Electronic Supplementary Material (ESI) for ChemComm.

Zinc-catalyzed C–H alkenylation of quinoline *N*-oxides with ynones: A new strategy toward quinoline-enol scaffolds

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Supporting Information

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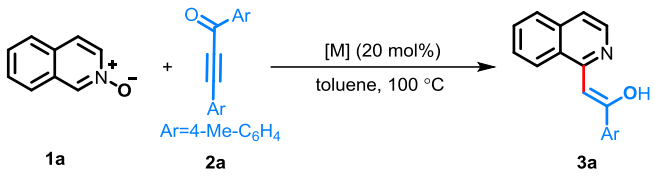
A. General information

All reagents were used as received unless otherwise noted. Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (TLC Silica Gel 60 F_{254}); visualization of the developed chromatogram was performed by fluorescence. Flash Chromatography was performed with silica gel (300-400 mesh). Proton-1 nuclear magnetic resonance (^{1}H NMR) data were acquired at 400 MHz on a Bruker Ascend 400 (400 MHz) spectrometer, and chemical shifts are reported in delta (δ) units, in parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, coupling constants *J* are quoted in Hz. Carbon-13 nuclear magnetic resonance (^{13}C NMR) data were acquired at 100 MHz on a Bruker Ascend 400 spectrometer, chemical shifts are reported in ppm relative to the center line of a triplet at 77.0 ppm for $CDCl_3$. Fluorine-19 nuclear magnetic resonance (^{19}F NMR) data were acquired at 376 MHz on a Bruker Ascend 400 spectrometer. Infrared spectra (IR) data were recorded on a TENSOR 27 FT-IR spectrometer and recorded in wave numbers (cm^{-1}). High resolution mass spectra were acquired on a Bruker Daltonics MicroTof-Q II mass spectrometer. **1a**[1], **1b**[2], **1c**[3], **1d**[4], **1e-1g**[5], **1h-1i**[6], **1j**[7], **1k**[6], **1l**[8], **1m-1n**[6], **1p**[6], **1q**[9], **2a**[11], **2b**[10], **2c-2g**[11], **2i**[11], **2j**[12], **2k-2m**[13], **2n**[14], and **2o**[15] were prepared according to literature methods.

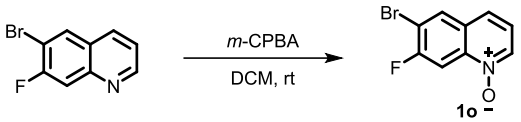
B. Complementary reaction optimization



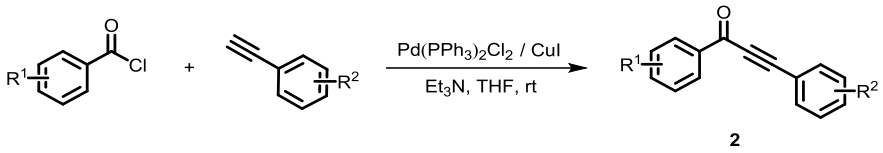
entry	catalyst	solvent	temp. (℃)	yield (%)[a]
1	$Co(OAc)_2$	toluene	100	8
2	$FeCl_3$	toluene	100	10
3	$Mn(OAc)_2$	toluene	100	12
4	$(C_6F_5)_3B$	toluene	100	35
5	AgOTf	toluene	100	26
6	NaOAc	toluene	100	16
7	$Sc(OTf)_3$	toluene	100	40
8	$In(OTf)_2$	toluene	100	38
9	$Zn(NO_3)_2$	toluene	100	7
10	$ZnSO_4$	toluene	100	43
11	$Zn(OAc)_2$	toluene	100	49

Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol) and catalyst (0.04 mmol) in toluene (2.0 mL) at 100 ℃ for 12 h. [a]Isolated yields.

C. Preparation of substrates

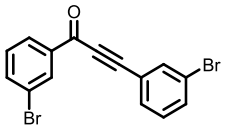


6-Bromo-7-fluoroquinoline (0.68 g, 3.0 mmol) was dissolved in DCM (15.0 mL). *m*-CPBA (1.22 g, 85%) was gradually added at 0 ℃. After reacting for five minutes, the reaction mixture was allowed to stir at room temperature overnight. When the starting material was completely converted, the reaction mixture was diluted with 60.0 mL aqueous saturated $NaHCO_3$ and extracted with DCM (20.0 mL × 3). The combined organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure. Then the residue was separated and purified on a silica gel column using DCM/MeOH eluent to obtain the product **1o**. White solid (0.47 g, 65% yield). DCM/MeOH = 30:1, R_f = 0.31. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, *J* = 6.1 Hz, 1H), 8.52 (d, *J* = 9.3 Hz, 1H), 8.18 (d, *J* = 6.7 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.34 (dd, *J* = 8.5, 6.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7 (d, *J* = 252.9 Hz), 141.6 (d, *J* = 9.4 Hz), 136.2, 133.0, 128.2, 124.2, 121.5 (d, *J* = 2.4 Hz), 113.4 (d, *J* = 24.5 Hz), 106.4 (d, *J* = 27.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -100.7. IR (KBr): 2985, 2377, 1639, 1496, 1397, 1261, 739 cm^{-1}. HRMS (ESI) m/z Calcd for C_9H_6BrFNO $[M+H]^+$ 241.9617, found 241.9619.



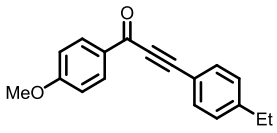
2

A round bottom flask equipped with stir bar was charged with $Pd(PPh_3)_2Cl_2$ (70.2 mg, 0.1 mmol), CuI (38.1 mg, 0.2 mmol), terminal alkyne (5.0 mmol) and anhydrous THF (15.0 mL). After stirring for 1 min under Ar atmosphere, Et_3N (1.0 mL, 7.5 mmol) and acid chloride (6.0 mmol) were added. The mixture was stirred at room temperature and monitored by TLC. When the reaction was complete, the reaction mixture was diluted with 90.0 mL H_2O and extracted with EtOAc (30.0 mL × 3). The combined organic layer was washed with brine and dried with $MgSO_4$. Then concentration in vacuo, the crude product was purified by silica gel column chromatography to obtain the corresponding ynones **2**.



1,3-Bis(3-bromophenyl)prop-2-yn-1-one (2h)

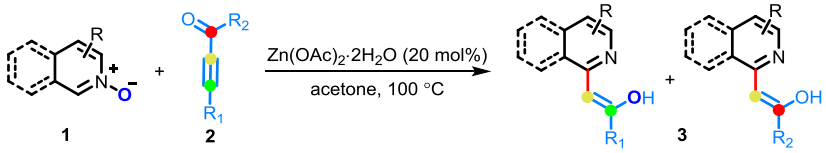
White solid (1.46 g, 80% yield). PE/EA = 40:1, R_f = 0.32. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 7.87 (s, 1H), 7.84–7.79 (m, 1H), 7.71–7.64 (m, 2H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.1, 138.4, 137.1, 135.6, 134.2, 132.3, 131.6, 130.3, 130.2, 128.2, 123.0, 122.6, 121.8, 91.6, 87.0. IR (KBr): 3218, 2985, 2208, 1636, 1398, 1264, 736 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{15}H_8Br_2OK$ $[M+K]^+$ 400.8579, found 400.8562.



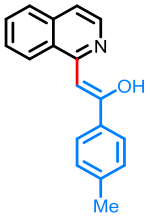
3-(4-Ethylphenyl)-1-(4-methoxyphenyl)prop-2-yn-1-one (2p)

Pale yellow solid (0.99 g, 75% yield). PE/EA = 30:1, R_f = 0.35. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26–8.20 (m, 2H), 7.69–7.59 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.05–7.01 (m, 2H), 3.94 (s, 3H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.7, 164.4, 147.5, 133.1, 131.9, 130.5, 128.2, 117.5, 113.9, 93.0, 86.8, 55.6, 29.0, 15.1. IR (KBr): 2966, 2931, 2204, 1632, 1259, 1160, 837 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{18}H_{16}O_2K$ $[M+K]^+$ 303.0787, found 303.0781.

D. Reaction results

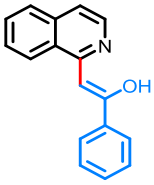


A pressure tube was charged with (iso)quinoline *N*-oxide **1** (0.2 mmol), ynone **2** (0.24 mmol) $Zn(OAc)_2$ $2H_2O$ (8.8 mg, 0.04 mmol), and acetone (2.0 mL). The reaction mixture was stirred at 100 ℃ for 12 h under air in an oil bath. After cooling to room temperature, the mixture was filtered through a short Celite pad and all volatiles were removed under reduced pressure. The residue was purified by silica gel chromatography using PE/EA eluent to afford the product **3**.



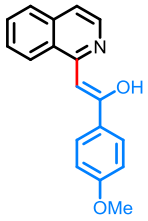
(*Z*)-2-(Isoquinolin-1-yl)-1-(*p*-tolyl)ethen-1-ol (3a)

Yellow solid (33.9 mg, 65% yield). PE/EA = 5:1, R_f = 0.25. ^{1}H NMR (400 MHz, DMSO): δ 15.92 (s, 1H), δ 8.60–8.53 (m, 1H), 8.03 (d, *J* = 7.8 Hz, 2H), 7.76 (d, *J* = 7.9 Hz, 3H), 7.63 (s, 1H), 7.31 (d, *J* = 7.7 Hz, 2H), 7.02–6.93 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, DMSO): δ 182.9, 154.0, 140.6, 137.7, 135.7, 132.6, 129.7, 129.3, 128.0, 127.5, 127.3, 125.5, 124.4, 111.0, 84.3, 21.5. IR (KBr): 3025, 2980, 1586, 1544, 1345, 1257, 1206, 794, 752 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{18}H_{15}NOK$ $[M+K]^+$ 300.0791, found 300.0785.



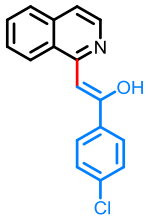
(*Z*)-2-(Isoquinolin-1-yl)-1-phenylethen-1-ol (3b)

Yellow solid (36.1 mg, 73% yield). PE/EA = 10:1, R_f = 0.31. ^{1}H NMR (400 MHz, $CDCl_3$): δ 16.27 (s, 1H), 8.26 (d, *J* = 8.3 Hz, 1H), 8.12–8.03 (m, 2H), 7.75–7.67 (m, 1H), 7.66–7.55 (m, 2H), 7.54–7.48 (m, 3H), 7.44 (d, *J* = 6.7 Hz, 1H), 6.86 (d, *J* = 6.7 Hz, 1H), 6.82 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.2, 154.5, 140.6, 135.6, 131.8, 130.3, 128.3, 128.2, 127.4, 127.1, 126.8, 124.6, 124.5, 111.2, 84.9. IR (KBr): 3062, 1634, 1544, 1259, 1208, 737 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{17}H_{13}NONa$ $[M+Na]^+$ 270.0895, found 270.0896.



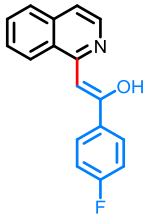
(*Z*)-2-(Isoquinolin-1-yl)-1-(4-methoxyphenyl)ethen-1-ol (3c)

Yellow solid (37.1 mg, 67% yield). PE/EA = 5:1, R_f = 0.24. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.3 Hz, 1H), 8.05 (d, *J* = 8.7 Hz, 2H), 7.73–7.67 (m, 1H), 7.64–7.55 (m, 2H), 7.41 (d, *J* = 6.8 Hz, 1H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.85–6.74 (m, 2H), 3.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.0, 161.6, 154.2, 135.6, 133.3, 131.7, 128.5, 128.1, 127.3, 127.1, 124.7, 124.4, 113.6, 110.6, 84.2, 55.4. IR (KBr): 2974, 2893, 1628, 1588, 1345, 1248, 1073, 755 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{18}H_{15}NO_2Na$ $[M+Na]^+$ 300.1000, found 300.1016.



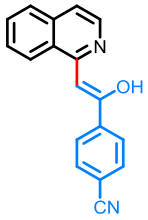
(*Z*)-1-(4-Chlorophenyl)-2-(isoquinolin-1-yl)ethen-1-ol (3d)

Yellow solid (35.5 mg, 63% yield). PE/EA = 10:1, R_f = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$): δ 16.25 (s, 1H), 8.23 (d, *J* = 8.3 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 2H), 7.75–7.68 (m, 1H), 7.65–7.54 (m, 2H), 7.49–7.40 (m, 3H), 6.87 (d, *J* = 6.7 Hz, 1H), 6.74 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.7, 154.6, 139.0, 136.3, 135.6, 132.0, 128.5, 128.2, 128.1, 127.5, 127.2, 124.5, 124.5, 111.5, 84.7. IR (KBr): 3060, 1608, 1543, 1345, 1213, 785, 743 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{17}H_{12}ClNOK$ $[M+K]^+$ 320.0244, found 320.0245.



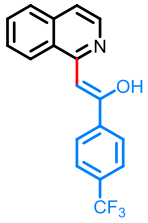
(*Z*)-1-(4-Fluorophenyl)-2-(isoquinolin-1-yl)ethen-1-ol (3e)

Yellow solid (32.9 mg, 62% yield). PE/EA = 5:1, R_f = 0.31. ^{1}H NMR (400 MHz, DMSO): δ 15.86 (s, 1H), 8.60 (d, *J* = 8.3 Hz, 1H), 8.22–8.16 (m, 2H), 7.81–7.74 (m, 3H), 7.66–7.60 (m, 1H), 7.31 (t, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 6.7 Hz, 1H), 6.98 (s, 1H). ^{13}C NMR (100 MHz, DMSO): δ 181.9, 164.0 (d, *J* = 246.2 Hz), 154.1, 137.0 (d, *J* = 2.6 Hz), 135.7, 132.7, 129.8, 129.7, 129.6, 128.0, 127.5, 125.7, 124.3, 115.5 (d, *J* = 21.3 Hz), 111.3, 84.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ -110.9. IR (KBr): 3057, 1637, 1491, 1264, 1070, 740 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{17}H_{12}FNONa$ $[M+Na]^+$ 288.0801, found 288.0809.



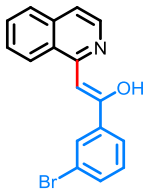
(*Z*)-4-(1-Hydroxy-2-(isoquinolin-1-yl)vinyl)benzonitrile (3f)

Yellow solid (31.0 mg, 57% yield). PE/EA = 5:1, R_f = 0.24. ^{1}H NMR (400 MHz, DMSO): δ 16.05 (s, 1H), 8.66 (d, *J* = 8.4 Hz, 1H), 8.30 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.89–7.80 (m, 3H), 7.71–7.64 (m, 1H), 7.16 (d, *J* = 7.0 Hz, 1H), 7.09 (s, 1H). ^{13}C NMR (100 MHz, DMSO): δ 180.2, 154.5, 144.4, 135.9, 133.0, 132.8, 129.8, 128.3, 127.9, 127.6, 125.9, 124.3, 119.3, 112.9, 112.5, 85.5. IR (KBr): 3060, 2223, 1596, 1519, 1211, 792, 754 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{18}H_{12}N_2ONa$ $[M+Na]^+$ 295.0847, found 295.0851.



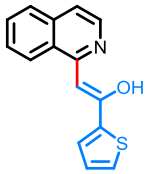
(*Z*)-2-(Isoquinolin-1-yl)-1-(4-(trifluoromethyl)phenyl)ethen-1-ol (3g)

Yellow solid (47.3 mg, 75% yield). PE/EA = 10:1, R_f = 0.25. ^{1}H NMR (400 MHz, $CDCl_3$): δ 16.37 (s, 1H), 8.25 (d, *J* = 8.3 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 2H), 7.75–7.71 (m, 3H), 7.68–7.63 (m, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 6.7 Hz, 1H), 6.93 (d, *J* = 6.7 Hz, 1H), 6.78 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.1, 154.8, 143.8, 135.7, 131.7 (q, *J* = 32 Hz), 132.1, 128.1, 127.6, 127.3, 127.0, 125.2 (q, *J* = 3.5 Hz), 124.5, 124.4, 124.1 (q, *J* = 270.4 Hz), 112.1, 85.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.6. IR (KBr): 3059, 1637, 1516, 1327, 1068, 742 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{18}H_{12}F_3NONa$ $[M+Na]^+$ 338.0769, found 338.0780.



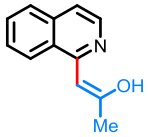
(*Z*)-1-(3-Bromophenyl)-2-(isoquinolin-1-yl)ethen-1-ol (3h)

Yellow solid (38.5 mg, 59% yield). PE/EA = 5:1, R_f = 0.29. ^{1}H NMR (400 MHz, $CDCl_3$): δ 16.23 (s, 1H), 8.25 (d, *J* = 8.3 Hz, 1H), 8.17 (s, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.76–7.69 (m, 1H), 7.66–7.57 (m, 3H), 7.46 (d, *J* = 6.8 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 6.7 Hz, 1H), 6.72 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.2, 154.6, 142.7, 135.6, 133.0, 132.0, 129.9, 129.8, 128.0, 127.6, 127.2, 125.3, 124.5, 124.5, 122.6, 111.8, 84.8. IR (KBr): 3058, 1591, 1543, 1342, 1210, 690, 603 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{17}H_{13}BrNO$ $[M+H]^+$ 326.0181, found 326.0185.



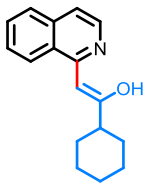
(*Z*)-2-(Isoquinolin-1-yl)-1-(thiophen-2-yl)ethen-1-ol (3i)

Yellow solid (32.9 mg, 65% yield). PE/EA = 5:1, R_f = 0.23. ^{1}H NMR (400 MHz, $CDCl_3$): δ 15.72 (s, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 7.76–7.67 (m, 2H), 7.63–7.54 (m, 2H), 7.51 (d, *J* = 5.0 Hz, 1H), 7.39–7.31 (m, 1H), 7.16 (t, *J* = 4.7 Hz, 1H), 6.79 (d, *J* = 6.8 Hz, 1H), 6.66 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.5, 154.0, 147.4, 135.5, 132.0, 129.2, 127.7, 127.7, 127.4, 127.1, 126.8, 124.5, 124.4, 110.7, 84.3. IR (KBr): 3062, 1592, 1544, 1348, 1209, 1073, 709 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{15}H_{11}NOSNa$ $[M+Na]^+$ 276.0459, found 276.0460.



(*Z*)-1-(Isoquinolin-1-yl)prop-1-en-2-ol (3j)

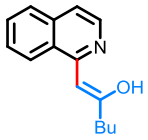
Yellow solid (21.5 mg, 58% yield). PE/EA = 5:1, R_f = 0.28. ^{1}H NMR (400 MHz, DMSO): δ 15.09 (s, 1H), 8.20 (d, *J* = 8.3 Hz, 1H), 7.72–7.65 (m, 2H), 7.62 (t, *J* = 6.8 Hz, 1H), 7.54 (t, *J* = 8.3 Hz, 1H), 6.84 (d, *J* = 6.8 Hz, 1H), 6.18 (s, 1H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, DMSO): δ 190.6, 152.6, 135.6, 132.4, 129.6, 127.8, 127.4, 124.9, 123.7, 109.9, 87.5, 29.0. IR (KBr): 3059, 2983, 2892, 1599, 1358, 1255, 1063, 737 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{12}H_{11}NONa$ $[M+Na]^+$ 208.0738, found 208.0743.



(*Z*)-1-Cyclohexyl-2-(quinolin-2-yl)ethen-1-ol (3k)

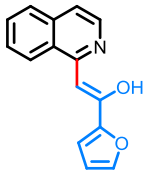
Yellow solid (33.9 mg, 67% yield). PE/EA = 10:1, R_f = 0.25. ^{1}H NMR (400 MHz, DMSO): δ 15.24 (s, 1H), 8.25 (d, *J* = 8.3 Hz, 1H), 7.74–7.65 (m, 2H), 7.60 (t, *J* = 5.9 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 6.8 Hz, 1H), 6.18 (s, 1H), 2.33 (t, *J* = 9.8 Hz, 1H), 1.88–1.73 (m, 4H), 1.53–1.40 (m, 2H), 1.39–1.17 (m, 4H). ^{13}C NMR (100 MHz, DMSO): δ 196.9, 153.2, 135.6, 132.3, 129.6, 127.7, 127.3, 125.0, 124.0, 109.8, 85.6, 49.5, 30.4, 26.2, 26.1. IR (KBr): 3061, 2989,

2890, 1596, 1350, 1245, 1053, 742 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{17}H_{20}NO$ $[M+H]^+$ 254.1545, found 254.1542.



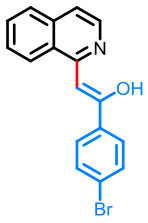
(*Z*)-1-(Isoquinolin-1-yl)hex-1-en-2-ol (3l)

Yellow solid (27.7 mg, 61% yield). PE/EA = 10:1, R_f = 0.24. ^1H NMR (400 MHz, DMSO): δ 15.18 (s, 1H), 8.25 (d, *J* = 8.3 Hz, 1H), 7.75–7.68 (m, 2H), 7.63 (t, *J* = 6.8 Hz, 1H), 7.61–7.53 (m, 1H), 6.87 (d, *J* = 6.8 Hz, 1H), 6.20 (s, 1H), 2.40 (t, *J* = 7.5 Hz, 2H), 1.69–1.59 (m, 2H), 1.43–1.35 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, DMSO): δ 193.7, 152.7, 135.6, 132.4, 129.6, 127.8, 127.4, 125.0, 123.8, 109.8, 87.1, 41.4, 28.8, 22.5, 14.4. IR (KBr): 3058, 2976, 2868, 1548, 1352, 1243, 1060, 713 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{15}H_{18}NO$ $[M+H]^+$ 228.1388, found 228.1385.



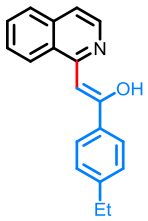
(*Z*)-1-(Furan-2-yl)-2-(isoquinolin-1-yl)ethen-1-ol (3m)

Yellow solid (18.5 mg, 39% yield). PE/EA = 5:1, R_f = 0.18. ^1H NMR (400 MHz, DMSO): δ 15.28 (s, 1H), 8.39 (d, *J* = 8.3 Hz, 1H), 7.88–7.83 (m, 1H), 7.82–7.69 (m, 3H), 7.66–7.59 (m, 1H), 7.24 (d, *J* = 3.4 Hz, 1H), 6.97 (d, *J* = 6.8 Hz, 1H), 6.73 (s, 1H), 6.69–6.65 (m, 1H). ^{13}C NMR (100 MHz, DMSO): δ 174.4, 154.7, 153.6, 145.1, 135.7, 132.8, 129.4, 128.1, 127.5, 125.2, 124.1, 112.5, 112.5, 110.7, 83.9. IR (KBr): 3052, 1637, 1491, 1210, 1071, 747 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{15}H_{12}NO_2$ $[M+H]^+$ 238.0868, found 238.0867.



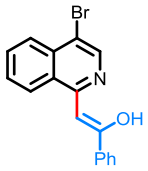
(*Z*)-1-(4-Bromophenyl)-2-(isoquinolin-1-yl)ethen-1-ol (3n)

Yellow solid (11.7 mg, 18% yield). PE/EA = 5:1, R_f = 0.26. ^1H NMR (400 MHz, DMSO): δ 15.92 (s, 1H), 8.60 (d, *J* = 8.3 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 2H), 7.84–7.77 (m, 3H), 7.72–7.62 (m, 3H), 7.07 (d, *J* = 6.8 Hz, 1H), 6.99 (s, 1H). ^{13}C NMR (100 MHz, DMSO): δ 181.5, 154.2, 139.6, 135.8, 132.8, 131.6, 129.7, 129.3, 128.1, 127.5, 125.7, 124.5, 124.3, 111.7, 84.5. IR (KBr): 3059, 1637, 1591, 1209, 747 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{17}H_{13}BrNO$ $[M+H]^+$ 326.0181, found 326.0170.



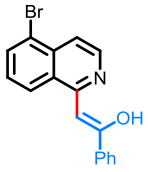
(*Z*)-1-(4-Ethylphenyl)-2-(isoquinolin-1-yl)ethen-1-ol (3o)

Yellow solid (18.7 mg, 34% yield). PE/EA = 10:1, R_f = 0.29. ^{1}H NMR (400 MHz, DMSO): δ 15.97 (s, 1H), 8.61 (d, *J* = 8.3 Hz, 1H), 8.09 (d, *J* = 8.2 Hz, 2H), 7.86–7.78 (m, 3H), 7.67 (t, *J* = 6.2 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 6.7 Hz, 1H), 7.01 (s, 1H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, DMSO): δ 183.0, 154.0, 146.9, 138.0, 135.7, 132.6, 129.7, 128.1, 128.0, 127.5, 127.3, 125.5, 124.4, 111.0, 84.4, 28.5, 15.9. IR (KBr): 3060, 2967, 2872, 1628, 1591, 1209, 1068, 746 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{19}H_{17}NOK$ $[M+K]^+$ 314.0947, found 314.0947.



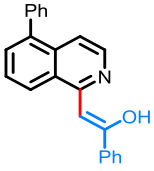
(*Z*)-2-(4-Bromoisoquinolin-1-yl)-1-phenylethen-1-ol (3a')

Yellow solid (42.4 mg, 65% yield). PE/EA = 10:1, R_f = 0.38. ^{1}H NMR (400 MHz, $CDCl_3$): δ 16.34 (s, 1H), 8.13 (s, 1H), 8.07–8.01 (m, 2H), 7.65–7.59 (m, 2H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.53–7.48 (m, 3H), 7.34 (t, *J* = 6.9 Hz, 1H), 6.66 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.4, 153.2, 139.0, 138.9, 138.4, 131.2, 130.7, 128.4, 126.8, 126.7, 124.3, 123.8, 119.7, 115.7, 90.4. IR (KBr): 3065, 1617, 1541, 1217, 1068, 748, 707 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{17}H_{13}BrNO$ $[M+H]^+$ 326.0181, found 326.0184.



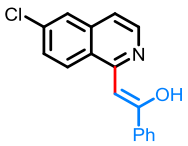
(*Z*)-2-(5-Bromoisoquinolin-1-yl)-1-phenylethen-1-ol (3b')

Yellow solid (37.2 mg, 57% yield). PE/EA = 5:1, R_f = 0.32. ^{1}H NMR (400 MHz, $CDCl_3$): δ 16.32 (s, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 8.07–7.99 (m, 2H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.56–7.48 (m, 4H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 7.0 Hz, 1H), 6.79 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.2, 154.2, 140.1, 135.6, 134.9, 130.5, 130.2, 128.4, 127.7, 126.8, 126.2, 123.9, 122.2, 109.8, 85.6. IR (KBr): 3059, 1591, 1535, 1344, 1206, 751, 616 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{17}H_{13}BrNO$ $[M+H]^+$ 326.0181, found 326.0184.



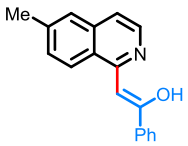
(*Z*)-1-Phenyl-2-(5-phenylisoquinolin-1-yl)ethen-1-ol (3c')

Yellow solid (38.8 mg, 60% yield). PE/EA = 5:1, R_f = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$): δ 16.43 (s, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 8.10–8.04 (m, 2H), 7.69–7.61 (m, 2H), 7.57–7.45 (m, 8H), 7.41 (d, *J* = 7.0 Hz, 1H), 6.92 (d, *J* = 7.0 Hz, 1H), 6.88 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.9, 154.8, 140.6, 139.9, 139.4, 133.8, 132.7, 130.3, 129.9, 128.5, 128.4, 128.3, 127.8, 126.9, 126.8, 125.0, 123.8, 109.4, 85.2. IR (KBr): 3058, 1635, 1549, 1350, 1205, 755, 697 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{23}H_{17}NONa$ $[M+Na]^+$ 346.1208, found 346.1208.



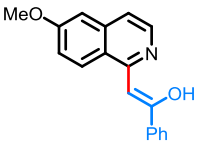
(*Z*)-2-(6-Chloroisoquinolin-1-yl)-1-phenylethen-1-ol (3d')

Yellow solid (38.3 mg, 68% yield). PE/EA = 5:1, R_f = 0.26. ^{1}H NMR (400 MHz, DMSO): δ 15.81 (s, 1H), 8.62 (d, *J* = 8.9 Hz, 1H), 8.18–8.08 (m, 2H), 7.89 (d, *J* = 2.2 Hz, 1H), 7.80 (t, *J* = 6.8 Hz, 1H), 7.62 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.56–7.46 (m, 3H), 7.00 (s, 1H), 6.98 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO): δ 183.3, 153.6, 140.2, 137.5, 137.3, 131.2, 131.0, 128.7, 128.0, 127.9, 127.3, 126.3, 123.1, 110.1, 85.0. IR (KBr): 3061, 1585, 1482, 1257, 1193, 781, 727 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{17}H_{12}ClNONa$ $[M+Na]^+$ 304.0505, found 304.0501.



(*Z*)-2-(6-Methylisoquinolin-1-yl)-1-phenylethen-1-ol (3e')

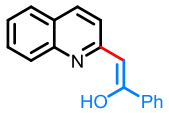
Yellow solid (35.0 mg, 67% yield). PE/EA = 5:1, R_f = 0.25. ^{1}H NMR (400 MHz, DMSO): δ 15.95 (s, 1H), 8.47 (d, *J* = 8.5 Hz, 1H), 8.17–8.06 (m, 2H), 7.75 (t, *J* = 5.4 Hz, 1H), 7.57 (s, 1H), 7.53–7.44 (m, 4H), 7.02–6.90 (m, 2H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, DMSO): δ 182.6, 154.1, 142.9, 140.5, 135.9, 130.7, 129.8, 129.7, 128.7, 127.2, 126.9, 125.5, 122.2, 111.1, 84.3, 21.7. IR (KBr): 2953, 1590, 1546, 1337, 1208, 719 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{18}H_{15}NONa$ $[M+Na]^+$ 284.1051, found 284.1052.



(*Z*)-2-(6-Methoxyisoquinolin-1-yl)-1-phenylethen-1-ol (3f')

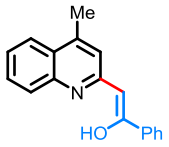
Yellow solid (32.7 mg, 59% yield). PE/EA = 5:1, R_f = 0.33. ^{1}H NMR (400 MHz, $CDCl_3$): δ 16.34 (s, 1H), 8.17 (d, *J* = 9.1 Hz, 1H), 8.08–8.00 (m, 2H), 7.55–7.40 (m, 4H), 7.18 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.98 (d, *J* = 2.6 Hz, 1H), 6.81 (d, *J* = 6.7 Hz, 1H), 6.70 (s, 1H), 3.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.6, 162.4, 154.4, 140.8, 137.8, 130.1, 128.8, 128.2, 126.7, 126.5,

118.6, 118.0, 111.0, 107.0, 84.3, 55.5. IR (KBr): 3063, 2977, 2892, 1623, 1588, 1223, 1067, 732 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{18}H_{15}NONa$ $[M+Na]^+$ 300.1000, found 300.1000.



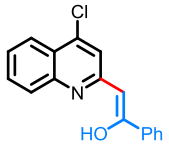
(*Z*)-1-Phenyl-2-(quinolin-2-yl)ethen-1-ol (3g')

Yellow solid (36.6 mg, 74% yield). PE/EA = 10:1, R_f = 0.29. ^1H NMR (400 MHz, $CDCl_3$): δ 15.75 (s, 1H), 8.03–7.97 (m, 2H), 7.70 (d, *J* = 9.2 Hz, 1H), 7.61–7.46 (m, 6H), 7.33–7.27 (m, 1H), 6.92 (d, *J* = 9.1 Hz, 1H), 6.13 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.9, 154.3, 139.8, 138.0, 136.1, 131.0, 130.4, 128.3, 127.6, 126.7, 123.7, 123.4, 122.3, 118.3, 90.0. IR (KBr): 3059, 1634, 1550, 1144, 1070 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{17}H_{13}NONa$ $[M+Na]^+$ 270.0895, found 270.0896.



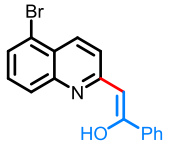
(*Z*)-2-(4-Methylquinolin-2-yl)-1-phenylethen-1-ol (3h')

Yellow solid (35.5 mg, 68% yield). PE/EA = 5:1, R_f = 0.30. ^1H NMR (400 MHz, $CDCl_3$): δ 15.70 (s, 1H), 8.05–7.96 (m, 2H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.62–7.45 (m, 5H), 7.34 (t, *J* = 8.1 Hz, 1H), 6.79 (s, 1H), 6.07 (s, 1H), 2.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.2, 153.9, 144.4, 140.1, 137.6, 130.7, 130.2, 128.2, 126.6, 124.0, 123.8, 123.5, 121.6, 118.5, 89.1, 19.0. IR (KBr): 3059, 2978, 2890, 1632, 1344, 1182, 1069, 696 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{18}H_{15}NONa$ $[M+Na]^+$ 284.1051, found 284.1050.



(*Z*)-2-(4-Chloroquinolin-2-yl)-1-phenylethen-1-ol (3i')

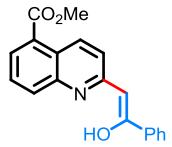
Yellow solid (34.3 mg, 61% yield). PE/EA = 10:1, R_f = 0.31. ^1H NMR (400 MHz, $CDCl_3$): δ 15.69 (s, 1H), 8.04–7.94 (m, 3H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.60–7.55 (m, 1H), 7.53–7.47 (m, 3H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.07 (s, 1H), 6.09 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.2, 154.1, 141.6, 139.6, 138.9, 131.9, 130.6, 128.3, 126.5, 124.6, 124.3, 121.9, 121.5, 119.4, 90.3. IR (KBr): 3062, 1591, 1479, 1254, 1191, 779, 731 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{17}H_{13}ClNO$ $[M+H]^+$ 282.0686, found 282.0680.



(*Z*)-2-(5-Bromoquinolin-2-yl)-1-phenylethen-1-ol (3j')

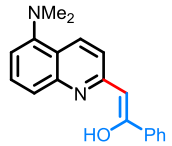
Yellow solid (42.4 mg, 65% yield). PE/EA = 10:1, R_f = 0.32. ^1H NMR (400 MHz, $CDCl_3$): δ 15.68 (s, 1H), 8.03 (d, *J* = 9.4 Hz, 1H), 7.99–7.91 (m, 2H), 7.51–7.43 (m, 5H), 7.36 (t, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 9.4 Hz, 1H), 6.13 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.6, 154.5, 140.0, 139.0, 134.8, 131.1, 130.6, 128.4, 127.5, 126.6, 123.6, 122.8, 122.4, 118.7, 90.9. IR (KBr): 3058,

1588, 1533, 1342, 1204, 749, 613 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{17}H_{13}BrNO$ $[M+H]^+$ 326.0181, found 326.0174.



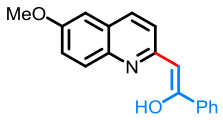
Methyl (*Z*)-2-(2-hydroxy-2-phenylvinyl)quinoline-5-carboxylate (3k')

Orange solid (40.9 mg, 67% yield). PE/EA = 5:1, R_f = 0.22. ^1H NMR (400 MHz, $CDCl_3$): δ 15.78 (s, 1H), 8.87 (d, *J* = 9.6 Hz, 1H), 8.03–7.93 (m, 3H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.60 (t, *J* = 7.9 Hz, 1H), 7.54–7.45 (m, 3H), 7.04 (d, *J* = 9.6 Hz, 1H), 6.16 (s, 1H), 4.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.0, 166.8, 154.0, 139.2, 139.1, 133.9, 130.5, 129.6, 128.3, 127.0, 126.6, 124.0, 123.5, 122.6, 90.4, 52.4. IR (KBr): 3061, 2954, 2828, 1715, 1632, 1547, 1266, 1138, 741 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{19}H_{16}NO_3$ $[M+H]^+$ 306.1130, found 306.1143.



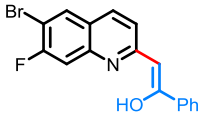
(*Z*)-2-(5-(Dimethylamino)quinolin-2-yl)-1-phenylethen-1-ol (3l')

Yellow oil (33.6 mg, 58% yield). PE/EA = 5:1, R_f = 0.28. ^1H NMR (400 MHz, $CDCl_3$): δ 15.75 (s, 1H), 8.10 (d, *J* = 9.4 Hz, 1H), 8.05–7.97 (m, 2H), 7.53–7.44 (m, 5H), 7.20 (d, *J* = 8.3 Hz, 1H), 6.94–6.87 (m, 2H), 6.12 (s, 1H), 2.89 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.0, 154.0, 151.5, 140.1, 139.0, 133.1, 131.1, 130.3, 128.3, 126.7, 120.7, 118.0, 112.8, 112.6, 89.3, 45.2. IR (KBr): 3060, 2968, 2895, 1639, 1356, 1153, 1089, 687 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{19}H_{19}N_2O$ $[M+H]^+$ 291.1497, found 291.1489.



(*Z*)-2-(6-Methoxyquinolin-2-yl)-1-phenylethen-1-ol (3m')

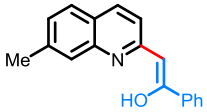
Yellow solid (24.9 mg, 45% yield). PE/EA = 5:1, R_f = 0.24. ^1H NMR (400 MHz, $CDCl_3$): δ 16.10 (s, 1H), 8.02–7.94 (m, 2H), 7.73 (d, *J* = 9.0 Hz, 1H), 7.58 (d, *J* = 9.0 Hz, 1H), 7.51–7.44 (m, 3H), 7.28 (d, *J* = 2.7 Hz, 1H), 7.02–6.96 (m, 2H), 6.13 (s, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.3, 156.4, 154.4, 139.0, 135.7, 134.6, 129.9, 128.3, 126.3, 124.9, 122.4, 121.6, 121.2, 107.8, 90.8, 55.6. IR (KBr): 3057, 2979, 2891, 1638, 1263, 1070, 739 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{18}H_{15}NO_2Na$ $[M+Na]^+$ 300.1000, found 300.0992.



(*Z*)-2-(6-Bromo-7-fluoroquinolin-2-yl)-1-phenylethen-1-ol (3n')

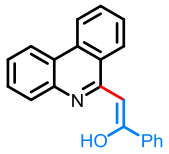
Yellow solid (37.2 mg, 54% yield). PE/EA = 10:1, R_f = 0.36. ^1H NMR (400 MHz, $CDCl_3$): δ 15.74 (s, 1H), 8.02–7.93 (m, 2H), 7.79 (d, *J* = 7.1 Hz, 1H), 7.63 (d, *J* = 9.2 Hz, 1H), 7.53–7.45 (m, 3H), 7.36–7.29 (m, 1H), 6.93 (d, *J* = 9.0 Hz, 1H), 6.16 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.1, 159.9 (d, *J* = 250.1 Hz), 155.2, 138.5, 134.4, 131.9, 130.7, 128.7 (d, *J* = 3.9 Hz), 128.4,

126.6, 122.4 (d, J = 2.4 Hz), 121.5, 106.4 (d, J = 25.3 Hz), 105.3 (d, J = 23.1 Hz), 91.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ -102.0. IR (KBr): 3058, 1638, 1552, 1254, 1202, 1070, 884, 740 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{17}H_{12}BrFNO$ $[M+H]^+$ 344.0086, found 344.0094.



(*Z*)-2-(7-Methylquinolin-2-yl)-1-phenylethen-1-ol (3o')

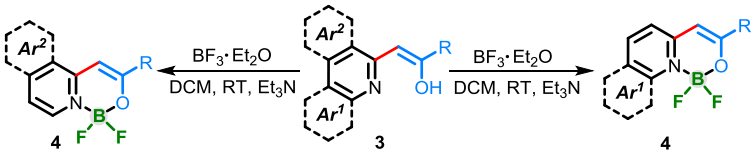
Yellow solid (37.1 mg, 71% yield). PE/EA = 10:1, R_f = 0.34. ^{1}H NMR (400 MHz, $CDCl_3$): δ 15.74 (s, 1H), 8.01–7.94 (m, 3H), 7.67 (d, J = 8.0 Hz, 1H), 7.54–7.48 (m, 4H), 7.23 (d, J = 8.0 Hz, 1H), 7.10 (d, J = 9.1 Hz, 1H), 6.34 (s, 1H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.8, 154.9, 142.1, 139.4, 138.4, 137.0, 130.8, 128.8, 128.1, 126.8, 126.2, 121.8, 121.7, 118.9, 90.2, 21.8. IR (KBr): 2956, 1593, 1548, 1347, 1216, 723 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{18}H_{16}NO$ $[M+H]^+$ 262.1232, found 262.1222.



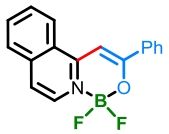
(*Z*)-2-(Phenanthridin-6-yl)-1-phenylethen-1-ol (3p')

Yellow solid (41.6 mg, 70% yield). PE/EA = 5:1, R_f = 0.38. ^{1}H NMR (400 MHz, DMSO): δ 16.00 (s, 1H), 8.71 (d, J = 8.4 Hz, 1H), 8.65 (d, J = 8.3 Hz, 1H), 8.51 (d, J = 8.1 Hz, 1H), 8.21–8.16 (m, 2H), 7.92 (t, J = 7.1 Hz, 1H), 7.74 (t, J = 7.1 Hz, 1H), 7.62 (d, J = 3.9 Hz, 2H), 7.59–7.51 (m, 3H), 7.45–7.38 (m, 1H), 7.12 (s, 1H). ^{13}C NMR (100 MHz, DMSO): δ 185.9, 153.0, 140.2, 134.6, 133.0, 132.0, 131.3, 130.6, 129.0, 128.8, 127.5, 126.4, 124.3, 124.3, 123.6, 123.5, 120.4, 118.4, 85.5. IR (KBr): 3063, 1599, 1547, 1348, 1213, 1070, 736 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{21}H_{16}NO$ $[M+H]^+$ 298.1232, found 298.1231.

E. Synthetic transformation of products

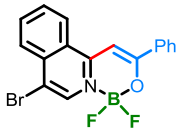


Enol **3** (0.2 mmol) was dissolved in dry dichloromethane (2.5 mL). Triethylamine (0.29 mL, 2.1 mmol) and boron trifluoride diethyl ether complex (0.26 mL, 2.0 mmol) were added to the solution and stirred at room temperature for 24 h. After completed, water was added into the solution, and the solution was extracted with DCM. The organic layer was washed with water and dried over $MgSO_4$. After concentration of solvent, the residue was purified by silica gel chromatography using PE/DCM to afford **4** as a light yellow solid.



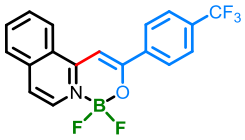
4,4-Difluoro-2-phenyl-4*H*-4λ^4,5λ^4-[1,3,2]oxazaborinino[4,3-*a*]isoquinoline (4a)

Light yellow solid (46.6 mg, 79% yield). PE/DCM = 1:4, R_f = 0.35. ^{1}H NMR (400 MHz, DMSO): δ 9.04 (d, *J* = 8.5 Hz, 1H), 8.30–8.24 (m, 3H), 8.14 (d, *J* = 8.1 Hz, 1H), 8.08 (t, *J* = 7.6 Hz, 1H), 7.96–7.89 (m, 2H), 7.75 (s, 1H), 7.65–7.56 (m, 3H). ^{13}C NMR (100 MHz, DMSO): δ 164.3, 152.6, 136.8, 134.7, 134.2, 132.1, 131.6, 129.9, 129.2, 128.0, 127.4, 127.3, 123.9, 120.0, 90.7. ^{19}F NMR (376 MHz, DMSO): δ -136.0. IR (KBr): 3061, 1637, 1543, 1052, 745, 690 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{17}H_{12}BF_2NONa$ $[M+Na]^+$ 318.0878, found 318.0877.



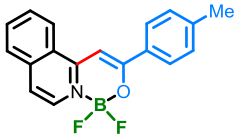
7-Bromo-4,4-difluoro-2-phenyl-4*H*-4λ^4,5λ^4-[1,3,2]oxazaborinino[4,3-*a*]isoquinoline (4b)

Light yellow solid (64.3 mg, 86% yield). PE/DCM = 1:4, R_f = 0.33. ^{1}H NMR (400 MHz, DMSO): δ 9.13 (d, *J* = 8.4 Hz, 1H), 8.43 (s, 1H), 8.30–8.19 (m, 4H), 8.07–7.99 (m, 1H), 7.77 (s, 1H), 7.68–7.54 (m, 3H). ^{13}C NMR (100 MHz, DMSO): δ 165.5, 152.6, 136.2, 135.2, 134.1, 132.6, 132.4, 130.8, 129.3, 128.3, 127.5, 126.7, 124.8, 114.9, 90.8. ^{19}F NMR (376 MHz, DMSO): δ -135.8. IR (KBr): 3062, 1636, 1543, 1261, 1070, 747, 688 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{17}H_{11}BBrF_2NOK$ $[M+K]^+$ 411.9722, found 411.9704.



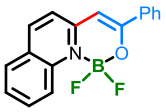
4,4-Difluoro-2-(4-(trifluoromethyl)phenyl)-4*H*-4λ^4,5λ^4-[1,3,2]oxazaborinino[4,3-*a*]isoquinolin e (4c)

Light yellow solid (65.3 mg, 90% yield). PE/DCM = 1:4, R_f = 0.37. ^{1}H NMR (400 MHz, DMSO): δ 9.10 (d, *J* = 8.5 Hz, 1H), 8.47 (d, *J* = 8.2 Hz, 2H), 8.34 (d, *J* = 6.7 Hz, 1H), 8.20 (d, *J* = 7.4 Hz, 1H), 8.12 (t, *J* = 7.0 Hz, 1H), 8.04 (d, *J* = 6.7 Hz, 1H), 8.00–7.94 (m, 3H), 7.91 (s, 1H). ^{13}C NMR (100 MHz, DMSO): δ 162.1, 152.2, 138.1, 136.9, 134.9, 131.7, 131.5 (q, J = 32 Hz), 130.0, 128.0, 128.0, 127.4, 126.1 (q, J = 3.8 Hz), 124.0, 124.4 (q, J = 270.8 Hz), 120.8, 92.4. ^{19}F NMR (376 MHz, DMSO): δ -61.20, -135.90. IR (KBr): 3058, 1638, 1551, 1326, 1116, 1070, 747 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{18}H_{11}BF_5NONa$ $[M+Na]^+$ 386.0752, found 386.0749.



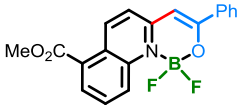
4,4-Difluoro-2-(p-tolyl)-4*H*-4λ^4,5λ^4-[1,3,2]oxazaborinino[4,3-*a*]isoquinoline (4d)

Light yellow solid (46.4 mg, 75% yield). PE/DCM = 1:4, R_f = 0.32. ^{1}H NMR (400 MHz, DMSO): δ 9.01 (d, *J* = 8.6 Hz, 1H), 8.23 (d, *J* = 6.7 Hz, 1H), 8.17–8.10 (m, 3H), 8.05 (t, *J* = 7.5 Hz, 1H), 7.93–7.86 (m, 2H), 7.68 (s, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, DMSO): δ 164.6, 152.7, 142.3, 136.7, 134.6, 131.6, 131.5, 129.8, 129.8, 128.0, 127.4, 127.3, 123.9, 119.7, 90.0, 21.5. ^{19}F NMR (376 MHz, DMSO): δ -136.0. IR (KBr): 3056, 2981, 2891, 1637, 1546, 1263, 1071, 739 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{18}H_{14}BF_2NONa$ $[M+Na]^+$ 332.1034, found 332.1033.



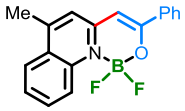
1,1-Difluoro-3-phenyl-1*H*-1λ^4,11λ^4-[1,3,2]oxazaborinino[3,4-*a*]quinoline (4e)

Light yellow solid (47.2 mg, 80% yield). PE/DCM = 1:4, R_f = 0.36. ^{1}H NMR (400 MHz, DMSO): δ 8.67 (d, *J* = 8.7 Hz, 1H), 8.55 (d, *J* = 8.2 Hz, 1H), 8.13–8.04 (m, 3H), 7.95 (t, *J* = 7.1 Hz, 1H), 7.75-7.67 (m, 2H), 7.64–7.56 (m, 3H), 7.07 (s, 1H). ^{13}C NMR (100 MHz, DMSO): δ 163.5, 154.3, 142.9, 138.9, 133.5, 132.9, 132.2, 129.7, 129.4, 127.2, 126.9, 122.2, 122.2, 122.1, 95.1. ^{19}F NMR (376 MHz, DMSO): δ -125.7. IR (KBr): 3061, 1639, 1553, 1263, 1069, 741 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{17}H_{12}BF_2NONa$ $[M+Na]^+$ 318.0878, found 318.0872.



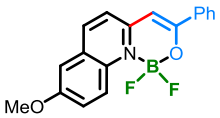
Methyl 1,1-difluoro-3-phenyl-1*H*-1λ^4,11λ^4-[1,3,2]oxazaborinino[3,4-*a*]quinoline-7-carboxylate (4f)

Light yellow solid (58.6 mg, 83% yield). PE/DCM = 1:4, R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.46 (d, *J* = 9.3 Hz, 1H), 9.03 (d, *J* = 9.0 Hz, 1H), 8.25 (d, *J* = 7.4 Hz, 1H), 8.06 (d, *J* = 7.4 Hz, 2H), 7.85 (t, *J* = 8.3 Hz, 1H), 7.59–7.47 (m, 3H), 7.38 (d, *J* = 9.3 Hz, 1H), 6.47 (s, 1H), 4.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 165.9, 153.9, 140.0, 138.9, 133.5, 131.7, 130.8, 129.7, 128.6, 127.6, 127.4, 127.0, 125.6, 122.7, 93.8, 52.5. ^{19}F NMR (376 MHz, DMSO): δ -127.2. IR (KBr): 3056, 2982, 2891, 1639, 1554, 1263, 1072, 739 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{19}H_{14}BF_2NO_3Na$ $[M+Na]^+$ 376.0932, found 376.0928.



1,1-Difluoro-6-methyl-3-phenyl-1*H*-1λ^4,11λ^4-[1,3,2]oxazaborinino[3,4-*a*]quinoline (4g)

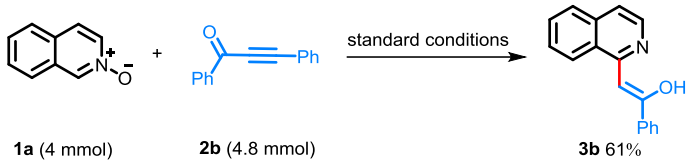
Light yellow solid (55.0 mg, 89% yield). PE/DCM = 1:4, R_f = 0.33. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 8.6 Hz, 1H), 8.02 (d, *J* = 6.3 Hz, 2H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.81 (t, *J* = 7.0 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.53–7.45 (m, 3H), 7.12 (s, 1H), 6.36 (s, 1H), 2.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 153.3, 150.1, 139.3, 133.8, 131.8, 131.3, 128.5, 126.7, 126.2, 124.2, 123.4, 121.4, 93.7, 19.3. ^{19}F NMR (376 MHz, DMSO): δ -128.4. IR (KBr): 3056, 2981, 2891, 1620, 1551, 1264, 1078, 740 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{18}H_{14}BF_2NONa$ $[M+Na]^+$ 332.1034, found 332.1027.



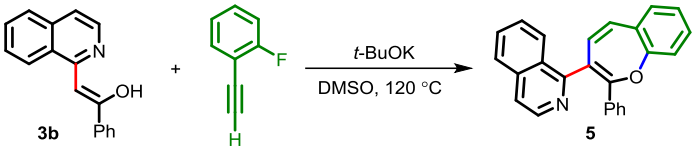
1,1-Difluoro-8-methoxy-3-phenyl-1*H*-1λ^4,11λ^4-[1,3,2]oxazaborinino[3,4-*a*]quinoline (4h)

Light yellow solid (49.4 mg, 76% yield). PE/DCM = 1:4, R_f = 0.32. ^{1}H NMR (400 MHz, DMSO): δ 8.58 (d, *J* = 8.7 Hz, 1H), 8.48 (d, *J* = 9.6 Hz, 1H), 8.07–7.99 (m, 2H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.63–7.54 (m, 5H), 6.99 (s, 1H), 3.96 (s, 3H). ^{13}C NMR (100 MHz, DMSO): δ 162.2, 157.8, 152.2, 141.9, 134.1, 133.8, 131.8, 129.3, 128.9, 126.7, 123.9, 123.8, 122.5, 108.9, 94.9,

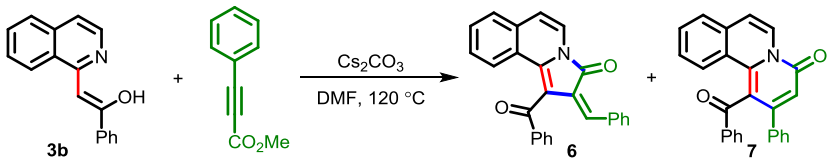
56.3. ^{19}F NMR (376 MHz, DMSO): δ -133.2. IR (KBr): 3060, 2978, 2891, 1624, 1552, 1252, 1057 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{18}H_{15}BF_2NO_2$ $[M+H]^+$ 326.1164, found 326.1177.



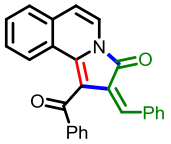
A pressure tube was charged with isoquinoline *N*-oxide **1a** (580.6 mg, 4.0 mmol), 1,3-diphenylprop-2-yn-1-one **2b** (990.0 mg, 4.8 mmol), $Zn(OAc)_2 \cdot 2H_2O$ (175.6 mg, 0.8 mmol) and acetone (20.0 mL). The reaction mixture was stirred at 100 ℃ for 12 h under air in an oil bath. After cooling to room temperature, the mixture was filtered through a short Celite pad and all volatiles were removed under reduced pressure. The residue was purified by silica gel chromatography using PE/EA eluent to afford the product **3b** (603.4 mg, 61% yield).



To a dried Schlenk tube was added the mixture of (*Z*)-2-(isoquinolin-1-yl)-1-phenylethen-1-ol **3b** (0.20 mmol), *o*-fluorophenylacetylene (0.22 mmol), potassium tert-butoxide (0.20 mmol) and DMSO (1.0 mL). The mixture was stirred at 120 ℃ for 12 h under Ar atmosphere. After the reaction was completed, a saturated aqueous solution (30.0 mL) of NH_4Cl was added, followed by extraction with EtOAc (10.0 mL × 3). The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to yield the crude product, which was further purified by silica gel chromatography using PE/EA to afford the product **5**: White solid (47.9 mg, 69% yield). PE/EA = 10:1, R_f = 0.32. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (d, *J* = 5.7 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.64–7.56 (m, 2H), 7.45–7.32 (m, 3H), 7.30–7.28 (m, 2H), 7.23 (t, *J* = 7.9 Hz, 1H), 7.11–6.99 (m, 5H), 6.49 (d, *J* = 11.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 155.5, 152.3, 142.5, 136.6, 135.4, 131.6, 131.3, 130.8, 130.4, 130.1, 128.9, 128.7, 128.5, 127.6, 127.3, 127.0, 126.8, 124.9, 124.8, 121.2, 120.5. IR (KBr): 3067, 1633, 1487, 1175, 1070, 755, 690 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{25}H_{18}NO$ $[M+H]^+$ 348.1388, found 348.1384.

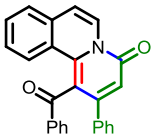


A dried Schlenk tube was charged with (*Z*)-2-(isoquinolin-1-yl)- 1-phenylethen-1-ol **3b** (49.5 mg, 0.20 mmol) and Cs_2CO_3 (130.3 mg, 0.40 mmol). The tube was then charged and recharged with Ar three times. Methyl 3-phenylpropiolate (38.4 mg, 0.22 mmol) and DMF (2.0 mL) were added into the tube and then heated at 120 ℃ overnight in an oil bath. After the reaction was completed, the resulting mixture was extracted with EtOAc (10.0 mL × 3) and dried with $MgSO_4$. Then the solvent was removed under reduced pressure and purified by silica gel column chromatography using PE/EA eluent to afford the product **6** and **7**.



(*Z*)-1-Benzoyl-2-benzylidenepyrrolo[2,1-*a*]isoquinolin-3(2H)-one (6)

Yellow solid (24.8 mg, 33% yield). PE/EA = 4:1, R_f = 0.18. ^{1}H NMR (400 MHz, DMSO): δ 8.86 (d, *J* = 8.3 Hz, 1H), 8.76 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.89–7.80 (m, 4H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.56–7.42 (m, 5H), 7.42–7.34 (m, 3H). ^{13}C NMR (100 MHz, DMSO): δ 195.5, 157.0, 150.0, 141.1, 138.4, 137.8, 133.8, 132.1, 131.3, 129.6, 129.5, 129.3, 129.2, 128.9, 128.9, 127.9, 126.3, 125.6, 122.7, 120.7, 116.1, 101.7. IR (KBr): 3060, 1753, 1640, 1375, 1242, 1050 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{26}H_{18}NO_2$ $[M+H]^+$ 376.1338, found 376.1327.



1-Benzoyl-2-phenyl-4H-pyrido[2,1-*a*]isoquinolin-4-one (7)

Yellow solid (36.8 mg, 49% yield). PE/EA = 4:1, R_f = 0.20. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.08 (d, *J* = 7.7 Hz, 1H), 8.06 (d, *J* = 8.6 Hz, 1H), 7.73 (d, *J* = 6.9 Hz, 2H), 7.68 (d, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.30–7.15 (m, 9H), 6.78 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 158.5, 151.6, 139.4, 138.3, 138.1, 133.4, 132.6, 131.0, 129.5, 128.6, 128.6, 128.6, 128.1, 127.9, 127.7, 127.1, 125.5, 123.3, 115.9, 115.4, 113.9. IR (KBr): 3057, 1663, 1462, 1263, 739 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{26}H_{17}NO_2Na$ $[M+Na]^+$ 376.1338, found 376.1331.

F. Fluorescence quantum yields

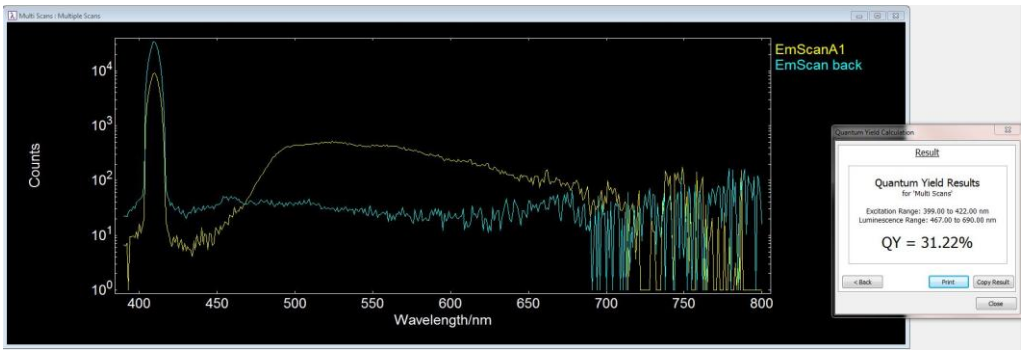


Figure S1. Quantum yield of compound **4a** in solid state

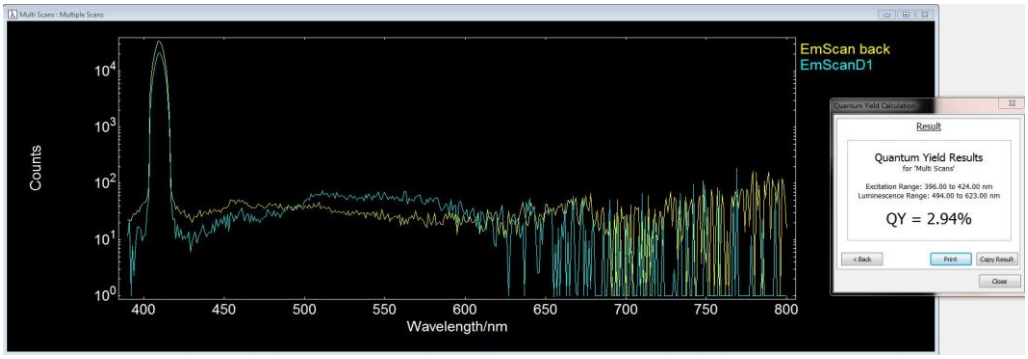


Figure S2. Quantum yield of compound **4b** in solid state

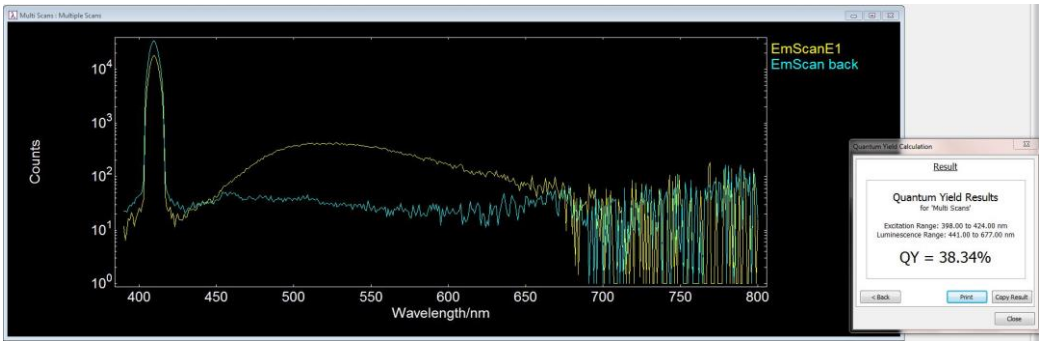


Figure S3. Quantum yield of compound **4c** in solid state

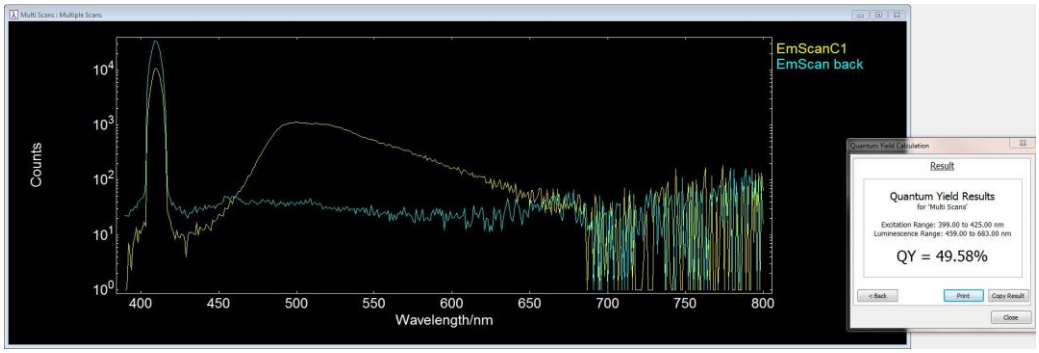


Figure S4. Quantum yield of compound **4d** in solid state

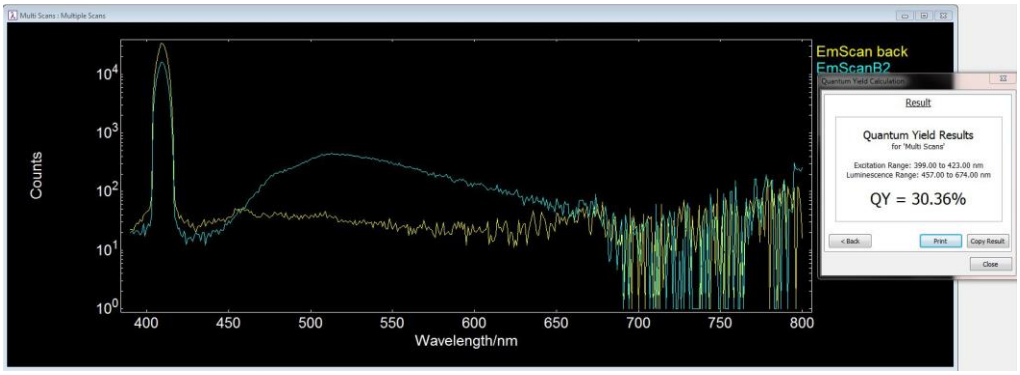


Figure S5. Quantum yield of compound **4e** in solid state

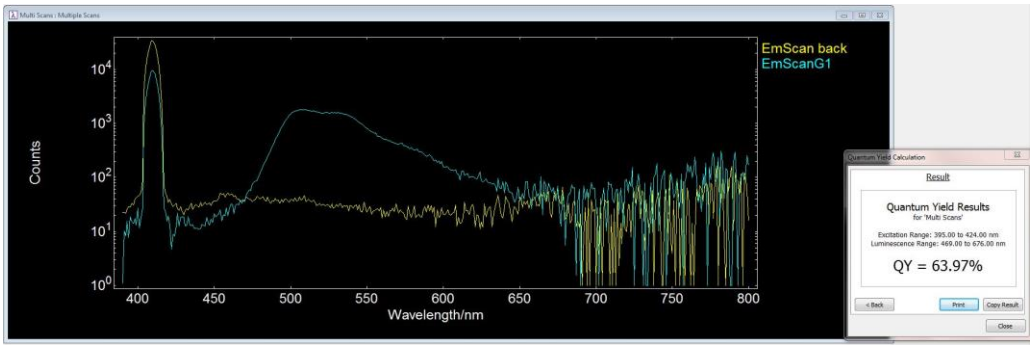


Figure S6. Quantum yields of compound **4f** in solid state

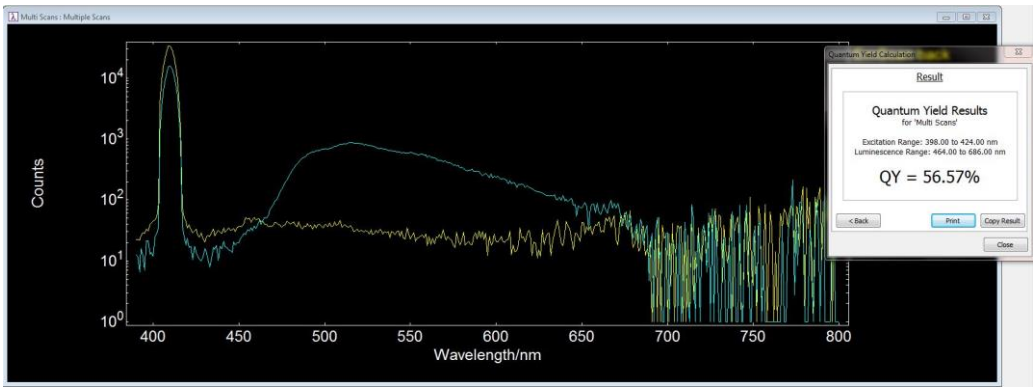


Figure S7. Quantum yields of compound **4g** in solid state

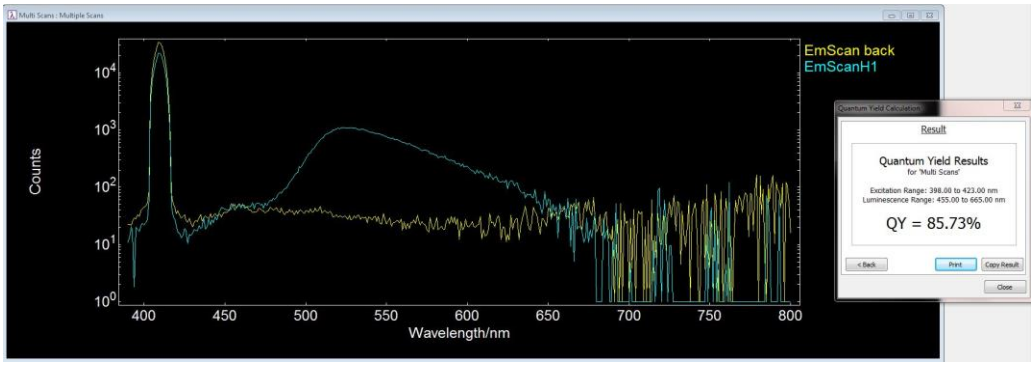


Figure S8. Quantum yields of compound **4h** in solid state

G. Stability study of products

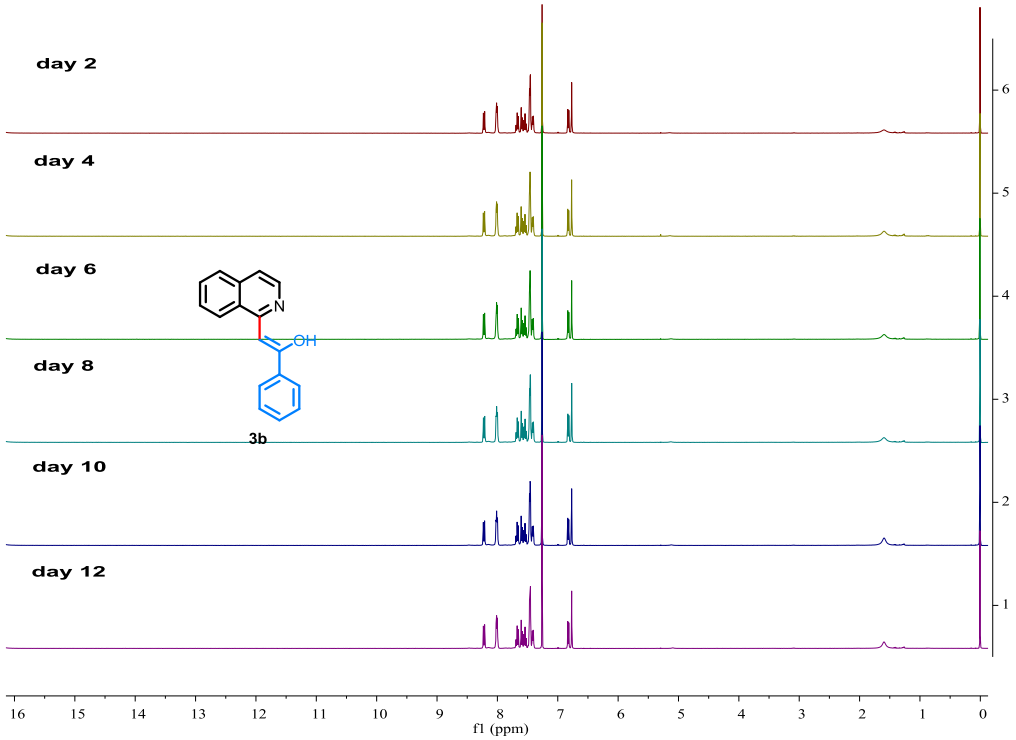


Figure S9. ^{1}H NMR spectra of product **3b** at different stage

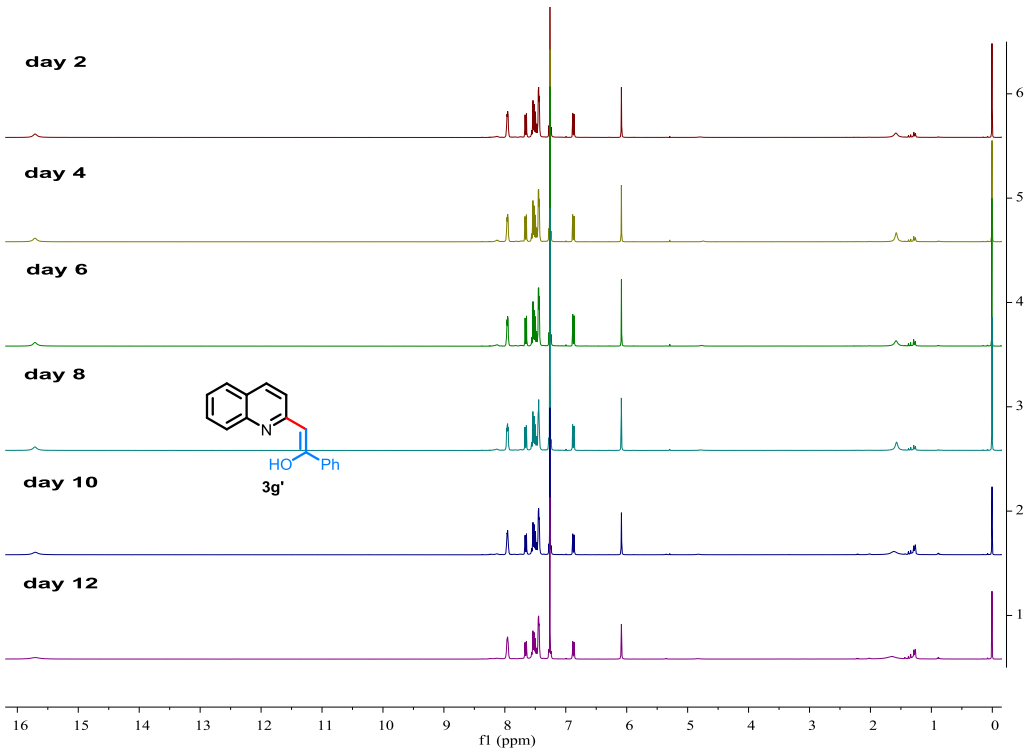


Figure S10. ^{1}H NMR spectra of product **3g′** at different stage

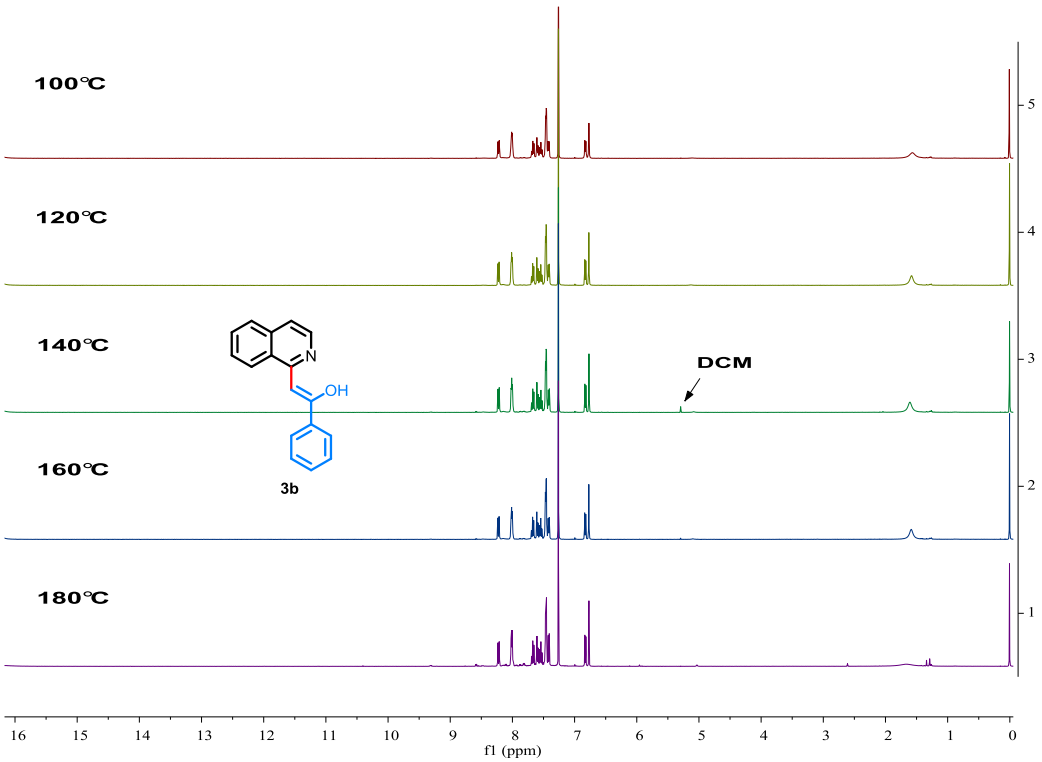


Figure S11. ^{1}H NMR spectra of product **3b** under different temperatures

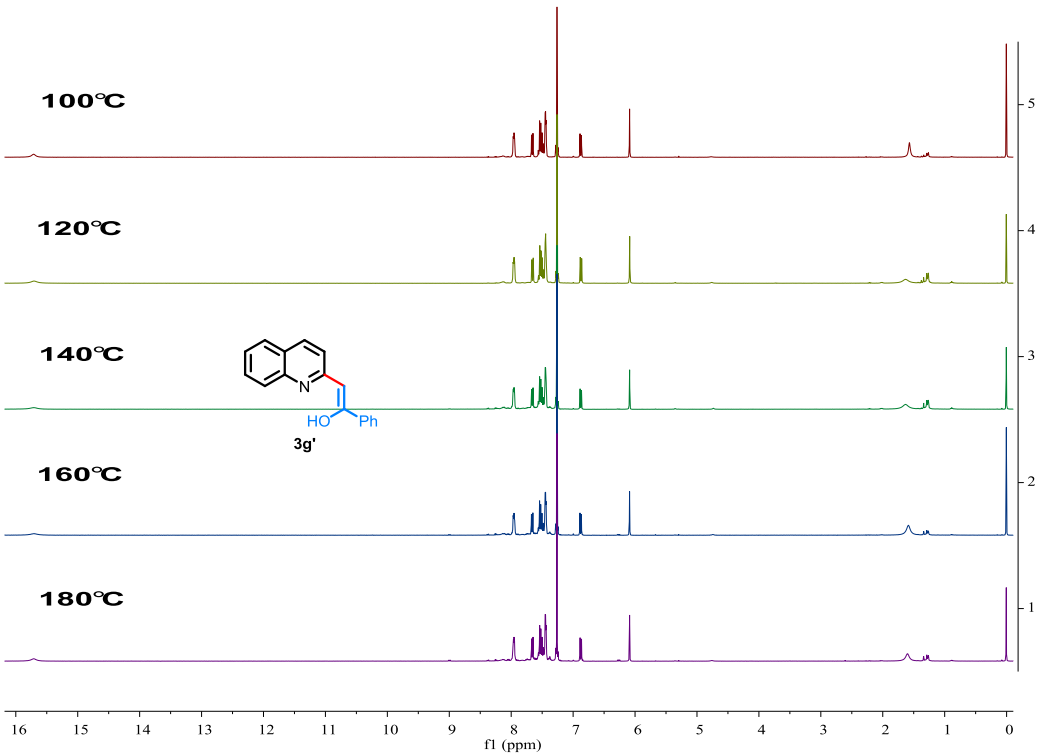
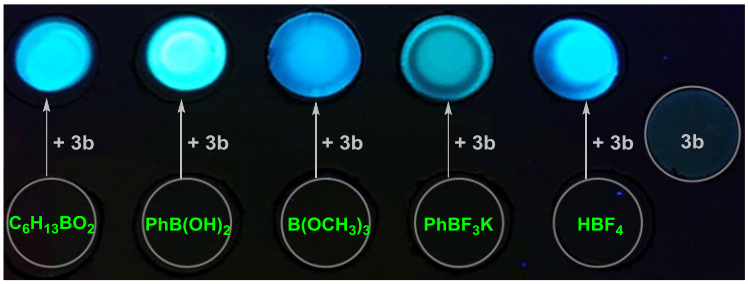


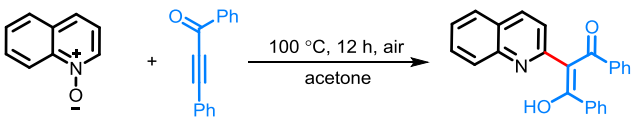
Figure S12. ^{1}H NMR spectra of product **3g′** under different temperatures

H. Detection experiment of boron compounds

We prepared solution of product **3b** and boron compounds, all the concentrations of the boron compounds and product **3b** were 10 mM. Among them, product **3b** was dissolved in EtOH, $C_6H_{13}BO_2$(BHpin), $PhB(OH)_2$ and $B(OCH_3)_3$ were dissolved in DCM, $PhBF_3K$ was dissolved in H_2O, and HBF_4 was dissolved in EtOH. Firstly, $C_6H_{13}BO_2$(BHpin), $PhB(OH)_2$, $B(OCH_3)_3$, $PhBF_3K$ and HBF_4 were spotted on the top of the TLC plate from left to right, and then boron compounds were spotted on the bottom of the TLC plate from left to right. Product **3b** was spotted on the right side of the TLC plate. Finally, the product **3b** was spotted on the top of the TLC plate from left to right, covering the previous boron compounds. The TLC plate was heated at 60 ℃ for ten minutes and placed under 365 nm UV lamp to observe the results.

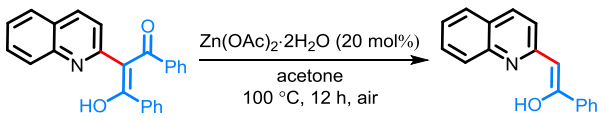


I. Mechanistic study



1h **2b** **8** 75%

A pressure tube was charged with quinoline *N*-oxide **1h** (0.05 mmol), ynone **2b** (0.06 mmol) and acetone (0.5 mL). The reaction mixture was stirred at 100 ℃ for 12 h under air atmosphere. After cooling to room temperature, the mixture was filtered through a short Celite pad and all volatiles were removed under reduced pressure. The residue was purified by silica gel chromatography using PE/EA eluent to afford the product **8**. Yellow solid (13.2 mg, 75% yield). PE/EA = 20:1, R_f = 0.32. ^{1}H NMR (400 MHz, $CDCl_3$): δ 17.12 (s, 1H), 7.96 (s, 2H), 7.73–7.69 (m, 3H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.47–7.42 (m, 3H), 7.27–7.21 (m, 1H), 7.18–7.12 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 192.6, 154.5, 142.6, 142.2, 138.3, 136.5, 131.6, 131.4, 129.8, 129.3, 128.2, 127.8, 127.7, 125.1, 123.7, 119.8, 118.7, 106.2. IR (KBr): 3215, 2988, 1633, 1588, 1400, 1372, 1267, 738 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{24}H_{17}NO_2Na$ $[M+Na]^+$ 374.1157, found 374.1150.



8 **3g'** 95%

A pressure tube was charged with $Zn(OAc)_2 \cdot 2H_2O$ (2.2 mg, 0.01 mmol), (*E*)-3-hydroxy-1,3-diphenyl-2-(quinolin-2-yl)prop-2-en-1-one **8** (17.6 mg, 0.05 mmol) and acetone (0.5 mL). The reaction mixture was stirred at 100 ℃ for 12 h under air atmosphere. After cooling to room temperature, the mixture was filtered through a short Celite pad and all volatiles were removed under reduced pressure. The residue was purified by silica gel chromatography using PE/EA eluent to afford the product **3g'**.

J. References

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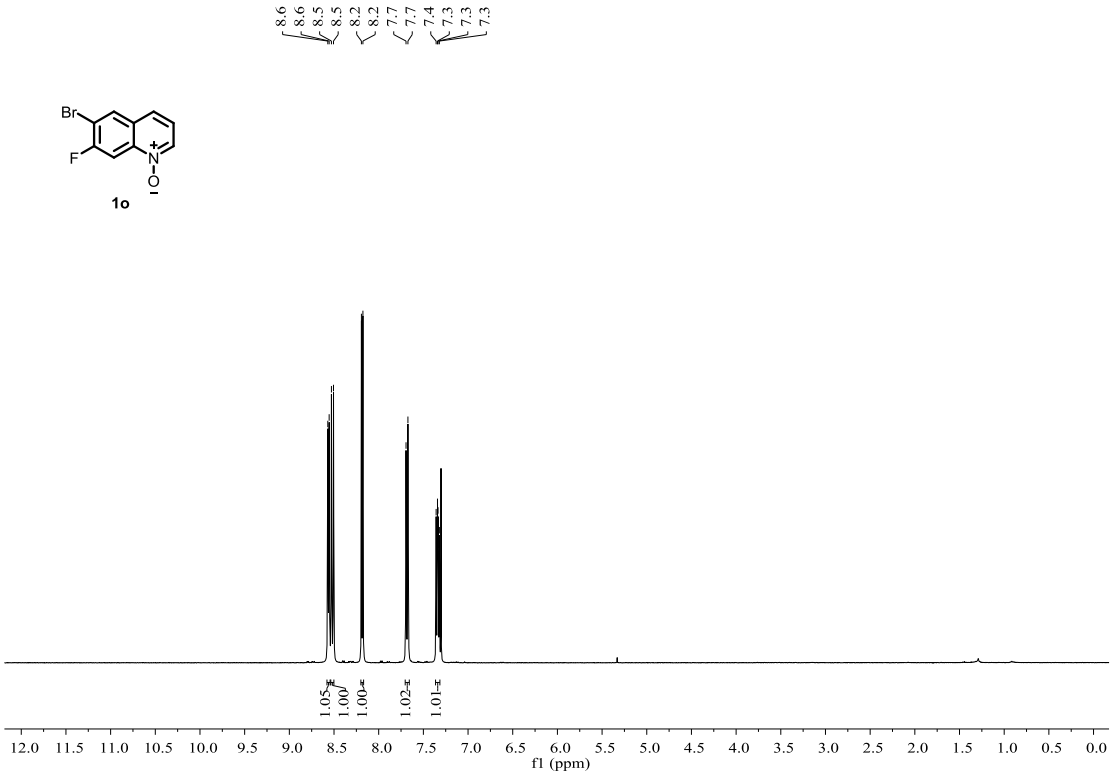
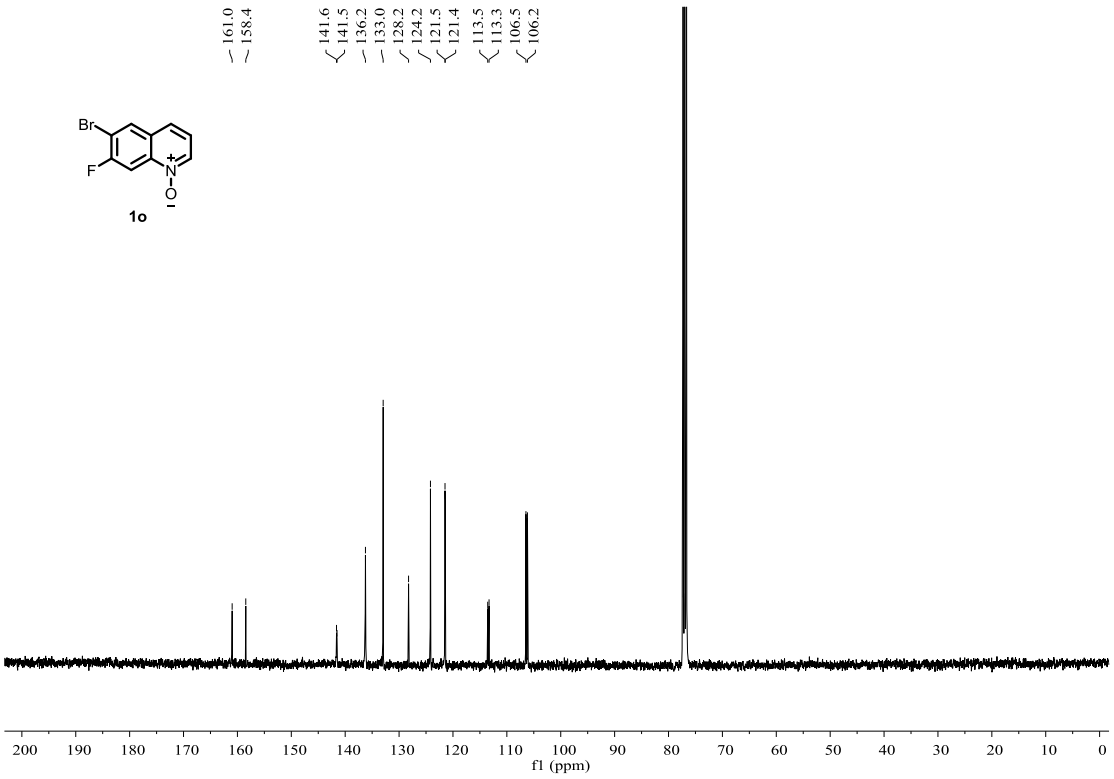
K. NMR spectra

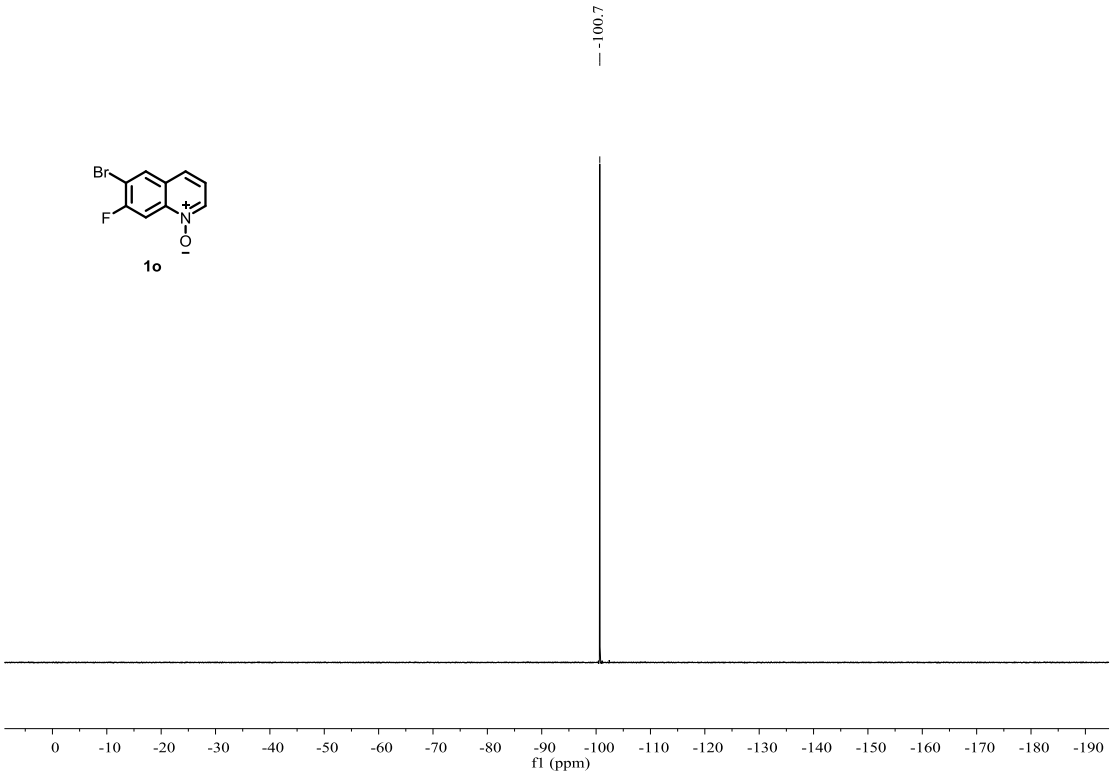
^{1}H NMR of **1o** (400 MHz, $CDCl_3$)



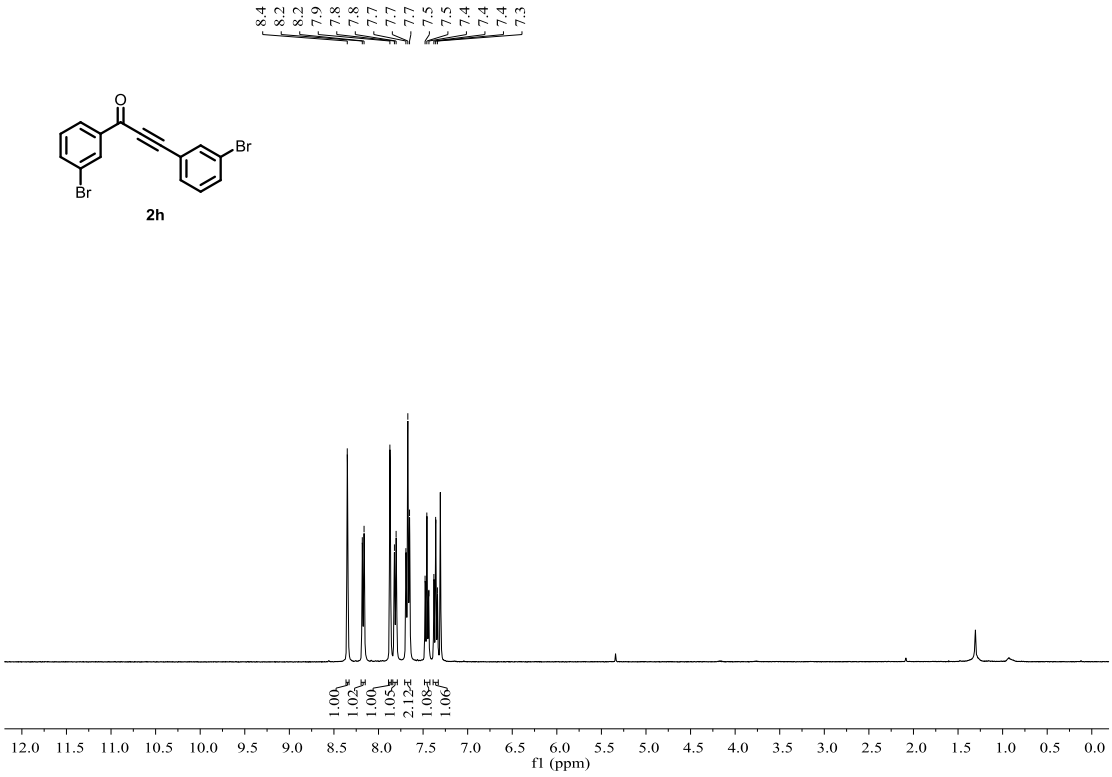
^{13}C NMR of **1o** (100 MHz, $CDCl_3$)



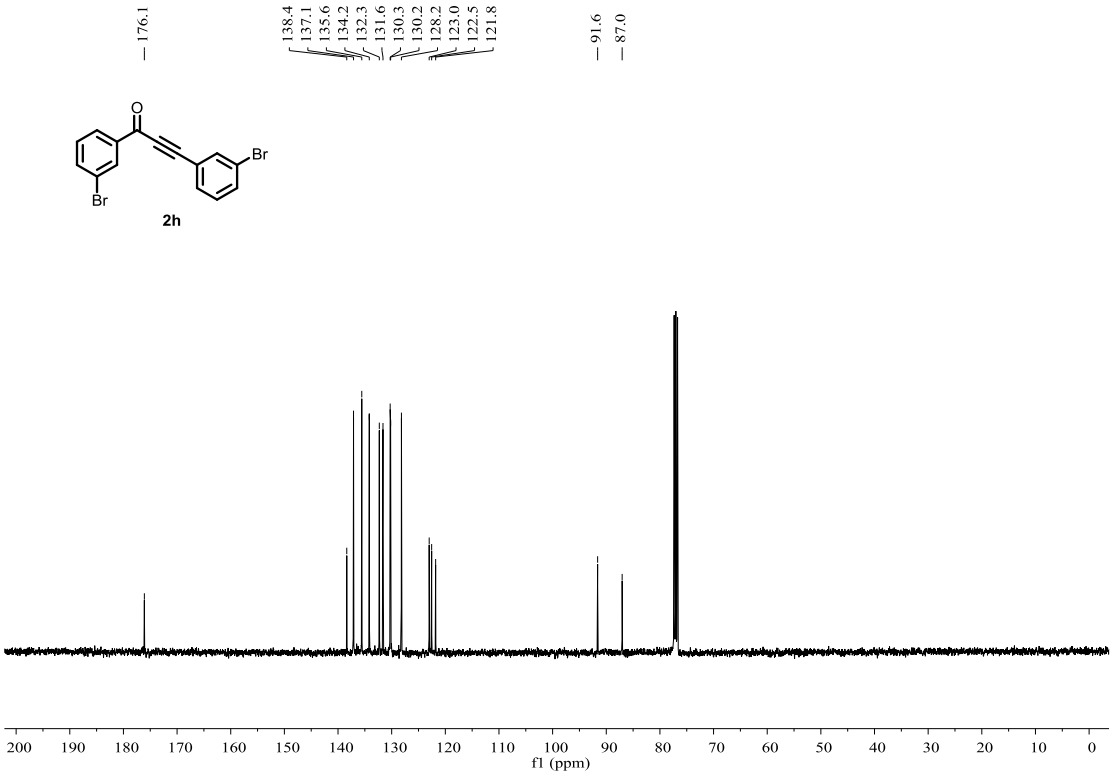
^{19}F NMR of **1o** (376 MHz, $CDCl_3$)



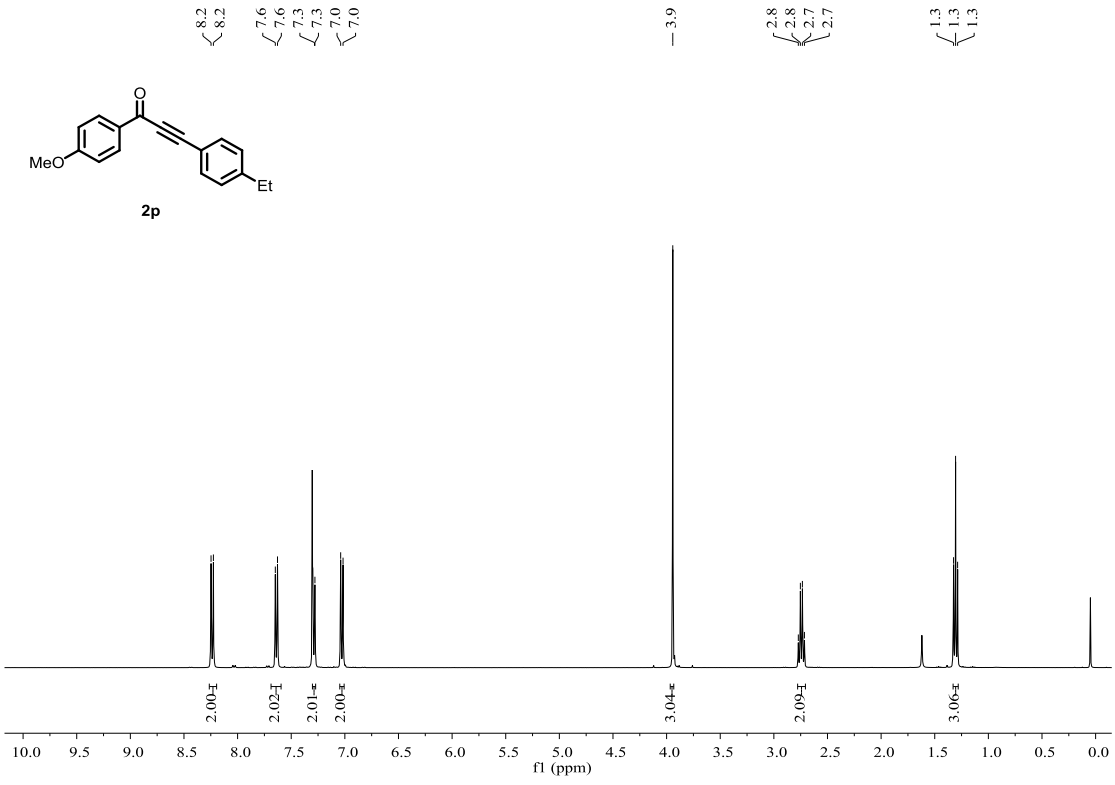
^{1}H NMR of **2h** (400 MHz, $CDCl_3$)



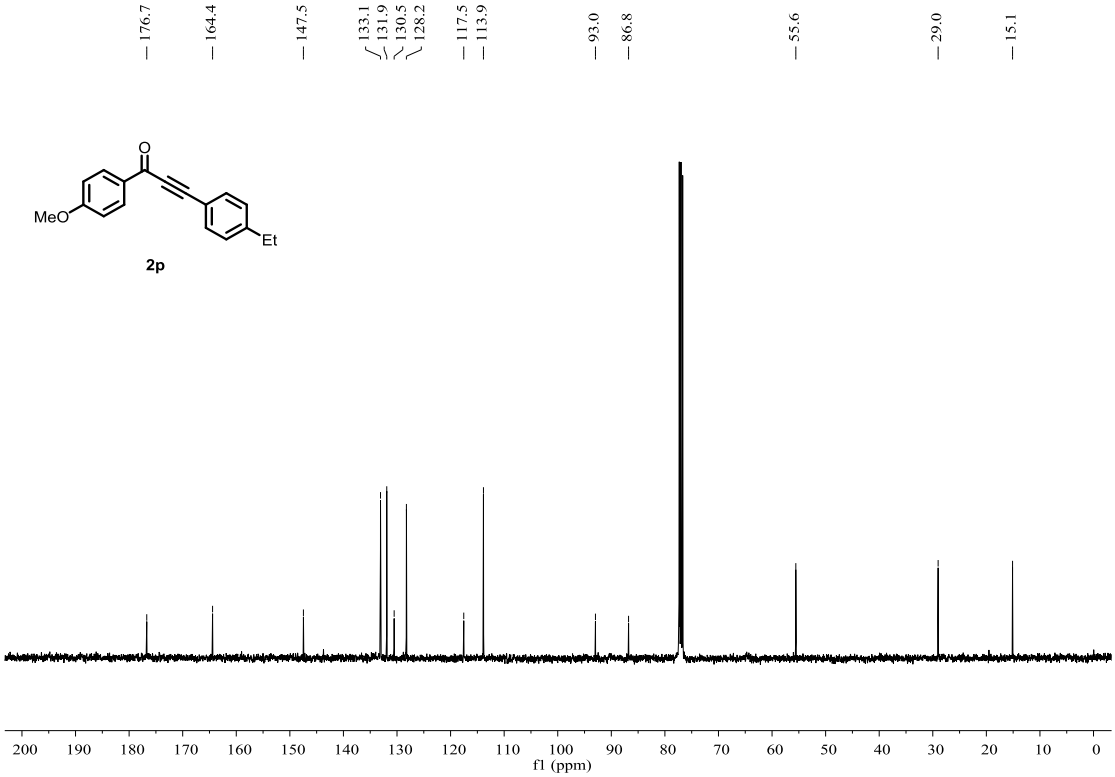
^{13}C NMR of **2h** (100 MHz, $CDCl_3$)



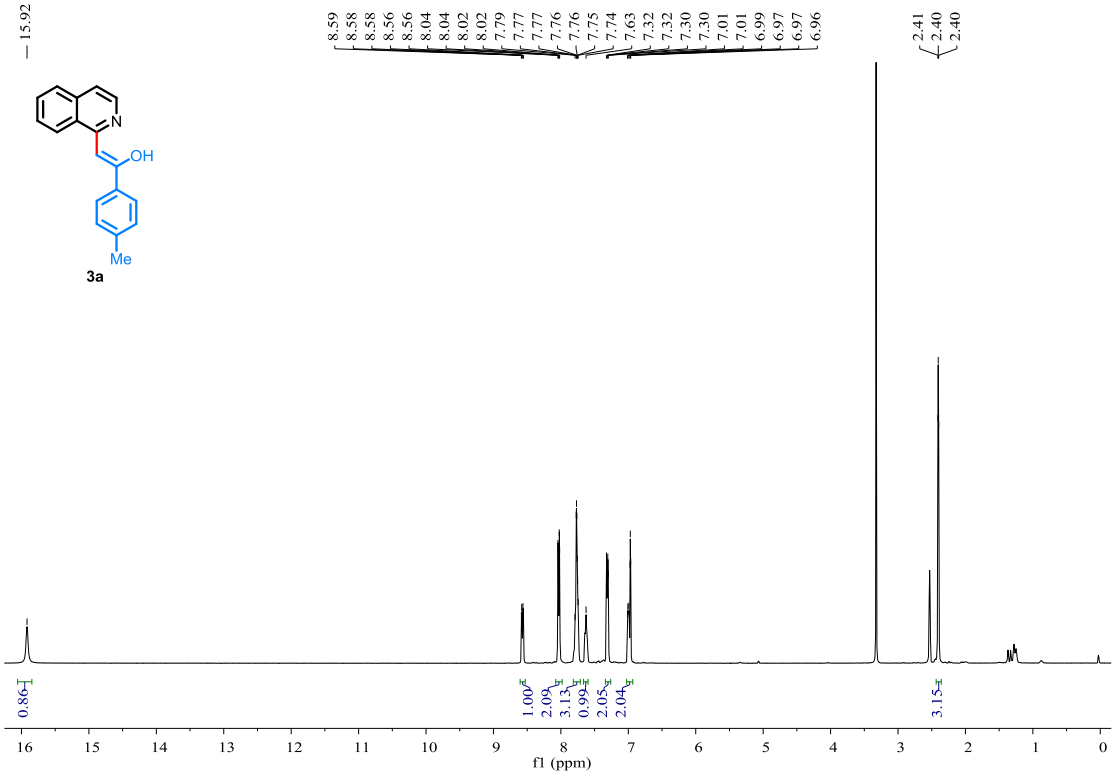
^{1}H NMR of **2p** (400 MHz, $CDCl_3$)



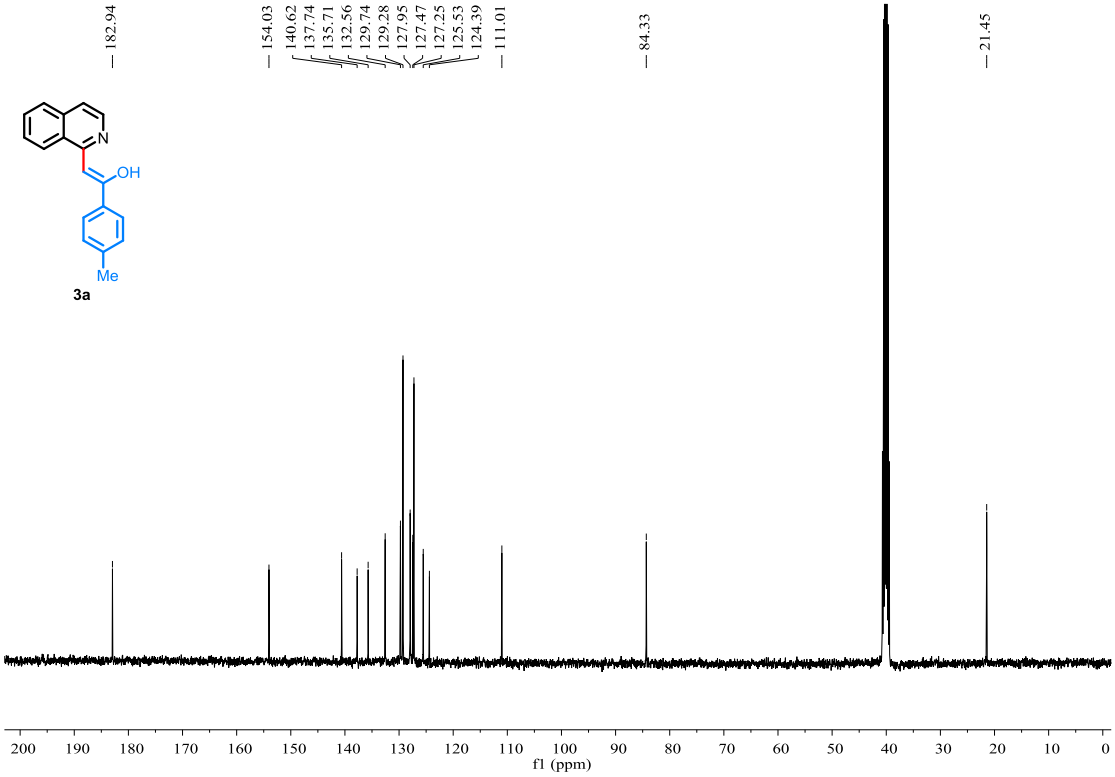
^{13}C NMR of **2p** (100 MHz, $CDCl_3$)



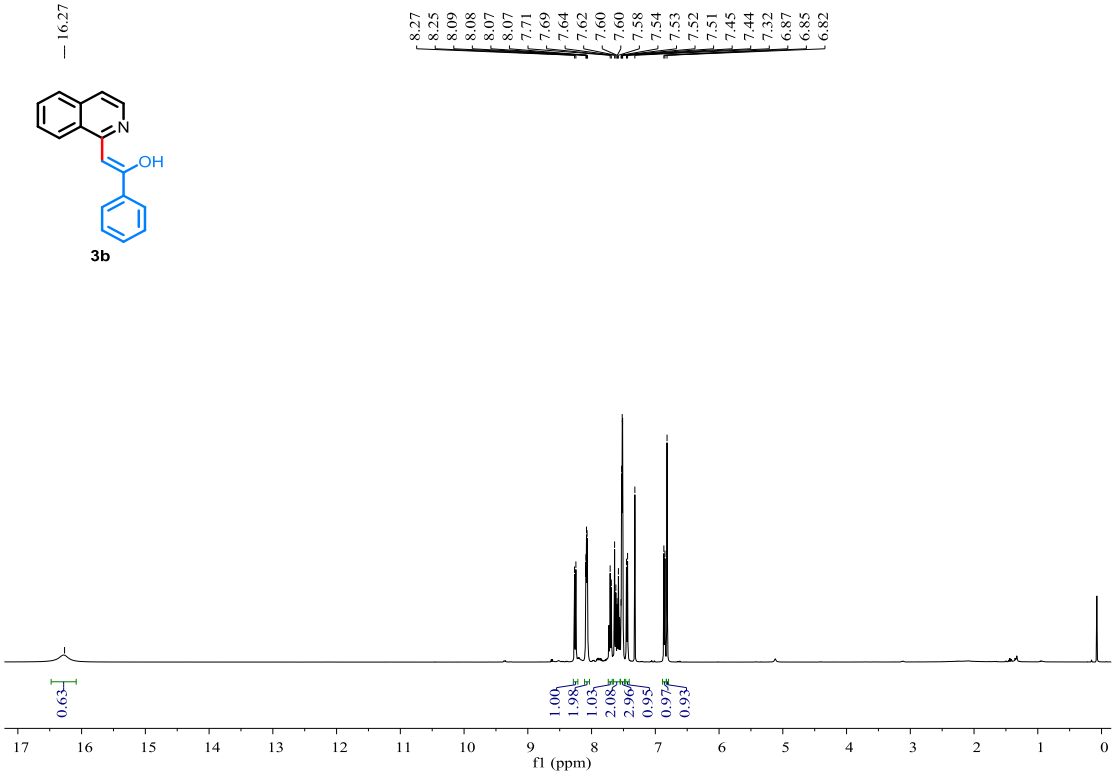
^{1}H NMR of **3a** (400 MHz, DMSO)



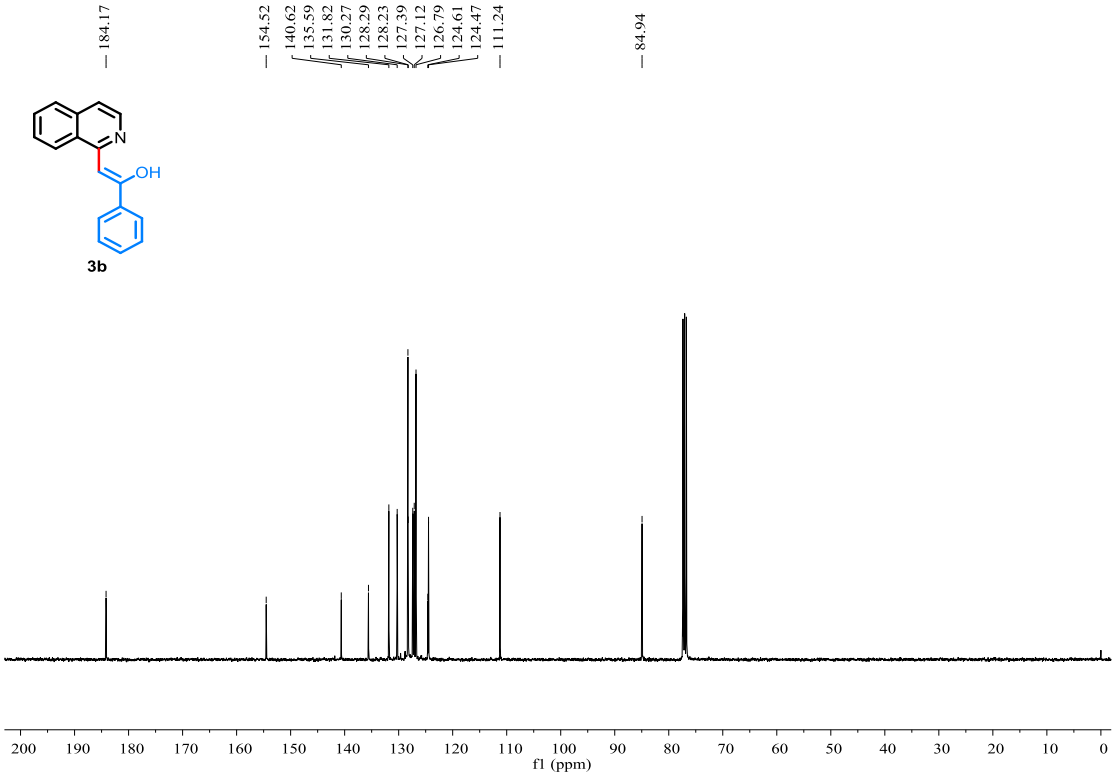
^{13}C NMR of **3a** (100 MHz, DMSO)



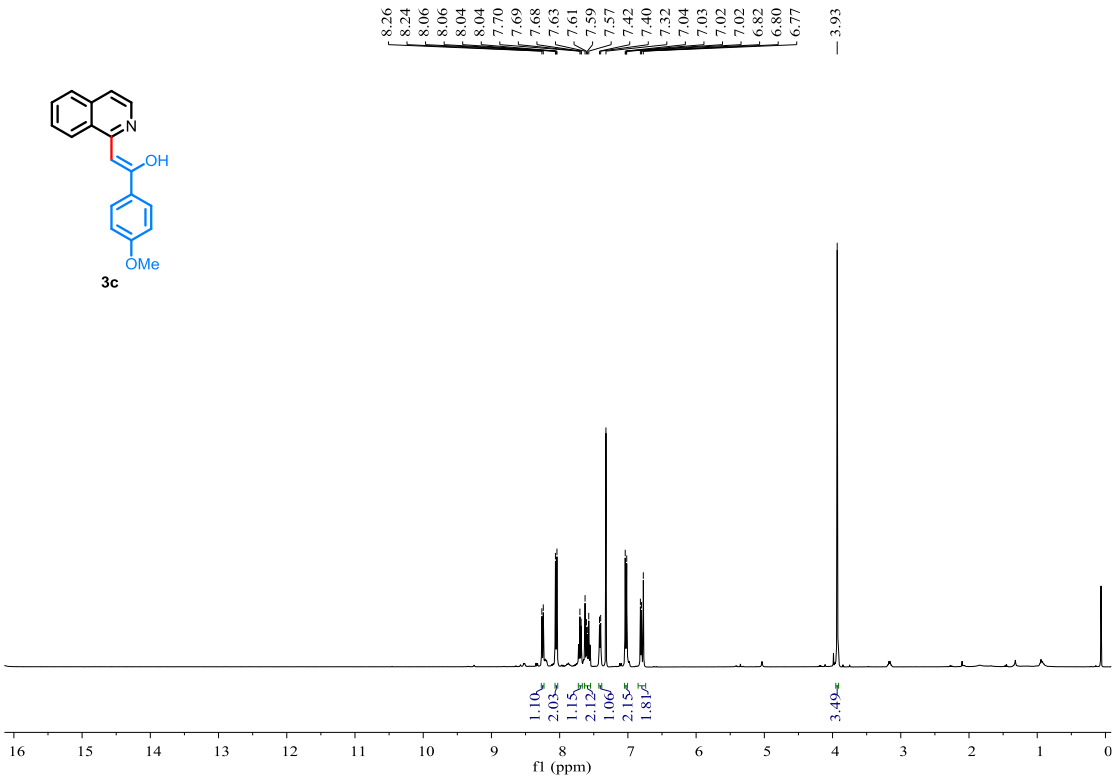
^{1}H NMR of **3b** (400 MHz, $CDCl_3$)



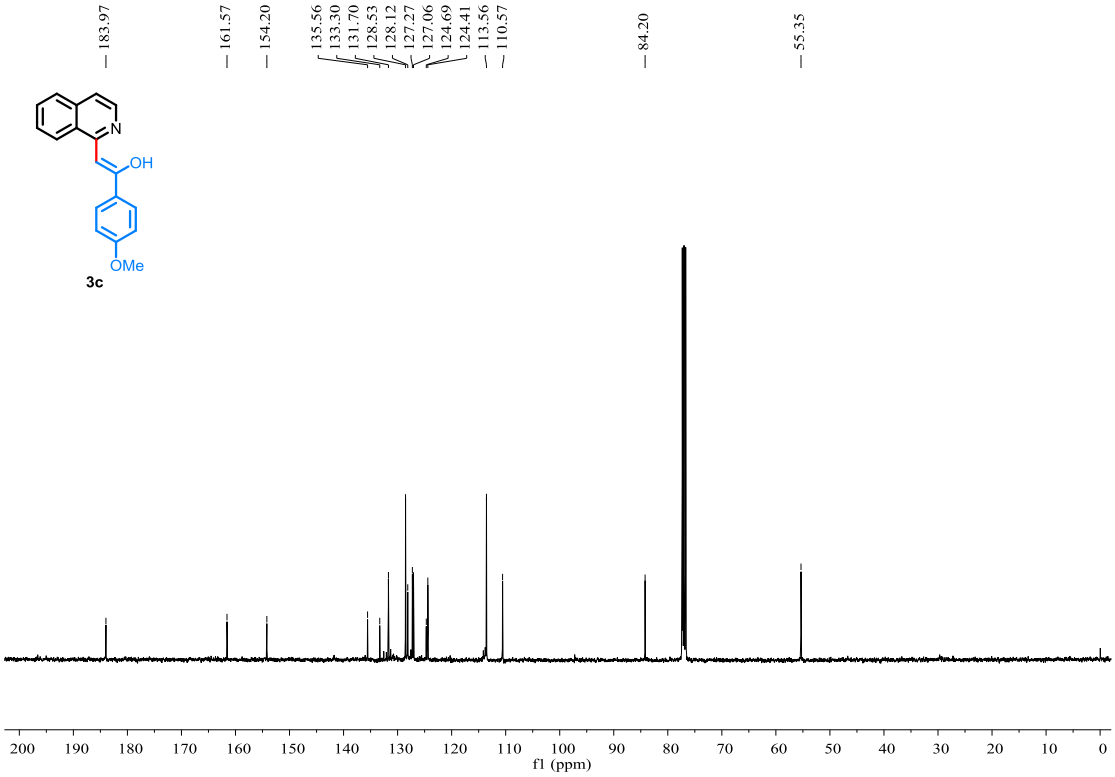
^{13}C NMR of **3b** (100 MHz, $CDCl_3$)



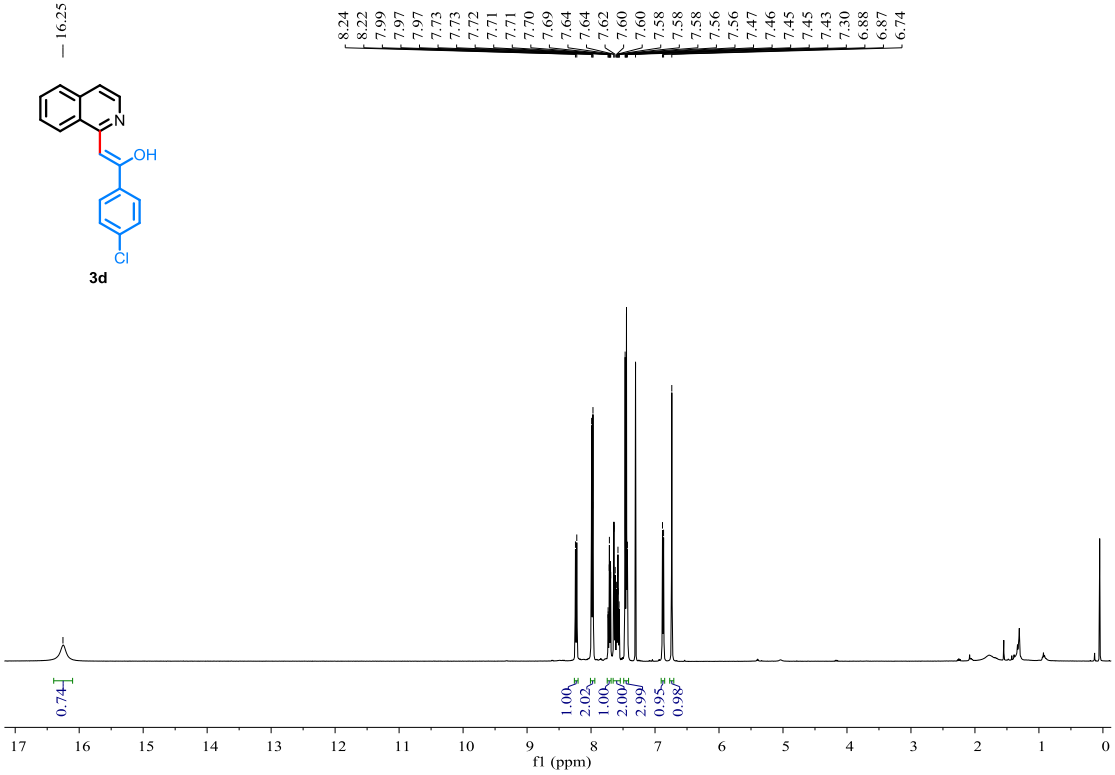
^{1}H NMR of **3c** (400 MHz, $CDCl_3$)



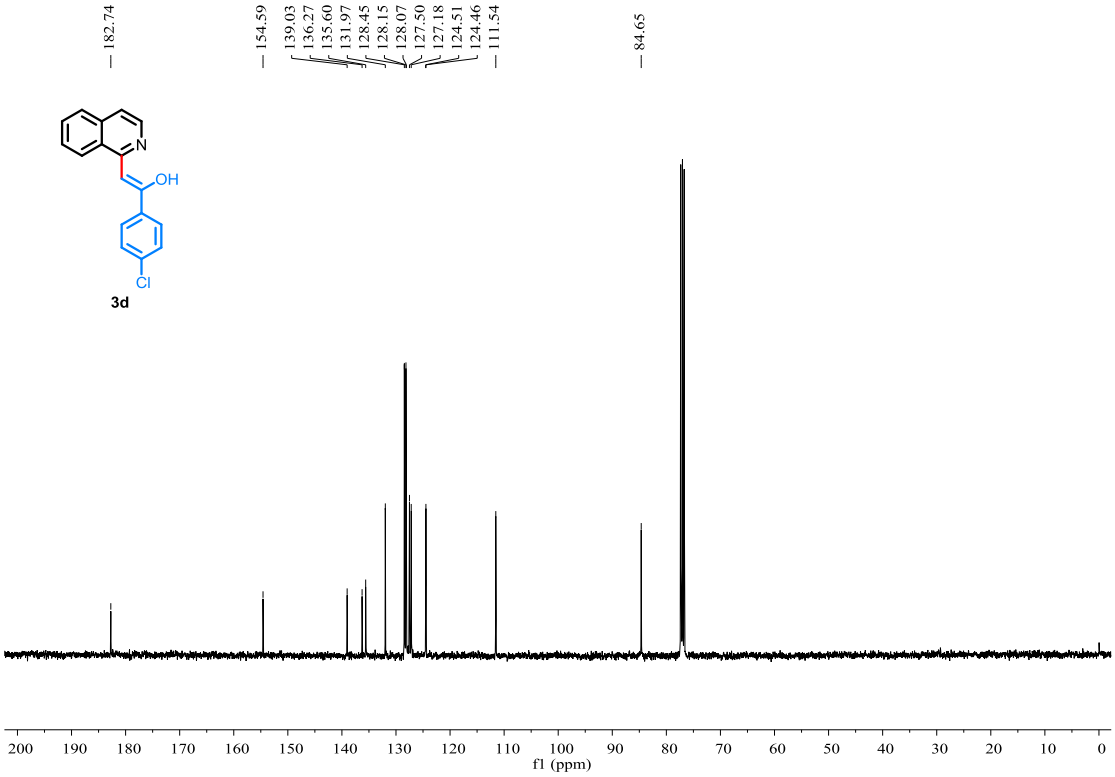
^{13}C NMR of **3c** (100 MHz, $CDCl_3$)



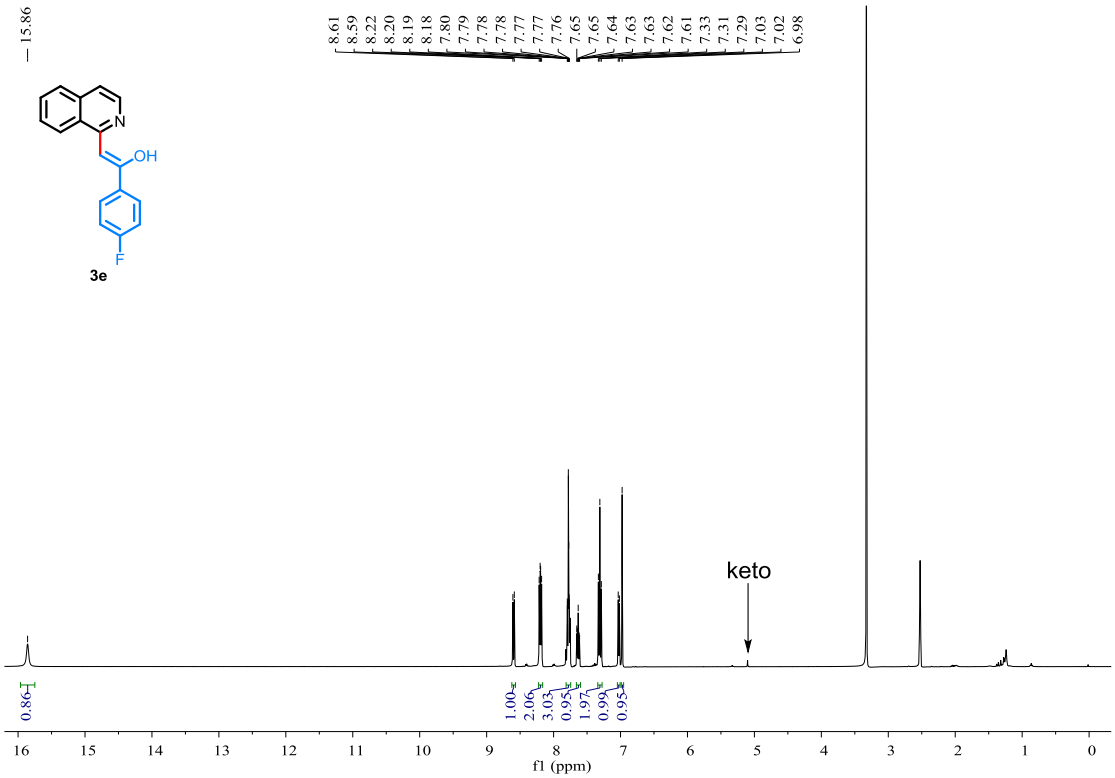
^{1}H NMR of **3d** (400 MHz, $CDCl_3$)



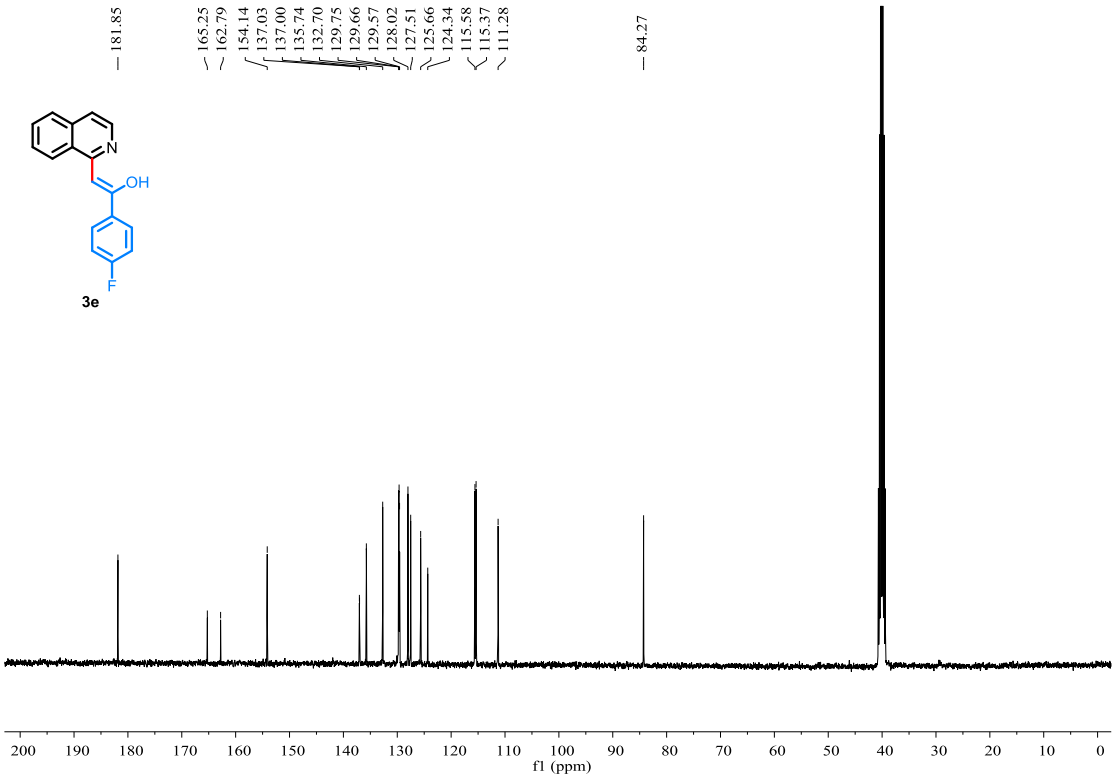
^{13}C NMR of **3d** (100 MHz, $CDCl_3$)



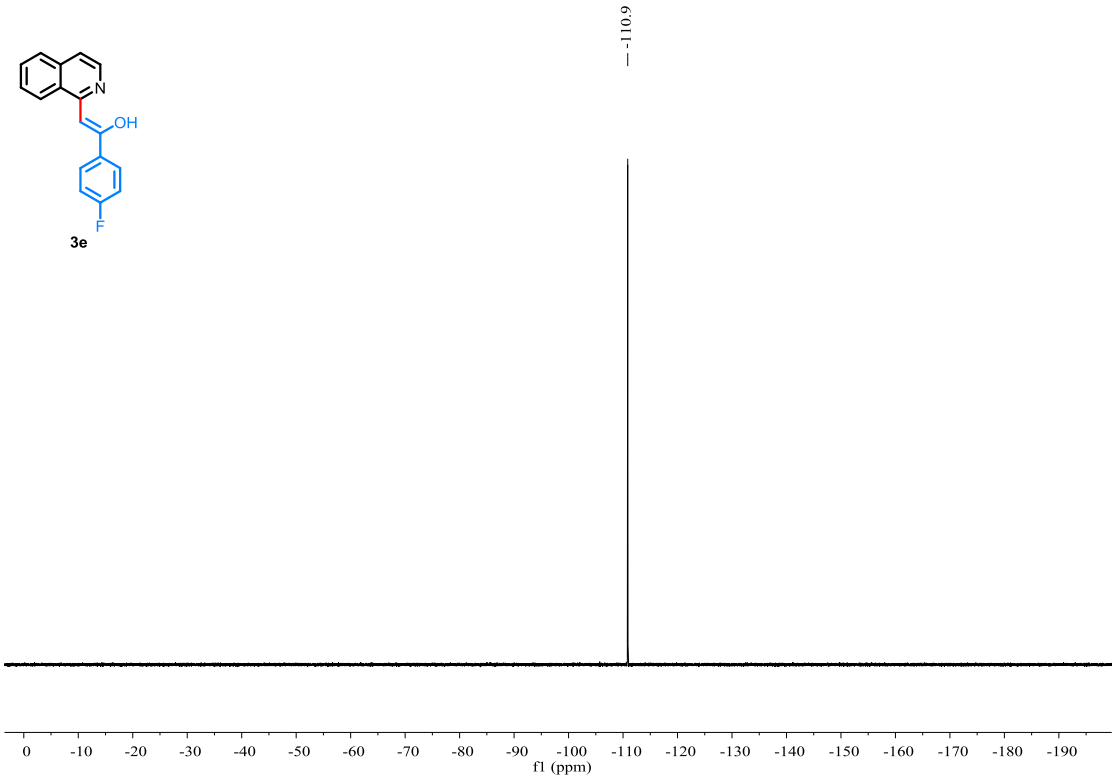
^{1}H NMR of **3e** (400 MHz, DMSO)



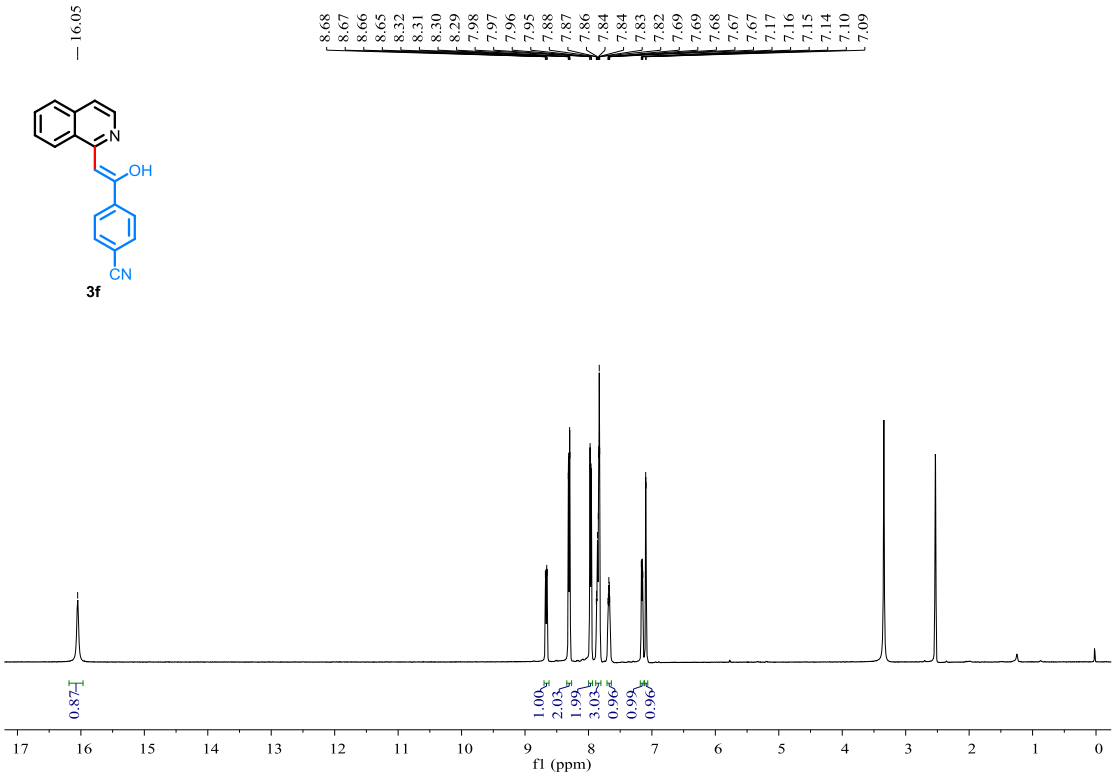
^{13}C NMR of **3e** (100 MHz, DMSO)



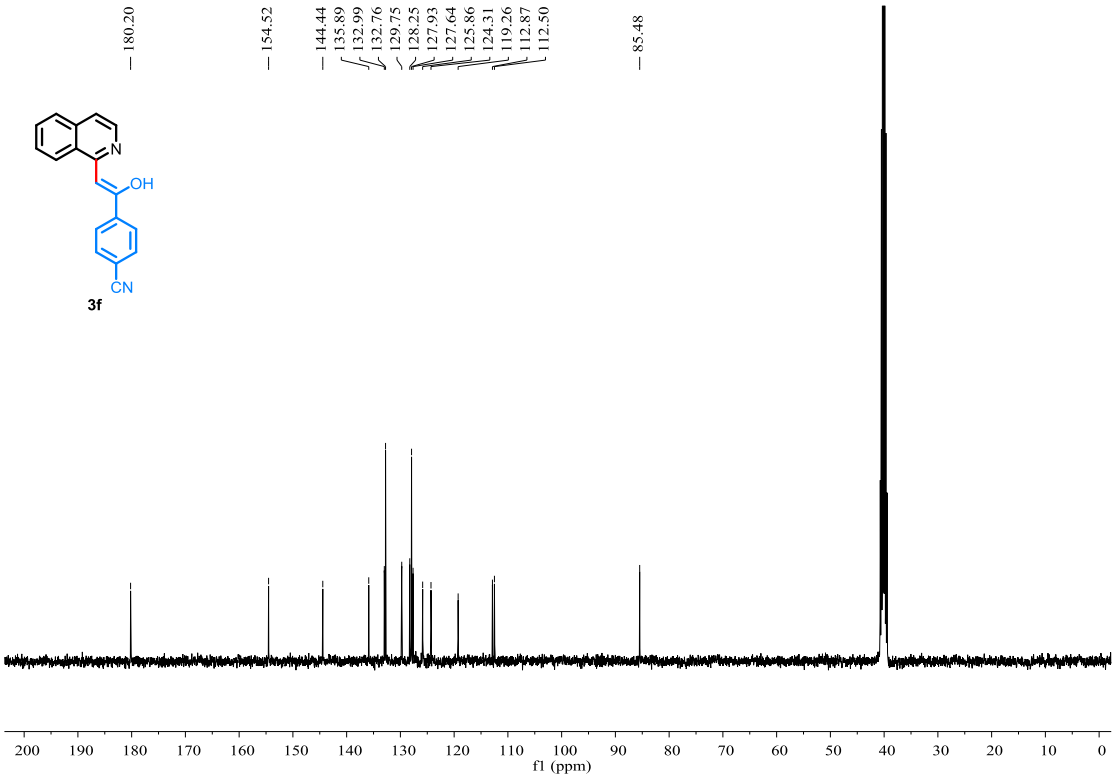
^{19}F NMR of **3e** (376 MHz, DMSO)



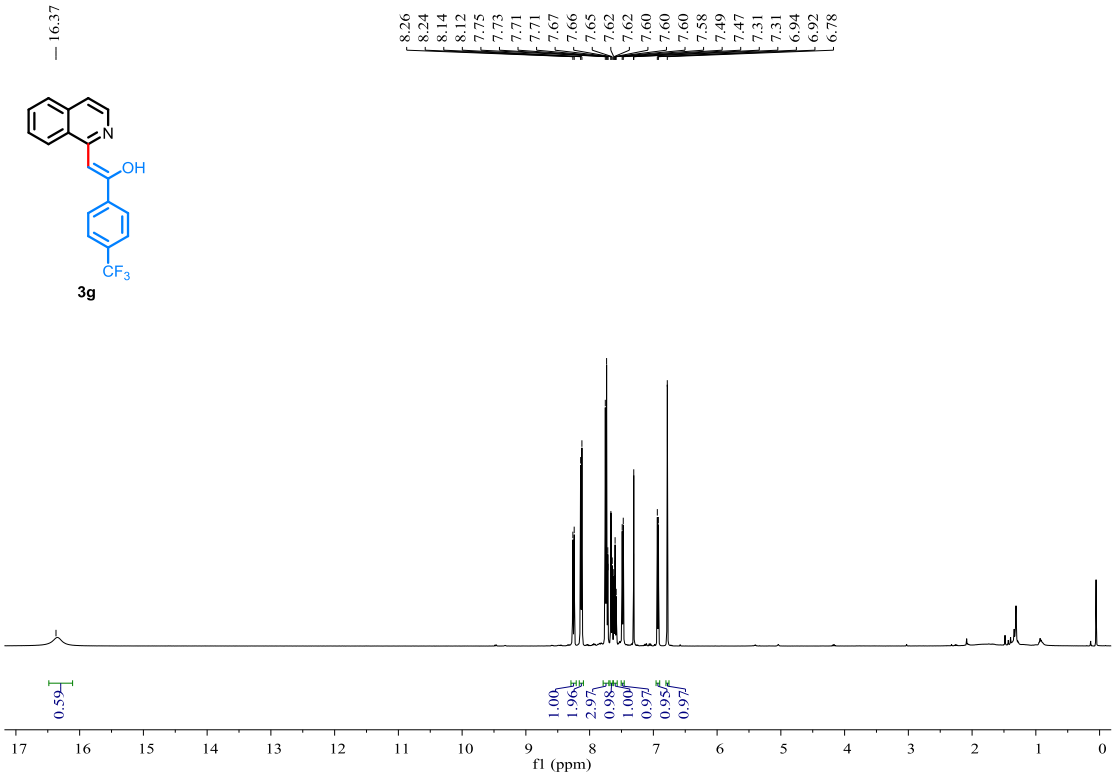
^{1}H NMR of **3f** (400 MHz, DMSO)



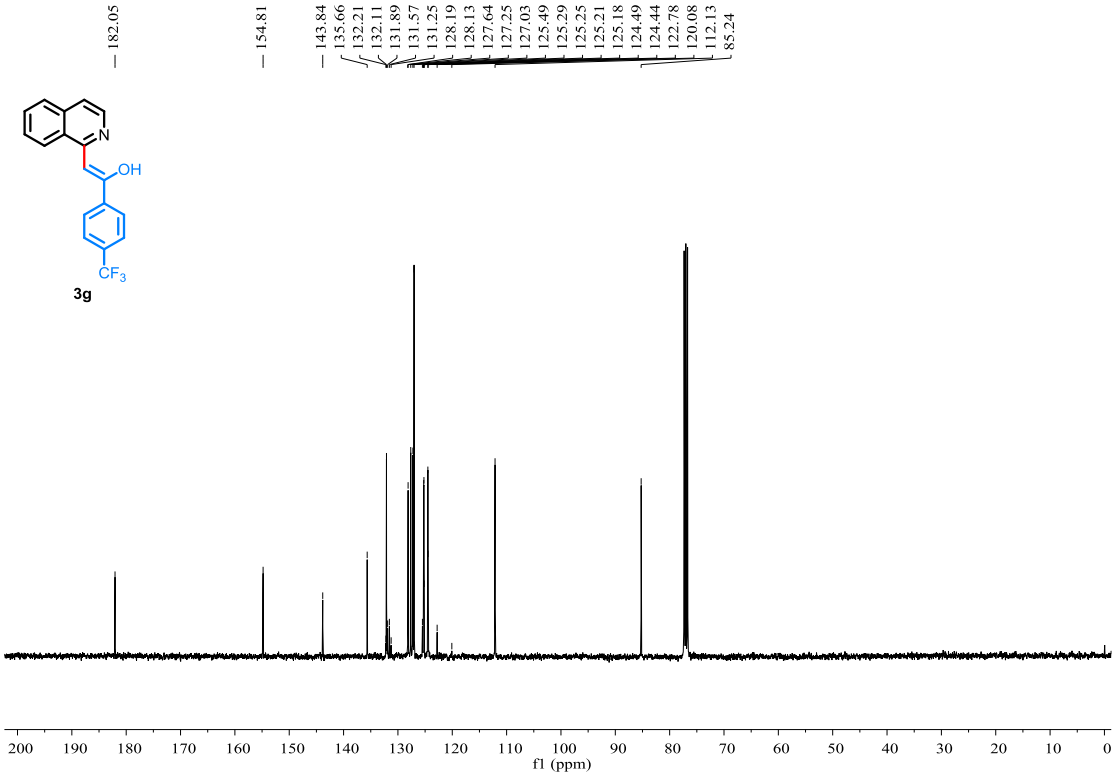
^{13}C NMR of **3f** (100 MHz, DMSO)



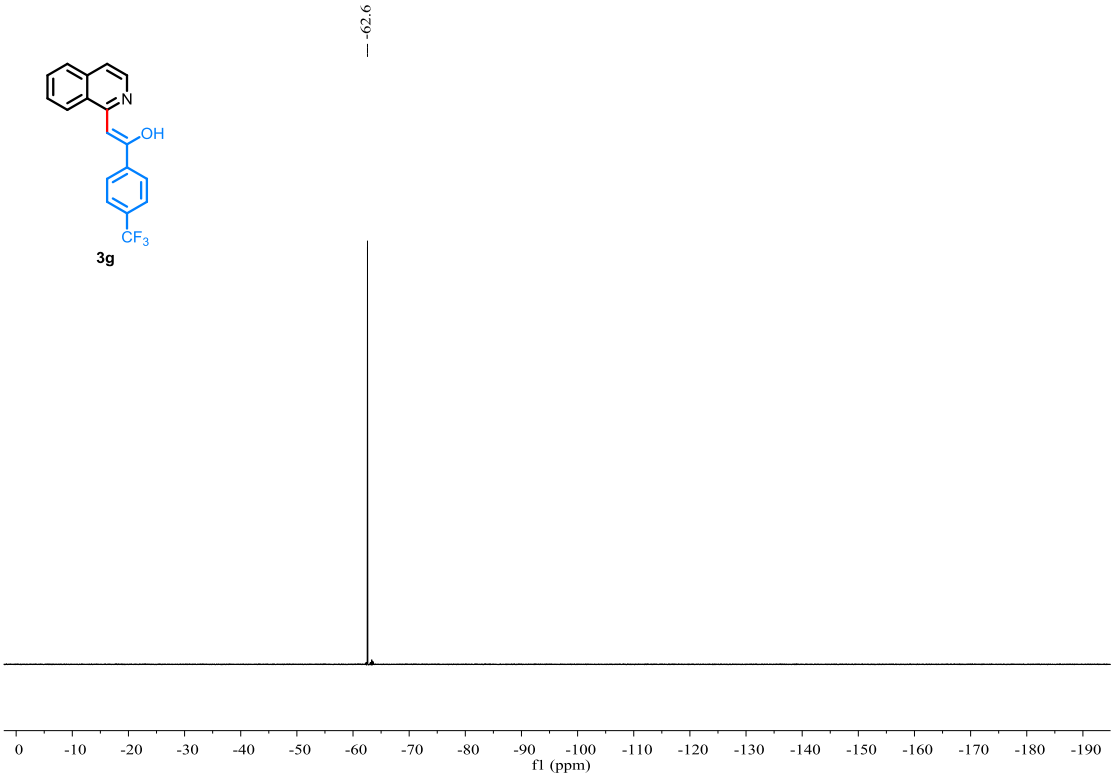
^{1}H NMR of **3g** (400 MHz, $CDCl_3$)



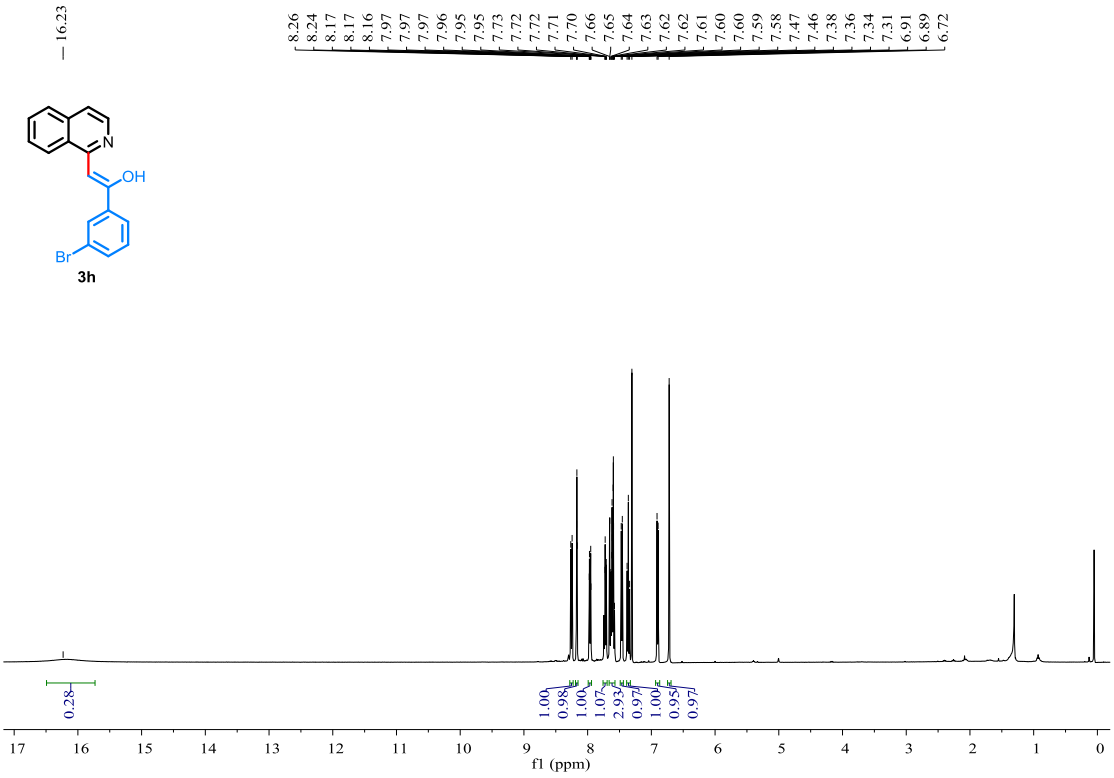
^{13}C NMR of **3g** (100 MHz, $CDCl_3$)



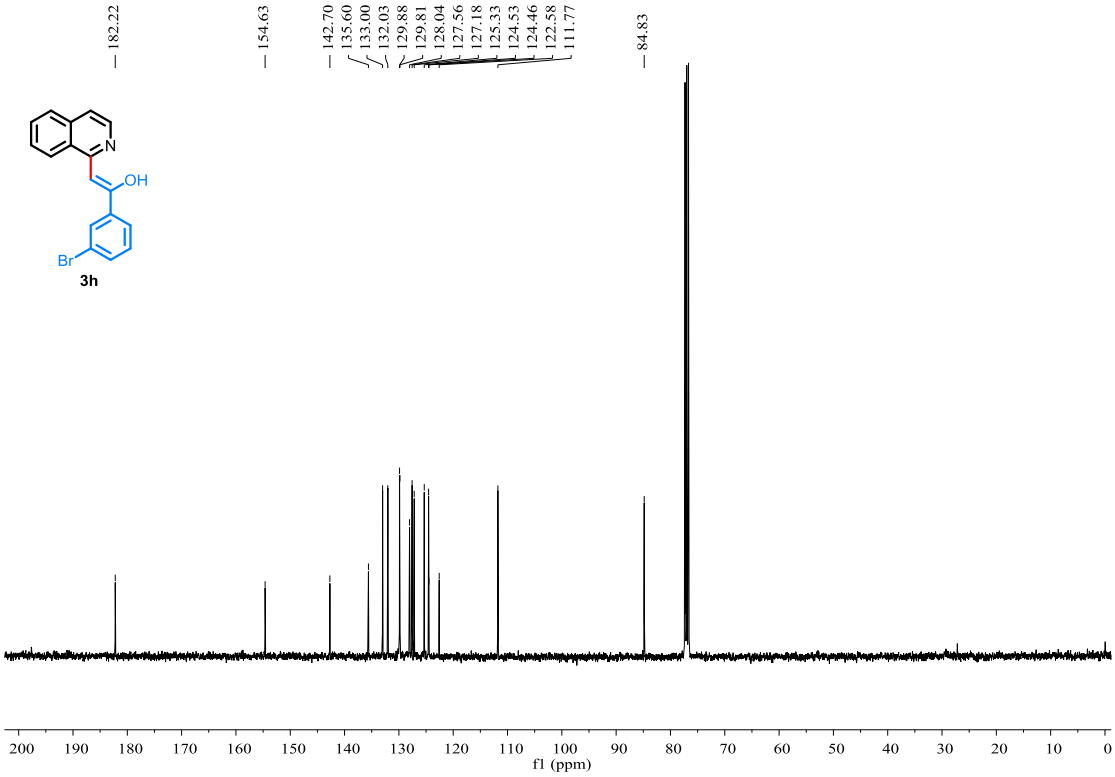
^{19}F NMR of **3g** (376 MHz, $CDCl_3$)



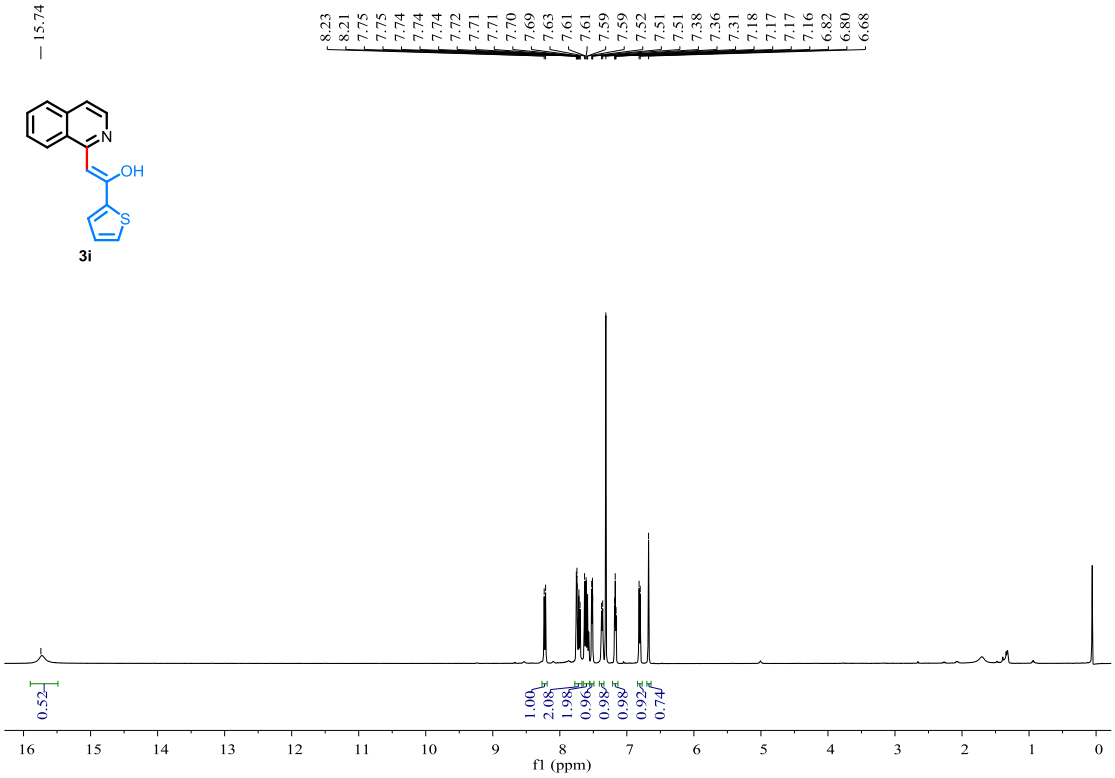
^{1}H NMR of **3h** (400 MHz, $CDCl_3$)



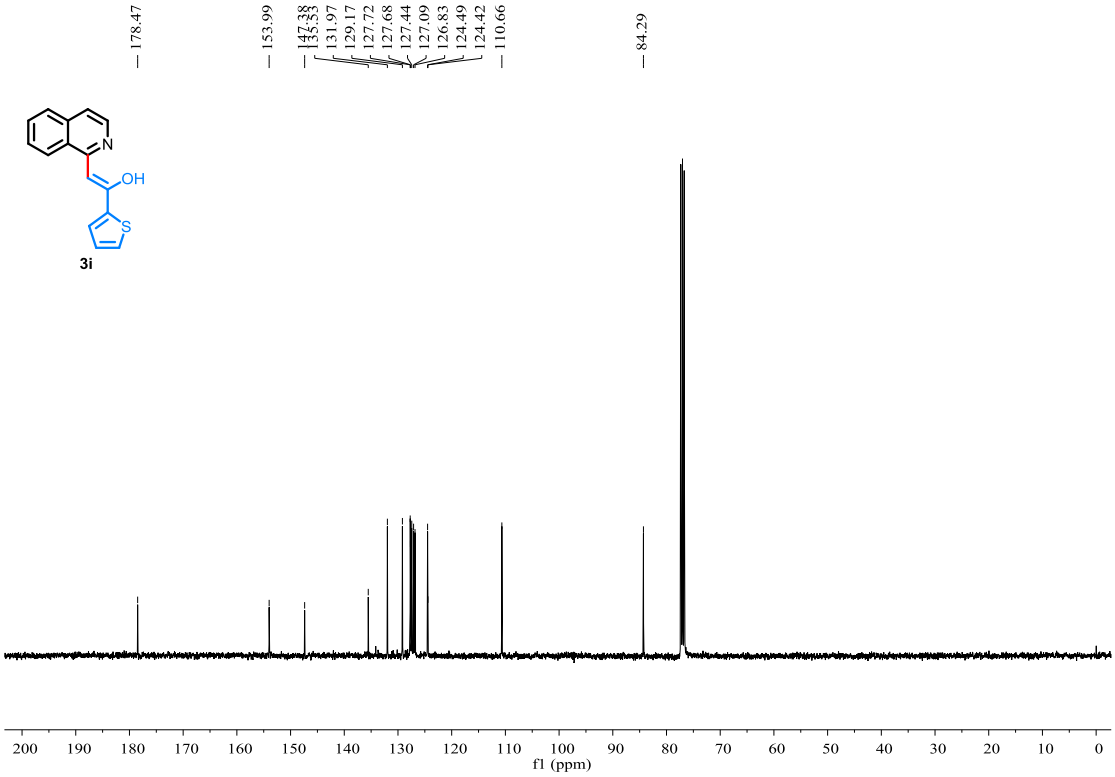
^{13}C NMR of **3h** (100 MHz, $CDCl_3$)



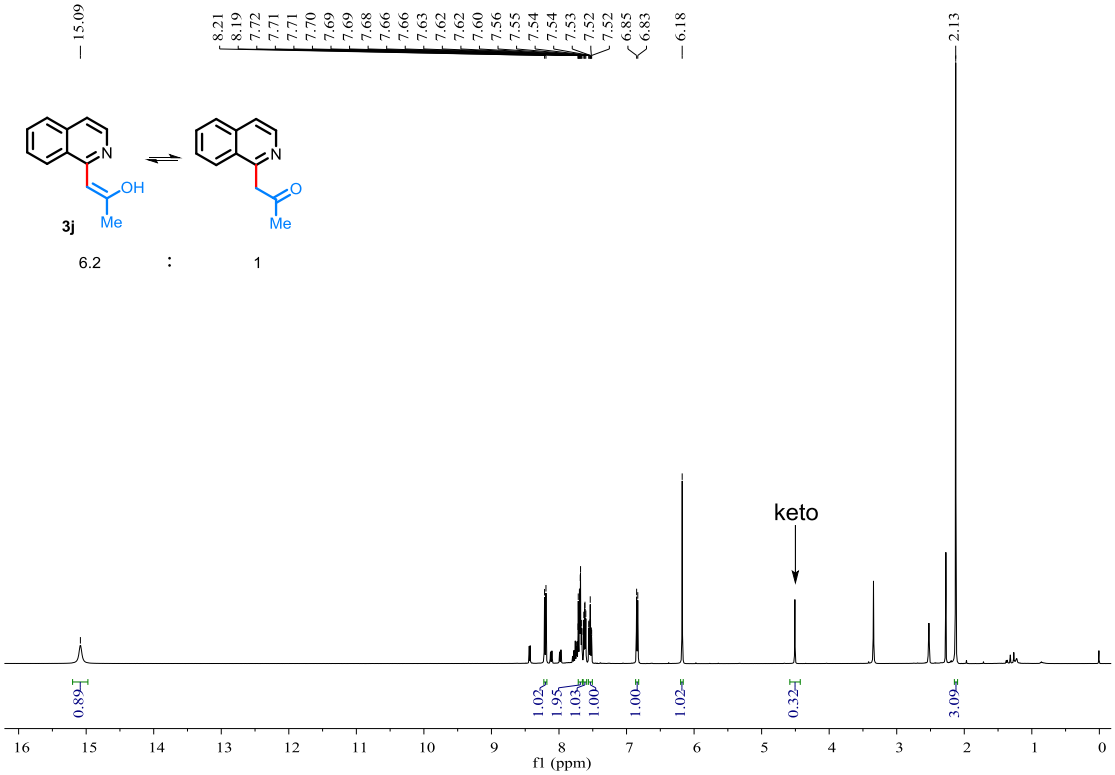
^{1}H NMR of **3i** (400 MHz, $CDCl_3$)



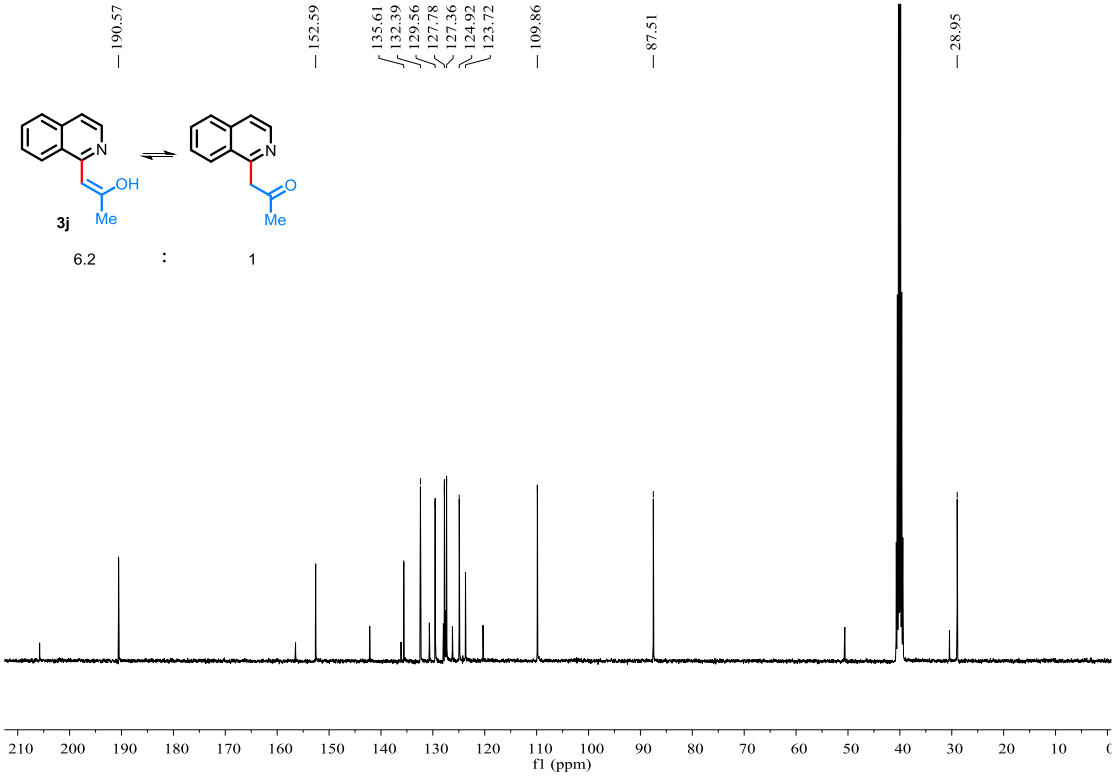
^{13}C NMR of **3i** (100 MHz, $CDCl_3$)



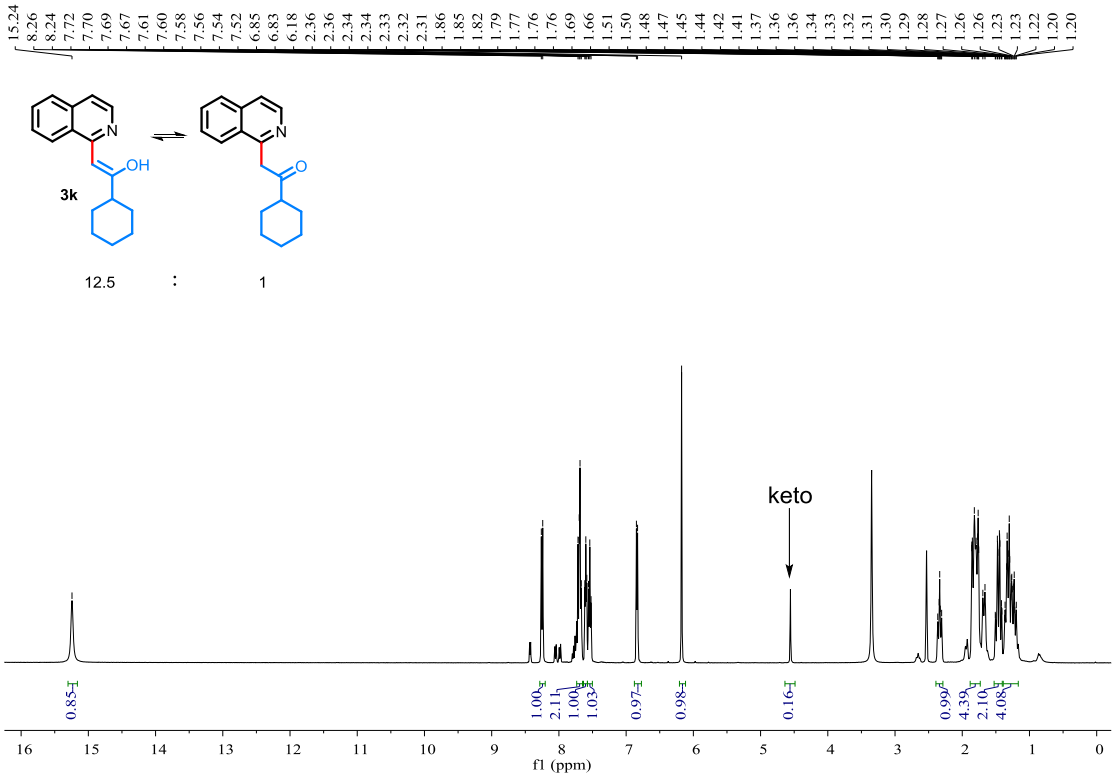
^{1}H NMR of **3j** (400 MHz, DMSO)



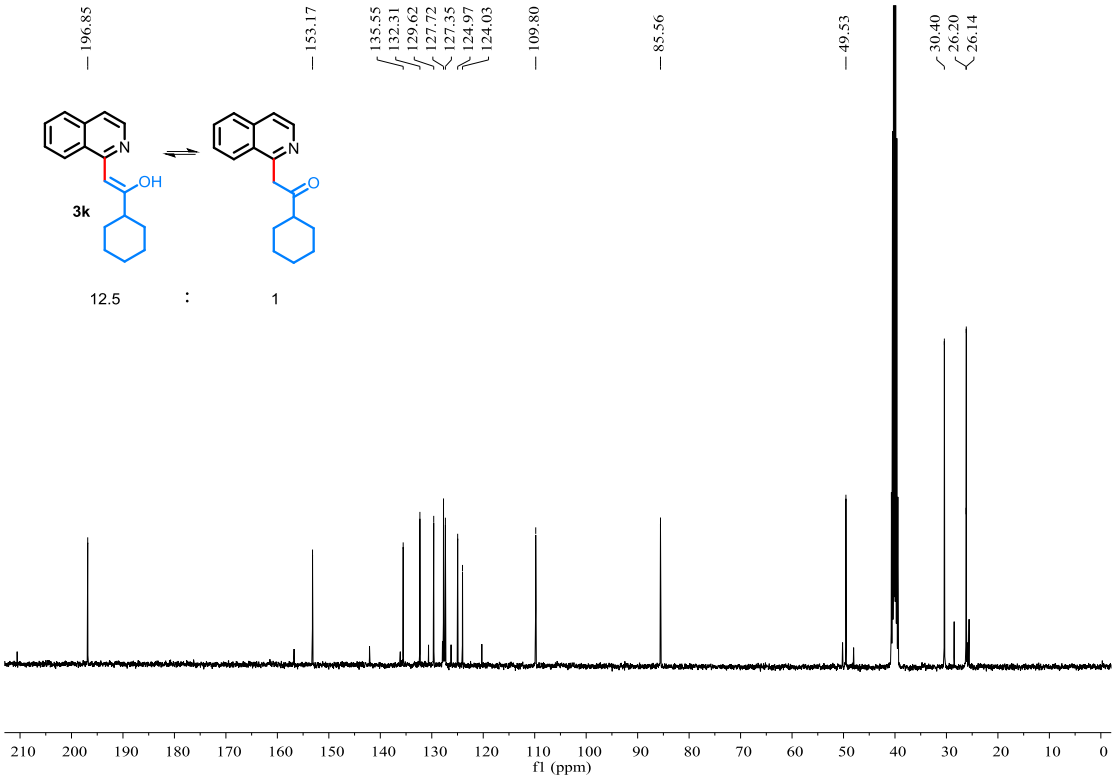
^{13}C NMR of **3j** (100 MHz, DMSO)



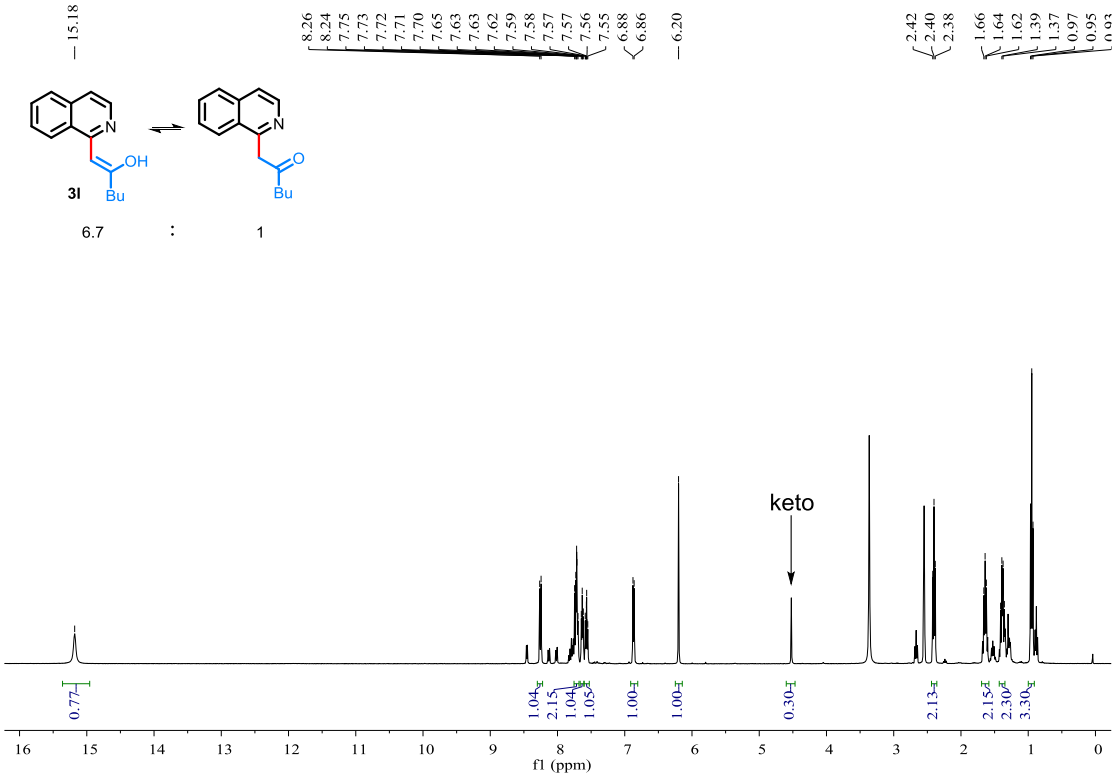
^{1}H NMR of **3k** (400 MHz, DMSO)



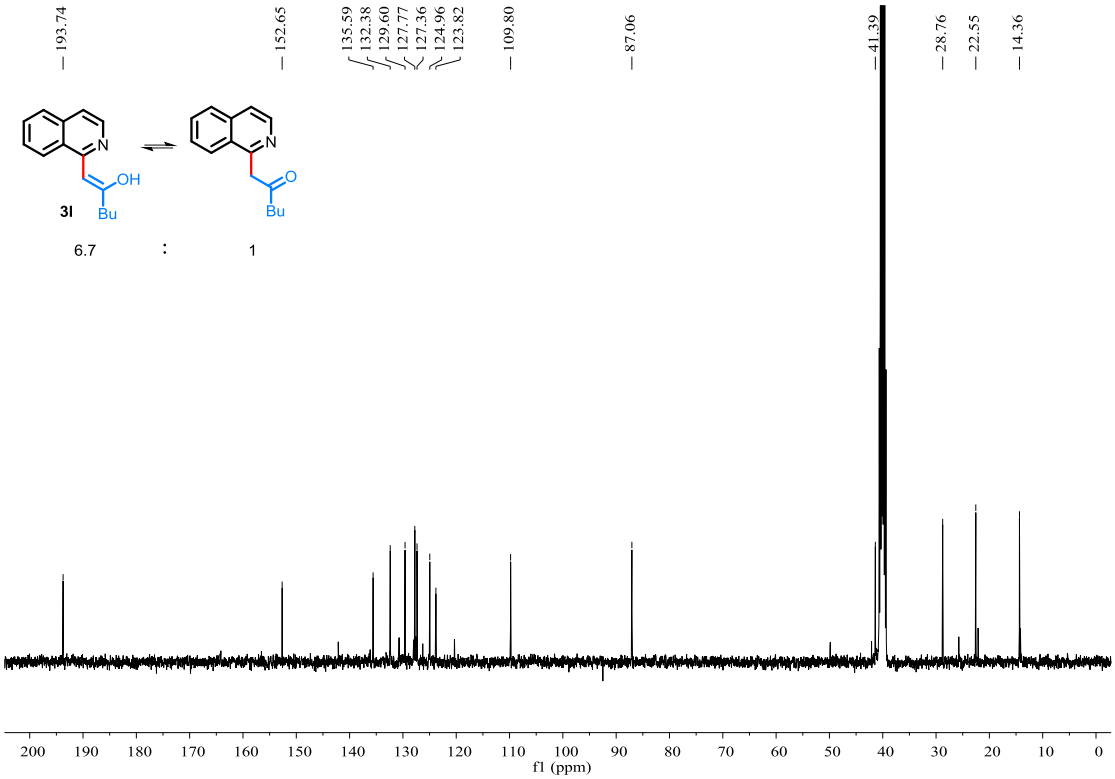
^{13}C NMR of **3k** (100 MHz, DMSO)



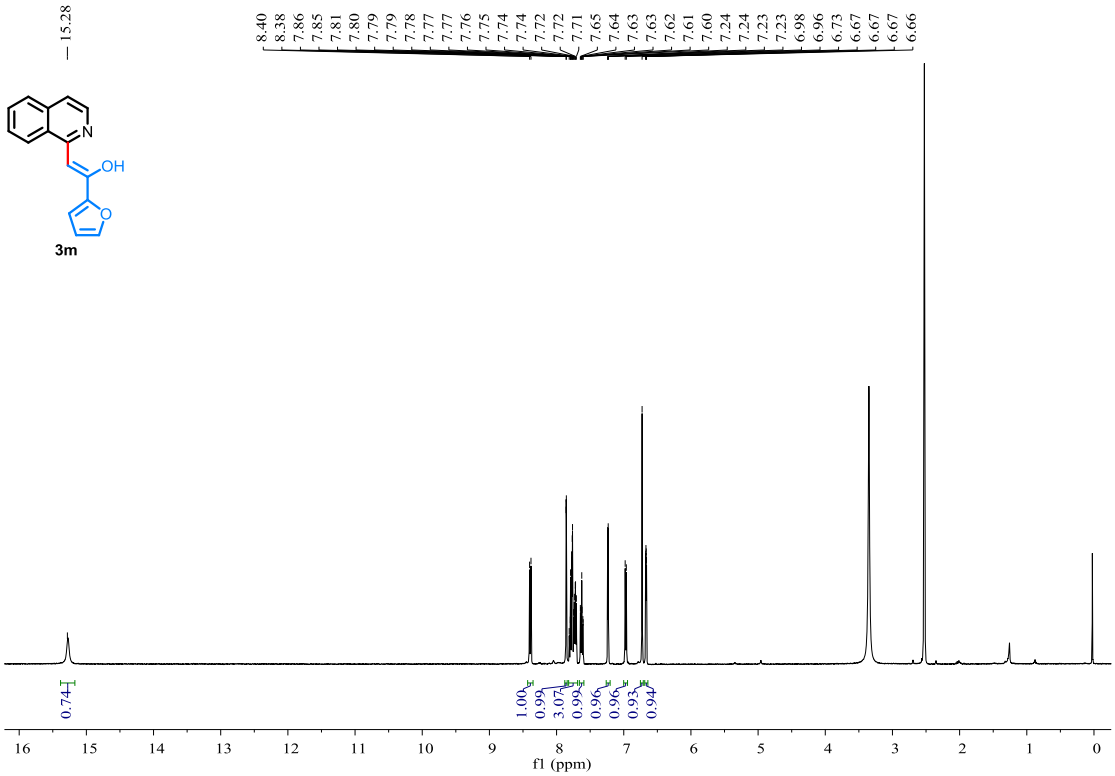
^{1}H NMR of **3l** (400 MHz, DMSO)



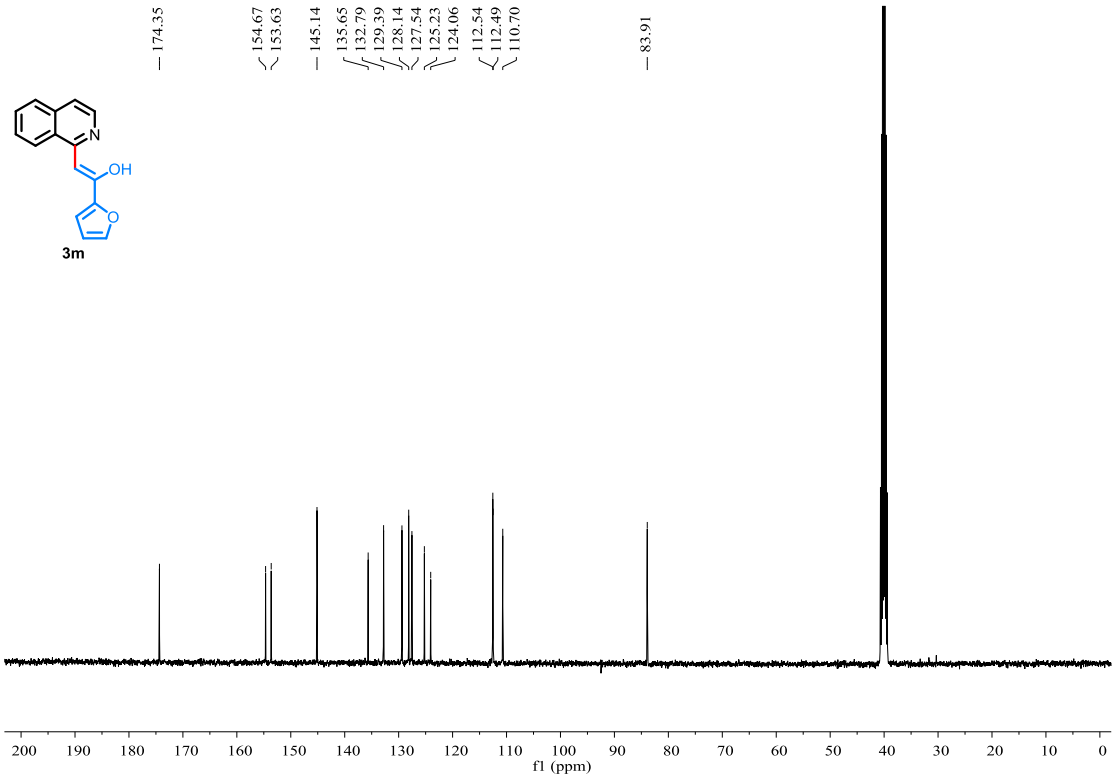
^{13}C NMR of **3l** (100 MHz, DMSO)



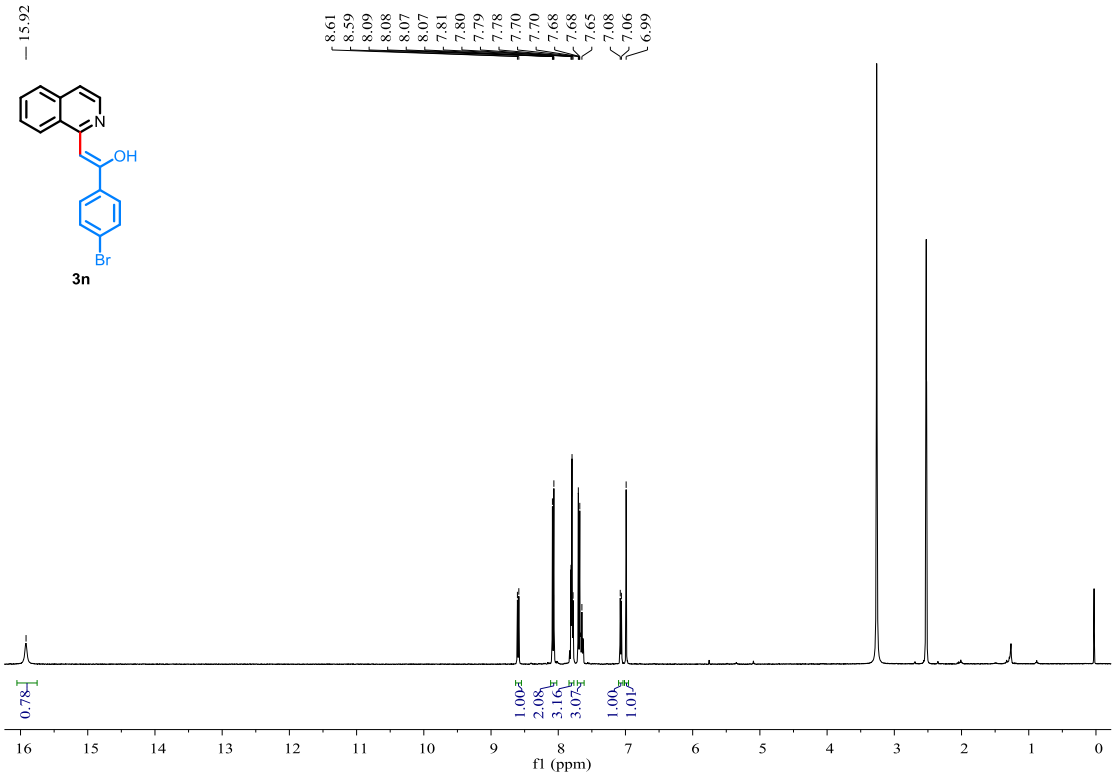
^{1}H NMR of **3m** (400 MHz, DMSO)



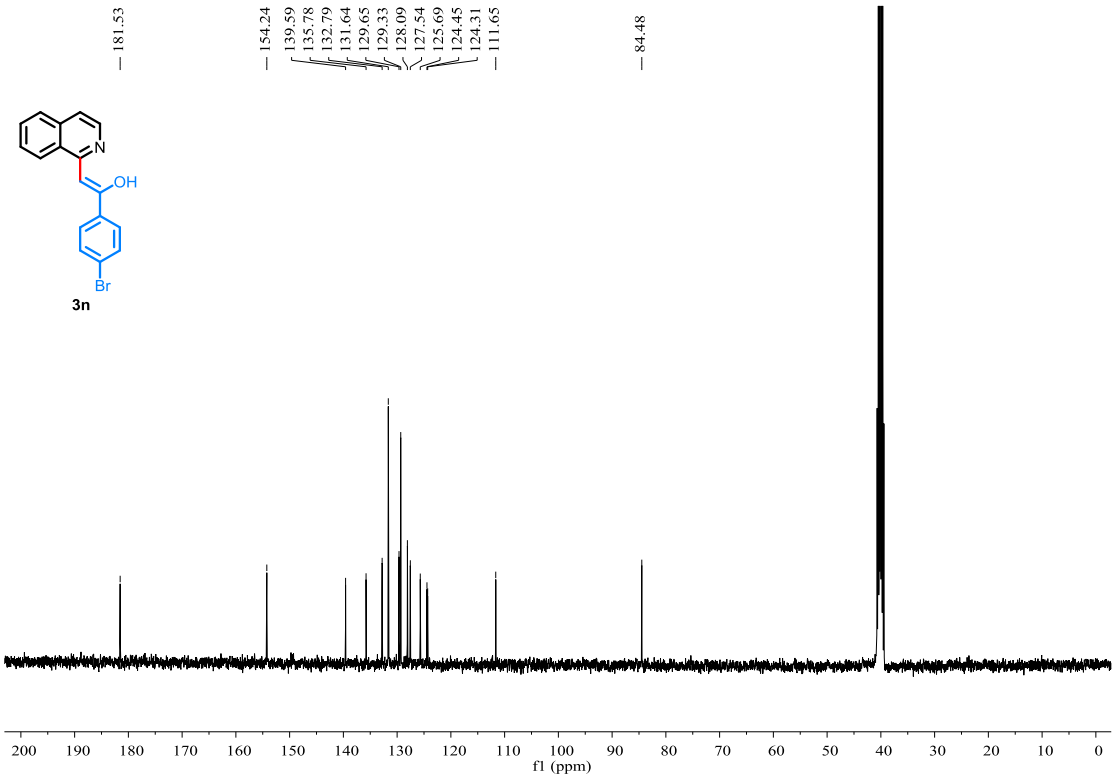
^{13}C NMR of **3m** (100 MHz, DMSO)



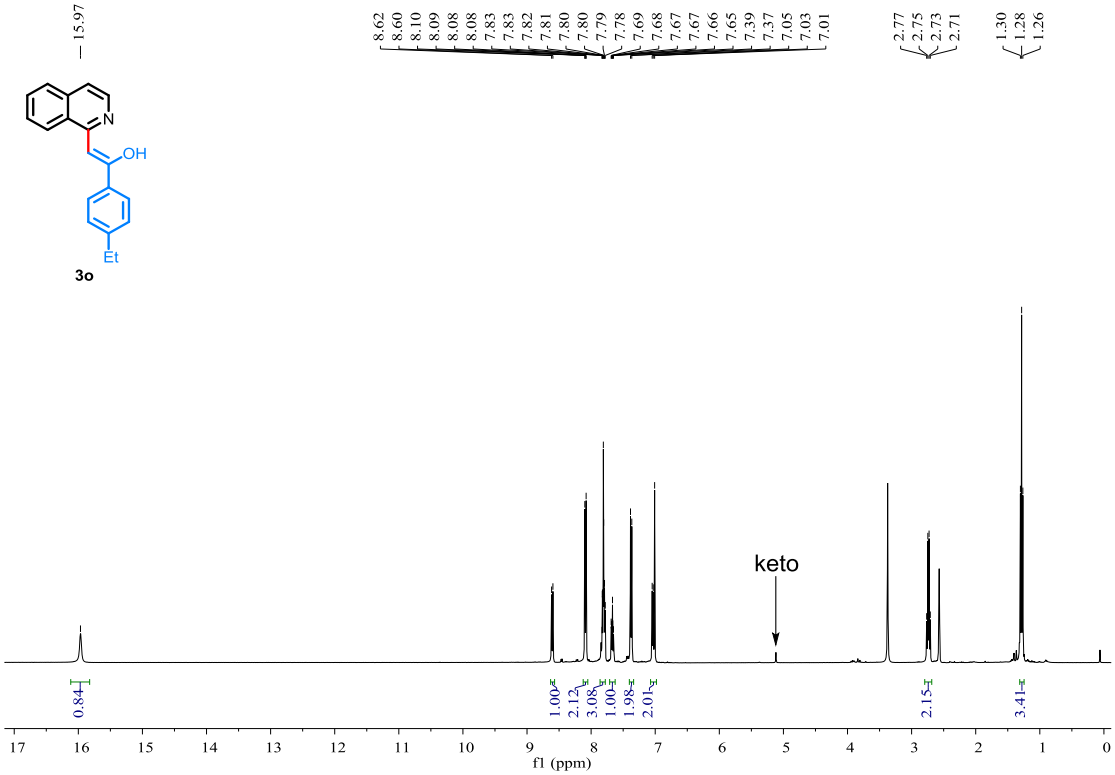
^{1}H NMR of **3n** (400 MHz, DMSO)



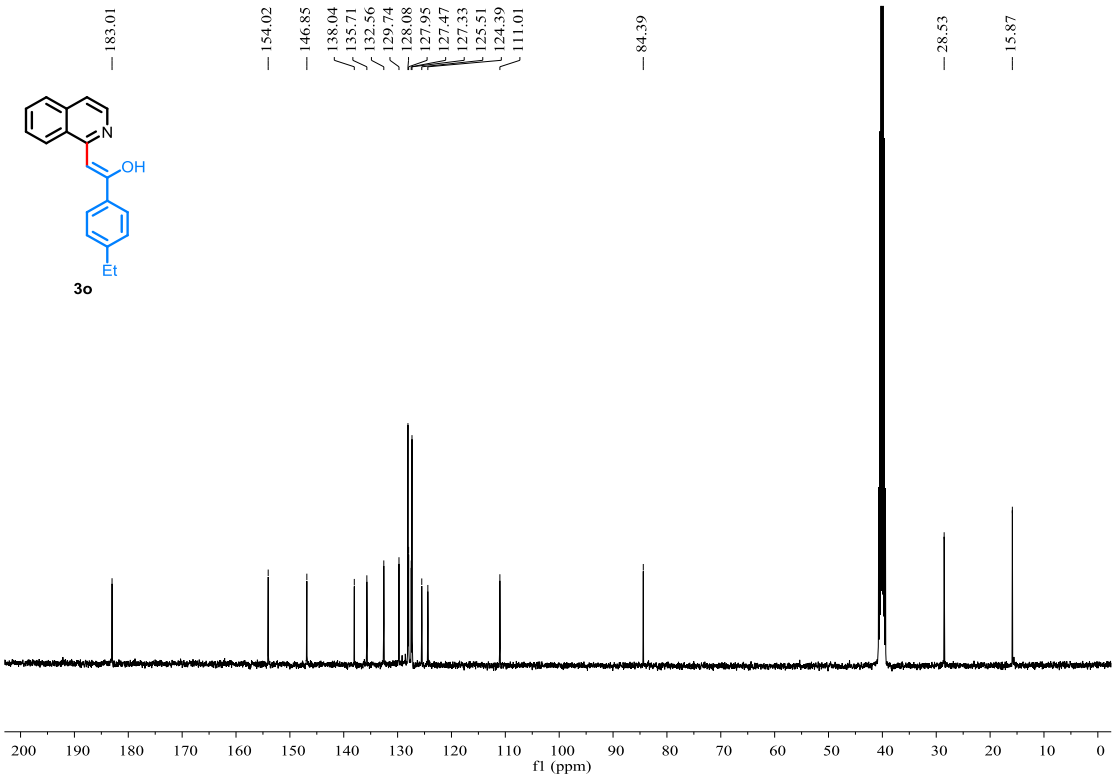
^{13}C NMR of **3n** (100 MHz, DMSO)



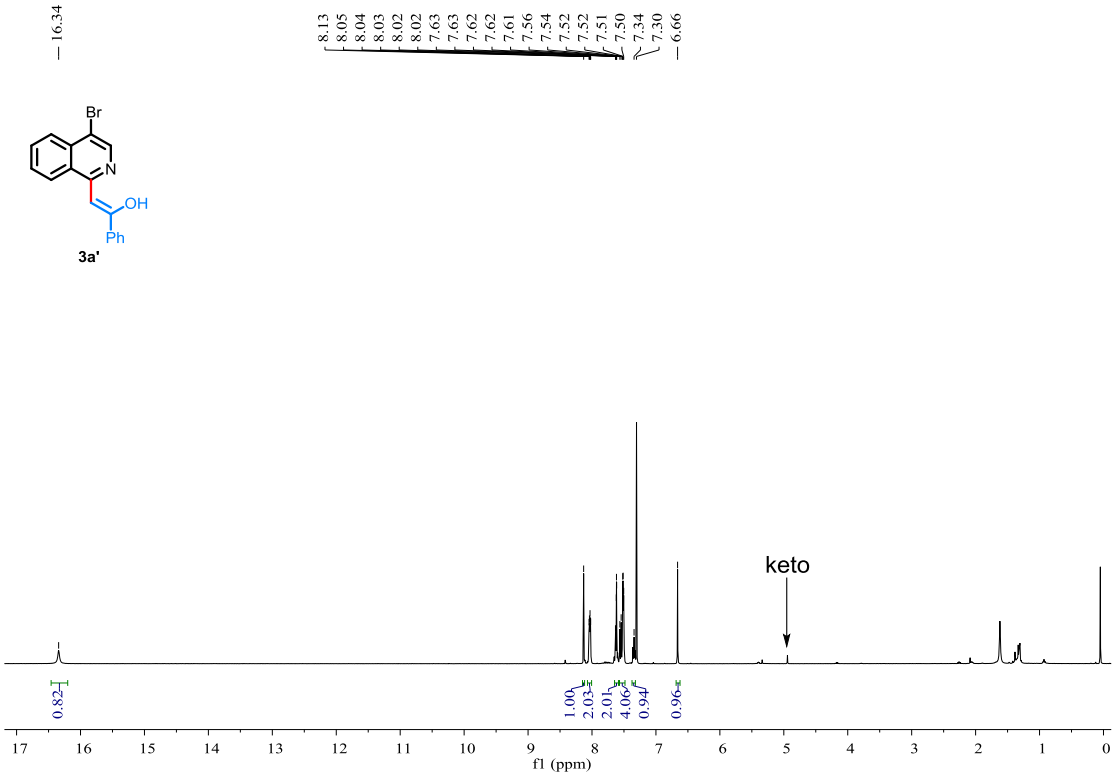
^{1}H NMR of **3o** (400 MHz, DMSO)



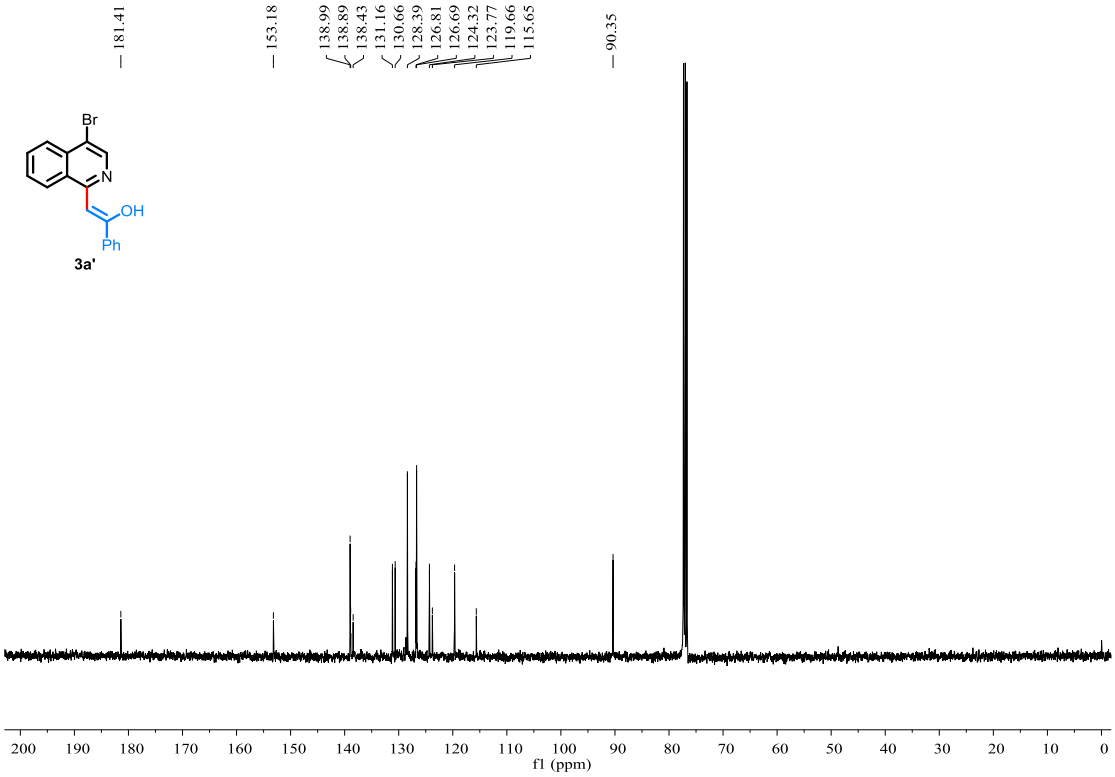
^{13}C NMR of **3o** (100 MHz, DMSO)



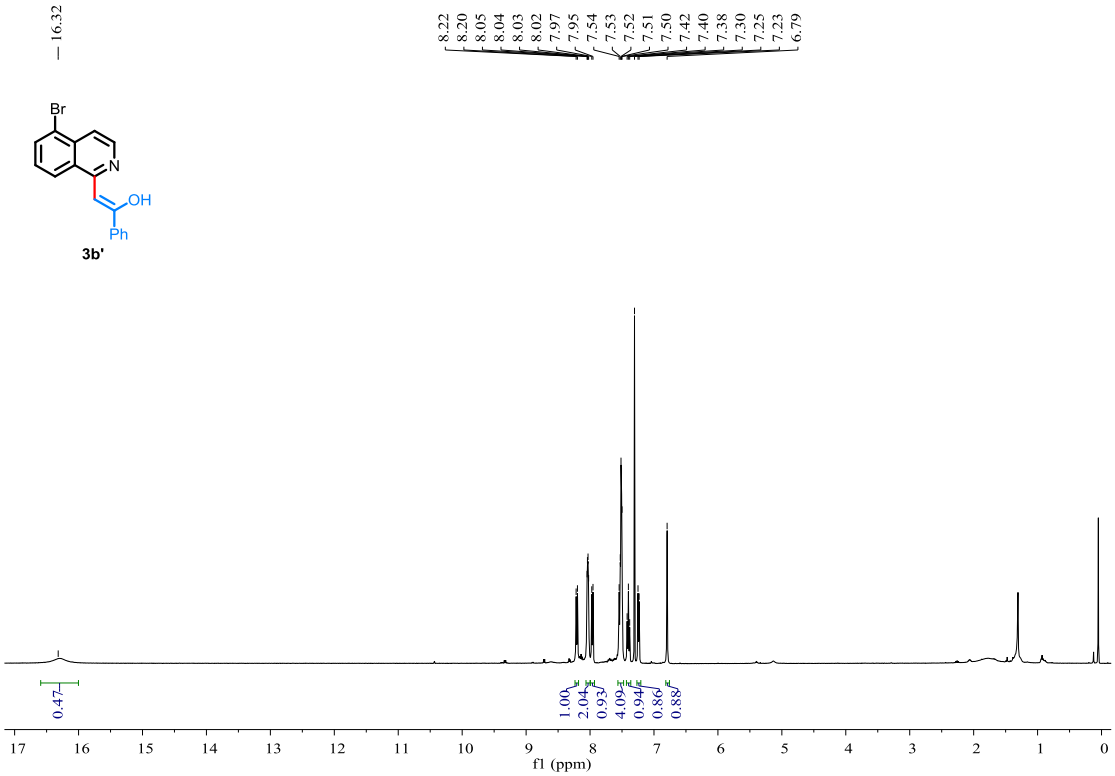
^{1}H NMR of **3a'** (400 MHz, $CDCl_3$)



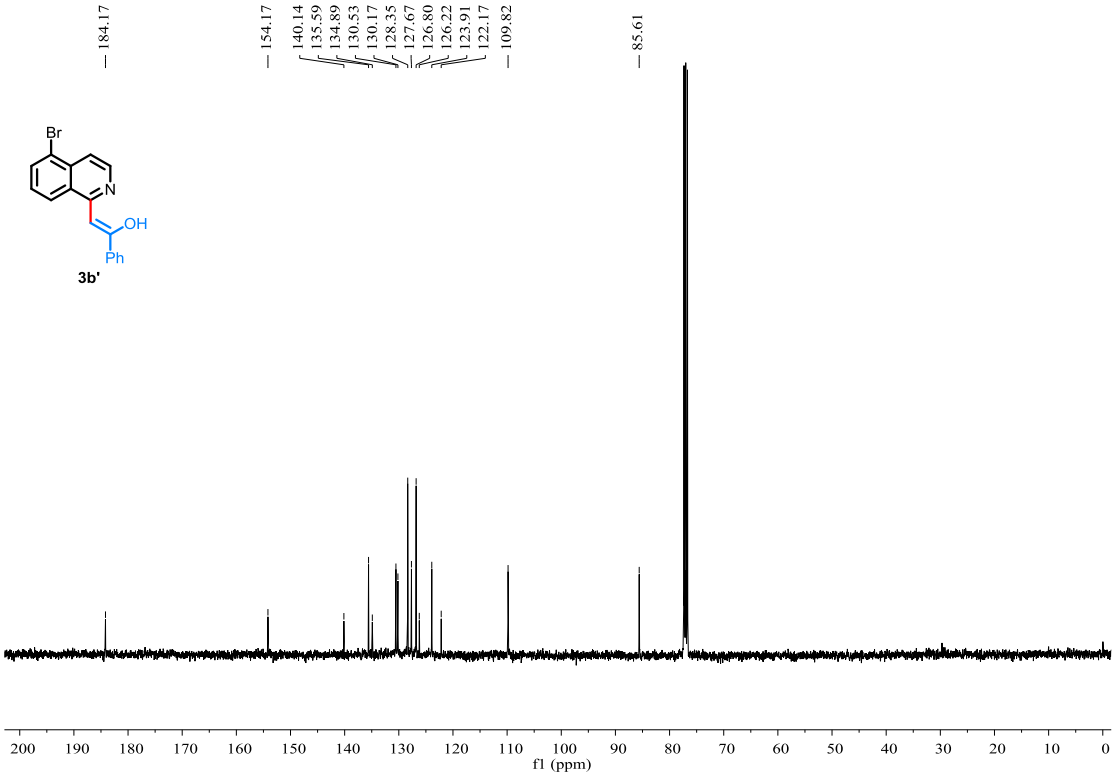
^{13}C NMR of **3a'** (100 MHz, $CDCl_3$)



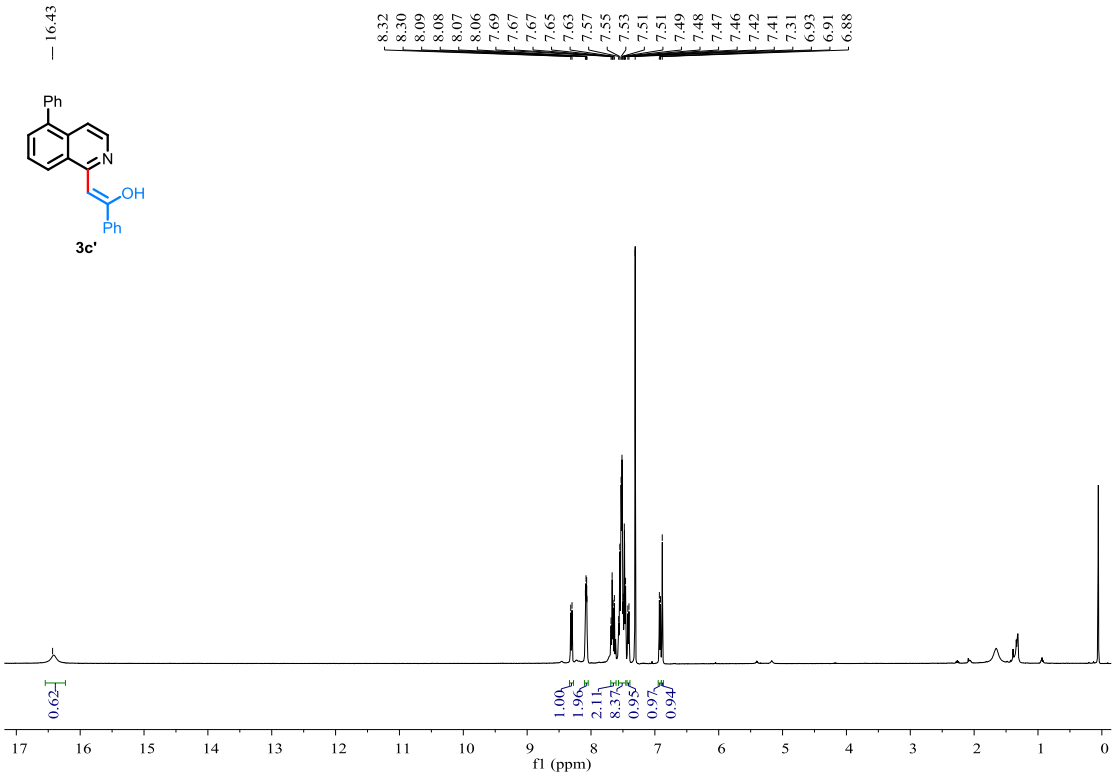
^{1}H NMR of **3b'** (400 MHz, $CDCl_3$)



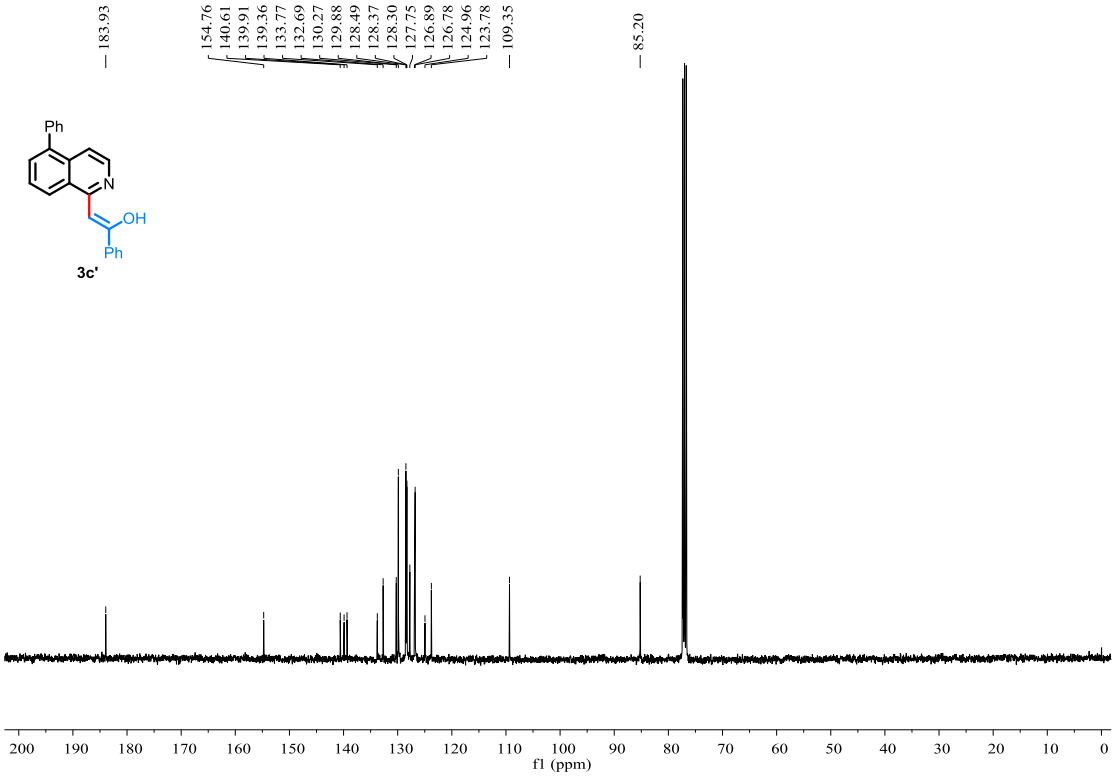
^{13}C NMR of **3b'** (100 MHz, $CDCl_3$)



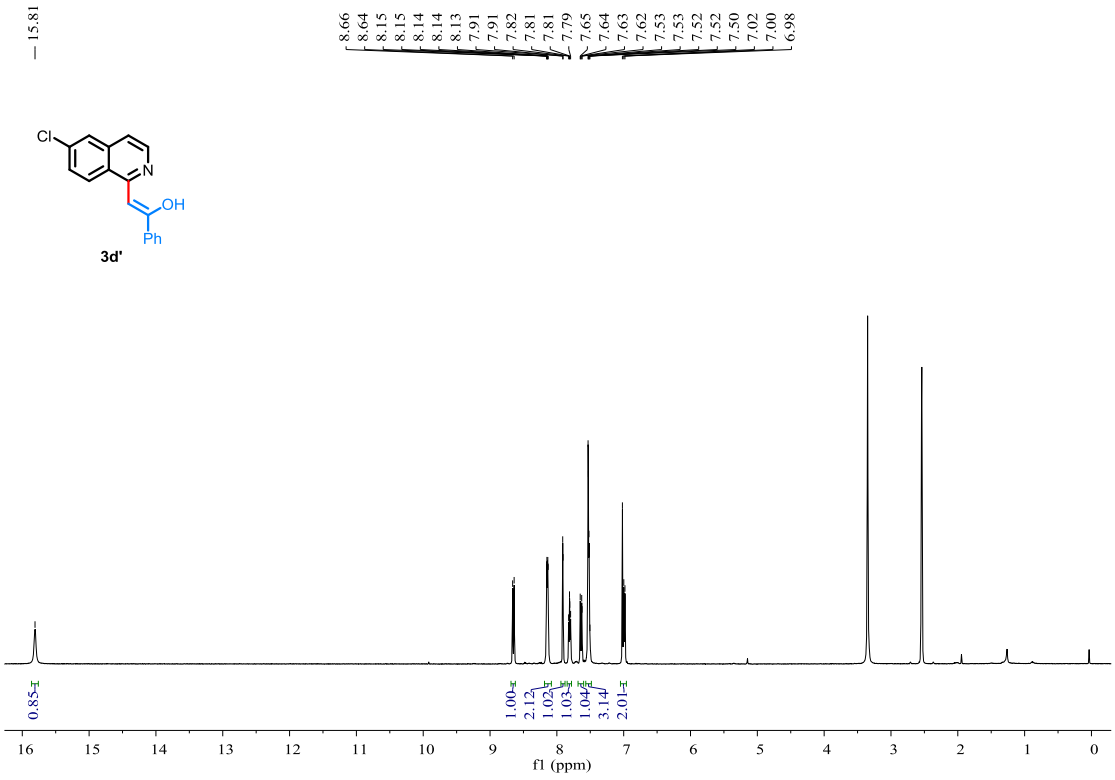
^{1}H NMR of **3c'** (400 MHz, $CDCl_3$)



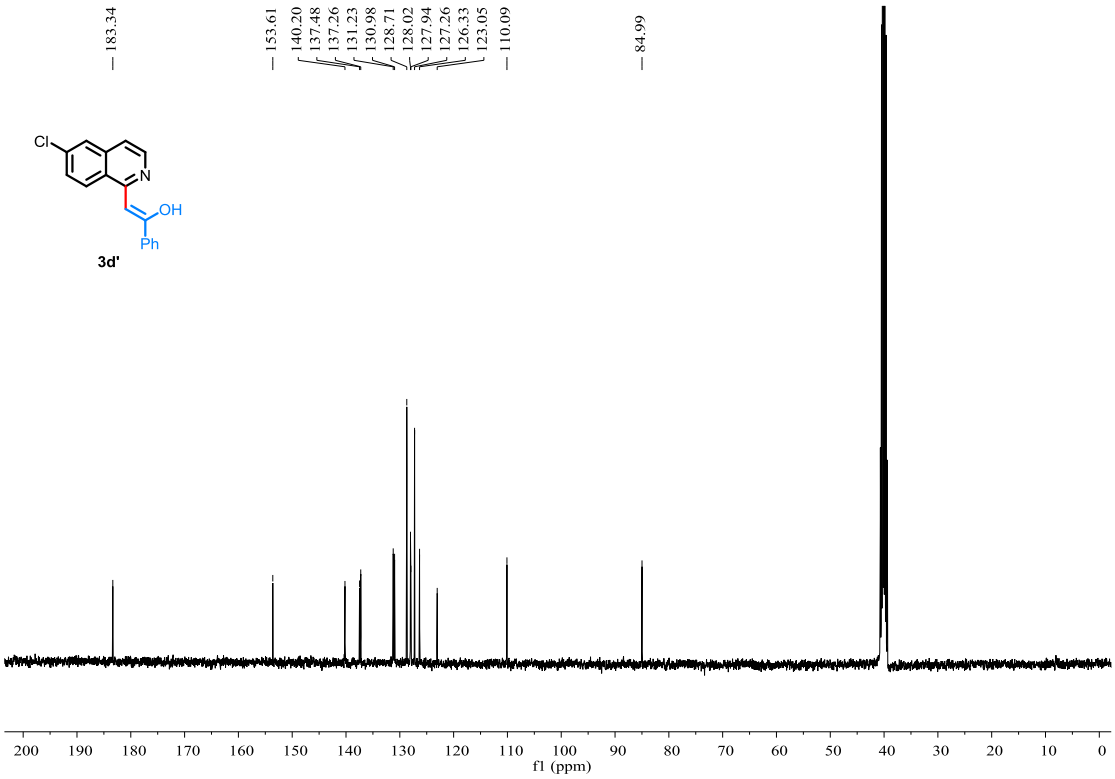
^{13}C NMR of **3c'** (100 MHz, $CDCl_3$)



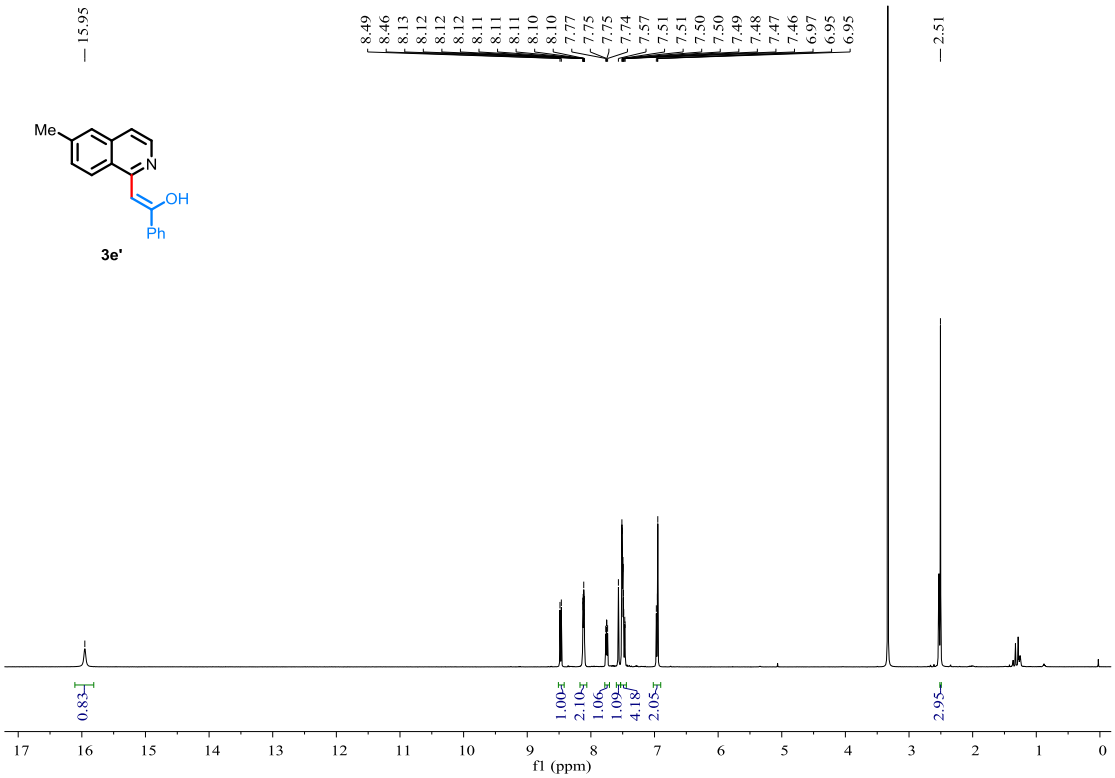
^{1}H NMR of **3d'** (400 MHz, DMSO)



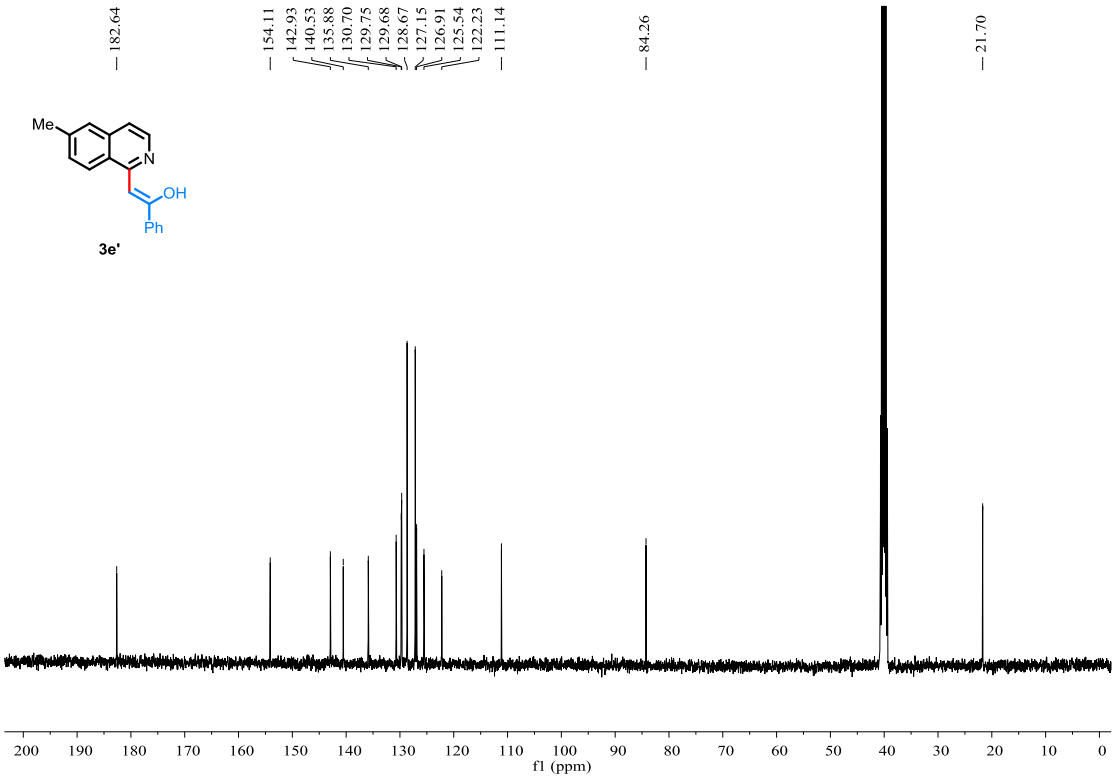
^{13}C NMR of **3d'** (100 MHz, DMSO)



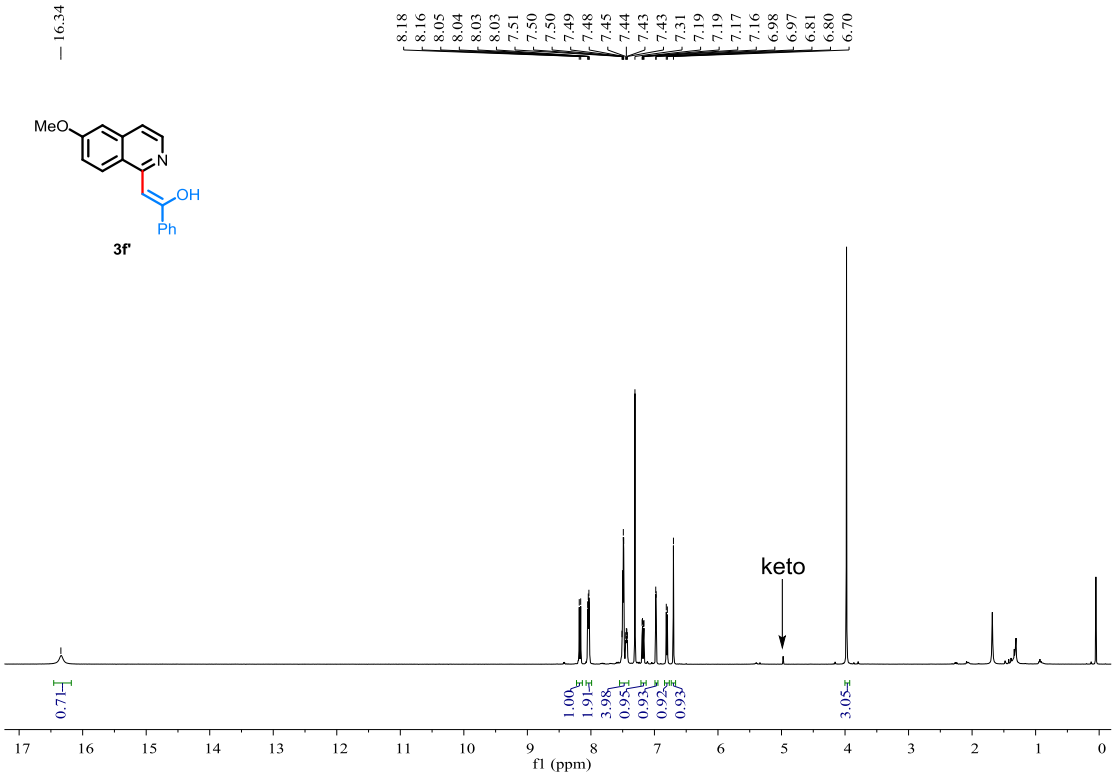
^{1}H NMR of **3e'** (400 MHz, DMSO)



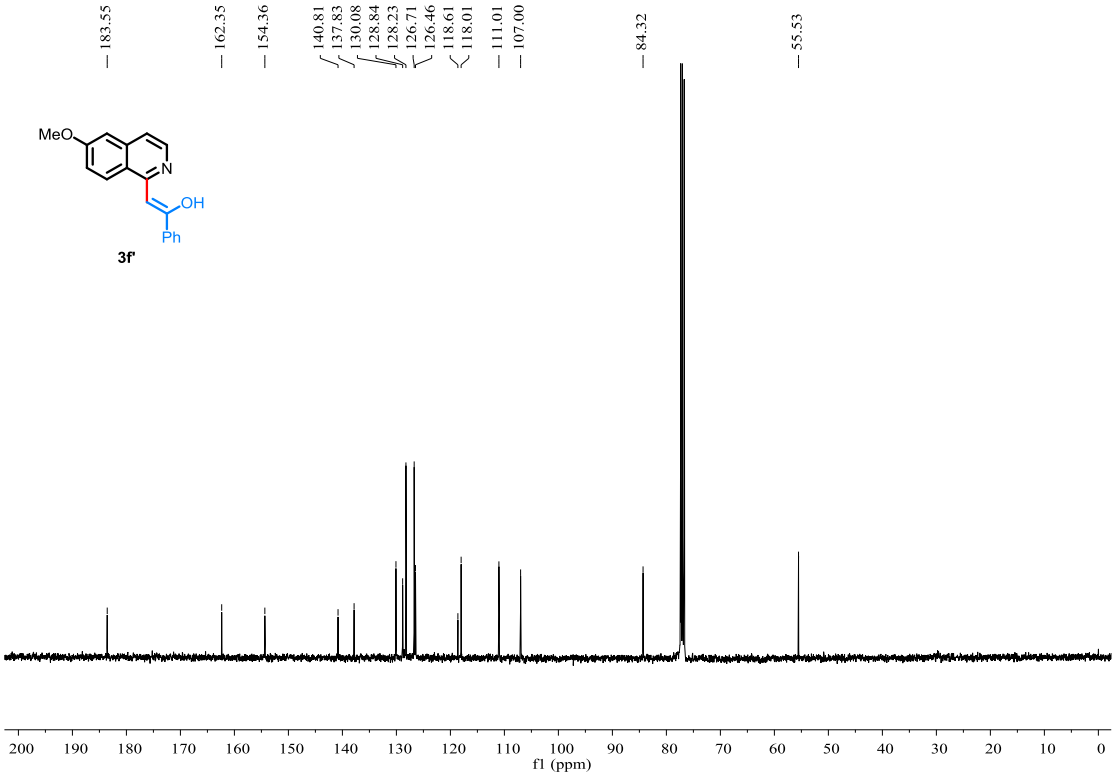
^{13}C NMR of **3e'** (100 MHz, DMSO)



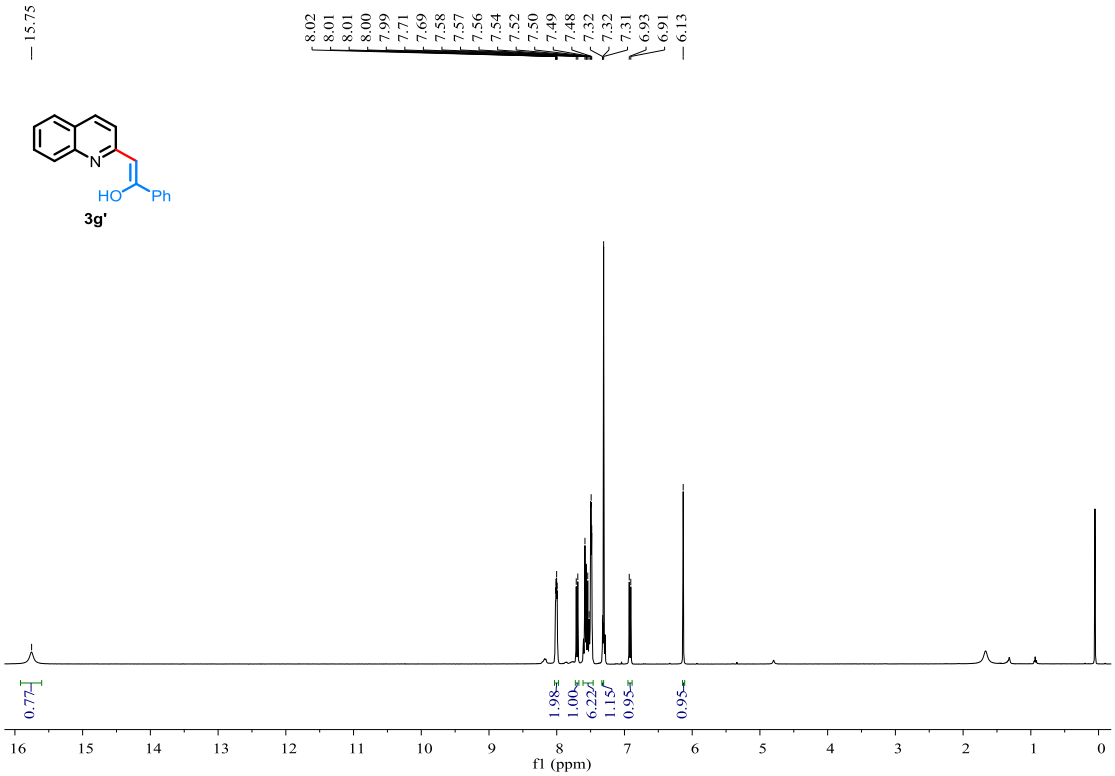
^{1}H NMR of **3f'** (400 MHz, $CDCl_3$)



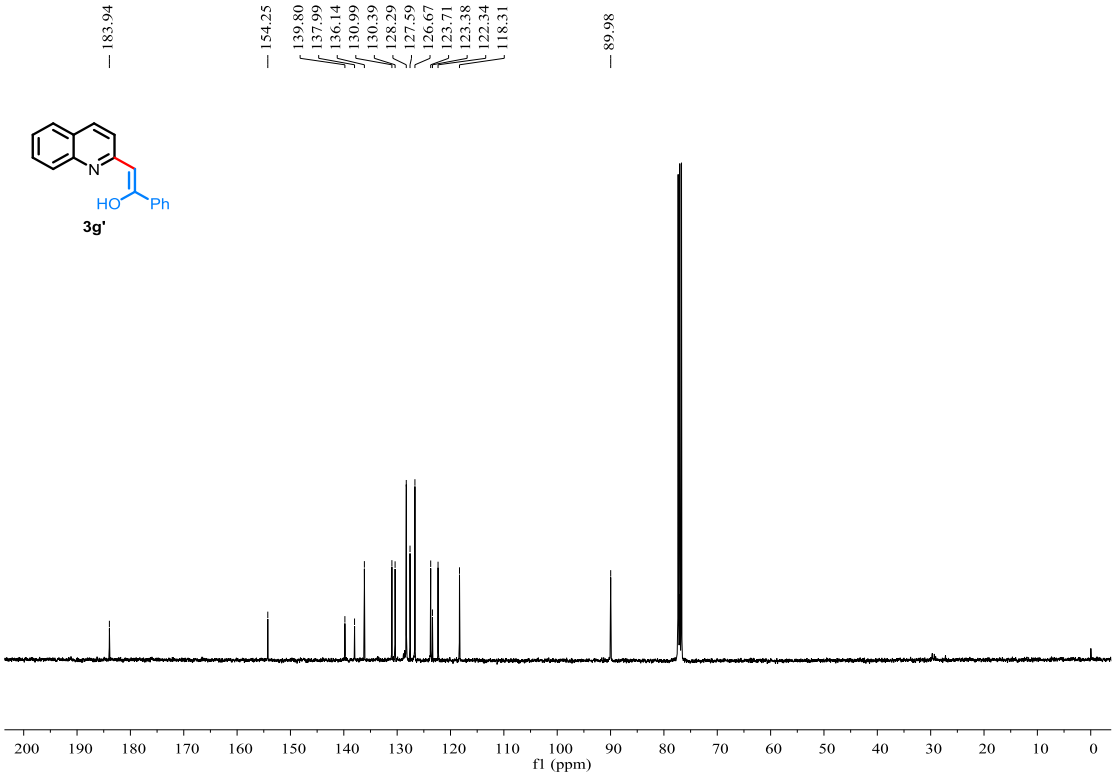
^{13}C NMR of **3f'** (100 MHz, $CDCl_3$)



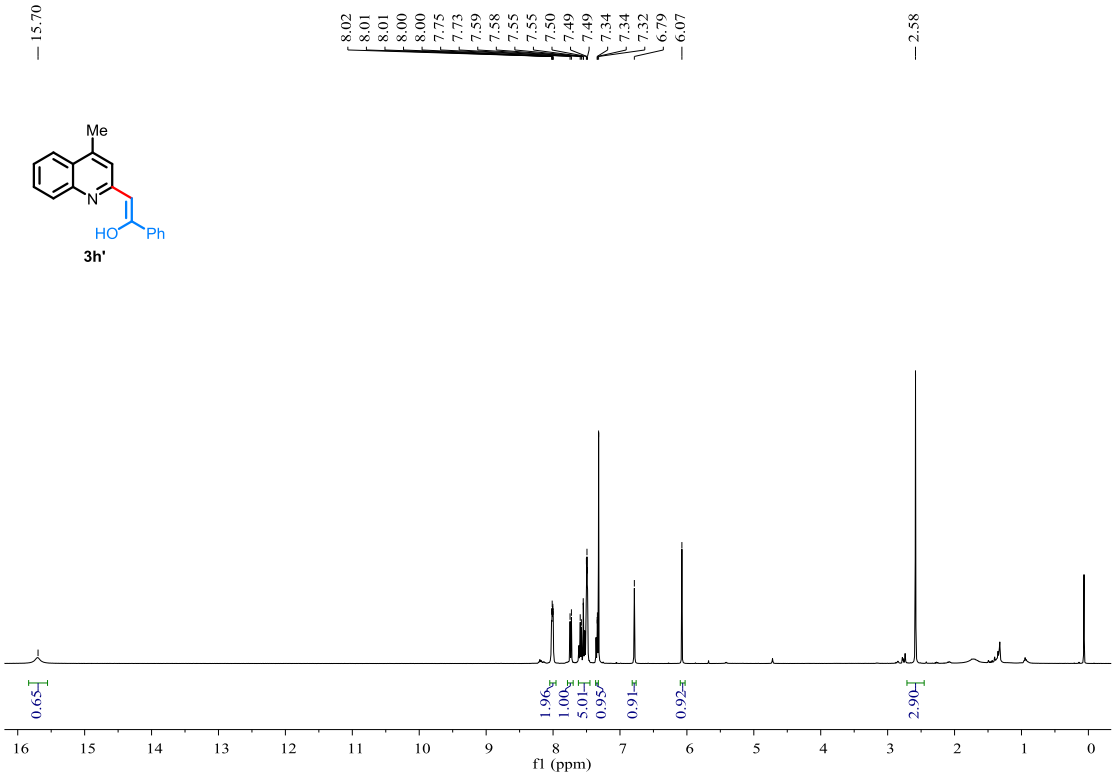
^{1}H NMR of **3g'** (400 MHz, $CDCl_3$)



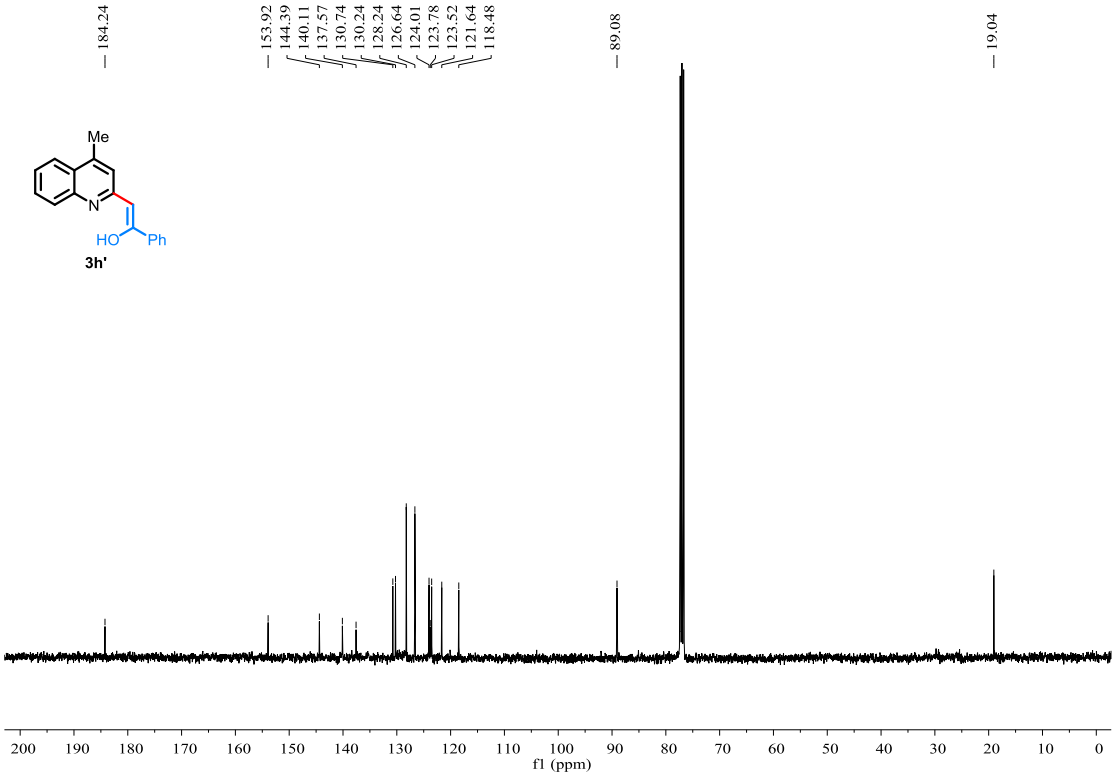
^{13}C NMR of **3g'** (100 MHz, $CDCl_3$)



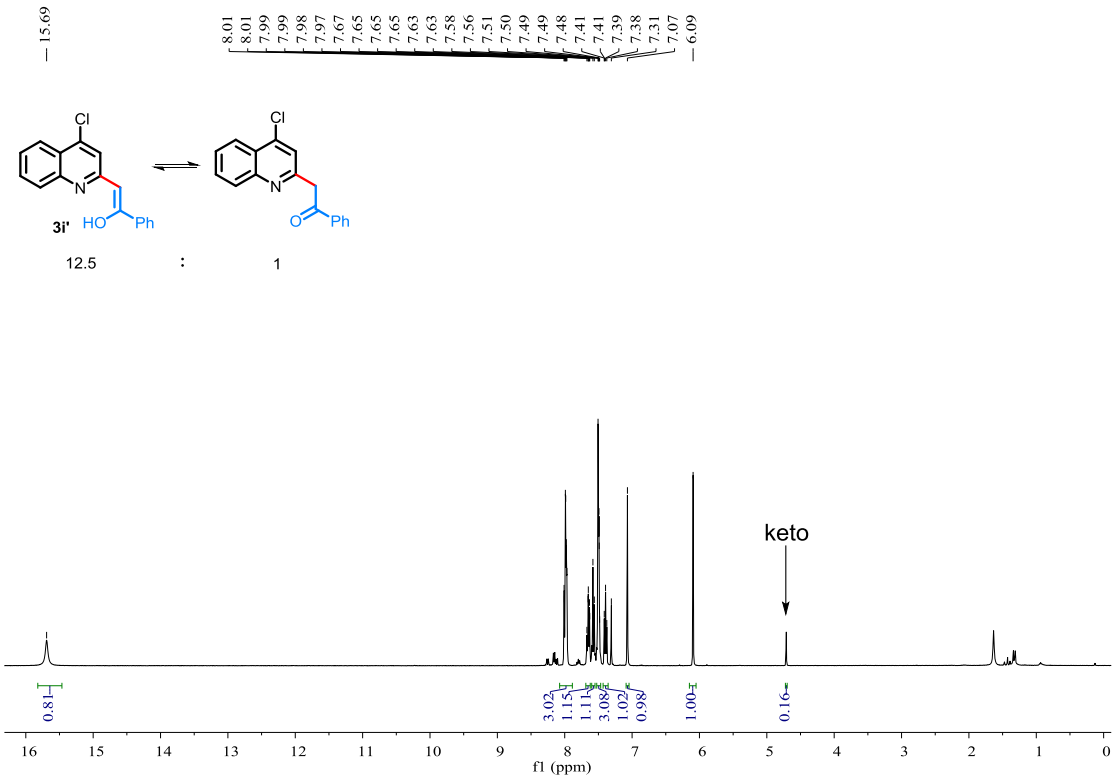
^{1}H NMR of **3h'** (400 MHz, $CDCl_3$)



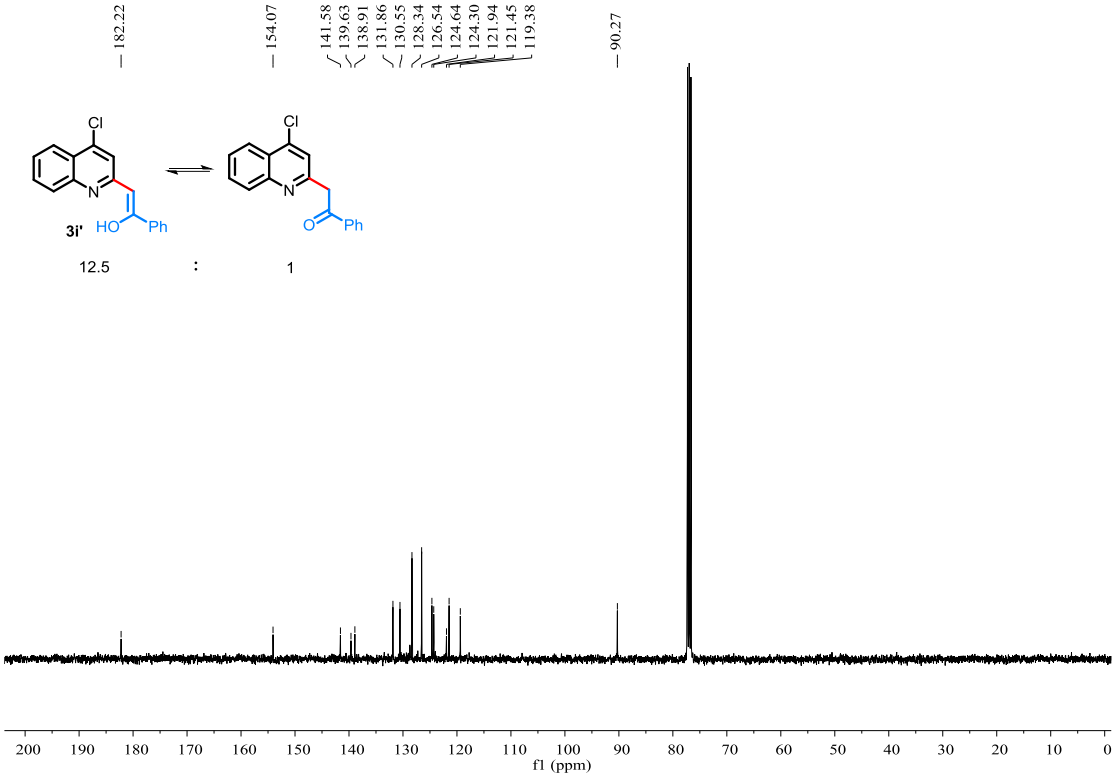
^{13}C NMR of **3h'** (100 MHz, $CDCl_3$)



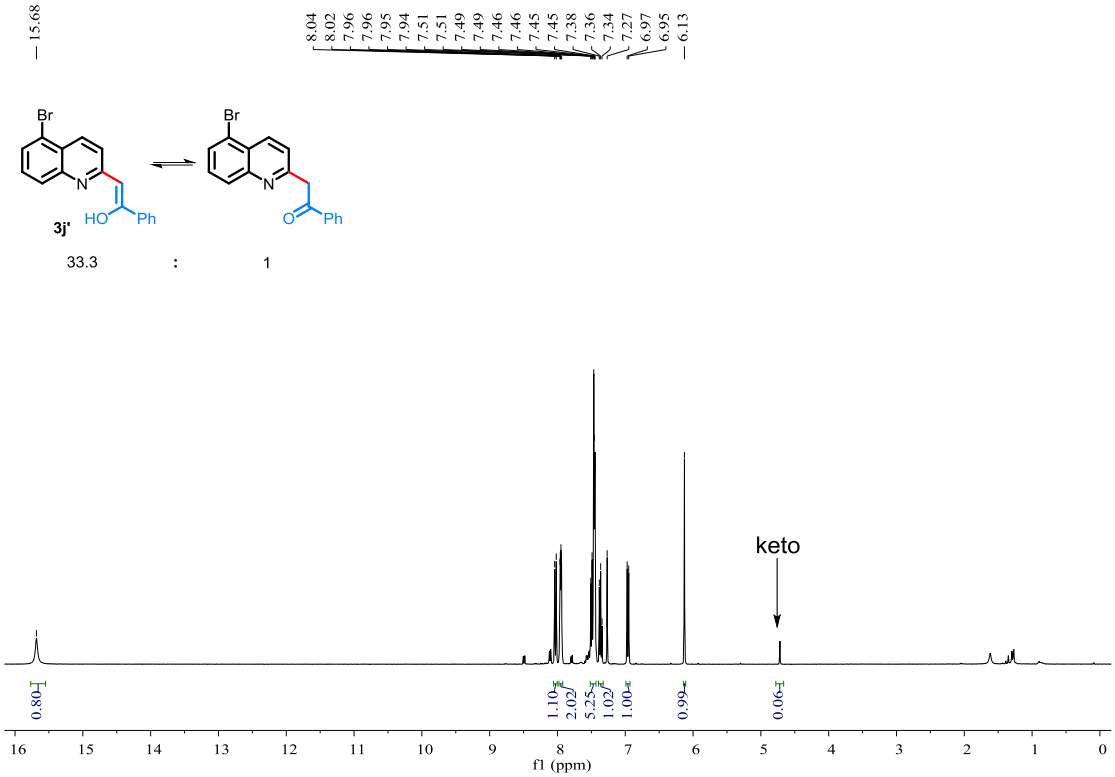
^{1}H NMR of **3i'** (400 MHz, $CDCl_3$)



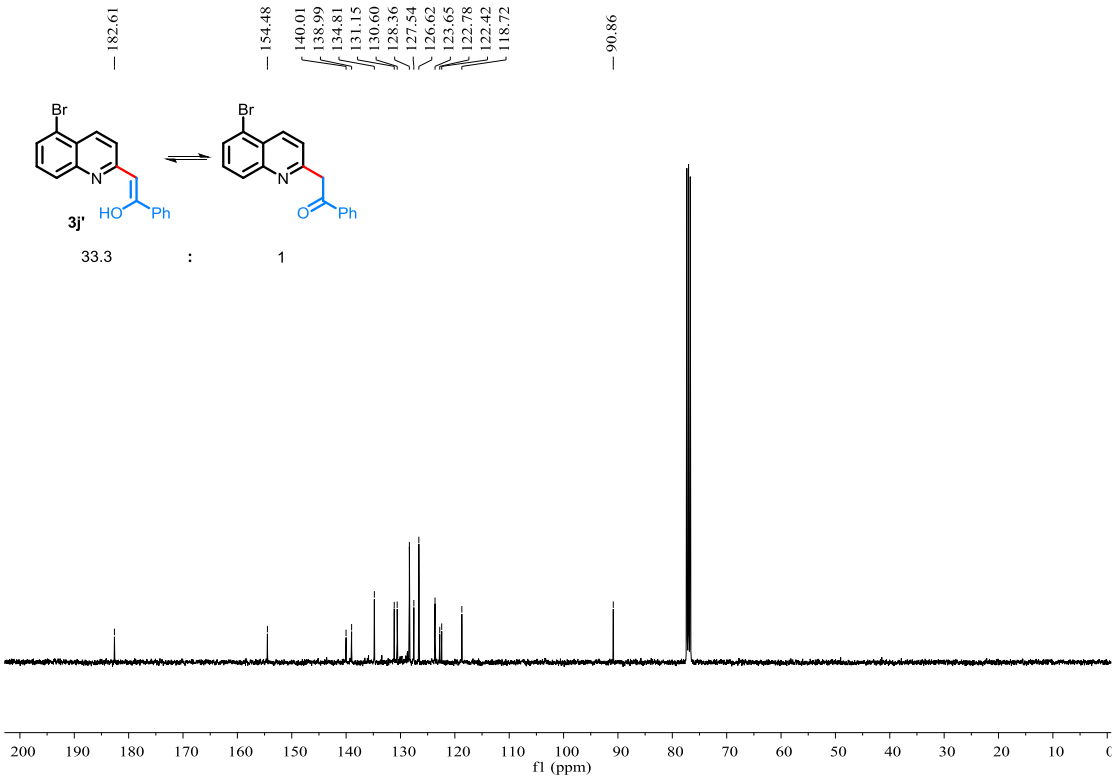
^{13}C NMR of **3i'** (100 MHz, $CDCl_3$)



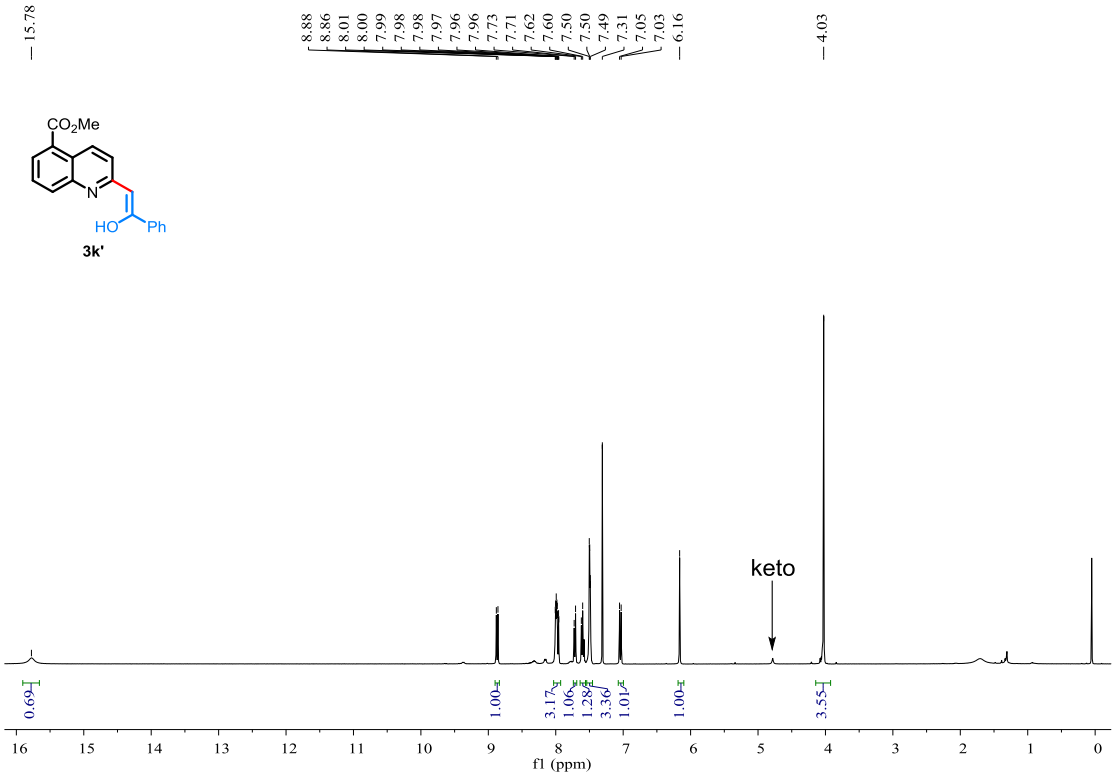
^{1}H NMR of **3j'** (400 MHz, $CDCl_3$)



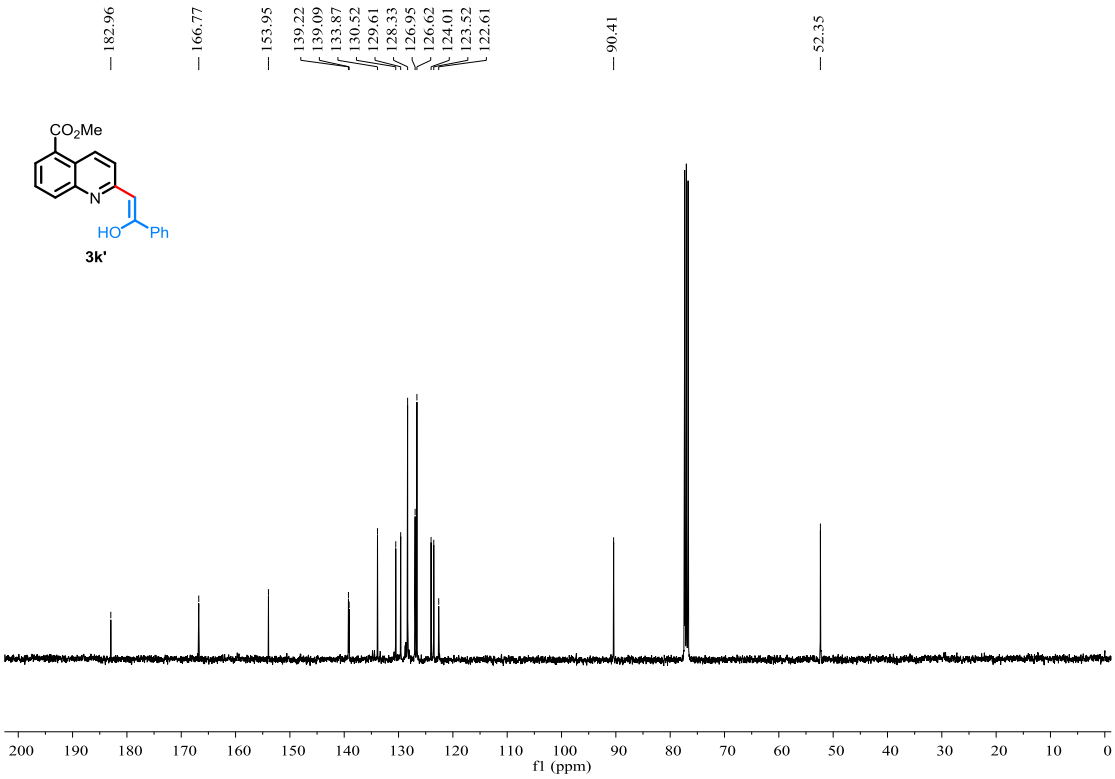
^{13}C NMR of **3j'** (100 MHz, $CDCl_3$)



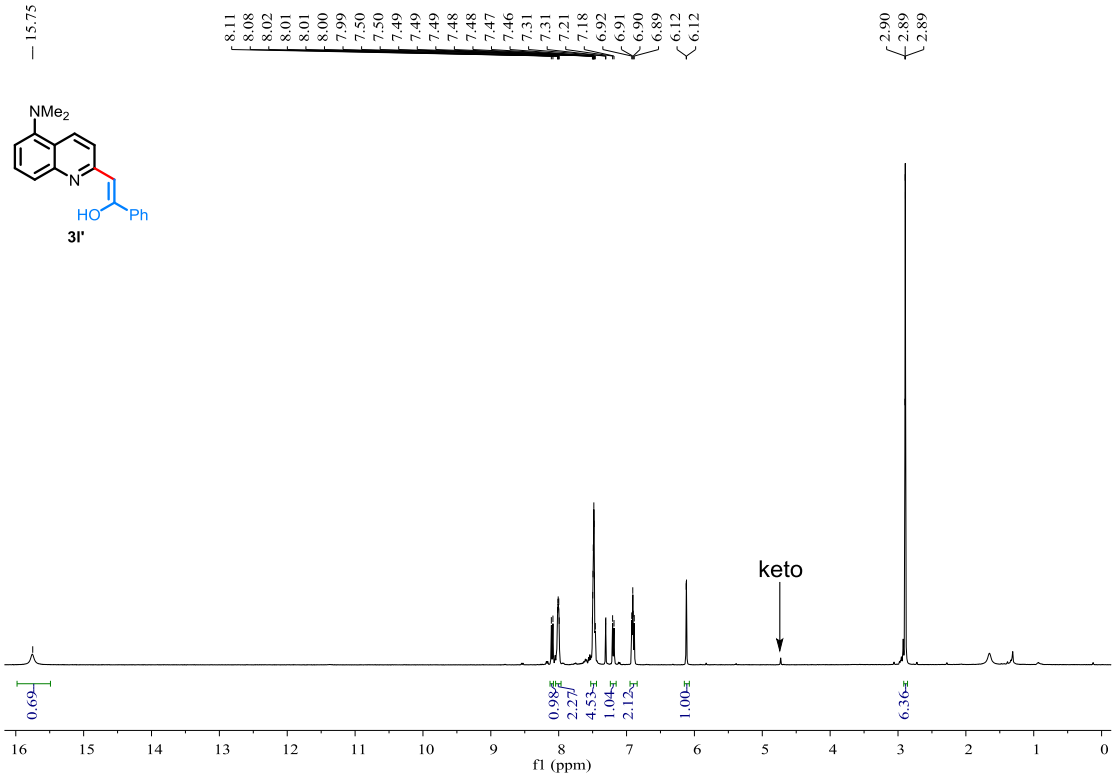
^{1}H NMR of **3k'** (400 MHz, $CDCl_3$)



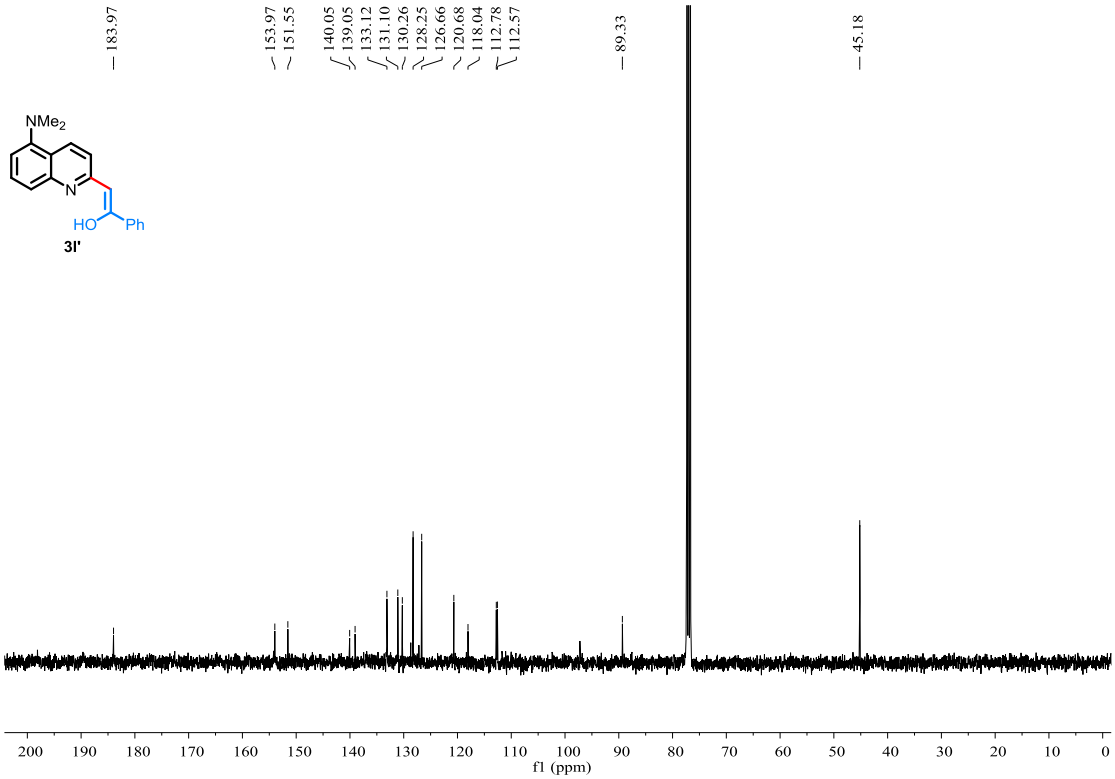
^{13}C NMR of **3k'** (100 MHz, $CDCl_3$)



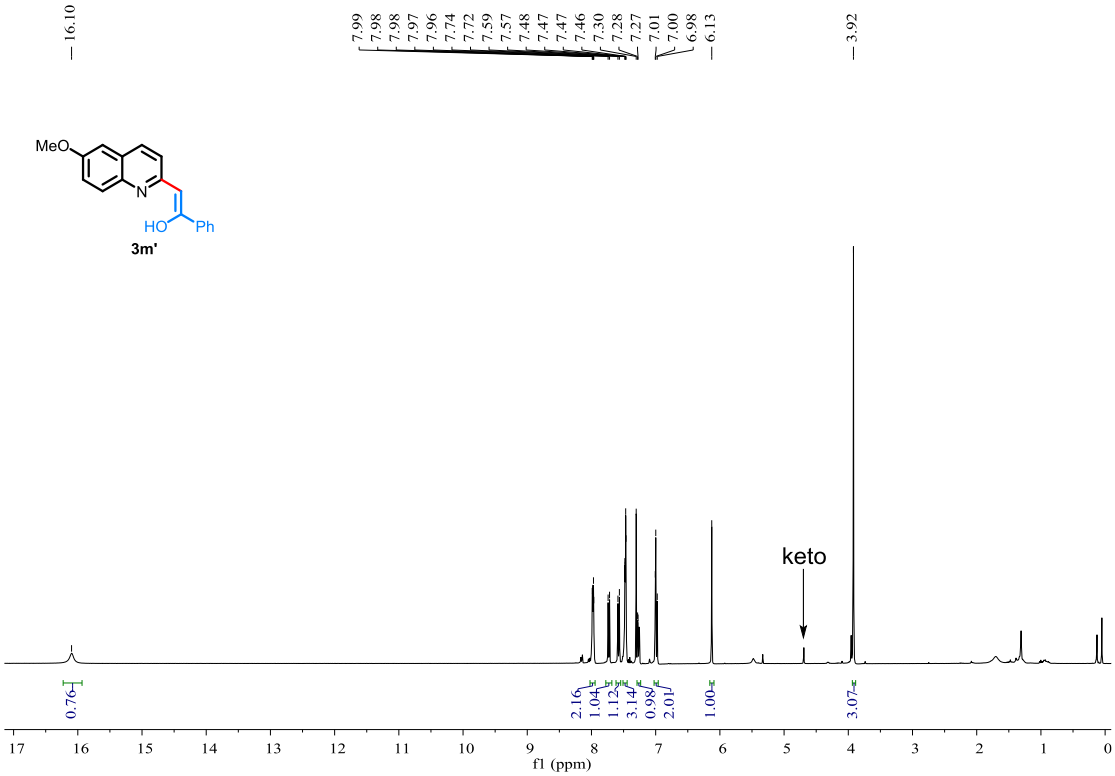
^{1}H NMR of **3l'** (400 MHz, $CDCl_3$)



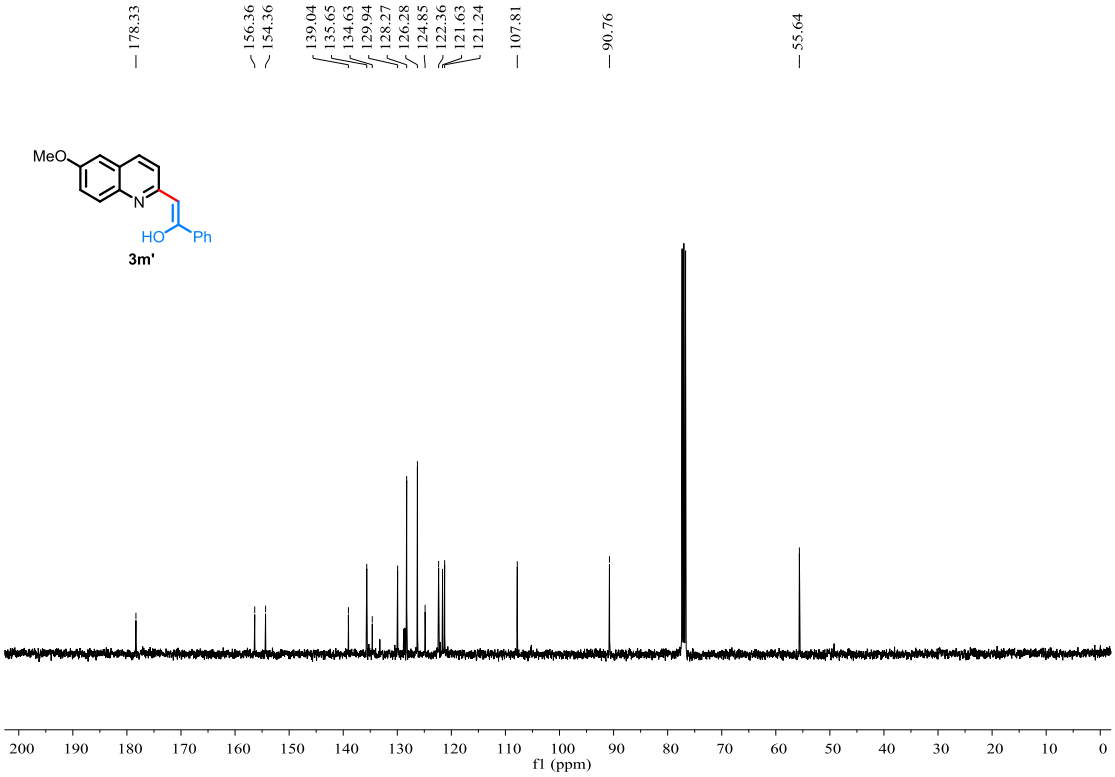
^{13}C NMR of **3l'** (100 MHz, $CDCl_3$)



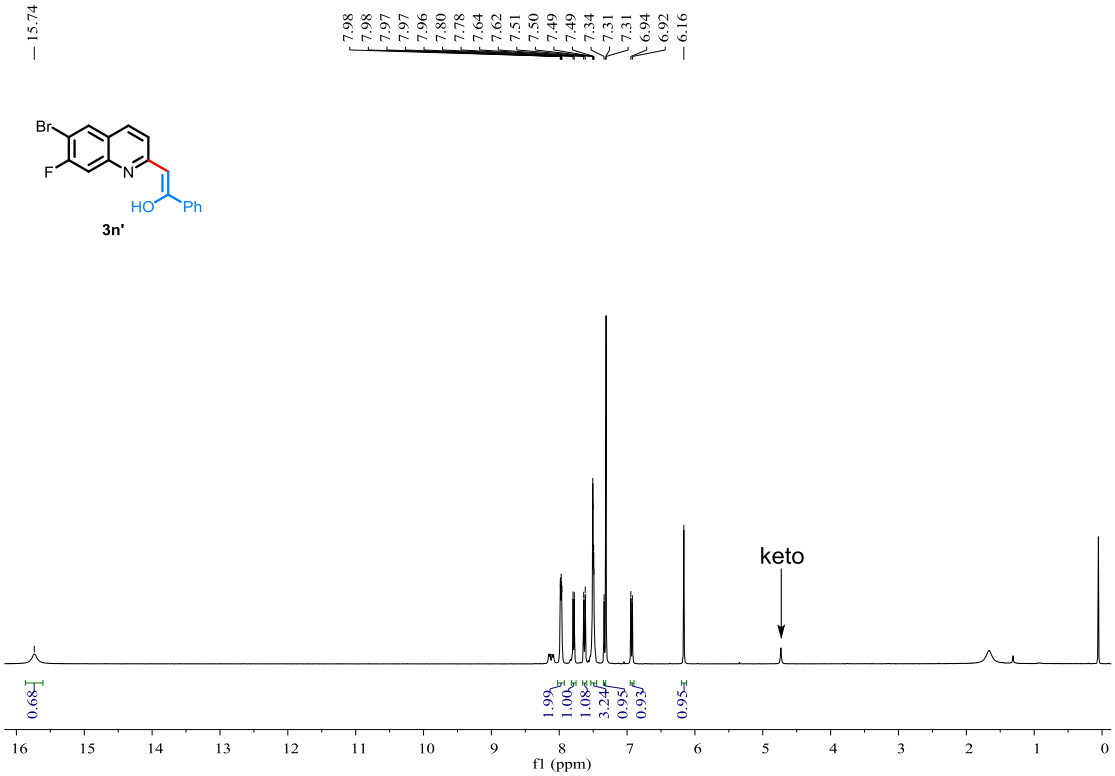
^{1}H NMR of **3m'** (400 MHz, $CDCl_3$)



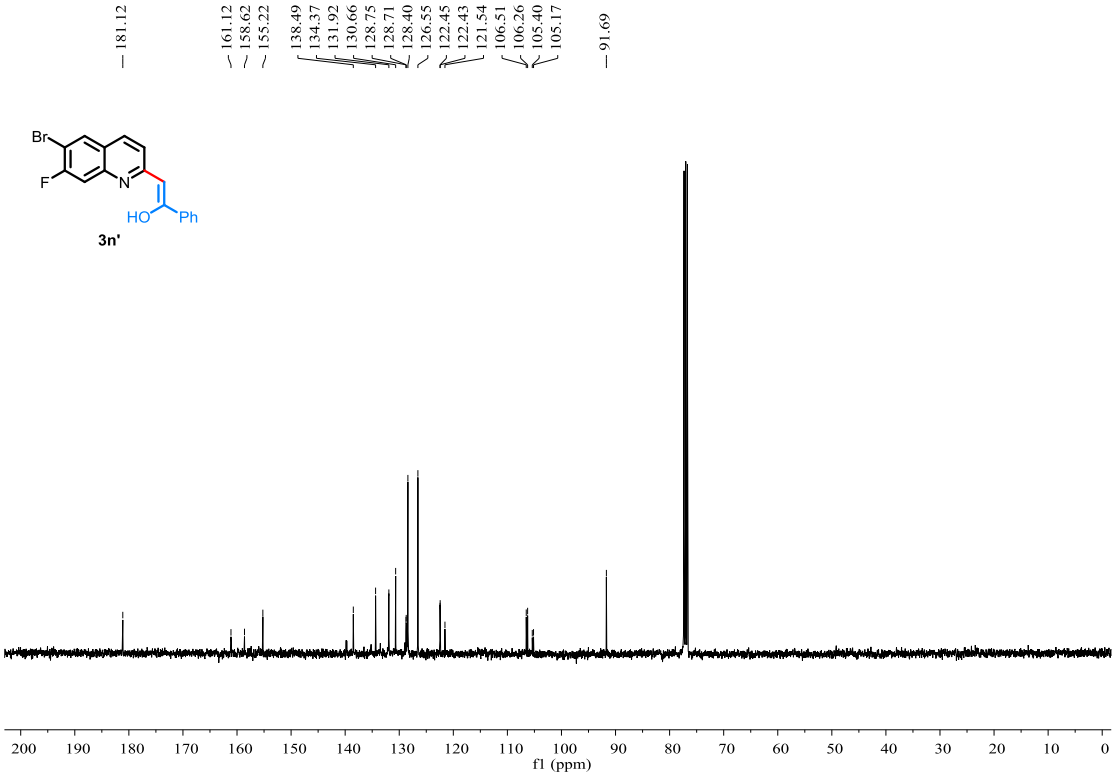
^{13}C NMR of **3m'** (100 MHz, $CDCl_3$)



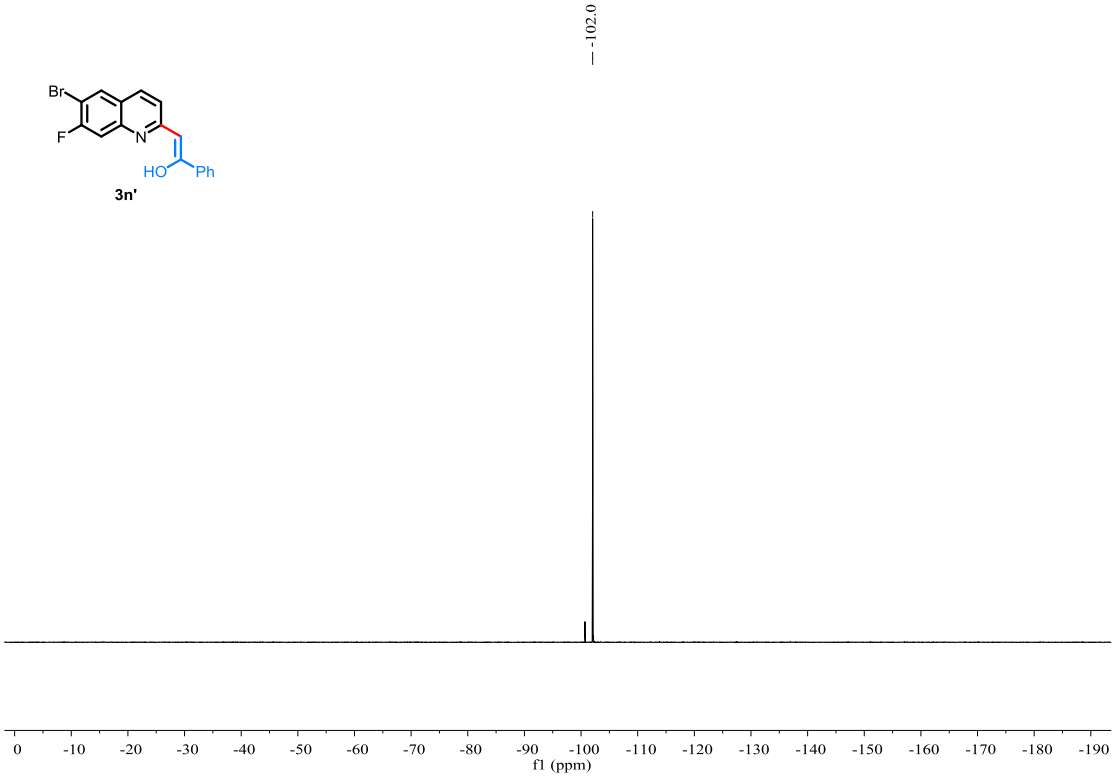
^{1}H NMR of **3n'** (400 MHz, $CDCl_3$)



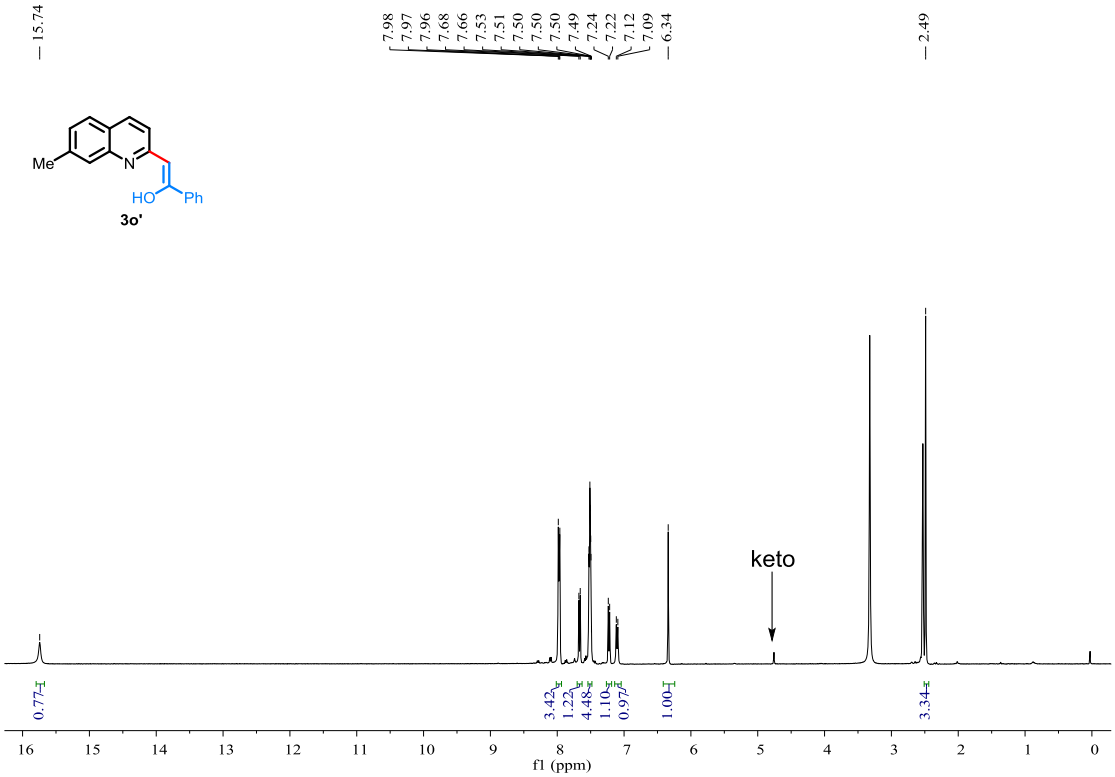
^{13}C NMR of **3n'** (100 MHz, $CDCl_3$)



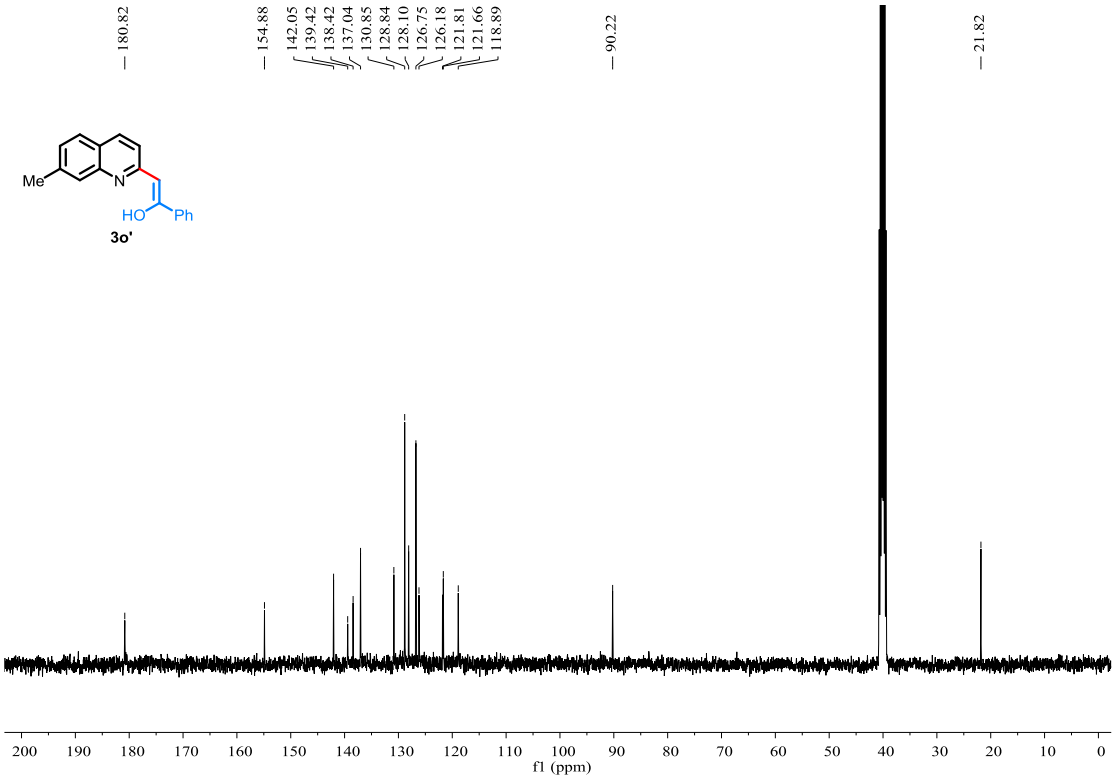
^{19}F NMR of **3n'** (376 MHz, $CDCl_3$)



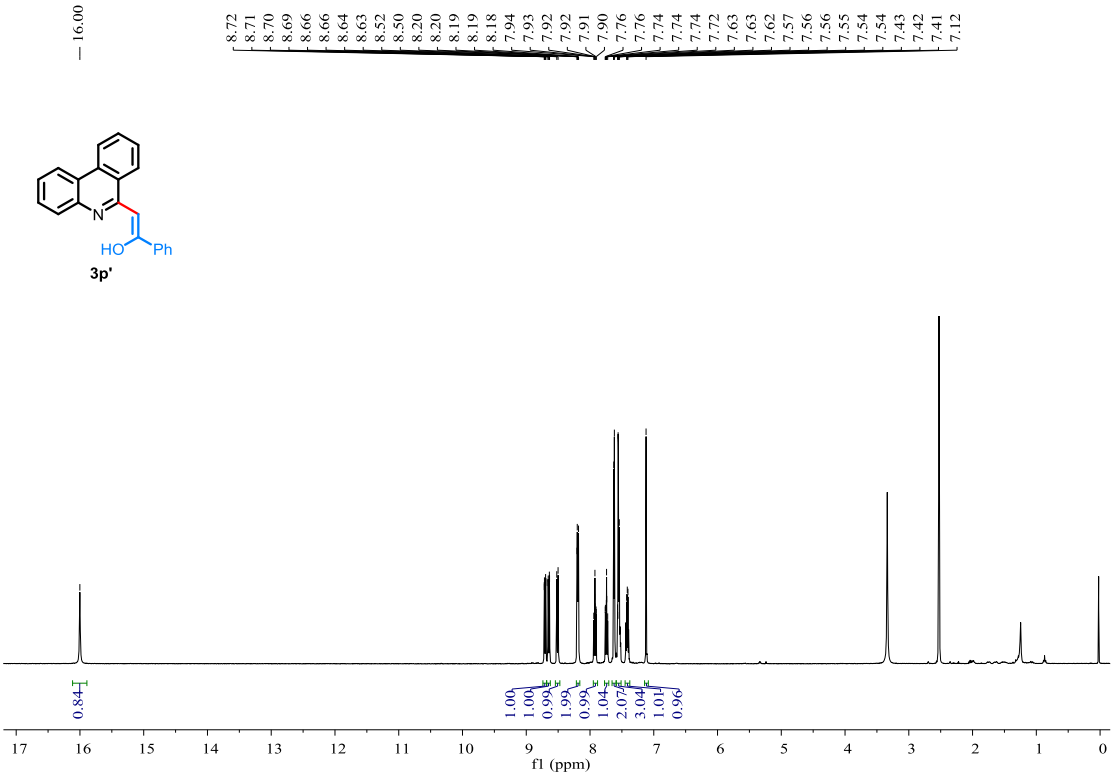
^{1}H NMR of **3o'** (400 MHz, DMSO)



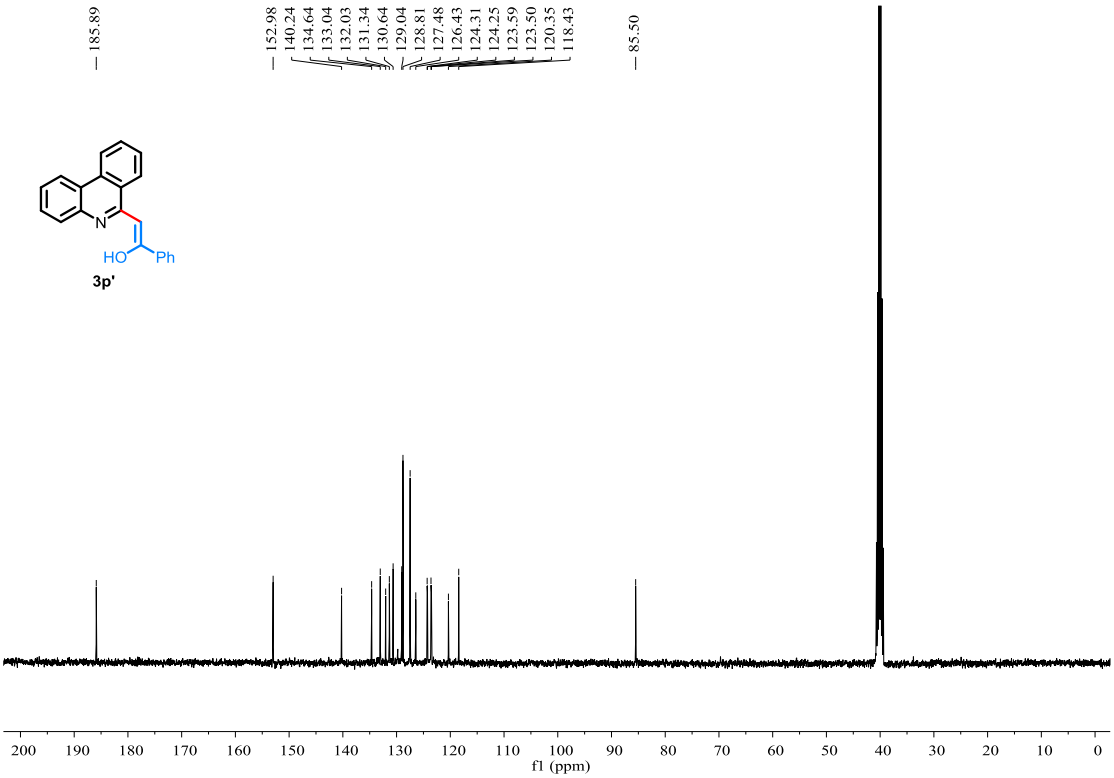
^{13}C NMR of **3o'** (100 MHz, DMSO)



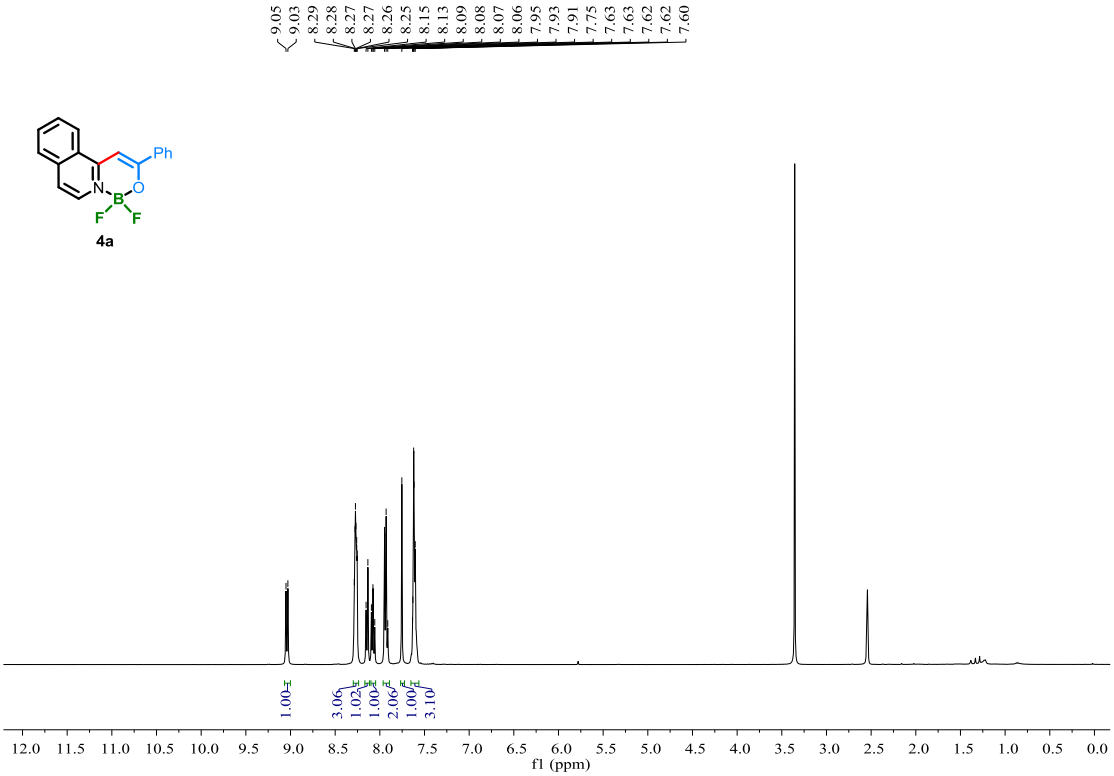
^{1}H NMR of **3p'** (400 MHz, DMSO)



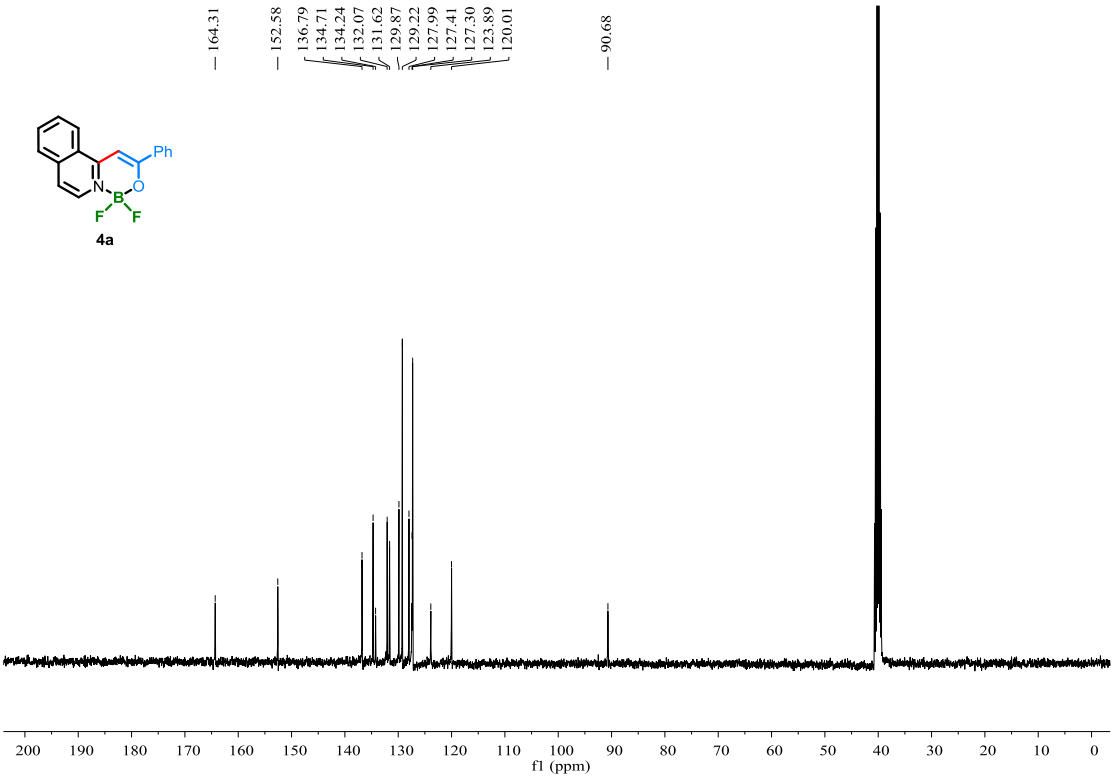
^{13}C NMR of **3p'** (100 MHz, DMSO)



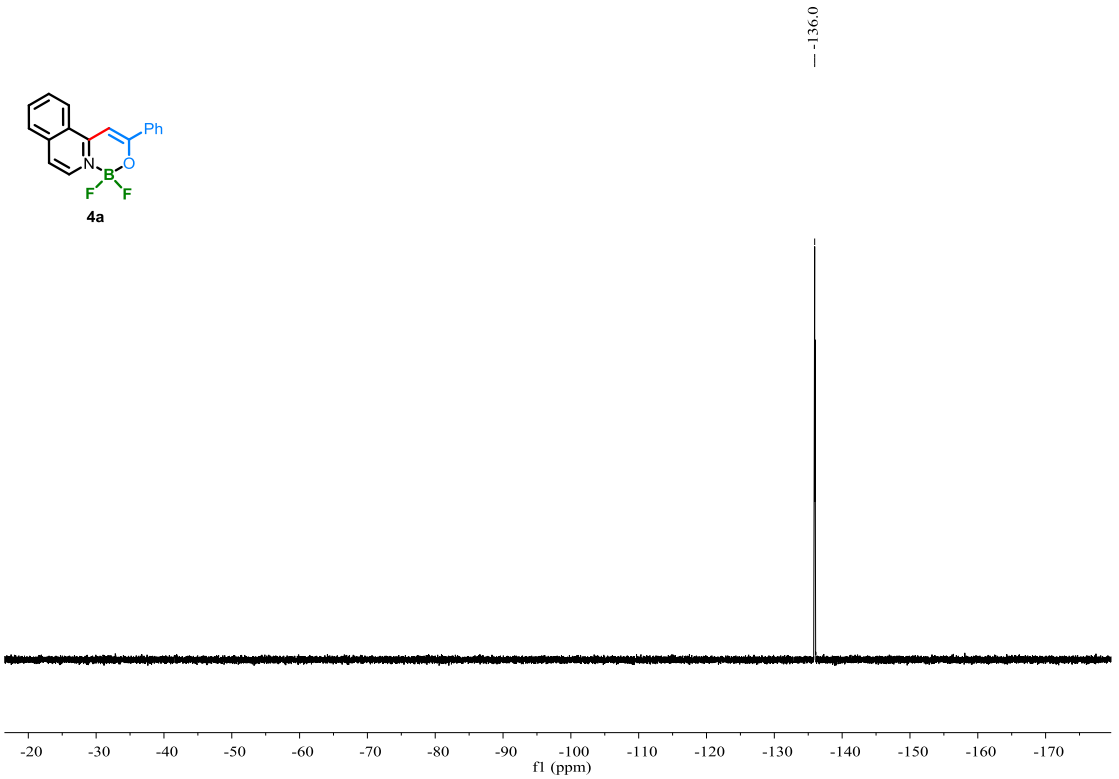
^{1}H NMR of **4a** (400 MHz, DMSO)



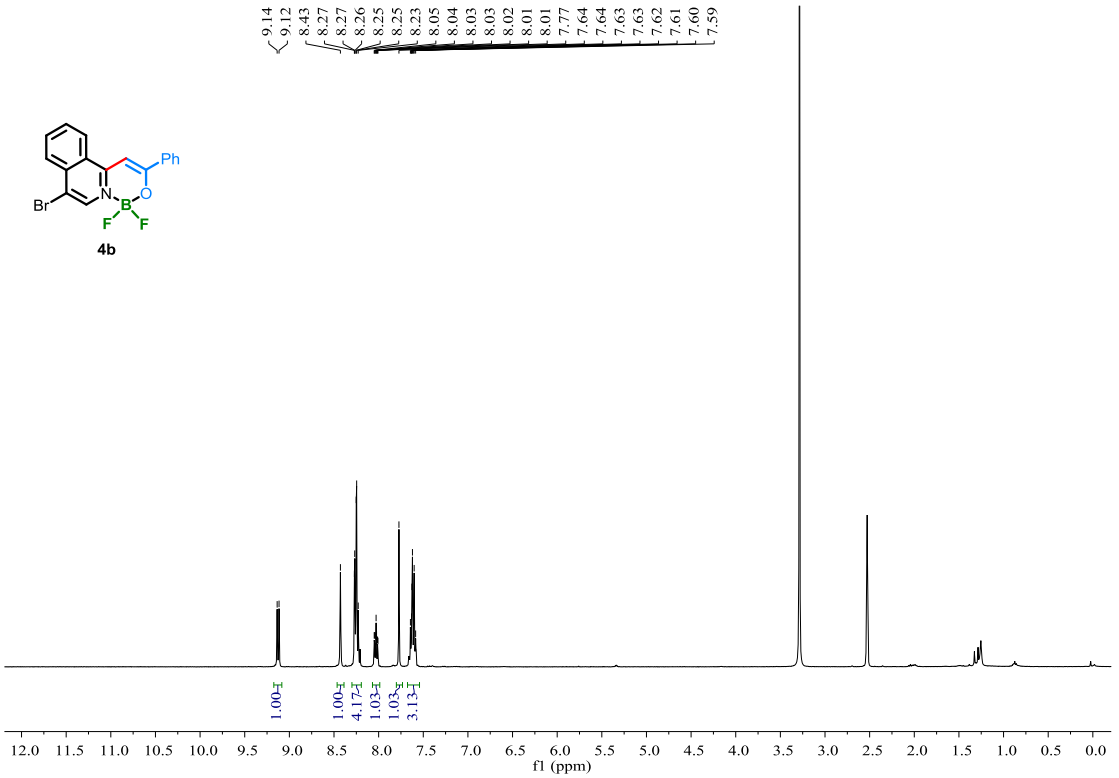
^{13}C NMR of **4a** (100 MHz, DMSO)



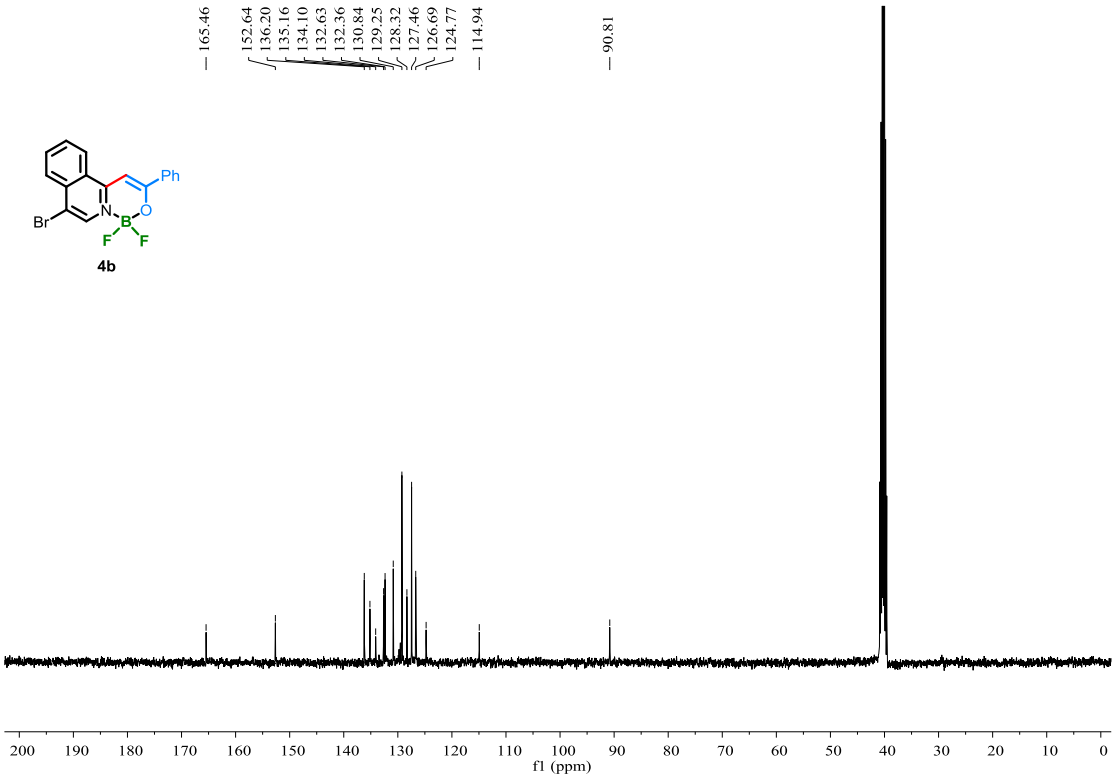
^{19}F NMR of **4a** (376 MHz, DMSO)



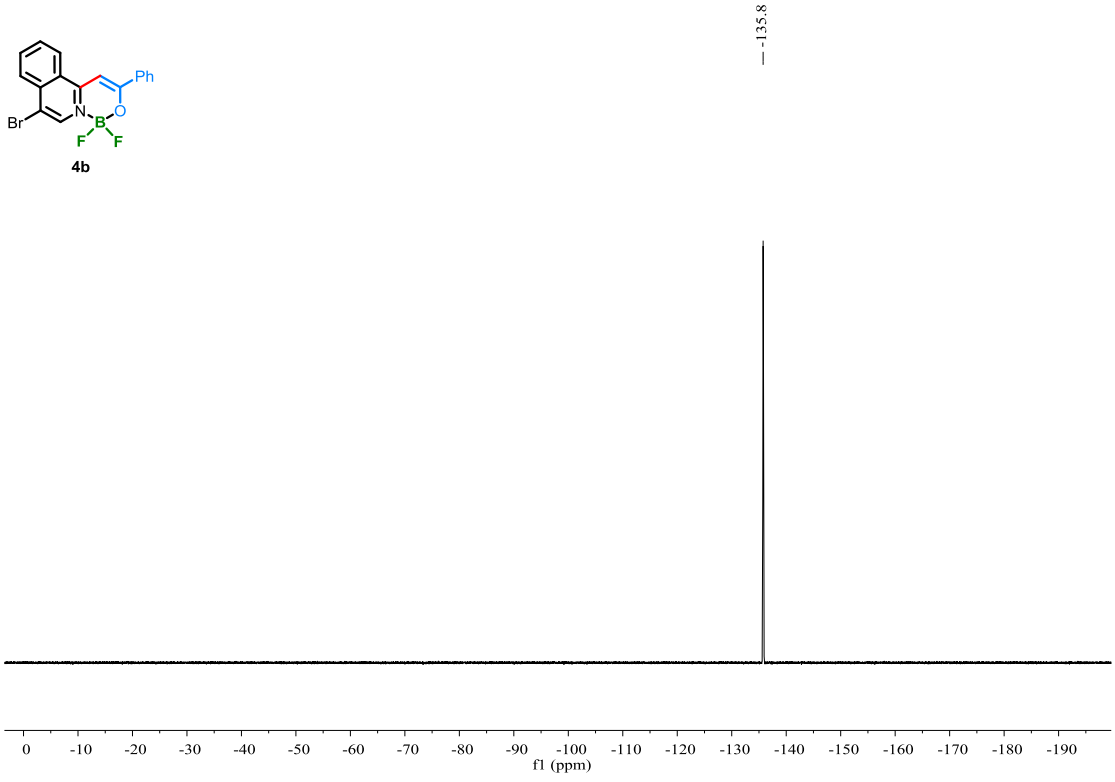
^{1}H NMR of **4b** (400 MHz, DMSO)



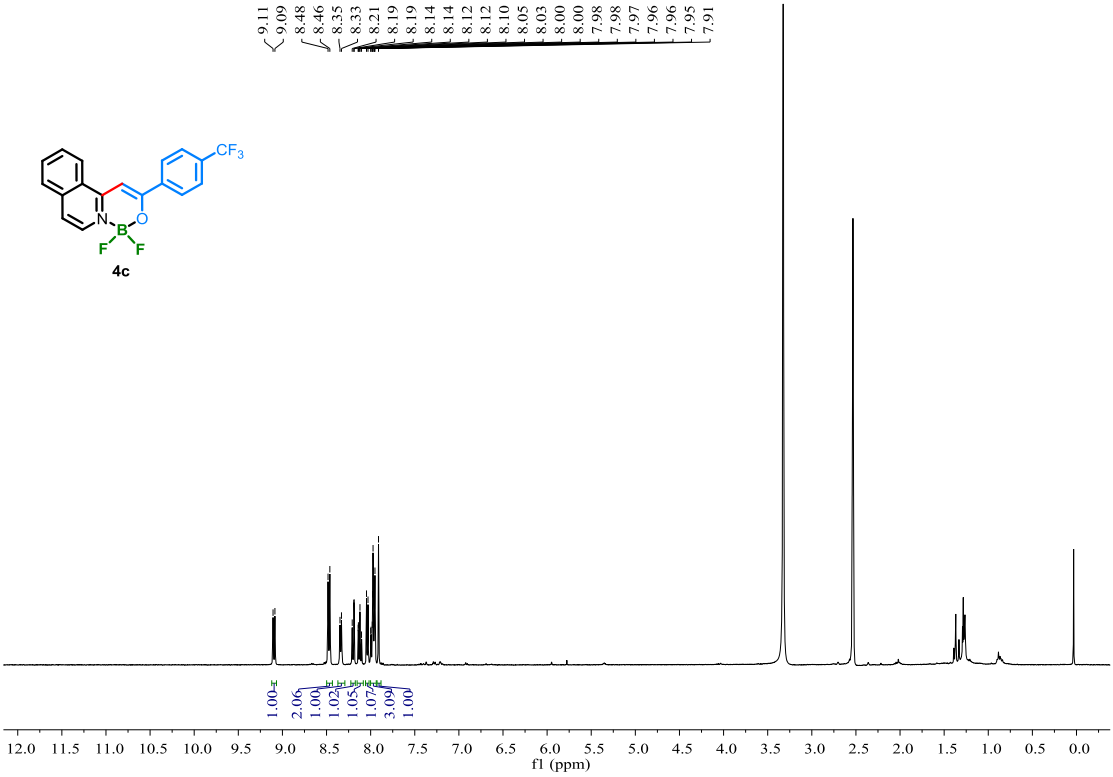
^{13}C NMR of **4b** (100 MHz, DMSO)



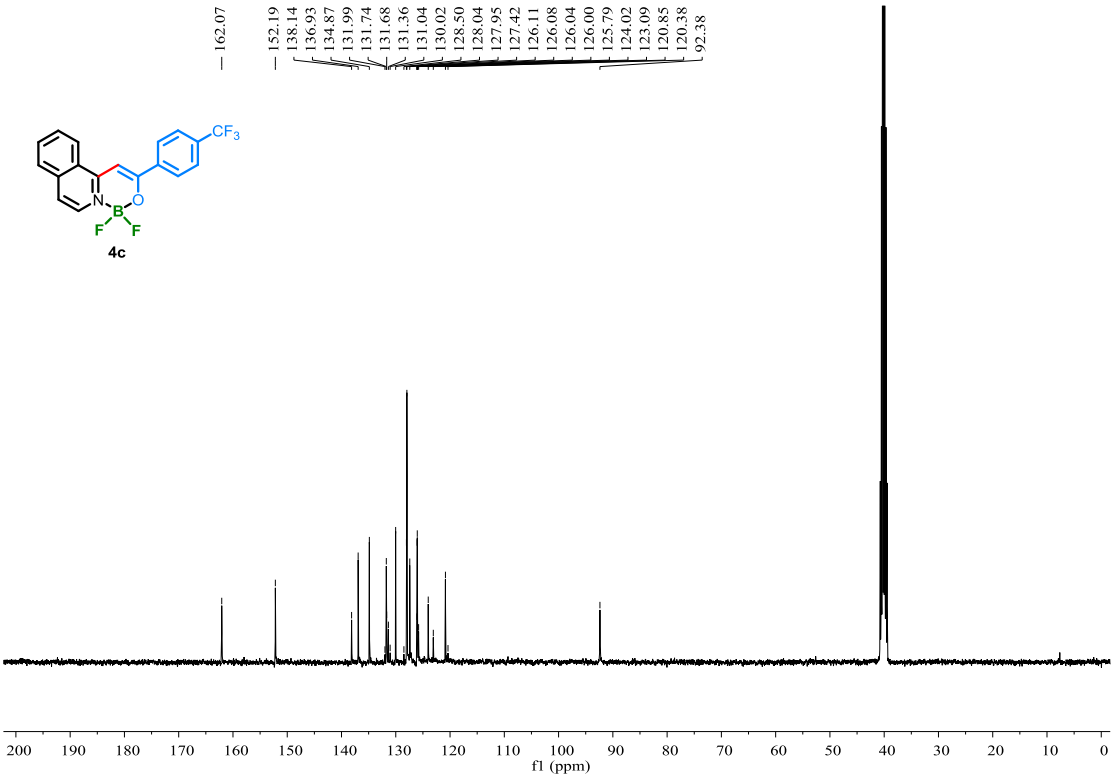
^{19}F NMR of **4b** (376 MHz, DMSO)



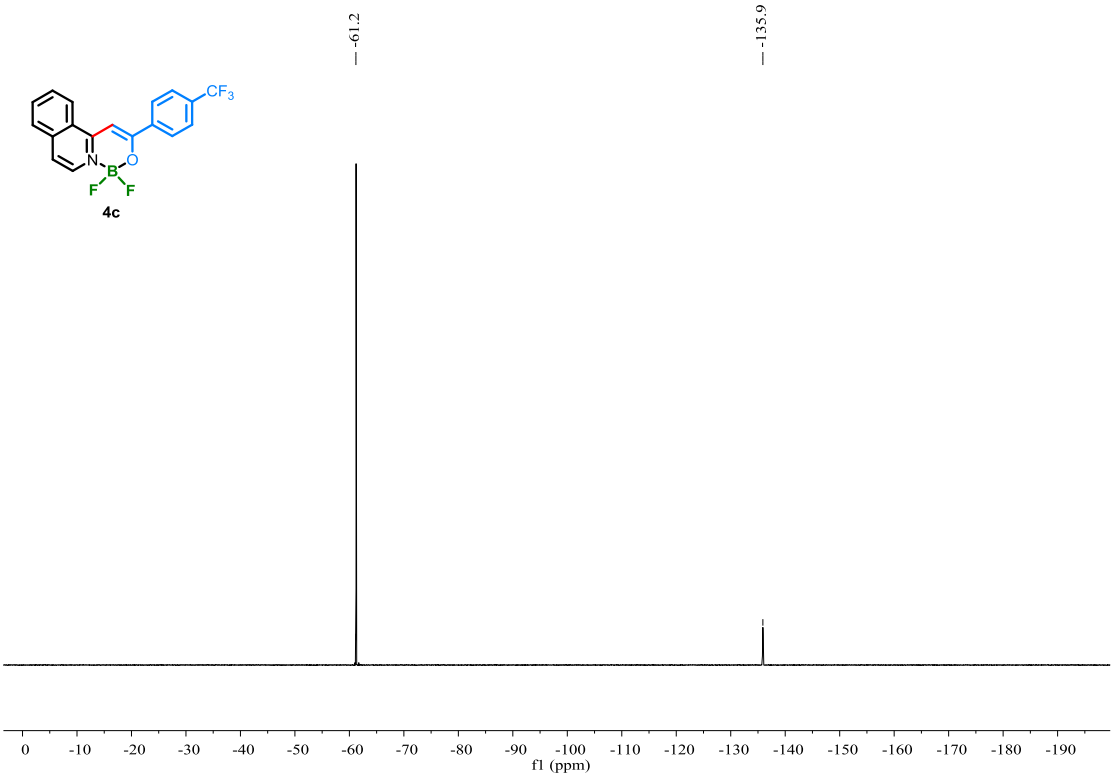
^{1}H NMR of **4c** (400 MHz, DMSO)



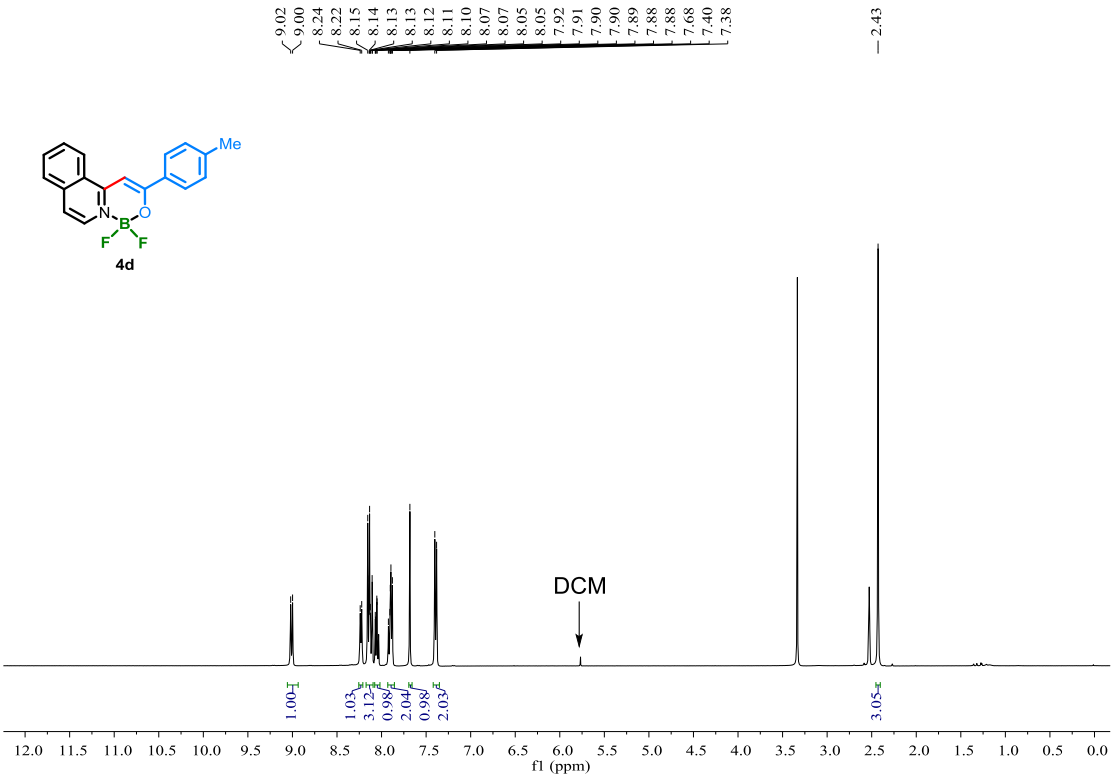
^{13}C NMR of **4c** (100 MHz, DMSO)



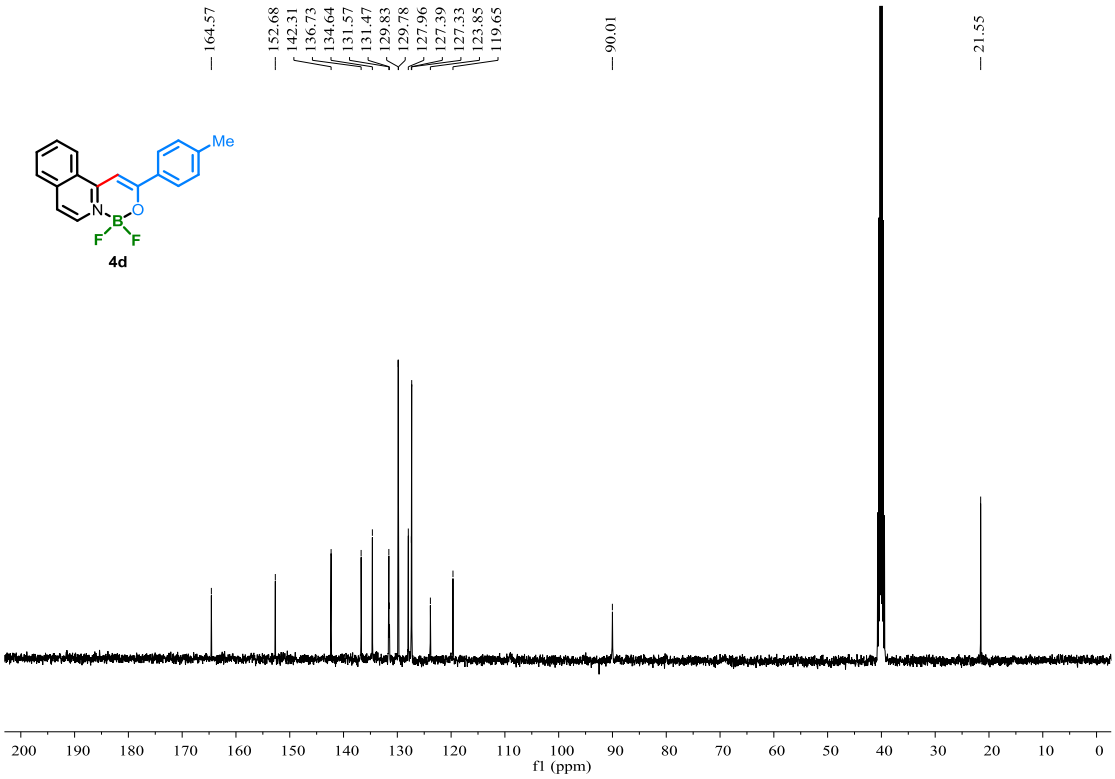
^{19}F NMR of **4c** (376 MHz, DMSO)



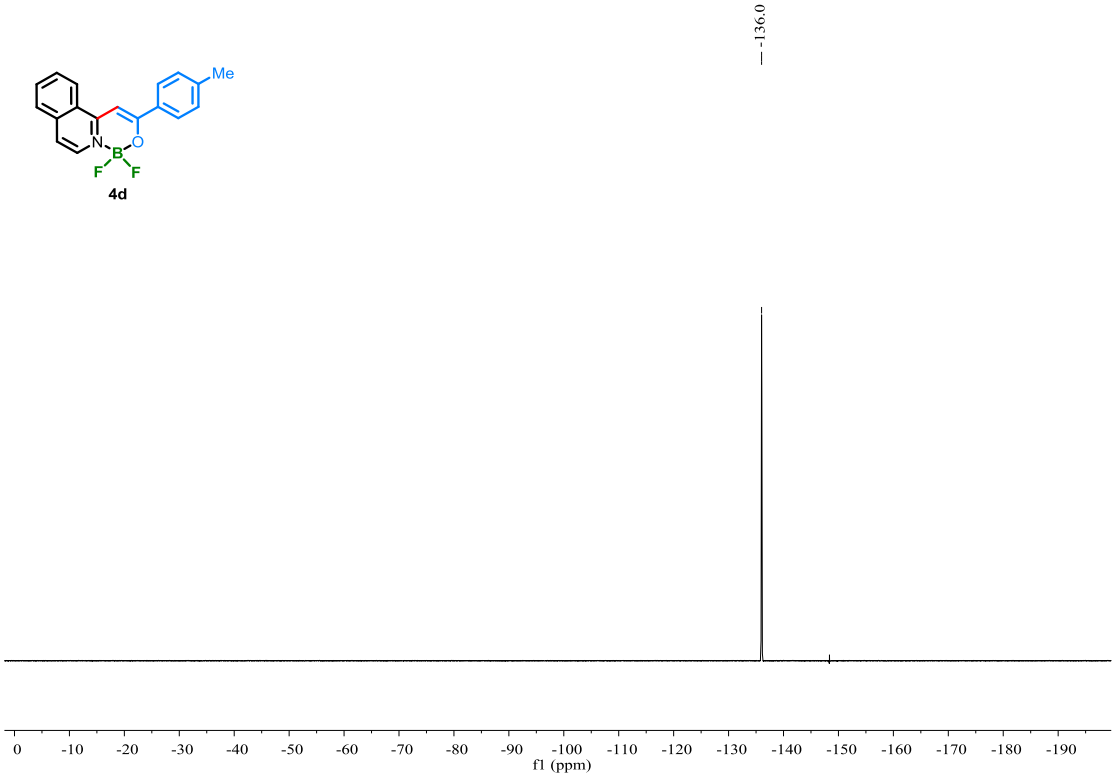
^{1}H NMR of **4d** (400 MHz, DMSO)



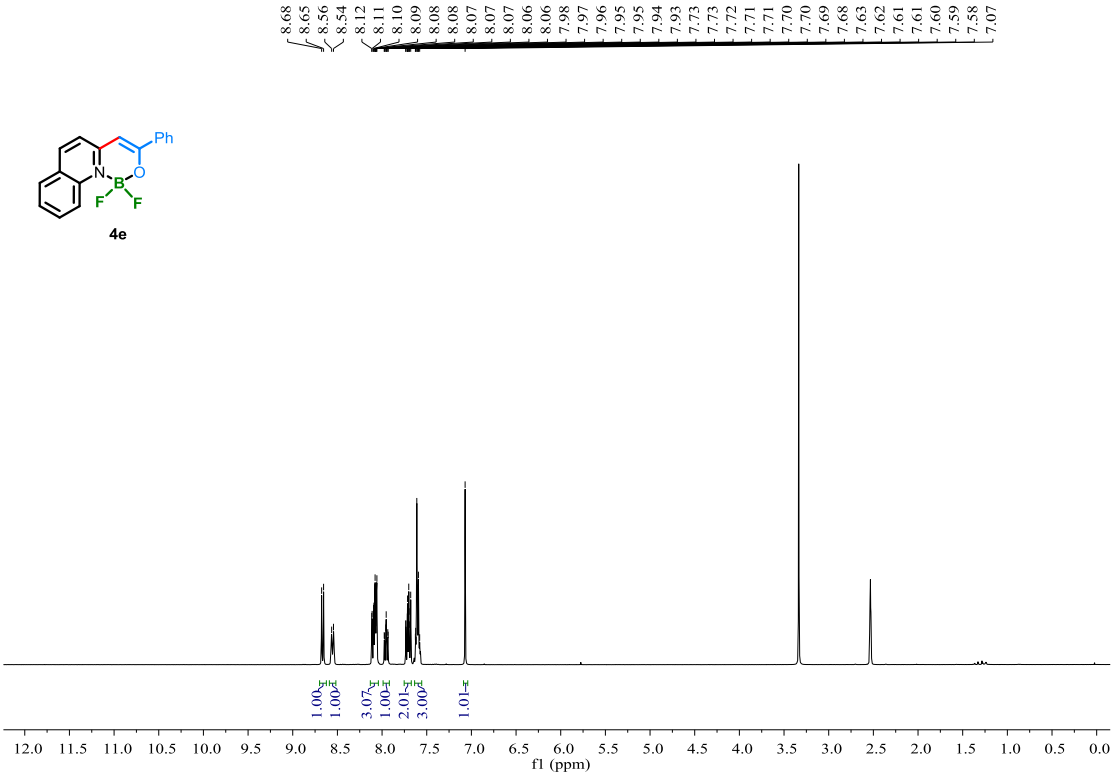
^{13}C NMR of **4d** (100 MHz, DMSO)



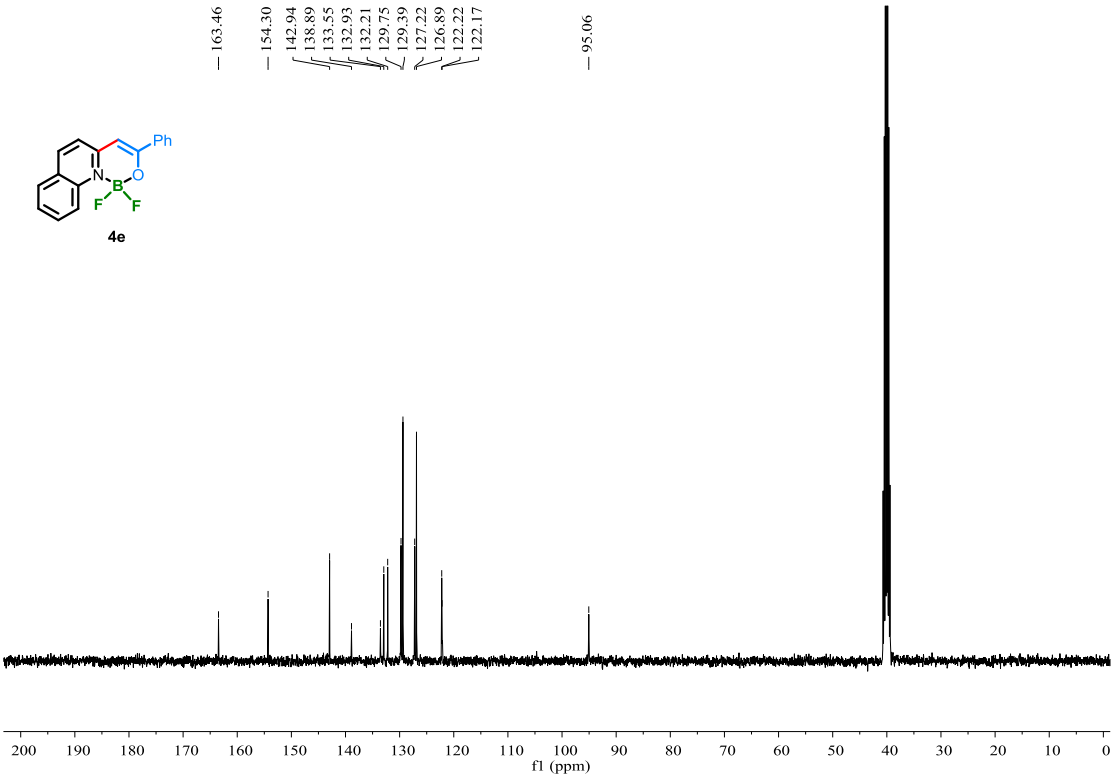
^{19}F NMR of **4d** (376 MHz, DMSO)



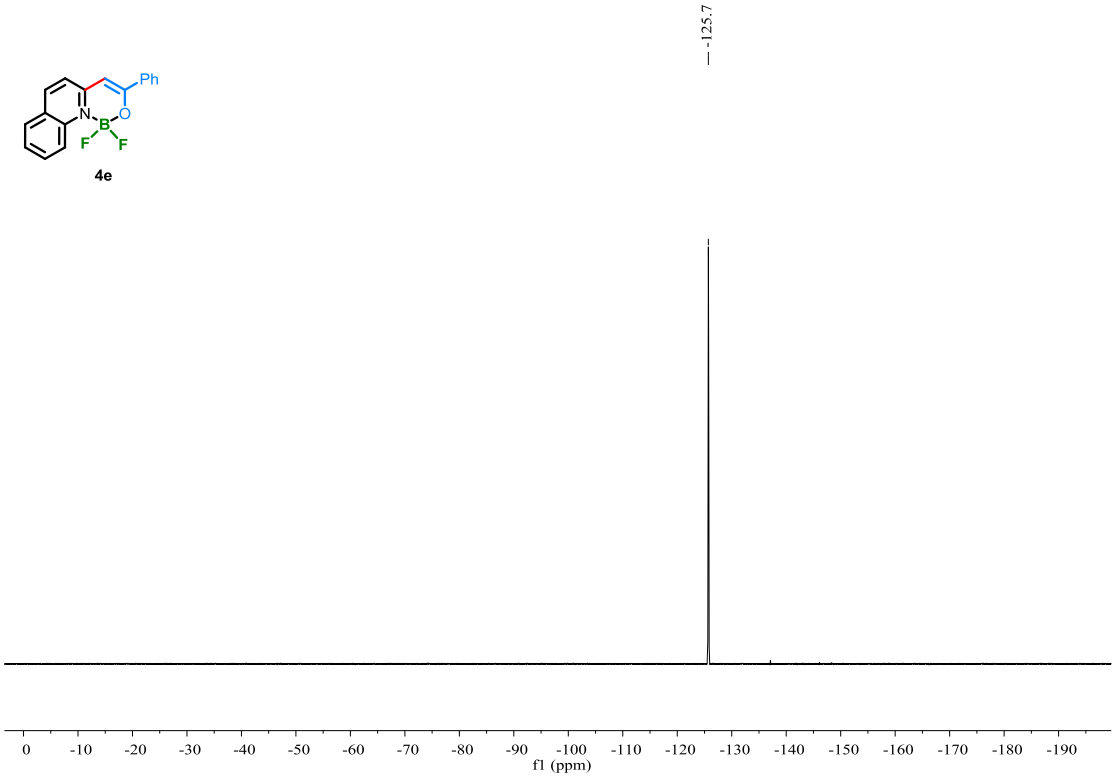
^{1}H NMR of **4e** (400 MHz, DMSO)



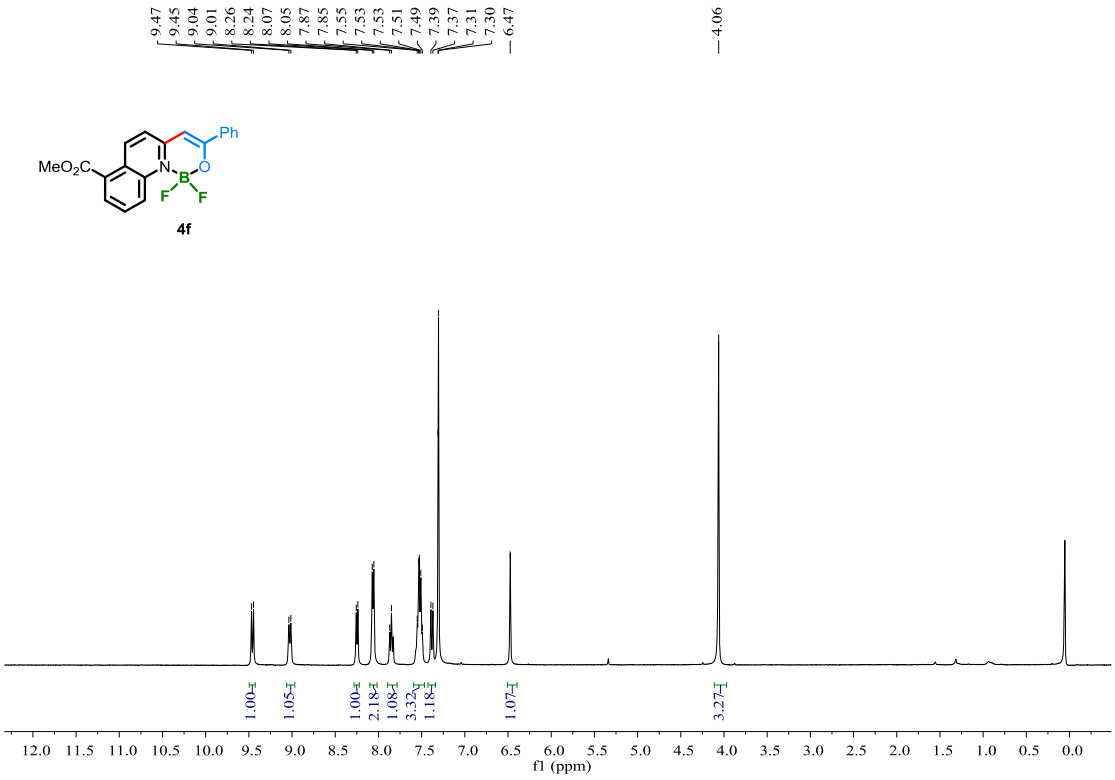
^{13}C NMR of **4e** (100 MHz, DMSO)



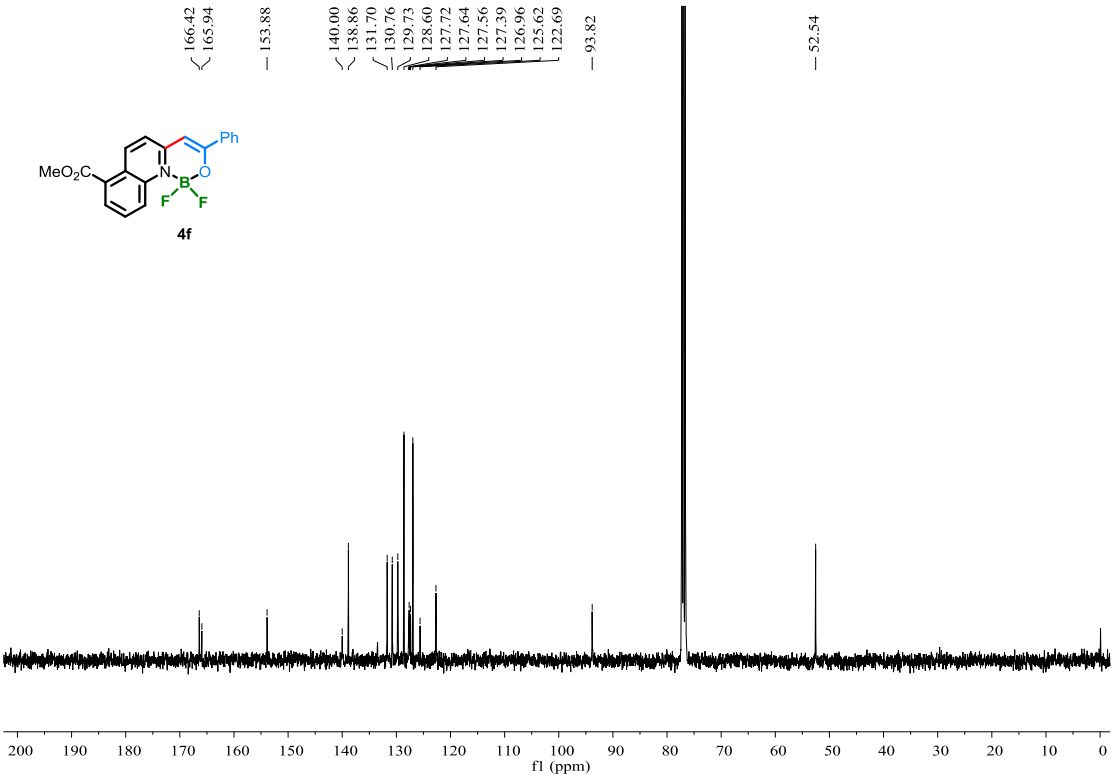
^{19}F NMR of **4e** (376 MHz, DMSO)



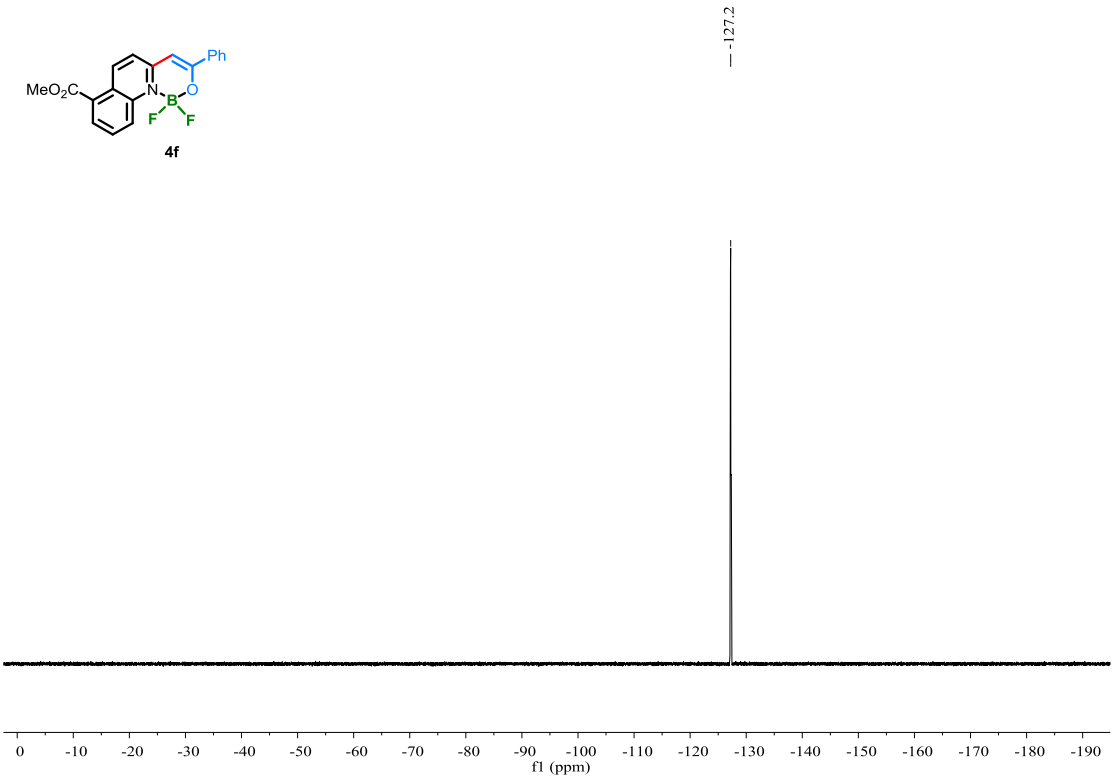
^{1}H NMR of **4f** (400 MHz, $CDCl_3$)



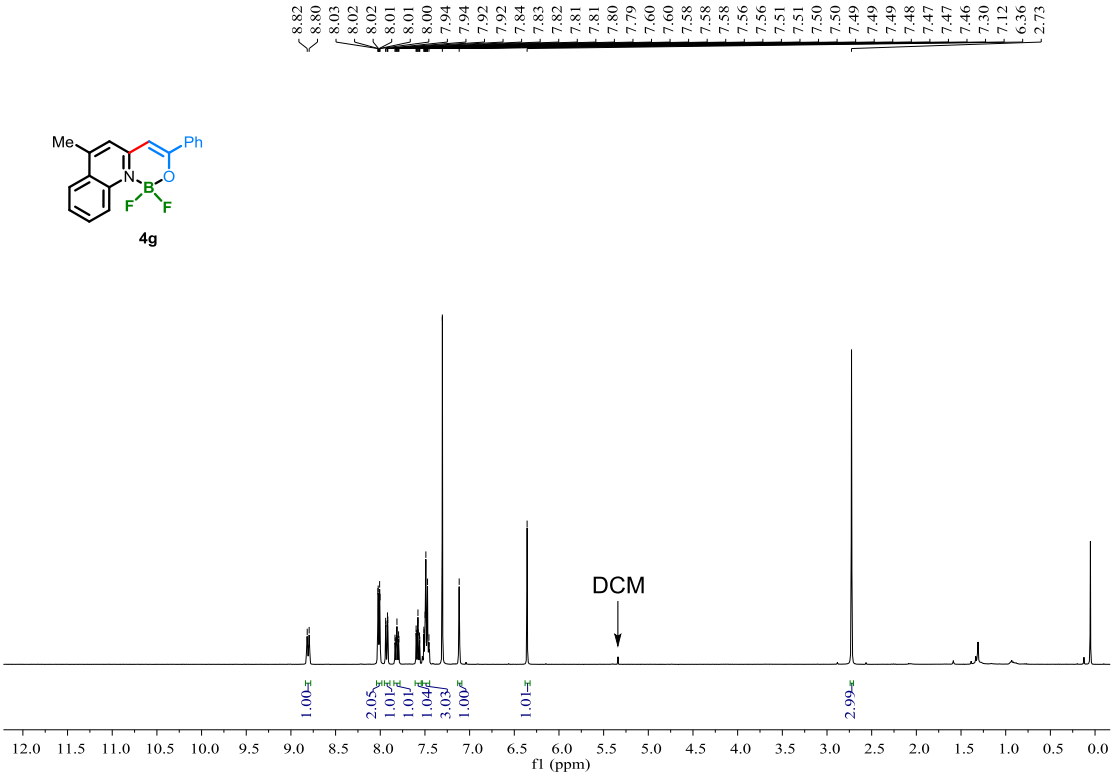
^{13}C NMR of **4f** (100 MHz, $CDCl_3$)



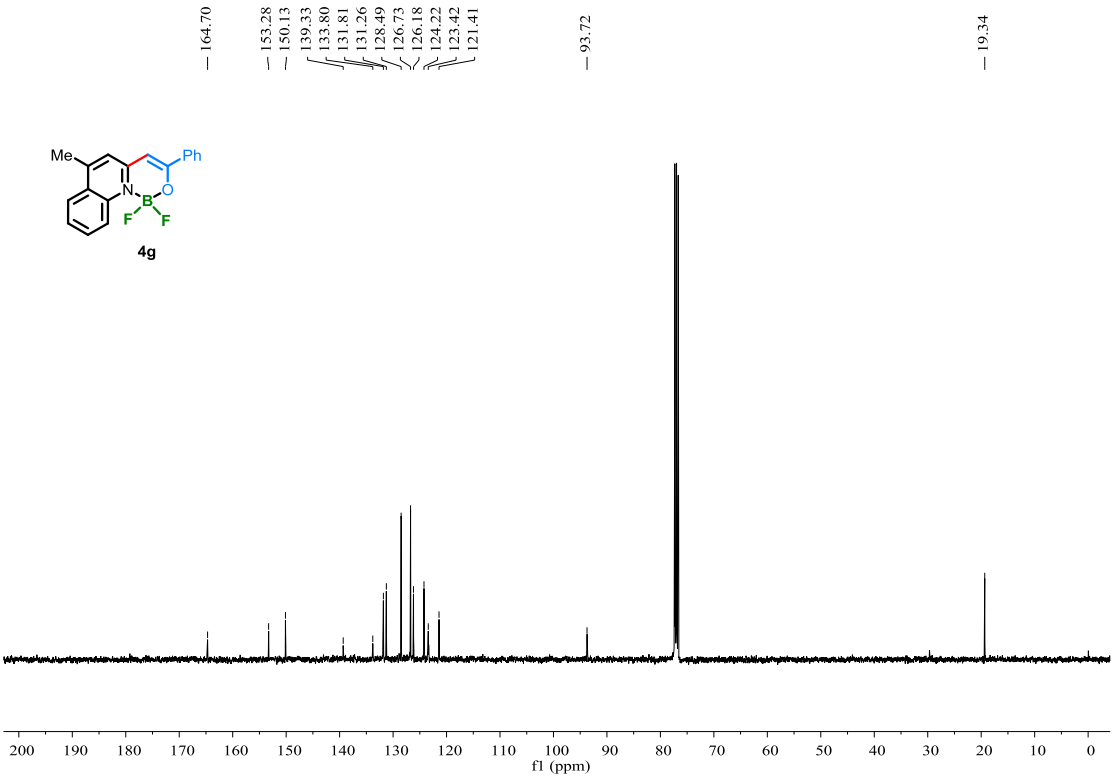
^{19}F NMR of **4f** (376 MHz, $CDCl_3$)



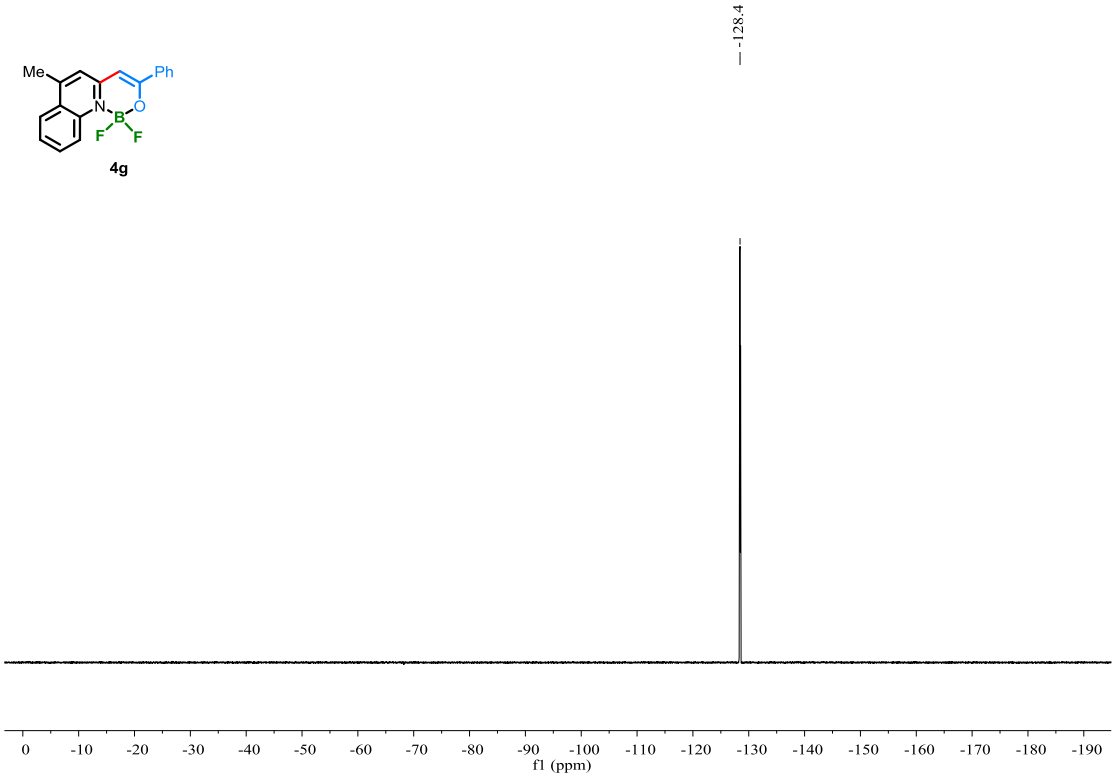
^{1}H NMR of **4g** (400 MHz, $CDCl_3$)



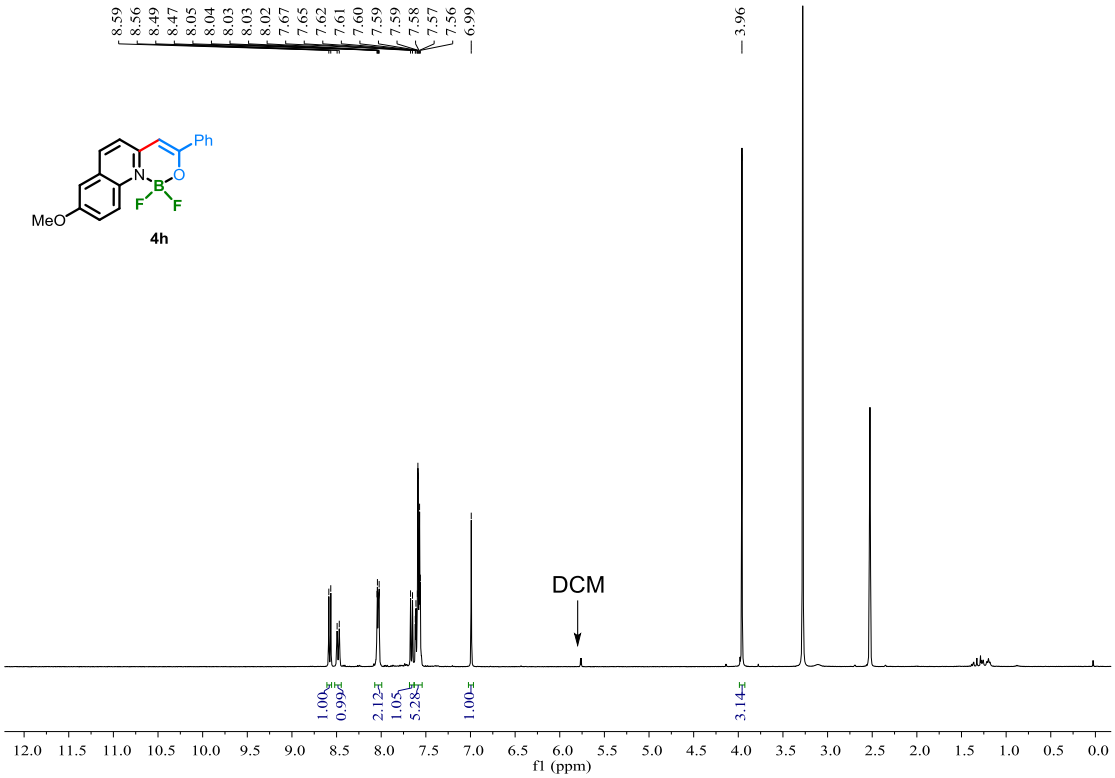
^{13}C NMR of **4g** (100 MHz, $CDCl_3$)



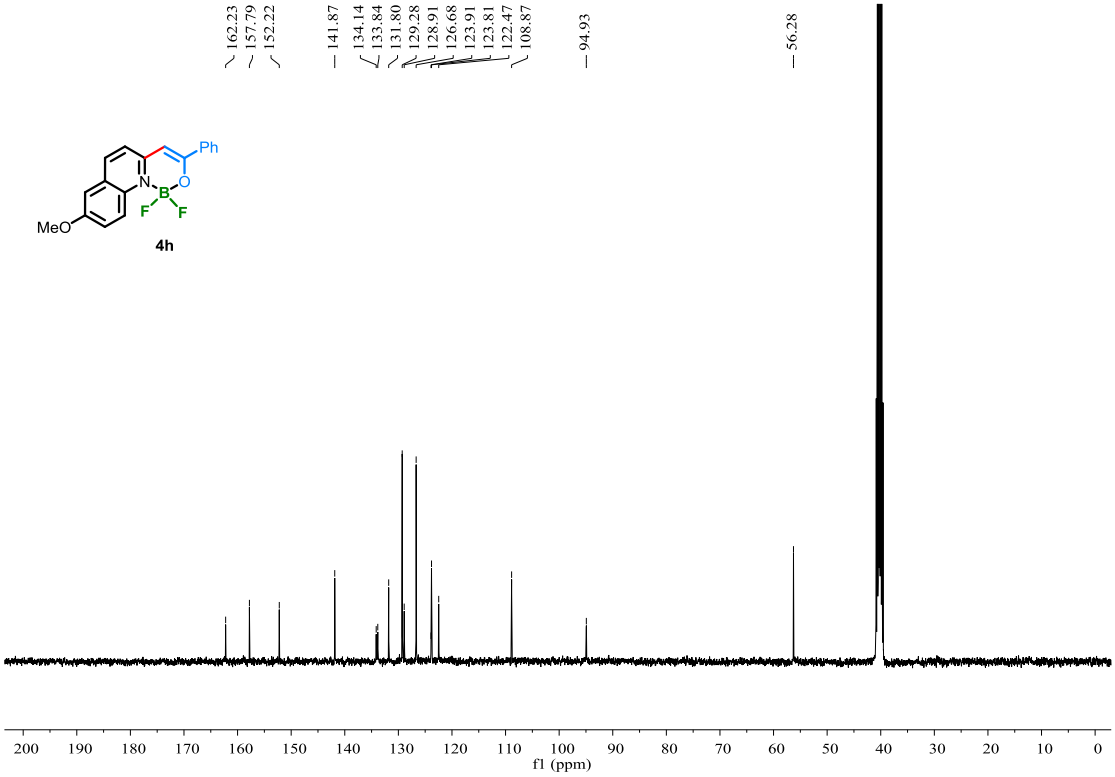
^{19}F NMR of **4g** (376 MHz, $CDCl_3$)



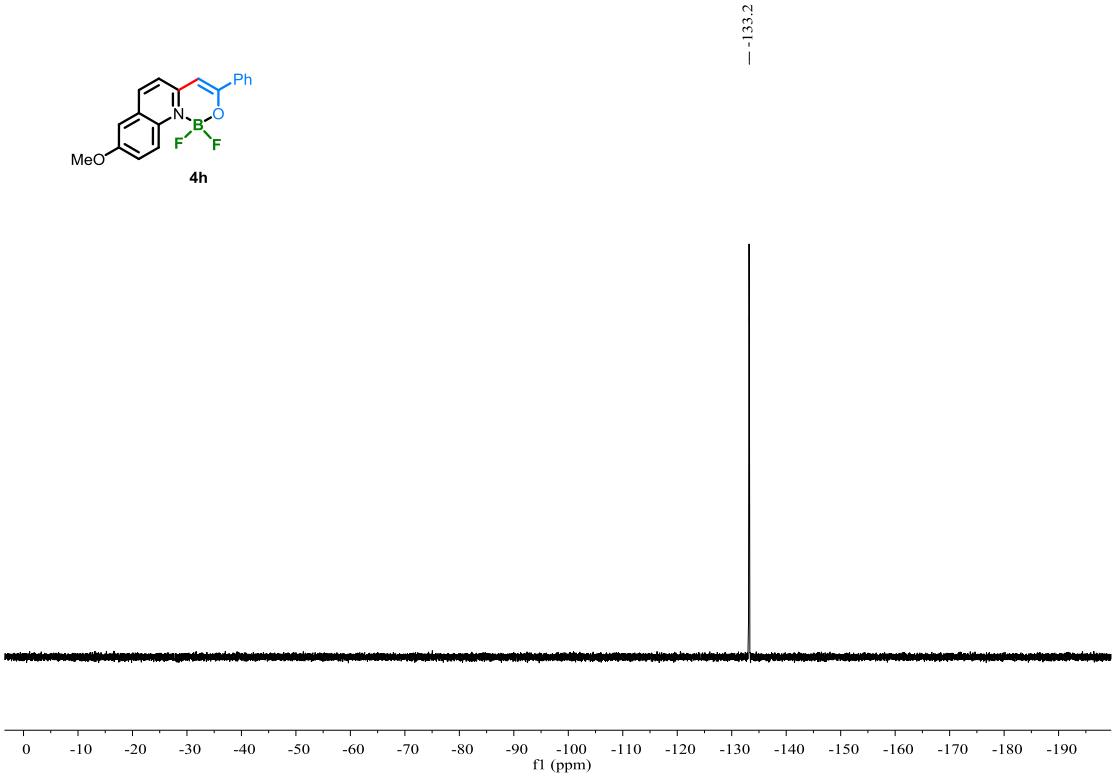
^{1}H NMR of **4h** (400 MHz, DMSO)



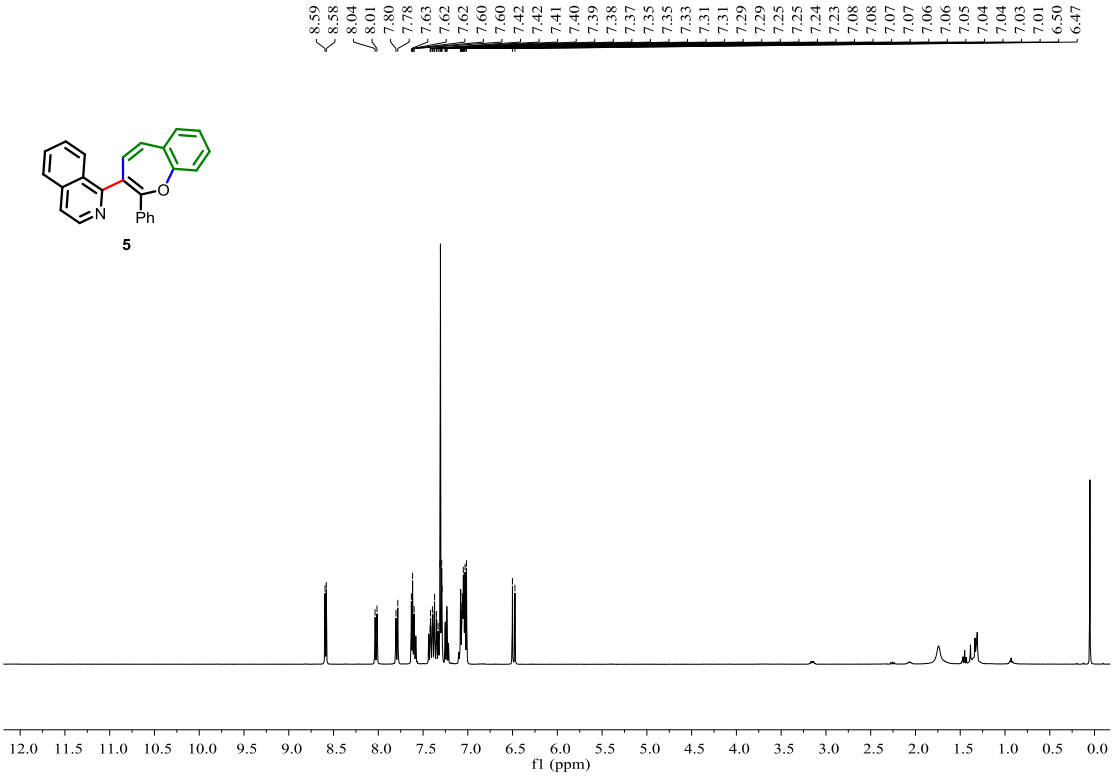
^{13}C NMR of **4h** (100 MHz, DMSO)



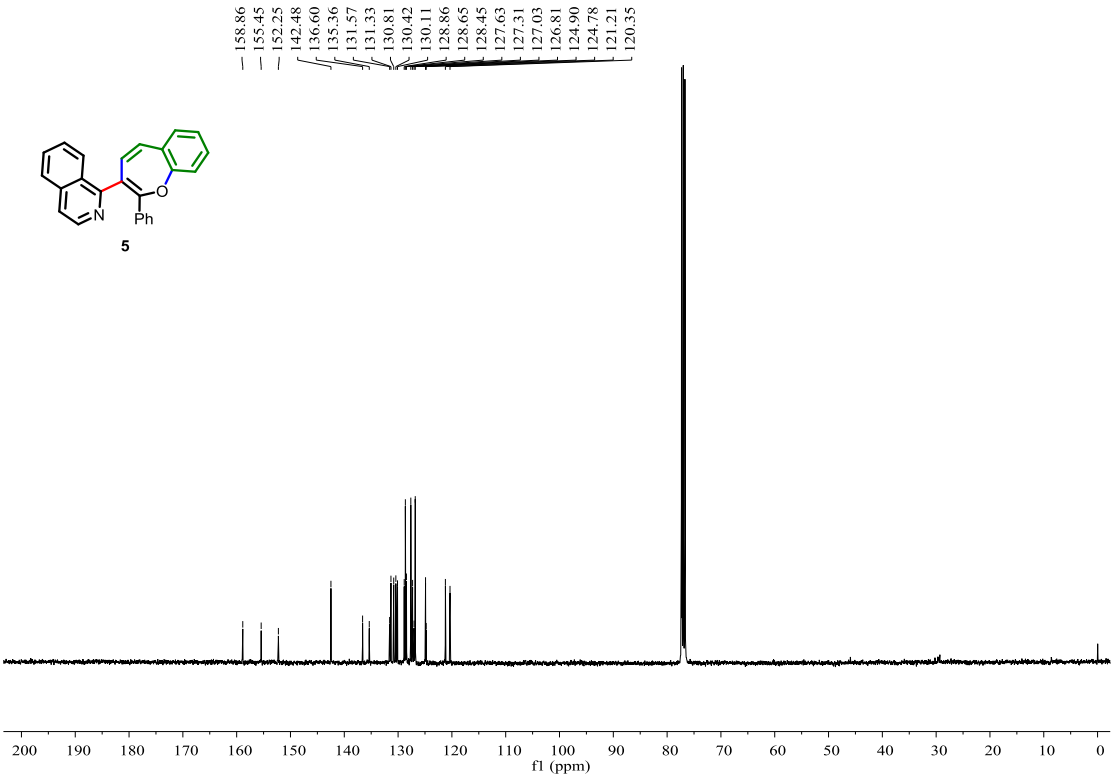
^{19}F NMR of **4h** (376 MHz, DMSO)



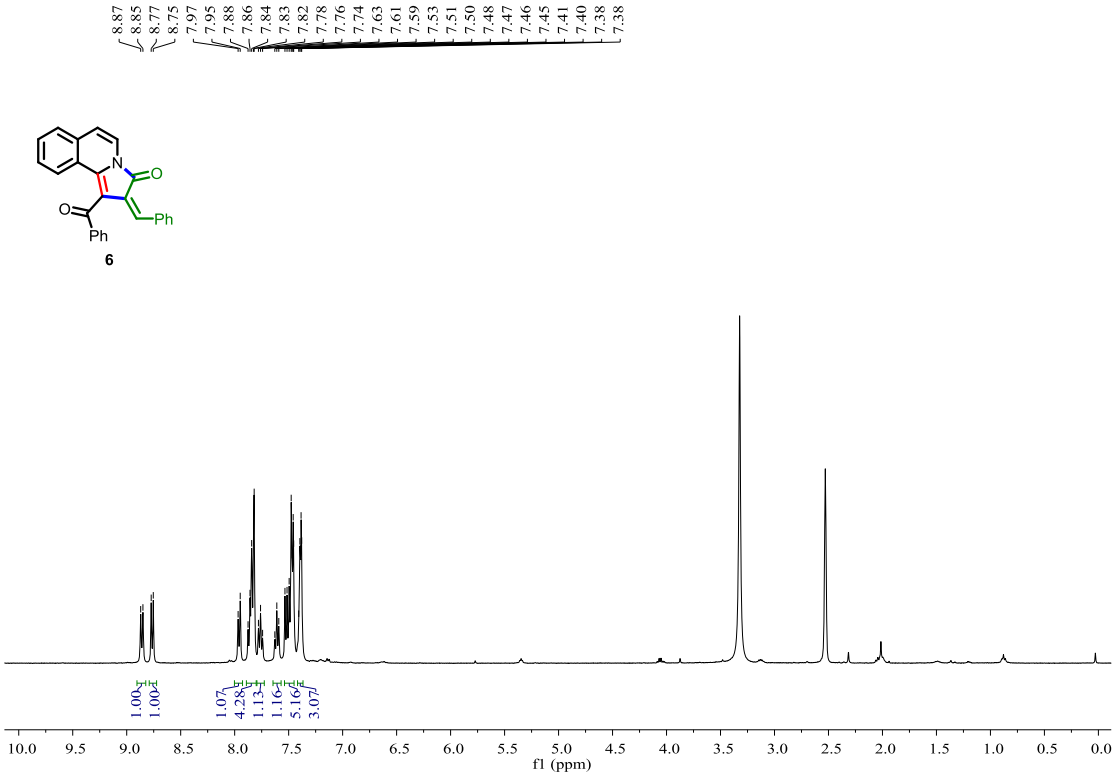
^{1}H NMR of **5** (400 MHz, $CDCl_3$)



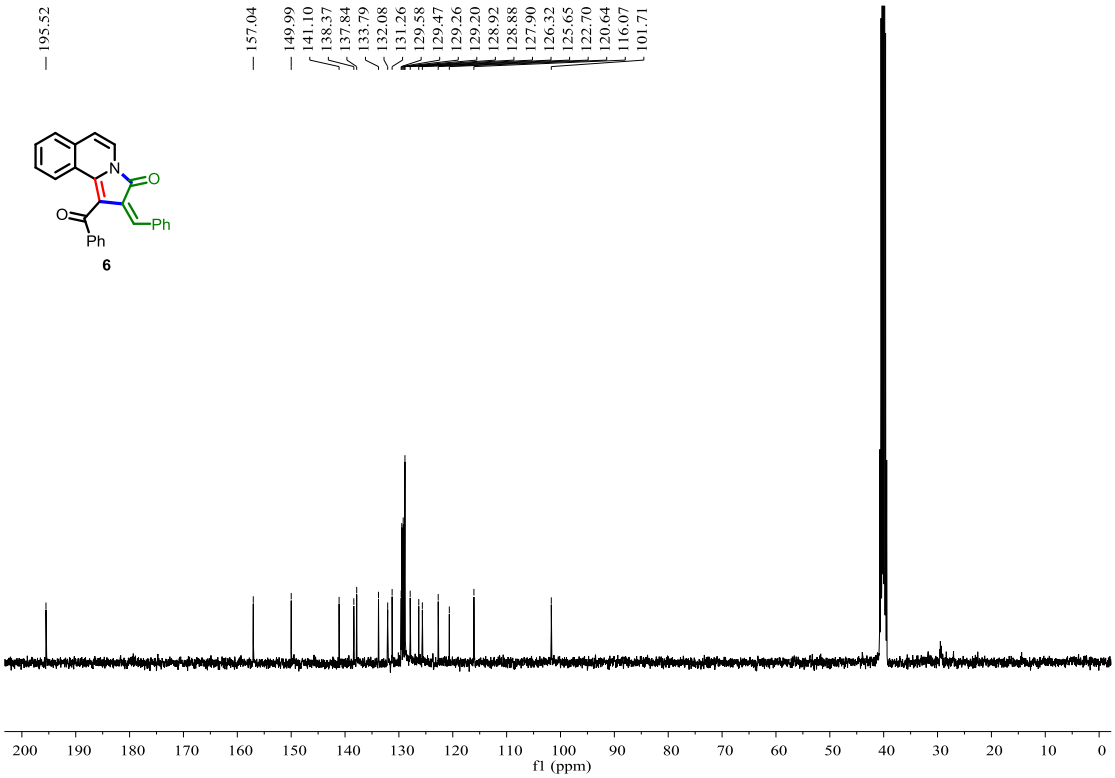
^{13}C NMR of **5** (100 MHz, $CDCl_3$)



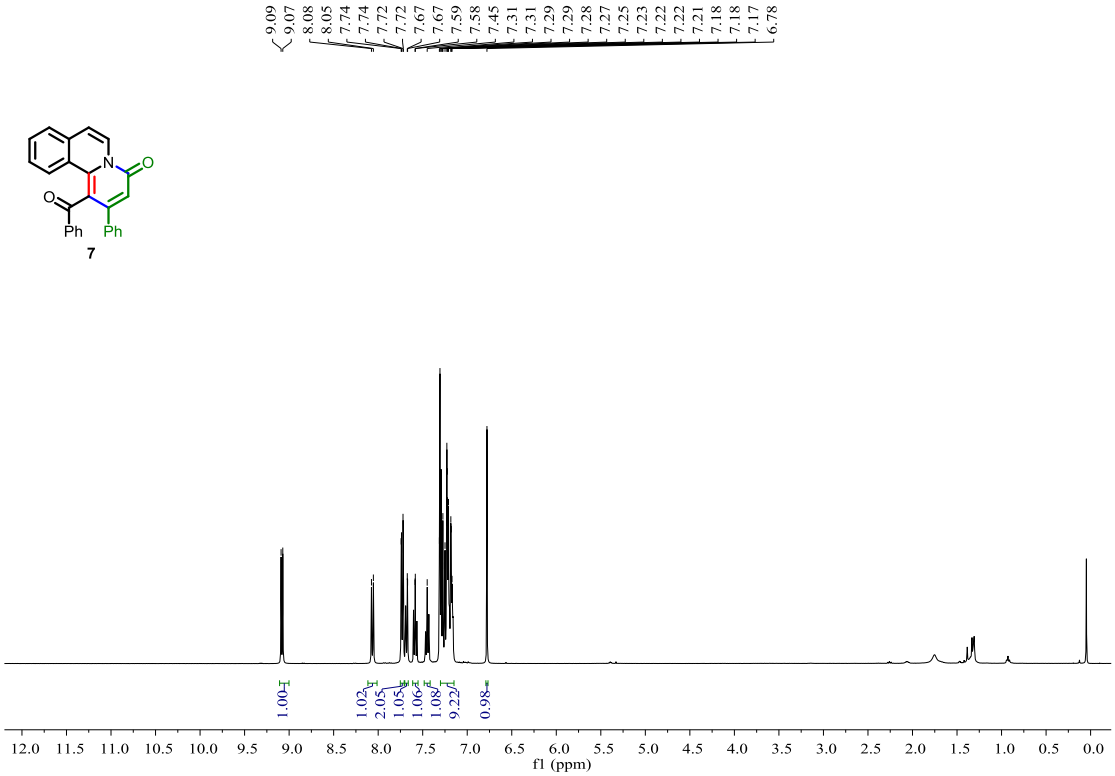
^{1}H NMR of **6** (400 MHz, DMSO)



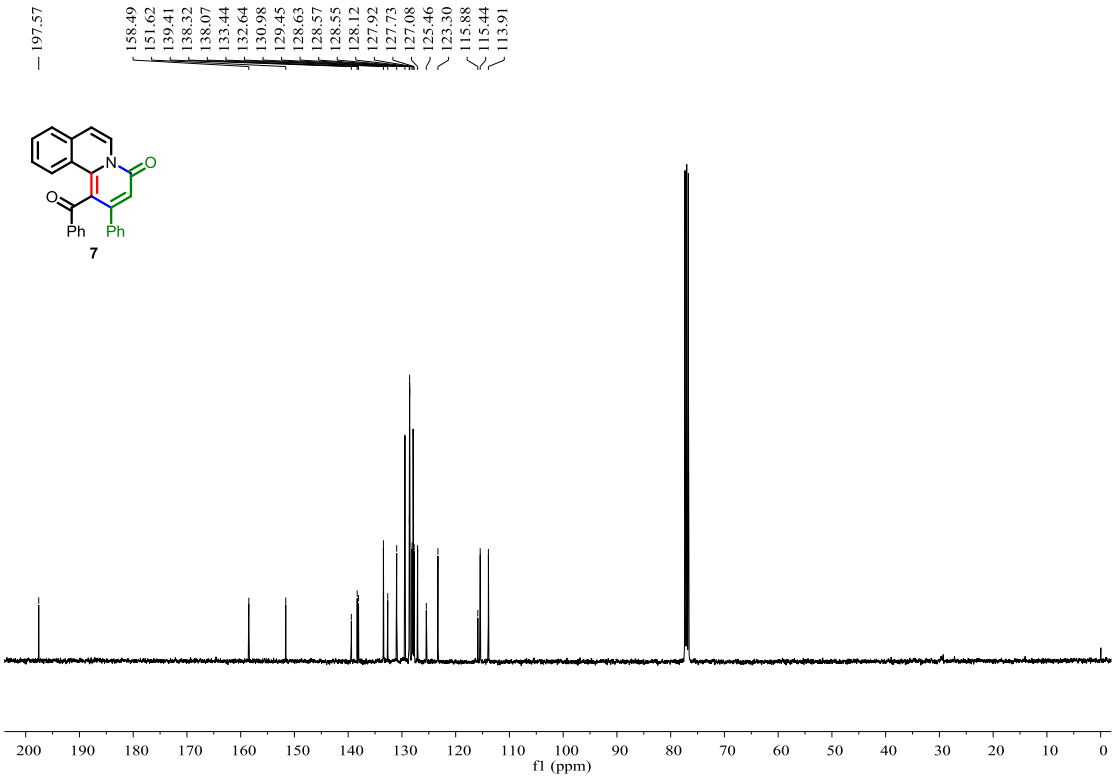
^{13}C NMR of **6** (100 MHz, DMSO)



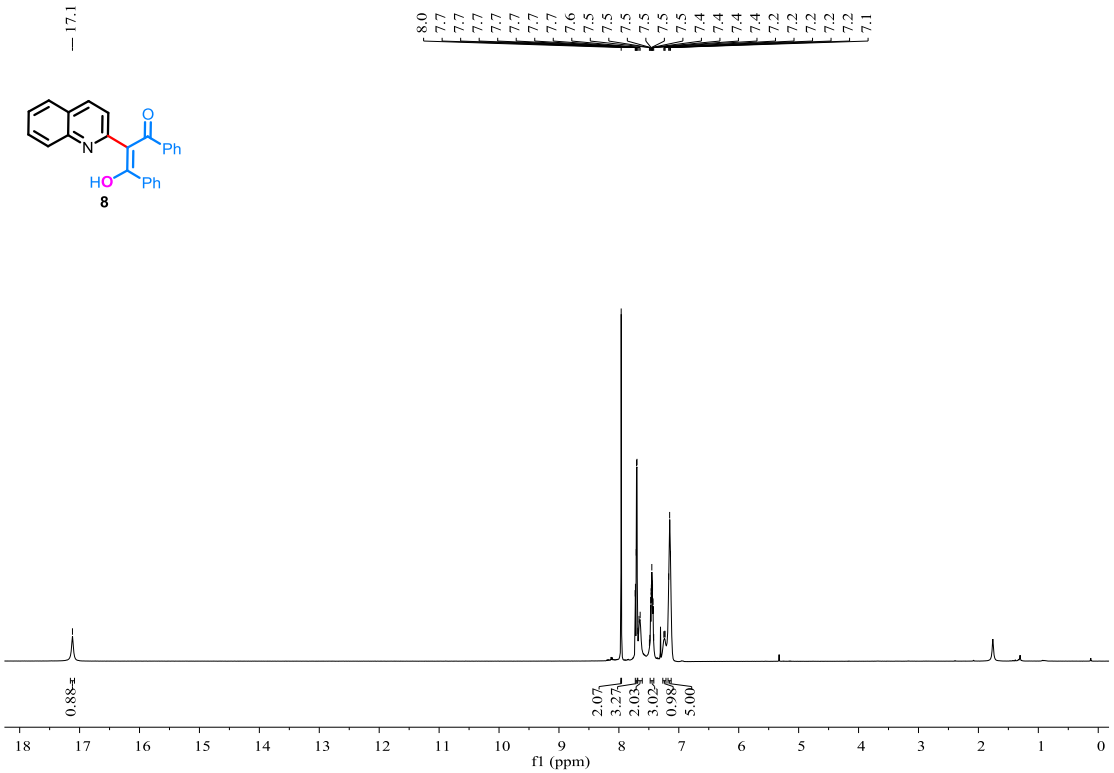
^{1}H NMR of **7** (400 MHz, $CDCl_3$)



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



^{1}H NMR of **8** (400 MHz, $CDCl_3$)



^{13}C NMR of **8** (100 MHz, $CDCl_3$)