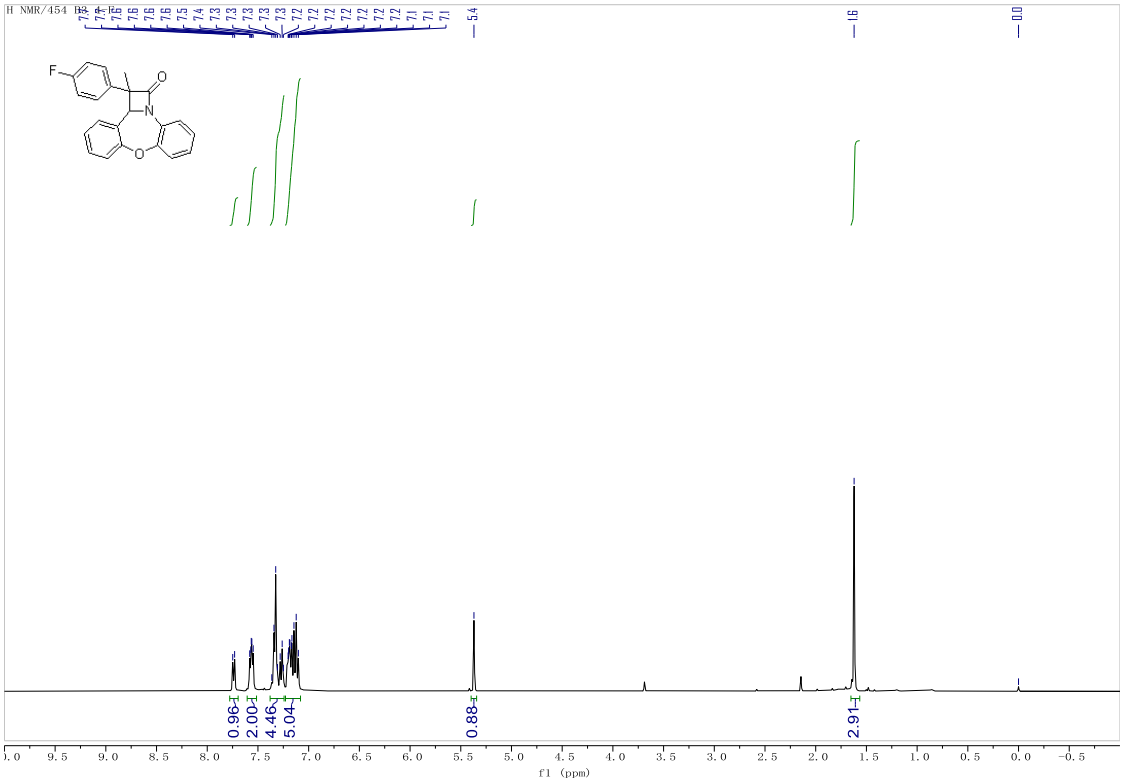
^{1}H NMR Spectrum of **3aa**



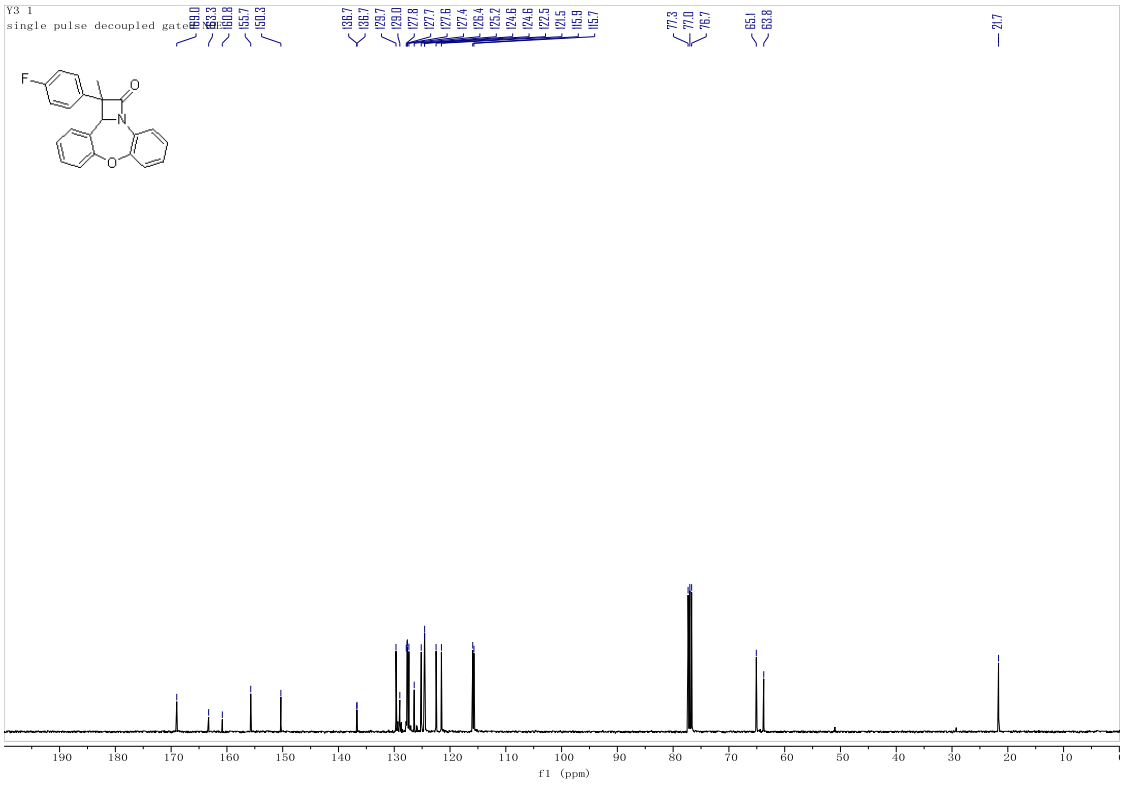
^{13}C NMR Spectrum of **3aa**

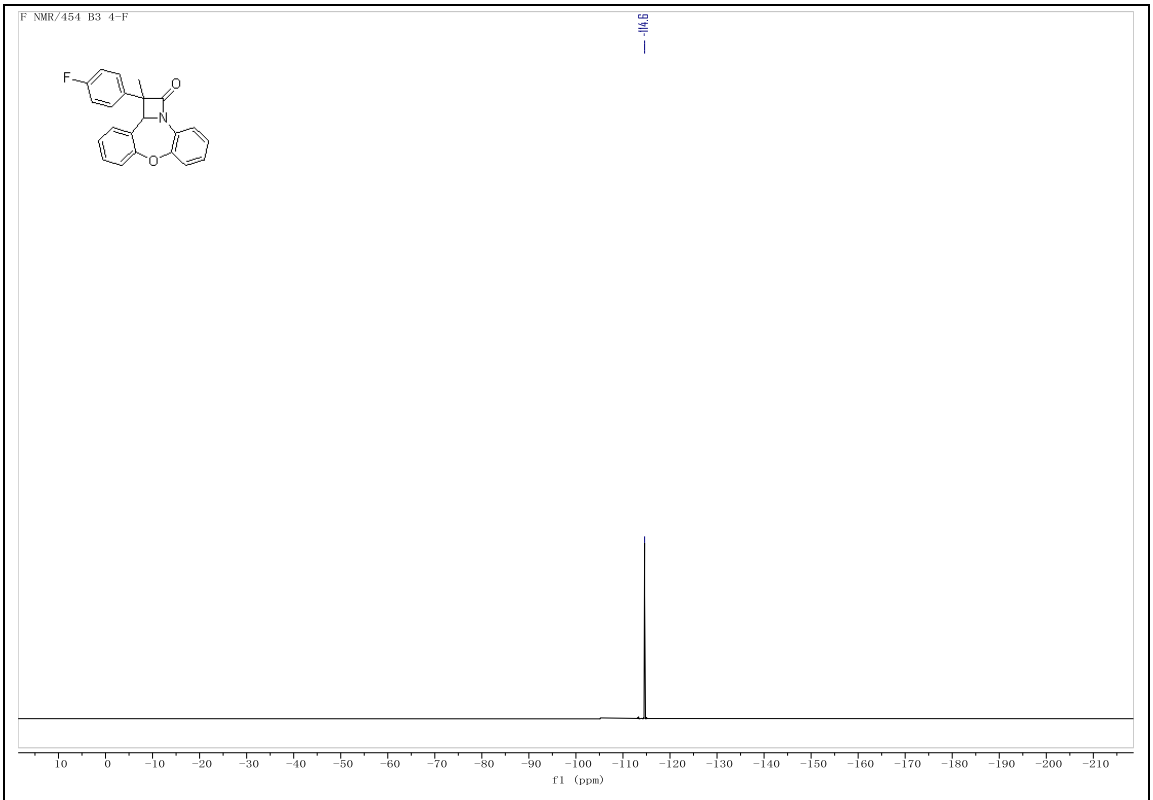


^{1}H NMR Spectrum of **3ab**

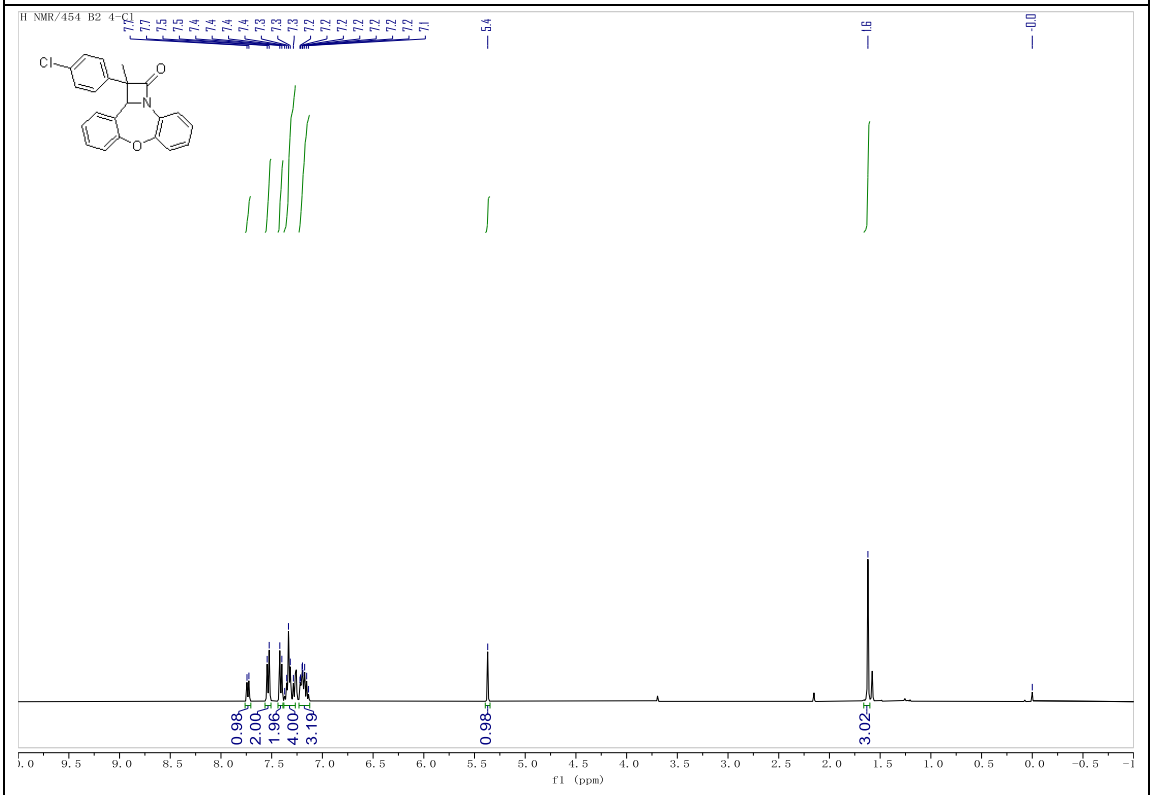


^{13}C NMR Spectrum of **3ab**

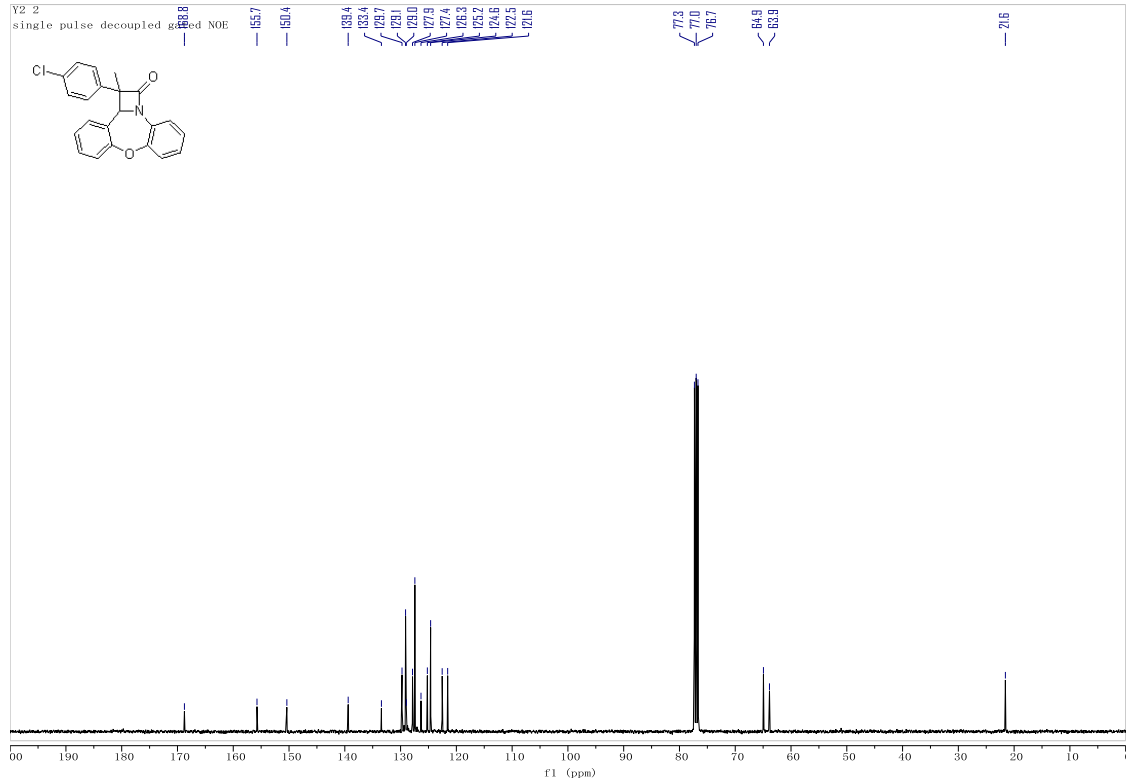



F NMR/454 B3 4-F
-114.6
F
O
N
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

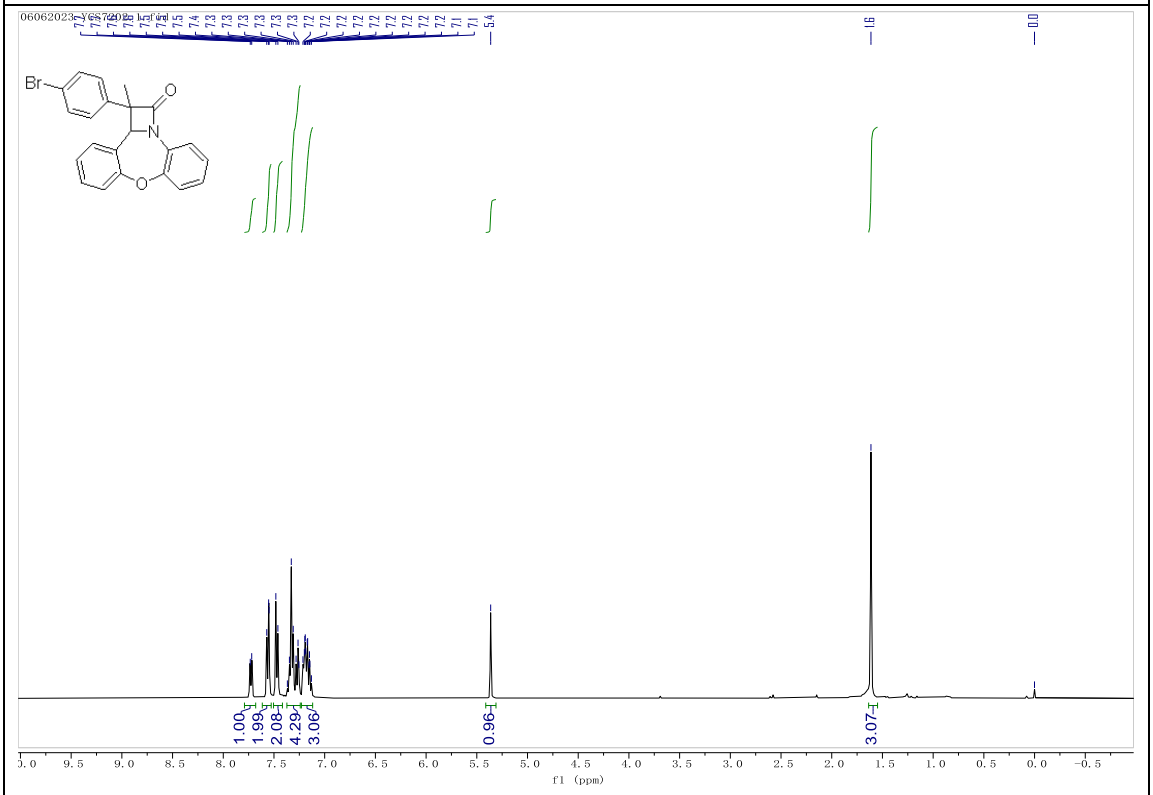
^{1}H NMR Spectrum of **3ac**



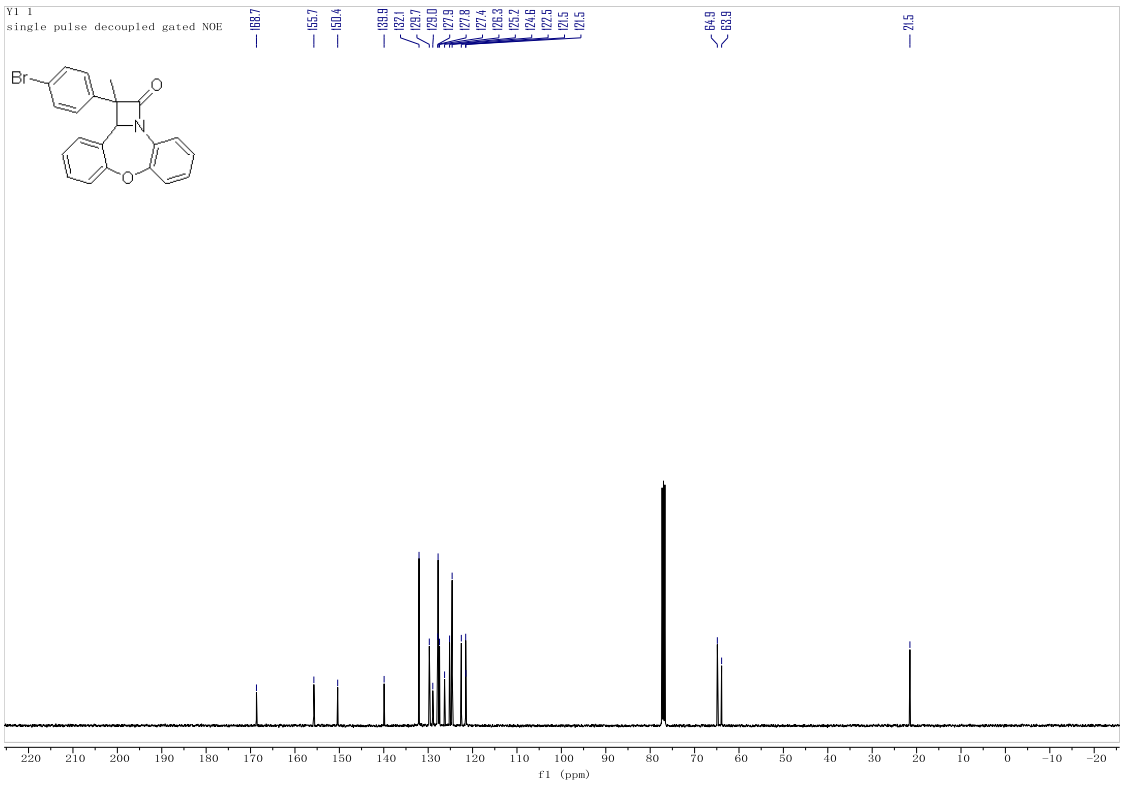
^{13}C NMR Spectrum of **3ac**



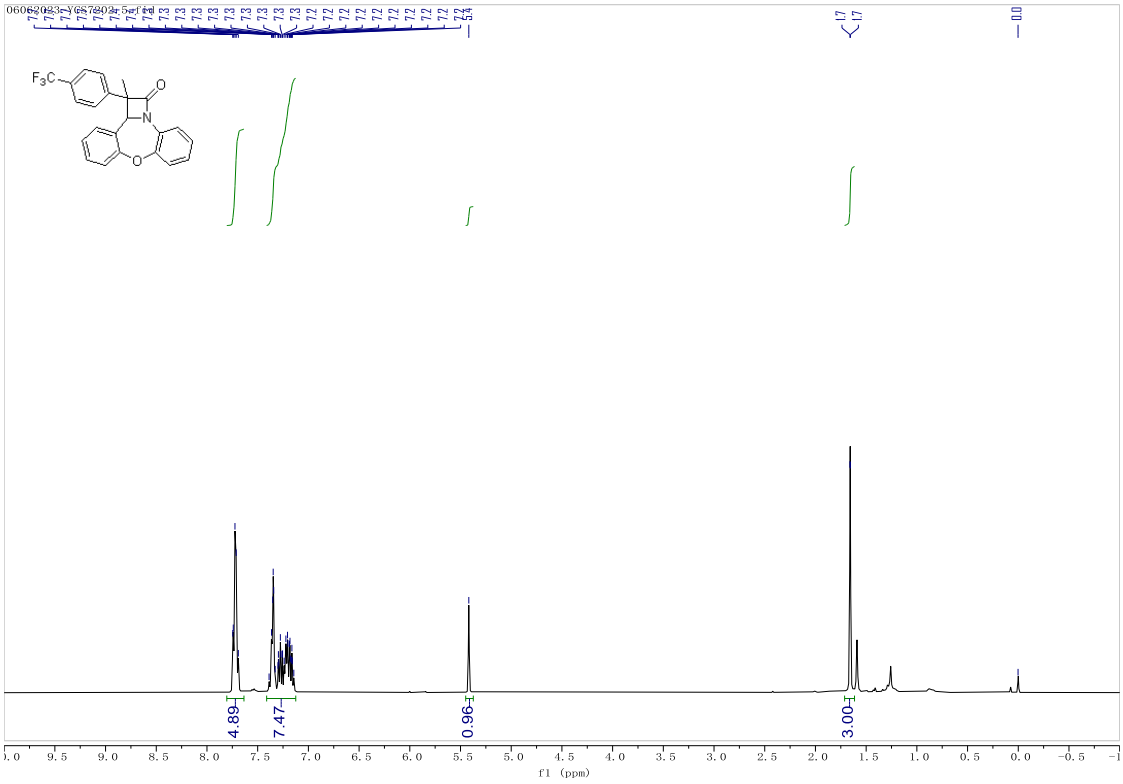
^{1}H NMR Spectrum of **3ad**



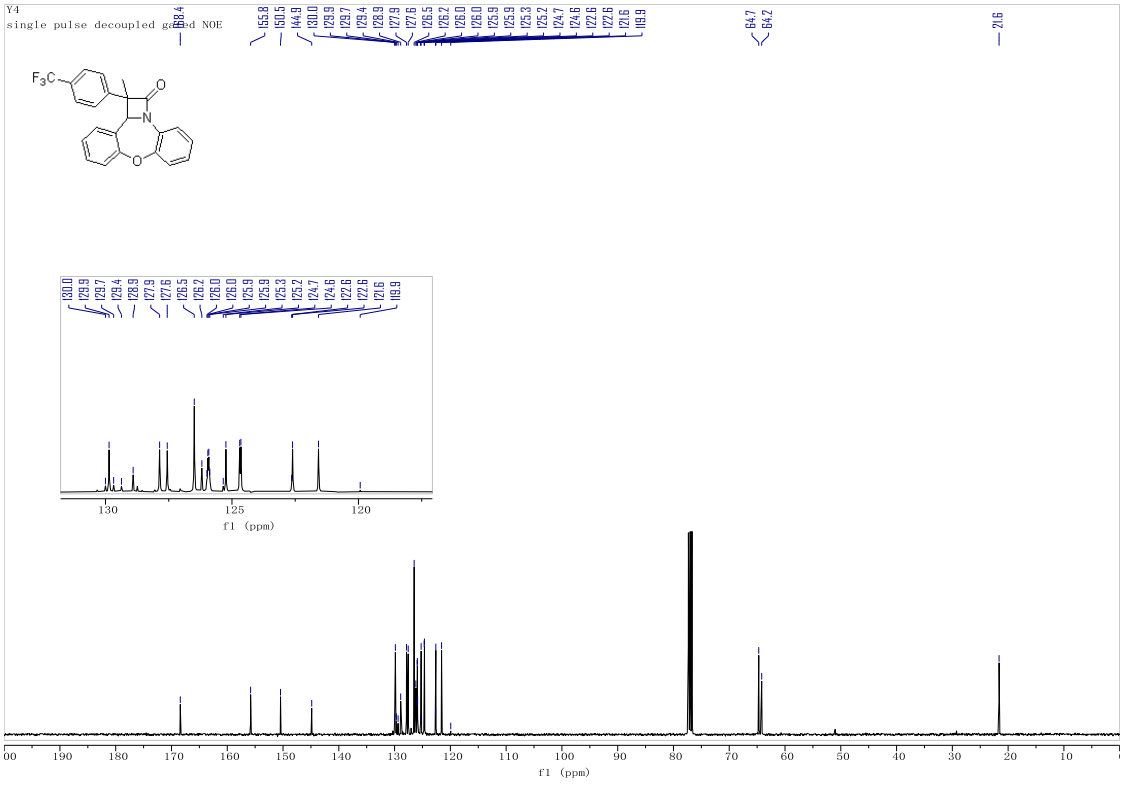
^{13}C NMR & F NMR Spectrum of **3ad**

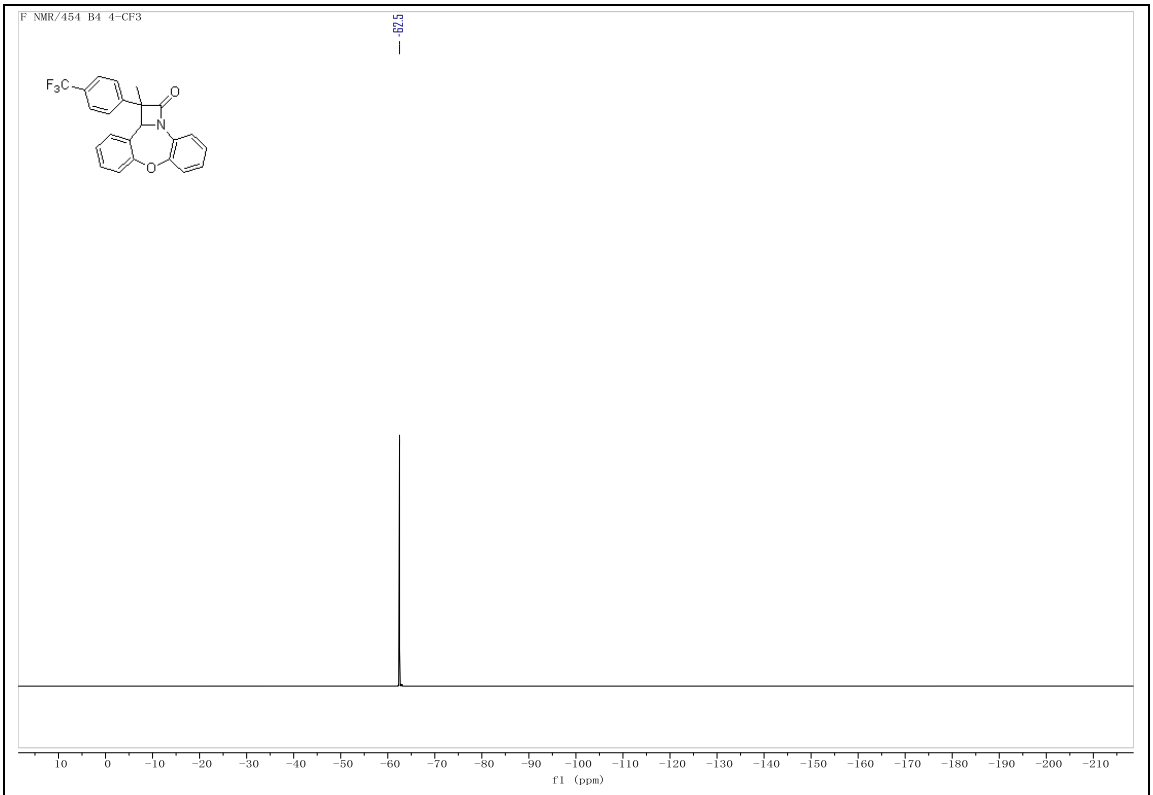


^{1}H NMR Spectrum of **3ae**

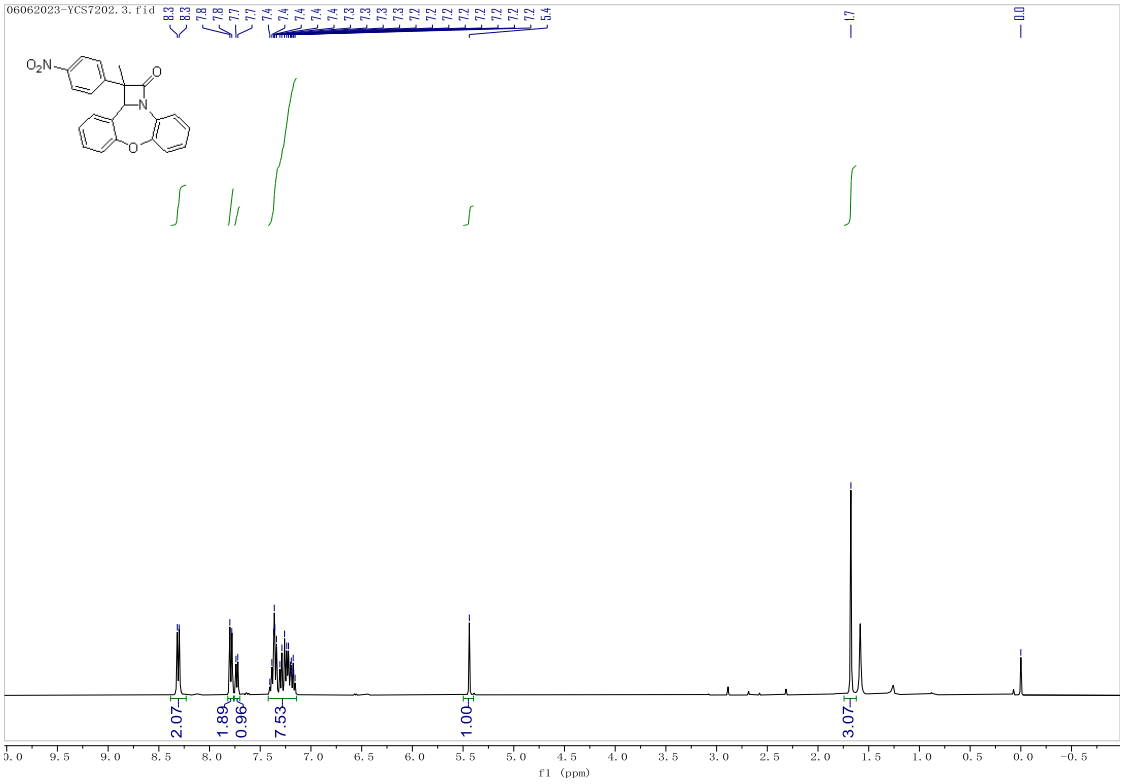


^{13}C NMR Spectrum of **3ae**

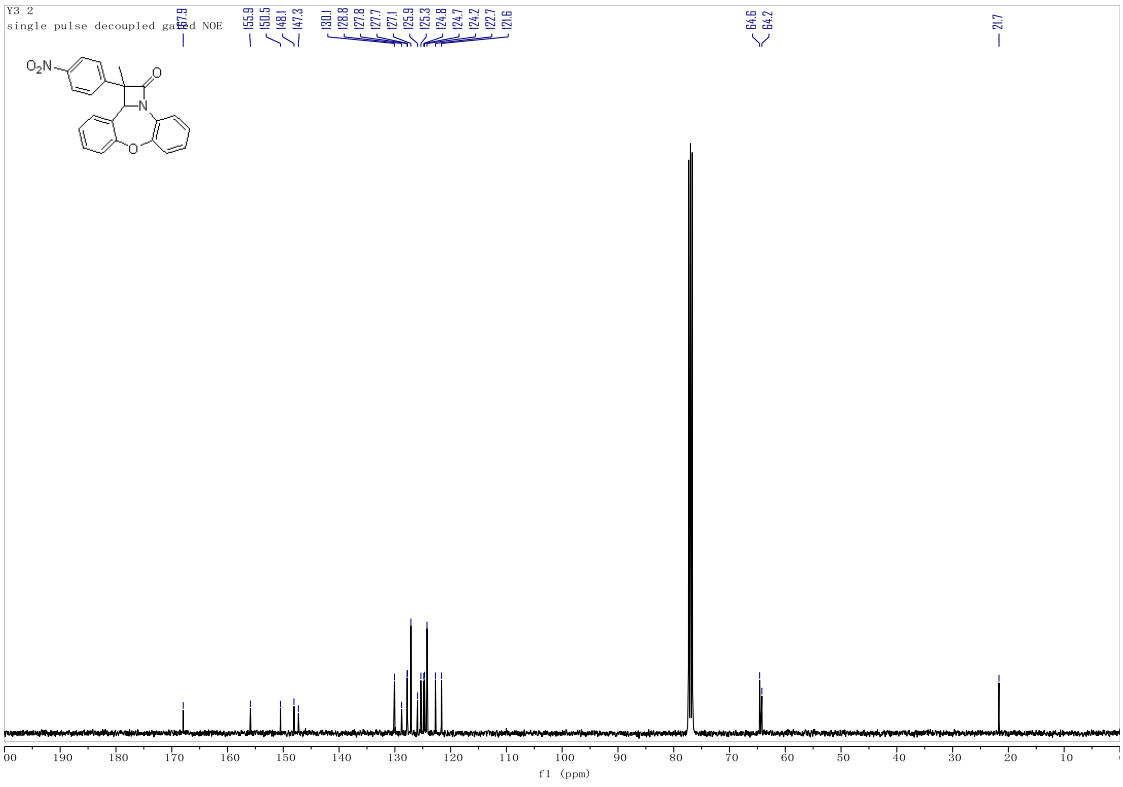



F NMR/454 B4 4-CF3
-62.5
F3C
O
N
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

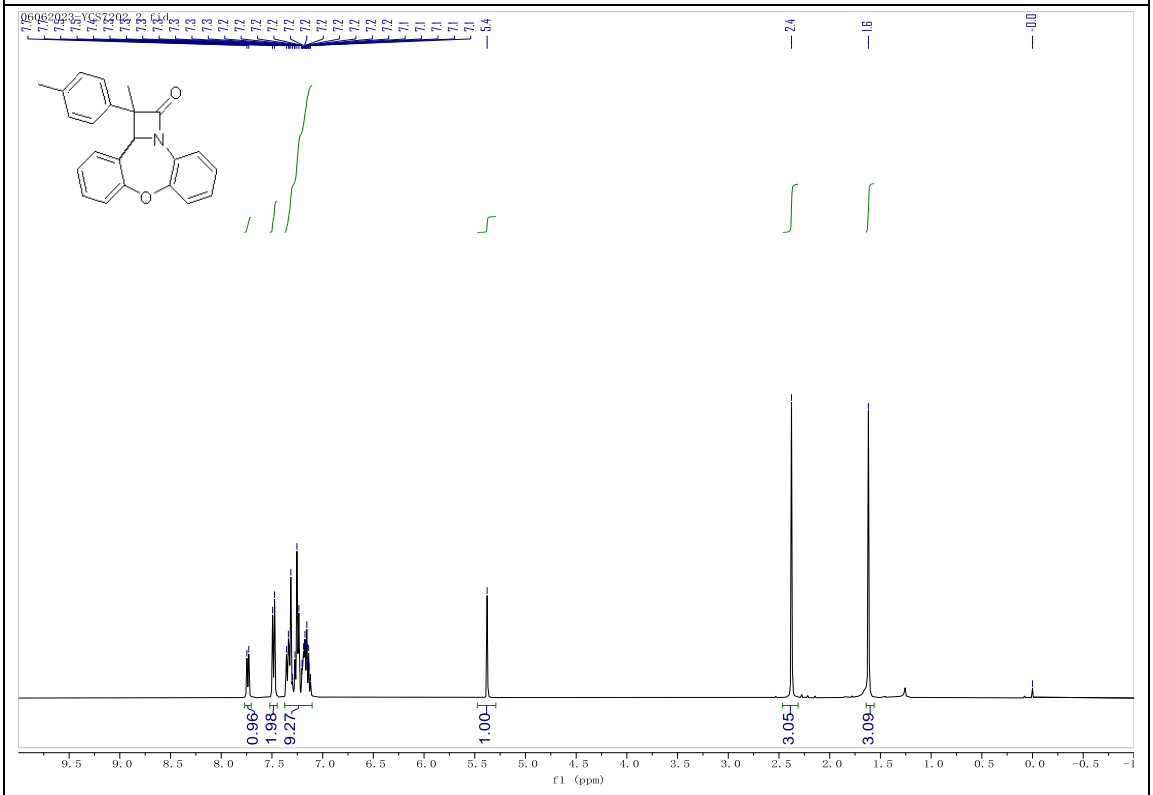
^{1}H NMR Spectrum of **3af**



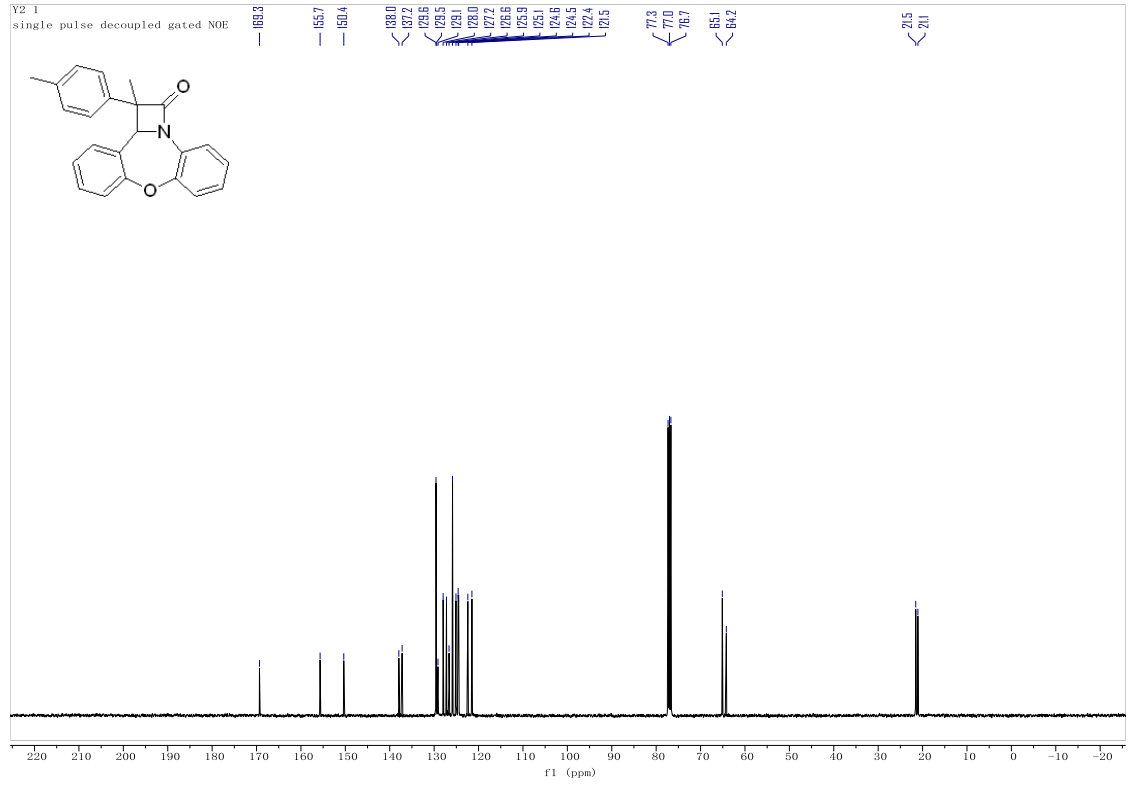
^{13}C NMR Spectrum of **3af**



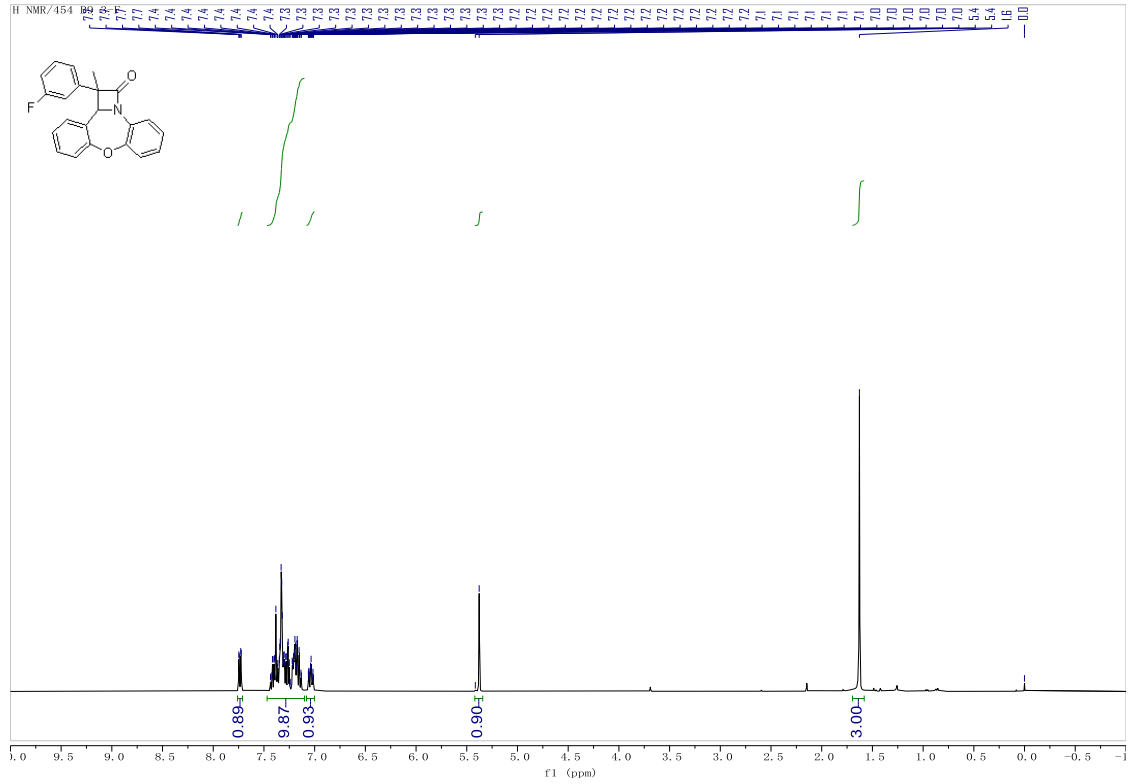
^{1}H NMR Spectrum of **3ag**



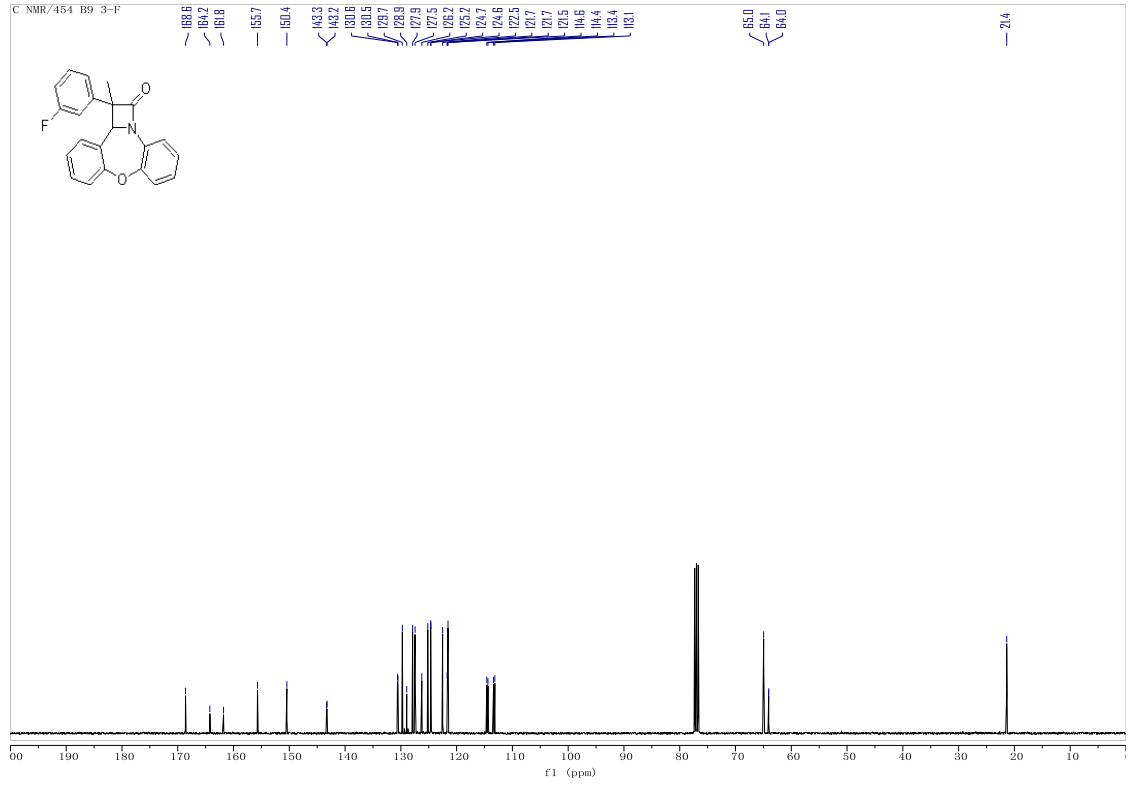
^{13}C NMR Spectrum of **3ag**

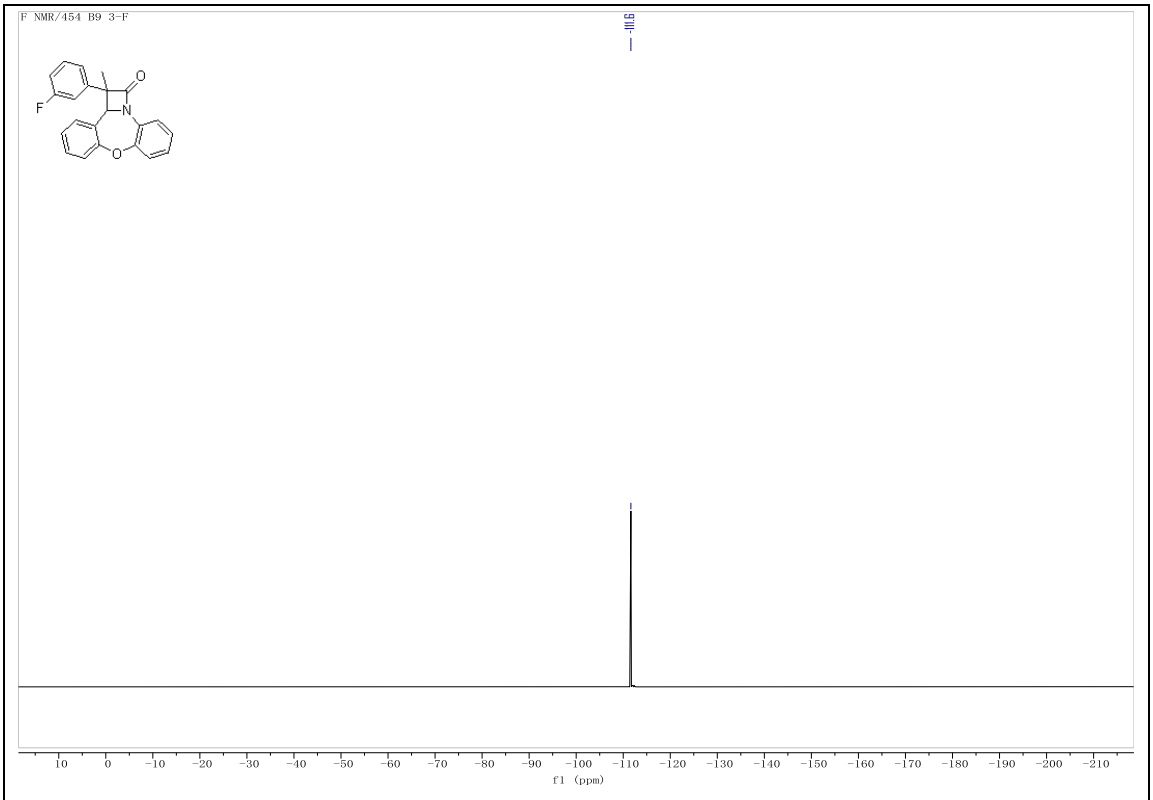


^{1}H NMR Spectrum of **3ah**



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

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N
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-90
-100
-110
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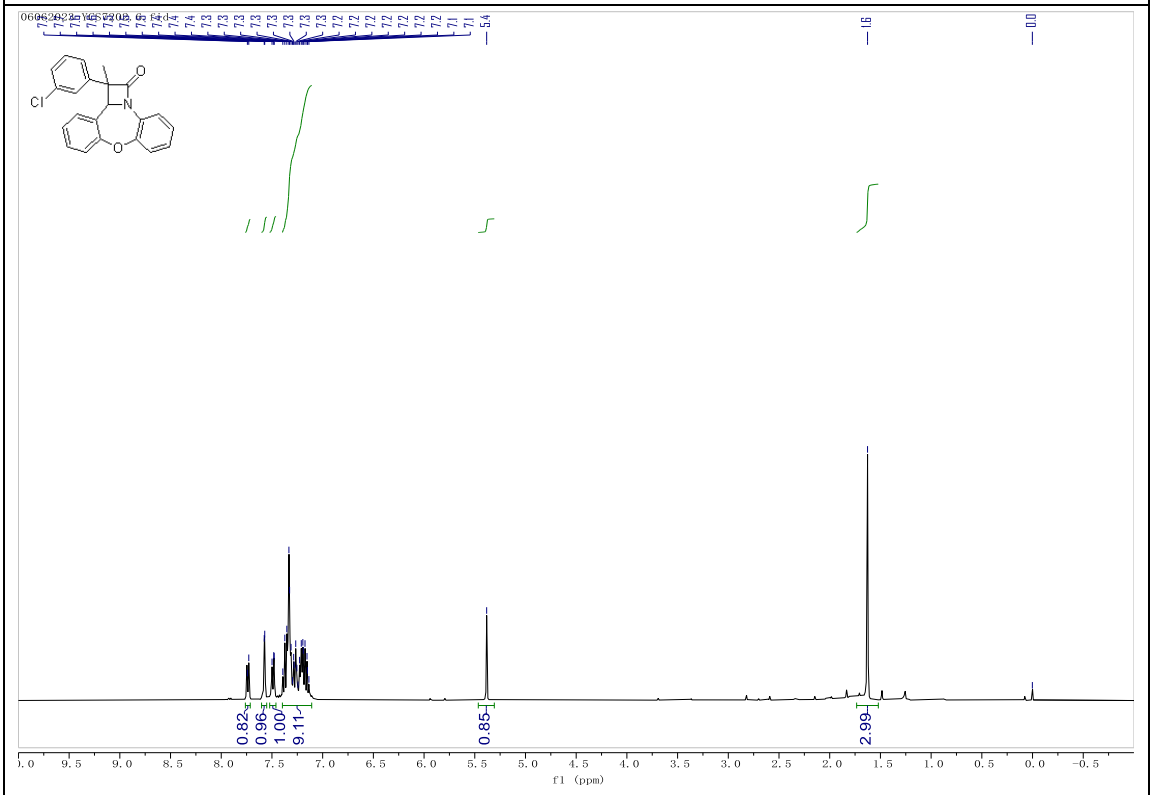
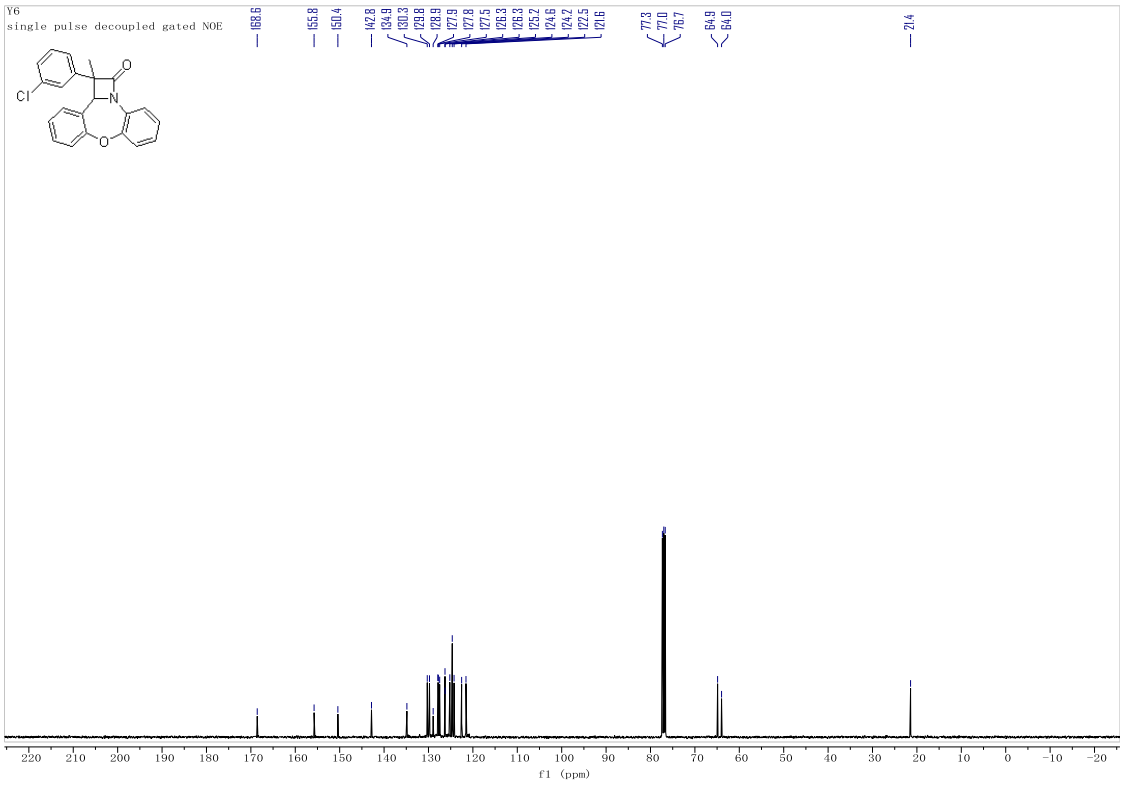
-180
-190
-200
-210
f1 (ppm)

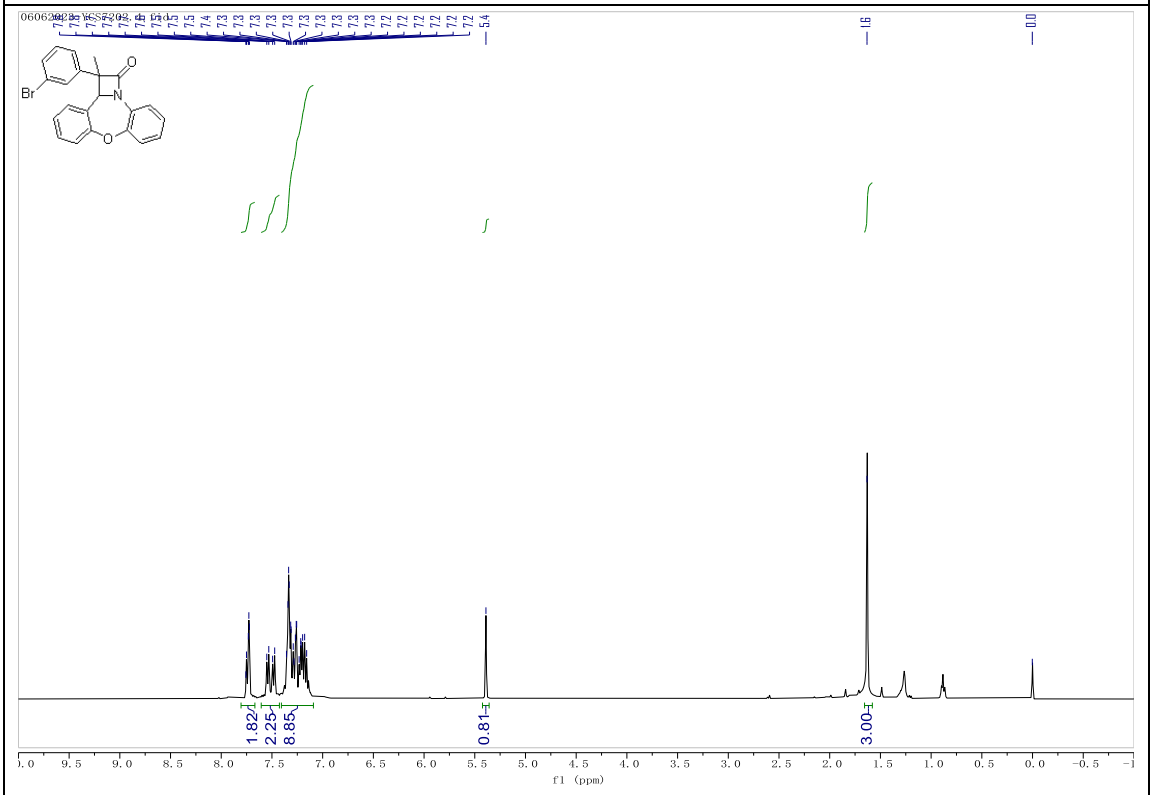
^{1}H NMR Spectrum of **3ai**



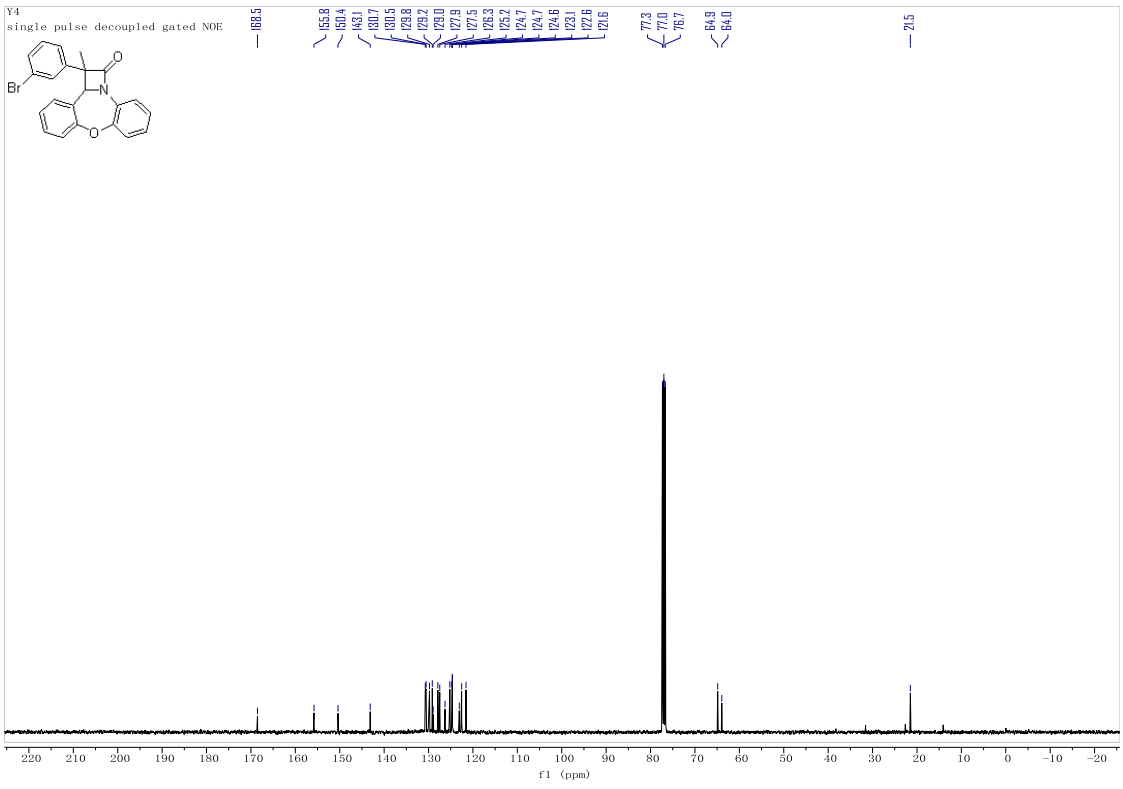
^{13}C NMR Spectrum of **3ai**



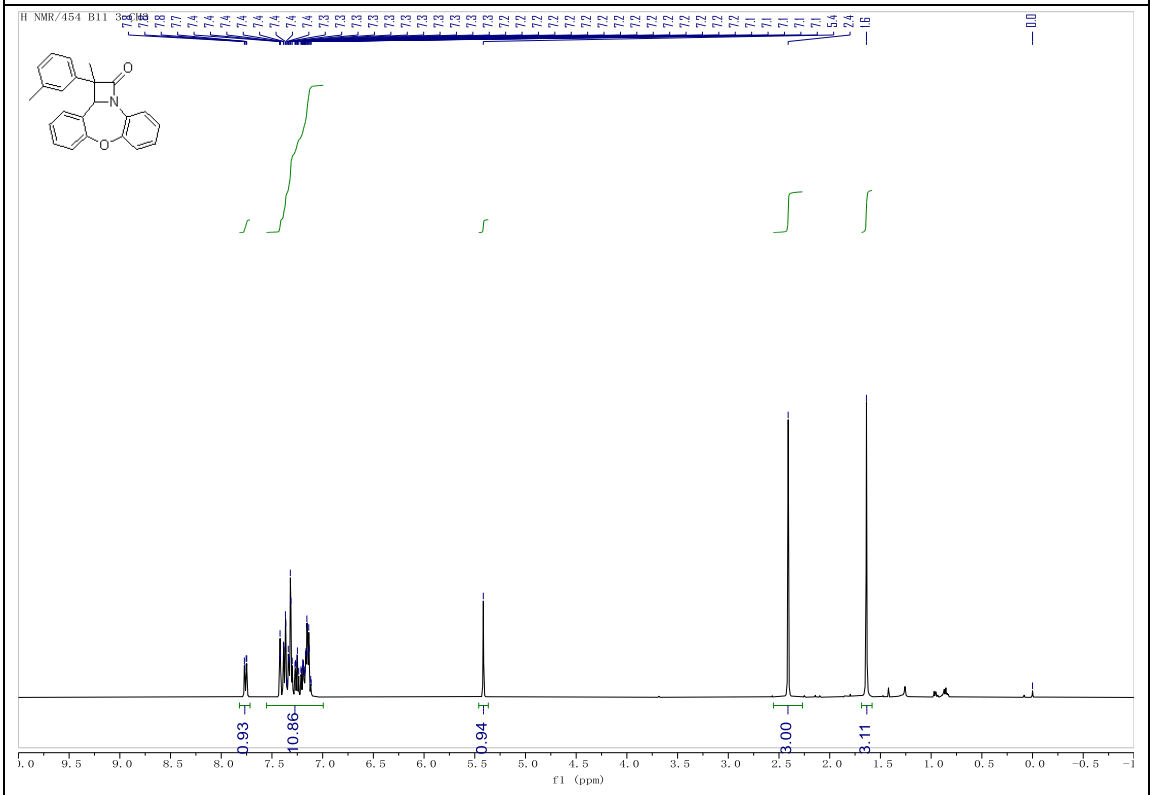
^{1}H NMR Spectrum of **3aj**



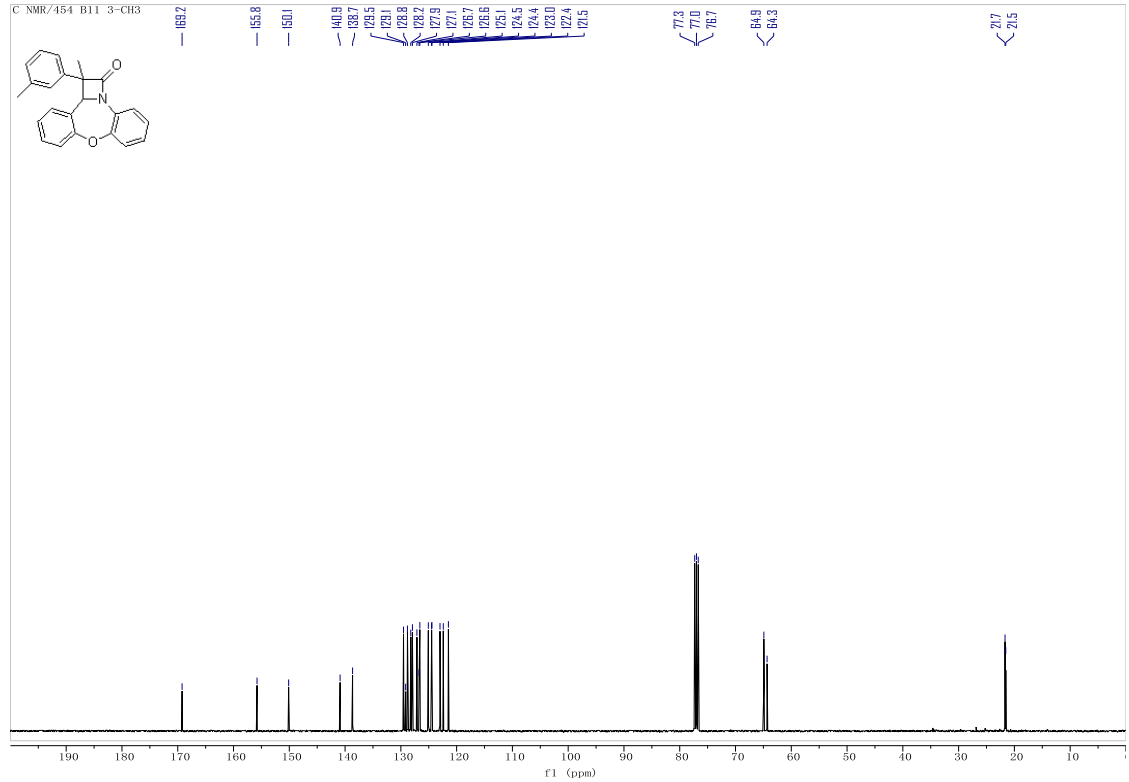
^{13}C NMR Spectrum of **3aj**



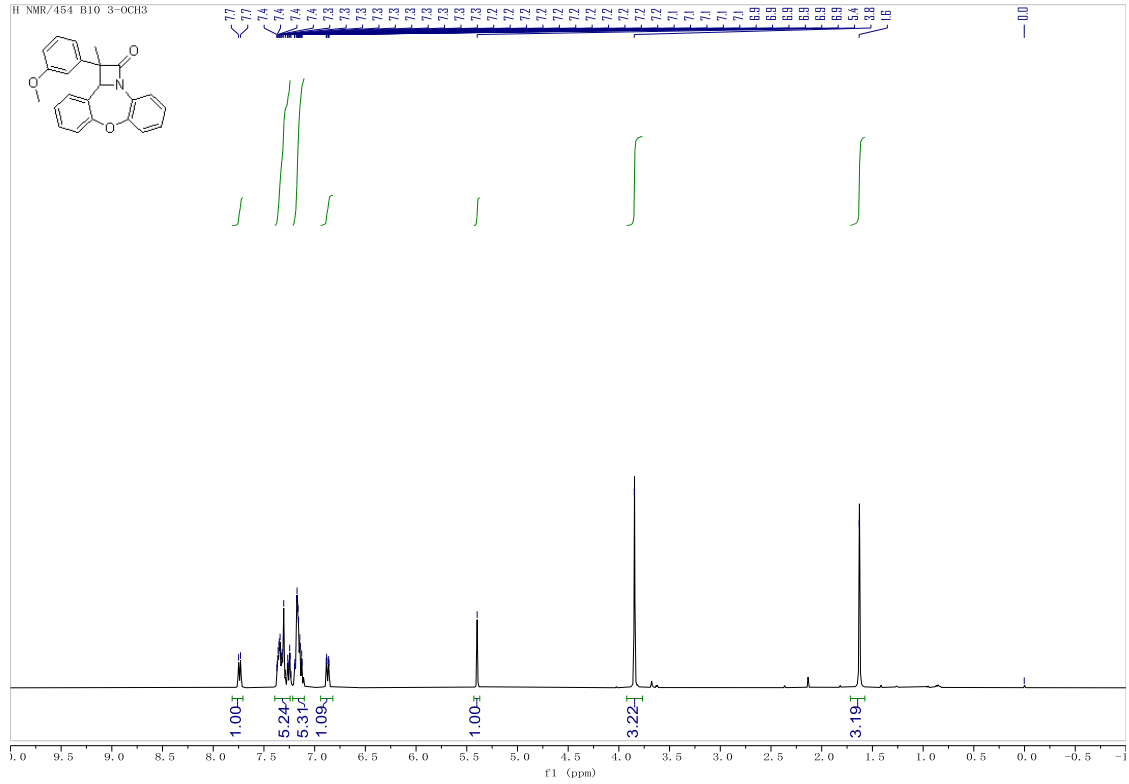
^{1}H NMR Spectrum of **3ak**



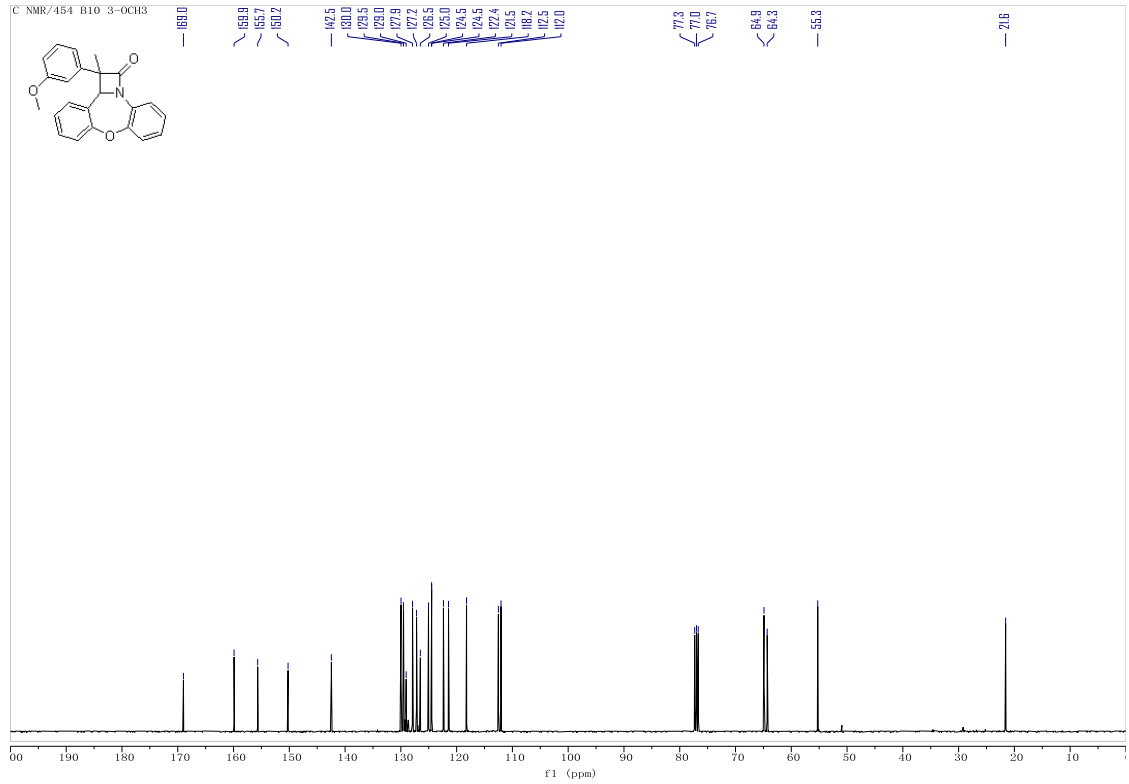
^{13}C NMR Spectrum of **3ak**



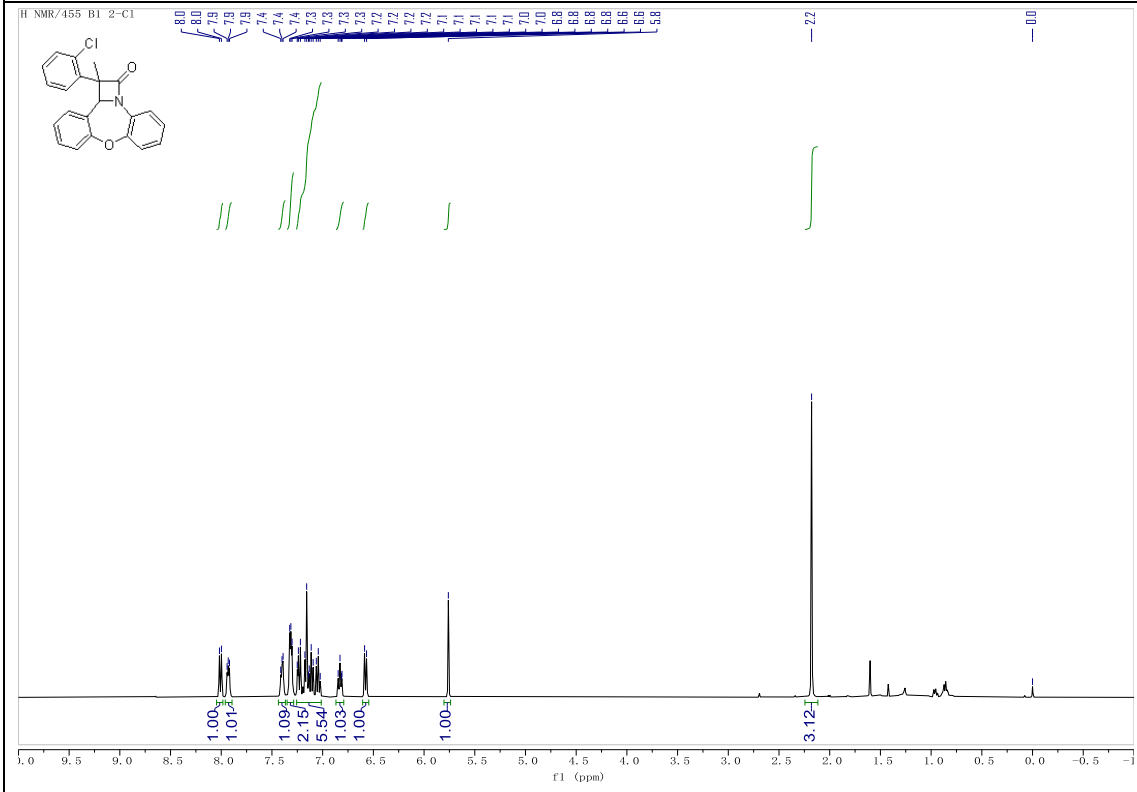
^{1}H NMR Spectrum of **3al**



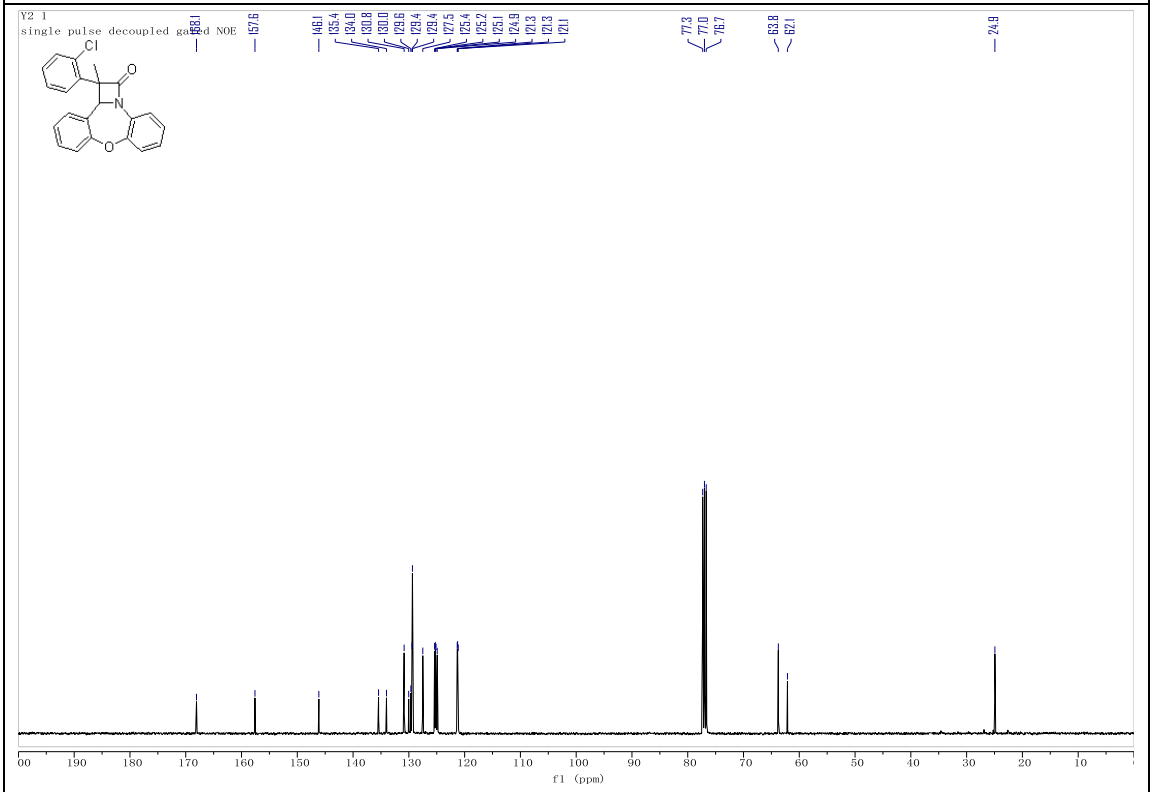
^{13}C NMR Spectrum of **3al**



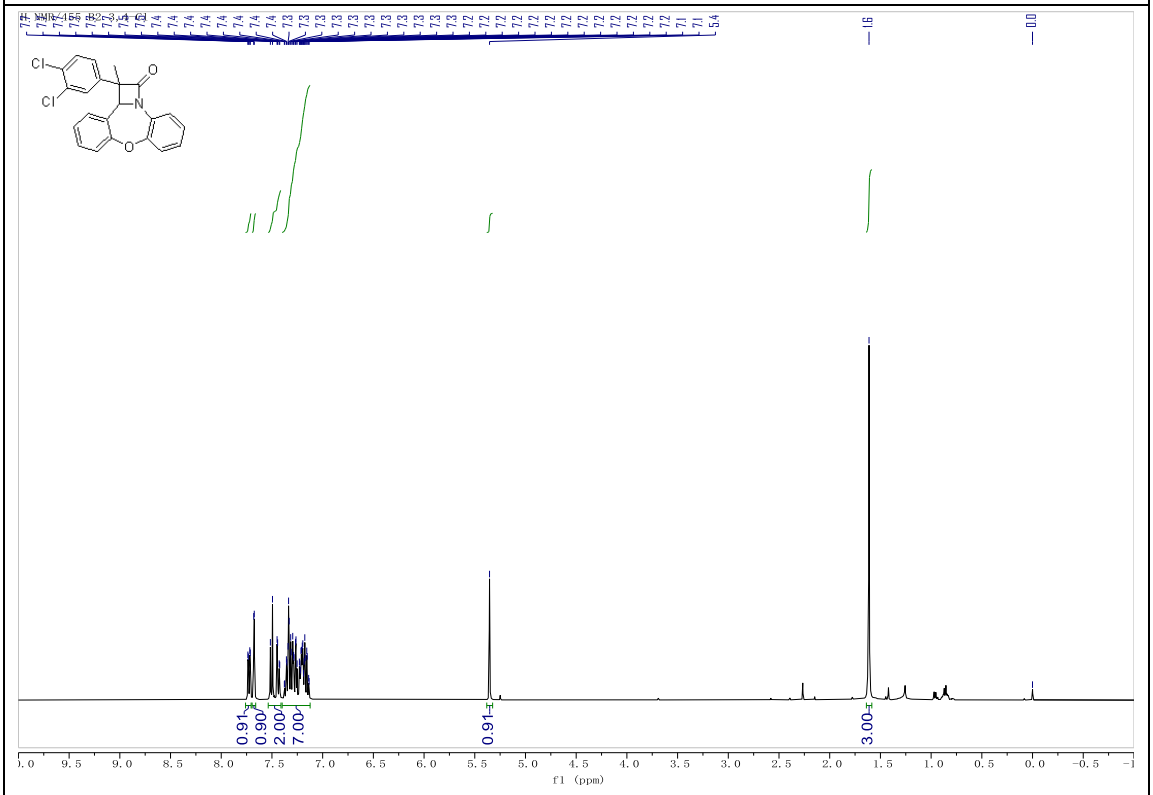
^{1}H NMR Spectrum of **3am**



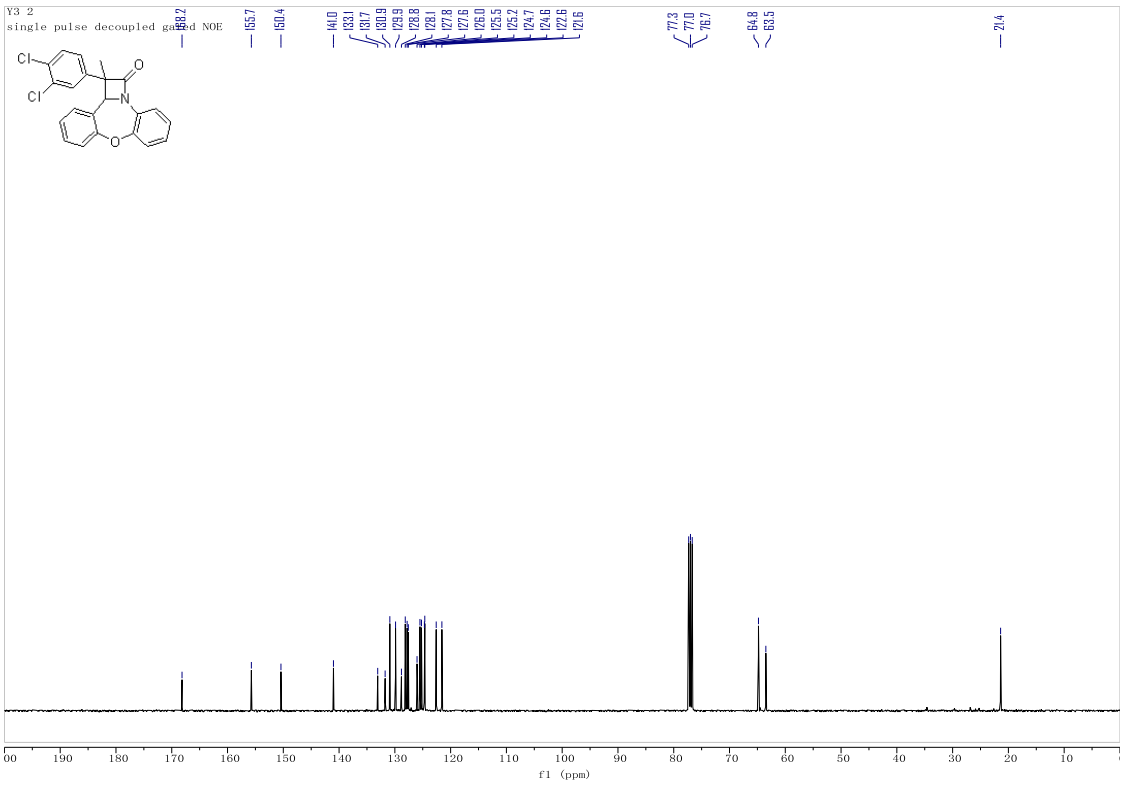
^{13}C NMR Spectrum of **3am**



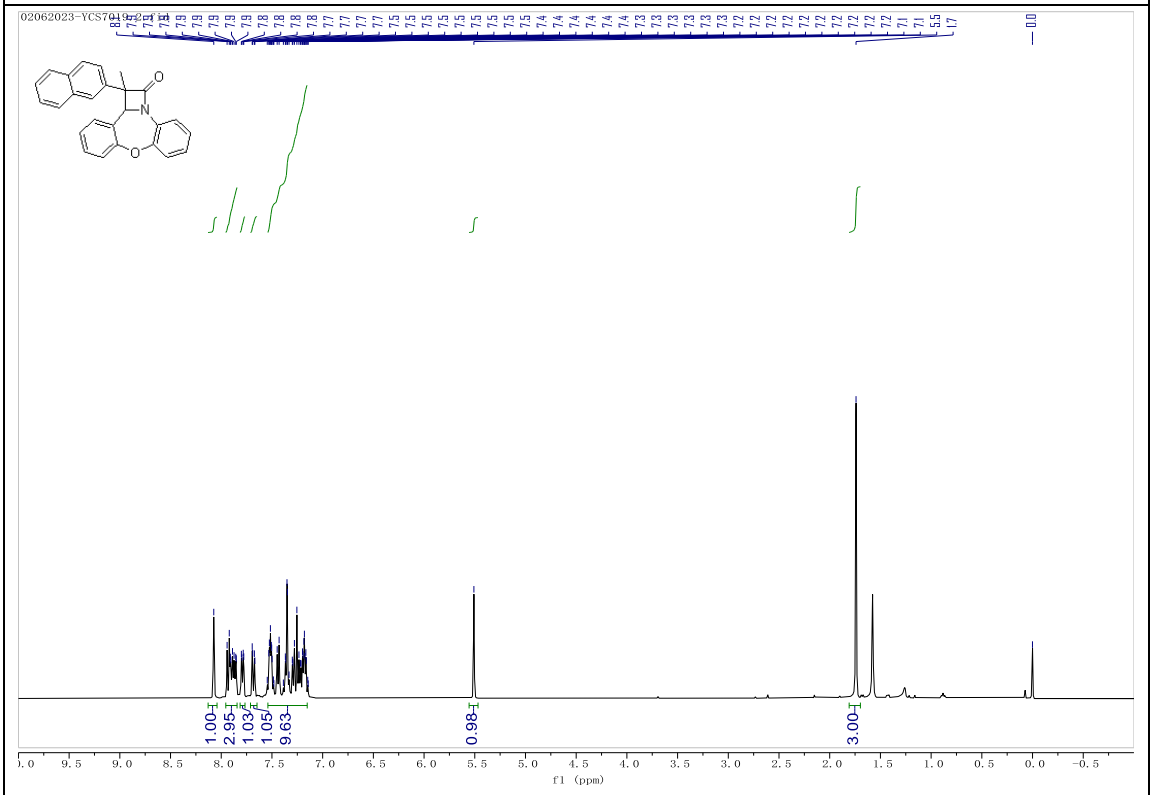
^{1}H NMR Spectrum of **3an**



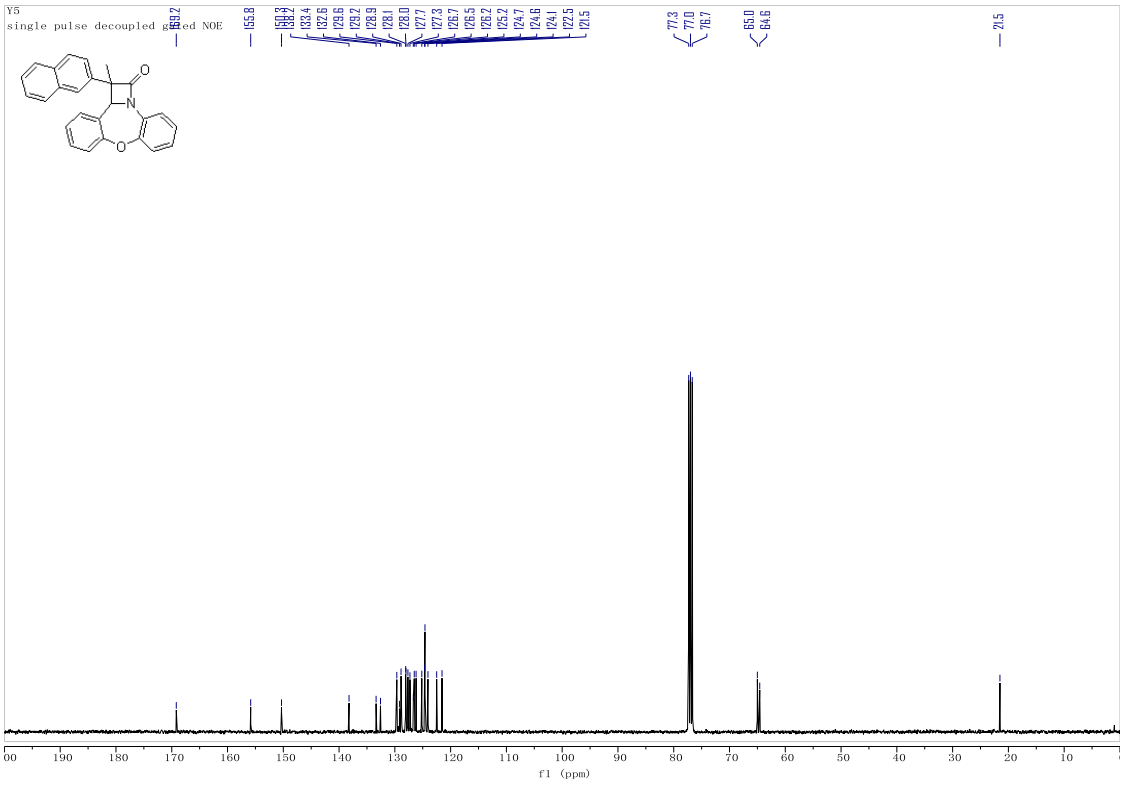
^{13}C NMR Spectrum of **3an**



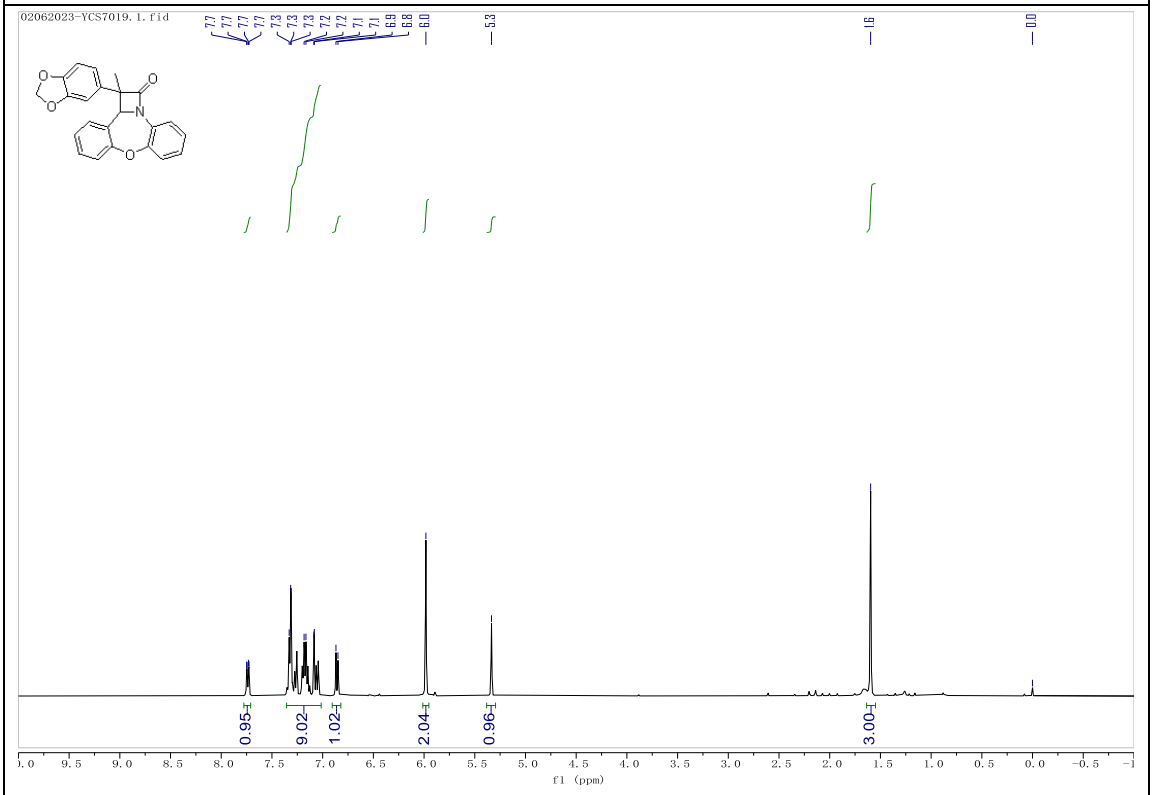
^{1}H NMR Spectrum of **3ao**



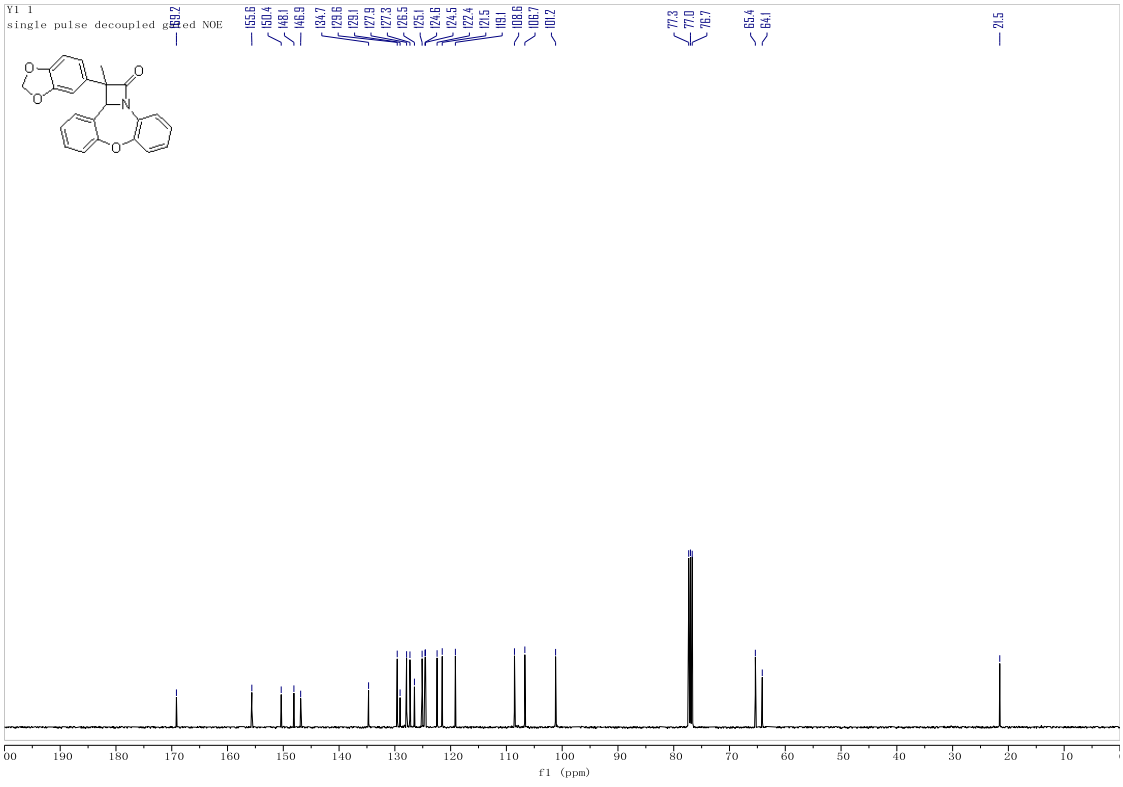
^{13}C NMR Spectrum of **3ao**



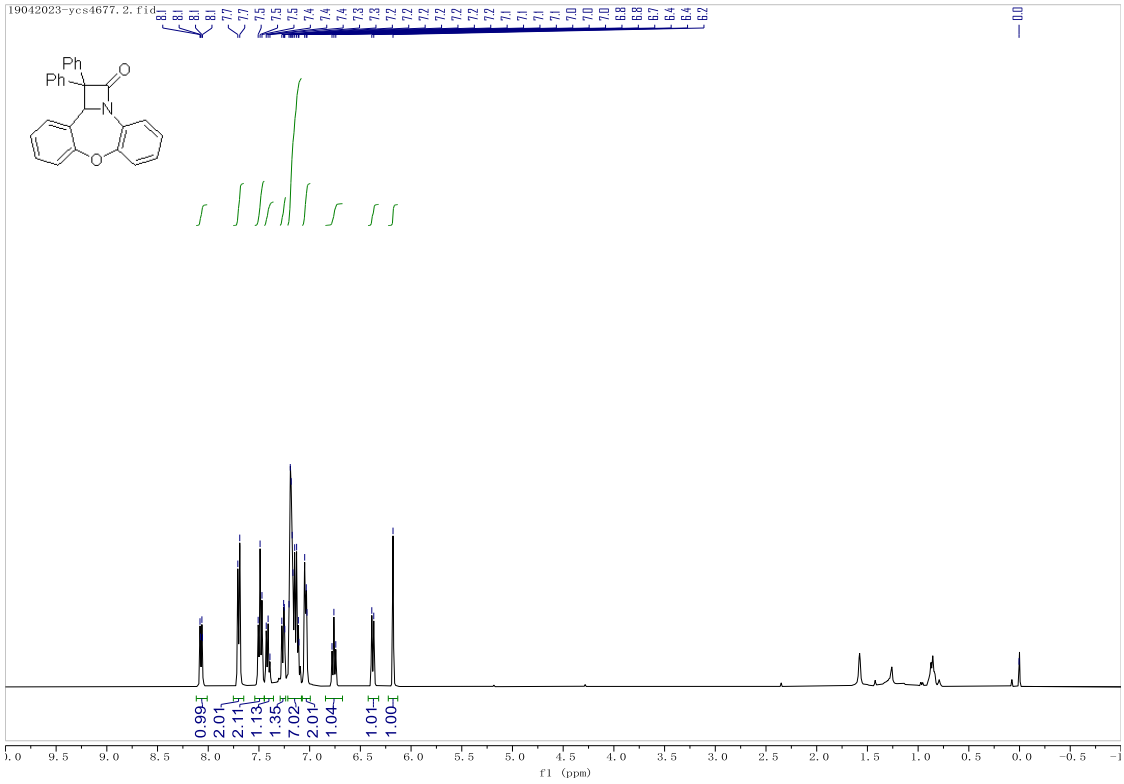
^{1}H NMR Spectrum of **3ap**



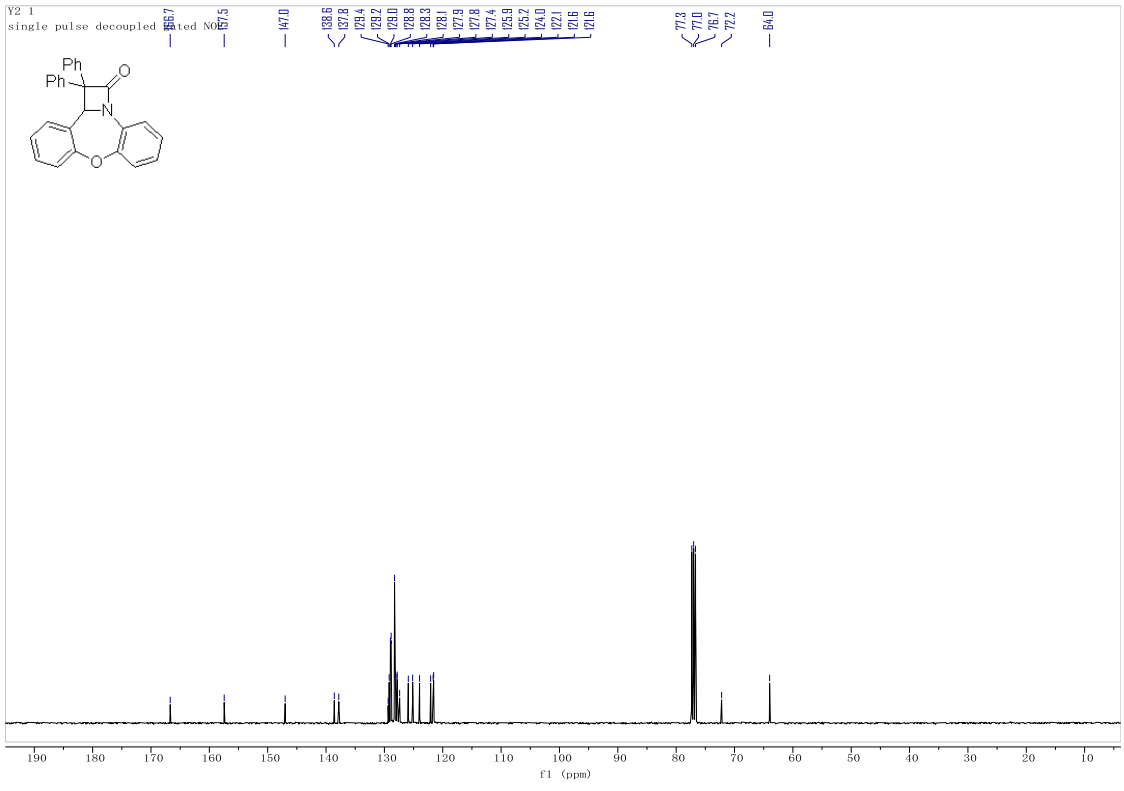
^{13}C NMR Spectrum of **3ap**



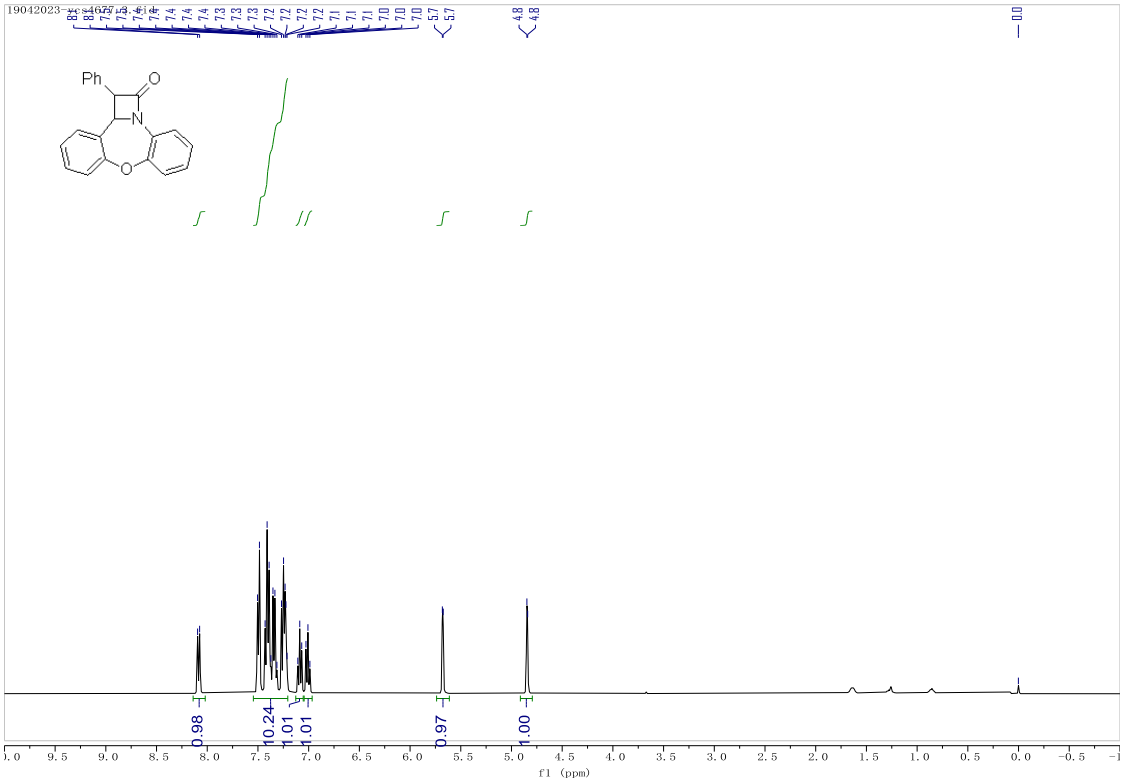
^{1}H NMR Spectrum of **3aq**



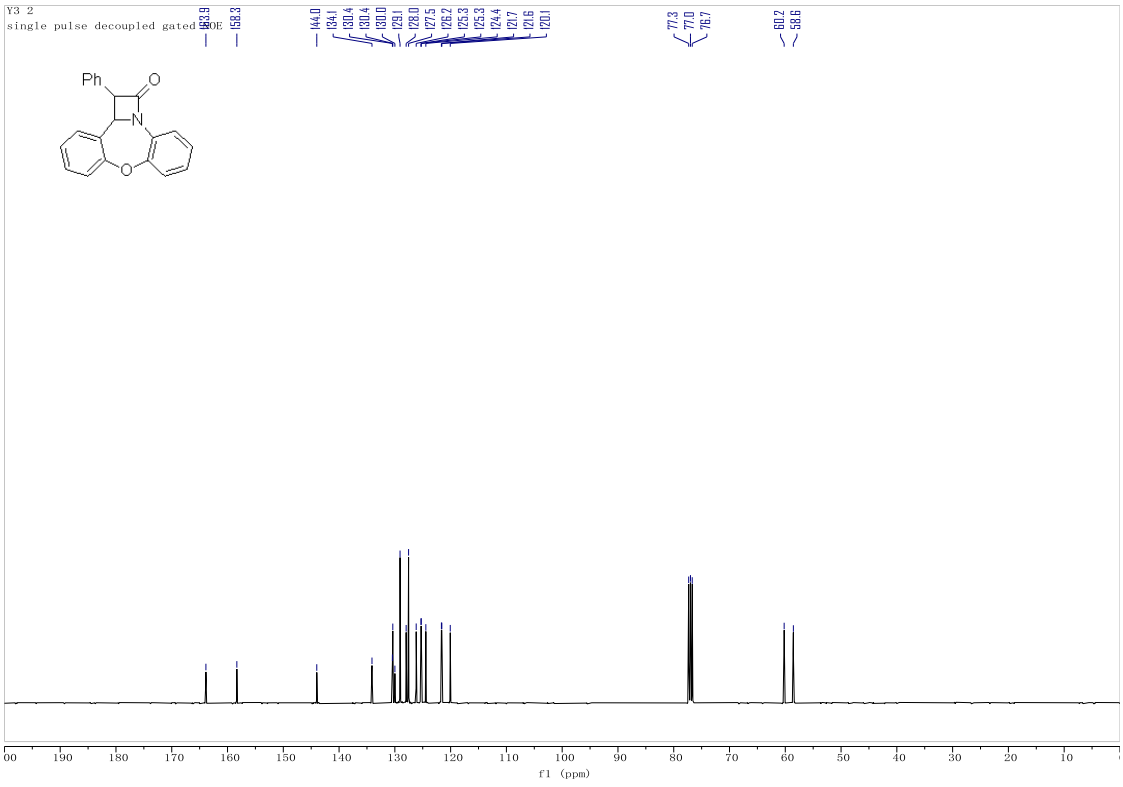
^{13}C NMR Spectrum of **3aq**



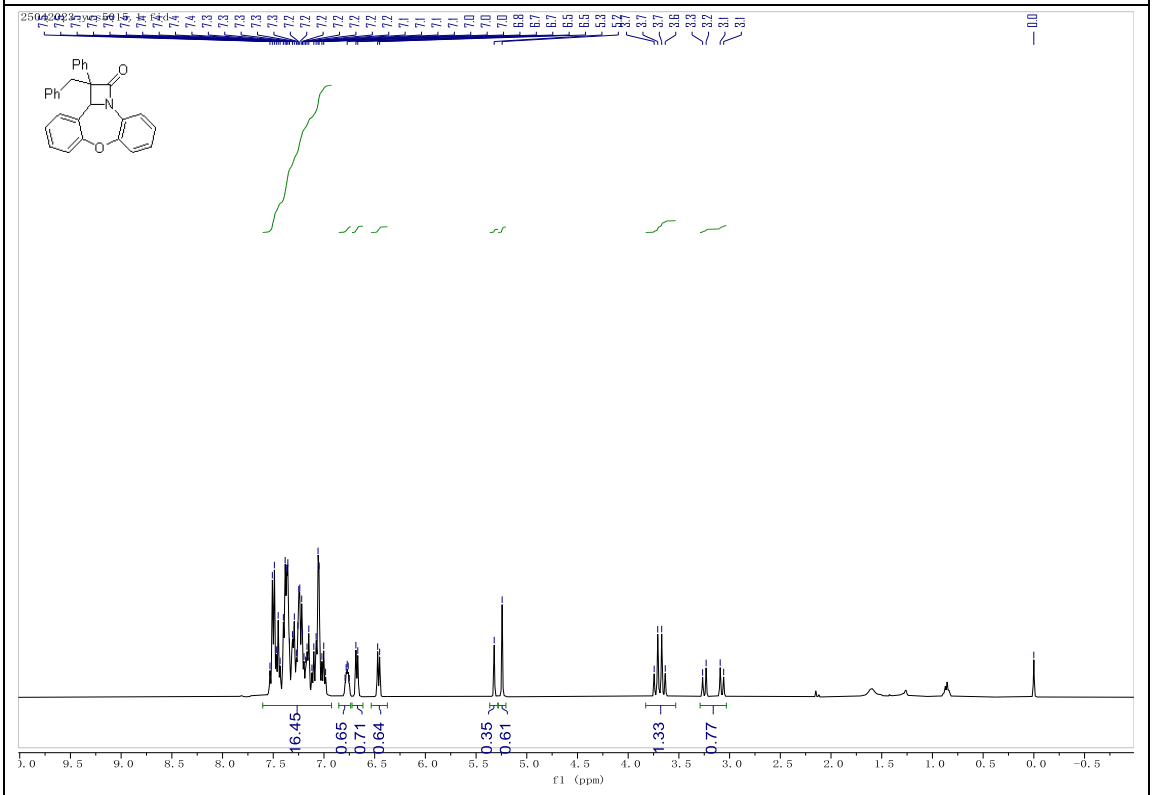
^{1}H NMR Spectrum of **3ar**



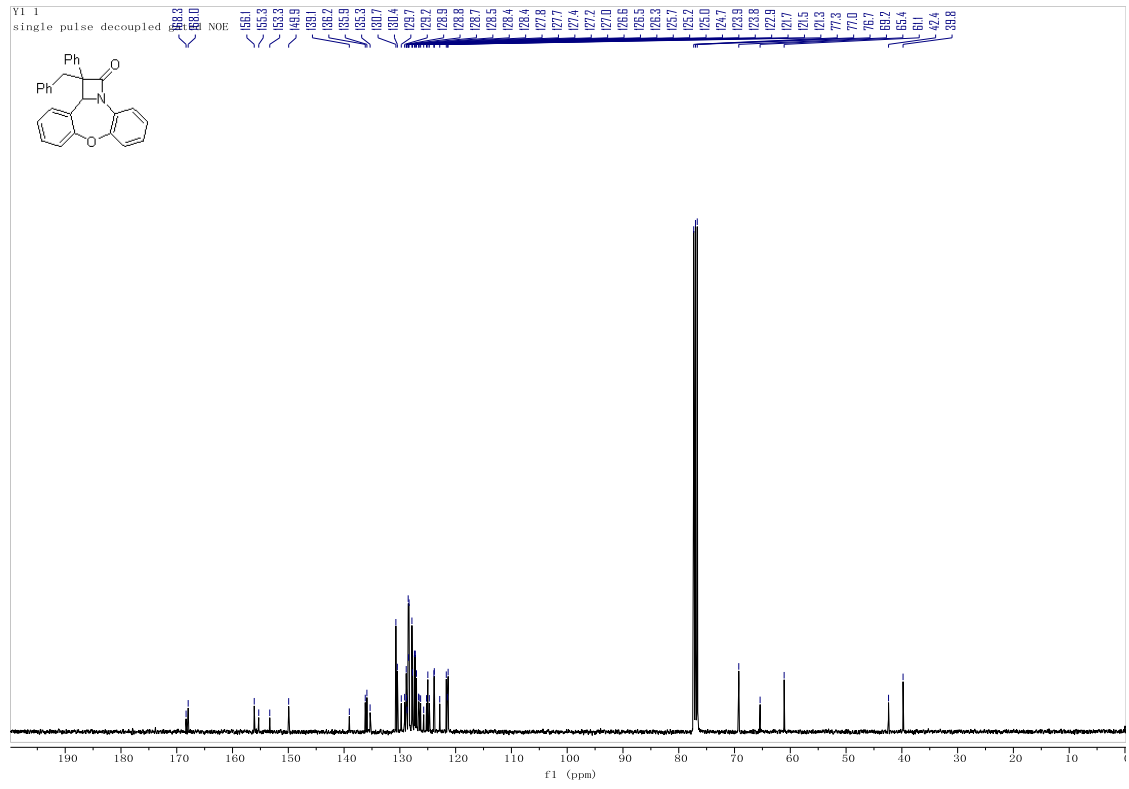
^{13}C NMR & ^{19}F NMR Spectrum of **3ar**



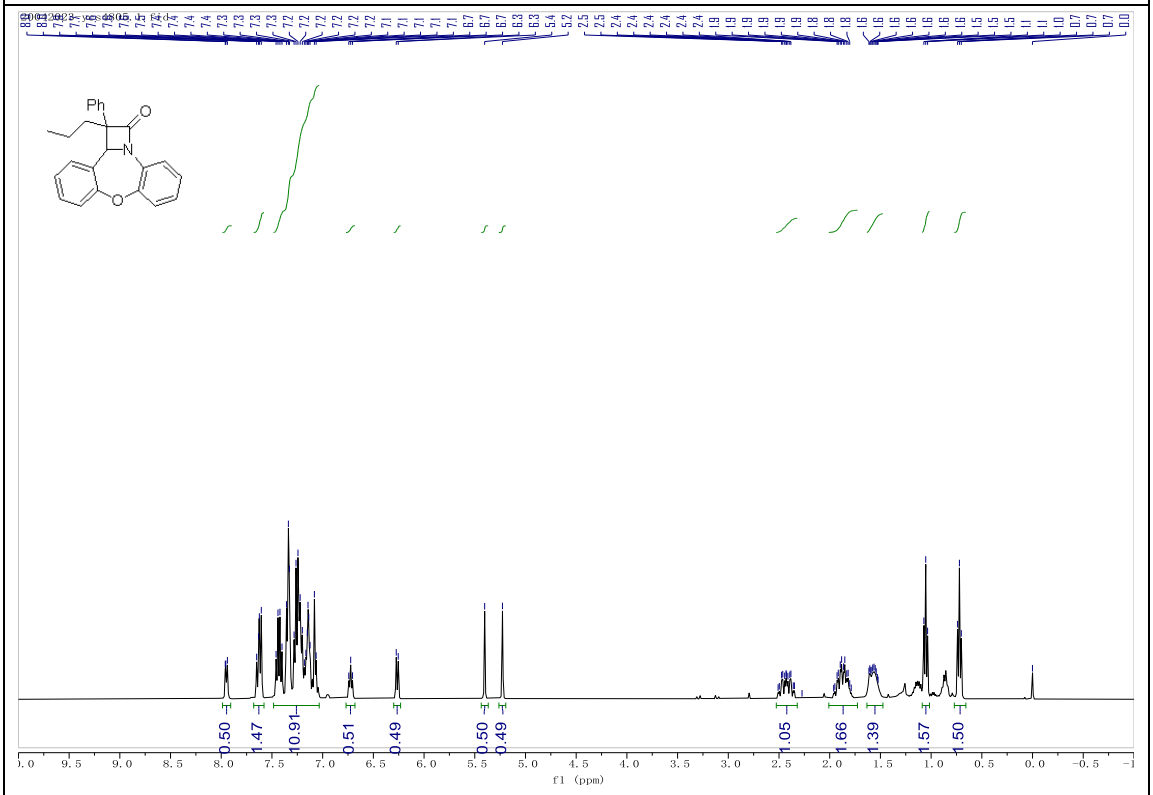
^{1}H NMR Spectrum of **3as**



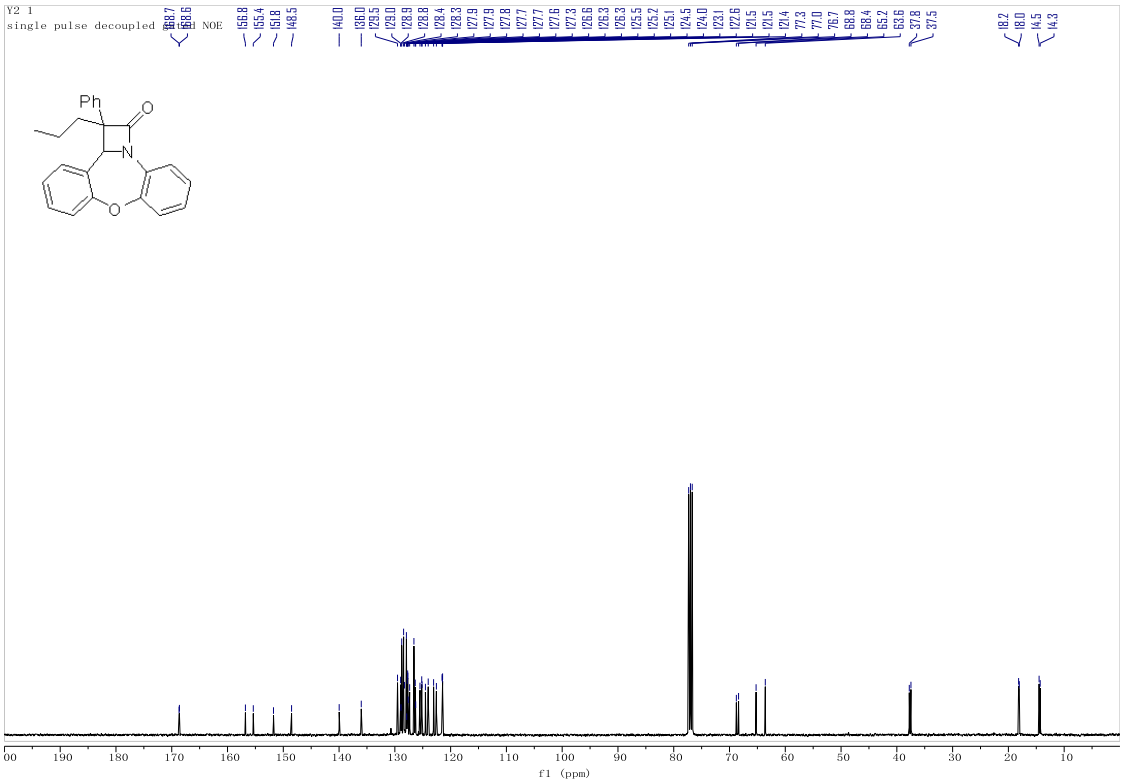
^{13}C NMR Spectrum of **3as**



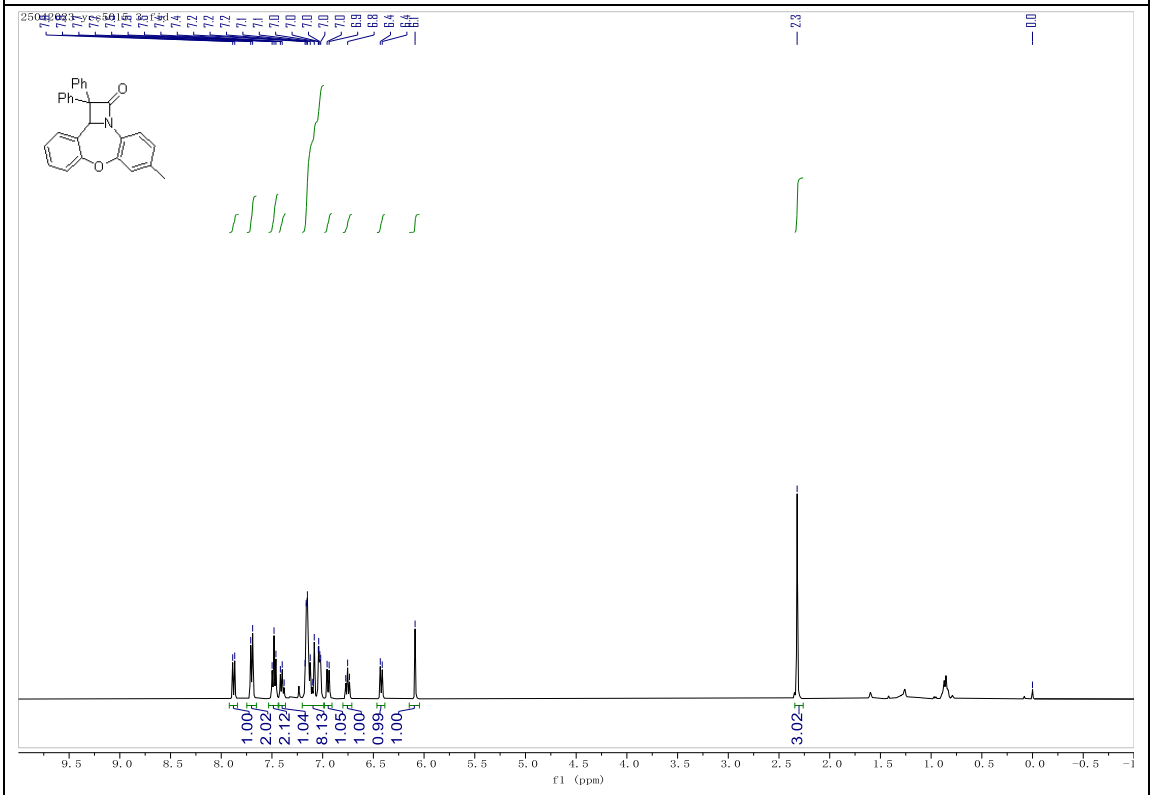
^{1}H NMR Spectrum of **3at**



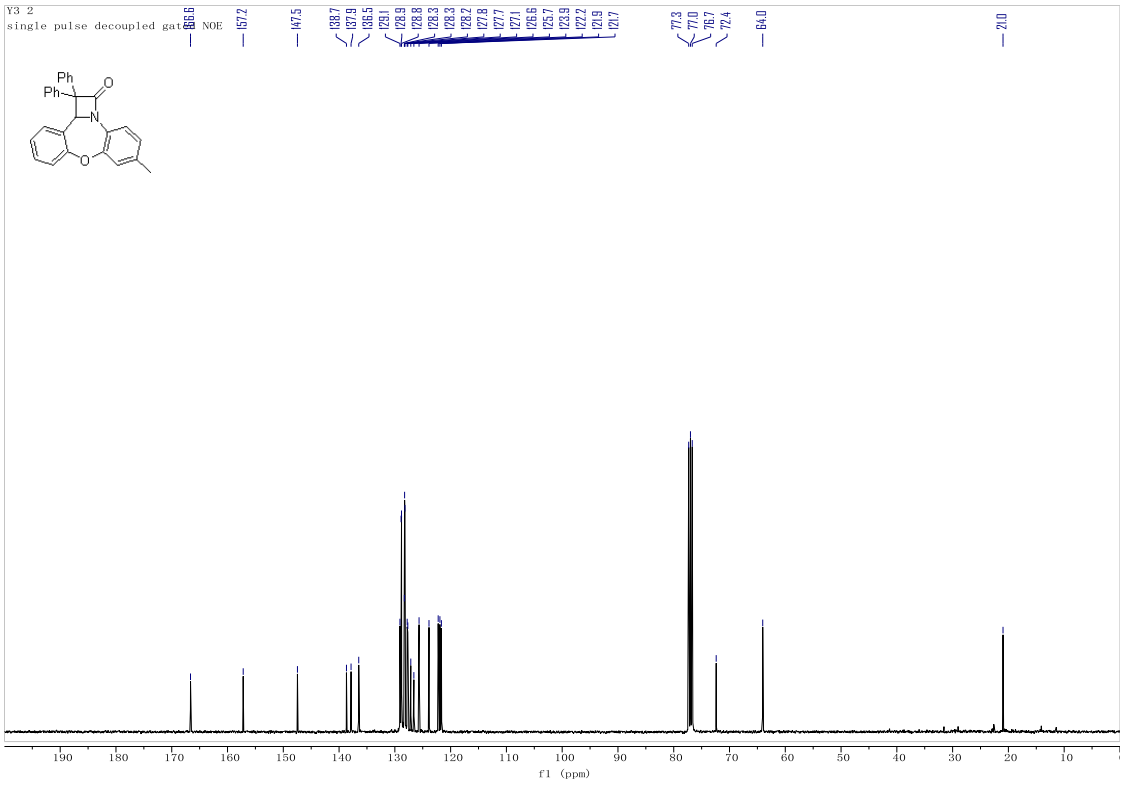
^{13}C NMR Spectrum of **3at**



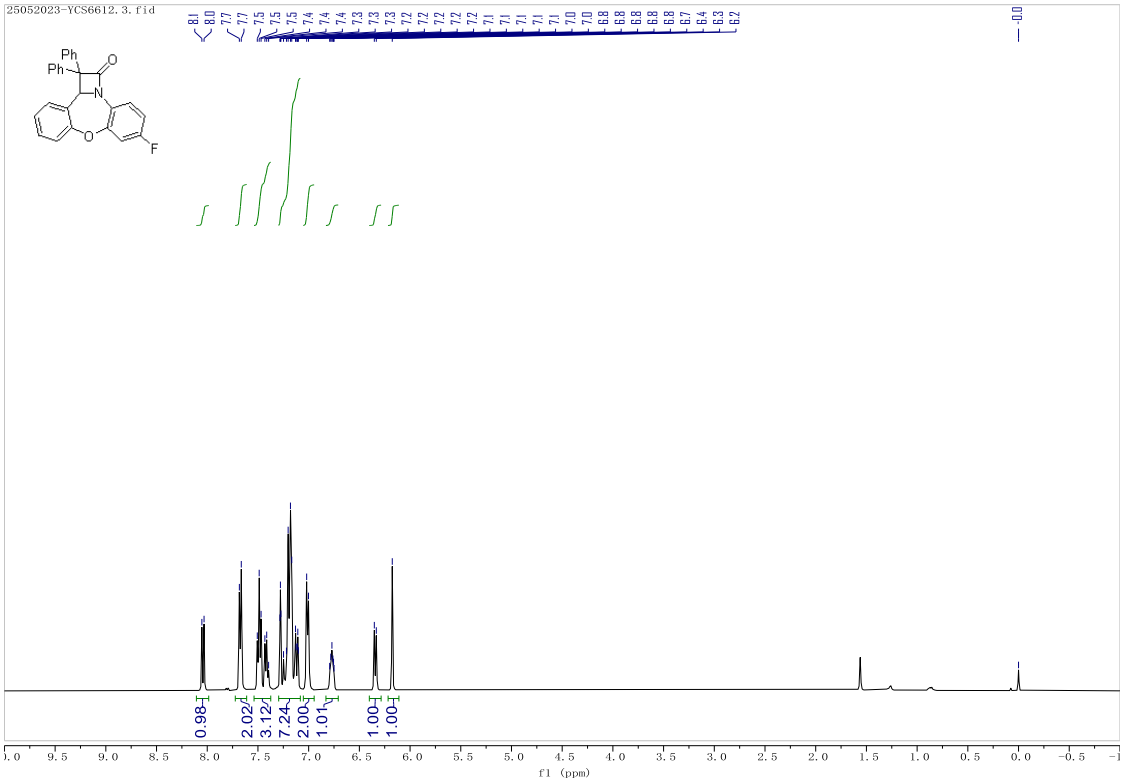
^{1}H NMR Spectrum of **3bq**



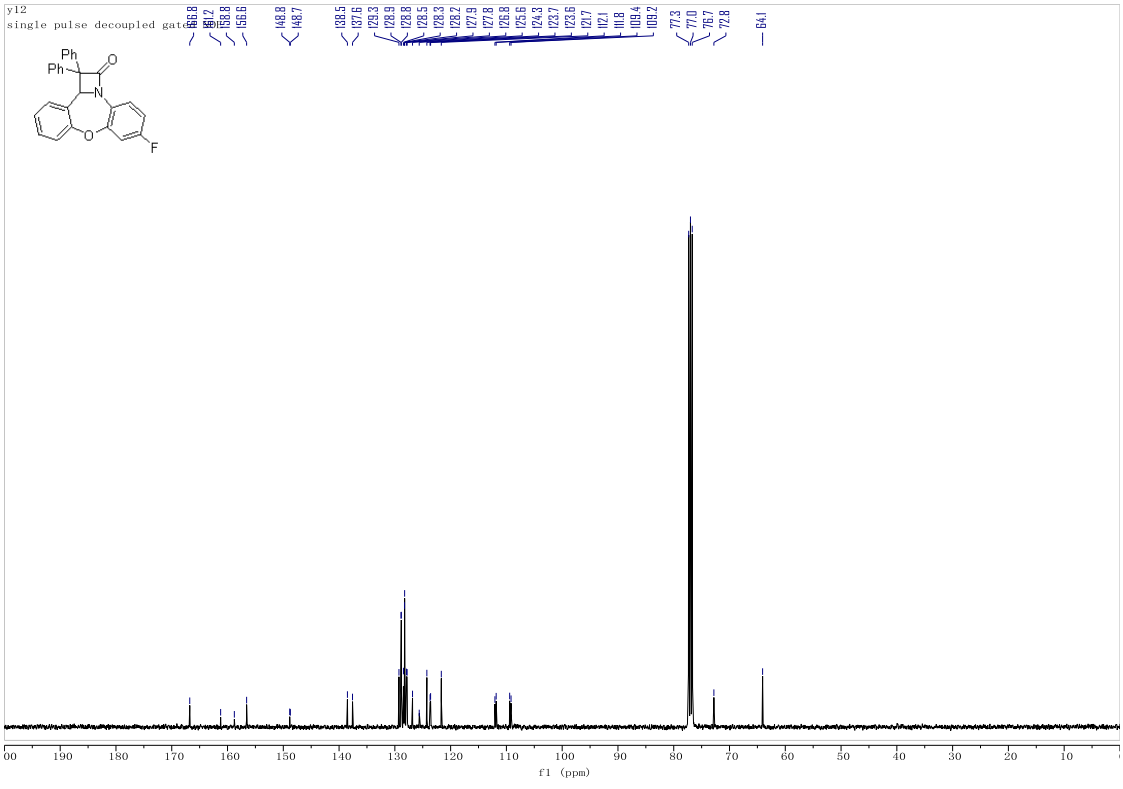
^{13}C NMR Spectrum of **3bq**

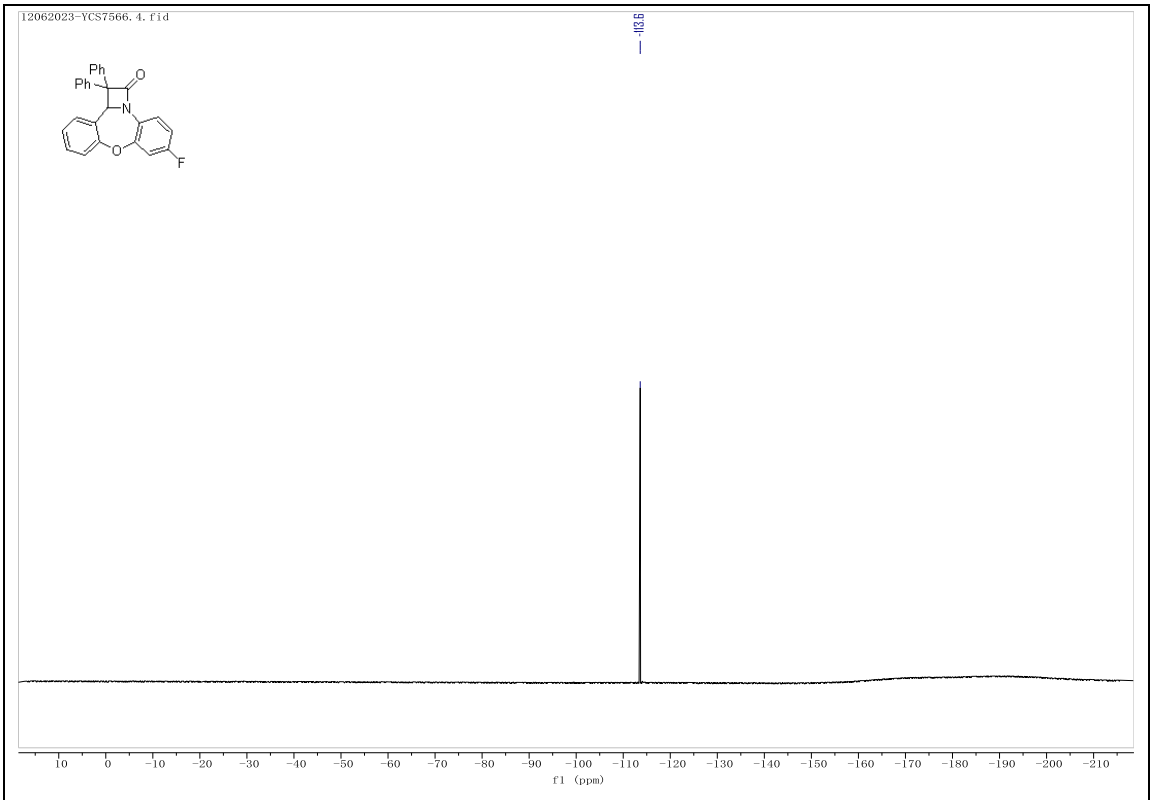


^{1}H NMR Spectrum of **3cq**



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

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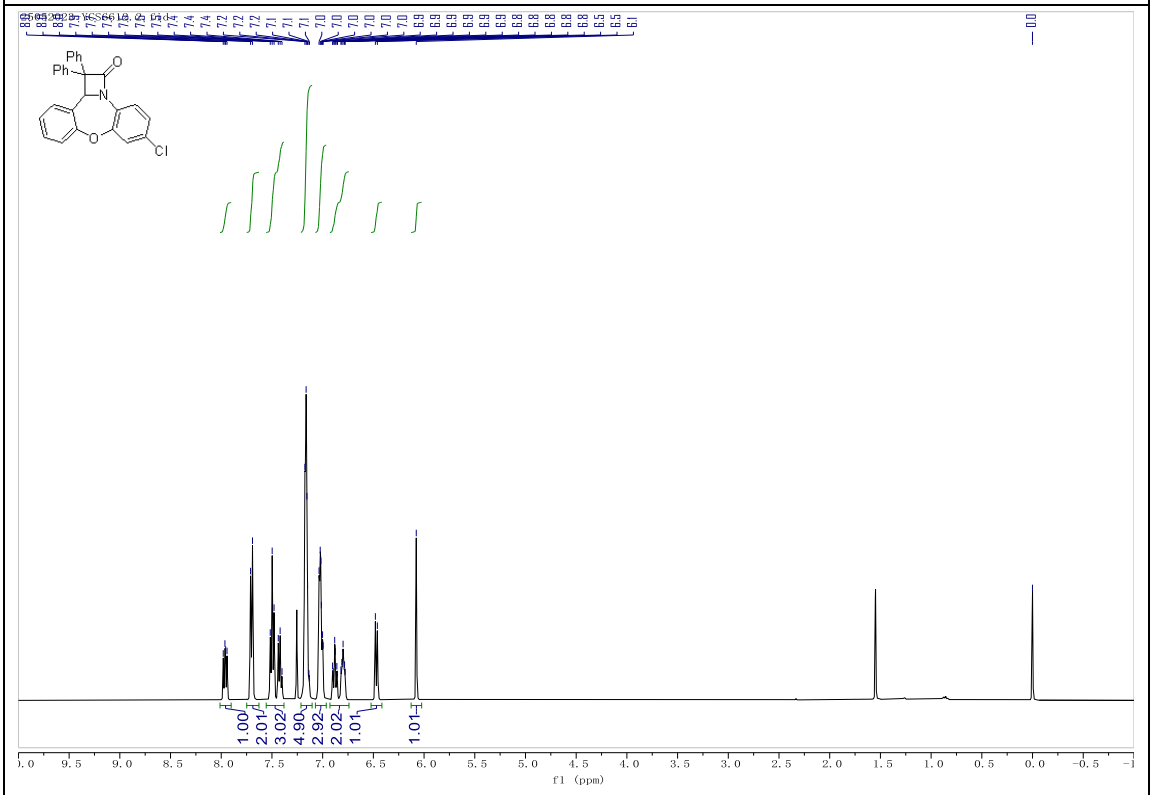
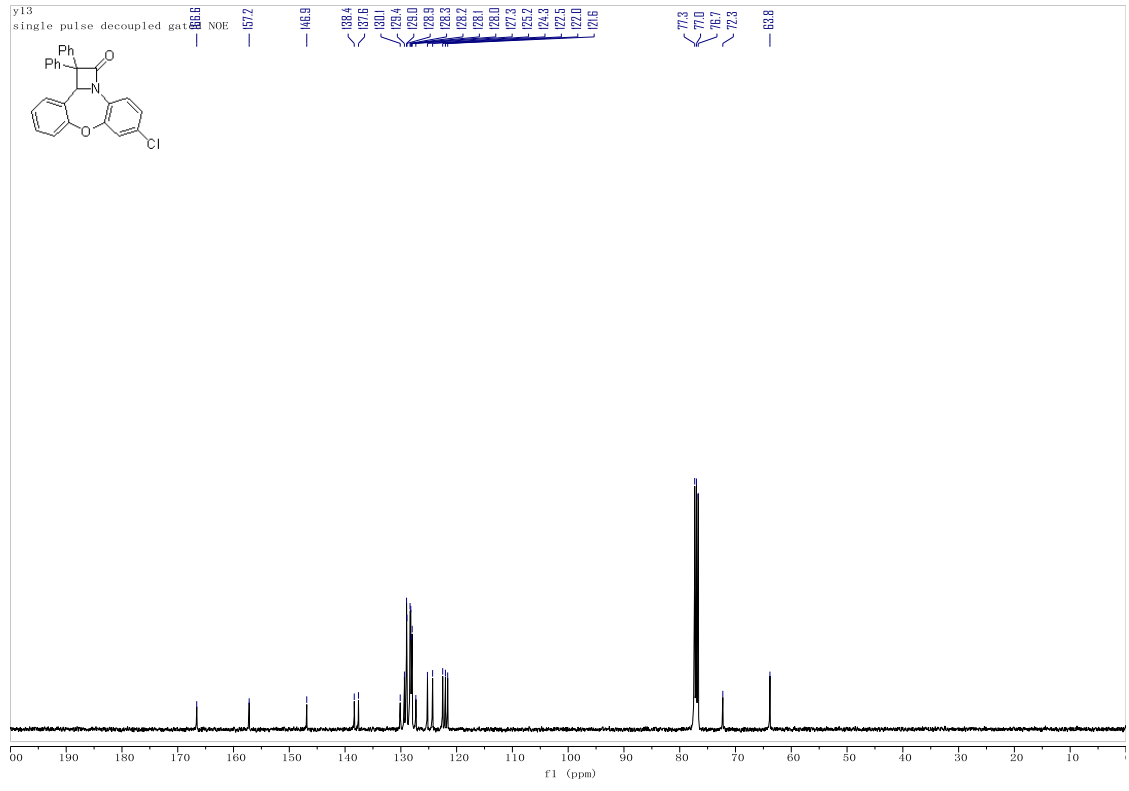
f1 (ppm)

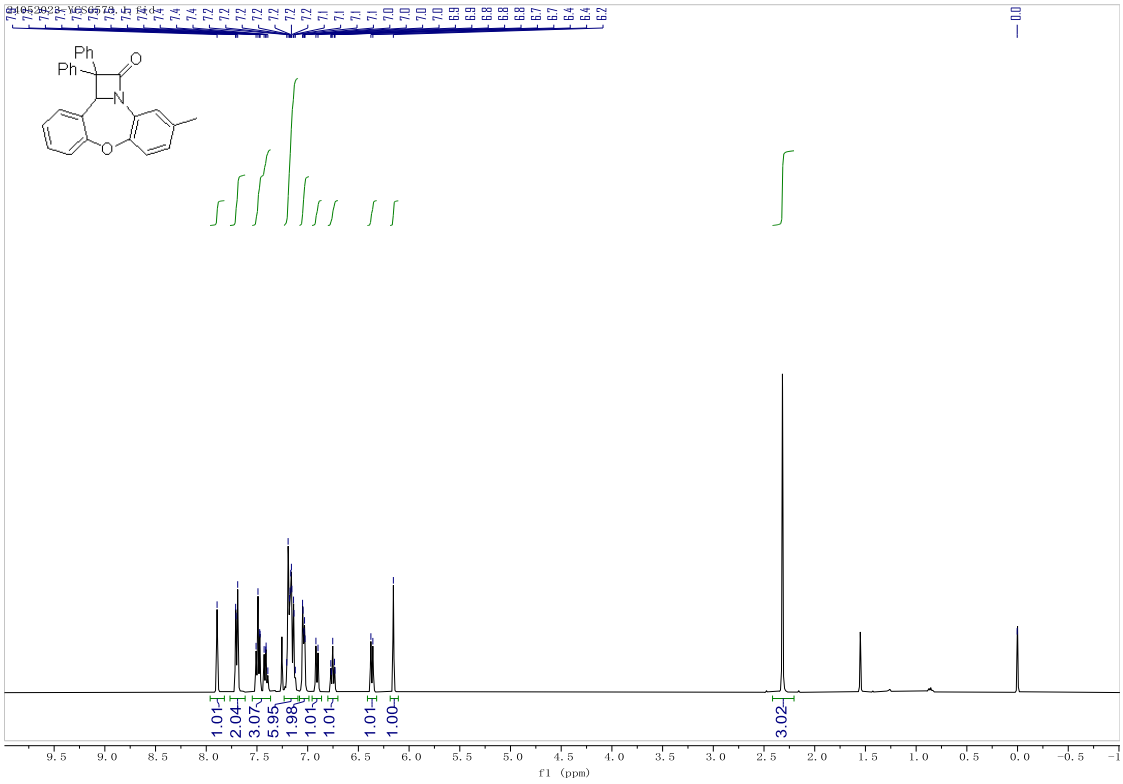
^{1}H NMR Spectrum of **3dq**



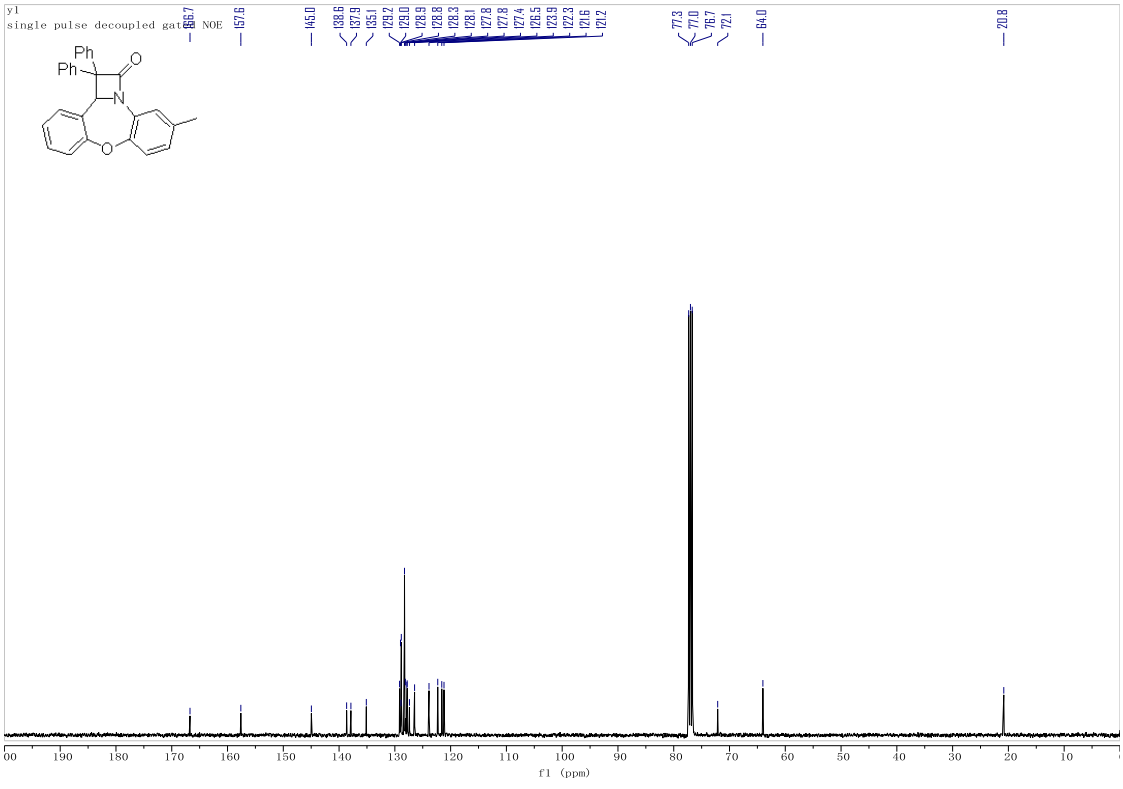
^{13}C NMR Spectrum of **3dq**



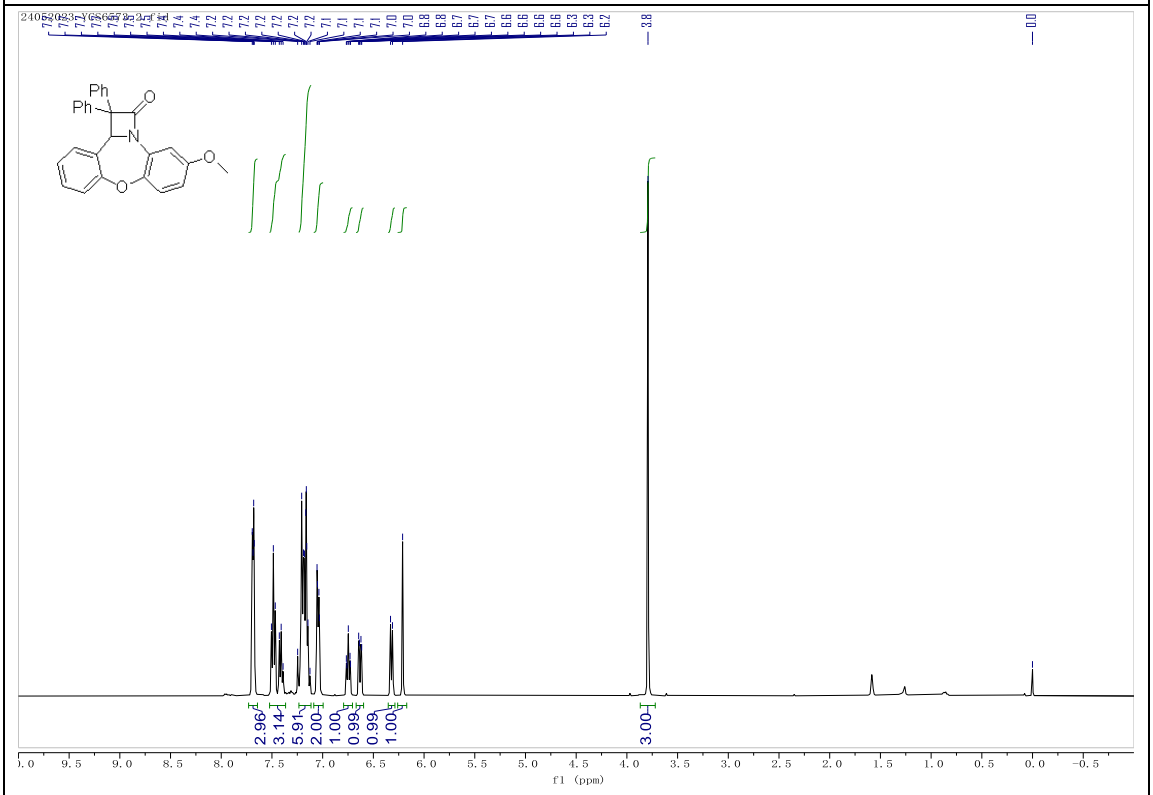
^{1}H NMR Spectrum of **3eq**



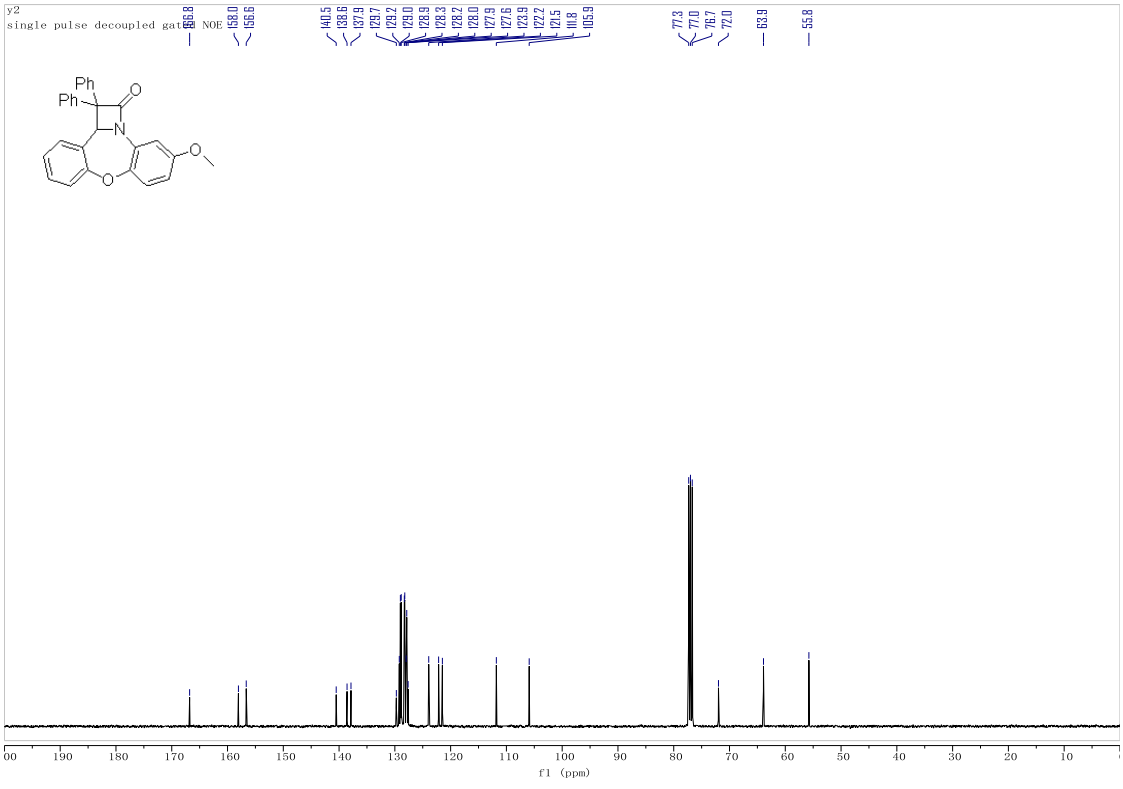
^{13}C NMR Spectrum of **3eq**



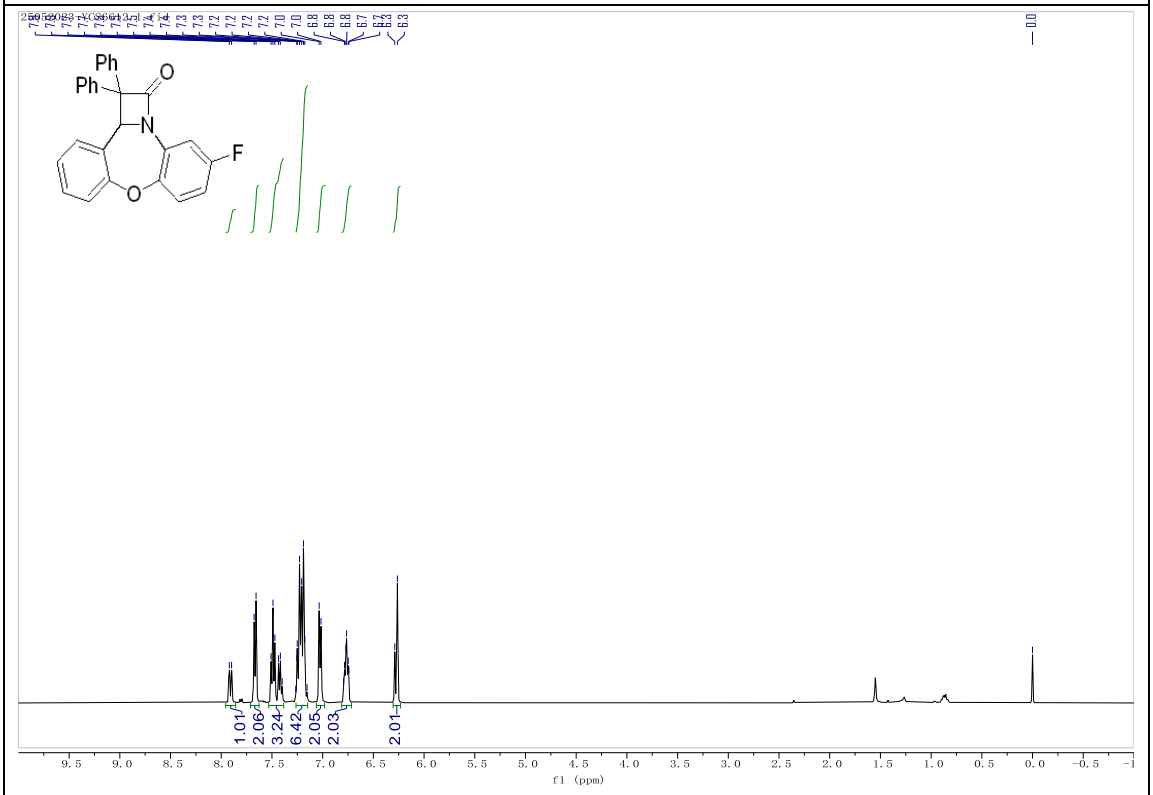
^{1}H NMR Spectrum of **3fq**



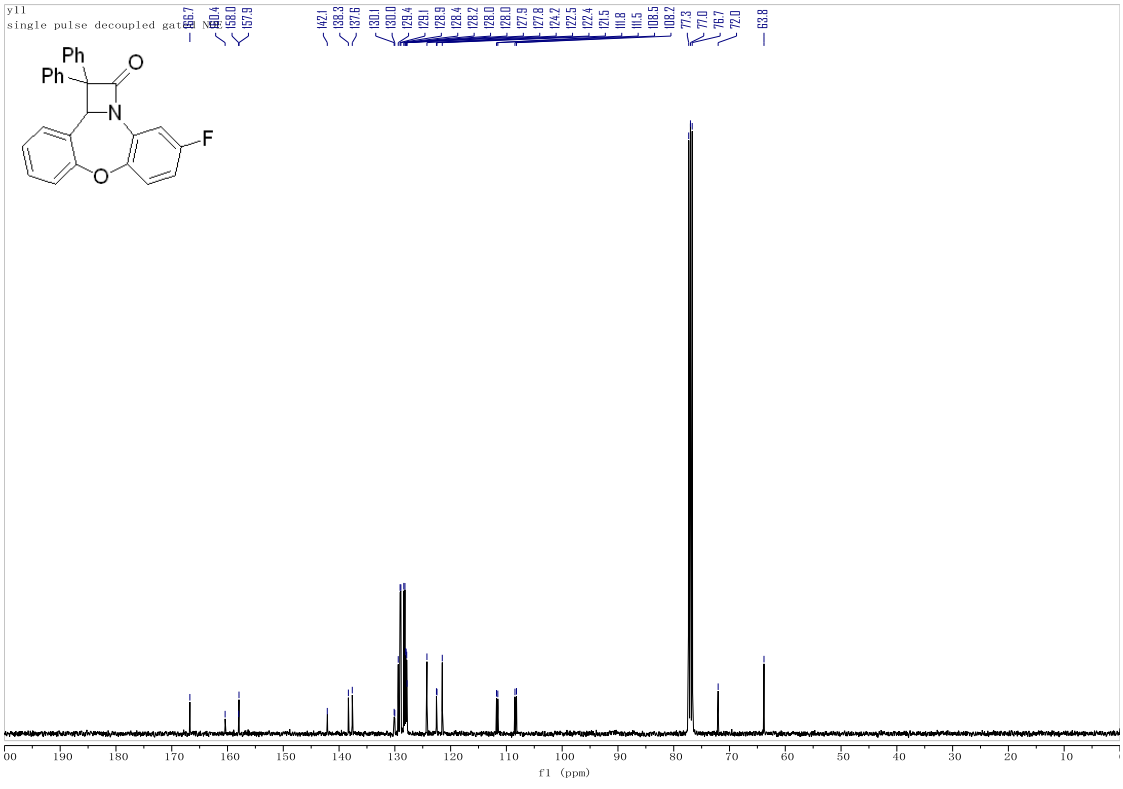
^{13}C NMR Spectrum of **3fq**

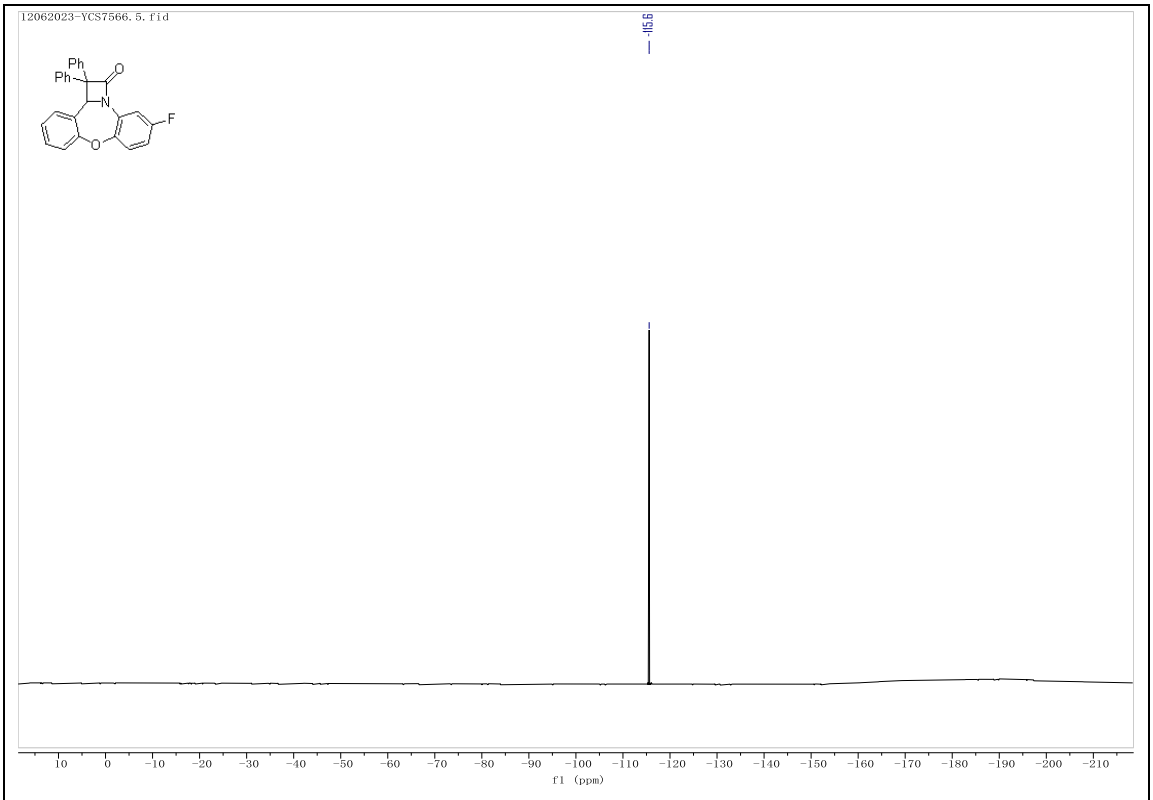


^{1}H NMR Spectrum of **3gq**



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

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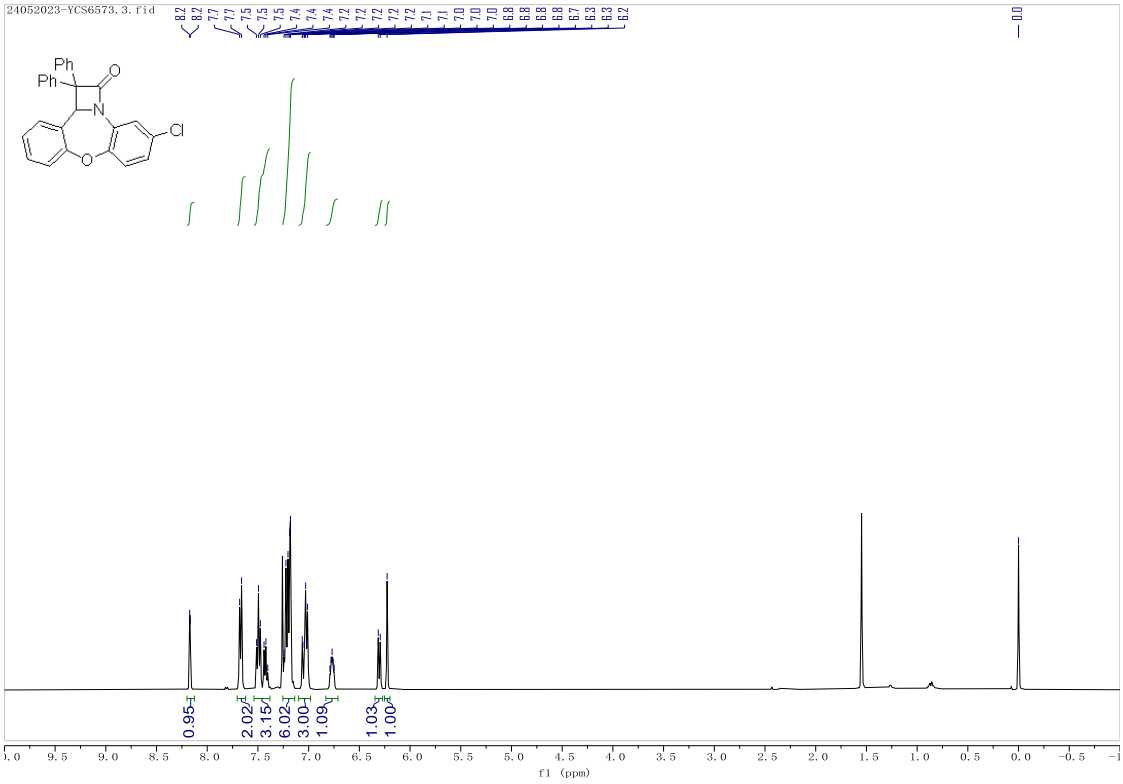
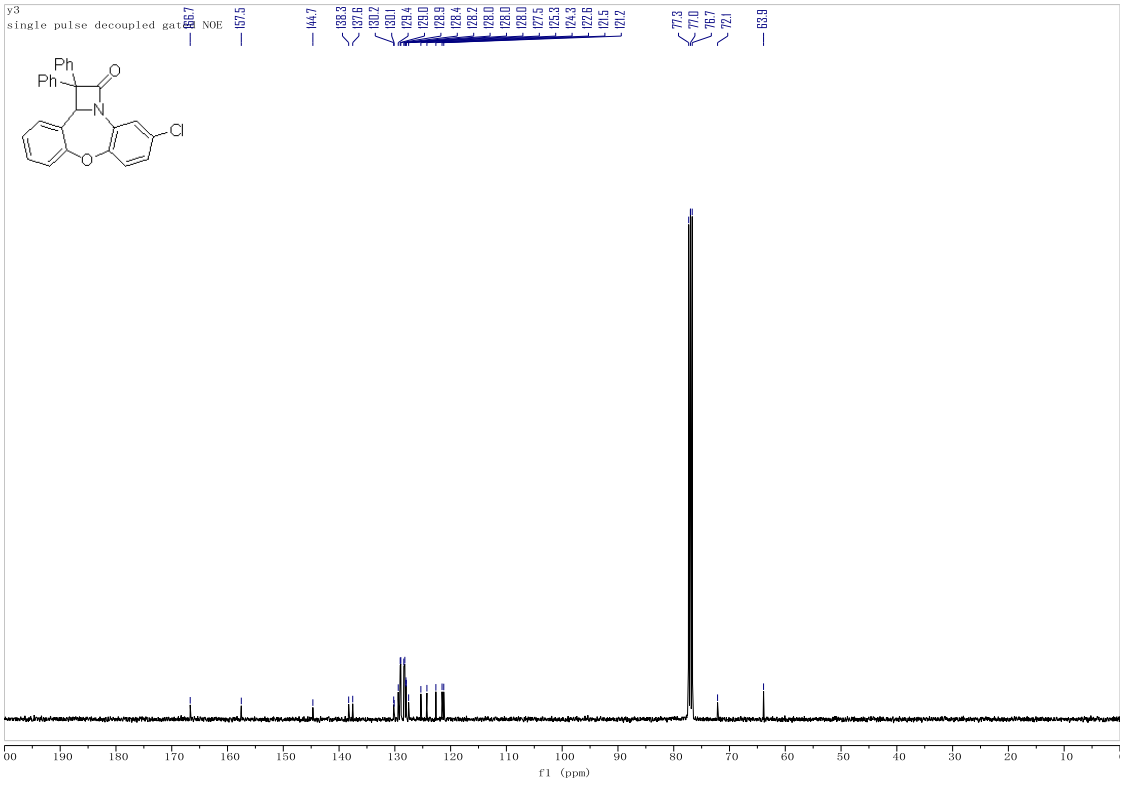
f1 (ppm)

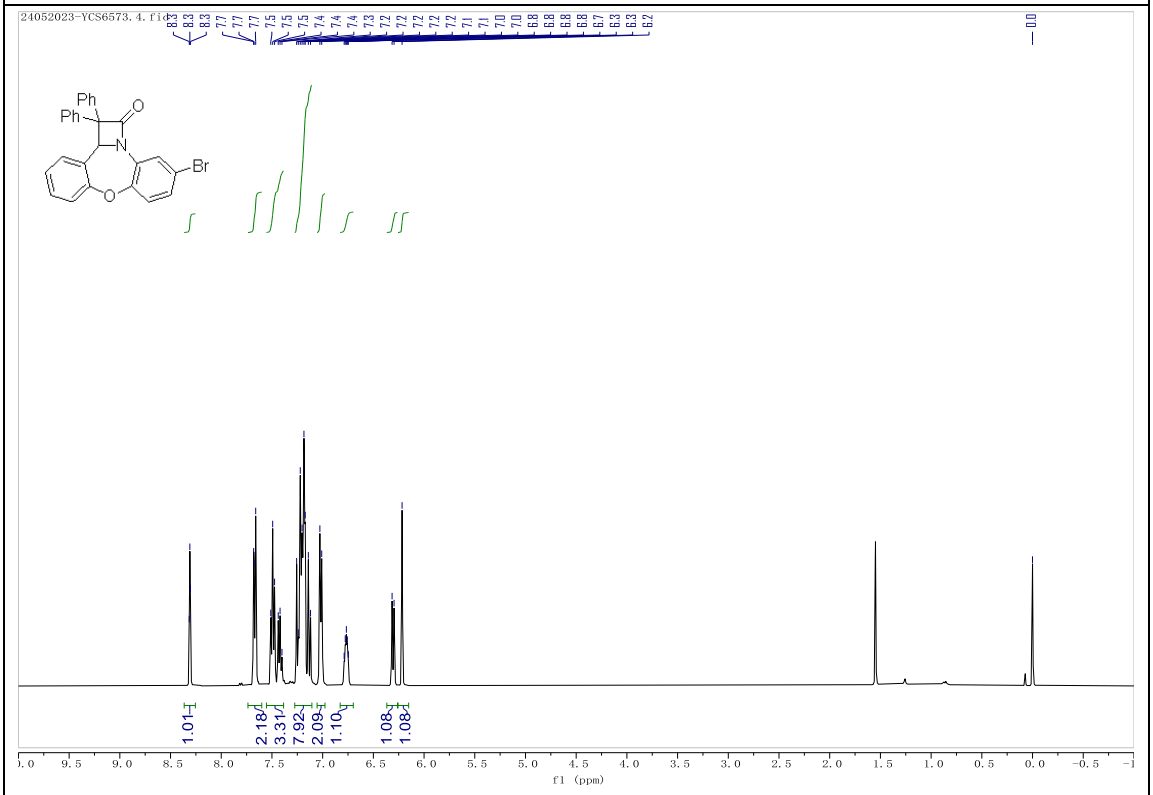
^{1}H NMR Spectrum of **3hq**



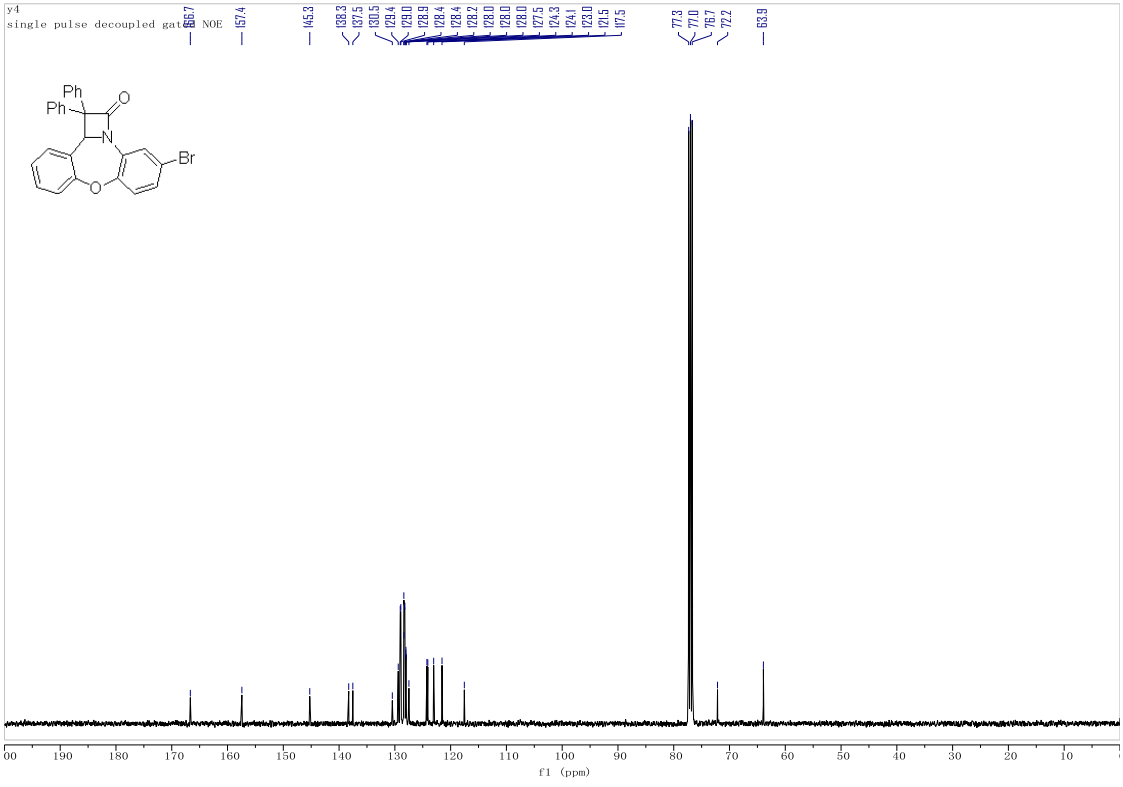
^{13}C NMR Spectrum of **3hq**



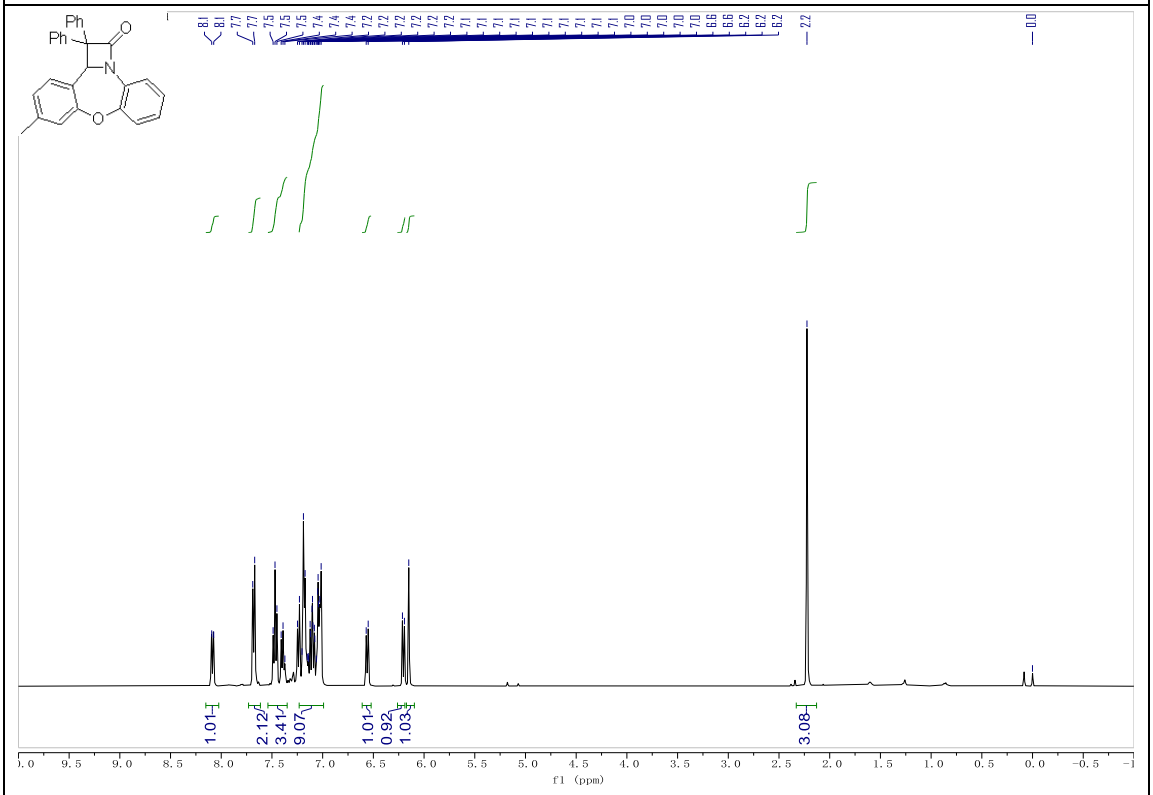
^{1}H NMR Spectrum of **3iq**



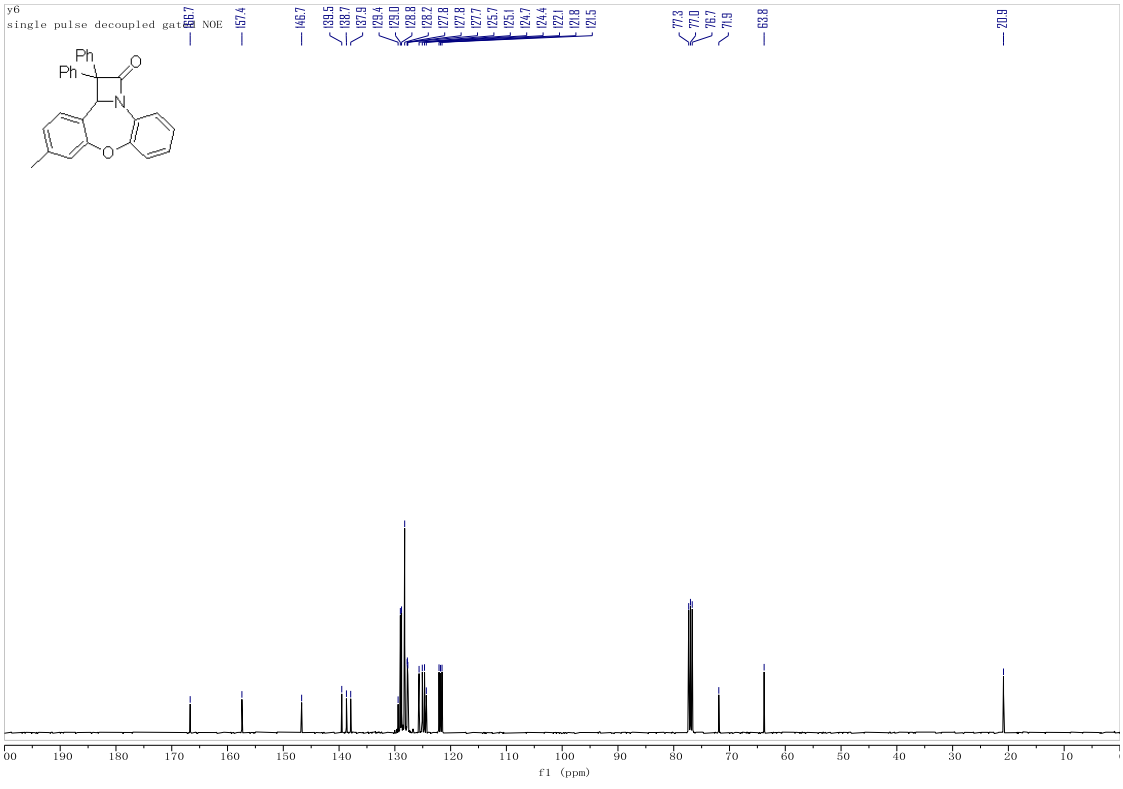
^{13}C NMR Spectrum of **3iq**



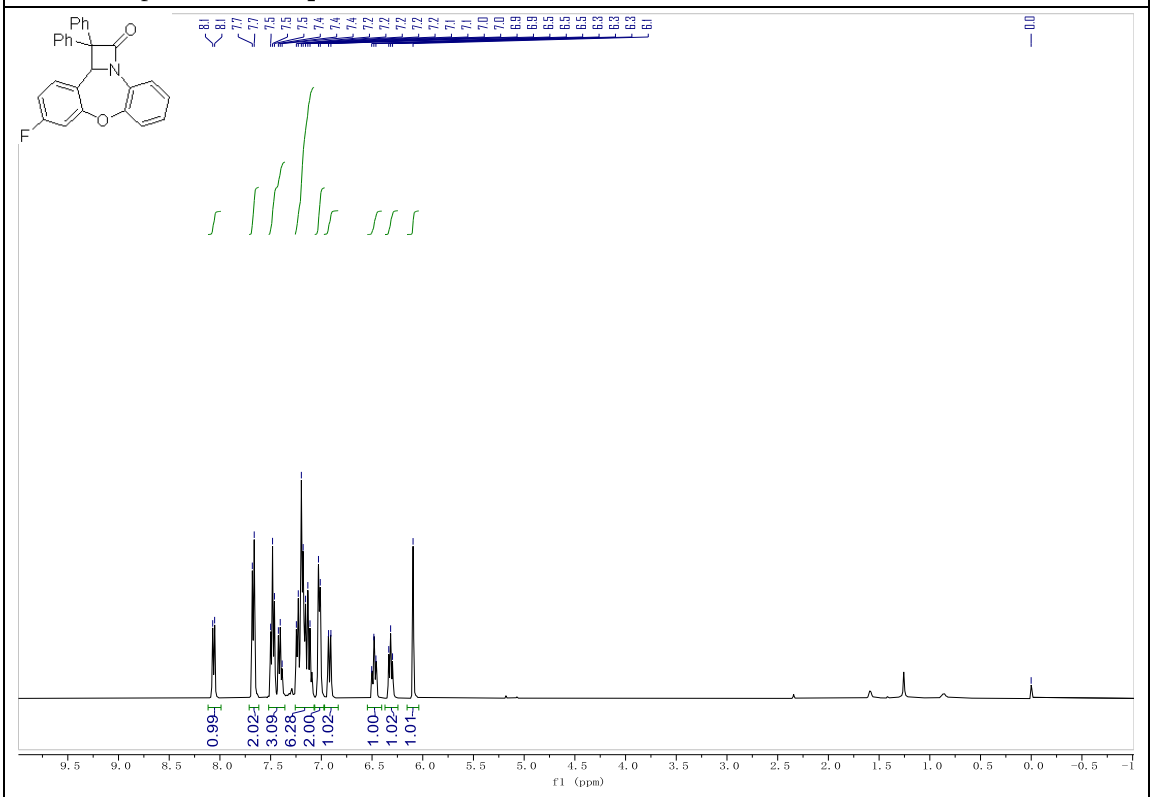
^{1}H NMR Spectrum of **3jq**



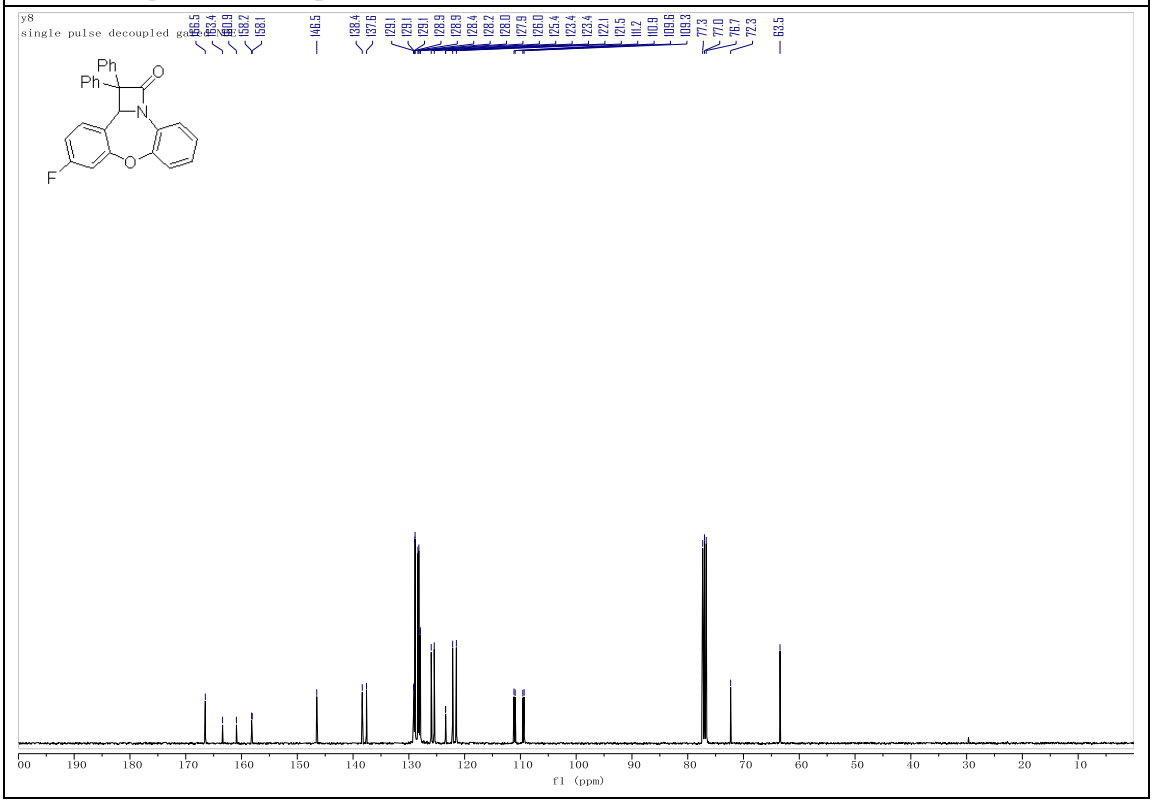
^{13}C NMR Spectrum of **3jq**

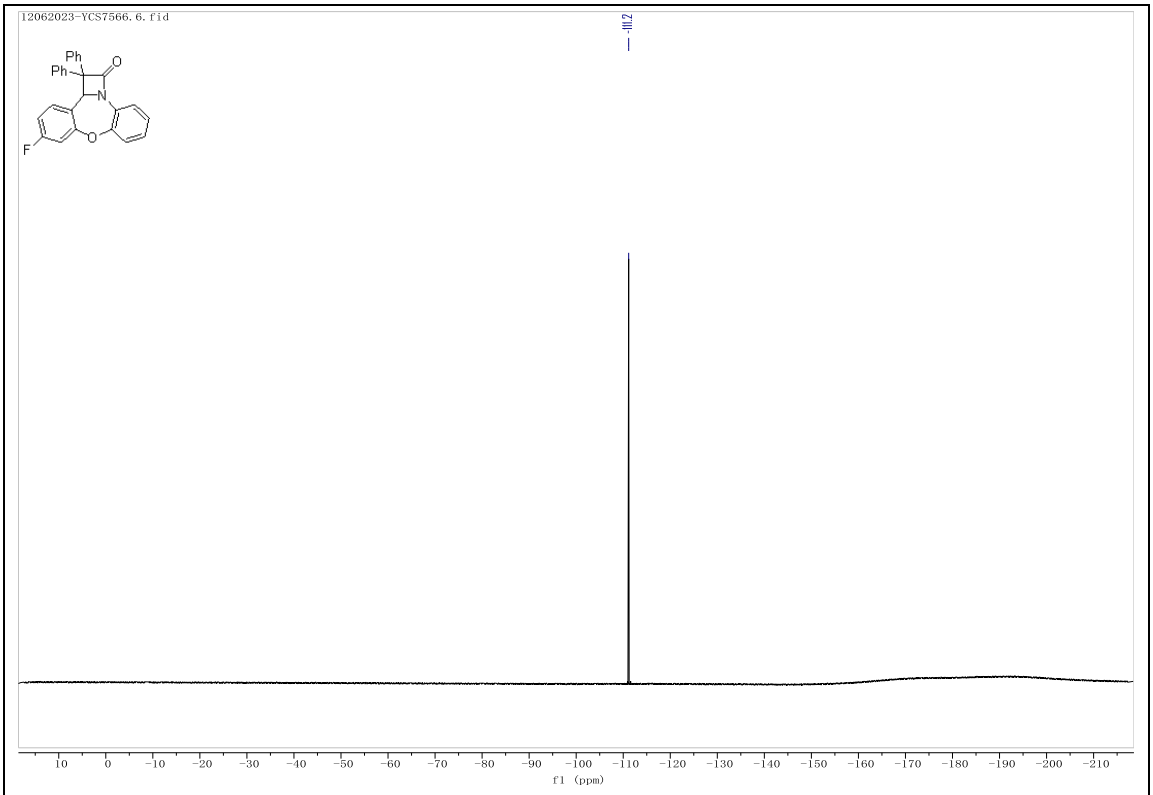


^{1}H NMR Spectrum of **3kq**



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

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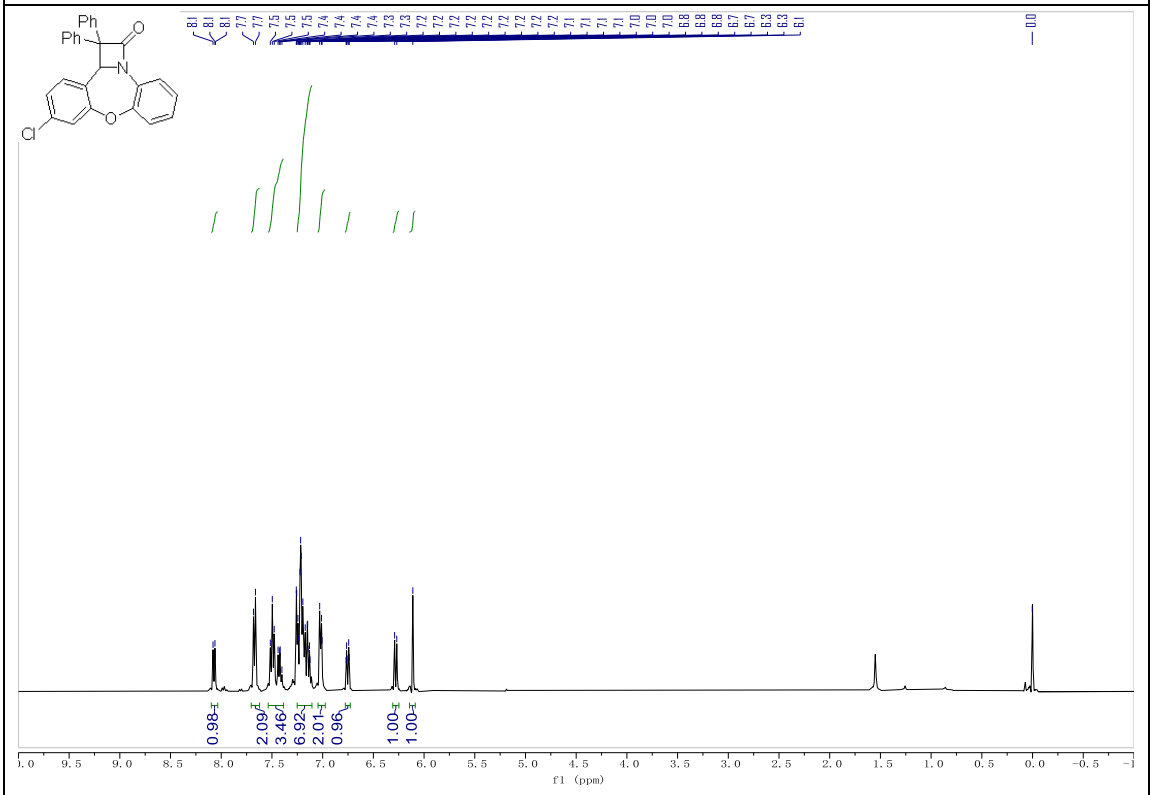
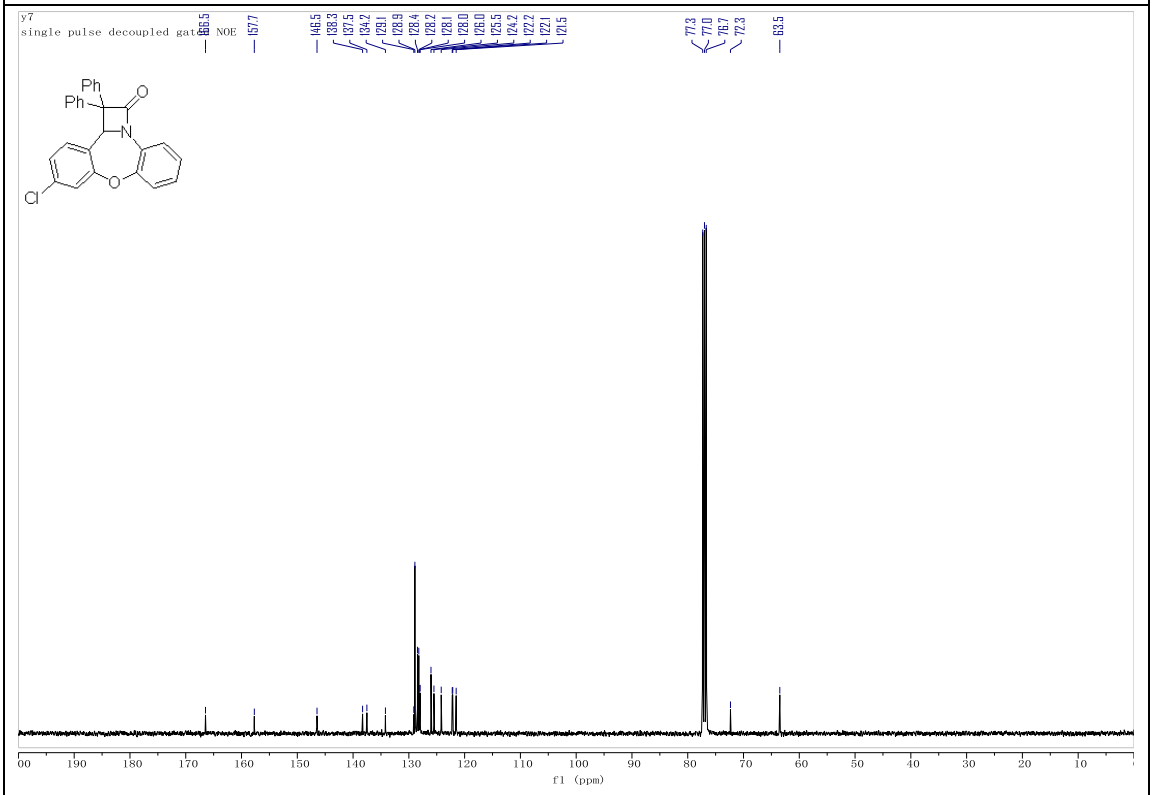
f1 (ppm)

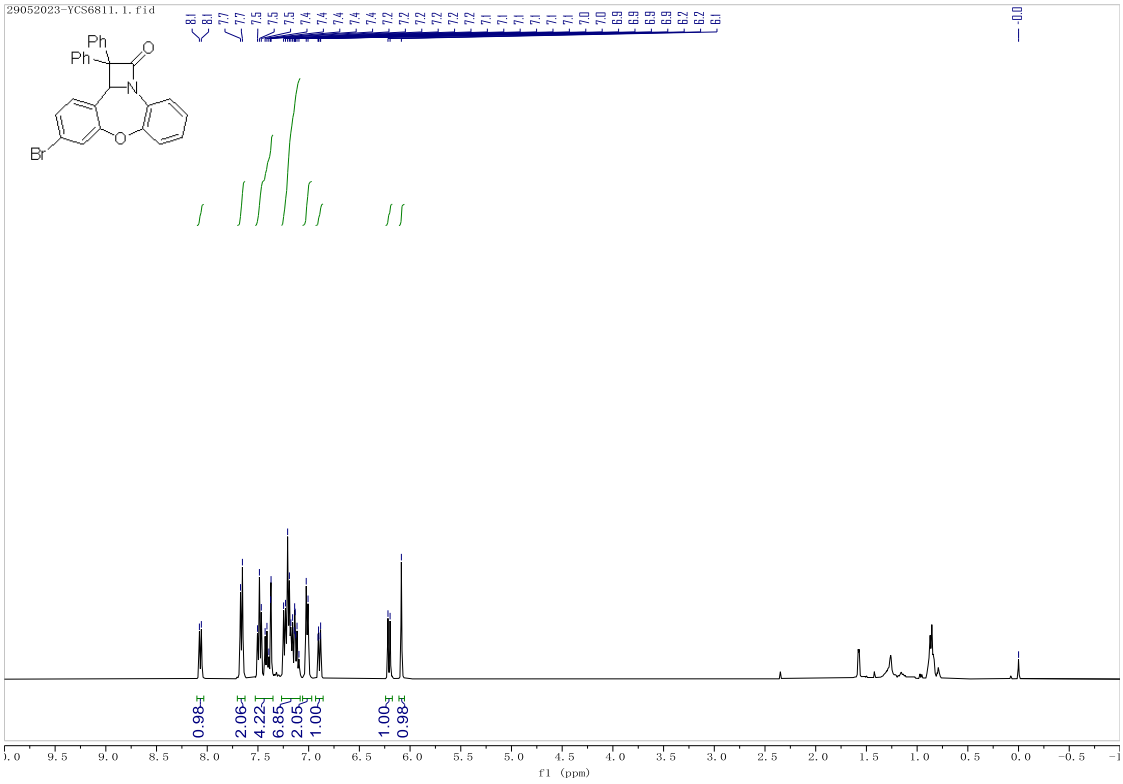
^{1}H NMR Spectrum of **3lq**



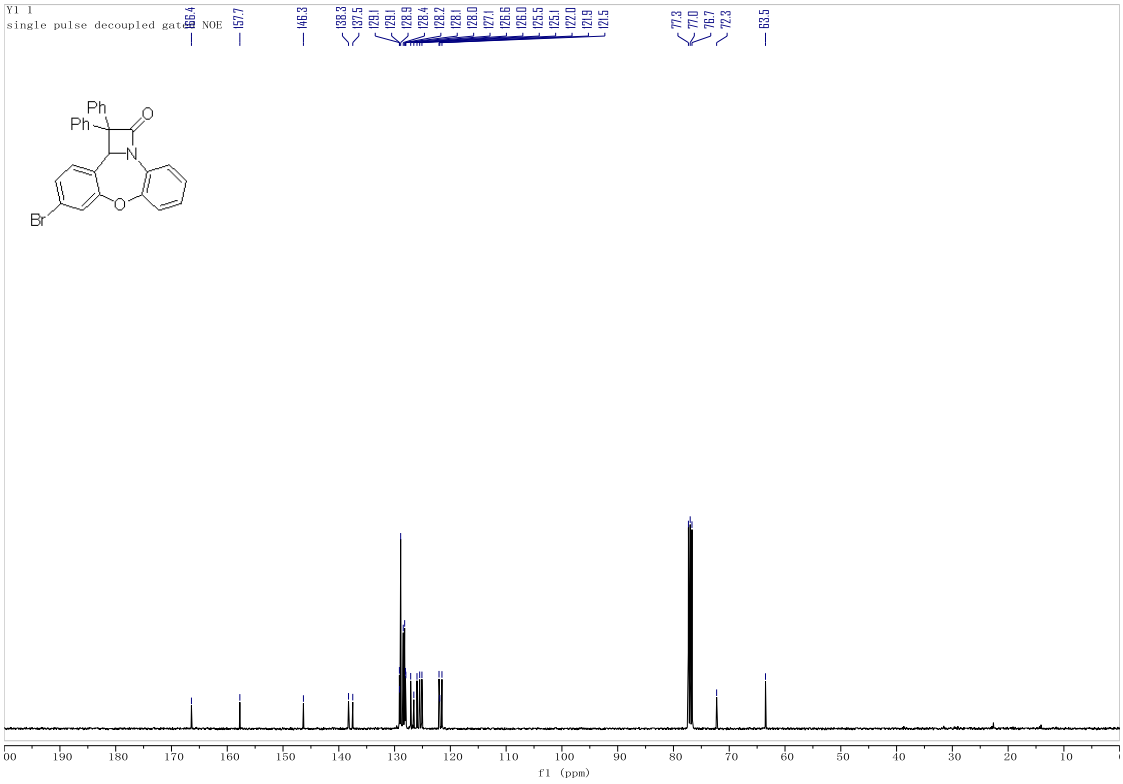
^{13}C NMR Spectrum of **3lq**



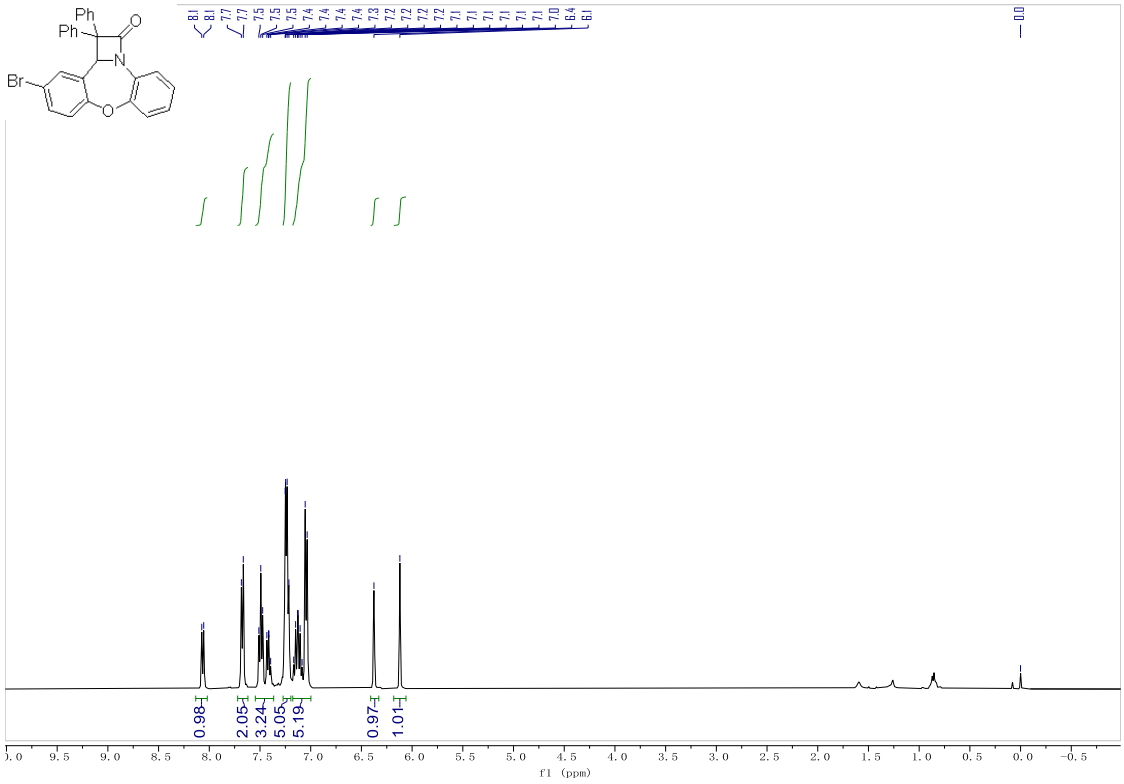
^{1}H NMR Spectrum of **3mq**



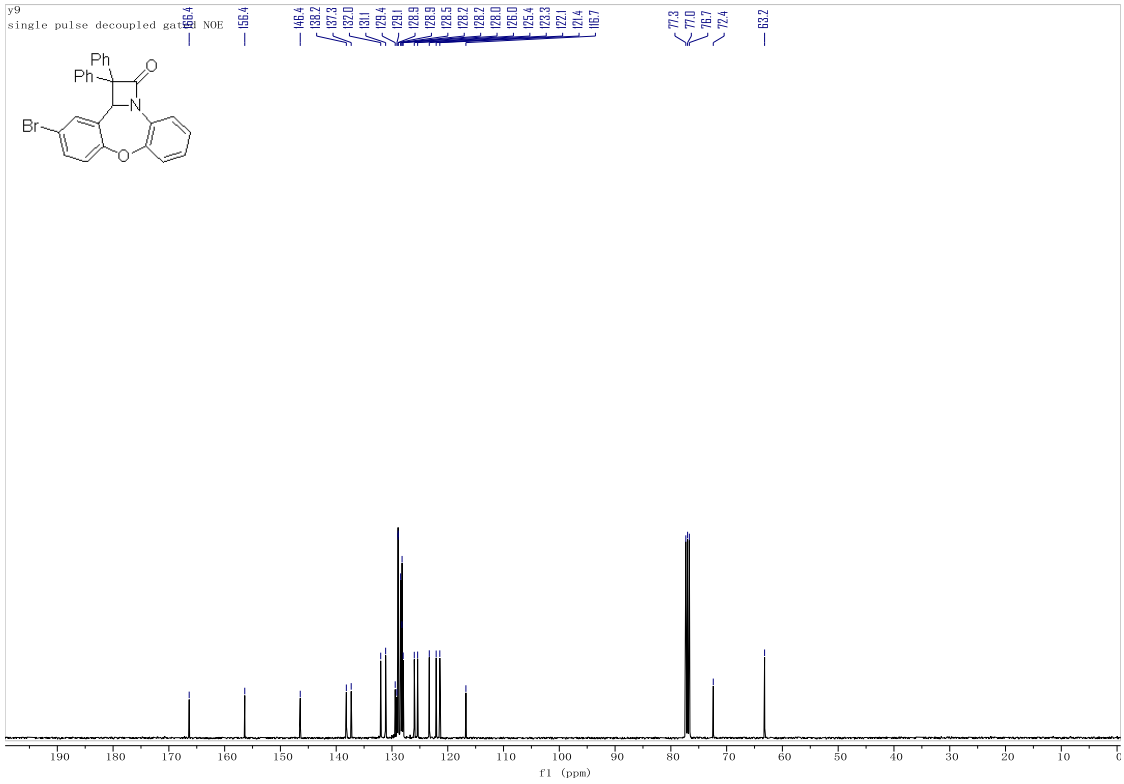
^{13}C NMR Spectrum of **3mq**



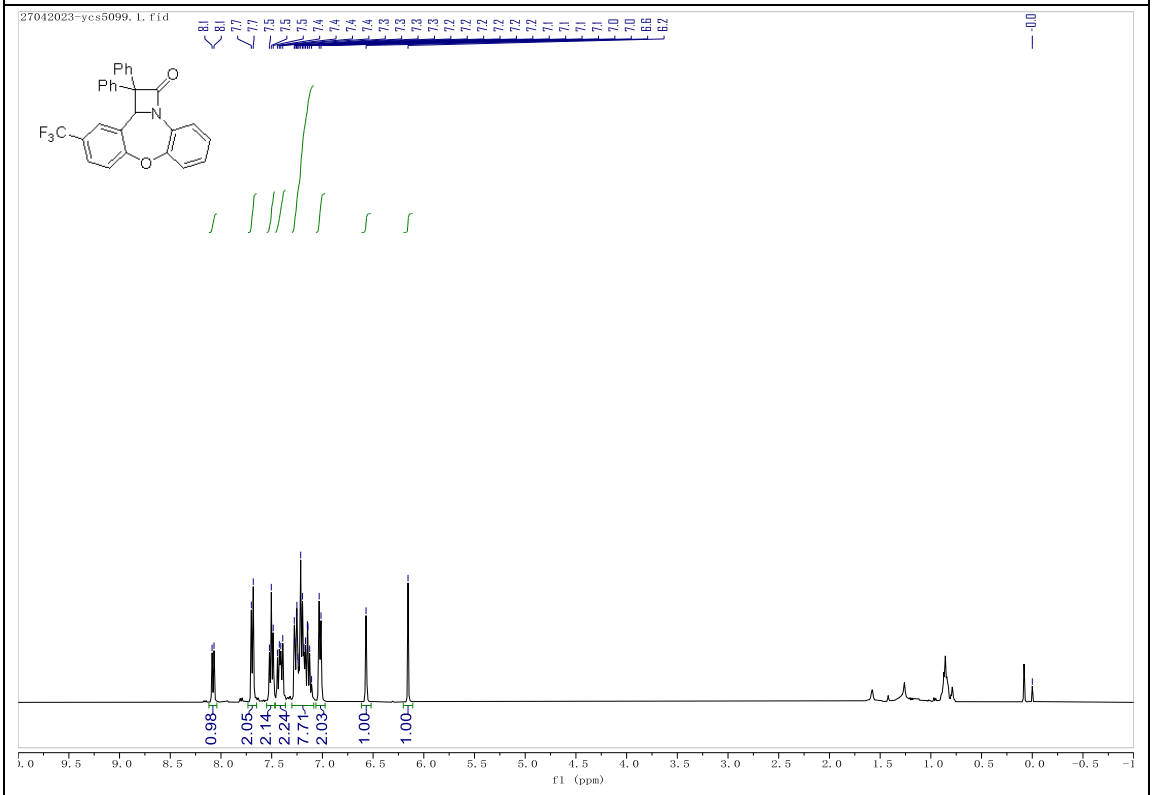
^{1}H NMR Spectrum of **3nq**



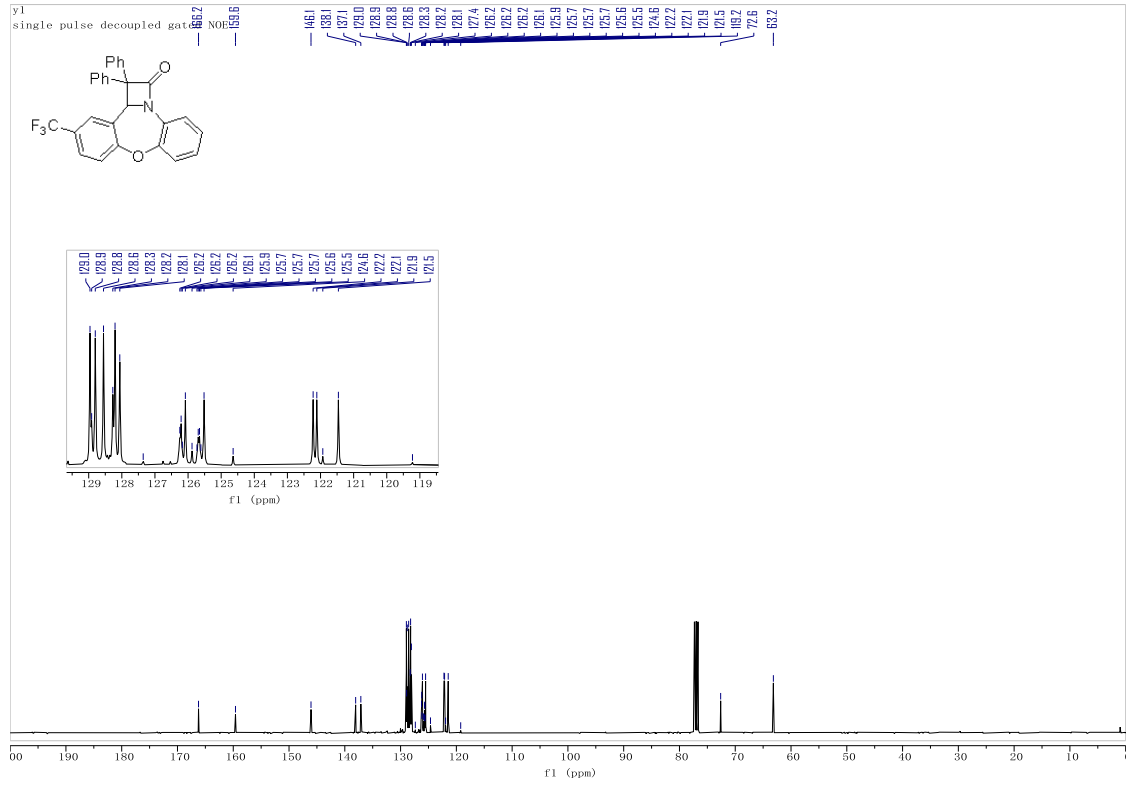
^{13}C NMR Spectrum of **3nq**

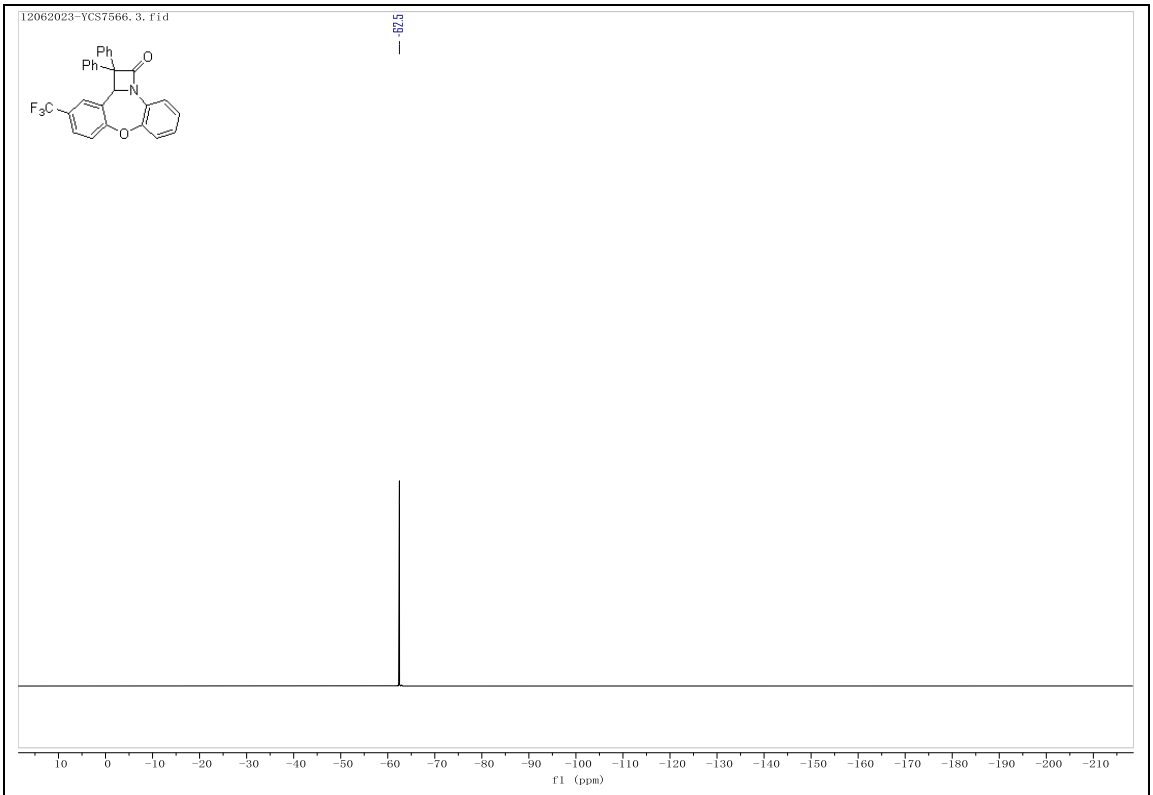


^{1}H NMR Spectrum of **3oq**



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

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F3C
O
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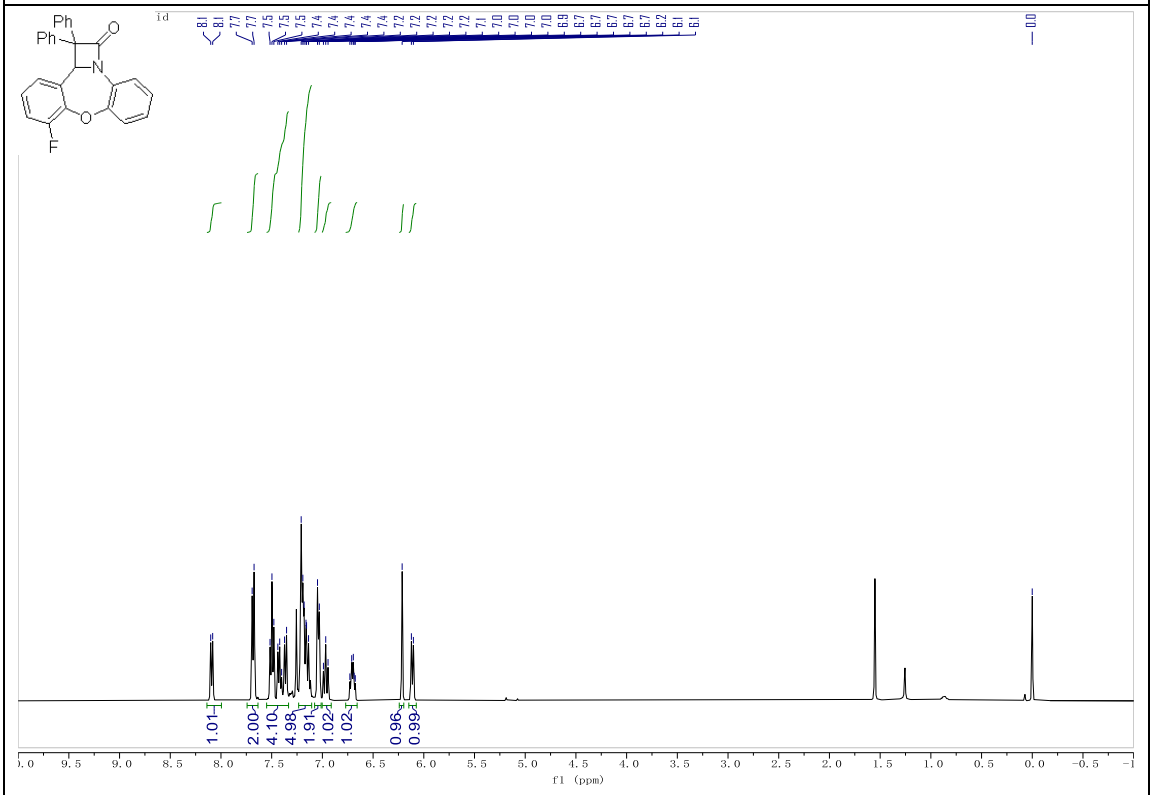
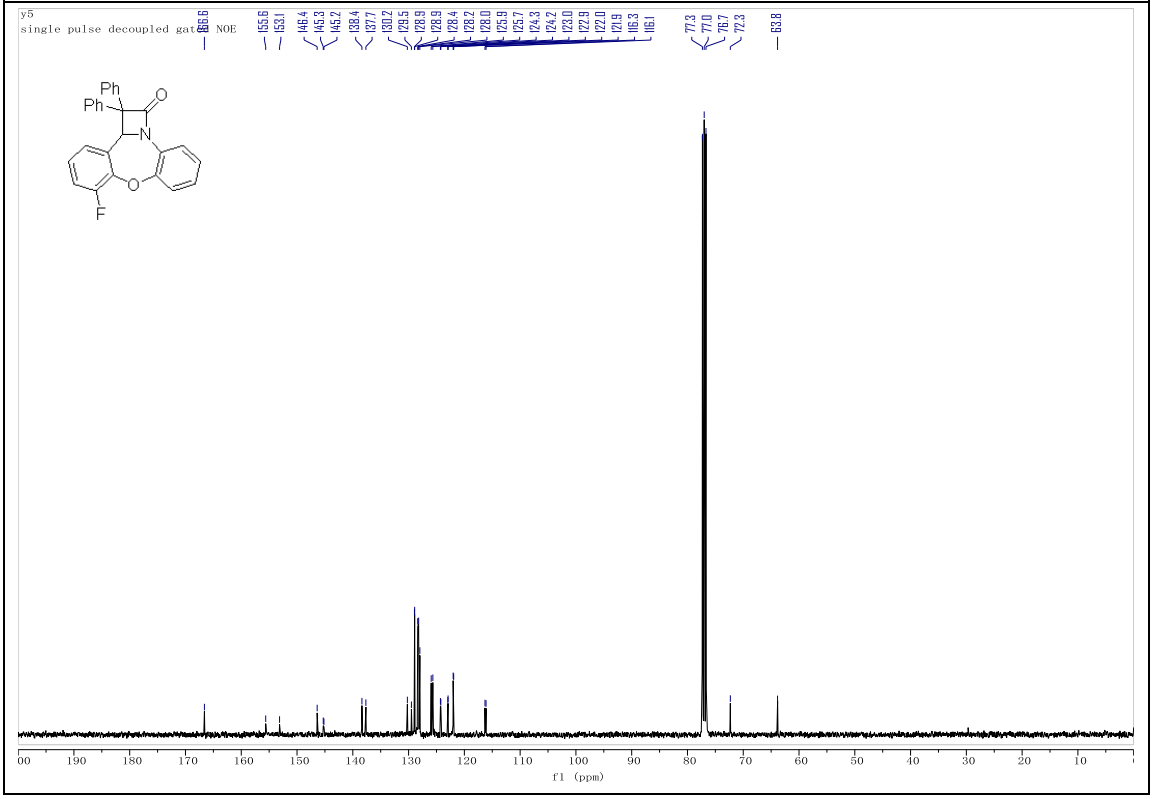
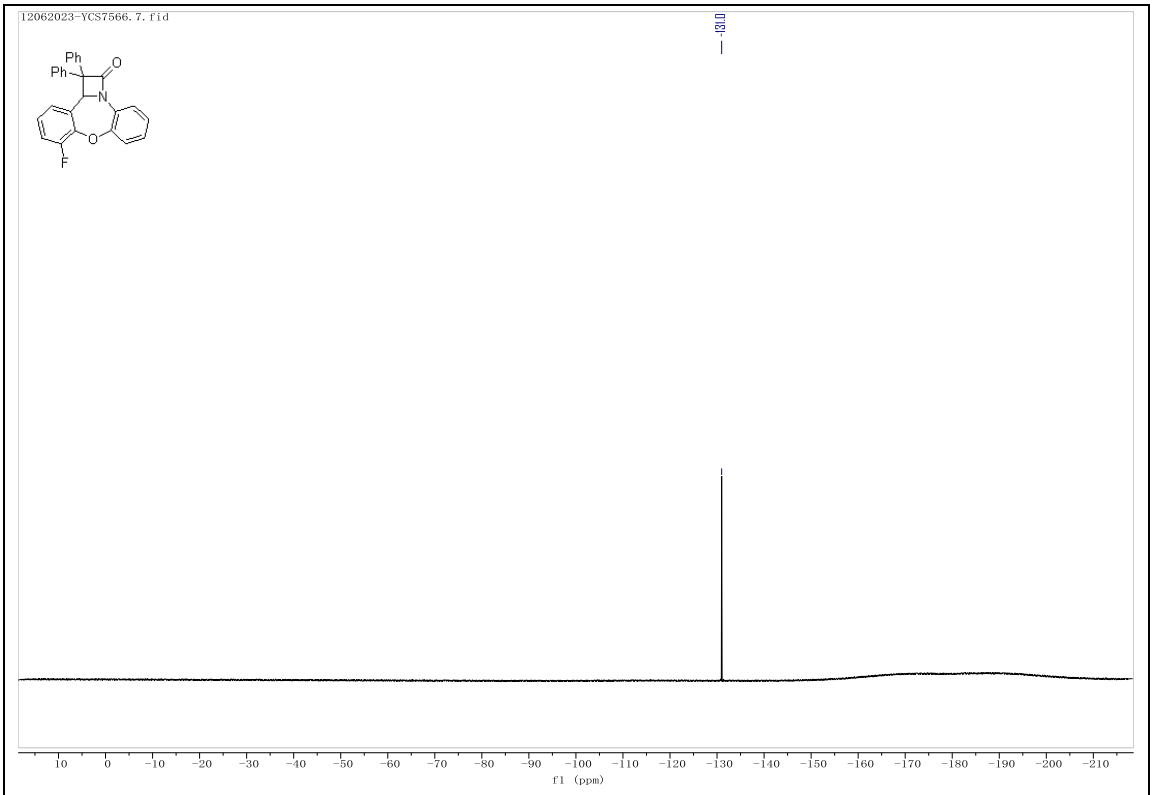
f1 (ppm)

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



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

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N
O
F
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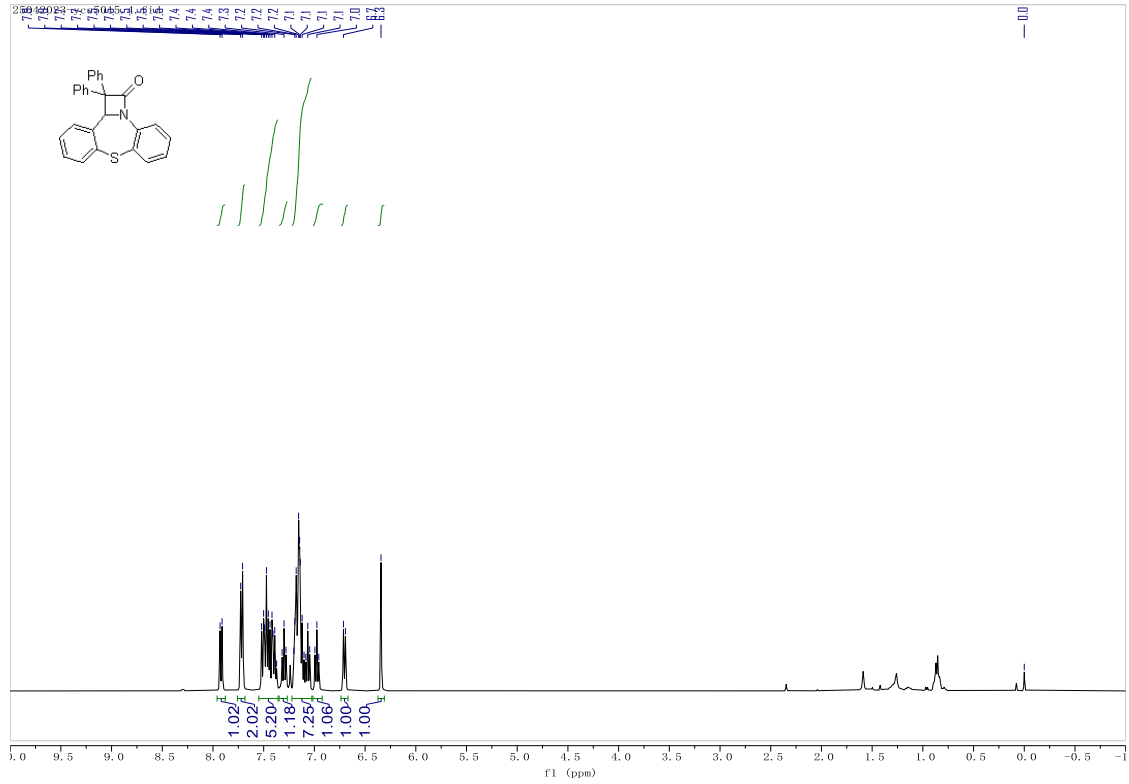
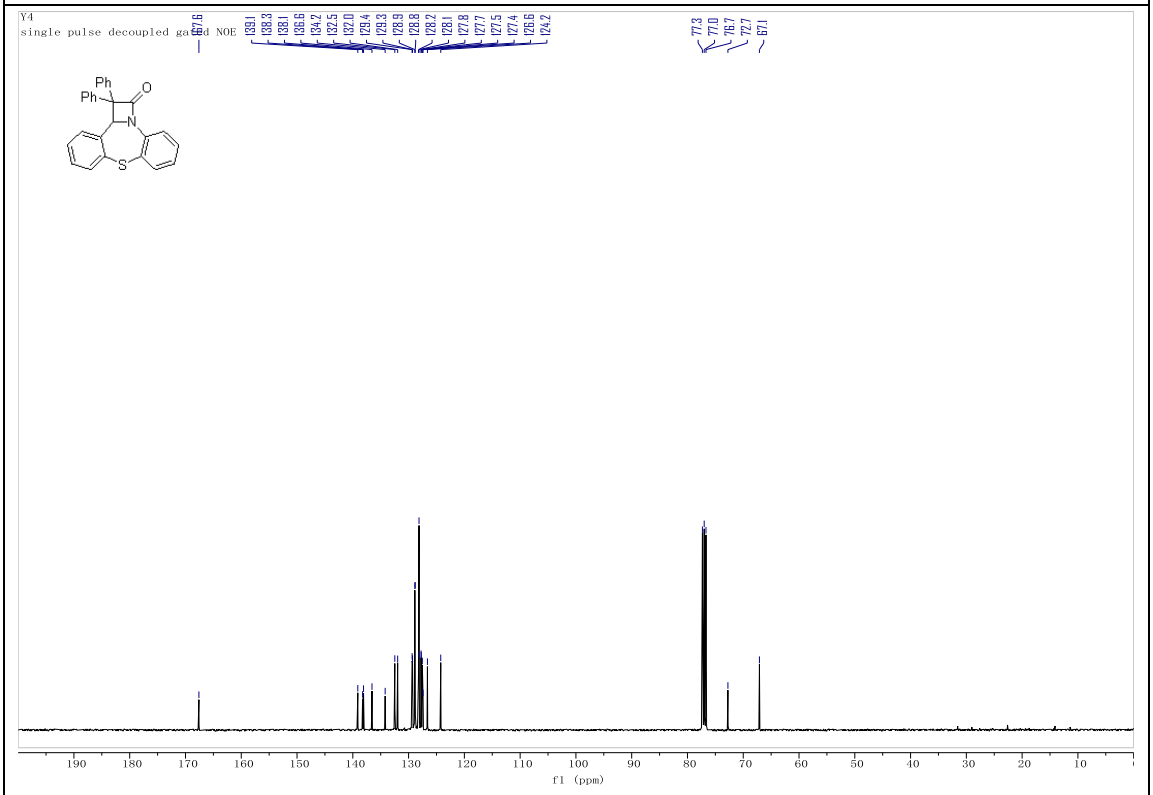
f1 (ppm)

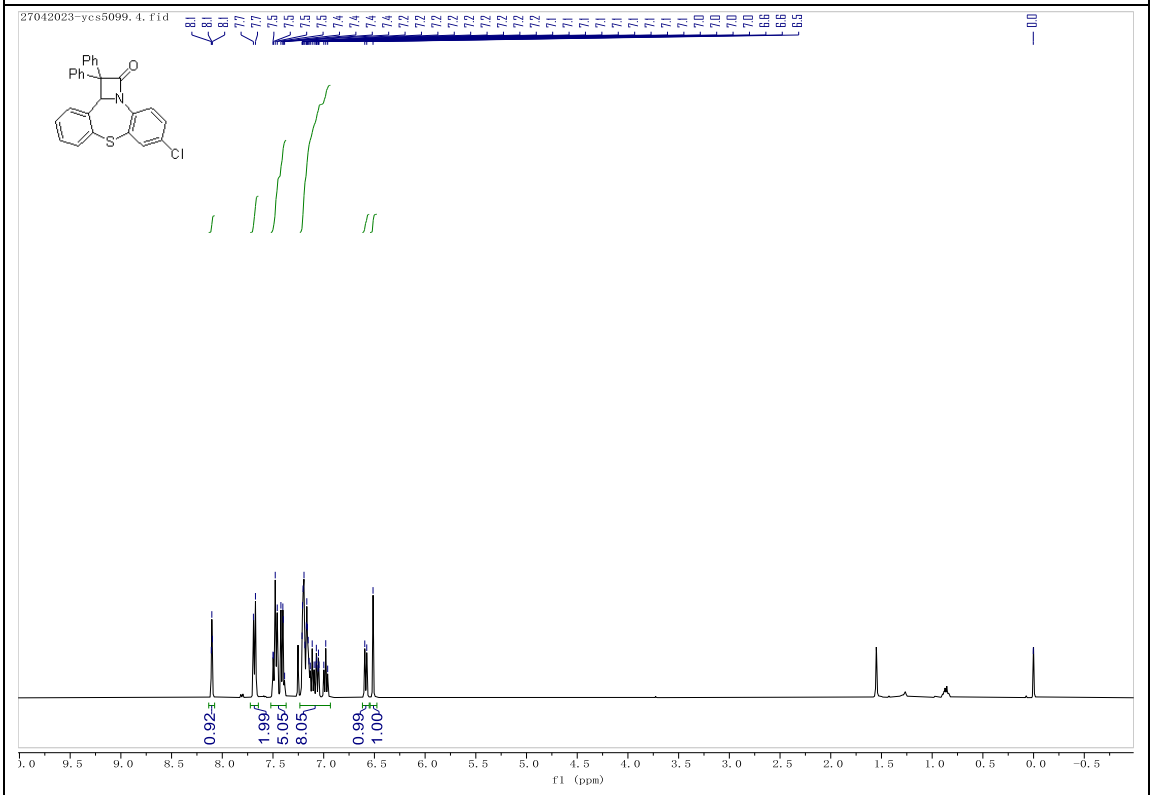
^{1}H NMR Spectrum of **3qq**



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



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



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