

Supporting Information

Palladium-Catalyzed Decarboxylative Domino Synthesis of Fused Quinolin-2(1*H*)-one Scaffolds Containing Perfluoroalkyl Unit

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Supporting Information Placeholder

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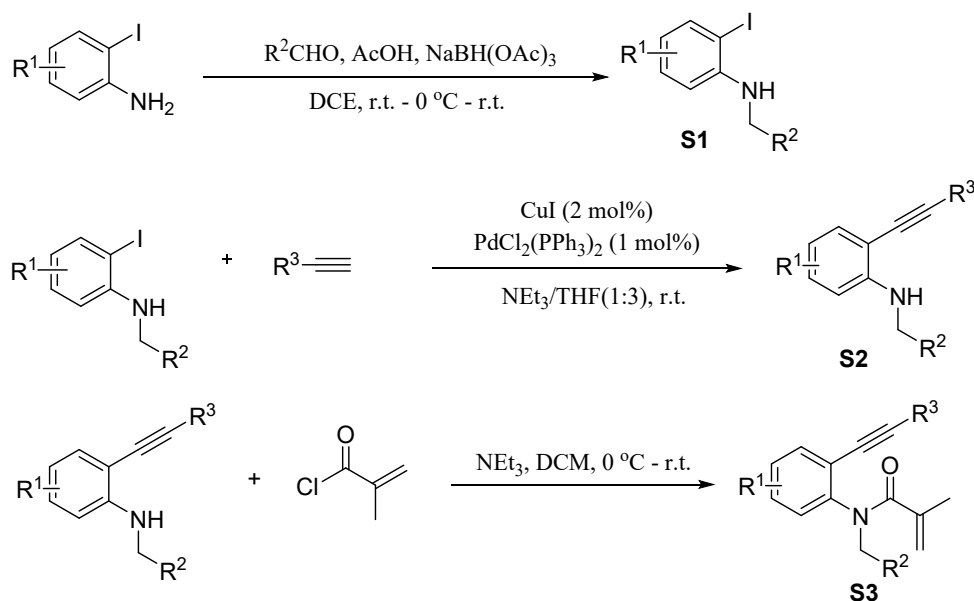
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1. General experimental information

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). ¹H NMR (400 MHz) chemical shifts were reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard. ¹³C NMR (100 MHz) chemical shifts were reported in ppm (δ) from tetramethylsilane (TMS) with the solvent resonance as the internal standard and ¹⁹F 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}

1a-h, 1n-1q, 1s (ref. 1)



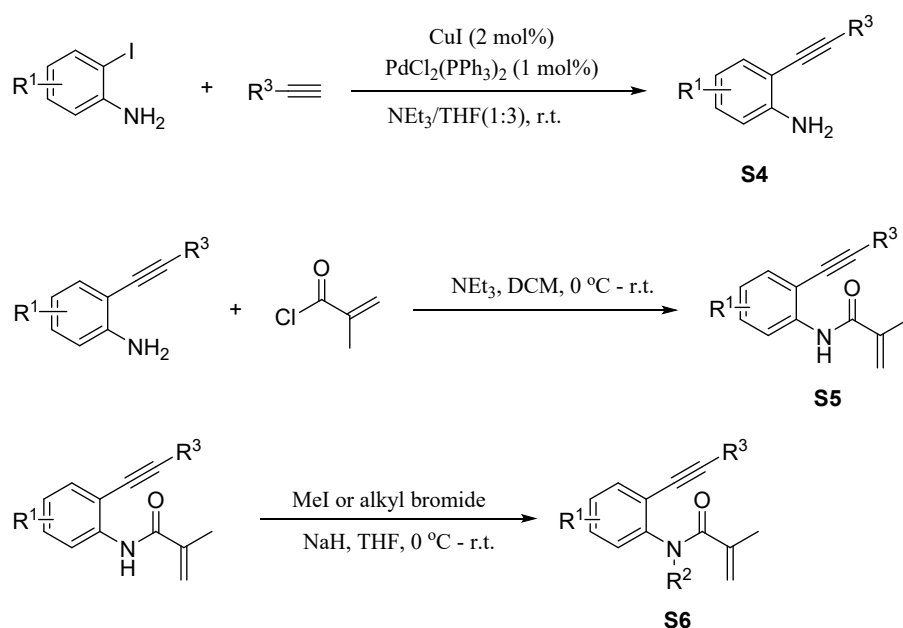
General procedure for synthesis of **S1**: To a 15 mL oven-dried tube charged with 2-iodoaniline (5.0 mmol, 1.0 equiv), aldehyde (6.0 mmol, 1.2 equiv) and dry 1,2-dichloroethane (8.0 mL) was added glacial acetic acid (30.0 μ L, 0.5 mmol, 10 mol%) at room temperature. The reaction was stirred at room 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 Na₂SO₄, 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 PdCl₂(PPh₃)₂ (0.1 mmol, 1 mol%) and CuI (0.2 mmol, 2 mol%) in a mixture of THF (30.0 mL) and Et₃N (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 CH₂Cl₂ (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 S2

CH₂Cl₂ (5.0 mL) was added methacryloyl chloride (1.5 equiv) and Et₃N (2.0 equiv) at 0 °C. The resulted mixture was stirred at room temperature for 12 h. Then, the reaction was quenched by saturated NaHCO₃ solution and the reaction mixture was extracted with CH₂Cl₂ for three times. The combined organic layer was dried over anhydrous Na₂SO₄ and concentrated in vacuo. The resulting crude mixture was purified by flash chromatography using petroleum ether / ethyl acetate = 10:1 as eluent.

1i-m (ref. 2)



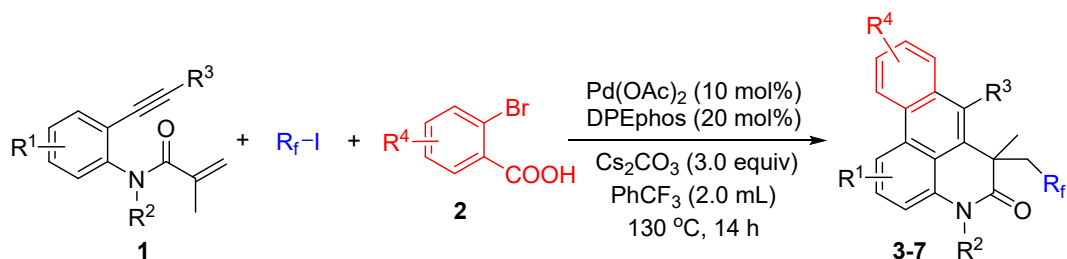
General procedure for synthesis of **S4**: To a suspension of PdCl₂(PPh₃)₂ (0.1 mmol, 1 mol%) and CuI (0.2 mmol, 2 mol%) in a mixture of THF (30.0 mL) and Et₃N (10.0 mL) was added 2-iodoaniline (10.0 mmol) and alkyne (12.0 mmol, 1.2 equiv). The reaction was allowed to react at room temperature for 12 h. Then, the crude mixture was filtered through a shot pad of Celite and washed with CH₂Cl₂ (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 CH₂Cl₂ (5.0 mL) was added methacryloyl chloride (1.5 equiv) and Et₃N (2.0 equiv) at 0 °C. The resulted mixture was stirred at room temperature for 12 h. Then, the reaction was quenched by saturated NaHCO₃ solution and the reaction mixture was extracted with CH₂Cl₂ 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.

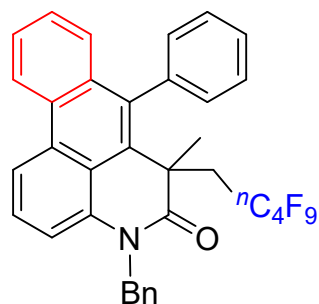
General procedure for the synthesis of substrates **S6**: To a solution of NaH (2.0 equiv) in THF (5.0 mL) at 0 °C was added a solution of **S5** (1.0 equiv) in THF dropwise and the reaction mixture was stirred for 30 min. Then, iodomethane or alkyl bromide (1.5 equiv) was added and the reaction mixture 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.

3. General procedure for synthesis of fused quinolin-2(1H)-one products (3aa-qa, 3sa, 4a-c, 5ab-ai, 6aj, 7a-e)

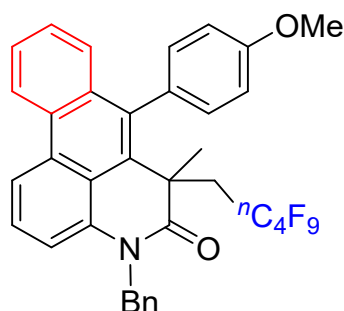


1,7-enyne **1** (0.2 mmol, 1.0 equiv), *o*-bromobenzoic acid **2** (0.4 mmol, 2.0 equiv), $Pd(OAc)_2$ (4.5 mg, 10 mol%), DPEphos (21.5 mg, 20 mol%), Cs_2CO_3 (195.0 mg, 0.6 mmol, 3.0 equiv), and perfluoroalkyl iodide (1.2 mmol, 6.0 equiv) were added to an oven-dried tube (15.0 mL) which was then placed 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 130 °C (oil bath) for 14 h. Upon the reaction was completed, the resulting mixture was purified by silica gel column using chromatography (petroleum ether / ethyl acetate = 20:1) to obtain products (**3aa-qa**, **3sa**, **4a-c**, **5ab-ai**, **6aj**, **7a-e**).

4. Characterization data of products (3aa-qa, 3sa, 4a-c, 5ab-ai, 6aj, 7a-e)

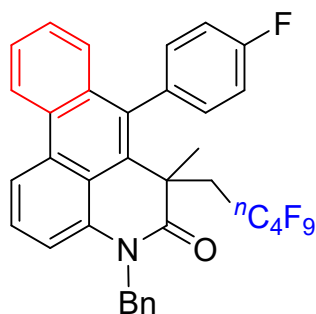


4-benzyl-6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-7-phenyl-4H-naphtho[3,2,1-de]quinolin-5(6H)-one (3aa). The product was purified by column chromatography (petroleum ether / ethyl acetate = 20:1); White solid, 91.9 mg, 71% yield; mp 154.8-156.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.68 (d, $J = 8.4$ Hz, 1H), 8.45 (d, $J = 8.4$ Hz, 1H), 7.61 (d, $J = 7.3$ Hz, 1H), 7.55 (m, 4H), 7.50 (d, $J = 6.5$ Hz, 1H), 7.41 – 7.36 (m, 2H), 7.34 (d, $J = 4.4$ Hz, 4H), 7.30 – 7.26 (m, 1H), 7.16 (d, $J = 7.9$ Hz, 1H), 6.94 (d, $J = 8.5$ Hz, 1H), 5.45 (dd, $J = 42.3, 14.4$ Hz, 2H), 3.26 (dd, $J = 34.7, 15.3$ Hz, 1H), 3.13 – 2.94 (m, 1H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.3, 139.9, 137.8, 136.6, 136.3, 134.0, 133.4, 131.99, 131.96, 131.1, 129.8, 129.2, 128.9, 128.25, 128.18, 127.9, 127.6, 127.32, 127.27, 127.1, 126.9, 126.5, 122.8, 118.0, 117.8, 112.6, 47.9, 45.3, 39.7 (t, $J = 18.1$ Hz), 31.9; ^{19}F NMR (377 MHz, CDCl_3) δ -80.99 (s, 3F), -108.88 – -110.15 (m, 1F), -110.98 – -112.17 (m, 1F), -123.33 – -125.42 (m, 2F), -125.87 (s, 2F); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{35}\text{H}_{24}\text{F}_9\text{NNaO}^+$: 668.1606; found: 668.1615.



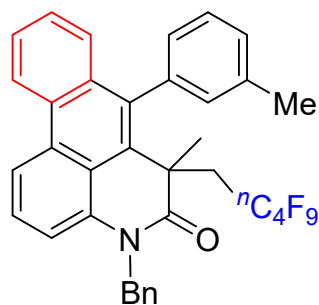
4-benzyl-7-(4-methoxyphenyl)-6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-4H-naphtho[3,2,1-de]quinolin-5(6H)-one (3ba). The product was purified by column chromatography (petroleum ether / ethyl acetate = 20:1); White solid, 74.6 mg, 55% yield; mp 212.5-213.7 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.71 (d, $J = 8.4$ Hz, 1H), 8.49 (d, $J = 8.5$ Hz, 1H), 7.63 (t, $J = 7.6$ Hz, 1H), 7.55 (t, $J = 8.1$ Hz, 1H), 7.43 (m, 2H), 7.37 (d, $J = 4.4$ Hz, 4H), 7.30 (dd, $J = 7.4, 3.6$ Hz, 2H),

7.18 (d, $J = 7.9$ Hz, 1H), 7.15 – 7.09 (m, 2H), 7.03 (d, $J = 8.4$ Hz, 1H), 5.47 (dd, $J = 43.6, 14.5$ Hz, 2H), 4.00 (s, 3H), 3.30 (dd, $J = 34.6, 15.0$ Hz, 1H), 3.11 (m, 1H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.4, 159.4, 137.6, 136.6, 136.3, 134.5, 134.4, 133.1, 133.0, 131.6, 131.0, 130.2, 129.3, 128.9, 127.6, 127.3, 127.0, 126.9, 126.5, 122.8, 117.95, 117.90, 113.6, 113.3, 112.6, 55.5, 47.8, 45.3, 39.6 (t, $J = 18.1$ Hz), 32.0; ^{19}F NMR (377 MHz, CDCl_3) δ -80.98 (s, 3F), -108.90 – -110.15 (m, 1F), -110.70 – -112.39 (m, 1F), -124.35 (dd, 2F), -125.84 (d, $J = 9.9$ Hz, 2F); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{36}\text{H}_{26}\text{F}_9\text{NNaO}_2^+$: 698.1712; found: 698.1721.

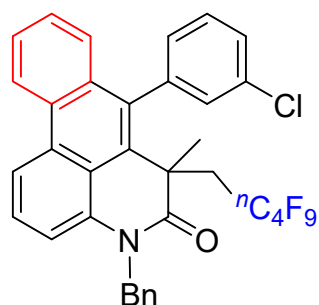


4-benzyl-7-(4-fluorophenyl)-6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-4H-

naphtho[3,2,1-*de*]quinolin-5(6H)-one (3ca). The product was purified by column chromatography (petroleum ether / ethyl acetate = 20:1); White solid, 84.5 mg, 64% yield; mp 190.8-192.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.69 (d, $J = 8.4$ Hz, 1H), 8.46 (d, $J = 8.4$ Hz, 1H), 7.61 (t, $J = 7.5$ Hz, 1H), 7.53 (t, $J = 8.1$ Hz, 1H), 7.49 – 7.45 (m, 1H), 7.42 (t, $J = 7.7$ Hz, 1H), 7.35 (d, $J = 4.3$ Hz, 5H), 7.31 – 7.23 (m, 3H), 7.17 (d, $J = 7.9$ Hz, 1H), 6.93 (d, $J = 8.4$ Hz, 1H), 5.45 (dd, $J = 40.8, 14.9$ Hz, 2H), 3.32 (dd, $J = 34.8, 15.3$ Hz, 1H), 2.97 (m, 1H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.1, 162.6 (d, $J = 248.7$ Hz), 136.7, 136.4 (d, $J = 20.3$ Hz), 135.7 (d, $J = 3.7$ Hz), 135.1 (d, $J = 7.7$ Hz), 134.0, 133.6, 131.1, 130.3, 129.3, 128.9, 127.4 (d, $J = 20.5$ Hz), 127.2, 127.0, 126.5, 122.9, 118.0, 117.7, 115.4, 115.3, 115.2, 115.1, 112.7, 47.9, 45.3, 39.7 (t, $J = 18.1$ Hz), 32.0; ^{19}F NMR (377 MHz, CDCl_3) δ -80.97 (s, 3F), -108.96 – -110.15 (m, 1F), -111.01 – -112.35 (m, 1F), -113.21 (s, 1F), -123.34 – -125.39 (m, 2F), -125.82 (d, $J = 11.1$ Hz, 2F); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{35}\text{H}_{23}\text{F}_{10}\text{NNaO}^+$: 686.1512; found: 686.1517.

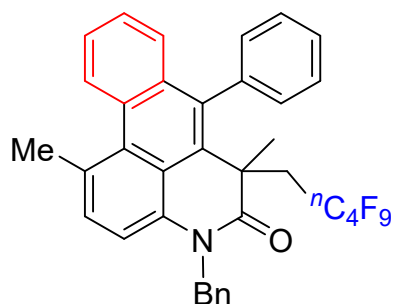


4-benzyl-6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-7-(*m*-tolyl)-4H-naphtho[3,2,1-*de*]quinolin-5(6H)-one (3da). The product was purified by column chromatography (petroleum ether / ethyl acetate = 20:1); White solid, 85.9 mg, 65% yield; mp 171.2-172.4 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.67 (d, *J* = 8.4 Hz, 1H), 8.45 (d, *J* = 8.4 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 8.1 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.35 (s, 1H), 7.33 (d, *J* = 4.3 Hz, 4H), 7.29 (s, 1H), 7.26 (s, 1H), 7.16 (dd, *J* = 13.2, 7.7 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 1H), 5.43 (dd, *J* = 52.4, 15.2 Hz, 2H), 3.36 – 2.82 (m, 2H), 2.44 (s, 3H), 1.91 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 173.3, 139.7, 138.0, 137.9, 136.6, 136.3, 134.0, 132.7, 131.0, 130.5, 129.7, 129.2, 128.9, 128.8, 127.8, 127.7, 127.3, 127.0, 126.9, 126.5, 122.8, 118.0, 117.8, 112.6, 47.8, 45.3, 39.5 (t, *J* = 17.7 Hz), 32.0, 21.4; ¹⁹F NMR (377 MHz, CDCl₃) δ -81.02 (s, 3F), -109.08 – -110.29 (m, 1F), -110.86 – -112.03 (m, 1F), -123.47 – -125.47 (m, 2F), -125.88 (s, 2F); HRMS (ESI-TOF) *m/z*: [M+Na]⁺ Calcd. for C₃₆H₂₆F₉NNaO⁺ : 682.1763; found: 682.1761.

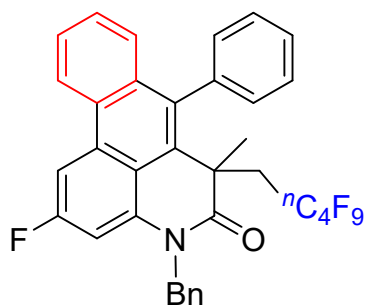


4-benzyl-7-(3-chlorophenyl)-6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-4H-naphtho[3,2,1-*de*]quinolin-5(6H)-one (3ea). The product was purified by column chromatography (petroleum ether / ethyl acetate = 20:1); White solid, 78.4 mg, 58% yield; mp 145.6-146.8 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.69 (d, *J* = 8.3 Hz, 1H), 8.45 (d, *J* = 8.3 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.54 (t, *J* = 8.2 Hz, 2H), 7.51 – 7.46 (m, 2H), 7.45 – 7.39 (m, 1H), 7.35 – 7.32 (m, 4H), 7.30 – 7.27 (m, 2H), 7.16 (d, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 5.44 (dd, *J* = 43.5, 15.0 Hz, 2H), 3.31

(dd, $J = 34.8, 15.3$ Hz, 1H), 3.06 – 2.82 (m, 1H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.0, 141.8, 136.5, 136.4, 136.2, 134.6, 133.5, 132.12, 132.08, 131.6, 131.2, 130.1, 129.3, 129.2, 129.0, 128.5, 127.6, 127.32, 127.29, 127.1, 126.5, 122.9, 118.0, 117.6, 112.8, 47.9, 45.2, 39.7 (t, $J = 18.4$ Hz), 32.0; ^{19}F NMR (377 MHz, CDCl_3) δ -80.98 (s, 3F), -109.14 – -110.21 (m, 1F), -111.19 – -112.38 (m, 1F), -123.99 – -124.76 (m, 2F), -125.83 (s, 2F); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{35}\text{H}_{23}\text{ClF}_9\text{NNaO}^+$: 702.1217; found: 702.1224.

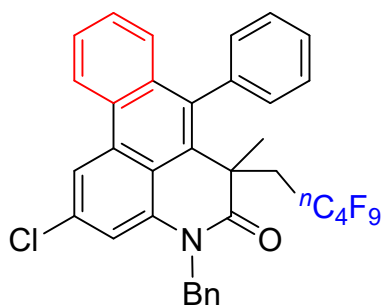


4-benzyl-1,6-dimethyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-7-phenyl-4H-naphtho[3,2,1-de]quinolin-5(6H)-one (3fa). The product was purified by column chromatography (petroleum ether / ethyl acetate = 20:1); White solid, 59.7 mg, 45% yield; mp 145.1-146.3 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.63 (d, $J = 8.5$ Hz, 1H), 7.52 (dt, $J = 9.4, 7.5$ Hz, 4H), 7.47 (d, $J = 6.5$ Hz, 1H), 7.36 (t, $J = 7.2$ Hz, 3H), 7.32 (d, $J = 4.5$ Hz, 4H), 7.24 (d, $J = 4.9$ Hz, 1H), 7.07 (d, $J = 8.2$ Hz, 1H), 6.99 (d, $J = 8.4$ Hz, 1H), 5.41 (dd, $J = 59.6, 16.1$ Hz, 2H), 3.22 (dd, $J = 34.9, 15.5$ Hz, 1H), 3.10 – 3.03 (m, 1H), 3.00 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.9, 139.9, 137.5, 136.7, 134.8, 134.2, 133.4, 132.1, 131.5, 131.4, 130.0, 129.9, 129.7, 128.9, 128.2, 128.1, 127.9, 127.6, 127.2, 126.8, 126.6, 126.4, 124.9, 119.3, 112.3, 47.8, 45.2, 39.7 (t, $J = 18.2$ Hz), 31.7, 26.9; ^{19}F NMR (377 MHz, CDCl_3) δ -81.00 (s, 3F), -108.91 – -110.13 (m, 1F), -111.11 – -112.46 (m, 1F), -123.53 – -125.42 (m, 2F), -125.86 (s, 2F); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{36}\text{H}_{26}\text{F}_9\text{NNaO}^+$: 682.1763; found: 682.1761.



4-benzyl-2-fluoro-6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-7-phenyl-4H-

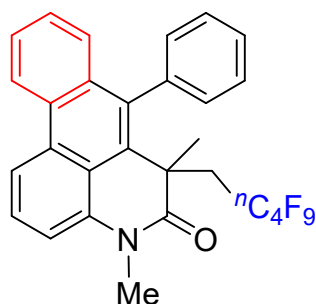
naphtho[3,2,1-*de*]quinolin-5(6*H*)-one (3ga). The product was purified by column chromatography (petroleum ether / ethyl acetate = 20:1); White solid, 74.1 mg, 56% yield; mp 159.4-160.6 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.52 (d, *J* = 8.4 Hz, 1H), 8.04 (dd, *J* = 10.4, 2.1 Hz, 1H), 7.63 – 7.52 (m, 4H), 7.45 (d, *J* = 5.2 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.29 (m, 6H), 6.92 (d, *J* = 8.5 Hz, 2H), 5.39 (dd, *J* = 53.0, 15.7 Hz, 2H), 3.21 (dd, *J* = 34.6, 15.1 Hz, 1H), 3.11 – 2.94 (m, 1H), 1.88 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 173.5, 161.7 (d, *J* = 244.2 Hz), 139.6, 138.7, 138.6, 136.9, 135.9, 134.3, 133.5, 132.8, 132.7, 132.0, 129.5, 129.1, 128.8 (d, *J* = 4.2 Hz), 128.4, 128.2 (d, *J* = 23.6 Hz), 127.7, 127.6, 127.0, 126.6, 122.9, 114.7, 102.5 (d, *J* = 22.7 Hz), 102.1, 48.1, 45.3, 39.8 (t, *J* = 17.5 Hz), 31.9; ¹⁹F NMR (377 MHz, CDCl₃) δ -80.99 (s, 3F), -108.94 – -110.05 (m, 1F), -110.95 – -112.19 (m, 2F), -123.44 – -125.40 (m, 2F), -125.87 (d, *J* = 9.9 Hz, 2F); HRMS (ESI-TOF) *m/z*: [M+Na]⁺ Calcd. for C₃₅H₂₃F₁₀NNaO⁺ : 686.1512; found: 686.1521.



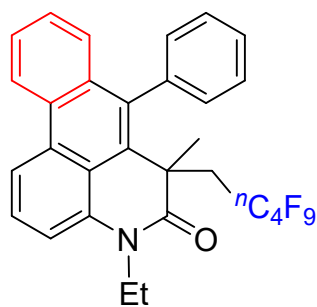
4-benzyl-2-chloro-6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-7-phenyl-4H-

naphtho[3,2,1-*de*]quinolin-5(6*H*)-one (3ha). The product was purified by column chromatography (petroleum ether / ethyl acetate = 20:1); White solid, 88.7 mg, 65% yield; mp 160.6-161.8 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.58 (d, *J* = 8.4 Hz, 1H), 8.39 (d, *J* = 1.7 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 5.3 Hz, 3H), 7.45 (s, 1H), 7.40 (t, 1H), 7.34 (m, 5H), 7.30 – 7.27 (m, 1H), 7.13 (d, *J* = 1.7 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 5.39 (dd, *J* = 51.9, 16.0 Hz, 2H), 3.20 (dd, *J* = 34.5, 15.2

Hz, 1H), 3.08 – 2.90 (m, 1H), 1.87 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.4, 139.5, 138.0, 137.8, 135.9, 134.3, 133.5, 133.4, 132.1, 131.9, 129.4, 129.1, 128.41, 128.35, 128.3, 128.0, 127.7, 127.6, 127.2, 126.7, 122.8, 117.3, 116.3, 113.0, 48.0, 45.2, 39.8 (t, $J = 18.7$ Hz), 31.9; ^{19}F NMR (377 MHz, CDCl_3) δ -80.99 (s, 3F), -108.18 – -110.12 (m, 1F), -110.60 – -112.31 (m, 1F), -123.32 – -125.35 (m, 2F), -125.87 (d, $J = 12.5$ Hz, 2F); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{35}\text{H}_{23}\text{ClF}_9\text{NNaO}^+$: 702.1217; found: 702.1216.

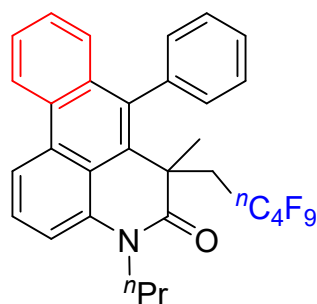


4,6-dimethyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-7-phenyl-4H-naphtho[3,2,1-*de*]quinolin-5(6H)-one (3ia). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); White solid, 83.5 mg, 73% yield; mp 204.5-205.7 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.69 (d, $J = 8.3$ Hz, 1H), 8.49 (d, $J = 8.3$ Hz, 1H), 7.66 (t, $J = 8.1$ Hz, 1H), 7.61 – 7.56 (m, 1H), 7.54 – 7.49 (m, 3H), 7.42 – 7.38 (m, 1H), 7.37 – 7.34 (m, 2H), 7.23 (d, $J = 8.1$ Hz, 1H), 6.92 (d, $J = 8.4$ Hz, 1H), 3.59 (s, 3H), 3.12 (dd, $J = 35.1, 15.1$ Hz, 1H), 3.03 – 2.87 (m, 1H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.8, 139.9, 137.7, 137.3, 134.0, 133.5, 131.8, 130.9, 130.0, 129.2, 128.21, 128.17, 127.9, 127.6, 127.4, 127.1, 126.9, 122.8, 117.9, 117.7, 111.3, 44.9, 40.0 (t, $J = 18.2$ Hz), 31.4, 31.1; ^{19}F NMR (377 MHz, CDCl_3) δ -81.02 (s, 3F), -109.41 – -110.92 (m, 1F), -112.33 – -113.79 (m, 1F), -124.43 (s, 2F), -125.57 – -126.80 (m, 2F); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{29}\text{H}_{20}\text{F}_9\text{NNaO}^+$: 592.1293; found: 592.1300.



4-ethyl-6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-7-phenyl-2,6-dihydro-1H-

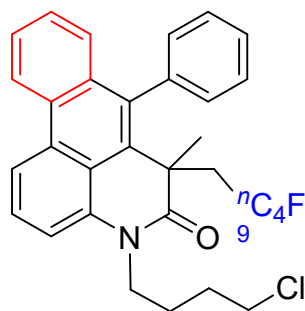
naphtho[3,2,1-*de*]quinolin-5(4*H*)-one (3ja). The product was purified by column chromatography (petroleum ether / ethyl acetate = 20:1); White solid, 71.0 mg, 61% yield; mp 164.1-165.3 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.70 (d, *J* = 8.3 Hz, 1H), 8.48 (d, *J* = 8.3 Hz, 1H), 7.68 (t, *J* = 8.2 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.51 (m, 3H), 7.43 – 7.33 (m, 3H), 7.25 (s, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 4.51 – 4.32 (m, 1H), 4.10 – 3.95 (m, 1H), 3.11 (dd, *J* = 35.0, 15.2 Hz, 1H), 3.01 – 2.86 (m, 1H), 1.79 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 172.1, 140.0, 137.6, 135.9, 134.0, 133.5, 131.8, 131.2, 130.1, 129.2, 128.2, 127.9, 127.5, 127.4, 127.0, 126.8, 122.8, 117.7, 111.2, 44.8, 40.1 (t, *J* = 17.7 Hz), 38.6, 31.4, 11.5; ¹⁹F NMR (377 MHz, CDCl₃) δ -81.04 (s, 3F), -109.55 – -110.57 (m, 1F), -111.84 – -113.01 (m, 1F), -124.30 – -124.63 (m, 2F), -125.89 (s, 2F); HRMS (ESI-TOF) *m/z*: [M+Na]⁺ Calcd. for C₃₀H₂₂F₉NNaO⁺ : 606.1450; found: 606.1456.



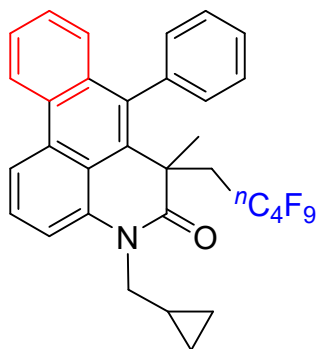
6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-7-phenyl-4-propyl-2,6-dihydro-1H-

naphtho[3,2,1-*de*]quinolin-5(4*H*)-one (3ka). The product was purified by column chromatography (petroleum ether / ethyl acetate = 20:1); White solid, 75.6mg, 63% yield; mp 120.8-122.0 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.70 (d, *J* = 8.3 Hz, 1H), 8.48 (d, *J* = 8.3 Hz, 1H), 7.67 (t, *J* = 8.2 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.54 – 7.48 (m, 3H), 7.43 – 7.38 (m, 1H), 7.38 – 7.34 (m, 2H), 7.21 (d, *J* = 7.9 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 4.28 – 4.12 (m, 1H), 4.04 – 3.91 (m, 1H), 3.12 (dd, *J* = 34.9, 15.1 Hz, 1H), 3.02 – 2.86 (m, 1H), 1.87 – 1.71 (m, 5H), 1.07 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100

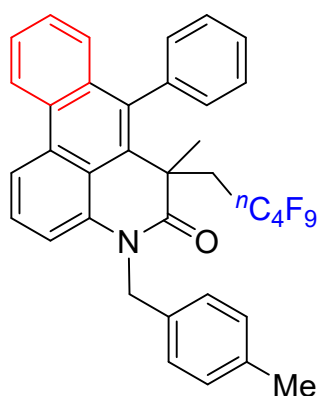
MHz, CDCl₃) δ 172.3, 140.0, 137.6, 136.2, 134.0, 133.5, 131.9, 131.2, 130.1, 129.2, 128.2, 128.1, 127.9, 127.5, 127.4, 127.0, 126.8, 122.8, 117.9, 117.7, 111.4, 45.3, 44.9, 40.0 (t, J = 18.1 Hz), 31.5, 19.4, 11.5.; ¹⁹F NMR (377 MHz, CDCl₃) δ -81.02 (s, 3F), -109.27 – -110.71 (m, 1F), -111.63 – -113.30 (m, 1F), -124.16 – -124.96 (m, 2F), -125.91 (d, J = 12.4 Hz, 2F); HRMS (ESI-TOF) m/z : [M+Na]⁺ Calcd. for C₃₁H₂₄F₉NNaO⁺ : 620.1606; found: 620.1610.



4-(4-chlorobutyl)-6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-7-phenyl-2,6-dihydro-1H-naphtho[3,2,1-*de*]quinolin-5(4H)-one (31a). The product was purified by column chromatography (petroleum ether / ethyl acetate = 20:1); Yellow oil, 83.5 mg, 65% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.70 (d, J = 8.4 Hz, 1H), 8.50 (d, J = 8.5 Hz, 1H), 7.68 (t, J = 8.1 Hz, 1H), 7.60 (dd, J = 8.1, 7.1 Hz, 1H), 7.56 – 7.50 (m, 3H), 7.46 – 7.39 (m, 1H), 7.39 – 7.33 (m, 2H), 7.24 (d, J = 8.0 Hz, 1H), 6.92 (d, J = 8.5 Hz, 1H), 4.45 – 3.91 (m, 2H), 3.65 (d, J = 2.7 Hz, 2H), 3.12 (dd, J = 34.7, 14.6 Hz, 1H), 3.04 – 2.86 (m, 1H), 1.97 (d, J = 5.5 Hz, 4H), 1.80 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 172.5, 139.9, 137.7, 136.0, 134.0, 133.5, 131.9, 131.3, 129.8, 129.2, 128.21, 128.16, 127.9, 127.6, 127.4, 127.1, 126.9, 122.8, 117.9, 111.3, 44.9, 44.6, 42.8, 40.0 (t, J = 17.7 Hz), 31.5, 30.1, 23.7; ¹⁹F NMR (377 MHz, CDCl₃) δ -81.02 (s, 3F), -109.04 – -110.70 (m, 1F), -111.61 – -113.35 (m, 1F), -124.01 – -124.95 (m, 2F), -125.89 (s, 2F); HRMS (ESI-TOF) m/z : [M+Na]⁺ Calcd. for C₃₂H₂₅ClF₉NNaO⁺ : 668.1373; found: 668.1382.

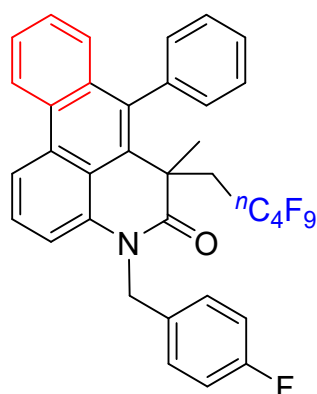


4-(cyclopropylmethyl)-6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-7-phenyl-2,6-dihydro-1H-naphtho[3,2,1-de]quinolin-5(4H)-one (3ma). The product was purified by column chromatography (petroleum ether / ethyl acetate = 20:1); White solid, 69.7 mg, 57% yield; mp 148.6-149.8 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.70 (d, $J = 8.3$ Hz, 1H), 8.49 (d, $J = 8.3$ Hz, 1H), 7.69 (t, $J = 8.2$ Hz, 1H), 7.62 – 7.56 (m, 1H), 7.54 – 7.50 (m, 3H), 7.42 (d, $J = 7.9$ Hz, 2H), 7.39 – 7.33 (m, 2H), 6.90 (d, $J = 8.4$ Hz, 1H), 4.24 – 4.00 (m, 2H), 3.13 (dd, $J = 35.0, 15.2$ Hz, 1H), 3.02 – 2.86 (m, 1H), 1.79 (s, 3H), 1.35 – 1.28 (m, 1H), 0.62 – 0.41 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.7, 140.0, 137.6, 136.5, 134.0, 133.5, 131.9, 131.2, 130.1, 129.2, 128.2, 128.1, 127.9, 127.5, 127.3, 127.0, 126.8, 122.8, 117.7, 111.8, 47.2, 45.0, 40.0 (t, $J = 18.5$ Hz), 31.5, 9.0, 4.3, 3.8; ^{19}F NMR (377 MHz, CDCl_3) δ -81.03 (s), -109.20 – -110.30 (m), -111.30 – -112.62 (m), -123.56 – -125.55 (m), -125.90 (s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{32}\text{H}_{24}\text{F}_9\text{NNaO}^+$: 632.1606; found: 632.1614.

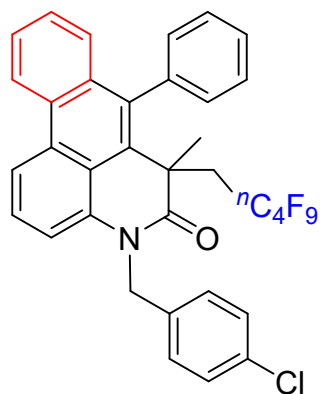


4-(3,5-dimethoxyphenyl)-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)cyclopenta[de]quinoline-2,5(1H,3H)-dione (3na). The product was purified by column chromatography (petroleum ether / ethyl acetate = 20:1); White solid, 83.5 mg, 63% yield; mp 209.7-210.9 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.68 (d, $J = 8.3$ Hz, 1H), 8.45 (d, $J = 8.4$ Hz,

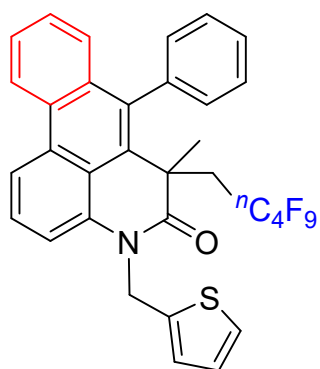
1H), 7.62 – 7.56 (m, 2H), 7.55 – 7.51 (m, 3H), 7.51 – 7.48 (m, 1H), 7.38 (t, $J = 7.3$ Hz, 2H), 7.23 (d, $J = 7.9$ Hz, 2H), 7.19 – 7.12 (m, 3H), 6.93 (d, $J = 8.5$ Hz, 1H), 5.50 – 5.33 (m, 2H), 3.25 (dd, $J = 34.7, 15.3$ Hz, 1H), 3.13 – 2.87 (m, 1H), 2.33 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.2, 139.9, 137.7, 136.9, 136.4, 134.0, 133.53, 133.46, 132.0, 131.0, 129.8, 129.6, 129.2, 128.23, 128.17, 127.9, 127.6, 127.3, 127.0, 126.9, 126.5, 122.8, 117.9, 117.8, 112.7, 47.6, 45.3, 39.7 (t, $J = 17.8$ Hz), 31.9, 21.2; ^{19}F NMR (377 MHz, CDCl_3) δ -80.99 (t, $J = 9.4$ Hz, 3F), -108.77 – -110.08 (m, 1F), -110.89 – -112.39 (m, 1F), -123.29 – -125.43 (m, 2F), -125.86 (dd, $J = 26.1, 12.0$ Hz, 2F); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{36}\text{H}_{26}\text{F}_9\text{NNaO}^+$: 682.1763; found: 682.1769.



4-(4-fluorobenzyl)-6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-7-phenyl-2,6-dihydro-1H-naphtho[3,2,1-de]quinolin-5(4H)-one (30a). The product was purified by column chromatography (petroleum ether / ethyl acetate = 20:1); White solid, 85.7 mg, 65% yield; mp 100.1-101.3 °C ^1H NMR (400 MHz, CDCl_3) δ 8.69 (d, $J = 8.3$ Hz, 1H), 8.47 (d, $J = 8.3$ Hz, 1H), 7.63 – 7.57 (m, 2H), 7.57 – 7.54 (m, 3H), 7.52 – 7.48 (m, 1H), 7.43 – 7.36 (m, 2H), 7.32 (dd, $J = 8.5, 5.3$ Hz, 2H), 7.13 (d, $J = 7.8$ Hz, 1H), 7.03 (t, $J = 8.7$ Hz, 2H), 6.95 (d, $J = 8.3$ Hz, 1H), 5.40 (s, 2H), 3.25 (dd, $J = 34.7, 15.2$ Hz, 1H), 3.14 – 2.97 (m, 1H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.3, 162.1 (d, $J = 245.3$ Hz), 139.8, 137.9, 136.2, 134.0, 133.4, 132.29, 132.26, 131.9 (d, $J = 3.3$ Hz), 131.1, 129.6, 129.2, 128.3, 128.2 (d, $J = 8.7$ Hz), 128.0, 127.6, 127.3, 127.1, 127.0, 122.8, 118.1, 117.8, 115.8 (d, $J = 21.6$ Hz), 112.4, 47.3, 45.3, 39.7 (t, $J = 18.0$ Hz), 31.9; ^{19}F NMR (377 MHz, CDCl_3) δ -80.99 (t, $J = 8.4$ Hz, 3F), -109.37 (d, $J = 273.3$ Hz, 1F), -111.59 (d, $J = 273.4$ Hz, 1F), -115.52 (d, $J = 4.1$ Hz, 1F), -123.24 – -125.56 (m, 2F), -125.86 (d, $J = 12.4$ Hz, 2F); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{35}\text{H}_{23}\text{F}_{10}\text{NNaO}^+$: 686.1512; found: 686.1519.

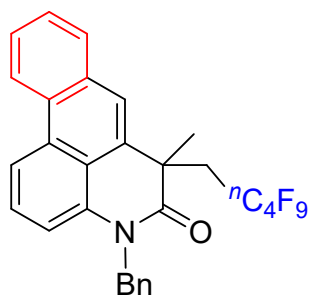


4-(4-chlorobenzyl)-6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-7-phenyl-2,6-dihydro-1H-naphtho[3,2,1-*de*]quinolin-5(4H)-one (3pa). The product was purified by column chromatography (petroleum ether / ethyl acetate = 20:1); White solid, 84.7 mg, 62% yield; mp 123.8-125.0 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.69 (d, *J* = 8.4 Hz, 1H), 8.47 (d, *J* = 8.5 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.57 – 7.53 (m, 4H), 7.48 (d, *J* = 6.1 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.33 – 7.26 (m, 4H), 7.08 (d, *J* = 7.9 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 1H), 5.39 (s, 2H), 3.23 (dd, *J* = 34.6, 15.2 Hz, 1H), 3.13 – 2.94 (m, 1H), 1.89 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 173.4, 139.8, 137.9, 136.1, 135.2, 134.0, 133.4, 133.1, 132.0, 131.1, 129.6, 129.2, 129.1, 128.3, 128.2, 128.03, 127.97, 127.6, 127.3, 127.2, 127.0, 122.8, 118.2, 117.8, 112.4, 47.3, 45.3, 39.7 (t, *J* = 17.4 Hz), 31.9; ¹⁹F NMR (377 MHz, CDCl₃) δ -80.98 (s, 3F), -108.69 – -110.15 (m, 1F), -110.96 – -112.41 (m, 1F), -123.27 – -125.52 (m, 2F), -125.86 (d, *J* = 9.4 Hz, 2F); HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd. for C₃₅H₂₃ClF₉NNaO⁺ : 702.1217; found: 702.1224.

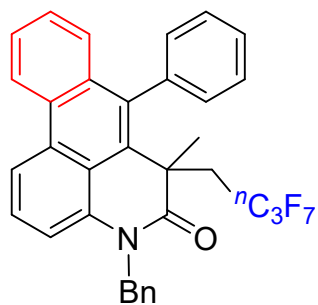


6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-7-phenyl-4-(thiophen-2-ylmethyl)-2,6-dihydro-1H-naphtho[3,2,1-*de*]quinolin-5(4H)-one (3qa). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); White solid, 70.0 mg, 54% yield; mp 133.2-134.4 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.68 (d, *J* = 8.4 Hz, 1H), 8.48 (d, *J* = 8.4 Hz, 1H),

7.61 (dd, $J = 16.5, 8.3$ Hz, 2H), 7.54 (t, $J = 6.6$ Hz, 3H), 7.46 (d, $J = 5.8$ Hz, 1H), 7.42 – 7.32 (m, 3H), 7.22 (d, $J = 5.0$ Hz, 1H), 7.13 (d, $J = 3.1$ Hz, 1H), 6.98 – 6.94 (m, 1H), 6.92 (d, $J = 8.5$ Hz, 1H), 5.54 (dd, $J = 43.9, 15.6$ Hz, 2H), 3.21 (dd, $J = 34.6, 15.1$ Hz, 1H), 3.08 – 2.90 (m, 1H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.8, 139.8, 139.2, 137.8, 136.0, 134.0, 133.4, 131.9, 131.2, 129.6, 129.2, 128.24, 128.16, 127.9, 127.6, 127.3, 127.1, 126.9, 126.8, 126.2, 125.2, 122.8, 118.1, 117.9, 111.9, 45.2, 43.2, 39.7 (t, $J = 18.0$ Hz), 31.6; ^{19}F NMR (377 MHz, CDCl_3) δ -80.97 (d, $J = 1.6$ Hz, 3F), -108.87 – -110.56 (m, 1F), -110.87 – -112.39 (m, 1F), -123.54 – -125.55 (m, 2F), -125.84 (s, 2F); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{33}\text{H}_{22}\text{F}_9\text{NNaOS}^+$: 674.1171; found: 674.1180.

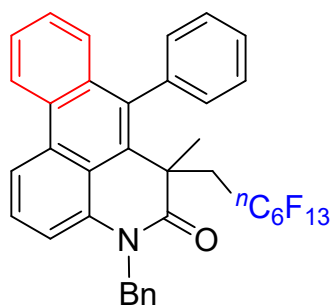


4-benzyl-6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-4H-naphtho[3,2,1-de]quinolin-5(6H)-one (3sa). The product was purified by column chromatography (petroleum ether / ethyl acetate = 20:1); Yellow oil, 47.1 mg, 41% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.68 – 8.59 (m, 1H), 8.38 (d, $J = 8.4$ Hz, 1H), 7.90 (dd, $J = 6.4, 2.8$ Hz, 1H), 7.77 (s, 1H), 7.70 – 7.60 (m, 2H), 7.51 (t, $J = 8.1$ Hz, 1H), 7.34 – 7.28 (m, 5H), 7.10 (d, $J = 7.9$ Hz, 1H), 5.45 (s, 2H), 3.75 (dd, $J = 32.4, 15.6$ Hz, 1H), 3.14 – 2.85 (m, 1H), 1.87 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.8, 136.6, 136.0, 133.1, 131.8, 131.0, 129.2, 129.0, 128.4, 127.5, 127.3, 127.1, 126.5, 124.4, 123.2, 118.0, 117.2, 112.2, 47.0, 44.2, 40.9 (t, $J = 19.5$ Hz), 34.8; ^{19}F NMR (377 MHz, CDCl_3) δ -81.03 (t, $J = 9.1$ Hz, 3F), -105.44 (d, $J = 281.2$ Hz, 1F), -111.37 (d, $J = 272.8$ Hz, 1F), -123.18 – -125.35 (m, 2F), -125.54 – -126.27 (m, 2F); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{29}\text{H}_{21}\text{F}_9\text{NO}^+$: 570.1474; found: 570.1470.



4-benzyl-6-(2,2,3,3,4,4,4-heptafluorobutyl)-6-methyl-7-phenyl-2,6-dihydro-1H-

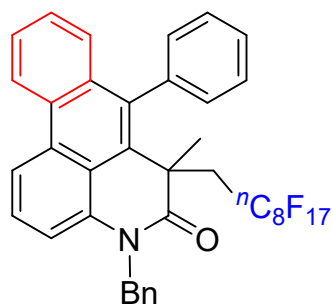
naphtho[3,2,1-*de*]quinolin-5(4H)-one (4a). The product was purified by column chromatography (petroleum ether / ethyl acetate = 30:1); White solid, 76.7 mg, 64% yield; mp 190.1-191.3 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.68 (d, *J* = 8.4 Hz, 1H), 8.45 (d, *J* = 8.4 Hz, 1H), 7.57 (m, 5H), 7.50 – 7.45 (m, 1H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.33 (d, *J* = 4.3 Hz, 4H), 7.29 – 7.25 (m, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 5.43 (dd, *J* = 61.7, 15.2 Hz, 2H), 3.23 (dd, *J* = 34.7, 15.2 Hz, 1H), 3.10 – 2.92 (m, 1H), 1.90 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 173.3, 139.9, 137.8, 136.6, 136.3, 134.0, 133.5, 132.0, 131.1, 129.8, 129.2, 128.9, 128.3, 128.2, 127.9, 127.6, 127.32, 127.28, 127.1, 126.9, 126.6, 122.8, 118.0, 117.8, 112.6, 47.9, 45.3, 39.6 (t, *J* = 17.5 Hz), 31.9; ¹⁹F NMR (377 MHz, CDCl₃) δ -80.26 (d, *J* = 1.4 Hz, 3F), -108.92 – -110.96 (m, 1F), -111.69 – -114.62 (m, 1F), -126.11 – -129.95 (m, 2F); HRMS (ESI-TOF) *m/z*: [M+Na]⁺ Calcd. for C₃₄H₂₄F₇NNaO⁺ : 618.1638; found: 618.1646.



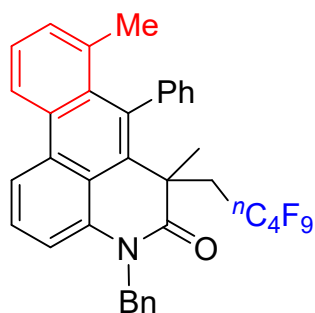
4-benzyl-6-methyl-7-phenyl-6-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-2,6-dihydro-1H-

naphtho[3,2,1-*de*]quinolin-5(4H)-one (4b). The product was purified by column chromatography (petroleum ether / ethyl acetate = 40:1); White solid, 100.5 mg, 67% yield; mp 208.7-209.9 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.69 (d, *J* = 8.4 Hz, 1H), 8.46 (d, *J* = 8.4 Hz, 1H), 7.63 – 7.56 (m, 3H), 7.55 – 7.50 (m, 3H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 4.3 Hz, 4H), 7.30 – 7.27 (m, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 6.96 (d, *J* = 8.5 Hz, 1H), 5.46 (dd, *J* = 47.0, 15.4 Hz, 2H), 3.28 (dd, *J* = 34.8, 15.1

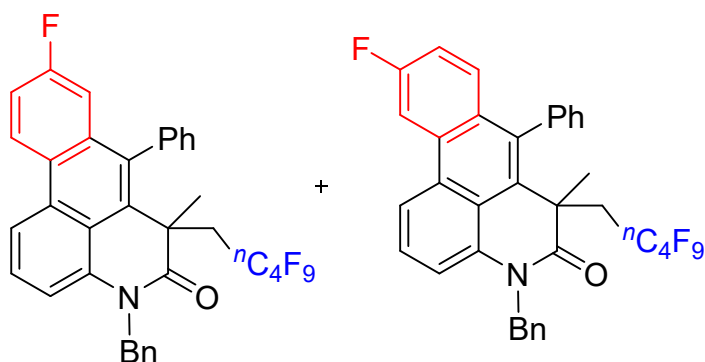
Hz, 1H), 3.15 – 2.95 (m, 1H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.3, 139.9, 137.8, 136.6, 136.4, 134.0, 133.5, 132.0, 131.1, 129.8, 129.3, 128.9, 128.3, 128.2, 127.9, 127.6, 127.32, 127.28, 127.1, 126.9, 126.6, 122.8, 118.0, 117.9, 112.6, 47.9, 45.3, 39.8 (t, $J = 18.0$ Hz), 31.9; ^{19}F NMR (377 MHz, CDCl_3) δ -80.80 (t, $J = 9.3$ Hz, 3F), -108.59 – -109.77 (m, 1F), -110.62 – -111.90 (m, 1F), -121.69 (s, 2F), -122.77 (s, 2F), -123.30 – -123.74 (m, 2F), -126.12 (s, 2F); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{34}\text{H}_{24}\text{F}_{13}\text{NNaO}^+$: 768.1543; found: 768.1552.



4-benzyl-6-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptafluorononyl)-6-methyl-7-phenyl-2,6-dihydro-1H-naphtho[3,2,1-de]quinolin-5(4H)-one (4c). The product was purified by column chromatography (petroleum ether / ethyl acetate = 30:1); White solid, 110.4 mg, 65% yield; mp 221.5-222.7 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.68 (d, $J = 8.3$ Hz, 1H), 8.45 (d, $J = 8.3$ Hz, 1H), 7.62 – 7.57 (m, 1H), 7.56 – 7.51 (m, 4H), 7.51 – 7.46 (m, 1H), 7.41 – 7.35 (m, 2H), 7.33 (d, $J = 4.4$ Hz, 4H), 7.26 – 7.23 (m, 1H), 7.14 (d, $J = 7.8$ Hz, 1H), 6.92 (d, $J = 8.0$ Hz, 1H), 5.43 (dd, $J = 46.0$, 15.1 Hz, 2H), 3.24 (dd, $J = 34.7$, 15.1 Hz, 1H), 3.10 – 2.89 (m, 1H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.3, 139.9, 137.8, 136.6, 136.4, 134.0, 133.5, 132.0, 131.1, 129.8, 129.3, 128.9, 128.3, 128.2, 127.9, 127.6, 127.33, 127.28, 127.1, 126.9, 126.6, 122.8, 118.0, 117.8, 112.6, 47.9, 45.3, 39.8 (t, $J = 14.7$ Hz), 31.9; ^{19}F NMR (377 MHz, CDCl_3) δ -80.76 (d, $J = 8.2$ Hz, 3F), -108.55 – -110.01 (m, 1F), -110.66 – -112.27 (m, 1F), -121.30 – -122.10 (m, 6F), -122.70 (s, 2F), -123.31 – -123.75 (m, 2F), -126.07 (s, 2F); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{39}\text{H}_{24}\text{F}_{17}\text{NNaO}^+$: 868.1479; found: 868.1487.

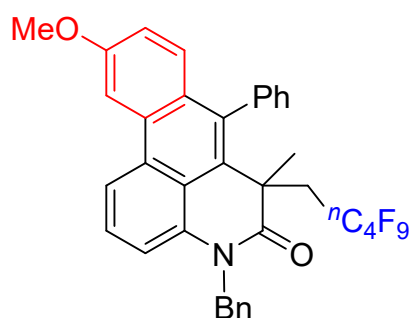


4-benzyl-6,8-dimethyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-7-phenyl-2,6-dihydro-1H-naphtho[3,2,1-*de*]quinolin-5(4H)-one (5ab)³. The product was purified by column chromatography (petroleum ether / ethyl acetate = 30:1); White solid, 81.4 mg, 62% yield; mp 176.4-177.6 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.60 (d, *J* = 8.3 Hz, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 7.54 – 7.47 (m, 3H), 7.47 – 7.40 (m, 4H), 7.35 – 7.30 (m, 4H), 7.27 (d, *J* = 3.4 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 5.40 (q, *J* = 16.3 Hz, 2H), 3.28 – 3.02 (m, 1H), 2.90 – 2.70 (m, 1H), 1.79 (s, 3H), 1.67 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 173.9, 141.6, 138.6, 137.1, 136.6, 135.8, 135.3, 133.5, 132.9, 131.6, 131.0, 130.7, 128.9, 128.6, 127.5, 127.3, 127.2, 126.9, 126.6, 122.1, 118.8, 117.8, 112.3, 48.0, 46.2, 39.9 (t, *J* = 17.9 Hz), 32.3, 25.5; ¹⁹F NMR (377 MHz, CDCl₃) δ -81.02 (s, 3F), -109.42 – -110.78 (m, 1F), -111.08 – -112.51 (m, 1F), -123.38 – -125.43 (m, 2F), -125.86 (d, *J* = 7.2 Hz, 2F); HRMS (ESI-TOF) *m/z*: [M+Na]⁺ Calcd. for C₃₆H₂₆F₉NNaO⁺: 682.1763; found: 682.1771.

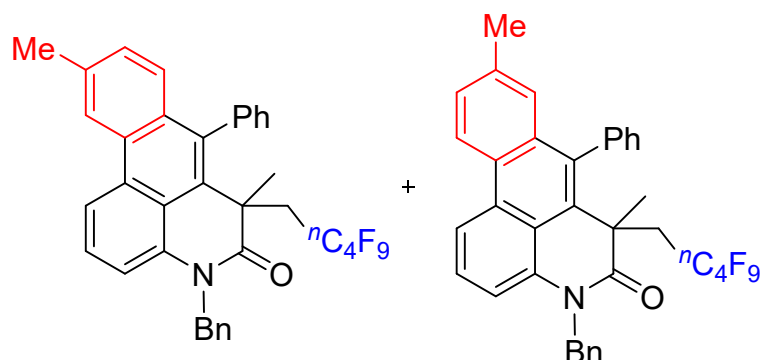


4-benzyl-9-fluoro-6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-7-phenyl-2,6-dihydro-1H-naphtho[3,2,1-*de*]quinolin-5(4H)-one and 4-benzyl-10-fluoro-6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-7-phenyl-2,6-dihydro-1H-naphtho[3,2,1-*de*]quinolin-5(4H)-one (5ac and 5ac')^{4,5}. The product was purified by column chromatography (petroleum ether / ethyl acetate = 20:1); White solid, 72.1 mg (5ac:5ac' = 4:1), 54% yield; mp 158.1-159.3 °C; ¹H NMR (400 MHz,

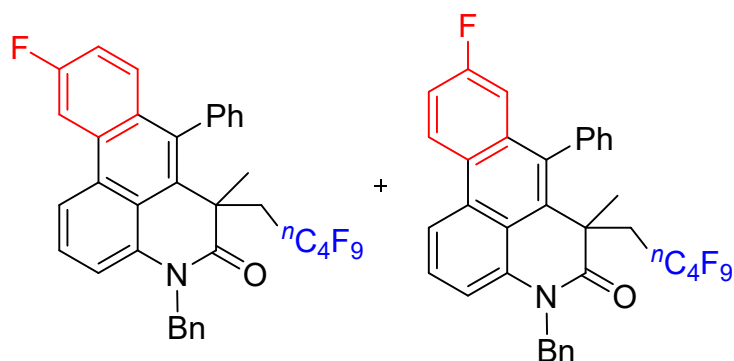
CDCl₃) δ 8.65 (dd, J = 9.2, 5.6 Hz, 0.2H), 8.35 (d, J = 8.5 Hz, 0.2H), 8.32 – 8.23 (m, 1.6H), 7.58 – 7.51 (m, 4H), 7.47 (d, J = 6.0 Hz, 1H), 7.37 – 7.31 (m, 5H), 7.29 – 7.24 (m, 1H), 7.16 (dd, J = 9.4, 5.0 Hz, 1H), 7.14 – 7.09 (m, 1H), 6.92 (dd, J = 9.3, 5.9 Hz, 0.8H), 6.54 (dd, J = 11.6, 2.6 Hz, 0.2H), 5.43 (dd, J = 45.5, 15.1 Hz, 2H), 3.24 (dd, J = 34.6, 15.2 Hz, 1H), 3.11 – 2.89 (m, 1H), 1.89 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 173.2, 161.7 (d, J = 247.0 Hz), 139.7, 136.5, 136.4, 133.4, 133.3, 131.8, 130.8, 130.4 (d, J = 4.3 Hz), 130.2 (d, J = 8.7 Hz), 129.0, 128.6, 128.4, 128.3, 128.2, 128.0, 127.8, 127.4 (d, J = 8.9 Hz), 126.5, 125.4, 125.3, 118.3, 118.1, 117.8, 116.1 (d, J = 23.5 Hz), 113.2, 112.5, 112.1, 111.9, 107.7 (d, J = 22.6 Hz), 47.9, 45.2, 39.7 (t, J = 17.9 Hz), 31.9; ¹⁹F NMR (377 MHz, CDCl₃) δ -80.99 (s, 3F), -108.89 – -110.20 (m, 1F), -110.91 – -112.27 (m, 1F), -112.75 – -113.03 (m, 0.2F), -113.59 (d, J = 3.9 Hz, 0.8F), -123.32 – -125.59 (m, 2F), -125.85 (d, J = 13.1 Hz, 2F); HRMS (ESI-TOF) m/z : [M+Na]⁺ Calcd. for C₃₅H₂₃F₁₀NNaO⁺: 686.1512; found: 686.1520.



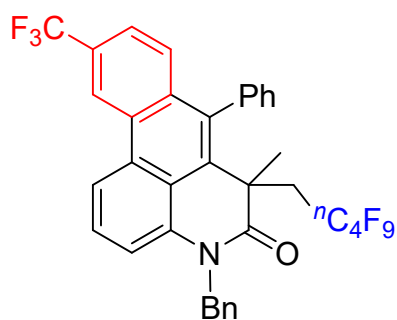
4-benzyl-10-methoxy-6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-7-phenyl-2,6-dihydro-1H-naphtho[3,2,1-de]quinolin-5(4H)-one (5ad)⁵. The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); White solid, 98.8 mg, 73% yield; mp 207.6-208.8 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.58 (d, J = 9.2 Hz, 1H), 8.33 (d, J = 8.4 Hz, 1H), 7.58 – 7.51 (m, 3H), 7.48 (m, 2H), 7.39 – 7.35 (m, 1H), 7.32 (d, J = 4.4 Hz, 4H), 7.25 – 7.20 (m, 2H), 7.07 (d, J = 7.8 Hz, 1H), 6.24 (d, J = 2.6 Hz, 1H), 5.56 – 5.28 (m, 2H), 3.58 (s, 3H), 3.23 (dd, J = 34.7, 15.4 Hz, 1H), 3.10 – 2.93 (m, 1H), 1.89 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 173.3, 158.4, 140.1, 137.2, 136.7, 136.4, 135.6, 133.4, 132.0, 131.1, 130.3, 128.9, 128.3, 128.1, 127.4, 127.2, 126.6, 124.5, 123.8, 117.5, 117.2, 116.8, 111.7, 108.2, 55.0, 47.8, 45.3, 39.7 (t, J = 18.6 Hz), 31.9; ¹⁹F NMR (377 MHz, CDCl₃) δ -81.00 (s, 3F), -108.88 – -110.09 (m, 1F), -111.04 – -112.40 (m, 1F), -123.44 – -125.38 (m, 2F), -125.87 (d, J = 10.7 Hz, 2F); HRMS (ESI-TOF) m/z : [M+Na]⁺ Calcd. for C₃₆H₂₆F₉NNaO₂⁺: 698.1712; found: 698.1719.



4-benzyl-6,10-dimethyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-7-phenyl-2,6-dihydro-1H-naphtho[3,2,1-*de*]quinolin-5(4H)-one and **4-benzyl-6,9-dimethyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-7-phenyl-2,6-dihydro-1H-naphtho[3,2,1-*de*]quinolin-5(4H)-one (5ae and 5ae')**^{3,5}. The product was purified by column chromatography (petroleum ether / ethyl acetate = 20:1); White solid, 76.7 mg (5ae:5ae' = 1:1), 58% yield; mp 183.1-184.3 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.49 (d, *J* = 8.6 Hz, 0.5H), 8.40 (s, 0.5H), 8.37 (d, *J* = 8.4 Hz, 0.5H), 8.33 (d, *J* = 8.3 Hz, 0.5H), 7.52 – 7.39 (m, 6H), 7.37 – 7.30 (m, 1H), 7.30 – 7.27 (m, 3H), 7.23 – 7.12 (m, 2H), 7.05 (t, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 8.6 Hz, 0.5H), 6.62 (s, 0.5H), 5.36 (dd, *J* = 40.9, 15.0 Hz, 2H), 3.18 (dd, *J* = 34.7, 15.1 Hz, 1H), 3.03 – 2.87 (m, 1H), 2.49 (s, 1.5H), 2.25 (s, 1.5H), 1.83 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 173.3, 140.1, 139.9, 137.7, 137.5, 136.8, 136.74, 136.68, 136.3, 134.1, 133.5, 133.4, 132.0, 131.9, 131.1, 130.7, 129.7, 129.3, 128.9, 128.75, 128.68, 128.20, 128.16, 128.1, 127.9, 127.5, 127.25, 127.22, 127.1, 126.6, 122.8, 122.5, 118.01, 117.96, 117.8, 117.5, 112.5, 112.2, 47.9, 47.8, 45.33, 45.25, 39.8 (t, *J* = 17.4 Hz), 31.93, 31.90, 21.9; ¹⁹F NMR (377 MHz, CDCl₃) δ -80.99 (s, 3F), -109.52 (d, *J* = 272.3 Hz, 1F), -110.92 – -112.41 (m, 1F), -123.40 – -125.42 (m, 2F), -125.85 (s, 2F); HRMS (ESI-TOF) *m/z*: [M+Na]⁺ Calcd. for C₃₆H₂₆F₉NNaO⁺: 682.1763; found: 682.1771.

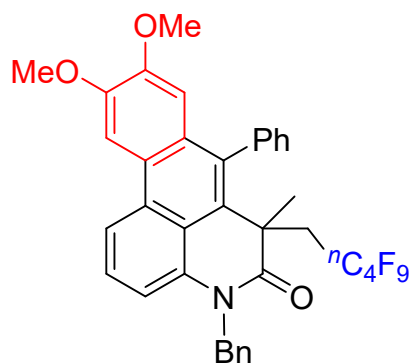


4-benzyl-10-fluoro-6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-7-phenyl-2,6-dihydro-1H-naphtho[3,2,1-*de*]quinolin-5(4H)-one and **4-benzyl-9-fluoro-6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-7-phenyl-2,6-dihydro-1H-naphtho[3,2,1-*de*]quinolin-5(4H)-one** (**5ac'** and **5ac**)^{4,5}. The product was purified by column chromatography (petroleum ether / ethyl acetate = 20:1); White solid, 86.8 mg (5af:5af' = 5.7:1), 65% yield; mp 151.8-153.0 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.65 (dd, *J* = 9.2, 5.7 Hz, 0.85H), 8.35 (d, *J* = 8.4 Hz, 0.85H), 8.29 – 8.20 (m, 0.3H), 7.58 – 7.51 (m, 4H), 7.45 (d, *J* = 6.1 Hz, 1H), 7.38 – 7.30 (m, 7H), 7.13 (d, *J* = 7.9 Hz, 1H), 6.94 – 6.87 (m, 0.15H), 6.53 (dd, *J* = 11.6, 2.6 Hz, 0.85H), 5.66 – 5.11 (m, 2H), 3.24 (dd, *J* = 34.9, 15.5 Hz, 1H), 3.08 – 2.91 (m, 1H), 1.88 (d, *J* = 2.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 173.1, 161.6 (d, *J* = 246.1 Hz), 139.4, 136.5, 135.7 (d, *J* = 8.2 Hz), 133.3, 131.8, 131.2, 130.8, 129.0, 128.6, 128.4, 128.2, 127.8, 127.3, 126.5, 125.9, 125.3 (d, *J* = 8.7 Hz), 118.1, 117.8, 117.4, 116.1 (d, *J* = 23.9 Hz), 113.2, 112.5, 112.0 (d, *J* = 22.9 Hz), 47.9, 45.3, 39.7 (t, *J* = 17.9 Hz), 31.8; ¹⁹F NMR (377 MHz, CDCl₃) δ -80.99 (s, 3F), -108.73 – -110.19 (m, 1F), -111.07 – -112.55 (m, 1F), -112.91 (d, *J* = 4.6 Hz, 0.85F), -113.62 (s, 0.15F), -123.33 – -125.55 (m, 2F), -125.87 (d, *J* = 12.1 Hz, 2F); HRMS (ESI-TOF) *m/z*: [M+Na]⁺ Calcd. for C₃₅H₂₃F₁₀NNaO⁺: 644.0866; found: 644.0875.

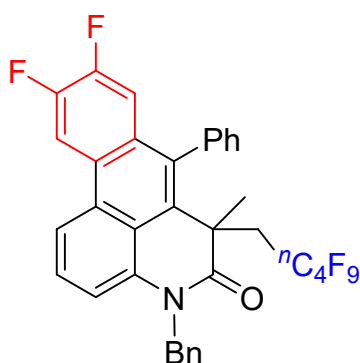


4-benzyl-6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-7-phenyl-10-(trifluoromethyl)-2,6-dihydro-1H-naphtho[3,2,1-*de*]quinolin-5(4H)-one (**5ag**)⁴. The product was purified by column

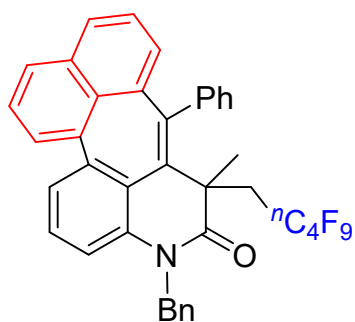
chromatography (petroleum ether / ethyl acetate = 10:1); White solid, 76.7 mg, 54% yield; mp 152.4-153.6 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.77 (d, *J* = 8.8 Hz, 1H), 8.45 (d, *J* = 8.3 Hz, 1H), 7.77 (dd, *J* = 8.7, 1.5 Hz, 1H), 7.60 – 7.54 (m, 4H), 7.47 (d, *J* = 4.8 Hz, 1H), 7.37 – 7.32 (m, 5H), 7.29 – 7.27 (m, 1H), 7.23 – 7.18 (m, 2H), 5.52 – 5.34 (m, 2H), 3.26 (dd, *J* = 34.9, 15.3 Hz, 1H), 3.10 – 2.92 (m, 1H), 1.90 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 173.1, 138.8, 137.7, 136.6, 136.3, 133.5, 133.3, 131.8 (d, *J* = 3.5 Hz), 131.4 (d, *J* = 32.9 Hz), 130.4, 129.0, 128.8, 128.5, 128.2, 127.9, 127.4, 125.2 (d, *J* = 264.9 Hz), 124.8 (d, *J* = 4.5 Hz), 122.72, 122.70, 118.6, 118.3, 113.6, 47.9, 45.4, 39.7 (t, *J* = 17.6 Hz), 31.9; ¹⁹F NMR (377 MHz, CDCl₃) δ -62.50 (s, 3F), -80.98 (s, 3F), -108.43 – -110.16 (m, 1F), -110.63 – -112.58 (m, 1F), -123.67 – -124.97 (m, 2F), -125.85 (s, 2F); HRMS (ESI-TOF) *m/z*: [M+Na]⁺ Calcd. for C₃₆H₂₃F₁₂NNaO⁺: 736.1480; found: 736.1488.



4-benzyl-9,10-dimethoxy-6-methyl-6-(2,2,3,3,4,4,5,5,5-nonfluoropentyl)-7-phenyl-2,6-dihydro-1H-naphtho[3,2,1-de]quinolin-5(4H)-one (5ah). The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 87.3 mg, 62% yield; mp 189.3-190.5 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, *J* = 8.4 Hz, 1H), 7.98 (s, 1H), 7.60 – 7.57 (m, 1H), 7.56 – 7.52 (m, 3H), 7.48 (t, *J* = 8.1 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.35 (d, *J* = 4.9 Hz, 4H), 7.32 – 7.26 (m, 1H), 7.09 (d, *J* = 7.9 Hz, 1H), 6.26 (s, 1H), 5.45 (dd, *J* = 40.5, 14.5 Hz, 2H), 4.09 (s, 3H), 3.58 (s, 3H), 3.28 (dd, *J* = 34.7, 15.1 Hz, 1H), 3.13 – 2.91 (m, 1H), 1.93 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 173.3, 149.6, 149.4, 140.4, 136.9, 136.7, 136.4, 133.3, 131.80, 131.77, 130.3, 129.4, 128.9, 128.21, 128.18, 128.0, 127.8, 127.2, 126.8, 126.5, 124.3, 117.5, 117.3, 111.5, 107.6, 103.0, 56.0, 55.2, 47.8, 45.2, 39.7 (t, *J* = 17.9 Hz), 32.0; ¹⁹F NMR (377 MHz, CDCl₃) δ -80.98 (t, *J* = 9.0 Hz, 3F), -109.58 (dd, *J* = 273.2, 32.4 Hz, 1F), -110.87 – -112.63 (m, 1F), -123.08 – -125.33 (m, 2F), -125.82 (dd, *J* = 26.6, 13.1 Hz, 2F); HRMS (ESI-TOF) *m/z*: [M+Na]⁺ Calcd. for C₃₇H₂₂F₉NNaO₃⁺: 728.1818; found: 728.1823.

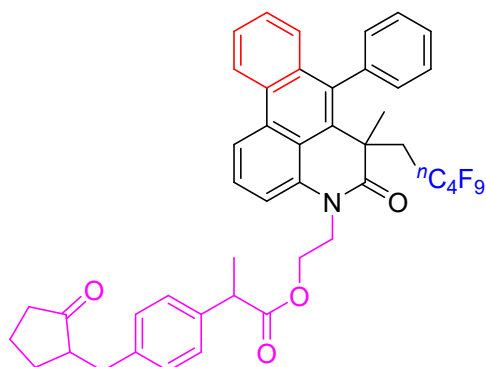


4-benzyl-9,10-difluoro-6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-7-phenyl-2,6-dihydro-1H-naphtho[3,2,1-*de*]quinolin-5(4H)-one (5ai). The product was purified by column chromatography (petroleum ether / ethyl acetate = 20:1); White solid, 79.5 mg, 58% yield; mp 147.1-148.3 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.36 (dd, *J* = 12.2, 8.0 Hz, 1H), 8.18 (d, *J* = 8.3 Hz, 1H), 7.61 – 7.55 (m, 3H), 7.52 (t, *J* = 8.1 Hz, 1H), 7.46 (d, *J* = 6.2 Hz, 1H), 7.37 – 7.32 (m, 5H), 7.29 – 7.26 (m, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 6.67 (dd, *J* = 12.9, 8.4 Hz, 1H), 5.44 (dd, *J* = 46.5, 15.2 Hz, 2H), 3.26 (dd, *J* = 34.9, 15.3 Hz, 1H), 3.09 – 2.86 (m, 1H), 1.89 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 173.1, 150.3 (dd, *J* = 250.1, 14.4 Hz), 150.0 (dd, *J* = 248.7, 13.7 Hz), 139.2, 136.7, 136.5, 136.4, 133.2, 131.7 (d, *J* = 3.3 Hz), 131.53, 131.48, 130.6, 130.1 (d, *J* = 3.5 Hz), 129.0, 128.8, 128.5, 128.3, 127.8, 127.4, 126.5, 117.9, 117.8, 114.7 (d, *J* = 18.7 Hz), 112.9, 110.4 (d, *J* = 18.3 Hz), 47.9, 45.3, 39.7 (t, *J* = 17.7 Hz), 31.8; ¹⁹F NMR (377 MHz, CDCl₃) δ -80.99 (s, 3F), -108.53 – -110.27 (m, 1F), -110.79 – -112.59 (m, 1F), -123.34 – -125.40 (m, 2F), -125.85 (d, *J* = 11.5 Hz, 2F), -135.98 (dd, *J* = 18.8, 10.6 Hz, 1F), -136.43 – -136.87 (m, 1F); HRMS (ESI-TOF) *m/z*: [M+Na]⁺ Calcd. for C₃₅H₂₂F₁₁NNaO⁺: 704.1418; found: 704.1426.



4-benzyl-6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-7-phenyl-2,4-dihydro-1H-naphtho[1',8':4,5,6]cyclohepta[1,2,3-*de*]quinolin-5(6H)-one (6aj). The product was purified by

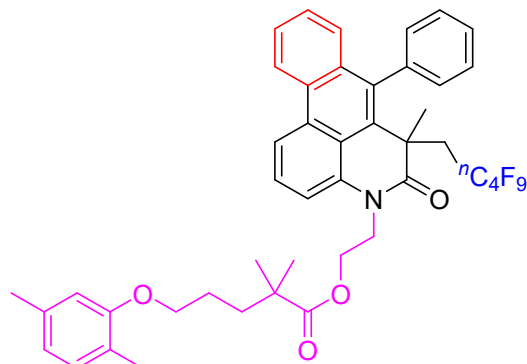
column chromatography (petroleum ether / ethyl acetate = 15:1); White oil, 72.6 mg, 52% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, $J = 7.9$ Hz, 1H), 7.60 (d, $J = 7.0$ Hz, 1H), 7.57 – 7.50 (m, 2H), 7.40 – 7.32 (m, 4H), 7.31 – 7.26 (m, 3H), 7.25 – 7.22 (m, 2H), 7.22 – 7.15 (m, 1H), 7.10 (t, $J = 7.7$ Hz, 1H), 6.97 (d, $J = 8.1$ Hz, 1H), 6.73 (d, $J = 7.4$ Hz, 1H), 6.67 (d, $J = 7.9$ Hz, 1H), 6.52 (d, $J = 7.3$ Hz, 1H), 5.46 (d, $J = 16.3$ Hz, 1H), 5.10 (d, $J = 16.3$ Hz, 1H), 2.71 (dd, $J = 35.5, 15.1$ Hz, 1H), 2.18 – 1.97 (m, 1H), 1.00 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.6, 147.9, 145.2, 141.9, 139.6, 137.7, 137.24, 137.17, 132.8, 132.7, 131.3, 131.2, 130.5, 129.3, 129.1, 129.0, 128.7, 128.0, 127.8, 127.61, 127.59, 127.55, 127.47, 126.50, 126.3, 124.8, 114.3, 48.1, 47.5, 38.7 (t, $J = 19.6$ Hz), 21.1; ^{19}F NMR (377 MHz, CDCl_3) δ -81.58 (s, 3F), -106.97 – -108.23 (m, 1F), -112.86 – -114.32 (m, 1F), -125.43 – -126.17 (m, 2F), -126.34 (s, 2F); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{39}\text{H}_{26}\text{F}_9\text{NNaO}^+$: 718.1763; found: 718.1771.



2-(6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-5-oxo-7-phenyl-5,6-dihydro-4H-naphtho[3,2,1-de]quinolin-4-yl)ethyl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate (7a).

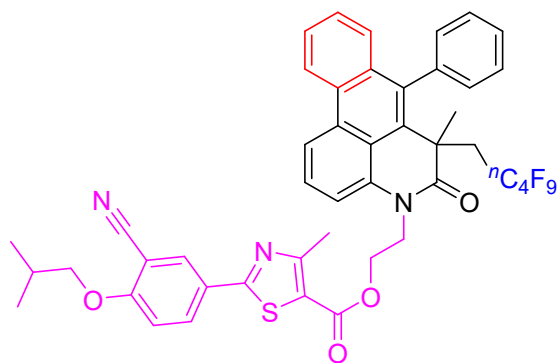
The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); White solid, 79.7 mg, 48% yield; mp 78.3-79.5 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.70 (d, $J = 8.4$ Hz, 1H), 8.50 (d, $J = 8.4$ Hz, 1H), 7.67 – 7.56 (m, 2H), 7.52 (m, 3H), 7.39 (dd, $J = 15.0, 7.7$ Hz, 4H), 7.18 (d, $J = 7.9$ Hz, 2H), 7.08 (d, $J = 7.9$ Hz, 2H), 6.91 (d, $J = 8.5$ Hz, 1H), 4.58 – 4.27 (m, 4H), 3.76 – 3.61 (m, 1H), 3.21 – 2.84 (m, 3H), 2.51 – 2.41 (m, 1H), 2.32 (m, 2H), 2.17 – 2.01 (m, 2H), 1.98 – 1.87 (m, 1H), 1.77 (s, 3H), 1.75 – 1.67 (m, 1H), 1.57 – 1.50 (m, 1H), 1.47 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 220.2, 174.9, 172.8, 139.8, 139.1, 138.2, 137.8, 136.2, 136.1, 133.9, 133.4, 131.8, 131.2, 129.6, 129.3, 129.2, 128.23, 128.16, 127.9, 127.65, 127.56, 127.5, 127.1, 127.0, 122.8, 118.1, 117.8, 111.6, 111.5, 60.7, 51.1, 51.0, 45.2, 44.9, 42.0, 41.8, 40.1 (t, $J = 17.9$ Hz), 38.3, 35.3, 31.4, 29.4, 20.6, 18.5; ^{19}F NMR (377 MHz, CDCl_3) δ -80.99 (s, 3F), -109.51 – -110.74 (m,

1F), -111.64 – -113.63 (m, 1F), -124.52 (s, 2F), -125.86 (d, $J = 30.3$ Hz, 2F); HRMS (ESI-TOF) m/z : $[M+Na]^+$ Calcd. for $C_{45}H_{38}F_9NNaO_4^+$: 850.2549; found: 850.2557.

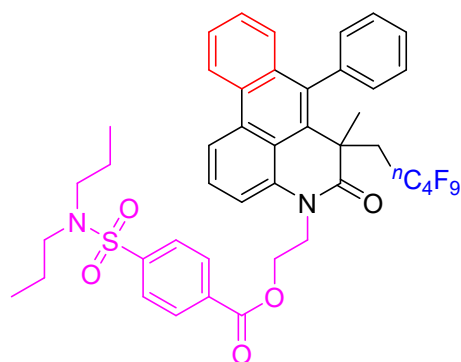


2-(6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-5-oxo-7-phenyl-5,6-dihydro-4H-naphtho[3,2,1-de]quinolin-4-yl)ethyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (7b).

The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); White solid, 103.6 mg, 62% yield; mp 107.6-109.8 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, $J = 8.4$ Hz, 1H), 8.51 (d, $J = 8.4$ Hz, 1H), 7.71 (t, $J = 8.1$ Hz, 1H), 7.61 (t, $J = 7.5$ Hz, 1H), 7.57 – 7.50 (m, 4H), 7.44 – 7.37 (m, 2H), 7.33 (d, $J = 6.9$ Hz, 1H), 7.00 (d, $J = 7.4$ Hz, 1H), 6.93 (d, $J = 8.4$ Hz, 1H), 6.65 (d, $J = 7.4$ Hz, 1H), 6.55 (s, 1H), 4.65 – 4.31 (m, 4H), 4.06 – 3.49 (m, 2H), 3.28 – 2.70 (m, 2H), 2.28 (s, 3H), 2.18 (s, 3H), 1.82 (s, 3H), 1.72 (s, 4H), 1.23 (d, $J = 2.4$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1, 172.7, 157.0, 139.9, 137.8, 136.6, 136.2, 134.0, 133.4, 131.8, 131.2, 130.4, 129.6, 129.2, 128.2, 128.1, 127.9, 127.6, 127.5, 127.1, 127.0, 123.7, 122.8, 120.8, 118.2, 117.8, 112.0, 111.7, 67.9, 60.6, 44.9, 42.3, 42.0, 40.1 (t, $J = 17.7$ Hz), 37.2, 31.4, 25.3, 25.2, 21.5, 15.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -80.97 (s, 3F), -109.06 – -111.27 (m, 1F), -111.45 – -113.99 (m, 1F), -124.47 (s, 2F), -125.40 – -126.53 (m, 2F); HRMS (ESI-TOF) m/z : $[M+Na]^+$ Calcd. for $C_{45}H_{42}F_9NNaO_4^+$: 854.2862; found: 854.2869.



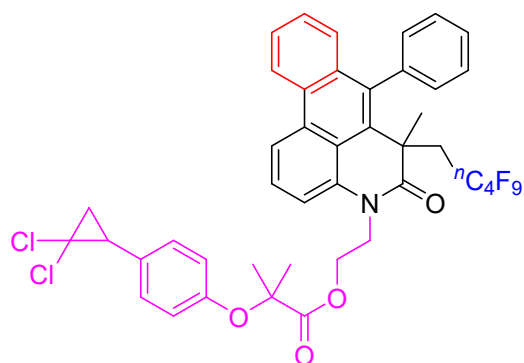
2-(6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-5-oxo-7-phenyl-5,6-dihydro-4H-naphtho[3,2,1-de]quinolin-4-yl)ethyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (7c). The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 82.1 mg, 46% yield; mp 162.5-163.7 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.71 (d, J = 8.4 Hz, 1H), 8.52 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 2.0 Hz, 1H), 8.02 (dd, J = 8.8, 2.0 Hz, 1H), 7.70 (t, J = 8.1 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.55 – 7.46 (m, 4H), 7.42 – 7.34 (m, 3H), 6.98 (d, J = 8.9 Hz, 1H), 6.91 (d, J = 8.5 Hz, 1H), 4.77 – 4.52 (m, 4H), 3.89 (d, J = 6.5 Hz, 2H), 3.25 – 2.86 (m, 2H), 2.73 (s, 3H), 2.30 – 2.14 (m, 1H), 1.80 (s, 3H), 1.09 (d, J = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.9, 167.7, 162.7, 162.1, 162.0, 139.8, 137.9, 136.2, 134.0, 133.4, 132.7, 132.2, 131.8, 131.3, 129.6, 129.2, 128.3, 128.2, 127.9, 127.6, 127.5, 127.2, 127.0, 126.1, 122.9, 121.2, 118.2, 117.9, 115.5, 112.8, 111.5, 103.2, 75.9, 61.3, 44.9, 42.0, 40.2 (t, J = 17.7 Hz), 31.4, 28.3, 19.2, 17.6; ^{19}F NMR (377 MHz, CDCl_3) δ -81.00 (s, 3F), -109.46 – -111.03 (m, 1F), -111.43 – -113.29 (m, 1F), -123.34 – -124.96 (m, 2F), -125.77 – -125.99 (m, 2F); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd. for $\text{C}_{46}\text{H}_{37}\text{F}_9\text{N}_3\text{O}_4\text{S}^+$: 898.2356; found: 898.2365.



2-(6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-5-oxo-7-phenyl-5,6-dihydro-4H-naphtho[3,2,1-de]quinolin-4-yl)ethyl 4-(N,N-dipropylsulfamoyl)benzoate--methane (1/1) (7d).

The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White

solid, 72.5 mg, 42% yield; mp 62.5-63.7 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.70 (d, *J* = 8.4 Hz, 1H), 8.52 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.67 (t, *J* = 8.1 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.55 – 7.51 (m, 3H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.33 (m, 3H), 6.92 (d, *J* = 8.4 Hz, 1H), 4.82 – 4.75 (m, 1H), 4.73 – 4.67 (m, 1H), 4.63 (t, *J* = 5.9 Hz, 2H), 3.15 – 3.05 (m, 5H), 3.05 – 2.90 (m, 1H), 1.80 (s, 3H), 1.54 (dd, *J* = 15.1, 7.5 Hz, 4H), 0.86 (t, *J* = 7.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 172.9, 165.4, 144.5, 139.8, 137.9, 136.1, 133.9, 133.4, 133.1, 131.7, 131.3, 130.4, 129.5, 129.1, 128.2, 128.1, 127.9, 127.6, 127.3, 127.2, 127.1, 127.0, 122.8, 118.3, 117.8, 111.3, 61.7, 50.0, 44.9, 41.9, 40.2 (t, *J* = 18.1 Hz), 31.4, 22.0, 11.2; ¹⁹F NMR (377 MHz, CDCl₃) δ -81.03 (t, *J* = 9.4 Hz, 3F), -109.35 – -110.70 (m, 1F), -111.79 – -113.03 (m, 1F), -124.49 (s, 2F), -125.70 – -126.14 (m, 2F); HRMS (ESI-TOF) *m/z*: [M+Na]⁺ Calcd. for C₄₄H₄₃F₁₀N₂NaO₅S⁺: 905.2641; found: 905.2638.

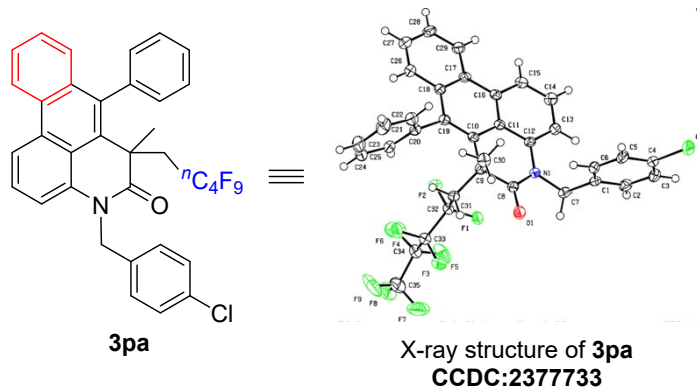


2-(6-methyl-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-5-oxo-7-phenyl-5,6-dihydro-4H-naphtho[3,2,1-de]quinolin-4-yl)ethyl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate (7e). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); White solid, 99.6 mg, 57% yield; mp 168. °C; ¹H NMR (400 MHz, CDCl₃) δ 8.70 (d, *J* = 8.3 Hz, 1H), 8.49 (d, *J* = 8.4 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.55 – 7.50 (m, 3H), 7.41 – 7.38 (m, 3H), 7.37 – 7.33 (m, 1H), 7.11 – 6.98 (m, 2H), 6.92 (d, *J* = 8.5 Hz, 1H), 6.84 – 6.76 (m, 2H), 4.57 – 4.33 (m, 4H), 3.17 – 2.89 (m, 2H), 2.78 – 2.70 (m, 1H), 1.89 – 1.81 (m, 1H), 1.79 (s, 3H), 1.68 (dd, *J* = 16.0, 8.4 Hz, 1H), 1.58 (d, *J* = 11.5 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 174.4, 172.8, 155.0, 139.8, 137.8, 136.0, 134.0, 133.4, 131.8, 131.2, 129.8, 129.7, 129.6, 129.2, 128.5, 128.4, 128.25, 128.17, 127.9, 127.6, 127.5, 127.2, 127.0, 122.8, 119.0, 118.9, 118.2, 117.7, 111.6, 79.3, 61.5, 60.9, 44.9, 41.8, 40.1 (t, *J* = 18.1 Hz), 34.9, 31.4, 25.9, 25.6, 25.4; ¹⁹F NMR (377 MHz, CDCl₃) δ -80.98 (s, 3F), -109.35 – -110.98 (m, 1F), -111.72 – -113.25 (m, 1F), -124.51 (s,

2F), -125.87 (d, $J = 14.7$ Hz, 2F); HRMS (ESI-TOF) m/z : $[M+Na]^+$ Calcd. for $C_{43}H_{34}Cl_2F_9NNaO_4^+$:
892.1613; found: 892.1616.

5. X-ray crystal data for product **3pa** (CCDC: 2377733)

Bruker Apex2 CCD was used for the crystal measurement and the ellipsoid contour is shown at 30% probability levels. Single crystals of compound **3pa** were obtained by slow evaporation of its hexane/dichloromethane solution.



Compound	3pa
Empirical formula	C ₃₅ H ₂₃ ClF ₉ NO
Formula weight	679.99
Temperature/K	150
Crystal system	monoclinic
Space group	P2 ₁
a/Å	14.7922(7)
b/Å	6.2915(3)
c/Å	19.9389(10)
α/°	90
β/°	106.376(2)
γ/°	90
Volume/Å ³	1780.34(15)
Z	2
ρ _{calc} /cm ³	1.268
μ/mm ⁻¹	0.181
F(000)	692.0
Crystal size/mm ³	0.15 × 0.06 × 0.05
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.026 to 52.916
Index ranges	-18 ≤ h ≤ 18, -7 ≤ k ≤ 7, -24 ≤ l ≤ 24
Reflections collected	21018
Independent reflections	6682 [R _{int} = 0.0644, R _{sigma} = 0.0669]
Data/restraints/parameters	6682/1/425

Goodness-of-fit on F^2	1.033
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0442$, $wR_2 = 0.1017$
Final R indexes [all data]	$R_1 = 0.0581$, $wR_2 = 0.1090$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.21/-0.25

6. References

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7. ^1H , ^{13}C , ^{19}F NMR spectra of products (3aa-qa, 3sa, 4a-c, 5ab-ai, 6aj, 7a-e)

