Supporting Information

Regioselective Cascade Annulations of Indoles with Alkynediones for Construction of Functionalized Tetrahydrocarbazoles Triggered by Cp*Rh^{III}-Catalyzed C−H Activation

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Contents

1. General methods

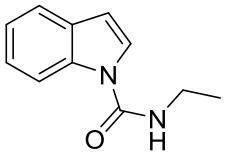
Unless otherwise noted, all reactions were performed using standard Schlenk techniques. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker AVANCE III 400 or JEOL JNM-ECZ400S/L1 400 MHz spectrometer or Bruker AVANCE III HD 600 MHz spectrometer. Chemical shifts (δ values) were reported in ppm with internal TMS (^{1}H NMR), DMSO-*d6* (^{13}C NMR) or external CF_3CO_2H (^{19}F NMR) references, respectively. Melting points were measured on a RY-I apparatus and uncorrected. IR spectra were measured on a NICOLET iS10 spectrometer. HRMS (high-resolution mass spectroscopy) were determined on a WATERS I-Class VION IMS Qtof. Column chromatography was performed on silica gel (200-300 mesh) using a mixture of petroleum ether (PE, 60-90 ℃)/ethyl acetate (EA) as the eluent. Unless otherwise noted, all reagents were purchased from commercial sources and used without further purification.

2. Synthesis of substrates

2.1 General procedure for the synthesis of *N*-substituted carboxamides indoles 1

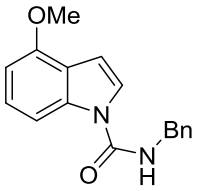
N-substituted carboxamides indoles **1** were prepared according to the literature[1] and all data were in agreement with these reported[1].

***N*-ethyl-1H-indole-1-carboxamide, 1c**



White solid, 463 mg, yield 82%, PE:EA = 10:1, M.p. 67-69 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (d, *J* = 8.3 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 3.6 Hz, 1H), 7.25 (t, *J* = 7.7 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.52 (d, *J* = 3.6 Hz, 1H), 6.11 (s, *1*H), 3.44 – 3.37 (m, 2H), 1.20 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2, 135.2, 130.3, 124.2, 122.3, 121.3, 114.1, 107.0, 36.0, 15.2; FTIR (neat) υ 3127, 3064, 2923, 2855, 1665, 1445, 1398, 1293, 1199, 1020, 780, 738, 691, 433 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{12}N_2ONa$ 211.0842; Found 211.0845.

***N*-benzyl-4-methoxy-1H-indole-1-carboxamide, 1e**

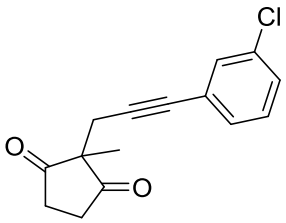


White solid, 615 mg, yield 73%, PE:EA = 5:1, M.p. 116-118 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.4 Hz, 1H), 7.31 (d, *J* = 3.6 Hz, 1H), 7.28 – 7.22 (m, 5H), 7.14 (d, *J* = 8.2 Hz, 1H), 6.66 (d, *J* = 3.6 Hz, 1H), 6.59 (d, *J* = 7.9 Hz, 1H), 6.32 (br, 1H), 4.46 (d, *J* = 5.6 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 152.4, 137.8, 136.5, 128.7, 127.6, 125.2, 122.6, 120.5, 107.4, 104.2, 102.5, 55.4, 44.8; FTIR (neat) υ 3147, 2939, 1666, 1533, 1493, 1329, 1228, 1065, 739, 698, 617, 617 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{16}N_2O_2Na$ 303.1104; Found 303.1107.

2.2 General procedure for the synthesis of alkynediones 2

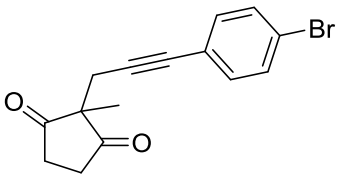
Alkynediones **2** were synthesized according to the literature[2, 3] and all data were in agreement with those reported.[2, 3] Alkynediones **2d**, **2h** and **2m** were synthesized according to the literature.[2, 4, 5]

2-(3-(3-chlorophenyl)prop-2-yn-1-yl)-2-methylcyclopentane-1,3-dione, 2d



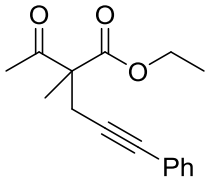
Brown solid, 208 mg, yield 83%, PE:EA = 5:1, M.p. 72-74 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 – 7.26 (m, 2H), 7.21 – 7.20 (m, 2H), 2.88 – 2.80 (m, 4H), 2.69 (s, 2H), 1.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.4, 134.2, 131.6, 129.9, 129.7, 128.8, 124.3, 85.5, 81.7, 55.5, 36.0, 25.6, 19.3; FTIR (neat) υ 2991, 2928, 1723, 1584, 1482, 1329, 1210, 1078, 994, 879, 790, 680, 444 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{14}ClO_2$ 261.0677; Found 261.0676.

2-(3-(4-bromophenyl)prop-2-yn-1-yl)-2-methylcyclopentane-1,3-dione, 2h



Brown solid, 243 mg, yield 80%, PE:EA = 5:1, M.p. 85-87 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.38 (m, 2H), 7.18 – 7.16 (m, 2H), 2.88 – 2.78 (m, 4H), 2.66 (s, 2H), 1.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.5, 133.2, 131.7, 122.6, 121.6, 85.4, 81.9, 55.5, 36.0, 25.7, 19.2; FTIR (neat) υ 2971, 1712, 1493, 1413, 1320, 1073, 1010, 827, 518, 397 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{13}BrO_2$ 305.0172; Found 305.0174

ethyl 2-acetyl-2-methyl-5-phenylpent-4-ynoate, 2m



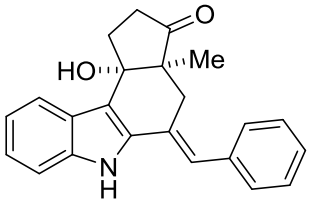
Brown liquid, 184 mg, yield 71%, PE:EA = 10:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (m, 2H), 7.28 – 7.26 (m, 3H), 4.28 – 4.19 (m, 2H), 3.00 – 2.89 (m, 2H), 2.22 (s, 3H), 1.54 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.1, 171.7, 131.7, 128.3, 128.1, 123.3 ,85.0, 83.6, 61.9, 59.4, 26.3, 26.0, 19.4, 14.2; FTIR (neat) υ 2981, 2939, 1712, 1493, 1440, 1356, 1277, 1188, 1099, 1015 758, 699, 522 cm^{-1}; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{18}O_3Na$ 281.1148; Found 281.1152.

3. General procedure for Cp*Rh^{III}-catalyzed cascade annulations

A seal tube charged with a stir bar was added *N*-substituted carboxamides indoles **1** (0.20 mmol, 1.0 equiv), alkynediones **2** (0.24 mmol, 1.2 equiv), $[RhCp^*Cl_2]_2$ (0.005 mmol, 2.5 mol%), $Cu(OAc)_2$ Ħ$_2$O (20.0 mg, 0.10 mmol, 0.5 equiv), and NaOAc (24.6 mg, 0.30 mmol, 1.5 equiv). The tube was purged three times by vacuum and N_2, then CH_3CN (2.0 mL, 0.1 M) was added. The mixture was stirred at 80 ℃ for 12 h, which was then concentrated in vacuum. The residue was purified by silica gel column chromatography (PE/EA = 20/1 to 10/1) to give products **3**.

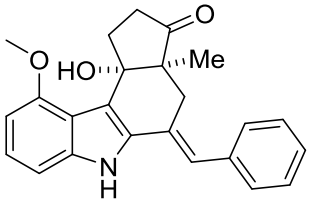
4. Characterization data for products 3

***Cis*-(*E*)-5-benzylidene-10c-hydroxy-3a-methyl-1,3a,4,5,6,10c-hexahydrocyclopent a[*c*]carbazol-3(2H)-one, 3a**



White solid, 61.0 mg, yield 89%, PE:EA = 5:1, M.p. 199-202 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.23 (s, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.45 – 7.41 (m, 4H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.08 (s, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 5.37 (s, 1H), 3.04 (d, *J* = 15.2 Hz, 1H), 2.89 – 2.56 (m, 1H), 2.58 (d, *J* = 15.3 Hz, 1H), 2.43 – 2.31 (m, 2H), 1.86 – 1.76 (m, 1H), 1.03 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 219.0, 137.8, 136.8, 134.7, 128.9, 128.4, 127.0, 126.7, 125.7, 122.4, 122.4, 120.4, 118.9, 116.3, 111.1, 75.4, 54.2, 34.7, 31.7, 31.6, 17.6; FTIR (neat) υ 3271, 3057, 2880, 1729, 1597, 1192, 1451, 1396, 1305, 1217, 1154, 1056, 798, 749, 702, 506 cm^{-1}. HRMS (ESI) m/z: [M + Na]$^{+}$ Calcd for $C_{23}H_{21}NO_2Na$ 366.1465; Found 366.1452.

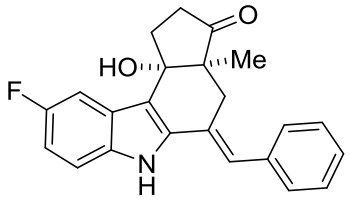
Cis-(_E_)-5-benzylidene-10c-hydroxy-10-methoxy-3a-methyl-1,3a,4,5,6,10c-hexahydrocyclopenta[_c_]carbazol-3(2H)-one, 3b



White solid, 53.7 mg, yield 72%, PE:EA = 4:1, M.p. 182-185 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.36 (s, 1H), 7.43 – 7.38 (d, *J* = 6.6 Hz, 4H), 7.31 – 7.26 (m, 1H), 7.11 (m, 2H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.61 (d, *J* = 7.7 Hz, 1H), 4.59 (s, 1H), 3.98 (s, 3H), 2.93 (d, *J* = 15.1 Hz, 1H), 2.57 – 2.52 (m, 2H), 2.46 – 2.42 (m, 1H), 2.38 – 2.32 (m, 1H), 2.27 – 2.19 (m, 1H), 0.93 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 219.6, 151.9, 139.2, 136.6, 132.1, 128.8, 128.5, 126.7, 126.4, 123.7, 122.7, 116.4, 115.7, 105.1, 100.1, 76.0, 55.6, 54.5, 35.2, 34.9, 33.1, 15.7. FTIR (neat) υ 3473, 3363, 2962, 1712, 1509, 1469, 1254, 1232, 1104, 1052, 745, 696, 547, 506 cm^{-1}. HRMS (ESI) m/z: [M + Na]$^{+}$ Calcd for $C_{24}H_{23}NO_3Na$ 396.1570; Found 396.1564.

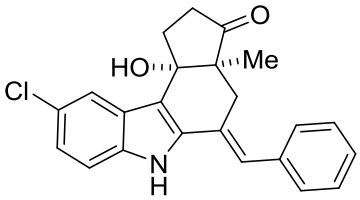
Cis-(_E_)-5-benzylidene-9-fluoro-10c-hydroxy-3a-methyl-1,3a,4,5,6,10c-hexahydroc

yclopenta[*c*]carbazol-3(2H)-one, 3c



White solid, 54.3 mg, yield 75%, PE:EA = 5:1, M.p. 204-206 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.33 (s, 1H), 7.48 (dd, J = 10.1, 2.1 Hz, 1H),7.44 –7.43 (m, 4H), 7.35 – 7.29 (m, 2H), 7.07 (s, 1H), 6.96 (t, J = 10.3 Hz 1H), 5.38 (s, 1H), 3.01 (d, J = 15.2 Hz, 1H), 2.60 – 2.52 (m, 2H), 2.42 – 2.32 (m, 2H), 1.91 – 1.82 (m, 1H), 1.00 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 219.0, 156.6 (C-F, $J_{C\text{-}F}$ = 231.8 Hz), 136.6, 136.4, 134.4, 129.0, 128.5, 126.9, 126.8, 125.8 (C-F, $J_{C\text{-}F}$ = 10.2 Hz), 123.1, 116.4 (C-F, $J_{C\text{-}F}$ = 4.8 Hz), 112.0 (C-F, $J_{C\text{-}F}$ = 9.7 Hz), 110.4 (C-F, $J_{C\text{-}F}$ = 25.9 Hz), 105.4 (C-F, $J_{C\text{-}F}$ = 23.5 Hz), 75.3, 54.3, 34.8 31.8, 31.7, 17.4; ^{19}F NMR (376 MHz, DMSO-d_6): δ -124.5. FTIR (neat) υ 3261, 2966, 1730, 1492, 1446, 1299, 1163, 1057, 1023, 845, 706 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{20}FNO_2Na$ 384.1370; Found 384.1350.

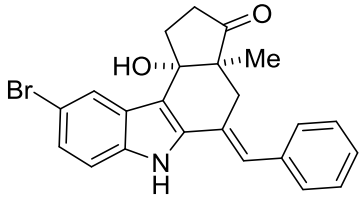
***Cis*-(*E*)-5-benzylidene-9-chloro-10c-hydroxy-3a-methyl-1,3a,4,5,6,10c-hexahydro cyclopenta[*c*]carbazol-3(2H)-one, 3d**



White solid, 59.1 mg, yield 78%, PE:EA = 5:1, M.p. 198-201 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 11.45 (s, 1H), 7.76 (s, 1H), 7.45 – 7.43 (m, 4H), 7.36 (d, J = 8.5 Hz, 1H), 7.31 – 7.30 (m, 1H), 7.14 (d, J = 8.0 Hz, 1H), 7.09 (s, 1H), 5.42 (s, 1H), 3.01 (d, J = 15.2 Hz, 1H), 2.57 – 2.52 (m, 2H), 2.41 – 2.33 (m, 2H), 1.91 – 1.85 (m, 1H), 0.99 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 219.0 136.5, 136.2, 136.1, 129.0, 128.5, 126.9, 126.8, 126.6, 123.5, 123.4, 122.3, 119.4, 116.0, 112.6, 75.4, 54.4, 34.8, 32.1, 31.8, 17.3. FTIR (neat) υ 3365, 2967, 1729, 1451, 1399, 1055, 1023, 853, 799, 749, 508 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{21}ClNO_2$ 378.1255; Found 378.1240.

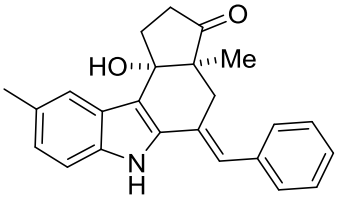
***Cis*-(*E*)-5-benzylidene-9-bromo-10c-hydroxy-3a-methyl-1,3a,4,5,6,10c-hexahydro**

cyclopenta[*c*]carbazol-3(2H)-one, 3e



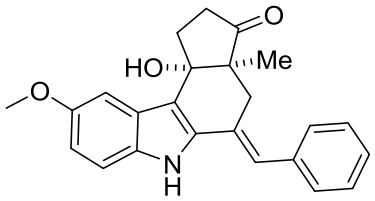
White solid, 66.2 mg, yield 79%, PE:EA = 5:1, M.p. 182-186 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.46 (s, 1H), 7.92 (s,1H), 7.44 – 7.43 (m, 4H), 7.33 – 7.28 (m, 2H), 7.25 (dd, *J* = 8.6 Hz, 1H), 7.10 (s, 1H), 5.43 (s, 1H), 3.01 (d, *J* = 15.2 Hz, 1H), 2.57 – 2.52 (m, 2H), 3.43 – 2.31 (m, 2H), 1.94 – 1.85 (m, 1H), 0.99 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 218.9, 136.5, 136.4, 135.9, 129.0, 128.5, 127.5, 126.9, 126.5, 124.8, 123.5, 122.4, 115.9, 113.1, 111.4, 75.3, 54.4, 34.7, 32.1, 31.8, 17.2. FTIR (neat) υ 3437, 3276, 1719, 1495, 1441, 1295, 1280, 1056, 855, 795, 694, 495 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{20}BrNO_2Na$ 444.0570; Found 444.0571.

***Cis*-(*E*)-5-benzylidene-10c-hydroxy-3a,9-dimethyl-1,3a,4,5,6,10c-hexahydrocyclopenta[*c*]carbazol-3(2H)-one, 3f**



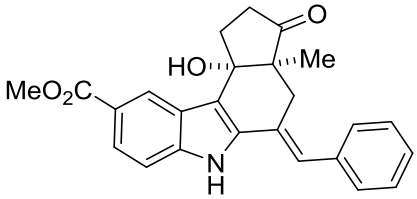
White solid, 51.6 mg, yield 72%, PE:EA = 5:1, M.p. 193-195 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.08 (s, 1H), 7.58 (s, 1H), 7.43 – 7.42 (m, 4H), 7.31 – 7.26 (m, 1H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.02 (s, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 5.29 (s, 1H), 3.01 (d, *J* = 15.2 Hz, 1H), 2.68 – 2.61 (m, 1H), 2.55 (d, *J* = 15.2 Hz, 1H), 2.40 (s, 3H), 2.37 – 2.28 (m, 2H), 1.83 – 1.73 (m, 1H), 1.01 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 219.0, 136.8, 136.8, 134.8, 128.9, 128.5, 127.3, 127.1, 126.6, 125.9, 124.0, 122.1, 120.1, 115.8, 110.9, 75.3, 54.2, 34.7, 31.6, 31.5, 21.3, 17.7. FTIR (neat) υ 3445, 3285, 2982, 1720, 1488, 1456, 1177, 1152, 1072, 793, 697, 601, 505 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{23}NO_2Na$ 380.1621; Found 380.1620.

***Cis*-(*E*)-5-benzylidene-10c-hydroxy-9-methoxy-3a-methyl-1,3a,4,5,6,10c-hexahydrocyclopenta[*c*]carbazol-3(2H)-one, 3g**



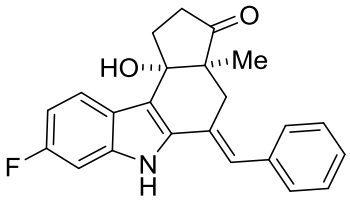
White solid, 49.2 mg, yield 66%, PE:EA = 4:1, M.p. 208-211 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.07 (s, 1H), 7.43 – 7.42 (m, 4H), 7.28 – 7.24 (m, 3H), 7.03 (s, 1H), 6.80 (d, *J* = 8.5, 1H), 5.33 (s, 1H), 3.79 (s, 3H), 3.01 (d, *J* = 15.1 Hz, 1H), 2.67 – 2.61 (m, 1H), 2.55 (d, *J* = 15.3 Hz, 1H), 2.41 – 2.30 (m, 2H), 1.88 – 1.78 (m, 1H), 1.01 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 219.1, 153.1, 136.9, 135.2, 132.9, 129.0, 128.5, 127.1, 126.6, 126.0, 122.1, 116.1, 112.4, 111.8, 102.3, 75.4, 55.4, 54.3, 34.8, 31.7, 31.6, 17.6. FTIR (neat) υ 3485, 3341, 2974, 1728, 1480, 1440, 1304, 1169, 1025, 848, 801, 713, 633 cm^{-1}. HRMS (ESI) m/z: [M + Na]$^{+}$ Calcd for $C_{24}H_{23}NO_3Na$ 396.1570; Found 396.1565.

***Cis*-Methyl (*E*)-5-benzylidene-10c-hydroxy-3a-methyl-3-oxo-1,2,3,3a,4,5,6,10c-octahydrocyclopenta[*c*]carbazole-9-carboxylate, 3h**



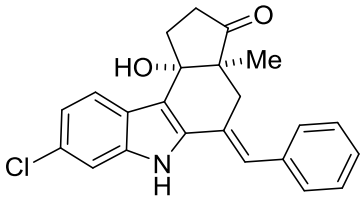
Purple solid, 51.2 mg, yield 64%, PE:EA = 3:1, M.p. 199-203 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 11.67 (s, 1H), 8.49 (s, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.49 – 7.44 (m, 5H), 7.31 (s, 1H), 7.11 (s, 1H), 5.51 (s, 1H), 3.87 (s, 3H), 3.02 (d, *J* = 15.2 Hz, 1H), 2.59 – 2.54 (m, 2H), 2.44 – 2.35 (m, 2H), 1.88 – 1.85 (m, 1H), 1.01 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 218.9, 167.2, 140.5, 136.5, 136.3, 129.0, 128.5, 127.0, 126.5, 125.3, 123.6, 123.5, 122.7, 120.3, 117.3, 111.1, 75.3, 54.3, 51.8, 34.7, 32.3, 31.7, 17.4. FTIR (neat) υ 3485, 2982, 2859, 1720, 1680, 1608, 1448, 1328, 1272, 1112, 1057, 769, 697, 492 cm^{-1}. HRMS (ESI) m/z: [M + Na]$^{+}$ Calcd for $C_{25}H_{23}NO_4Na$ 424.1519; Found 424.1515.

***Cis*-(*E*)-5-benzylidene-8-fluoro-10c-hydroxy-3a-methyl-1,3a,4,5,6,10c-hexahydrocyclopenta[*c*]carbazol-3(2H)-one, 3i**



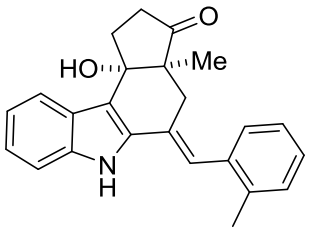
White solid, 56.3 mg, yield 78%, PE:EA = 5:1, M.p. 184-186 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.34 (s, 1H), 7.70 – 7.74 (m, 1H), 7.43 – 7.42 (m, 4H), 7.30 – 7.29 (m, 1H), 7.09 (d, J = 9.8 Hz, 1H), 7.02 (s, 1H), 6.89 (t, *J* = 9.2 Hz, 1H), 5.38 (s, 1H), 3.0 (d, *J* = 15.2 Hz, 1H), 2.61 – 2.56 (m, 2H), 2.41 – 2.30 (m, 2H), 1.87 – 1.77 (m, 1H), 0.99 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 218.9, 159.5 (C-F, $J_{C\text{-}F}$ = 236.3 Hz), 138.0 (C-F, $J_{C\text{-}F}$ = 12.6 Hz), 136.7, 135.4 (C-F, $J_{C\text{-}F}$ = 3.1 Hz), 129.0, 128.5, 126.8, 126.7, 122.6, 122.5, 121.4 (C-F, $J_{C\text{-}F}$ = 10.1 Hz), 116.4, 107.3 (C-F, $J_{C\text{-}F}$ = 24.2 Hz), 97.2 (C-F, $J_{C\text{-}F}$ = 25.2 Hz), 75.3, 54.3, 34.7, 31.9, 31.6, 17.6. ^{19}F NMR (376 MHz, DMSO-d_6) : δ -119.8. FTIR (neat) υ 3366, 2971, 1724, 1455, 1270, 1047, 1022, 783, 746, 511 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{20}FNO_2Na$ 384.1370; Found 384.1366.

Cis-(_E_)-5-benzylidene-8-chloro-10c-hydroxy-3a-methyl-1,3a,4,5,6,10c-hexahydro cyclopenta[_c_]carbazol-3(2H)-one, 3j



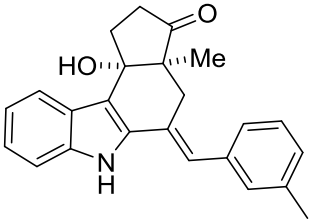
White solid, 54.5 mg, yield 72%, PE:EA = 5:1, M.p. 152-154 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.42 (s, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.44 – 7.43 (m, 4H), 7.36 (s, 1H), 7.31 – 7.29 (m, 1H), 7.07 – 7.04 (m, 2H), 5.43 (s, 1H), 3.03 (d, *J* = 15.2 Hz, 1H), 2.62 – 2.55 (m, 2H), 2.42 – 2.31 (m, 2H), 1.87 – 1.78 (m, 1H), 1.02 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 218.9, 138.3, 136.6, 135.7, 129.0, 128.5, 127.1, 126.9, 126.7, 124.5, 123.1, 121.7, 119.3, 116.4, 110.7, 75.2, 54.2, 34.7, 31.8, 31.6, 17.5. FTIR (neat) υ 3397, 3253, 2926, 1720, 1456, 1192, 1152, 1065, 801, 753, 593, 505 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{20}ClNO_2Na$ 400.1075; Found 400.1077.

Cis-(_E_)-10c-hydroxy-3a-methyl-5-(2-methylbenzylidene)-1,3a,4,5,6,10c-hexahydr ocyclopenta[_c_]carbazol-3(2H)-one, 3k



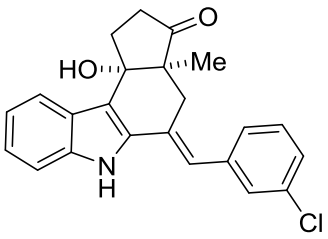
White solid, 38.7 mg, yield 54%, PE:EA = 5:1, M.p. 185-188 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.24 (s, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.37 – 7.35 (m, 2H), 7.27 – 7.24 (m, 3H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.07 (s, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 5.30 (s, 1H), 2.79 (d, *J* = 14.9 Hz, 1H), 2.65 – 2.59 (m, 1H), 2.42 – 2.36 (m, 3H), 2.29 (s, 3H), 1.88 – 1.80 (m, 1H), 0.96 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 219.1, 137.7, 136.5, 135.8, 134.5, 129.9, 128.9, 127.0, 126.9, 125.7, 125.5, 122.4, 121.6, 120.4, 118.9, 116.2, 111.1, 75.6, 54.3, 34.8, 31.9, 31.6, 19.8, 17.4. FTIR (neat) υ 3415, 3290, 2972, 1729, 1452, 1396, 1150, 1052, 1023, 744, 725, 627 cm^{-1}. HRMS (ESI) m/z: [M + Na]$^{+}$ Calcd for $C_{24}H_{23}NO_2Na$ 380.1621; Found 380.1623.

Cis-(_E_)-10c-hydroxy-3a-methyl-5-(3-methylbenzylidene)-1,3a,4,5,6,10c-hexahydrocyclopenta[_c_]carbazol-3(2H)-one, 3l



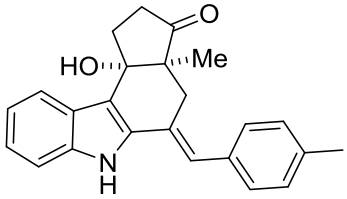
White solid, 52.8 mg, yield 74%, PE:EA = 5:1, M.p. 181-183 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.19 (s, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.24 – 7.21 (m, 2H), 7.15 – 7.09 (m, 2H), 7.03 – 3.99 (m, 2H), 5.33 (s, 1H), 3.01 (d, *J* = 15.2 Hz, 1H), 2.66 – 2.59 (m, 1H), 2.54 (d, *J* = 15.8 Hz, 1H), 7.38 – 7.31 (m, 5H), 1.85 – 1.77 (m, 1H), 1.00 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 219.1, 137.8, 137.5, 136.7, 134.8, 129.6, 128.3, 127.4, 126.8, 126.1, 125.7, 122.5, 122.4, 120.4, 118.9, 116.2, 111.1, 75.4, 54.3, 34.8, 31.8, 31.6, 21.2, 17.6. FTIR (neat) υ 3412, 3282, 2953, 1734, 1708, 1449, 1397, 1241, 1060, 1025, 860, 748, 731, 697 cm^{-1}. HRMS (ESI) m/z: [M + Na]$^{+}$ Calcd for $C_{24}H_{23}NO_3Na$ 380.1621; Found 380.1619.

Cis-(_E_)-5-(3-chlorobenzylidene)-10c-hydroxy-3a-methyl-1,3a,4,5,6,10c-hexahydrocyclopenta[_c_]carbazol-3(2H)-one, 3m



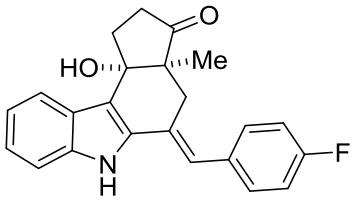
White solid, 54.2 mg, yield 72%, PE:EA = 5:1, M.p. 139-143 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.24 (s, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.41 – 7.40 (m, 1H), 7.38 – 7.34 (m, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.05 – 7.01 (m, 2H), 5.39 (s, 1H), 3.00 (d, *J* = 15.2 Hz, 1H), 2.68 – 2.62 (m, 1H), 2.56 (d, *J* = 15.2 Hz, 1H) 2.43 – 2.32 (m, 2H), 1.86 – 1.76 (m, 1H), 1.03 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 219.0, 139.0, 137.9, 134.3, 133.2, 130.3, 128.6, 128.3, 127.6, 126.5, 125.6, 122.7, 120.9, 120.6, 119.0, 116.9, 111.3, 75.3, 54.3, 34.8, 31.8, 31.5, 17.7. FTIR (neat) υ 3386, 2880, 2867, 1734, 1587, 1443, 1232, 1042, 878, 757, 697, 437 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{20}ClNO_2Na$ 400.1075; Found 400.1072.

Cis-(_E_)-10c-hydroxy-3a-methyl-5-(4-methylbenzylidene)-1,3a,4,5,6,10c-hexahydrocyclopenta[_c_]carbazol-3(2H)-one, 3n



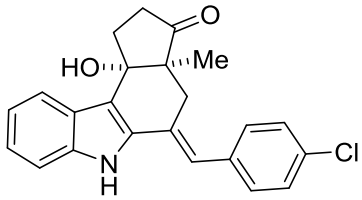
White solid, 60.2 mg, yield 84%, PE:EA = 5:1, M.p. 183-186 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 11.19 (s, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.34 – 7.31 (m, 3H), 7.24 – 7.23 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.02 – 7.00 (m, 2H), 5.32 (s, 1H), 3.01 (d, *J* = 15.1, 1H), 2.65 – 2.62 (m, 1H), 2.54 (d, *J* = 15.1 Hz, 1H), 2.39 – 2.30 (m, 5H), 1.82 – 1.76 (m, 1H), 1.01 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 219.0, 137.8, 136.0, 134.9, 133.9, 129.1, 128.9, 126.3, 125.7, 122.4, 122.3, 120.4, 118.8, 116.0, 111.1, 75.3, 54.2, 34.7, 31.8, 31.6, 20.8, 17.7. FTIR (neat) υ 3386, 3282, 2962, 2876, 1717, 1457, 1146, 1060, 870, 739, 627, 506 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{23}NO_2Na$ 380.1621; Found 380.1601.

Cis-(_E_)-5-(4-fluorobenzylidene)-10c-hydroxy-3a-methyl-1,3a,4,5,6,10c-hexahydrocyclopenta[_c_]carbazol-3(2H)-one, 3o



White solid, 50.7 mg, yield 70%, PE:EA = 5:1, M.p. 182-185 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 11.21 (s, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.47 (t, J = 6.9 Hz, 2H), 7.34 (d, J = 8.1 Hz, 1H), 7.26 (t, J = 8.6 Hz, 2H), 7.14 (t, J = 7.6 Hz, 1H), 7.03 – 7.01 (m, 2H), 5.35 (s, 1H), 2.97 (d, J = 15.0 Hz, 1H), 2.66 – 2.61 (m, 1H), 2.52 (d, J = 17.3 Hz, 1H), 2.39 – 2.31 (m, 2H), 1.82 – 1.75 (m, 1H), 1.01 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 219.1, 160.9 (C-F, $J_{C\text{-}F}$ = 244.6 Hz), 137.8, 134.7,133.2 (C-F, $J_{C\text{-}F}$ = 3.3 Hz), 130.9 (C-F, $J_{C\text{-}F}$ = 7.8 Hz), 127.0, 125.7, 122.5, 121.3, 120.5, 118.9, 116.3, 115.4 (C-F, $J_{C\text{-}F}$ = 21.3 Hz), 111.2, 75.3, 54.2, 34.7, 31.7, 31.4, 17.7. ^{19}F NMR (376 MHz, DMSO-d_6) : δ -115.0. FTIR (neat) υ 3262, 2964, 1729, 1502, 1452, 1410, 1339, 1242, 1060, 1024, 847, 736, 715, 517 cm^{-1}. HRMS (ESI) m/z: [M + Na]$^{+}$ Calcd for $C_{23}H_{20}FNO_2Na$ 384.1370; Found 384.1362.

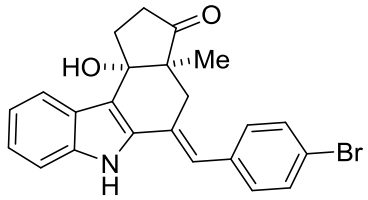
Cis-(_E_)-5-(4-chlorobenzylidene)-10c-hydroxy-3a-methyl-1,3a,4,5,6,10c-hexahydro cyclopenta[_c_]carbazol-3(2H)-one, 3p



White solid, 47.4 mg, yield 63%, PE:EA = 5:1, M.p. 139-143 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.22 (s, 1H), 7.79 (d, J = 7.9 Hz, 1H), 7.49 – 7.44 (m, 4H), 7.35 (d, J = 8.0 Hz, 1H), 7.14 (t, J = 7.0 Hz, 1H), 7.04 – 7.02 (m, 2H), 5.36 (s, 1H), 2.98 (d, J = 15.2 Hz, 1H), 2.67 – 2.61 (m, 1H), 2.53 (d, J = 19.4 Hz, 1H), 2.41 – 2.30 (m, 2H), 1.83 – 1.75 (m, 1H), 1.02 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 218.9, 137.9, 135.6, 134.5, 131.2, 130.6, 128.5, 127.8, 125.6, 122.6, 121.1, 120.5, 118.9, 116.6, 111.2, 75.3, 54.2, 34.7, 31.7, 31.5, 17.7. FTIR (neat) υ 3371, 3278, 2910, 2880, 1727, 1457, 1395, 1149, 1093, 1056, 1014, 870, 806, 770, 511 cm^{-1}. HRMS (ESI) m/z: [M + Na]$^{+}$ Calcd for $C_{23}H_{20}ClNO_2Na$ 400.1075; Found 400.1065.

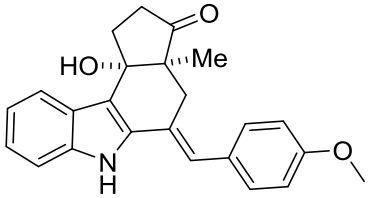
Cis-(_E_)-5-(4-bromobenzylidene)-10c-hydroxy-3a-methyl-1,3a,4,5,6,10c-hexahydr

ocyclopenta[*c*]carbazol-3(2H)-one, 3q



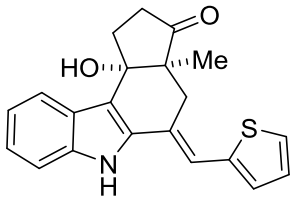
White solid, 41.2 mg, yield 49%, PE:EA = 5:1, M.p. 143-145 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 11.23 (s, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.62 (d, *J* = 5.9 Hz, 2H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H) 7.04 – 7.00 (m, 2H), 5.37 (s, 1H), 2.98 (d, *J* = 15.1 Hz, 1H), 2.67 – 2.62 (m, 1H), 2.54 (d, *J* = 15.2 Hz, 1H), 2.40 – 2.31 (m, 2H), 1.82 – 1.75 (m, 1H), 1.02 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 219.0, 137.9, 136.0, 134.5, 131.4, 131.0, 127.9, 125.6, 122.7, 121.2, 120.5, 119.8, 119.0, 116.6, 111.2, 75.3, 54.2, 34.7, 31.7, 31.5, 17.7. FTIR (neat) υ 3280, 2969, 1723, 1485, 1396, 1244, 1192, 1055, 1026, 866, 803, 746, 527 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{20}BrNO_2Na$ 444.0570; Found 444.0568.

***Cis*-(*E*)-10c-hydroxy-5-(4-methoxybenzylidene)-3a-methyl-1,3a,4,5,6,10c-hexahydrocyclopenta[*c*]carbazol-3(2H)-one, 3r**



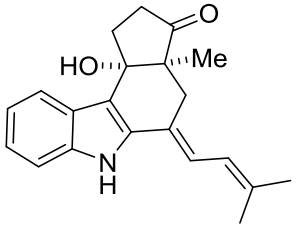
Blue solid, 42.3 mg, yield 57%, PE:EA = 5:1, M.p. 153-156 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.15 (s, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.38 – 7.32 (m, 3H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.01 – 6.99 (m, 4H), 5.30 (s, 1H), 3.79 (s, 3H), 3.00 (d, *J* = 15.1 Hz, 1H), 2.72 – 2.60 (m, 1H), 2.53 (d, *J* = 15.1 Hz, 1H), 2.40 – 2.26 (m, 2H), 1.84 – 1.76 (m, 1H), 1.01 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 219.1, 158.1, 137.8, 135.1, 130.3, 129.3, 125.8, 125.2, 122.2, 122.2, 120.3, 118.8, 115.6, 114.0, 111.1, 75.4, 55.2, 54.2, 34.8, 31.7, 31.6, 17.7. FTIR (neat) υ 3744, 3273, 2964, 1723, 1538, 1459, 1394, 1249, 1175, 1056, 1024, 864, 768, 572 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{23}NO_3Na$ 396.1570; Found 396.1563.

***Cis*-(*E*)-10c-hydroxy-3a-methyl-5-(thiophen-2-ylmethylene)-1,3a,4,5,6,10c-hexahydrocyclopenta[*c*]carbazol-3(2H)-one, 3s**



White solid, 45.4 mg, yield 65%, PE:EA = 5:1, M.p. 183-186 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.18 (s, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.61 (s, 1H), 7.54 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.26 (d, *J* = 5.0 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.02 – 6.99 (m, 2H), 5.33 (s, 1H), 3.07 (d, *J* = 15.4 Hz, 1H), 2.68 – 2.65 (m, 1H), 2.54 (d, *J* = 15.4 Hz, 1H), 2.40 – 2.30 (m, 2H), 1.82 – 1.71 (m, 1H), 1.05 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 219.0, 137.9, 137.8, 134.9, 128.9, 126.1, 126.0, 125.7, 123.7, 122.4, 120.3, 118.8, 116.7, 116.0, 111.1, 75.3, 54.1, 34.7, 31.8, 31.6, 17.8. FTIR (neat) υ 3385, 2973, 2877, 1722, 1454, 1394, 1143, 1047, 1022, 752, 735, 623 cm^{-1}. HRMS (ESI) m/z: [M + Na]$^{+}$ Calcd for $C_{21}H_{19}NO_2SNa$ 372.1028; Found 372.1023.

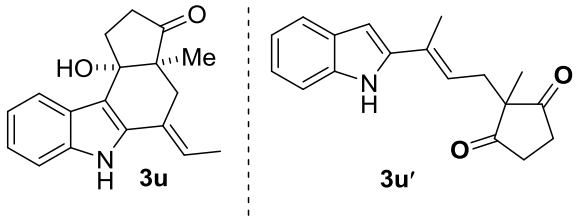
Cis-(_E_)-10c-hydroxy-3a-methyl-5-(3-methylbut-2-en-1-ylidene)-1,3a,4,5,6,10c-hexahydrocyclopenta[_c_]carbazol-3(2H)-one, 3t



White solid, 41.8 mg, 65% yield, PE:EA = 5:1, M.p. 196-198 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.10 (s, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.0 (t, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 11.5 Hz, 1H), 6.26 (d, *J* = 11.6 Hz, 1H), 5.22 (s, 1H), 2.84 (d, *J* = 15.2 Hz, 1H), 2.64 – 2.57 (m, 1H), 2.38 – 2.34 (m, 2H), 2.32 – 2.20 (m, 1H), 1.90 (s, 3H), 1.89 (s, 3H), 1.81 – 1.75 (m, 1H), 1.04 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 219.2, 137.7, 136.4, 135.4, 125.9, 123.0, 122.1, 121.1, 120.2, 119.2, 118.7, 115.4, 110.9, 75.7, 54.1, 34.7, 31.8, 30.4, 26.4, 18.5, 17.6. FTIR (neat) υ 3464, 3300, 2962, 2893, 1726, 1630, 1449, 1310, 1042, 731, 713, 566 cm^{-1}. HRMS (ESI) m/z: [M + Na]$^{+}$ Calcd for $C_{21}H_{23}NO_2Na$ 344.1621; Found 344.1617.

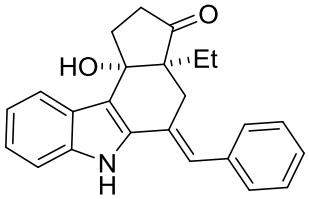
Cis-(_E_)-5-ethylidene-10c-hydroxy-3a-methyl-1,3a,4,5,6,10c-hexahydrocyclopenta[_c_]carbazol-3(2H)-one/(_E_)-2-(3-(1H-indol-2-yl)but-2-en-1-yl)-2-methylcyclopentan

e-1,3-dione, 3u/3u′



3u and **3u′** were obtained in 50% total yield (41.7 mg) with two isomers that cannot be separated on column chromatography, White solid, **3u**/**3u′** = 2/1, PE:EA = 5:1. ^{1}H NMR (600 MHz, DMSO-d_6): δ 11.07 (s, 0.5H), 10.96 (s, 1H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.8, 0.5H), 7.31 – 7.28 (m, 1.5H), 7.09–7.04 (m, 1.5H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 0.5H), 6.43 (s, 0.5H), 6.06 (q, *J* = 6.2 Hz, 1H), 5.88 (t, *J* = 7.7 Hz, 0.5H), 5.21 (s, 1H), 2.75 – 2.74 (m, 2H), 2.69 (d, *J* = 15.0 Hz, 1H), 2.59 – 2.55(m, 1H), 2.48 (s, 0.5H), 2.36 – 2.29 (m, 2H), 2.20 (d, *J* = 15.0 Hz, 1H), 1.96 (s, 1.5H), 1.80 – 1.79 (m, 3.5H), 1.10 (s, 1.5H), 1.03 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 219.2, 216.4, 139.5, 137.3, 136.8, 134.7, 129.4, 128.0, 126.0, 125.7, 121.7, 121.5, 120.1, 119.8, 118.8, 118.6, 118.5, 117.9, 114.0, 110.9, 110.8, 99.7, 75.6, 56.2, 54.0, 39.4, 35.2, 34.7, 34.2, 31.7, 30.1, 17.9, 17.5, 14.1, 12.9. FTIR (neat) υ 3417, 3294, 2979, 2883, 1731, 1722, 1498, 1451, 1390, 1309, 1273, 1187, 1156, 1069, 1004, 857, 744, 632, 576 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{19}NO_2Na$ 282.1489; Found 282.1487.

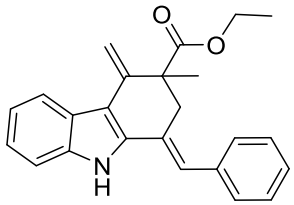
***Cis*-(*E*)-5-benzylidene-3a-ethyl-10c-hydroxy-1,3a,4,5,6,10c-hexahydrocyclopenta[*c*]carbazol-3(2H)-one, 3v**



White solid, 52.2 mg, yield 73%, PE:EA = 5:1, M.p. 182-185 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.19 (s, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.48 – 7.42 (m, 4H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.13 (t, *J* = 7.1 Hz, 1H), 7.04 – 7.00 (m, 2H), 5.30 (s, 1H), 3.22 (d, *J* = 15.2 Hz, 1H), 2.71 (t, *J* = 10.1 Hz, 1H), 2.45 – 2.36 (m, 2H), 2.32 – 2.25 (m, 1H), 1.72 – 1.60 (m, 3H), 0.79 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz,

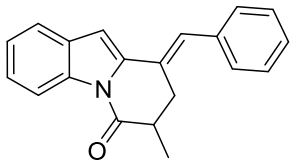
DMSO-d_6): δ 217.6, 137.9, 136.9, 135.2, 129.0, 128.5, 127.2, 126.63, 125.6, 122.5, 122.3, 120.4, 118.8, 116.5, 111.2, 75.5, 56.6, 34.6, 31.2, 27.4, 23.5, 8.2. FTIR (neat) υ 3328, 2921, 2849, 1712, 1452, 1185, 1295, 1082, 967, 779, 748, 696 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{23}NO_2$ Na 380.1621; Found 380.1618.

Ethyl (*E*)-1-benzylidene-3-methyl-4-methylene-2,3,4,9-tetrahydro-1H-carbazole-3-carboxylate, 3w



White solid, 25 mg, yield 35%, PE:EA = 10:1, M.p. 145-147 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 11.47 (s, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.44 – 7.42 (m, 4H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.30 – 7.29 (m, 1H), 7.20 – 7.16 (m, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 5.62 (s, 1H), 5.11 (s, 1H), 3.99 – 3.85 (m, 2H), 3.41 (d, *J* = 15.0 Hz, 1H), 2.76 (d, *J* = 15.0, 1H), 1.41 (s, 3H), 0.95 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 174.4, 142.3, 138.0, 136.7, 135.4, 128.9, 128.5, 127.3, 126.8, 124.8, 123.0, 122.9, 120.0, 120.0, 112.7, 111.4, 105.8, 60.2, 49.3, 37.6, 23.2, 13.8. FTIR (neat) υ 3378, 2980, 1699, 1613, 1440, 1224, 1263, 1111, 1016, 860, 731, 705, 532 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{23}NO_2$Na 380.1621; Found 380.1618.

(*E*)-9-benzylidene-7-methyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one, 3x



Yellow oil, 34 mg, yield 59%, PE:EA = 5:1. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.35 (t, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 7.3 Hz, 1H), 7.44 – 7.41 (m, 5H), 7.33 – 7.25 (m, 3H), 7.09 (s, 1H), 3.17 (dd, *J* = 13.7, 4.0 Hz, 1H), 2.96 – 2.83 (m, 2H), 1.23 (d, *J* = 6.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 171.8, 139.3, 136.0, 134.7, 129.9, 129.2, 128.5, 127.4, 126.4, 126.3, 124.6, 124.0, 120.5, 115.6, 102.9, 37.3, 32.2, 15.7. FTIR (neat) υ 3054, 3023, 2967, 1704, 1598, 1552, 1473, 1352, 1304, 1184, 803, 698, 515 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{18}NO$ 288.1383; Found 288.1371.

5. Preliminary mechanistic studies

5.1 Synthesis of deuterium *N*-benzyl-1H-indole-1-carboxamide 1a-D

The C3-deuterated indole was prepared according to the literature[1, 6]. And then the C3-deuterated *N*-benzyl-1H-indole-1-carboxamide **1a-D** is synthesized as following procedure. To a stirred solution of the C3-deuterated 1H-indole (0.71 g, 2.85 mmol) in anhydrous CH_3CN (5.0 mL) was added 1,1'-Carbonyldiimidazole (0.49 g, 3.02 mmol, 1.06 equiv) followed by 4-dimethylaminopyridine (DMAP, 10 mg). The resulted solution was stirred at reflux under N_2 until C3-deuterated 1H-indole was consumed by TLC. The resulted reaction solution was cooled and benzylamine (0.40 g, 3.70 mmol) was added, and the resulted solution was again heated at reflux under N_2 overnight (16 h). Then the resulted reaction was cooled and evaporated under reduced pressure. The residue was purified via column chromatography (silica gel, PE/EA = 10:1) and afforded the desired **1a-D** in 85% yield (0.62g) with 82% deuterium at C3 position of indole. The deuterated ratio of **1a-D** was determined by ^{1}H NMR analysis, with the spectra shown as Figure S1

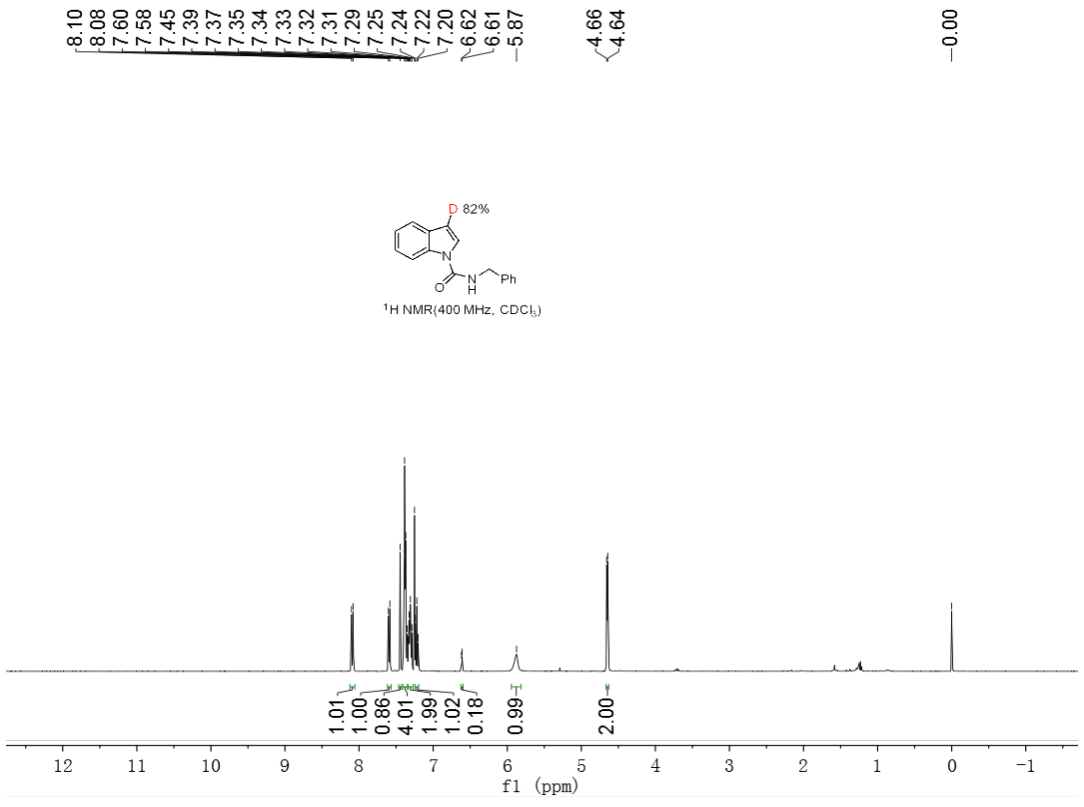
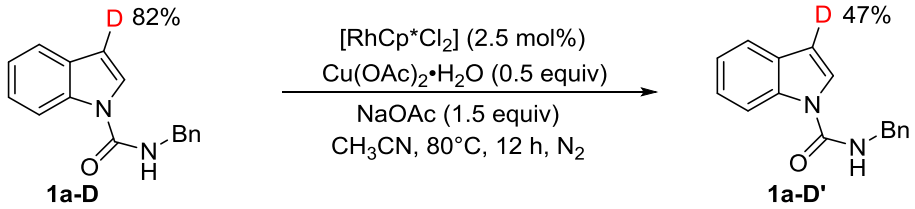


Figure S1. ^{1}H NMR spectra of deuterated substrate **1a-D**

5.2 Procedure for deuterium-labeling studies



A seal tube charged with a stir bar was added **1a-D** (50.2 mg, 0.20 mmol, 1 equiv) $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol%), $Cu(OAc)_2 H_2O$ (20.0 mg, 0.10 mmol, 0.5 equiv), NaOAc (24.6 mg, 0.30 mmol, 1.5 equiv) and CH_3CN (2.0 mL). The mixture was stirred at 80 ℃ under N_2 for 12 h. Then water (10 mL) was added and the resulted mixture was extracted with EA for three times. The organic layer was then dried (Na_2SO_4) and removed in vacuo by rotary evaporation to give product **1a-D'**. The deuterated ratio of product **1a-D'** was determined by ^1H NMR analysis, with the spectra shown as Figure S2.

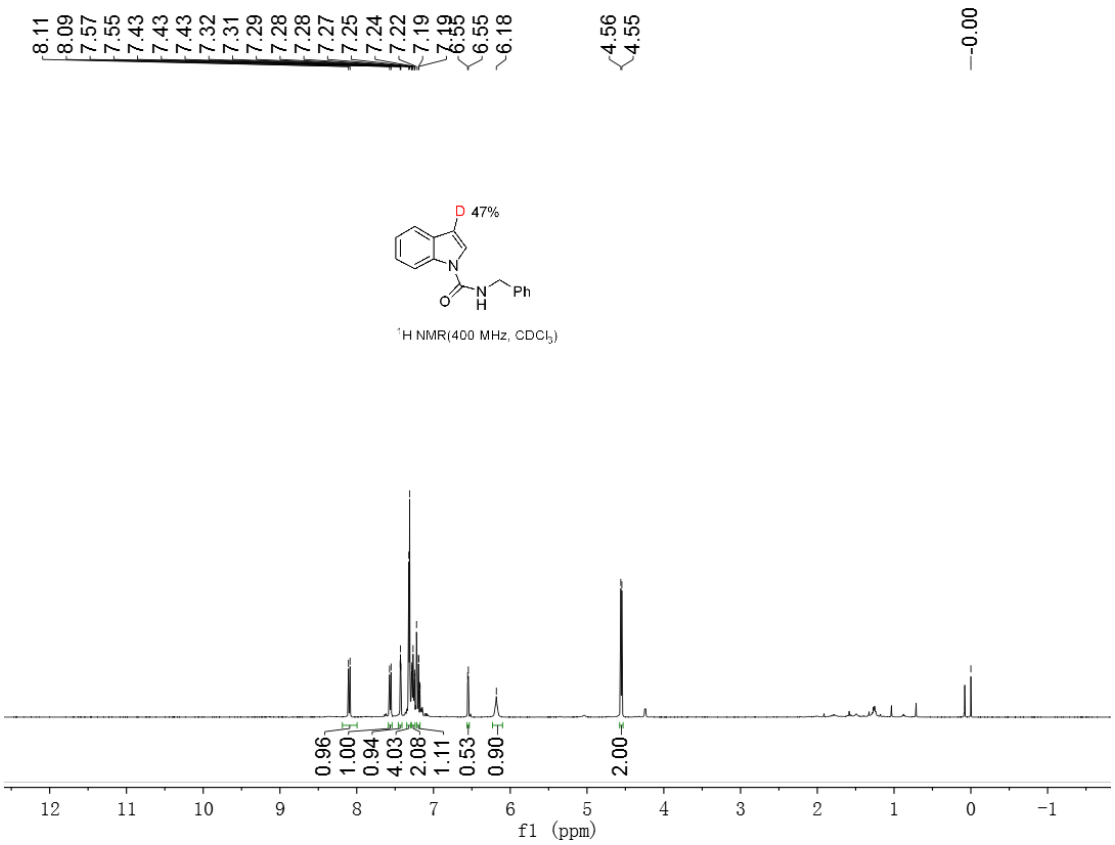
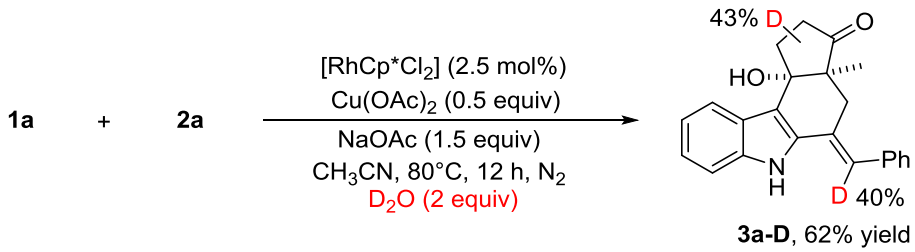


Figure S2. Deuterated ratio of product **1a-D'**



A seal tube charged with a stir bar was added **1a** (50.0mg, 0.20 mmol, 1 equiv), **2a** (54.3 mg, 0.24 mmol, 1.2 equiv), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol%), $Cu(OAc)_2$ (18.1 mg, 0.10 mmol, 0.5 equiv), NaOAc (24.6 mg, 0.30 mmol, 1.5 equiv), D_2O (8.0 mg, 0.40 mmol, 2.0 equiv) and CH_3CN (2 mL). The mixture was stirred at 80 ℃ under N_2 for 12 h, which was then concentrated in vacuum. The residue was purified by silica gel column chromatography (PE/EA = 10/1) to give product **3a-D**. The deuterated ratio of **3a-D** was determined by ^1H NMR analysis, with the spectra shown as Figure S3.

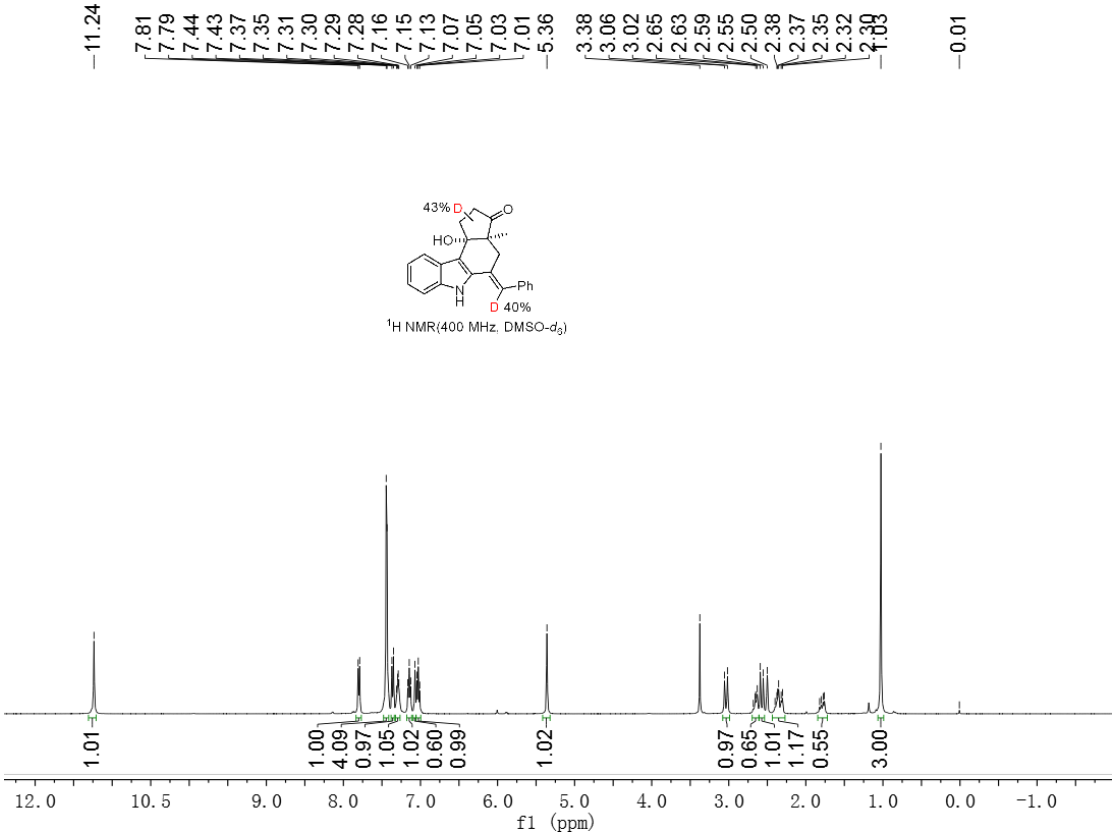


Figure S3. ^1H NMR spectra of deuterated product **3a-D**

5.3 Analysis of the reaction solution of standard reaction by GC-MS

To confirm the reaction intermediates, the standard reaction solution was analysed by

GC-MS (Agilent 5977B GC/MSD). Both benzyl isocyanate and *N*-benzyl acetamide were detected, which are shown as Figure S4. The MS data is in agreement with those reported.[7]

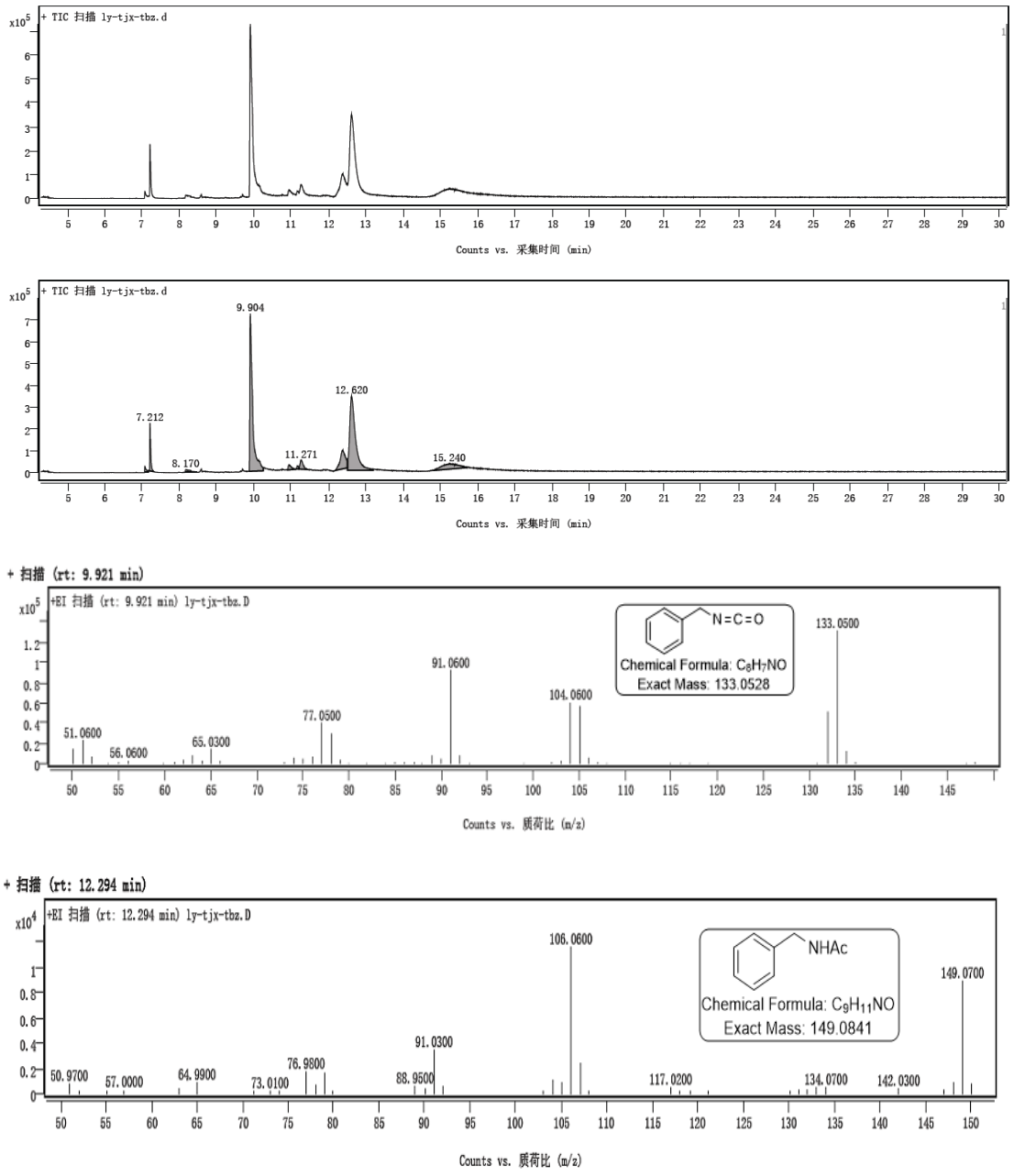


Figure S4. MS spectra of benzyl isocyanate and *N*-benzyl acetamide

6. Crystal structural data of 3a

Single crystal of compounds **3a** was obtained by recrystallization from MeOH. The structure is shown in Figure S5. X-ray diffractional data and the refinement are shown in Table S1.

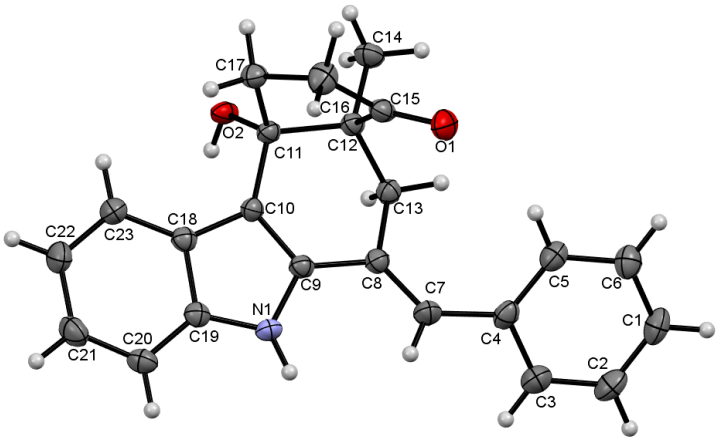


Figure S5. X-ray single crystal structure of **3a**

Table S1. Crystal data and structure refinement for 3a.

CCDC 2071594	
Empirical formula	$C_{23}H_{21}NO_2$
Formula weight	343.41
Temperature/k	296.15
Wavelength	0.71073 Å
Crystal system	monoclinic
space group	P21/n
a/Å	11.796(2)
b/Å	12.945(2)
c/Å	12.662(2)
α/°	90
β/ °	108.737(2)
γ/ °	90
Volume/ $Å^3$	1831.0(6)
Z	4
p_{calc} g/cm^3	1.2457
μ /mm^{-1}	0.079
F(000)	728.3
Crystal size/mm^3	0.26× 0.24 × 0.2

2Θ range for data collection/°	4.1 to 53.22
Index ranges	-14 ≤ h ≤ 14, -16 ≤ k ≤ 16, -15 ≤ l ≤ 15
Reflections collected	19094
Max. and min. transmission	0.984 and 0.980
Data/restraints/parameters	3809/0/237
Goodness-of-fit on F^2	1.040
Final R indices [I>2sigma(I)]	R_1 = 0.0375, wR_2 = 0.0890
R indices (all data)	R_1 = 0.0515, wR_2 = 0.0984
Largest diff. peak and hole/ e ·$Å^{-3}$	0.28/-0.26

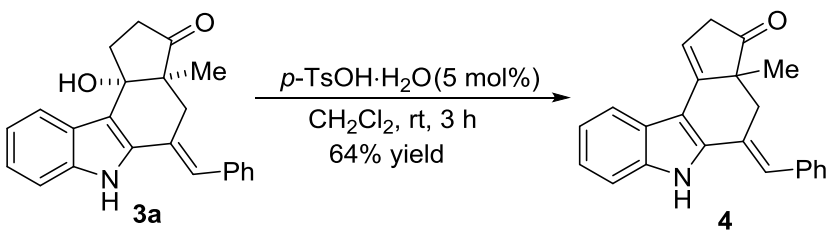
CIF files of **3a** can be obtained from the Cambridge Crystallographic Data Centre using deposition numbers 2071594. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: deposit@ccdc.cam.ac.uk, fax: +44 (1223) 336 033].

7. Scale up synthesis and applications

7.1 General procedure for Scale up synthesis

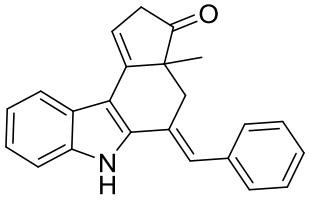
A Schlenk flask (50 mL) charged with a stir bar was added *N*-benzyl-1H-indole -1-carboxamide **1a** (0.75 g, 3 mmol, 1 equiv), 2-methyl-2-(3-phenylprop-2-yn-1-yl) cyclopentane-1,3-dione **2a** (0.81 g, 3.6 mmol, 1.2 equiv), $[RhCp^*Cl_2]_2$ (46.4 mg, 0.075 mmol, 2.5 mol%), $Cu(OAc)_2·H_2O$ (300 mg, 1.5 mmol, 0.5 equiv), NaOAc (0.37 g, 4.5 mmol, 1.5 equiv) and CH_3CN (30 mL). The mixture was stirred at 60 ℃ under N_2 for 48 h, which was then concentrated in vacuum. The residue was purified by silica gel column chromatography (PE:EA = 5:1) to give products **3a** in 57% yield (0.59 g).

7.2 General procedure for dehydration of tetrahydrocarbazole 3a



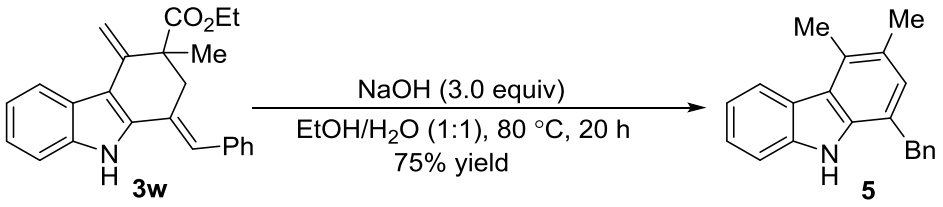
A seal tube charged with a stir bar was added **3a** (68.6 mg, 0.20 mmol, 1 equiv), *p*-toluenesulfonic acid monohydrate (1.90 mg, 0.01 mmol, 0.05 equiv) and CH_2Cl_2 (2.0 mL). The mixture was stirred at room temperature under N_2 for 3 h, which was then concentrated in vacuum. The residue was purified by silica gel column chromatography (PE/EA = 10/1) to give product **4** in 64% yield.

(*E*)-5-benzylidene-3a-methyl-3a,4,5,6-tetrahydrocyclopenta[*c*]carbazol-3(2H)-one, 4



White solid, 42 mg, yield 64%, PE:EA = 10:1, M.p. 132-136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (s, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.40 – 7.35 (m, 5H), 7.30 – 7.28 (m, 1H), 7.25 (s, 1H), 7.20 (t, *J* = 7.0 Hz, 1H), 6.93 (d, *J* = 2.2 Hz, 1H), 6.14 (s, 1H), 3.41 (dd, *J* = 23.2, 1.8 Hz, 1H), 3.21 (d, *J* = 14.6 Hz, 1H), 3.08 (dd, *J* = 23.2, 2.9 Hz, 1H), 2.57 (dd, *J* = 14.6, 2.3 Hz, 1H), 1.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 219.5, 140.8, 137.7, 136.2, 135.5, 129.3, 128.6, 127.3, 126.9, 125.6, 124.8, 123.9, 120.9, 120.3, 111.7, 111.3, 110.3, 51.9, 42.5, 32.9, 22.7. FTIR (neat) υ 3407, 2985, 2917, 2860, 1758, 1715, 1444, 1305, 1241, 1203, 1044, 741, 706 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}NO$ 325.1539; Found 326.1527.

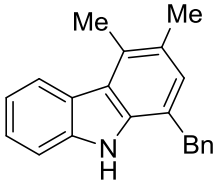
7.3 General procedure for hydrolysis and decarboxylation of product 3w



A seal tube charged with a stir bar was added NaOH (6.8 mg, 0.17 mmol, 3.0 equiv) followed by EtOH (1.0 mL) and water (1.0 mL), which was stirred for 5 min. Then **3w** (20.0 mg, 0.056 mmol, 1.0 equiv) was added. The mixture was heated to 80 ℃ and stirred for 20 h. After that the reaction was cooled and quenched with HCl (1 mL, 1M). Then water (10 mL) was added and extracted with EA for three times. The organic layer was dried (Na_2SO_4) and the solvent was removed in vacuum. The

residue was purified by silica gel column chromatography (PE/EA = 15/1) to give the carbazole product **5** in 75% yield.

1-Benzyl-3,4-dimethyl-9H-carbazole, 5



White solid, 12.1 mg, yield 75%, PE:EA = 15:1. M.p. 129-131 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 8.0 Hz, 1H), 7.69 (s, 1H), 7.35 – 7.25 (m, 5H), 7.25 – 7.18 (m, 3H), 7.10 (s, 1H), 4.24 (s, 2H), 2.80 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.93, 139.90, 137.3, 129.8, 129.3, 128.9, 128.7, 127.1, 126.6, 125.0, 124.3, 122.9, 122.6, 119.3, 119.2, 110.7, 38.0, 19.7, 16.5; FTIR (neat) υ 3432, 2917, 2858, 1597, 1445, 1392, 1267, 1078, 717, 720, 701, 606, 533, 465, 407 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{20}N$ 286.1590; Found 286.1584.

8. References

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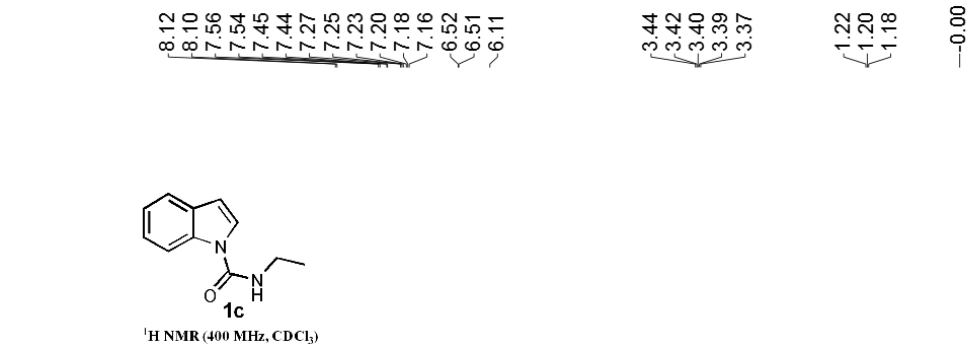
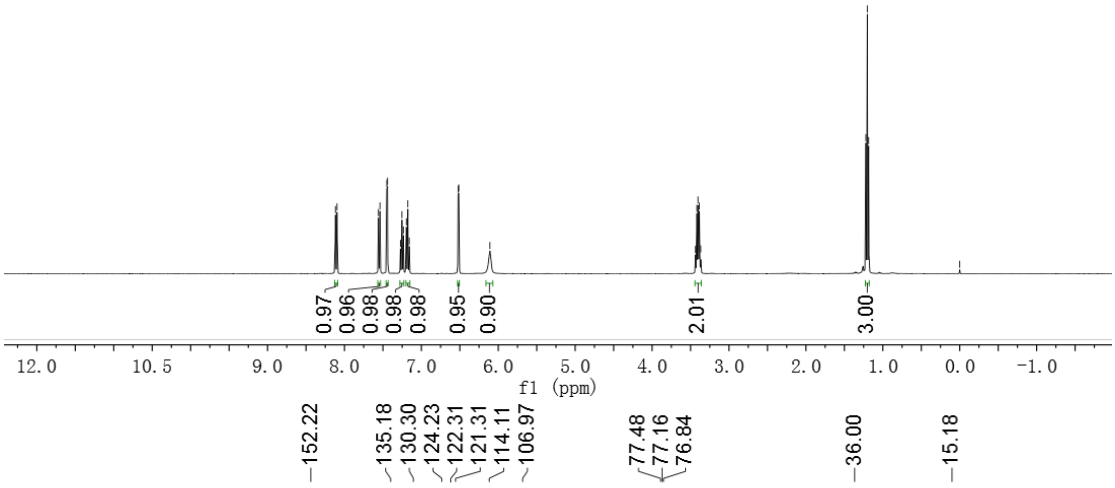
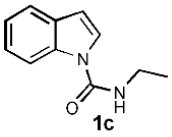
6. Dong, B.; Cong, X.; Hao, N. Silver-catalyzed regioselective deuteration of (hetero)arenes and α-deuteration of 2-alkyl azaarenes. *RSC Adv.* **2020**, *10*, 25475.
7. For benzyl isocyanate: Artuso, E.; Degani, I.; Fochi, Rita.; Magistris, C. One-Pot Three-Step Preparation of Alkyl and Aryl Alkylcarbamates from *S*-Methyl *N*-Alkylthiocarbamates. *Synthesis* **2008**, 1612.

9. NMR spectra of new compounds

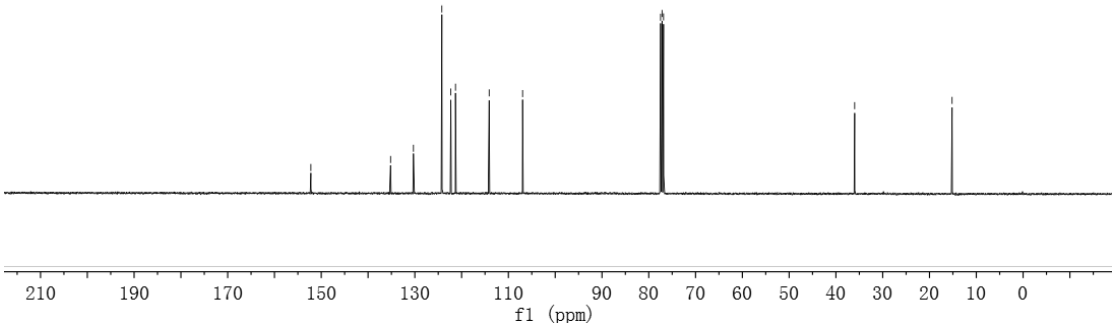


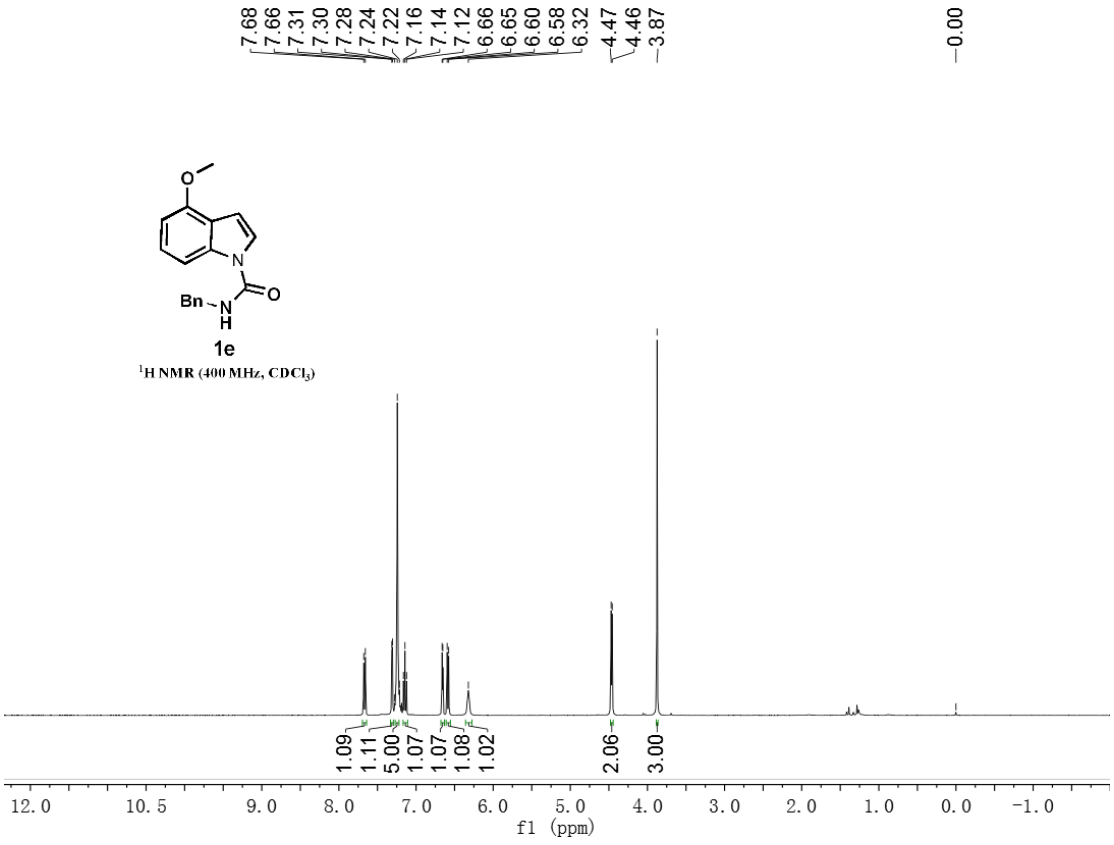
^{1}H NMR (400 MHz, $CDCl_3$)

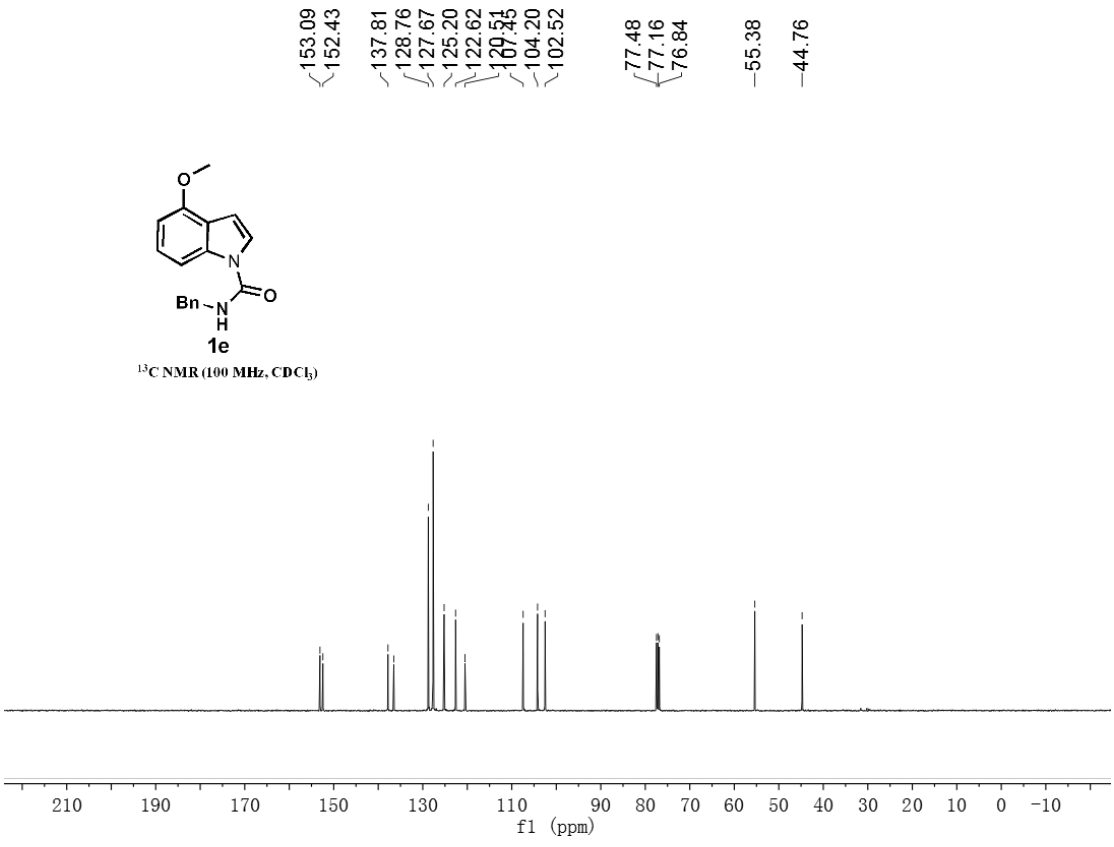


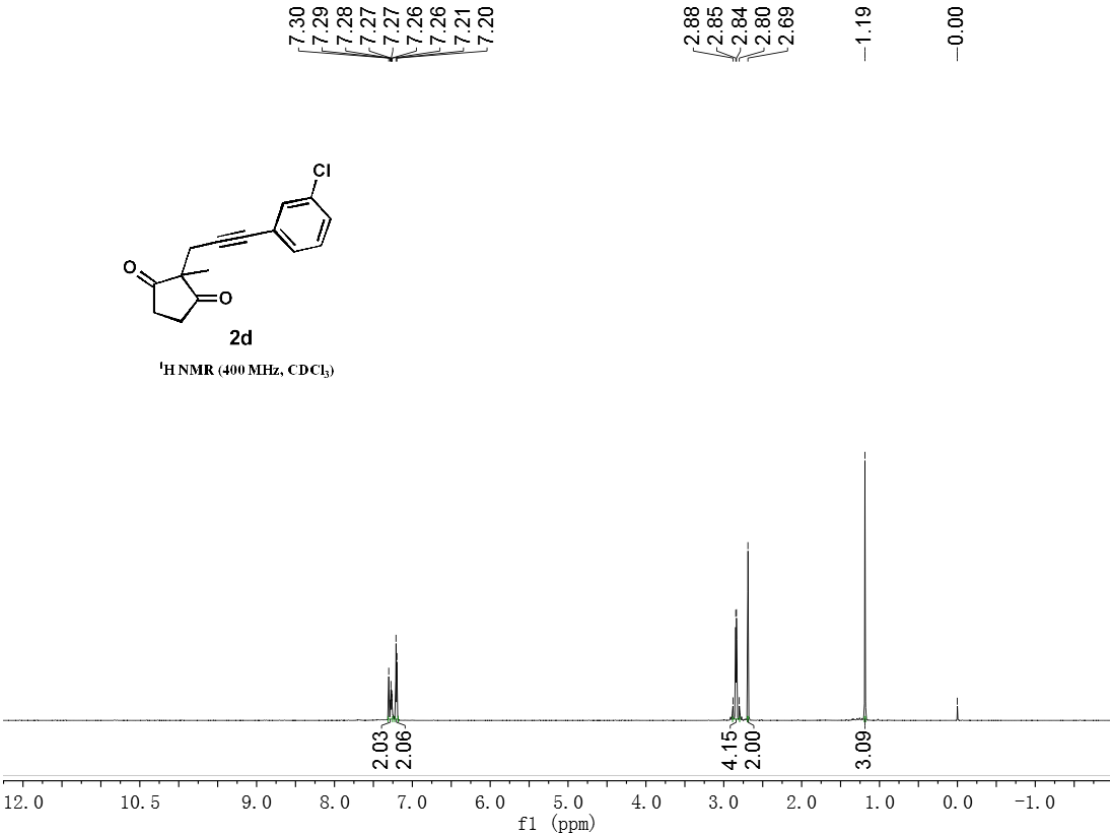


^{13}C NMR (400 MHz, $CDCl_3$)



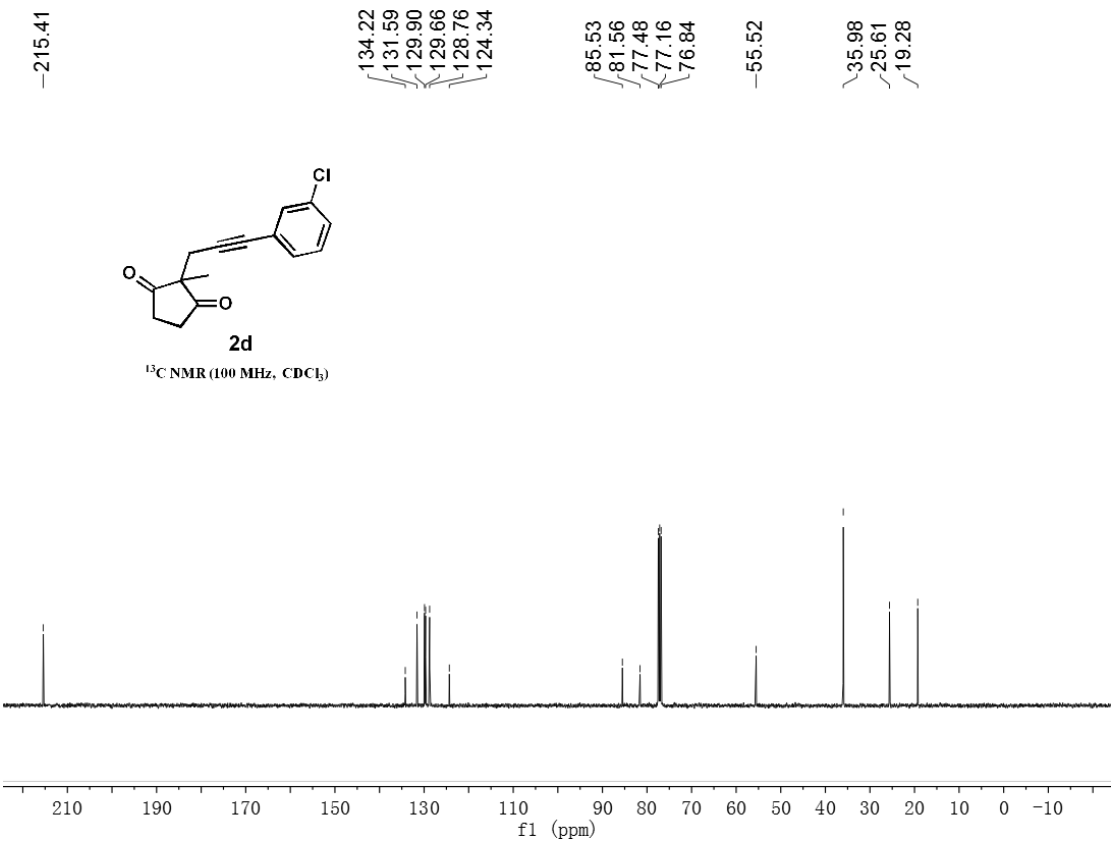

7.68
7.66
7.31
7.30
7.28
7.24
7.22
7.16
7.14
7.12
6.66
6.65
6.60
6.58
6.32
4.47
4.46
3.87
0.00
1e
1H NMR (400 MHz, CDCl3)
1.09
1.11
5.00
1.07
1.07
1.08
1.02
2.06
3.00
f1 (ppm)


153.09
152.43
137.81
128.76
127.67
125.20
122.62
120.51
107.45
104.20
102.52
77.48
77.16
76.84
55.38
44.76
1e
13C NMR (100 MHz, CDCl3)
f1 (ppm)



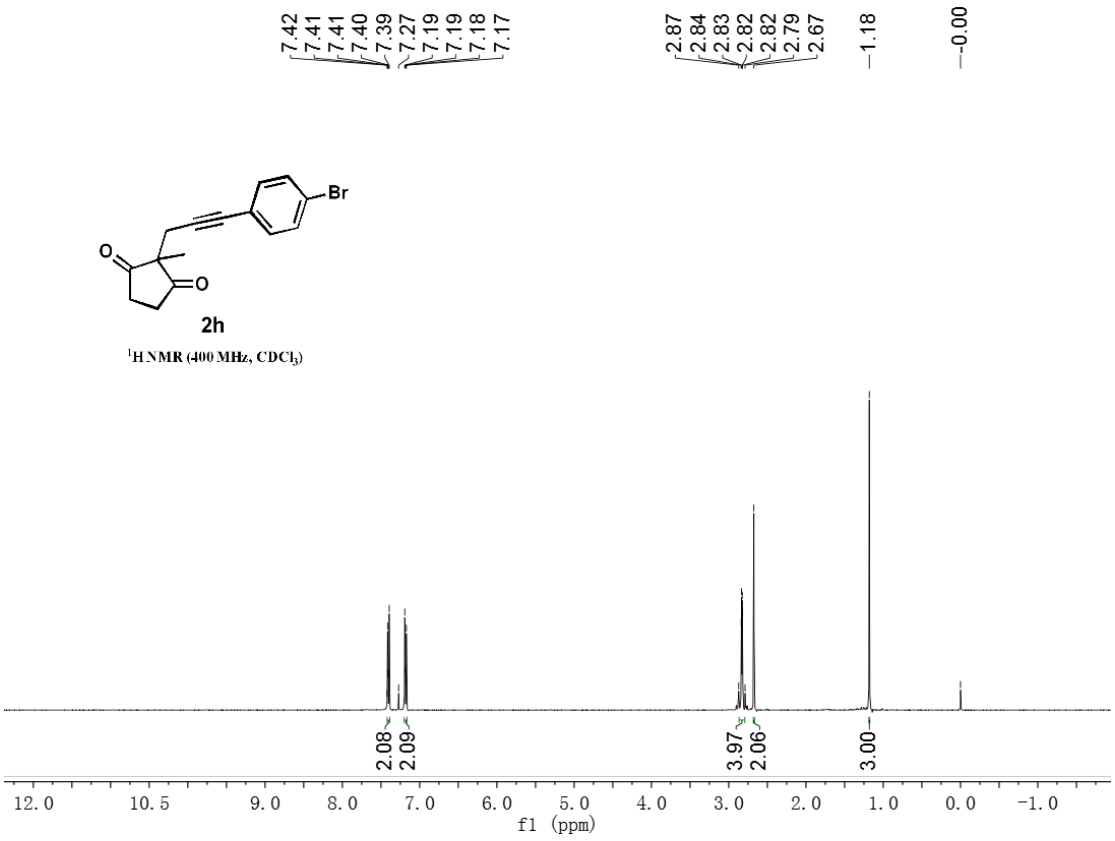
2d

^{1}H NMR (400 MHz, $CDCl_3$)



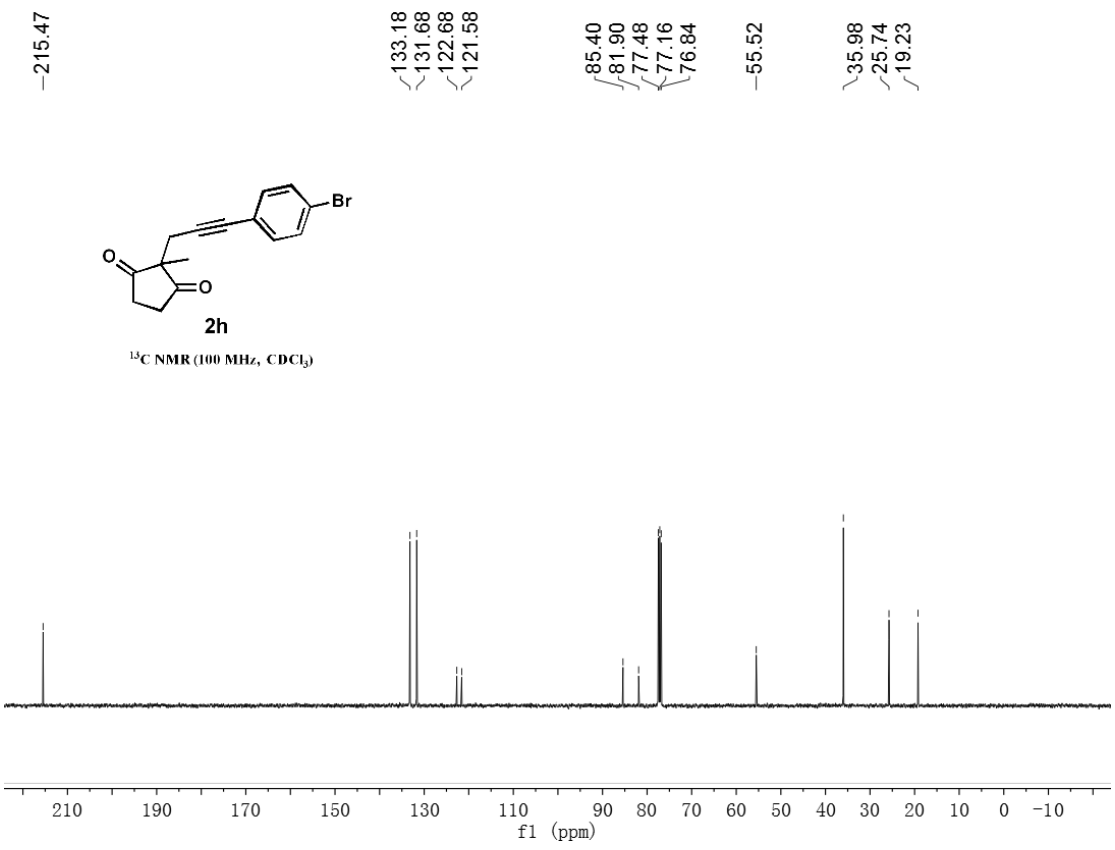
2d

^{13}C NMR (100 MHz, $CDCl_3$)



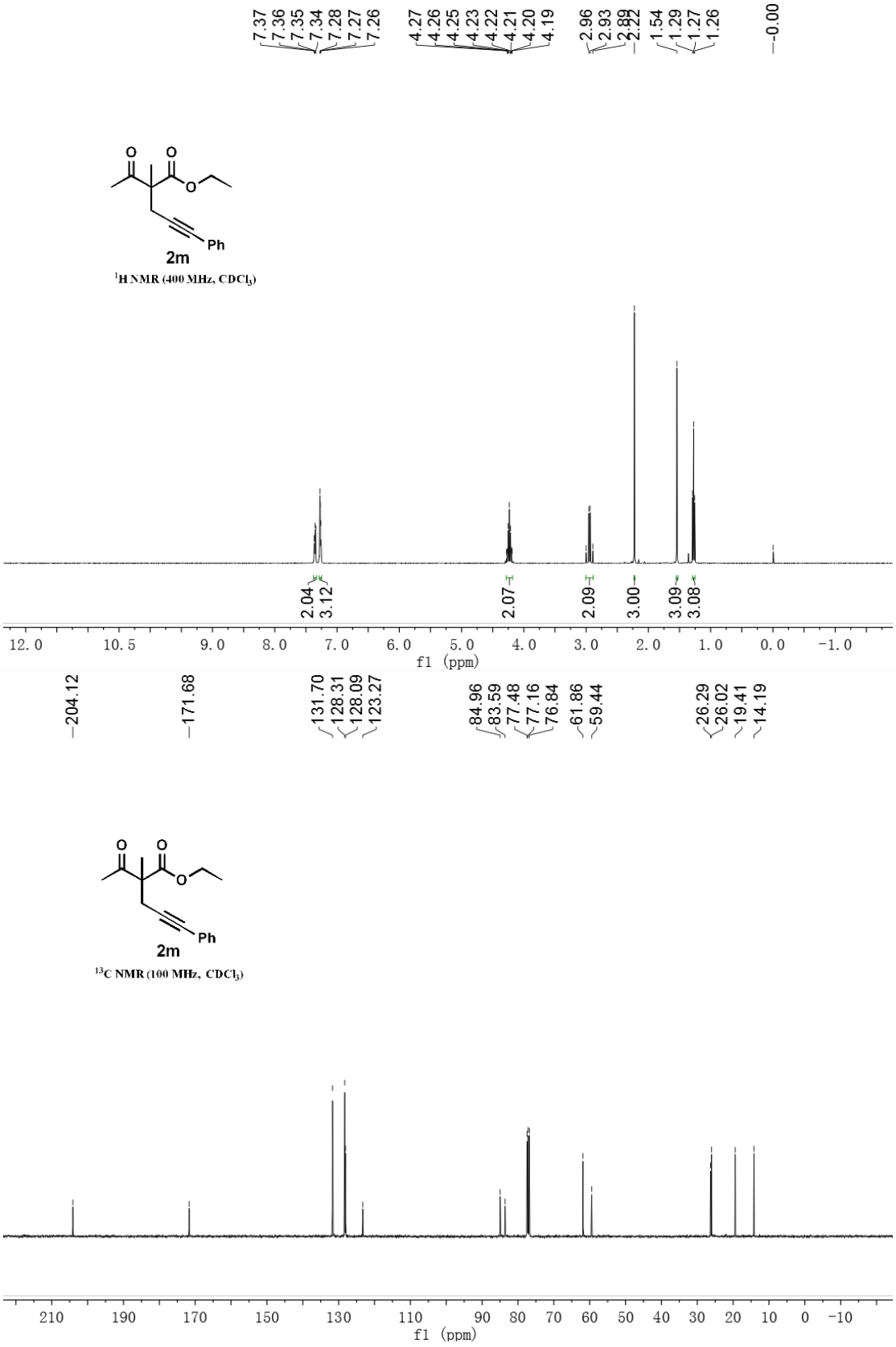
2h

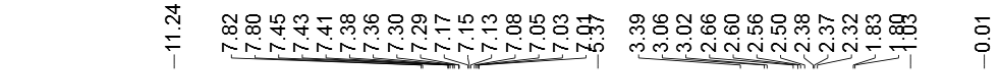
^{1}H NMR (400 MHz, $CDCl_3$)

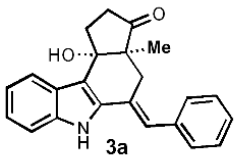


2h

^{13}C NMR (100 MHz, $CDCl_3$)

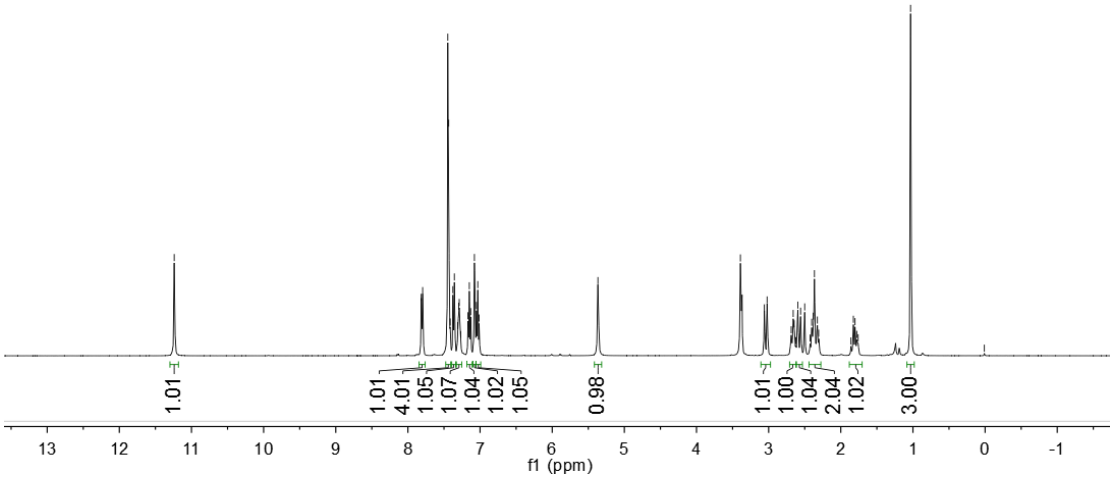

7.37
7.36
7.35
7.34
7.28
7.27
7.26
4.27
4.26
4.25
4.23
4.22
4.21
4.20
4.19
2.96
2.93
2.89
2.22
1.54
1.29
1.27
1.26
0.00
Ph
2m
^{1}H NMR (400 MHz, CDCl$_3$)
2.04
3.12
2.07
2.09
3.00
3.09
3.08
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)
204.12
171.68
131.70
128.31
128.09
123.27
84.96
83.59
77.48
77.16
76.84
61.86
59.44
26.29
26.02
19.41
14.19
Ph
2m
^{13}C NMR (100 MHz, CDCl$_3$)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

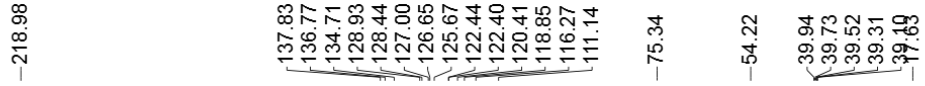


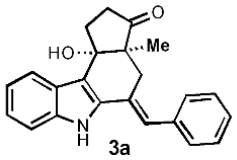


3a

^{1}H NMR (400 MHz, DMSO-d_6)

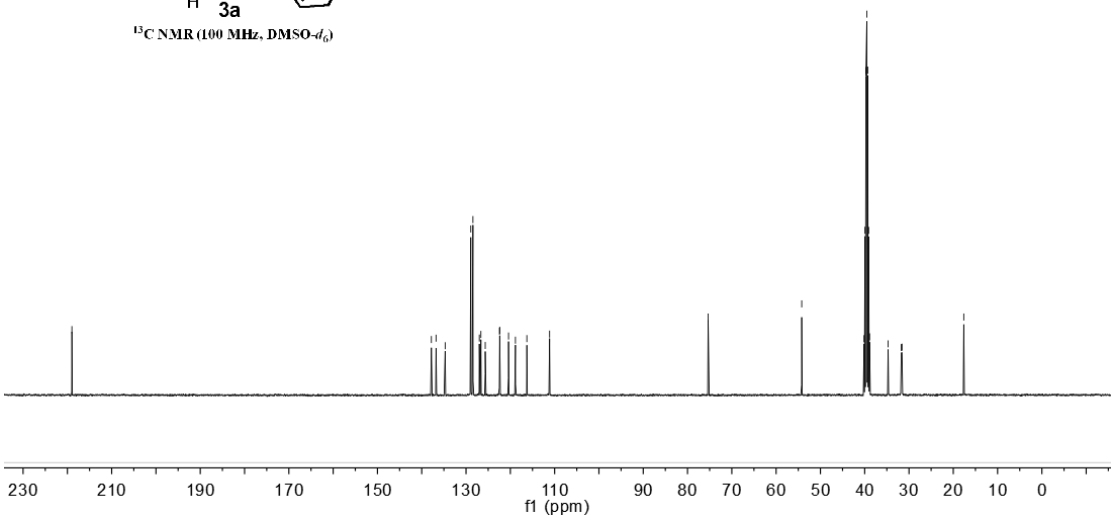


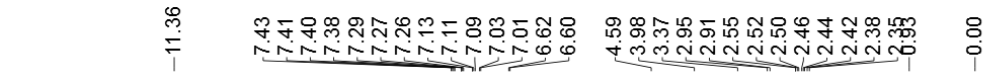


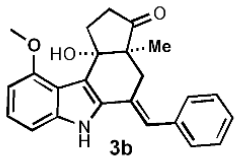


3a

^{13}C NMR (100 MHz, DMSO-d_6)

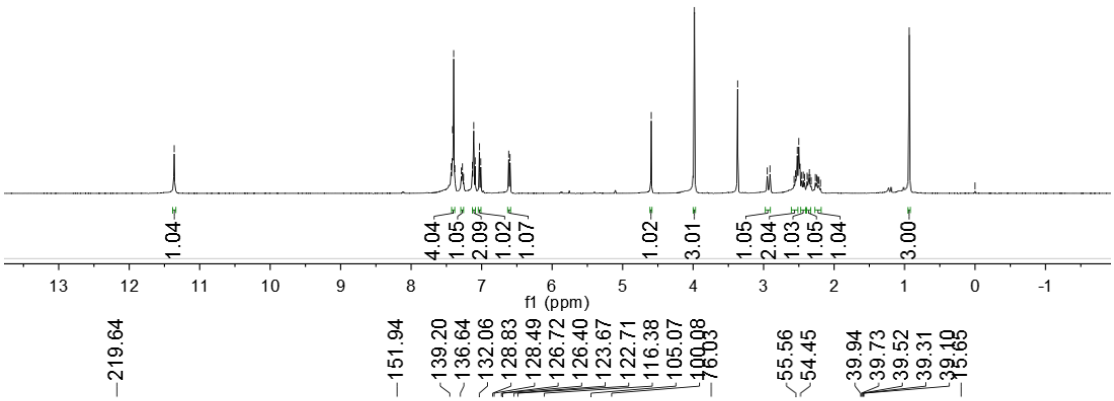


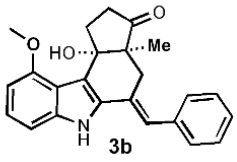




3b

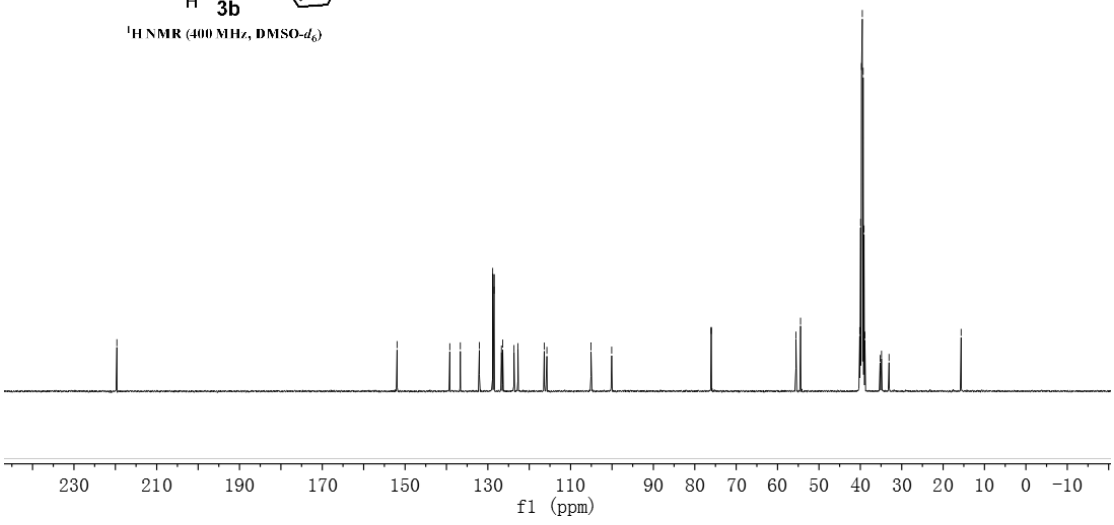
^{1}H NMR (400 MHz, DMSO-d_6)

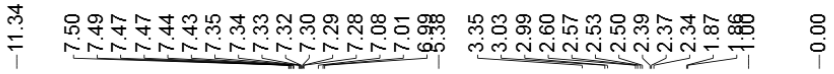


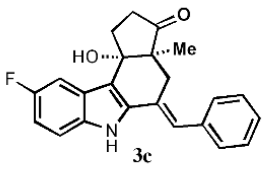


3b

^{1}H NMR (400 MHz, DMSO-d_6)

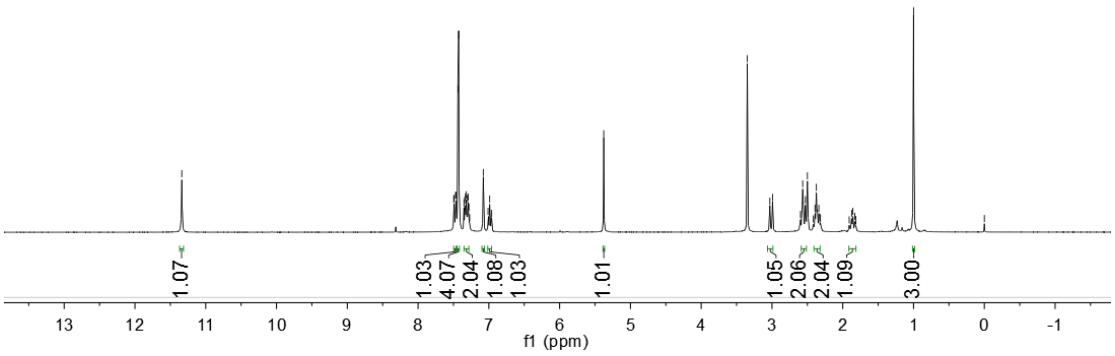


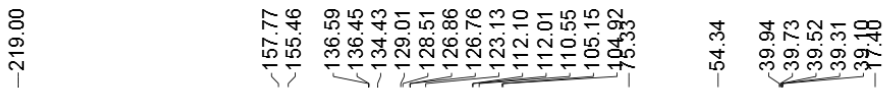


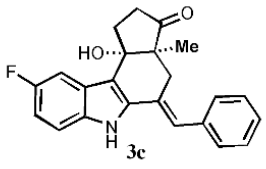


3c

^{1}H NMR (400 MHz, DMSO-d_6)

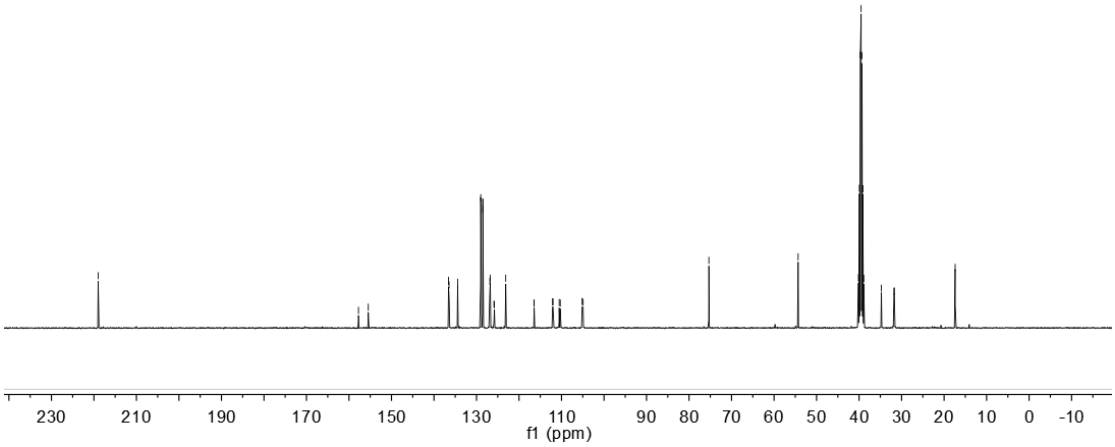


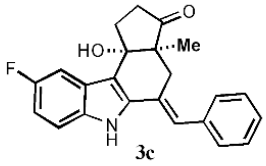




3c

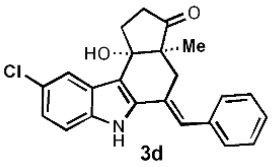
^{13}C NMR (100 MHz, DMSO-d_6)





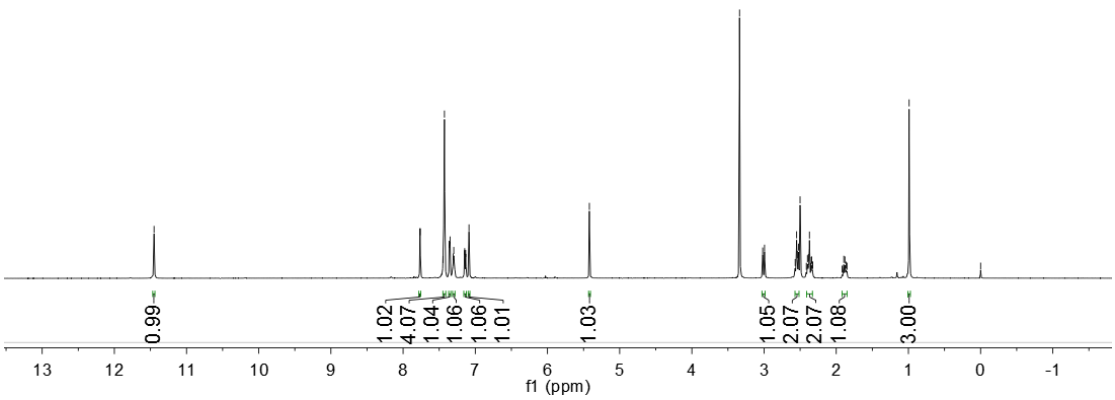
3c

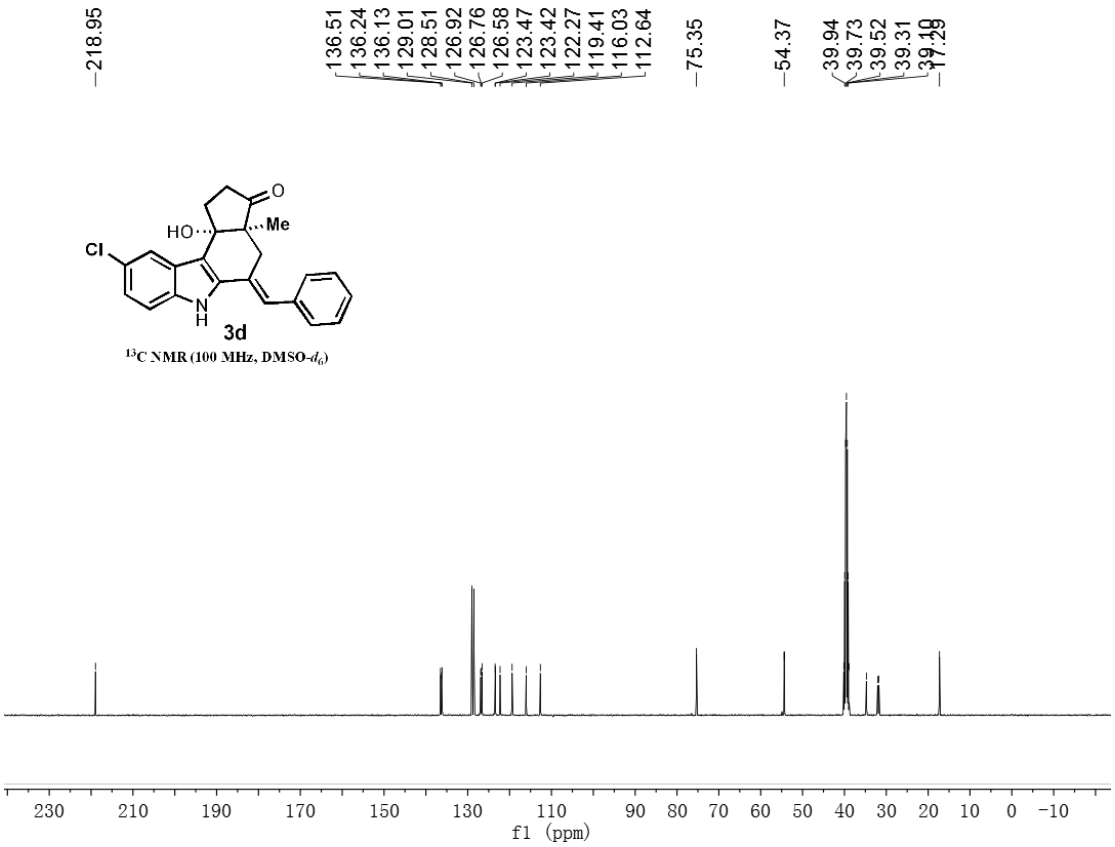
^{19}F NMR (376 MHz, DMSO-d_6)



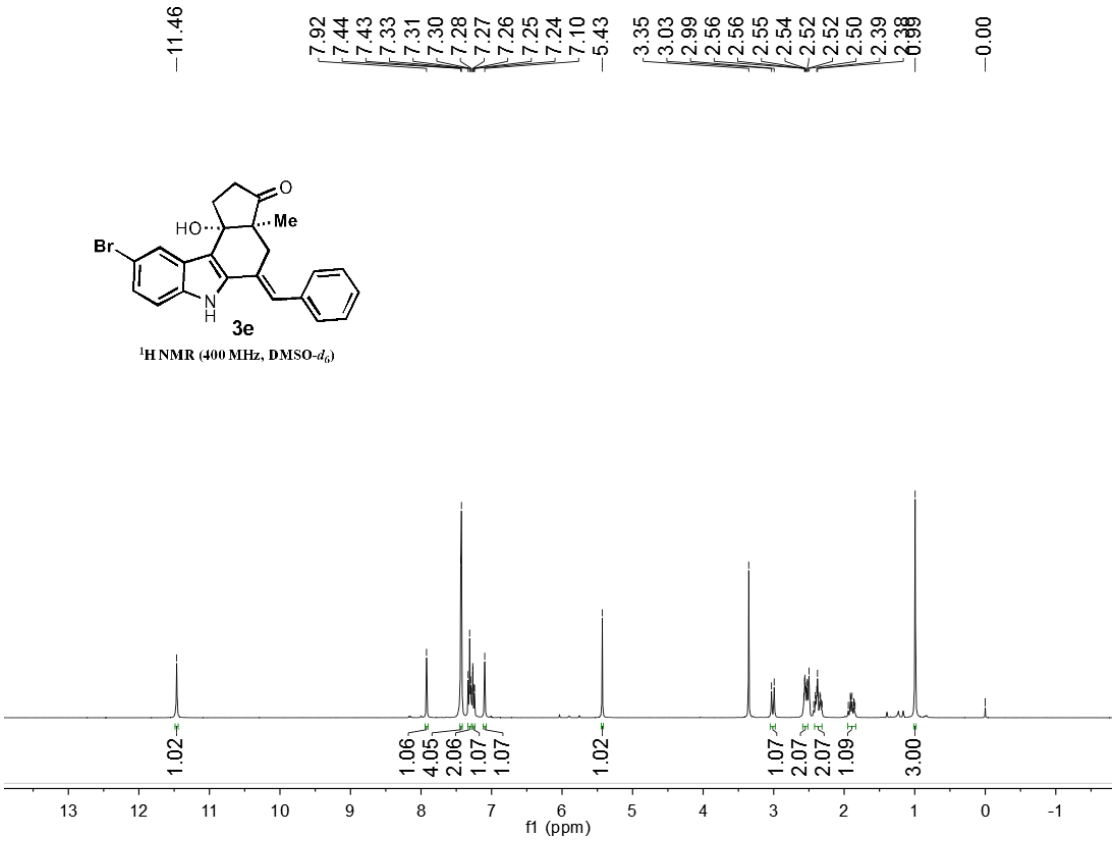
3d

^{1}H NMR (600 MHz, DMSO-d_6)





^{13}C NMR (100 MHz, DMSO-d_6)



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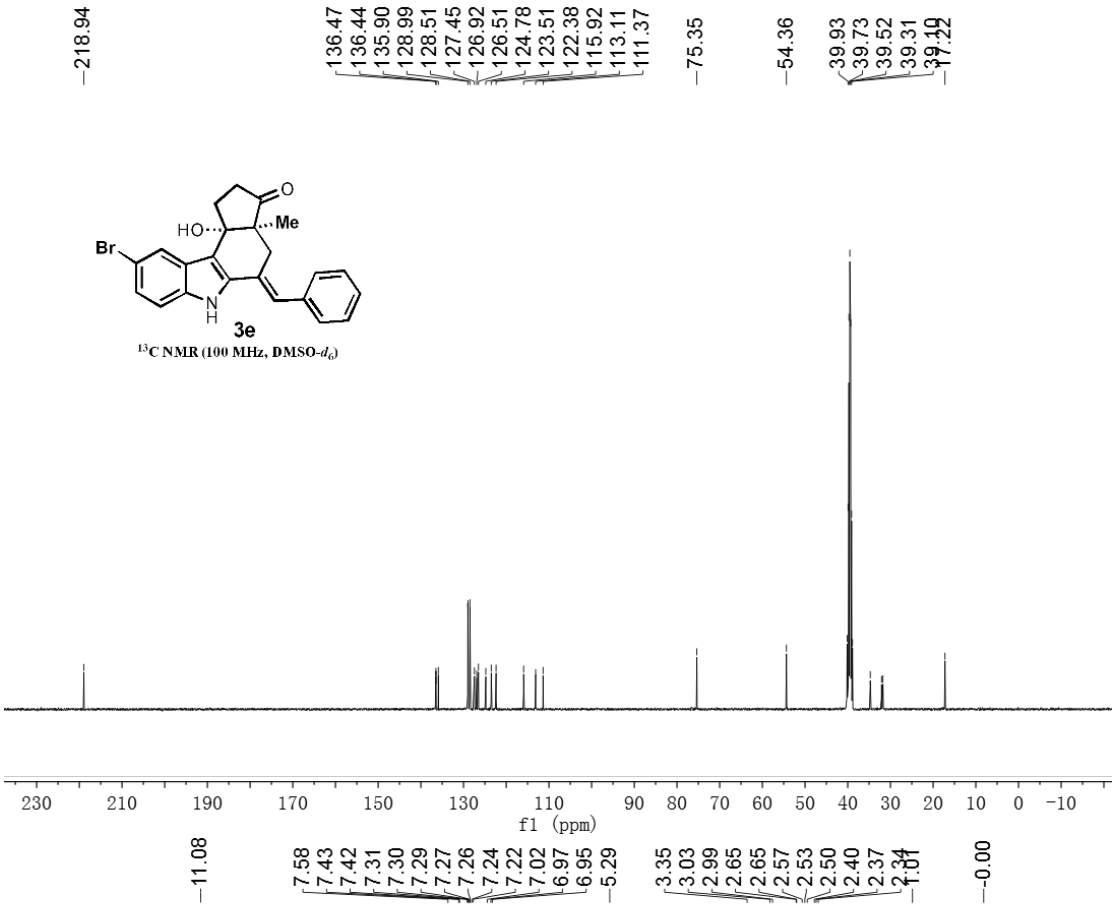
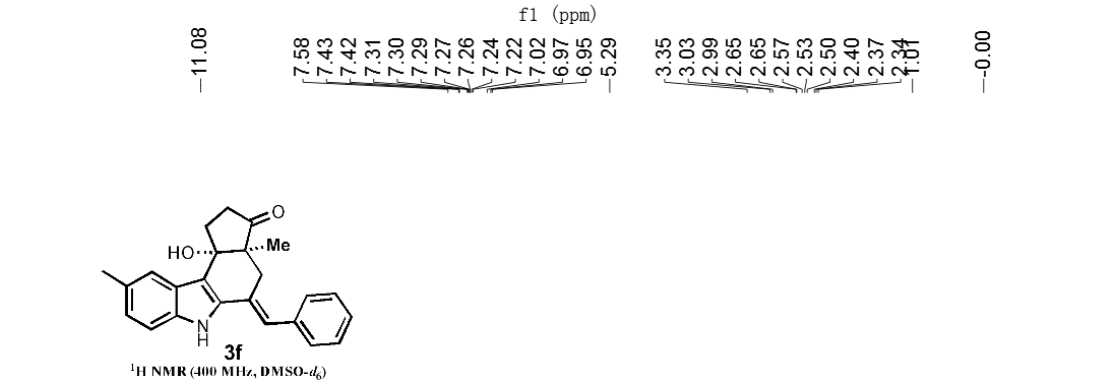


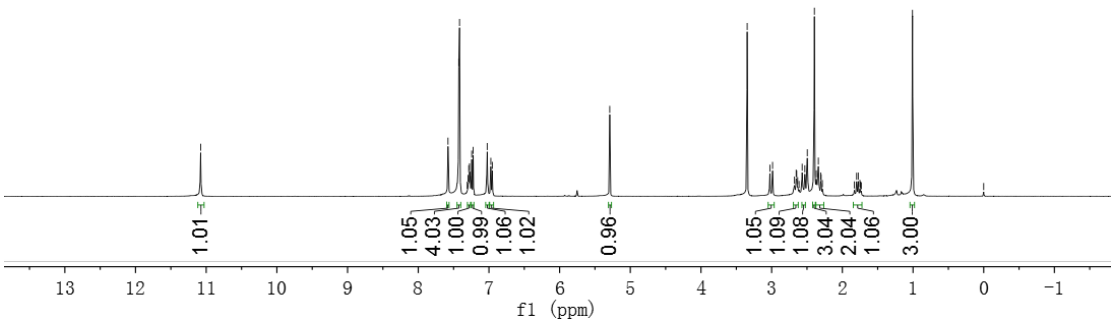
3e

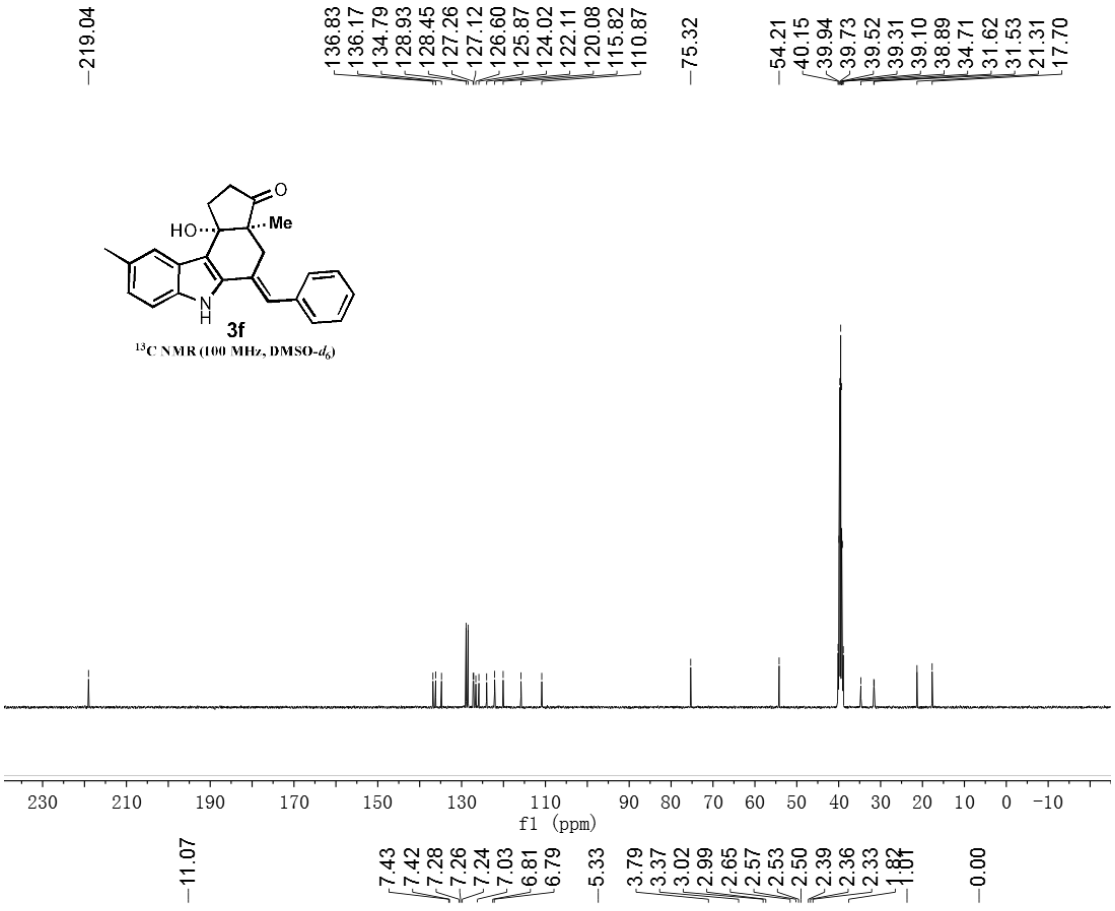
^{13}C NMR (100 MHz, DMSO-d_6)



3f

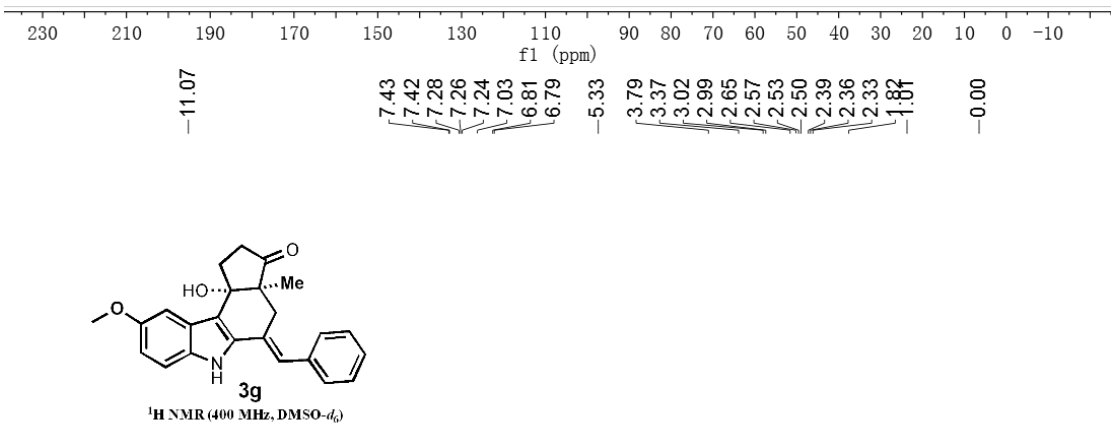
^{1}H NMR (400 MHz, DMSO-d_6)





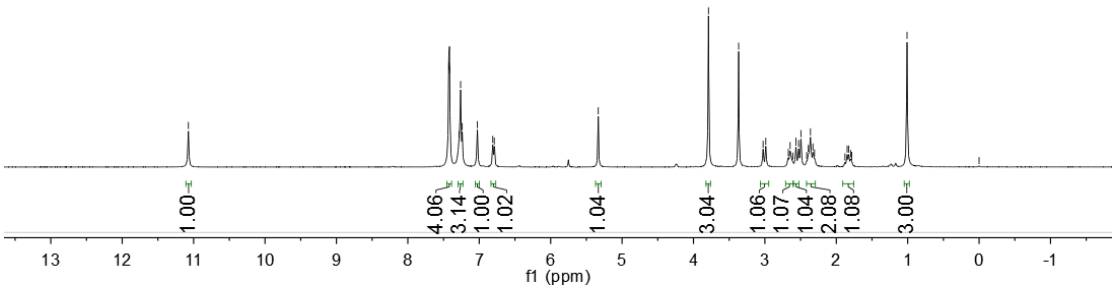
3f

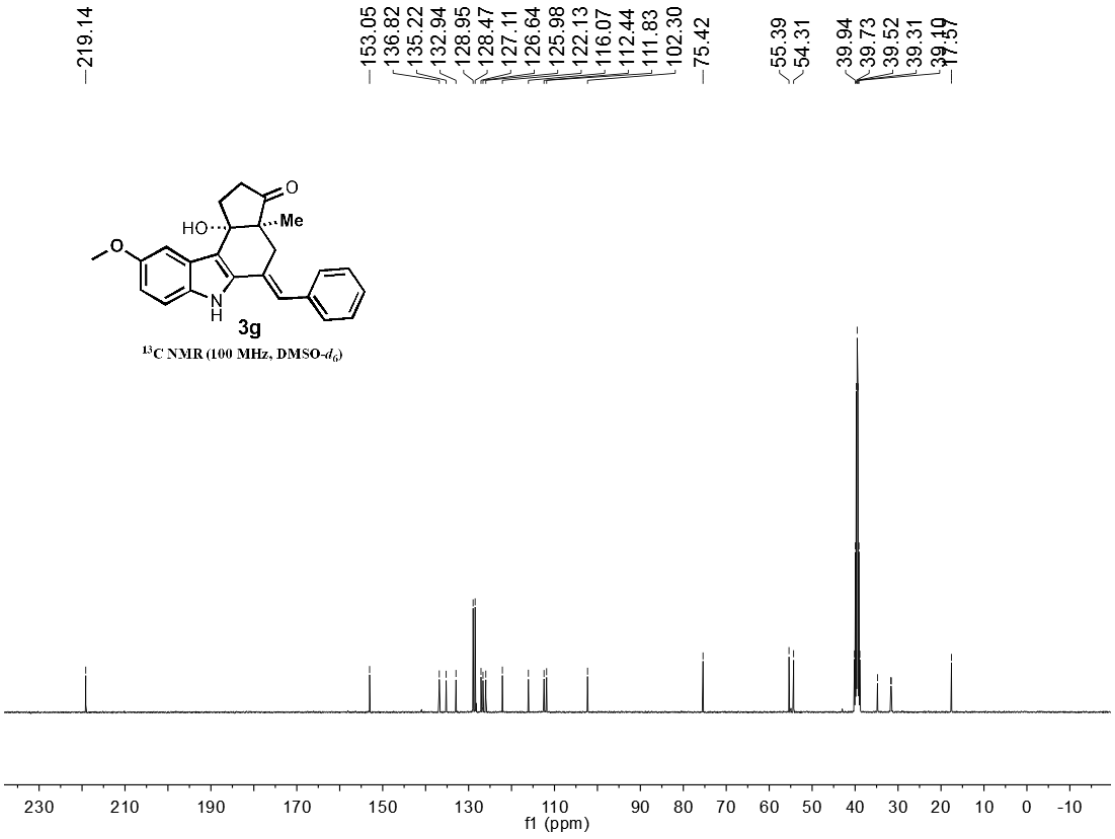
^{13}C NMR (100 MHz, DMSO-d_6)



3g

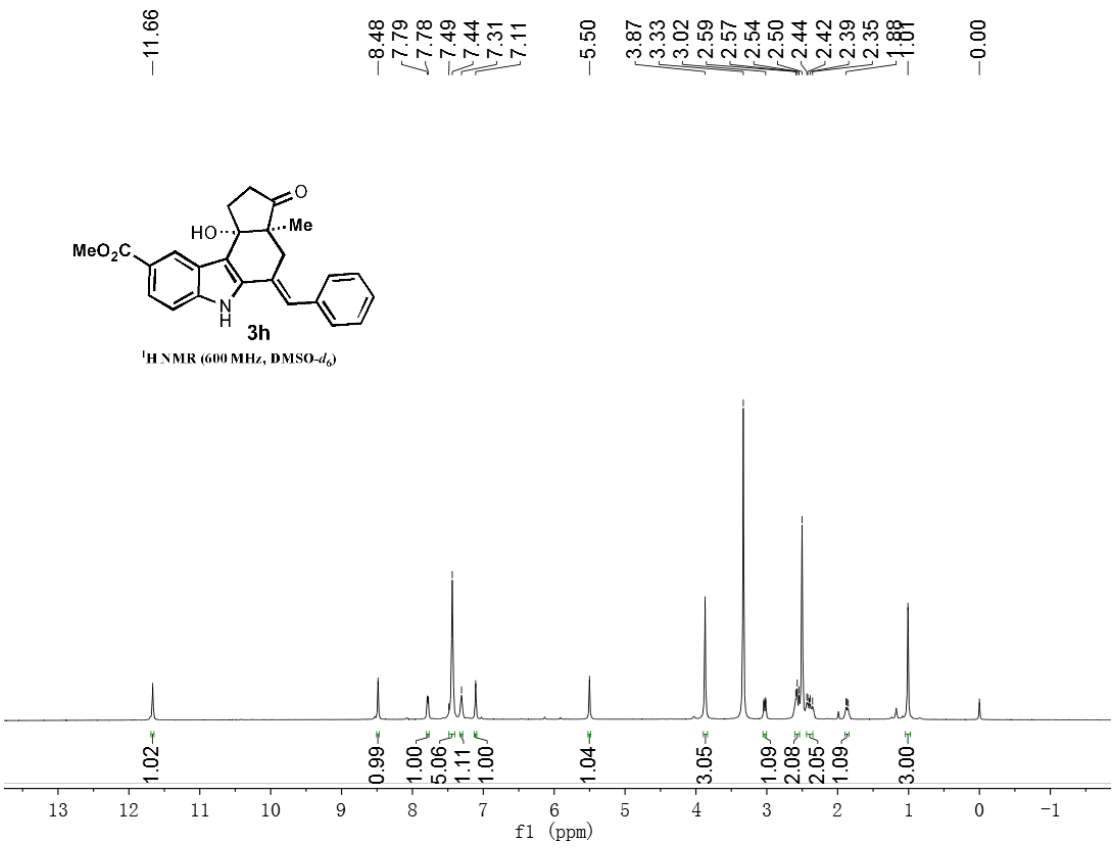
^{1}H NMR (400 MHz, DMSO-d_6)





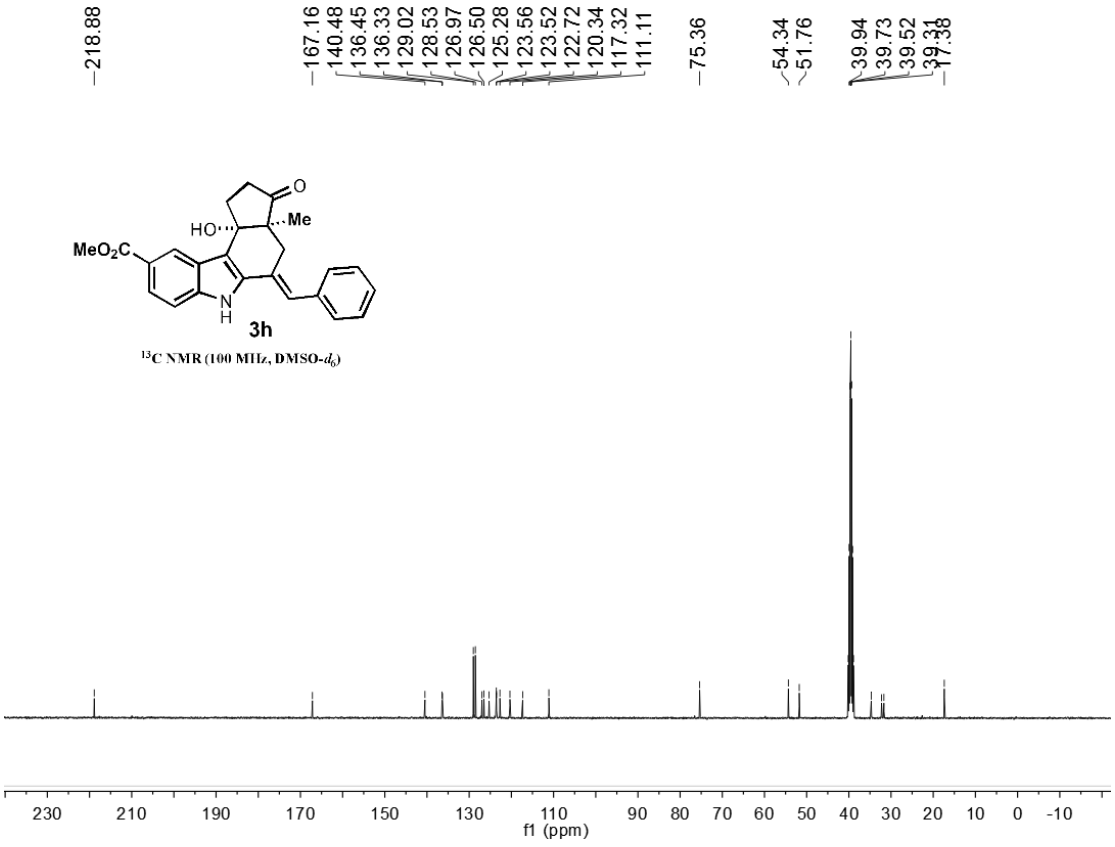
3g

^{13}C NMR (100 MHz, DMSO-d_6)



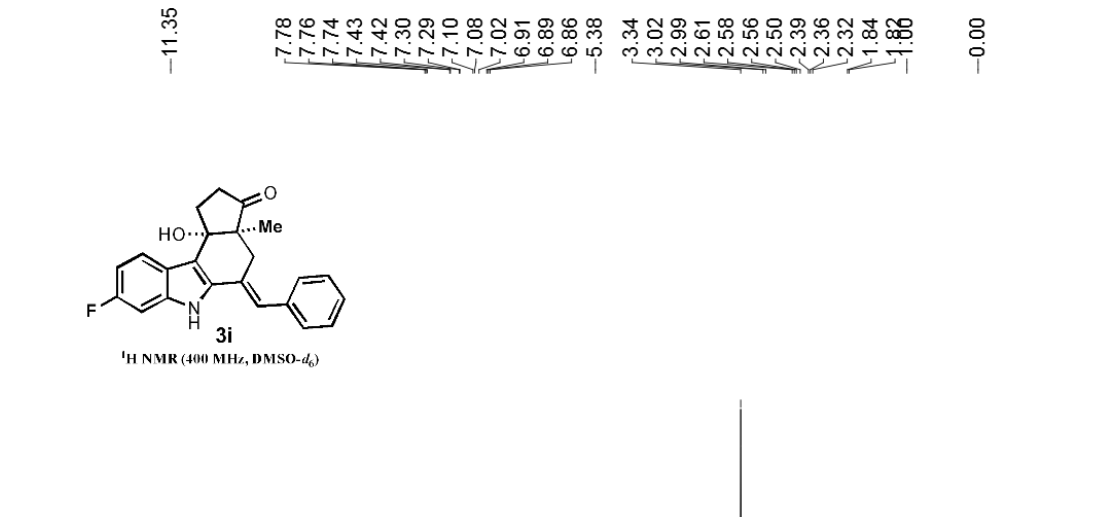
3h

^{1}H NMR (600 MHz, DMSO-d_6)



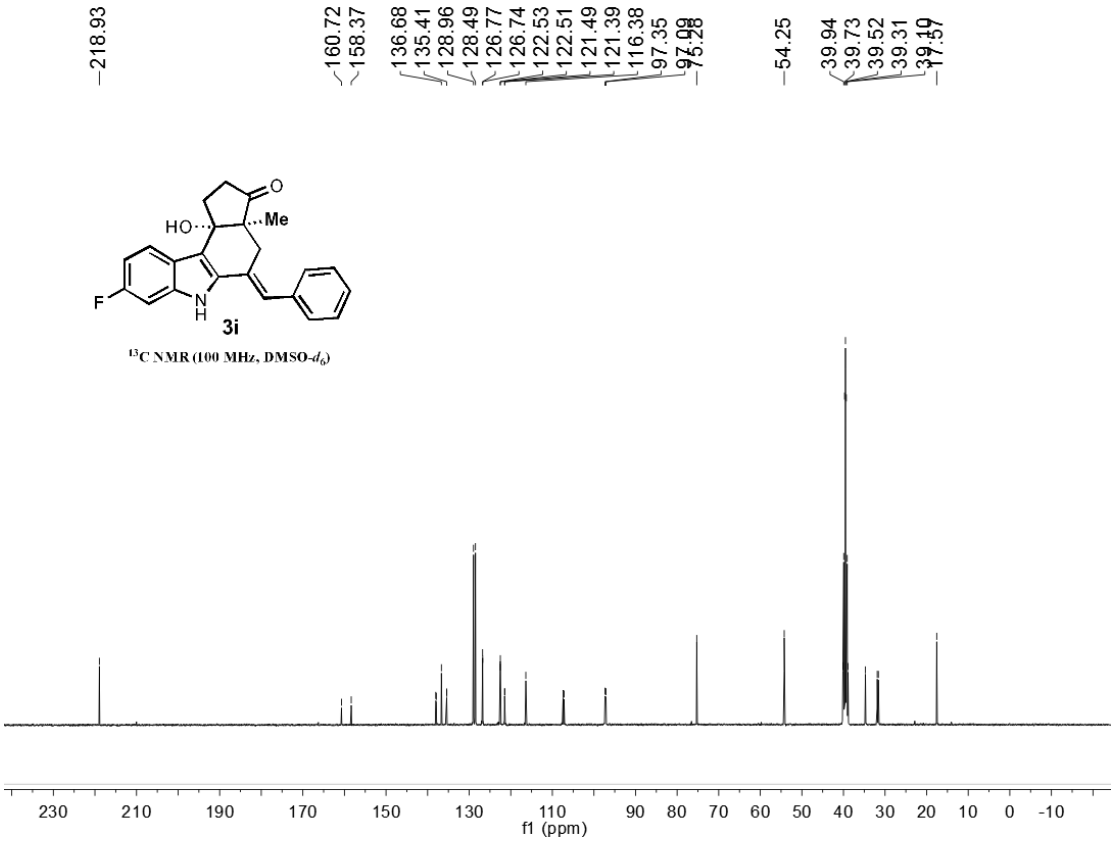
3h

^{13}C NMR (100 MHz, DMSO-d_6)

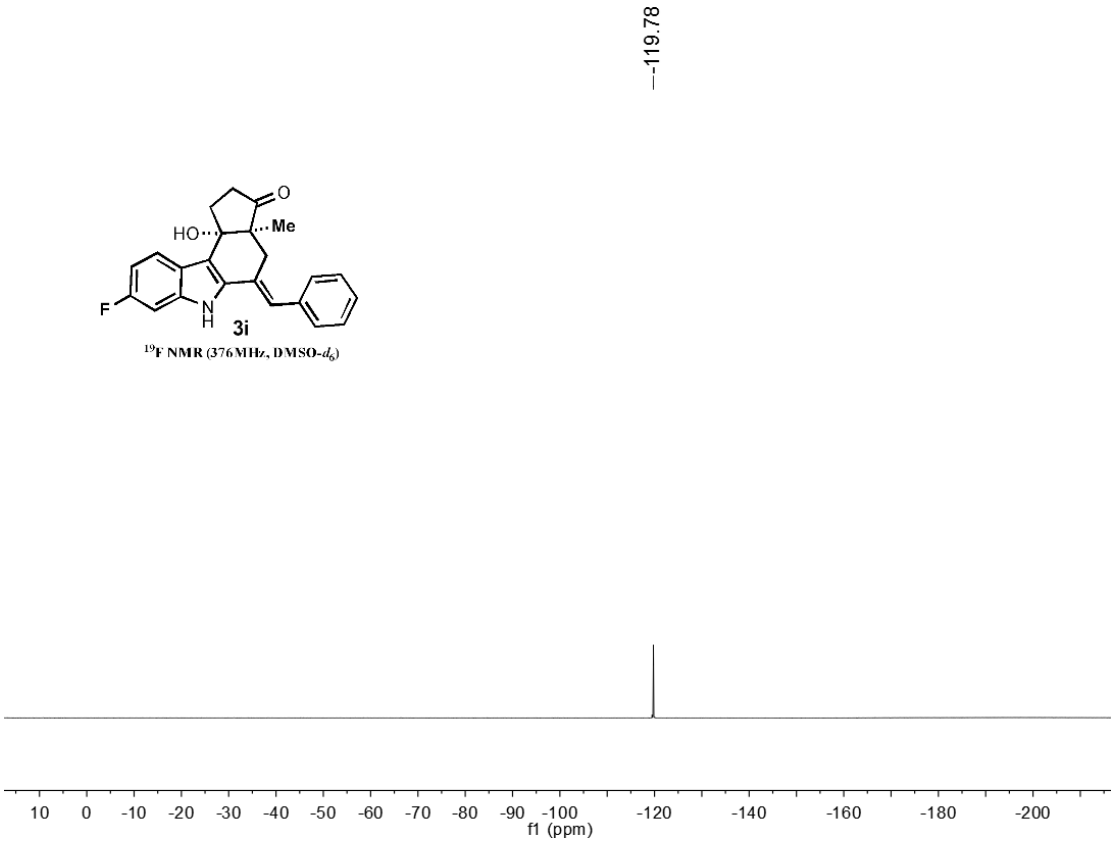


3i

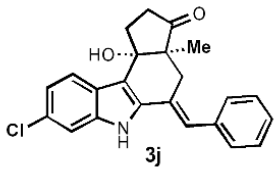
^{1}H NMR (400 MHz, DMSO-d_6)



^{13}C NMR (100 MHz, DMSO-d_6)

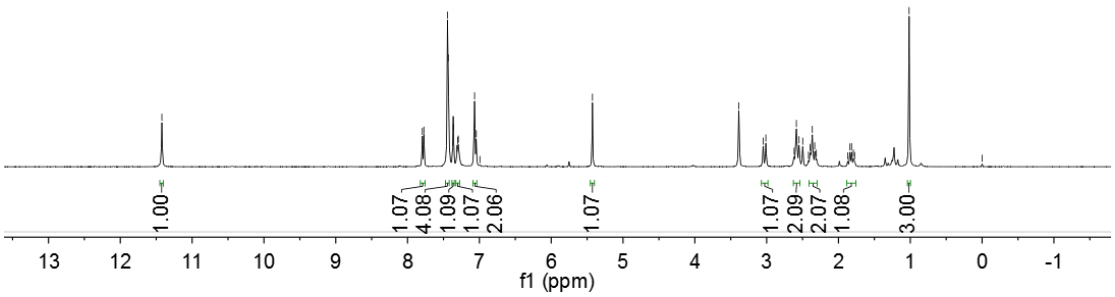


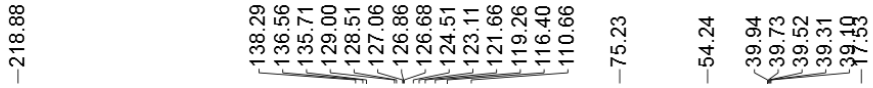
^{19}F NMR (376 MHz, DMSO-d_6)

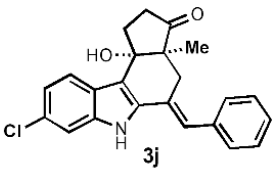


3j

^{1}H NMR (400 MHz, DMSO-d_6)

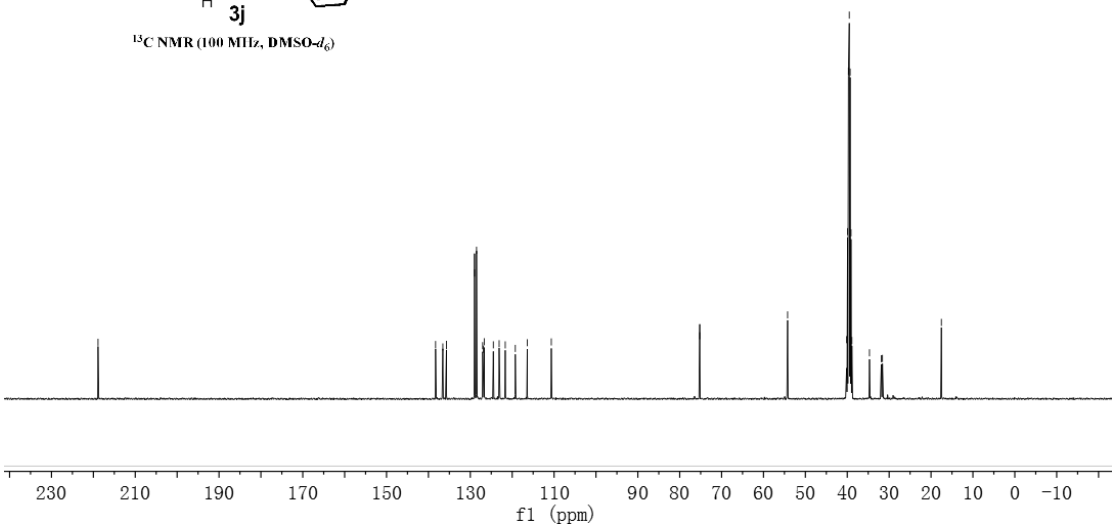


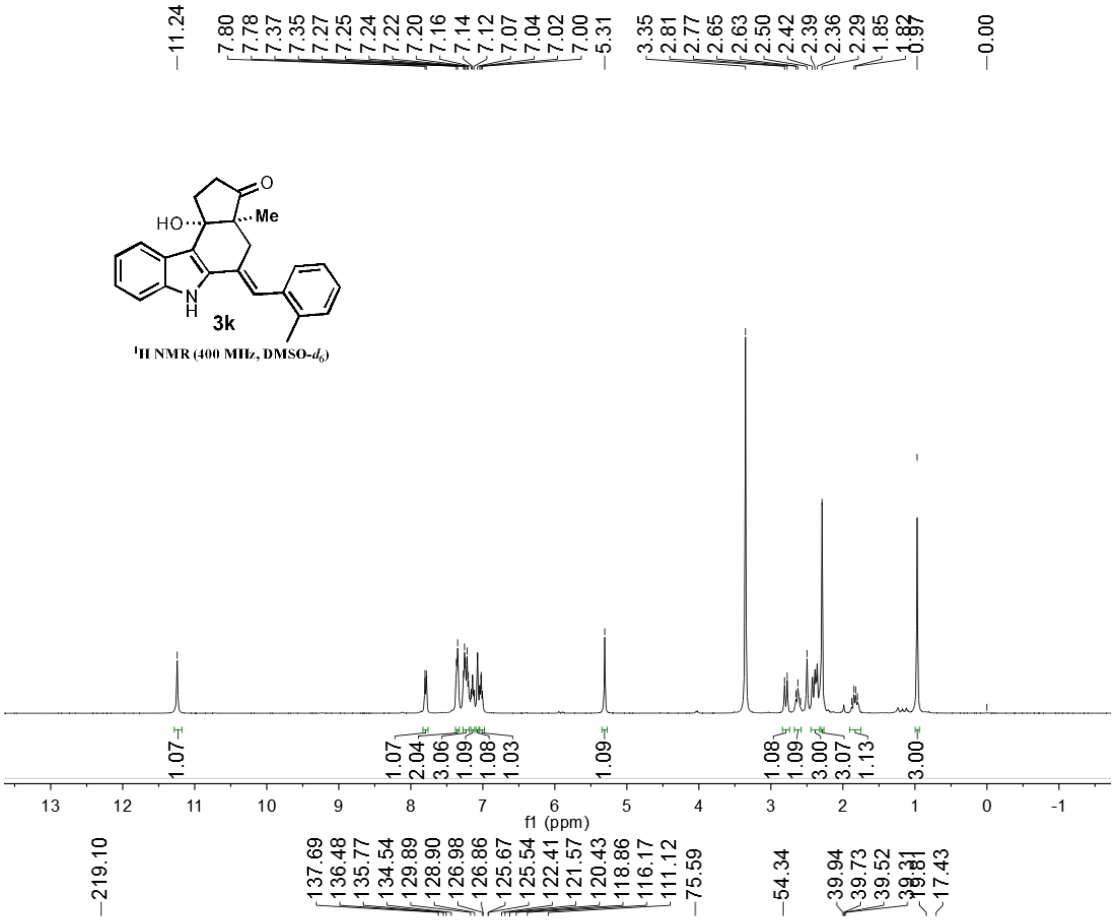


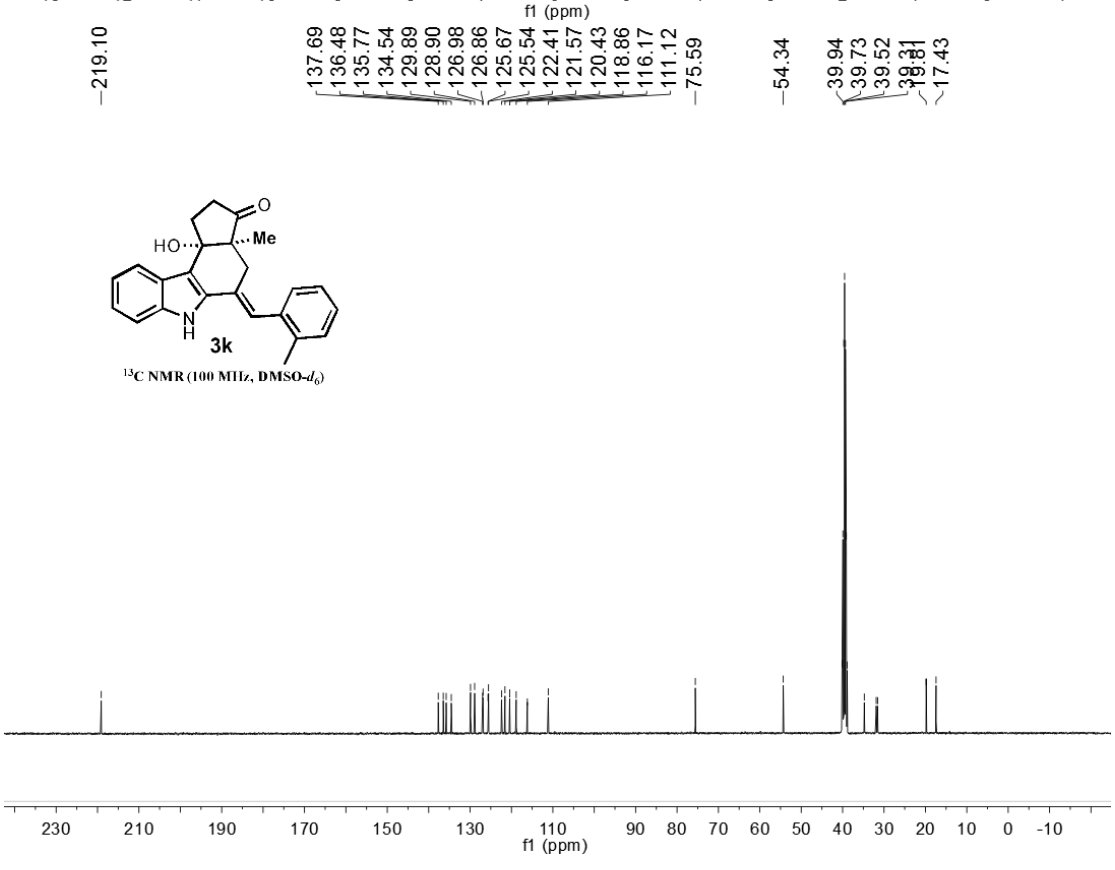


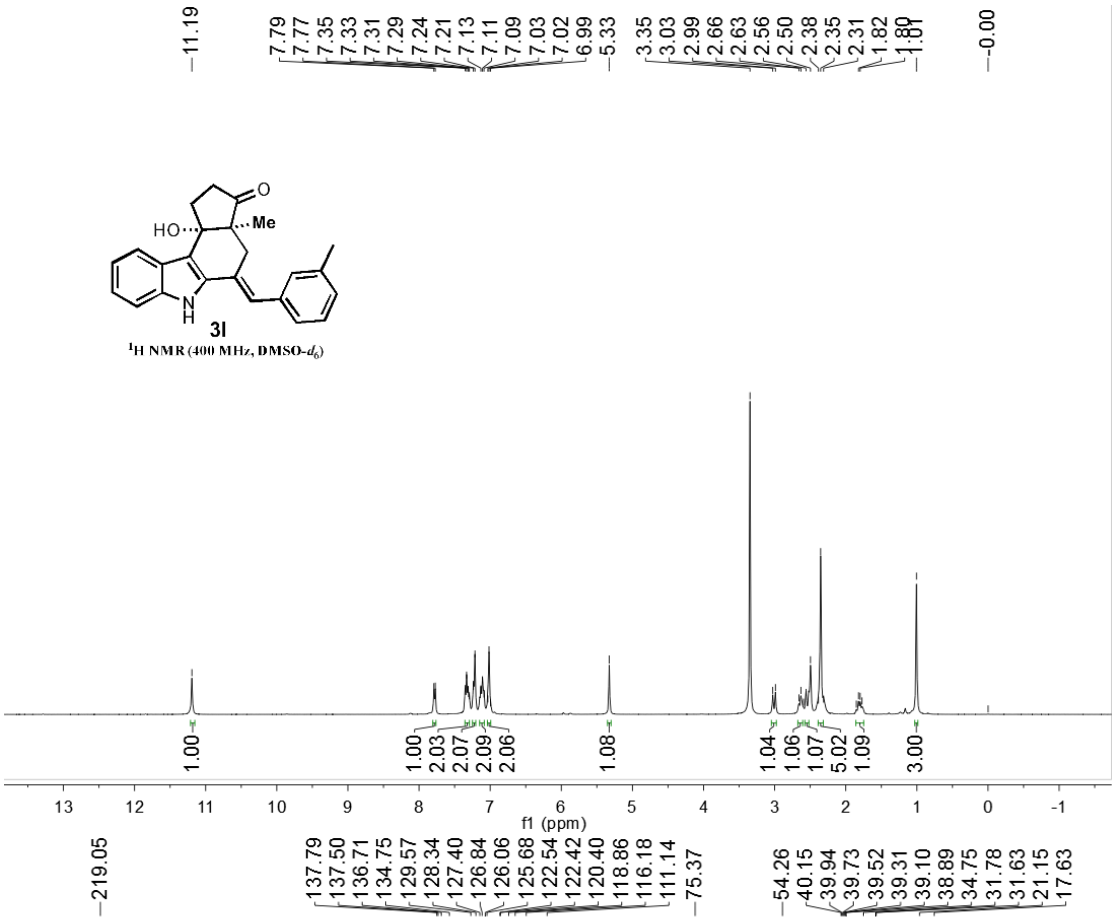
3j

^{13}C NMR (100 MHz, DMSO-d_6)



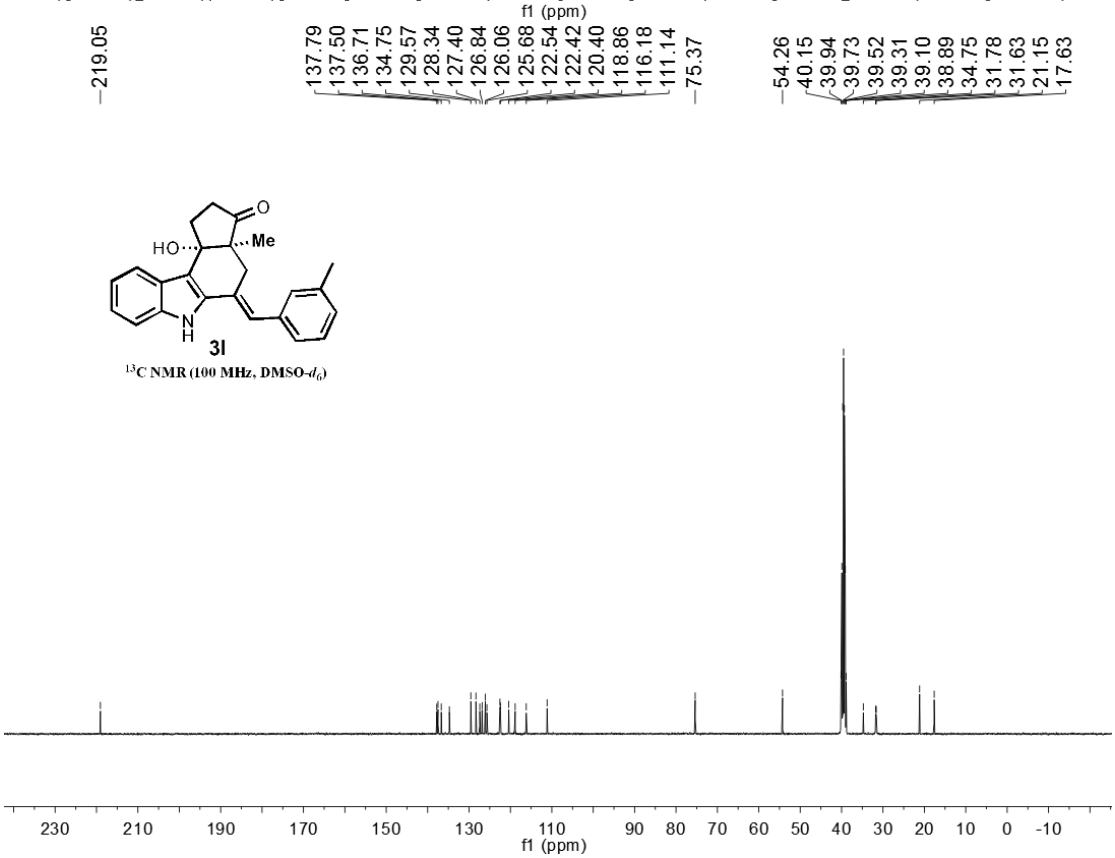

11.24
7.80
7.78
7.37
7.35
7.27
7.25
7.24
7.22
7.20
7.16
7.14
7.12
7.07
7.04
7.02
7.00
5.31
3.35
2.81
2.77
2.65
2.63
2.50
2.42
2.39
2.36
2.29
1.85
1.82
0.97
0.00
HO
Me
O
N
H
3k
1H NMR (400 MHz, DMSO-d6)
1.07
1.07
2.04
3.06
1.09
1.08
1.03
1.09
1.08
1.09
3.00
3.07
1.13
3.00
f1 (ppm)


219.10
137.69
136.48
135.77
134.54
129.89
128.90
126.98
126.86
125.67
125.54
122.41
121.57
120.43
118.86
116.17
111.12
75.59
54.34
39.94
39.73
39.52
39.31
39.10
17.43
HO
Me
O
N
H
3k
13C NMR (100 MHz, DMSO-d6)
f1 (ppm)



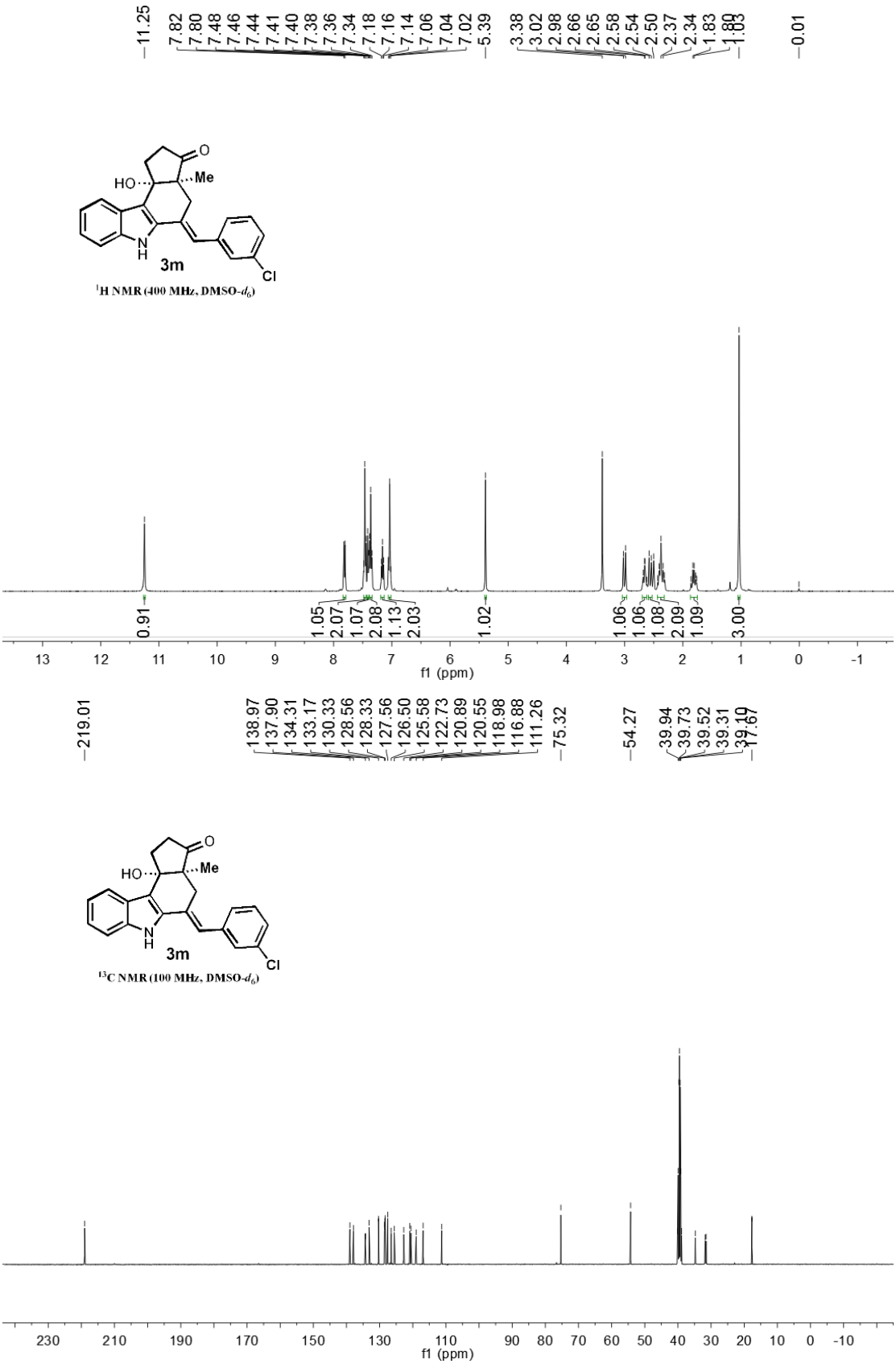
3l

^{1}H NMR (400 MHz, DMSO-d_6)



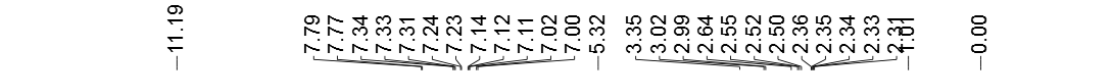
3l

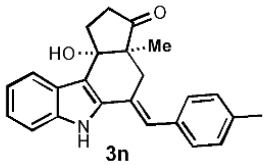
^{13}C NMR (100 MHz, DMSO-d_6)



^{1}H NMR (400 MHz, DMSO-d_6)

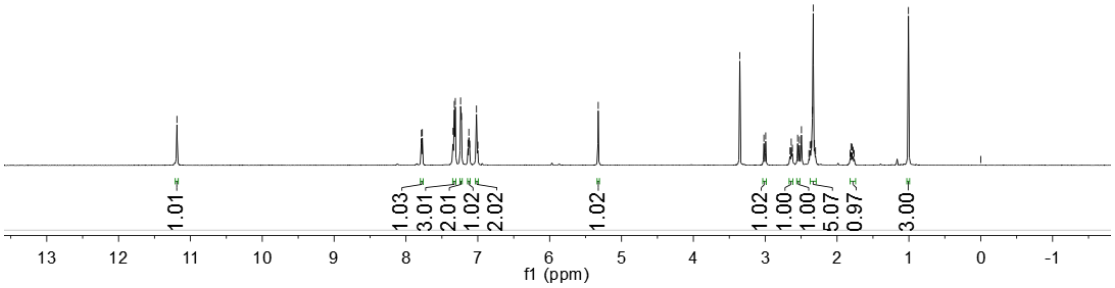
^{13}C NMR (100 MHz, DMSO-d_6)

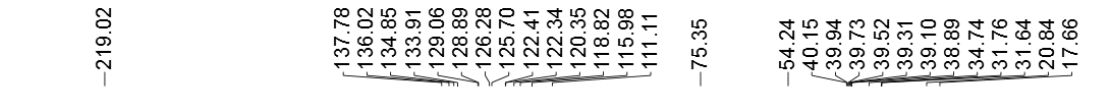


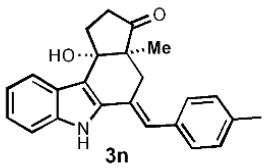


3n

^{1}H NMR (600 MHz, DMSO-d_6)

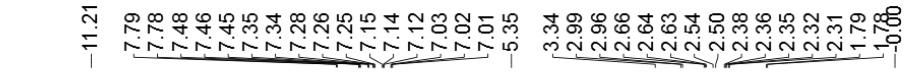


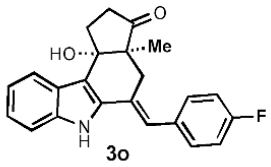




3n

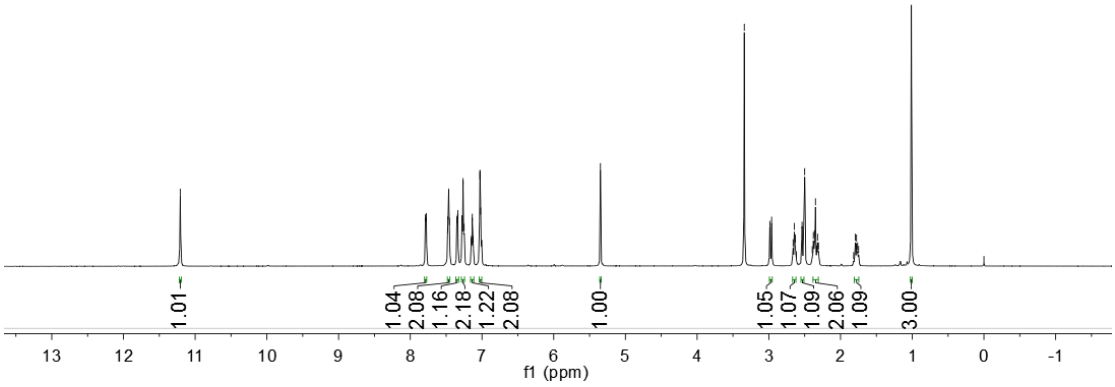
^{13}C NMR (100 MHz, DMSO-d_6)

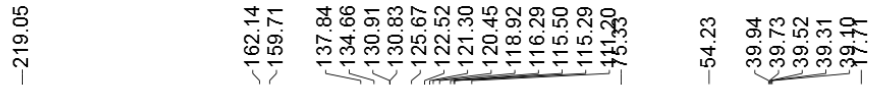


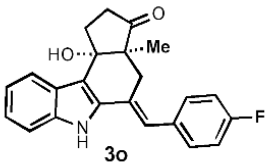


3o

^{1}H NMR (600 MHz, DMSO-d_6)

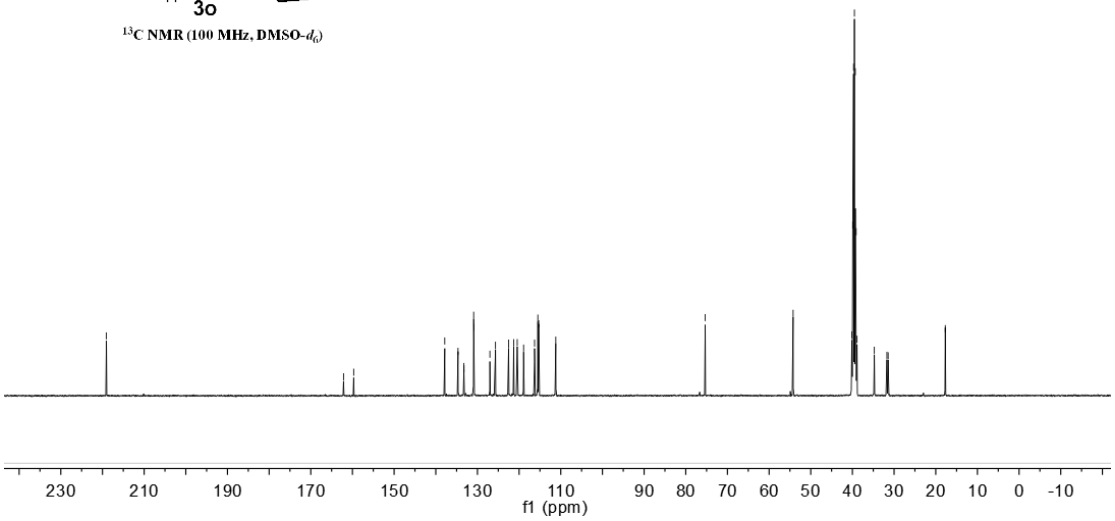


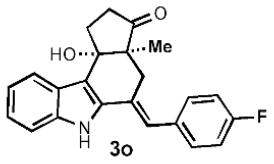




3o

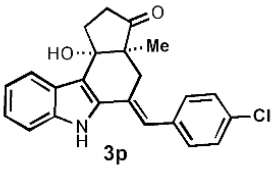
^{13}C NMR (100 MHz, DMSO-d_6)





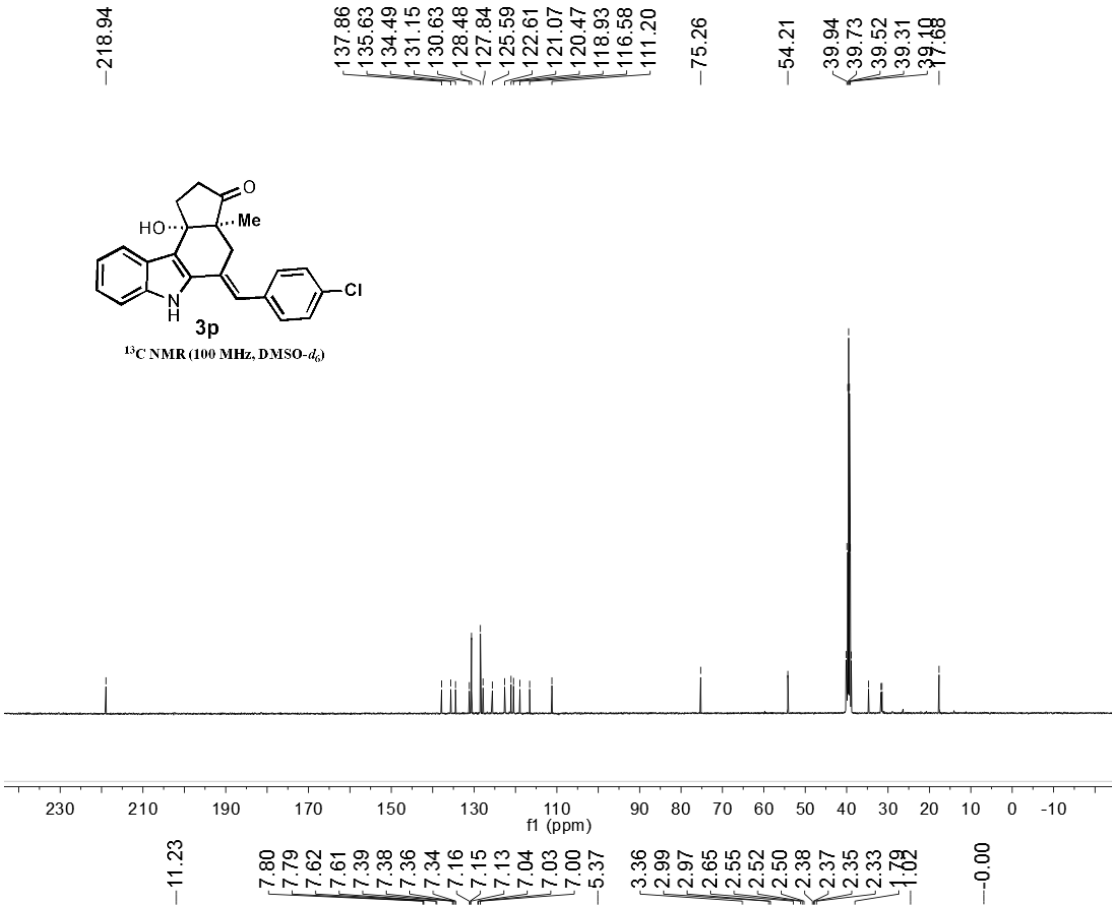
3o

^{19}F NMR (376 MHz, DMSO-d_6)



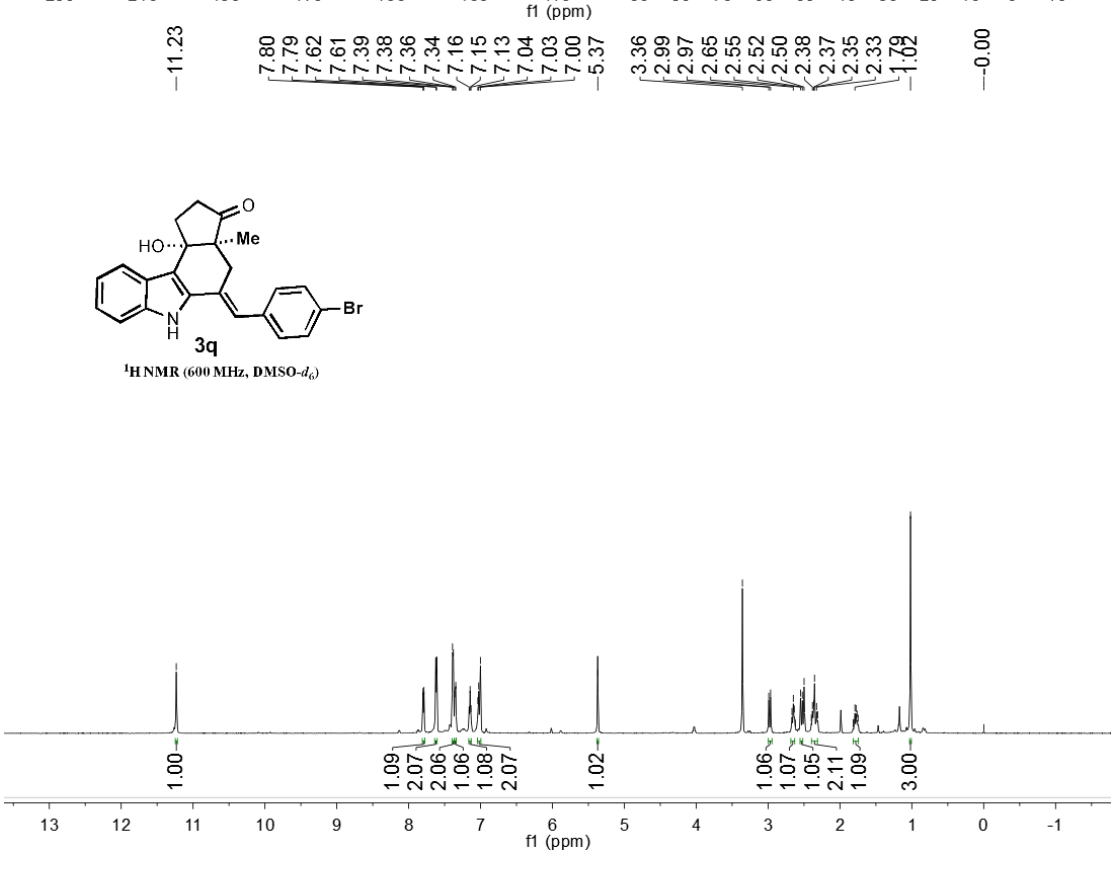
3p

^{1}H NMR (400 MHz, DMSO-d_6)



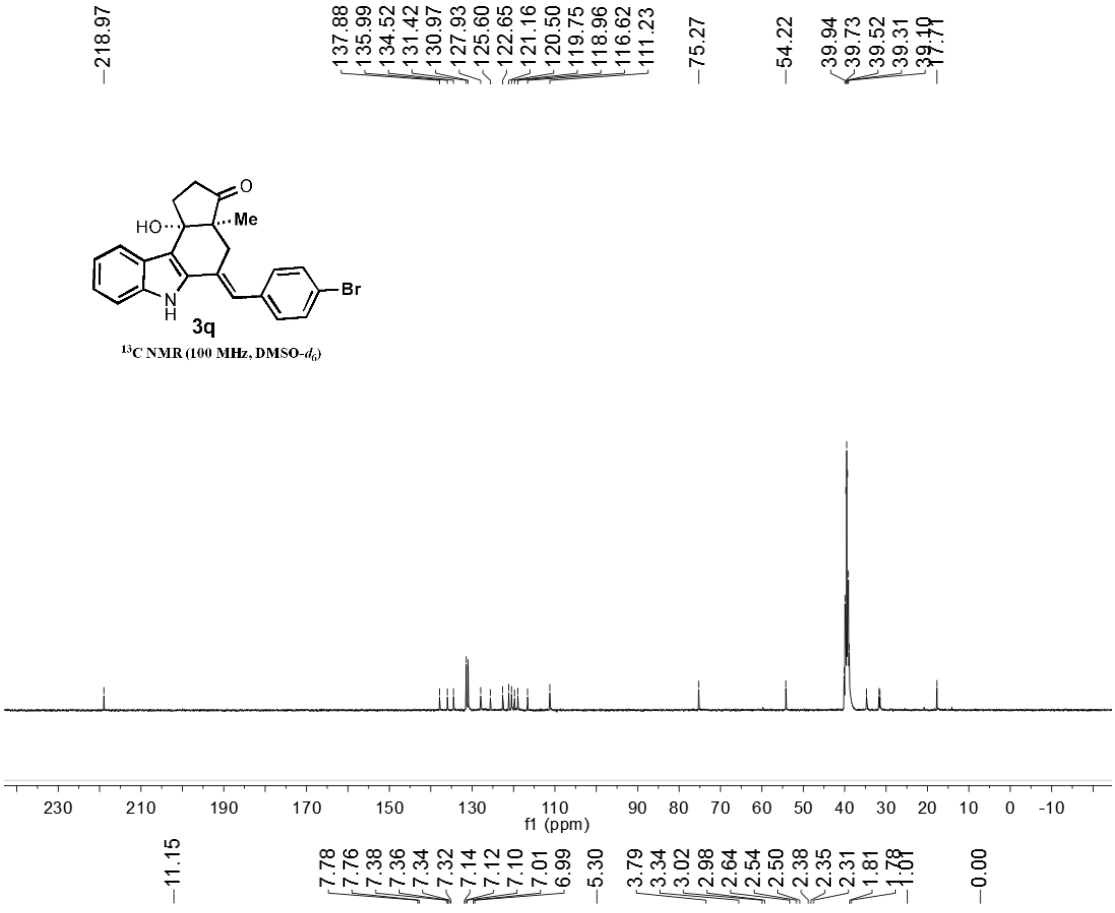
3p

^{13}C NMR (100 MHz, DMSO-d_6)

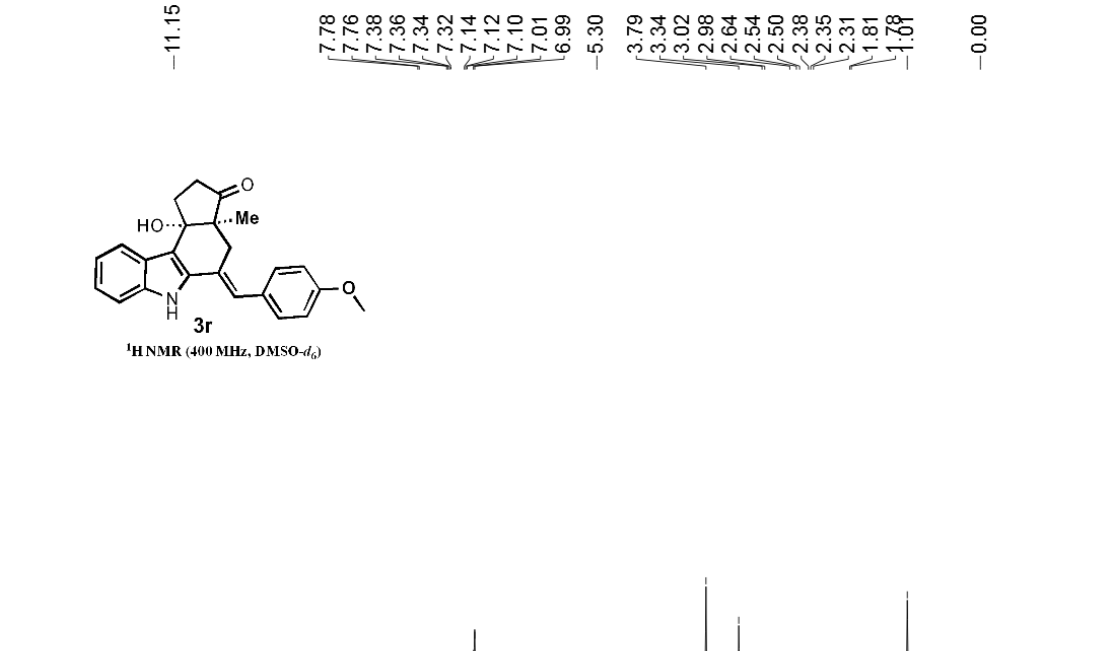


3q

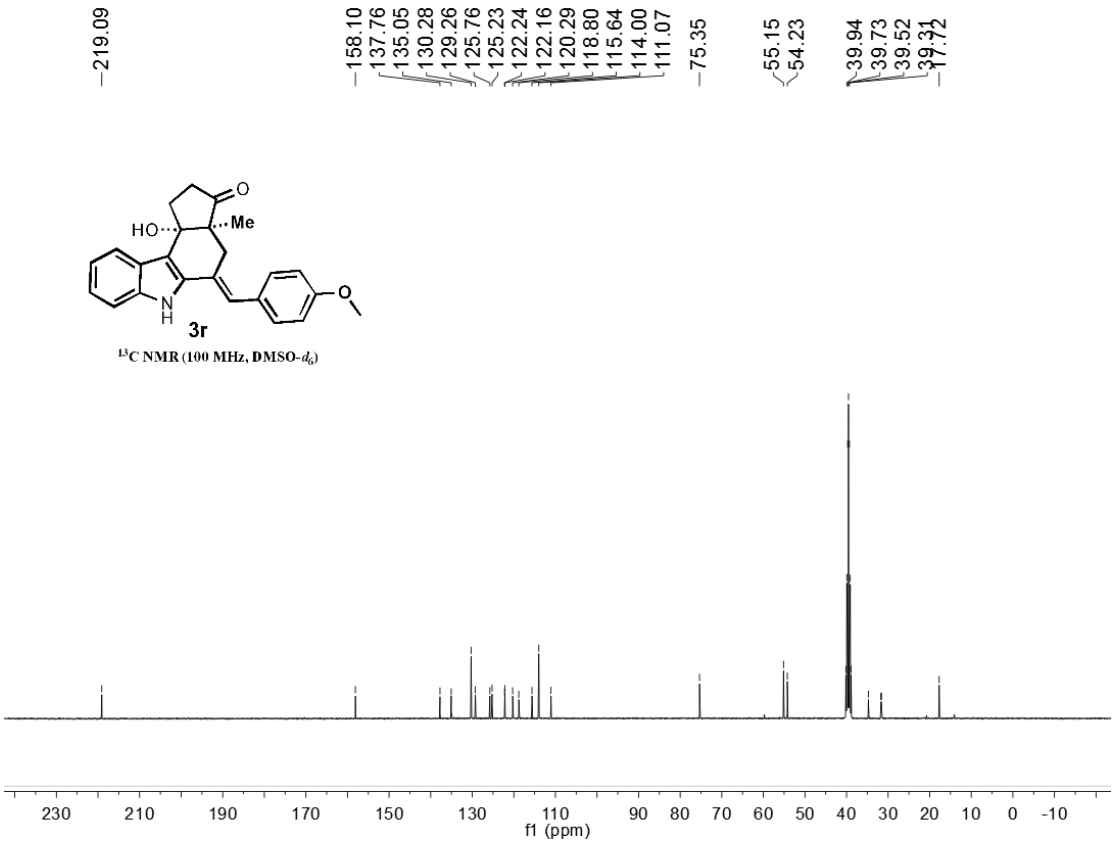
^{1}H NMR (600 MHz, DMSO-d_6)



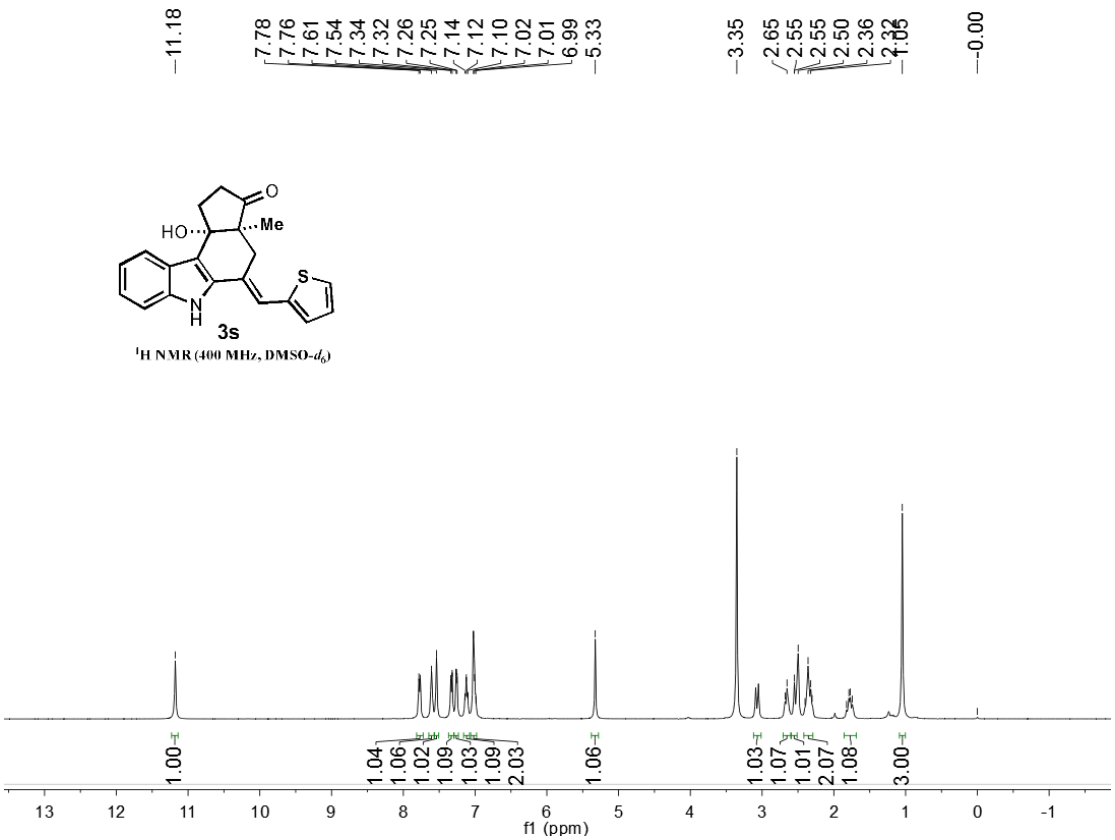
^{13}C NMR (100 MHz, DMSO-d_6)



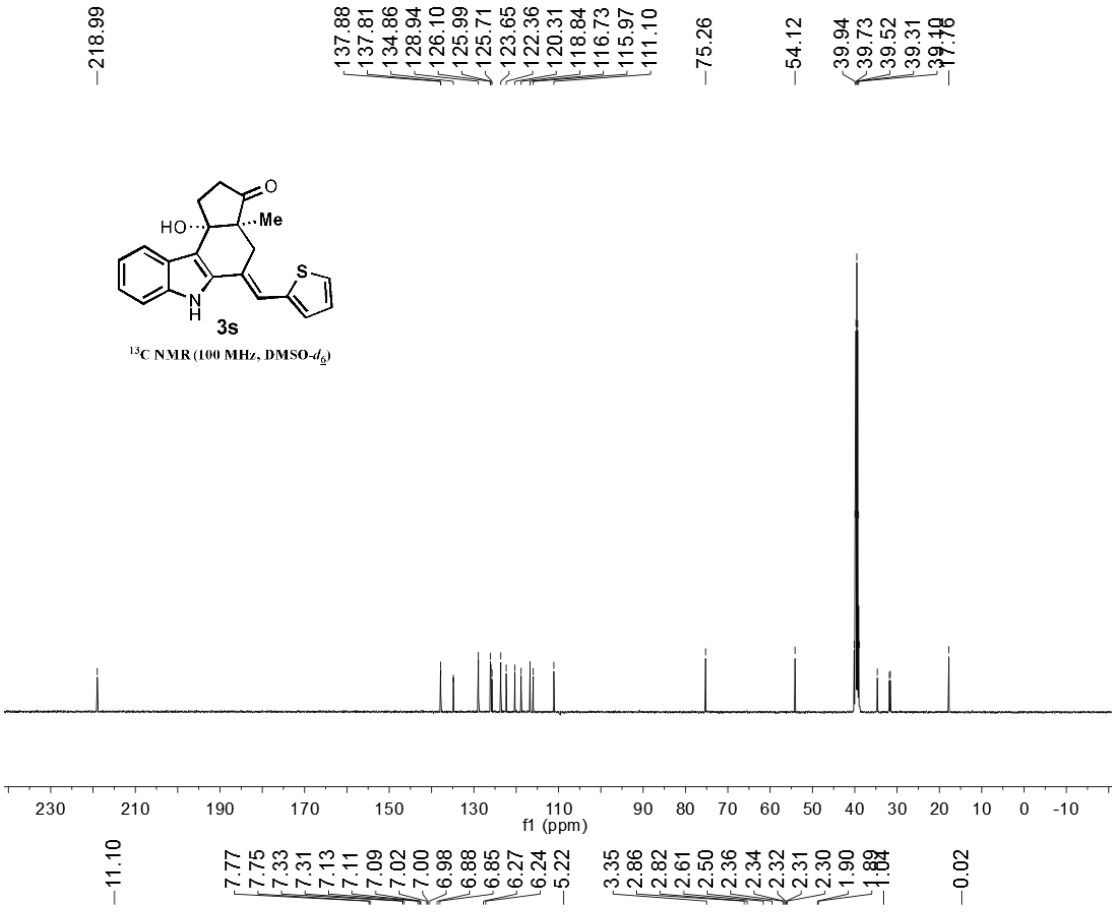
^{1}H NMR (400 MHz, DMSO-d_6)



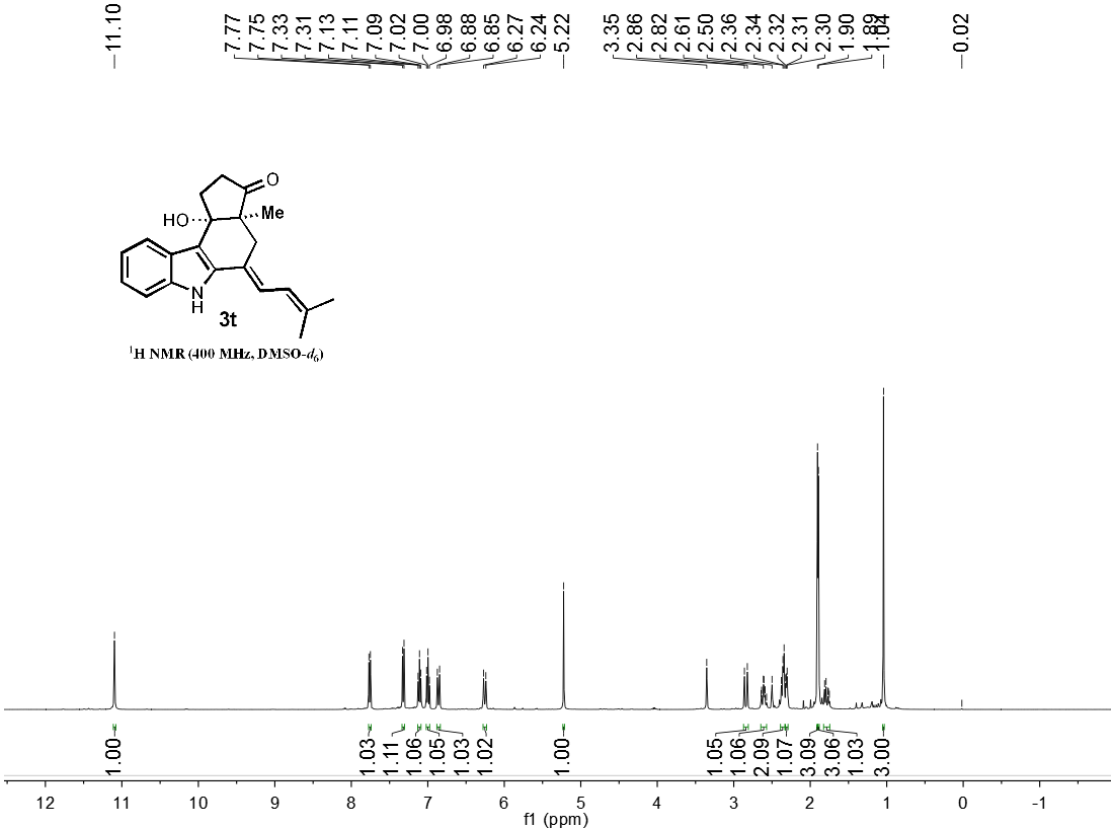
^{13}C NMR (100 MHz, DMSO-d_6)



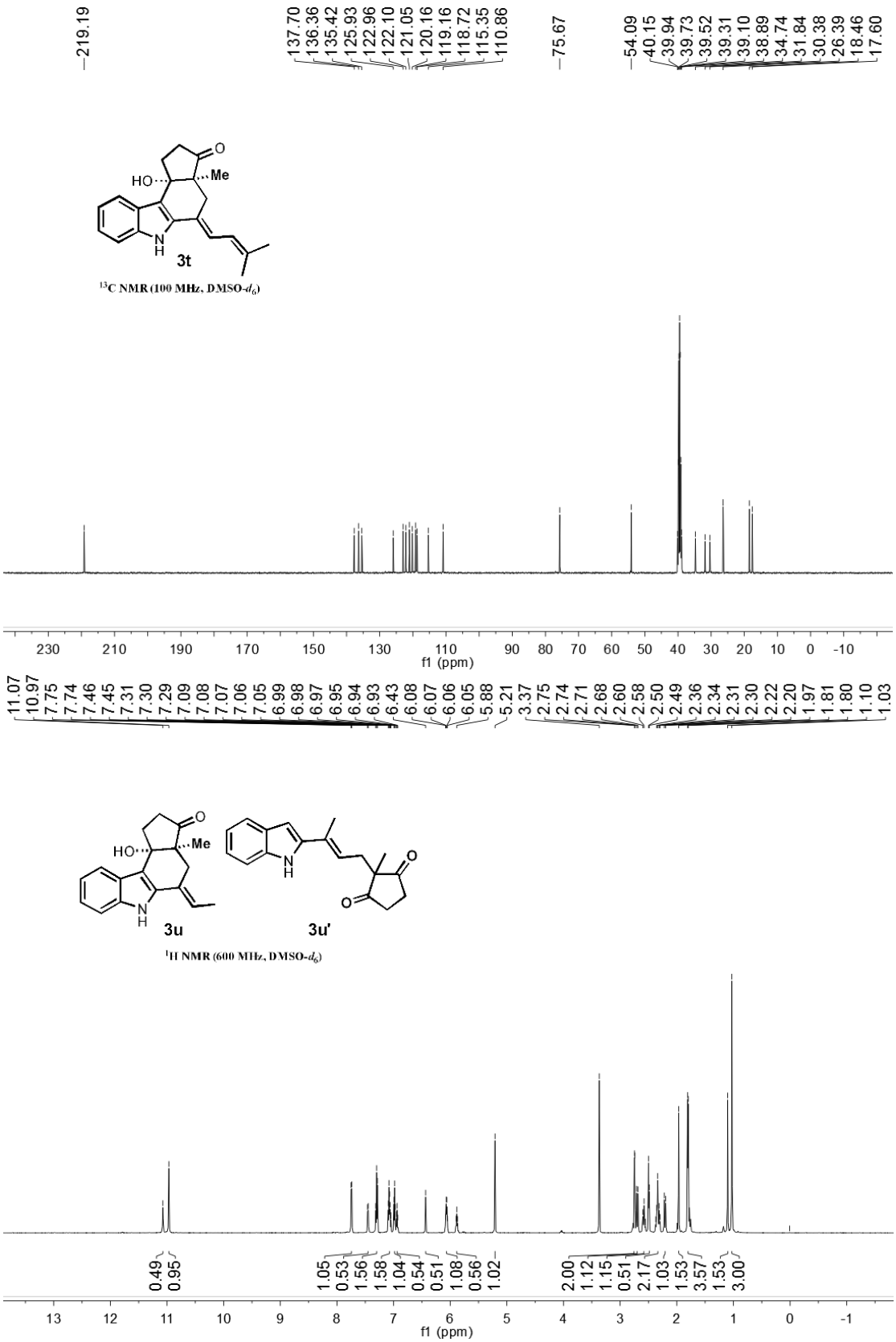
^{1}H NMR (400 MHz, DMSO-d_6)

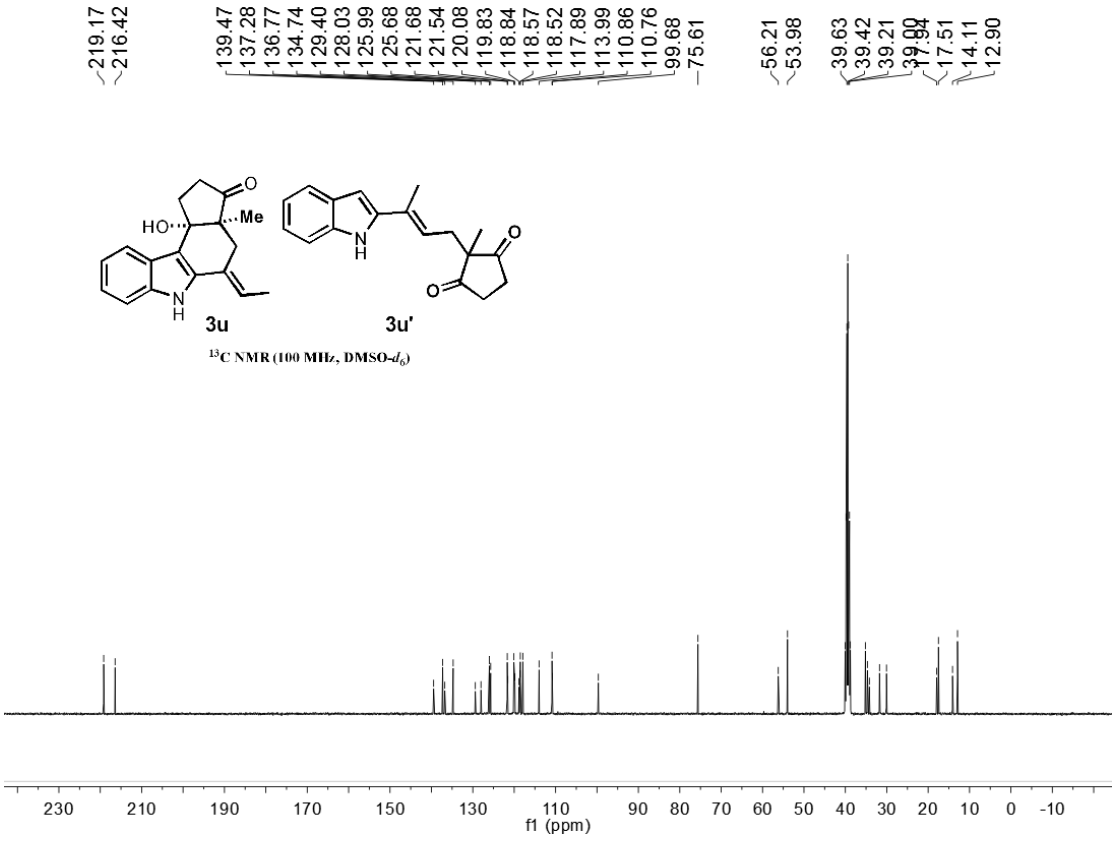


^{13}C NMR (100 MHz, DMSO-d_6)

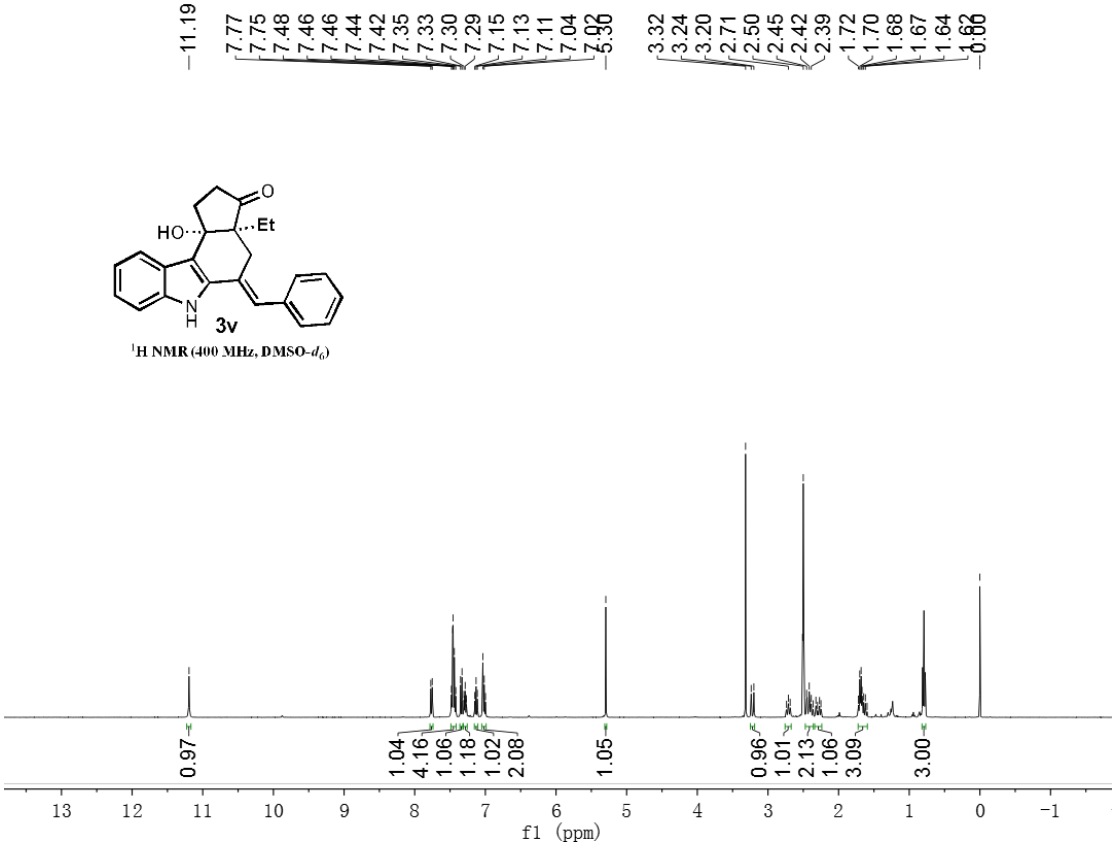


^{1}H NMR (400 MHz, DMSO-d_6)

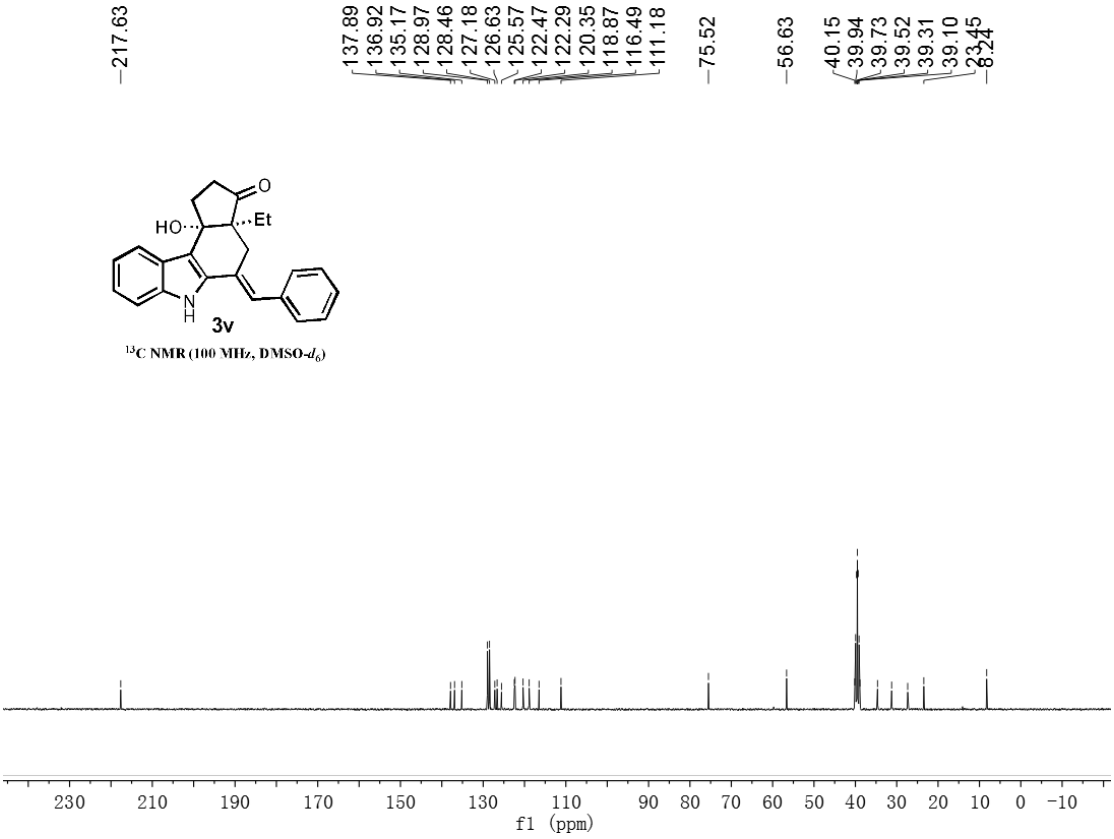

219.19
137.70
136.36
135.42
125.93
122.96
122.10
121.05
120.16
119.16
118.72
115.35
110.86
75.67
54.09
40.15
39.94
39.73
39.52
39.31
39.10
38.89
34.74
31.84
30.38
26.39
18.46
17.60
HO
Me
O
N
H
3t
13C NMR (100 MHz, DMSO-d6)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
11.07
10.97
7.75
7.74
7.46
7.45
7.31
7.30
7.29
7.09
7.08
7.07
7.06
7.05
6.99
6.98
6.97
6.95
6.94
6.93
6.43
6.08
6.07
6.06
6.05
5.88
5.21
3.37
2.75
2.74
2.71
2.68
2.60
2.58
2.50
2.49
2.36
2.34
2.31
2.30
2.22
2.20
1.97
1.81
1.80
1.10
1.03
HO
Me
O
N
H
3u
O
O
N
H
3u'
1H NMR (600 MHz, DMSO-d6)
0.49
0.95
1.05
0.53
1.56
1.58
1.04
0.54
0.51
1.08
0.56
1.02
2.00
1.12
1.15
0.51
2.17
1.03
1.53
3.57
1.53
3.00
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

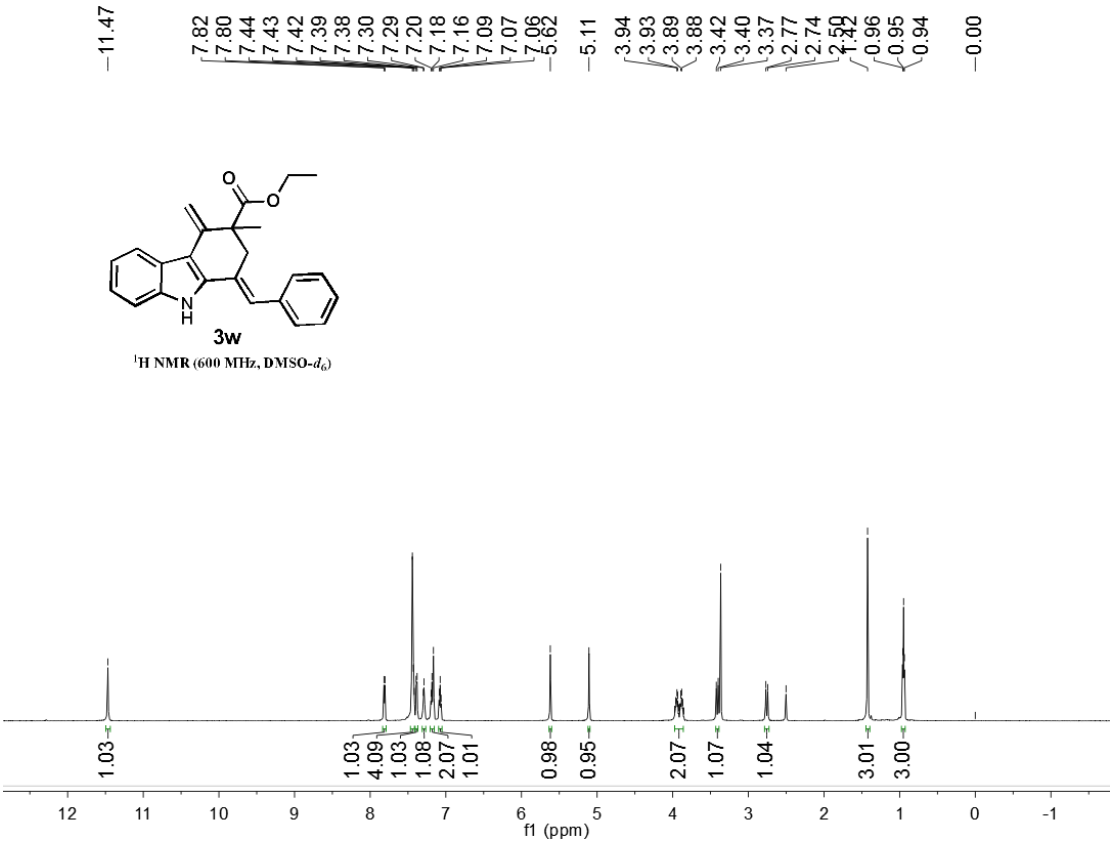


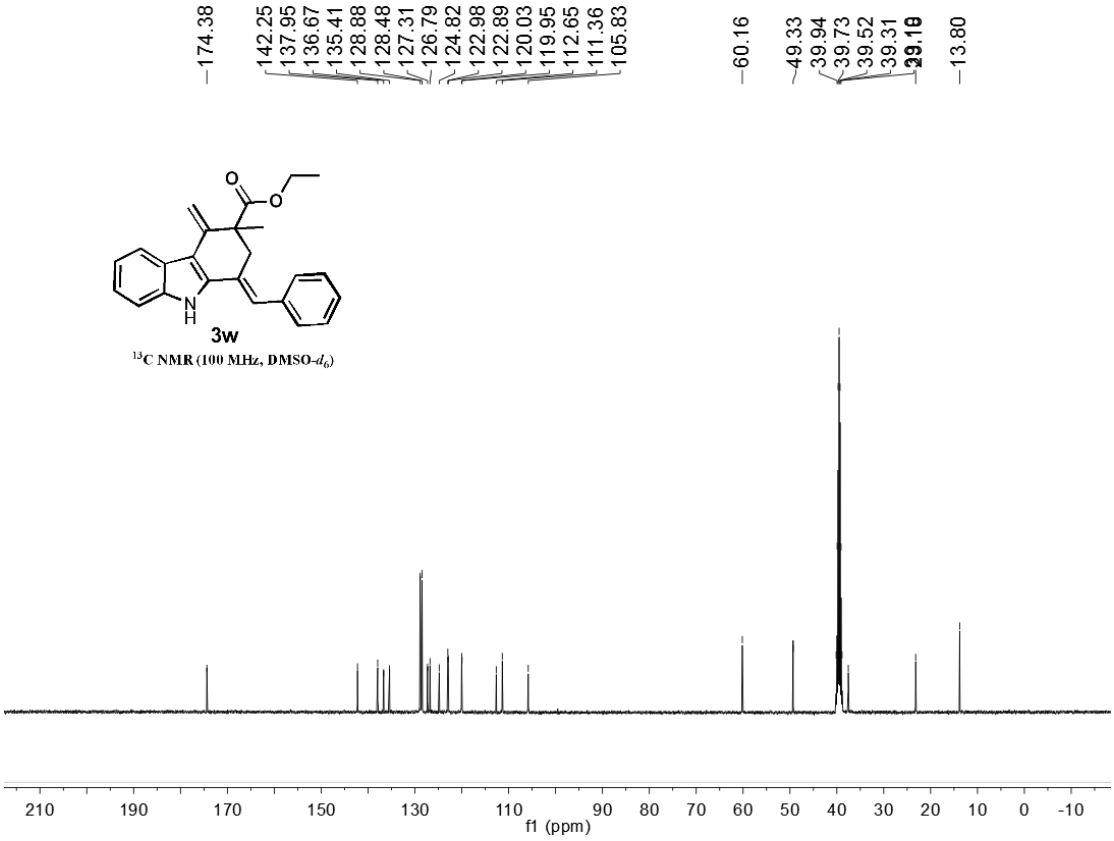
^{13}C NMR (100 MHz, DMSO-d_6)



^{1}H NMR (400 MHz, DMSO-d_6)

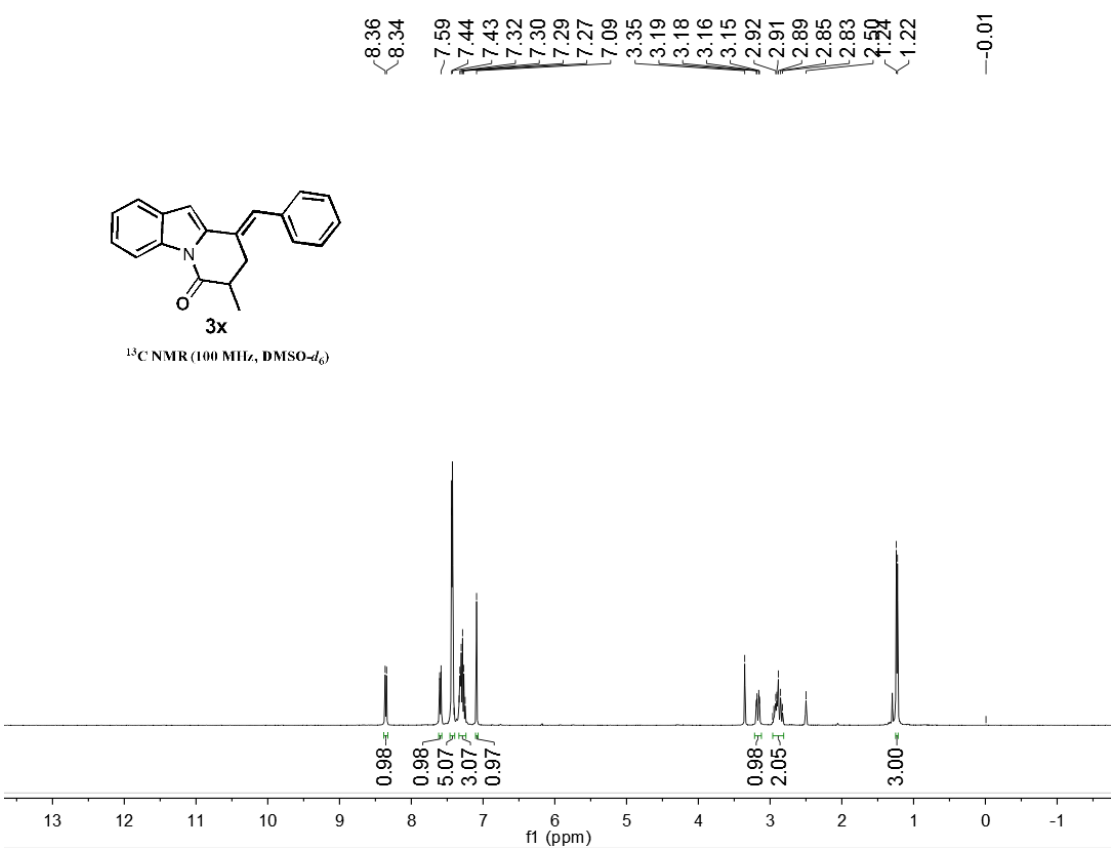

217.63
137.89
136.92
135.17
128.97
128.46
127.18
126.63
125.57
122.47
122.29
120.35
118.87
116.49
111.18
75.52
56.63
40.15
39.94
39.73
39.52
39.31
39.10
23.45
8.24
HO
Et
O
N
H
3v
13C NMR (100 MHz, DMSO-d6)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


11.47
7.82
7.80
7.44
7.43
7.42
7.39
7.38
7.30
7.29
7.20
7.18
7.16
7.09
7.07
7.06
5.62
5.11
3.94
3.93
3.89
3.88
3.42
3.40
3.37
2.77
2.74
2.50
1.42
0.96
0.95
0.94
0.00
O
O
N
H
3w
1H NMR (600 MHz, DMSO-d6)
1.03
1.03
4.09
1.03
1.08
2.07
1.01
0.98
0.95
2.07
1.07
1.04
3.01
3.00
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)



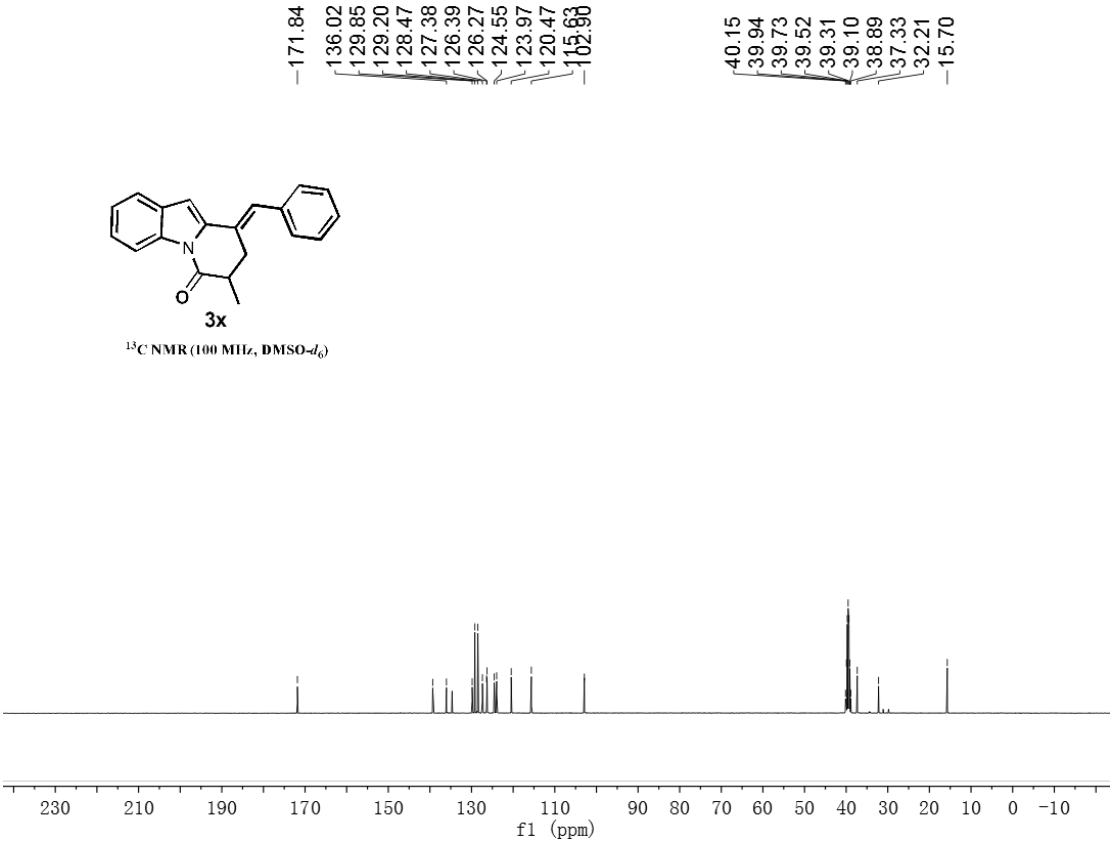
3w

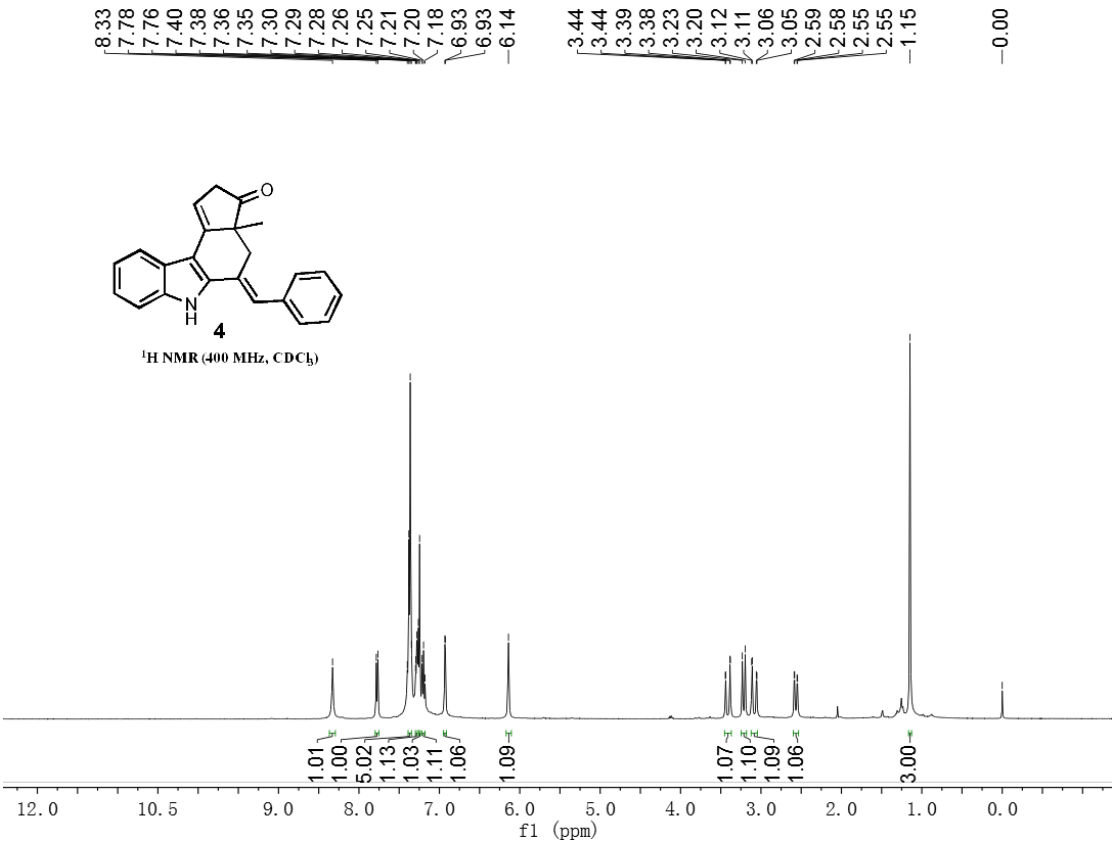
^{13}C NMR (100 MHz, DMSO-d_6)

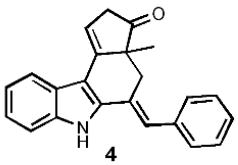


3x

^{13}C NMR (100 MHz, DMSO-d_6)

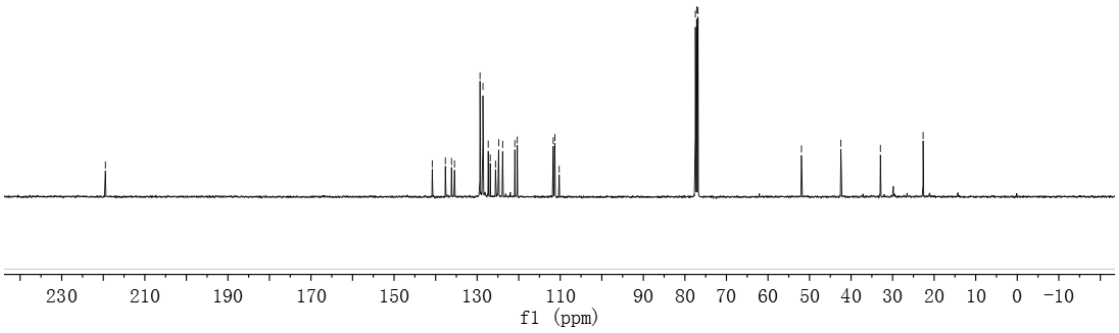

171.84
136.02
129.85
129.20
128.47
127.38
126.39
126.27
124.55
123.97
120.47
115.63
102.90
40.15
39.94
39.73
39.52
39.31
39.10
38.89
37.33
32.21
15.70
O
N
3x
13C NMR (100 MHz, DMSO-d6)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

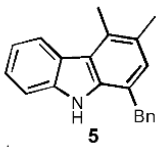

8.33
7.78
7.76
7.40
7.38
7.36
7.35
7.30
7.29
7.28
7.26
7.25
7.21
7.20
7.18
6.93
6.93
6.14
3.44
3.44
3.39
3.38
3.23
3.20
3.12
3.11
3.06
3.05
2.59
2.58
2.55
2.55
1.15
0.00
O
N
H
4
1H NMR (400 MHz, CDCl3)
1.01
1.00
5.02
1.13
1.03
1.11
1.06
1.09
1.07
1.10
1.09
1.06
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)



4

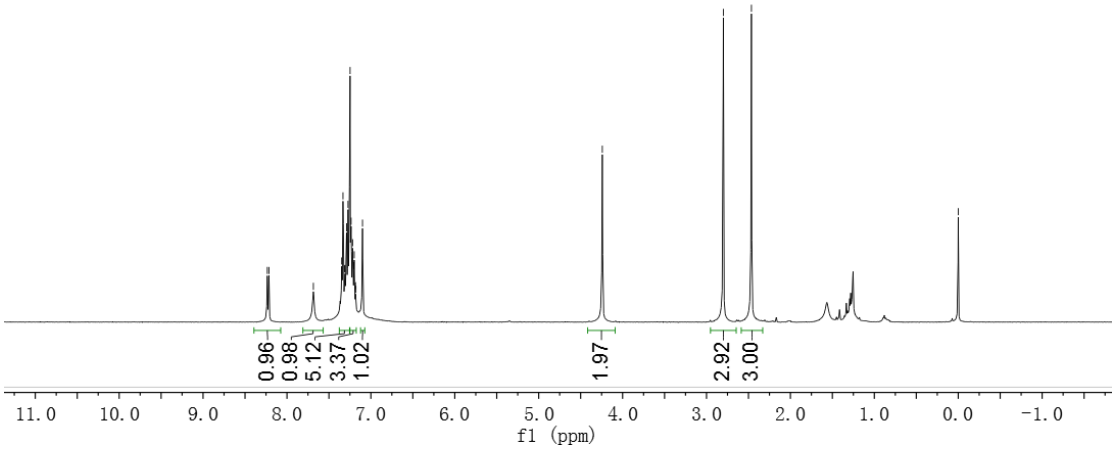
^{13}C NMR (100 MHz, $CDCl_3$)

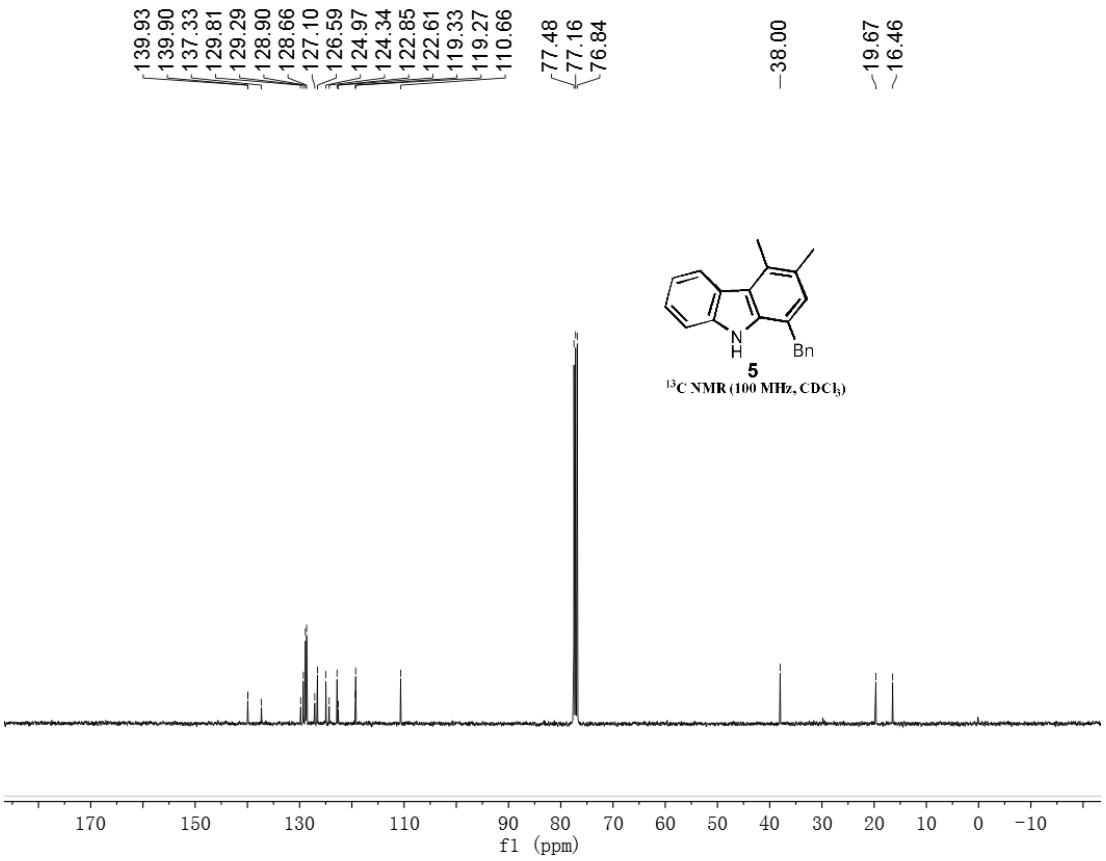




5

^{1}H NMR (400 MHz, $CDCl_3$)




139.93
139.90
137.33
129.81
129.29
128.90
128.66
127.10
126.59
124.97
124.34
122.85
122.61
119.33
119.27
110.66
77.48
77.16
76.84
38.00
19.67
16.46
N
H
Bn
5
13C NMR (100 MHz, CDCl3)
170
150
130
110
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)