Supporting Information

Photoinitiated Three Component α -Perfluoroalkyl- β -Heteroarylation of Unactivated Alkenes via Electron Catalysis

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1. General Experimental Methods

All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in pre-heated glassware under an argon atmosphere using standard *Schlenk* techniques. All commercially available reagents were purchased from TCI, Sigma-Aldrich, Alfa Aesar, Acros or ABCR in the highest purity grade and used directly without further purification. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F-254 plates and visualized by fluorescence quenching under UV light or staining with the standard solution of KMnO4. Column chromatography was performed on Merck or Fluka silica gel 60 (40-63 μm) using a forced flow of 0.5 bar. ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were recorded on *DPX* 300, *AV* 400 or 600 at 300 K. Chemical shifts were expressed in parts per million (ppm) with respect to the residual solvent peak. Coupling constants were reported as Hertz (Hz), signal shapes and splitting patterns were indicated as follows: s, singlet; brs, broad singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra were recorded on a *Finnigan MAT* 4200S, a *Bruker Daltonics Micro Tof*, a *Waters-Micromass Quatro LCZ* (ESI); peaks are given in *m/z* (% of basis peak).

2. General experimental procedure

Quinoxalin-2(1*H*)-ones **1aa-1am**¹, **1an**² were prepared according to the reported procedures.

General experimental procedure for the reaction of quinoxalin-2(1*H*)-ones **1**, alkenes **2** and perfluoroalkyl iodides **3**

A Schlenk-tube equipped with a magnetic stir bar was charged with a quinoxalin-2(1*H*)-one **1** (0.2 mmol) and then evacuated and backfilled with Ar 3 times. Afterwards, NMP (0.5 mL), an alkene **2** (2.5 equiv, 0.50 mmol), a perfluoroalkyl iodide **3** (2.0 equiv, 0.4 mmol) and DBU (3.0 equiv, 0.6 mmol) were added by syringe under Ar atmosphere.

The tightly sealed tube was then irradiated with a 5 W blue LEDs (the distance between the tube and the light source was about 5 cm) and simultaneously cooled by a fan to keep the reaction temperature at 25 °C. After 16 hours, the mixture was transferred into a 100 mL separating funnel which contained 20 mL H₂O. The mixture was extracted twice with Et₂O (20 mL each) 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 (EtOAc:pentane = 1:8 to 1:1) to give the product 4.

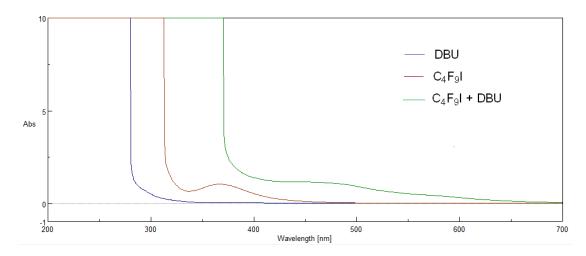
Scaled-up synthesis of compound 4a

A Schlenk-tube equipped with a magnetic stir bar was charged with a quinoxalin-2(1*H*)-one 1 (1 mmol, 160 mg) and then evacuated and backfilled with Ar 3 times. Afterwards, NMP (2.5 mL), allylbenzene 2a (2.5 equiv, 2.50 mmol, 295mg), perfluorobutyl iodide 3 (2.0 equiv, 2 mmol, 692 mg) and DBU (3.0 equiv, 3 mmol, 456 mg) were added by syringe under Ar atmosphere. The tightly sealed tube was then irradiated with a 5 W blue LEDs (the distance between the tube and the light source was about 5 cm) and simultaneously cooled by a fan to keep the reaction temperature at 25 °C. After 16 hours, the mixture was transferred into a 100 mL separating funnel which contained 30 mL H₂O. The mixture was extracted twice with Et₂O (30 mL each) and the combined organic layer was washed with brine (30 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 (EtOAc:pentane = 1:8) to give the product 4a as a colloidal solid in 84% yield (415.6 mg).

3. UV/Vis absorption spectra

The UV/Vis absorption spectra of NMP solutions of DBU (0.1 M), C₄F₉I (0.1 M), and

a mixture of C₄F₉I and DBU are shown in Figure S1. A bathochromic shift can be observed, indicating the formation of an EDA complex.



Reference:

- 1. A. Carrër, J.-D. Brion, S. Messaoudi, and M. Alami, Org. Lett., 2013, 15, 5606.
- 2. M. Kaftory, V. Shteiman, T. Lavy, J. R. Scheffer, J. Yang, and V. Enkelmann, *Eur. J. Org. Chem.*, 2005, 847.

$$C_4F_5$$

yl)quinoxalin-2(1*H*)-one (**4a**): According to the General Procedure, **4a** (87.6 mg, 88%) was prepared as a colloidal solid. 1 H NMR (300 MHz, CDCl₃) δ 7.76 (dd, J = 8.0, 1.4 Hz, 1H), 7.52 – 7.42 (m, 1H), 7.31 – 7.09 (m, 7H), 4.26 – 4.17 (m, 1H), 3.62 (s, 3H), 3.27 – 2.93 (m, 2H), 2.73 (dd, J = 13.6, 8.9 Hz, 1H), 2.22 (dd, J = 37.6, 17.7 Hz, 1H); 13 C NMR (75 MHz, CDCl₃) δ 160.28, 154.26, 138.42, 133.09, 132.46, 130.14, 129.96, 129.23, 128.50, 126.60, 123.64, 113.61, 39.82, 36.41, 31.71 (s), 31.44 (t, J = 21.0 Hz), 29.15, 13 C-NMR for CF₂CF₂CF₂CF₃ could not be assigned; 19 F NMR (282 MHz, CDCl₃) δ -81.09 (tt, J = 9.7, 3.1 Hz, 3F), -112.47 (t, J = 12.7 Hz, 2F), -124.45 (m, 2F), -125.71 – -126.12 (m, 2F); FTIR (neat): \tilde{v} = 2951, 1652, 1603, 1474, 1216, 1131, 1100, 749, 701; HRMS (ESI): Calcd for [C₂₂H₁₇F₉N₂O+Na] +: 519.1089, found: 519.1082.

$$C_4F_5$$

yl)quinoxalin-2(1*H*)-one (**4b**): According to the General Procedure, **4b** (98.3 mg, 97%) was prepared as a colorless oil. 1 H NMR (300 MHz, CDCl₃) δ 7.75 (dd, J = 8.0, 1.5 Hz, 1H), 7.45 (td, J = 8.7, 1.5 Hz, 1H), 7.25 (td, J = 8.0, 1.2 Hz, 1H), 7.21 – 6.96 (m, 6H), 4.04 – 3.91 (m, 1H), 3.58 (s, 3H), 3.20 – 2.95 (m, 1H), 2.72 – 2.11 (m, 4H), 1.95 (m, 1H); 19 F NMR (282 MHz, CDCl₃) δ -81.05 (tt, J = 9.7, 3.1 Hz, 3F), -111.44 – -114.09 (m, 2F), -124.42 (dd, J = 18.2, 8.9 Hz, 2F), -125.59 – -125.99 (m, 2F); 13 C NMR (75 MHz, CDCl₃) δ 160.6, 154.3, 141.2, 133.1, 132.4, 130.1, 129.7, 128.3, 128.2, 125.8, 123.6, 113.5, 35.7, 35.0, 33.3, 32.8 (t, J = 20.25 Hz), 32.6, 29.1, 13 C-NMR for CF₂CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2940, 1653, 1603, 1474, 1217,

1199, 1165, 1131, 878, 751, 698; HRMS (ESI): Calcd for $[C_{23}H_{19}F_{9}N_{2}O+Na]^{+}$: 533.1246, found: 533.1238.

$$C_4F_9$$

1-Methyl-3-(7,7,7,7,7,7,7,7,7,7-nonafluoro-1-(naphthalen-1-yl)-7λ¹²-hepta-4,6-diyn-2-yl)quinoxalin-2(1*H*)-one (**4c**): According to the General Procedure, **4c** (82.8 mg, 76%) was prepared as a colorless oil. 1 H NMR (300 MHz, CDCl₃) δ 8.48 (d, J = 8.4 Hz, 1H), 7.95 – 7.84 (m, 2H), 7.79 (dd, J = 7.3, 2.1 Hz, 1H), 7.68 – 7.49 (m, 3H), 7.29 – 7.45 (m, 4H), 4.63 – 4.46 (m, 1H), 3.89 – 3.70 (m, 4H), 3.50 – 3.09 (m, 2H), 2.37 (dd, J = 37.8, 17.9 Hz, 1H); 19 F NMR (282 MHz, CDCl₃) δ -81.11 (tt, J = 9.7, 3.1 Hz, 3F), -112.35 (s, 2F), -124.30 – -124.70 (m, 2F), -125.80 – -126.10 (m, 2F); 13 C NMR (75 MHz, CDCl₃) δ 160.4, 154.4, 134.4, 134.0, 133.1, 132.5, 132.2, 130.1, 129.9, 128.7, 127.74, 127.70, 126.3, 125.7, 125.1, 124.0, 123.6, 113.6, 37.3, 35.6, 31.6, 31.3 (t, J = 20.3 Hz), 29.2, 13 C-NMR for CF₂CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2951, 1651, 1603, 1474, 1219, 1166, 1133, 1101, 778, 754, 723; HRMS (ESI): Calcd for [C₂₆H₁₉F₉N₂O+Na] $^+$: 569.1246, found: 569.1237.

$$C_4F_9$$

1-Methyl-3-(10,10,10,10,10,10,10,10,10-nonafluoro- $10\lambda^{12}$ -deca-7,9-diyn-5-yl)quinoxalin-2(1*H*)-one (**4d**): According to the General Procedure, **4d** (86.9 mg, 94%) was prepared as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.76 (dd, J = 7.9, 1.5 Hz, 1H), 7.50 – 7.40 (m, 1H), 7.31 – 7.17 (m, 2H), 3.89 (m, 1H), 3.63 (s, 3H), 3.21 – 2.94

(m, 1H), 2.37 - 2.14 (m, 1H), 1.85 - 1.50 (m, 2H), 1.35 - 1.11 (m, 4H), 0.79 (t, J = 6.9 Hz, 3H); 19 F NMR (282 MHz, CDCl3) δ -81.10 (tt, J = 9.7, 3.2 Hz, 3F), -111.41 – -114.33 (m, 2F), -124.49 (m, 2F), -125.67 – -126.10 (m); 13 C NMR (75 MHz, CDCl₃) δ 161.1, 154.4, 133.0, 132.4, 129.96, 129.92, 123.5, 113.5, 34.5, 34.1, 32.5 (t, J = 21.0 Hz), 29.1, 29.0, 22.5, 13.8, 13 C-NMR for CF₂CF₂CF₂CF₃ could not be assigned; FTIR (neat): $\tilde{v} = 2960$, 2937, 1656, 1604, 1475, 1217, 1132, 1088, 877, 752, 722; HRMS (ESI): Calcd for [C₁₉H₁₉F₉N₂O+Na] $^+$: 485.1246, found: 485.1250.

$$C_4F_9$$

$$C_4F_9$$

1-Methyl-3-(9,9,9,9,9,9,9,9,9-nonafluoro-2-methyl-9λ¹²-nona-6,8-diyn-4-yl)quinoxalin-2(1*H*)-one (**4f**): According to the General Procedure, **4f** (90.7 mg, 98%) was prepared as a colorless oil. 1 H NMR (300 MHz, CDCl₃) δ 7.75 (dd, J = 7.9, 1.5 Hz, 1H), 7.46 (ddd, J = 8.6, 7.5, 1.5 Hz, 1H), 7.30 – 7.17 (m, 2H), 4.05 – 3.89 (m, 1H), 3.64 (s, 3H), 3.20 – 2.93 (m, 1H), 2.37 – 2.10 (m, 1H), 1.78 – 1.32 (m, 3H), 0.89 (d, J = 6.3 Hz, 3H), 0.88(d, J = 6.3 Hz, 3H); 19 F NMR (282 MHz, CDCl₃) δ -81.08 (tt, J = 9.7, 3.2 Hz, 3F), -111.32 – -114.55 (m, 2F), -123.97 – -125.28 (m, 2F), -125.55 – -126.32 (m, 2F); 13 C NMR (75 MHz, CDCl₃) δ 161.4, 154.3, 133.0, 132.5, 129.96, 129.90, 123.5, 113.5, 43.6, 32.87 (t, J = 21.0 Hz), 29.1, 25.9, 22.6, 22.2, 13 C-NMR for CF₂CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2960, 1654, 1604, 1474, 1216, 1165, 1132, 1089, 881, 752, 723; HRMS (ESI): Calcd for [C₁₉H₁₉F₉N₂O+Na] $^+$: 485.1246, found: 485.1256.

$$C_4F_9$$

1-Methyl-3-(1,1,1,1,1,1,1,1,1,1,1-nonafluoro-12-hydroxy- $1\lambda^{12}$ -dodeca-1,3-diyn-6-yl)quinoxalin-2(1*H*)-one (**4g**): According to the General Procedure, **4g** (99.0 mg, 98%) was prepared as a colorless oil. 1 H NMR (300 MHz, CDCl₃) δ 7.76 (dd, J = 7.9, 1.5 Hz, 1H), 7.52 – 7.42 (m, 1H), 7.33 – 7.18 (m, 2H), 3.96 – 3.80 (m, 1H), 3.64 (s, 3H), 3.59 – 3.47 (m, 2H), 2.97 – 3.18 (m, 1H), 2.37 – 2.13 (m, 1H), 1.74 – 1.84 (m, 1H), 1.60 – 1.14 (m, 10H); 19 F NMR (282 MHz, CDCl₃) δ -81.09 (tt, J = 9.7, 3.2 Hz, 3F), -111.51 – -114.11 (m, 2F), -124.52 – -124.43 (m, 2F), -125.94 – 125.86 (m, 2F); 13 C NMR (75 MHz, CDCl₃) δ 161.0, 154.4, 133.0, 132.4, 130.0, 129.9, 123.6, 113.6, 62.7, 34.4, 34.1, 32.8, 32.5, 29.1, 29.0, 26.8, 25.3, 13 C-NMR for CF₂CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2933, 2860, 1651, 1603, 1217, 1131, 1086, 753, 722; HRMS (ESI): Calcd for [C₂₁H₂₃F₉N₂O₂+Na] $^+$: 529.1508, found: 529.1503.

$$\begin{array}{c} O \\ Ph \\ O \\ N \\ O \end{array}$$

$$C_4F_9$$

Ethyl 9,9,9,9,9,9,9,9,9-nonafluoro-4-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-9 λ^{12} -nona-6,8-diynoate (**4i**): According to the General Procedure, **4i** (91.8 mg, 91%) was prepared as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.76 (dd, J = 7.9, 1.5 Hz, 1H), 7.48 (ddd, J = 8.6, 7.5, 1.5 Hz, 1H), 7.23 – 7.30 (m, 2H), 4.03 – 3.87 (m, 3H), 3.64 (s, 3H), 3.19 – 2.92 (m, 1H), 2.40 – 2.00 (m, 5H), 1.11 (t, J = 7.1 Hz, 3H); ¹⁹F NMR (282 MHz, CDCl₃) δ -81.07 (tt, J = 9.7, 3.2 Hz, 3F), -111.53 – -114.58 (m, 2F), -124.15 – -124.71 (m, 2F), -125.94 – -125.85 (m, 2F); ¹³C NMR (75 MHz, CDCl₃) δ 172.6, 159.9, 154.3, 133.1, 132.3, 130.2, 130.0, 123.6, 113.6, 60.4, 34.0, 32.99 (t, J = 21.0 Hz),

 $31.5, 29.1, 28.9, 14.0, ^{13}$ C-NMR for $CF_2CF_2CF_2CF_3$ could not be assigned; FTIR (neat): $\tilde{v}=2984, 1732, 1653, 1604, 1474, 1216, 1164, 1131, 1107, 754;$ HRMS (ESI): Calcd for $[C_{20}H_{19}F_9N_2O_3+Na]^+$: 529.1144, found: 529.1135.

Diethyl (8,8,8,8,8,8,8,8,8,8-nonafluoro-3-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-8 λ^{12} -octa-5,7-diyn-1-yl)phosphonate (**4j**): According to the General Procedure, **4j** (101.8 mg, 89%) was prepared as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.76 (dd, J = 8.0, 1.4 Hz, 1H), 7.53 – 7.45 (m, 1H), 7.32 – 7.20 (m, 2H), 4.04 – 3.91 (m, 5H), 3.64 (s, 3H), 3.15 – 2.86 (m, 1H), 2.32 – 1.98 (m, 4H), 1.86 – 1.52 (m, 2H), 1.21 (td, J = 7.1, 2.7 Hz, 6H); ¹⁹F NMR (282 MHz, CDCl₃) δ -81.10 (tt, J = 9.7, 3.1 Hz, 3F), -111.30 – -114.54 (m, 2F), -124.31 – -124.68 (m, 2F), -125.94 – 125.87 (m, 2F); ¹³C NMR (75 MHz, CDCl₃) δ 159.5, 154.3, 133.0, 132.3, 130.4, 130.0, 123.7, 113.6, 61.6 (d, J = 6.5 Hz), 34.8 (d, J = 18.4 Hz), 32.68 (t, J = 21.0 Hz), 29.2, 26.78 (d, J = 4.0 Hz), 24.0, 22.1, 16.33 (d, J = 5.9 Hz), ¹³C-NMR for CF₂CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2984, 1651, 1603, 1218, 1132, 1055, 1024, 959, 756, 722; HRMS (ESI): Calcd for [C₂₁H₂₄F₉N₂PO₄+Na] +: 593.1222, found: 593.1219.

$$C_4F_9$$

10,10,10,10,10,10,10,10,10,10. Nonafluoro-5-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)- $10\lambda^{12}$ -deca-7,9-diynenitrile (**4k**): According to the General Procedure, **4k** (57.9 mg, 61%) was prepared as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.77 (dd, J = 8.0, 1.4 Hz, 1H), 7.55 – 7.46 (m, 1H), 7.34 – 7.23 (m, 2H), 3.89 – 3.98 (m, 1H), 3.65 (s,

3H), 3.17 - 2.88 (m, 1H), 2.39 - 2.16 (m, 3H), 2.08 - 1.90 (m, 1H), 1.74 - 1.86 (m, 1H), 1.72 - 1.51 (m, 2H); ¹⁹F NMR (282 MHz, CDCl₃) δ -81.05 (tt, J = 9.7, 3.1 Hz, 3F), -111.44 – -114.44 (m, 2F), -123.91 – -124.69 (m, 2F), -125.91 – -125.83 (m, 2F); ¹³C NMR (75 MHz, CDCl₃) δ 159.7, 154.3, 133.0, 132.3, 130.4, 130.0, 123.8, 119.1, 113.7, 33.7, 33.1, 33.0 (t, J = 21.0 Hz), 29.2, 22.9, 16.9, ¹³C-NMR for CF₂CF₂CF₂CF₃ could not be assigned; FTIR (neat): $\tilde{v} = 2943$, 1653, 1604, 1220, 1133, 880, 755, 723; HRMS (ESI): Calcd for [C₁₉H₁₆F₉N₃O+Na] +: 496.1042, found: 496.1034.

$$CI$$
 C_4F_9

3-(1-Chloro-10,10,10,10,10,10,10,10,10,10-nonafluoro-10λ¹²-deca-7,9-diyn-5-yl)-1-methylquinoxalin-2(1*H*)-one (**4l**): According to the General Procedure, **4l** (84.3 mg, 85%) was prepared as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.76 (dd, J = 8.0, 1.5 Hz, 1H), 7.48 (ddd, J = 8.6, 7.4, 1.5 Hz, 1H), 7.22 – 7.30 (m, 2H), 4.00 – 3.83 (m, 1H), 3.64 (s, 3H), 3.43 (t, J = 6.6 Hz, 2H), 3.21 – 2.94 (m, 1H), 2.43 – 2.13 (m, 1H), 1.94 – 1.30 (m, 6H); ¹⁹F NMR (282 MHz, CDCl₃) δ -81.07 (tt, J = 9.7, 3.2 Hz, 3F), -111.43 – -114.41 (m, 2F), -124.27 – -124.62 (m, 2F), -125.89 (t, J = 10.6 Hz, 2F); ¹³C NMR (75 MHz, CDCl₃) δ 160.6, 154.3, 133.0, 132.4, 130.1, 129.9, 123.6, 113.6, 44.5, 34.3, 33.3, 32.6 (t, J = 21.7 Hz), 32.2, 29.1, 24.1, ¹³C-NMR for CF₂CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2950, 1652, 1603, 1217, 1131, 880, 753, 722; HRMS (ESI): Calcd for [C₁₉H₁₈CIF₉N₂O+Na] +: 519.0856, found: 519.0856.

$$C_4F_9$$

3-(1-Bromo-10,10,10,10,10,10,10,10,10,10-nonafluoro-10λ¹²-deca-7,9-diyn-5-yl)-1-methylquinoxalin-2(1*H*)-one (**4m**): According to the General Procedure, **4m** (56.9 mg, 53%) was prepared as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.77 (dd, J = 8.0, 1.4 Hz, 1H), 7.48 (ddd, J = 8.6, 7.4, 1.5 Hz, 1H), 7.23 – 7.31 (m, 2H), 3.97 – 3.83 (m, 1H), 3.65 (s, 3H), 3.30 (t, J = 6.7 Hz, 2H), 3.21 – 2.92 (m, 1H), 2.45 – 2.12 (m, 1H), 1.88 – 1.31 (m, 7H); ¹⁹F NMR (282 MHz, CDCl₃) δ -81.05 (tt, J = 9.7, 3.1 Hz, 3F), -111.48 – -114.12 (m, 2F), -124.27 – -124.62 (m, 2F), -125.87 (t, J = 10.5 Hz, 2F); ¹³C NMR (75 MHz, CDCl₃) δ 160.5, 154.3, 133.0, 132.4, 130.1, 129.9, 123.6, 113.6, 34.3, 33.2, 33.1, 32.63 (t, J = 21.0 Hz), 32.3, 29.2, 25.3, ¹³C-NMR for CF₂CF₂CF₃ could not be assigned; FTIR (neat): $\tilde{v} = 2941$, 1652, 1604, 1474, 1218, 1132, 880, 754, 722; HRMS (ESI): Calcd for [C₁₉H₁₈BrF₉N₂O+Na] +: 563.0351, found: 563.0345.

$$C_4F_9$$

1-Methyl-3-(7,7,7,7,7,7,7,7,7,7-nonafluoro-1-(thiophen-2-yl)-7λ¹²-hepta-4,6-diyn-2-yl)quinoxalin-2(1*H*)-one (**4n**): According to the General Procedure, **4n** (59.0 mg, 57%) was prepared as a colorless oil. 1 H NMR (300 MHz, CDCl₃) δ 7.65 (dd, J = 8.0, 1.4 Hz, 1H), 7.42 – 7.32 (m, 1H), 7.11 – 7.19 (m, 2H), 6.91 (dd, J = 5.1, 1.1 Hz, 1H), 6.64 – 6.71 (m, 2H), 4.09 (ddd, J = 12.0, 9.8, 3.8 Hz, 1H), 3.52 (s, 3H), 3.25 (dd, J = 14.7, 6.4 Hz, 1H), 3.10 – 2.79 (m, 2H), 2.39 – 2.11 (m, 1H); 19 F NMR (282 MHz, CDCl₃) δ - 81.06 (tt, J = 9.7, 3.1 Hz, 3F), -111.30 – -113.66 (m, 2F), -124.16 – -124.64 (m, 2F), -125.72 – -126.05 (m, 2F); 13 C NMR (75 MHz, CDCl₃) δ 159.6, 154.2, 140.6, 133.1, 132.4, 130.2, 130.0, 126.8, 126.1, 124.2, 123.6, 113.6, 36.9, 33.5, 31.7 (d, J = 21.0 Hz), 29.1, 13 C-NMR for CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2952, 1652, 1603, 1474, 1217, 1132, 1095, 884, 752, 726; HRMS (ESI): Calcd for [C₂₀H₁₅F₉N₂O+Na]⁺: 525.0654, found: 525.0652.

$$C_4F_5$$

3-(1-(9*H*-Carbazol-9-yl)-9,9,9,9,9,9,9,9,9,9-nonafluoro-9λ¹²-nona-6,8-diyn-4-yl)-1-methylquinoxalin-2(1*H*)-one (**4o**): According to the General Procedure, **4o** (85.0 mg, 70%) was prepared as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.96 (d, *J* = 7.7 Hz, 2H), 7.67 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.43 (ddd, *J* = 8.6, 7.4, 1.5 Hz, 1H), 7.35 – 7.05 (m, 8H), 4.29 – 3.83 (m, 2H), 4.05 – 3.89 (m, 1H), 3.57 (s, 3H), 3.09 – 2.88 (m, 1H), 2.35 – 1.63 (m, 5H); ¹⁹F NMR (282 MHz, CDCl₃) δ -81.02 (tt, *J* = 9.7, 3.1 Hz, 3F), -111.31 – -114.14 (m, 2F), -124.22 – -124.61 (m, 2F), -125.88 – -125.81 (m, 2F); ¹³C NMR (75 MHz, CDCl₃) δ 160.2, 154.3, 140.3, 133.0, 132.4, 130.2, 130.0, 125.6, 123.6, 122.8, 120.3, 118.8, 113.6, 108.6, 42.6, 34.2, 33.13 (t, *J* = 21.0 Hz), 31.6, 29.1, 25.9, ¹³C-NMR for CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2950, 1649, 1602, 1464, 1217, 1132, 748, 723; HRMS (ESI): Calcd for [C₃₀H₂₄F₉N₃O+Na] ⁺: 636.1668, found: 636.1671.

$$C_4F_9$$

1-Methyl-3-(9,9,9,9,9,9,9,9,9-nonafluoro-1-((2-oxo-2*H*-chromen-4-yl)oxy)-9 λ^{12} -nona-6,8-diyn-4-yl)quinoxalin-2(1*H*)-one (**4p**): According to the General Procedure, **4p** (111.2 mg, 92%) was prepared as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.61 (ddd, J = 17.7, 7.9, 1.5 Hz, 2H), 7.43 – 7.28 (m, 2H), 7.21 – 7.01 (m, 4H), 5.39 (s, 1H), 4.00 – 3.85 (m, 3H), 3.51 (s, 3H), 3.14 – 2.78 (m, 1H), 1.96 – 2.34 m, 2H), 1.85 – 1.68

(m, 3H); ¹⁹F NMR (282 MHz, CDCl₃) δ -81.06 (tt, J = 9.7, 3.1 Hz, 3F), -111.34 – -114.21 (m, 2F), -124.24 – -124.72 (m, 2F), -125.91 – -125.83 (m, 2F); ¹³C NMR (75 MHz, CDCl₃) δ 165.4, 162.7, 160.1, 154.3, 153.3, 133.0, 132.3, 132.2, 130.4, 129.9, 123.7, 122.9, 116.6, 115.6, 113.6, 90.4, 68.6, 34.3, 33.05 (t, J = 21.0 Hz) , 30.2, 29.2, 25.9, ¹³C-NMR for CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2956, 1722, 1653, 1624, 1236, 1184, 1133, 1109, 752; HRMS (ESI): Calcd for [C₂₇H₂₁F₉N₂O₄+Na] $^+$: 631.1250, found: 631.1255.

$$C_4F_9$$

2-(9,9,9,9,9,9,9,9,9,9,9,9-Nonafluoro-4-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-9 λ^{12} -nona-6,8-diyn-1-yl)isoindoline-1,3-dione (**4q**): According to the General Procedure, **4q** (112.5 mg, 97%) was prepared as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.75 – 7.66 (m, 3H), 7.64 – 7.55 (m, 2H), 7.50 – 7.41 (m, 1H), 7.19 – 7.26 (m, 2H), 3.89 – 3.96 (m, 1H), 3.67 – 3.53 (m, 5H), 3.17 – 2.91 (m, 1H), 2.16 – 2.35 (m, 1H), 1.92 – 1.79 (m, 1H), 1.80 – 1.48 (m, 3H); ¹⁹F NMR (282 MHz, CDCl₃) δ -81.08 (tt, J = 9.7, 3.1 Hz, 3F), -111.28 – -114.27 (m, 2F), -124.29 – -124.66 (m, 2F), -125.89 (t, J = 10.8 Hz, 2F); ¹³C NMR (75 MHz, CDCl₃) δ 168.2, 160.2, 154.3, 133.8, 133.0, 132.4, 132.1, 130.1, 129.9, 123.5, 123.1, 113.6, 37.76 (s), 34.29 (s), 32.88 (t, J = 21.1 Hz), 31.5, 29.1, 25.9, ¹³C-NMR for CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2942, 1710, 1653, 1604, 1397, 1219, 1133, 755, 720; HRMS (ESI): Calcd for [C₂₆H₂₀F₉N₃O₃+Na] ⁺: 616.1253, found: 616.1255.

$$C_4F_9$$

yl)quinoxalin-2(1*H*)-one (**4r**): According to the General Procedure, **4r** (32.8 mg, 34%) was prepared as a colorless oil. 1 H NMR (300 MHz, CDCl₃) δ 7.85 (dd, J = 8.0, 1.5 Hz, 1H), 7.47 (ddd, J = 8.7, 7.4, 1.5 Hz, 1H), 7.38 – 7.41 (m, 2H), 7.34 – 7.25 (m, 1H), 7.25 – 7.09 (m, 4H), 5.15 (dd, J = 8.4, 4.9 Hz, 1H), 3.69 – 3.43 (m, 1H), 3.56 (s, 3H), 2.75 – 2.49 (m, 1H); 19 F NMR (282 MHz, CDCl₃) δ -81.02 (tt, J = 9.7, 3.2 Hz, 3F), -111.15 – -114.79 (m, 2F), -124.45 (d, J = 9.4 Hz, 2F), -125.85 – -125.73 (m, 2F); 13 C NMR (75 MHz, CDCl₃) δ 158.6, 154.0, 139.8, 133.2, 132.3, 130.2, 130.1, 128.7, 128.4, 127.3, 123.6, 113.6, 39.7, 34.32 (t, J = 21.0 Hz), 29.1, 13 C-NMR for CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2956, 1654, 1604, 1474, 1218, 1132, 1076, 879, 753, 699; HRMS (ESI): Calcd for [C₂₁H₁₅F₉N₂O+Na] $^+$: 505.0933, found: 505.0931.

$$\bigcap_{N \to 0}^{OMe} C_4 F_9$$

1-Methyl-3-(6,6,6,6,6,6,6,6,6,6,6-nonafluoro-1-(4-methoxyphenyl)-6 λ^{12} -hexa-3,5-diyn-1-yl)quinoxalin-2(1*H*)-one (**4s**): According to the General Procedure, **4s** (73.6 mg, 72%) was prepared as a colorless oil. 1 H NMR (300 MHz, CDCl₃) δ 7.95 (dd, J = 8.0, 1.5 Hz, 1H), 7.62 – 7.51 (m, 1H), 7.47 – 7.36 (m, 3H), 7.34 – 7.25 (m, 1H), 6.90 – 6.82 (m, 2H), 5.21 (dd, J = 8.3, 5.1 Hz, 1H), 3.78 (s, 3H), 3.71 – 3.52 (m, 1H), 3.67 (s, 3H), 2.61 – 2.81 (m, 1H); 19 F NMR (282 MHz, CDCl₃) δ -81.04 (tt, J = 9.7, 3.2 Hz, 3F), -111.03 – -114.82 (m, 2F), -124.47 (d, J = 9.2 Hz, 2F), -125.64 – -126.01 (m, 2F); 13 C NMR (75 MHz, CDCl₃) δ 158.87, 158.80, 154.0, 133.1, 132.3, 131.7, 130.1, 129.4, 123.6, 114.1, 113.5, 55.1, 38.9, 34.3 (t, J = 21.0 Hz), 29.1, 13 C-NMR for CF₂CF₂CF₂CF₃ could

not be assigned; FTIR (neat): $\tilde{v}=2957,\,1656,\,1604,\,1512,\,1231,\,1180,\,1133,\,1095,\,1036,\,879,\,751;$ HRMS (ESI): Calcd for $[C_{22}H_{17}F_9N_2O_2+Na]^+$: 535.1039, found: 535.1033.

$$\begin{array}{c|c} & \text{Et} & \text{Et} \\ & & \\ &$$

$$C_4F_9$$

 $1\text{-Methyl-}3\text{-}(1\text{-}(5,5,5,5,5,5,5,5,5,5-nonafluoro-}5\lambda^{12}\text{-penta-}2,4\text{-diyn-}1\text{-}$

yl)cyclohexyl)quinoxalin-2(1*H*)-one (**4u**): According to the General Procedure, **4u** (88.5 mg, 93%) was prepared as a white solid. 1 H NMR (300 MHz, CDCl₃) δ 7.80 (dd, J = 7.9, 1.5 Hz, 1H), 7.45 (ddd, J = 8.6, 7.4, 1.5 Hz, 1H), 7.30 – 7.17 (m, 2H), 3.59 (s, 3H), 3.01 (t, J = 21.6 Hz, 2H), 2.53 – 2.35 (m, 2H), 1.93 – 1.75 (m, 2H), 1.38 – 1.62 (m, 6H); 19 F NMR (282 MHz, CDCl₃) δ -81.13 (tt, J = 9.8, 3.0 Hz, 3F), -110.60 – 111.81 (m, 2F), -124.53 – -124.5 (m, 2F), -125.55 – -126.01 (m, 2F); 13 C NMR (75

MHz, CDCl₃) δ 161.2, 153.8, 133.1, 132.2, 130.3, 129.9, 123.3, 113.3, 44.2, 35.41 (t, J = 19.5), 34.8, 28.8, 26.2, 22.2, ¹³C-NMR for CF₂CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2942, 1650, 1603, 1591, 1218, 1130, 1081, 878, 751, 724; HRMS (ESI): Calcd for [C₂₀H₁₉F₉N₂O+Na] +: 497.1246, found: 497.1242.

$$N$$
 C_4F_9

3-(5-Ethyl-10,10,10,10,10,10,10,10,10,10,10-nonafluoro-10λ¹²-deca-7,9-diyn-5-yl)-1-methylquinoxalin-2(1*H*)-one (**4v**): According to the General Procedure, **4v** (86.7 mg, 88%) was prepared as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.91 (dd, J = 7.9, 1.3 Hz, 1H), 7.61 – 7.51 (m, 1H), 7.42 – 7.28 (m, 2H), 3.71 (s, 3H), 3.28 – 2.94 (m, 2H), 2.46 – 1.97 (m, 4H), 1.43 – 1.00 (m, 4H), 0.92 (t, J = 7.3 Hz, 3H), 0.83 (t, J = 7.5 Hz, 3H); ¹⁹F NMR (282 MHz, CDCl₃) δ -81.13 (tt, J = 9.8, 2.8 Hz, 3F), -111.55 (t, J = 12.8 Hz, 2F), -124.57 – -124.68 (m, 2F), -125.50 – -125.96 (m, 2F); ¹³C NMR (75 MHz, CDCl₃) δ 161.3, 153.7, 133.0, 132.0, 130.4, 129.8, 123.2, 113.3, 47.0, 33.0, 32.66 (t, J = 19.0 Hz), 28.8, 26.2, 25.6, 23.1, 13.9, 7.9, ¹³C-NMR for CF₂CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2960, 1652, 1472, 1230, 1216, 1130, 1080, 877, 752, 19; HRMS (ESI): Calcd for [C₂₁H₂₃F₉N₂O+Na] +: 513.1559, found: 513.1563.

$$N$$
 \tilde{C}_4F_9

1-Methyl-3-(2-(4,4,4,4,4,4,4,4,4-nonafluoro- $4\lambda^{12}$ -buta-1,3-diyn-1-

yl)cyclohexyl)quinoxalin-2(1*H*)-one (**4w**): According to the General Procedure, **4w** (49.0 mg, 53%) was prepared as a colorless oil. 1 H NMR (300 MHz, CDCl₃) δ 7.83 (dd, J = 7.9, 1.5 Hz, 1H), 7.55 (ddd, J = 8.6, 7.4, 1.5 Hz, 1H), 7.41 – 7.29 (m, 2H), 3.82 – 3.66 (m, 1H), 3.73 (s, 3H), 3.51 – 3.25 (m, 1H), 2.16 – 1.43 (m, 8H); 19 F NMR (282 MHz, CDCl₃) δ -80.95 (tt, J = 10.2, 2.9 Hz, 3F), -106.80 (dt, J = 279.4, 22.4 Hz, 2F), -

117.38 – -128.15 (m, 4F); ¹³C NMR (75 MHz, CDCl₃) δ 162.3, 154.2, 132.9, 132.6, 129.6, 123.5, 113.5, 41.70 (dd, J = 20.5, 16.5 Hz), 39.2, 31.7, 29.1, 25.0, 24.9, 24.5, ¹³C-NMR for CF₂CF₂CF₃ could not be assigned; FTIR (neat): $\tilde{v} = 2937$, 1653, 1603, 1474, 1232, 1212, 1131, 752, 738, 721; HRMS (ESI): Calcd for [C₁₉H₁₇F₉N₂O+Na] ⁺: 483.1089, found: 483.1089.

$$C_4F_9$$

1-Methyl-3-(7,7,7,7,7,7,7,7,7,7-nonafluoro-2,3-dimethyl-7 λ^{12} -hepta-4,6-diyn-2-yl)quinoxalin-2(1*H*)-one (**4x**): According to the General Procedure, **4x** (38.5 mg, 43%) was prepared as a white solid. 1 H NMR (300 MHz, CDCl₃) δ 7.77 (dd, J = 7.9, 1.5 Hz, 1H), 7.50 – 7.40 (m, 1H), 7.31 – 7.18 (m, 2H), 4.37 – 4.12 (m, 1H), 3.60 (s, 3H), 1.49 (s, 3H), 1.41 (s, 3H), 1.12 (d, J = 7.1 Hz, 3H); 19 F NMR (282 MHz, CDCl₃) δ -80.97 (tt, J = 10.2, 3.0 Hz, 3F), -107.32 – -117.10 (m, 2F), -121.20 – -121.15 (m, 2F), -123.67 – -127.93 (m, 2F); 13 C NMR (75 MHz, CDCl₃) δ 163.4, 153.8, 133.1, 132.1, 130.3, 129.7, 123.3, 113.3, 45.1, 38.22 (t, J = 18.75 Hz), 28.8, 24.7, 21.9, 9.4, 13 C-NMR for CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2987, 1652, 1604, 1232, 1217, 1166, 1131, 1081, 839, 752, 721; HRMS (ESI): Calcd for [C₁₈H₁₇F₉N₂O+Na] ${}^{+}$: 471.1089, found: 471.1093.

$$C_4F_9$$

 $3\hbox{-}(1\hbox{-}Butoxy\hbox{-}6,6,6,6,6,6,6,6,6-nonafluoro\hbox{-}6\lambda^{12}\hbox{-}hexa\hbox{-}3,5\hbox{-}diyn\hbox{-}1\hbox{-}yl)\hbox{-}1\hbox{-}$

methylquinoxalin-2(1H)-one (**4y**): According to the General Procedure, **4y** (93.5 mg, 98%) was prepared as a colorless oil. 1 H NMR (300 MHz, CDCl₃) δ 7.88 (dd, J = 8.0, 1.5 Hz, 1H), 7.52 (ddd, J = 8.7, 7.4, 1.5 Hz, 1H), 7.25 – 7.33 (m, 2H), 5.28 (dd, J = 7.2, 4.9 Hz, 1H), 3.74 – 3.37 (m, 2H), 3.65 (s, 3H), 3.06 – 2.40 (m, 2H), 1.61 – 1.20 (m,

4H), 0.93 - 0.73 (m, 3H); ¹⁹F NMR (282 MHz, CDCl₃) δ -81.09 (tt, J = 9.7, 3.2 Hz, 3F), -110.91 – -114.24 (m, 2F), -124.49 (dd, J = 17.7, 9.4 Hz, 2F), -125.91 – -125.84 (m, 2F); ¹³C NMR (75 MHz, CDCl₃) δ 156.5, 154.2, 133.4, 132.4, 130.9, 130.7, 123.8, 113.6, 71.2, 70.6, 34.08 (t, J = 21.0 Hz), 31.8, 29.0, 19.0, 13.7, ¹³C-NMR for CF₂CF₂CF₃ could not be assigned; FTIR (neat): $\tilde{v} = 2962$, 1657, 1603, 1470, 1218, 1132, 1028, 882, 752; HRMS (ESI): Calcd for [C₁₉H₁₉F₉N₂O₂+Na] +: 501.1195, found: 501.1186.

$$C_4F_9$$

1-Methyl-3-(6,6,6,6,6,6,6,6,6,6-nonafluoro-1-(2-oxopyrrolidin-1-yl)-6 λ^{12} -hexa-3,5-diyn-1-yl)quinoxalin-2(1*H*)-one (**4z**): According to the General Procedure, **4z** (94.9 mg, 98%) was prepared as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.90 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.67 – 7.55 (m, 1H), 7.44 – 7.31 (m, 2H), 5.86 (dd, *J* = 9.1, 4.3 Hz, 1H), 3.79 – 3.54 (m, 2H), 3.72 (s, 3H), 3.35 – 2.85 (m, 2H), 2.40 (t, *J* = 8.0 Hz, 2H), 2.08 (dd, *J* = 14.4, 7.1 Hz, 2H); ¹⁹F NMR (282 MHz, CDCl₃) δ -81.02 (tt, *J* = 9.7, 3.1 Hz, 3F), -112.87 – -115.47 (m, 2F), -124.00 – -124.64 (m, 2F), -125.53 – -126.06 (m, 2F); ¹³C NMR (75 MHz, CDCl₃) δ 175.0, 154.5, 153.6, 133.5, 131.9, 130.9, 130.5, 123.7, 113.6, 47.6, 46.0, 31.1, 29.3, 29.1, 18.6, ¹³C-NMR for CF₂CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2970, 1685, 1649, 1603, 1420, 1216, 1131, 1092, 879, 758, 734; HRMS (ESI): Calcd for [C₁₉H₁₆F₉N₃O₂+Na] +: 512.0991, found: 512.0987.

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N-(6,6,6,6,6,6,6,6,6,6,6,6-nonafluoro-1-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-6 λ^{12} -hexa-3,5-diyn-1-yl)acetamide (**4aa**): According to the General Procedure, **4aa** (69.6 mg, 75%) was prepared as a colorless oil. 1 H NMR (300 MHz, CDCl₃) δ 7.93 (dd, J = 8.0, 1.4 Hz, 1H), 7.69 – 7.59 (m, 1H), 7.48 – 7.35 (m, 2H), 7.07 (d, J = 8.2 Hz, 1H), 5.86 (dt, J = 8.2, 5.7 Hz, 1H), 3.75 (s, 3H), 3.13 – 2.88 (m, 2H), 2.11 (s, 3H); 19 F NMR (282 MHz, CDCl₃) δ -81.08 (tt, J = 9.7, 2.9 Hz, 3F), -111.04 – -114.82 (m, 2F), -124.21 – 124.72 (m, 2F), -125.92 (t, J = 10.9 Hz, 2F); 13 C NMR (75 MHz, CDCl₃) δ 169.2, 155.1, 153.7, 133.2, 132.0, 131.0, 130.3, 124.1, 113.8, 47.1, 32.43 (t, J = 19.7 Hz), 29.0, 23.3, 13 C-NMR for CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 3277, 1658, 1604, 1474, 1232, 1220, 1133, 881, 755; HRMS (ESI): Calcd for [C₁₇H₁₄F₉N₃O₂+Na] $^+$: 486.0835, found: 486.0860.

$$\begin{array}{c|c}
 & \text{N} & \text{O} \\
 & \text{N} & \text{O} \\
 & \text{H} & \text{O}
\end{array}$$

3-(10,10,10,10,10,10,10,10,10,10,10-Nonafluoro-10λ¹²-deca-7,9-diyn-5-yl)quinoxalin-2(1*H*)-one (**4ab**): According to the General Procedure, **4ab** (47.9 mg, 53%) was prepared as a white solid. ¹H NMR (300 MHz, CDCl₃) δ 12.53 (s, 1H), 7.82 – 7.72 (m, 1H), 7.51 – 7.39 (m, 1H), 7.25 – 7.30 (m, 2H), 4.08 – 3.88 (m, 1H), 3.29 – 2.95 (m, 1H), 2.31 (dt, J = 26.7, 14.5 Hz, 1H), 1.90 – 1.59 (m, 2H), 1.18 – 1.36 (m, 4H), 0.80 (t, J = 6.9 Hz, 3H); ¹⁹F NMR (282 MHz, CDCl₃) δ -81.07 (tt, J = 9.7, 3.1 Hz, 3F), -112.75 (dt, J = 25.4, 11.7 Hz, 2F), -124.27 – -124.72 (m, 2F), -125.84 – -125.93 (m, 2F); ¹³C NMR (75 MHz, CDCl₃) δ 161.6, 156.3, 132.7, 130.8, 130.1, 128.9, 124.2, 115.6, 34.2, 33.7, 32.94 (d, J = 21.7 Hz), 29.0, 22.5, 13.8, ¹³C-NMR for CF₂CF₂CF₂CF₃ could not be assigned; FTIR (neat): $\tilde{v} = 2961$, 1662, 1611, 1218, 1132, 1095, 877, 754, 721; HRMS (ESI): Calcd for [C₁₈H₁₇F₉N₂O+Na] +: 471.1089, found: 471.1094.

$$N$$
 C_4F_9
 C_9

1-Benzyl-3-(10,10,10,10,10,10,10,10,10)-nonafluoro- $10\lambda^{12}$ -deca-7,9-diyn-5-

yl)quinoxalin-2(1*H*)-one (**4ac**): According to the General Procedure, **4ac** (101.1 mg, 94%) was prepared as a colorless oil. 1 H NMR (300 MHz, CDCl₃) δ 7.76 (dd, J = 7.9, 1.5 Hz, 1H), 7.36 – 7.26 (m, 1H), 7.26 – 7.07 (m, 7H), 5.51 – 5.35 (m, 2H), 4.05 – 3.86 (m, 1H), 3.26 – 2.95 (m, 1H), 2.46 – 2.15 (m, 1H), 1.94 – 1.55 (m, 2H), 1.44 – 1.08 (m, 4H), 0.79 (t, J = 7.0 Hz, 3H); 19 F NMR (282 MHz, CDCl₃) δ -81.05 (tt, J = 9.7, 3.2 Hz, 3F), -111.45 – -113.93 (m, 2F), -124.27 – -124.74 (m, 2F), -125.91 – -125.83 (m, 2F); 13 C NMR (75 MHz, CDCl₃) δ 161.3, 154.5, 135.2, 132.7, 132.3, 130.0, 129.9, 128.9, 127.6, 126.7, 123.6, 114.4, 45.8, 34.7, 34.2, 32.86 (t, J = 21.0 Hz), 29.2, 22.5, 13.8, 13 C-NMR for CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2933, 1653, 1604, 1217, 1132, 1096, 878, 751, 695; HRMS (ESI): Calcd for [C₂₅H₂₃F₉N₂O+Na] $^+$: 561.1559, found: 561.1551.

$$\begin{array}{c|c}
 & \text{N} & \text{O} \\
 & \text{N} & \text{O} \\
 & \text{CO}_2\text{Et}
\end{array}$$

Ethyl 2-(3-(10,10,10,10,10,10,10,10,10,10-nonafluoro-10λ¹²-deca-7,9-diyn-5-yl)-2-oxoquinoxalin-1(2*H*)-yl)acetate (**4ad**): According to the General Procedure, **4ad** (98.0 mg, 92%) was prepared as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.78 (dd, J = 8.0, 1.5 Hz, 1H), 7.43 (ddd, J = 8.6, 7.4, 1.5 Hz, 1H), 7.31 – 7.22 (m, 1H), 7.00 (dd, J = 8.4, 0.8 Hz, 1H), 5.02 (d, J = 17.2 Hz, 1H), 4.89 (d, J = 17.2 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.83 – 3.92 (m, 1H), 3.26 – 2.86 (m, 1H), 2.43 – 2.13 (m, 1H), 1.58 – 1.82 (m, 2H), 1.28 – 1.08 (m, 7H), 0.79 (t, J = 9.1, 3H); ¹⁹F NMR (282 MHz, CDCl₃) δ -81.11 (tt, J = 9.7, 3.1 Hz, 3F), -111.48 – -114.06 (m, 2F), -124.35 – -124.74 (m, 2F), -125.95 – -125.88 (m, 2F); ¹³C NMR (75 MHz, CDCl₃) δ 166.9, 161.0, 154.0, 132.5, 132.1,

130.2, 130.1, 123.8, 113.0, 62.0, 43.6, 34.5, 34.1, 32.6, 29.0, 22.5, 13.9, 13.7, 13 C-NMR for CF₂CF₂CF₂CF₃ could not be assigned; FTIR (neat): $\tilde{v} = 2934$, 1751, 1658, 1605, 1214, 1178, 1133, 1099, 1022, 878, 753, 721; HRMS (ESI): Calcd for [C₂₂H₂₃F₉N₂O₃+Na] $^+$: 557.1457, found: 557.1458.

$$N$$
 C_4F_5

1,6,7-Trimethyl-3-(10,10,10,10,10,10,10,10,10,10-nonafluoro-10λ¹²-deca-7,9-diyn-5-yl)quinoxalin-2(1*H*)-one (**4ae**): According to the General Procedure, **4ae** (94.2 mg, 96%) was prepared as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.51 (s, 1H), 6.99 (s, 1H), 3.82 – 3.90 (m, 1H), 3.60 (s, 3H), 3.19 – 2.91 (m, 1H), 2.35 (s, 3H), 2.29 – 2.08 (m, 1H), 2.26 (s, 3H), 1.87 – 1.49 (m, 2H), 1.33 – 1.11 (m, 4H), 0.78 (t, J = 6.9 Hz, 3H); ¹⁹F NMR (282 MHz, CDCl₃) δ -81.11 (tt, J = 9.7, 3.2 Hz, 3F), -111.55 – -114.41 (m, 2F), -124.47 (dd, J = 18.4, 9.2 Hz, 2F), -125.77 – -126.09 (m, 2F); ¹³C NMR (75 MHz, CDCl₃) δ 159.8, 154.4, 139.7, 132.4, 131.0, 130.9, 130.0, 114.1, 34.4, 34.1, 32.65 (t, J = 21.0 Hz), 29.07, 29.04, 22.5, 20.4, 19.0, 13.8, ¹³C-NMR for CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2932, 1652, 1622, 1470, 1217, 1182, 1132, 1078, 1006, 880, 845, 734, 721; HRMS (ESI): Calcd for [C₂₁H₂₃F₉N₂O+Na] ⁺: 513.1559, found: 513.1566.

$$CI$$
 N
 O
 C_4F_5

6,7-Dichloro-1-methyl-3-(10,10,10,10,10,10,10,10,10,10-nonafluoro- $10\lambda^{12}$ -deca-7,9-diyn-5-yl)quinoxalin-2(1*H*)-one (**4af**): According to the General Procedure, **4af** (90.0 mg, 85%) was prepared as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.83 (s, 1H), 7.31 (s, 1H), 3.92 – 3.79 (m, 1H), 3.59 (s, 3H), 3.13 – 2.88 (m, 1H), 2.16 – 12.34 (m, 1H), 1.84 – 1.48 (m, 2H), 1.34 – 1.15 (m, 4H), 0.79 (t, J = 6.9 Hz, 3H); ¹⁹F NMR (282

MHz, CDCl₃) δ -81.10 (tt, J = 9.7, 3.2 Hz, 3F), -112.56 – -112.99 (m, 2F), -124.33 – 124.76 (m, 2F), -125.91 (t, J = 12.8 Hz, 2F); ¹³C NMR (75 MHz, CDCl₃) δ 162.8, 153.8, 134.1, 132.4, 131.4, 130.6, 127.4, 115.1, 34.5, 34.0, 32.57 (t, J = 21.0 Hz), 29.4, 29.0, 22.5, 13.7, ¹³C-NMR for CF₂CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2933, 1662, 1599, 1465, 1217, 1181, 1132, 1094, 1019, 879, 845, 719; HRMS (ESI): Calcd for [C₁₉H₁₇C₁₂F₉N₂O+Na] +: 553.0466, found: 553.0471.

$$\begin{array}{c|c}
 & \text{Bu} \\
 & \text{C}_4F_9 \\
 & \text{O}
\end{array}$$

7-Fluoro-1-methyl-3-(10,10,10,10,10,10,10,10,10,10-nonafluoro-10λ¹²-deca-7,9-diyn-5-yl)quinoxalin-2(1*H*)-one (**4ag**): According to the General Procedure, **4ag** (75.0 mg, 78%) was prepared as a colorless oil. 1 H NMR (300 MHz, CDCl₃) δ 7.83 (dd, J = 8.8, 6.0 Hz, 1H), 7.13 – 6.98 (m, 2H), 3.91 – 4.00 (m, 1H), 3.70 (s, 3H), 3.04 – 3.25 (m, 1H), 2.35 (dt, J = 15.1, 13.9 Hz, 1H), 1.98 – 1.58 (m, 2H), 1.44 – 1.23 (m, 4H), 0.89 (t, J = 6.9 Hz, 3H); 19 F NMR (282 MHz, CDCl₃) δ -81.13 (tt, J = 9.7, 3.1 Hz, 3F), -107.74 (s, 1F), -111.57 – -114.28 (m, 2F), -124.32 – -124.85 (m, 2F), -125.96 (t, J = 11.1 Hz, 2F); 13 C NMR (75 MHz, CDCl₃) δ 163.2 (d, J = 250.4 Hz), 159.9 (d, J = 3.5 Hz), 154.2, 134.46 (d, J = 11.6 Hz), 131.76 (d, J = 10.4 Hz), 129.20 (d, J = 2.2 Hz), 111.3 (d, J = 23.4 Hz), 100.5 (d, J = 27.8 Hz), 34.4, 34.0, 32.52 (t, J = 20.9 Hz), 29.3, 29.0, 22.5, 13.8, 13 C-NMR for CF₂CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2935, 1657, 1502, 1215, 1163, 1131, 1082, 877, 720; HRMS (ESI): Calcd for [C₁₉H₁₈F₁₀N₂O+Na] $^{+}$: 503.1152, found: 503.1157.

$$C_4$$
Fg

7-Chloro-1-methyl-3-(10,10,10,10,10,10,10,10,10,10)-nonafluoro- $10\lambda^{12}$ -deca-7,9-diyn-5-yl)quinoxalin-2(1H)-one (**4ah**): According to the General Procedure, **4ah** (85.6 mg,

86%) was prepared as a colorless oil. 1 H NMR (300 MHz, CDCl₃) δ 7.85 – 7.71 (m, 1H), 7.29 – 7.34 (m, 2H), 3.92 – 4.01 (m, 1H), 3.71 (s, 3H), 3.04 – 3.25 (m, 1H), 2.26 – 2.45 (m, 1H), 1.95 – 1.58 (m, 2H), 1.45 – 1.24 (m, 4H), 0.90 (t, J = 9.1, 3H); 19 F NMR (282 MHz, CDCl₃) δ -81.09 (tt, J = 9.7, 3.2 Hz, 3F), -111.59 – -114.11 (m, 2F), -124.20 – -124.79 (m, 2F), -125.73 – -126.19 (m, 2F); 13 C NMR (75 MHz, CDCl₃) δ 161.3, 154.1, 135.9, 133.9, 130.9, 123.9, 113.6, 34.5, 34.0, 32.56 (t, J = 21.0 Hz), 29.3, 29.0, 22.5, 13.8, 13 C-NMR for CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2936, 1601, 1217, 1184, 1132, 1084, 877, 733, 720; HRMS (ESI): Calcd for $[C_{19}H_{18}ClF_{9}N_{2}O+Na]^{+}$: 519.0856, found: 519.0856.

$$\begin{array}{c|c} F & & \\ & & \\ & & \\ N & \\ O & \\ \end{array} C_4 F_9$$

6-Fluoro-1-methyl-3-(10,10,10,10,10,10,10,10,10,10-nonafluoro-10λ¹²-deca-7,9-diyn-5-yl)quinoxalin-2(1*H*)-one (**4ai**): According to the General Procedure, **4ai** (68.0 mg, 71%) was prepared as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.60 – 7.51 (m, 1H), 7.34 – 7.27 (m, 2H), 4.06 – 3.92 (m, 1H), 3.74 (s, 3H), 3.30 – 2.97 (m, 1H), 2.51 – 2.22 (m, 1H), 1.97 – 1.60 (m, 2H), 1.42 – 1.16 (m, 4H), 0.90 (t, J = 6.9 Hz, 3H); ¹⁹F NMR (282 MHz, CDCl₃) δ -81.11 (tt, J = 9.7, 3.2 Hz, 3F), -112.76 (dt, J = 46.0, 12.7 Hz, 2F), -119.18 (s, 1F), -124.33 – -124.64 (m, 2F), -125.76 – -126.07 (m, 2F); ¹³C NMR (75 MHz, CDCl₃) δ 162.8, 158.6 (d, J = 242.3 Hz), 154.0, 133.0 (d, J = 11.2 Hz), 129.7, 117.6 (d, J = 24.0 Hz), 115.3 (d, J = 22.5 Hz), 114.6 (d, J = 8.7 Hz), 34.6, 34.0, 32.5 (t, J = 21.0 Hz), 29.4, 29.0, 22.5, 13.7, ¹³C-NMR for CF₂CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2937, 1654, 1502, 1217, 1162, 1130, 1089, 877, 810, 720; HRMS (ESI): Calcd for [C₁₉H₁₈F₁₀N₂O+Na] ⁺: 503.1152, found: 503.1160.

$$CI$$
 N
 O
 C_4F_5

6-Chloro-1-methyl-3-(10,10,10,10,10,10,10,10,10,10-nonafluoro-10λ¹²-deca-7,9-diyn-5-yl)quinoxalin-2(1*H*)-one (**4aj**): According to the General Procedure, **4aj** (78.9 mg, 80%) was prepared as a colorless oil. 1 H NMR (300 MHz, CDCl₃) δ 7.76 (d, J = 2.4 Hz, 1H), 7.42 (dd, J = 8.9, 2.4 Hz, 1H), 7.15 – 7.19 (m, 1H), 3.95 – 3.83 (m, 1H), 3.62 (s, 3H), 2.94 – 3.15 (m, 1H), 2.38 – 2.10 (m, 1H), 1.86 – 1.53 (m, 2H), 1.33 – 1.16 (m, 4H), 0.79 (t, J = 6.9 Hz, 3H); 19 F NMR (282 MHz, CDCl₃) δ -81.08 (tt, J = 9.7, 3.2 Hz, 3F), -111.56 – -114.16 (m, 2F), -124.27 – -124.66 (m, 2F), -125.90 (dd, J = 12.6, 9.8 Hz, 2F); 13 C NMR (75 MHz, CDCl₃) δ 162.7, 154.0, 132.9, 131.7, 129.9, 129.2, 128.9, 114.7, 34.5, 34.0, 32.5, 29.3, 29.0, 22.5, 13.8, 13 C-NMR for CF₂CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2934, 1657, 1491, 1216, 1182, 1132, 1096, 879, 808, 719; HRMS (ESI): Calcd for [C₁₉H₁₈ClF₉N₂O+Na] $^+$: 519.0856, found: 519.0857.

$$\mathsf{Br} \bigvee_{\mathsf{N}} \mathsf{O} \mathsf{C_4} \mathsf{F_9}$$

6-Bromo-1-methyl-3-(10,10,10,10,10,10,10,10,10,10-nonafluoro- $10\lambda^{12}$ -deca-7,9-diyn-5-yl)quinoxalin-2(1*H*)-one (**4ak**): According to the General Procedure, **4ak** (70 mg, 65%) was prepared as a white solid. ¹H NMR (300 MHz, CDCl₃) δ 7.91 (d, J = 2.6 Hz, 1H), 7.55 (dd, J = 8.9, 2.3 Hz, 1H), 7.10 (d, J = 8.9 Hz, 1H), 3.94 – 3.80 (m, 1H), 3.62 (s, 3H), 2.93 – 3.14 (m, 1H), 2.40 – 2.11 (m, 1H), 1.85 – 1.54 (m, 2H), 1.31 – 1.15 (m, 4H), 0.79 (t, J = 6.9 Hz, 3H); ¹⁹F NMR (282 MHz, CDCl₃) δ -81.08 (tt, J = 9.7, 3.2 Hz, 3F), -111.56 – -114.18 (m, 2F), -124.30 – -124.65 (m, 2F), -125.92 (dd, J = 17.6, 7.7 Hz, 2F); ¹³C NMR (75 MHz, CDCl₃) δ 162.6, 154.0, 133.2, 132.7, 132.3, 132.1, 116.1, 115.0, 34.5, 34.1, 32.56 (t, J = 21.0 Hz), 29.3, 29.0, 22.5, 13.8, ¹³C-NMR for CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2936, 1657, 1487, 1217, 1133, 1093, 879, 806, 718; HRMS (ESI): Calcd for [C₁₉H₁₈BrF₉N₂O+Na] ⁺: 563.0351, found: 563.0357.

$$O_2N$$
 N
 O_4F_9

1-Methyl-6-nitro-3-(10,10,10,10,10,10,10,10,10,10,10-nonafluoro- $10\lambda^{12}$ -deca-7,9-diyn-5-yl)quinoxalin-2(1*H*)-one (**4al**): According to the General Procedure, **4al** (41.6 mg, 41%) was prepared as a yellow solid. ¹H NMR (300 MHz, CDCl₃) δ 8.64 (d, J = 2.6 Hz, 1H), 8.32 (dd, J = 9.2, 2.6 Hz, 1H), 7.34 (d, J = 9.2 Hz, 1H), 3.98 – 3.84 (m, 1H), 3.70 (s, 3H), 3.20 – 2.92 (m, 1H), 2.40 – 2.12 (m, 1H), 1.88 – 1.54 (m, 2H), 1.35 – 1.15 (m, 4H), 0.80 (t, J = 6.9 Hz, 3H); ¹⁹F NMR (282 MHz, CDCl₃) δ -81.06 (tt, J = 9.7, 3.1 Hz, 3F), -112.69 (d, J = 6.6 Hz, 2F), -124.48 – -124.38 (m, 2F), -125.68 – -126.17 (m, 2F); ¹³C NMR (75 MHz, CDCl₃) δ 164.1, 153.9, 143.4, 137.6, 131.5, 125.5, 124.5, 114.2, 34.5, 34.1, 32.60 (t, J = 20.5 Hz), 29.8, 29.0, 22.4, 13.7, ¹³C-NMR for CF₂CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2961, 1667, 1614, 1341, 1218, 1132, 1077, 820, 727; HRMS (ESI): Calcd for [C₁₉H₁₈F₉N₃O₃+Na] +: 530.1097, found: 530.1091.

$$MeO_2C$$
 N
 O
 C_4F_5

Methyl 1-methyl-3-(10,10,10,10,10,10,10,10,10,10-nonafluoro- $10\lambda^{12}$ -deca-7,9-diyn-5-yl)-2-oxo-1,2-dihydroquinoxaline-6-carboxylate (**4am**): According to the General Procedure, **4am** (74.0 mg, 71%) was prepared as a white solid. ¹H NMR (300 MHz, CDCl₃) δ 8.43 (d, J = 2.0 Hz, 1H), 8.12 (dd, J = 8.8, 2.0 Hz, 1H), 7.27 (d, J = 8.8 Hz, 1H), 3.96 – 3.84 (m, 1H), 3.89 (s, 3H), 3.66 (s, 3H), 3.22 – 2.88 (m, 1H), 2.42 – 2.08 (m, 1H), 1.87 – 1.51 (m, 2H), 1.17 – 1.26 (m, 4H), 0.79 (t, J = 6.9 Hz, 3H); ¹⁹F NMR (282 MHz, CDCl₃) δ -81.09 (tt, J = 9.7, 3.2 Hz, 3F), -111.58 – -114.19 (m, 2F), -124.32 – -124.68 (m, 2F), -125.92 (t, J = 11.3 Hz, 2F); ¹³C NMR (75 MHz, CDCl₃) δ 166.0, 162.2, 154.3, 136.3, 131.7, 131.6, 130.7, 125.5, 113.6, 52.2, 34.4, 34.1, 32.56 (t, J = 21.0 Hz), 29.4, 29.0, 22.5, 13.7, ¹³C-NMR for CF₂CF₂CF₂CF₃ could not be assigned;

FTIR (neat): $\tilde{v} = 2959$, 1723, 1662, 1611, 1437, 1286, 1215, 1132, 1105, 878, 766, 734; HRMS (ESI): Calcd for $[C_{21}H_{21}F_{9}N_{2}O_{3}+Na]^{+}$: 543.1301, found: 543.1310.

$$\begin{array}{c|c} & & & & \\ & & & \\ Ph & & & \\ \hline Ph & & & \\ \hline \end{array}$$

1-Methyl-3-(10,10,10,10,10,10,10,10,10,10-nonafluoro- $10\lambda^{12}$ -deca-7,9-diyn-5-yl)-5,6-diphenylpyrazin-2(1*H*)-one (**4an**): According to the General Procedure, **4an** (101.6 mg, 90%) was prepared as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.52 – 7.31 (m, 4H), 7.16 – 7.20 (m, 6H), 3.91 – 3.99 (m, 1H), 3.37 (s, 3H), 3.10 – 3.32 (m, 1H), 2.53 – 2.22 (m, 1H), 2.01 – 1.61 (m, 2H), 1.51 – 1.29 (m, 4H), 0.94 (t, J = 6.9 Hz, 3H); ¹⁹F NMR (282 MHz, CDCl₃) δ -81.03 (tt, J = 9.7, 3.1 Hz, 3F), -111.43 – -114.47 (m, 2F), -124.43 (dd, J = 17.7, 8.7 Hz, 2F), -125.68 – -126.11 (m, 2F); ¹³C NMR (75 MHz, CDCl₃) δ 157.7, 155.1, 137.8, 136.7, 132.6, 131.9, 130.1, 129.4, 129.2, 128.9, 127.6, 126.8, 34.3, 34.0, 33.9, 32.14 (t, J = 21.0 Hz), 29.2, 22.6, 13.9, ¹³C-NMR for CF₂CF₂CF₂CF₃ could not be assigned; FTIR (neat): $\tilde{v} = 2959$, 1647, 1586, 1417, 1216, 1131, 877, 703; HRMS (ESI): Calcd for [C₂₇H₂₅F₉N₂O+Na] ⁺: 587.1715, found: 587.1741.

1-Methyl-3-(1,1,1-trifluoroheptan-3-yl)quinoxalin-2(1*H*)-one (**4ao**): According to the General Procedure, **4ao** (52.0mg, 83%) was prepared as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.77 (dd, J = 8.0, 1.5 Hz, 1H), 7.51 – 7.42 (m, 1H), 7.22 – 7.29 (m, 2H), 3.82 – 3.69 (m, 1H), 3.63 (s, 3H), 2.90 – 3.03 (m, 1H), 2.24 – 2.42 (m, 1H), 1.84 – 1.55 (m, 2H), 1.32 – 1.13 (m, 4H), 0.78 (t, J = 6.9 Hz, 3H); ¹⁹F NMR (282 MHz, CDCl₃) δ -64.39 (s); ¹³C NMR (75 MHz, CDCl₃) δ 160.9, 154.4, 133.0, 132.5, 129.99, 129.96, 126.9 (q, J = 277.5), 123.5, 113.5, 36.0, 35.8 (q, J = 27.7 Hz), 33.5, 29.1, 29.0,

22.5, 13.8, 13 C-NMR for CF₂CF₂CF₂CF₃ could not be assigned; FTIR (neat): $\tilde{v} = 2959$, 2933, 1653, 1603, 1474, 1258, 1149, 1118, 1086, 754; HRMS (ESI): Calcd for $[C_{16}H_{19}F_3N_2O+Na]^+$: 335.1342, found: 335.1354.

$$N$$
 C_3F_7

3-(1,1,1,1,1,1,1-Heptafluoro-1λ⁸-non-2-yn-5-yl)-1-methylquinoxalin-2(1*H*)-one (**4ap**): According to the General Procedure, **4ap** (79.1 mg, 96%) was prepared as a colorless oil. 1 H NMR (300 MHz, CDCl₃) δ 7.87 (dd, J = 7.9, 1.5 Hz, 1H), 7.62 – 7.51 (m, 1H), 7.32 – 7.40 (m, 2H), 3.95 – 4.04 (m, 1H), 3.75 (s, 3H), 3.33 – 3.02 (m, 1H), 2.51 – 2.22 (m, 1H), 2.00 – 1.64 (m, 2H), 1.45 – 1.27 (m, 4H), 0.90 (t, J = 6.9 Hz, 3H); 19 F NMR (282 MHz, CDCl₃) δ -80.47 (t, J = 9.7 Hz, 3F), -112.28 – -114.85 (m, 2F), -127.81 (s, 2F); 13 C NMR (75 MHz, CDCl₃) δ 161.1, 154.4, 133.0, 132.4, 129.98, 129.92, 123.5, 113.5, 34.5, 34.0, 32.4 (t, J = 21.0 Hz), 29.1, 29.0, 22.5, 13.8, 13 C-NMR for CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2936, 1653, 1603, 1474, 1352, 1218, 1170, 1110, 1086, 752, 729; HRMS (ESI): Calcd for [C₁₈H₁₉F₇N₂O+Na] $^+$: 453.1278, found: 453.1268.

$$N$$
 C_6F_{13}
 C_6F_{13}

 124.00 (m, 2F), -125.99 – -126.37 (m, 2F); 13 C NMR (75 MHz, CDCl₃) δ 161.1, 154.4, 133.0, 132.5, 129.94, 129.91, 123.5, 113.5, 34.5, 34.1, 32.69 (t, J = 21.0 Hz), 29.1, 29.0, 22.5, 13.7, 13 C-NMR for CF₂CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2960, 1655, 1604, 1234, 1189, 1143, 1120, 1087, 752, 731, 707; HRMS (ESI): Calcd for [C₂₁H₁₉F₁₃N₂O+Na] $^+$: 585.1182, found: 585.1193.

$$N$$
 C_8F_{17}
 C_8F_{17}

$$\begin{array}{c|c}
 & \text{N} & \text{O} \\
 & \text{N} & \text{O}
\end{array}$$

3-(1-Chloro-1,1,2,2-tetrafluorooctan-4-yl)-1-methylquinoxalin-2(1*H*)-one (**4as**): According to the General Procedure, **4as** (54.0 mg, 71%) was prepared as a colorless oil. 1 H NMR (300 MHz, CDCl₃) δ 7.87 (dd, J = 7.9, 1.5 Hz, 1H), 7.57 (ddd, J = 8.6, 7.4, 1.5 Hz, 1H), 7.42 – 7.30 (m, 2H), 3.94 – 4.03 (m, 1H), 3.75 (s, 3H), 3.30 – 3.02 (m,

1H), 2.52 - 2.26 (m, 1H), 1.98 - 1.60 (m, 2H), 1.46 - 1.22 (m, 4H), 0.89 (t, J = 6.9 Hz, 3H); 19 F NMR (282 MHz, CDCl₃) δ -71.21 – -71.18 (m, 2F), -111.16 – -113.42 (m, 2F); 13 C NMR (75 MHz, CDCl₃) δ 161.2, 154.4, 133.0, 132.5, 129.95, 129.92, 123.5, 113.5, 35.0, 34.0, 32.54 (t, J = 21.0 Hz), 29.1, 29.0, 22.5, 13.8, 13 C-NMR for CF₂CF₂CF₃ could not be assigned; FTIR (neat): $\tilde{v} = 2960$, 1655, 1603, 1474, 1150, 1084, 936, 753; HRMS (ESI): Calcd for [C₁₇H₁₉ClF₄N₂O+Na] $^+$: 401.1014, found: 401.1022.

$$C_4F_9$$

$$\begin{array}{c|c}
 & C_4 F_9 \\
 & C_{0_2} Et \\
 & C_{0_2} Et
\end{array}$$

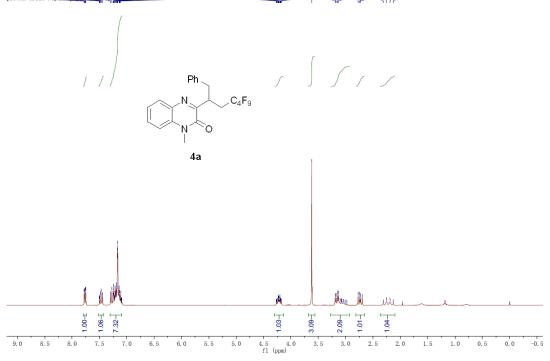
 NMR (300 MHz, CDCl₃) δ 7.83 (dd, J = 7.9, 1.3 Hz, 1H), 7.56 (ddd, J = 8.7, 7.4, 1.5 Hz, 1H), 7.40 – 7.30 (m, 2H), 4.31 – 4.12 (m, 4H), 3.72 (s, 3H), 3.06 – 2.79 (m, 3H), 2.69 – 2.05 (m, 7H), 1.27 (td, J = 6.9, 1.8 Hz, 6H); ¹⁹F NMR (282 MHz, CDCl₃) δ - 81.05 (tt, J = 9.6, 3.2 Hz, 3F), -111.62 – -115.01 (m, 2F), -124.35 (d, J = 9.1 Hz, 2F), -125.85 (dd, J = 13.9, 8.6 Hz, 2F); ¹³C NMR (75 MHz, CDCl₃) δ 172.4, 172.3, 170.4, 158.8, 154.8, 133.0, 132.6, 129.8, 123.6, 113.5, 61.62, 61.55, 58.7, 39.6, 39.0, 38.6, 34.7, 33.4, 29.0, 13.9, ¹³C-NMR for CF₂CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 1644, 1601, 1474, 1318, 1159, 1069, 755, 731; HRMS (ESI): Calcd for [C₂6H₂7F₉N₂O₅+Na] +: 641.1668, found: 641.1683.

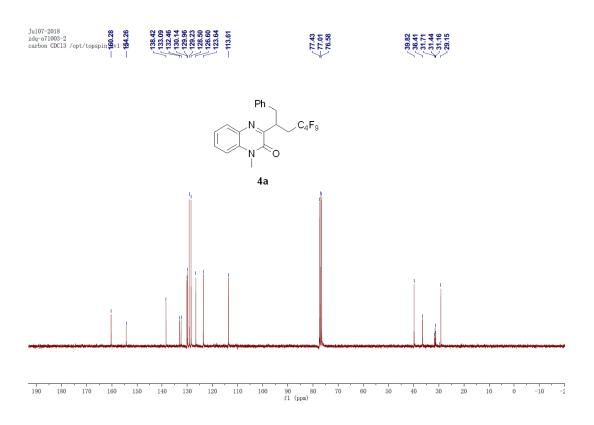
$$C_4F_9$$

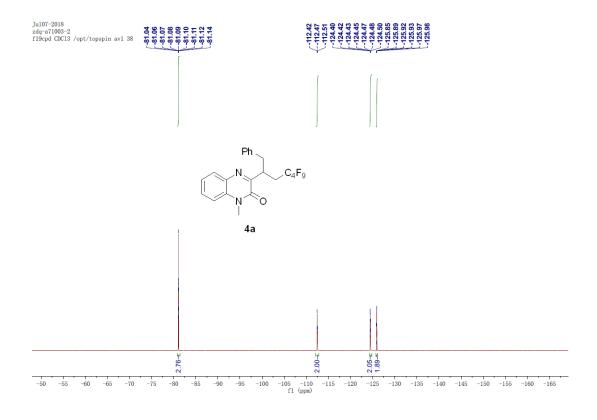
2-Chloro-3- $(10,10,10,10,10,10,10,10,10-nonafluoro-<math>10\lambda^{12}$ -deca-7,9-diyn-5-

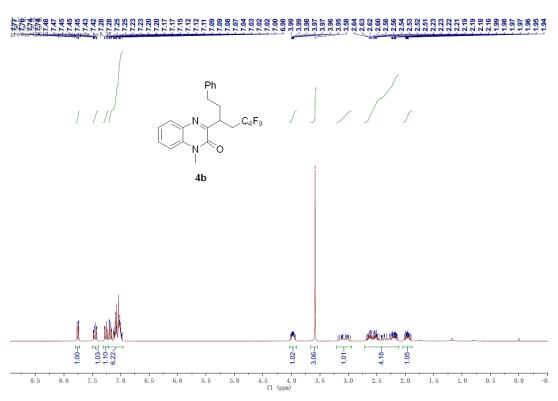
yl)quinoxaline (**9**): 9 was prepared with the reaction of **4ab** (448.0 mg, 1mmol), POCl₃ (0.11 mL, 1.2 mmol), and pyridine (0.08 mL, 1.0 mL, 1.0 mmol) under 160 °C for 2 hours. 1 H NMR (300 MHz, CDCl₃) δ 8.13 – 8.01 (m, 2H), 7.76 – 7.80 (M, 2H), 4.17 – 4.04 (m, 1H), 3.17 – 3.38 (m, 1H), 2.60 – 2.35 (m, 1H), 2.00 – 1.71 (m, 2H), 1.49 – 1.15 (m, 4H), 0.89 (t, J = 7.1 Hz, 3H); 19 F NMR (282 MHz, CDCl₃) δ -81.19 (tt, J = 9.7, 3.1 Hz, 3F), -111.37 – -114.39 (m, 2F), -124.57 (dd, J = 17.7, 9.3 Hz, 2F), -126.02 (t, J = 10.4 Hz, 2F); 13 C NMR (75 MHz, CDCl₃) δ 156.4, 147.2, 140.9, 140.8, 130.4, 130.1, 128.7, 128.1, 35.7, 35.5, 33.98 (t, J = 21.0 Hz), 28.8, 22.4, 13.7, 13 C-NMR for CF₂CF₂CF₃ could not be assigned; FTIR (neat): \tilde{v} = 2935, 1353, 1217, 1185, 1129, 1035, 878, 760, 719, 596; HRMS (ESI): Calcd for [C₁₈H₁₆ClF₉N₂+Na] +: 489.0751, found: 489.0759.

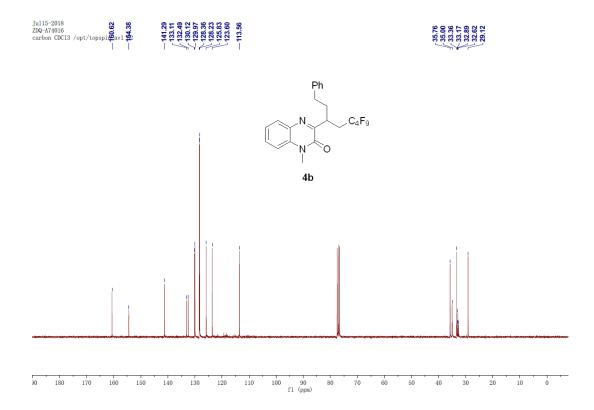


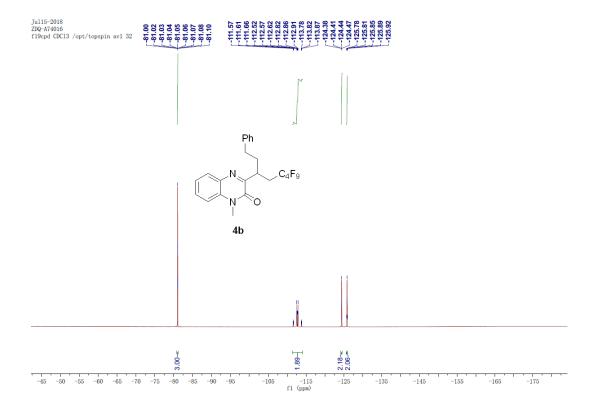


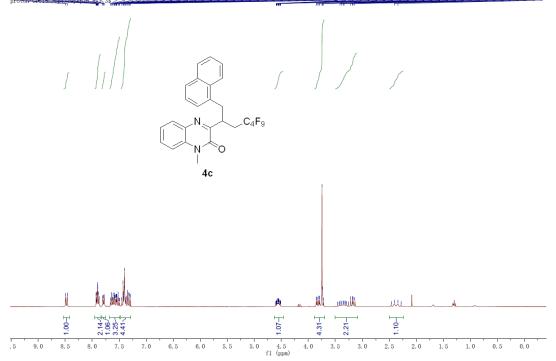


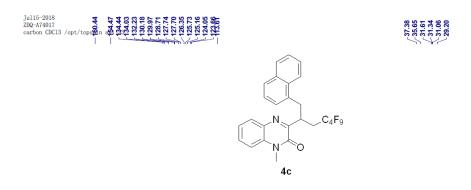


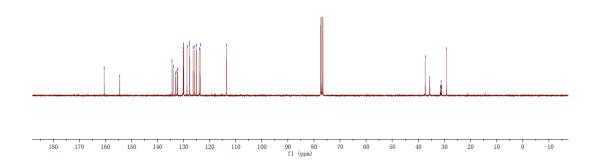


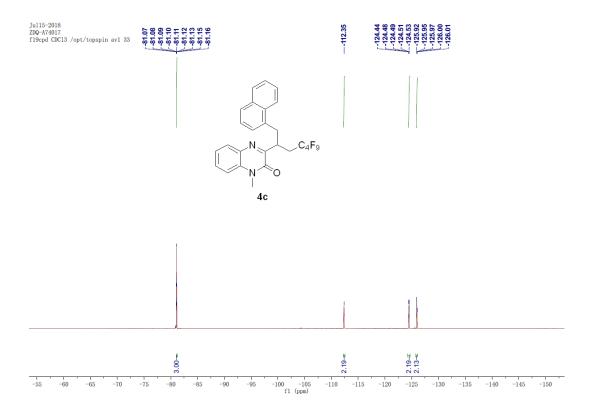


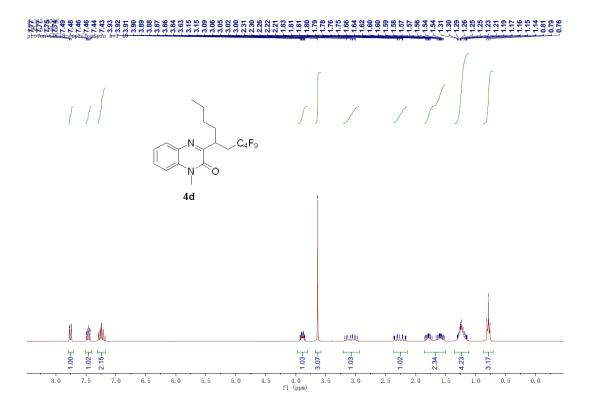


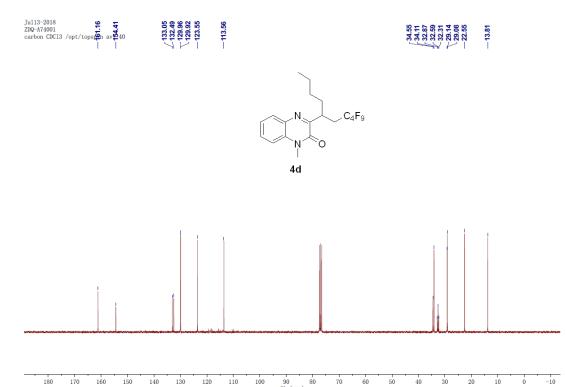


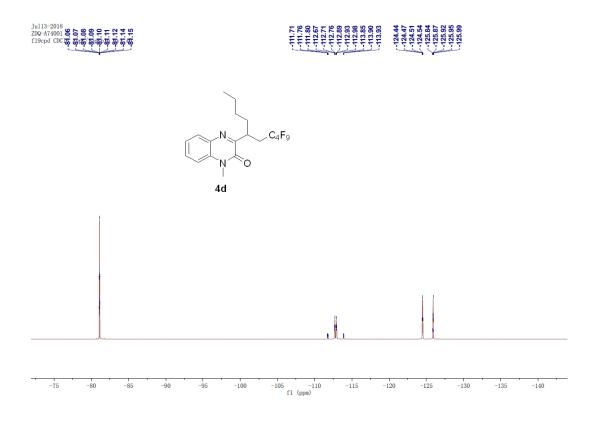


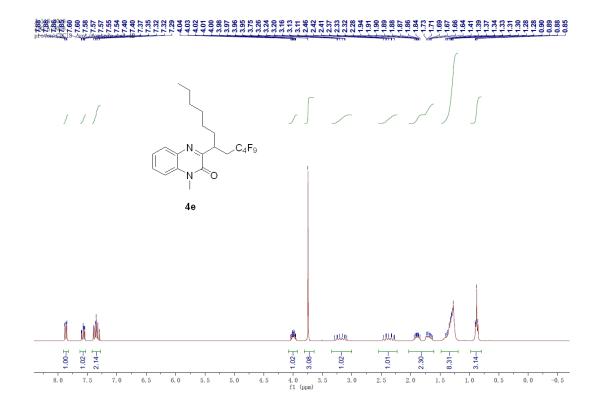


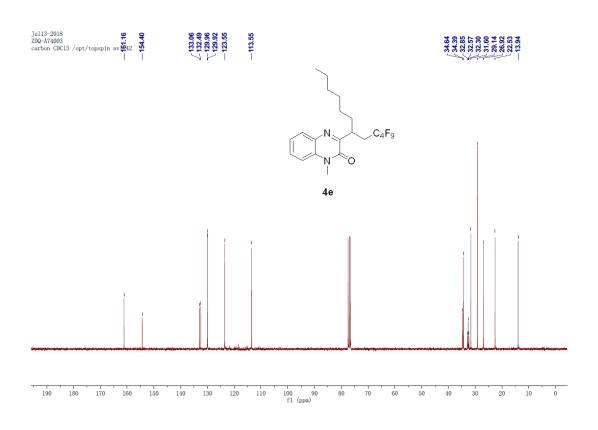


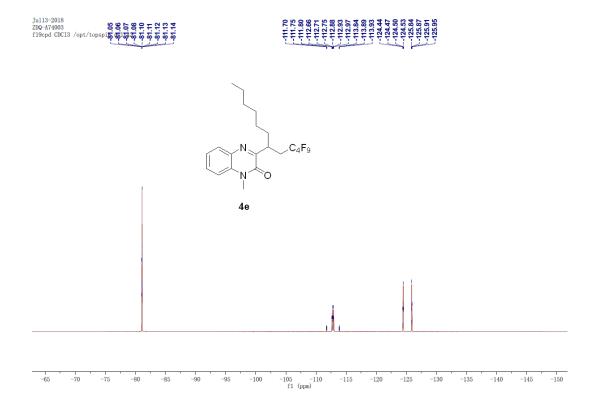


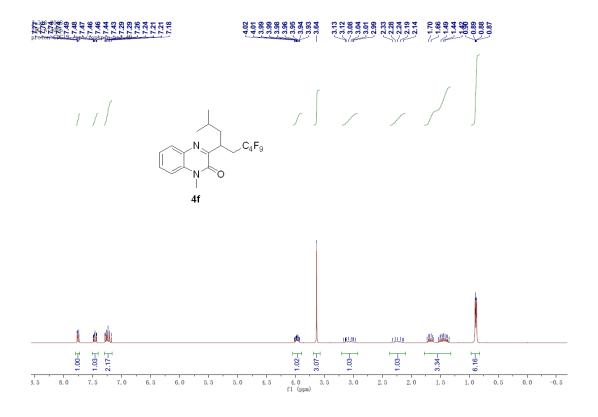




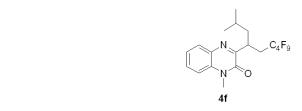


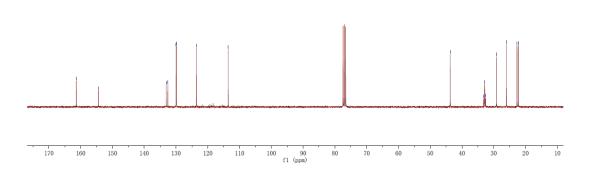


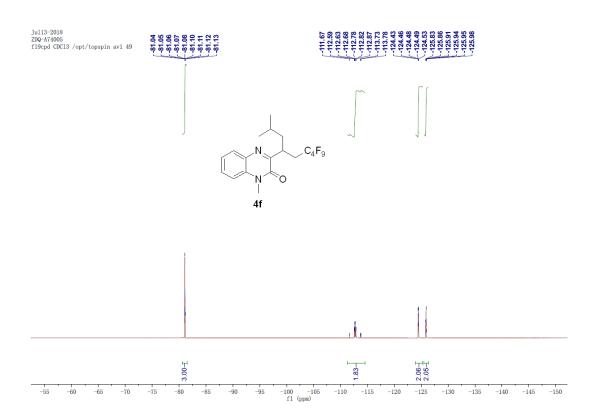


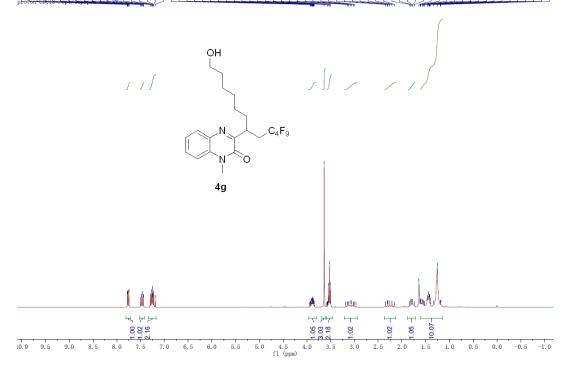


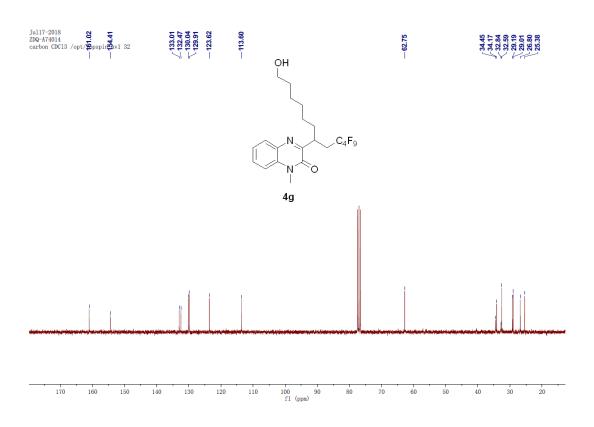


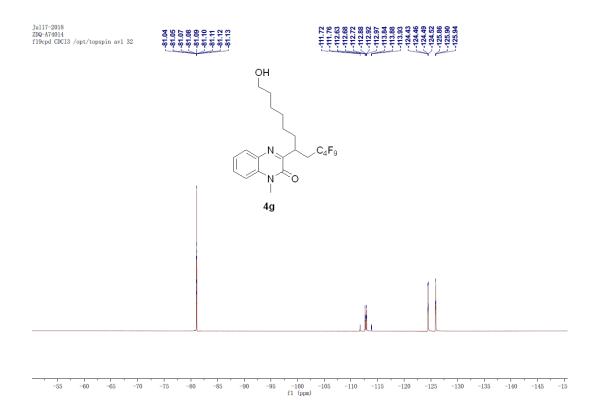


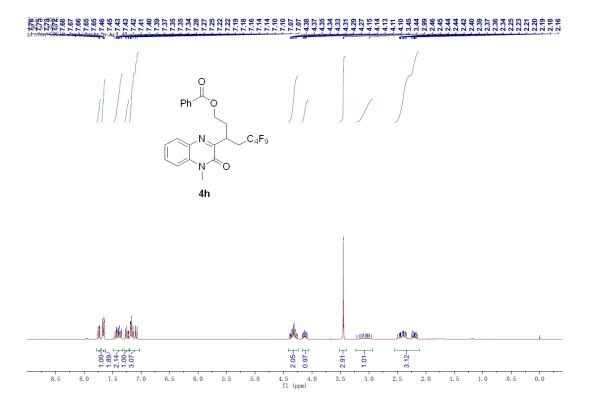


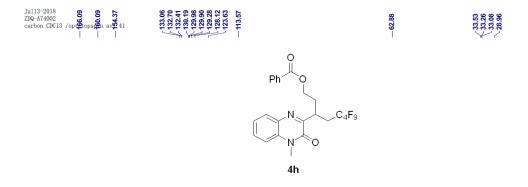


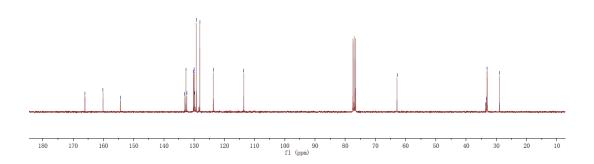


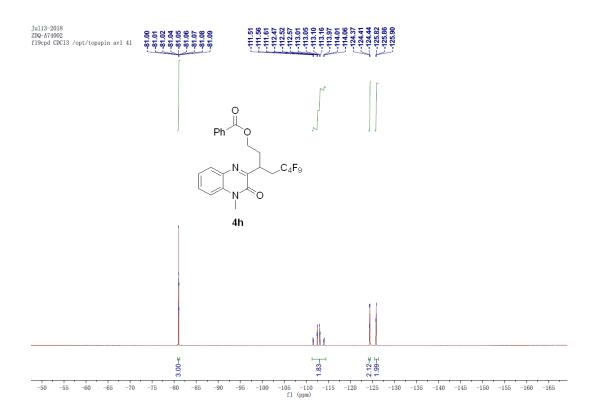




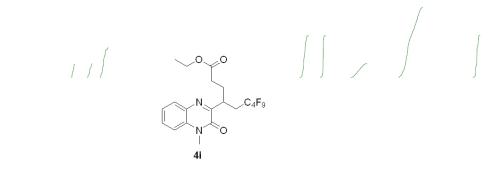


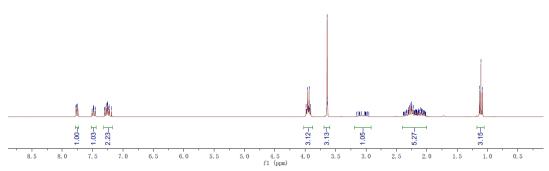


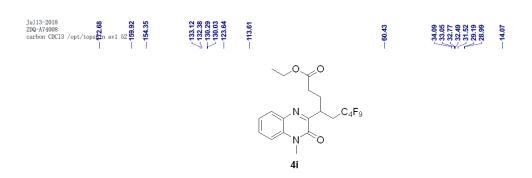


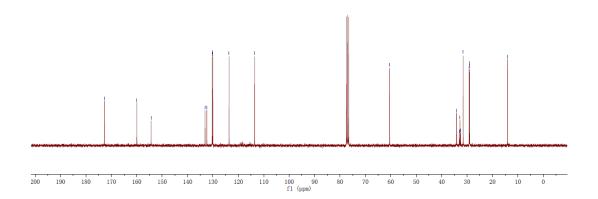


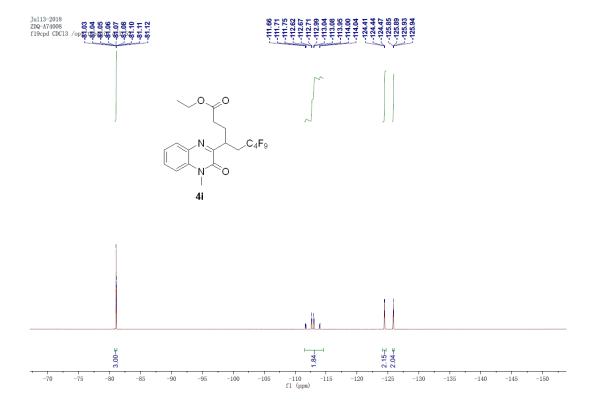
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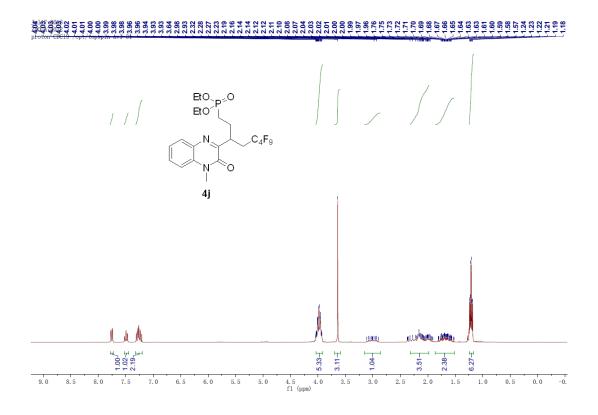




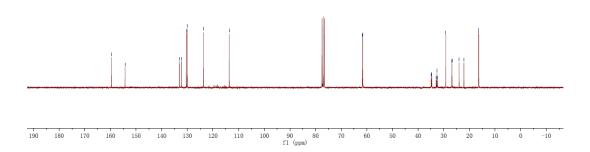


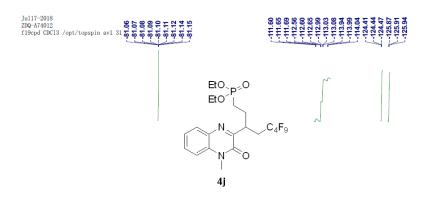


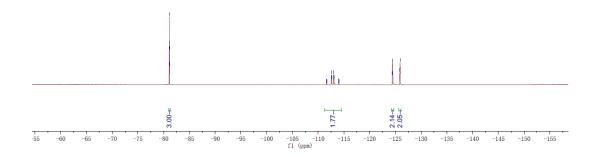


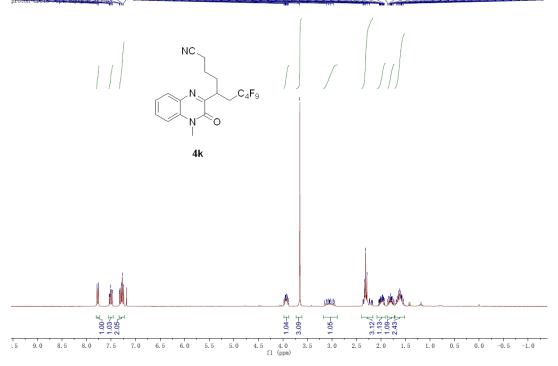


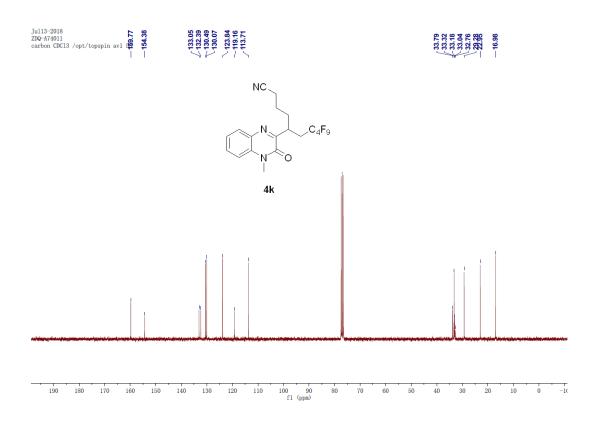


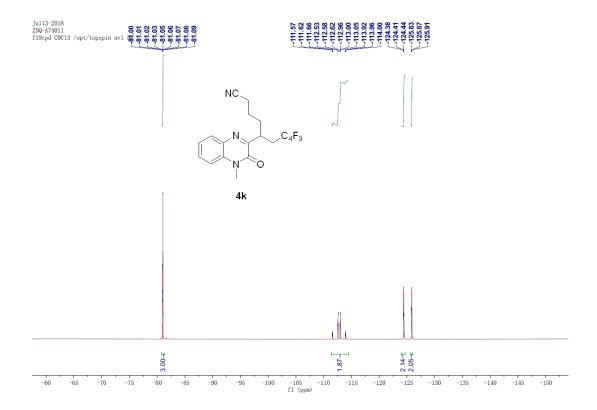




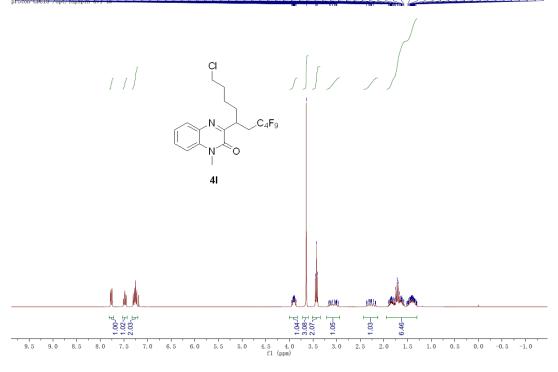


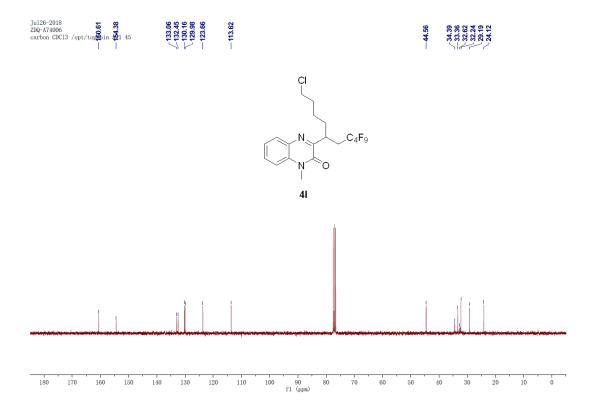


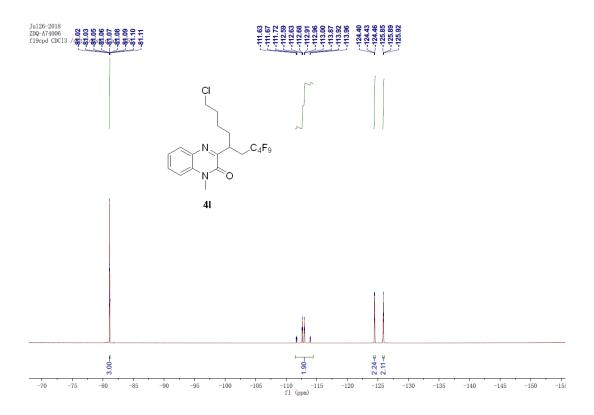


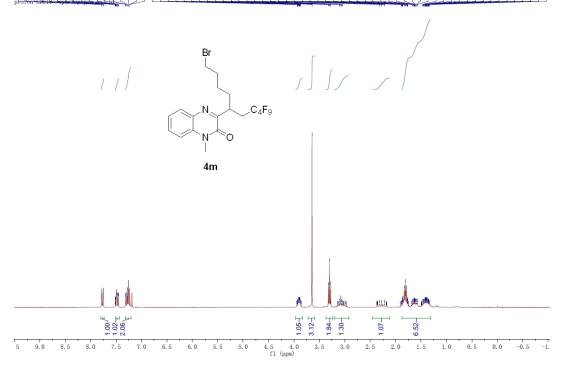


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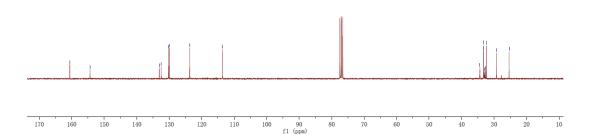


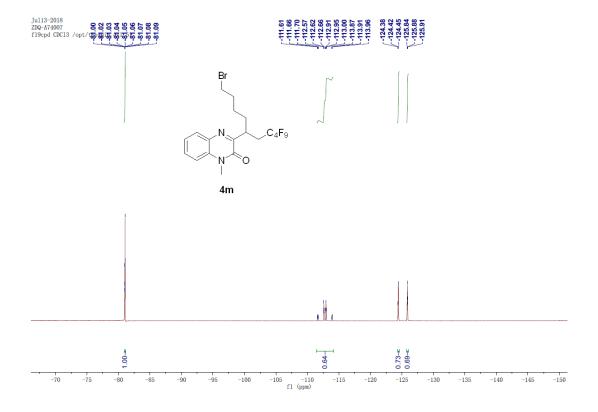
Jul13-2018 **80 87** ZDQ-A74007 **90** Pt Spin av1 51

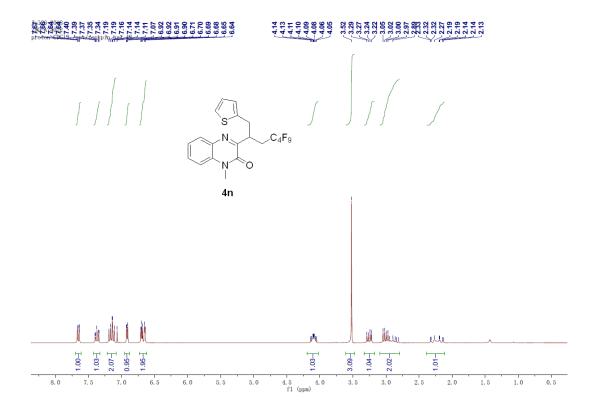
—113.62

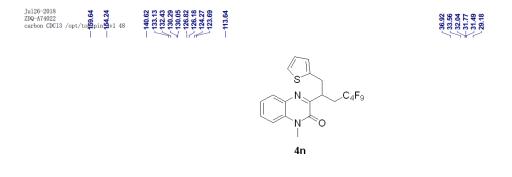
33.21 33.21 33.19 32.91 32.63 32.36 29.21 29.21

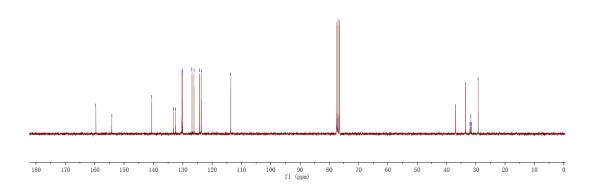
$$C_4F_9$$

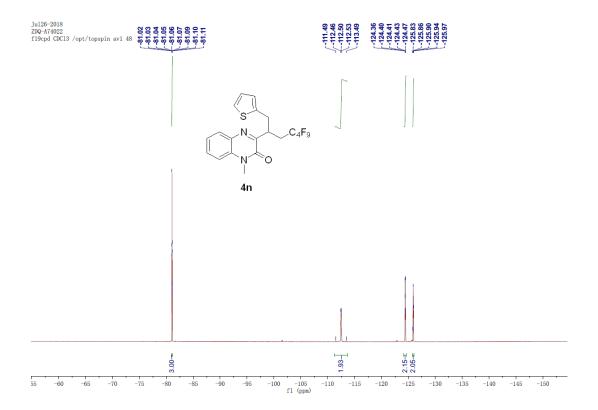


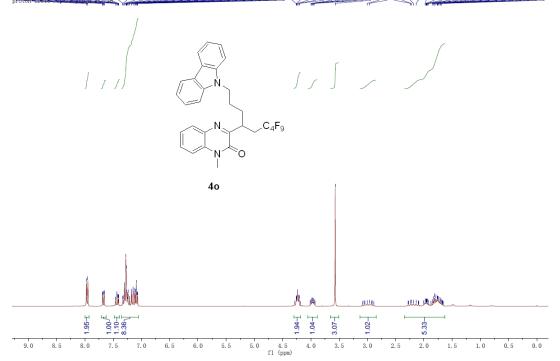


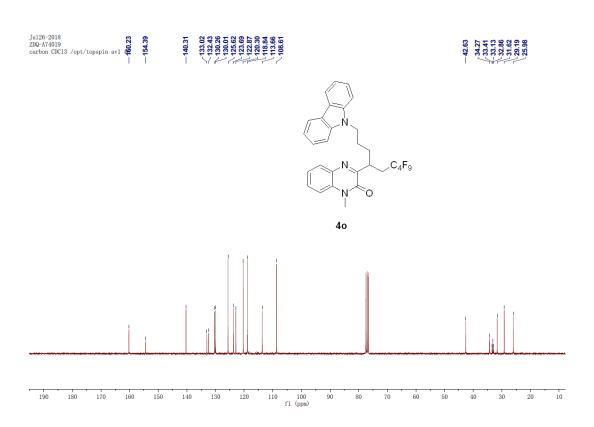


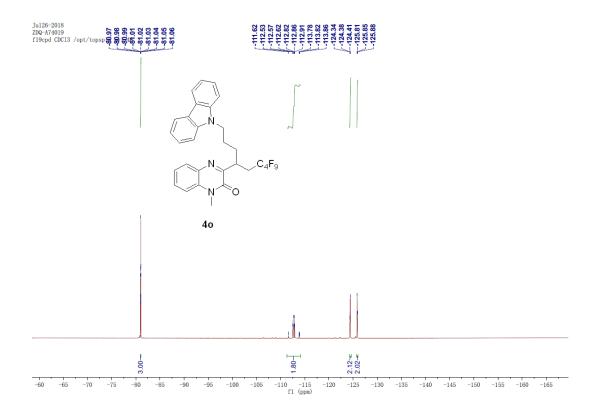


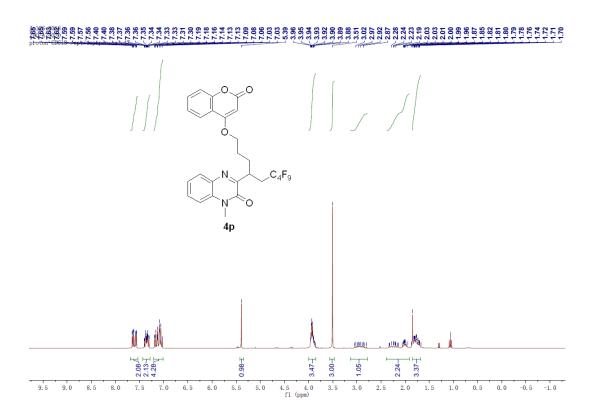


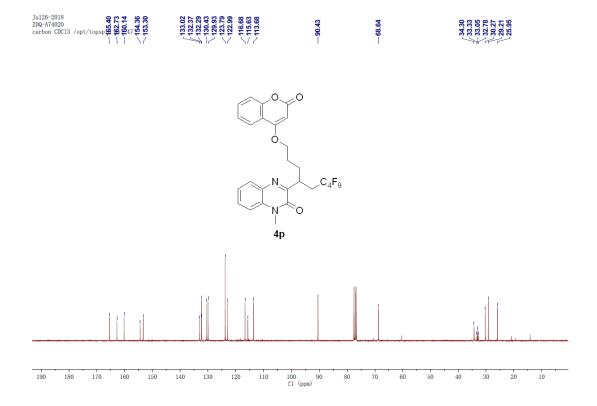


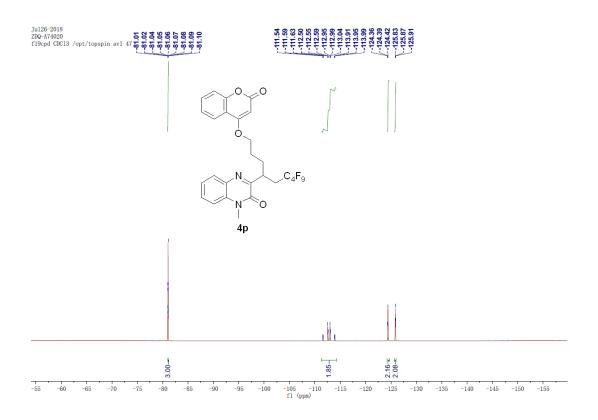


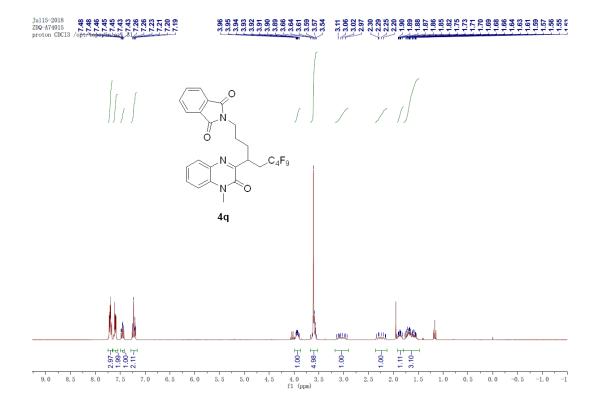


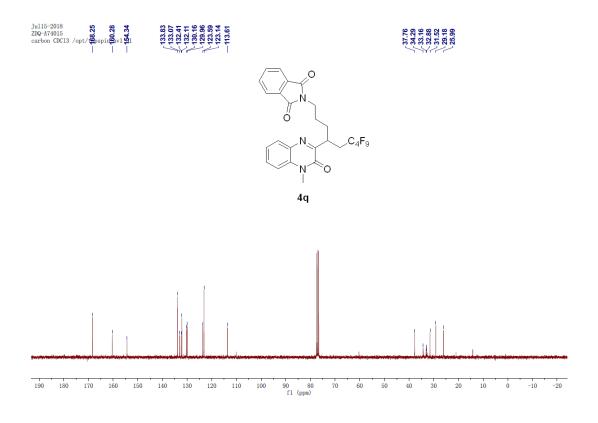


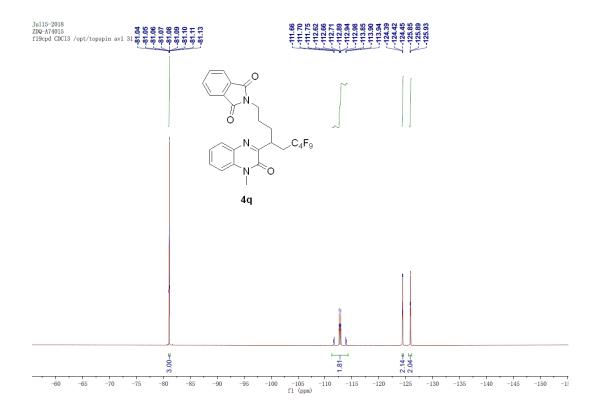


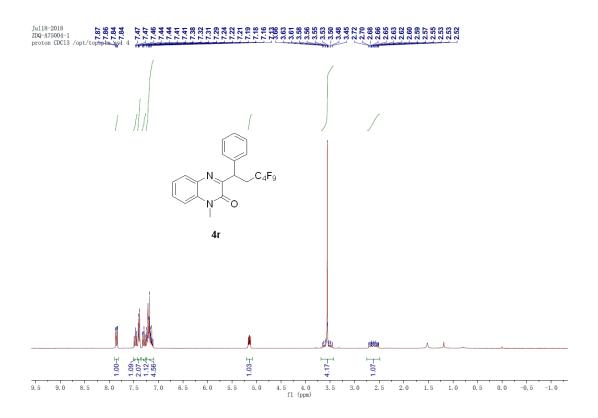


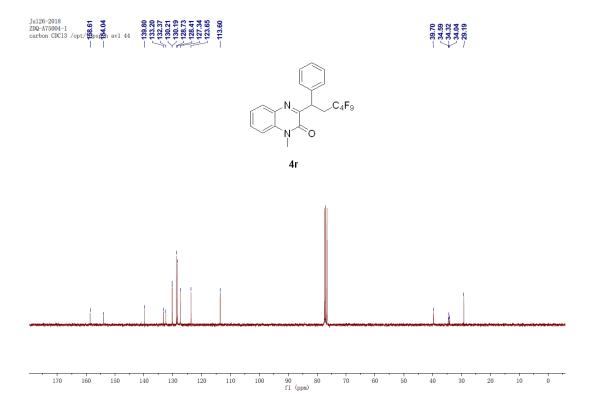


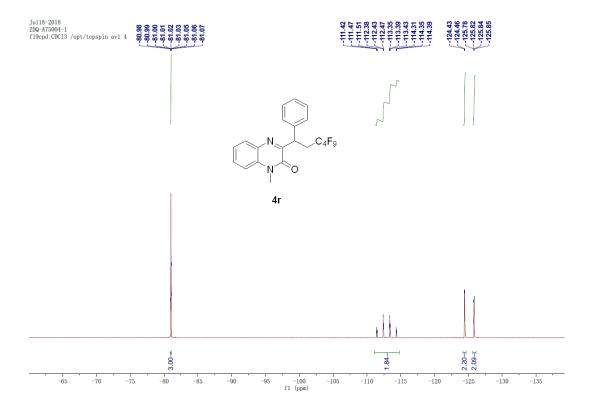


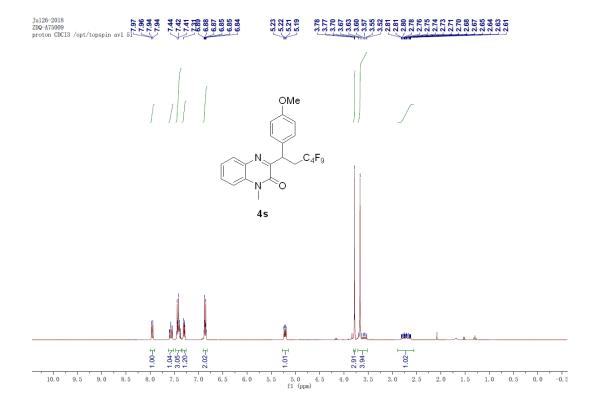


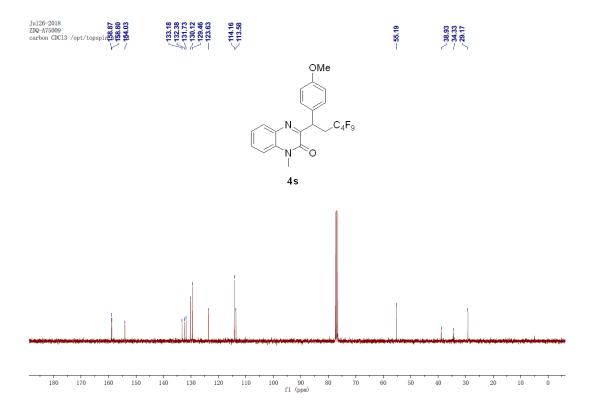


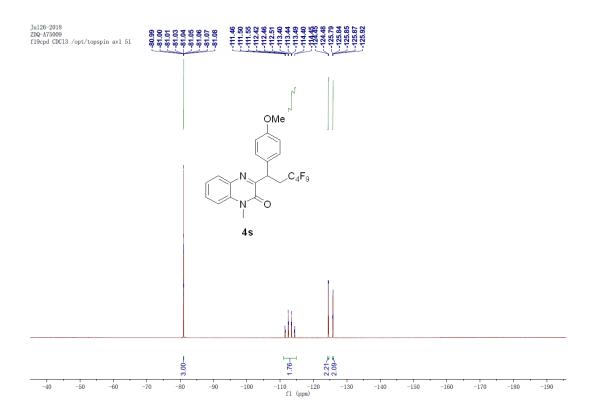


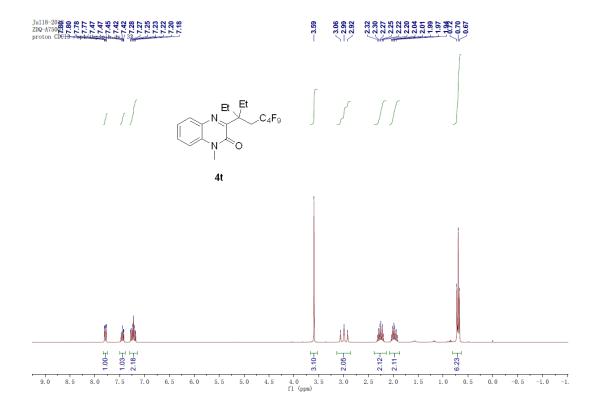


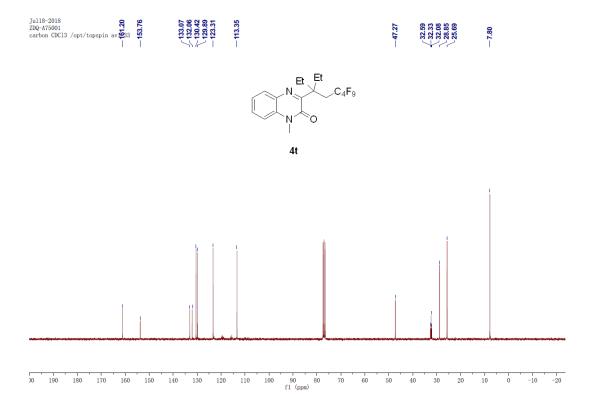


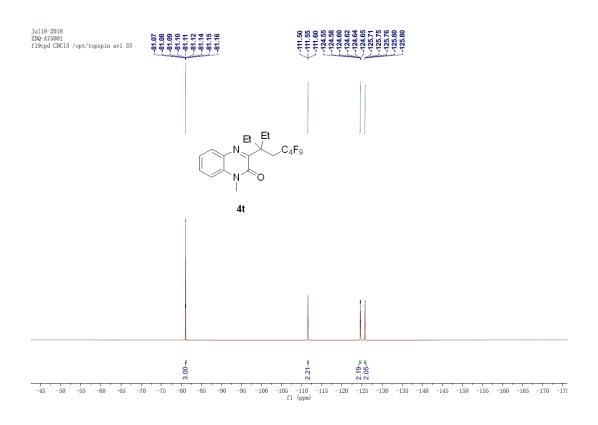


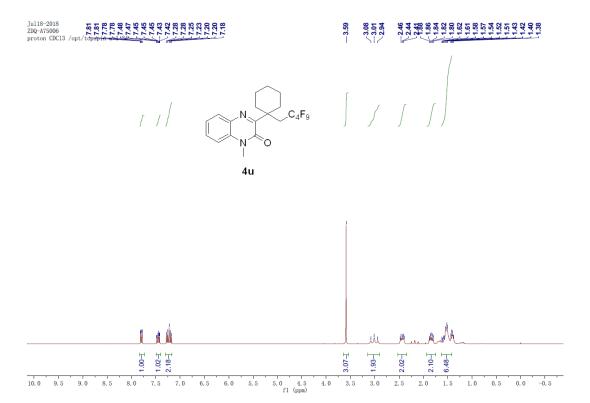




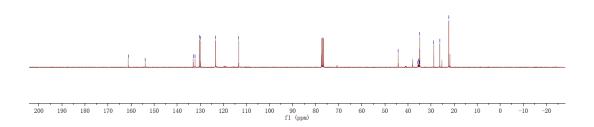


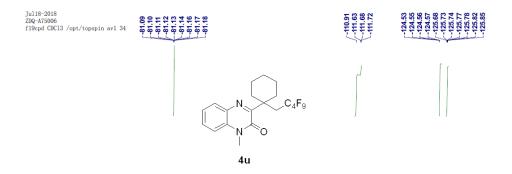


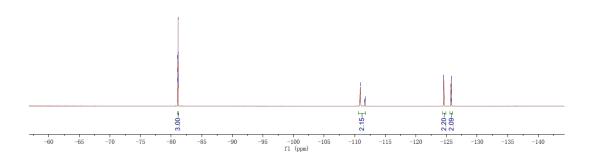


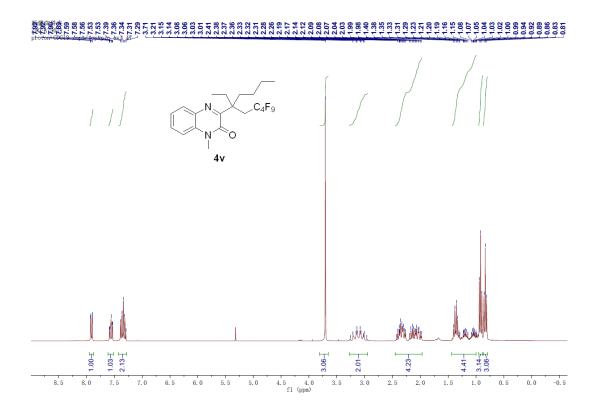


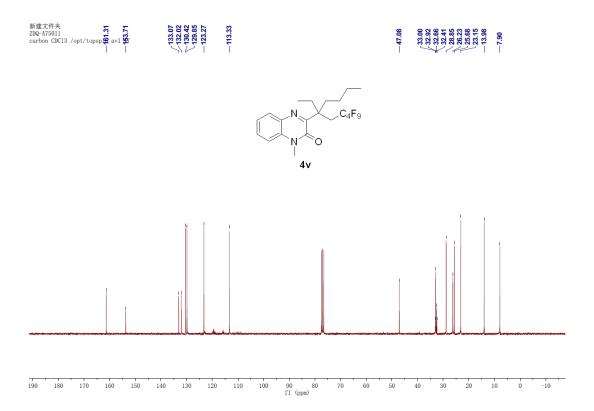


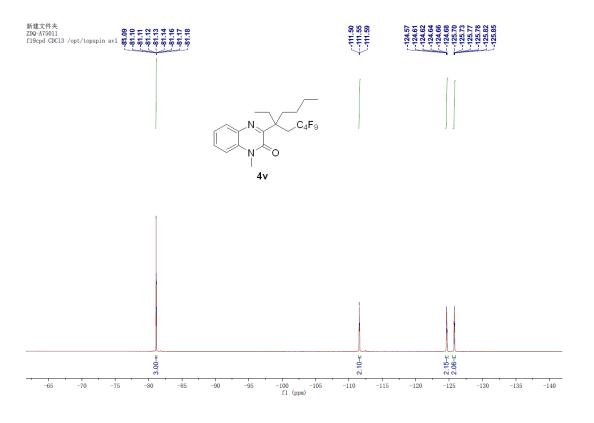


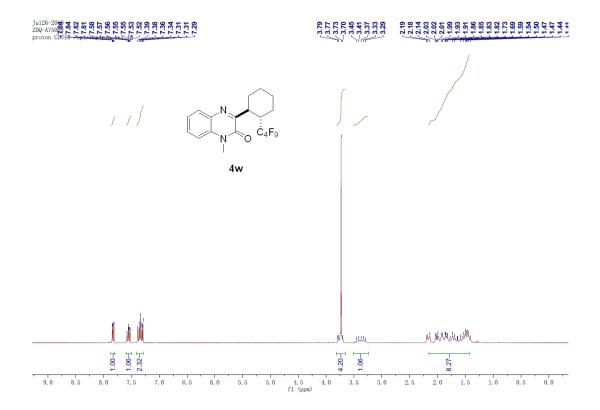


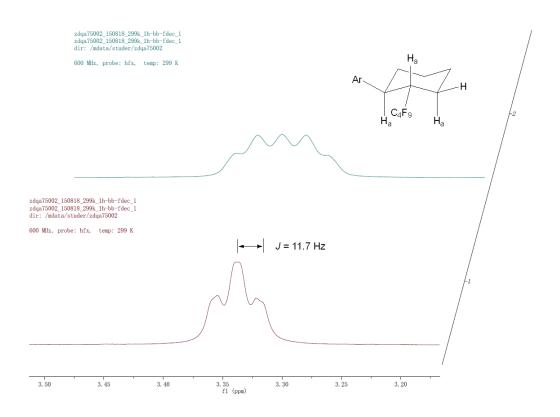


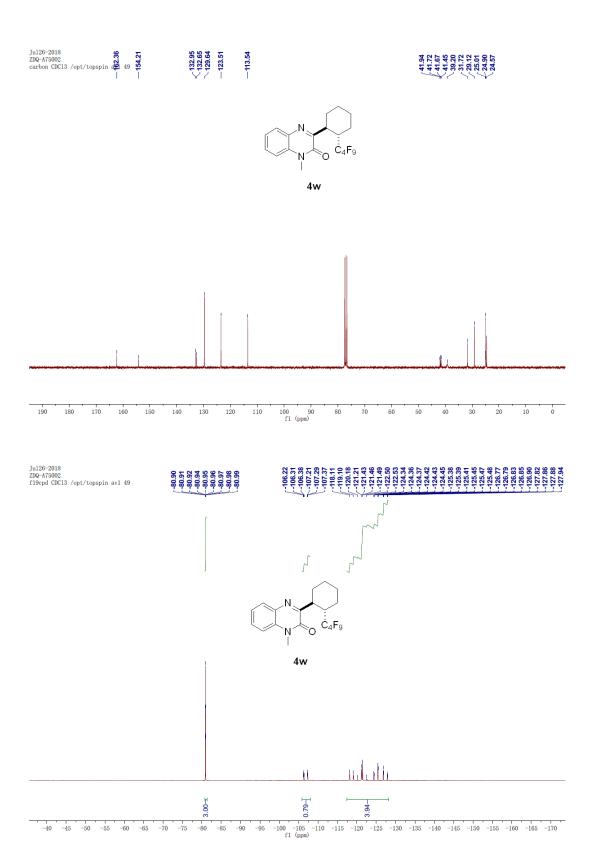


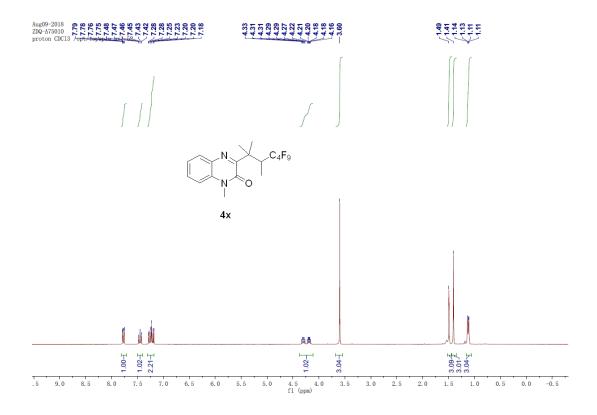


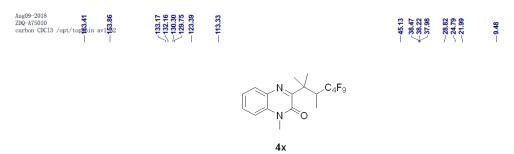


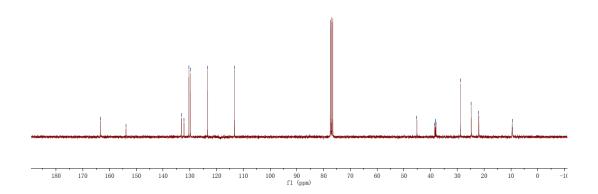


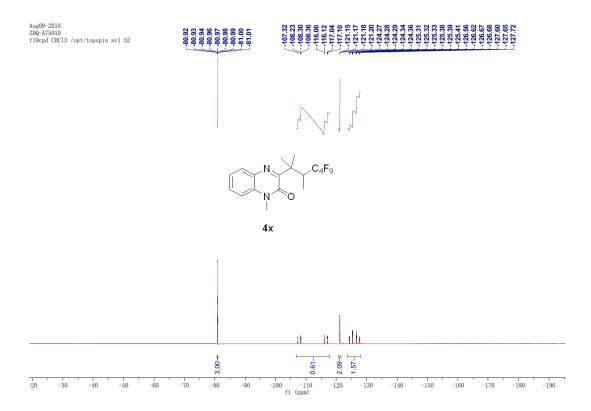


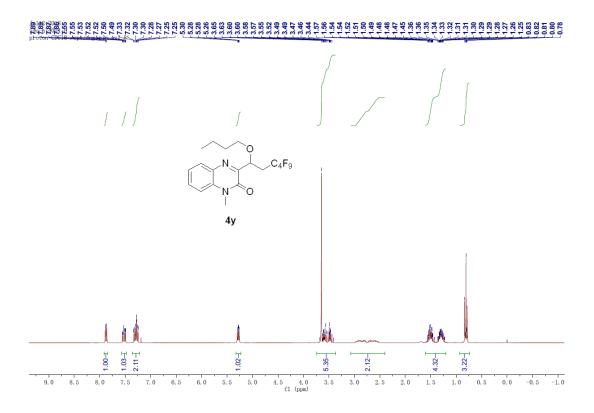


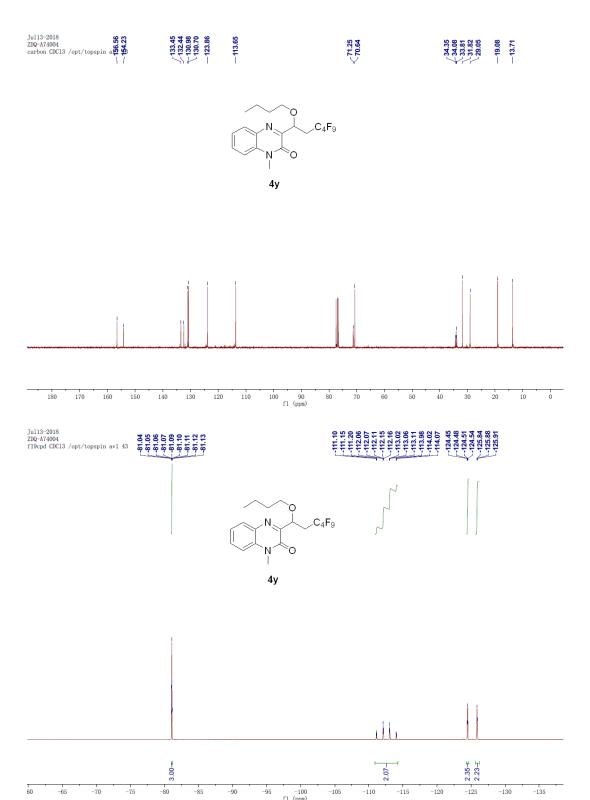






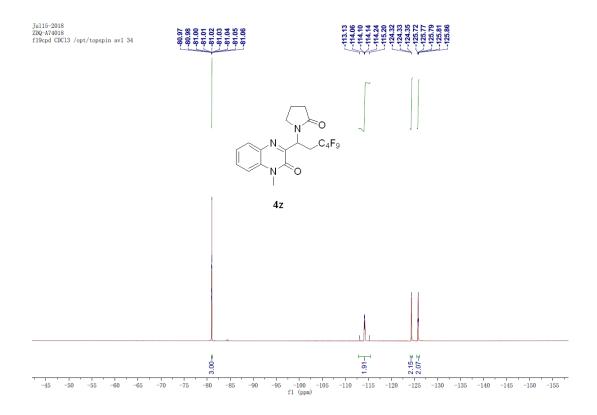


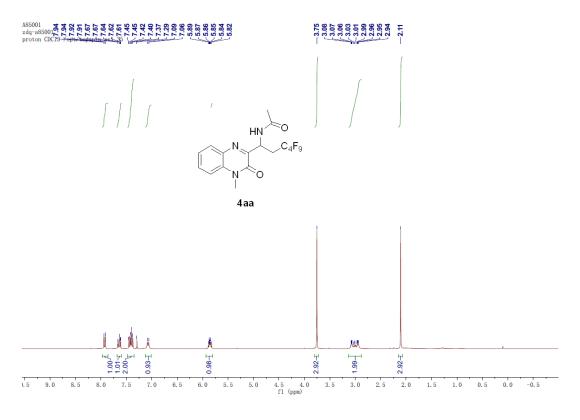


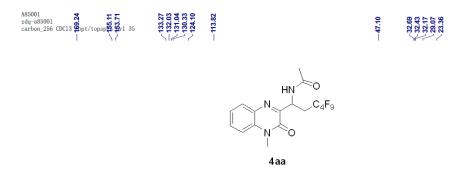


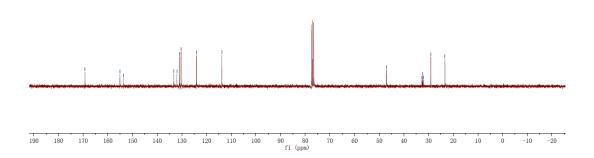
5.589 4z

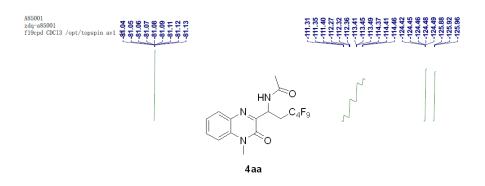
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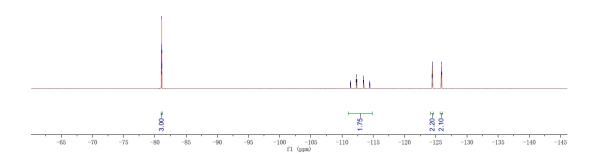


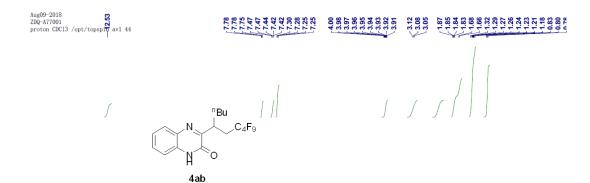


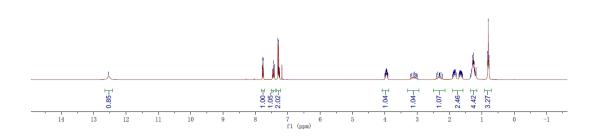




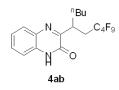


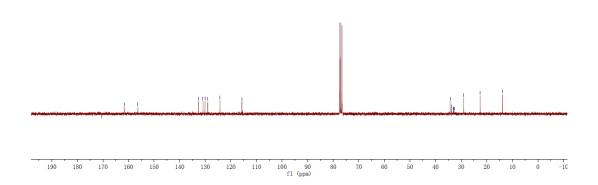


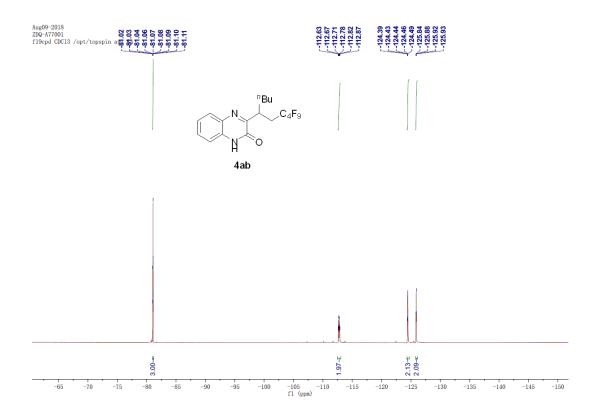


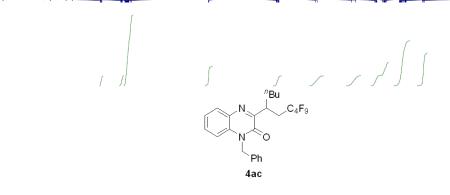


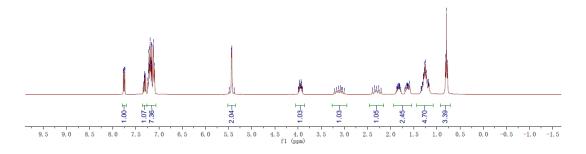


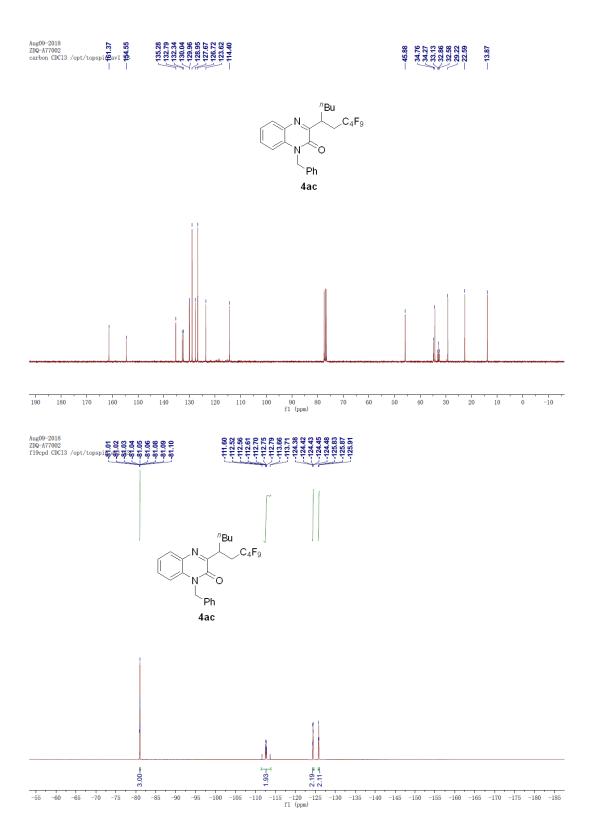


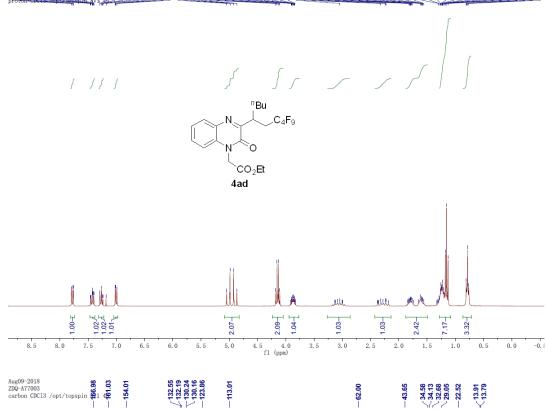




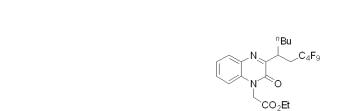




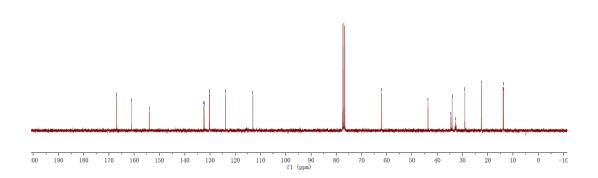




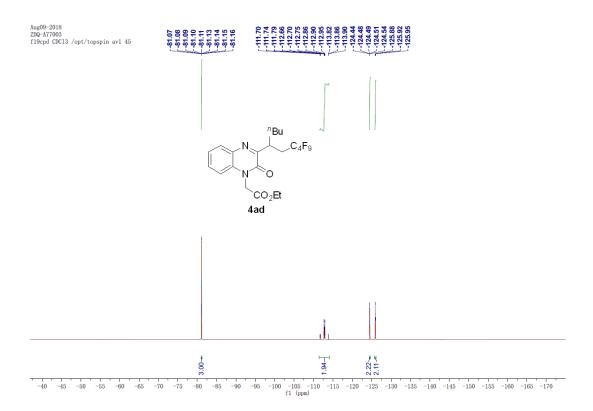
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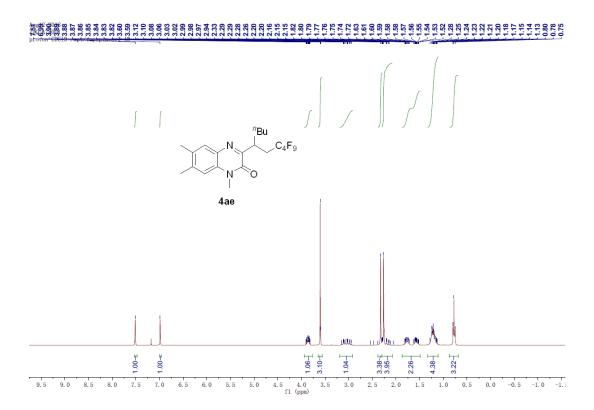


-113.01



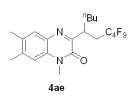
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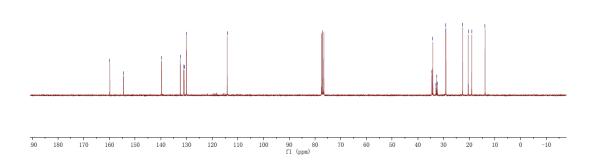


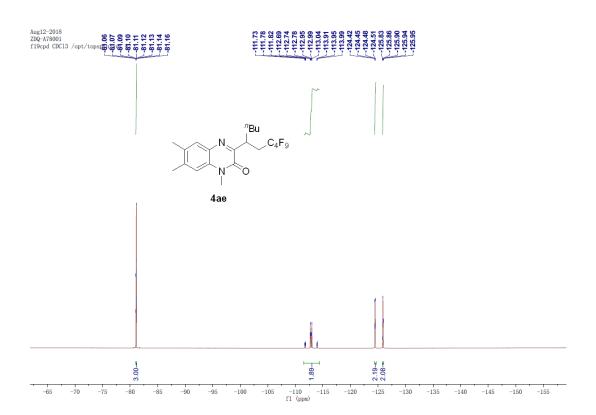


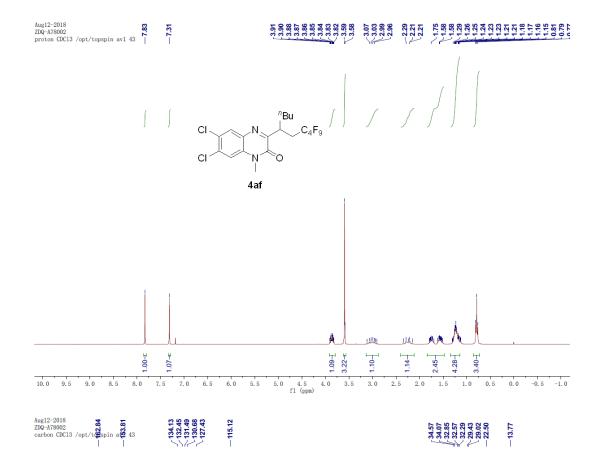


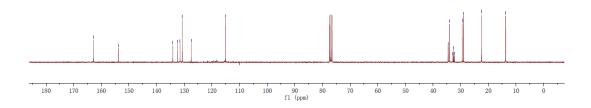


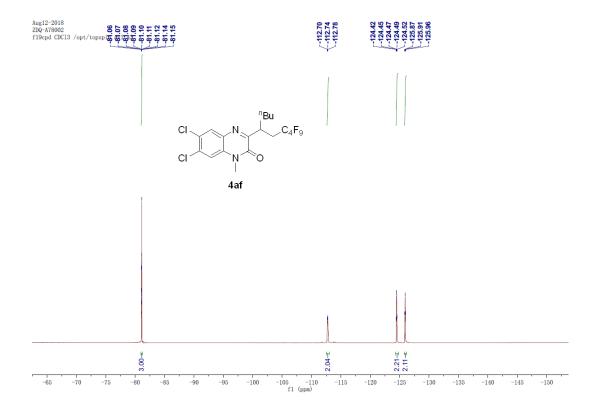


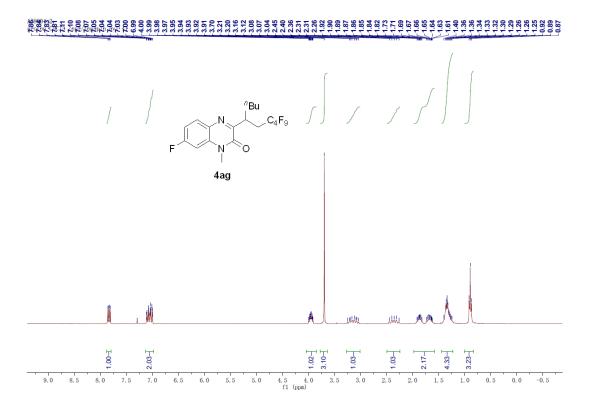


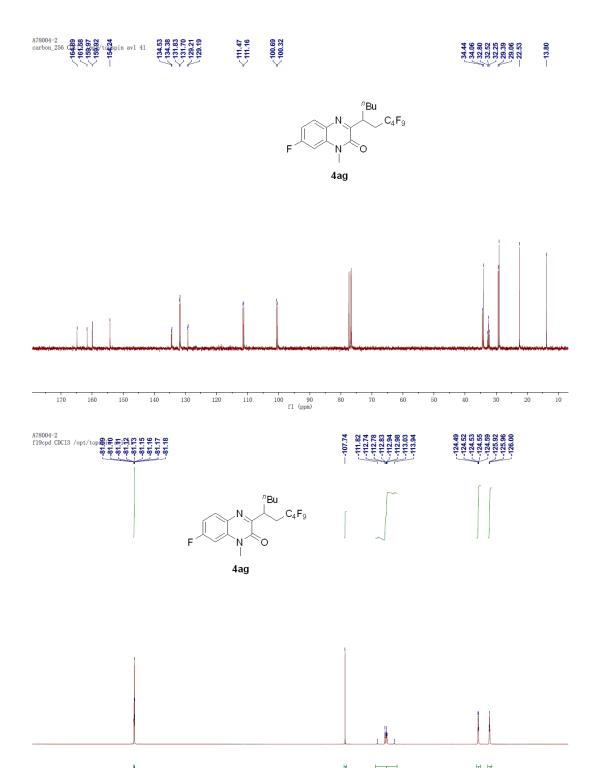




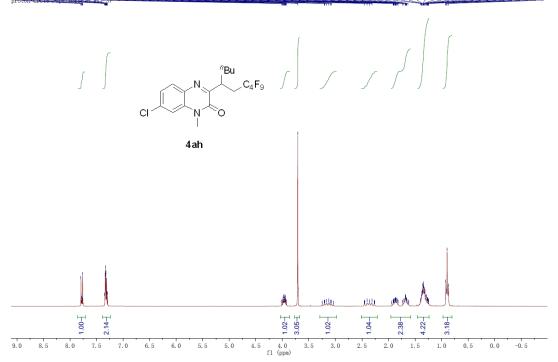


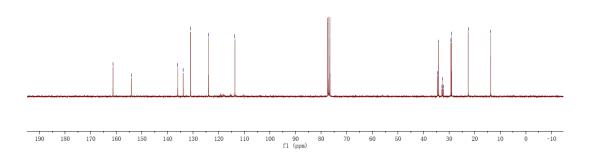


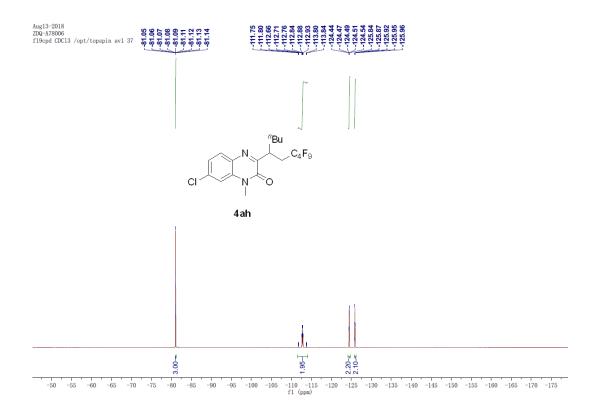


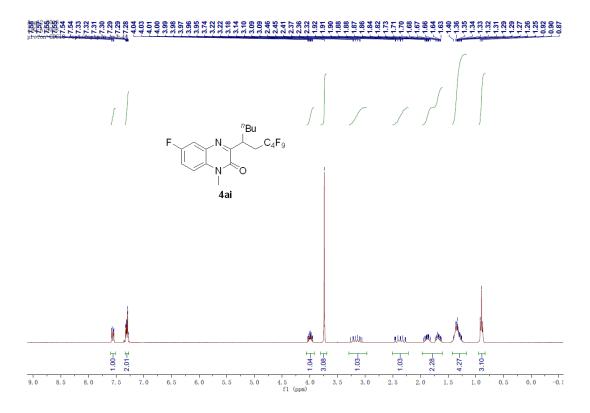


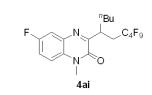
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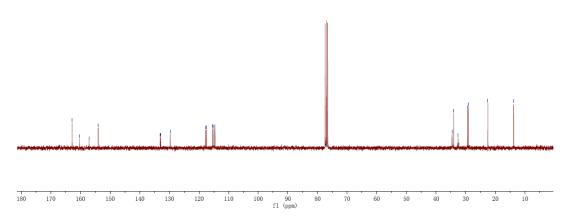


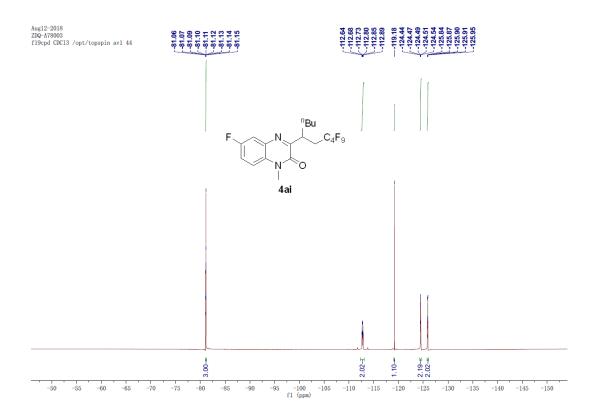


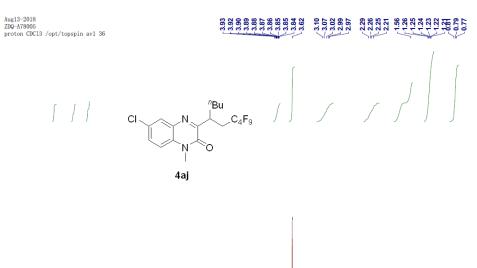


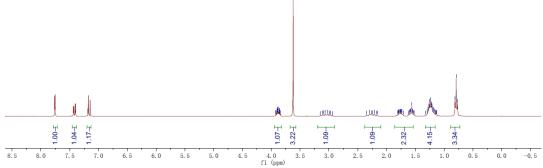




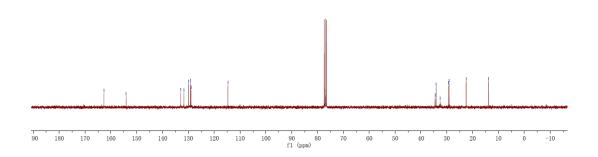


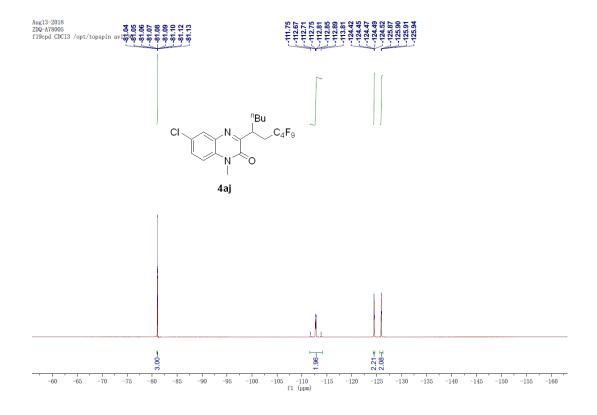


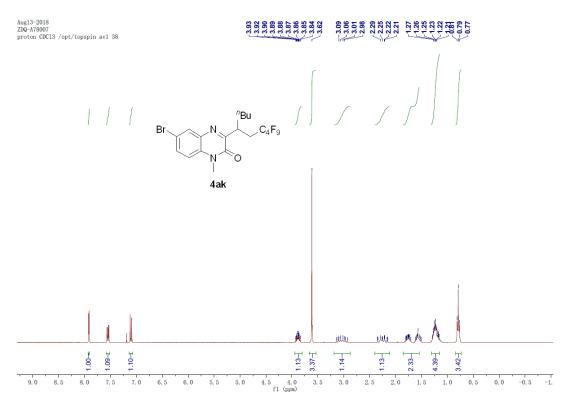


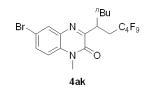


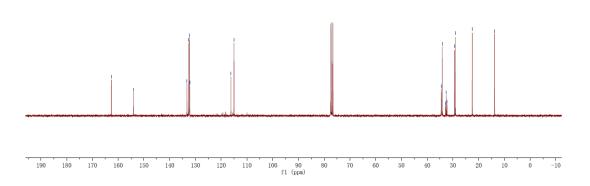
$$CI$$
 N
 C_4F_9
 C_4F_9
 C_4F_9

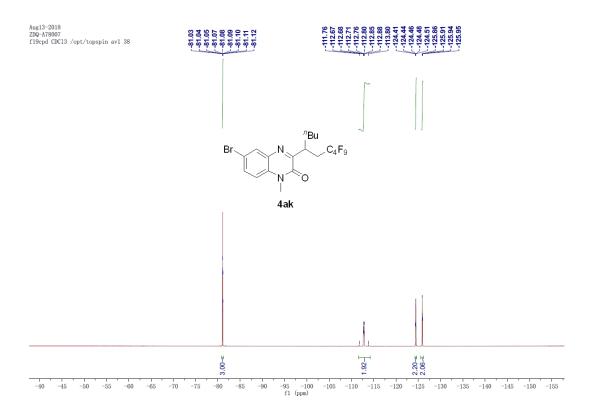


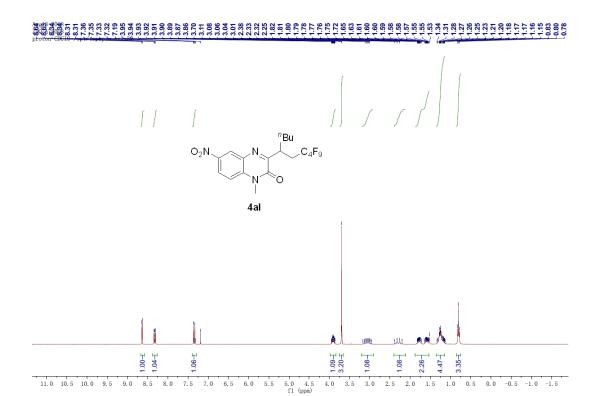








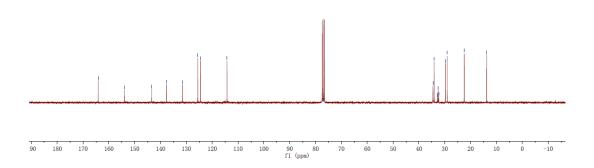


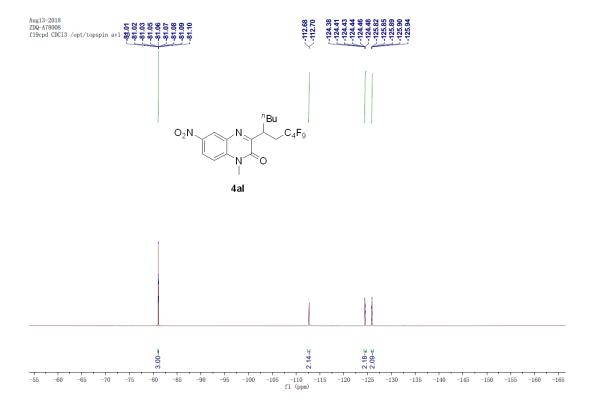


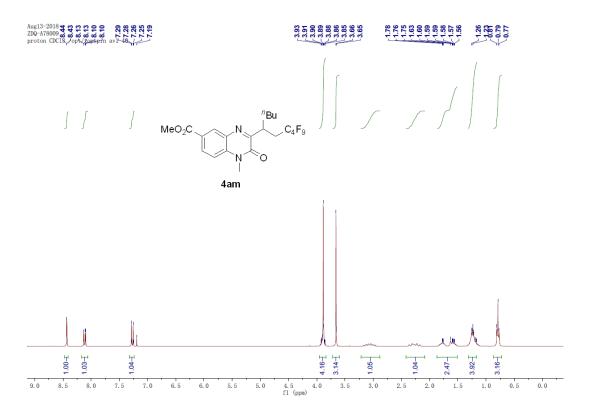


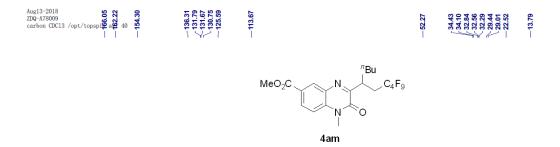
$$O_2N$$
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 O_4F_9

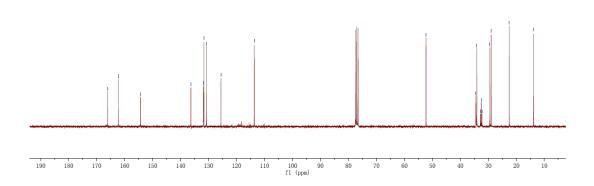
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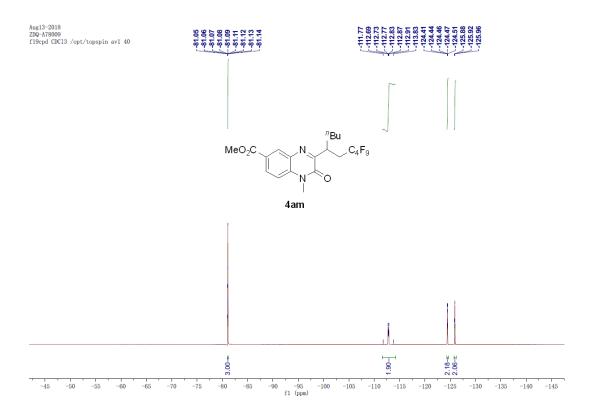


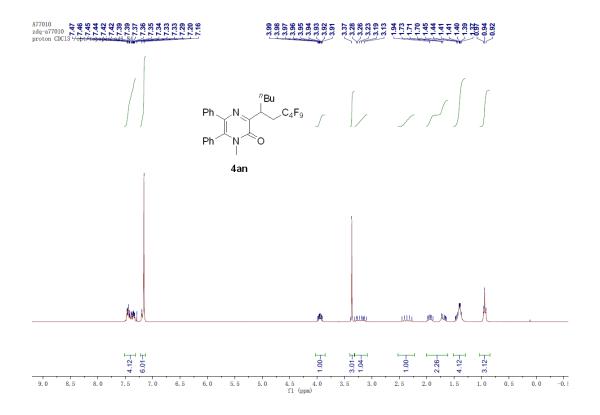






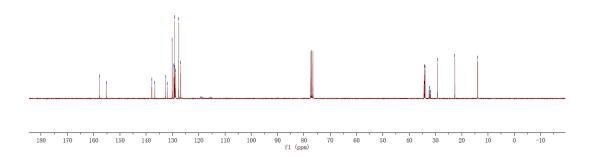


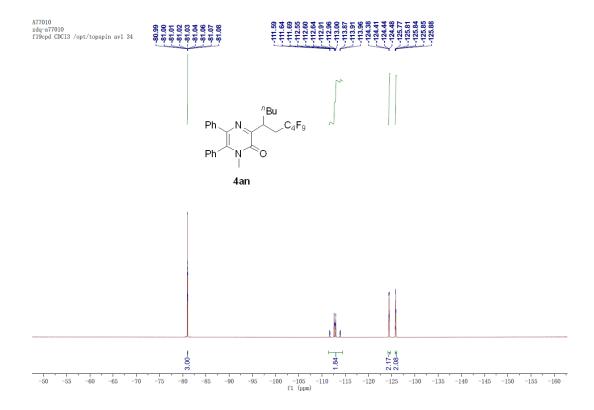


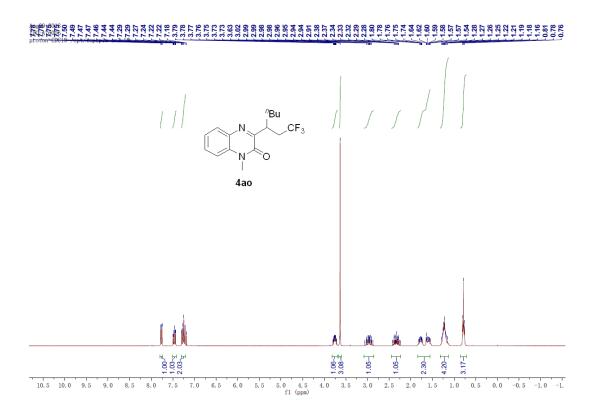


32.42 32.42 32.42 32.14 31.87 29.20 22.60

$$\begin{array}{c|c} & & & & \\ Ph & & & & \\ Ph & & & \\ Ph & & & \\$$

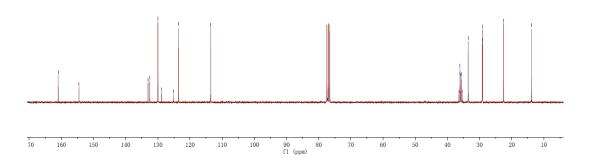






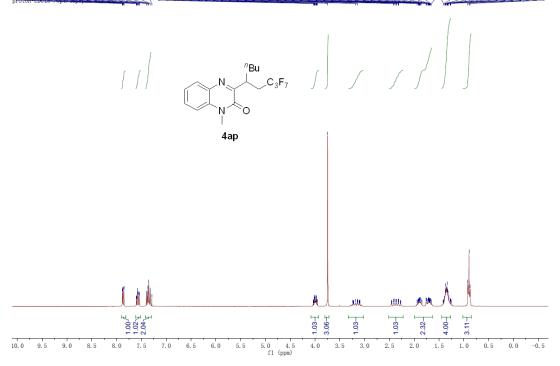






Aug09-2018 ZDQ-A76006 f19cpd CDC13 /opt/topspin av1 50

-64.39



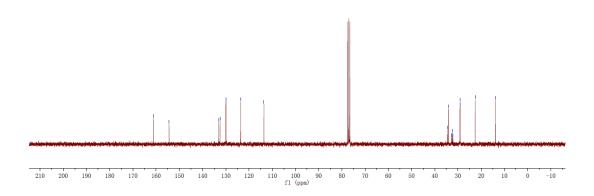
Aug09-2018 ZDQ-A76001 carbon CDC13 /opt/topspin av1 46

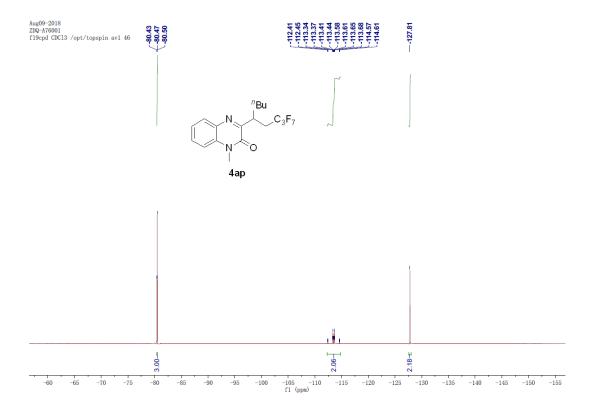


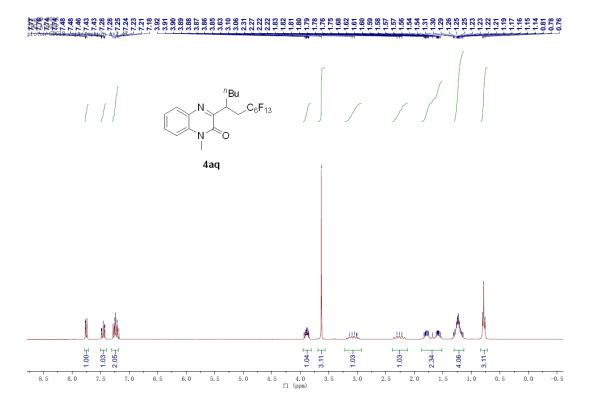




$$N$$
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 C_3F_7
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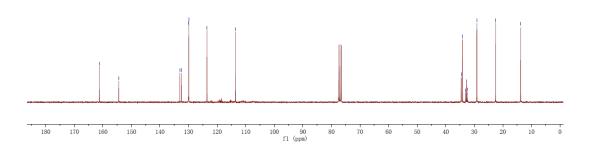


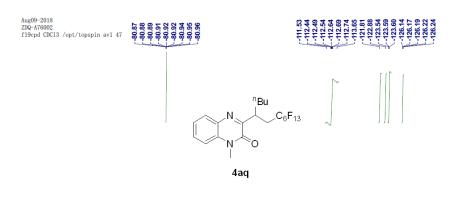


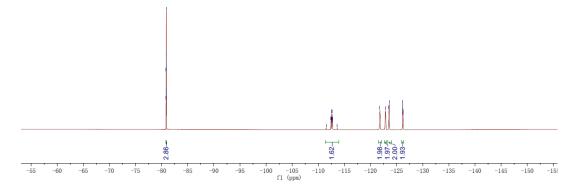


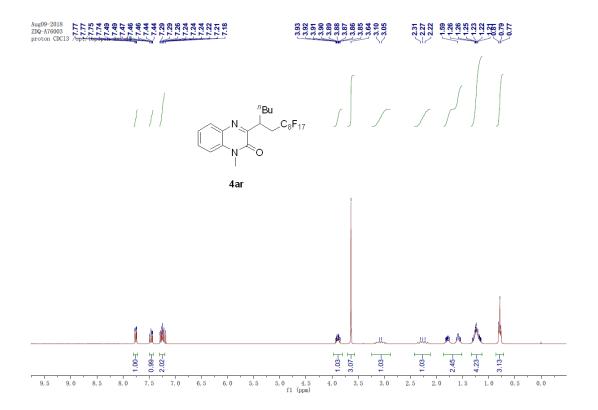


$$\begin{array}{c|c}
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 & \text{V} & \text{O} \\
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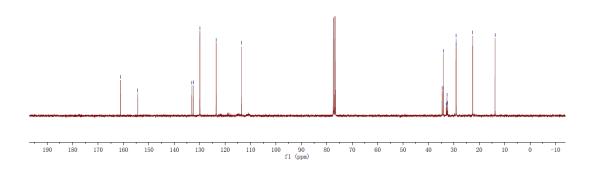


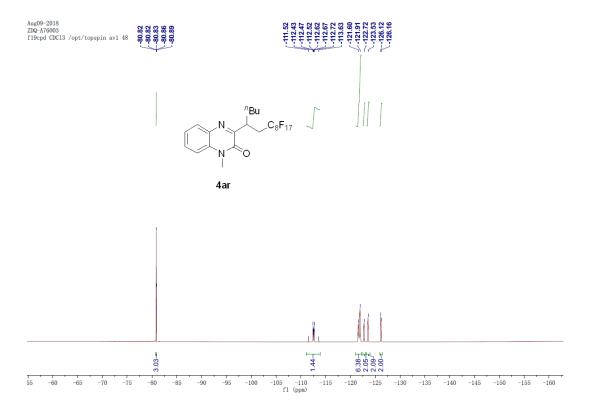


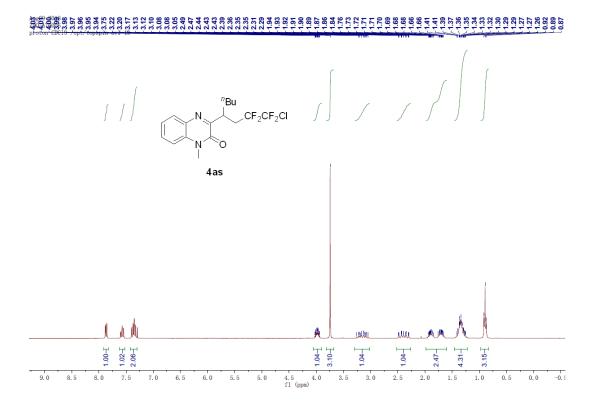


Aug09-2018 ZDQ-A76003 carbon CDC13 /opt/topspin av 48 1

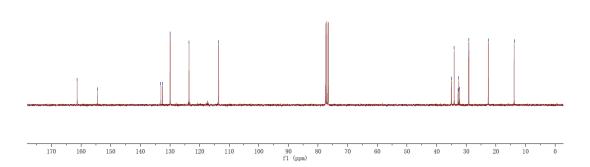
7 129.95 7 129.95 - 123.54 34.59 32.43 32.43 7.29.13 7.29.08

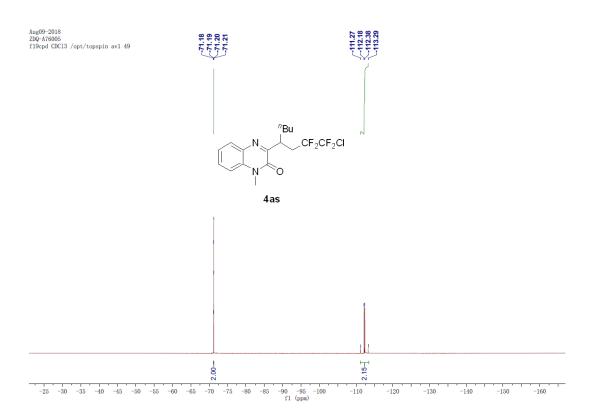


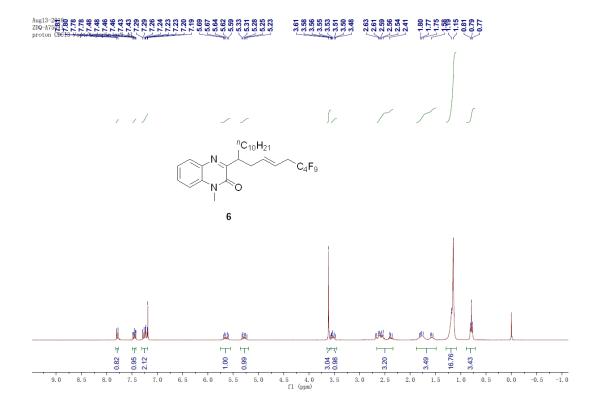


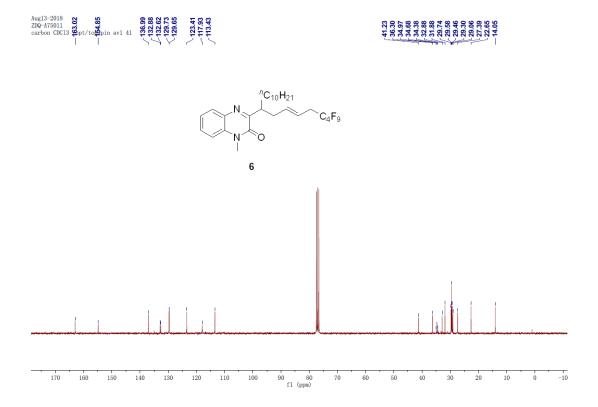


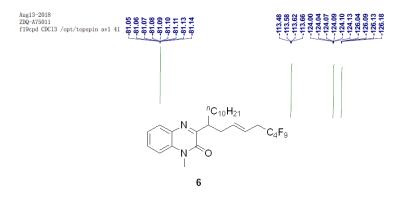


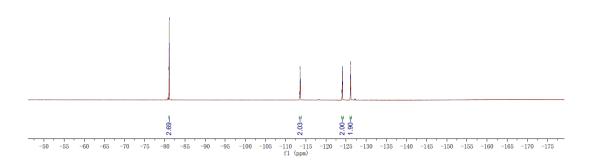


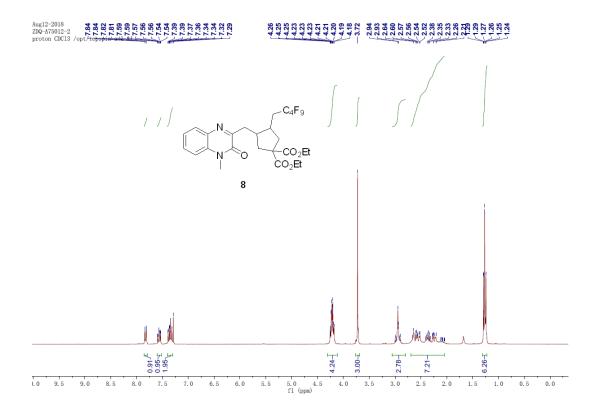




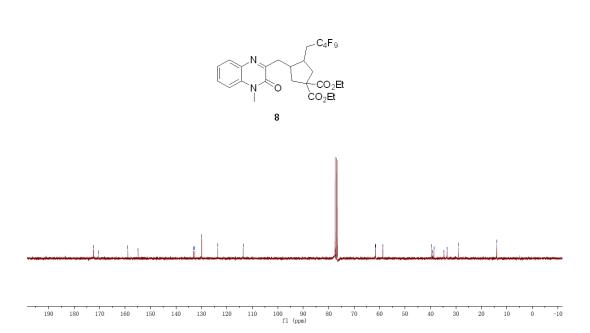


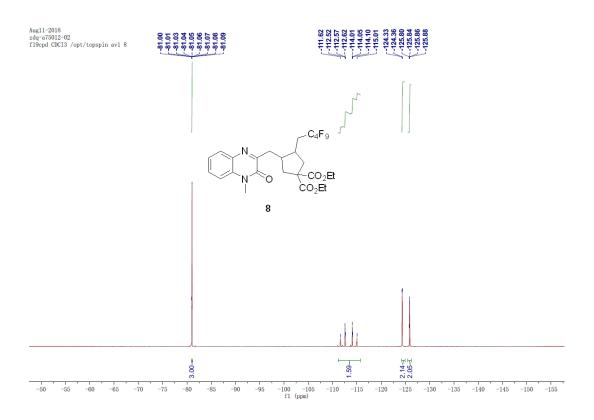




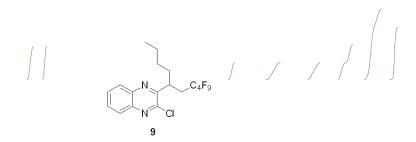


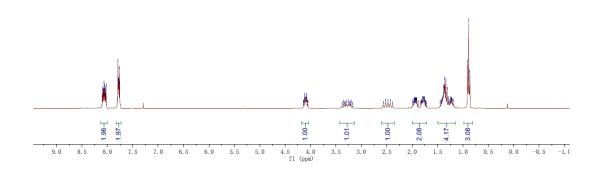






88.89 88.80 88





33.70 33.70 28.87 22.49

$$C_4F_9$$

