

Supporting Information

Palladium-Catalyzed Cascade Carbonylative Synthesis of Perfluoroalkyl and Carbonyl-Containing 3,4-Dihydroquinolin-2(1H)- one Derivatives

Shangyuan Wang,^a Jiangjie Zhang,^a Jian-Shu Wang,^a Jun Ying,^{*,a} and Xiao-Feng Wu^{*,b,c}

^a Department of Chemistry, Key Laboratory of Surface & Interface Science of Polymer Materials of Zhejiang Province, Zhejiang Sci-Tech University, Hangzhou 310018, China. E-mail: yingjun@zstu.edu.cn

^b Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 116023 Dalian, Liaoning, China. E-mail: xwu2020@dicp.ac.cn

^c Leibniz-Institut für Katalyse e. V., Albert-Einstein-Straße 29a, 18059 Rostock, Germany.

Supporting Information Placeholder

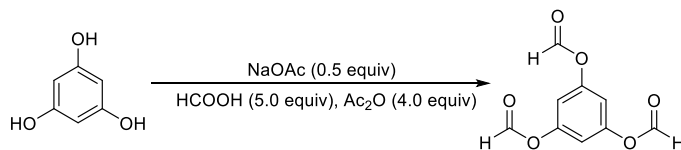
Table of Contents

1. General experimental information	S1
2. Preparation of benzene-1,3,5-triyl triformate (TFBen)	S2
3. General procedure for the synthesis of substrates	S3
4. General procedure for cascade carbonylative synthesis of products (2a-m, 3a-o)	S4
5. Characterization data of products (2a-m, 3a-o)	S5
6. X-ray crystal data for product 3c (CCDC: 2213275)	S22
7. References	S23
8. ¹ H, ¹³ C, ¹⁹ F NMR spectra of products (2a-m, 3a-o)	S24

1. General experimental information

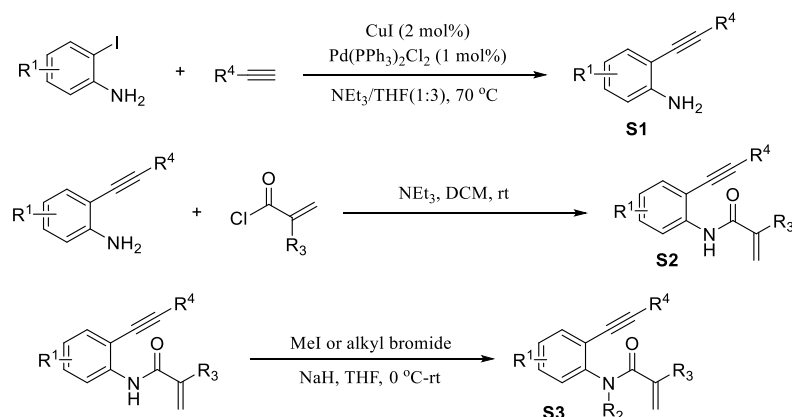
Unless otherwise noted, all reactions were carried out under nitrogen atmosphere. The chemicals were ordered from Bidepharm and Energy Chemicals. All commercially available reagents were used without further purification. All of the solvents were treated according to known methods. Column chromatography 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. ^{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. Preparation of benzene-1,3,5-triyl triformate (TFBen)¹



Formic acid (8.4 mL, 222.8 mmol, 5.0 equiv) was added to acetic anhydride (16.8 mL, 178.2 mmol, 4.0 equiv) at r.t. The mixture was stirred at 60 °C (oil bath) for 1 h and cooled to r.t. The resulting solution was poured into a flask containing 1,3,5-trihydroxybenzene (5.62 g, 44.6 mmol, 1.0 equiv) and AcONa (1.83 g, 22.3 mmol, 0.5 equiv). The mixture was stirred for 4 h in a water bath and then diluted with toluene (100 mL), washed with H₂O (50.0 mL) twice. Keep the organic phase in fridge (2-8 °C) for overnight. Then filtered and dried in vacuo to afford the desired product benzene-1,3,5-triyl triformate (TFBen) as a white solid (5.1 g, 55%).

3. General procedure for the synthesis of substrates²

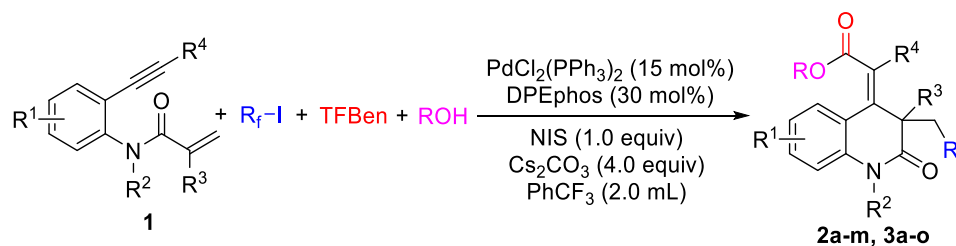


General procedure for synthesis of **S1**: To a suspension of Pd(PPh₃)₂Cl₂ (0.1 mmol, 1 mol%) and CuI (0.2 mmol, 2 mol%) in a mixture of THF (20.0 mL) and Et₃N (20.0 mL), was added 2-iodoaniline (10.0 mmol) and alkyne (12.0 mmol). The reaction was allowed to react at 70 °C (oil bath) for 12 h. Then, 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 ethyl acetate and petroleum ether as eluent.

General procedure for synthesis of **S2**: To a stirred solution of **S1** (1.0 equiv) in CH₂Cl₂ (5.0 mL) was added methacryloyl chloride (1.5 equiv) and Et₃N (2.0 equiv). 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 ethyl acetate and petroleum as eluent.

General procedure for the synthesis of substrates **S3**: To a solution of NaH (2.0 equiv) in THF (5.0 mL) at 0 °C was added a solution of **S2** (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 CH₂Cl₂ for three times. The combined organic layer was washed with brine and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel using ethyl acetate and petroleum as eluent.

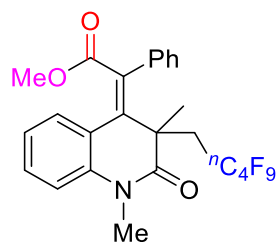
4. General procedure for cascade carbonylative synthesis of products (2a-m, 3a-o)



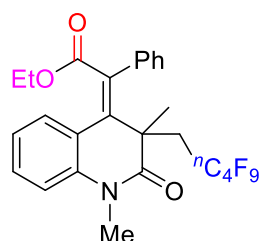
1,7-enyne **1** (0.2 mmol, 1.0 equiv), perfluoroalkyl iodide (0.4 mmol, 2.0 equiv), Pd(PPh₃)₂Cl₂ (14.0 mg, 10 mol%), DPEphos (21.5 mg, 20 mol%), and Cs₂CO₃ (130.0 mg, 0.4 mmol, 2.0 equiv) were added to an oven-dried tube (15.0 mL) which was then placed under vacuum and refilled with nitrogen three times. PhCF₃ (2.0 mL) was added into the tube via syringe and the tube was sealed and stirred at 50 °C (oil bath) for 6 h. Then alcohol (0.3 mL), Pd(PPh₃)₂Cl₂ (7.0 mg, 5 mol%), DPEphos (10.8 mg, 10 mol%), Cs₂CO₃ (130.0 mg, 0.4 mmol, 2.0 equiv), NIS (45.0 mg, 0.2 mmol, 1.0 equiv), and TFBen (210.0 mg, 1.0 mmol, 5.0 equiv) were added into the tube which was then placed under vacuum and refilled with nitrogen three times. The tube was sealed and stirred at 90 °C for 22 h. Upon the reaction was completed, the resulting mixture was purified by silica gel column using chromatography (petroleum ether / ethyl acetate = 10:1) to obtain products (**2a-m**, **3a-o**).

2 mmol scale procedure: 1,7-enyne **1a** (2 mmol, 1.0 equiv), perfluoroalkyl iodide (2.0 equiv), Pd(PPh₃)₂Cl₂ (14.0 mg, 10 mol%), DPEphos (21.5 mg, 20 mol%), and Cs₂CO₃ (130.0 mg, 0.4 mmol, 2.0 equiv) were added to an oven-dried tube (25.0 mL) which was then placed under vacuum and refilled with nitrogen three times. PhCF₃ (10.0 mL) was added into the tube via syringe and the tube was sealed and stirred at 50 °C (oil bath) for 6 h. Then alcohol (3 mL), Pd(PPh₃)₂Cl₂ (5 mol%), DPEphos (10 mol%), Cs₂CO₃ (4 mmol, 2.0 equiv), NIS (2 mmol, 1.0 equiv), and TFBen (10.0 mmol, 5.0 equiv) were added into the tube which was then placed under vacuum and refilled with nitrogen three times. The tube was sealed and stirred at 90 °C for 22 h. Upon the reaction was completed, the resulting mixture was purified by silica gel column using chromatography (petroleum ether / ethyl acetate = 10:1) to obtain product **2a** in 65% yield (719 mg).

5. Characterization data of products (2a-m, 3a-o)

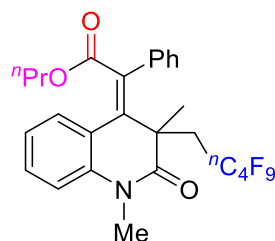


methyl (E)-2-(1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)-2-phenylacetate (2a). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow liquid, 77.4 mg, 70% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.44 (m, 2H), 7.42 – 7.36 (m, 2H), 7.36 – 7.28 (m, 2H), 7.27 – 7.23 (m, 1H), 7.09 (t, J = 7.4 Hz, 1H), 7.04 (d, J = 8.1 Hz, 1H), 3.46 (s, 3H), 3.41 (s, 3H), 2.39 – 2.22 (m, 1H), 2.06 – 1.90 (m, 1H), 1.17 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.5, 170.1, 137.9, 137.1, 136.6, 130.2, 129.9, 128.4, 128.38, 128.3, 128.1, 126.0, 123.7, 114.4, 52.3, 47.6, 36.9 (t, J = 19.8 Hz), 31.0, 21.8 (d, J = 4.5 Hz); ^{19}F NMR (377 MHz, CDCl_3) δ -81.04 – -81.17 (m, 3F), -108.67 – -109.72 (m, 1F), -113.65 – -114.57 (m, 1F), -124.79 – -124.98 (m, 2F), -125.83 (dt, J = 46.7, 14.1 Hz, 2F); HRMS (ESI-TOF) Calcd. for $\text{C}_{25}\text{H}_{20}\text{F}_9\text{NO}_3^+ [\text{M}+\text{H}]^+$: 554.1372; found: 554.1379.

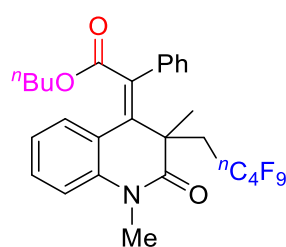


ethyl (E)-2-(1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)-2-phenylacetate (2b). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow liquid, 59.0 mg, 52%; ^1H NMR (400 MHz, CDCl_3) δ 7.48 (t, J = 8.3 Hz, 2H), 7.39 (q, J = 6.4 Hz, 2H), 7.38 – 7.25 (m, 2H), 7.28 – 7.21 (m, 1H), 7.08 (t, J = 7.5 Hz, 1H), 7.03 (d, J = 8.1 Hz, 1H), 4.04 – 3.82 (m, 2H), 3.42 (s, 3H), 2.37 – 2.18 (m, 1H), 2.05 – 1.89 (m, 1H), 1.16 (s, 3H), 0.95 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.6, 169.7, 137.9, 137.0, 136.9, 136.7, 130.1, 130.0, 128.7, 128.3, 128.2, 128.1, 126.1, 123.7, 114.3, 61.4, 47.6, 36.9 (t, J = 19.9 Hz), 31.1, 21.8 (d, J = 4.6 Hz), 13.7; ^{19}F NMR (377 MHz, CDCl_3) δ -

81.1(m, 3F), -108.7 – -109.7 (m, 1F), -113.6 – -114.6 (m, 1F), -124.9, -125.9(m, 2F) (dt, $J = 46.0$, 13.4 Hz, 2F); HRMS (ESI-TOF) Calcd. for $C_{26}H_{23}F_9NO_3^+$ $[M+H]^+$: 568.1529; found: 568.1543.

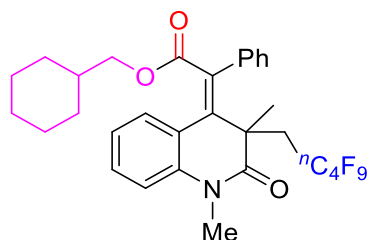


propyl (E)-2-(1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)-2-phenylacetate (2c). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow liquid, 69.7 mg, 60% yield; 1H NMR (400 MHz, $CDCl_3$) δ 7.48 (t, $J = 8.1$ Hz, 2H), 7.42 – 7.36 (m, 2H), 7.36 – 7.28 (m, 2H), 7.28 – 7.24 (m, 1H), 7.08 (t, $J = 7.6$ Hz, 1H), 7.03 (d, $J = 8.3$ Hz, 1H), 3.90 – 3.82 (m, 1H), 3.80 – 3.72 (m, 1H), 3.41 (s, 3H), 2.37 – 2.19 (m, 1H), 2.06 – 1.89 (m, 1H), 1.40 – 1.30 (m, 2H), 1.17 (s, 3H), 0.60 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 169.8, 138.0, 137.0, 136.8, 136.7, 130.1, 130.0, 128.6, 128.3, 128.3, 128.1, 126.2, 123.8, 114.3, 67.1, 47.6, 36.9 (t, $J = 19.9$ Hz), 31.1, 21.8 (d, $J = 4.5$ Hz), 21.6, 10.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.1 (m, 3F), -108.7 – -109.7 (m, 1F), -113.6 – -114.6 (m, 1F), -124.8 – -125.0 (m, 2F), -125.8 (dt, $J = 44.2$, 12.8 Hz, 2F); HRMS (ESI-TOF) Calcd. for $C_{27}H_{25}F_9NO_3^+$ $[M+H]^+$: 582.1685; found: 582.1695.

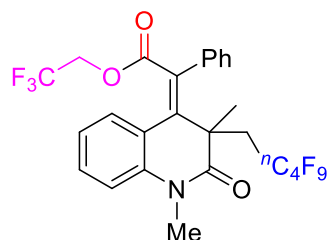


butyl (E)-2-(1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)-2-phenylacetate (2d). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow liquid, 78.5 mg, 66% yield; 1H NMR (400 MHz, $CDCl_3$) δ 7.48 (t, $J = 8.3$ Hz, 2H), 7.39 (q, $J = 7.0$, 6.4 Hz, 2H), 7.36 – 7.27 (m, 2H), 7.26 – 7.22 (m, 1H), 7.08 (t, $J = 7.5$ Hz, 1H), 7.03 (d, $J = 8.1$ Hz, 1H), 3.93 – 3.78 (m, 2H), 3.41 (s, 3H), 2.36 – 2.20 (m, 1H), 2.05 – 1.90 (m, 1H), 1.38 – 1.28 (m, 2H), 1.17 (s, 3H), 1.06 – 0.93 (m, 2H), 0.74 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 169.8, 138.0, 137.1, 136.8, 136.7, 130.1, 130.0,

128.7, 128.32, 128.26, 128.1, 126.2, 123.9, 114.3, 65.3, 47.6, 36.9 (t, $J = 19.8$ Hz), 31.1, 30.3, 21.8 (d, $J = 4.6$ Hz), 18.9, 13.7; ^{19}F NMR (377 MHz, CDCl_3) δ -81.05 – -81.16 (m, 3F), -108.73 – -109.69 (m, 1F), -113.62 – -114.61 (m, 1F), -124.81 – -124.98 (m, 2F), -125.84 (dt, $J = 44.2$, 14.0 Hz, 2F); HRMS (ESI-TOF) Calcd. for $\text{C}_{28}\text{H}_{27}\text{F}_9\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 596.1842; found: 596.1846.

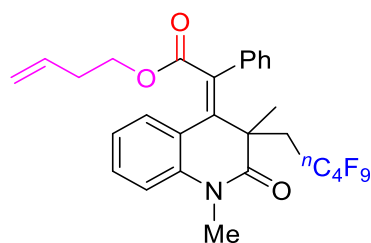


cyclohexylmethyl (E)-2-(1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)-2-phenylacetate (2e). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow liquid, 66.1 mg, 52% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.47 (t, $J = 7.2$ Hz, 2H), 7.43 – 7.36 (m, 2H), 7.35 – 7.27 (m, 2H), 7.26 – 7.23 (m, 1H), 7.09 (t, $J = 7.6$ Hz, 1H), 7.03 (d, $J = 8.1$ Hz, 1H), 3.65 (d, $J = 5.7$ Hz, 2H), 3.41 (s, 3H), 2.35 – 2.20 (m, 1H), 2.05 – 1.87 (m, 1H), 1.58 (d, $J = 10.3$ Hz, 2H), 1.39 – 1.22 (m, 5H), 1.17 (s, 3H), 1.06 (t, $J = 9.7$ Hz, 2H), 0.70 – 0.56 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.6, 169.9, 138.0, 137.1, 136.8, 136.7, 130.1, 130.0, 128.7, 128.32, 128.27, 128.1, 126.3, 124.0, 114.3, 70.6, 47.6, 36.8 (t, $J = 19.6$ Hz), 36.7, 31.1, 29.4, 29.3, 26.3, 25.8, 25.7, 21.9 (d, $J = 3.9$ Hz); ^{19}F NMR (377 MHz, CDCl_3) δ -80.65 – -81.74 (m, 3F), -108.54 – -109.84 (m, 1F), -113.58 – -114.63 (m, 1F), -124.83 – -125.00 (m, 2F), -125.82 (dt, $J = 42.3$, 14.0 Hz, 2F); HRMS (ESI-TOF) Calcd. for $\text{C}_{31}\text{H}_{31}\text{F}_9\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 636.2155; found: 636.2158.

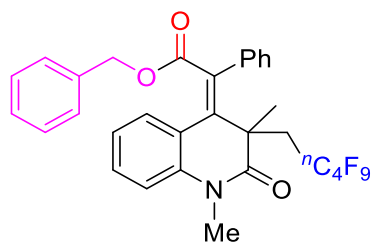


2,2,2-trifluoroethyl (E)-2-(1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)-2-phenylacetate (2f). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow liquid, 74.5 mg, 60% yield; ^1H

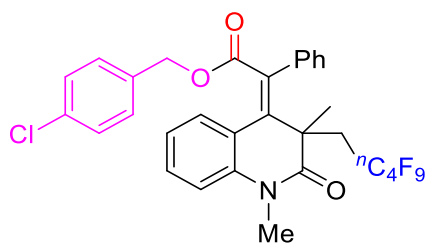
NMR (400 MHz, CDCl₃) δ 7.48 (d, J = 7.6 Hz, 1H), 7.44 – 7.39 (m, 3H), 7.38 – 7.35 (m, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.10 (t, J = 7.6 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 4.38 (dq, J = 12.6, 8.4 Hz, 1H), 4.02 (dq, J = 12.6, 8.4 Hz, 1H), 3.42 (s, 3H), 2.39 – 2.22 (m, 1H), 2.08 – 1.91 (m, 1H), 1.18 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.3, 168.0, 139.8, 138.0, 135.9, 134.7, 130.7, 130.2, 128.8, 128.5, 128.4, 125.7, 124.1, 121.3, 114.6, 61.0 (q, J = 36.8 Hz), 47.9, 37.0 (t, J = 19.9 Hz), 31.1, 21.7 (d, J = 4.7 Hz); ¹⁹F NMR (377 MHz, CDCl₃) δ -73.6 (t, J = 8.4 Hz, 3F), -81.1 (t, J = 10.0 Hz, 3F), -108.6 – -109.5 (m, 1F), -113.6 – -114.5 (m, 1F), -124.9 (m, 2F), -125.8 (dt, J = 51.4, 14.0 Hz, 2F); HRMS (ESI-TOF) Calcd. for C₂₆H₂₀F₁₂NO₃⁺ [M+H]⁺: 622.1246; found: 622.1256.



but-3-en-1-yl (E)-2-(1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)-2-phenylacetate (2g). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow liquid, 60.5 mg, 51% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.47 (t, J = 7.9 Hz, 2H), 7.44 – 7.34 (m, 2H), 7.38 – 7.25 (m, 2H), 7.24 (d, J = 7.8 Hz, 1H), 7.09 (t, J = 7.6 Hz, 1H), 7.04 (d, J = 8.1 Hz, 1H), 5.49 – 5.34 (m, 1H), 4.92 – 4.82 (m, 2H), 3.96 (dt, J = 10.7, 6.6 Hz, 1H), 3.85 (dt, J = 10.8, 6.7 Hz, 1H), 3.41 (s, 3H), 2.36 – 2.20 (m, 1H), 2.14 – 2.03 (m, 2H), 2.02 – 1.89 (m, 1H), 1.17 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.6, 169.7, 138.0, 137.0, 136.8, 136.7, 133.7, 130.2, 130.0, 128.6, 128.38, 128.35, 128.3, 128.1, 126.2, 123.8, 117.1, 114.4, 64.5, 47.6, 36.8 (t, J = 19.9 Hz), 32.6, 31.1, 21.8 (d, J = 4.6 Hz); ¹⁹F NMR (377 MHz, CDCl₃) δ -80.06 – -82.34 (m, 3F), -108.55 – -109.98 (m, 1F), -113.45 – -115.01 (m, 1F), -124.83 – -124.96 (m, 2F), -125.84 (dt, J = 43.8, 13.2 Hz, 2F); HRMS (ESI-TOF) Calcd. for C₂₈H₂₄F₉NO₃⁺ [M+H]⁺: 594.1685; found: 594.1695.

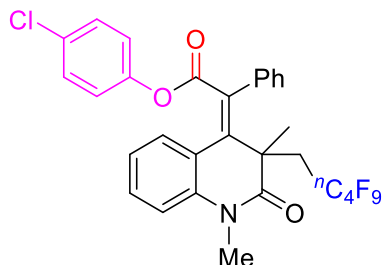


benzyl (E)-2-(1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)-2-phenylacetate (2h). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow solid, 62.9 mg, 50% yield; mp 111.5-116.6 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.49 (d, J = 7.6 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.35 (t, J = 7.8 Hz, 2H), 7.30 (t, J = 7.4 Hz, 1H), 7.27 – 7.20 (m, 4H), 7.03 (d, J = 8.1 Hz, 1H), 6.95 – 6.90 (m, 3H), 4.94 (d, J = 12.3 Hz, 1H), 4.84 (d, J = 12.3 Hz, 1H), 3.39 (s, 3H), 2.37 – 2.19 (m, 1H), 2.07 – 1.89 (m, 1H), 1.17 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.5, 169.5, 138.0, 137.5, 136.6, 136.5, 135.2, 130.2, 130.1, 128.6, 128.5, 128.42, 128.35, 128.3, 128.2, 126.0, 124.0, 114.3, 67.3, 47.8, 36.9 (t, J = 19.8 Hz), 31.1, 21.9 (d, J = 3.8 Hz); ^{19}F NMR (377 MHz, CDCl_3) δ -80.07 – -81.87 (m, 3F), -107.92 – -110.40 (m, 1F), -113.33 – -115.13 (m, 1F), -124.62 – -125.18 (m, 2F), -125.81 (dt, J = 45.6, 13.0 Hz, 2F); HRMS (ESI-TOF) Calcd. for $\text{C}_{31}\text{H}_{24}\text{F}_9\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 630.1685; found: 630.1696.

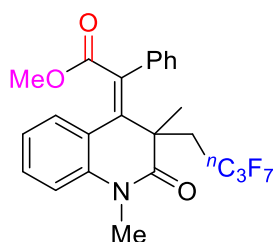


4-chlorobenzyl (E)-2-(1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)-2-phenylacetate (2i). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow solid, 61.0 mg, 46% yield; mp 118.3-119.8 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, J = 7.6 Hz, 1H), 7.42 (t, J = 7.7 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.34 – 7.27 (m, 2H), 7.22 (d, J = 7.6 Hz, 1H), 7.18 (d, J = 8.3 Hz, 2H), 7.02 (d, J = 8.1 Hz, 1H), 6.91 (t, J = 7.6 Hz, 1H), 6.83 (d, J = 8.3 Hz, 2H), 4.85 (s, 2H), 3.39 (s, 3H), 2.35 – 2.17 (m, 1H), 2.06 – 1.88 (m, 1H), 1.16 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.5, 169.3, 138.0, 137.8, 136.5, 136.3, 134.2, 133.7, 130.3, 130.1, 129.8, 128.7, 128.6, 128.5, 128.4, 128.2, 125.9, 123.9, 114.3, 66.4, 47.7, 36.9 (t, J = 19.1 Hz), 31.2, 21.9 (d, J = 4.3 Hz); ^{19}F NMR (377 MHz, CDCl_3) δ -80.98 – -81.17 (m, 3F), -108.63 – -109.60 (m, 1F), -113.63 – -114.66 (m, 1F), -124.64 – -125.10

(m, 2F), -125.57 – -126.04 (m, 2F); HRMS (ESI-TOF) Calcd. for $C_{31}H_{24}ClF_9NO_3^+$ $[M+H]^+$: 664.1296; found: 664.1299.

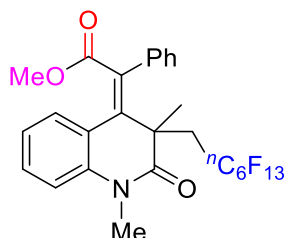


4-chlorophenyl **(E)-2-(1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)-2-phenylacetate (2j)**. The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow liquid, 72.7 mg, 56% yield; 1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.6 Hz, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.41 – 7.35 (m, 3H), 7.20 (d, J = 8.7 Hz, 2H), 7.16 (t, J = 7.6 Hz, 1H), 7.10 (d, J = 8.1 Hz, 1H), 6.59 (d, J = 8.7 Hz, 2H), 3.44 (s, 3H), 2.42 – 2.19 (m, 1H), 2.08 – 1.95 (m, 1H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 167.7, 148.9, 138.8, 138.2, 136.2, 135.7, 131.5, 130.7, 130.2, 129.5, 128.9, 128.8, 128.6, 128.43, 128.38, 125.9, 124.0, 122.7, 114.6, 47.8, 37.1 (t, J = 19.8 Hz), 31.2, 21.8 (d, J = 4.1 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -80.29 – -81.64 (m), -107.47 – -111.30 (m), -112.88 – -114.91 (m), -124.71 – -125.07 (m), -125.78 (dt, J = 51.8, 14.1 Hz); HRMS (ESI-TOF) Calcd. for $C_{30}H_{21}ClF_9NO_3^+$ $[M+H]^+$: 650.1139; found: 650.1135.

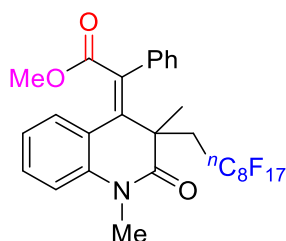


methyl **(E)-2-(3-(2,2,3,3,4,4,4-heptafluorobutyl)-1,3-dimethyl-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)-2-phenylacetate (2k)**. The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow liquid, 66.4 mg, 66% yield; 1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.6 Hz, 2H), 7.43 – 7.36 (m, 2H), 7.35 – 7.30 (m, 2H), 7.26 – 7.21 (m, 1H), 7.10 (t, J = 7.5 Hz, 1H), 7.04 (d, J = 8.2 Hz, 1H), 3.47 (s, 3H), 3.42 (s, 3H), 2.38 – 2.19 (m, 1H), 2.03 – 1.88 (m, 1H), 1.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.2, 138.0, 137.1, 136.6,

131.8, 130.2, 130.0, 129.4, 128.6, 128.4, 128.3, 128.2, 127.6, 126.0, 123.8, 114.4, 52.4, 47.6, 36.8 (t, $J = 19.8$ Hz), 31.1, 21.8 (d, $J = 4.5$ Hz); ^{19}F NMR (377 MHz, CDCl_3) δ -80.20 (t, $J = 9.8$ Hz, 3F), -109.34 – -110.34 (m, 1F), -114.61 – -115.58 (m, 1F), -128.19 (dd, $J = 35.2, 6.2$ Hz, 2F); HRMS (ESI-TOF) Calcd. for $\text{C}_{24}\text{H}_{20}\text{F}_7\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 504.1404; found: 504.1411.

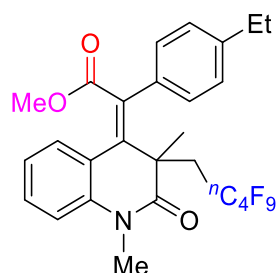


methyl (E)-2-(1,3-dimethyl-2-oxo-3-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-2,3-dihydroquinolin-4(1H)-ylidene)-2-phenylacetate (2l). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow liquid, 75.7 mg, 58% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.47 (t, $J = 6.8$ Hz, 2H), 7.43 – 7.37 (m, 2H), 7.36 – 7.28 (m, 2H), 7.24 (d, $J = 7.4$ Hz, 1H), 7.10 (t, $J = 7.6$ Hz, 1H), 7.04 (d, $J = 8.2$ Hz, 1H), 3.47 (s, 3H), 3.42 (s, 3H), 2.38 – 2.17 (m, 1H), 2.07 – 1.87 (m, 1H), 1.16 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.6, 170.2, 138.0, 137.2, 136.7, 136.6, 130.2, 130.0, 128.42, 128.35, 128.3, 128.2, 126.0, 123.8, 114.4, 52.4, 47.6, 37.1 (t, $J = 19.8$ Hz), 31.1, 21.9 (d, $J = 4.7$ Hz); ^{19}F NMR (377 MHz, CDCl_3) δ -80.84 (t, $J = 10.1$ Hz, 3F), -108.11 – -109.51 (m, 1F), -112.99 – -114.45 (m, 1F), -121.70 (s, 2F), -122.92 (s, 2F), -123.73 – -124.32 (m, 2F), -125.94 – -126.54 (m, 2F); HRMS (ESI-TOF) Calcd. for $\text{C}_{27}\text{H}_{20}\text{F}_{13}\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 654.1308; found: 654.1310.

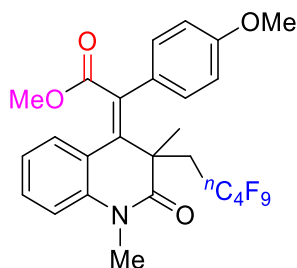


methyl (E)-2-(3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptafluorononyl)-1,3-dimethyl-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)-2-phenylacetate (2m). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow liquid, 75.3 mg, 50% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.46 (t, $J = 7.1$ Hz, 2H), 7.43 – 7.37 (m, 2H), 7.36 – 7.28 (m, 2H), 7.27 – 7.23 (m, 1H), 7.10 (t, $J = 7.6$ Hz, 1H), 7.04 (d, $J = 8.2$ Hz, 1H), 3.47 (s, 3H), 3.42 (s, 3H), 2.39 –

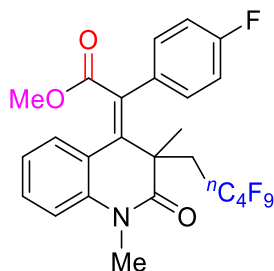
2.19 (m, 1H), 2.06 – 1.88 (m, 1H), 1.17 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.6, 170.2, 138.0, 137.2, 136.6, 136.6, 130.2, 123.0, 128.4, 128.3, 128.2, 126.0, 123.8, 114.5, 52.4, 47.6, 37.1 (t, $J = 19.8$ Hz), 31.1, 21.8 (d, $J = 4.4$ Hz); ^{19}F NMR (377 MHz, CDCl_3) δ -80.28 – -81.44 (m, 3F), -108.16 – -109.80 (m, 1F), -112.83 – -114.61 (m, 1F), -121.50, (s, 2F) -121.98 (s, 2F), -122.75 (s, 4F), -123.96 (s, 2F), -126.16 (s, 2F); HRMS (ESI-TOF) Calcd. for $\text{C}_{29}\text{H}_{20}\text{F}_{17}\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 754.1244; found: 754.1245.



methyl (E)-2-(1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)-2-(4-ethylphenyl)acetate (3a). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow solid; 88.3 mg, 76%, mp 109.3–110.7 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.45 (d, $J = 7.6$ Hz, 1H), 7.38 (t, $J = 8.5$ Hz, 2H), 7.23 (d, $J = 7.8$ Hz, 1H), 7.14 (s, 2H), 7.09 (t, $J = 7.6$ Hz, 1H), 7.03 (d, $J = 8.1$ Hz, 1H), 3.47 (s, 3H), 3.41 (s, 3H), 2.67 (q, $J = 7.6$ Hz, 2H), 2.37 – 2.18 (m, 1H), 2.05 – 1.89 (m, 1H), 1.25 (t, $J = 7.6$ Hz, 3H), 1.18 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.7, 170.4, 144.6, 137.9, 137.0, 136.8, 133.8, 130.1, 129.8, 128.4, 128.3, 127.8, 127.7, 126.1, 123.8, 114.4, 52.3, 47.6, 37.0 (t, $J = 20.1$ Hz), 31.1, 28.7, 21.9 (d, $J = 3.8$ Hz), 15.4; ^{19}F NMR (377 MHz, CDCl_3) δ -81.1 (t, $J = 9.9$ Hz, 3F), -108.8 – -109.7 (m, 1F), -113.7 – -114.5 (m, 1F), -124.9 (m, 2F), -125.8 (dt, $J = 46.1, 14.1$ Hz, 2F); HRMS (ESI-TOF) Calcd. for $\text{C}_{27}\text{H}_{25}\text{F}_9\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 582.1685; found: 582.1696.

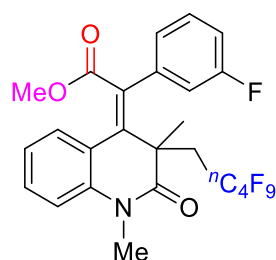


methyl (E)-2-(1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)-2-(4-methoxyphenyl)acetate (3b). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow solid; 82.8 mg, 71%, mp 135.1-132.8 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.44 (d, J = 7.6 Hz, 1H), 7.42 – 7.33 (m, 2H), 7.14 (d, J = 8.5 Hz, 1H), 7.08 (t, J = 7.6 Hz, 1H), 7.03 (d, J = 8.2 Hz, 1H), 6.94 (dd, J = 8.5, 2.7 Hz, 1H), 6.84 (dd, J = 8.4, 2.7 Hz, 1H), 3.82 (s, 3H), 3.47 (s, 3H), 3.41 (s, 3H), 2.37 – 2.19 (m, 1H), 2.05 – 1.90 (m, 1H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.7, 170.4, 159.7, 137.9, 137.3, 136.4, 131.2, 130.2, 129.6, 128.7, 128.4, 126.1, 123.8, 114.4, 113.8, 113.6, 55.4, 52.3, 47.6, 37.0 (t, J = 19.7 Hz), 31.1, 22.0 (d, J = 4.4 Hz); ^{19}F NMR (377 MHz, CDCl_3) δ -81.1 (t, J = 9.9 Hz, 3F), -108.7 – -109.7 (m, 1F), -113.7 – -114.6 (m, 1F), -124.9 (m, 2F), -125.8 (dt, J = 47.6, 14.1 Hz, 2F); HRMS (ESI-TOF) Calcd. for $\text{C}_{26}\text{H}_{22}\text{F}_9\text{NO}_4\text{Na}^+ [\text{M}+\text{Na}]^+$: 606.1297; found: 606.1300.

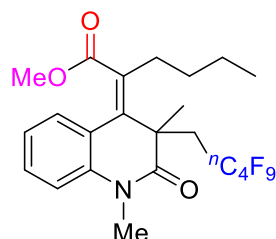


methyl (E)-2-(1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)-2-(4-fluorophenyl)acetate (3c). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow solid, 65.1 mg, 57% yield, mp 132.4-133.1 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.46 – 7.41 (m, 2H), 7.38 (d, J = 7.7 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.13 – 7.07 (m, 2H), 7.06 – 7.03 (m, 1H), 7.02 – 6.97 (m, 1H), 3.47 (s, 3H), 3.42 (s, 3H), 2.37 – 2.19 (m, 1H), 2.04 – 1.88 (m, 1H), 1.16 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.4, 170.1, 162.8 (d, J = 248.1 Hz), 138.0, 137.9, 135.4, 132.4 (d, J = 3.5 Hz), 131.8 (d, J = 8.2 Hz), 130.4, 130.2 (d, J = 8.2 Hz), 128.3, 125.9, 123.9, 115.5 (d, J = 21.6 Hz), 115.3 (d, J = 21.6 Hz),

114.5, 52.4, 47.7, 36.9 (t, $J = 19.9$ Hz), 31.1, 22.0 (d, $J = 4.6$ Hz); ^{19}F NMR (377 MHz, CDCl_3) δ -80.55 – -81.58 (m, 3F), -108.23 – -110.13 (m, 1F), -112.35 – -113.44 (m, 1F), -113.32 – -114.98 (m, 1F), -124.20 – -125.39 (m, 2F), -125.84 (dt, $J = 50.9, 13.0$ Hz, 2F); HRMS (ESI-TOF) Calcd. for $\text{C}_{25}\text{H}_{19}\text{F}_{10}\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 572.1278; found: 572.1285.

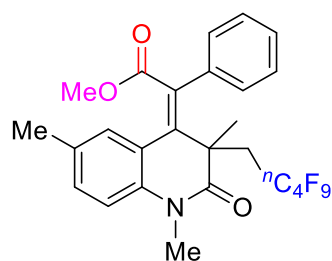


methyl (E)-2-(1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)-2-(3-fluorophenyl)acetate (3d). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow liquid, 68.5 mg, 60% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.43 (d, $J = 7.3$ Hz, 1H), 7.42 – 7.33 (m, 1H), 7.31 – 7.24 (m, 1H), 7.25 – 7.17 (m, 1H), 7.10 (t, $J = 7.7$ Hz, 1H), 7.07 – 7.03 (m, 2H), 7.03 – 6.95 (m, 1H), 3.47 (s, 3H), 3.42 (s, 3H), 2.37 – 2.20 (m, 1H), 2.06 – 1.88 (m, 1H), 1.19 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.3, 169.7, 162.5 (d, $J = 247.9$ Hz), 138.7 – 138.4 (m), 138.1, 137.9, 135.1, 130.5, 130.0 (d, $J = 8.4$ Hz), 129.8 (d, $J = 8.3$ Hz), 128.3 (d, $J = 3.9$ Hz), 126.0, 125.7, 124.5, 123.9, 115.8, 115.59, 115.55 (d, $J = 20.8$ Hz), 114.5, 52.5, 47.7, 36.9 (t, $J = 19.6$ Hz), 31.2, 21.7 (d, $J = 3.9$ Hz); ^{19}F NMR (377 MHz, CDCl_3) δ -80.70 – -81.85 (m, 3F), -107.90 – -109.87 (m, 1F), -112.27 – -112.97 (m, 1F), -113.47 – -114.71 (m, 1F), -124.72 – -125.21 (m, 2F), -125.68 – -125.95 (m, 2F); HRMS (ESI-TOF) Calcd. for $\text{C}_{25}\text{H}_{19}\text{F}_{10}\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 572.1278; found: 572.1283.

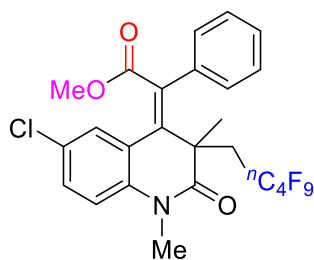


methyl (E)-2-(1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)hexanoate (3e). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow liquid, 49.0 mg, 46% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.31

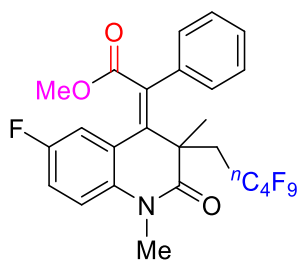
(t, $J = 7.9$ Hz, 1H), 7.21 (d, $J = 7.5$ Hz, 1H), 7.02 (d, $J = 7.7$ Hz, 1H), 6.98 (t, $J = 7.2$ Hz, 1H), 3.41 (s, 3H), 3.38 (s, 3H), 2.87 – 2.75 (m, 1H), 2.62 – 2.52 (m, 1H), 2.29 – 2.15 (m, 1H), 2.10 – 1.98 (m, 1H), 1.94 (s, 3H), 1.48 – 1.41 (m, 2H), 1.39 – 1.32 (m, 2H), 0.91 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.3, 170.6, 137.9, 137.5, 135.4, 129.7, 128.5, 127.2, 123.6, 118.7, 117.7, 114.2, 52.0, 47.9, 36.6 (t, $J = 19.6$ Hz), 31.1, 30.9, 22.9, 21.1 (d, $J = 4.2$ Hz), 13.9; ^{19}F NMR (377 MHz, CDCl_3) δ -81.09 – -81.21 (m, 3F), -108.12 – -109.33 (m, 1F), -113.98 – -115.37 (m, 1F), -124.77 – -125.29 (m, 2F), -125.90 (dt, $J = 41.0, 13.2$ Hz, 2F); HRMS (ESI-TOF) Calcd. for $\text{C}_{23}\text{H}_{24}\text{F}_9\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 534.1685; found: 534.1682.



methyl (E)-2-phenyl-2-(1,3,6-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)acetate (3f). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow liquid, 62.4 mg, 55% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.46 (d, $J = 7.5$ Hz, 1H), 7.40 (t, $J = 7.4$ Hz, 1H), 7.37 – 7.33 (m, 1H), 7.31 (d, $J = 8.1$ Hz, 1H), 7.27 (s, 1H), 7.24 (d, $J = 7.4$ Hz, 1H), 7.18 (d, $J = 8.4$ Hz, 1H), 6.92 (d, $J = 8.2$ Hz, 1H), 3.48 (s, 3H), 3.39 (s, 3H), 2.32 (s, 3H), 2.31 – 2.21 (m, 1H), 2.06 – 1.89 (m, 1H), 1.15 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.4, 170.3, 137.4, 136.6, 136.4, 135.6, 133.4, 131.8, 130.7, 123.0, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 125.9, 114.3, 52.2, 47.6, 37.0 (t, $J = 19.9$ Hz), 31.1, 21.8 (d, $J = 4.5$ Hz), 20.7; ^{19}F NMR (377 MHz, CDCl_3) δ -81.12 – -81.26 (m, 3F), -108.70 – -109.76 (m, 1F), -113.55 – -114.59 (m, 1F), -124.93 – -125.07 (m, 2F), -125.93 (dt, $J = 39.4, 12.5$ Hz, 2F); HRMS (ESI-TOF) Calcd. for $\text{C}_{26}\text{H}_{22}\text{F}_9\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 568.1529; found: 568.1520.

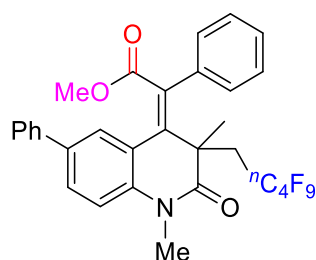


methyl (E)-2-(6-chloro-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)-2-phenylacetate (3g). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow liquid, 71.6 mg, 61% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.47 (s, 1H), 7.46 – 7.39 (m, 1H), 7.39 – 7.32 (m, 3H), 7.31 – 7.27 (m, 1H), 7.24 (d, J = 7.6 Hz, 1H), 6.97 (d, J = 8.7 Hz, 1H), 3.55 (s, 3H), 3.39 (s, 3H), 2.37 – 2.20 (m, 1H), 2.10 – 1.92 (m, 1H), 1.16 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.3, 169.7, 138.0, 136.6, 136.1, 135.6, 131.9, 129.9, 129.7, 129.5, 129.3, 129.1, 128.7, 128.6, 128.4, 128.3, 128.0, 127.4, 115.6, 52.4, 47.4, 37.1 (t, J = 19.9 Hz), 31.2, 22.0 (d, J = 4.4 Hz); ^{19}F NMR (377 MHz, CDCl_3) δ -81.03 – -81.14 (m, 3F), -108.80 – -110.09 (m, 1F), -113.20 – -114.36 (m, 1F), -124.74 – -124.89 (m, 2F), -125.80 (dt, J = 41.8, 12.8 Hz, 2F); HRMS (ESI-TOF) Calcd. for $\text{C}_{25}\text{H}_{19}\text{ClF}_9\text{NO}_3^+ [\text{M}+\text{H}]^+$: 588.0983; found: 588.0979.

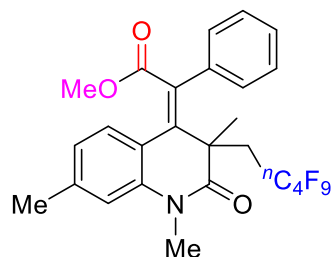


methyl (E)-2-(6-fluoro-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)-2-phenylacetate (3h). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow solid, 60.5 mg, 53% yield; mp 115.3-116.6 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.48 – 7.38 (m, 2H), 7.39 – 7.33 (m, 1H), 7.35 – 7.27 (m, 1H), 7.27 – 7.18 (m, 2H), 7.10 (td, J = 8.4, 8.0, 2.9 Hz, 1H), 7.00 (dd, J = 8.9, 4.6 Hz, 1H), 3.54 (s, 3H), 3.40 (s, 3H), 2.37 – 2.19 (m, 1H), 2.06 – 1.90 (m, 1H), 1.15 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.2, 169.7, 159.0 (d, J = 244.1 Hz), 137.9, 136.1, 135.8, 134.3, 131.9, 129.8, 128.6, 128.4, 128.3 (d, J = 5.0 Hz), 127.6 (d, J = 7.9 Hz), 116.7 (d, J = 22.7 Hz), 115.8 (d, J = 8.1

Hz), 115.2 (d, $J = 24.5$ Hz), 52.5, 47.4, 37.0 (t, $J = 19.7$ Hz), 31.4, 21.9 (d, $J = 4.6$ Hz); ^{19}F NMR (377 MHz, CDCl_3) δ -80.96 – -81.21 (m, 3F), -108.56 – -110.12 (m, 1F), -113.21 – -114.82 (m, 1F), -118.59 – -119.22 (m, 1F), -124.57 – -125.01 (m, 2F), -125.79 (dt, $J = 47.4, 14.0$ Hz, 2F); $\text{C}_{25}\text{H}_{19}\text{F}_{10}\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 572.1278; found: 572.1283.

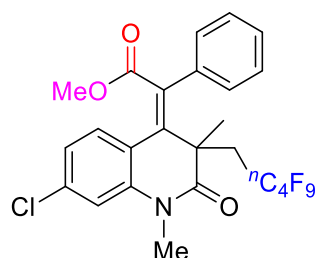


methyl (E)-2-(1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxo-6-phenyl-2,3-dihydroquinolin-4(1H)-ylidene)-2-phenylacetate (3i). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow solid, 75.5 mg, 60% yield; mp 114.7-115.9 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.77 (s, 1H), 7.65 (dd, $J = 8.4, 1.9$ Hz, 1H), 7.58 (d, $J = 7.5$ Hz, 2H), 7.51 (d, $J = 7.5$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 2H), 7.43 – 7.39 (m, 1H), 7.38 – 7.31 (m, 3H), 7.31 – 7.26 (m, 1H), 7.12 (d, $J = 8.4$ Hz, 1H), 3.46 (s, 3H), 3.43 (s, 3H), 2.45 – 2.28 (m, 1H), 2.12 – 1.93 (m, 1H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.6, 170.2, 139.6, 137.2, 137.1, 137.0, 136.7, 136.5, 120.0, 129.1, 128.6, 128.5, 128.42, 128.36, 128.2, 127.6, 126.9, 126.7, 126.4, 114.8, 52.5, 47.7, 37.1 (t, $J = 19.8$ Hz), 31.2, 21.9 (d, $J = 4.0$ Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -80.37 – -81.69 (m, 3F), -108.57 – -110.00 (m, 1F), -113.20 – -114.58 (m, 1F), -124.47 – -125.22 (m, 2F), -125.77 (dt, $J = 38.5, 13.9$ Hz, 2F); HRMS (ESI-TOF) Calcd. for $\text{C}_{31}\text{H}_{24}\text{F}_9\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 630.1685; found: 630.1680.

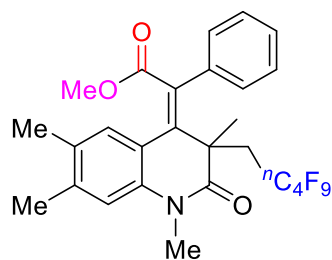


methyl (E)-2-phenyl-2-(1,3,7-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)acetate (3j). The product was purified by column

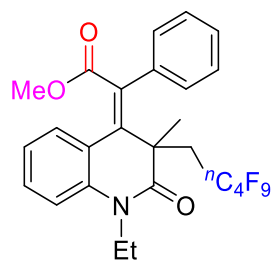
chromatography (petroleum ether / ethyl acetate = 10:1); Yellow liquid, 63.5 mg, 56% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.46 (d, $J = 7.7$ Hz, 1H), 7.39 (t, $J = 7.4$ Hz, 1H), 7.35 – 7.27 (m, 3H), 7.24 (d, $J = 7.3$ Hz, 1H), 6.90 (d, $J = 7.8$ Hz, 1H), 6.84 (s, 1H), 3.48 (s, 3H), 3.40 (s, 3H), 2.40 (s, 3H), 2.34 – 2.21 (m, 1H), 2.05 – 1.89 (m, 1H), 1.15 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.7, 170.3, 140.5, 137.8, 137.3, 136.8, 136.0, 131.7, 130.0, 128.6, 128.5, 128.32, 128.27, 128.2, 128.1, 124.5, 123.1, 115.3, 52.3, 47.7, 37.0 (t, $J = 19.8$ Hz), 31.1, 21.9 (d, $J = 4.9$ Hz), 21.8; ^{19}F NMR (377 MHz, CDCl_3) δ -81.01 – -81.17 (m, 3F), -108.72 – -109.97 (m, 1F), -113.42 – -114.57 (m, 1F), -124.71 – -124.85 (m, 2F), -125.83 (dt, $J = 52.2, 14.3$ Hz, 2F); HRMS (ESI-TOF) Calcd. for $\text{C}_{26}\text{H}_{22}\text{F}_9\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 568.1529; found: 568.1532.



methyl (E)-2-(7-chloro-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)-2-phenylacetate (3k). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow solid, 70.4 mg, 60% yield; mp 118.7-119.9 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.43 (d, $J = 4.2$ Hz, 1H), 7.41 – 7.36 (m, 2H), 7.36 – 7.27 (m, 2H), 7.23 (d, $J = 7.6$ Hz, 1H), 7.08 (dd, $J = 8.2, 1.9$ Hz, 1H), 7.04 (d, $J = 1.9$ Hz, 1H), 3.50 (s, 3H), 3.39 (s, 3H), 2.36 – 2.18 (m, 1H), 2.07 – 1.90 (m, 1H), 1.15 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.6, 169.9, 139.2, 137.4, 136.3, 136.1, 135.9, 131.8, 129.8, 129.4, 128.7, 128.6, 128.4, 128.33, 128.27, 124.3, 123.7, 114.9, 52.5, 47.6, 37.1 (t, $J = 20.0$ Hz), 31.2, 22.0 (d, $J = 4.7$ Hz); ^{19}F NMR (377 MHz, CDCl_3) δ -80.65 – -81.35 (m, 3F), -108.71 – -109.97 (m, 1F), -113.42 – -114.49 (m, 1F), -124.60 – -124.87 (m, 2F), -125.60 – -125.98 (m, 2F); HRMS (ESI-TOF) Calcd. for $\text{C}_{25}\text{H}_{19}\text{ClF}_9\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 588.0983; found: 588.0975.

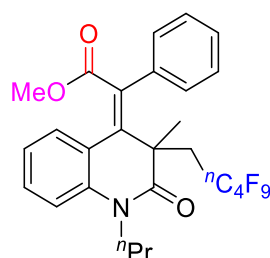


methyl (E)-2-phenyl-2-(1,3,6,7-tetramethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)acetate (3l). The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow liquid, 58.1 mg, 50% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.45 (d, $J = 7.6$ Hz, 1H), 7.39 (t, $J = 7.4$ Hz, 1H), 7.35 – 7.27 (m, 2H), 7.24 (d, $J = 7.4$ Hz, 1H), 7.20 (s, 1H), 6.80 (s, 1H), 3.49 (s, 3H), 3.38 (s, 3H), 2.31 (s, 3H), 2.29 – 2.23 (m, 1H), 2.22 (s, 3H), 2.06 – 1.90 (m, 1H), 1.14 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.6, 170.4, 138.8, 137.4, 136.8, 135.8, 135.7, 132.0, 130.0, 129.3, 128.6, 128.30, 128.26, 128.2, 123.3, 115.9, 52.2, 47.7, 37.1 (t, $J = 19.7$ Hz), 31.1, 22.0 (d, $J = 4.3$ Hz), 20.3, 19.1; ^{19}F NMR (377 MHz, CDCl_3) δ -80.58 – -81.53 (m, 3F), -109.02 – -110.16 (m, 1F), -113.38 – -114.47 (m, 1F), -124.40 – -125.16 (m, 2F), -125.82 (dt, $J = 45.6, 13.9$ Hz, 2F); HRMS (ESI-TOF) Calcd. for $\text{C}_{27}\text{H}_{25}\text{F}_9\text{NO}_3^+ [\text{M}+\text{H}]^+$: 582.1685; found: 582.1691.

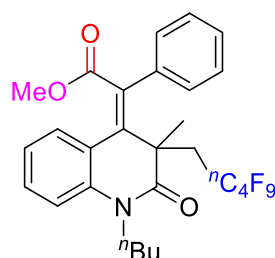


methyl (E)-2-(1-ethyl-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)-2-phenylacetate (3m) The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow liquid, 69.2 mg, 61% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.48 – 7.43 (m, 2H), 7.41 (d, $J = 8.1$ Hz, 1H), 7.37 (d, $J = 7.8$ Hz, 1H), 7.33 (d, $J = 8.0$ Hz, 1H), 7.29 (d, $J = 7.2$ Hz, 1H), 7.24 (d, $J = 7.6$ Hz, 1H), 7.10 – 7.04 (m, 2H), 4.21 – 4.10 (m, 1H), 3.90 – 3.79 (m, 1H), 3.46 (s, 3H), 2.36 – 2.20 (m, 1H), 2.06 – 1.90 (m, 1H), 1.29 (t, $J = 7.1$ Hz, 3H), 1.15 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.2, 169.9, 137.6, 137.0, 136.6, 136.5, 130.3, 130.0, 128.6, 128.5, 128.4, 128.3, 128.2, 126.3, 123.7, 114.3, 52.4, 47.5, 39.3,

36.8 (t, $J = 20.0$ Hz), 21.6(d, $J = 4.1$ Hz), 12.5; ^{19}F NMR (377 MHz, CDCl_3) δ -80.99 – -81.21 (m, 3F), -108.55 – -109.65 (m, 1F), -113.37 – -114.60 (m, 1F), -124.71 – -125.15 (m, 2F), -125.86 (dt, $J = 42.8, 13.4$ Hz, 2F); HRMS (ESI-TOF) Calcd. for $\text{C}_{26}\text{H}_{22}\text{F}_9\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 568.1529; found: 568.1536.



methyl **(E)-2-(3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxo-1-propyl-2,3-dihydroquinolin-4(1H)-ylidene)-2-phenylacetate (3n).** The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow liquid, 73.2 mg, 63% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.45 (t, $J = 7.8$ Hz, 2H), 7.42 – 7.36 (m, 2H), 7.35 – 7.28 (m, 2H), 7.22 (d, $J = 7.3$ Hz, 1H), 7.08 (t, $J = 7.7$ Hz, 1H), 7.04 (d, $J = 8.3$ Hz, 1H), 3.96 – 3.88 (m, 2H), 3.45 (s, 3H), 2.38 – 2.23 (m, 1H), 2.05 – 1.88 (m, 1H), 1.78 – 1.66 (m, 2H), 1.14 (s, 3H), 0.98 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.3, 170.2, 137.6, 137.1, 136.6, 136.4, 130.1, 130.0, 128.51, 128.46, 128.4, 128.3, 128.2, 126.7, 123.7, 114.8, 52.4, 47.6, 45.3, 36.8 (t, $J = 19.9$ Hz), 21.7 (d, $J = 4.6$ Hz), 20.4, 11.0; ^{19}F NMR (377 MHz, CDCl_3) δ -81.03 – -81.14 (m, 3F), -108.43 – -109.47 (m, 1F), -113.64 – -114.60 (m, 1F), -124.79 – -125.06 (m, 2F), -125.86 (dt, $J = 45.8, 14.2$ Hz, 2F); HRMS (ESI-TOF) Calcd. for $\text{C}_{27}\text{H}_{25}\text{F}_9\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 582.1685; found: 582.1685.

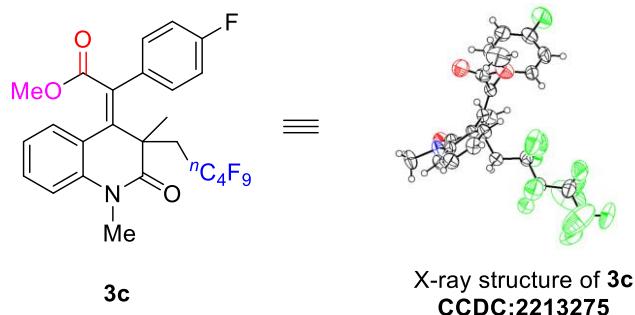


methyl **(E)-2-(1-butyl-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)-2-phenylacetate (3o).** The product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1); Yellow liquid, 73.8 mg, 62% yield; ^1H

NMR (400 MHz, CDCl₃) δ 7.45 (t, J = 8.1 Hz, 2H), 7.44 – 7.36 (m, 1H), 7.39 – 7.30 (m, 2H), 7.33 – 7.26 (m, 1H), 7.22 (d, J = 7.3 Hz, 1H), 7.07 (q, 2H), 4.03 – 3.86 (m, 2H), 3.45 (s, 3H), 2.39 – 2.19 (m, 1H), 2.05 – 1.87 (m, 1H), 1.73 – 1.60 (m, 2H), 1.47 – 1.37 (m, 2H), 1.15 (s, 3H), 0.98 (t, J = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.2, 137.5, 137.1, 136.6, 136.4, 130.1, 130.0, 128.51, 128.45, 128.4, 128.3, 128.2, 126.7, 123.7, 114.7, 52.4, 47.6, 43.7, 36.8 (t, J = 19.9 Hz), 29.2, 21.7 (d, J = 4.6 Hz), 20.1, 13.9; ¹⁹F NMR (377 MHz, CDCl₃) δ -80.96 – -81.34 (m, 3F), -108.37 – -109.62 (m, 1F), -113.27 – -114.93 (m, 1F), -124.82 – -125.10 (m, 2F), -125.86 (dt, J = 45.4, 14.2 Hz, 2F); HRMS (ESI-TOF) Calcd. for C₂₈H₂₆F₉NO₃⁺ [M+H]⁺: 596.1842; found: 596.1846.

6. X-ray crystal data for product 3c (CCDC: 2213275)

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



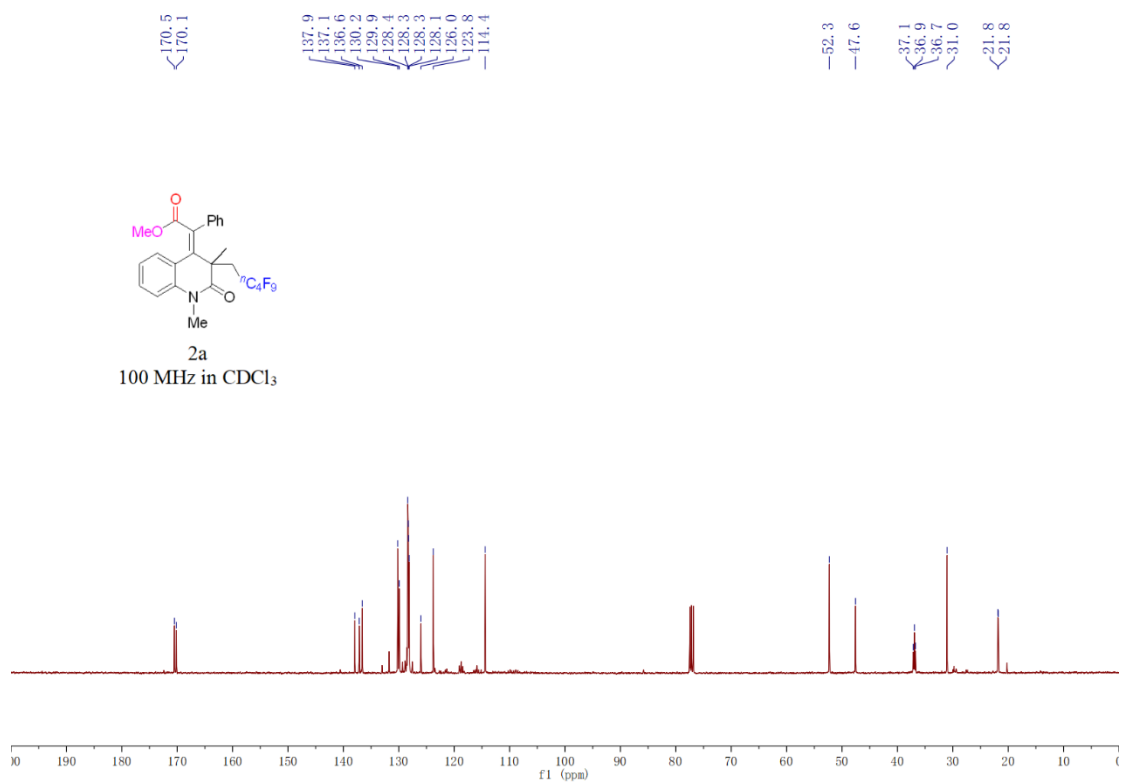
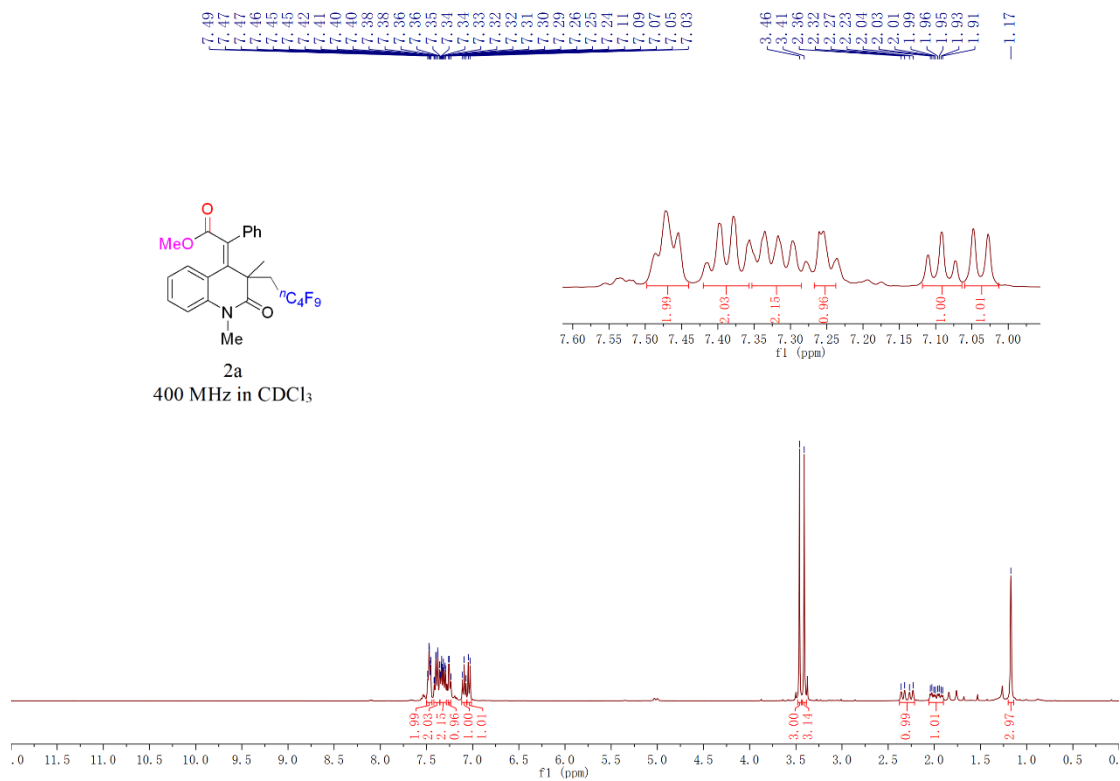
Compound	3c
Empirical formula	C ₂₅ H ₁₉ F ₁₀ NO ₃
Formula weight	571.41
Temperature/K	596.15
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	22.355(5)
b/Å	9.885(2)
c/Å	22.471(5)
α /°	90
β /°	92.523(3)
γ /°	90
Volume/Å ³	4960.9(19)
Z	8
$\rho_{\text{calc}}/\text{cm}^3$	1.530
μ/mm^{-1}	0.150
F(000)	2320.0
Crystal size/mm ³	0.19 × 0.18 × 0.17
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	2.682 to 54.662
Index ranges	-28 ≤ h ≤ 28, -12 ≤ k ≤ 12, -28 ≤ l ≤ 18
Reflections collected	29616
Independent reflections	11064 [R _{int} = 0.0394, R _{sigma} = 0.0486]
Data/restraints/parameters	11064/849/764
Goodness-of-fit on F ²	1.068
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0863, wR ₂ = 0.2533
	S22

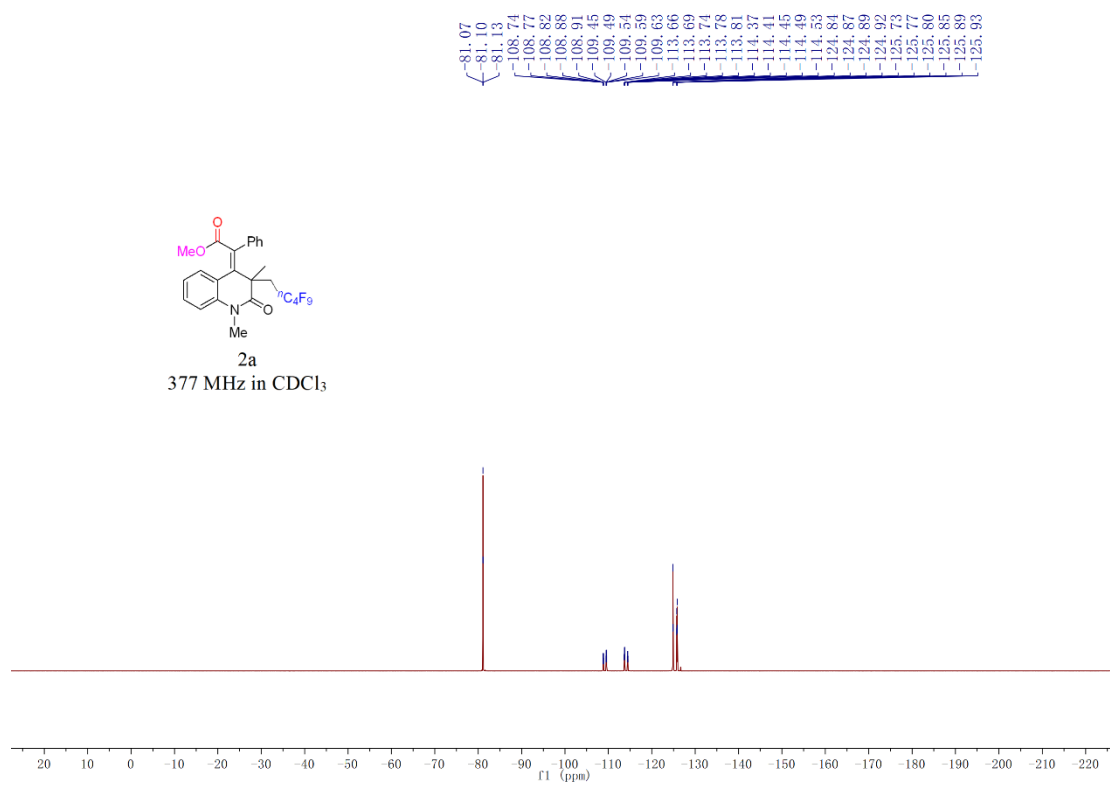
Final R indexes [all data]	$R_1 = 0.1371$, $wR_2 = 0.2977$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.73/-0.44

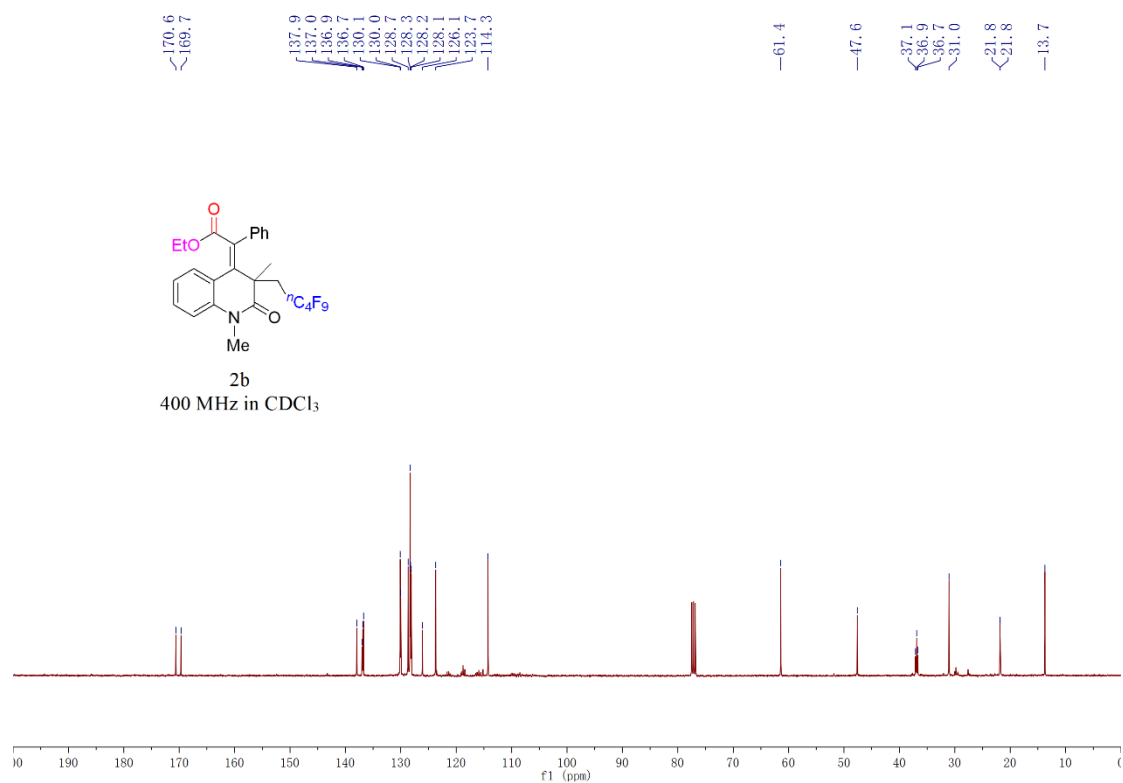
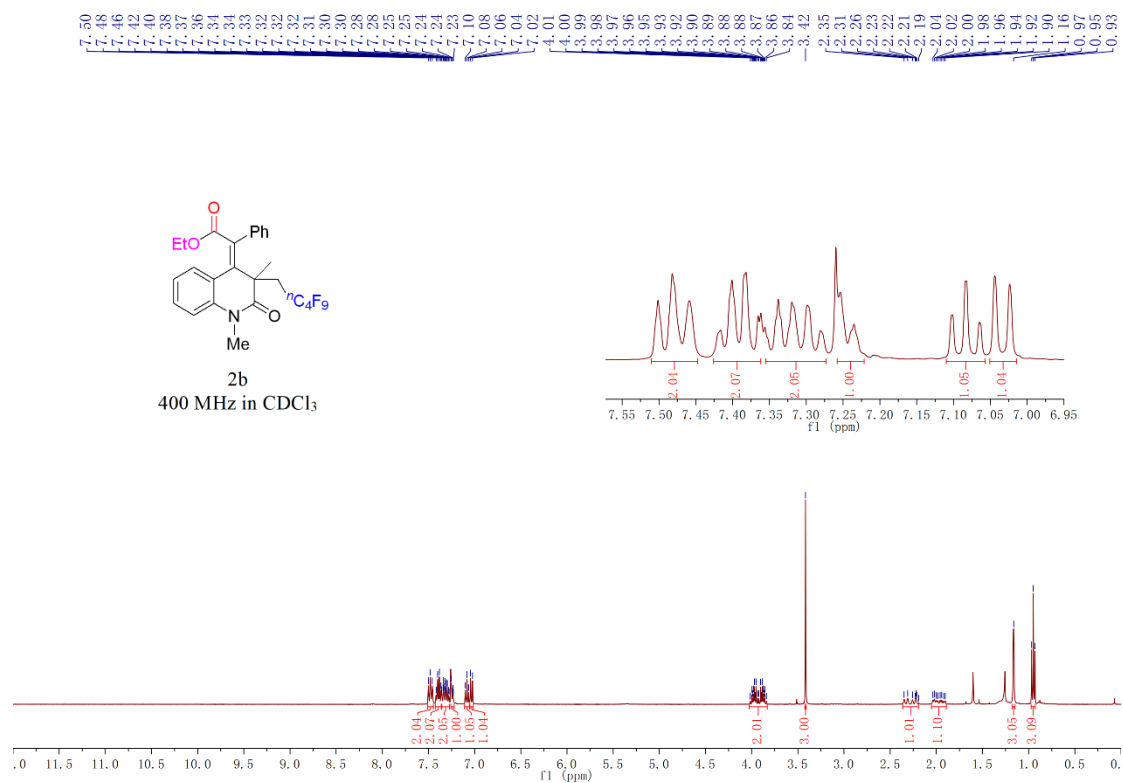
7. References

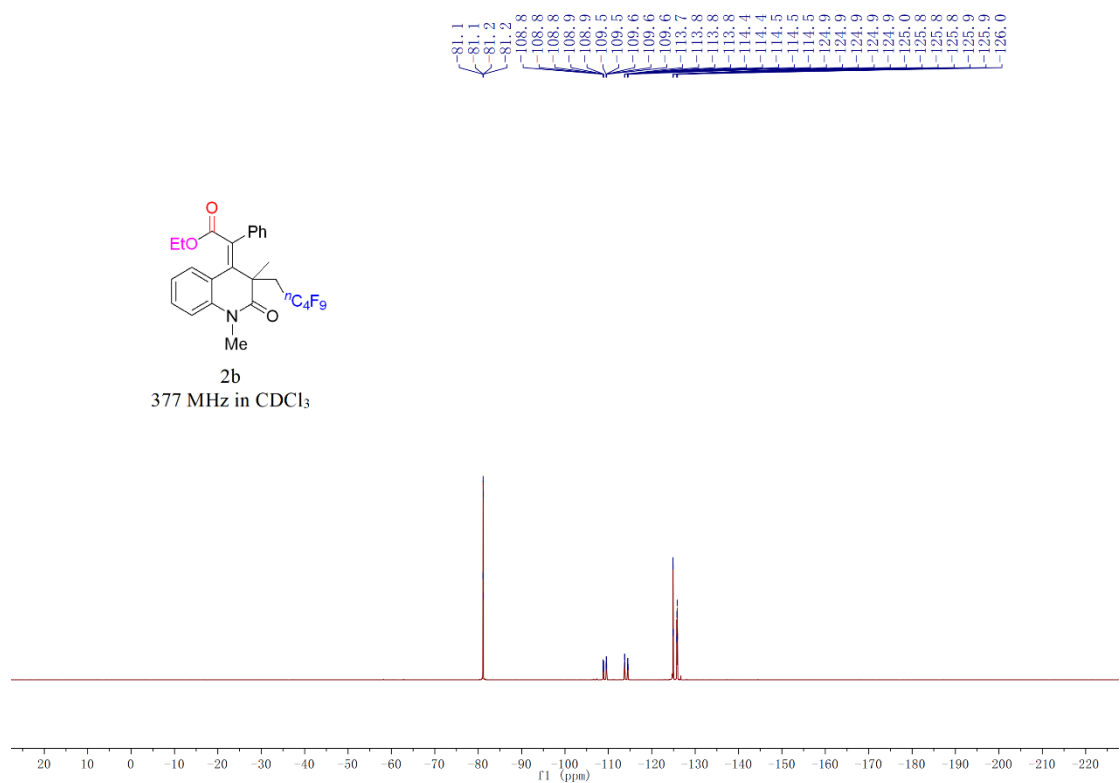
1. Jiang, L.-B.; Qi, X.; Wu, X.-F. Benzene-1,3,5-triyl triformate (TFBen): A convenient, efficient, and non-reacting CO source in carbonylation reactions. *Tetrahedron Lett.* **2016**, *57*, 3368-3370.
2. Li, Q.; Cai, Y.; Hu, Y.; Jin, H.; Chen, F.; Liu, Y.; Zhou, B. Nickel-catalyzed cyclization of 1,7-enynes for the selective synthesis of dihydrocyclobuta[*c*]quinolin-3-ones and benzo[*b*]azocin-2-ones. *Chem. Commun.* **2021**, *57*, 11657-11660.

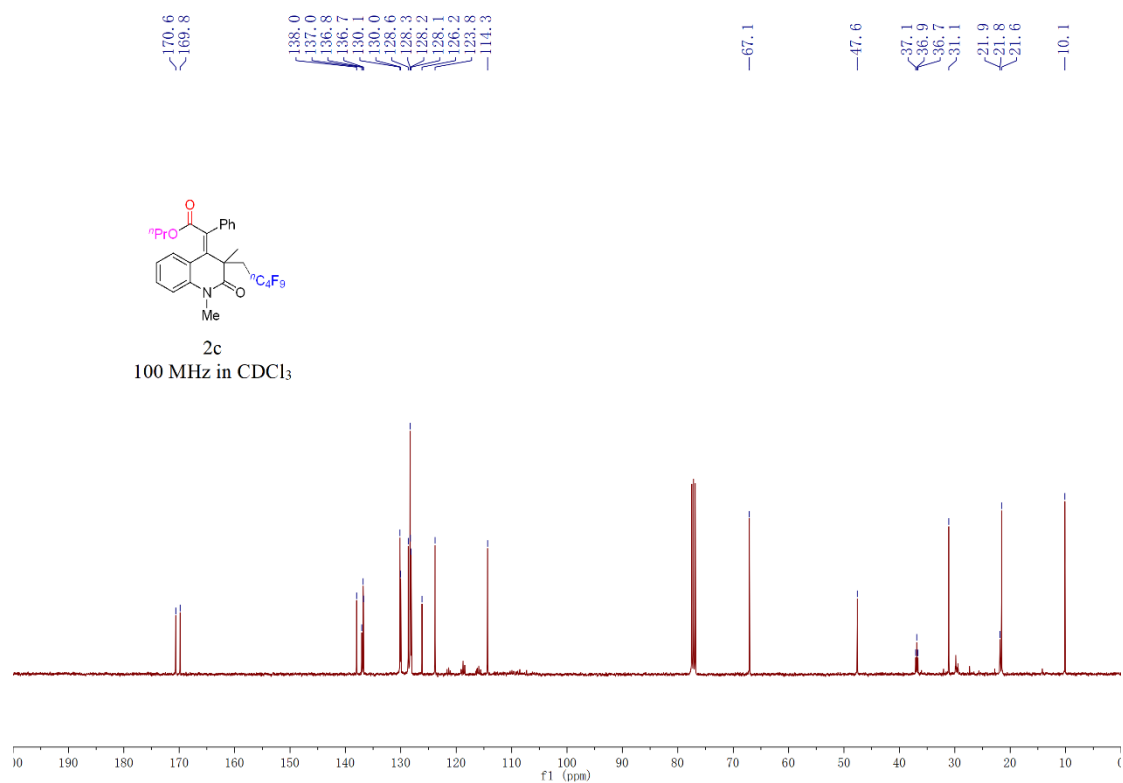
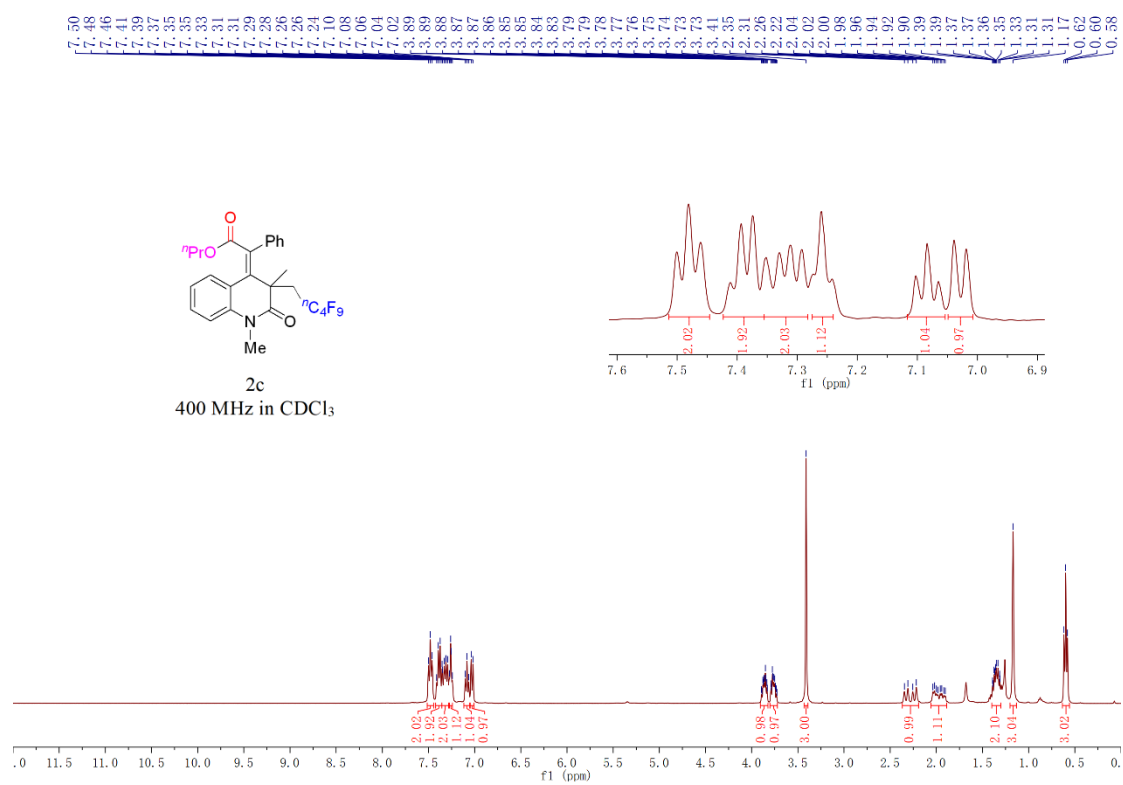
8. ^1H , ^{13}C , ^{19}F NMR spectra of products (2a-m, 3a-o)

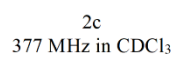


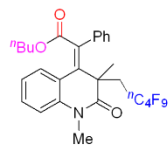
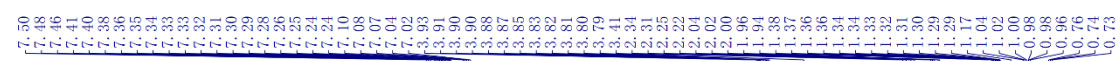




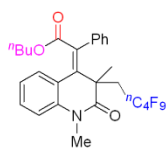
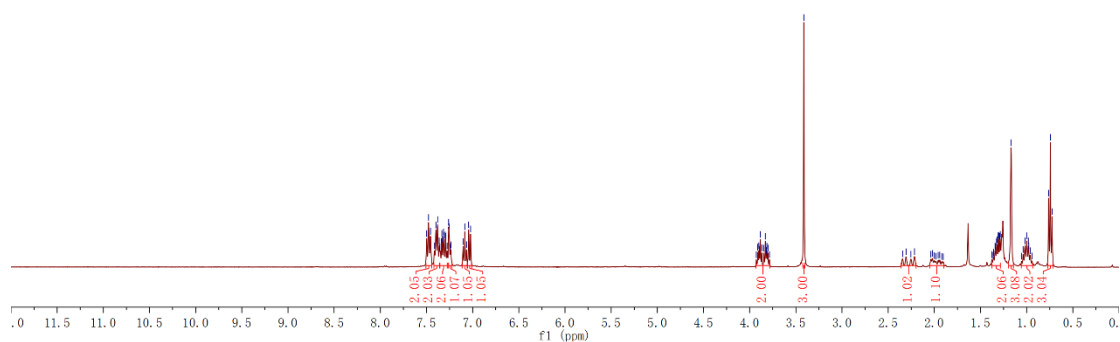
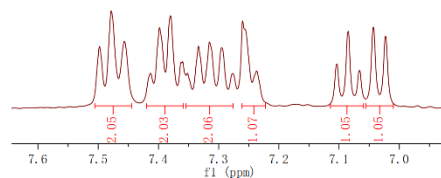




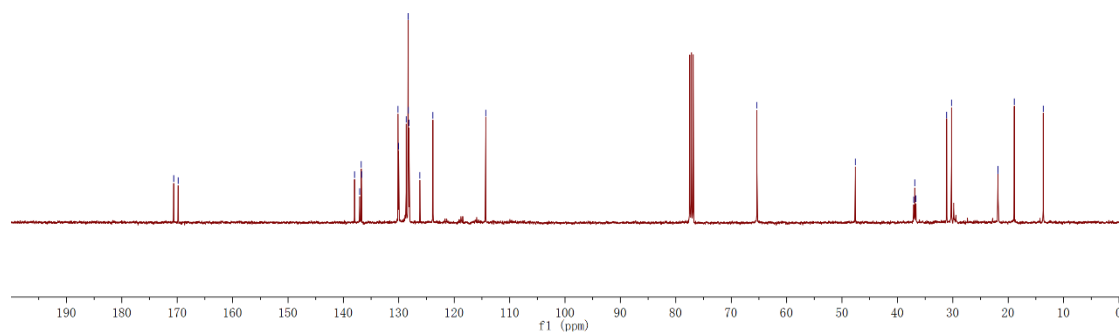


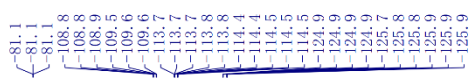
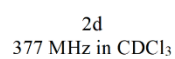


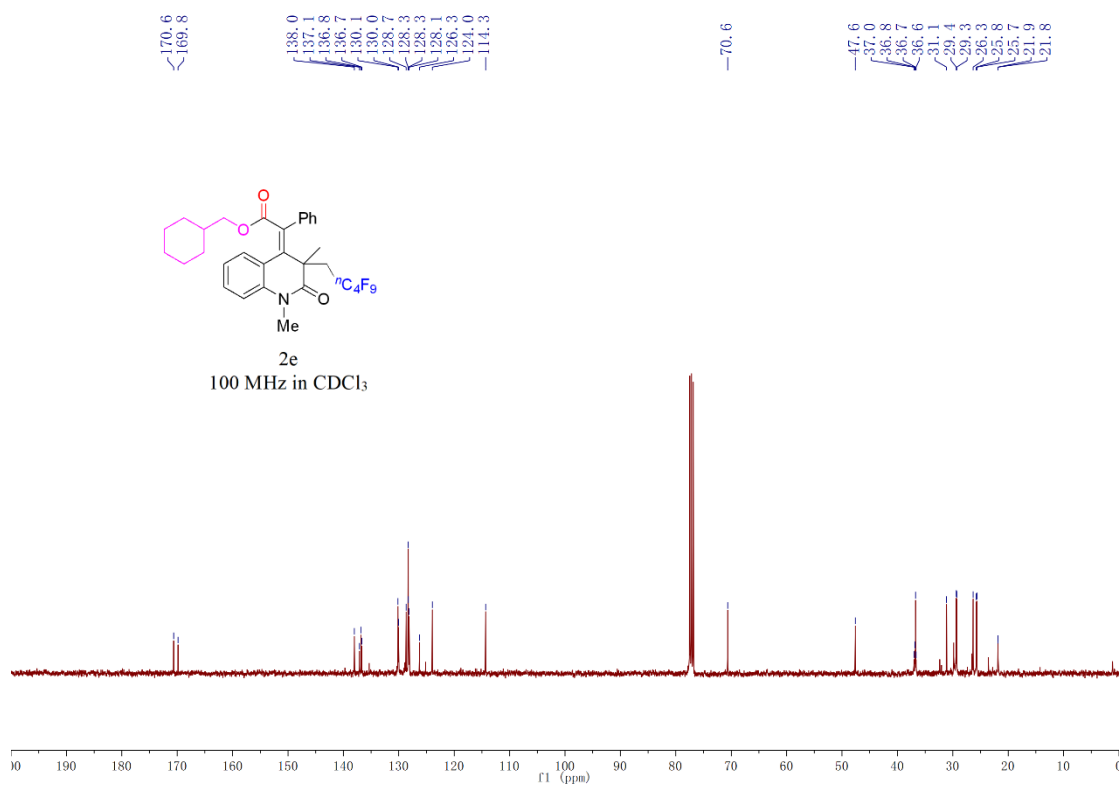
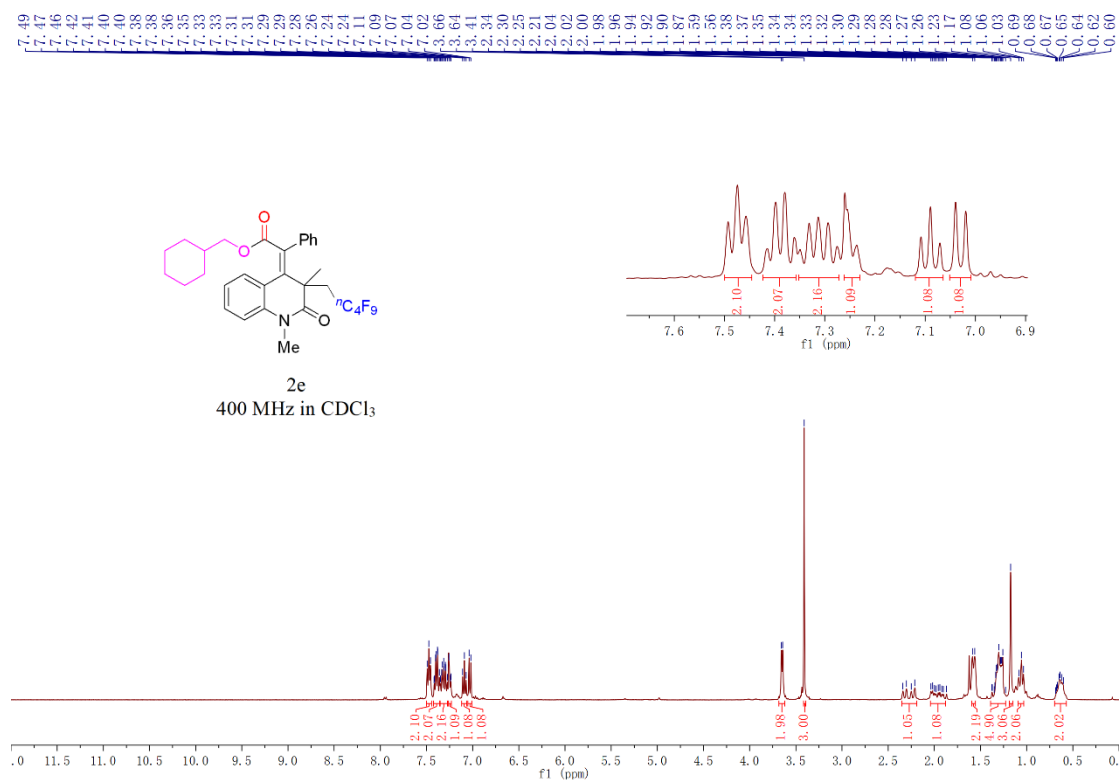
2d
400 MHz in CDCl₃

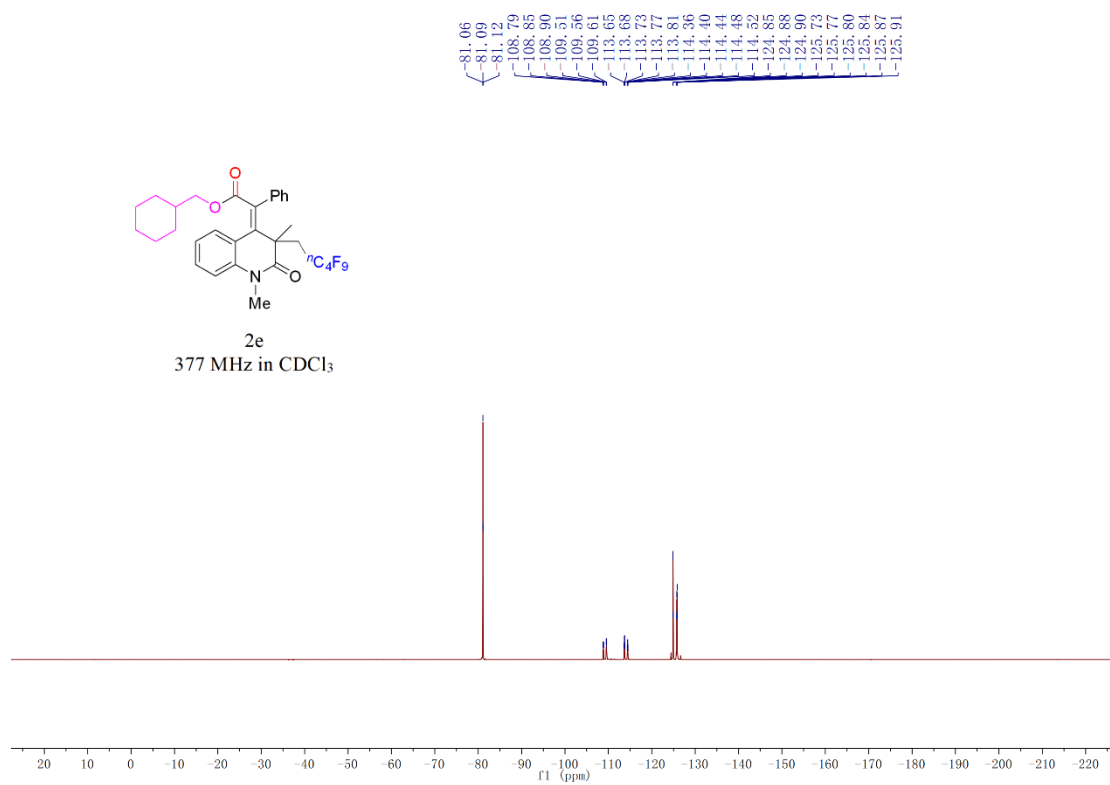


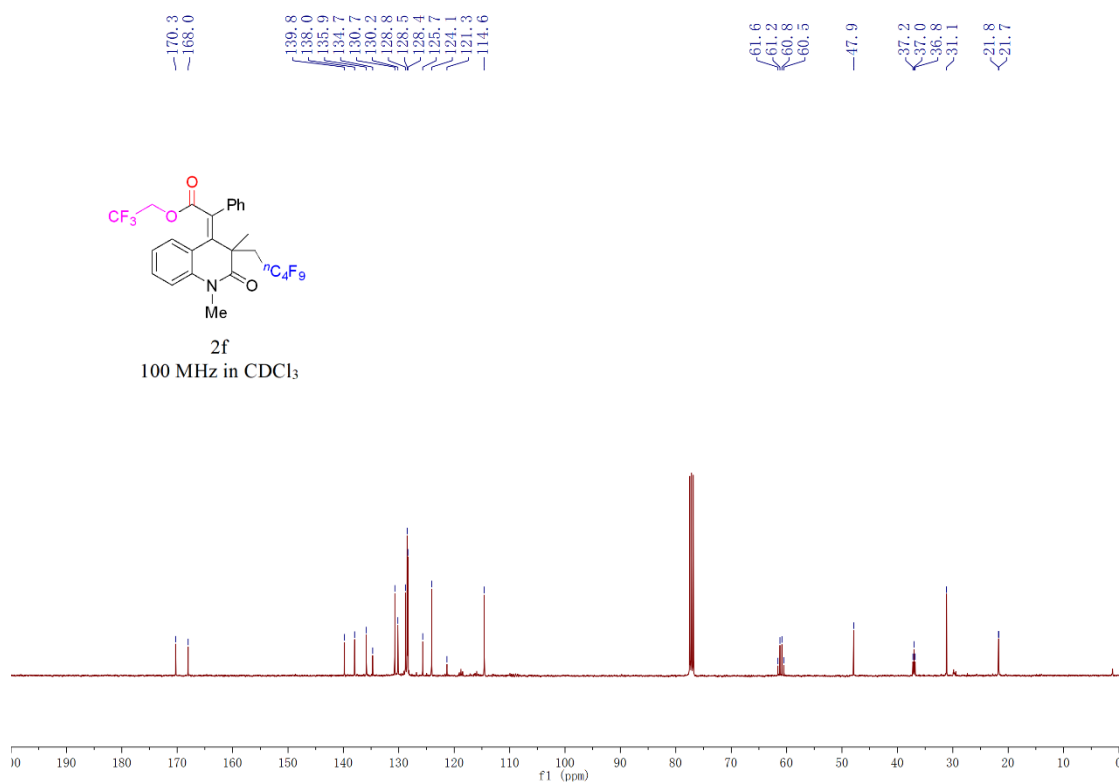
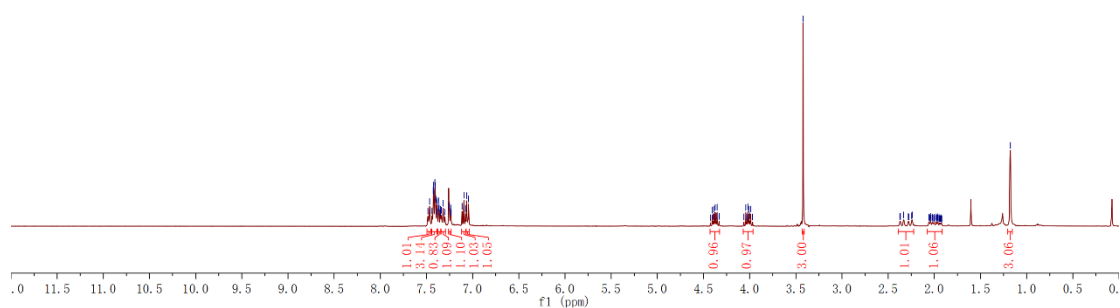
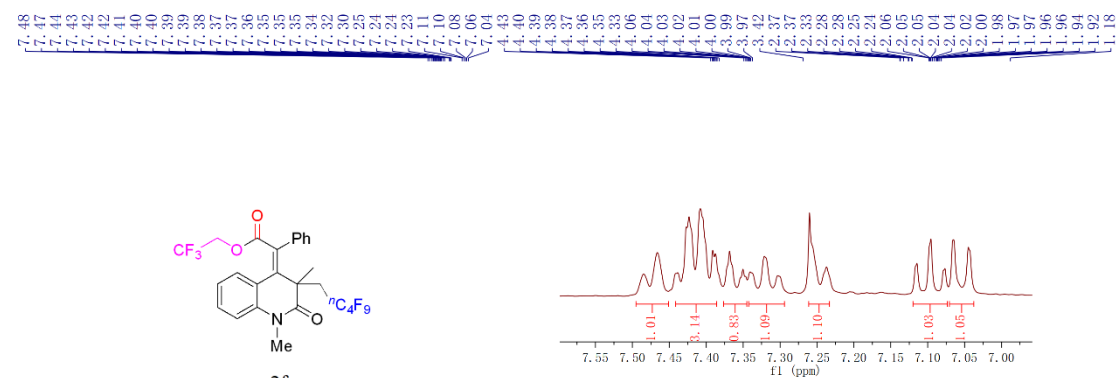
2d
100 MHz in CDCl₃





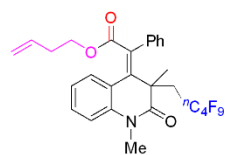




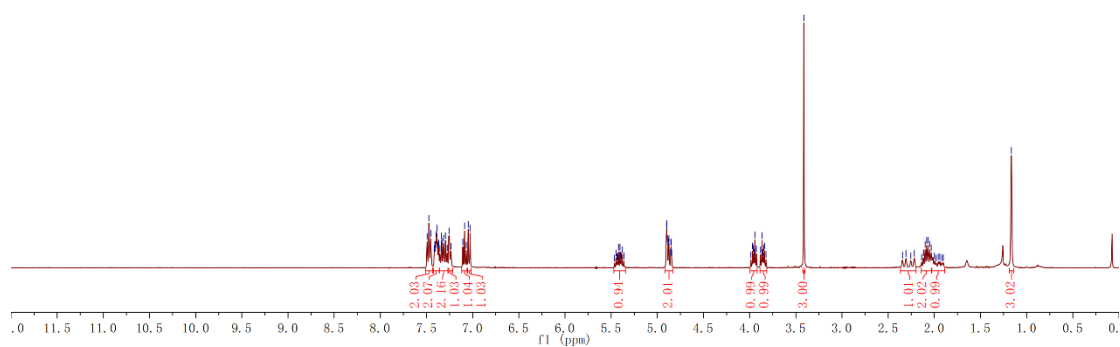
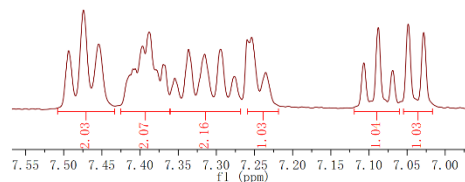




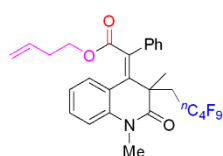
7.49
7.47
7.45
7.42
7.41
7.40
7.39
7.38
7.37
7.35
7.34
7.33
7.32
7.29
7.25
7.24
7.21
7.07
7.05
5.45
5.43
5.41
5.40
5.39
5.38
5.36
4.90
4.89
4.88
4.87
4.86
4.85
4.85
3.99
3.97
3.96
3.95
3.94
3.93
3.88
3.87
3.86
3.85
3.84
3.82
3.41
2.35
2.31
2.25
2.22
2.12
2.10
2.08
2.07
2.05
2.03
2.00
1.94
1.17



2g
400 MHz in CDCl_3



170.6
169.7
138.0
137.0
136.8
136.7
133.7
130.2
130.0
128.6
128.4
128.3
128.1
126.1
123.8
117.1
114.4



2g
100 MHz in CDCl_3

