

Supporting Information

Photoredox-catalyzed 2,2,2-trifluoroethylation and 2,2-difluoroethylation of alkenes with concomitant introduction of a quinoxalin-2(1*H*)-one moiety

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1. General information

¹H NMR (TMS as the internal standard) were recorded on a Bruker AM 400 or 600 spectrometer, ¹³C NMR and ¹⁹F NMR (CFCl₃ as outside standard and low field is positive) spectra were recorded on a Bruker AM 400 or 600 spectrometer. For the determination of ¹⁹F NMR yield, PhCF₃ was used as an internal standard and the relaxation delay (d1) was set to 5 s. Chemical shifts (δ) were reported in per million (ppm), and coupling constants (J) were in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High resolution mass spectra (HRMS) were obtained on a GC-TOF mass spectrometer.

Materials: Unless otherwise noted, all reagents were obtained commercially and used without further purification. Substrates were purchased from commercial sources or prepared according to literature procedures. Reactions were performed using glassware that was flame-dried under vacuum.

2. Preparation of Substrates

Substrates **1a** (*CAS*: 100-42-5), **1b** (*CAS*: 611-15-4), **1c** (*CAS*: 1746-23-2), **1d** (*CAS*: 637-69-4), **1e** (*CAS*: 2626-16-2), **1f** (*CAS*: 405-99-2), **1g** (*CAS*: 2039-82-9), **1h** (*CAS*: 2039-86-3), **1i** (*CAS*: 2234-20-0), **1l** (*CAS*: 768-56-9) and **5** (*CAS*: 3195-24-2) were obtained commercially and used without further purification.

Substrates **1j** were prepared according to the reported literature.¹

Substrates **1k** were prepared according to the reported literature.²

Substrates **1m** were prepared according to the reported literature.³

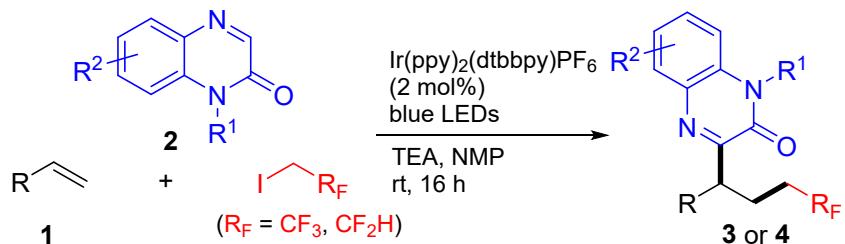
Substrates **2a**, **2c**, **2e** - **2n** were prepared according to the reported literature.⁴

Substrates **2q**, **2r** were prepared according to the reported literature.⁵

Substrates **2b** were prepared according to the reported literature.⁶

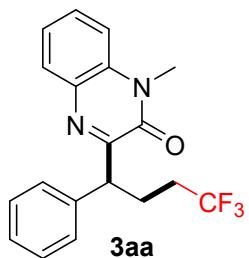
Substrates **2d** were prepared according to the reported literature.⁷

3. General procedure for the three-component coupling reaction of alkenes, quinoxalin-2(1*H*)-ones, and ICH₂CF₃/ICH₂CF₂H



To a sealed tube equipped with a stir bar were added quinoxalin-2(1*H*)-ones **2** (0.2 mmol, 1.0 equiv), Ir(ppy)₂(dtbbpy)PF₆ (3.7 mg, 0.004 mmol, 2 mol %). The tube was evacuated and backfilled with pure N₂ for three times. Afterwards, NMP (0.5 mL), alkenes **1** (2.5 equiv, 0.5 mmol), ICH₂CF₃/ICH₂CF₂H (2.0 equiv, 0.4 mmol) and TEA (3.0 equiv, 0.6 mmol) were added by syringe under N₂ atmosphere. The tightly sealed tube was then irradiated with a 20 W blue LEDs (the distance between the tube and the light source was about 7 cm) and simultaneously cooled by a fan to keep the reaction temperature at 25 °C. After 16 hours, the mixture was transferred into a 125 mL separating funnel which contained 20 mL H₂O. The mixture was extracted with DCM (20 mL each) for three times and the combined organic layer was washed with brine (20 mL) once and dried by Na₂SO₄. After filtration, the filtrate was concentrated under reduced pressure to give the crude product, which was purified by flash chromatography on silica gel (PE/EtOAc = 10: 1) to give the product **3** or **4**.

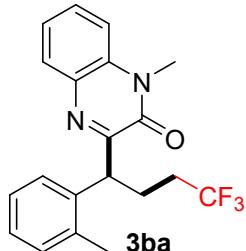
1-Methyl-3-(4,4,4-trifluoro-1-phenylbutyl)quinoxalin-2(1*H*)-one (3aa**)**



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3aa** (49.1 mg, 71%) as a yellow solid. Mp 125–127 °C; **1H NMR** (400 MHz, CDCl₃) δ 7.88 – 7.76 (m, 1H), 7.59 – 6.95 (m, 8H), 4.59 (t, *J* = 7.8 Hz, 1H), 3.48 (s, 3H), 2.55 – 2.18 (m, 2H), 2.14 – 1.77 (m, 2H); **19F NMR** (376 MHz, CDCl₃) δ -66.07 (t, *J* = 10.9 Hz, 3F); **13C NMR** (101 MHz, CDCl₃) δ 158.7, 153.3, 139.0, 131.9, 131.5, 129.1, 129.0, 127.6, 127.5, 126.2 (q, *J* = 277.3 Hz), 126.1, 122.5, 112.5, 45.2, 31.0 (q, *J* = 28.6 Hz), 28.0, 25.0 (q, *J* = 2.9 Hz); **IR** (thin film) ν 2944, 1648,

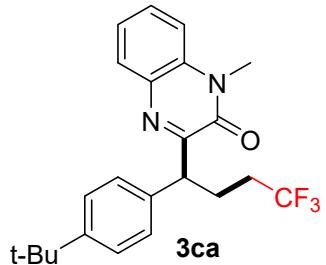
1602, 1252, 1132, 1104, 1018, 962, 763, 744, 515 cm⁻¹; **MS** (ESI): *m/z* 347.1 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₁₉H₁₈F₃N₂O [M+H]⁺: 347.1366; Found: 347.1374.

1-Methyl-3-(4,4,4-trifluoro-1-(o-tolyl)butyl)quinoxalin-2(1*H*)-one (3ba)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3ba** (33.1 mg, 46%) as a white solid. Mp 114–116 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.89 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.53 – 7.41 (m, 1H), 7.30 (*t*, *J* = 7.6 Hz, 1H), 7.22 – 7.16 (m, 1H), 7.14 – 7.05 (m, 2H), 7.04 – 6.91 (m, 2H), 4.83 (*t*, *J* = 7.3 Hz, 1H), 3.53 (s, 3H), 2.57 (s, 3H), 2.52 – 2.38 (m, 1H), 2.17 – 2.13 (m, 2H), 1.98 – 1.94 (m, 1H); **¹⁹F NMR** (377 MHz, CDCl₃) δ -66.14 (*t*, *J* = 10.5 Hz, 3F); **¹³C NMR** (101 MHz, CDCl₃) δ 160.1, 154.5, 138.9, 137.0, 133.0, 132.5, 130.8, 130.3, 130.1, 127.3 (*q*, *J* = 277.3 Hz), 126.8 (*d*, *J* = 12.1 Hz), 126.1, 123.6, 113.6, 41.6, 31.9 (*q*, *J* = 28.5 Hz), 29.7, 29.1, 26.4 (*d*, *J* = 3.1 Hz), 19.9; **IR** (thin film) ν 2920, 1650, 1597, 1471, 1295, 1256, 1132, 1085, 973, 749, 562 cm⁻¹; **MS** (ESI): *m/z* 361.2 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₂₀H₂₀F₃N₂O [M+H]⁺: 361.1522; Found: 361.1529.

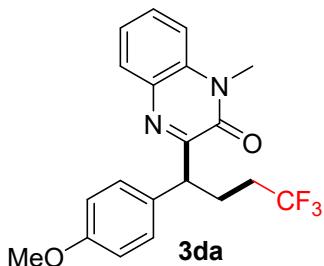
3-(1-(4-(*Tert*-butyl)phenyl)-4,4,4-trifluorobutyl)-1-methylquinoxalin-2(1*H*)-one (3ca)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3ca** (61.1 mg, 76%) as a white powder. Mp 109–111 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.86 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.34 – 7.08 (m, 6H), 4.59 (*t*, *J* = 7.8 Hz, 1H), 3.54 (s, 3H), 2.50 – 2.18 (m, 2H), 2.13 – 1.86 (m, 2H), 1.19 (s, 9H); **¹⁹F NMR** (376 MHz, CDCl₃) δ -66.11 (*t*, *J* = 11.0 Hz, 3F); **¹³C**

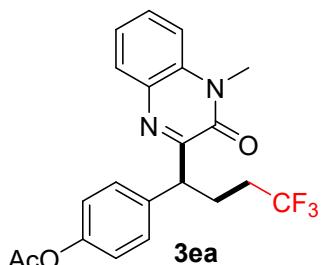
NMR (101 MHz, CDCl₃) δ 158.9, 153.4, 148.8, 135.9, 132.0, 131.6, 129.2, 129.0, 127.1, 126.3 (q, *J* = 277.3 Hz), 124.5, 122.5, 112.5, 44.6, 33.4, 31.1 (q, *J* = 28.5 Hz), 30.3, 28.1, 25.1 (q, *J* = 2.7 Hz); **IR** (thin film) ν 2963, 1653, 1603, 1526, 1256, 1099, 1019, 980, 795, 757, 582, 459 cm⁻¹; **MS** (ESI): *m/z* 403.2 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₂₃H₂₆F₃N₂O [M+H]⁺: 403.1992; Found: 403.1988.

1-Methyl-3-(4,4,4-trifluoro-1-(4-methoxyphenyl)butyl)quinoxalin-2(1*H*)-one (3da)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3da** (75.3 mg, 77%) as a brown liquid. **1H NMR** (400 MHz, CDCl₃) δ 7.82 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.47 – 7.32 (m, 1H), 7.31 – 7.18 (m, 3H), 7.16 – 7.07 (m, 1H), 6.82 – 6.67 (m, 2H), 4.53 (t, *J* = 7.8 Hz, 1H), 3.63 (s, 3H), 3.49 (s, 3H), 2.45 – 2.18 (m, 2H), 2.14 – 1.83 (m, 2H); **19F NMR** (377 MHz, CDCl₃) δ -66.03 (t, *J* = 10.9 Hz, 3F); **13C NMR** (101 MHz, CDCl₃) δ 158.9, 157.6, 153.3, 132.0, 131.5, 130.9, 129.1, 128.9, 128.5, 126.3 (q, *J* = 276.5 Hz), 122.5, 113.0, 112.5, 54.1, 44.3, 31.0 (q, *J* = 28.4 Hz), 28.0, 25.0 (t, *J* = 2.9 Hz); **IR** (thin film) ν 2940, 1651, 1603, 1509, 1247, 1134, 1034, 981, 833, 752, 559 cm⁻¹; **MS** (ESI): *m/z* 377.1 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₂₀H₂₀F₃N₂O₂ [M+H]⁺: 377.1471; Found: 377.1471.

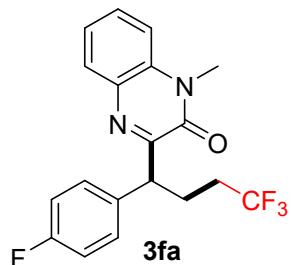
4-(4,4,4-Trifluoro-1-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butyl)phenyl acetate (3ea)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3ea** (47.5 mg, 59%) as a yellow solid. Mp 187-189 °C; **1H NMR** (400 MHz, CDCl₃) δ 7.83 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.62 – 7.32 (m, 3H), 7.30 – 7.10 (m, 2H), 6.99 – 6.77 (m, 2H), 4.62 (t, *J* = 7.9 Hz, 1H), 3.53 (s, 3H), 2.46 – 2.43 (m, 1H),

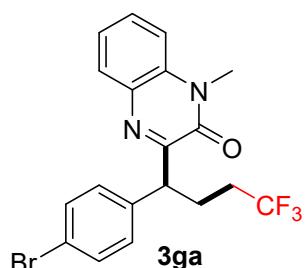
2.29 – 2.26 (m, 1H), 2.16 (s, 3H), 2.11 – 1.88 (m, 2H); **¹⁹F NMR** (377 MHz, CDCl₃) δ -66.07 (t, *J* = 10.9 Hz, 3F); **¹³C NMR** (101 MHz, CDCl₃) δ 168.4, 158.4, 153.3, 148.7, 136.5, 132.0, 131.5, 129.1, 128.5, 126.2 (q, *J* = 276.3 Hz), 122.6, 120.6, 112.6, 44.4, 31.0 (q, *J* = 28.6 Hz), 28.1, 25.0 (d, *J* = 2.9 Hz), 20.1; **IR** (thin film) ν 2962, 1769, 1645, 1602, 1471, 1258, 1188, 1016, 981, 795, 752, 570 cm⁻¹; **MS** (ESI): *m/z* 405.1 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₂₁H₂₀F₃N₂O₃ [M+H]⁺: 405.1421; Found: 405.1416.

1-Methyl-3-(4,4,4-trifluoro-1-(4-fluorophenyl)butyl)quinoxalin-2(1*H*)-one (3fa)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3fa** (51.6 mg, 71%) as a brown liquid. **¹H NMR** (400 MHz, CDCl₃) δ 7.83 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.50 – 7.34 (m, 1H), 7.35 – 7.22 (m, 3H), 7.21 – 7.10 (m, 1H), 6.87 (t, *J* = 8.5 Hz, 2H), 4.58 (t, *J* = 7.8 Hz, 1H), 3.52 (s, 3H), 2.51 – 2.33 (m, 1H), 2.33 – 2.15 (m, 1H), 2.06 – 1.90 (m, 2H); **¹⁹F NMR** (377 MHz, CDCl₃) δ -66.08 (t, *J* = 10.8 Hz, 3F), -115.53 (m, 1F); **¹³C NMR** (101 MHz, CDCl₃) δ 160.9 (d, *J* = 245.5 Hz), 158.5, 153.3, 134.7 (d, *J* = 3.2 Hz), 132.0, 131.5, 129.2, 129.0 (d, *J* = 8.0 Hz), 126.2 (q, *J* = 276.3 Hz), 122.7, 114.4 (d, *J* = 21.3 Hz), 112.6, 44.4, 30.9 (q, *J* = 28.6 Hz), 28.1, 25.1 (d, *J* = 3.1 Hz); **IR** (thin film) ν 2946, 1650, 1601, 1505, 1258, 1219, 1131, 979, 843, 749, 559 cm⁻¹; **MS** (ESI): *m/z* 387.1 [M+Na]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₁₉H₁₆F₄N₂ONa [M+ Na]⁺: 387.1091; Found: 387.1090.

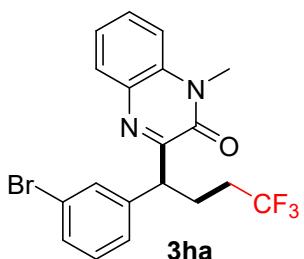
3-(1-(4-Bromophenyl)-4,4,4-trifluorobutyl)-1-methylquinoxalin-2(1*H*)-one (3ga)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3ga** (49.1 mg, 71%) as a brown liquid. **¹H NMR** (400 MHz, CDCl₃) δ

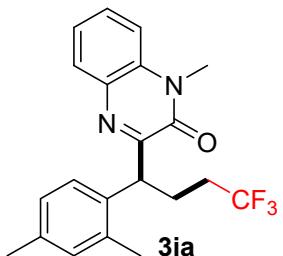
7.84 (d, $J = 7.9$ Hz, 1H), 7.46 (t, $J = 7.9$ Hz, 1H), 7.33 – 7.18 (m, 6H), 4.56 (t, $J = 7.7$ Hz, 1H), 3.54 (s, 3H), 2.48 – 2.39 (m, 1H), 2.29 – 2.19 (m, 1H), 2.12 – 1.87 (m, 2H); **^{19}F NMR** (376 MHz, CDCl_3) δ -66.11 (t, $J = 10.6$ Hz, 3F); **^{13}C NMR** (101 MHz, CDCl_3) δ 158.2, 153.2, 138.1, 132.0, 131.5, 130.7, 129.3, 129.2, 126.1 (q, $J = 276.3$ Hz), 122.7, 120.1, 112.6, 44.6, 30.9 (q, $J = 28.7$ Hz), 28.1, 24.9 (d, $J = 3.1$ Hz); **IR** (thin film) ν 2925, 1652, 1601, 1472, 1255, 1135, 1010, 981, 753, 556 cm^{-1} ; **MS** (ESI): m/z 447.0 [M+Na] $^+$; **HRMS** (ESI-TOF): m/z Calculated for $\text{C}_{19}\text{H}_{16}\text{BrF}_3\text{N}_2\text{O}\text{Na}$ [M+Na] $^+$: 447.0290; Found: 447.0302.

3-(1-(3-Bromophenyl)-4,4,4-trifluorobutyl)-1-methylquinoxalin-2(1*H*)-one (**3ha**)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3ha** (45.8 mg, 54%) as a white solid. Mp 89-91 °C; **^1H NMR** (400 MHz, CDCl_3) δ 7.87 (dd, $J = 8.0, 1.4$ Hz, 1H), 7.58 – 7.41 (m, 2H), 7.35 – 7.15 (m, 4H), 7.09 (t, $J = 7.8$ Hz, 1H), 4.57 (t, $J = 7.8$ Hz, 1H), 3.56 (s, 3H), 2.52 – 2.37 (m, 1H), 2.29 – 2.19 (m, 1H), 2.13 – 1.91 (m, 2H); **^{19}F NMR** (377 MHz, CDCl_3) δ -66.12 (t, $J = 10.8$ Hz, 3F); **^{13}C NMR** (101 MHz, CDCl_3) δ 158.0, 153.2, 141.5, 132.0, 131.5, 130.2, 129.3, 129.2, 126.4, 126.1 (q, $J = 277.3$ Hz), 122.7, 121.7, 112.6, 44.8, 31.0 (q, $J = 28.7$ Hz), 28.2, 25.1 (d, $J = 3.0$ Hz); **IR** (thin film) ν 2951, 1650, 1599, 1470, 1293, 1135, 984, 787, 749, 560 cm^{-1} ; **MS** (ESI): m/z 447.0 [M+Na] $^+$; **HRMS** (ESI-TOF): m/z Calculated for $\text{C}_{19}\text{H}_{16}\text{BrF}_3\text{N}_2\text{O}\text{Na}$ [M+Na] $^+$: 447.0290; Found: 447.0296.

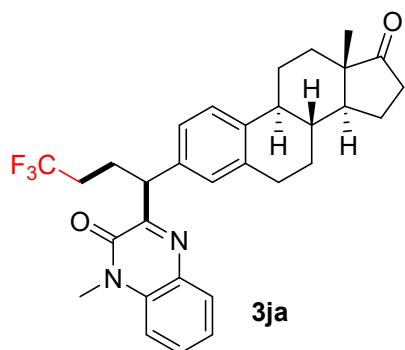
3-(1-(2,4-Dimethylphenyl)-4,4,4-trifluorobutyl)-1-methylquinoxalin-2(1*H*)-one (**3ia**)



The product mixture was purified by silica gel column chromatography (PE/EtOAc =

10:1) to afford **3ia** (35.9 mg, 48%) as a white solid. Mp 131–133 °C; **1H NMR** (400 MHz, CDCl₃) δ 7.88 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.50 – 7.42 (m, 1H), 7.35 – 7.25 (m, 1H), 7.23 – 7.14 (m, 1H), 6.99 – 6.90 (m, 2H), 6.78 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.78 (t, *J* = 7.3 Hz, 1H), 3.53 (s, 3H), 2.53 (s, 3H), 2.47 – 2.37 (m, 1H), 2.20 – 2.09 (m, 5H), 1.99 – 1.91 (m, 1H); **19F NMR** (377 MHz, CDCl₃) δ -66.14 (t, *J* = 10.5 Hz, 3F); **13C NMR** (101 MHz, CDCl₃) δ 159.2, 153.4, 135.7, 135.3, 134.7, 132.0, 131.5, 130.5, 129.2, 128.9, 126.3 (q, *J* = 277.3 Hz), 125.8, 125.7, 122.5, 112.5, 40.3, 30.9 (q, *J* = 28.4 Hz), 28.9, 25.3 (d, *J* = 2.9 Hz), 19.9, 18.8; **IR** (thin film) ν 2956, 1654, 1604, 1255, 1122, 1092, 1000, 966, 820, 753, 580 cm⁻¹; **MS** (ESI): *m/z* 375.2 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₂₁H₂₂F₃N₂O [M+H]⁺: 375.1679; Found: 375.1676.

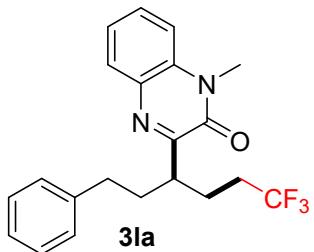
1-Methyl-3-(4,4,4-trifluoro-1-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)butyl)quinoxalin-2(1*H*)-one (3ja)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3ja** (61.0 mg, 60%) as a white solid. Mp 119–121 °C; **1H NMR** (400 MHz, CDCl₃) δ 7.87 (dt, *J* = 8.1, 1.6 Hz, 1H), 7.47 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.33 – 7.26 (m, 1H), 7.20 (d, *J* = 9.1 Hz, 1H), 7.15 – 7.11 (m, 2H), 7.08 – 7.04 (m, 1H), 4.54 (td, *J* = 7.8, 1.7 Hz, 1H), 3.55 (s, 3H), 2.91 – 2.65 (m, 2H), 2.50 – 2.36 (m, 2H), 2.34 – 2.20 (m, 2H), 2.20 – 1.81 (m, 6H), 1.59 – 1.26 (m, 7H), 0.80 (d, *J* = 1.4 Hz, 3H); **19F NMR** (377 MHz, CDCl₃) δ -66.10 (td, *J* = 10.6, 2.3 Hz, 3F); **13C NMR** (101 MHz, CDCl₃) δ 158.8 (d, *J* = 2.2 Hz), 153.4, 137.5, 136.5 (d, *J* = 1.7 Hz), 135.7 (d, *J* = 1.6 Hz), 132.0, 131.6, 129.2, 129.0, 128.0, 126.3 (d, *J* = 276.3 Hz), 124.8, 124.7, 124.6, 122.6, 112.5, 49.5, 46.9, 44.8 (d, *J* = 3.3 Hz), 43.3, 37.0, 34.8, 31.1 (q, *J* = 28.6 Hz), 30.6, 28.4, 28.1, 25.5, 24.6 (d, *J* = 4.3 Hz), 20.6, 12.8; **IR** (thin film) ν 2924, 1737, 1655, 1602, 1472, 1256, 1133, 1006, 755, 582 cm⁻¹; **MS** (ESI): *m/z* 523.3 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₃₁H₃₄F₃N₂O₂ [M+H]⁺: 523.2567; Found: 523.2567.

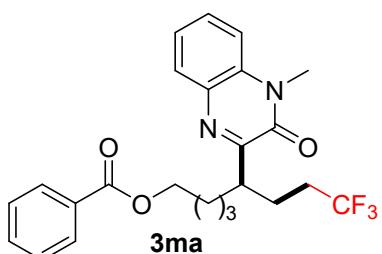
523.2563.

1-Methyl-3-(6,6,6-trifluoro-1-phenylhexan-3-yl)quinoxalin-2(1H)-one (3la)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3la** (32.2 mg, 43%) as a white solid. Mp 75–77 °C; **1H NMR** (400 MHz, CDCl₃) δ 7.78 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.30 – 7.26 (m, 1H), 7.22 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.15 – 7.10 (m, 2H), 7.08 – 6.99 (m, 3H), 3.61 (s, 3H), 3.53 (tt, *J* = 8.2, 5.3 Hz, 1H), 2.64 – 2.48 (m, 2H), 2.26 – 2.08 (m, 2H), 2.06 – 1.96 (m, 2H), 1.94 – 1.82 (m, 2H); **19F NMR** (376 MHz, CDCl₃) δ -66.44 (t, *J* = 10.6 Hz, 3F); **13C NMR** (101 MHz, CDCl₃) δ 160.6, 153.7, 140.8, 131.9, 131.5, 129.0, 128.9, 127.4, 127.2, 126.2 (q, *J* = 277.1 Hz), 124.7, 122.6, 112.5, 39.2, 33.8, 32.6, 30.6 (q, *J* = 28.5 Hz), 28.2, 23.9 (t, *J* = 3.0 Hz); **IR** (thin film) ν 2933, 1645, 1593, 1258, 1134, 1034, 964, 751, 699, 458 cm⁻¹; **MS** (ESI): *m/z* 375 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₂₁H₂₂F₃N₂O [M+H]⁺: 375.1679; Found: 375.1679.

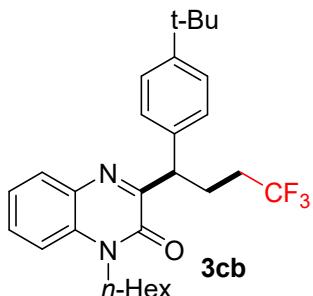
8,8,8-Trifluoro-5-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)octyl benzoate (3ma)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3ma** (29.4 mg, 33%) as a brown liquid. **1H NMR** (400 MHz, CDCl₃) δ 7.89 (d, *J* = 7.7 Hz, 2H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.52 – 7.39 (m, 2H), 7.37 – 7.11 (m, 4H), 4.32 – 4.07 (m, 2H), 3.61 (s, 3H), 3.50 (t, *J* = 7.3 Hz, 1H), 2.15 – 1.94 (m, 4H), 1.95 – 1.81 (m, 2H), 1.71 (q, *J* = 7.1 Hz, 1H), 1.66 – 1.55 (m, 3H), 1.44 – 1.34 (m, 3H); **19F NMR** (377 MHz, CDCl₃) δ -66.42 (t, *J* = 10.5 Hz, 3F); **13C NMR** (101 MHz, CDCl₃) δ 166.6, 161.7, 154.8, 132.9, 132.8, 132.6, 130.4, 130.1, 130.0, 129.5, 128.3,

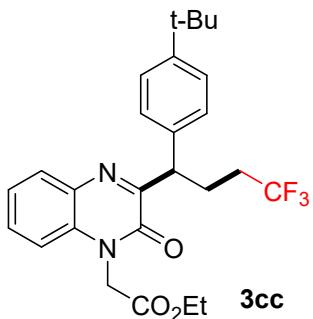
127.2 (q, $J = 277.3$ Hz), 123.7, 113.6, 64.7, 40.0, 32.8, 31.7 (q, $J = 28.5$ Hz), 29.2, 28.7, 24.7 (d, $J = 3.0$ Hz), 23.6; **IR** (thin film) ν 2946, 1716, 1650, 1602, 1472, 1272, 1116, 754, 711, 426 cm^{-1} ; **MS** (ESI): m/z 447.2 [M+H] $^+$; **HRMS** (ESI-TOF): m/z Calculated for C₂₄H₂₆F₃N₂O₃ [M+H] $^+$: 447.1890; Found: 447.1890.

3-(1-(4-(*Tert*-butyl)phenyl)-4,4,4-trifluorobutyl)-1-hexylquinoxalin-2(1*H*)-one (3cb)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3cb** (57.6 mg, 61%) as a white solid. Mp 139–141 °C; **¹H NMR** (400 MHz, CDCl₃) δ ppm 7.85 (d, $J = 7.7$ Hz, 1H), 7.42 (t, $J = 7.5$ Hz, 1H), 7.30 – 7.13 (m, 6H), 4.59 (t, $J = 7.8$ Hz, 1H), 4.20 – 4.10 (m, 1H), 4.03 – 3.93 (m, 1H), 2.47 – 2.38 (m, 1H), 2.35 – 2.23 (m, 1H), 2.15 – 1.87 (m, 2H), 1.64 – 1.56 (m, 2H), 1.29 (q, $J = 7.6$, 7.0 Hz, 6H), 1.18 (s, 9H), 0.79 (t, $J = 6.8$ Hz, 3H); **¹⁹F NMR** (376 MHz, CDCl₃) δ ppm -66.12 (t, $J = 10.9$ Hz, 3F); **¹³C NMR** (101 MHz, CDCl₃) δ ppm 159.0, 153.1, 148.7, 135.9, 131.9, 131.2, 129.4, 128.8, 127.1, 126.3 (q, $J = 277.3$ Hz), 124.5, 122.3, 112.5, 44.5, 41.5, 33.4, 31.1 (q, $J = 28.6$ Hz), 30.4, 30.3, 26.1, 25.6, 25.1 (d, $J = 2.9$ Hz), 21.5, 12.9; **IR** (thin film) ν 2960, 1651, 1602, 1308, 1257, 1099, 1002, 756, 587, 465 cm^{-1} ; **MS** (ESI): m/z 473.3 [M+H] $^+$; **HRMS** (ESI-TOF): m/z Calculated for C₂₈H₃₇F₃N₂O [M+H] $^+$: 473.2774; Found: 473.2774.

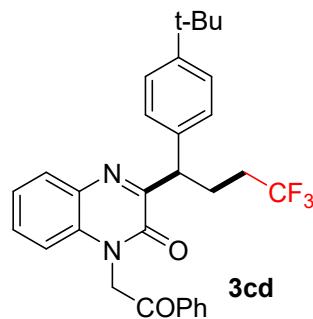
Ethyl 2-(3-(1-(4-(*tert*-butyl)phenyl)-4,4,4-trifluorobutyl)-2-oxoquinoxalin-1(2*H*)-yl)acetate (3cc)



The product mixture was purified by silica gel column chromatography (PE/EtOAc =

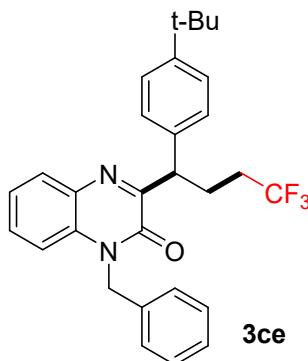
10:1) to afford **3cc** (68.3 mg, 72%) as a white powder. Mp 127–129 °C; **1H NMR** (400 MHz, CDCl₃) δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.30 – 7.15 (m, 5H), 6.94 (d, *J* = 8.3 Hz, 1H), 4.98 (d, *J* = 17.3 Hz, 1H), 4.72 (d, *J* = 17.3 Hz, 1H), 4.56 (t, *J* = 7.8 Hz, 1H), 4.17 – 4.02 (m, 2H), 2.46 – 2.38 (m, 1H), 2.35 – 2.25 (m, 1H), 2.13 – 1.88 (m, 2H), 1.18 (s, 9H), 1.12 (t, *J* = 7.1 Hz, 3H); **19F NMR** (377 MHz, CDCl₃) δ -66.08 (t, *J* = 10.9 Hz, 3F); **13C NMR** (101 MHz, CDCl₃) δ 166.0, 158.8, 152.9, 148.9, 135.6, 131.6, 131.1, 129.5, 129.1, 127.1, 126.3 (q, *J* = 277.3 Hz), 124.6, 122.9, 112.0, 61.0, 44.7, 42.6, 33.4, 31.0 (q, *J* = 28.7 Hz), 30.3, 25.0 (d, *J* = 3.0 Hz), 13.0; **IR** (thin film) ν 2964, 1755, 1657, 1258, 1202, 1097, 1019, 794, 757, 575 cm⁻¹; **MS** (ESI): *m/z* 497.2 [M+Na]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₂₆H₂₉F₃N₂O₃Na [M+Na]⁺: 497.2023; Found: 497.2021.

3-(1-(4-(*Tert*-butyl)phenyl)-4,4,4-trifluorobutyl)-1-(2-oxo-2-phenylethyl)quinoxalin-2(1*H*)-one (3cd)



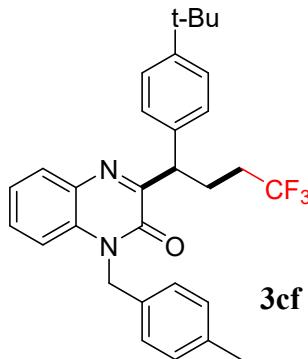
The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3cd** (51.6 mg, 51%) as a white solid. Mp 179–181 °C; **1H NMR** (400 MHz, CDCl₃) δ 7.90 – 7.86 (m, 3H), 7.57 – 7.47 (m, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.32 – 7.16 (m, 6H), 6.78 (dd, *J* = 8.2, 1.3 Hz, 1H), 5.65 (d, *J* = 17.6 Hz, 1H), 5.36 (d, *J* = 17.5 Hz, 1H), 4.55 (t, *J* = 7.8 Hz, 1H), 2.49 – 2.39 (m, 1H), 2.35 – 2.25 (m, 1H), 2.13 – 1.87 (m, 2H), 1.18 (s, 9H); **19F NMR** (376 MHz, CDCl₃) δ -66.03 (t, *J* = 10.9 Hz, 3F); **13C NMR** (101 MHz, CDCl₃) δ 190.1, 158.6, 153.1, 148.8, 135.7, 133.4, 132.2, 131.7, 131.4, 129.4, 129.0, 128.0, 127.1, 127.0, 126.3 (q, *J* = 277.3 Hz), 124.6, 122.7, 112.4, 47.6, 44.7, 33.4, 31.0 (q, *J* = 28.5 Hz), 30.3, 25.0 (d, *J* = 3.1 Hz); **IR** (thin film) ν 2966, 1705, 1656, 1600, 1297, 1220, 981, 842, 751, 583 cm⁻¹; **MS** (ESI): *m/z* 507.2 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₃₀H₃₀F₃N₂O₂ [M+H]⁺: 507.2254; Found: 507.2243.

1-Benzyl-3-(1-(4-(*tert*-butyl)phenyl)-4,4,4-trifluorobutyl)quinoxalin-2(1*H*)-one (3ce)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3ce** (51.6 mg, 54%) as a yellow solid. Mp 155–157 °C; **1H NMR** (400 MHz, CDCl₃) δ 7.85 (d, *J* = 7.7 Hz, 1H), 7.41 – 6.91 (m, 14H), 5.44 (d, *J* = 15.6 Hz, 1H), 5.17 (d, *J* = 15.6 Hz, 1H), 4.65 (t, *J* = 7.7 Hz, 1H), 2.51 – 2.25 (m, 2H), 2.18 – 1.88 (m, 2H), 1.19 (s, 9H); **19F NMR** (376 MHz, CDCl₃) δ -66.04 (t, *J* = 10.9 Hz, 3F); **13C NMR** (101 MHz, CDCl₃) δ 159.2, 153.4, 148.8, 135.8, 134.1, 131.8, 131.3, 129.3, 128.9, 127.8, 127.1, 126.6, 126.3 (q, *J* = 277.3 Hz), 125.8, 124.5, 122.6, 113.3, 44.9, 44.7, 33.4, 31.1 (q, *J* = 28.5 Hz), 30.3, 25.1 (d, *J* = 3.1 Hz); **IR** (thin film) ν 2967, 1650, 1602, 1452, 1256, 1132, 1003, 756, 697, 581 cm⁻¹; **MS** (ESI): *m/z* 479.2 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₂₉H₃₀F₃N₂O [M+H]⁺: 479.2305; Found: 479.2299.

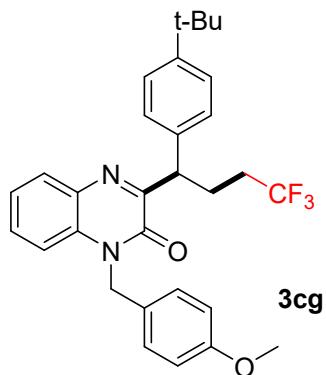
3-(1-(4-(*Tert*-butyl)phenyl)-4,4,4-trifluorobutyl)-1-(4-methylbenzyl)quinoxalin-2(1*H*)-one (3cf)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3cf** (56.1 mg, 57%) as a white solid. Mp 169–171°C; **1H NMR** (400 MHz, CDCl₃) δ 7.83 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.31 – 7.08 (m, 7H), 6.95 (s, 4H), 5.39 (d, *J* = 15.5 Hz, 1H), 5.10 (d, *J* = 15.5 Hz, 1H), 4.64 (t, *J* = 7.8 Hz, 1H), 2.49 – 2.24 (m, 2H), 2.16 (s, 3H), 2.11 – 1.88 (m, 2H), 1.18 (s, 9H); **19F NMR** (376 MHz, CDCl₃) δ -66.02 (t, *J* = 10.8 Hz, 3F); **13C NMR** (101 MHz, CDCl₃) δ 159.2, 153.4, 148.8, 136.3, 135.8, 131.8, 131.3, 131.2, 129.2, 128.9, 128.5, 127.1, 126.3 (q, *J* = 277.3 Hz),

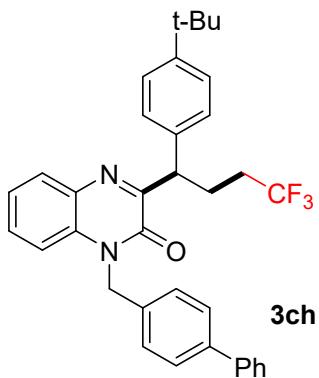
125.8, 124.5, 122.5, 113.3, 44.7, 44.6, 33.4, 31.1 (q, $J = 28.5$ Hz), 30.3, 25.1 (d, $J = 3.0$ Hz), 21.3; **IR** (thin film) ν 2961, 1651, 1602, 1257, 1169, 1099, 1005, 795, 757, 580 cm^{-1} ; **MS** (ESI): m/z 493.2 [M+H]⁺; **HRMS** (ESI-TOF): m/z Calculated for C₃₀H₃₂F₃N₂O [M+H]⁺: 493.2461; Found: 493.2449.

3-(1-(4-(*Tert*-butyl)phenyl)-4,4,4-trifluorobutyl)-1-(4-methoxybenzyl)quinoxalin-2(1*H*)-one (3cg)



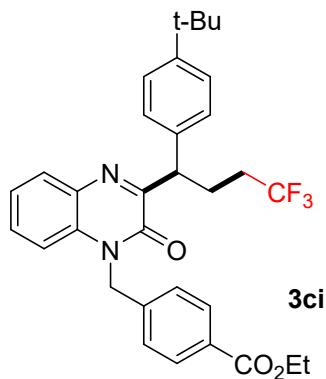
The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3cg** (52.9 mg, 52%) as a yellow solid. Mp 137-139 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.83 (dd, $J = 7.9, 1.6$ Hz, 1H), 7.31 – 7.09 (m, 7H), 7.00 (d, $J = 8.7$ Hz, 2H), 6.68 (d, $J = 8.7$ Hz, 2H), 5.36 (d, $J = 15.4$ Hz, 1H), 5.09 (d, $J = 15.3$ Hz, 1H), 4.64 (t, $J = 7.8$ Hz, 1H), 3.61 (s, 3H), 2.53 – 2.20 (m, 2H), 2.18 – 1.83 (m, 2H), 1.18 (s, 9H); **¹⁹F NMR** (376 MHz, CDCl₃) δ -66.02 (t, $J = 10.9$ Hz, 3F); **¹³C NMR** (101 MHz, CDCl₃) δ 159.2, 158.0, 153.4, 148.8, 135.9, 131.8, 131.3, 129.3, 128.8, 127.3, 127.1, 126.3 (q, $J = 277.3$ Hz), 126.2, 124.5, 122.5, 113.2, 113.1, 54.1, 44.7, 44.4, 33.4, 31.1 (q, $J = 28.7$ Hz), 30.3, 25.1 (d, $J = 3.0$ Hz); **IR** (thin film) ν 2962, 1652, 1602, 1516, 1254, 1099, 809, 758, 581 cm^{-1} ; **MS** (ESI): m/z 509.2 [M+H]⁺; **HRMS** (ESI-TOF): m/z Calculated for C₃₀H₃₂F₃N₂O₂ [M+H]⁺: 509.2410; Found: 509.2406.

1-([1,1'-Biphenyl]-4-ylmethyl)-3-(1-(4-(*tert*-butyl)phenyl)-4,4,4-trifluorobutyl)quinoxalin-2(1*H*)-one (3ch)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3ch** (59.8 mg, 54%) as a white solid. Mp 189–191 °C; **1H NMR** (400 MHz, CDCl₃) δ 7.95 – 7.79 (m, 1H), 7.55 – 6.95 (m, 16H), 5.46 (d, *J* = 15.7 Hz, 1H), 5.16 (d, *J* = 15.8 Hz, 1H), 4.65 (t, *J* = 7.8 Hz, 1H), 2.52 – 2.25 (m, 2H), 2.15 – 1.84 (m, 2H), 1.18 (s, 9H); **19F NMR** (377 MHz, CDCl₃) δ -65.93 (t, *J* = 10.8 Hz, 3F); **13C NMR** (101 MHz, CDCl₃) δ 159.1, 153.4, 148.8, 139.6, 139.4, 135.8, 133.1, 131.8, 131.3, 129.3, 128.9, 127.7, 127.1, 126.5, 126.4, 126.3 (q, *J* = 277.3 Hz), 126.2, 125.9, 124.5, 122.6, 44.7, 33.4, 31.1 (q, *J* = 28.5 Hz), 30.3, 25.1 (d, *J* = 3.1 Hz); **IR** (thin film) ν 2947, 1656, 1257, 1144, 1001, 959, 823, 757, 701, 583 cm⁻¹; **MS** (ESI): *m/z* 555.3 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₃₅H₃₄F₃N₂O [M+H]⁺: 555.2618; Found: 555.2632.

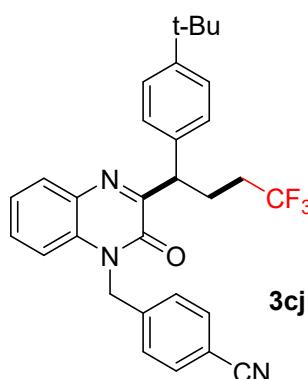
Ethyl 4-((3-(1-(4-(*tert*-butyl)phenyl)-4,4,4-trifluorobutyl)-2-oxoquinalin-1(2*H*)-yl)methyl)benzoate (3ci)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3ci** (66.0 mg, 60%) as a white solid. Mp 150–152 °C; **1H NMR** (400 MHz, CDCl₃) δ 7.85 (t, *J* = 8.6 Hz, 3H), 7.46 – 7.14 (m, 6H), 7.05 (dd, *J* = 27.8, 8.1 Hz, 3H), 5.47 (d, *J* = 16.1 Hz, 1H), 5.23 (d, *J* = 16.0 Hz, 1H), 4.63 (t, *J* = 7.8 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 1H), 2.54 – 2.24 (m, 2H), 2.13 – 1.84 (m, 2H), 1.25 (t, *J* = 7.1 Hz,

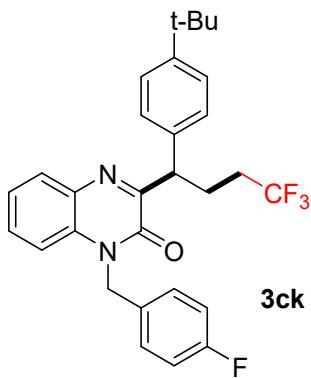
3H), 1.19 (s, 9H); **¹⁹F NMR** (377 MHz, CDCl₃) δ -66.02 (t, *J* = 10.8 Hz, 3F); **¹³C NMR** (101 MHz, CDCl₃) δ 165.0, 159.1, 153.3, 148.9, 139.2, 135.7, 131.8, 131.1, 129.4, 129.1, 129.0, 128.9, 127.1, 126.3 (q, *J* = 277.3 Hz), 125.7, 124.6, 122.8, 113.0, 60.0, 44.8, 44.7, 33.4, 31.1 (q, *J* = 28.6 Hz), 30.3, 25.0 (d, *J* = 3.0 Hz), 13.2; **IR** (thin film) ν 2965, 1716, 1664, 1602, 1468, 1277, 1255, 1103, 820, 750, 579 cm⁻¹; **MS** (ESI): *m/z* 573.2 [M+Na]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₃₂H₃₃F₃N₂O₃Na [M+Na]⁺: 573.2336; Found: 573.2325.

4-((3-(1-(*Tert*-butyl)phenyl)-4,4,4-trifluorobutyl)-2-oxoquinoxalin-1(2*H*)-yl)methylbenzonitrile (3cj)



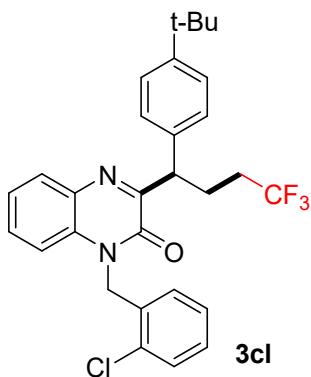
The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3cj** (43.3 mg, 43%) as a white solid. Mp 153–155 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.90 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.39 – 7.09 (m, 8H), 6.99 (dd, *J* = 8.3, 1.2 Hz, 1H), 5.47 (d, *J* = 16.3 Hz, 1H), 5.25 (d, *J* = 16.3 Hz, 1H), 4.62 (t, *J* = 7.8 Hz, 1H), 2.53 – 2.26 (m, 2H), 2.14 – 1.95 (m, 2H), 1.20 (s, 9H); **¹⁹F NMR** (377 MHz, CDCl₃) δ -66.01 (t, *J* = 10.9 Hz, 3F); **¹³C NMR** (101 MHz, CDCl₃) δ 159.1, 153.2, 149.0, 139.5, 135.5, 131.8, 131.7, 130.9, 129.6, 129.2, 127.1, 126.5, 126.3 (q, *J* = 277.3 Hz), 124.6, 123.0, 117.3, 112.7, 110.7, 44.7, 44.6, 33.4, 31.0 (q, *J* = 28.6 Hz), 30.3, 25.0 (d, *J* = 3.0 Hz); **IR** (thin film) ν 2963, 2229, 1671, 1604, 1255, 1099, 962, 811, 760, 580 cm⁻¹; **MS** (ESI): *m/z* 504.2 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₃₀H₂₉F₃N₃O [M+H]⁺: 504.2257; Found: 504.2256.

3-(1-(*Tert*-butyl)phenyl)-4,4,4-trifluorobutyl)-1-(4-fluorobenzyl)quinoxalin-2(1*H*)-one (3ck)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3ck** (39.7 mg, 40%) as a white solid. Mp 149–151 °C; **1H NMR** (400 MHz, CDCl₃) δ 7.86 (d, *J* = 7.9 Hz, 1H), 7.43 – 6.95 (m, 9H), 6.84 (t, *J* = 8.4 Hz, 2H), 5.38 (d, *J* = 15.5 Hz, 1H), 5.28 – 5.07 (m, 1H), 4.63 (t, *J* = 7.8 Hz, 1H), 2.50 – 2.23 (m, 2H), 2.18 – 1.85 (m, 2H), 1.19 (s, 9H); **19F NMR** (376 MHz, CDCl₃) δ -66.04 (t, *J* = 11.0 Hz, 3F), -114.37 (m, 1F); **13C NMR** (101 MHz, CDCl₃) δ 162.4, 159.9, 159.2, 153.4, 148.9, 135.7, 131.9, 131.2, 129.9 (d, *J* = 3.3 Hz), 129.4, 129.0, 127.7, 127.6, 127.1, 126.1 (q, *J* = 277.3 Hz), 124.6, 122.7, 114.9, 114.7, 113.0, 44.7, 44.3, 33.4, 31.1 (q, *J* = 28.5 Hz), 30.3, 25.0; **IR** (thin film) ν 2962, 1651, 1603, 1256, 1095, 1002, 820, 765, 580, 499 cm⁻¹; **MS** (ESI): *m/z* 519.2 [M+Na]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₂₉H₂₈F₄N₂O_{Na} [M+Na]⁺: 519.2030; Found: 519.2016.

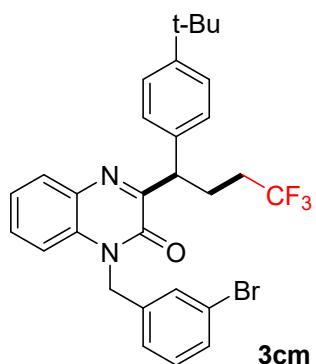
3-(1-(4-(*Tert*-butyl)phenyl)-4,4,4-trifluorobutyl)-1-(2-chlorobenzyl)quinoxalin-2(1*H*)-one (3cl)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3cl** (64.8 mg, 64%) as a white solid. Mp 182–184 °C; **1H NMR** (400 MHz, CDCl₃) δ 7.87 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.46 – 7.17 (m, 7H), 7.10 – 6.99 (m, 1H), 6.96 – 6.82 (m, 2H), 6.48 (d, *J* = 7.8 Hz, 1H), 5.47 (d, *J* = 16.8 Hz, 1H), 5.28 (d, *J* = 16.7 Hz, 1H), 4.64 (t, *J* = 7.8 Hz, 1H), 2.51 – 2.29 (m, 2H), 2.18 – 1.86 (m, 2H),

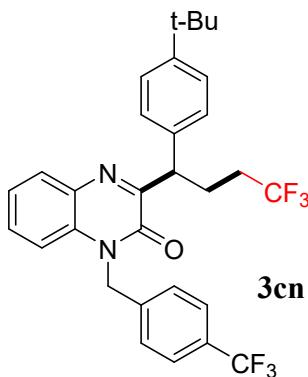
1.18 (s, 9H); **¹⁹F NMR** (377 MHz, CDCl₃) δ -66.01 (t, *J* = 10.9 Hz, 3F); **¹³C NMR** (101 MHz, CDCl₃) δ 159.1, 153.4, 148.9, 135.7, 131.8, 131.6, 131.1, 131.0, 129.3, 129.1, 128.7, 127.7, 127.1, 126.3 (q, *J* = 277.3 Hz), 126.2, 125.7, 124.6, 122.8, 113.2, 44.7, 42.6, 33.4, 31.1 (q, *J* = 28.7 Hz), 30.3, 25.0 (d, *J* = 3.0 Hz); **IR** (thin film) ν 2963, 1655, 1604, 1447, 1258, 1099, 961, 822, 760, 582 cm⁻¹; **MS** (ESI): *m/z* 535.2 [M+Na]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₂₉H₂₈ClF₃N₂ONa [M+Na]⁺: 535.1735; Found: 535.1746.

1-(3-Bromobenzyl)-3-(1-(*tert*-butyl)phenyl)-4,4,4-trifluorobutyl)quinoxalin-2(1*H*)-one (3cm**)**



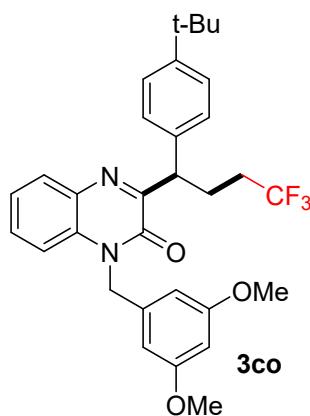
The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3cm** (70.1 mg, 63%) as a white solid. Mp 157-159 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.84 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.31 – 7.14 (m, 8H), 7.03 – 6.90 (m, 3H), 5.35 (d, *J* = 15.8 Hz, 1H), 5.09 (d, *J* = 15.8 Hz, 1H), 4.62 (t, *J* = 7.8 Hz, 1H), 2.49 – 2.26 (m, 2H), 2.14 – 1.90 (m, 2H), 1.17 (s, 9H); **¹⁹F NMR** (377 MHz, CDCl₃) δ -65.95 (t, *J* = 10.9 Hz, 3F); **¹³C NMR** (101 MHz, CDCl₃) δ 159.1, 153.3, 148.9, 136.5, 135.7, 131.8, 131.0, 129.8, 129.4, 129.0, 128.8, 127.1, 126.3 (q, *J* = 277.3 Hz), 124.6, 124.4, 122.8, 121.9, 113.0, 44.7, 44.3, 33.4, 31.0 (q, *J* = 28.5 Hz), 30.3, 25.0 (d, *J* = 3.0 Hz); **IR** (thin film) ν 2965, 1647, 1601, 1256, 1099, 1002, 821, 759, 582 cm⁻¹; **MS** (ESI): *m/z* 579.1 [M+Na]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₂₉H₂₈BrF₃N₂ONa [M+Na]⁺: 579.1229; Found: 579.1225.

3-(1-(*Tert*-butyl)phenyl)-4,4,4-trifluorobutyl)-1-(4-(trifluoromethyl)benzyl)quinoxalin-2(1*H*)-one (3cn**)**



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3cn** (61.2 mg, 56%) as a white solid. Mp 166–168 °C; **1H NMR** (400 MHz, CDCl₃) δ 7.87 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.09 (m, 8H), 7.01 (d, *J* = 8.3 Hz, 1H), 5.45 (d, *J* = 16.1 Hz, 1H), 5.22 (d, *J* = 16.0 Hz, 1H), 4.62 (t, *J* = 7.8 Hz, 1H), 2.53 – 2.22 (m, 2H), 2.12 – 1.87 (m, 2H), 1.18 (s, 9H); **19F NMR** (376 MHz, CDCl₃) δ -62.63 (s, 3F), -66.02 (t, *J* = 10.8 Hz, 3F); **13C NMR** (101 MHz, CDCl₃) δ 159.1, 153.3, 149.0, 138.2 (d, *J* = 1.5 Hz), 135.6, 131.8, 131.0, 129.5, 129.1 (d, *J* = 3.7 Hz), 128.8, 126.3 (q, *J* = 277.3 Hz), 126.1, 124.8 (q, *J* = 3.9 Hz), 124.6, 122.9, 122.8 (q, *J* = 273.1 Hz), 112.9, 44.7, 44.48, 33.4, 31.0 (q, *J* = 28.6 Hz), 30.3, 25.1 (d, *J* = 2.9 Hz); **IR** (thin film) ν 2965, 1649, 1603, 1325, 1256, 1119, 1098, 818, 756, 584 cm⁻¹; **MS** (ESI): *m/z* 547.2 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₃₀H₂₉F₆N₂O [M+H]⁺: 547.2179; Found: 547.2170.

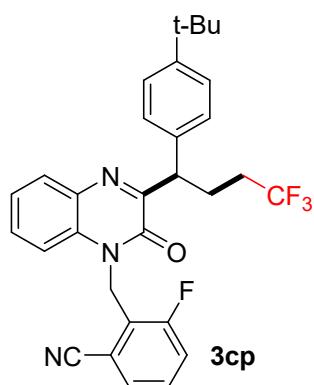
3-(1-(4-(*Tert*-butyl)phenyl)-4,4,4-trifluorobutyl)-1-(3,5-dimethoxybenzyl)quinoxalin-2(1*H*)-one (3co)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3co** (57.3 mg, 53%) as a white solid. Mp 146–148 °C; **1H NMR** (400 MHz, CDCl₃) δ 7.84 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.29 – 7.25 (m, 3H), 7.23 – 7.18 (m, 3H), 7.14 – 7.08 (m, 1H), 6.24 – 6.08 (m, 3H), 5.23 (s, 2H), 4.63 (t, *J* = 7.8 Hz, 1H),

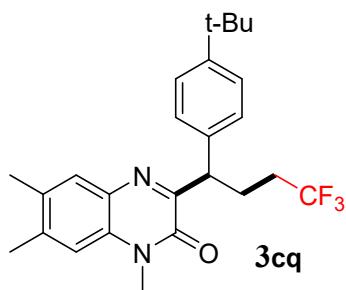
3.53 (s, 6H), 2.51 – 2.24 (m, 2H), 2.14 – 1.89 (m, 2H), 1.17 (s, 9H); **¹⁹F NMR** (376 MHz, CDCl₃) δ -65.99 (t, *J* = 10.8 Hz, 3F); **¹³C NMR** (101 MHz, CDCl₃) δ 160.1, 159.0, 153.4, 148.8, 136.5, 135.9, 131.8, 131.3, 129.2, 129.0, 127.0, 126.3 (q, *J* = 277.3 Hz), 124.5, 122.6, 113.3, 103.7, 98.2, 54.1, 44.9, 44.7, 33.4, 31.1 (q, *J* = 28.6 Hz), 30.3, 25.0 (d, *J* = 3.2 Hz); **IR** (thin film) ν 2960, 1651, 1596, 1472, 1258, 1138, 960, 822, 753, 584 cm⁻¹; **MS** (ESI): *m/z* 539.3 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₃₁H₃₄F₃N₂O₃ [M+H]⁺: 539.2516; Found: 539.2517.

2-((3-(1-(*Tert*-butyl)phenyl)-4,4,4-trifluorobutyl)-2-oxoquinoxalin-1(2*H*)-yl)methyl)-3-fluorobenzonitrile (3cp)



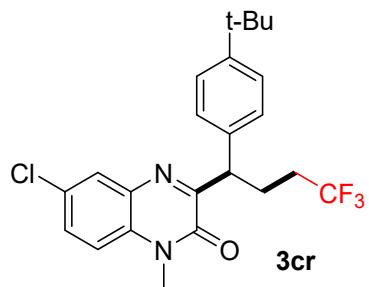
The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3cp** (60.5 mg, 58%) as a yellow solid. Mp 184–186 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.92 (d, *J* = 7.8 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.31 – 7.22 (m, 5H), 6.99 – 6.90 (m, 2H), 6.41 (d, *J* = 8.8 Hz, 1H), 5.59 (d, *J* = 16.8 Hz, 1H), 5.44 (d, *J* = 16.8 Hz, 1H), 4.62 (t, *J* = 7.8 Hz, 1H), 2.55 – 2.26 (m, 2H), 2.16 – 1.96 (m, 2H), 1.19 (s, 9H); **¹⁹F NMR** (377 MHz, CDCl₃) δ -66.04 (td, *J* = 11.7, 3.8 Hz, 3F), -100.58 (q, *J* = 8.1 Hz, 1F); **¹³C NMR** (101 MHz, CDCl₃) δ 164.4 (d, *J* = 258.6 Hz), 159.1, 153.2, 149.1, 141.3 (d, *J* = 8.6 Hz), 135.4, 134.6 (d, *J* = 9.7 Hz), 131.8, 129.7, 129.5, 127.0, 126.3 (q, *J* = 277.3 Hz), 124.7, 123.3, 115.2 (d, *J* = 14.1 Hz), 114.9, 113.6 (d, *J* = 24.3 Hz), 112.4, 106.1, 44.9, 42.9, 33.4, 31.0 (q, *J* = 28.4 Hz), 30.3, 24.9 (d, *J* = 3.0 Hz); **IR** (thin film) ν 2962, 1658, 1606, 1587, 1435, 1257, 1174, 1021, 824, 760, 582 cm⁻¹; **MS** (ESI): *m/z* 522.2 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₃₀H₂₈F₄N₃O [M+H]⁺: 522.2163; Found: 522.2177.

3-(1-(*Tert*-butyl)phenyl)-4,4,4-trifluorobutyl)-1,6,7-trimethylquinoxalin-2(1*H*)-one (3cq)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3cq** (39.6 mg, 46%) as a white solid. Mp 160–162 °C; **1H NMR** (400 MHz, CDCl₃) δ ppm 7.61 (s, 1H), 7.28 – 7.24 (m, 2H), 7.22 – 7.16 (m, 2H), 6.93 (s, 1H), 4.56 (t, *J* = 7.8 Hz, 1H), 3.50 (s, 3H), 2.44 – 2.37 (m, 1H), 2.31 (s, 3H), 2.28 (s, 3H), 2.26 – 2.20 (m, 1H), 2.12 – 1.87 (m, 2H), 1.18 (s, 9H); **19F NMR** (376 MHz, CDCl₃) δ ppm -66.11 (t, *J* = 11.0 Hz, 3F); **13C NMR** (101 MHz, CDCl₃) δ ppm 157.6, 153.4, 148.6, 138.7, 136.2, 131.4, 130.0, 129.9, 129.3, 127.0, 126.3 (q, *J* = 277.3 Hz), 124.5, 113.1, 44.5, 33.4, 31.1 (q, *J* = 28.5 Hz), 30.3, 28.0, 25.1 (d, *J* = 2.9 Hz), 19.5, 18.1; **IR** (thin film) ν 2964, 1643, 1620, 1258, 1136, 995, 793, 583 cm⁻¹; **MS** (ESI): *m/z* 431.2 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₂₅H₃₀F₃N₂O [M+H]⁺: 431.2305; Found: 431.2302.

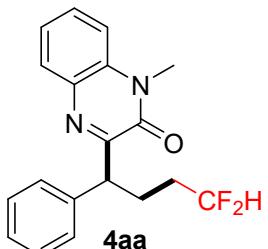
3-(1-(4-(*Tert*-butyl)phenyl)-4,4,4-trifluorobutyl)-6-chloro-1-methylquinoxalin-2(1*H*)-one (3cr)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **3cr** (36.6 mg, 42%) as a white solid. Mp 136–138 °C; **1H NMR** (400 MHz, CDCl₃) δ ppm 7.86 (d, *J* = 2.4 Hz, 1H), 7.40 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.24 (q, *J* = 8.5 Hz, 4H), 7.10 (d, *J* = 8.9 Hz, 1H), 4.58 (t, *J* = 7.8 Hz, 1H), 3.52 (s, 3H), 2.45 – 2.18 (m, 2H), 2.12 – 1.84 (m, 2H), 1.19 (s, 9H); **19F NMR** (376 MHz, CDCl₃) δ ppm -66.11 (t, *J* = 10.9 Hz, 3F); **13C NMR** (101 MHz, CDCl₃) δ ppm 160.4, 153.0, 149.0, 135.4, 132.1, 130.7, 128.9, 128.5, 127.9, 127.1, 126.2 (q, *J* = 277.3 Hz), 124.6, 113.7, 44.7, 33.4, 31.0 (q, *J* = 28.6 Hz), 30.3, 28.3, 25.0 (d, *J* = 3.0 Hz); **IR** (thin film) ν 2962, 1655, 1256, 1216, 1145, 1099, 1004, 823, 797, 591 cm⁻¹; **MS** (ESI): *m/z* 437.2

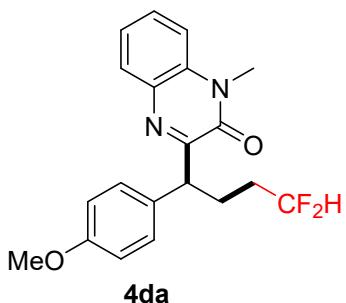
$[M+H]^+$; **HRMS** (ESI-TOF): m/z Calculated for $C_{23}H_{25}ClF_3N_2O$ $[M+H]^+$: 437.1602; Found: 437.1613.

3-(4, 4-Difluoro-1-phenylbutyl)-1-methylquinoxalin-2(1*H*)-one (4aa)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **4aa** (39.4 mg, 60%) as a yellow solid. Mp 123–125 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.83 (dd, J = 7.9, 1.5 Hz, 1H), 7.43 – 7.36 (m, 1H), 7.37 – 7.32 (m, 2H), 7.28 – 7.06 (m, 6H), 5.73 (tt, J = 56.9, 4.5 Hz, 1H), 4.59 (t, J = 7.8 Hz, 1H), 3.50 (s, 3H), 2.39 – 2.27 (m, 1H), 2.22 – 2.13 (m, 1H), 1.88 – 1.62 (m, 2H); **¹⁹F NMR** (376 MHz, CDCl₃) δ -115.59 (dt, J = 56.9, 17.6 Hz, 2F); **¹³C NMR** (101 MHz, CDCl₃) δ 160.2, 154.4, 140.6, 133.0, 132.6, 130.2, 130.0, 128.6 (d, J = 4.1 Hz), 127.0, 123.6, 117.4 (t, J = 239.0 Hz), 113.6, 46.67, 32.4 (t, J = 21.0 Hz), 29.2, 26.4 (t, J = 5.5 Hz); **IR** (thin film) ν 2925, 1651, 1602, 1472, 1122, 957, 753, 701, 571 cm⁻¹; **MS** (ESI): m/z 329.1 [M+H]⁺; **HRMS** (ESI-TOF): m/z Calculated for C₁₉H₁₉F₂N₂O [M+H]⁺: 329.1460; Found: 329.1458.

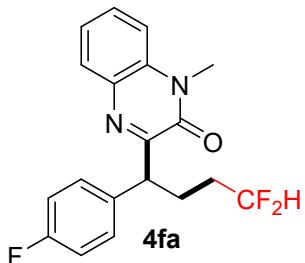
3-(4, 4-Difluoro-1-(4-methoxyphenyl)butyl)-1-methylquinoxalin-2(1*H*)-one (4da)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **4da** (53.0 mg, 74%) as a brown liquid. **¹H NMR** (400 MHz, CDCl₃) δ 7.91 (dd, J = 8.0, 1.5 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.42 – 7.28 (m, 3H), 7.23 (dd, J = 9.7, 1.5 Hz, 1H), 6.91 – 6.72 (m, 2H), 5.82 (tt, J = 56.9, 4.5 Hz, 1H), 4.62 (dd, J = 8.5, 7.2 Hz, 1H), 3.73 (s, 3H), 3.59 (s, 3H), 2.39 – 2.34 (m, 1H), 2.27 – 2.23 (m, 1H), 1.93 – 1.71 (m, 2H); **¹⁹F NMR** (376 MHz, CDCl₃) δ -115.53 (dt, J = 56.9, 17.6 Hz, 2F);

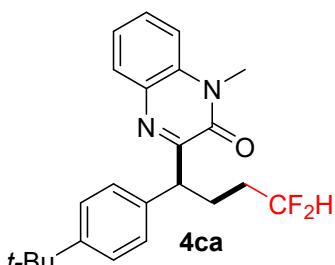
¹³C NMR (101 MHz, CDCl₃) δ 160.4, 158.6, 154.4, 133.0, 132.6, 132.5, 130.0 (d, *J* = 19.5 Hz), 129.6, 127.0, 123.6, 117.4 (t, *J* = 238.9 Hz), 114.0, 113.6, 55.2, 45.8, 32.4 (t, *J* = 20.9 Hz), 29.1, 26.4 (t, *J* = 5.5 Hz); **IR** (thin film) ν 2928, 1651, 1602, 1508, 1471, 1246, 1034, 832, 752, 576 cm⁻¹; **MS** (ESI): *m/z* 359.2 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₂₀H₂₁F₂N₂O₂ [M+H]⁺: 359.1566; Found: 359.1563.

3-(4, 4-Difluoro-1-(4-fluorophenyl)butyl)-1-methylquinoxalin-2(1*H*)-one (4fa)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **4fa** (49.8 mg, 72%) as a brown liquid. **¹H NMR** (400 MHz, CDCl₃) δ 7.91 (d, *J* = 7.9 Hz, 1H), 7.52 (t, *J* = 7.9 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 7.1 Hz, 1H), 6.96 (t, *J* = 8.2 Hz, 2H), 6.05 – 5.50 (m, 1H), 4.67 (t, *J* = 7.8 Hz, 1H), 3.61 (s, 3H), 2.41 (tt, *J* = 12.7, 6.0 Hz, 1H), 2.28 – 2.18 (m, 1H), 1.96 – 1.66 (m, 2H); **¹⁹F NMR** (377 MHz, CDCl₃) δ -115.62 (dt, *J* = 56.9, 17.5 Hz, 2F), -115.82 (m, 1F); **¹³C NMR** (101 MHz, CDCl₃) δ 161.9 (d, *J* = 245.2 Hz), 160.0, 154.4, 136.3 (d, *J* = 3.2 Hz), 133.0, 132.6, 130.2 – 130.0 (m), 123.7, 117.3 (t, *J* = 239.0 Hz), 115.5, 115.3, 113.6, 45.9, 32.3 (t, *J* = 21.0 Hz), 29.2, 26.4 (t, *J* = 5.5 Hz); **IR** (thin film) ν 2923, 1650, 1602, 1472, 1221, 1122, 834, 752, 734, 527 cm⁻¹; **MS** (ESI): *m/z* 347.1 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₁₉H₁₈F₃N₂O [M+H]⁺: 347.1366; Found: 347.1364.

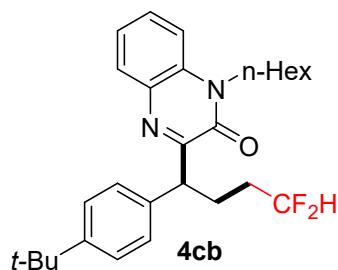
3-(1-(4-(*Tert*-butyl)phenyl)-4,4-difluorobutyl)-1-methylquinoxalin-2(1*H*)-one (4ca)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **4ca** (46.9 mg, 61%) as a brown liquid. **¹H NMR** (400 MHz, CDCl₃) δ 7.82 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.42 – 7.35 (m, 1H), 7.30 – 7.18 (m, 5H), 7.15 – 7.09

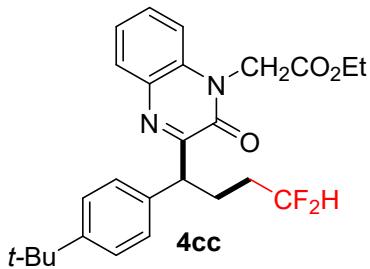
(m, 1H), 5.73 (tt, $J = 56.9, 4.5$ Hz, 1H), 4.58 (t, $J = 7.8$ Hz, 1H), 3.50 (s, 3H), 2.37 – 2.25 (m, 1H), 2.23 – 2.10 (m, 1H), 1.84 – 1.62 (m, 2H), 1.17 (s, 9H); **^{19}F NMR** (376 MHz, CDCl_3) δ -115.51 (dt, $J = 56.9, 17.6$ Hz, 2F); **^{13}C NMR** (101 MHz, CDCl_3) δ 160.4, 154.5, 149.7, 137.4, 133.0, 132.7, 130.1, 129.9, 128.2, 125.5, 123.5, 117.4 (t, $J = 239.0$ Hz), 113.5, 46.1, 34.4, 32.4 (t, $J = 20.9$ Hz), 31.4, 29.1, 26.4 (t, $J = 5.5$ Hz); **IR** (thin film) ν 2962, 1655, 1603, 1471, 1122, 1025, 931, 831, 756, 584 cm^{-1} ; **MS** (ESI): m/z 385.2 [M+H] $^+$; **HRMS** (ESI-TOF): m/z Calculated for $\text{C}_{23}\text{H}_{27}\text{F}_2\text{N}_2\text{O}$ [M+H] $^+$: 385.2086; Found: 385.2085.

3-(1-(*Tert*-butyl)phenyl)-4,4-difluorobutyl)-1-hexylquinoxalin-2(1*H*)-one (**4cb**)



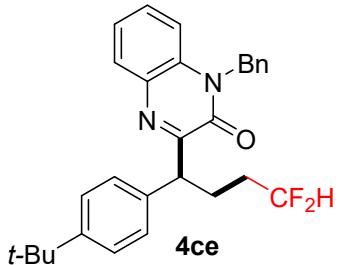
The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **4cb** (49.1 mg, 54%) as a white solid. Mp 130–132 °C; **^1H NMR** (400 MHz, CDCl_3) δ 7.92 (d, $J = 7.9$ Hz, 1H), 7.49 (t, $J = 8.1$ Hz, 1H), 7.37 – 7.23 (m, 6H), 6.19 – 5.42 (m, 1H), 4.67 (t, $J = 7.8$ Hz, 1H), 4.23 (dt, $J = 15.1, 7.9$ Hz, 1H), 4.07 (dt, $J = 14.2, 7.8$ Hz, 1H), 2.40 (tt, $J = 12.6, 6.3$ Hz, 1H), 2.29 – 2.24 (m, 1H), 1.89 – 1.75 (m, 2H), 1.67 (dd, $J = 15.7, 8.0$ Hz, 3H), 1.43 – 1.28 (m, 5H), 1.26 (s, 9H), 0.91 – 0.79 (m, 3H); **^{19}F NMR** (377 MHz, CDCl_3) δ -115.52 (dt, $J = 57.0, 17.5$ Hz, 2F); **^{13}C NMR** (101 MHz, CDCl_3) δ 160.5, 154.2, 149.6, 137.5, 132.9, 132.2, 130.4, 129.8, 128.1, 125.5, 123.3, 117.4 (t, $J = 239.0$ Hz), 113.5, 45.9, 42.5, 34.4, 32.5 (t, $J = 20.9$ Hz), 31.4, 31.3, 27.2, 26.7, 26.5 (t, $J = 5.4$ Hz), 22.6, 13.9; **IR** (thin film) ν 2960, 1650, 1603, 1468, 1121, 1023, 757, 587, 443 cm^{-1} ; **MS** (ESI): m/z 455.3 [M+H] $^+$; **HRMS** (ESI-TOF): m/z Calculated for $\text{C}_{28}\text{H}_{37}\text{F}_2\text{N}_2\text{O}$ [M+H] $^+$: 455.2868; Found: 455.2867.

Ethyl 2-(3-(1-(*tert*-butyl)phenyl)-4,4-difluorobutyl)-2-oxoquinoxalin-1(2*H*)-ylacetate (**4cc**)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **4cc** (48.4 mg, 53%) as a brown liquid. **1H NMR** (400 MHz, CDCl₃) δ 7.86 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.30 – 7.23 (m, 3H), 7.23 – 7.18 (m, 2H), 6.94 (dd, *J* = 8.4, 1.2 Hz, 1H), 5.74 (tt, *J* = 56.9, 4.5 Hz, 1H), 4.97 (d, *J* = 17.3 Hz, 1H), 4.73 (d, *J* = 17.3 Hz, 1H), 4.56 (dd, *J* = 8.4, 7.2 Hz, 1H), 4.20 – 3.98 (m, 2H), 2.45 – 2.36 (m, 1H), 2.31 – 2.22 (m, 1H), 1.87 – 1.63 (m, 2H), 1.18 (s, 9H), 1.11 (t, *J* = 7.1 Hz, 3H); **19F NMR** (376 MHz, CDCl₃) δ -115.58 (dt, *J* = 56.9, 17.5 Hz, 2F); **13C NMR** (101 MHz, CDCl₃) δ 167.1, 160.3, 154.1, 149.7, 137.1, 132.7, 132.2, 130.5, 130.1, 128.2, 125.5, 123.9, 117.4 (t, *J* = 239.0 Hz), 113.0, 62.0, 46.2, 43.6, 34.4, 32.4 (t, *J* = 21.0 Hz), 31.4, 26.4 (t, *J* = 5.5 Hz), 14.1; **IR** (thin film) ν 2963, 1749, 1658, 1604, 1469, 1203, 1121, 755, 582 cm⁻¹; **MS** (ESI): *m/z* 457.2 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₂₆H₃₁F₂N₂O₃ [M+H]⁺: 457.2297; Found: 457.2298.

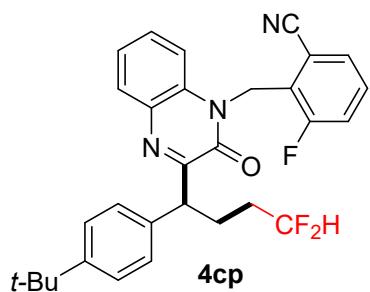
1-Benzyl-3-(1-(4-(*tert*-butyl)phenyl)-4,4-difluorobutyl)quinoxalin-2(1*H*)-one (4ce)



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 15:1) to afford **4ce** (58.9 mg, 64%) as a yellow solid. Mp 137-139 °C; **1H NMR** (400 MHz, CDCl₃) δ 7.92 (d, *J* = 7.8 Hz, 1H), 7.42 – 7.33 (m, 3H), 7.32 – 7.15 (m, 8H), 7.12 (d, *J* = 7.3 Hz, 2H), 6.02 – 5.65 (m, 1H), 5.52 (d, *J* = 15.7 Hz, 1H), 5.25 (d, *J* = 15.7 Hz, 1H), 4.73 (t, *J* = 7.8 Hz, 1H), 2.48 – 2.39 (m, 1H), 2.35 – 2.25 (m, 1H), 1.95 – 1.27 (m, 2H), 1.27 (s, 9H); **19F NMR** (377 MHz, CDCl₃) δ -115.45 (dt, *J* = 56.9, 17.8 Hz, 2F); **13C NMR** (101 MHz, CDCl₃) δ 160.7, 154.6, 149.8, 137.4, 135.3, 132.9, 132.4, 130.3, 129.9, 128.9, 128.2, 127.7, 126.9, 125.5, 123.6, 117.5 (t, *J* = 239.0 Hz), 114.3, 46.1 (d, *J* = 20.6 Hz), 34.5, 32.5 (t, *J* = 20.9 Hz), 31.4, 26.4 (t, *J* = 5.4 Hz); **IR** (thin film) ν 2964, 1654, 1603, 1455, 1122, 909, 733, 583, 421 cm⁻¹; **MS** (ESI): *m/z*

461.2 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₂₉H₃₁F₂N₂O [M+H]⁺: 461.2399; Found: 461.2401.

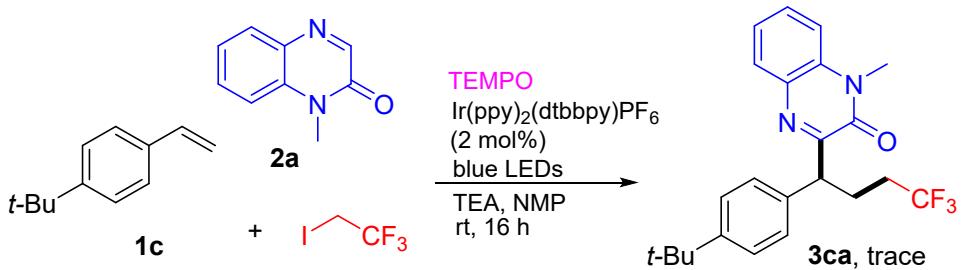
2-((3-(1-(*Tert*-butyl)phenyl)-4,4-difluorobutyl)-2-oxoquinoxalin-1(2*H*)-yl)methyl)-3-fluorobenzonitrile (4cp**)**



The product mixture was purified by silica gel column chromatography (PE/EtOAc = 10:1) to afford **4cp** (49.1 mg, 48%) as a white solid. Mp 176–178 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.99 (d, *J* = 7.9 Hz, 1H), 7.71 (dd, *J* = 8.7, 5.3 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.38 – 7.25 (m, 5H), 7.15 – 6.91 (m, 2H), 6.57 – 6.36 (m, 1H), 5.85 (tt, *J* = 56.7, 4.5 Hz, 1H), 5.66 (d, *J* = 16.8 Hz, 1H), 5.52 (d, *J* = 16.8 Hz, 1H), 4.70 (t, *J* = 7.8 Hz, 1H), 2.46 (tt, *J* = 12.4, 6.3 Hz, 1H), 2.36 – 2.27 (m, 1H), 1.99 – 1.79 (m, 2H), 1.27 (s, 9H); **¹⁹F NMR** (377 MHz, CDCl₃) δ -100.59 (td, *J* = 8.4, 5.6 Hz, 2F), -115.52 (dt, *J* = 56.9, 17.6 Hz, 1F); **¹³C NMR** (101 MHz, CDCl₃) δ 165.4 (d, *J* = 258.3 Hz), 160.6, 154.3, 149.9, 142.4 (d, *J* = 8.6 Hz), 136.9, 135.6 (d, *J* = 9.5 Hz), 132.9, 131.6, 130.7, 130.4, 128.1, 125.6, 124.3, 117.4 (t, *J* = 239.0 Hz), 116.4 – 115.8 (m), 114.7 (d, *J* = 24.3 Hz), 113.5, 107.1 (d, *J* = 3.6 Hz), 46.4, 43.9, 34.4, 32.4 (t, *J* = 20.9 Hz), 31.3, 26.2 (t, *J* = 5.4 Hz); **IR** (thin film) ν 2963, 2228, 1658, 1606, 1123, 932, 831, 758, 586 cm⁻¹; **MS** (ESI): *m/z* 504.2 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₃₀H₂₉F₃N₃O [M+H]⁺: 504.2257; Found: 504.2258.

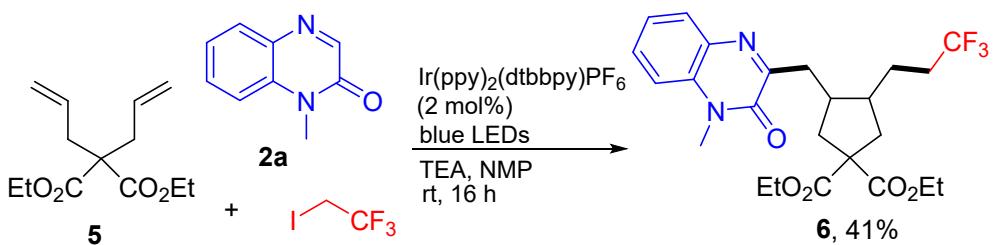
4. Control Experiments

Radical Inhibition Experiments



To a sealed tube equipped with a stir bar were added **2a** (0.2 mmol, 1.0 equiv), Ir(ppy)₂(dtbbpy)PF₆ (3.7 mg, 0.004 mmol, 2 mol %) and TEMPO (125.0mg, 0.8 mmol, 4.0 equiv). The tube was evacuated and backfilled with pure N₂ for three times. Afterwards, NMP (0.5 mL), 4-*tert*-Butylstyrene **1c** (2.5 equiv, 0.5 mmol), ICH₂CF₃ (2.0 equiv, 0.4 mmol) and TEA (3.0 equiv, 0.6 mmol) were added by syringe under N₂ atmosphere. The tightly sealed tube was then irradiated with a 20 W blue LEDs (the distance between the tube and the light source was about 7 cm) and simultaneously cooled by a fan to keep the reaction temperature at 25 °C. After 16 hours, the mixture was transferred into a 125 mL separating funnel which contained 20 mL H₂O. The mixture was extracted with DCM (20 mL each) for three times and the combined organic layer was washed with brine (20 mL) once and dried by Na₂SO₄. After filtration, the filtrate was concentrated under reduced pressure to give the crude product. The ¹⁹F NMR spectroscopy of the crude product indicated that only trace of product **3ca** was formed.

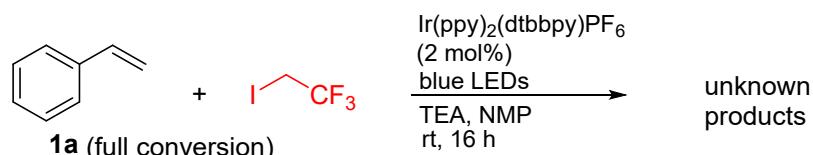
Radical Clock Experiments



To a sealed tube equipped with a stir bar were added **2a** (0.2 mmol, 1.0 equiv), Ir(ppy)₂(dtbbpy)PF₆ (3.7 mg, 0.004 mmol, 2 mol %). The tube was evacuated and backfilled with pure N₂ for three times. Afterwards, NMP (0.5 mL), Diethyl 2,2-Diallylmalonate **5** (2.5 equiv, 0.5 mmol), ICH₂CF₃ (2.0 equiv, 0.4 mmol) and TEA

(3.0 equiv, 0.6 mmol) were added by syringe under N₂ atmosphere. The tightly sealed tube was then irradiated with a 20 W blue LEDs (the distance between the tube and the light source was about 7 cm) and simultaneously cooled by a fan to keep the reaction temperature at 25 °C. After 16 hours, the mixture was transferred into a 125 mL separating funnel which contained 20 mL H₂O. The mixture was extracted with DCM (20 mL each) for three times and the combined organic layer was washed with brine (20 mL) once and dried by Na₂SO₄. After filtration, the filtrate was concentrated under reduced pressure to give the crude product, which was purified by flash chromatography on silica gel (PE/EtOAc = 10: 1) to give the product **6** (39.6 mg, 41%) as a brown liquid. **¹H NMR** (400 MHz, CDCl₃) δ 7.72 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.24 (dd, *J* = 16.0, 8.0 Hz, 2H), 4.11 (s, 4H), 3.61 (s, 3H), 3.01 – 2.85 (m, 1H), 2.83 – 2.63 (m, 2H), 2.41 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.28 (dd, *J* = 10.8, 6.1 Hz, 1H), 2.18 – 2.00 (m, 5H), 1.80 – 1.60 (m, 1H), 1.52 – 1.36 (m, 1H), 1.16 (q, *J* = 7.2 Hz, 6H); **¹⁹F NMR** (377 MHz, CDCl₃) δ -66.34 (t, *J* = 10.9 Hz); **¹³C NMR** (101 MHz, CDCl₃) δ 172.5 (d, *J* = 10.5 Hz), 159.4, 154.8, 133.0, 132.6, 129.8, 127.2 (q, *J* = 276.4 Hz), 123.5, 113.6, 61.6, 61.5, 58.7, 41.3, 39.0, 38.4, 38.1, 33.1, 32.5 (q, *J* = 28.5 Hz), 29.0, 21.5 (d, *J* = 2.9 Hz), 14.0; **IR** (thin film) ν 2981, 1726, 1652, 1602, 1473, 1250, 1035, 860, 754, 561, 459 cm⁻¹; **MS** (ESI): *m/z* 483 [M+H]⁺; **HRMS** (ESI-TOF): *m/z* Calculated for C₂₄H₃₀F₃N₂O₅ [M+H]⁺: 483.2101; Found: 483.2103.

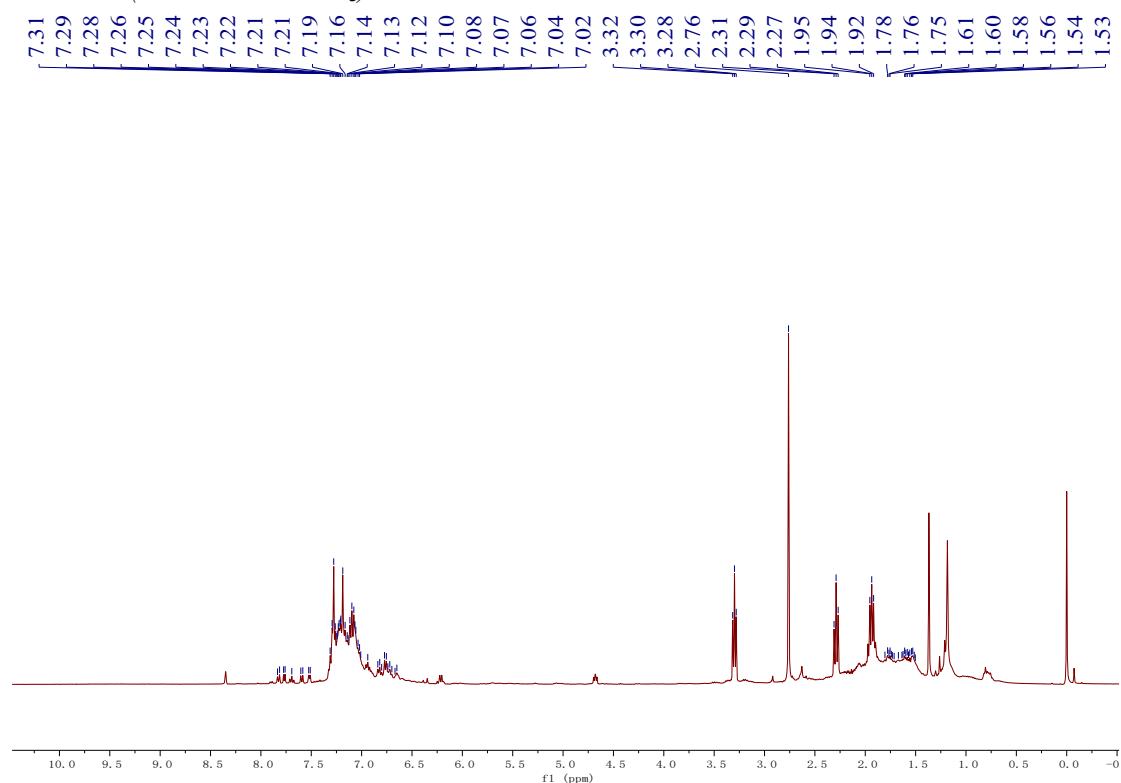
Two-Component reaction of **1a** and ICH₂CF₃



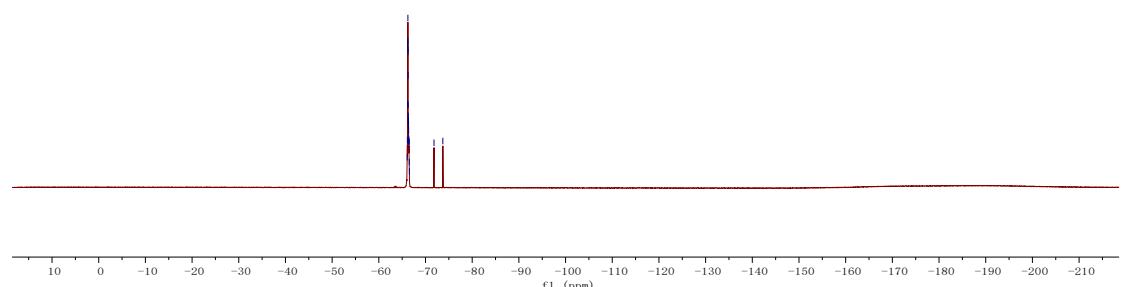
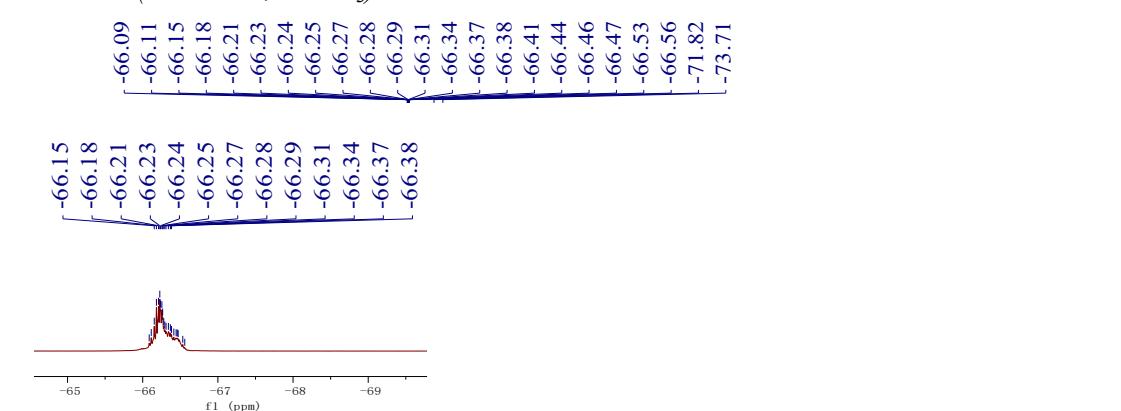
To a sealed tube equipped with a stir bar was added Ir(ppy)₂(dtbbpy)PF₆ (3.7 mg, 0.004 mmol, 2 mol %). The tube was evacuated and backfilled with pure N₂ for three times. Afterwards, NMP (0.5 mL), styrene **1a** (2.5 equiv, 0.5 mmol), ICH₂CF₃ (2.0 equiv, 0.4 mmol) and TEA (3.0 equiv, 0.6 mmol) were added by syringe under N₂ atmosphere. The tightly sealed tube was then irradiated with a 20 W blue LEDs (the distance between the tube and the light source was about 7 cm) and simultaneously cooled by a fan to keep the reaction temperature at 25 °C. After 16 hours, the mixture was transferred into a 125 mL separating funnel which contained 20 mL H₂O. The mixture was extracted with DCM (20 mL each) for three times and the combined organic layer was washed with brine (20 mL) once and dried by Na₂SO₄. After

filtration, the filtrate was concentrated under reduced pressure to give the crude product. Styrene **1a** was completely converted to unknown products.

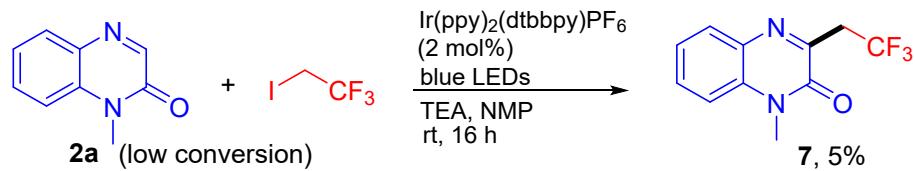
¹H NMR (400 MHz, CDCl₃)



¹⁹F NMR (377 MHz, CDCl₃)

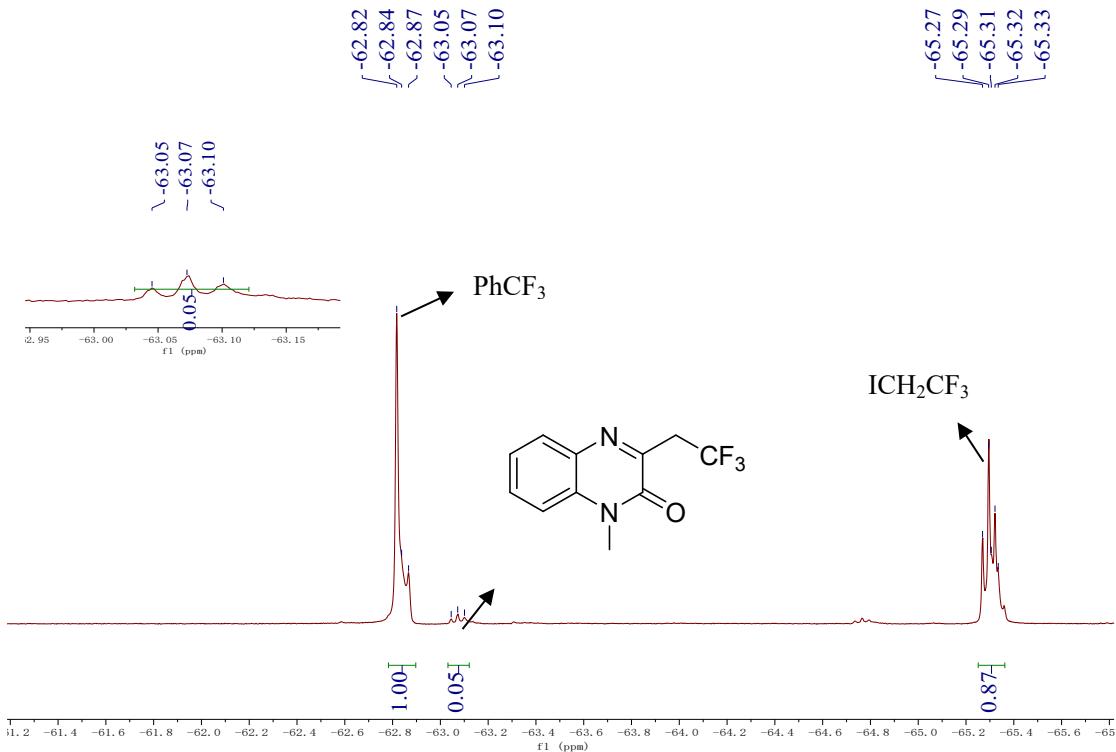


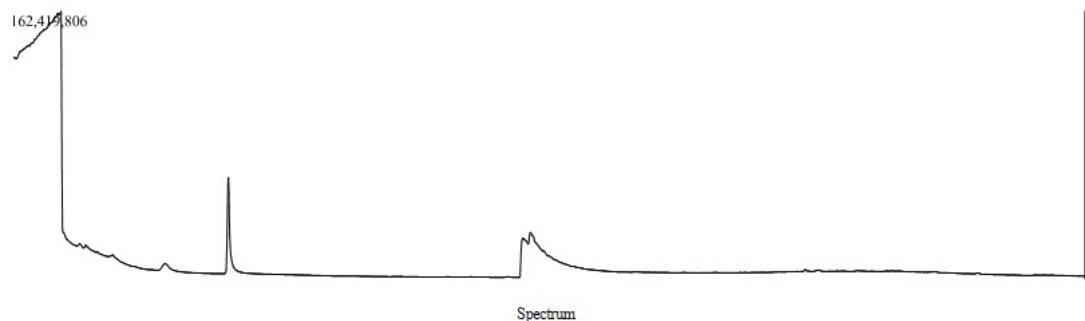
*Two-Component reaction of **2a** and ICH_2CF_3*



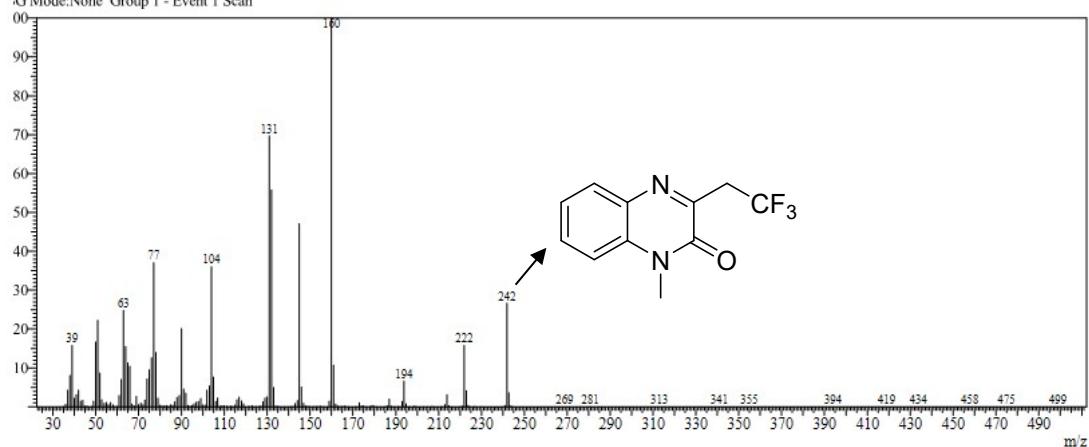
To a sealed tube equipped with a stir bar were added **2a** (0.2 mmol, 1.0 equiv) and $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ (3.7 mg, 0.004 mmol, 2 mol %). The tube was evacuated and backfilled with pure N_2 for three times. Afterwards, NMP (0.5 mL), ICH_2CF_3 (3.0 equiv, 0.6 mmol) and TEA (3.0 equiv, 0.6 mmol) were added by syringe under N_2 atmosphere. The tightly sealed tube was then irradiated with a 20 W blue LEDs (the distance between the tube and the light source was about 7 cm) and simultaneously cooled by a fan to keep the reaction temperature at 25 °C. After 16 hours, the reaction mixture was monitored by TLC, ^{19}F NMR, and GC-MS. The TLC indicated that most of **2a** was not converted, whereas ^{19}F NMR⁸ and GC-MS showed that trace of product **7** was formed.

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



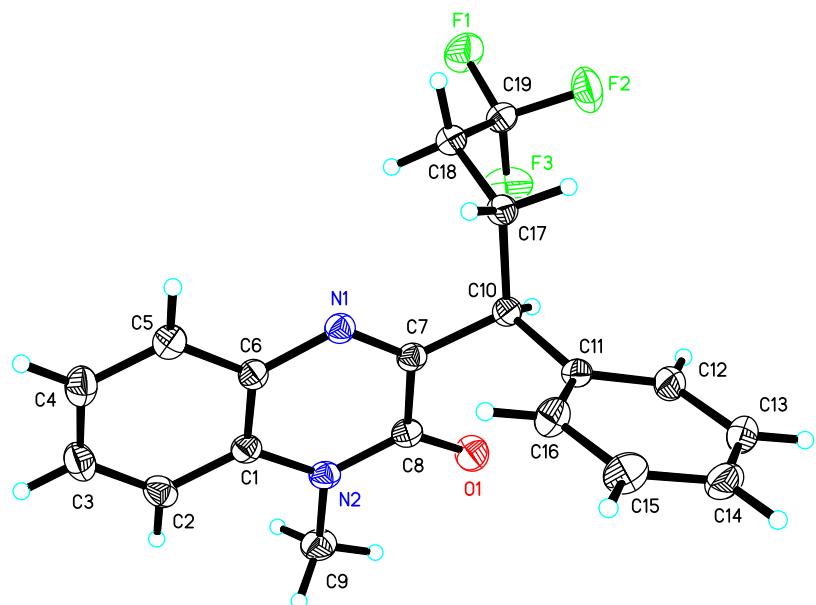
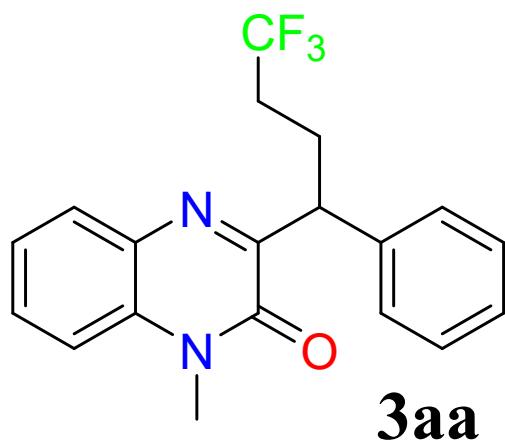


ine#:1 R.Time:8.830(Scan#:1167)
IassPeaks:465
awMode:Single 8.830(1167) BasePeak:160(3518791)
G Mode:None Group 1 - Event 1 Scan



5. ORTEP Drawing of the X-Ray Crystallographic Structure of Product 3aa

The crystals were obtained from a solution of Toluene slow volatilization. The X-ray intensity data were measured at 213(2) K



The crystal structure has been deposited at the Cambridge Crystallographic Data Center and allocated the deposition number CCDC 2100730

This data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif

Crystal data and structure refinement for 3aa

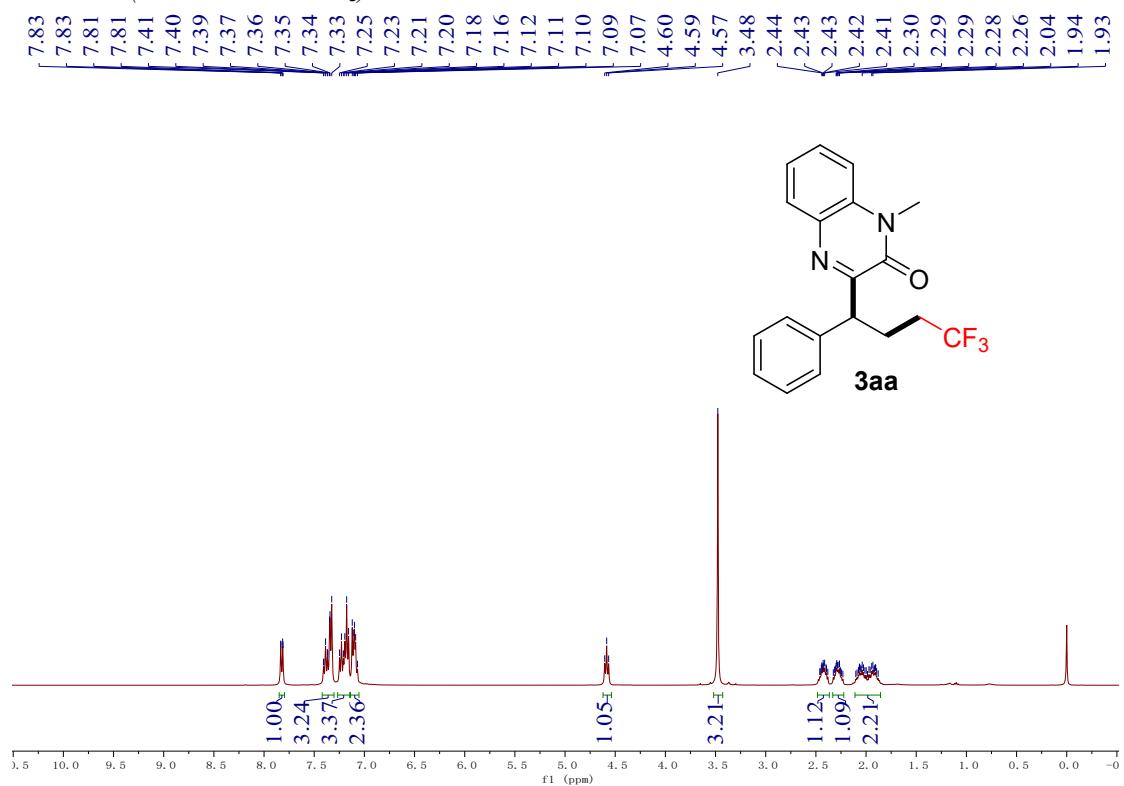
Identification code	3aa
Empirical formula	C19 H17 F3 N2 O
Formula weight	346.34
Temperature	213(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 11.9256(4) Å b = 11.4661(4) Å c = 12.6607(4) Å
Volume	1640.65(10) Å ³
Z	4
Density (calculated)	1.402 Mg/m ³
Absorption coefficient	0.111 mm ⁻¹
F(000)	720
Crystal size	0.190 x 0.150 x 0.110 mm ³
Theta range for data collection	3.353 to 26.000°.
Index ranges	-14<=h<=13, -11<=k<=14, -15<=l<=15
Reflections collected	8037
Independent reflections	3205 [R(int) = 0.0222]
Completeness to theta = 25.242°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6765
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3205 / 0 / 228
Goodness-of-fit on F ²	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0399, wR2 = 0.0881
R indices (all data)	R1 = 0.0528, wR2 = 0.0980
Extinction coefficient	0.025(4)
Largest diff. peak and hole	0.219 and -0.269 e.Å ⁻³

6. References

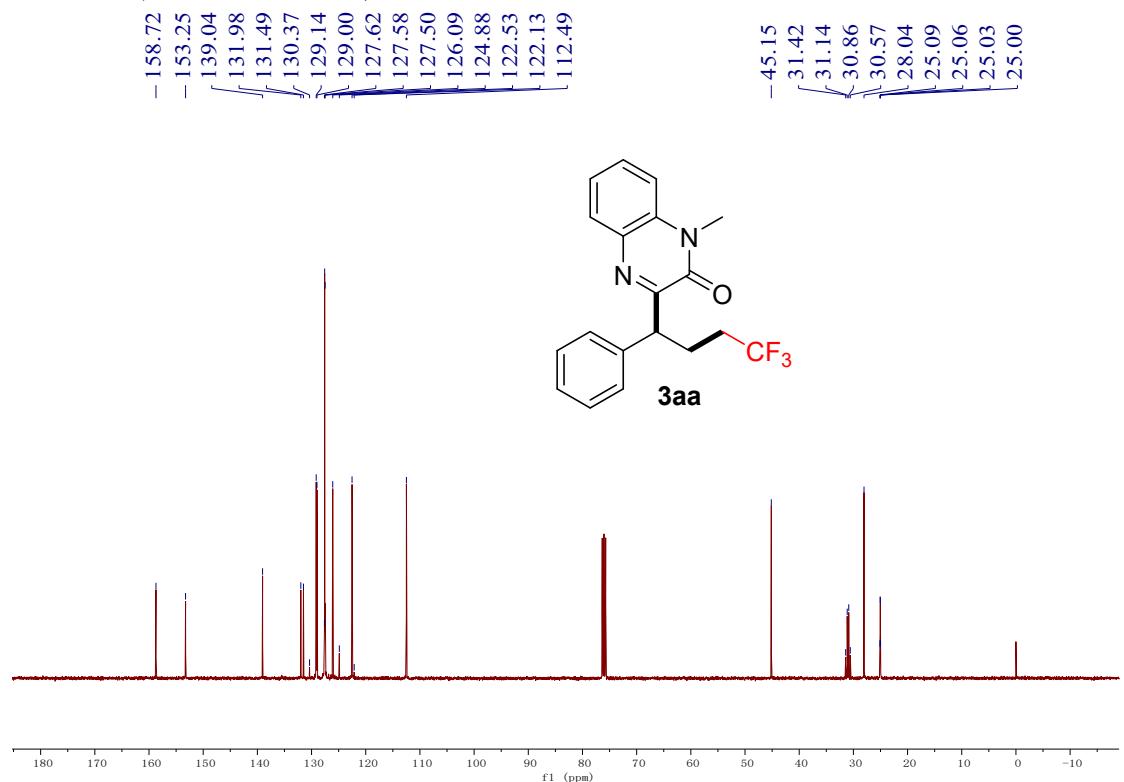
- (1) M. Mato, B. Herle and A. M. Echavarren, Cyclopropanation by Gold- or Zinc-Catalyzed Retro-Buchner Reaction at Room Temperature, *Org. Lett.*, 2018, **20**, 4341-4345.
- (2) M. Schedler, D. S. Wang and F. Glorius, NHC-catalyzed hydroacylation of styrenes. *Angew. Chem. Int. Ed.*, 2013, **52**, 2585-2589.
- (3) Y. Liu, H. Wu, Y. Guo, J.-C. Xiao, Q.-Y. Chen and C. Liu, Trifluoromethylfluorosulfonylation of Unactivated Alkenes Using Readily Available Ag(O₂CCF₂SO₂F) and N-Fluorobenzenesulfonimide. *Angew. Chem. Int. Ed.*, 2017, **56**, 15432-15435.
- (4) S. Liu, Y. Huang, F.-L. Qing and X.-H. Xu, Transition-Metal-Free Decarboxylation of 3,3,3-Trifluoro-2,2-dimethylpropanoic Acid for the Preparation of C(CF₃)Me₂-Containing Heteroarenes. *Org. Lett.*, 2018, **20**, 5497-5501.
- (5) J. Xu, H. Yang, H. Cai, H. Bao, W. Li and P. Zhang, Transition-Metal and Solvent-Free Oxidative C-H Fluoroalkoxylation of Quinoxalinones with Fluoroalkyl Alcohols. *Org. Lett.*, 2019, **21**, 4698-4702.
- (6) H.-Y. Su, X.-L. Zhu, Y. Huang, X.-H. Xu, and F.-L. Qing, Copper-catalyzed chemoselective C-H functionalization of quinoxalin-2(1H)-ones with hexafluoroisopropanol. *Chem. Commun.*, 2020, **56**, 12805-12808.
- (7) J. Wang, B. Sun, L. Zhang, T. Xu, Y. Xie and C. Jin, Transition-metal-free direct C-3 cyanation of quinoxalin-2(1H)-ones with ammonium thiocyanate as the “CN” source. *Org. Chem. Front.*, 2020, **7**, 113-118.
- (8) T. Yang, H. Zhu and W. Yu, Copper-catalyzed radical reactions of 2-azido-N-arylacrylamides with 1-(trifluoromethyl)-1,2-benziodoxole and 1-azidyl-1,2-benziodoxole. *Org. Chem. Chem.*, 2016, **14**, 3376-3384.

7. Copies of ¹H NMR, ¹⁹F NMR and ¹³C NMR Spectra of Products

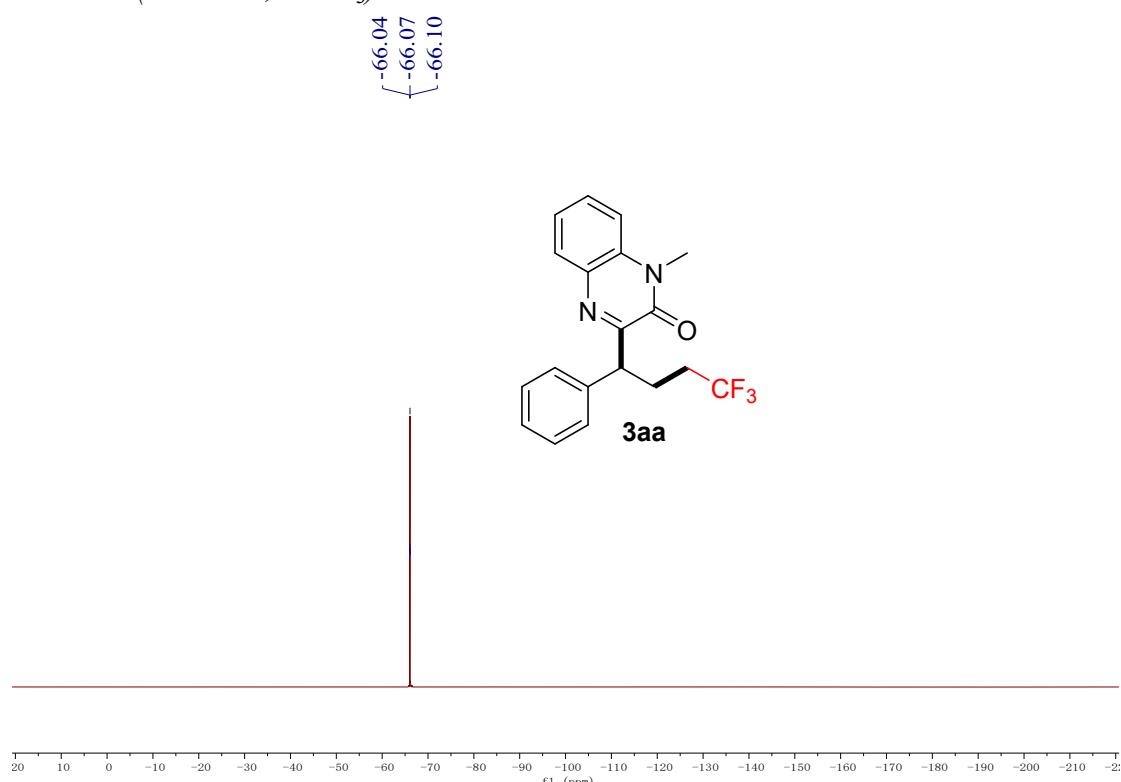
*1*H NMR (400 MHz, CDCl₃)



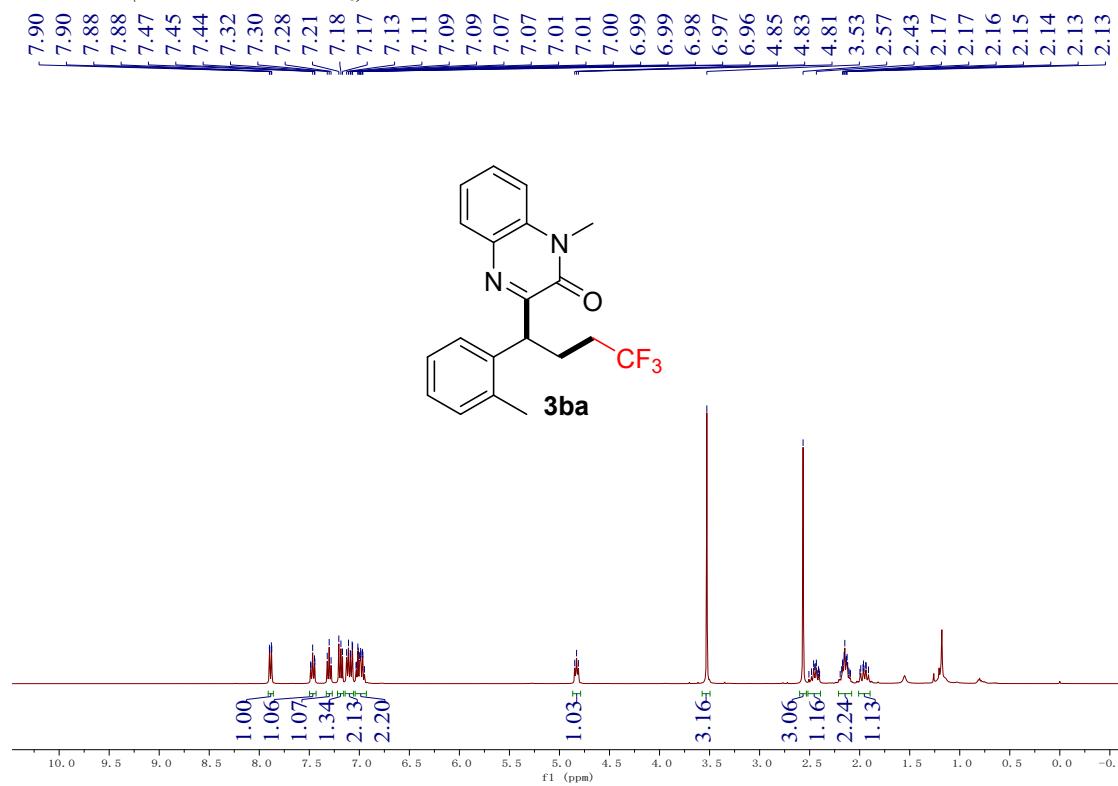
*13*C NMR (101 MHz, CDCl₃)



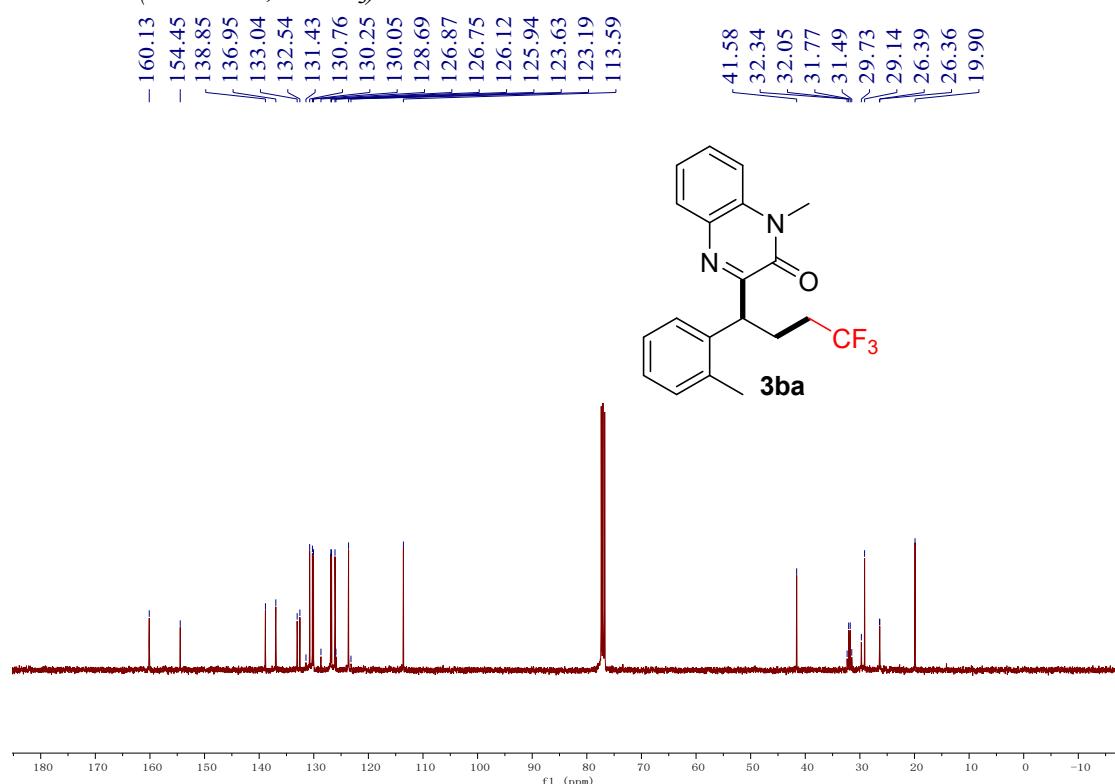
^{19}F NMR ($377\text{ MHz, } \text{CDCl}_3$)



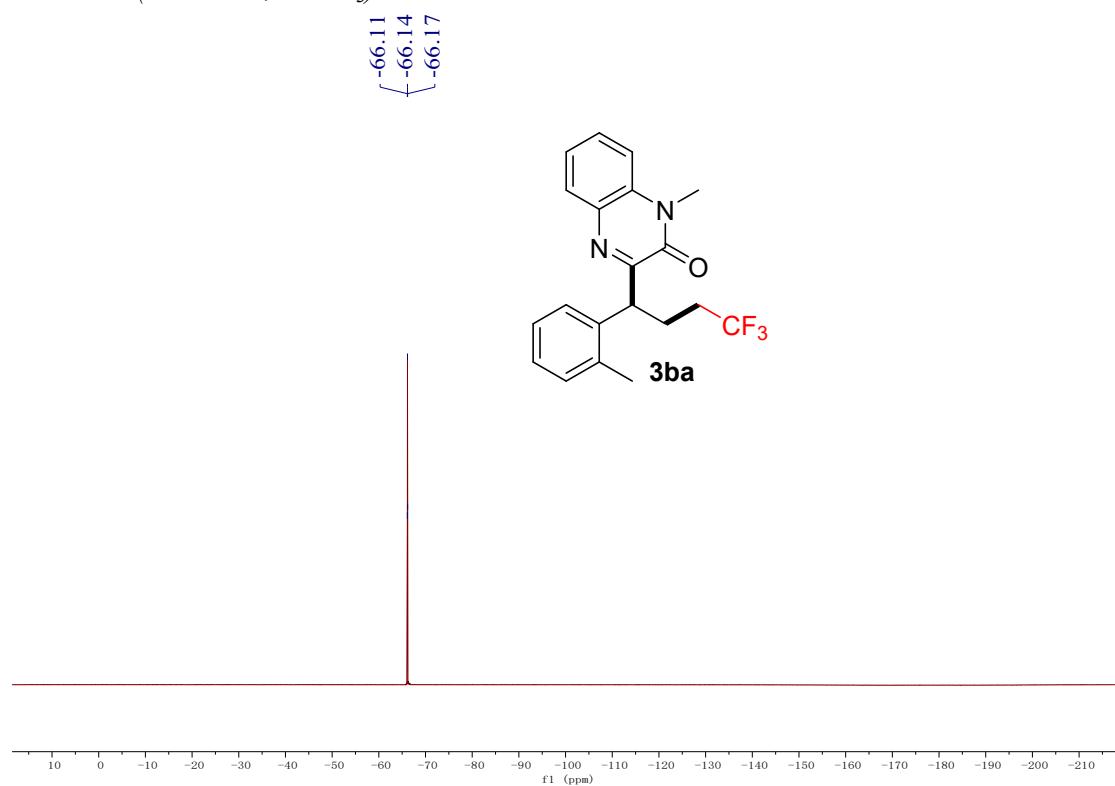
^1H NMR ($400\text{ MHz, } \text{CDCl}_3$)



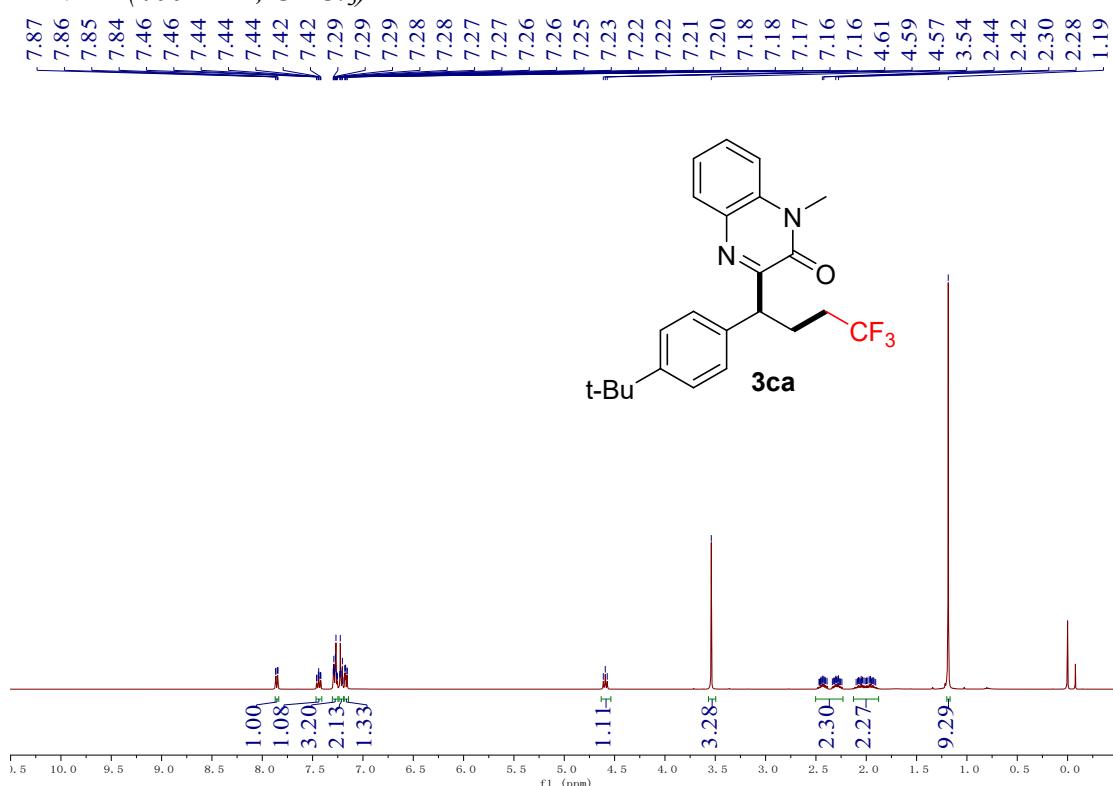
¹³C NMR (101 MHz, CDCl₃)



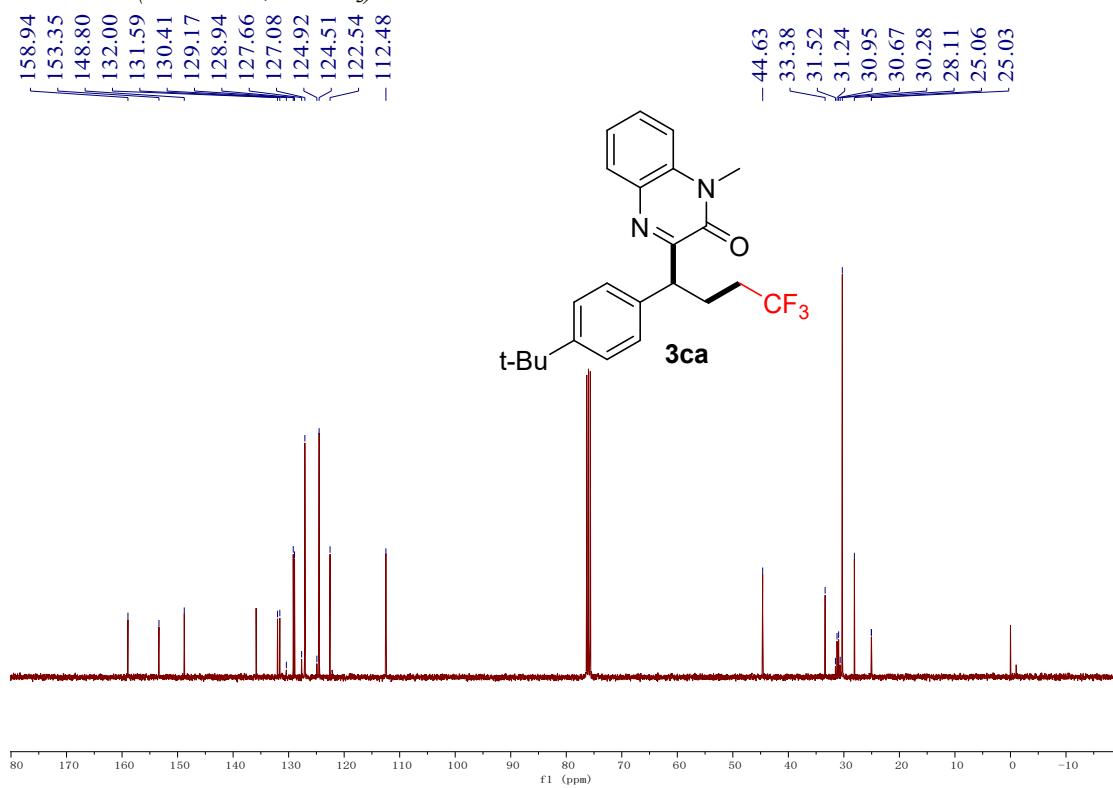
¹⁹F NMR (377 MHz, CDCl₃)



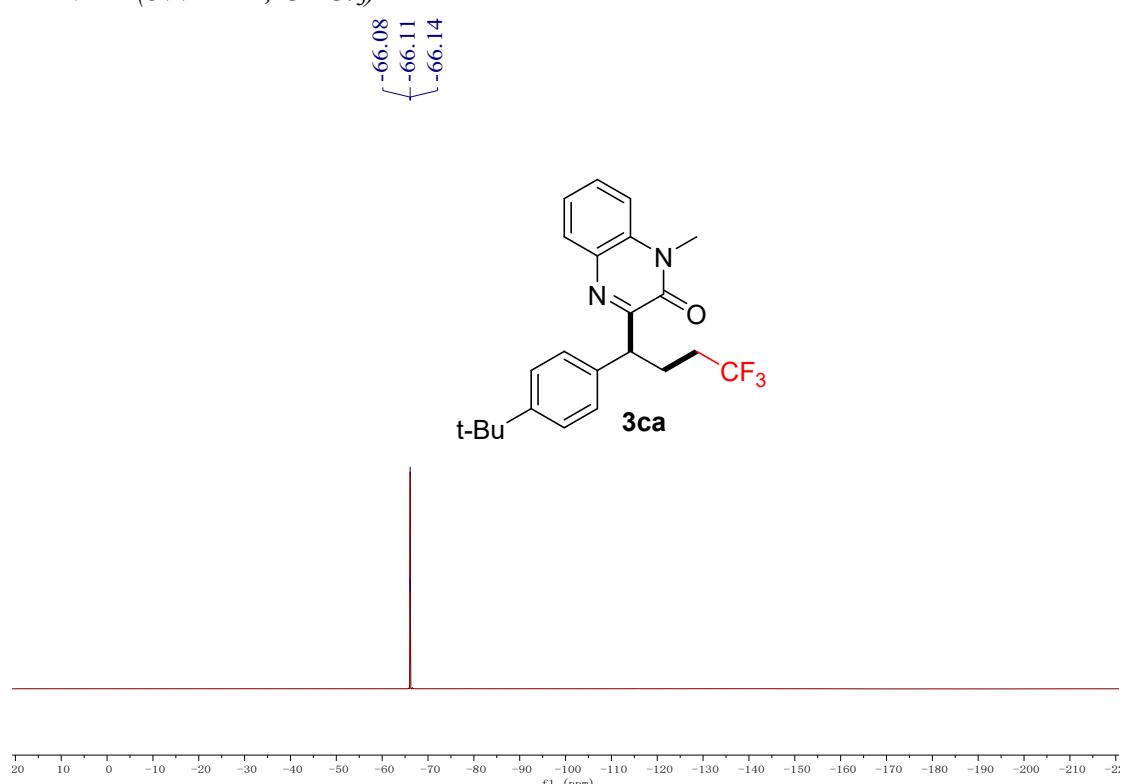
¹H NMR (400 MHz, $CDCl_3$)



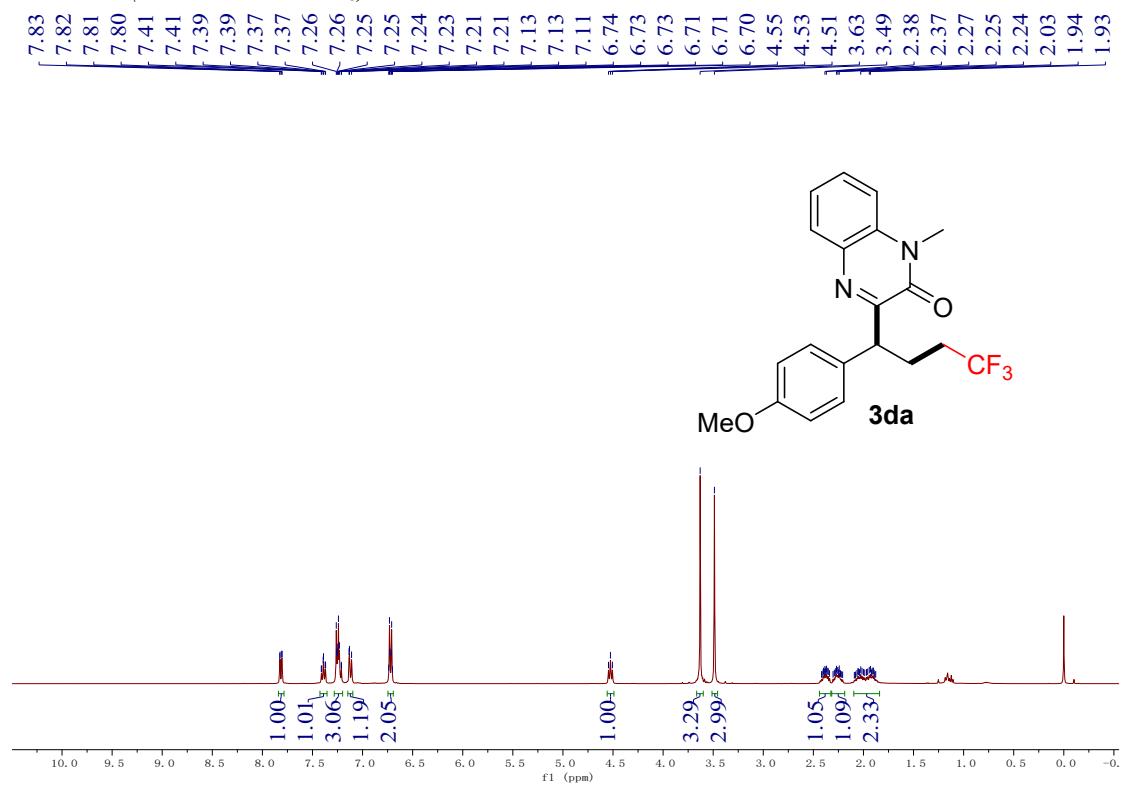
^{13}C NMR (101 MHz, CDCl_3)



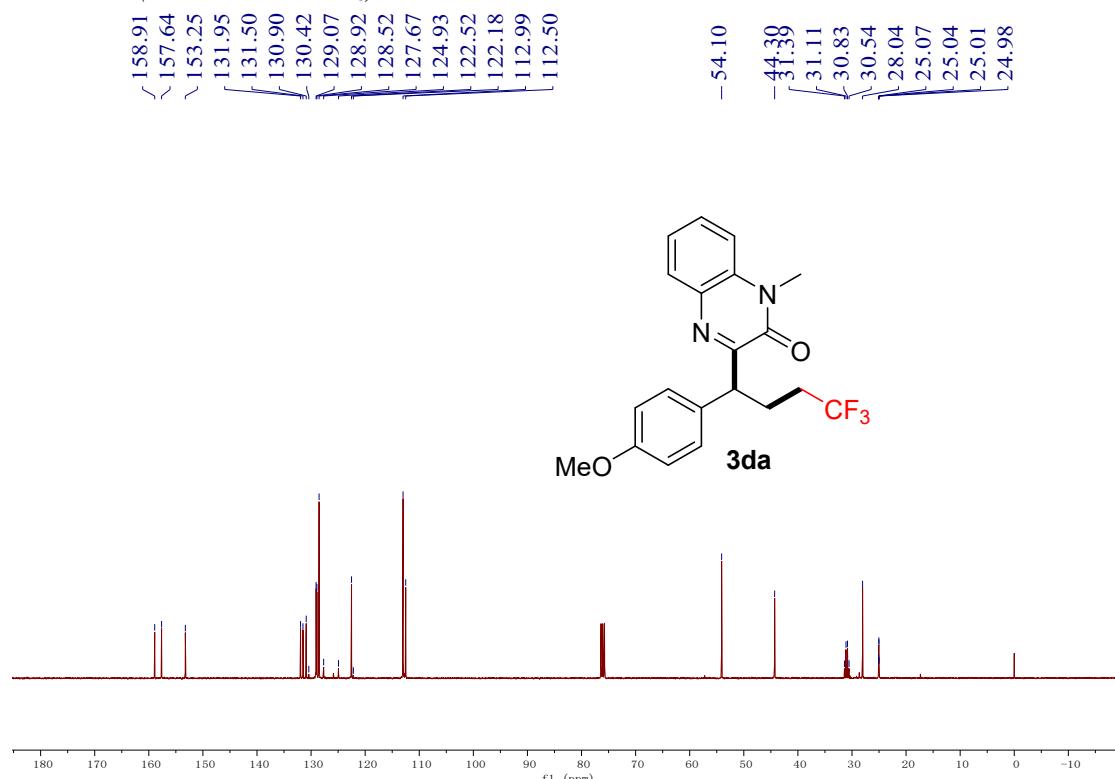
¹⁹F NMR (377 MHz, CDCl₃)



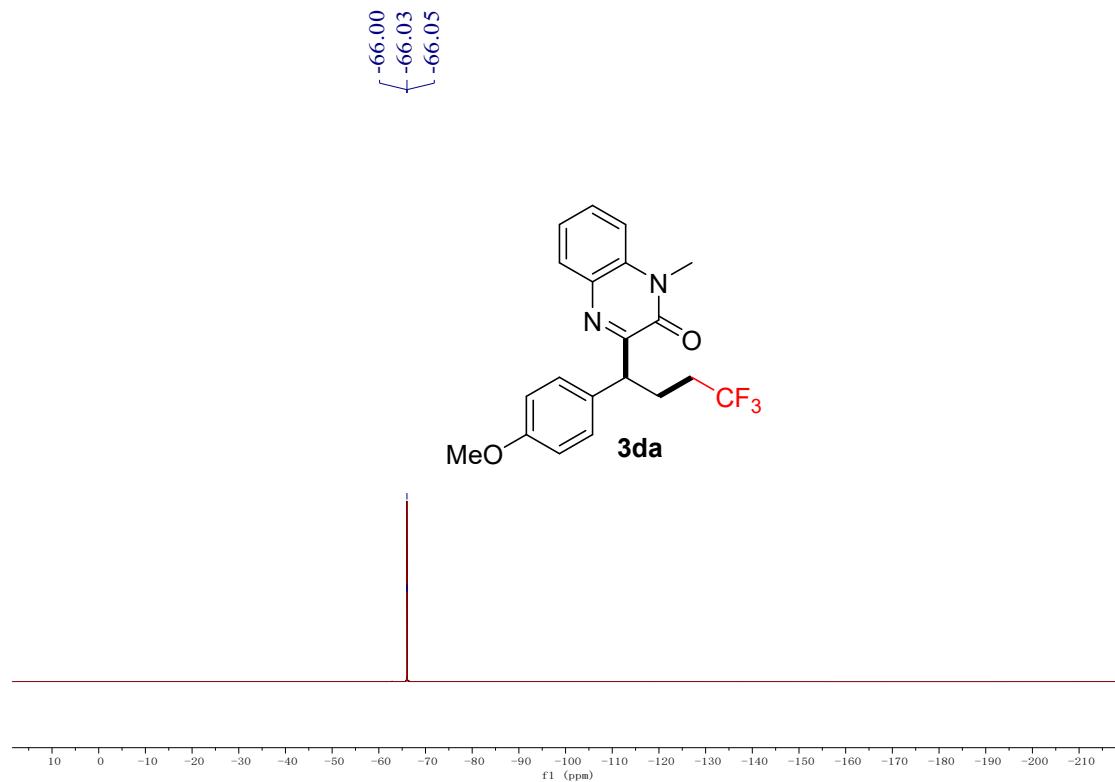
¹H NMR (400 MHz, CDCl₃)



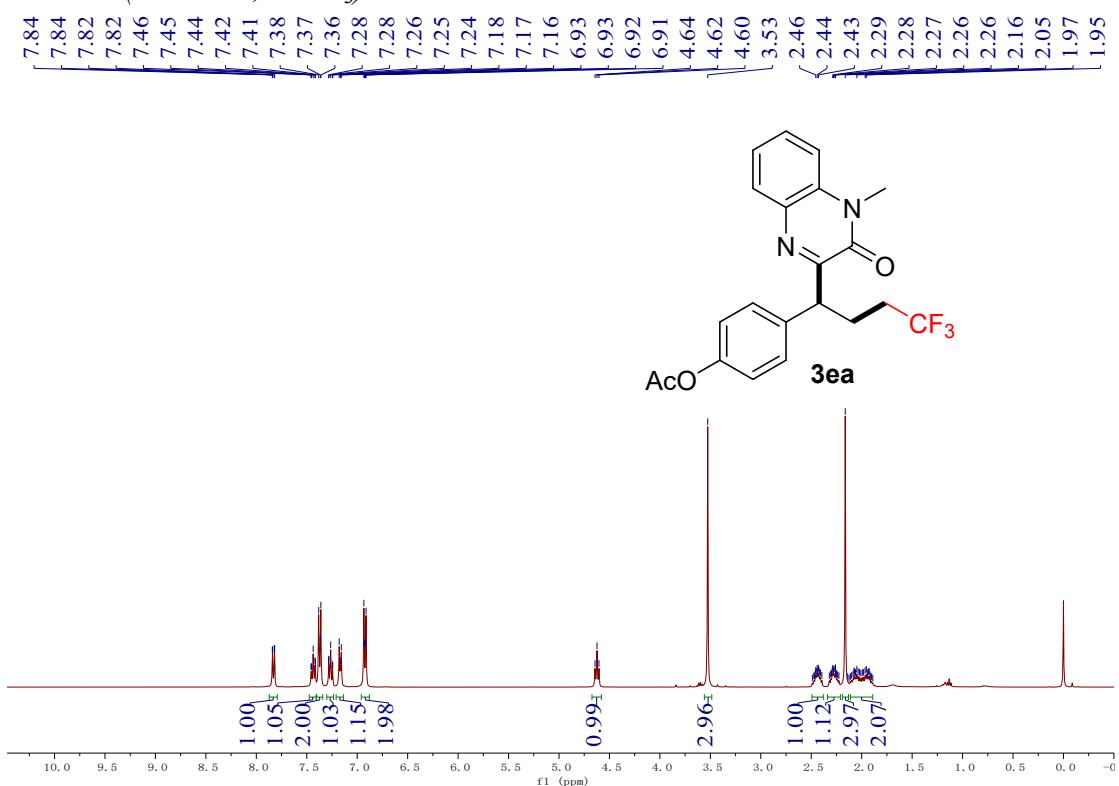
¹³C NMR (101 MHz, CDCl₃)



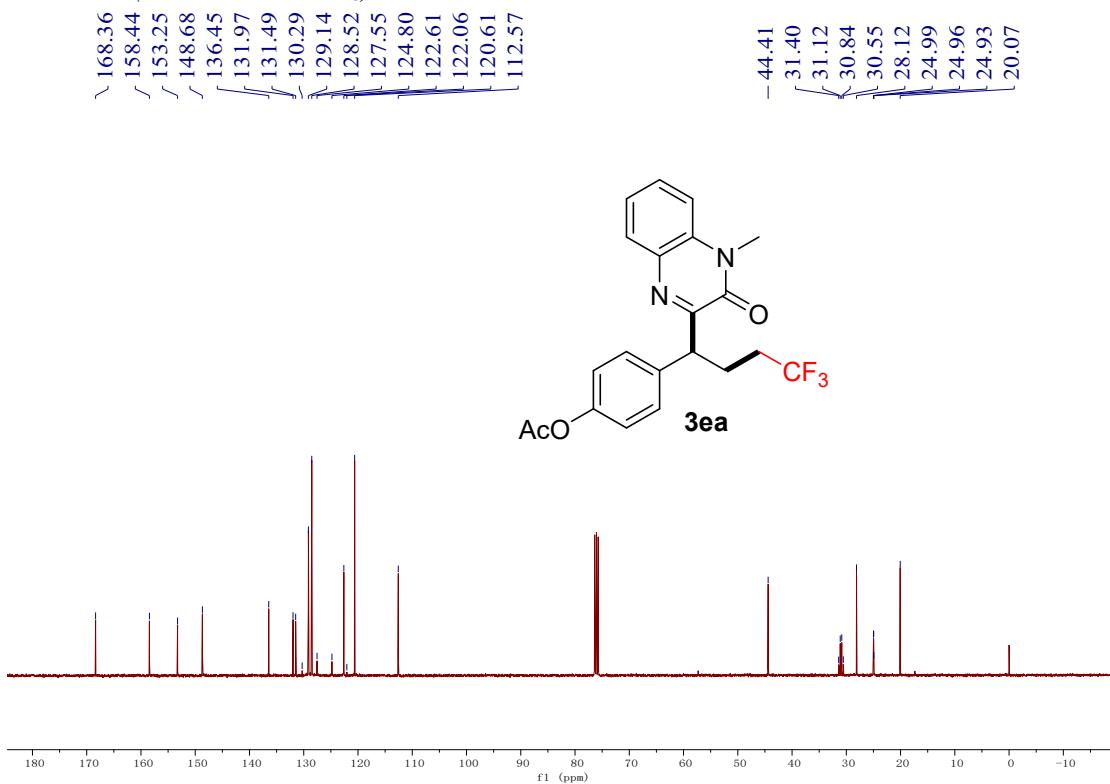
¹⁹F NMR (377 MHz, CDCl₃)



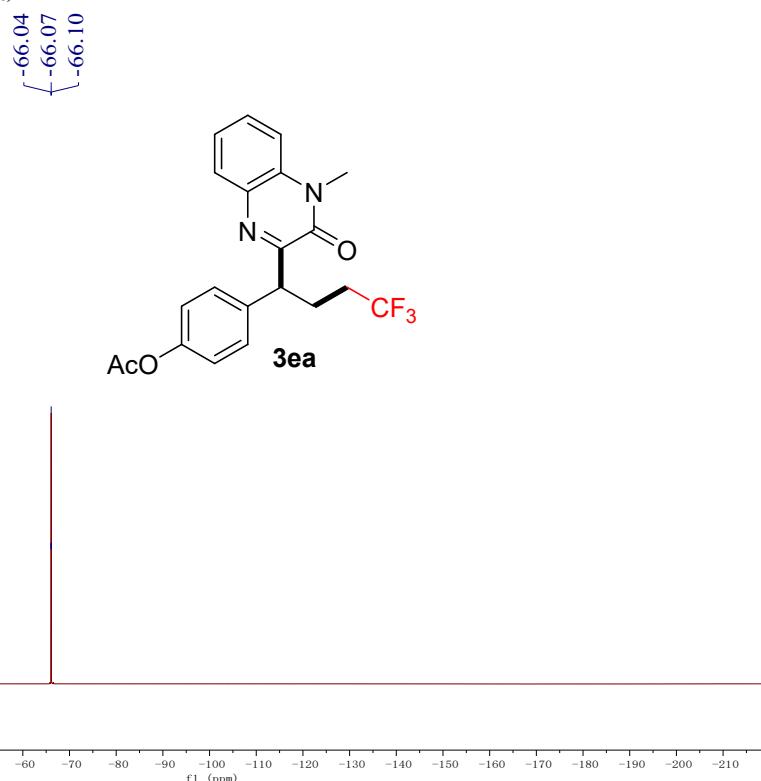
¹H NMR (400 MHz, CDCl₃)



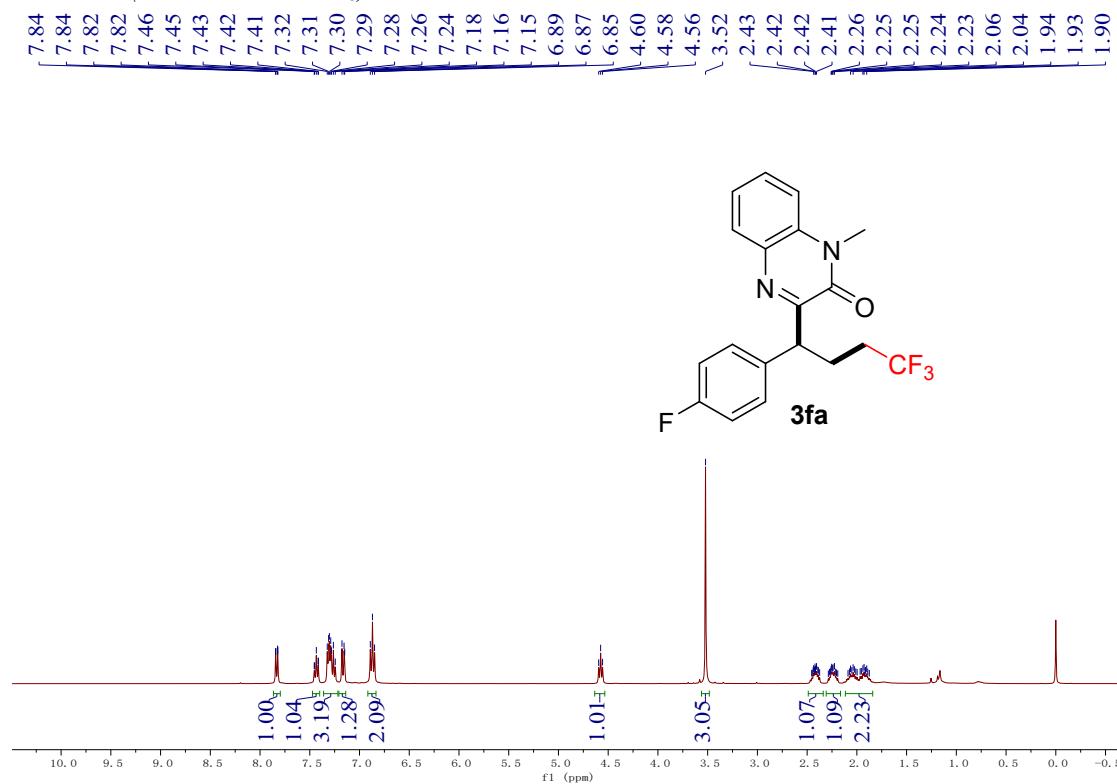
¹³C NMR (101 MHz, CDCl₃)



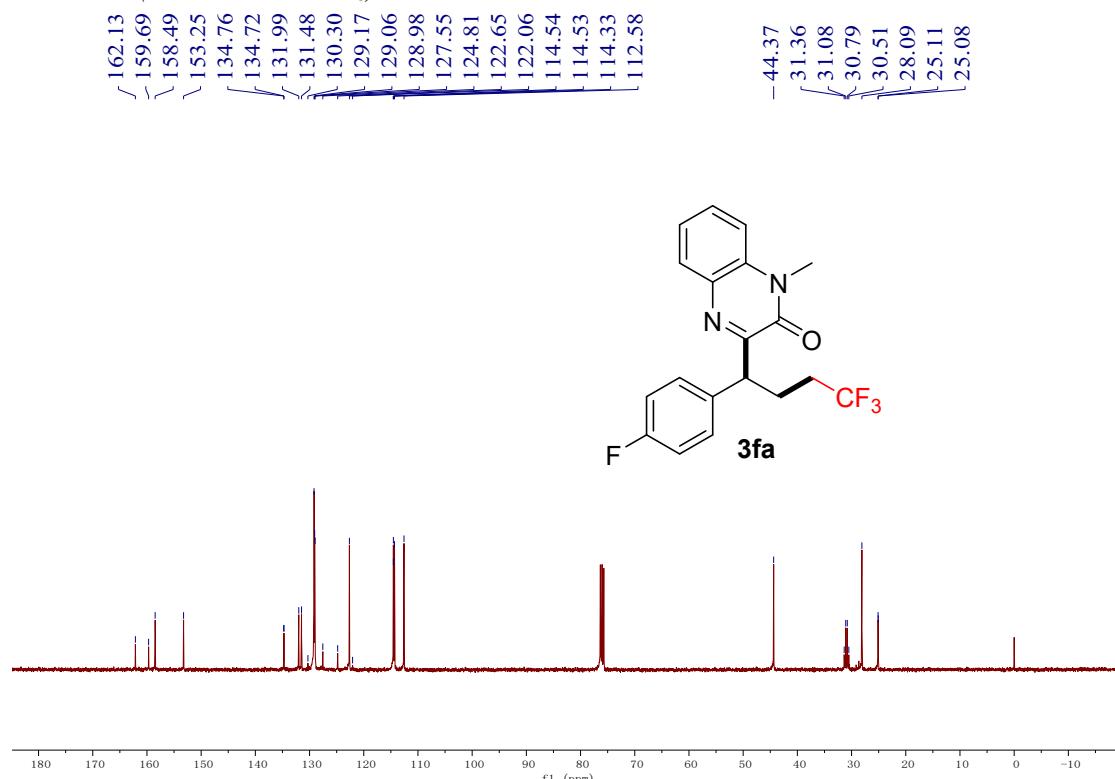
^{19}F NMR ($377\text{ MHz, } \text{CDCl}_3$)



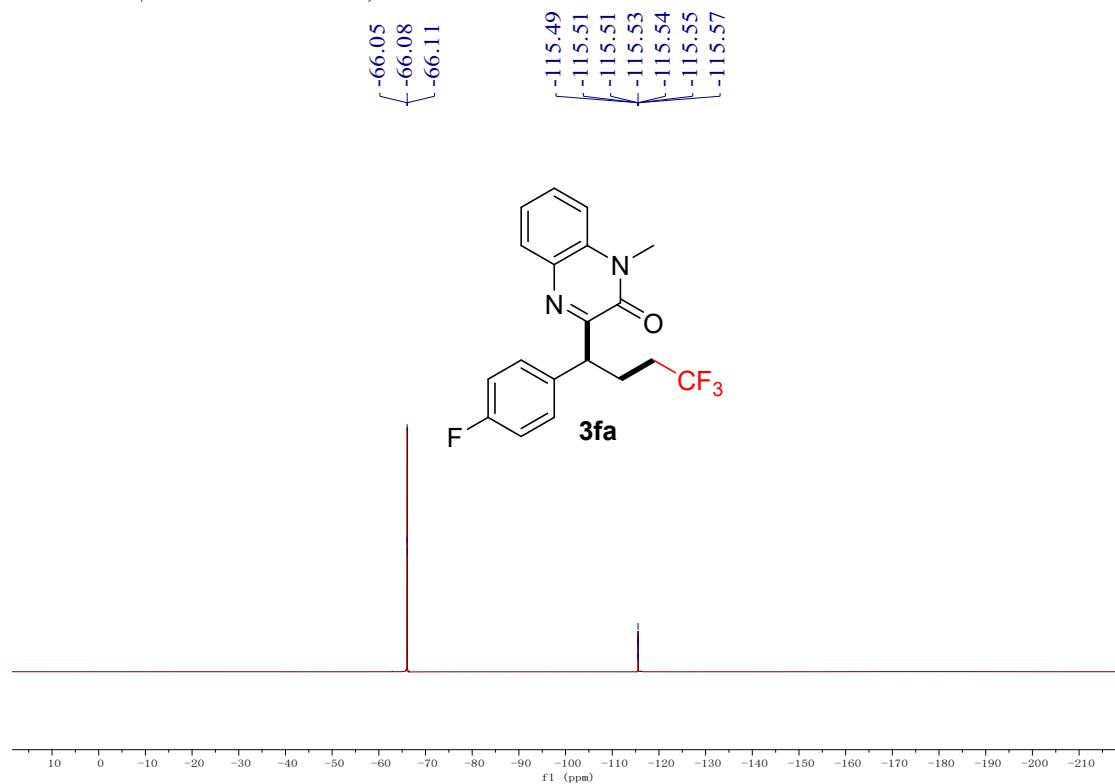
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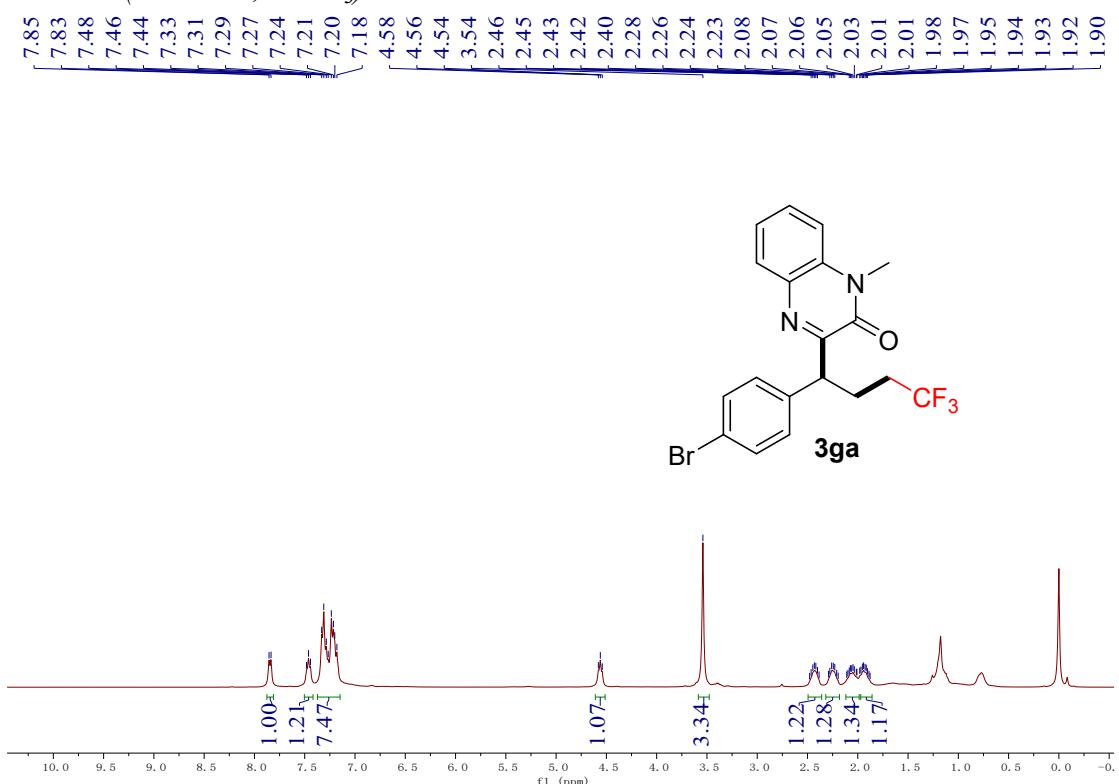
^{13}C NMR (101 MHz, CDCl_3)



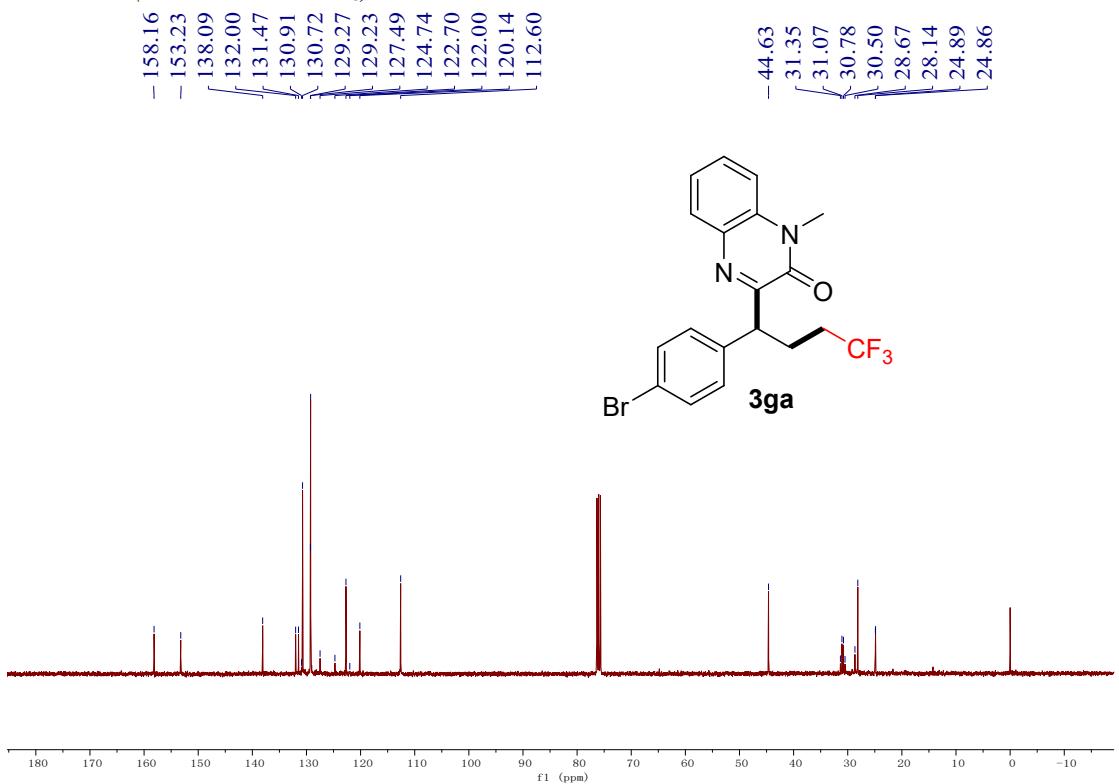
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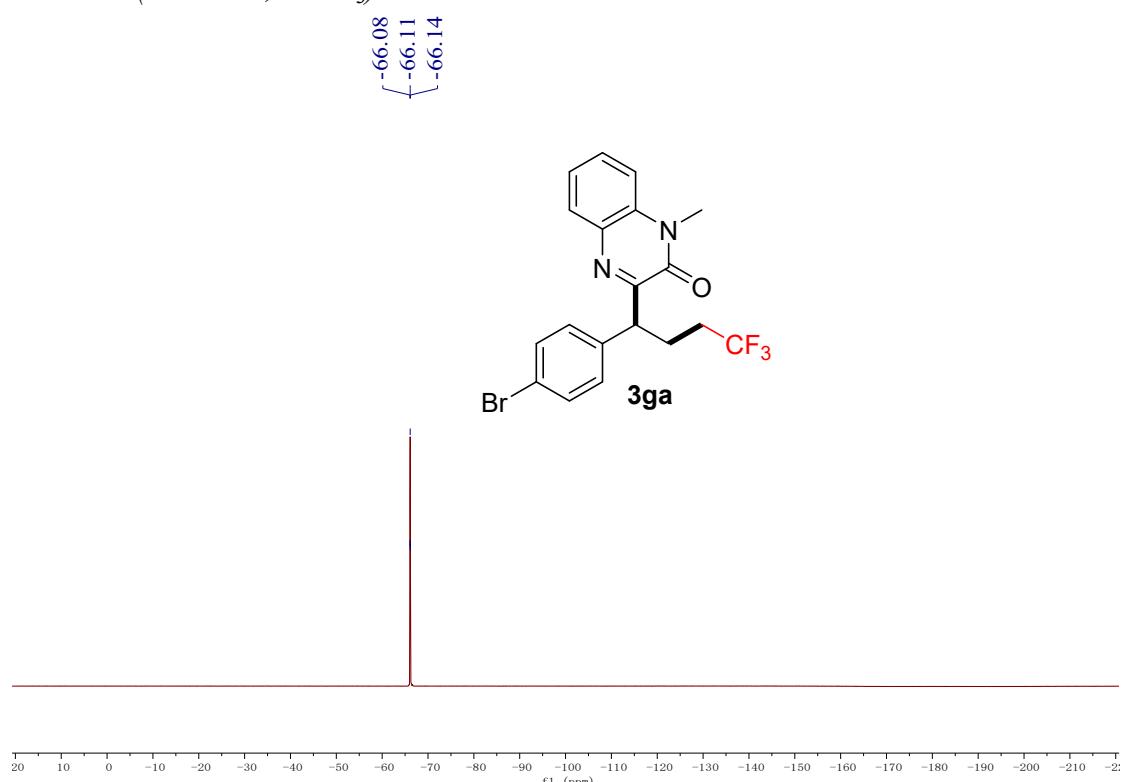
¹H NMR (400 MHz, CDCl₃)



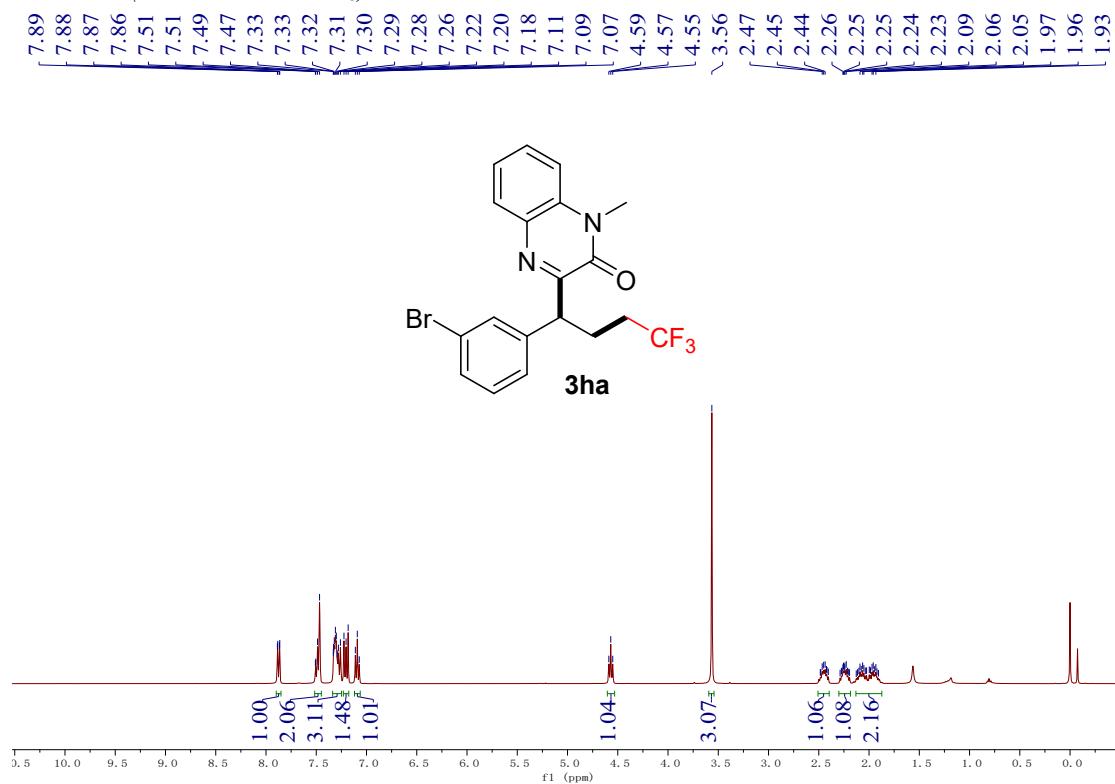
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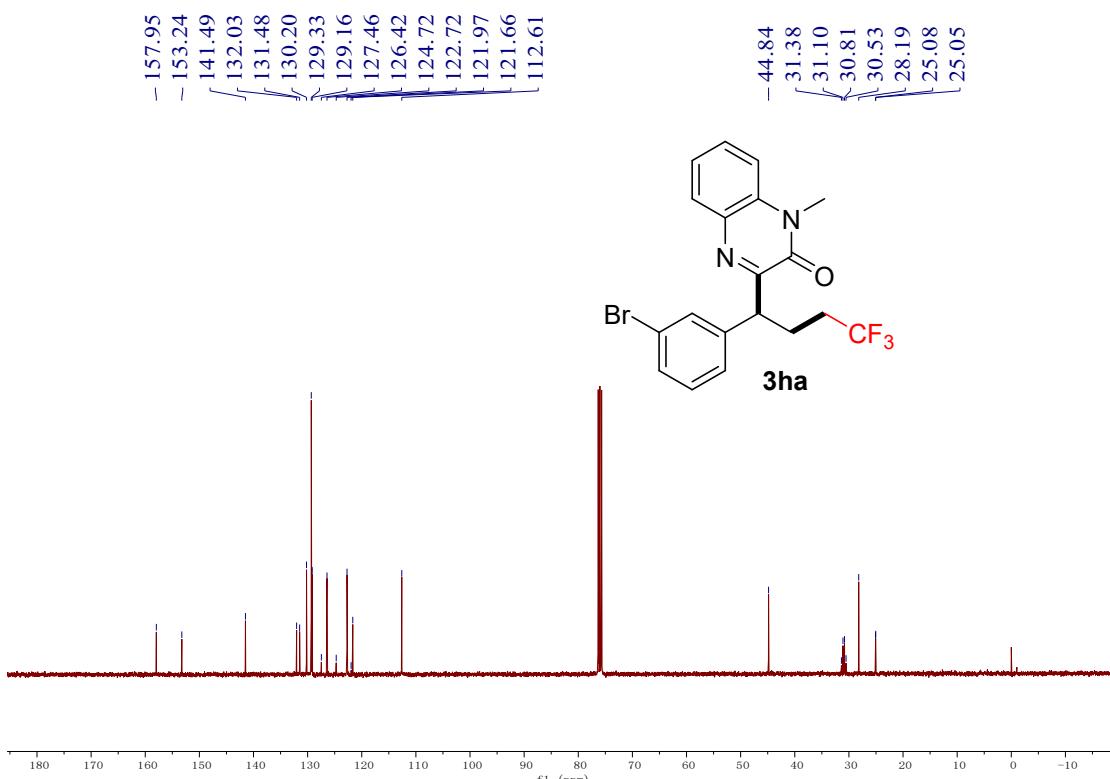
^{19}F NMR (377 MHz, $CDCl_3$)



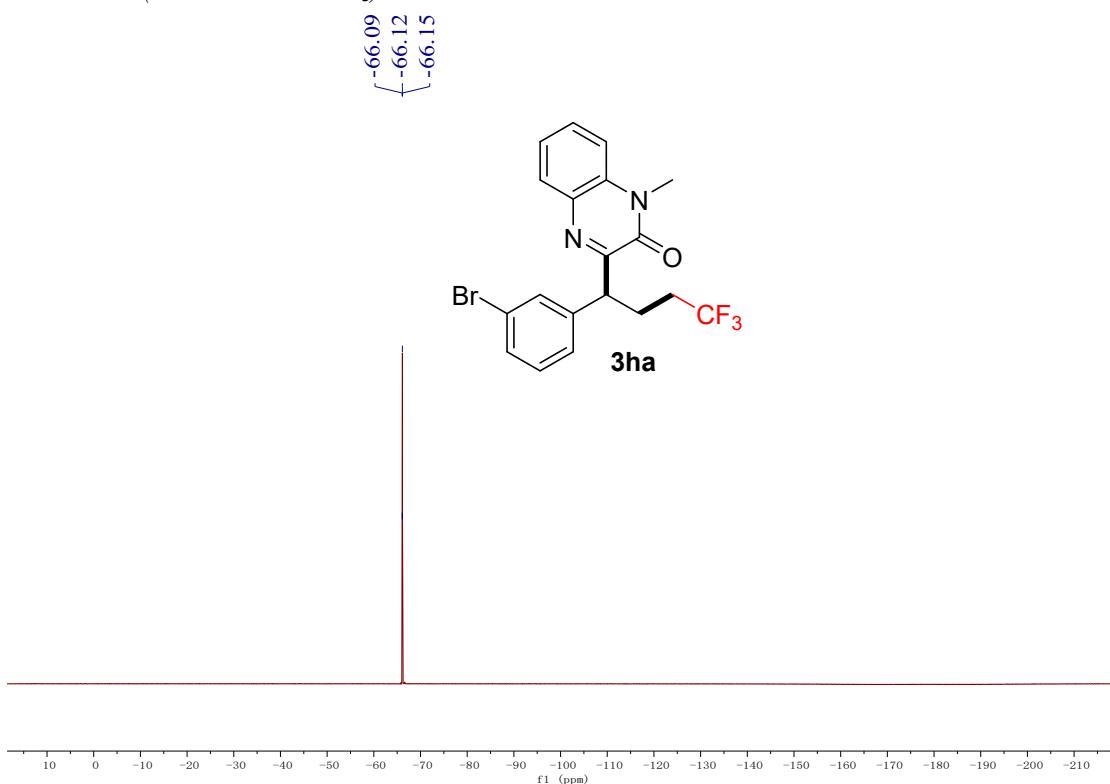
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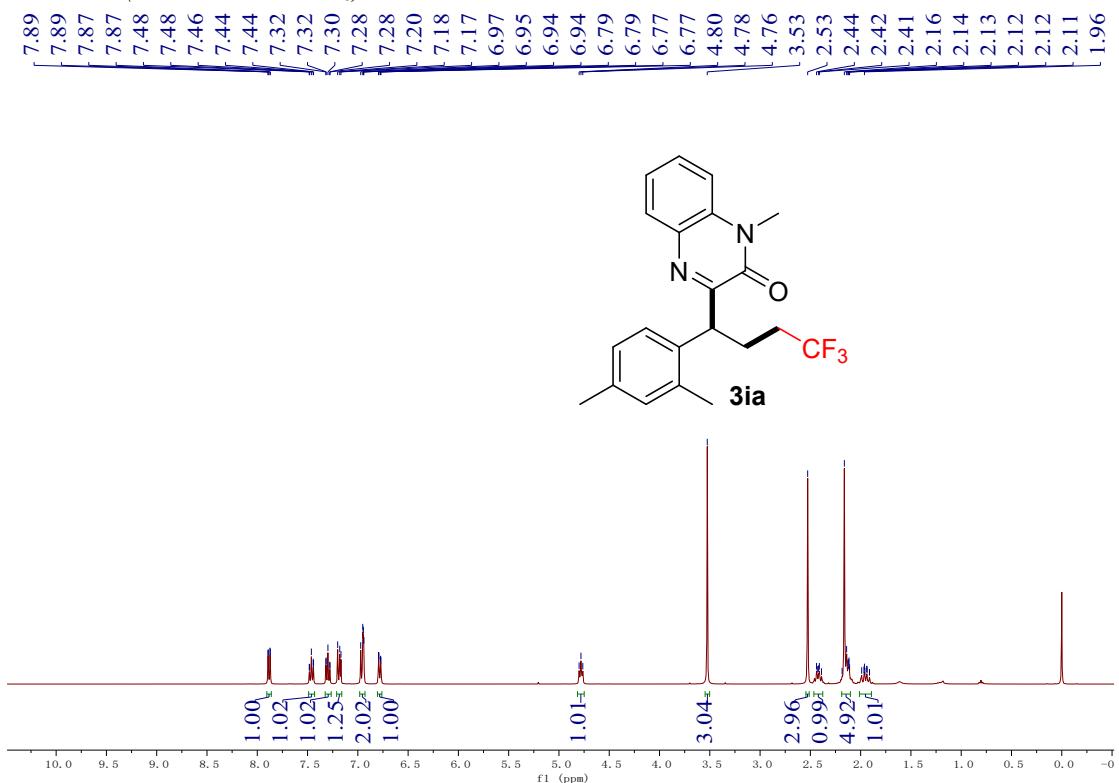
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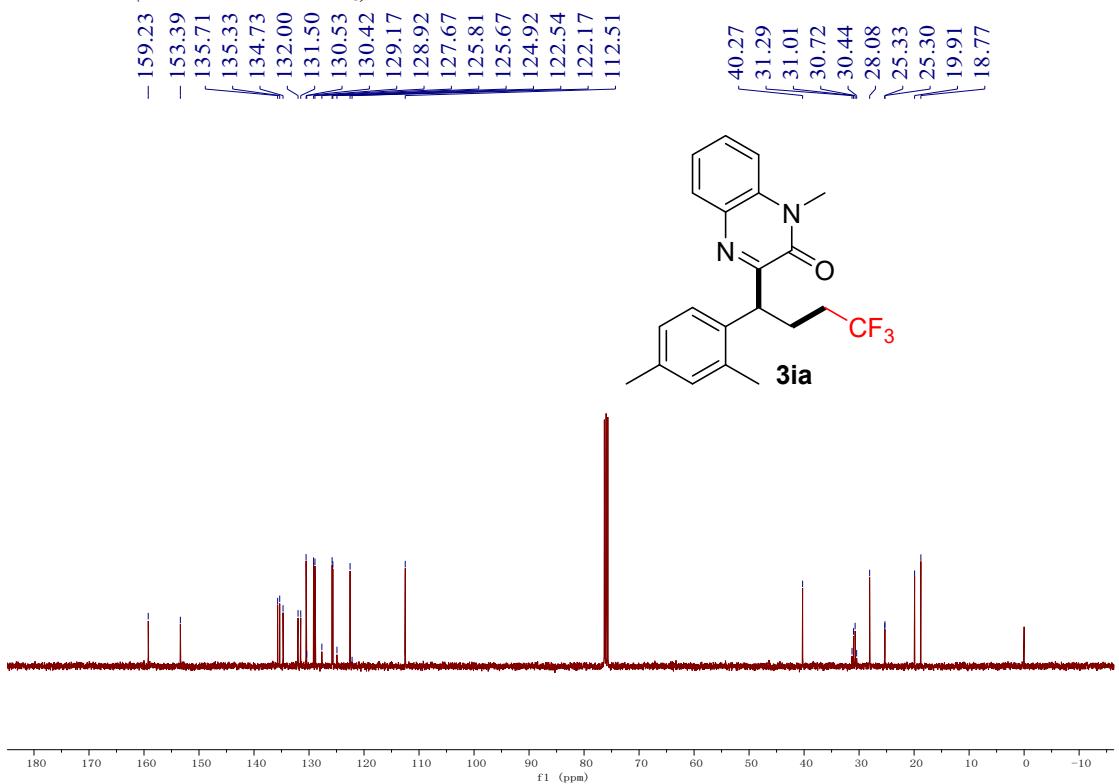
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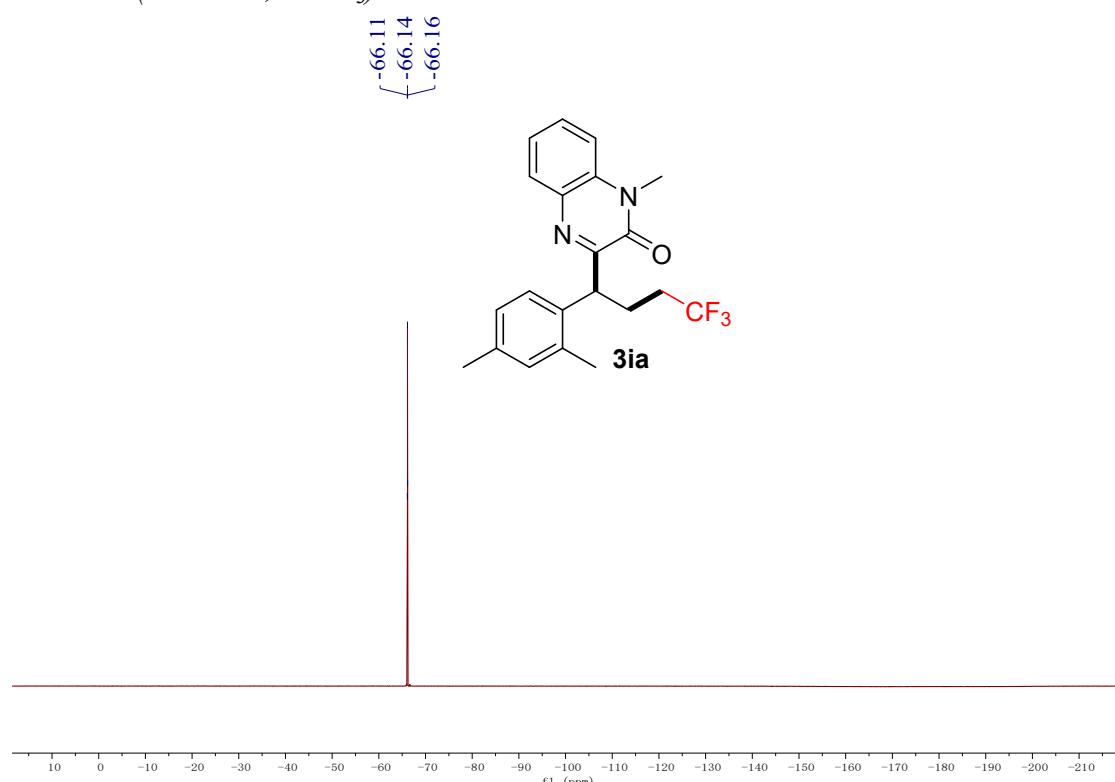
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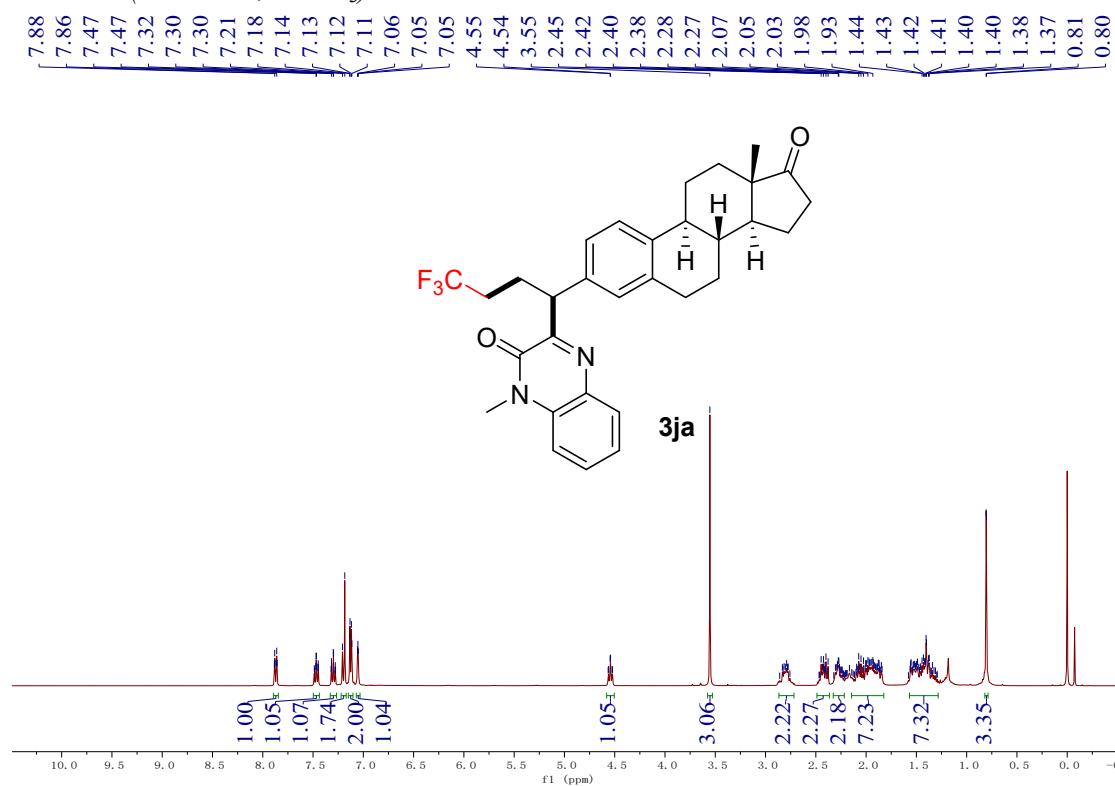
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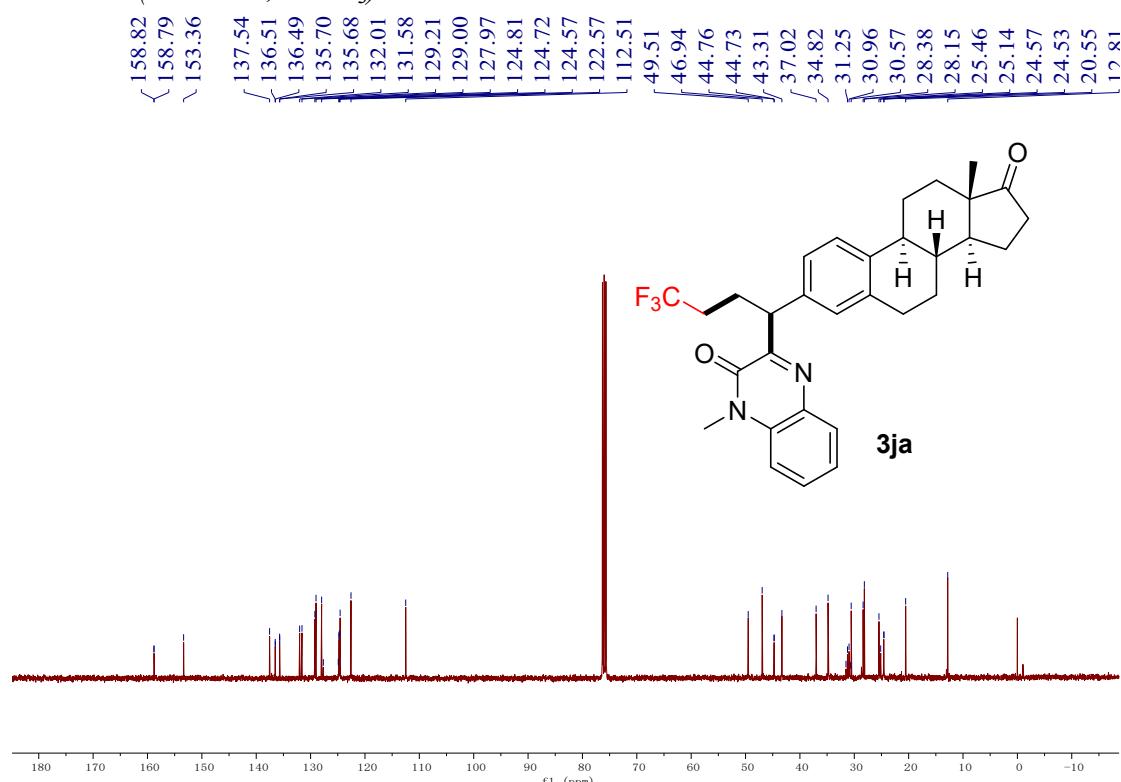
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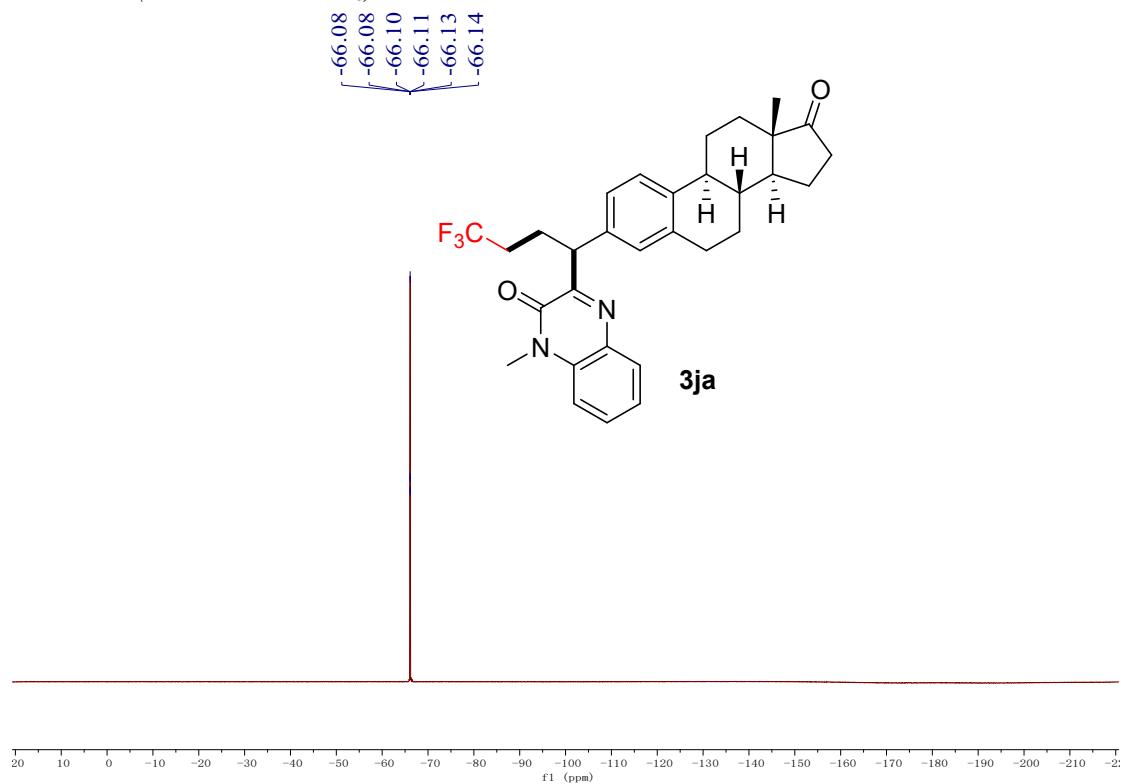
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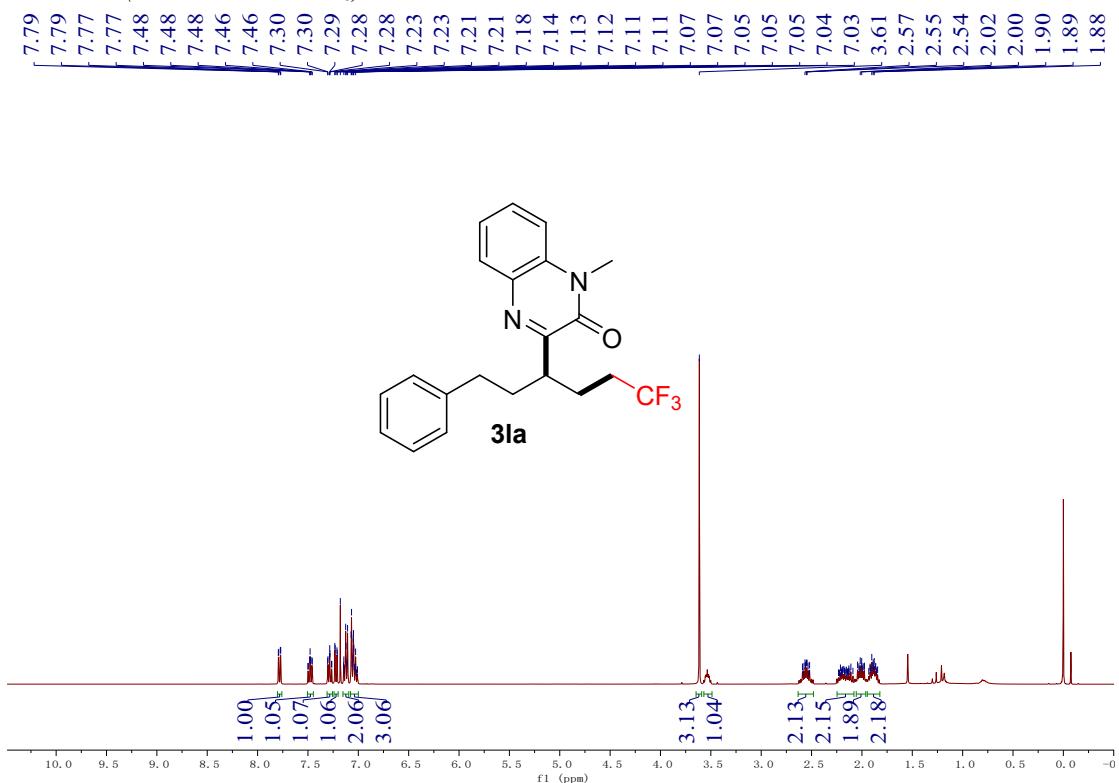
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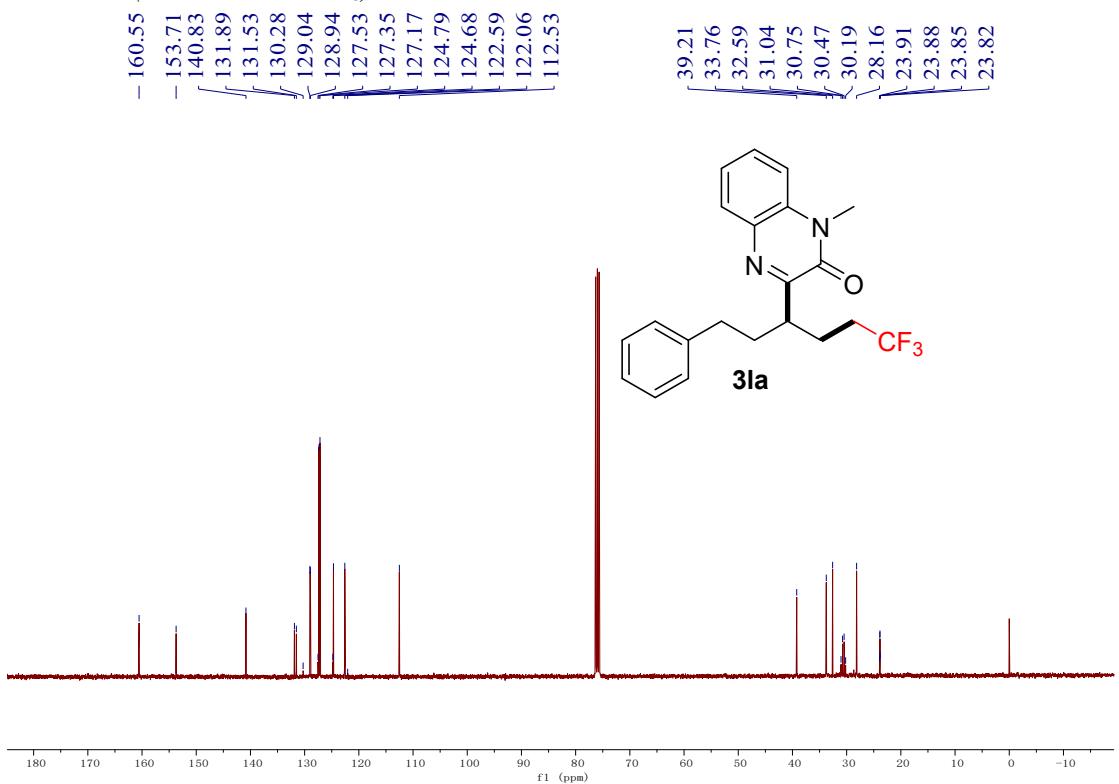
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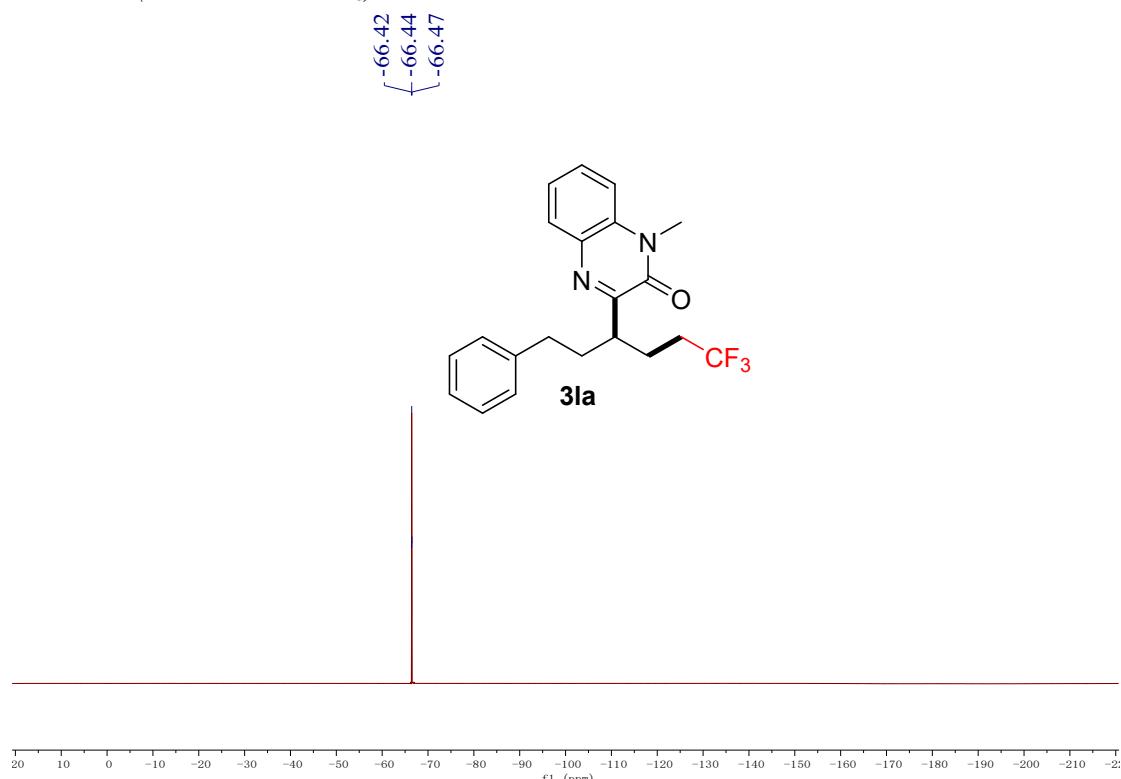
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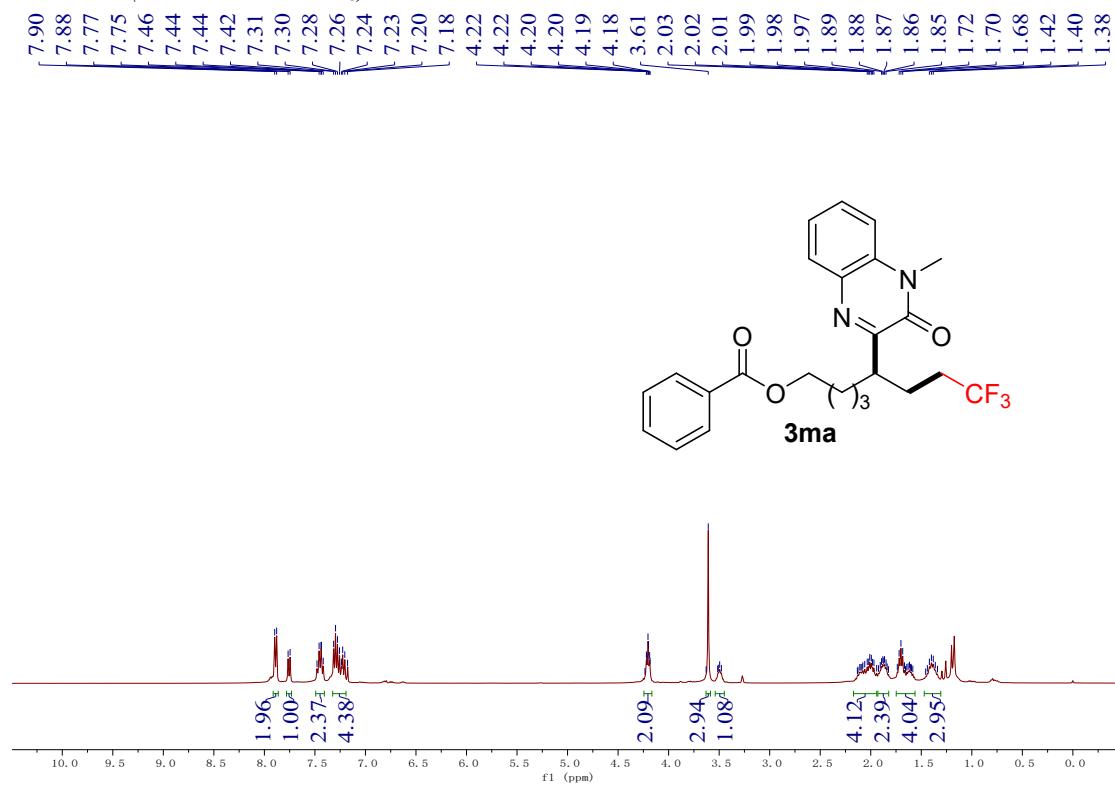
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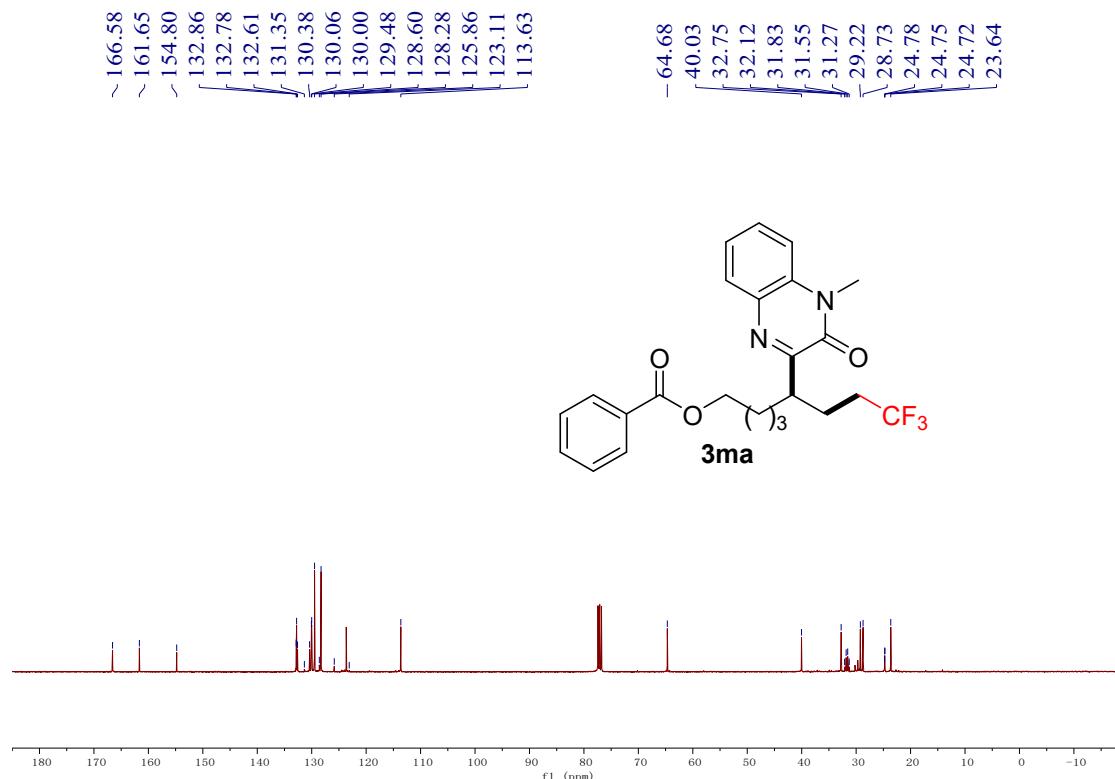
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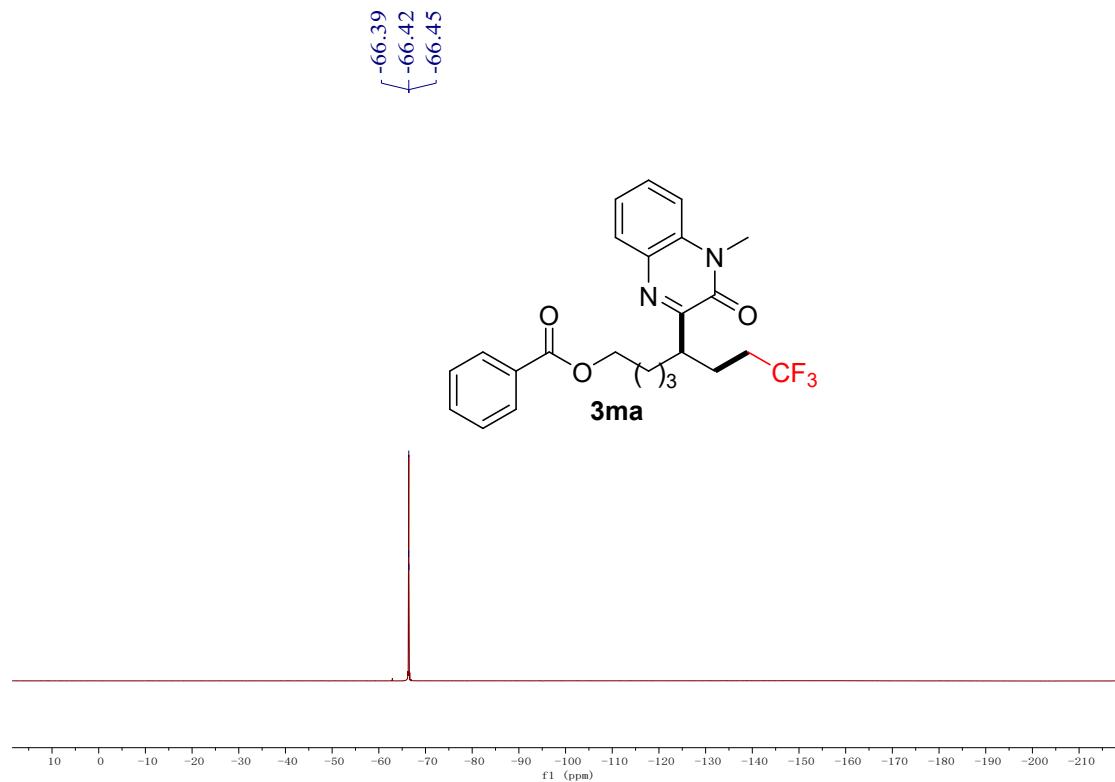
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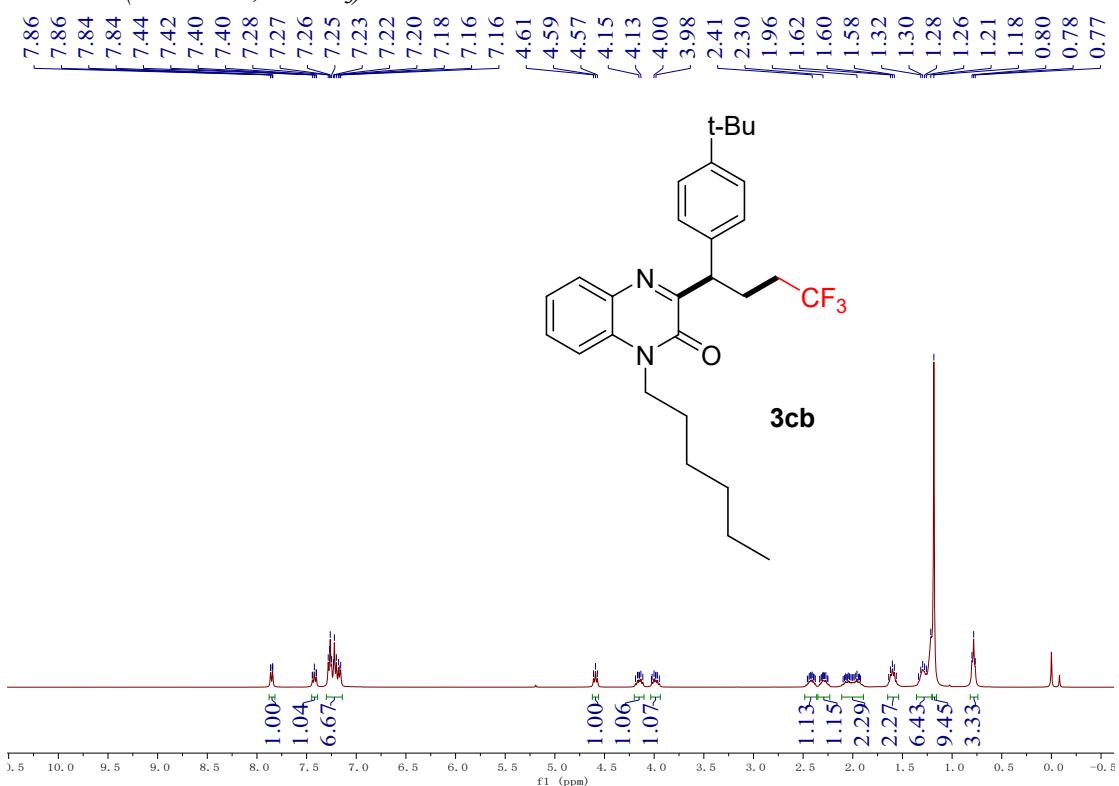
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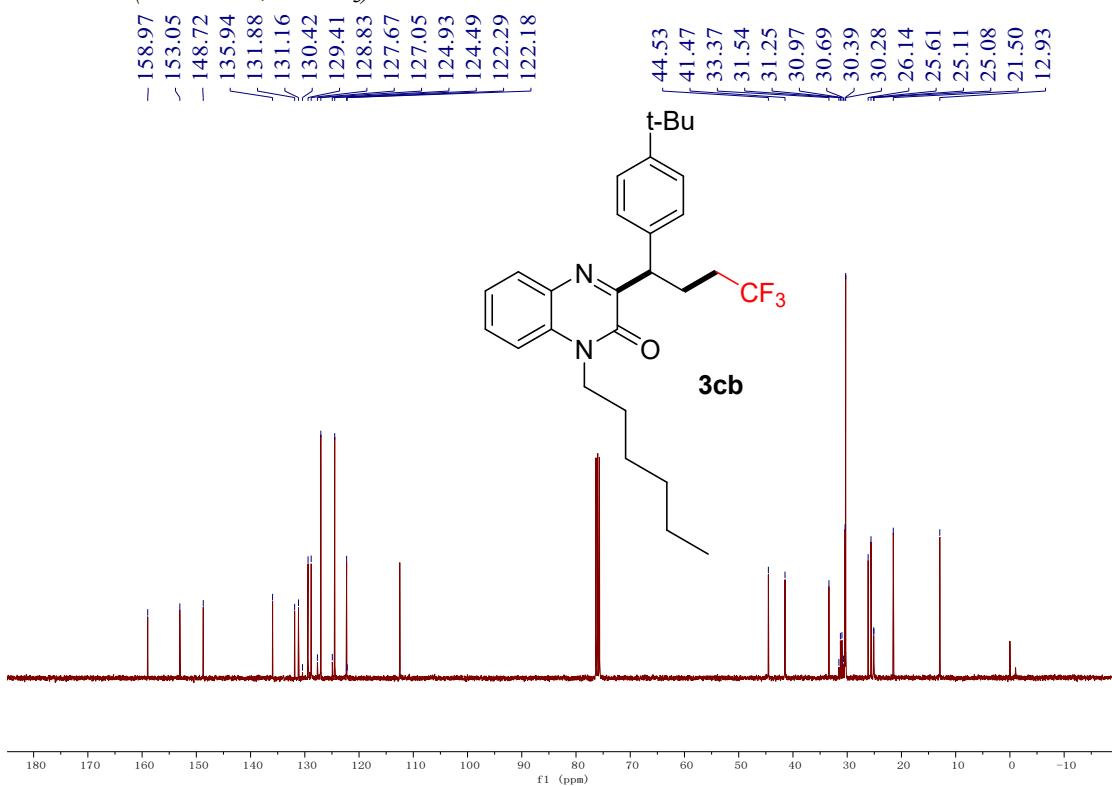
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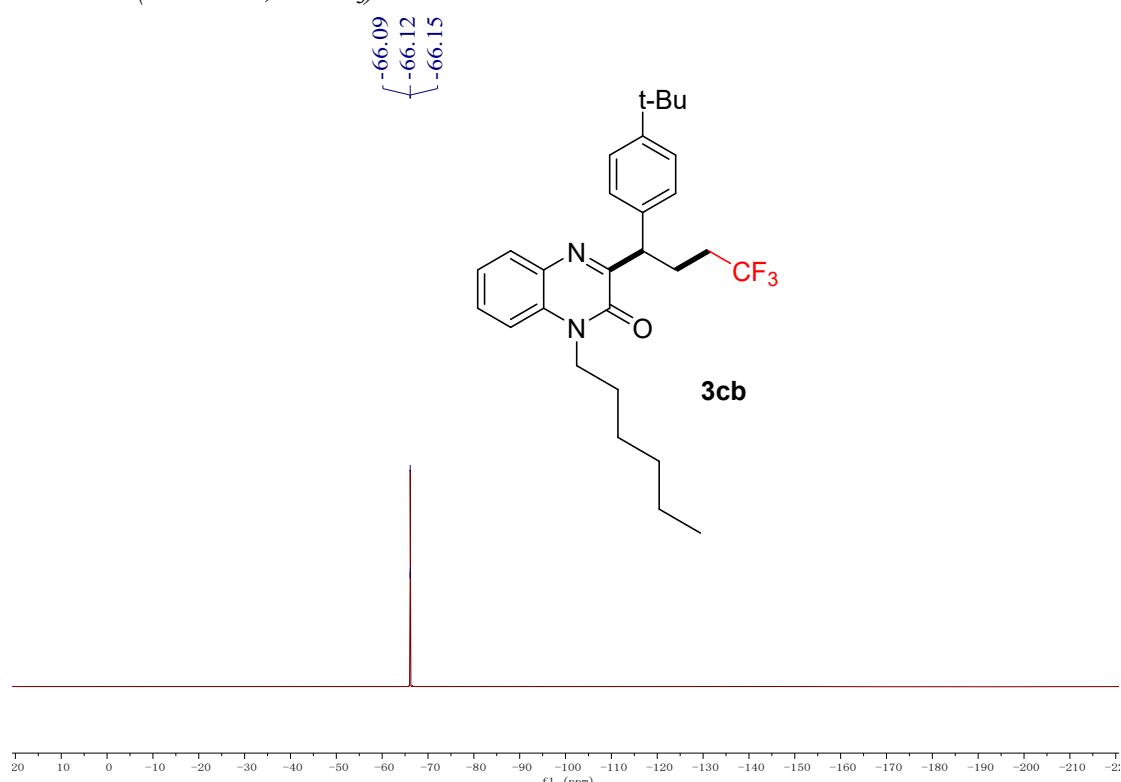
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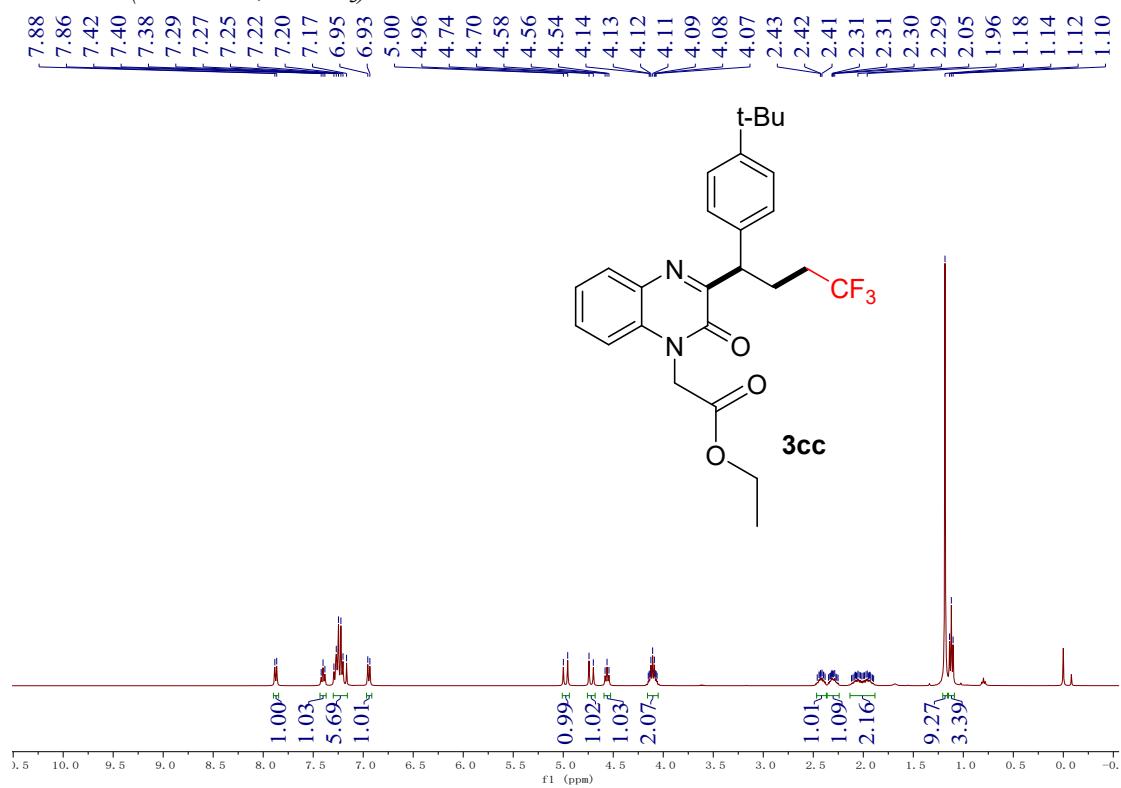
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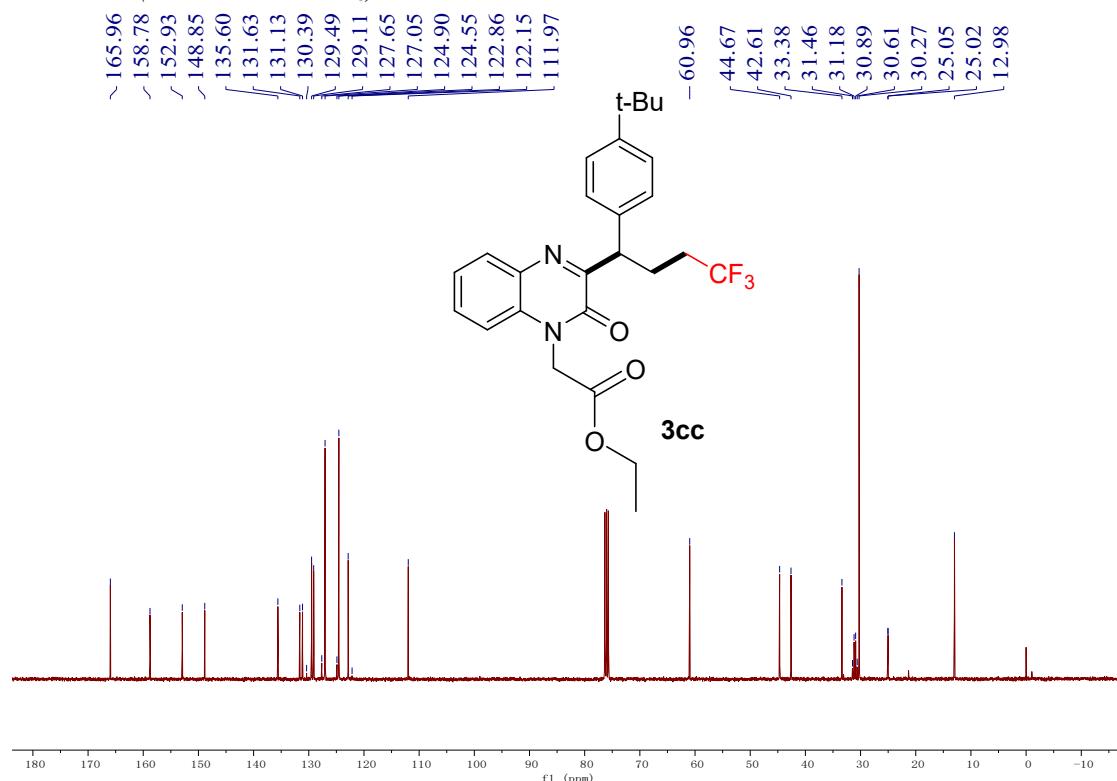
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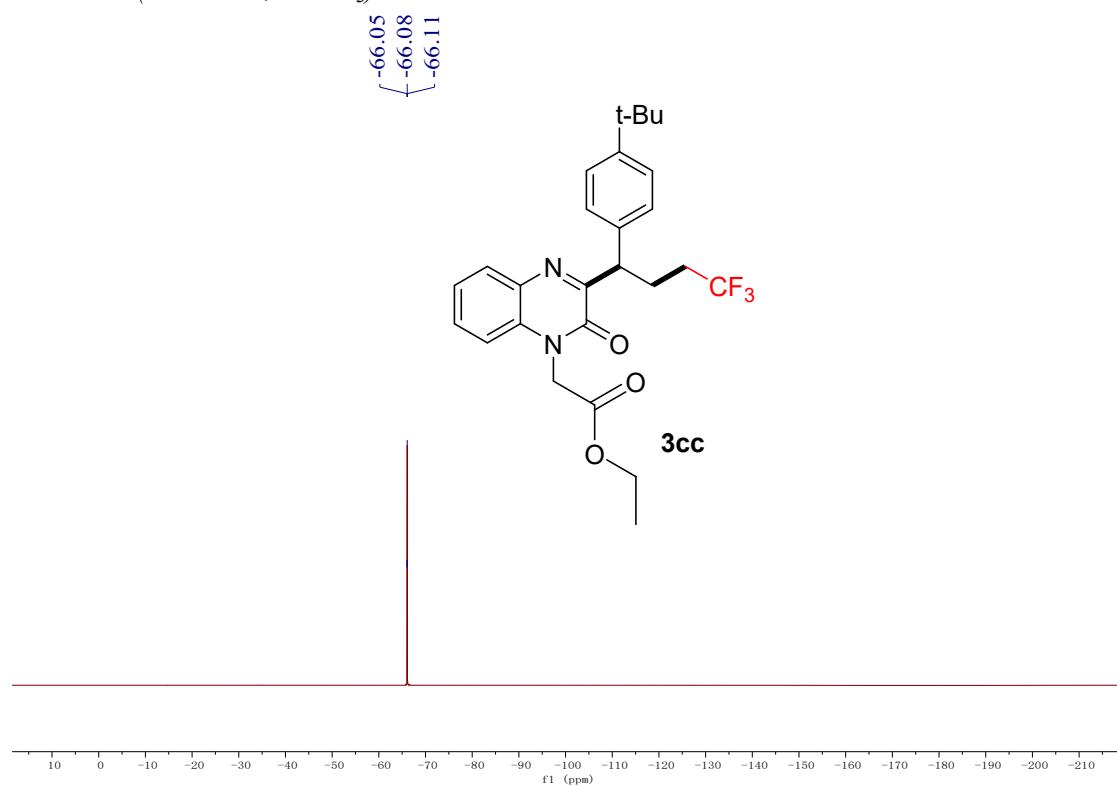
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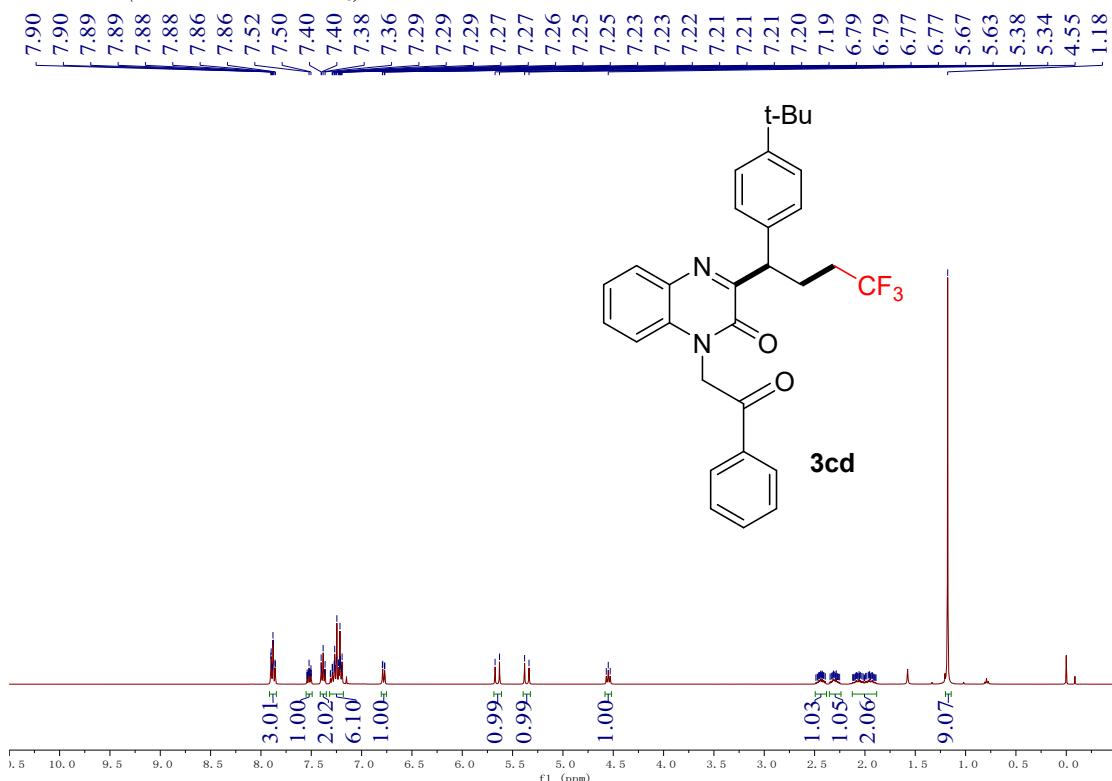
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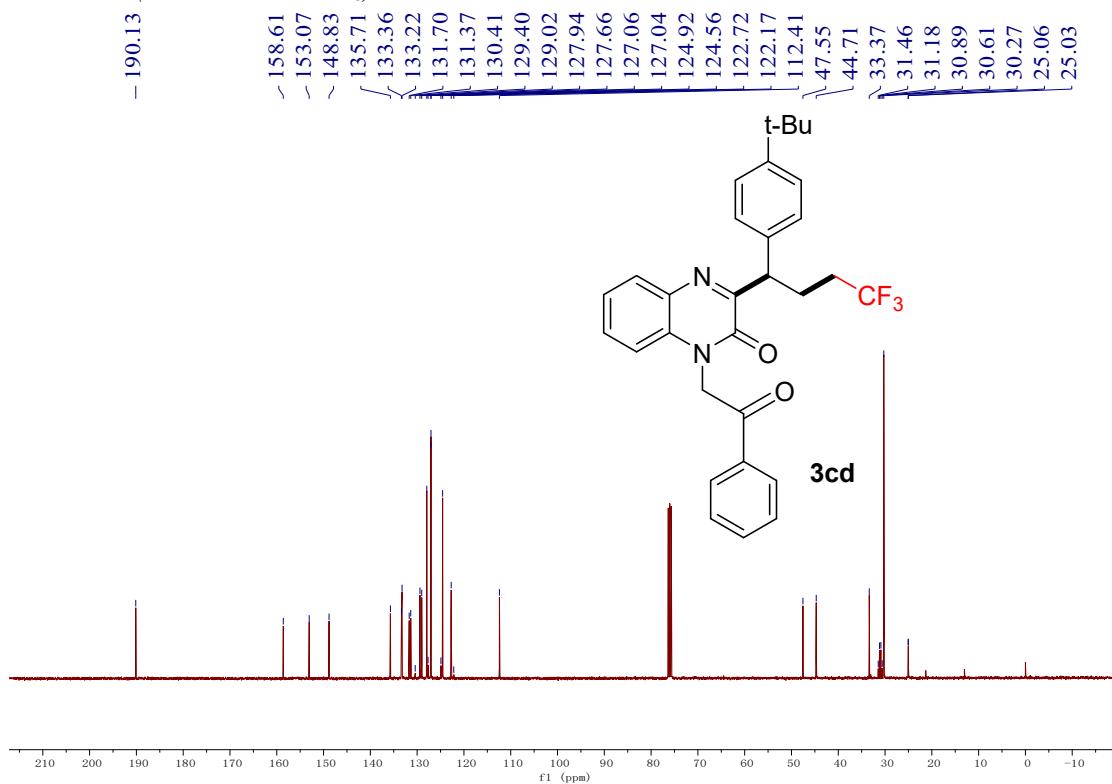
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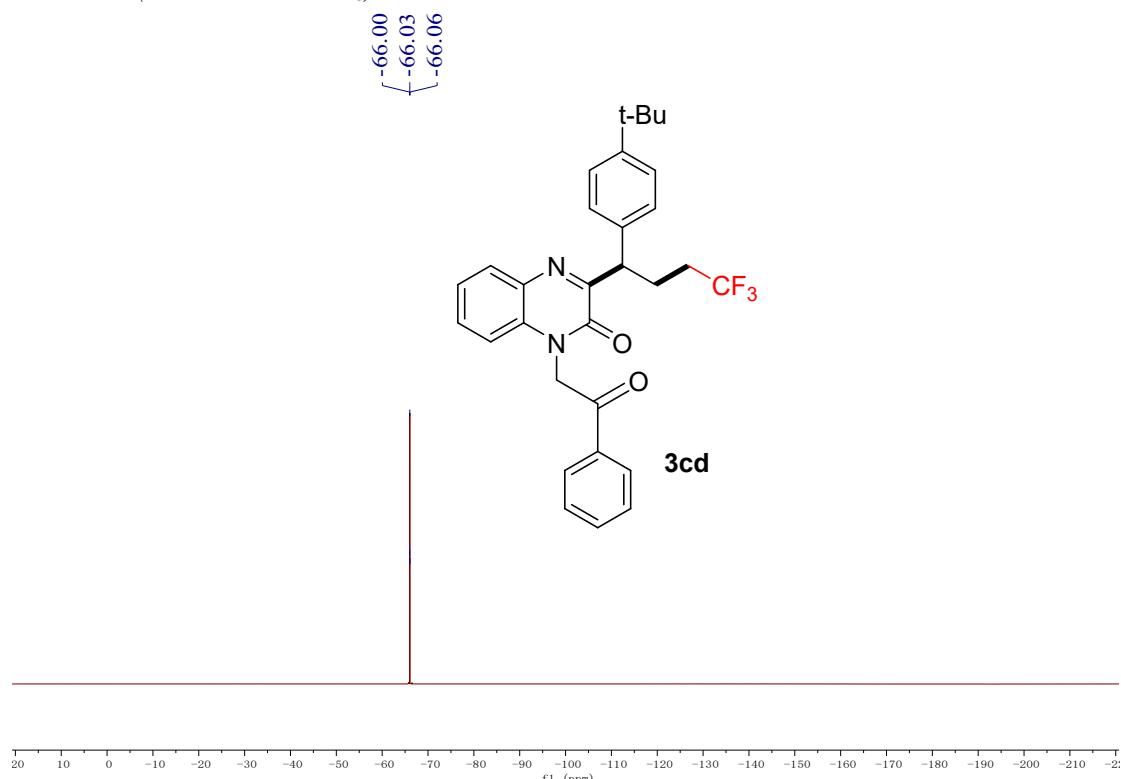
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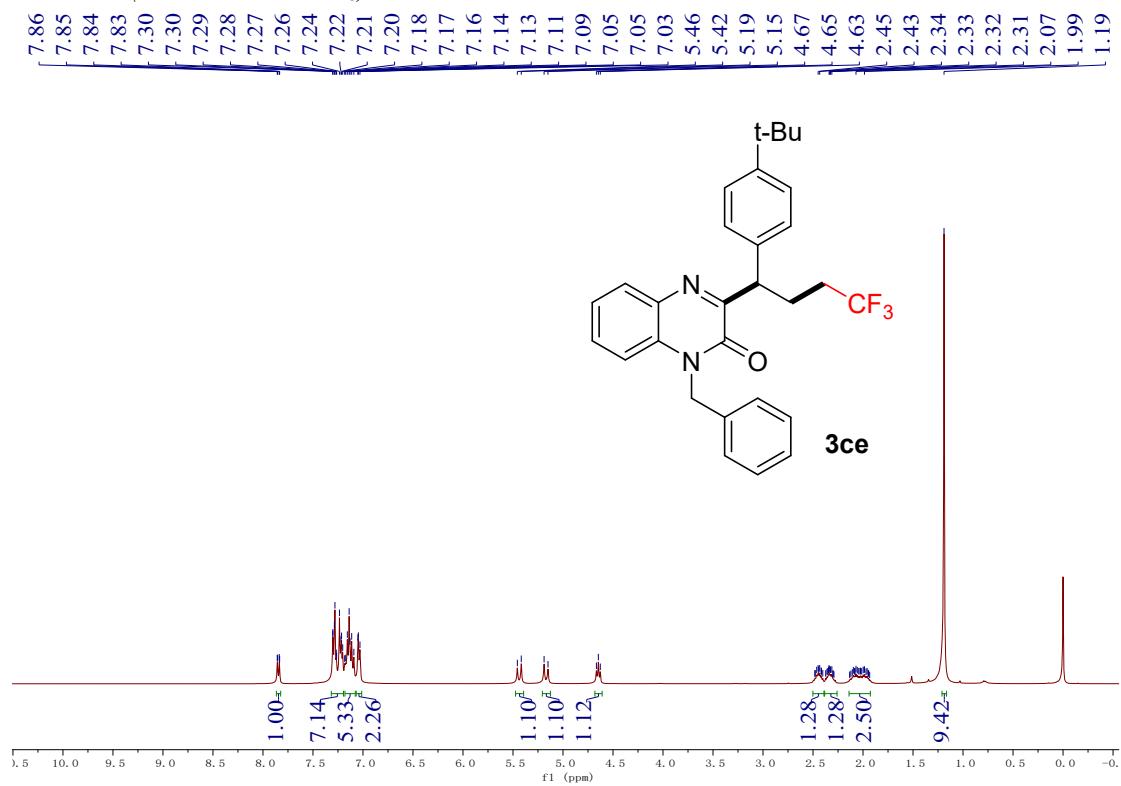
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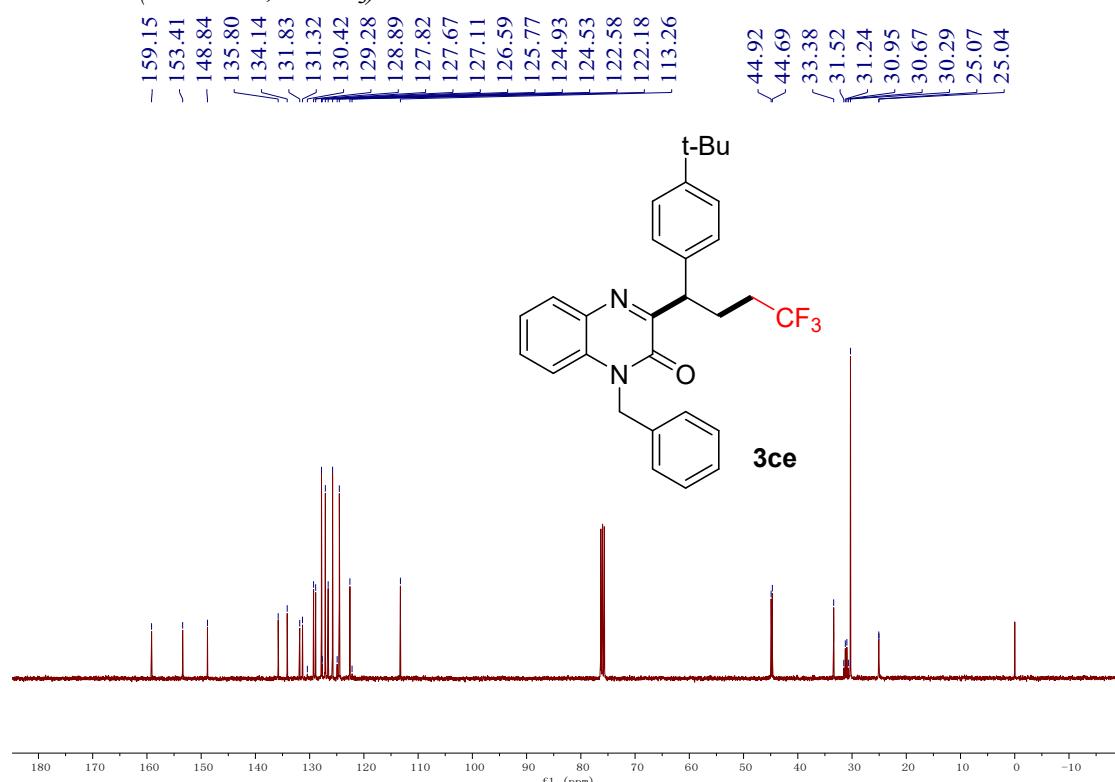
^{19}F NMR ($377\text{ MHz, } \text{CDCl}_3$)



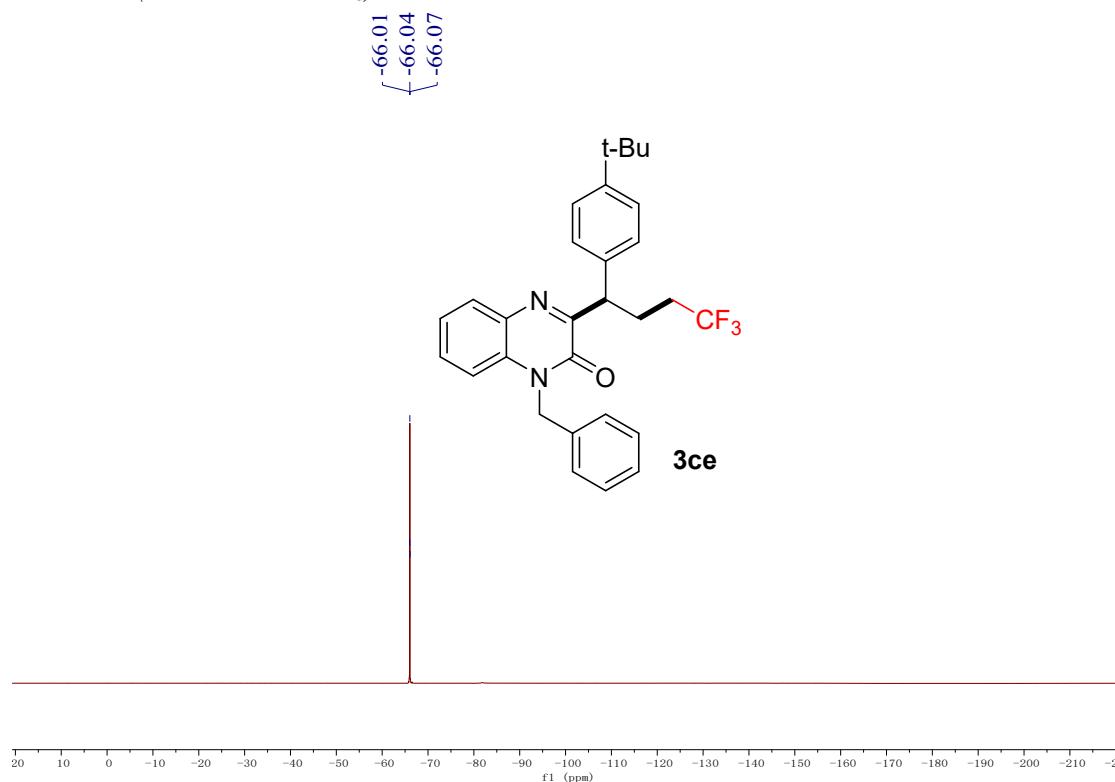
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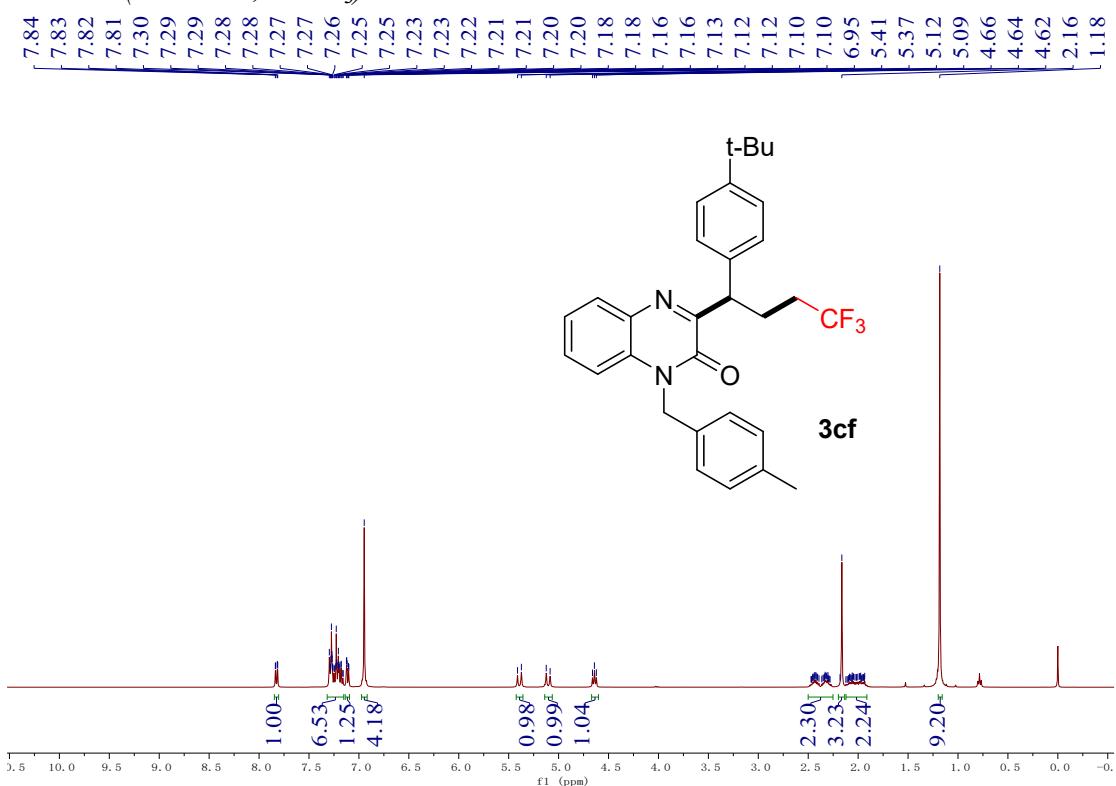
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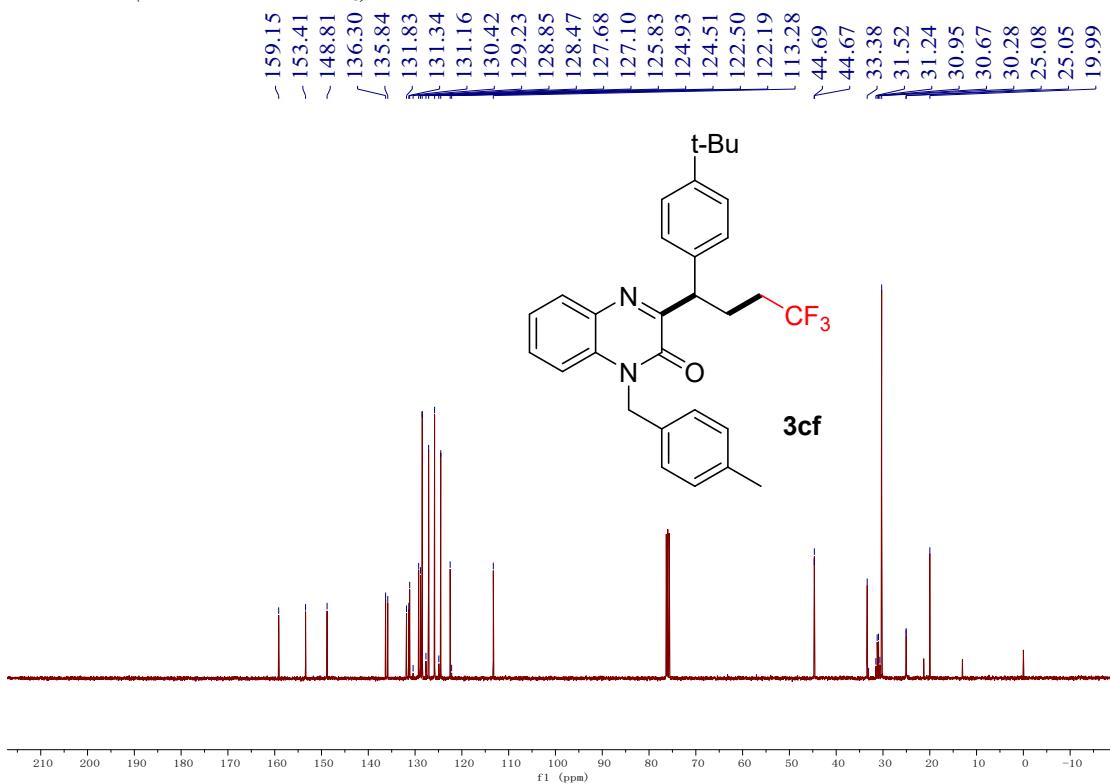
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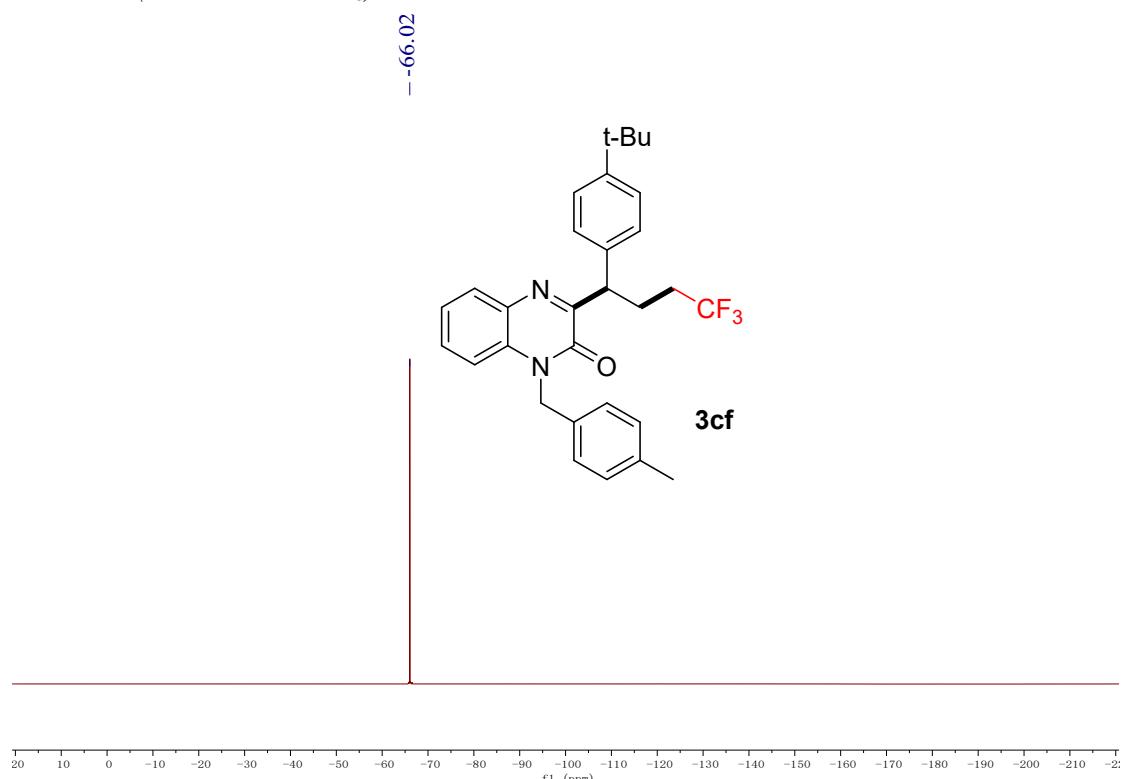
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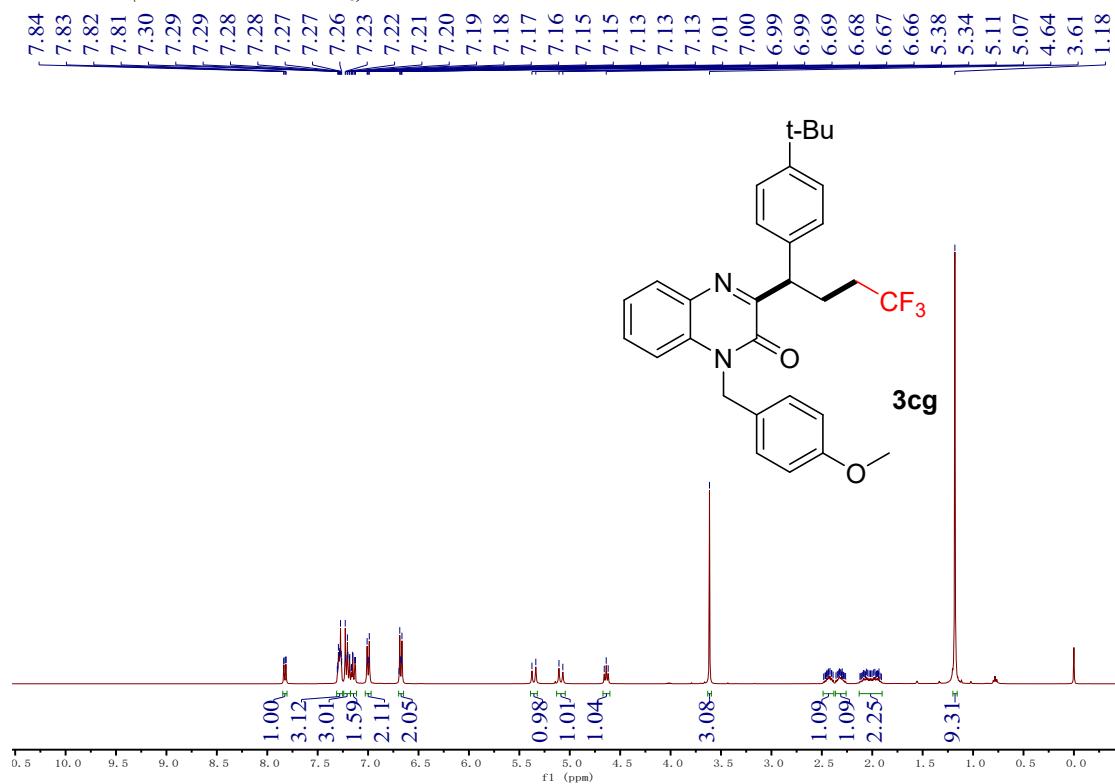
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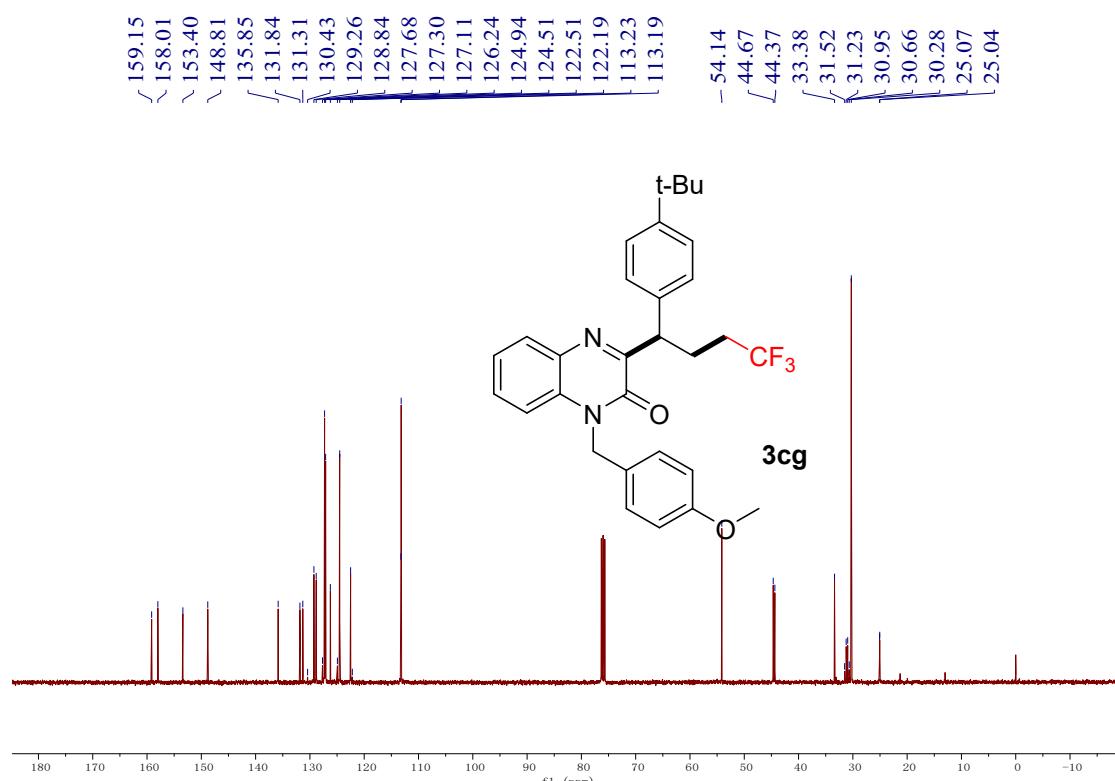
^{19}F NMR ($377\text{ MHz, } \text{CDCl}_3$)



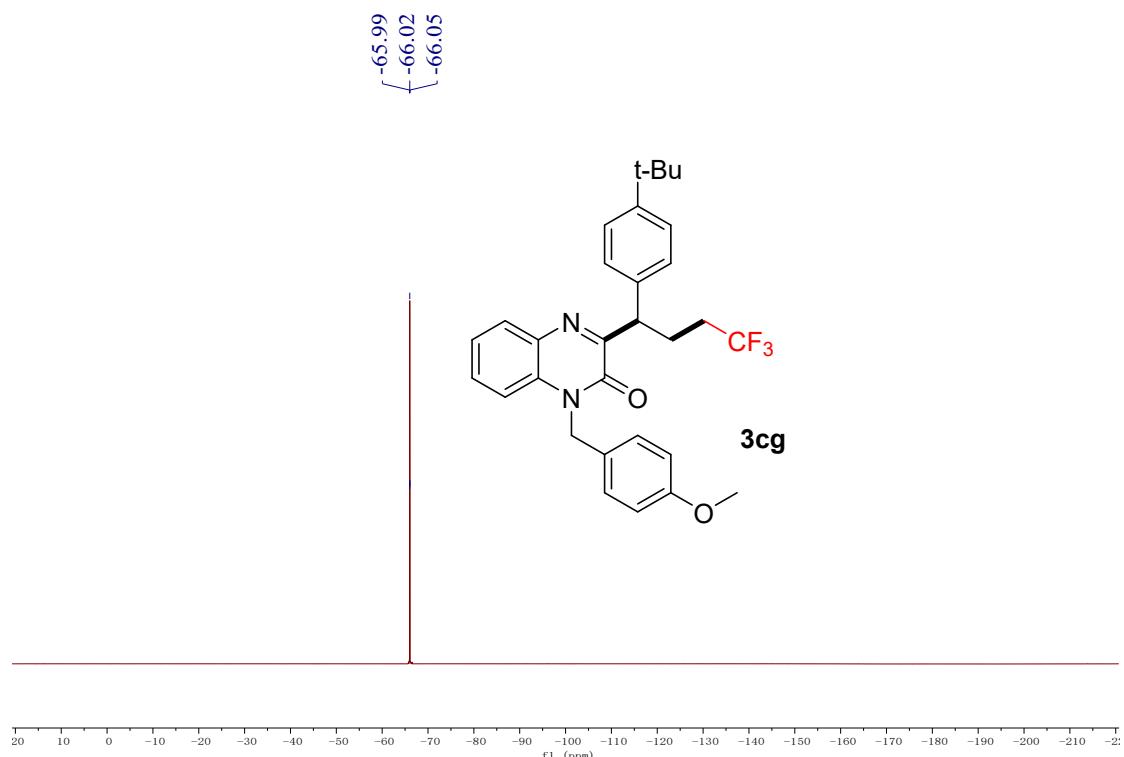
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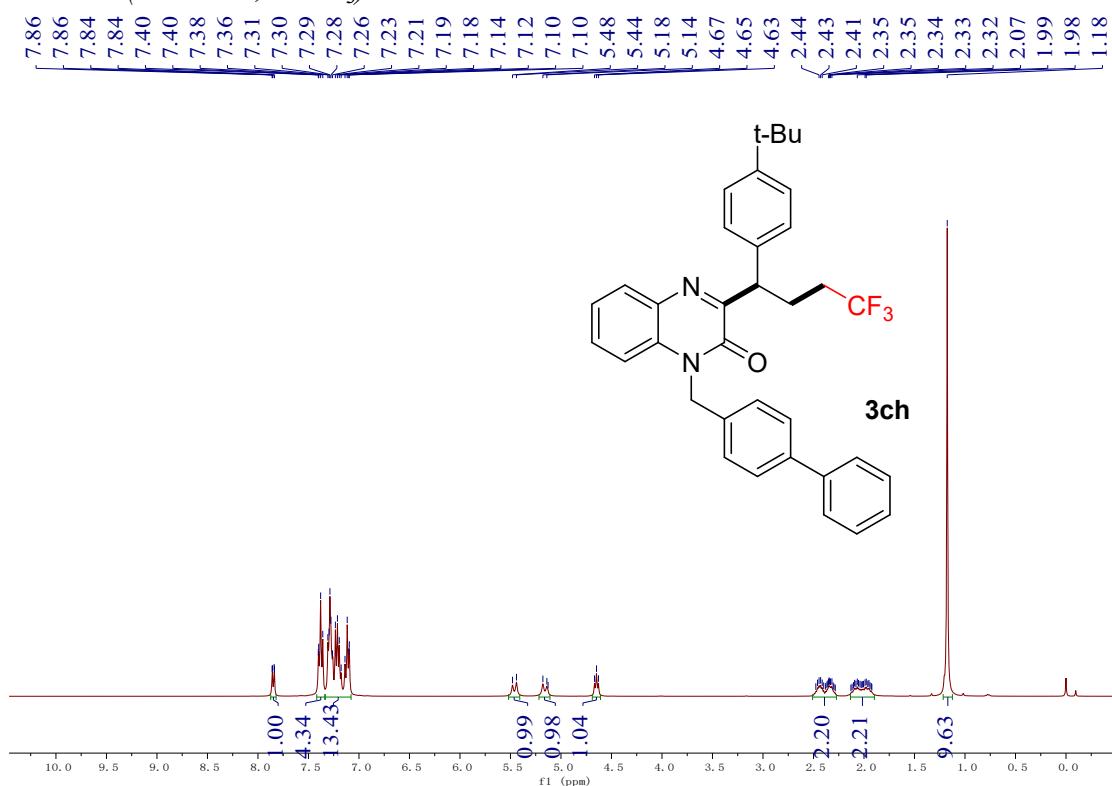
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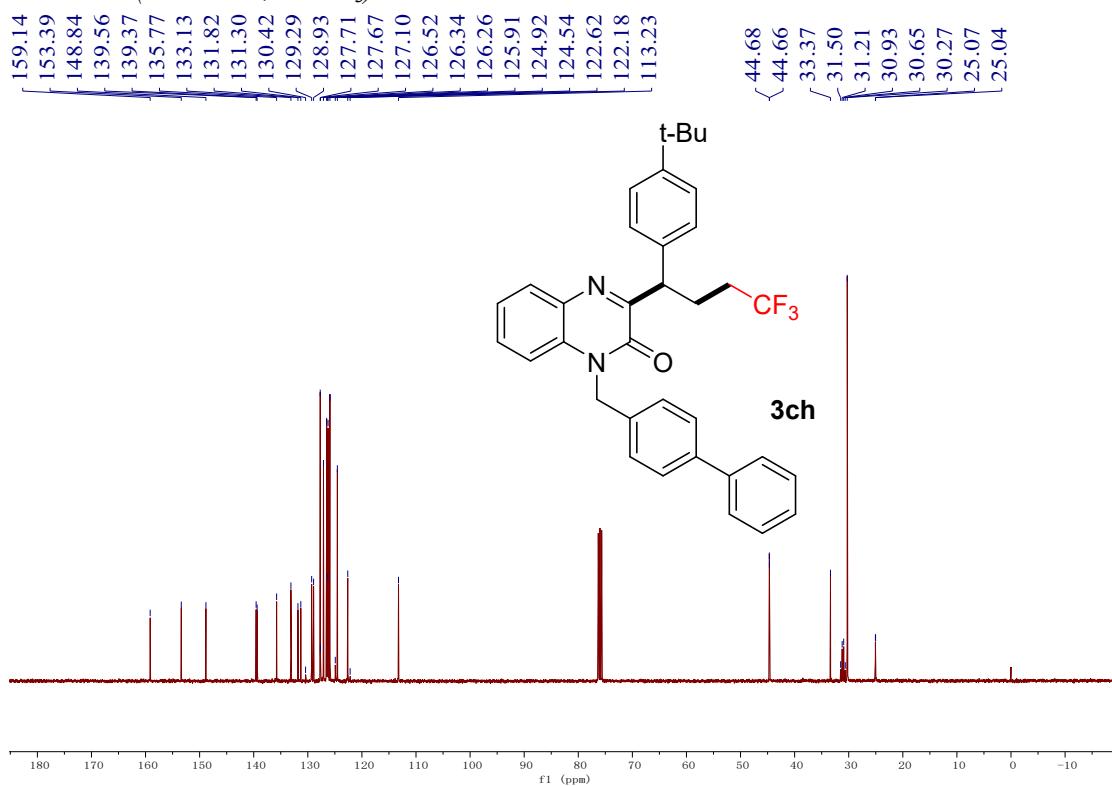
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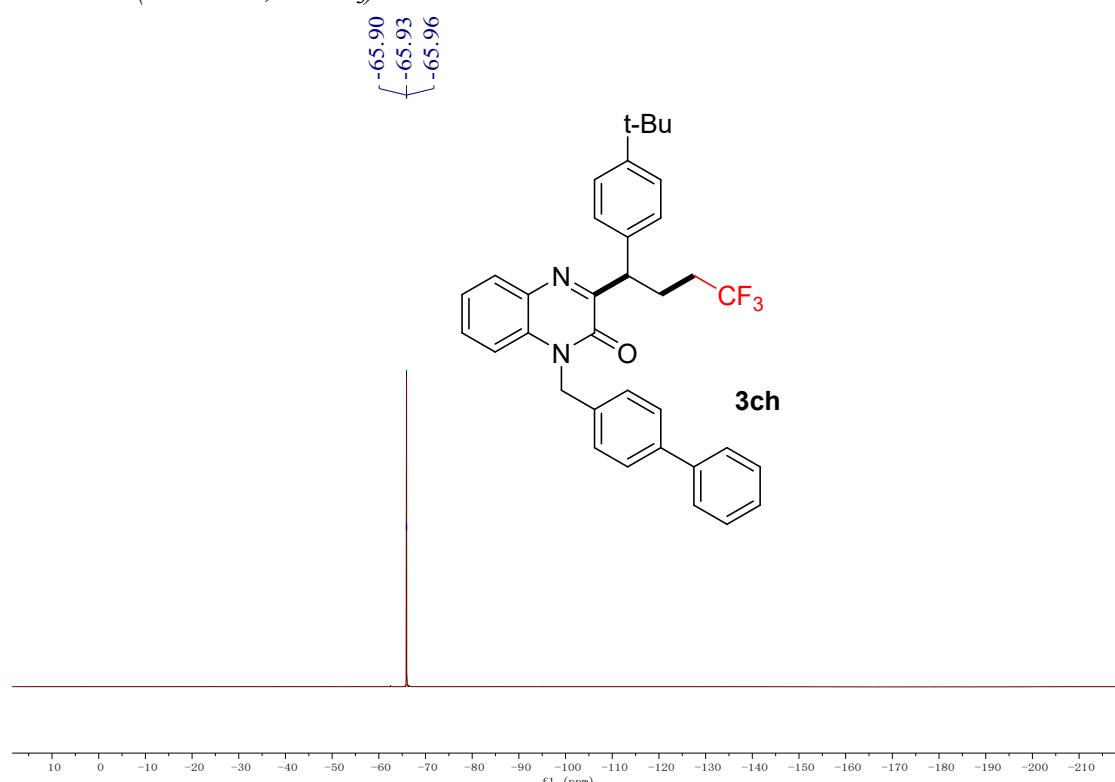
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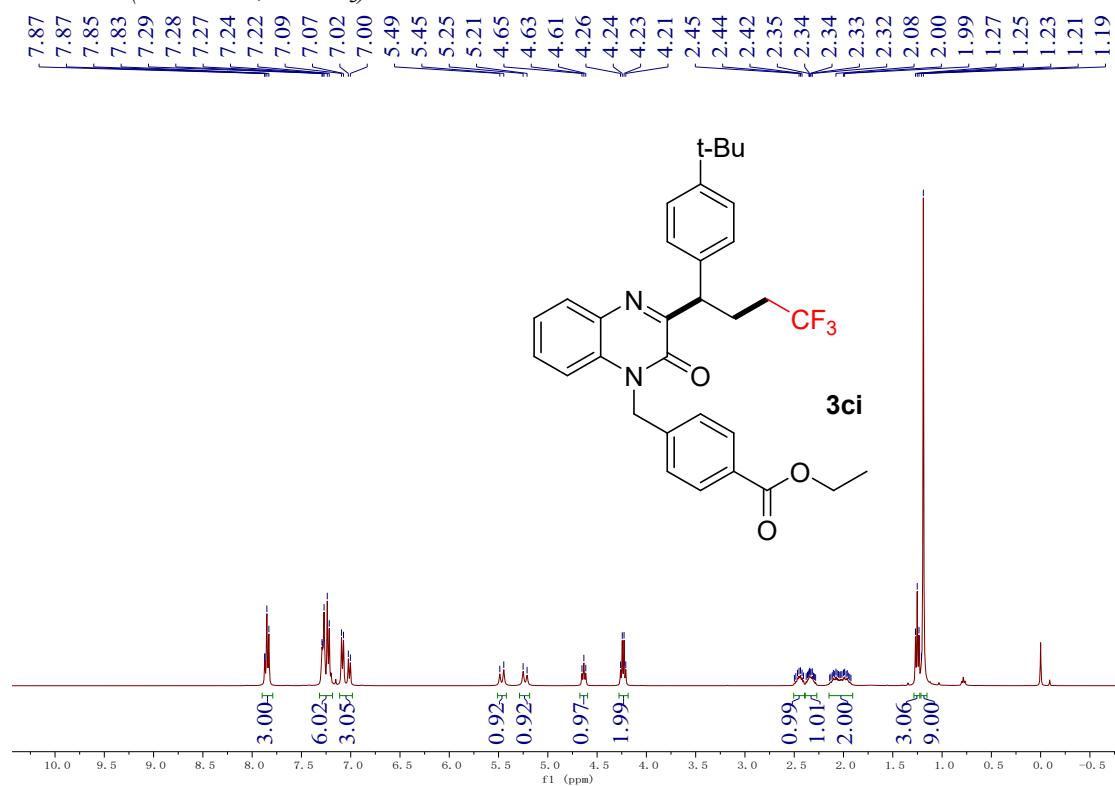
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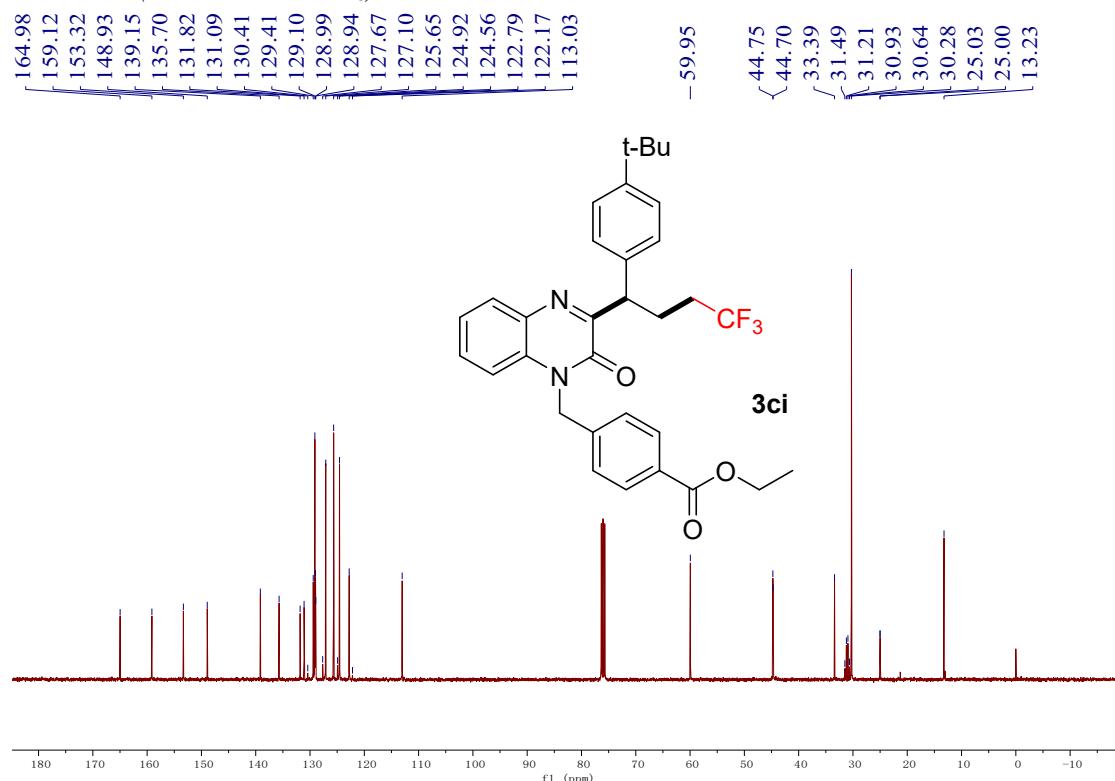
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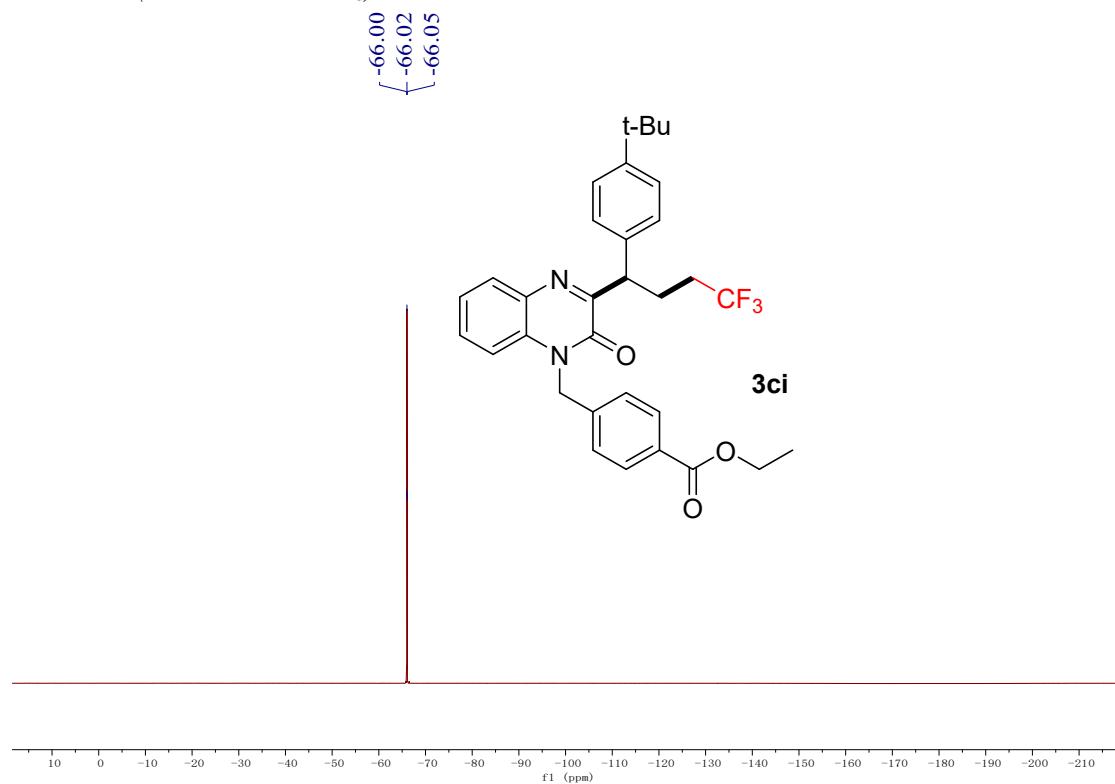
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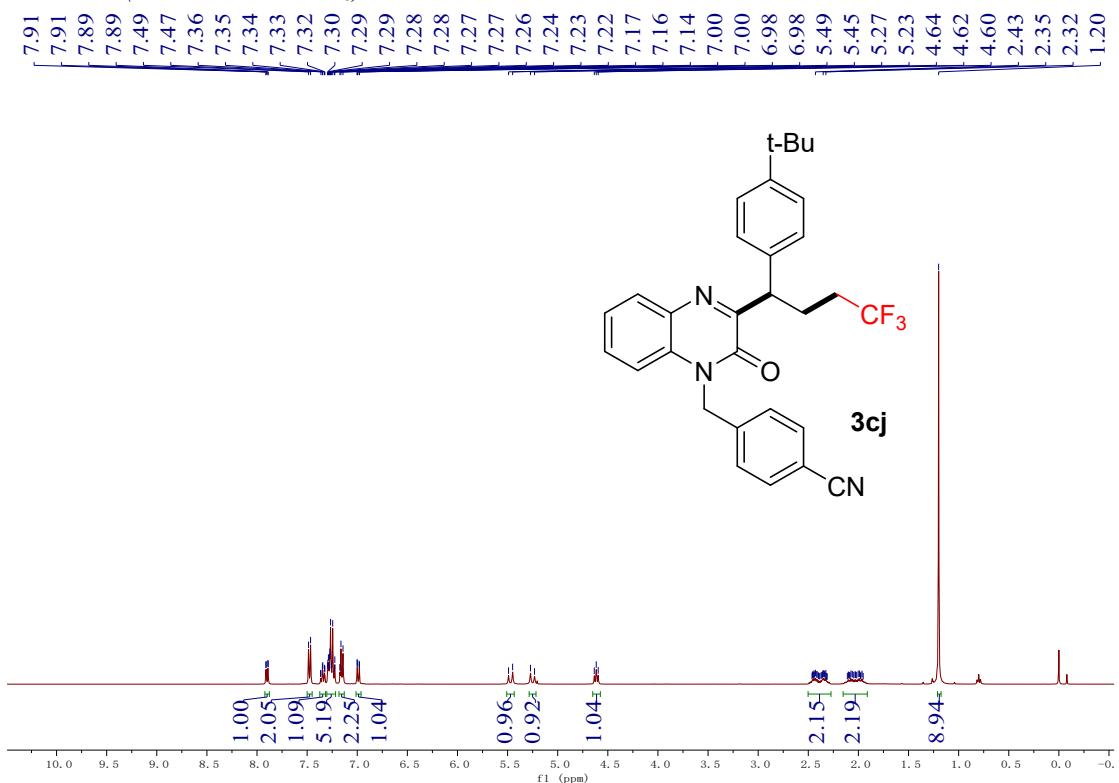
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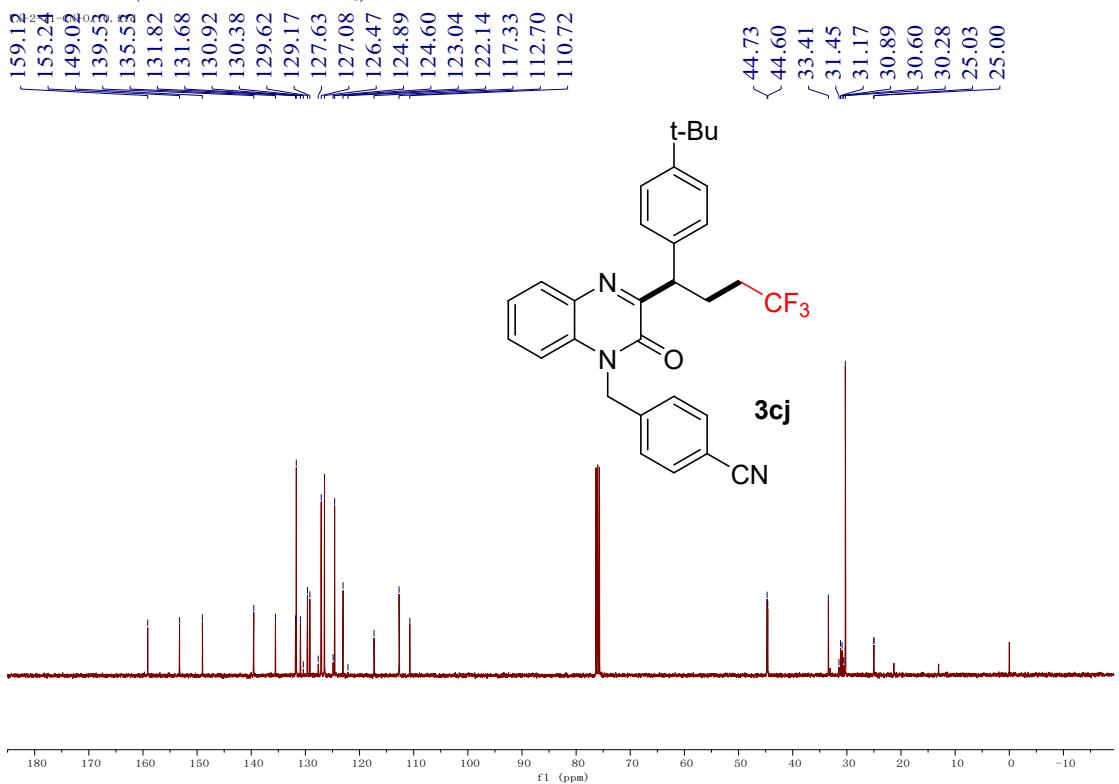
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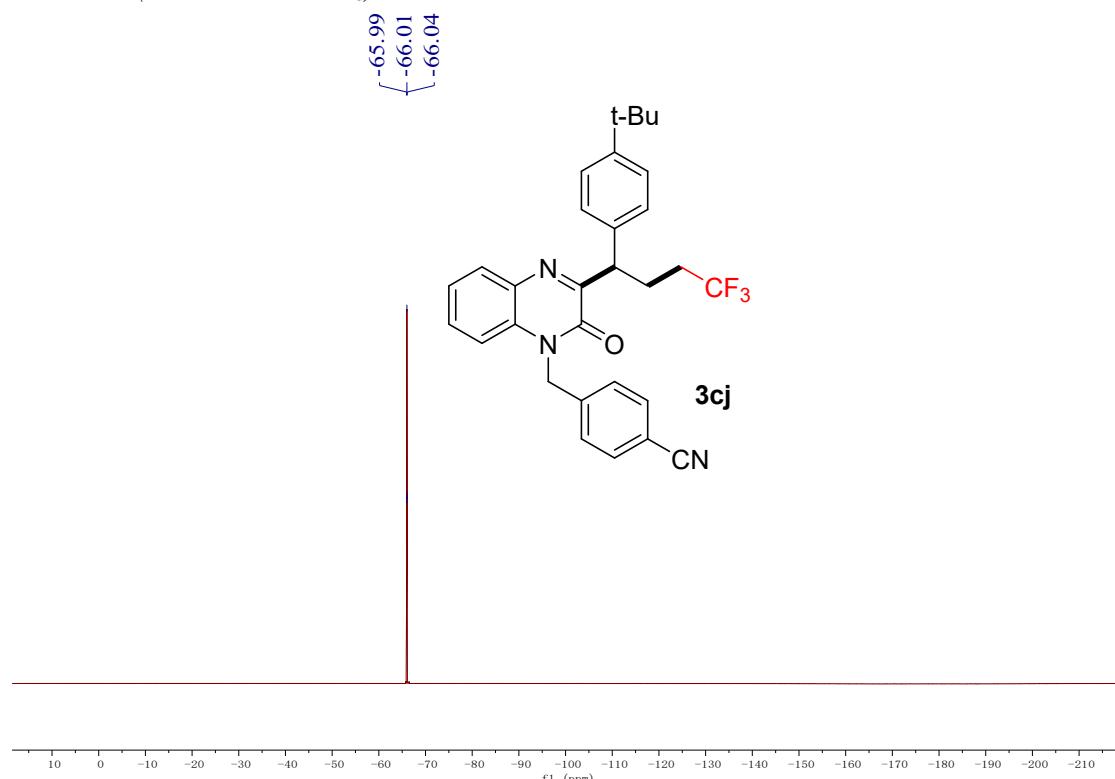
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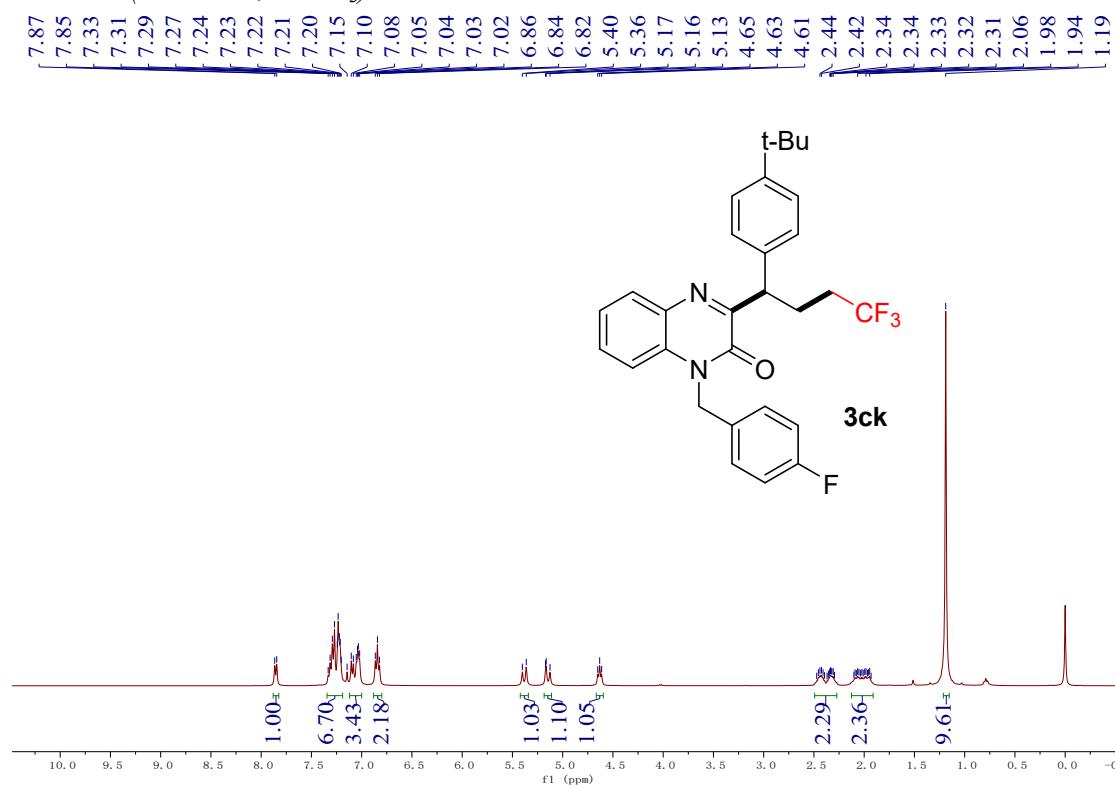
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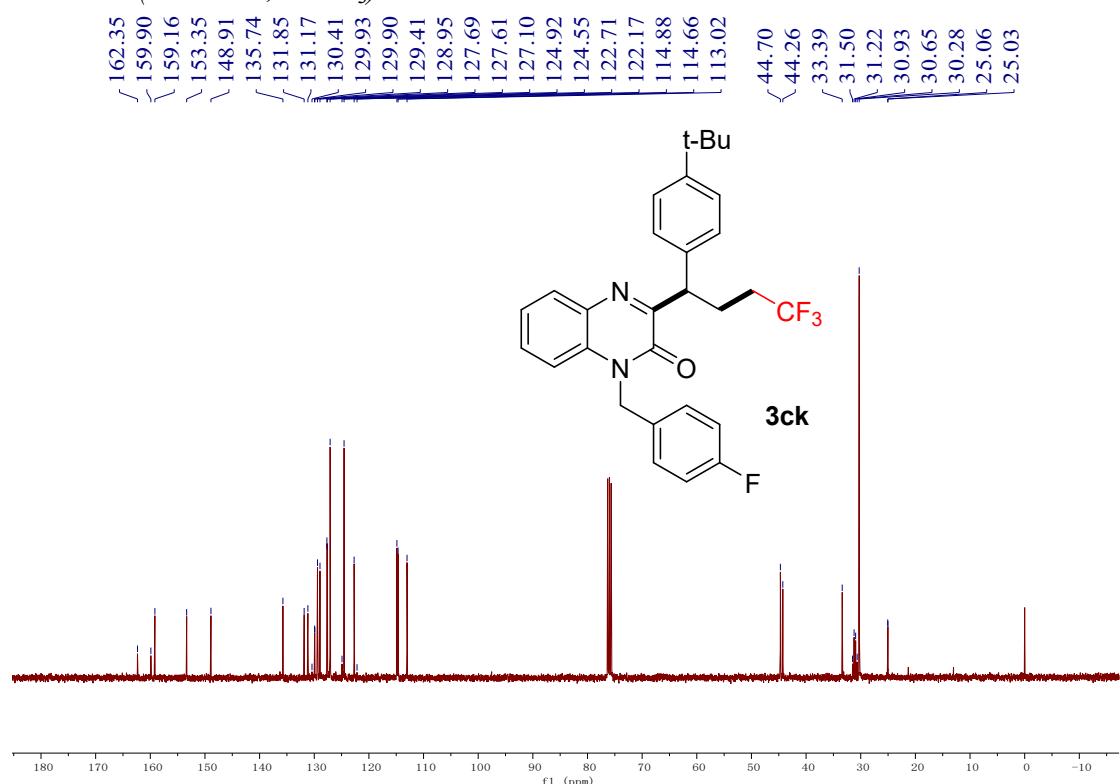
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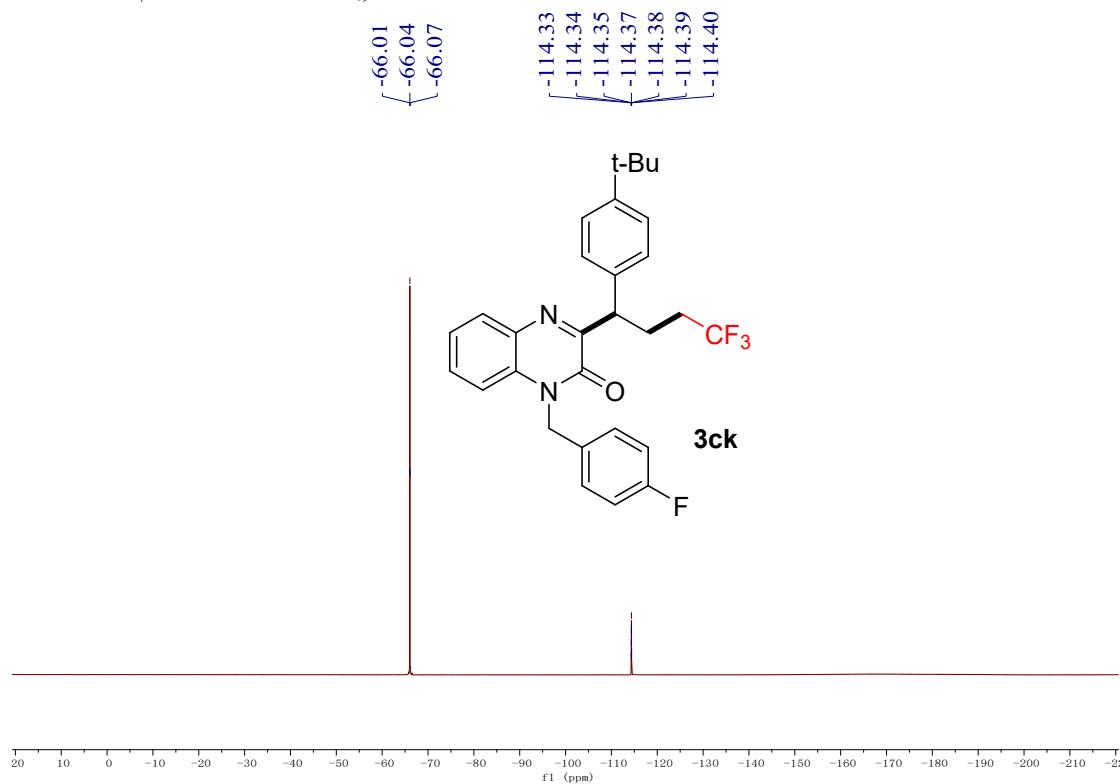
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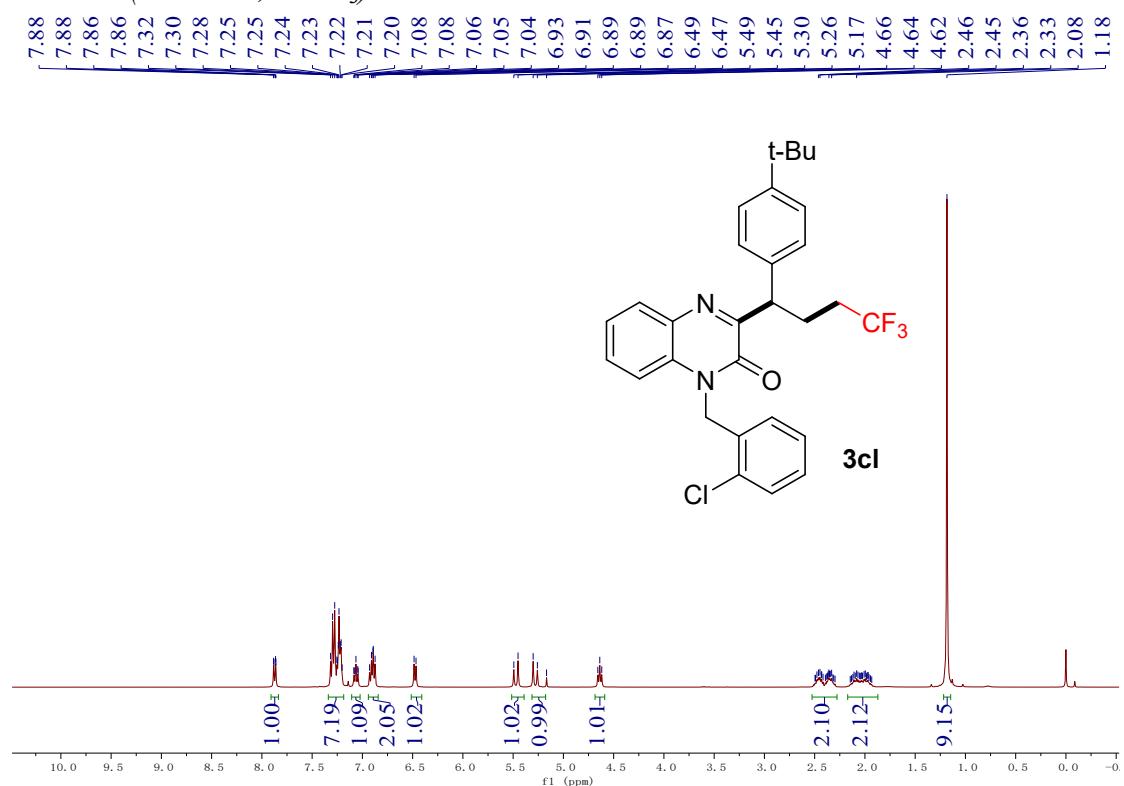
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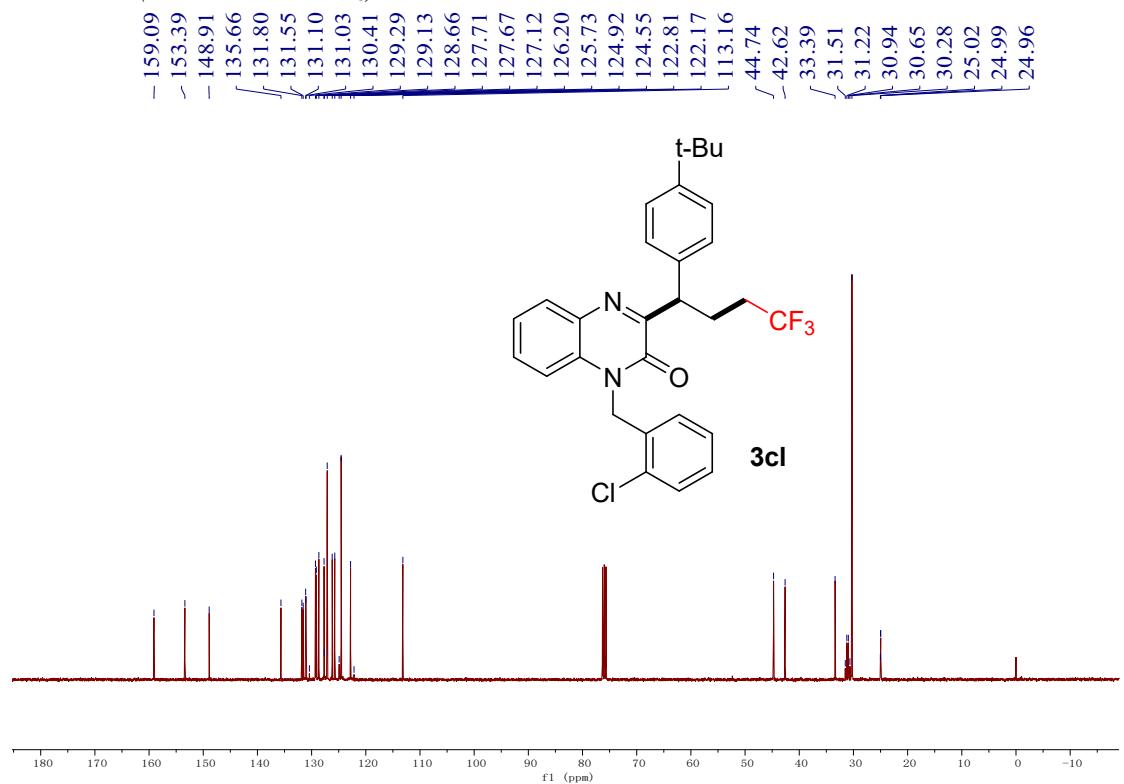
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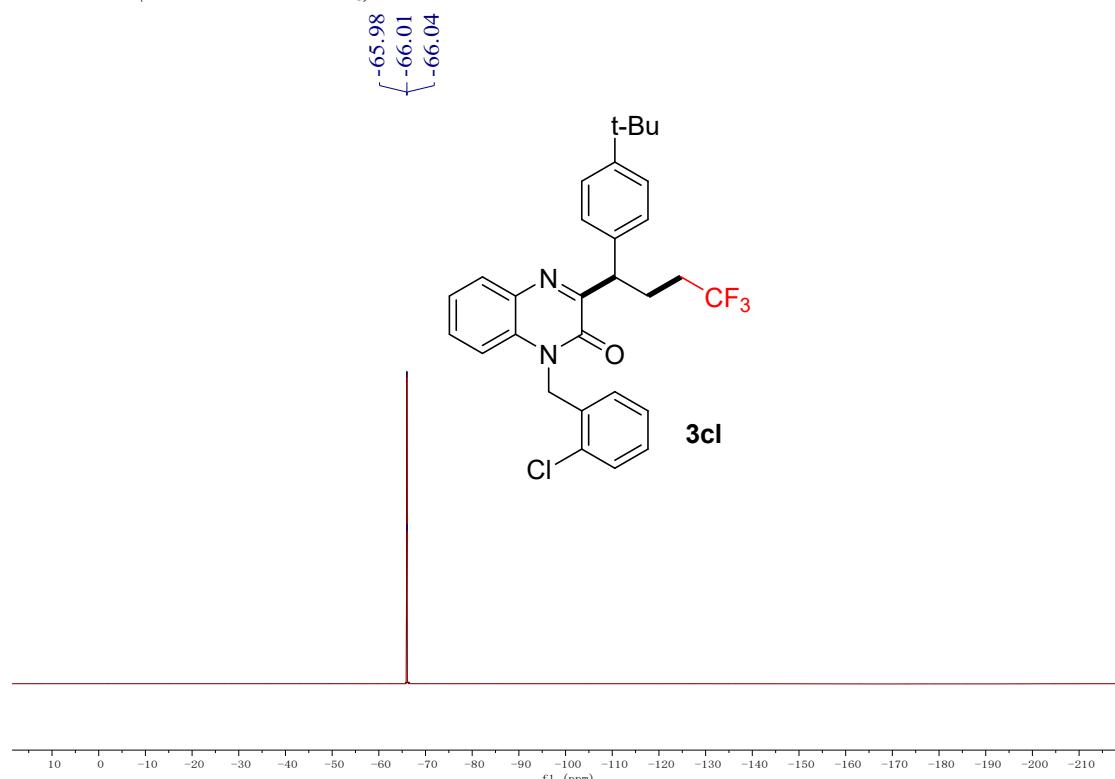
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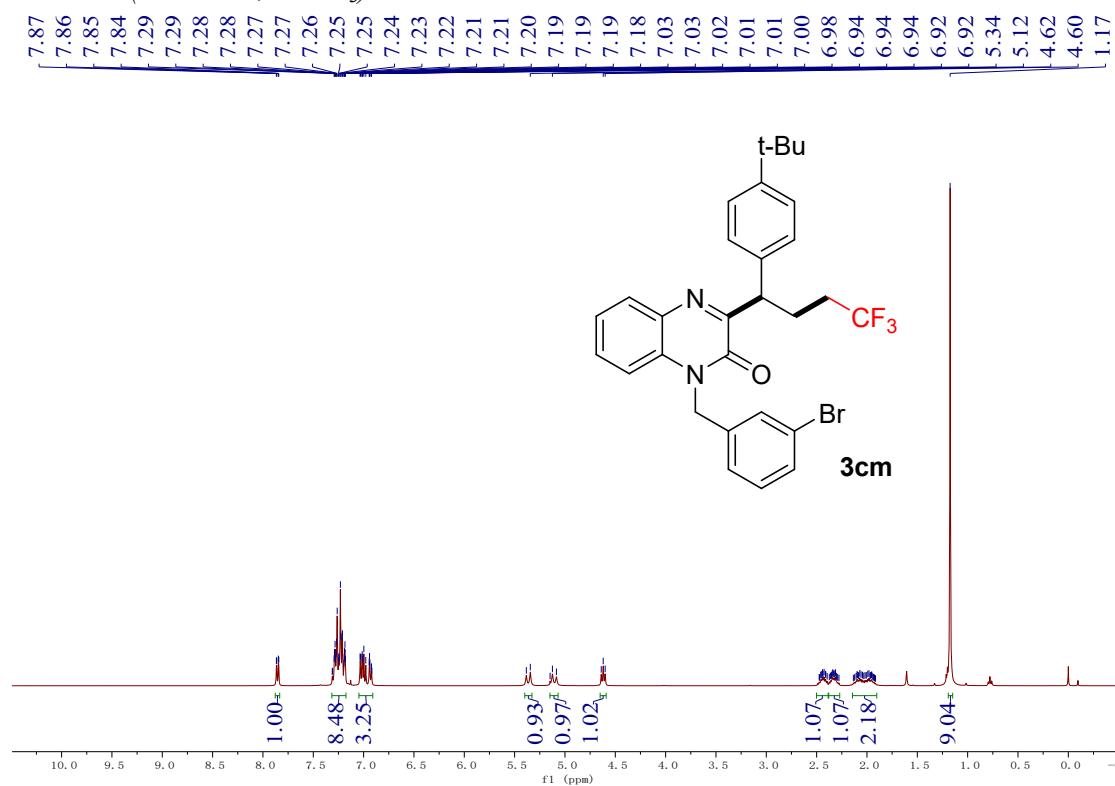
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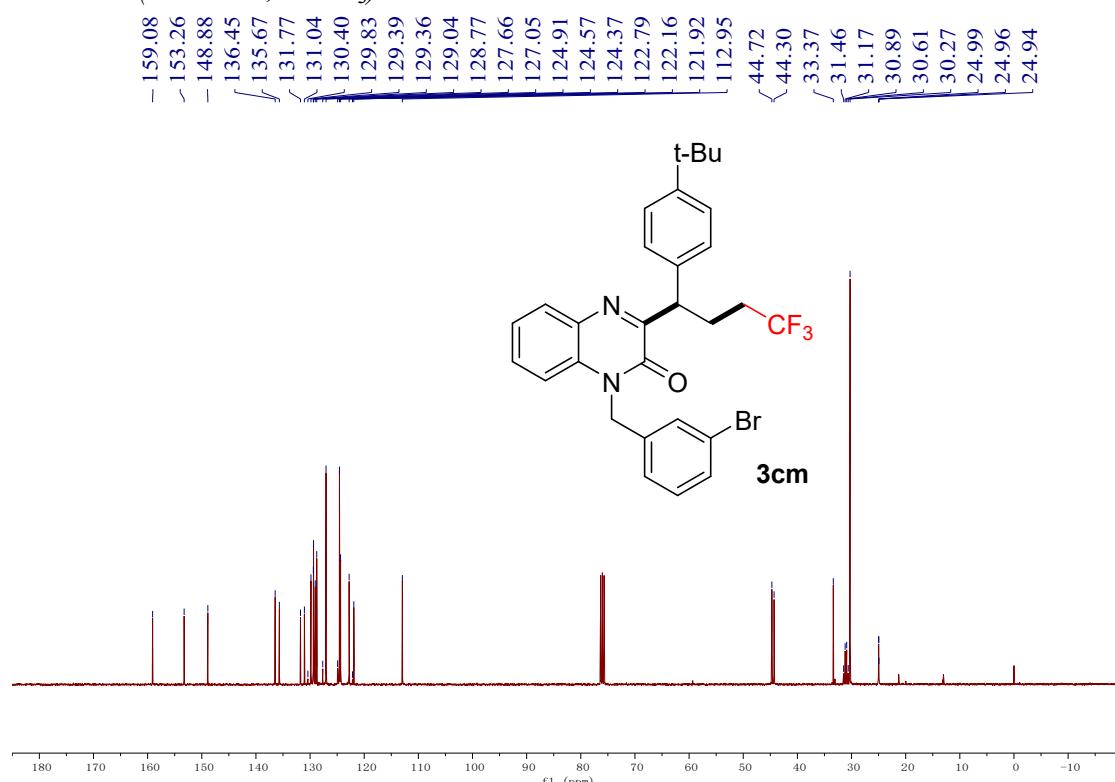
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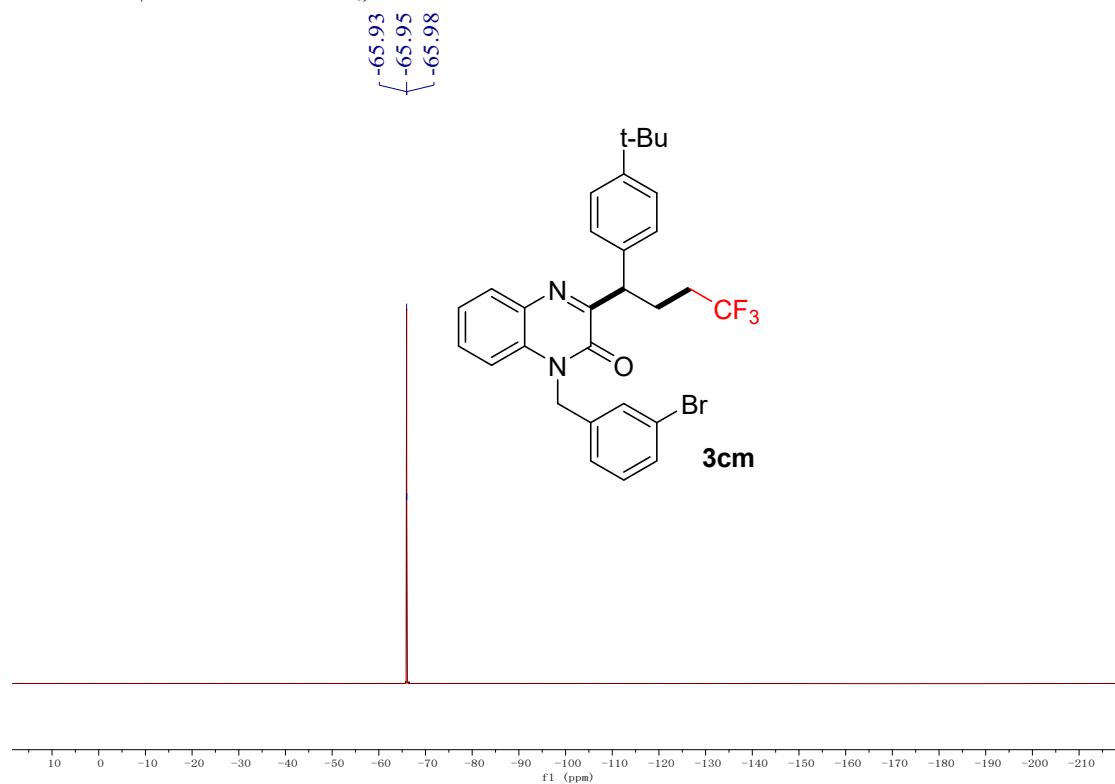
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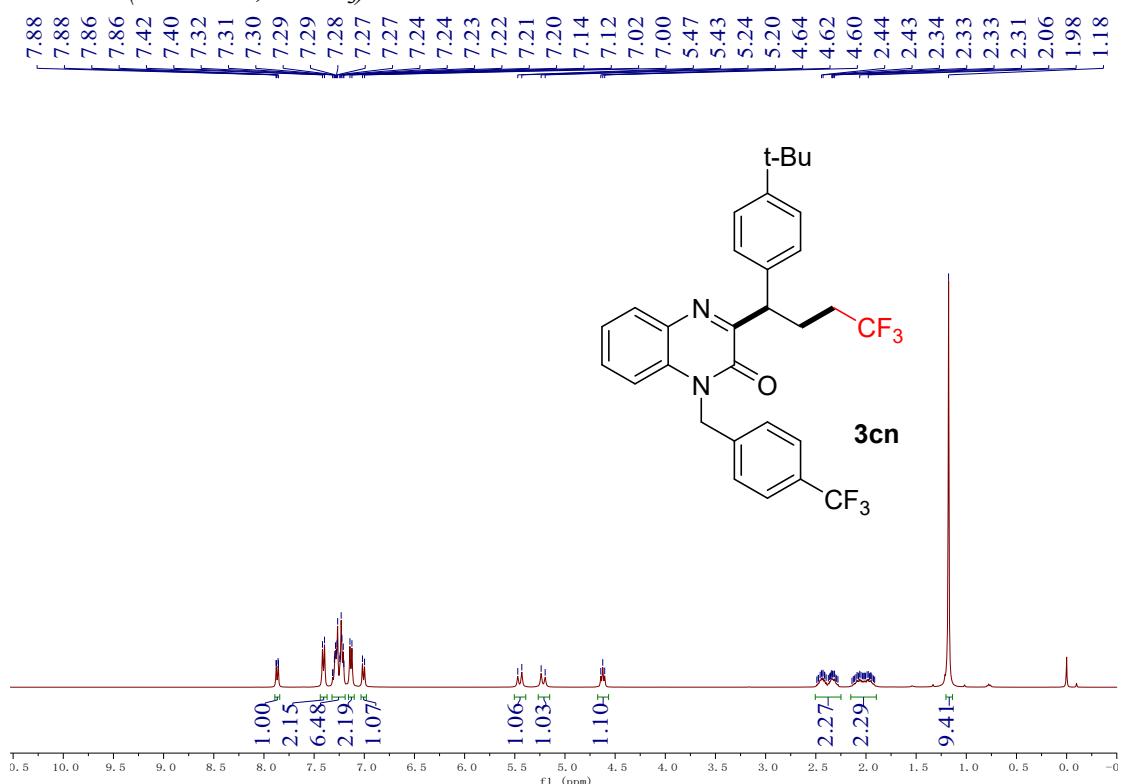
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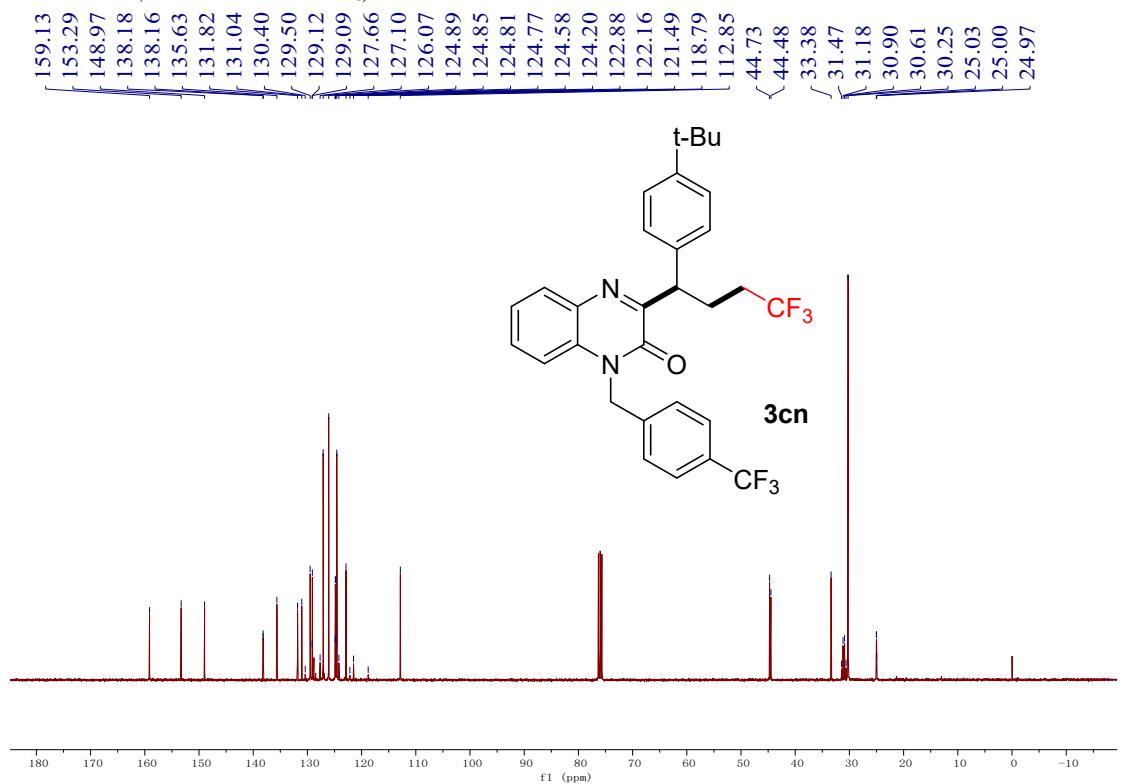
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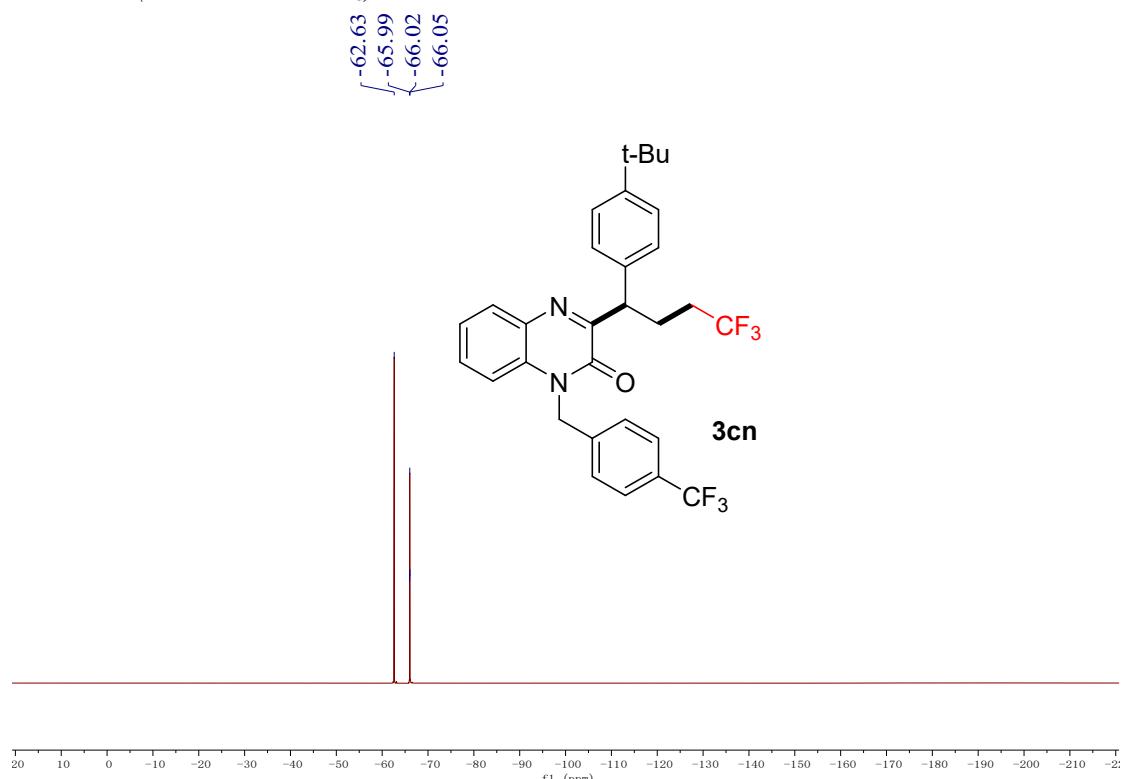
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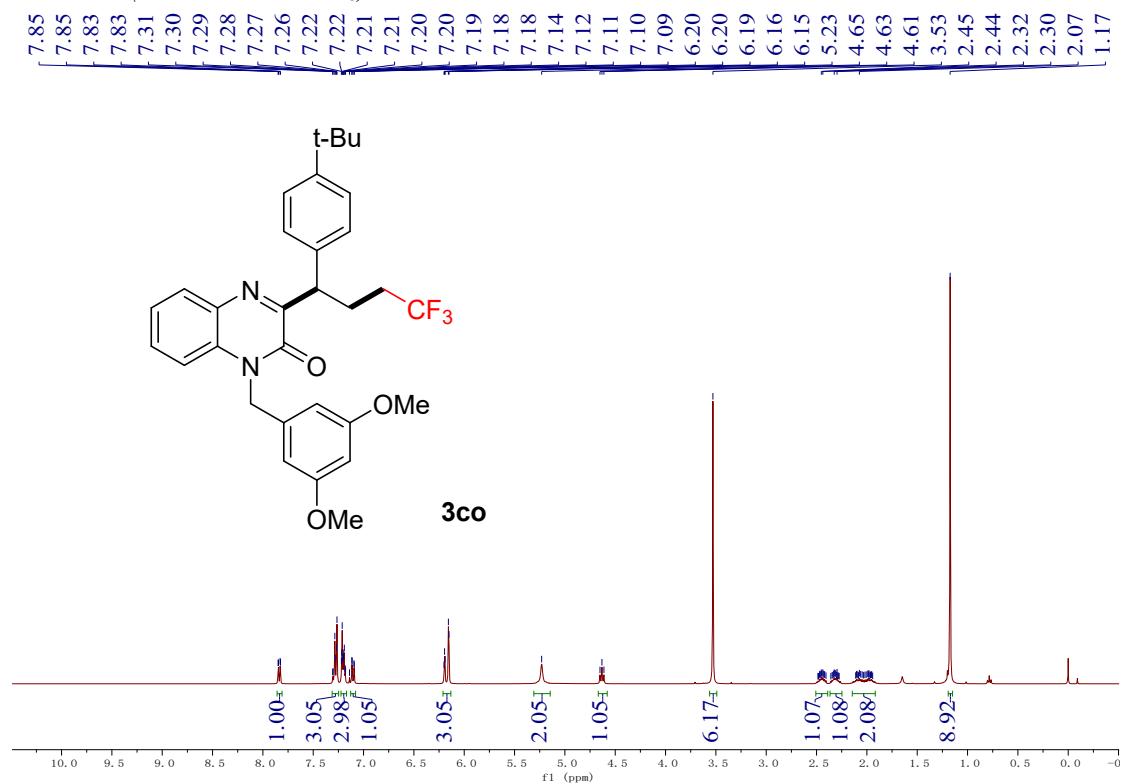
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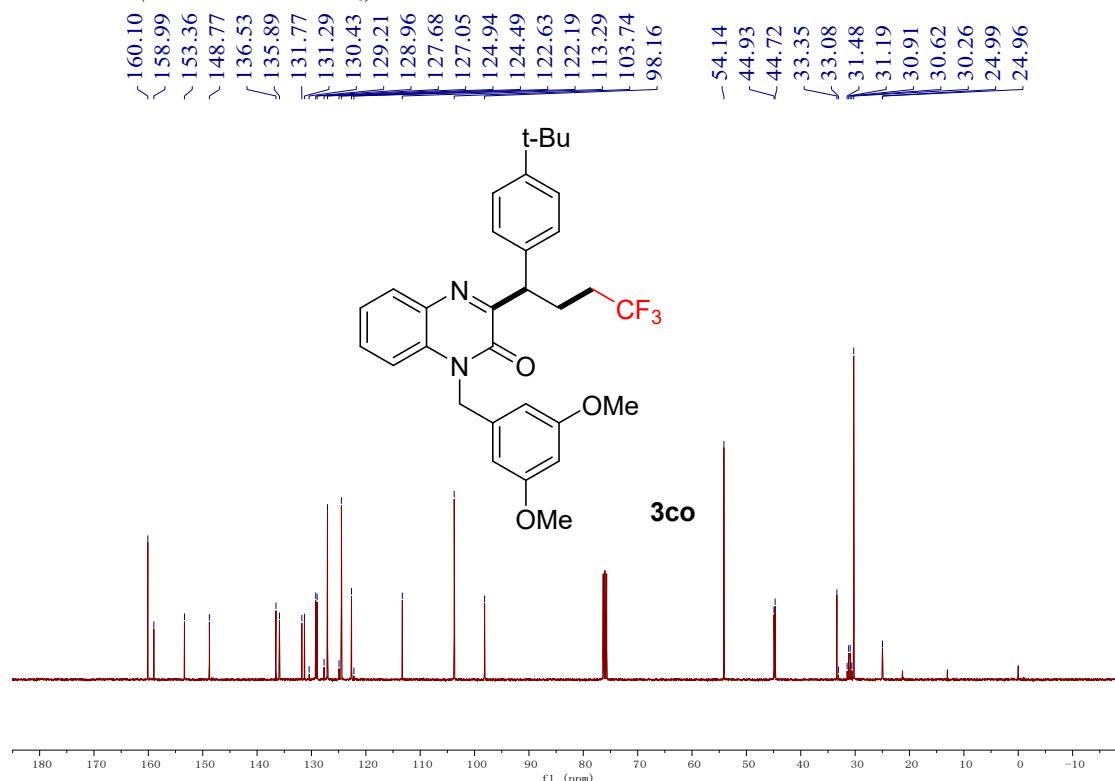
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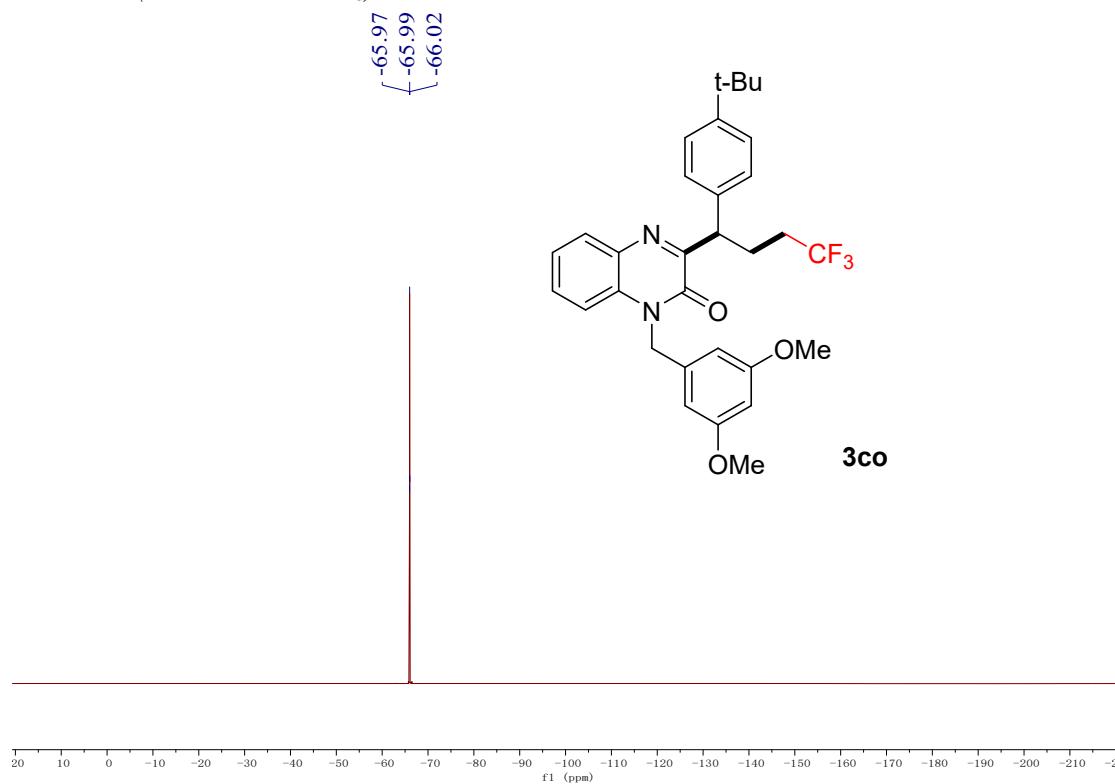
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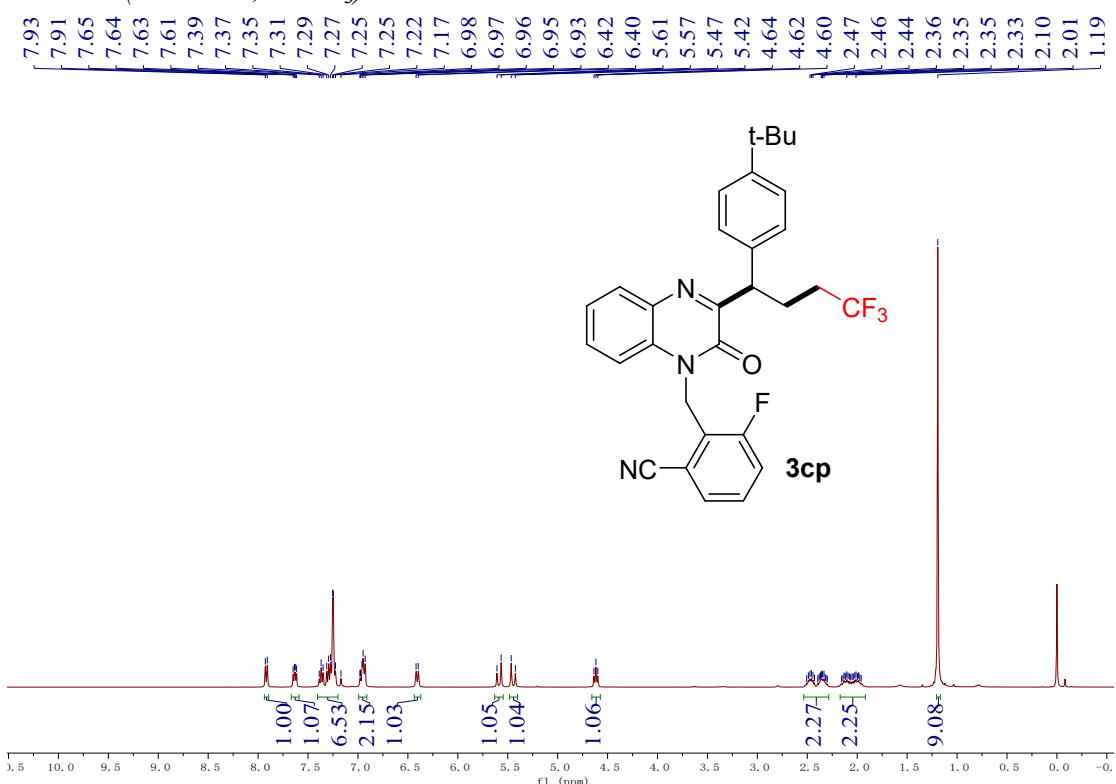
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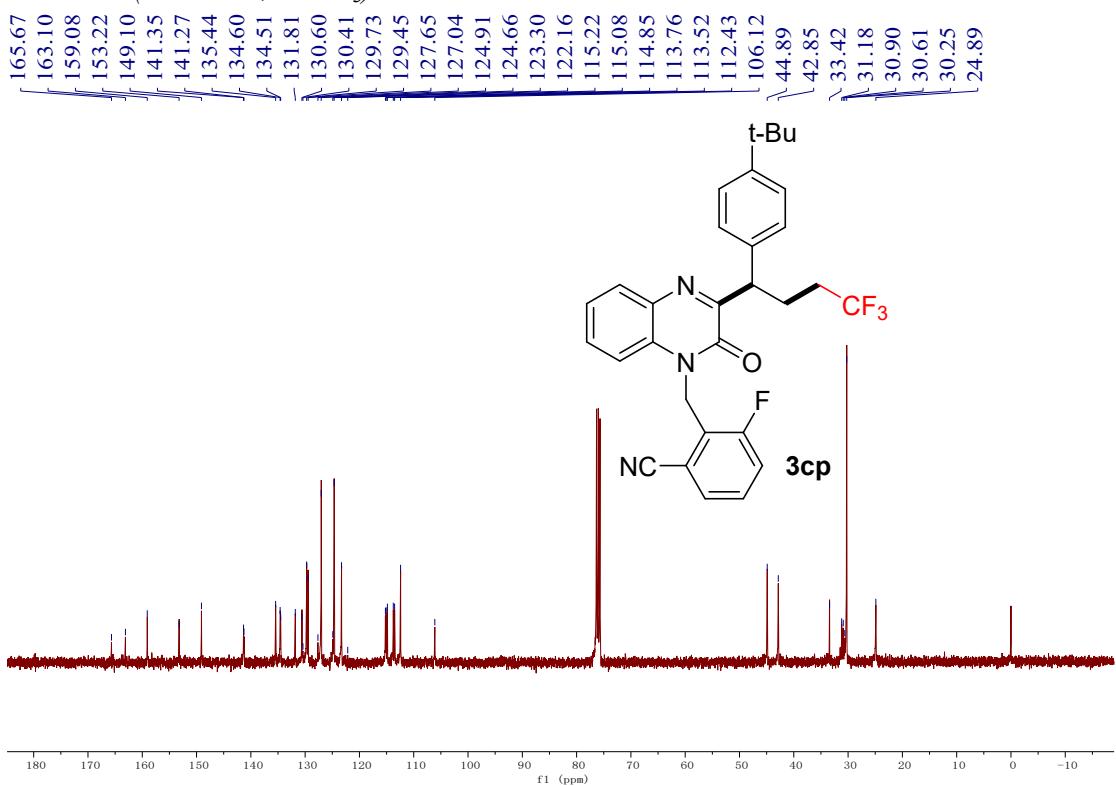
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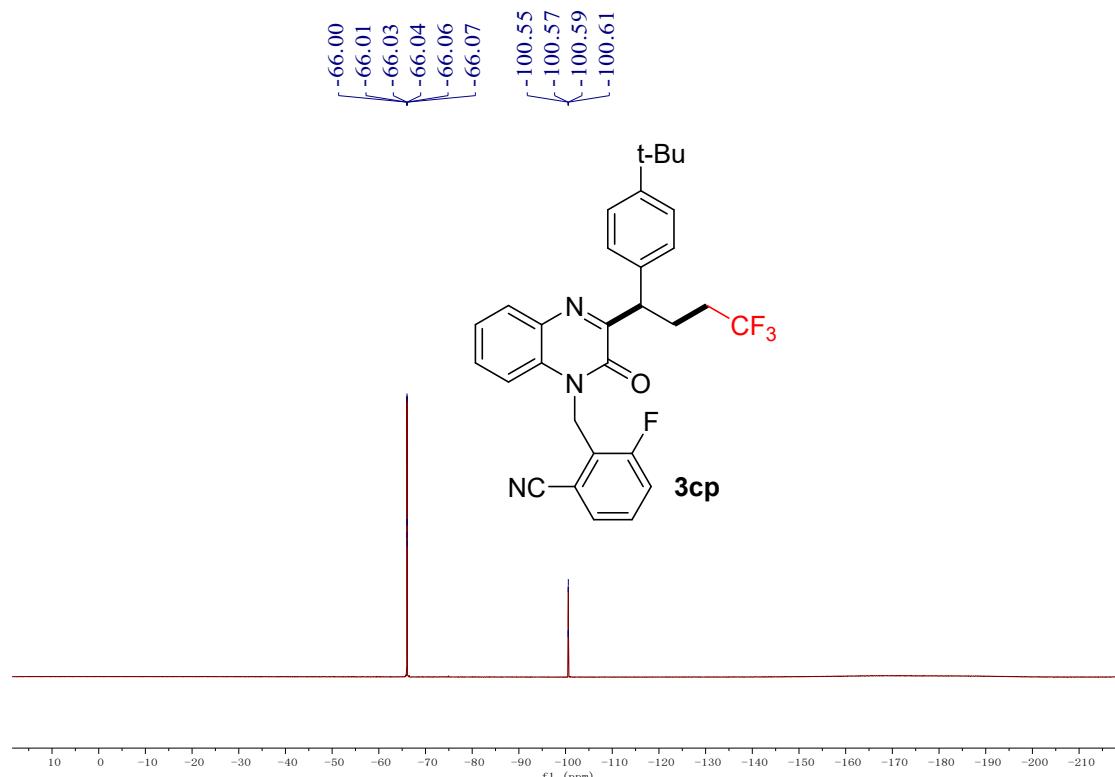
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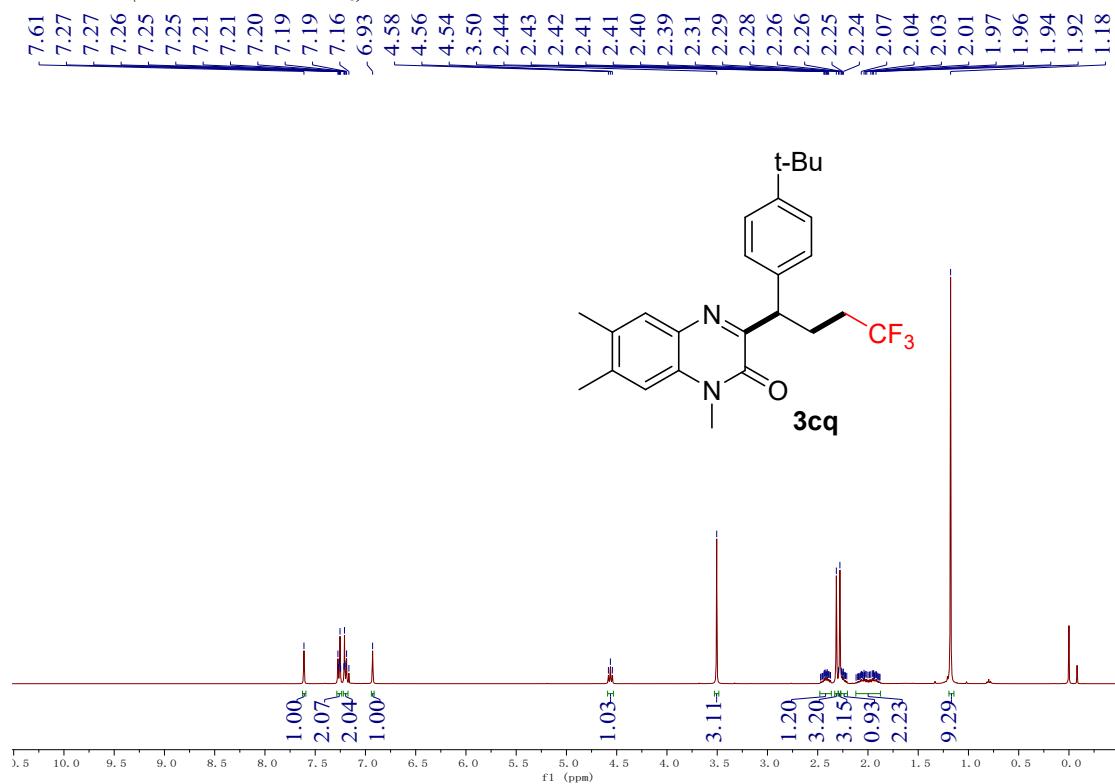
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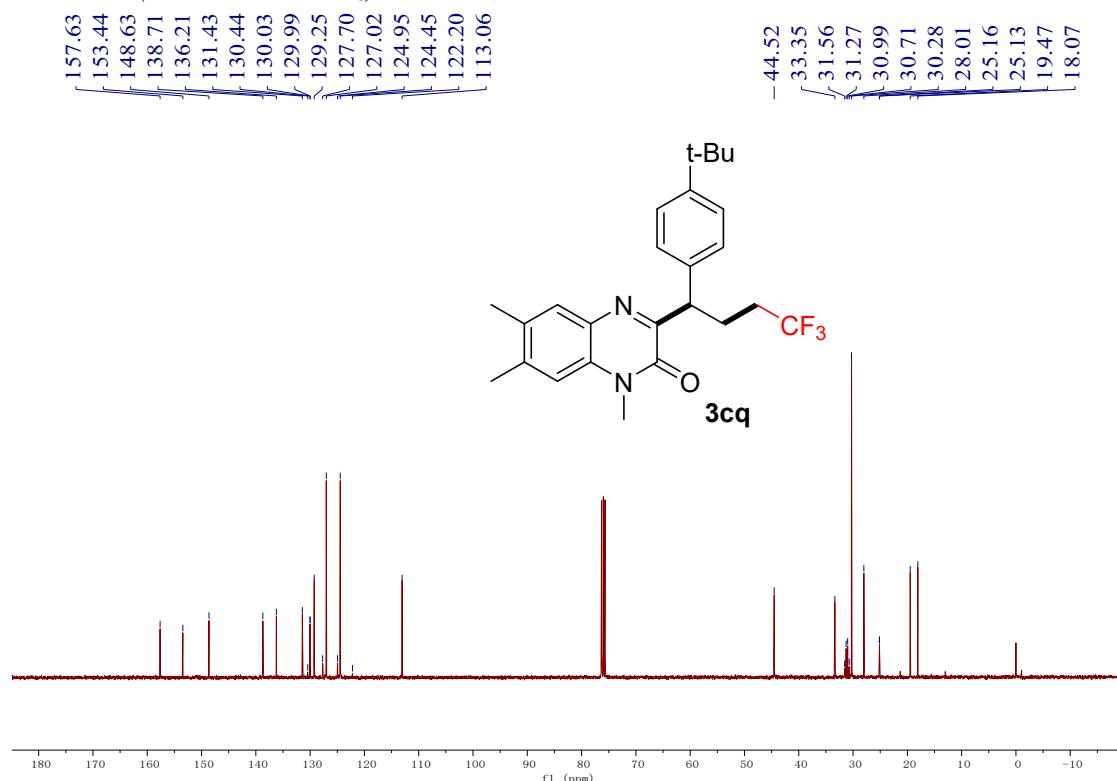
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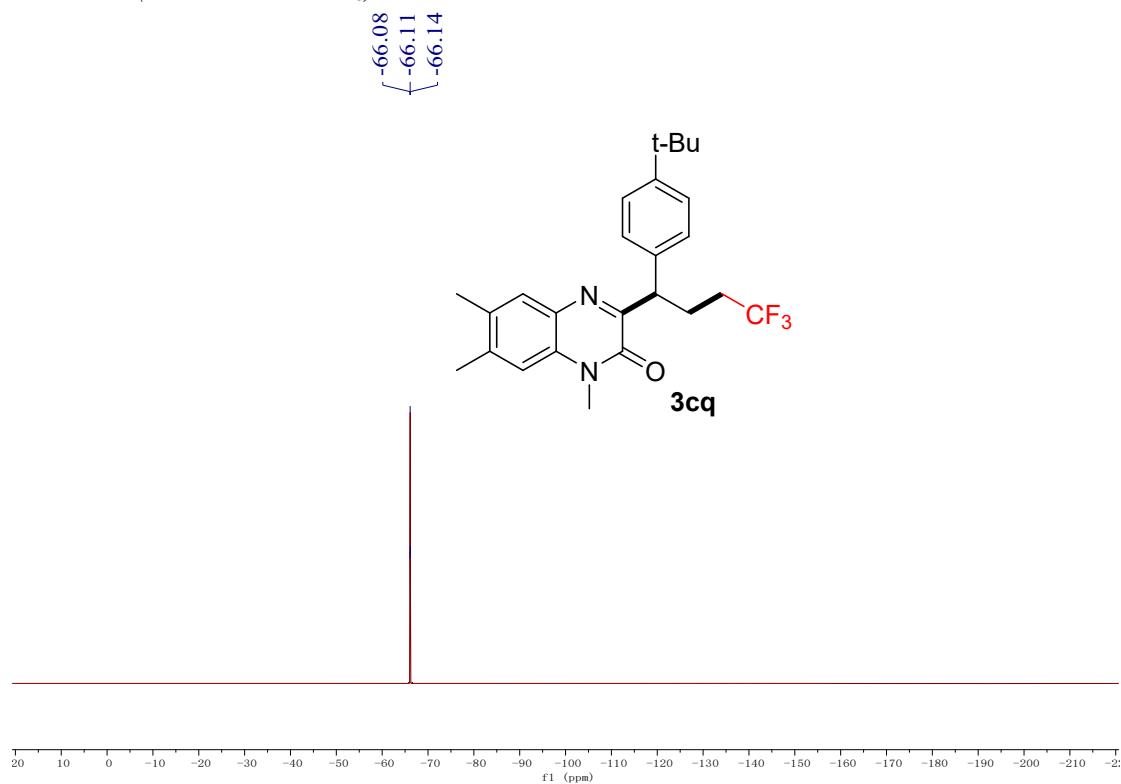
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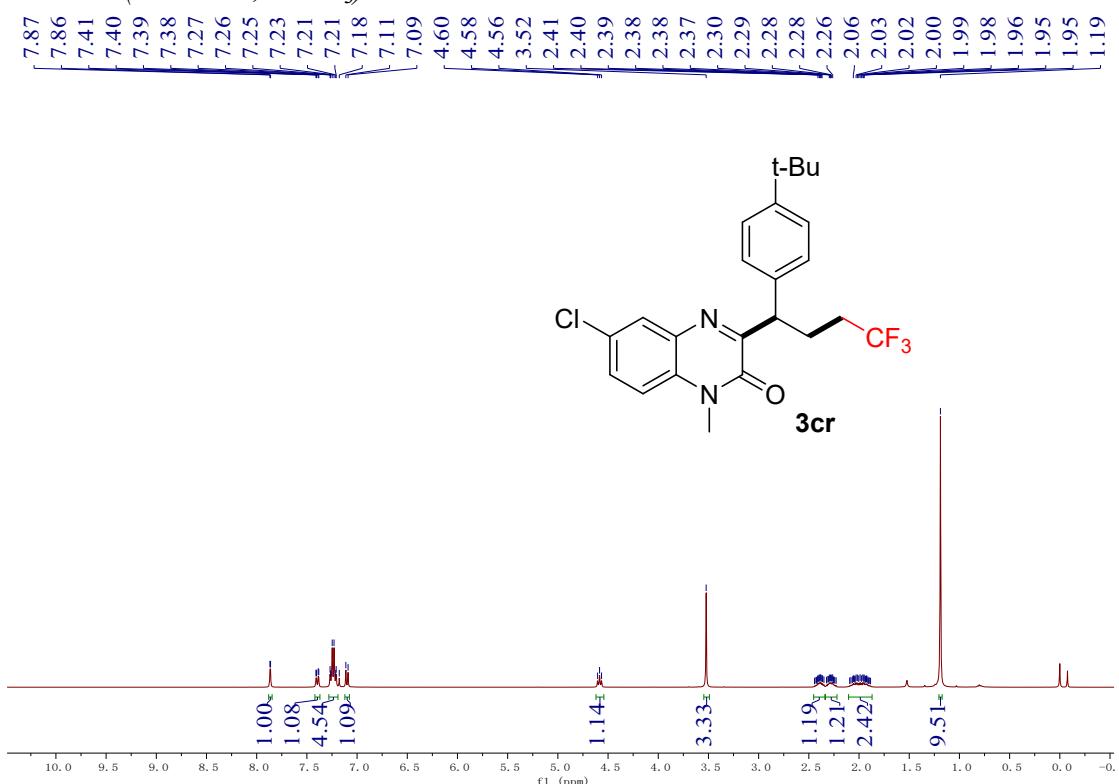
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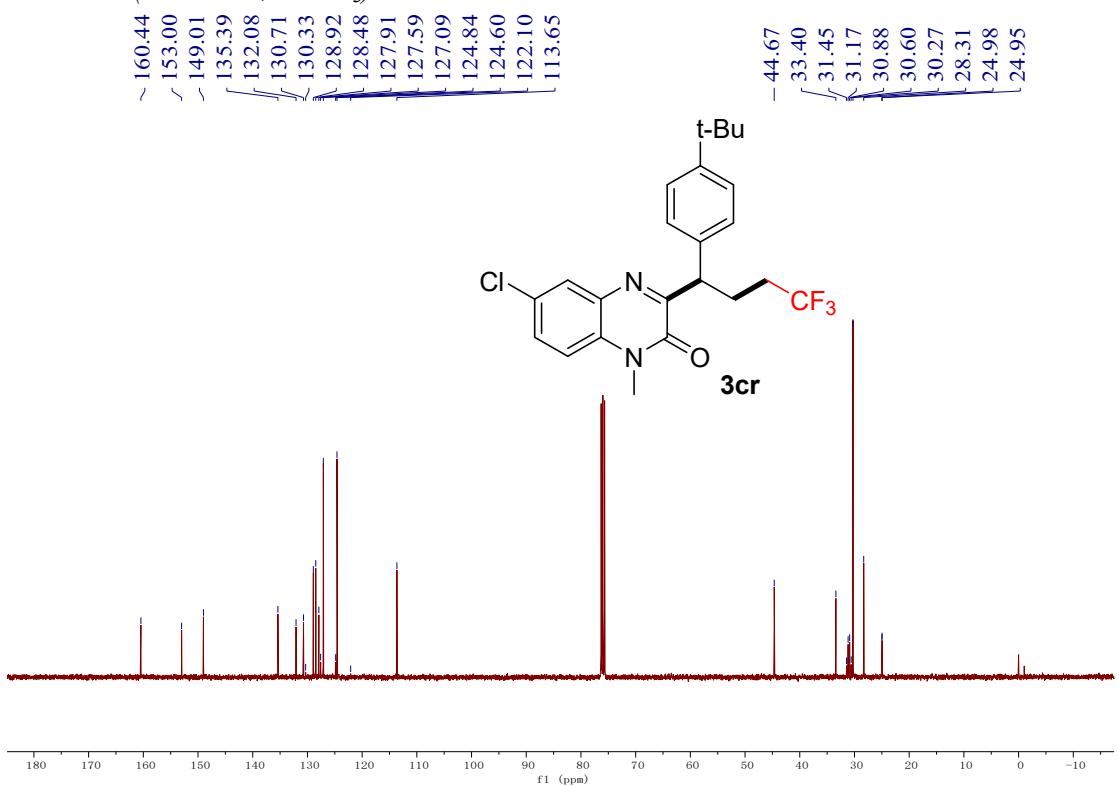
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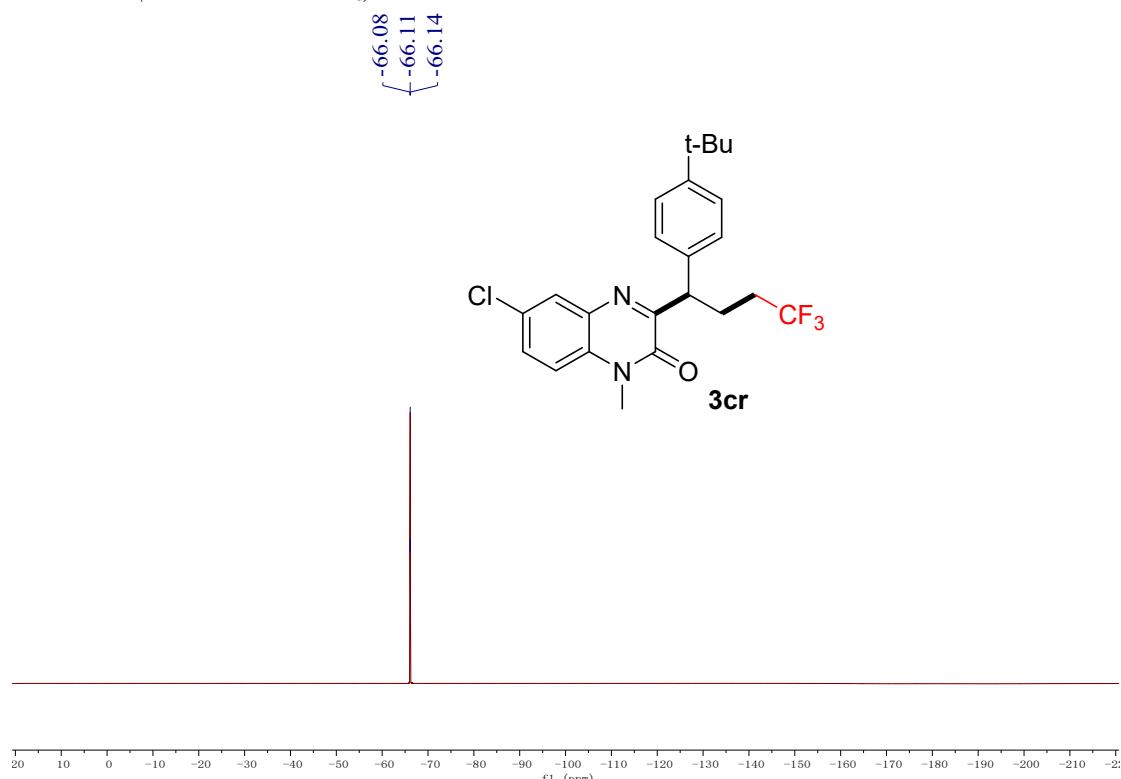
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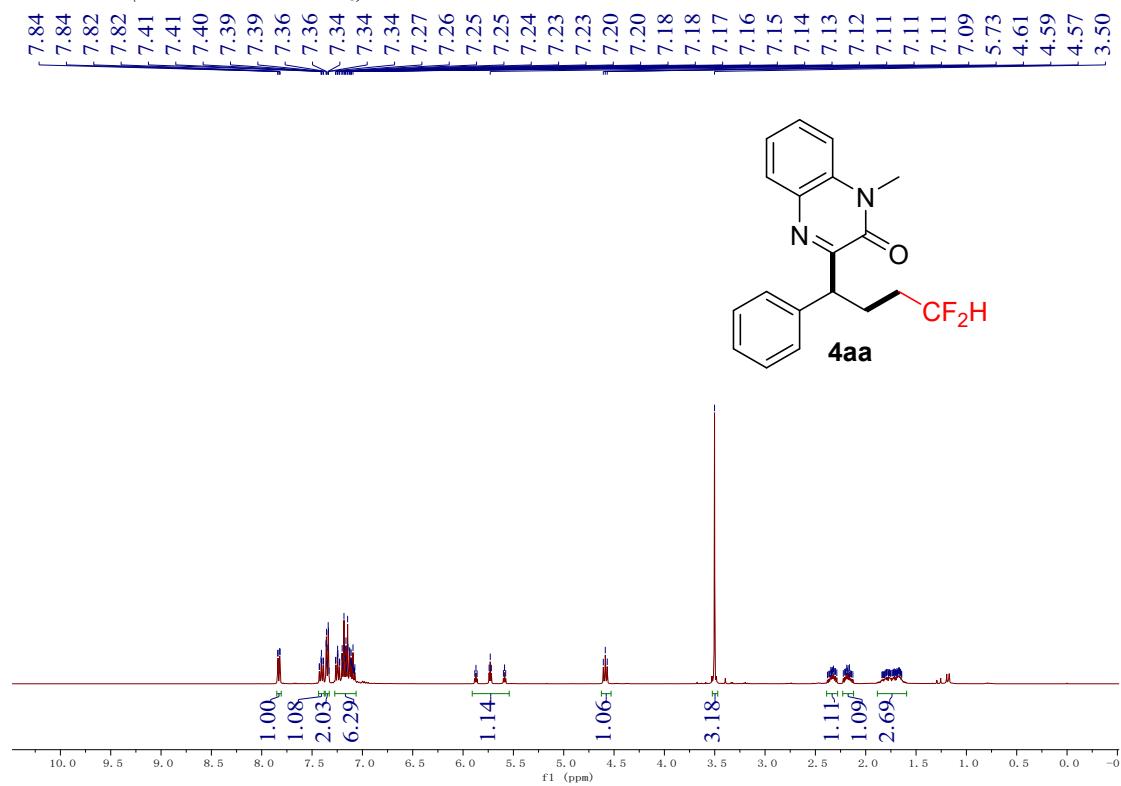
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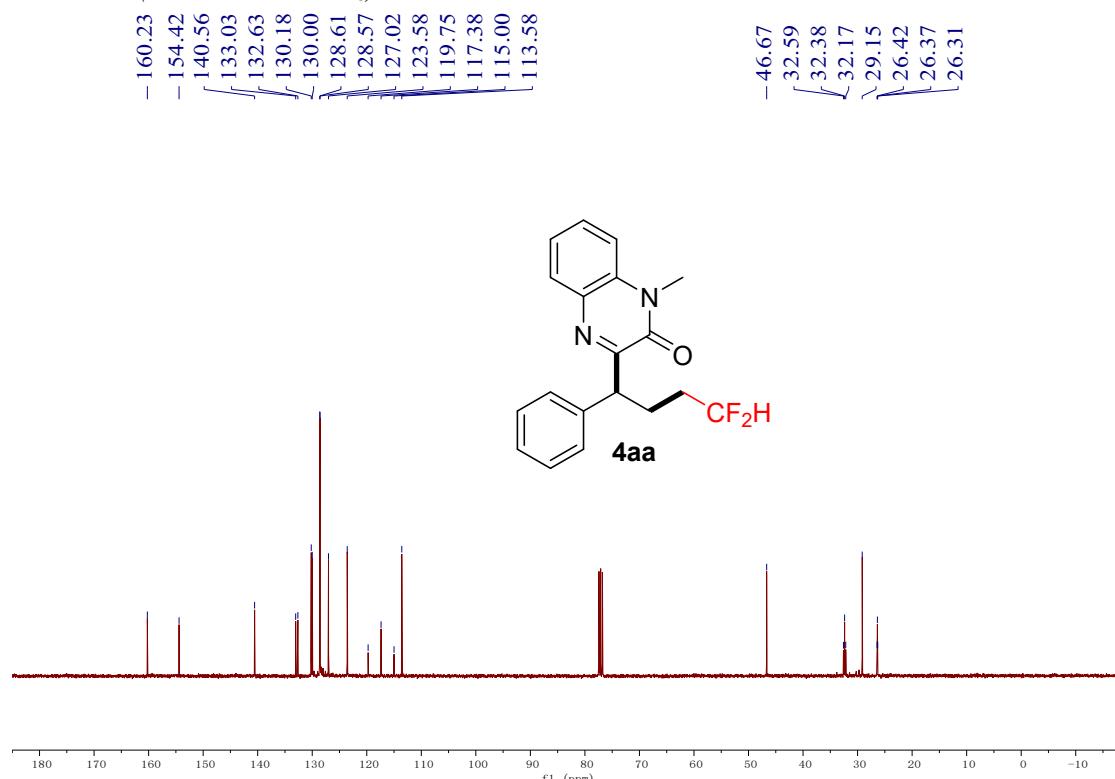
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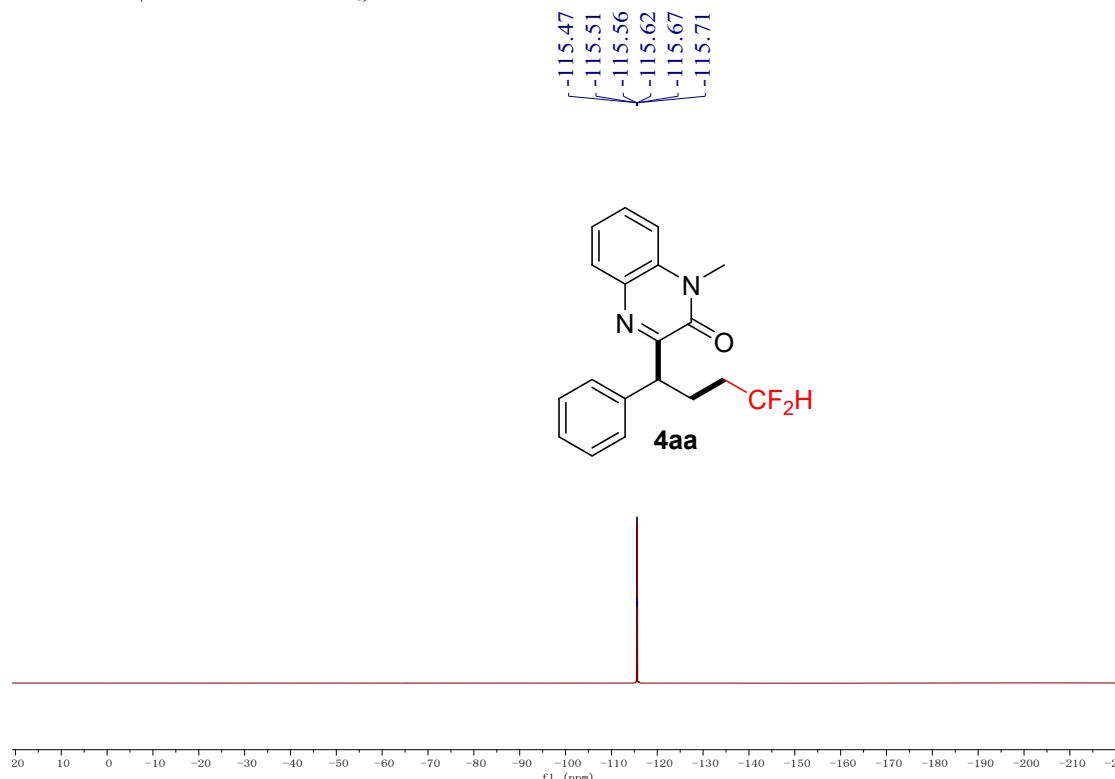
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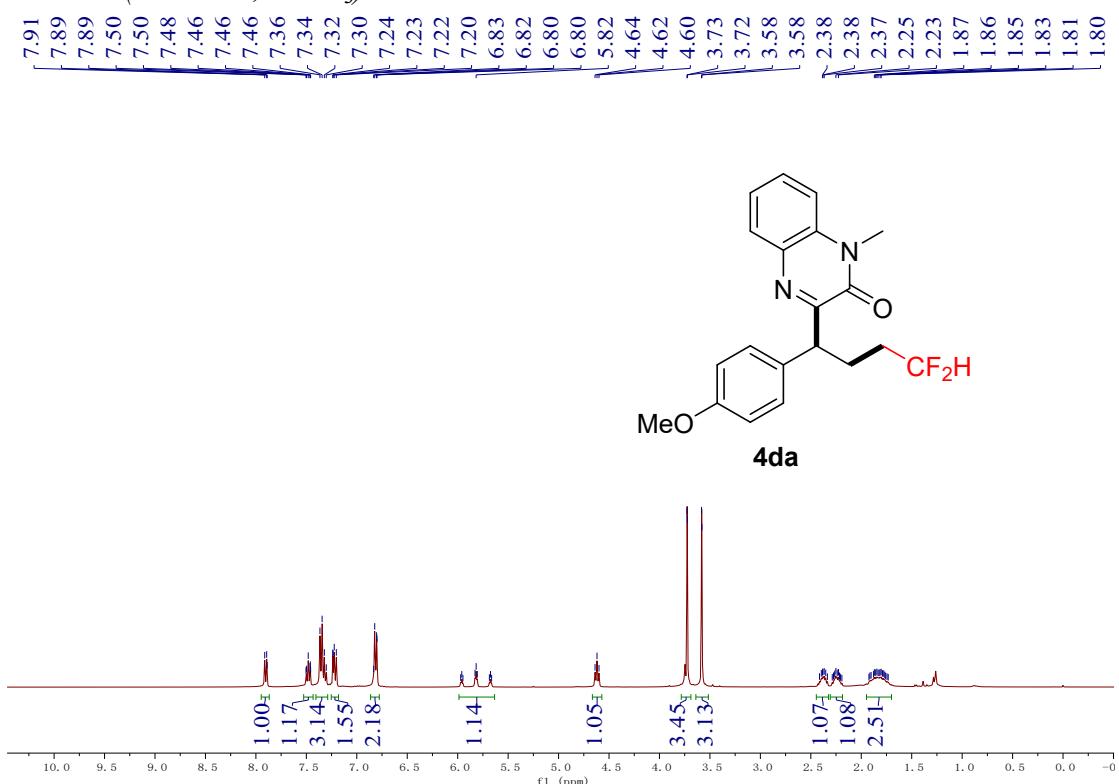
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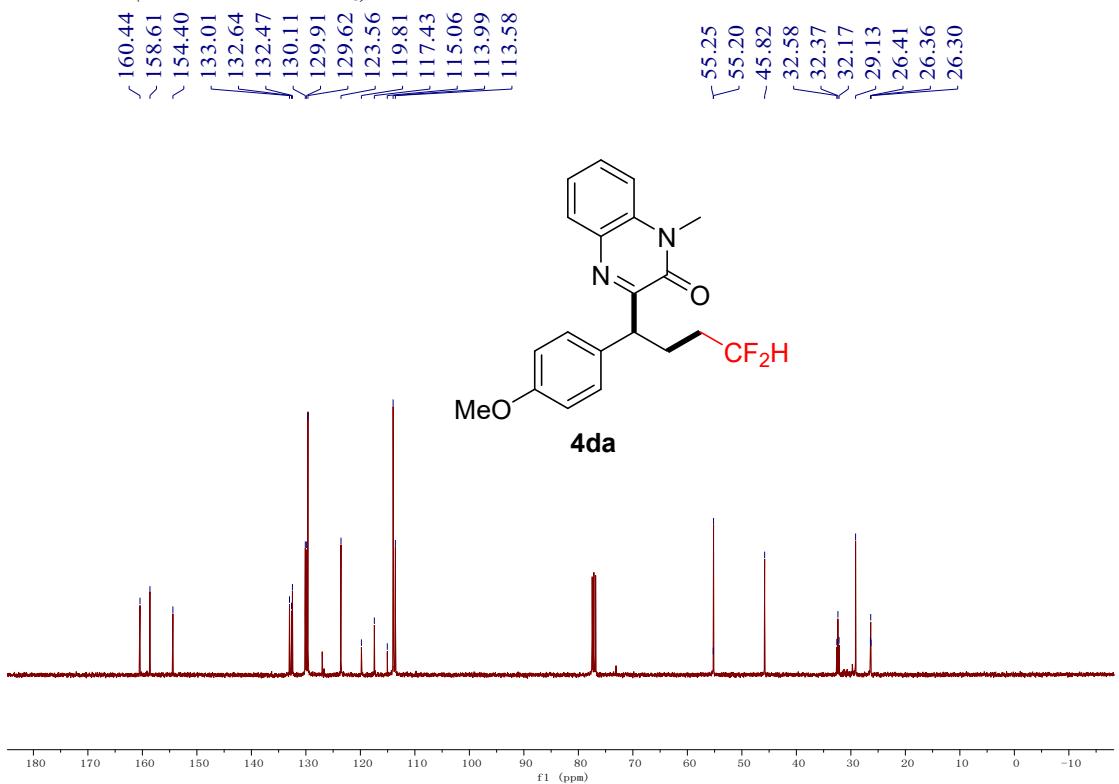
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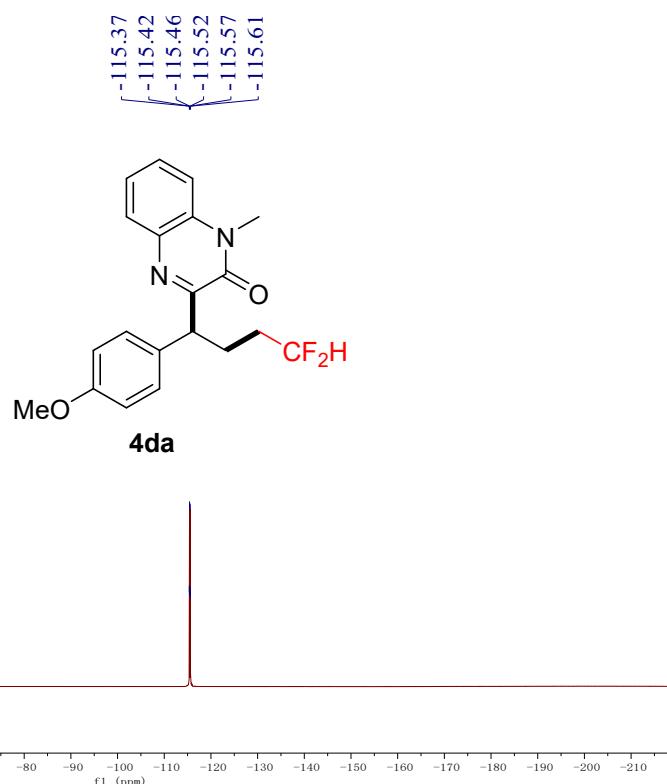
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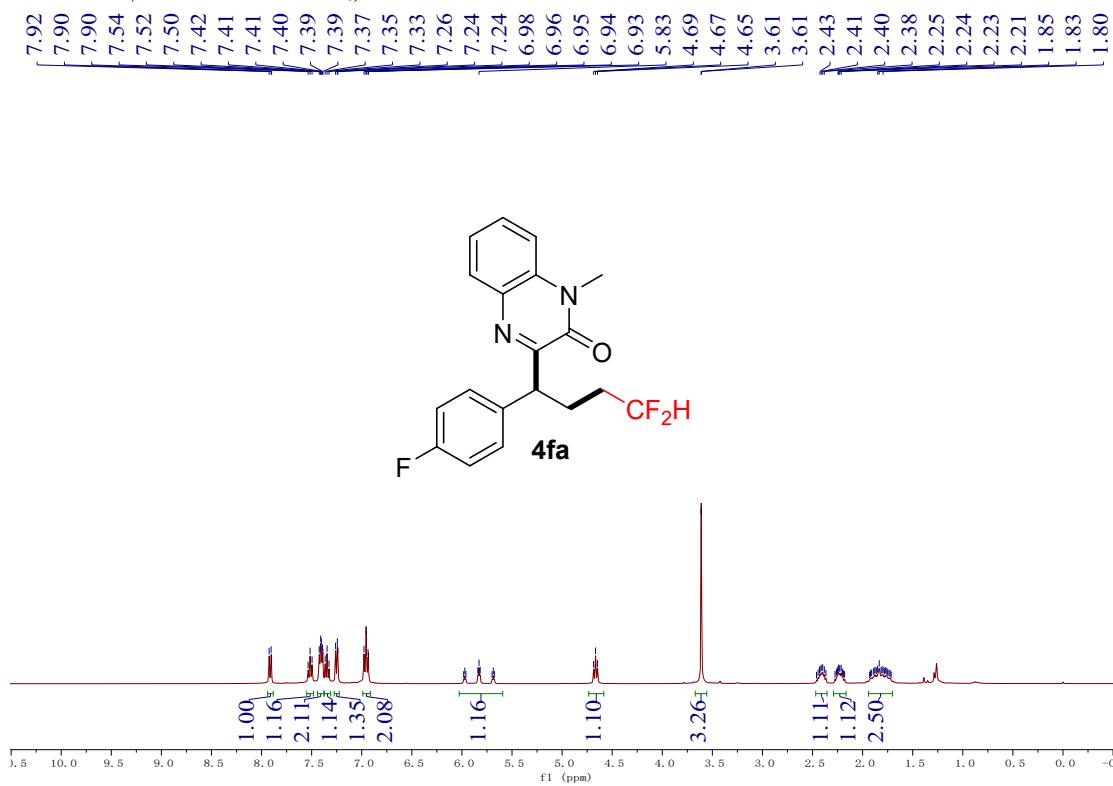
¹³C NMR (101 MHz, CDCl₃)



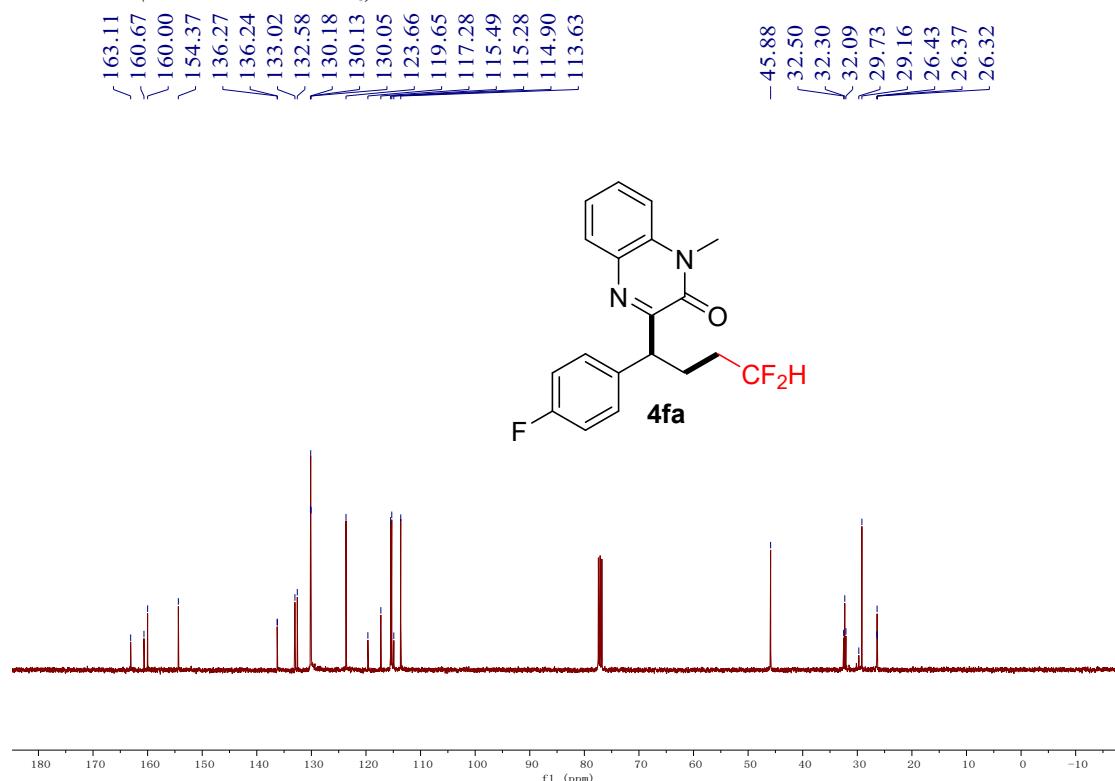
^{19}F NMR ($377\text{ MHz, } \text{CDCl}_3$)



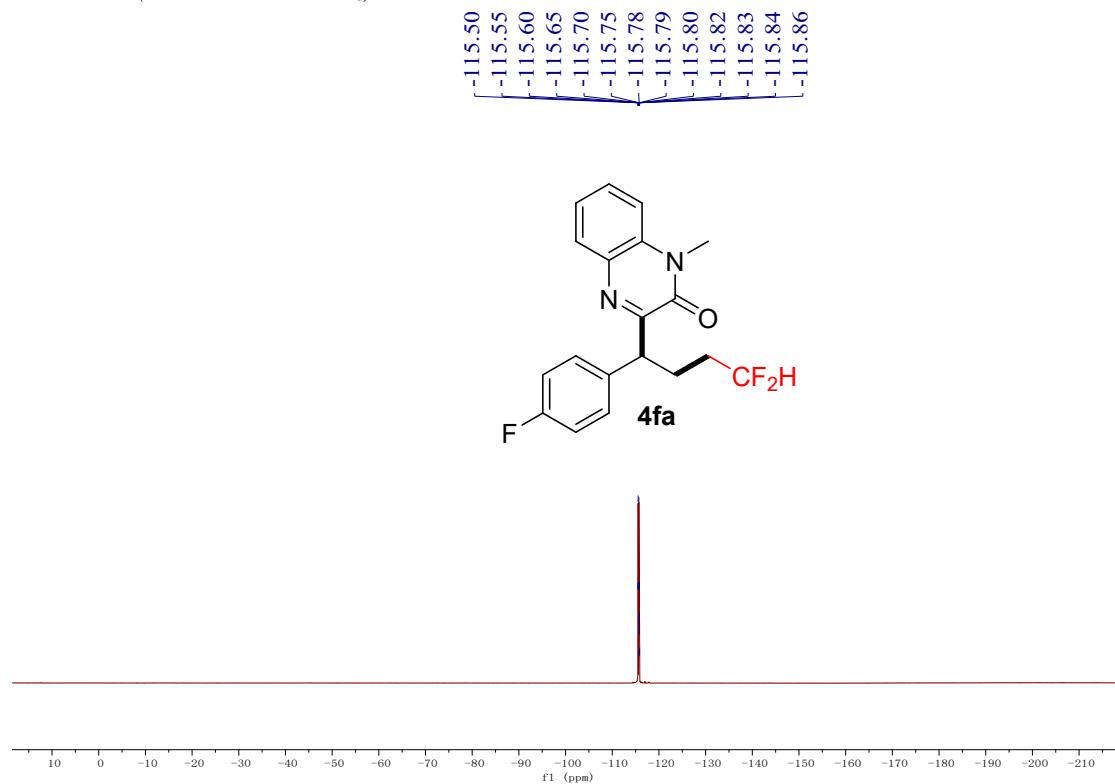
^1H NMR ($400\text{ MHz, } \text{CDCl}_3$)



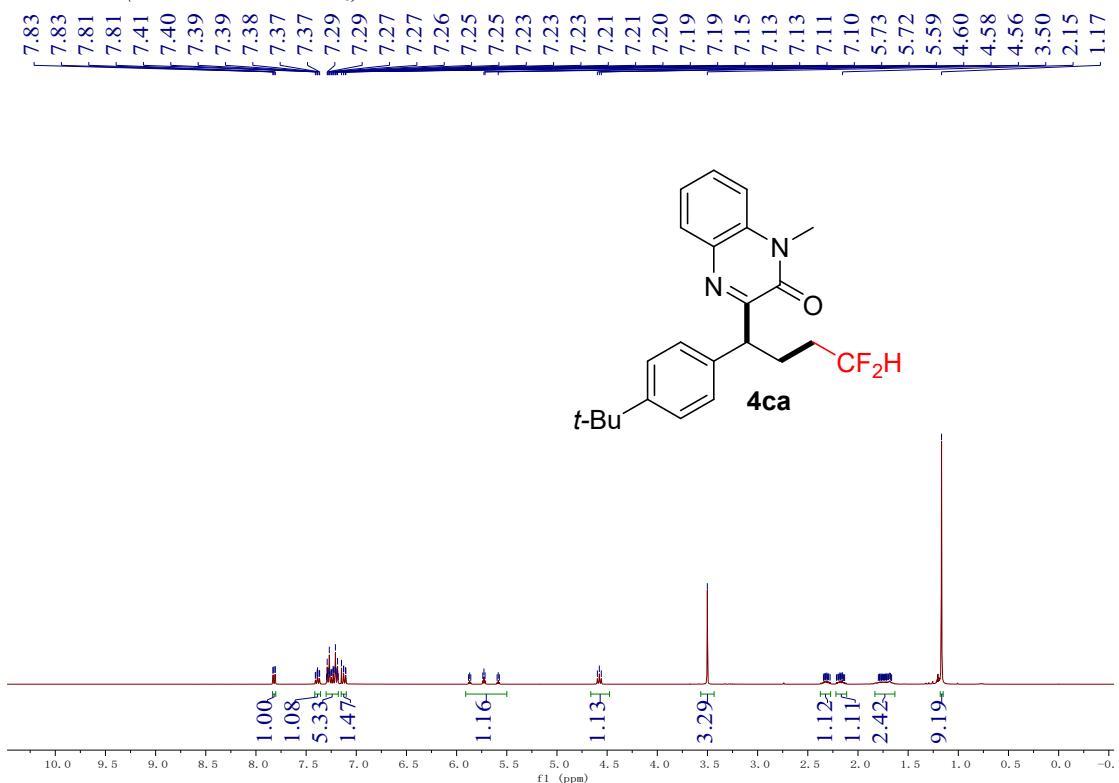
¹³C NMR (101 MHz, CDCl₃)



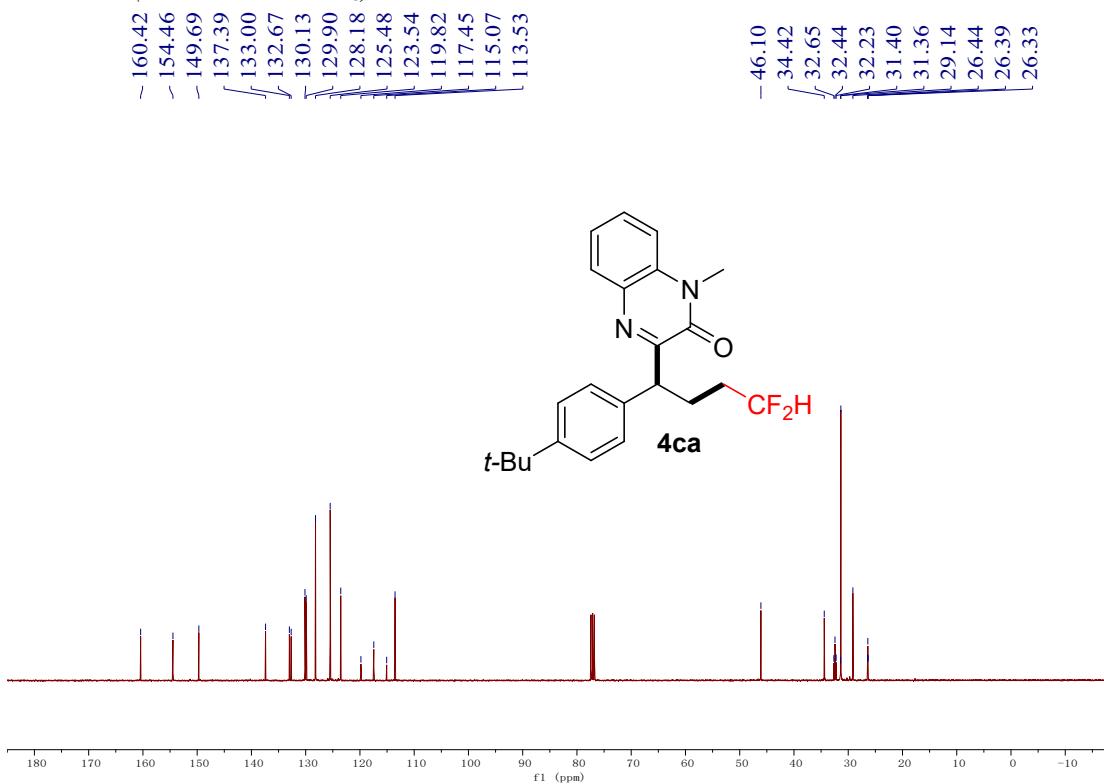
¹⁹F NMR (377 MHz, CDCl₃)



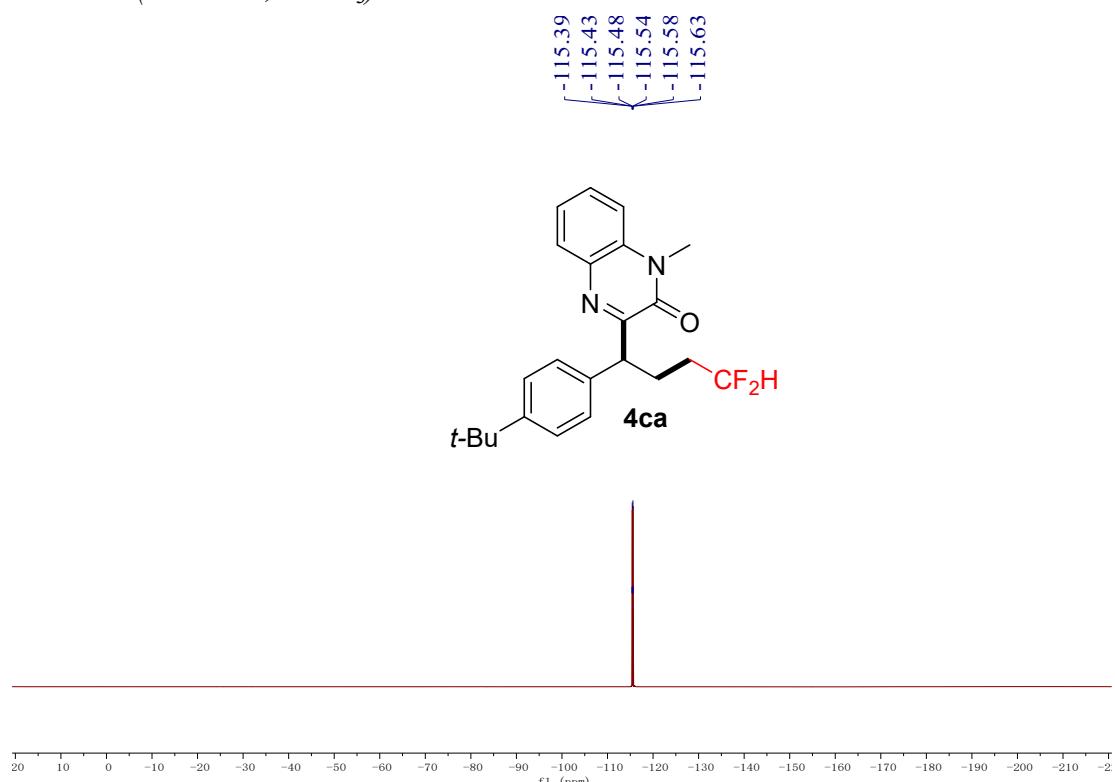
¹H NMR (400 MHz, CDCl₃)



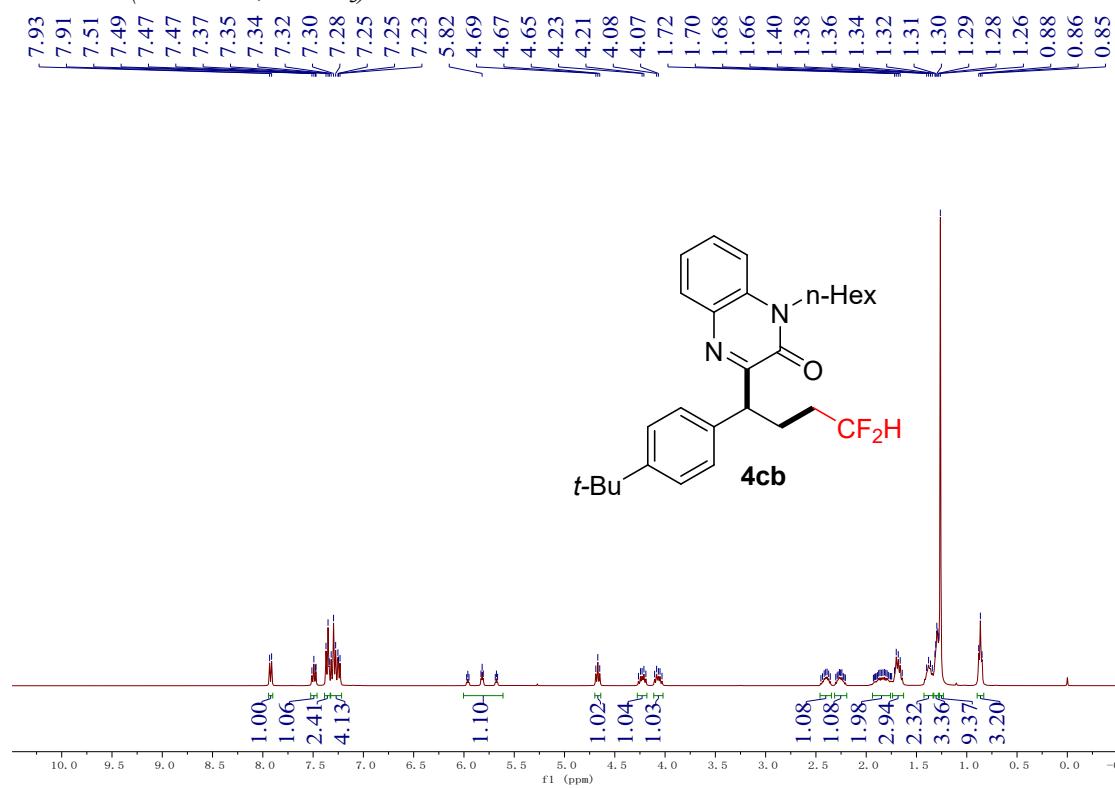
¹³C NMR (101 MHz, CDCl₃)



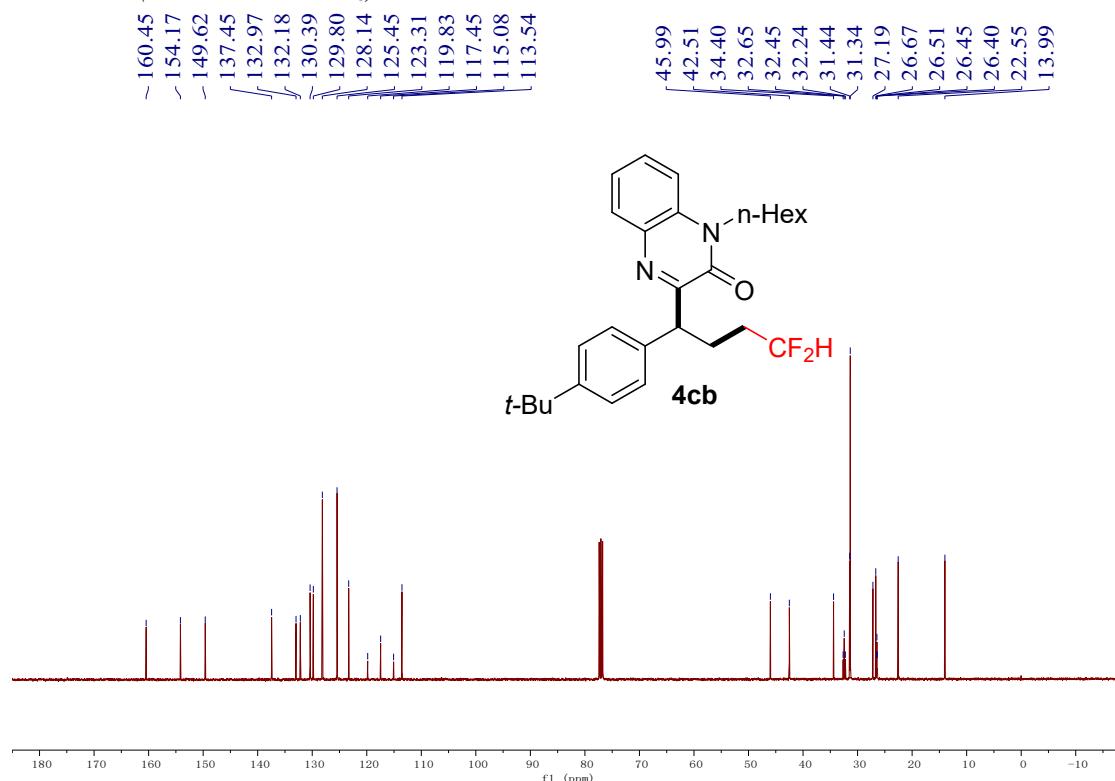
¹⁹F NMR (377 MHz, CDCl₃)



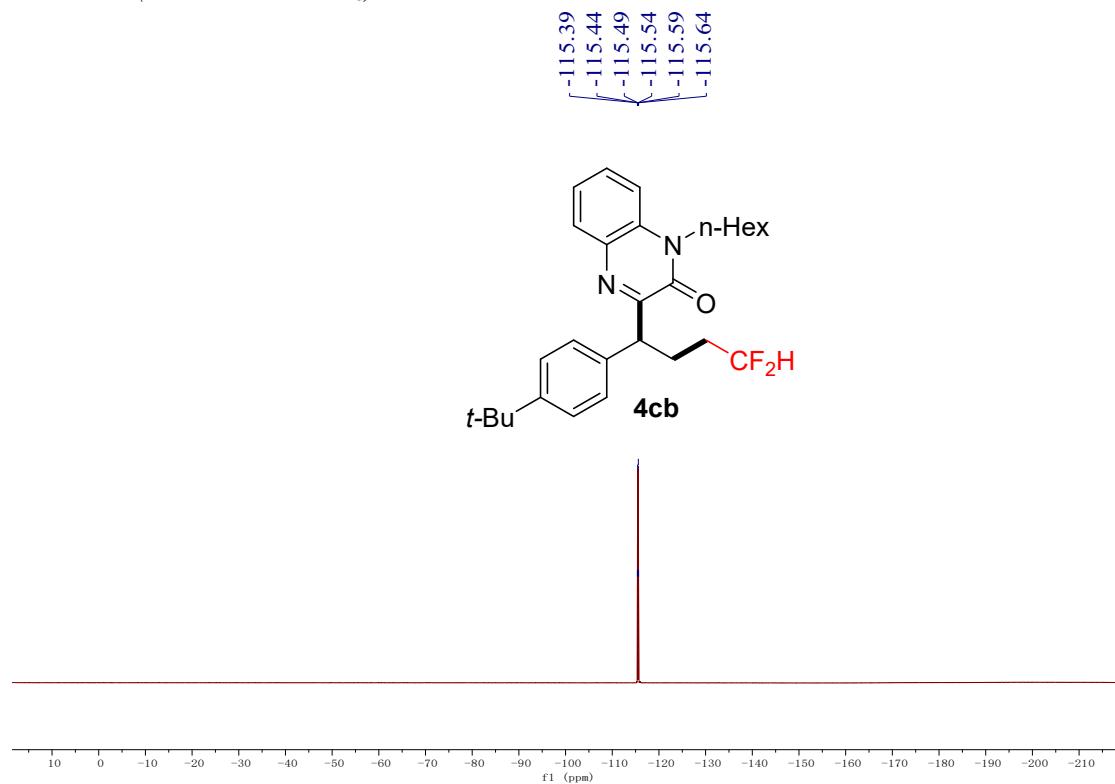
¹H NMR (400 MHz, CDCl₃)



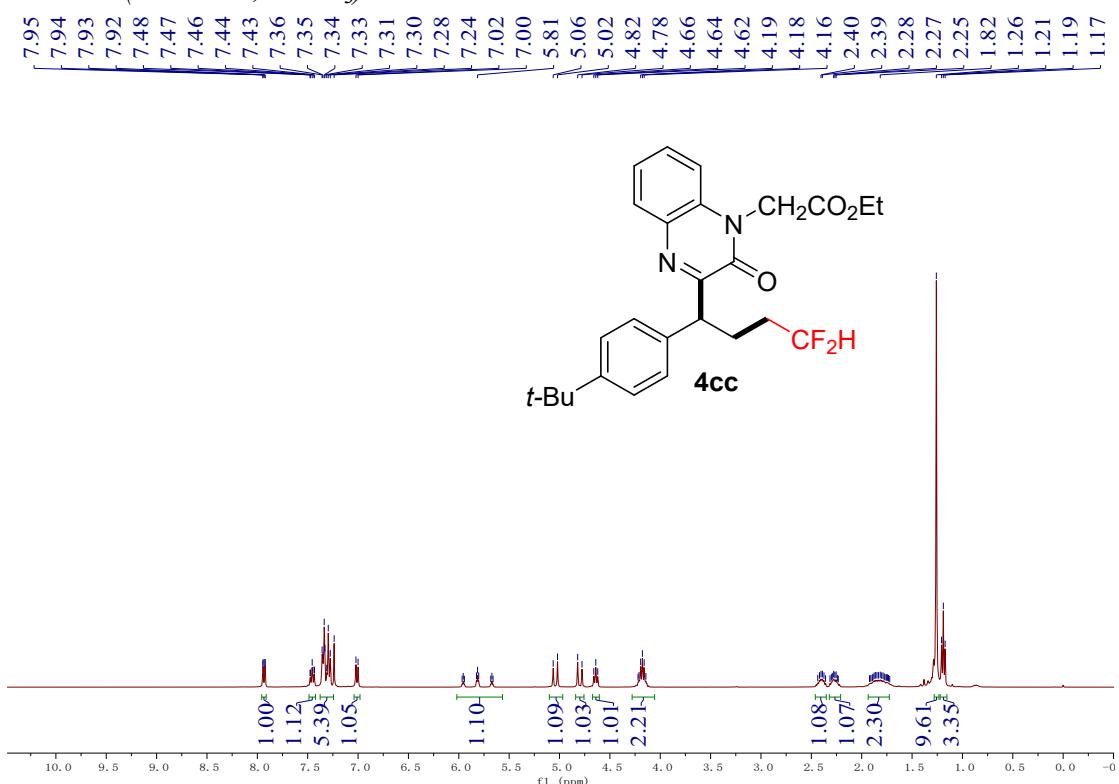
¹³C NMR (101 MHz, CDCl₃)



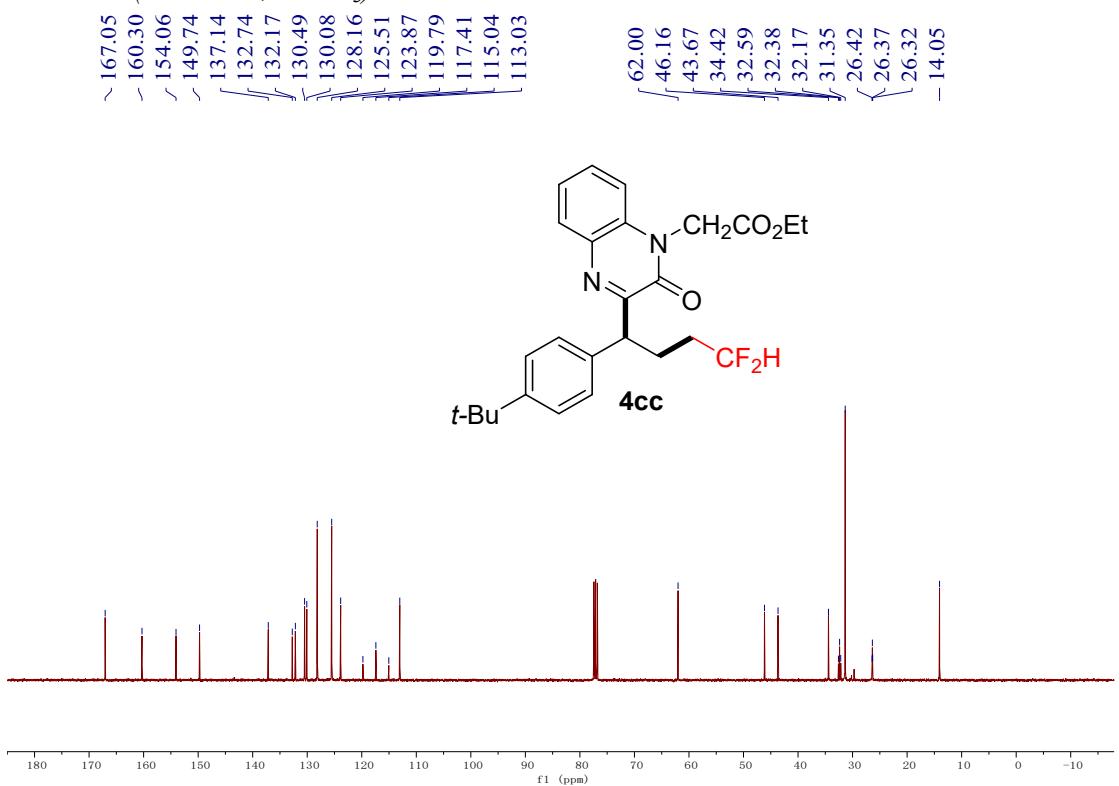
¹⁹F NMR (377 MHz, CDCl₃)



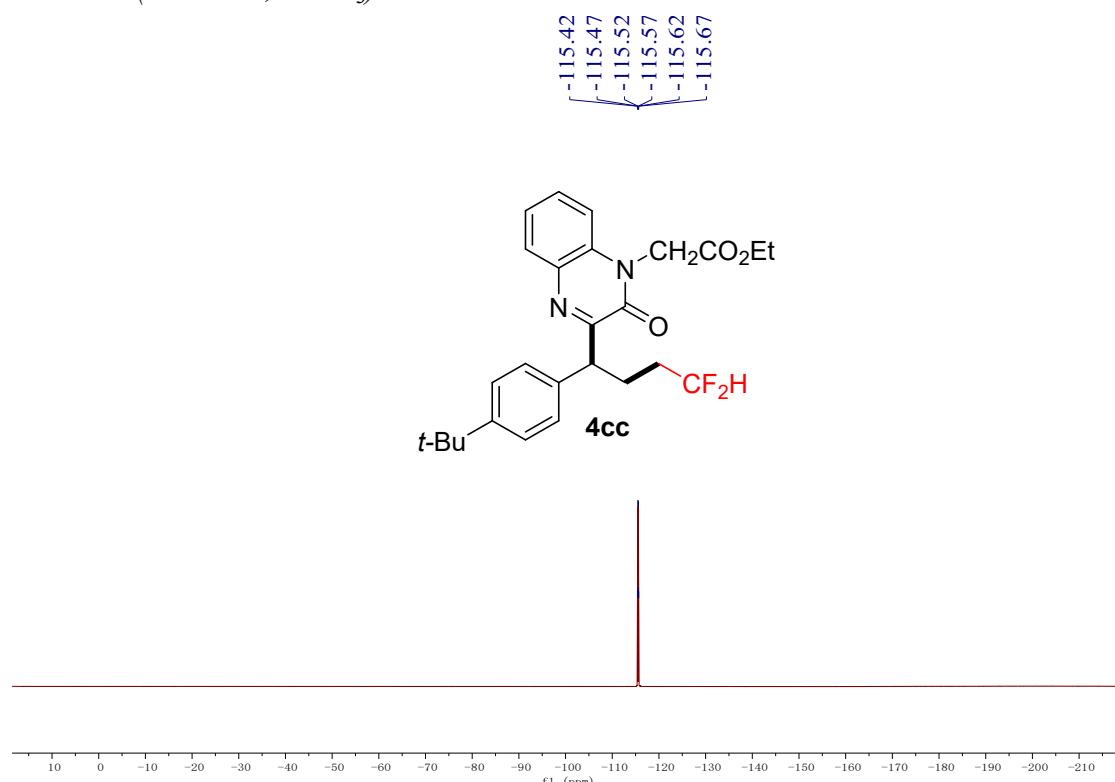
¹H NMR (400 MHz, CDCl₃)



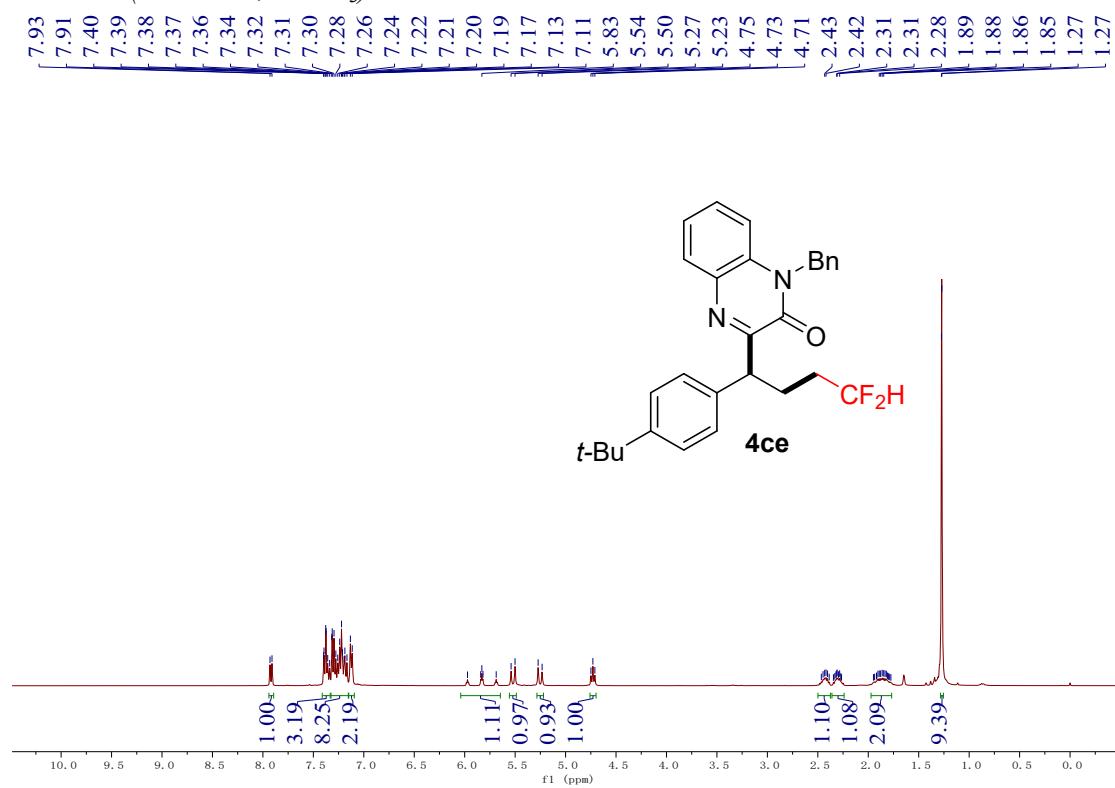
¹³C NMR (101 MHz, CDCl₃)



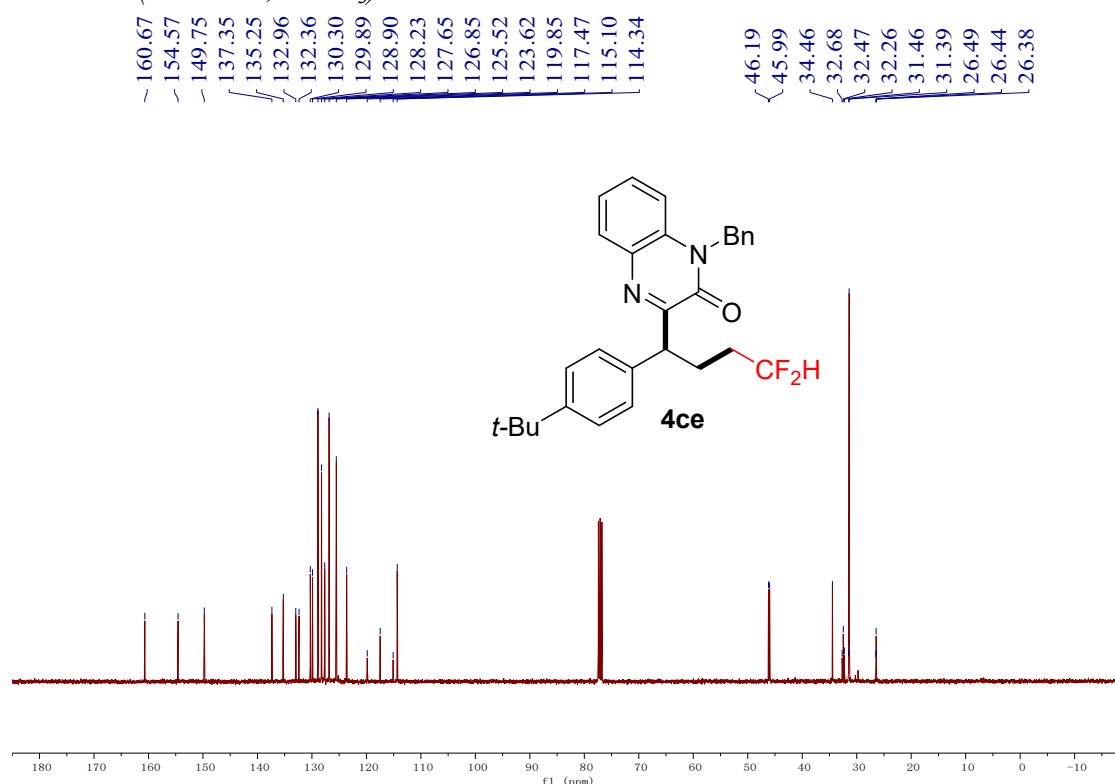
¹⁹F NMR (377 MHz, CDCl₃)



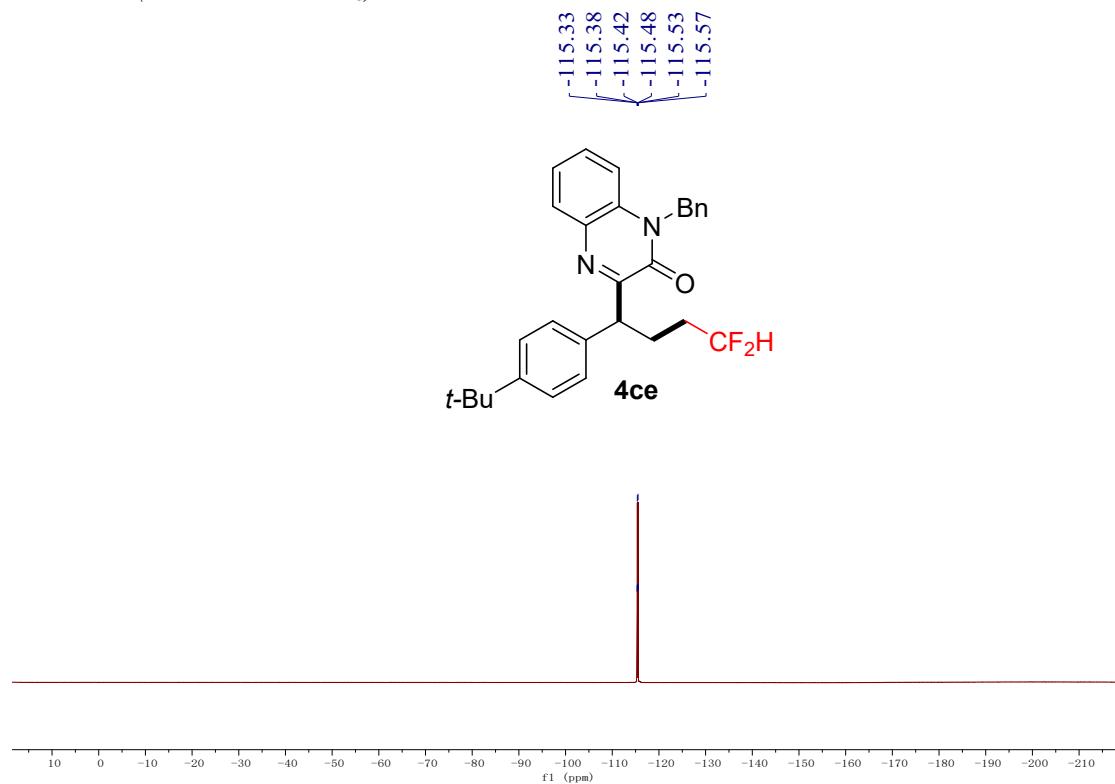
¹H NMR (400 MHz, CDCl₃)



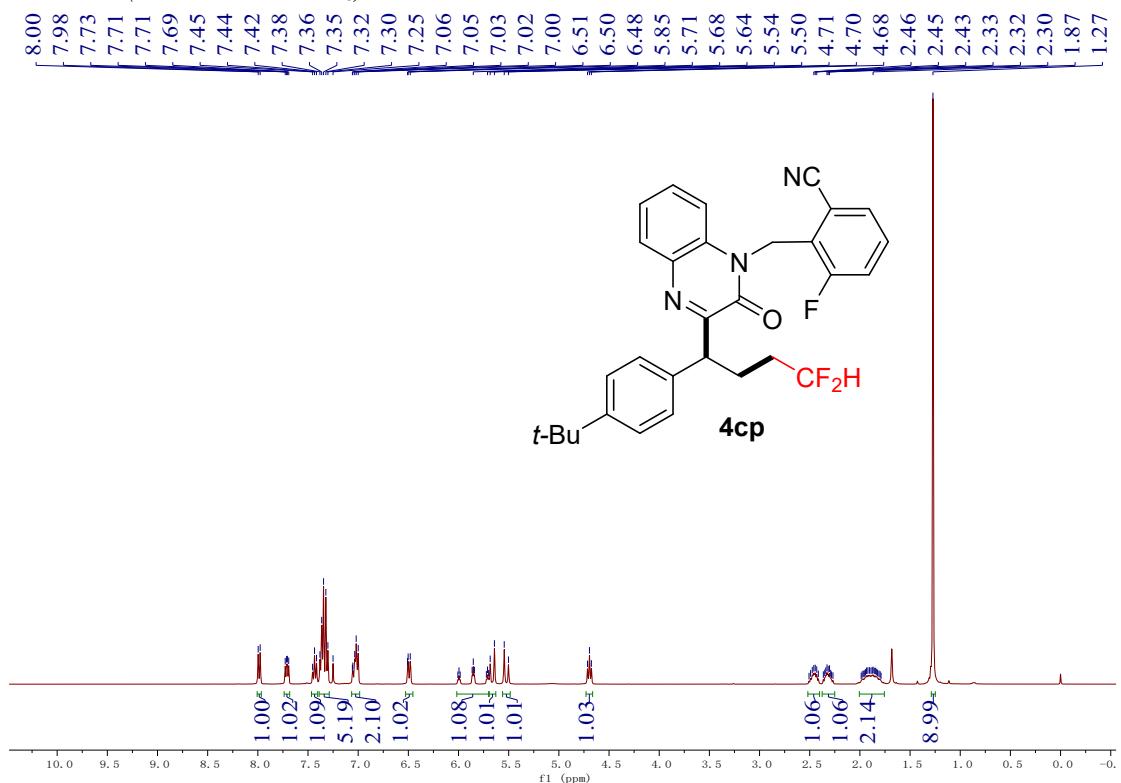
¹³C NMR (101 MHz, CDCl₃)



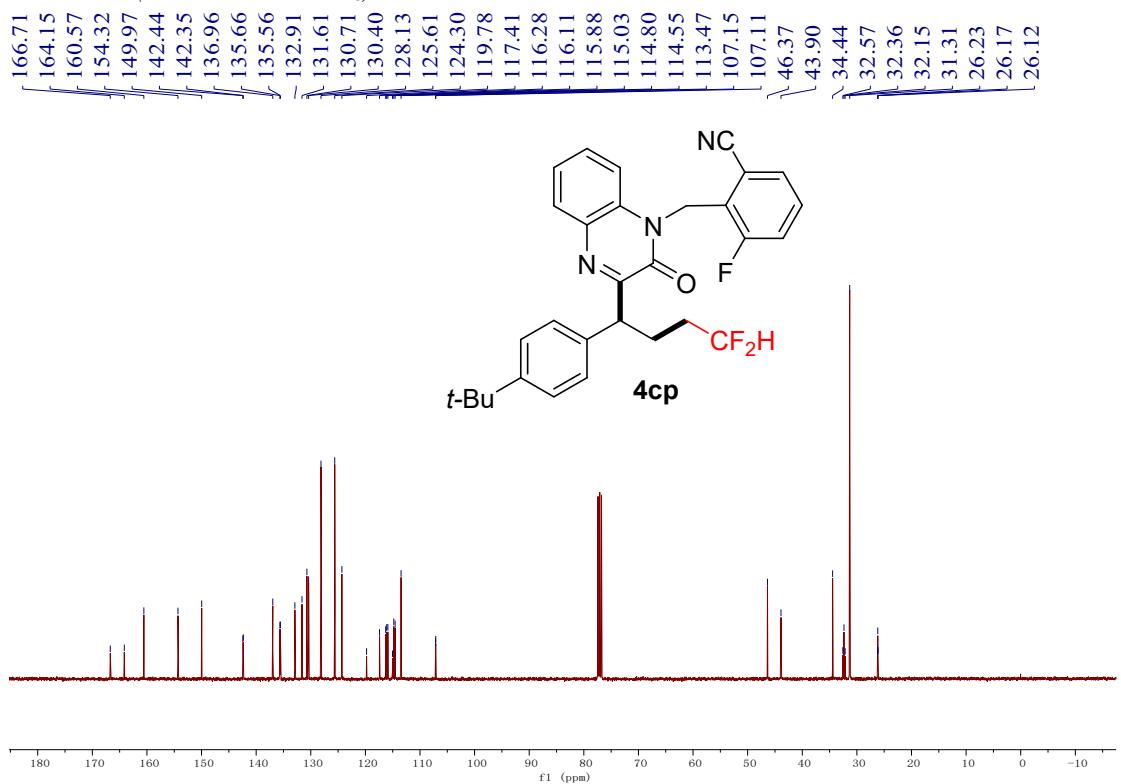
¹⁹F NMR (377 MHz, CDCl₃)



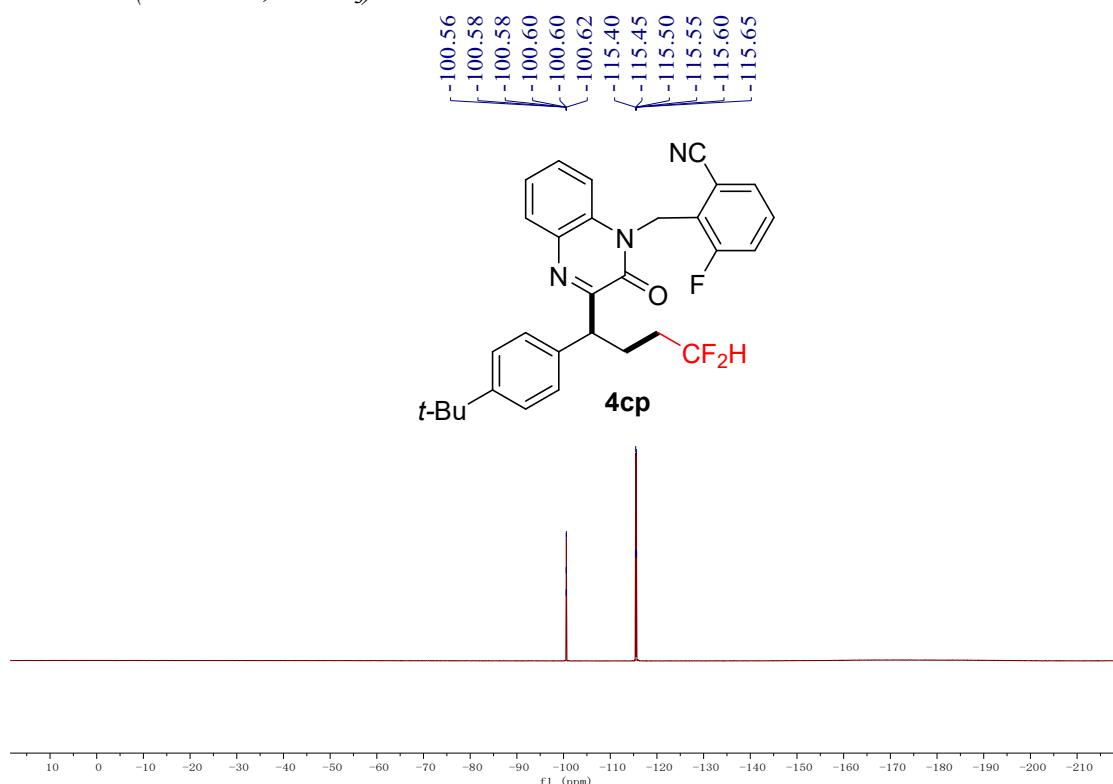
¹H NMR (400 MHz, CDCl₃)



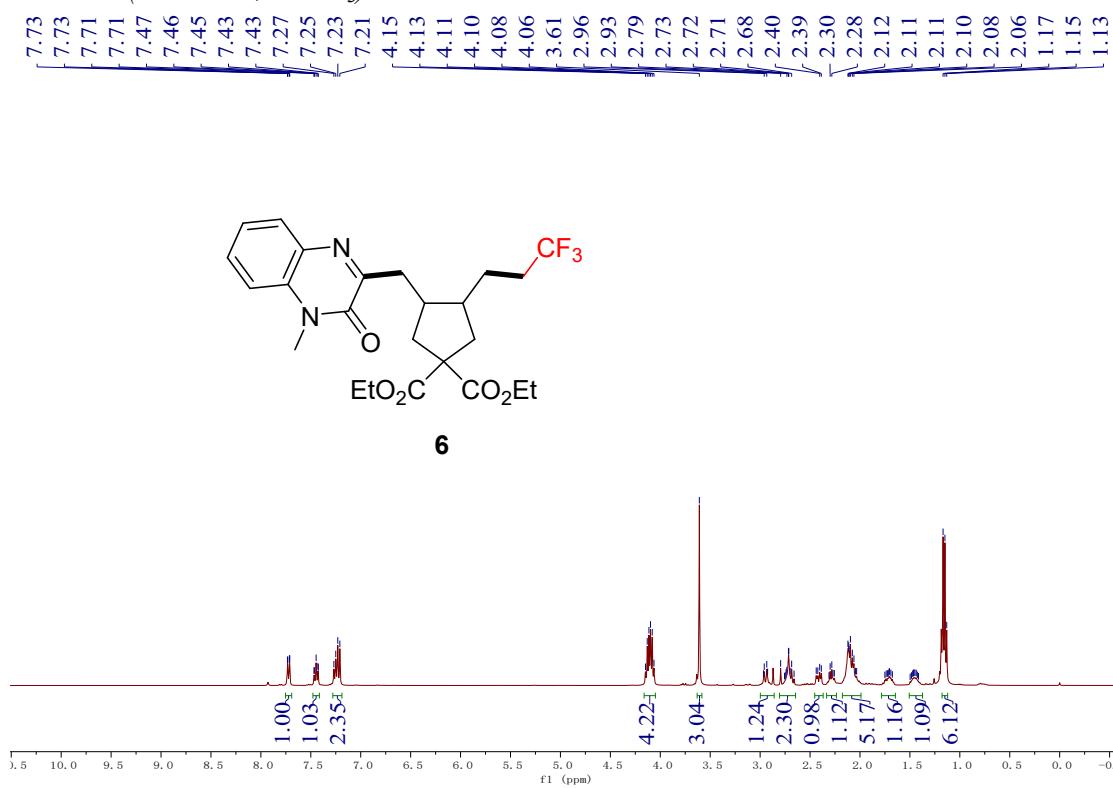
¹³C NMR (101 MHz, CDCl₃)



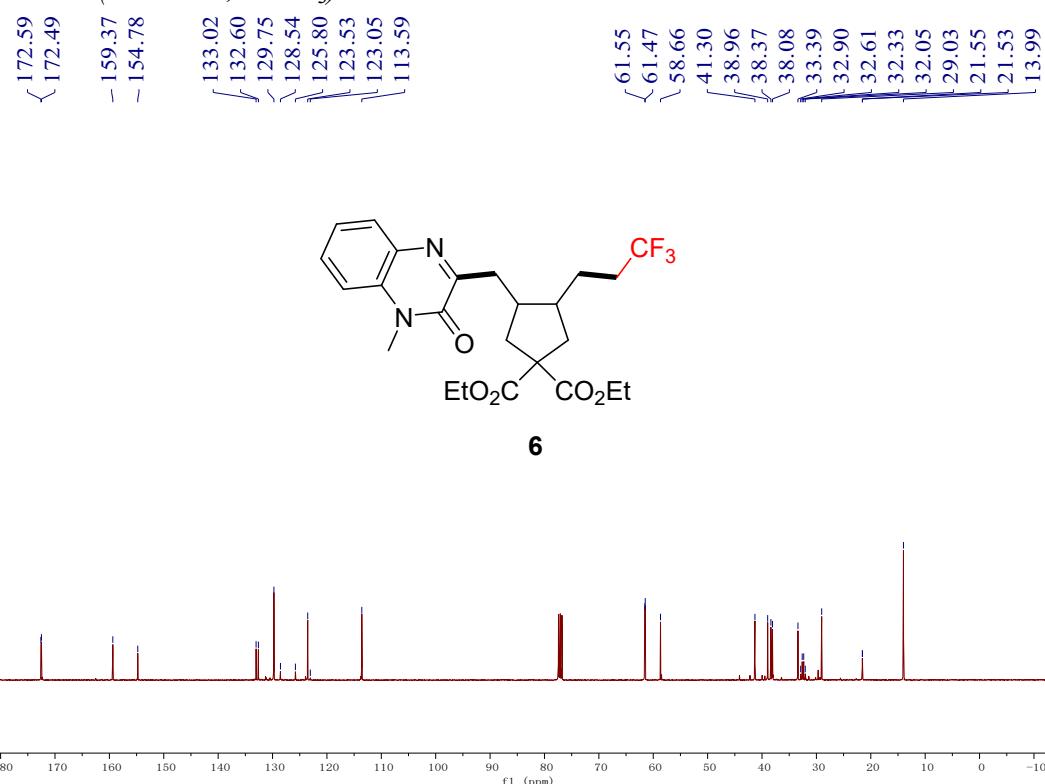
¹⁹F NMR (377 MHz, CDCl₃)



¹H NMR (400 MHz, CDCl₃)



^{13}C NMR (101 MHz, CDCl_3)



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

