Supporting Information

Palladium-Catalyzed Trifluoroethylation of Terminal Alkynes with 1,1,1-Trifluoro-2-iodoethane

Yi-Si Feng[†], Chuan-Qi Xie[†], Wen-Long Qiao[†], and Hua-Jian Xu[*,‡]

[†]*School of Chemical Engineering, School of Medical Engineering, Hefei University of Technology,* [‡]*Key Laboratory of Advanced Functional Materials and Devices, Anhui Province, Hefei 230009, P. R. China.*

E-mail: hjxu@hfut.edu.cn

Table of Contents

Part 1. General Information

a. Materials

All solvents were obtained from commercial suppliers and used without further purification. All the catalysts , ligands and bases were obtained from commercial suppliers. Aryl and alkyl alkynes were obtained from commercial suppliers or prepared according to standard procedures unless otherwise stated.[1]

b. Methods

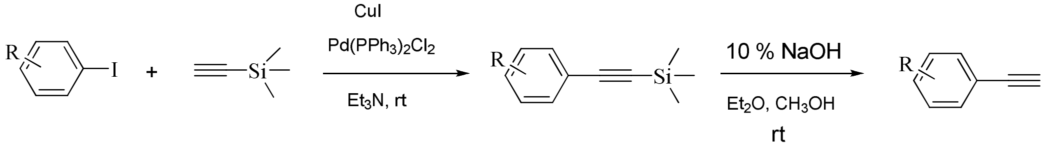
^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts of ^{19}F NMR spectra ($CFCl_3$ as outside standard and low field is positive) were recorded with ^{1}H-coupling on a Bruker 377 MHz spectrometer. ^{13}C-NMR spectra were recorded with on a Brucker 101 MHz spectrometer. Chemical shifts were reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Coupling constants (J) are reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. GC-MS analysis was performed on Thermo Scientific AS 3000 Series GC-MS System. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

Reference: (1) (a) Li, H.-B.; Jeffrey, L.; Wang, K.-K. *J. Org. Chem.* **2001**, *66*, 7804. (b) Achard, T.; Lepronier, A.; Gimbert, Y.; Clavier, H.; Giordano, L.; Tenaglia, A.; Buono, G. *Angew. Chem. Int. Ed.* **2011**, *50*, 3552. (c) Weyrauch, J. P.; Hashmi, A. S. K.; Schuster, A.; Hengst, T.; Schetter, S.; Littmann, A.; Rudolph, M.; Hamzic, M.; Visus, J.; Rominger, F.; Frey, W.; Bats, J. W. *Chem.-Eur. J.* **2010**, *16*, 956. (d) Trost, B. M.; Fandrick, D. R.; Dinh, D. C. J. *Am. Chem. Soc.* **2005**, *127*, 14186. (e) Li, C.-H.; Liu, X.-F.; Yuan, M.-J.; Li, J.-B.; Guo, Y.-B.; Xu, J.-L.; Zhu, M.; Lv, J.; Liu, H.-B.; Li, Y.-L. *Langmuir* **2007**, *23*, 6754. (f) Tiecco, M.; Testaferri, L.; Temperini, A.; Bagnoli, L.; Marini, F.; Santi, C.; Terlizzi, R. *Eur. J. Org. Chem.* **2004**, 3447.

Part 2. Experimental Section

a. General procedure for preparation of various terminal alkynes (1a-1s)

1. Preparation of aryl alkynes (1a-1b, 1e-1l)



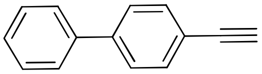
Preparation of Aryl (Trimethylsilyl)Acetylenes: To a mixture of varoius aryl iodide (7 mmol) compounds, Pd(PPh$_3$)$_2$C1$_2$ (3 mol %), and copper(I) iodide (5 mol%) in 30 mL of triethylamine was added dropwise via cannula a solution of (trimethylsilyl)acetylene (1.1 equiv) in 5 mL of triethylamine. The reaction mixture was stirred at room temperature for one hour before 50 mL of a saturated ammonium chloride solution and 50 mL of diethyl ether were introduced. The organic layer was separated, and the aqueous layerwas back extracted with diethyl ether. The combined organic layers were washed with brine and water, dried over sodium sulfate, and concentrated. Purification of the residue by flash column chromatography afforded various (trimethylsilyl)acetylenes.

General Procedure for the Formation of Aryl Alkynes: To a solution of aryl(trimethylsilyl)acetylenes (5-7 mmol) in 30-50 mL of diethy1 ether was added 30-50 mL of methanol and 15-20 mL of a 10% sodium hydroxide solution. After 10 min of stirring at room temperature, the reaction mixture was neutralized with a 1 M HCl solution. The organic layer was separated, and the aqueous layer was back extracted with diethyl ether. The combined organic layers were washed with brine and water, dried over sodium sulfate, and concentrated. Purification of the residue by flash column chromatography afforded various aryl alkynes. Substrates **1b-1c** were purchased from commercial sources.

2. Preparation of alkyl alkynes

Alkyl alkynes **1m**[b] ,**1n**[c], **1o**[d], **1p**[b], and **1q**[e] were prepared according to literature procedures. **1r-1s**[f] were obtained by conventional acylation of commercially available alkynols.

4-ethynylbiphenyl (1a)



1a

The mixture of 4-iodobiphenyl (1.96 g, 7 mmol), Pd(PPh$_3$)$_2$C1$_2$ (3 mol %, 147 mg) and CuI (5 mol %, 67 mg) in Et$_3$N (30 mL) was added dropwise via cannula a solution of (trimethylsilyl)acetylene (1.1 equiv, 1.93 mg) in Et$_3$N (5 mL) at rt for 2 h (Monitored by TLC), purification of the residue by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 100:1) afforded 1.4 g of (biphenyl-4-ylethynyl)trimethylsilane (5.6 mmol, 80% yield).

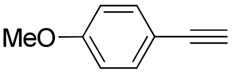
To a solution of (biphenyl-4-ylethynyl)triethylsilane (1.25 g 5 mmol) in 50 mL of diethyl ether was added 50 mL of methanol and 20 mL of a 10% sodium hydroxide solution at rt for 30 min (Monitored by TLC). The reaction mixture was neutralized with a 1 M HCl solution. Flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate 100:1) afforded the product **1a** as yellow solid. Yield: 0.756 g (90%).

This compound is known.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.5 Hz,2H), 7.56 (s, 4H), 7.45 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 3.13 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.58, 140.25, 132.55, 128.87, 127.73, 127.03, 120.96, 83.54, 77.74.

1-ethynyl-4-methoxybenzene (1b)



1b

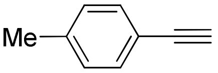
The mixture of 1-iodo-4-methoxybenzene (1.638 g, 7 mmol), $Pd(PPh_3)_2C1_2$ (3 mol %, 147 mg) and CuI (5 mol %, 67 mg) in Et_3N (30 mL) was added dropwise via cannula a solution of (trimethylsilyl)acetylene (1.1 equiv, 1.93 mg) in Et_3N (5 mL) at rt for 1.5 h (Monitored by TLC), purification of the residue by column chromatography on silica gel (eluent: petroleum ether) afforded 1.17 g of ((4-methoxyphenyl)ethynyl)trimethylsilane (5.7 mmol, 82% yield).

To a solution of ((4-methoxyphenyl)ethynyl)trimethylsilane (1.25 g 5 mmol) in 50 mL of diethyl ether was added 50 mL of methanol and 20 mL of a 10% sodium hydroxide solution at rt for 30 min (Monitored by TLC). The reaction mixture was neutralized with a 1 M HCl solution. Flash chromatography on silica gel (eluent: petroleum ether) afforded the product **1b** as yellow oil. Yield: 0.561 g (85%).

This compound is known.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 3.81 (s, 3H), 3.00 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.90, 132.56, 113.12, 112.90, 82.63, 74.74, 54.26.

1-ethynyl-4-methylbenzene (1c)



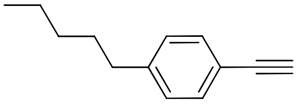
1c

This compound were purchased from Energy Chemical Tedia Company Inc. Yellow oil.

This compound is known.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 3.02 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.94, 132.01, 129.06, 119.01, 83.83, 76.46, 21.49.

1-ethynyl-4-pentylbenzene (1d)



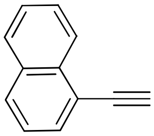
1d

This compound were purchased from Energy Chemical Tedia Company Inc. Yellow oil. Yellow oil.

This compound is known.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40 (d, J = 7.1 Hz, 2H), 7.13 (d, J = 7.1 Hz, 2H), 3.03 (s, 1H), 2.59 (t, J = 6.9 Hz,2H), 1.59 (s, 2H), 1.31 (s, 4H), 0.88 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 143.97, 132.02, 128.41, 119.16, 83.86, 76.45, 35.85, 31.41, 30.93, 22.52, 14.03.

1-ethynylnaphthalene (1e)



1e

The mixture of 4-iodobiphenyl (1.78 g, 7 mmol), Pd(PPh$_3$)$_2$C1$_2$ (3 mol %, 147mg) and CuI (5 mol%, 67mg) in Et$_3$N (30 mL) was added dropwise via cannula a solution of (trimethylsilyl)acetylene (1.1 equiv, 1.93 mg) in Et$_3$N (5 mL) at rt for 2 h (Monitored by TLC), and a purification by column chromatography on silica gel (eluent: petroleum ether) to give trimethyl(naphthalen-1-ylethynyl)silane (1.348 g, 6.0 mmol, 86% yield).

To a solution of trimethyl(naphthalen-1-ylethynyl)silane (1.348 g 6 mmol) in 50 mL of diehy1 ether was added 50 mL of methanol and 20 mL of a 10% sodium hydroxide solution at rt for 25 min (Monitored by TLC). The reaction mixture was neutralized with a 1 M HCl solution. Flash chromatography on silica gel (eluent: petroleum ether) afforded the product **1e** as a yellow oil. Yield: 0.839 g (92%).

This compound is known.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.36 (d, *J* = 7.9 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 6.2 Hz, 1H), 7.53 (dd, *J* = 19.3, 7.3 Hz, 2H), 7.39 (t, *J* = 7.1 Hz, 1H), 3.46 (s, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 133.43, 132.99, 131.19, 129.24, 128.25, 126.91, 126.44, 125.98, 125.05, 119.68, 81.98, 81.71.

4-ethynylbenzonitrile (1f)

1f

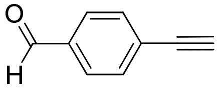
The mixture of 4-iodobenzonitrile (1.603 g, 7 mmol), $Pd(PPh_3)_2C1_2$ (3 mol %, 147mg) and CuI (5 mol%, 67mg) in Et_3N (30 mL) was added dropwise via cannula a solution of (trimethylsilyl)acetylene (1.1 equiv, 1.93 mg) in Et_3N (5 mL) at rt for 3 h (Monitored by TLC), and a purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 25:1) to give 4-((trimethylsilyl)ethynyl)benzonitrile (1.08 g, 5.43 mmol, 78% yield).

To a solution of 4-((trimethylsilyl)ethynyl)benzonitrile (0.995 g 5 mmol) in 50 mL of diehyl ether was added 50 mL of methanol and 20 mL of a 10% sodium hydroxide solution at rt for 20 min (Monitored by TLC). The reaction mixture was neutralized with a 1 M HCl solution. Flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate 25:1) afforded the product **1f** as yellow solid. Yield: 0.552 g (87%).

This compound is known.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, J = 20.1, 8.0 Hz, 4H), 3.31 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.67, 132.03, 126.97, 118.29, 112.28, 81.84, 81.56.

4-ethynylbenzaldehyde (1g)



1g

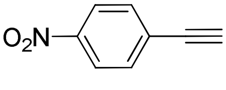
The mixture of 4-iodobenzaldehyde (1.63 g, 7 mmol), $Pd(PPh_3)_2C1_2$ (3 mol %, 147mg) and CuI (5 mol%, 67mg) in Et_3N (30 mL) was added dropwise via cannula a solution of (trimethylsilyl)acetylene (1.1 equiv, 1.93 mg) in Et_3N (5 mL) at rt for 2 h (Monitored by TLC), and a purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 20:1) to give 4-((trimethylsilyl)ethynyl)benzaldehyde (1.2 g, 5.94 mmol, 85% yield).

To a solution of 4-((trimethylsilyl)ethynyl)benzaldehyde (1.25 g 5 mmol) in 50 mL of diehyl ether was added 50 mL of methanol and 20 mL of a 10% sodium hydroxide solution at rt for 15 min (Monitored by TLC). The reaction mixture was neutralized with a 1 M HCl solution. Flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate 20:1) afforded the product **1g** as yellow solid. Yield: 0.572 g (88%).

This compound is known.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.85 (d, J = 8.1 Hz, 2H), 7.65 (d, J = 8.1 Hz, 2H), 3.30 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.42, 135.91, 132.71, 129.50, 128.29, 82.60, 81.07.

1-ethynyl-4-nitrobenzene (1h)



1h

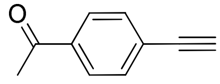
The mixture of 1-iodo-4-nitrobenzene (1.743 g, 7 mmol), $Pd(PPh_3)_2C1_2$ (3 mol %, 147mg) and CuI (5 mol%, 67mg) in Et_3N (30 mL) was added dropwise via cannula a solution of (trimethylsilyl)acetylene (1.1 equiv, 1.93 mg) in Et_3N (5 mL) at rt for 4 h (Monitored by TLC), and a purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 50:1) to give trimethyl((4-nitrophenyl)ethynyl)silane (1.24 g, 5.66 mmol, 81% yield).

To a solution of trimethyl((4-nitrophenyl)ethynyl)silane (1.095 g 5 mmol) in 50 mL of diehy1 ether was added 50 mL of methanol and 20 mL of a 10% sodium hydroxide solution at rt for 35 min (Monitored by TLC). The reaction mixture was neutralized with a 1 M HCl solution. Flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate 50:1) afforded the product **1h** as yellow solid. Yield: 0.63 g (86%).

This compound is known.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.7 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 2H), 3.37 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.49, 132.97, 128.91, 123.57, 82.35, 81.59.

1-(4-ethynylphenyl)ethanone (1i)



1i

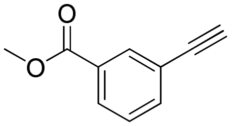
The mixture of 1-(4-iodophenyl)ethanone (1.722g, 7 mmol), $Pd(PPh_3)_2C1_2$ (3 mol %, 147mg) and CuI (5 mol%, 67mg) in Et_3N (30 mL) was added dropwise via cannula a solution of (trimethylsilyl)acetylene (1.1 equiv, 1.93 mg) in Et_3N (5 mL) at rt for 1.5 h (Monitored by TLC), and a purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1) to give 1-(4-((trimethylsilyl)ethynyl)phenyl)ethanone (1.285 g, 5.95 mmol, 85% yield).

To a solution of 1-(4-((trimethylsilyl)ethynyl)phenyl)ethanone (1.23 g, 5 mmol) in 50 mL of diehy1 ether was added 50 mL of methanol and 20 mL of a 10% sodium hydroxide solution at rt for 10 min (Monitored by TLC). The reaction mixture was neutralized with a 1 M HCl solution. Flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1) afforded the product **1i** as yellow solid. Yield: 0.64 g (89%).

This compound is known.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 2H), 3.26 (s, 1H), 2.61 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.2, 136.7, 132.2, 128.1, 126.9, 82.7, 80.3, 26.6.

methyl 3-ethynylbenzoate (1j)



1j

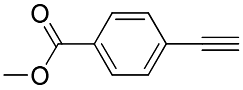
The mixture of methyl 3-iodobenzoate (1.834 g, 7 mmol), Pd(PPh_3)$_2$Cl_2 (3 mol %, 147mg) and CuI (5 mol%, 67mg) in Et_3N (30 mL) was added dropwise via cannula a solution of (trimethylsilyl)acetylene (1.1 equiv, 1.93 mg) in Et_3N (5 mL) at rt for 2 h (Monitored by TLC), and a purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 50:1) to give methyl 3-((trimethylsilyl)ethynyl)benzoate (1.4 g, 6.03 mmol, 86% yield).

To a solution of methyl 3-((trimethylsilyl)ethynyl)benzoate (1.16 g, 5 mmol) in 50 mL of diehy1 ether was added 50 mL of methanol and 20 mL of a 10% sodium hydroxide solution at rt for 15 min (Monitored by TLC). The reaction mixture was neutralized with a 1 M HCl solution. Flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate 50:1) afforded the product **1j** as yellow solid. Yield: 0.696 g (87%).

This compound is known.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 3.85 (s, 3H), 3.05 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.23, 135.21, 132.23, 129.41, 128.77, 127.46, 121.53, 81.51, 77.12, 51.29.

methyl 4-ethynylbenzoate (1k)



1k

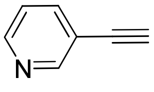
The mixture of methyl 4-iodobenzoate (1.834 g, 7 mmol), Pd(PPh_3)$_2$Cl_2 (3 mol %, 147mg) and CuI (5 mol%, 67mg) in Et_3N (30 mL) was added dropwise via cannula a solution of (trimethylsilyl)acetylene (1.1 equiv, 1.93 mg) in Et_3N (5 mL) at rt for 2 h (Monitored by TLC), and a purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 50:1) to give methyl 4-((trimethylsilyl)ethynyl)benzoate (1.445 g, 6.23 mmol, 89% yield).

To a solution of methyl 4-((trimethylsilyl)ethynyl)benzoate (1.392 g, 6 mmol) in 50 mL of diehy1 ether was added 50 mL of methanol and 20 mL of a 10% sodium hydroxide solution at rt for 15 min (Monitored by TLC). The reaction mixture was neutralized with a 1 M HCl solution. Flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate 50:1) afforded the product **1j** as yellow solid. Yield: 0.806 g (84%).

This compound is known.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 3.92 (d, *J* = 0.5 Hz, 3H), 3.23 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.42, 132.08, 130.12, 129.46, 126.74, 82.79, 80.05, 52.30.

3-ethynylpyridine (1l)



1l

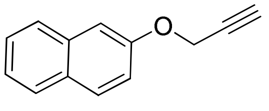
The mixture of methyl 3-iodopyridine (1.435 g, 7 mmol), Pd(PPh$_3$)$_2$C1$_2$ (3 mol %, 147mg) and CuI (5 mol%, 67mg) in Et$_3$N (30 mL) was added dropwise via cannula a solution of (trimethylsilyl)acetylene (1.1 equiv, 1.93 mg) in Et$_3$N (5 mL) at rt for 3 h (Monitored by TLC), and a purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1) to give methyl 3-((trimethylsilyl)ethynyl)pyridine (0.98 g, 5.6 mmol, 80% yield).

To a solution of methyl 3-((trimethylsilyl)ethynyl)pyridine (0.875 g, 5 mmol) in 50 mL of diehy1 ether was added 50 mL of methanol and 20 mL of a 10% sodium hydroxide solution at rt for 50 min (Monitored by TLC). The reaction mixture was neutralized with a 1 M HCl solution. Flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1) afforded the product **1l** as white solid. Yield: 0.427 g (83%).

This compound is known.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.72 (s, 1H), 8.57 (d, *J* = 4.8 Hz, 1H), 7.77 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.29 – 7.23 (m, 1H), 3.22 (s, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 152.51, 149.08, 138.87, 123.06, 81.22, 81.11.

2-(prop-2-ynyloxy)naphthalene (1m)



1m

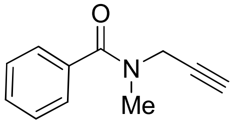
A solution of naphthalen-2-ol (2.88 g, 20 mmol), propargyl choride (2.9 mL, 40 mmol, 2 equiv) and potassium carbonate (6.9 g, 50 mmol, 2.5 equiv) in DMF (20 mL) was stirred 16 h at 50ºC. The reaction was cooled to rt and poured into HCl 1N (50 mL) and extracted with Et$_2$O.The organic phase was washed with HCl 1 N, then brine, dried over anhydrous MgSO$_4$ and the volatiles removed under reduced pressure. Flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate 50:1) afforded the product **1m** as yellow solid. Yield: 2.4 g (84%).

This compound is known.

Reference: Achard, T.; Lepronier, A.; Gimbert, Y.; Clavier, H.; Giordano, L.; Tenaglia, A.; Buono, G. *Angew. Chem. Int. Ed.* **2011**, *50*, 3552.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.79 – 7.71 (m, 3H), 7.45 (t, J = 7.5 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.23 (d, J = 2.9 Hz, 1H), 7.19 (dd, J = 8.9, 2.5 Hz, 1H), 4.80 (d, J = 2.3 Hz, 2H), 2.55 (t, J = 2.3 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 155.44, 134.26, 129.57, 129.31, 127.66, 126.92, 126.46, 124.01, 118.72, 107.42, 78.48, 75.65, 55.82.

N-methyl-N-(prop-2-ynyl)benzamide (1n)



1n

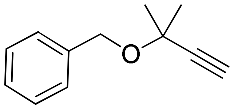
Benzoylchloride (1.69 g 12.0 mmol), N-methylprop-2-yn-1-amine (830 mg 12.0 mmol), Et_3N (1.21 g, 12.0 mmol) and DMAP (29.3 mg, 240 µmol) were employed. Flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1) afforded the product **1n** as a brownish oil. Yield: 1.92 g (93%).

This compound is known.

Reference: Weyrauch, J. P.; Hashmi, A. S. K.; Schuster, A.; Hengst, T.; Schetter, S.; Littmann, A.; Rudolph, M.; Hamzic, M.; Visus, J.; Rominger, F.; Frey, W.; Bats, J. W. *Chem.- Eur. J.* **2010**, *16*, 956.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.34 (m, 5H), 4.36 (s, 1H), 3.99 (s, 1H), 3.09 (d, J = 29.6 Hz, 3H), 2.34 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 169.44, 133.53, 128.13, 126.59, 125.27, 125.14, 125.10, 76.56, 70.88, 39.62, 34.7.

((2-methylbut-3-yn-2-yloxy)methyl)benzene (1o)



1o

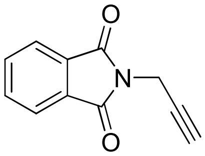
2-Methyl-3-butyn-2-ol (8 mL, 9.94g, 83 mmol) was added to a heterogeneous mixture of NaH (60% in mineral oil, 4g, 0.1 mol) in anhydrous THF (400 mL). After stirring the mixture for 1 hour under nitrogen at room temperature, tetrabutylammonium iodide (1.5g, 4 mmol) followed by benzylbromide (12 mL, 17g, 0.1 mol) were added to the above alkoxide mixture. The mixture was stirred under nitrogen for 18 hours. After which, the reaction was diluted with diethyl ether (300 mL), washed with water (3x100 mL), brine (100 mL), dried with MgSO4, filtered and concentrated to an oil. Silica chromatography (eluent: petroleum ether/ diethyl ether 50:1) provided the product **1o** as a clear oil. Yield: 12.2 g (85%).

This compound is known.

Reference: Trost, B. M.; Fandrick, D. R.; Dinh, D. C. J. *Am. Chem. Soc.,* **2005**, *127*, 14186.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.22 (m, 5H), 4.63 (s, 2H), 2.47 (s, 1H), 1.55 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 138.84, 128.29, 127.71, 127.37, 86.05, 72.29, 70.45, 66.50, 28.83.

2-(prop-2-ynyl)isoindoline-1,3-dione (1p)



1p

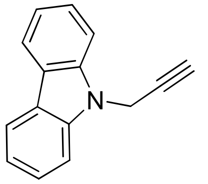
A solution of isoindoline-1,3-dione (2.94 g, 20 mmol), propargyl choride (2.9 mL, 40 mmol, 2 equiv) and potassium carbonate (6.9 g, 50 mmol, 2.5 equiv) in DMF (20 mL) was stirred 16 h at 50ºC. The reaction was cooled to rt and poured into HCl 1N (50 mL) and extracted with Et_2O.The organic phase was washed with HCl 1 N, then brine, dried over anhydrous $MgSO_4$ and the volatiles removed under reduced pressure. Flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate 15:1) afforded the product **1p** as White solid. Yield: 2.96 g (80%).

This compound is known.

Reference: Achard, T.; Lepronier, A.; Gimbert, Y.; Clavier, H.; Giordano, L.; Tenaglia, A.; Buono, G. *Angew. Chem. Int. Ed.* **2011**, *50*, 3552.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 2H), 7.77 – 7.72 (m, 2H), 4.46 (s, 2H), 2.23 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.02, 134.26, 131.98, 123.62, 77.17, 71.51, 27.01.

9-(prop-2-ynyl)-9H-carbazole (1q)



1q

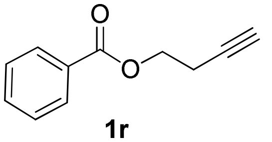
To a solution of carbazole 1 (1.67 g, 10 mmol) in 30 mL of acetone, K_2CO_3 (2.76 g, 20 mmol) was added. After the mixture was stirred for 15 min, 3-bromopropyne (2.25 mL of an 80 wt % solution in toluene, 15 mmol) was added dropwise for 30 min. After it was stirred for 3 h at room temperature, the mixture was filtered, the filtrate was rotoevaporated, and the crude product was separated by silica gel column chromatography (eluent: petroleum ether) to give the product **1q** as a white solid. Yield: 1.55 g (75%).

This compound is known.

Reference: Li, C.-H.; Liu, X.-F.; Yuan, M.-J.; Li, J.-B.; Guo, Y.-B.; Xu, J.-L.; Zhu, M.; Lv, J.; Liu, H.-B.; Li, Y.-L. *Langmuir* **2007**, *23*, 6754.

^{1}HNMR (CDCl3): δ 8.09 (2H, d); 7.48 (4H, t); 7.27 (2H, t); 5.04 (2H, d); 2.24 (1H, s).^{13}C NMR (CDCl3) δ 138.79, 124.87, 122.19, 119.38, 118.54, 107.65, 77.68, 71.53, 31.31.

but-3-ynyl benzoate (1r)



1r

Benzoyl chloride (5.8 mL, 50 mmol), but-3-yn-1-ol (4.5 mL, 60 mmol, 1.2 equiv), Et_3N (14 mL, 2 equiv) in DCM (100 mL) from 0 ^{o}C to rt for 16 h. Flash chromatography on silica gel (eluent: petroleum ether) afforded the product **1r** as colourless oil. Yield: 6.173 g (71.9%).

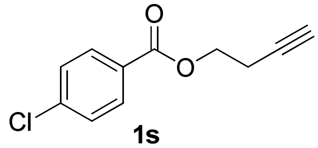
This compound is known.

Reference: Tiecco, M.; Testaferri, L.; Temperini, A.; Bagnoli, L.; Marini, F.; Santi, C.; Terlizzi, R. Eur. *J. Org. Chem.* **2004**, 3447.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 2H), 4.32 (t, *J* = 6.7 Hz, 2H), 2.57 (t, *J* = 6.6 Hz, 2H), 1.96 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.21, 132.03, 128.86, 128.60, 127.33, 79.00, 69.04, 61.53, 18.03.

but-3-ynyl 4-chlorobenzoate (1s)



1s

4-chlorobenzoyl chloride (6.34 mL, 50 mmol), but-3-yn-1-ol (4.5 mL, 60 mmol, 1.2 equiv), Et_3N (14 mL, 2 equiv) in DCM (100 mL) from 0 °C to rt for 16 h. Flash chromatography on silica gel (eluent: petroleum ether) afforded the product **1s** as colourless oil. Yield: 6.76 g (65%).

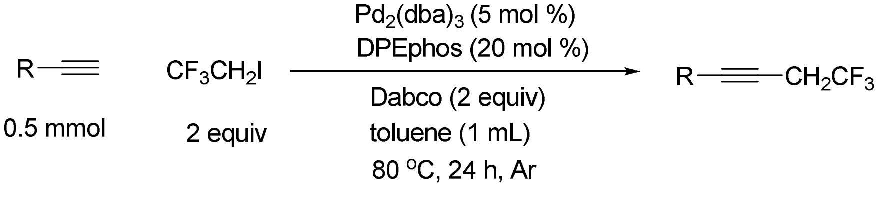
This compound is **new**.

Reference: Tiecco, M.; Testaferri, L.; Temperini, A.; Bagnoli, L.; Marini, F.; Santi, C.; Terlizzi, R. Eur. *J. Org. Chem.* **2004**, 3447.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 4.42 (t, *J* = 6.8 Hz, 2H), 2.67 (td, *J* = 6.8, 2.7 Hz, 2H), 2.04 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.42, 139.54, 131.06, 128.74, 128.34, 79.90, 70.12, 62.78, 19.06.

HRMS calcd for $C_{11}H_9ClO_2$: 208.0291; found: 208.0293.

3. General procedure for the synthesis of trifluoroethylated alkynes (3a-3s)

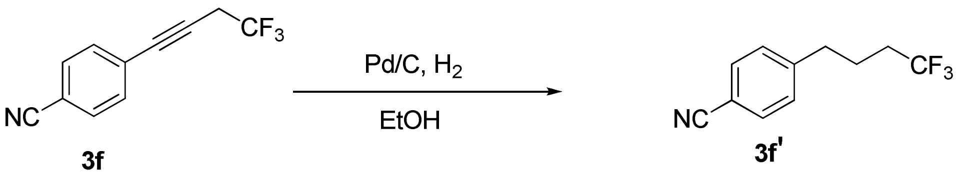


After standard cycles of evacuation and back-filling with dry and pure argon, an oven-dried Schlenk tube equipped with a magnetic stirring bar was combined $Pd_2(dba)_3$ (5 mol %), DPEphos (20 mol %), Dabco (2 equiv).The tube was evacuated and backfilled with argon (this procedure was repeated three times). Under a counter flow of argon, CF_3CH_2I (100 uL, 2 equiv), aryl or alkyl alkynes (55 uL, 0.5 mmol) and solvent toluene (1 mL) were added by syringe. The tube was sealed and the mixture was allowed to stir at 80 °C for 24 h. At the conclusion of the reaction, ethyl acetate was added to the mixture at room temperature. The organic layer was separated, and washed with water. The combined organic extracts were washed with brine, and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by chromatography on silica gel to give the product.

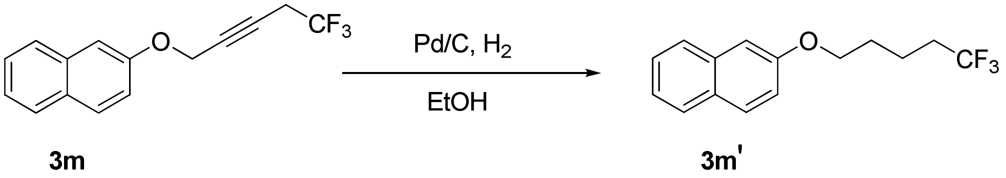
Products **3b, 3c, 3e, 3h, 3k** are known compounds.

c. Further synthetic applications of trifluoroethylated alkynes

1. General procedure for the reduction of aryl or alkyl 2,2,2,-trifluoroethylation product:

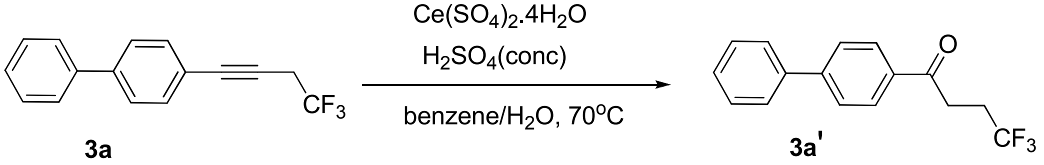


To a solution of 3f (105 mg, 0.5 mmol) in ethanol (15 mL) was added Pd/C 10% (50 mg). The reaction mixture was stirred under H_2 balloon overnight at room temperature. The reaction mixture was filtered through a silica gel pad, washed with CH_2Cl_2,and filtrate was concentrated. The residue was purified using chromatography on silica gel (eluent: petroleum ether/ethyl acetate 50:1) to give the hydrogenated product **3f**' (97 mg, 91% yield). Yellow oil;



To a solution of 3m (132 mg, 0.5 mmol) in ethanol (15 mL) was added Pd/C 10% (50 mg). The reaction mixture was stirred under H_2 balloon overnight at room temperature. The reaction mixture was filtered through a silica gel pad, washed with CH_2Cl_2, and filtrate was concentrated. The residue was purified using chromatography on silica gel (eluent: petroleum ether/ethyl acetate 100:1) to give the hydrogenated product **3m'** (126 mg, 94% yield). Yellow solid;

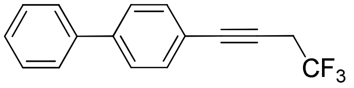
2. General procedure for the oxidation of aryl 2,2,2,-trifluoroethylation product:



A mixture of 3a (0.5 mmol, 130 mg) and $Ce(SO_4)_2.4H_2O$ (98%, 0.05 mmol, 20 mg) was added into a 25-mL one-necked round bottom flask. Then H_2O (10 μL), 98% H_2SO_4 (30 μL) and benzene (1.0 mL) were added into the mixture in turn. The reaction flask was immersed in a 70 °C oil bath with stirring under Ar atmosphere for 24 hours. The reaction mixture was extracted with ethyl acetate, dried with anhydrous magnesium sulfate and then concentrated in vacuo. The residue was purified on silic gel (eluent: petroleum ether/ethyl acetate 100:1) to afford the product **3a'** (68 mg, 49% yield). White solid;

Part 3. Characterization of the Products

1. 4-(4,4,4-trifluorobut-1-ynyl)biphenyl (3a)



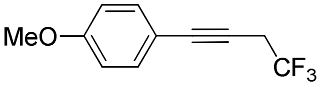
3a

According to the general procedure **b**, the mixture of $Pd_2(dba)_3$ (22.9 mg, 5 mol %), DPEphos (53.9 mg, 20 mol %), Dabco (112.2 mg, 2 equiv) were added into oven-dried Schlenk tube. The tube was evacuated and backfilled with argon (this procedure was repeated three times). Then, CF_3CH_2I (100 uL, 2 equiv), 4-ethynylbiphenyl (89 mg, 0.5 mmol) and toluene (1 mL) were added by syringe under argon , the tube was sealed and allowed to stir at 80 °C for 24 h. After column chromatography on silica gel (eluent: petroleum ether) afforded the product **3a** as a white solid. Yield: 74.1 mg, 57%.

This compound is **new**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.0 Hz, 2H), 7.53 (q, J = 8.6 Hz, 4H), 7.44 (t, J = 7.5 Hz, 2H), 7.35 (t, J = 7.3 Hz, 1H), 3.29 (q, J = 9.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.50, 140.26, 132.28, 128.88, 127.74, 127.04 (d, J = 3.8 Hz), 124.24 (q, J = 276.9 Hz), 121.07, 84.25, 78.12 (q, J = 5.1 Hz), 26.88 (q, J = 34.8 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.40 (t, J = 9.5 Hz). HRMS calcd for $C_{16}H_{11}F_3$: 260.0813; found: 260.0815.

2. 1-methoxy-4-(4,4,4-trifluorobut-1-ynyl)benzene (3b)



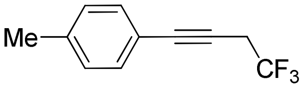
3b

According to the general procedure **b**, the mixture of $Pd_2(dba)_3$ (22.9 mg, 5 mol %), DPEphos (53.9 mg, 20 mol %), Dabco (112.2 mg, 2 equiv) were added into oven-dried Schlenk tube. The tube was evacuated and backfilled with argon (this procedure was repeated three times). Then, CF_3CH_2I (100 uL, 2 equiv), 1-ethynyl-4-methoxybenzene (66 mg, 0.5 mmol) and toluene (1 mL) were added by syringe under argon , the tube was sealed and allowed to stir at 80 °C for 24 h. After column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 100:1) afforded the product **3b** as a yellow oil. Yield: 90 mg, 84%.

This compound is known.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.9 Hz, 2H), 6.83 (d, J = 8.9 Hz, 2H), 3.80 (s,3H),3.25 (q, J = 9.6 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.90, 133.30, 124.31(q, J = 276.8 Hz), 114.29, 113.95, 84.24, 76.04 (q, J = 5.1 Hz), 55.26, 26.78 (q, J = 34.7 Hz).^{19}F NMR (377 MHz, $CDCl_3$) δ -66.58 (t, J = 9.7 Hz). HRMS calcd for $C_{11}H_9F_3O$: 214.0605; found: 214.0603.

3. 1-methyl-4-(4,4,4-trifluorobut-1-ynyl)benzene (3c)



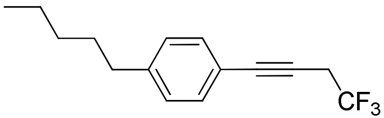
3c

According to the general procedure **b**, the mixture of $Pd_2(dba)_3$ (22.9 mg, 5 mol %), DPEphos (53.9 mg, 20 mol %), Dabco (112.2 mg, 2 equiv) were added into oven-dried Schlenk tube. The tube was evacuated and backfilled with argon (this procedure was repeated three times). Then, CF_3CH_2I (100 uL, 2 equiv), 1-ethynyl-4-methylbenzene (58 mg, 0.5 mmol) and toluene (1 mL) were added by syringe under argon , the tube was sealed and allowed to stir at 80 °C for 24 h. After column chromatography on silica gel (eluent: petroleum ether) afforded the product **3c** as a yellow oil. Yield: 80.2 mg, 81%.

This compound is known.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 3.25 (q, *J* = 9.6 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.86, 131.74, 129.08, 124.27 (q, *J* = 275.0 Hz), 119.13, 84.47, 76.81 (q, *J* = 5.1 Hz), 26.82 (q, *J* = 34.8 Hz), 21.48. ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.51 (t, *J* = 9.6 Hz). HRMS calcd for $C_{11}H_9F_3$: 198.0656; found: 198.0657.

4. 1-pentyl-4-(4,4,4-trifluorobut-1-ynyl)benzene (3d)



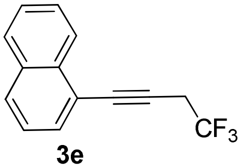
3d

According to the general procedure **b**, the mixture of $Pd_2(dba)_3$ (22.9 mg, 5 mol %), DPEphos (53.9 mg, 20 mol %), Dabco (112.2 mg, 2 equiv) were added into oven-dried Schlenk tube. The tube was evacuated and backfilled with argon (this procedure was repeated three times). Then, CF_3CH_2I (100 uL, 2 equiv), 1-ethynyl-4-pentylbenzene (86 mg, 0.5 mmol) and toluene (1 mL) were added by syringe under argon , the tube was sealed and allowed to stir at 80 °C for 24 h. After column chromatography on silica gel (eluent: petroleum ether) afforded the product **3d** as yellow oil. Yield: 92.7 mg, 73%.

This compound is **new.**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 3.26 (q, *J* = 9.6 Hz, 2H), 2.59 (t, *J* = 10.2 Hz, 2H), 1.64 – 1.57 (m, 2H), 1.34 – 1.28 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 143.90, 131.75, 128.44, 125.38 (q, *J* = 275.0 Hz), 119.31, 84.51, 69.42 (q, *J* = 5.1 Hz), 35.85, 31.41, 30.90, 26.81 (q, *J* = 34.8 Hz), 22.51, 14.00.^{19}F NMR (377 MHz, $CDCl_3$) δ -66.52 (t, *J* = 9.5 Hz). HRMS calcd for$C_{15}H_{17}F_3$: 254.1282; found: 254.1285.

5. 2-(4,4,4-trifluorobut-1-ynyl)naphthalene (3e)



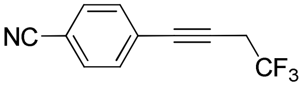
3e

According to the general procedure **b**, the mixture of $Pd_2(dba)_3$ (22.9 mg, 5 mol %), DPEphos (53.9 mg, 20 mol %), Dabco (112.2 mg, 2 equiv) were added into oven-dried Schlenk tube. The tube was evacuated and backfilled with argon (this procedure was repeated three times). Then, CF_3CH_2I (100 uL, 2 equiv), 1-ethynylnaphthalene (76.1 mg, 0.5 mmol) and toluene (1 mL) were added by syringe under argon , the tube was sealed and allowed to stir at 80 °C for 24 h. After column chromatography on silica gel (eluent: petroleum ether) afforded the product **3e** as yellow oil. Yield: 52.6 mg, 45%.

This compound is known

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 7.1 Hz, 1H), 7.57 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.51 (t, *J* = 6.8 Hz, 1H), 7.44 – 7.38 (m, 1H), 3.43 (q, *J* = 9.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.37, 132.09, 129.77, 128.17, 127.28, 125.96, 125.47, 124.86, 124.07, 123.13 (q, *J* = 275.0 Hz), 118.76, 81.59, 81.26 (q, *J* = 5.2 Hz), 26.08 (q, *J* = 34.8 Hz).^{19}F NMR (377 MHz, $CDCl_3$) δ -66.31 (t, *J* = 9.5 Hz). HRMS calcd for$C_{14}H_9F_3$: 234.0656; found: 234.0658.

6. 4-(4,4,4-trifluorobut-1-ynyl)benzonitrile (3f)



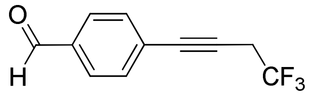
3f

According to the general procedure **b**, the mixture of $Pd_2(dba)_3$ (22.9 mg, 5 mol %), DPEphos (53.9 mg, 20 mol %), Dabco (112.2 mg, 2 equiv) were added into oven-dried Schlenk tube. The tube was evacuated and backfilled with argon (this procedure was repeated three times). Then, CF_3CH_2I (100 uL, 2 equiv), 4-ethynylbenzonitrile (63.5 mg, 0.5 mmol) and toluene (1 mL) were added by syringe under argon , the tube was sealed and allowed to stir at 80 °C for 24 h. After column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 50:1) afforded the product **3f** as yellow oil; Yield: 62.7 mg, 60%.

This compound is **new**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 3.31 (q, *J* = 9.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.43, 132.06, 127.01, 123.91 (q, *J* = 274.8 Hz), 118.26, 112.28, 82.84, 82.10 (q, *J* = 5.2 Hz), 26.89 (q, *J* = 35.1 Hz).^{19}F NMR (377 MHz, $CDCl_3$) δ -66.15 (t, *J* = 9.5 Hz). HRMS calcd for $C_{11}H_6F_3N$: 209.0452; found: 209.045.

7. 4-(4,4,4-trifluorobut-1-ynyl)benzaldehyde (3g)



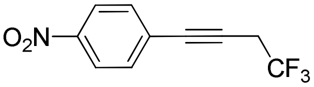
3g

According to the general procedure **b**, the mixture of $Pd_2(dba)_3$ (22.9 mg, 5 mol %), DPEphos (53.9 mg, 20 mol %), Dabco (112.2 mg, 2 equiv) were added into oven-dried Schlenk tube. The tube was evacuated and backfilled with argon (this procedure was repeated three times). Then, CF_3CH_2I (100 uL, 2 equiv), 4-ethynylbenzaldehyde (65 mg, 0.5 mmol) and toluene (1 mL) were added by syringe under argon , the tube was sealed and allowed to stir at 80 °C for 24 h. After column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 40:1) afforded the product **3g** as yellow oil; Yield: 60.4 mg, 57%.

This compound is **new**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 3.32 (q, *J* = 9.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.34, 135.87, 132.42, 129.49, 128.31, 123.98 (q, *J* = 276.7 Hz), 83.52, 81.57 (q, *J* = 5.0 Hz), 26.88 (q, *J* = 35.0 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.21 (t, *J* = 9.5 Hz). HRMS calcd for $C_{11}H_7F_3O$: 212.0449; found: 212.04.

8. 1-nitro-4-(4,4,4-trifluorobut-1-ynyl)benzene (3h)



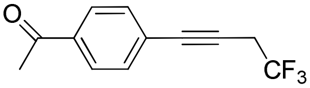
3h

According to the general procedure **b**, the mixture of $Pd_2(dba)_3$ (22.9 mg, 5 mol %), DPEphos (53.9 mg, 20 mol %), Dabco (112.2 mg, 2 equiv) were added into oven-dried Schlenk tube. The tube was evacuated and backfilled with argon (this procedure was repeated three times). Then, CF_3CH_2I (100 uL, 2 equiv), 1-ethynyl-4-nitrobenzene (73.5 mg, 0.5 mmol) and toluene (1 mL) were added by syringe under argon , the tube was sealed and allowed to stir at 80 °C for 24 h. After column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 50:1) afforded the product **3h** as yellow solid. Yield: 49.2 mg, 43%.

This compound is known.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.9 Hz, 2H), 7.60 (d, *J* = 8.9 Hz, 2H), 3.33 (q, *J* = 9.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.50, 132.71, 128.93, 123.90 (q, *J* = 276.9 Hz), 123.61, 82.94 (q, *J* = 5.0 Hz), 82.63, 26.93 (q, *J* = 35.1 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.09 (t, *J* = 9.4 Hz). HRMS calcd for $C_{10}H_6F_3NO_2$: 229.0351; found: 229.0352.

9. 1-(4-(4,4,4-trifluorobut-1-ynyl)phenyl)ethanone (3i)



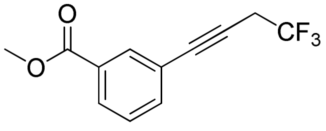
3i

According to the general procedure **b**, the mixture of $Pd_2(dba)_3$ (22.9 mg, 5 mol %), DPEphos (53.9 mg, 20 mol %), Dabco (112.2 mg, 2 equiv) were added into oven-dried Schlenk tube. The tube was evacuated and backfilled with argon (this procedure was repeated three times). Then, CF_3CH_2I (100 uL, 2 equiv), 1-(4-ethynylphenyl)ethanone (72 mg, 0.5 mmol) and toluene (1 mL) were added by syringe under argon , the tube was sealed and allowed to stir at 80 °C for 24 h. After column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 20:1) afforded the product **3i** as yellow oil. Yield: 92.7 mg, 82%.

This compound is **new**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 3.31 (q, *J* = 9.5 Hz, 2H), 2.60 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.27, 136.74, 132.03, 128.23, 126.97, 123.92 (q, *J* = 274.0 Hz), 83.64, 80.86 (q, *J* = 5.0 Hz), 26.90 (q, *J* = 35.0 Hz), 26.63. ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.24 (t, *J* = 9.5 Hz). HRMS calcd for $C_{12}H_9F_3O$: 226.0605; found: 226.0604.

10. methyl 3-(4,4,4-trifluorobut-1-ynyl)benzoate (3j)



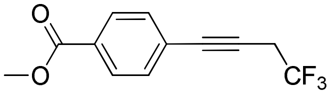
3j

According to the general procedure **b**, the mixture of $Pd_2(dba)_3$ (22.9 mg, 5 mol %), DPEphos (53.9 mg, 20 mol %), Dabco (112.2 mg, 2 equiv) were added into oven-dried Schlenk tube. The tube was evacuated and backfilled with argon (this procedure was repeated three times). Then, CF_3CH_2I (100 uL, 2 equiv), methyl 3-ethynylbenzoate (80 mg, 0.5 mmol) and toluene (1 mL) were added by syringe under argon , the tube was sealed and allowed to stir at 80 °C for 24 h. After column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 30:1) afforded the product **3j** as yellow oil. Yield: 99 mg, 82%.

This compound is **new**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 3.85 (s, 3H), 3.21 (q, *J* = 9.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.29, 135.98, 133.01, 130.49, 129.73, 128.52, 124.13 (q, *J* = 276.9 Hz), 122.63, 83.39, 78.55 (q, *J* = 5.1 Hz), 52.32, 26.79 (q, *J* = 34.9 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.34 (t, *J* = 9.4 Hz).HRMS calcd for $C_{12}H_9F_3O_2$: 242.0555; found: 242.0552.

11. methyl 4-(4,4,4-trifluorobut-1-ynyl)benzoate (3k)



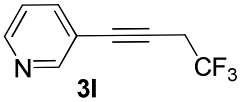
3k

According to the general procedure **b**, the mixture of $Pd_2(dba)_3$ (22.9 mg, 5 mol %), DPEphos (53.9 mg, 20 mol %), Dabco (112.2 mg, 2 equiv) were added into oven-dried Schlenk tube. The tube was evacuated and backfilled with argon (this procedure was repeated three times). Then, CF_3CH_2I (100 uL, 2 equiv), methyl 4-ethynylbenzoate (73.5 mg, 0.5 mmol) and toluene (1 mL) were added by syringe under argon , the tube was sealed and allowed to stir at 80 °C for 24 h. After column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 30:1) afforded the product **3k** as yellow oil. Yield: 96.8 mg, 80%.

This compound is known.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.6 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 3.84 (s, 3H), 3.22 (q, J = 9.5 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 165.39, 130.78, 129.05, 128.46, 125.77, 123.05 (q, J = 276.9 Hz), 82.64, 79.50 (q, J = 5.1 Hz), 51.23, 25.83 (q, J = 35.0 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.24 (t, J = 9.5 Hz). HRMS calcd for $C_{12}H_9F_3O_2$: 242.0555; found: 242.0554.

12. 3-(4,4,4-trifluorobut-1-ynyl)pyridine (3l)



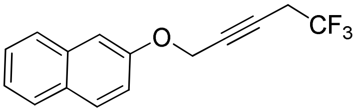
3l

According to the general procedure **b**, the mixture of $Pd_2(dba)_3$ (22.9 mg, 5 mol %), DPEphos (53.9 mg, 20 mol %), Dabco (112.2 mg, 2 equiv) were added into oven-dried Schlenk tube. The tube was evacuated and backfilled with argon (this procedure was repeated three times). Then, CF_3CH_2I (100 uL, 2 equiv), 3-ethynylpyridine (51.5 mg, 0.5 mmol) and toluene (1 mL) were added by syringe under argon , the tube was sealed and allowed to stir at 80 °C for 24 h. After column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 20:1) afforded the product **3l** as yellow oil. Yield: 70 mg, 76%.

This compound is **new**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J = 51.0 Hz, 2H), 7.74 (d, J = 7.9 Hz, 1H), 7.26 (m, 1H), 3.31 (q, J = 9.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.51, 149.08, 138.87, 124.02 (q, J = 276.9 Hz), 123.06, 81.22, 81.11 (q, J = 5.1 Hz), 26.86 (q, J = 35.0 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.28 (t, J = 9.5 Hz). HRMS calcd for $C_9H_6F_3N$: 185.0452; found: 185.0457.

13. 2-(5,5,5-trifluoropent-2-ynyloxy)naphthalene (3m)



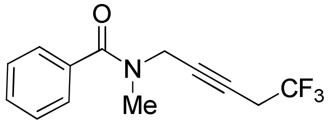
3m

According to the general procedure **b**, the mixture of $Pd_2(dba)_3$ (22.9 mg, 5 mol %), DPEphos (53.9 mg, 20 mol %), Dabco (112.2 mg, 2 equiv) were added into oven-dried Schlenk tube. The tube was evacuated and backfilled with argon (this procedure was repeated three times). Then, CF_3CH_2I (100 uL, 2 equiv), 2-(prop-2-ynyloxy)naphthalene (91 mg, 0.5 mmol) and toluene (1 mL) were added by syringe under argon , the tube was sealed and allowed to stir at 80 °C for 24 h. After column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 50:1) afforded the product **3m** as yellow solid. Yield: 118.8 mg, 90%.

This compound is **new**.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.69 (dd, *J* = 14.3, 6.0 Hz, 3H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 2.3 Hz, 1H), 7.10 (dd, *J* = 8.9, 2.5 Hz, 1H), 4.74 (s, 2H), 3.03 (q, *J* = 9.5 Hz, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 155.44, 134.29, 129.57, 129.31, 127.65, 126.93, 126.49, 124.05 (q, *J* = 274.7 Hz), 124.03, 118.68, 107.49, 79.41, 76.14 (q, *J* = 5.1 Hz), 55.97, 26.27 (q, *J* = 35.0 Hz) . ^{19}F NMR (376 MHz, CDCl$_3$) δ -66.36 (t, *J* = 9.5 Hz). HRMS calcd for $C_{15}H_{11}F_3O$: 264.0762; found: 264.0763.

14. N-methyl-N-(5,5,5-trifluoropent-2-ynyl)benzamide (3n)



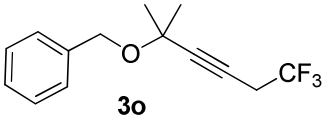
3n

According to the general procedure **b**, the mixture of Pd$_2$(dba)$_3$ (22.9 mg, 5 mol %), DPEphos (53.9 mg, 20 mol %), Dabco (112.2 mg, 2 equiv) were added into oven-dried Schlenk tube. The tube was evacuated and backfilled with argon (this procedure was repeated three times). Then, CF$_3$CH$_2$I (100 uL, 2 equiv), N-methyl-N-(prop-2-ynyl)benzamide (86.5 mg, 0.5 mmol) and toluene (1 mL) were added by syringe under argon , the tube was sealed and allowed to stir at 80 °C for 24 h. After column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1) afforded the product **3n** as yellow oil. Yield: 114.7 mg, 90%.

This compound is **new**.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.51 – 7.36 (m, 5H), 4.39 (s, 1H), 4.01 (s, 1H), 3.09 (q, *J* = 9.5 Hz, 5H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 171.36, 135.47, 130.02, 128.49, 127.09, 124.13 (q, *J* = 274.7 Hz), 79.36, 73.01 (q, *J* = 5.1 Hz), 41.66, 36.78, 26.18 (q, *J* = 35.0 Hz). ^{19}F NMR (377 MHz, CDCl$_3$) δ -66.59 (t, *J* = 9.5 Hz). HRMS calcd for $C_{13}H_{12}F_3NO$: 255.0871; found: 255.0874.

15. ((6,6,6-trifluoro-2-methylhex-3-yn-2-yloxy)methyl)benzene (3o)



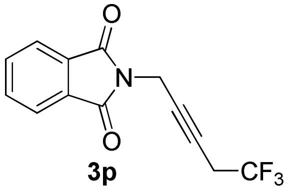
3o

According to the general procedure **b**, the mixture of Pd$_2$(dba)$_3$ (22.9 mg, 5 mol %), DPEphos (53.9 mg, 20 mol %), Dabco (112.2 mg, 2 equiv) were added into oven-dried Schlenk tube. The tube was evacuated and backfilled with argon (this procedure was repeated three times). Then, CF$_3$CH$_2$I (100 uL, 2 equiv), ((2-methylbut-3-yn-2-yloxy)methyl)benzene (87 mg, 0.5 mmol) and toluene (1 mL) were added by syringe under argon , the tube was sealed and allowed to stir at 80 °C for 24 h. After column chromatography on silica gel (eluent: petroleum ether) afforded the product **3o** as yellow oil. Yield: 114 mg, 89%.

This compound is **new**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 4H), 7.18 (d, *J* = 6.8 Hz, 1H), 4.52 (s, 2H), 2.99 (q, *J* = 9.6 Hz, 2H), 1.45 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.87, 127.30, 126.74, 126.40, 123.01 (q, *J* = 274.7 Hz), 85.89, 71.75 (q, *J* = 5.0 Hz), 69.57, 65.58, 27.71, 25.07 (q, *J* = 34.8 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.72 (t, *J* = 9.7 Hz). HRMS calcd for $C_{14}H_{15}F_3O$: 256.1075; found: 256.1074.

16. 2-(5,5,5-trifluoropent-2-ynyl)isoindoline-1,3-dione (3p)



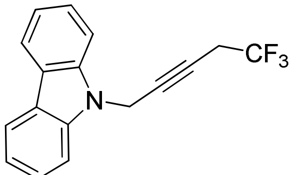
3p

According to the general procedure **b**, the mixture of $Pd_2(dba)_3$ (22.9 mg, 5 mol %), DPEphos (53.9 mg, 20 mol %), Dabco (112.2 mg, 2 equiv) were added into oven-dried Schlenk tube. The tube was evacuated and backfilled with argon (this procedure was repeated three times). Then, CF_3CH_2I (100 uL, 2 equiv), 2-(prop-2-ynyl)isoindoline-1,3-dione (92.5 mg, 0.5 mmol) and toluene (1 mL) were added by syringe under argon , the tube was sealed and allowed to stir at 80 °C for 24 h. After column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1) afforded the product **3p** as white crystal. Yield: 108 mg, 81%.

This compound is **new**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.47 (t, *J* = 2.2 Hz, 2H), 3.03 (q, *J* = 9.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.00, 134.27, 132.01, 123.99 (q, *J* = 276.8 Hz), 123.62, 78.09, 71.78 (q, *J* = 5.1 Hz), 27.13, 26.11 (q, *J* = 34.9 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.39 (t, *J* = 9.4 Hz). HRMS calcd for $C_{13}H_8F_3NO_2$: 267.0507; found: 267.0509.

17. 9-(5,5,5-trifluoropent-2-ynyl)-9,9a-dihydro-4aH-carbazole (3q)



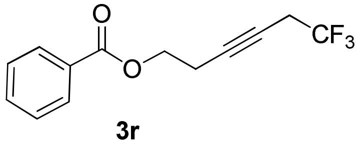
3q

According to the general procedure **b**, the mixture of $Pd_2(dba)_3$ (22.9 mg, 5 mol %), DPEphos (53.9 mg, 20 mol %), Dabco (112.2 mg, 2 equiv) were added into oven-dried Schlenk tube. The tube was evacuated and backfilled with argon (this procedure was repeated three times). Then, CF_3CH_2I (100 uL, 2 equiv), 9-(prop-2-ynyl)-9H-carbazole (102.5 mg, 0.5 mmol) and toluene (1 mL) were added by syringe under argon , the tube was sealed and allowed to stir at 80 °C for 24 h. After column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 20:1) afforded the product **3q** as yellow oil. Yield: 136 mg, 95%.

This compound is **new**.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.97 (d, *J* = 7.8 Hz, 2H), 7.41 – 7.27 (m, 4H), 7.15 (t, *J* = 7.3 Hz, 2H), 4.87 (t, *J* = 2.1 Hz, 2H), 2.82 (q, *J* = 9.6 Hz, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 138.79, 124.87, 122.97 (q, *J* = 276.8 Hz), 122.19, 119.38, 118.54, 107.65, 77.68 , 71.53 (q, *J* = 5.1 Hz), 31.31, 24.96 (q, *J* = 34.8 Hz). ^{19}F NMR (377 MHz, CDCl$_3$) δ -66.35 (t, *J* = 9.6 Hz). HRMS calcd for $C_{17}H_{12}F_3N$: 287.0922; found: 287.0925.

18. 6,6,6-trifluorohex-3-ynyl benzoate (3r)



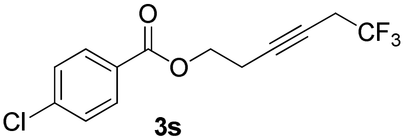
3r

According to the general procedure **b**, the mixture of Pd$_2$(dba)$_3$ (22.9 mg, 5 mol %), DPEphos (53.9 mg, 20 mol %), Dabco (112.2 mg, 2 equiv) were added into oven-dried Schlenk tube. The tube was evacuated and backfilled with argon (this procedure was repeated three times). Then, CF$_3$CH$_2$I (100 uL, 2 equiv), but-3-ynyl benzoate (87 mg, 0.5 mmol) and toluene (1 mL) were added by syringe under argon , the tube was sealed and allowed to stir at 80 °C for 24 h. After column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 50:1) afforded the product **3r** as yellow oil. Yield: 71.7 mg, 56%.

This compound is **new**.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.98 (d, *J* = 7.1 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 4.34 (t, *J* = 6.8 Hz, 2H), 2.94 (q, *J* = 9.6 Hz, 2H), 2.60 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 166.32, 133.10, 129.98, 129.68, 128.40, 124.25 (q, *J* = 274.7 Hz), 80.57, 70.18 (q, *J* = 5.1 Hz), 62.49, 26.15 (q, *J* = 34.7 Hz), 19.29. ^{19}F NMR (376 MHz, CDCl$_3$) δ -66.36 (t, *J* = 9.5 Hz). HRMS calcd for $C_{13}H_{11}F_3O_2$: 256.0711; found: 256.0716.

19. 6,6,6-trifluorohex-3-ynyl 4-chlorobenzoate (3s)



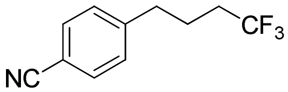
3s

According to the general procedure **b**, the mixture of Pd$_2$(dba)$_3$ (22.9 mg, 5 mol %), DPEphos (53.9 mg, 20 mol %), Dabco (112.2 mg, 2 equiv) were added into oven-dried Schlenk tube. The tube was evacuated and backfilled with argon (this procedure was repeated three times). Then, CF$_3$CH$_2$I (100 uL, 2 equiv), but-3-ynyl 4-chlorobenzoate (104 mg, 0.5 mmol) and toluene (1 mL) were added by syringe under argon , the tube was sealed and allowed to stir at 80 °C for 24 h. After column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 20:1) afforded the product **3s** as yellow oil. Yield: 136.3 mg, 94%.

This compound is **new**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 4.32 (t, *J* = 6.7 Hz, 2H), 2.94 (q, *J* = 9.6 Hz, 2H), 2.59 (t, *J* = 6.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.41, 138.57, 130.04, 127.73, 127.39, 123.33 (q, *J* = 274.7 Hz), 79.42, 69.26 (q, *J* = 5.1 Hz), 61.65, 25.09 (q, *J* = 34.7 Hz), 18.22. ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.87 (t, *J* = 9.5 Hz). HRMS calcd for $C_{13}H_{10}ClF_3O_2$: 290.0321; found: 290.0321.

20. 4-(4,4,4-trifluorobutyl)benzonitrile (3f')



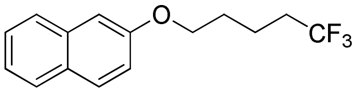
3f'

Yellow oil; Yield: 97 mg, 91%.

This compound is **new**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.4 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 2.68 (t, *J* = 7.7 Hz, 2H), 2.07 – 1.95 (m, 2H), 1.87 – 1.79 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.30, 131.39, 128.17, 125.93 (q, *J* = 276.4 Hz), 117.84, 109.33, 33.67, 32.00 (q, *J* = 28.8 Hz), 28.69, 22.08 (q, *J* = 2.9 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.15 (t, *J* = 10.7 Hz). HRMS calcd for $C_{11}H_{10}F_3N$: 213.0765; found: 213.0766.

21. 2-(5,5,5-trifluoropentyloxy)naphthalene (3m')



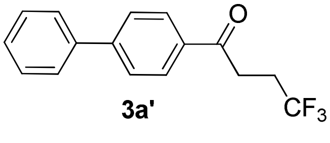
3m'

Yellow solid; Yield: 126 mg, 94%.

This compound is **new**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 17.1, 8.2 Hz, 3H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 9.1 Hz, 1H), 7.02 (s, 1H), 3.99 (t, *J* = 6.0 Hz, 2H), 2.16 – 2.02 (m, 2H), 1.87 – 1.77 (m, 2H), 1.76 – 1.67 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.78, 133.54, 128.41, 128.00, 126.63, 126.12 (q, *J* = 276.3 Hz), 125.68, 125.36, 122.62, 117.82, 105.57, 66.11, 32.50 (q, *J* = 28.6 Hz), 28.69, 27.27, 17.95 (q, *J* = 3.0 Hz). ^{19}F NMR(377 MHz, $CDCl_3$) δ -66.30 (t, *J* = 10.8 Hz). HRMS calcd for $C_{15}H_{15}F_3O$: 268.1075; found: 268.1078.

22. 1-(biphenyl-4-yl)-4,4,4-trifluorobutan-1-one (3a')



3a'

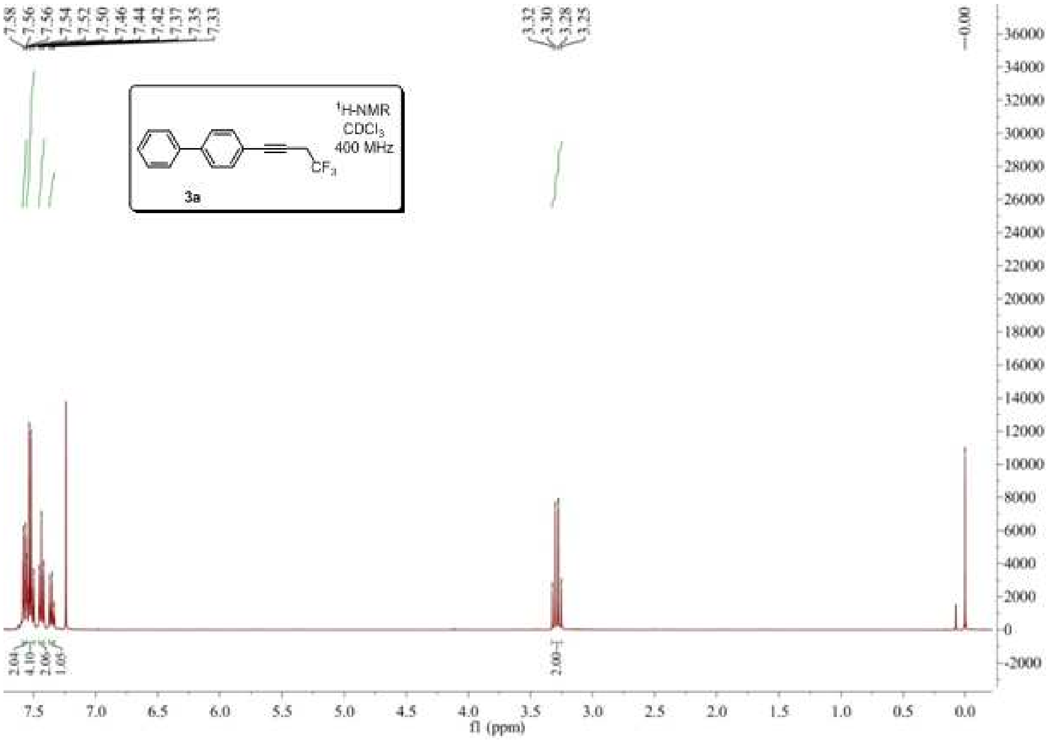
White solid; Yield: 68 mg, 49%.

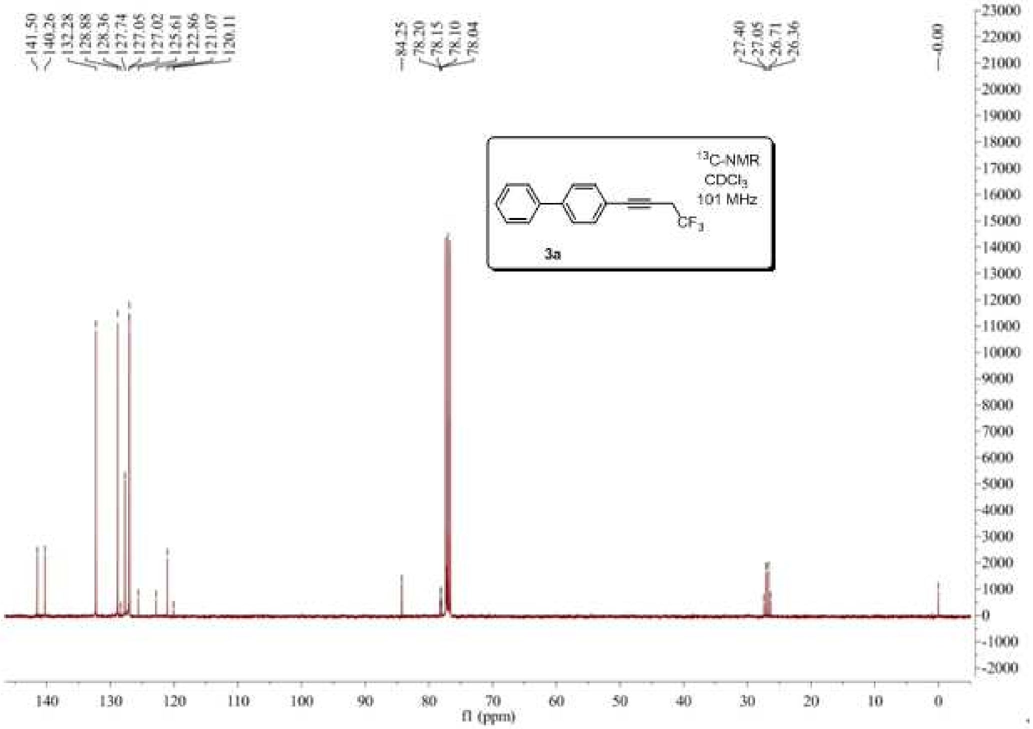
This compound is **new**.

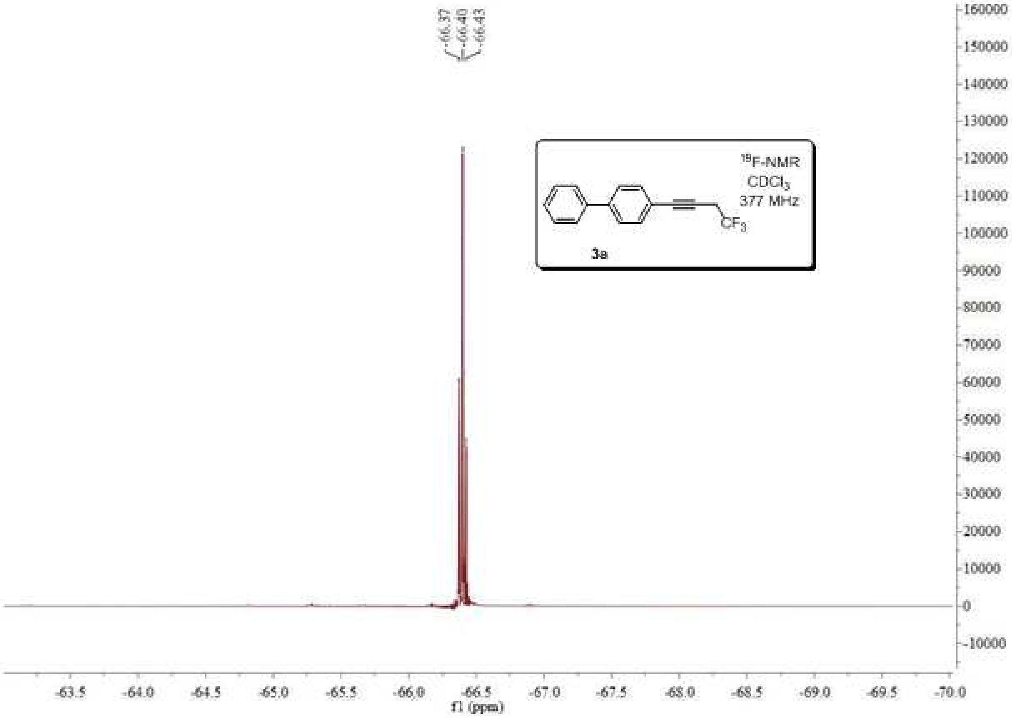
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, *J* = 8.6 Hz, 2H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 7.0 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 1H), 3.32 – 3.25 (m, 2H), 2.68 – 2.55 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 194.89, 145.29, 138.65, 133.79, 127.98, 127.60, 127.37, 126.36, 126.25, 126.17 (q, *J* = 275.7 Hz), 30.22 (q, *J* = 2.6 Hz), 28.69, 27.38 (q, *J* = 29.7 Hz). ^{19}F N MR (377 MHz, CDCl$_3$) δ -66.38 (t, *J* = 10.9 Hz). HRMS calcd for $C_{16}H_{13}F_3O$: 278.0918; found: 278.0916.

Part 4. Copies of ^{1}H-NMR and ^{13}C-NMR Spectra the Products

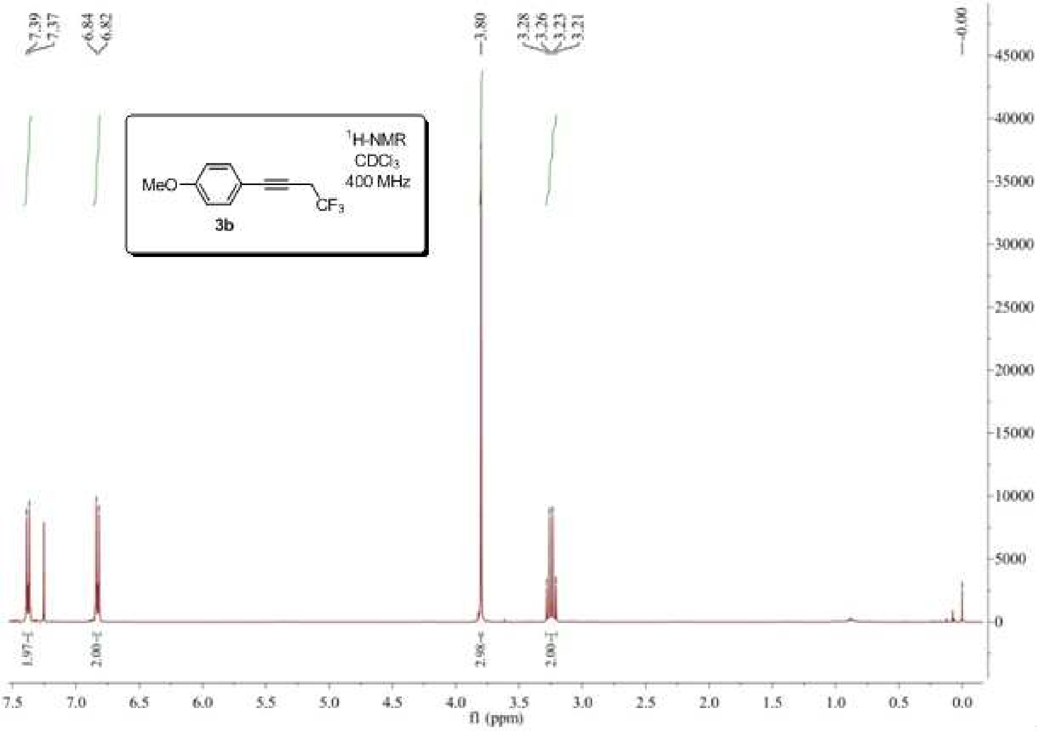
4-(4,4,4-trifluorobut-1-ynyl)biphenyl (3a)

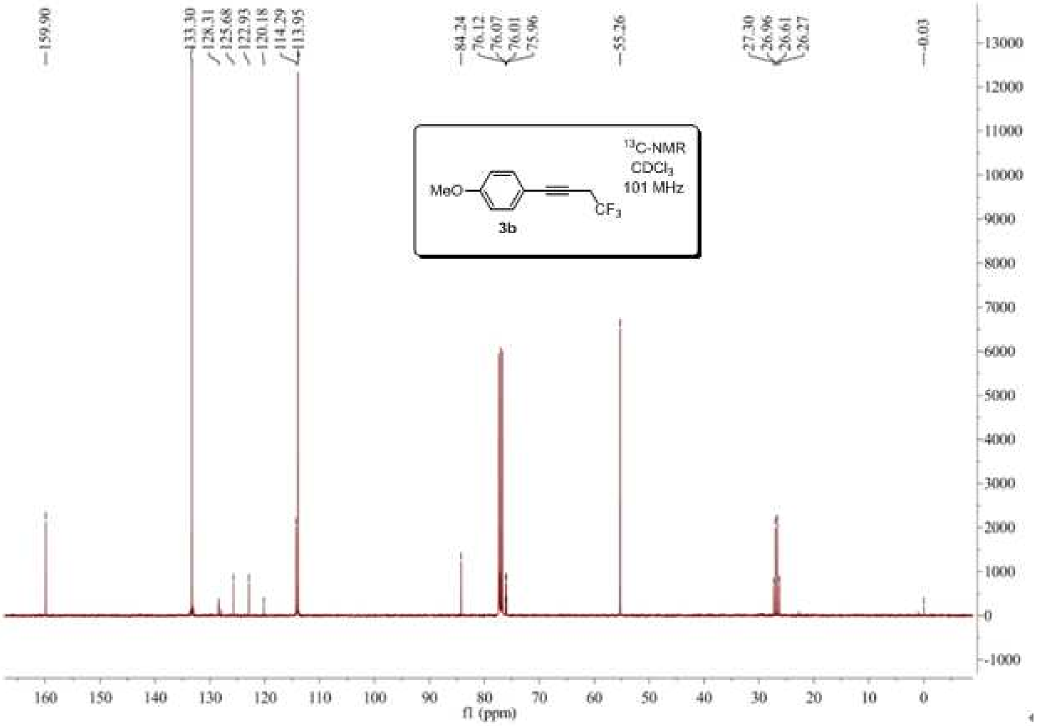


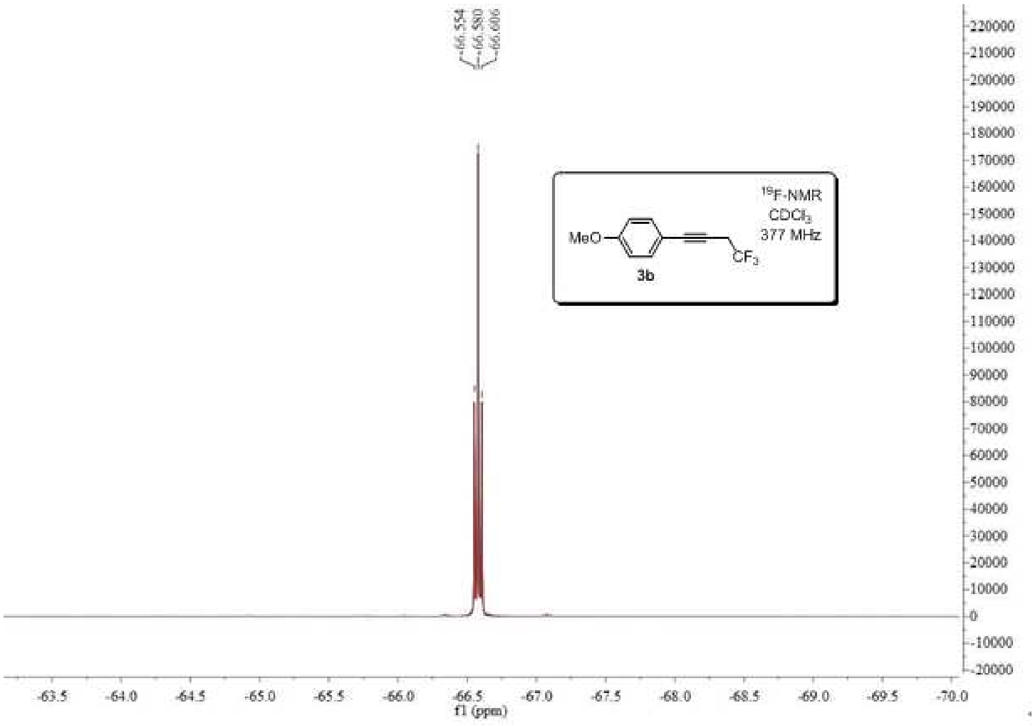




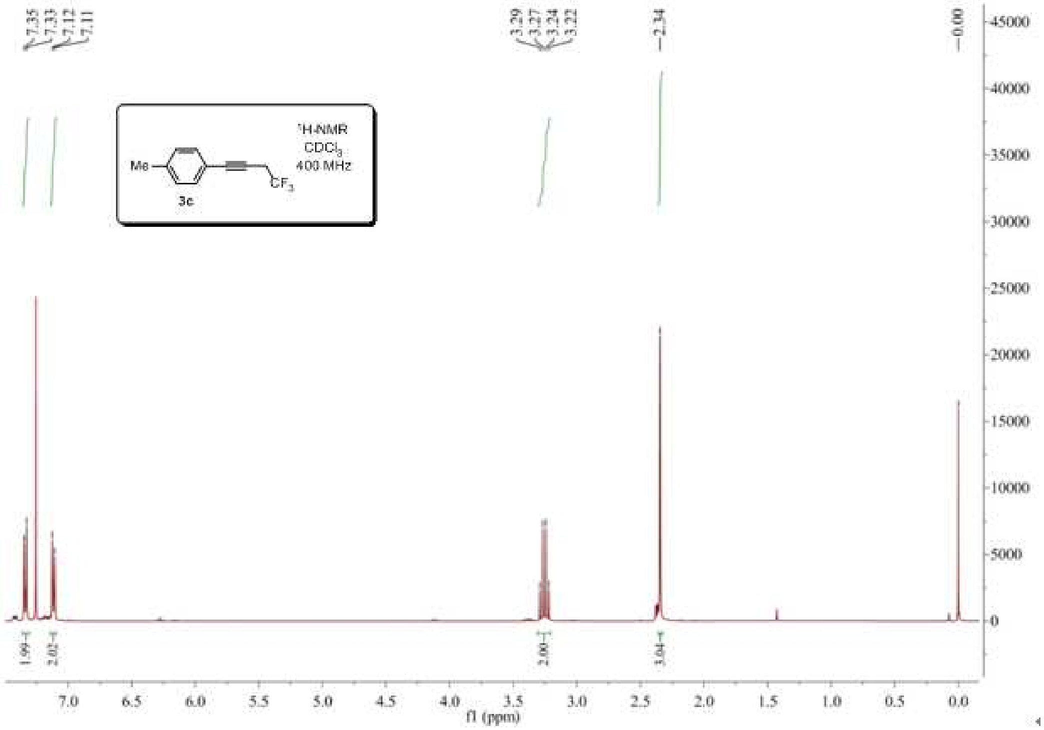
1-methoxy-4-(4,4,4-trifluorobut-1-ynyl)benzene (3b)

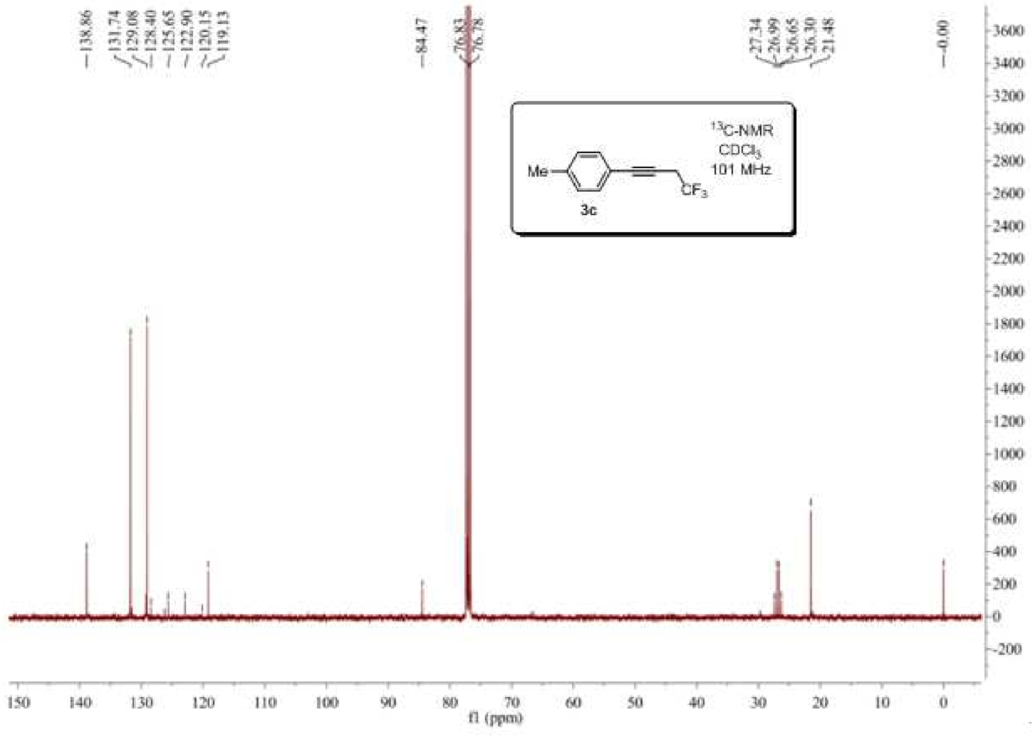


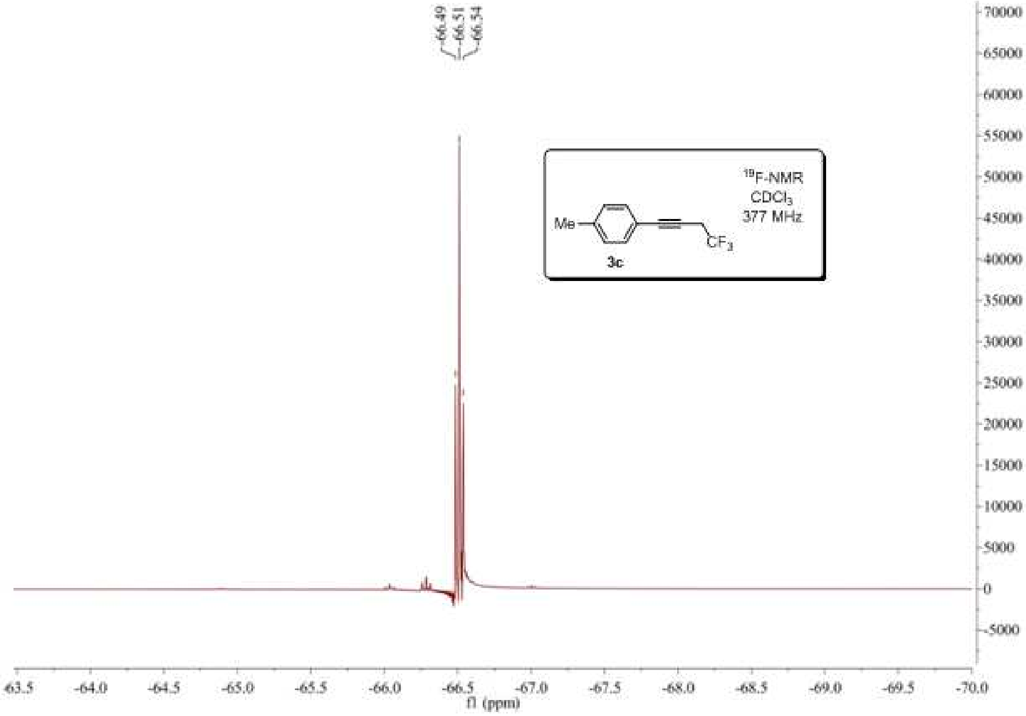

159.90
133.30
128.31
125.68
122.93
120.18
114.29
113.95
84.24
76.12
76.07
76.01
75.96
55.26
27.30
26.96
26.61
26.27
-0.03
^{13}C-NMR
$CDCl_3$
101 MHz
MeO
CF_3
3b
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-66.554
-66.580
-66.606
^{19}F-NMR
$CDCl_3$
377 MHz
MeO
CF_3
3b
220000
210000
200000
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
-63.5
-64.0
-64.5
-65.0
-65.5
-66.0
-66.5
-67.0
-67.5
-68.0
-68.5
-69.0
-69.5
-70.0
f1 (ppm)

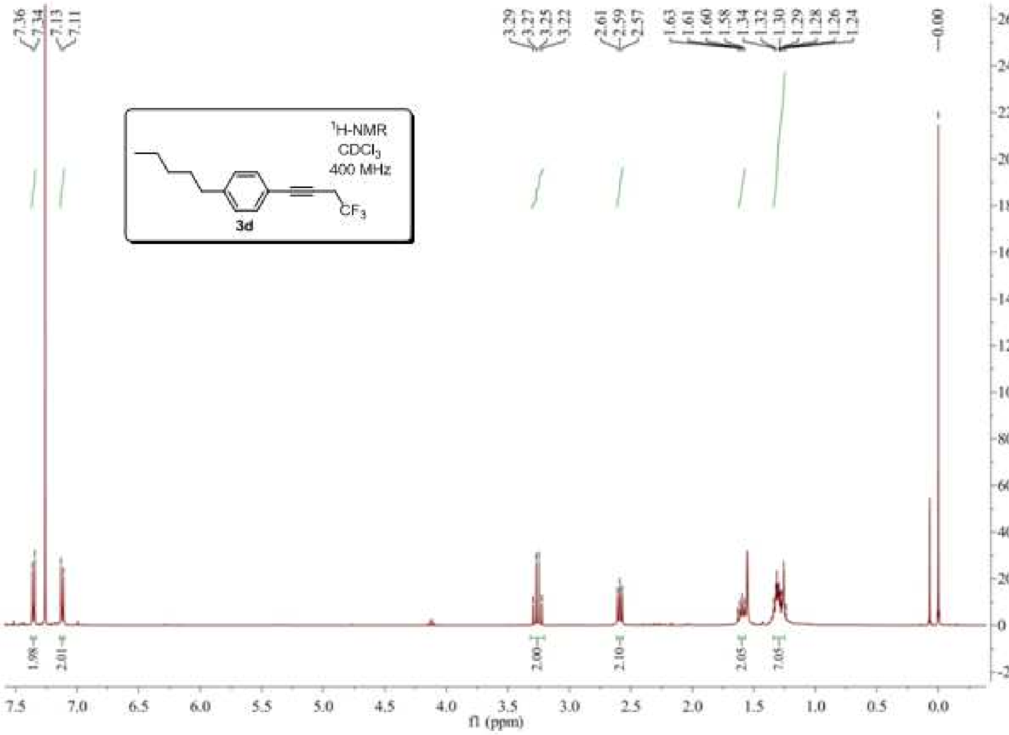
1-methyl-4-(4,4,4-trifluorobut-1-ynyl)benzene (3c)

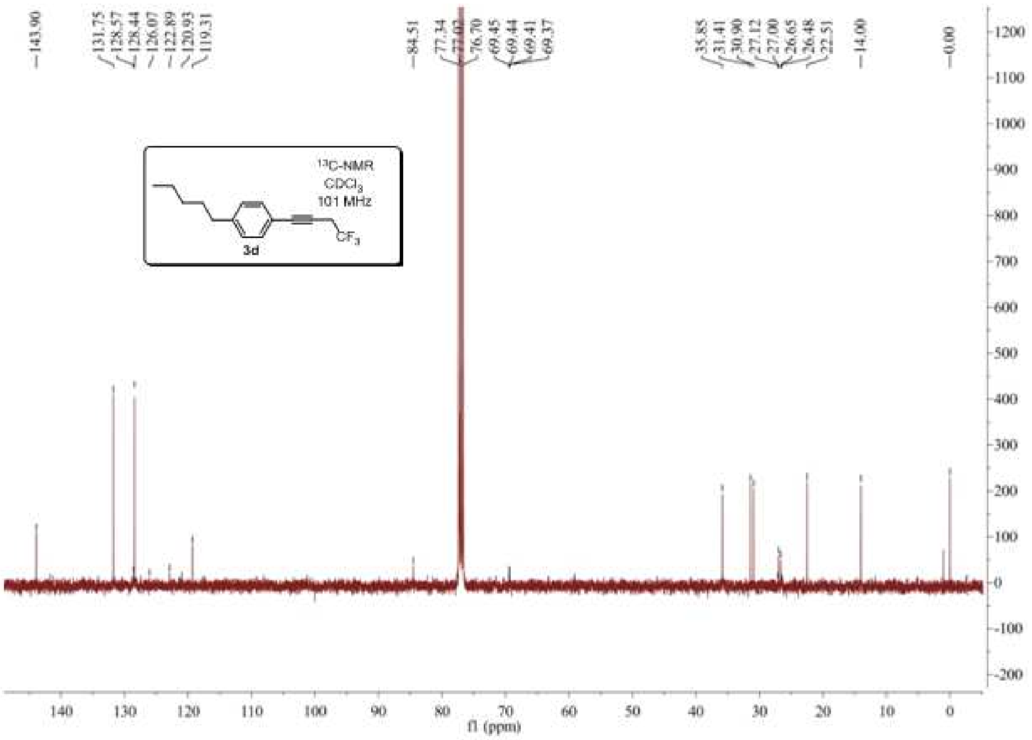


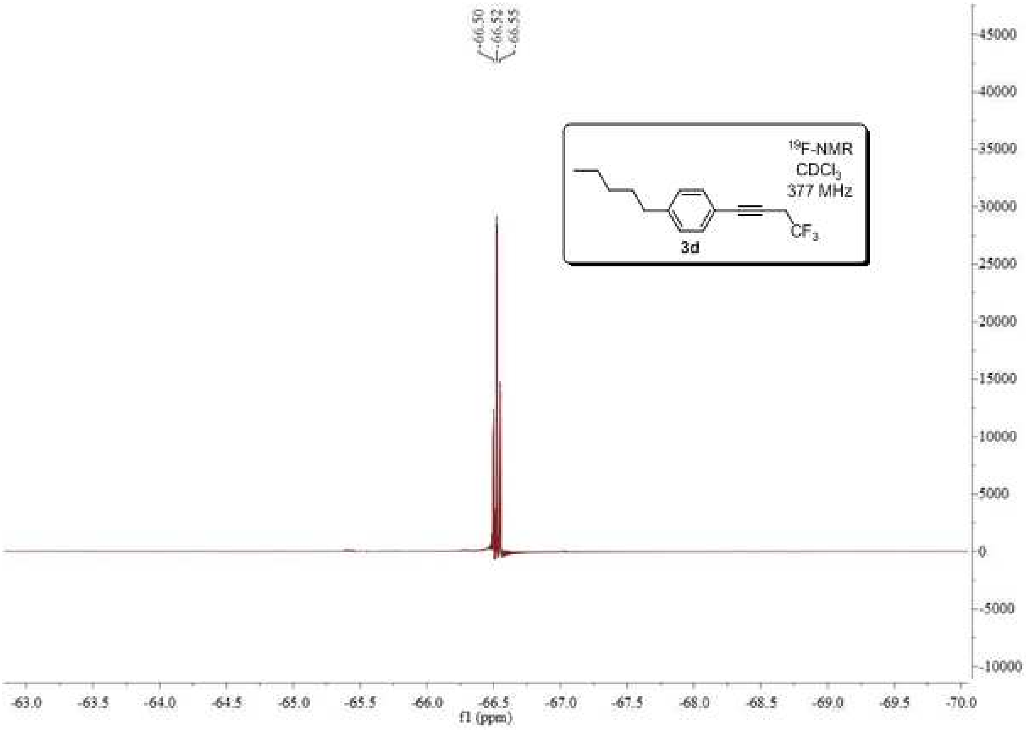




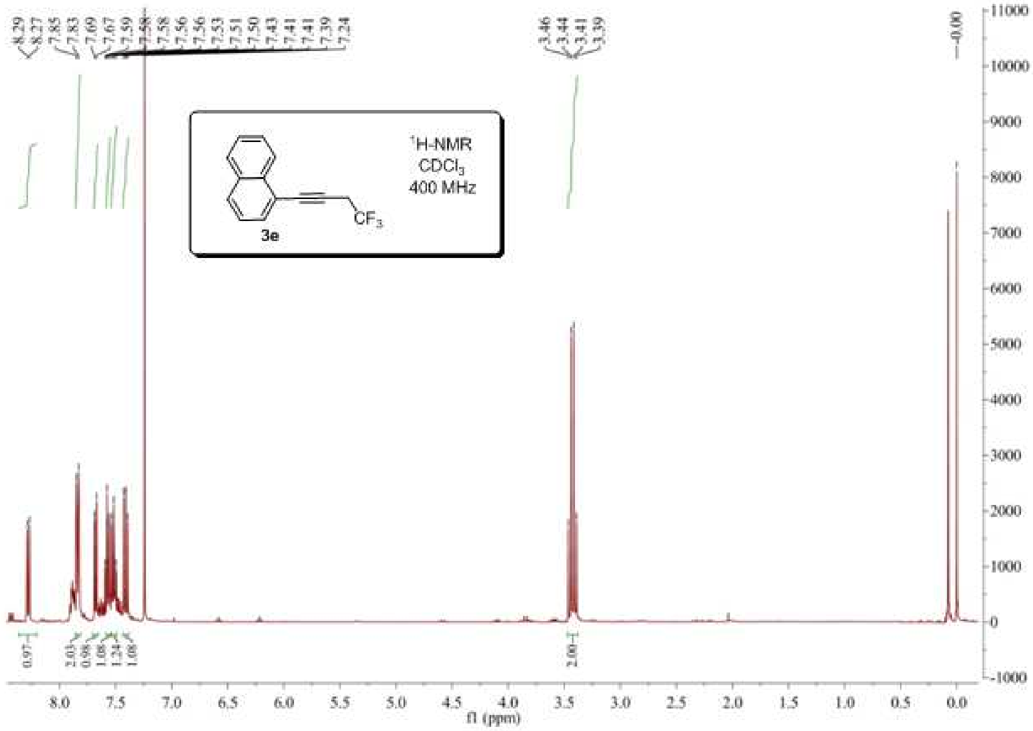
1-pentyl-4-(4,4,4-trifluorobut-1-ynyl)benzene (3d)

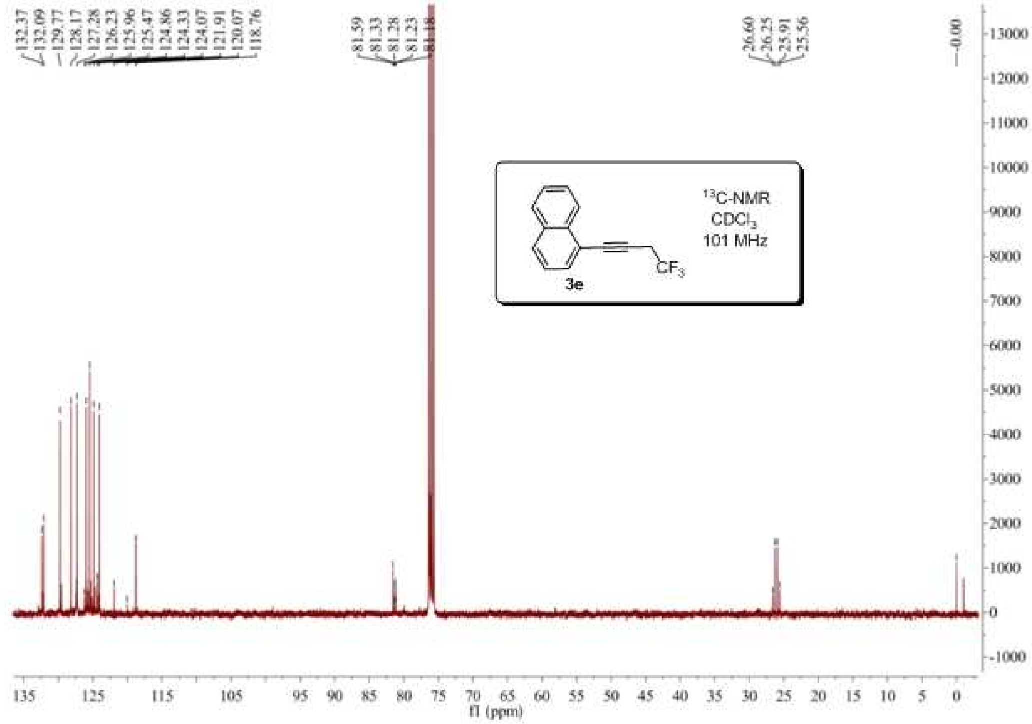


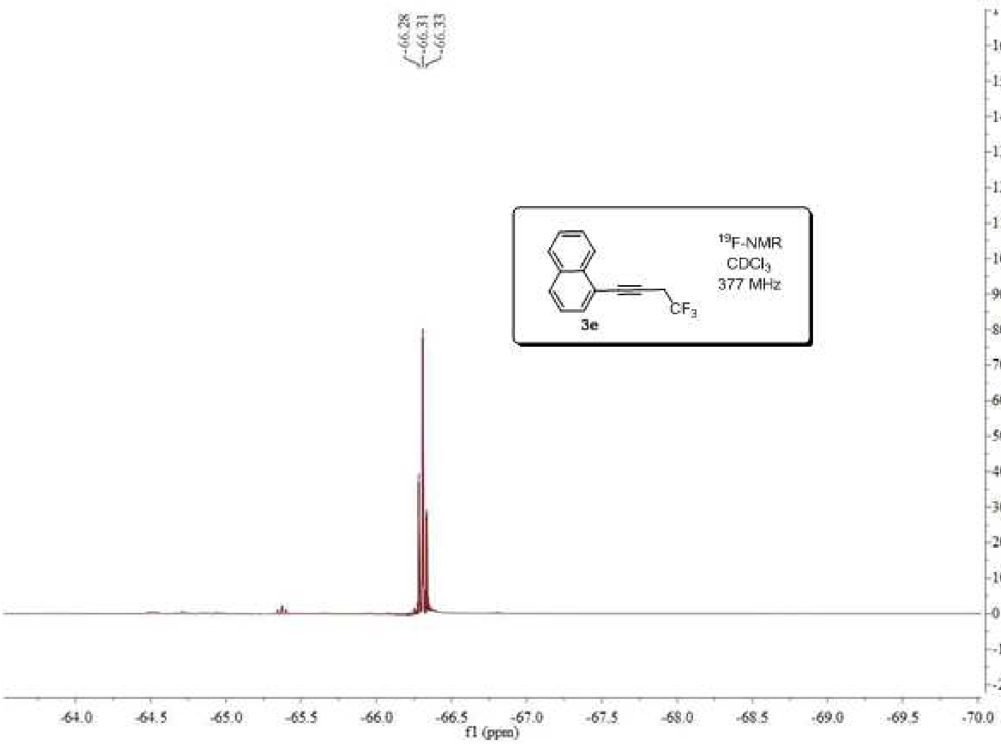

143.90
131.75
128.57
128.44
126.07
122.89
120.93
119.31
84.51
77.34
77.02
76.70
69.45
69.44
69.41
69.37
35.85
31.41
30.90
27.12
27.00
26.65
26.48
22.51
14.00
0.00
^{13}C-NMR
CDCl$_3$
101 MHz
CF$_3$
3d
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-66.50
-66.52
-66.55
^{19}F-NMR
CDCl$_3$
377 MHz
CF$_3$
3d
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
-63.0
-63.5
-64.0
-64.5
-65.0
-65.5
-66.0
-66.5
-67.0
-67.5
-68.0
-68.5
-69.0
-69.5
-70.0
f1 (ppm)

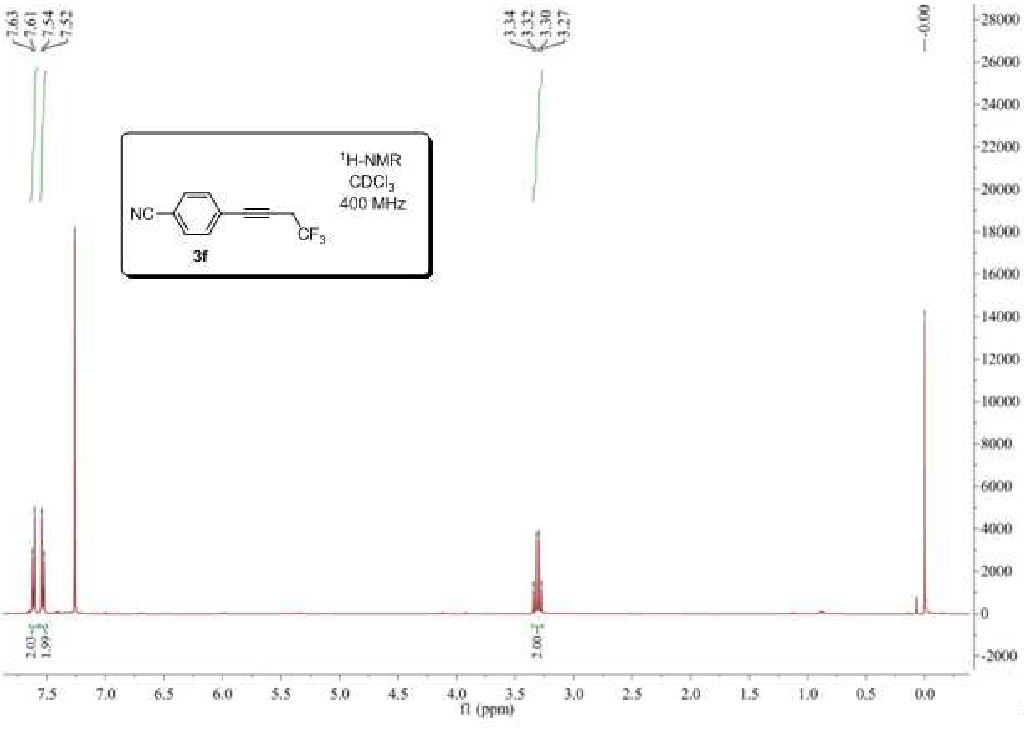
2-(4,4,4-trifluorobut-1-ynyl)naphthalene (3e)

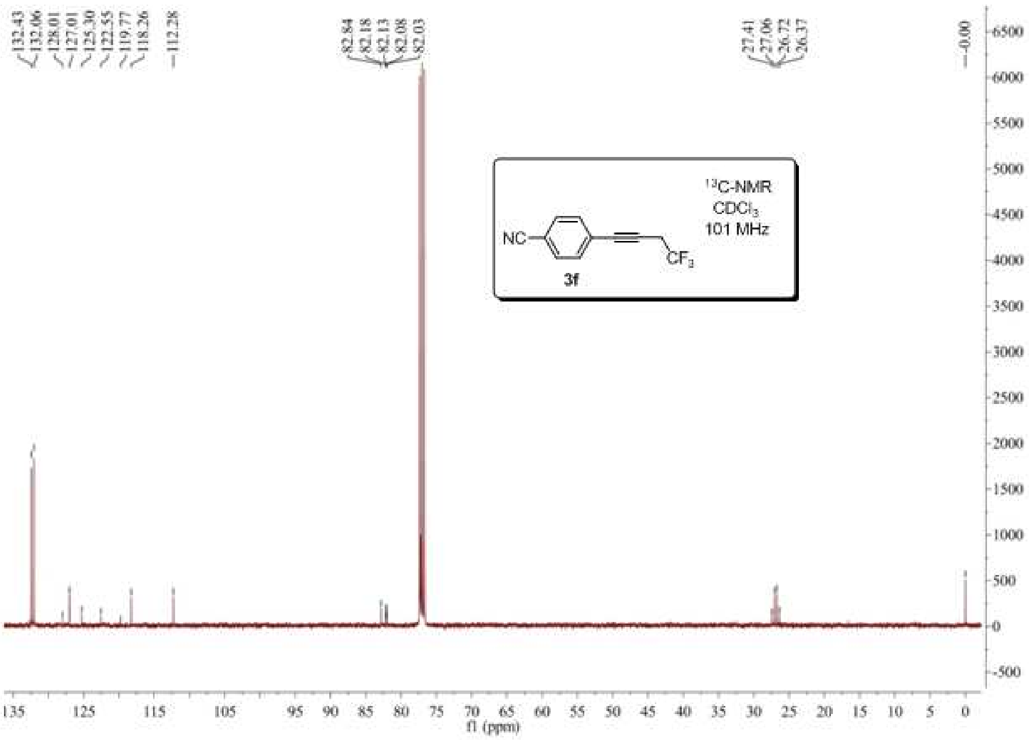


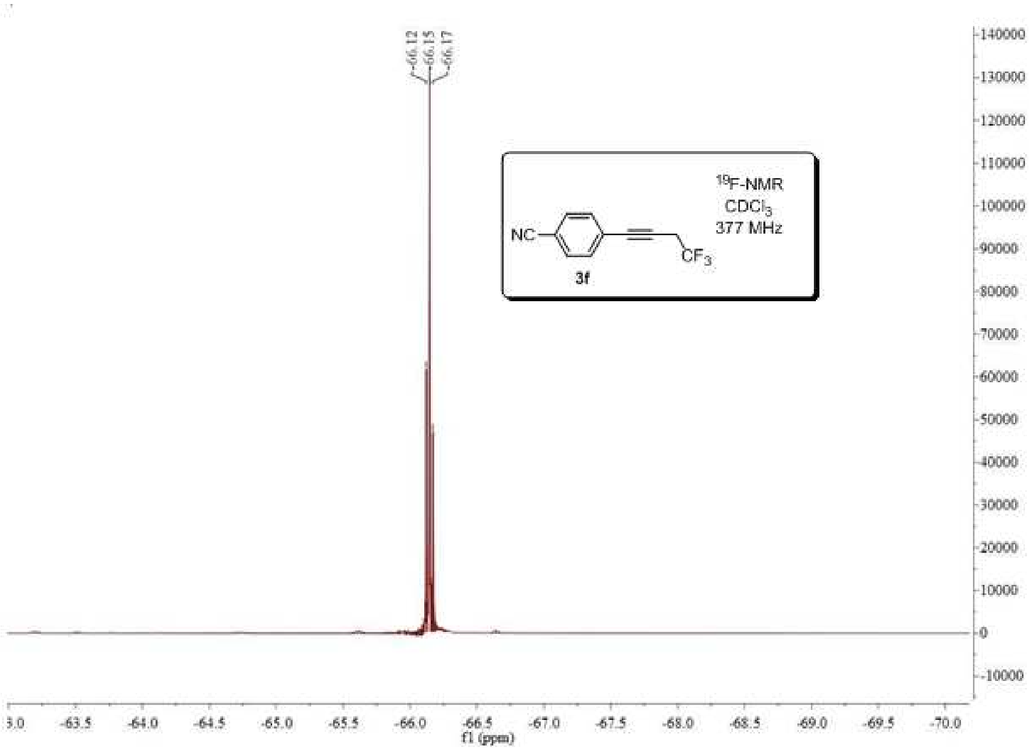




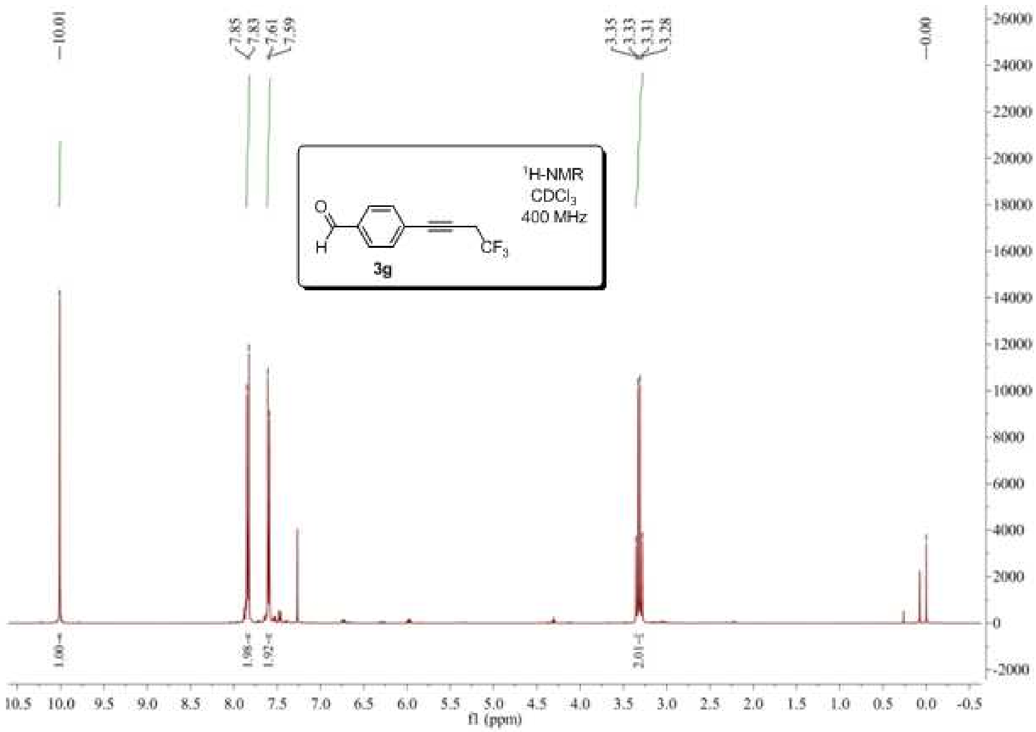
4-(4,4,4-trifluorobut-1-ynyl)benzonitrile (3f)

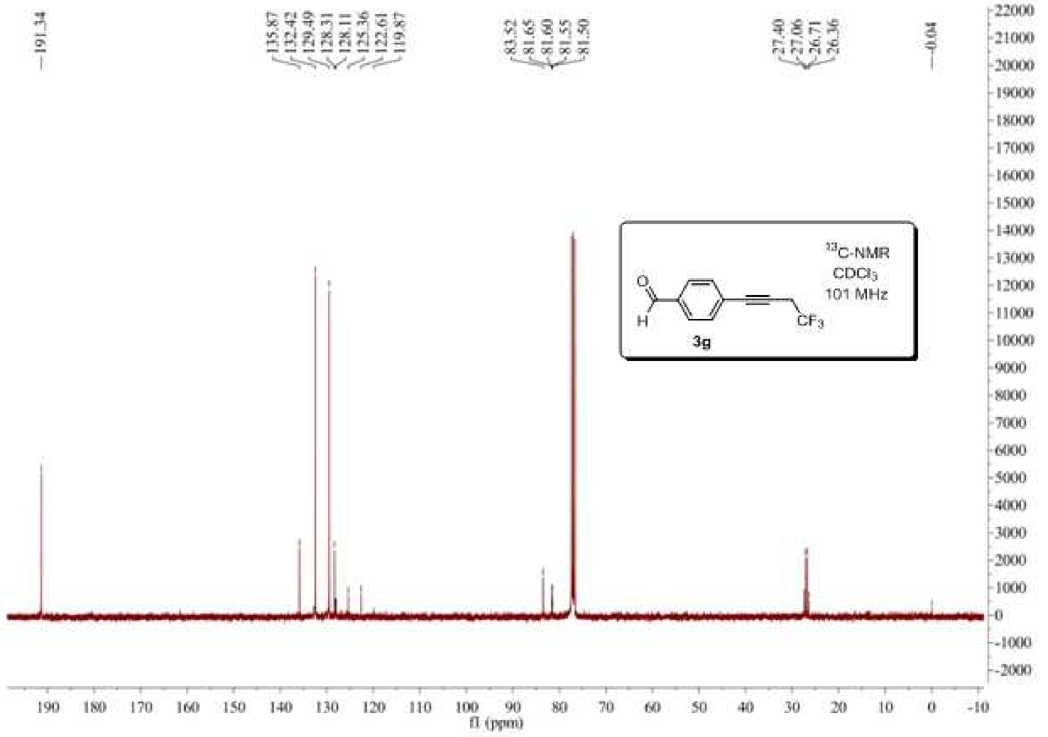


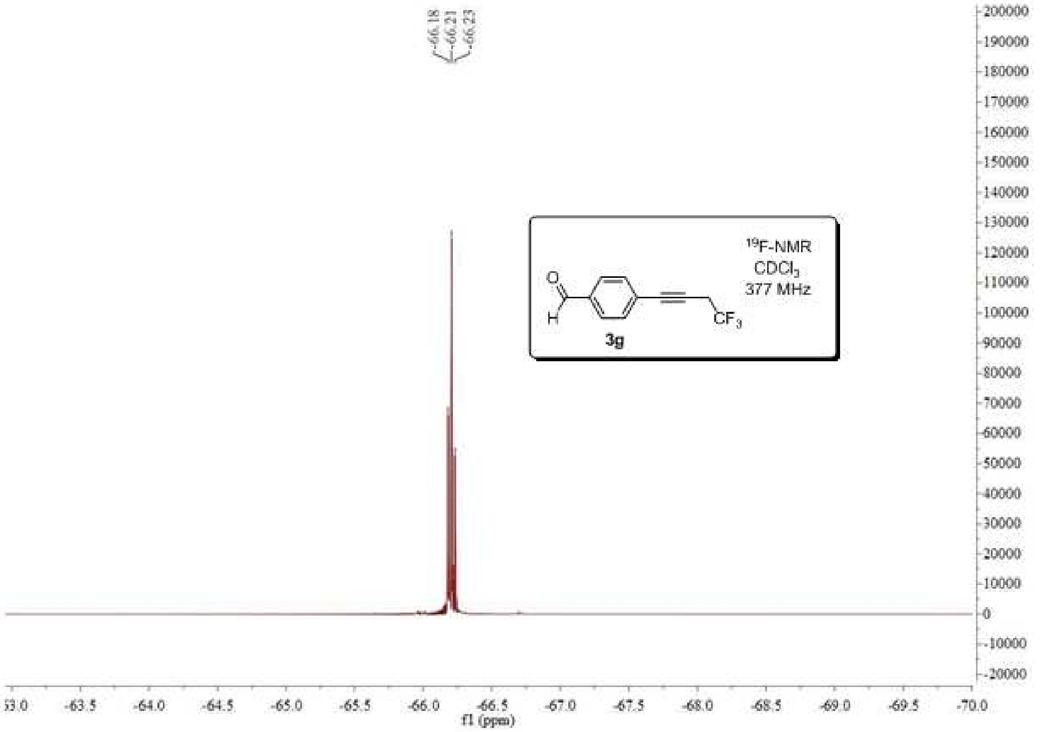

132.43
132.06
128.01
127.01
125.30
122.55
119.77
118.26
112.28
82.84
82.18
82.13
82.08
82.03
27.41
27.06
26.72
26.37
-0.00
¹³C-NMR
CDCl₃
101 MHz
NC
CF₃
3f
f1 (ppm)


-66.12
-66.15
-66.17
¹⁹F-NMR
CDCl₃
377 MHz
NC
CF₃
3f
f1 (ppm)

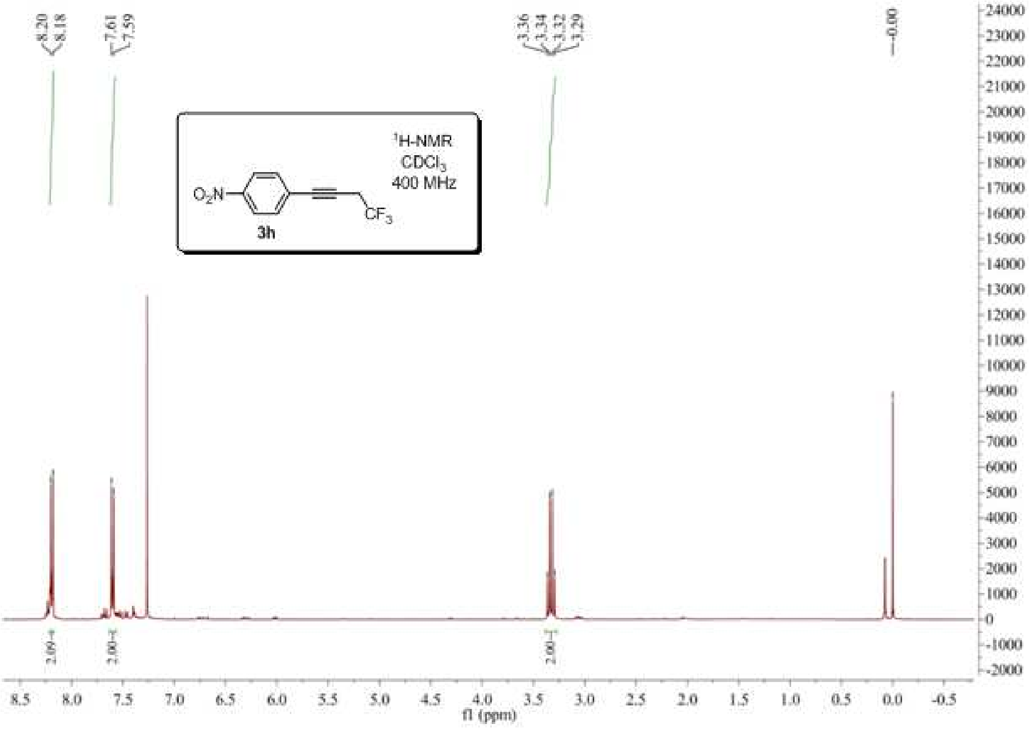
4-(4,4,4-trifluorobut-1-ynyl)benzaldehyde (3g)

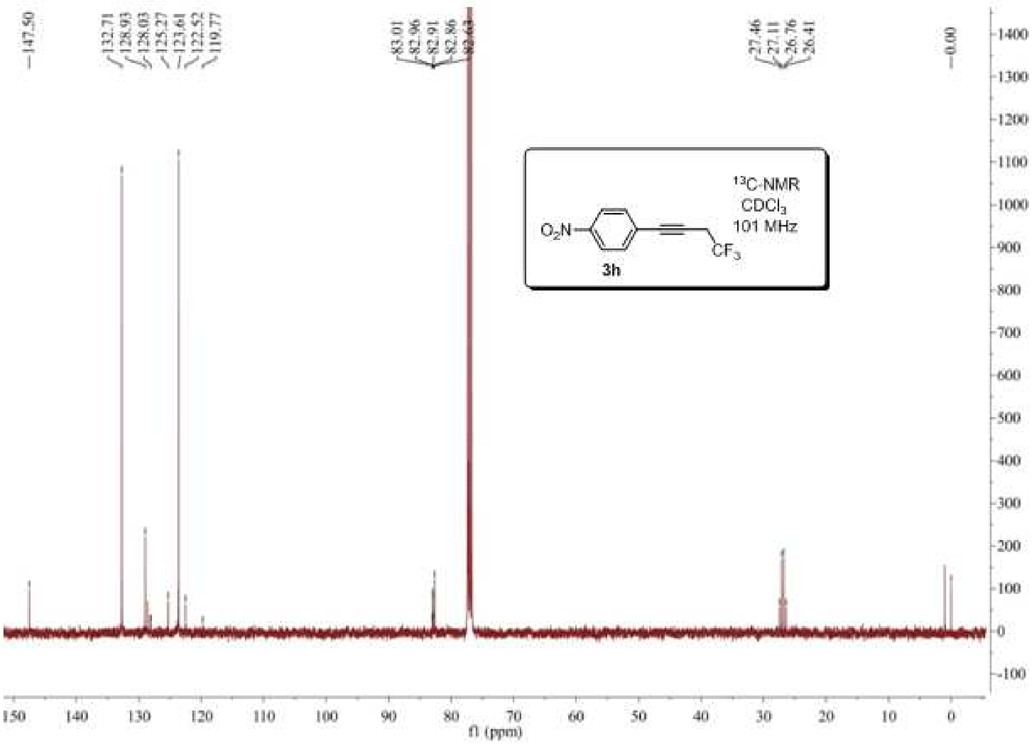




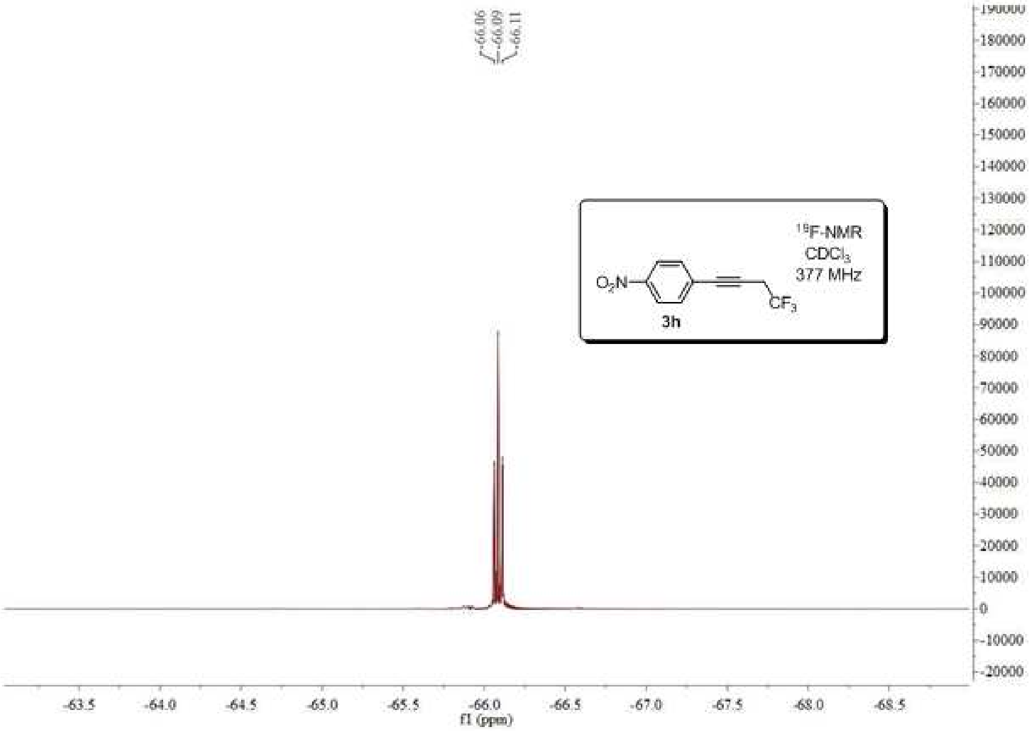


1-nitro-4-(4,4,4-trifluorobut-1-ynyl)benzene (3h)



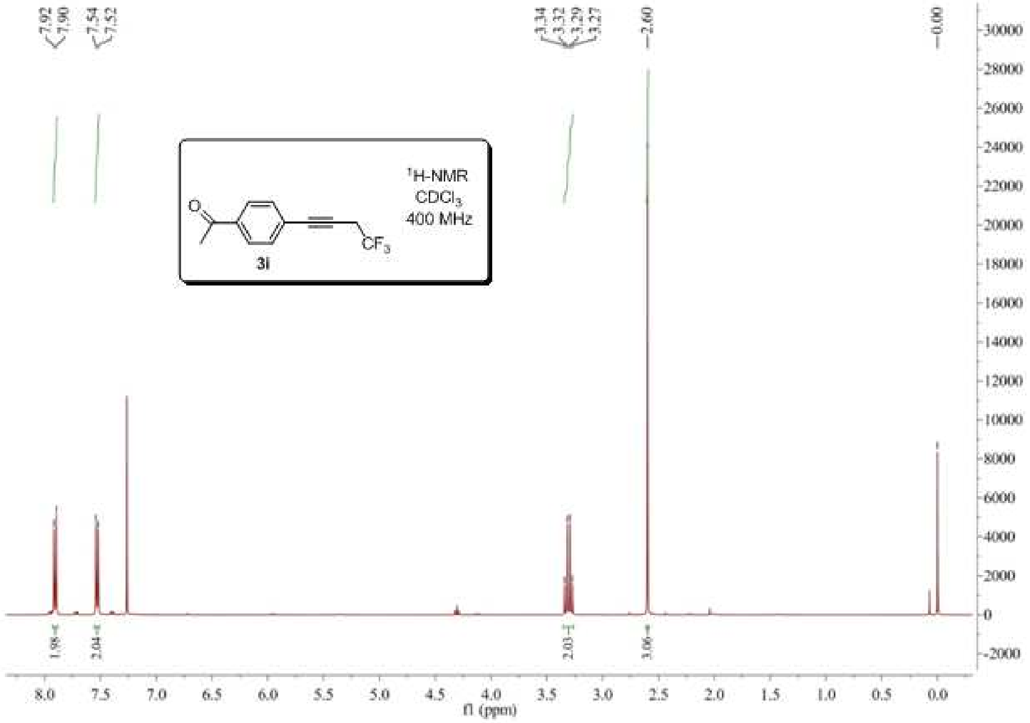


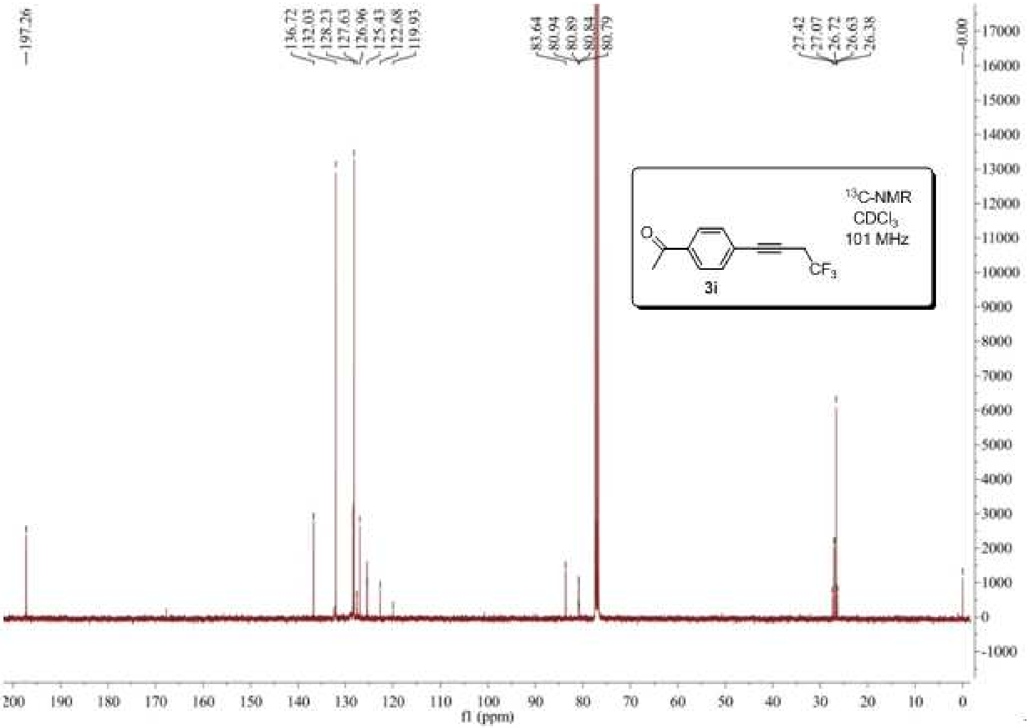
147.50
132.71
128.93
128.03
125.27
123.61
122.52
119.77
83.01
82.96
82.91
82.86
82.63
27.46
27.11
26.76
26.41
0.00
^{13}C-NMR
CDCl$_3$
101 MHz
O$_2$N
CF$_3$
3h
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

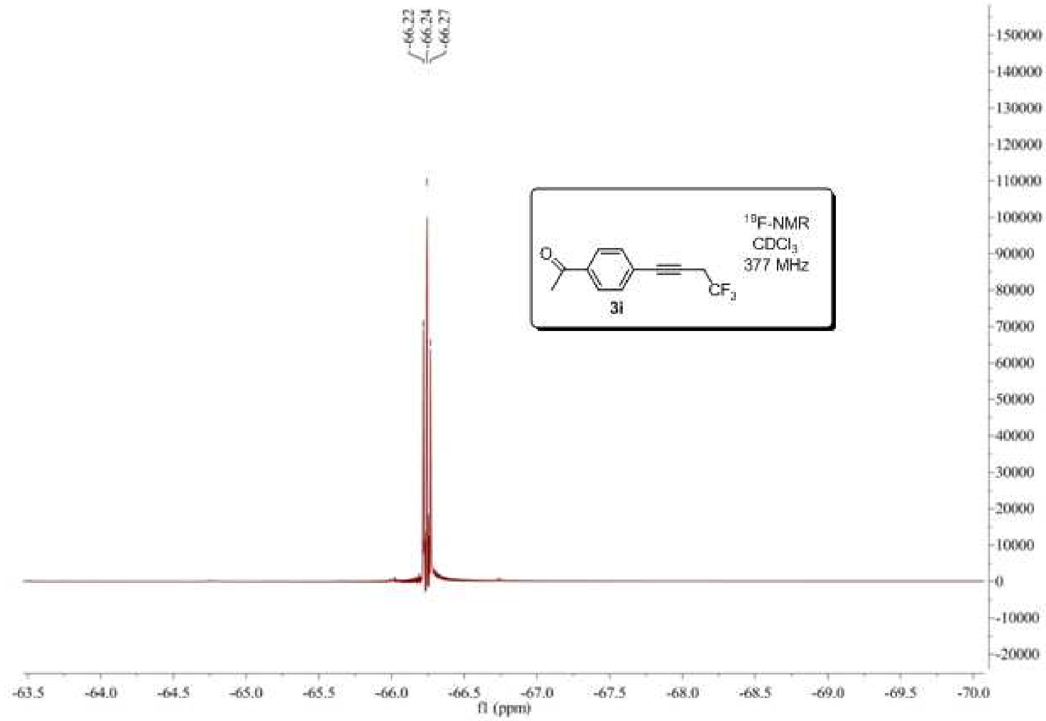


-66.06
-66.09
-66.11
^{19}F-NMR
CDCl$_3$
377 MHz
O$_2$N
CF$_3$
3h
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
-63.5
-64.0
-64.5
-65.0
-65.5
-66.0
-66.5
-67.0
-67.5
-68.0
-68.5
f1 (ppm)

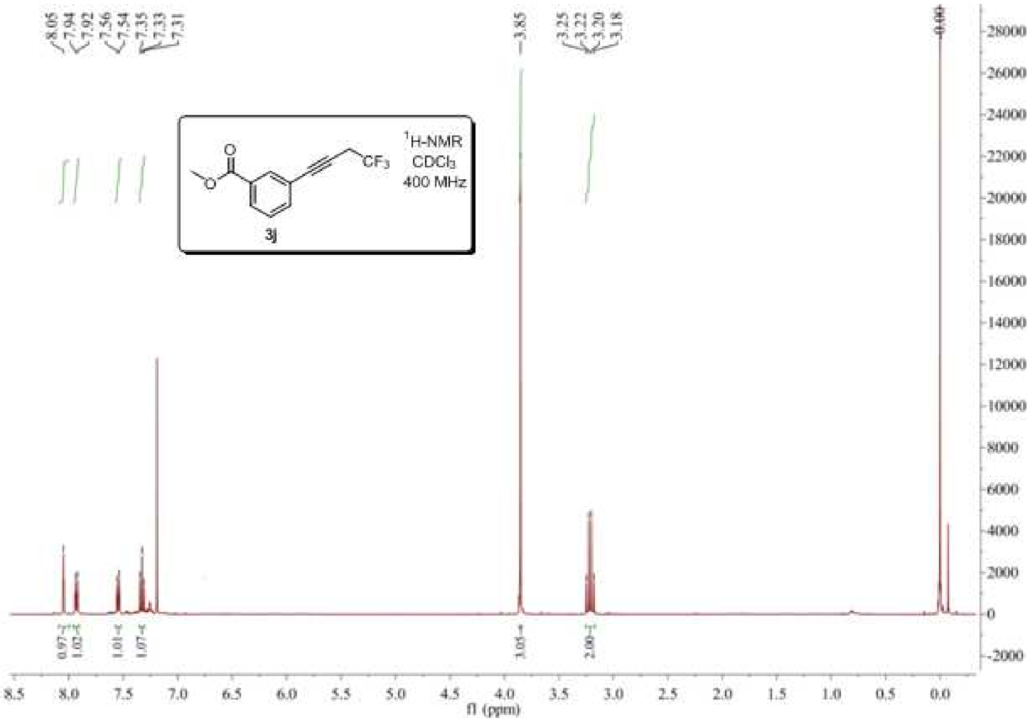
1-(4-(4,4,4-trifluorobut-1-ynyl)phenyl)ethanone (3i)

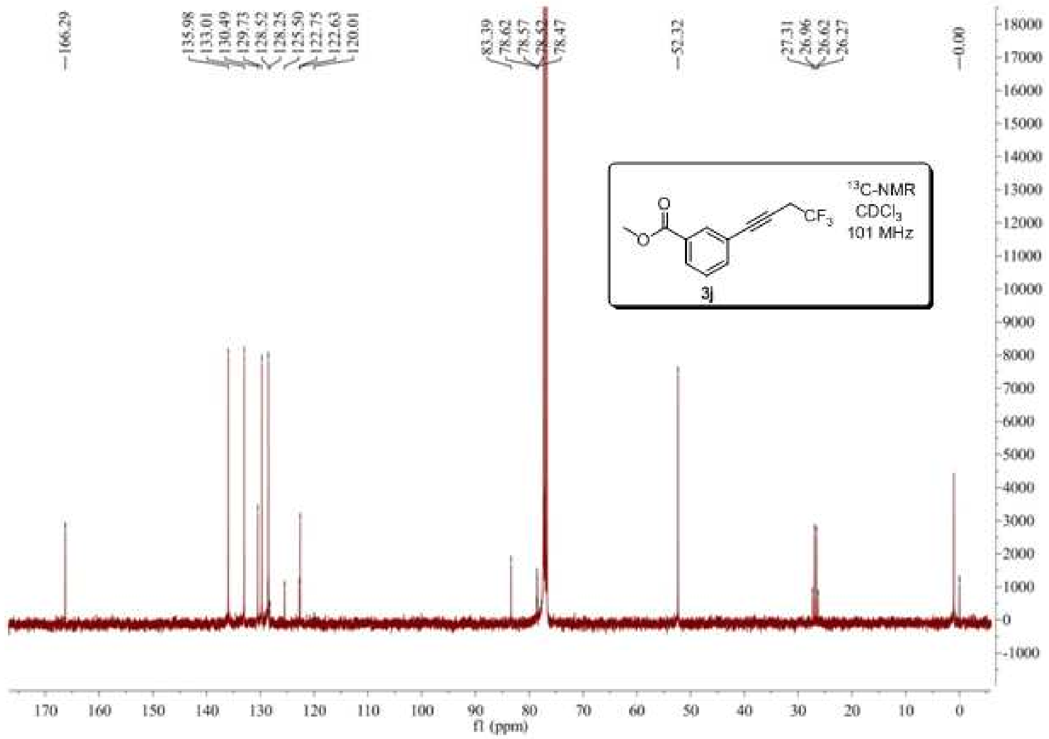




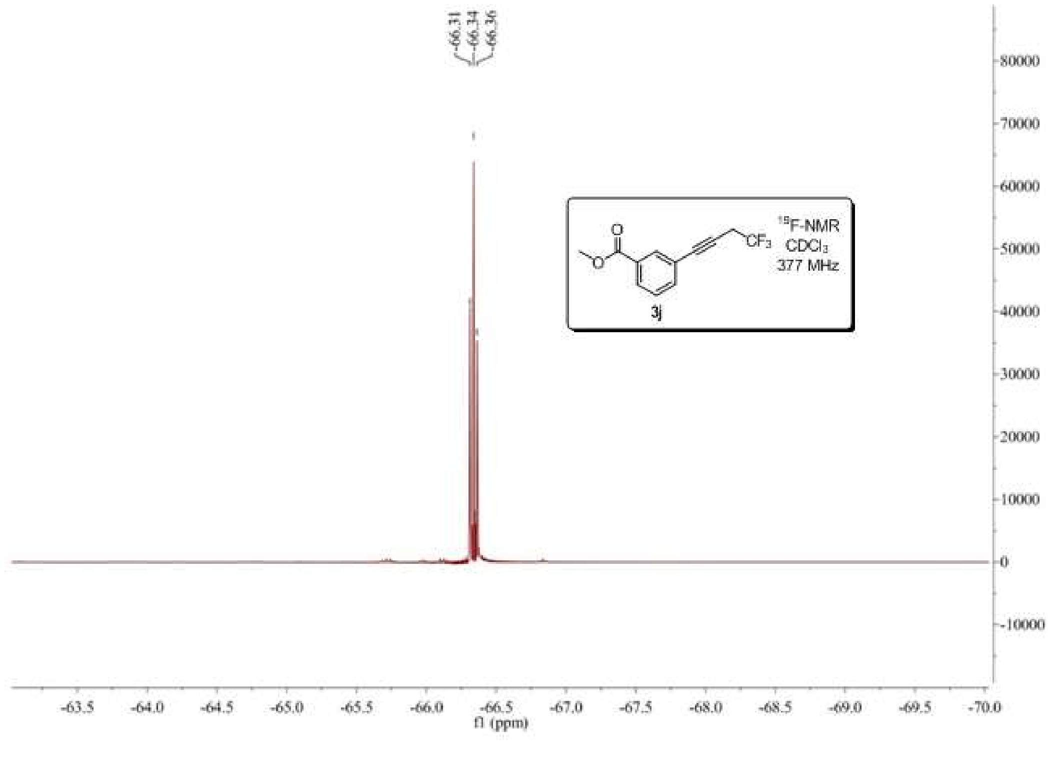


methyl 3-(4,4,4-trifluorobut-1-ynyl)benzoate (3j)



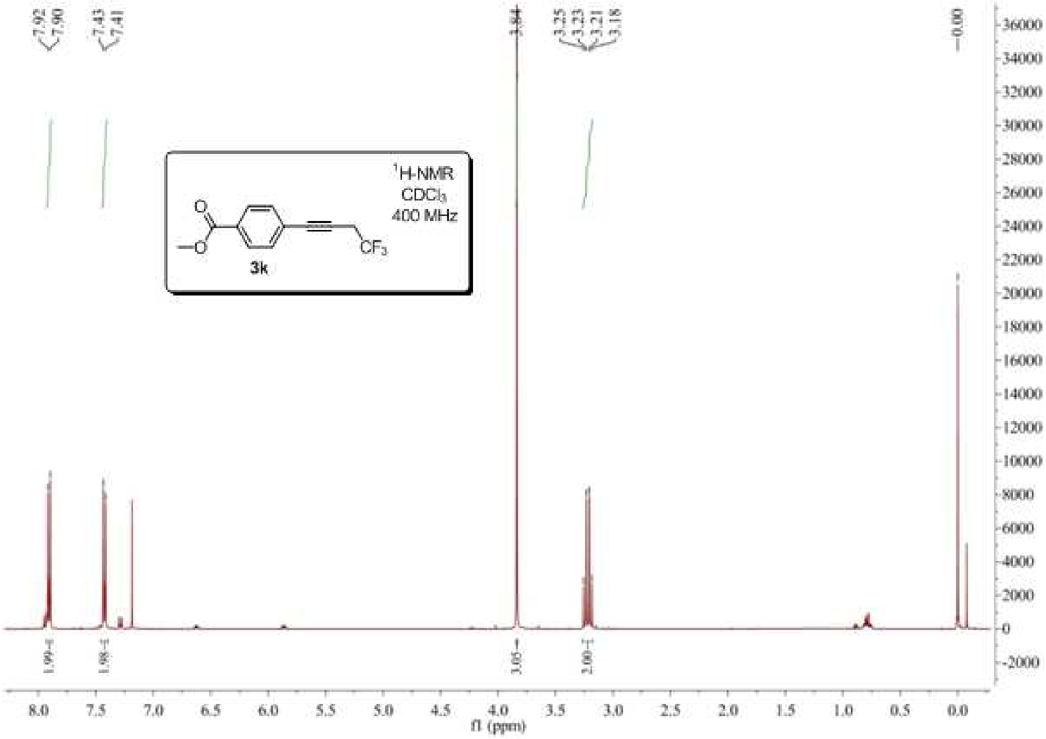


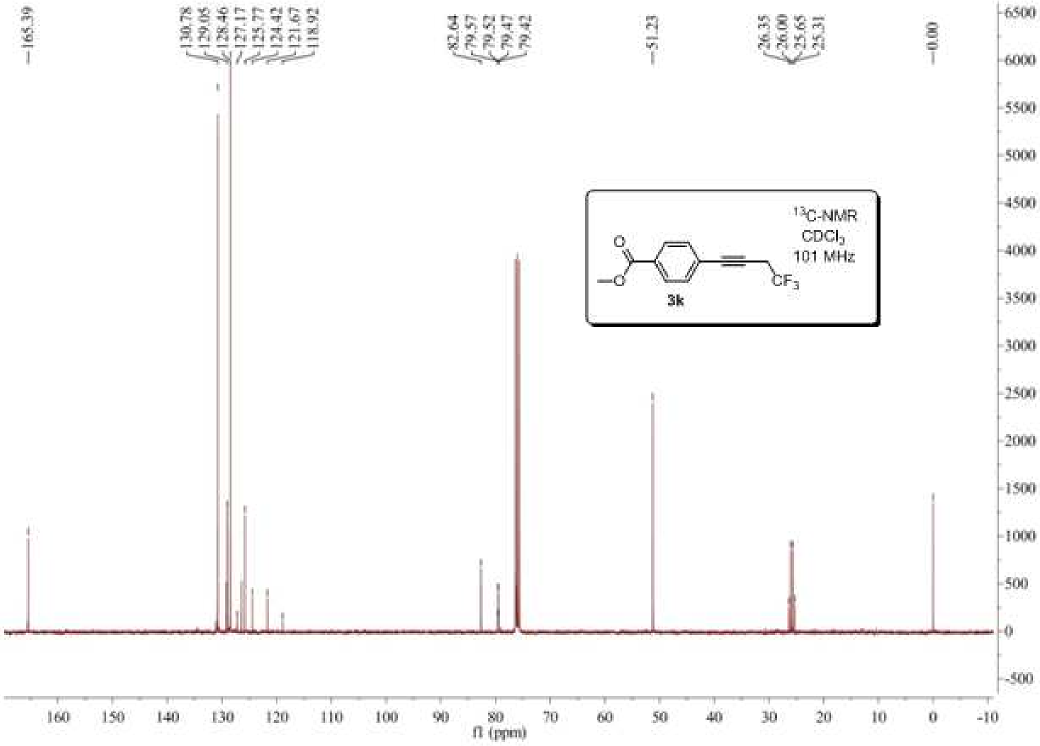
166.29
135.98
133.01
130.49
129.73
128.52
128.25
125.50
122.75
122.63
120.01
83.39
78.62
78.57
78.52
78.47
52.32
27.31
26.96
26.62
26.27
0.00
^{13}C-NMR
CDCl$_3$
101 MHz
CF$_3$
3j
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
18000 17000 16000 15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000

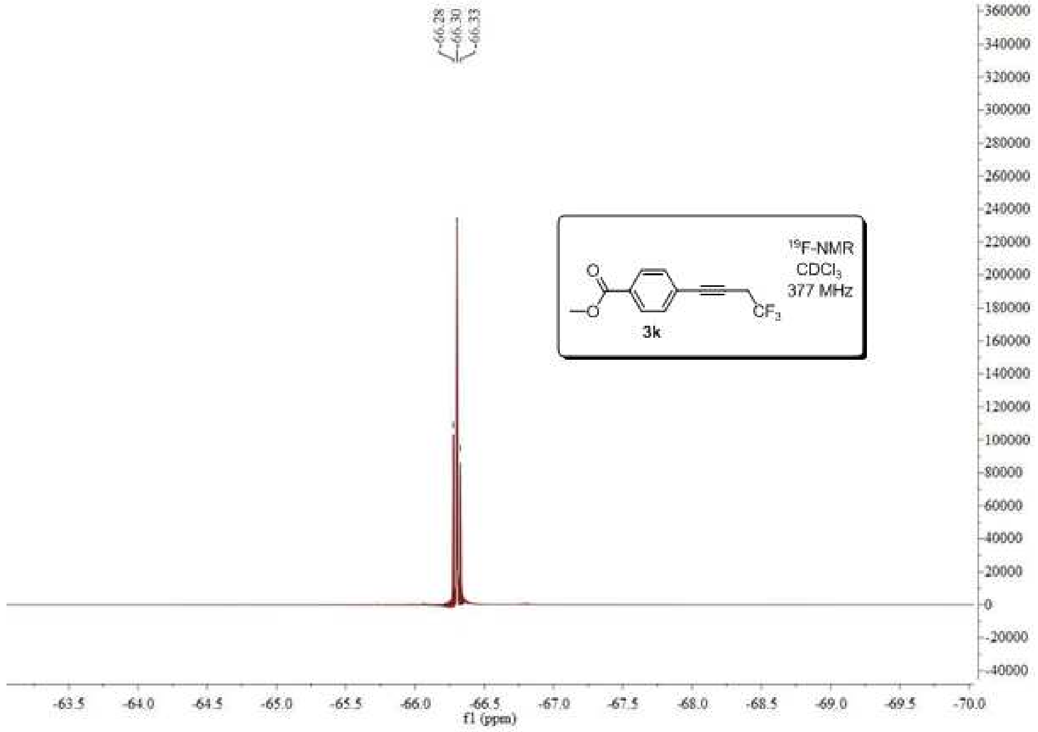


-66.31
-66.34
-66.36
^{19}F-NMR
CDCl$_3$
377 MHz
CF$_3$
3j
f1 (ppm)
-63.5 -64.0 -64.5 -65.0 -65.5 -66.0 -66.5 -67.0 -67.5 -68.0 -68.5 -69.0 -69.5 -70.0
80000 70000 60000 50000 40000 30000 20000 10000 0 -10000

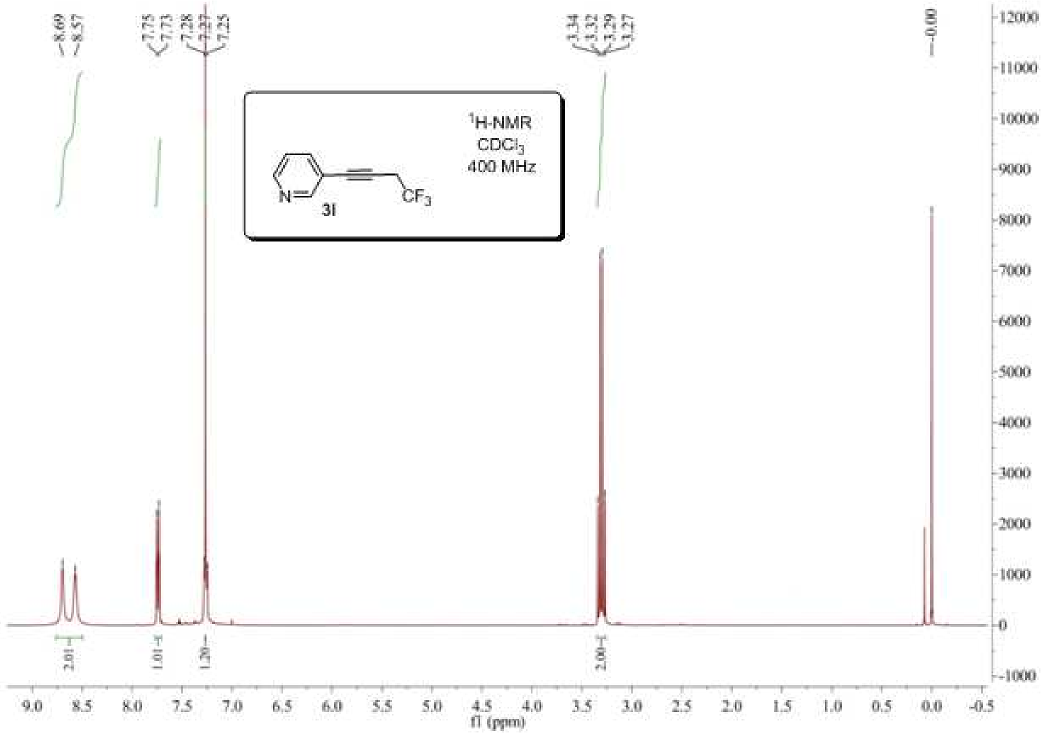
methyl 4-(4,4,4-trifluorobut-1-ynyl)benzoate (3k)

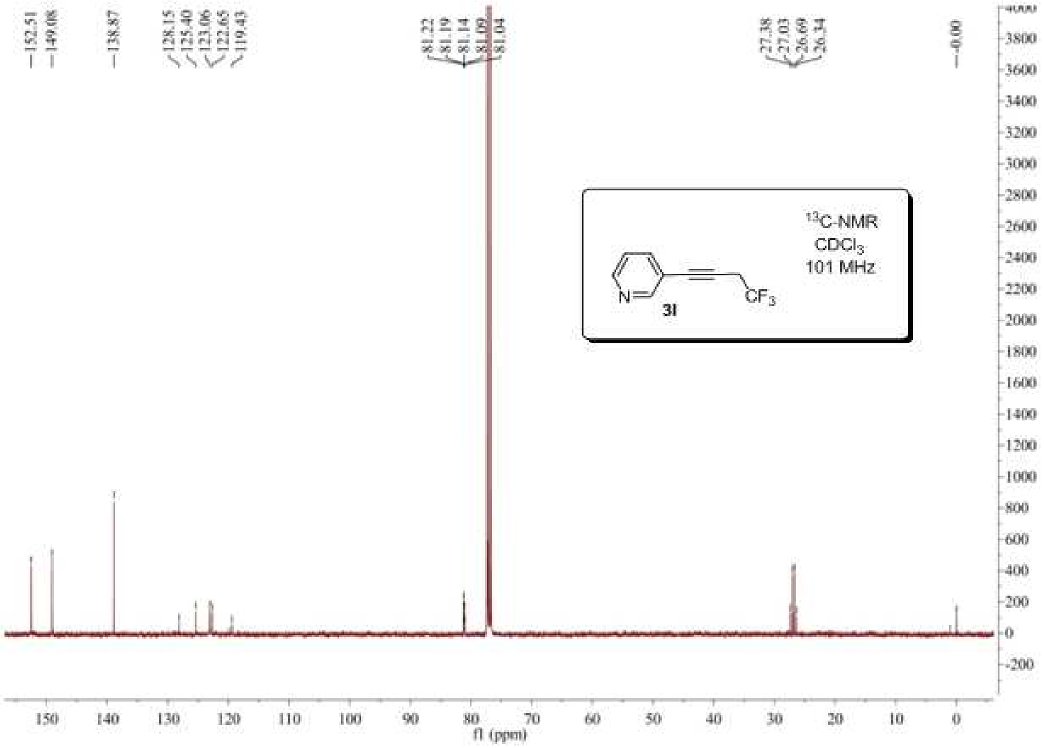


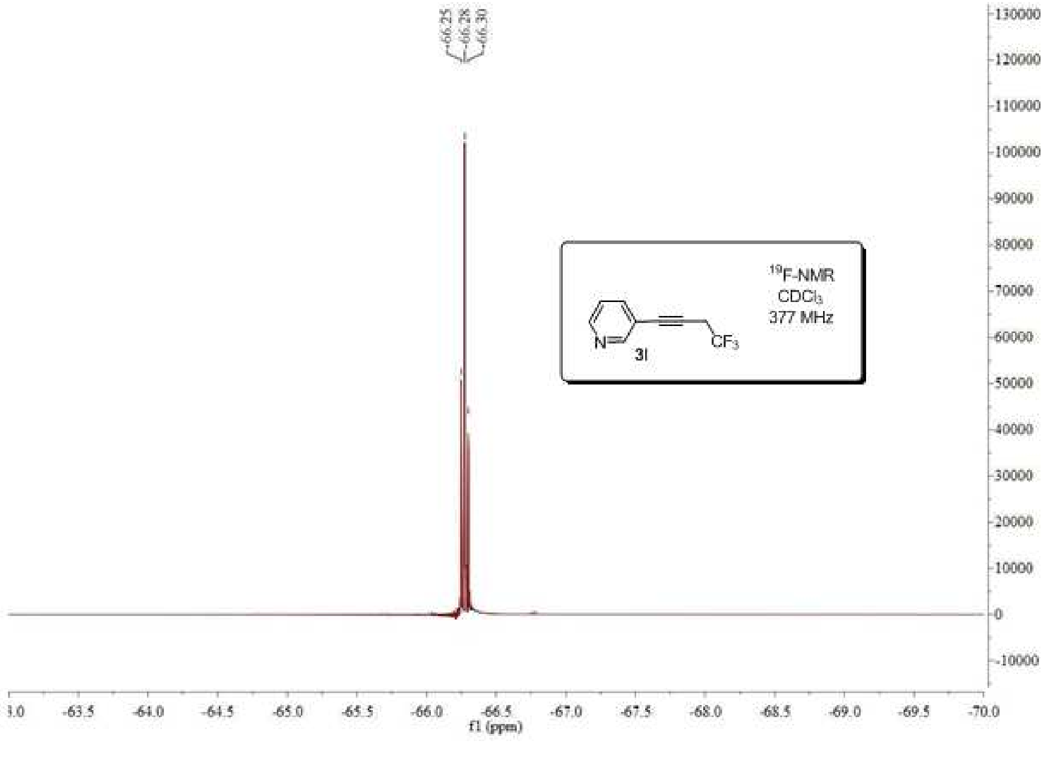




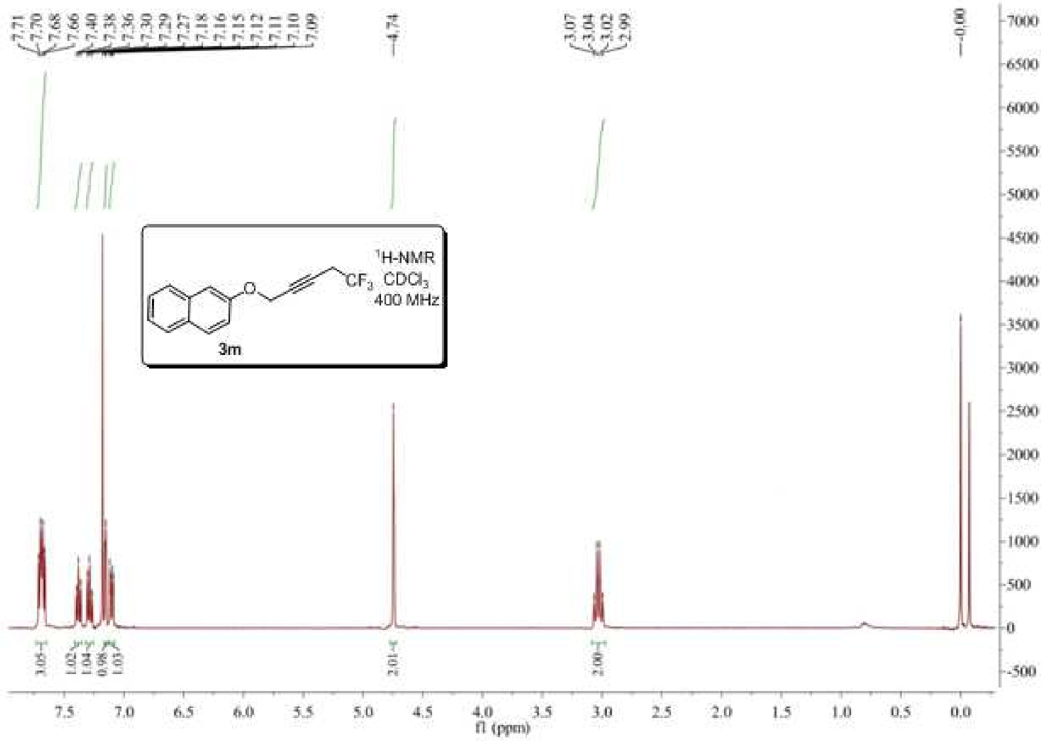
3-(4,4,4-trifluorobut-1-ynyl)pyridine (3l)

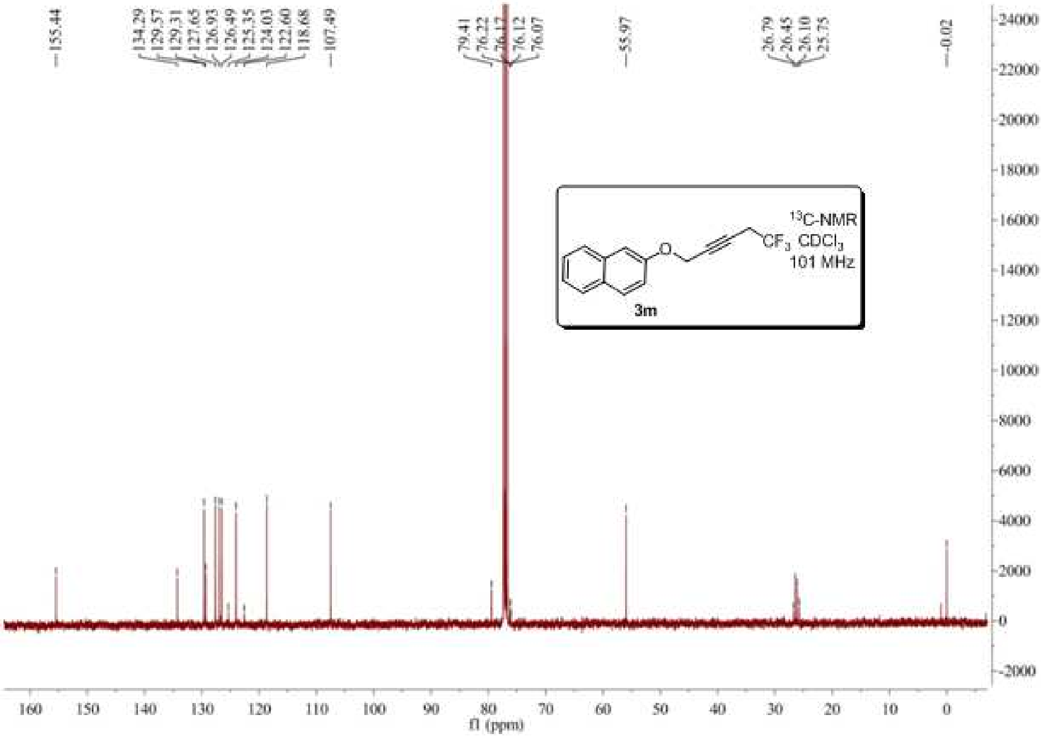


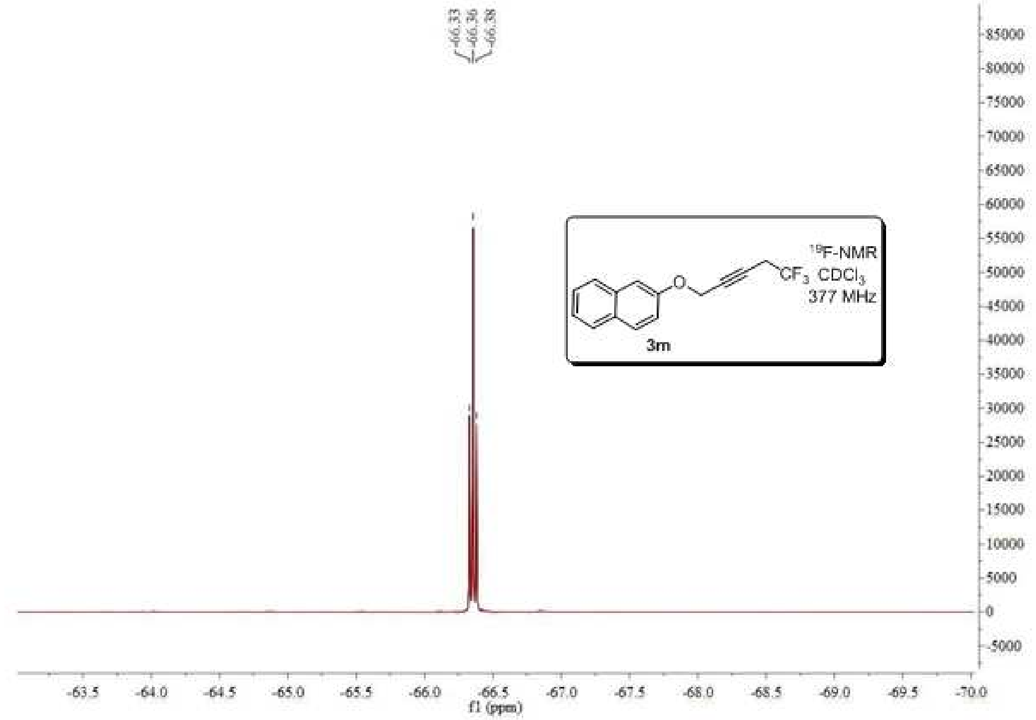

152.51
149.08
138.87
128.15
125.40
123.06
122.65
119.43
81.22
81.19
81.14
81.09
81.04
27.38
27.03
26.69
26.34
0.00
^{13}C-NMR
CDCl$_3$
101 MHz
N
CF$_3$
3l
f1 (ppm)
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200


-66.25
-66.28
-66.30
^{19}F-NMR
CDCl$_3$
377 MHz
N
CF$_3$
3l
f1 (ppm)
3.0 -63.5 -64.0 -64.5 -65.0 -65.5 -66.0 -66.5 -67.0 -67.5 -68.0 -68.5 -69.0 -69.5 -70.0
130000 120000 110000 100000 90000 80000 70000 60000 50000 40000 30000 20000 10000 0 -10000

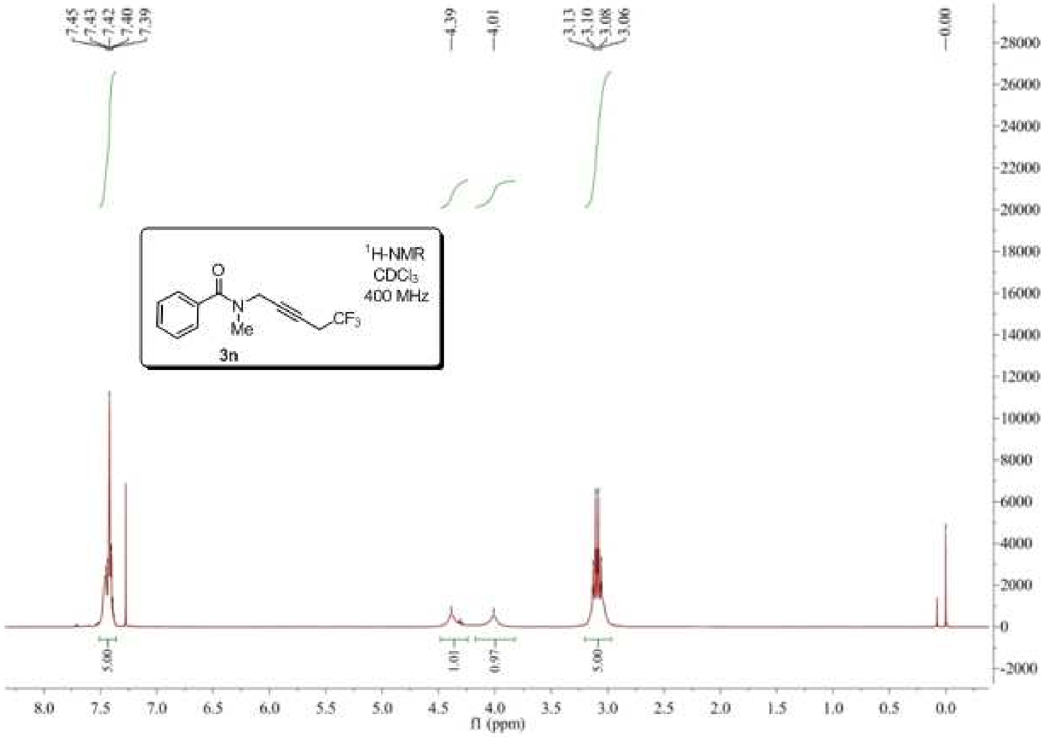
2-(5,5,5-trifluoropent-2-ynyloxy)naphthalene (3m)

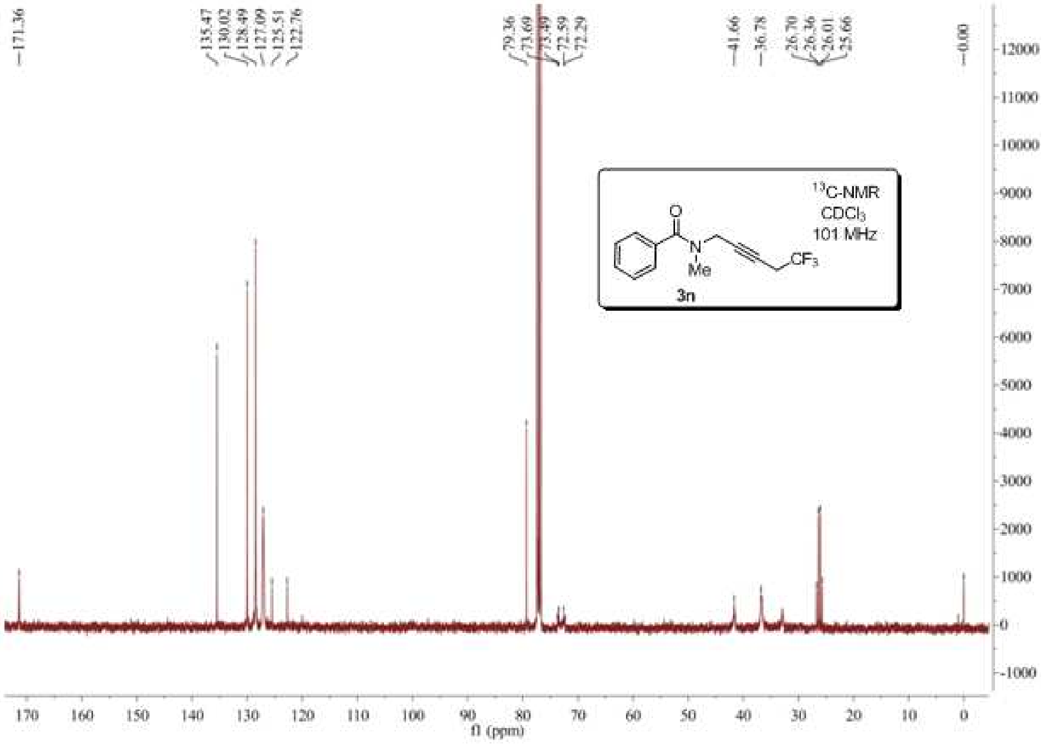


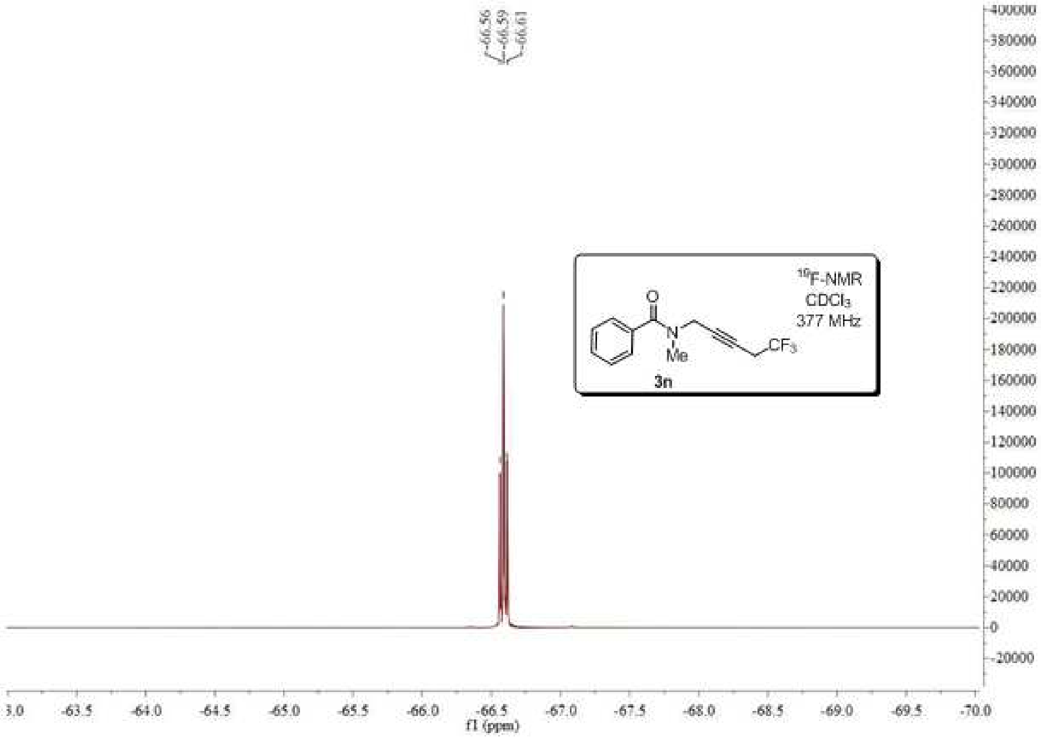




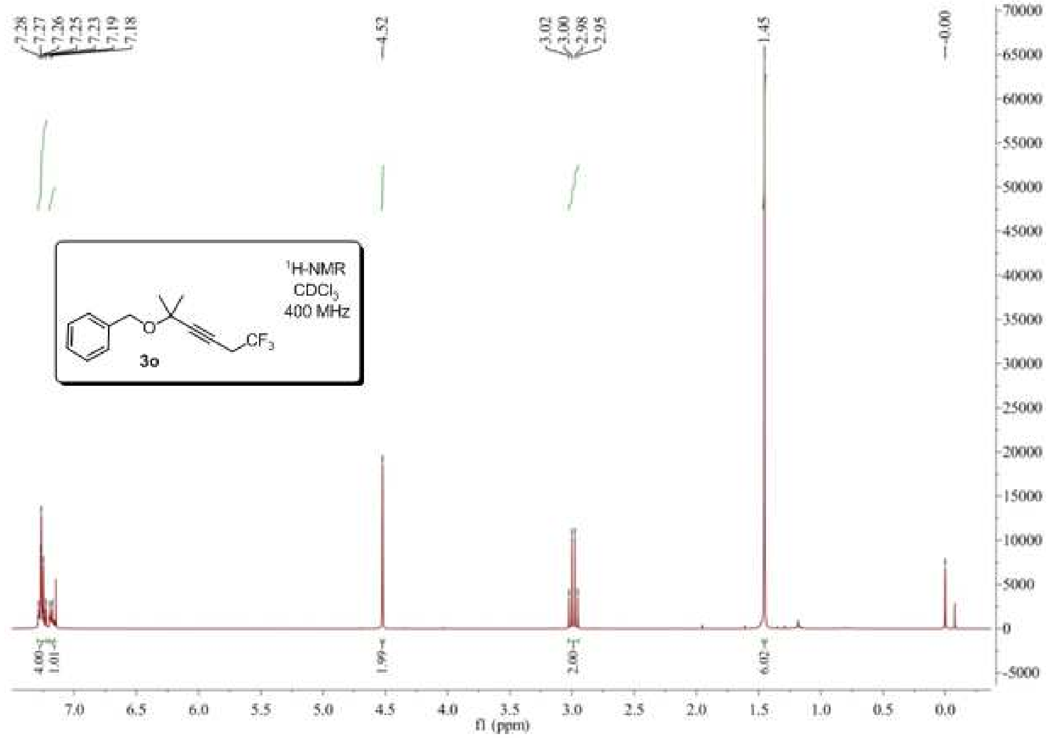
N-methyl-N-(5,5,5-trifluoropent-2-ynyl)benzamide(3n)

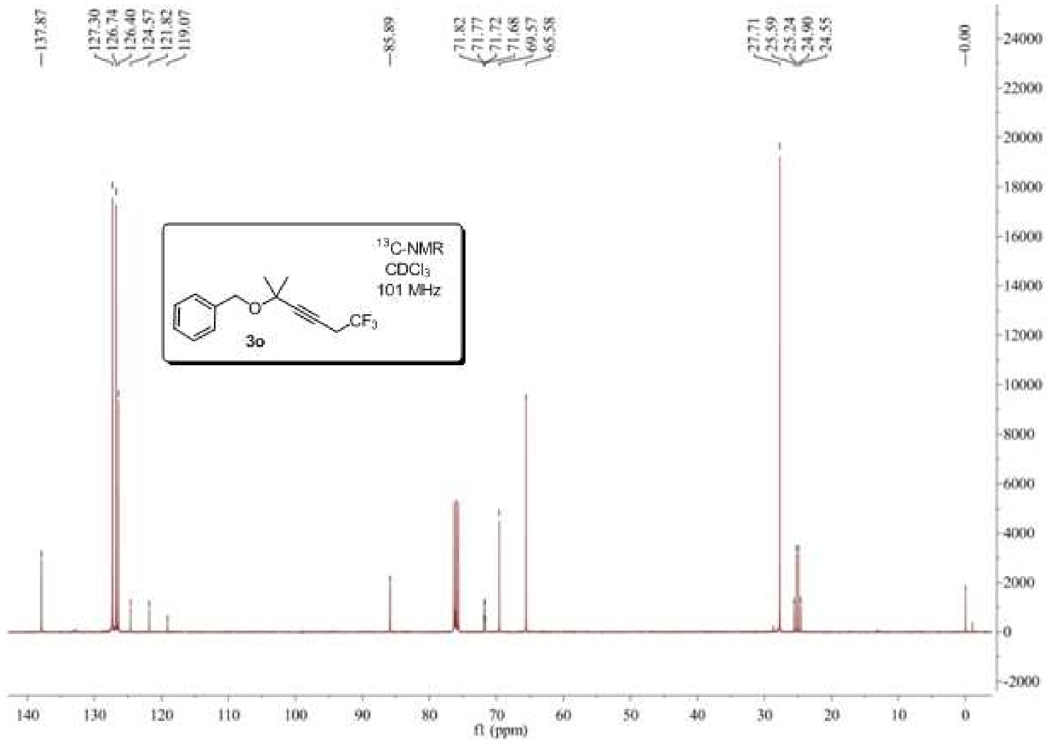


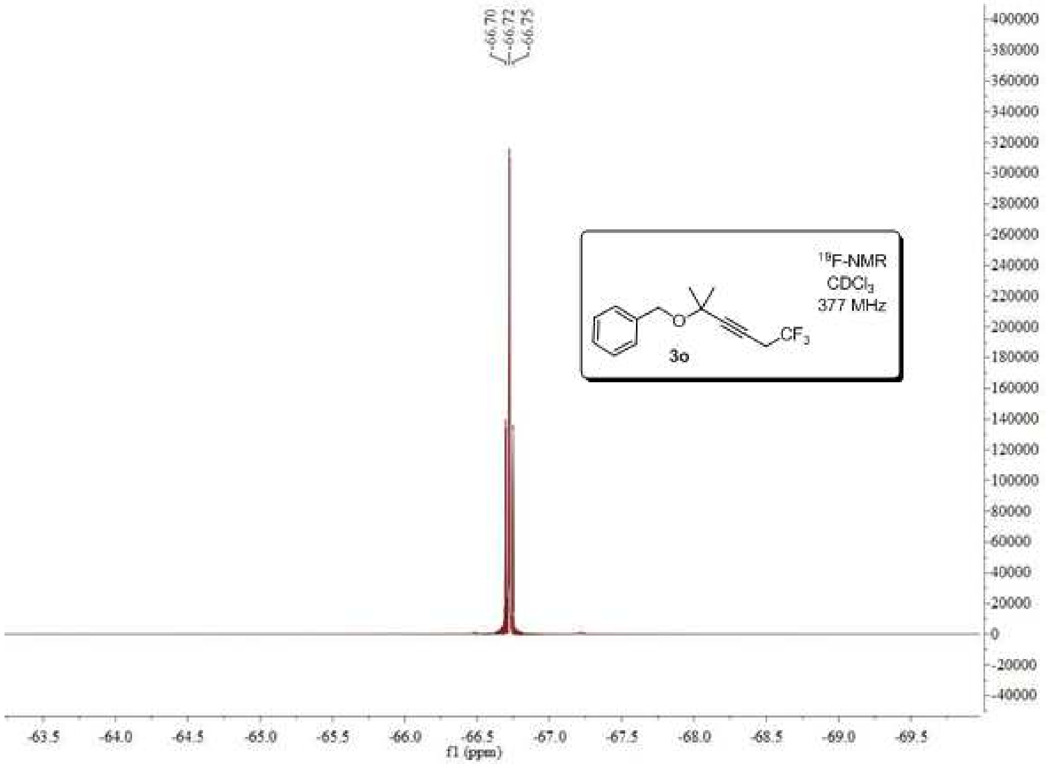

171.36
135.47
130.02
128.49
127.09
125.51
122.76
79.36
73.69
73.49
72.59
72.29
41.66
36.78
26.70
26.36
26.01
25.66
0.00
^{13}C-NMR
CDCl$_3$
101 MHz
O
N
Me
CF$_3$
3n
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-66.56
-66.59
-66.61
^{19}F-NMR
CDCl$_3$
377 MHz
O
N
Me
CF$_3$
3n
400000
380000
360000
340000
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
3.0
-63.5
-64.0
-64.5
-65.0
-65.5
-66.0
-66.5
-67.0
-67.5
-68.0
-68.5
-69.0
-69.5
-70.0
f1 (ppm)

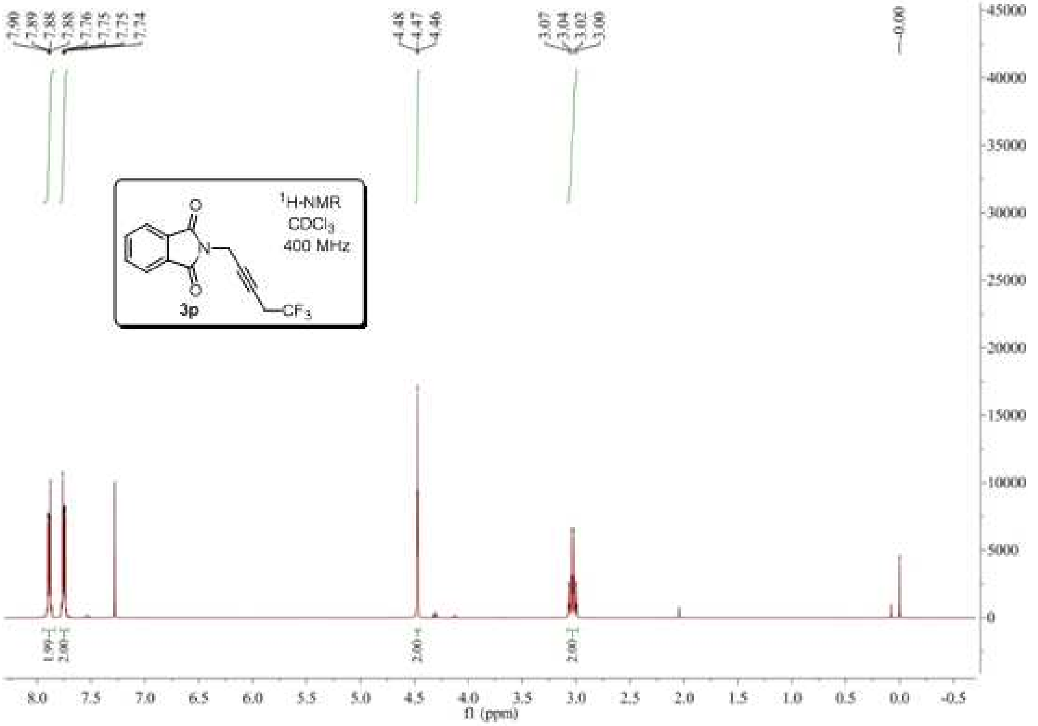
((6,6,6-trifluoro-2-methylhex-3-yn-2-yloxy)methyl)benzene (3o)

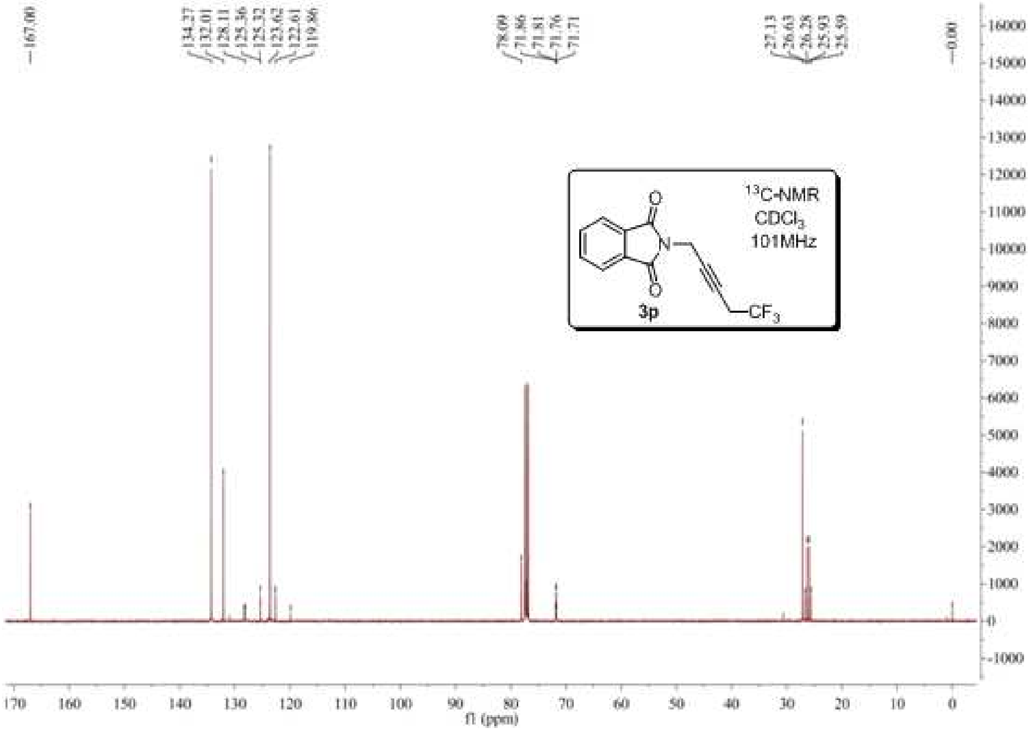


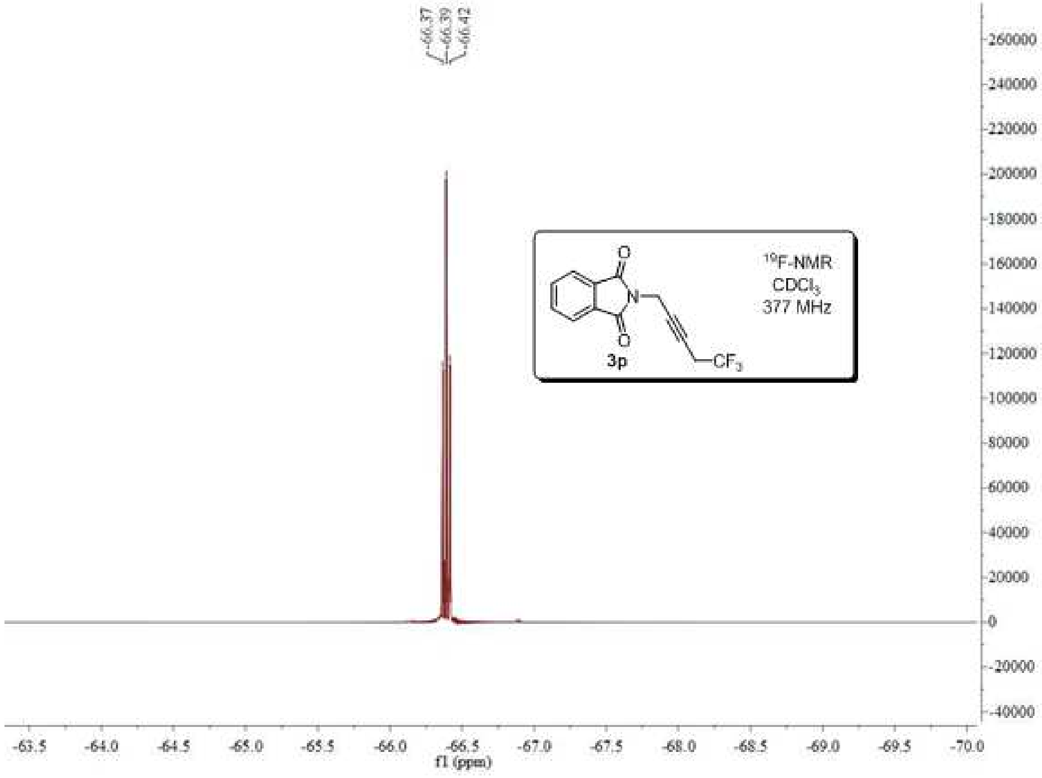




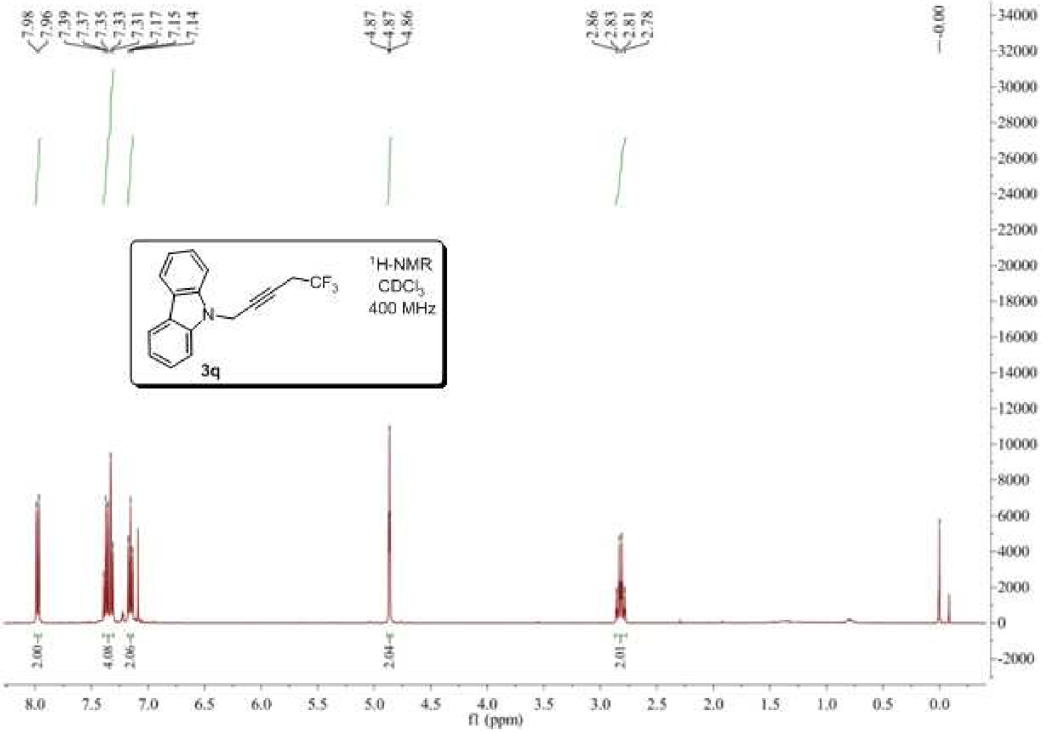
2-(5,5,5-trifluoropent-2-ynyl)isoindoline-1,3-dione(3p)

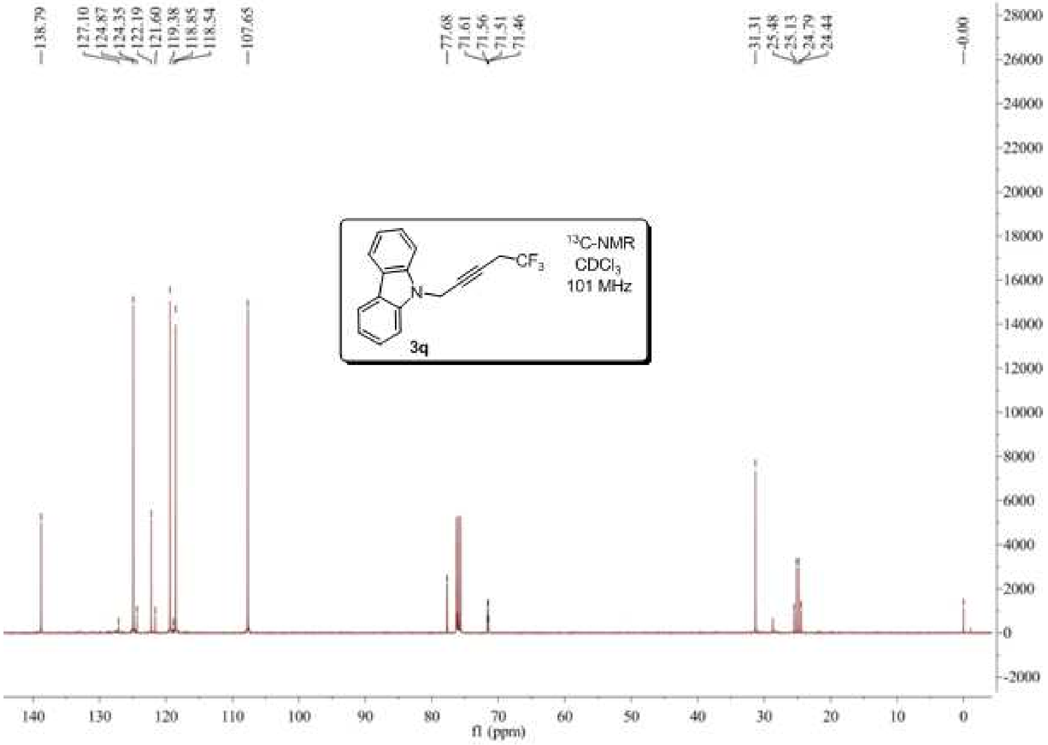


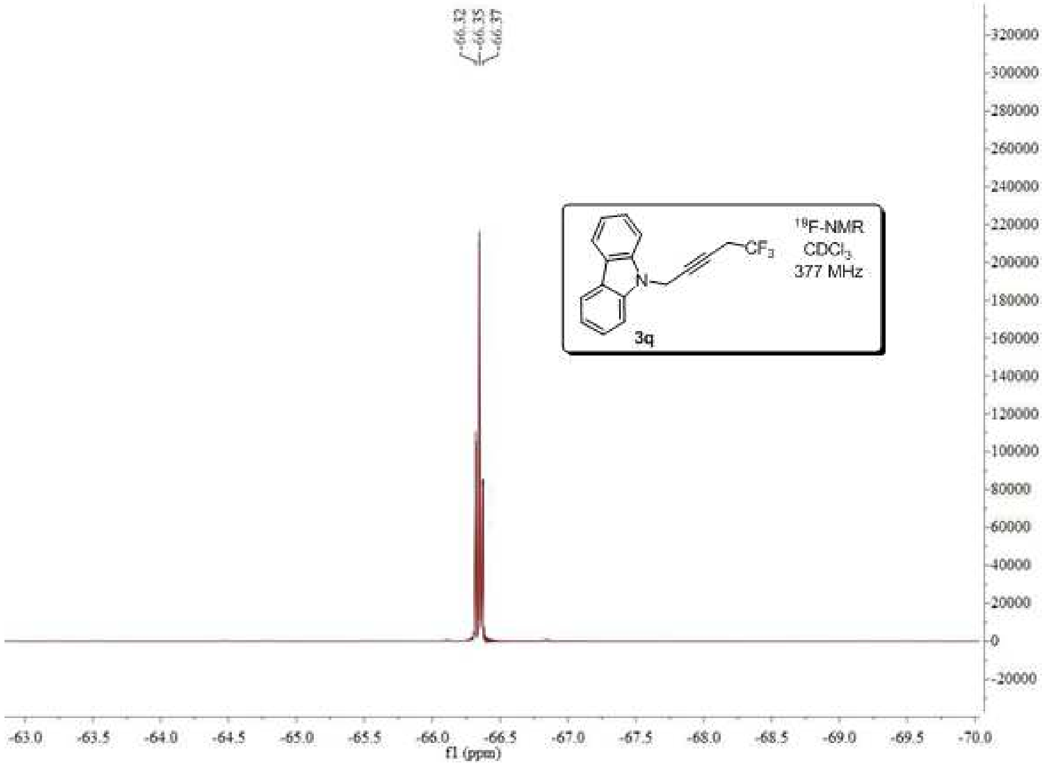




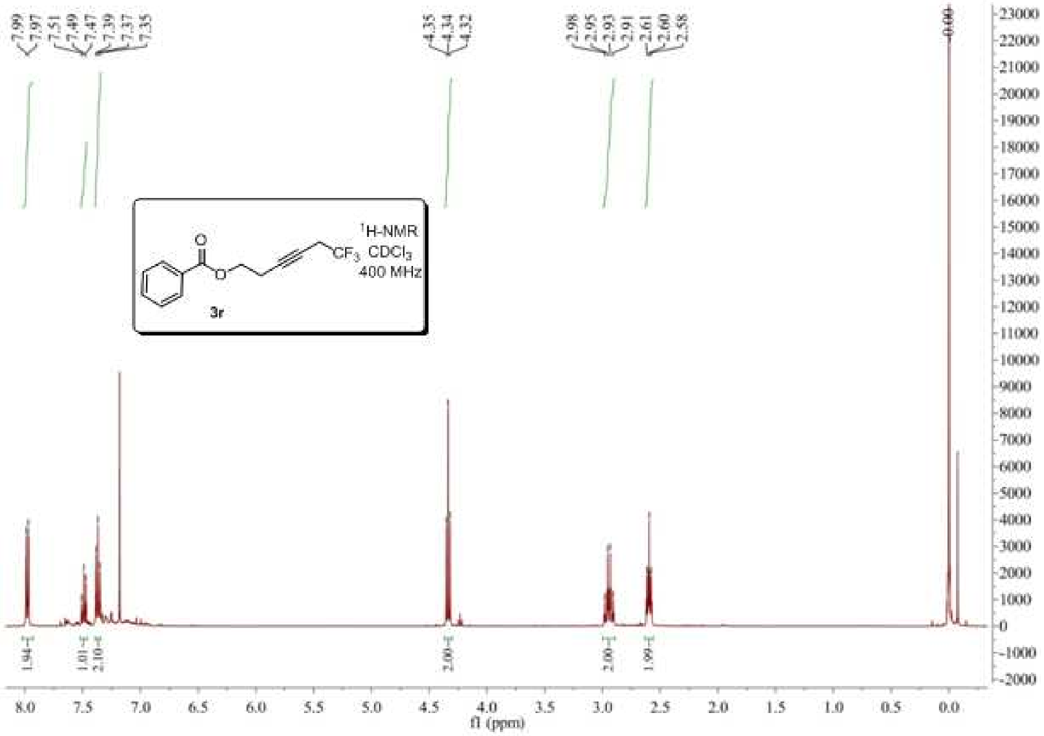
9-(5,5,5-trifluoropent-2-ynyl)-9H-carbazole(3q)

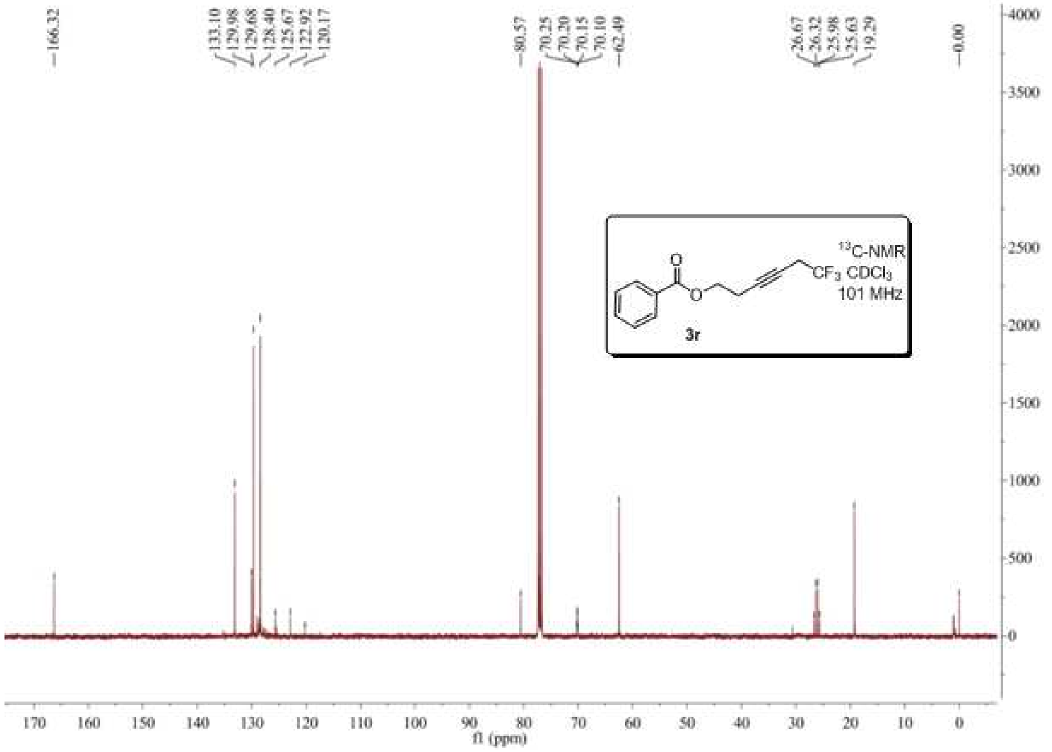

7.98
7.96
7.39
7.37
7.35
7.33
7.31
7.17
7.15
7.14
4.87
4.87
4.86
2.86
2.83
2.81
2.78
0.00
CF3
N
3q
1H-NMR
CDCl3
400 MHz
2.00
4.08
2.06
2.04
2.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000

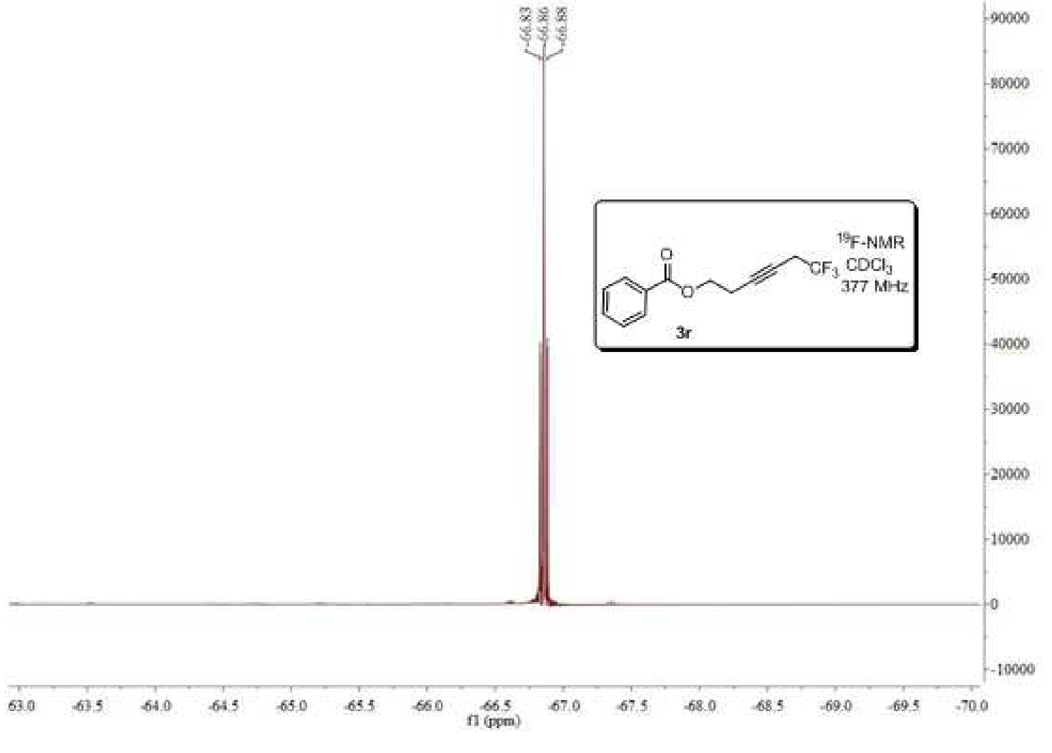

138.79
127.10
124.87
124.35
122.19
121.60
119.38
118.85
118.54
107.65
77.68
71.61
71.56
71.51
71.46
31.31
25.48
25.13
24.79
24.44
0.00
CF3
N
3q
13C-NMR
CDCl3
101 MHz
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000



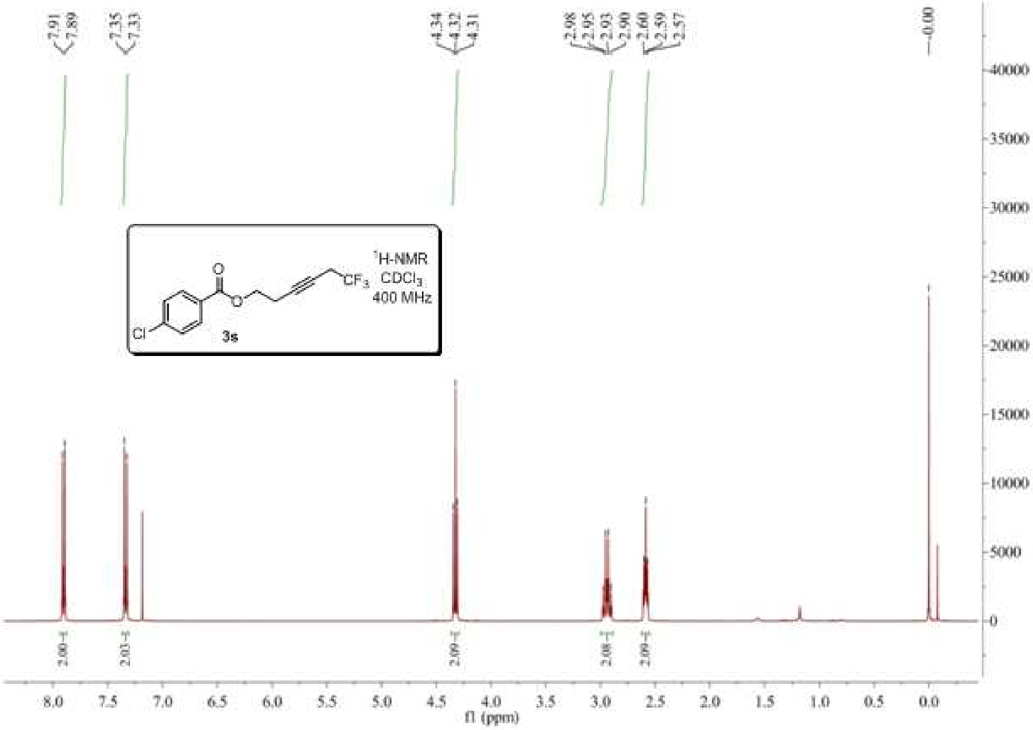
6,6,6-trifluorohex-3-ynyl benzoate (3r)

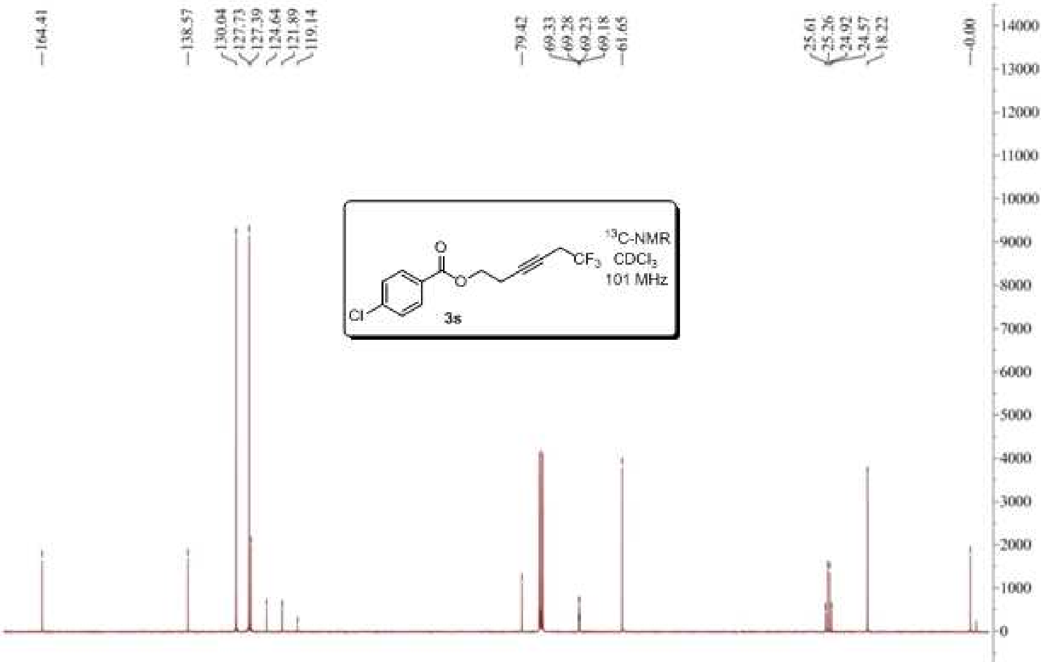


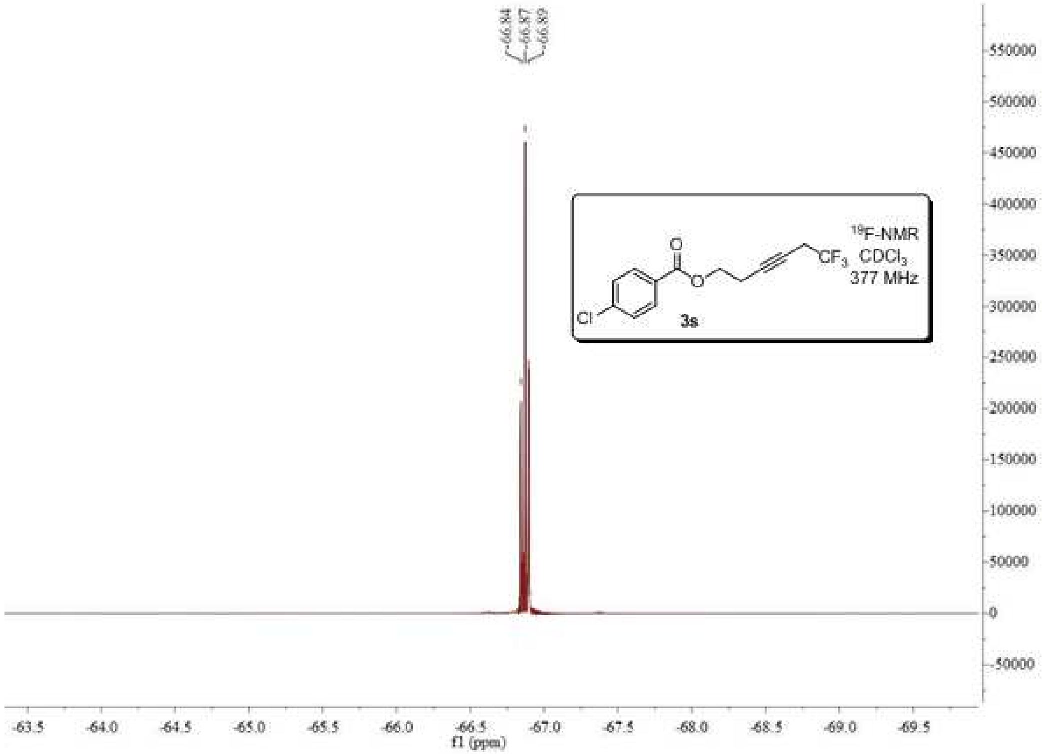




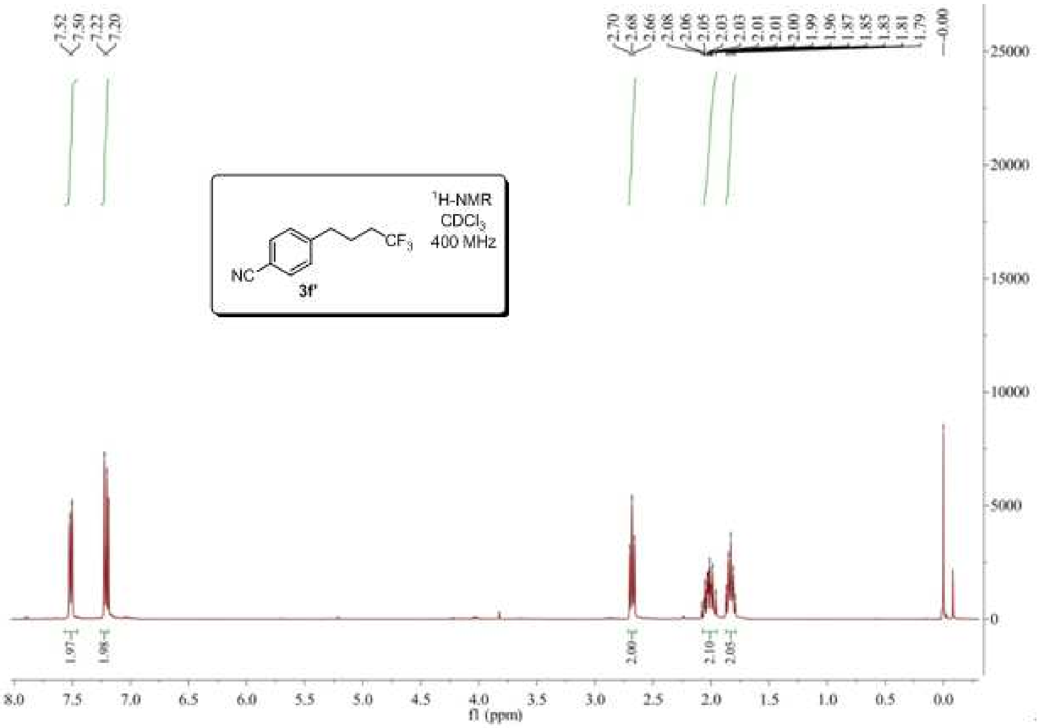
6,6,6-trifluorohex-3-ynyl 4-chlorobenzoate (3s)

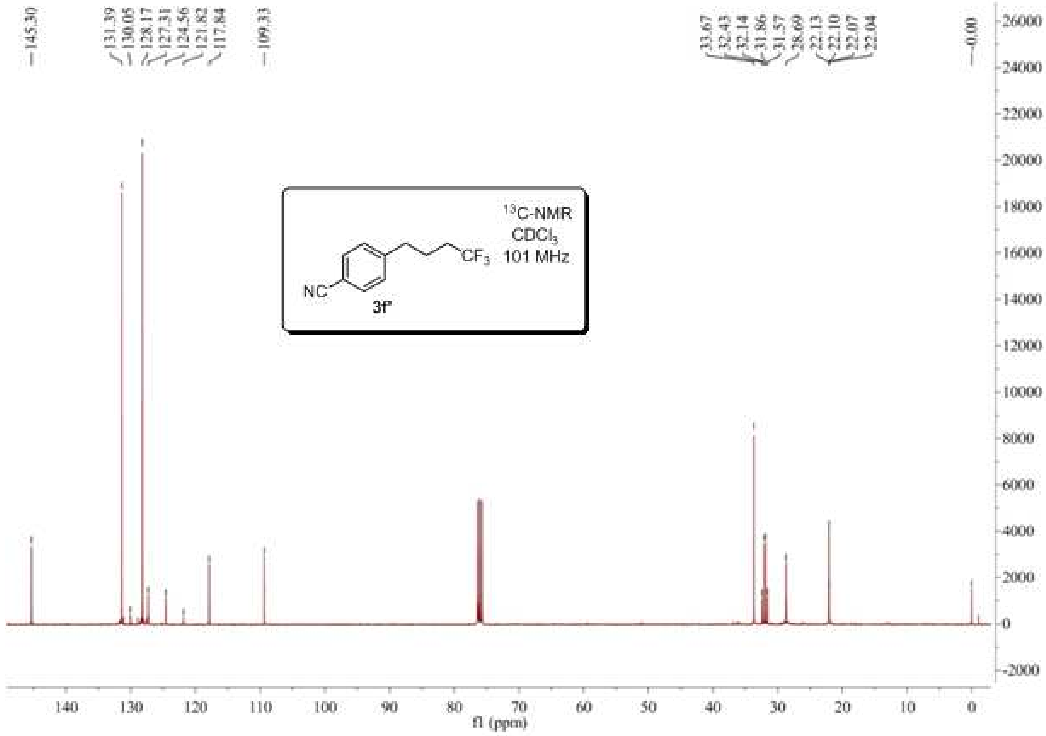

7.91
7.89
7.35
7.33
4.34
4.32
4.31
2.98
2.95
2.93
2.90
2.60
2.59
2.57
-0.00
Cl
O
O
CF3
3s
1H-NMR
CDCl3
400 MHz
2.00
2.03
2.09
2.08
2.09
40000
35000
30000
25000
20000
15000
10000
5000
0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

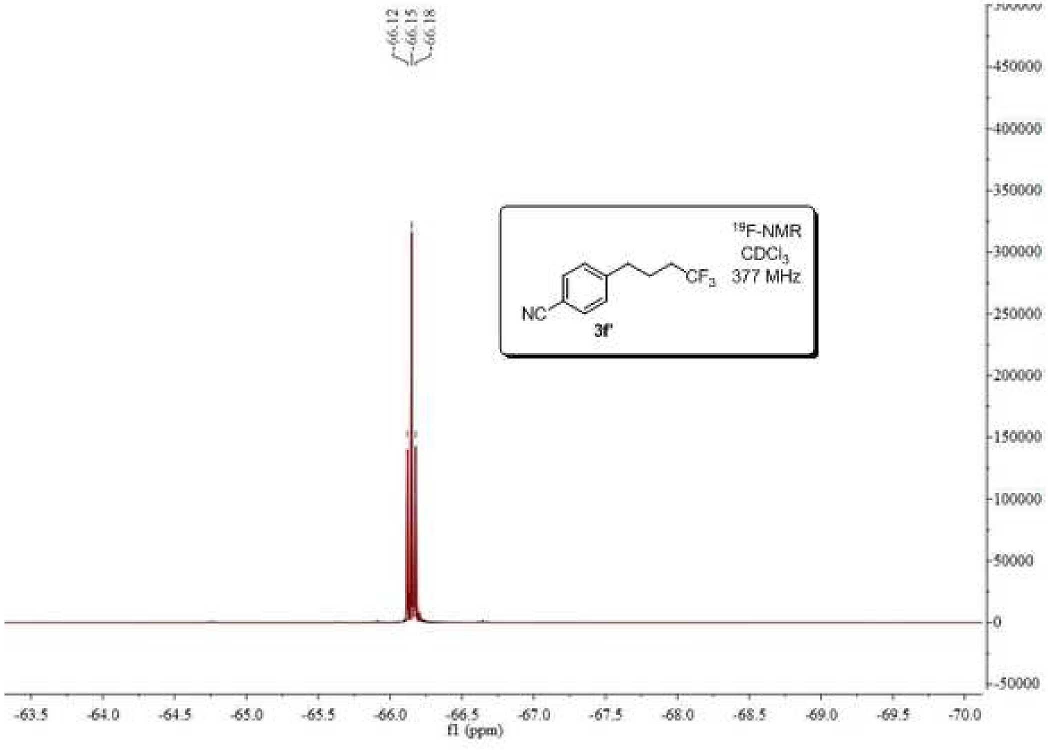

164.41
138.57
130.04
127.73
127.39
124.64
121.89
119.14
79.42
69.33
69.28
69.23
69.18
61.65
25.61
25.26
24.92
24.57
18.22
-0.00
Cl
O
O
CF3
3s
13C-NMR
CDCl3
101 MHz
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



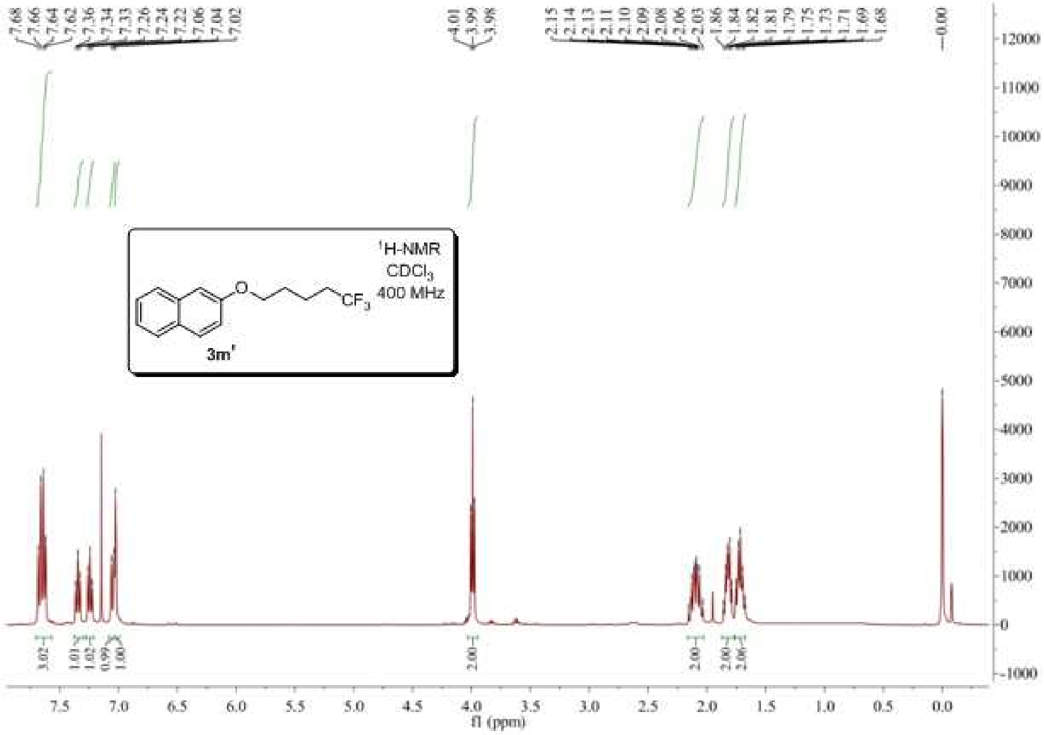
4-(4,4,4-trifluorobutyl)benzonitrile (3f')

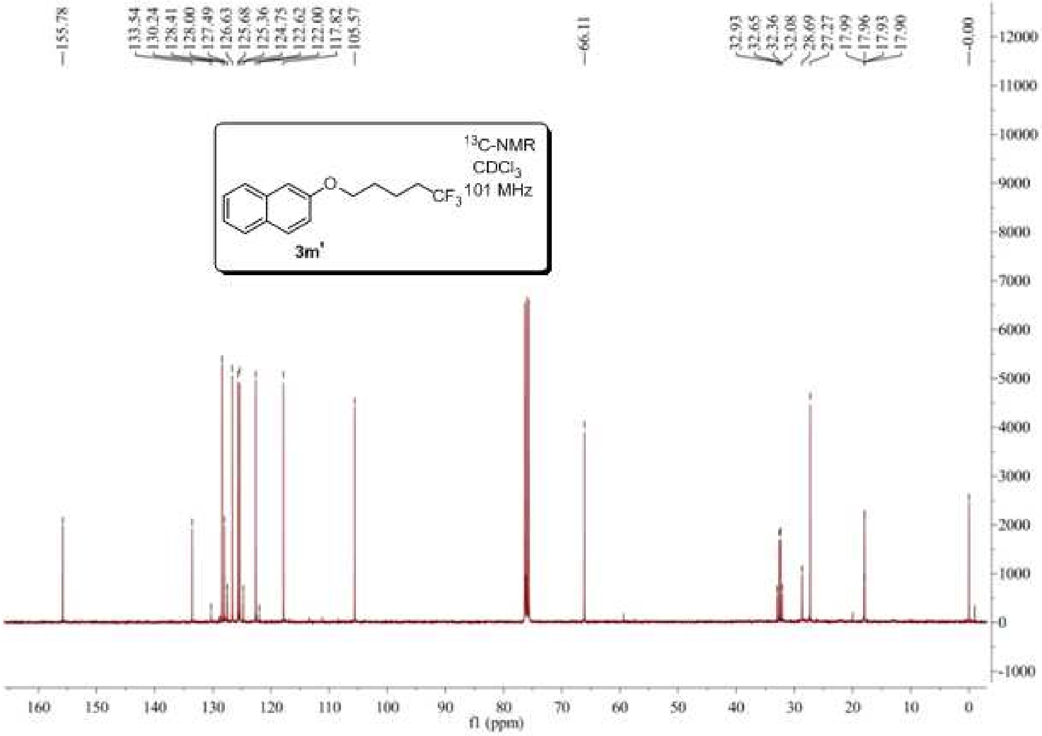


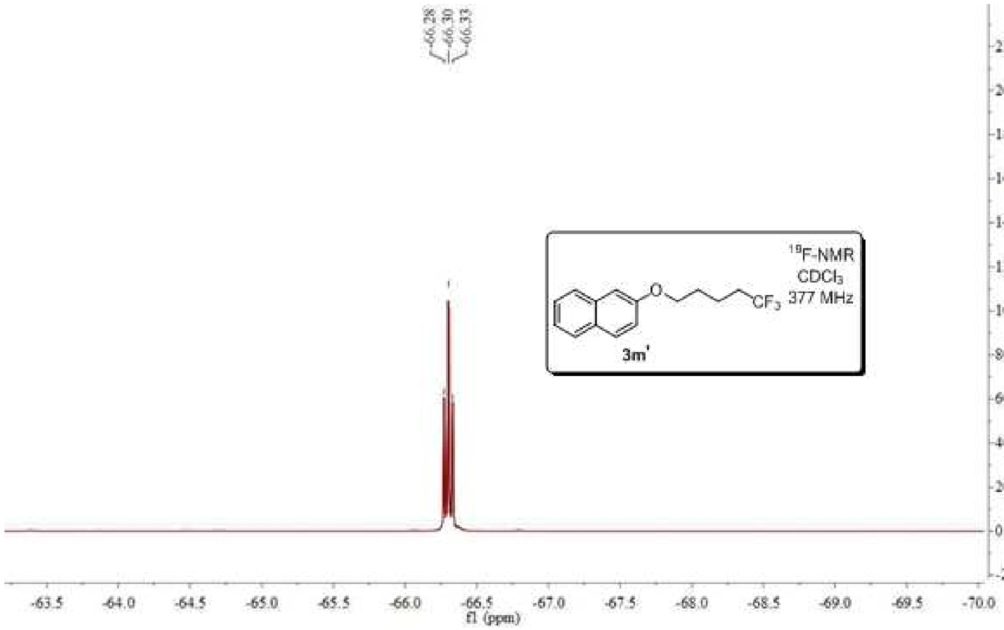

145.30
131.39
130.05
128.17
127.31
124.56
121.82
117.84
109.33
33.67
32.43
32.14
31.86
31.57
28.69
22.13
22.10
22.07
22.04
0.00
13C-NMR
CDCl3
101 MHz
NC
CF3
3f'
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-66.12
-66.15
-66.18
19F-NMR
CDCl3
377 MHz
NC
CF3
3f'
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
-63.5
-64.0
-64.5
-65.0
-65.5
-66.0
-66.5
-67.0
-67.5
-68.0
-68.5
-69.0
-69.5
-70.0
f1 (ppm)

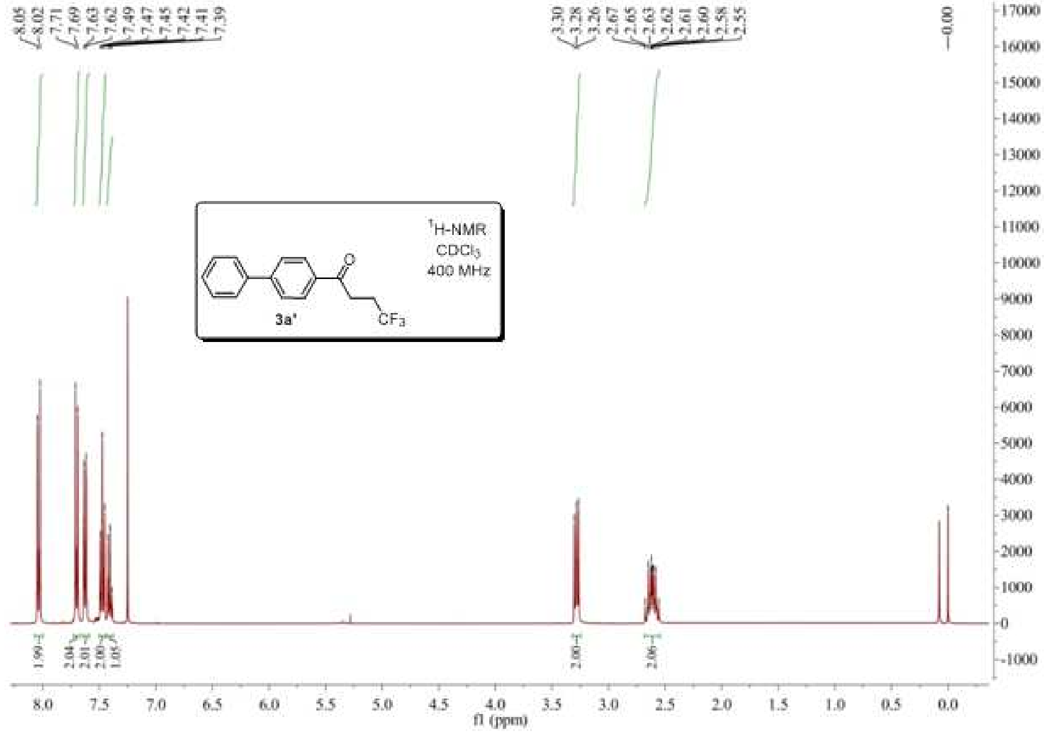
2-(5,5,5-trifluoropentyloxy)naphthalene (3m')

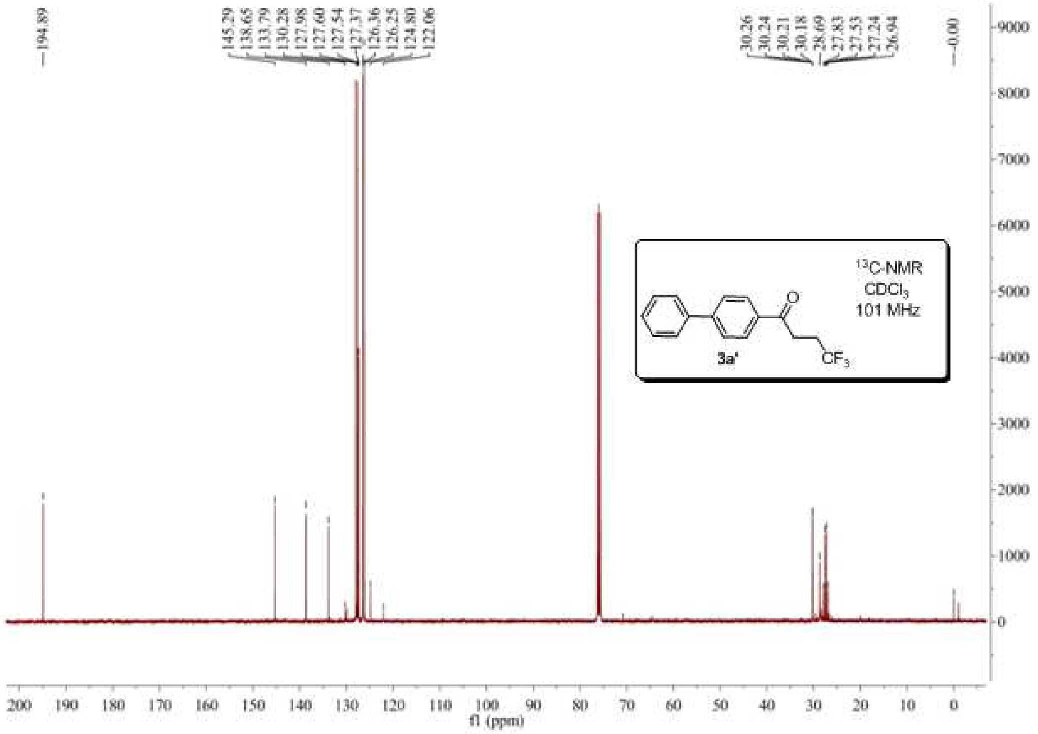


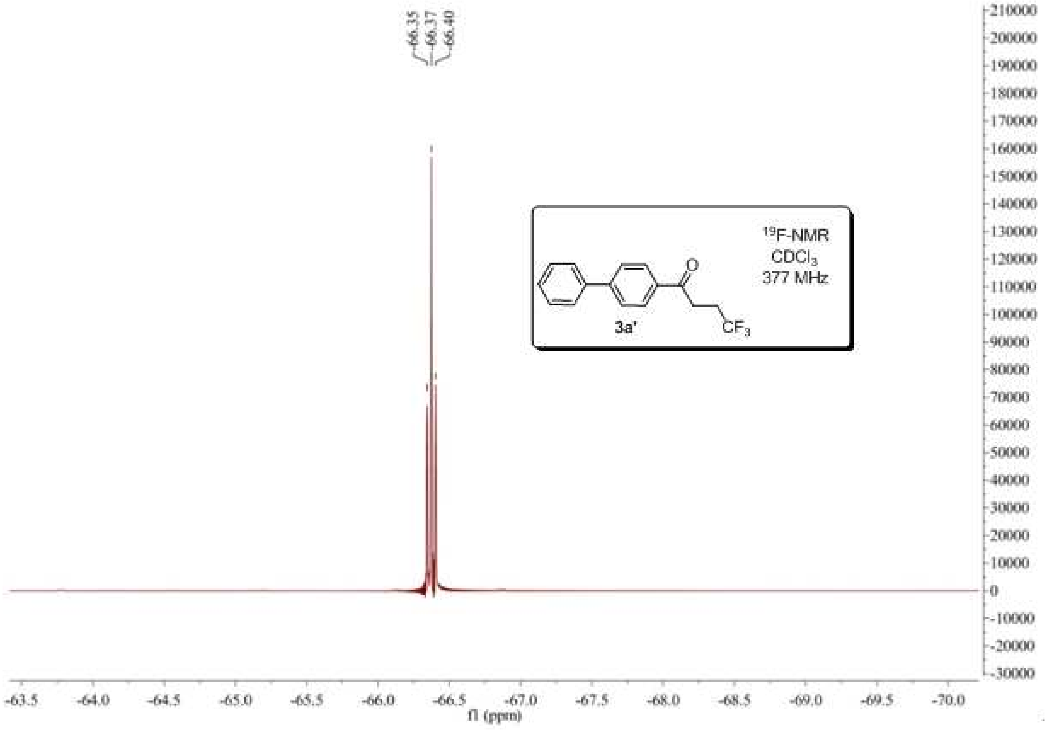




1-(biphenyl-4-yl)-4,4,4-trifluorobutan-1-one (3a′)




194.89
145.29
138.65
133.79
130.28
127.98
127.60
127.54
127.37
126.36
126.25
124.80
122.06
30.26
30.24
30.21
30.18
28.69
27.83
27.53
27.24
26.94
0.00
^{13}C-NMR
CDCl$_3$
101 MHz
O
CF$_3$
3a'
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-66.35
-66.37
-66.40
^{19}F-NMR
CDCl$_3$
377 MHz
O
CF$_3$
3a'
210000
200000
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
-30000
-63.5 -64.0 -64.5 -65.0 -65.5 -66.0 -66.5 -67.0 -67.5 -68.0 -68.5 -69.0 -69.5 -70.0
f1 (ppm)