Supporting Information

Palladium-Catalyzed Domino Cyclization and C-H Amination of 1,7-Enynes Toward *N*-containing Fused Quinolin-2(1*H*)-ones

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Supporting Information Placeholder

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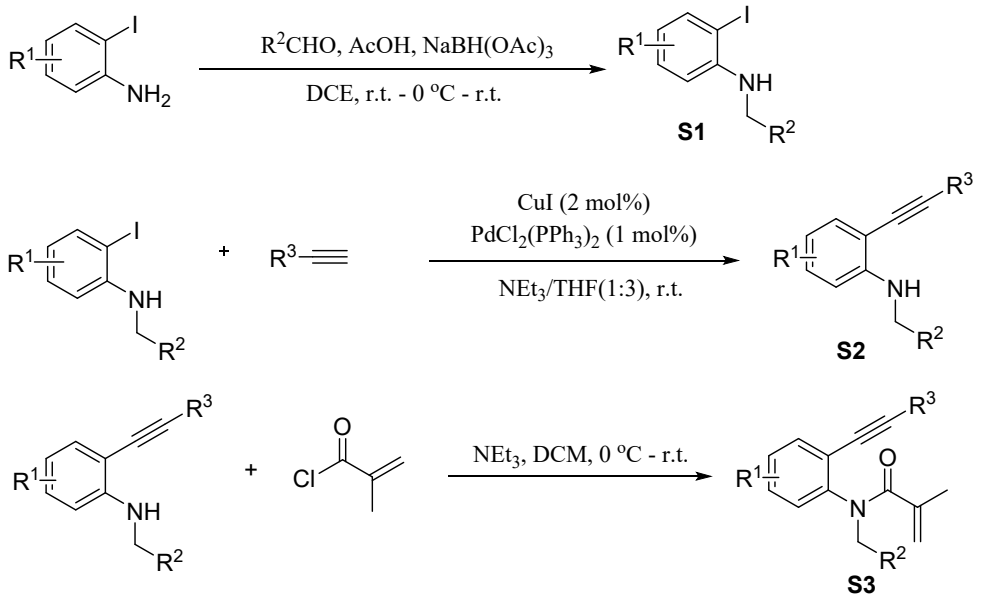
1. General experimental information

Unless otherwise noted, all reactions were carried out under nitrogen atmosphere. All commercially available reagents were used without further purification. All of the solvents were treated according to known methods. Column chromatography was performed on silica gel (200-400 mesh). ^{1}H NMR (400 MHz) chemical shifts were reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard. ^{13}C NMR (100 MHz) chemical shifts were reported in ppm (δ) from tetramethylsilane (TMS) with the solvent resonance as the internal standard and ^{19}F NMR at (377 MHz) chemical shifts were reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, qd = quartet of doublets, m = multiplet), coupling constants (Hz) and integration. HRMS measurements were obtained on a TOF analyzer.

2. General procedure for the synthesis of substrates[1,2,3]

1a-l, 1r-z, 1A-B (ref. 1)



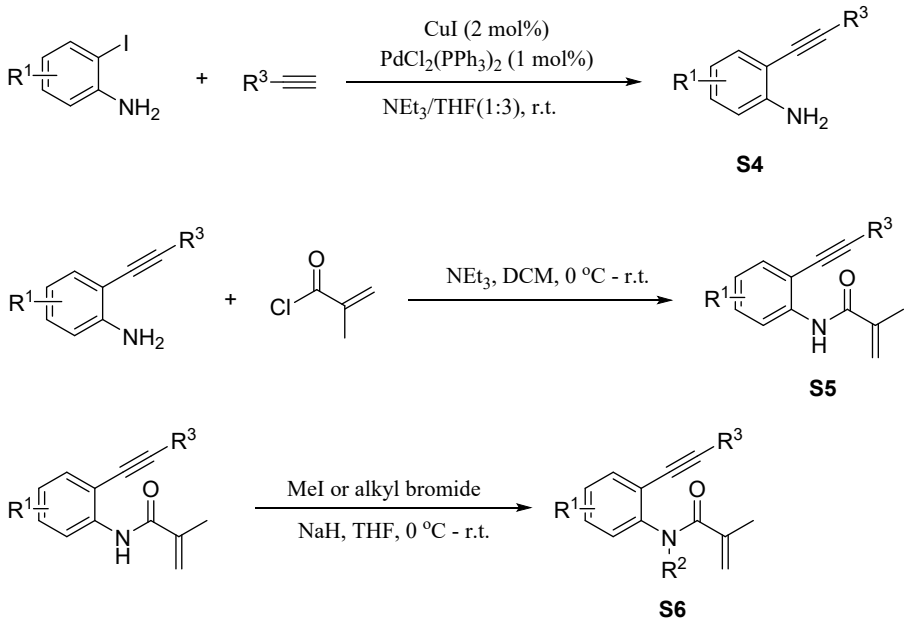
General procedure for synthesis of **S1**: To a 15 mL oven-dried tube charged with 2-iodoaniline (5.0 mmol, 1.0 equiv), aldehyde (6.0 mmol, 1.2 equiv) and dry 1,2-dichloroethane (8.0 mL) was added glacial acetic acid (30.0 μL, 0.5 mmol, 10 mol%) at room temperature. The reaction was stirred at room temperature for 1 h. Then $NaBH(OAc)_3$ (2.1 g, 10.0 mmol, 2.0 equiv) was added for portions at 0 °C. The mixture was allowed to stir at room temperature for 12 h. The resulting reaction mixture was cooled to 0 °C and water (2.0 mL) was added. The residue was extracted with ethyl acetate twice and the combined organic phase was dried over anhydrous Na_2SO_4, filtrated and concentrated. The resulting crude mixture was purified by flash chromatography using petroleum ether / ethyl acetate = 50:1 as eluent.

General procedure for synthesis of **S2**: To a suspension of $PdCl_2(PPh_3)_2$ (0.1 mmol, 1 mol%) and CuI (0.2 mmol, 2 mol%) in a mixture of THF (30.0 mL) and Et_3N (10.0 mL) was added **S1** (10.0 mmol) and alkyne (12.0 mmol, 1.2 equiv). The reaction was allowed to react at room temperature for 12 h. Then, the crude mixture was filtered through a shot pad of Celite and washed with CH_2Cl_2 (10.0 mL) for three times, and the combined organic layer was concentrated under reduced pressure. The resulting mixture was purified by flash chromatography using petroleum ether / ethyl acetate = 50:1 as eluent.

General procedure for the synthesis of substrates **S3**: To a stirred solution of **S2** (1.0 equiv) in

CH_2Cl_2 (5.0 mL) was added methacryloyl chloride (1.5 equiv) and Et_3N (2.0 equiv) at 0 °C. The resulted mixture was stirred at room temperature for 12 h. Then, the reaction was quenched by saturated $NaHCO_3$ solution and the reaction mixture was extracted with CH_2Cl_2 for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting crude mixture was purified by flash chromatography using petroleum ether / ethyl acetate = 10:1 as eluent.

1m-q (ref. 2)

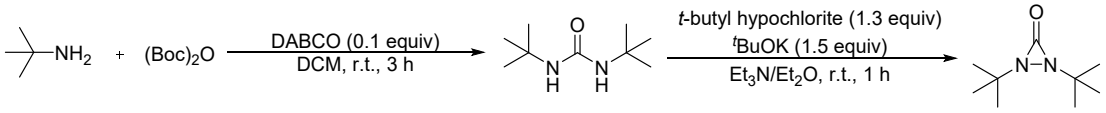


General procedure for synthesis of **S4**: To a suspension of $PdCl_2(PPh_3)_2$ (0.1 mmol, 1.0 mol%) and CuI (0.2 mmol, 2.0 mol%) in a mixture of THF (30.0 mL) and Et_3N (10.0 mL) was added 2-iodoaniline (10.0 mmol) and alkyne (12.0 mmol, 1.2 equiv). The reaction was allowed to react at room temperature for 12 h. Then, the crude mixture was filtered through a shot pad of Celite and washed with CH_2Cl_2 (10.0 mL) for three times, and the combined organic layer was concentrated under reduced pressure. The resulting mixture was purified by flash chromatography using petroleum ether / ethyl acetate = 50:1 as eluent.

General procedure for synthesis of **S5**: To a stirred solution of **S4** (1.0 equiv) in CH_2Cl_2 (5.0 mL) was added methacryloyl chloride (1.5 equiv) and Et_3N (2.0 equiv) at 0 °C. The resulted mixture was stirred at room temperature for 12 h. Then, the reaction was quenched by saturated $NaHCO_3$ solution and the reaction mixture was extracted with CH_2Cl_2 for three times. The combined organic

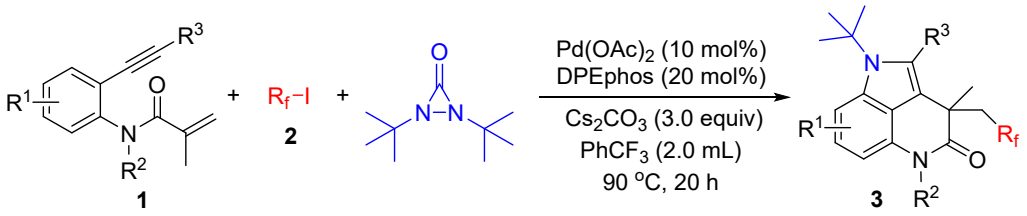
layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting crude mixture was purified by flash chromatography using petroleum ether / ethyl acetate = 20:1 as eluent.

General procedure for the synthesis of substrates **S6**: To a solution of NaH (2.0 equiv) in THF (5.0 mL) at 0 °C was added a solution of **S5** (1.0 equiv) in THF dropwise and the reaction mixture was stirred for 30 min. Then, iodomethane or alkyl bromide (1.5 equiv) was added and the reaction mixture was stirred at room temperature. Upon completion, the reaction was quenched by water and extracted with CH_2Cl_2 for three times. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 as eluent. **Di-*t*-butyldiaziridinone (ref. 3)**



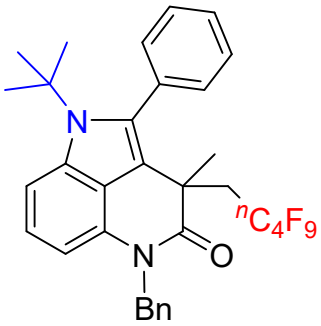
To a solution of *t*-butylamine (100 mmol, 2.0 equiv), DABCO (560 mg, 5 mmol, 0.1 equiv) in CH_2Cl_2 (50 mL) was added carefully $(Boc)_2O$ (11.5 mL, 50 mmol, 1.0 equiv). Then the solution was stirred at room temperature for 3 h. Then the reaction mixture was cooled to 0 °C and hexane was added. The resulting solid was collected and further washed with cold water and diethyl ether to afford the 1,3-di-*t*-butylurea as a white solid in 84% yield (7.2 g). Then *t*-butyl hypochlorite (5.6 g, 52 mmol, 1.3 equiv) was added dropwise by syringe to a viscous suspension of 1,3-di-*t*-butylurea (6.9 g, 40 mmol, 1.0 equiv) in dry ether (40 mL) with stirring at 0 °C. To the resulting clear pale yellow-green solution was added KO^{t}Bu (6.7 g, 60 mmol, 1.5 equiv) in small portions followed by 5 drops of triethylamine. The resulting mixture was stirred at room temperature for 1 h, then diluted with hexane (20 mL), washed with water (3 × 30 mL) and brine (20 mL), dried over Na_2SO_4, filtered and concentrated, cooled to 0 °C, then filtered again by filtering membrane to give di-*t*-butyldiaziridinone as colorless liquid in 74% yield (5.0 g).

3. General procedure for synthesis of fused quinolin-2(1*H*)-one products (3aa-za, 3ab-ac, 3Aa, 4a-e)

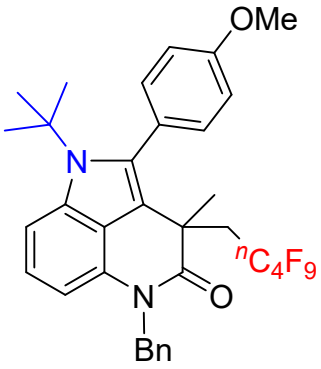


1,7-enyne **1** (0.2 mmol, 1.0 equiv), perfluoroalkyl iodide **2** (1.2 mmol, 6.0 equiv), $Pd(OAc)_2$ (4.5 mg, 10 mol%), DPEphos (21.5 mg, 20 mol%), Cs_2CO_3 (195.0 mg, 0.6 mmol, 3.0 equiv), and di-*t*-butyldiaziridinone (68.0 mg, 0.4 mmol, 2.0 equiv) were added to an oven-dried tube (15.0 mL) which was then placed under vacuum and refilled with nitrogen three times. $PhCF_3$ (2.0 mL) was added into the tube via syringe and the tube was sealed and stirred at 90 °C (oil bath) for 20 h. Upon the reaction was completed, the resulting mixture was purified by silica gel column using chromatography (petroleum ether / ethyl acetate = 30:1) to obtain products (**3aa-za, 3ab-ac, 3Aa, 4a-e**).

4. Characterization data of products (3aa-za, 3ab-ac, 3Aa, 4a-e, 3A, 5)[4]

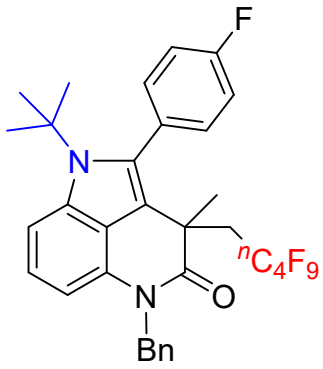


5-benzyl-1-(*tert*-butyl)-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-phenyl-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3aa). The product was purified by column chromatography (petroleum ether / ethyl acetate = 30:1); White solid, 89.6 mg, 70% yield; mp 144.6-145.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 7.4 Hz, 1H), 7.47 – 7.35 (m, 4H), 7.36 – 7.25 (m, 5H), 7.22 (d, J = 7.2 Hz, 1H), 7.01 (t, J = 8.0 Hz, 1H), 6.47 (d, J = 7.5 Hz, 1H), 5.23 (s, 2H), 3.09 – 2.94 (m, 1H), 2.21 – 2.05 (m, 1H), 1.53 (s, 9H), 1.46 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.7, 137.3, 136.1, 135.3, 134.2, 133.0, 132.7, 132.0, 129.0, 128.7, 127.8, 127.6, 127.1, 127.0, 122.5, 115.2, 112.3, 110.3, 102.4, 60.0, 46.3, 42.8, 39.9 – 39.5 (m), 32.1, 30.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ -80.98 (s, 3F), -109.61 – -111.13 (m, 1F), -111.82 – -112.89 (m, 1F), -124.46 – -125.08 (m, 2F), -125.60 – -126.34 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{33}H_{29}F_9N_2ONa^+$: 663.2028; found: 663.2037.

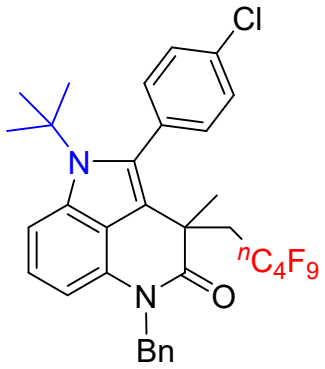


5-benzyl-1-(*tert*-butyl)-2-(4-methoxyphenyl)-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3ba). The product was purified by column chromatography (petroleum ether / ethyl acetate = 30:1); Yellow oil, 77.7 mg, 58% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 6.5 Hz, 1H), 7.36 – 7.28 (m, 3H), 7.28 (dd, J = 6.0, 2.1 Hz, 2H), 7.25 (d, J = 2.9 Hz, 1H), 7.25 – 7.17 (m, 1H), 7.02 – 6.98 (m, 1H), 6.96 – 6.91 (m, 2H), 6.46 (d, J

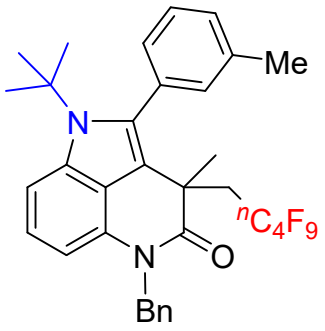
= 7.6 Hz, 1H), 5.23 (d, J = 3.9 Hz, 2H), 3.89 (s, 3H), 3.11 – 2.95 (m, 1H), 2.25 – 2.10 (m, 1H), 1.54 (s, 9H), 1.49 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.8, 160.1, 137.4, 135.3, 134.1, 133.1, 132.6, 128.7, 127.9, 127.1, 127.0, 122.3, 115.2, 113.2, 113.1, 112.4, 110.2, 102.3, 59.9, 55.4, 46.3, 42.8, 39.7 (t, J = 18.2 Hz), 32.2, 30.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.51 (t, J = 9.6 Hz, 3F), -110.48 – -111.48 (m, 1F), -112.46 – -113.40 (m, 1F), -125.22 (s, 2F), -126.22 – -126.43 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{34}H_{31}F_9N_2O_2Na^+$: 693.2134; found: 693.2139.



5-benzyl-1-(*tert*-butyl)-2-(4-fluorophenyl)-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3ca). The product was purified by column chromatography (petroleum ether / ethyl acetate = 30:1); Yellow solid, 68.4 mg, 52% yield; mp 154.3-155.5 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 1H), 7.40 – 7.27 (m, 6H), 7.23 (d, J = 7.1 Hz, 1H), 7.13 (dt, J = 8.6, 6.1 Hz, 2H), 7.03 (t, J = 8.1 Hz, 1H), 6.49 (d, J = 7.6 Hz, 1H), 5.24 (s, 2H), 3.16 – 3.00 (m, 1H), 2.19 – 2.02 (m, 1H), 1.54 (s, 9H), 1.49 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.6, 163.1 (d, J = 249.6 Hz), 137.3, 134.6 (d, J = 8.1 Hz), 134.2, 134.0, 133.72, 133.68, 132.7, 132.0 (d, J = 3.8 Hz), 128.7, 127.1, 127.0, 122.7, 114.9 (d, J = 21.1 Hz), 112.7, 110.3, 102.5, 60.0, 46.3, 42.7, 39.7 (t, J = 18.3 Hz), 32.2, 30.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -80.99 (t, J = 9.5 Hz, 3F), -109.81 – -111.01 (m, 1F), -111.79 – -111.98 (m, 1F), -112.03 – -113.02 (m, 1F), -124.76 (s, 2F), -125.66 – -125.91 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{33}H_{28}F_{10}N_2ONa^+$: 681.1934; found: 681.1943.

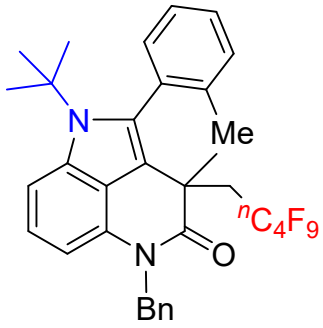


5-benzyl-1-(*tert*-butyl)-2-(4-chlorophenyl)-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3da). The product was purified by column chromatography (petroleum ether / ethyl acetate = 30:1); Yellow solid, 72.8 mg, 54% yield; mp 165.9-167.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 13.1 Hz, 3H), 7.34 – 7.27 (m, 6H), 7.22 (t, J = 7.0 Hz, 1H), 7.03 (t, J = 8.1 Hz, 1H), 6.48 (d, J = 7.6 Hz, 1H), 5.24 (s, 2H), 3.15 – 3.01 (m, 1H), 2.19 – 2.04 (m, 1H), 1.54 (s, 9H), 1.48 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.5, 137.2, 135.2, 134.7, 134.3, 134.2, 133.7, 133.2, 132.7, 128.7, 128.13, 128.07, 127.1, 127.0, 122.8, 115.1, 112.7, 110.3, 102.5, 60.1, 46.3, 42.7, 39.9 (t, J = 18.5 Hz), 32.2, 30.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.49 (t, J = 9.3 Hz, 3F), -110.03 – -111.47 (m, 1F), -112.43 – -113.68 (m, 1F), -125.04 – -125.43 (m, 2F), -126.09 – -126.47 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{33}H_{28}ClF_9N_2ONa^+$: 697.1639; found: 697.1643.

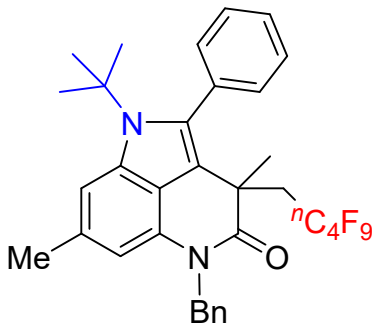


5-benzyl-1-(*tert*-butyl)-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-(*m*-tolyl)-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3ea). The product was purified by column chromatography (petroleum ether / ethyl acetate = 30:1); White solid, 90.3 mg, 69% yield; mp 160.3-161.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 7.6 Hz, 2H), 7.31 – 7.27 (m, 4H), 7.26 (d, J = 2.2 Hz, 2H), 7.23 – 7.13 (m, 2H), 7.00 (t, J = 8.1 Hz, 1H), 6.46 (d, J = 7.5 Hz, 1H), 5.23 (s, 2H), 3.08 – 2.91 (m, 1H), 2.39 (d, J = 7.1 Hz, 3H), 2.26 – 2.09 (m, 1H), 1.54 (d, J = 2.0 Hz, 9H),

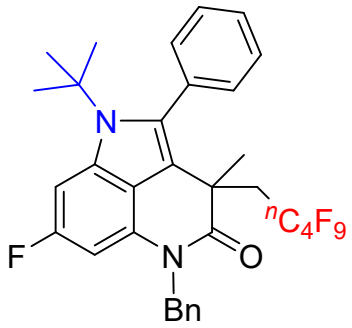
1.47 (d, J = 5.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 173.7, 137.5, 137.2, 137.1, 135.9, 134.0, 133.4, 132.5, 129.9, 129.52, 129.45, 128.6, 127.6, 127.4, 127.0, 126.9, 122.2, 115.1, 112.0, 110.2, 102.2, 59.9, 46.1, 42.6, 39.4 (t, J = 18.2 Hz), 32.0, 30.8, 21.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.52 (t, J = 10.2 Hz, 3F), -110.53 – -111.99 (m, 1F), -112.23 – -113.51 (m, 1F), -125.08 – -125.45 (m, 2F), -126.35 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{34}H_{31}F_9N_2ONa^+$: 677.2185; found: 677.2188.



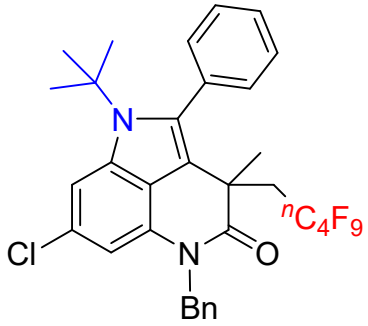
5-benzyl-1-(*tert*-butyl)-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-(*o*-tolyl)-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3fa). The product was purified by column chromatography (petroleum ether / ethyl acetate = 30:1); White solid, 86.3 mg, 66% yield; mp 171.3-172.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.3 Hz, 1H), 7.35 (d, J = 7.4 Hz, 3H), 7.29 (t, J = 8.0 Hz, 4H), 7.23 (d, J = 7.4 Hz, 2H), 7.01 (t, J = 8.1 Hz, 1H), 6.48 (d, J = 7.6 Hz, 1H), 5.23 (s, 2H), 3.06 – 2.91 (m, 1H), 2.39 – 2.24 (m, 1H), 2.11 (s, 3H), 1.52 (s, 9H), 1.34 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 173.8, 139.6, 137.3, 135.9, 134.3, 134.1, 132.7, 131.88, 131.85, 130.0, 129.4, 128.7, 127.1, 125.3, 122.2, 115.6, 110.8, 110.3, 102.2, 59.9, 46.4, 42.8, 40.4 (t, J = 18.0 Hz), 31.4, 28.2, 20.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.49 (t, J = 9.2 Hz, 3F), -110.64 – -112.15 (m, 1F), -112.25 – -113.43 (m, 1F), -125.24 (s, 2F), -126.21 – -126.54 (m, 2F); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{34}H_{32}F_9N_2O^+$: 655.2365; found: 655.2368.



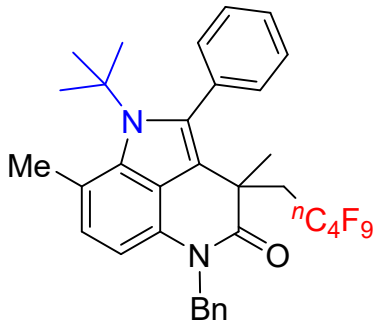
5-benzyl-1-(*tert*-butyl)-3,7-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-phenyl-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3ga). The product was purified by column chromatography (petroleum ether / ethyl acetate = 30:1); White solid, 81.1 mg, 62% yield; mp 142.6-143.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 1H), 7.42 (dt, J = 6.1, 1.8 Hz, 2H), 7.40 – 7.32 (m, 4H), 7.29 (d, J = 6.4 Hz, 2H), 7.23 (dt, J = 8.5, 3.8 Hz, 1H), 7.13 (s, 1H), 6.35 (s, 1H), 5.22 (d, J = 7.7 Hz, 2H), 3.09 – 2.93 (m, 1H), 2.43 (s, 3H), 2.22 – 2.06 (m, 1H), 1.53 (s, 9H), 1.46 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.9, 137.4, 136.3, 134.6, 134.5, 133.0, 132.4, 132.3, 132.0, 128.8, 128.6, 127.8, 127.6, 127.1, 127.0, 113.3, 112.1, 110.2, 104.1, 59.8, 46.2, 42.7, 39.7 (t, J = 18.2 Hz), 32.1, 30.7, 23.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ -80.99 (t, J = 10.2 Hz, 3F), -109.87 – -110.99 (m, 1F), -111.70 – -112.98 (m, 1F), -124.74 (s, 2F), -125.44 – -126.07 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{34}H_{31}F_9N_2ONa^+$: 677.2185; found: 677.2191.



5-benzyl-1-(*tert*-butyl)-7-fluoro-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-phenyl-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3ha). The product was purified by column chromatography (petroleum ether / ethyl acetate = 30:1); White solid, 75.0 mg, 57% yield; mp 150.6-151.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (t, J = 7.4 Hz, 2H), 7.43 (d, J = 4.6 Hz, 1H), 7.40 (d, J = 9.5 Hz, 2H), 7.33 – 7.29 (m, 4H), 7.23 (d, J = 6.3 Hz, 1H), 7.01 (d, J = 11.5 Hz, 1H), 6.31 (d, J = 10.7 Hz, 1H), 5.18 (d, J = 3.3 Hz, 2H), 3.08 – 2.92 (m, 1H), 2.22 – 2.05 (m, 1H), 1.50 (s, 9H), 1.47 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.0, 160.2 (d, J = 234.1 Hz), 136.8, 135.9, 135.4, 133.0, 132.1 (d, J = 3.6 Hz), 129.1, 128.8, 127.9, 127.7, 127.3, 127.0, 112.2, 111.4, 96.4 (d, J = 29.0 Hz), 92.9 (d, J = 31.4 Hz), 60.2, 46.4, 42.8, 39.8 (t, J = 18.2 Hz), 32.0, 30.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.01 (t, J = 11.9 Hz, 3F), -109.96 – -111.15 (m, 1F), -111.72 – -113.00 (m, 1F), -118.12 (s, 1F), -124.77 (s, 2F), -125.50 – -126.05 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{33}H_{28}F_{10}N_2ONa^+$: 681.1934; found: 681.1943.

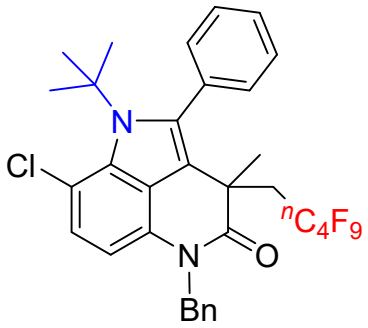


5-benzyl-1-(*tert*-butyl)-7-chloro-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-phenyl-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3ia). The product was purified by column chromatography (petroleum ether / ethyl acetate = 30:1); White solid, 87.6 mg, 65% yield; mp 147.5-148.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 4H), 7.40 – 7.34 (m, 2H), 7.33 – 7.30 (m, 4H), 7.24 (dd, J = 6.3, 2.8 Hz, 1H), 6.50 (s, 1H), 5.19 (s, 2H), 3.06 – 2.91 (m, 1H), 2.20 – 2.04 (m, 1H), 1.51 (s, 9H), 1.46 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.8, 136.7, 135.9, 135.6, 134.0, 133.2, 132.8, 131.9, 129.2, 128.8, 128.2, 127.9, 127.8, 127.3, 127.0, 113.6, 112.4, 110.0, 103.6, 60.3, 46.3, 42.7, 39.7 (t, J = 18.1 Hz), 32.1, 30.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ -80.93 – -81.06 (m, 3F), -109.78 – -111.19 (m, 1F), -111.68 – -112.93 (m, 1F), -124.74 (s, 2F), -125.43 – -126.33 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{33}H_{28}ClF_9N_2ONa^+$: 697.1639; found: 697.1645.

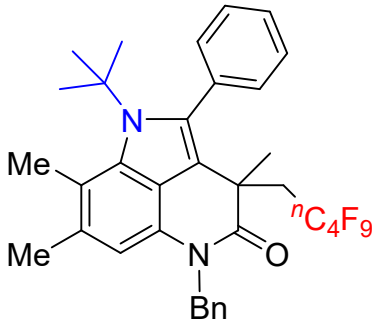


5-benzyl-1-(*tert*-butyl)-3,8-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-phenyl-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3ja). The product was purified by column chromatography (petroleum ether / ethyl acetate = 40:1); White solid, 81.1 mg, 62% yield; mp 140.1-141.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 4.5 Hz, 1H), 7.45 – 7.39 (m, 3H), 7.37 – 7.27 (m, 5H), 7.22 (t, J = 7.1 Hz, 1H), 6.88 (d, J = 7.7 Hz, 1H), 6.46 (d, J = 7.7 Hz, 1H), 5.23 (s, 2H), 3.25 – 3.09 (m, 1H), 2.77 (s, 3H), 2.41 – 2.26 (m, 1H), 1.52 (s, 9H), 1.44 (s, 3H); ^{13}C{^{1}H}

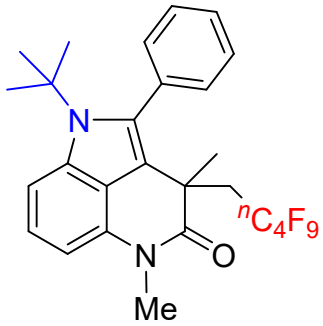
NMR (100 MHz, $CDCl_3$) δ 173.3, 137.6, 137.34, 137.25, 136.9, 132.0, 131.0, 130.8, 128.7, 128.4, 128.0, 127.9, 127.5, 127.1, 127.0, 117.6, 116.7, 113.5, 103.9, 58.7, 46.3, 42.4, 40.3 (t, J = 18.1 Hz), 34.4, 30.5, 25.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.52 (t, J = 9.9 Hz, 3F), -110.33 – -111.55 (m, 1F), -112.28 – -113.47 (m, 1F), -125.27 (s, 2F), -126.25 – -126.48 (m, 2F); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{34}H_{32}F_9N_2O^+$: 655.2365; found: 655.2374.



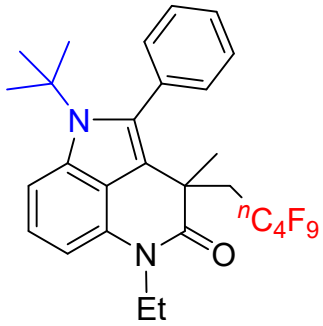
5-benzyl-1-(*tert*-butyl)-8-chloro-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-phenyl-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3ka). The product was purified by column chromatography (petroleum ether / ethyl acetate = 40:1); Yellow solid, 91.7mg, 68% yield; mp 137.7-138.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.37 (m, 4H), 7.35 (dd, J = 6.4, 1.7 Hz, 1H), 7.29 (d, J = 4.5 Hz, 4H), 7.27 – 7.19 (m, 1H), 7.09 (d, J = 8.2 Hz, 1H), 6.43 (d, J = 8.2 Hz, 1H), 5.22 (d, J = 3.7 Hz, 2H), 3.19 – 3.03 (m, 1H), 2.36 – 2.20 (m, 1H), 1.59 (s, 9H), 1.44 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.2, 138.3, 136.9, 136. 5, 133.2, 132.0, 131.5, 131.1, 128.79, 128.77, 128.1, 128.0, 127.3, 126.9, 126.6, 118.3, 113.5, 112.4, 104.7, 60.3, 46.4, 42.3, 40.2 (t, J = 17.6 Hz), 34.5, 30.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.50 (t, J = 9.2 Hz, 3F), -110.40 – -111.51 (m, 1F), -112.12 – -113.40 (m, 1F), -125.24 (s 2F), -126.15 – -126.57 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{33}H_{28}ClF_9N_2ONa^+$: 697.1639; found: 697.1645.



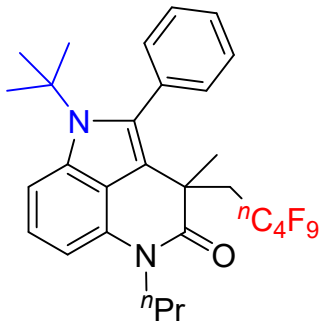
5-benzyl-1-(*tert*-butyl)-3,7,8-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-phenyl-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3la). The product was purified by column chromatography (petroleum ether / ethyl acetate = 40:1); Yellow solid, 82.8 mg, 62% yield; mp 149.5-150.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.3 Hz, 1H), 7.47 – 7.35 (m, 3H), 7.38 – 7.31 (m, 3H), 7.28 (d, J = 7.7 Hz, 2H), 7.25 – 7.19 (m, 1H), 6.46 (s, 1H), 5.21 (q, J = 15.9 Hz, 2H), 3.30 – 3.13 (m, 1H), 2.59 (s, 3H), 2.47 – 2.35 (m, 1H), 2.32 (s, 3H), 1.51 (s, 9H), 1.38 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.4, 139.1, 138.6, 137.5, 137.4, 133.2, 131.9, 130.6, 130.0, 128.7, 128.2, 128.1, 128.0, 127.04, 126.99, 116.8, 115.4, 114.2, 107.2, 59.1, 46.2, 42.5, 40.7 (t, J = 18.5 Hz), 34.5, 30.1, 22.3, 20.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.52 (t, J = 10.1 Hz, 3F), -109.61 – -111.23 (m, 1F), -112.12 – -114.17 (m, 1F), -125.27 (s, 2F), -126.20 – -126.44 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{35}H_{33}F_9N_2ONa^+$: 691.2341; found: 691.2349.



1-(*tert*-butyl)-3,5-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-phenyl-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3ma). The product was purified by column chromatography (petroleum ether / ethyl acetate = 30:1); White solid, 75.6 mg, 67% yield; mp 118.5-119.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.1 Hz, 2H), 7.44 – 7.35 (m, 3H), 7.35 (d, J = 8.6 Hz, 1H), 7.13 (t, J = 8.0 Hz, 1H), 6.54 (d, J = 7.5 Hz, 1H), 3.44 (s, 3H), 3.01 – 2.85 (m, 1H), 2.17 – 2.01 (m, 1H), 1.54 (s, 9H), 1.42 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.4, 136.2, 135.3, 134.0, 133.4, 132.9, 131.9, 128.9, 127.8, 127.6, 122.5, 115.1, 112.4, 110.3, 101.3, 60.0, 42.4, 39.9 (t, J = 17.9 Hz), 32.1, 30.3, 29.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.56 (t, J = 9.5 Hz, 3F), -111.28 – -112.38 (m, 1F), -113.52 – -114.77 (m, 1F), -125.23 – -125.40 (m, 2F), -126.09 – -126.63 (m, 2F); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{26}F_9N_2O^+$: 565.1896; found: 565.1895.

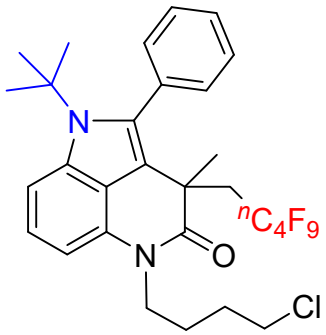


1-(*tert*-butyl)-5-ethyl-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-phenyl-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3na). The product was purified by column chromatography (petroleum ether / ethyl acetate = 30:1); White solid, 70.5 mg, 61% yield; mp 112.2-113.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (td, J = 6.0, 2.0 Hz, 2H), 7.41 – 7.35 (m, 3H), 7.33 (d, J = 8.6 Hz, 1H), 7.15 – 7.09 (m, 1H), 6.55 (d, J = 7.6 Hz, 1H), 4.25 – 4.12 (m, 1H), 3.96 – 3.83 (m, 1H), 3.02 – 2.84 (m, 1H), 2.17 – 1.99 (m, 1H), 1.54 (s, 9H), 1.41 (s, 3H), 1.27 (t, J = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.8, 136.2, 135.3, 134.2, 132.9, 132.2, 132.0, 128.9, 127.8, 127.6, 122.5, 115.3, 112.4, 110.0, 101.2, 60.0, 42.3, 39.9 (t, J = 18.4 Hz), 37.2, 32.1, 30.3, 12.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.45 – -81.58 (m, 3F), -111.01 – -112.11 (m, 1F), -112.95 – -114.20 (m, 1F), -125.34 (s, 2F), -126.06 – -126.67 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{28}H_{27}F_9N_2ONa^+$: 601.1872; found: 601.1881.

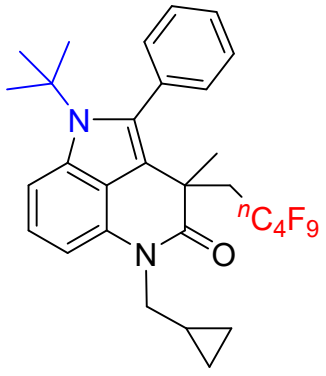


1-(*tert*-butyl)-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-phenyl-5-propyl-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3oa). The product was purified by column chromatography (petroleum ether / ethyl acetate = 30:1); White solid, 77.0 mg, 65% yield; mp 115.2-116.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.44 – 7.34 (m, 3H), 7.32 (d, J = 8.5 Hz, 1H), 7.11 (t, J = 8.0 Hz, 1H), 6.53 (d, J = 7.6 Hz, 1H), 4.08 – 3.95 (m, 1H), 3.90 – 3.78 (m, 1H), 3.03 – 2.81 (m, 1H), 2.15 – 2.01 (m, 1H), 1.77 – 1.69 (m, 2H), 1.53 (s, 9H), 1.40 (s, 3H), 1.01 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.0, 136.2, 135.2, 134.2, 132.9,

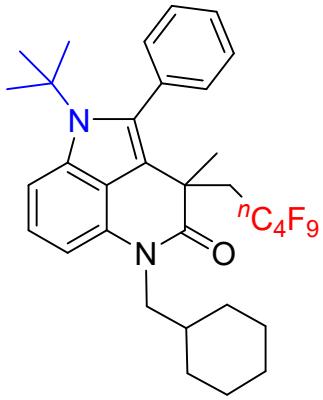
132.6, 132.0, 128.9, 127.8, 127.6, 122.5, 115.2, 112.4, 110.0, 101.3, 60.0, 44.1, 42.3, 39.8 (t, J = 18.2 Hz), 32.1, 30.4, 20.2, 11.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.03 (t, J = 10.2 Hz, 3F), -110.39 – -111.61 (m, 1F), -112.49 – -113.58 (m, 1F), -124.78 – -124.90 (m, 2F), -125.71 – -125.96 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{29}H_{29}F_9N_2ONa^+$: 615.2028; found: 615.2037.



1-(*tert*-butyl)-5-(4-chlorobutyl)-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-phenyl-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3pa). The product was purified by column chromatography (petroleum ether / ethyl acetate = 30:1); White solid, 70.4 mg, 55% yield; mp 102.5-103.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.30 (m, 6H), 7.12 (td, J = 8.1, 2.0 Hz, 1H), 6.54 (dd, J = 7.6, 2.0 Hz, 1H), 4.14 – 4.02 (m, 1H), 3.99 – 3.89 (m, 1H), 3.59 (t, J = 5.0 Hz, 2H), 3.01 – 2.84 (m, 1H), 2.17 – 1.99 (m, 1H), 1.95 – 1.83 (m, 4H), 1.53 (s, 9H), 1.40 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.3, 136.1, 135.4, 134.2, 132.9, 132.3, 131.9, 128.9, 127.8, 127.6, 122.5, 115.2, 112.2, 110.2, 101.3, 60.0, 42.4, 41.5, 39.8 (t, J = 18.0 Hz), 32.1, 30.4, 30.1, 24.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.52 (t, J = 10.1 Hz, 3F), -110.87 – -111.95 (m, 1F), -112.97 – -114.05 (m, 1F), -125.35 (s, 2F), -126.22 – -126.54 (m, 2F); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{30}H_{30}ClF_9N_2ONa^+$: 663.1795; found: 663.1804.

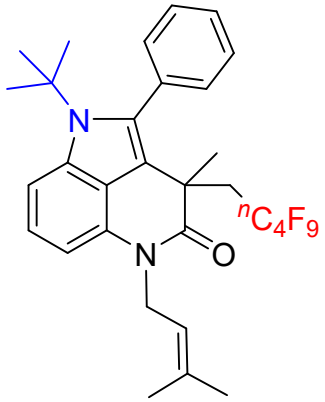


1-(*tert*-butyl)-5-(cyclopropylmethyl)-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-phenyl-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3qa). The product was purified by column chromatography (petroleum ether / ethyl acetate = 50:1); Yellow oil, 62.8 mg, 52% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.4 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.41 – 7.34 (m, 2H), 7.33 (d, J = 8.6 Hz, 1H), 7.13 (t, J = 8.1 Hz, 1H), 6.64 (d, J = 7.6 Hz, 1H), 3.98 (dd, J = 14.3, 7.2 Hz, 1H), 3.87 (dd, J = 14.3, 6.6 Hz, 1H), 3.10 (dt, J = 10.5, 6.5 Hz, 1H), 3.04 – 2.86 (m, 1H), 2.16 – 2.02 (m, 1H), 1.54 (s, 9H), 1.40 (s, 3H), 0.48 – 0.42 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.4, 136.2, 135.2, 134.2, 133.0, 131.99, 131.96, 128.9, 127.8, 127.6, 122.5, 115.2, 112.5, 110.0, 101.6, 60.0, 46.2, 42.4, 40.0 (t, J = 18.4 Hz), 32.1, 30.3, 9.5, 3.9, 3.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.54 (t, J = 10.4 Hz, 3F), -110.64 – -111.67 (m, 1F), -112.76 – -113.77 (m, 1F), -125.42 (s, 2F), -126.21 – -126.47 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{30}H_{29}F_9N_2ONa^+$: 627.2028; found: 627.2037.

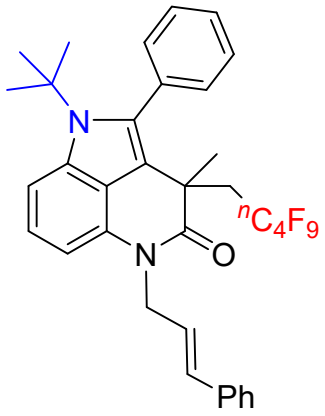


1-(*tert*-butyl)-5-(cyclohexylmethyl)-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-phenyl-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3ra). The product was purified by column chromatography (petroleum ether / ethyl acetate = 50:1); Yellow oil, 95.6 mg, 74% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.0 Hz, 1H), 7.43 – 7.35 (m, 4H), 7.32 (dd, J = 8.8, 2.9 Hz, 1H), 7.11 (td, J = 8.1, 3.0 Hz, 1H), 6.54 (dd, J = 7.8, 3.1 Hz, 1H), 3.96 – 3.88 (m, 1H), 3.81 – 3.69 (m, 1H), 3.04 – 2.87 (m, 1H), 2.16 – 2.00 (m, 1H), 1.96 – 1.85 (m, 1H), 1.81 – 1.60 (m, 6H), 1.53 (s, 9H), 1.41 (s, 3H), 1.20 – 1.08 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.5, 136.2, 135.2, 134.2, 133.2, 133.0, 132.0, 128.9, 127.8, 127.6, 122.3, 115.2, 112.4, 109.9, 101.9, 59.9, 48.5, 42.4, 39.7 (t, J = 18.3 Hz), 36.5, 32.1, 31.32, 31.25, 30.7, 26.6, 26.13, 26.07; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.56 (t, J = 10.2 Hz, 3F), -110.53 – -111.68 (m, 1F), -112.94 – -114.02 (m, 1F), -125.32 (s, 2F),

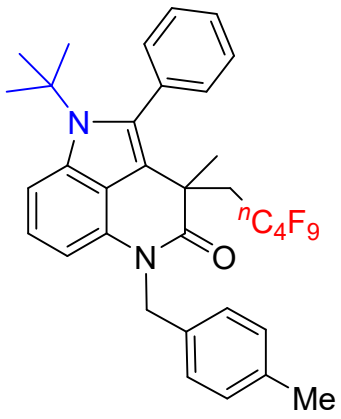
-126.25 – -126.57 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{33}H_{35}F_9N_2ONa^+$: 669.2498; found: 669.2505.



1-(*tert*-butyl)-3-methyl-5-(3-methylbut-2-en-1-yl)-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-phenyl-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3sa). The product was purified by column chromatography (petroleum ether / ethyl acetate = 40:1); White solid, 64.3 mg, 52% yield; mp 124.6-125.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.43 – 7.36 (m, 2H), 7.39 – 7.33 (m, 1H), 7.32 (d, J = 8.5 Hz, 1H), 7.10 (t, J = 8.1 Hz, 1H), 6.49 (d, J = 7.6 Hz, 1H), 5.16 (t, J = 5.6 Hz, 1H), 4.69 (dd, J = 16.1, 6.2 Hz, 1H), 4.54 (dd, J = 15.6, 6.5 Hz, 1H), 3.01 – 2.86 (m, 1H), 2.16 – 2.01 (m, 1H), 1.84 (s, 3H), 1.69 (s, 3H), 1.53 (s, 9H), 1.40 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.0, 136.2, 135.2, 134.1, 133.0, 132.5, 132.0, 131.9, 128.9, 127.8, 127.6, 122.5, 119.9, 115.3, 112.4, 110.1, 101.7, 59.9, 42.5, 40.7, 39.9 (t, J = 16.3 Hz), 32.1, 30.3, 25.7, 18.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.53 (t, J = 10.2 Hz, 3F), -111.05 – -112.26 (m, 1F), -112.93 – -114.38 (m, 1F), -125.27 (s, 2F), -126.21 – -126.46 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{31}H_{31}F_9N_2ONa^+$: 641.2185; found: 641.2182.

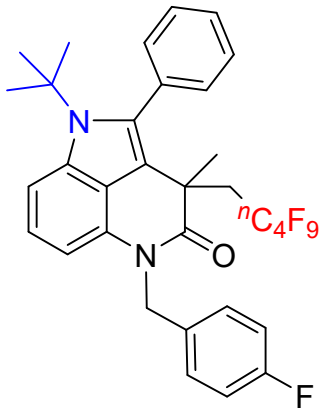


1-(*tert*-butyl)-5-cinnamyl-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-phenyl-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3ta). The product was purified by column chromatography (petroleum ether / ethyl acetate = 30:1); White solid, 66.6 mg, 50% yield; mp 167.9-169.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.35 (m, 5H), 7.34 (d, J = 4.1 Hz, 1H), 7.32 (d, J = 2.4 Hz, 2H), 7.26 (t, J = 7.4 Hz, 2H), 7.20 (d, J = 7.0 Hz, 1H), 7.10 (t, J = 8.1 Hz, 1H), 6.64 (d, J = 16.4 Hz, 1H), 6.60 (d, J = 7.7 Hz, 1H), 6.26 (dt, J = 16.0, 5.7 Hz, 1H), 4.89 (dd, J = 16.0, 5.2 Hz, 1H), 4.69 (dd, J = 16.1, 6.1 Hz, 1H), 3.04 – 2.89 (m, 1H), 2.19 – 2.04 (m, 1H), 1.54 (s, 9H), 1.44 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.2, 136.9, 136.1, 135.3, 134.2, 132.9, 132.43, 132.36, 132.0, 128.9, 128.5, 127.8, 127.63, 127.56, 126.5, 124.1, 122.5, 115.2, 112.2, 110.2, 102.0, 60.0, 44.3, 42.6, 39.9 (t, J = 18.5 Hz), 32.1, 30.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.53 (t, J = 9.9 Hz, 3F), -110.93 – -111.96 (m, 1F), -112.71 – -113.73 (m, 1F), -125.28 (s, 2F), -126.22 – -126.57 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{35}H_{31}F_9N_2ONa^+$: 689.2185; found: 689.2184.

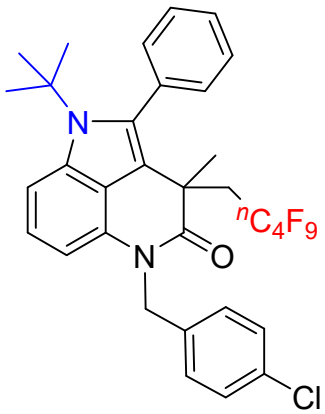


1-(*tert*-butyl)-3-methyl-5-(4-methylbenzyl)-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-phenyl-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3ua). The product was purified by column chromatography (petroleum ether / ethyl acetate = 30:1); Yellow oil, 78.5 mg, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 7.2 Hz, 1H), 7.48 – 7.39 (m, 2H), 7.39 (d, J = 6.4 Hz, 2H), 7.30 (d, J = 8.5 Hz, 1H), 7.23 (d, J = 7.6 Hz, 2H), 7.10 (d, J = 7.6 Hz, 2H), 7.02 (t, J = 8.1 Hz, 1H), 6.49 (d, J = 7.6 Hz, 1H), 5.20 (d, J = 5.0 Hz, 2H), 3.11 – 2.93 (m, 1H), 2.30 (s, 3H), 2.22 – 2.06 (m, 1H), 1.54 (s, 9H), 1.47 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.7, 136.6, 136.2, 135.3, 134.3, 134.2, 133.0, 132.7, 132.0, 129.3, 128.9, 127.8, 127.6, 127.0, 122.5, 115.2, 112.3, 110.2, 102.4, 60.0, 46.0, 42.7, 39.7 (t, J = 18.3 Hz), 32.1, 30.8, 21.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.00 (t, J = 8.8 Hz, 3F), -109.94 – -111.06 (m, 1F), -111.87 – -113.01 (m, 1F), -124.74 (s, 2F), -125.69 – -

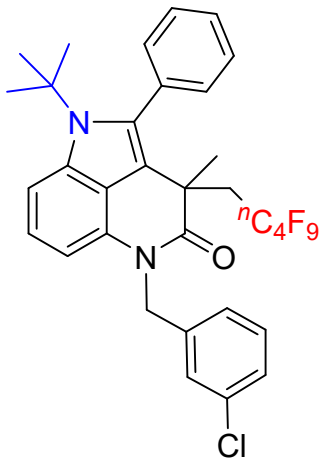
126.01 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{34}H_{31}F_9N_2ONa^+$: 677.2185; found: 677.2192.



1-(*tert*-butyl)-5-(4-fluorobenzyl)-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-phenyl-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3va). The product was purified by column chromatography (petroleum ether / ethyl acetate = 40:1); White solid, 72.4 mg, 55% yield; mp 123.1-124.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, J = 7.8, 1.8 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.37 (td, J = 8.6, 1.9 Hz, 2H), 7.33 – 7.28 (m, 3H), 7.05 – 7.00 (m, 1H), 6.96 (t, J = 8.7 Hz, 2H), 6.46 (d, J = 7.6 Hz, 1H), 5.27 – 5.09 (m, 2H), 3.07 – 2.91 (m, 1H), 2.20 – 2.05 (m, 1H), 1.53 (s, 9H), 1.45 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.8, 162.1 (d, J = 244.3 Hz), 136.0, 135.5, 134.2, 133.0, 132.9, 132.5, 132.0 (d, J = 3.3 Hz), 129.0, 128.8 (d, J = 8.1 Hz), 127.8, 127.7, 122.4, 115.5 (d, J = 21.5 Hz), 115.2, 112.1, 110.4, 102.1, 60.1, 45.6, 42.8, 39.7 (t, J = 18.0 Hz), 32.1, 30.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.52 (t, J = 8.1 Hz, 3F), -110.29 – -111.58 (m, 1F), -112.17 – -113.64 (m, 1F), -116.28 – -116.68 (m, 1F), -125.29 (s, 2F), -126.15 – -126.47 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{33}H_{28}F_{10}N_2ONa^+$: 681.1934; found: 681.1943.

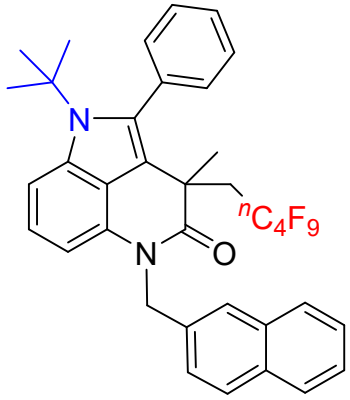


1-(*tert*-butyl)-5-(4-chlorobenzyl)-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-phenyl-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3wa). The product was purified by column chromatography (petroleum ether / ethyl acetate = 30:1); White solid, 87.6 mg, 65% yield; mp 148.8-150.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.3 Hz, 1H), 7.48 – 7.39 (m, 2H), 7.42 – 7.34 (m, 2H), 7.32 (d, J = 8.5 Hz, 1H), 7.26 (d, J = 1.5 Hz, 4H), 7.02 (t, J = 8.1 Hz, 1H), 6.43 (d, J = 7.5 Hz, 1H), 5.24 (d, J = 15.9 Hz, 1H), 5.13 (d, J = 16.0 Hz, 1H), 3.07 – 2.92 (m, 1H), 2.22 – 2.06 (m, 1H), 1.54 (s, 9H), 1.46 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.8, 136.0, 135.9, 135.5, 134.2, 132.9, 132.4, 131.98, 131.95, 129.0, 128.8, 128.5, 127.8, 127.7, 122.4, 115.2, 112.1, 110.4, 102.1, 60.1, 45.7, 42.8, 39.7 (t, J = 18.1 Hz), 32.1, 30.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.54 (t, J = 10.1 Hz, 3F), -110.44 – -111.47 (m, 1F), -112.41 – -113.47 (m, 1F), -125.32 (s, 2F), -126.28 – -126.48 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{33}H_{28}ClF_9N_2ONa^+$: 697.1639; found: 697.1645.

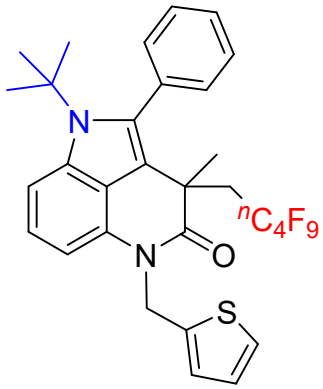


1-(*tert*-butyl)-5-(3-chlorobenzyl)-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-phenyl-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3xa). The product was purified by column chromatography (petroleum ether / ethyl acetate = 30:1); White solid, 72.8 mg, 54% yield; mp 163.5-164.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.0 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.40 (d, J = 6.5 Hz, 2H), 7.33 (d, J = 8.7 Hz, 2H), 7.25 – 7.17 (m, 3H), 7.03 (t, J = 8.1 Hz, 1H), 6.42 (d, J = 7.5 Hz, 1H), 5.25 (d, J = 16.0 Hz, 1H), 5.14 (d, J = 16.1 Hz, 1H), 3.08 – 2.93 (m, 1H), 2.23 – 2.06 (m, 1H), 1.54 (s, 9H), 1.47 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.8, 139.4, 136.0, 135.5, 134.6, 134.2, 132.9, 132.4, 132.0, 129.9, 129.0, 127.8, 127.7, 127.4, 127.1, 125.2, 122.5, 115.2, 112.1, 110.5, 102.1, 60.1, 45.8, 42.8, 39.7 (t, J = 18.4 Hz), 32.1, 30.8; ^{19}F NMR (377 MHz,

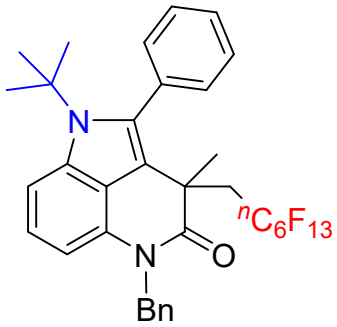
$CDCl_3$) δ -81.52 (t, J = 9.9 Hz, 3F), -110.39 – -111.57 (m, 1F), -112.29 – -113.38 (m, 1F), -125.15 – -125.43 (m, 2F), -126.18 – -126.49 (m, 2F); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{33}H_{29}ClF_9N_2O^+$: 675.1819; found: 675.1824.



1-(*tert*-butyl)-3-methyl-5-(naphthalen-2-ylmethyl)-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-phenyl-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3ya). The product was purified by column chromatography (petroleum ether / ethyl acetate = 30:1); Yellow solid, 74.5 mg, 54% yield; mp 151.3-152.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.76 (m, 3H), 7.74 (t, J = 4.6 Hz, 1H), 7.51 (d, J = 7.2 Hz, 1H), 7.48 – 7.39 (m, 7H), 7.30 (d, J = 8.6 Hz, 1H), 6.99 (t, J = 8.1 Hz, 1H), 6.51 (d, J = 7.6 Hz, 1H), 5.47 (d, J = 16.0 Hz, 1H), 5.33 (d, J = 16.1 Hz, 1H), 3.13 – 2.99 (m, 1H), 2.25 – 2.09 (m, 1H), 1.54 (s, 9H), 1.51 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.9, 136.1, 135.4, 134.8, 134.2, 133.6, 133.0, 132.8, 132.6, 132.0, 129.0, 128.5, 127.9, 127.8, 127.74, 127.65, 126.1, 125.7, 125.6, 125.3, 122.5, 115.2, 112.2, 110.3, 102.5, 60.0, 46.5, 42.8, 39.7 (t, J = 18.1 Hz), 32.1, 30.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.50 (t, J = 10.2 Hz, 3F), -110.35 – -111.55 (m, 1F), -112.01 – -113.23 (m, 1F), -124.99 – -125.36 (m, 2F), -126.12 – -126.47 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{37}H_{31}F_9N_2ONa^+$: 713.2185; found: 713.2191.

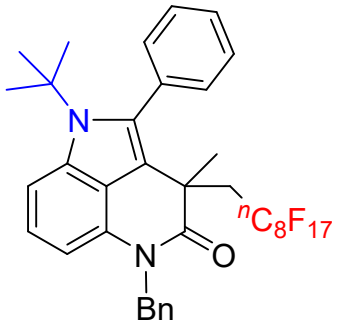


1-(*tert*-butyl)-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-phenyl-5-(thiophen-2-ylmethyl)-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3za). The product was purified by column chromatography (petroleum ether / ethyl acetate = 40:1); White solid, 78.8 mg, 61% yield; mp 131.1-132.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 6.9 Hz, 1H), 7.43 (td, J = 7.9, 1.4 Hz, 2H), 7.40 – 7.30 (m, 3H), 7.17 (dt, J = 5.2, 1.4 Hz, 1H), 7.10 (t, J = 7.6 Hz, 2H), 6.91 (td, J = 4.2, 3.3, 1.5 Hz, 1H), 6.70 (dd, J = 7.6, 1.5 Hz, 1H), 5.39 (d, J = 15.6 Hz, 1H), 5.30 (d, J = 15.7 Hz, 1H), 3.08 – 2.92 (m, 1H), 2.21 – 2.05 (m, 1H), 1.53 (s, 9H), 1.44 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.3, 139.5, 136.1, 135.4, 134.2, 132.9, 132.1, 132.0, 129.0, 127.8, 127.6, 126.5, 125.0, 122.4, 115.2, 112.1, 110.4, 101.8, 60.0, 42.6, 41.2, 39.7 (t, J = 18.5 Hz), 32.1, 30.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.54 (t, J = 10.1 Hz, 3F), -110.55 – -111.62 (m, 1F), -112.55 – -113.58 (m, 1F), -125.20 – -125.46 (m, 2F), -126.20 – -126.58 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{31}H_{27}F_9N_2OSNa^+$: 669.1593; found: 669.1600.

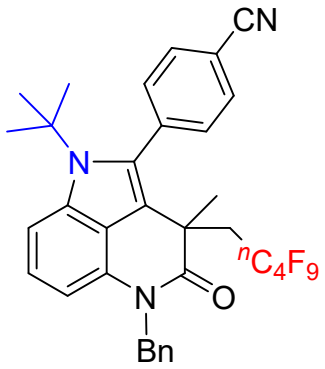


5-benzyl-1-(*tert*-butyl)-3-methyl-2-phenyl-3-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3ab). The product was purified by column chromatography (petroleum ether / ethyl acetate = 30:1); Yellow oil, 79.9 mg, 54% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 7.1 Hz, 1H), 7.46 – 7.37 (m, 4H), 7.35 – 7.29 (m, 4H), 7.27 (d, J = 7.9 Hz, 1H), 7.22 (d, J = 7.1 Hz, 1H), 7.01 (t, J = 8.1 Hz, 1H), 6.48 (d, J = 7.6 Hz, 1H), 5.24 (s,

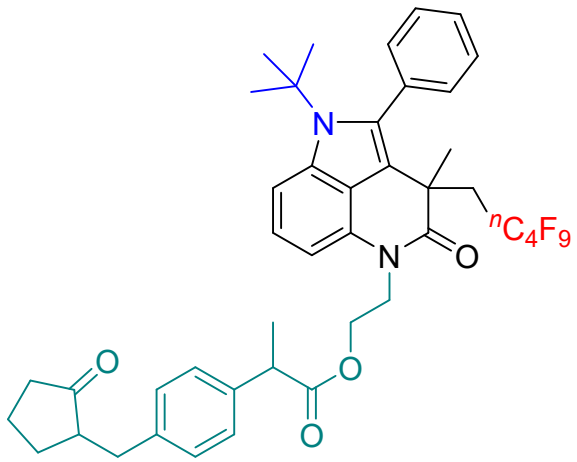
2H), 3.10 – 2.95 (m, 1H), 2.23 – 2.07 (m, 1H), 1.54 (s, 9H), 1.48 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 173.8, 137.3, 136.1, 135.3, 134.1, 132.9, 132.7, 132.0, 129.0, 128.7, 127.8, 127.6, 127.1, 127.0, 122.5, 115.2, 112.2, 110.3, 102.4, 60.0, 46.3, 42.8, 39.8 (t, J = 18.2 Hz), 32.1, 30.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.32 (t, J = 10.3 Hz, 3F), -110.23 – -111.32 (m, 1F), -112.03 – -113.37 (m, 1F), -122.23 (s, 2F), -123.33 (s, 2F), -124.30 – -124.64 (m, 2F), -126.48 – -126.86 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{35}H_{29}F_{13}N_2ONa^+$: 763.1965; found: 763.1971.



5-benzyl-1-(*tert*-butyl)-3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl)-3-methyl-2-phenyl-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3ac). The product was purified by column chromatography (petroleum ether / ethyl acetate = 30:1); Yellow oil, 97.4 mg, 58% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 7.1 Hz, 1H), 7.46 – 7.38 (m, 4H), 7.35 – 7.29 (m, 4H), 7.28 (d, J = 8.4 Hz, 1H), 7.22 (d, J = 6.8 Hz, 1H), 7.02 (t, J = 8.1 Hz, 1H), 6.48 (d, J = 7.6 Hz, 1H), 5.24 (s, 2H), 3.12 – 2.84 (m, 1H), 2.27 – 2.05 (m, 1H), 1.54 (s, 9H), 1.48 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 173.8, 137.3, 136.1, 135.3, 134.2, 133.0, 132.7, 132.0, 129.0, 128.7, 127.8, 127.6, 127.1, 127.0, 122.5, 115.2, 112.3, 110.3, 102.4, 60.0, 46.3, 42.8, 39.8 (t, J = 18.2 Hz), 32.1, 30.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.30 (t, J = 10.1 Hz, 3F), -110.23 – -111.29 (m, 1F), -112.04 – -113.19 (m, 1F), -121.90 – -122.13 (m, 2F), -122.17 – -122.66 (m, 4F), -123.22 (s, 2F), -124.28 – -124.48 (m, 2F), -126.62 (t, J = 14.6 Hz, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{37}H_{29}F_{17}N_2ONa^+$: 863.1901; found: 863.1899.

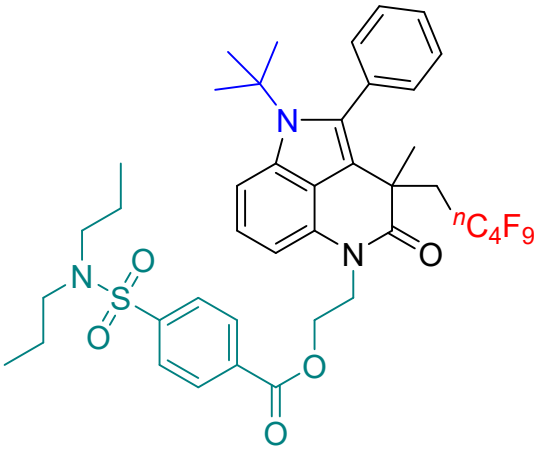


4-(5-benzyl-1-(*tert*-butyl)-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-4-oxo-1,3,4,5-tetrahydropyrrolo[4,3,2-*de*]quinolin-2-yl)benzonitrile (3Aa). The product was purified by column chromatography (petroleum ether / ethyl acetate = 15:1); White solid, 61.2 mg, 46% yield; mp 164.3-165.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (t, J = 7.2 Hz, 2H), 7.64 (d, J = 7.8 Hz, 1H), 7.54 (d, J = 7.9 Hz, 1H), 7.34 – 7.28 (m, 5H), 7.22 (t, J = 6.8 Hz, 1H), 7.06 (t, J = 8.1 Hz, 1H), 6.51 (d, J = 7.6 Hz, 1H), 5.24 (s, 2H), 3.19 – 3.03 (m, 1H), 2.07 – 1.90 (m, 1H), 1.53 (s, 9H), 1.46 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.6, 137.0, 134.6, 133.6, 132.8, 132.7, 132.6, 132.5, 131.6, 131.4, 128.7, 127.2, 127.0, 123.3, 118.3, 115.1, 113.3, 113.0, 110.3, 102.8, 60.2, 46.3, 42.6, 40.0 (t, J = 18.3 Hz), 32.2, 31.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.48 (t, J = 10.0 Hz, 3F), -110.08 – -111.33 (m, 1F), -112.52 – -113.60 (m, 1F), -125.12 – -125.32 (m, 2F), -126.32 (dt, J = 26.9, 13.3 Hz, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{34}H_{28}F_9N_3NaO^+$: 688.1981; found: 688.1985.



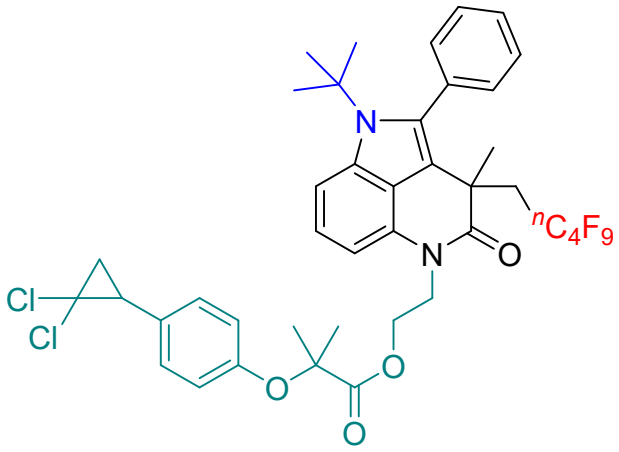
2-(1-(*tert*-butyl)-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-4-oxo-2-phenyl-3,4-dihydropyrrolo[4,3,2-*de*]quinolin-5(1*H*)-yl)ethyl 2-(4-((2-

oxocyclopentyl)methyl)phenyl)propanoate (4a). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow oil, 87.1 mg, 53% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 6.6 Hz, 2H), 7.42 – 7.37 (m, 3H), 7.34 (d, J = 8.7 Hz, 1H), 7.16 (d, J = 7.9 Hz, 2H), 7.12 – 7.06 (m, 3H), 6.60 (d, J = 7.6 Hz, 1H), 4.41 – 4.07 (m, 4H), 3.64 (q, J = 7.2 Hz, 1H), 3.13 (dd, J = 13.9, 4.0 Hz, 1H), 2.98 – 2.80 (m, 1H), 2.55 – 2.43 (m, 1H), 2.39 – 2.29 (m, 2H), 2.11 (dt, J = 18.7, 9.9 Hz, 3H), 2.00 – 1.92 (m, 1H), 1.80 – 1.69 (m, 1H), 1.54 (s, 9H), 1.47 – 1.42 (m, 4H), 1.39 (d, J = 5.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 220.2, 174.7, 173.4, 138.9, 138.3, 136.0, 135.3, 134.1, 132.8, 132.4, 131.9, 129.1, 128.9, 127.70, 127.65, 127.6, 122.5, 115.0, 112.0, 110.2, 101.4, 61.3, 60.0, 51.1, 45.1, 42.3, 40.8, 39.8 (t, J = 18.1 Hz), 38.2, 35.3, 32.0, 30.3, 29.3, 20.6, 18.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.00 (t, J = 10.3 Hz, 3F), -110.62 – -111.66 (m, 1F), -112.57 – -113.68 (m, 1F), -124.91 (s, 2F), -125.65 – -126.14 (m, 2F); HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd. for $C_{43}H_{43}F_9N_2O_4Na^+$: 845.2971; found: 845.2975.

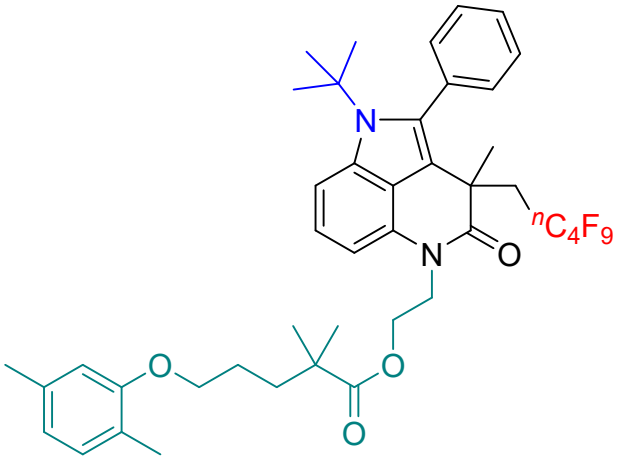


2-(1-(*tert*-butyl)-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-4-oxo-2-phenyl-3,4-dihydropyrrolo[4,3,2-*de*]quinolin-5(1*H*)-yl)ethyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (4b). The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 82.7 mg, 48% yield; mp 116.2-117.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, J = 8.4, 2.4 Hz, 2H), 7.79 (dd, J = 8.4, 2.4 Hz, 2H), 7.46 – 7.32 (m, 6H), 7.09 (td, J = 8.1, 2.4 Hz, 1H), 6.66 (dd, J = 7.7, 2.4 Hz, 1H), 4.69 – 4.59 (m, 2H), 4.47 – 4.35 (m, 2H), 3.07 (dt, J = 5.7, 3.8 Hz, 4H), 2.98 – 2.83 (m, 1H), 2.16 – 2.00 (m, 1H), 1.56 – 1.54 (m, 4H), 1.53 (s, 9H), 1.40 (s, 3H), 0.85 (td, J = 7.4, 2.4 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.7, 165.4, 157.2, 144.2, 135.9, 135.5, 134.2, 133.4, 132.9, 132.4, 131.9, 130.5, 129.0, 127.8, 127.7, 127.0, 122.4, 115.1, 111.9, 110.5,

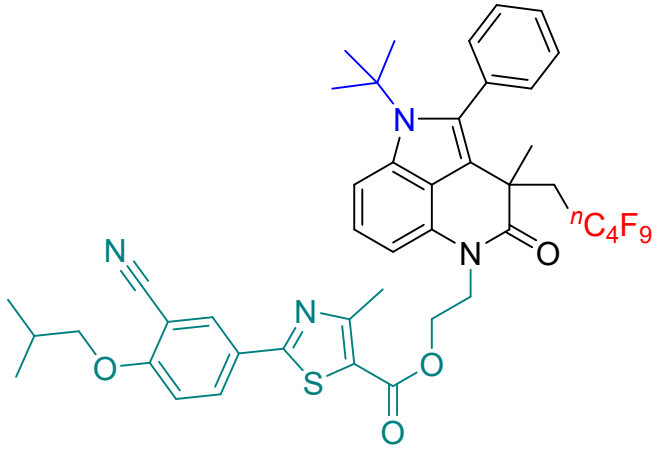
101.3, 62.5, 60.1, 50.0, 42.4, 40.8, 39.9 (t, J = 18.3 Hz), 32.1, 29.7, 22.0, 11.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.55 (t, J = 10.1 Hz, 3F), -111.28 – -112.42 (m, 1F), -113.67 (m, 1F), -125.08 – -125.49 (m, 2F), -126.22 – -126.62 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{41}H_{44}F_9N_3O_5SNa^+$: 884.2750; found: 884.2755.



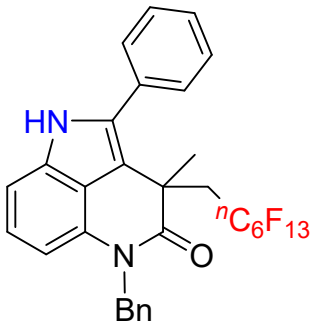
2-(1-(*tert*-butyl)-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-4-oxo-2-phenyl-3,4-dihydropyrrolo[4,3,2-*de*]quinolin-5(1*H*)-yl)ethyl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate (4c). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow oil, 82.9 mg, 48% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 5H), 7.33 (d, J = 8.6 Hz, 1H), 7.10 (dd, J = 8.7, 2.7 Hz, 3H), 6.82 (dd, J = 8.8, 2.4 Hz, 2H), 6.59 (dd, J = 7.6, 1.6 Hz, 1H), 4.41 (q, J = 7.1 Hz, 2H), 4.29 – 4.12 (m, 2H), 2.98 – 2.85 (m, 1H), 2.82 (dd, J = 10.7, 8.4 Hz, 1H), 2.17 – 1.99 (m, 1H), 1.93 (dd, J = 10.7, 7.4 Hz, 1H), 1.77 (t, J = 7.8 Hz, 1H), 1.54 (s, 6H), 1.53 (s, 9H), 1.40 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.2, 173.5, 155.0, 136.0, 135.4, 134.2, 132.9, 132.3, 131.9, 129.8, 129.0, 128.4, 127.8, 127.7, 122.6, 119.2, 115.1, 112.0, 110.4, 101.5, 79.4, 61.9, 61.0, 60.0, 42.4, 40.7, 39.9 (t, J = 18.3 Hz), 35.0, 32.1, 30.3, 26.0, 25.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.53 (t, J = 10.1 Hz, 3F), -111.20 – -112.27 (m, 1F), -113.19 – -114.41 (m, 1F), -125.39 (s, 2F), -126.10 – -126.53 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{41}H_{39}Cl_2F_9N_2O_4Na^+$: 887.2035; found: 887.2044.



2-(1-(*tert*-butyl)-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-4-oxo-2-phenyl-3,4-dihydropyrrolo[4,3,2-*de*]quinolin-5(1*H*)-yl)ethyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (4d). The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); Yellow oil, 61.1 mg, 37% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, J = 6.7, 3.2 Hz, 1H), 7.42 (t, J = 5.8 Hz, 2H), 7.38 (d, J = 9.0 Hz, 1H), 7.32 (d, J = 8.5 Hz, 2H), 7.11 (t, J = 8.0 Hz, 1H), 6.99 (d, J = 7.4 Hz, 1H), 6.67 (dd, J = 15.8, 7.7 Hz, 2H), 6.58 (s, 1H), 4.34 (q, J = 6.0, 4.9 Hz, 2H), 4.29 – 4.20 (m, 2H), 3.87 – 3.73 (m, 2H), 2.99 – 2.82 (m, 1H), 2.30 (s, 3H), 2.16 (s, 3H), 2.12 – 2.00 (m, 1H), 1.82 (t, J = 12.9 Hz, 1H), 1.67 – 1.63 (m, 3H), 1.52 (s, 9H), 1.41 (s, 3H), 1.16 (d, J = 2.7 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 178.0, 173.5, 157.1, 136.5, 136.1, 135.4, 134.2, 132.9, 132.6, 132.0, 130.4, 129.0, 127.8, 127.6, 123.8, 122.6, 120.8, 115.1, 112.1, 110.3, 107.7, 101.7, 68.0, 61.2, 60.0, 56.4, 42.4, 42.2, 40.9, 39.9 (t, J = 18.9 Hz), 37.1, 32.1, 30.4, 25.2, 21.5, 15.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.00 (t, J = 10.1 Hz, 3F), -110.51 – -111.79 (m, 1F), -112.64 – -114.11 (m, 1F), -124.75 – -125.20 (m, 2F), -125.59 – -126.05 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{43}H_{47}F_9N_2O_4Na^+$: 849.3284; found: 849.3292.

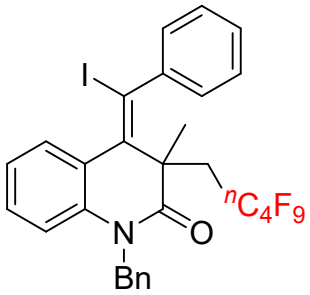


2-(1-(*tert*-butyl)-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-4-oxo-2-phenyl-3,4-dihydropyrrolo[4,3,2-*de*]quinolin-5(1*H*)-yl)ethyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (4e). The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 76.7 mg, 43% yield; mp 107.5-108.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (t, J = 2.3 Hz, 1H), 8.10 (dd, J = 8.8, 2.3 Hz, 1H), 7.52 (d, J = 6.5 Hz, 1H), 7.47 (dd, J = 7.5, 5.5 Hz, 2H), 7.44 – 7.40 (m, 2H), 7.38 (s, 1H), 7.15 (t, J = 8.0 Hz, 1H), 7.04 (d, J = 8.9 Hz, 1H), 6.72 (d, J = 7.3 Hz, 1H), 4.61 (t, J = 5.6 Hz, 2H), 4.42 (t, J = 5.8 Hz, 2H), 3.94 (d, J = 6.5 Hz, 2H), 3.11 – 2.83 (m, 1H), 2.73 (s, 3H), 2.28 – 2.20 (m, 1H), 2.19 – 2.05 (m, 1H), 1.57 (s, 9H), 1.47 (s, 3H), 1.13 (d, J = 6.7 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.5, 167.5, 162.5, 162.0, 161.6, 135.9, 135.4, 134.1, 132.8, 132.6, 132.1, 131.8, 128.9, 128.4, 127.6, 126.1, 122.4, 121.5, 115.4, 115.0, 112.6, 111.9, 110.3, 107.7, 103.0, 101.4, 75.8, 61.9, 60.0, 42.4, 40.8, 39.8 (t, J = 18.1 Hz), 32.0, 30.2, 28.2, 19.1, 17.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.55 (t, J = 9.6 Hz, 3F), -110.99 – -112.32 (m, 1F), -113.06 – -114.52 (m, 1F), -125.17 – -125.74 (m, 2F), -126.05 – -126.71 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{44}H_{41}F_9N_4O_4SNa^+$: 915.2597; found: 915.2595.



5-benzyl-3-methyl-2-phenyl-3-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-1,5-dihydropyrrolo[4,3,2-*de*]quinolin-4(3*H*)-one (3A). The product was purified by column

chromatography (petroleum ether / ethyl acetate = 10:1); White solid, 127.2 mg, 93% yield; mp 195.3-197.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.50 (d, J = 1.9 Hz, 2H), 7.47 (d, J = 3.1 Hz, 2H), 7.32 (t, J = 6.6 Hz, 3H), 7.28 (d, J = 7.8 Hz, 2H), 7.25 – 7.22 (m, 1H), 7.06 (t, J = 7.8 Hz, 1H), 6.98 (d, J = 8.1 Hz, 1H), 6.49 (d, J = 7.5 Hz, 1H), 5.26 (s, 2H), 3.40 – 3.23 (m, 1H), 2.50 – 2.36 (m, 1H), 1.78 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.7, 137.2, 133.2, 133.1, 132.8, 132.7, 129.9, 129.0, 128.8, 128.7, 127.2, 127.0, 124.1, 115.5, 110.9, 105.9, 102.9, 46.2, 43.2, 39.8 (t, J = 18.6 Hz), 33.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.30 (t, J = 10.1 Hz, 3F), -109.38 – -110.63 (m, 1F), -112.64 – -113.91 (m, 1F), -122.33 (s, 2F), -123.36 (s, 2F), -124.43 – -124.90 (m, 2F), -126.42 – -126.83 (m, 2F); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{31}H_{21}F_{13}N_2ONa^+$: 707.1339; found: 707.1332.



(*E*)-1-benzyl-4-(iodo(phenyl)methylene)-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-3,4-dihydroquinolin-2(1*H*)-one (5) (ref. 4). The product was purified by column chromatography (petroleum ether / ethyl acetate = 20:1); Yellow oil, 121.3 mg, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 7.7 Hz, 1H), 7.38 – 7.33 (m, 6H), 7.30 – 7.28 (m, 2H), 7.26 (d, J = 7.1 Hz, 1H), 7.19 (d, J = 7.5 Hz, 2H), 7.14 (d, J = 7.5 Hz, 1H), 6.97 (d, J = 8.1 Hz, 1H), 5.30 (d, J = 16.3 Hz, 1H), 5.11 (d, J = 16.2 Hz, 1H), 2.46 – 2.31 (m, 1H), 2.10 – 1.92 (m, 1H), 1.18 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.1, 146.4, 139.6, 137.4, 136.7, 132.2, 131.4, 130.1, 129.1, 128.5, 128.4, 128.3, 128.0, 127.7, 127.5, 126.3, 123.5, 115.4, 101.0, 48.7, 47.6, 37.3 (t, J = 19.8 Hz), 21.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.02 (t, J = 10.1 Hz, 3F), -107.46 – -108.54 (m, 1F), -113.77 – -114.78 (m, 1F), -124.95 – -125.19 (m, 2F), -125.86 (dt, J = 59.6, 13.3 Hz, 2F).

5. References

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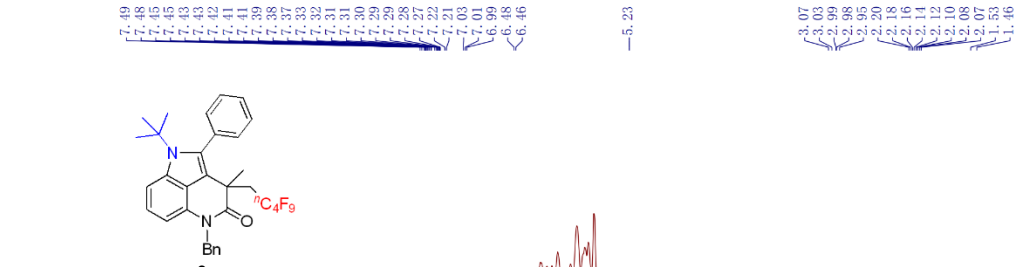
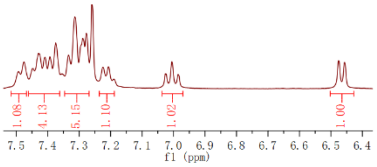
3. Li, R.; Li, B.; Zhang, H.; Ju, C.-W.; Qin, Y.; Xue, X.-S.; Zhao, D. A ring expansion strategy towards diverse azaheterocycles. *Nat. Chem.* **2021**, *13,* 1006-1016.
4. Wang, S.-W.; Yu, J.; Zhou, Q.-Y.; Chen, S.-Y.; Xu Z.-H.; Tang, S.; *ACS Sustainable Chem. Eng.* **2019**, *7*, 10154-10162.

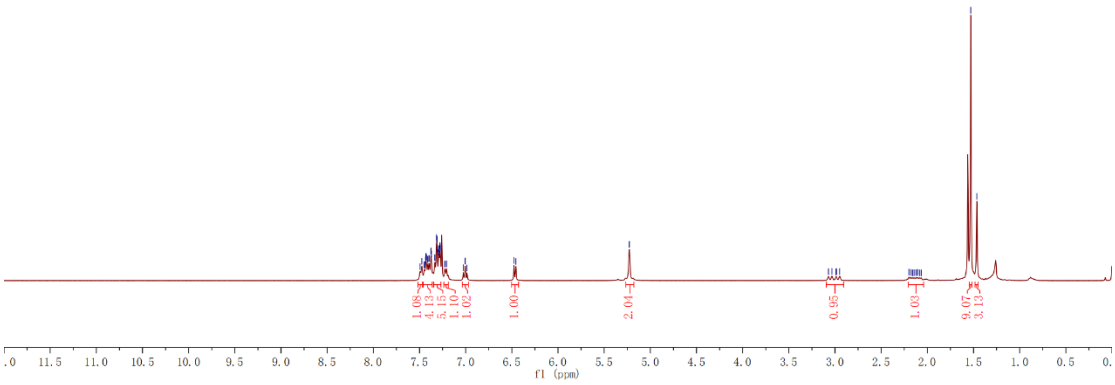
6. ^{1}H, ^{13}C, ^{19}F NMR spectra of products (3aa-za, 3ab-ac, 3Aa, 4a-e, 3A, 5)

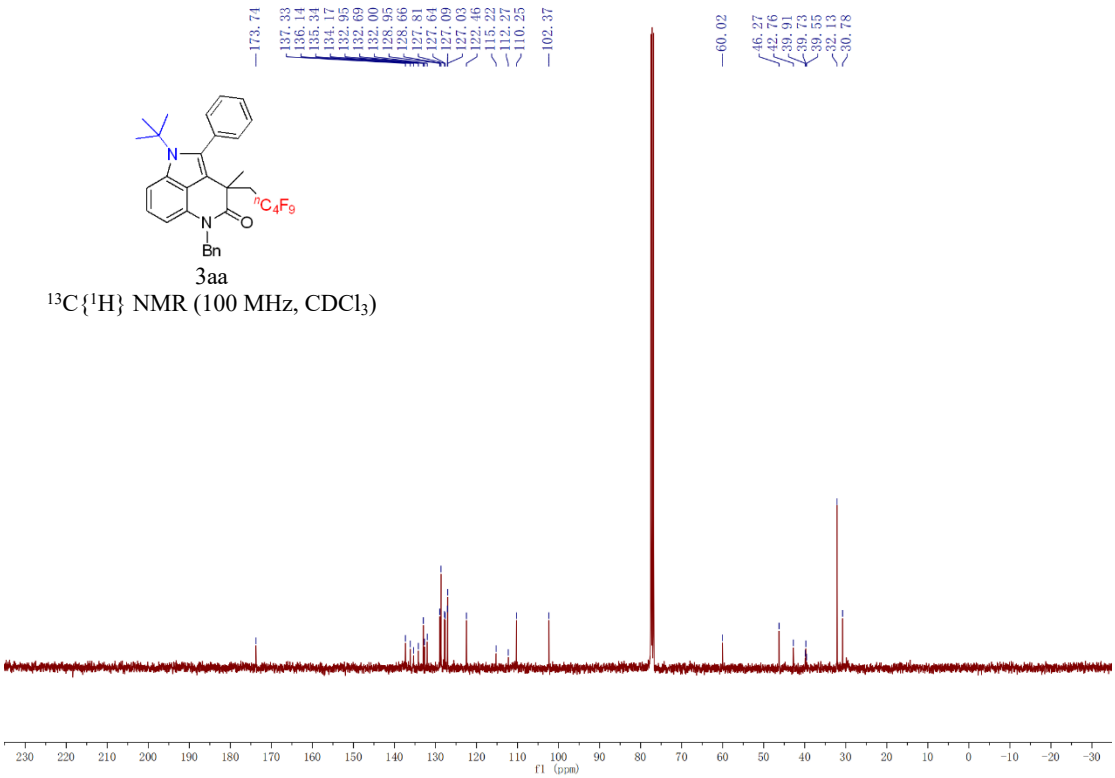


3aa

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

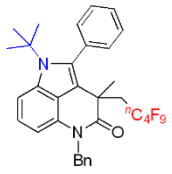






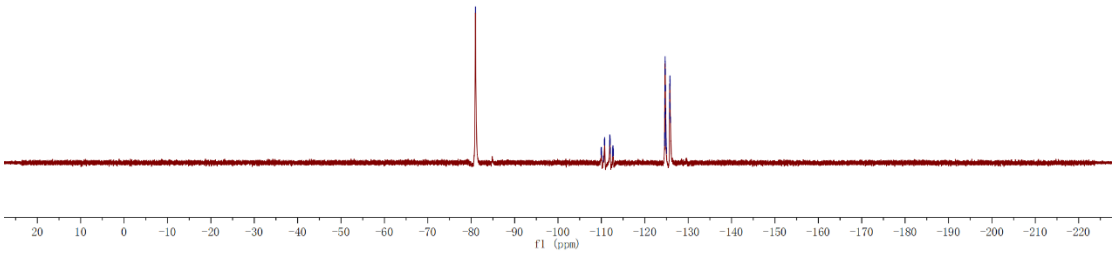
3aa

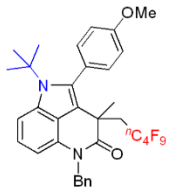
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



3aa

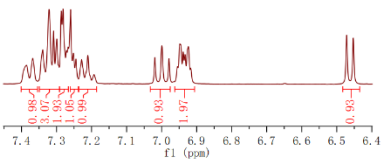
^{19}F NMR (377 MHz, $CDCl_3$)

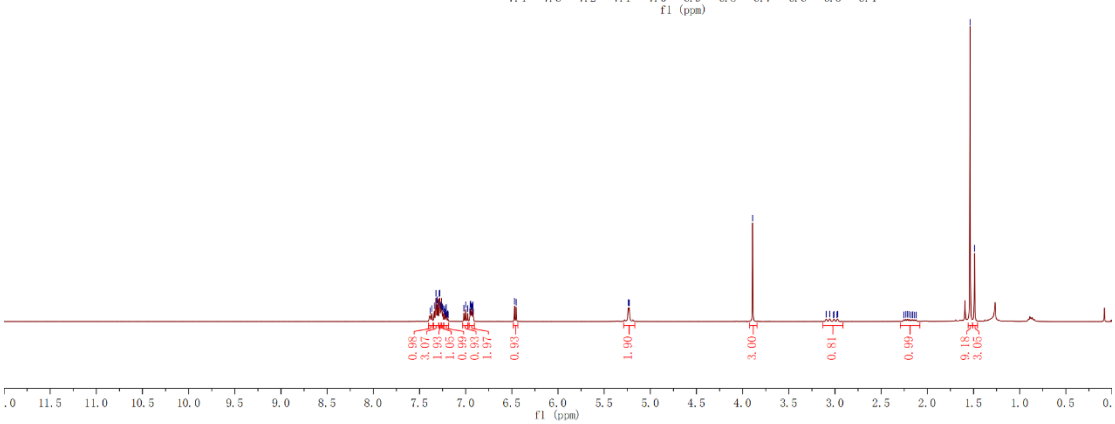


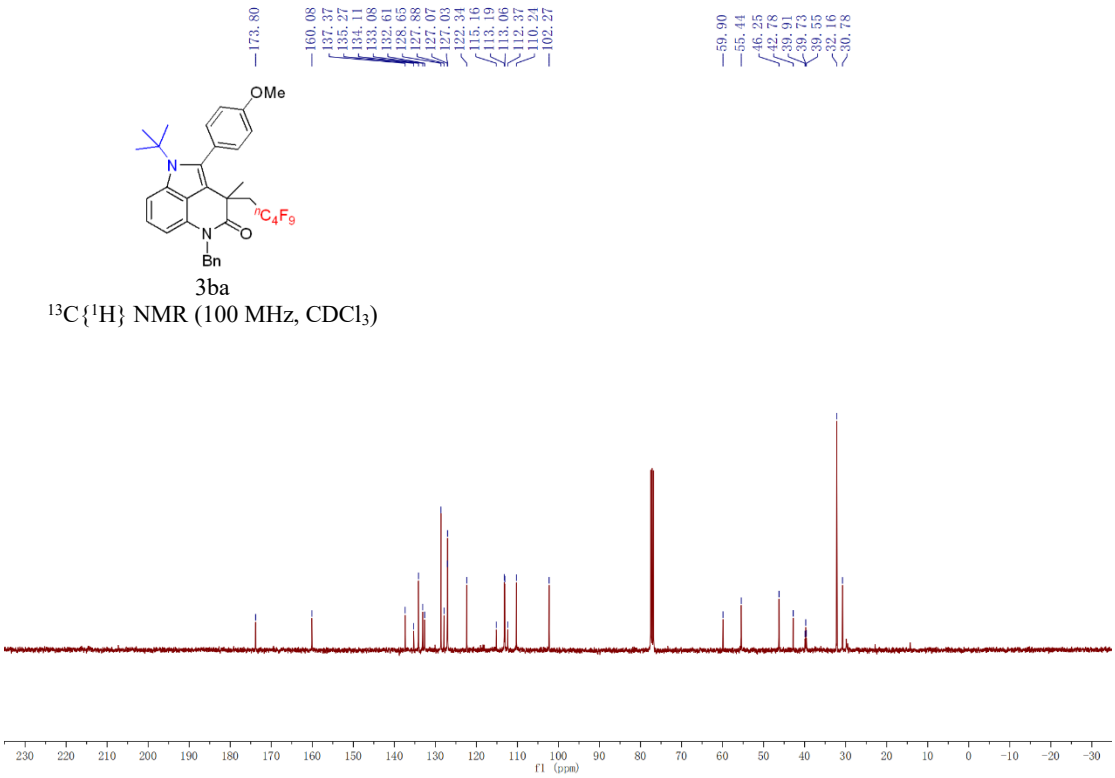


3ba

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

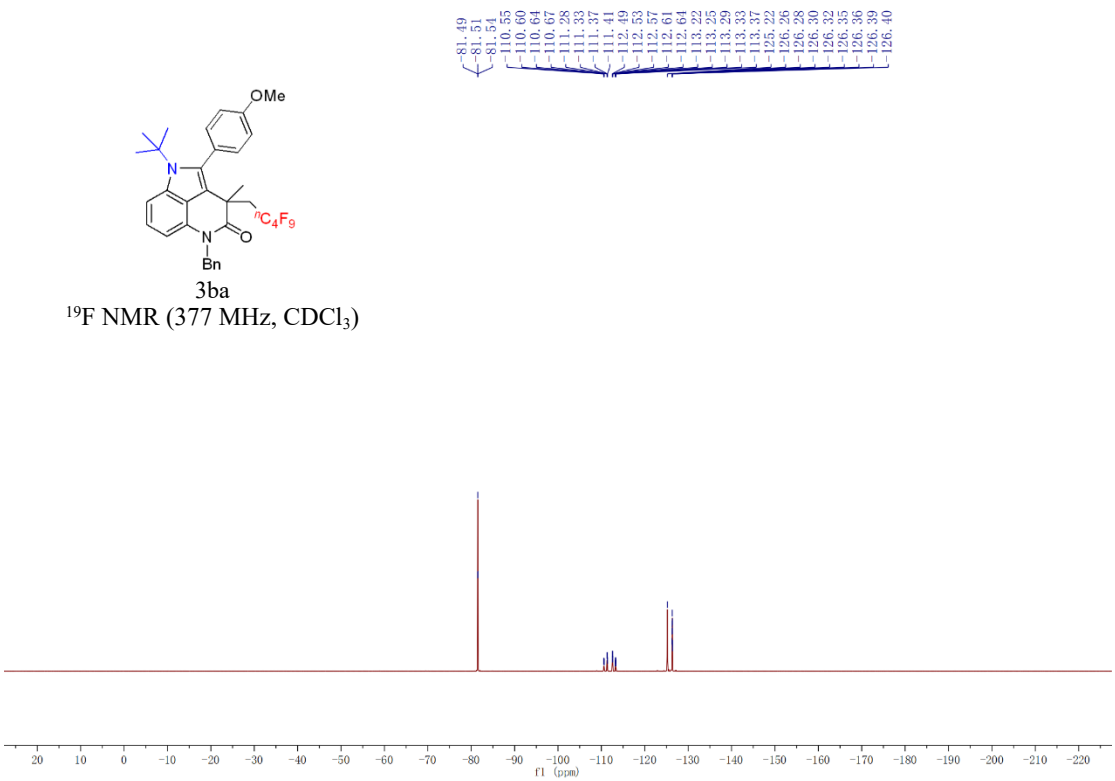






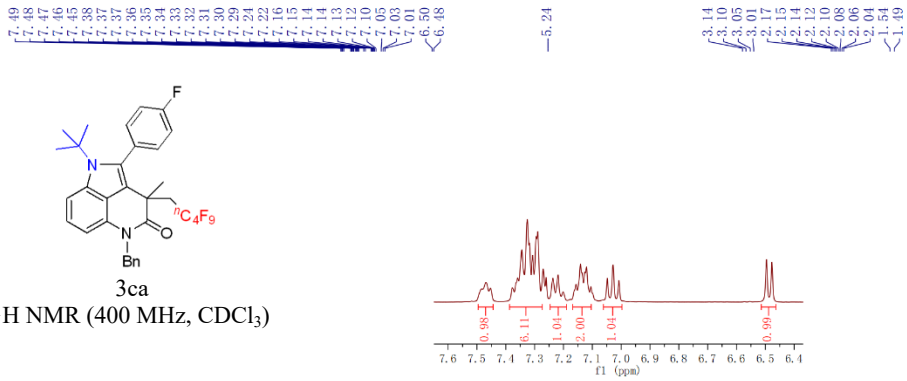
3ba

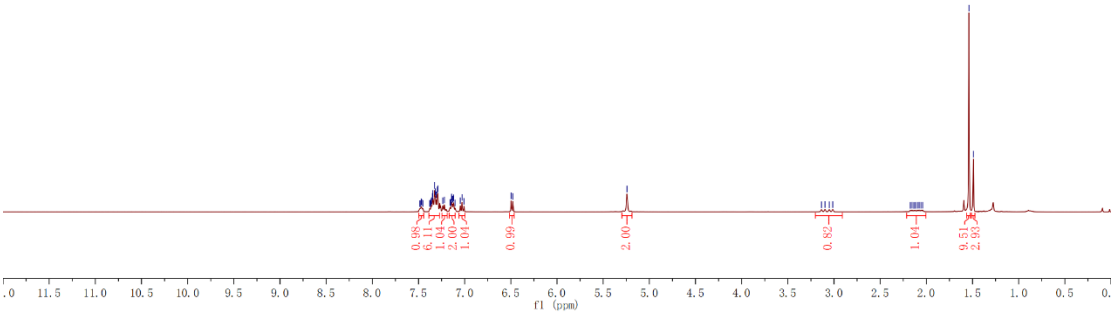
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



3ba

^{19}F NMR (377 MHz, $CDCl_3$)



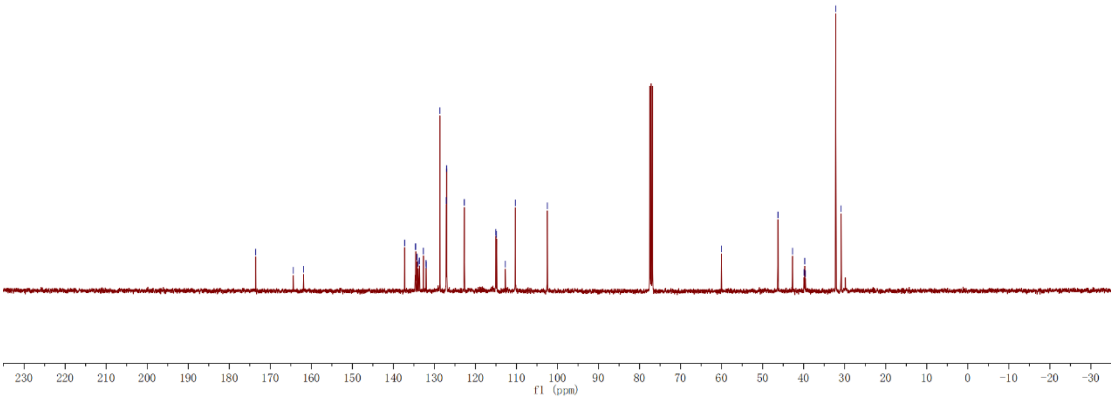


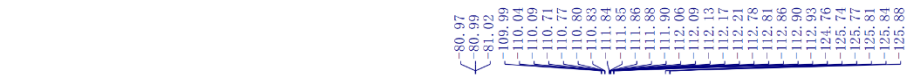
3ca

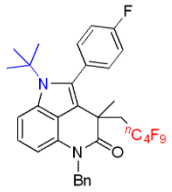
^{1}H NMR (400 MHz, $CDCl_3$)

3ca

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

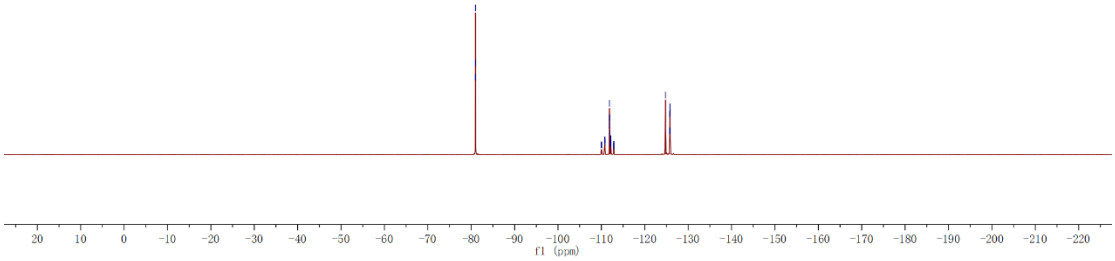


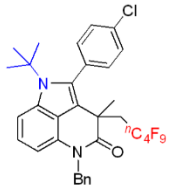




3ca

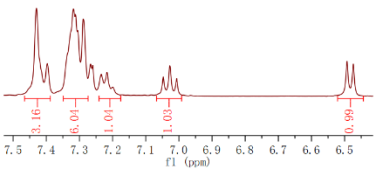
^{19}F NMR (377 MHz, $CDCl_3$)

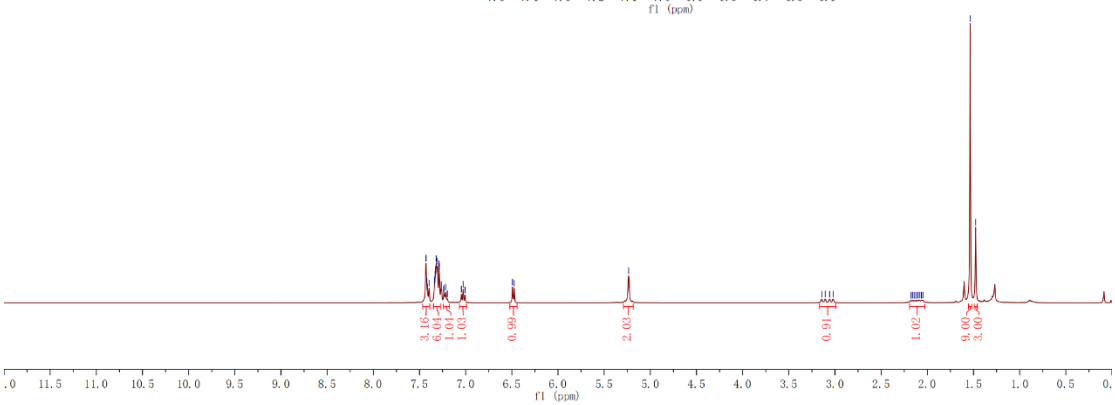


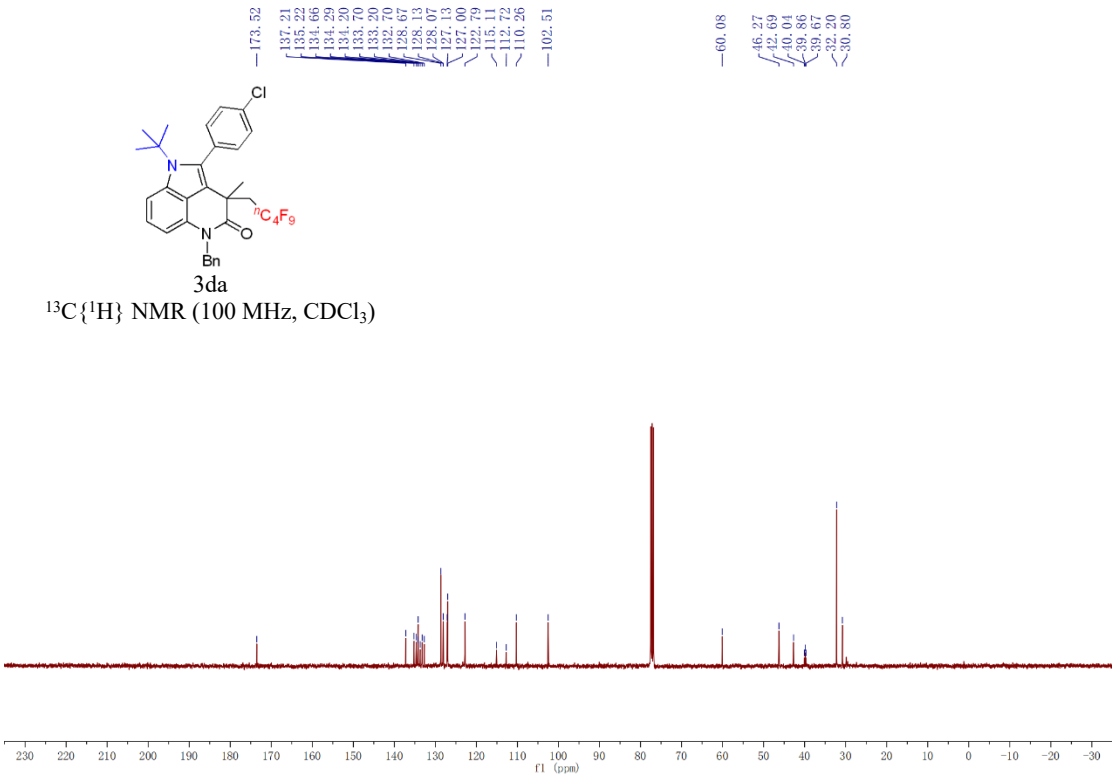


3da

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

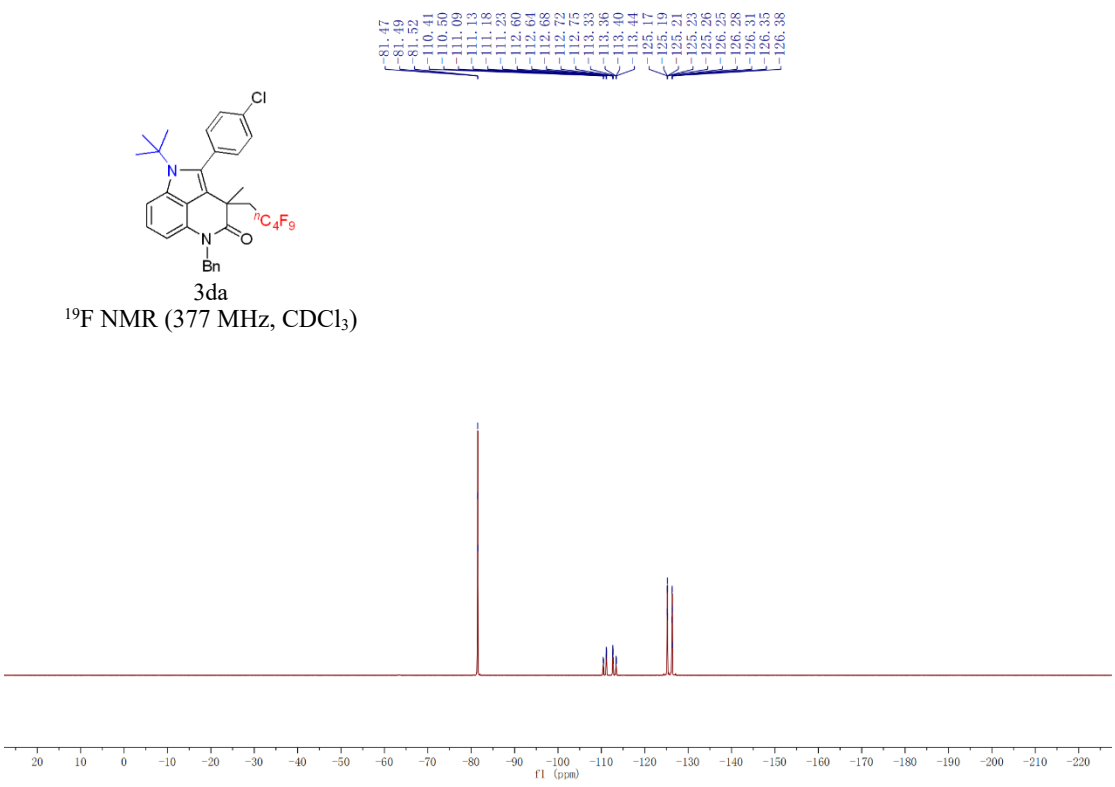






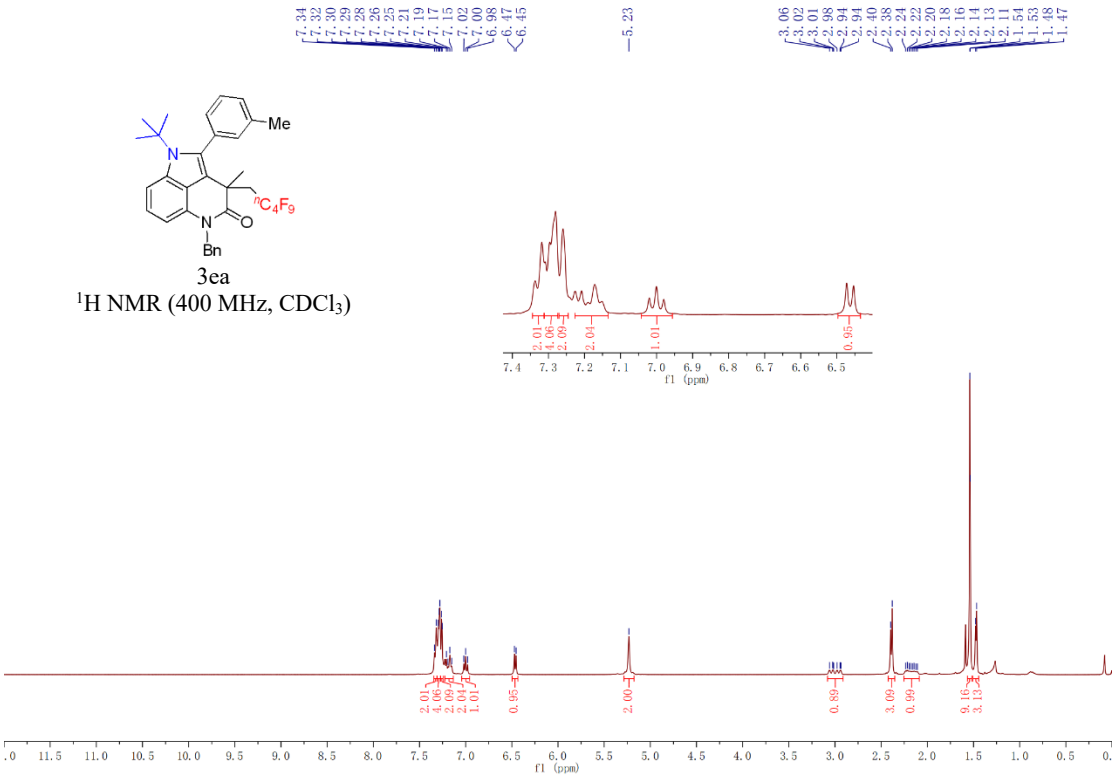
3da

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



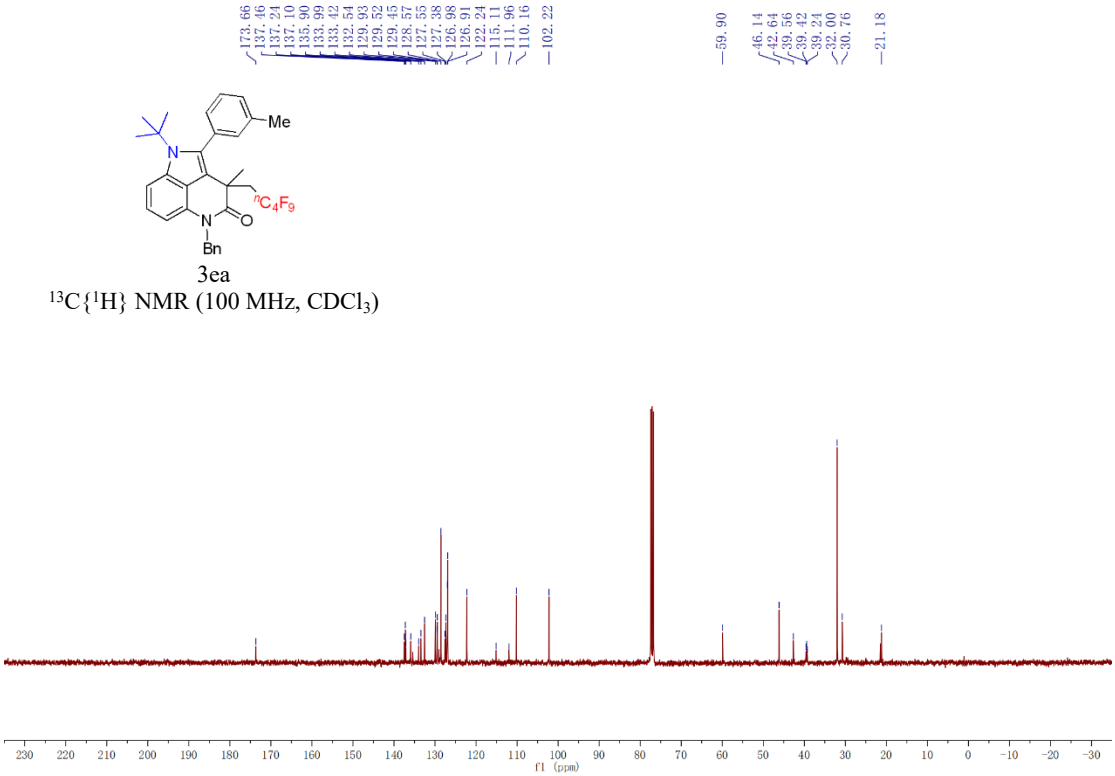
3da

^{19}F NMR (377 MHz, $CDCl_3$)



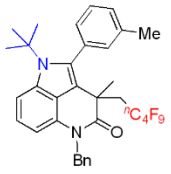
3ea

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



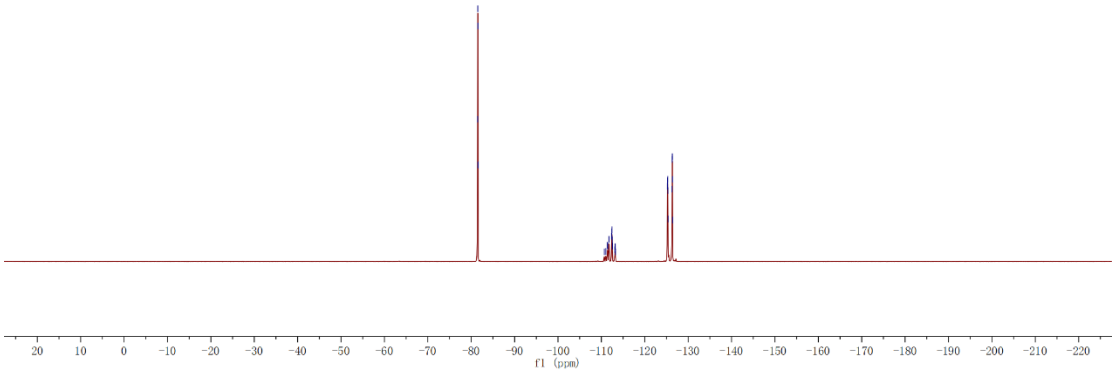
3ea

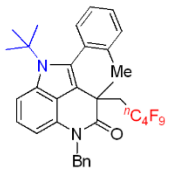
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



3ea

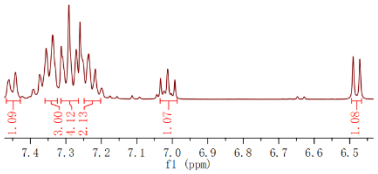
^{19}F NMR (377 MHz, $CDCl_3$)

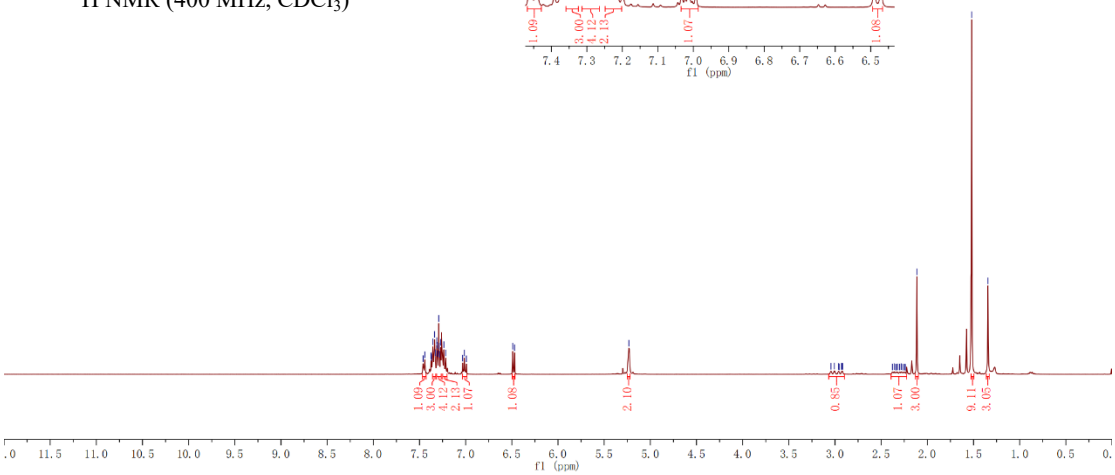


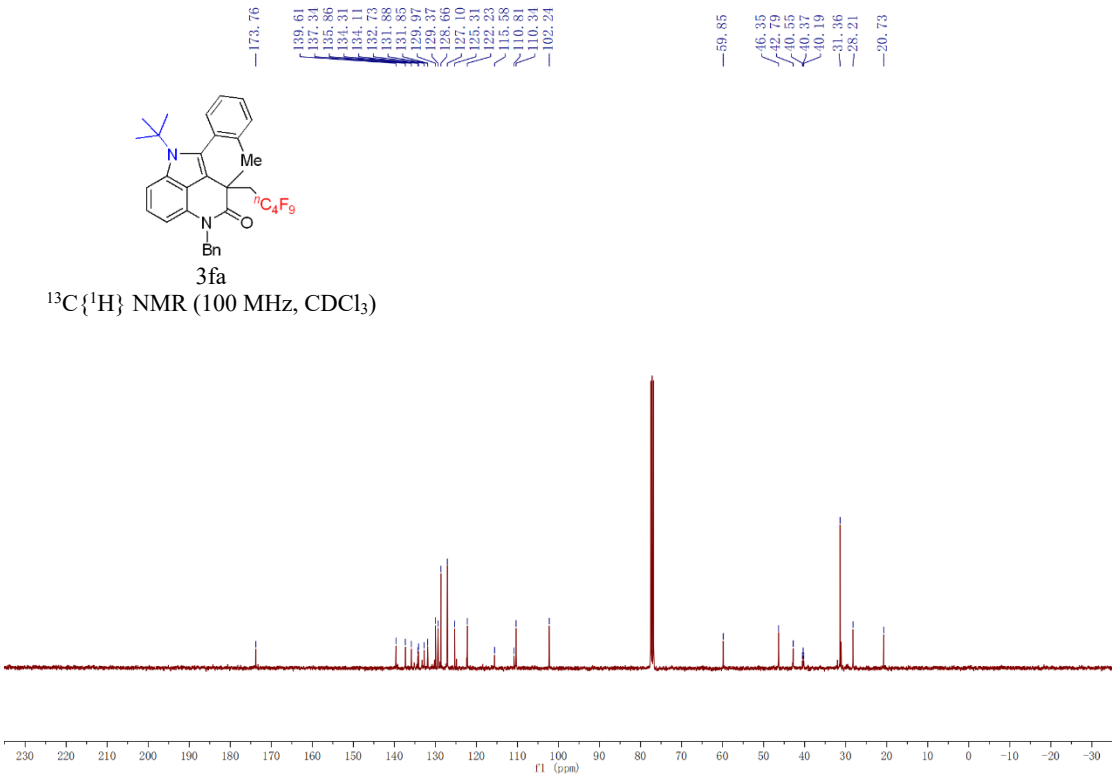


3fa

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

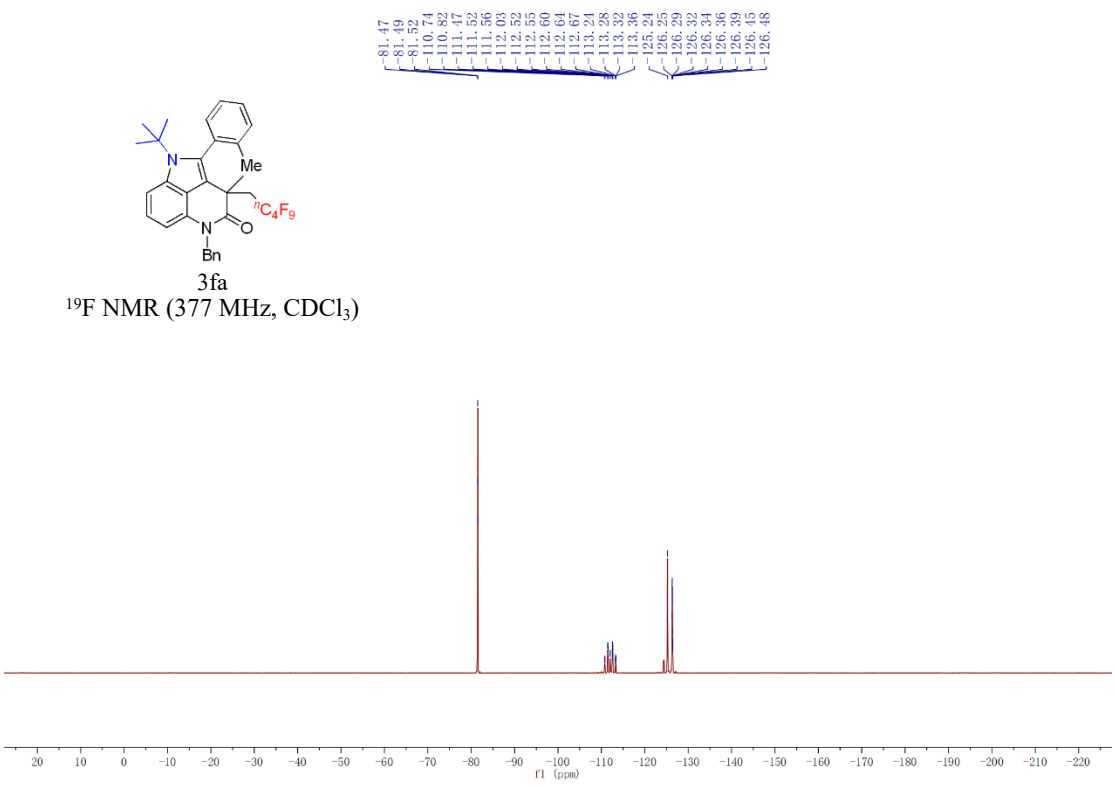






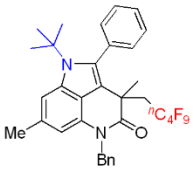
3fa

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



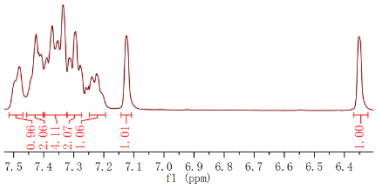
3fa

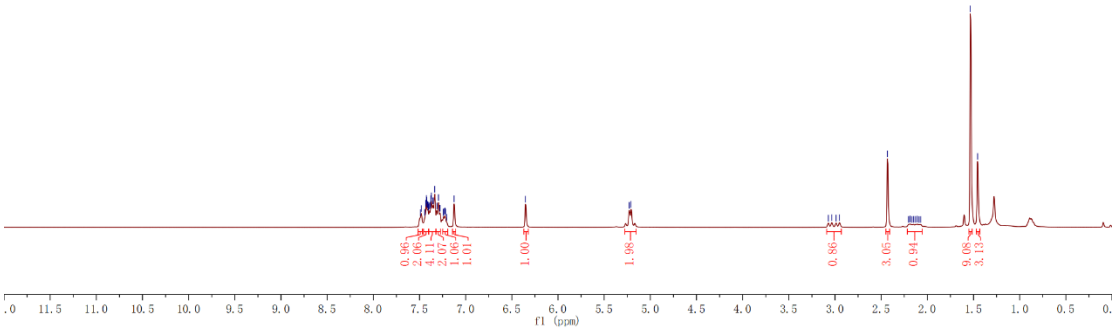
^{19}F NMR (377 MHz, $CDCl_3$)

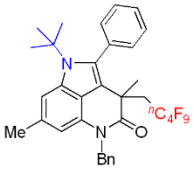


3ga

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

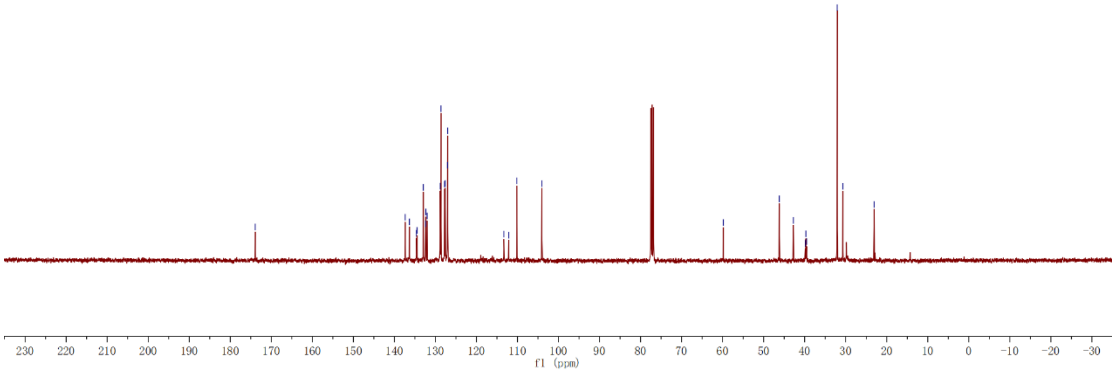


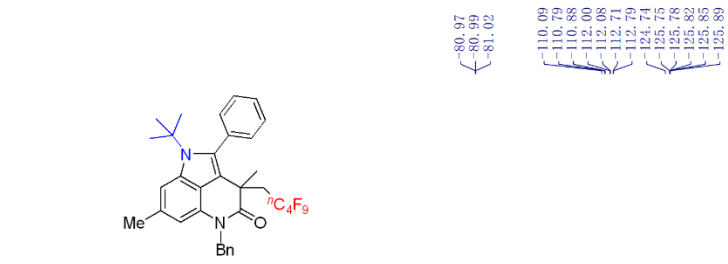




3ga

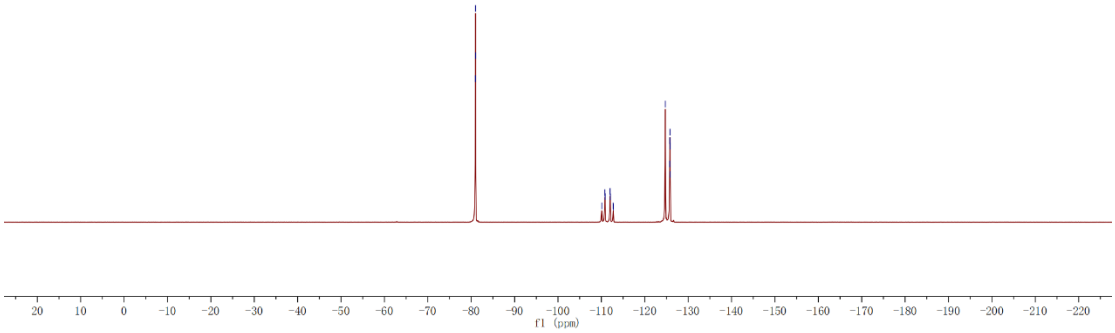
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)





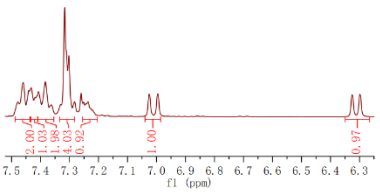
3ga

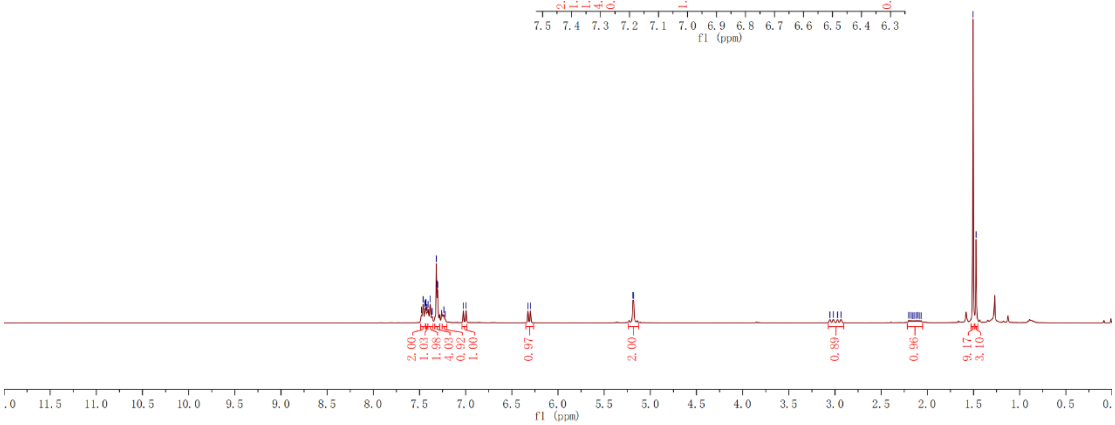
^{19}F NMR (377 MHz, $CDCl_3$)

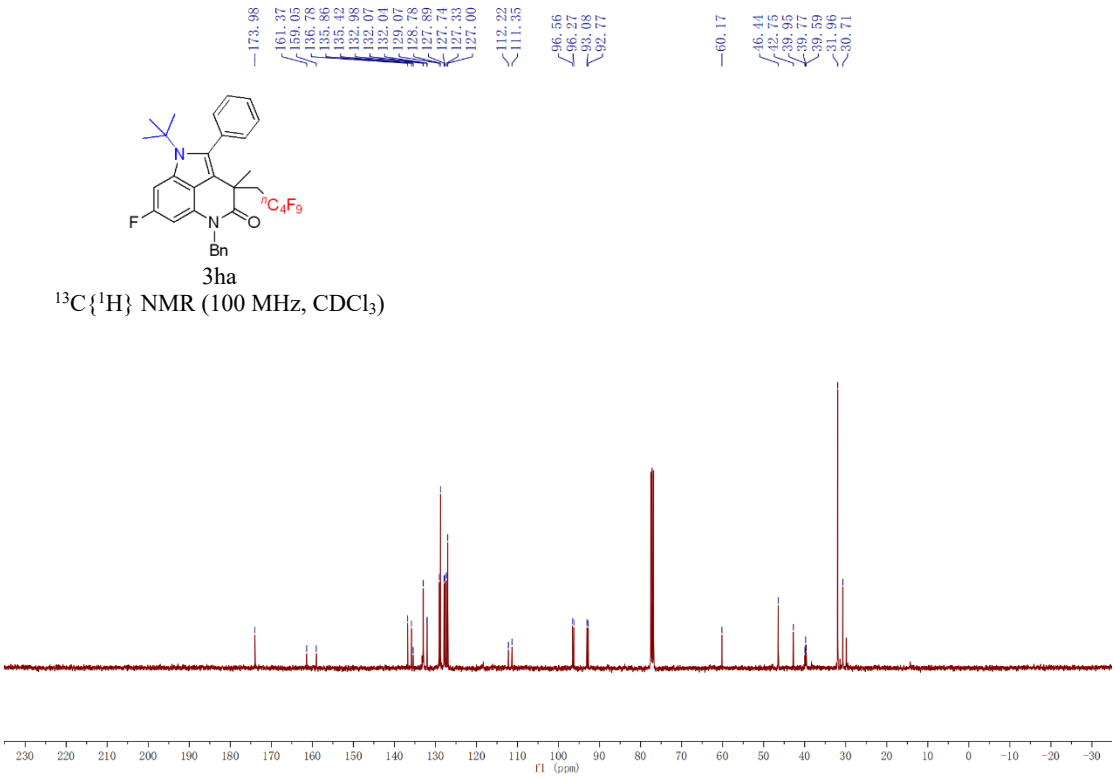


3ha

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

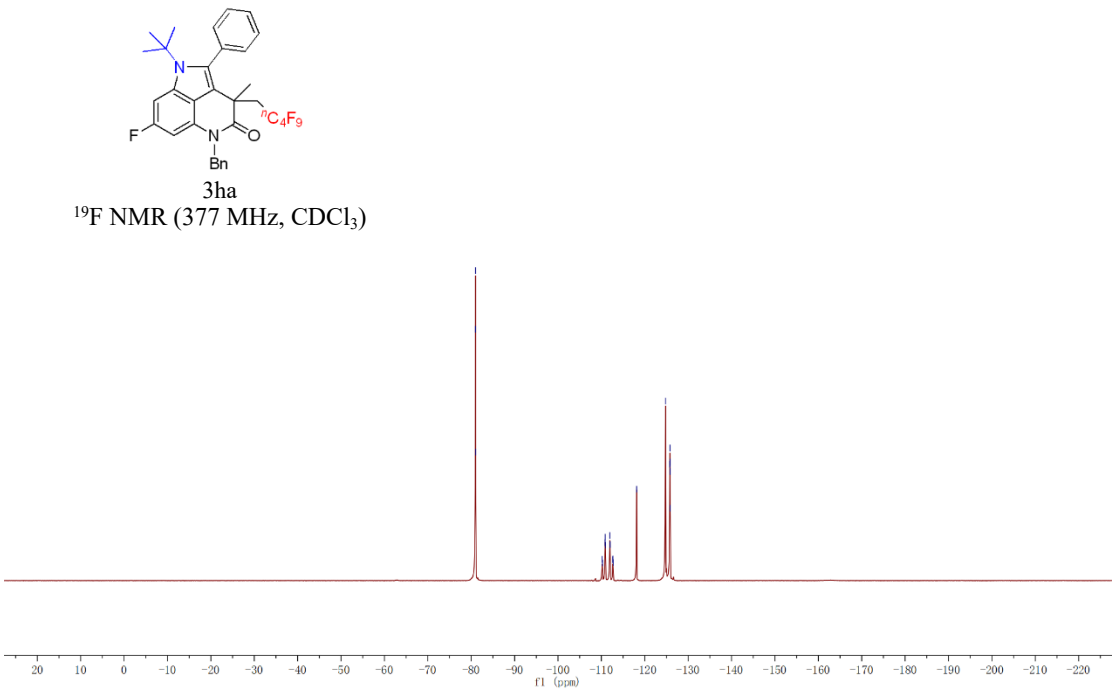






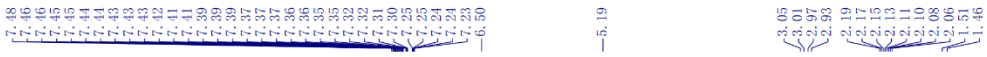
3ha

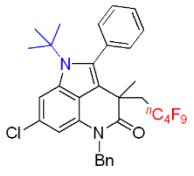
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



3ha

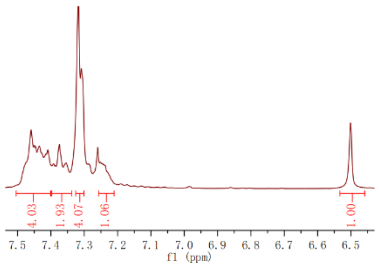
^{19}F NMR (377 MHz, $CDCl_3$)

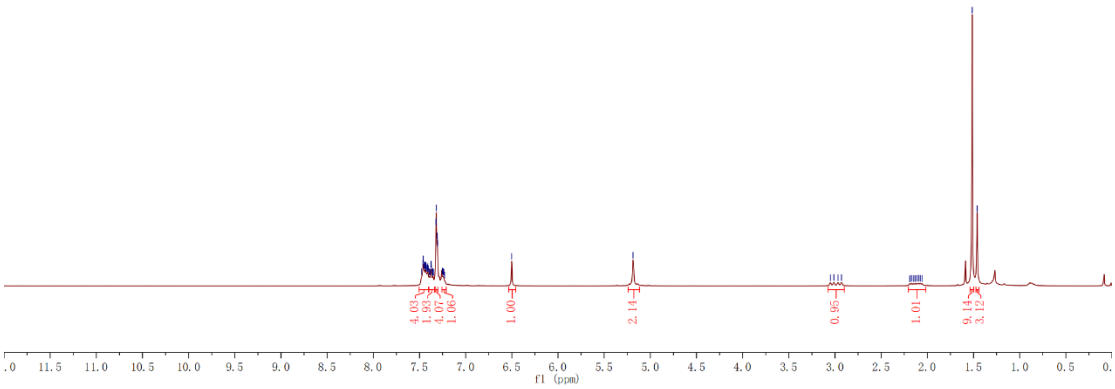


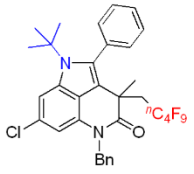


3ia

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

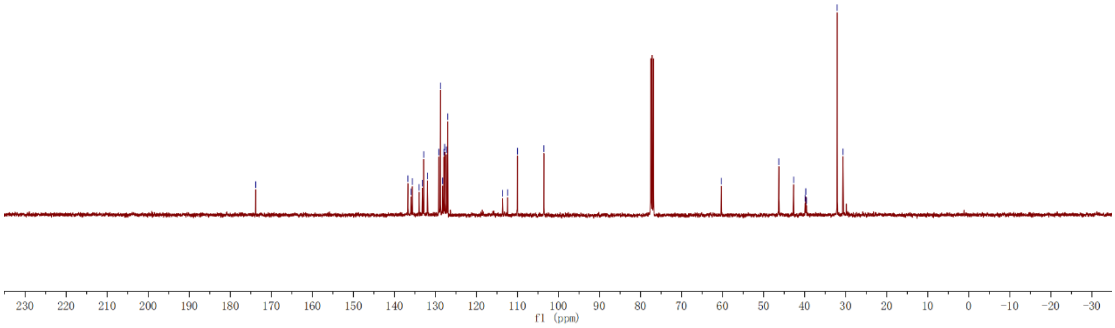


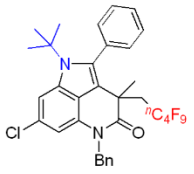




3ia

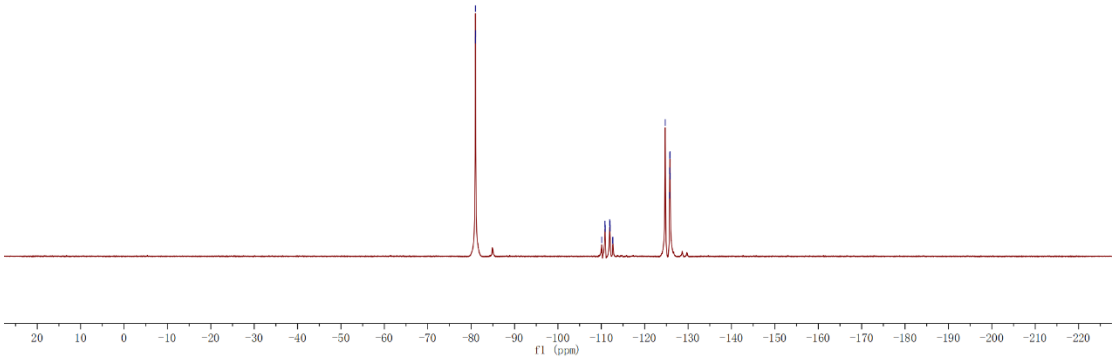
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

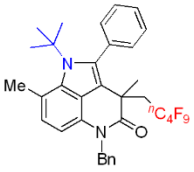




3ia

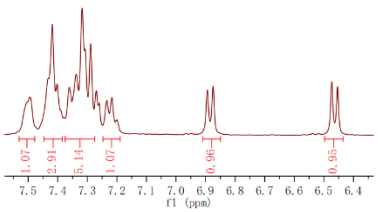
^{19}F NMR (377 MHz, $CDCl_3$)

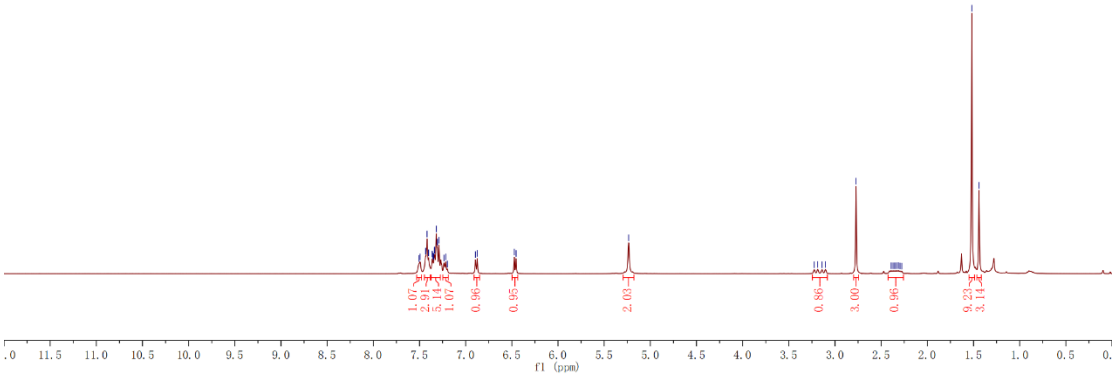


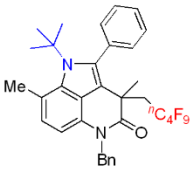


3ja

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

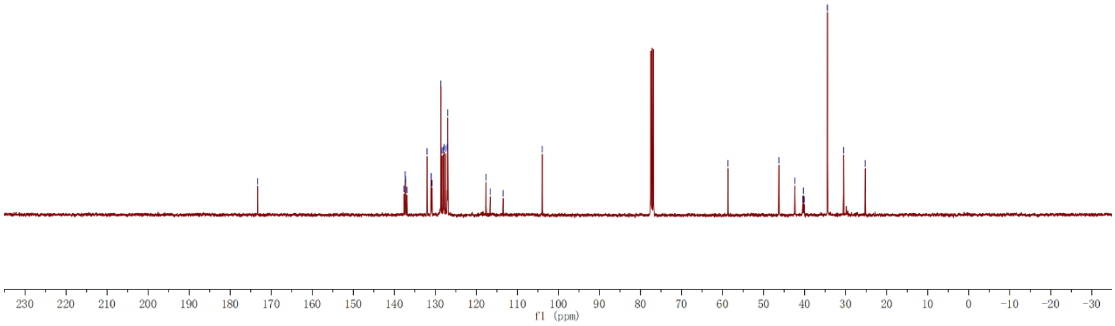


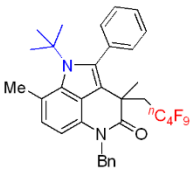




3ja

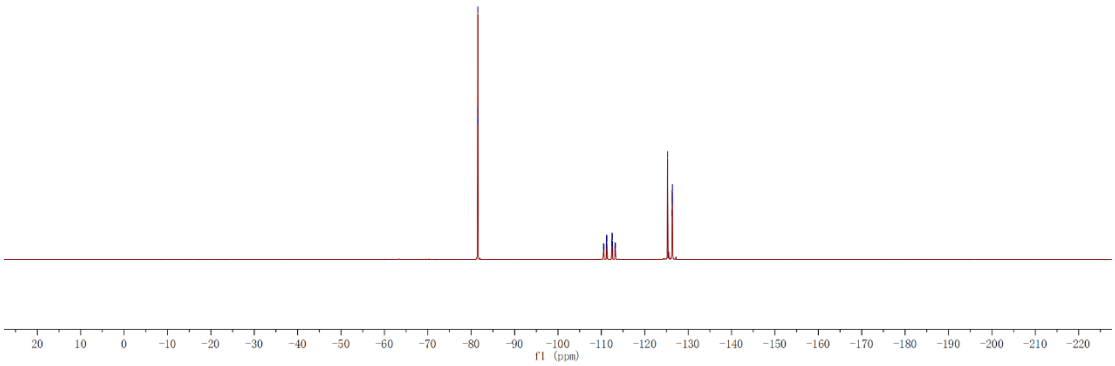
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

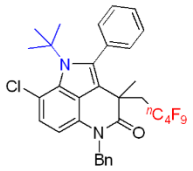




3ja

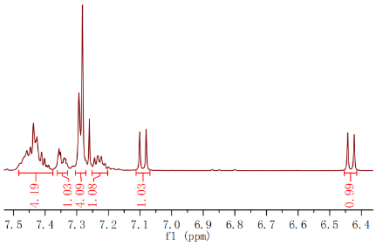
^{19}F NMR (377 MHz, $CDCl_3$)

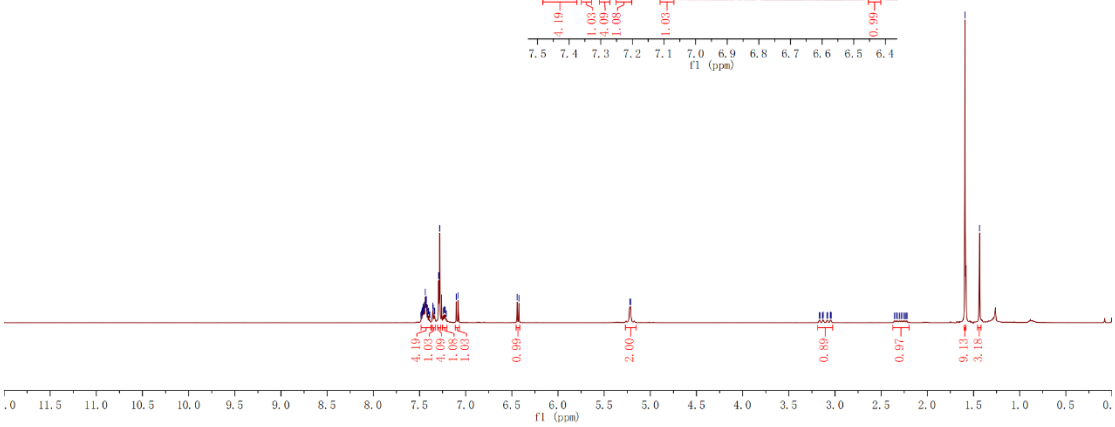


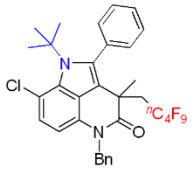


3ka

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

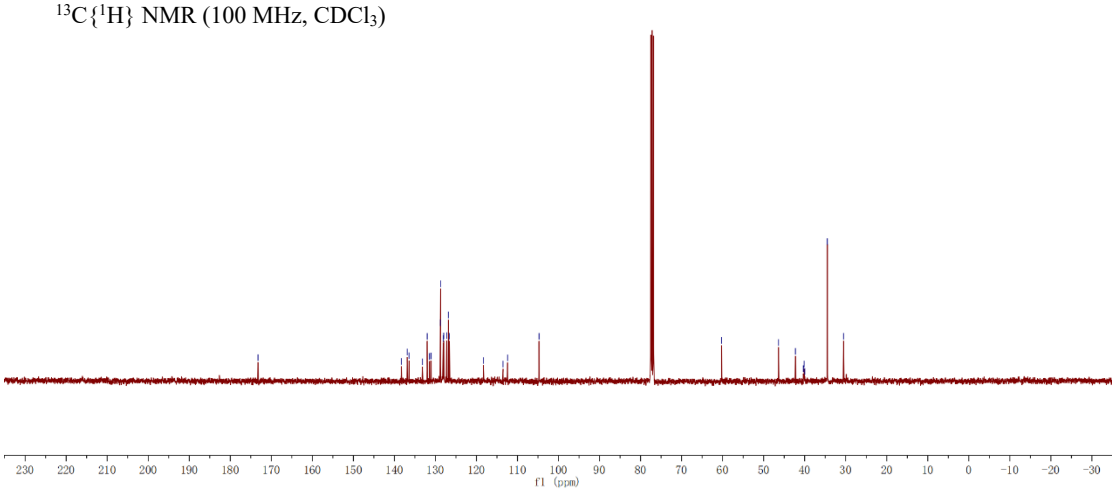


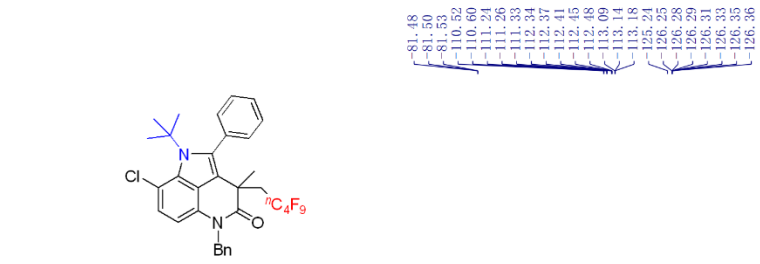




3ka

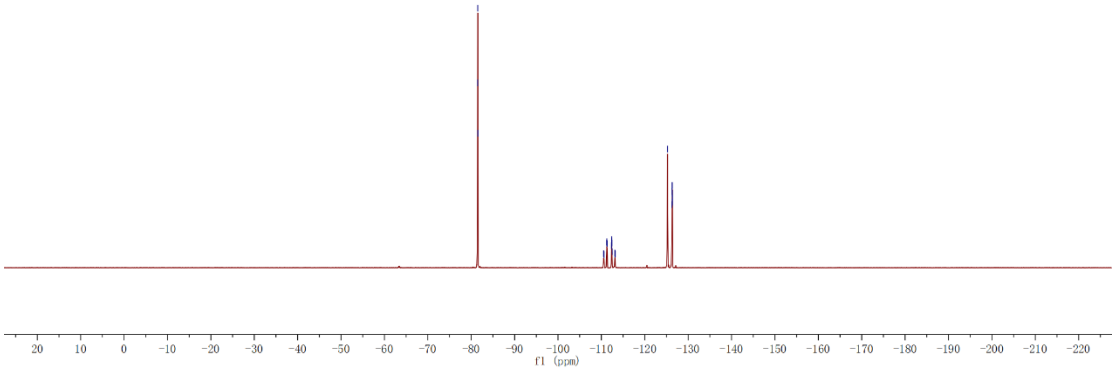
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

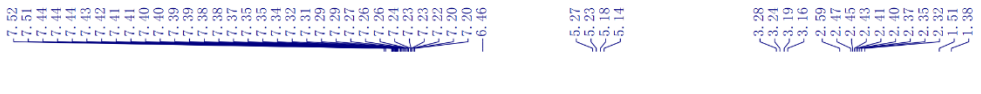


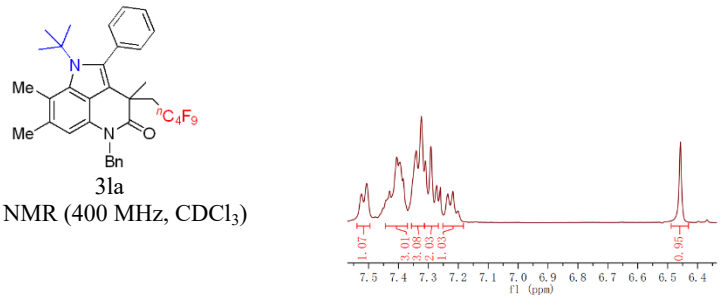


3ka

^{19}F NMR (377 MHz, $CDCl_3$)

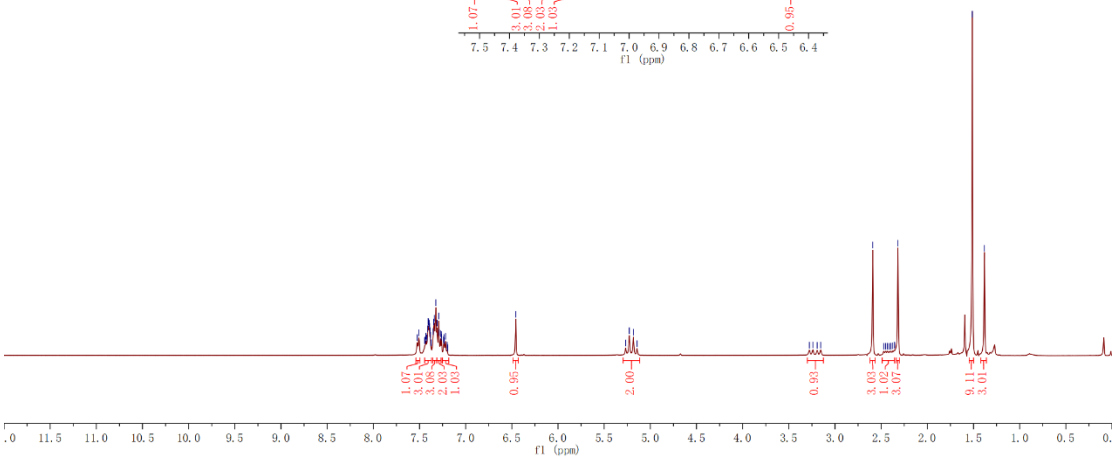


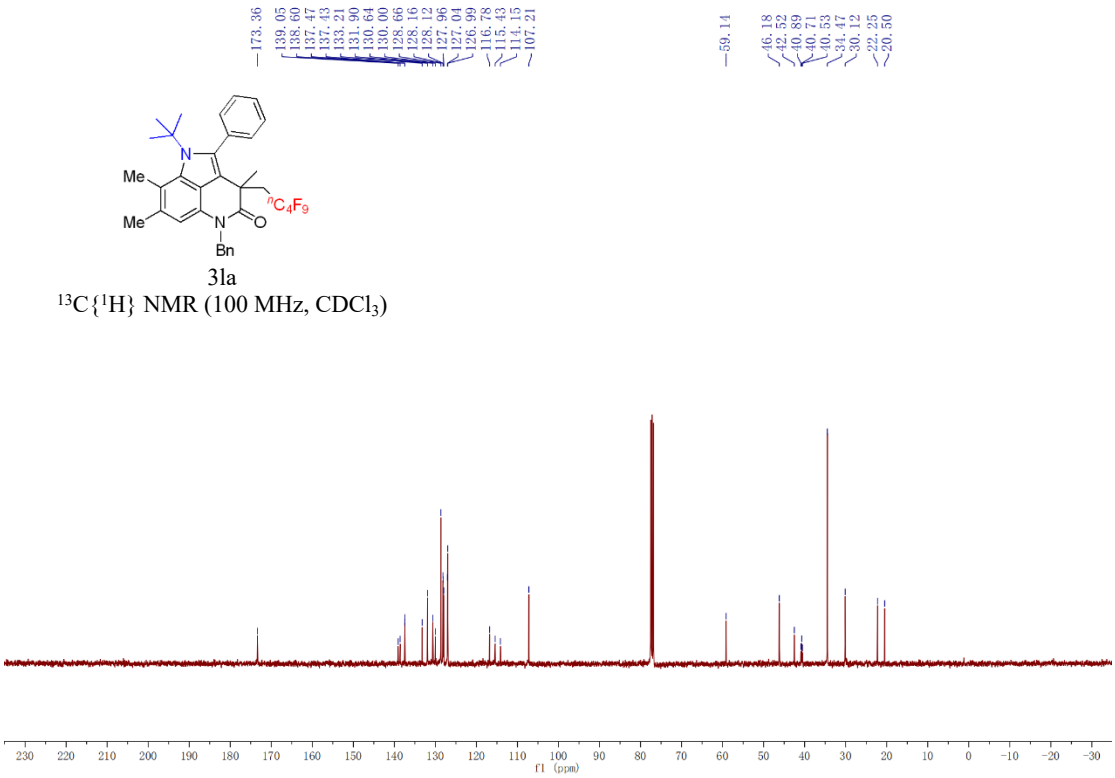




3la

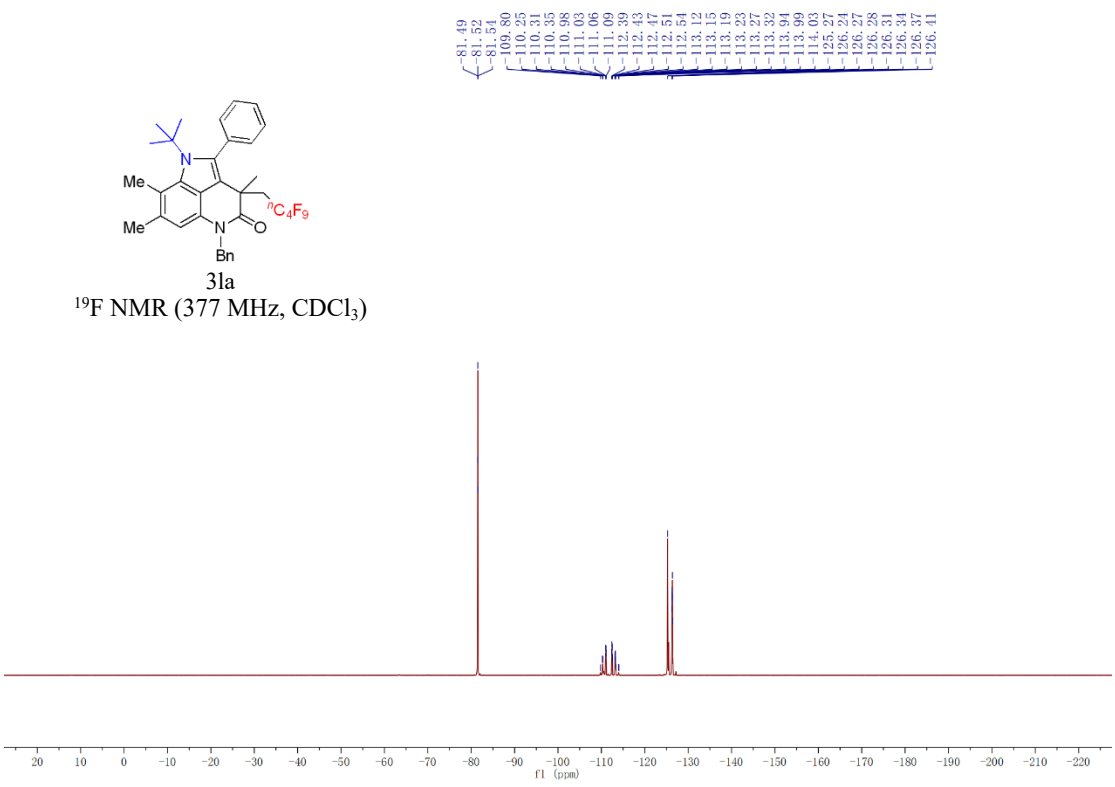
^{1}H NMR (400 MHz, $CDCl_3$)





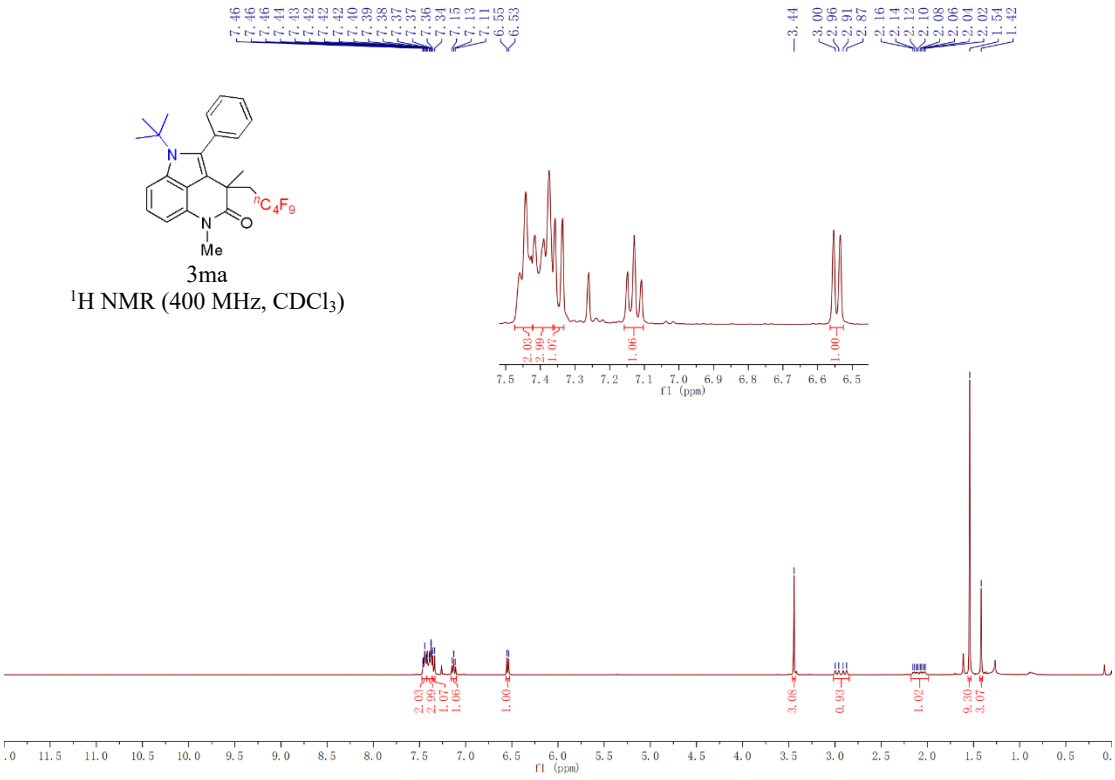
3la

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



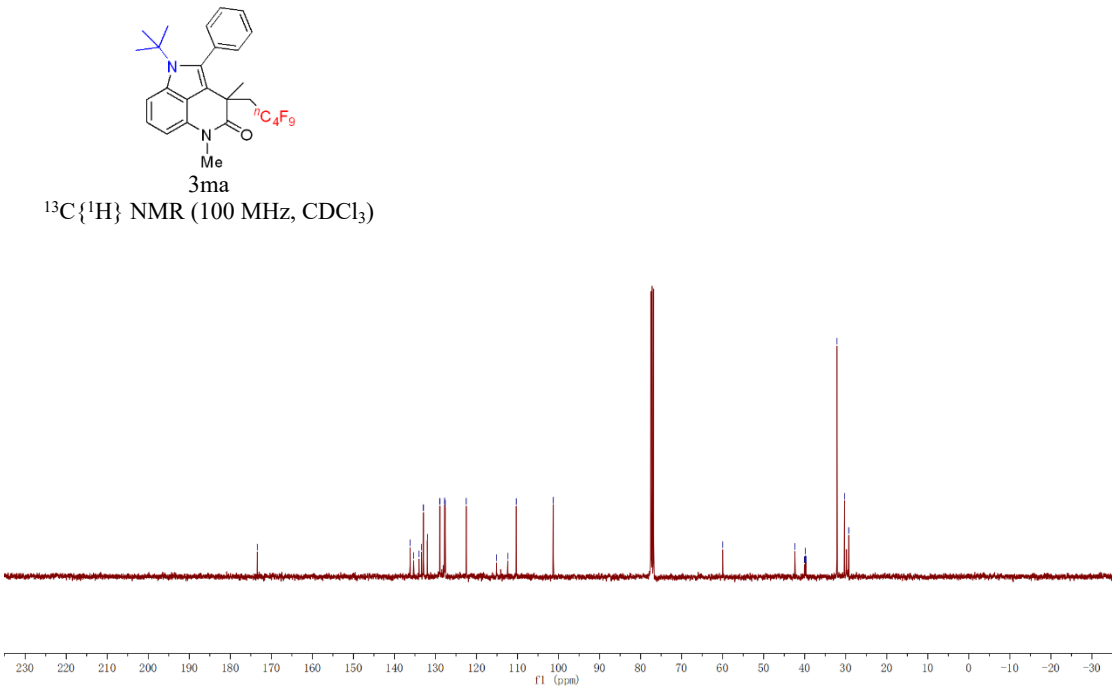
3la

^{19}F NMR (377 MHz, $CDCl_3$)



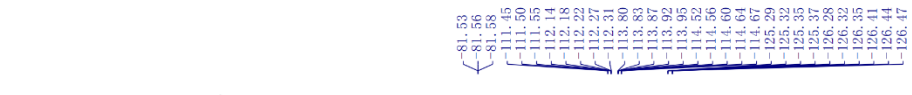
3ma

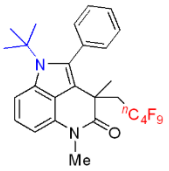
^{1}H NMR (400 MHz, $CDCl_3$)



3ma

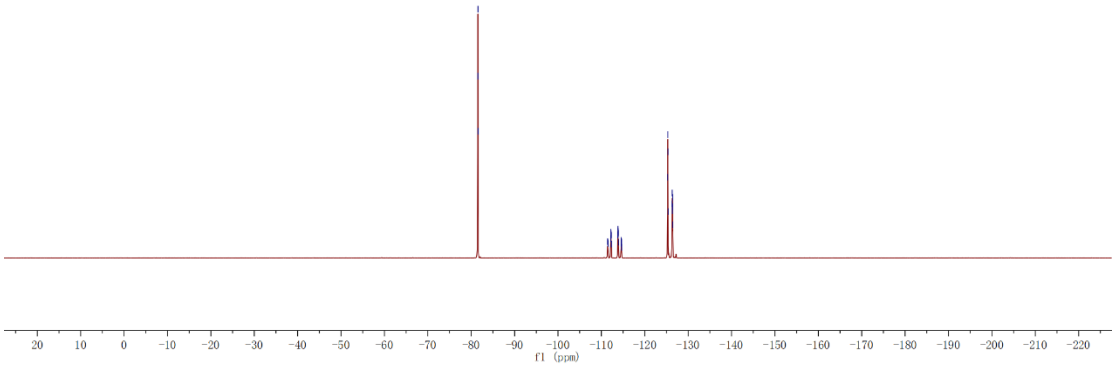
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

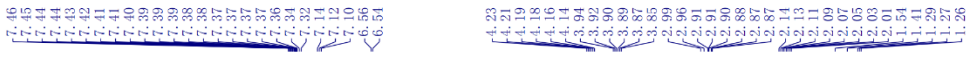


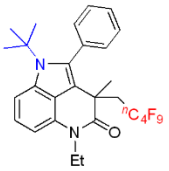


3ma

^{19}F NMR (377 MHz, $CDCl_3$)

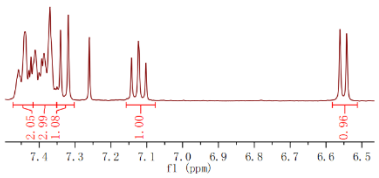


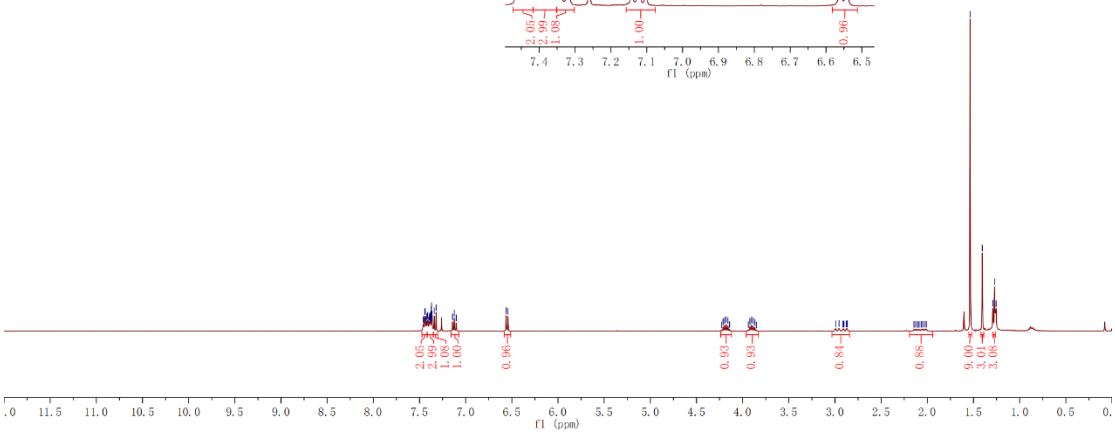


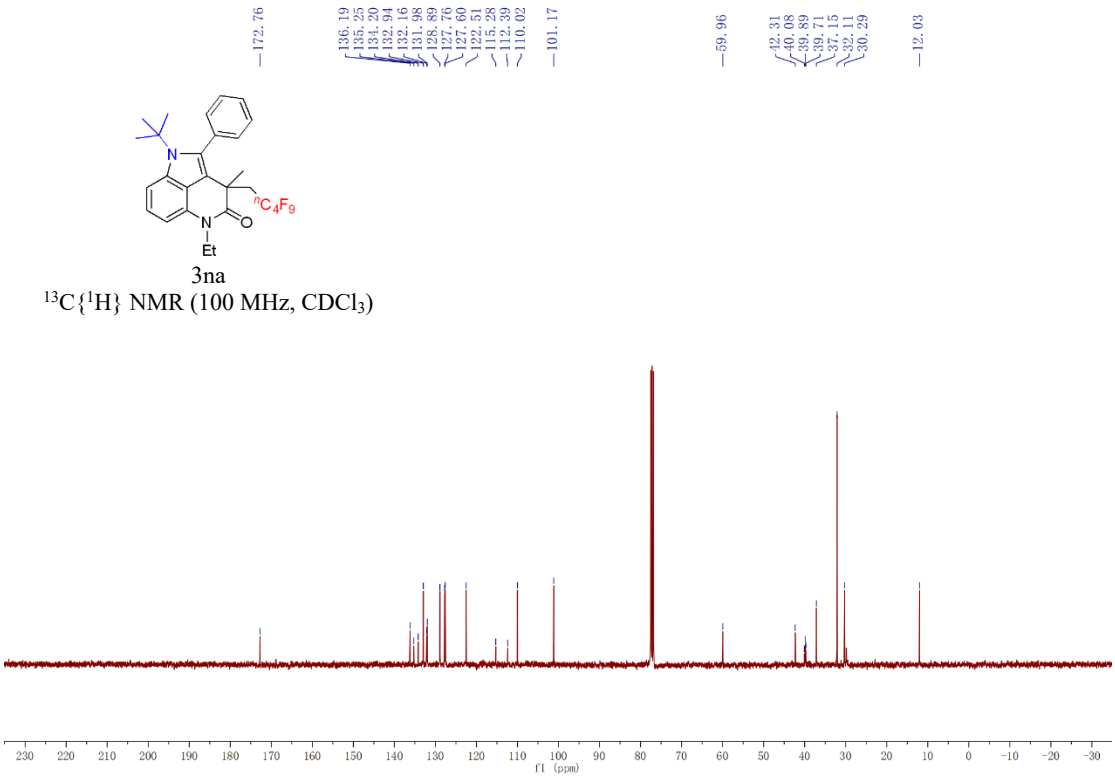


3na

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

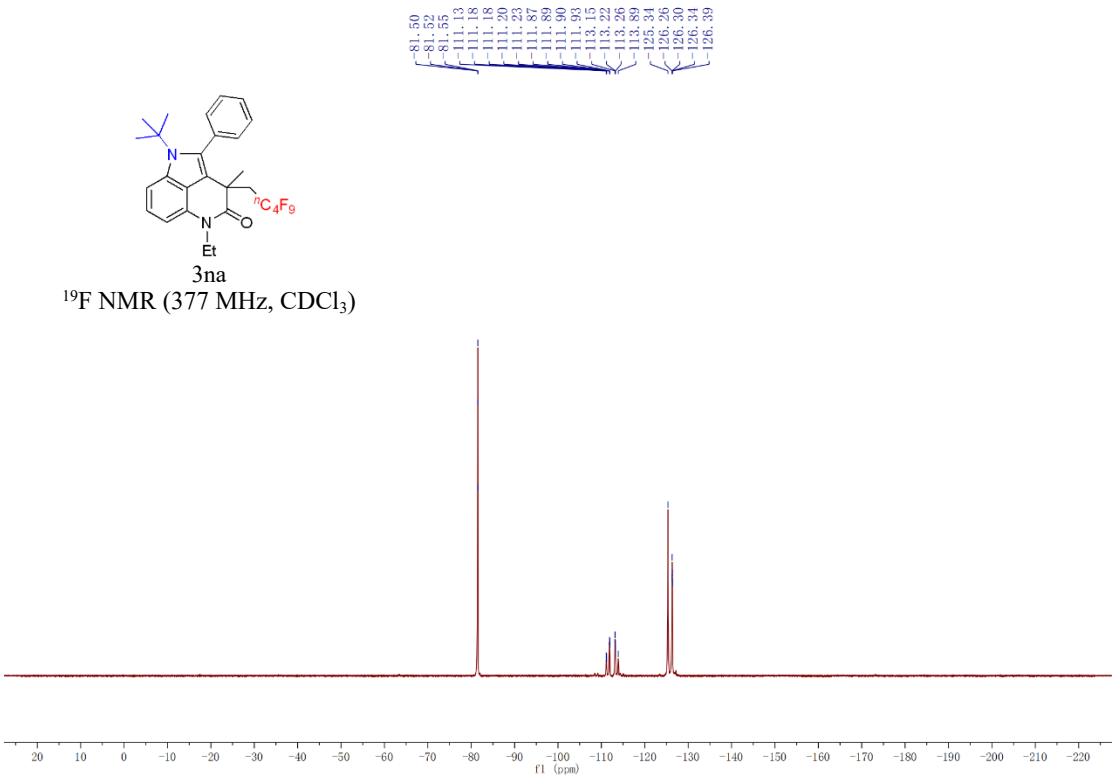






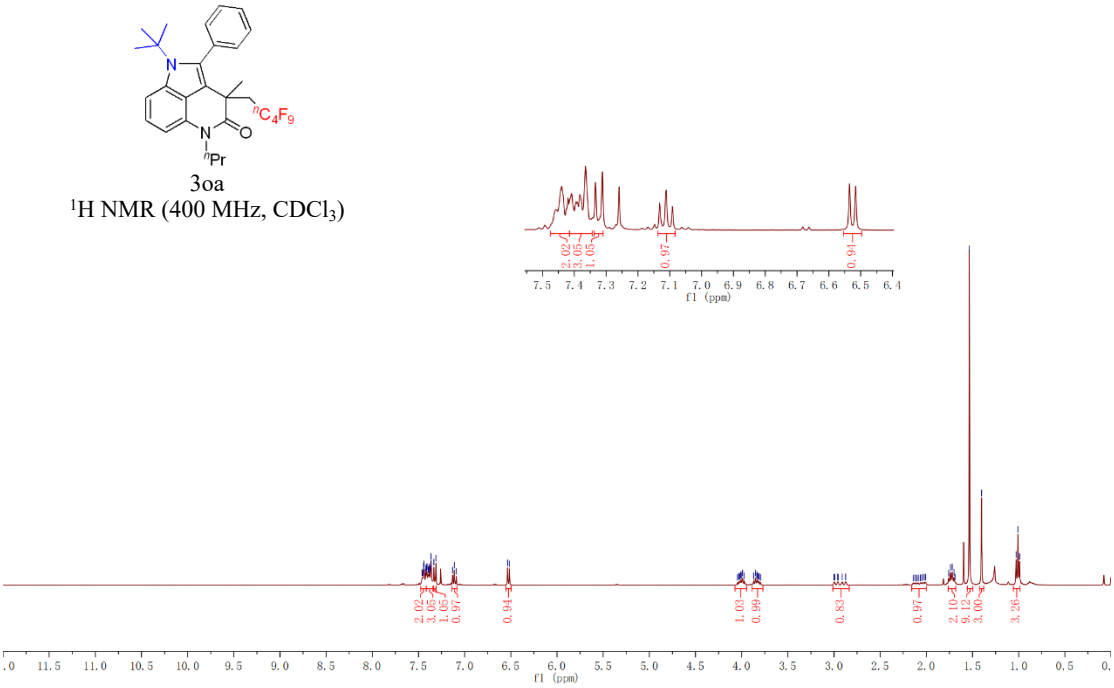
3na

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



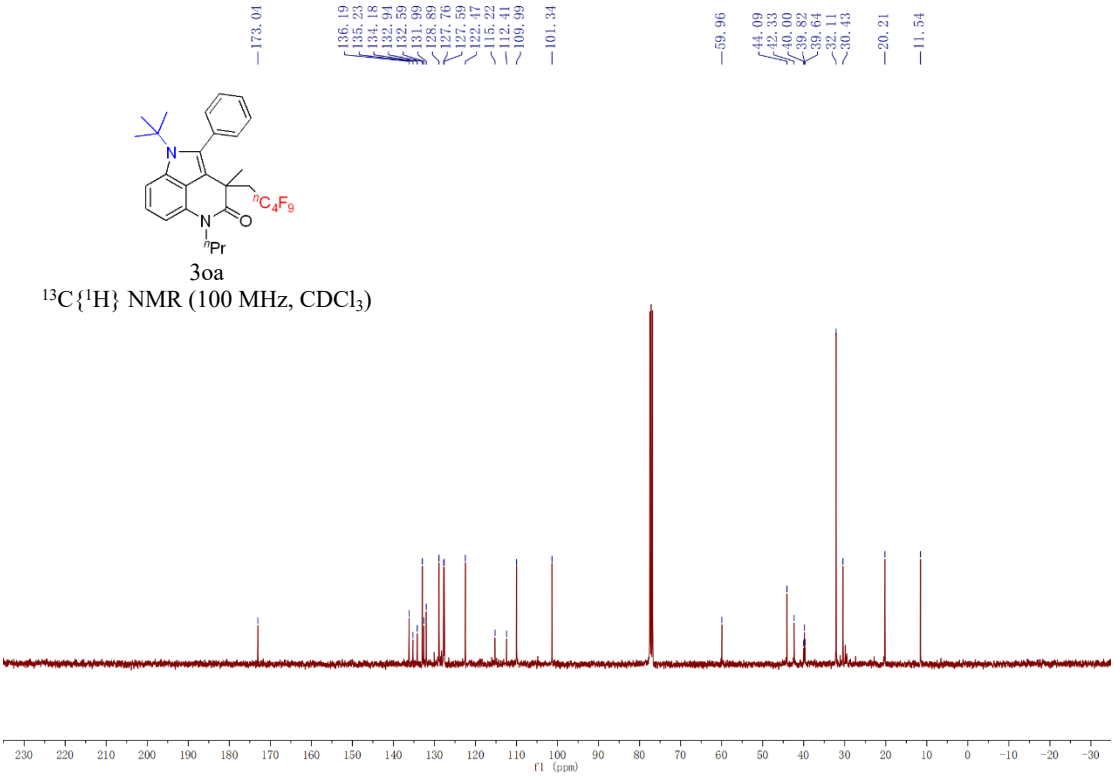
3na

^{19}F NMR (377 MHz, $CDCl_3$)



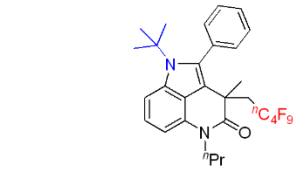
3oa

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



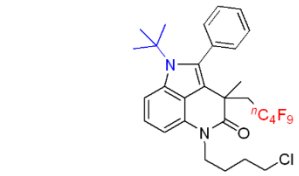
3oa

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)



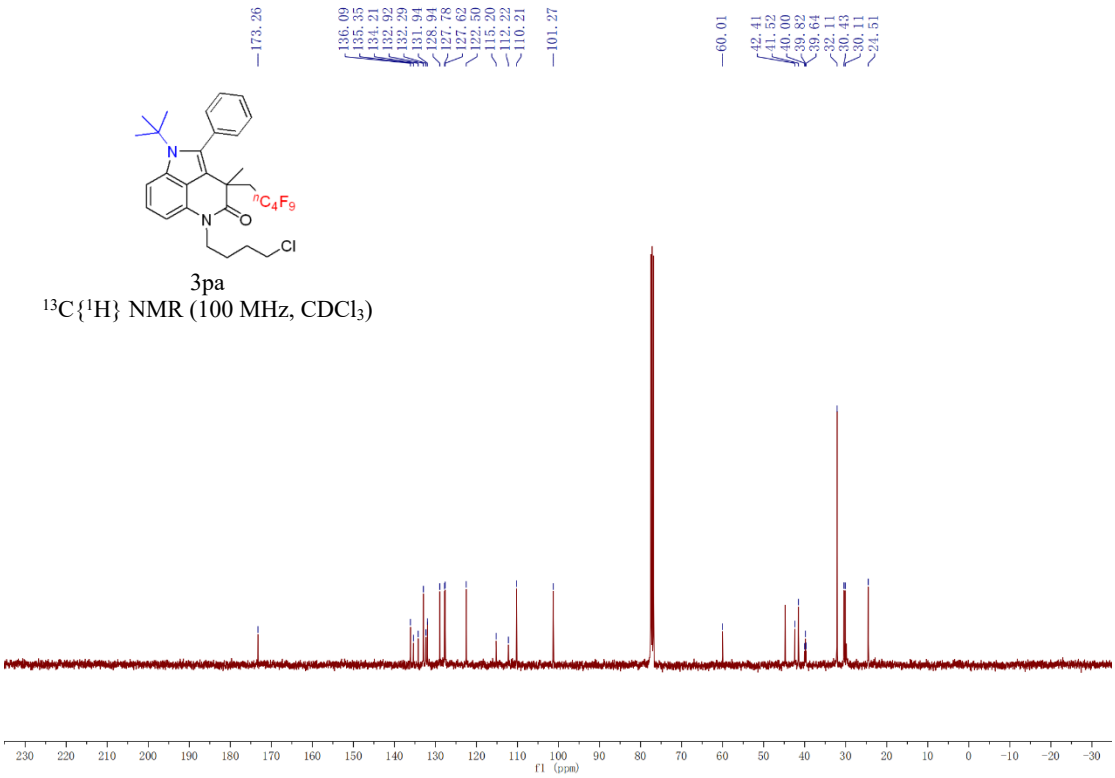
3oa

^{19}F NMR (377 MHz, $CDCl_3$)



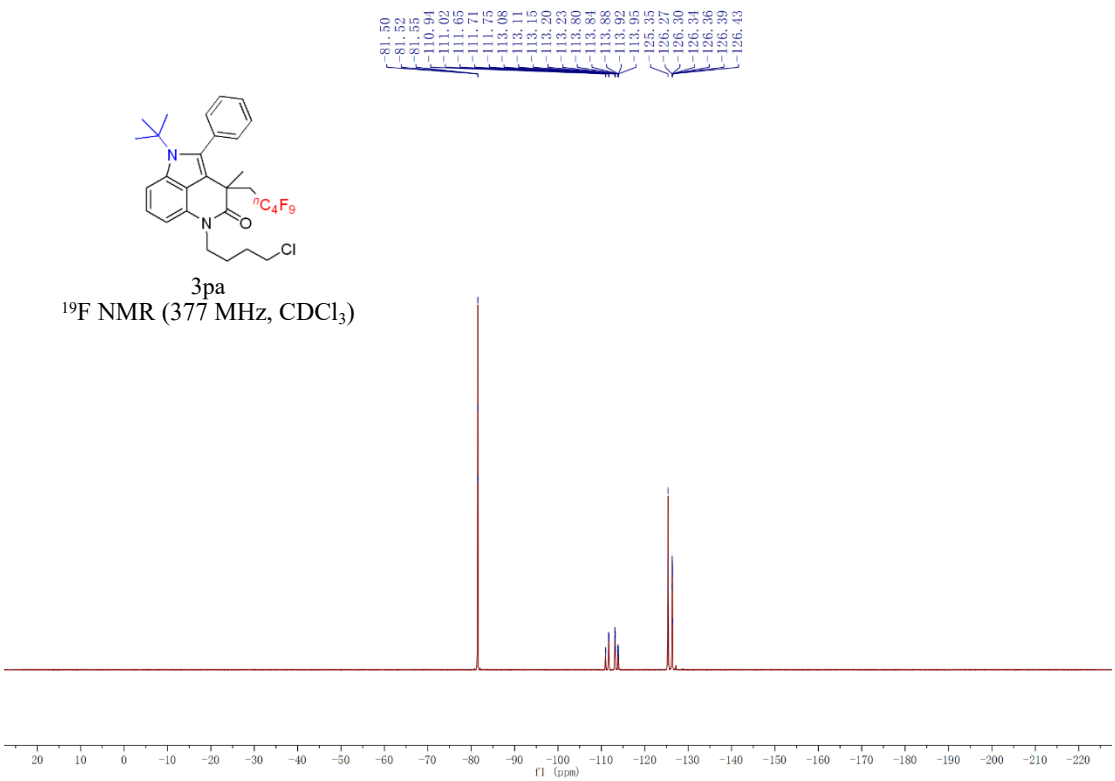
3pa

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



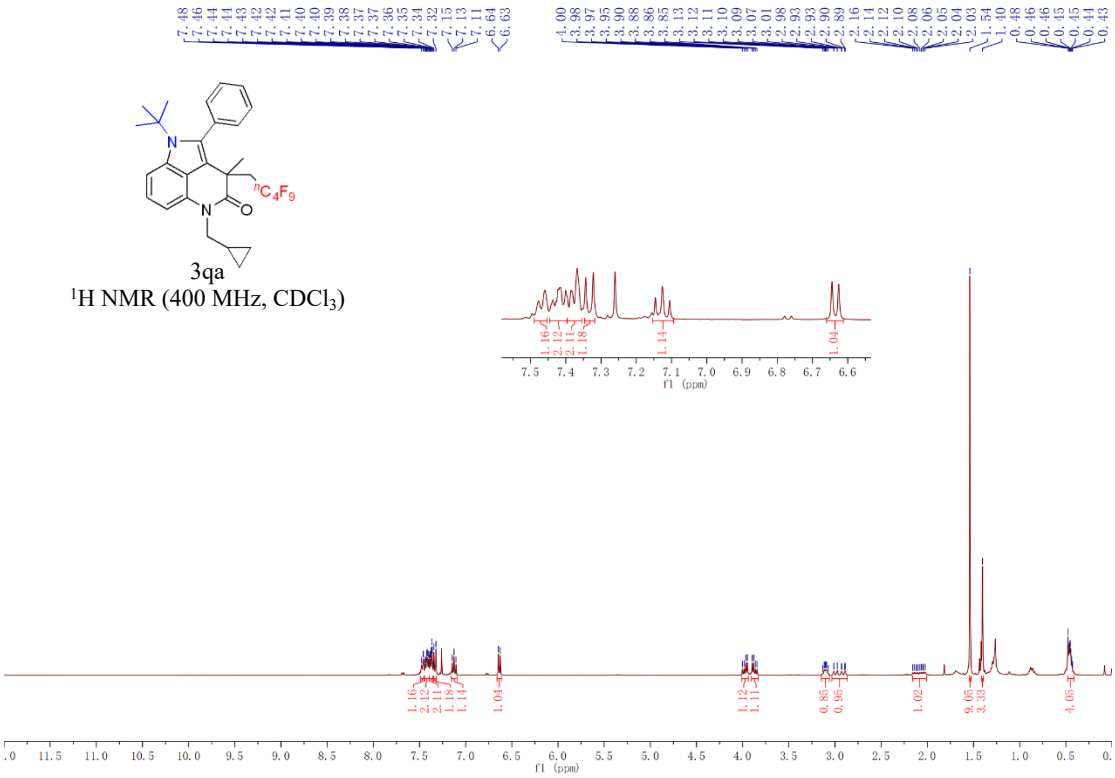
3pa

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



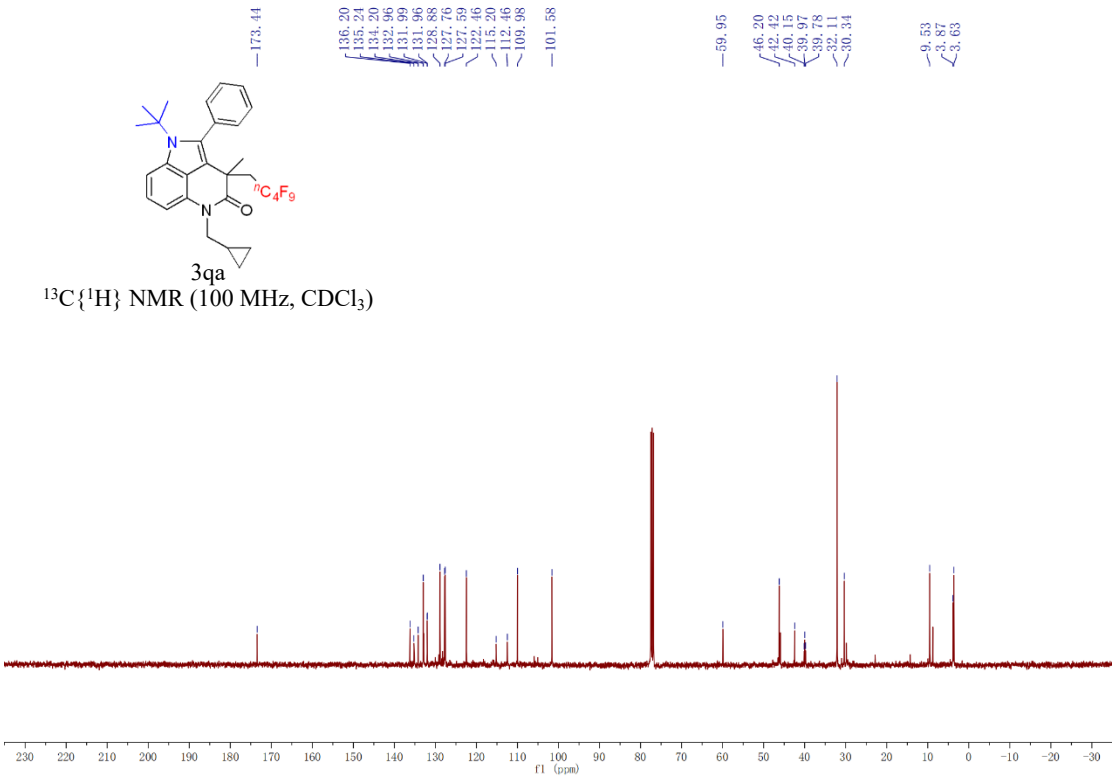
3pa

^{19}F NMR (377 MHz, $CDCl_3$)



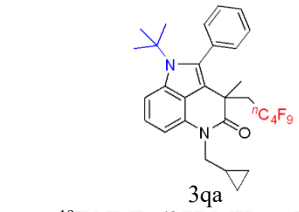
3qa

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



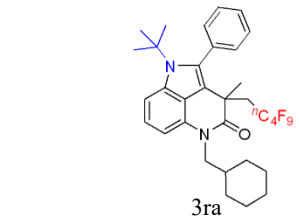
3qa

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)



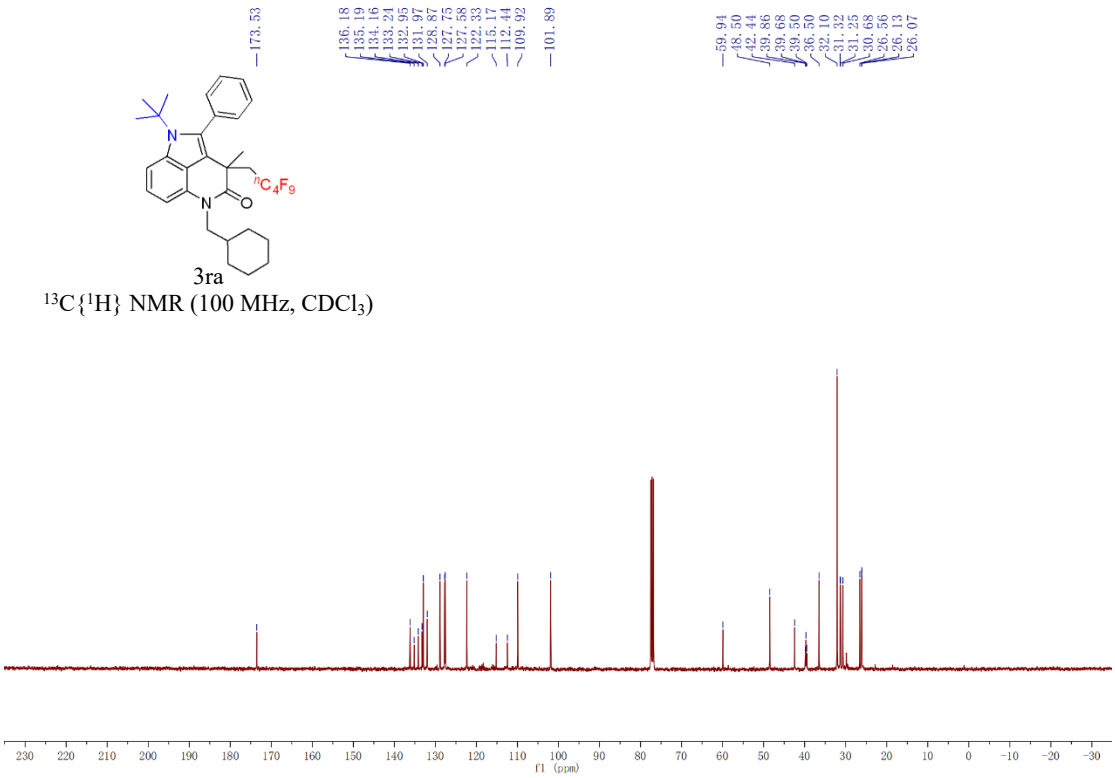
3qa

^{19}F NMR (377 MHz, $CDCl_3$)



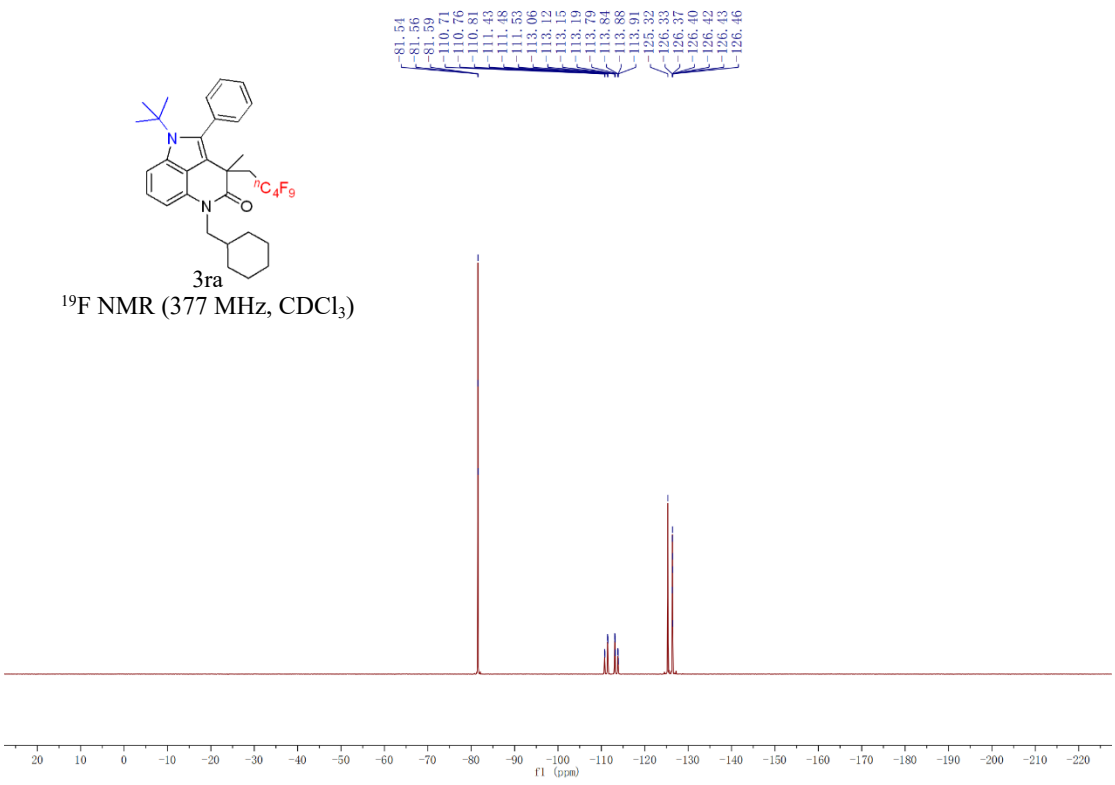
3ra

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



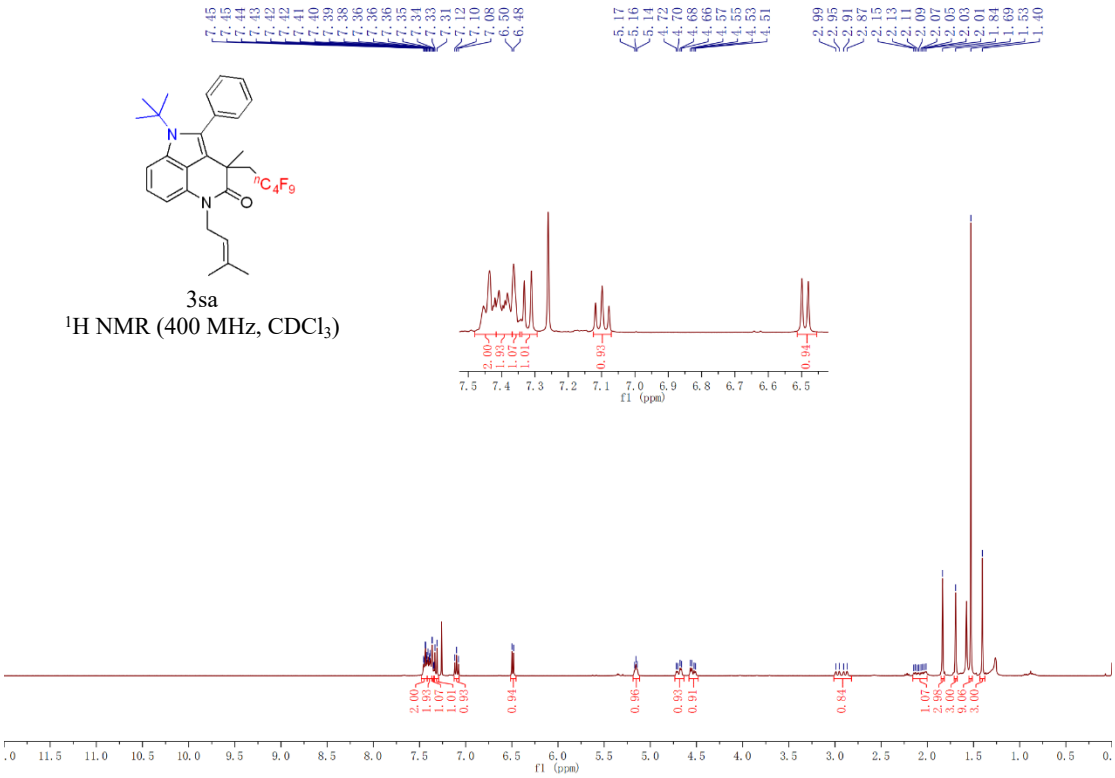
3ra

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



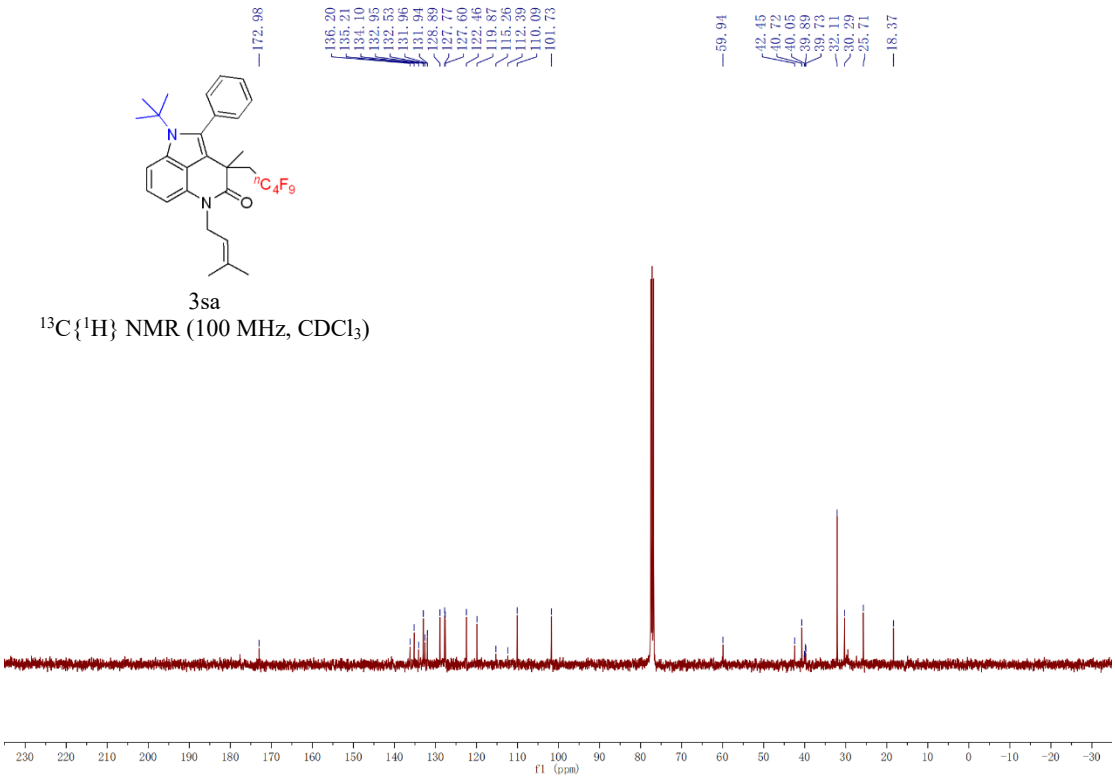
3ra

^{19}F NMR (377 MHz, $CDCl_3$)



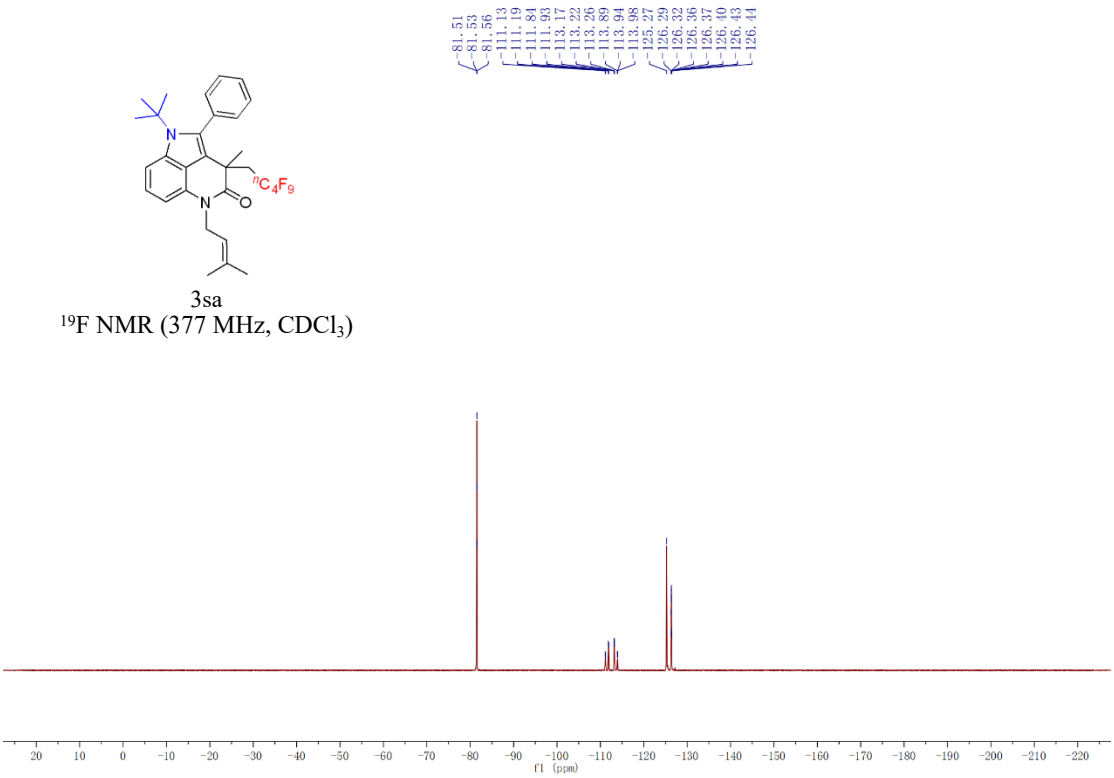
3sa

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



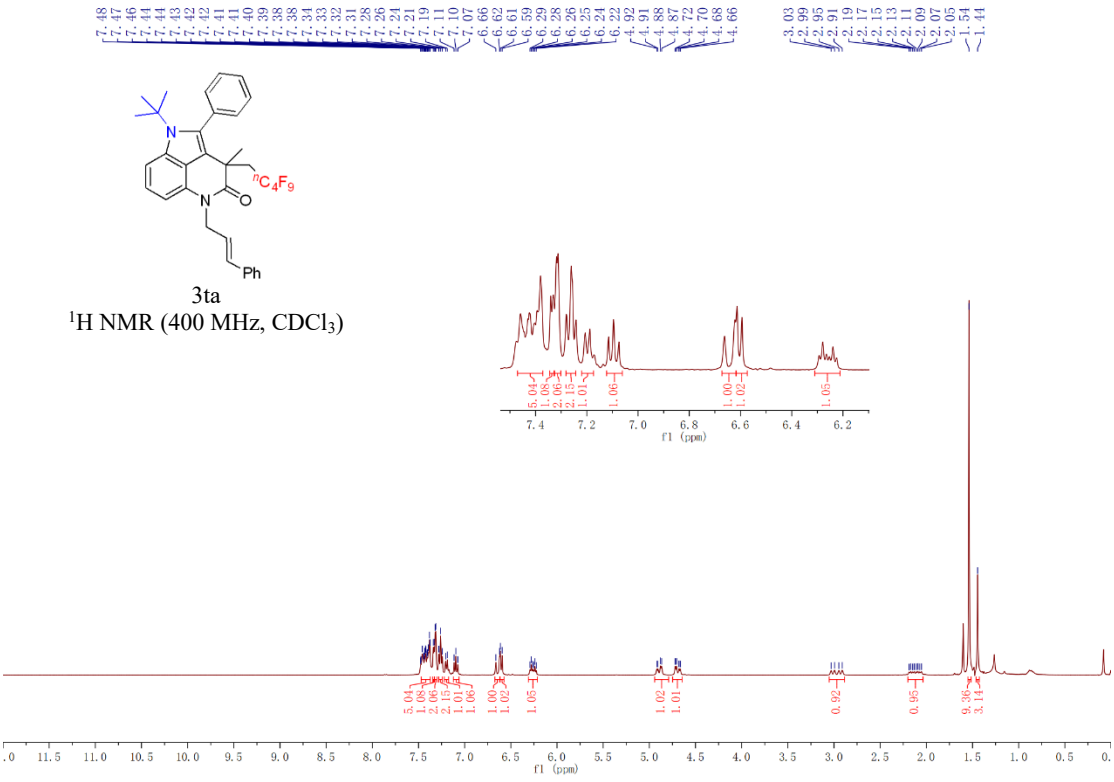
3sa

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



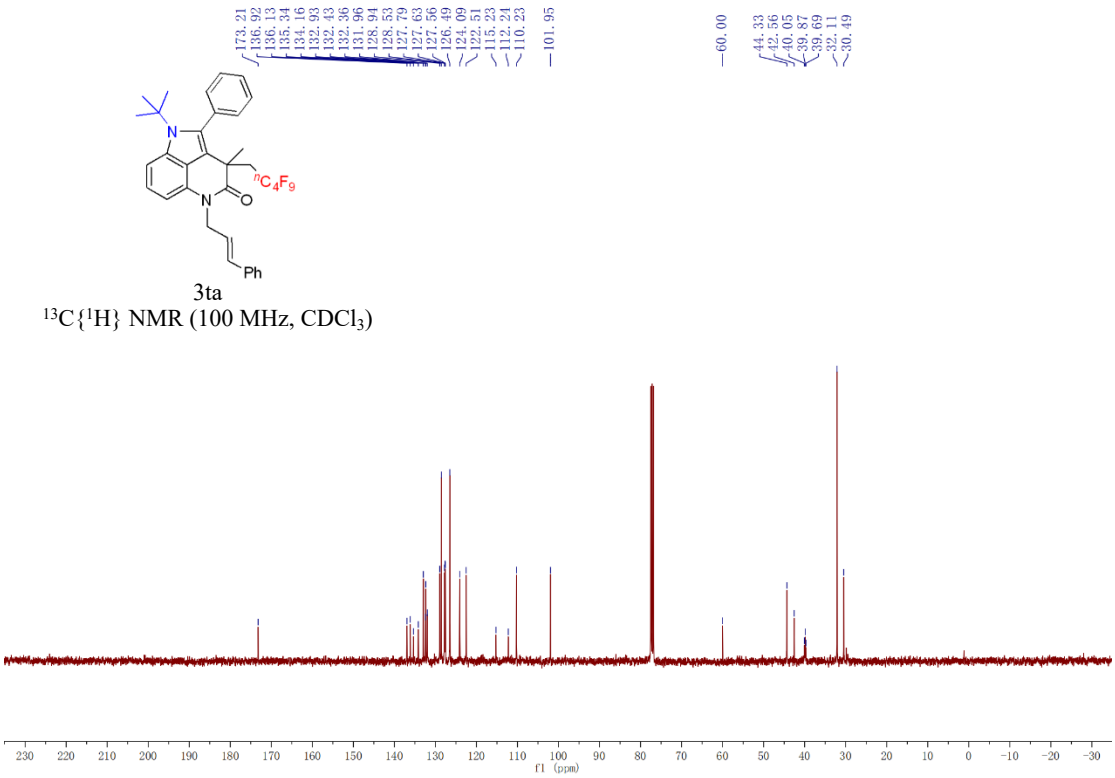
3sa

^{19}F NMR (377 MHz, $CDCl_3$)



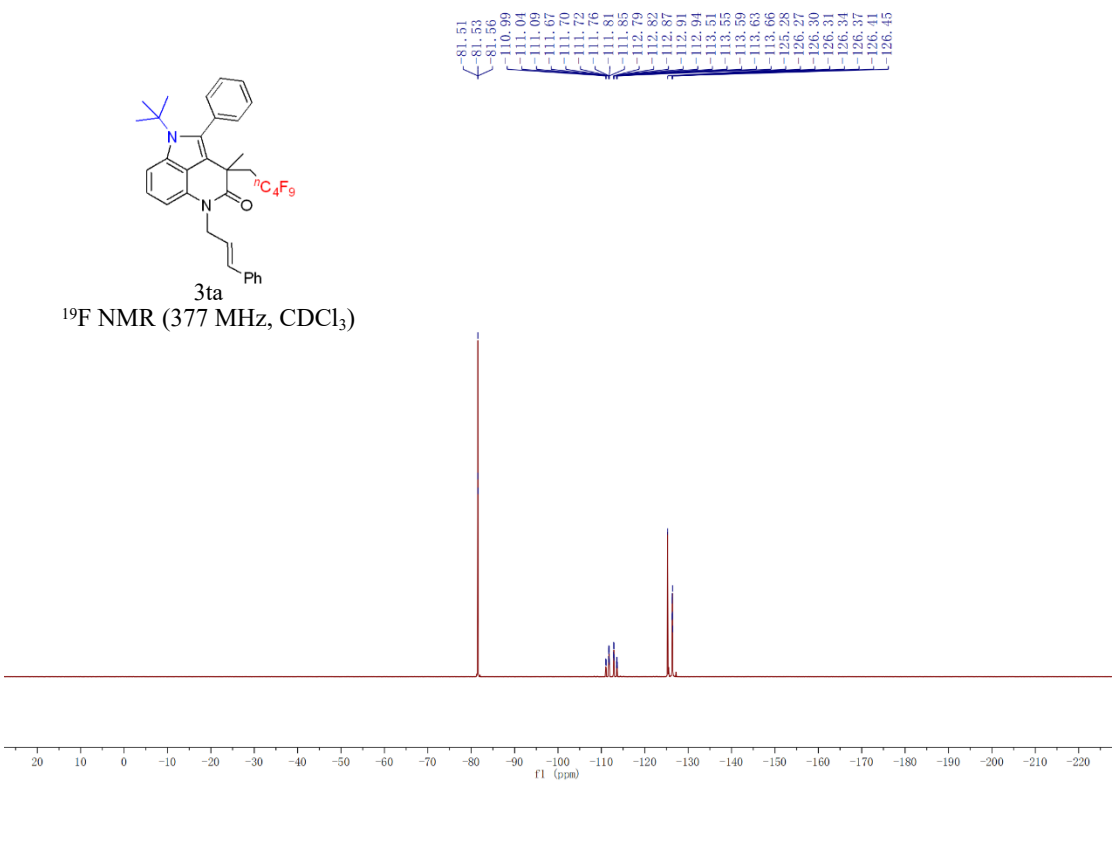
3ta

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



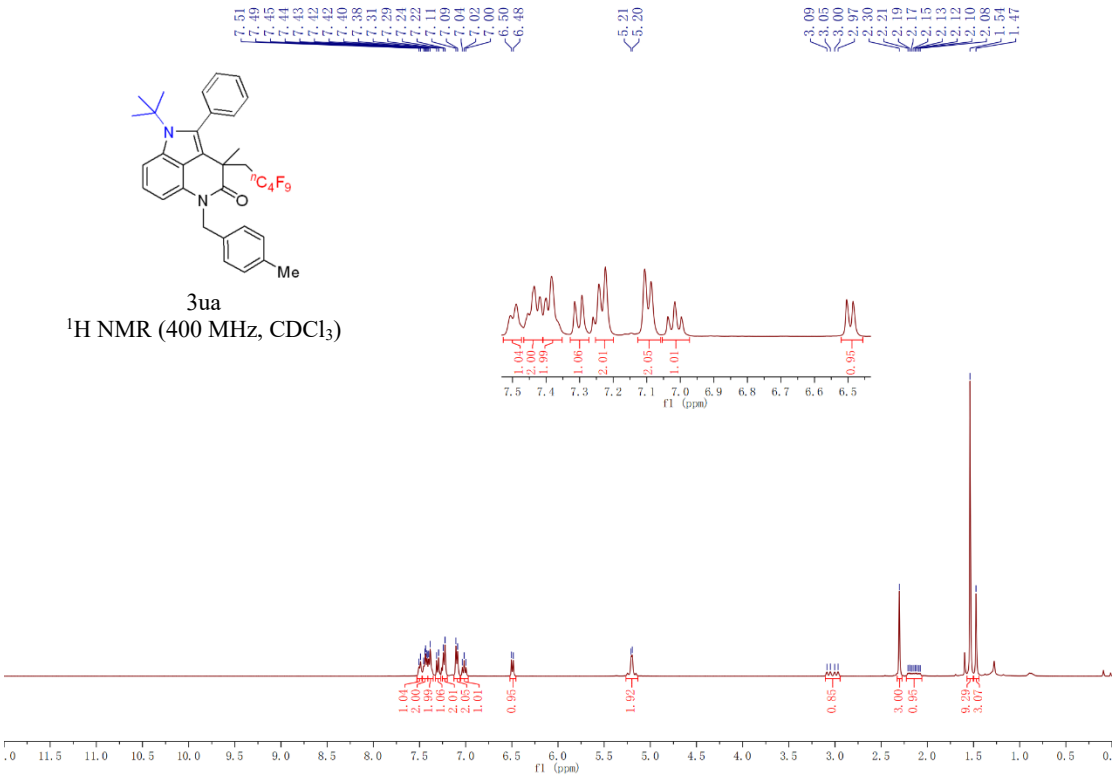
3ta

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



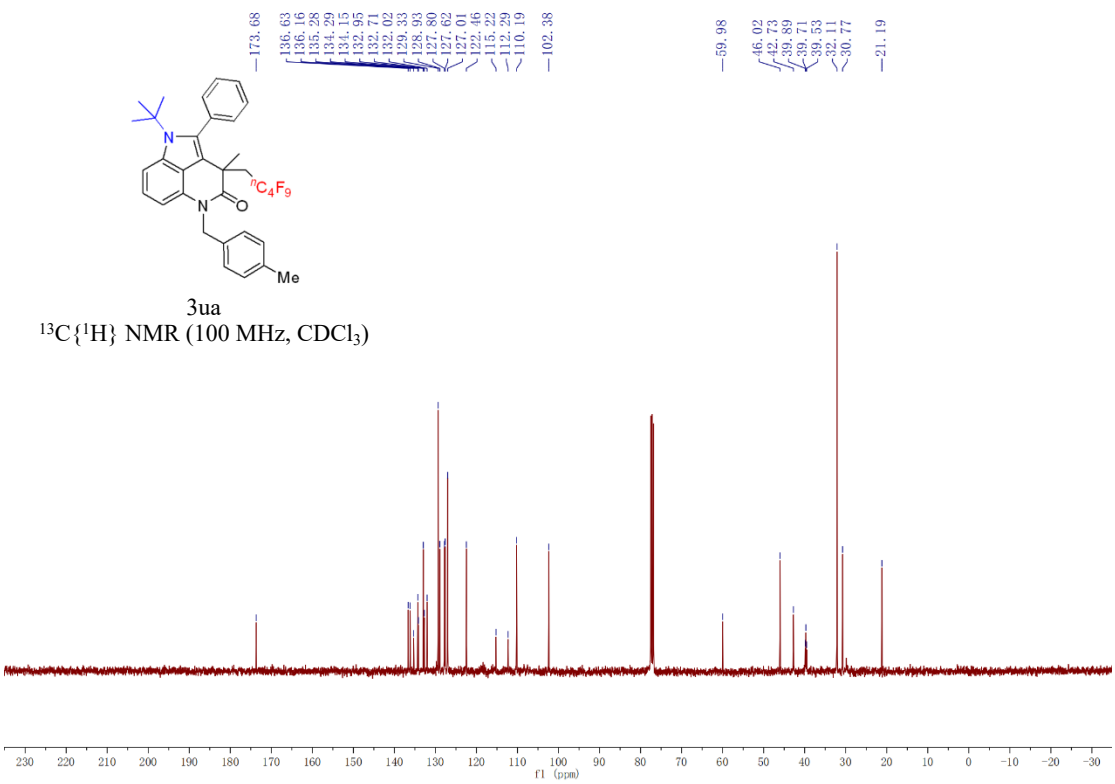
3ta

^{19}F NMR (377 MHz, $CDCl_3$)



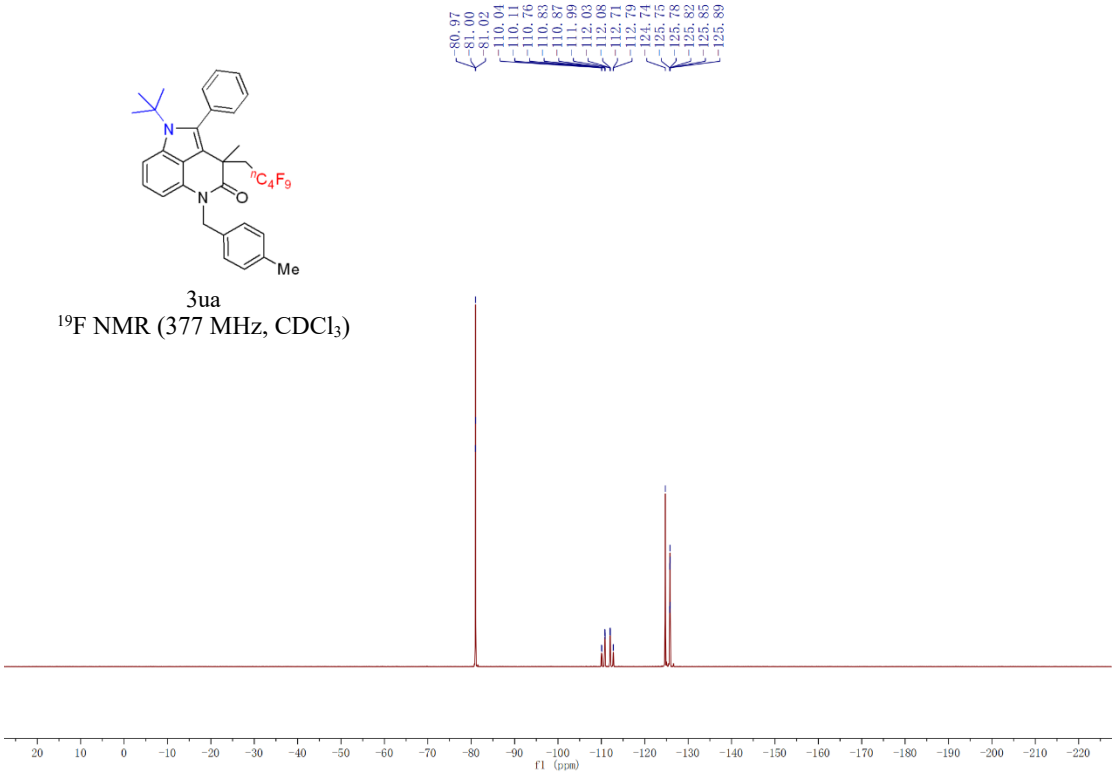
3ua

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



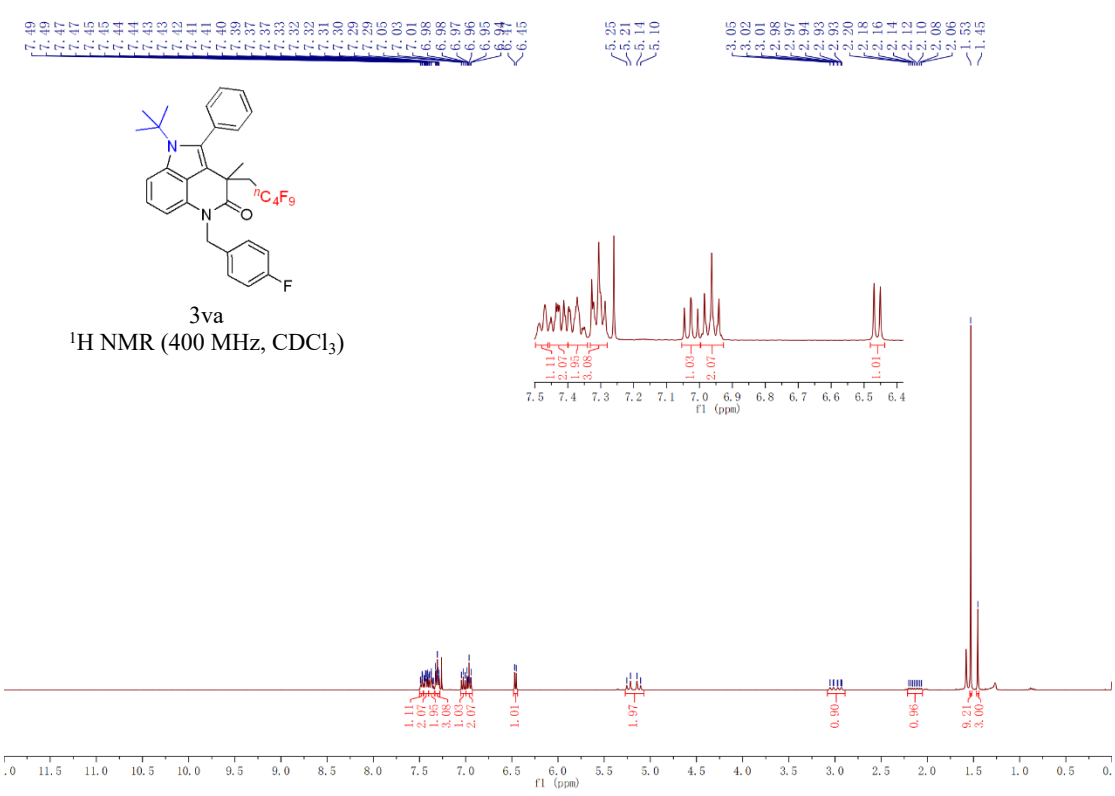
3ua

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



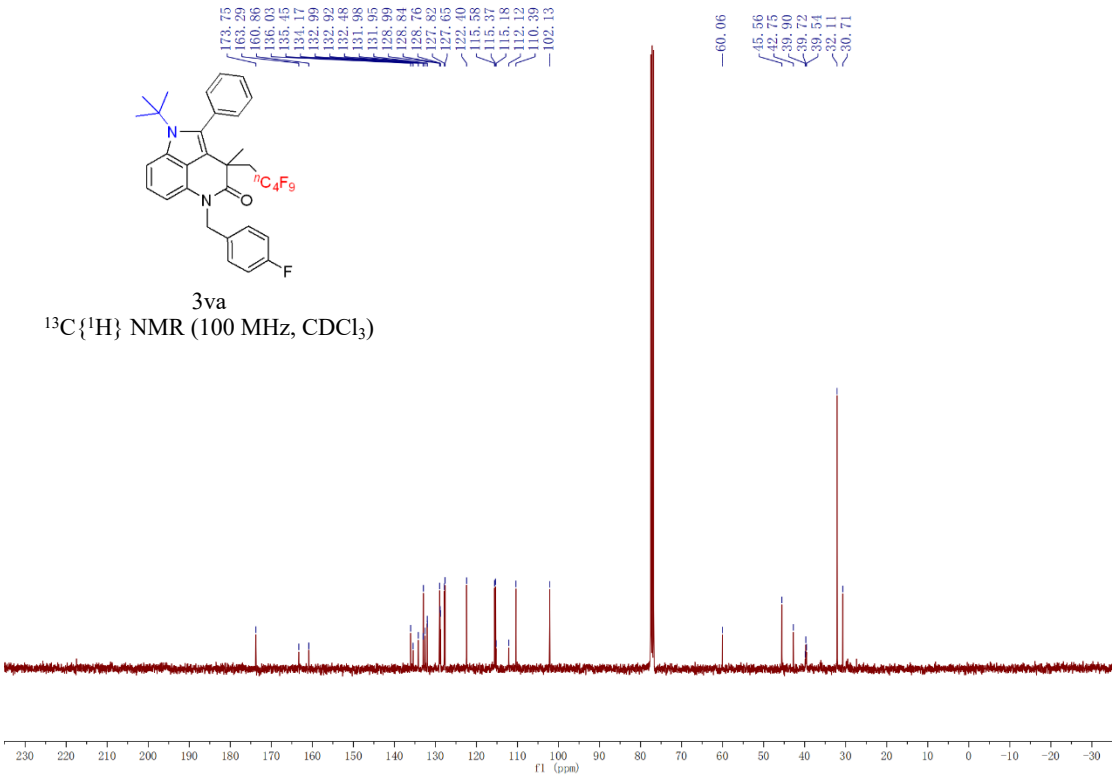
3ua

^{19}F NMR (377 MHz, $CDCl_3$)



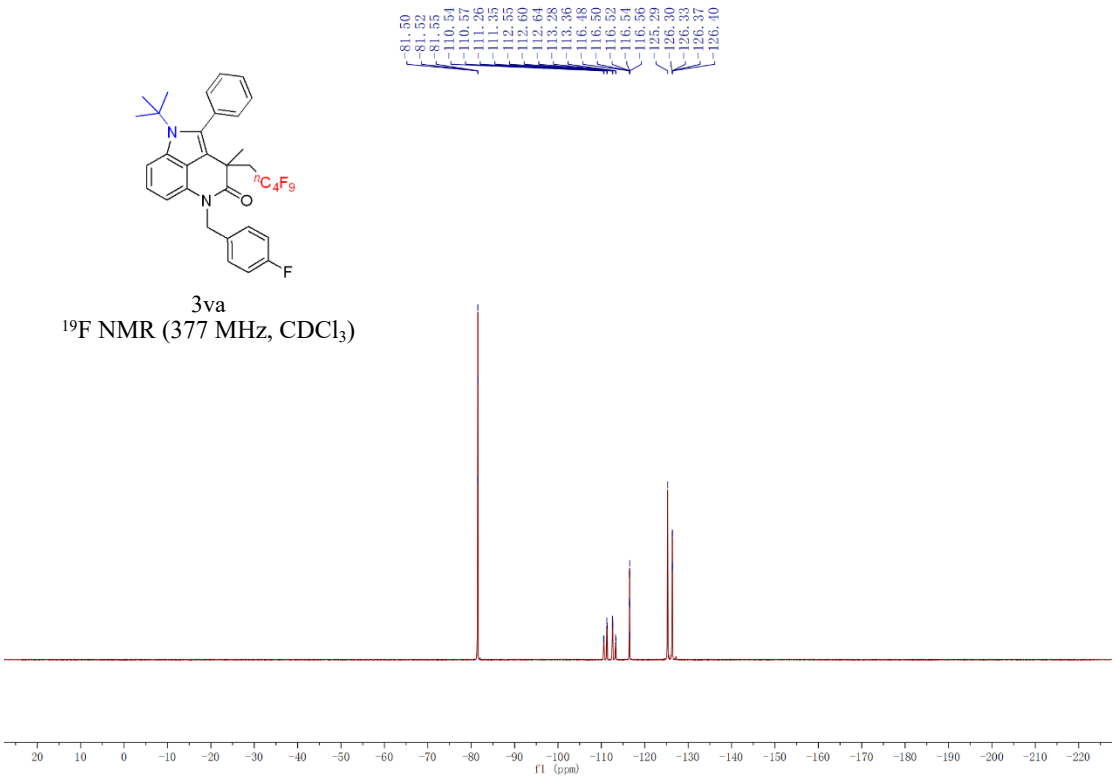
3va

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



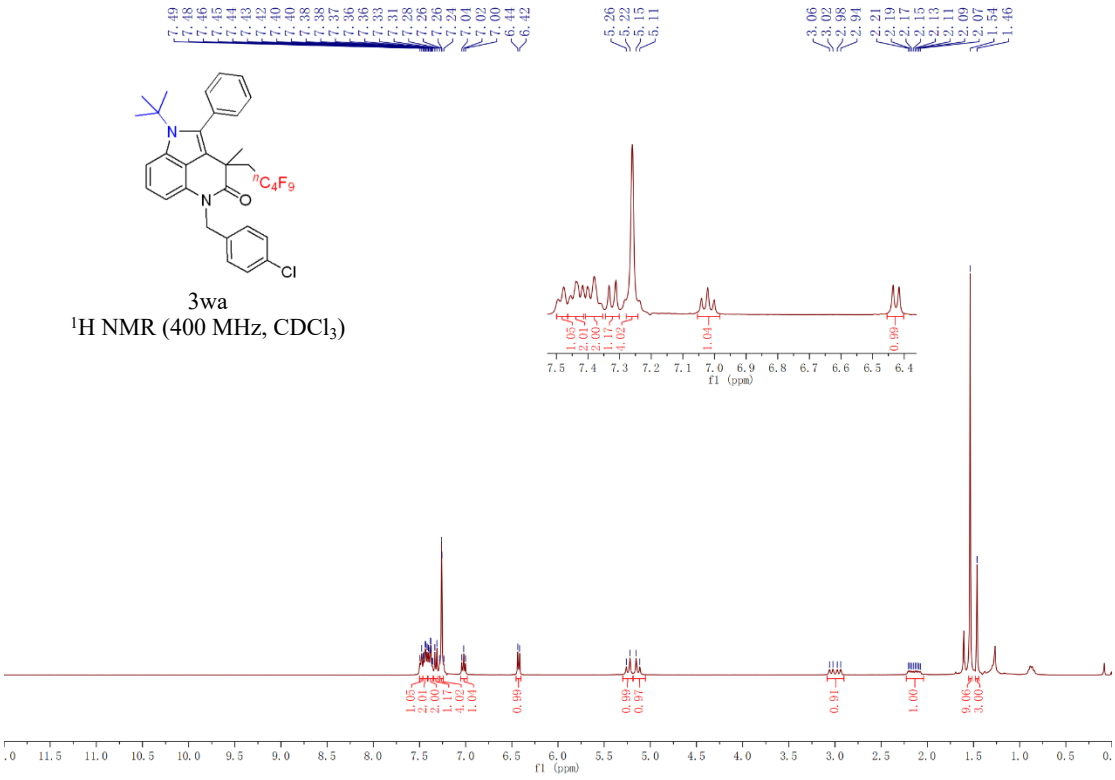
3va

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



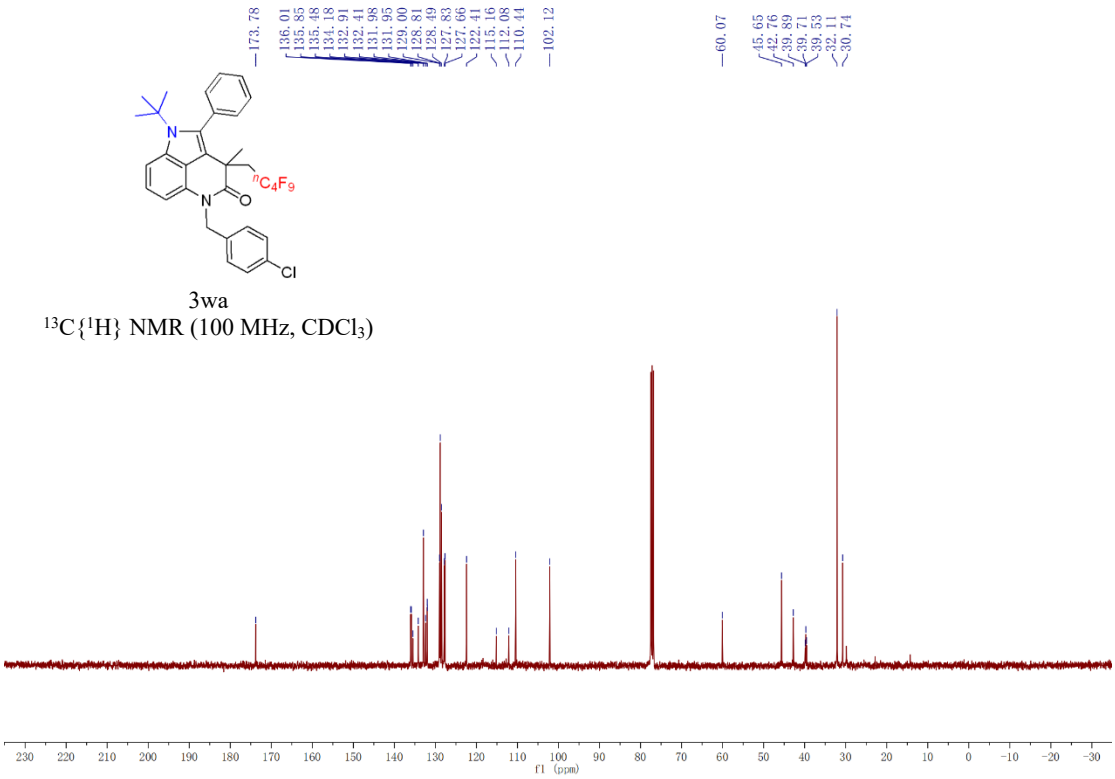
3va

^{19}F NMR (377 MHz, $CDCl_3$)



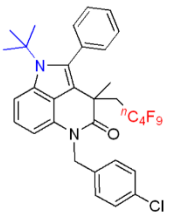
3wa

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



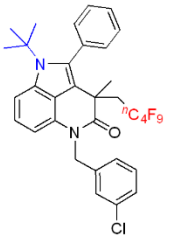
3wa

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



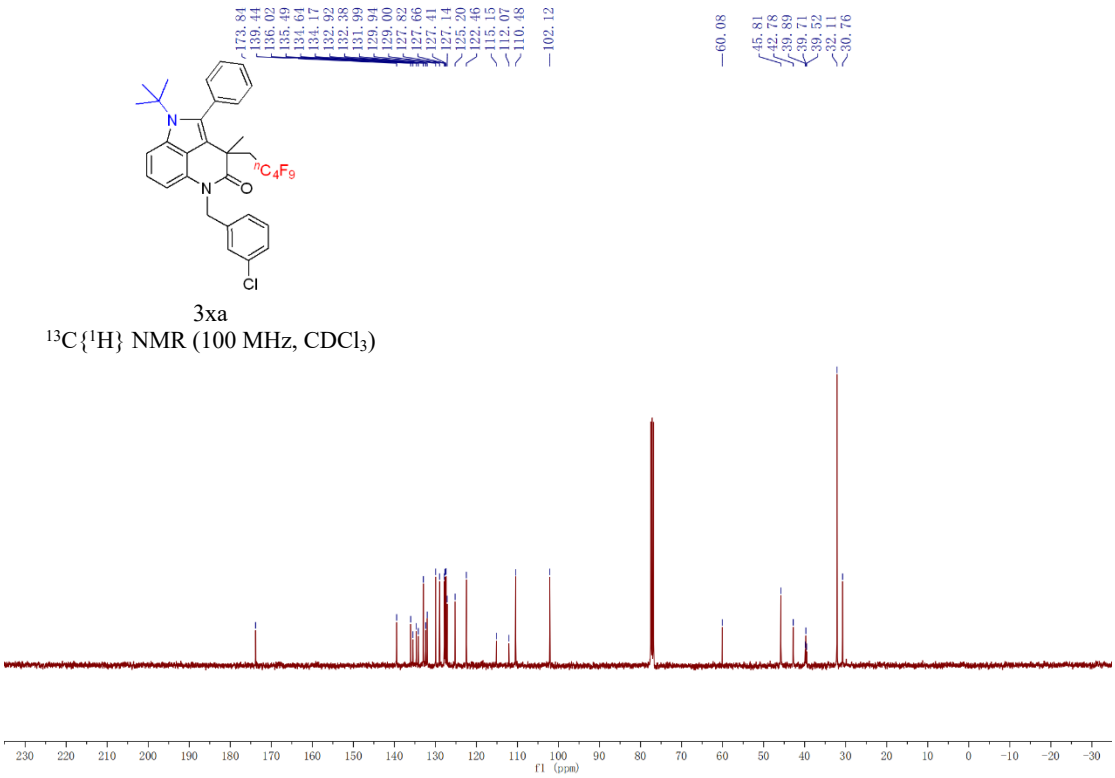
3wa

^{19}F NMR (377 MHz, $CDCl_3$)



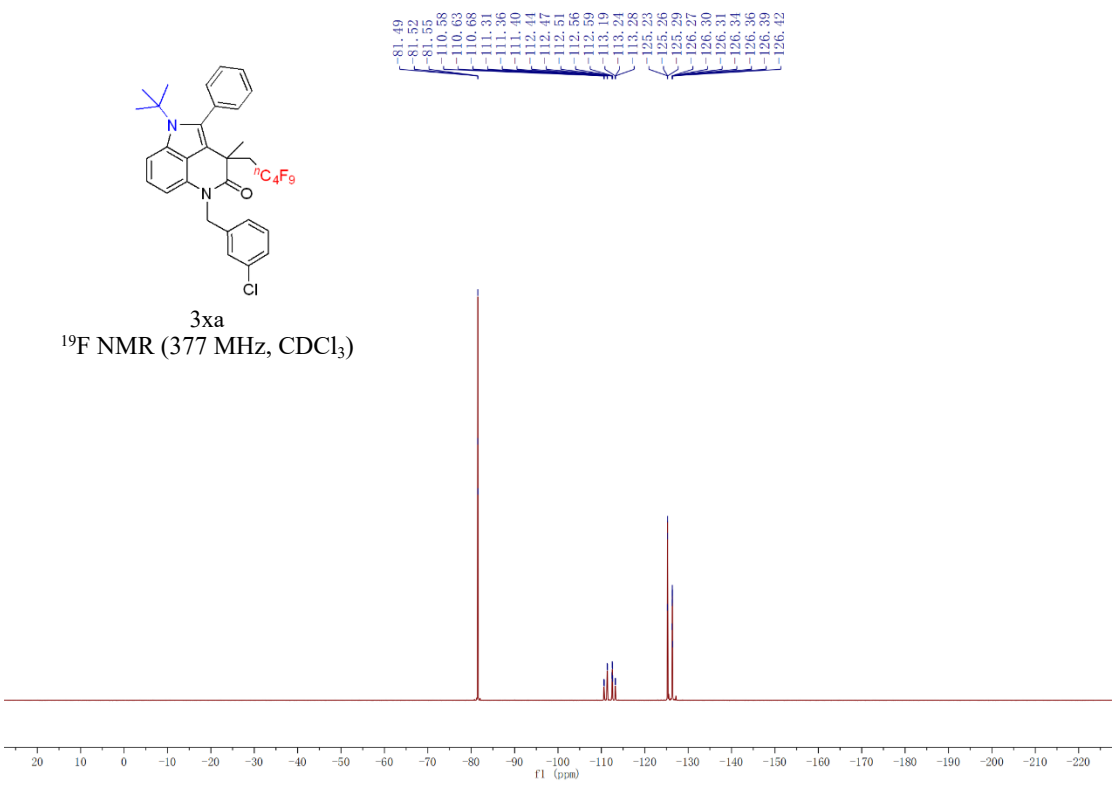
3xa

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



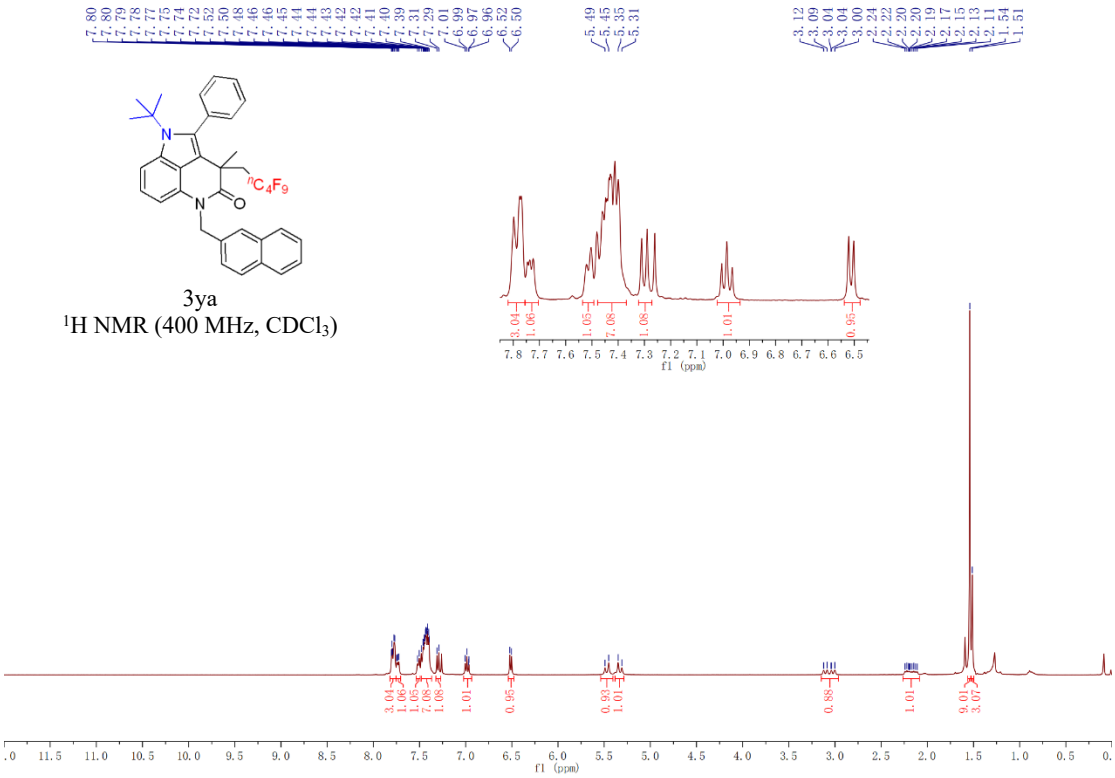
3xa

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



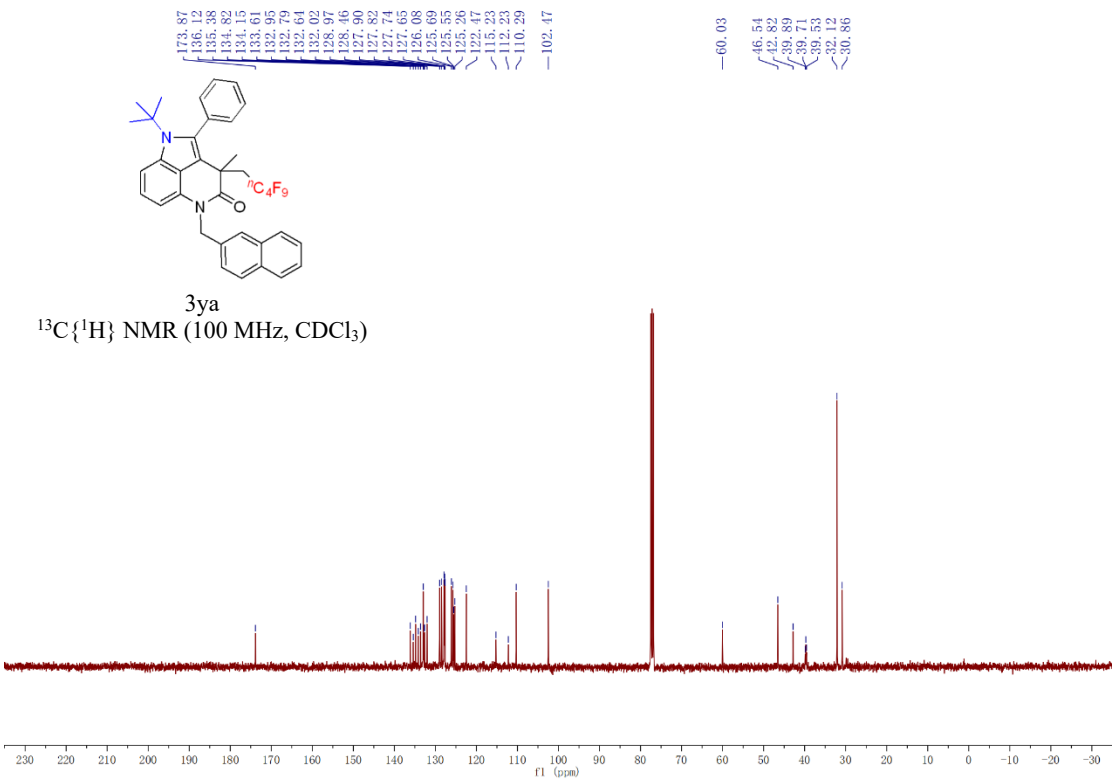
3xa

^{19}F NMR (377 MHz, $CDCl_3$)



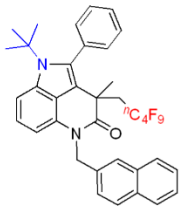
3ya

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



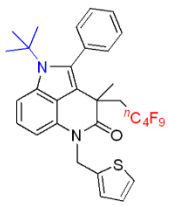
3ya

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



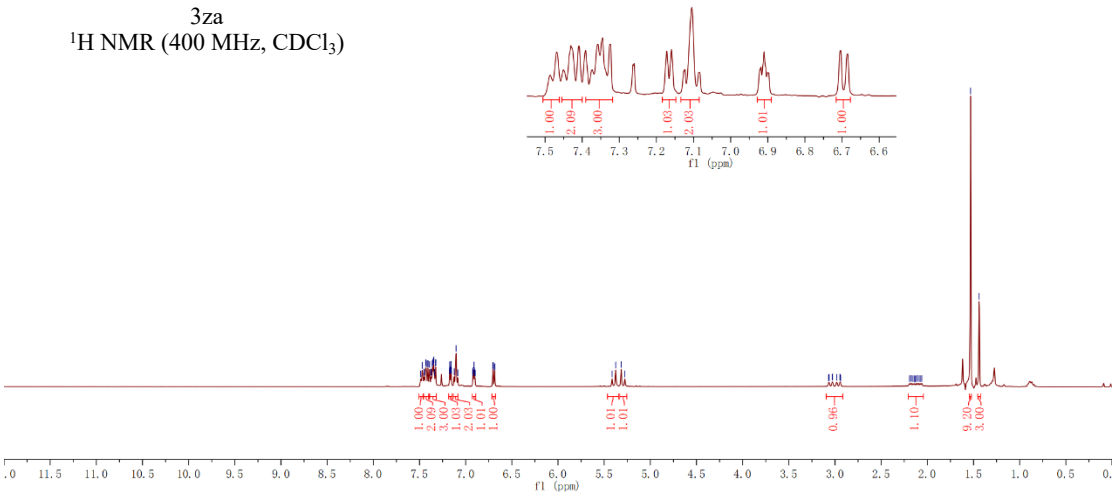
3ya

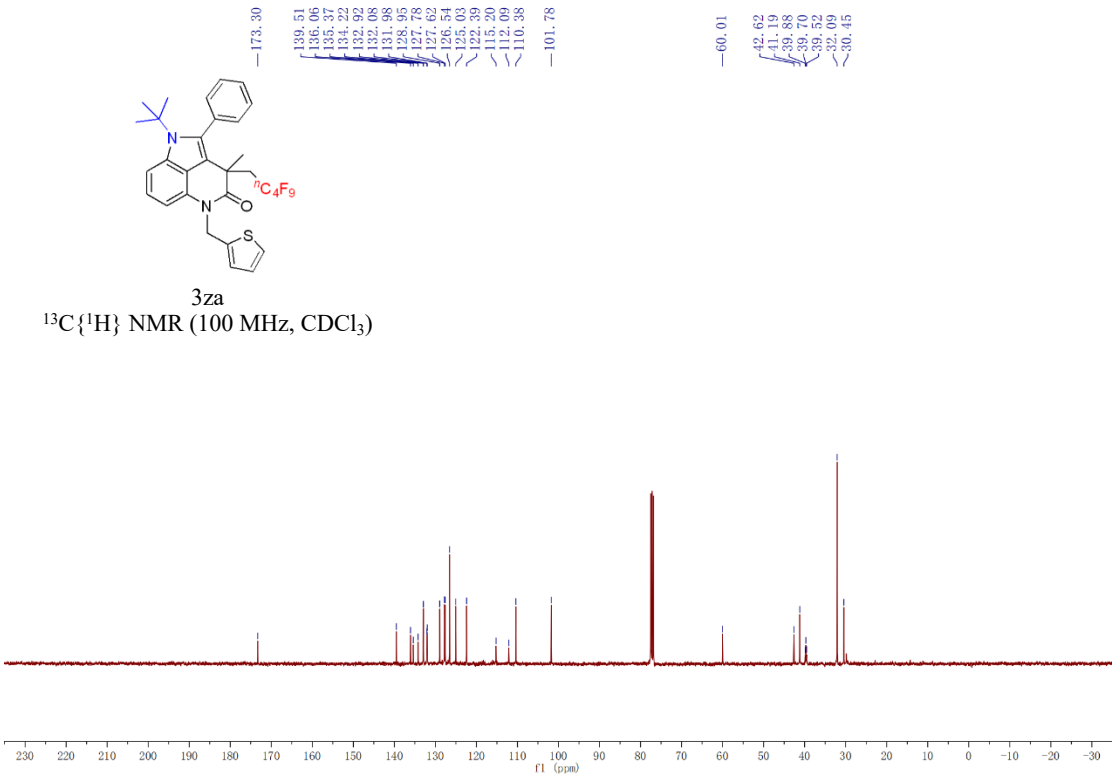
^{19}F NMR (377 MHz, $CDCl_3$)



3za

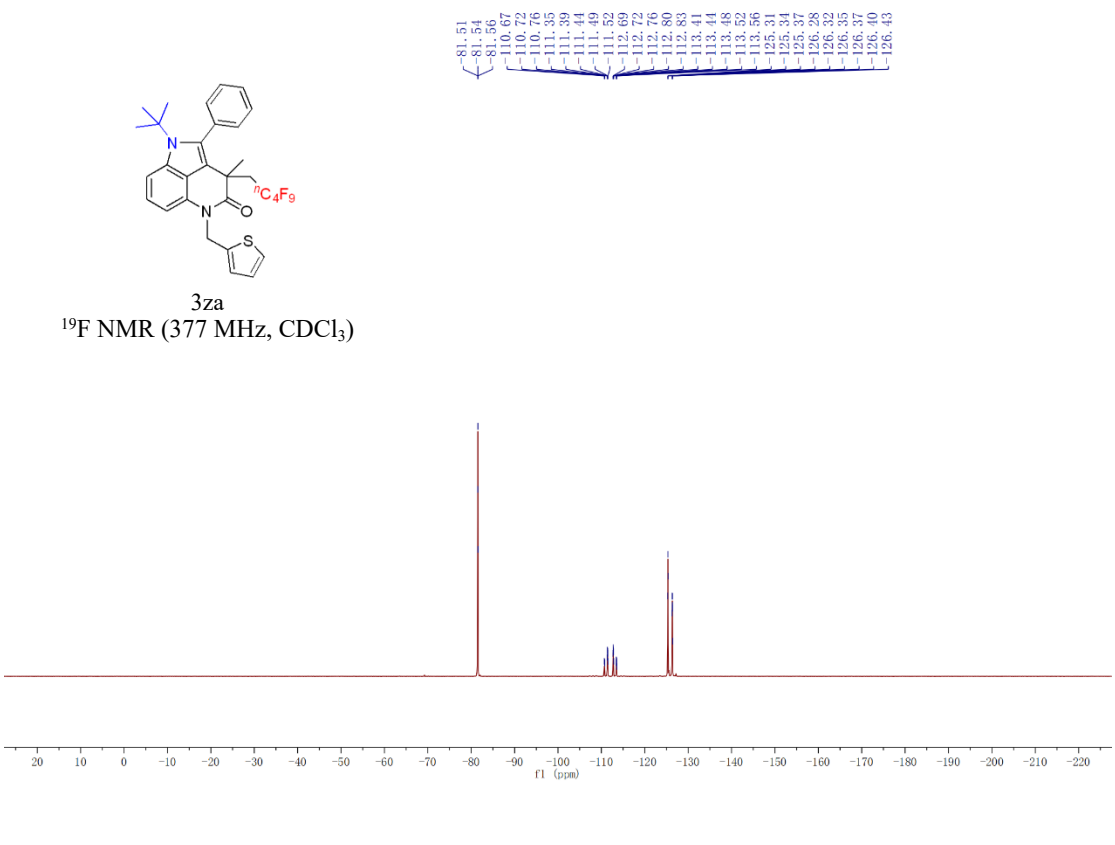
^{1}H NMR (400 MHz, $CDCl_3$)





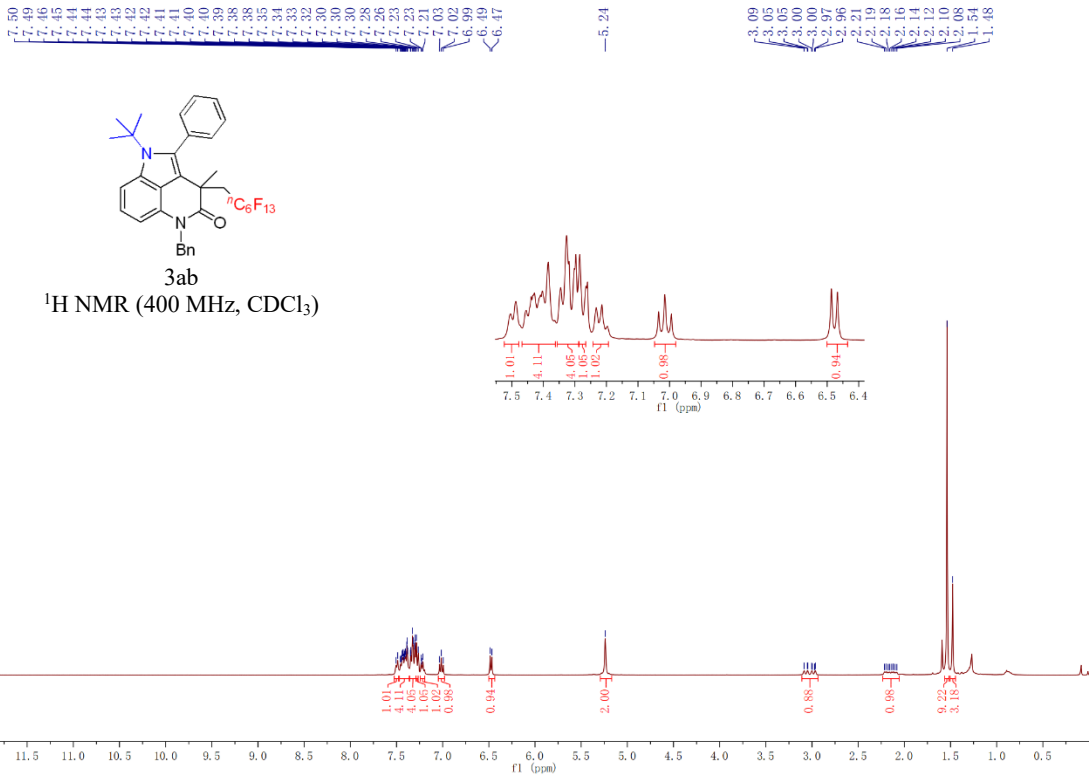
3za

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



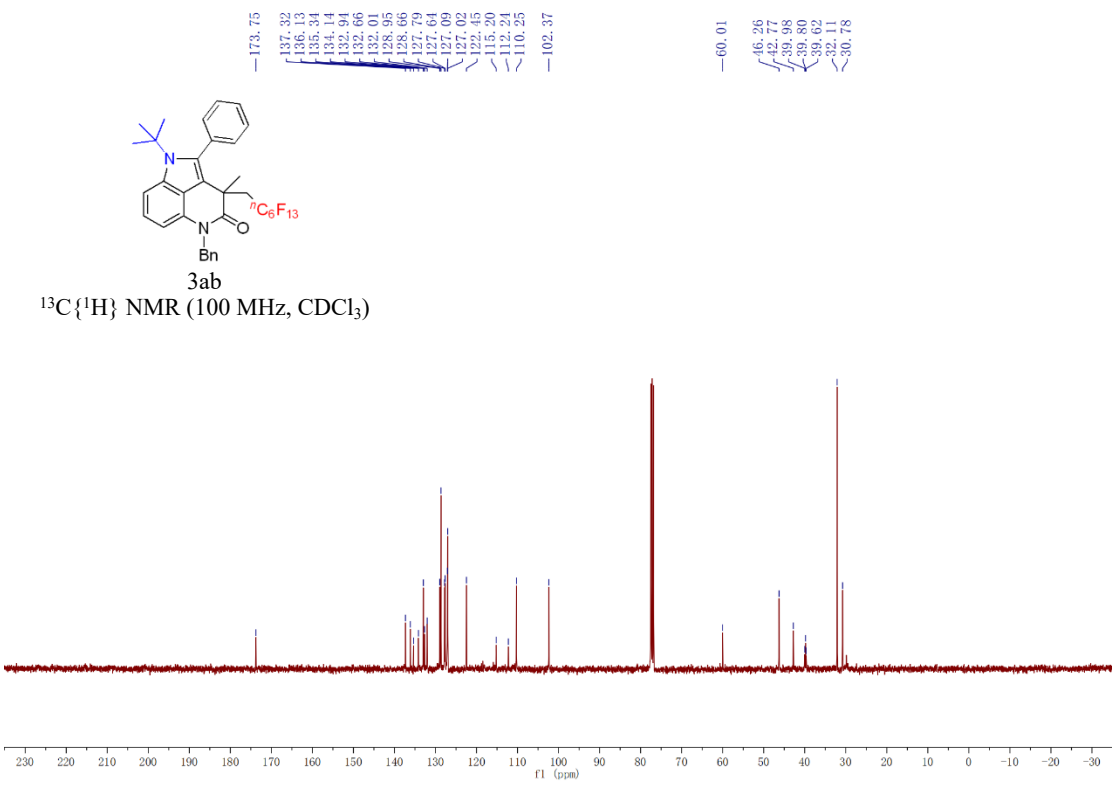
3za

^{19}F NMR (377 MHz, $CDCl_3$)



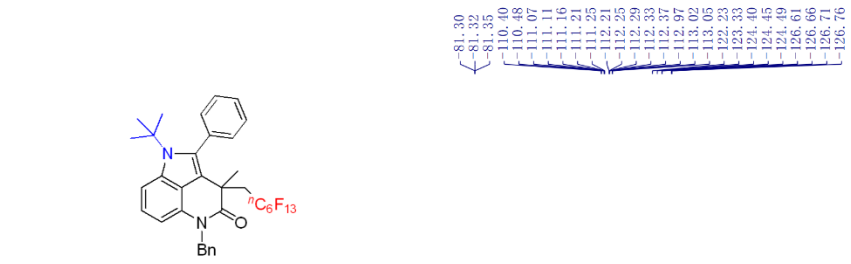
3ab

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



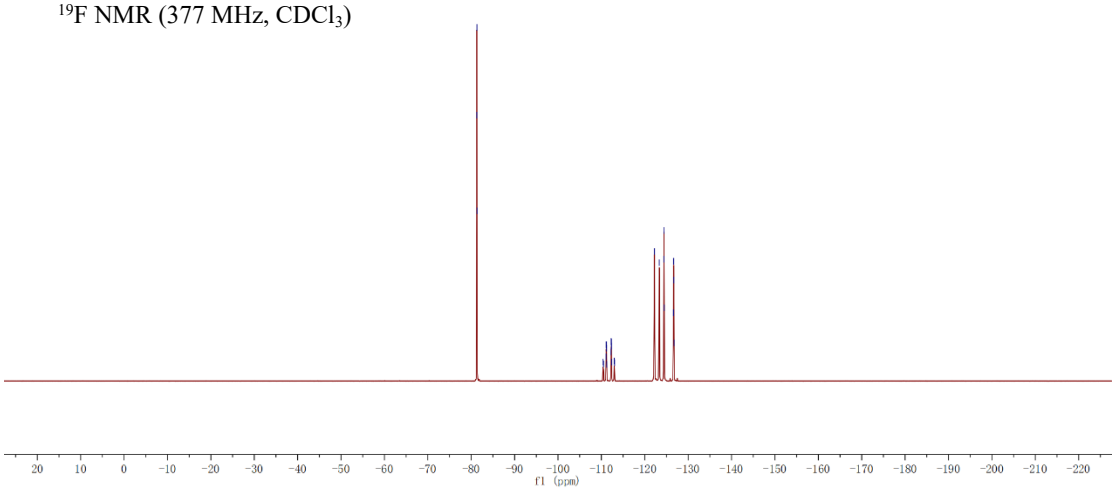
3ab

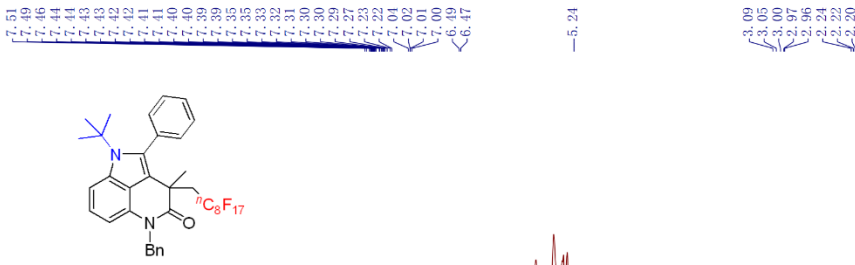
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)



3ab

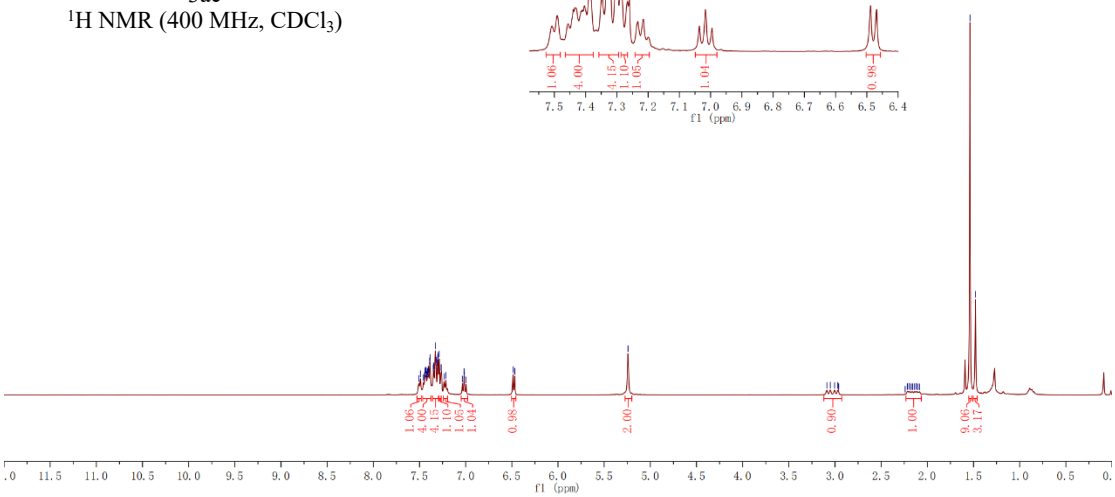
^{19}F NMR (377 MHz, $CDCl_3$)

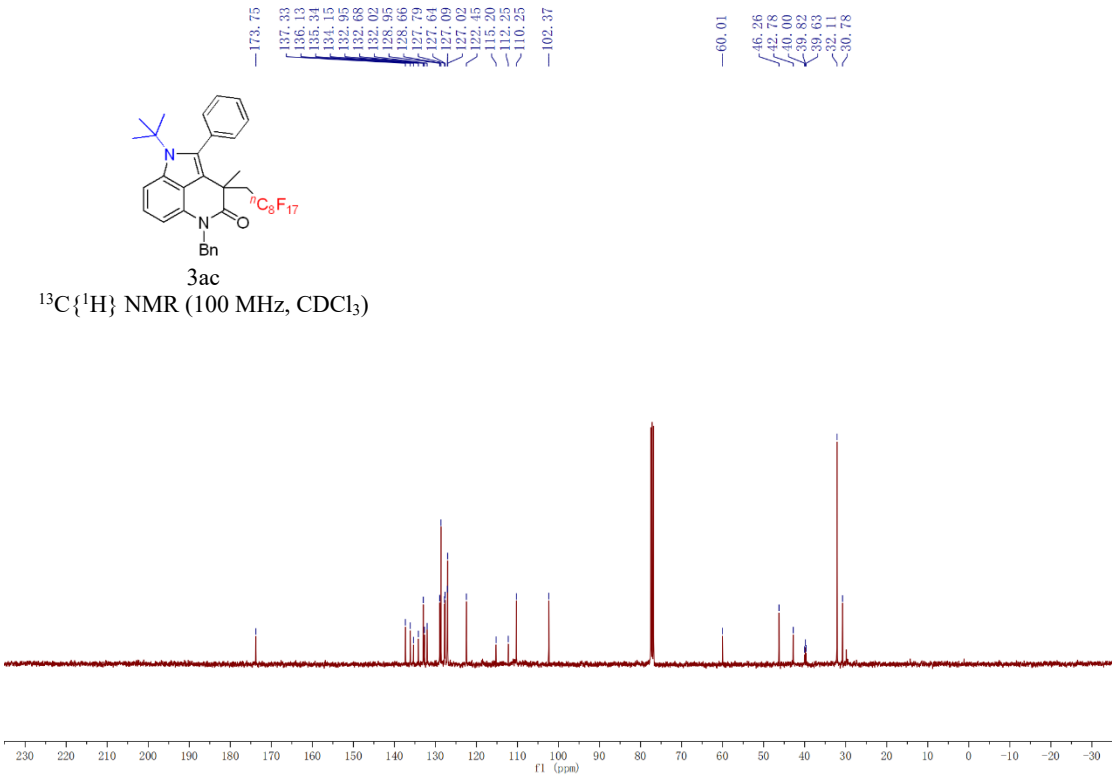




3ac

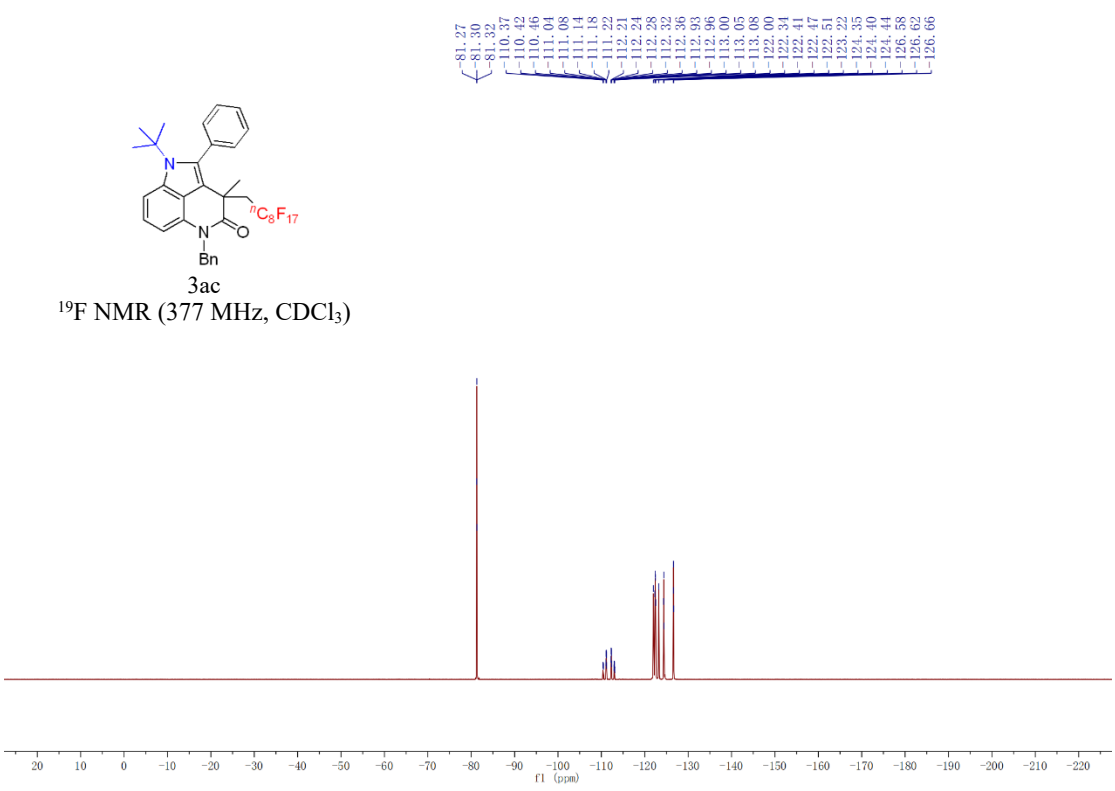
^{1}H NMR (400 MHz, $CDCl_3$)





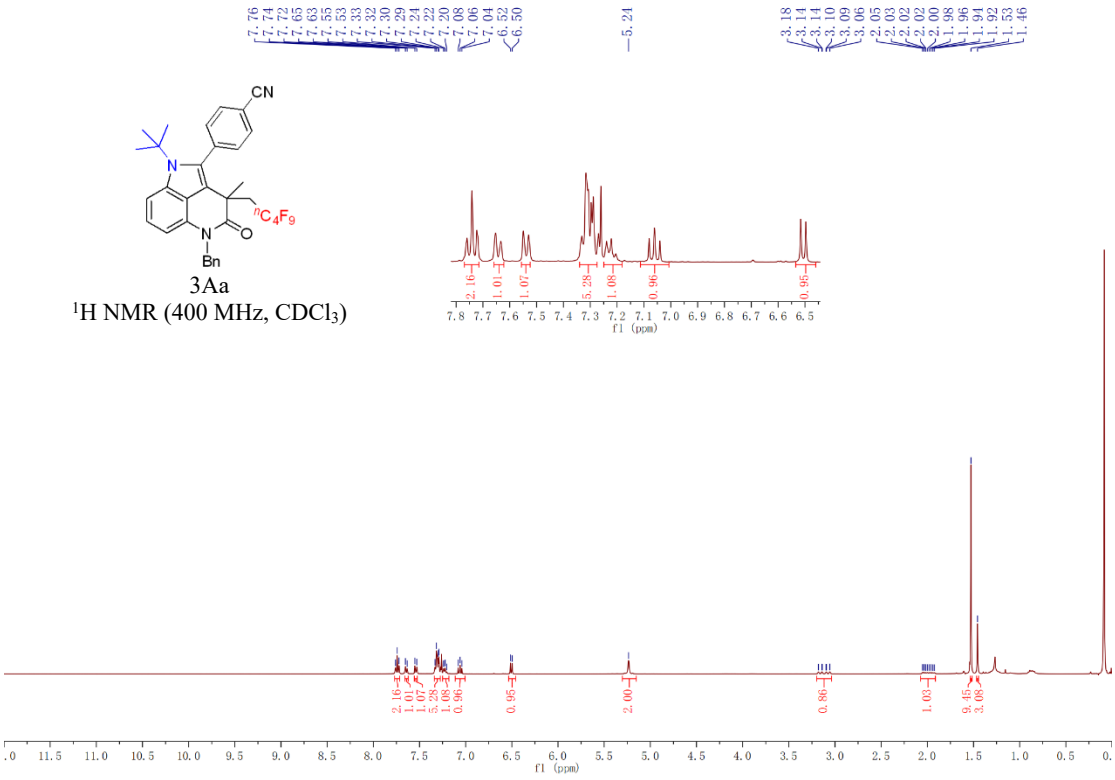
3ac

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



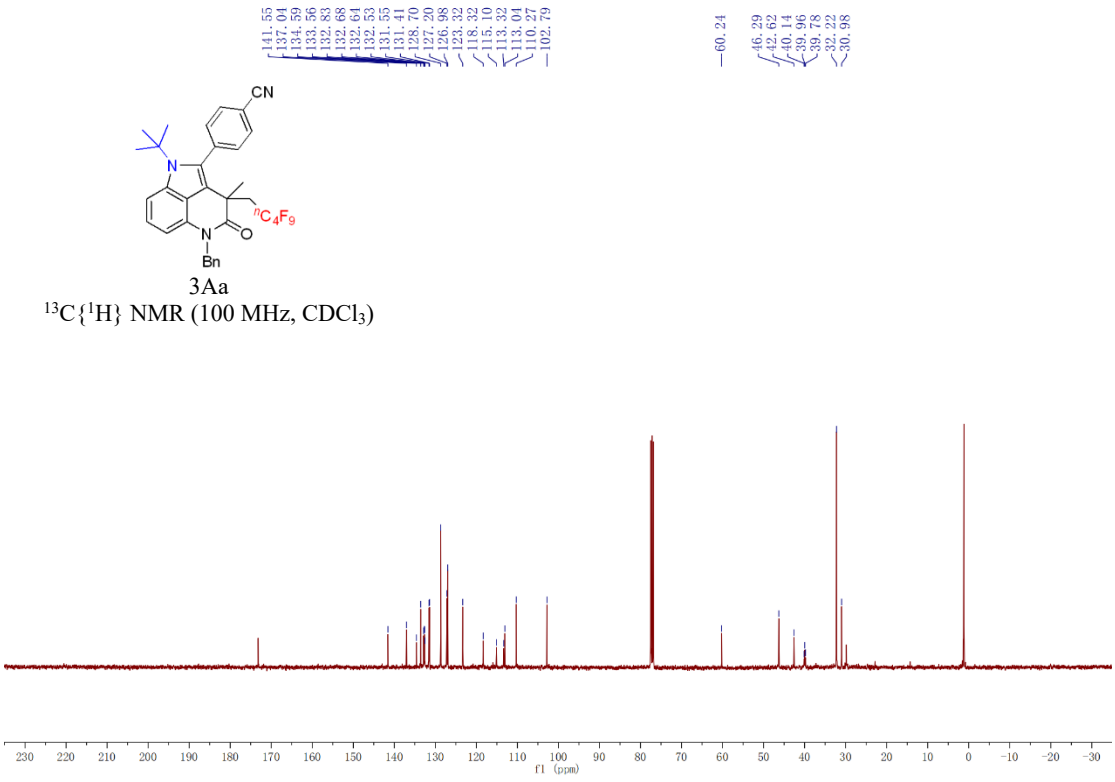
3ac

^{19}F NMR (377 MHz, $CDCl_3$)



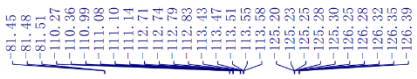
3Aa

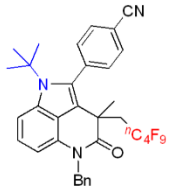
^{1}H NMR (400 MHz, $CDCl_3$)



3Aa

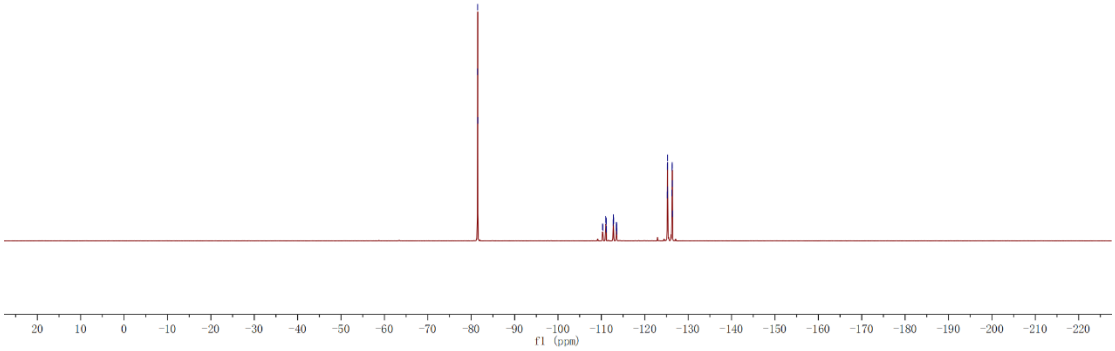
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

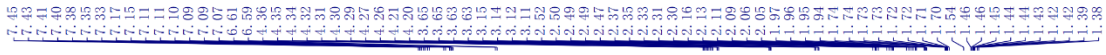


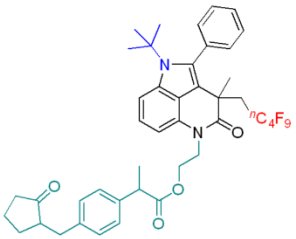


3Aa

^{19}F NMR (377 MHz, $CDCl_3$)

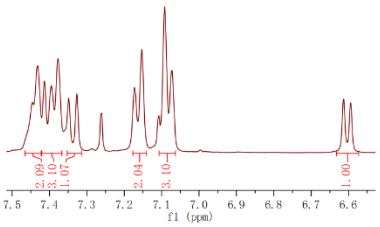


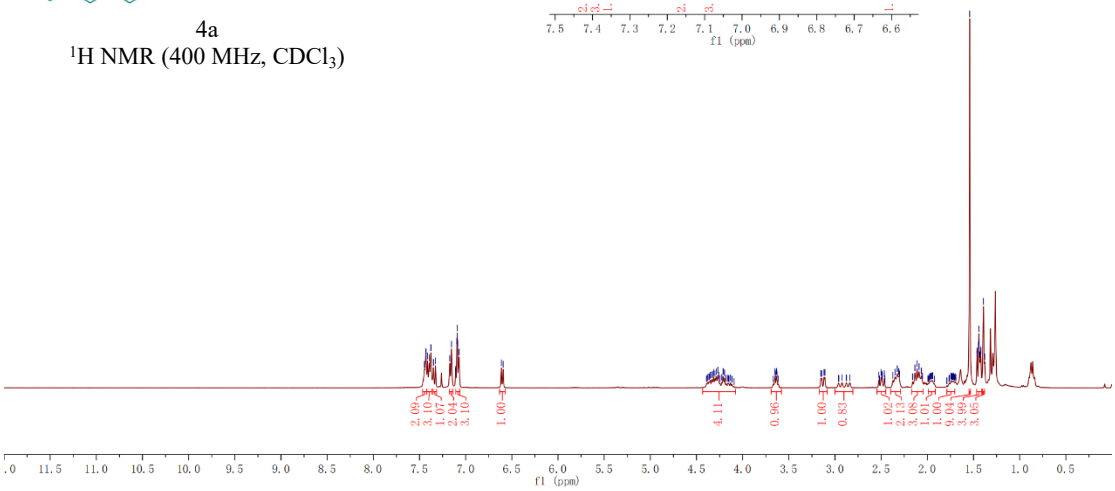


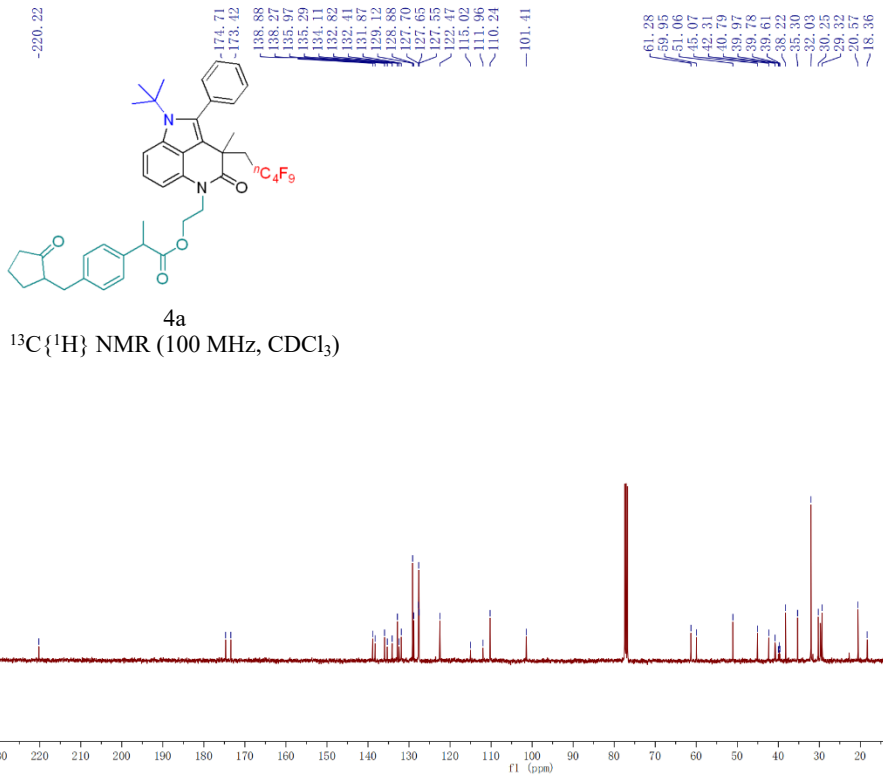


4a

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

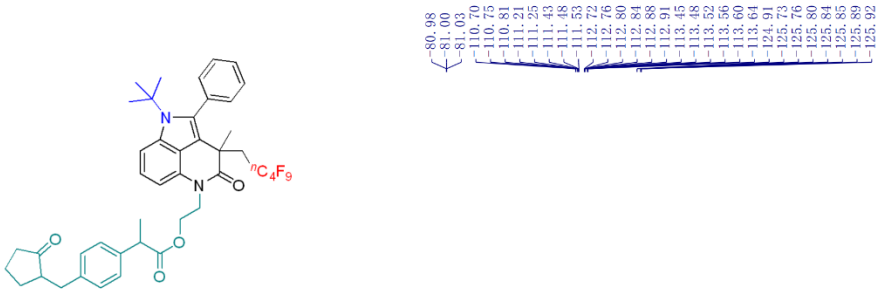






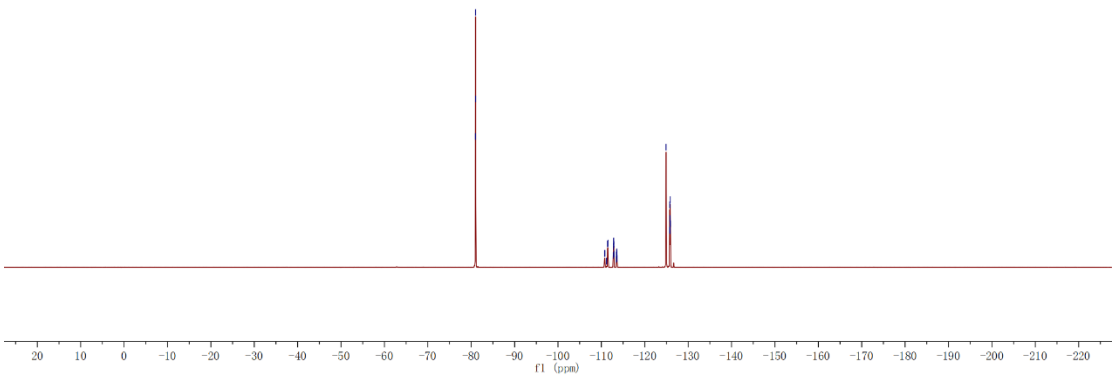
4a

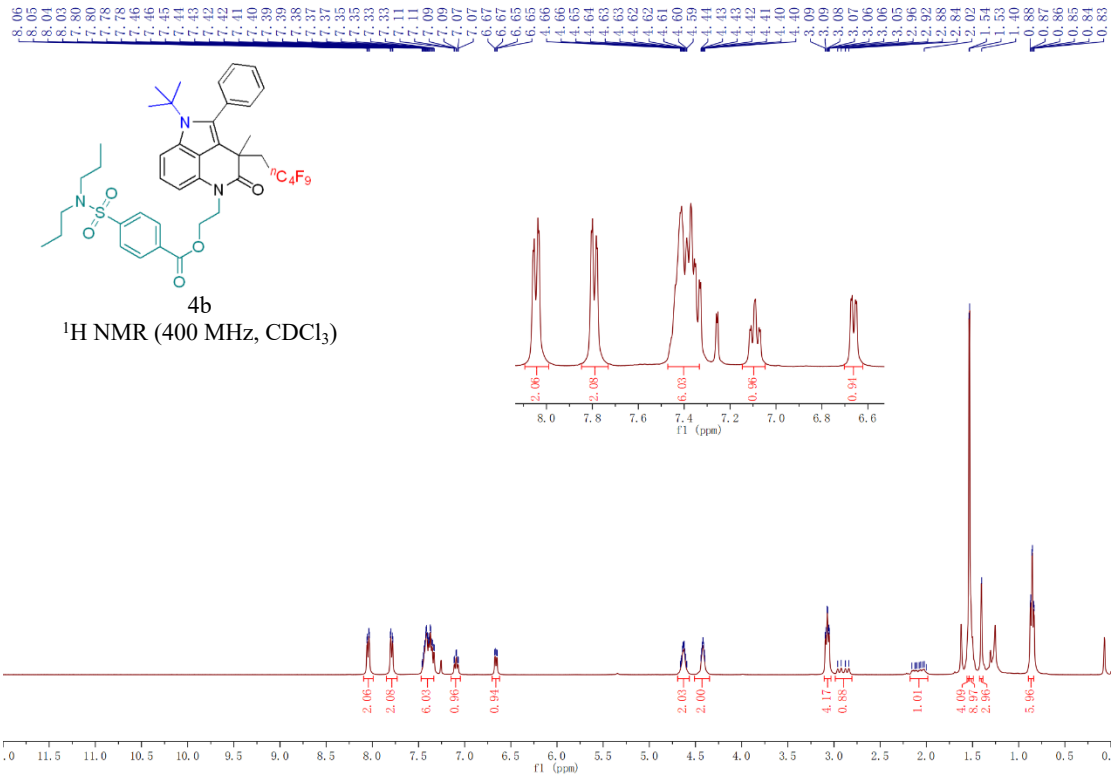
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



4a

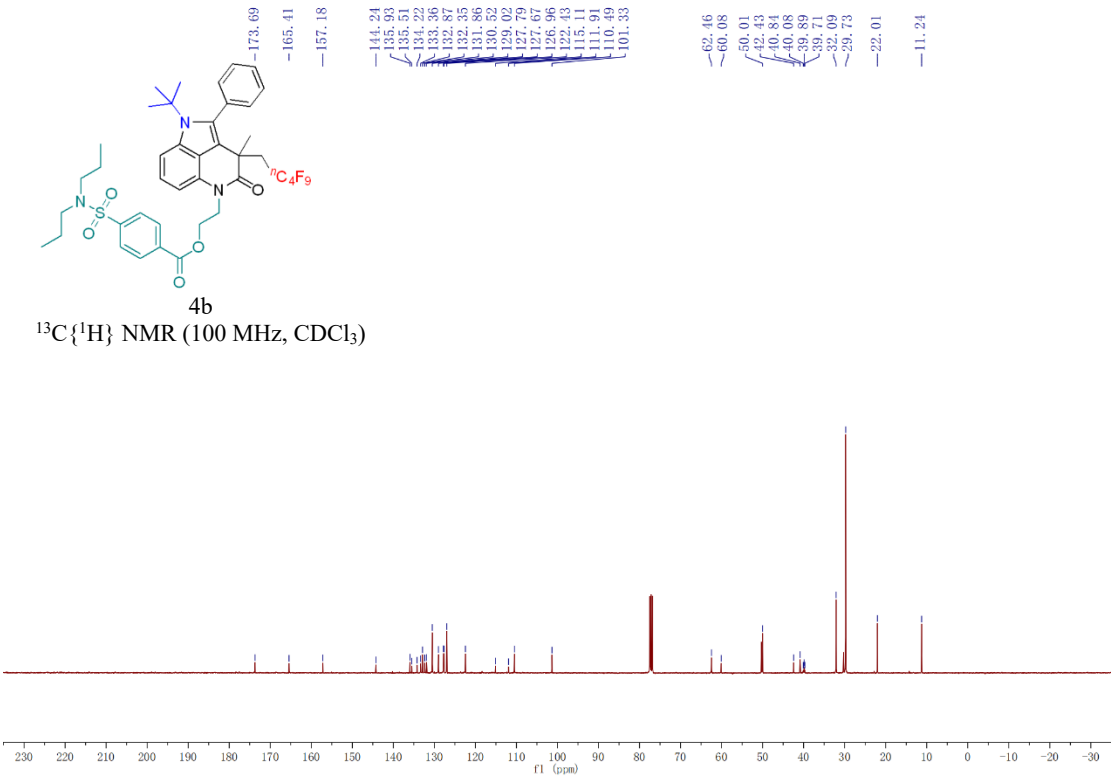
^{19}F NMR (377 MHz, $CDCl_3$)





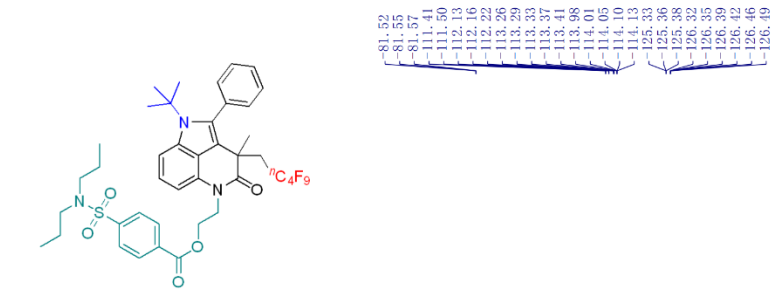
4b

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



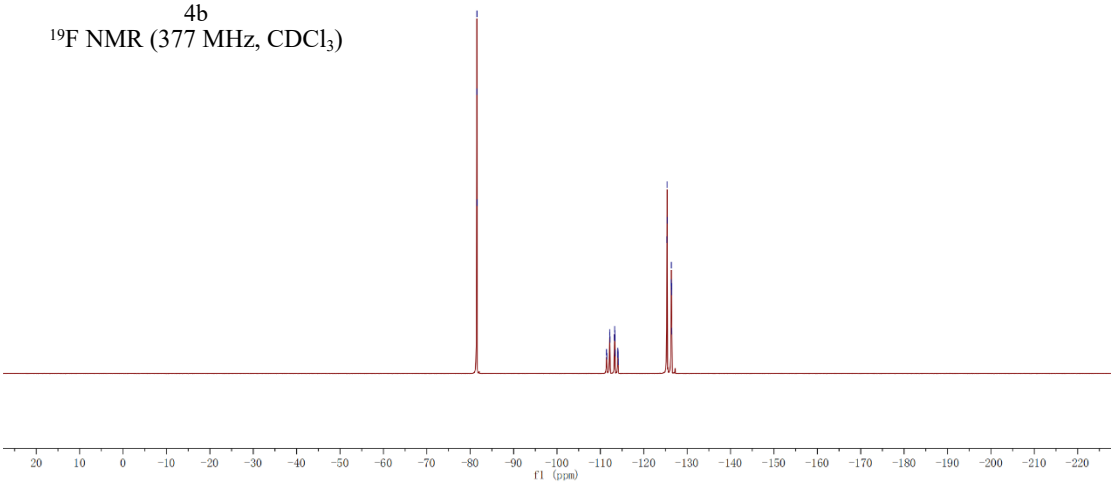
4b

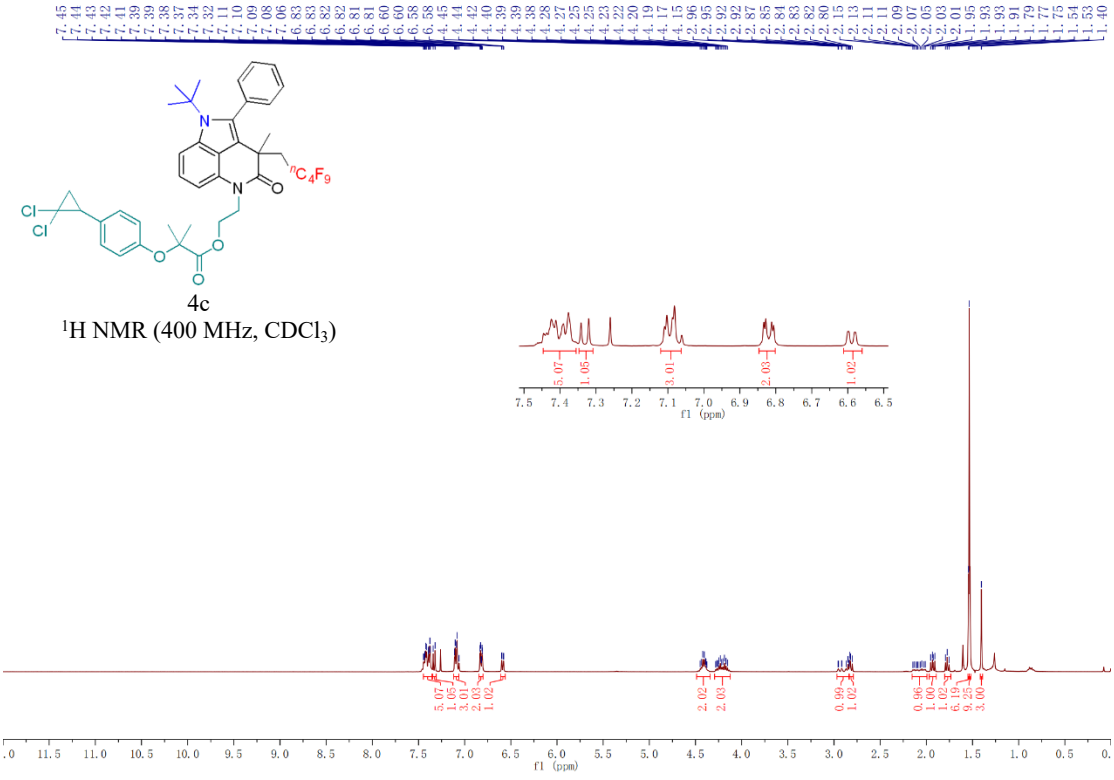
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



4b

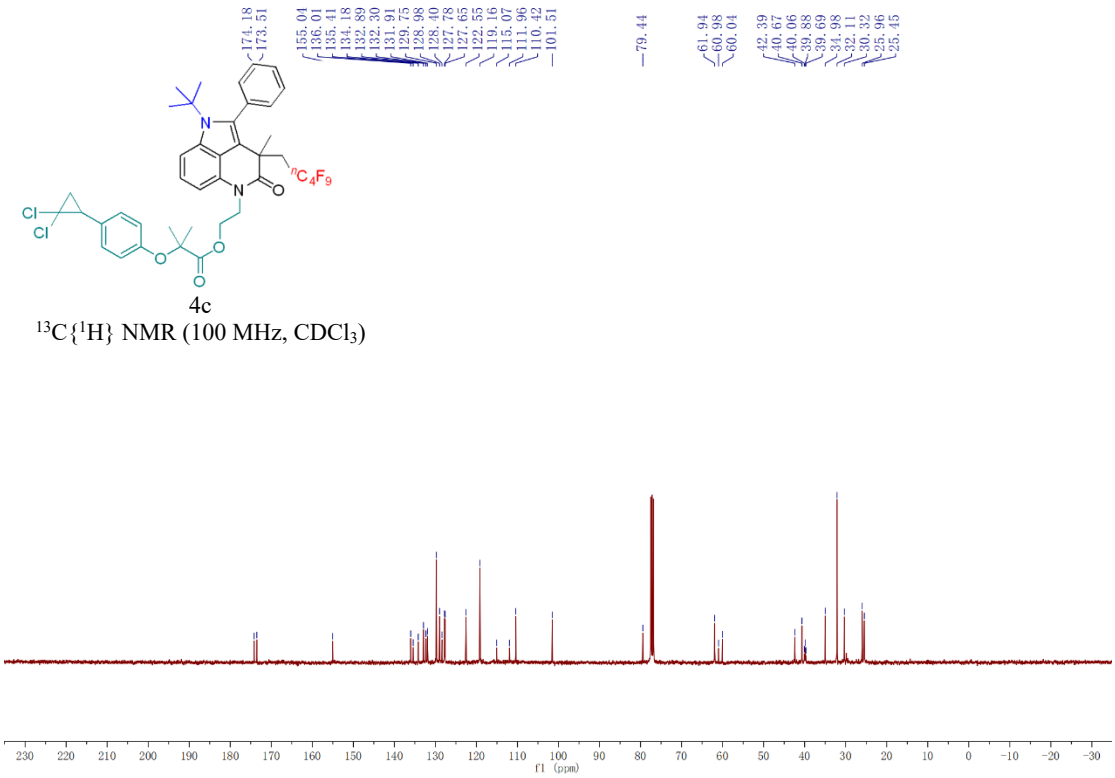
^{19}F NMR (377 MHz, $CDCl_3$)





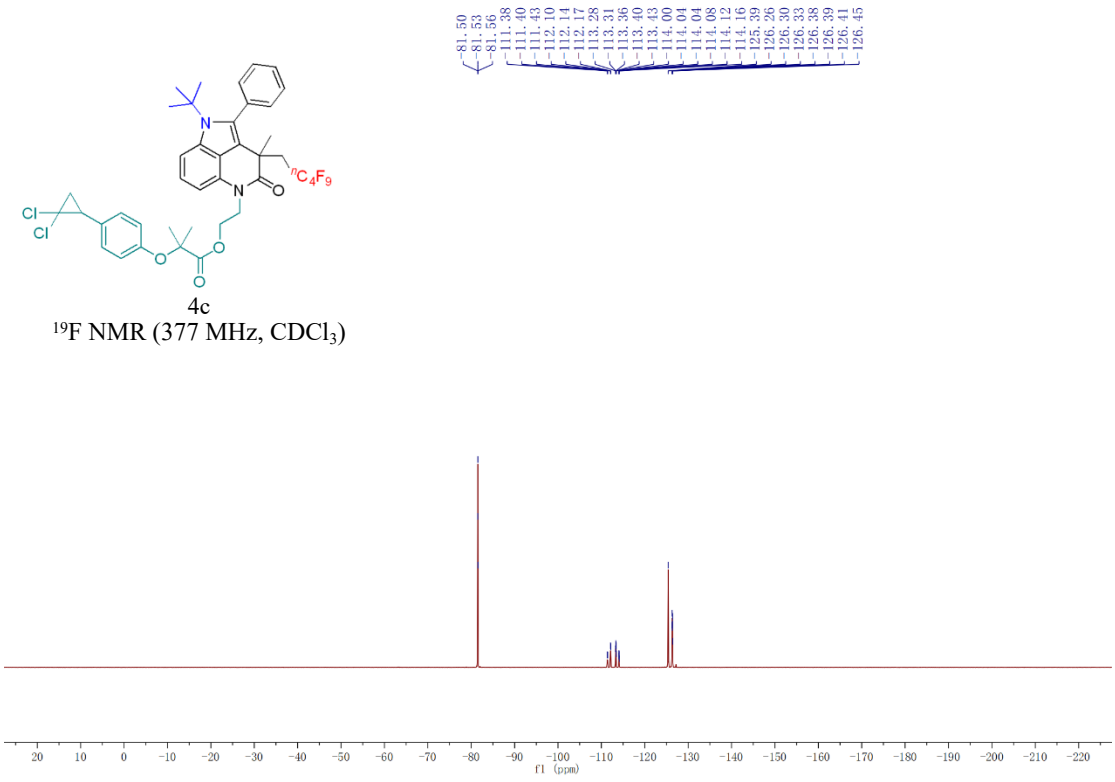
4c

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



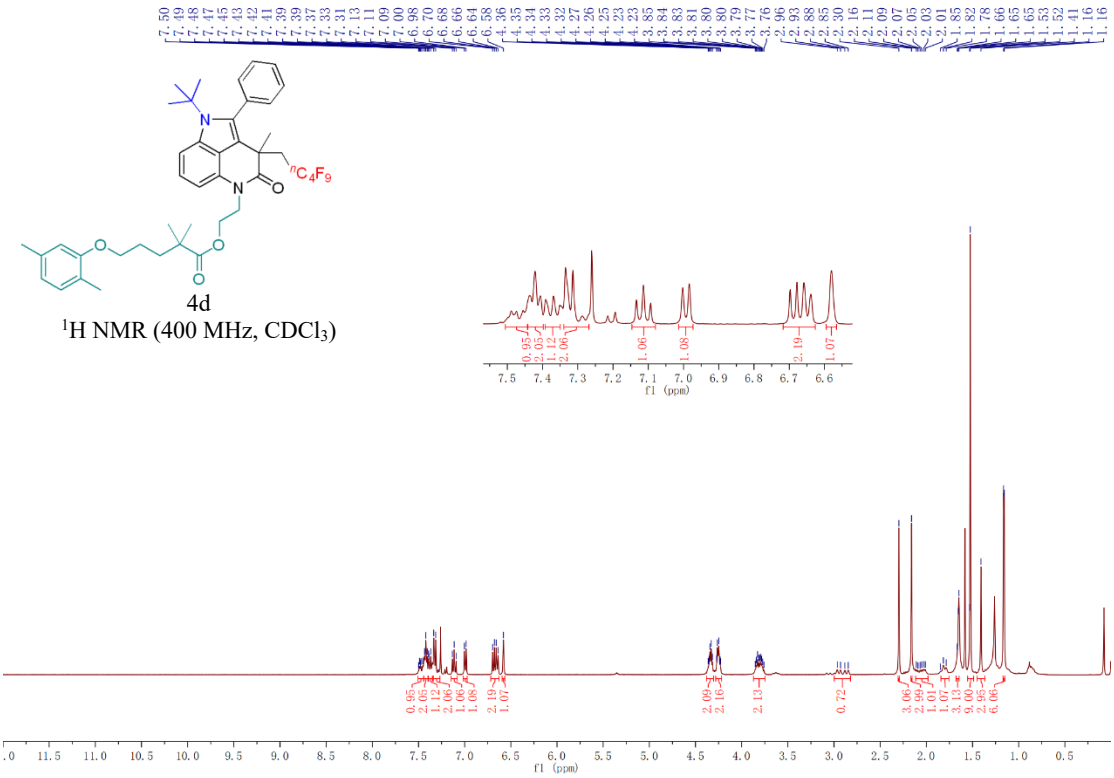
4c

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



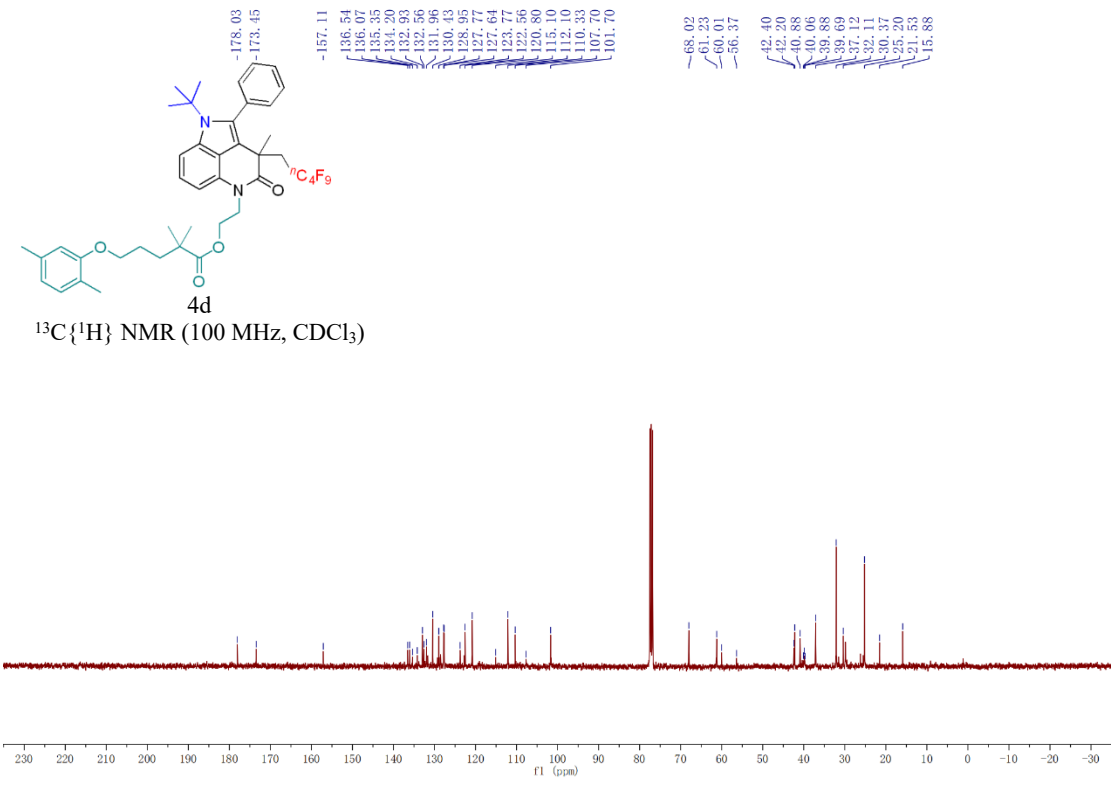
4c

^{19}F NMR (377 MHz, $CDCl_3$)



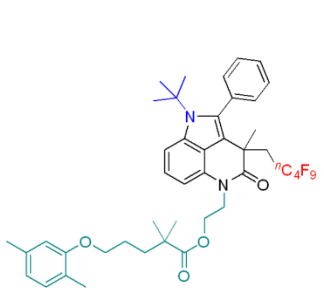
4d

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



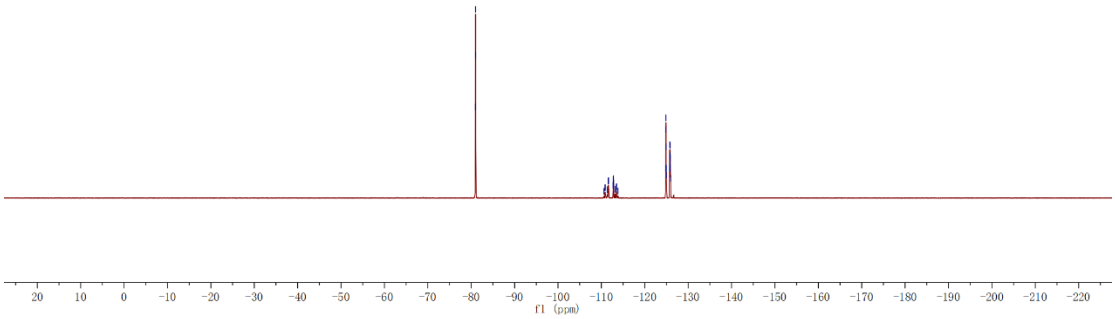
4d

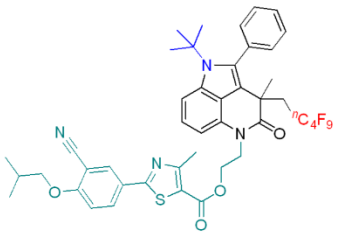
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)



4d

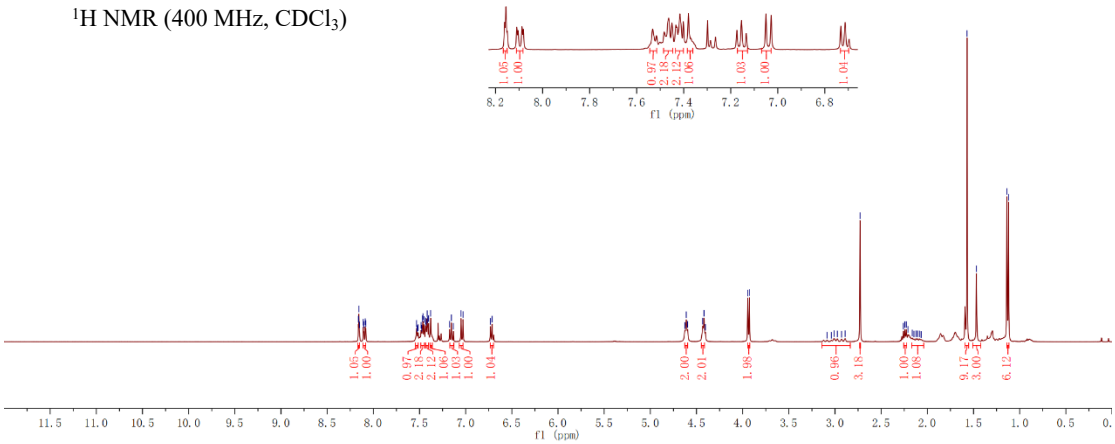
^{19}F NMR (377 MHz, $CDCl_3$)

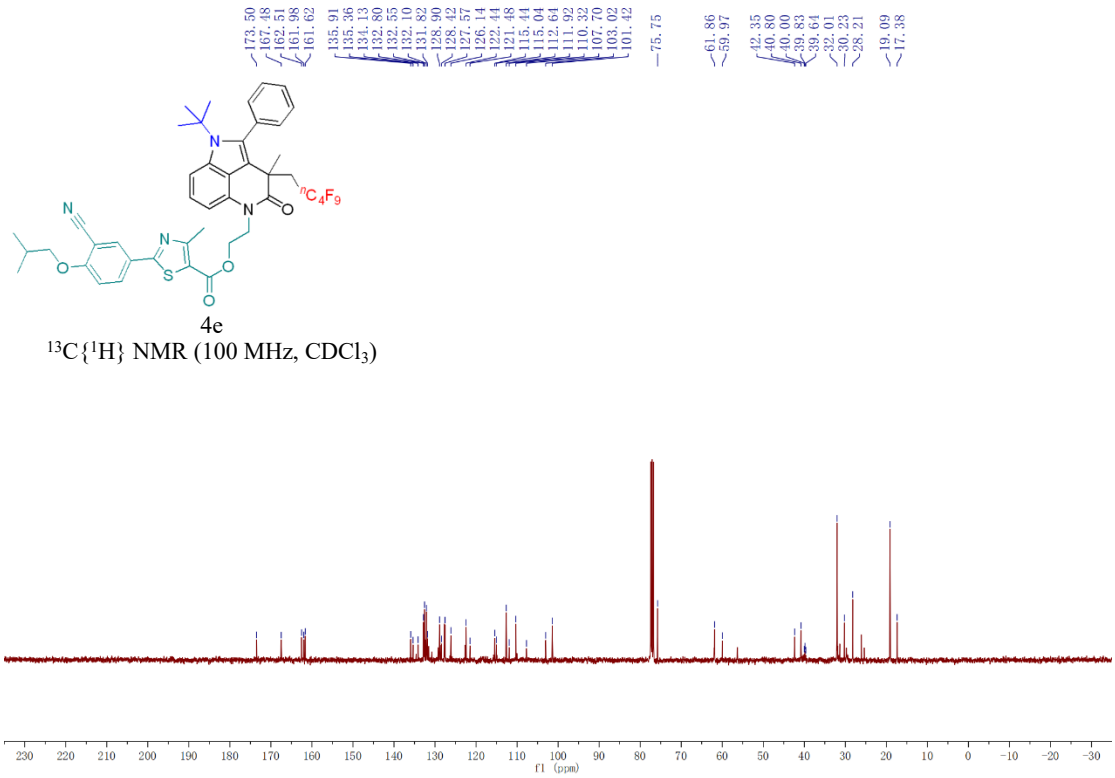




4e

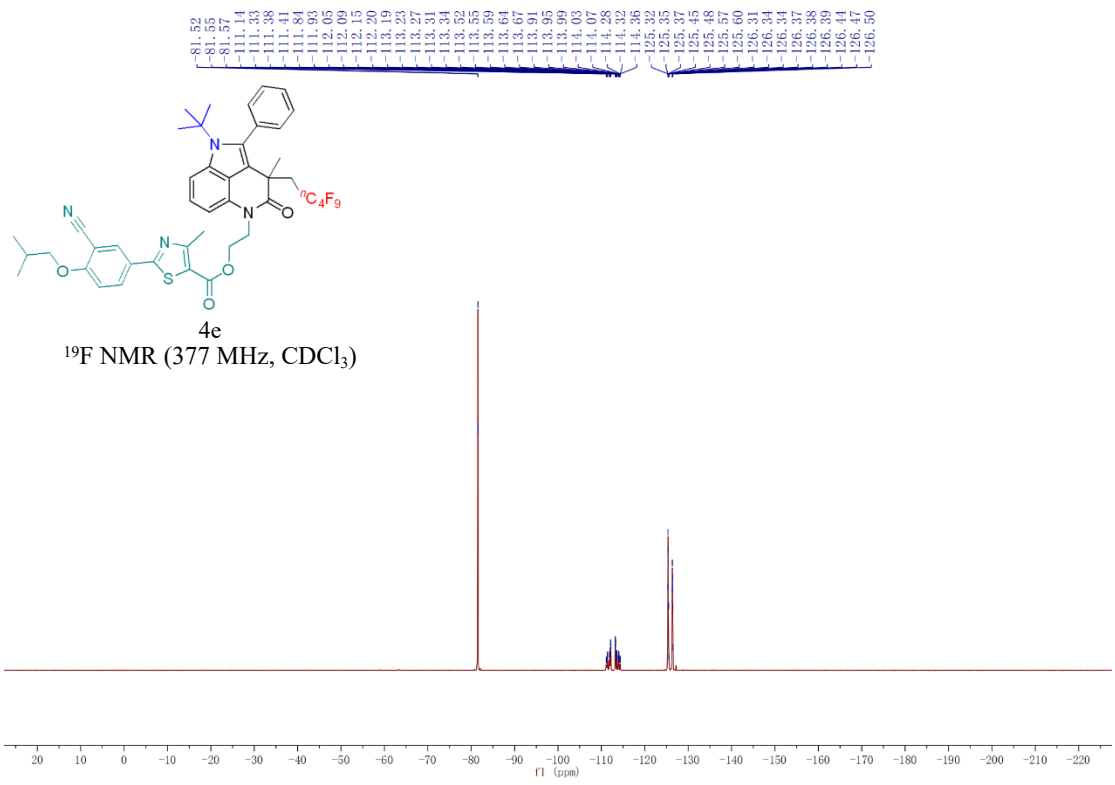
^{1}H NMR (400 MHz, $CDCl_3$)





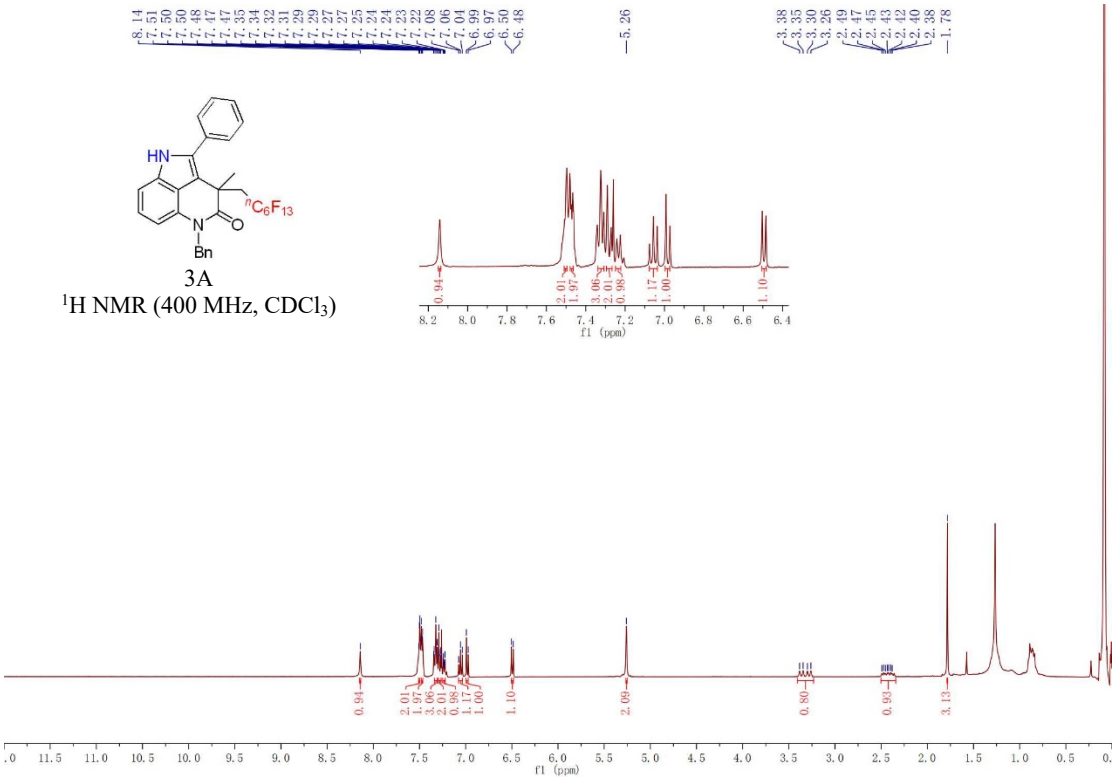
4e

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



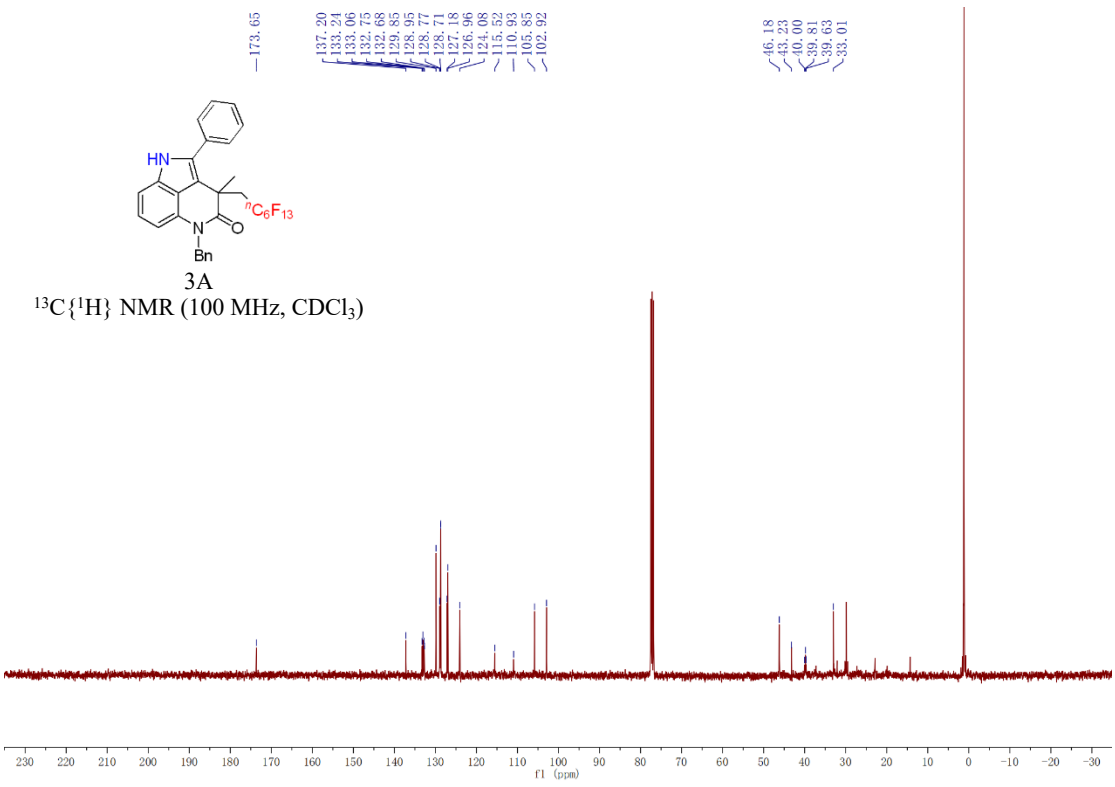
4e

^{19}F NMR (377 MHz, $CDCl_3$)



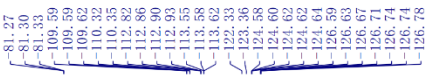
3A

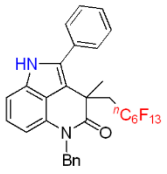
^{1}H NMR (400 MHz, $CDCl_3$)



3A

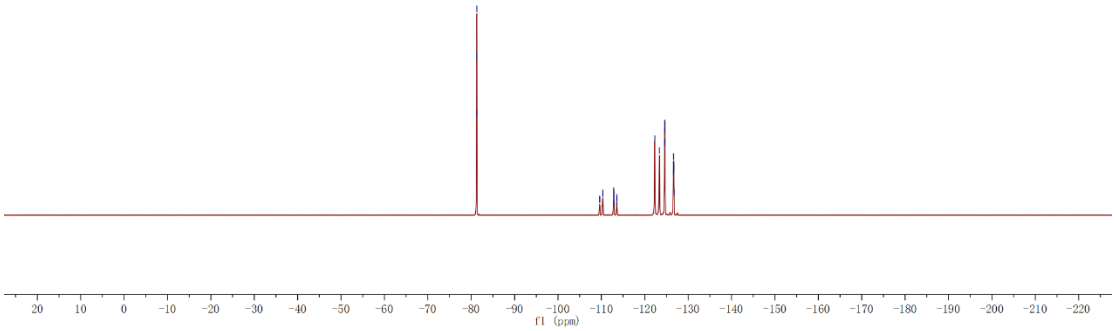
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

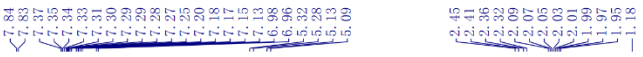


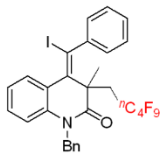


3A

^{19}F NMR (377 MHz, $CDCl_3$)

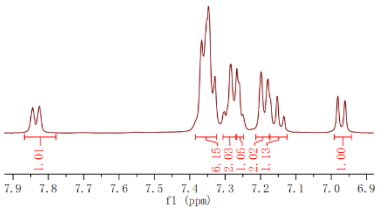


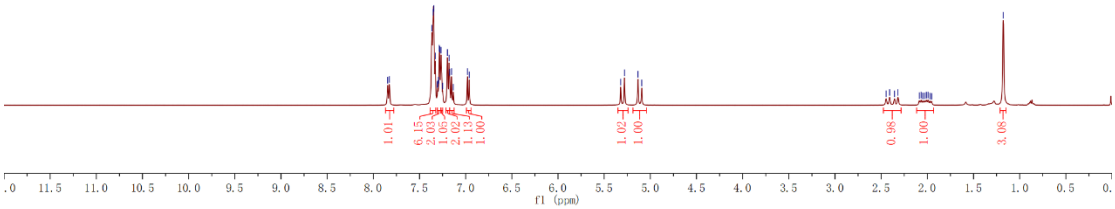


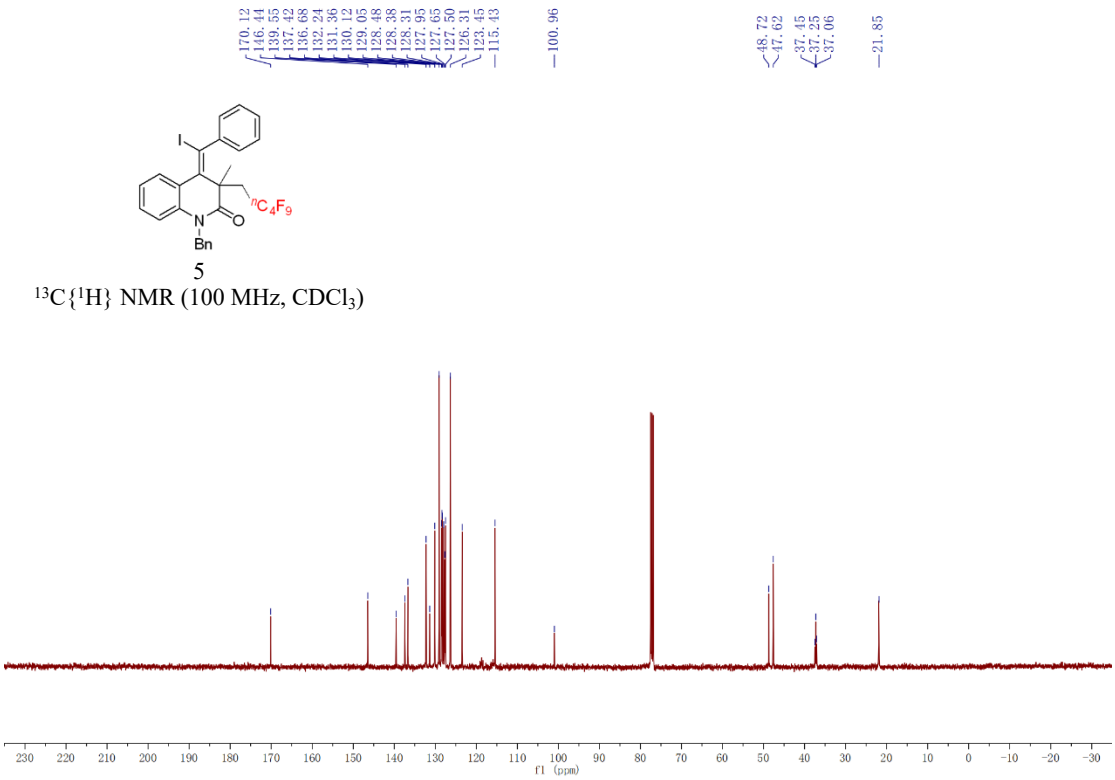


5

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

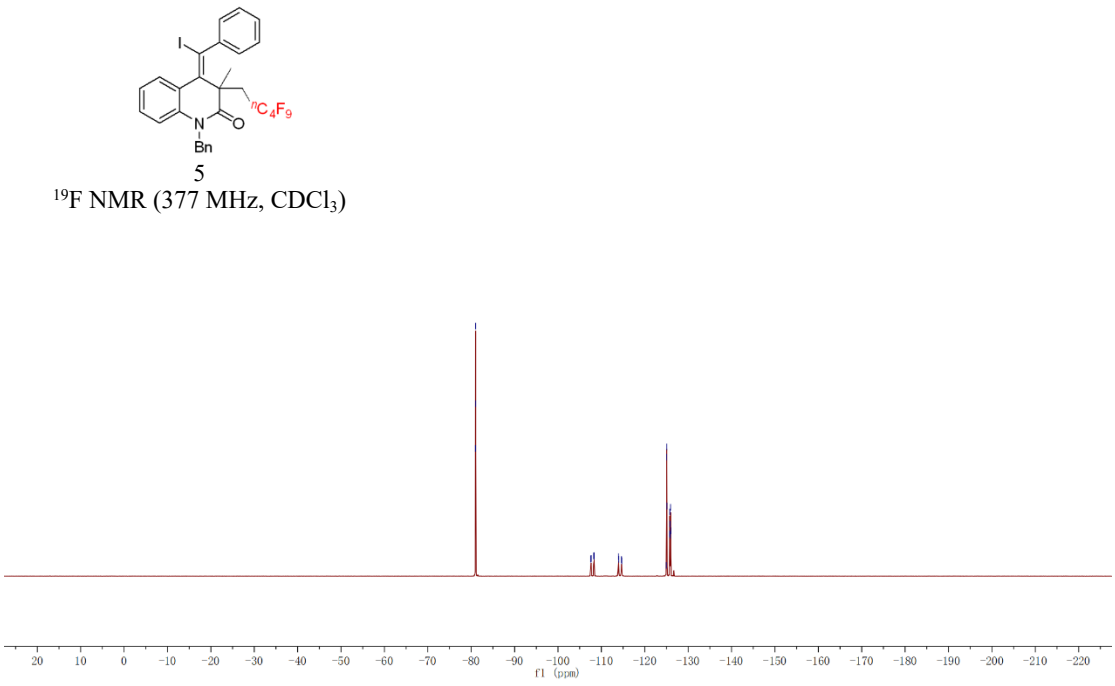






5

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



5

^{19}F NMR (377 MHz, $CDCl_3$)