

Palladium/norbornene-catalyzed C–H/N–H cycloaddition of carbazoles with 2-halobenzoic acid derivatives

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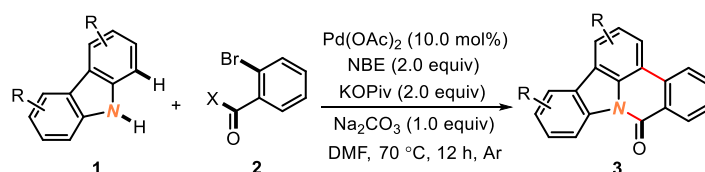
1. General information

All reagents were used from commercial received unless otherwise noted. Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (TLC Silica Gel 60 F₂₅₄); visualization of the developed chromatogram was performed by fluorescence. Flash Chromatography was performed with silica gel (300-400 mesh). Proton-1 nuclear magnetic resonance (¹H 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 (¹³C 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 CDCl₃. High resolution mass spectra (HRMS) were acquired on a Bruker Daltonics MicroTof-Q II mass spectrometer. The Fourier IR data was determined on a VECTOR II spectrometer in Bruker Germany.

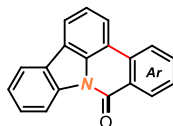
2. General procedure for the synthesis of substrates

The substrates **1a-d**, **1f**, **1i**, **1l-1m**, **1t** and **1u** were commercially available, and the Others (including **1e**^[1], **1k**^[1], **1g-h**^[2] and **1j**^[2]) were prepared according to the reported procedures.

3. General procedure for the synthesis of products 3

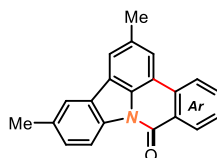


A 15 mL pressure tube was charged with Pd(OAc)₂ (0.02 mmol, 4.5 mg, 0.1 equiv.), KOPiv (0.4 mmol, 56.0 mg, 2.0 equiv.), Na₂CO₃ (0.2 mmol, 21.2 mg, 1.0 equiv.), NBE (0.4 mmol, 37.6 mg, 2.0 equiv.), **1** (0.2 mmol, 1.0 equiv.), **2** (0.4 mmol, 2.0 equiv.) and DMF (2 mL) under Ar atmosphere. The reaction mixture was stirred at 70 °C for 12 h under Ar atmosphere in an oil bath. After cooling to room temperature, neutralized by a saturated aqueous NaCl solution, and extracted with EtOAc. The organic layers were dried over anhydrous Na₂SO₄ and concentrated to dryness under reduced pressure. The crude product was purified by silica gel flash chromatography (PE/EA as the eluent) to give the products **3**.



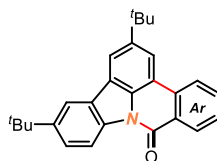
8H-indolo[3,2,1-de]phenanthridin-8-one (3a)

White solid (42.1 mg, 78% yield). M.p.: 218-220 °C. PE / EA = 20:1, $R_f = 0.32$. $^1\text{H NMR}$ (400 MHz, $\text{CDCl}_3 + 10\% \text{CF}_3\text{COOD}$): δ 8.50 (d, $J = 7.6$ Hz, 1H), 8.35 (d, $J = 7.3$ Hz, 1H), 7.96 (d, $J = 7.4$ Hz, 1H), 7.77 (s, 2H), 7.67 (d, $J = 6.8$ Hz, 2H), 7.50 (dt, $J = 14.8, 7.1$ Hz, 2H), 7.37 (t, $J = 6.7$ Hz, 1H), 7.27 (d, $J = 7.2$ Hz, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 160.8, 138.1, 133.8, 133.4, 133.1, 129.0, 128.5, 128.3, 126.6, 126.4, 125.7, 124.7, 124.5, 122.4, 121.1, 120.8, 120.3, 117.5, 116.8. IR (KBr): 3468, 2924, 1750, 1663, 1599, 1498, 1434, 1343, 1304, 1267, 759, cm^{-1} .



2,12-dimethyl-8H-indolo[3,2,1-de]phenanthridin-8-one (3b)

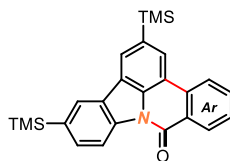
White solid (46.8 mg, 78% yield). M.p.: 266-269 °C. PE / EA = 20:1, $R_f = 0.32$. $^1\text{H NMR}$ (400 MHz, $\text{CDCl}_3 + 10\% \text{CF}_3\text{COOD}$): δ 8.39 (d, $J = 8.0$ Hz, 1H), 8.32 (d, $J = 8.3$ Hz, 1H), 8.06 (d, $J = 8.0$ Hz, 1H), 7.75 (t, $J = 7.5$ Hz, 1H), 7.62 (s, 1H), 7.58 (t, $J = 7.6$ Hz, 1H), 7.52 (s, 1H), 7.49 (s, 1H), 7.26 (t, $J = 3.9$ Hz, 1H), 2.48 (s, 3H), 2.45 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 161.2, 136.4, 136.2, 135.3, 134.1, 133.7, 131.5, 129.4, 129.1, 128.6, 127.2, 126.2, 125.0, 122.6, 122.1, 121.2, 120.9, 117.4, 116.8, 22.1, 21.7. IR (KBr): 3684, 2921, 2857, 1753, 1667, 1595, 1490, 1453, 1350, 857, 812, 768, 684, 573 cm^{-1} .



2,12-di-tert-butyl-8H-indolo[3,2,1-de]phenanthridin-8-one (3c)

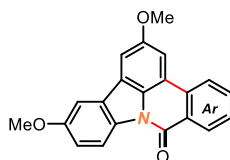
White solid (53.3 mg, 70% yield). M.p.: 212-214 °C. PE / EA = 20:1, $R_f = 0.32$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.70 (d, $J = 8.6$ Hz, 1H), 8.65 (d, $J = 7.9$ Hz, 1H), 8.33 (d, $J = 8.0$ Hz, 1H), 8.21 (s, 1H), 8.16 (s, 1H), 8.11 (s, 1H), 7.78 (t, $J = 7.5$ Hz, 1H), 7.66 (d, $J = 8.6$ Hz, 1H), 7.60 (t, $J = 7.6$ Hz, 1H), 1.57 (s, 9H), 1.50 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 159.9, 148.3, 147.7, 136.9, 134.3, 133.0, 132.8, 129.5, 128.2, 128.1, 126.7, 125.7, 124.7, 122.4, 118.4, 117.3, 117.3,

116.9, 116.5, 35.7, 35.3, 32.3, 32.0. IR (KBr): 2954, 2863, 1674, 1489, 1452, 1362, 1274, 872, 824, 765, 685, 631 cm⁻¹.



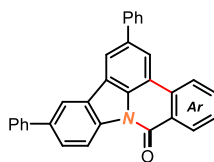
2,12-bis(trimethylsilyl)-8H-indolo[3,2,1-de]phenanthridin-8-one (3d)

White solid (57.4 mg, 71% yield). M.p.: 263-270 °C. PE / EA = 20:1, R_f = 0.32. ¹H NMR (400 MHz, CDCl₃): δ 8.79 (d, *J* = 8.0 Hz, 1H), 8.64 (d, *J* = 7.9 Hz, 1H), 8.35 (d, *J* = 7.9 Hz, 1H), 8.29 (s, 1H), 8.26 – 8.22 (m, 2H), 7.85 – 7.72 (m, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 0.48 (s, 9H), 0.43 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): ¹³C NMR (101 MHz, CDCl₃) δ 160.7, 139.8, 137.6, 136.5, 135.6, 134.6, 133.8, 133.6, 130.1, 128.9, 128.5, 126.6, 126.4, 126.3, 125.7, 124.8, 123.0, 117.4, 117.3, 0.0. IR (KBr): 2952, 1677, 1599, 1487, 1357, 1260, 1158, 1108, 841, 763, 689, 621 cm⁻¹.



2,12-dimethoxy-8H-indolo[3,2,1-de]phenanthridin-8-one (3e)

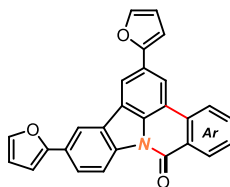
Yellow solid (39.6 mg, 60% yield). M.p.: 192-195 °C. PE / EA = 5:1, R_f = 0.32. ¹H NMR (400 MHz, CDCl₃): δ 8.59 (d, *J* = 7.5, 2.8 Hz, 2H), 8.10 (d, *J* = 7.9 Hz, 1H), 7.74 (t, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.51 (s, 1H), 7.39 (s, 1H), 7.34 (s, 1H), 7.10 (d, *J* = 8.9 Hz, 1H), 3.95 (s, 3H), 3.93 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 159.2, 157.6, 157.6, 133.6, 133.5, 132.7, 129.8, 129.4, 128.5, 128.4, 127.7, 125.2, 122.6, 118.2, 117.7, 115.5, 106.8, 106.8, 104.9, 56.5, 56.1. IR (KBr): 2924, 1695, 1599, 1499, 1464, 1422, 1367, 1327, 1263, 1199, 1163, 826, 774, 690 cm⁻¹.



2,12-diphenyl-8H-indolo[3,2,1-de]phenanthridin-8-one (3f)

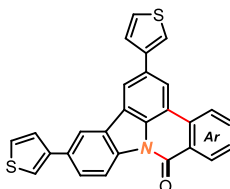
White solid (56.3 mg, 67% yield). M.p.: 215-220 °C. PE / EA = 20:1, R_f = 0.32. ¹H NMR (400 MHz, CDCl₃ + 10% CF₃COOD): δ 8.37 (d, *J* = 8.4 Hz, 1H), 8.28 (d, *J* = 7.9 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.92 (s, 1H), 7.87 (s, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.56 (t, *J* = 8.3 Hz, 5H), 7.45 (dq, *J* = 19.5, 6.1, 5.6 Hz, 7H). ¹³C NMR (100 MHz, CDCl₃): δ 160.4, 140.8, 140.6, 138.8,

138.5, 137.5, 133.6, 133.4, 132.9, 129.2, 129.2, 129.1, 128.7, 127.8, 127.7, 127.6, 127.5, 127.4, 127.1, 126.5, 124.9, 122.4, 120.0, 119.4, 119.1, 117.6, 117.0. IR (KBr): 2923, 2856, 1674, 1597, 1474, 1361, 1273, 1200, 1137, 830, 740, 693 cm^{-1} .



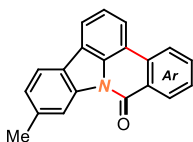
2,12-di(furan-2-yl)-8H-indolo[3,2,1-de]phenanthridin-8-one (3g)

Yellow solid (48.0 mg, 60% yield). M.p.: 259-264 °C. PE / EA = 5:1, $R_f = 0.32$. ^1H NMR (400 MHz, $\text{CDCl}_3 + 10\% \text{CF}_3\text{COOD}$): δ 8.34 (d, $J = 8.0$ Hz, 2H), 8.03 (d, $J = 7.9$ Hz, 1H), 7.82 (s, 1H), 7.76 (s, 1H), 7.71 (d, $J = 7.8$ Hz, 4H), 7.55 (d, $J = 7.0$ Hz, 3H), 7.45 (d, $J = 8.4$ Hz, 1H), 6.78 – 6.68 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 160.5, 144.2, 144.1, 144.1, 144.1, 139.0, 138.9, 137.3, 133.7, 133.5, 132.8, 130.4, 129.9, 129.4, 128.8, 127.0, 126.8, 126.5, 126.4, 126.3, 126.2, 125.0, 122.5, 118.6, 118.0, 117.8, 117.3, 109.2, 109.1. IR (KBr): 3452, 2925, 2859, 1777, 1668, 1498, 1361, 1281, 1156, 1047, 870, 773, 590, cm^{-1} .



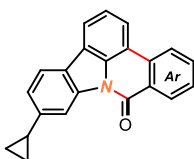
2,12-di(thiophen-3-yl)-8H-indolo[3,2,1-de]phenanthridin-8-one (3h)

Yellow solid (53.3 mg, 62% yield). M.p.: 258-262 °C. PE / EA = 5:1, $R_f = 0.32$. ^1H NMR (400 MHz, $\text{CDCl}_3 + 10\% \text{CF}_3\text{COOD}$): δ 8.35 (d, $J = 7.3$ Hz, 2H), 8.04 (d, $J = 7.6$ Hz, 1H), 7.97 (s, 1H), 7.87 (s, 2H), 7.72 (t, $J = 7.4$ Hz, 1H), 7.61 (d, $J = 8.2$ Hz, 1H), 7.55 (t, $J = 7.4$ Hz, 1H), 7.36 (dd, $J = 12.9, 5.1$ Hz, 3H), 7.30 (s, 1H), 7.15 (dd, $J = 11.1, 3.8$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 159.5, 144.1, 144.0, 137.6, 133.7, 133.6, 133.2, 132.6, 132.1, 129.5, 129.0, 128.5, 128.4, 128.3, 128.3, 127.1, 126.8, 126.6, 125.4, 125.4, 125.1, 123.9, 123.8, 122.7, 118.9, 118.4, 118.0, 117.9, 117.4. IR (KBr): 3064, 2953, 2868, 1673, 1591, 1483, 1452, 1411, 1348, 1326, 1276, 1209, 1144, 861, 807, 760, 684, 549 cm^{-1} .



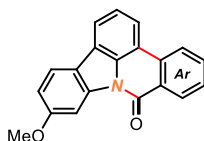
11-methyl-8H-indolo[3,2,1-de]phenanthridin-8-one (3i)

White solid (35.3 mg, 63% yield). M.p.: 181-183 °C. PE / EA = 20:1, R_f = 0.32. ^1H NMR (400 MHz, CDCl_3): δ 8.59 (d, J = 8.0 Hz, 1H), 8.56 (s, 1H), 8.21 – 8.13 (m, 1H), 7.97 (d, J = 7.8 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.74 (t, J = 7.6 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.7 Hz, 1H), 7.22 (d, J = 7.8 Hz, 1H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 156.7, 136.4, 136.1, 131.9, 131.6, 130.7, 127.2, 126.2, 125.7, 124.2, 122.7, 122.2, 122.2, 120.6, 118.9, 118.7, 118.0, 116.1, 115.5, 24.6. IR (KBr): 3481, 2925, 2855, 1668, 1503, 1420, 1344, 1294, 872, 821, 796, 752, 693 cm^{-1} .



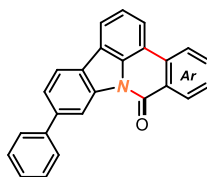
11-cyclopropyl-8H-indolo[3,2,1-de]phenanthridin-8-one (3j)

White solid (36.0 mg, 60% yield). M.p.: 172-177 °C. PE / EA = 20:1, R_f = 0.32. ^1H NMR (400 MHz, CDCl_3): δ 8.57 (d, J = 7.9 Hz, 1H), 8.45 (s, 1H), 8.15 (d, J = 7.9 Hz, 1H), 7.94 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 7.5 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.73 (t, J = 7.6 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.16 (d, J = 8.0 Hz, 1H), 2.17 – 2.06 (m, 1H), 1.10 (q, J = 5.3 Hz, 2H), 0.89 (q, J = 5.0 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 159.8, 144.8, 138.8, 133.9, 133.6, 132.6, 129.0, 128.0, 127.5, 124.3, 123.8, 123.8, 122.9, 122.2, 120.3, 120.2, 119.4, 116.7, 113.8, 16.2, 10.0. IR (KBr): 3462, 2923, 1678, 1606, 1502, 1423, 1344, 1276, 1148, 1032, 967, 803, 749, 689 cm^{-1} .



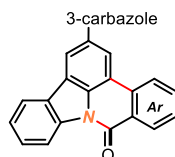
11-methoxy-8H-indolo[3,2,1-de]phenanthridin-8-one (3k)

White solid (40.8 mg, 68% yield). M.p.: 165-172 °C. PE / EA = 10:1, R_f = 0.32. ^1H NMR (400 MHz, CDCl_3): δ 8.51 (d, J = 6.7 Hz, 1H), 8.23 (s, 1H), 8.09 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.74 – 7.65 (m, 3H), 7.58 – 7.50 (m, 1H), 7.33 (t, J = 7.7 Hz, 1H), 6.94 (d, J = 6.2 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 160.3, 160.1, 139.8, 134.0, 133.9, 132.9, 129.2, 128.2, 127.6, 124.4, 124.1, 122.4, 121.3, 120.0, 119.6, 118.8, 116.8, 113.6, 101.3, 56.0. IR (KBr): 3466, 2924, 1668, 1660, 1501, 1466, 1427, 1345, 1272, 1166, 1074, 854, 751, 691 cm^{-1} .



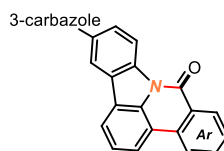
11-phenyl-8H-indolo[3,2,1-de]phenanthridin-8-one (3l)

White solid (33.3 mg, 49% yield). M.p.: 187-190 °C. PE / EA = 10:1, $R_f = 0.32$. $^1\text{H NMR}$ (400 MHz, $\text{CDCl}_3 + 10\% \text{CF}_3\text{COOD}$): δ 8.71 (s, 1H), 8.38 (d, $J = 7.7$ Hz, 1H), 8.03 (d, $J = 7.8$ Hz, 1H), 7.81 (d, $J = 7.7$ Hz, 1H), 7.76 (d, $J = 8.0$ Hz, 1H), 7.71 (d, $J = 7.1$ Hz, 4H), 7.59 (d, $J = 8.0$ Hz, 1H), 7.52 (q, $J = 7.4$ Hz, 3H), 7.42 (t, $J = 7.3$ Hz, 1H), 7.33 (d, $J = 7.6$ Hz, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 160.4, 140.8, 139.7, 138.0, 133.2, 132.8, 132.8, 128.3, 128.2, 127.8, 127.1, 126.6, 125.5, 124.9, 124.2, 124.0, 123.7, 121.7, 120.3, 120.1, 119.5, 116.3, 115.0. IR (KBr): 3435, 2949, 1669, 1602, 1418, 1341, 1286, 889, 747, 693, 639 cm^{-1} .



2-(9H-carbazol-3-yl)-8H-indolo[3,2,1-de]phenanthridin-8-one (3m)

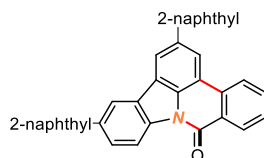
White solid (29.5 mg, 34% yield). M.p.: 242-247 °C. PE / EA = 2:1, $R_f = 0.30$. $^1\text{H NMR}$ (400 MHz, $\text{CDCl}_3 + 10\% \text{CF}_3\text{COOD}$): δ 8.83 (d, $J = 8.1$ Hz, 1H), 8.71 (d, $J = 7.8$ Hz, 1H), 8.53 (d, $J = 8.1$ Hz, 2H), 8.42 (d, $J = 10.6$ Hz, 2H), 8.19 (dd, $J = 14.8, 5.9$ Hz, 2H), 7.95 (t, $J = 7.5$ Hz, 1H), 7.83 (d, $J = 6.8$ Hz, 1H), 7.77 (t, $J = 7.5$ Hz, 1H), 7.68 (t, $J = 7.7$ Hz, 1H), 7.59 (t, $J = 7.2$ Hz, 2H), 7.52 (s, 2H), 7.35 – 7.30 (m, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 159.9, 140.3, 140.1, 139.1, 138.8, 134.4, 133.7, 133.0, 129.5, 128.8, 128.6, 127.2, 126.9, 126.3, 126.0, 125.9, 125.6, 124.2, 123.4, 122.9, 122.8, 121.1, 120.8, 120.4, 120.0, 119.4, 118.6, 117.8, 117.5, 111.0, 110.1. IR (KBr): 3321, 2975, 2854, 1747, 1665, 1602, 1454, 1423, 1424, 1353, 1237, 1127, 772, 727, 589, 512 cm^{-1} .



2-(9H-carbazol-3-yl)-8H-indolo[3,2,1-de]phenanthridin-8-one (3m')

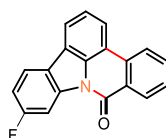
White solid (38.7 mg, 45% yield). M.p.: 256-258 °C. PE / EA = 2:1, $R_f = 0.32$. $^1\text{H NMR}$ (400 MHz, $\text{CDCl}_3 + 10\% \text{CF}_3\text{COOD}$): δ 8.63 (d, $J = 7.2$ Hz, 1H), 8.51 (d, $J = 7.1$ Hz, 1H), 8.21 (s, 2H),

8.12 – 7.99 (m, 4H), 7.86 – 7.76 (m, 2H), 7.65 (s, 2H), 7.59 (s, 1H), 7.40 (s, 3H), 7.25 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 161.9, 140.8, 140.4, 139.5, 137.3, 134.6, 134.1, 132.6, 129.5, 129.0, 128.1, 128.0, 126.4, 126.3, 125.8, 125.7, 125.5, 124.4, 123.8, 123.0, 121.8, 121.0, 120.7, 120.6, 120.0, 119.7, 119.2, 118.1, 117.8, 111.2, 111.0. IR (KBr): 3361, 2950, 2925, 1660, 1591, 1448, 1341, 1275, 1240, 1140, 874, 801, 747, 592 cm⁻¹.



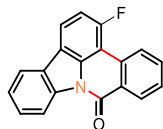
2,12-di(naphthalen-2-yl)-8H-indolo[3,2,1-de]phenanthridin-8-one (3t)

White solid (52.0 mg, 50% yield). M.p.: 255-257 °C. PE / EA = 10:1, R_f = 0.32. ¹H NMR (400 MHz, CDCl₃ + 10% CF₃COOD): δ 8.24 (d, *J* = 8.3 Hz, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.88 (s, 1H), 7.83 – 7.69 (m, 9H), 7.64 (d, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 2H), 7.45 (p, *J* = 7.0 Hz, 6H), 7.36 (t, *J* = 7.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 160.5, 138.6, 138.3, 137.7, 137.4, 137.3, 133.8, 133.8, 133.6, 133.5, 132.8, 132.6, 129.1, 128.8, 128.7, 128.6, 128.4, 128.4, 127.8, 127.8, 127.6, 127.1, 126.7, 126.5, 126.4, 126.3, 126.1, 126.0, 125.8, 125.5, 125.3, 125.0, 122.4, 120.0, 119.4, 119.0, 117.7, 116.9. IR (KBr): 3048, 1667, 1599, 1486, 1439, 1355, 1275, 1138, 855, 808, 738, 681, 607, 466 cm⁻¹.



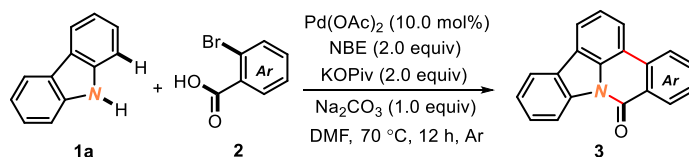
11-fluoro-8H-indolo[3,2,1-de]phenanthridin-8-one (3u)

White solid (25.7 mg, 46% yield). M.p.: 244-246 °C. PE / EA = 50:1, R_f = 0.32. ¹H NMR (400 MHz, CDCl₃ + 10% CF₃COOD): δ 8.45 (d, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 11.2 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.81 (dd, *J* = 10.1, 2.8 Hz, 3H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.14 (t, *J* = 8.7 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 162.8 (d = 244.9 Hz), 161.2, 138.8 (d = 12.7 Hz), 134.1, 134.0, 133.8, 129.4, 128.9, 126.3, 125.2, 124.1, 123.0, 122.8, 121.9 (d = 9.8 Hz), 121.1, 120.2, 117.2, 113.4 (d = 23.8 Hz), 105.6 (d = 28.4 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -111.5. IR (KBr): 3675, 2954, 1677, 1602, 1427, 1348, 1293, 1254, 853, 802, 745, 690, 551 cm⁻¹.

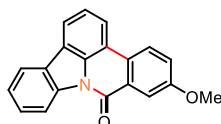


3-fluoro-8H-indolo[3,2,1-de]phenanthridin-8-one (3u')

White solid (16.8 mg, 30% yield). M.p.: 220-224 °C. PE / EA = 50:1, R_f = 0.28. ^1H NMR (400 MHz, CDCl_3): δ 8.76 (d, J = 8.1 Hz, 1H), 8.67 (d, J = 7.8 Hz, 1H), 8.58 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.90 (dd, J = 8.1, 4.2 Hz, 1H), 7.81 (t, J = 7.5 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.4 Hz, 1H), 7.25 – 7.17 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 159.9, 159.6 (d = 251.8 Hz), 139.5 (d = 1.5 Hz), 135.2 (d = 9.4 Hz), 133.7, 131.7 (d = 4.2 Hz), 129.5, 128.7, 127.7, 127.3 (d = 16.7 Hz), 126.0, 125.3, 121.4 (d = 10.6 Hz), 120.7 (d = 2.5 Hz), 120.4, 117.5, 112.5, 112.2, 106.5 (d = 15 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -114.2. IR (KBr): 3053, 2923, 1677, 1611, 1503, 1459, 1365, 1336, 1308, 1203, 1097, 813, 745, 692, 588 cm^{-1} .



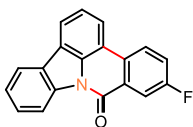
A 15 mL pressure tube was charged with $\text{Pd}(\text{OAc})_2$ (0.02 mmol, 4.5 mg, 0.1 equiv.), KOPIV (0.4 mmol, 56.0 mg, 2.0 equiv.), Na_2CO_3 (0.2 mmol, 21.2 mg, 1.0 equiv.), NBE (0.4 mmol, 37.6 mg, 2.0 equiv.), **1a** (0.2 mmol, 33.4 mg, 1.0 equiv.), **2** (0.4 mmol, 2.0 equiv.) and DMF (2 mL) under Ar atmosphere. The reaction mixture was stirred at 70 °C for 12 h under Ar atmosphere in an oil bath. After cooling to room temperature, neutralized by a saturated aqueous NaCl solution, and extracted with EtOAc. The organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by silica gel flash chromatography (PE/EA as the eluent) to give the products **3**.



6-methoxy-8H-indolo[3,2,1-de]phenanthridin-8-one (3n)

White solid (43.2 mg, 72% yield). M.p.: 170-176 °C. PE / EA = 10:1, R_f = 0.32. ^1H NMR (400 MHz, CDCl_3): δ 8.60 (d, J = 8.0 Hz, 1H), 7.78 (t, J = 11.1 Hz, 3H), 7.62 (t, J = 8.8 Hz, 2H),

7.47 (t, $J = 7.6$ Hz, 1H), 7.34 (t, $J = 7.4$ Hz, 1H), 7.20 (t, $J = 7.3$ Hz, 1H), 7.07 (d, $J = 8.4$ Hz, 1H), 3.87 (d, $J = 2.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 159.7, 159.4, 138.5, 133.1, 128.9, 127.8, 126.9, 126.6, 124.8, 124.0, 123.8, 123.7, 121.7, 120.6, 119.7, 119.4, 117.2, 116.9, 110.3, 55.7. IR (KBr): 3464, 2854, 1671, 1600, 1510, 1441, 1343, 1270, 1115, 1031, 830, 743, 567, 554 cm^{-1} .



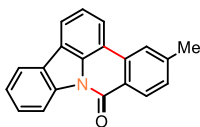
6-fluoro-8H-indolo[3,2,1-de]phenanthridin-8-one (3o)

White solid (39.0 mg, 68% yield). M.p.: 230-235 $^{\circ}\text{C}$. PE / EA = 20:1, $R_f = 0.32$. ^1H NMR (400 MHz, $\text{CDCl}_3 + 10\% \text{CF}_3\text{COOD}$): δ 8.42 (d, $J = 8.0$ Hz, 1H), 7.94 (dt, $J = 10.1, 5.9$ Hz, 2H), 7.78 (d, $J = 7.6$ Hz, 1H), 7.70 (t, $J = 7.9$ Hz, 2H), 7.47 (t, $J = 7.6$ Hz, 1H), 7.43 – 7.28 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 161.8 (d = 248.8 Hz), 159.8, 137.9, 132.6, 130.2 (d = 2.4 Hz), 128.5, 128.3 (d = 7.6 Hz), 126.8, 126.1, 125.2, 124.8 (d = 8.0 Hz), 124.7, 121.9, 121.6, 121.1, 121.0, 120.2, 117.6, 116.3. ^{19}F NMR (376 MHz, CDCl_3) δ -111.3. IR (KBr): 3453, 2924, 1670, 1611, 1512, 1445, 1361, 1241, 1122, 827, 745, 554 cm^{-1} .



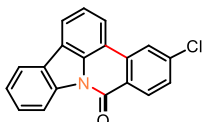
6-(trifluoromethyl)-8H-indolo[3,2,1-de]phenanthridin-8-one (3p)

White solid (42.9 mg, 65% yield). M.p.: 233-236 $^{\circ}\text{C}$. PE / EA = 20:1, $R_f = 0.32$. ^1H NMR (400 MHz, $\text{CDCl}_3 + 10\% \text{CF}_3\text{COOD}$): δ 8.64 (s, 1H), 8.49 (d, $J = 8.1$ Hz, 1H), 8.14 (d, $J = 8.3$ Hz, 1H), 7.87 (dt, $J = 21.0, 7.4$ Hz, 4H), 7.52 (t, $J = 7.7$ Hz, 1H), 7.43 (q, $J = 7.4$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 159.8, 138.0, 136.6, 133.7, 130.7 (q = 33.6 Hz), 129.7, 129.7, 128.8, 126.8, 126.7 (q = 4.1 Hz), 126.5, 126.2, 125.3, 124.9, 123.4, 122.5, 121.1, 121.0, 117.6, 115.9. ^{19}F NMR (376 MHz, CDCl_3) δ -62.6. IR (KBr): 3023, 2854, 1715, 1663, 1639, 1514, 1444, 1345, 749, 550 cm^{-1} .



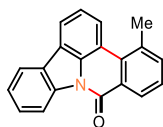
5-methyl-8H-indolo[3,2,1-de]phenanthridin-8-one (3q)

White solid (40.3 mg, 72% yield). M.p.: 188-190 °C. PE / EA = 20:1, R_f = 0.32. ^1H NMR (400 MHz, CDCl_3): δ 8.74 (d, J = 8.1 Hz, 1H), 8.41 (d, J = 8.1 Hz, 1H), 7.93 (t, J = 8.5 Hz, 2H), 7.87 (d, J = 6.8 Hz, 2H), 7.55 (t, J = 7.7 Hz, 1H), 7.41 (q, J = 8.0 Hz, 2H), 7.33 (d, J = 8.1 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 160.2, 143.8, 138.8, 134.5, 133.9, 129.8, 129.4, 128.2, 126.6, 125.6, 125.0, 124.5, 124.1, 122.8, 121.0, 120.9, 120.3, 117.5, 117.3, 22.4. IR (KBr): 3029, 2950, 1671, 1608, 1506, 1442, 1334, 1255, 1169, 1116, 834, 752 cm^{-1} .



5-chloro-8H-indolo[3,2,1-de]phenanthridin-8-one (3r)

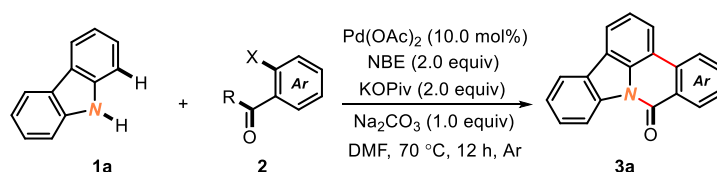
White solid (37.8 mg, 63% yield). M.p.: 241-245 °C. PE / EA = 20:1, R_f = 0.32. ^1H NMR (400 MHz, CDCl_3 + 10% CF_3COOD): δ 8.36 (d, J = 6.6 Hz, 1H), 8.18 (d, J = 8.9 Hz, 1H), 7.76 (s, 1H), 7.71 (d, J = 8.9 Hz, 1H), 7.62 (d, J = 23.2 Hz, 2H), 7.48 – 7.40 (m, 1H), 7.34 (t, J = 7.5 Hz, 2H), 7.24 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 160.1, 140.7, 140.7, 138.1, 135.2, 133.5, 130.7, 129.0, 128.6, 126.6, 126.0, 125.0, 124.8, 122.4, 121.8, 120.9, 120.4, 117.6, 115.9. IR (KBr): 3430, 3050, 2963, 1668, 1595, 1503, 1441, 1342, 1298, 1264, 1124, 888, 831, 743 cm^{-1} .



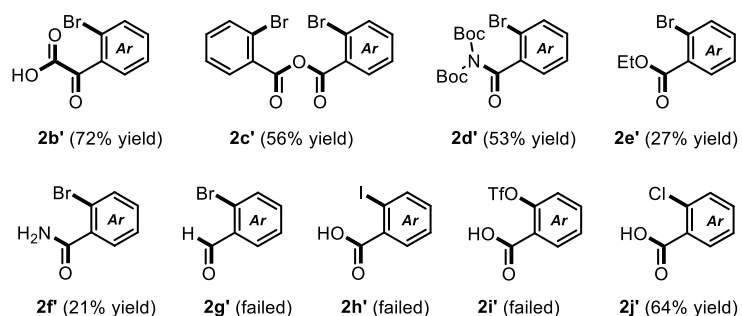
8H-indolo[3,2,1-de]phenanthridin-8-one (3s)

White solid (29.1 mg, 52% yield). M.p.: 195-200 °C. PE / EA = 20:1, R_f = 0.32. ^1H NMR (400 MHz, CDCl_3): δ 8.70 (d, J = 8.1 Hz, 1H), 8.48 (d, J = 8.8 Hz, 1H), 8.09 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 7.5 Hz, 1H), 7.53 (t, J = 7.7 Hz, 1H), 7.45 – 7.35 (m, 3H), 7.29 (t, J = 7.8 Hz, 1H), 2.75 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 159.9, 137.9, 136.9, 135.9, 134.1, 132.4, 128.9, 127.8, 127.7, 127.4, 126.4, 125.0, 124.7, 124.3, 123.4, 120.2, 120.1, 118.6, 117.3, 25.3. IR (KBr): 3429, 2924, 2854, 1692, 1604, 1501, 1438, 1440, 1367, 1267, 745 cm^{-1} .

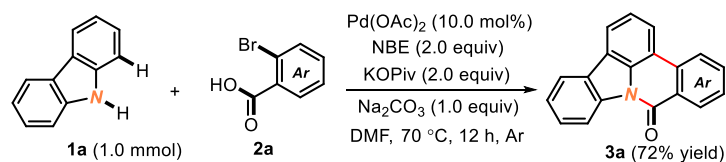
4. General procedure for further substrate scope



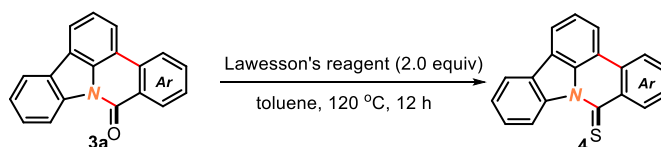
A 15 mL pressure tube was charged with Pd(OAc)₂ (0.02 mmol, 4.5 mg, 0.1 equiv.), KOPiv (0.4 mmol, 56.0 mg, 2.0 equiv.), Na₂CO₃ (0.2 mmol, 21.2 mg, 1.0 equiv.), NBE (0.4 mmol, 37.6 mg, 2.0 equiv.), **1a** (0.2 mmol, 33.4 mg, 1.0 equiv.), **2** (0.4 mmol, 2.0 equiv.) and DMF (2 mL) under Ar atmosphere. The reaction mixture was stirred at 70 °C for 12 h under nitrogen atmosphere in an oil bath. After cooling to room temperature, neutralized by a saturated aqueous NaCl solution, and extracted with EtOAc. The organic layers were dried over anhydrous Na₂SO₄ and concentrated to dryness under reduced pressure. The crude product was purified by silica gel flash chromatography (PE/EA as the eluent) to give the products **3a**.



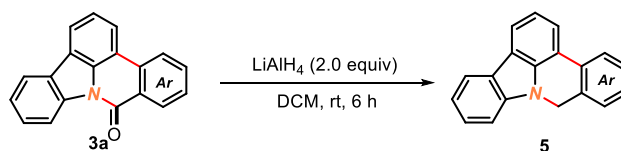
5. Scale-up reaction and derivatizations



A 75 mL pressure tube was charged with Pd(OAc)₂ (0.1 mmol, 22.5 mg, 0.1 equiv.), KOPiv (2.0 mmol, 280.0 mg, 2.0 equiv.), Na₂CO₃ (1.0 mmol, 106.0 mg, 1.0 equiv.), NBE (2.0 mmol, 188.0 mg, 2.0 equiv.), **1a** (1.0 mmol, 167.0 mg, 1.0 equiv.), **2a** (2.0 mmol, 398.0 mg, 2.0 equiv.) and DMF (10 mL) under Ar atmosphere. The reaction mixture was stirred at 70 °C for 12 h under nitrogen atmosphere in an oil bath. After cooling to room temperature, neutralized by a saturated aqueous NaCl solution, and extracted with EtOAc. The organic layers were dried over anhydrous Na₂SO₄ and concentrated to dryness under reduced pressure. The crude product was purified by silica gel flash chromatography (PE/EA as the eluent) to give the product **3a** (0.22 g, 72% yield).

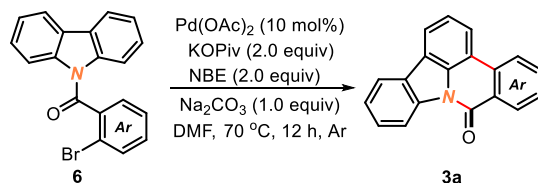


To a solution of **3a** (60.1 mg, 0.2 mmol), Lawesson's reagent (161.6 mg, 0.4 mmol), and toluene (2 mL) were successively added under air. The tube was sealed with a Teflon-coated cap and the reaction solution was heated at 120 °C for 12 h. The reaction mixture was filtered through a pad of celite and washed with DCM (10 mL). The combined organic layer was concentrated in vacuo. The crude product was purified by silica gel flash chromatography (PE:EA = 20:1 as the eluent) to give **4** as a product. Product **4**: Yellow solid (55.6 mg, 85% yield). M.p.: 225-230 °C. PE / EA = 50:1, $R_f = 0.32$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 10.03 (d, $J = 8.3$ Hz, 1H), 9.26 (d, $J = 8.3$ Hz, 1H), 8.24 (d, $J = 7.9$ Hz, 1H), 8.12 (d, $J = 7.8$ Hz, 1H), 8.02 (d, $J = 7.5$ Hz, 1H), 7.96 (d, $J = 7.5$ Hz, 1H), 7.77 (t, $J = 7.4$ Hz, 1H), 7.64 – 7.51 (m, 4H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 186.5, 141.7, 134.8, 134.5, 133.7, 132.8, 129.0, 128.5, 128.3, 128.2, 126.7, 125.8, 124.3, 122.3, 120.8, 120.8, 120.7, 120.1, 119.5. IR (KBr): 3453, 2924, 2853, 1663, 1557, 1501, 1447, 1347, 1399, 1249, 1167, 1006, 757 cm^{-1} .

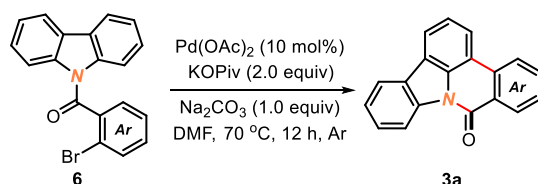


To a solution of **3a** (60.1 mg, 0.2 mmol), LiAlH_4 (15.2 mg, 0.4 mmol), and DCM (2 mL) were successively added under air. The tube was sealed with a Teflon-coated cap and the reaction solution was heated at room temperature for 6 h. The reaction mixture was filtered through a pad of celite and washed with DCM (2 mL). The combined organic layer was concentrated in vacuo. The crude product was purified by silica gel flash chromatography (PE:EA = 50:1 as the eluent) to give **5** as a product. Product **5**: White solid (53.0 mg, 90% yield). M.p.: 153-160 °C. PE / EA = 50:1, $R_f = 0.32$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.11 (d, $J = 7.8$ Hz, 1H), 7.94 (dd, $J = 11.3, 7.8$ Hz, 2H), 7.74 (d, $J = 7.4$ Hz, 1H), 7.51 (t, $J = 7.6$ Hz, 1H), 7.41 (d, $J = 8.1$ Hz, 1H), 7.37 (d, $J = 7.4$ Hz, 1H), 7.30 (dd, $J = 13.0, 5.7$ Hz, 3H), 7.21 (t, $J = 7.6$ Hz, 1H), 5.54 (s, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 140.2, 137.3, 130.2, 130.0, 127.8, 125.8, 123.6, 122.9, 121.4, 121.2, 120.5, 119.9, 119.7, 117.9, 117.8, 108.9, 45.8. IR (KBr): 3453, 2924, 2853, 1669, 1597, 1551, 1437, 1340, 1236, 1119, 824, 748, 555 cm^{-1} .

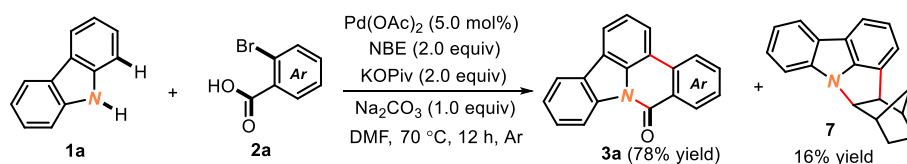
6. Mechanistic Studies



A 15 mL pressure tube was charged with Pd(OAc)₂ (0.02 mmol, 4.5 mg, 0.1 equiv.), KOPIv (0.4 mmol, 56.0 mg, 2.0 equiv.), Na₂CO₃ (0.2 mmol, 21.2 mg, 1.0 equiv.), NBE (0.4 mmol, 37.6 mg, 2.0 equiv.), **6** (0.2 mmol, 77.6 mg, 1.0 equiv.) and DMF (2 mL) under Ar atmosphere. The reaction mixture was stirred at 70 °C for 12 h under nitrogen atmosphere in an oil bath. After cooling to room temperature, neutralized by a saturated aqueous NaCl solution, and extracted with EtOAc. The organic layers were dried over anhydrous Na₂SO₄ and TLC analysis indicated the absence of product **3a**.

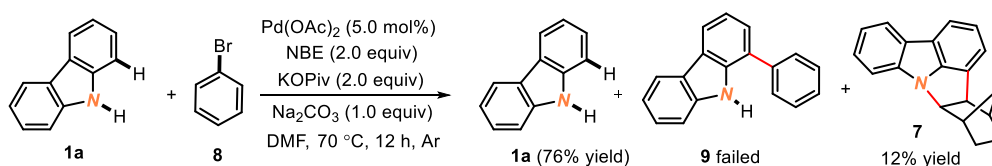


A 15 mL pressure tube was charged with Pd(OAc)₂ (0.02 mmol, 4.5 mg, 0.1 equiv.), KOPIv (0.4 mmol, 56.0 mg, 2.0 equiv.), Na₂CO₃ (0.2 mmol, 21.2 mg, 1.0 equiv.), **6** (0.2 mmol, 77.6 mg, 1.0 equiv.) and DMF (2 mL) under Ar atmosphere. The reaction mixture was stirred at 70 °C for 12 h under nitrogen atmosphere in an oil bath. After cooling to room temperature, neutralized by a saturated aqueous NaCl solution, and extracted with EtOAc. The organic layers were dried over anhydrous Na₂SO₄ and concentrated to dryness under reduced pressure. The organic layers were dried over anhydrous Na₂SO₄ and TLC analysis indicated the absence of product **3a**.

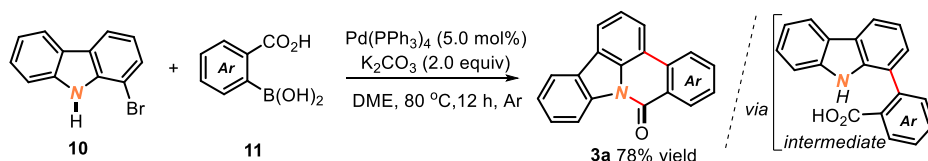


A 15 mL pressure tube was charged with Pd(OAc)₂ (0.01 mmol, 2.3 mg, 0.05 equiv.), KOPIv (0.4 mmol, 56.0 mg, 2.0 equiv.), Na₂CO₃ (0.2 mmol, 21.2 mg, 1.0 equiv.), NBE (0.4 mmol, 37.6 mg, 2.0 equiv.), **1a** (0.2 mmol, 33.4 mg, 1.0 equiv.), **2** (0.4 mmol, 79.6 mg, 2.0 equiv.) and DMF (2

mL) under Ar atmosphere. The reaction mixture was stirred at 70 °C for 12 h under nitrogen atmosphere in an oil bath. After cooling to room temperature, neutralized by a saturated aqueous NaCl solution, and extracted with EtOAc. The organic layers were dried over anhydrous Na₂SO₄ and concentrated to dryness under reduced pressure. The crude product was purified by silica gel flash chromatography (PE/EA as the eluent) to give the products **3a** and **7**. Product **7**: White solid (8.32 mg, 16% yield). PE / EA = 50:1, R_f = 0.32. M.p.: 54-56 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.16 (d, *J* = 7.9 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 4.0 Hz, 2H), 7.30 (dt, *J* = 8.2, 4.1 Hz, 1H), 7.24 (d, *J* = 6.8 Hz, 1H), 7.18 (t, *J* = 7.3 Hz, 1H), 4.83 (d, *J* = 6.5 Hz, 1H), 4.07 (d, *J* = 6.5 Hz, 1H), 2.91 (s, 1H), 2.61 (s, 1H), 1.79 (t, *J* = 11.3, 5.9 Hz, 2H), 1.58 – 1.47 (m, 2H), 1.25 (t, *J* = 8.8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 152.3, 138.2, 127.2, 126.7, 124.9, 122.5, 120.6, 119.4, 118.7, 118.2, 114.5, 109.7, 69.2, 59.2, 42.1, 40.4, 33.5, 28.6, 25.7. IR (KBr): 3053, 2924, 2873, 1643, 1577, 1492, 1447, 1321, 1255, 1119, 1041, 918, 744, 622 cm⁻¹.



A 15 mL pressure tube was charged with Pd(OAc)₂ (0.01 mmol, 2.3 mg, 0.05 equiv.), KOPIV (0.4 mmol, 56.0 mg, 2.0 equiv.), Na₂CO₃ (0.2 mmol, 21.2 mg, 1.0 equiv.), NBE (0.4 mmol, 37.6 mg, 2.0 equiv.), **1a** (0.2 mmol, 33.4 mg, 1.0 equiv.), **8** (0.4 mmol, 62.8 mg, 2.0 equiv.) and DMF (2 mL) under Ar atmosphere. The reaction mixture was stirred at 70 °C for 12 h under nitrogen atmosphere in an oil bath. After cooling to room temperature, neutralized by a saturated aqueous NaCl solution, and extracted with EtOAc. The organic layers were dried over anhydrous Na₂SO₄ and concentrated to dryness under reduced pressure. The crude product was purified by silica gel flash chromatography (PE/EA as the eluent) to give the products **1a** and **7**. And the wanted compound **9** was did not detected.



A 15 mL pressure tube was charged with Pd(PPh₃)₄ (0.01 mmol, 11.5 mg, 0.05 equiv.),

K_2CO_3 (0.2 mmol, 27.6 mg, 2.0 equiv.), **8** (0.2 mmol, 44.8 mg, 1.0 equiv.), **11** (0.24 mmol, 39.8 mg, 1.2 equiv.) and DME (2 mL) under Ar atmosphere. The reaction mixture was stirred at 80 °C for 12 h under nitrogen atmosphere in an oil bath. After cooling to room temperature, neutralized by a saturated aqueous NaHCO_3 solution, and extracted with EtOAc. The organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by silica gel flash chromatography (PE/EA as the eluent) to give the products **3a**.

7. Crystallographic data

Methods to get single crystals suitable for X-ray diffraction test: **3c** was dissolved in 2 mL of CH_2Cl_2 , filtered, and then injected into a 20 mL vial. Subsequently, 5 mL of hexane was slowly added to the vial without shaking and the solution was allowed to evaporate slowly over the course of 2 days to give yellow single crystal.

Single crystal structures were measured on a Bruker D8 Venture with TXS diffractometer with a graphite monochromated Mo $\text{K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$, at 296(2) K) radiation. The structure was solved by direct methods and refined anisotropically based on F^2 by a full-matrix least-squares refinement with the SHELXL-2014 program. Anisotropic thermal parameters were applied to non-hydrogen atoms, and all hydrogen atoms of organic ligands were calculated and added at the theoretical positions.

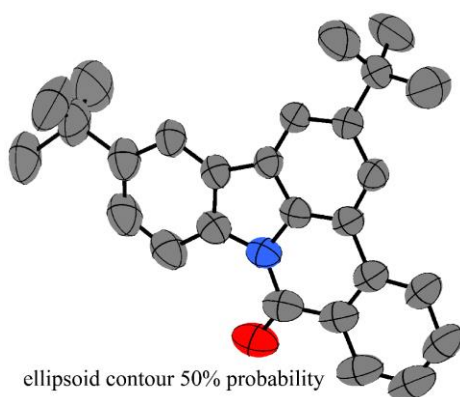


Figure S2 Molecular structure of $\text{C}_{27}\text{H}_{27}\text{NO}$, (**3c**). The thermal ellipsoids are shown at 50% probability.

Table S2 Crystal, Intensity Collection, and Refinement Data for Complexes 3c.

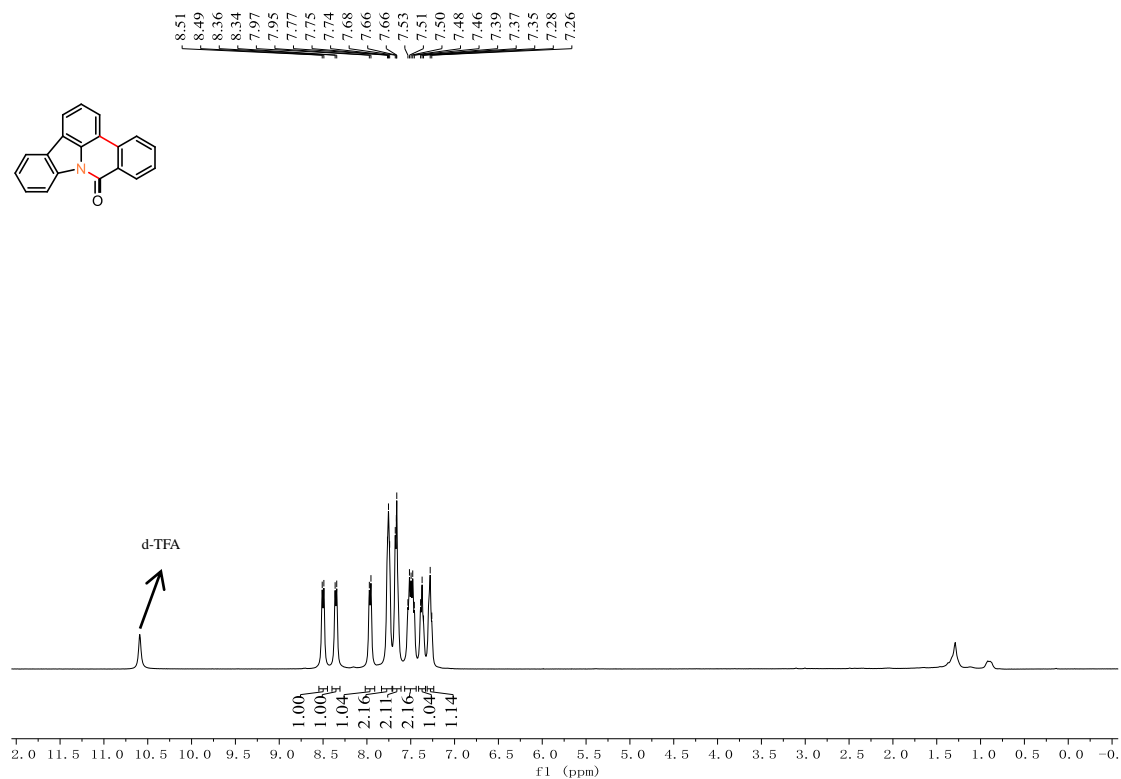
complex	3c
CCDC number	2366116
Empirical formula	C ₂₇ H ₁₇ NO
Formula weight	381.49
Temperature [K]	293.00
Crystal system	triclinic
Space group (number)	P-1 (2)
<i>a</i> [Å]	7.057(3)
<i>b</i> [Å]	12.282(4)
<i>c</i> [Å]	13.493 (5)
α [°]	76.338(13)
β [°]	79.786(14)
γ [°]	78.458(14)
Volume [Å ³]	1103.0(8)
<i>Z</i>	2
ρ_{calc} [gcm ⁻³]	1.149
μ [mm ⁻¹]	0.069
<i>F</i> (000)	408.0
Crystal size [mm ³]	0.13×0.12×0.1
Crystal colour	clear light colourless
Crystal shape	block
Radiation	MoK α (λ = 0.71073)
2 θ range [°]	5.948 to 55.196 -9 ≤ <i>h</i> ≤ 9
Index ranges	-15 ≤ <i>k</i> ≤ 15 -17 ≤ <i>l</i> ≤ 17
Reflections collected	32354 5054
Independent reflections	<i>R</i> _{int} = 0.1207 <i>R</i> _{sigma} = 0.0655
Completeness to θ = 53.594°	99.7 %
Data / Restraints / Parameters	5054/87/299
Goodness-of-fit on <i>F</i> ²	1.031
<i>R</i> ₁ [<i>I</i> ≥ 2 σ (<i>I</i>)] ^[a]	0.0746
<i>wR</i> ₂ [<i>I</i> ≥ 2 σ (<i>I</i>)] ^[b]	0.2036
<i>R</i> ₁ [<i>I</i> ≥ 2 σ (<i>I</i>)] ^[a]	0.1377
<i>R</i> ₁ [all data] ^[b]	0.2676
<i>R</i> ₁ Largest peak/hole [eÅ ⁻³]	0.27/-0.21

$$^{[a]}R_1 = F_o - F_c / F_o$$

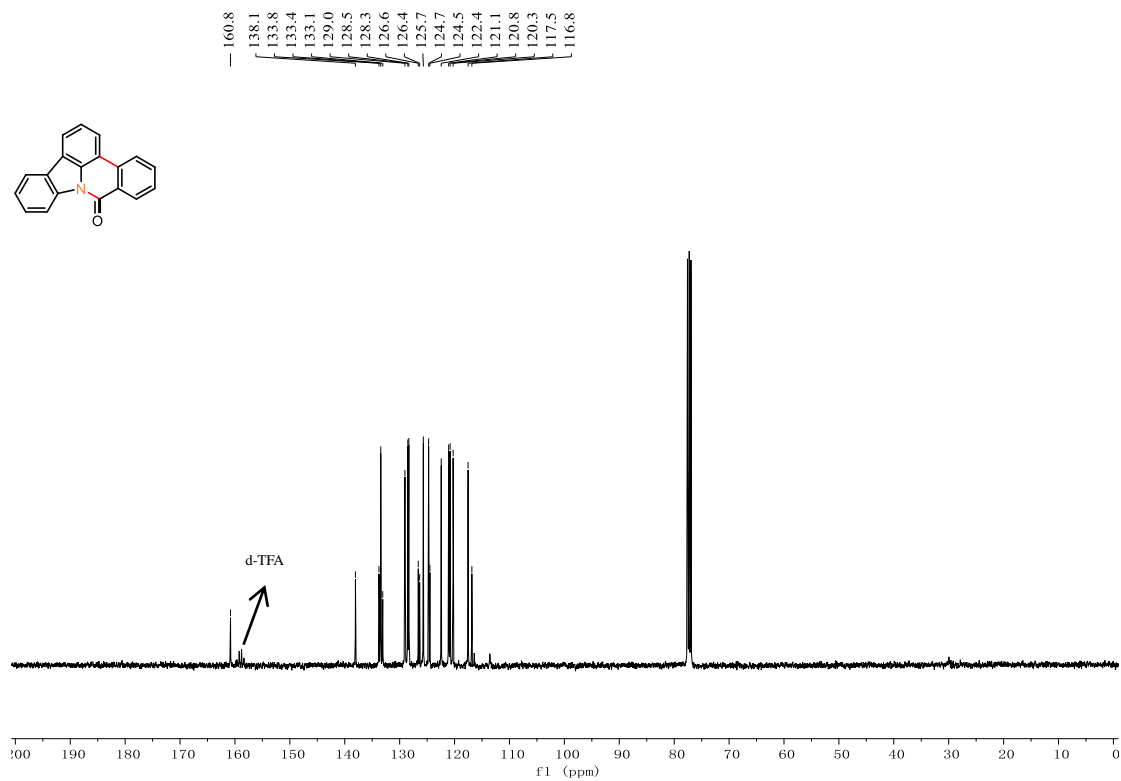
$$^{[b]}wR_2 = \{w[(F_o)^2 - (F_c)^2]^2 / w[(F_o)^2]^2\}^{1/2}$$

8. NMR and HRMS spectra

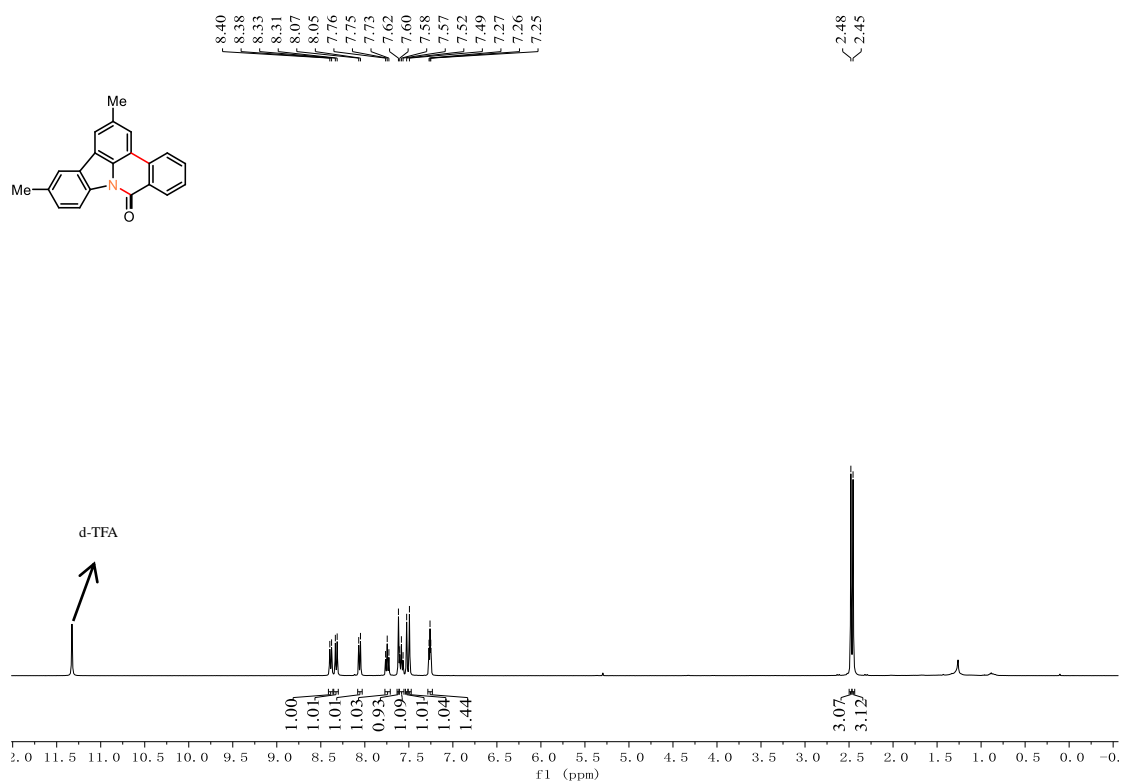
The HRMS spectra of compounds **3a**^[3] and **7**^[4] have been reported in relevant literatures.
¹H NMR of **3a** (400 MHz, CDCl₃ + CF₃COOD)



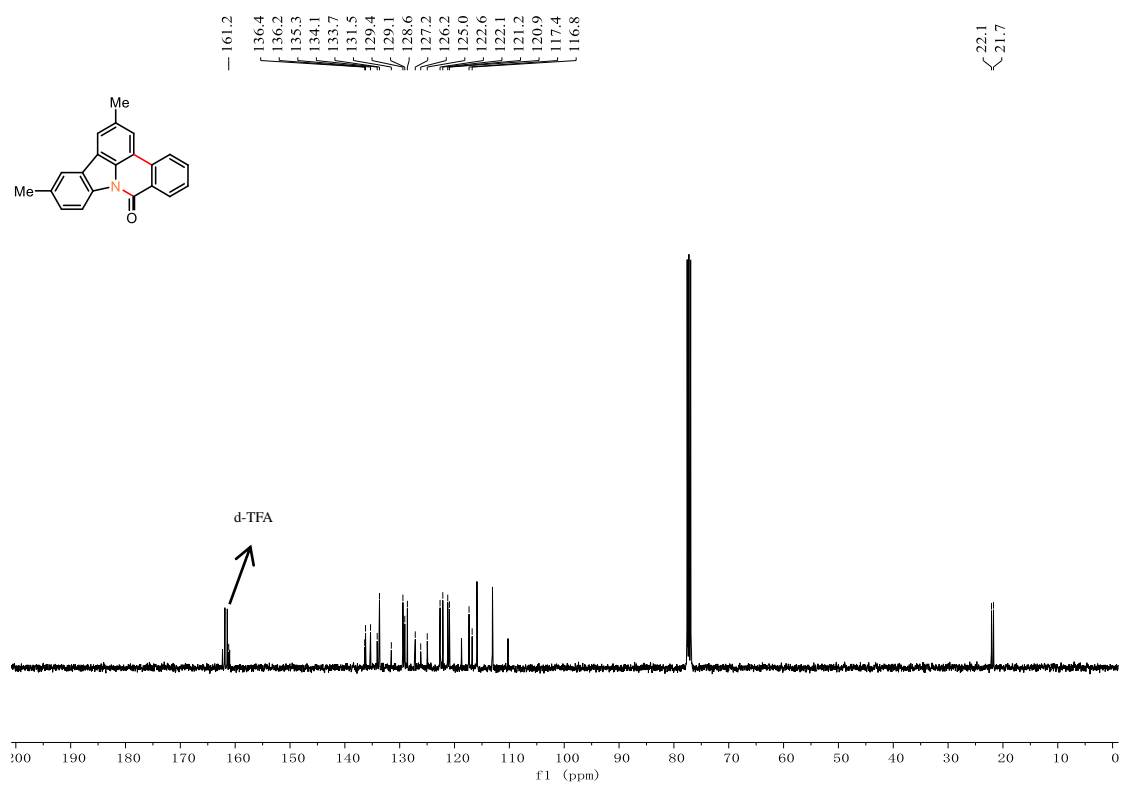
¹³C NMR of **3a** (100 MHz, CDCl₃ + CF₃COOD)



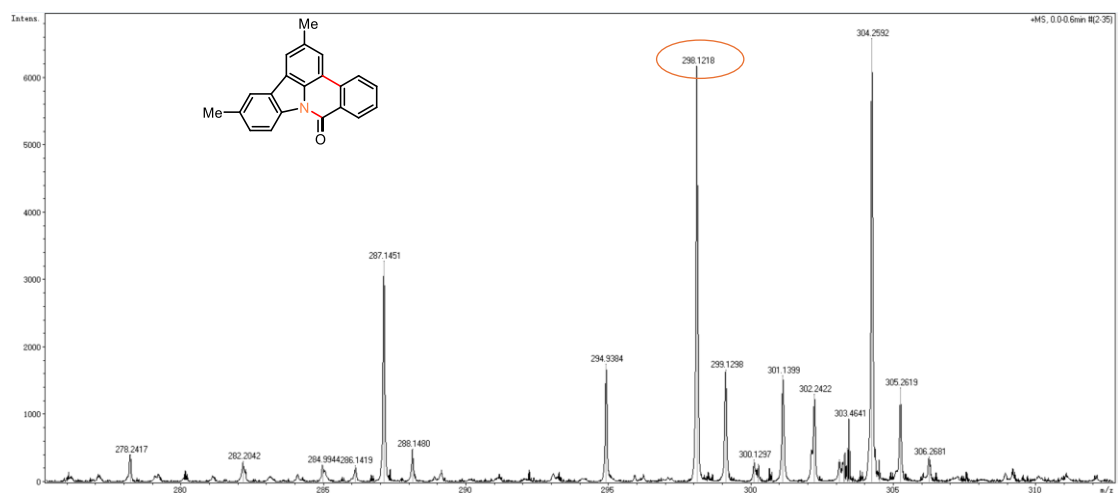
^1H NMR of **3b** (400 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$)



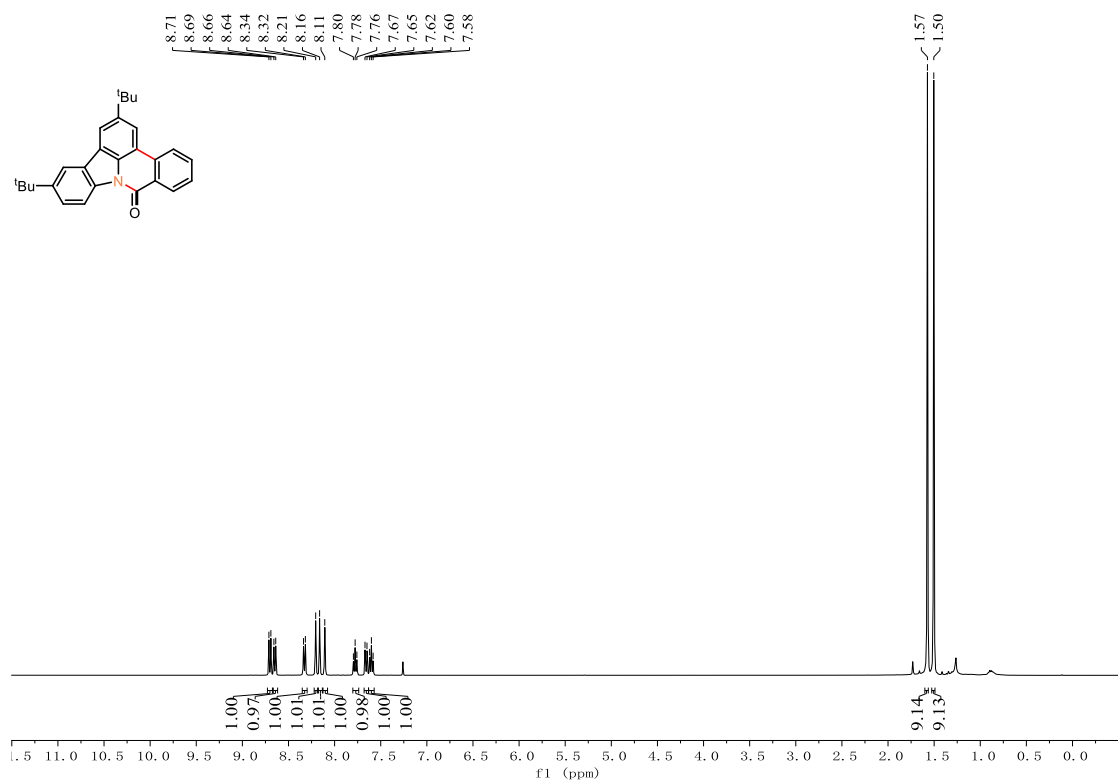
^{13}C NMR of **3b** (100 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$)



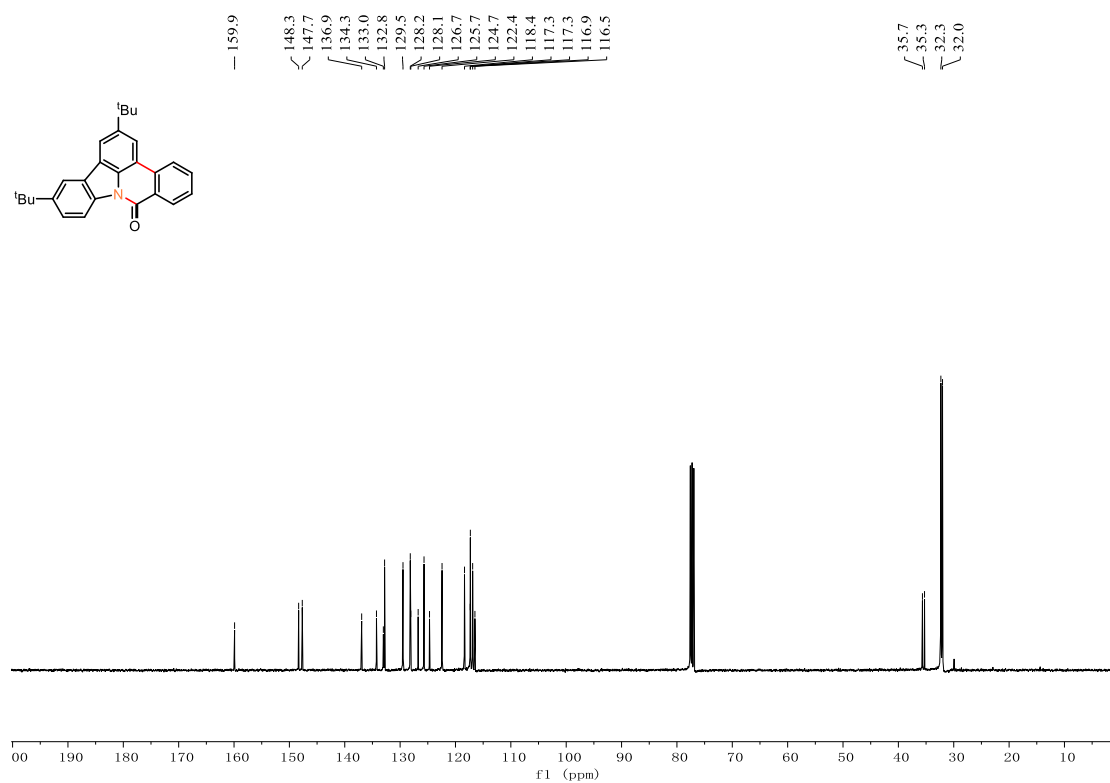
HRMS (ESI) m/z Calcd for $C_{12}H_{16}NO$ $[M+H]^+$ 298.1226, found 298.1218.



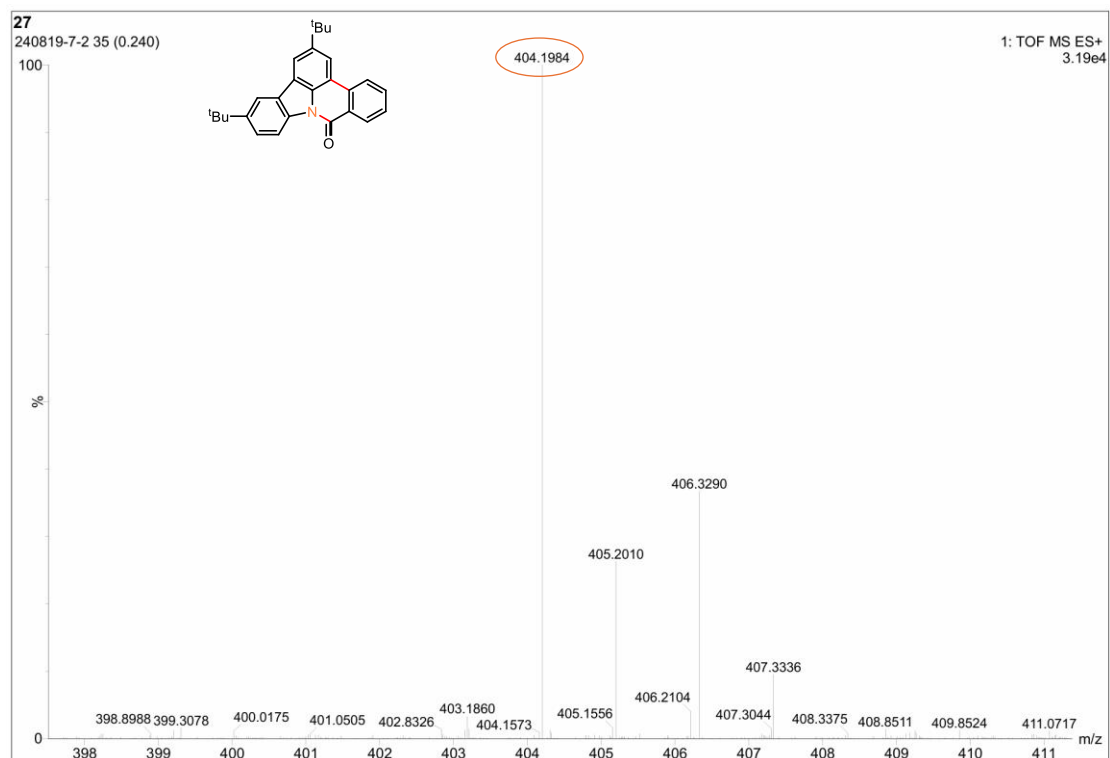
1H NMR of **3c** (400 MHz, $CDCl_3$)



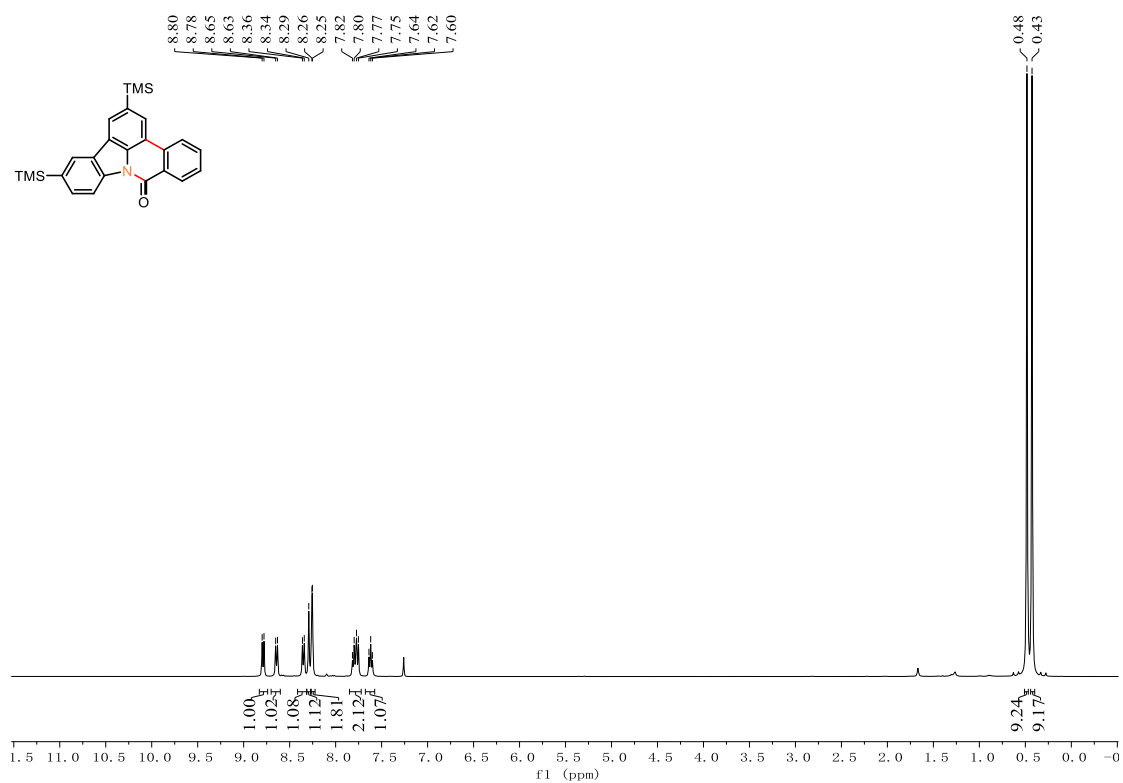
^{13}C NMR of **3c** (100 MHz, CDCl_3)



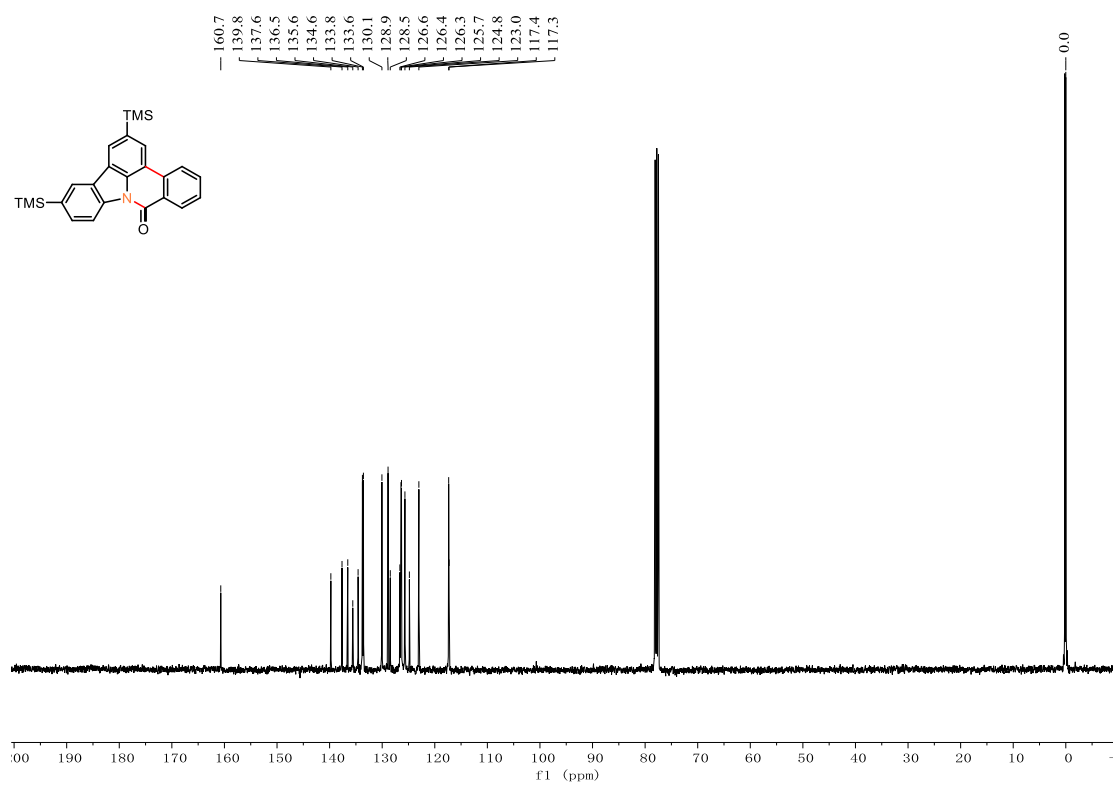
HRMS (ESI) m/z Calcd for $\text{C}_{27}\text{H}_{28}\text{NO}$ $[\text{M}+\text{Na}]^+$ 404.1985, found 404.1984.



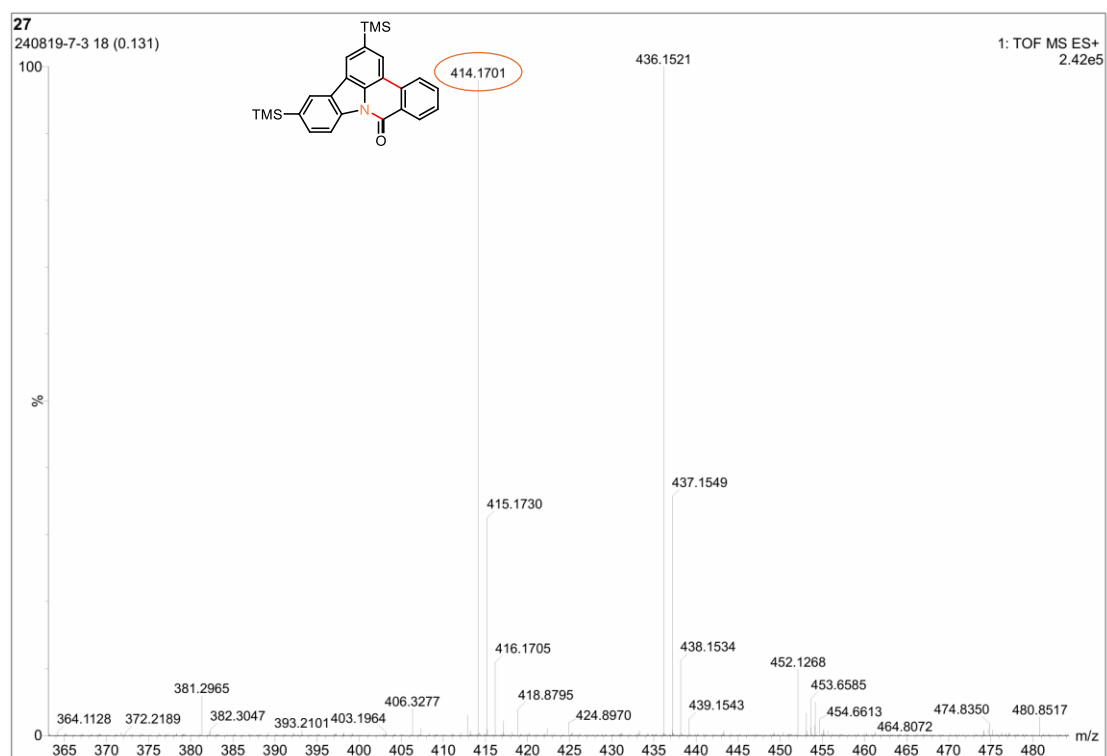
¹H NMR of **3d** (400 MHz, CDCl₃)



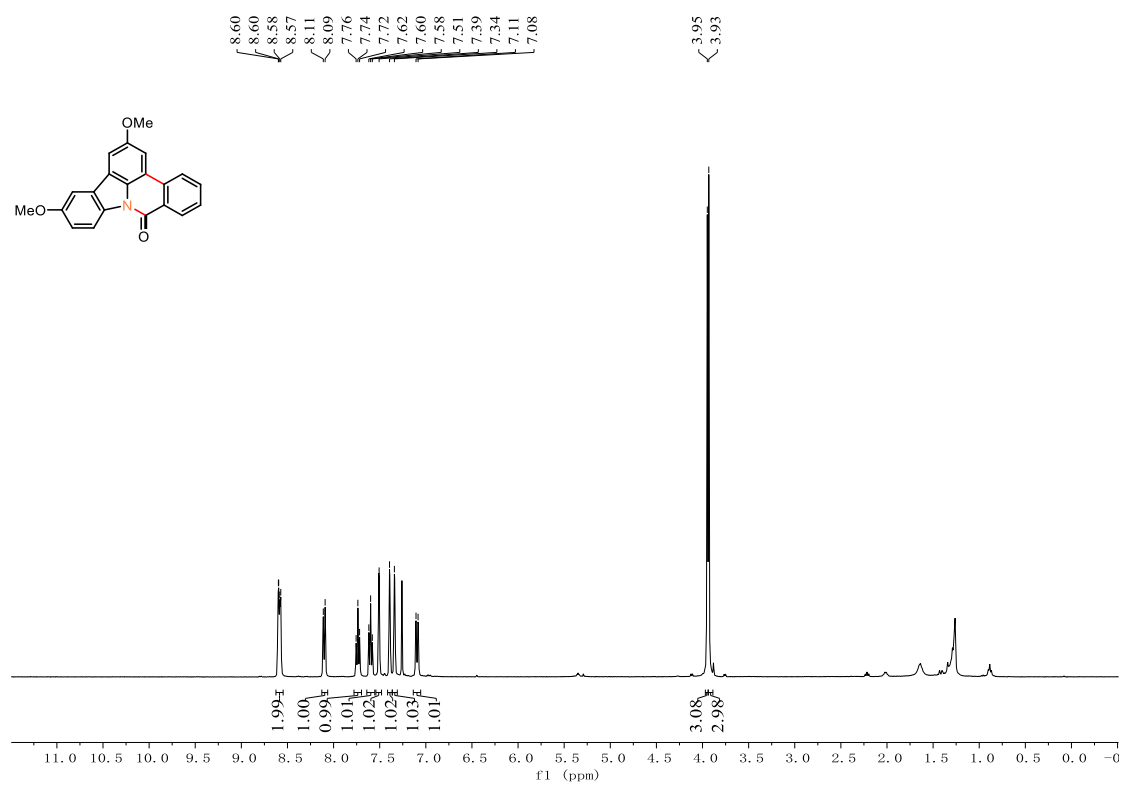
¹³C NMR of **3d** (100 MHz, CDCl₃)



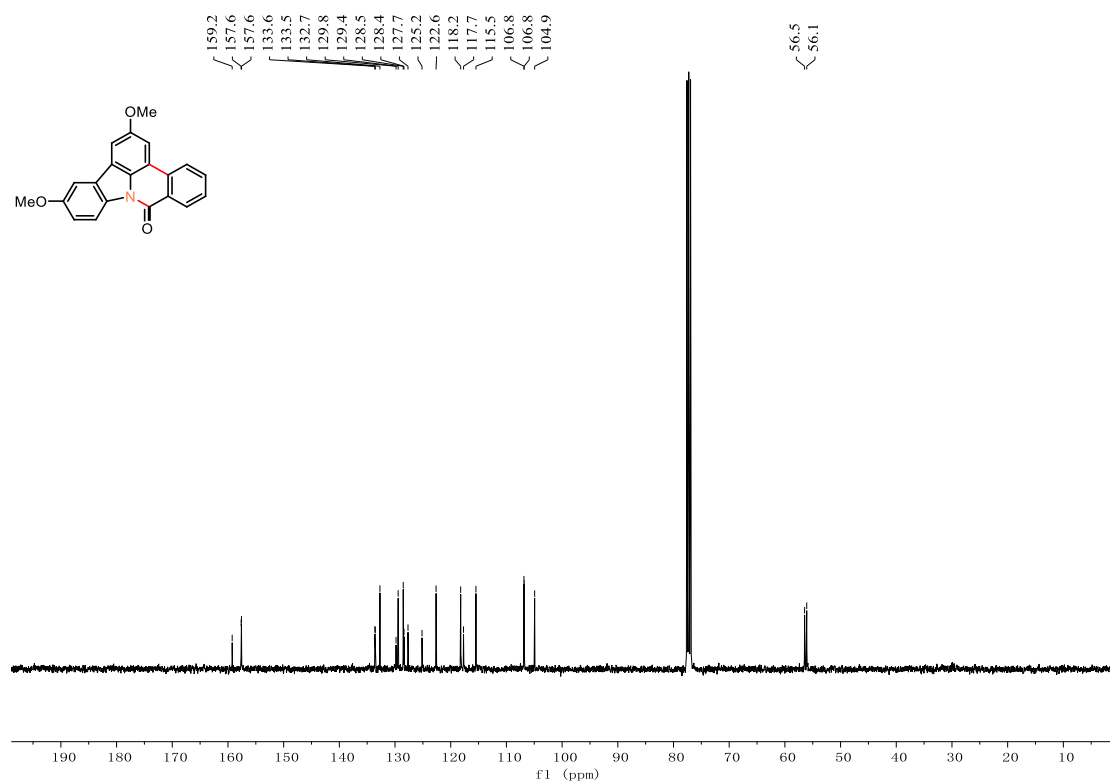
HRMS (ESI) (ESI) m/z Calcd for $C_{25}H_{28}NOSi_2$ $[M+H]^+$ 414.1704, found 414.1701.



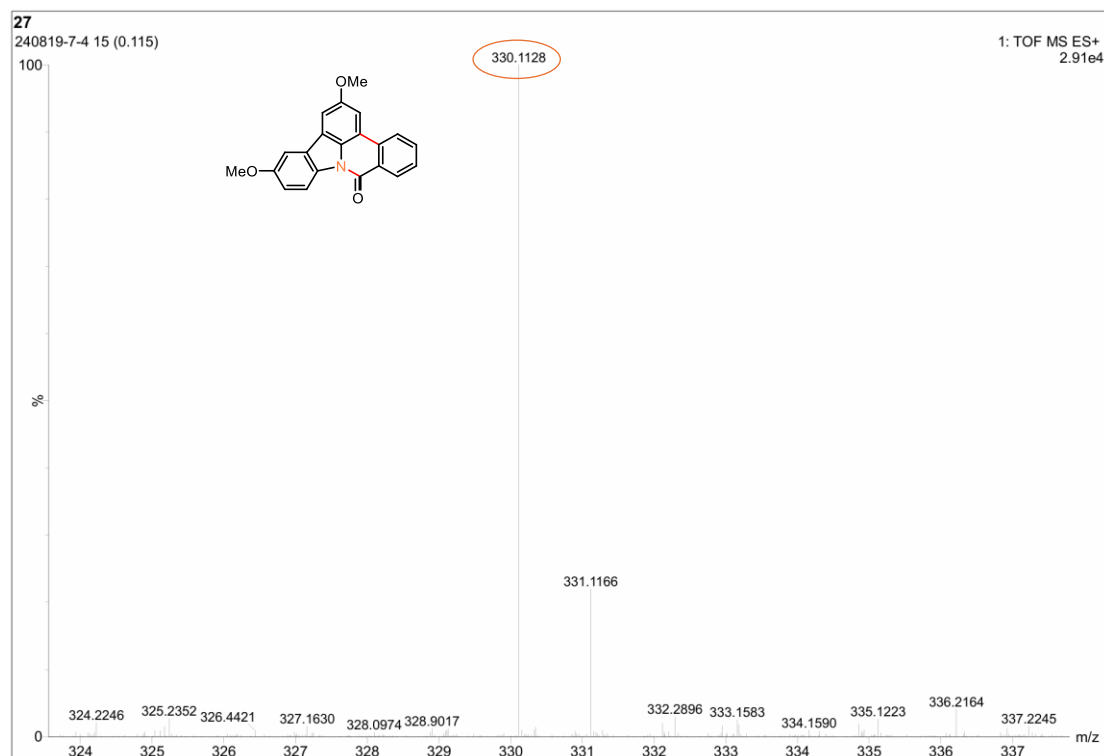
1H NMR of **3e** (400 MHz, $CDCl_3$)



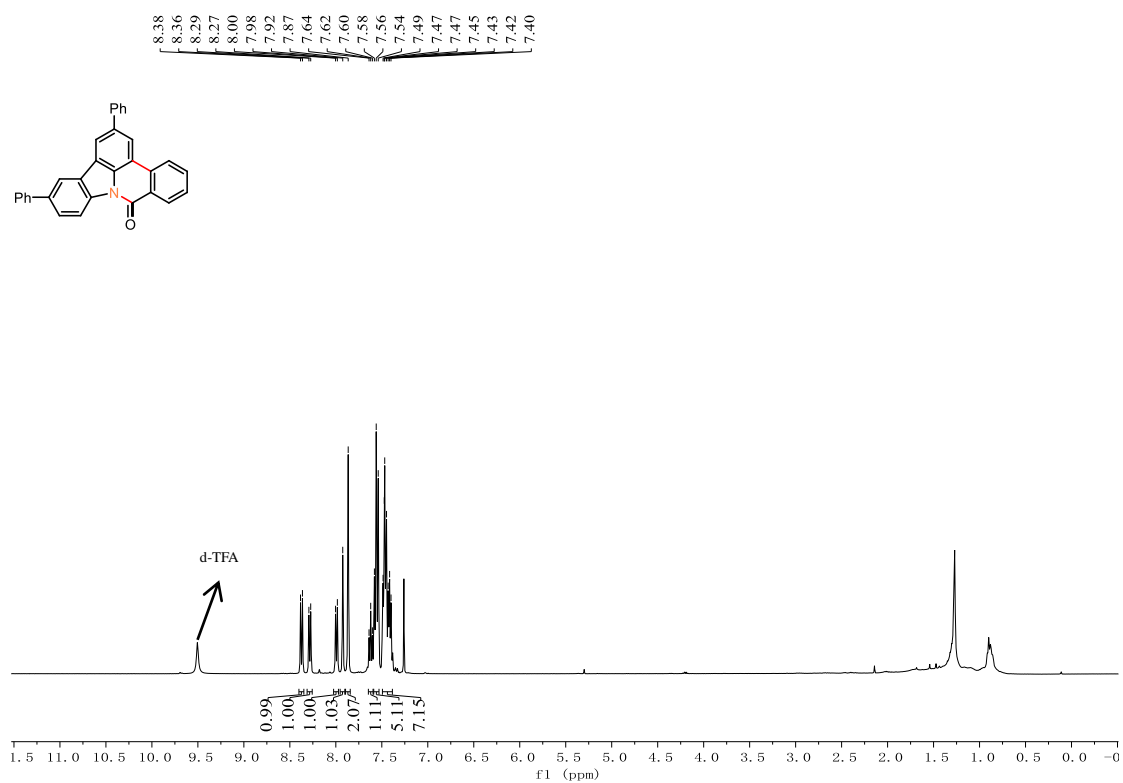
^{13}C NMR of **3e** (100 MHz, CDCl_3)



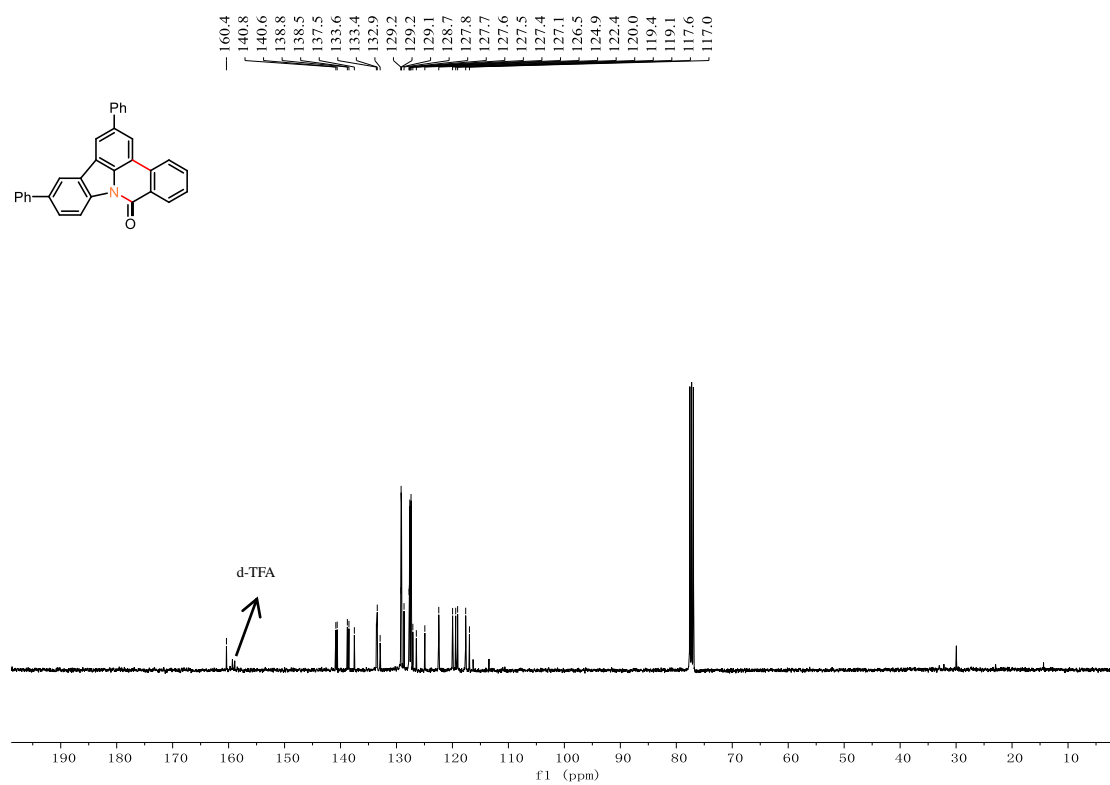
HRMS (ESI) m/z Calcd for $\text{C}_{21}\text{H}_{16}\text{NO}_3$ $[\text{M}+\text{H}]^+$ 330.1125, found 330.1128.



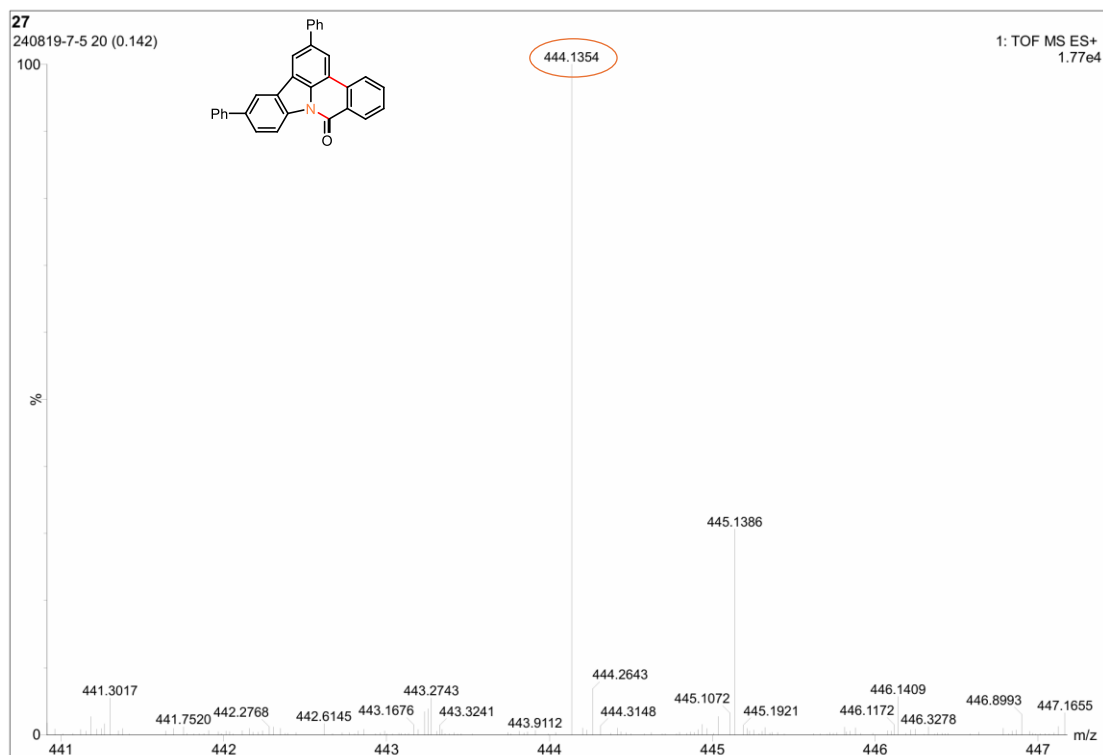
¹H NMR of **3f** (400 MHz, CDCl₃ + CF₃COOD)



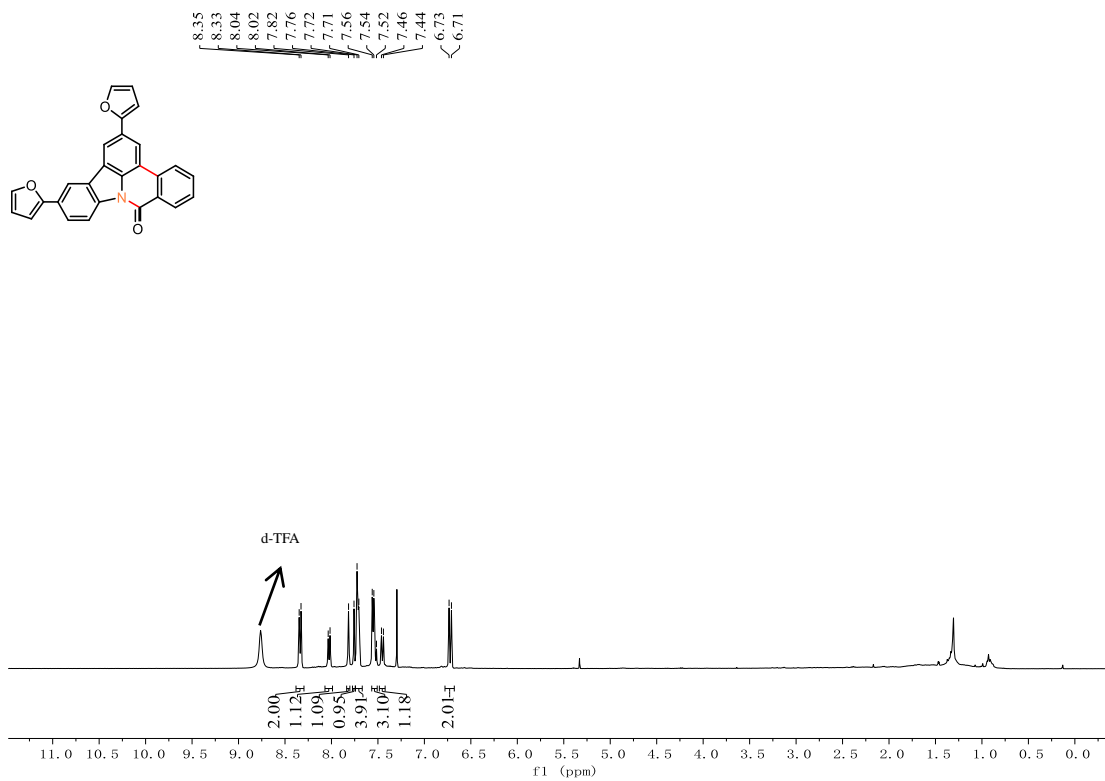
¹³C NMR of **3f** (100 MHz, CDCl₃ + CF₃COOD)



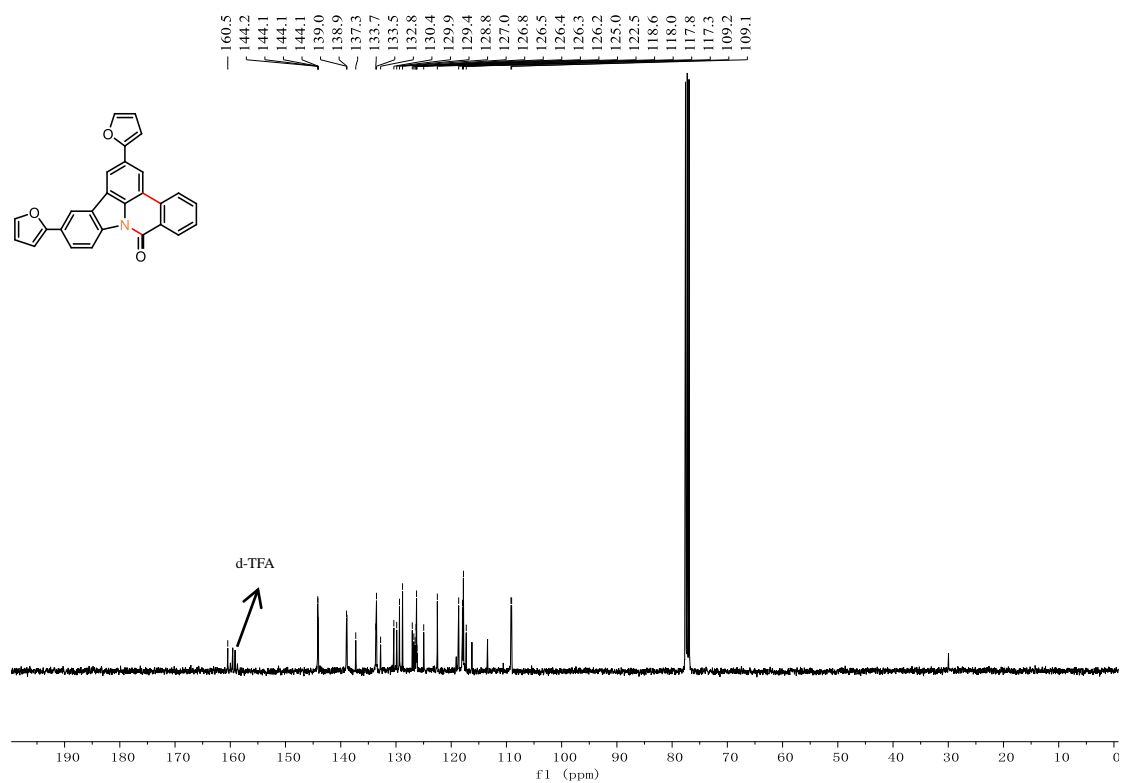
HRMS (ESI) m/z Calcd for $C_{31}H_{20}NO$ $[M+Na]^+$ 444.1359, found 444.1354.



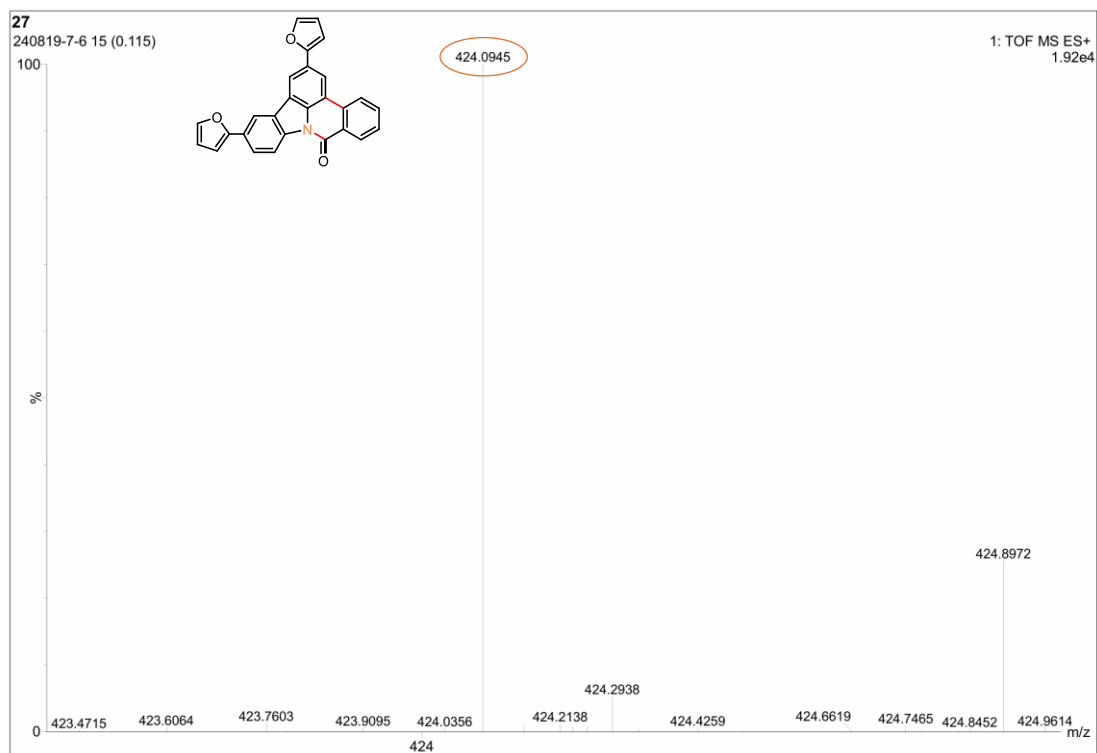
1H NMR of **3g** (400 MHz, $CDCl_3$ + CF_3COOD)



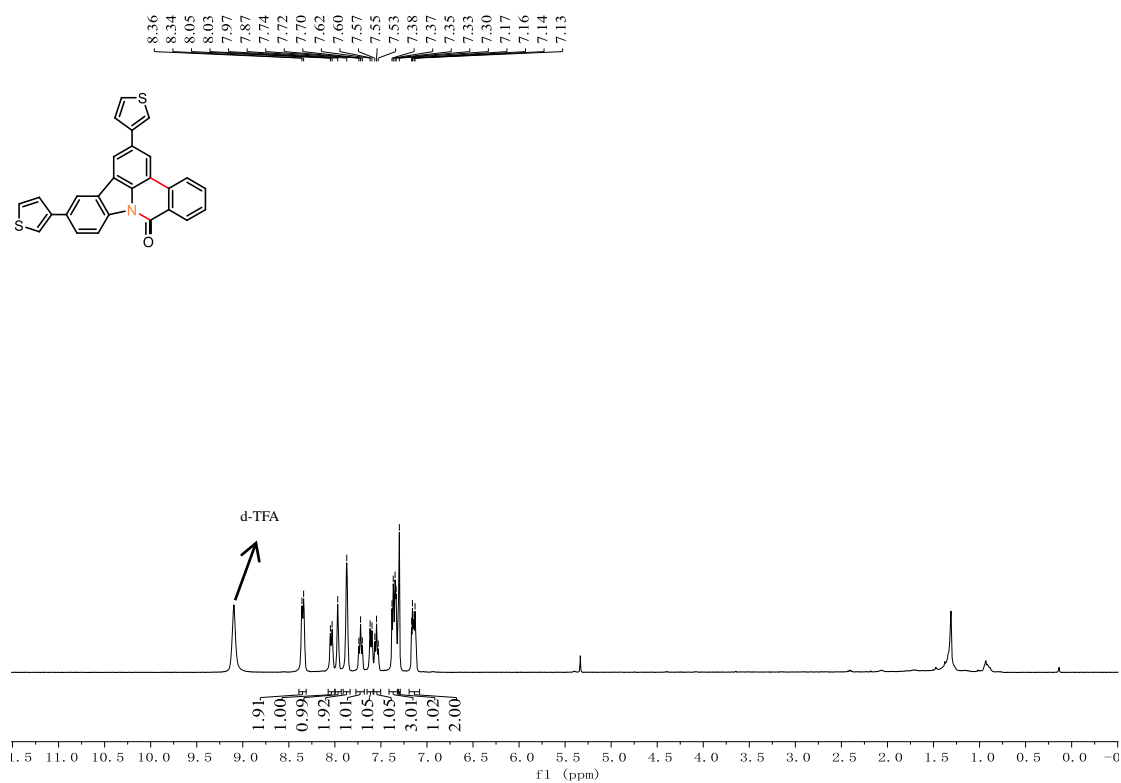
^{13}C NMR of **3g** (100 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$)



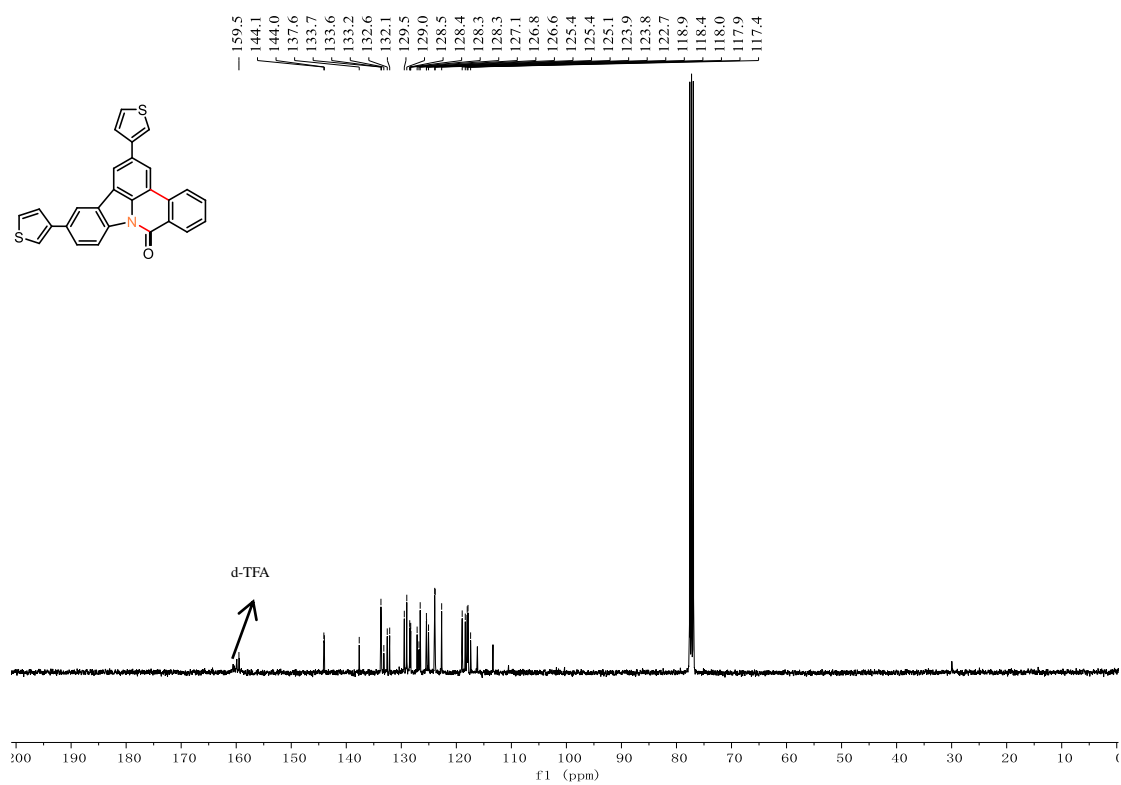
HRMS (ESI) m/z Calcd for $\text{C}_{27}\text{H}_{16}\text{NO}_3$ $[\text{M}+\text{Na}]^+$ 424.0944, found 424.0945.



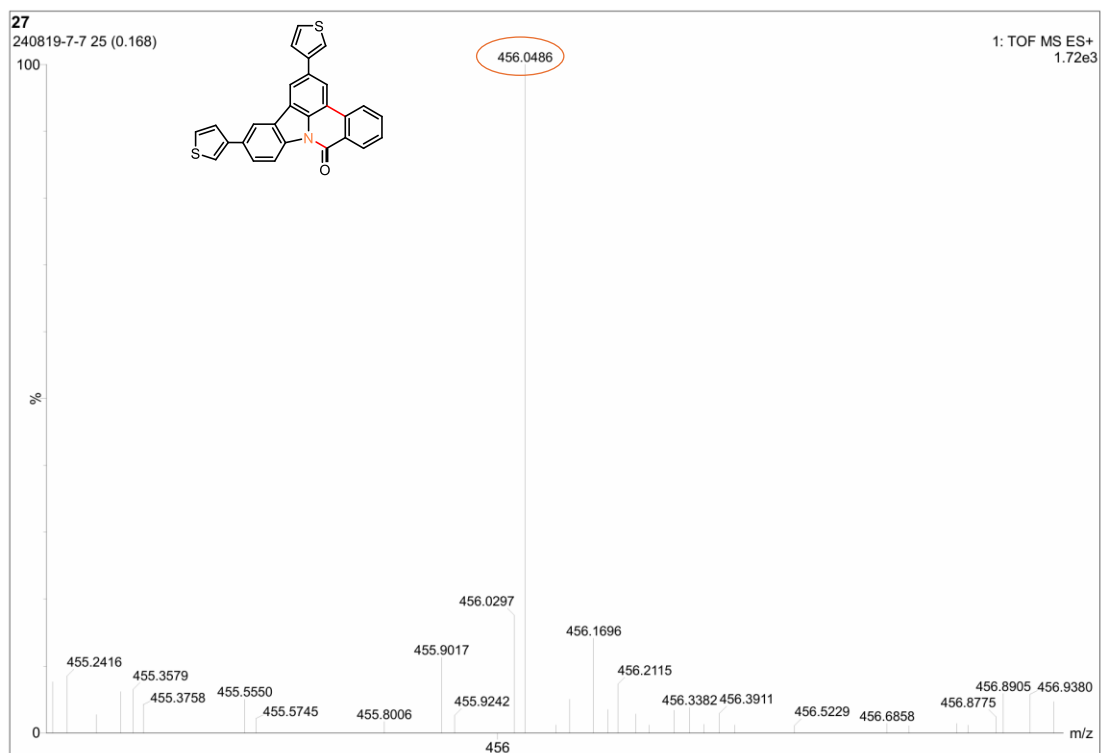
¹H NMR of **3h** (400 MHz, CDCl₃ + CF₃COOD)



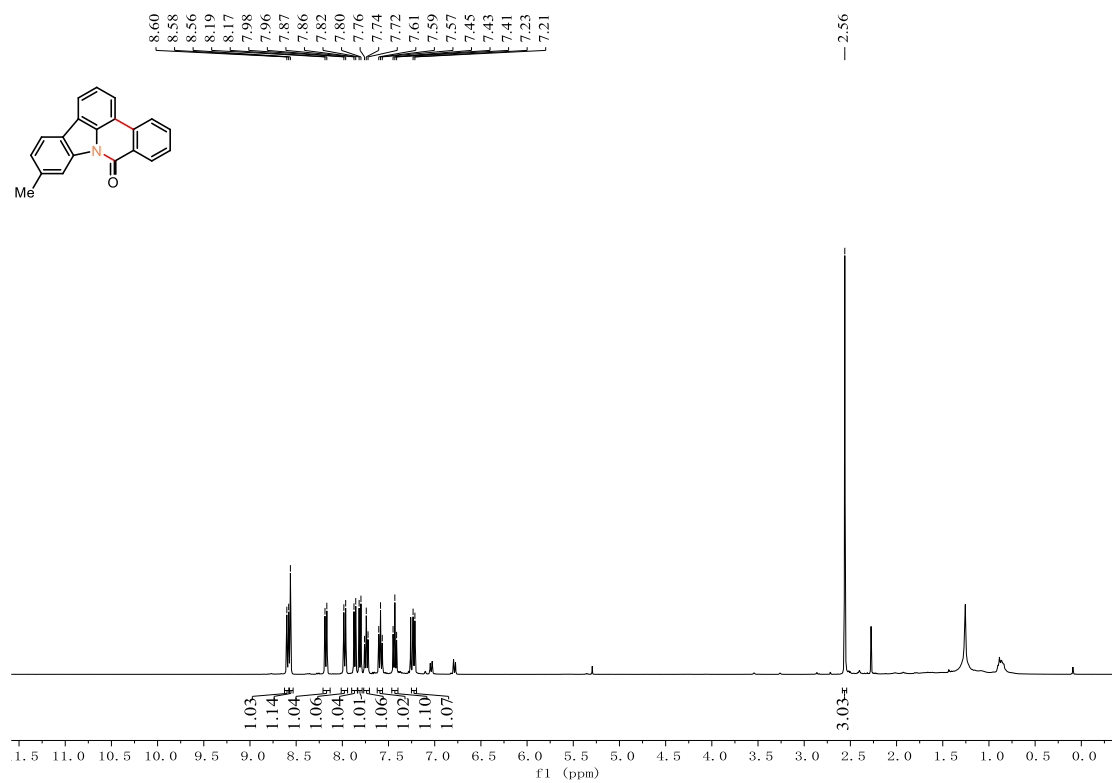
¹³C NMR of **3h** (100 MHz, CDCl₃ + CF₃COOD)



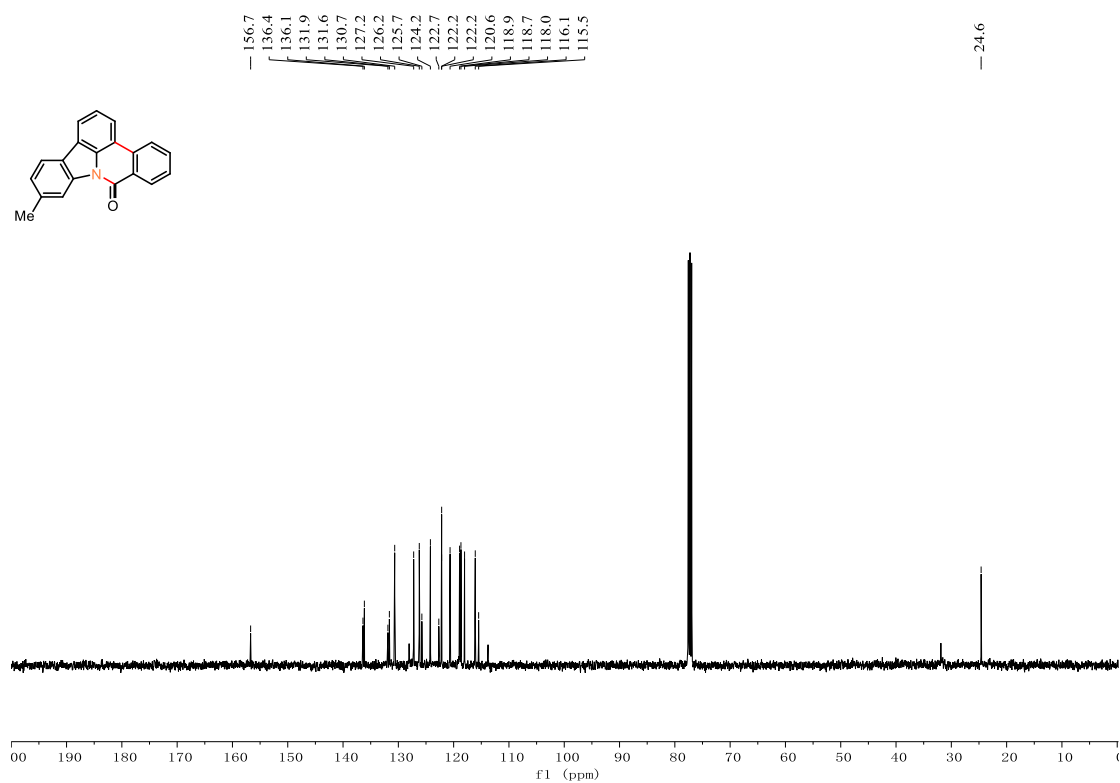
HRMS (ESI) m/z Calcd for C₂₇H₁₆NOS₂ [M+Na]⁺ 456.0487, found 456.0486.



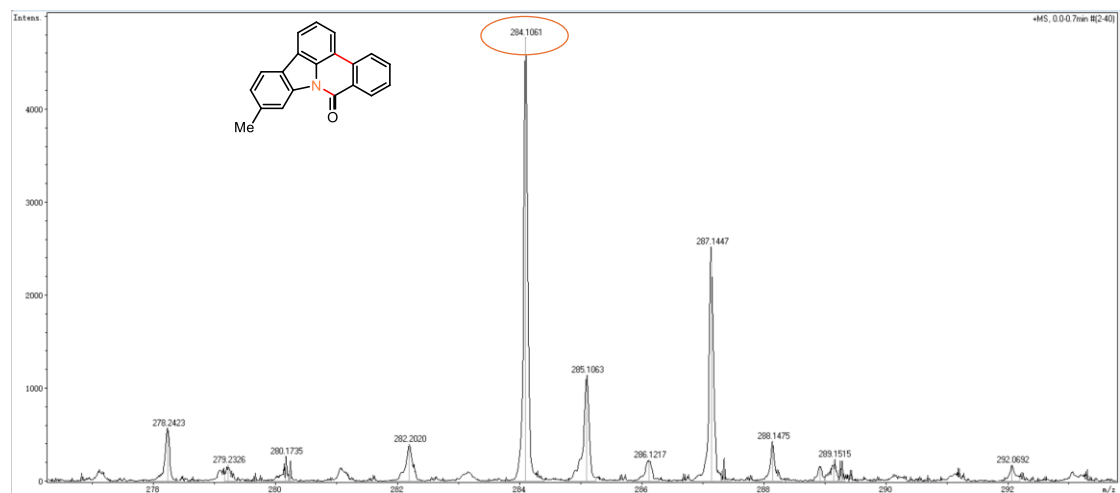
¹H NMR of **3i** (400 MHz, CDCl₃)



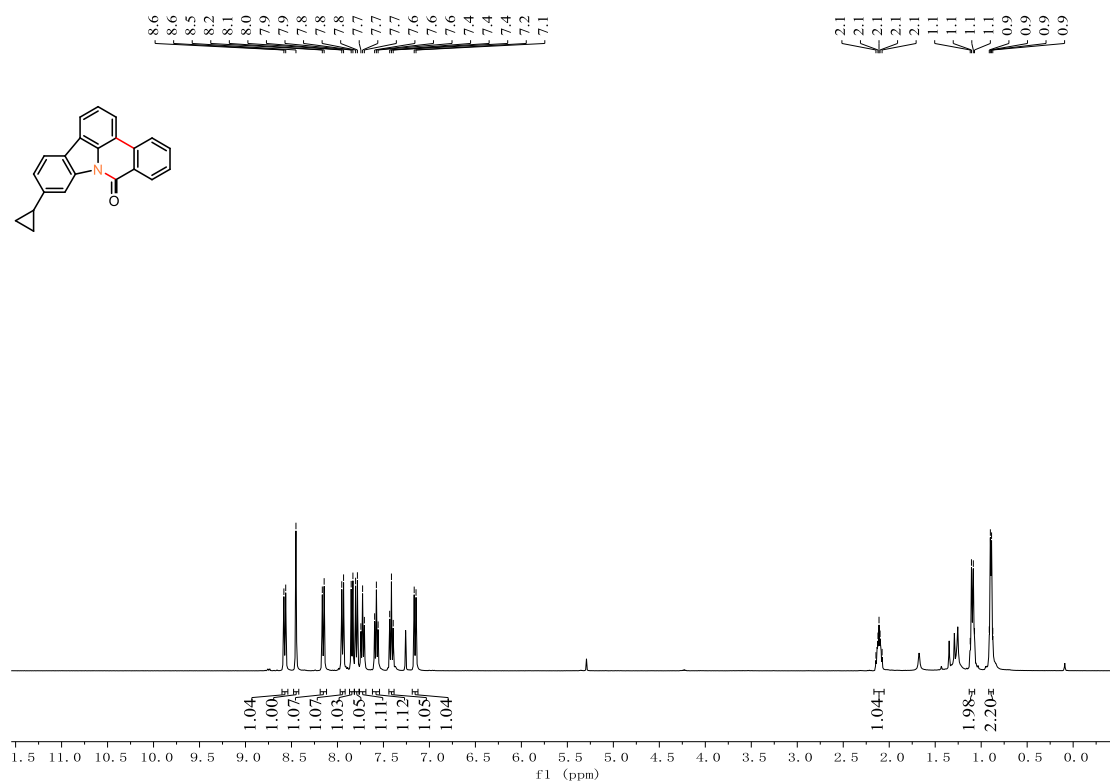
^{13}C NMR of **3i** (100 MHz, CDCl_3)



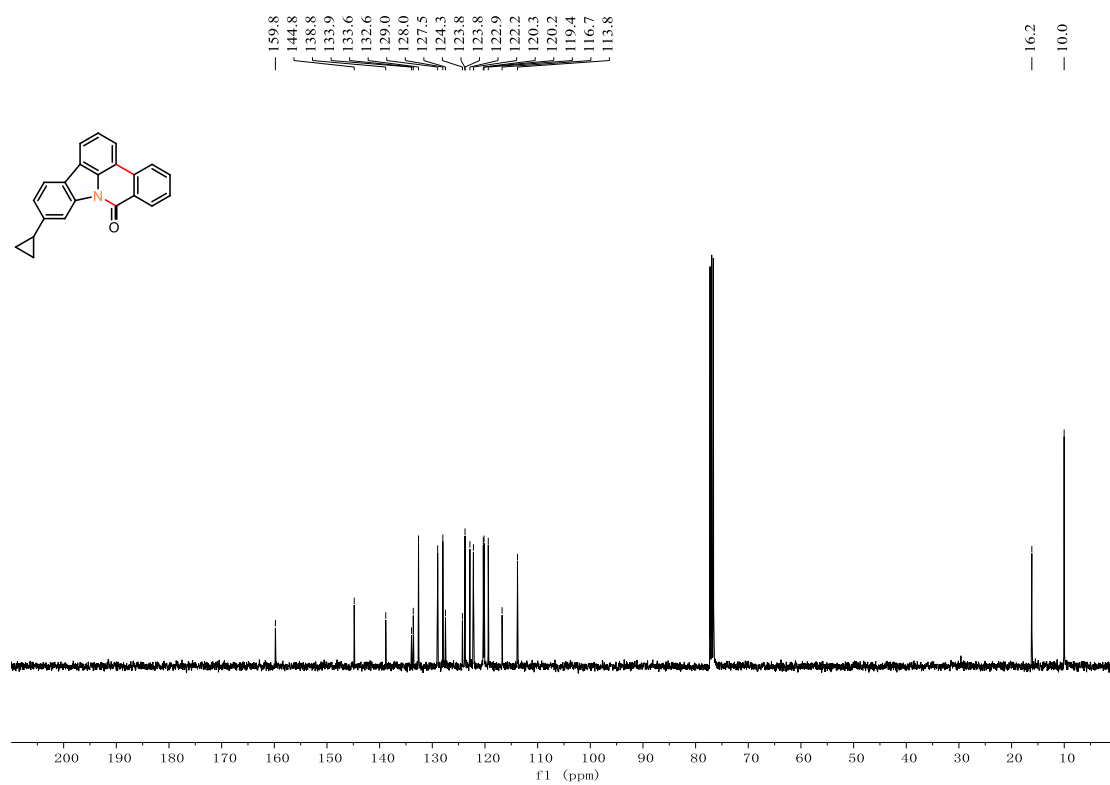
HRMS (ESI) m/z Calcd for $\text{C}_{20}\text{H}_{14}\text{NO}$ $[\text{M}+\text{H}]^+$ 284.1070, found 284.1061.



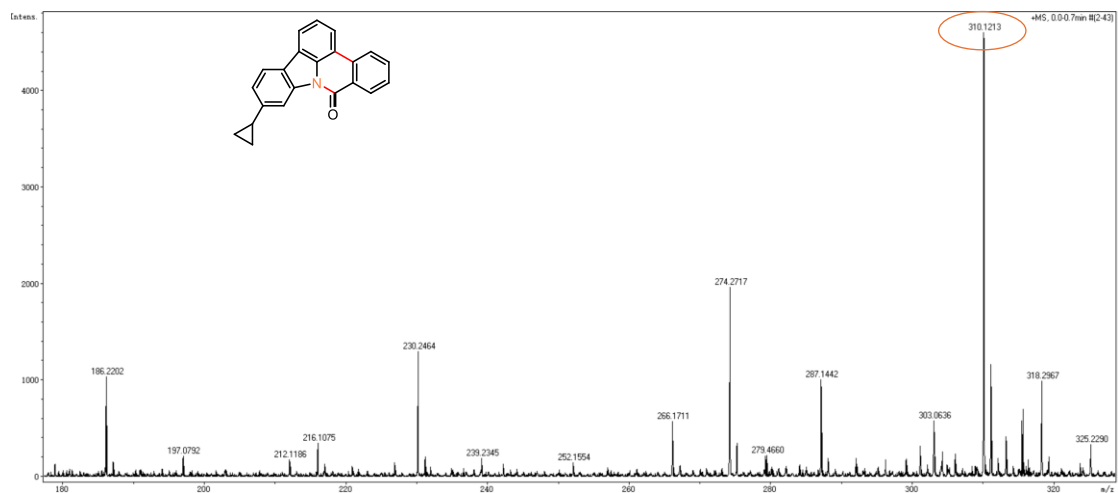
¹H NMR of **3j** (400 MHz, CDCl₃)



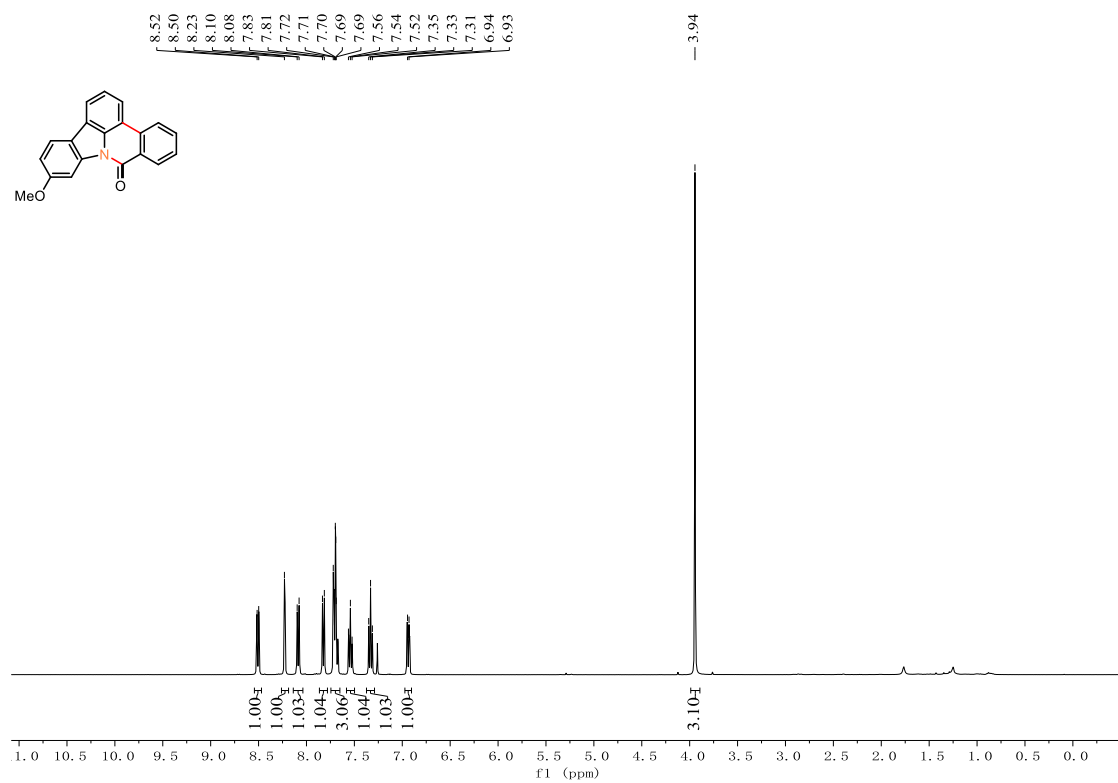
¹³C NMR of **3j** (100 MHz, CDCl₃)



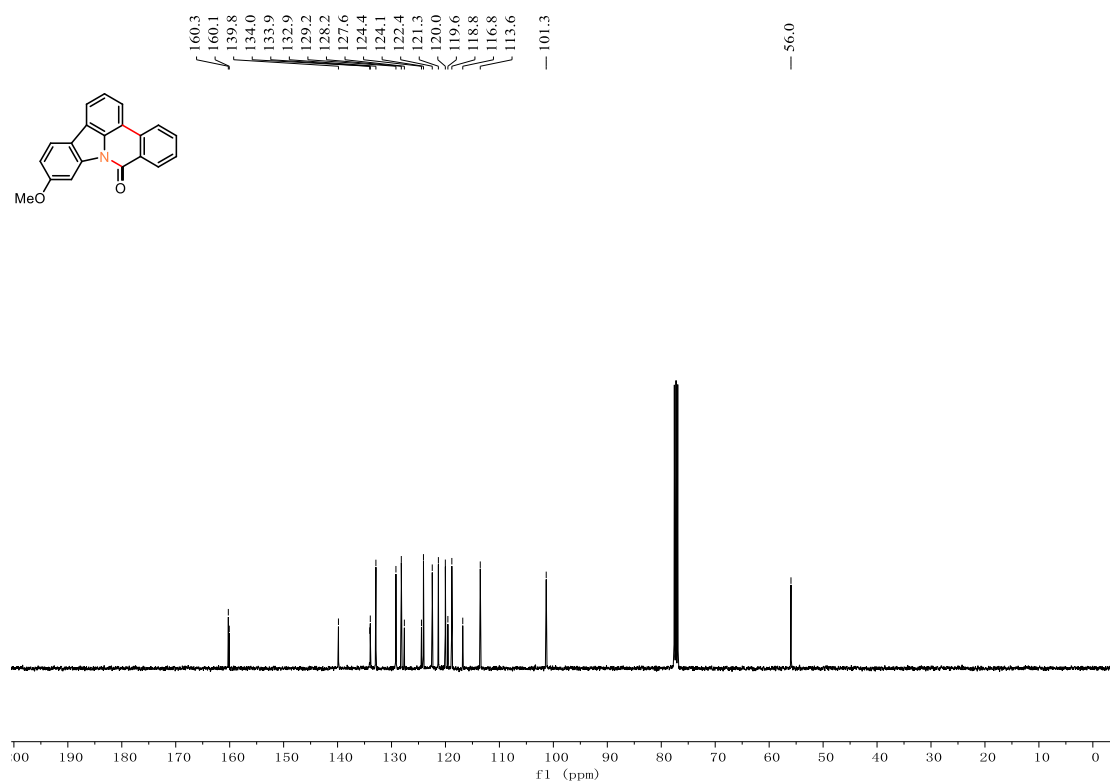
HRMS (ESI) m/z Calcd for C₂₂H₁₆NO [M+H]⁺ 310.1226, found 310.1213.



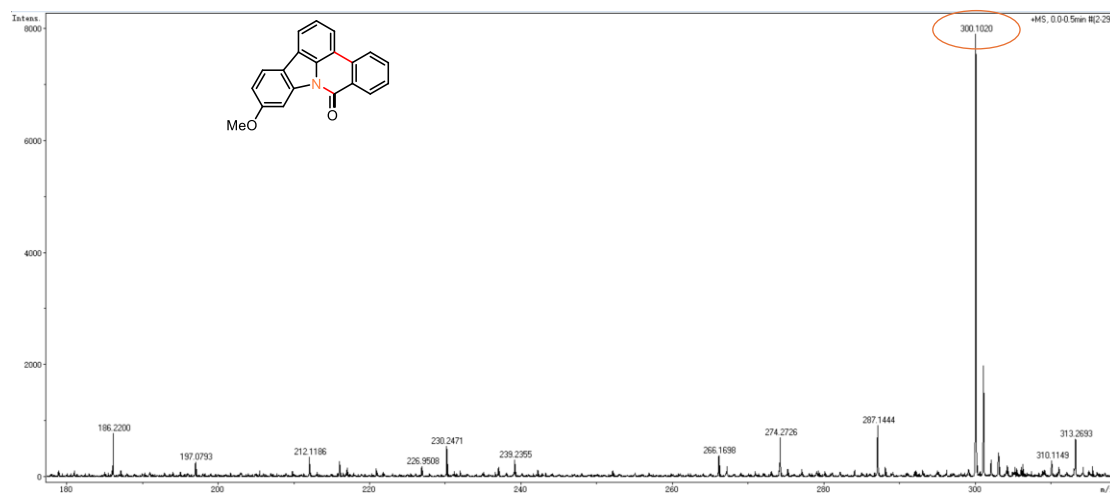
¹H NMR of **3k** (400 MHz, CDCl₃)



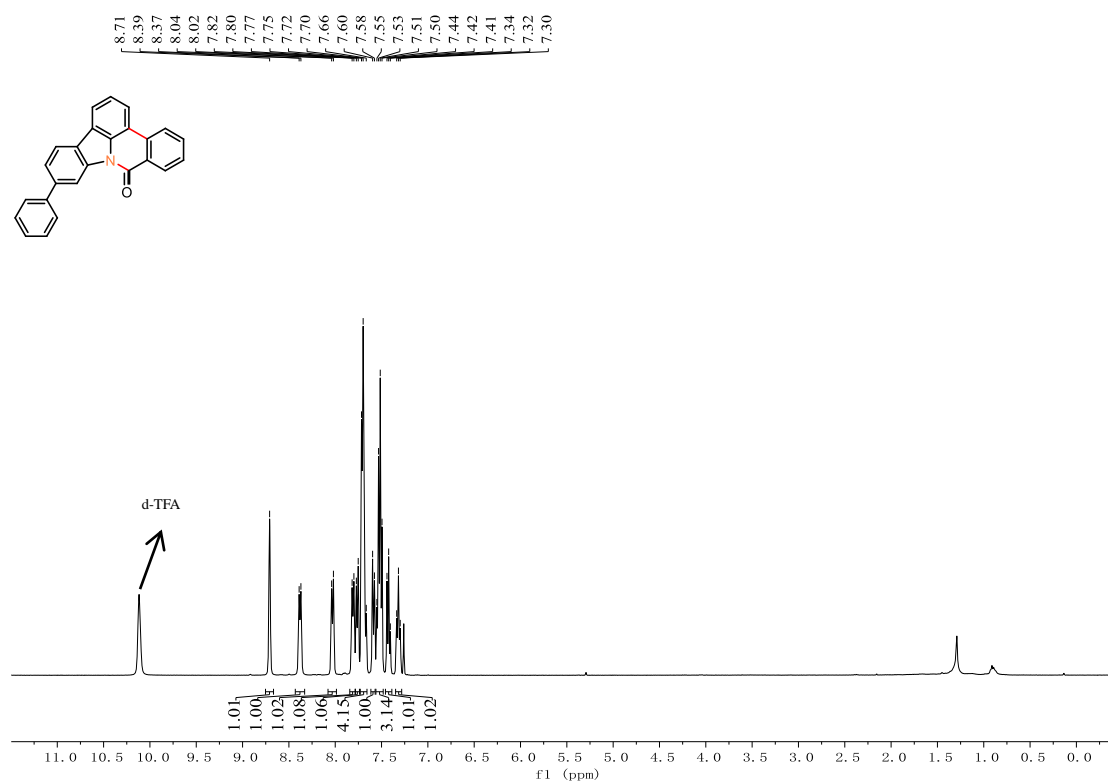
^{13}C NMR of **3k** (100 MHz, CDCl_3)



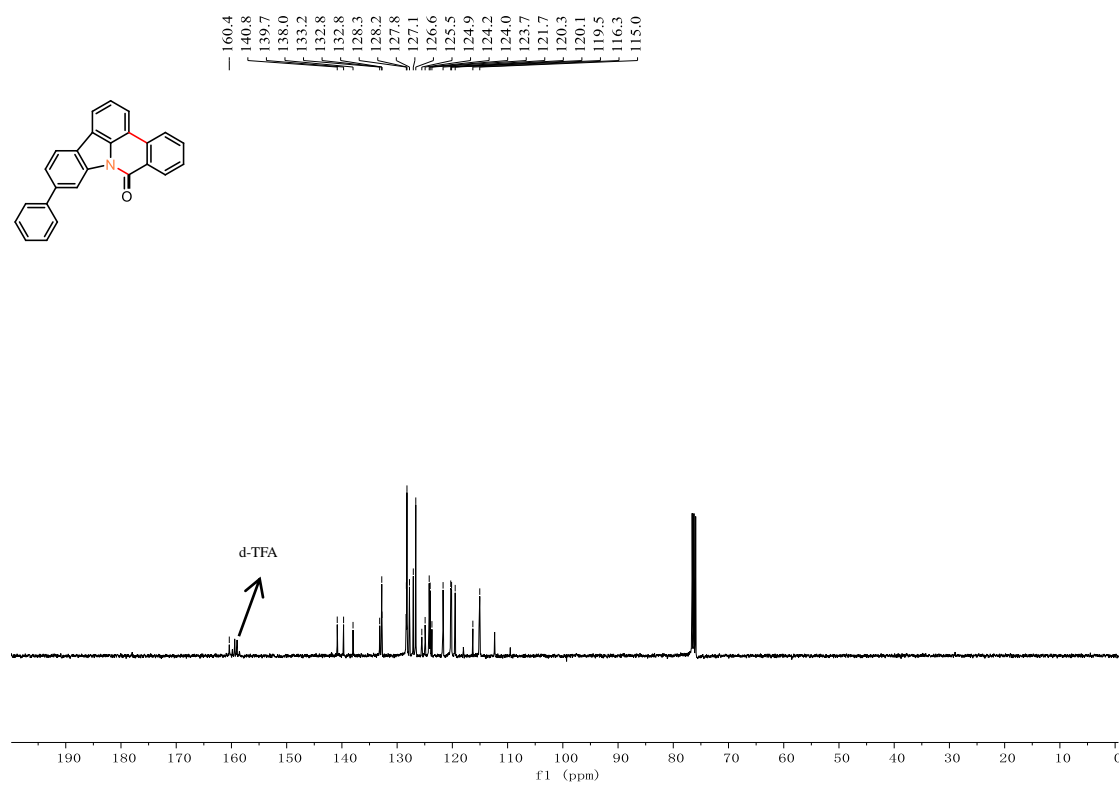
HRMS (ESI) m/z Calcd for $\text{C}_{20}\text{H}_{14}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 300.1019, found 300.1020.



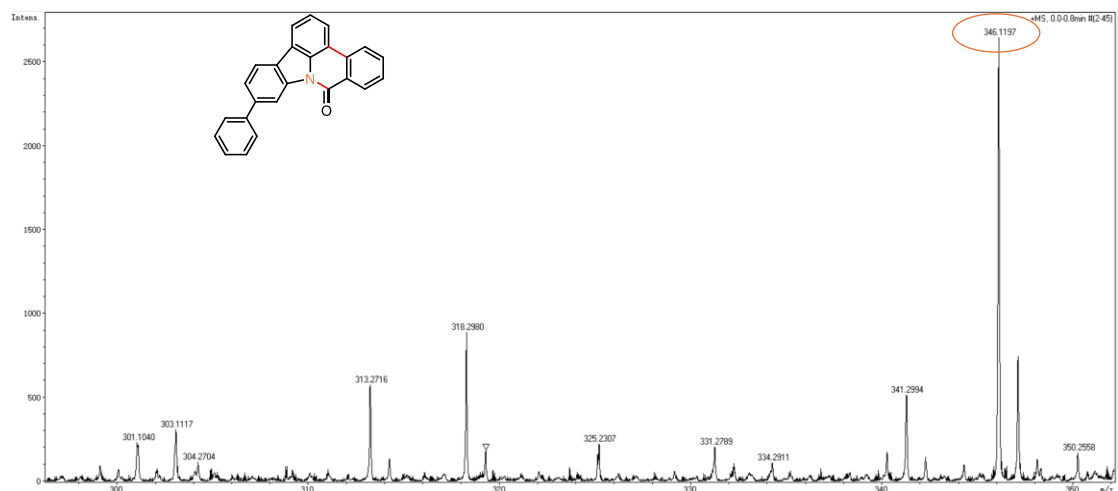
¹H NMR of **31** (400 MHz, CDCl₃ + CF₃COOD)



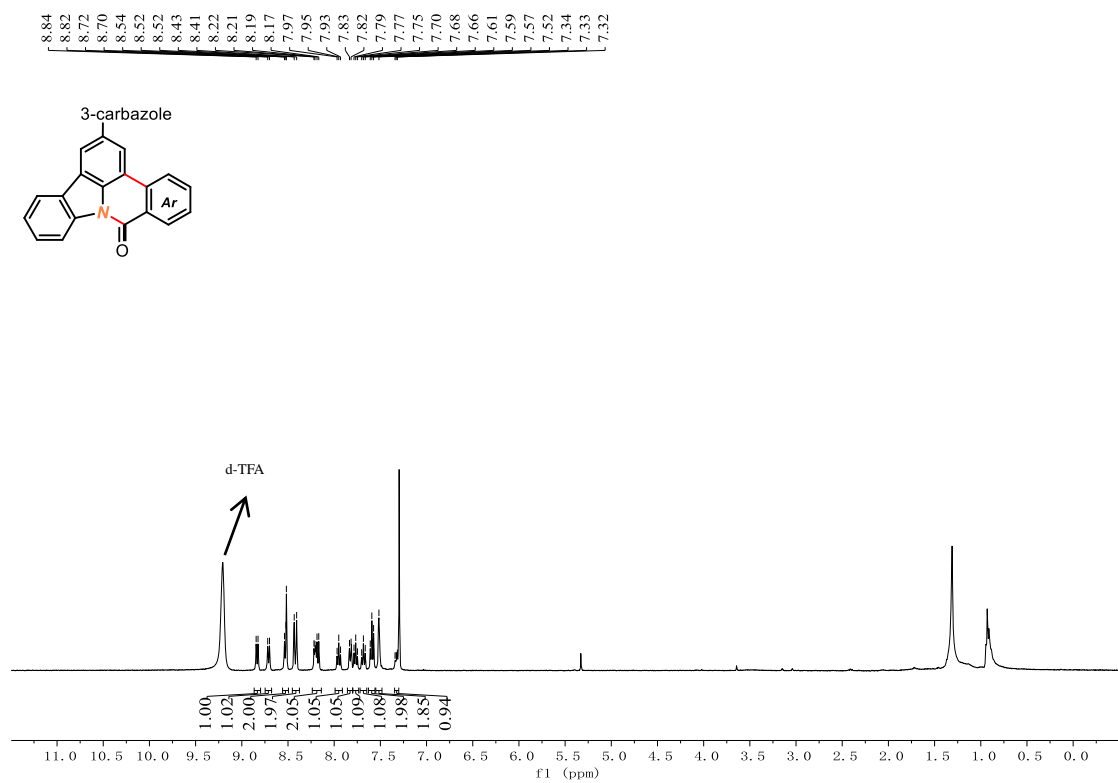
¹³C NMR of **31** (100 MHz, CDCl₃ + CF₃COOD)



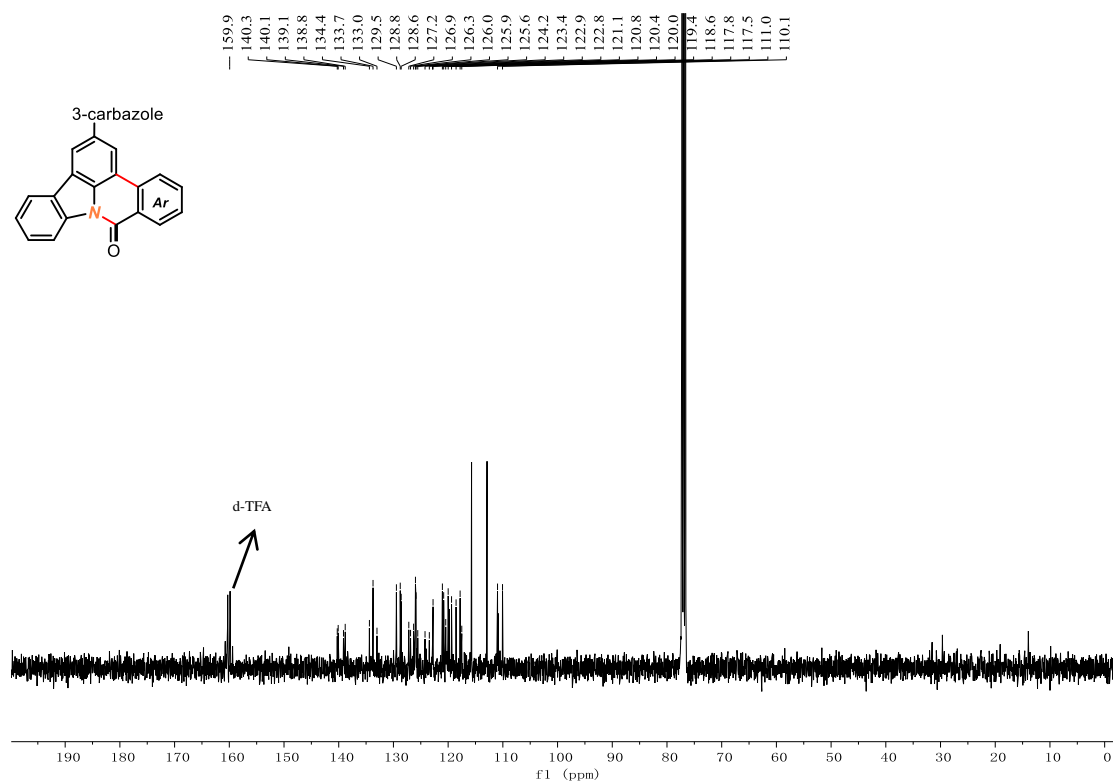
HRMS (ESI) m/z Calcd for $C_{25}H_{16}NO$ $[M+H]^+$ 346.1226, found 346.1197.



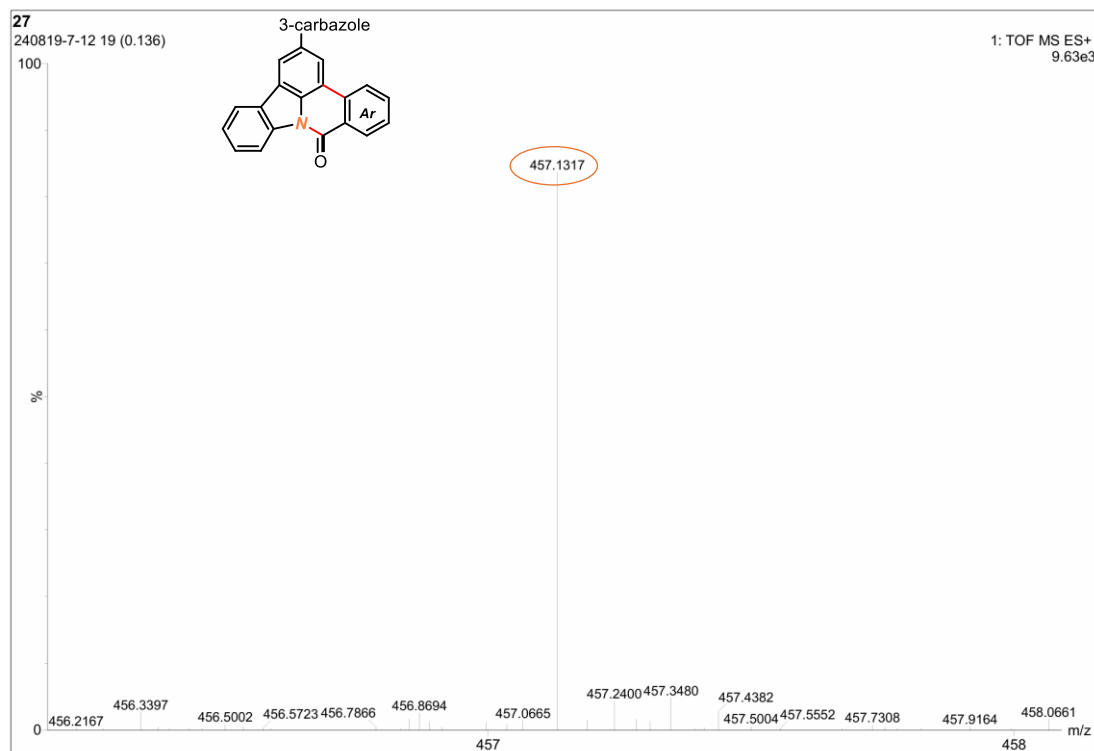
1H NMR of **3m** (400 MHz, $CDCl_3$ + CF_3COOD)



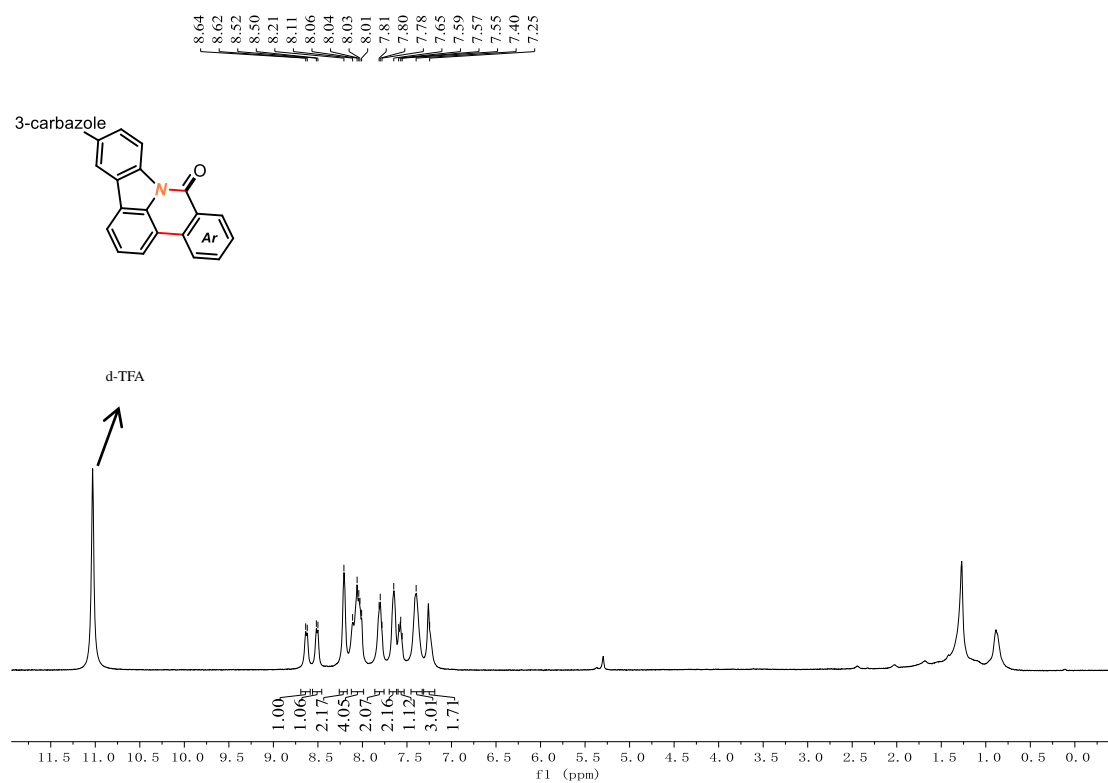
^{13}C NMR of **3m** (100 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$)



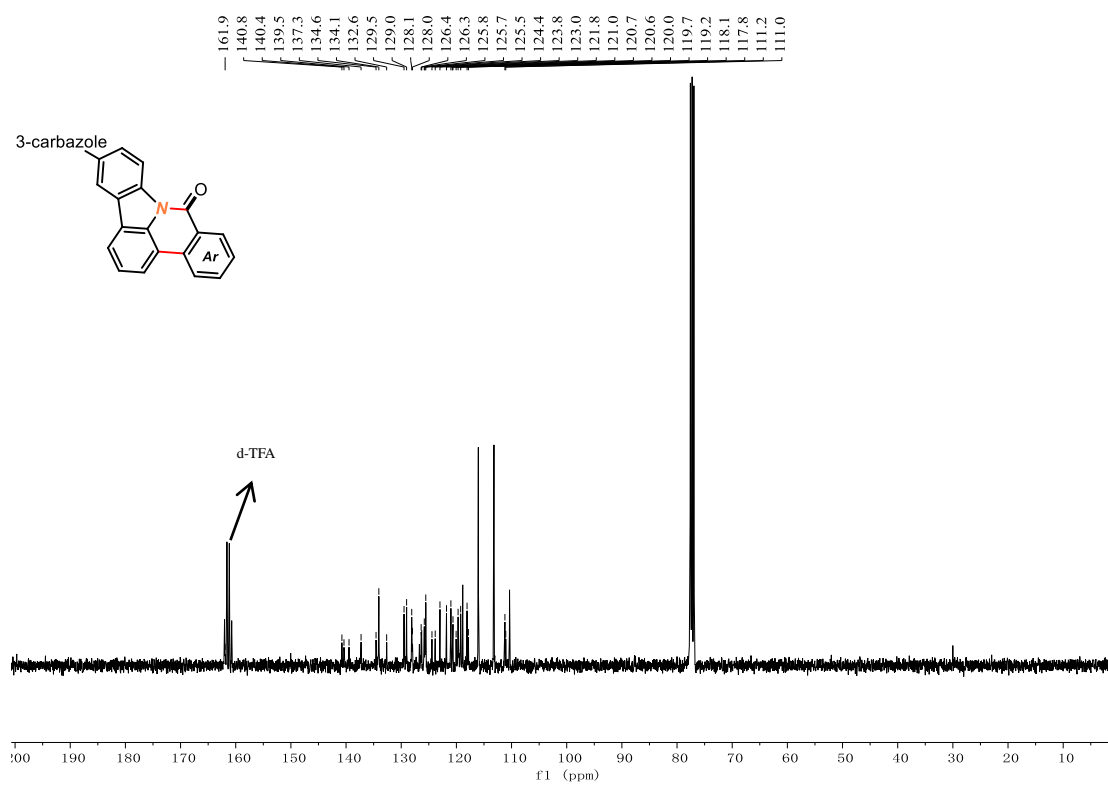
HRMS (ESI) m/z Calcd for $\text{C}_{31}\text{H}_{19}\text{N}_2\text{O}$ $[\text{M}+\text{Na}]^+$ 457.1311, found 457.1317.



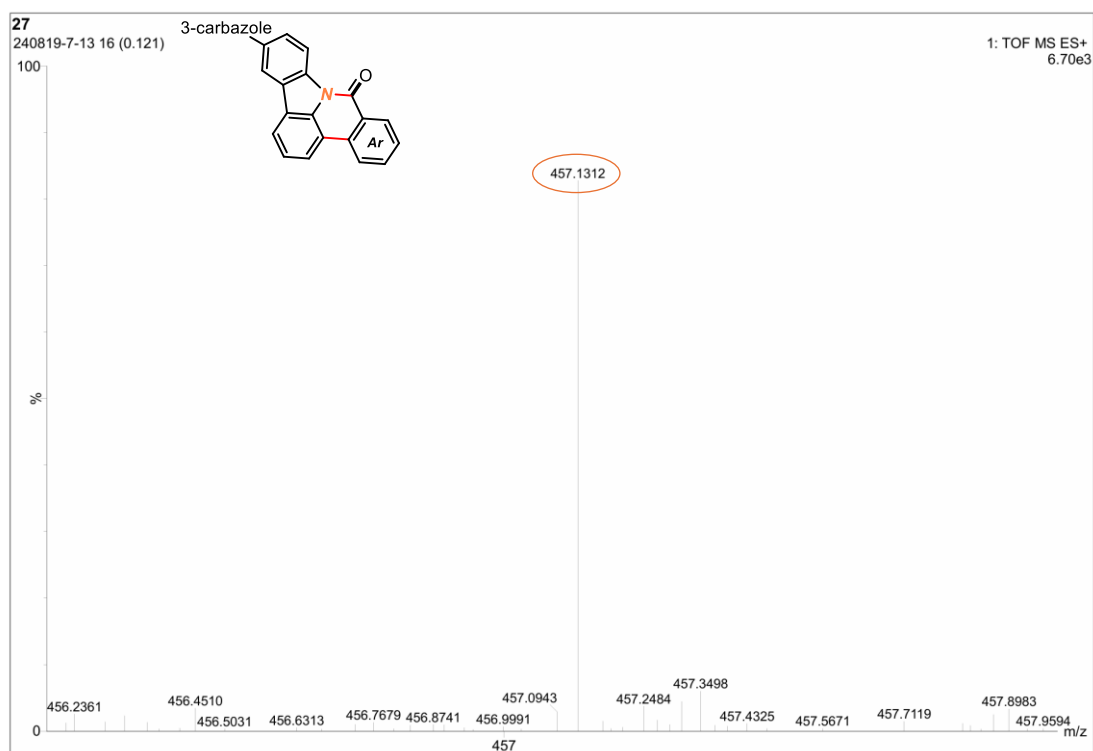
¹H NMR of **3m'** (400 MHz, CDCl₃ + CF₃COOD)



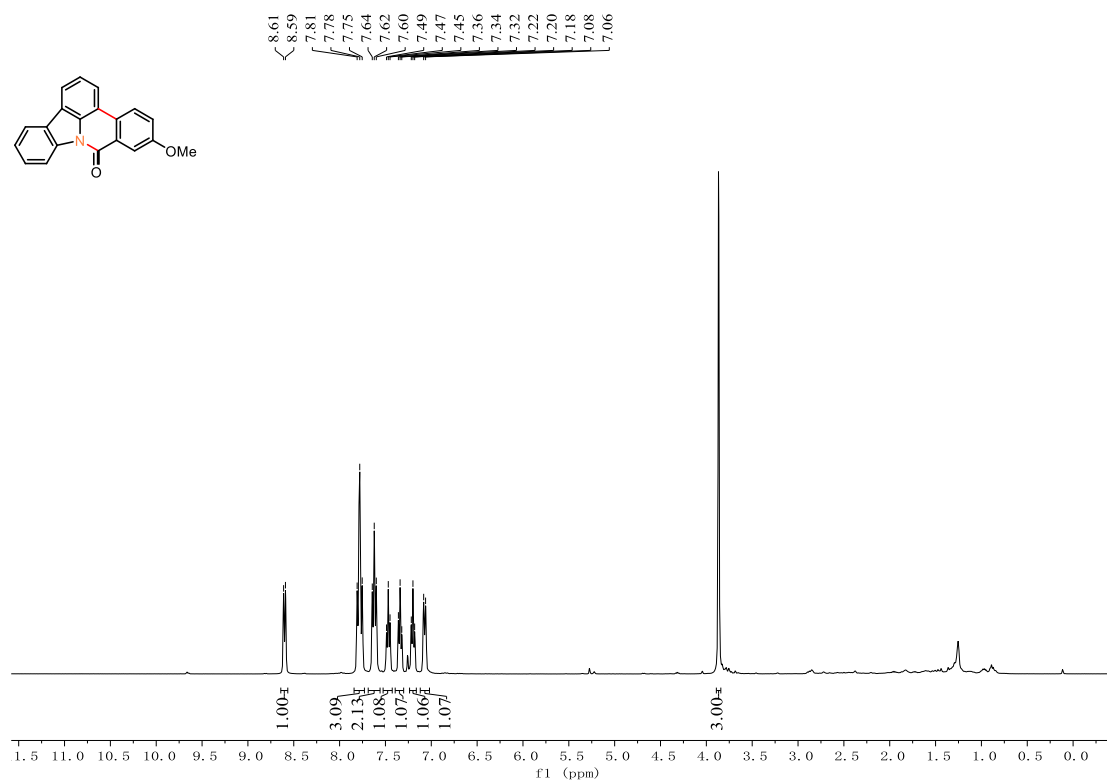
¹³C NMR of **3m'** (100 MHz, CDCl₃ + CF₃COOD)



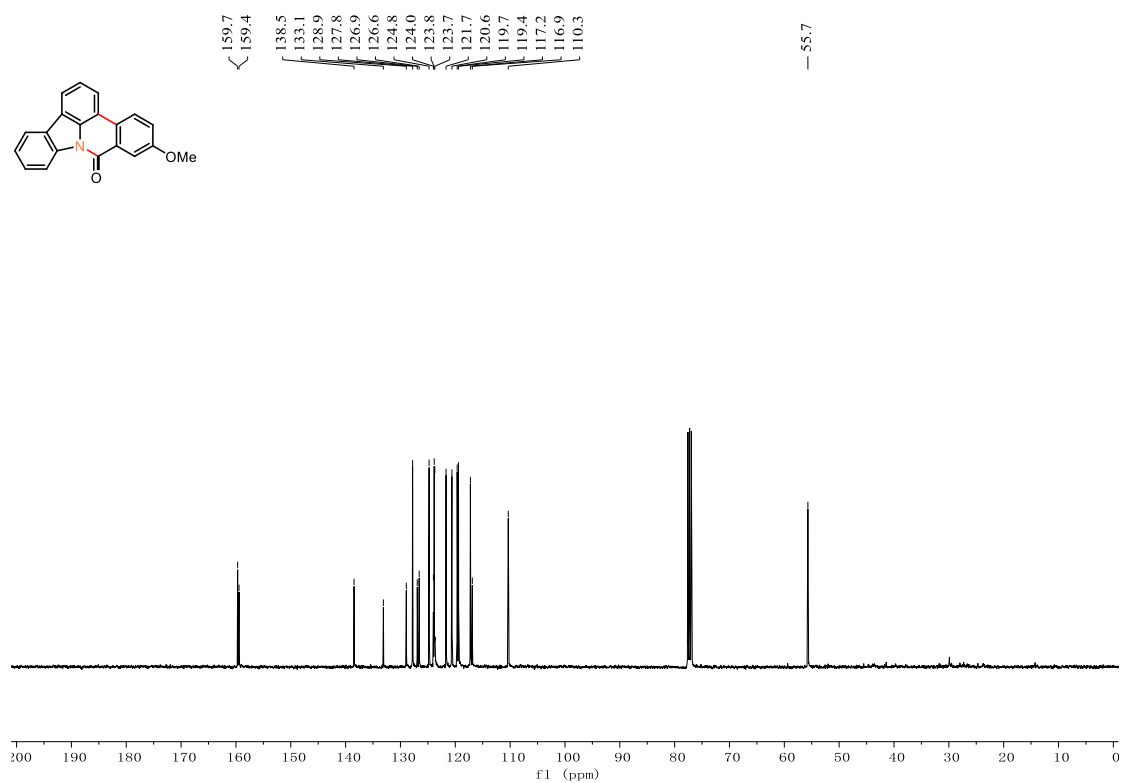
HRMS (ESI) m/z Calcd for $C_{31}H_{19}N_2O$ $[M+Na]^+$ 457.1311, found 457.1312.



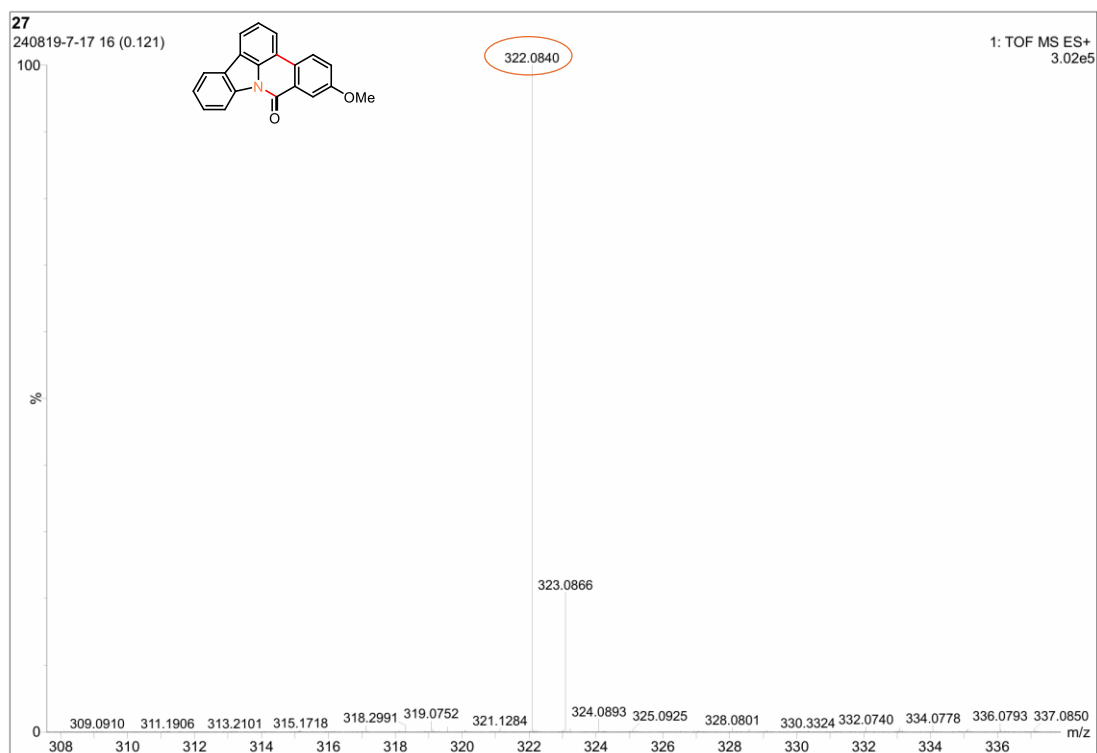
1H NMR of **3n** (400 MHz, $CDCl_3$)



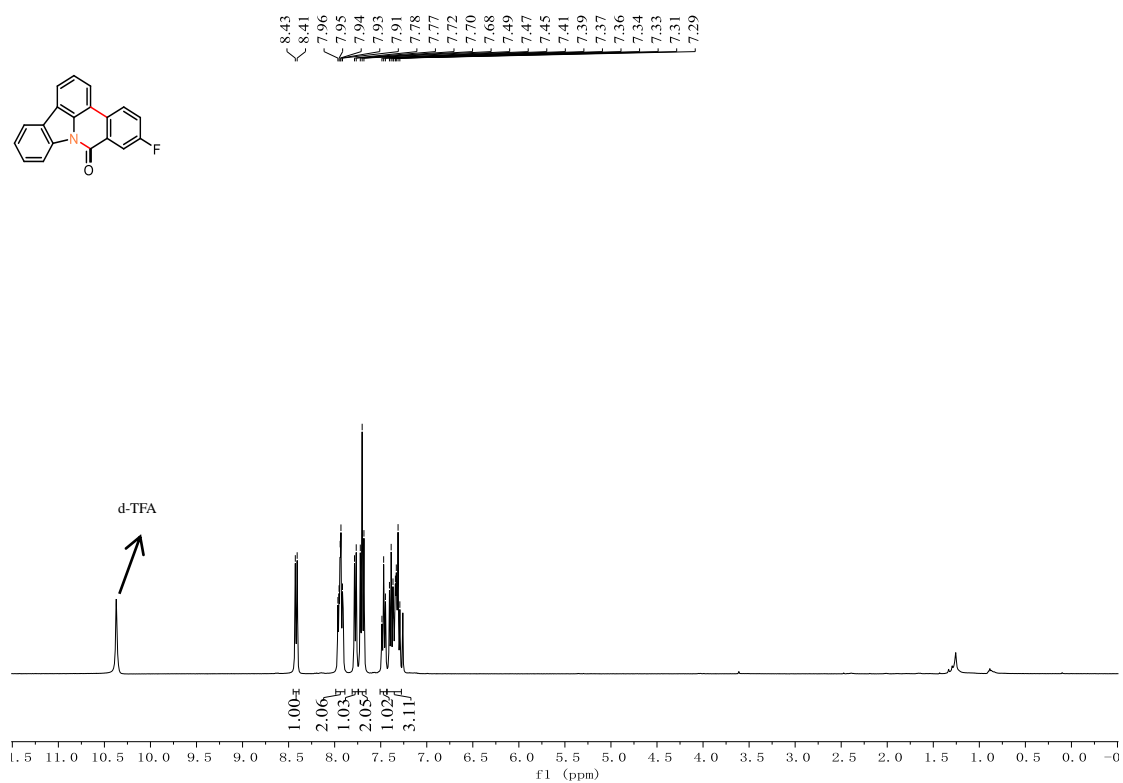
^{13}C NMR of **3n** (100 MHz, CDCl_3)



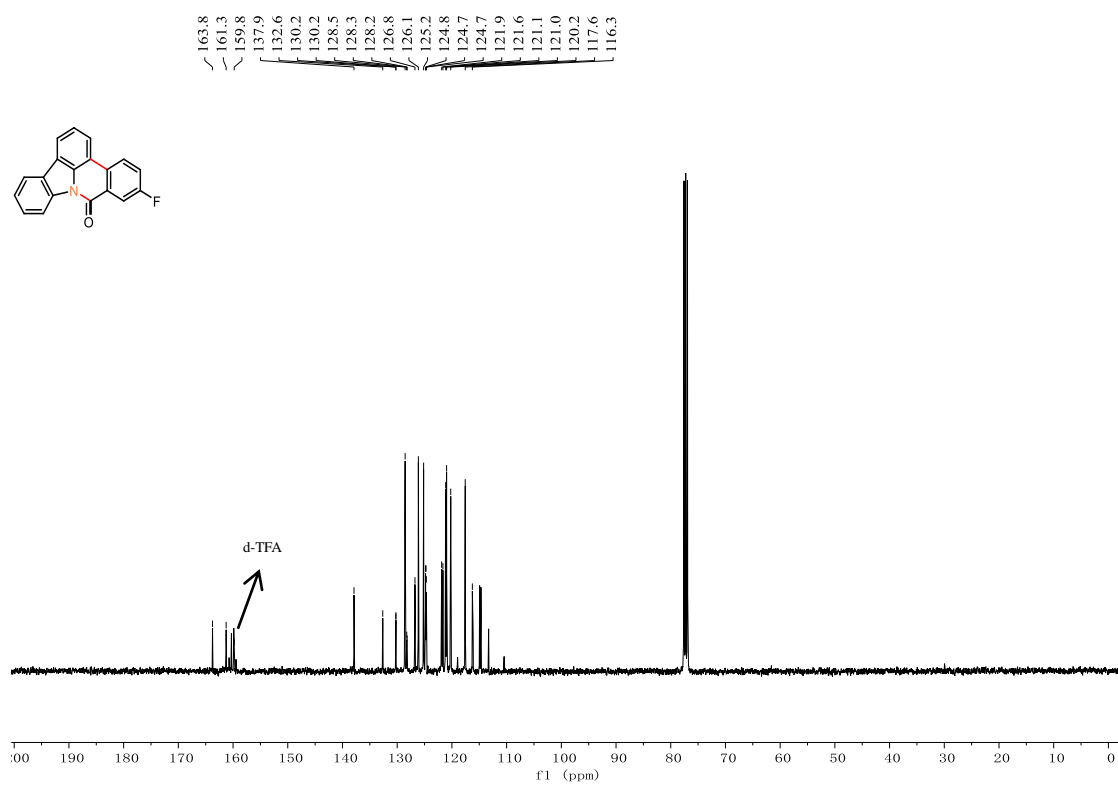
HRMS (ESI) m/z Calcd for $\text{C}_{20}\text{H}_{14}\text{NO}_2$ $[\text{M}+\text{Na}]^+$ 322.0838, found 322.0840.



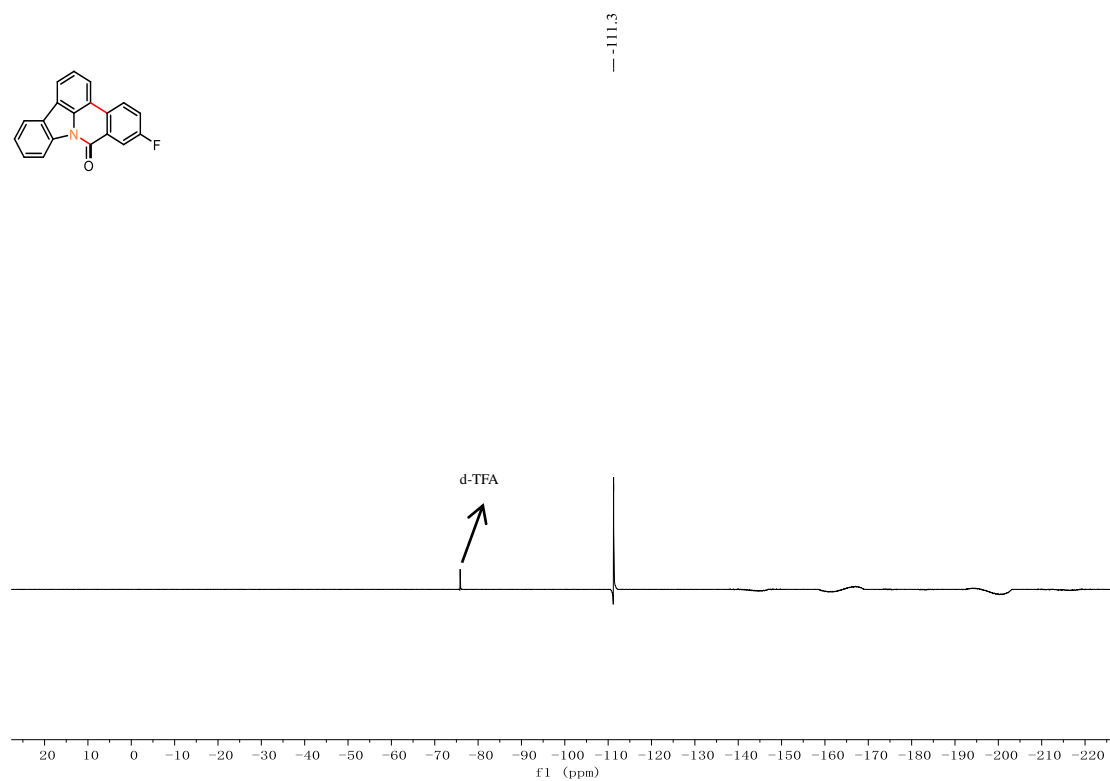
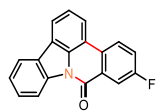
^1H NMR of **3o** (400 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$)



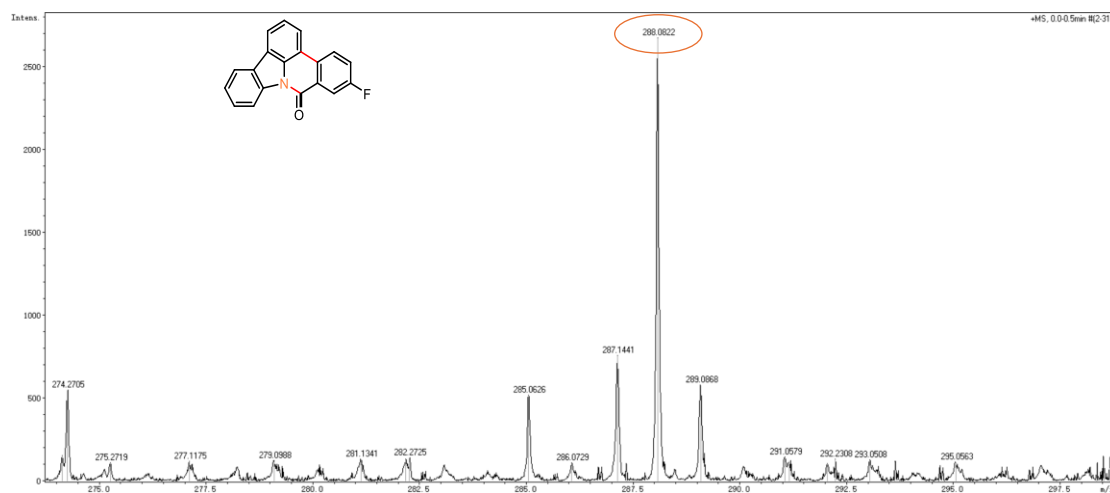
^{13}C NMR of **3o** (100 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$)



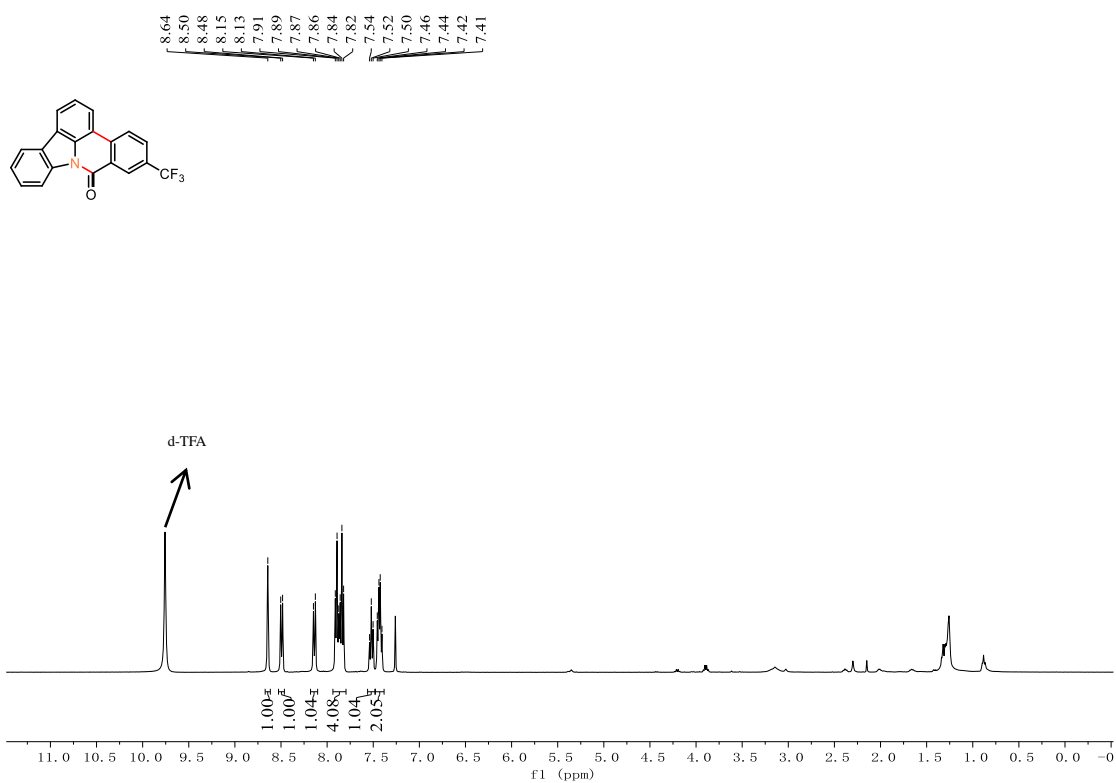
^{19}F NMR of **3o** (376 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$)



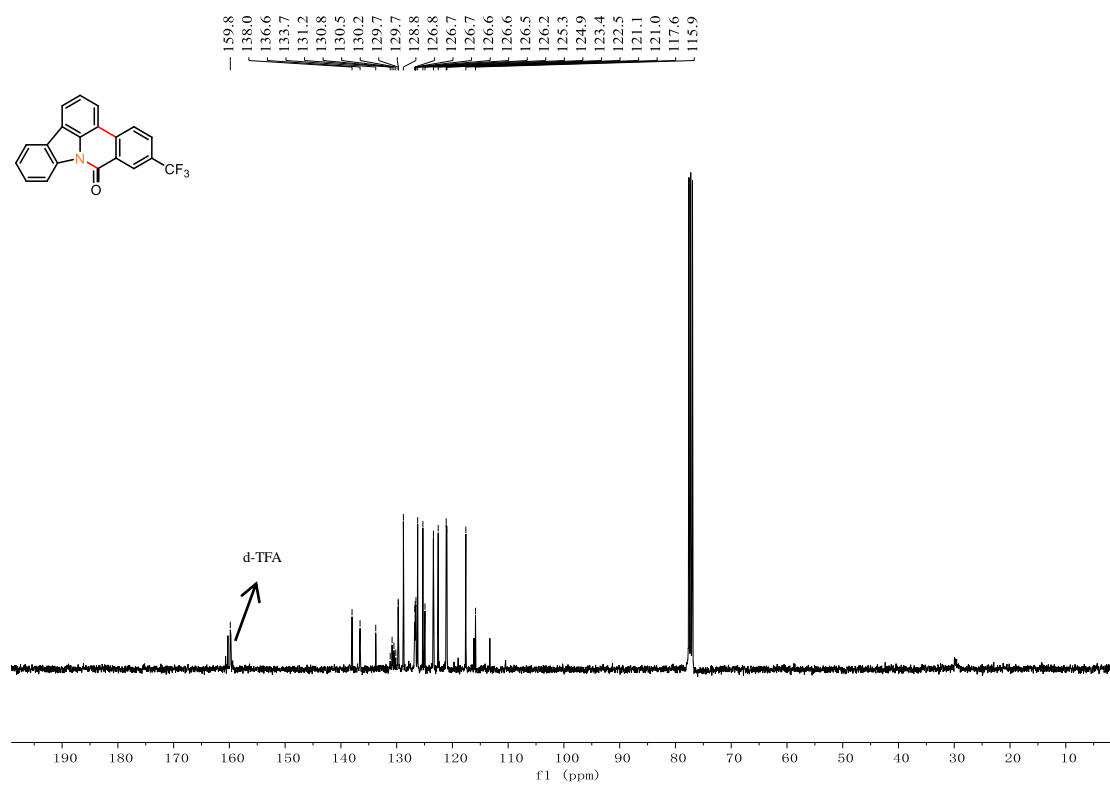
HRMS (ESI) m/z Calcd for $\text{C}_{19}\text{H}_{11}\text{FNO}$ $[\text{M}+\text{H}]^+$ 288.0819, found 288.0822.



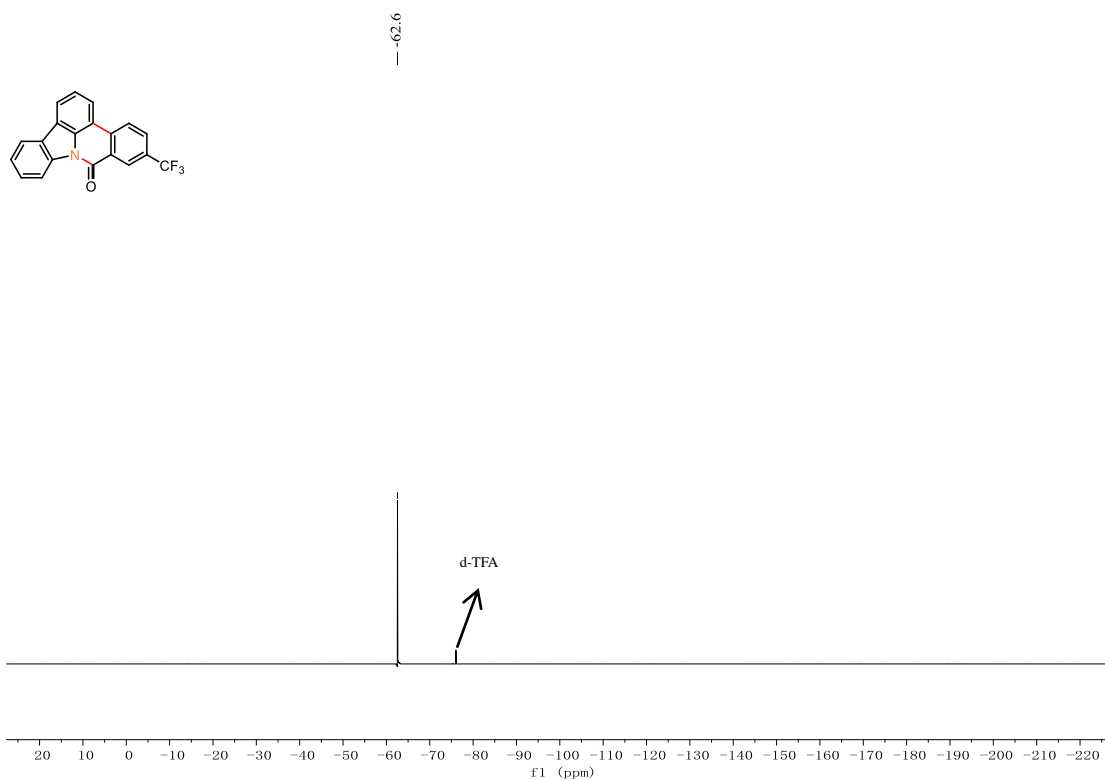
¹H NMR of **3p** (400 MHz, CDCl₃ + CF₃COOD)



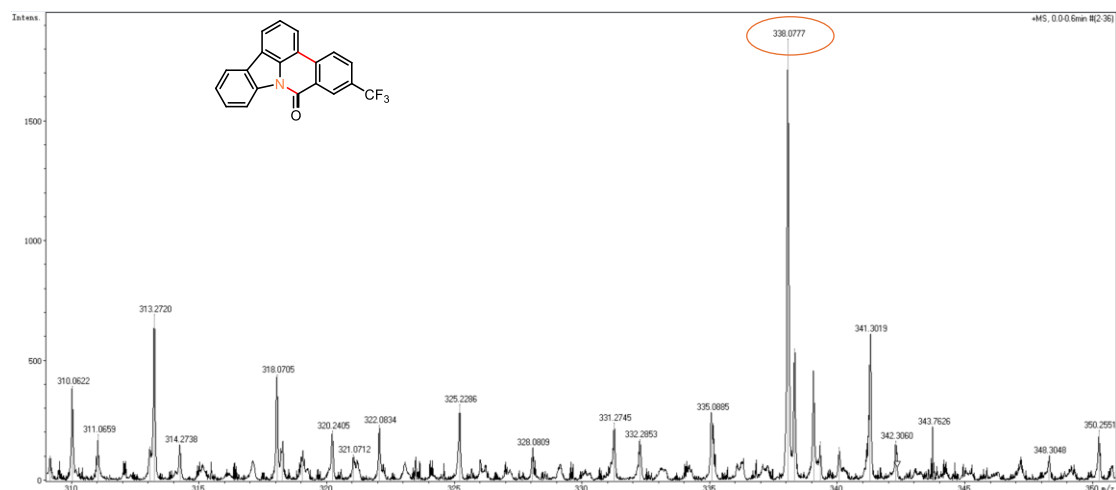
¹³C NMR of **3p** (100 MHz, CDCl₃ + CF₃COOD)



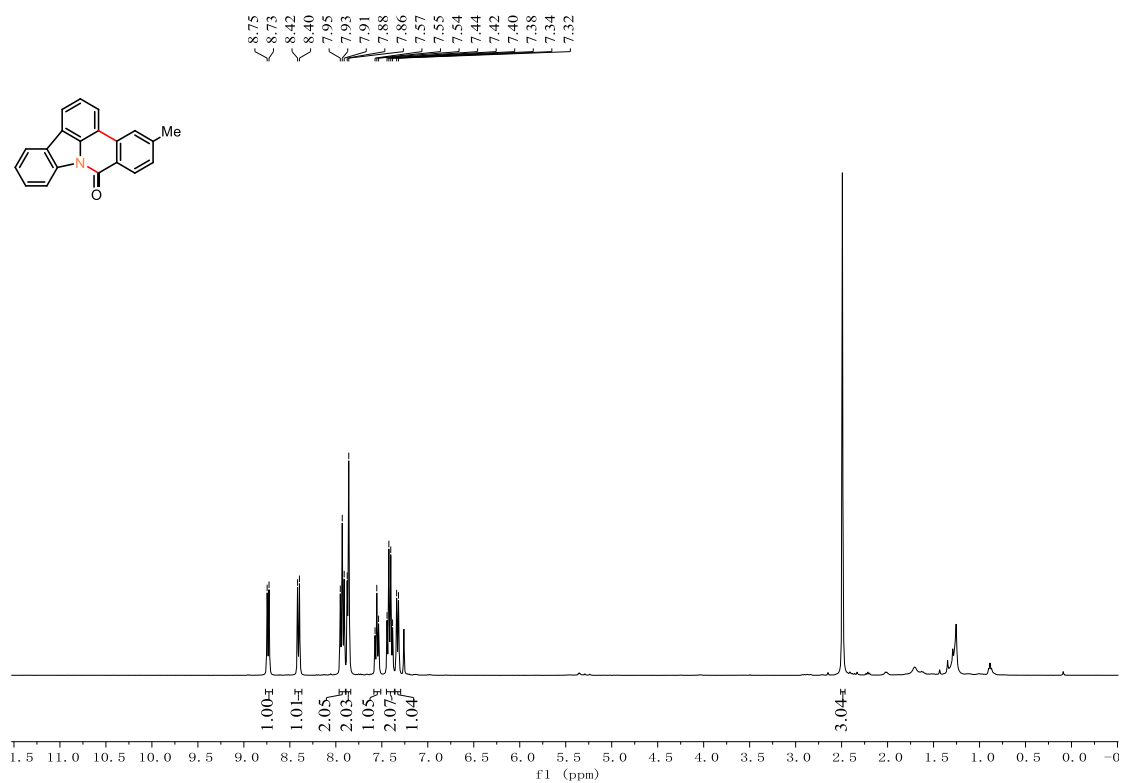
^{19}F NMR of **3p** (376 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$)



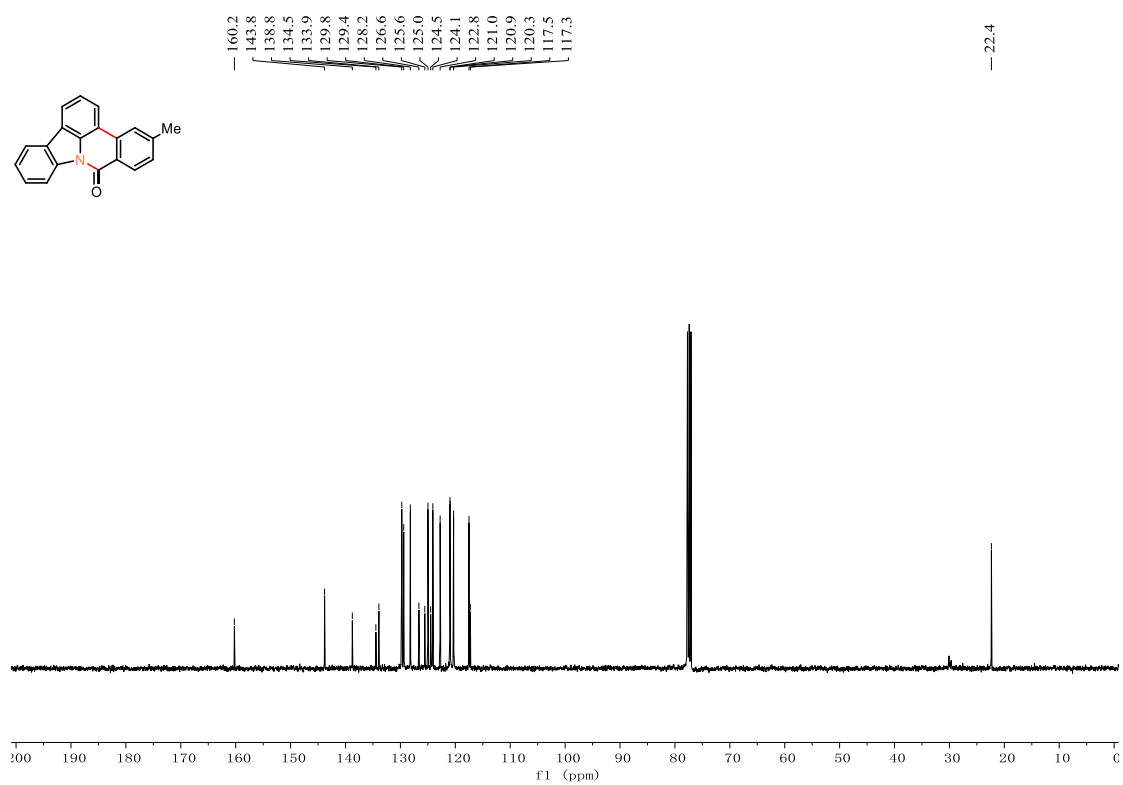
HRMS (ESI) m/z Calcd for $\text{C}_{20}\text{H}_{11}\text{F}_3\text{NO}$ $[\text{M}+\text{H}]^+$ 338.0787, found 338.0777.



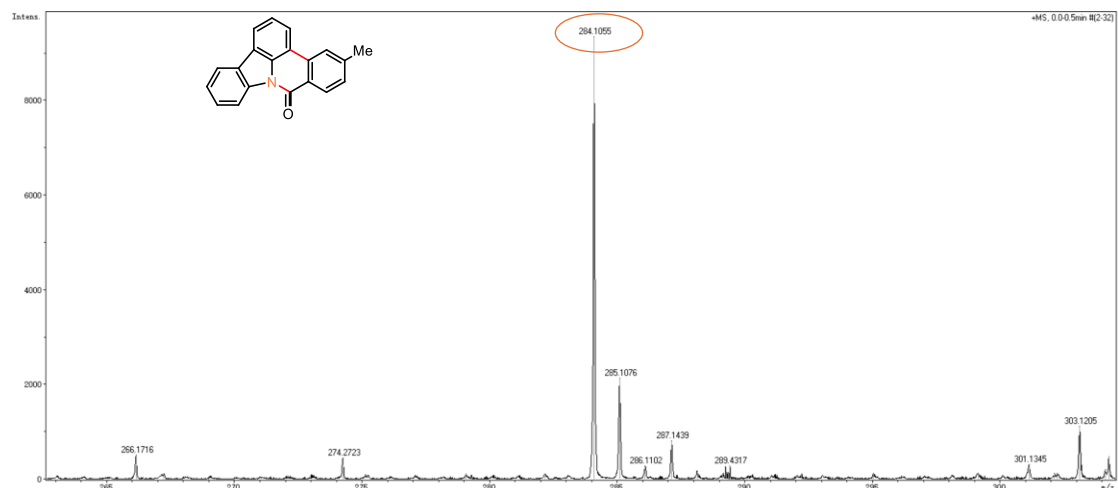
¹H NMR of **3q** (400 MHz, CDCl₃)



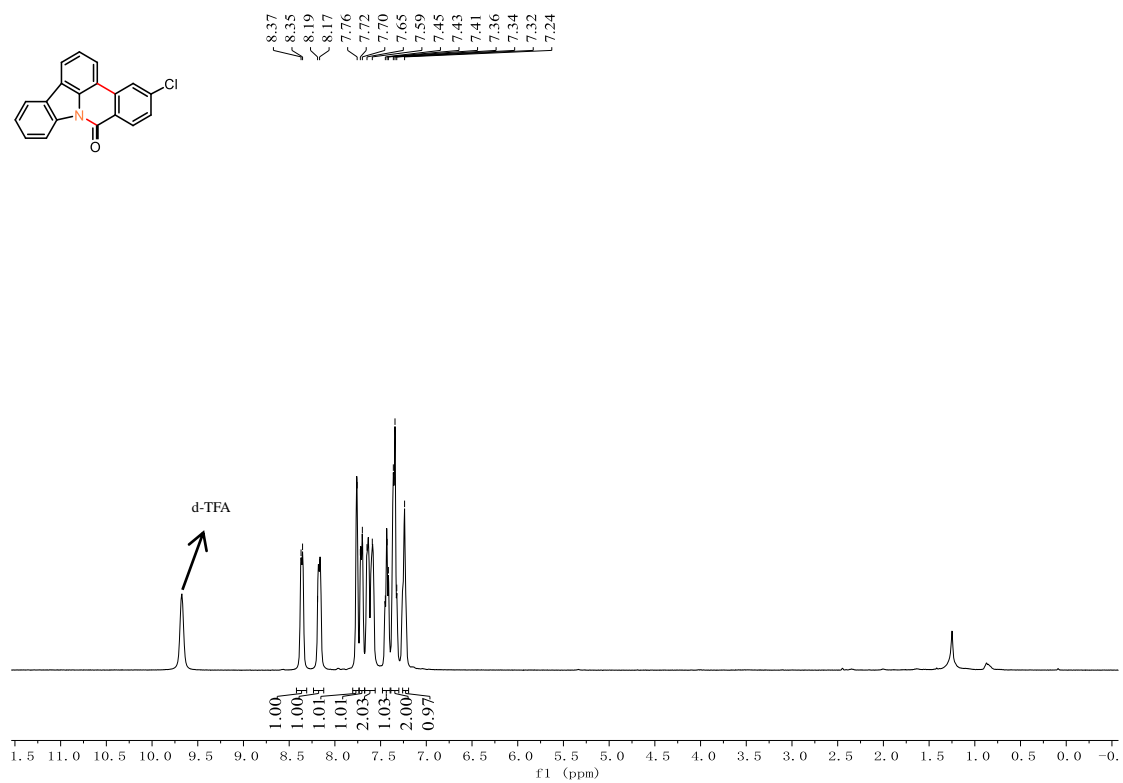
¹³C NMR of **3q** (100 MHz, CDCl₃)



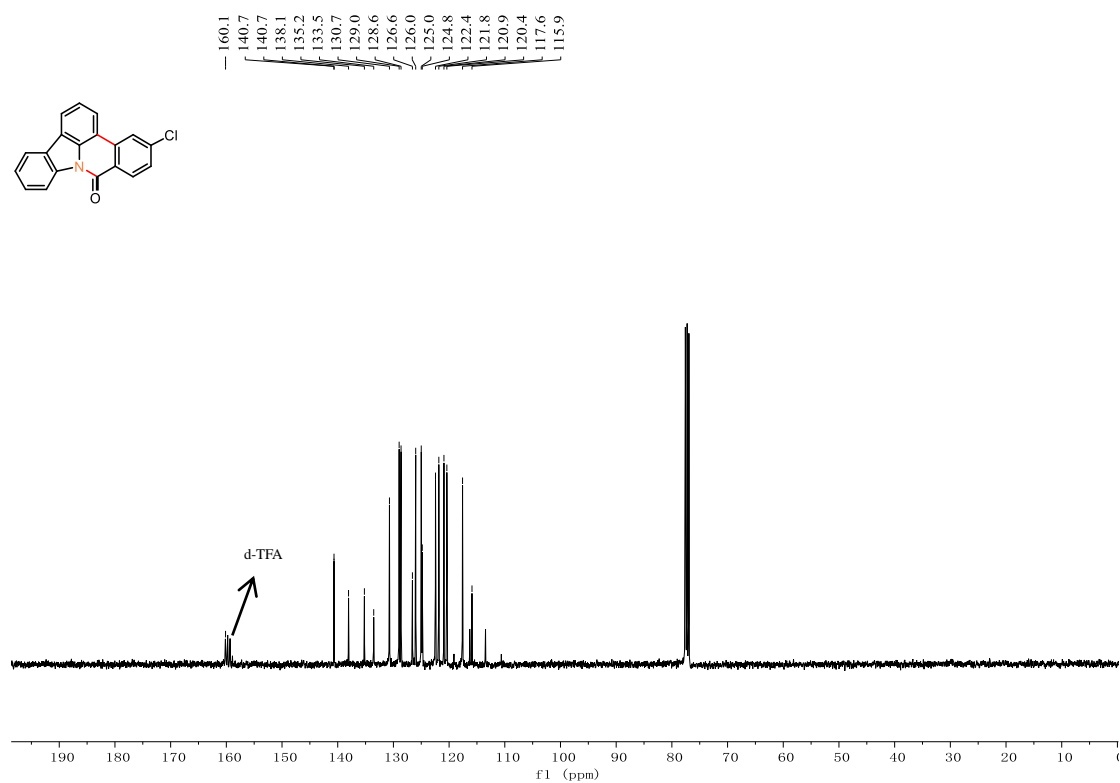
HRMS (ESI) m/z Calcd for $C_{20}H_{14}NO$ $[M+H]^+$ 284.1070, found 284.1055.



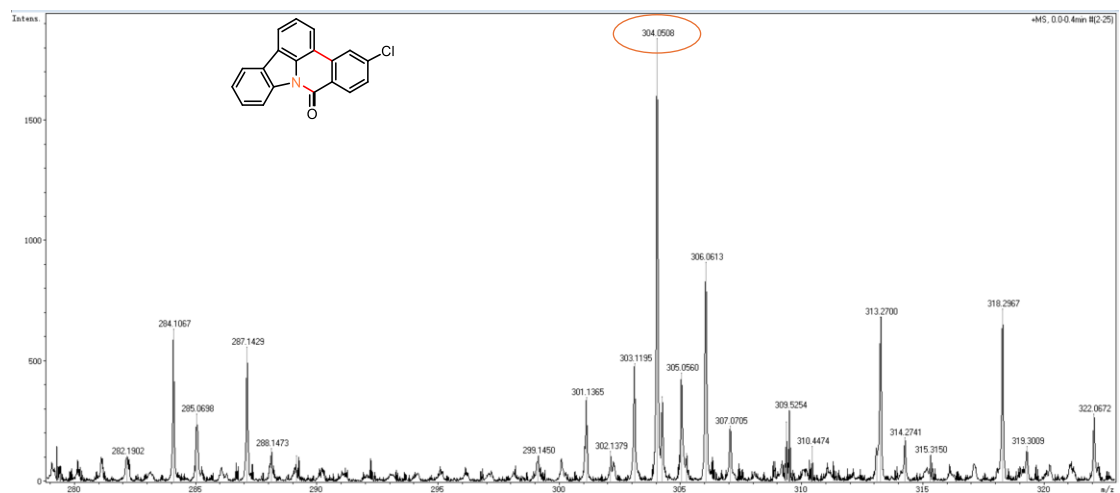
1H NMR of **3r** (400 MHz, $CDCl_3 + CF_3COOD$)



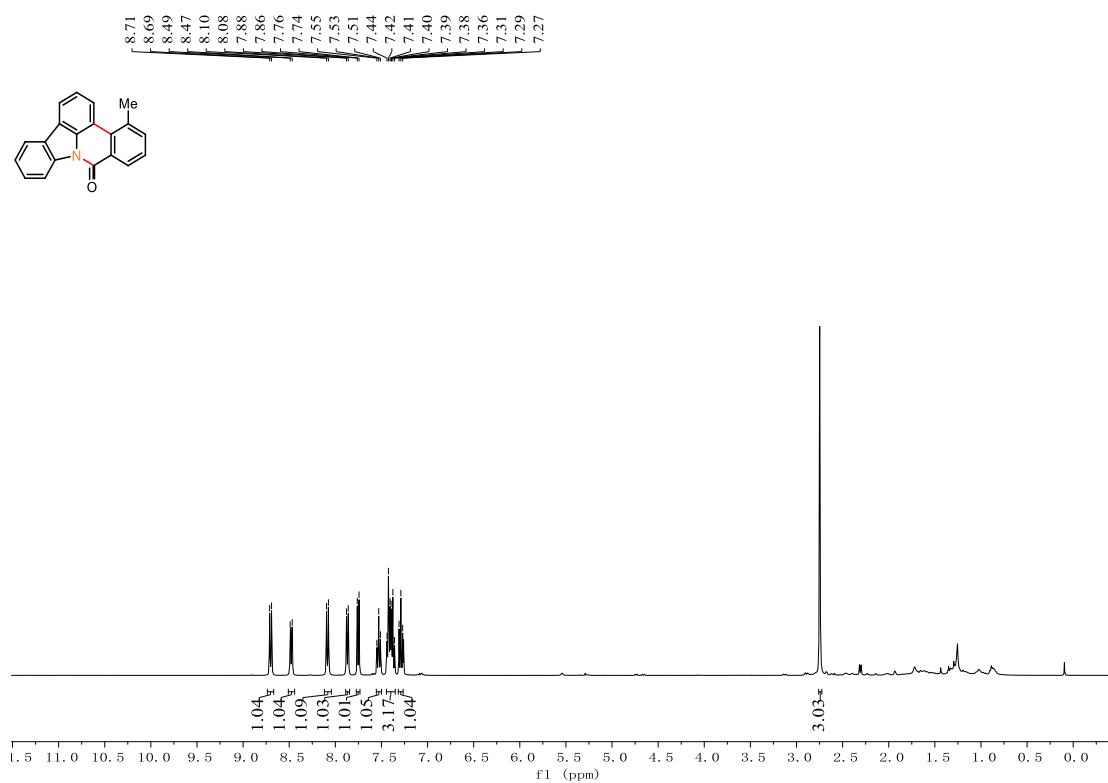
^{13}C NMR of **3r** (100 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$)



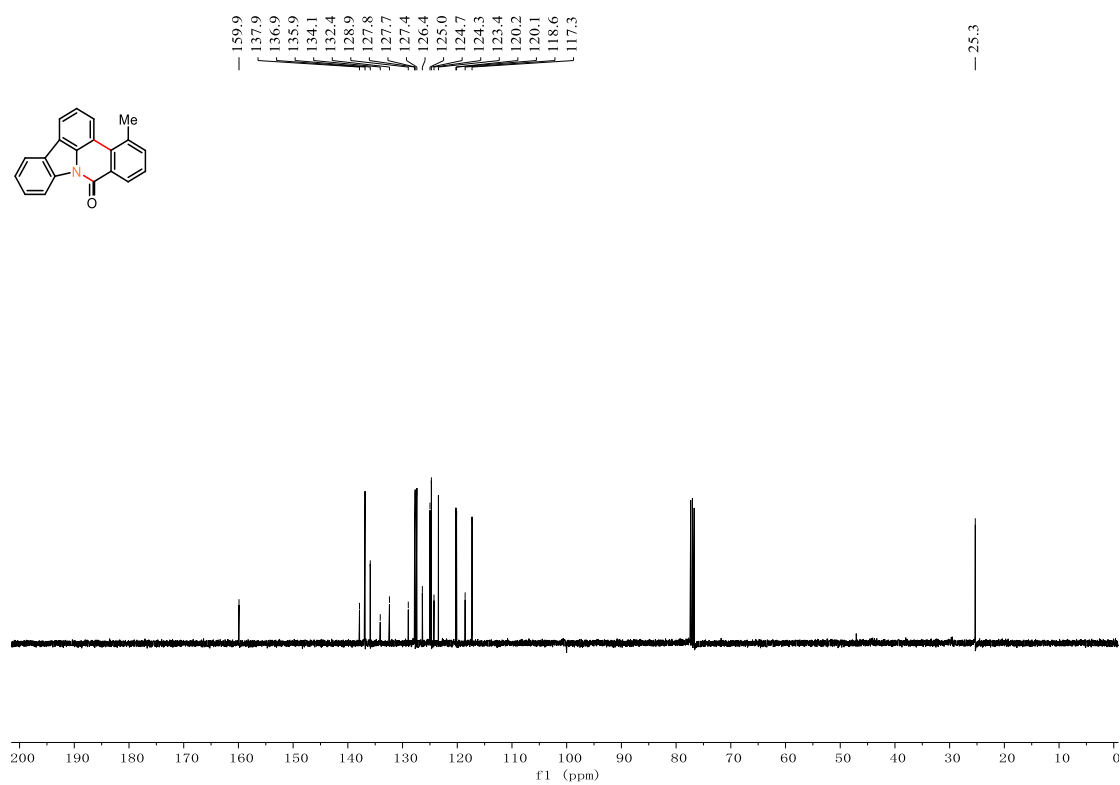
HRMS (ESI) m/z Calcd for $\text{C}_{19}\text{H}_{11}\text{ClNO}$ $[\text{M}+\text{H}]^+$ 304.0524, found 304.0508.



¹H NMR of **3s** (400 MHz, CDCl₃)



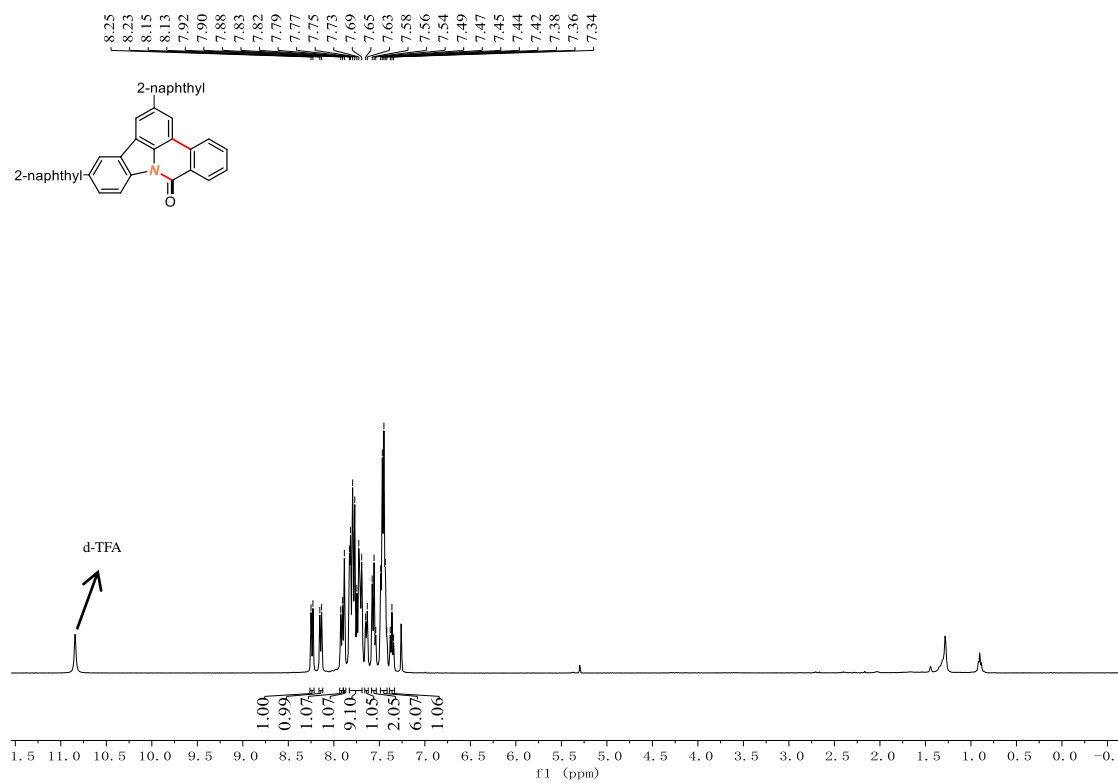
¹³C NMR of **3s** (100 MHz, CDCl₃)



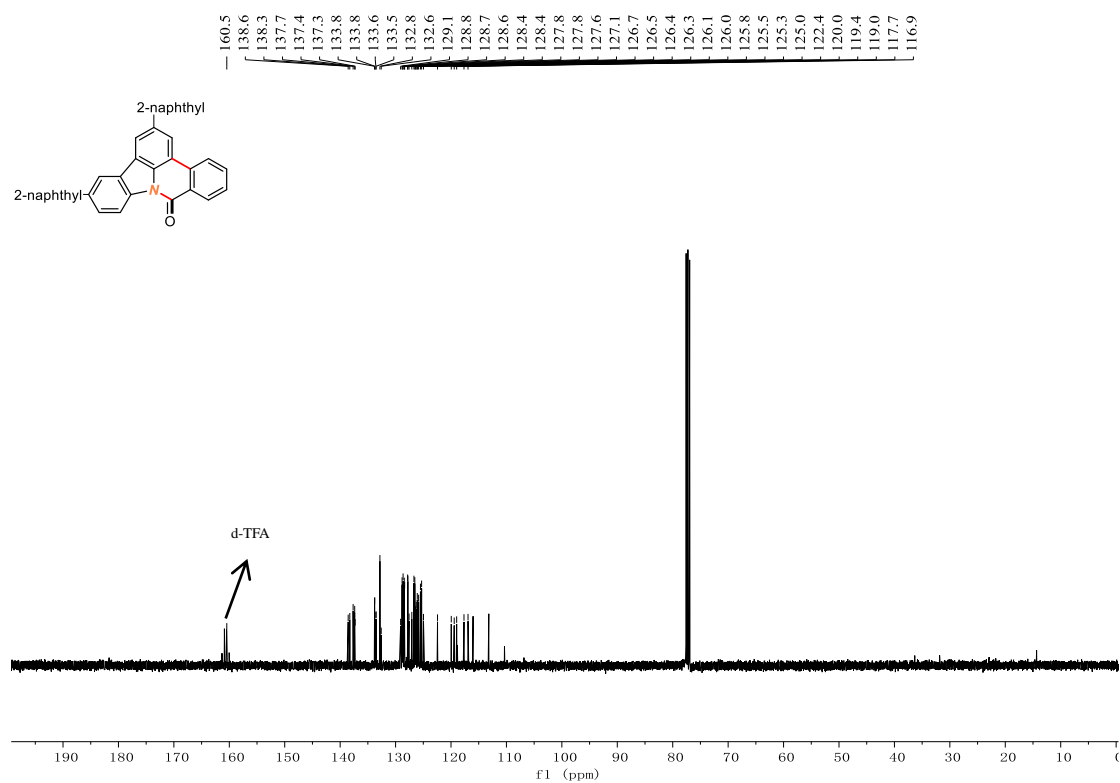
HRMS (ESI) m/z Calcd for $C_{20}H_{14}NO$ $[M+H]^+$ 284.1070, found 284.1055.



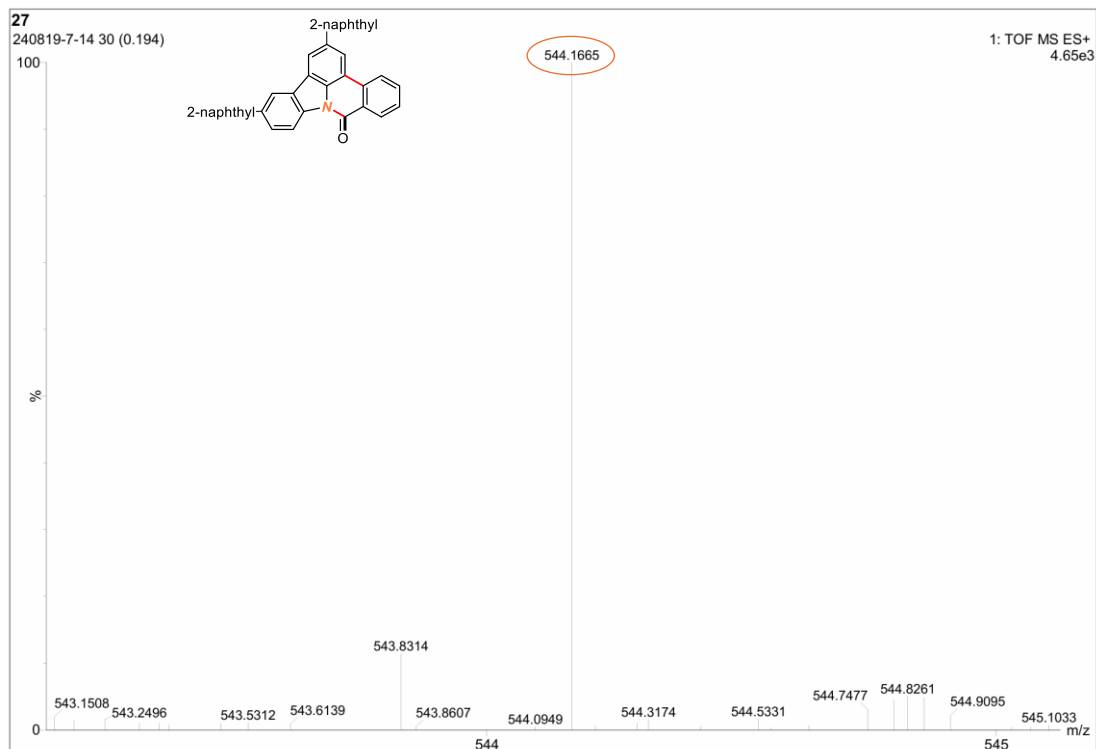
1H NMR of **3t** (400 MHz, $CDCl_3 + CF_3COOD$)



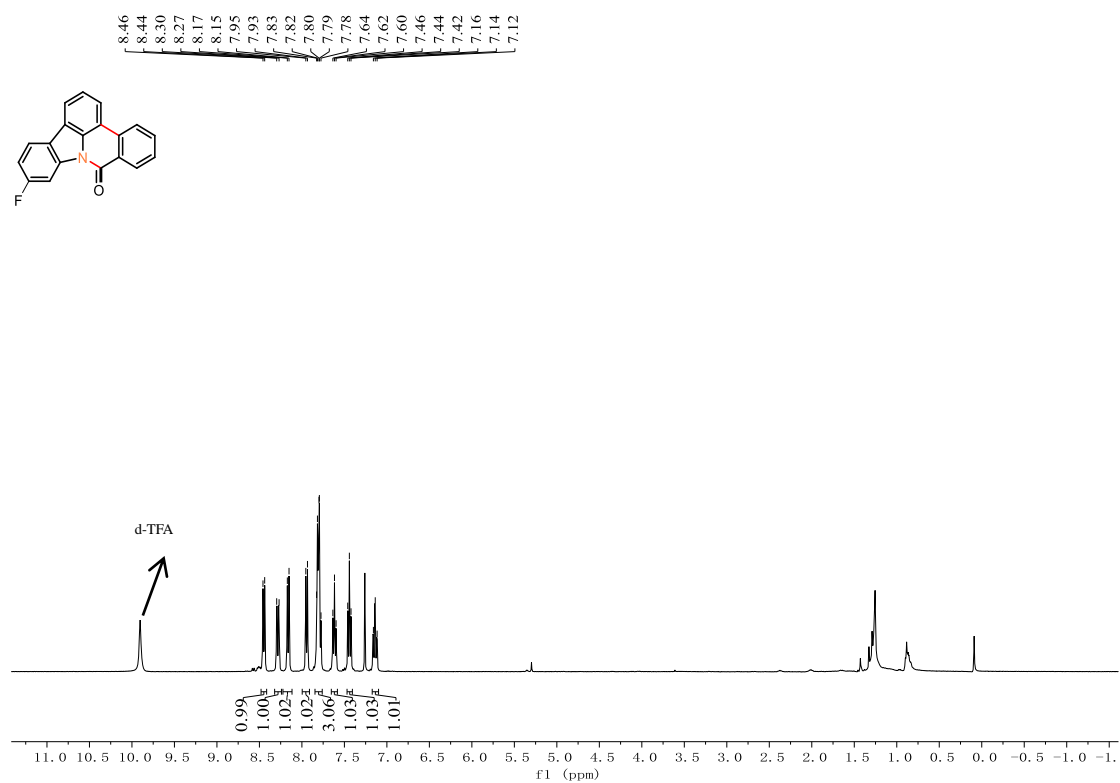
^{13}C NMR of **3t** (100 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$)



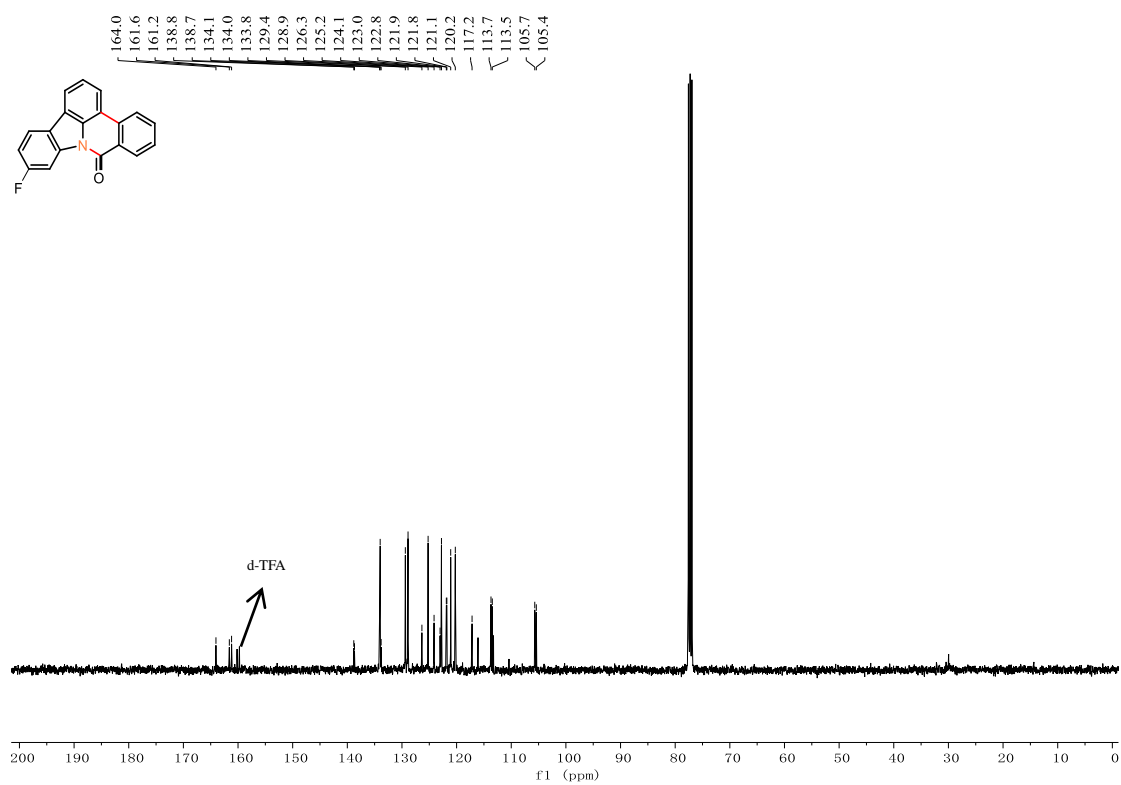
HRMS (ESI) m/z Calcd for $\text{C}_{39}\text{H}_{23}\text{NO}$ $[\text{M}+\text{Na}]^+$ 544.1672, found 544.1665.



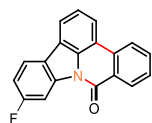
¹H NMR of **3u** (400 MHz, CDCl₃ + CF₃COOD)



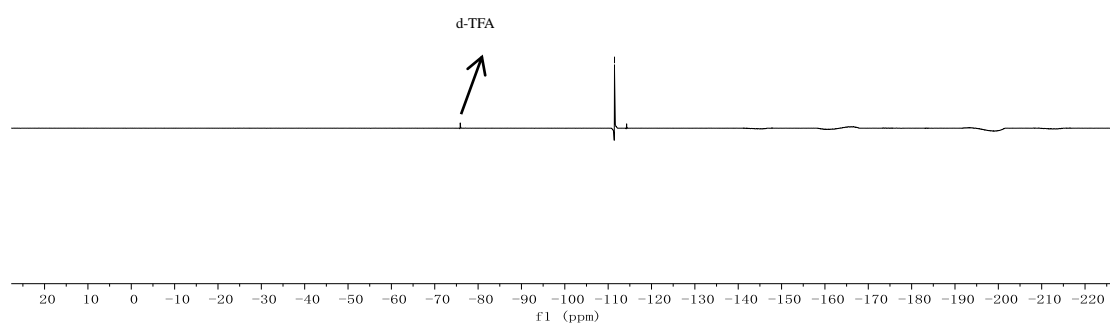
¹³C NMR of **3u** (100 MHz, CDCl₃ + CF₃COOD)



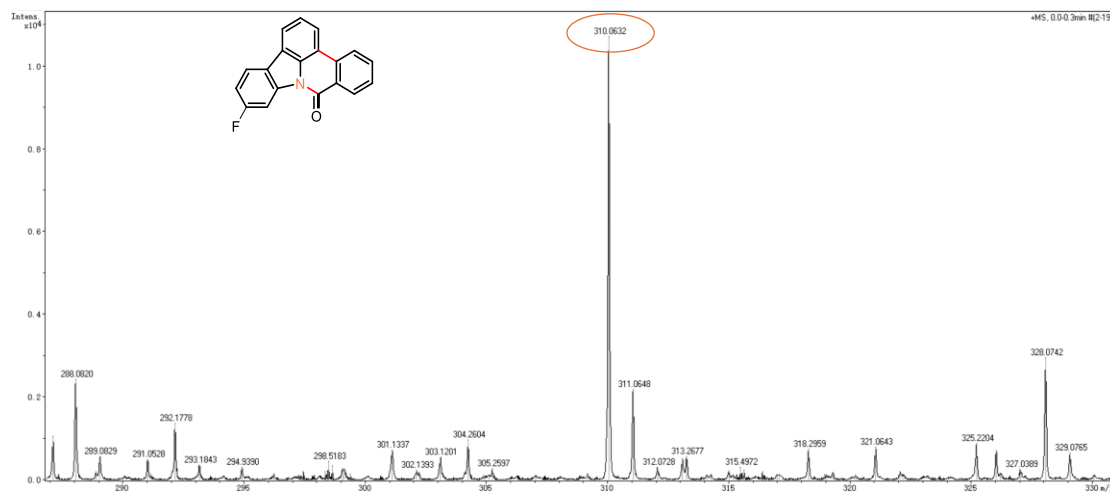
^{19}F NMR of **3u** (376 MHz, $\text{CDCl}_3 + \text{CF}_3\text{COOD}$)



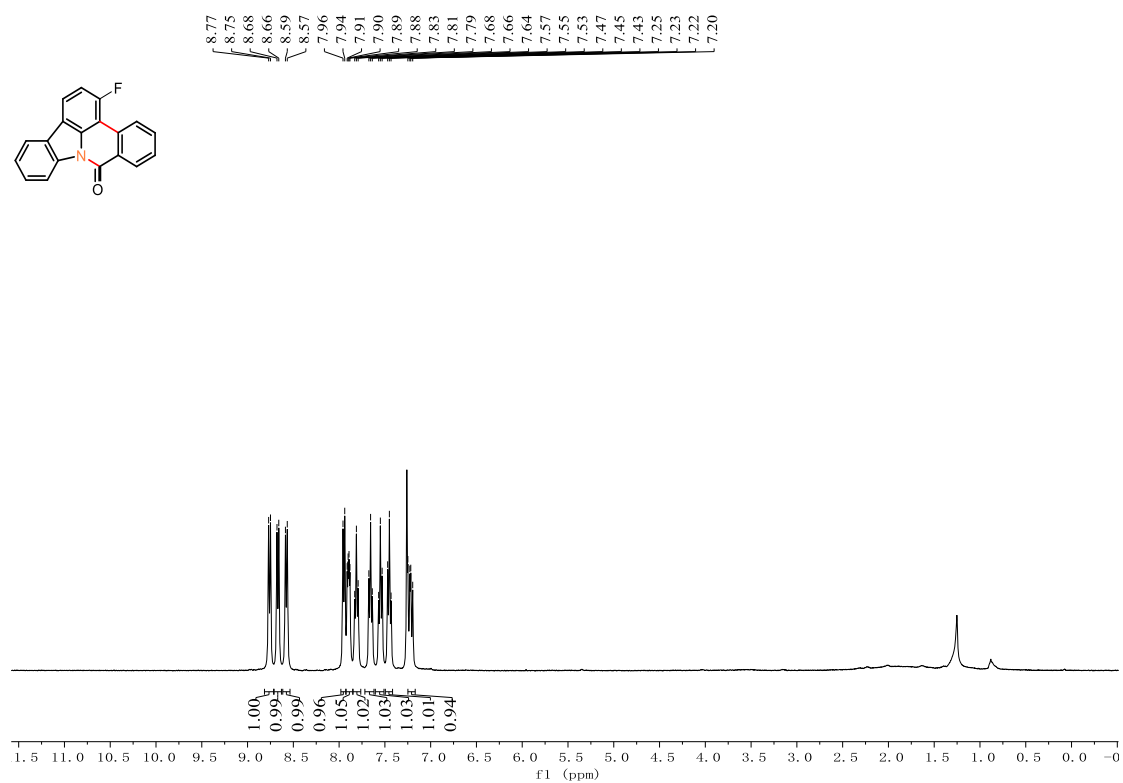
-111.5



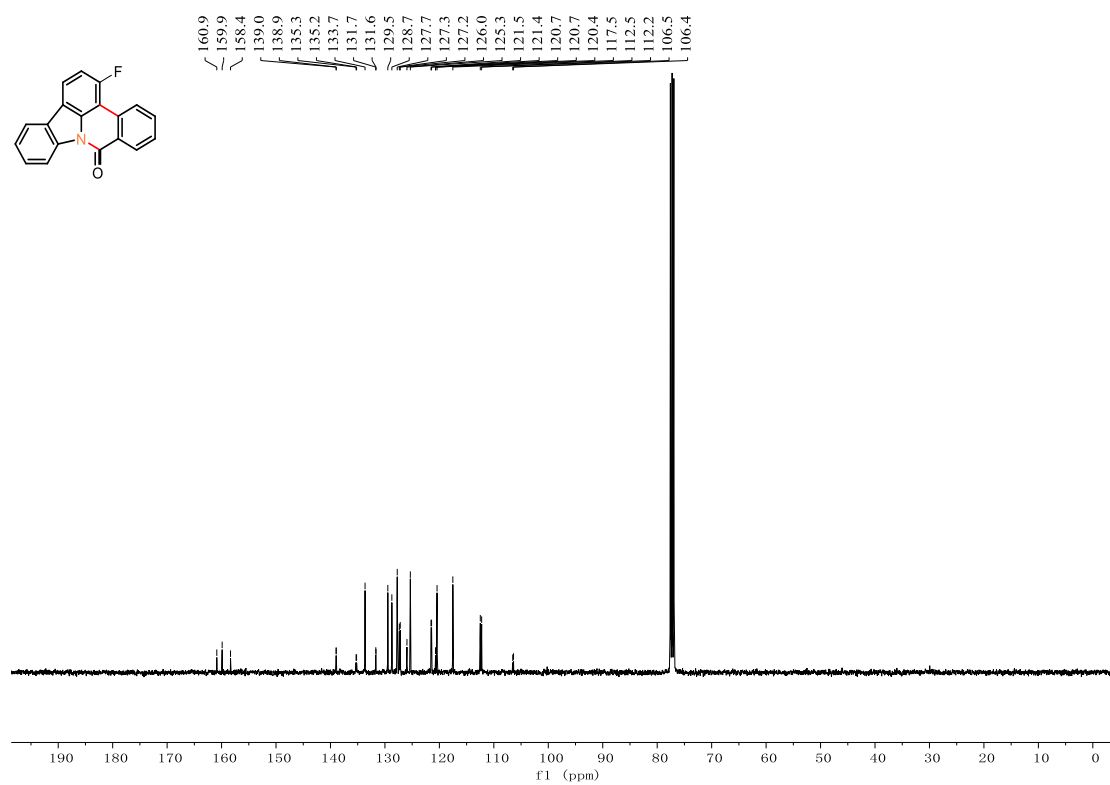
HRMS (ESI) m/z Calcd for $\text{C}_{19}\text{H}_{11}\text{FNO}$ $[\text{M}+\text{Na}]^+$ 310.0639, found 310.0632.



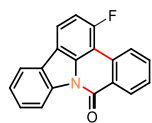
¹H NMR of **3u'** (400 MHz, CDCl₃)



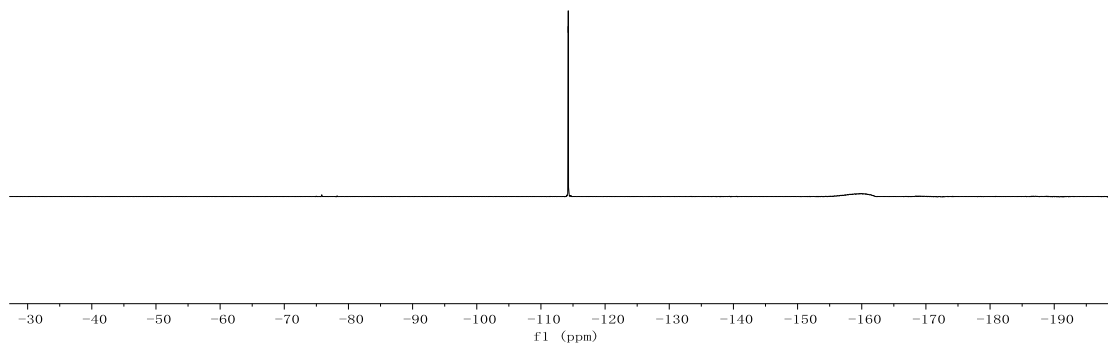
¹³C NMR of **3u'** (100 MHz, CDCl₃)



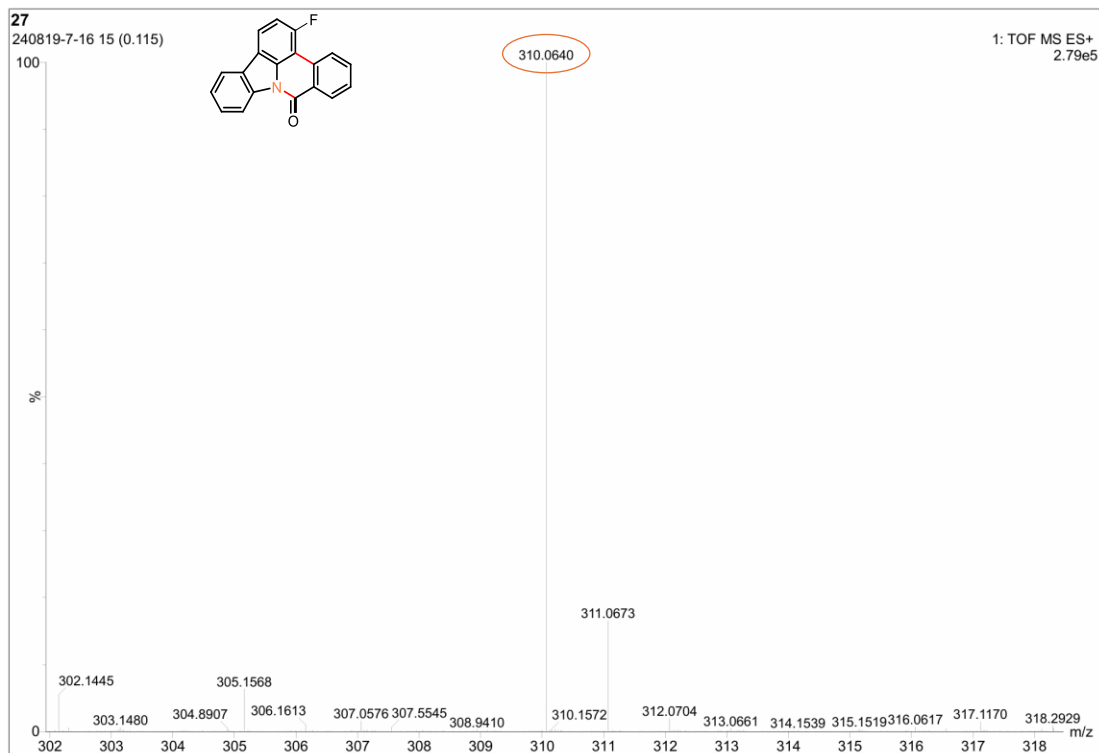
^{19}F NMR of **3u'** (376 MHz, CDCl_3)



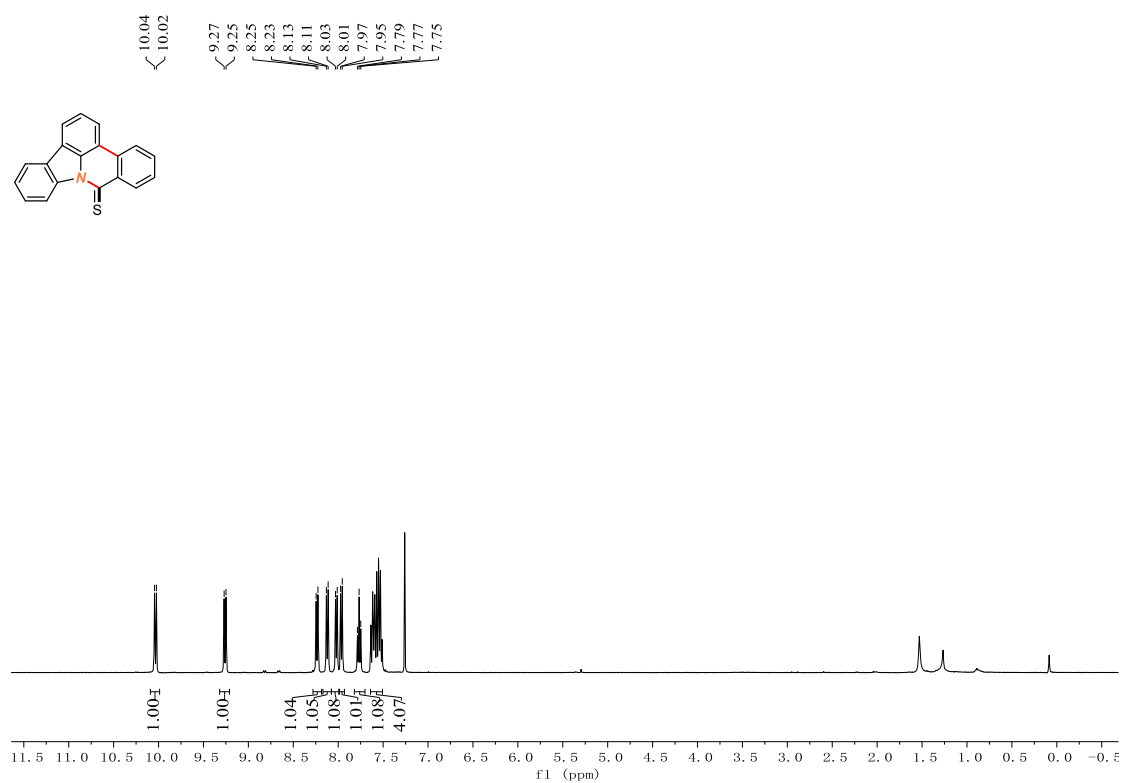
-114.2



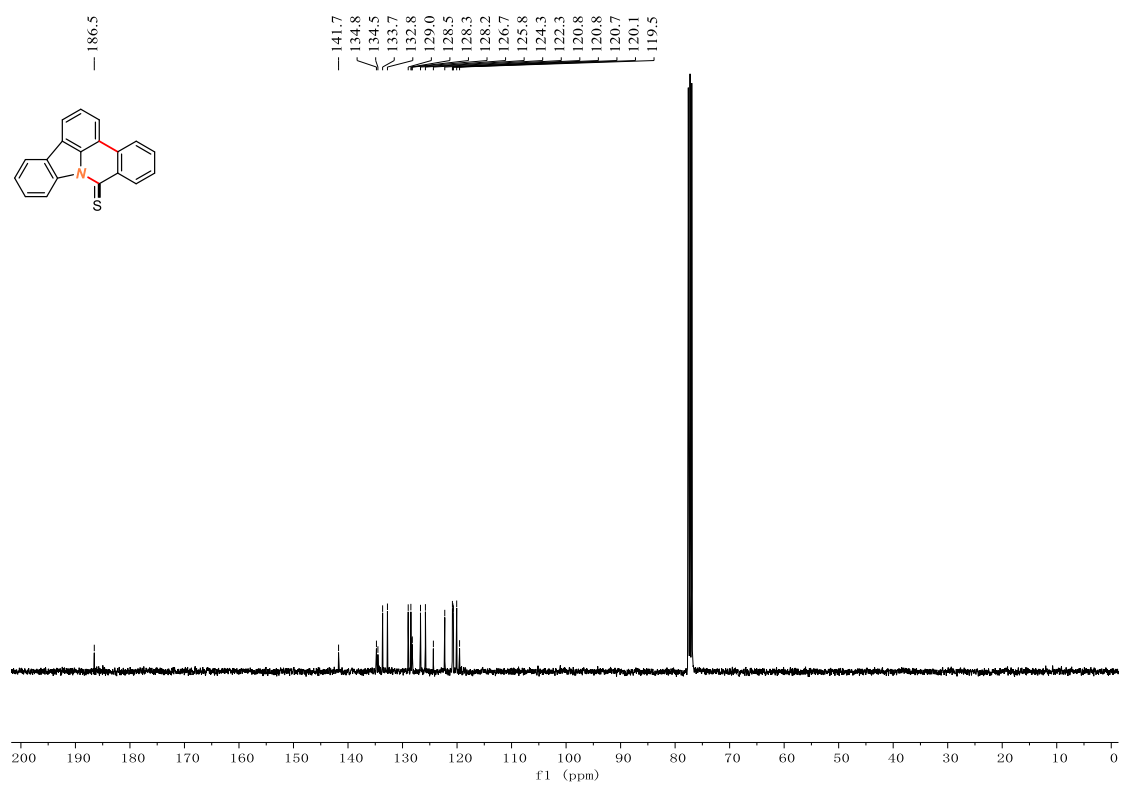
HRMS (ESI) m/z Calcd for $\text{C}_{19}\text{H}_{11}\text{FNO}$ $[\text{M}+\text{Na}]^+$ 310.0639, found 310.0640.



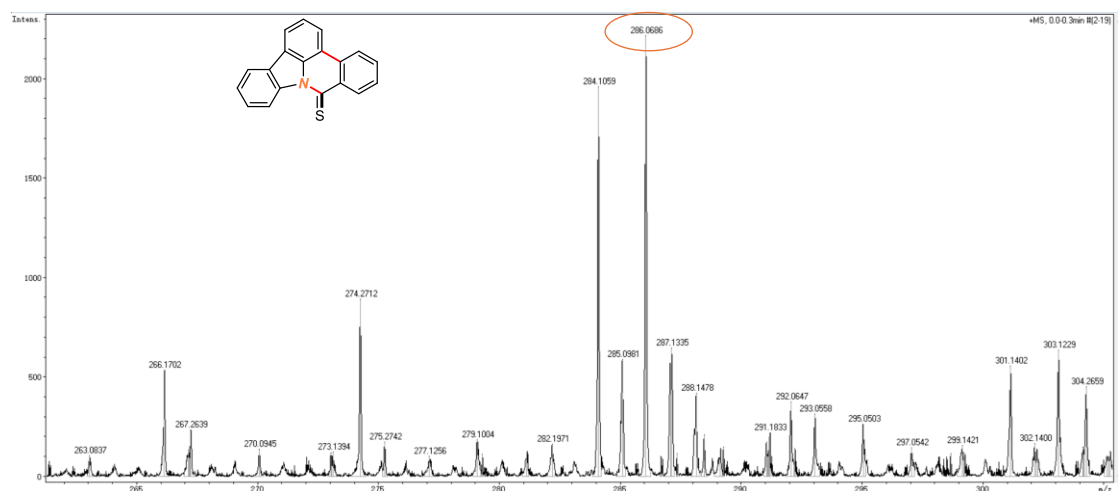
¹H NMR of **4** (400 MHz, CDCl₃)



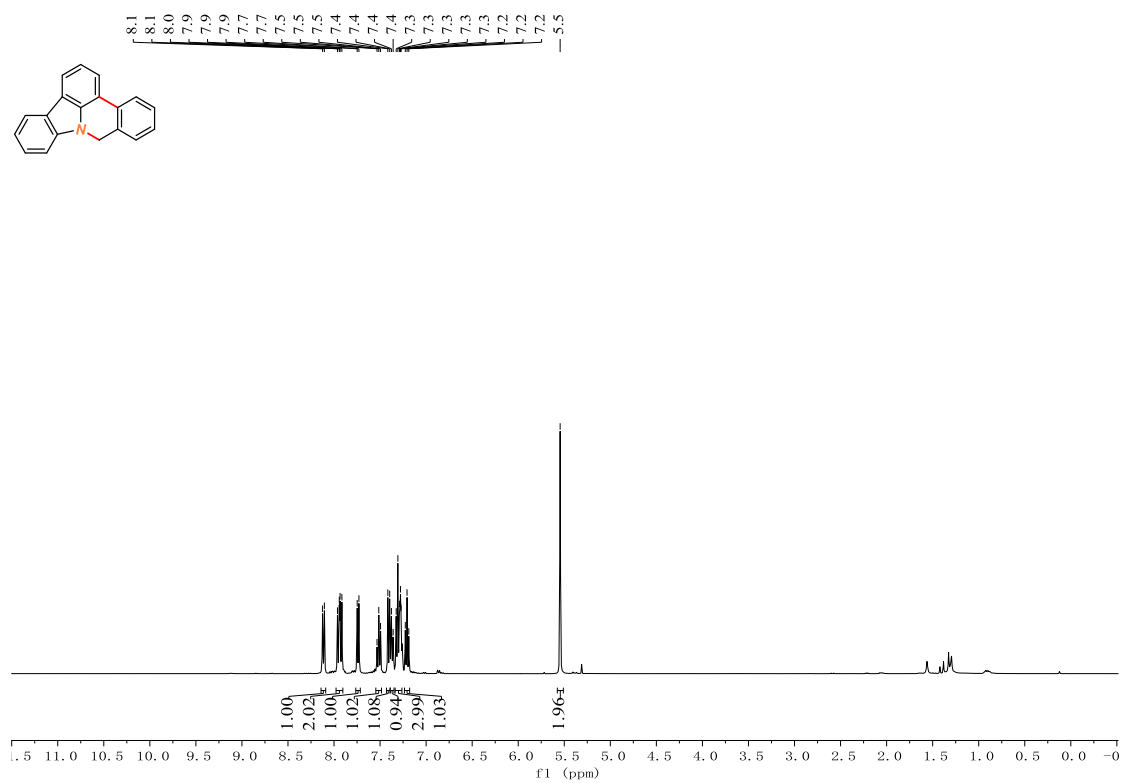
¹³C NMR of **4** (100 MHz, CDCl₃)



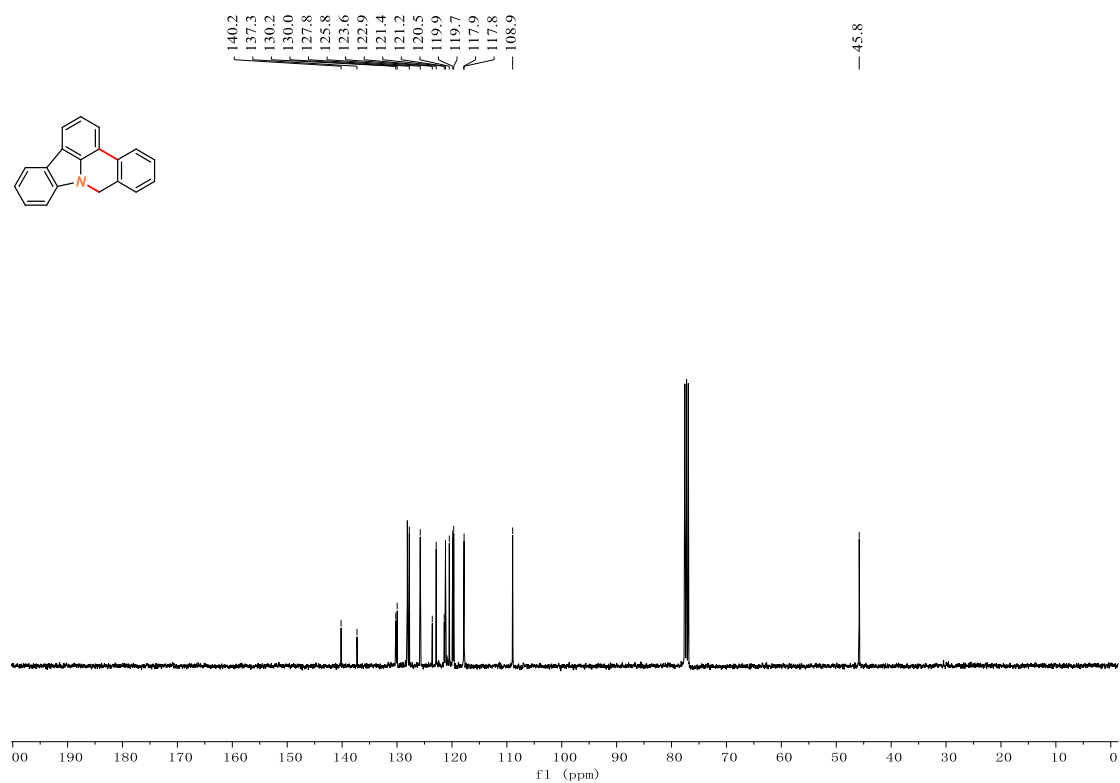
HRMS (ESI) m/z Calcd for C₁₉H₁₂NS [M+H]⁺ 286.0685, found 286.0686.



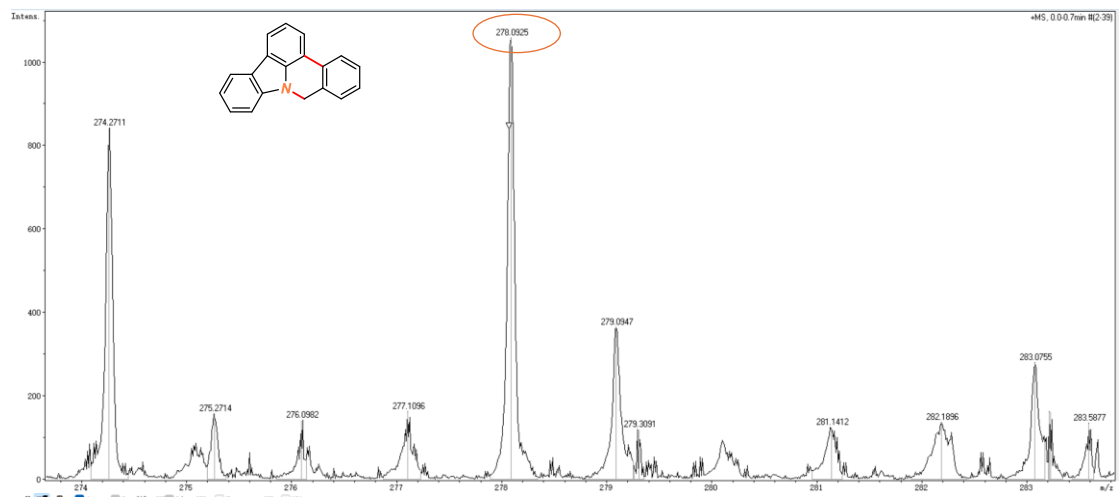
¹H NMR of **5** (400 MHz, CDCl₃)



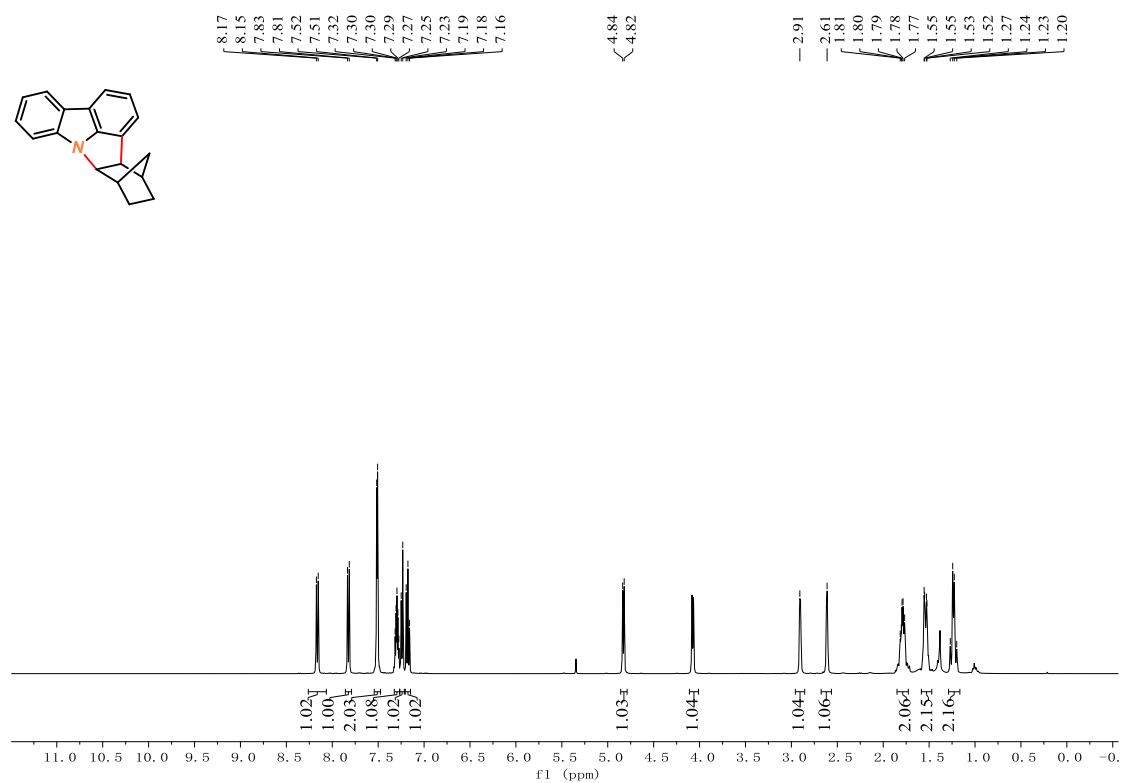
^{13}C NMR of **5** (100 MHz, CDCl_3)



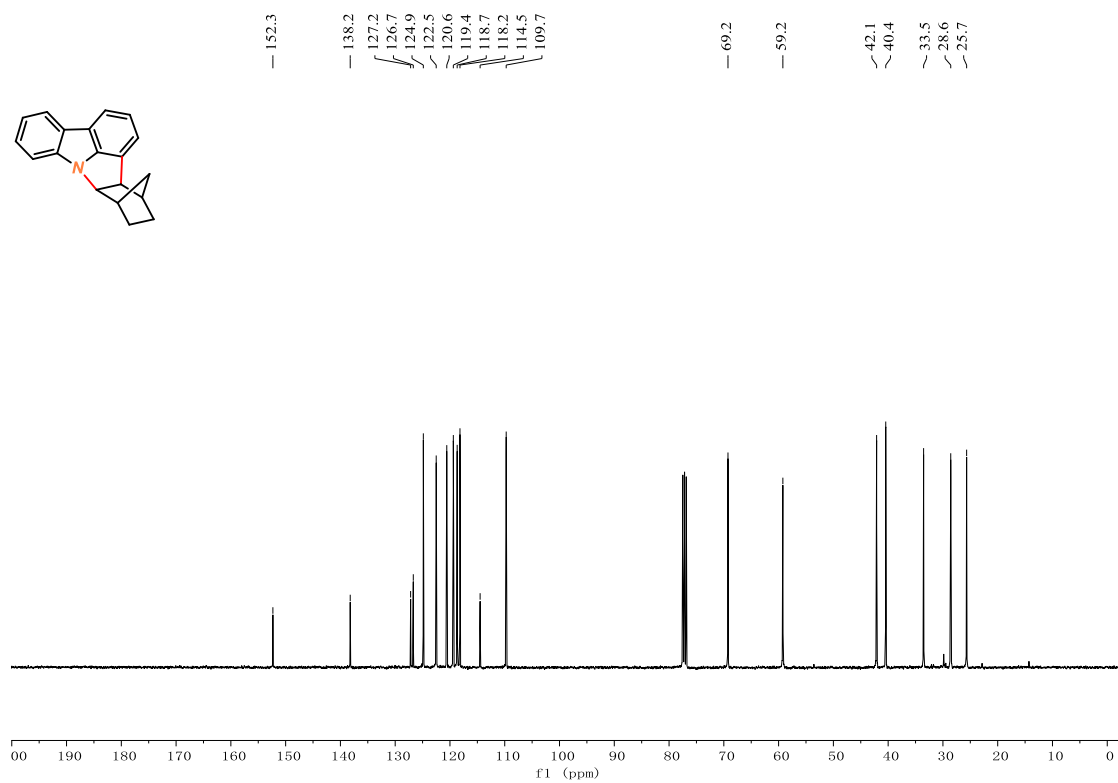
HRMS (ESI) m/z Calcd for $\text{C}_{19}\text{H}_{14}\text{N}$ $[\text{M}+\text{Na}]^+$ 278.0940, found 278.0925.



¹H NMR of 7 (400 MHz, CDCl₃)



¹³C NMR of 7 (100 MHz, CDCl₃)



9. References

- [1] M. Holzapfel, C. Lambert, *J. Phys. Chem. C.*, **2008**, *112*, 1227.
- [2] N. Miyaura, K. Yamada, A. Suzuki, *Tetrahedron Lett.*, **1979**, *20*, 3437.
- [3] L. Qiao, K. Zhang, H. J. Li, P. Lu, Y. G. Wang, *Tetrahedron Lett.*, **2022**, *91*, 153648.
- [4] P. Annamalai, H. C. Hisao, S. Raju, Y. H. Fu, P. L. Chen, J. C. Horng, Y. H. Li, S. C. Chuang, *Org. Lett.*, **2019**, *21*, 1182.