Supporting Information

Visible-Light-Induced Difunctionalization of β-CF_2H-1,3-Enynes to Access CF_2H-Containing All-Carbon Quaternary Centers

Shu-Jie Chen,[a] Jin-Hao Lin,[a] Jia-Ming Wu,[a] You-Hong Li,[a] Bao-Le Dong,[a] Guo-Shu Chen,[a] and Yun-Lin Liu*[a,b]

[a] School of Chemistry and Chemical Engineering, Guangzhou University, Guangzhou, 510006, P. R. China

[b] Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

Email: ylliu@gzhu.edu.cn

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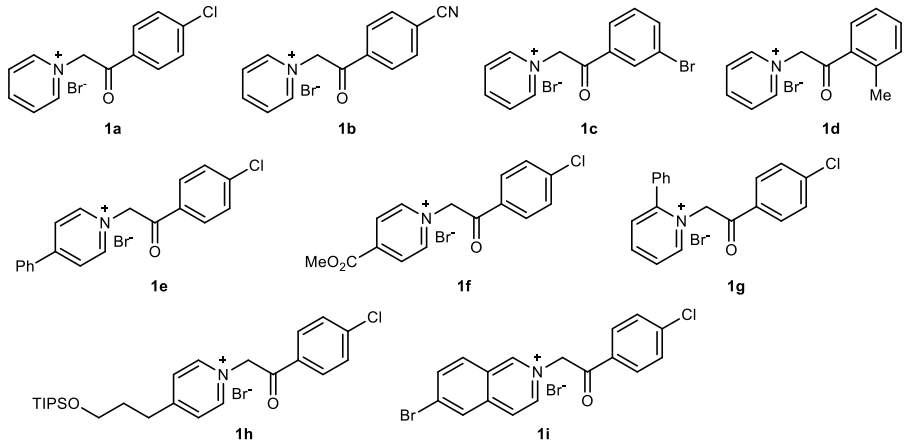
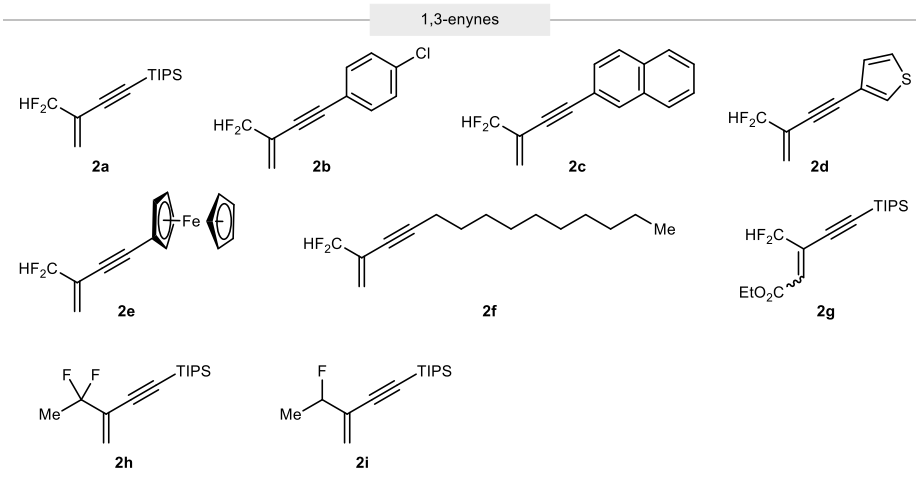
1. General Information

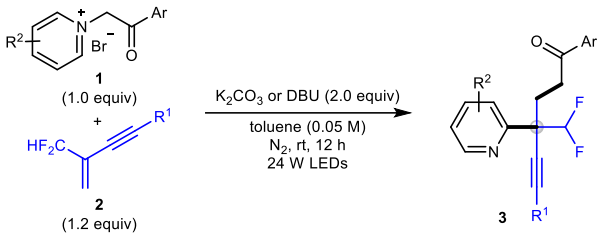
Unless otherwise mentioned, all reactions were performed in oven-dried glassware under N_2. NMR spectra were recorded on Bruker AV III, Ascend 500 HD, or Bruker AVANCE III HD 400. The chemical shifts (δ) for ^1H, ^{13}C, and ^{19}F are given in ppm relative to residual signals of the solvents ($CDCl_3$ δ 7.26 ppm for ^1H NMR and δ 77.16 ppm for ^{13}C NMR). Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. Data for ^{13}C NMR and ^{19}F NMR are reported in terms of chemical shift and multiplicity where appropriate. NMR yields were calculated by using 3,4,5-trichloropyridine as an internal standard. High-resolution mass spectra were performed on Agilent Q-TOF 6545 (ESI Source). Flash chromatography was performed on silica gel (200-300 mesh). Thin-layer chromatography (TLC) was carried out using commercial silica gel-precoated glass plates, and compounds were visualized under UV light (254 nm). The starting materials *N*-benzoylmethylpyridinium bromides **1**[1] and β-CF_2H-1,3-enynes **2**[2] were synthesized according to the literature. A household 24 W LED lamp from Philips was used as the source of light.

N-benzoylmethylpyridinium bromides





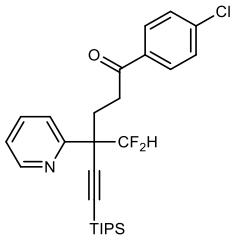
2. General Procedure for Carbopyridylation of β-CF_2H-1,3-Enynes



To an oven-dried Schlenk tube was charged with pyridinium salt **1** (0.10 mmol, 1.0 equiv), and K_2CO_3 (0.20 mmol, 2.0 equiv, if K_2CO_3 was used). The tube was capped, evacuated, and filled with nitrogen (three cycles). To these solids, degassed toluene (2 mL, 0.05 M), β-CF_2H-1,3-enyne **2** (0.12 mmol, 1.2 equiv), and DBU (0.20 mmol, 2.0 equiv, if DBU was used) were added sequentially under N_2 atmosphere. The mixture was stirred and irradiated with a 24 W LED lamp (PHILIPS, 5 cm away) at room temperature for 12 h. The reaction mixture was passed through a plug of silica eluting with petroleum ether-EtOAc (1/1), and the eluent was concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2, petroleum ether/EtOAc) to afford the desired product **3**.

Characterization Data:

1-(4-chlorophenyl)-4-(difluoromethyl)-4-(pyridin-2-yl)-6-(triisopropylsilyl)hex-5-yn-1-one (**3a**)



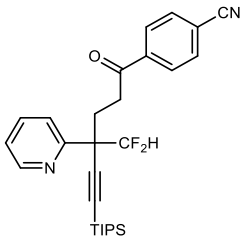
Following the general procedure, the reaction of pyridinium salt **1a** (31 mg, 0.10 mmol, 1.0 equiv), β-CF_2H-1,3-enyne **2a** (31 mg, 0.12 mmol, 1.2 equiv), and DBU (30 µL, 0.20 mmol, 2.0 equiv) in toluene (2 mL) at room temperature for 12 h afford **3a** (36 mg, 73%) as a white solid after purification by flash chromatography (5% EtOAc in petroleum ether).

mp 64-65 °C

TLC (SiO_2) R_f = 0.54 (hexanes/ethyl acetate = 9:1), [UV light]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (ddd, *J* = 4.7, 1.9, 0.9 Hz, 1H), 7.91 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.82-7.77 (m, 2H), 7.74 (td, *J* = 7.7, 1.8 Hz, 1H), 7.423-7.35 (m, 2H), 7.24 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 6.19 (dd, *J* = 57.3, 55.6 Hz, 1H), 3.30-3.17 (m, 1H), 2.77-2.57 (m, 2H), 2.48-2.35 (m, 1H), 1.17-1.10 (m, 21H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.8, 156.3, 149.3, 139.4, 136.9, 135.0, 129.4, 128.8, 123.7, 122.8, 117.3 (t, *J* = 250.5 Hz), 103.0, 90.1, 52.7 (t, *J* = 19.2 Hz), 34.2, 30.0, 18.7, 11.2. **^{19}F NMR** (with ^{1}H decoupling) (376 MHz, $CDCl_3$) δ -121.4, -122.1, -125.5, -126.2. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{27}H_{34}ClF_2NNaOSi$ 512.1958; found 512.1952.

4-(4-(Difluoromethyl)-4-(pyridin-2-yl)-6-(triisopropylsilyl)hex-5-ynoyl)benzonitrile (**3b**)



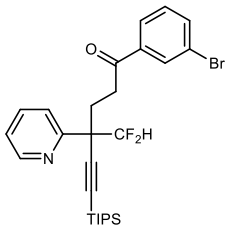
Following the general procedure, the reaction of corresponding pyridinium salt **1b** (30

mg, 0.10 mmol, 1.0 equiv), β-CF_2H-1,3-enyne **2a** (31 mg, 0.12 mmol, 1.2 equiv), and DBU (30 μL, 0.20 mmol, 2.0 equiv) in toluene (2 mL) at room temperature for 12 h afford **3b** (28 mg, 59%) as a colorless oil after purification by flash chromatography (10% EtOAc in petroleum ether).

TLC (SiO_2) R_f = 0.27 (hexanes/ethyl acetate = 9:1), [UV light]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (ddd, *J* = 4.8, 1.9, 0.9 Hz, 1H), 7.97-7.89 (m, 3H), 7.78 -7.70 (m, 3H), 7.27-7.22 (m, 1H), 6.16 (dd, *J* = 57.2, 55.5 Hz, 1H), 3.34-3.17 (m, 1H), 2.79-2.67 (m, 2H), 2.49-2.40 (m, 1H), 1.15-1.11 (m, 21H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.6, 156.2, 149.3, 139.6, 136.9, 132.4, 128.4, 123.8, 122.9, 117.9, 117.2 (t, *J* = 250.5 Hz), 116.3, 102.9, 90.3, 52.6 (t, *J* = 19.2 Hz), 34.6, 29.7, 18.6, 11.2. **^{19}F NMR** (with ^{1}H decoupling) (376 MHz, $CDCl_3$) δ -121.4, -122.1, -125.3, -126.0. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{35}F_2N_2OSi$ 481.2481; found 481.2481.

1-(3-Bromophenyl)-4-(difluoromethyl)-4-(pyridin-2-yl)-6-(triisopropylsilyl)hex-5-yn-1-one (**3c**)



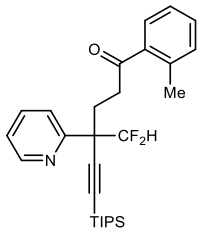
Following the general procedure, the reaction of corresponding pyridinium salt **1c** (35.7 mg, 0.10 mmol, 1.0 equiv), β-CF_2H-1,3-enyne **2a** (31 mg, 0.12 mmol, 1.2 equiv), DBU (30 μL, 0.20 mmol, 2.0 equiv), and toluene (2 mL) at room temperature for 12 h afford **3c** (36 mg, 68%) as a colorless oil after purification by flash chromatography (2-4% EtOAc in petroleum ether).

TLC (SiO_2) R_f = 0.54 (hexanes/ethyl acetate = 9:1), [UV light]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (ddd, *J* = 4.8, 1.9, 0.9 Hz, 1H), 7.98 (t, *J* = 1.8 Hz, 1H), 7.92 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.80-7.72 (m, 2H), 7.65 (ddd, *J* = 7.9, 2.0, 1.0 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.24 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 6.18 (dd, *J* = 57.2, 55.6 Hz, 1H), 3.30-3.17 (m, 1H), 2.77-2.62 (m, 2H), 2.46-2.36 (m, 1H), 1.15-1.12 (m, 21H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.7, 156.3, 149.3, 138.4, 136.9, 135.9, 131.1, 130.1, 126.5, 123.7, 122.9, 122.8, 117.3 (t, *J* = 250.5 Hz), 102.9, 90.2, 52.7 (t, *J* = 19.2 Hz), 34.3, 29.8, 18.7,

11.2. **^{19}F NMR** (with ^{1}H decoupling) (376 MHz, $CDCl_3$) δ -121.4, -122.2, -125.4, -126.1. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{27}H_{35}BrF_2NOSi$ 534.1634; found 534.1647.

4-(Difluoromethyl)-4-(pyridin-2-yl)-1-(o-tolyl)-6-(triisopropylsilyl)hex-5-yn-1-one (**3d**)

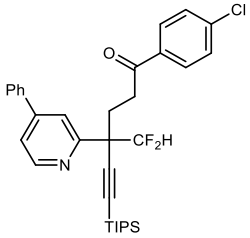


Following the general procedure, the reaction of corresponding pyridinium salt **1d** (29 mg, 0.10 mmol, 1.0 equiv), β-CF_2H-1,3-enyne **2a** (31 mg, 0.12 mmol, 1.2 equiv), and DBU (30 µL, 0.20 mmol, 2.0 equiv) in toluene (2 mL) at room temperature for 12 h afford **3d** (29 mg, 62%) as a pale yellow oil after purification by flash chromatography (3-5% EtOAc in petroleum ether).

TLC (SiO_2) R_f = 0.57 (hexanes/ethyl acetate = 9:1), [UV light]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (dd, *J* = 4.9, 1.9 Hz, 1H), 7.90-7.86 (m, 1H), 7.70 (td, *J* = 7.8, 1.9 Hz, 1H), 7.48 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.31 (td, *J* = 7.5, 1.5 Hz, 1H), 7.23-7.14 (m, 3H), 6.19 (dd, *J* = 57.3, 55.6 Hz, 1H), 3.18 (ddd, *J* = 16.1, 11.3, 4.1 Hz, 1H), 2.69-2.50 (m, 2H), 2.44-2.40 (m, 4H), 1.13-1.10 (m, 21H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.2, 156.6, 149.4, 138.1, 137.8, 136.9, 132.0, 131.3, 128.4, 125.6, 123.7, 122.7, 117.5 (t, *J* = 251.5 Hz), 103.1 (t, *J* = 4.0 Hz), 90.0, 52.7 (t, *J* = 19.2 Hz), 37.1, 30.3, 21.3, 18.7, 11.3. **^{19}F NMR** (with ^{1}H decoupling) (376 MHz, $CDCl_3$) δ -121.4, -122.2, -125.7, -126.4. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{38}F_2NOSi$ 470.2685; found 470.2685.

1-(4-Chlorophenyl)-4-(difluoromethyl)-4-(4-phenylpyridin-2-yl)-6-(triisopropylsilyl)hex-5-yn-1-one (**3e**)



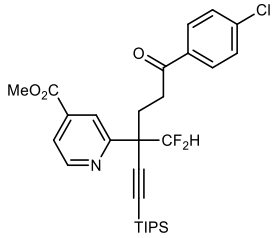
Following the general procedure, the reaction of corresponding pyridinium salt **1e** (39 mg, 0.10 mmol, 1.0 equiv), β-CF_2H-1,3-enyne **2a** (31 mg, 0.12 mmol, 1.2 equiv), and

DBU (30 μL, 0.20 mmol, 2.0 equiv) in toluene (2 mL) at room temperature for 12 h afford **3e** (37 mg, 65%) as a white solid after purification by flash chromatography (3-5% EtOAc in petroleum ether).

TLC (SiO_2) R_f = 0.48 (hexanes/ethyl acetate = 9:1), [UV light]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 5.1, 0.8 Hz, 1H), 8.21 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.83-7.77 (m, 2H), 7.69-7.64 (m, 2H), 7.52-7.45 (m, 4H), 7.39-7.34 (m, 2H), 6.23 (dd, *J* = 57.3, 55.6 Hz, 1H), 3.29-3.19 (m, 1H), 2.80-2.67 (m, 2H), 2.51-2.41 (m, 1H), 1.17-1.13 (m, 21H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.8, 156.9, 149.8, 149.2, 139.4, 137.9, 135.0, 129.4, 129.3, 129.1, 128.8, 127.1, 121.8, 120.6, 117.3 (t, *J* = 250.5 Hz), 103.0, 90.4, 52.9 (t, *J* = 19.2 Hz), 34.2, 30.1, 18.7, 11.2. **^{19}F NMR** (with ^{1}H decoupling) (376 MHz, $CDCl_3$) δ -121.2, -121.9, -125.4, -126.1. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{33}H_{39}ClF_2NOSi$ 566.2452; found 566.2466.

Methyl 2-(6-(4-chlorophenyl)-3-(difluoromethyl)-6-oxo-1-(triisopropylsilyl)hex-1-yn-3-yl)isonicotinate (**3f**)



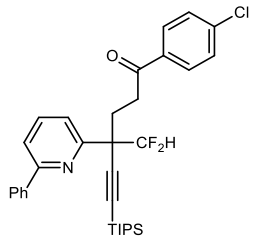
Following the general procedure, the reaction of corresponding pyridinium salt **1f** (37 mg, 0.10 mmol, 1.0 equiv), β-CF_2H-1,3-enyne **2a** (31 mg, 0.12 mmol, 1.2 equiv), and DBU (30 μL, 0.20 mmol, 2.0 equiv) in toluene (2 mL) at room temperature for 12 h afford **3f** (39 mg, 71%) as a crimson oil after purification by flash chromatography (5-10% EtOAc in petroleum ether).

TLC (SiO_2) R_f = 0.43 (hexanes/ethyl acetate = 9:1), [UV light]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 5.0 Hz, 1H), 8.53-8.48 (m, 1H), 7.82-7.73 (m, 3H), 7.40-7.34 (m, 2H), 6.17 (dd, *J* = 57.1, 55.5 Hz, 1H), 3.93 (d, *J* = 2.1 Hz, 3H), 3.21 (ddd, *J* = 16.2, 10.4, 4.5 Hz, 1H), 2.75-2.57 (m, 2H), 2.43 (ddd, *J* = 13.7, 11.1, 4.3 Hz, 1H), 1.16-1.11 (m, 21H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.6, 165.3, 157.8, 150.3, 139.6, 138.4, 135.0, 129.5, 128.9, 123.2, 122.2, 117.2 (t, *J* = 250.5 Hz), 102.4 (t, *J* = 3.0 Hz), 91.1, 52.9 (t, *J* = 19.2 Hz), 52.8, 34.1, 30.0, 18.7, 11.2. **^{19}F NMR** (with ^{1}H decoupling)

(376 MHz, $CDCl_3$) δ -121.2, -121.9, -125.2, -125.9. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{29}H_{36}ClF_2NNaO_3Si$ 570.2013; found 570.2013.

1-(4-Chlorophenyl)-4-(difluoromethyl)-4-(6-phenylpyridin-2-yl)-6-(triisopropylsilyl)hex-5-yn-1-one (**3g**)

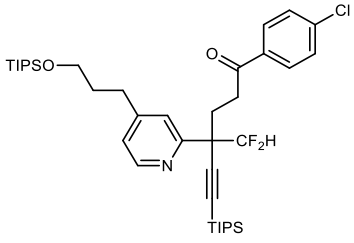


Following the general procedure, the reaction of corresponding pyridinium salt **1g** (39 mg, 0.10 mmol, 1.0 equiv), β-CF_2H-1,3-enyne **2a** (31 mg, 0.12 mmol, 1.2 equiv), and DBU (30 μL, 0.40 mmol, 2.0 equiv) in toluene (2 mL) at room temperature for 12 h afford **3g** (47.5 mg, 84%) as a colorless oil after purification by flash chromatography (3% EtOAc in petroleum ether).

TLC (SiO_2) R_f = 0.71 (hexanes/ethyl acetate = 3:1), [UV light]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-7.98 (m, 2H), 7.87-7.74 (m, 4H), 7.70 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.49-7.40 (m, 3H), 7.31-7.25 (m, 2H), 6.28 (dd, *J* = 57.3, 55.6 Hz, 1H), 3.24 (ddd, *J* = 16.1, 11.4, 4.5 Hz, 1H), 2.86 (ddd, *J* = 13.0, 11.4, 4.5 Hz, 1H), 2.71 (ddd, *J* = 16.2, 11.5, 4.6 Hz, 1H), 2.47 (td, *J* = 12.3, 4.5 Hz, 1H), 1.18-1.12 (m, 21H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.0, 156.6, 156.1, 139.4, 138.6, 137.8, 134.9, 129.5, 129.4, 128.8, 128.8, 126.9, 122.0, 119.2, 117.5 (t, *J* = 250.5 Hz), 103.0, 90.1, 52.9 (t, *J* = 19.2 Hz), 34.3, 30.4, 18.7, 11.2. **^{19}F NMR** (with ^{1}H decoupling) (376 MHz, $CDCl_3$) δ -121.3, -122.0, -125.5, -126.2. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{33}H_{39}ClF_2NOSi$ 566.2452; found 566.2437.

1-(4-Chlorophenyl)-4-(difluoromethyl)-6-(triisopropylsilyl)-4-(4-(3-((triisopropylsilyl)oxy)propyl)pyridin-2-yl)hex-5-yn-1-one (**3h**)

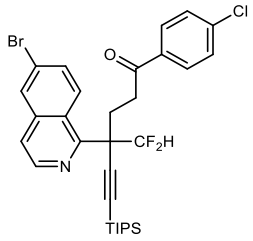


Following the general procedure, the reaction of corresponding pyridinium salt **1h** (53 mg, 0.10 mmol, 1.0 equiv), β-CF_2H-1,3-enyne **2a** (31 mg, 0.12 mmol, 1.2 equiv), and K_2CO_3 (28 mg, 0.20 mmol, 2.0 equiv) in toluene (2 mL) at room temperature for 12 h afford **3h** (29 mg, 41%) as a white solid after purification by flash chromatography (4% EtOAc in petroleum ether).

TLC (SiO_2) R_f = 0.51 (hexanes/ethyl acetate = 9:1), [UV light]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 5.0 Hz, 1H), 7.83-7.77 (m, 3H), 7.42-7.35 (m, 2H), 7.07 (dd, *J* = 5.0, 1.6 Hz, 1H), 6.16 (dd, *J* = 57.3, 55.5 Hz, 1H), 3.74 (t, *J* = 6.1 Hz, 2H), 3.20 (ddd, *J* = 16.0, 11.8, 4.5 Hz, 1H), 2.78-2.60 (m, 4H), 2.40 (td, *J* = 13.7, 12.7, 4.4 Hz, 1H), 1.88 (ddt, *J* = 9.3, 7.8, 6.2 Hz, 2H), 1.14 (s, 21H), 1.10-1.03 (m, 21H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.9, 156.2, 152.4, 149.1, 139.4, 135.0, 129.4, 128.8, 123.9, 123.0, 117.3 (t, *J* = 250.5 Hz), 103.2, 90.0, 62.4, 52.6 (t, *J* = 19.2 Hz), 34.2, 33.2, 31.9, 30.0, 18.7, 18.0, 12.0, 11.2. **^{19}F NMR** (with ^{1}H decoupling) (376 MHz, $CDCl_3$) δ -121.3, -122.1, -125.4, -126.2. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{39}H_{60}ClF_2NNaO_2Si_2$ 726.3711; found 726.3714.

4-(6-Bromoisoquinolin-1-yl)-1-(4-chlorophenyl)-4-(difluoromethyl)-6-(triisopropylsilyl)hex-5-yn-1-one (**3i**)



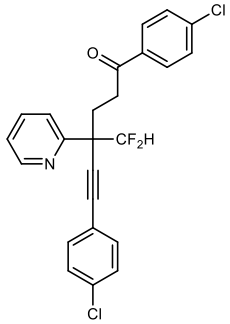
Following the general procedure, the reaction of corresponding pyridinium salt **1i** (44 mg, 0.10 mmol, 1.0 equiv), β-CF_2H-1,3-enyne **2a** (31 mg, 0.12 mmol, 1.2 equiv), and K_2CO_3 (28 mg, 0.20 mmol, 2.0 equiv) in toluene (2 mL) at room temperature for 12 h afford **3i** (40 mg, 65%) as a pale yellow oil after purification by flash chromatography (3.5% EtOAc in petroleum ether).

TLC (SiO_2) R_f = 0.65 (hexanes/ethyl acetate = 9:1), [UV light]

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (d, *J* = 9.3 Hz, 1H), 8.47 (d, *J* = 5.6 Hz, 1H), 8.00 (d, *J* = 2.1 Hz, 1H), 7.84 (dd, *J* = 8.8, 2.2 Hz, 2H), 7.60 (dd, *J* = 9.3, 2.1 Hz, 1H), 7.52 (d, *J* = 5.6 Hz, 1H), 7.38 (dd, *J* = 8.8, 2.2 Hz, 2H), 6.60-6.29 (m, 1H), 3.31-3.14 (m, 2H), 3.10-3.01

(m, 1H), 2.54-2.44 (m, 1H), 1.07-1.04 (m, 21H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.0, 155.2, 141.8, 139.6, 138.7, 135.1, 130.1, 129.8, 129.5, 128.9, 125.9, 124.8, 120.5, 117.1 (t, *J* = 251.5 Hz), 104.5, 91.6, 51.6 (t, *J* = 19.2 Hz), 34.7, 30.1, 18.7, 11.2. **^{19}F NMR** (with ^{1}H decoupling) (376 MHz, $CDCl_3$) δ -120.3, -121.0, -124.7, -125.5. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{31}H_{36}BrClF_2NOSi$ 618.1401; found 618.1406.

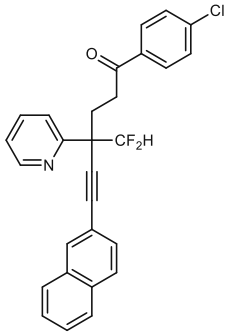
1,6-Bis(4-chlorophenyl)-4-(difluoromethyl)-4-(pyridin-2-yl)hex-5-yn-1-one (**3j**)



Following the general procedure, the reaction of corresponding pyridinium salt **1a** (31 mg, 0.10 mmol, 1.0 equiv), β-CF_2H-1,3-enyne **2b** (26 mg, 0.12 mmol, 1.2 equiv), and DBU (30 µL, 0.20 mmol, 2.0 equiv) in toluene (2 mL) at room temperature for 12 h afford **3j** (20 mg, 45%) as a pale yellow oil after purification by flash chromatography (5% EtOAc in petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (ddd, *J* = 4.8, 1.9, 0.9 Hz, 1H), 7.89 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.82-7.73 (m, 3H), 7.48-7.42 (m, 2H), 7.39-7.35 (m, 2H), 7.34-7.30 (m, 2H), 7.27 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 6.27 (dd, *J* = 57.2, 55.6 Hz, 1H), 3.20-3.11 (m, 1H), 2.84-2.66 (m, 2H), 2.60-2.47 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.7, 156.2 (d, *J* = 4.3 Hz), 149.5, 139.5, 137.0, 135.0, 134.9, 133.2, 129.5, 128.9, 128.7, 123.7, 123.0, 120.8, 117.4 (t, *J* = 250.5 Hz), 87.3, 85.8 (t, *J* = 3.1 Hz), 52.4 (t, *J* = 19.1 Hz), 34.0, 30.0 (d, *J* = 3.7 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -121.1 (d, *J* = 55.7 Hz), -121.8 (d, *J* = 55.5 Hz), -125.3 (d, *J* = 57.3 Hz), -126.0 (d, *J* = 57.2 Hz). **HRMS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{24}H_{18}Cl_2F_2NO$ 444.0728; found 444.0720.

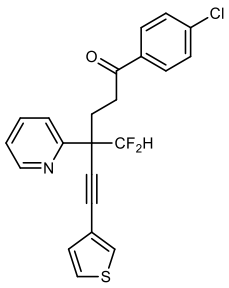
1-(4-Chlorophenyl)-4-(difluoromethyl)-6-(naphthalen-2-yl)-4-(pyridin-2-yl)hex-5-yn-1-one (**3k**)



Following the general procedure, the reaction of corresponding pyridinium salt **1a** (31 mg, 0.10 mmol, 1.0 equiv), β-CF_2H-1,3-enyne **2c** (27 mg, 0.12 mmol, 1.2 equiv), and K_2CO_3 (28 mg, 0.20 mmol, 2.0 equiv) in toluene (2 mL) at room temperature for 12 h afford **3k** (22 mg, 48%) as a yellow oil after purification by flash chromatography (5% EtOAc in petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58-8.50 (m, 1H), 7.95 (d, *J* = 1.5 Hz, 1H), 7.93-7.88 (m, 1H), 7.74-7.67 (m, 6H), 7.47 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.41 (dt, *J* = 6.3, 3.5 Hz, 2H), 7.29-7.23 (m, 2H), 7.2 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 6.23 (dd, *J* = 57.2, 55.6 Hz, 1H), 3.18-3.11 (m, 1H), 2.79-2.62 (m, 2H), 2.56-2.46 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.9, 156.5 (d, *J* = 4.3 Hz), 149.5, 139.5, 137.0, 135.0, 133.0, 132.9, 132.0, 129.5, 128.9, 128.5, 128.1, 127.8, 127.8, 126.9, 126.7, 123.9, 123.0, 119.5, 117.6 (t, *J* = 249.5 Hz), 88.9, 85.0 (d, *J* = 2.9 Hz), 52.4 (t, *J* = 19.1 Hz), 34.1, 30.1 (d, *J* = 3.9 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -121.0 (d, *J* = 55.7 Hz), -121.8 (d, *J* = 55.5 Hz), -125.2 (d, *J* = 57.3 Hz), -125.9 (d, *J* = 57.3 Hz). **HRMS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{21}ClF_2NO$ 460.1274; found 460.1265.

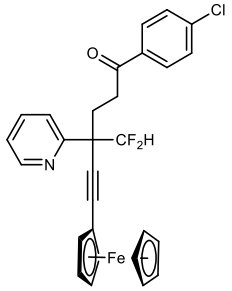
1-(4-chlorophenyl)-4-(difluoromethyl)-4-(pyridin-2-yl)-6-(thiophen-3-yl)hex-5-yn-1-one (**3l**)



Following the general procedure, the reaction of corresponding pyridinium salt **1a** (31 mg, 0.10 mmol, 1.0 equiv), β-CF_2H-1,3-enyne **2d** (22 mg, 0.12 mmol, 1.2 equiv), and K_2CO_3 (28 mg, 0.20 mmol, 2.0 equiv) in toluene (2 mL) at room temperature for 12 h afford **3l** (22 mg, 53%) as a pale yellow oil after purification by flash chromatography (5-10% EtOAc in petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (ddd, *J* = 4.8, 1.9, 0.9 Hz, 1H), 7.91 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.83-7.78 (m, 2H), 7.76 (td, *J* = 7.7, 1.8 Hz, 1H), 7.54 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.40-7.34 (m, 2H), 7.30 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.28-7.24 (m, 1H), 7.19 (dd, *J* = 5.0, 1.2 Hz, 1H), 6.26 (dd, *J* = 57.3, 55.6 Hz, 1H), 3.23-3.12 (m, 1H), 2.82-2.65 (m, 2H), 2.58-2.47 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.8, 156.4 (d, *J* = 4.3 Hz), 149.4, 139.5, 137.0, 135.0, 130.0, 129.6, 129.5, 128.8, 125.5, 123.8, 122.9, 121.3, 117.5 (t, *J* = 249.3 Hz), 84.3 (t, *J* = 3.2 Hz), 83.6, 52.3 (t, *J* = 19.1 Hz), 34.0, 30.0 (d, *J* = 3.6 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -121.2 (d, *J* = 55.5 Hz), -121.9 (d, *J* = 55.7 Hz), -125.3 (d, *J* = 57.3 Hz), -126.0 (d, *J* = 57.3 Hz). **HRMS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{17}ClF_2NOS$ 416.0682; found 416.0678.

(6-(4-Chlorophenyl)-3-(difluoromethyl)-6-oxo-3-(pyridin-2-yl)hex-1-yn-1-yl)ferrocene (3m)

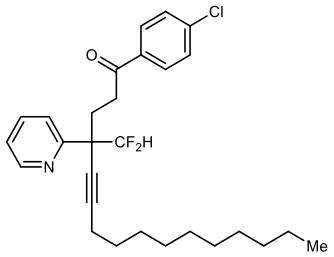


Following the general procedure, the reaction of corresponding pyridinium salt **1a** (31 mg, 0.10 mmol, 1.0 equiv), β-CF_2H-1,3-enyne **2e** (34 mg, 0.12 mmol, 1.2 equiv), and K_2CO_3 (28 mg, 0.20 mmol, 2.0 equiv) in toluene (2 mL) at room temperature for 12 h afford **3m** (36 mg, 70%) as a yellow oil after purification by flash chromatography (5% EtOAc in petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 7.92 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.86-7.80 (m, 2H), 7.77 (td, *J* = 7.7, 1.8 Hz, 1H), 7.42-7.36 (m, 2H), 7.25 (ddd, *J* =

7.2, 4.8, 1.2 Hz, 1H), 6.25 (dd, *J* = 57.5, 55.8 Hz, 1H), 4.52-4.49 (m, 2H), 4.23-4.22 (m, 7H), 3.25-3.11 (m, 1H), 2.81-2.61 (m, 2H), 2.56-2.41 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.9, 156.8, 149.4, 139.5, 136.9, 135.0, 129.5, 128.9, 123.8, 122.8, 117.4 (t, *J* = 249.0 Hz), 87.1, 80.6, 71.7, 70.0, 68.9, 64.1, 52.4 (t, *J* = 19.1 Hz), 34.1, 30.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -121.3 (d, *J* = 55.7 Hz), -122.0 (d, *J* = 55.8 Hz), -125.4 (d, *J* = 57.6 Hz), -126.2 (d, *J* = 57.7 Hz). **HRMS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{23}ClF_2FeNO$ 518.0780; found 518.0784.

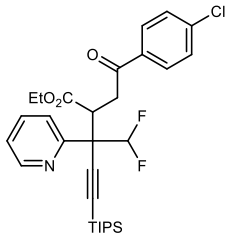
1-(4-Chlorophenyl)-4-(difluoromethyl)-4-(pyridin-2-yl)hexadec-5-yn-1-one (**3n**)



Following the general procedure, the reaction of corresponding pyridinium salt **1a** (31 mg, 0.10 mmol, 1.0 equiv), β-CF_2H-1,3-enyne **2f** (29 mg, 0.12 mmol, 1.2 equiv), and DBU (30 μL, 0.20 mmol, 2.0 equiv) in toluene (2 mL) at room temperature for 12 h afford **3n** (27.5 mg, 58%) as a pale yellow oil after purification by flash chromatography (5% EtOAc in petroleum ether).

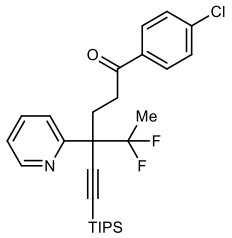
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (dt, *J* = 4.7, 1.3 Hz, 1H), 7.86 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.82-7.78 (m, 2H), 7.73 (td, *J* = 7.7, 1.9 Hz, 1H), 7.41-7.35 (m, 2H), 7.23 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 6.17 (dd, *J* = 57.5, 55.9 Hz, 1H), 3.18-3.07 (m, 1H), 2.72-2.57 (m, 2H), 2.43-2.31 (m, 3H), 1.59 (p, *J* = 7.1 Hz, 2H), 1.47-1.41 (m, 2H), 1.32-1.24 (m, 12H), 0.87 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.0, 157.0 (d, *J* = 4.5 Hz), 149.2, 139.4, 136.7, 135.1, 129.4, 128.8, 123.7, 122.7, 117.6 (t, *J* = 248.9 Hz), 89.2, 75.4 (t, *J* = 2.9 Hz), 51.7 (t, *J* = 19.2 Hz), 34.1, 31.9, 30.1 (d, *J* = 3.9 Hz), 29.6, 29.3, 29.1, 28.9, 28.7, 22.7, 18.9, 14.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -121.7 (d, *J* = 55.9 Hz), -122.4 (d, *J* = 55.9 Hz), -125.7 (d, *J* = 57.2 Hz), -126.4 (d, *J* = 57.3 Hz). **HRMS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{35}ClF_2NO$ 474.2370; found 474.2365.

Ethyl 2-(2-(4-chlorophenyl)-2-oxoethyl)-3-(difluoromethyl)-3-(pyridin-2-yl)-5-(triisopropylsilyl)pent-4-ynoate (3o)



Following the general procedure, the reaction of pyridinium salt **1a** (31 mg, 0.10 mmol, 1.0 equiv), enyne **2i** (40 mg, 0.12 mmol, 1.2 equiv), and DBU (30 µL, 0.20 mmol, 2.0 equiv) in toluene (2 mL) at room temperature for 12 h afford **3o** (30 mg, 53%) as a pale yellow oil after purification by flash chromatography (2-5% EtOAc in petroleum ether). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.61-8.53 (m, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.82-7.71 (m, 3H), 7.41-7.33 (m, 2H), 7.24 (d, *J* = 6.3 Hz, 1H), 6.51 (t, *J* = 55.4 Hz, 1H), 4.14 (t, *J* = 10.1 Hz, 3H), 3.83 (dd, *J* = 17.9, 11.3 Hz, 1H), 2.69 (d, *J* = 17.7 Hz, 1H), 1.23 (dt, *J* = 8.4, 4.1 Hz, 3H), 1.19-1.12 (m, 21H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.4, 171.2, 155.7, 149.1, 139.6, 136.9, 134.8, 129.3, 128.8, 123.8, 123.0, 115.9 (t, *J* = 248.6 Hz), 100.4, 92.1, 61.2, 54.7 (t, *J* = 20.1 Hz), 45.9, 38.2, 18.6, 13.9, 11.2. **^{19}F NMR** (with ^{1}H decoupling) (471 MHz, $CDCl_3$) δ -121.1, -121.7, -121.8, -122.4. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{30}H_{38}ClF_2NNaO_3Si$ 584.2170; found 584.2171.

1-(4-Chlorophenyl)-4-(1,1-difluoroethyl)-4-(pyridin-2-yl)-6-(triisopropylsilyl)hex-5-yn-1-one (3p)



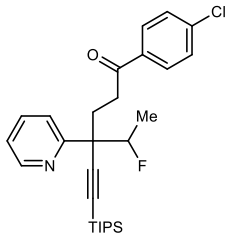
Following the general procedure, the reaction of pyridinium salt **1a** (31 mg, 0.10 mmol, 1.0 equiv), enyne **2g** (33 mg, 0.12 mmol, 1.2 equiv), and DBU (30 µL, 0.20 mmol, 2.0 equiv) in toluene (2 mL) at room temperature for 12 h afford **3p** (17 mg, 33%) as a white solid after purification by flash chromatography (3.5% EtOAc in petroleum ether).

mp 81-82 °C

TLC (SiO_2) R_f = 0.54 (hexanes/ethyl acetate = 9:1), [UV light]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (ddd, *J* = 4.8, 1.9, 0.9 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.87-7.81 (m, 2H), 7.73 (td, *J* = 7.7, 1.9 Hz, 1H), 7.41-7.35 (m, 2H), 7.26-7.22 (m, 1H), 3.25-3.02 (m, 2H), 2.77 (ddd, *J* = 15.9, 11.8, 4.1 Hz, 1H), 2.50-2.37 (m, 1H), 1.65 (t, *J* = 18.6 Hz, 3H), 1.13-1.09 (m, 21H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.4, 156.0, 148.8, 139.3, 136.4, 135.1, 129.5, 128.1, 125.3, 123.5 (t, *J* = 251.5 Hz), 122.7, 106.2, 88.6, 55.4 (t, *J* = 23.2 Hz), 35.1, 28.0 (t, *J* = 3.0 Hz), 20.7 (t, *J* = 27.3 Hz), 18.7, 11.3. **^{19}F NMR** (with ^{1}H decoupling) (376 MHz, $CDCl_3$) δ -94.8 (d, *J* = 8.0 Hz). **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{28}H_{36}ClF_2NNaOSi$ 526.2115; found 526.2115.

1-(4-Chlorophenyl)-4-(1-fluoroethyl)-4-(pyridin-2-yl)-6-(triisopropylsilyl)hex-5-yn-1-one (**3q**)



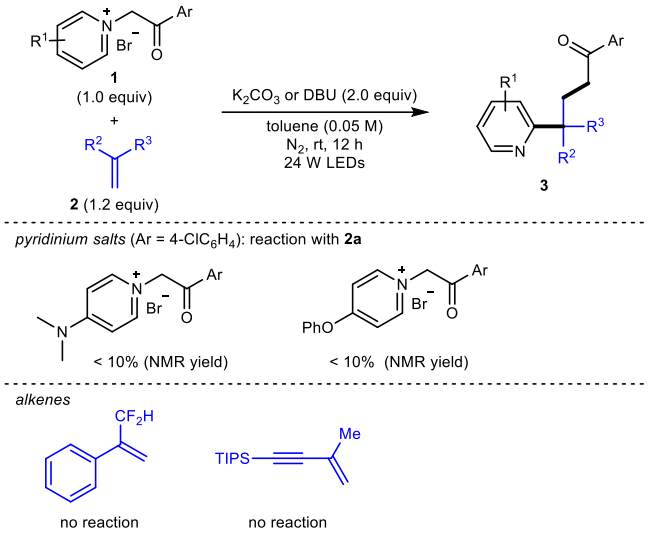
Following the general procedure, the reaction of pyridinium salt **1a** (31 mg, 0.10 mmol, 1.0 equiv), enyne **2h** (31 mg, 0.12 mmol, 1.2 equiv), and DBU (30 µL, 0.20 mmol, 2.0 equiv) in toluene (2 mL) at room temperature for 12 h afford **3q** (9 mg, 18%, dr = 1.1:1) as a colorless oil after purification by flash chromatography (5% EtOAc in petroleum ether).

TLC (SiO_2) R_f = 0.53 (hexanes/ethyl acetate = 9:1), [UV light]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (ddd, *J* = 17.1, 4.7, 1.7 Hz, 1H), 7.95-7.87 (m, 1H), 7.83 -7.74 (m, 2H), 7.70 (tdd, *J* = 7.9, 4.1, 1.8 Hz, 1H), 7.40-7.33 (m, 2H), 7.23-7.16 (m, 1H), 5.10 (ddq, *J* = 46.1, 20.4, 6.1 Hz, 1H), 3.29-3.08 (m, 1H), 2.67-2.44 (m, 2.5H), 2.09 (td, *J* = 12.3, 3.9 Hz, 0.5H), 1.57 (dd, *J* = 24.5, 6.2 Hz, 1.8H), 1.21-1.10 (m, 22.2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.6, (198.3), 159.0, (158.9), 149.4, (149.3), 139.4, (139.2), 136.6, (136.3), 135.1, (135.0), 129.5, (129.4), 128.8, (128.8), 124.0, (123.2), 122.2, (122.1), 106.6, (106.5), 95.1 (d, *J* = 8.1 Hz), {93.4 (d, *J* = 7.1 Hz)}, 89.0, (88.9), 53.7 (d, *J* = 14.1 Hz), {53.5 (d, *J* = 14.1 Hz)}, 35.1, (34.6), 32.6 (d, *J* = 3.0 Hz), {(31.19, 31.15) (d, *J* = 6.1 Hz)}, 18.7, (18.7), 17.0 (d, *J* = 6.1 Hz), {16.8 (d, *J* = 6.1 Hz)}, 11.3, (11.3). **^{19}F NMR** (with ^{1}H decoupling) (376 MHz, $CDCl_3$) δ -173.5 (-180.5). **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ calcd

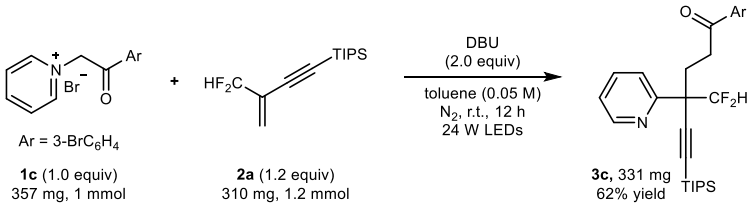
for $C_{28}H_{37}ClFNNaOSi$ 508.2209; found 508.2208.

Substrates Limitation



3. Scale-Up Synthesis and Derivatization of the Products

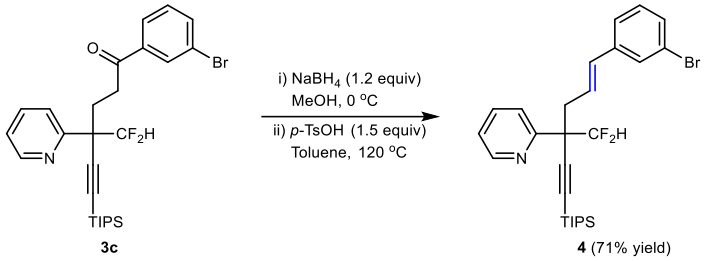
Scale-Up Synthesis of 3c



A 100 mL oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with pyridinium salt **1c** (357 mg, 1 mmol, 1.0 equiv). The tube was capped, evacuated, and filled with nitrogen (three cycles). To these solids, degassed toluene (20 mL, 0.05 M), β-CF_3-1,3-enyne **2a** (310 mg, 1.2 mmol, 1.2 equiv), and DBU (299 μL, 2.0 mmol, 2.0 equiv) was added sequentially under nitrogen atmosphere. The mixture was stirred and irradiated with a 24 W white LED bulb (PHILIPS, 5 cm away) at room temperature for 12 h. The reaction mixture was passed through a short pad of silica eluting with petroleum ether-EtOAc (1/1) to remove the salts and unreacted DBU. After the eluent was concentrated under reduced pressure, the residue was purified by flash chromatography (SiO_2, petroleum ether/EtOAc = 96:4) to afford product **3c** (331 mg, 62% yield) as a colorless oil.

Derivatization of the Product 3c

(*E*)-2-(6-(3-bromophenyl)-3-(difluoromethyl)-1-(triisopropylsilyl)hex-5-en-1-yn-3-yl)pyridine (4)



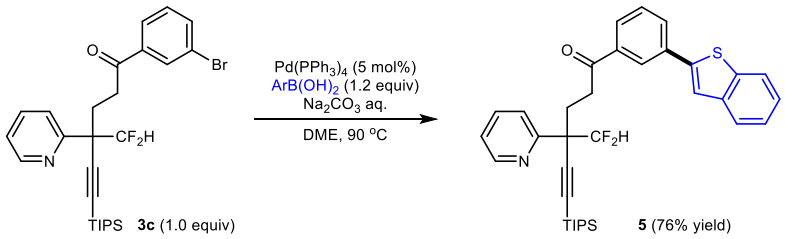
To a solution of **3c** (53 mg, 0.10 mmol) in MeOH (2 mL) was added $NaBH_4$ (4.5 mg, 0.12 mmol) in one portion at 0 °C, and the resulting mixture was stirred until full conversion as judged by TLC analysis. Then, the reaction was quenched with water (5 mL) and extracted with EtOAc (5 mL × 3). The combined organics were dried over Na_2SO_4 and concentrated to give the crude alcohol, which was directly used in the next step without further purification.

The crude alcohol was dissolved in toluene (2 mL), and *p*-TsOH (26 mg, 0.15 mmol) was added. The reaction was stirred under reflux for 12 h in an oil bath maintained at 120 °C. The mixture was cooled to room temperature, filtered through a short SiO_2 plug (eluting with EtOAc), and concentrated *in vacuo*. Purification by column chromatography over silica gel (PE/EtOAc = 97.5:2.5) gave the compound **4** (37 mg, 71%) as a yellowish oil.

Characterization data of **4**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 7.76 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.62 (td, *J* = 7.7, 1.9 Hz, 1H), 7.29-7.27 (m, 1H), 7.22-7.20 (m, 1H), 7.14 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 7.02-7.00 (m, 2H), 6.32-5.93 (m, 3H), 3.08-3.03 (m, 1H), 2.91-2.78 (m, 1H), 1.07-1.03 (m, 21H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.5 (d, *J* = 4.3 Hz), 149.0, 139.4, 136.8, 132.3, 130.0, 129.9, 128.9, 125.8, 124.9, 123.8, 122.6, 122.6, 117.1 (t, *J* = 249.3 Hz), 102.9, 90.1, 53.3 (t, *J* = 19.0 Hz), 29.7, 18.6, 11.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -122.0 (d, *J* = 55.4 Hz), -122.7 (d, *J* = 55.4 Hz), -126.4 (d, *J* = 57.3 Hz), -127.1 (d, *J* = 57.4 Hz). **HRMS** (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{27}H_{34}BrF_2NNaSi$ 540.1504; found 540.1501.

1-(3-(Benzo[*b*]thiophen-2-yl)phenyl)-4-(difluoromethyl)-4-(pyridin-2-yl)-6-(triisopropylsilyl)hex-5-yn-1-one (5)

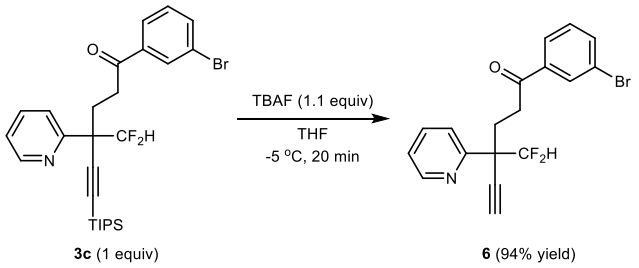


To a 25 mL Schlenk tube equipped with a stirrer bar was added aryl boronic acid (21.5 mg, 0.12 mmol) and $Pd(PPh_3)_4$ (6 mg, 0.005 mmol). The system was purged with nitrogen three times, and then Na_2CO_3 (2 M in H_2O, 200 uL) and a degassed solution of **3c** (53 mg, 0.1 mmol) in 1,2-dimethoxyethane (3 mL) was added under nitrogen. The resulting mixture was stirred in an oil bath maintained at 90 °C for 24 h. After cooling to room temperature, the reaction mixture was poured into water and extracted with ethyl acetate (5 mL × 3). The combined organics were dried over Na_2SO_4 and concentrated under reduced pressure. Purification by column chromatography over silica gel (PE/EtOAc = 96:4) gave the compound **5** (45 mg, 76%) as a colorless oil.

Characterization data of **5:**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (ddd, *J* = 4.8, 1.9, 0.9 Hz, 1H), 8.12 (t, *J* = 1.8 Hz, 1H), 7.86 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.79-7.64 (m, 5H), 7.50 (d, *J* = 0.7 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.31-7.24 (m, 2H), 7.15 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 6.14 (dd, *J* = 57.3, 55.6 Hz, 1H), 3.31-3.18 (m, 1H), 2.75-2.60 (m, 2H), 2.39 (ddd, *J* = 13.8, 11.8, 4.5 Hz, 1H), 1.09-1.04 (m, 21H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.6, 155.4, 148.3, 141.9, 139.5, 138.6, 136.3, 135.8, 133.8, 129.7, 128.1, 126.6, 124.7, 123.7, 122.7, 122.7, 121.7, 121.3, 119.3, 116.3 (t, *J* = 250.5), 102.0, 89.1, 51.7 (t, *J* = 19.1 Hz), 33.3, 29.1, 17.6, 10.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -121.4 (d, *J* = 55.6 Hz), -122.1 (d, *J* = 55.7 Hz), -125.5 (d, *J* = 57.2 Hz), -126.2 (d, *J* = 57.1 Hz). **HRMS (ESI-TOF)** *m/z*: $[M + Na]^+$ calcd for $C_{35}H_{39}F_2NNaOSSi$ 610.2382; found 610.2391.

1-(3-Bromophenyl)-4-(difluoromethyl)-4-(pyridin-2-yl)hex-5-yn-1-one (6)



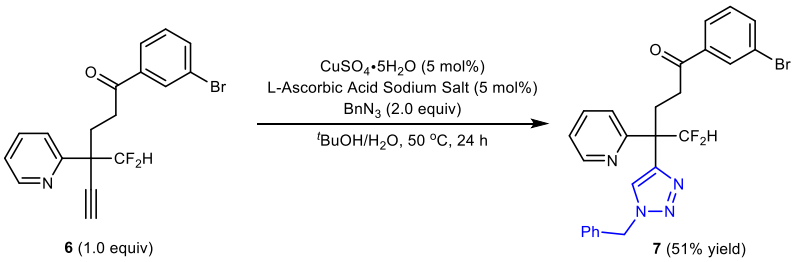
3c (1 equiv) **6** (94% yield)

To a solution of **3c** (160 mg, 0.3 mmol) in THF (4 mL) was added TBAF (0.33 mmol, 1 M in THF) dropwise at -5 °C. The solution was stirred until full conversion as judged by TLC analysis (with 20 minutes). Then, the reaction was quenched with saturated NH_4Cl solution (5 mL) and extracted with EtOAc (5 mL × 3). The combined organic extract was dried over Na_2SO_4 and concentrated in *vacuo*. The crude product was purified by flash chromatography on silica gel (PE/EtOAc = 95/5) to give compound **6** as a colorless oil (107 mg, 94% yield).

Characterization data of **6**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 7.91 (t, *J* = 1.8 Hz, 1H), 7.80 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.73-7.66 (m, 2H), 7.58 (ddd, *J* = 7.9, 2.0, 1.0 Hz, 1H), 7.25-7.17 (m, 2H), 6.13 (dd, *J* = 57.1, 55.4 Hz, 1H), 3.07 (ddd, *J* = 16.9, 11.0, 4.5 Hz, 1H), 2.70-2.52 (m, 3H), 2.40-2.33 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.5, 155.6, 149.5, 138.4, 137.0, 135.9, 131.1, 130.2, 126.6, 123.6, 123.0, 122.9, 117.3 (t, *J* = 249.8 Hz), 79.5 (t, *J* = 3.1 Hz), 76.8, 51.7 (t, *J* = 19.1 Hz), 34.0, 29.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -121.5 (d, *J* = 55.4 Hz), -122.3 (d, *J* = 55.6 Hz), -125.6 (d, *J* = 57.2 Hz), -126.3 (d, *J* = 57.0 Hz). **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ calcd for $C_{18}H_{15}BrF_2NO$ 378.0300; found 378.0294.

4-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)-1-(3-bromophenyl)-5,5-difluoro-4-(pyridin-2-yl)pentan-1-one (7)



6 (1.0 equiv) **7** (51% yield)

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added $CuSO_4·5H_2O$ (1.3

mg, 0.05 equiv) and L-Ascorbic acid sodium salt (1.0 mg, 0.05 equiv). The system was purged with nitrogen three times, and then a solution of **6** (37.8 mg, 0.1 mmol, 1.0 equiv) in *t*-BuOH (0.5 mL), H_2O (0.5 mL) was added in sequence, followed by a quick evacuate-refill cycle. BnN_3 (25 μL, 0.2 mmol, 2.0 equiv) was added *via* microsyringe, and the reaction mixture was stirred in an oil bath maintained at 50 ^oC for 24 h. After the reaction was complete, the reaction mixture was diluted with H_2O (5 mL) and extracted with EtOAc (5 mL × 3). The combined organic layers were washed with brine and dried over Na_2SO_4. After the solvent was evaporated under reduced pressure, the residue was purified by silica gel column chromatography (PE/EtOAc = 3:1) to deliver product **7** (26 mg, 51%) as a yellowish oil.

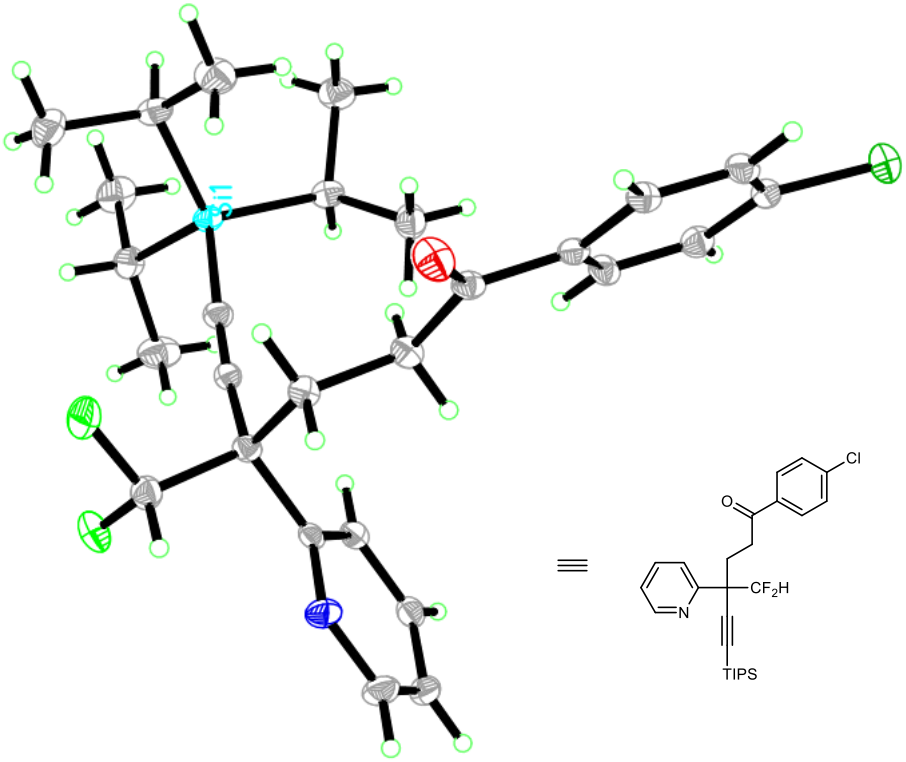
Characterization data of **7**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 1H), 7.92 (t, *J* = 1.8 Hz, 1H), 7.73 (dt, *J* = 7.9, 1.3 Hz, 1H), 7.58-7.50 (m, 3H), 7.353-7.26 (m, 3H), 7.24-7.17 (m, 3H), 7.12 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 7.06-7.01 (m, 1H), 6.57 (t, *J* = 52 Hz, 1H), 5.50 (d, *J* = 3.1 Hz, 2H), 3.27-3.11 (m, 1H), 2.86-2.64 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.2, 158.7, 149.0, 145.2, 138.5, 136.7, 135.8, 134.5, 131.1, 130.1, 129.2, 128.8, 128.0, 126.7, 123.7, 123.5, 122.8, 122.5, 119.0 (t, *J* = 248.1 Hz), 54.3, 52.8 (t, *J* = 18.7 Hz), 34.2, 29.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -122.6 (d, *J* = 55.2 Hz), -123.3 (d, *J* = 55.4 Hz), -127.0 (d, *J* = 56.5 Hz), -127.7 (d, *J* = 56.5 Hz). **HRMS** (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{25}H_{21}BrF_2N_4NaO$ 533.0759; found 533.0766.

4. Single Crystal X-ray Structural Analysis

Crystal Structure of 3a

A view of the molecular structure of compound **3a** (thermal ellipsoids are shown with a 30% probability level). Single crystals of compound **3a** suitable for the X-ray crystal structure analysis were obtained by the slow evaporation of a solution of compound **3a** in PE/dichloromethane.



X-Ray Crystallographic Data of 3a

Crystal data and structure refinement for 3a	
CCDC	2117234
Empirical formula	$C_{27}H_{34}ClF_2NOSi$
Formula weight	490.10
Temperature/K	149.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	7.4228(3)
b/Å	12.3770(4)
c/Å	15.3766(5)
α/°	76.468(3)
β/°	76.054(3)
γ/°	81.669(3)
Volume/Å^3	1327.10(9)
Z	2
ρ_{calc}g/cm^3	1.226
μ/mm^{-1}	0.222
F(000)	520.0
Crystal size/mm^3	0.14 × 0.13 × 0.12
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.926 to 58.798
Index ranges	-9 ⩽ h ⩽ 9, -16 ⩽ k ⩽ 15, -19 ⩽ l ⩽ 19
Reflections collected	18104
Independent reflections	6397 [R_{int} = 0.0518, R_{sigma} = 0.0568]
Data/restraints/parameters	6397/0/304
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0482, wR_2 = 0.1146
Final R indexes [all data]	R_1 = 0.0657, wR_2 = 0.1298
Largest diff. peak/hole / e Å^{-3}	0.31/-0.42

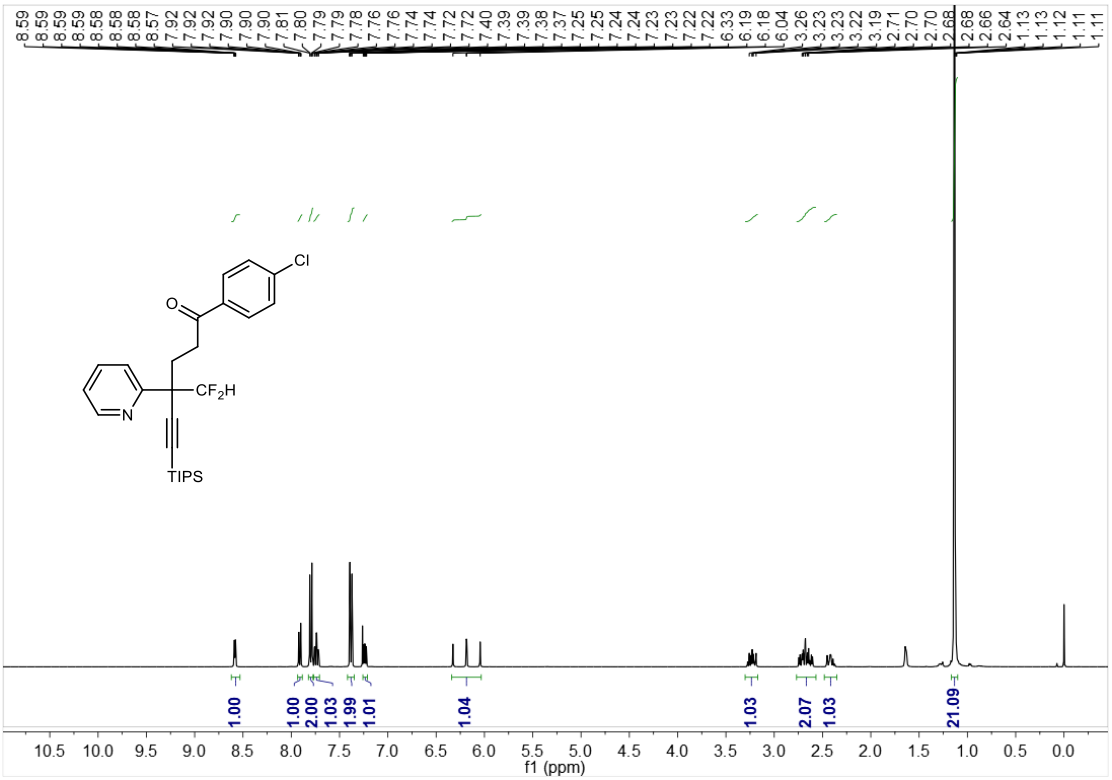
5. References

[1] S.-J. Chen, G.-S. Chen, T. Deng, J.-H. Li, Z.-Q. He, L.-S. Liu, H. Ren, Y.-L. Liu, 1,2-Dicarbofunctionalization of trifluoromethyl alkenes with pyridinium salts via a cycloaddition/visible-light-enabled fragmentation cascade. *Org. Lett.* 2022, **24**, 702-707.

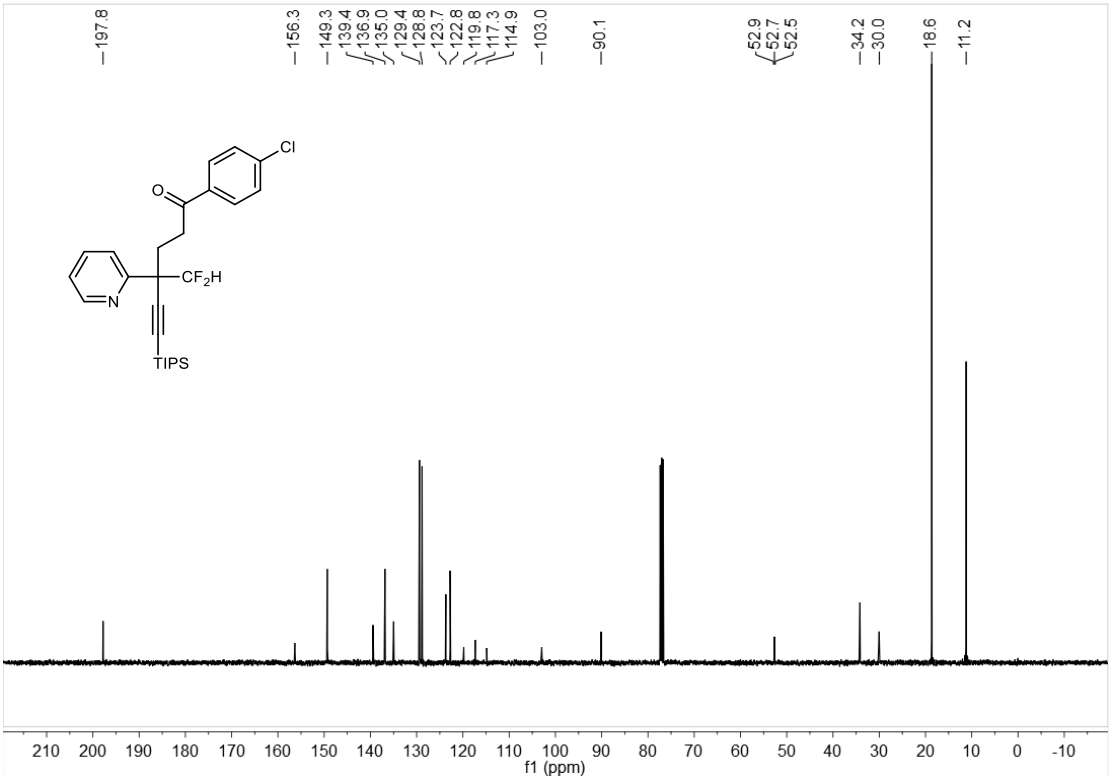
[2] Z.-Q. He, S.-J. Chen, G.-S. Chen, B.-L. Dong, J.-H. Lin, Y. Zhong, J.-M. Wu, Z. Ren, Y.-L. Liu, Base-mediated allylic defluorinative functionalizations of β-CF_2H-1,3-enynes enables the construction of terminal monofluoroenynes. *Org. Lett.* 2024, **26**, 7468-7473.

6. Copies of NMR Spectra

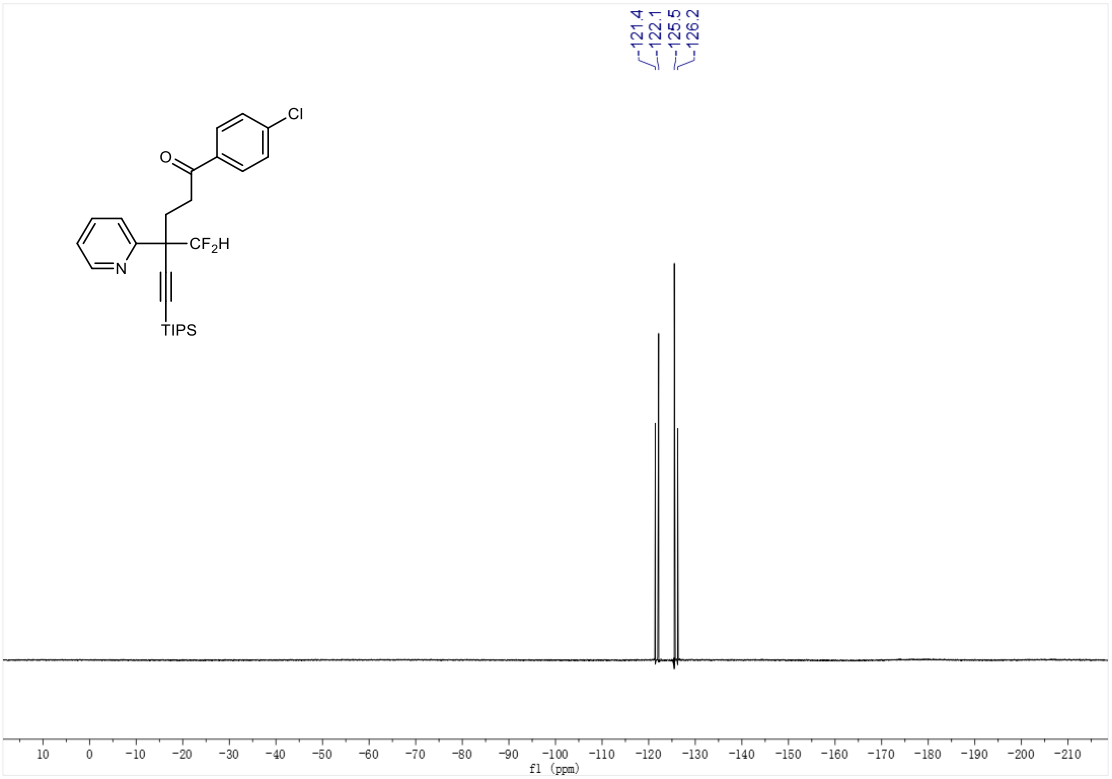
^{1}H NMR spectra of compound **3a** in $CDCl_3$ (400 MHz):



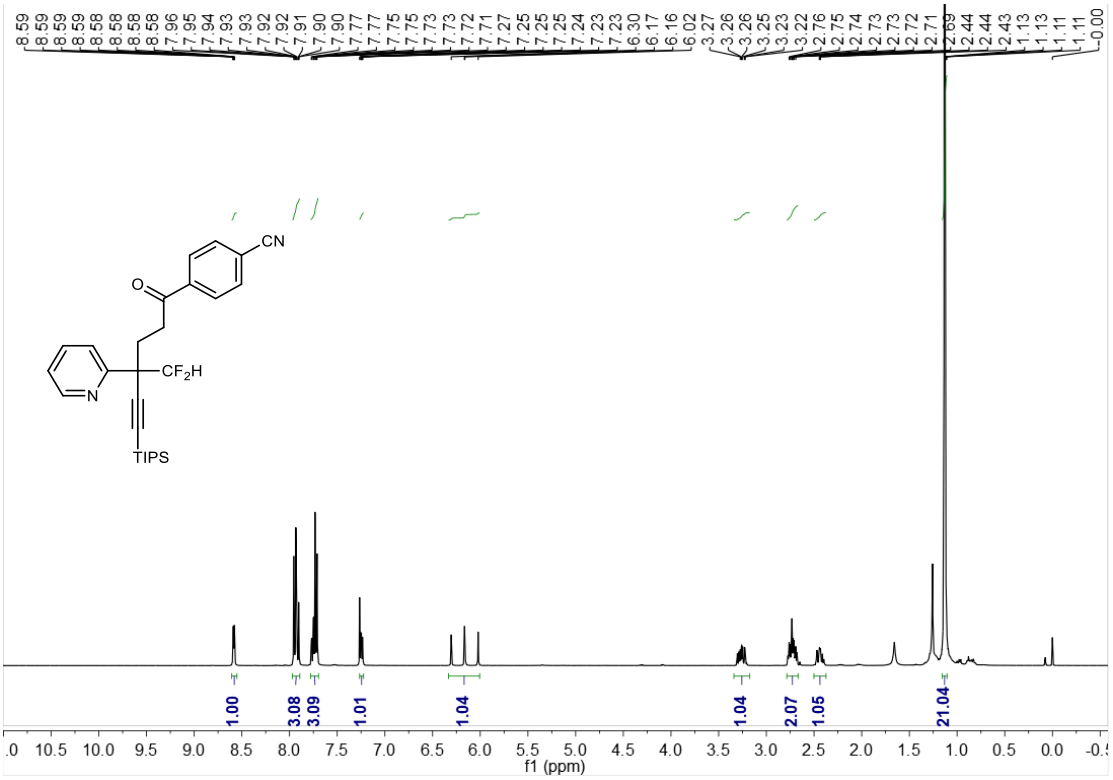
^{13}C NMR spectra of compound **3a** in $CDCl_3$ (101 MHz):



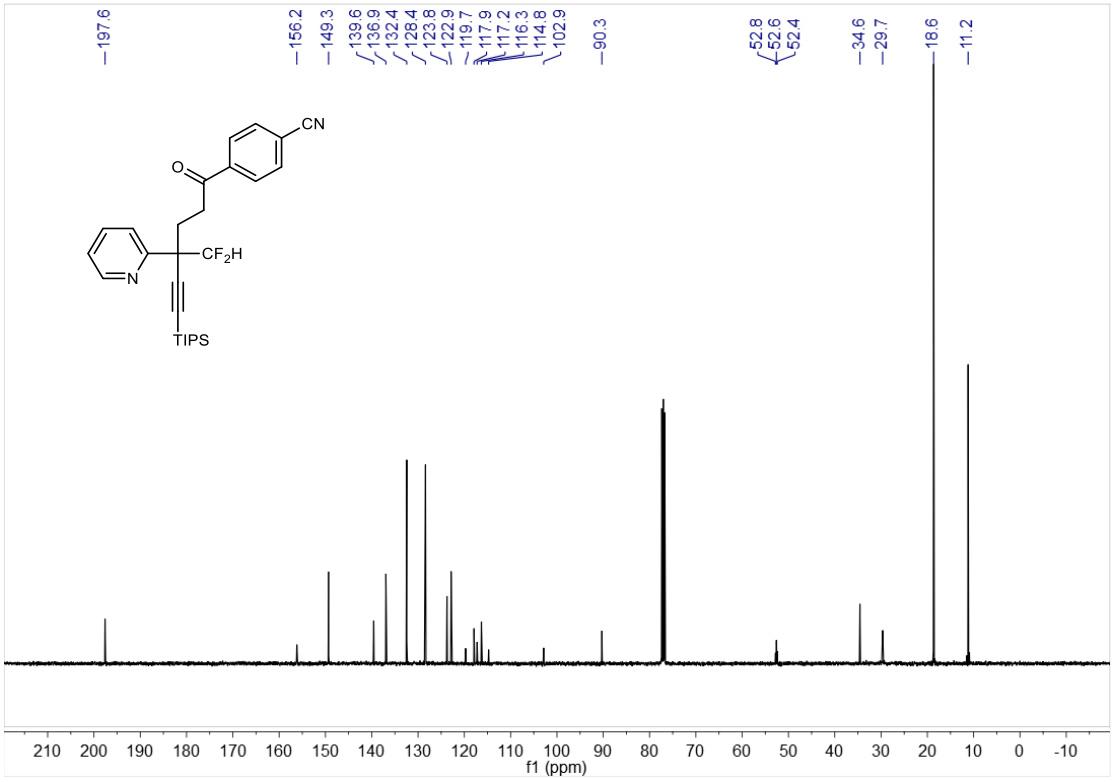
^{19}F NMR (with ^{1}H decoupling) spectra of compound **3a** in $CDCl_3$ (376 MHz):



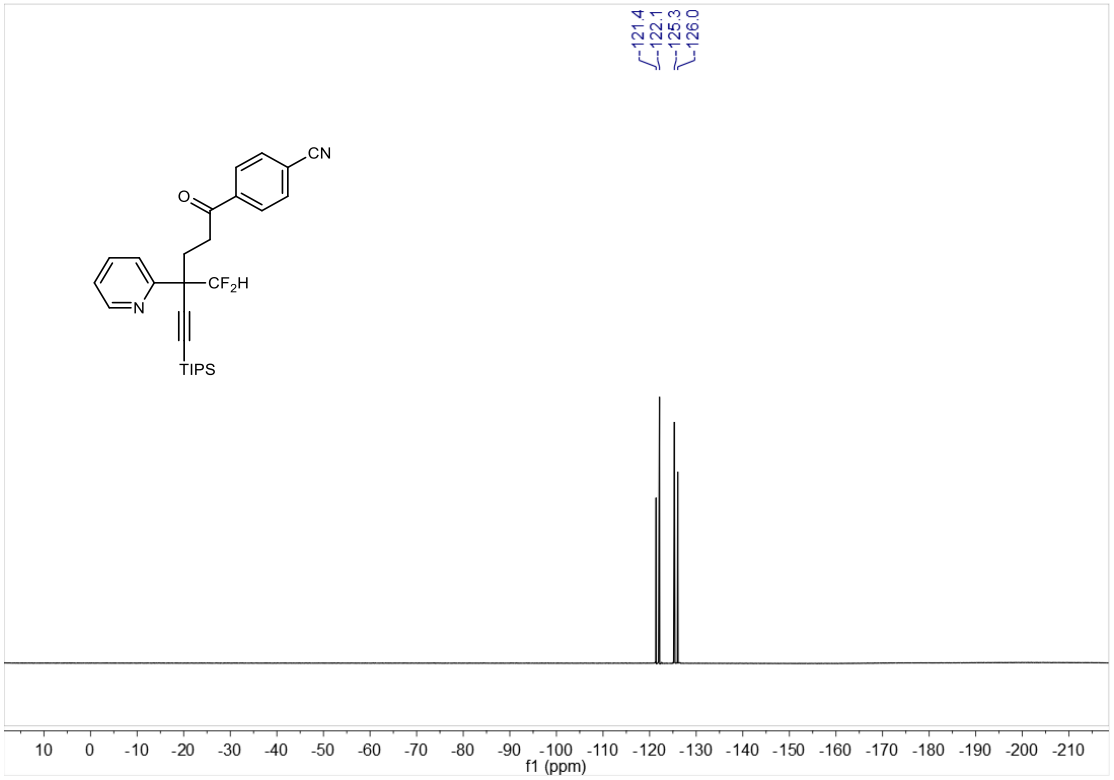
^{1}H NMR spectra of compound **3b** in $CDCl_3$ (400 MHz):



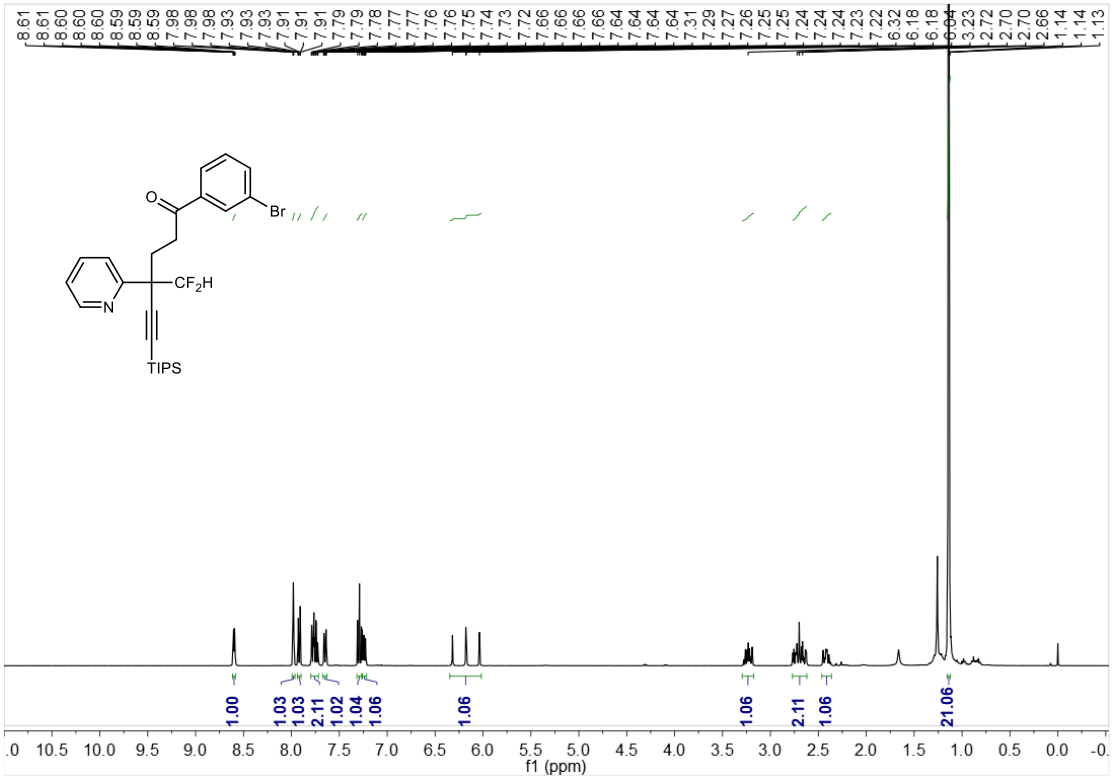
^{13}C NMR spectra of compound **3b** in $CDCl_3$ (101 MHz):



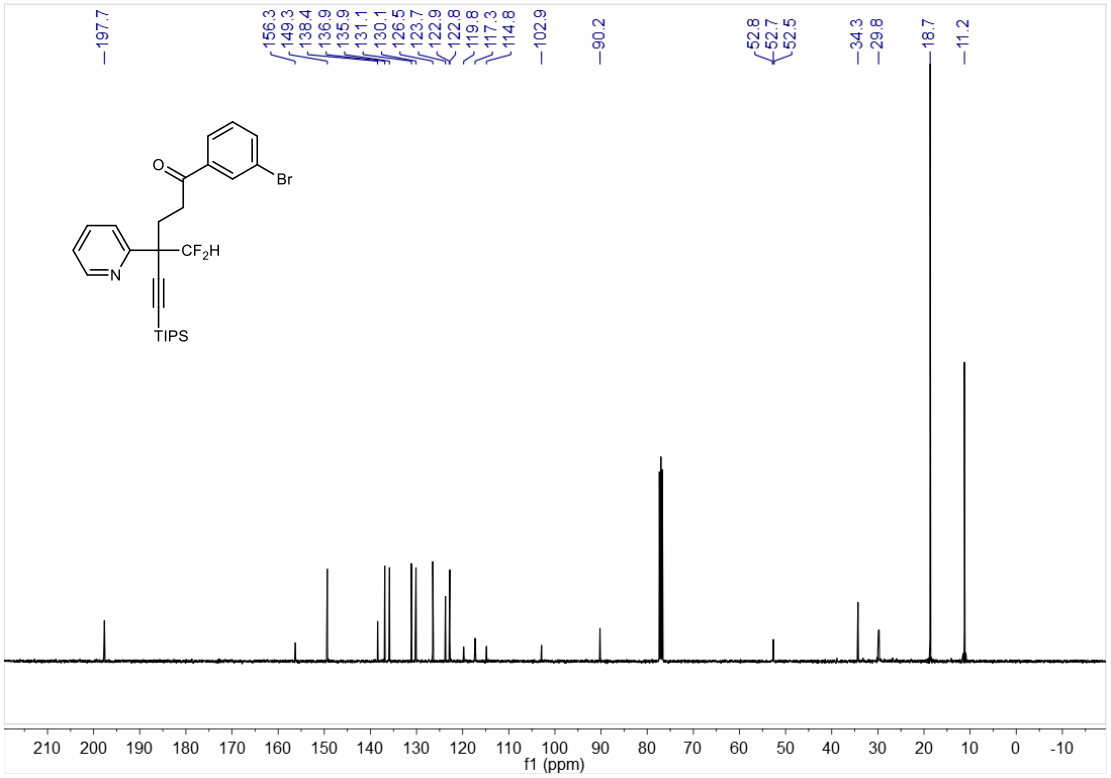
^{19}F NMR (with ^{1}H decoupling) spectra of compound **3b** in $CDCl_3$ (376 MHz):



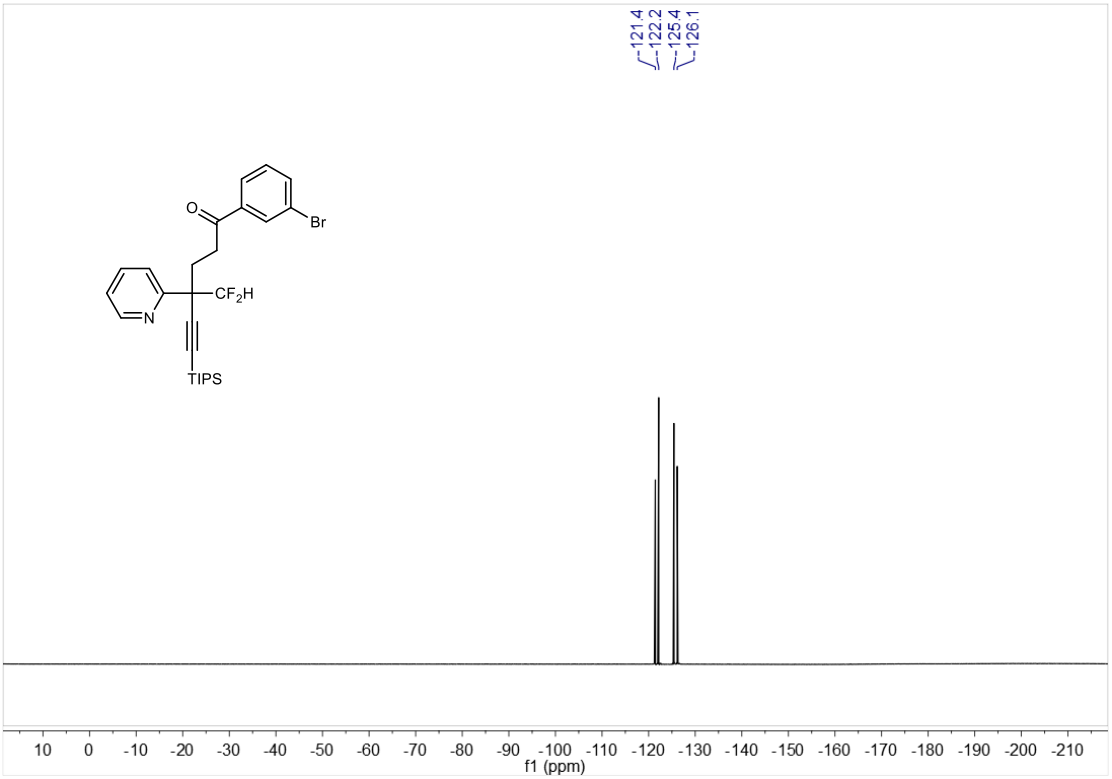
^{1}H NMR spectra of compound **3c** in $CDCl_3$ (400 MHz):



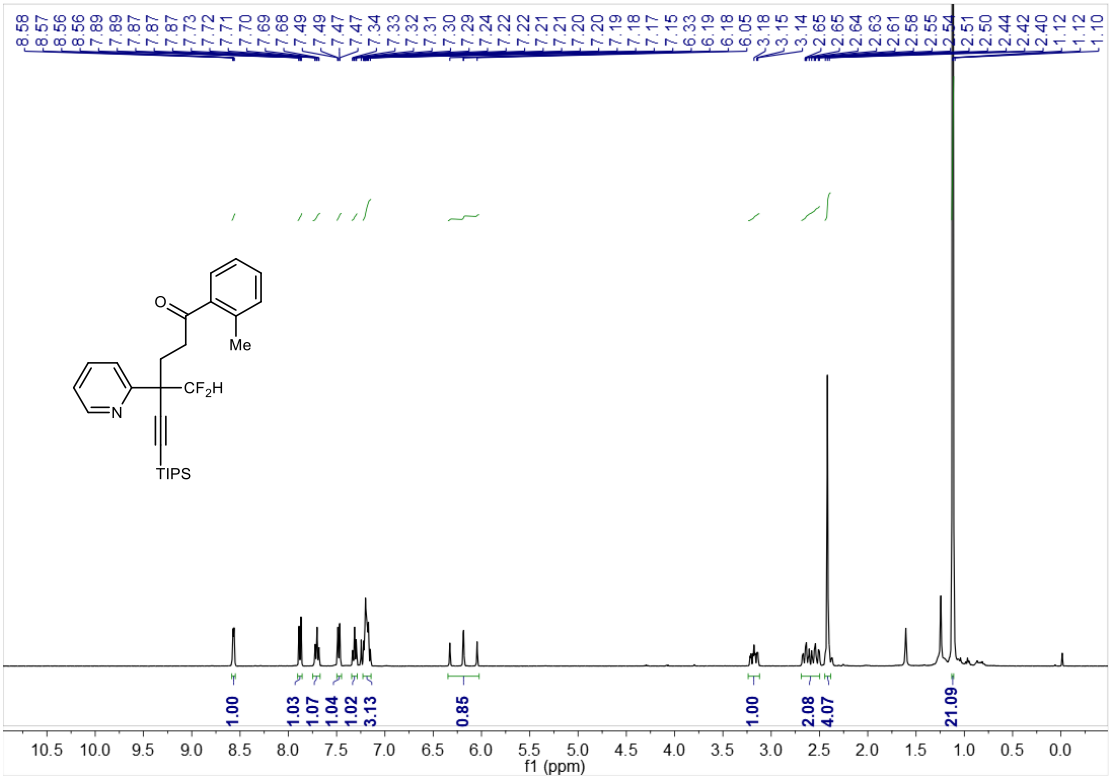
^{13}C NMR spectra of compound **3c** in $CDCl_3$ (101 MHz):



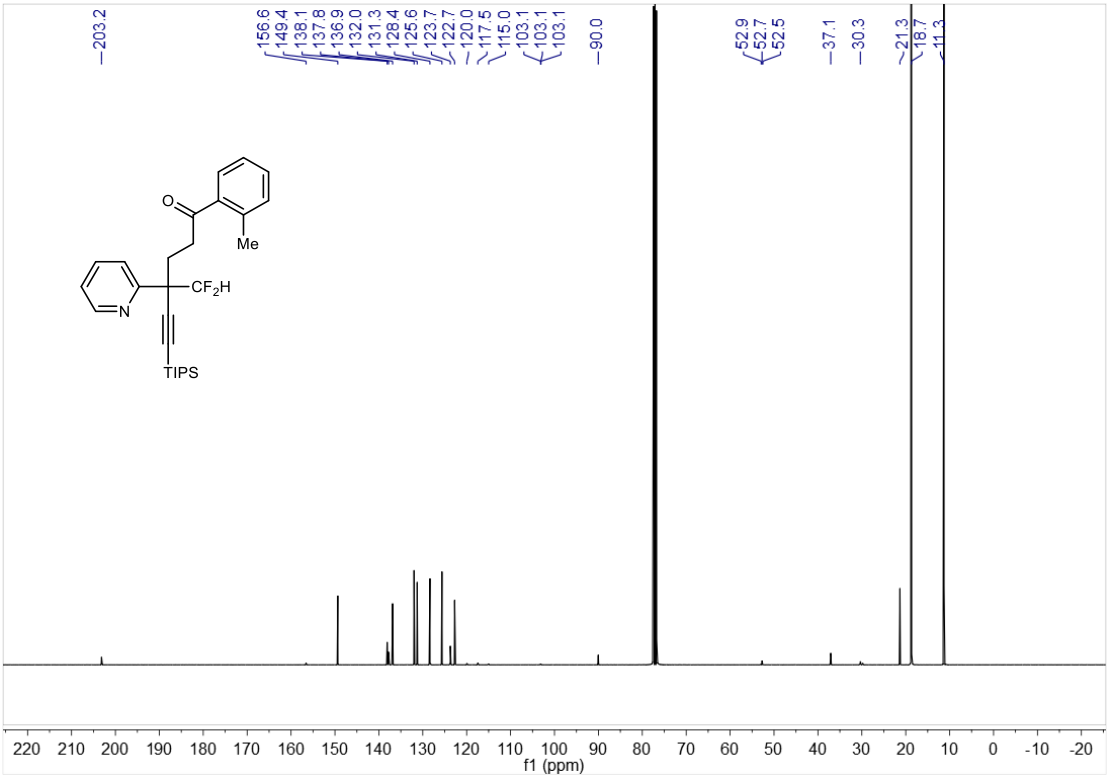
^{19}F NMR (with ^{1}H decoupling) spectra of compound **3c** in $CDCl_3$ (376 MHz):



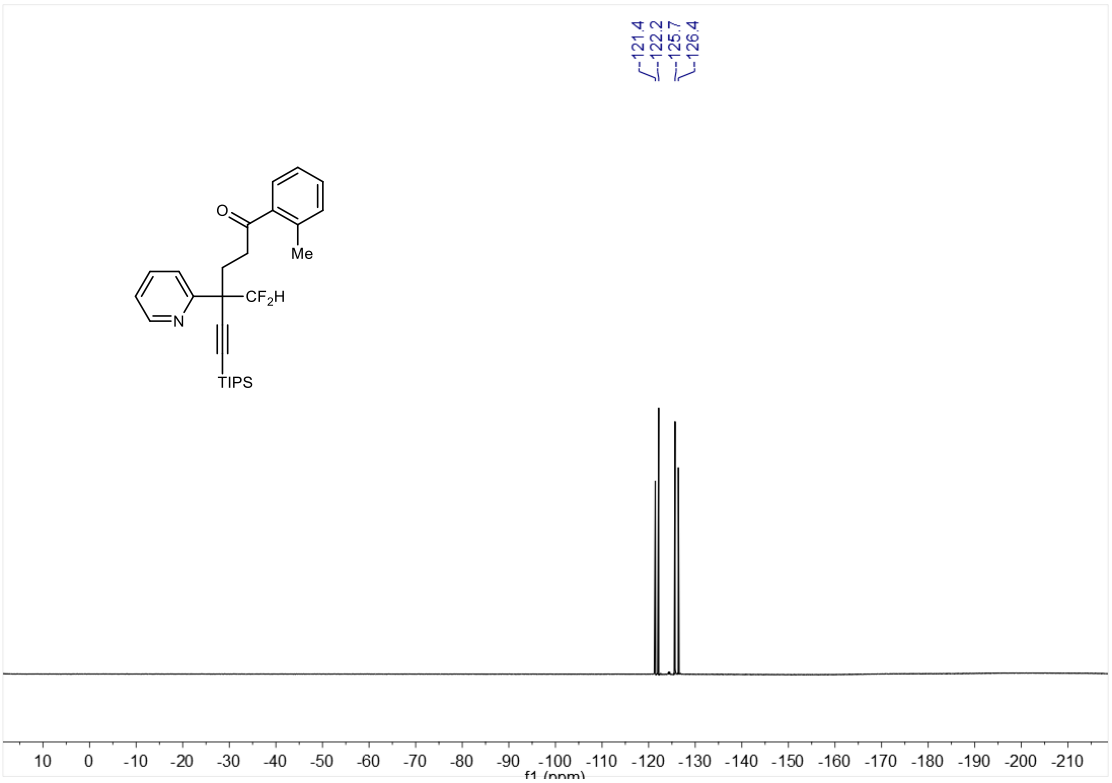
^{1}H NMR spectra of compound **3d** in $CDCl_3$ (400 MHz):



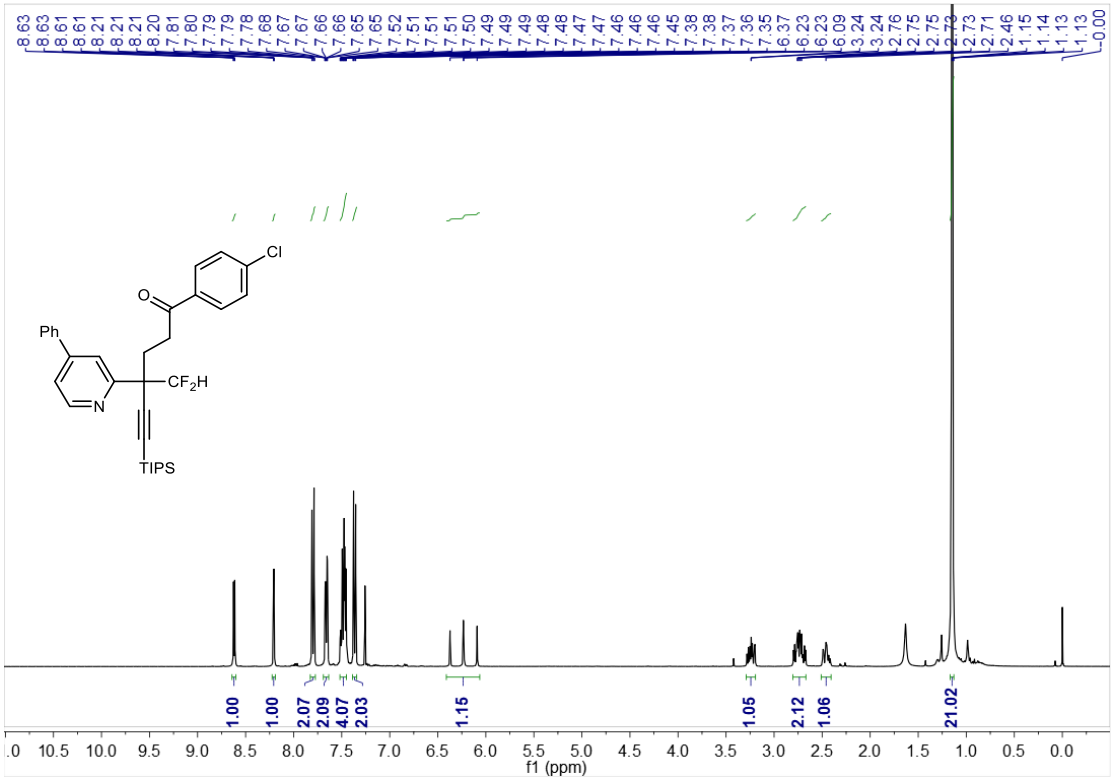
^{13}C NMR spectra of compound **3d** in $CDCl_3$ (101 MHz):



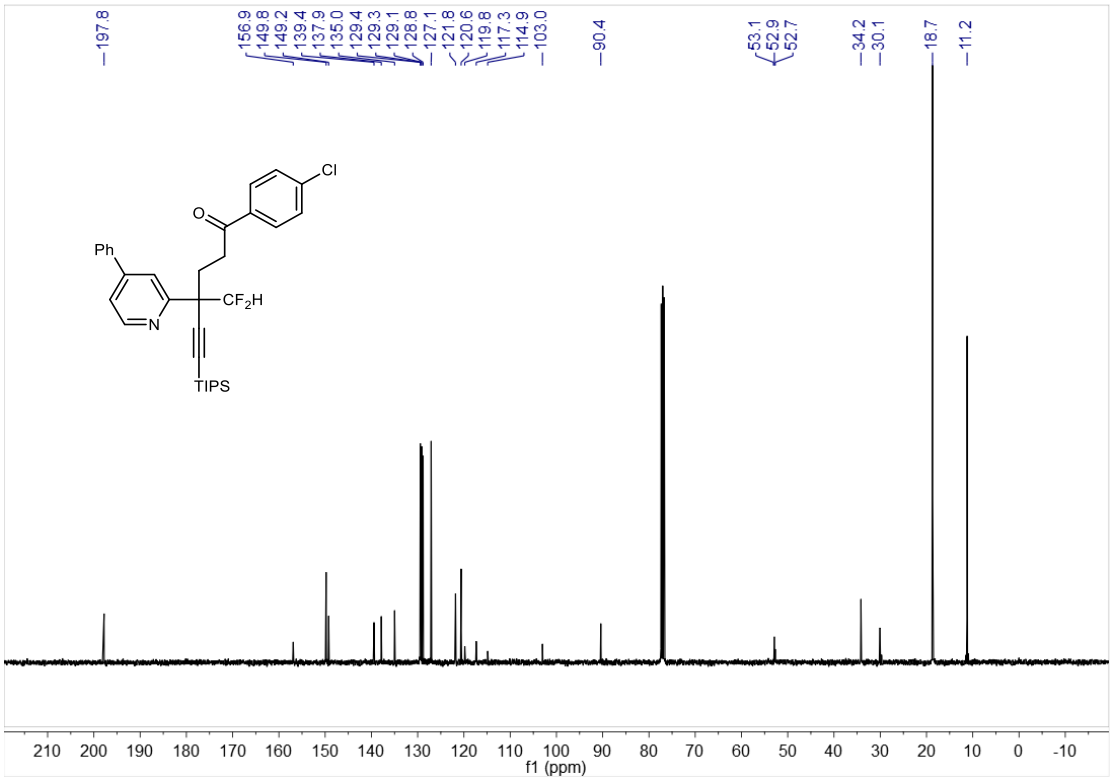
^{19}F NMR (with ^{1}H decoupling) spectra of compound **3d** in $CDCl_3$ (376 MHz):



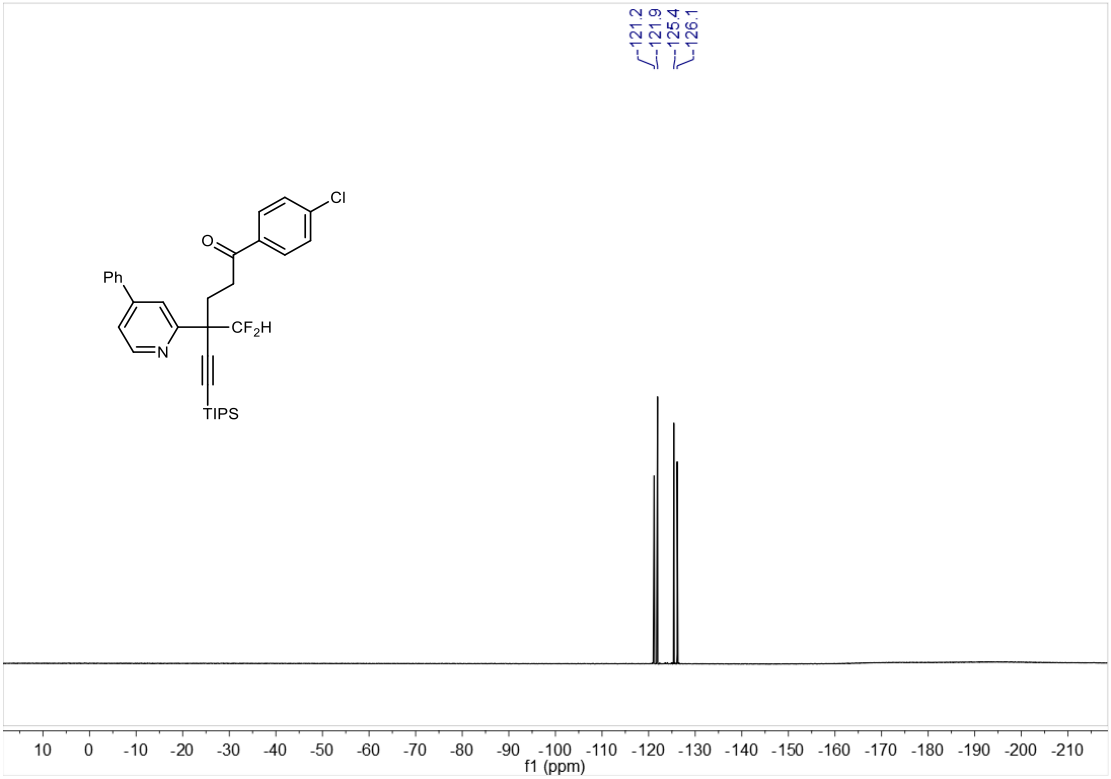
^{1}H NMR spectra of compound **3e** in $CDCl_3$ (400 MHz):



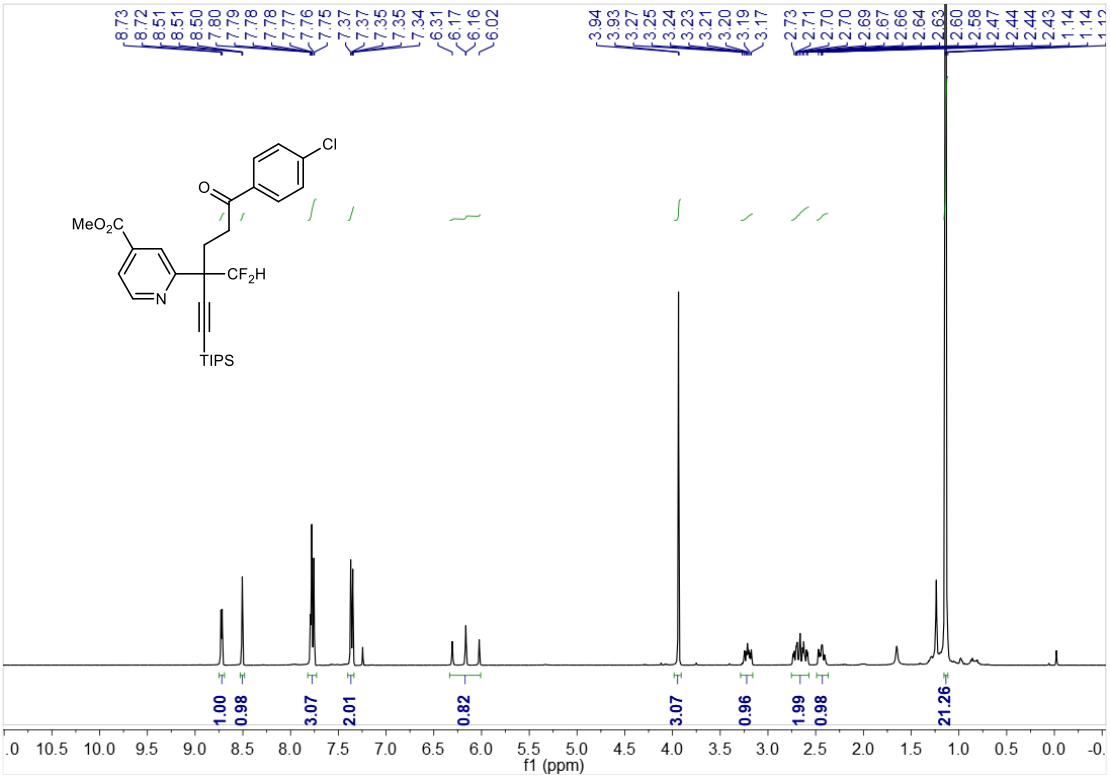
^{13}C NMR spectra of compound **3e** in $CDCl_3$ (101 MHz):



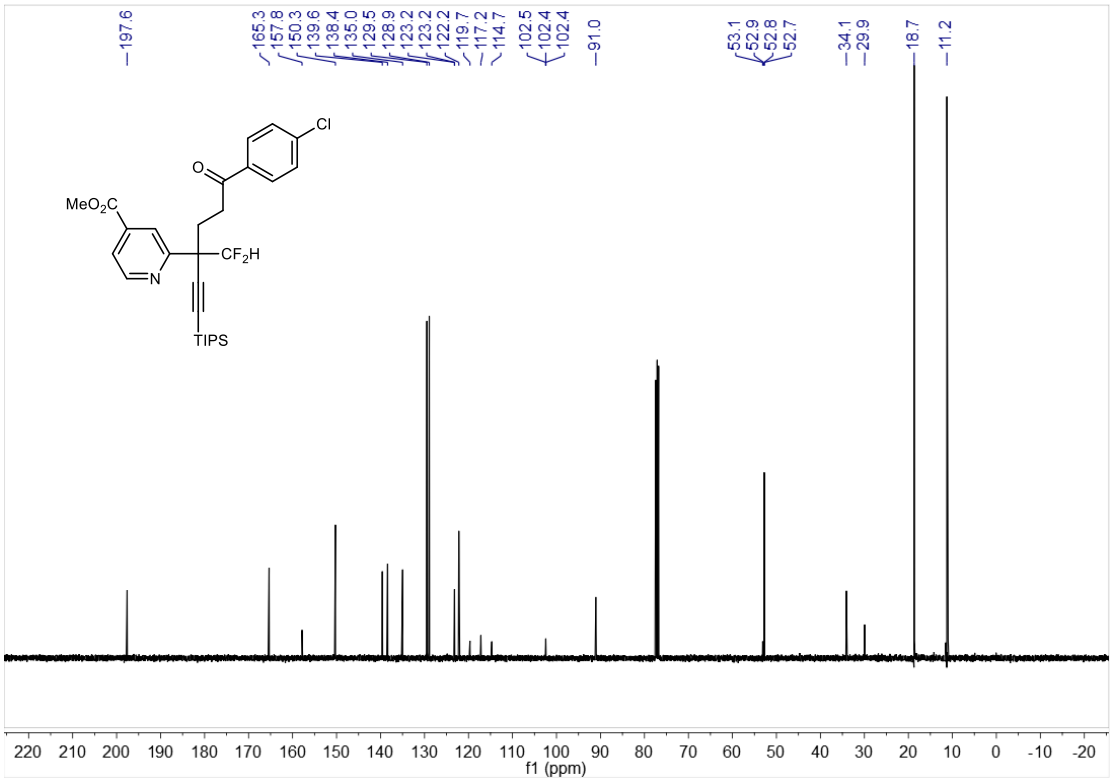
^{19}F NMR (with ^{1}H decoupling) spectra of compound **3e** in $CDCl_3$ (376 MHz):



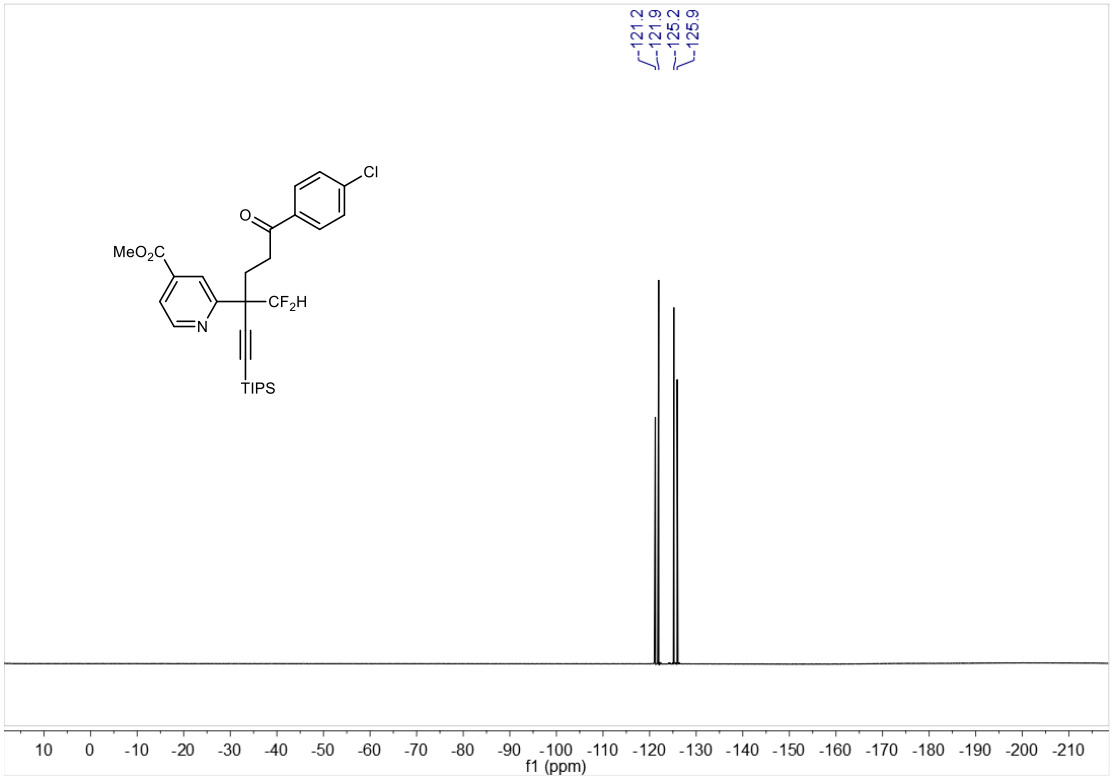
^{1}H NMR spectra of compound **3f** in $CDCl_3$ (400 MHz):



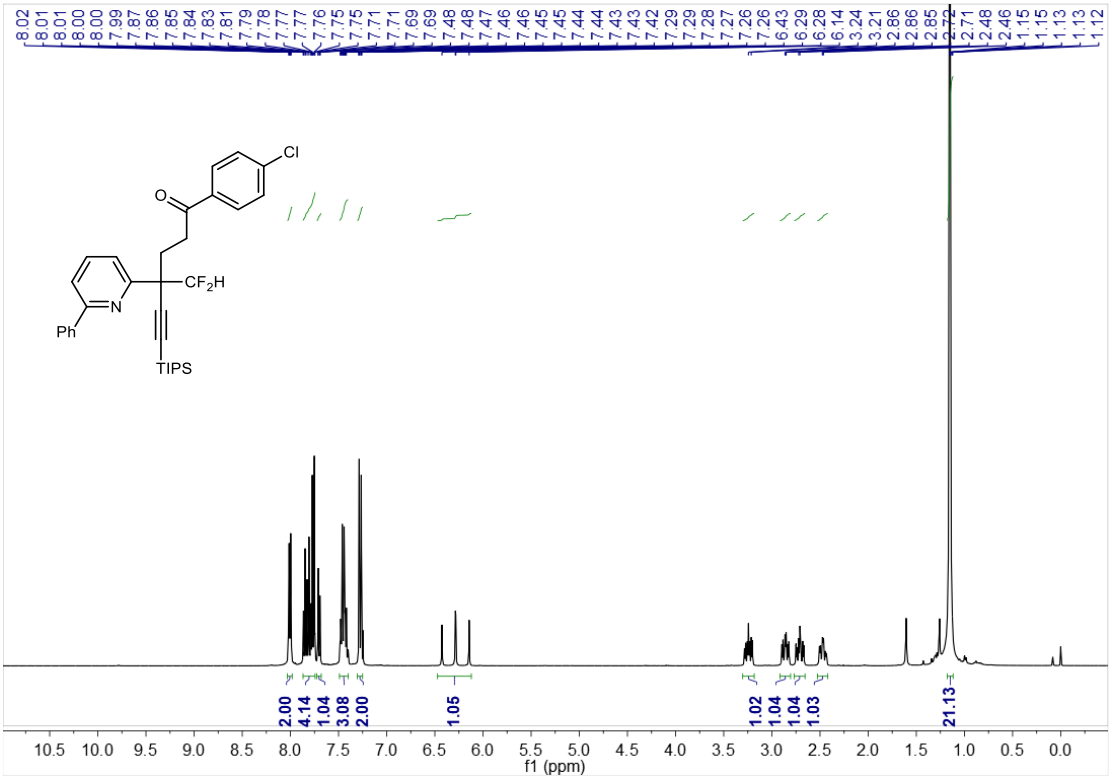
^{13}C NMR spectra of compound **3f** in $CDCl_3$ (101 MHz):



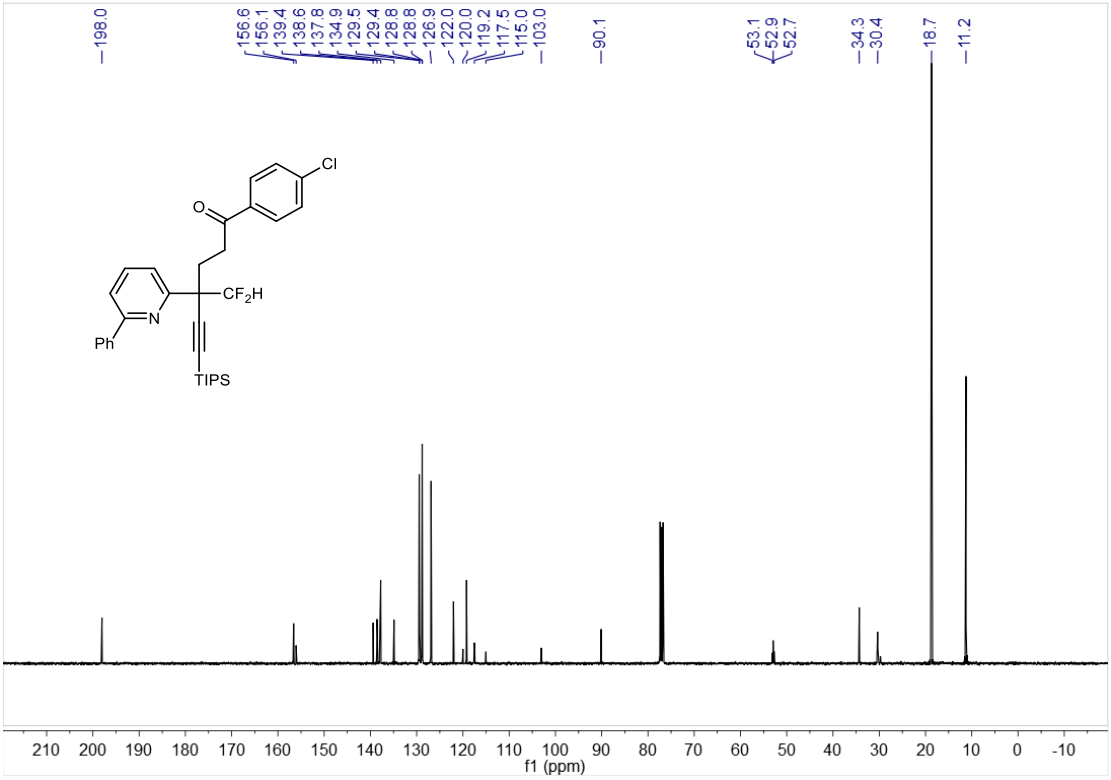
^{19}F NMR (with ^{1}H decoupling) spectra of compound **3f** in $CDCl_3$ (376 MHz):



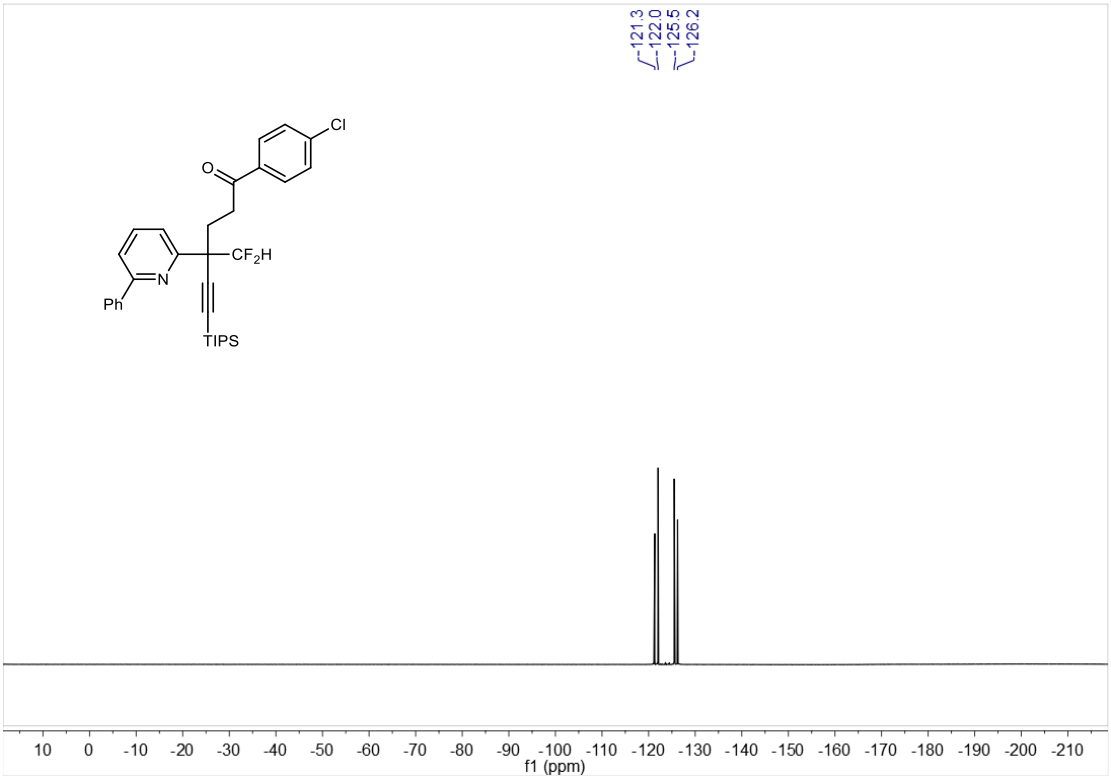
^{1}H NMR spectra of compound **3g** in $CDCl_3$ (400 MHz):



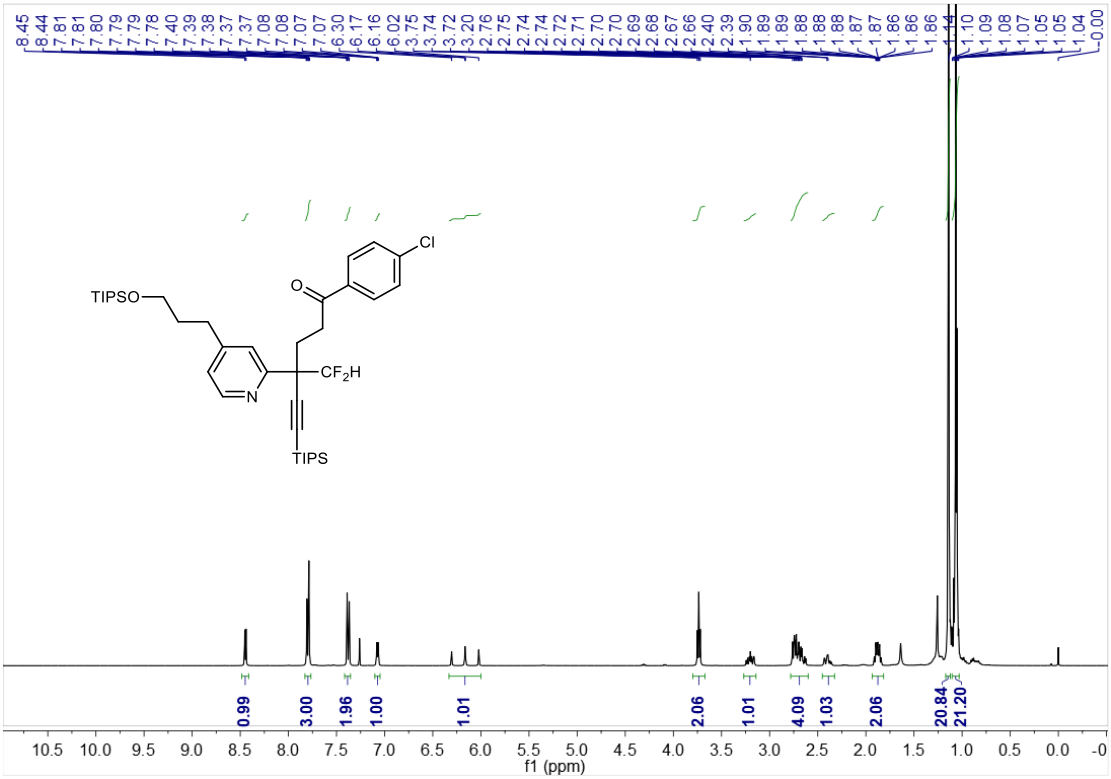
^{13}C NMR spectra of compound **3g** in $CDCl_3$ (101 MHz):



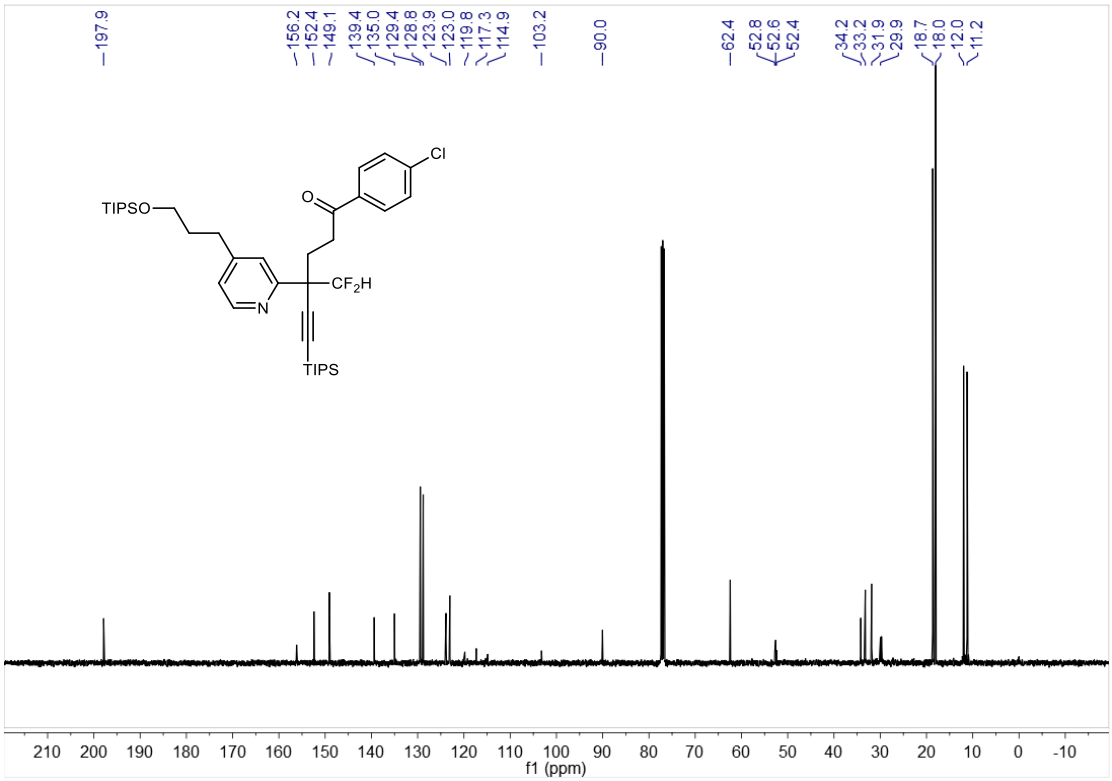
^{19}F NMR (with ^{1}H decoupling) spectra of compound **3g** in $CDCl_3$ (376 MHz):



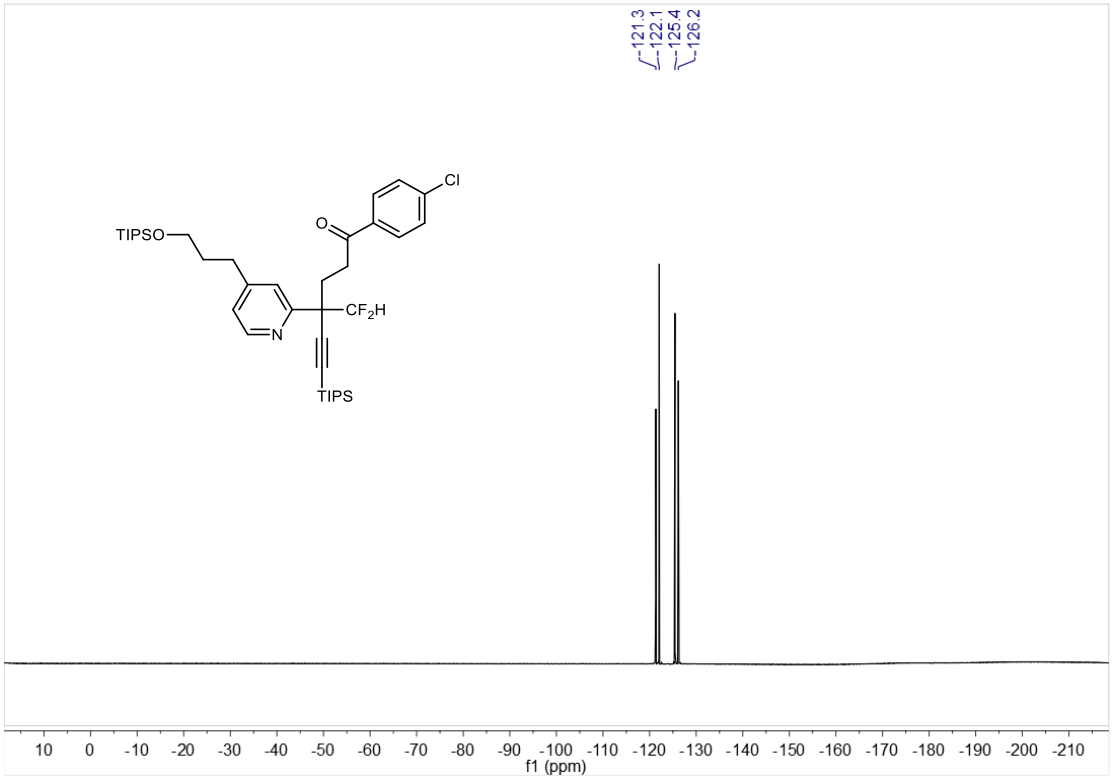
^{1}H NMR spectra of compound **3h** in $CDCl_3$ (400 MHz):



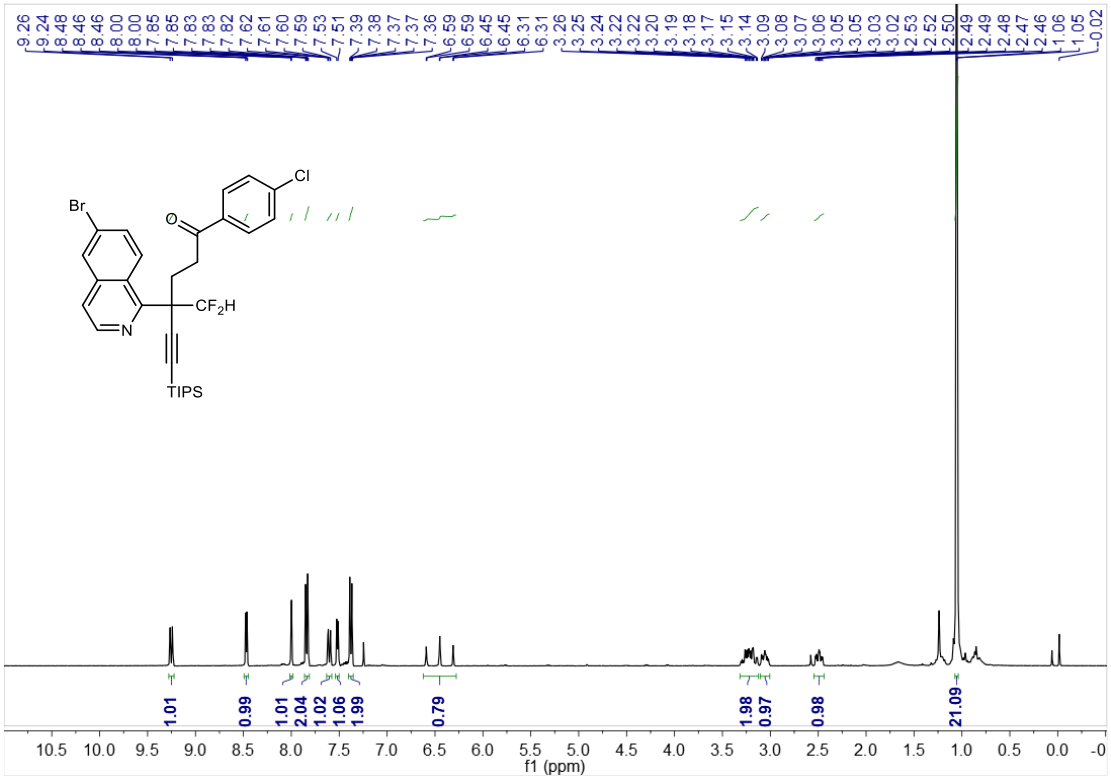
^{13}C NMR spectra of compound **3h** in $CDCl_3$ (101 MHz):



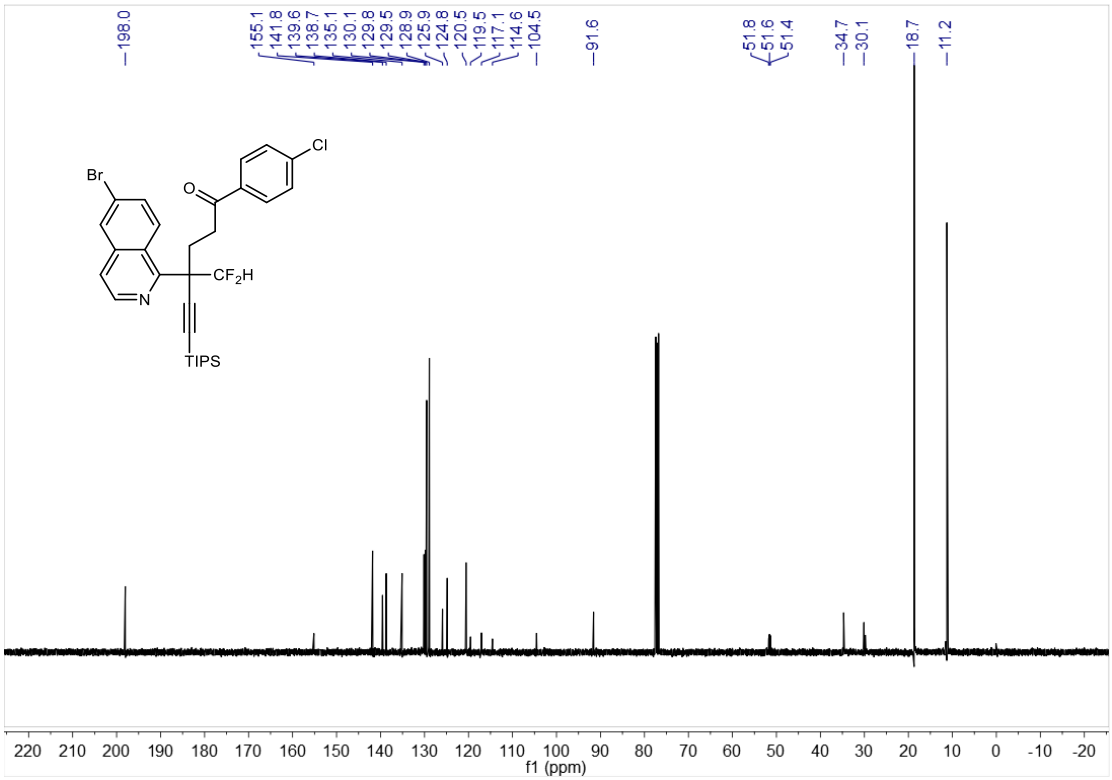
^{19}F NMR (with ^{1}H decoupling) spectra of compound **3h** in $CDCl_3$ (376 MHz):



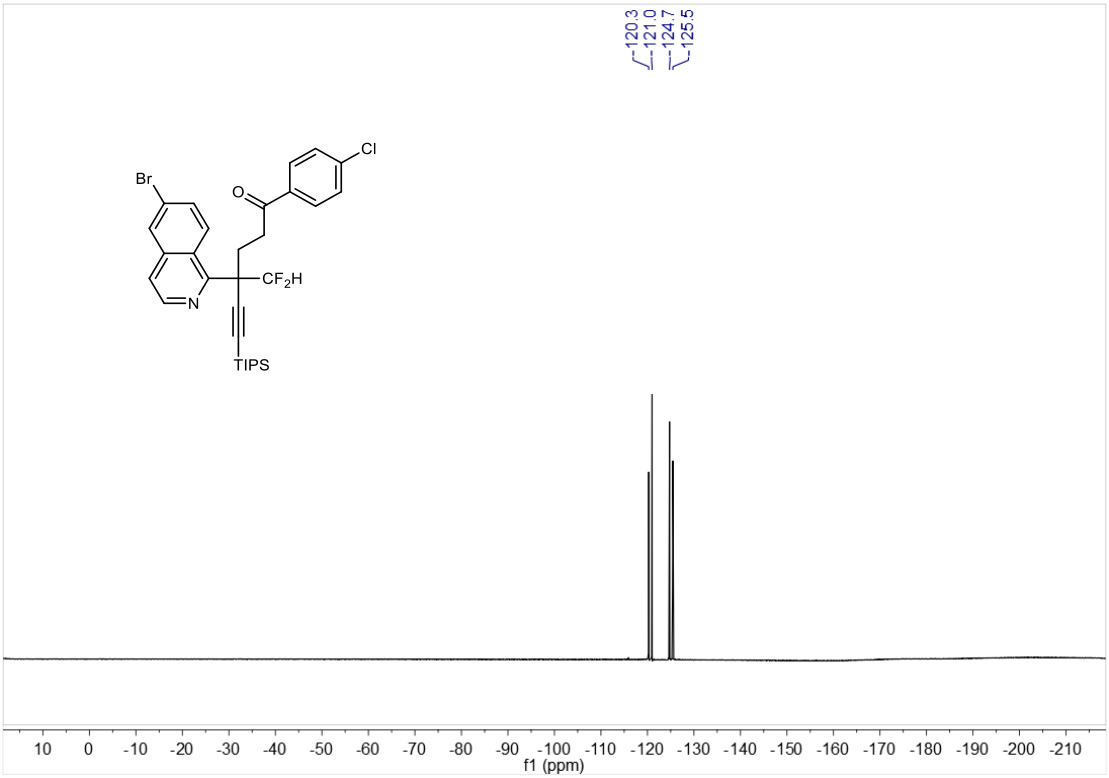
^{1}H NMR spectra of compound **3i** in $CDCl_3$ (400 MHz):



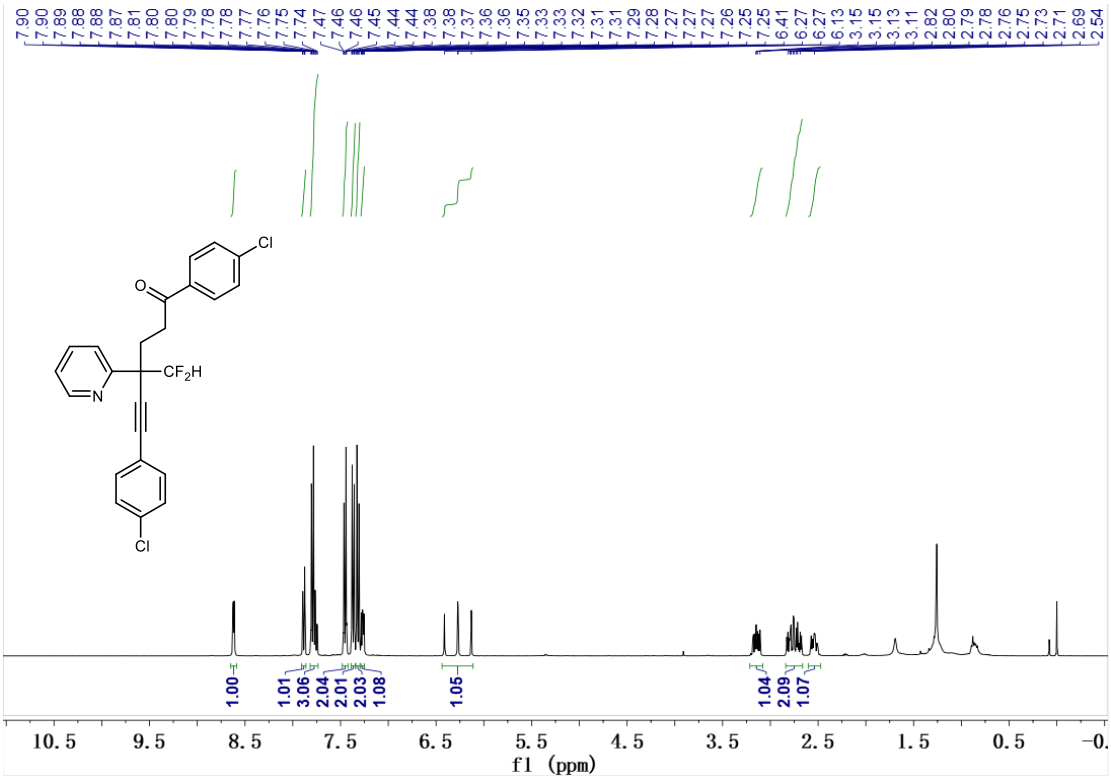
^{13}C NMR spectra of compound **3i** in $CDCl_3$ (101 MHz):



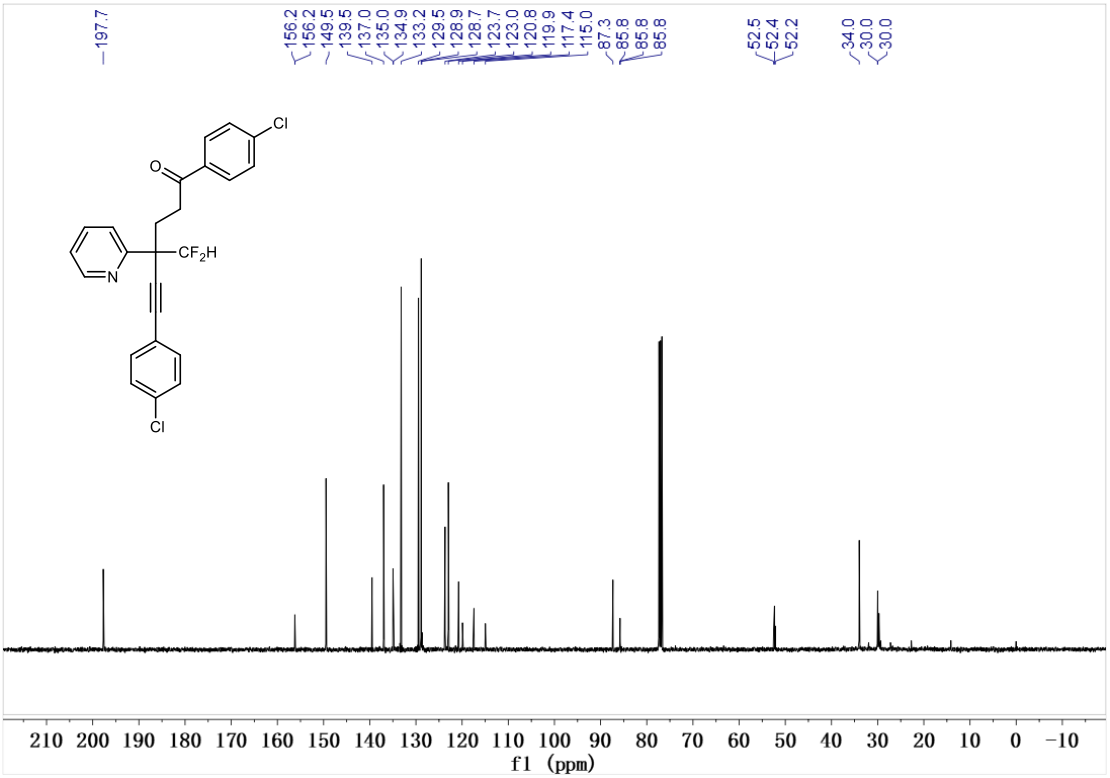
^{19}F NMR (with ^{1}H decoupling) spectra of compound **3i** in $CDCl_3$ (376 MHz):



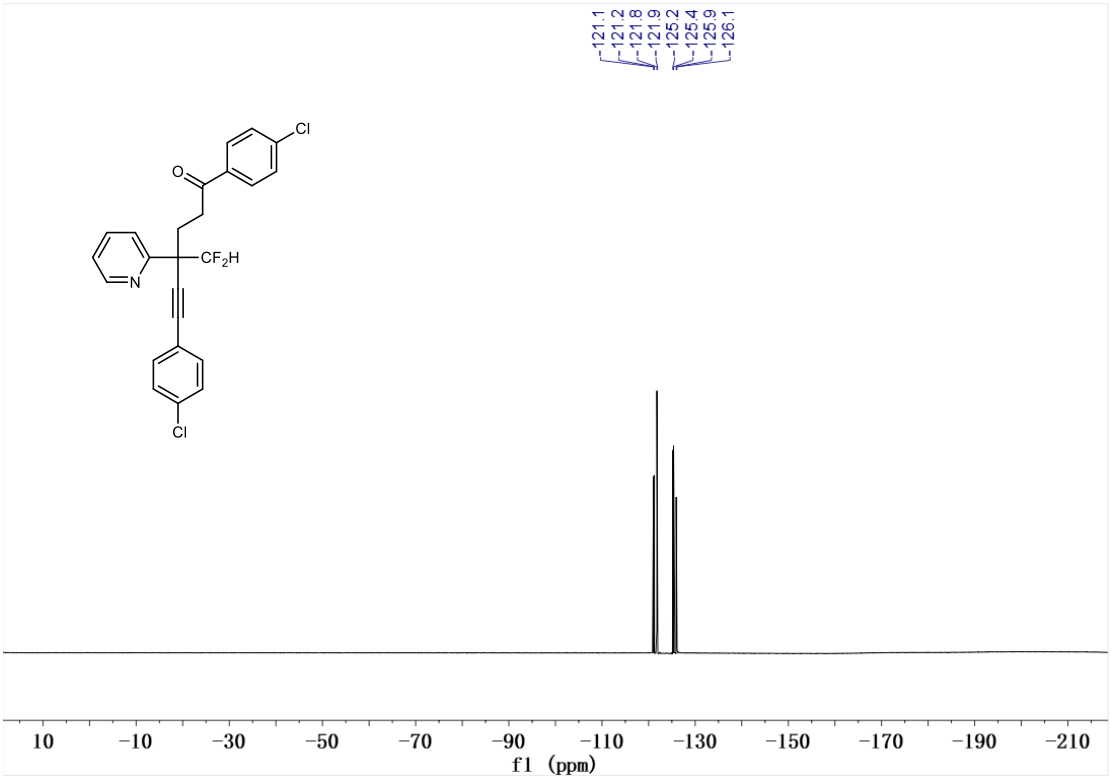
^{1}H NMR spectra of compound **3j** in $CDCl_3$ (400 MHz):



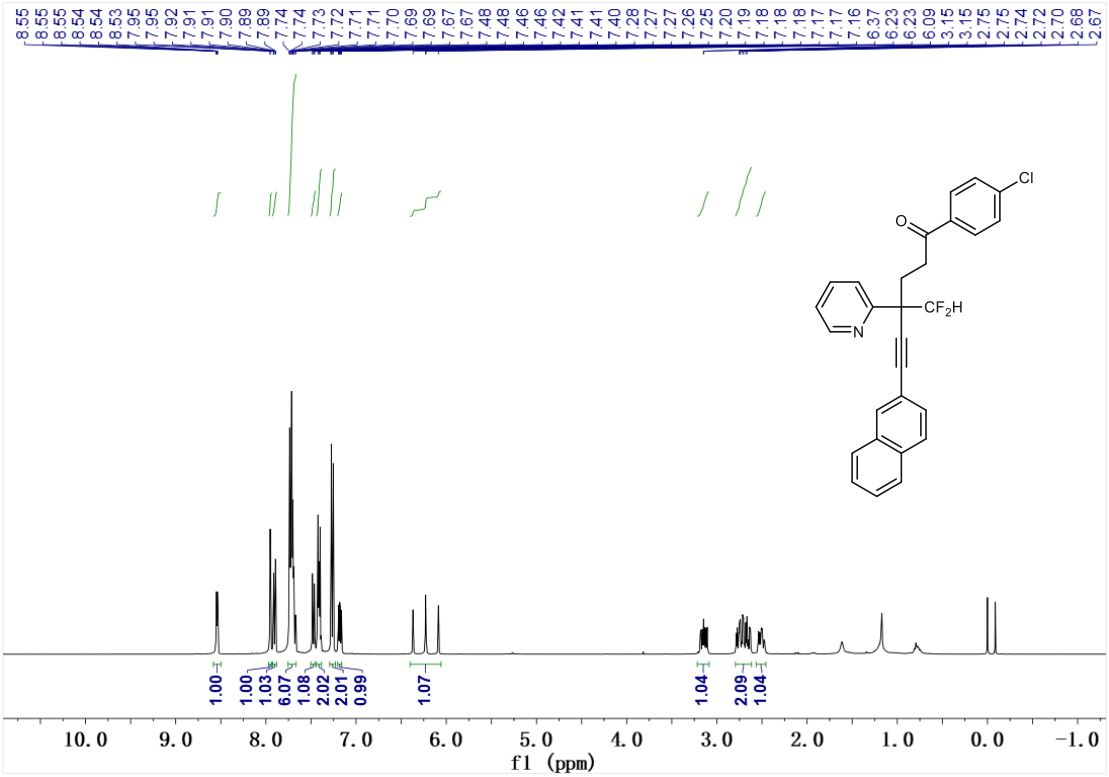
^{13}C NMR spectra of compound **3j** in $CDCl_3$ (101 MHz):



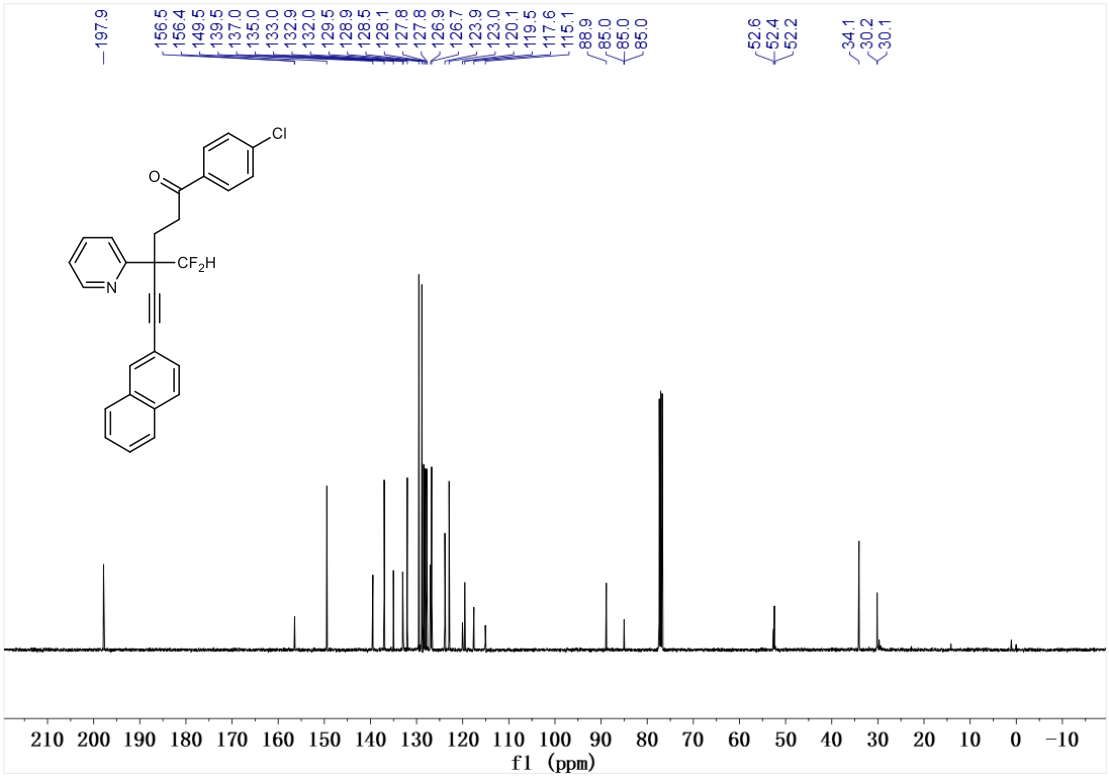
^{19}F NMR spectra of compound **3j** in $CDCl_3$ (376 MHz):



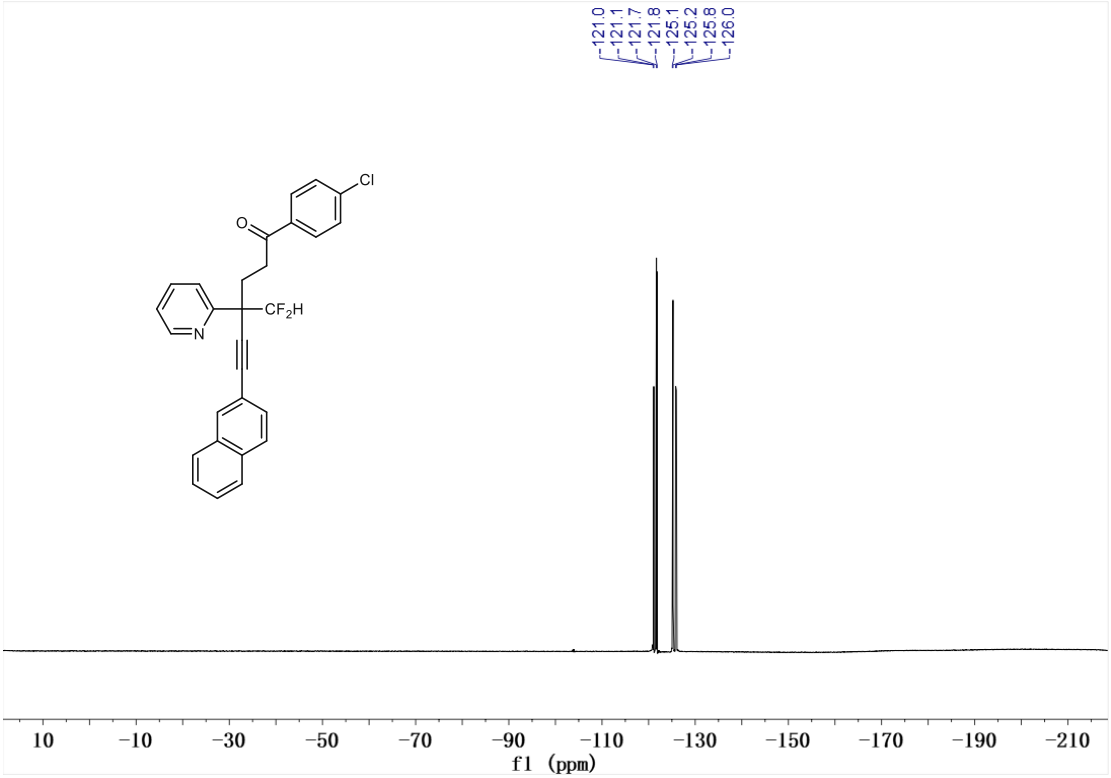
^{1}H NMR spectra of compound **3k** in $CDCl_3$ (400 MHz):



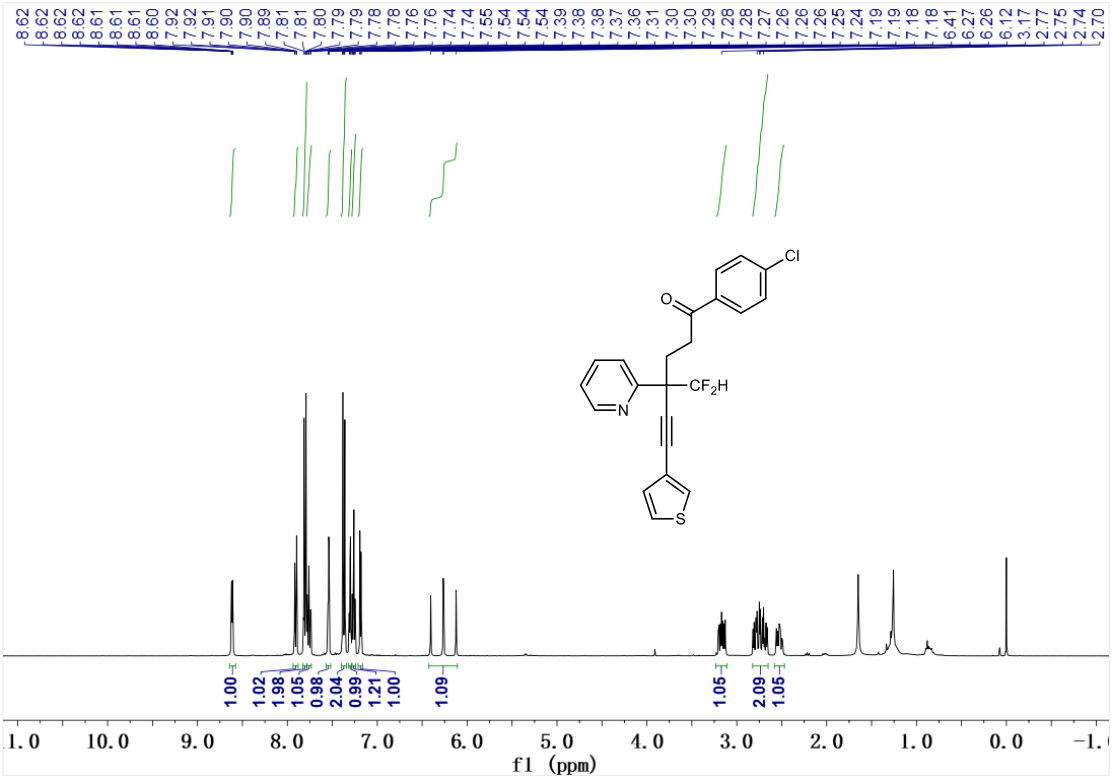
^{13}C NMR spectra of compound **3k** in $CDCl_3$ (101 MHz):



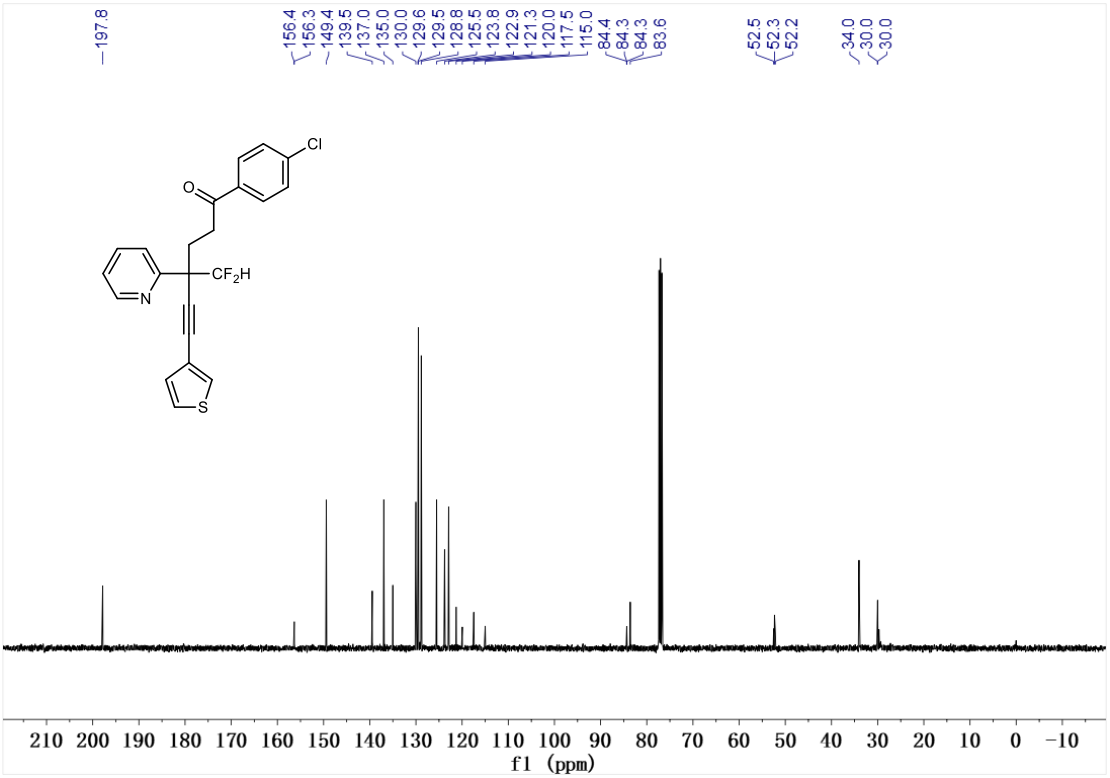
^{19}F NMR spectra of compound **3k** in $CDCl_3$ (376 MHz):



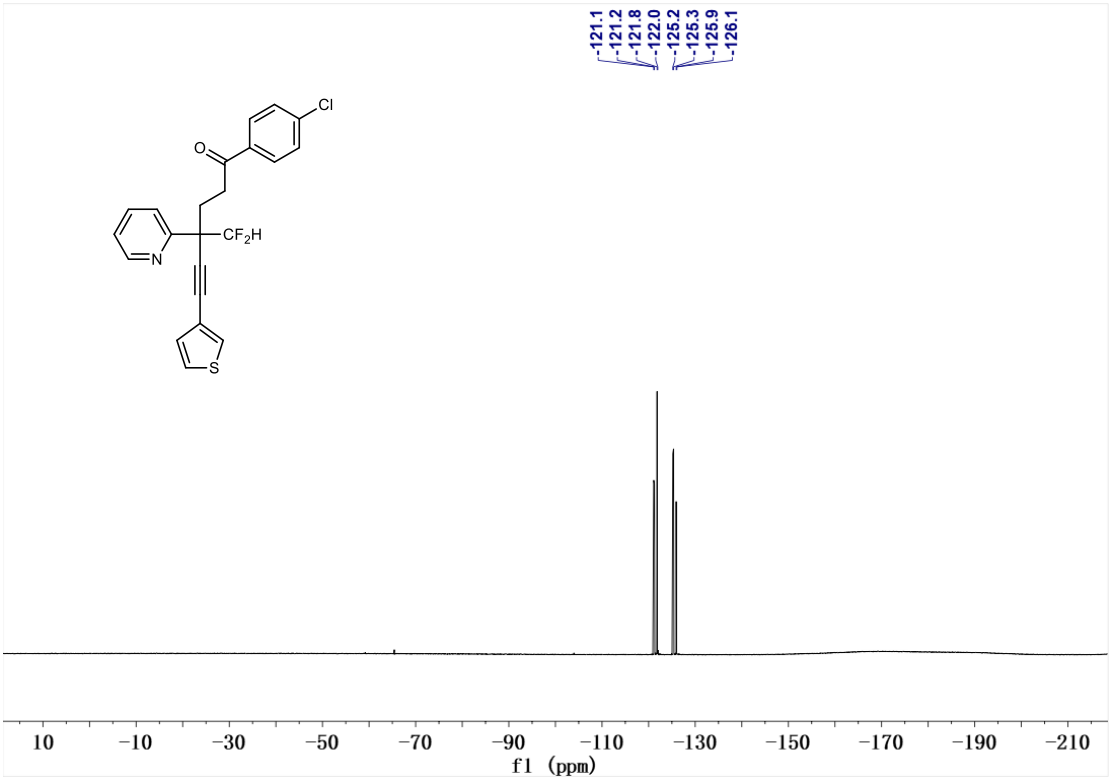
^{1}H NMR spectra of compound **3l** in $CDCl_3$ (400 MHz):



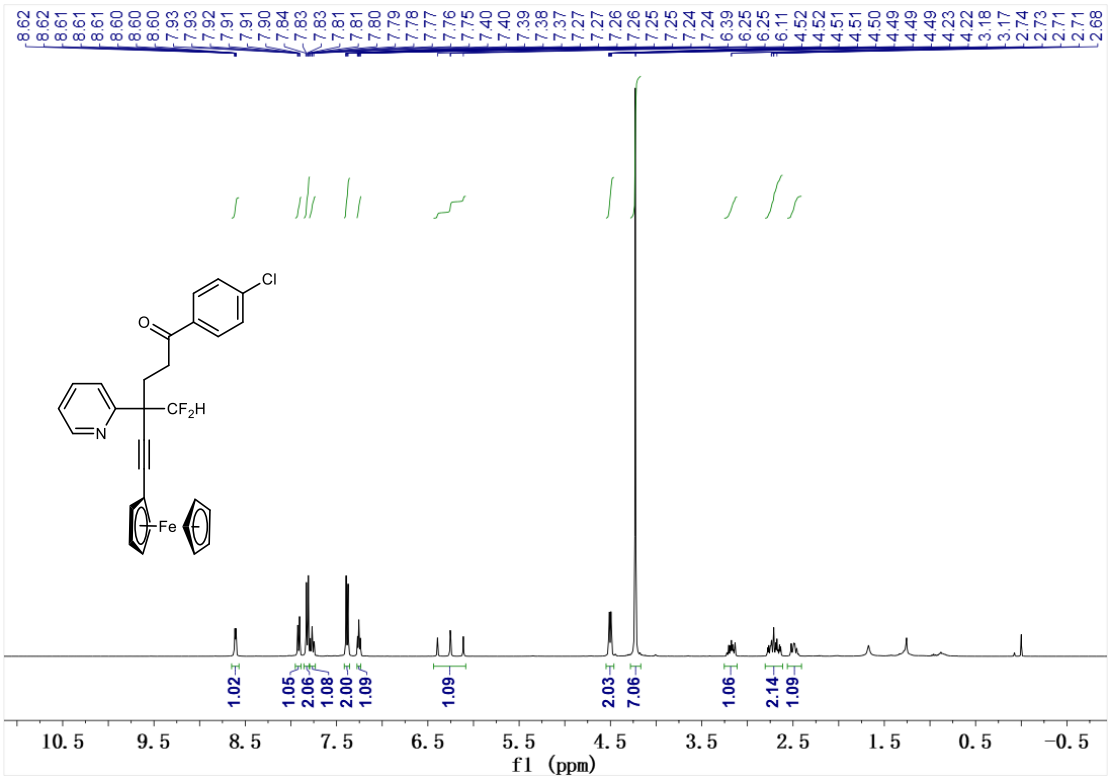
^{13}C NMR spectra of compound **3l** in $CDCl_3$ (101 MHz):



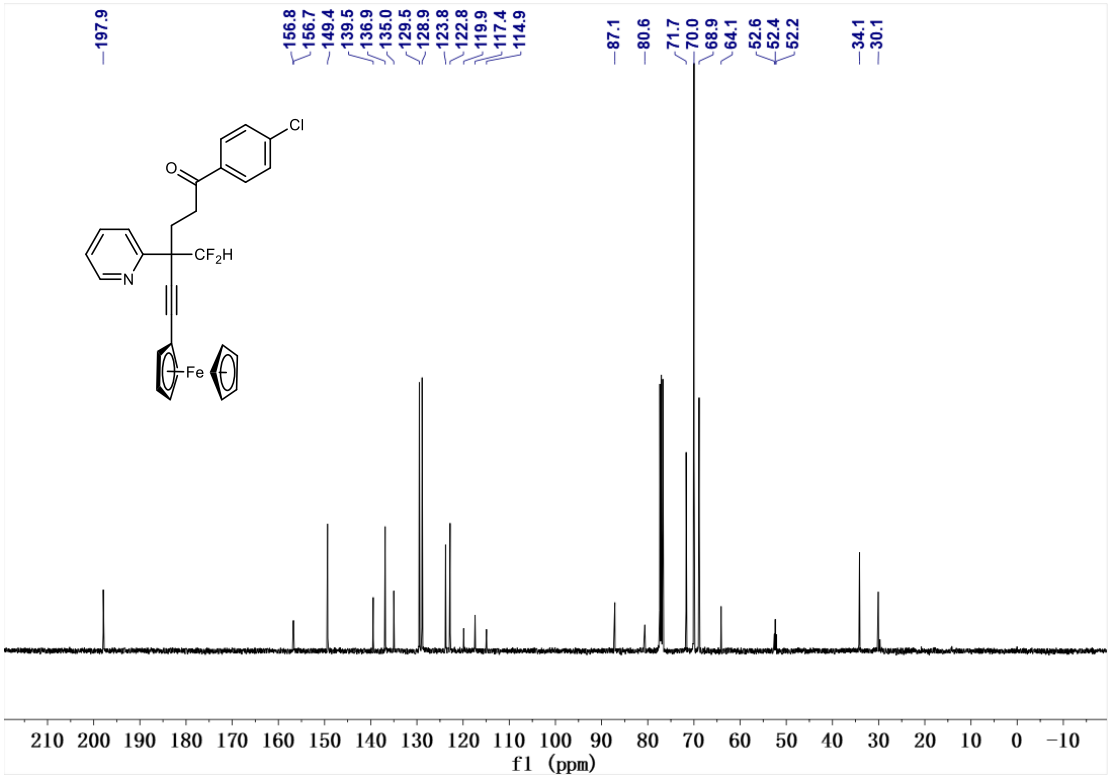
^{19}F NMR spectra of compound **3l** in $CDCl_3$ (376 MHz):



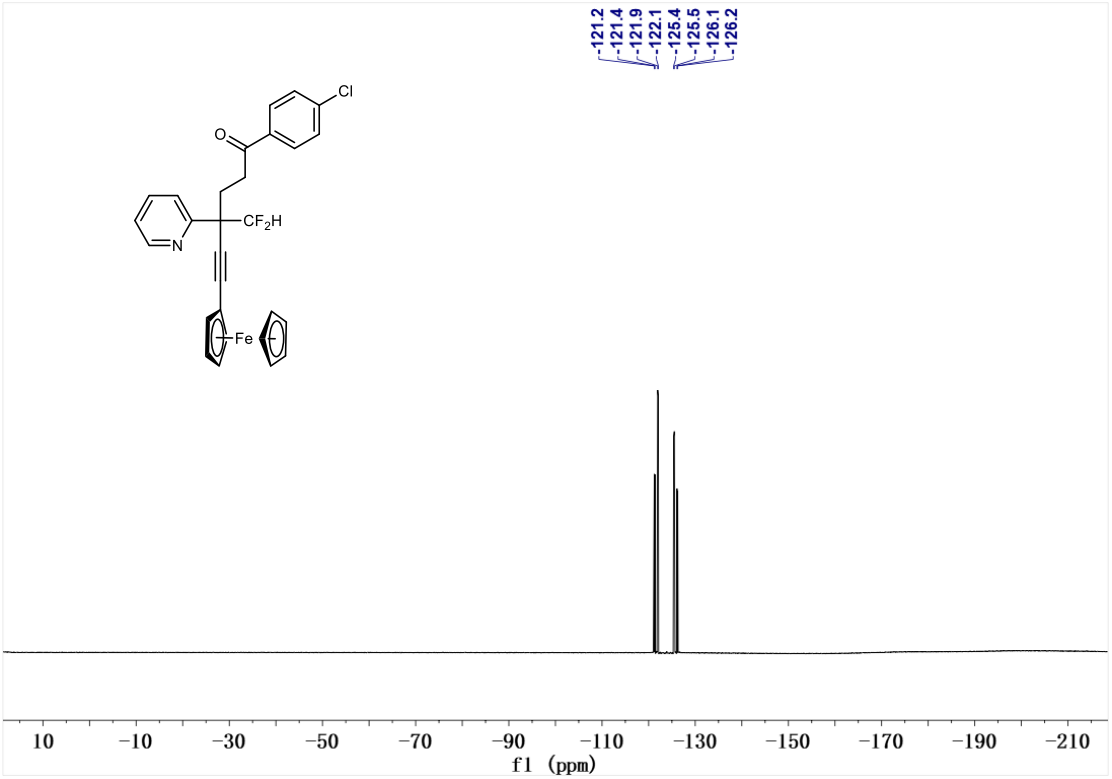
^{1}H NMR spectra of compound **3m** in $CDCl_3$ (400 MHz):



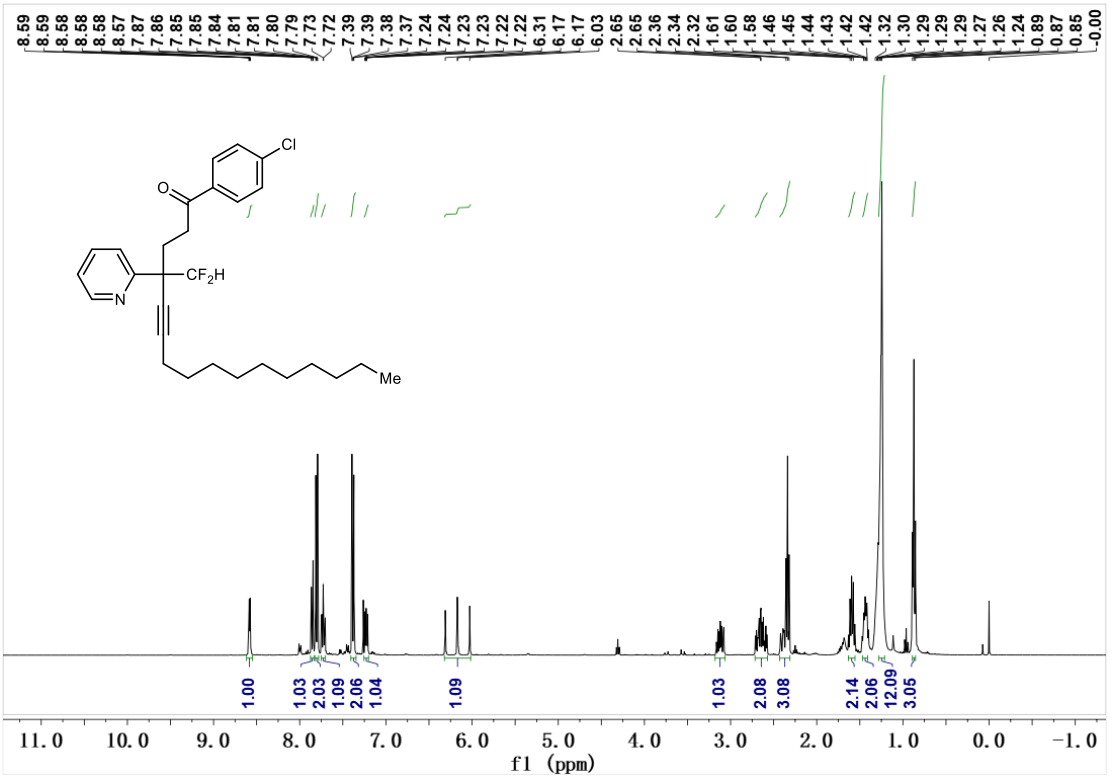
^{13}C NMR spectra of compound **3m** in $CDCl_3$ (101 MHz):



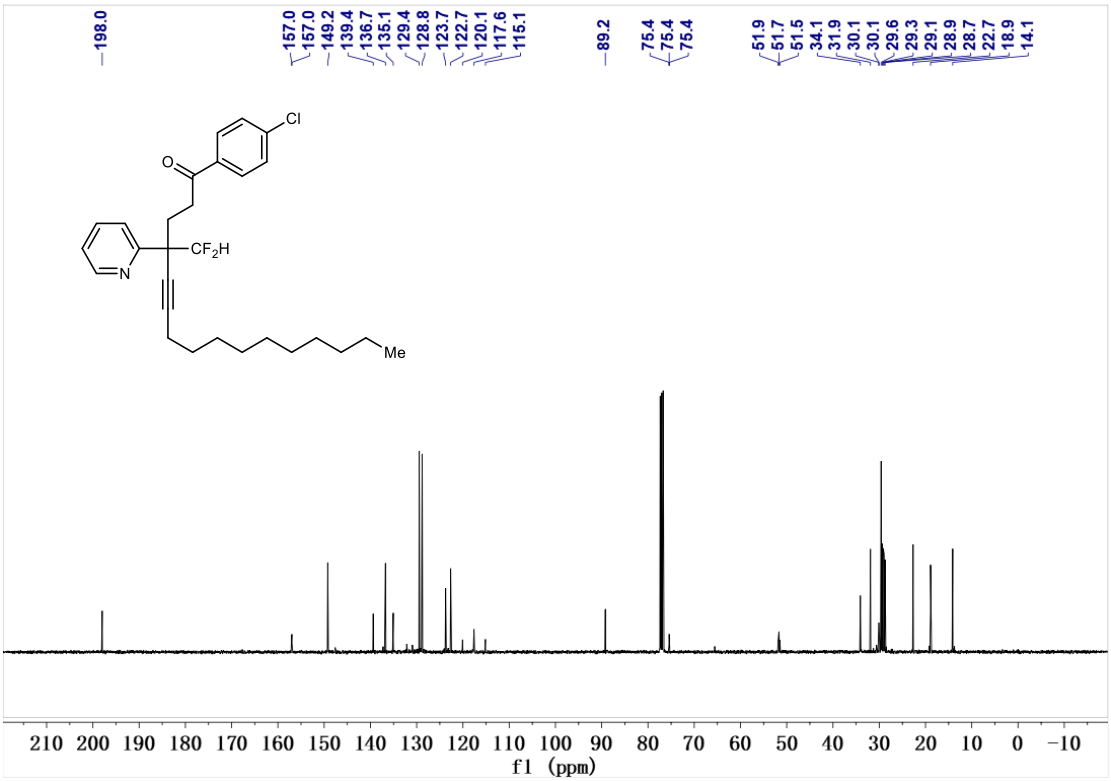
^{19}F NMR spectra of compound **3m** in $CDCl_3$ (376 MHz):



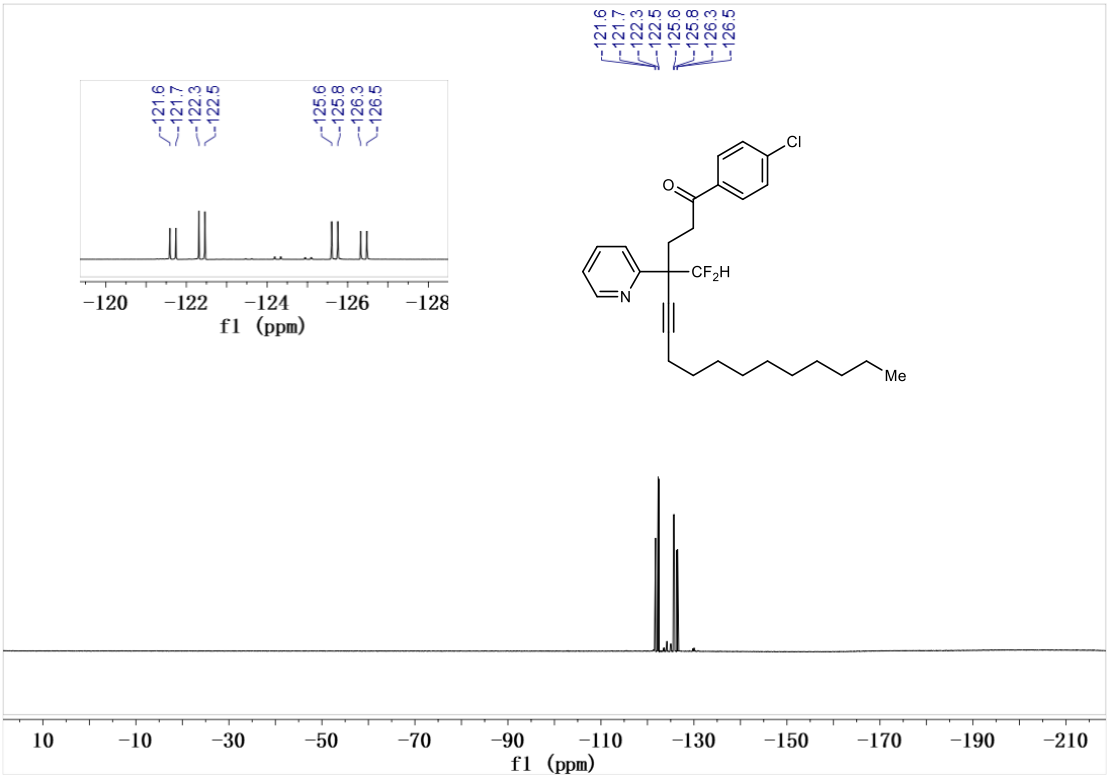
^{1}H NMR spectra of compound **3n** in $CDCl_3$ (400 MHz):



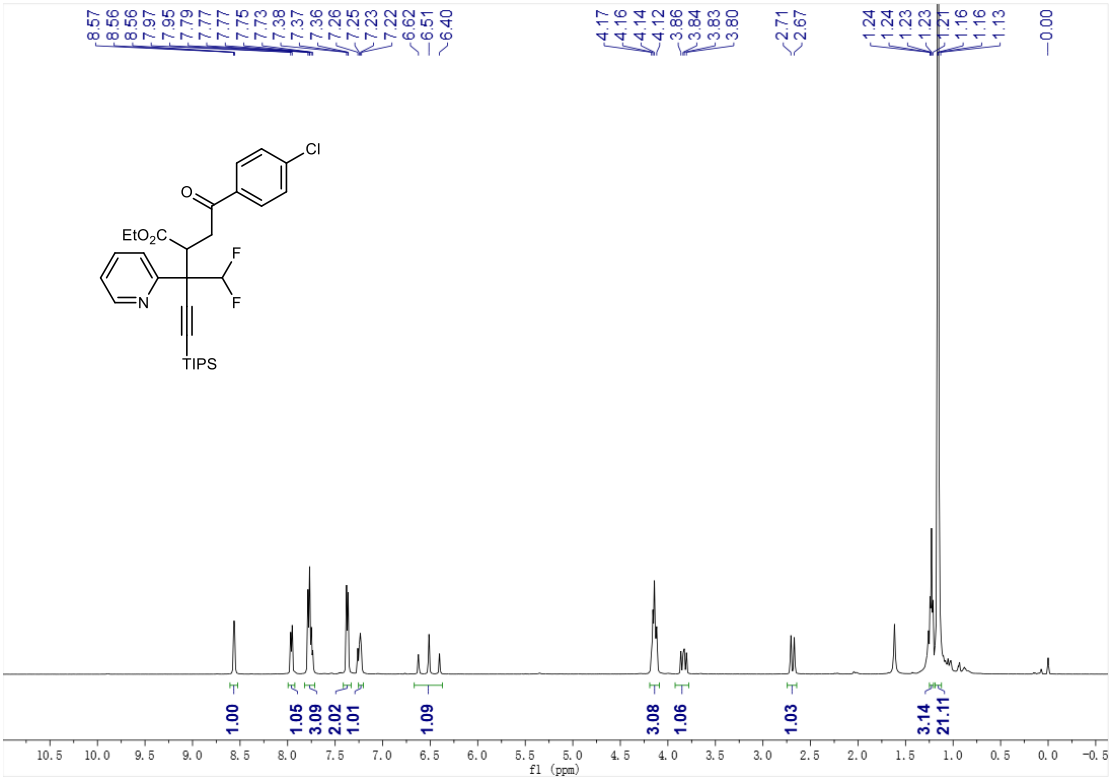
^{13}C NMR spectra of compound **3n** in $CDCl_3$ (101 MHz):



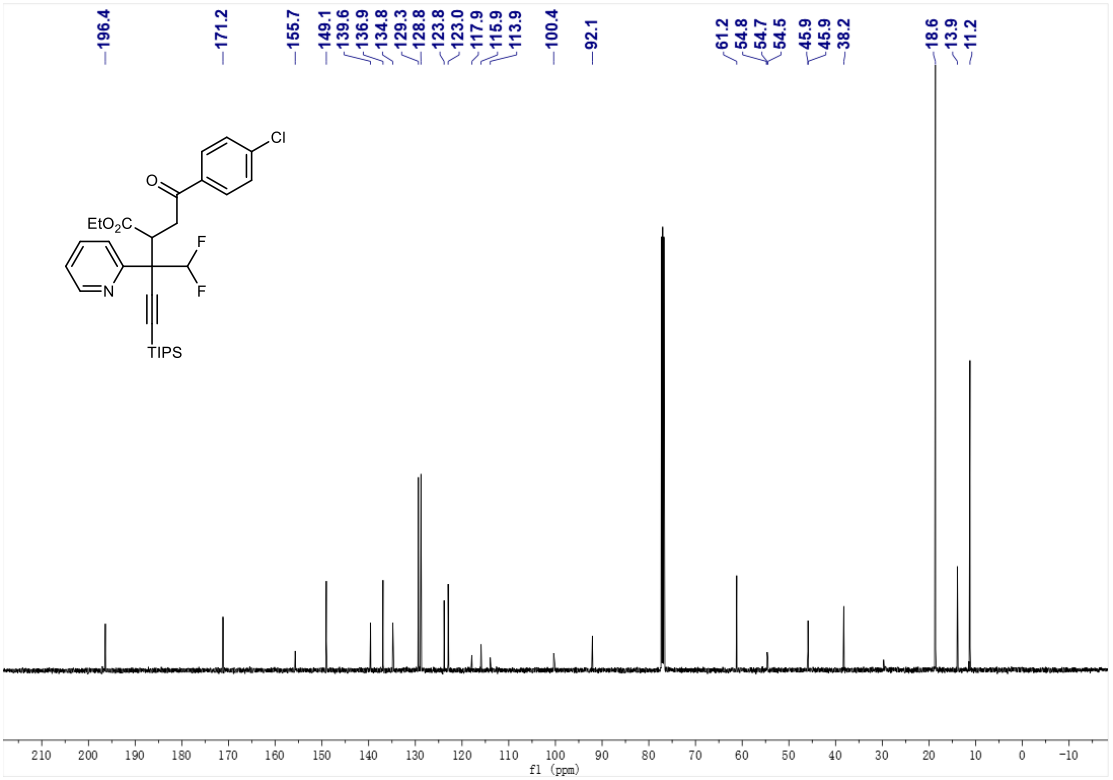
^{19}F NMR spectra of compound **3n** in $CDCl_3$ (376 MHz):



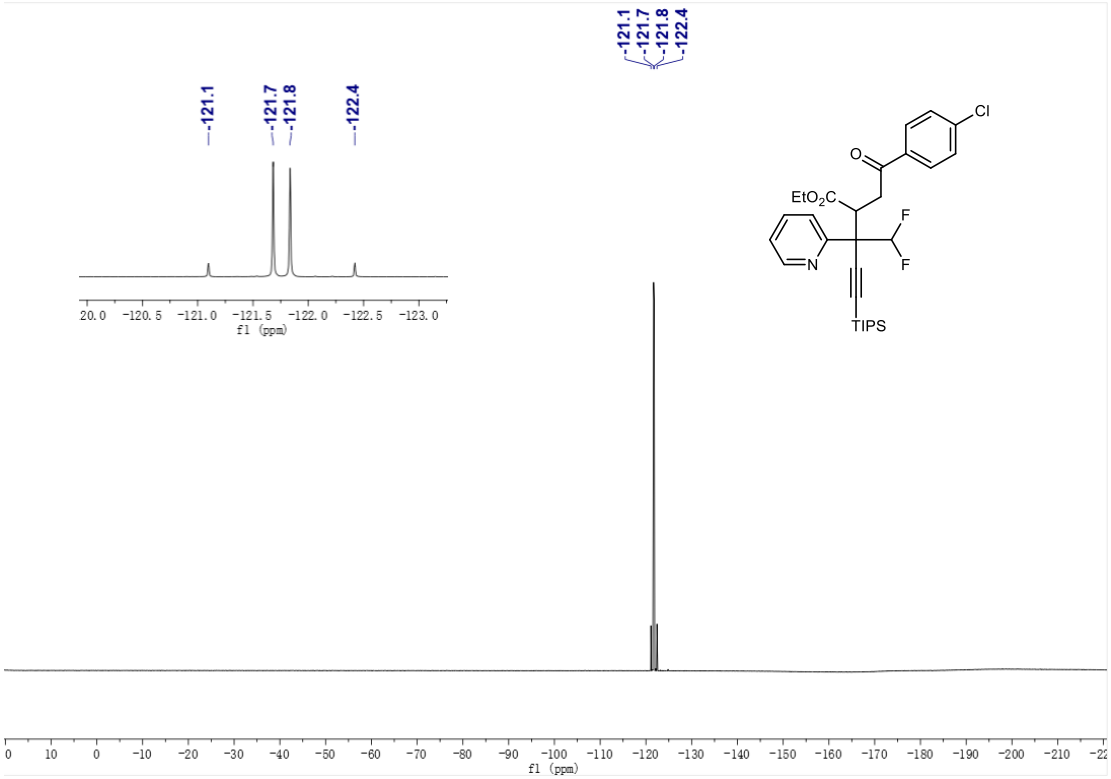
^{1}H NMR spectra of compound **3o** in $CDCl_3$ (500 MHz):



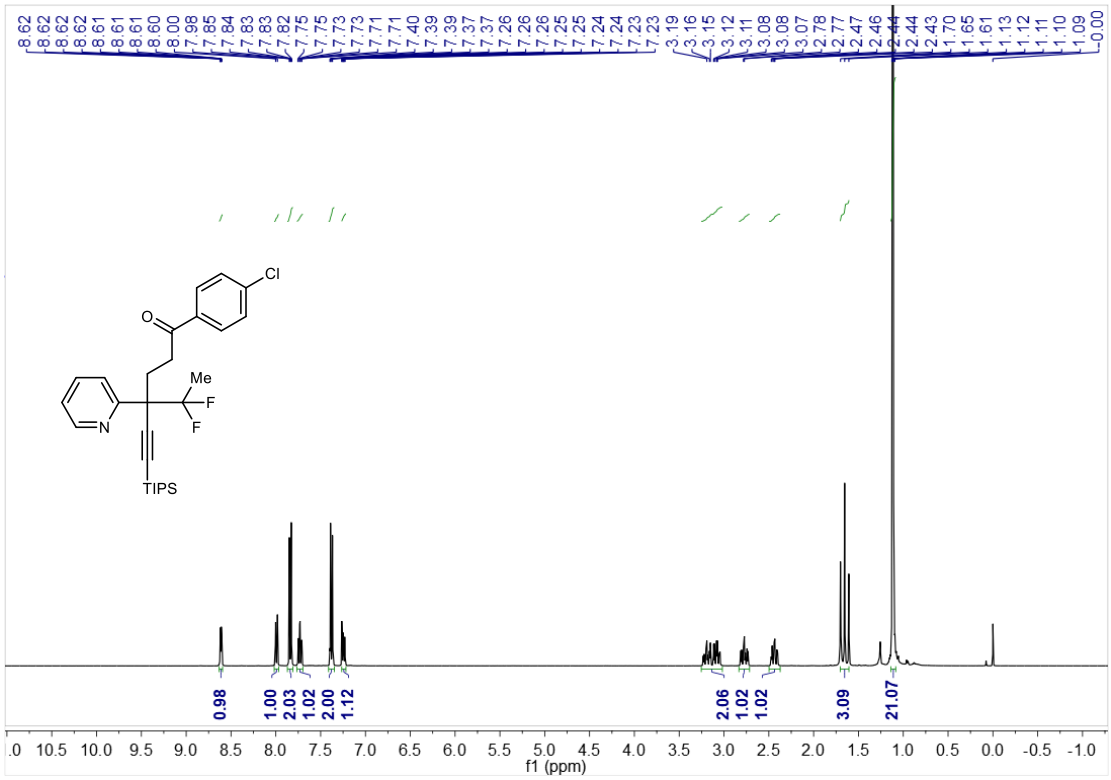
^{13}C NMR spectra of compound **3o** in $CDCl_3$ (126 MHz):



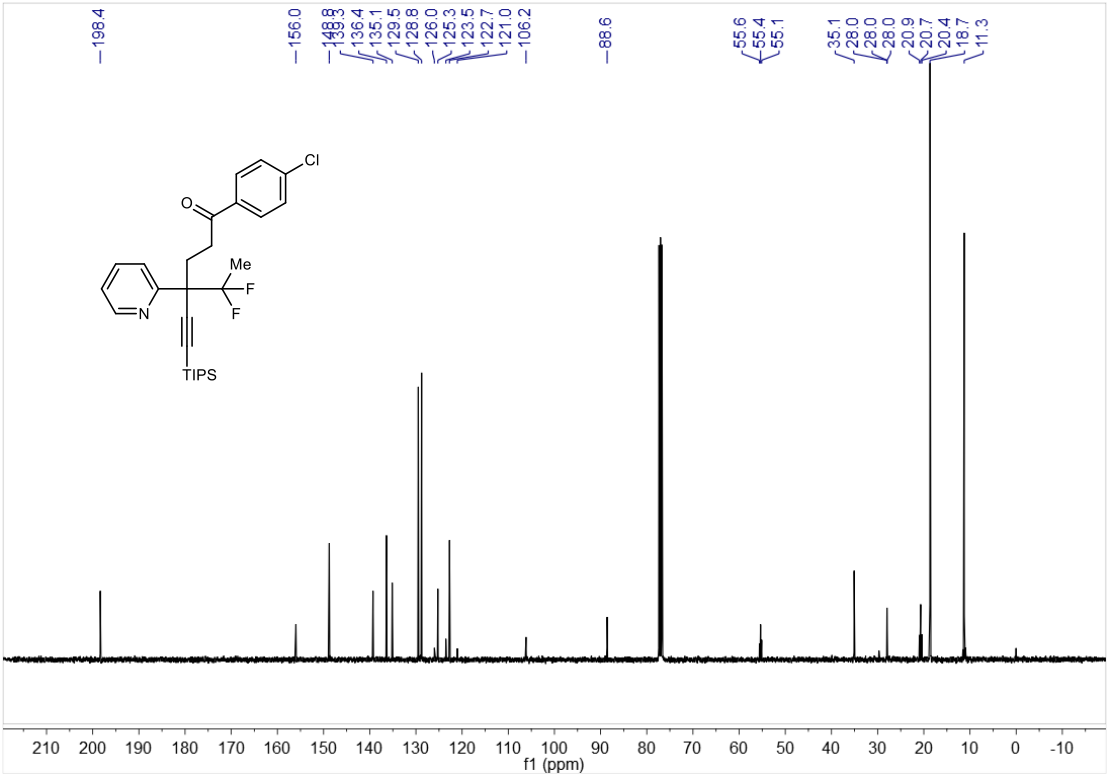
^{19}F NMR (with ^{1}H decoupling) spectra of compound **3o** in $CDCl_3$ (471 MHz):



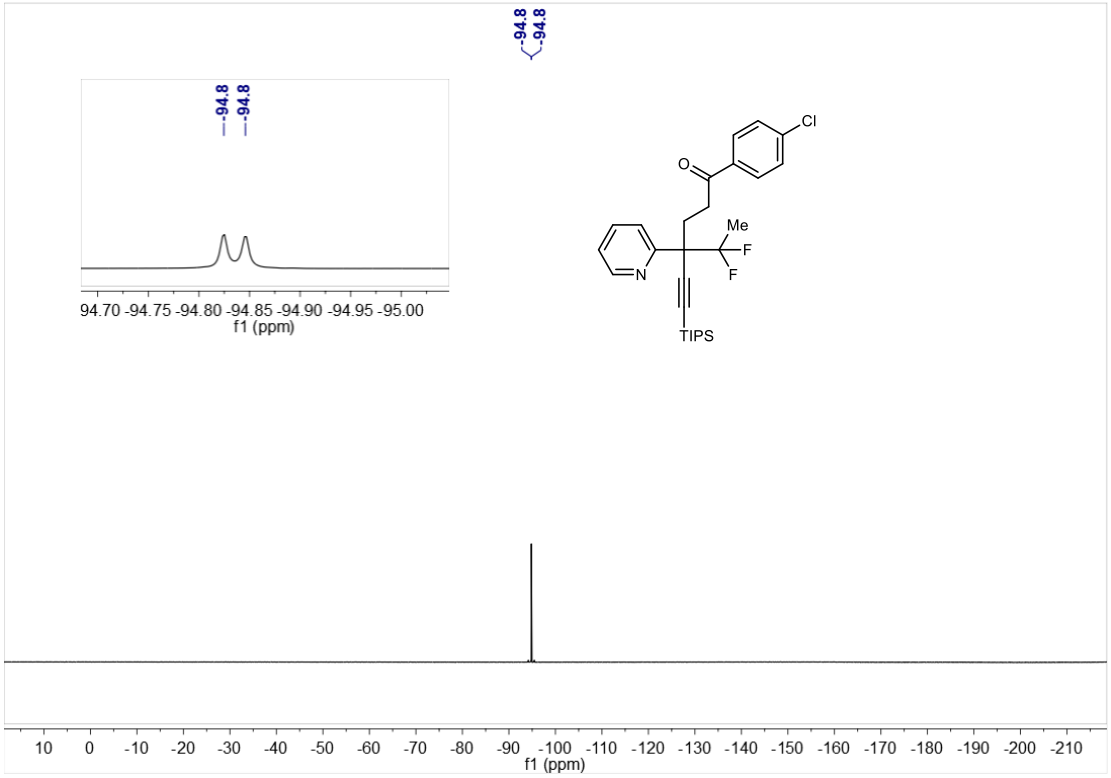
^{1}H NMR spectra of compound **3p** in $CDCl_3$ (400 MHz):



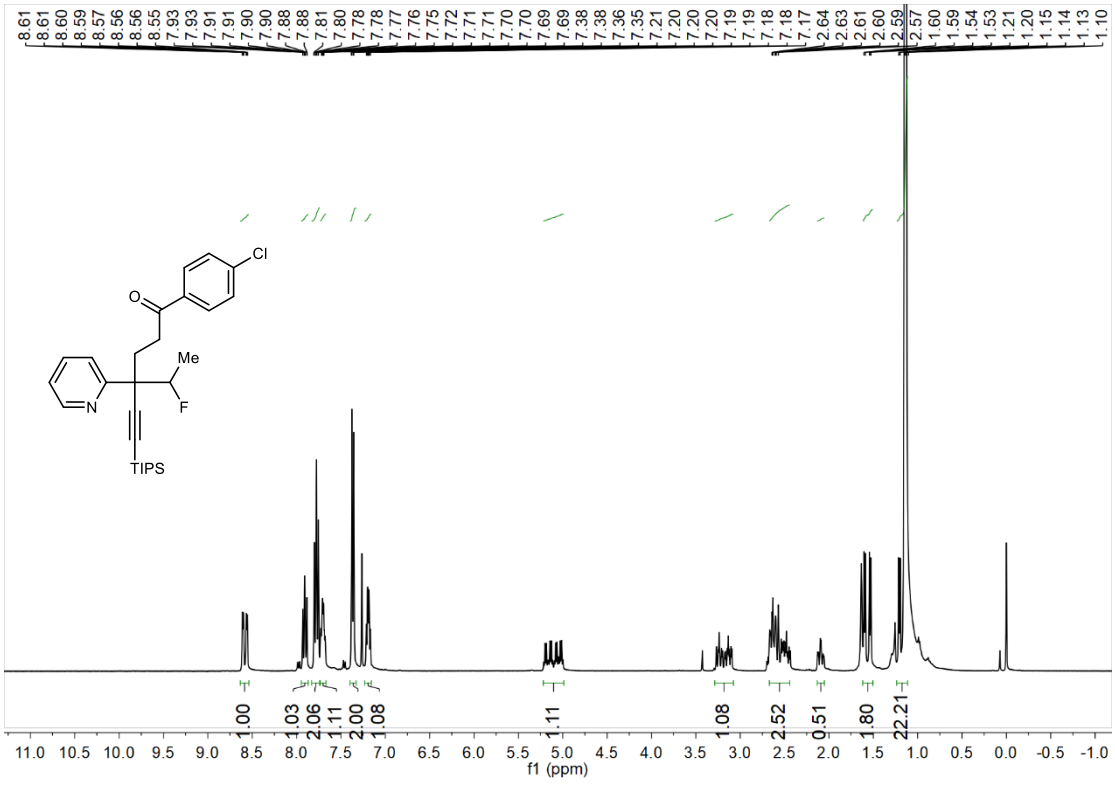
^{13}C NMR spectra of compound **3p** in $CDCl_3$ (101 MHz):



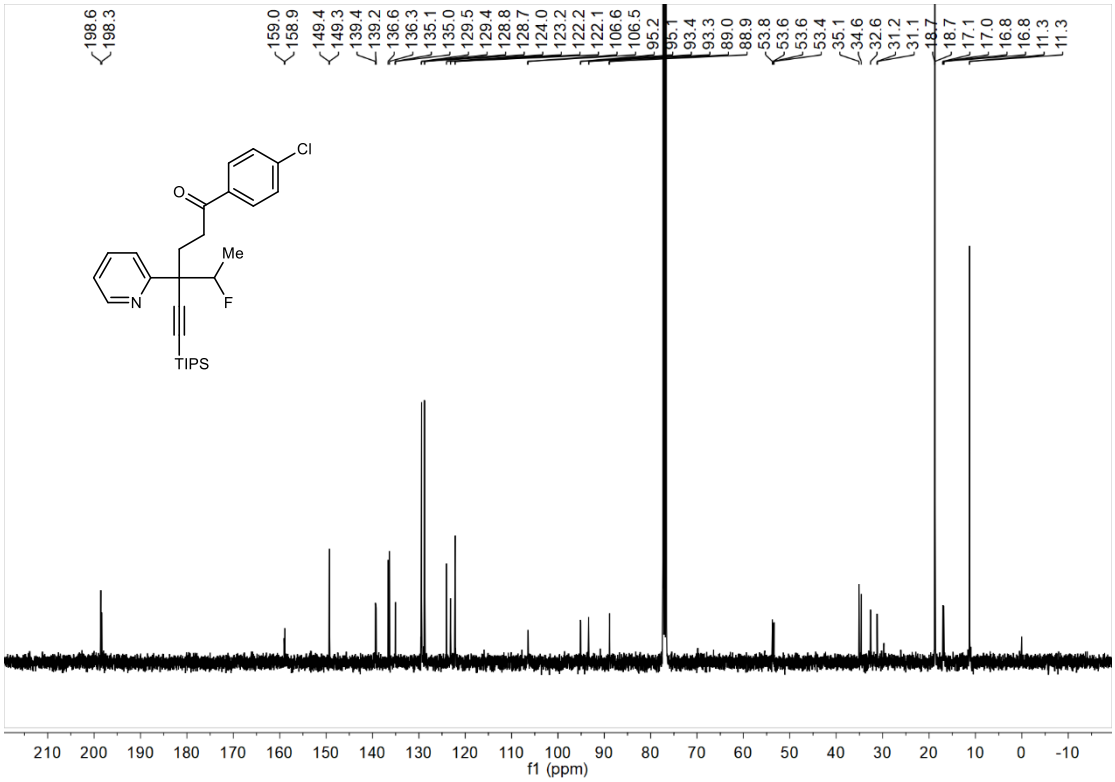
^{19}F NMR (with ^{1}H decoupling) spectra of compound **3p** in $CDCl_3$ (376 MHz):



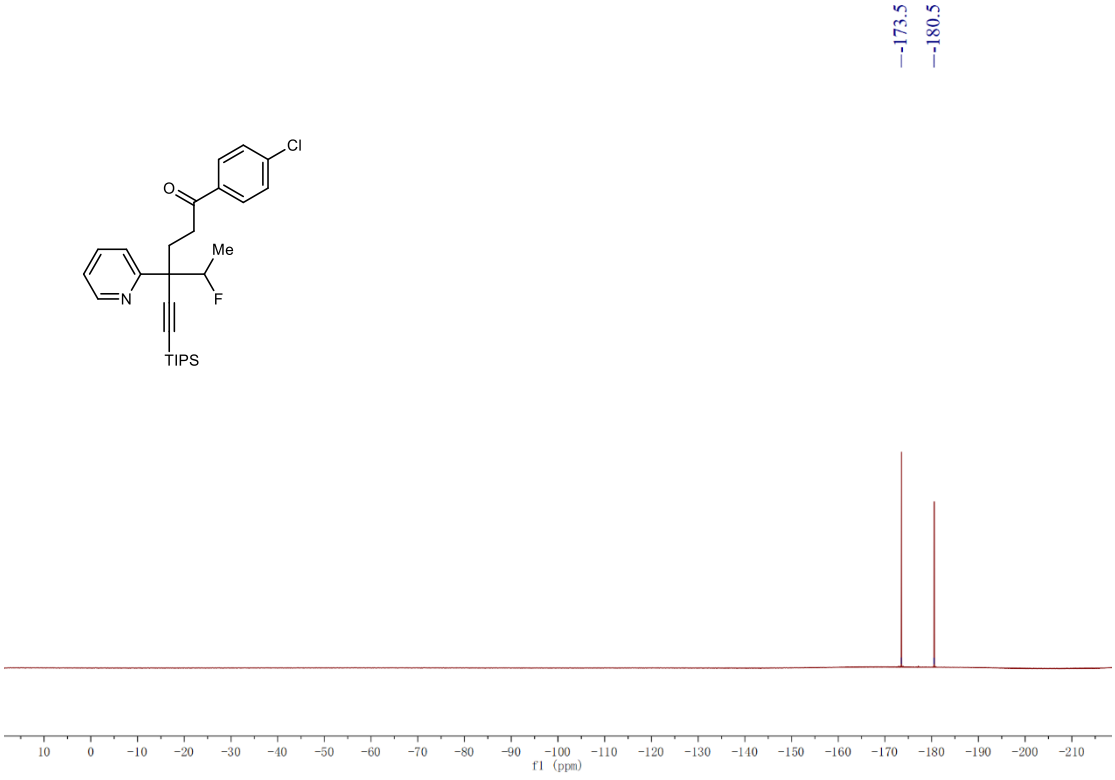
^{1}H NMR spectra of compound **3q** in $CDCl_3$ (400 MHz):



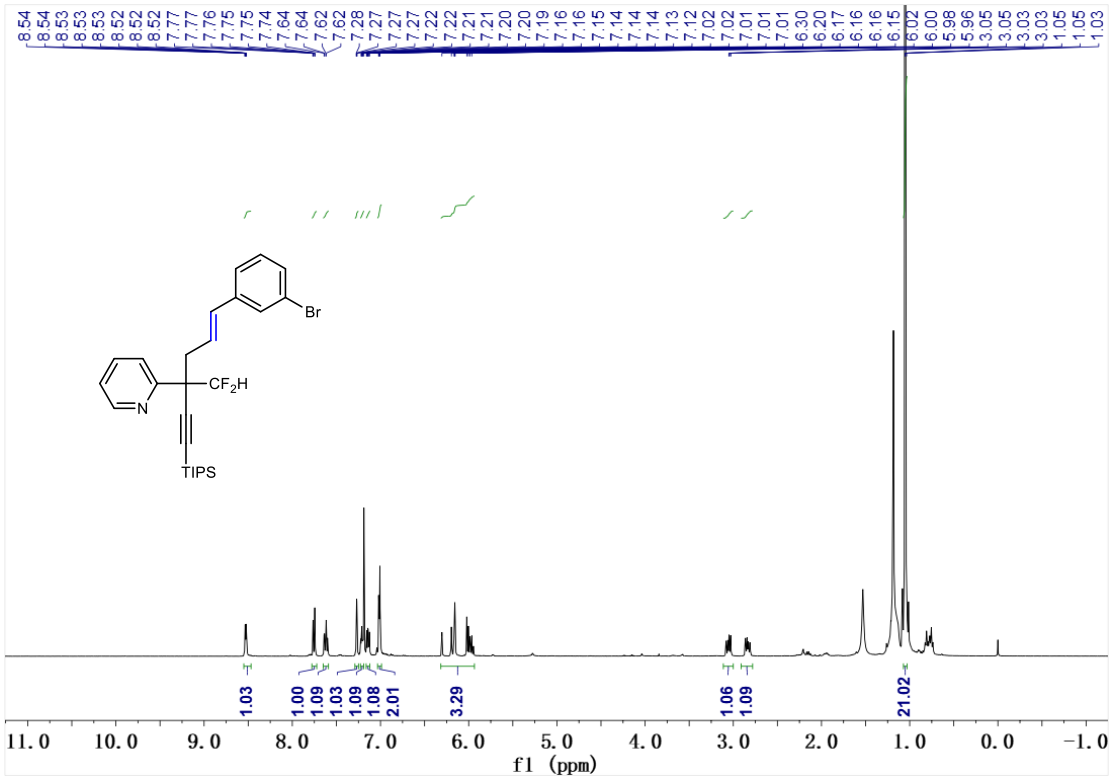
^{13}C NMR spectra of compound **3q** in $CDCl_3$ (101 MHz):



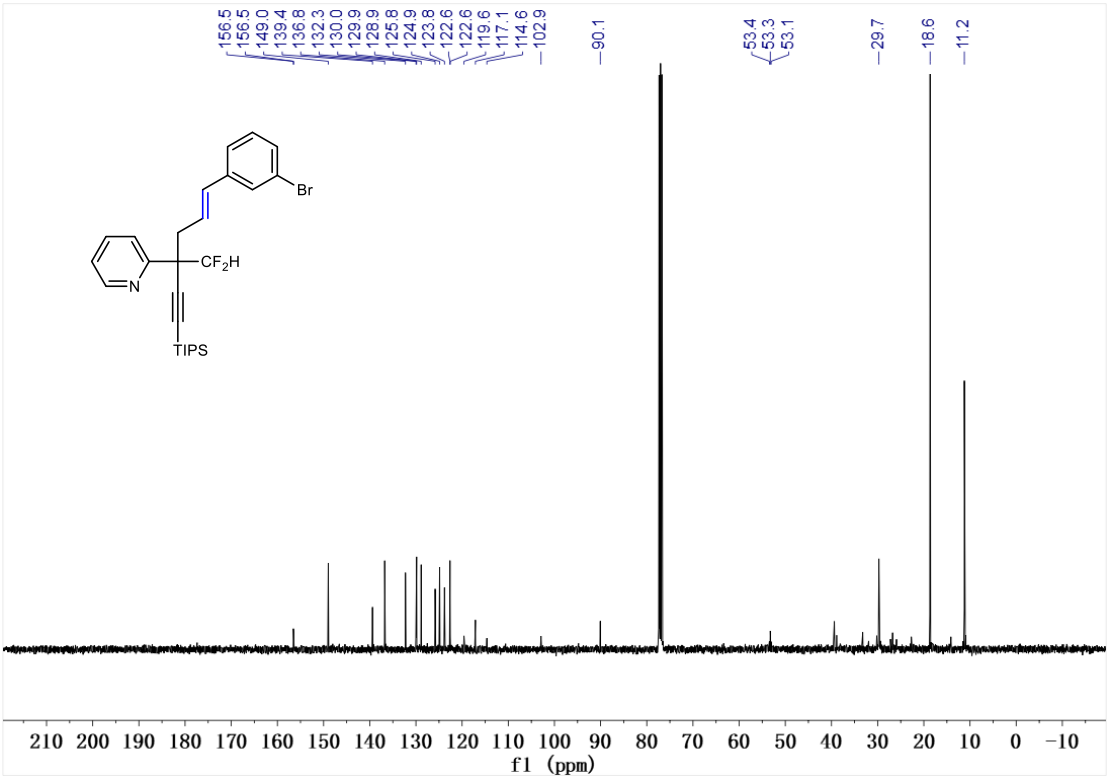
^{19}F NMR (with ^{1}H decoupling) spectra of compound **3q** in $CDCl_3$ (376 MHz):



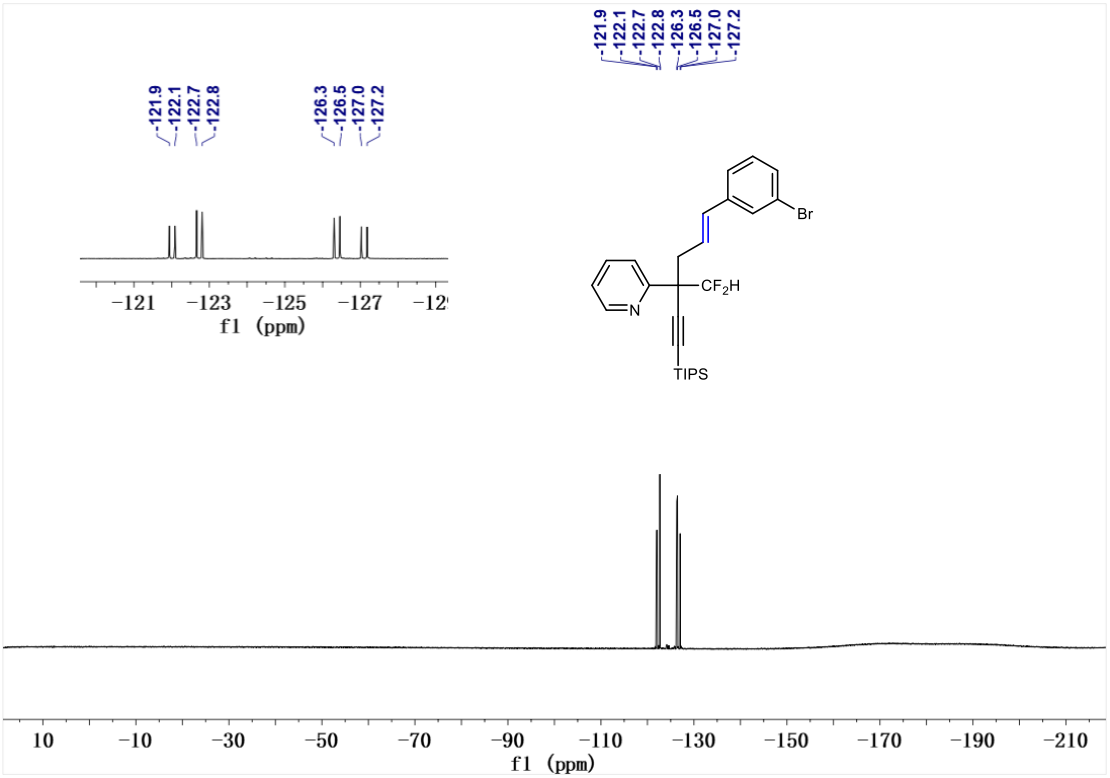
^{1}H NMR spectra of compound **4** in $CDCl_3$ (400 MHz):



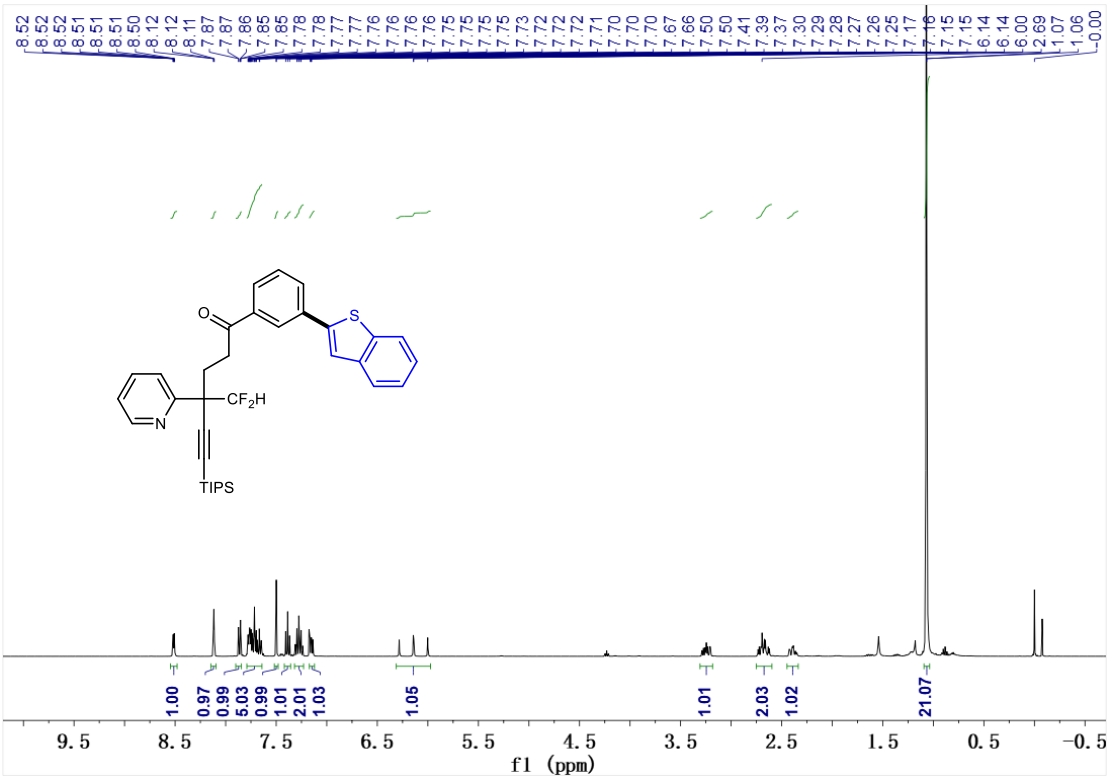
^{13}C NMR spectra of compound **4** in $CDCl_3$ (101 MHz):



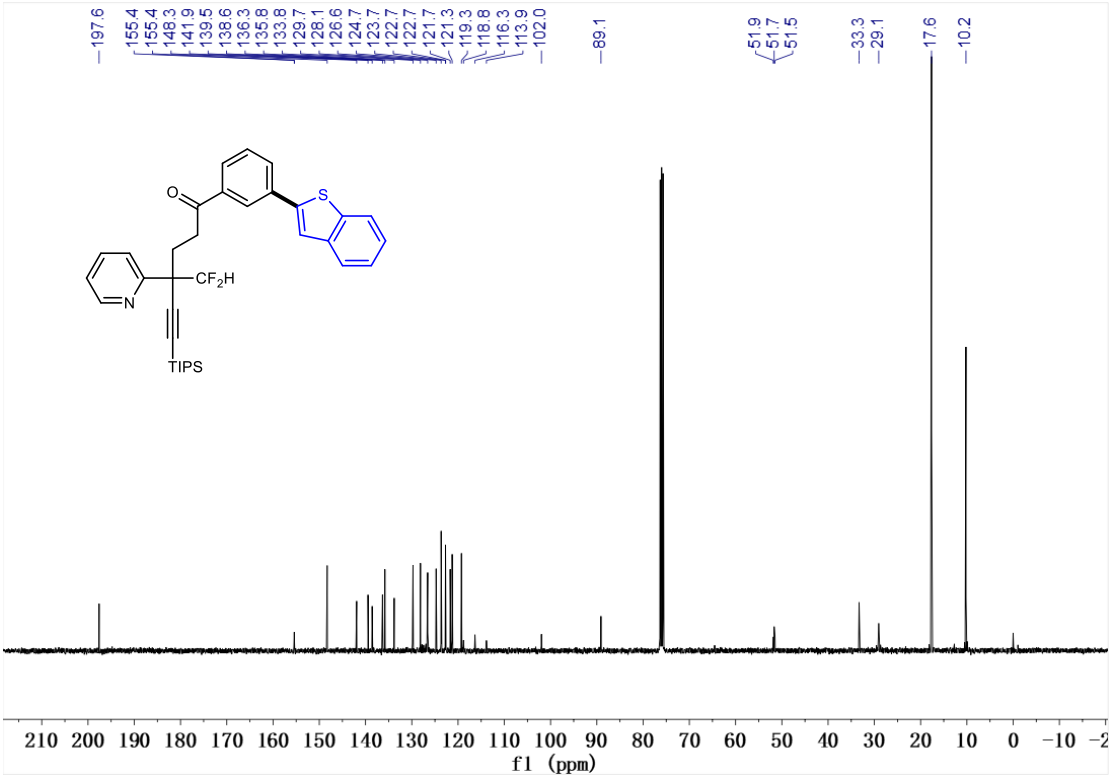
^{19}F NMR spectra of compound **4** in $CDCl_3$ (376 MHz):



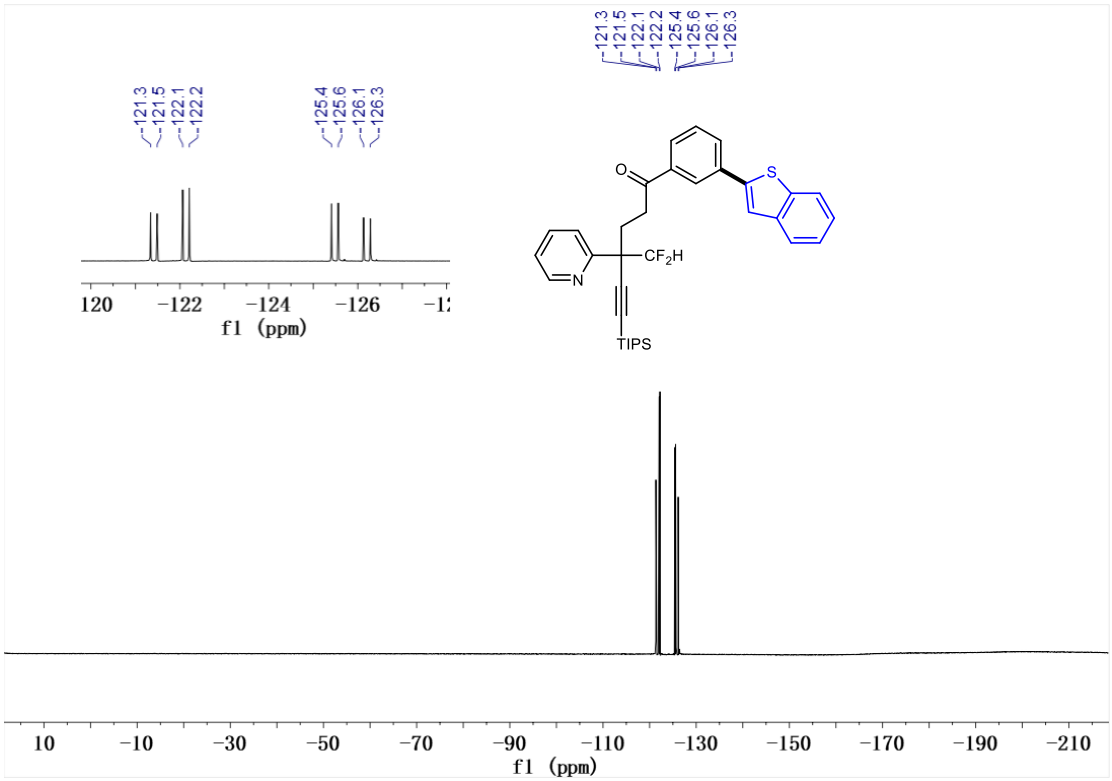
^{1}H NMR spectra of compound **5** in $CDCl_3$ (400 MHz):



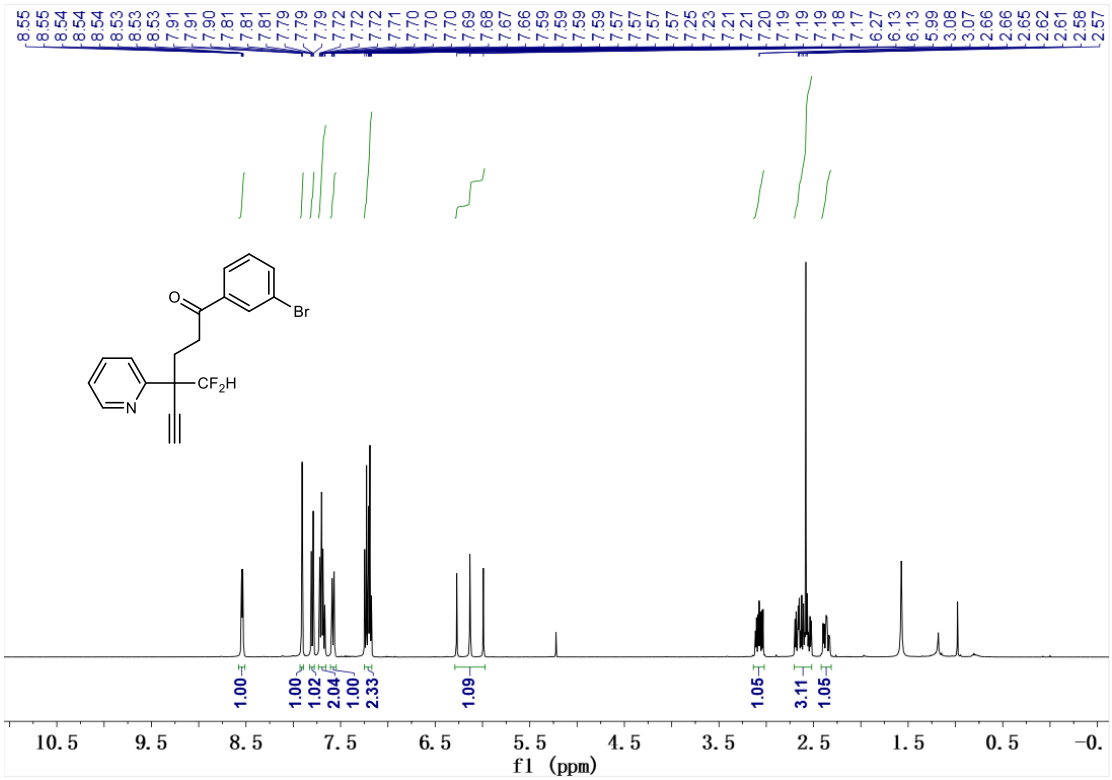
^{13}C NMR spectra of compound **5** in $CDCl_3$ (101 MHz):



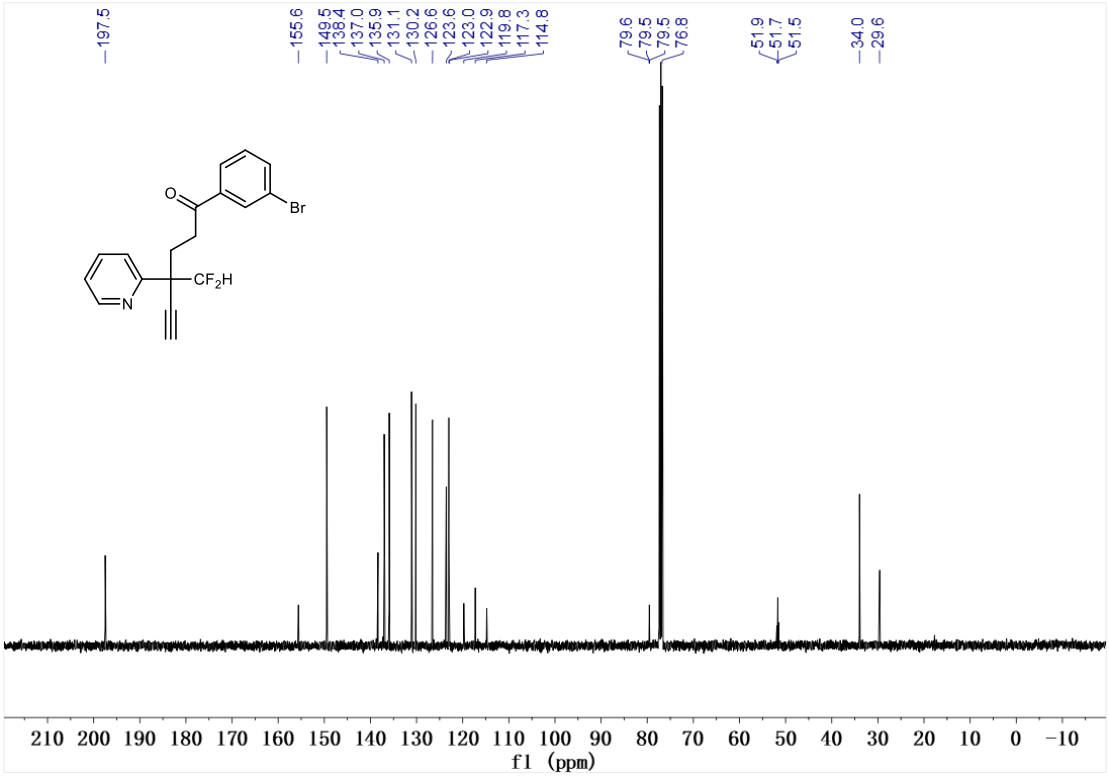
^{19}F NMR spectra of compound **5** in $CDCl_3$ (376 MHz):



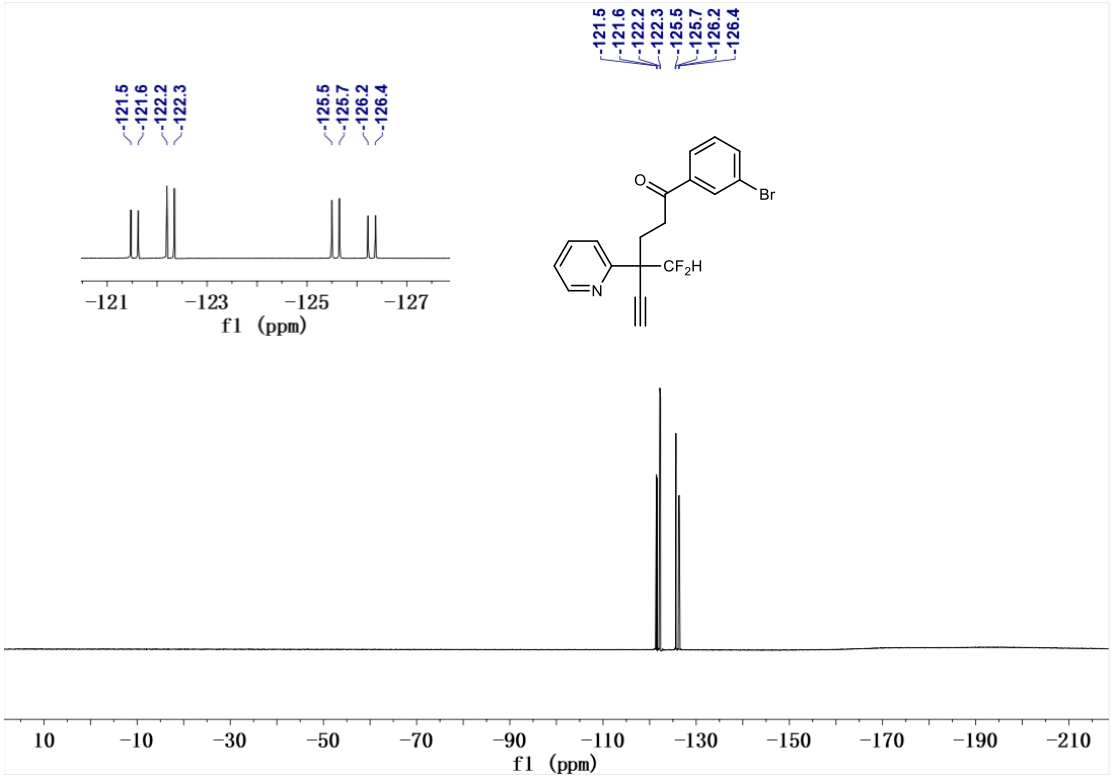
^{1}H NMR spectra of compound **6** in $CDCl_3$ (400 MHz):



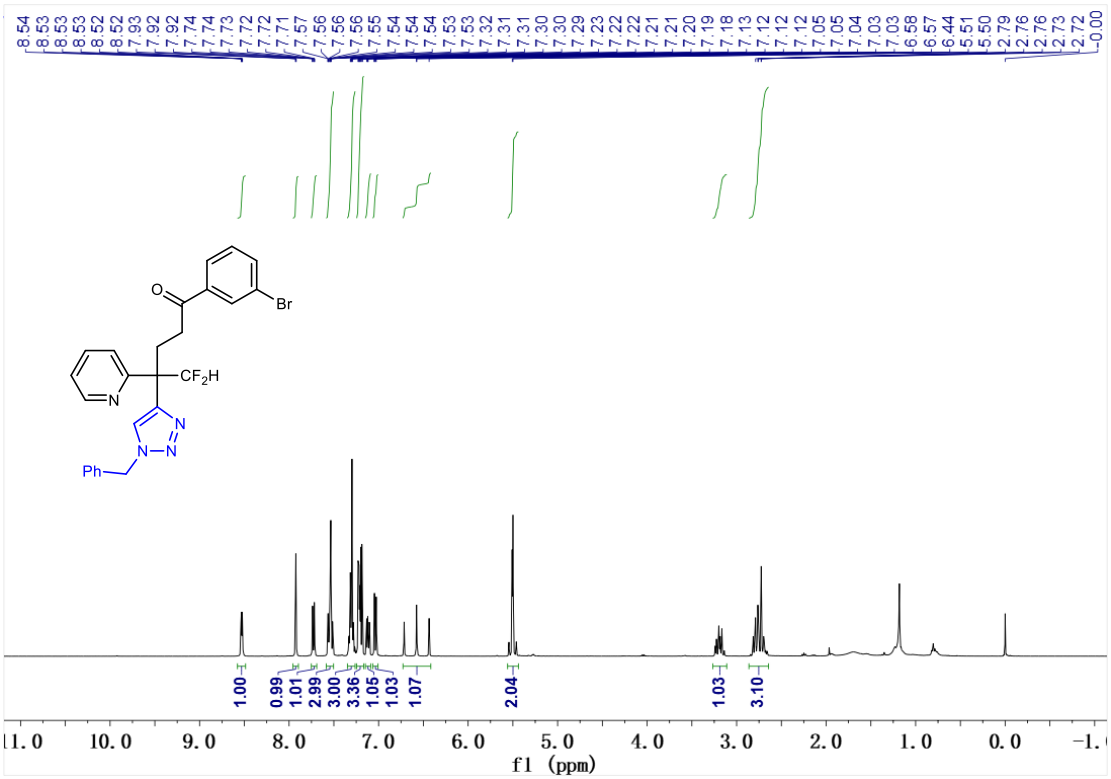
^{13}C NMR spectra of compound **6** in $CDCl_3$ (101 MHz):



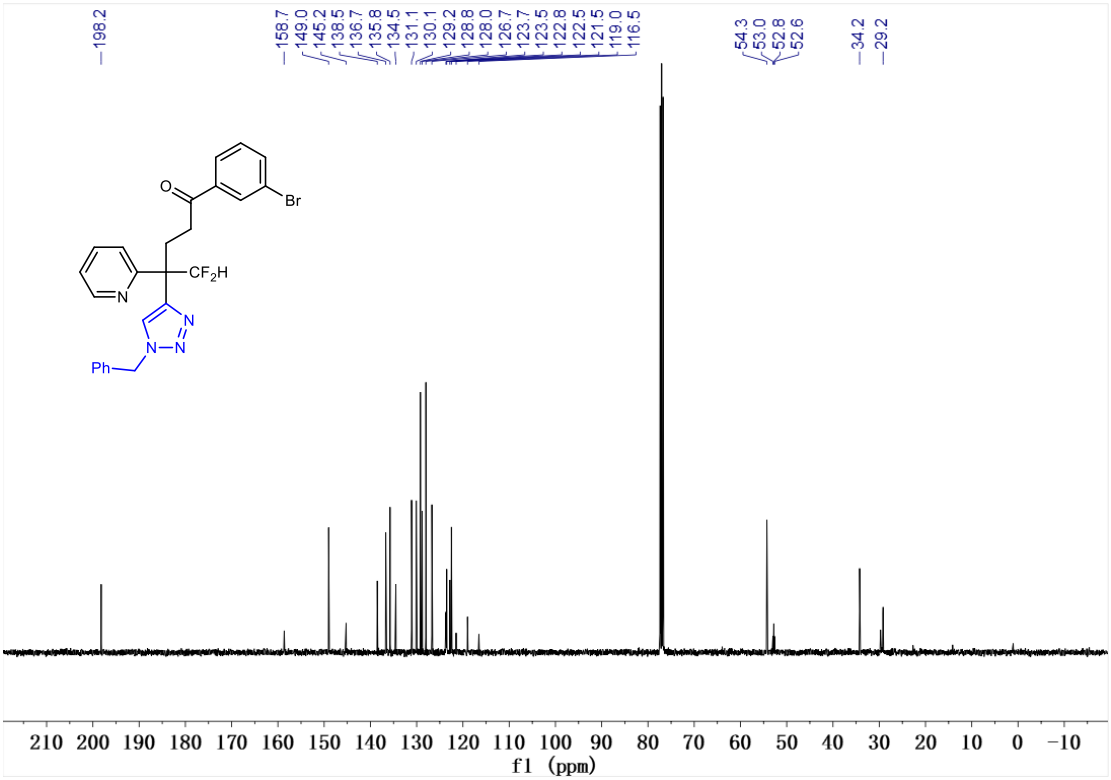
^{19}F NMR spectra of compound **6** in $CDCl_3$ (376 MHz):



^{1}H NMR spectra of compound **7** in $CDCl_3$ (400 MHz):



^{13}C NMR spectra of compound **7** in $CDCl_3$ (101 MHz):



^{19}F NMR spectra of compound **7** in $CDCl_3$ (376 MHz):