

Supporting Information to

Visible-light induced three-component alkynyl-difluoroalkylation of unactivated alkenes

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General information

Unless otherwise noted, starting materials **1-3** were used directly from commercial suppliers without further purification. ^1H , ^{13}C , and ^{19}F NMR spectra were measured on a 600 or 400 MHz NMR spectrometer using CDCl_3 as the solvent with tetramethylsilane (TMS) as the internal standard. Chemical shifts (δ) are given in parts per million relative to TMS, and the coupling constants are given in hertz. High-resolution mass spectrometry (HRMS) analyses were carried out using a TOF MS instrument with an ESI source. Infrared (IR) spectra were recorded on a Nicolet 670 spectrophotometer and reported as wavenumber (cm^{-1}). Column chromatography was performed using silica gel (300–400 mesh). Compounds **1d**¹, **1r**², **2a-i**³, **2j**⁴, and **3b-f**⁵ were prepared according to the methods reported in the literature.

Quenching experiments

A Hitachi RF-6000 fluorescence spectrometer was used to record the emission intensities. All the solutions were excited at 463 nm and emission intensity at 534 nm was observed. DMF was degassed with a stream of N_2 for 30 min. In a typical experiment, the emission spectrum of a 1×10^{-5} M solution of $\text{Ir}(\text{ppy})_3$ in DMF was collected. Then, $\text{BrCF}_2\text{CO}_2\text{Et}$ or NEt_3 was added to the measured solution in a quartz cuvette and the emission spectrum of the sample was collected. I_0 and I represent the intensities of the emission in the absence and presence of the quencher at 534 nm. (a) Emission spectra of 1×10^{-5} $\text{Ir}(\text{ppy})_3$ at $\lambda_{\text{ex}} = 463$ nm showing the quenching effect of increasing $\text{BrCF}_2\text{CO}_2\text{Et}$ or NEt_3 , respectively. (b) The Stern-Volmer plot.

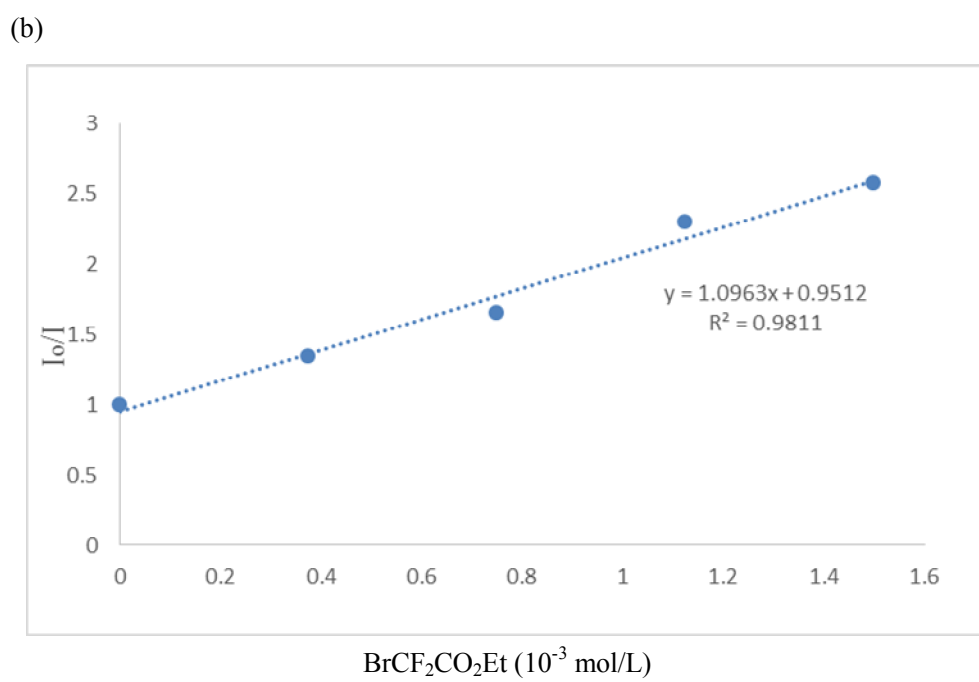
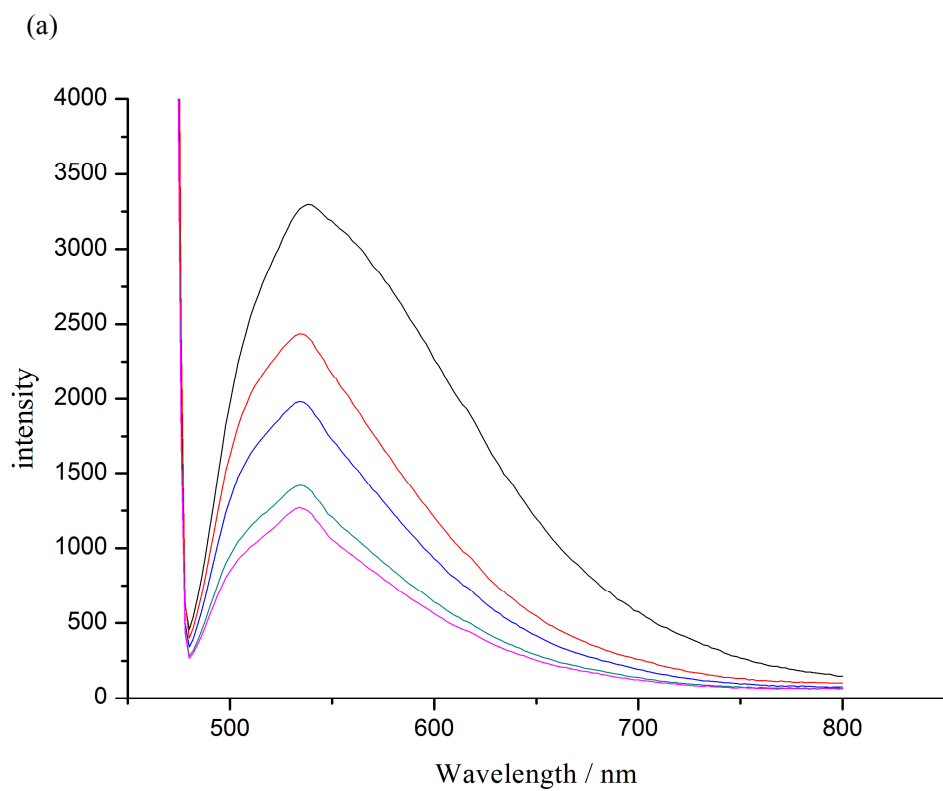
¹ S. L. Rossler, B. S. Schreib, M. Ginterseder, J. Y. Hamilton and E. M. Carreira, *Org. Lett.*, 2017, **19**, 5533.

² X. Wang and Y. Wu, *Chem. Commun.*, 2018, **54**, 1877.

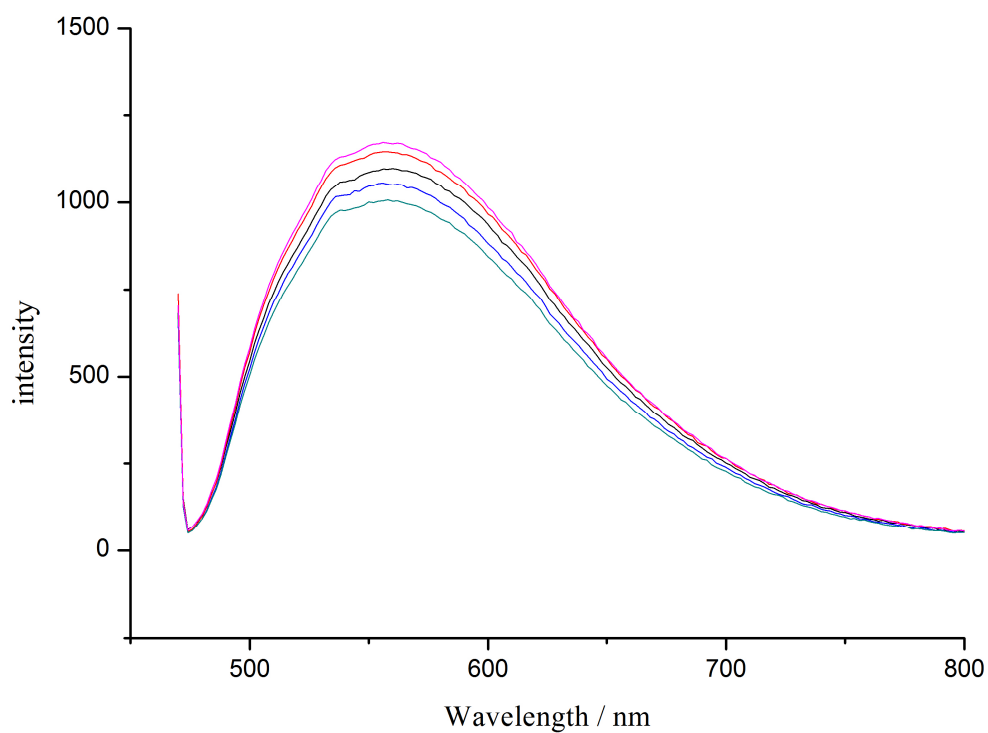
³ J. Meesin, P. Kattun, C. Pareseecharoen, M. Pomakotr, V. Reutralul, D. Soorukram and C. Kuhakarn, *J. Org. Chem.*, 2016, **81**, 2744.

⁴ C. C. Chen and J. Waser, *Org. Lett.*, 2015, **17**, 736.

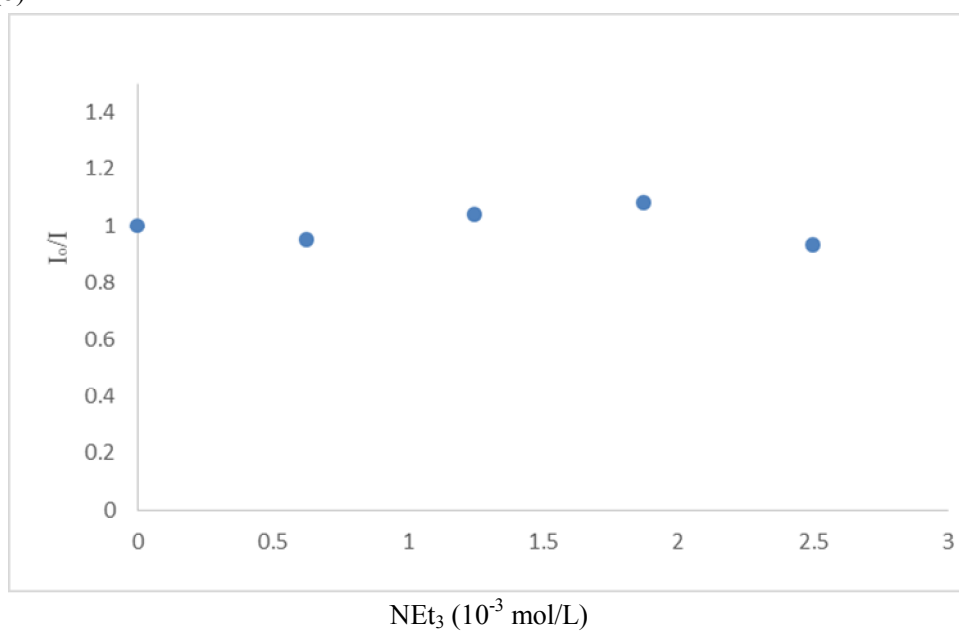
⁵ L. Wang, X.-L. Jia, J.-J. Zhong, L.-Z. Wu and Q. Liu, *Org. Lett.*, 2014, **15**, 5842.



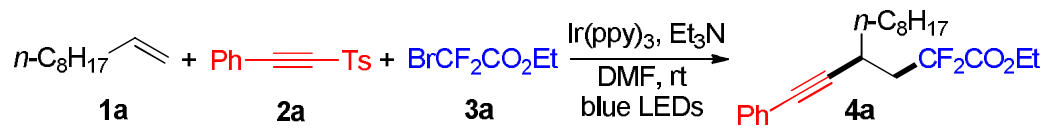
(a)



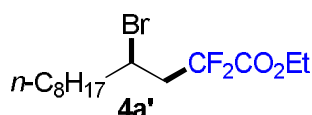
(b)



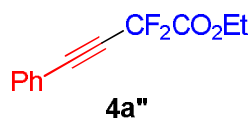
General procedure for the visible-light induced three-component alkynyl-difluoroalkylation of unactivated alkenes



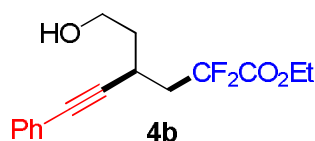
To a mixture of Ir(ppy)₃ (2.6 mg, 0.02 mmol), **1a** (28.0 mg, 0.2 mmol), **2a** (102.4 mg, 0.4 mmol), and Et₃N (139 mg, 1.0 mmol) in 2 mL of DMF was added **3a** (151.2 mg, 0.6 mmol) under a nitrogen atmosphere. After 36 h of irradiation with 15 W of blue LEDs at 25°C, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 20:1) gave 55 mg of **4a** (75% yield) as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.39–7.38 (m, 2H), 7.28–7.27 (m, 3H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.89–2.84 (m, 1H), 2.51–2.41 (m, 1H), 2.30–2.22 (m, 1H), 1.60–1.53 (m, 3H), 1.47–1.44 (m, 1H), 1.30–1.26 (m, 13H), 0.88 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 164.0 (t, *J* = 31.3 Hz), 131.5, 128.2, 127.9, 123.4, 115.6 (t, *J* = 249.2 Hz), 90.6, 82.7, 62.9, 39.8 (t, *J* = 22.8 Hz), 35.4, 31.8, 29.4, 29.2, 29.2, 26.9, 26.1 (dd, *J* = 6.1, 3.2 Hz), 22.6, 14.1, 13.8; ¹⁹F NMR (565 MHz, CDCl₃) δ -100.8 (d, *J* = 261.8 Hz), -107.0 (d, *J* = 261.8 Hz); IR (KBr) ν: 2925, 2855, 1768, 1599, 1490, 1089, 756, 691 cm⁻¹; HRMS (ESI) calcd for C₂₂H₃₀F₂NaO₂ (M+Na)⁺ 387.2106 found 387.2105.



Compound 4a''⁶: It was obtained in 28% yield (13 mg) as a colorless oil using 3 equiv of K₂HPO₄ instead of Et₃N; ¹H NMR (600 MHz, CDCl₃) δ 4.35 (q, *J* = 7.1 Hz, 2H), 4.19–4.14 (m, 1H), 2.86–2.77 (m, 1H), 2.68–2.60 (m, 1H), 1.89–1.83 (m, 2H), 1.56–1.50 (m, 1H), 1.47–1.42 (m, 1H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.31–1.28 (m, 10H), 0.88 (t, *J* = 7.0 Hz, 3H); ¹⁹F NMR (565 MHz, CDCl₃) δ -101.4 (d, *J* = 264.4 Hz), -107.3 (d, *J* = 264.4 Hz).



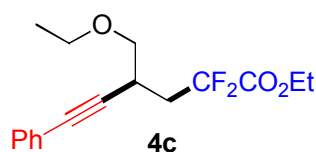
Compound 4a'''⁷: 7 mg, 15% yield, colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.54 (d, *J* = 7.3 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H); ¹⁹F NMR (565 MHz, CDCl₃) δ -90.0.



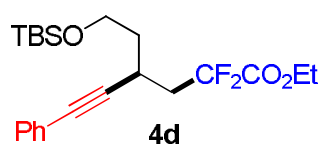
⁶ C. Yu, N. Lqbal, S. Park and E. J. Cho, *Chem. Commun.*, 2014, **50**, 12884.

⁷ T. Besset, T. Poisson and X. Pannecoucke. *Eur. J. Org. Chem.*, 2014, **32**, 7220.

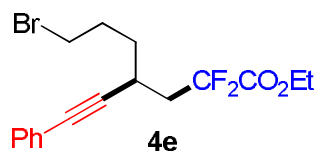
Compound 4b: 31 mg, 52% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.40–7.38 (m, 2H), 7.30–7.27 (m, 3H), 4.22 (q, $J = 7.1$ Hz, 2H), 3.90–3.88 (m, 2H), 3.15–3.10 (m, 1H), 2.57–2.47 (m, 1H), 2.36–2.28 (m, 1H), 1.93–1.88 (m, 1H), 1.85–1.80 (m, 1H), 1.77 (s, 1H), 1.27 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 163.9 (t, $J = 32.7$ Hz), 131.5, 128.2, 128.1, 122.9, 115.4 (t, $J = 249.5$ Hz), 89.5, 83.3, 63.0, 60.4, 39.7 (t, $J = 23.2$ Hz), 37.8, 23.1 (dd, $J = 6.3, 3.8$ Hz), 13.8; ^{19}F NMR (565 MHz, CDCl_3) δ -101.1 (d, $J = 262.8$ Hz), -106.6 (d, $J = 262.8$ Hz); IR (KBr) ν : 3500, 2935, 2213, 1760, 1598, 1491, 1442, 1095, 756, 691 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{19}\text{F}_2\text{O}_3$ ($\text{M}+\text{H}$) $^+$ 297.1297 found 297.1297.



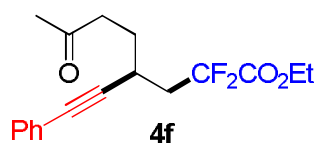
Compound 4c: 29 mg, 47% yield, colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.43–7.40 (m, 2H), 7.32–7.29 (m, 3H), 4.25 (q, $J = 7.1$ Hz, 2H), 3.69–3.49 (m, 4H), 3.19–3.12 (m, 1H), 2.65–2.53 (m, 1H), 2.49–2.35 (m, 1H), 1.30 (t, $J = 6.9$ Hz, 3H), 1.24 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 164.0 (t, $J = 32.9$ Hz), 131.6, 128.2, 128.1, 123.0, 115.6 (t, $J = 249.3$ Hz), 87.8, 83.0, 72.3, 66.5, 62.9, 36.5 (t, $J = 23.4$ Hz), 26.9 (dd, $J = 5.9, 3.3$ Hz), 15.0, 13.8; ^{19}F NMR (565 MHz, CDCl_3) δ -101.8 (d, $J = 262.0$ Hz), -106.1 (d, $J = 262.2$ Hz); IR (KBr) ν : 2959, 2362, 1755, 1599, 1490, 1095, 756, 690 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{21}\text{F}_2\text{O}_3$ ($\text{M}+\text{H}$) $^+$ 311.1453 found 311.1448.



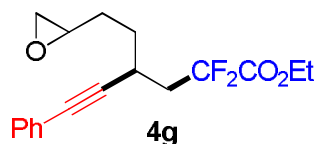
Compound 4d: 38 mg, 46% yield, colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.39–7.37 (m, 2H), 7.29–7.27 (m, 3H), 4.21 (q, $J = 7.2$ Hz, 2H), 3.85–3.80 (m, 2H), 3.15–3.08 (m, 1H), 2.53–2.45 (m, 1H), 2.38–2.26 (m, 1H), 1.87–1.74 (m, 2H), 1.27 (t, $J = 7.2$ Hz, 3H), 0.90 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 164.0 (t, $J = 32.4$ Hz), 131.5, 128.2, 127.9, 123.3, 115.5 (t, $J = 246.3$ Hz), 89.9, 82.9, 62.9, 60.3, 39.8 (t, $J = 23.4$ Hz), 38.2, 25.9, 22.9 (dd, $J = 6.0, 3.4$ Hz), 18.3, 13.8, -5.4, -5.4; ^{19}F NMR (565 MHz, CDCl_3) δ -101.0 (d, $J = 262.0$ Hz), -106.8 (d, $J = 262.0$ Hz); IR (KBr) ν : 2953, 2928, 2240, 1769, 1491, 1091, 755, 691 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{32}\text{F}_2\text{NaO}_3\text{Si}$ ($\text{M}+\text{Na}$) $^+$ 433.1981 found 433.1975.



Compound 4e: 49 mg, 66% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.40–7.38 (m, 2H), 7.30–7.28 (m, 3H), 4.23 (q, $J = 7.2$ Hz, 2H), 3.49–3.46 (m, 2H), 2.95–2.91 (m, 1H), 2.55–2.46 (m, 1H), 2.32–2.24 (m, 1H), 2.18–2.15 (m, 1H), 2.09–2.02 (m, 1H), 1.85–1.79 (m, 1H), 1.74–1.68 (m, 1H), 1.28 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 163.8 (t, $J = 32.1$ Hz), 131.5, 128.2, 128.1, 122.9, 115.3 (t, $J = 251.9$ Hz), 89.4, 83.3, 63.0, 39.8 (t, $J = 23.1$ Hz), 33.8, 33.2, 30.2, 25.6 (dd, $J = 6.1, 3.5$ Hz), 13.8; ^{19}F NMR (565 MHz, CDCl_3) δ -101.1 (d, $J = 262.7$ Hz), -106.9 (d, $J = 262.7$ Hz); IR (KBr) ν : 2953, 2928, 2240, 1769, 1598, 1493, 1012, 755, 693 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{19}\text{BrF}_2\text{NaO}_2$ ($\text{M}+\text{Na}$) $^+$ 395.0429 found 395.0429.

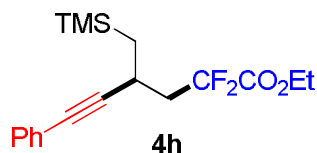


Compound 4f: 50 mg, 78% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.39–7.38 (m, 2H), 7.30–7.29 (m, 3H), 4.22 (q, $J = 7.1$ Hz, 2H), 2.95–2.91 (m, 1H), 2.75–2.66 (m, 2H), 2.52–2.44 (m, 1H), 2.32–2.24 (m, 1H), 2.18 (s, 3H), 1.99–1.93 (m, 1H), 1.81–1.75 (m, 1H), 1.27 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 207.7, 163.8 (t, $J = 32.5$ Hz), 131.5, 128.2, 128.1, 122.9, 115.3 (t, $J = 252.8$ Hz), 89.3, 83.5, 62.9, 40.9, 39.8 (t, $J = 23.3$ Hz), 30.1, 29.0, 25.5 (dd, $J = 6.1, 3.5$ Hz), 13.8; ^{19}F NMR (565 MHz, CDCl_3) δ -101.2 (d, $J = 263.1$ Hz), -106.7 (d, $J = 263.0$ Hz); IR (KBr) ν : 2925, 2240, 1761, 1710, 1599, 1091, 753, 694 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{21}\text{F}_2\text{O}_3$ ($\text{M}+\text{H}$) $^+$ 323.1453 found 323.1453.

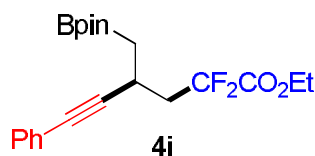


Compound 4g: 46 mg, 72% yield, colorless oil; dr = 1:1; ^1H NMR (600 MHz, CDCl_3) δ 7.39–7.38 (m, 2H), 7.29–7.28 (m, 3H), 4.22 (q, $J = 7.2$ Hz, 2H), 2.99–2.92 (m, 2H), 2.80–2.77 (m, 1H), 2.55–2.45 (m, 2H), 2.33–2.24 (m, 1H), 1.94–1.66 (m, 4H), 1.28 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 163.8 (t, $J = 32.3$ Hz), 131.5, 128.2, 128.0, 128.0, 123.0, 123.0, 115.3 (t, $J = 252.7$ Hz), 89.6, 89.4, 83.3, 83.2, 62.9, 51.8, 51.5, 47.1, 47.0, 39.8 (t, $J = 23.1$ Hz), 39.7 (t, $J = 23.1$ Hz), 31.8, 31.4, 30.2, 29.7, 26.1 (dd, $J = 6.0, 3.4$ Hz), 25.7 (dd, $J = 6.1, 3.5$ Hz), 13.7; ^{19}F

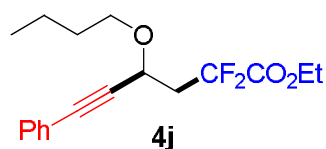
NMR (565 MHz, CDCl₃) δ -101.0 (dd, J = 262.5, 5.9 Hz), -107.0 (dd, J = 262.6, 29.6 Hz); IR (KBr) ν : 2983, 2931, 1762, 1598, 1490, 1095, 757, 692 cm⁻¹; HRMS (ESI) calcd for C₁₈H₂₁F₂O₃ (M+H)⁺ 323.1453 found 323.1449.



Compound 4h: 47 mg, 70% yield, colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.38–7.36 (m, 2H), 7.29–7.27 (m, 3H), 4.23–4.19 (m, 2H), 3.00–2.96 (m, 1H), 2.59–2.49 (m, 1H), 2.30–2.23 (m, 1H), 1.27 (t, J = 7.1 Hz, 3H), 1.03–0.99 (m, 1H), 0.90–0.87 (m, 1H), 0.11 (s, 9H); ¹³C NMR (151 MHz, CDCl₃) δ 164.0 (t, J = 32.0 Hz), 131.4, 128.2, 127.9, 123.4, 115.4 (t, J = 249.1 Hz), 91.9, 82.4, 62.7, 43.4 (t, J = 22.8 Hz), 24.0, 22.3 (dd, J = 6.6, 3.9 Hz), 13.8, -0.9; ¹⁹F NMR (565 MHz, CDCl₃) δ -100.6 (d, J = 262.8 Hz), -107.1 (d, J = 262.8 Hz); IR (KBr) ν : 2951, 2891, 2175, 1743, 1599, 1491, 1077, 753, 715, 688 cm⁻¹; HRMS (ESI) calcd for C₁₈H₂₄F₂NaO₂Si (M+Na)⁺ 361.1406 found 361.1398.



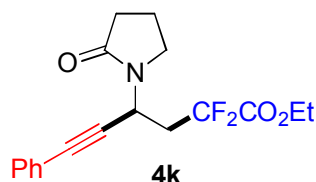
Compound 4i: 49 mg, 63% yield, colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.38–7.35 (m, 2H), 7.27–7.25 (m, 3H), 4.20 (q, J = 7.2 Hz, 2H), 3.16–3.08 (m, 1H), 2.61–2.47 (m, 1H), 2.38–2.26 (m, 1H), 1.28–1.20 (m, 17H); ¹³C NMR (151 MHz, CDCl₃) δ 164.0 (t, J = 33.2 Hz), 131.5, 128.1, 127.7, 123.4, 115.5 (t, J = 252.6 Hz), 91.7, 83.5, 81.8, 62.8, 41.4 (t, J = 22.9 Hz), 24.8, 24.7, 22.0 (dd, J = 6.7, 3.7 Hz), 13.8; ¹⁹F NMR (565 MHz, CDCl₃) δ -100.9 (d, J = 262.6 Hz), -107.0 (d, J = 262.3 Hz); IR (KBr) ν : 2989, 2325, 1765, 1598, 1493, 1086, 756, 696 cm⁻¹; HRMS (ESI) calcd for C₂₁H₂₈BF₂O₄ (M+H)⁺ 393.2043 found 393.2042.



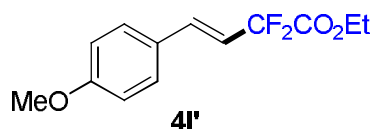
Compound 4j: 43 mg, 67% yield, colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.44–7.42 (m, 2H), 7.34–7.30 (m, 3H), 4.49–4.47 (m, 1H), 4.30–4.25 (m, 2H), 3.77–3.74 (m, 1H), 3.39–3.36 (m, 1H), 2.85–2.76 (m, 1H), 2.57–2.50 (m, 1H), 1.56–1.51 (m, 2H), 1.38–1.33 (m, 5H), 0.92 (t, J = 7.4 Hz); ¹³C NMR (151 MHz, CDCl₃) δ 163.6 (t, J = 31.1 Hz), 131.7, 128.6, 128.3, 122.2, 114.4 (t, J =

S8

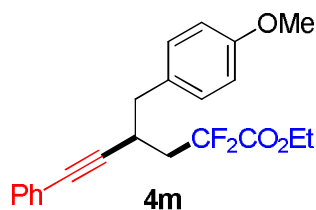
248.5 Hz), 86.2, 86.2, 69.2, 64.4 (dd, $J = 10.2, 4.6$ Hz), 62.6, 41.1 (t, $J = 23.5$ Hz), 31.4, 19.1, 13.9, 13.8; ^{19}F NMR (565 MHz, CDCl_3) δ -101.9 (d, $J = 264.0$ Hz), -108.7 (d, $J = 264.2$ Hz); IR (KBr) ν : 2959, 2872, 2362, 1754, 1599, 1490, 1098, 755, 715, 690 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{23}\text{F}_2\text{O}_3$ ($\text{M}+\text{H}$) $^+$ 325.1610 found 325.1607.



Compound 4k: 48 mg, 72% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.42–7.41 (m, 2H), 7.35–7.30 (m, 3H), 5.55–5.52 (m, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 3.63–3.59 (m, 1H), 3.48–3.44 (m, 1H), 2.71–2.57 (m, 2H), 2.42–2.39 (m, 2H), 2.10–2.03 (m, 2H), 1.33 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 174.2, 163.3 (t, $J = 32.2$ Hz), 131.7, 128.8, 128.3, 121.9, 114.3 (t, $J = 251.4$ Hz), 85.2, 84.1, 63.2, 43.1, 38.6 (t, $J = 5.8$ Hz), 37.7 (t, $J = 23.4$ Hz), 30.8, 17.8, 13.8; ^{19}F NMR (565 MHz, CDCl_3) δ -103.3 (d, $J = 271.0$ Hz), -105.3 (d, $J = 271.0$ Hz); IR (KBr) ν : 2932, 2221, 1743, 1675, 1599, 1492, 1085, 754, 692 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{20}\text{F}_2\text{NO}_3$ ($\text{M}+\text{H}$) $^+$ 336.1406 found 336.1405.



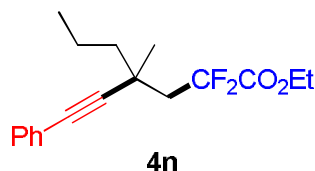
Compound 4l':⁸ 26 mg, 51% yield, colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, $J = 8.7$ Hz, 2H), 7.03–6.99 (m, 1H), 6.89 (d, $J = 8.7$ Hz, 2H), 6.20–6.11 (m, 1H), 4.34 (q, $J = 7.1$ Hz, 2H), 3.82 (s, 3H), 1.36 (t, $J = 7.1$ Hz, 3H).



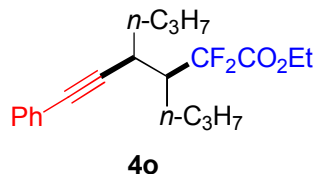
Compound 4m: 37 mg, 50% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.36–7.33 (m, 2H), 7.28–7.26 (m, 3H), 7.19 (d, $J = 8.5$ Hz, 2H), 6.86 (d, $J = 8.6$ Hz, 2H), 4.19 (q, $J = 7.1$ Hz, 2H), 3.80 (s, 3H), 3.11–3.07 (m, 1H), 2.92–2.83 (m, 2H), 2.47–2.37 (m, 1H), 2.33–2.25 (m, 1H), 1.24 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 163.9 (t, $J = 32.7$ Hz), 158.4, 131.5, 130.4, 130.1,

⁸ X. Wang, S. Zhao, J. Liu, D. Zhu, M. Guo, X. Tang and G Wang, *Org. Lett.*, 2017, **19**, 4187.

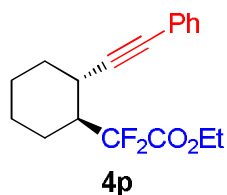
128.2, 128.0, 123.2, 115.5 (t, $J = 252.8$ Hz), 113.7, 90.1, 83.51, 62.9, 55.2, 40.6, 38.8 (t, $J = 23.2$ Hz), 28.2 (dd, $J = 6.0, 3.2$ Hz), 13.8; ^{19}F NMR (565 MHz, CDCl_3) δ -100.7 (d, $J = 262.1$ Hz), -106.7 (d, $J = 262.3$ Hz); IR (KBr) ν : 2934, 2836, 2364, 1762, 1611, 1245, 1086, 755, 691 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{23}\text{F}_2\text{O}_3$ ($\text{M}+\text{H}$) $^+$ 373.1610 found 373.1609.



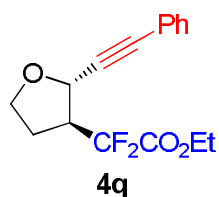
Compound 4n: 29 mg, 47% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.39–7.38 (m, 2H), 7.28–7.27 (m, 3H), 4.14 (q, $J = 7.1$ Hz, 2H), 2.53–2.45 (m, 1H), 2.30–2.20 (m, 1H), 1.64–1.61 (m, 1H), 1.55–1.50 (m, 3H), 1.40 (s, 3H), 1.22 (t, $J = 7.1$ Hz, 3H), 0.96 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 164.1 (t, $J = 32.4$ Hz), 131.5, 128.1, 127.8, 123.4, 116.0 (t, $J = 249.0$ Hz), 93.4, 82.7, 62.8, 45.2, 44.4 (t, $J = 22.2$ Hz), 32.5 (dd, $J = 4.7, 1.7$ Hz), 27.2 (d, $J = 2.7$ Hz), 17.9, 14.3, 13.7; ^{19}F NMR (565 MHz, CDCl_3) δ -97.6 (d, $J = 264.9$ Hz), -101.8 (d, $J = 264.9$ Hz); IR (KBr) ν : 2960, 2933, 1767, 1598, 1491, 1056, 755, 715, 691 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{22}\text{F}_2\text{NaO}_2$ ($\text{M}+\text{Na}$) $^+$ 331.1480 found 331.1488.



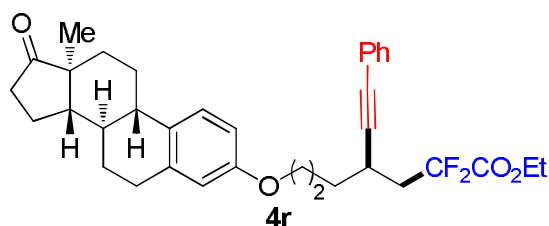
Compound 4o: 10 mg, 15% yield, colorless oil; dr = 3:1; ^1H NMR (600 MHz, CDCl_3) δ 7.40–7.38 (m, 2H), 7.29–7.27 (m, 3H), 4.27–4.23 (m, 2H), 2.90–2.87 (m, 1H), 2.55–2.47 (m, 1H), 1.71–1.64 (m, 3H), 1.58–1.53 (m, 2H), 1.51–1.40 (m, 3H), 1.30 (t, $J = 7.2$ Hz, 3H), 0.97–0.94 (m, 6H); ^{13}C NMR (151 MHz, CDCl_3) of major isomer δ 164.8 (t, $J = 32.9$ Hz), 131.5, 128.2, 127.8, 123.6, 117.6 (t, $J = 254.0$ Hz), 90.5, 83.0, 62.8, 45.8 (t, $J = 20.4$ Hz), 36.6, 33.2, 31.3 (t, $J = 3.7$ Hz), 27.8 (t, $J = 3.8$ Hz), 21.2, 14.2, 13.9, 13.8; ^{19}F NMR (565 MHz, CDCl_3) δ -105.6 (d, $J = 260.0$ Hz), -107.8 (d, $J = 260.0$ Hz); IR (KBr) ν : 2935, 2845, 1760, 1599, 1492, 756, 691 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{27}\text{F}_2\text{O}_2$ ($\text{M}+\text{H}$) $^+$ 337.1974 found 337.1973.



Compound 4p: 24 mg, 40% yield, colorless oil; dr > 20:1; ^1H NMR (600 MHz, CDCl_3) δ 7.39–7.38 (m, 2H), 7.28–7.26 (m, 3H), 4.09 (q, $J = 7.1$ Hz, 2H), 2.58–2.54 (m, 1H), 2.45–2.39 (m, 1H), 2.15–2.12 (m, 1H), 2.03–2.02 (m, 1H), 1.85–1.84 (m, 1H), 1.79–1.76 (m, 1H), 1.57–1.51 (m, 1H), 1.33–1.28 (m, 3H), 1.20 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 164.4 (t, $J = 33.7$ Hz), 131.5, 128.1, 127.9, 123.3, 116.4 (t, $J = 248.1$ Hz), 90.6, 82.8, 62.7, 45.5 (t, $J = 21.5$ Hz), 33.3, 29.6 (dd, $J = 5.2, 2.5$ Hz), 25.1, 24.5, 23.5 (dd, $J = 6.4, 2.3$ Hz), 13.7; ^{19}F NMR (565 MHz, CDCl_3) δ -105.8, -106.2; IR (KBr) ν : 2957, 2933, 2355, 1745, 1599, 1495, 1056, 755, 698 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{20}\text{F}_2\text{NaO}_2$ ($\text{M}+\text{Na}$) $^+$ 329.1324 found 329.1321.

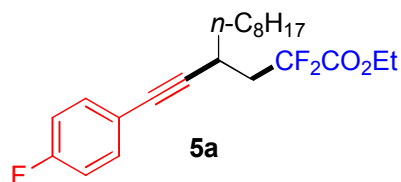


Compound 4q: 30 mg, 51% yield, colorless oil; dr > 20:1; ^1H NMR (400 MHz, CDCl_3) δ 7.44–7.42 (m, 3H), 7.34–7.28 (m, 3H), 4.95 (d, $J = 5.4$ Hz, 1H), 4.34 (q, $J = 7.2$ Hz, 2H), 4.08–3.94 (m, 2H), 3.23–3.10 (m, 1H), 2.31–2.22 (m, 1H), 2.18–2.11 (m, 1H), 1.35 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 163.4 (t, $J = 32.5$ Hz), 131.7, 128.7, 128.3, 122.1, 115.1 (t, $J = 253.5$ Hz), 86.7, 85.7, 68.2 (t, $J = 4.8$ Hz), 67.6, 63.2, 51.2 (t, $J = 22.6$ Hz), 26.0, 13.9; ^{19}F NMR (565 MHz, CDCl_3) δ -110.3 (d, $J = 258.4$ Hz), -111.5 (d, $J = 258.5$ Hz); IR (KBr) ν : 2945, 1767, 1598, 1491, 1150, 1056, cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{16}\text{F}_2\text{NaO}_3$ ($\text{M}+\text{Na}$) $^+$ 317.0960 found 317.0954.

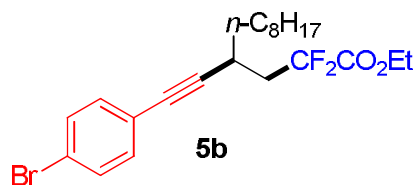


Compound 4r: 74 mg, 66% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.39–7.38 (m, 2H), 7.29–7.28 (m, 3H), 7.19 (d, $J = 8.6$ Hz, 1H), 6.72–6.71 (m, 1H), 6.65 (d, $J = 2.5$ Hz, 1H), 4.22 (q,

$J = 7.1$ Hz, 2H), 4.00 (t, $J = 6.2$ Hz, 2H), 2.99–2.94 (m, 1H), 2.90–2.87 (m, 2H), 2.54–2.48 (m, 2H), 2.40–2.37 (m, 1H), 2.31–2.22 (m, 2H), 2.17–2.11 (m, 1H), 2.07–2.04 (m, 2H), 2.02–1.93 (m, 3H), 1.86–1.81 (m, 1H), 1.75–1.73 (m, 1H), 1.62–1.55 (m, 2H), 1.52–1.48 (m, 3H), 1.45–1.41 (m, 1H), 1.27 (t, $J = 7.2$ Hz, 3H), 0.90 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 220.9, 163.9 (t, $J = 32.6$ Hz), 156.9, 137.7, 132.0, 131.5, 128.4, 128.0, 126.3, 123.1, 115.4 (t, $J = 252.5$ Hz), 114.5, 112.1, 89.9, 83.1, 67.2, 62.9, 50.3, 47.9, 43.9, 39.8 (t, $J = 23.0$ Hz), 38.3, 35.8, 32.0, 31.5, 29.6, 26.9, 26.5, 25.9, 21.5, 13.8, 13.8; ^{19}F NMR (565 MHz, CDCl_3) δ -100.9 (d, $J = 262.0$ Hz), -106.9 (d, $J = 262.3$ Hz); IR (KBr) ν : 2950, 2933, 2295, 1745, 1700, 1597, 1500, 1140, 860, 698 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{35}\text{H}_{40}\text{F}_2\text{NaO}_4$ ($\text{M}+\text{Na}$) $^+$ 585.2787 found 585.2790.

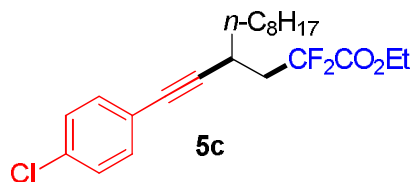


Compound 5a: 55 mg, 72% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.38–7.35 (m, 2H), 6.99–6.96 (m, 2H), 4.23–4.20 (m, 2H), 2.87–2.83 (m, 1H), 2.49–2.40 (m, 1H), 2.29–2.21 (m, 1H), 1.58–1.52 (m, 3H), 1.46–1.43 (m, 1H), 1.32–1.25 (m, 13H), 0.88 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 164.0 (t, $J = 32.4$ Hz), 162.3 (d, $J = 249.0$ Hz), 133.4 (d, $J = 8.3$ Hz), 119.5 (d, $J = 3.5$ Hz), 115.5 (t, $J = 249.0$ Hz), 115.4 (d, $J = 22.0$ Hz), 90.3, 81.6, 62.9, 39.8 (t, $J = 23.1$ Hz), 35.4, 31.9, 29.5, 29.2, 29.2, 26.9, 26.0 (dd, $J = 5.9, 3.3$ Hz), 22.7, 14.1, 13.8; ^{19}F NMR (565 MHz, CDCl_3) δ -101.1 (d, $J = 262.0$ Hz), -106.9 (d, $J = 262.0$ Hz); IR (KBr) ν : 2927, 2855, 1765, 1489, 1089, 827, 775, 722 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{30}\text{F}_3\text{O}_2$ ($\text{M}+\text{H}$) $^+$ 383.2192 found 383.2191.

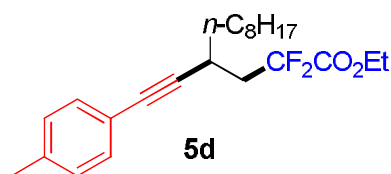


Compound 5b: 54 mg, 61% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.42 (d, $J = 8.4$ Hz, 2H), 7.25 (d, $J = 8.4$ Hz, 2H), 4.23–4.20 (m, 2H), 2.87–2.83 (m, 1H), 2.49–2.40 (m, 1H), 2.29–2.21 (m, 1H), 1.58–1.51 (m, 3H), 1.45–1.42 (m, 1H), 1.34–1.27 (m, 13H), 0.88 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 164.0 (t, $J = 32.8$ Hz), 133.0, 131.4, 122.3, 122.0, 115.5 (t, $J = 249.0$ Hz), 91.8, 81.7, 62.9, 39.7 (t, $J = 23.1$ Hz), 35.3, 31.8, 29.4, 29.2, 29.2, 26.9, 26.1 (dd, $J =$

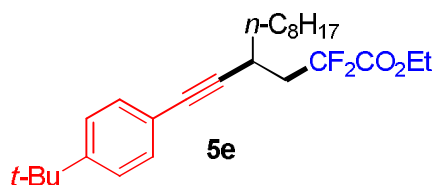
6.0, 3.4 Hz), 22.6, 14.1, 13.8; ^{19}F NMR (565 MHz, CDCl_3) δ -101.1 (d, J = 262.0 Hz), -106.9 (d, J = 262.0 Hz); IR (KBr) ν : 2926, 1764, 1491, 1088, 828, 775, 723 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{29}\text{BrF}_2\text{NaO}_2$ ($\text{M}+\text{Na}$) $^{+}$ 465.1211 found 465.1211.



Compound 5c: 54 mg, 68% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.31 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.3 Hz, 2H), 4.22 (q, J = 7.1 Hz, 2H), 2.88–2.84 (m, 1H), 2.49–2.40 (m, 1H), 2.29–2.21 (m, 1H), 1.60–1.52 (m, 3H), 1.47–1.43 (m, 1H), 1.29–1.27 (m, 13H), 0.88 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 164.0 (t, J = 32.8 Hz), 133.9, 132.8, 128.5, 121.9, 115.5 (t, J = 252.5 Hz), 91.7, 81.6, 62.9, 39.7 (t, J = 23.1 Hz), 35.4, 31.9, 29.7, 29.5, 29.3, 29.2, 27.0, 26.1 (dd, J = 6.0, 3.3 Hz), 22.7, 14.1, 13.9; ^{19}F NMR (565 MHz, CDCl_3) δ -101.2 (d, J = 262.3 Hz), -106.8 (d, J = 262.3 Hz); IR (KBr) ν : 2925, 1763, 1489, 1466, 1089, 828, 775, 723 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{30}\text{ClF}_2\text{O}_2$ ($\text{M}+\text{H}$) $^{+}$ 399.1897 found 399.1897.

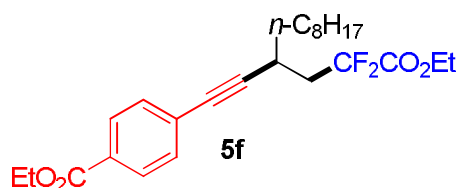


Compound 5d: 49 mg, 65% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.27 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 4.21 (q, J = 7.1 Hz, 2H), 2.86–2.83 (m, 1H), 2.49–2.46 (m, 1H), 2.33 (s, 3H), 2.28–2.23 (m, 1H), 1.59–1.53 (m, 3H), 1.46–1.43 (m, 1H), 1.29–1.26 (m, 13H), 0.88 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 164.0 (t, J = 32.0 Hz), 137.9, 131.4, 128.9, 120.3, 115.59 (d, J = 248.8 Hz), 89.7, 82.7, 62.9, 39.9 (t, J = 23.1 Hz), 35.5, 31.8, 29.4, 29.2, 26.9, 26.1 (dd, J = 6.3, 3.3 Hz), 22.7, 21.4, 14.1, 13.8; ^{19}F NMR (565 MHz, CDCl_3) δ -100.6 (d, J = 261.4 Hz), -107.1 (d, J = 261.5 Hz); IR (KBr) ν : 2924, 2854, 1761, 1509, 1464, 1089, 815, 774, 723 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{32}\text{F}_2\text{NaO}_2$ ($\text{M}+\text{Na}$) $^{+}$ 401.2263 found 401.2260.

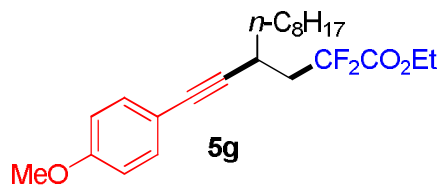


Compound 5e: 61 mg, 73% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.33–7.29 (m, 4H),

4.22 (q, $J = 7.1$ Hz, 2H), 2.88–2.83 (m, 1H), 2.50–2.41 (m, 1H), 2.29–2.21 (m, 1H), 1.59–1.53 (m, 3H), 1.48–1.44 (m, 1H), 1.30–1.26 (m, 22H), 0.88 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 164.0 (t, $J = 32.9$ Hz), 151.1, 131.2, 125.1, 120.4, 115.6 (t, $J = 248.9$ Hz), 89.8, 82.7, 62.9, 39.9 (t, $J = 22.9$ Hz), 35.5, 34.7, 31.8, 31.2, 29.5, 29.2, 26.9, 26.1 (dd, $J = 6.2, 3.1$ Hz), 22.6, 14.1, 13.8; ^{19}F NMR (565 MHz, CDCl_3) δ -100.9 (d, $J = 261.5$ Hz), -107.0 (d, $J = 261.4$ Hz); IR (KBr) ν : 2923, 2851, 1760, 1501, 1466, 1089, 813, 773, 722 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{38}\text{F}_2\text{NaO}_2$ ($\text{M}+\text{Na}$) $^{+}$ 443.2732 found 443.2726.

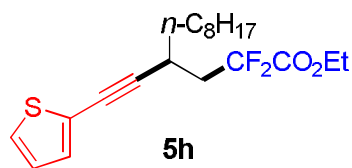


Compound 5f: 39 mg, 45% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.96 (d, $J = 8.3$ Hz, 2H), 7.44 (d, $J = 8.3$ Hz, 2H), 4.37 (q, $J = 7.0$ Hz, 2H), 4.24–4.20 (m, 2H), 2.92–2.87 (m, 1H), 2.52–2.42 (m, 1H), 2.31–2.23 (m, 1H), 1.63–1.53 (m, 3H), 1.48–1.45 (m, 1H), 1.39 (t, $J = 7.1$ Hz, 3H), 1.30–1.26 (m, 13H), 0.88 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 166.1, 163.9 (t, $J = 32.8$ Hz), 131.4, 129.6, 129.3, 128.0, 115.4 (t, $J = 249.7$ Hz), 93.8, 82.1, 62.9, 61.1, 39.6 (t, $J = 23.0$ Hz), 35.3, 31.8, 29.4, 29.2, 29.2, 26.9, 26.1 (dd, $J = 5.5, 2.9$ Hz), 22.6, 14.3, 14.1, 13.8; ^{19}F NMR (565 MHz, CDCl_3) δ -101.2 (d, $J = 262.0$ Hz), -106.9 (d, $J = 262.1$ Hz); IR (KBr) ν : 2931, 2854, 1761, 1725, 1499, 1466, 1089, 822, 773, 722 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{34}\text{F}_2\text{NaO}_4$ ($\text{M}+\text{Na}$) $^{+}$ 459.2317 found 459.2305.

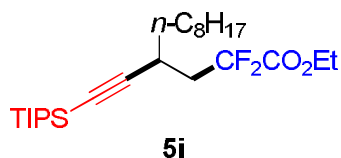


Compound 5g: 58 mg, 74% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.32 (d, $J = 8.8$ Hz, 2H), 6.81 (d, $J = 8.8$ Hz, 2H), 4.22–4.19 (m, 2H), 3.80 (s, 3H), 2.86–2.82 (m, 1H), 2.50–2.40 (m, 1H), 2.28–2.20 (m, 1H), 1.58–1.52 (m, 3H), 1.46–1.44 (m, 1H), 1.31–1.26 (m, 13H), 0.88 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 164.0 (t, $J = 32.2$ Hz), 159.3, 132.9, 115.6 (t, $J = 248.8$ Hz), 115.6, 113.8, 89.0, 82.5, 62.9, 55.2, 39.9 (t, $J = 23.1$ Hz), 35.5, 31.8, 29.5, 29.2, 26.9, 26.1 (dd, $J = 6.1, 3.3$ Hz), 22.7, 14.1, 13.8; ^{19}F NMR (565 MHz, CDCl_3) δ -100.6 (d, $J = 261.5$ Hz), -107.1 (d, $J = 261.5$ Hz); IR (KBr) ν : 2935, 2854, 1762, 1511, 1245, 1086, 820, 777, 755 cm^{-1} ;

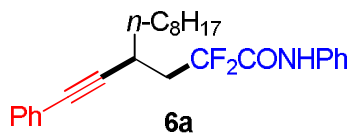
HRMS (ESI) calcd for $C_{23}H_{33}F_2O_3$ ($M+H$)⁺ 395.2392 found 395.2393.



Compound 5h: 34 mg, 46% yield, colorless oil; 1H NMR (600 MHz, $CDCl_3$) δ 7.20–7.19 (m, 1H), 7.13–7.13 (m, 1H), 6.94–6.93 (m, 1H), 4.26 (q, J = 7.2 Hz, 2H), 2.91–2.86 (m, 1H), 2.50–2.39 (m, 1H), 2.29–2.21 (m, 1H), 1.60–1.49 (m, 3H), 1.46–1.43 (m, 1H), 1.32–1.27 (m, 13H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.9 (t, J = 32.8 Hz), 131.5, 126.8, 126.4, 123.4, 115.4 (t, J = 249.2 Hz), 94.5, 75.9, 63.0, 39.6 (t, J = 23.1 Hz), 35.3, 31.8, 29.4, 29.2, 29.2, 26.9, 26.3 (dd, J = 6.2, 3.3 Hz), 22.6, 14.1, 13.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ -101.0 (d, J = 261.8 Hz), -107.1 (d, J = 261.9 Hz); IR (KBr) ν : 2923, 2854, 1754, 1642, 1413, 1190, 1082, 722, 697 cm^{-1} ; HRMS (ESI) calcd for $C_{20}H_{28}F_2NaO_2S$ ($M+Na$)⁺ 393.1670 found 393.1670.

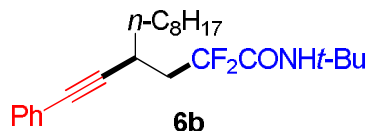


Compound 5i: 47 mg, 53% yield, colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ 4.32 (q, J = 7.1 Hz, 2H), 2.72 (brs, 1H), 2.43–2.30 (m, 1H), 2.25–2.12 (m, 1H), 1.54–1.44 (m, 4H), 1.36 (t, J = 7.2 Hz, 3H), 1.27 (brs, 10H), 1.08–1.00 (m, 21H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.1 (t, J = 32.8 Hz), 115.4 (t, J = 251.6 Hz), 109.7, 82.1, 62.8, 39.9 (t, J = 22.6 Hz), 35.5, 31.9, 29.5, 29.2, 29.1, 26.8, 26.3 (t, J = 4.1 Hz), 22.7, 18.6, 14.1, 13.9, 11.2; ^{19}F NMR (565 MHz, $CDCl_3$) δ -103.7 (d, J = 261.4 Hz), 104.7 (d, J = 261.4 Hz); IR (KBr) ν : 2924, 2863, 2167, 1770, 1375, 1192, 777, 723 cm^{-1} ; HRMS (ESI) calcd for $C_{25}H_{46}F_2NaO_2Si$ ($M+Na$)⁺ 467.3127 found 467.3117.

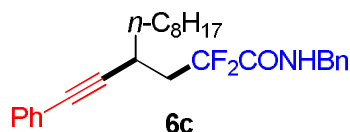


Compound 6a: 42 mg, 61% yield, colorless oil; 1H NMR (600 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.53–7.51 (m, 2H), 7.31–7.25 (m, 4H), 7.22–7.13 (m, 4H), 2.91–2.87 (m, 1H), 2.58–2.53 (m, 1H), 2.44–2.36 (m, 1H), 1.61–1.56 (m, 3H), 1.48–1.45 (m, 1H), 1.29–1.26 (m, 10H), 0.87 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.8 (t, J = 28.0 Hz), 136.0, 131.5, 129.1, 128.0, 127.7, 125.4, 123.2, 120.2, 117.6 (t, J = 254.2 Hz), 90.5, 82.9, 38.9 (t, J = 22.7 Hz), 35.6, 31.8, 29.4, 29.3,

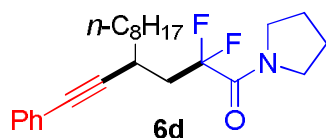
29.2, 26.9, 26.2 (t, $J = 4.8$ Hz), 22.6, 14.0; ^{19}F NMR (565 MHz, CDCl_3) δ -101.2 (d, $J = 256.3$ Hz), -105.0 (d, $J = 256.3$ Hz); IR (KBr) ν : 3305, 2919, 2852, 2361, 1686, 1600, 1541, 1446, 1117, 745, 686 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{32}\text{F}_2\text{NO}$ ($\text{M}+\text{H}$) $^+$ 412.2446 found 412.2439.



Compound 6b: 41 mg, 52% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.40–7.38 (m, 2H), 7.29–7.27 (m, 3H), 6.23 (s, 1H), 2.85–2.80 (m, 1H), 2.39–2.31 (m, 2H), 1.61–1.54 (m, 3H), 1.47–1.44 (m, 1H), 1.37 (s, 9H), 1.30–1.26 (m, 10H), 0.88 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 163.0 (t, $J = 27.1$ Hz), 131.5, 128.2, 127.7, 123.6, 117.4 (t, $J = 254.3$ Hz), 91.3, 82.2, 51.8, 38.9 (t, $J = 22.8$ Hz), 35.4, 31.8, 29.4, 29.2, 29.2, 28.3, 26.9, 26.2 (dd, $J = 5.3, 3.1$ Hz), 22.6, 14.0; ^{19}F NMR (565 MHz, CDCl_3) δ 102.7 (d, $J = 253.1$ Hz), 104.0 (d, $J = 253.1$ Hz); IR (KBr) ν : 3470, 2925, 2854, 2345, 1704, 1490, 1457, 1226, 1082, 755, 691 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{36}\text{F}_2\text{NO}$ ($\text{M}+\text{H}$) $^+$ 392.2759 found 392.2757.

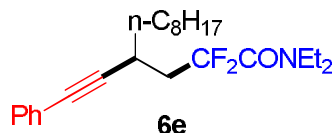


Compound 6c: 56 mg, 66% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.31–7.30 (m, 2H), 7.25–7.19 (m, 6H), 7.16–7.15 (m, 2H), 6.60 (s, 1H), 4.47–4.43 (m, 1H), 4.29–4.25 (m, 1H), 2.78–2.74 (m, 1H), 2.46–2.36 (m, 1H), 2.32–2.24 (m, 1H), 1.53–1.47 (m, 3H), 1.39–1.35 (m, 1H), 1.26–1.19 (m, 10H), 0.81 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 163.9 (t, $J = 28.3$ Hz), 136.6, 131.6, 128.8, 128.2, 127.9, 127.8, 127.8, 123.5, 115.9 (t, $J = 253.2$ Hz), 90.8, 82.6, 43.6, 39.0 (t, $J = 22.8$ Hz), 35.5, 31.8, 29.5, 29.2, 29.2, 26.9, 26.2 (t, $J = 4.7$ Hz), 22.6, 14.1; ^{19}F NMR (565 MHz, CDCl_3) δ -102.5 (d, $J = 256.7$ Hz), -104.8 (d, $J = 256.9$ Hz); IR (KBr) ν : 3310, 2914, 2849, 2359, 1674, 1597, 1552, 1185, 1050, 758, 692 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{33}\text{F}_2\text{NONa}$ ($\text{M}+\text{Na}$) $^+$ 448.2422 found 448.2420.

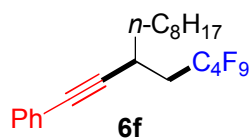


Compound 6d: 44 mg, 51% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.39–7.38 (m, 2H), 7.28–7.27 (m, 3H), 3.72 (t, $J = 6.8$ Hz, 2H), 3.50–3.48 (m, 2H), 2.97–2.92 (m, 1H), 2.52–2.35 (m,

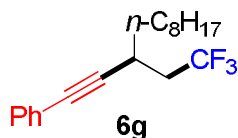
2H), 1.96–1.89 (m, 2H), 1.81–1.76 (m, 2H), 1.64–1.55 (m, 3H), 1.50–1.45 (m, 1H), 1.30–1.25 (m, 10H), 0.88 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 162.2 (t, $J = 29.0$ Hz), 131.6, 128.1, 127.6, 123.8, 118.5 (t, $J = 253.5$ Hz), 91.9, 81.8, 47.5, 46.7 (t, $J = 6.5$ Hz), 39.6 (t, $J = 22.5$ Hz), 35.7, 31.9, 29.5, 29.3, 29.3, 27.0, 26.5, 26.0 (t, $J = 4.2$ Hz), 23.2, 22.7, 14.1; ^{19}F NMR (565 MHz, CDCl_3) δ -101.4, -101.4; IR (KBr) ν : 2924, 2854, 1659, 1598, 1489, 1203, 755, 691 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{34}\text{F}_2\text{NO}$ ($\text{M}+\text{H}$) $^+$ 390.2603 found 390.2599.



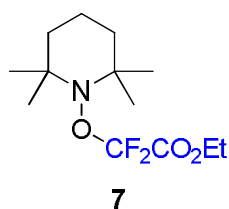
Compound 6e: 36 mg, 46% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.39–7.38 (m, 2H), 7.28–7.26 (m, 3H), 3.58–3.50 (m, 2H), 3.41–3.35 (m, 2H), 2.98–2.97 (m, 1H), 2.51–2.38 (m, 2H), 1.63–1.58 (m, 3H), 1.48 (brs, 1H), 1.30–1.27 (m, 10H), 1.21 (t, $J = 6.7$ Hz, 3H), 1.16–1.13 (m, 3H), 0.89–0.87 (m, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 162.8 (t, $J = 29.1$ Hz), 131.5, 128.1, 127.5, 123.9, 119.0 (t, $J = 255.6$ Hz), 92.3, 81.7, 41.9 (t, $J = 6.3$ Hz), 41.6, 40.1 (t, $J = 22.4$ Hz), 35.7, 31.9, 29.5, 29.3, 29.3, 27.0, 26.0 (t, $J = 3.9$ Hz), 22.7, 14.3, 14.1, 12.3; ^{19}F NMR (565 MHz, CDCl_3) δ -98.2 (d, $J = 278.1$ Hz), -99.9 (d, $J = 278.1$ Hz); IR (KBr) ν : 2924, 2855, 1670, 1489, 1463, 1194, 1070, 755, 691 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{36}\text{F}_2\text{NO}$ ($\text{M}+\text{H}$) $^+$ 392.2759 found 392.2755.



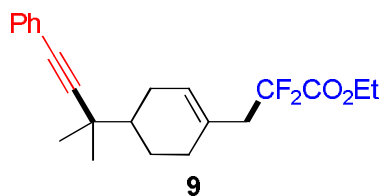
Compound 6f: It was prepared according the general procedure from $\text{C}_4\text{F}_9\text{I}$ (**3g**) using 1.5 equiv of **1a** and 2.0 equiv of **2a** in 64 mg (70% yield, based on **3g**) as a colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.41–7.39 (m, 2H), 7.29–7.28 (m, 3H), 3.06–3.01 (m, 1H), 2.47–2.40 (m, 1H), 2.30–2.21 (m, 1H), 1.68–1.57 (m, 3H), 1.50–1.49 (m, 1H), 1.31–1.26 (m, 10H), 0.88 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 131.6, 128.1, 127.9, 123.5, 117.9, 110.5, 108.9, 90.6, 82.5, 36.1, 35.5, 31.9, 29.7, 29.4, 29.2, 27.0, 25.2, 22.7, 14.0; ^{19}F NMR (565 MHz, CDCl_3) δ -81.0 (t, $J = 9.3$ Hz), -113.5–113.6 (m), -124.5–124.6 (m), -125.9 (t, $J = 11.5$ Hz); IR (KBr) ν : 2927, 2857, 2359, 1599, 1490, 1218, 1132, 755, 722, 690 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{26}\text{F}_5$ ($\text{M}+\text{H}$) $^+$ 461.1885 found 461.1886.



Compound 6g: 36 mg, 59% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.40–7.39 (m, 2H), 7.29–7.28 (m, 3H), 2.94–2.90 (m, 1H), 2.47–2.38 (m, 1H), 2.32–2.24 (m, 1H), 1.64–1.55 (m, 3H), 1.49–1.45 (m, 1H), 1.35–1.27 (m, 10H), 0.88 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 131.6, 128.2, 127.9, 126.3 (q, $J = 277.6$ Hz), 123.4, 90.2, 82.5, 39.2 (q, $J = 27.4$ Hz), 34.8, 31.8, 29.4, 29.2, 29.2, 26.9, 26.5 (q, $J = 3.0$ Hz), 22.7, 14.0; ^{19}F NMR (565 MHz, CDCl_3) δ -64.1; IR (KBr) ν : 2927, 2228, 1598, 1218, 1140, 757, 690 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{26}\text{F}_3(\text{M}+\text{H})^+$ 311.1981 found 311.1980.

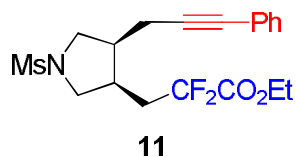


Compound 7:⁹ 31 mg, 55% yield, colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 4.36 (q, $J = 7.1$ Hz, 2H), 1.62–1.55 (m, 6H), 1.37 (t, $J = 7.2$ Hz, 3H), 1.20–1.17 (m, 12H); ^{19}F NMR (565 MHz, CDCl_3) δ -74.4; HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{24}\text{F}_2\text{NO}_3(\text{M}+\text{H})^+$ 280.1719 found 280.1722.

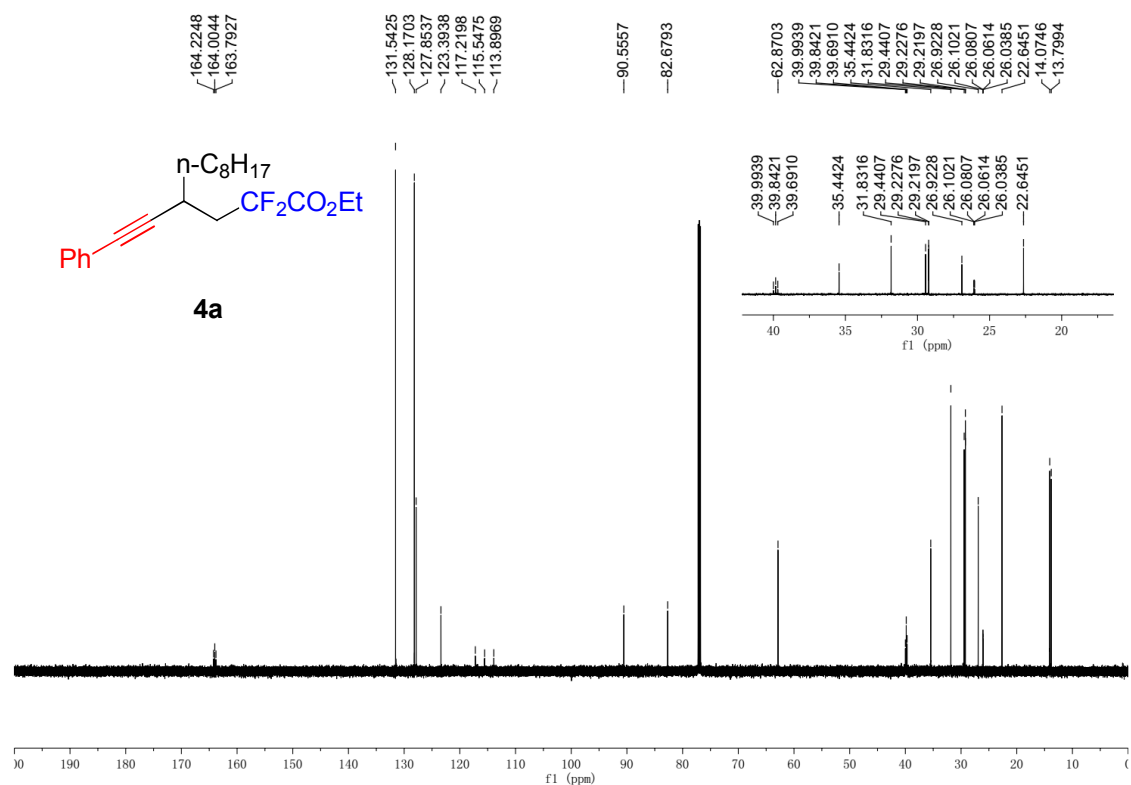
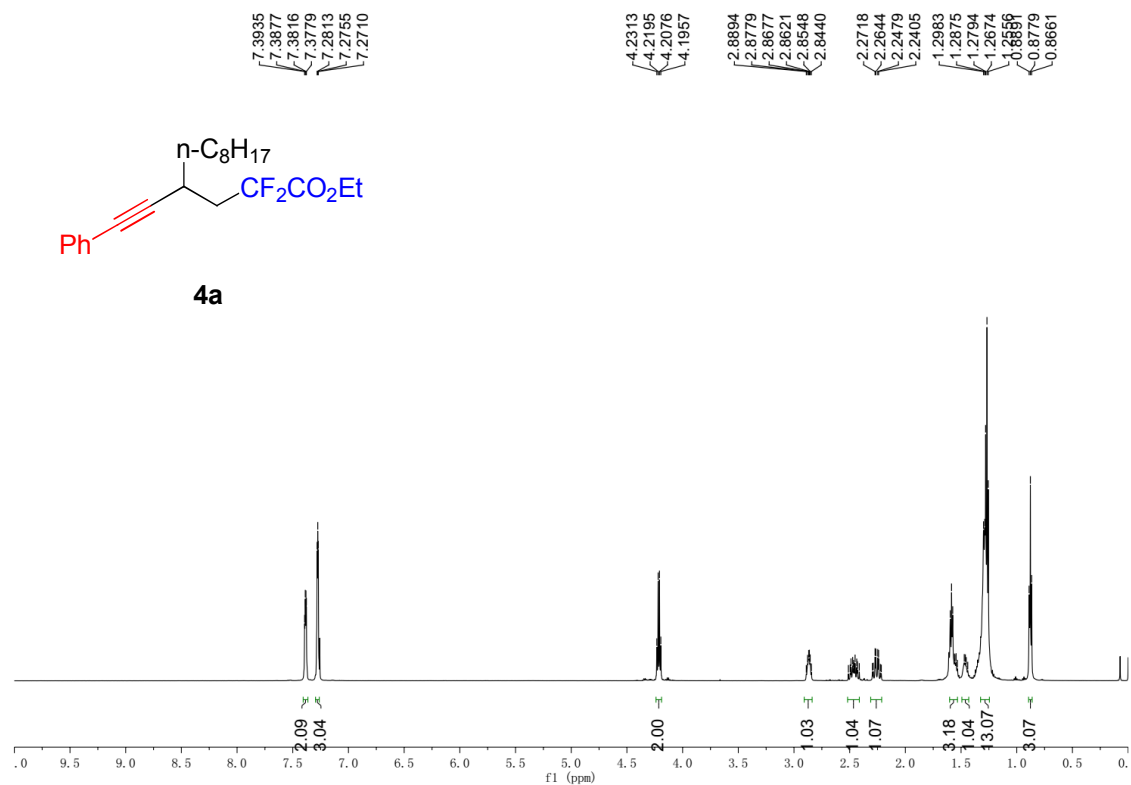


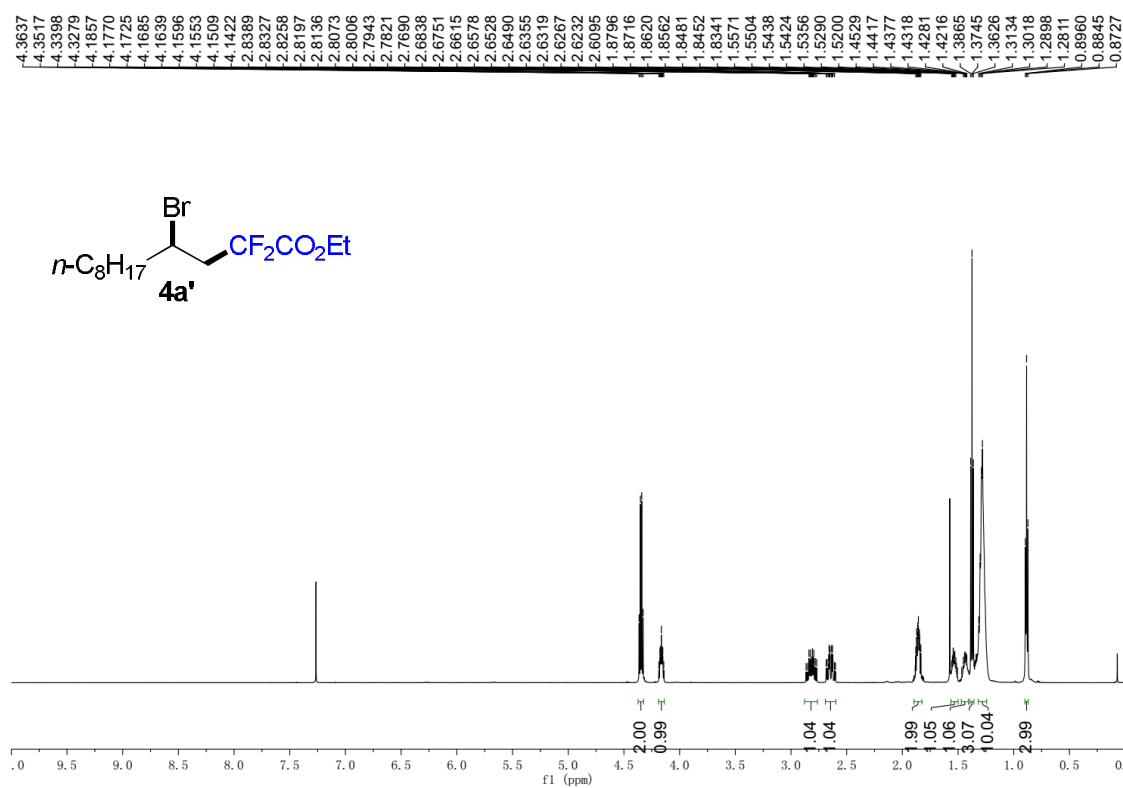
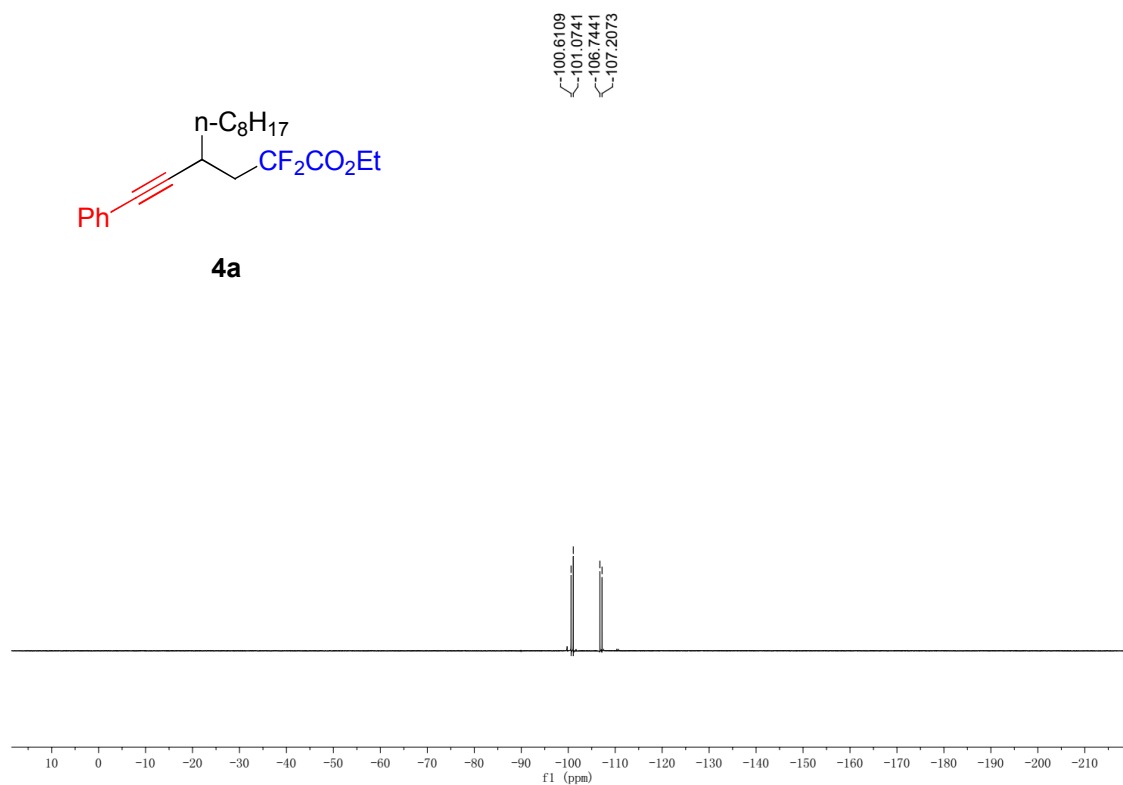
Compound 9: 37 mg, 52% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.38–7.36 (m, 2H), 7.28–7.25 (m, 3H), 5.63 (d, $J = 2.2$ Hz, 1H), 4.30 (q, $J = 7.1$ Hz, 2H), 2.77–2.70 (m, 2H), 2.23–2.09 (m, 3H), 2.03–1.99 (m, 2H), 1.49–1.39 (m, 2H), 1.33 (t, $J = 7.1$ Hz, 3H), 1.29 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 164.2 (t, $J = 32.8$ Hz), 131.6, 128.5, 128.3 (t, $J = 3.9$ Hz), 128.1, 127.4, 124.0, 116.1 (t, $J = 252.5$ Hz), 96.1, 81.1, 62.6, 43.3, 42.6 (t, $J = 23.1$ Hz), 34.6, 30.0, 27.8, 27.2, 27.0, 24.7, 14.0; ^{19}F NMR (565 MHz, CDCl_3) δ -102.8 (d, $J = 253.7$ Hz), -103.6 (d, $J = 253.7$ Hz); IR (KBr) ν : 2924, 1762, 1598, 1219, 1183, 1059, 755, 691 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{26}\text{F}_2\text{NaO}_2(\text{M}+\text{Na})^+$ 383.1793 found 383.1795.

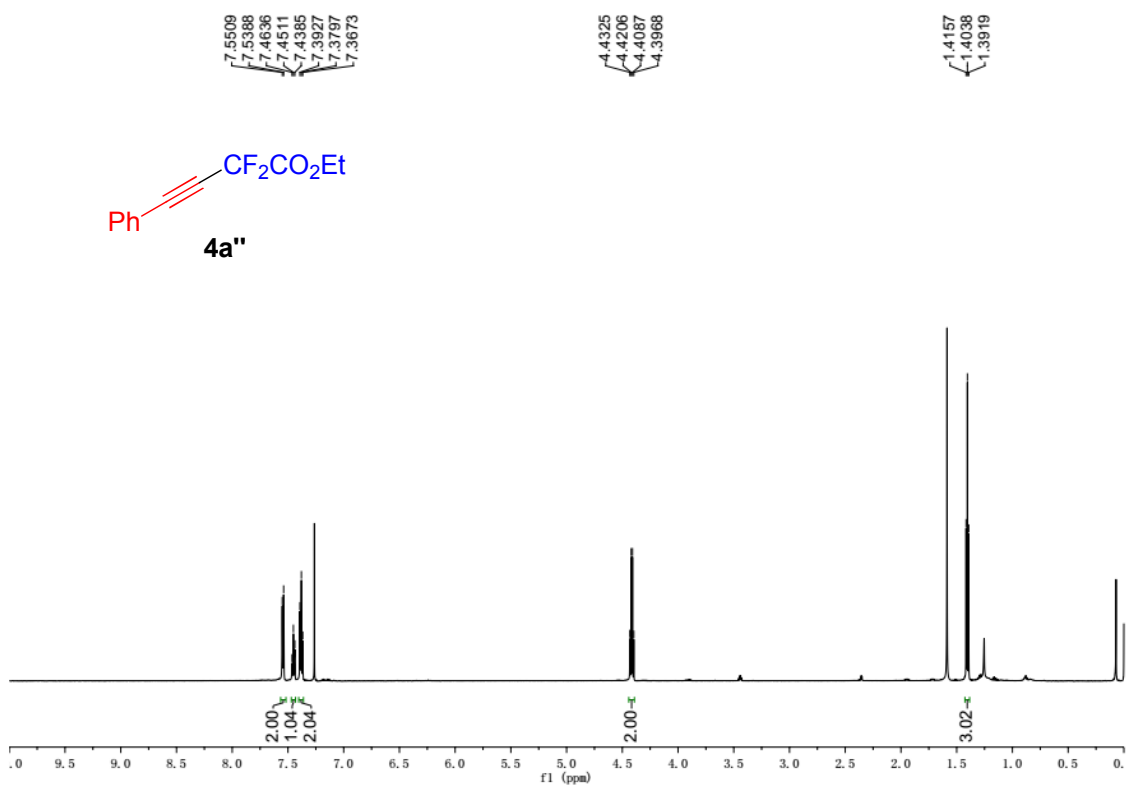
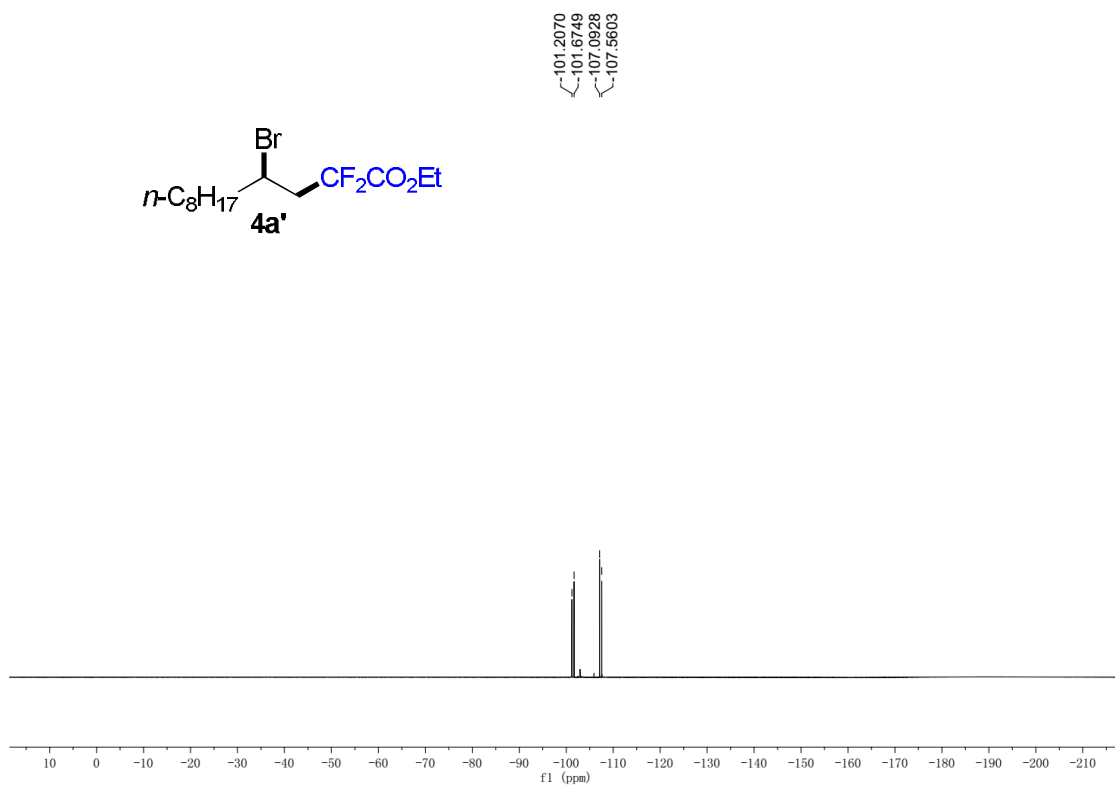
⁹ G. Ma, W. Wan, J. Li, Q. Hu, H. Jiang, S. Zhu, J. Wang and J. Hao, *Chem. Commun.*, 2014, **50**, 9749.

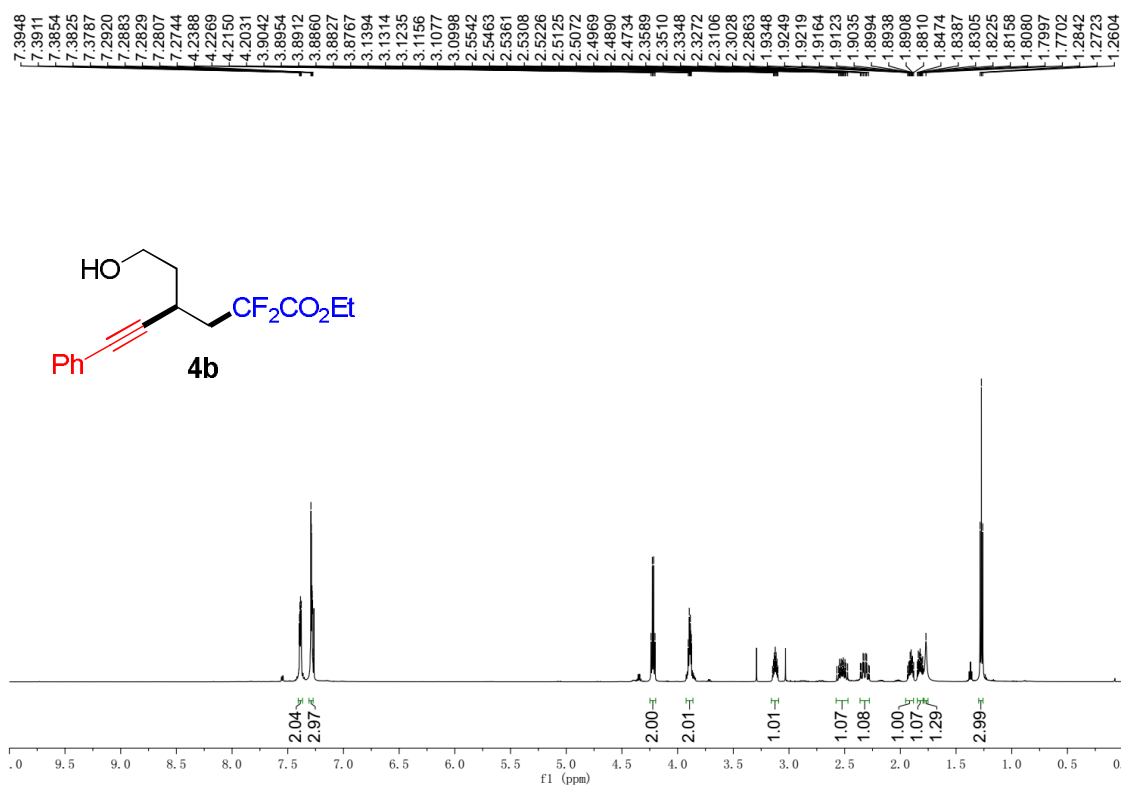
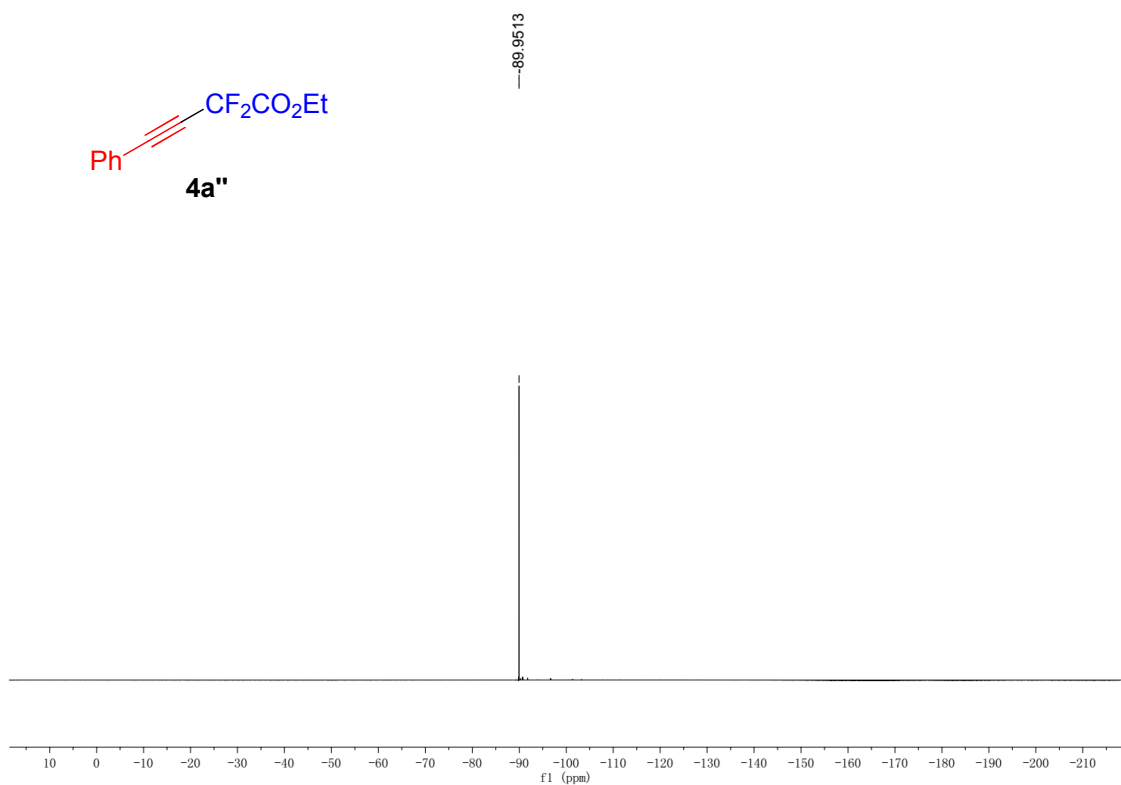


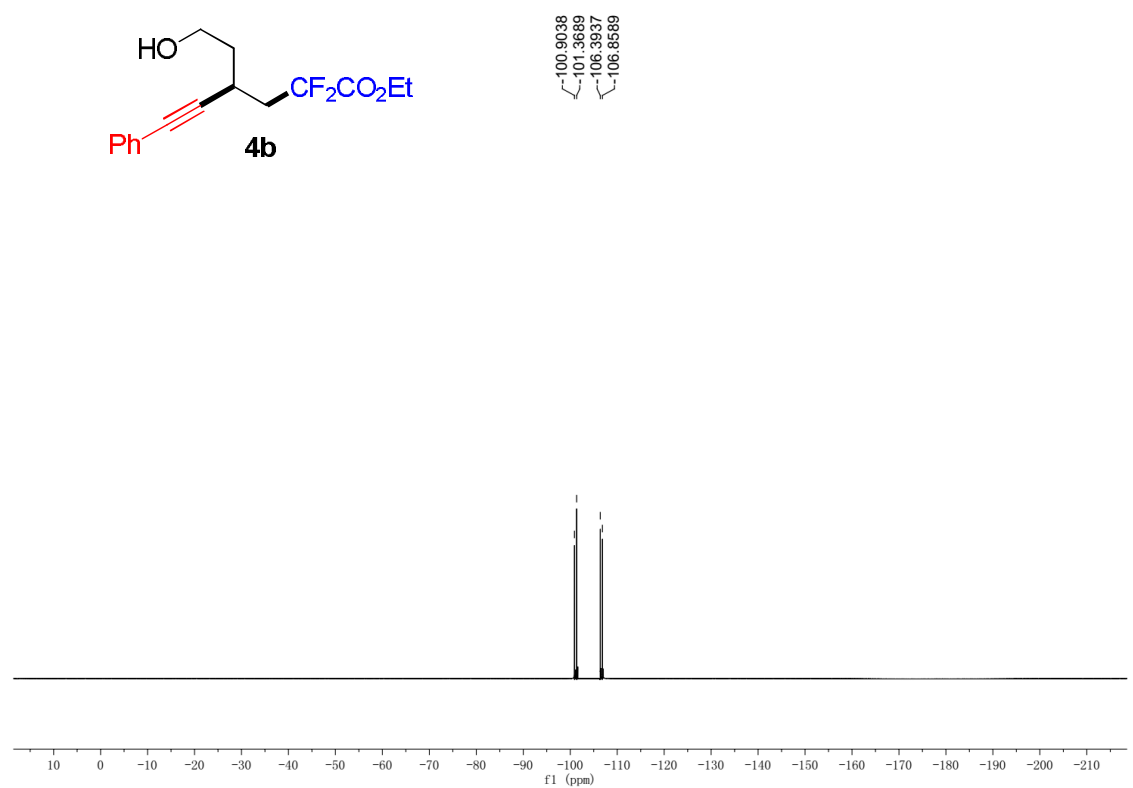
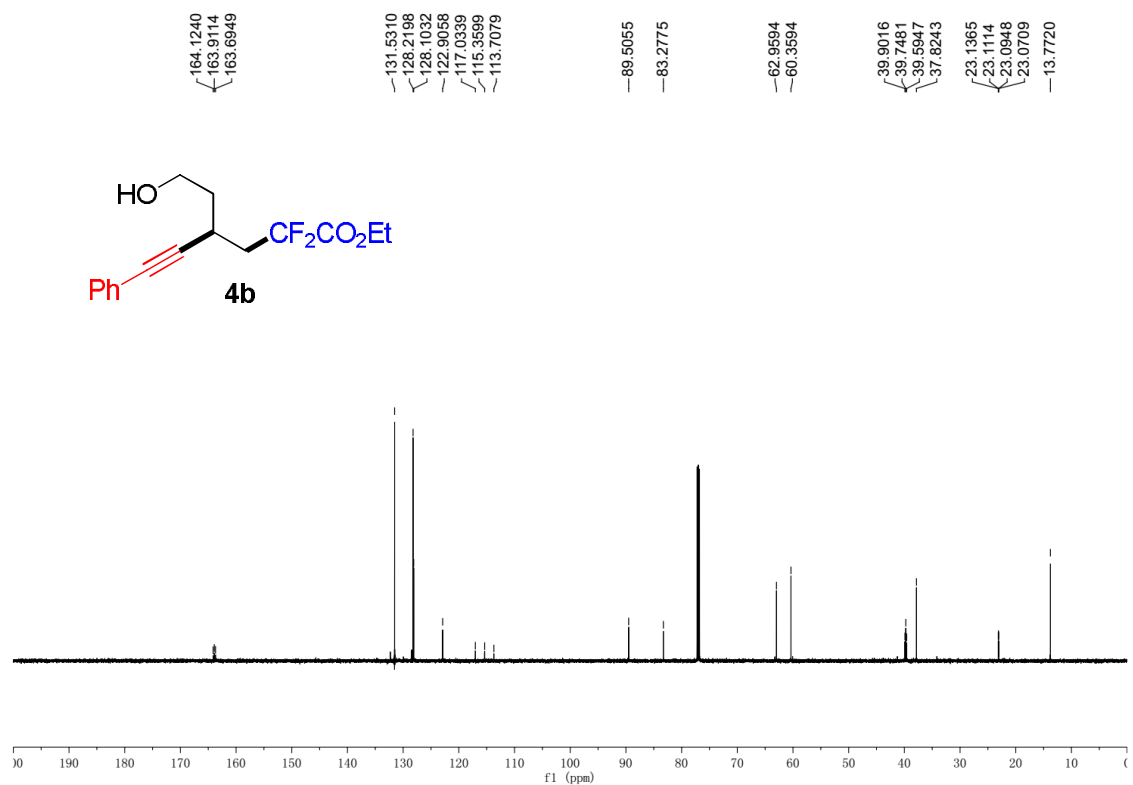
Compound 11: 36 mg, 45% yield, colorless oil; dr > 20:1; ^1H NMR (600 MHz, CDCl_3) δ 7.39–7.37 (m, 2H), 7.31–7.29 (m, 3H), 4.34 (q, $J = 7.1$ Hz, 2H), 3.64–3.61 (m, 1H), 3.55–3.54 (m, 2H), 3.26 (t, $J = 9.6$ Hz, 1H), 2.86 (s, 3H), 2.72–2.69 (m, 1H), 2.66–2.62 (m, 1H), 2.58–2.54 (m, 1H), 2.46–2.37 (m, 2H), 2.25–2.17 (m, 1H), 1.36 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 163.7 (t, $J = 32.6$ Hz), 131.5, 128.3, 128.1, 122.9, 115.5 (t, $J = 251.8$ Hz), 86.4, 82.6, 63.3, 51.8, 51.0, 40.7, 35.3, 35.3 (t, $J = 2.8$ Hz), 32.6 (t, $J = 23.4$ Hz), 18.9, 13.9; ^{19}F NMR (565 MHz, CDCl_3) δ -104.5 (d, $J = 262.5$ Hz), -106.0 (d, $J = 262.6$ Hz); IR (KBr) ν : 2933, 2860, 1760, 1597, 1490, 1328, 757, 693 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{23}\text{F}_2\text{NO}_4\text{SNa}$ ($\text{M}+\text{Na}$) $^+$ 422.1208 found 422.1208.

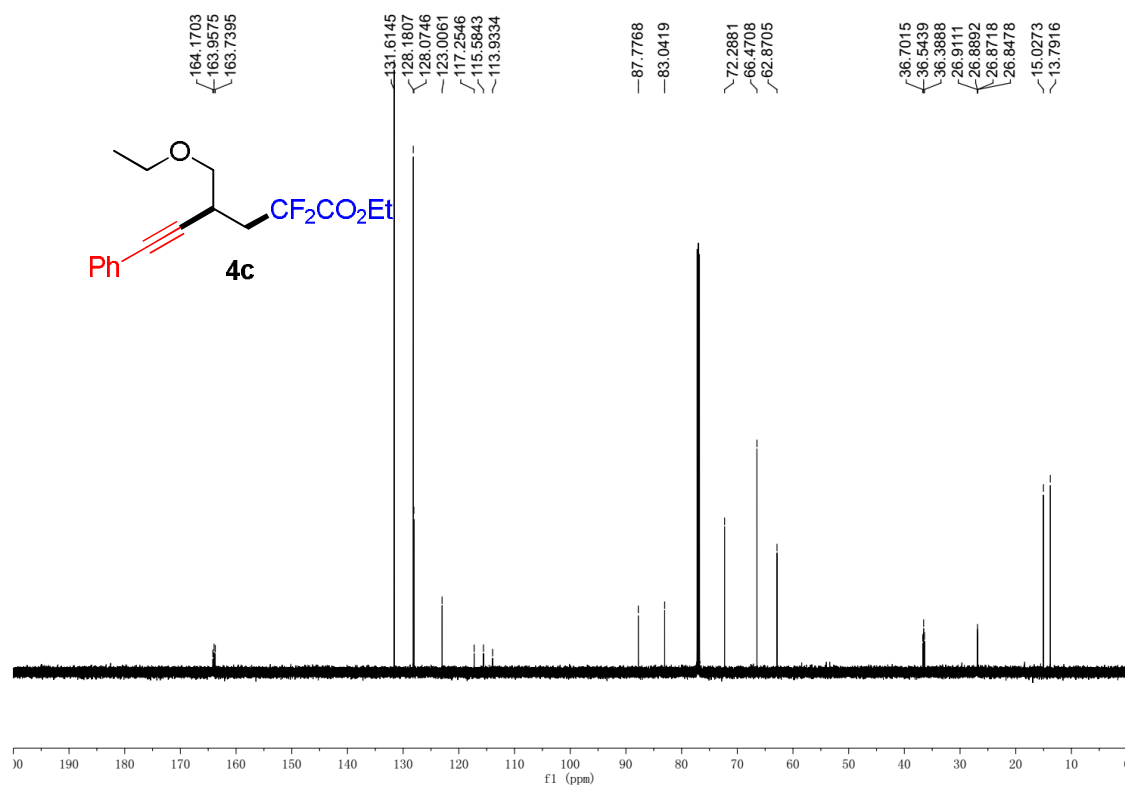
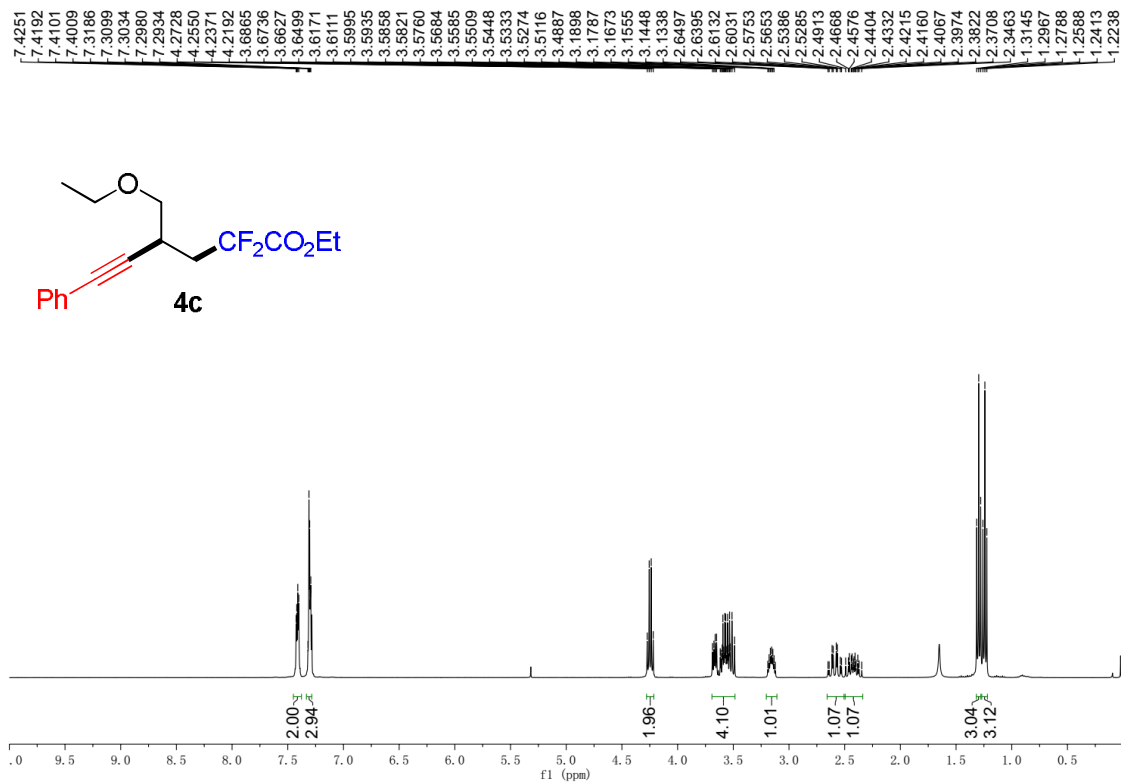


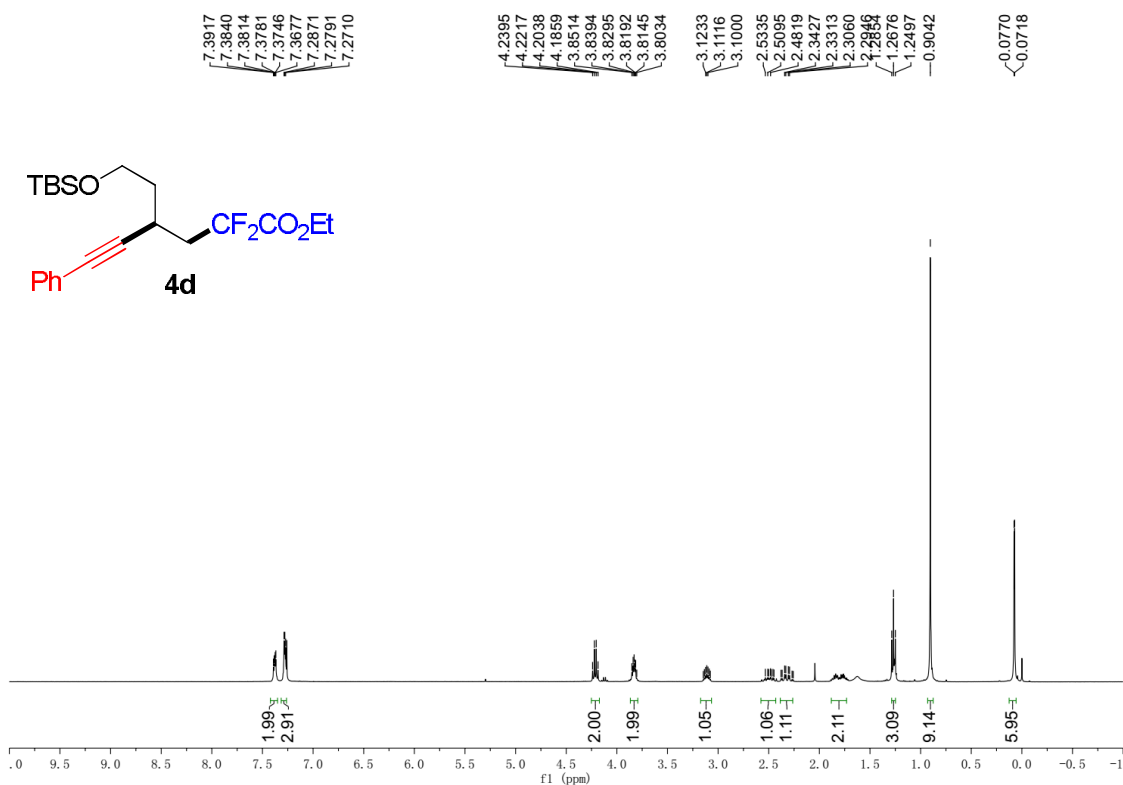
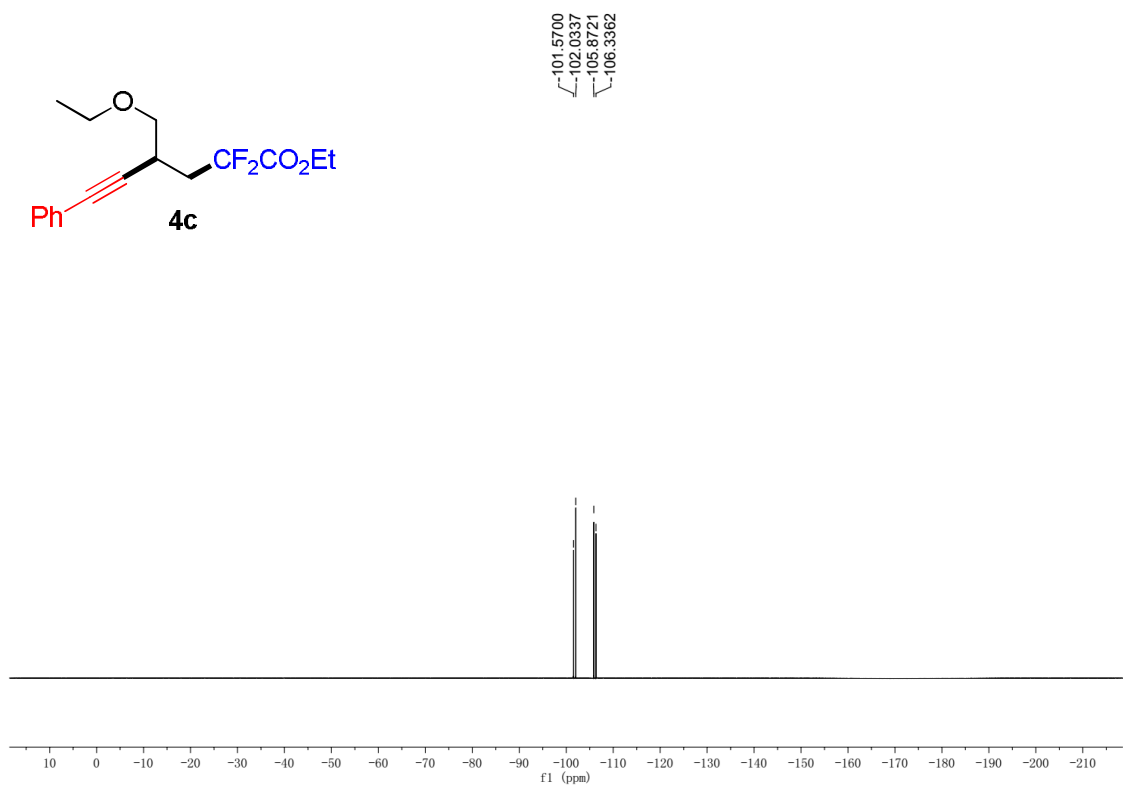


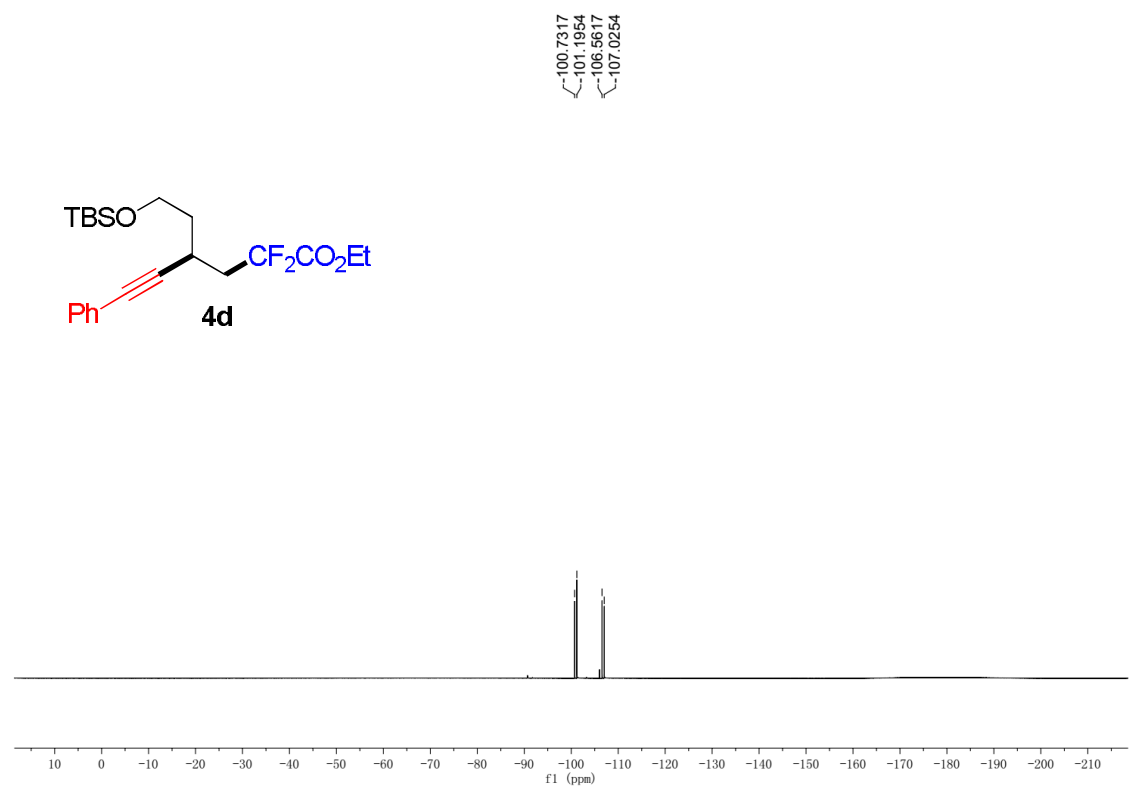
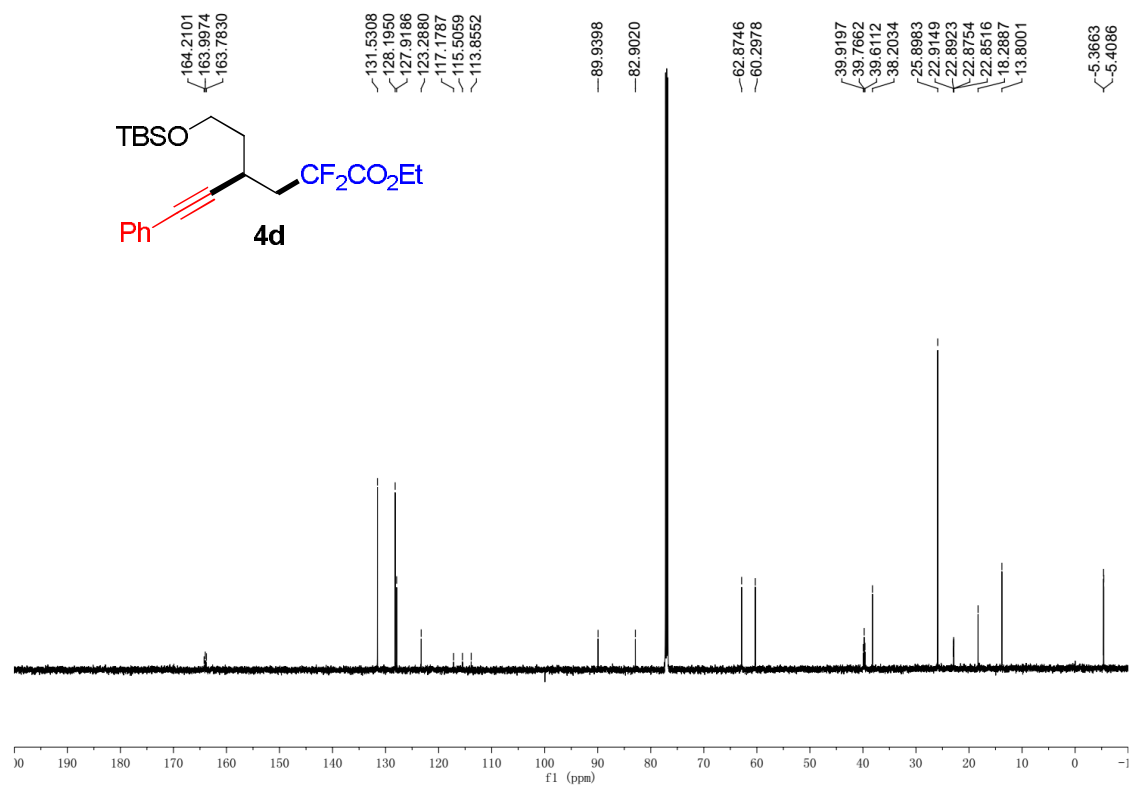


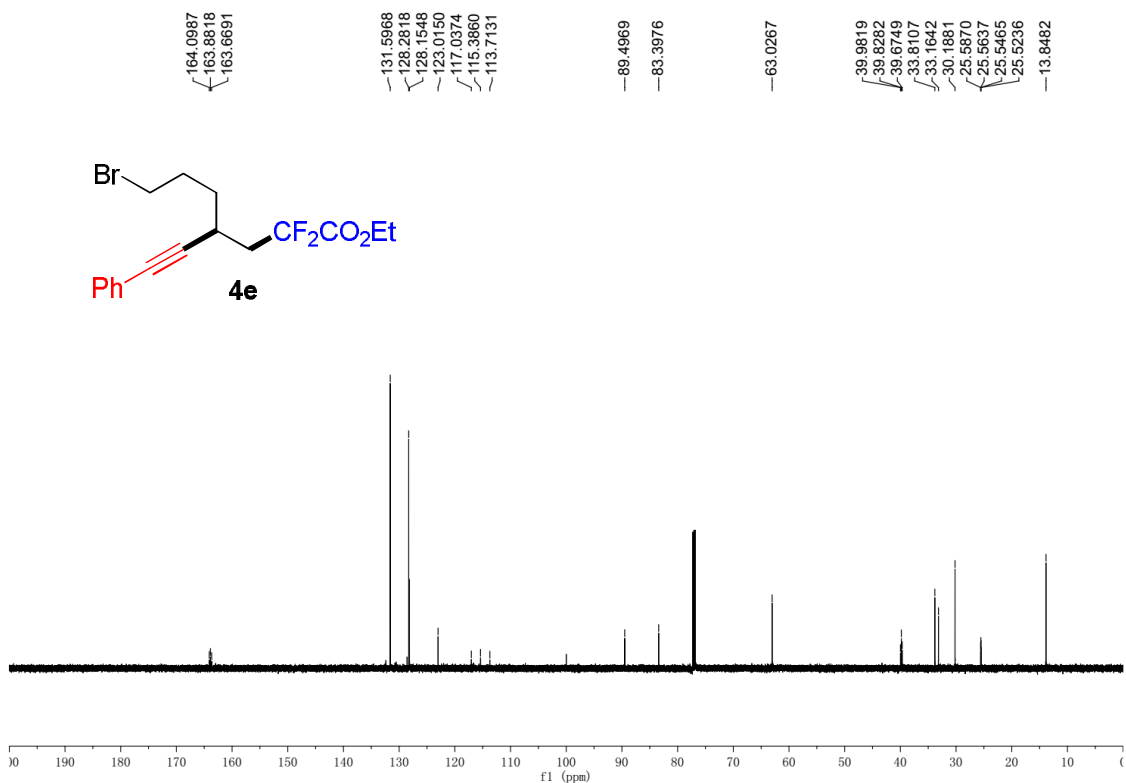
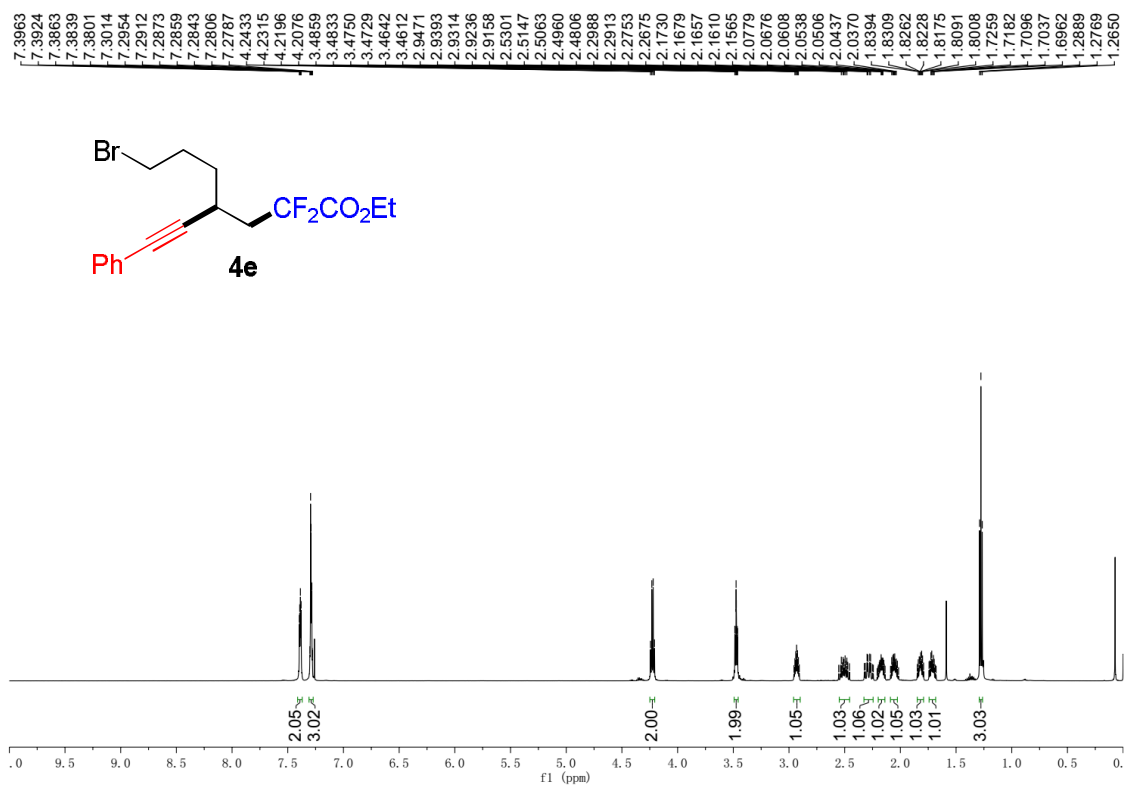


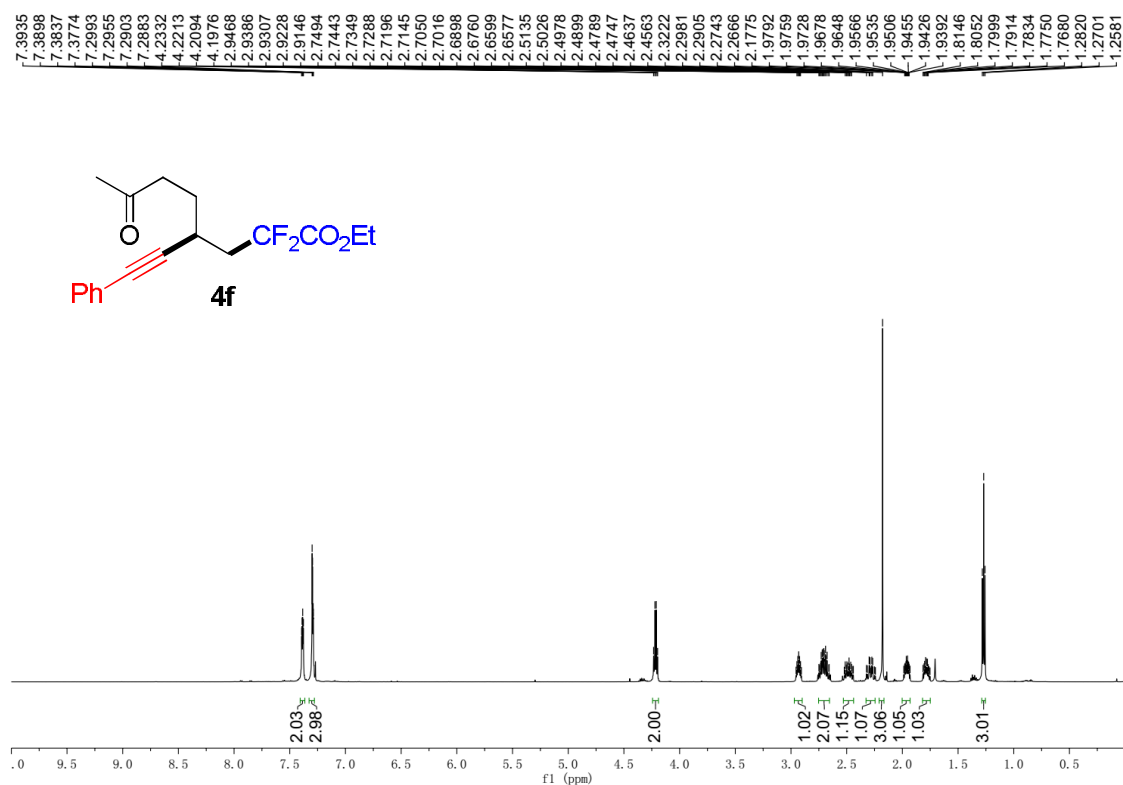
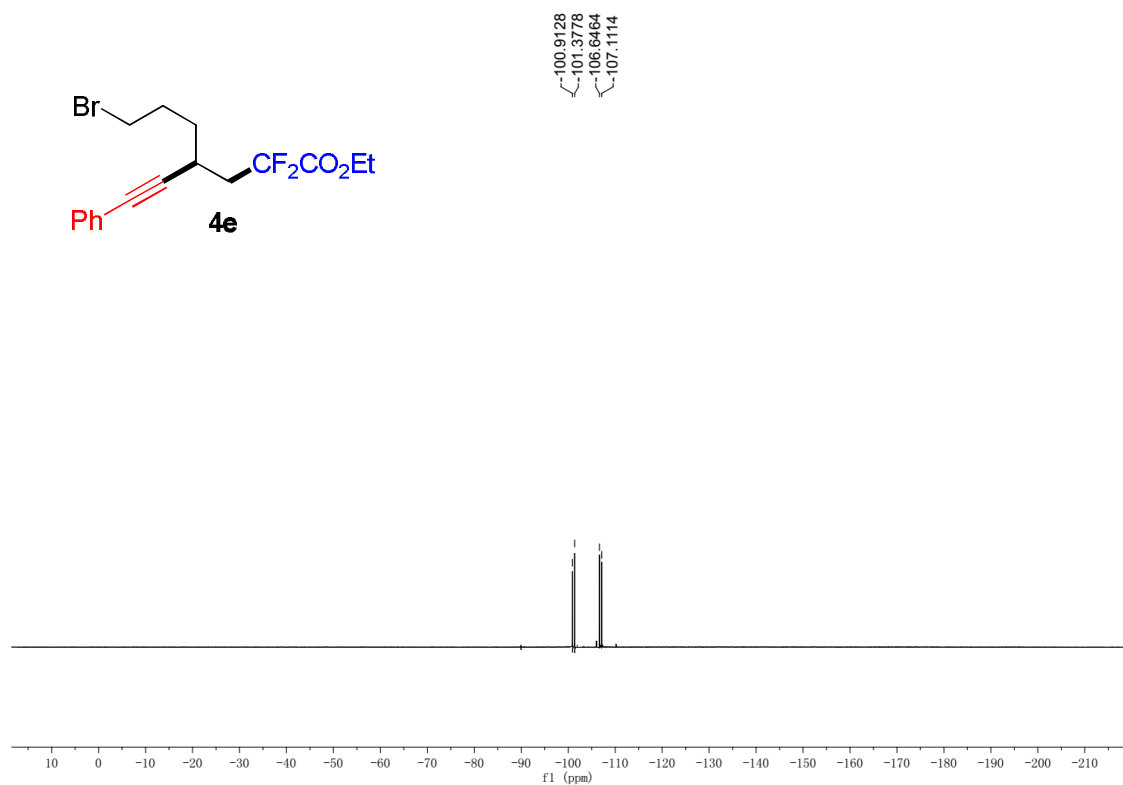


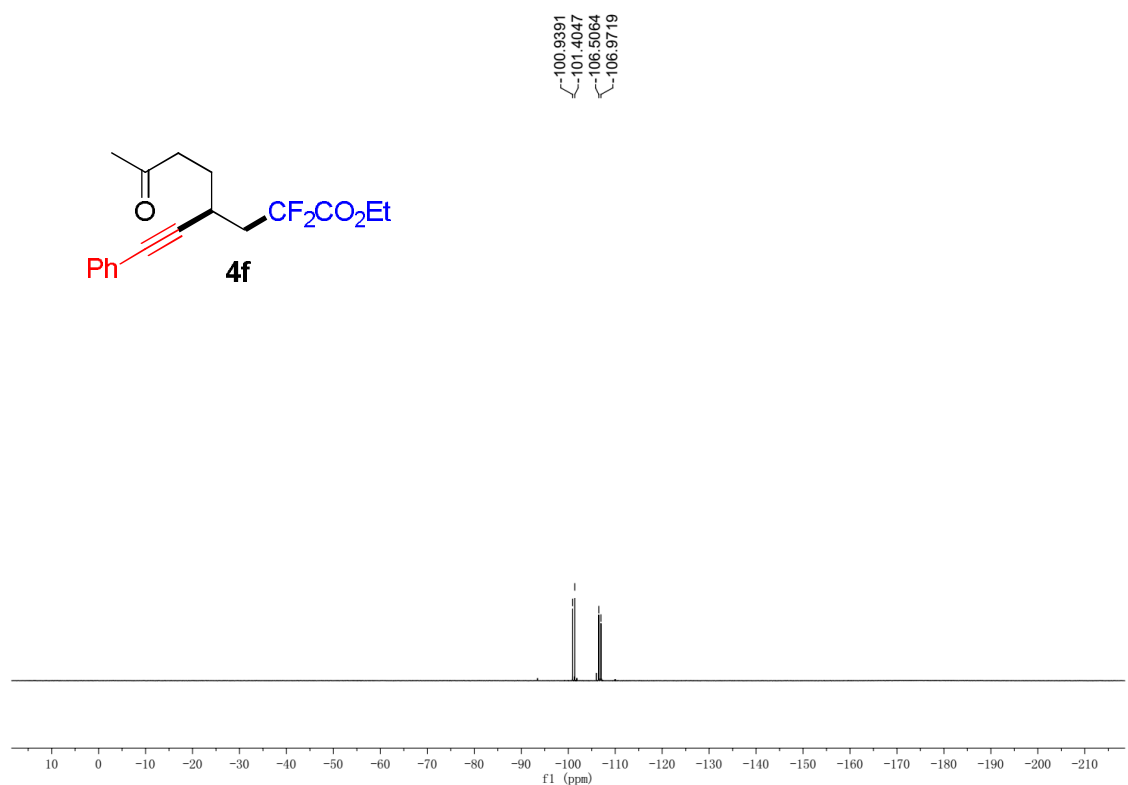
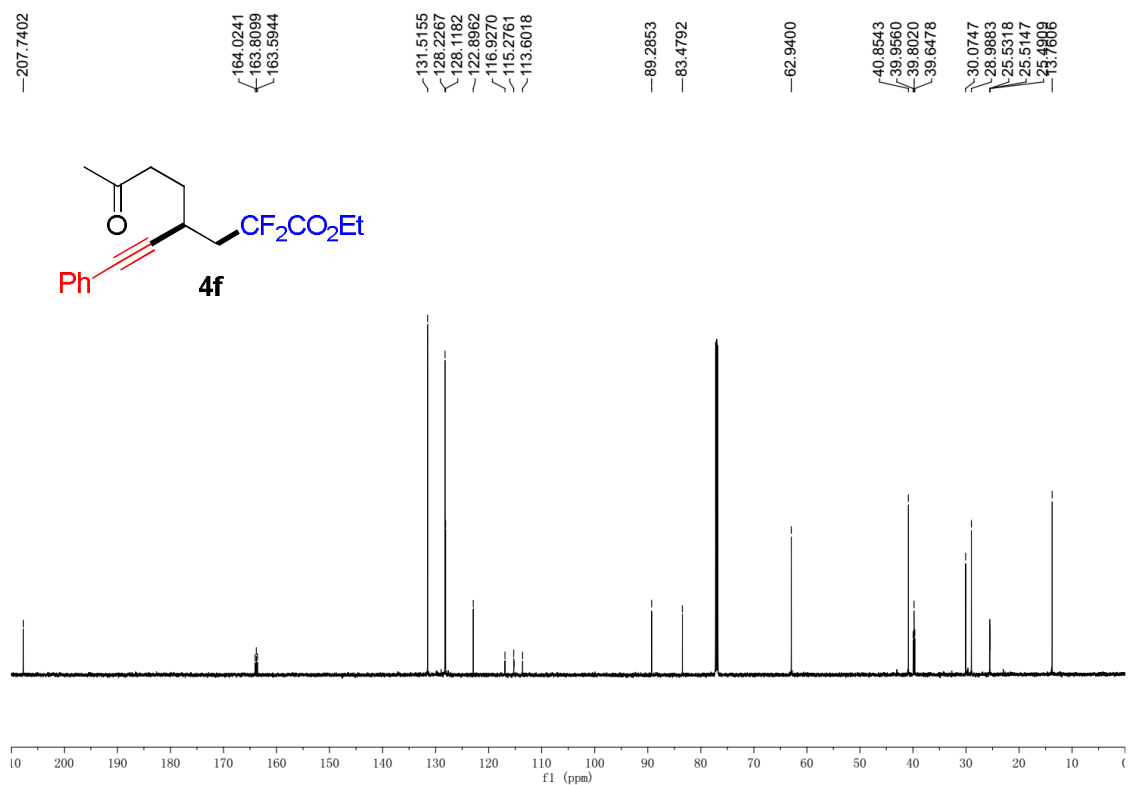


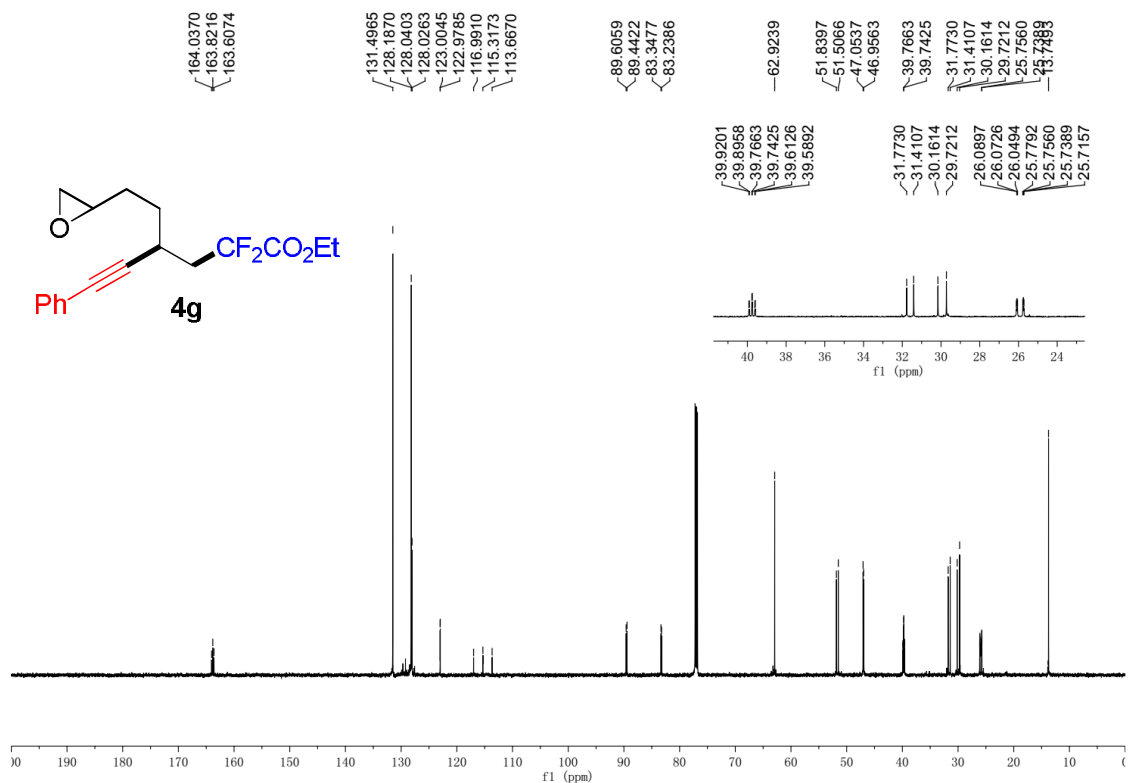
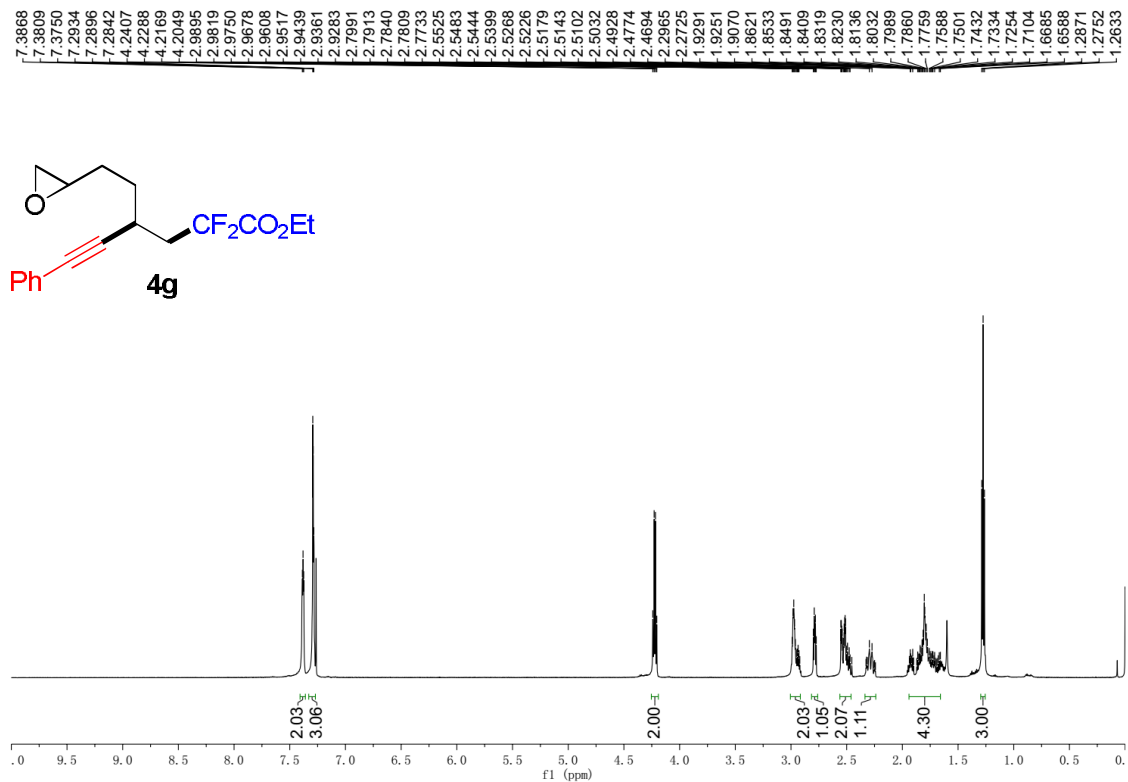


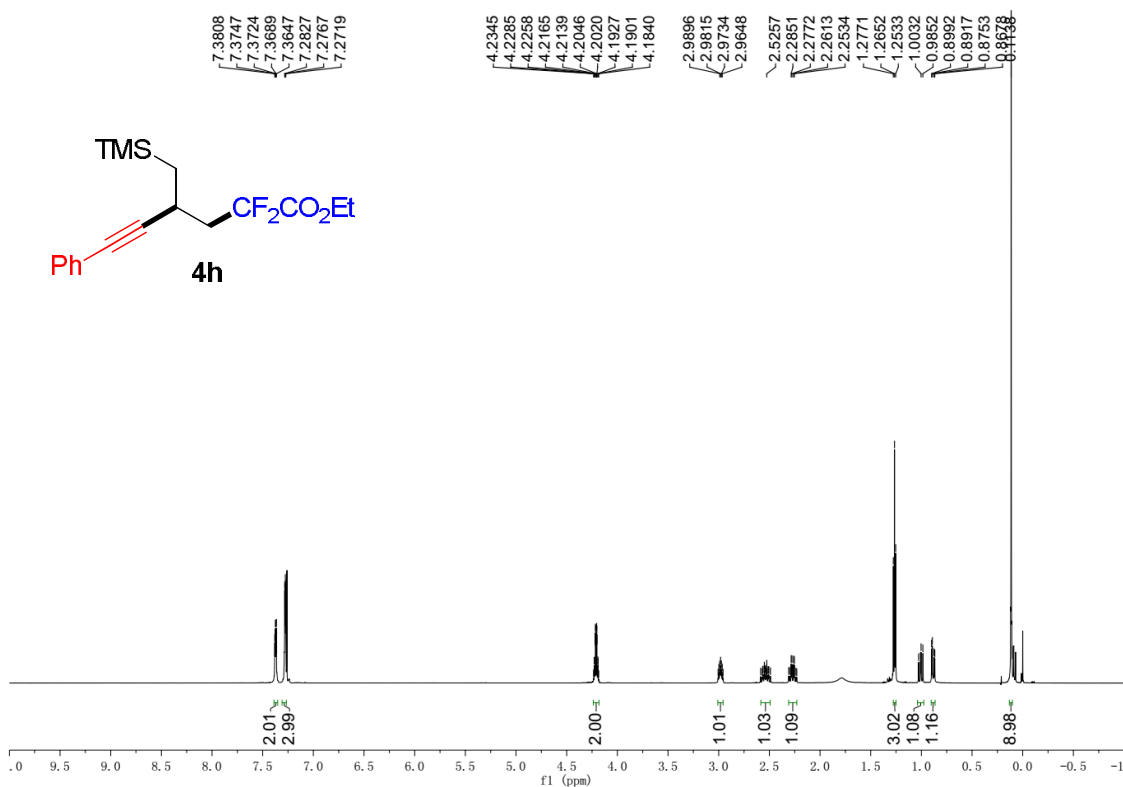
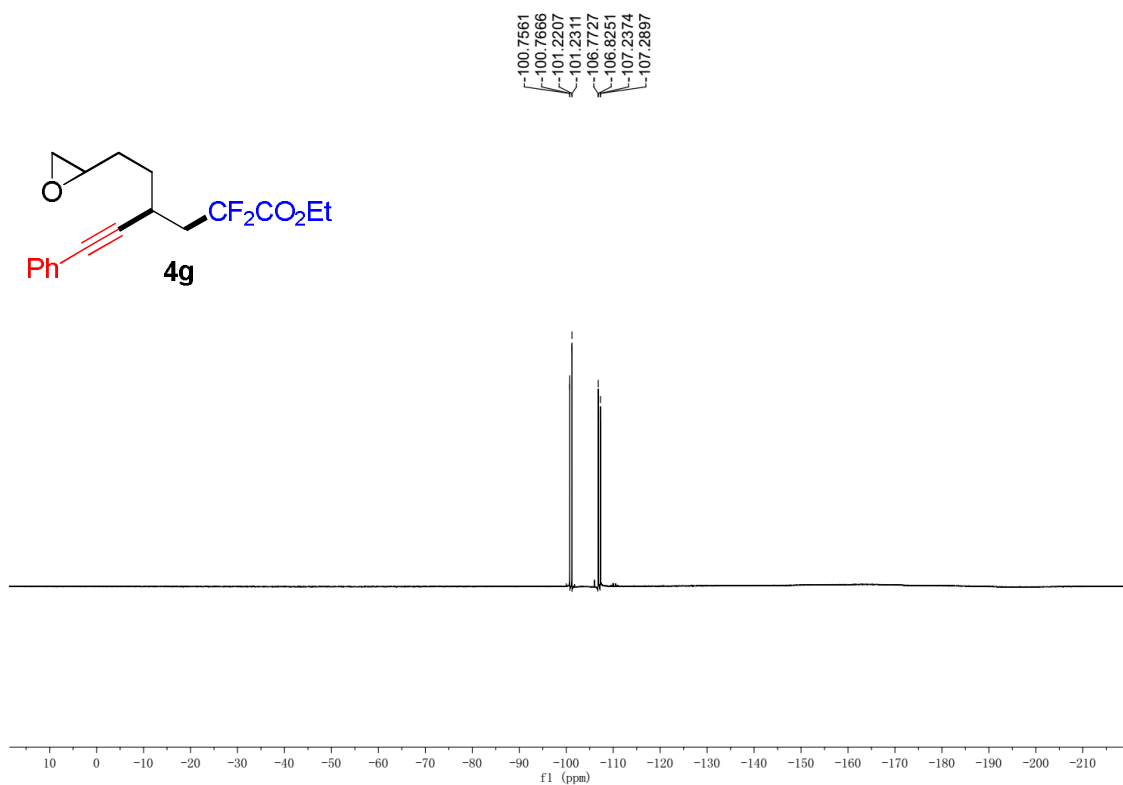


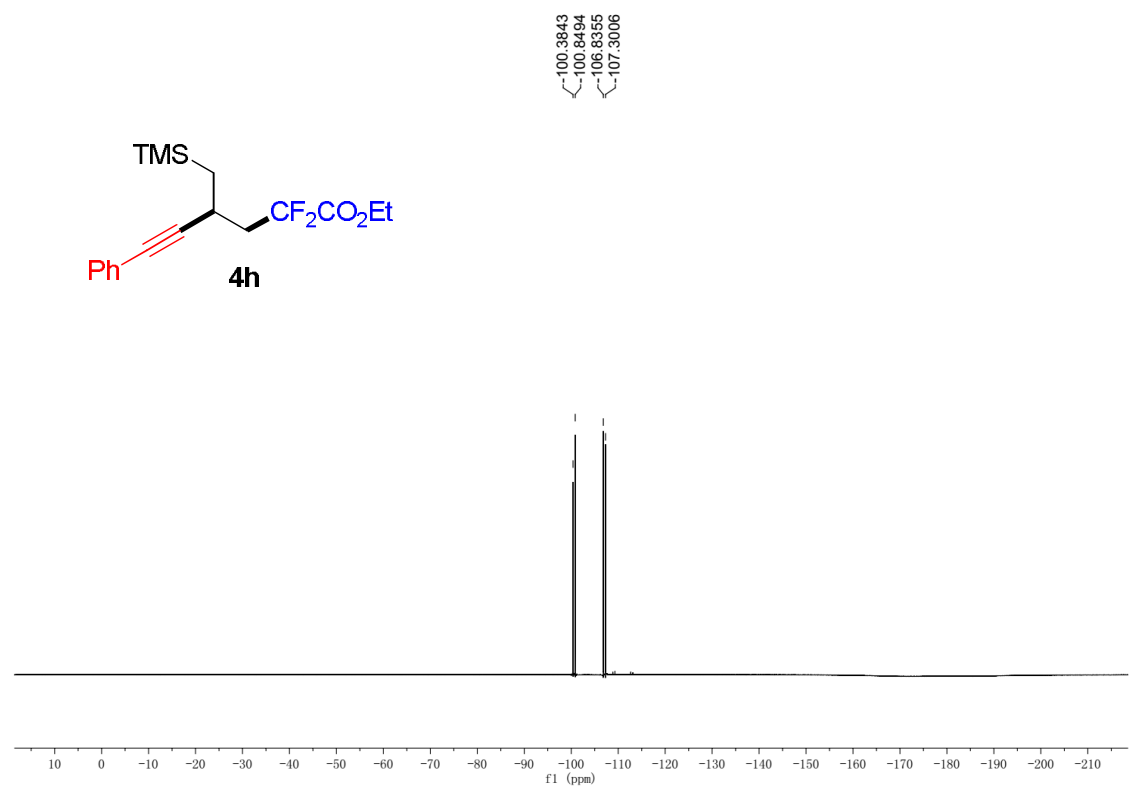
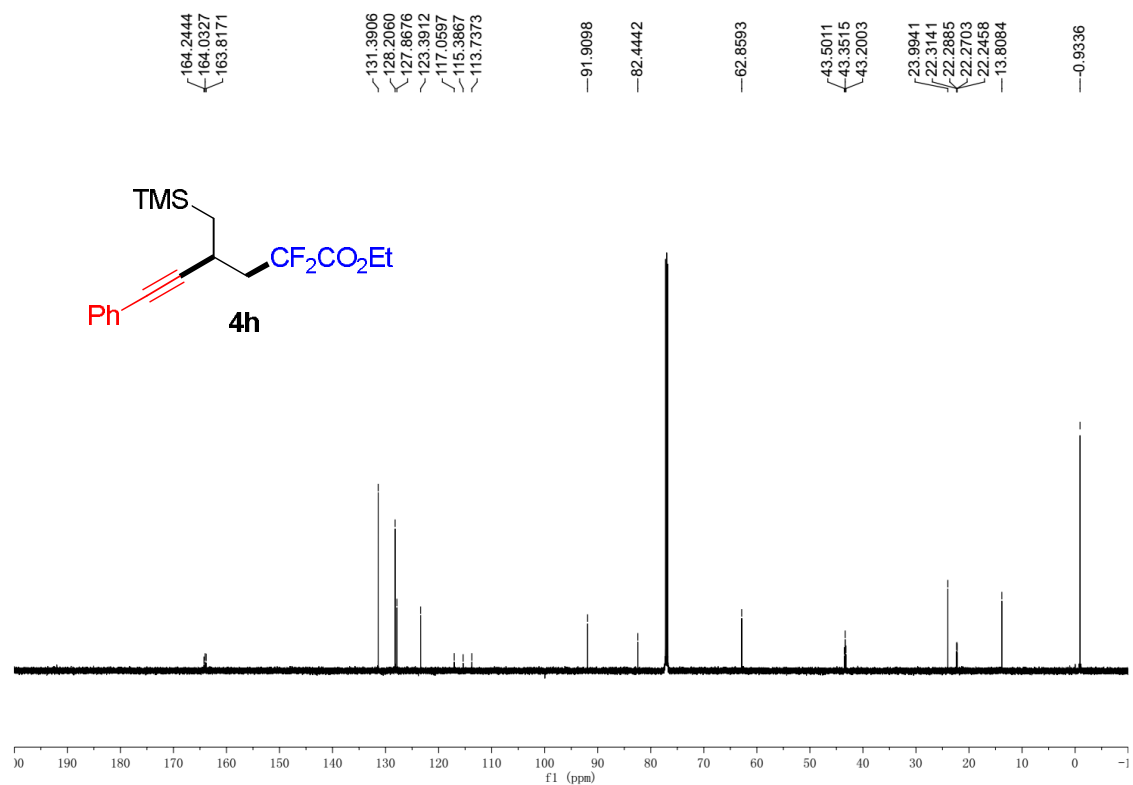


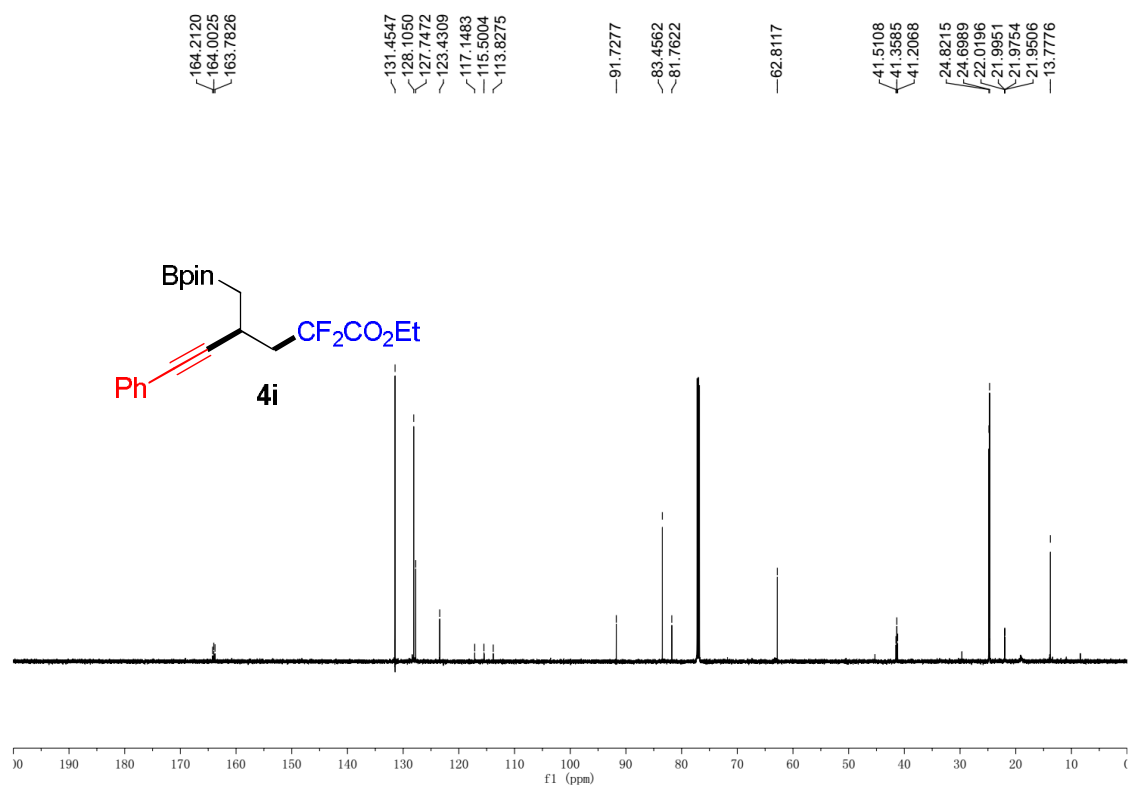
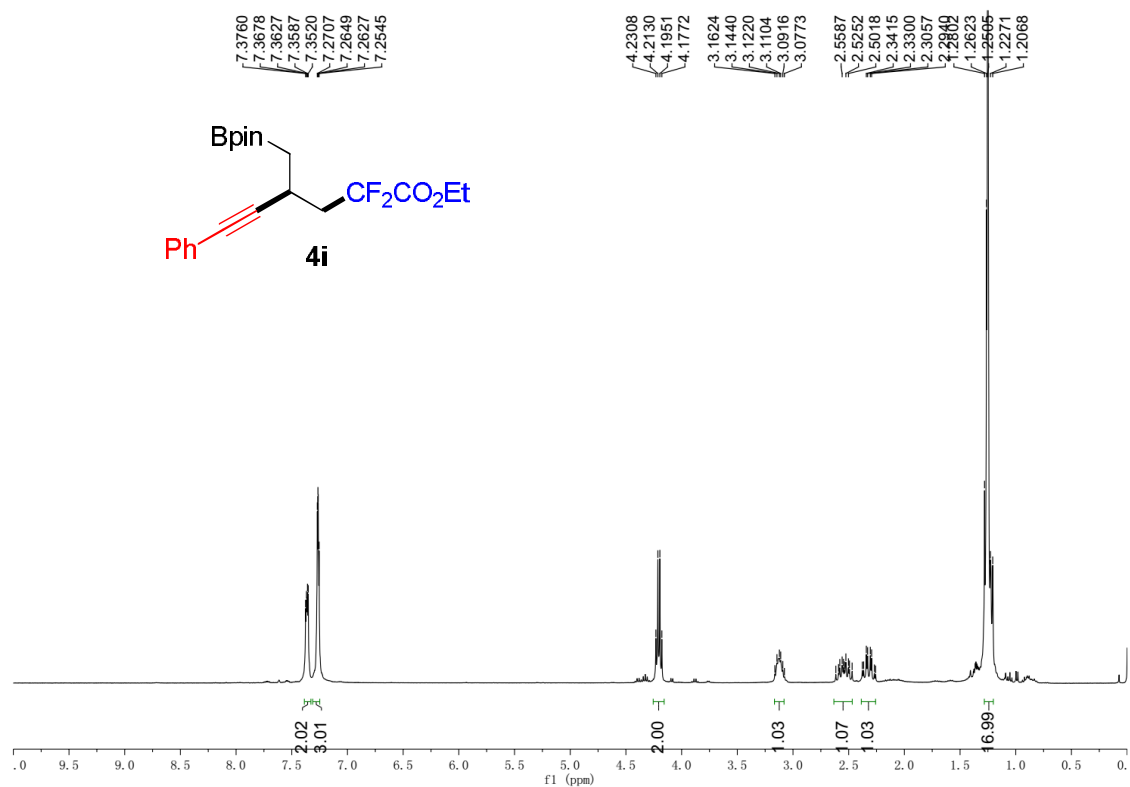


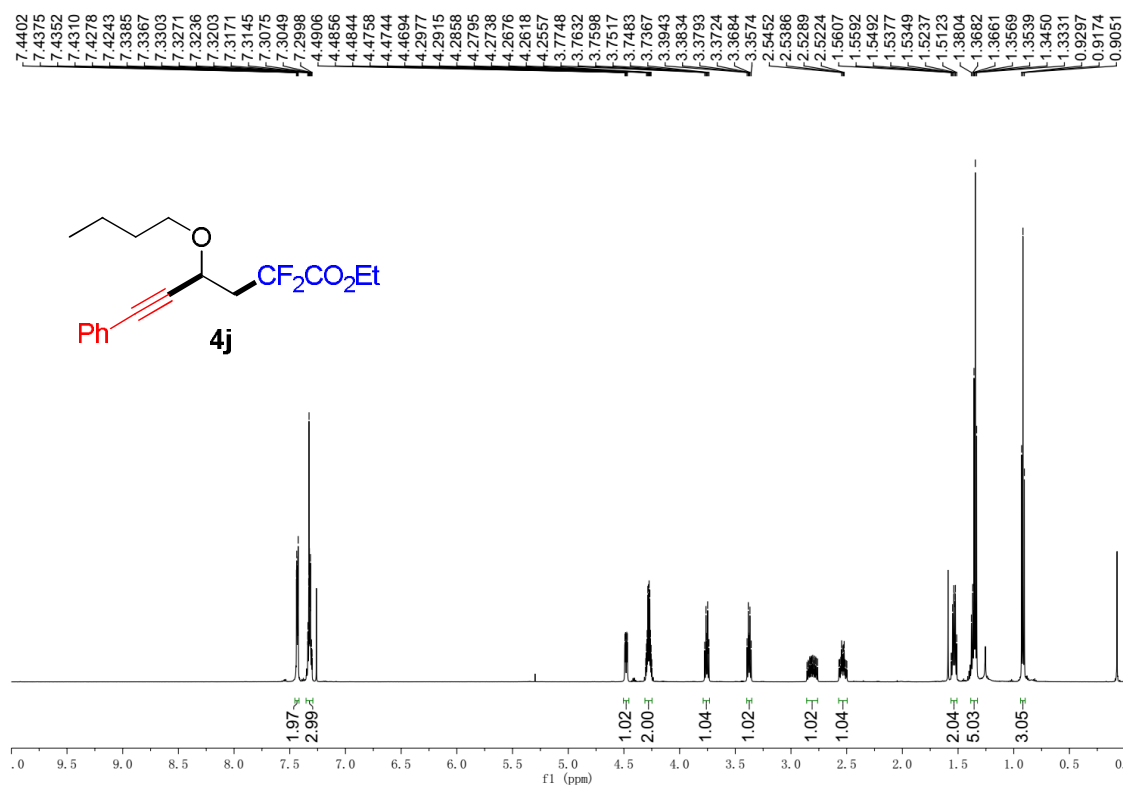
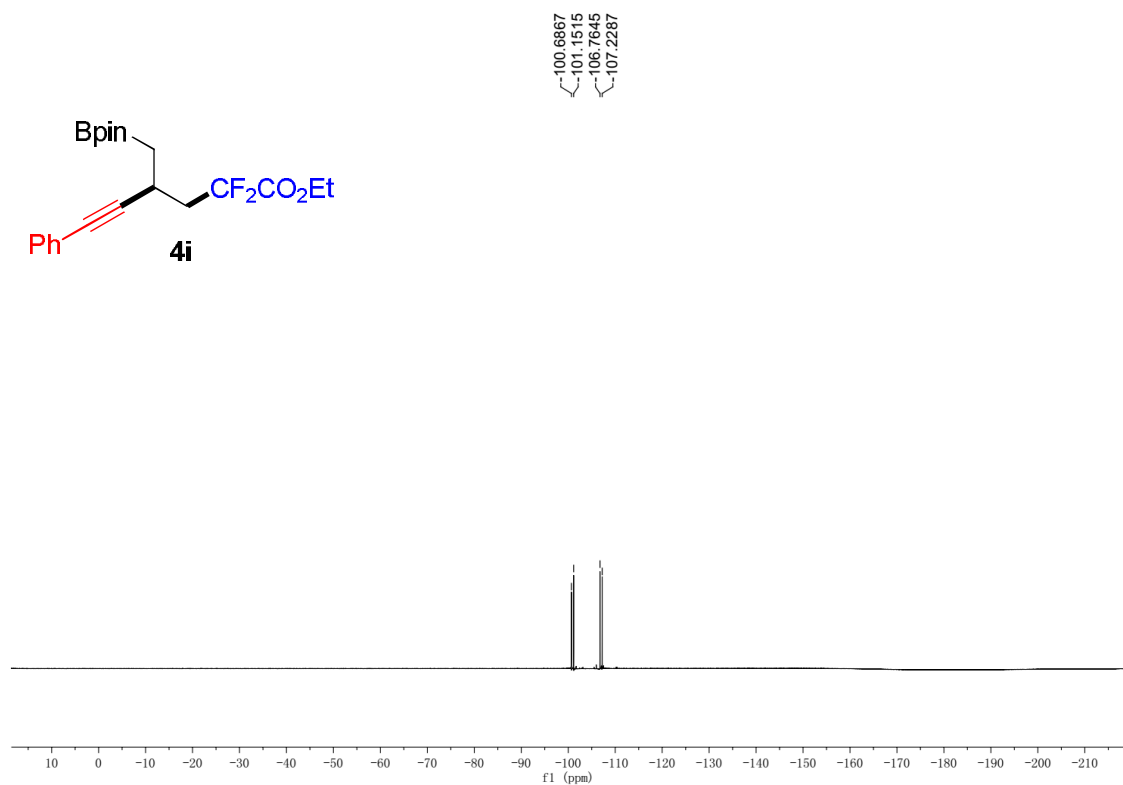


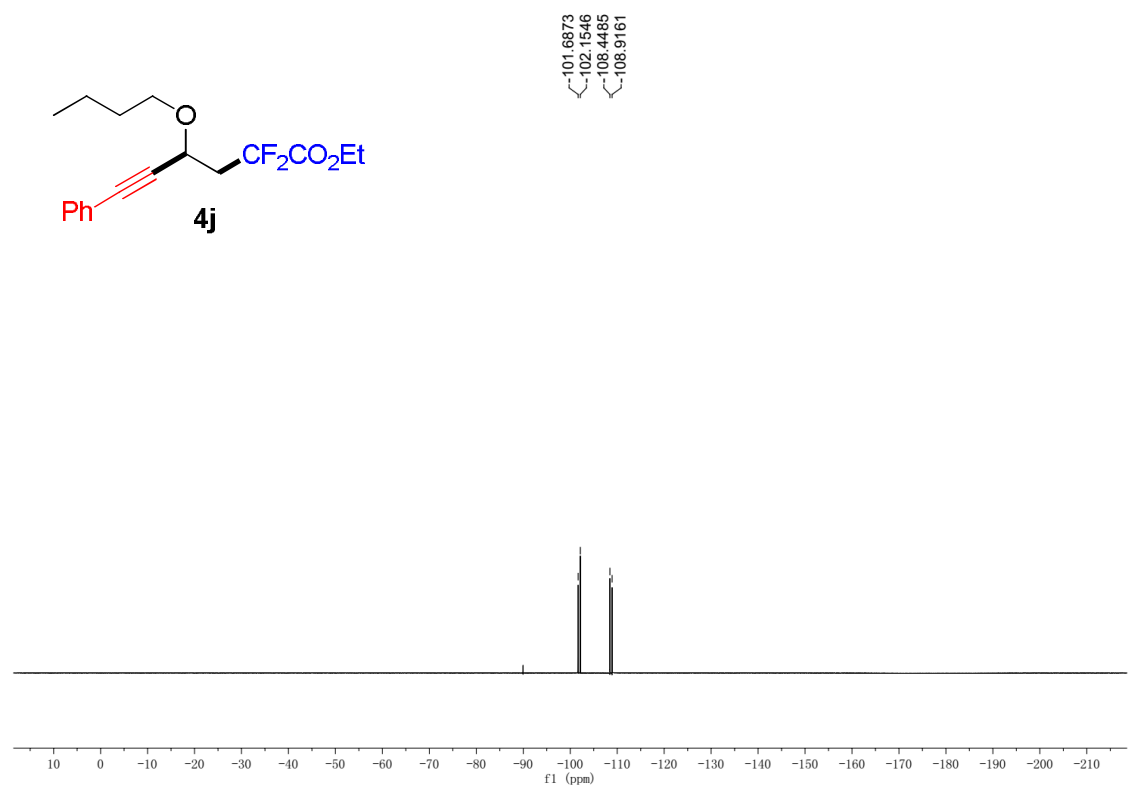
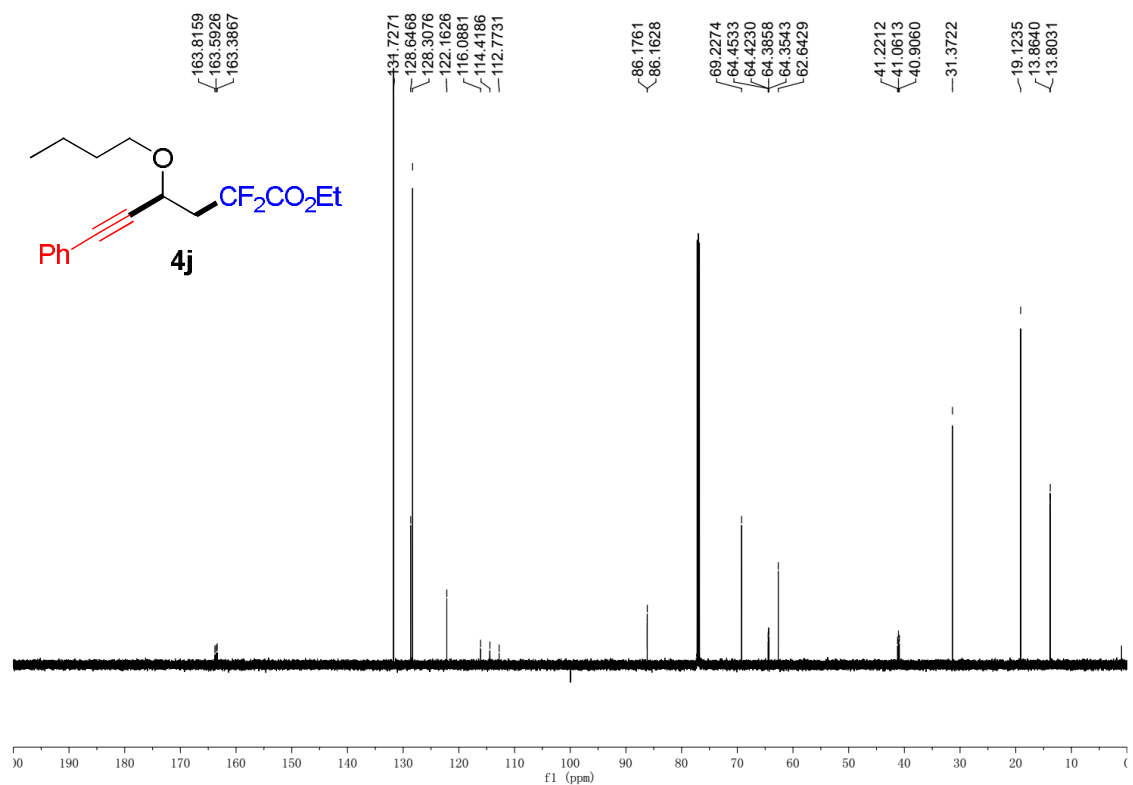


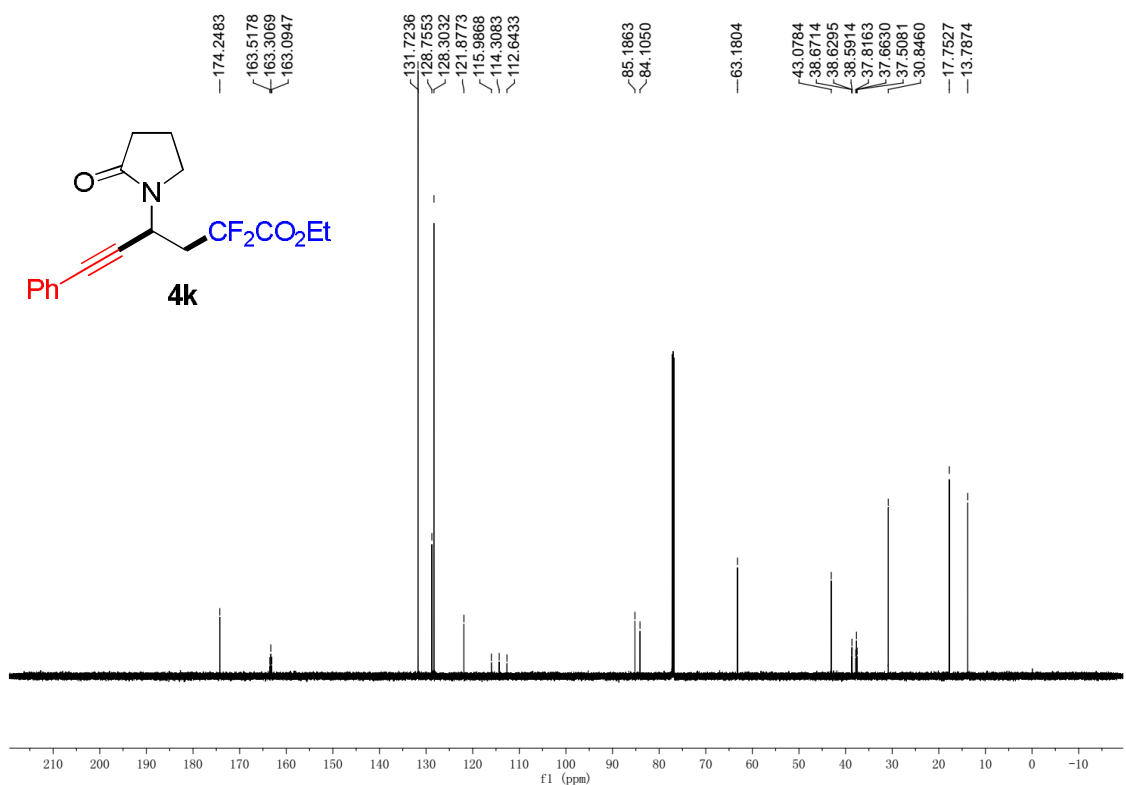
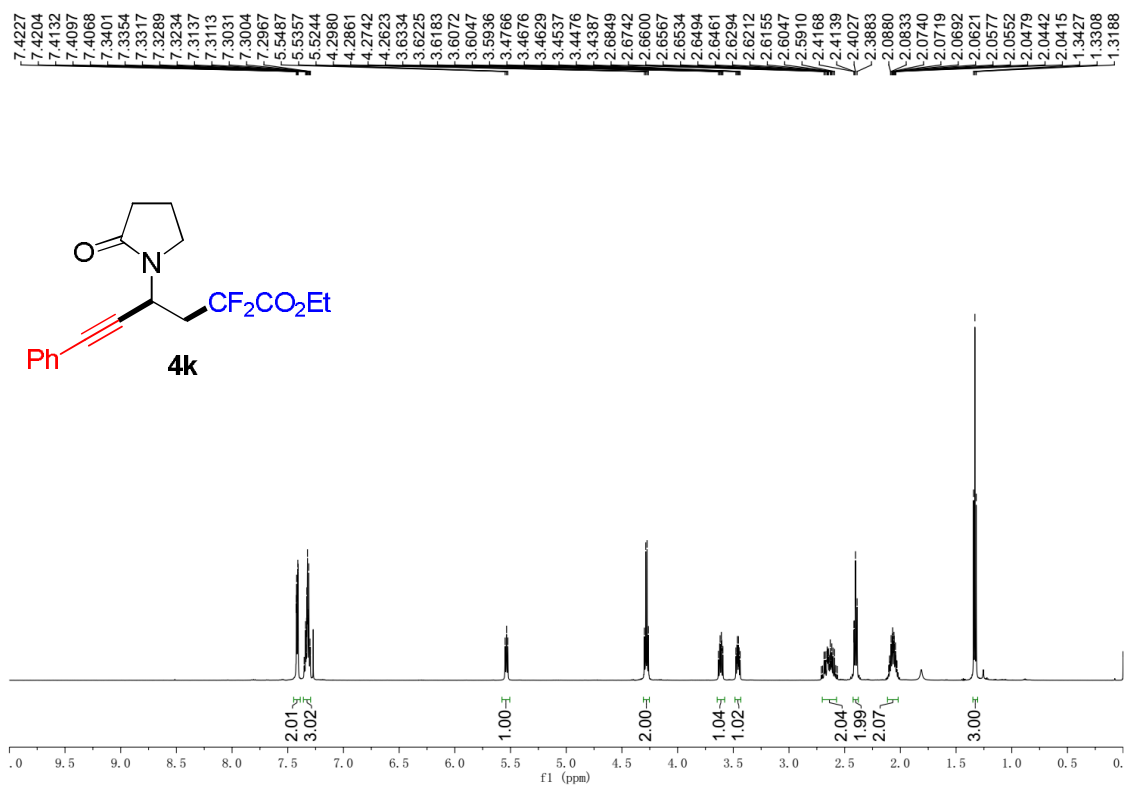


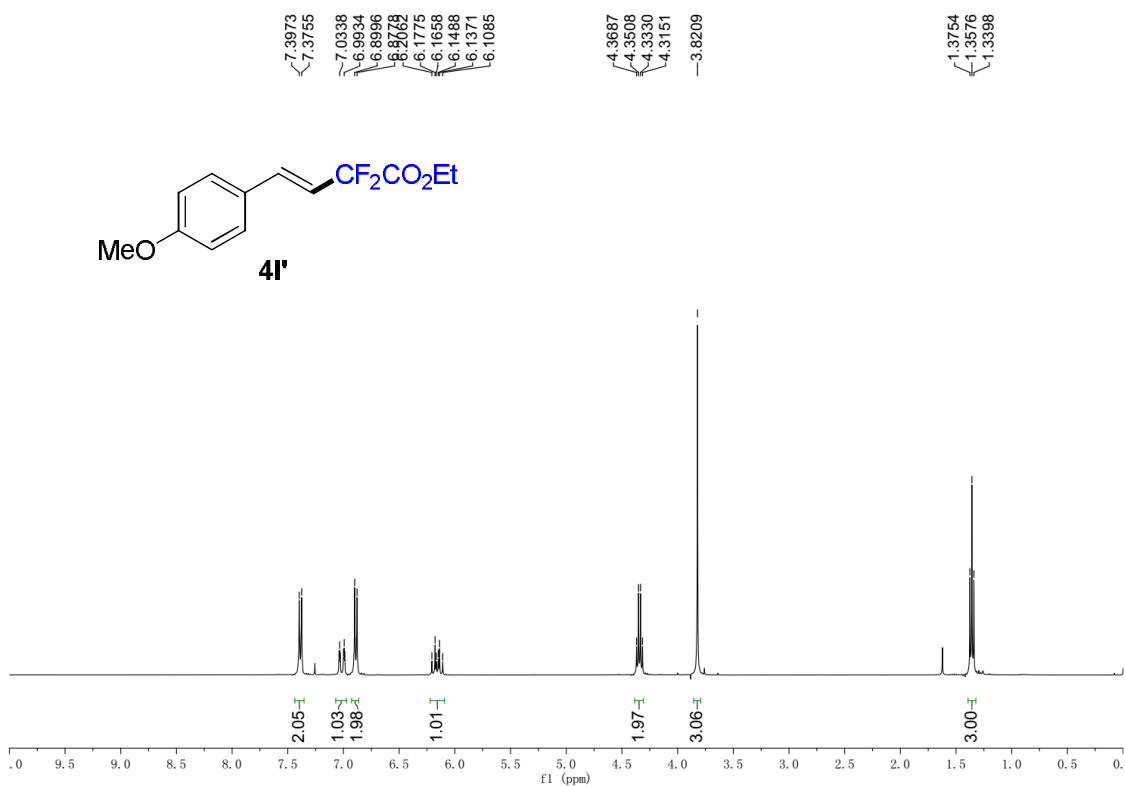
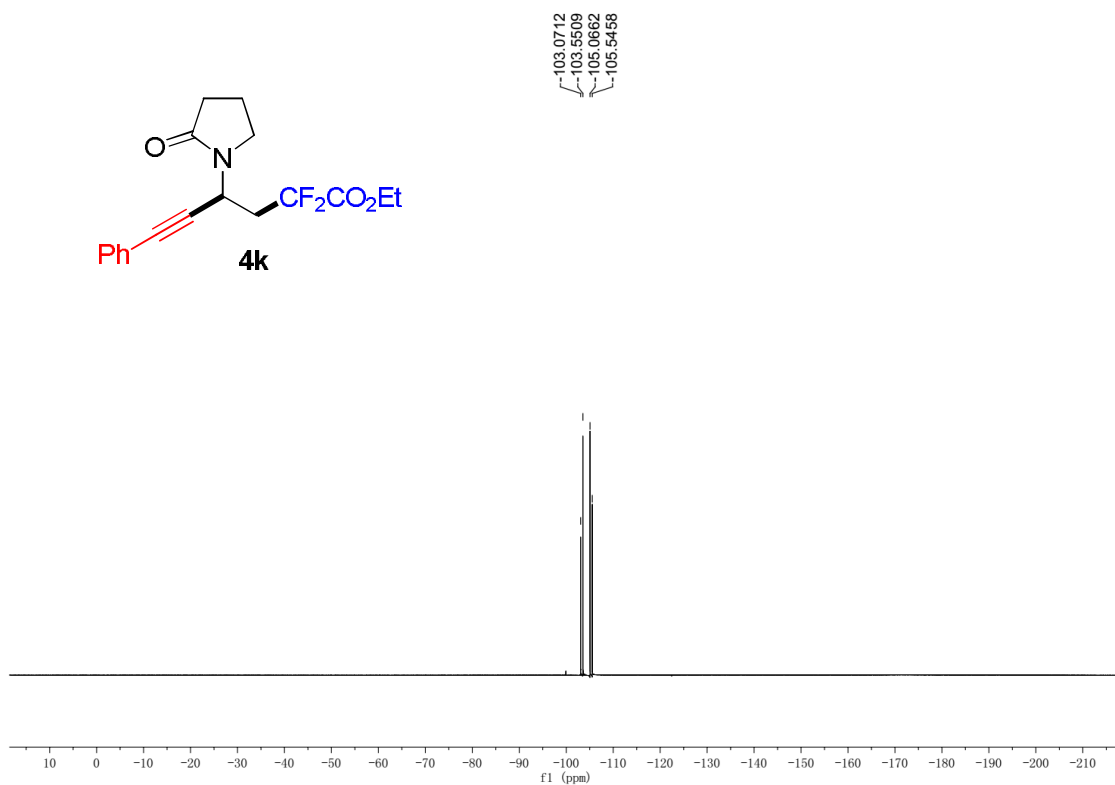


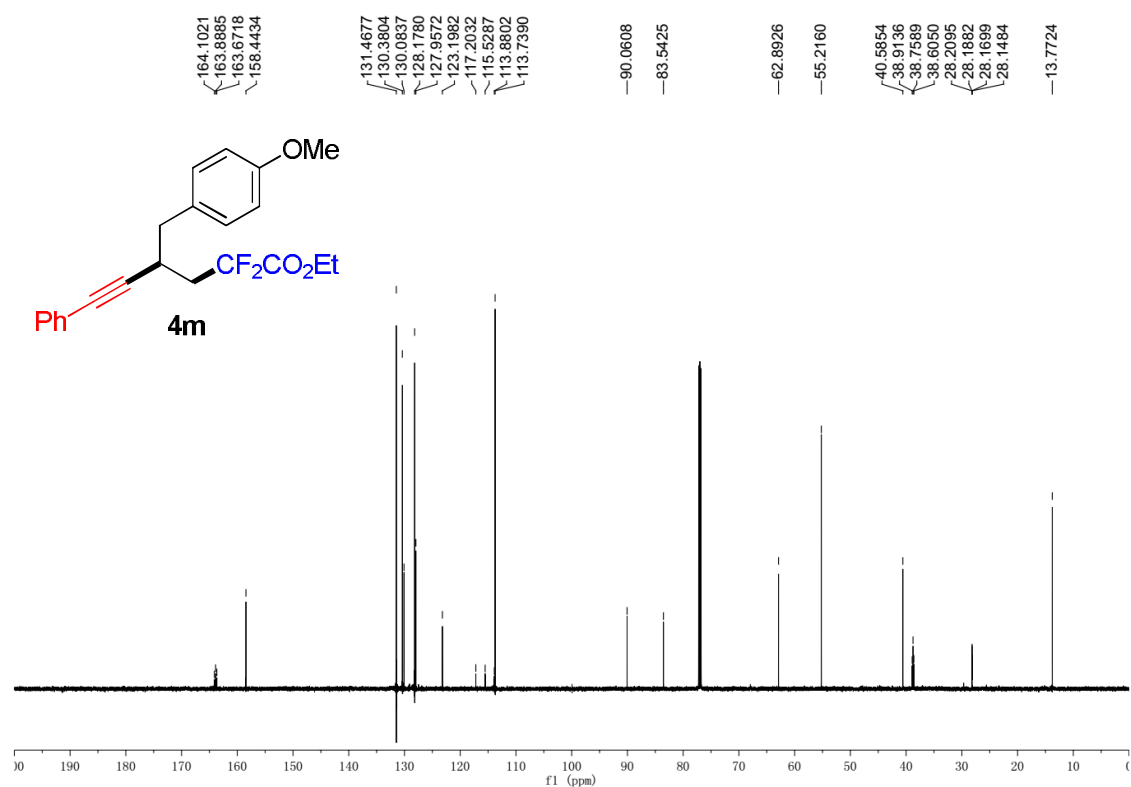
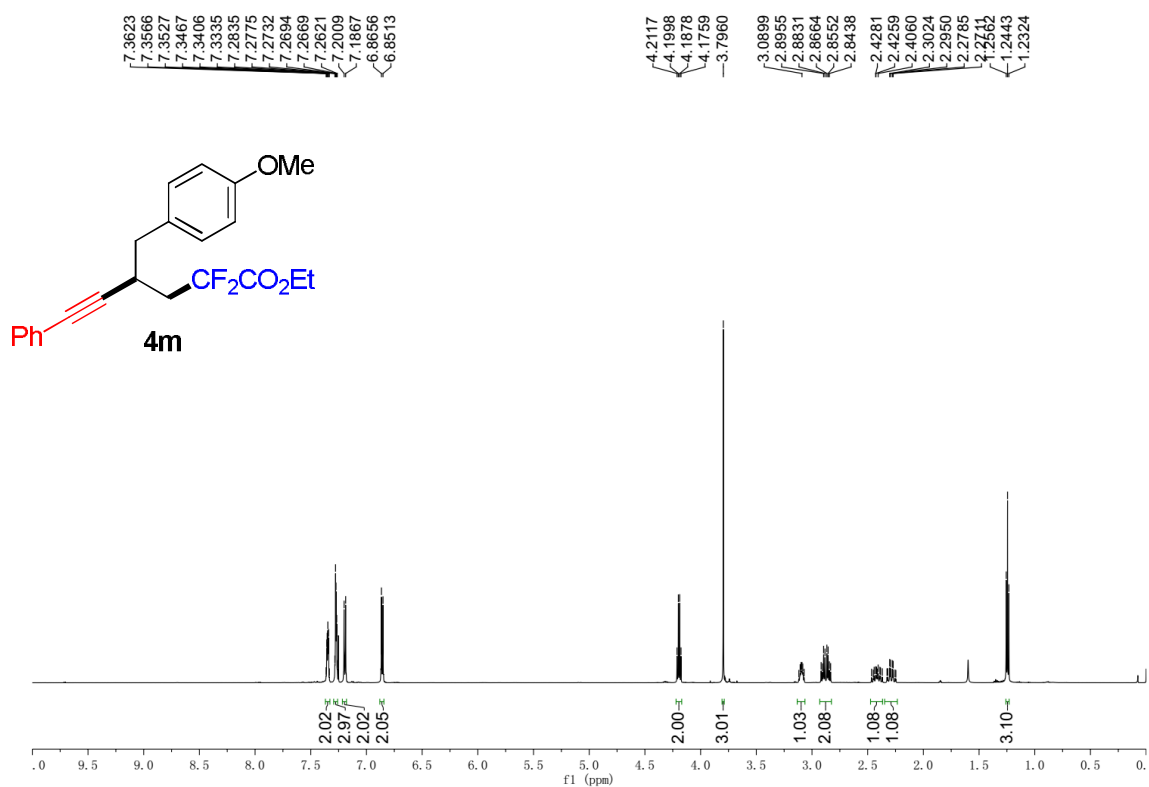


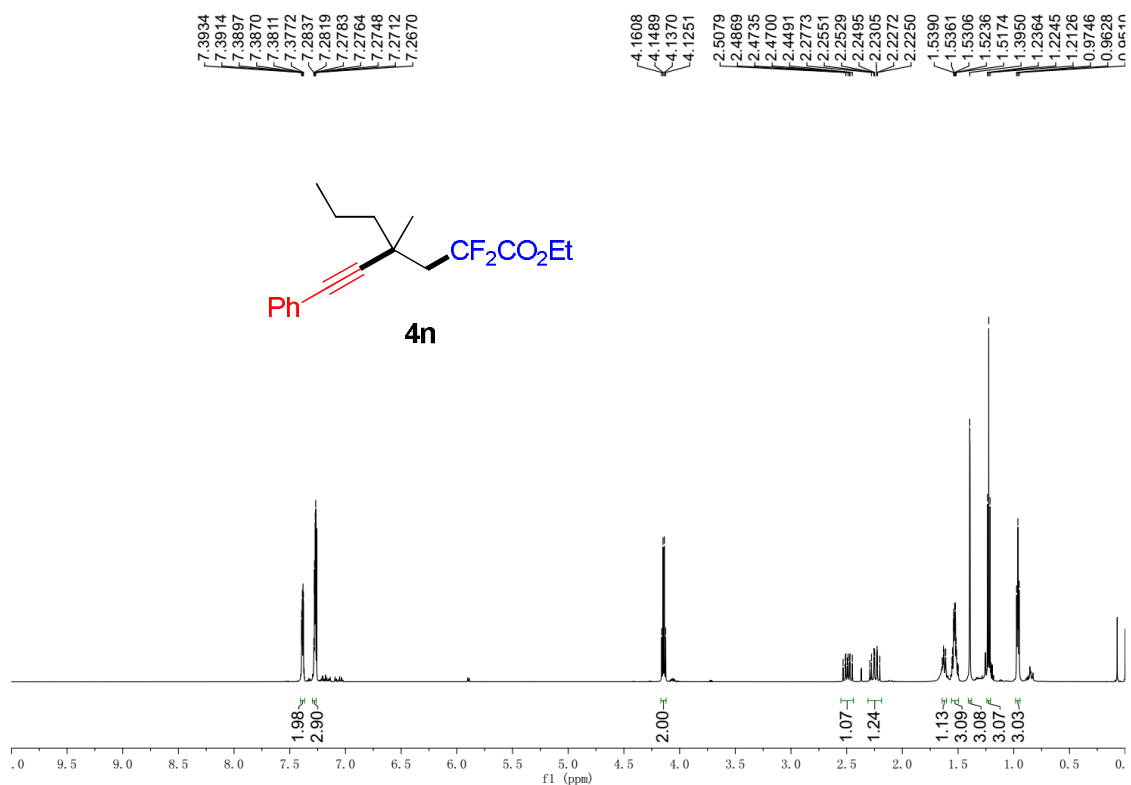
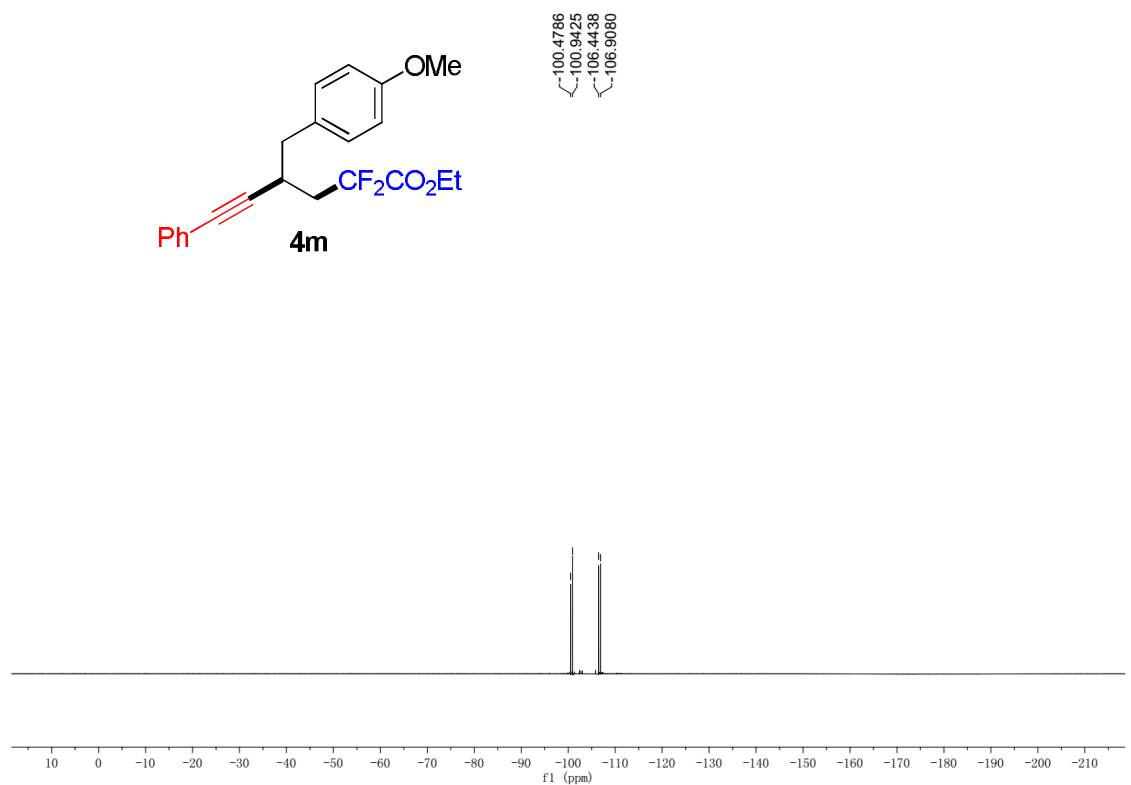


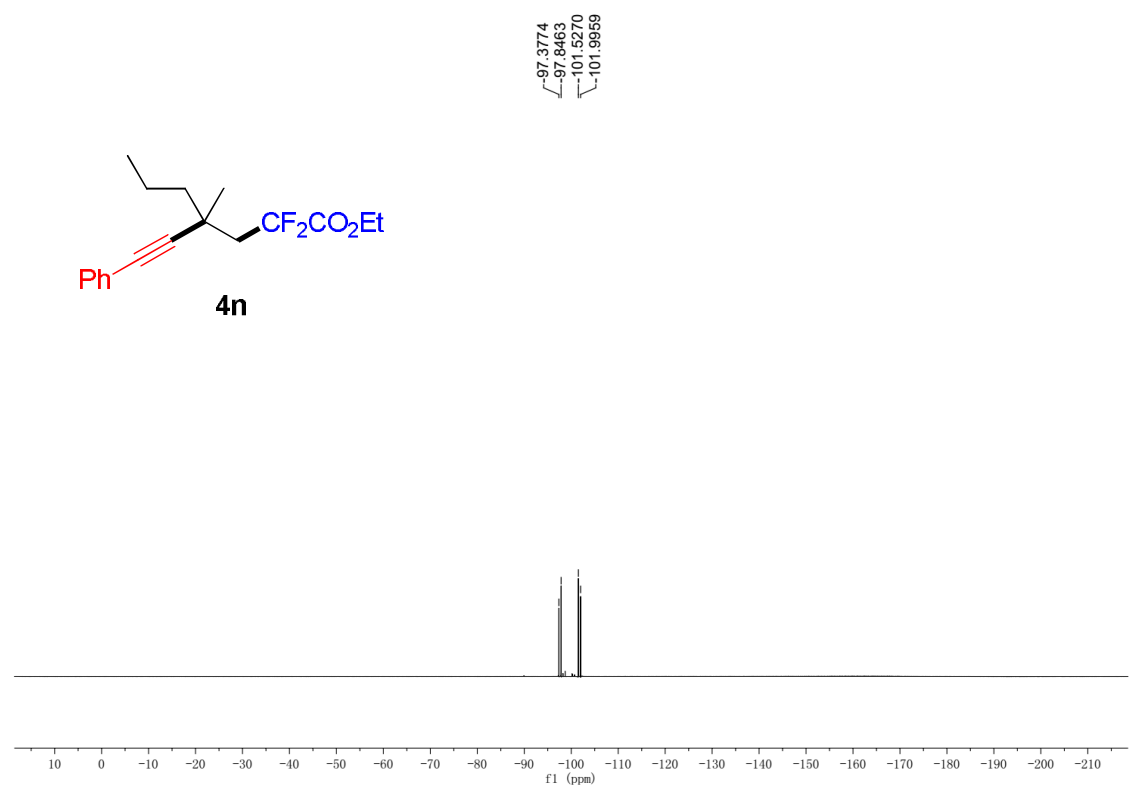
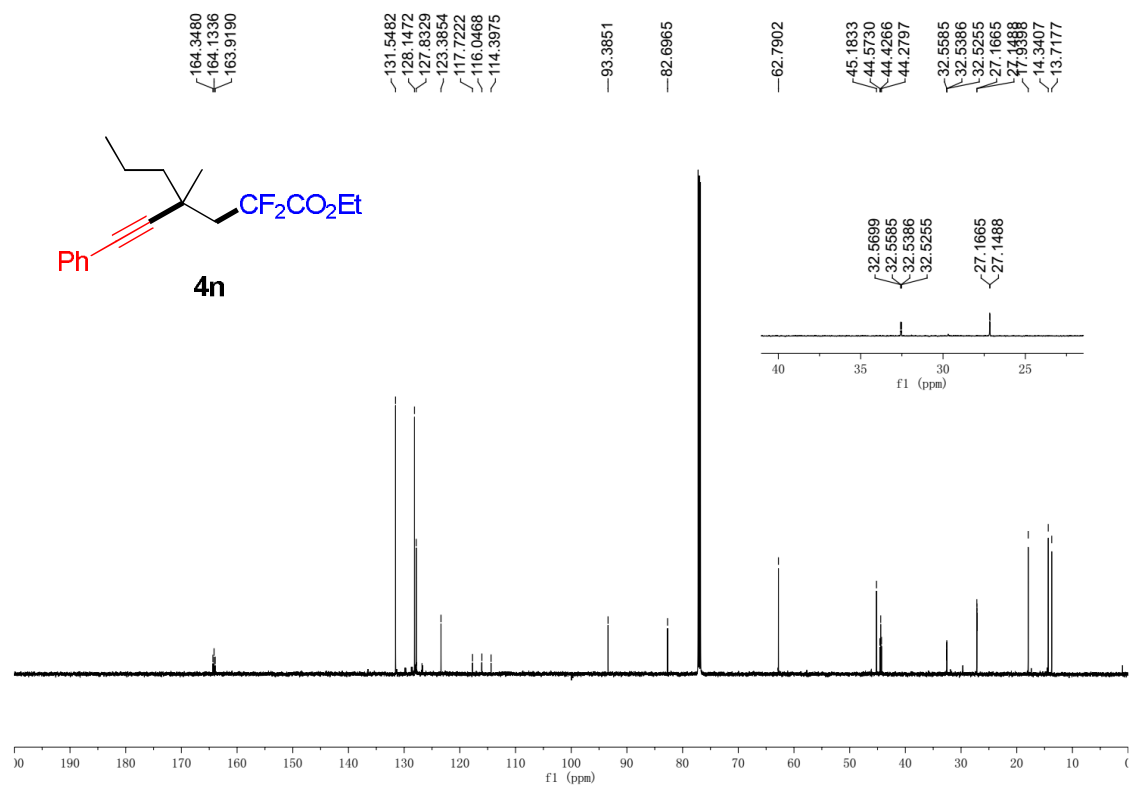


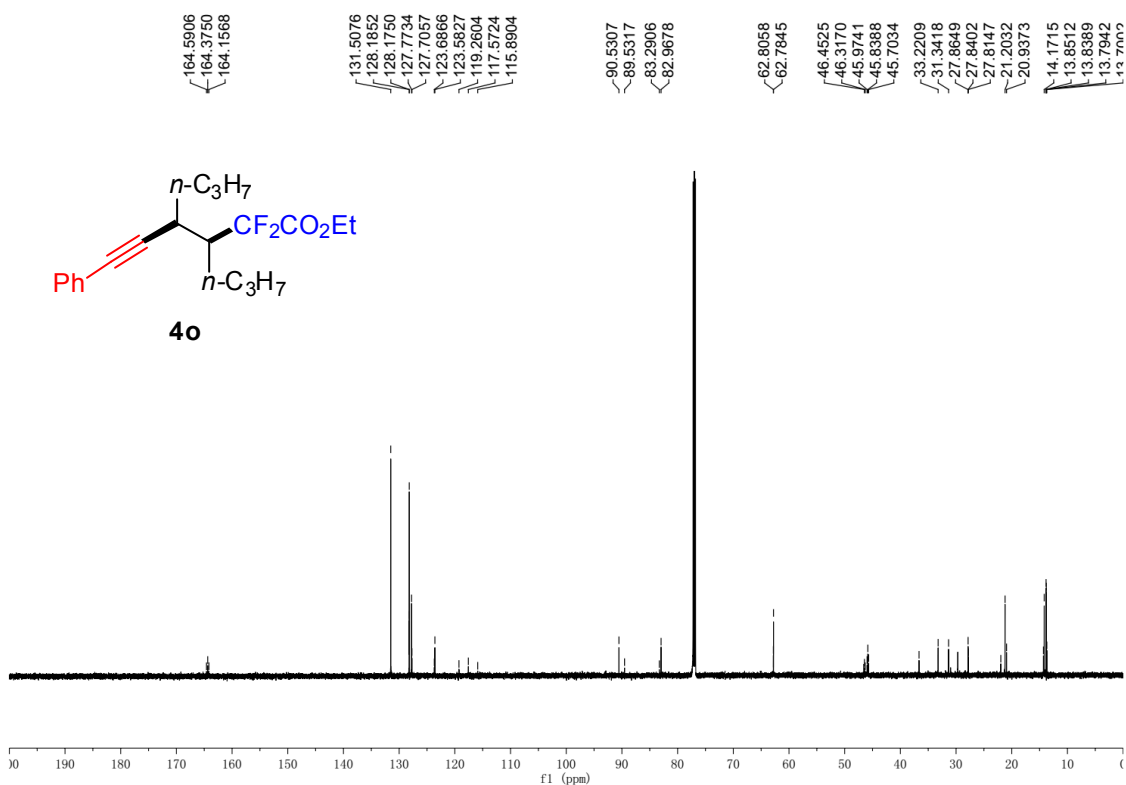
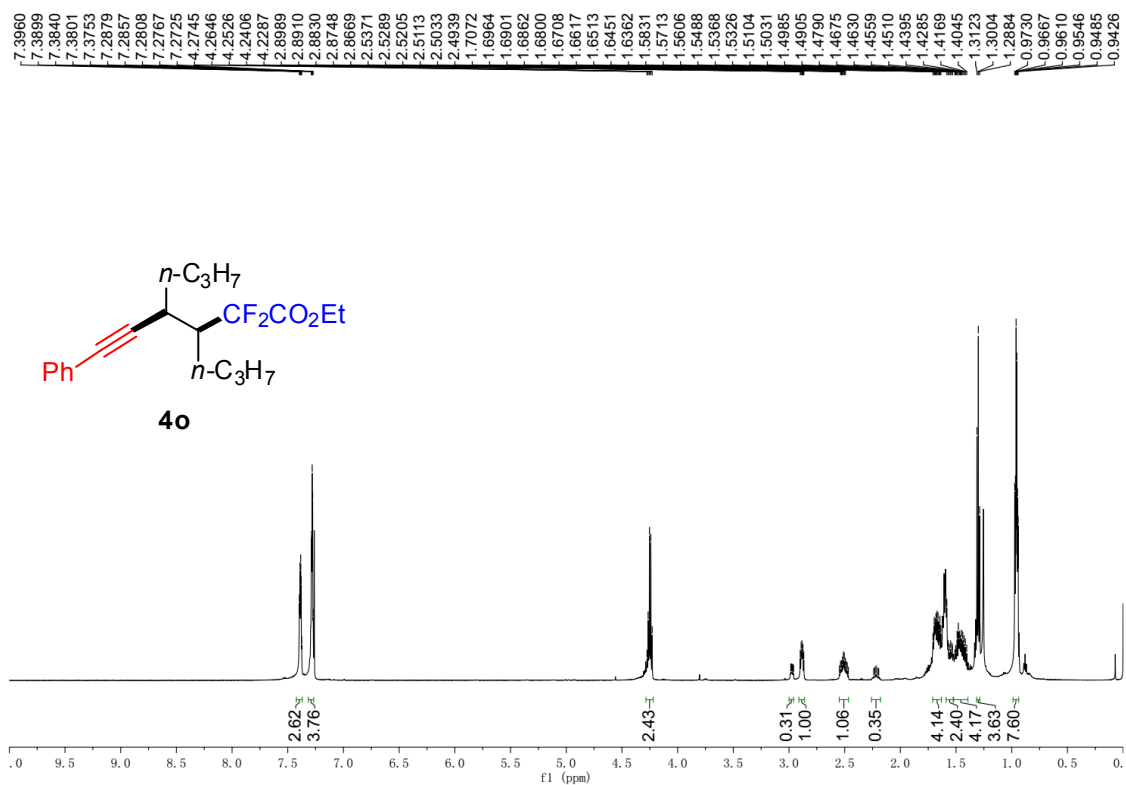


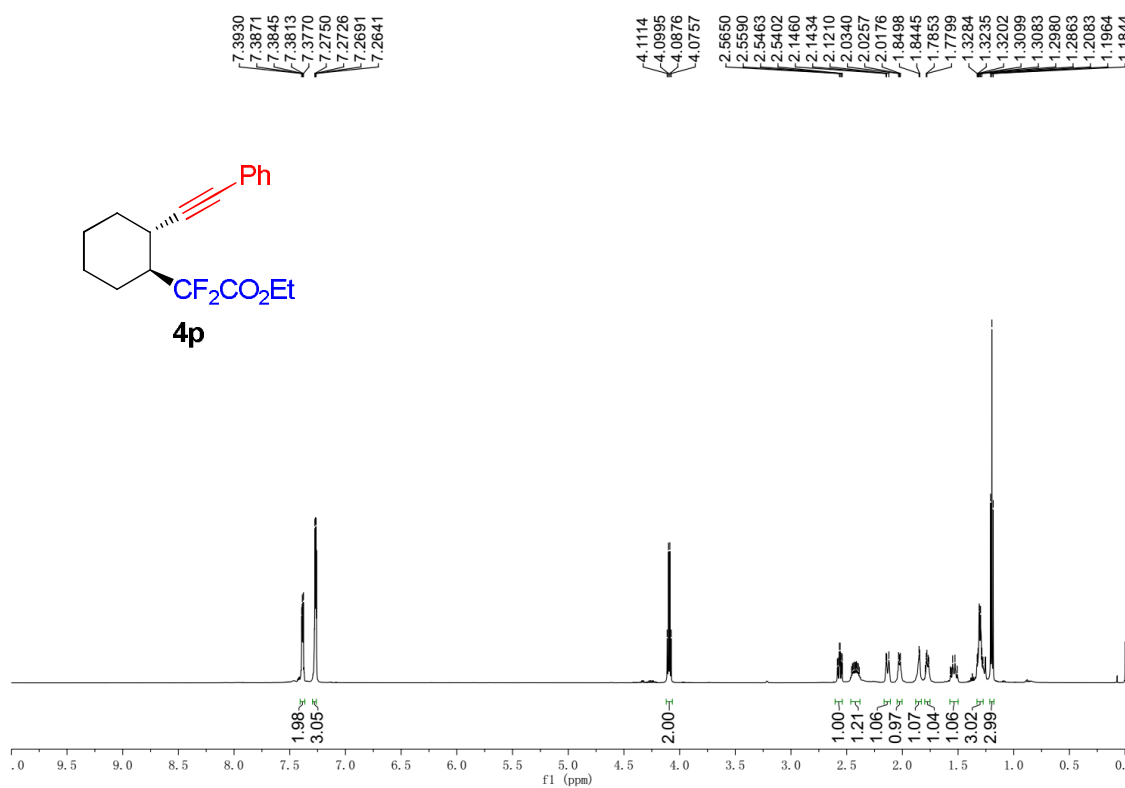
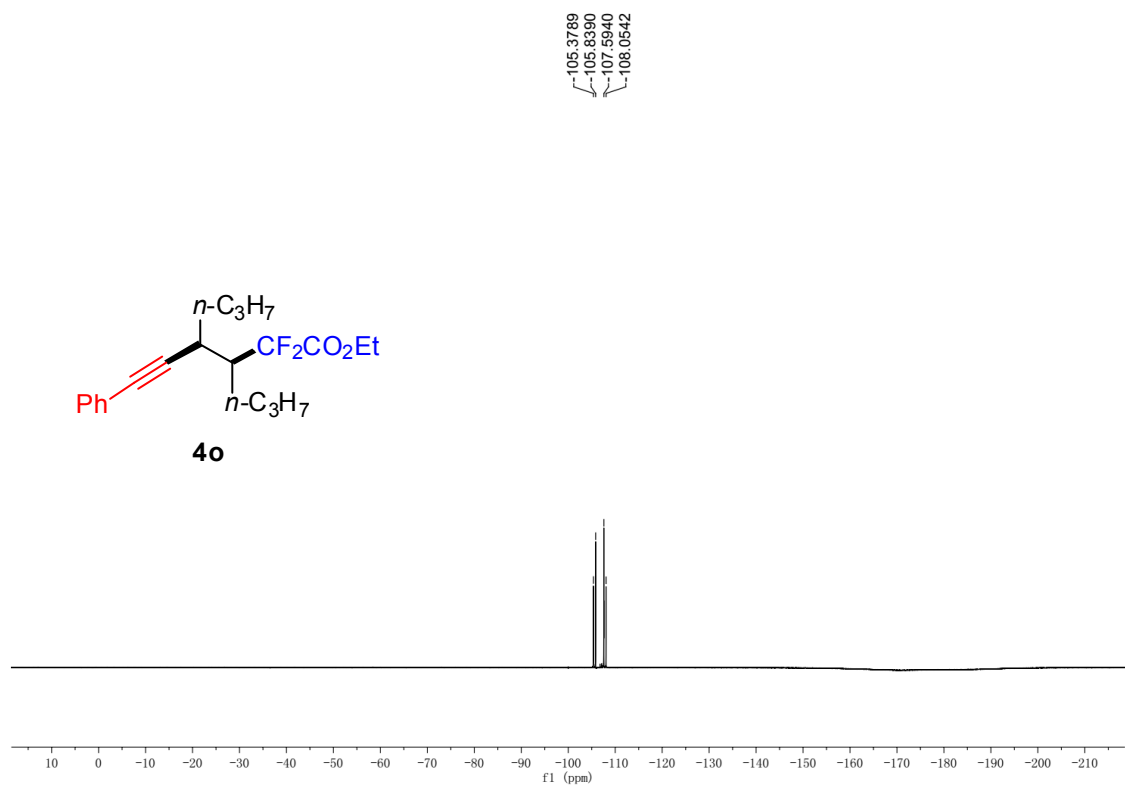


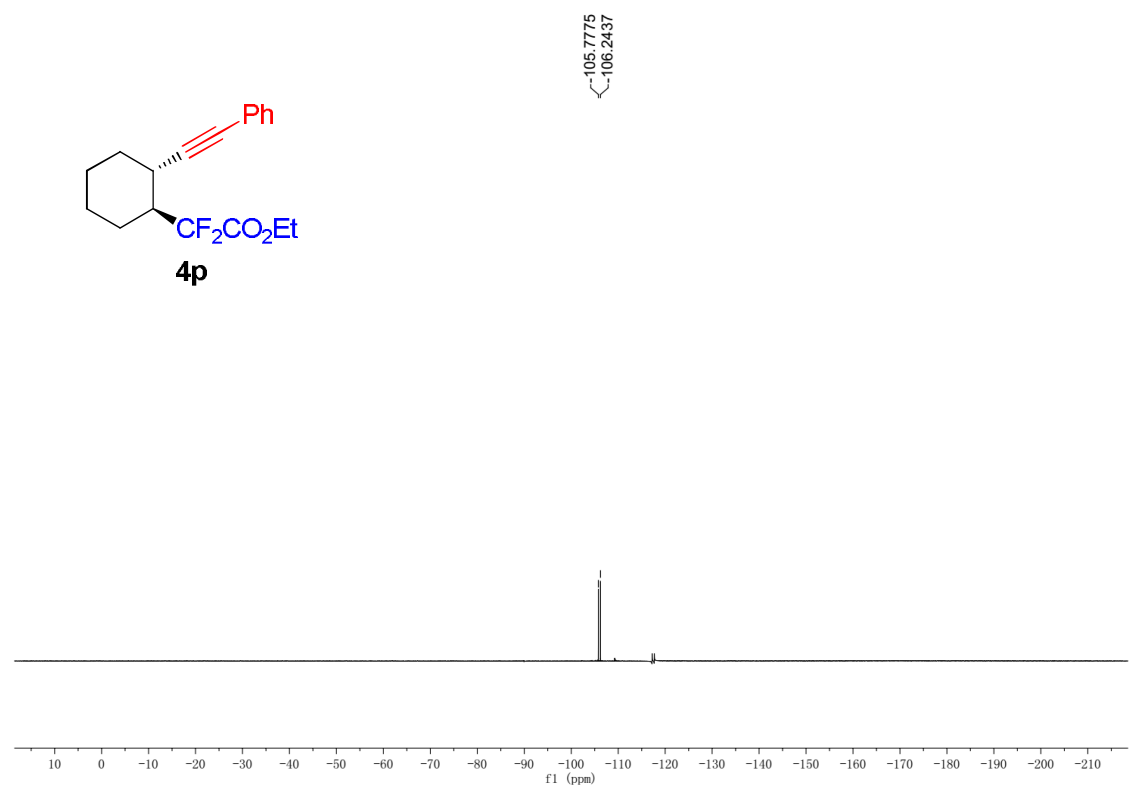
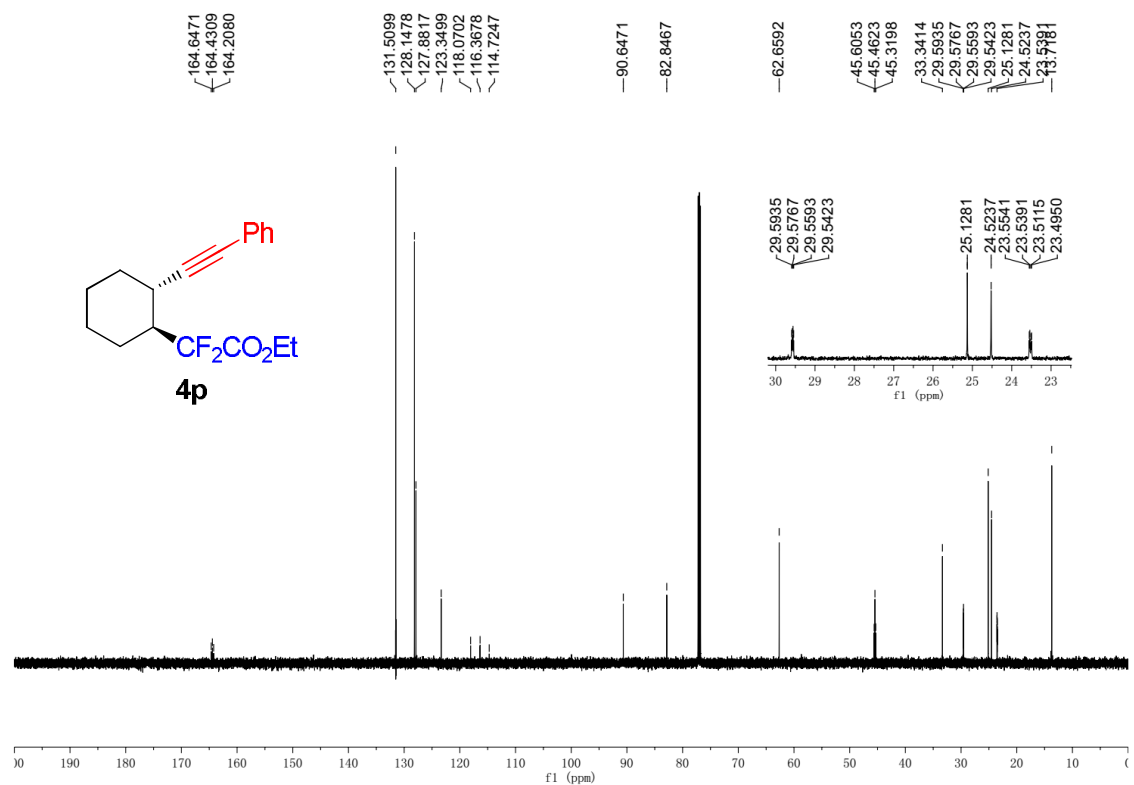


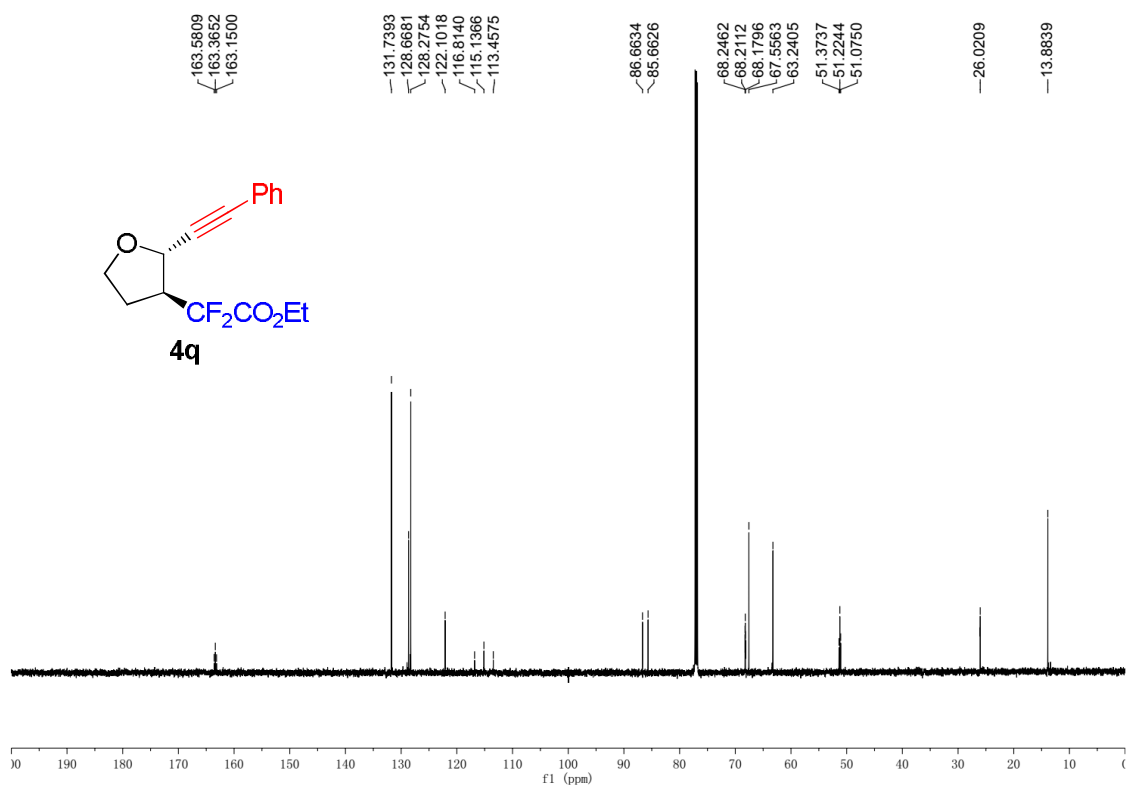
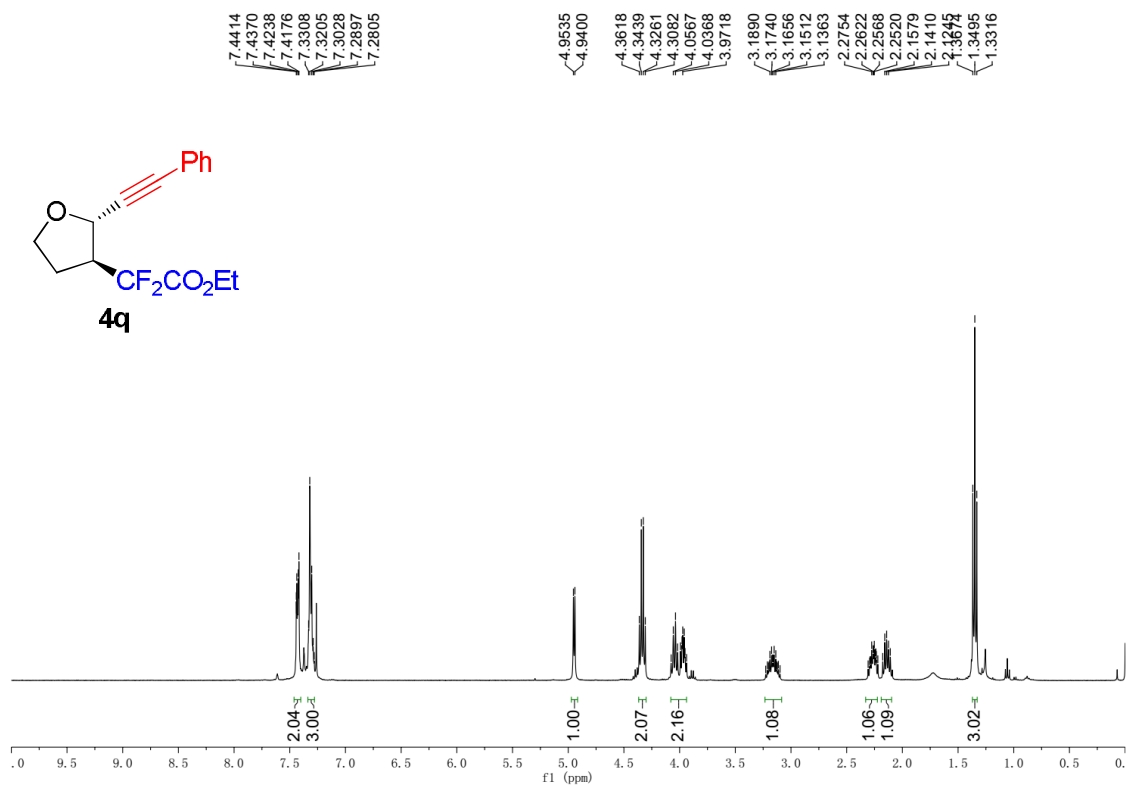


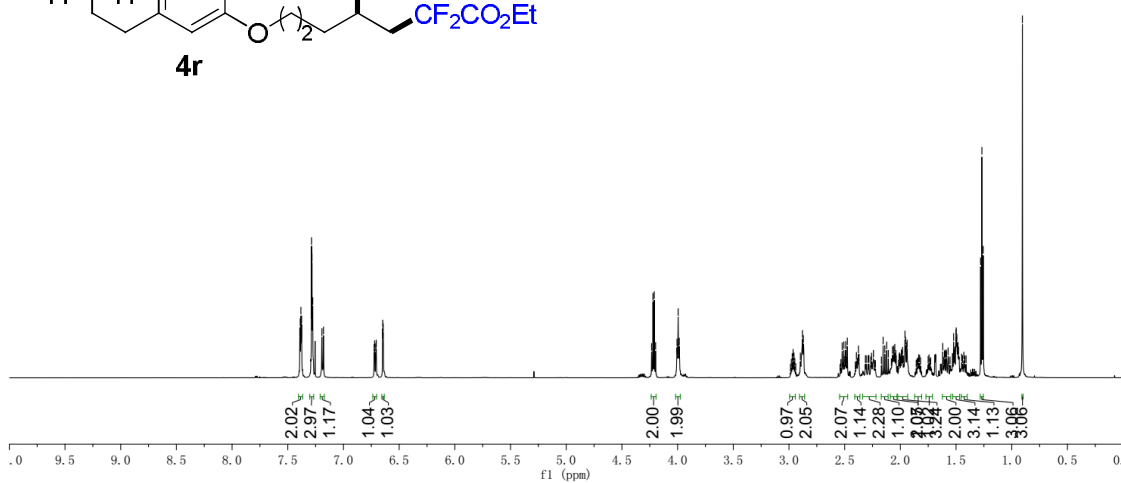
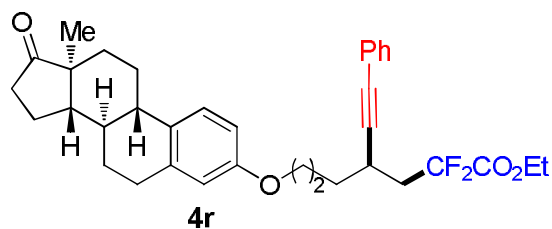
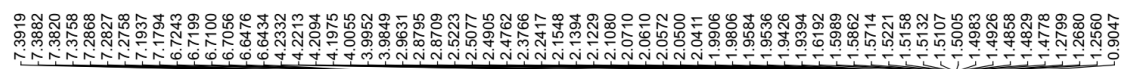
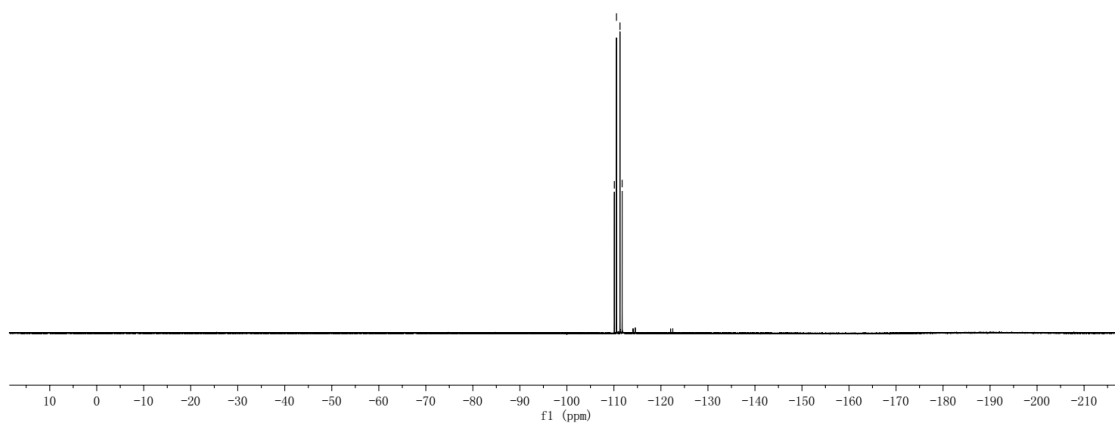


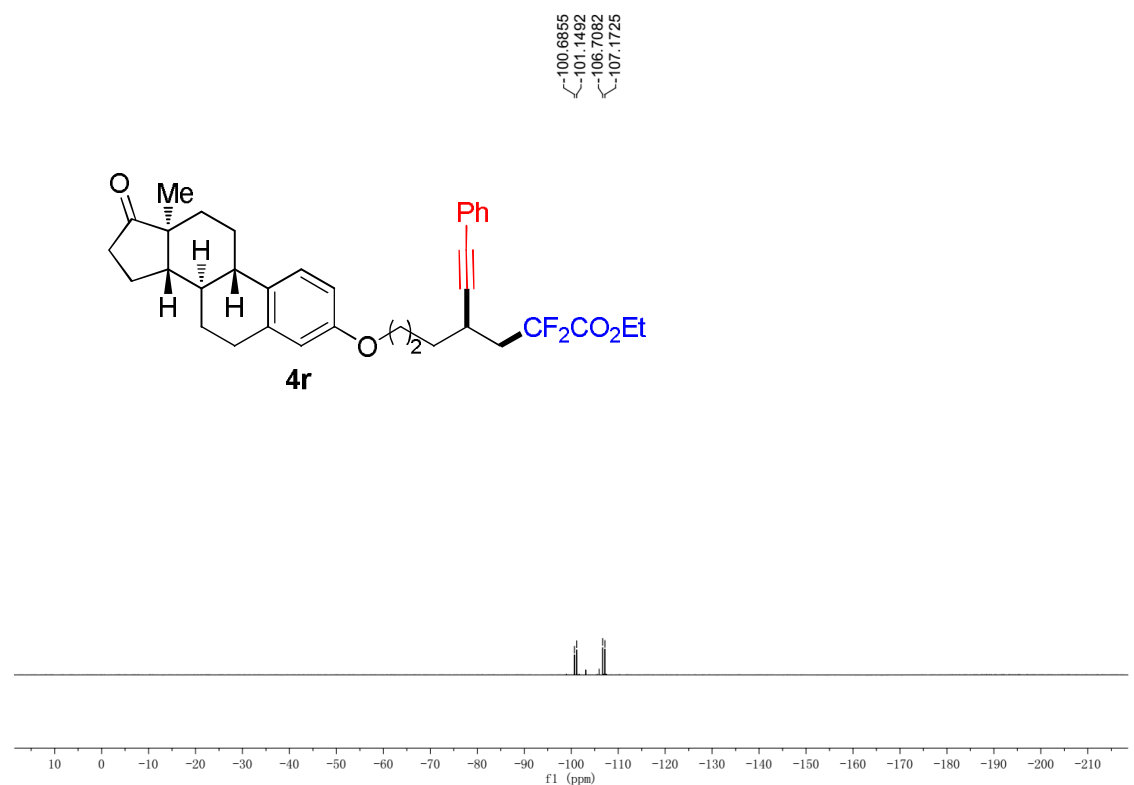
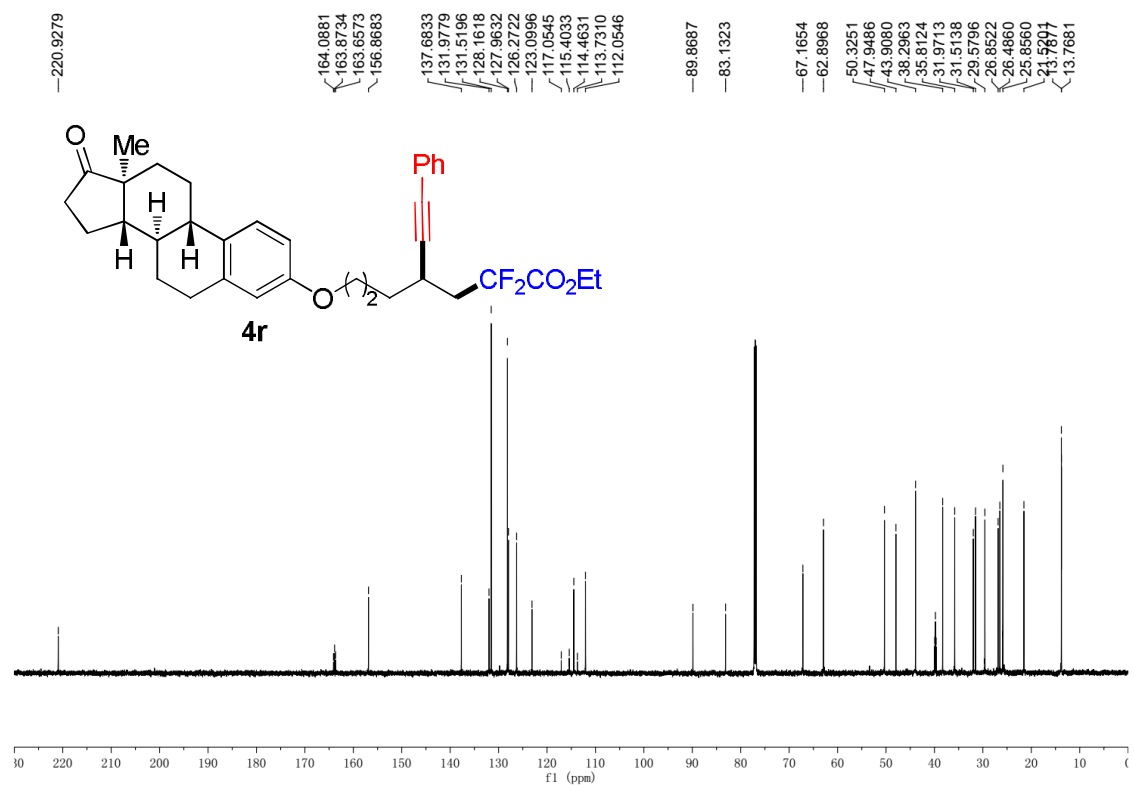


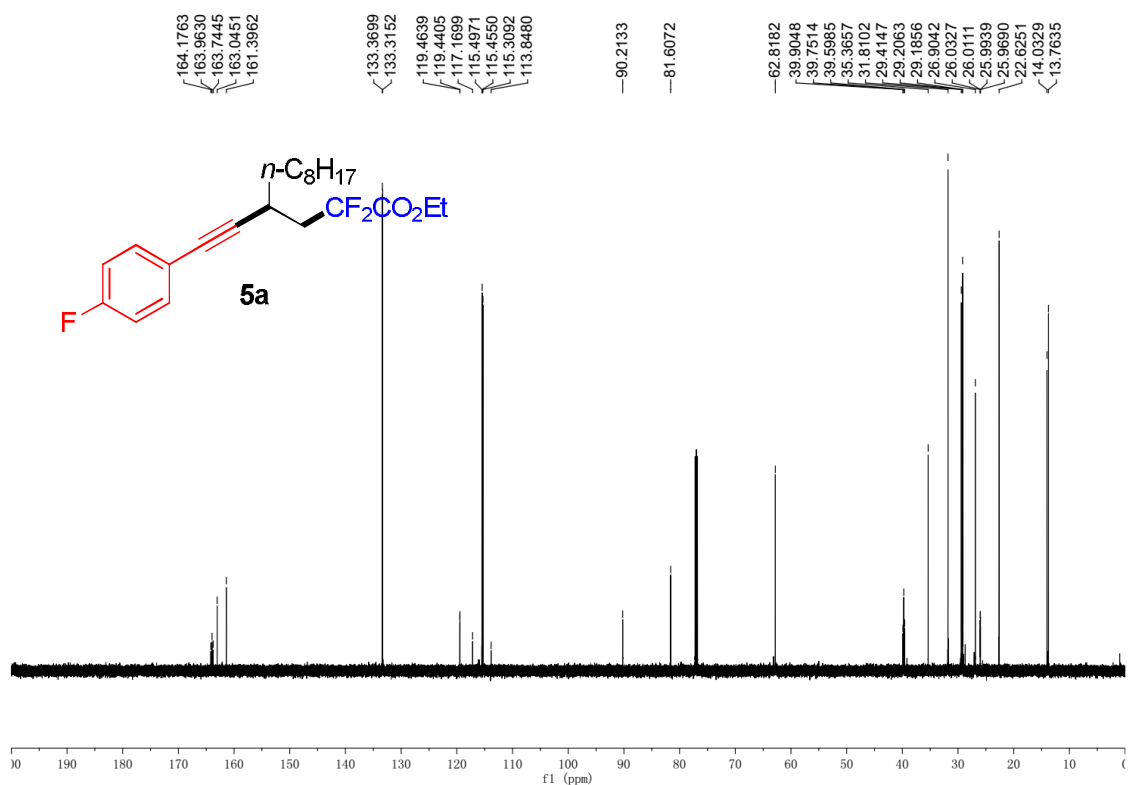
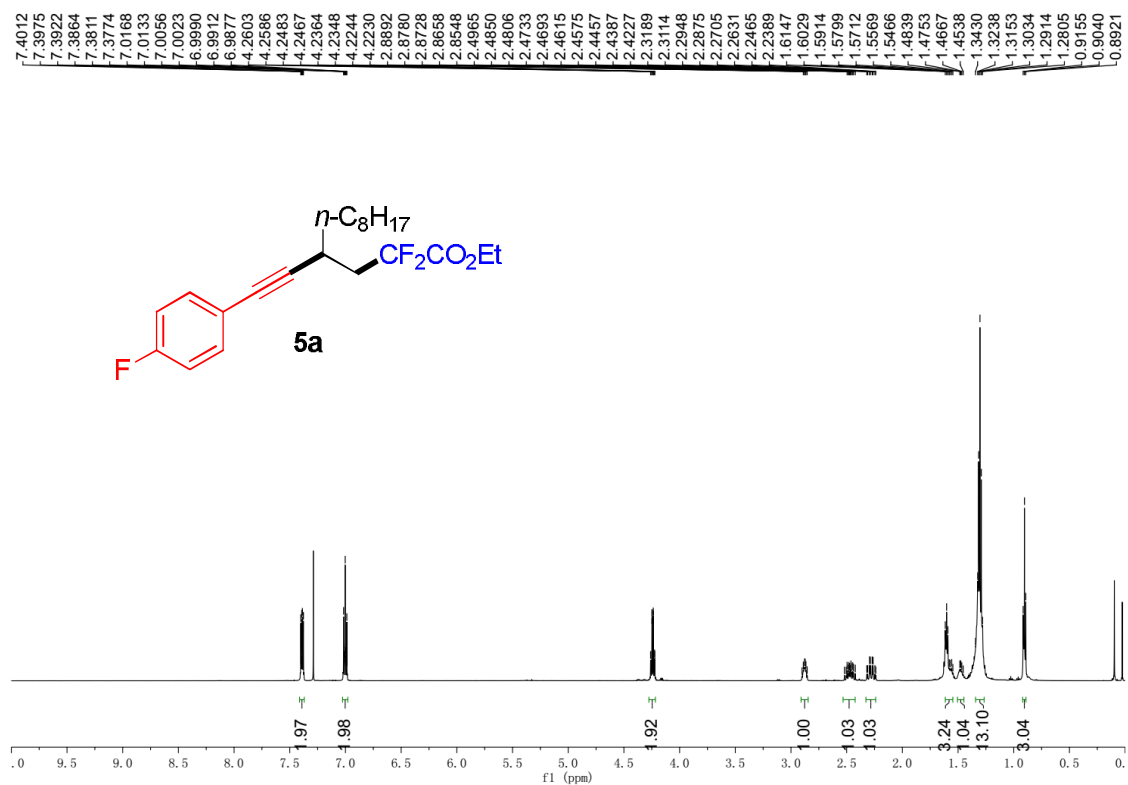


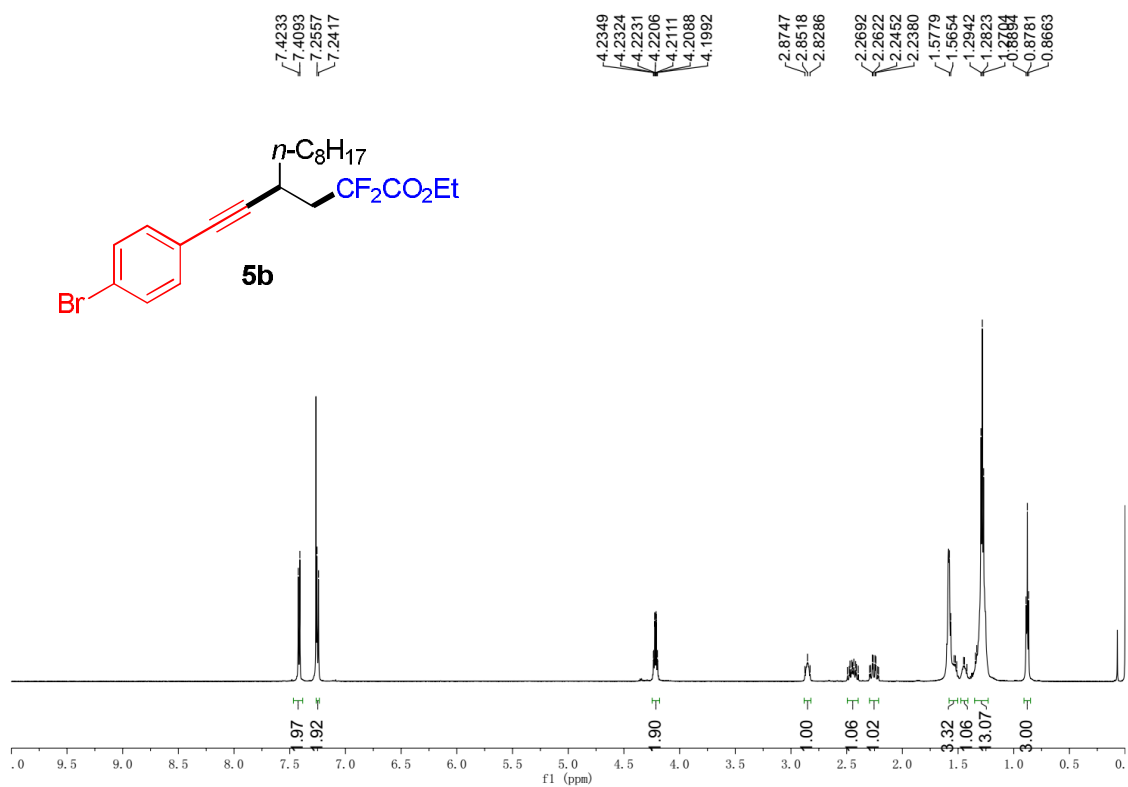
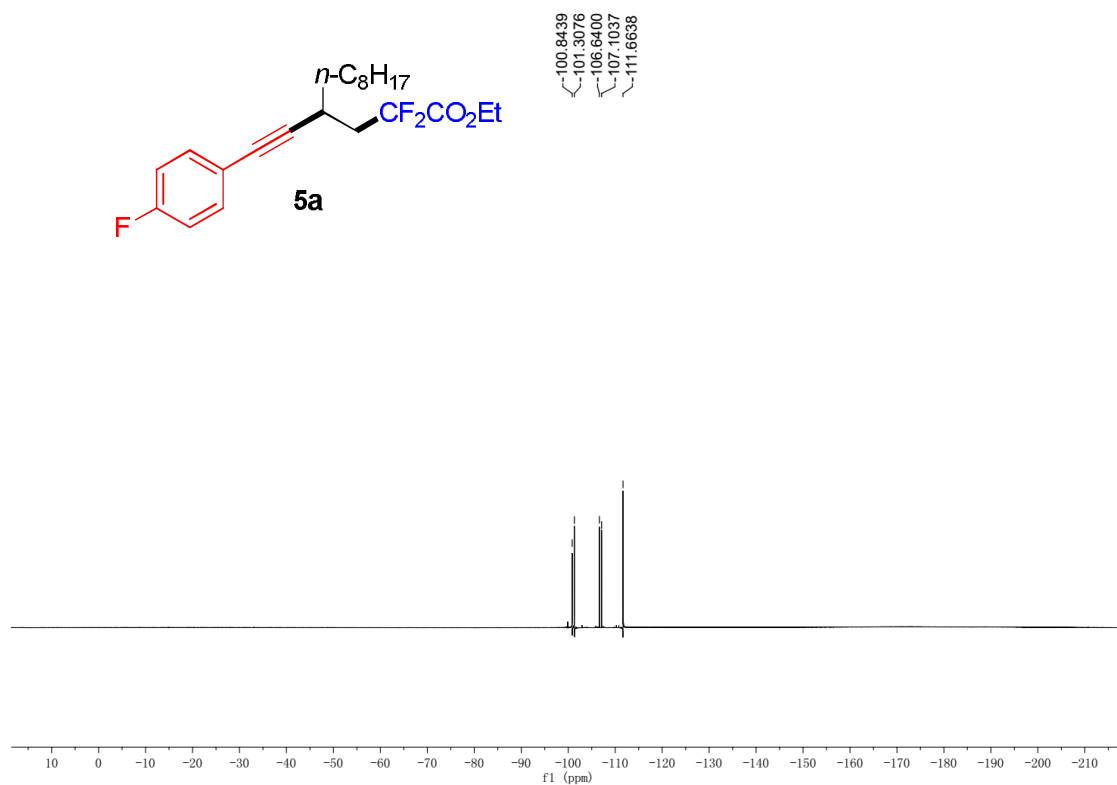


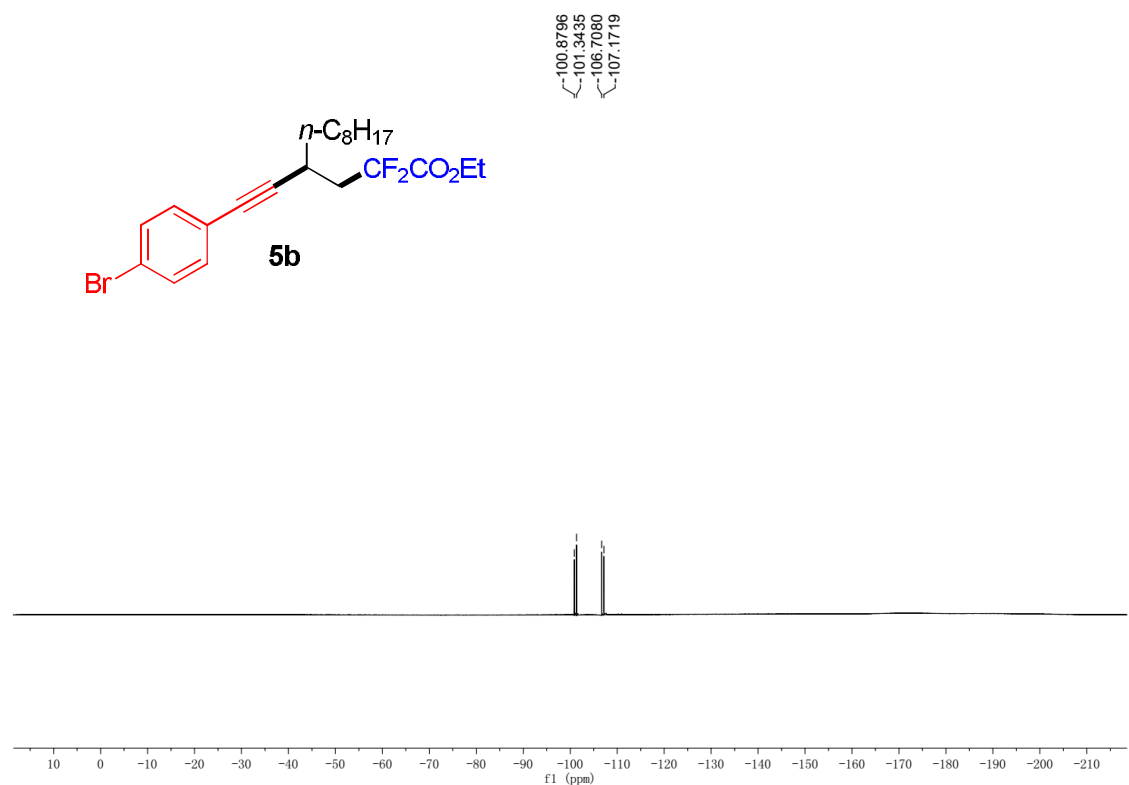
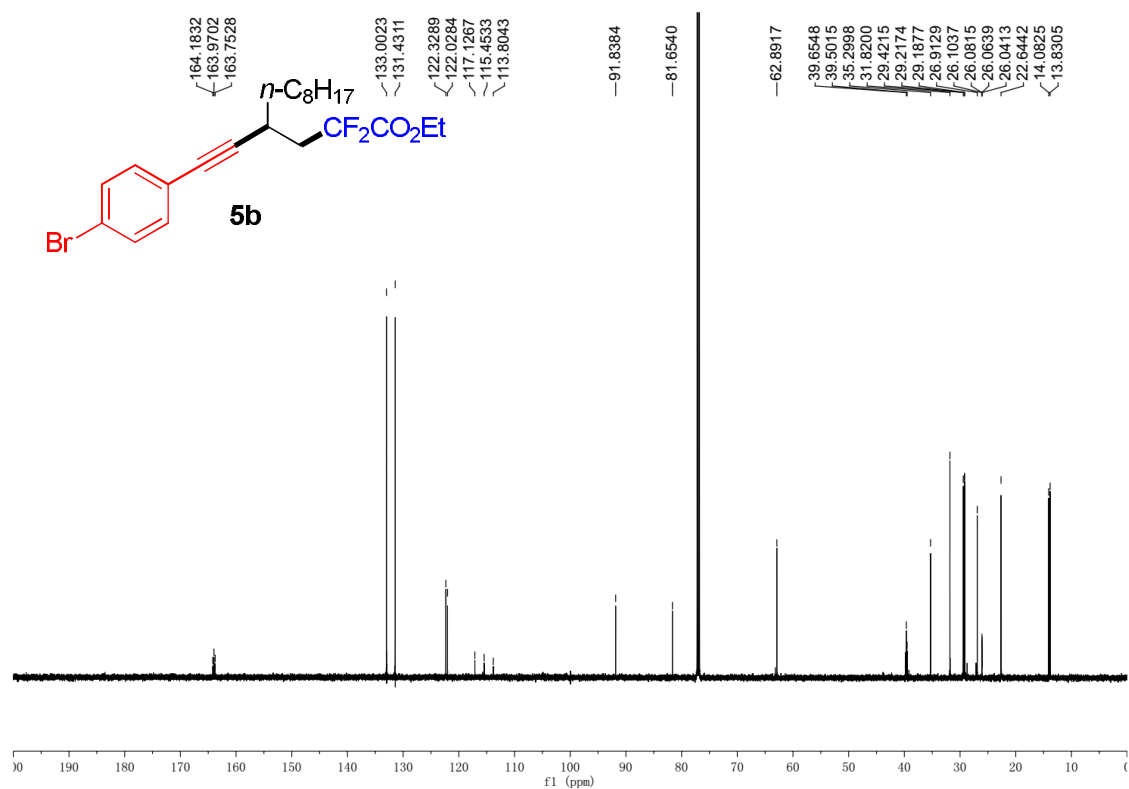


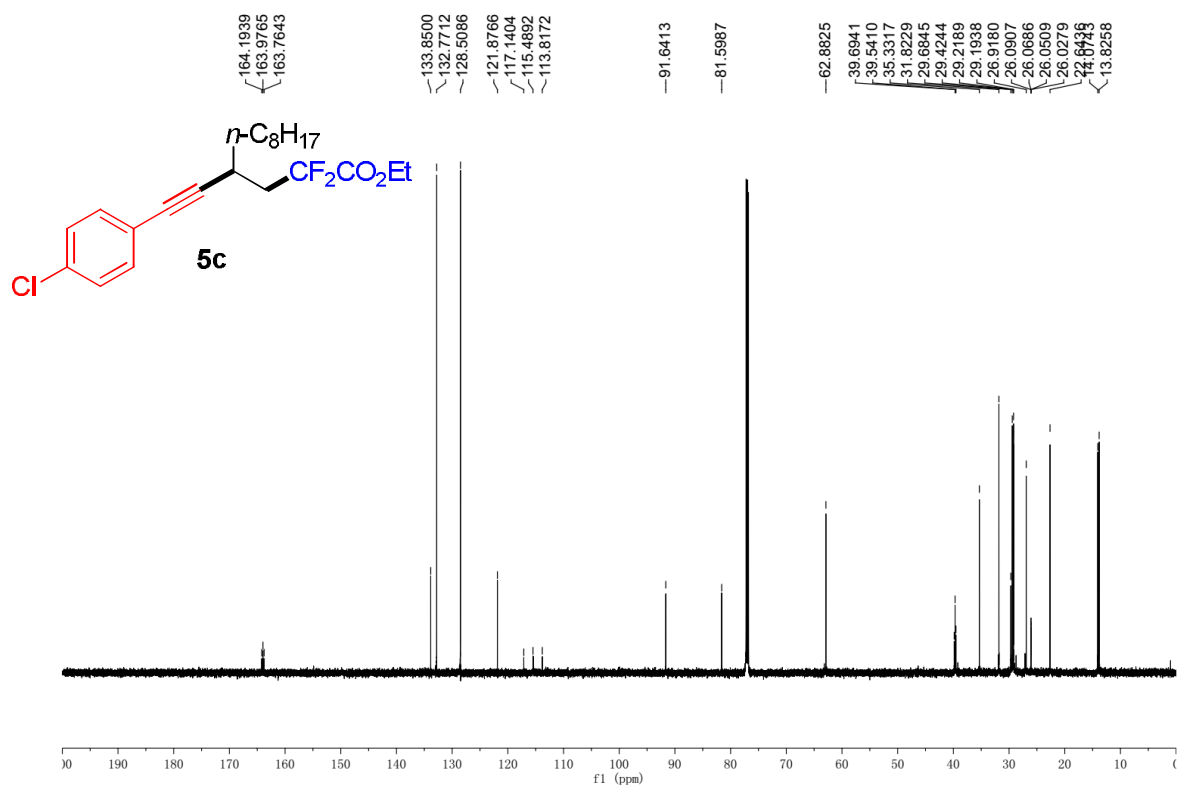
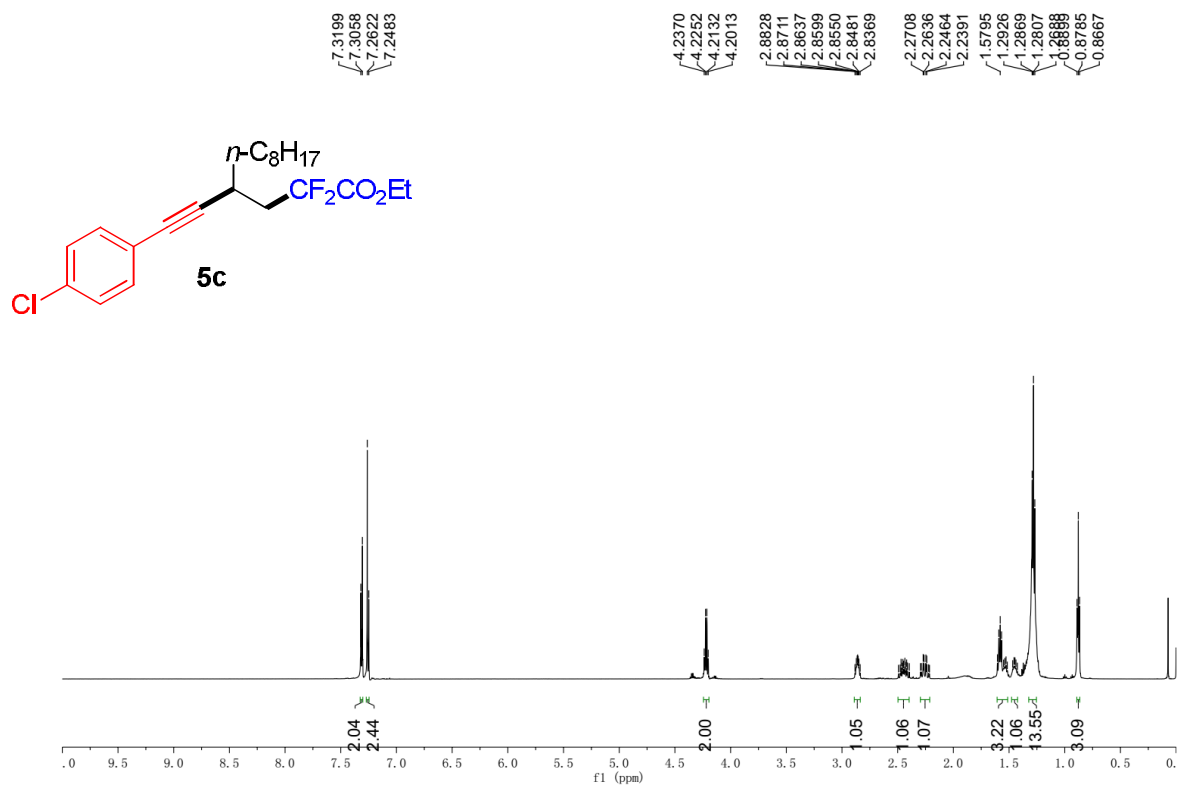


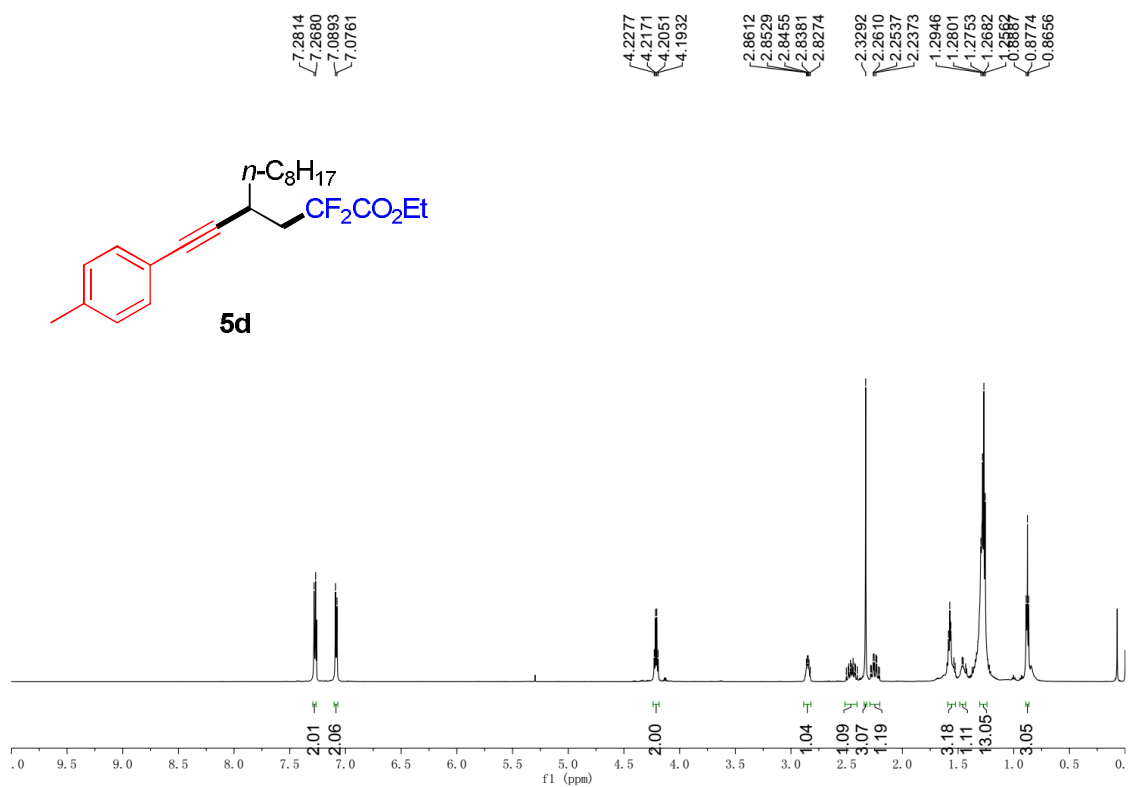
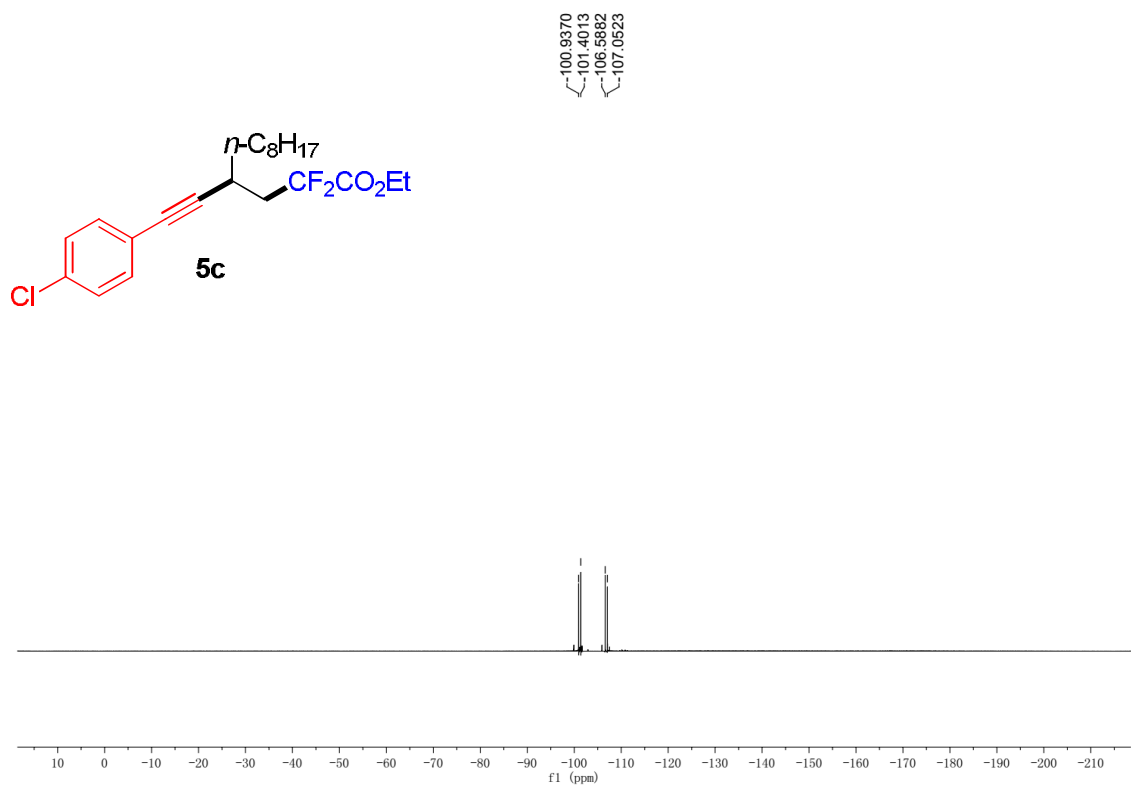


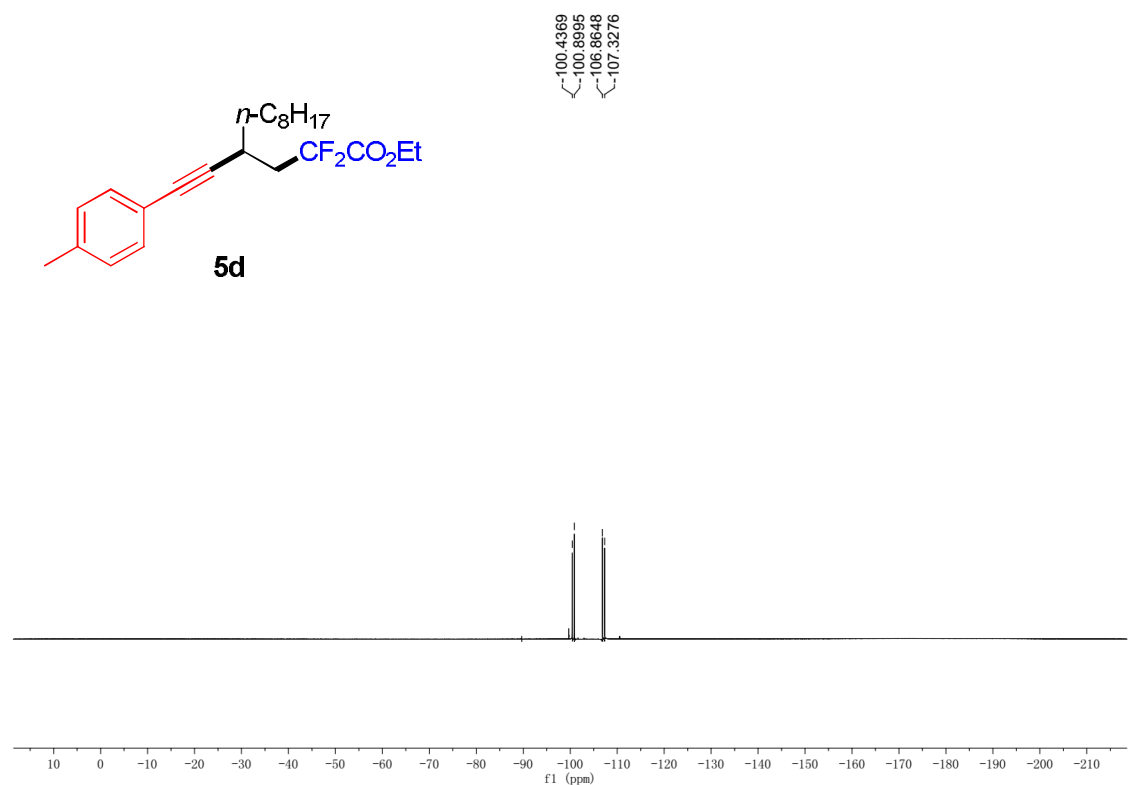
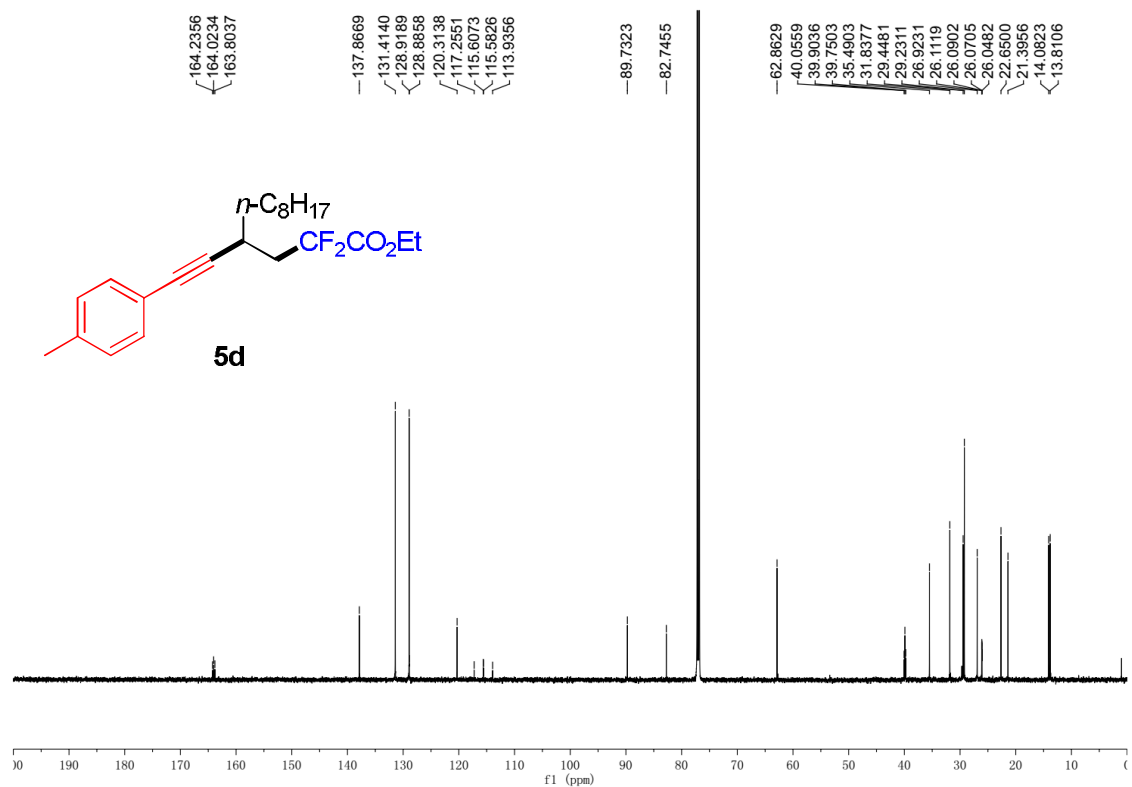


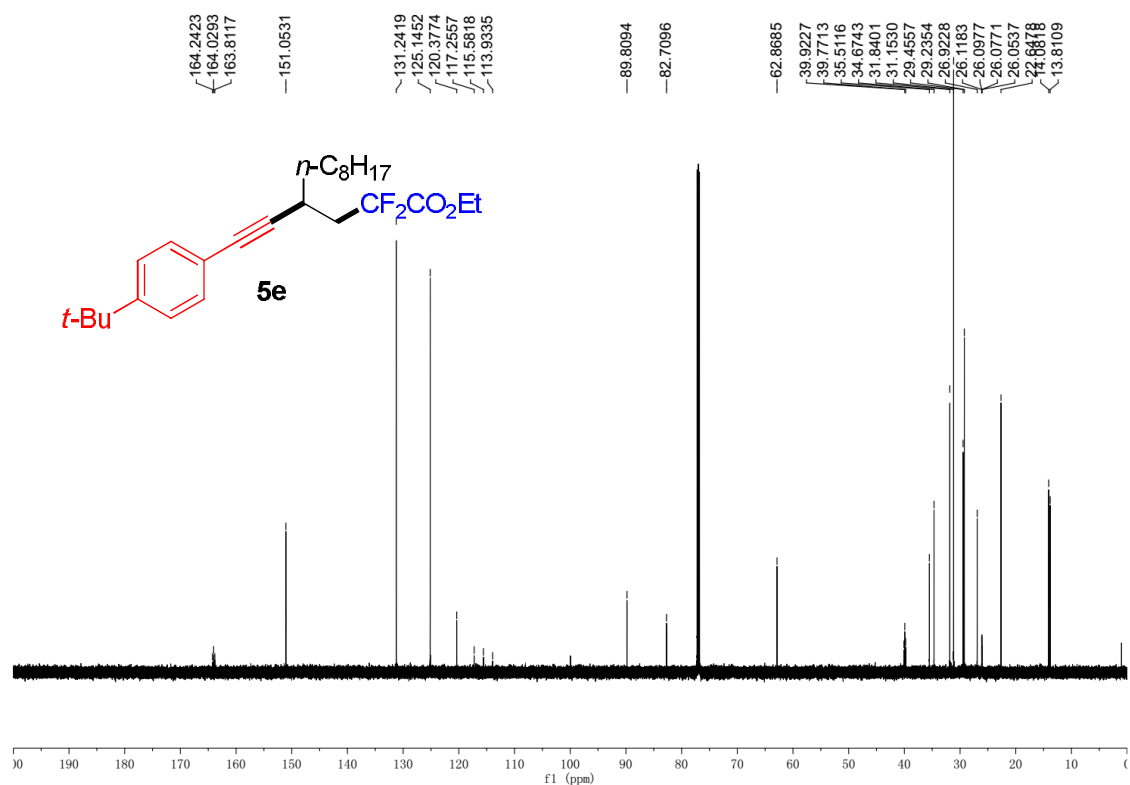
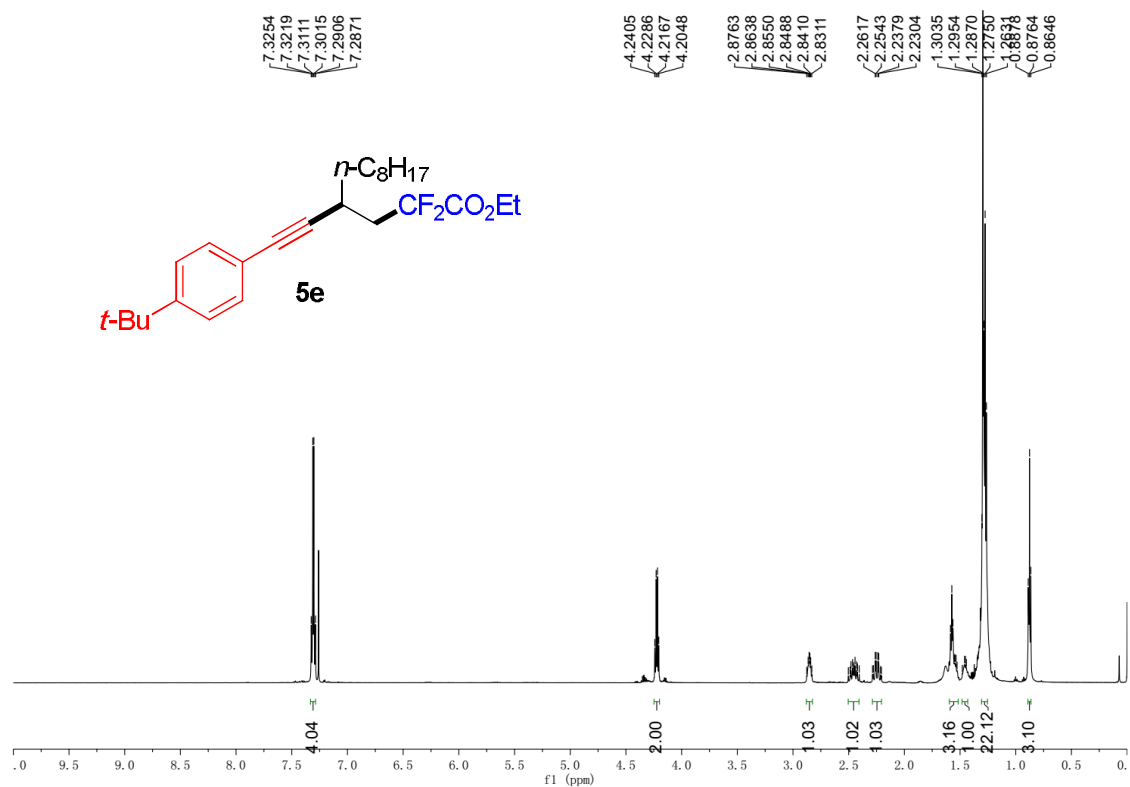


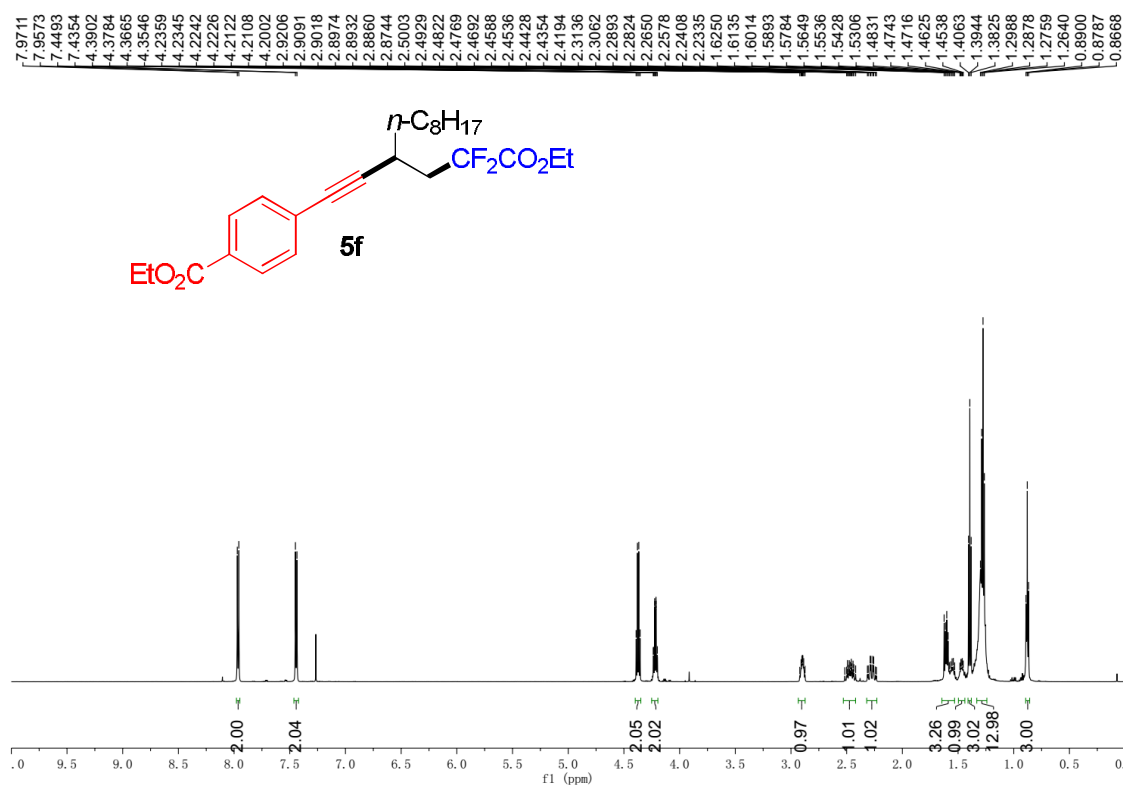
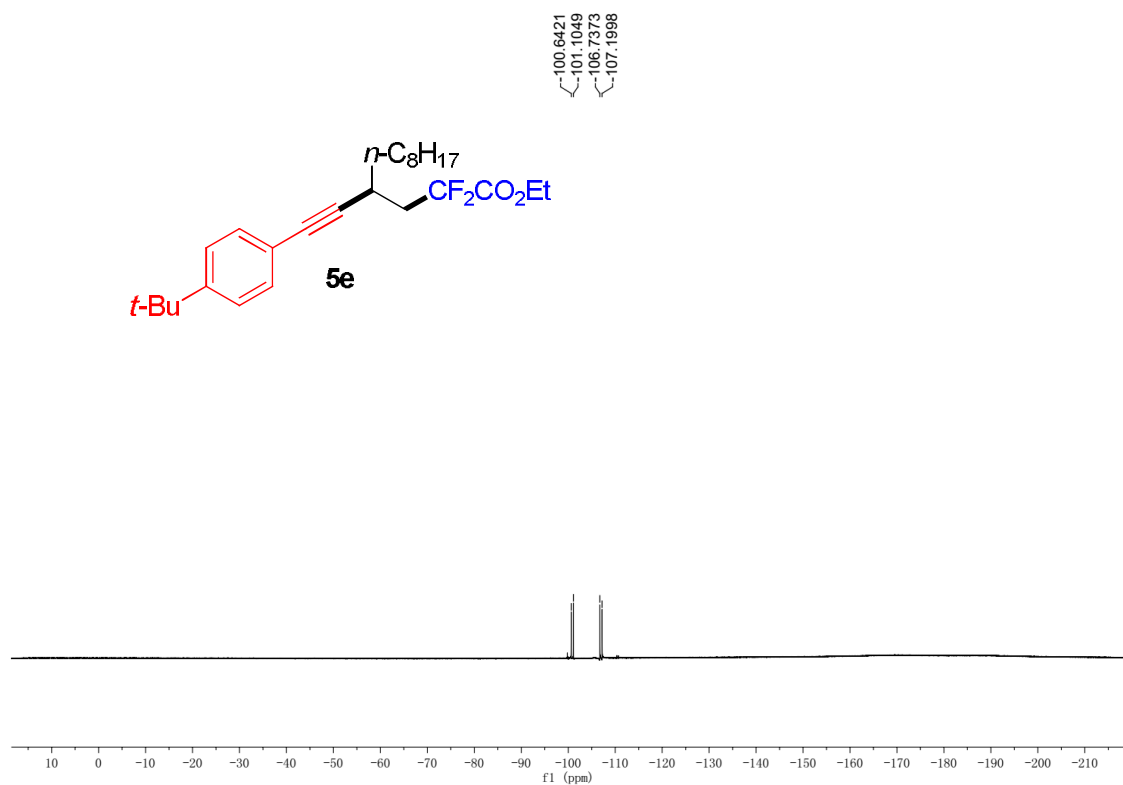


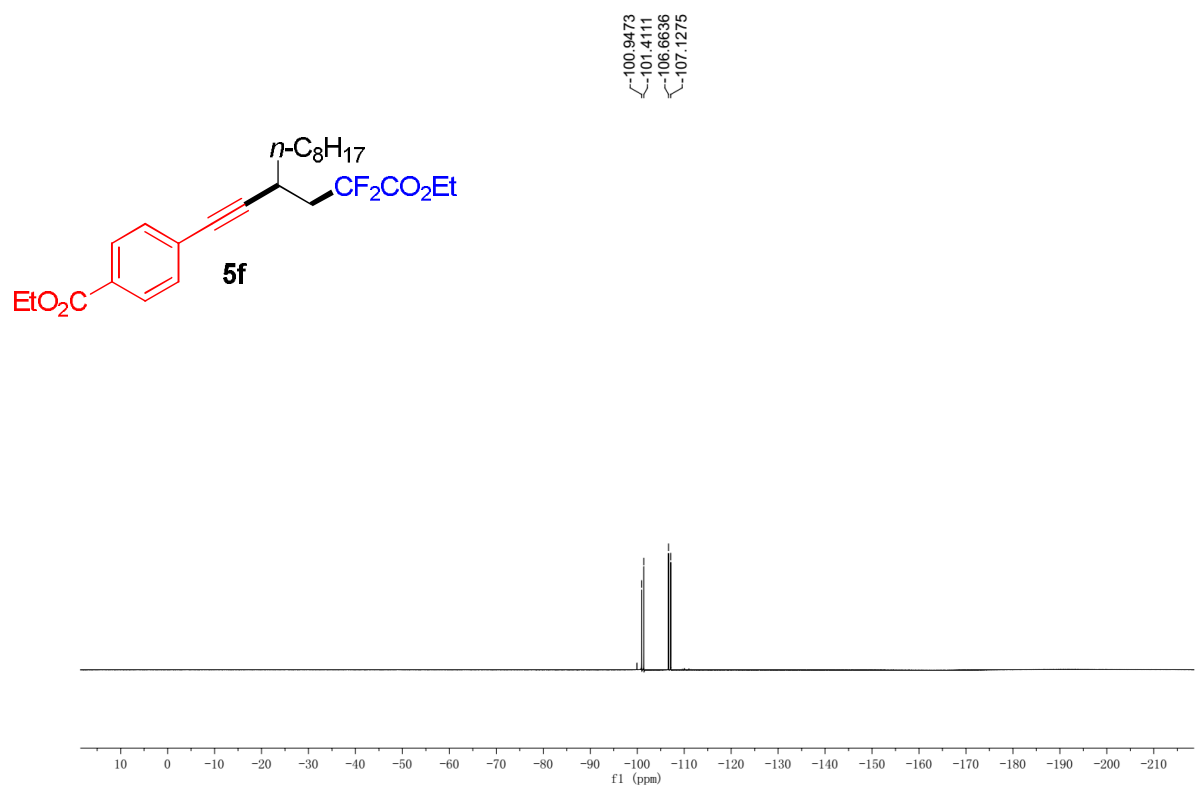
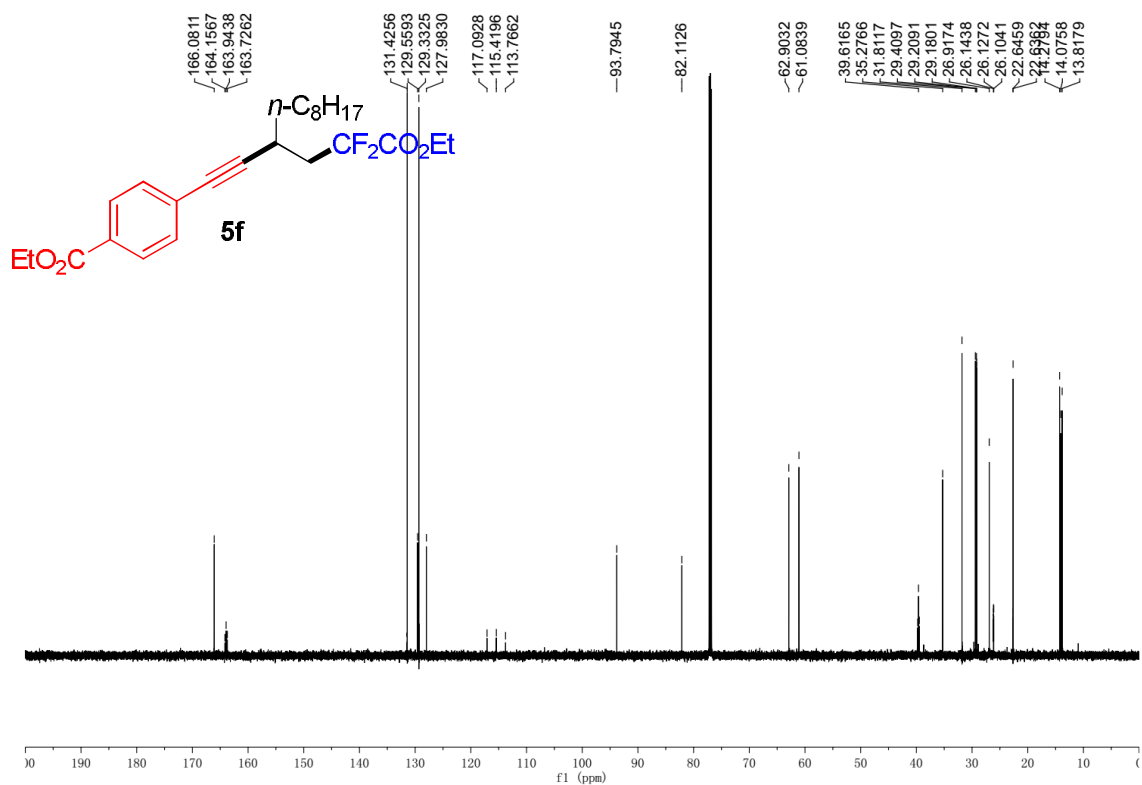


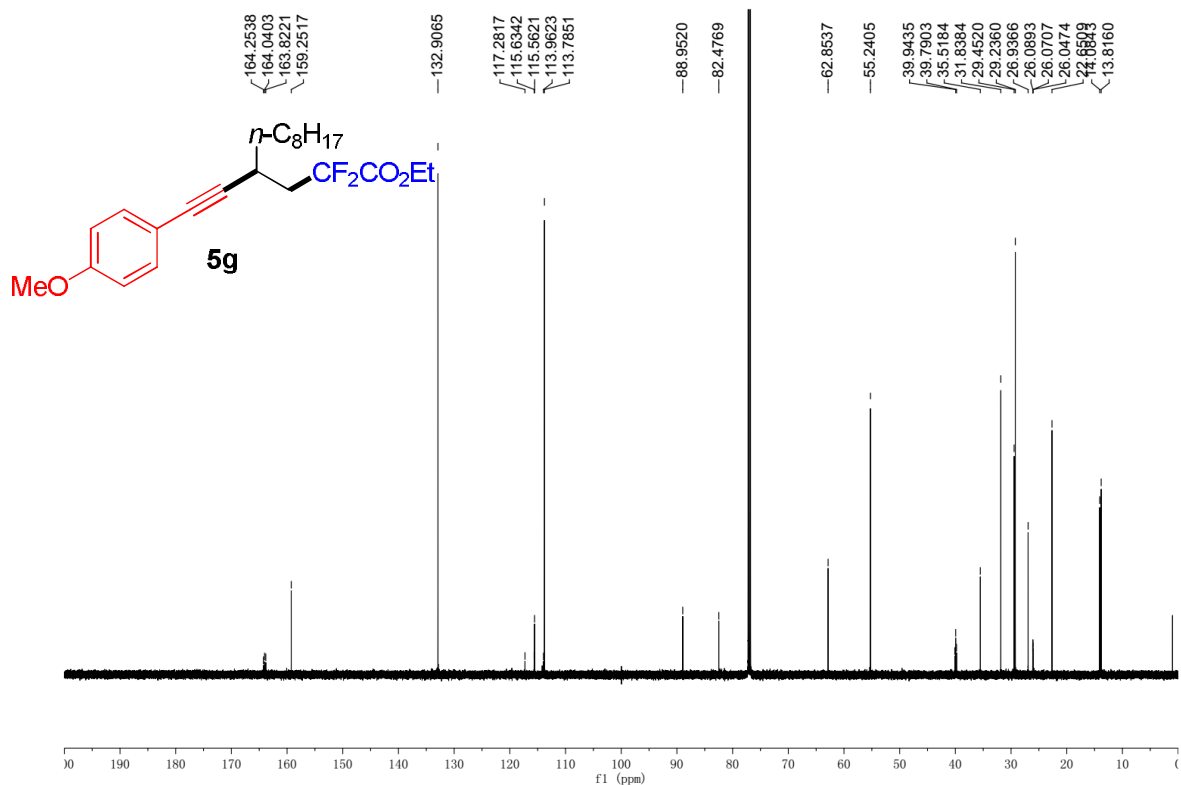
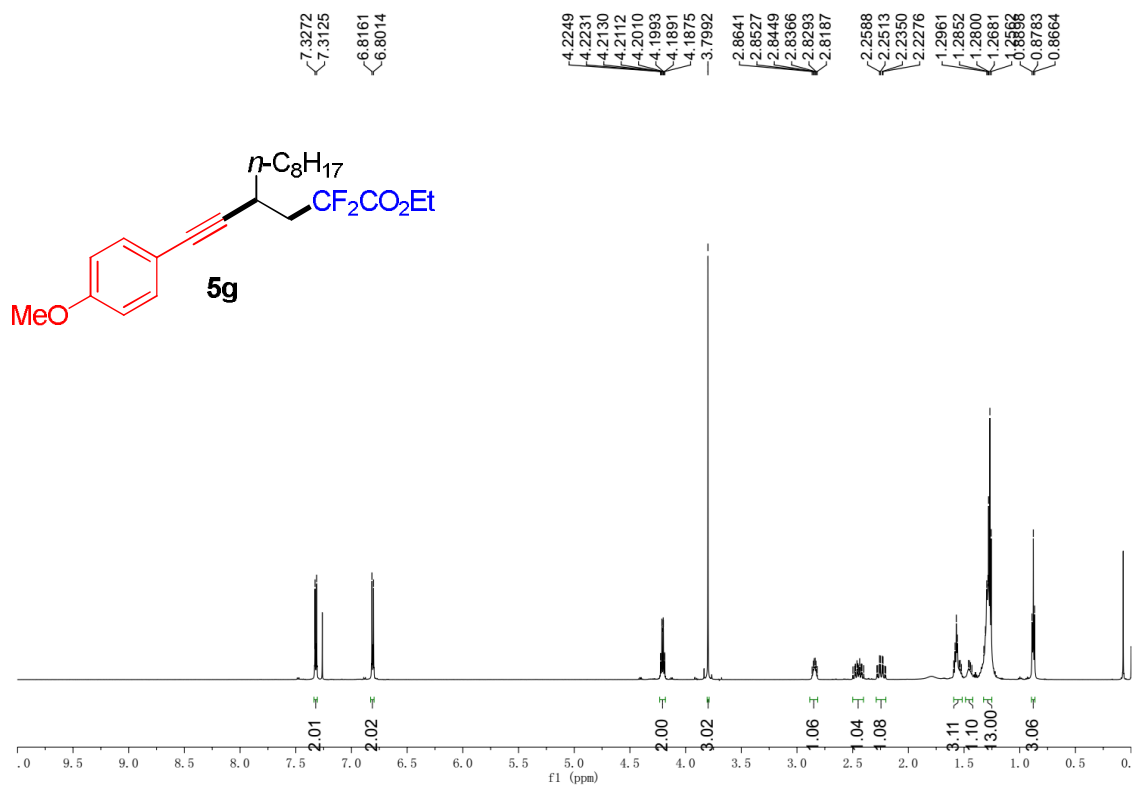


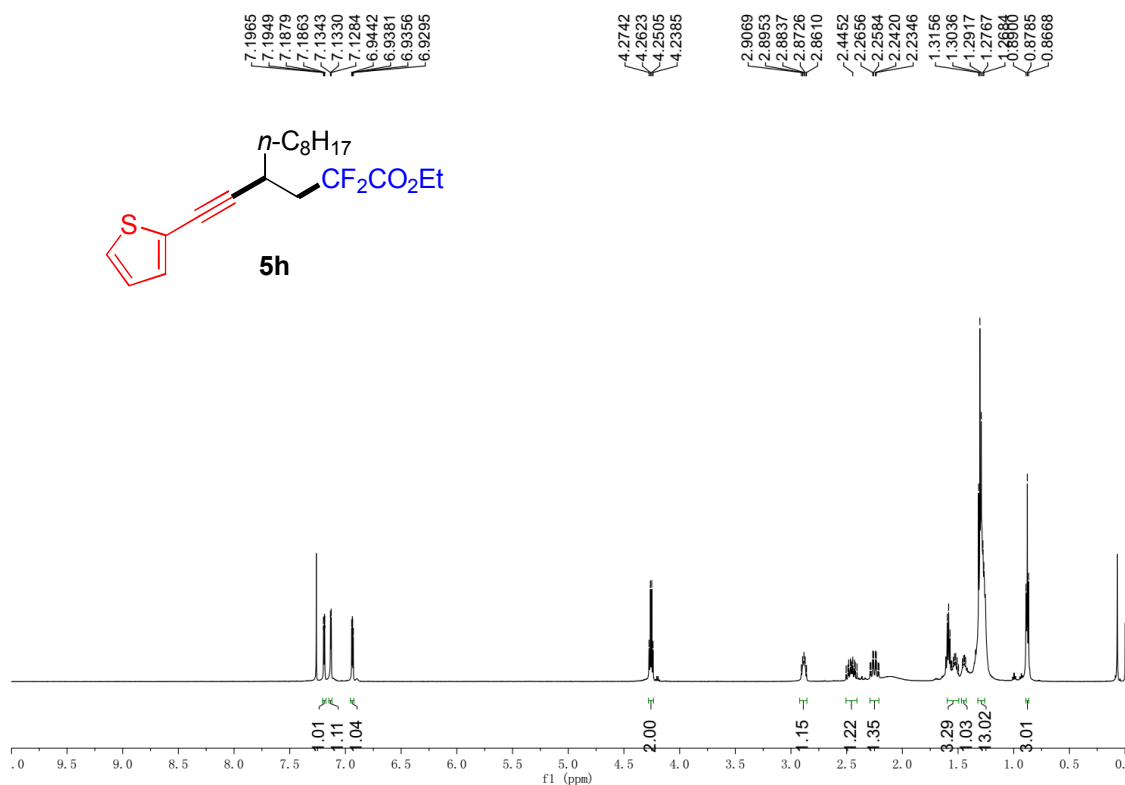
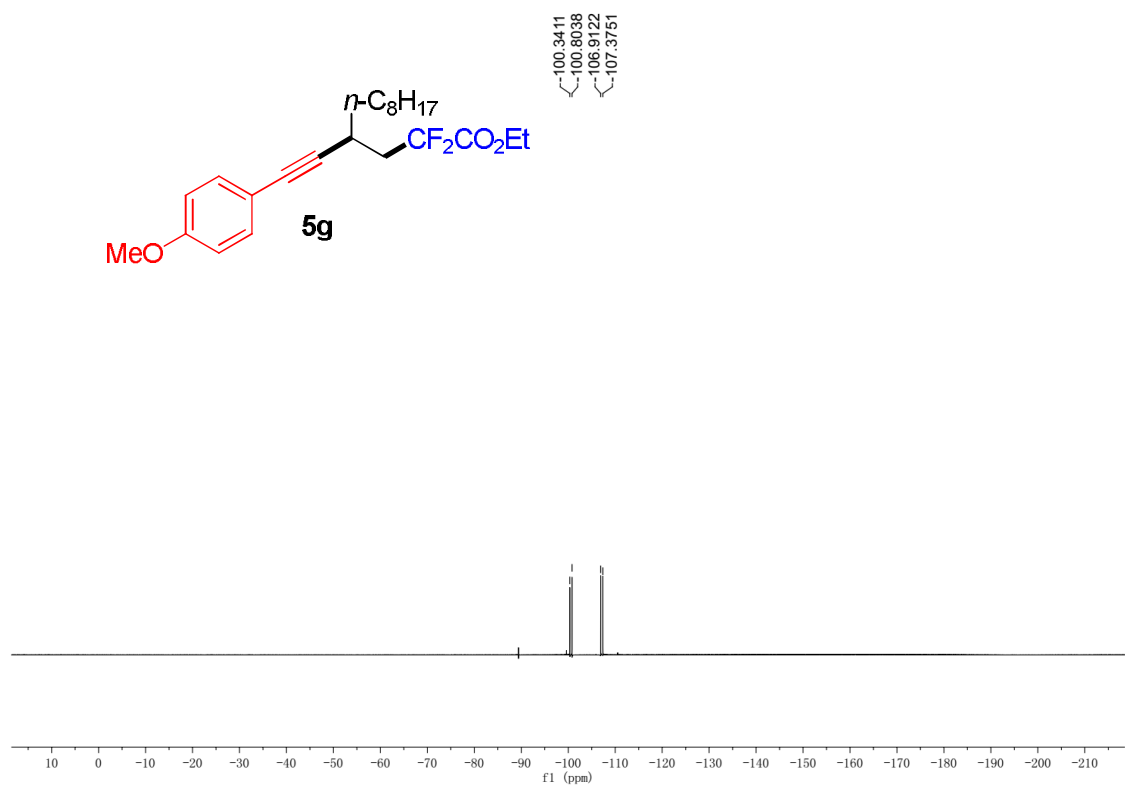


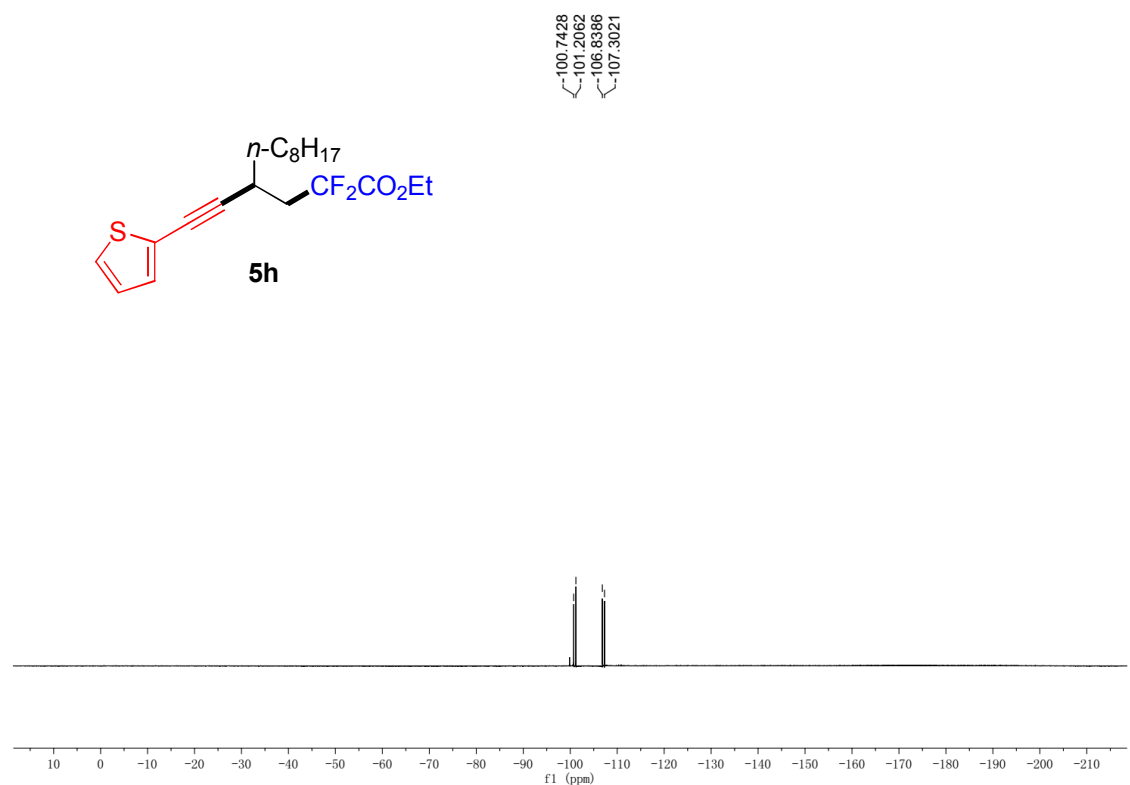
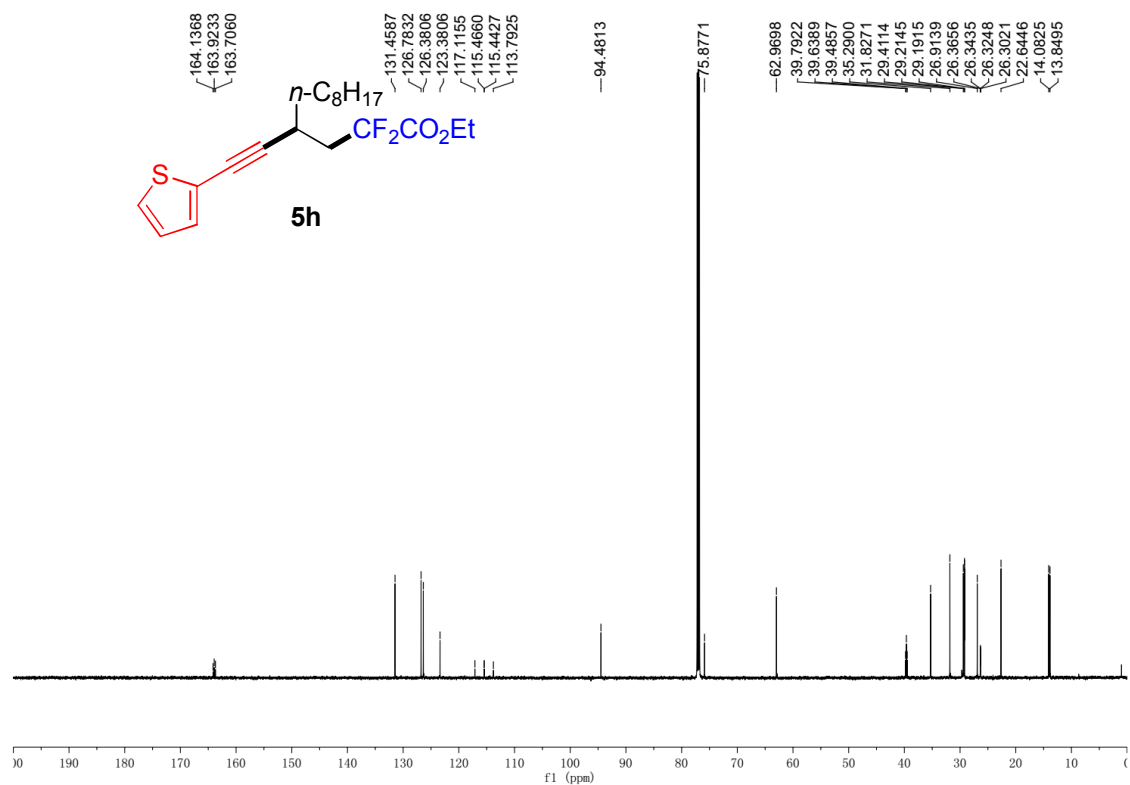


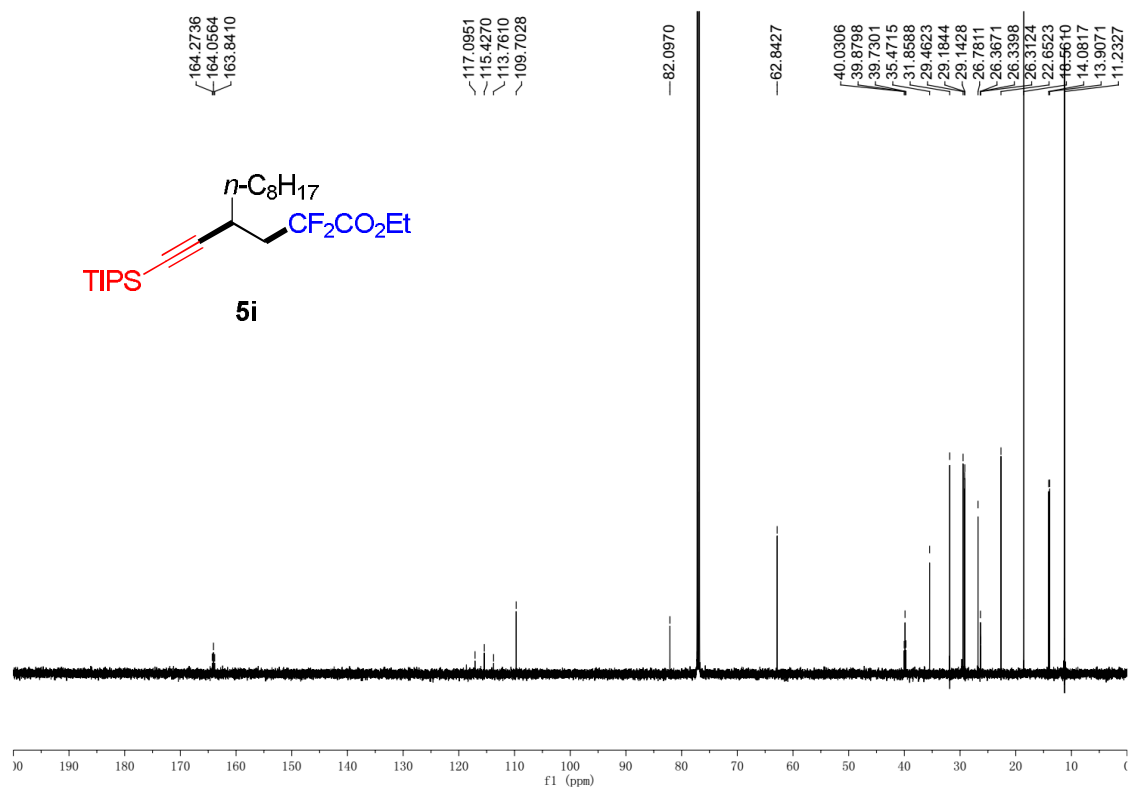
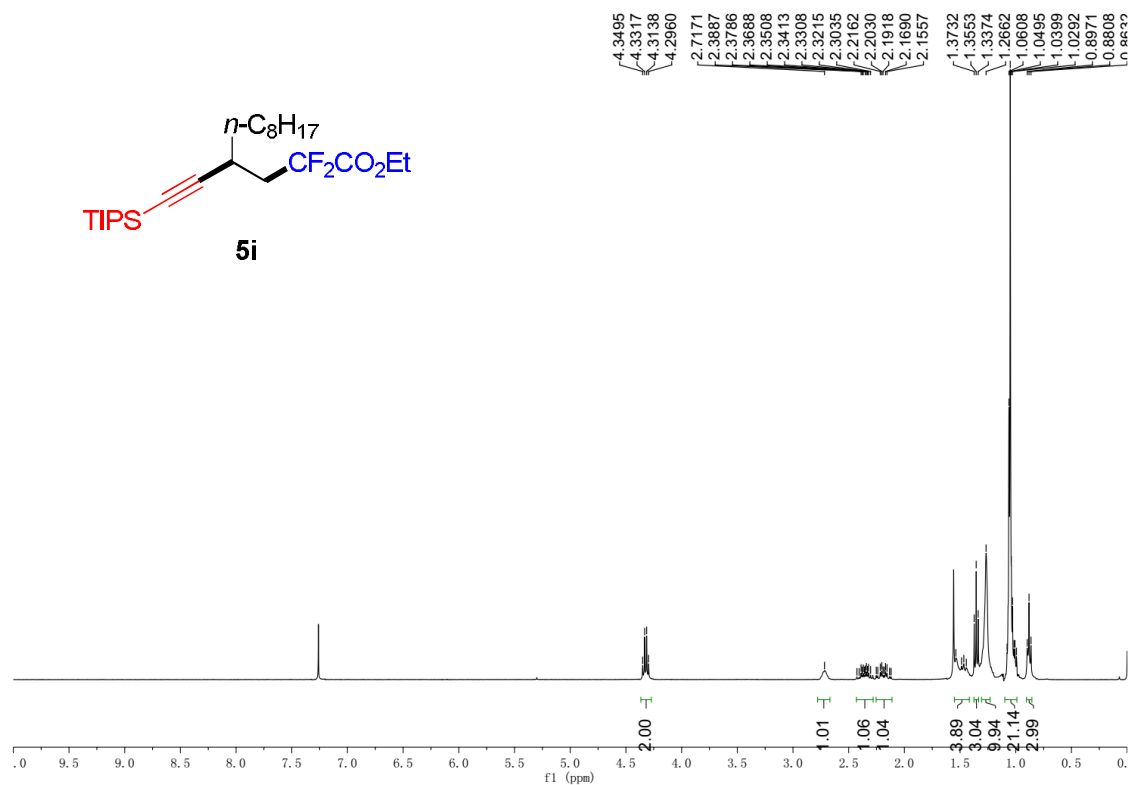


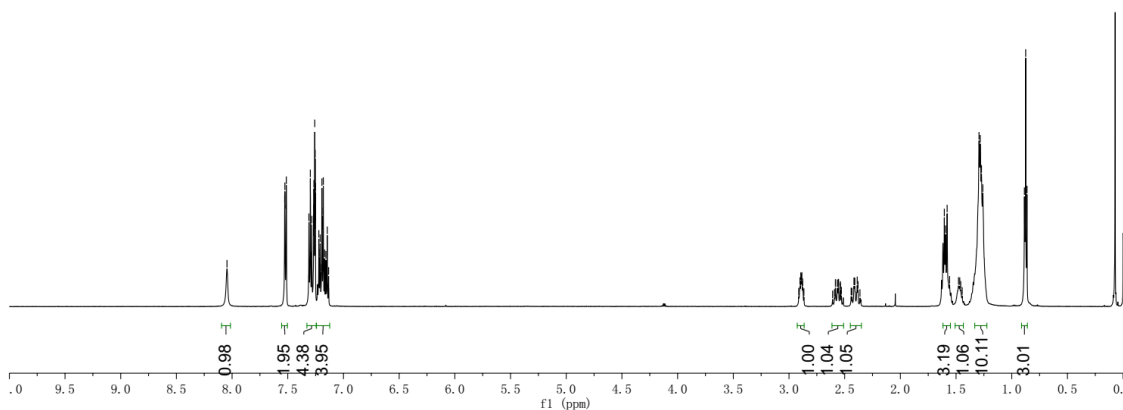
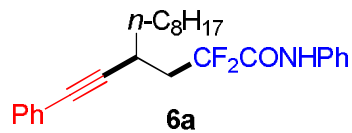
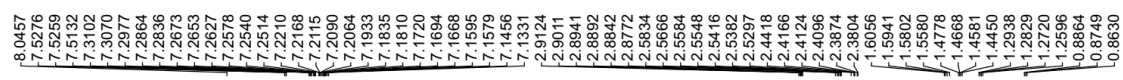
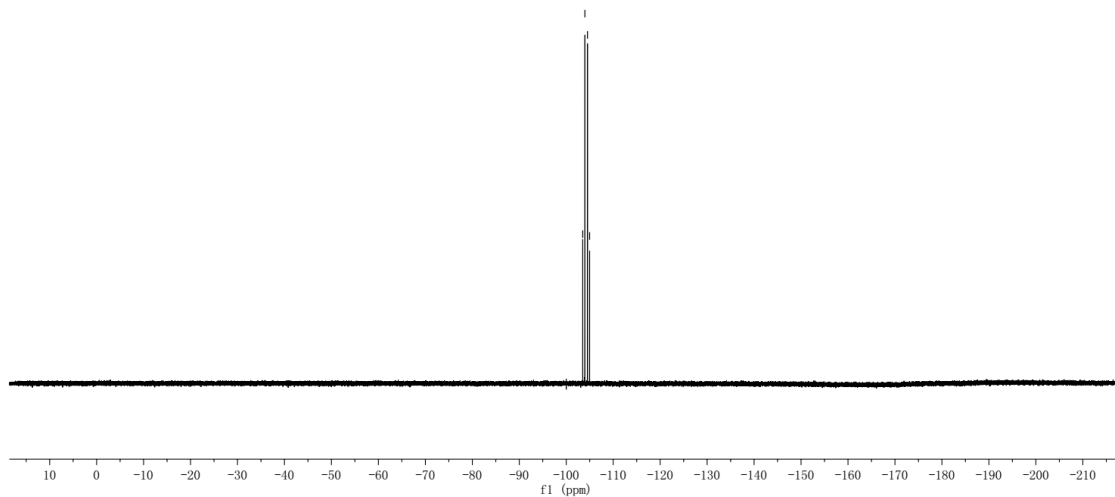


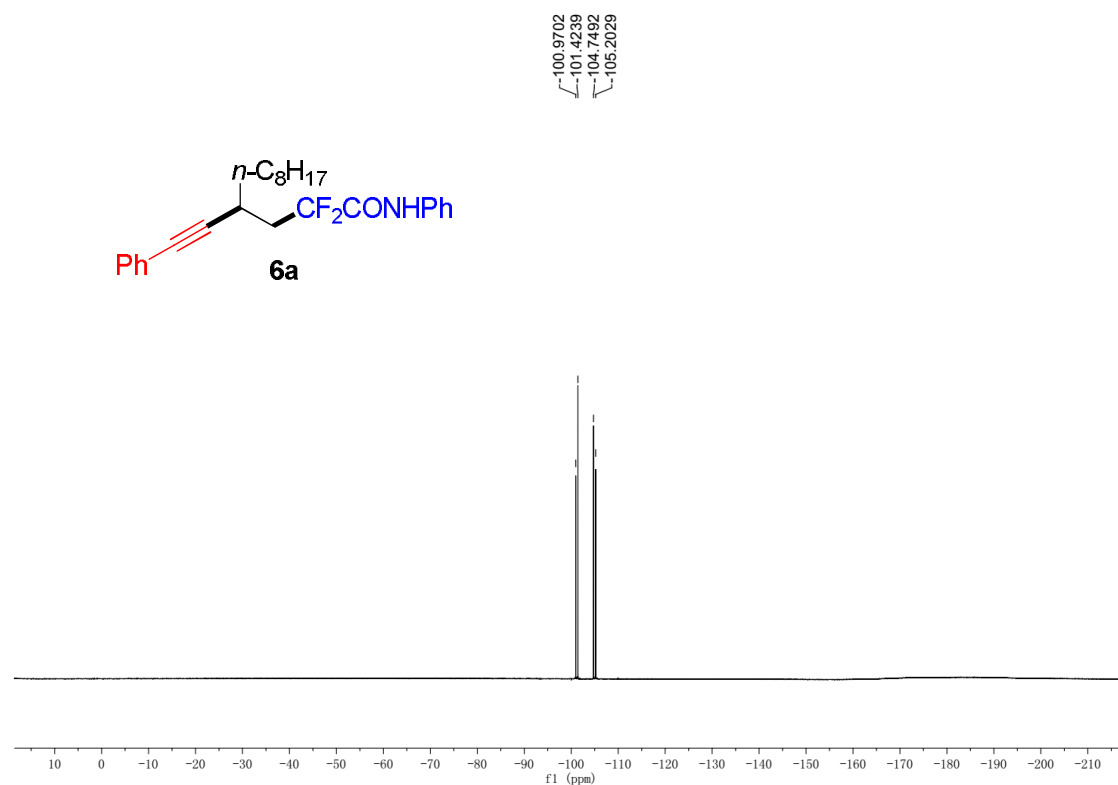
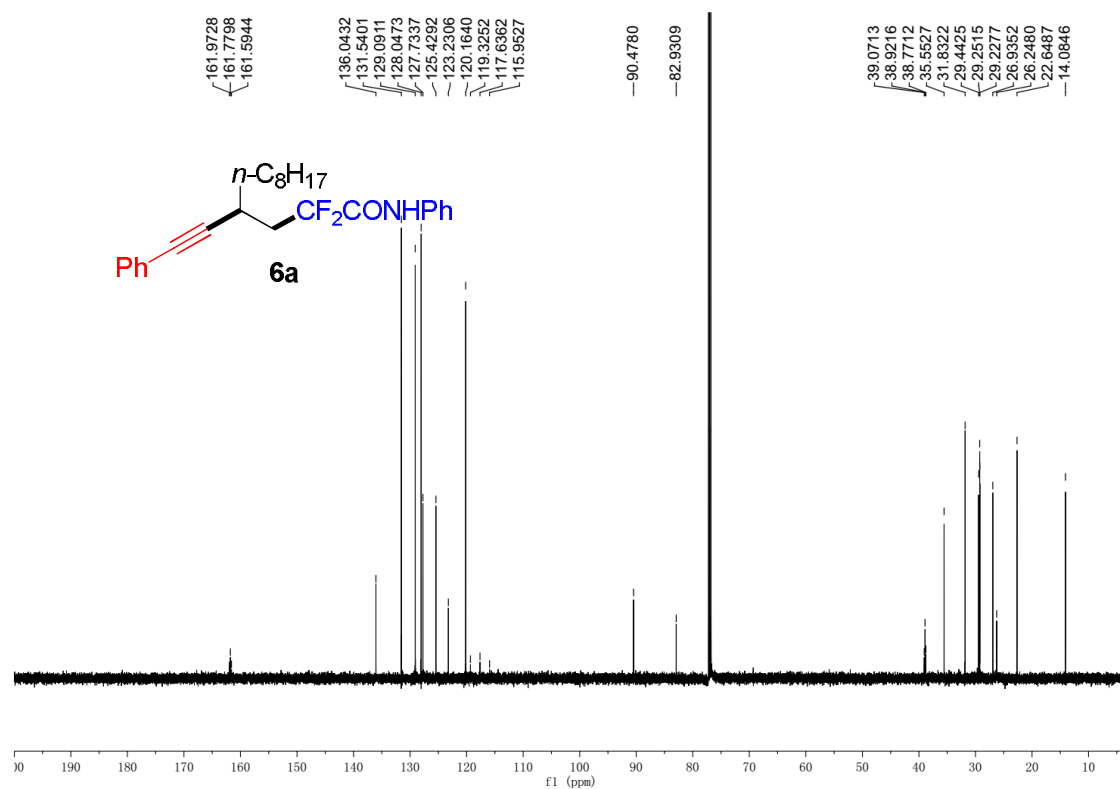


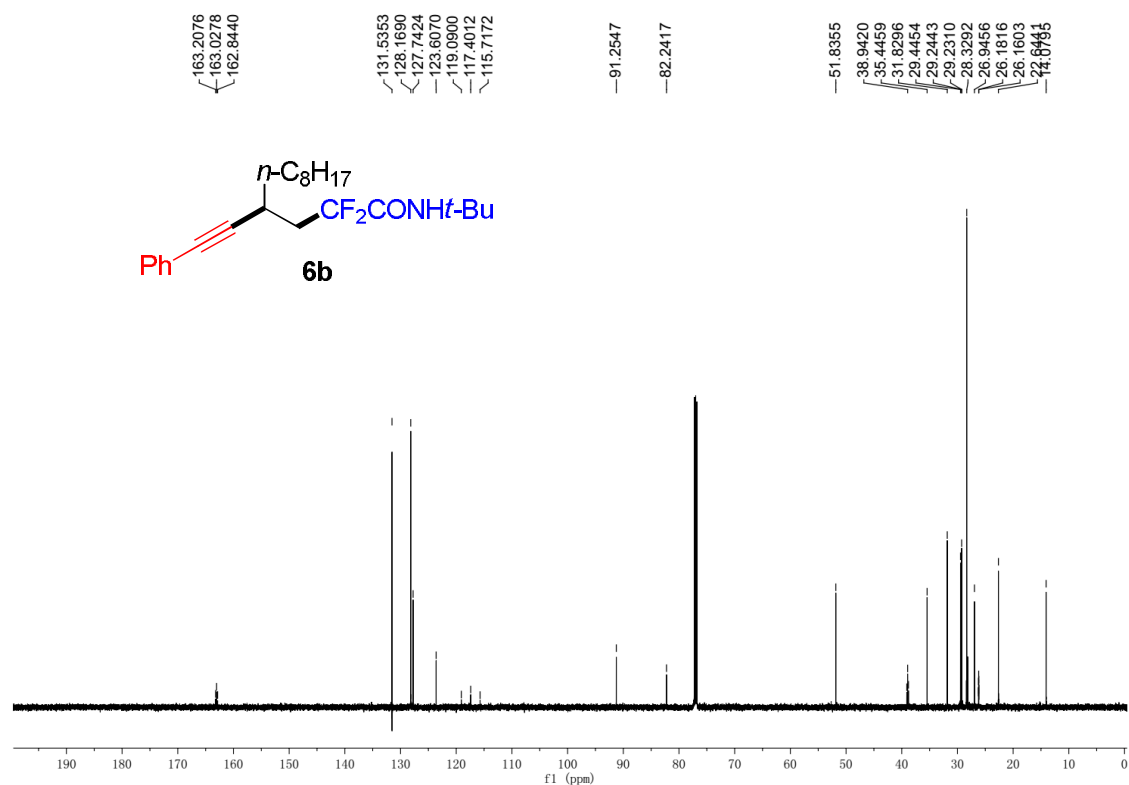
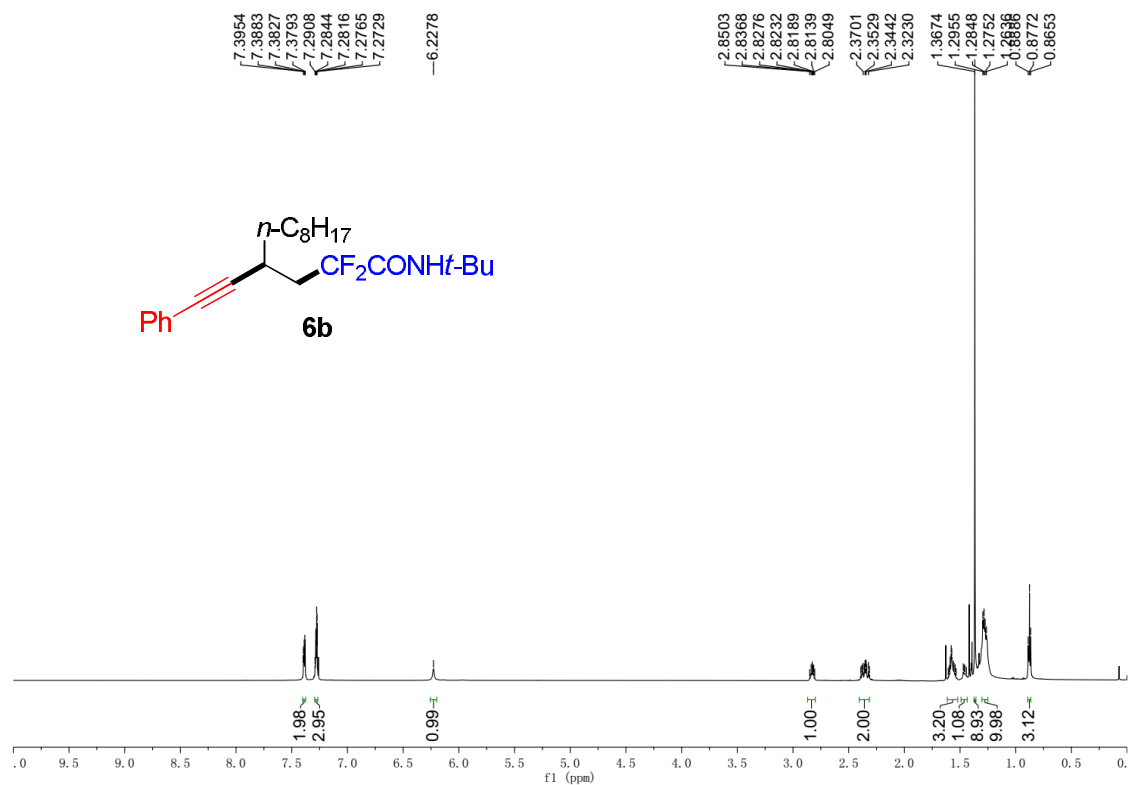


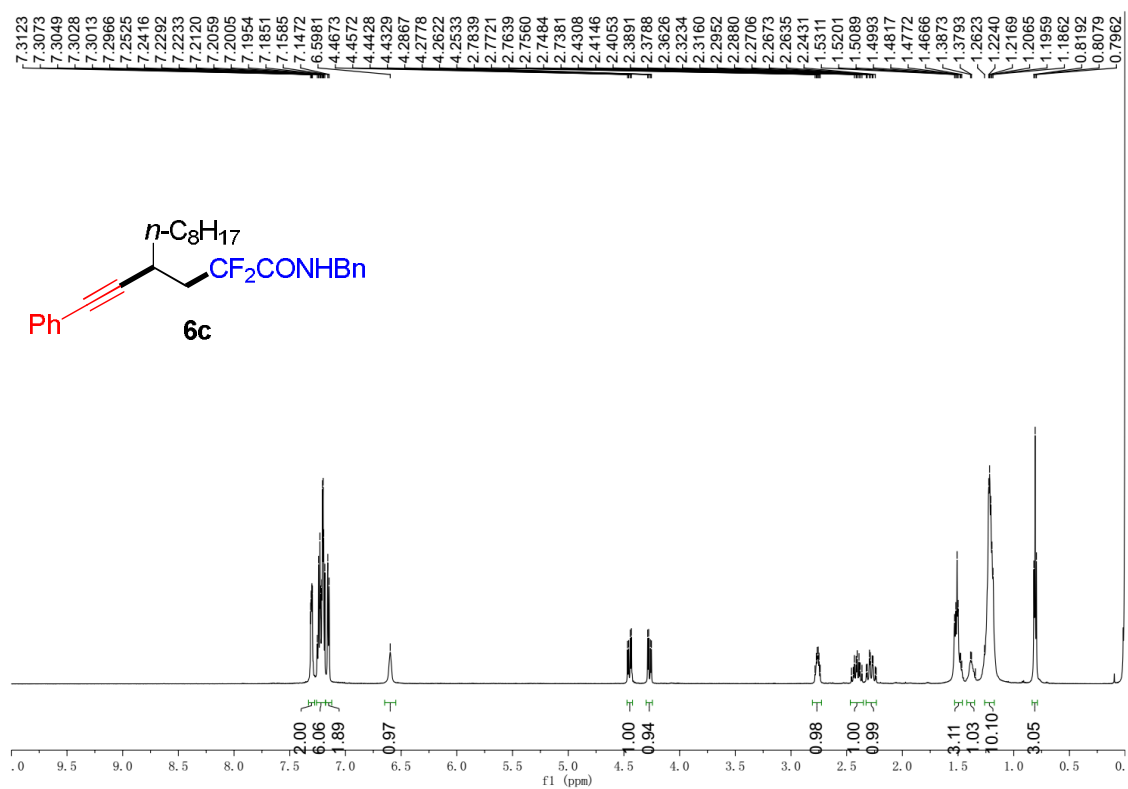
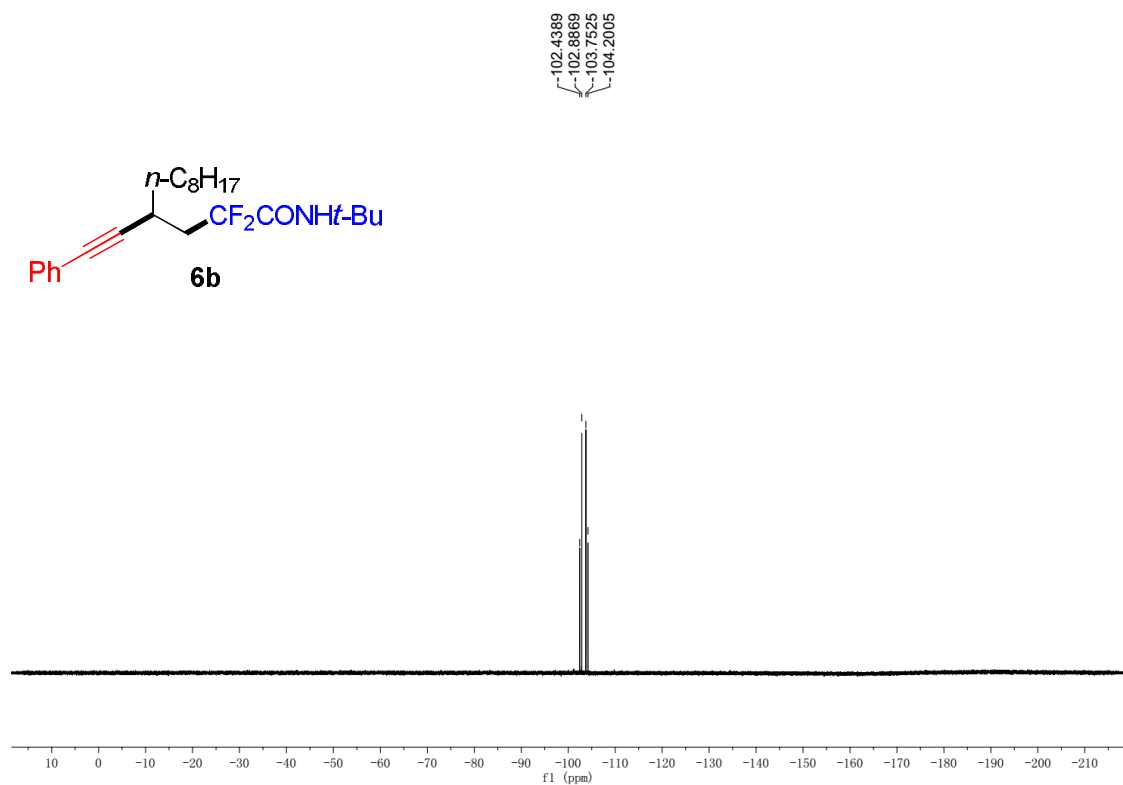


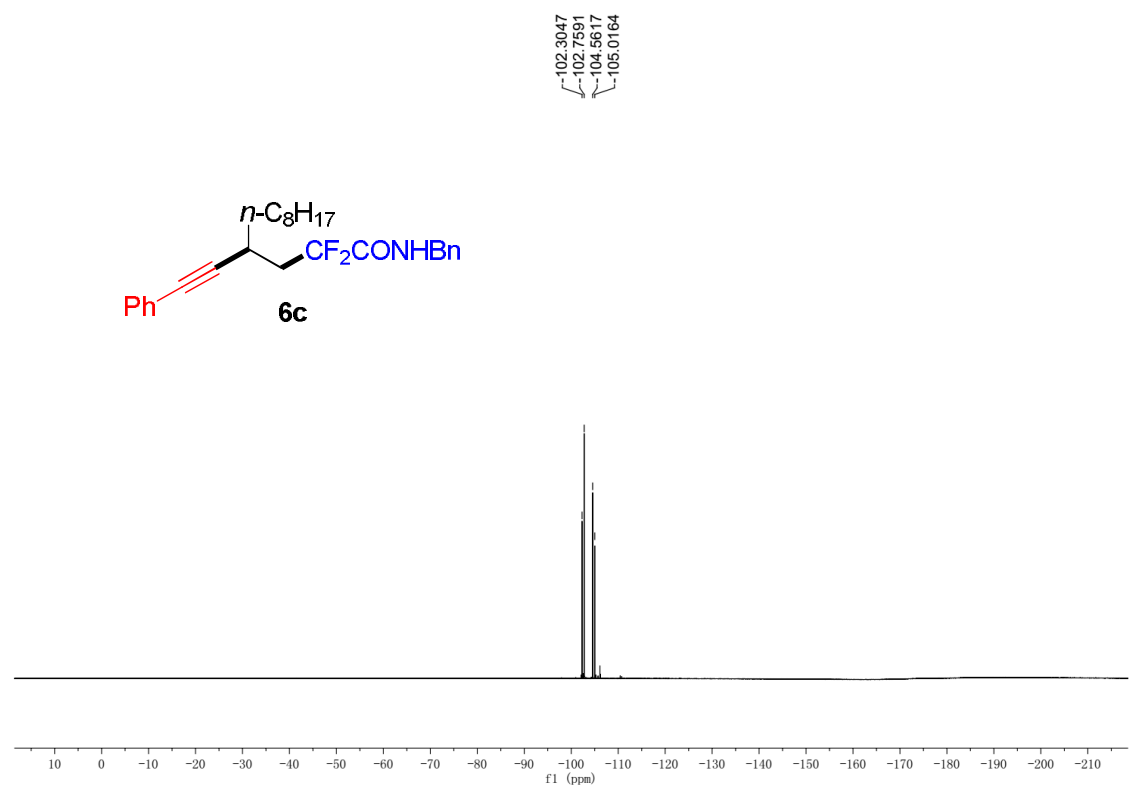
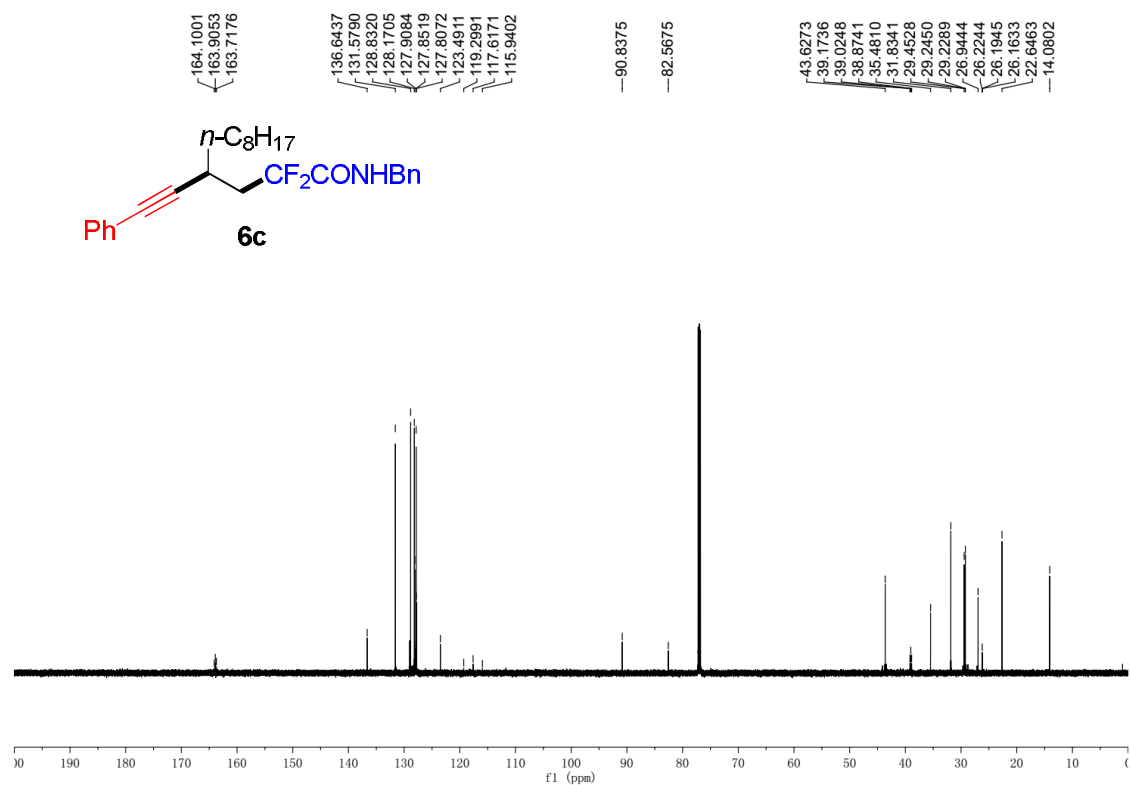


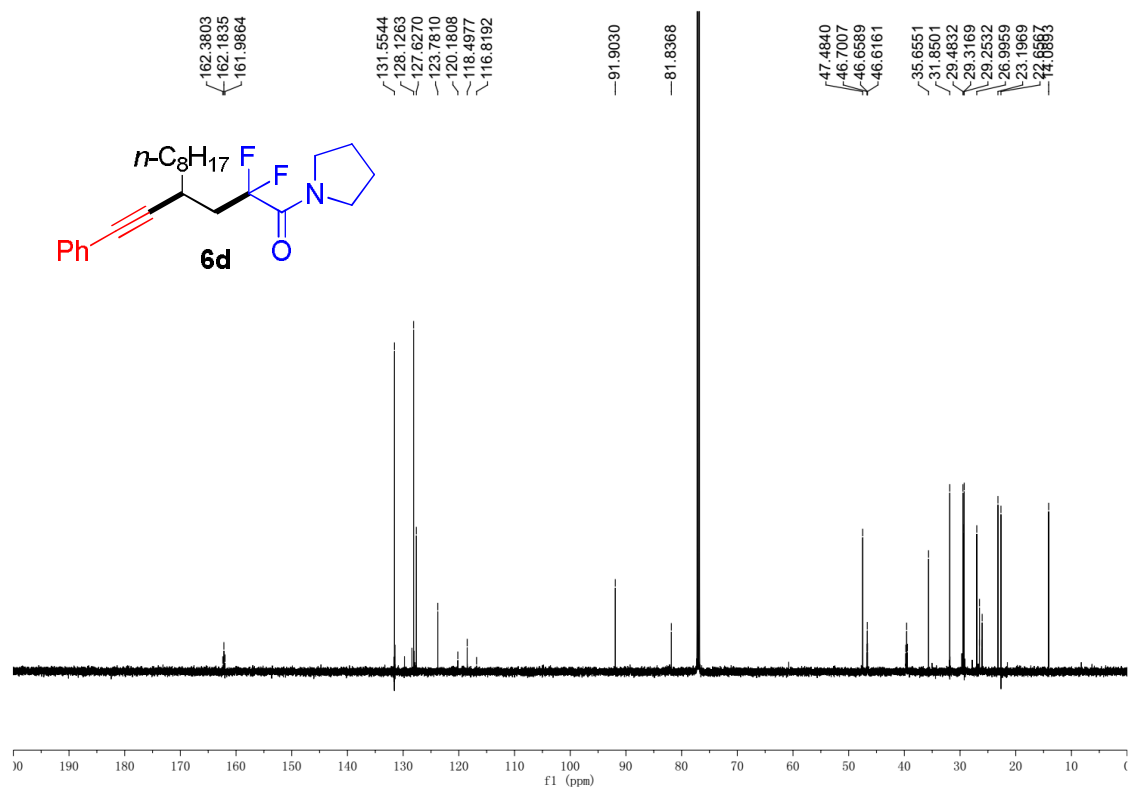
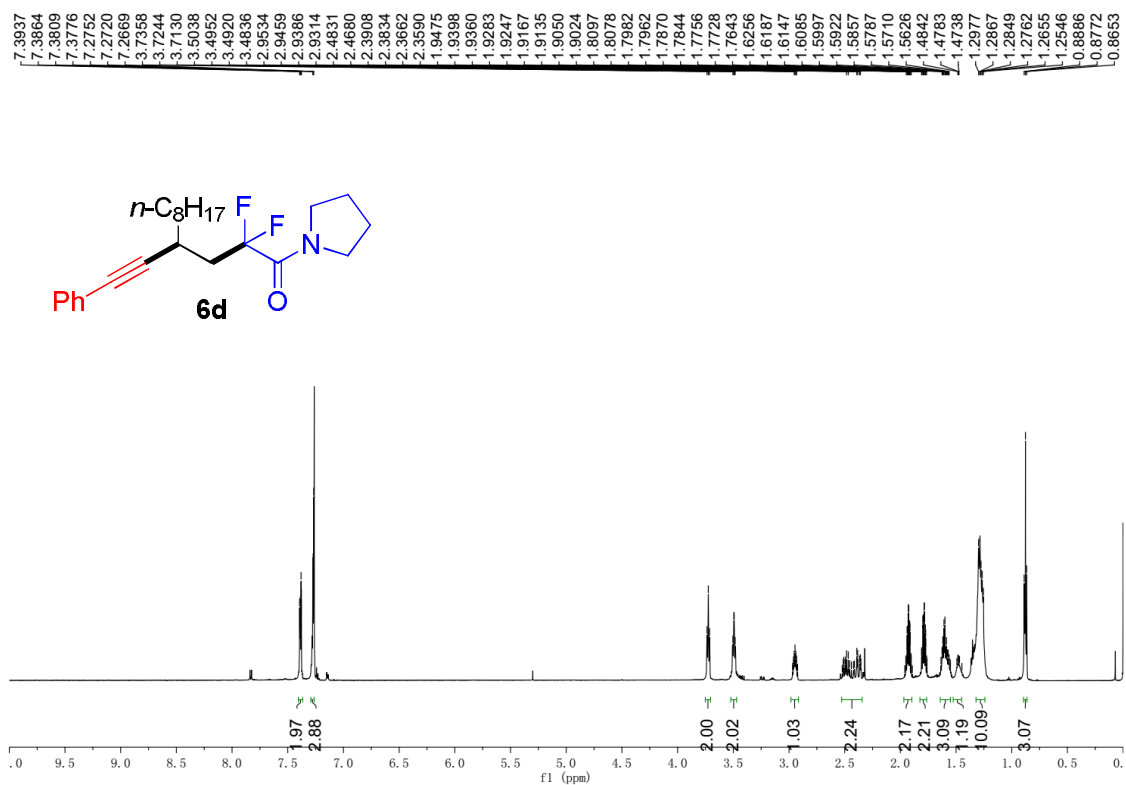


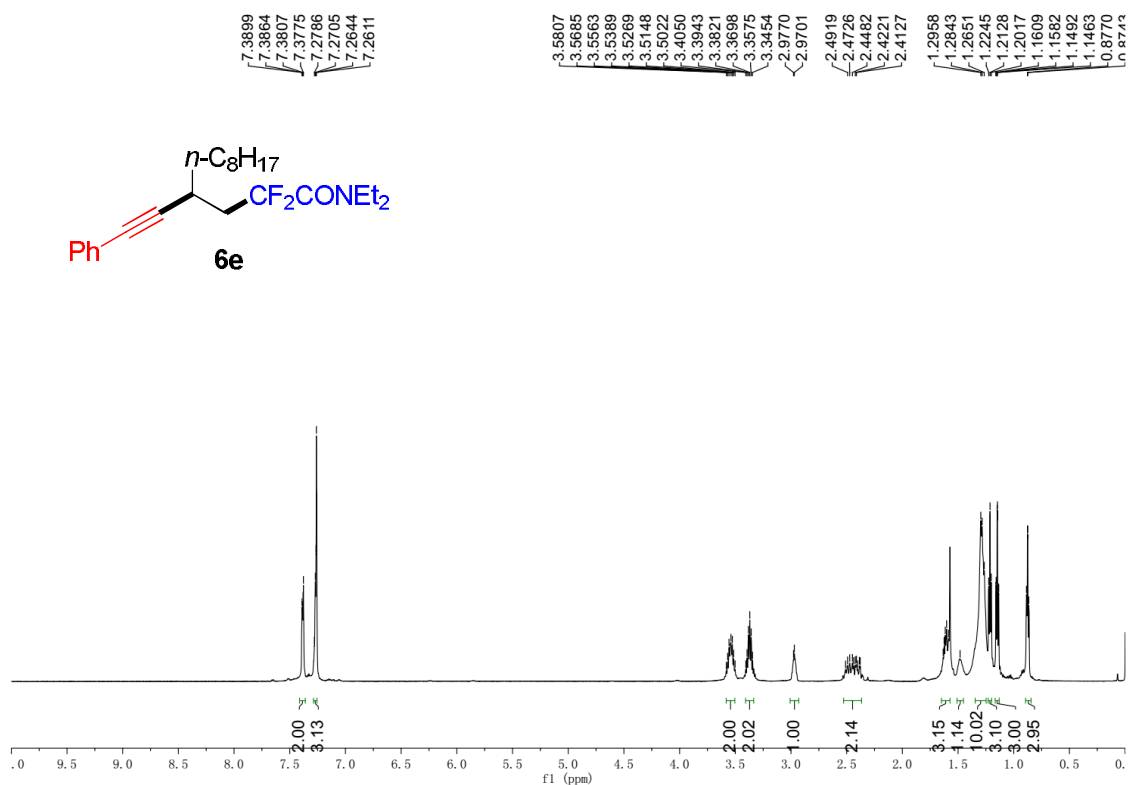
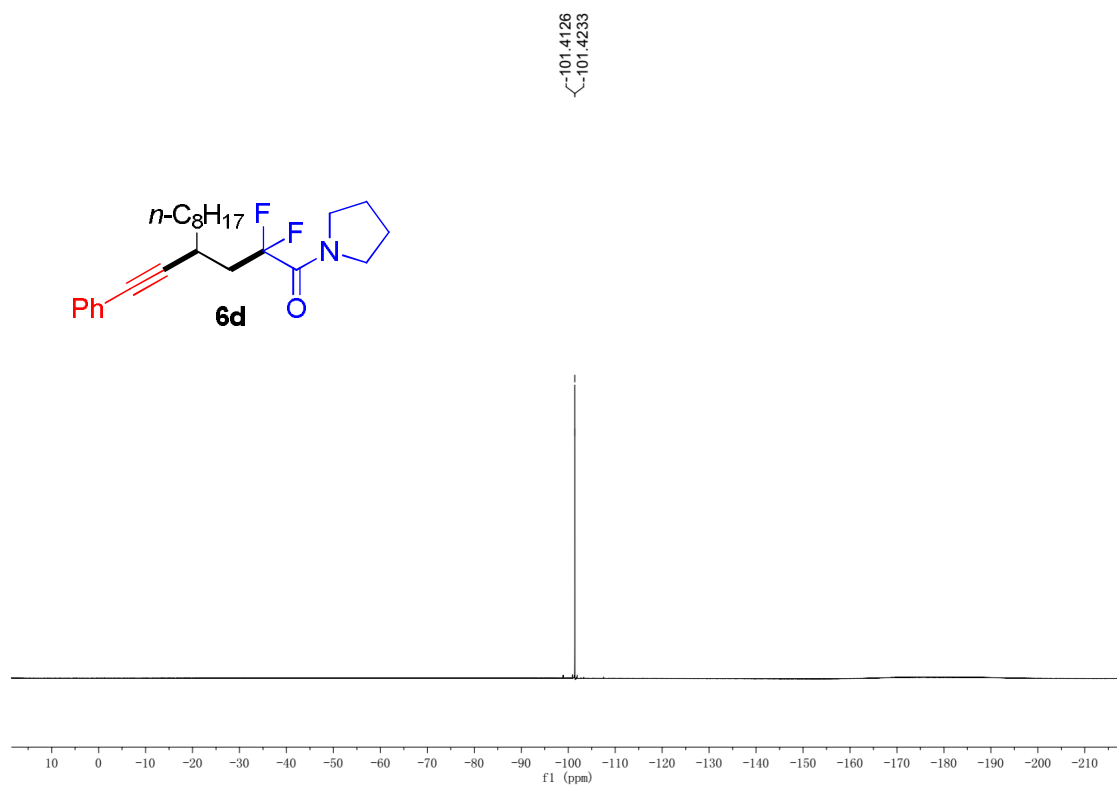


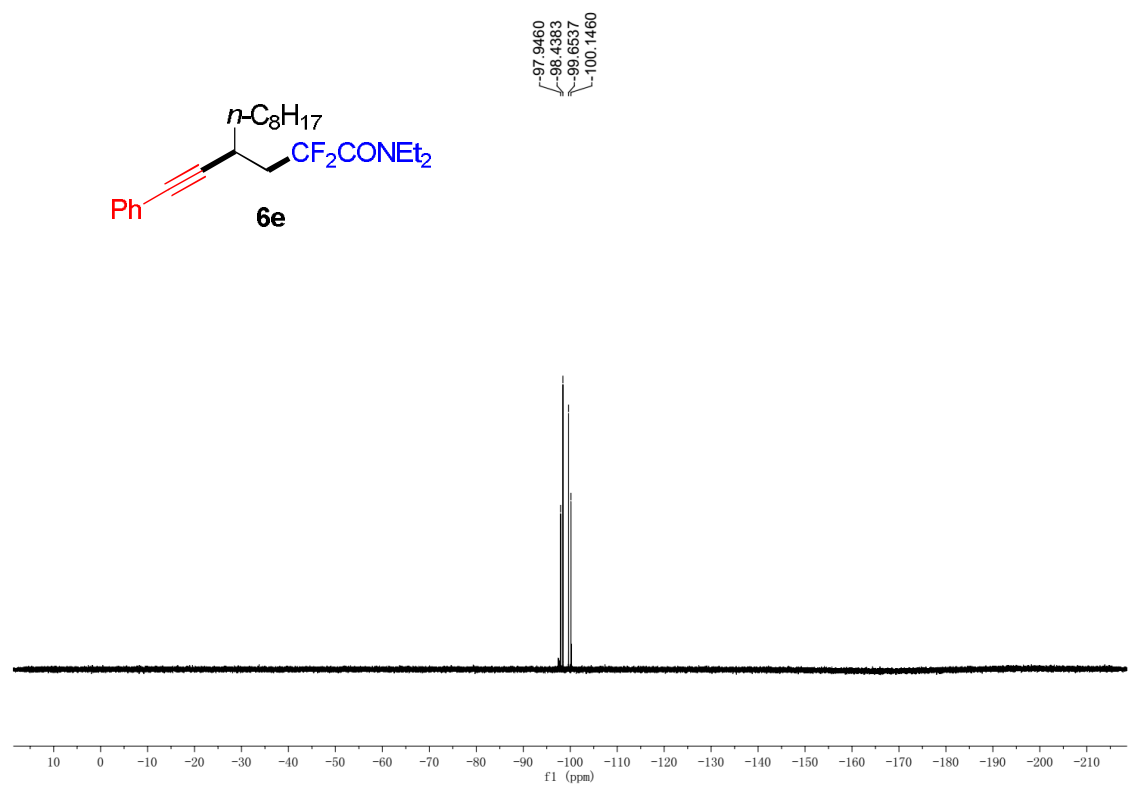
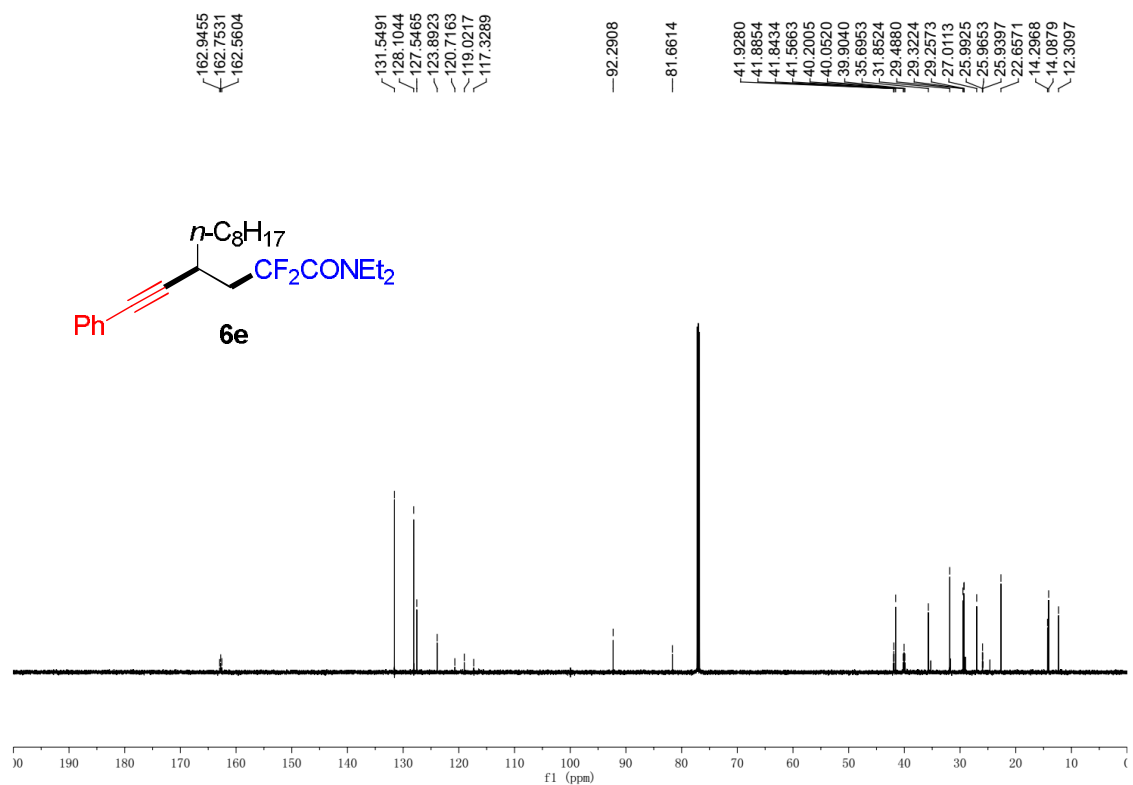


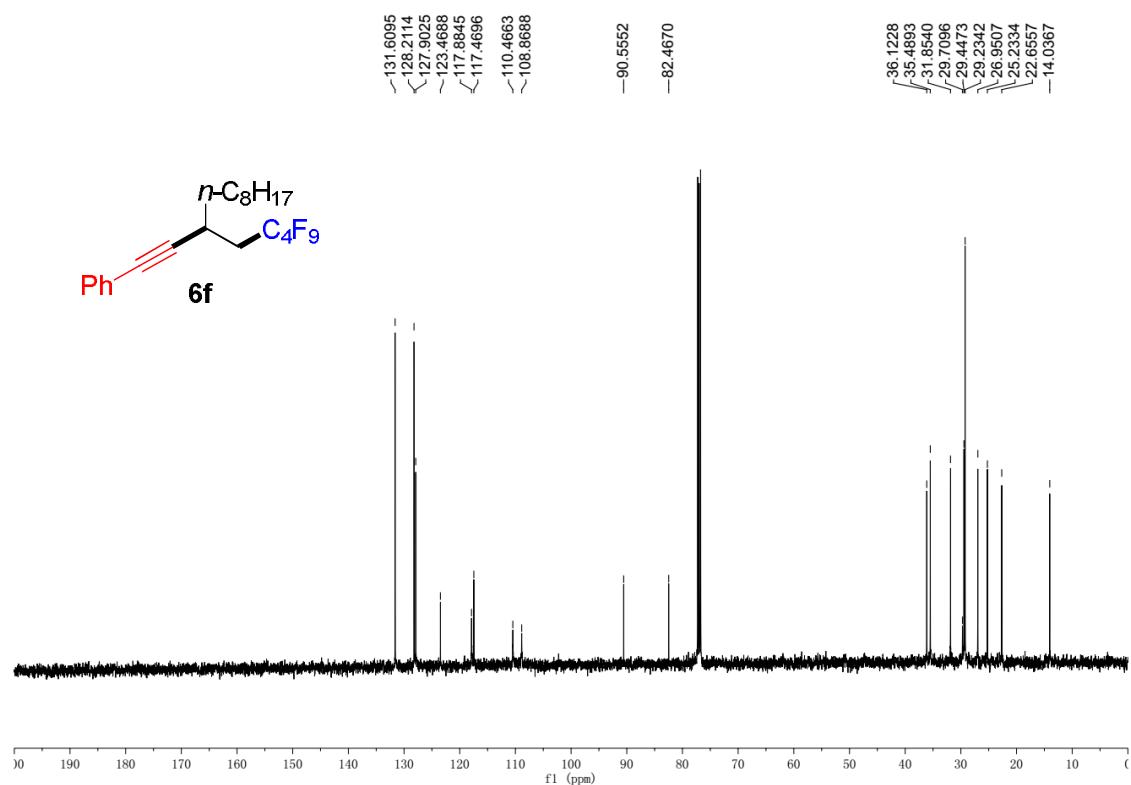
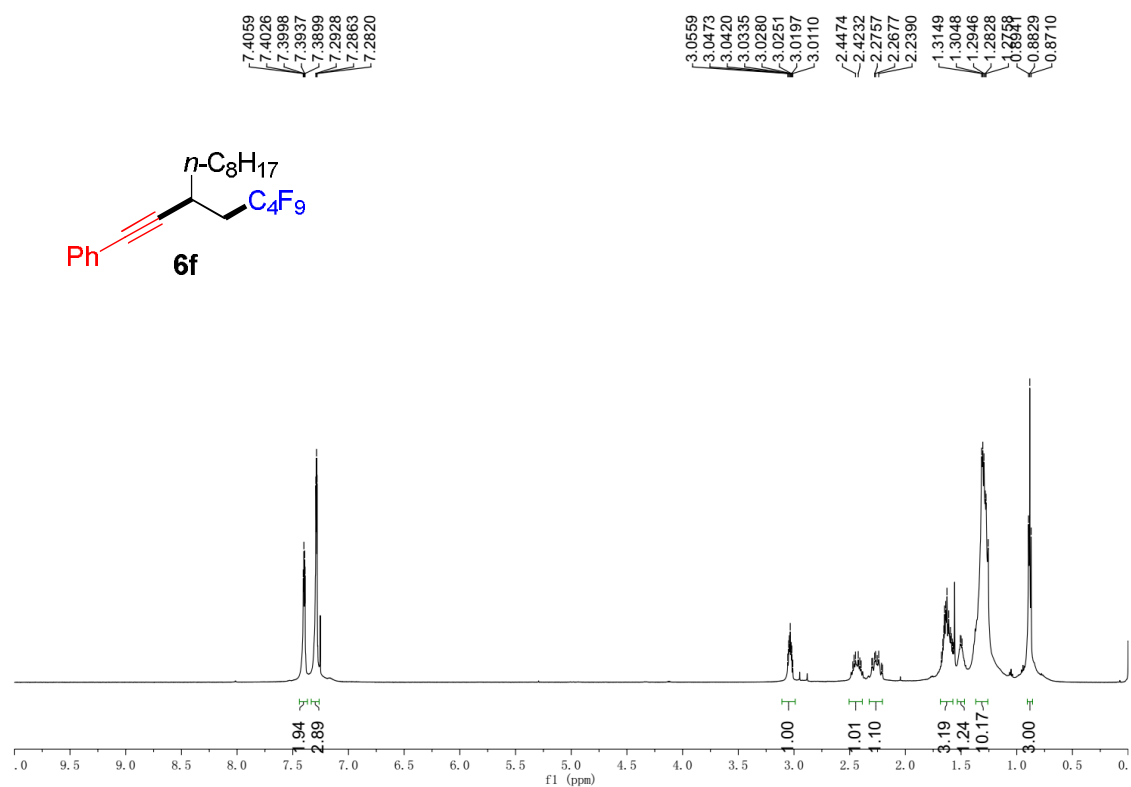


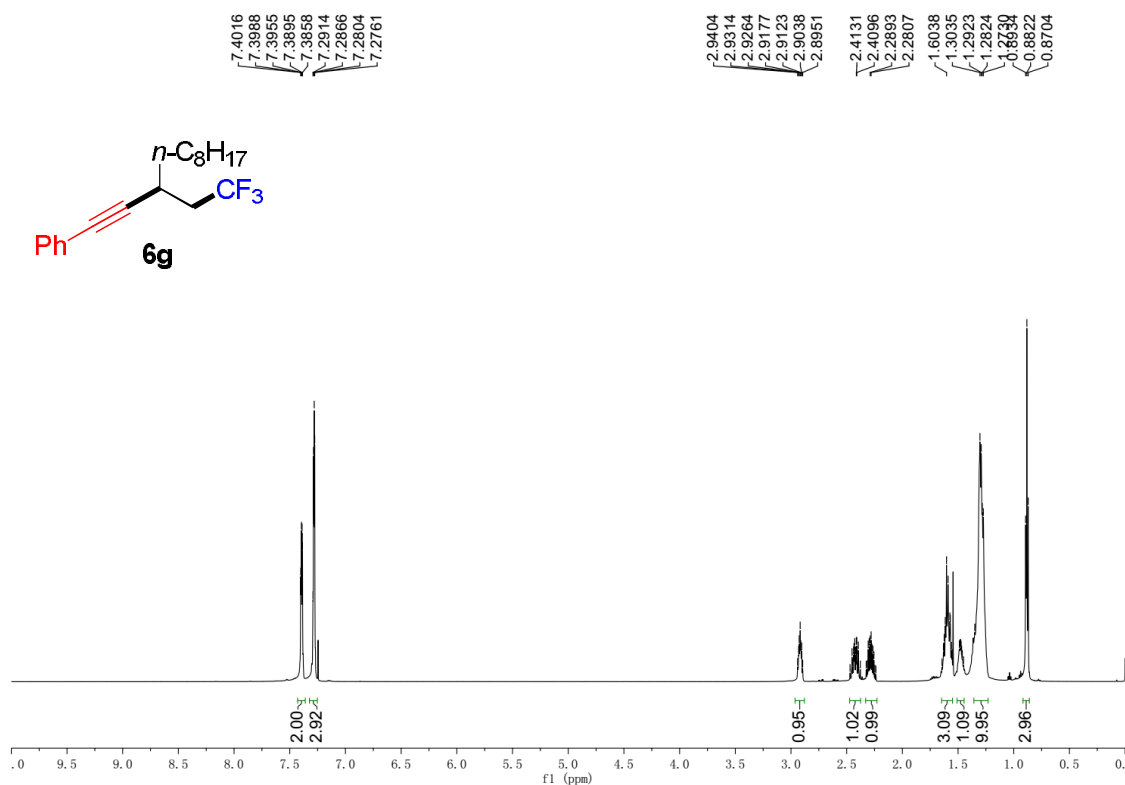
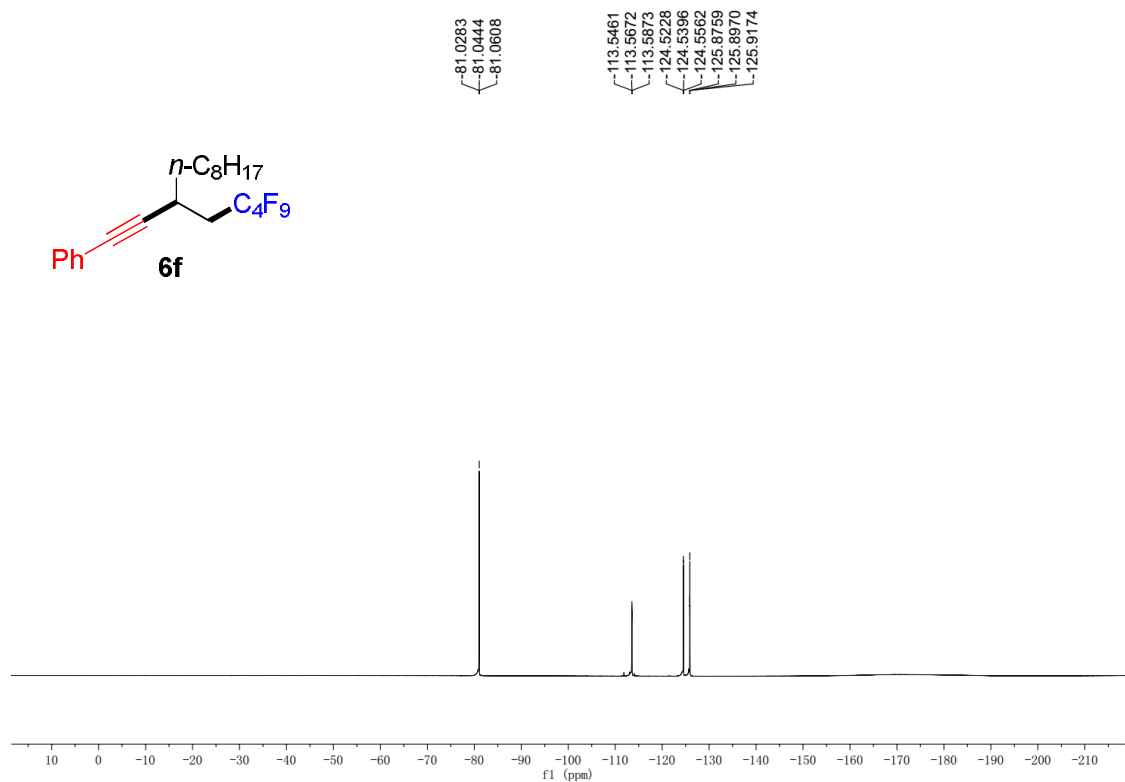


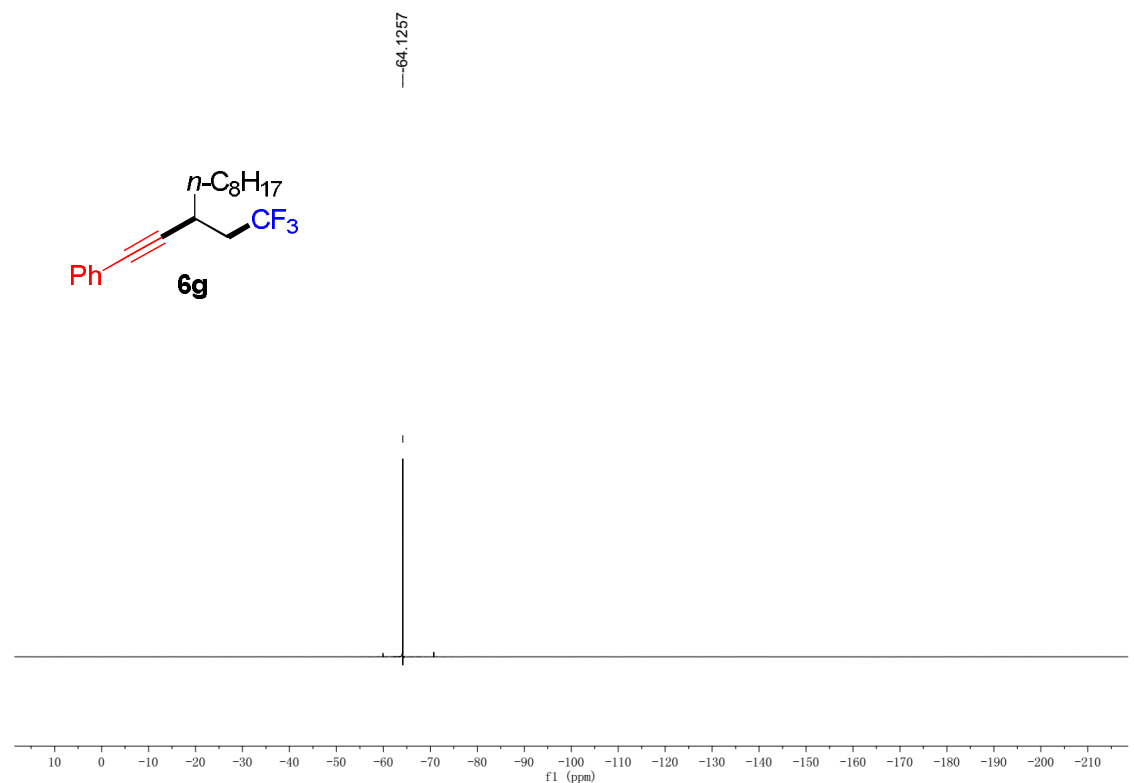
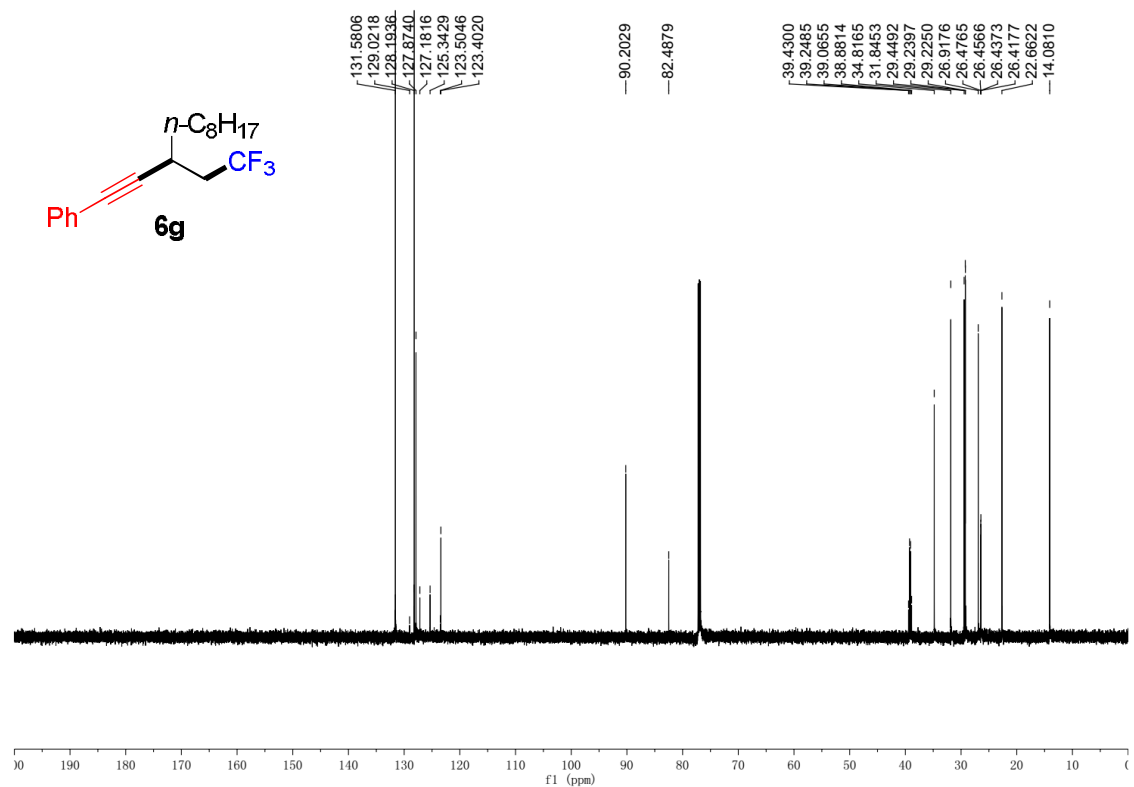


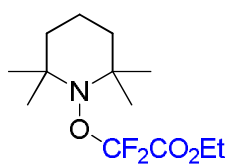




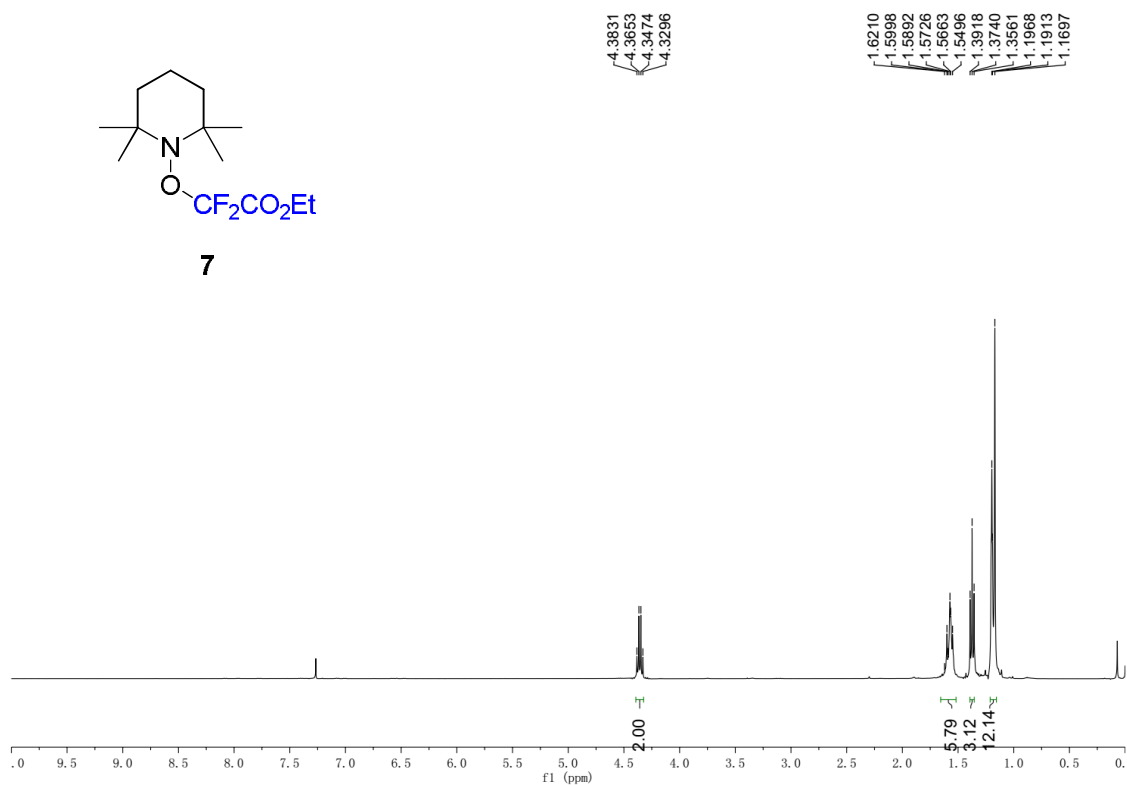




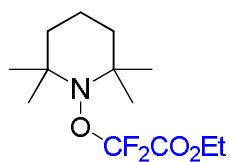




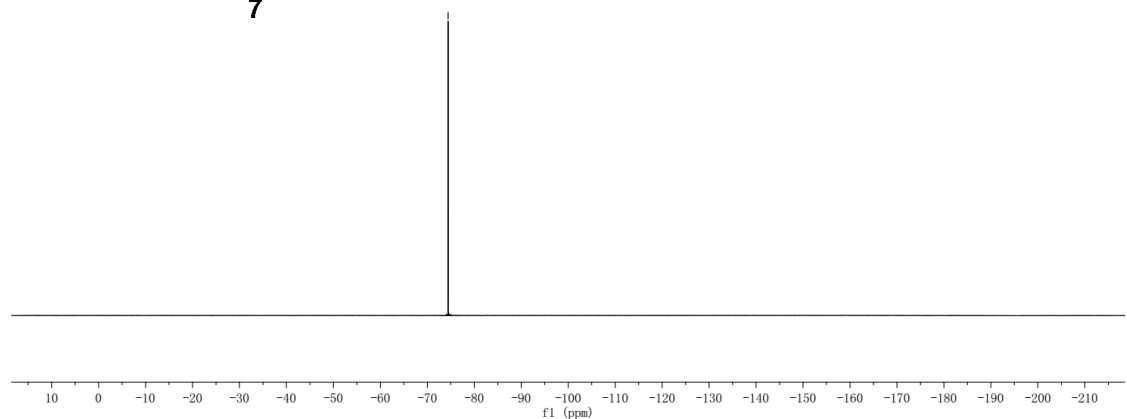
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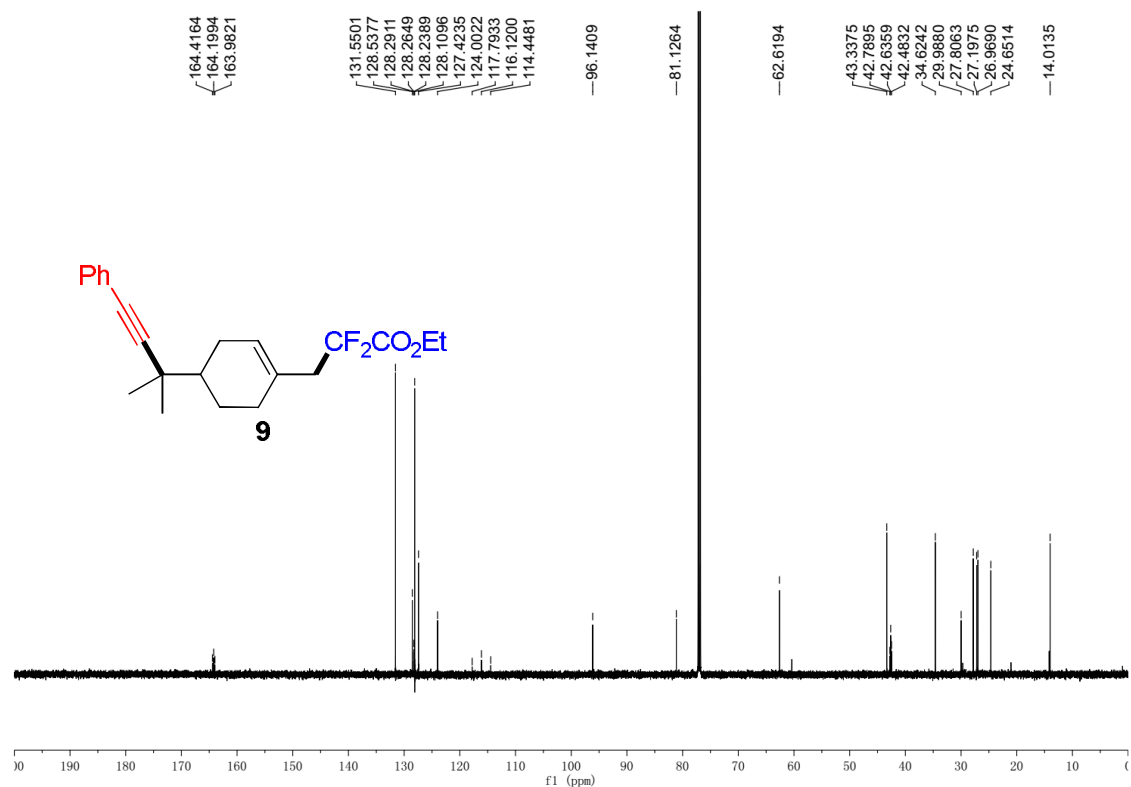
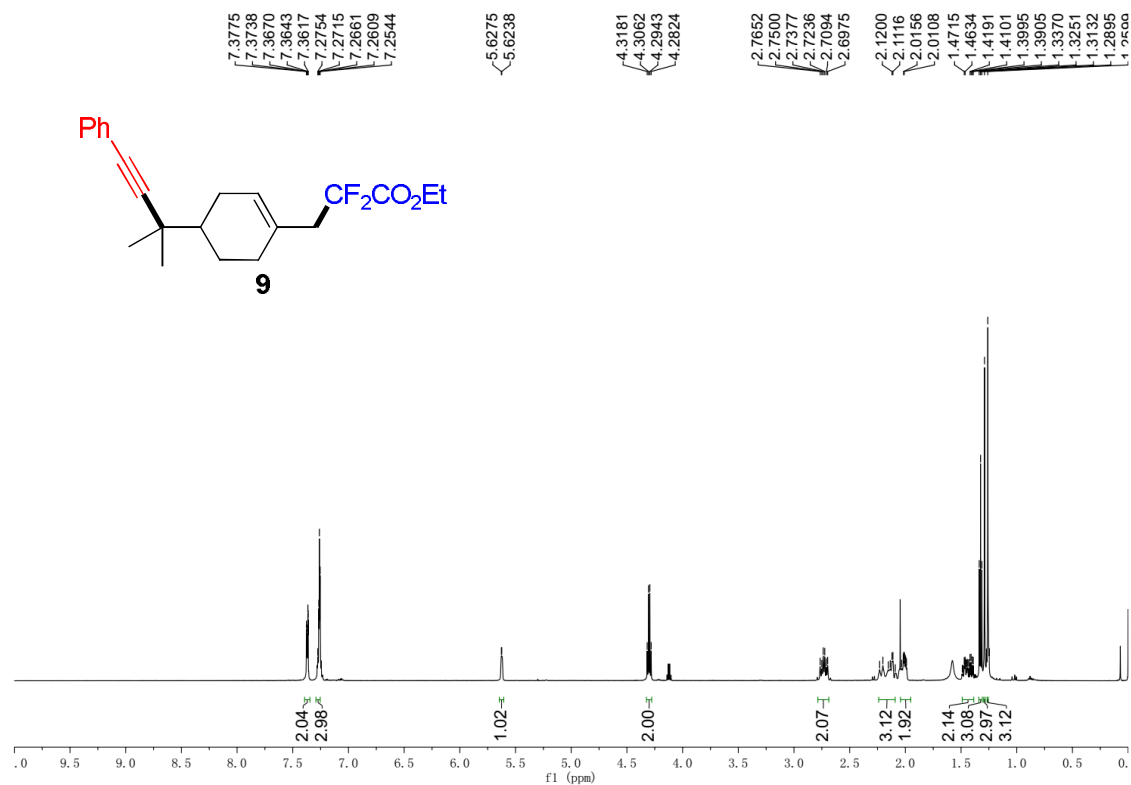


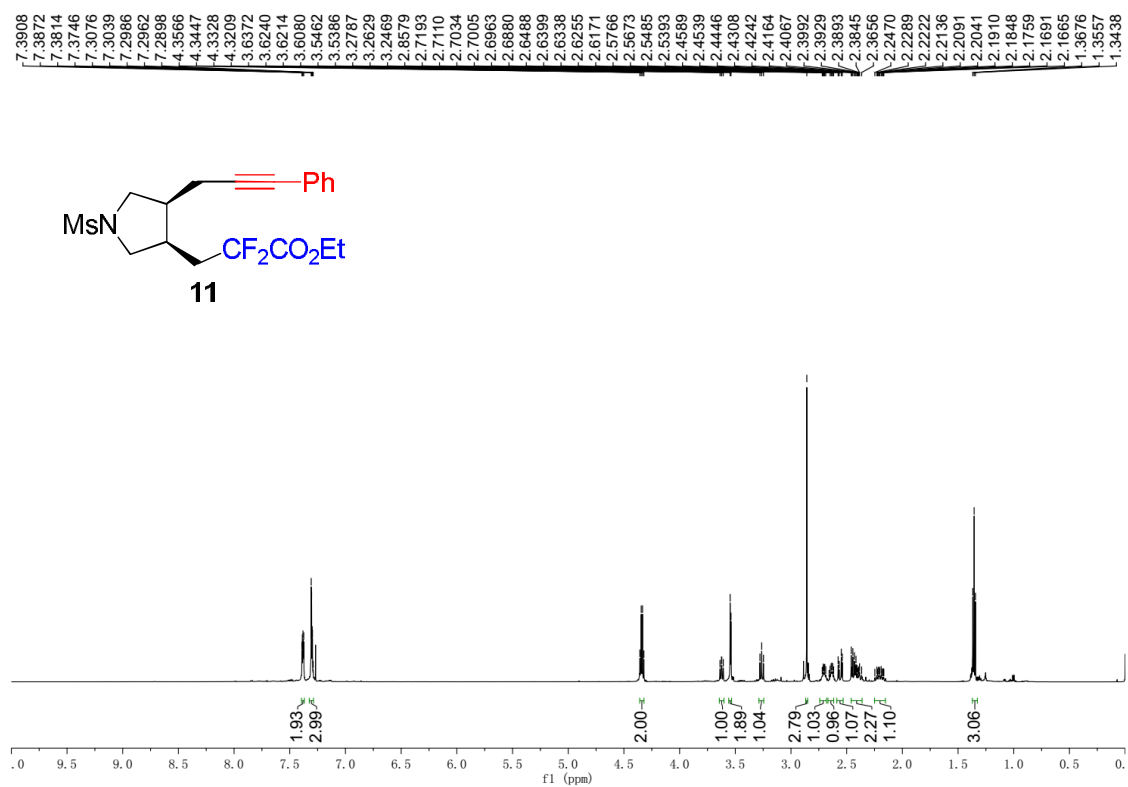
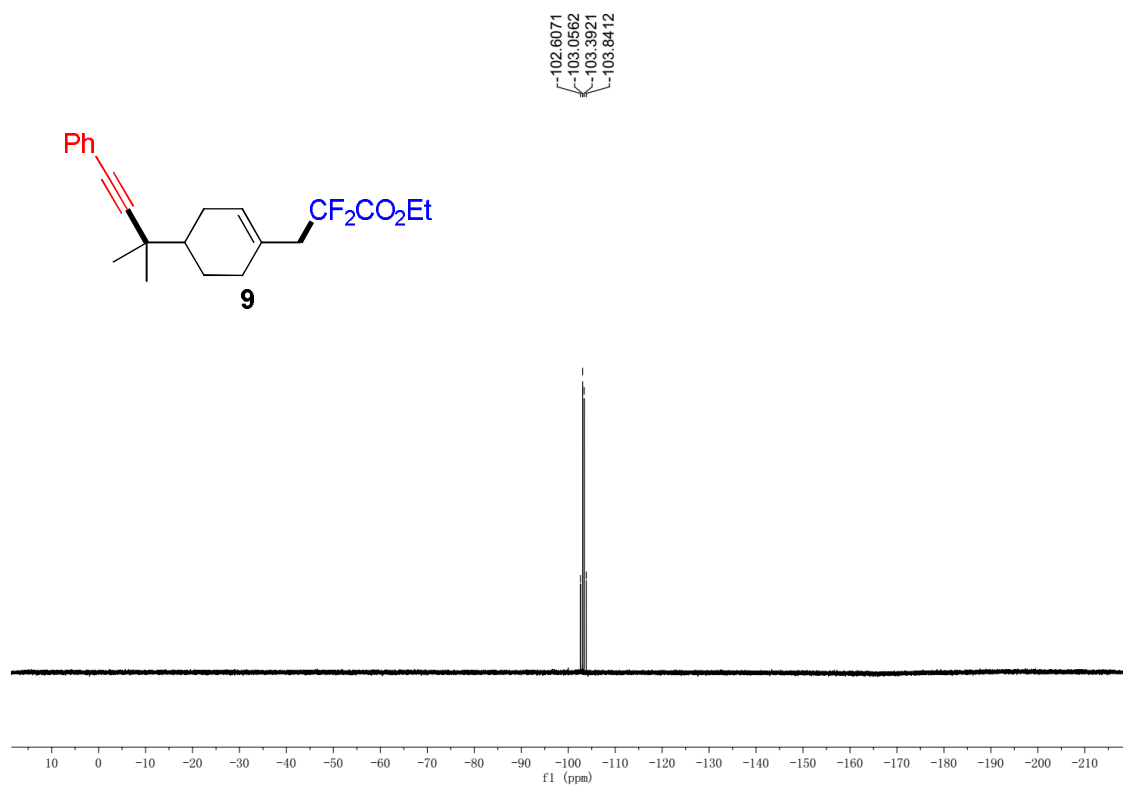
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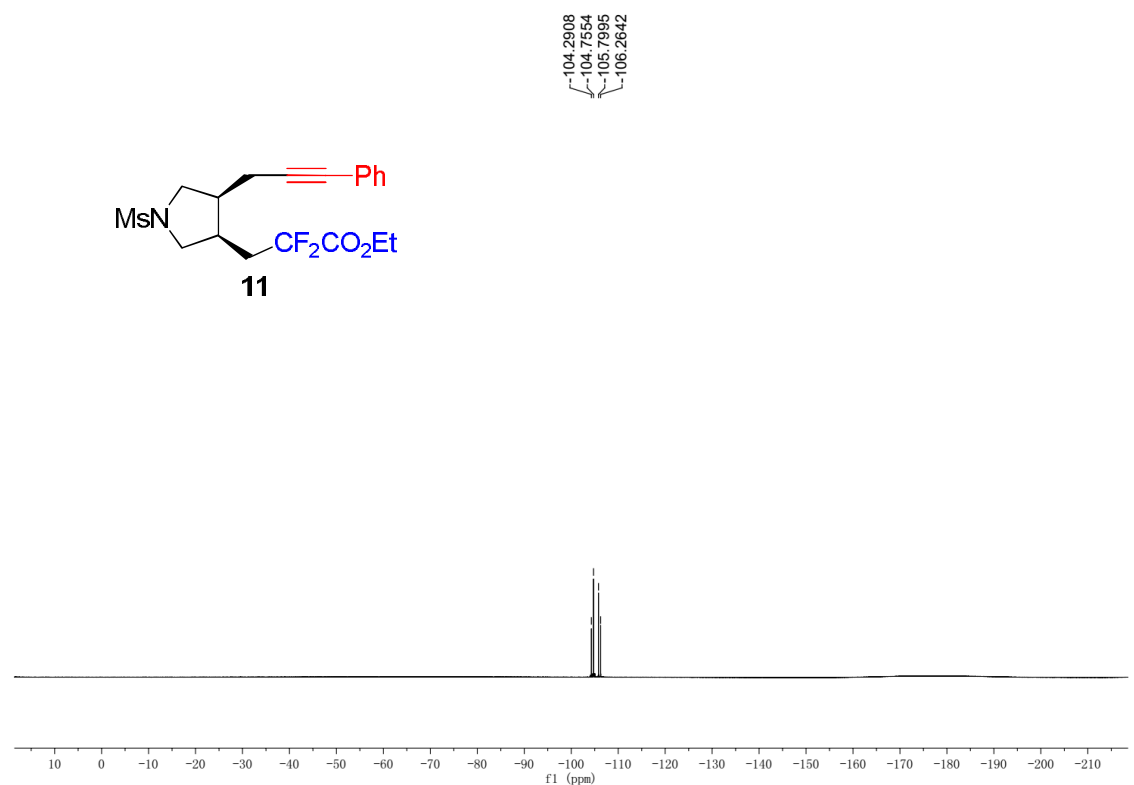
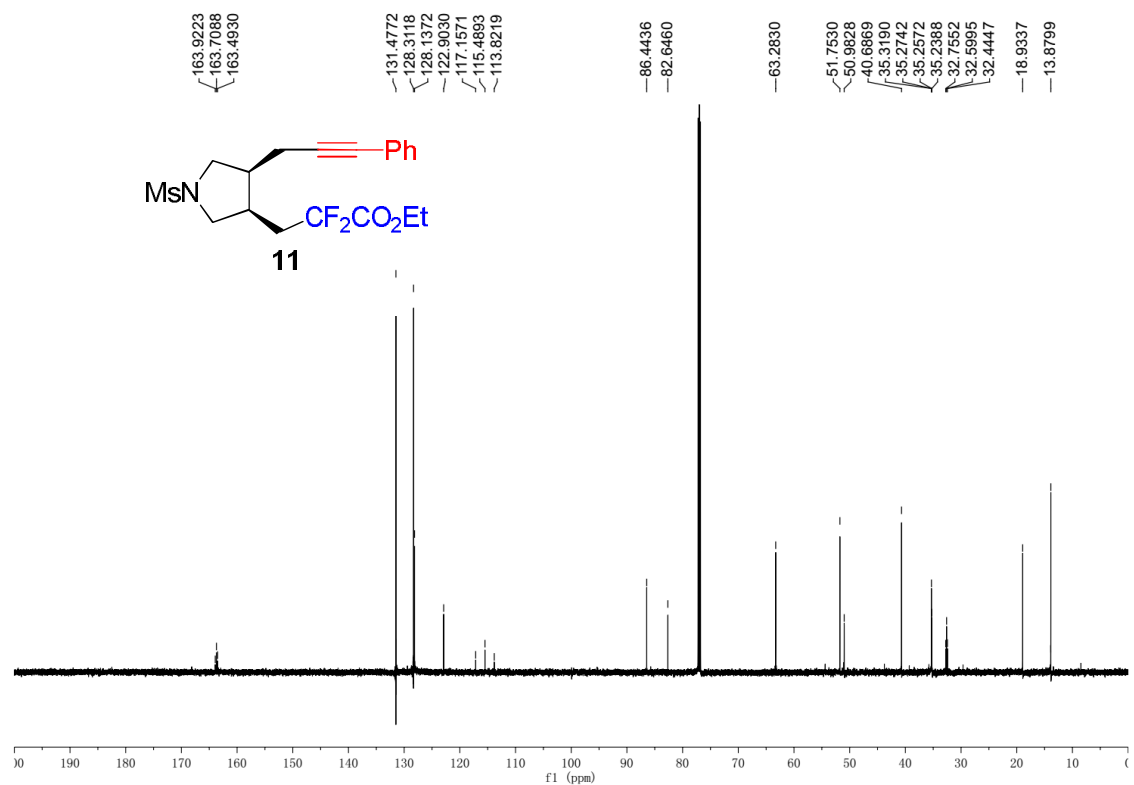


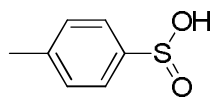
7











HRMS (ESI) calcd for C₇H₈SO₂ (M-H)⁻ 155.0172 found 155.0172.

