Supplementary Material

Copper-Catalyzed Radical Trifluoromethylalkynylation of Unactivated Alkenes with Terminal Alkynes

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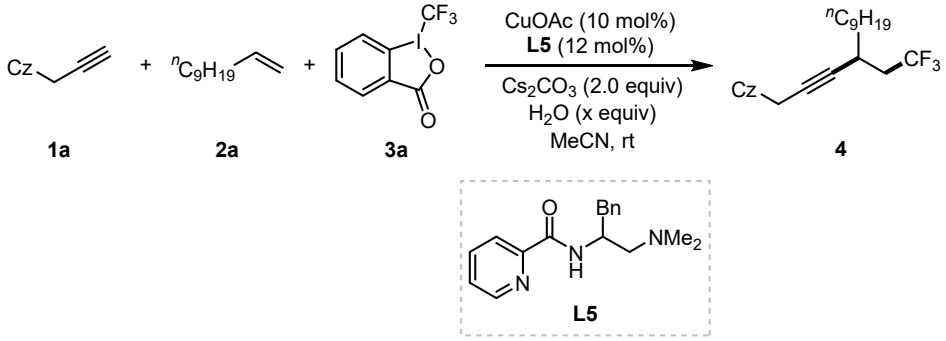
General information

All reactions were carried out under argon atmosphere using Schlenk techniques unless otherwise noted. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. CuOAc was purchased from TCI chemicals. Cs_2CO_3 was purchased from Bide Pharmatech Ltd. Anhydrous 1,4-dioxane, THF and MeCN were purchased from J&K Scientific. Other solvents and reagents were purchased from Aladdin, J&K Scientific, Leyan, and Bidepharm. or reactions that need heating, an oil bath was employed and the temperature of the oil bath was denoted. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). Visualization on TLC was achieved by use of UV colorless (254 nm), iodine, or basic $KMnO_4$ indicator.

NMR spectra were recorded on Bruker DRX-400 spectrometers at 400 MHz for ^1H NMR, 101 MHz for ^{13}C NMR, and 376 MHz for ^{19}F NMR, respectively, in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. Data for ^1H NMR were recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; p, pentet, m, multiplet; br, broad), coupling constant (Hz), integration. Data for ^{13}C NMR were reported in terms of chemical shift (δ, ppm). High-resolution mass spectrometry (HRMS) was performed on an Agilent Technologies 6230 TOF LC/MS under the conditions of electrospray ionization (ESI)/ atmospheric pressure chemical ionization (APCI) in a positive/negative mode using isopropyl alcohol or DCM as the solvent.

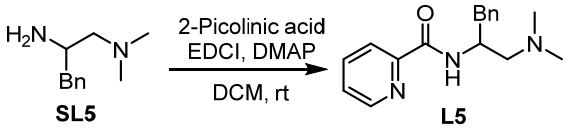
Table S1. The effect of water on the reaction efficiency



Entry	H_2O (equiv)	Yield (%)
1	--	80
2	1.0	78
3	2.0	77
4	5.0	78
5	10	79
6	100	54

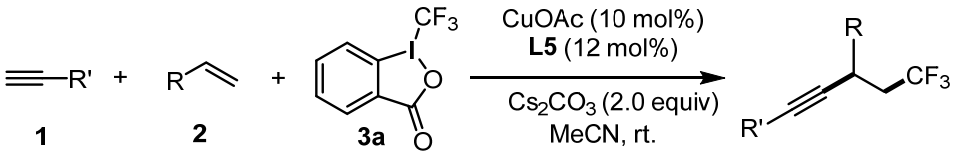
The synthesis of ligand L5

N-(1-(dimethylamino)-3-phenylpropan-2-yl)picolinamide (L5)



To a solution of **SL5** (1.78 g, 10 mmol) in anhydrous CH_2Cl_2 (70 mL) was added 2-picolinic acid (1.35 g, 11 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI, 2.11 g, 11 mmol), and 4-dimethylaminopyridine (DMAP, 1.34 g, 11 mmol). The reaction mixture was stirred at ambient temperature for 12 h. After completion, water was poured to above mixture, and the mixture was extracted with CH_2Cl_2. The combined organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 9/1 to petroleum ether/ethyl acetate 2/1) to provide the product **L5**. Yield: 1.72 g (61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 – 8.50 (m, 1H), 8.21 – 8.14 (m, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.87 – 7.79 (m, 1H), 7.47 – 7.37 (m, 1H), 7.35 – 7.17 (m, 5H), 4.54 – 4.41 (m, 1H), 3.13 – 2.90 (m, 2H), 2.49 (dd, *J* = 12.4, 8.4 Hz, 1H), 2.35 (dd, *J* = 12.4, 6.2 Hz, 1H), 2.27 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.1, 149.9, 148.1, 137.8, 137.3, 129.7, 128.4, 126.4, 126.1, 122.2, 62.0, 48.4, 45.7, 38.9. HRMS (ESI) *m/z* calcd. for $C_{17}H_{22}N_3O$ $[M+H]^+$ 284.1757, found 284.1749.

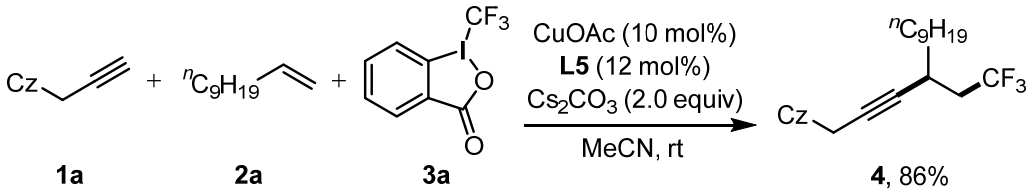
General procedure



General procedure A:
An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with radical precursor **3a** (0.24 mmol, 1.2 equiv), CuOAc (2.5 mg, 0.02 mmol, 10 mol%), **L5** (6.8 mg, 0.024 mmol, 12 mol%), and anhydrous Cs_2CO_3 (130.3 mg, 0.40 mmol, 2.0 equiv). The tube was evacuated and backfilled with argon three times. Then MeCN (2.0 mL) was added by syringe under argon atmosphere. Finally, alkene **2** (0.30 mmol, 1.5 equiv), and alkyne **1** (0.20 mmol, 1.0 equiv) were sequentially added into the mixture and the reaction mixture was stirred at room temperature for 3.5-7 d. Upon completion of the reaction (monitored by TLC), the reaction mixture was filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product.

General procedure B:
An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with radical precursor **3a** (0.24 mmol, 1.2 equiv), alkynes **1** (0.20 mmol, 1.0 equiv), CuOAc (2.5 mg, 0.02 mmol, 10 mol%), **L5** (6.8 mg, 0.024 mmol, 12 mol%), and anhydrous Cs_2CO_3 (130.3 mg, 0.40 mmol, 2.0 equiv). The tube was evacuated and backfilled with argon three times. Then MeCN (2.0 mL) was added by syringe under argon atmosphere. Finally, alkenes **2** (0.30 mmol, 1.5 equiv) were sequentially added into the mixture and the reaction mixture was stirred at room temperature for 3.5 d. Upon completion of the reaction (monitored by TLC), the reaction mixture was filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product.

Gram-scale reaction

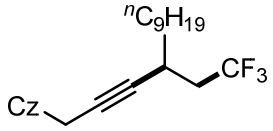


An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with radical precursor **3a** (6.0 mmol, 1.2 equiv), alkynes **1a** (5.0 mmol, 1.0 equiv), CuOAc (30.7 mg, 0.25 mmol, 5 mol%), **L5** (85.0 mg, 0.30 mmol, 6 mol%), and anhydrous Cs_2CO_3 (3.3 g, 10 mmol, 2.0 equiv). The tube was evacuated and backfilled with argon three times. Then MeCN (50 mL) was added by syringe under argon

atmosphere. Finally, alkenes **2a** (7.5 mmol, 1.5 equiv) were sequentially added into the mixture and the reaction mixture was stirred at room temperature for 5 d. Upon completion of the reaction (monitored by TLC), the reaction mixture was filtered through a short plug of silica gel eluted with EtOAc and purified by column chromatography to afford **4** as a colorless oil (1.84 g, 86% yield).

Analytical data

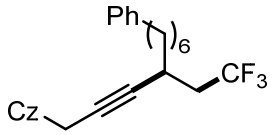
9-(4-(2,2,2-trifluoroethyl)tridec-2-yn-1-yl)-9H-carbazole (4)



4

68.4 mg, 80% yield (General procedure B). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 – 8.04 (m, 2H), 7.51 – 7.42 (m, 4H), 7.28 – 7.18 (m, 2H), 4.99 (d, *J* = 1.9 Hz, 2H), 2.65 – 2.58 (m, 1H), 2.28 – 2.00 (m, 2H), 1.44 – 1.08 (m, 16H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.0, 126.1 (q, *J* = 277.5 Hz), 125.8, 123.2, 120.4, 119.4, 108.8, 84.9, 76.3, 38.9 (q, *J* = 27.8 Hz), 34.5, 32.7, 31.9, 29.5, 29.4, 29.3, 29.1, 26.8, 25.8 (q, *J* = 3.0 Hz), 22.7, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.18. HRMS (ESI) *m/z* calcd. for $C_{27}H_{33}F_3N$ $[M+H]^+$ 428.2560, found 428.2554.

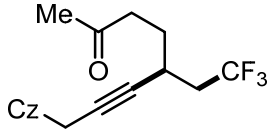
9-(10-phenyl-4-(2,2,2-trifluoroethyl)dec-2-yn-1-yl)-9H-carbazole (5)



5

70.7 mg, 77% yield (General procedure B). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.03 (m, 2H), 7.49 – 7.31 (m, 4H), 7.29 – 7.11 (m, 7H), 4.98 (d, *J* = 2.0 Hz, 2H), 2.66 – 2.57 (m, 1H), 2.56 – 2.49 (m, 2H), 2.27 – 1.99 (m, 2H), 1.62 – 1.02 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 140.0, 128.5, 128.3, 126.2 (q, *J* = 277.4 Hz), 125.8, 125.7, 123.2, 120.4, 119.4, 108.9, 84.8, 76.4, 38.9 (q, *J* = 27.7 Hz), 36.0, 34.5, 32.7, 31.4, 29.1, 29.0, 26.7, 25.8 (q, *J* = 3.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.11. HRMS (ESI) *m/z* calcd. for $C_{30}H_{31}F_3N$ $[M+H]^+$ 462.2403, found 462.2401.

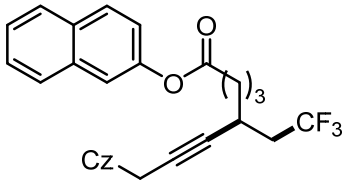
8-(9H-carbazol-9-yl)-5-(2,2,2-trifluoroethyl)oct-6-yn-2-one (6)



6

49.8 mg, 67% yield (General procedure B). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 – 8.10 (m, 2H), 7.56 – 7.46 (m, 4H), 7.34 – 7.22 (m, 2H), 5.06 (d, *J* = 2.1 Hz, 2H), 2.75 – 2.69 (m, 1H), 2.41 – 2.09 (m, 4H), 1.89 (s, 3H), 1.86 – 1.76 (m, 1H), 1.58 – 1.44 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 207.7, 139.9, 125.9 (q, *J* = 277.4 Hz), 125.9, 123.2, 120.5, 119.5, 108.8, 83.8, 77.4, 40.4, 39.0 (q, *J* = 28.0 Hz), 32.6, 29.8, 28.1, 25.1 (q, *J* = 3.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.17. HRMS (ESI) *m/z* calcd. for $C_{22}H_{21}F_3NO$ $[M+H]^+$ 372.1570, found 372.1568.

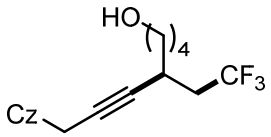
naphthalen-2-yl 8-(9H-carbazol-9-yl)-5-(2,2,2-trifluoroethyl)oct-6-ynoate (7)



7

55.7 mg, 54% yield (General procedure B). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 7.8 Hz, 2H), 7.94 – 7.77 (m, 3H), 7.62 – 7.46 (m, 7H), 7.37 – 7.26 (m, 2H), 7.22 (dd, *J* = 8.9, 2.4 Hz, 1H), 5.08 (d, *J* = 1.9 Hz, 2H), 2.85 – 2.72 (m, 1H), 2.57 (t, *J* = 7.3 Hz, 2H), 2.44 – 2.13 (m, 2H), 2.00 – 1.74 (m, 2H), 1.72 – 1.51 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.8, 148.3, 139.9, 133.8, 131.5, 129.5, 127.8, 127.7, 126.6, 126.0 (q, *J* = 277.6 Hz), 125.9, 125.8, 123.2, 121.1, 120.4, 119.5, 118.5, 108.9, 84.0, 77.3, 38.8 (q, *J* = 28.0 Hz), 33.7, 33.7, 32.7, 25.7 (q, *J* = 3.2 Hz), 22.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.02. HRMS (ESI) *m/z* calcd. for $C_{32}H_{27}F_3NO_2$ $[M+H]^+$ 514.1988, found 514.1973.

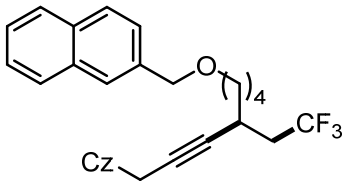
8-(9H-carbazol-9-yl)-5-(2,2,2-trifluoroethyl)oct-6-yn-1-ol (8)



8

57.7 mg, 77% yield (General procedure B). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 – 8.06 (m, 2H), 7.54 – 7.42 (m, 4H), 7.30 – 7.21 (m, 2H), 5.02 (d, *J* = 2.0 Hz, 2H), 3.43 (t, *J* = 6.2 Hz, 2H), 2.75 – 2.56 (m, 1H), 2.34 – 2.02 (m, 2H), 1.61 – 1.16 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.9, 126.1 (q, *J* = 277.5 Hz), 125.8, 123.2, 120.4, 119.4, 108.9, 84.5, 76.6, 62.6, 38.8 (q, *J* = 27.9 Hz), 34.2, 32.6, 32.1, 25.8 (q, *J* = 3.0 Hz), 23.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.18. HRMS (ESI) *m/z* calcd. for $C_{22}H_{23}F_3NO$ $[M+H]^+$ 374.1726, found 374.1724.

9-(8-(naphthalen-2-ylmethoxy)-4-(2,2,2-trifluoroethyl)oct-2-yn-1-yl)-9H-carbazole (9)

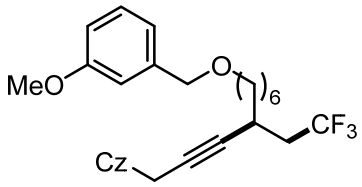


9

60.8 mg, 59% yield (General procedure B). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 – 8.01 (m, 2H), 7.83 – 7.76 (m, 3H), 7.75 – 7.70 (m, 1H), 7.49 – 7.38 (m, 7H), 7.25 – 7.18 (m, 2H), 4.95 (d, *J* = 1.9 Hz, 2H), 4.57 (brs, 2H), 3.36 – 3.28 (m, 2H), 2.64 – 2.60 (m, 1H), 2.26 – 1.97 (m, 2H), 1.55 – 1.28 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$):

δ 140.0, 136.1, 133.4, 133.0, 128.2, 127.9, 127.8, 126.4, 126.2, 126.2 (q, *J* = 277.6 Hz), 125.9, 125.8, 123.2, 120.4, 119.4, 108.9, 84.6, 76.6, 73.0, 70.0, 38.8 (q, *J* = 27.8 Hz), 34.3, 32.7, 29.3, 25.8 (q, *J* = 3.0 Hz), 23.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.07. HRMS (ESI) *m/z* calcd. for $C_{33}H_{31}F_3NO$ $[M+H]^+$ 514.2352, found 514.2350.

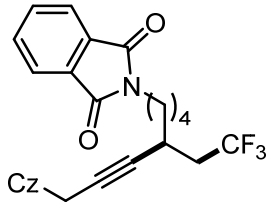
9-(10-((3-methoxybenzyl)oxy)-4-(2,2,2-trifluoroethyl)dec-2-yn-1-yl)-9H-carbazole (10)



10

74.6 mg, 74% yield (General procedure B). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 – 8.04 (m, 2H), 7.49 – 7.42 (m, 4H), 7.29 – 7.18 (m, 3H), 6.93 – 6.87 (m, 2H), 6.85 – 6.78 (m, 1H), 5.00 (d, *J* = 2.0 Hz, 2H), 4.46 (d, *J* = 1.7 Hz, 2H), 3.79 (s, 3H), 3.43 – 3.33 (m, 2H), 2.70 – 2.54 (m, 1H), 2.28 – 2.00 (m, 2H), 1.55 – 1.46 (m, 2H), 1.44 – 1.12 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.8, 140.4, 139.9, 129.4, 126.1 (q, *J* = 277.3 Hz), 125.8, 123.2, 120.4, 119.9, 119.4, 113.1, 113.0, 108.9, 84.7, 76.4, 72.8, 70.4, 55.2, 38.8 (q, *J* = 27.7 Hz), 34.5, 32.7, 29.6, 28.9, 26.7, 26.0, 25.8 (q, *J* = 3.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.08. HRMS (ESI) *m/z* calcd. for $C_{32}H_{35}F_3NO_2$ $[M+H]^+$ 522.2614, found 522.2613.

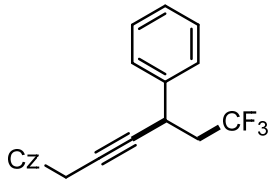
2-(8-(9H-carbazol-9-yl)-5-(2,2,2-trifluoroethyl)oct-6-yn-1-yl)isoindoline-1,3-dione (11)



11

70.4 mg, 70% yield (General procedure B). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.8 Hz, 2H), 7.84 – 7.77 (m, 2H), 7.70 – 7.62 (m, 2H), 7.50 – 7.40 (m, 4H), 7.27 – 7.19 (m, 2H), 4.98 (d, *J* = 1.9 Hz, 2H), 3.54 (t, *J* = 7.3 Hz, 2H), 2.68 – 2.56 (m, 1H), 2.30 – 2.00 (m, 2H), 1.66 – 1.20 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.4, 139.9, 133.9, 132.1, 126.0 (q, *J* = 277.5 Hz), 125.8, 123.2, 123.2, 120.4, 119.4, 108.9, 84.3, 76.7, 38.8 (q, *J* = 27.8 Hz), 37.6, 33.9, 32.6, 28.1, 25.8 (q, *J* = 3.1 Hz), 24.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.11. HRMS (ESI) *m/z* calcd. for $C_{30}H_{26}F_3N_2O_2$ $[M+H]^+$ 503.1941, found 503.1936.

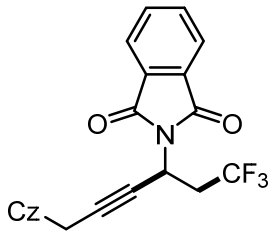
9-(6,6,6-trifluoro-4-phenylhex-2-yn-1-yl)-9H-carbazole (12)



12

45.3 mg, 60% yield (General procedure B). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.48 (d, *J* = 4.0 Hz, 4H), 7.30 – 7.20 (m, 7H), 5.08 (d, *J* = 1.9 Hz, 2H), 3.96 – 3.88 (m, 1H), 2.59 – 2.32 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.9, 138.1, 127.8, 126.5, 126.2, 124.8, 124.4 (q, *J* = 278.1 Hz), 122.2, 119.3, 118.4, 107.8, 82.3, 77.1, 40.8 (q, *J* = 27.7 Hz), 31.7, 30.8 (q, *J* = 3.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.39. HRMS (ESI) *m/z* calcd. for $C_{24}H_{19}F_3N$ $[M+H]^+$ 378.1464, found 378.1456.

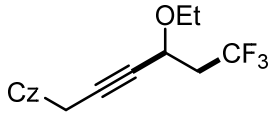
2-(6-(9H-carbazol-9-yl)-1,1,1-trifluorohex-4-yn-3-yl)isoindoline-1,3-dione (13)



13

51.0 mg, 57% yield (General procedure B). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.8 Hz, 2H), 7.87 – 7.79 (m, 2H), 7.74 – 7.68 (m, 2H), 7.49 – 7.39 (m, 4H), 7.27 – 7.20 (m, 2H), 5.41 – 5.33 (m, 1H), 5.04 (d, *J* = 2.1 Hz, 2H), 3.27 – 3.11 (m, 1H), 2.84 – 2.62 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.4, 139.8, 134.4, 131.6, 125.9, 124.8 (q, *J* = 277.6 Hz), 123.7, 123.2, 120.4, 119.6, 108.8, 78.8, 78.3, 36.7 (q, *J* = 28.7 Hz), 35.8 (q, *J* = 4.0 Hz), 32.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ -65.17. HRMS (ESI) *m/z* calcd. for $C_{26}H_{18}F_3N_2O_2$ $[M+H]^+$ 447.1315, found 447.1319.

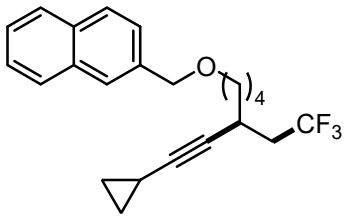
9-(4-ethoxy-6,6,6-trifluorohex-2-yn-1-yl)-9H-carbazole (14)



14

56.4 mg, 82% yield (General procedure B). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.8 Hz, 2H), 7.50 – 7.36 (m, 4H), 7.24 (t, *J* = 7.3 Hz, 2H), 4.98 (d, *J* = 1.6 Hz, 2H), 4.24 (t, *J* = 6.6 Hz, 1H), 3.68 – 3.56 (m, 1H), 3.34 – 3.22 (m, 1H), 2.56 – 2.28 (m, 2H), 1.10 (t, *J* = 7.0, 1.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.9, 125.9, 125.1 (q, *J* = 277.2 Hz), 123.3, 120.5, 119.6, 108.7, 81.0, 80.7, 64.7, 63.3 (q, *J* = 3.9 Hz), 40.1 (q, *J* = 28.2 Hz), 32.5, 14.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.77. HRMS (ESI) *m/z* calcd. for $C_{20}H_{19}F_3NO$ $[M+H]^+$ 346.1413, found 346.1410.

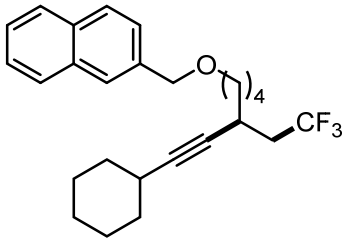
2-(((7-cyclopropyl-5-(2,2,2-trifluoroethyl)hept-6-yn-1-yl)oxy)methyl)naphthalene (17)



17

38.4 mg, 51% yield (General procedure A). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 – 7.80 (m, 3H), 7.78 (s, 1H), 7.51 – 7.43 (m, 3H), 4.66 (s, 2H), 3.51 (t, *J* = 6.3 Hz, 2H), 2.72 – 2.58 (m, 1H), 2.35 – 2.05 (m, 2H), 1.74 – 1.37 (m, 6H), 1.23 – 1.13 (m, 1H), 0.73 – 0.67 (m, 2H), 0.63 – 0.56 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.6, 133.8, 133.5, 128.7, 128.4, 128.2, 126.8, 126.8 (q, *J* = 277.4 Hz), 126.6, 126.3, 126.3, 86.2, 76.1, 73.5, 70.7, 39.9 (q, *J* = 27.4 Hz), 35.4, 29.9, 26.4 (q, *J* = 3.0 Hz), 24.2, 8.67, 8.65. ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.08. HRMS (ESI) *m/z* calcd. for $C_{23}H_{26}F_3O$ $[M+H]^+$ 375.1930, found 375.1921.

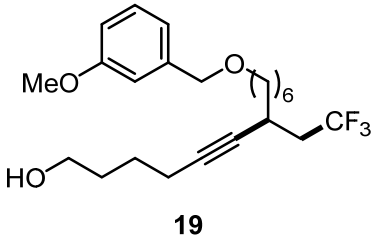
2-(((7-cyclohexyl-5-(2,2,2-trifluoroethyl)hept-6-yn-1-yl)oxy)methyl)naphthalene (18)



18

42.8 mg, 51% yield (General procedure A). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 – 7.80 (m, 3H), 7.78 (s, 1H), 7.52 – 7.37 (m, 3H), 4.67 (s, 2H), 3.52 (t, *J* = 6.2 Hz, 2H), 2.73 – 2.62 (m, 1H), 2.37 – 2.05 (m, 3H), 1.81 – 1.16 (m, 16H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.1, 133.3, 133.0, 128.1, 127.9, 126.3 (q, *J* = 278.8 Hz), 127.7, 126.3, 126.1, 125.8, 125.8, 86.9, 80.3, 73.0, 70.2, 39.6 (q, *J* = 27.3 Hz), 34.9, 32.9, 29.4, 28.9, 25.9, 25.9 (q, *J* = 3.0 Hz), 24.8, 23.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.99. HRMS (ESI) *m/z* calcd. for $C_{26}H_{32}F_3O$ $[M+H]^+$ 417.2400, found 417.2389.

13-((3-methoxybenzyl)oxy)-7-(2,2,2-trifluoroethyl)tridec-5-yn-1-ol (19)

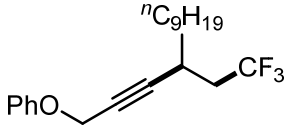


19

44.8 mg, 54% yield (General procedure A). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$):

δ 7.30 – 7.21 (m, 1H), 6.94 – 6.88 (m, 2H), 6.86 – 6.78 (m, 1H), 4.48 (s, 2H), 3.81 (s, 3H), 3.63 (t, *J* = 6.4 Hz, 2H), 3.46 (t, *J* = 6.6 Hz, 2H), 2.67 – 2.63 (m, 1H), 2.39 – 2.08 (m, 4H), 1.92 – 1.76 (m, 1H), 1.71 – 1.19 (m, 14H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.7, 140.2, 129.4, 126.3 (q, *J* = 277.6 Hz), 119.9, 113.1, 113.0, 82.1, 80.9, 72.8, 70.4, 62.4, 55.2, 39.4 (q, *J* = 27.4 Hz), 35.0, 31.8, 29.7, 29.0, 26.8, 26.1, 25.8 (q, *J* = 3.0 Hz), 25.2, 18.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.07. HRMS (ESI) *m/z* calcd. for $C_{23}H_{34}F_3O_3$ $[M+H]^+$ 415.2455, found 415.2450.

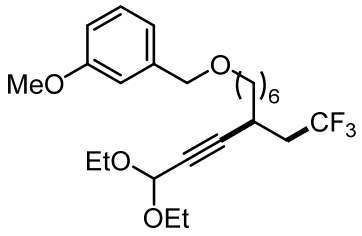
((4-(2,2,2-trifluoroethyl)tridec-2-yn-1-yl)oxy)benzene (20)



20

59.0 mg, 83% yield (General procedure A). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.21 (m, 2H), 7.07 – 6.88 (m, 3H), 4.68 (d, J = 2.0 Hz, 2H), 2.76 – 2.69 (m, 1H), 2.42 – 2.04 (m, 2H), 1.60 – 1.15 (m, 16H), 0.89 (t, J = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.7, 129.4, 126.1 (q, *J* = 277.4 Hz), 121.3, 115.0, 88.2, 77.2, 56.1, 38.8 (q, *J* = 27.8 Hz), 34.6, 31.9, 29.6, 29.5, 29.3, 29.2, 26.8, 25.9 (q, *J* = 3.0 Hz), 22.7, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.25. HRMS (ESI) *m/z* calcd. for $C_{21}H_{30}F_3O$ $[M+H]^+$ 355.2243, found 355.2240.

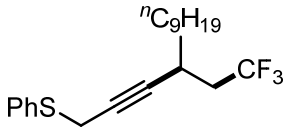
1-(((10,10-diethoxy-7-(2,2,2-trifluoroethyl)dec-8-yn-1-yl)oxy)methyl)-3-methoxybenzene (21)



21

71.0 mg, 80% yield (General procedure A). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 – 7.20 (m, 1H), 6.94 – 6.87 (m, 2H), 6.85 – 6.78 (m, 1H), 5.26 (d, *J* = 1.4 Hz, 1H), 4.47 (s, 2H), 3.80 (s, 3H), 3.77 – 3.67 (m, 2H), 3.63 – 3.51 (m, 2H), 3.46 (t, *J* = 6.5 Hz, 2H), 2.82 – 2.71 (m, 1H), 2.47 – 2.12 (m, 2H), 1.70 – 1.27 (m, 12H), 1.22 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.71, 140.29, 129.36, 126.09 (q, *J* = 277.4 Hz), 119.83, 113.05, 112.90, 91.29, 86.11, 77.92, 72.74, 70.33, 60.67, 55.16, 38.70 (q, *J* = 27.9 Hz), 34.33, 29.68, 29.02, 26.82, 26.07, 25.75 (q, *J* = 3.0 Hz), 15.08. ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.24. HRMS (ESI) *m/z* calcd. for $C_{24}H_{36}F_3O_4$ $[M+H]^+$ 445.2560, found 445.2572.

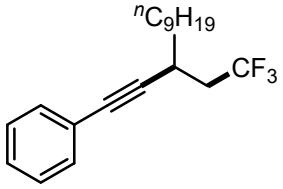
phenyl(4-(2,2,2-trifluoroethyl)tridec-2-yn-1-yl)sulfane (22)



22

52.3 mg, 71% yield (General procedure A). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.30 (dd, *J* = 8.6, 6.8 Hz, 2H), 7.26 – 7.20 (m, 1H), 3.62 (d, *J* = 2.2 Hz, 2H), 2.69 – 2.62 (m, 1H), 2.30 – 2.04 (m, 2H), 1.50 – 1.16 (m, 16H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 135.3, 130.0, 128.8, 126.7, 126.2 (q, *J* = 277.5 Hz), 84.3, 77.8, 39.0 (q, *J* = 27.6 Hz), 34.8, 31.9, 29.6, 29.5, 29.3, 29.2, 26.8, 25.9 (q, *J* = 3.0 Hz), 22.9, 22.7, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.23. HRMS (ESI) *m/z* calcd. for $C_{21}H_{30}F_3S$ $[M+H]^+$ 371.2015, found 371.2012.

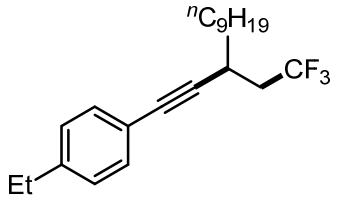
(3-(2,2,2-trifluoroethyl)dodec-1-yn-1-yl)benzene (23)



23

35.2 mg, 54% yield (General procedure A). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.36 (m, 2H), 7.31 – 7.25 (m, 3H), 2.98 – 2.86 (m, 1H), 2.52 – 2.20 (m, 2H), 1.66 – 1.43 (m, 4H), 1.40 – 1.20 (m, 12H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 131.6, 128.2, 127.9, 126.3 (q, *J* = 277.5 Hz), 123.4, 90.2, 82.5, 39.2 (q, *J* = 27.6 Hz), 34.8, 31.9, 29.6, 29.5, 29.3, 29.3, 26.9, 26.5 (q, *J* = 3.0 Hz), 22.7, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.14. HRMS (APCI) *m/z* calcd. for $C_{20}H_{28}F_3$ $[M+H]^+$ 325.2138, found 325.2134.

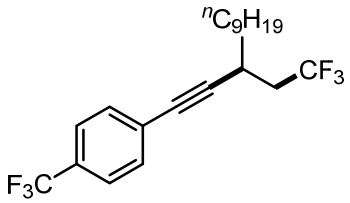
1- ethyl-4-(3-(2,2,2-trifluoroethyl)dodec-1-yn-1-yl)benzene (24)



24

38.8 mg, 55% yield (General procedure A). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 2.96 – 2.85 (m, 1H), 2.63 (q, *J* = 7.6 Hz, 2H), 2.50 – 2.19 (m, 2H), 1.65 – 1.41 (m, 4H), 1.36 – 1.17 (m, 15H), 0.88 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.3, 131.6, 127.8, 126.3 (q, *J* = 277.4 Hz), 120.6, 89.5, 82.6, 39.2 (q, *J* = 27.5 Hz), 34.9, 31.9, 29.6, 29.5, 29.3, 29.3, 28.8, 27.0, 26.5 (q, *J* = 3.0 Hz), 22.7, 15.5, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.12. HRMS (ESI) *m/z* calcd. for $C_{22}H_{32}F_3$ $[M+H]^+$ 353.2451, found 353.2444.

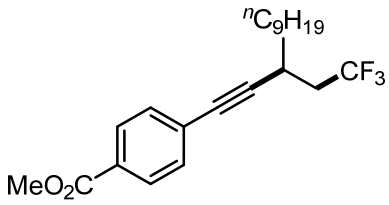
1-(3-(2,2,2-trifluoroethyl)dodec-1-yn-1-yl)-4-(trifluoromethyl)benzene (25)



25

53.1 mg, 68% yield (General procedure A). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 3.00 – 2.88 (m, 1H), 2.49 – 2.21 (m, 2H), 1.76 – 1.43 (m, 4H), 1.39 – 1.20 (m, 12H), 0.93 – 0.81 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 131.8, 129.7 (q, *J* = 32.6 Hz), 127.21 (q, *J* = 1.1 Hz), 126.2 (q, *J* = 277.4 Hz), 125.1 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.2 Hz), 92.9, 81.4, 39.0 (q, *J* = 27.7 Hz), 34.7, 31.9, 29.5, 29.5, 29.3, 29.2, 26.9, 26.5 (q, *J* = 3.0 Hz), 22.7, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.80, -64.20. HRMS (ESI) *m/z* calcd. for $C_{21}H_{27}F_6$ $[M+H]^+$ 393.2012, found 393.2012.

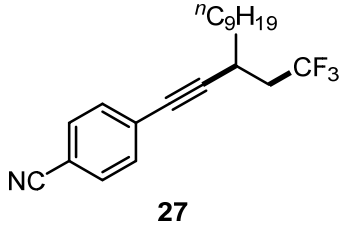
methyl 4-(3-(2,2,2-trifluoroethyl)dodec-1-yn-1-yl)benzoate (26)



26

41.0 mg, 54% yield (General procedure A). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 – 7.94 (m, 2H), 7.47 – 7.42 (m, 2H), 3.91 (s, 3H), 2.99 – 2.89 (m, 1H), 2.52 – 2.22 (m, 2H), 1.68 – 1.42 (m, 4H), 1.39 – 1.19 (m, 12H), 0.91 – 0.82 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.6, 131.5, 129.4, 129.2, 128.1, 126.2 (q, *J* = 277.4 Hz), 93.5, 82.0, 52.2, 39.0 (q, *J* = 27.7 Hz), 34.7, 31.9, 29.5, 29.5, 29.3, 29.2, 26.9, 26.6 (q, *J* = 3.0 Hz), 22.7, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.17. HRMS (ESI) *m/z* calcd. for $C_{22}H_{30}F_3O_2$ $[M+H]^+$ 383.2192, found 383.2187.

4-(3-(2,2,2-trifluoroethyl)dodec-1-yn-1-yl)benzonitrile (27)

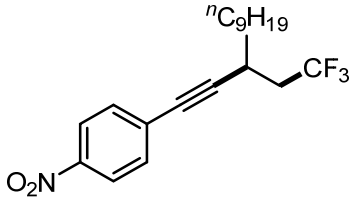


27

39.8 mg, 57% yield (General procedure B). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 3.04 – 2.87 (m, 1H), 2.49 – 2.23 (m, 2H), 1.68 – 1.41 (m, 4H), 1.39 – 1.19 (m, 12H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 132.2, 131.9, 128.3, 126.1 (q, *J* = 277.5 Hz), 118.5, 111.3, 95.1, 81.3, 38.9 (q, *J* = 27.9 Hz), 34.6, 31.9, 29.5, 29.5, 29.3, 29.2, 26.9, 26.6 (q, *J* = 3.0 Hz), 22.7, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.20. HRMS (ESI) *m/z* calcd. for

$C_{21}H_{27}F_3N$ $[M+H]^+$ 350.2090, found 350.2089.

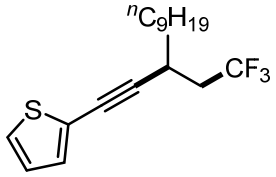
1- nitro-4-(3-(2,2,2-trifluoroethyl)dodec-1-yn-1-yl)benzene (28)



28

40.0 mg, 54% yield (General procedure B). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 3.04 – 2.93 (m, 1H), 2.52 – 2.25 (m, 2H), 1.71 – 1.44 (m, 4H), 1.42 – 1.21 (m, 12H), 0.90 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.9, 132.4, 130.3, 126.1 (q, *J* = 277.5 Hz), 123.5, 96.0, 81.1, 38.8 (q, *J* = 27.9 Hz), 34.6, 31.9, 29.5, 29.5, 29.3, 29.2, 27.0, 26.6 (q, *J* = 3.0 Hz), 22.7, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.21. HRMS (ESI) *m/z* calcd. for $C_{20}H_{27}F_3NO_2$ $[M+H]^+$ 370.1988, found 370.1984.

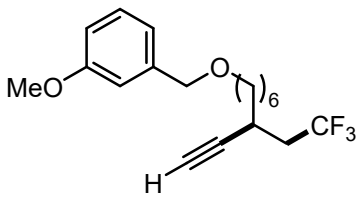
2-(3-(2,2,2-trifluoroethyl)dodec-1-yn-1-yl)thiophene (29)



29

24.6 mg, 37% yield (General procedure A). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (dd, *J* = 5.2, 1.1 Hz, 1H), 7.14 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.94 (dd, *J* = 5.2, 3.6 Hz, 1H), 2.99 – 2.88 (m, 1H), 2.51 – 2.19 (m, 2H), 1.69 – 1.40 (m, 4H), 1.37 – 1.21 (m, 12H), 0.91 – 0.85 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 131.5, 126.8, 126.4, 126.2 (q, *J* = 277.5 Hz), 123.4, 94.2, 75.7, 39.0 (q, *J* = 27.7 Hz), 34.7, 31.9, 29.5, 29.5, 29.3, 29.2, 26.9, 26.7 (q, *J* = 2.9 Hz), 22.7, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.21. HRMS (ESI) *m/z* calcd. for $C_{18}H_{26}F_3S$ $[M+H]^+$ 331.1702, found 331.1694.

1- methoxy-3-(((7-(2,2,2-trifluoroethyl)non-8-yn-1-yl)oxy)methyl)benzene (30)



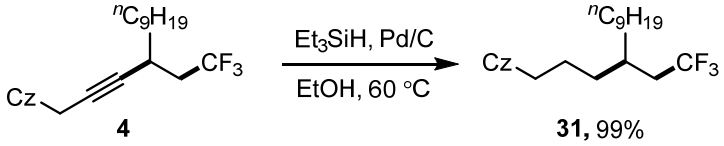
30

32.1 mg, 47% yield (General procedure A). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 – 7.22 (m, 1H), 6.94 – 6.88 (m, 2H), 6.86 – 6.79 (m, 1H), 4.48 (s, 2H), 3.81 (s, 3H), 3.52 – 3.43 (m, 2H), 2.75 – 2.63 (m, 1H), 2.43 – 2.30 (m, 1H), 2.27 – 2.16 (m, 1H), 2.14 – 2.11 (m, 1H), 1.68 – 1.28 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.7,

140.3, 129.4, 126.1 (q, J = 277.4 Hz), 119.9, 113.1, 112.9, 84.7, 72.8, 70.4, 70.4, 55.2, 39.0 (q, J = 27.9 Hz), 34.5, 29.7, 29.0, 26.7, 26.1, 25.6 (q, J = 3.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.26.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{26}F_3O_2$ $[M+H]^+$ 343.1879, found 343.1870.

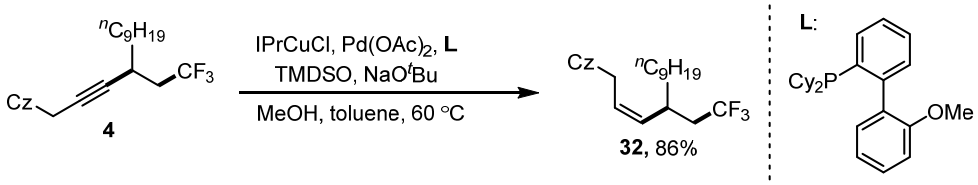
Synthetic applications

9-(4-(2,2,2-trifluoroethyl)tridecyl)-9H-carbazole (31)



To a mixture of Pd/C (5.0 mg, 10% w/w Pd on carbon) in MeOH (1.0 mL) was added **4** (42.8 mg, 0.10 mmol, 1.0 equiv.) under argon atmosphere. Then Et_3SiH (118.7 mg, 1.00 mmol, 10.0 equiv) were sequentially added into the mixture. The resulting reaction mixture was stirred under the hydrogen atmosphere at room temperature for 24 h. After completion, the reaction mixture was filtered and rinsed with CH_2Cl_2. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to afford **31** as a colorless oil (42.8 mg, 99% yield). 42.8 mg, 99% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.7 Hz, 2H), 7.42 – 7.34 (m, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 2H), 4.20 (t, *J* = 7.3 Hz, 2H), 2.00 – 1.81 (m, 2H), 1.84 – 1.71 (m, 2H), 1.72 – 1.61 (m, 1H), 1.44 – 1.33 (m, 2H), 1.24 – 1.06 (m, 16H), 0.85 – 0.76 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.3, 126.2 (q, *J* = 277.5 Hz), 124.6, 121.8, 119.4, 117.8, 107.5, 42.0, 36.3 (q, *J* = 26.9 Hz), 32.2, 31.0 (q, *J* = 2.2 Hz), 30.9, 29.7, 28.6, 28.5, 28.5, 28.3, 25.0, 24.3, 21.7, 13.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.35. HRMS (ESI) *m/z* calcd. for $C_{27}H_{37}F_3N$ $[M+H]^+$ 432.2873, found 432.2862.

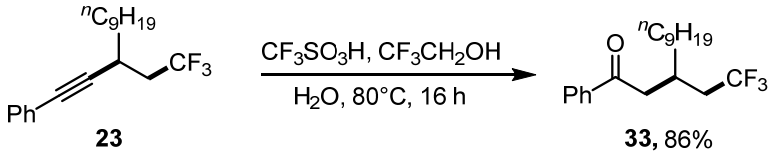
(Z)-9-(4-(2,2,2-trifluoroethyl)tridec-2-en-1-yl)-9H-carbazole (32)



To a flamed Schlenk tube charged with a stir bar were added NaO^{t}Bu (19.2 mg, 0.20 mmol, 2.0 equiv.), **4** (42.8 mg, 0.10 mmol, 1.0 equiv), $Pd(OAc)_2$ (1.12 mg, 0.005 mmol, 5.0 mol%), **L** (3.8 mg, 0.010 mmol, 10 mol%), IPrCuCl (4.88 mg, 0.010 mmol, 10 mol%), TMDSO (1,1,3,3-tetramethyldisiloxane) (26.9 mg, 0.20 mmol, 2.0 S49 equiv.), MeOH (16.0 mg, 0.5 mmol, 5.0 equiv.), and toluene (1.0 mL). The reaction mixture was stirred at 60 °C for 1.5 h. Upon completion, the reaction mixture was filtered through a short plug of silica gel eluted with EtOAc (3 mL) and purified by column chromatography to afford **32** as a colorless oil (36.9 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 7.8 Hz, 2H), 7.49 – 7.40 (m, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 2H), 5.60 – 5.49 (m, 1H), 5.37 – 5.25 (m, 1H), 4.93 (dd, *J* = 5.9, 2.0 Hz, 2H), 3.01 – 2.87 (m, 1H), 2.37 – 2.02 (m, 2H), 1.42 – 1.20 (m, 16H), 0.93 – 0.85 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.2, 134.8, 126.8 (q, *J* = 277.6 Hz), 126.6,

125.7, 123.0, 120.4, 119.1, 108.7, 40.3, 39.3 (q, J = 26.9 Hz), 35.7, 32.6 (q, J = 2.5 Hz), 32.0, 29.7, 29.7, 29.6, 29.4, 27.2, 22.8, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.36. HRMS (ESI) *m/z* calcd. for $C_{27}H_{35}F_3N$ $[M+H]^+$ 430.2716, found 430.2702.

1-phenyl-3-(2,2,2-trifluoroethyl)dodecan-1-one (33)

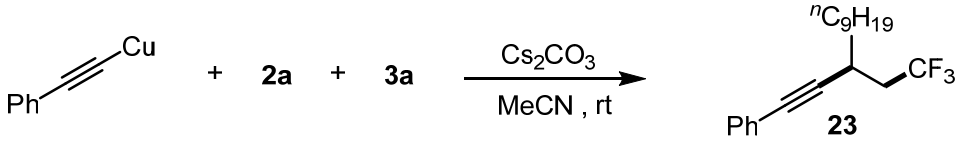


23 **33,** 86%

To a solution of **23** (32.4 mg, 0.10 mmol, 1.0 equiv.) in CF_3CH_2OH (0.5 mL) were added CF_3SO_3H (3.06 mg, 0.020 mmol, 0.2 equiv.) and H_2O (3.6 mg, 0.20 mmol, 2.0 equiv.). And the reaction mixture was stirred at 80 °C for 16 h. After evaporation under reduced pressure, the residue was purified with column chromatography on silica gel to yield the product **33** as a colorless oil (20.9 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 – 7.90 (m, 2H), 7.61 – 7.54 (m, 1H), 7.51 – 7.43 (m, 2H), 3.13 – 2.98 (m, 2H), 2.55 – 2.41 (m, 1H), 2.31 – 2.16 (m, 2H), 1.51 – 1.41 (m, 2H), 1.35 – 1.19 (m, 14H), 0.87 (t, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.8, 137.0, 133.2, 128.6, 127.9, 127.2 (q, J = 277.5 Hz), 42.1, 37.1 (q, J = 27.0 Hz), 33.9, 31.9, 29.6, 29.5, 29.5, 29.3, 28.9 (q, J = 2.1 Hz), 26.6, 22.7, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.86. HRMS (ESI) *m/z* calcd. for $C_{20}H_{30}F_3O$ $[M+H]^+$ 343.2243, found 343.2232.

Mechanistic studies

Control experiment with copper phenylacetylide



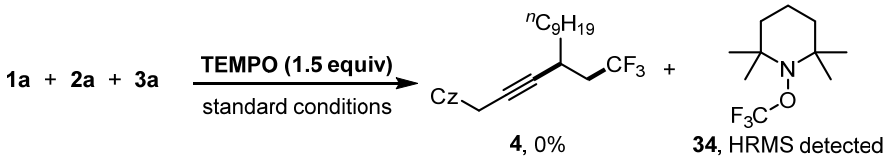
With **L5** (1 equiv.): **23**, 36%

Without **L5: 23,** 0%

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with copper phenylacetylide (8.2 mg, 0.05 mmol, 1.0 equiv.), alkene **2a** (11.6 mg, 0.075 mmol, 1.5 equiv.), radical precursor **3a** (19.0 mg, 0.06 mmol, 1.2 equiv.), **L5** (17.0 mg, 0.06 mmol, 1.2 equiv.), Cs_2CO_3 (32.6 mg, 0.10 mmol, 2.0 equiv.), and anhydrous MeCN (0.5 mL). The resulting reaction mixture was stirred at room temperature for 3.5 d. Upon completion of the reaction (monitored by TLC), the reaction mixture was filtered and washed by EtOAc. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to afford **23** (5.84 mg, 36% yield).

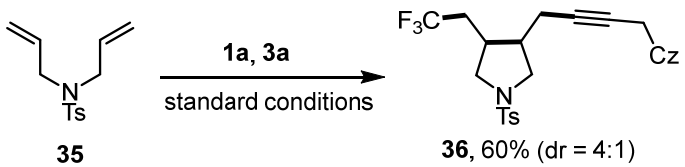
The procedure for the reaction without **L5** was the same with that described above except that **L5** was not added. No desired product **23** was observed.

Radical-trapping experiment



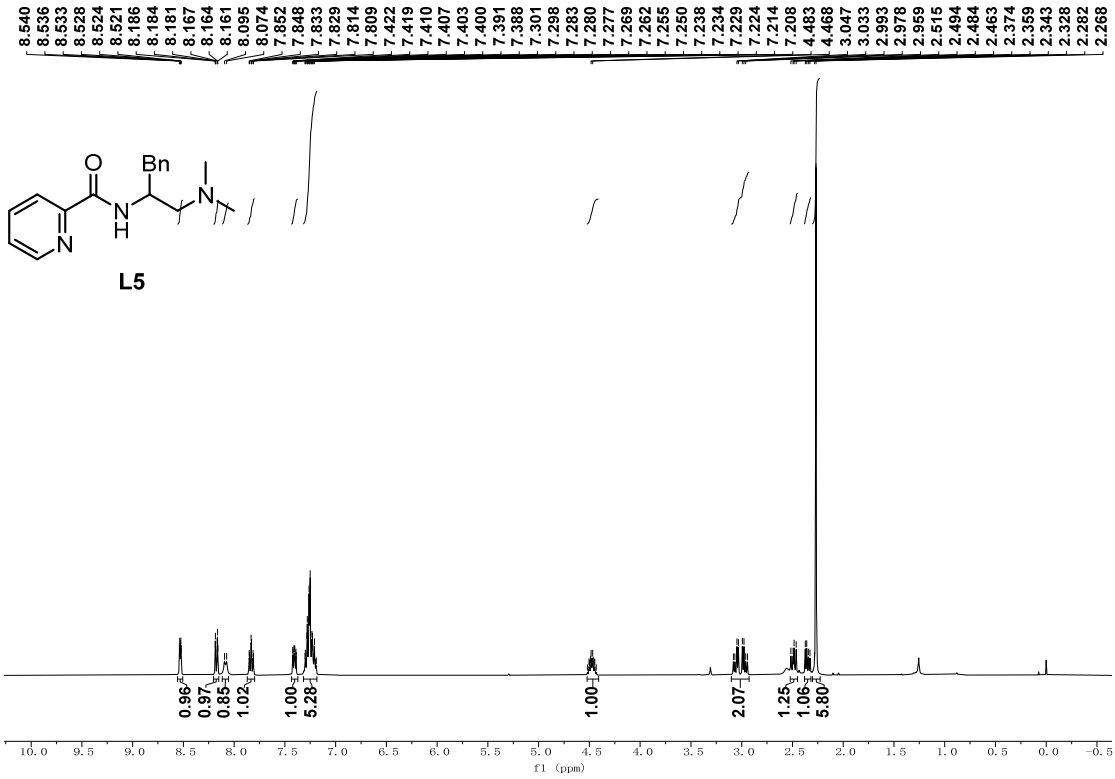
According to General Procedure **B** with alkyne **1a** (20.5 mg, 0.10 mmol, 1.0 equiv.), alkene **2a** (23.1 mg, 0.15 mmol, 1.5 equiv.), radical precursor **3a** (38.0 mg, 0.12 mmol, 1.2 equiv.), and 2,2,6,6- tetramethylpiperidinyloxy (TEMPO) (23.4 mg, 0.15 mmol, 1.5 equiv.) after 3.5 d, the reaction mixture was monitored by TLC. There was no product **4** observed, TEMPO-CF_3 product **34** was detected by HRMS, HRMS (ESI) *m/z* calcd. for $C_{10}H_{19}F_3NO$ $[M+H]^+$ 226.1413, found 226.1410.

Clock experiment



According to General Procedure **B** with alkyne **1a** (41.0 mg, 0.20 mmol, 1.0 equiv.),

alkene **35** (75.4 mg, 0.30 mmol, 1.5 equiv.), and radical precursor **3a** (75.8 mg, 0.24 mmol, 1.2 equiv.) after 3.5 d, Upon completion of the reaction (monitored by TLC), the reaction mixture was filtered and washed by EtOAc. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to afford a colorless oil **36** (62.9 mg, 60% yield, dr = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 – 8.04 (m, 2.00H), 7.64 – 7.44 (m, 4.17H), 7.44 – 7.36 (m, 2.00H), 7.30 – 7.18 (m, 3.02H), 7.01 (d, *J* = 8.0 Hz, 1.54H), 4.99 – 4.70 (m, 2.05H), 3.53 – 3.31 (m, 1.33H), 3.30 – 3.21 (m, 1.63H), 2.97 – 2.81 (m, 1.23H), 2.43 – 2.25 (m, 1.77H), 2.25 – 2.05 (m, 3.69H), 2.05 – 1.85 (m, 2.10H), 1.83 – 1.68 (m, 1.30H), 1.56 – 1.45 (m, 0.81H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.8, 143.7, 139.9, 139.8, 133.3, 133.0, 129.8, 129.7, 127.6, 127.5, 127.3, 126.4 (q, *J* = 276.9 Hz), 126.0, 126.0, 123.2, 120.5, 120.5, 119.6, 119.6, 108.7, 108.7, 80.8, 80.1, 77.3, 76.6, 76.4, 52.8, 51.7, 51.6, 50.6, 42.3, 40.2, 37.1 (q, *J* = 2.5 Hz), 36.1 (q, *J* = 28.8 Hz), 35.1 (q, *J* = 2.5 Hz), 32.4, 32.2 (q, *J* = 28.9 Hz), 21.6, 21.4, 20.7, 17.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.81, -64.83. HRMS (ESI) *m/z* calcd. for $C_{30}H_{29}F_3NO_2S$ $[M+H]^+$ 525.1818, found 525.1811.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7.848
7.833
7.829
7.814
7.809
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7.419
7.410
7.407
7.403
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Bn
N
H
N
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0.97
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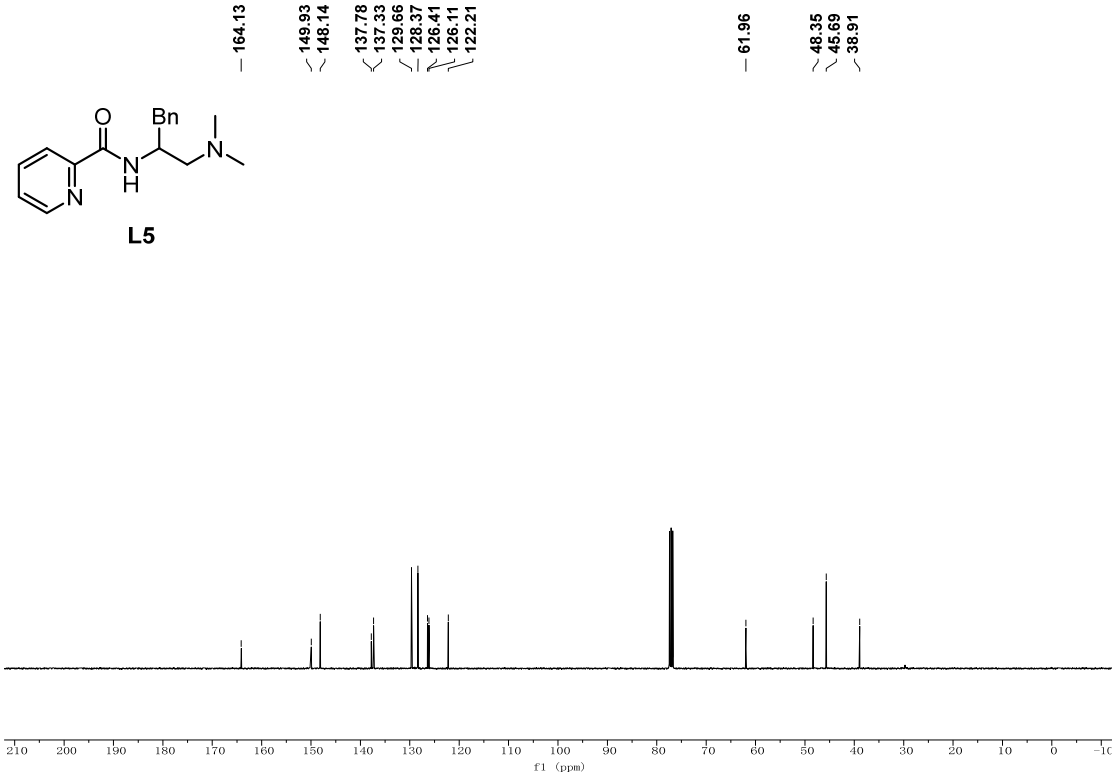
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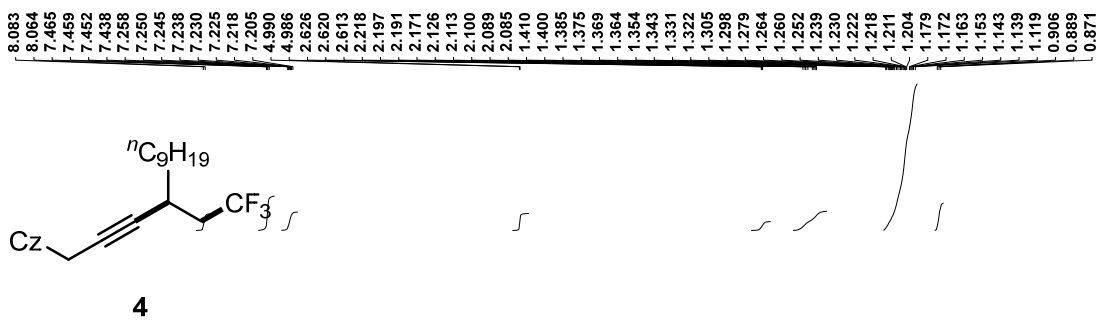
O
Bn
N
H
N
L5
f1 (ppm)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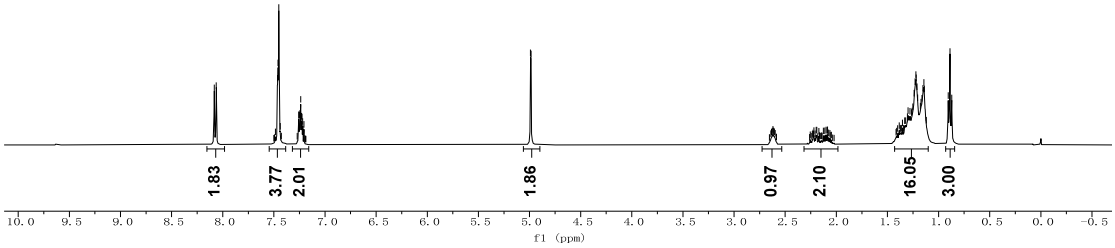
CF3
Cz

4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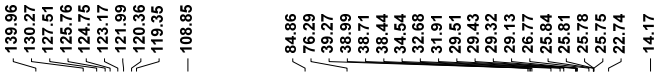
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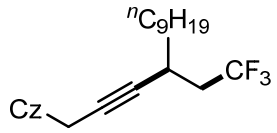
nC9H19
CF3
Cz

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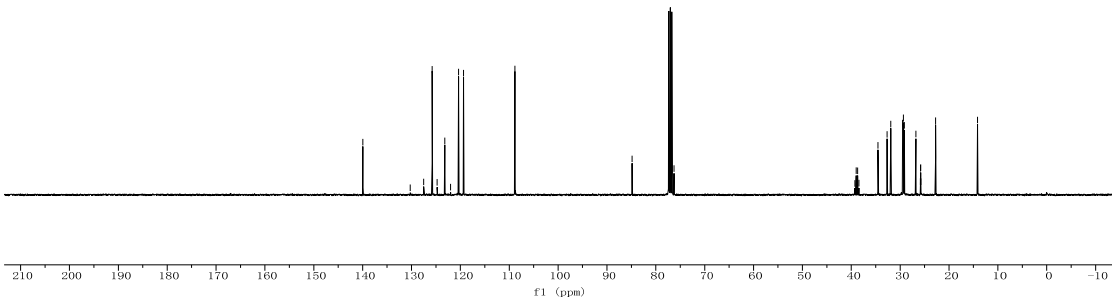
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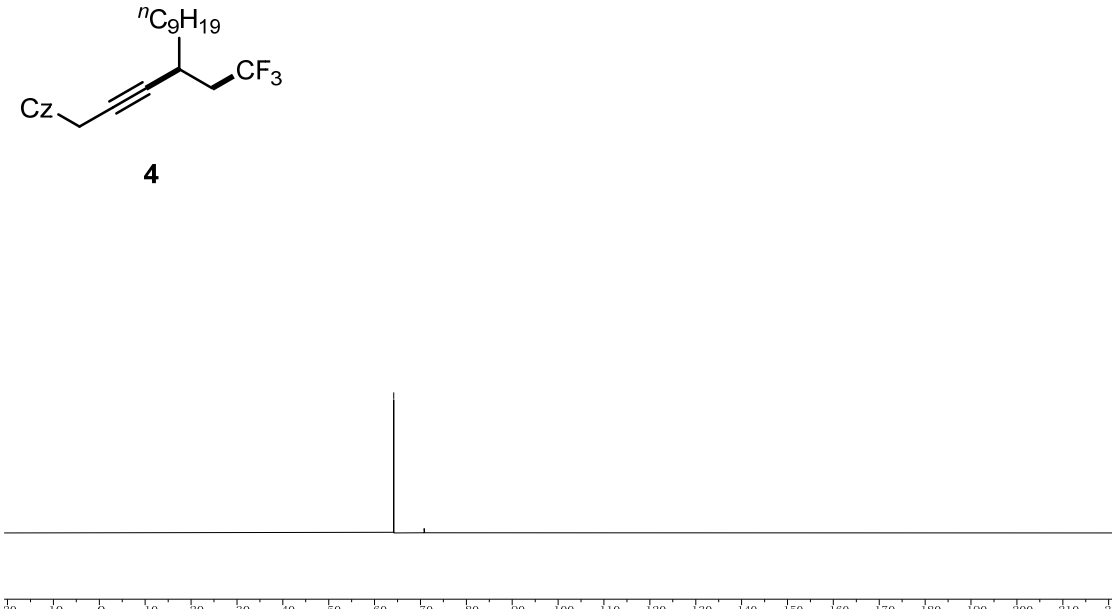
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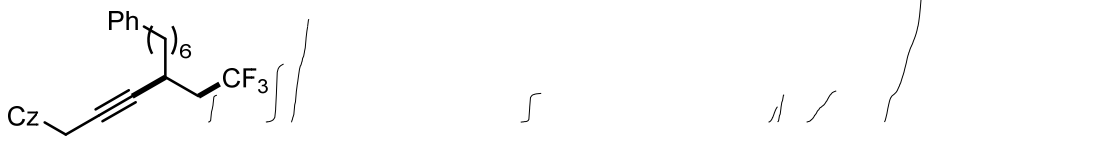
f1 (ppm)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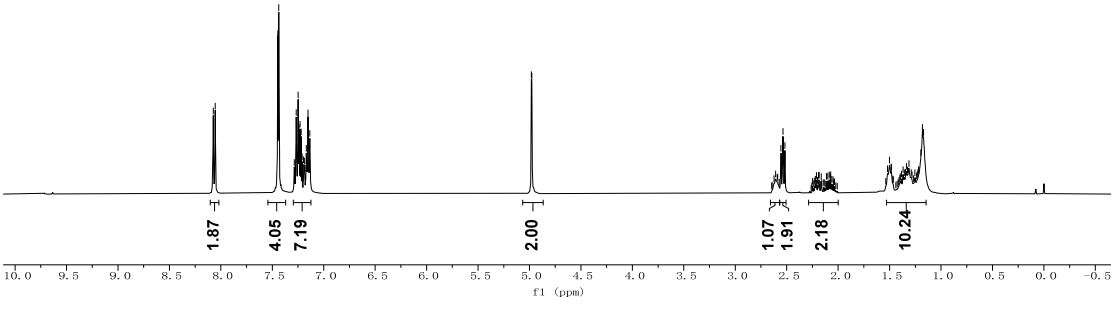
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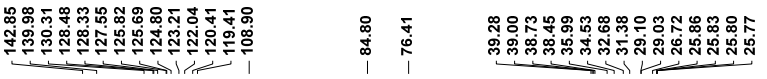
1.07
1.91
2.18
10.24
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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127.55
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125.69
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123.21
122.04
120.41
119.41
108.90
84.80
76.41
39.28
39.00
38.73
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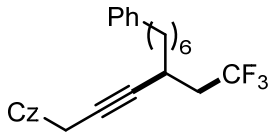
29.03
26.72
25.86
25.83
25.80
25.77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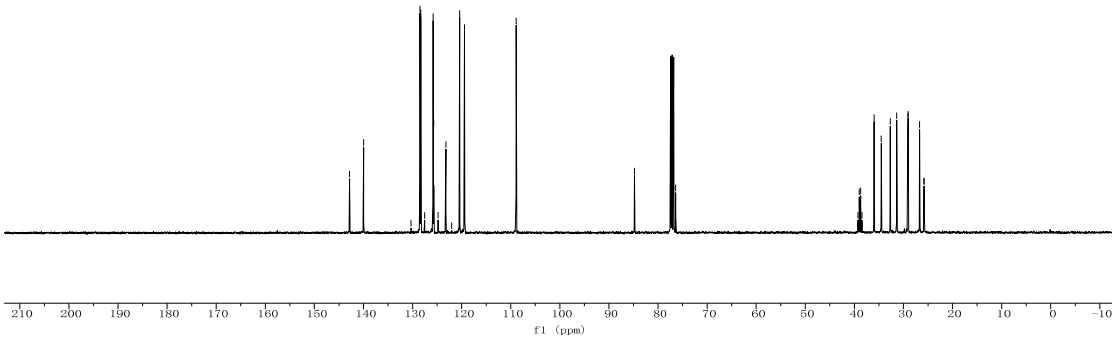
CF3
Cz

5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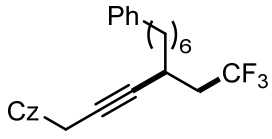
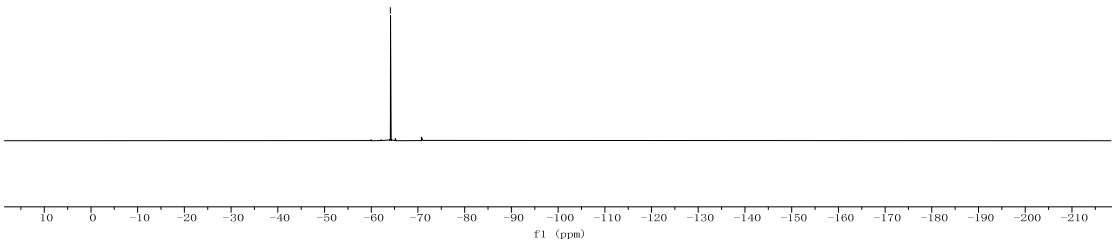
-64.112


Ph
6
CF3
Cz

5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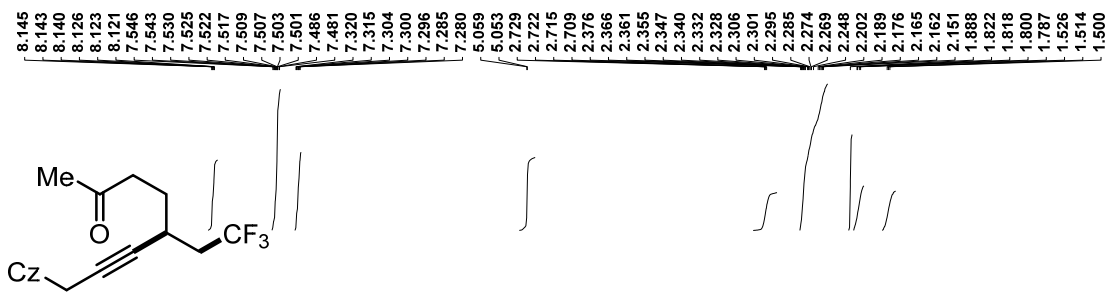
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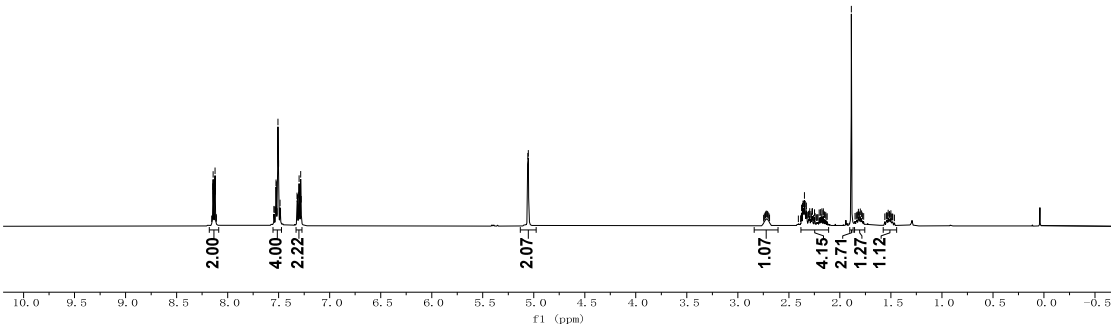
CF3
Cz

6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f1 (ppm)


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123.24
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119.55
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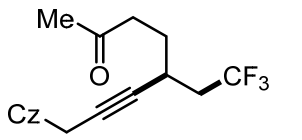
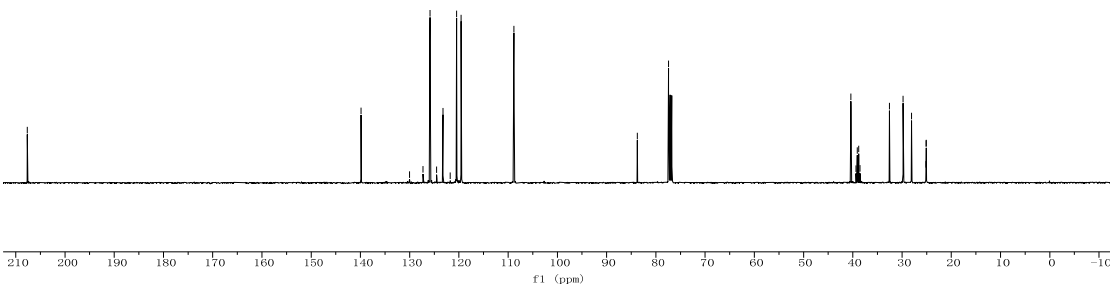
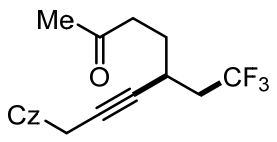
83.76
77.43
40.39
39.37
39.09
38.81
38.53
32.57
29.79
28.08
25.15
25.12
25.09
25.06


Me
O
CF3
Cz

6

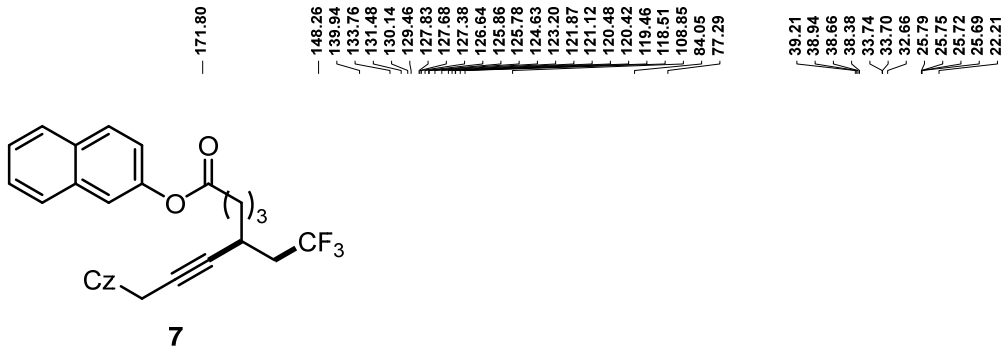

f1 (ppm)


Me
O
CF3
Cz

6

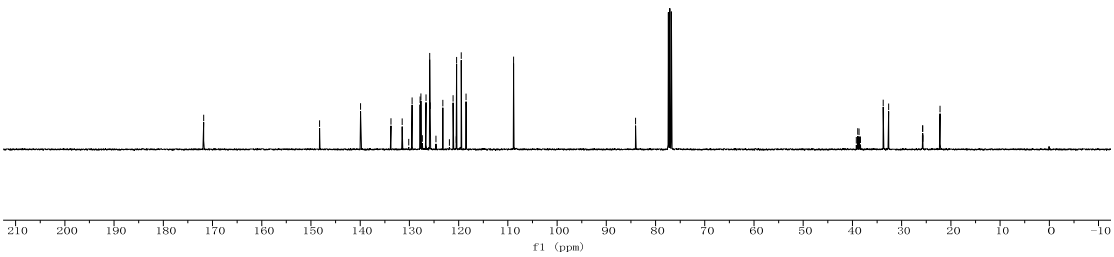
-64.173
f1 (ppm)
8.149
8.130
7.905
7.889
7.883
7.861
7.857
7.843
7.838
7.566
7.559
7.555
7.550
7.535
7.525
7.516
7.502
7.498
7.322
7.312
7.302
7.294
7.291
7.285
7.237
7.231
7.214
7.209
5.085
5.081
2.796
2.787
2.779
2.773
2.589
2.571
2.552
2.352
2.332
2.326
2.306
2.256
2.242
2.229
2.216
2.204
1.930
1.916
1.826
1.815
1.799
1.688
1.681
1.674
1.661
1.648
1.598
1.586
1.574
1.550
O
O
3
CF3
Cz
1.90
2.82
6.80
1.95
0.93
2.07
0.97
1.88
2.16
2.00
2.23
f1 (ppm)

7

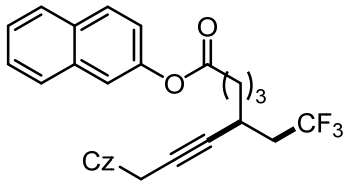

171.80
148.26
139.94
133.76
131.48
130.14
129.46
127.83
127.68
127.38
126.64
125.86
125.78
124.63
123.20
121.87
121.12
120.48
120.42
119.46
118.51
108.85
84.05
77.29
39.21
38.94
38.66
38.38
33.74
33.70
32.66
25.79
25.75
25.72
25.69
22.21

O
O
3
CF3
Cz

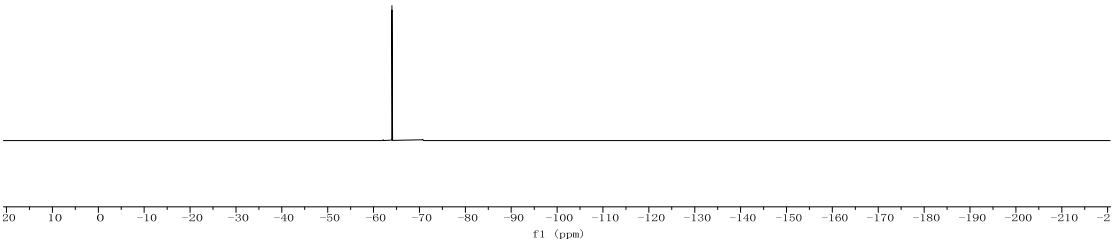
7

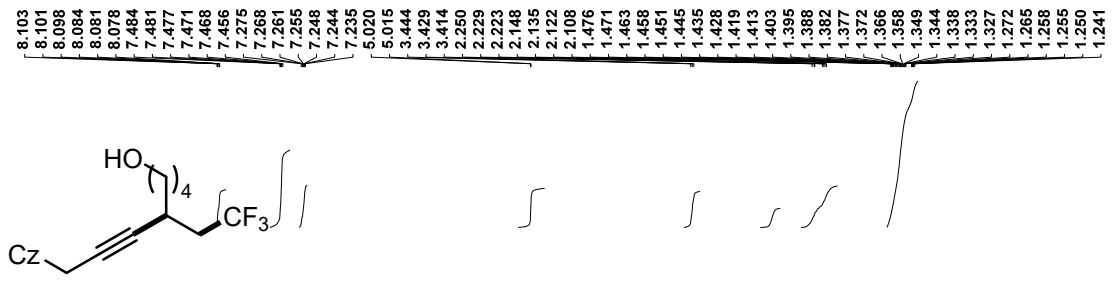

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-64.016

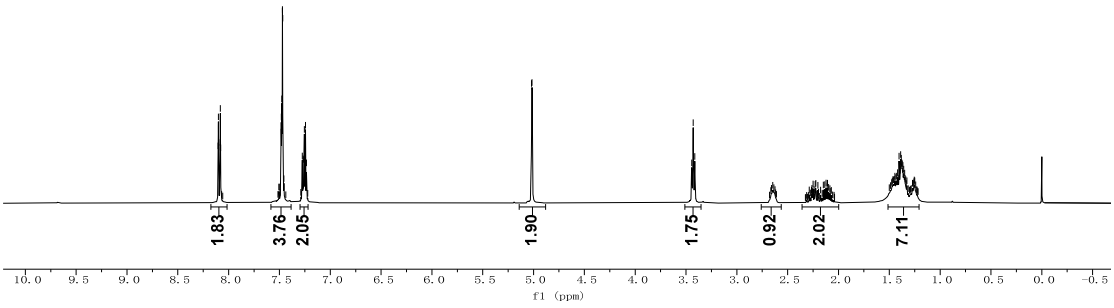

O
O
3
CF3
Cz

7

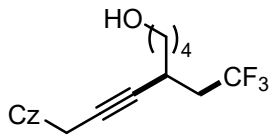

20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)


8.103
8.101
8.098
8.084
8.081
8.078
7.484
7.481
7.477
7.471
7.468
7.456
7.275
7.268
7.261
7.255
7.248
7.244
7.235
5.020
5.015
3.444
3.429
3.414
2.250
2.229
2.223
2.148
2.135
2.122
2.108
1.476
1.471
1.463
1.458
1.451
1.445
1.435
1.428
1.419
1.413
1.403
1.395
1.388
1.382
1.377
1.372
1.366
1.358
1.349
1.344
1.338
1.333
1.327
1.272
1.265
1.258
1.255
1.250
1.241
HO
4
CF3
Cz

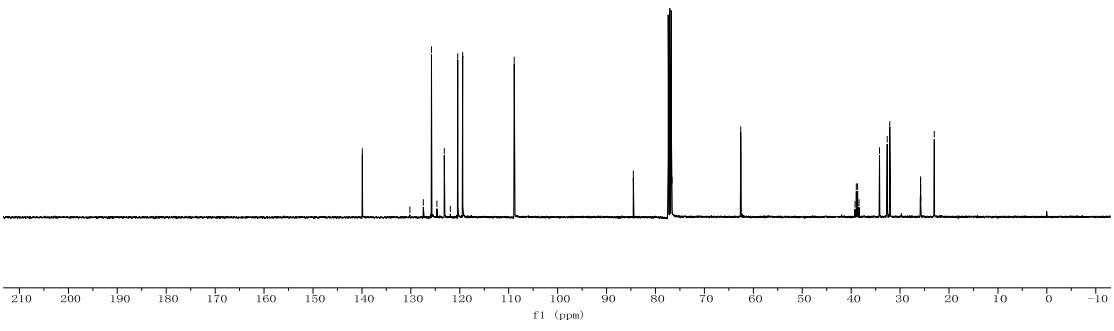
8

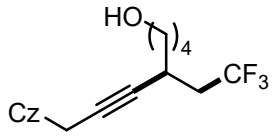

1.83
3.76
2.05
1.90
1.75
0.92
2.02
7.11
f1 (ppm)


139.92
130.20
127.44
125.78
124.68
123.16
121.92
120.41
119.41
108.87
84.54
76.60
62.58
39.22
38.94
38.67
38.39
34.21
32.64
32.10
25.85
25.82
25.79
25.76
23.02


HO
4
CF3
Cz

8


f1 (ppm)

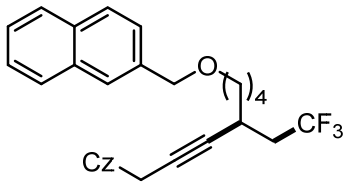

HO
4
CF3
Cz

8

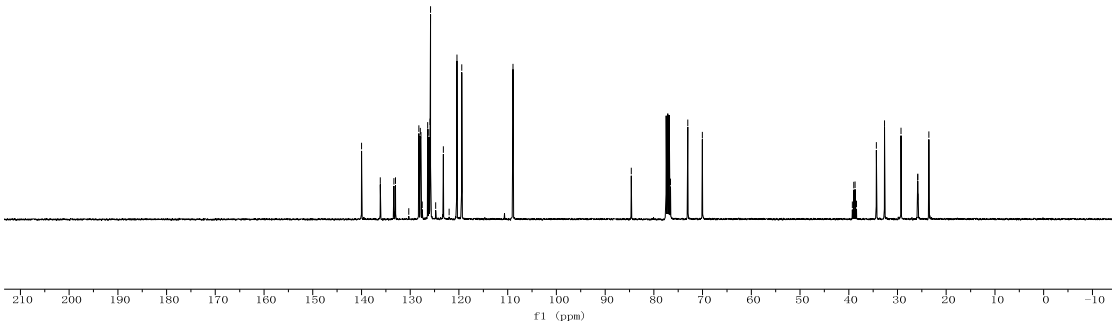
-64.184
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
8.057 8.050 8.037 8.031 7.823 7.817 7.810 7.803 7.799 7.792 7.786 7.780 7.733 7.724 7.468 7.462 7.457 7.448 7.439 7.434 7.429 7.421 7.406 7.400 7.235 7.227 7.219 7.216 7.207 7.198 7.190 4.957 4.952 4.572 4.566 3.339 3.333 3.323 3.317 3.307 3.301 1.513 1.504 1.496 1.489 1.477 1.439 1.430 1.415 1.408 1.389 1.388 1.382 1.358 1.354 1.344 1.338 1.333 1.324 1.313
O
4
CF3
Cz
2.06 3.06 1.03 7.17 2.25 2.02 2.03 2.00 1.00 2.16 6.21
10.0 9.5 9.0 8.5 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 -0.5
f1 (ppm)

9

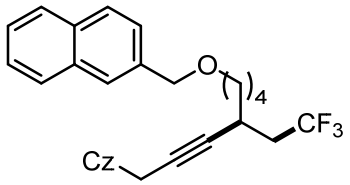

139.97
136.14
133.36
133.03
130.30
128.22
127.93
127.79
127.54
126.40
126.18
125.91
125.84
124.78
123.21
122.02
120.42
119.43
108.92
84.64
76.59
73.04
70.04
39.25
38.97
38.70
38.42
34.33
32.66
29.27
25.89
25.86
25.83
25.80
23.56


O
4
CF3
Cz

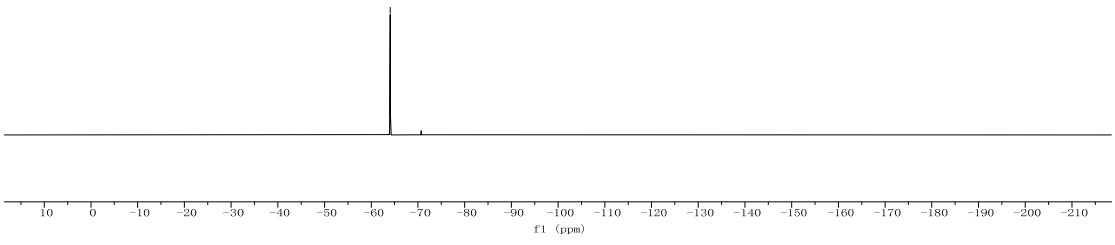
9

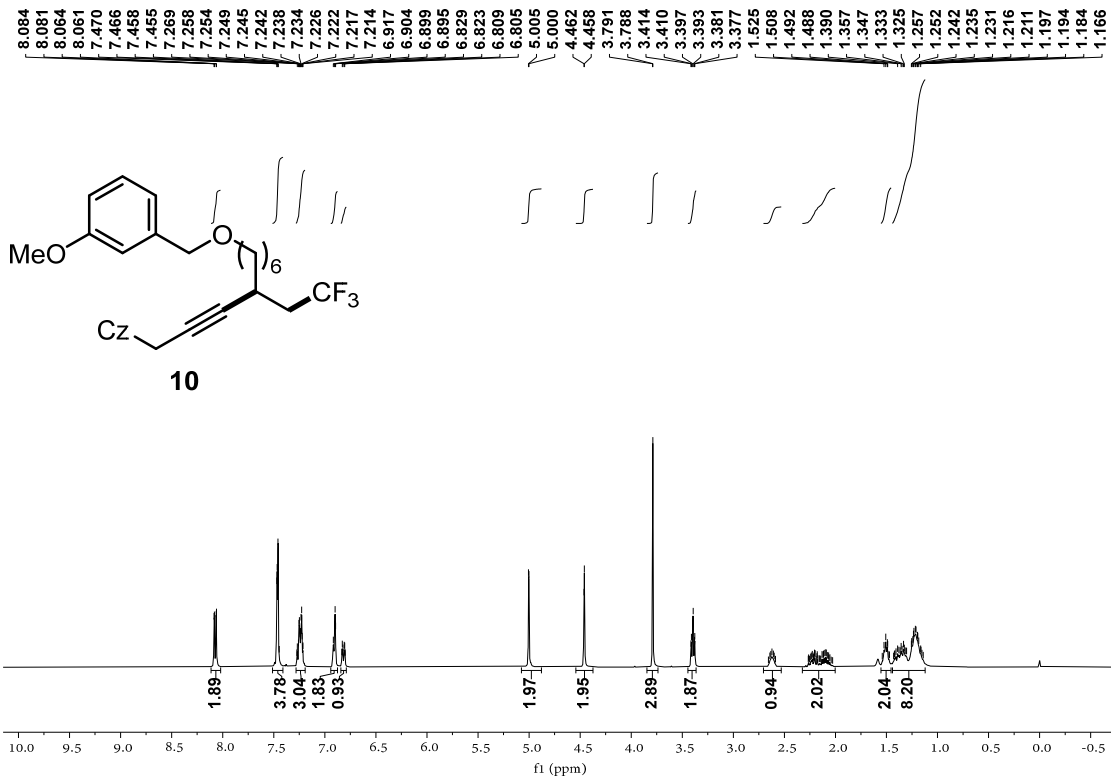

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


-64.071


O
4
CF3
Cz

9


10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)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8.061
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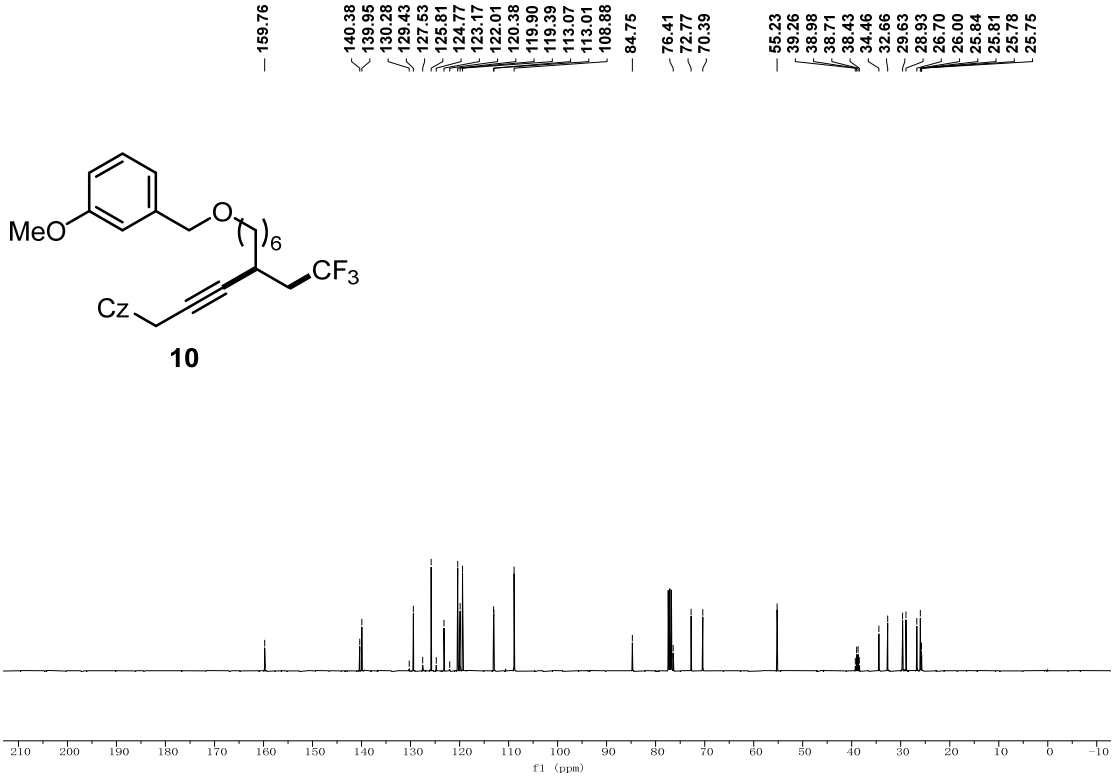
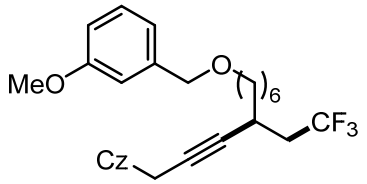
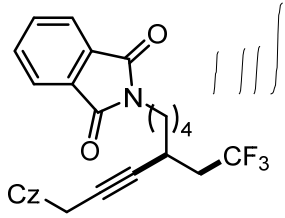
7.466
7.458
7.455
7.269
7.258
7.254
7.249
7.245
7.242
7.238
7.234
7.226
7.222
7.217
7.214
6.917
6.904
6.899
6.895
6.829
6.823
6.809
6.805
5.005
5.000
4.462
4.458
3.791
3.788
3.414
3.410
3.397
3.393
3.381
3.377
1.525
1.508
1.492
1.488
1.390
1.357
1.347
1.333
1.325
1.257
1.252
1.242
1.235
1.231
1.216
1.211
1.197
1.194
1.184
1.166
MeO
O
6
CF3
Cz
10
1.89
3.78
3.04
1.83
0.93
1.97
1.95
2.89
1.87
0.94
2.02
2.04
8.20
10.0 9.5 9.0 8.5 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 -0.5
f1 (ppm)


159.76
140.38
139.95
130.28
129.43
127.53
125.81
124.77
123.17
122.01
120.38
119.90
119.39
113.07
113.01
108.88
84.75
76.41
72.77
70.39
55.23
39.26
38.98
38.71
38.43
34.46
32.66
29.63
28.93
26.70
26.00
25.84
25.81
25.78
25.75
MeO
O
6
CF3
Cz
10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

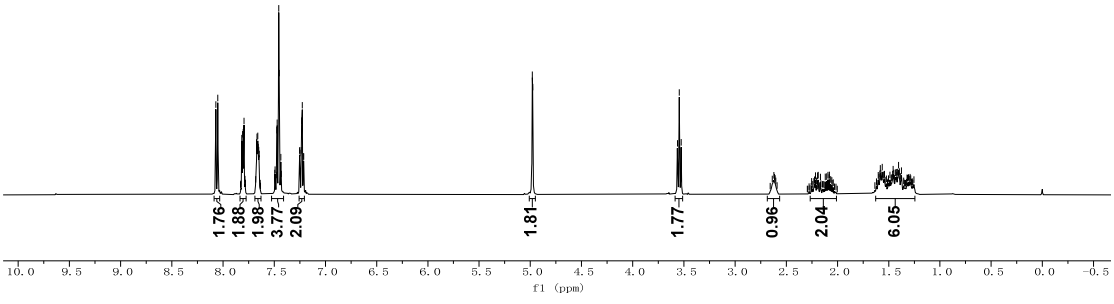

MeO
O
6
CF3
Cz

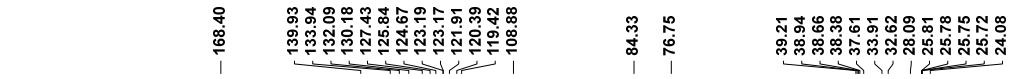
10

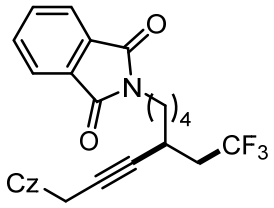
-64.082
f1 (ppm)
8.071
8.051
7.817
7.809
7.803
7.796
7.673
7.669
7.665
7.661
7.656
7.651
7.647
7.496
7.493
7.480
7.475
7.472
7.457
7.452
7.436
7.431
7.252
7.248
7.237
7.232
7.227
7.217
7.212
4.981
4.976
3.563
3.545
3.527
2.622
2.215
2.194
2.188
2.093
2.079
1.602
1.588
1.582
1.577
1.564
1.554
1.546
1.541
1.488
1.462
1.457
1.451
1.435
1.426
1.421
1.414
1.404
1.397
1.384
1.376


O
N
4
O
CF3
Cz

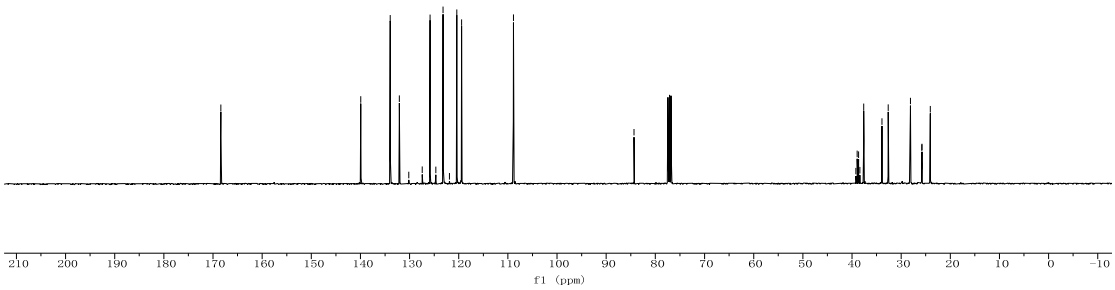
11


1.76
1.88
1.98
3.77
2.09
1.81
1.77
0.96
2.04
6.05
f1 (ppm)

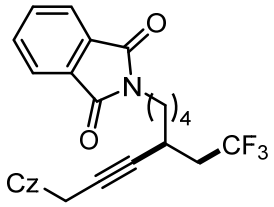

168.40
139.93
133.94
132.09
130.18
127.43
125.84
124.67
123.19
123.17
121.91
120.39
119.42
108.88
84.33
76.75
39.21
38.94
38.66
38.38
37.61
33.91
32.62
28.09
25.81
25.78
25.75
25.72
24.08


O
N
4
O
CF3
Cz

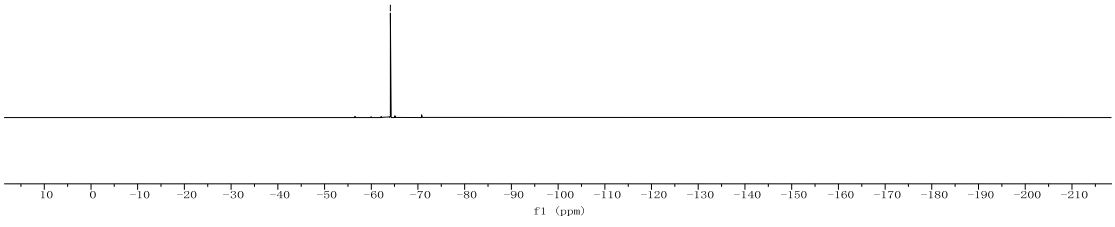
11

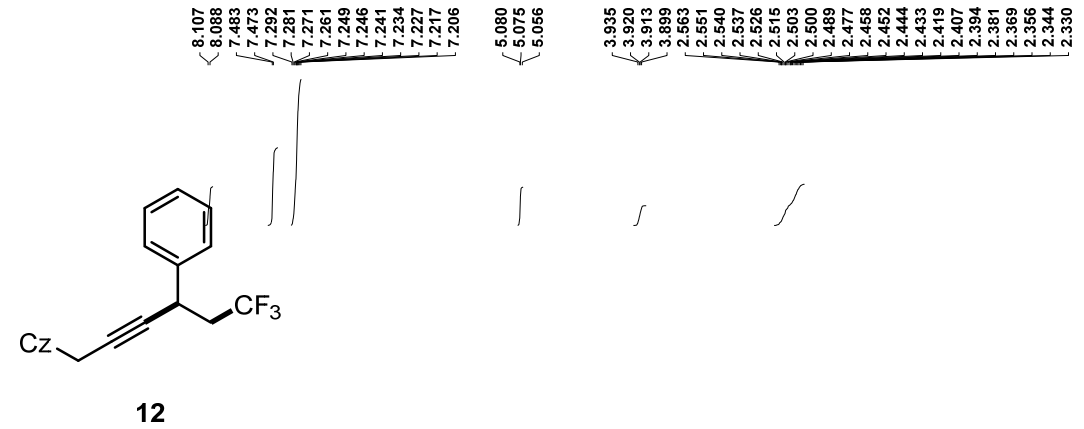

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


-64.110


O
N
4
O
CF3
Cz

11


10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)


8.107
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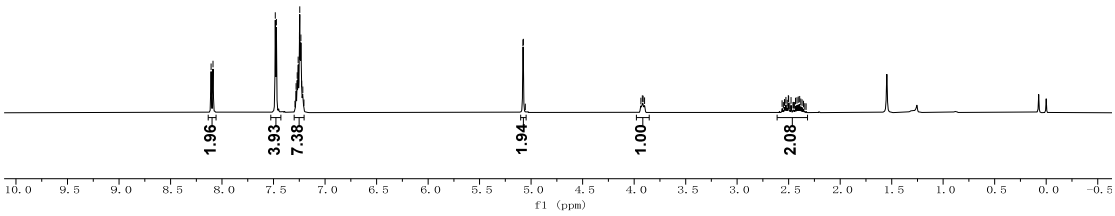
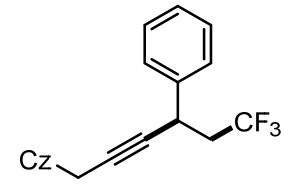
7.473
7.292
7.281
7.271
7.261
7.249
7.246
7.241
7.234
7.227
7.217
7.206
5.080
5.075
5.056
3.935
3.920
3.913
3.899
2.563
2.551
2.540
2.537
2.526
2.515
2.503
2.500
2.489
2.477
2.458
2.452
2.444
2.433
2.419
2.407
2.394
2.381
2.369
2.356
2.344
2.330
CF3
Cz

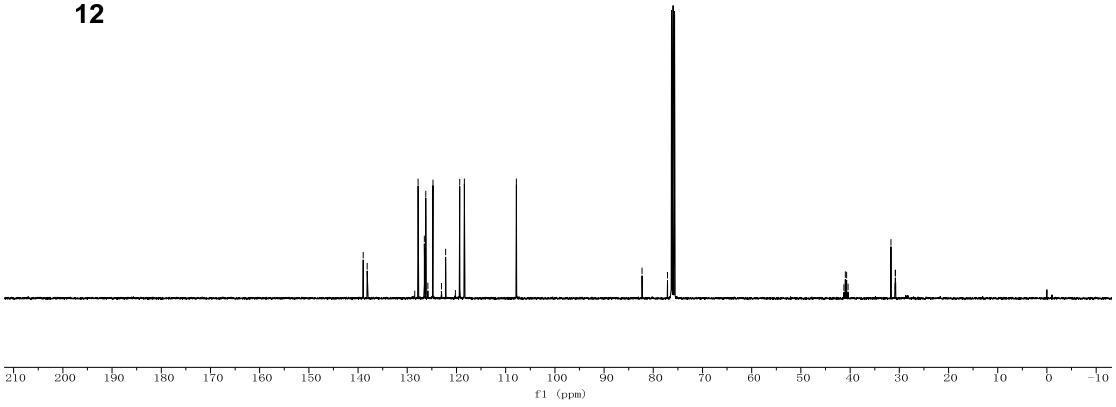
12

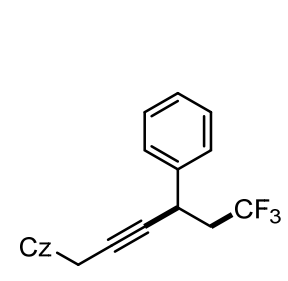

1.96
3.93
7.38
1.94
1.00
2.08
f1 (ppm)


138.95
138.14
128.49
127.79
126.53
126.23
125.83
124.79
123.06
122.20
120.22
119.34
118.41
107.83
82.27
77.10
41.26
40.98
40.71
40.43
31.71
30.87
30.83
30.80
30.77


CF3
Cz

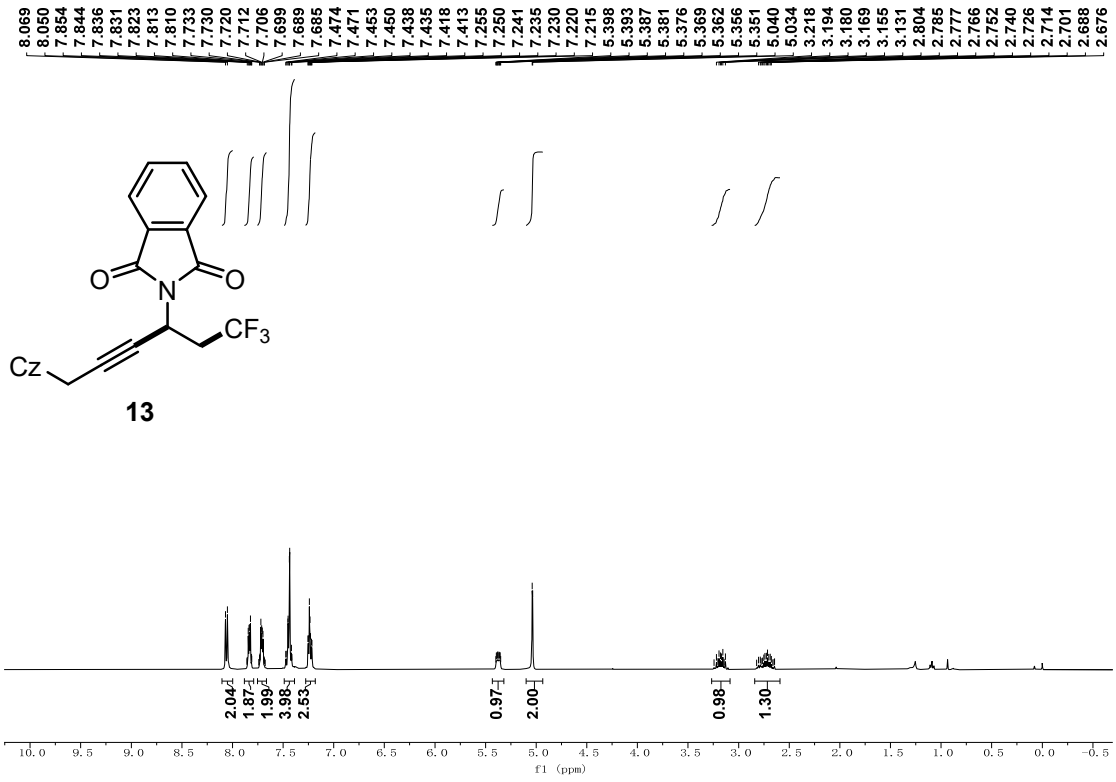
12


f1 (ppm)


Cz
CF3

12

-64.391
f1 (ppm)


8.069
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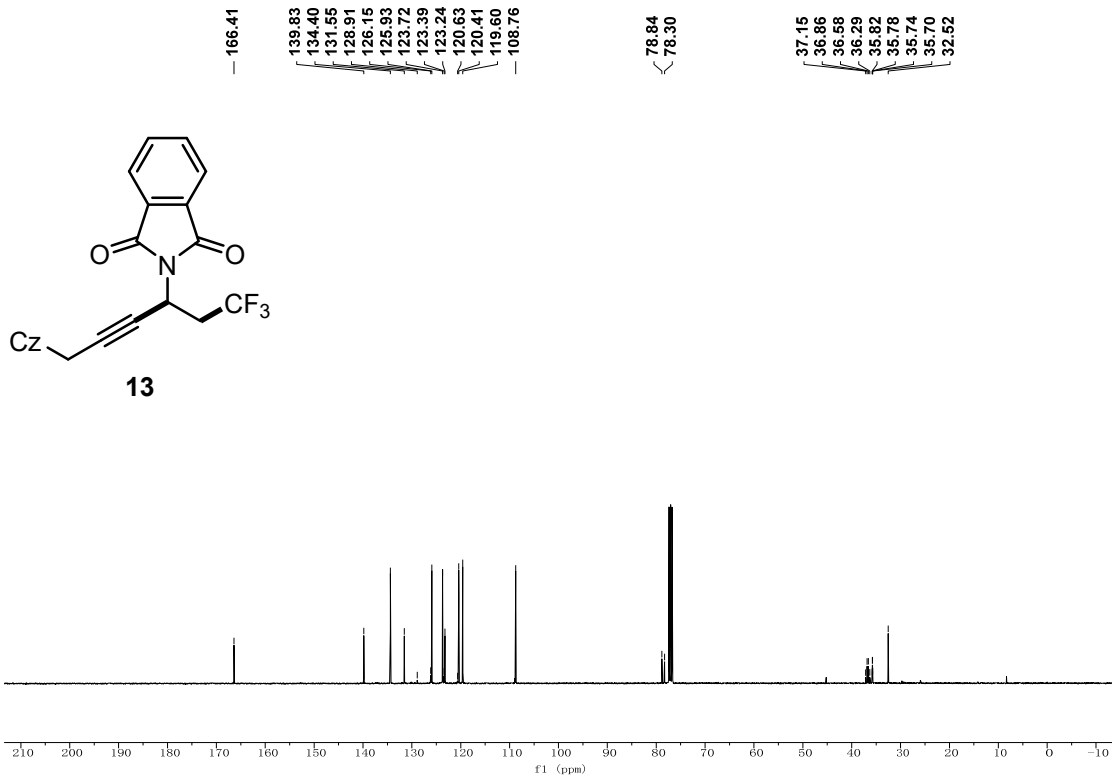
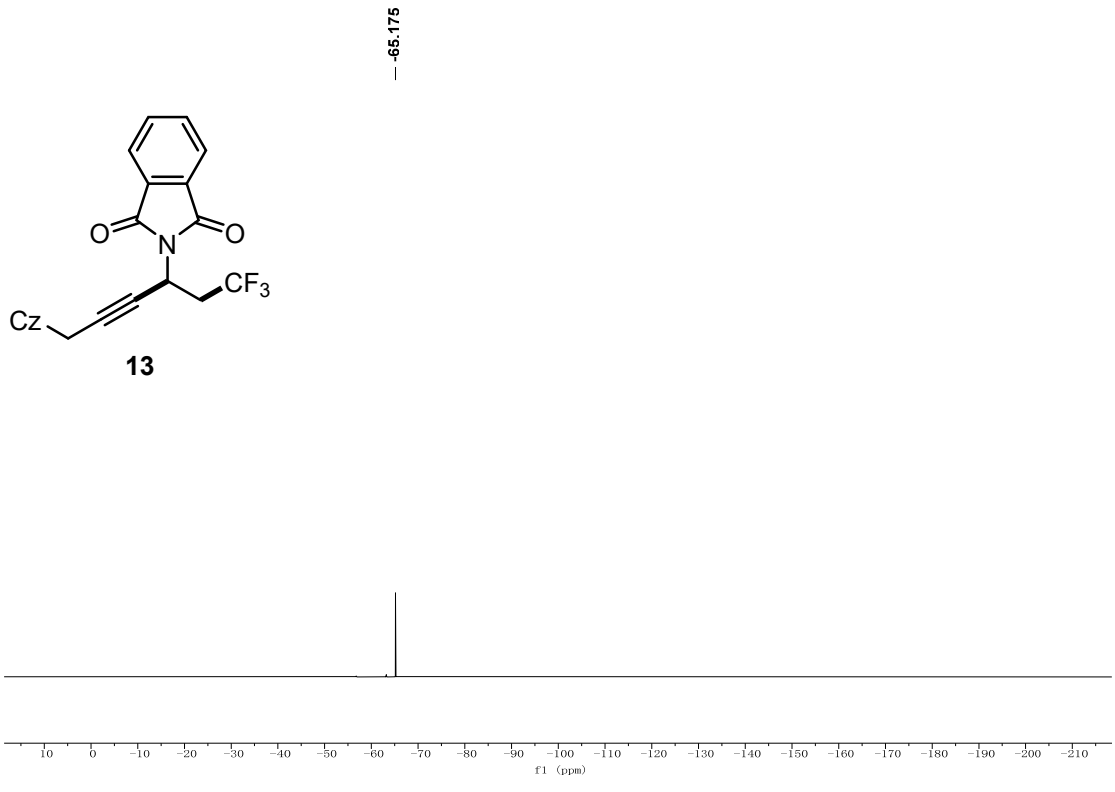
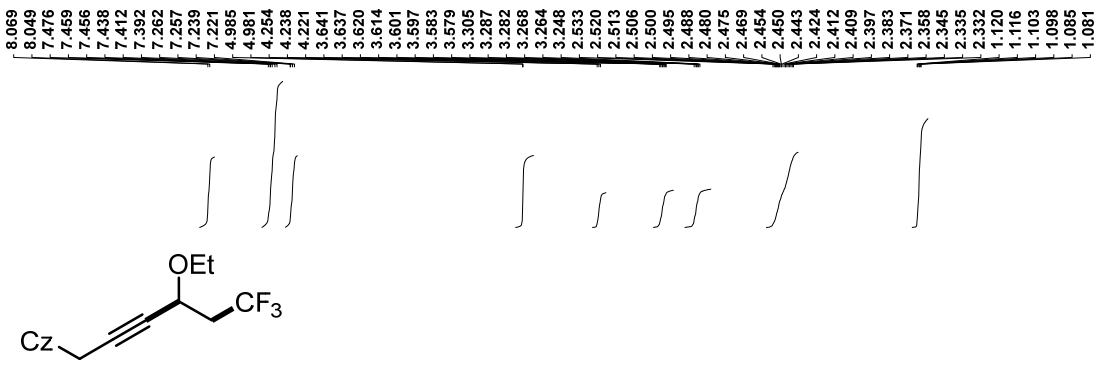
7.854
7.844
7.836
7.831
7.823
7.813
7.810
7.733
7.730
7.720
7.712
7.706
7.699
7.689
7.685
7.474
7.471
7.453
7.450
7.438
7.435
7.418
7.413
7.255
7.250
7.241
7.235
7.230
7.220
7.215
5.398
5.393
5.387
5.381
5.376
5.369
5.362
5.356
5.351
5.040
5.034
3.218
3.194
3.180
3.169
3.155
3.131
2.804
2.785
2.777
2.766
2.752
2.740
2.726
2.714
2.701
2.688
2.676
2.04
1.87
1.99
3.98
2.53
0.97
2.00
0.98
1.30
f1 (ppm)

O
N
O
CF3
Cz

13

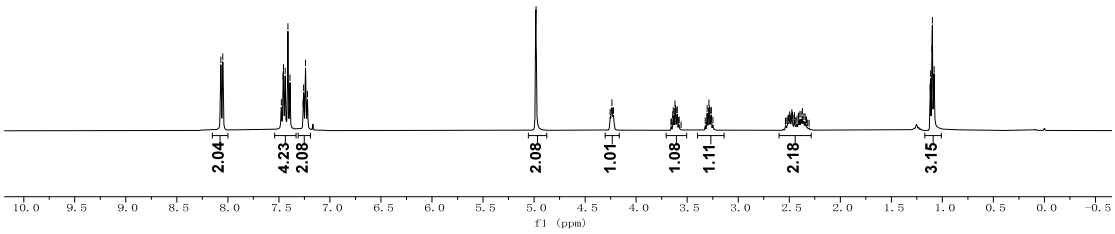

166.41
139.83
134.40
131.55
128.91
126.15
125.93
123.72
123.39
123.24
120.63
120.41
119.60
108.76
78.84
78.30
37.15
36.86
36.58
36.29
35.82
35.78
35.74
35.70
32.52
O
N
O
CF3
Cz
13
f1 (ppm)

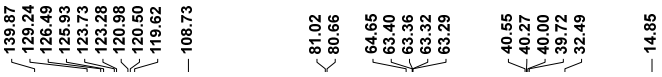

-65.175
O
N
O
CF3
Cz
13
f1 (ppm)

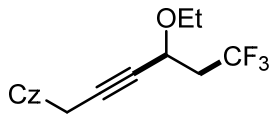

8.069
8.049
7.476
7.459
7.456
7.438
7.412
7.392
7.262
7.257
7.239
7.221
4.985
4.981
4.254
4.238
4.221
3.641
3.637
3.620
3.614
3.601
3.597
3.583
3.579
3.305
3.287
3.282
3.268
3.264
3.248
2.533
2.520
2.513
2.506
2.500
2.495
2.488
2.480
2.475
2.469
2.454
2.450
2.443
2.424
2.412
2.409
2.397
2.383
2.371
2.358
2.345
2.335
2.332
1.120
1.116
1.103
1.098
1.085
1.081

OEt
CF3
Cz

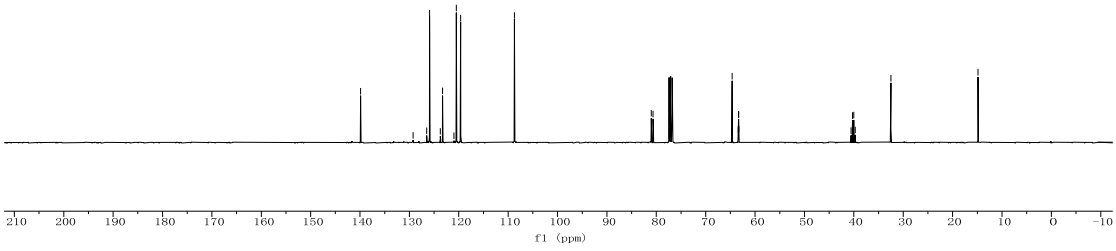
14

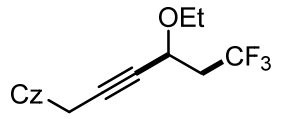

2.04
4.23
2.08
2.08
1.01
1.08
1.11
2.18
3.15
f1 (ppm)


139.87
129.24
126.49
125.93
123.73
123.28
120.98
120.50
119.62
108.73
81.02
80.66
64.65
63.40
63.36
63.32
63.29
40.55
40.27
40.00
39.72
32.49
14.85


OEt
CF3
Cz

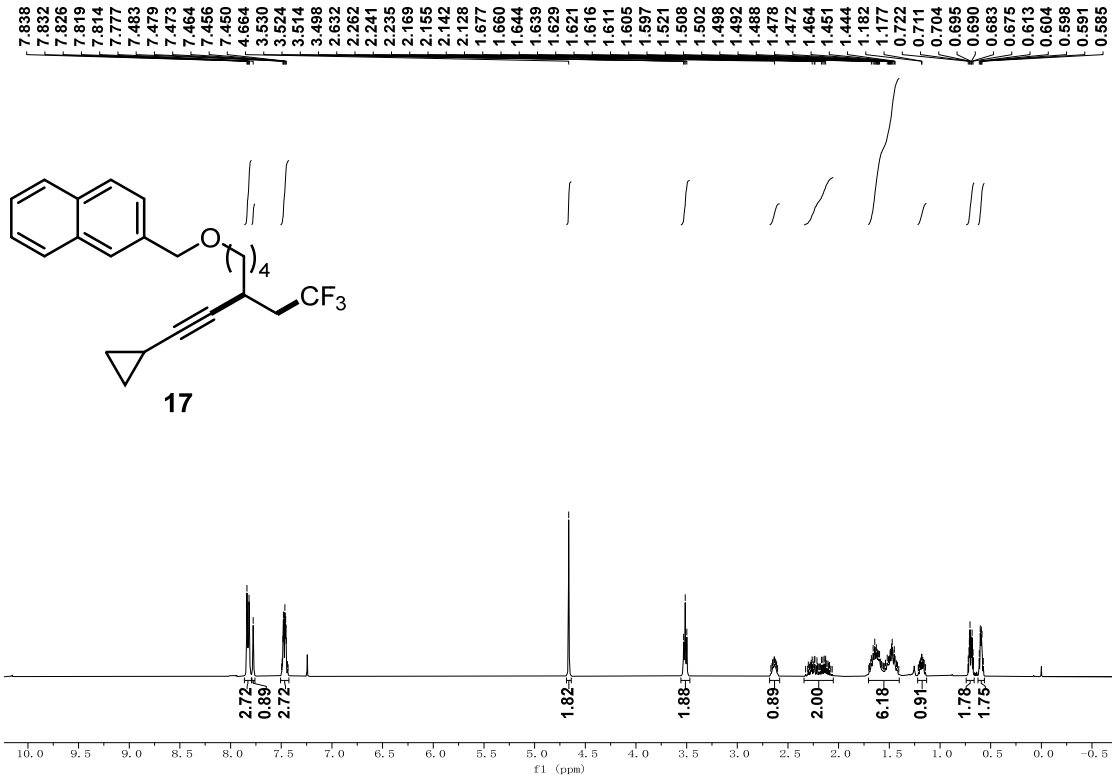
14


f1 (ppm)


OEt
CF3
Cz

14

-63.769
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.838
7.832
7.826
7.819
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7.777
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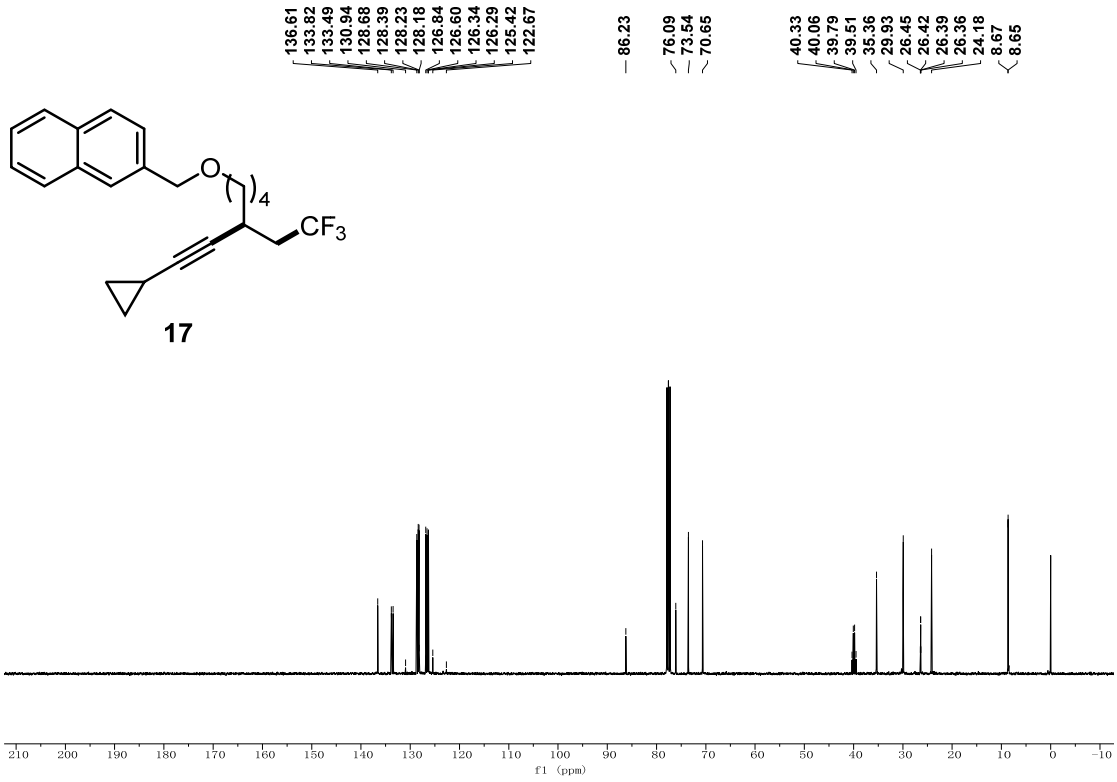
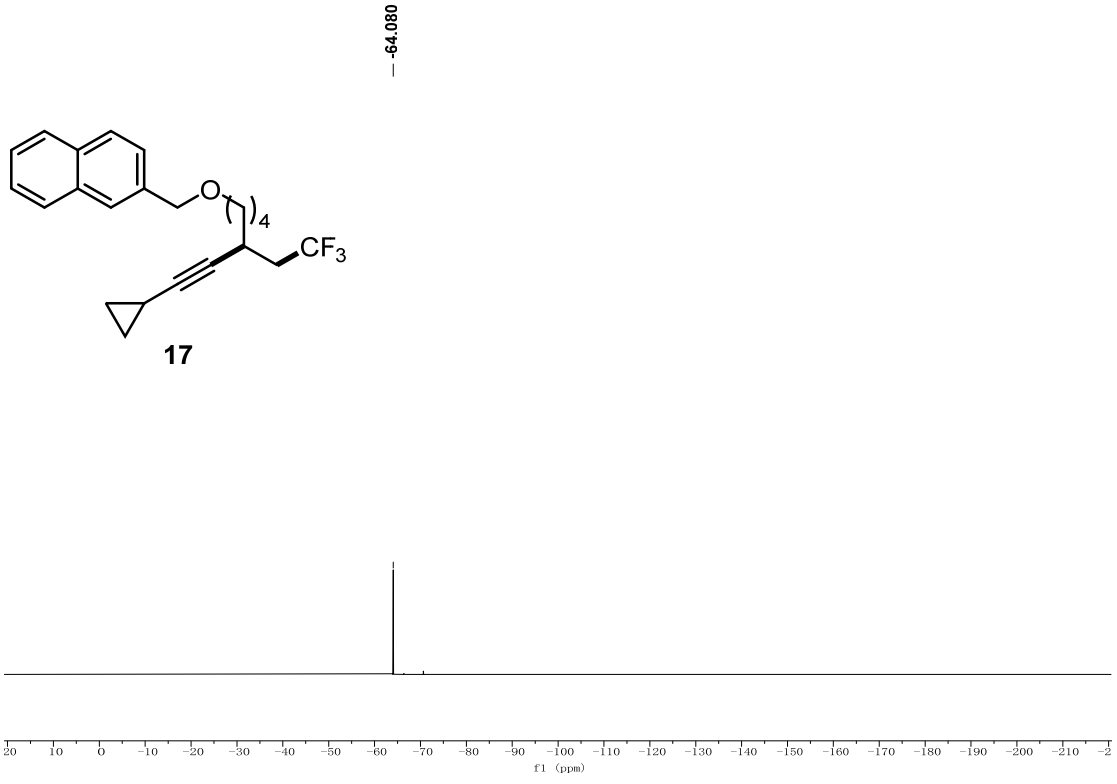
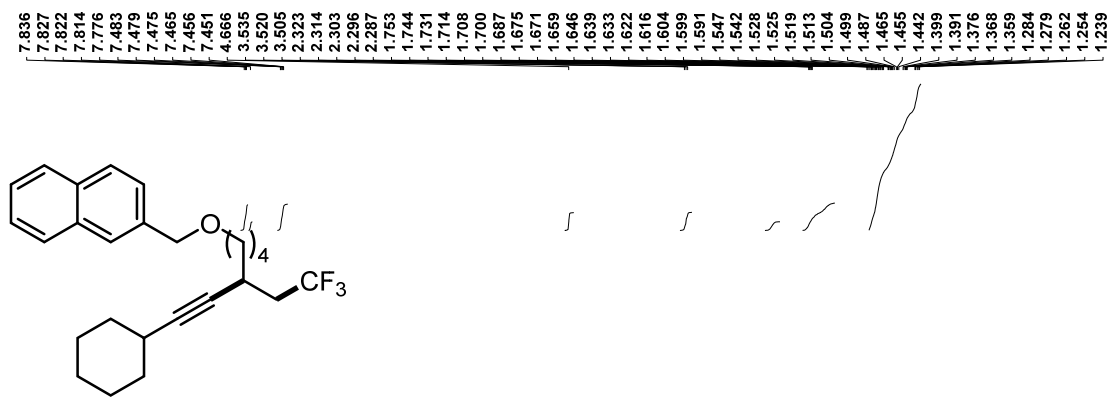
7.479
7.473
7.464
7.456
7.450
4.664
3.530
3.524
3.514
3.498
2.632
2.262
2.241
2.235
2.169
2.155
2.142
2.128
1.677
1.660
1.644
1.639
1.629
1.621
1.616
1.611
1.605
1.597
1.521
1.508
1.502
1.498
1.492
1.488
1.478
1.472
1.464
1.451
1.444
1.182
1.177
0.722
0.711
0.704
0.695
0.690
0.683
0.675
0.613
0.604
0.598
0.591
0.585
2.72
0.89
2.72
1.82
1.88
0.89
2.00
6.18
0.91
1.78
1.75
10.0 9.5 9.0 8.5 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 -0.5
f1 (ppm)

O
4
CF3

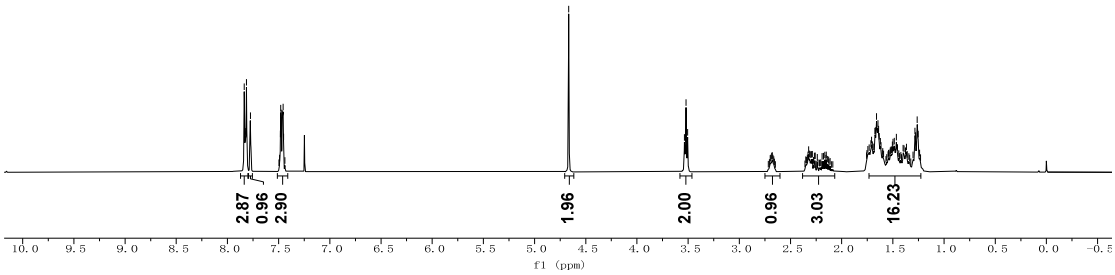
17


136.61
133.82
133.49
130.94
128.68
128.39
128.23
128.18
126.84
126.60
126.34
126.29
125.42
122.67
86.23
76.09
73.54
70.65
40.33
40.06
39.79
39.51
35.36
29.93
26.45
26.42
26.39
26.36
24.18
8.67
8.65
O
4
CF3
17
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-64.080
O
4
CF3
17
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)


7.836
7.827
7.822
7.814
7.776
7.483
7.479
7.475
7.465
7.456
7.451
4.666
3.535
3.520
3.505
2.323
2.314
2.303
2.296
2.287
1.753
1.744
1.731
1.714
1.708
1.700
1.687
1.675
1.671
1.659
1.646
1.639
1.633
1.622
1.616
1.604
1.599
1.591
1.547
1.542
1.528
1.525
1.519
1.513
1.504
1.499
1.487
1.465
1.455
1.442
1.399
1.391
1.376
1.368
1.359
1.284
1.279
1.262
1.254
1.239
O
4
CF3

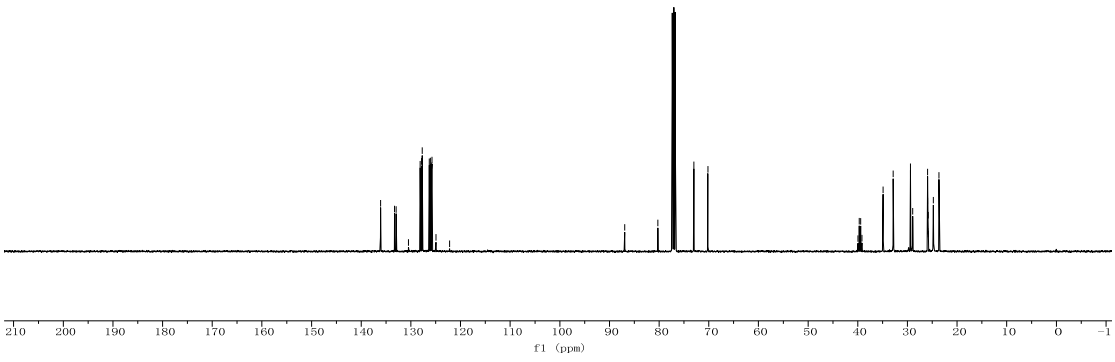
18

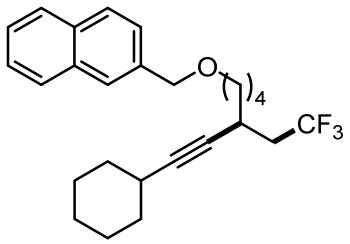

2.87
0.96
2.90
1.96
2.00
0.96
3.03
16.23
f1 (ppm)


136.10
133.29
132.96
130.47
128.14
127.85
127.70
126.29
126.08
125.81
125.75
124.96
122.20
86.92
80.27
73.00
70.18
39.97
39.70
39.43
39.15
34.90
32.87
29.40
28.94
25.94
25.93
25.90
25.87
25.84
25.81
24.77
23.64


O
4
CF3

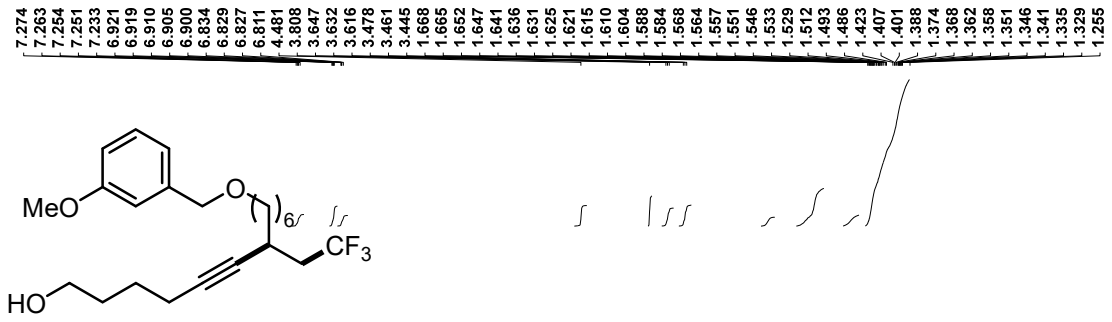
18


f1 (ppm)


O
4
CF3

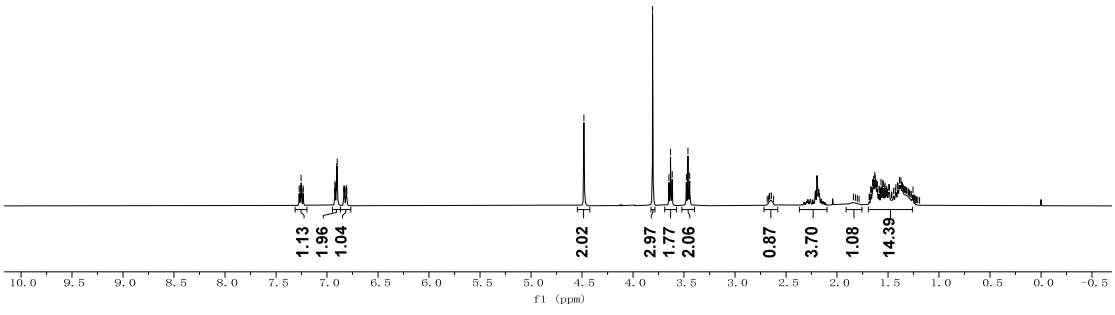
18

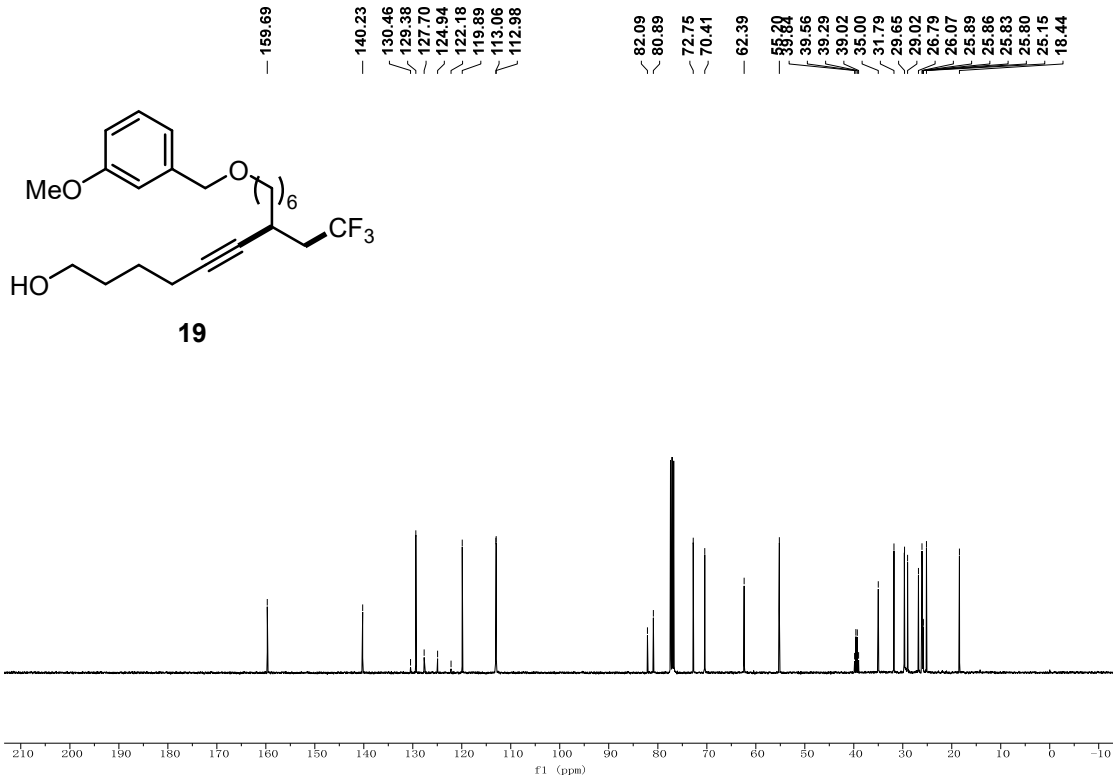
-63.990
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

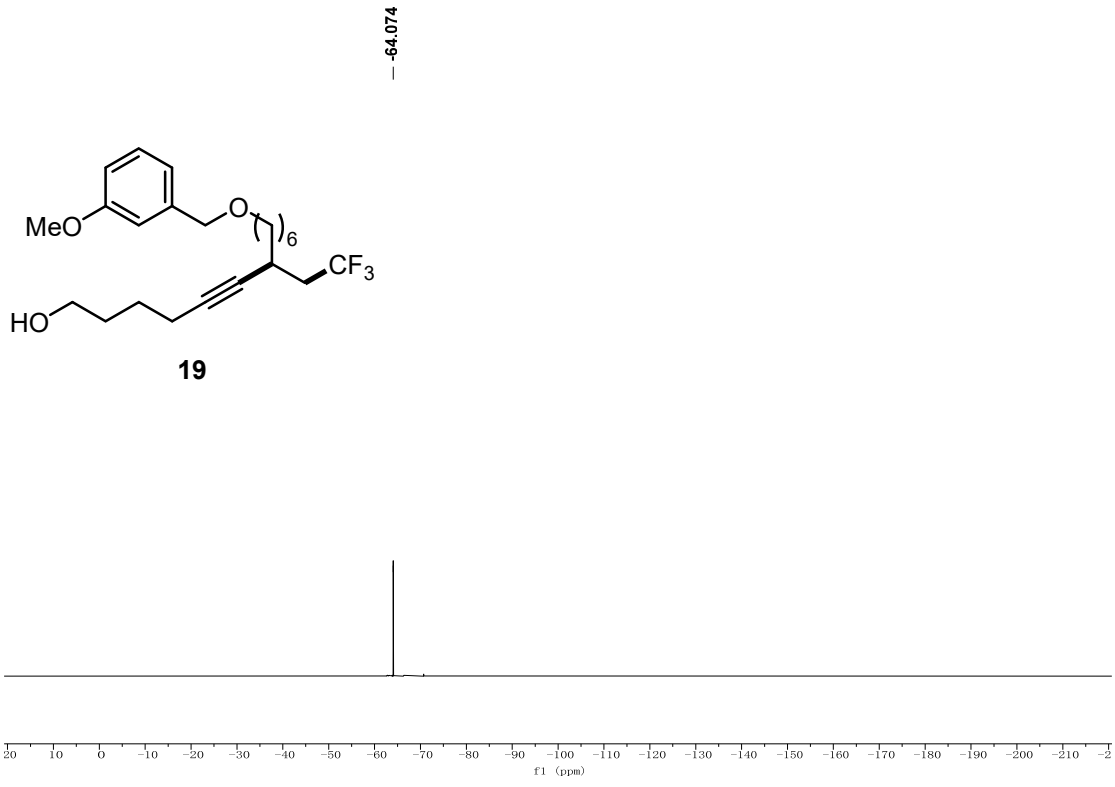

7.274
7.263
7.254
7.251
7.233
6.921
6.919
6.910
6.905
6.900
6.834
6.829
6.827
6.811
4.481
3.808
3.647
3.632
3.616
3.478
3.461
3.445
1.668
1.665
1.652
1.647
1.641
1.636
1.631
1.625
1.621
1.615
1.610
1.604
1.588
1.584
1.568
1.564
1.557
1.551
1.546
1.533
1.529
1.512
1.493
1.486
1.423
1.407
1.401
1.388
1.374
1.368
1.362
1.358
1.351
1.346
1.341
1.335
1.329
1.255

MeO
O
6
CF3
HO

19


1.13
1.96
1.04
2.02
2.97
1.77
2.06
0.87
3.70
1.08
14.39
10.0 9.5 9.0 8.5 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 -0.5
f1 (ppm)


159.69
140.23
130.46
129.38
127.70
124.94
122.18
119.89
113.06
112.98
82.09
80.89
72.75
70.41
62.39
55.20
39.84
39.56
39.29
39.02
35.00
31.79
29.65
29.02
26.79
26.07
25.89
25.86
25.83
25.80
25.15
18.44
MeO
O
6
CF3
HO
19
f1 (ppm)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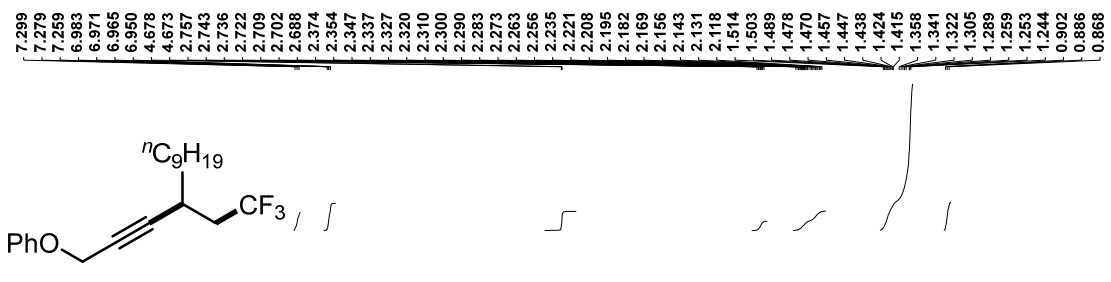
O
6
CF3
HO
19
f1 (ppm)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7.259
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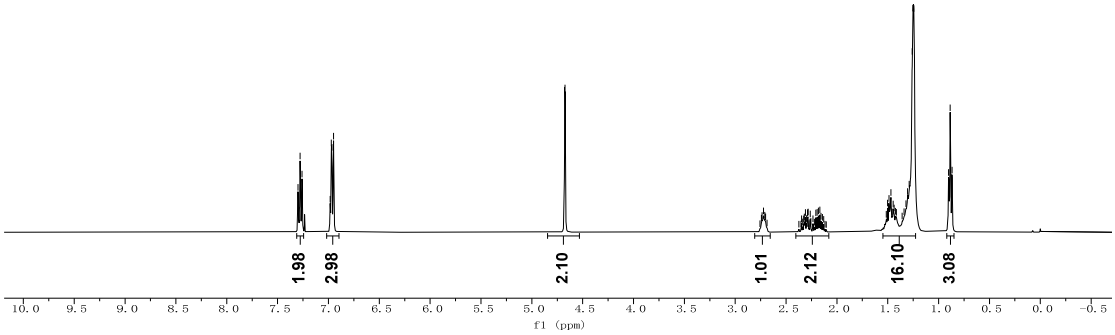
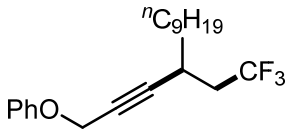
6.971
6.965
6.950
4.678
4.673
2.757
2.743
2.736
2.722
2.709
2.702
2.688
2.374
2.354
2.347
2.337
2.327
2.320
2.310
2.300
2.290
2.283
2.273
2.263
2.256
2.235
2.221
2.208
2.195
2.182
2.169
2.156
2.143
2.131
2.118
1.514
1.503
1.489
1.478
1.470
1.457
1.447
1.438
1.424
1.415
1.358
1.341
1.322
1.305
1.289
1.259
1.253
1.244
0.902
0.886
0.868
nC9H19
CF3
PhO

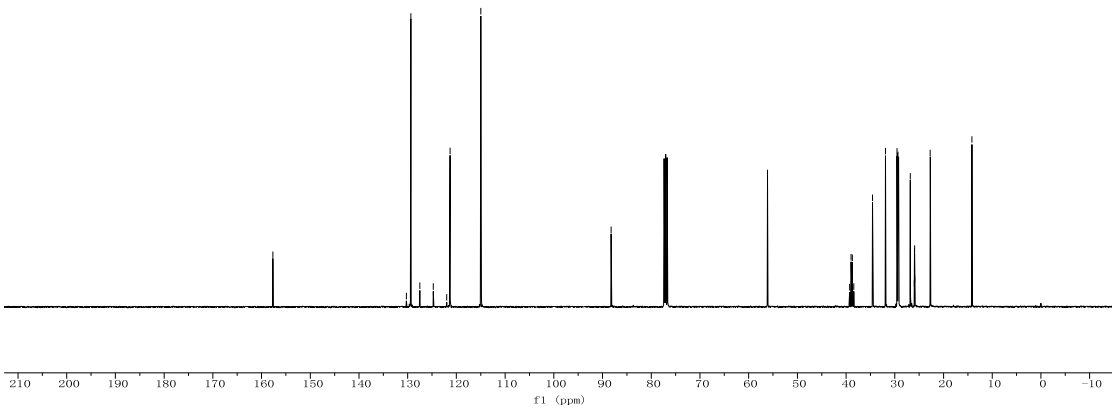
20

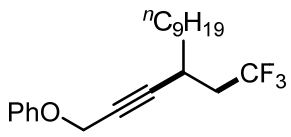

1.98
2.98
2.10
1.01
2.12
16.10
3.08
f1 (ppm)


157.69
130.27
129.36
127.52
124.76
122.00
121.31
114.98
88.23
77.17
56.15
39.26
38.98
38.71
38.43
34.58
31.92
29.56
29.49
29.34
29.21
26.81
25.98
25.96
25.93
25.90
22.73
14.15


nC9H19
CF3
PhO

20


f1 (ppm)


^{n}C$_9$H$_{19}$
CF$_3$
PhO

20

-64.253
f1 (ppm)
7.268
7.265
7.247
7.227
6.917
6.913
6.900
6.896
6.828
6.822
6.808
6.804
6.799
5.263
5.260
4.474
3.800
3.739
3.733
3.721
3.715
3.697
3.587
3.581
3.569
3.563
3.552
3.546
3.472
3.456
3.439
1.632
1.615
1.611
1.596
1.551
1.537
1.532
1.522
1.513
1.507
1.419
1.406
1.399
1.388
1.380
1.373
1.368
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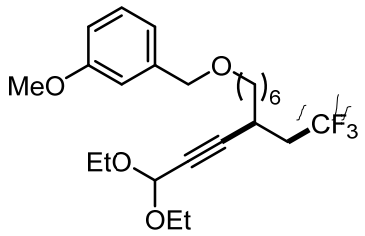
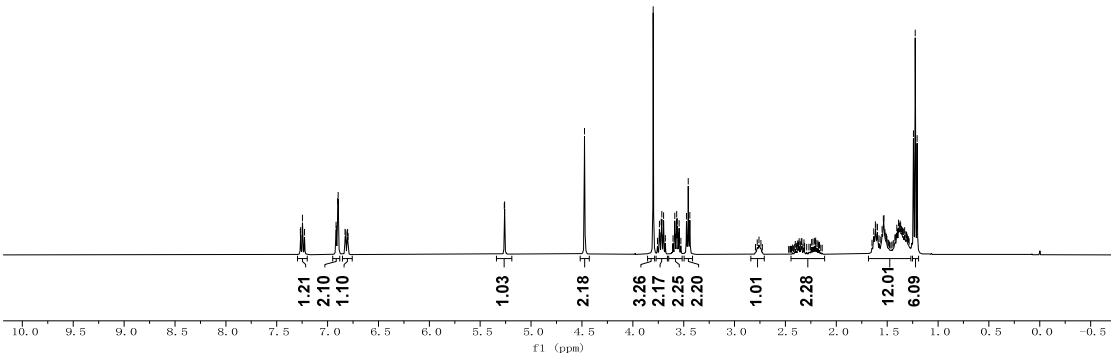
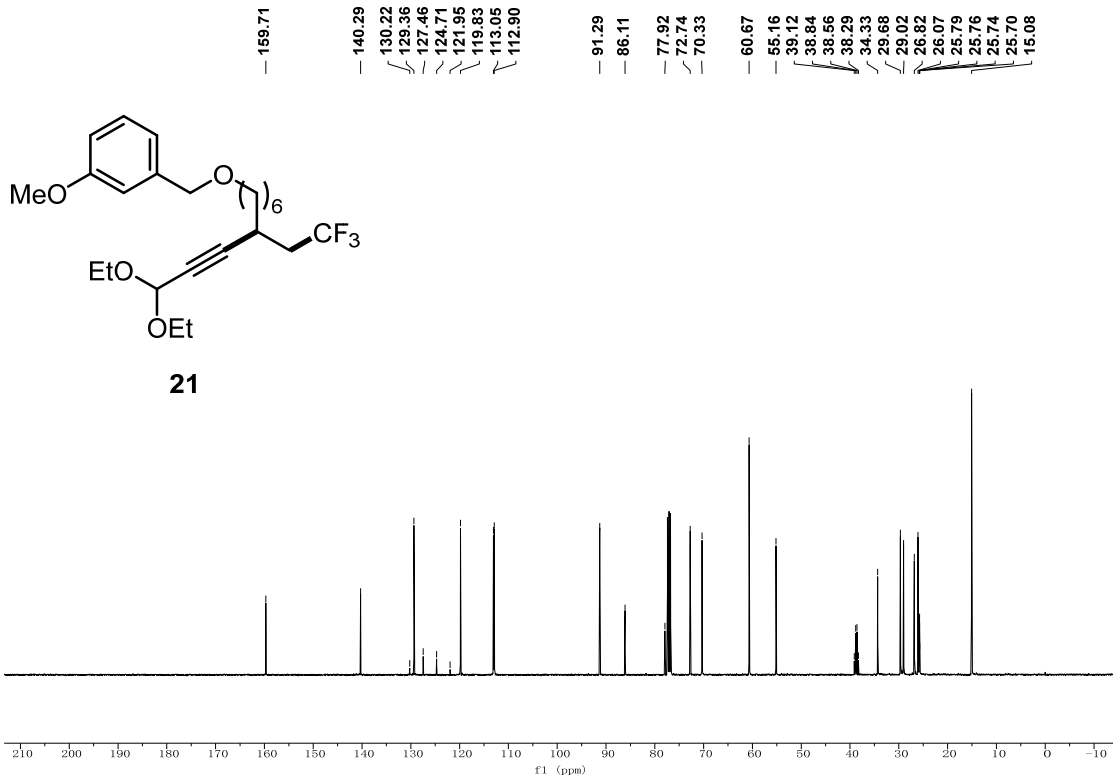
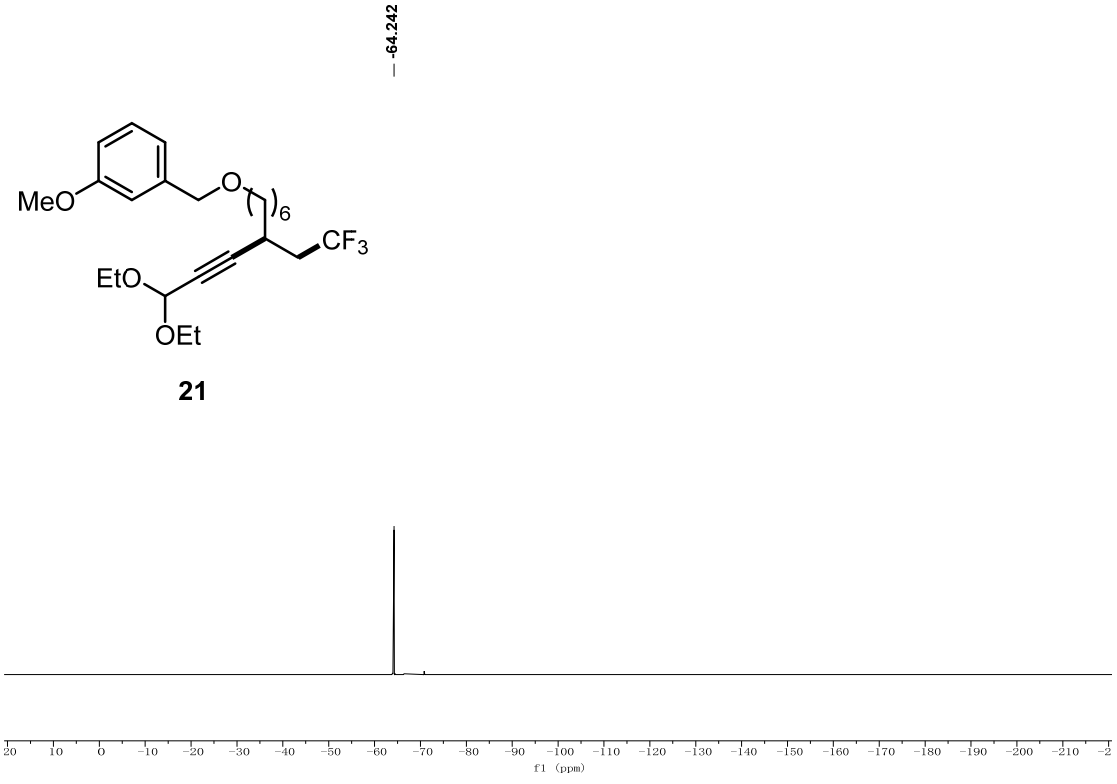
1.323
1.312
1.309
1.305
1.241
1.224
1.206


MeO
O
6
CF$_3$
EtO
OEt

21


1.21
2.10
1.10
1.03
2.18
3.26
2.17
2.25
2.20
1.01
2.28
12.01
6.09
f1 (ppm)


159.71
140.29
130.22
129.36
127.46
124.71
121.95
119.83
113.05
112.90
91.29
86.11
77.92
72.74
70.33
60.67
55.16
39.12
38.84
38.56
38.29
34.33
29.68
29.02
26.82
26.07
25.79
25.76
25.74
25.70
15.08
MeO
O
6
CF3
EtO
OEt
21
f1 (ppm)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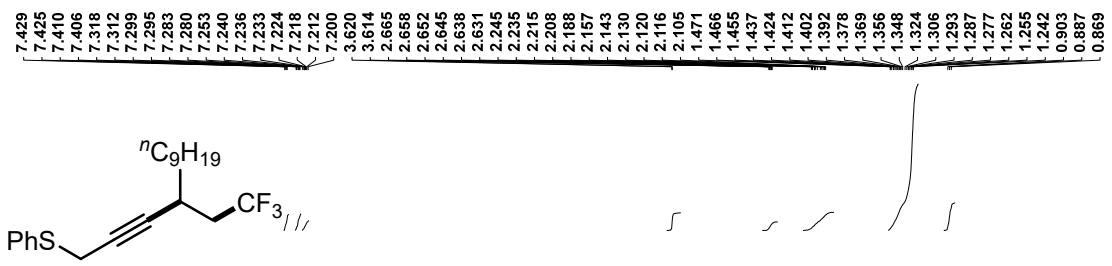
MeO
O
6
CF3
EtO
OEt
21
f1 (ppm)


7.429
7.425
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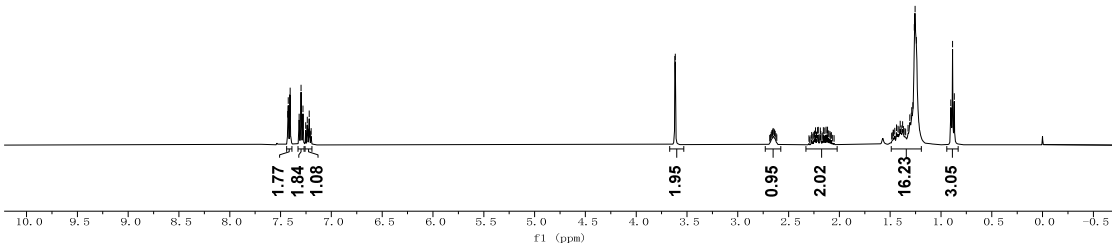
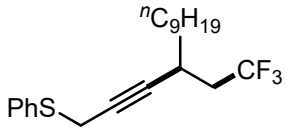
7.280
7.253
7.240
7.236
7.233
7.224
7.218
7.212
7.200
3.620
3.614
2.665
2.658
2.652
2.645
2.638
2.631
2.245
2.235
2.215
2.208
2.188
2.157
2.143
2.130
2.120
2.116
2.105
1.471
1.466
1.455
1.437
1.424
1.412
1.402
1.392
1.378
1.369
1.356
1.348
1.324
1.306
1.293
1.287
1.277
1.262
1.255
1.242
0.903
0.887
0.869
$^{n}C_9H_{19}$
CF_3
PhS

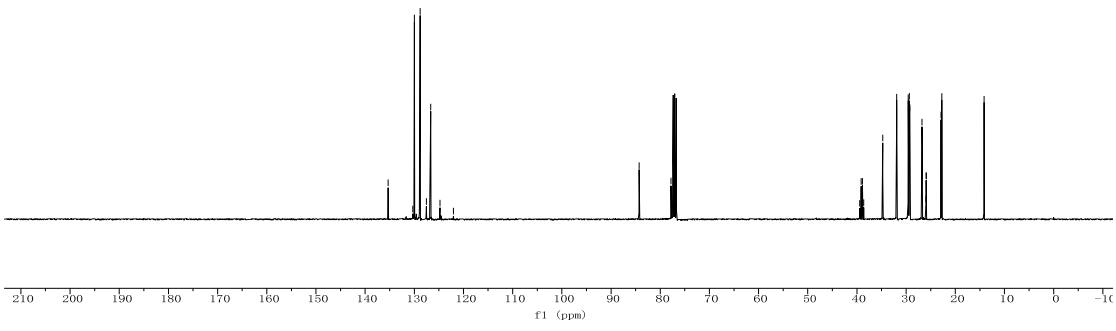
22

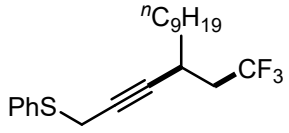

1.77
1.84
1.08
1.95
0.95
2.02
16.23
3.05
f1 (ppm)


135.32
130.31
129.99
128.83
127.55
126.67
124.79
122.04
84.30
77.80
39.43
39.16
38.88
38.61
34.75
31.93
29.58
29.50
29.34
29.24
26.78
25.97
25.94
25.91
25.88
22.89
22.73
14.16


$^{n}C_9H_{19}$
CF_3
PhS

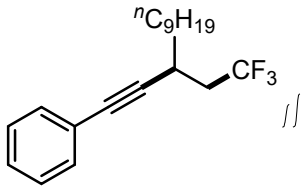
22


f1 (ppm)

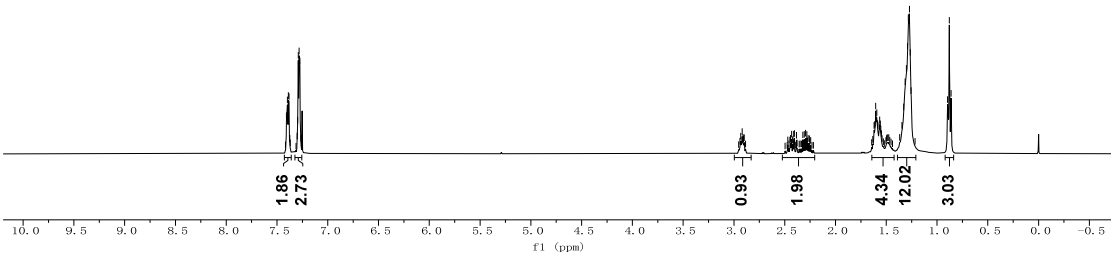

^{n}C$_9$H$_{19}$
CF$_3$
PhS

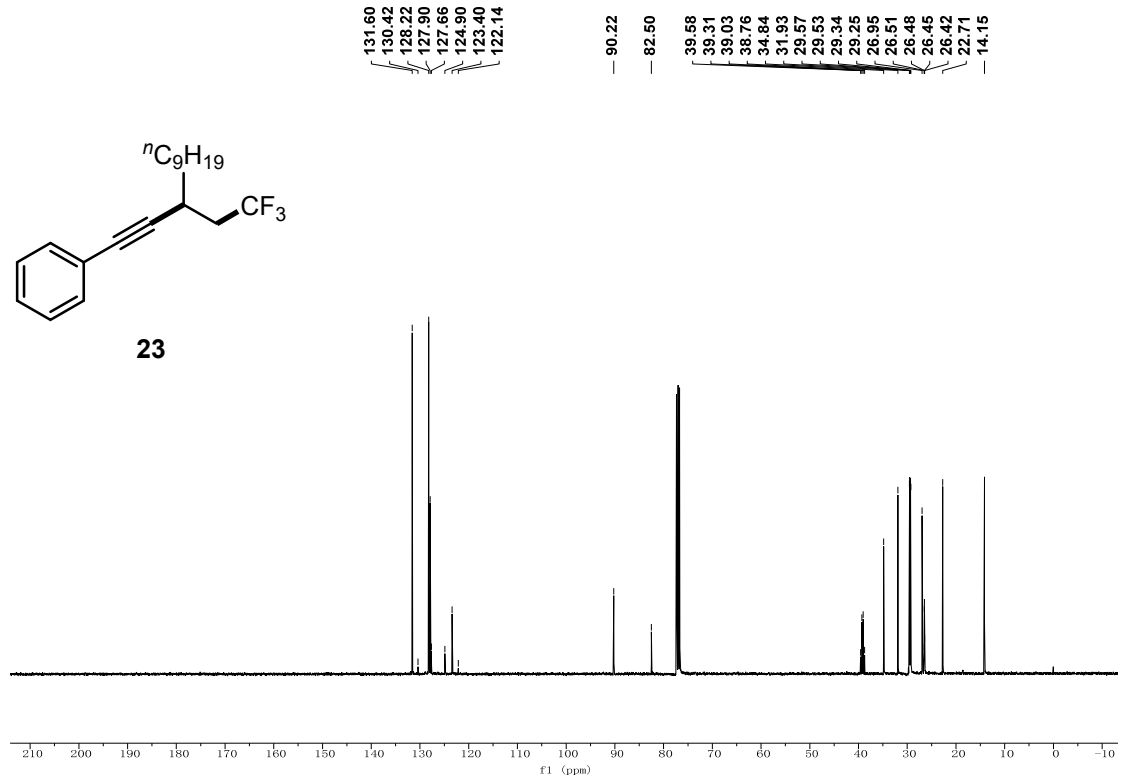
22

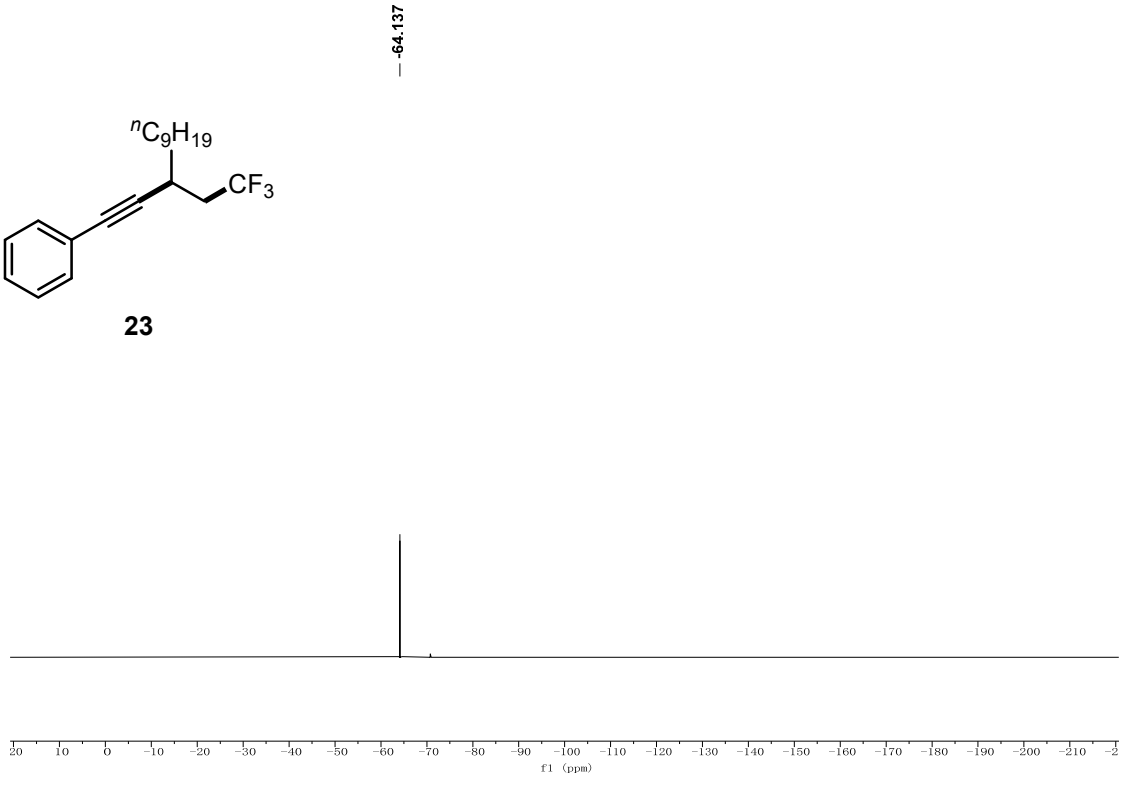
-64.234
f1 (ppm)
7.406
7.397
7.388
7.382
7.374
7.301
7.297
7.291
7.282
7.275
7.265
2.933
2.919
2.912
2.906
2.898
2.469
2.448
2.443
2.432
2.422
2.411
2.406
2.385
2.321
2.307
2.295
2.282
2.270
2.257
1.633
1.620
1.614
1.604
1.594
1.585
1.570
1.564
1.559
1.554
1.548
1.540
1.498
1.492
1.484
1.475
1.465
1.367
1.346
1.329
1.314
1.302
1.290
1.282
1.272
1.263
1.255
0.896
0.880
0.862

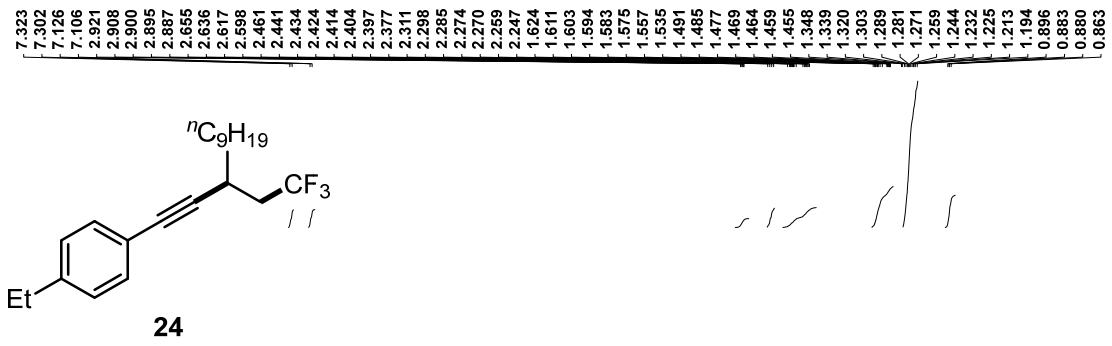

^{n}C$_9$H$_{19}$
CF$_3$

23

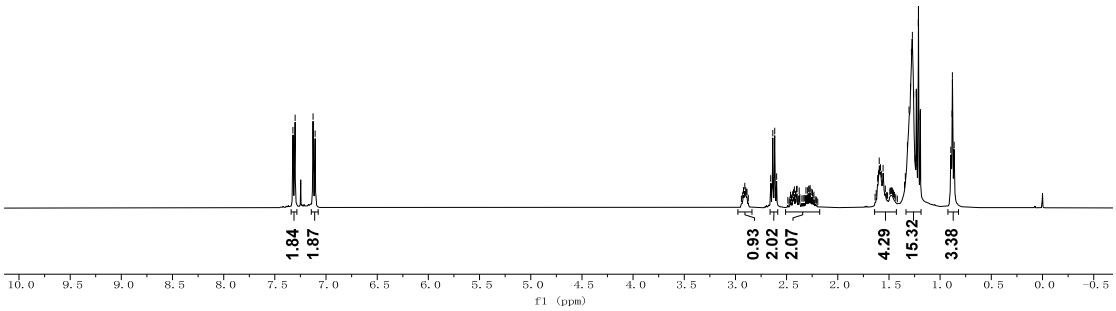

1.86
2.73
0.93
1.98
4.34
12.02
3.03
f1 (ppm)


131.60
130.42
128.22
127.90
127.66
124.90
123.40
122.14
90.22
82.50
39.58
39.31
39.03
38.76
34.84
31.93
29.57
29.53
29.34
29.25
26.95
26.51
26.48
26.45
26.42
22.71
14.15
$^{n}C_9H_{19}$
CF_3
23
f1 (ppm)


-64.137
$^{n}C_9H_{19}$
CF_3
23
f1 (ppm)


7.323
7.302
7.126
7.106
2.921
2.908
2.900
2.895
2.887
2.655
2.636
2.617
2.598
2.461
2.441
2.434
2.424
2.414
2.404
2.397
2.377
2.311
2.298
2.285
2.274
2.270
2.259
2.247
1.624
1.611
1.603
1.594
1.583
1.575
1.557
1.535
1.491
1.485
1.477
1.469
1.464
1.459
1.455
1.348
1.339
1.320
1.303
1.289
1.281
1.271
1.259
1.244
1.232
1.225
1.213
1.194
0.896
0.883
0.880
0.863
nC9H19
CF3
Et

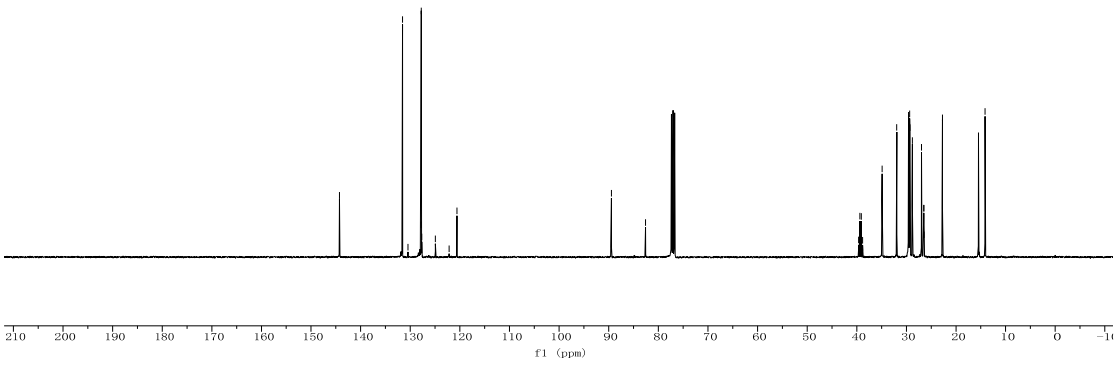
24

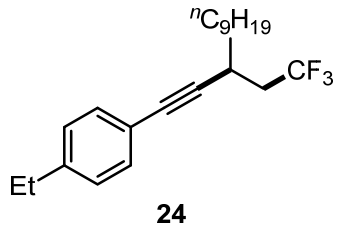

1.84
1.87
0.93
2.02
2.07
4.29
15.32
3.38
f1 (ppm)


144.27
131.57
130.45
127.82
127.79
127.69
124.93
122.17
120.59
89.46
82.57
39.64
39.37
39.09
38.82
34.89
31.94
29.58
29.54
29.35
29.27
28.80
26.95
26.53
26.50
26.47
26.44
22.72
15.46
14.15


nC9H19
CF3
Et

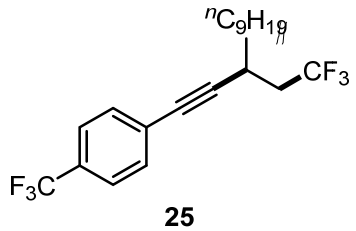
24


f1 (ppm)

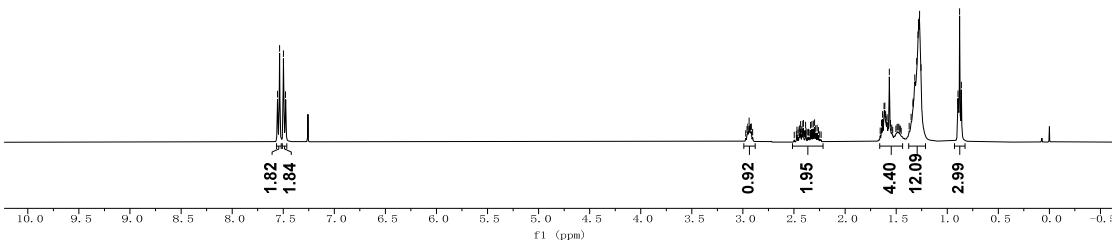

$^{n}C_9H_{19}$
CF_3
Et

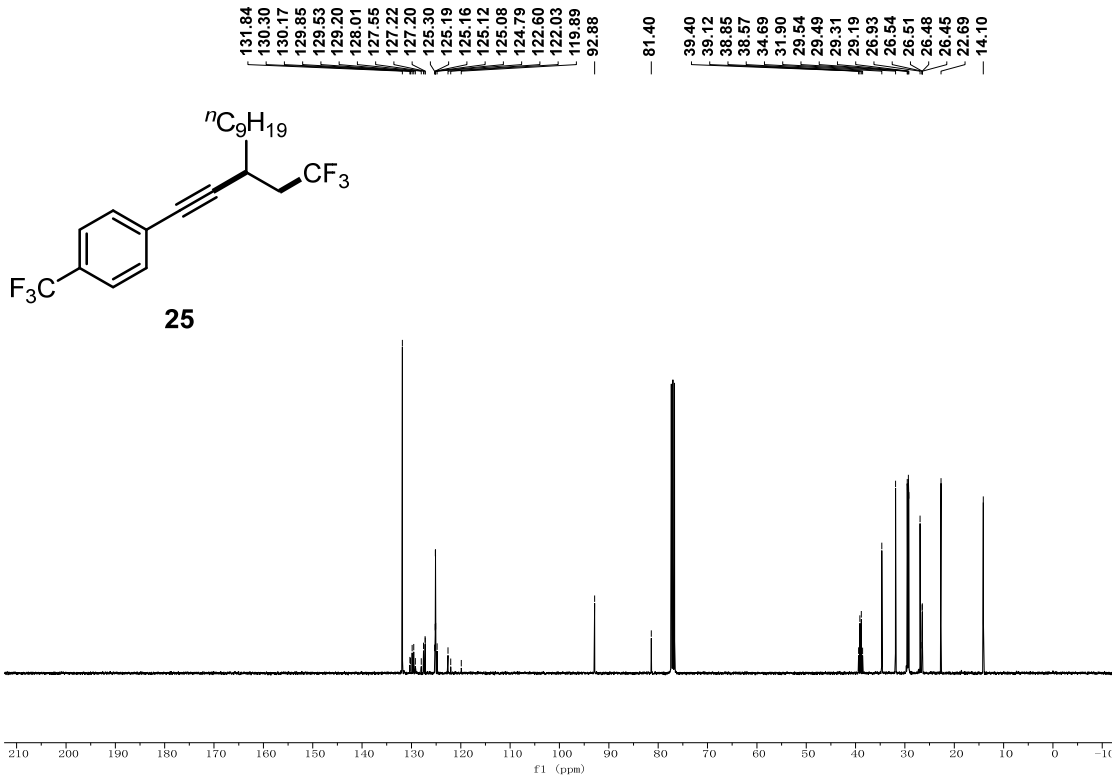
24

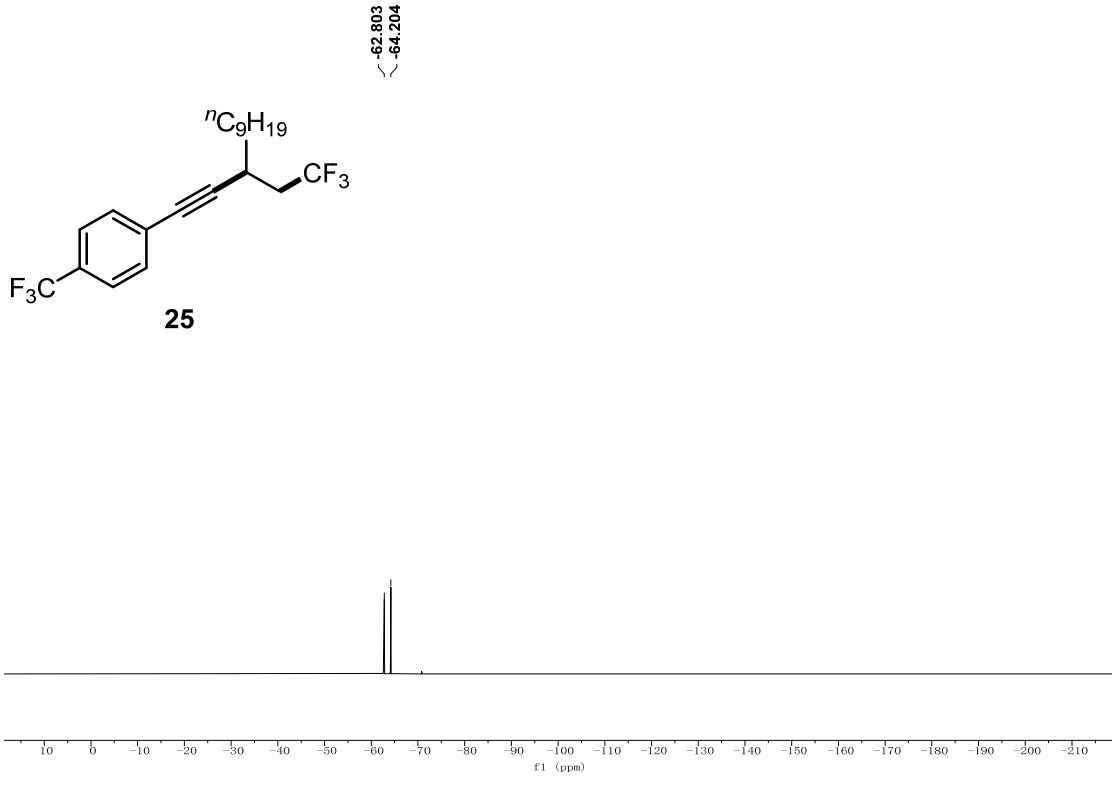
-64.117
f1 (ppm)
7.556
7.536
7.497
7.477
2.960
2.952
2.939
2.931
2.925
2.918
2.471
2.450
2.445
2.439
2.434
2.423
2.413
2.408
2.386
2.381
2.338
2.325
2.312
2.299
2.287
2.274
2.261
1.657
1.643
1.632
1.618
1.610
1.603
1.597
1.589
1.578
1.566
1.556
1.543
1.533
1.502
1.492
1.483
1.473
1.464
1.459
1.451
1.373
1.353
1.335
1.333
1.317
1.298
1.287
1.282
1.270
1.257
0.895
0.879
0.861

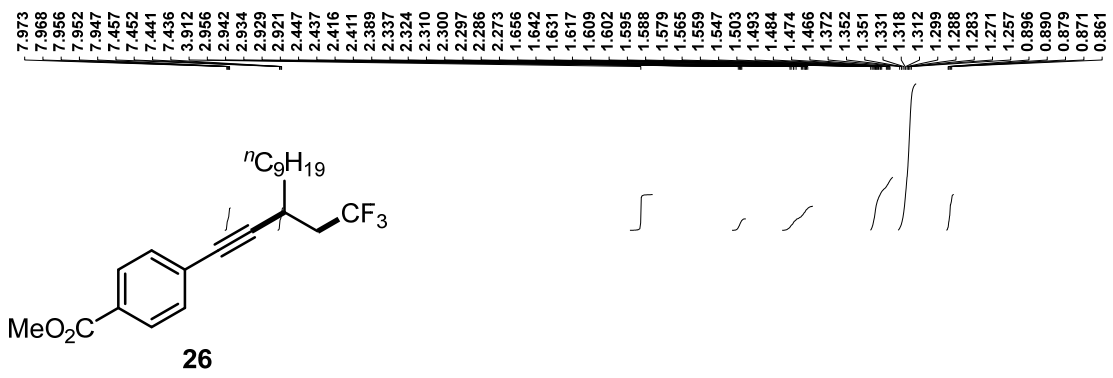

$^{n}C_9H_{19}$
CF_3
F_3C

25

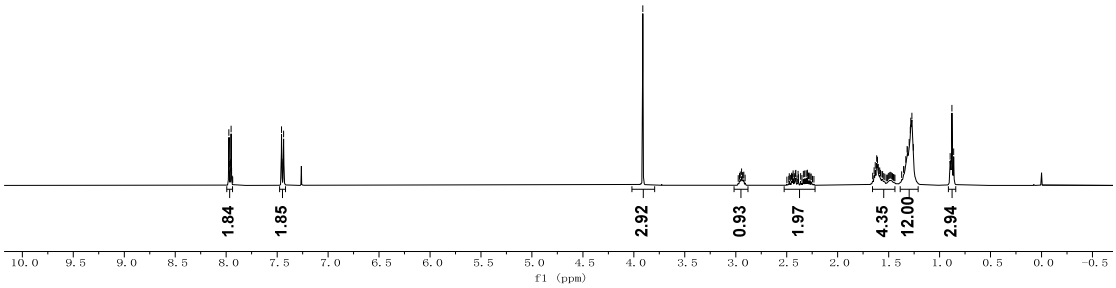

1.82
1.84
0.92
1.95
4.40
12.09
2.99
f1 (ppm)

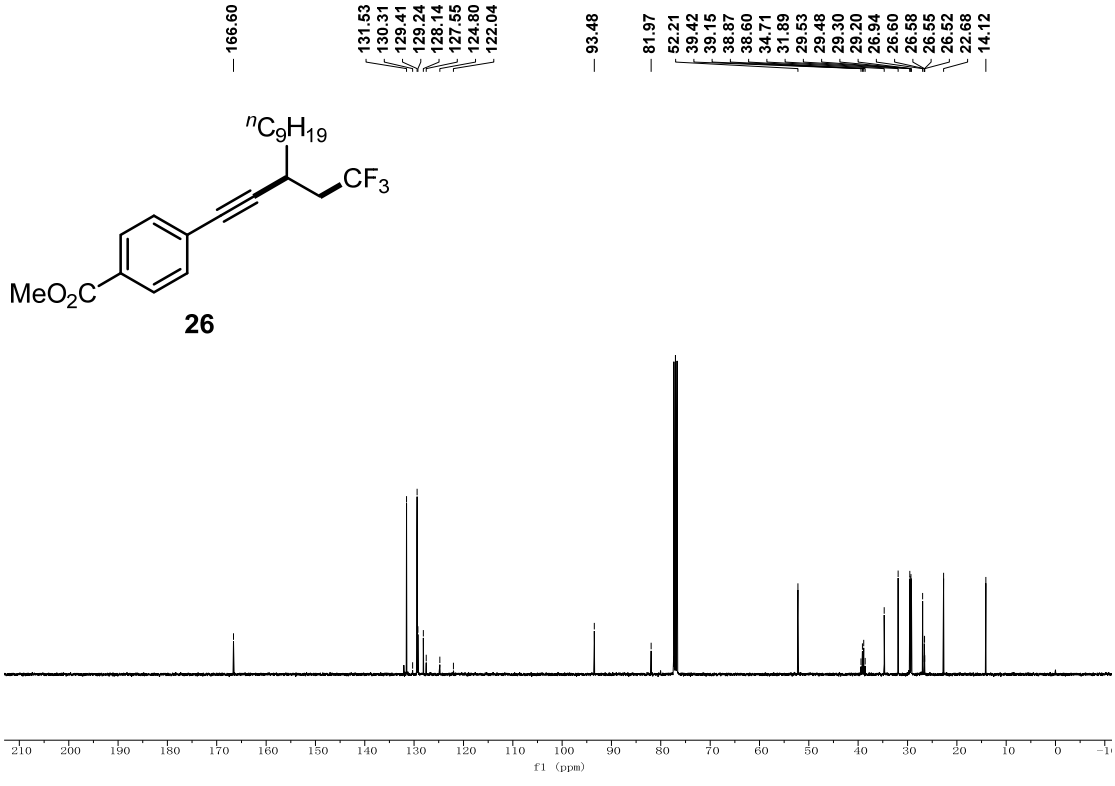

131.84
130.30
130.17
129.85
129.53
129.20
128.01
127.55
127.22
127.20
125.30
125.19
125.16
125.12
125.08
124.79
122.60
122.03
119.89
92.88
81.40
39.40
39.12
38.85
38.57
34.69
31.90
29.54
29.49
29.31
29.19
26.93
26.54
26.51
26.48
26.45
22.69
14.10
^{n}C$_9$H$_{19}$
CF$_3$
F$_3$C
25
f1 (ppm)


-62.803
-64.204
^{n}C$_9$H$_{19}$
CF$_3$
F$_3$C
25
f1 (ppm)

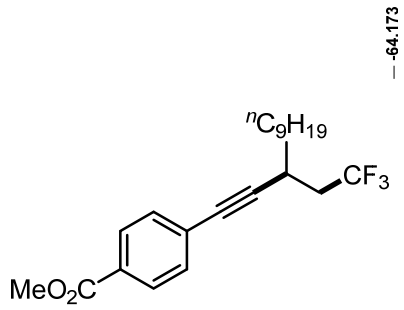

7.973
7.968
7.956
7.952
7.947
7.457
7.452
7.441
7.436
3.912
2.956
2.942
2.934
2.929
2.921
2.447
2.437
2.416
2.411
2.389
2.337
2.324
2.310
2.300
2.297
2.286
2.273
1.656
1.642
1.631
1.617
1.609
1.602
1.595
1.588
1.579
1.565
1.559
1.547
1.503
1.493
1.484
1.474
1.466
1.372
1.352
1.351
1.331
1.318
1.312
1.299
1.288
1.283
1.271
1.257
0.896
0.890
0.879
0.871
0.861
$^{n}C_9H_{19}$
CF_3
MeO_2C

26

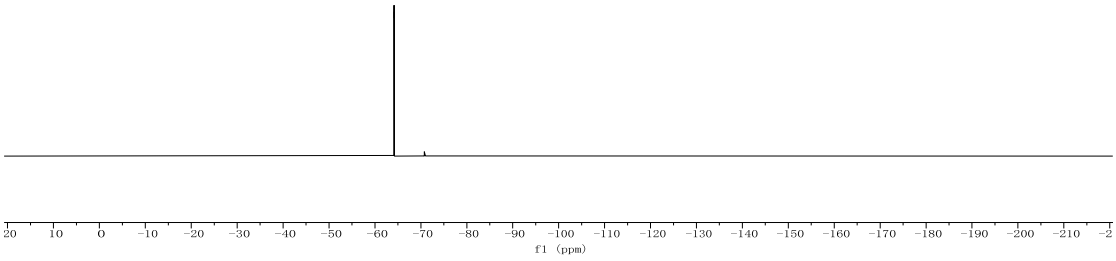

1.84
1.85
2.92
0.93
1.97
4.35
12.00
2.94
f1 (ppm)

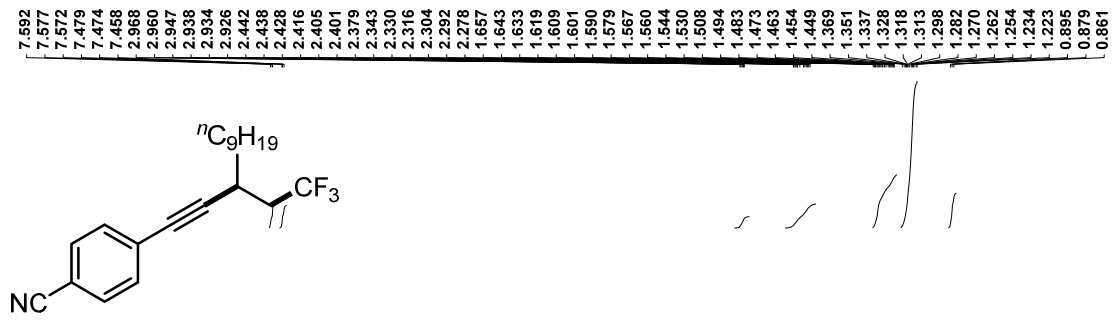

166.60
131.53
130.31
129.41
129.24
128.14
127.55
124.80
122.04
93.48
81.97
52.21
39.42
39.15
38.87
38.60
34.71
31.89
29.53
29.48
29.30
29.20
26.94
26.60
26.58
26.55
26.52
22.68
14.12
$^{n}C_9H_{19}$
CF_3
MeO_2C
f1 (ppm)

26


-64.173
^{n}C$_9$H$_{19}$
CF$_3$
MeO$_2$C

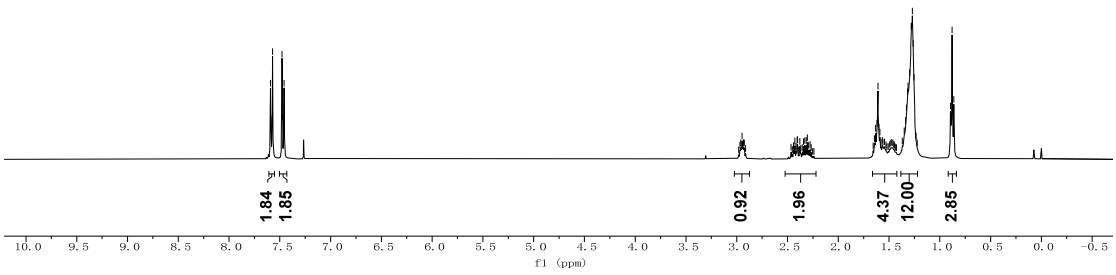
26

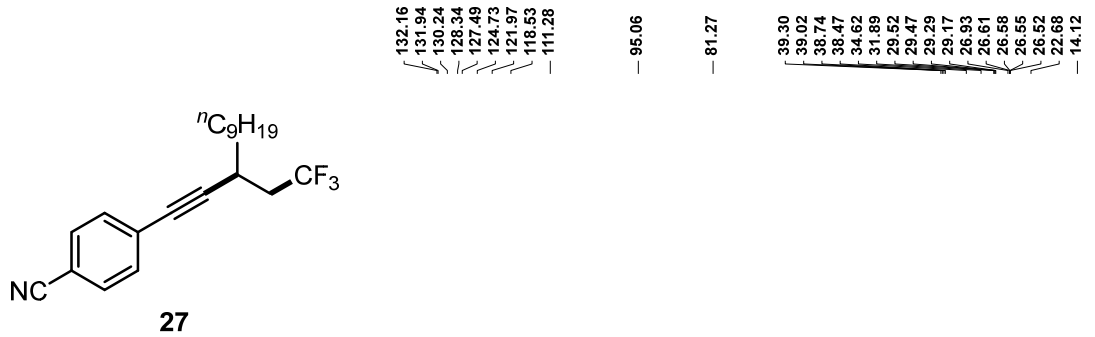

f1 (ppm)


7.592
7.577
7.572
7.479
7.474
7.458
2.968
2.960
2.947
2.938
2.934
2.926
2.442
2.438
2.428
2.416
2.405
2.401
2.379
2.343
2.330
2.316
2.304
2.292
2.278
1.657
1.643
1.633
1.619
1.609
1.601
1.590
1.579
1.567
1.560
1.544
1.530
1.508
1.494
1.483
1.473
1.463
1.454
1.449
1.369
1.351
1.337
1.328
1.318
1.313
1.298
1.282
1.270
1.262
1.254
1.234
1.223
0.895
0.879
0.861

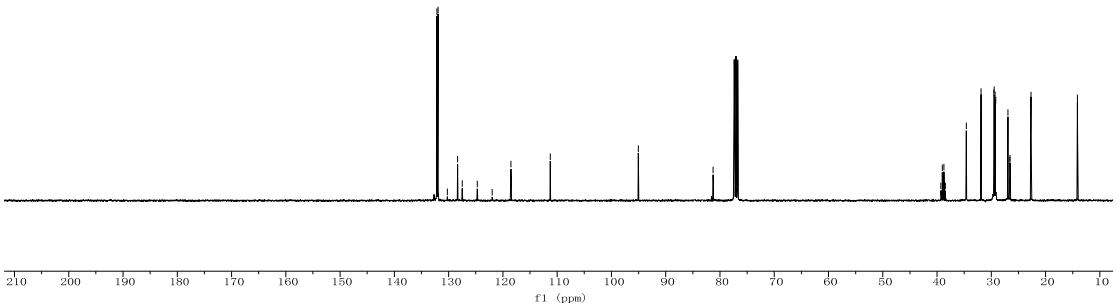
^{n}C$_9$H$_{19}$
CF$_3$
NC

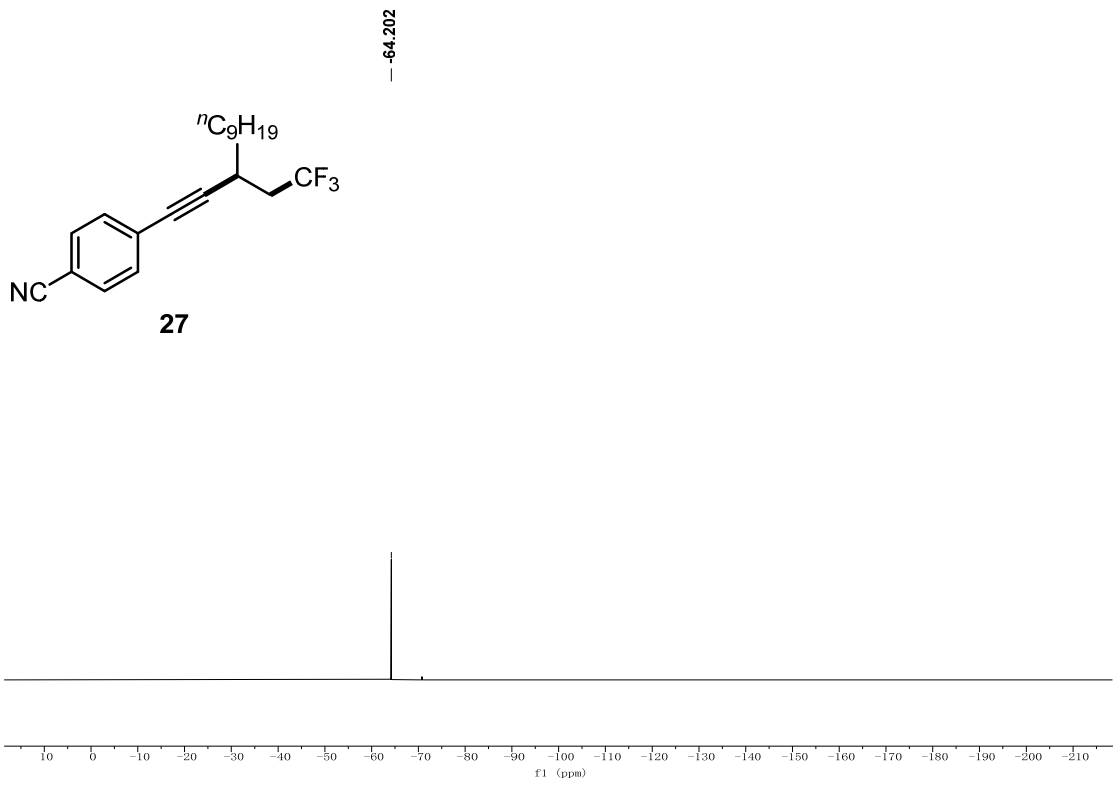
27


1.84
1.85
0.92
1.96
4.37
12.00
2.85
f1 (ppm)

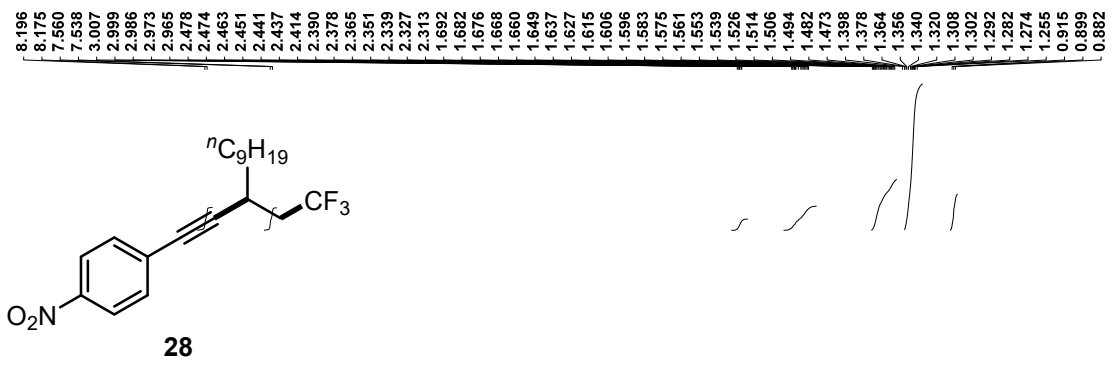

132.16
131.94
130.24
128.34
127.49
124.73
121.97
118.53
111.28
95.06
81.27
39.30
39.02
38.74
38.47
34.62
31.89
29.52
29.47
29.29
29.17
26.93
26.61
26.58
26.55
26.52
22.68
14.12
$^{n}C_9H_{19}$
CF_3
NC

27

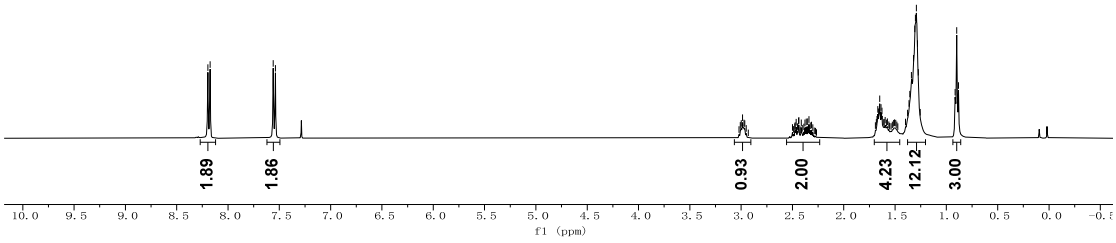

f1 (ppm)

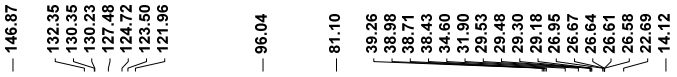

-64.202
$^{n}C_9H_{19}$
CF_3
NC
f1 (ppm)

27


8.196
8.175
7.560
7.538
3.007
2.999
2.986
2.973
2.965
2.478
2.474
2.463
2.451
2.441
2.437
2.414
2.390
2.378
2.365
2.351
2.339
2.327
2.313
1.692
1.682
1.676
1.668
1.660
1.649
1.637
1.627
1.615
1.606
1.596
1.583
1.575
1.561
1.553
1.539
1.526
1.514
1.506
1.494
1.482
1.473
1.398
1.378
1.364
1.356
1.340
1.320
1.308
1.302
1.292
1.282
1.274
1.255
0.915
0.899
0.882
$^{n}C_9H_{19}$
CF_3
O_2N

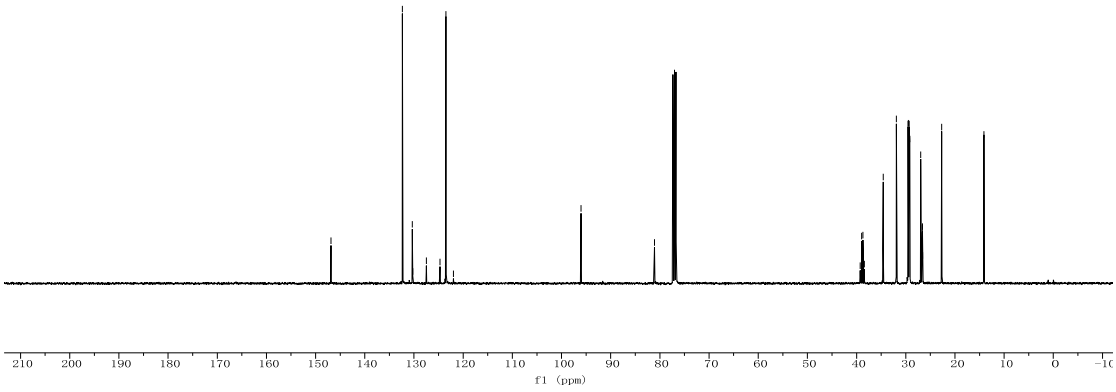
28

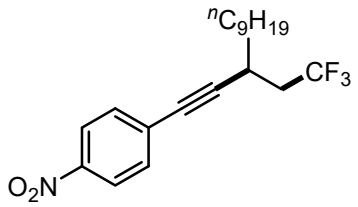

1.89
1.86
0.93
2.00
4.23
12.12
3.00
f1 (ppm)


146.87
132.35
130.35
130.23
127.48
124.72
123.50
121.96
96.04
81.10
39.26
38.98
38.71
38.43
34.60
31.90
29.53
29.48
29.30
29.18
26.95
26.67
26.64
26.61
26.58
22.69
14.12


$^{n}C_9H_{19}$
CF_3
O_2N

28


f1 (ppm)

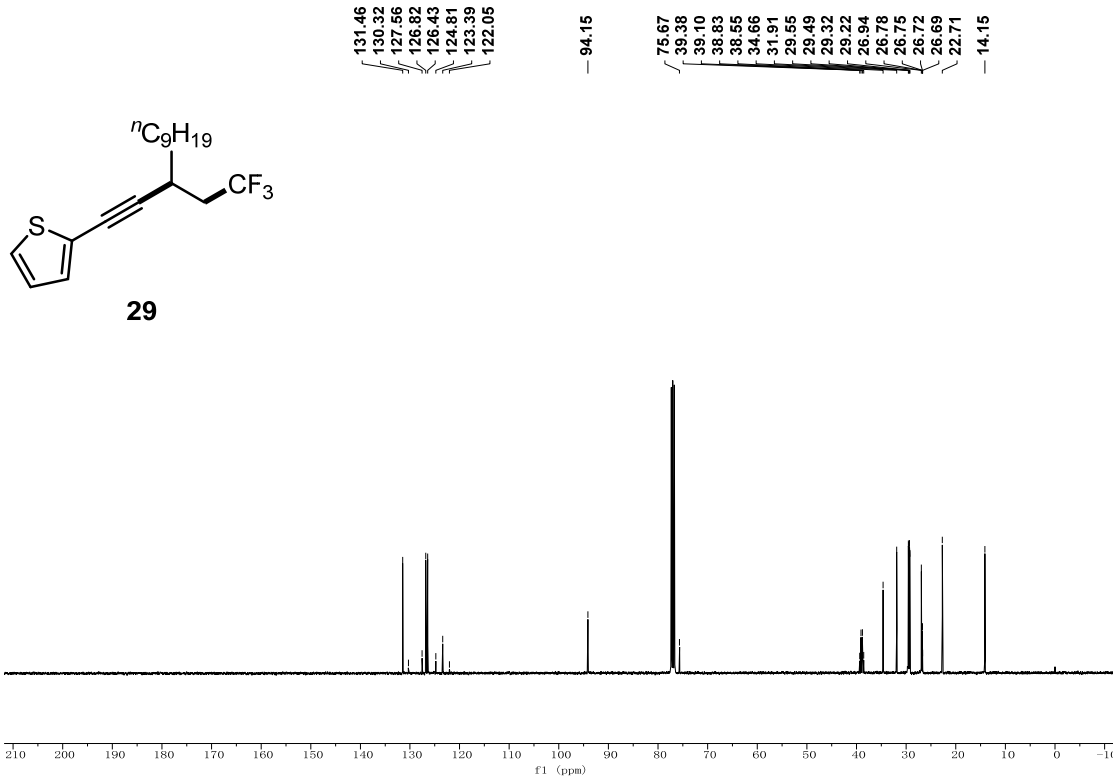

^{n}C$_9$H$_{19}$
CF$_3$
O$_2$N

28

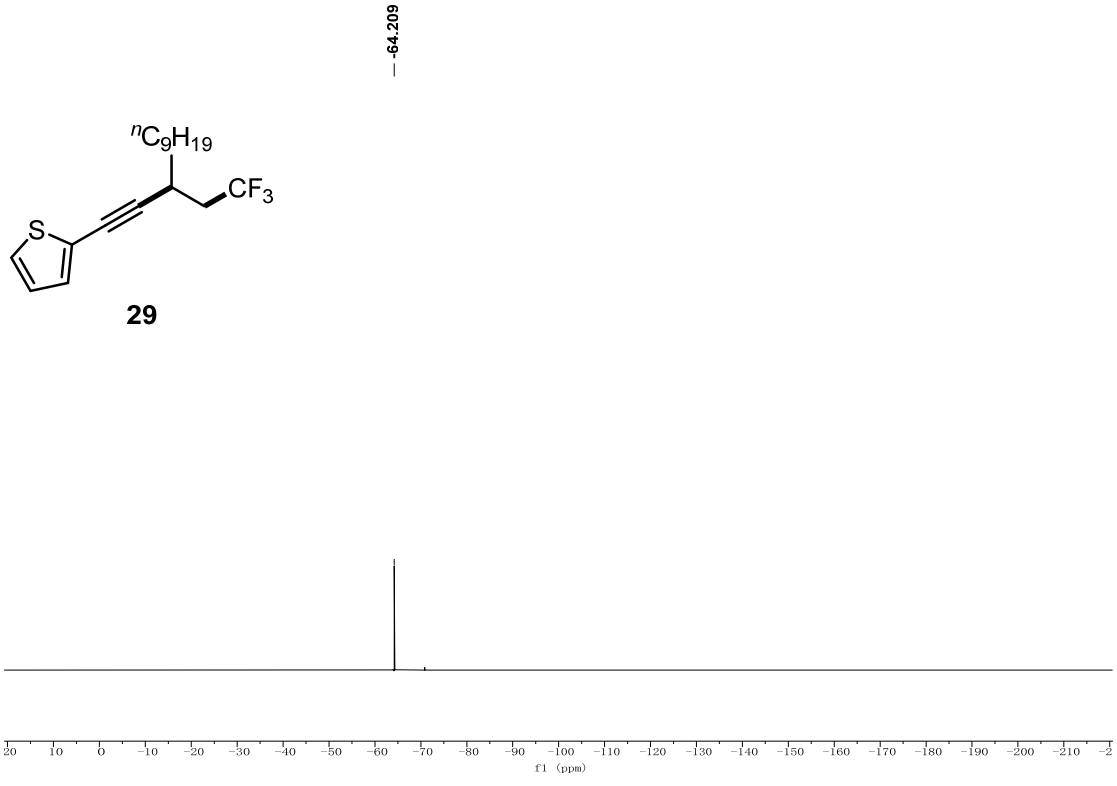
-64.212
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
7.203 7.200 7.190 7.187 7.142 7.139 7.133 7.130 6.952 6.943 6.939 6.930 2.948 2.934 2.927 2.921 2.914 2.465 2.438 2.428 2.418 2.407 2.401 2.381 2.317 2.303 2.291 2.280 2.277 2.265 2.253 1.641 1.626 1.617 1.612 1.602 1.590 1.579 1.570 1.560 1.547 1.539 1.471 1.465 1.461 1.453 1.359 1.339 1.318 1.306 1.301 1.289 1.281 1.272 1.260 1.225 0.897 0.892 0.880 0.862
0.90 0.94 0.94 0.93 1.99 4.41 12.25 2.98
10.0 9.5 9.0 8.5 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 -0.5
f1 (ppm)

^{n}C$_9$H$_{19}$
CF$_3$
S

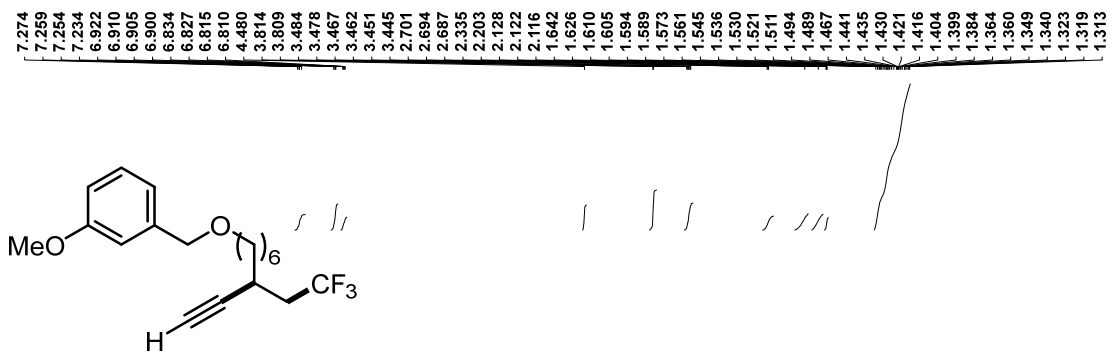
29


131.46
130.32
127.56
126.82
126.43
124.81
123.39
122.05
94.15
75.67
39.38
39.10
38.83
38.55
34.66
31.91
29.55
29.49
29.32
29.22
26.94
26.78
26.75
26.72
26.69
22.71
14.15
$^{n}C_9H_{19}$
CF_3
S
f1 (ppm)

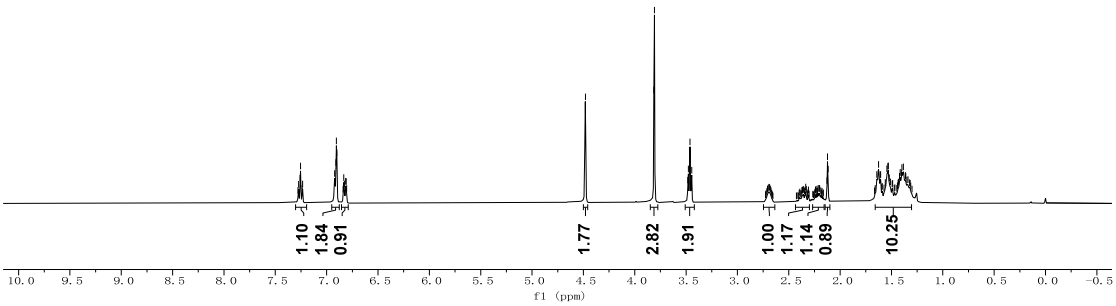
29

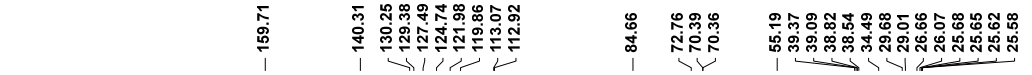

-64.209
$^{n}C_9H_{19}$
CF_3
S
f1 (ppm)

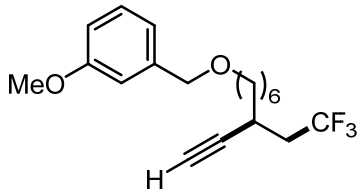
29


7.274
7.259
7.254
7.234
6.922
6.910
6.905
6.900
6.834
6.827
6.815
6.810
4.480
3.814
3.809
3.484
3.478
3.467
3.462
3.451
3.445
2.701
2.694
2.687
2.335
2.203
2.128
2.122
2.116
1.642
1.626
1.610
1.605
1.594
1.589
1.573
1.561
1.545
1.536
1.530
1.521
1.511
1.494
1.489
1.467
1.441
1.435
1.430
1.421
1.416
1.404
1.399
1.384
1.364
1.360
1.349
1.340
1.323
1.319
1.313
MeO
O
6
CF3
H

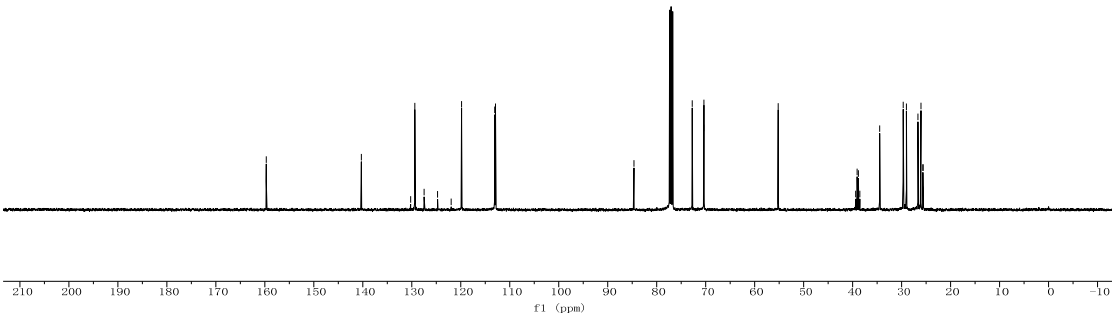
30

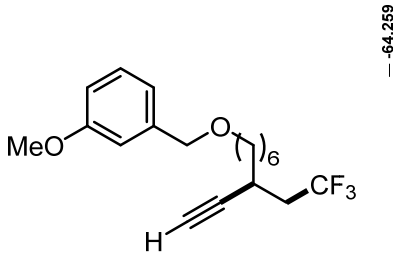

1.10
1.84
0.91
1.77
2.82
1.91
1.00
1.17
1.14
0.89
10.25
f1 (ppm)


159.71
140.31
130.25
129.38
127.49
124.74
121.98
119.86
113.07
112.92
84.66
72.76
70.39
70.36
55.19
39.37
39.09
38.82
38.54
34.49
29.68
29.01
26.66
26.07
25.68
25.65
25.62
25.58


MeO
O
6
CF3
H

30


f1 (ppm)

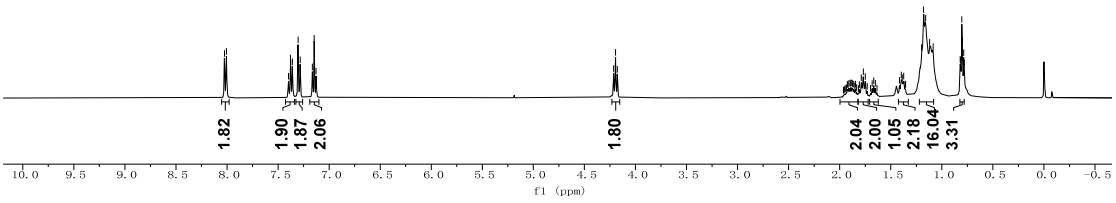

MeO
O
6
CF3
H

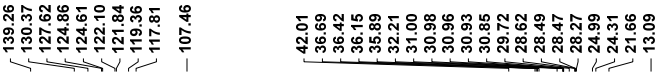
30

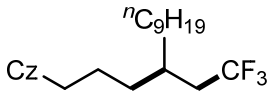
-64.259
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
8.025
8.006
7.398
7.378
7.359
7.304
7.284
7.164
7.146
7.127
4.214
4.196
4.177
1.963
1.954
1.948
1.939
1.935
1.925
1.919
1.910
1.897
1.891
1.881
1.874
1.862
1.852
1.846
1.835
1.817
1.808
1.789
1.769
1.750
1.731
1.698
1.682
1.667
1.651
1.636
1.415
1.397
1.387
1.374
1.360
1.355
1.198
1.179
1.159
1.119
1.085
0.821
0.816
0.804
0.799
0.786
0.781

nC9H19
Cz
CF3

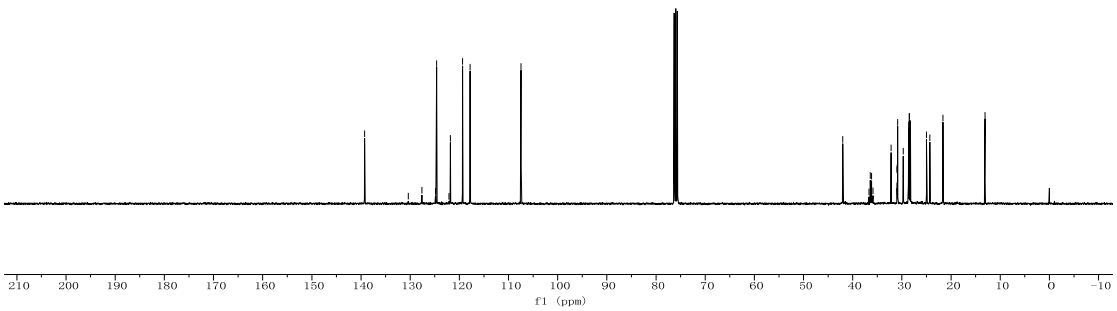
31


1.82
1.90
1.87
2.06
1.80
2.04
2.00
1.05
2.18
16.04
3.31
10.0 9.5 9.0 8.5 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 -0.5
f1 (ppm)

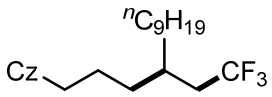

139.26
130.37
127.62
124.86
124.61
122.10
121.84
119.36
117.81
107.46
42.01
36.69
36.42
36.15
35.89
32.21
31.00
30.98
30.96
30.93
30.85
29.72
28.62
28.49
28.47
28.27
24.99
24.31
21.66
13.09


$^{n}C_9H_{19}$
Cz
CF_3

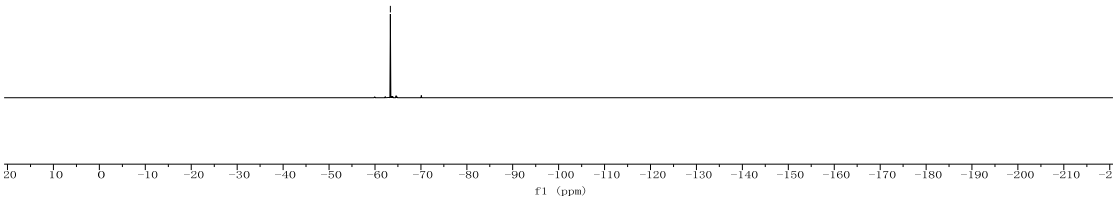
31

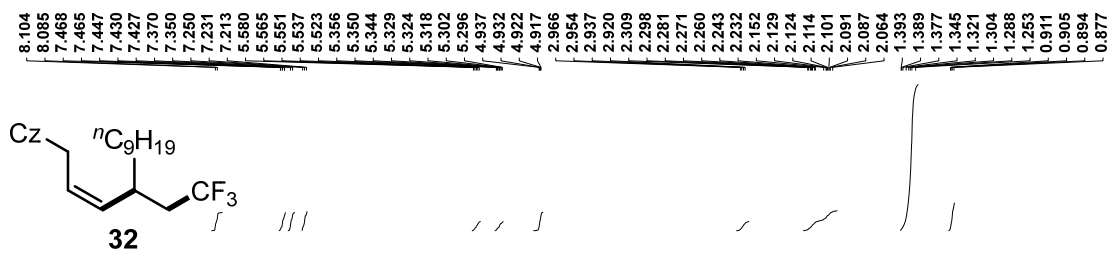

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-63.354


$^{n}C_9H_{19}$
Cz
CF_3

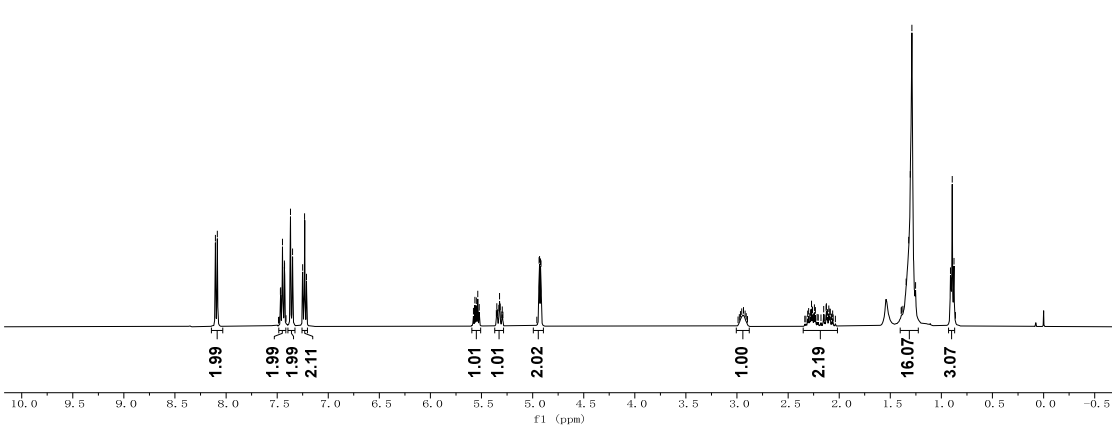
31

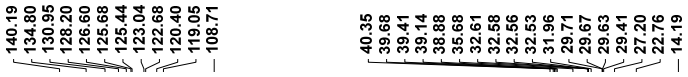

20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

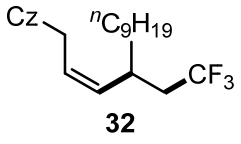

8.104
8.085
7.468
7.465
7.447
7.430
7.427
7.370
7.350
7.250
7.231
7.213
5.580
5.565
5.551
5.537
5.523
5.356
5.350
5.344
5.329
5.324
5.318
5.302
5.296
4.937
4.932
4.922
4.917
2.966
2.954
2.937
2.920
2.309
2.298
2.281
2.271
2.260
2.243
2.232
2.152
2.129
2.124
2.114
2.101
2.091
2.087
2.064
1.393
1.389
1.377
1.345
1.321
1.304
1.288
1.253
0.911
0.905
0.894
0.877

Cz
nC9H19
CF3

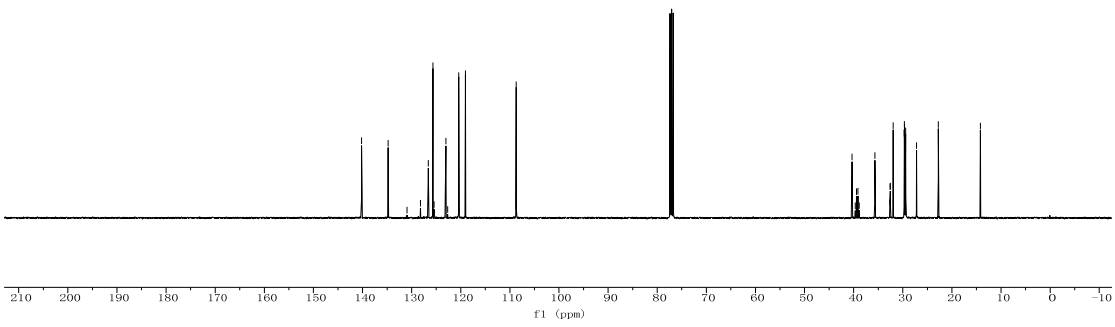
32

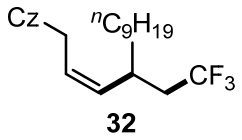

1.99
1.99
1.99
2.11
1.01
1.01
2.02
1.00
2.19
16.07
3.07
f1 (ppm)


140.19
134.80
130.95
128.20
126.60
125.68
125.44
123.04
122.68
120.40
119.05
108.71
40.35
39.68
39.41
39.14
38.88
35.68
32.61
32.58
32.56
32.53
31.96
29.71
29.67
29.63
29.41
27.20
22.76
14.19


Cz
nC9H19
CF3

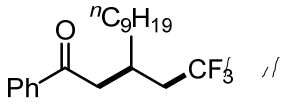
32


f1 (ppm)

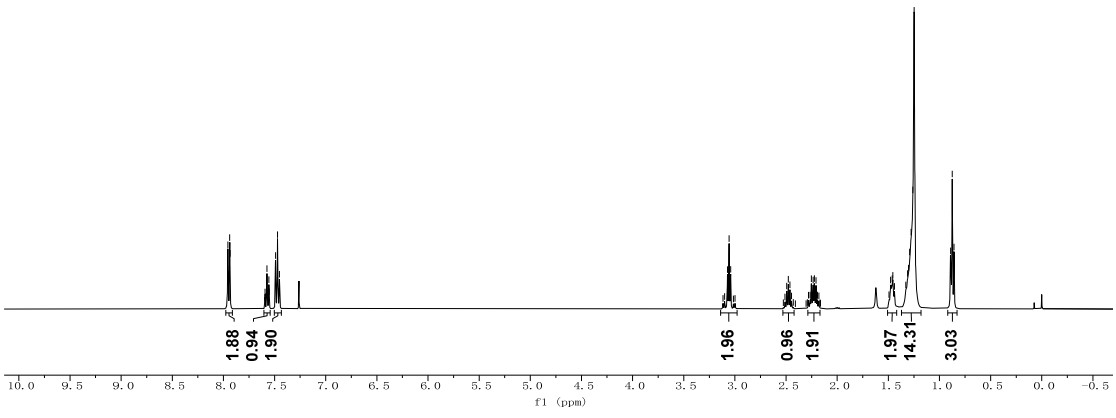

Cz
^{n}C$_9$H$_{19}$
CF$_3$

32

-63.356
f1 (ppm)
7.957
7.952
7.938
7.934
7.596
7.593
7.589
7.580
7.574
7.569
7.559
7.556
7.552
7.490
7.471
7.457
7.452
3.116
3.100
3.073
3.057
3.042
3.015
2.999
2.526
2.510
2.494
2.478
2.462
2.446
2.430
2.410
2.303
2.291
2.280
2.264
2.252
2.236
2.223
2.207
2.196
2.193
2.179
2.168
2.164
1.493
1.477
1.462
1.455
1.440
1.328
1.312
1.303
1.291
1.278
1.260
1.247
0.892
0.875
0.858


O
^{n}C$_9$H$_{19}$
Ph
CF$_3$

33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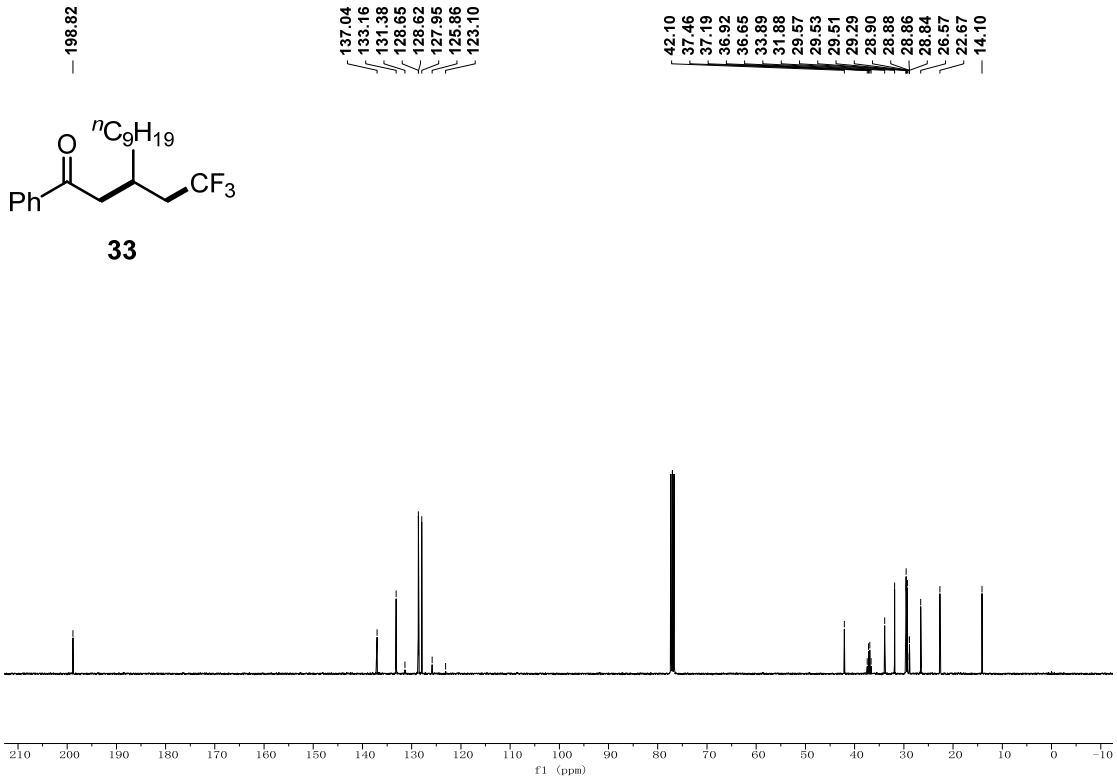
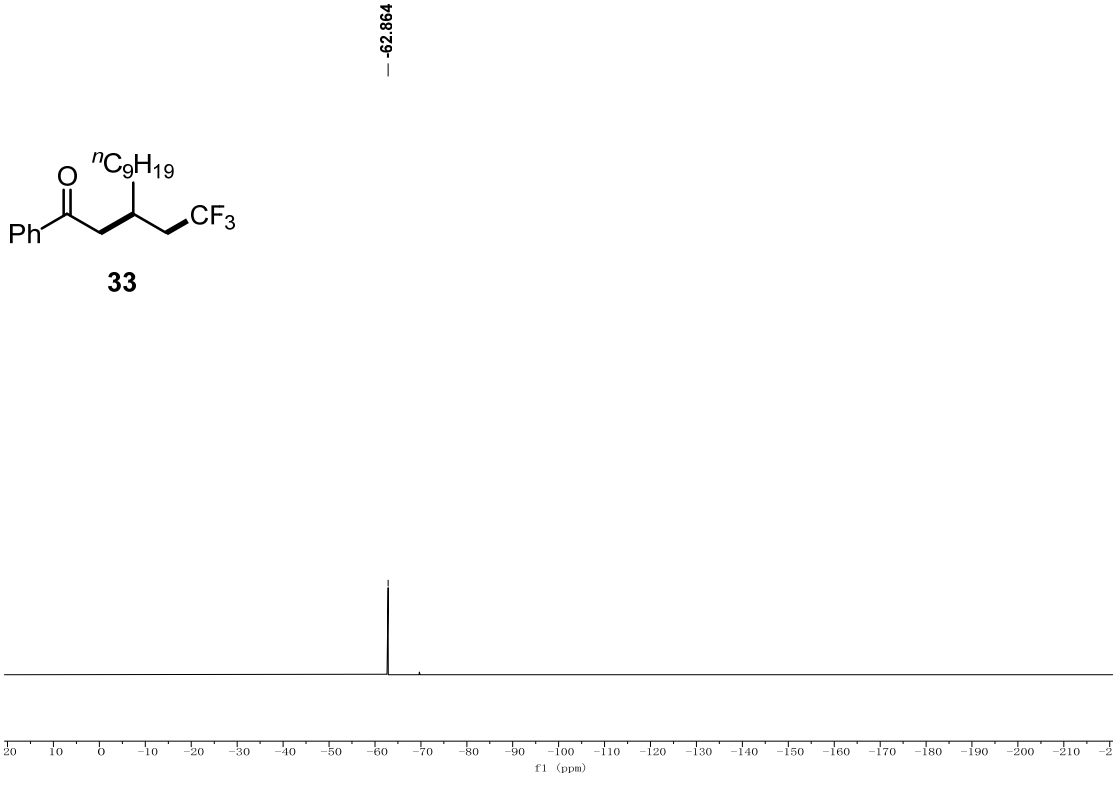
0.94
1.90
1.96
0.96
1.91
1.97
14.31
3.03
f1 (ppm)


198.82
137.04
133.16
131.38
128.65
128.62
127.95
125.86
123.10
42.10
37.46
37.19
36.92
36.65
33.89
31.88
29.57
29.53
29.51
29.29
28.90
28.88
28.86
28.84
26.57
22.67
14.10
O
nC9H19
Ph
CF3
33
f1 (ppm)


-62.864
O
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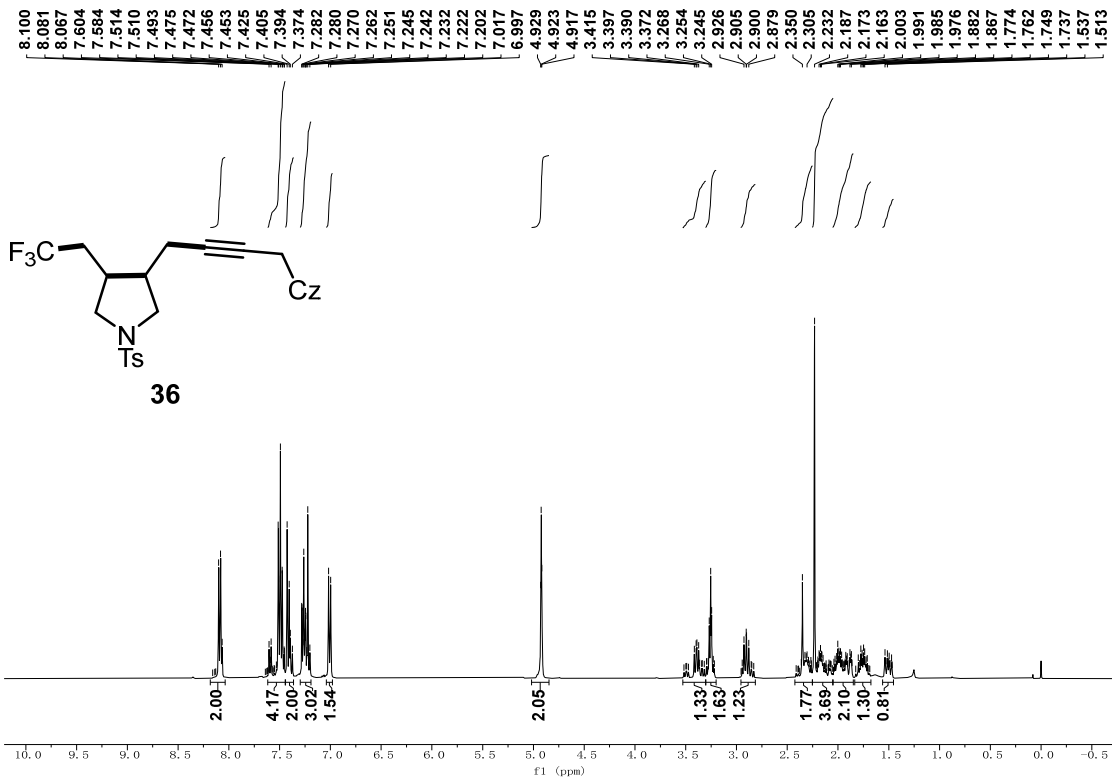
Ph
CF3
33
f1 (ppm)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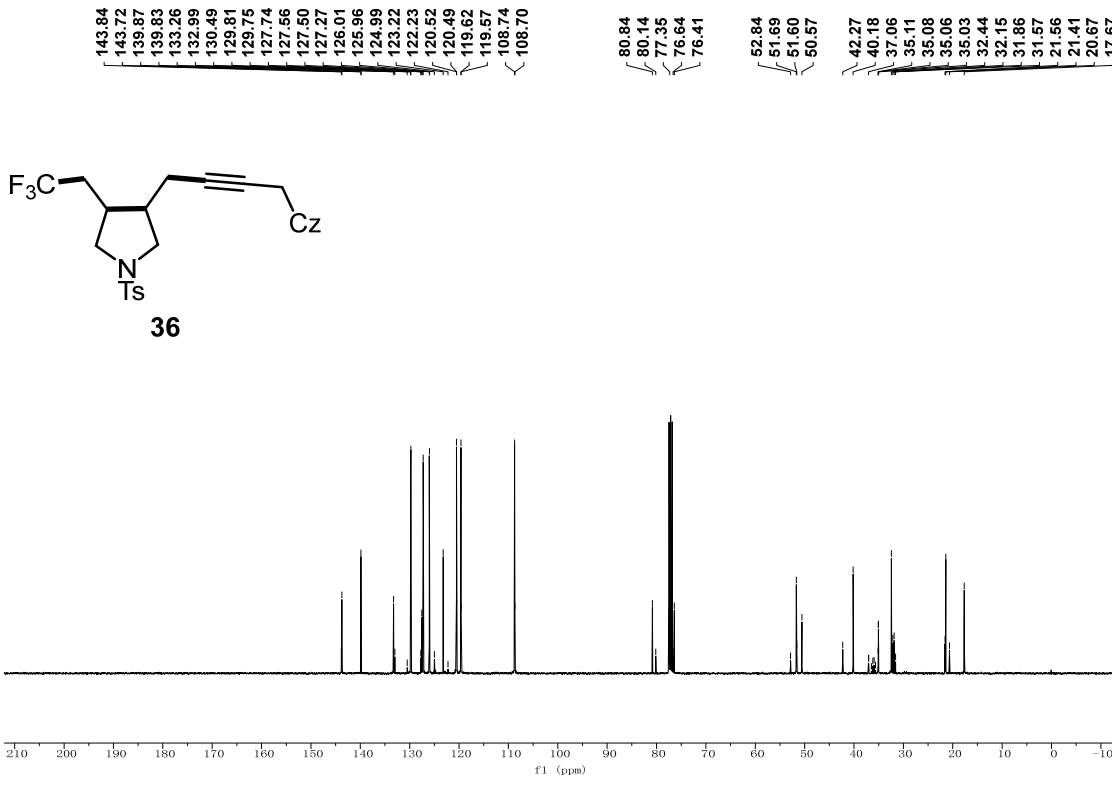
8.067
7.604
7.584
7.514
7.510
7.493
7.475
7.472
7.456
7.453
7.425
7.405
7.394
7.374
7.282
7.280
7.270
7.262
7.251
7.245
7.242
7.232
7.222
7.202
7.017
6.997
4.929
4.923
4.917
3.415
3.397
3.390
3.372
3.268
3.254
3.245
2.926
2.905
2.900
2.879
2.350
2.305
2.232
2.187
2.173
2.163
2.003
1.991
1.985
1.976
1.882
1.867
1.774
1.762
1.749
1.737
1.537
1.513
F3C
Cz
N
Ts
36
2.00
4.17
2.00
3.02
1.54
2.05
1.33
1.63
1.23
1.77
3.69
2.10
1.30
0.81
f1 (ppm)


143.84
143.72
139.87
139.83
133.26
132.99
130.49
129.81
129.75
127.74
127.56
127.50
127.27
126.01
125.96
124.99
123.22
122.23
120.52
120.49
119.62
119.57
108.74
108.70
80.84
80.14
77.35
76.64
76.41
52.84
51.69
51.60
50.57
42.27
40.18
37.06
35.11
35.08
35.06
35.03
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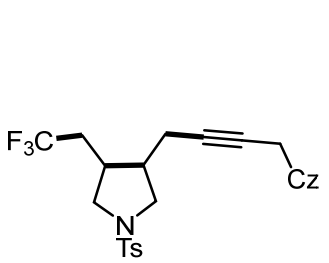
20.67
F3C
Cz
N
Ts
36
f1 (ppm)


F3C
Cz
N
Ts

36

-64.805
-64.831
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)