Supporting Information

Hydroazidation of trifluoromethyl alkenes with trimethylsilyl azide enabled by organic photoredox catalysis

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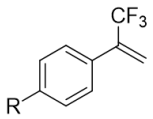
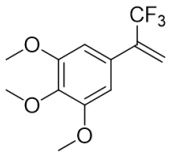
1. General information

Reactions via general procedure were carried out under an Ar atmosphere unless otherwise noted. Column chromatography was performed using silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 101 MHz, respectively) instrument using $CDCl_3$ as solvent, Chemical shifts are given in ppm and coupling constants in 400Hz. ^{1}H spectra and ^{13}C spectra were calibrated in relation to the reference measurement of $CDCl_3$ (7.260 ppm) and $CDCl_3$ (77.00 ppm), respectively. In order to indicate the signal multiplicity, the following abbreviations were used: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet) as well as combinations of them. Mass spectra were measured on Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra (ESI) were obtained with the Thermo Scientific LTQ Orbitrap XL mass spectrometer. Melting points were measured with a YUHUA X-5 melting point instrument and were uncorrected.

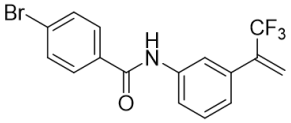
2. Synthesis and characterization of substrates.



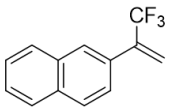
1a, R = Ph, 79%
1b, R = OMe, 52%
1d, R = OPh, 67%
1e, R = SMe, 75%
1f, R = Ac, 60%
1g, R = NO_2, 43%



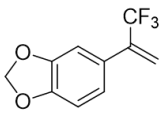
1c, 70%



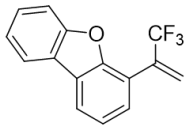
1h, 72%



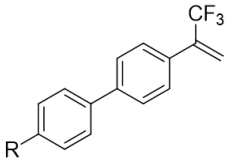
1i, 42%



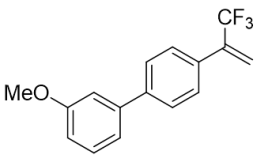
1j, 64%



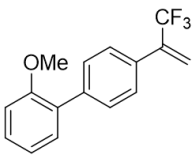
1k, 55%



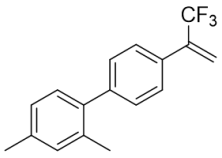
1l, R = OMe, 84%
1o, R = ^{t}Bu, 56%
1r, R = F, 65%
1s, R = Br, 56%
1t, R = CF_3, 72%
1u, R = COOMe, 66%
1v, R = CN, 78%



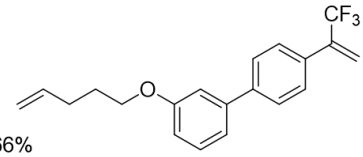
1m, 72%



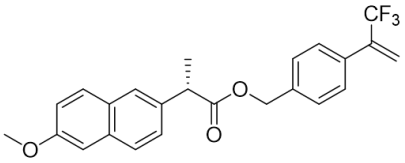
1n, 70%



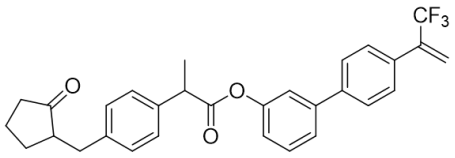
1p, 72%



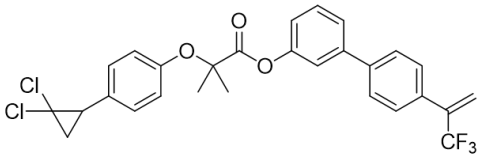
1q, 62%



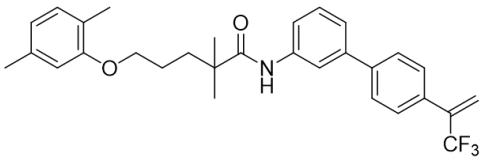
1w, 68%



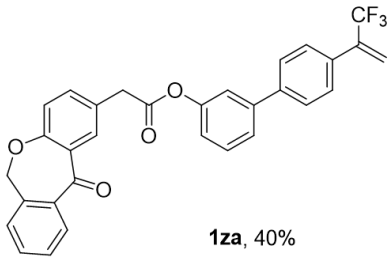
1x, 45%



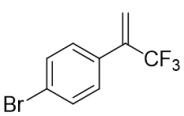
1y, 46%



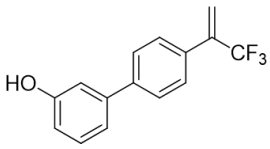
1z, 45%



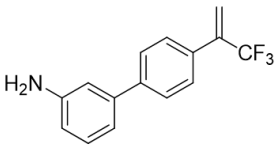
1za, 40%



M1, 50%

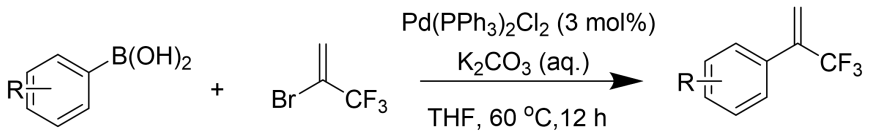


M2, 70%



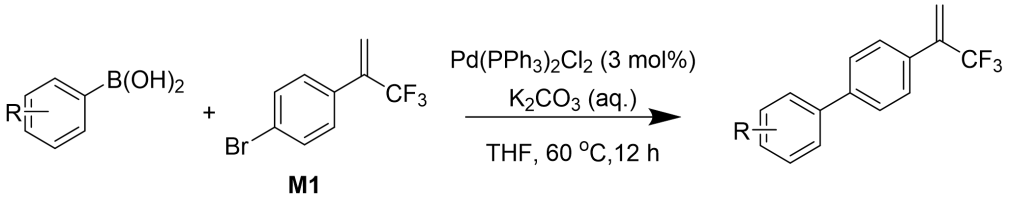
M3, 68%

Procedure A for preparation of trifluoromethyl alkenes (1a-1g, 1i-1k and M1)[1]



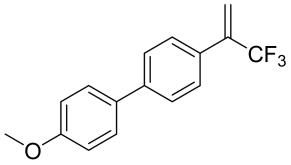
Procedure A: To a Schlenk tube equipped with a magnetic stir bar were added aqueous K_2CO_3 (2.00 M, 8 mL), THF (12 mL), arylboronic acid (4.00 mmol), 2-bromo-3,3,3-trifluoropropene (1391.4 mg, 2.0 equiv, 8.00 mmol) and $Pd(PPh_3)_2Cl_2$ (3 mol%, 84.2 mg, 0.12 mmol). The resulting solution was stirred at 60 °C with oil bath for 12 h. After the reaction mixture was cooled to room temperature, the reaction mixture was quenched with saturated aqueous NH_4Cl, and extracted with EtOAc (3 x 20 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed under reduced pressure. The resultant crude product material was purified by flash chromatography using the appropriate gradient of petroleum ether and ethyl acetate.

Procedure B for preparation of trifluoromethyl alkenes (1l-1v, M2 and M3)[2]



Procedure B: To a Schlenk tube equipped with a magnetic stir bar were added aqueous K_2CO_3 (2.00 M, 8 mL), THF (12 mL), arylboronic acid (4.00 mmol), 1-bromo-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (999.8 mg, 1.0 equiv, 4.00 mmol) and $Pd(PPh_3)_2Cl_2$ (3 mol%, 84.2 mg, 0.12 mmol). The resulting solution was stirred at 60 °C with oil bath for 12 h. After the reaction mixture was cooled to room temperature, the reaction mixture was quenched with saturated aqueous NH_4Cl, and extracted with EtOAc (3 x 20 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed under reduced pressure. The resultant crude product material was purified by flash chromatography using the appropriate gradient of petroleum ether and ethyl acetate.

4-methoxy-4'-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (1l)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 150/1) to yield **1l** (934.1 mg, 84%) as a white solid, mp: 107 - 111 °C

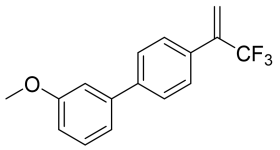
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.42 (m, 6H), 6.91 – 6.89 (m, 2H), 5.88 (s, 1H), 5.73 (s, 1H), 3.76 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.5, 141.4, 138.5 (q, J = 29.8 Hz), 132.7, 131.8, 128.1, 127.7, 126.7, 123.4 (q, J = 274.1 Hz), 119.9 (q, J = 5.8 Hz), 114.3, 55.3.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.56.

HRMS (APCI) m/z: $[M]^+$ calcd for $C_{16}H_{13}F_3O^+$ 278.0913; found 278.0911.

3-methoxy-4'-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (1m)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 150/1) to yield **1m** (778.4 mg, 70%) as a colorless liquid.

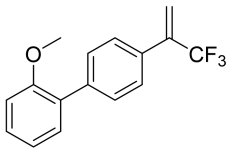
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.59 (m, 2H), 7.53 – 7.51 (m, 2H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 1H), 7.13 – 7.12 (m, 1H), 6.91 (dd, *J* = 8.2, 2.5 Hz, 1H), 5.96 (s, 1H), 5.81 (s, 1H), 3.85 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.0, 141.7, 141.7, 138.5 (q, *J* = 30.1 Hz), 132.6, 129.9, 127.7, 127.3, 123.4 (q, *J* = 274.1 Hz), 120.2 (q, *J* = 5.8 Hz), 119.6, 113.0, 112.9, 55.3.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.56.

HRMS (APCI) m/z: $[M]^+$ calcd for $C_{16}H_{13}F_3O^+$ 278.0913; found 278.0910.

2-methoxy-4'-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (1n)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 150/1) to yield **1n** (800.6 mg, 72%) as a colorless liquid.

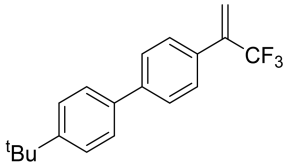
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.54 (m, 2H), 7.50 – 7.48 (m, 2H), 7.34 – 7.30 (m, 2H), 7.04 – 7.02 (m, 1H), 6.98 – 6.96 (m, 1H), 5.94 (s, 1H), 5.80 (s, 1H), 3.79 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.4, 139.3, 138.7 (q, *J* = 29.9 Hz), 132.0, 130.7, 129.7, 129.7, 129.0, 126.9, 123.4 (q, *J* = 274.1 Hz), 120.9, 120.0 (q, *J* = 5.8 Hz), 111.2, 55.5.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.42.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{13}F_3ONa^+$ 301.0811; found 301.0813.

4-(tert-butyl)-4'-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (1o)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 250/1) to yield **1o** (681.0 mg, 56%) as a white solid, mp: 68 - 72 °C

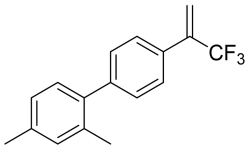
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.59 (m, 2H), 7.55 – 7.51 (m, 4H), 7.48 – 7.46 (m, 2H), 5.95 (s, 1H), 5.81 (s, 1H), 1.36 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.8, 141.7, 138.6 (q, *J* = 30.1 Hz), 137.3, 132.1, 127.7, 127.1, 126.7, 125.8, 123.4 (q, *J* = 274.1 Hz), 120.0 (q, *J* = 5.7 Hz), 34.6, 31.3.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.52.

HRMS (APCI) m/z: $[M+H]^+$ calcd for $C_{19}H_{20}F_3^+$ 305.1512; found 305.1509.

2,4-dimethyl-4'-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (1p)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 150/1) to yield **1p** (794.9 mg, 72%) as a colorless liquid.

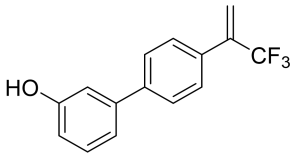
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.49 (m, 2H), 7.34 – 7.32 (m, 2H), 7.14 – 7.06 (m, 3H), 5.96 (s, 1H), 5.83 (s, 1H), 2.36 (s, 3H), 2.26 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.7, 138.6 (q, *J* = 29.9 Hz), 138.2, 137.3, 135.1, 131.8, 131.2, 129.6, 129.5, 127.0, 126.6, 123.4 (q, *J* = 274.0 Hz), 120.1 (q, *J* = 5.8 Hz), 21.0, 20.4.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.53.

HRMS (APCI) m/z: $[M]^+$ calcd for $C_{17}H_{15}F_3^+$ 276.1120; found 276.1117.

4'-(3,3,3-trifluoroprop-1-en-2-yl)-[1,1'-biphenyl]-3-ol (M2)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 8/1) to yield **M2** (739.2 mg, 70%) as a white solid, mp: 63 - 67 ºC

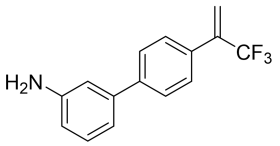
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.50 (m, 4H), 7.33 – 7.29 (m, 1H), 7.18 – 7.16 (m, 1H), 7.07 (s, 1H), 6.84 (dd, *J* = 8.0, 2.4 Hz, 1H), 5.97 (s, 1H), 5.81 (s, 1H), 5.18 (s, 0.87H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.8, 142.0, 141.2, 138.4 (q, *J* = 30.1 Hz), 132.6, 130.1, 127.7, 127.2, 123.3 (q, *J* = 274.1 Hz), 120.3 (q, *J* = 5.8 Hz), 119.7, 114.6, 114.0.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.57.

HRMS (APCI) m/z: $[M-H]^-$ calcd for $C_{15}H_{10}F_3O^-$ 263.0689; found 263.0685.

4'-(3,3,3-trifluoroprop-1-en-2-yl)-[1,1'-biphenyl]-3-amine (M3)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 5/1) to yield **M3** (715.4 mg, 68%) as a yellow liquid.

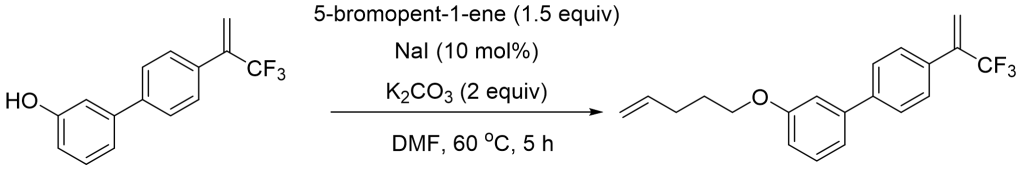
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.54 (m, 2H), 7.50 – 7.48 (m, 2H), 7.23 – 7.19 (m, 1H), 6.99 – 6.97 (m, 1H), 6.87 (s, 1H), 6.68 – 6.65 (m, 1H), 5.94 (s, 1H), 5.79 (s, 1H), 3.60 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.8, 141.9, 141.4, 138.5 (q, *J* = 29.8 Hz), 132.3, 129.8, 127.5, 127.1, 123.4 (q, *J* = 274.1 Hz), 120.1 (q, *J* = 5.7 Hz), 117.5, 114.5, 113.7.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.48.

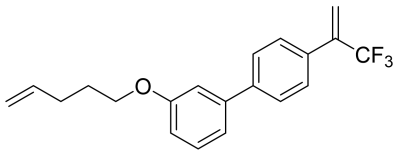
HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{13}F_3N^+$ 264.0995; found 264.0996.

Procedure C for preparation of trifluoromethyl alkenes (1q)[3]



Procedure C: A mixture of **M2** (1.056 g, 4.00 mmol, 1.0 equiv), NaI (60.0 mg, 10 mol%) K_2CO_3 (1.104 g, 8.00 mmol, 2.0 equiv) in DMF (15 mL) was stirred at 60 °C with oil bath for 30 minutes before 5-bromopent-1-ene (0.711 mL, 6.00 mmol, 1.5 equiv) was added. After the reaction mixture was cooled to room temperature, the reaction mixture was quenched with saturated H_2O, and extracted with EtOAc (3 x 20 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed under reduced pressure. The resultant crude product material was purified by flash chromatography using the appropriate gradient of petroleum ether and ethyl acetate.

3-(pent-4-en-1-yloxy)-4'-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (1q)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 50/1) to yield **1q** (823.4 mg, 62%) as a colorless liquid.

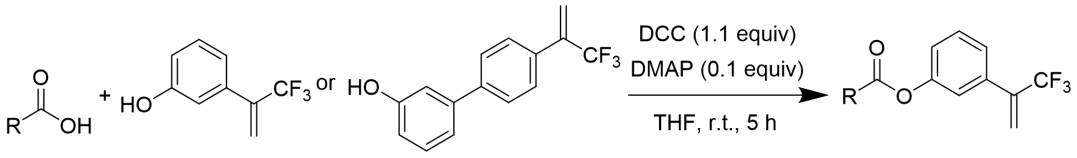
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.58 (m, 2H), 7.53 – 7.50 (m, 2H), 7.36 – 7.32 (m, 1H), 7.17 – 7.15 (m, 1H), 7.12 (s, 1H), 6.90 (dd, *J* = 8.2, 2.3 Hz, 1H), 5.96 (s, 1H), 5.91 – 5.83 (m, 1H), 5.81 (s, 1H), 5.09 (m, 1H), 5.05 – 4.99 (m, 1H), 4.03 (t, *J* = 6.4 Hz, 2H), 2.26 (q, *J* = 7.1 Hz, 2H), 1.91 (p, *J* = 6.7 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.5, 141.7, 141.7, 138.5 (q, *J* = 30.2 Hz), 137.8, 132.5, 129.8, 127.7, 127.3, 123.4 (q, *J* = 274.0 Hz), 120.2 (q, *J* = 5.8 Hz), 119.4, 115.2, 113.6, 113.5, 67.2, 30.1, 28.5.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.64.

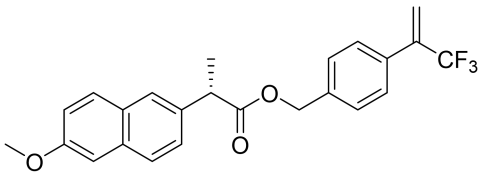
HRMS (APCI) m/z: $[M+H]^+$ calcd for $C_{20}H_{20}F_3O^+$ 333.1461; found 333.1455.

Procedure D for preparation of trifluoromethyl alkenes (1w, 1x, 1y and 1za)[4]



Procedure D: To a solution of carboxylic acid (4.50 mmol, 1.0 equiv), 4-dimethylaminopyridine (DMAP) (55.6 mg, 0.45 mmol, 0.1 equiv) and 3-(3,3,3-trifluoroprop-1-en-2-yl)phenol or 4'-(3,3,3-trifluoroprop-1-en-2-yl)-[1,1'-biphenyl]-3-ol (5.00 mmol, 1.1 equiv) in DMF (12 mL), *N*, *N*-dicyclohexylcarbodimide (DCC) (1.032 g, 5.00 mmol, 1.1 equiv) was added. The reaction mixture was stirred at room temperature for 5 hours. The reaction mixture was washed with water, and extracted with EtOAc (3 x 20 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed under reduced pressure. The resultant crude product material was purified by flash chromatography using the appropriate gradient of petroleum ether and ethyl acetate.

4-(3,3,3-trifluoroprop-1-en-2-yl)benzyl (S)-2-(6-methoxynaphthalen-2-yl)propanoate (1w)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **1w** (1266.8 mg, 68%) as a colorless oil.

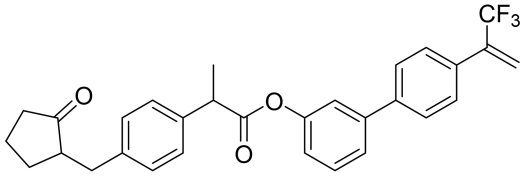
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.62 (m, 3H), 7.40 – 7.37 (m, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.14 – 7.09 (m, 2H), 5.91 (s, 1H), 5.70 (s, 1H), 5.10 (d, *J* = 3.1 Hz, 2H), 3.93 – 3.87 (m, 4H), 1.59 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.3, 157.6, 138.4 (q, *J* = 30.2 Hz), 136.8, 135.4, 133.7, 133.2, 129.2, 128.9, 127.9, 127.4, 127.1, 126.2, 125.9, 123.2 (q, *J* = 275.1 Hz), 120.5 (q, *J* = 5.8 Hz), 119.0, 105.5, 65.7, 55.1, 45.4, 18.4.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.66.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{24}H_{21}F_3O_3Na^+$ 437.1335; found 437.1348.

4'-(3,3,3-trifluoroprop-1-en-2-yl)-[1,1'-biphenyl]-3-yl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate (1x)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **1x** (996.3 mg, 45%) as a colorless oil.

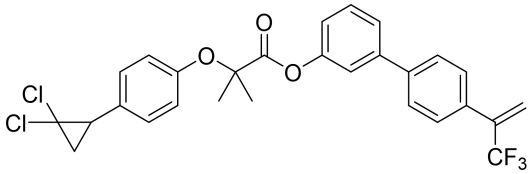
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.49 (m, 4H), 7.40 – 7.36 (m, 2H), 7.34 – 7.32 (m, 2H), 7.21 (s, 1H), 7.18 – 7.16 (m, 2H), 7.00 (dt, *J* = 6.8, 2.1 Hz, 1H), 5.95 (s, 1H), 5.79 (s, 1H), 3.96 (q, *J* = 7.1 Hz, 1H), 3.14 (dd, *J* = 13.9, 4.1 Hz, 1H), 2.53 (dd, *J* = 13.9, 9.5 Hz, 1H), 2.37 – 2.28 (m, 2H), 2.13 – 2.03 (m, 2H), 1.96 – 1.89 (m, 1H), 1.73 – 1.66 (m, 1H), 1.61 (d, *J* = 7.2 Hz, 3H), 1.57 – 1.48 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.9, 151.2, 141.6, 140.6, 139.1, 138.2 (q, *J* = 30.1 Hz), 137.7, 132.7, 129.6, 129.2, 127.6, 127.5, 127.1, 124.3, 123.2 (d, *J* = 274.1 Hz), 120.5, 120.3 (q, *J* = 5.7 Hz), 119.9, 50.8, 45.1, 38.0, 35.1, 29.1, 20.4, 18.4.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.50.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{30}H_{27}F_3O_3Na^+$ 515.1805; found 515.1817.

4'-(3,3,3-trifluoroprop-1-en-2-yl)-[1,1'-biphenyl]-3-yl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate (1y)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 8/1) to yield **1y** (1105.4 mg, 46%) as a colorless oil.

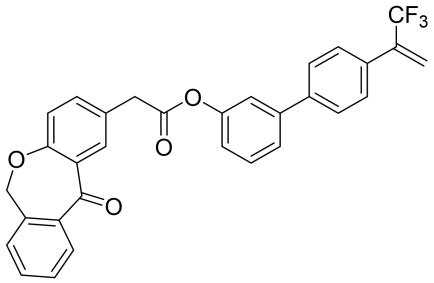
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (s, 4H), 7.43 – 7.36 (m, 2H), 7.17 – 7.14 (m, 3H), 6.97 – 6.95 (m, 3H), 5.95 (s, 1H), 5.79 (s, 1H), 2.84 – 2.79 (m, 1H), 1.91 – 1.87 (m, 1H), 1.77 – 1.73 (m, 7H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.8, 154.9, 150.9, 141.8, 140.4, 138.2 (q, *J* = 29.8 Hz), 132.8, 129.8, 129.8, 128.4, 127.7, 127.2, 124.7, 123.3 (q, *J* = 274.0 Hz), 120.4 (q, *J* = 5.8 Hz), 120.4, 119.8, 118.5, 79.2, 60.8, 34.7, 25.7, 25.4 (d, *J* = 3.7 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.39.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{28}H_{23}Cl_2F_3O_3Na^+$ 557.0869; found 557.0877.

4'-(3,3,3-trifluoroprop-1-en-2-yl)-[1,1'-biphenyl]-3-yl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (1za)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **1za** (925.2 mg, 40%) as a colorless oil.

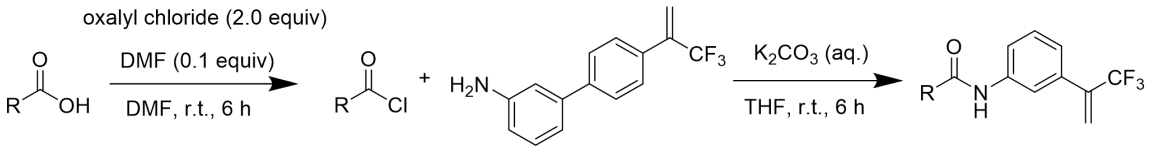
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 (s, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.54 – 7.45 (m, 6H), 7.41 – 7.36 (m, 3H), 7.31 (s, 1H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 6.8 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 5.93 (s, 1H), 5.77 (s, 1H), 5.10 (s, 2H), 3.88 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.5, 169.7, 160.5, 151.0, 141.5, 140.4, 140.2, 138.1 (q, *J* = 29.9 Hz), 136.2, 135.4, 132.7, 132.6, 132.5, 129.7, 129.3, 129.1, 127.7, 127.6, 127.1, 127.0, 125.1, 124.4, 123.2 (q, *J* = 273.9 Hz), 121.1, 120.5, 120.3 (q, *J* = 5.8 Hz), 119.9, 73.4, 40.0.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.37.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{31}H_{21}F_3O_4Na^+$ 537.1284; found 537.1294.

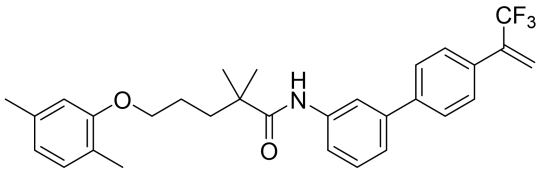
Procedure E for preparation of trifluoromethyl alkenes (1h and 1z)[2]



Procedure E: To a mixture of carboxylic acid (3.00 mmol, 1.0 equiv) and oxalylchloride (0.51 mL, 6.00 mmol, 2.0 equiv) in dry CH_2Cl_2 (12 mL) was added dropwise DMF (23.4 μL, 0.30 mmol, 0.1 equiv). The reaction mixture was stirred at room temperature for 6 h. Removal of the solvent in vacuo afforded the desired acid chloride which was used in the next step without further purification. To a mixture of 3-(3,3,3-trifluoroprop-1-en-2-yl)aniline or 4'-(3,3,3-trifluoroprop-1-en-2-yl)-[1,1'-biphenyl]-3-amine (3.00 mmol, 1.0 equiv) and K_2CO_3 (414.6 mg, 3.00 mmol, 1.0 equiv) in dry THF (6 mL) was added dropwise a solution of the freshly prepared acid chloride (3.00 mmol, 1.0 equiv) in dry THF (6 mL). This mixture was stirred at room temperature for 6 hours before water was added to quench the reaction. The resultant mixture was extracted with

EtOAc (3 x 20 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure.

5-(2,5-dimethylphenoxy)-2,2-dimethyl-N-(4'-(3,3,3-trifluoroprop-1-en-2-yl)-[1,1'-biphenyl]-3-yl)pentanamide (1z)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **1z** (668.3 mg, 45%) as a white solid, mp: 89 - 93 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.60 – 7.55 (m, 3H), 7.48 – 7.46 (m, 3H), 7.37 – 7.30 (m, 2H), 6.98 – 6.96 (m, 1H), 6.64 (d, *J* = 7.5 Hz, 1H), 6.59 (s, 1H), 5.94 (s, 1H), 5.78 (s, 1H), 3.90 (s, 2H), 2.26 (s, 3H), 2.16 (s, 3H), 1.82 (s, 4H), 1.33 (s, 6H).

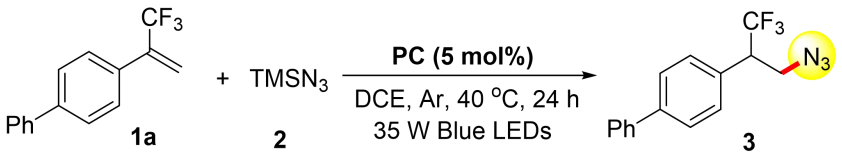
^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.9, 156.8, 141.2, 141.0, 138.5, 138.5 (q, *J* = 30.2 Hz), 136.5, 132.5, 130.3, 129.3, 127.6, 127.2, 123.5, 123.3 (q, *J* = 274.1 Hz), 122.8, 120.9, 120.2 (q, *J* = 5.9 Hz), 119.4, 118.9, 112.3, 67.9, 42.8, 37.6, 25.5, 25.1, 21.3, 15.7.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.49.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{30}H_{32}F_3NO_2Na^+$ 518.2277; found 518.2287.

3. Optimization of the reaction conditions and control experiments

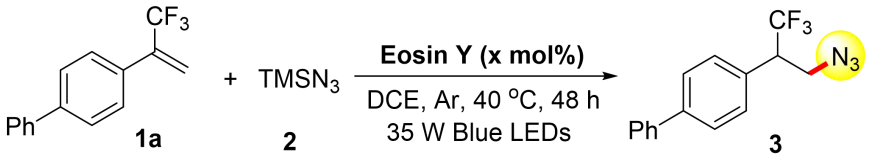
Table S1. Optimization of photocatalyst [a]



Entry	PC	Yield (%) [b]
1	Eosin Y	28
2[c]	Eosin Y	52
3	$Ir(ppy)_3$	trace
4	4CzIPN	8
5	$Ru(bpy)_3(PF_6)_2$	N.R
6	$[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$	trace
7	Rose Bengal	N.R.
8	9-Fluorenone	N.R.

[a] reaction conditions: **1a** (0.20 mmol), **2** (2 equiv), PC (5 mol%), DCE (2 mL), 35 W blue LEDs, Ar, 40 °C, 24 h. N.R. refers to no reaction. [b] Yields of the isolated products were given. [c] reaction 48 h.

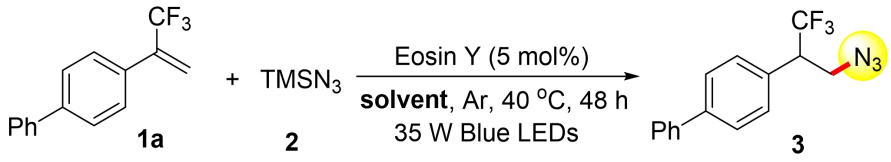
Table S2. Optimization of amount of photocatalyst [a]



Entry	Amount (mol%)	Yield (%) [b]
1	2	43
2	5	52
3	8	53
4	10	52

[a] reaction conditions: **1a** (0.20 mmol), **2** (2 equiv), Eosin Y (x mol%), DCE (2 mL), 35 W blue LEDs, Ar, 40 ºC, 48 h. [b] Yields of the isolated products were given.

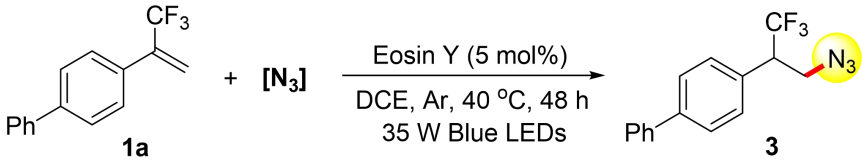
Table S3. Optimization of solvent [a] **.**



Entry	Solvent	Yield (%) [b]
1	DCE	52
2	DCE (1 mL)	61
3	DCE (0.5 mL)	40
4	CH_3CN	N.R.
5	Acetone	N.R.
6	THF	N.D.
7	PhCl	50
8	benzene	22
9	Et_2O	trace
10	DMF	trace
11	DMSO	trace
12	1,4-Dioxane	trace

[a] reaction conditions: **1a** (0.20 mmol), **2** (2 equiv), Eosin Y (5 mol%), solvent (2 mL), 35 W blue LEDs, Ar, 40 ºC, 48 h. N.R. refers to no reaction. N.D. refers to not detected. [b] Yields of the isolated products were given. PhCl= Chlorobenzene, CH_3CN= Acetonitrile, DCE= 1,2-Dichloroethane, THF= Tetrahydrofuran.

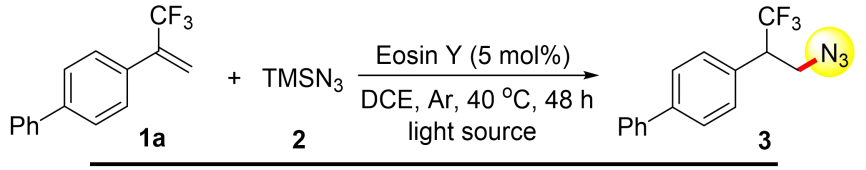
Table S4. Optimization of the azide sources [a]



Entry	Azide sources	Yield (%) [b]
1	TsN_3	0
2	Azidobenziodoxolone (ABX)	9
3	$TMSN_3$ (2 equiv)	61
4	$TMSN_3$ (3 equiv)	68
5	$TMSN_3$ (4 equiv)	69

[a] reaction conditions: **1a** (0.20 mmol), **azide source** (x equiv), Eosin Y (5 mol%), DCE (1 mL), 35 W blue LEDs, Ar, 40 ºC, 48 h. [b] Yields of the isolated products were given.

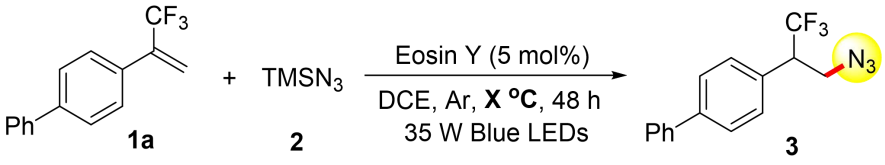
Table S5. Optimization of the light source [a]



Entry	Light source	Yield (%) [b]
1	35 W blue LEDs	68
2	35 W white LEDs	53
3	35 W purple LEDs	21
4	35 W yellow LEDs	16
5	35 W red LEDs	0

[a] reaction conditions: **1a** (0.20 mmol), **2** (3 equiv), Eosin Y (5 mol%), DCE (1 mL), light source, Ar, 40 ºC, 48 h. [b] Yields of the isolated products were given.

Table S6. Optimization of the temperature [a]

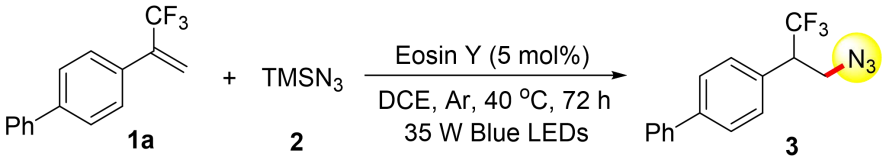


Entry	Temperature (ºC)	Yield (%) [b]
1	30	66
2	40	68
3	50	64

4	70	50
5[c]	40	74

[a] reaction conditions: **1a** (0.20 mmol), **2** (3 equiv), Eosin Y (5 mol%), DCE (1 mL), 35 W blue LEDs, Ar, X ºC, 48 h. [b] Yields of the isolated products were given. [c] 72 h.

Table S7. Controlled experiment [a]



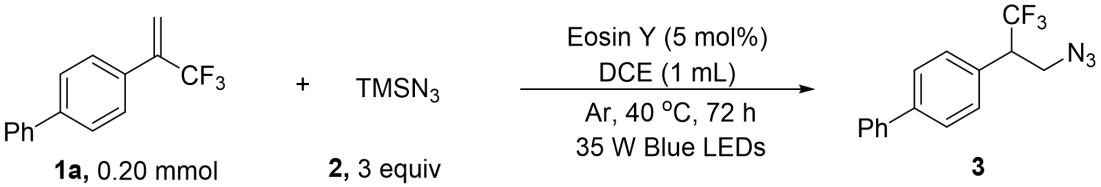
Entey	Variation from standard conditions	Yield (%) [b]
1	none	74
2	No PC or no light	N.R
3	air	50
4	Anhydrous DCE and H_2O (5 equiv)	72

[a] Standard conditions: **1a** (0.20 mmol), **2** (3 equiv), Eosin Y (5 mol%), DCE (1 mL), 35 W blue LEDs, Ar, 40 ºC, 72 h. [b] Yields of the isolated products were given.

4. General procedures

4.1 Reaction for the synthesis of 3

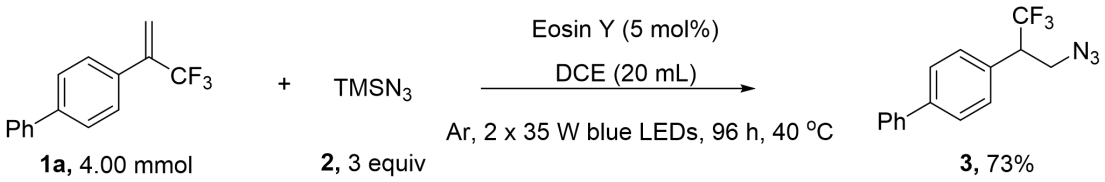
General procedure: 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (49.6 mg, 0.20 mmol), $TMSN_3$ (69.1 mg, 3.0 equiv), Eosin Y (6.5 mg, 5 mol%) and DCE (1 mL) were added into a 10 mL tube successively. The tube was charged with argon, which repeated three times. The reaction mixture was stirred at 40 ºC under the irradiation by 35 W Blue LEDs for 72 h. The reaction was monitored by TLC. The crude reaction mixture was quenched with saturated sodium carbonate and extracted with EtOAc (3 x 20 mL). The extracts were combined, dried over sodium sulfate, filtered, and the volatiles were removed under reduced pressure. Column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254) to give product **3.**



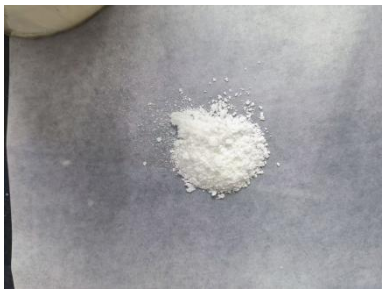
A commercially available 35W (HIPAR30) blue LED lamp was used as the light source, and the reaction setup was provided as the figure above. The sample was about 4 cm from the lamp under ambient temperature with the equipment of a fan.

4.2 Scale-up reaction for the synthesis of 3

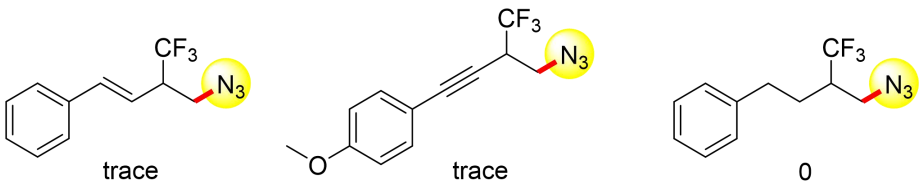
4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (4.00 mmol, 0.992 g), $TMSN_3$ (1.382 g, 3.0 equiv), Eosin Y (5 mol%, 129.6 mg) and DCE (20 mL) were added into a 100 mL reaction vessel successively. The vessel was charged with argon, which repeated three times. The reaction mixture was stirred at 40 ºC under the irradiation by 2 x 35 W Blue LEDs for 96 h. The reaction was monitored by TLC. After completion, the solvent was evaporated under vacuum, and the crude product was purified using Column chromatography on silica gel (200-300 mesh) to obtain product **3** in 73% yield **(**0.853 g**)**.



1a, 4.00 mmol **2,** 3 equiv **3,** 73%



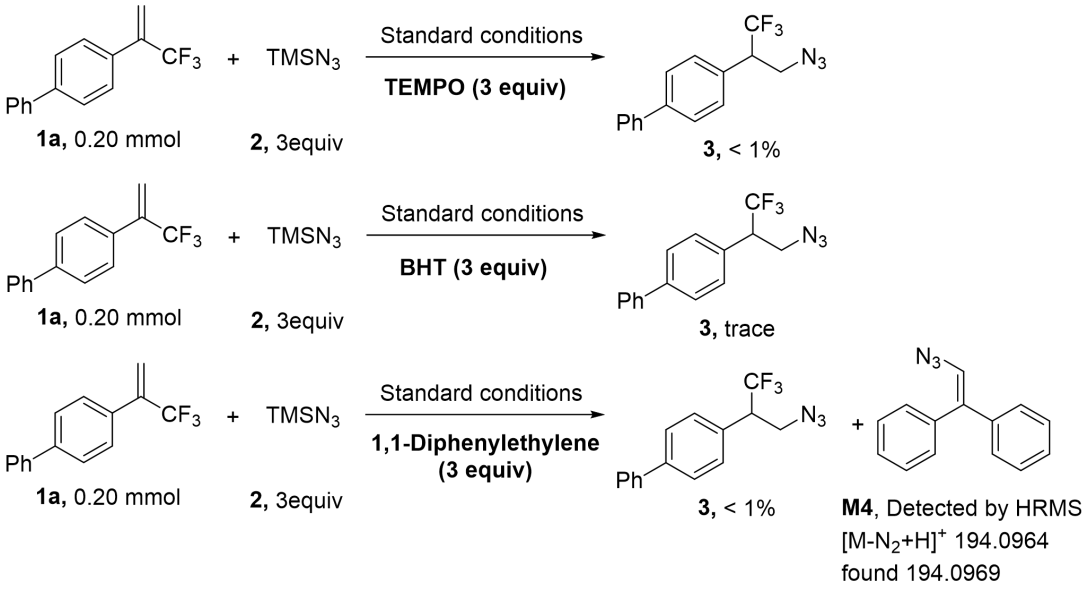
Limitations of the scope:



5. Mechanistic investigations

5.1 Free radical capture experiments

The following reaction was carried out under general procedure: 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (49.6 mg, 0.20 mmol), $TMSN_3$ (69.1 mg, 3.0 equiv), Eosin Y (6.5 mg, 5 mol%) and DCE (1 mL), and radical inhibitor TEMPO (93.8 mg, 3.0 equiv), BHT (132.2 mg, 3.0 equiv) or 1,1-diphenylethene (108.2 mg, 3.0 equiv) were added into a 10 mL tube successively. The tube was charged with argon, which repeated three times. The reaction mixture was stirred at 40 ºC under the irradiation by 35 W Blue LEDs for 72 h. After completion, product **3** was not detected, and (2-azidoethene-1,1-diyl)dibenzene (**M4)** was detected by HRMS (positive mode ESI).



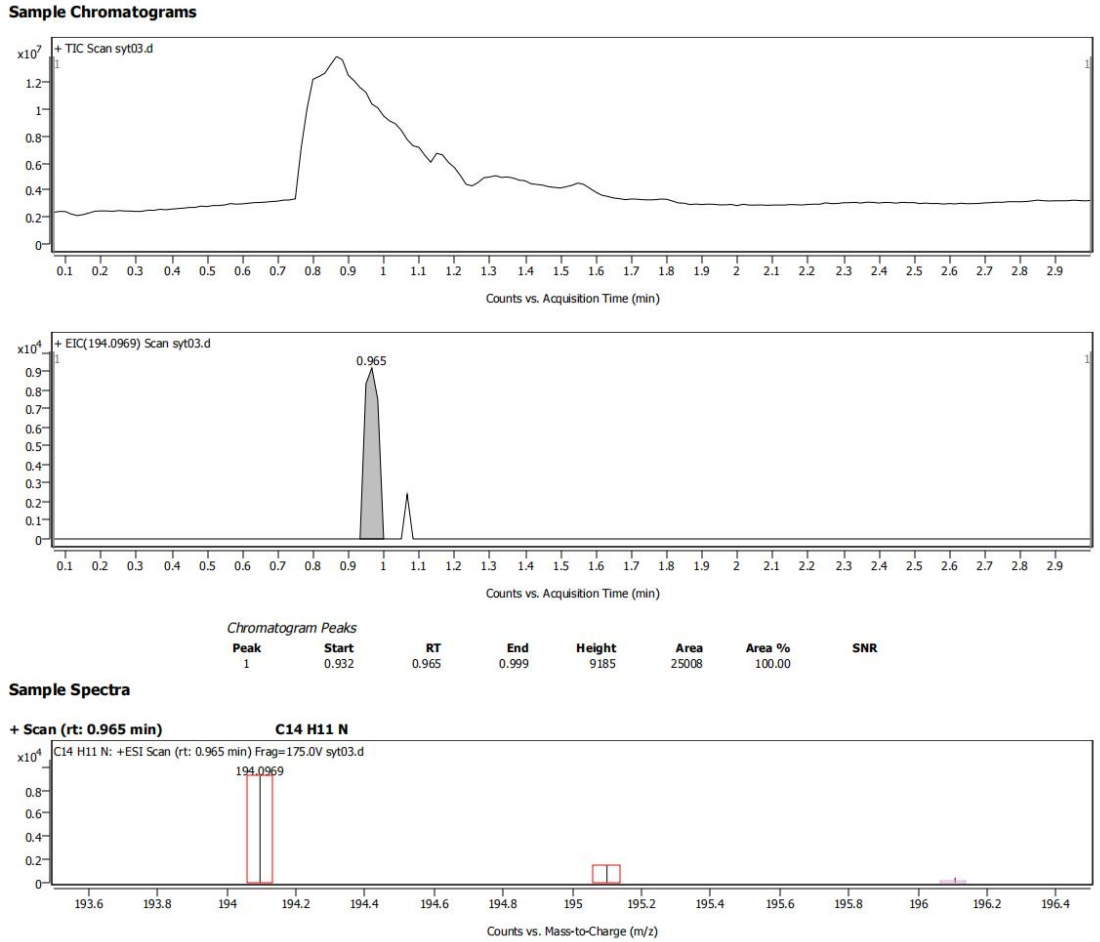
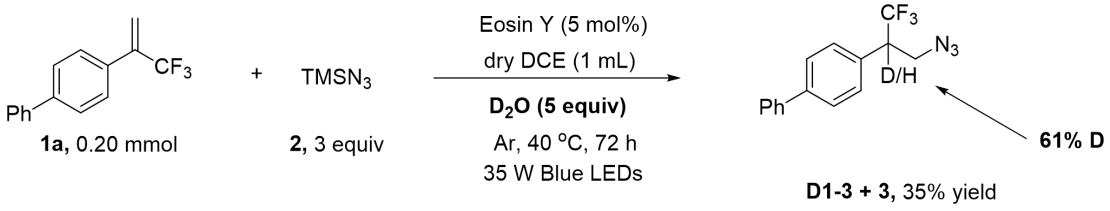
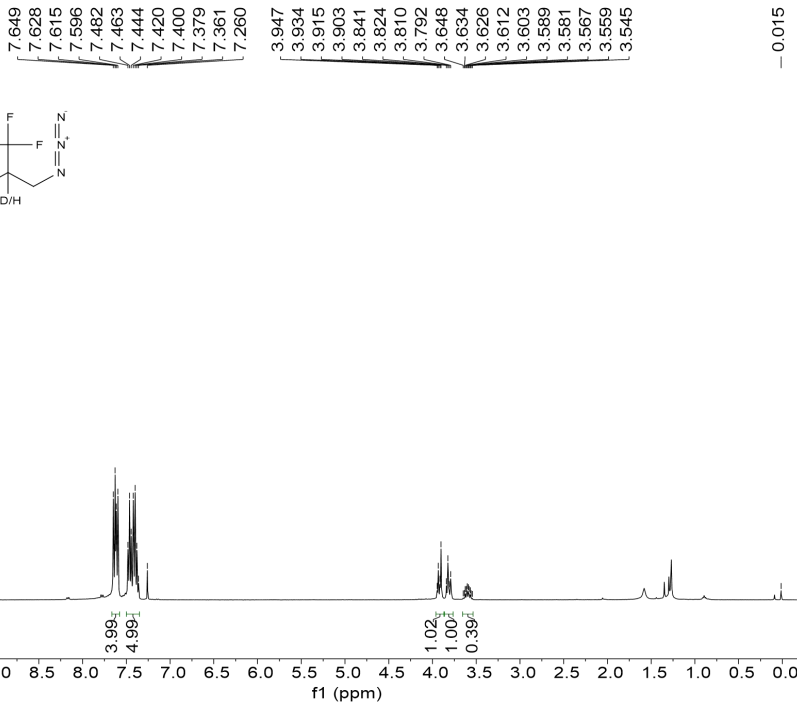


Figure S1. HRMS spectra of M4

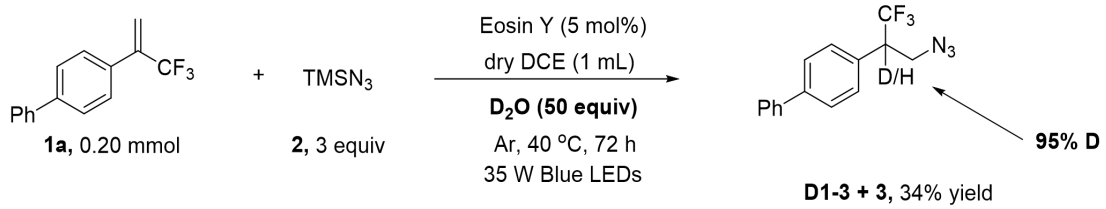
5.2. Deuterium-labelling experiments

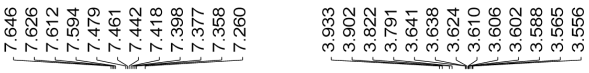
(a): 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (49.6 mg, 0.20 mmol), $TMSN_3$ (69.1 mg, 3.0 equiv), Eosin Y (6.5 mg, 5 mol%), DCE (1 mL) and D_2O (20 mg, 5.0 equiv) were added into a 10 mL tube successively. The tube was charged with argon, which repeated three times. The reaction mixture was stirred at 40 ºC under the irradiation by 35 W Blue LEDs for 72 h. The reaction was monitored by TLC. The crude reaction mixture was quenched with saturated sodium carbonate and extracted with EtOAc (3 x 20 mL). The extracts were combined, dried over sodium sulfate, filtered, and the volatiles were removed under reduced pressure. Column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254) to give product **D1-3+3** (35%, 61% D).

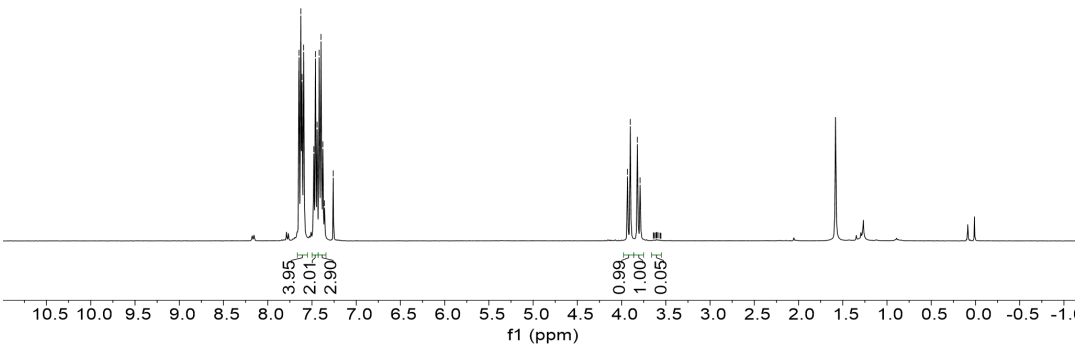




(b): 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (49.6 mg, 0.20 mmol), $TMSN_3$ (69.1 mg, 3.0 equiv), Eosin Y (6.5 mg, 5 mol%), DCE (1 mL) and D_2O (200 mg, 50 equiv) were added into a 10 mL tube successively. The tube was charged with argon, which repeated three times. The

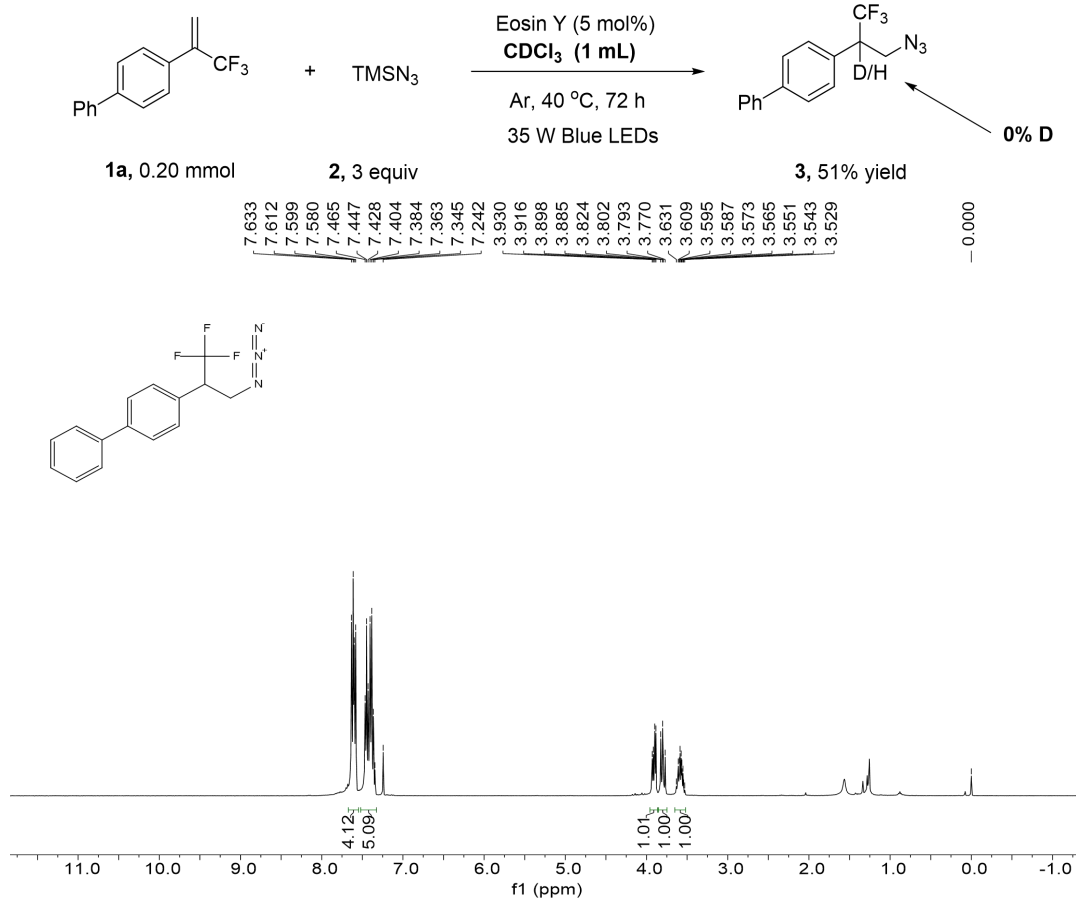






reaction mixture was stirred at 40 ºC under the irradiation by 35 W Blue LEDs for 72 h. The reaction was monitored by TLC. The crude reaction mixture was quenched with saturated sodium carbonate and extracted with EtOAc (3 x 20 mL). The extracts were combined, dried over sodium sulfate, filtered, and the volatiles were removed under reduced pressure. Column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254) to give product **D1-3+3** (34%, 95% D).

(c): 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (49.6 mg, 0.20 mmol), $TMSN_3$ (69.1 mg, 3.0 equiv), Eosin Y (6.5 mg, 5 mol%) and $CDCl_3$ (1 mL) were added into a 10 mL tube successively. The tube was charged with argon, which repeated three times. The reaction mixture was stirred at 40 ºC under the irradiation by 35 W Blue LEDs for 72 h. The reaction was monitored by TLC. The crude reaction mixture was quenched with saturated sodium carbonate and extracted with EtOAc (3 x 20 mL). The extracts were combined, dried over sodium sulfate, filtered, and the volatiles were removed under reduced pressure. Column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254) to give product **3** (51%, 0% D).



5.3. Radical clock experiment.

(1-cyclopropylvinyl)benzene (28.8 mg, 0.20 mmol), $TMSN_3$ (69.1 mg, 3.0 equiv), Eosin Y (6.5 mg, 5 mol%) and DCE (1 mL) were added into a 10 mL tube successively. The tube was charged with argon, which repeated three times. The reaction mixture was stirred at 40 ºC under the irradiation by 35 W Blue LEDs for 72 h. The extracts were combined, dried over sodium

sulfate, filtered, and the volatiles were removed under reduced pressure. However, complex products were obtained, and it could not be purified by column chromatography as pure compounds. The ring-opened compounds were formed, thus supporting the involvement of the azide radical ($N_3^{\bullet}$) in the catalytic reaction.

0.2 mmol **2**, 3 equiv **39**, Detected by HRMS $[M-N_3]^+$ 145.1012 found 145.1012

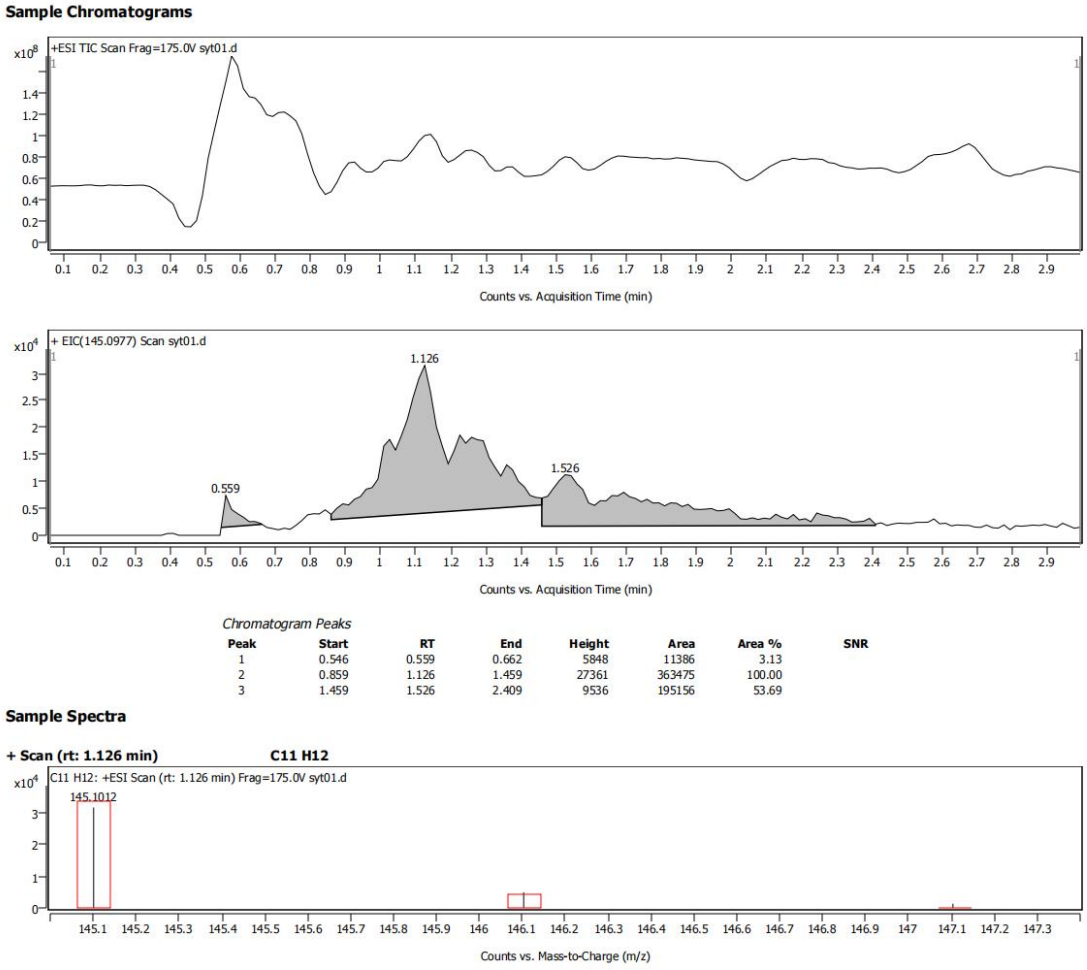


Figure S2. HRMS of compounds 39

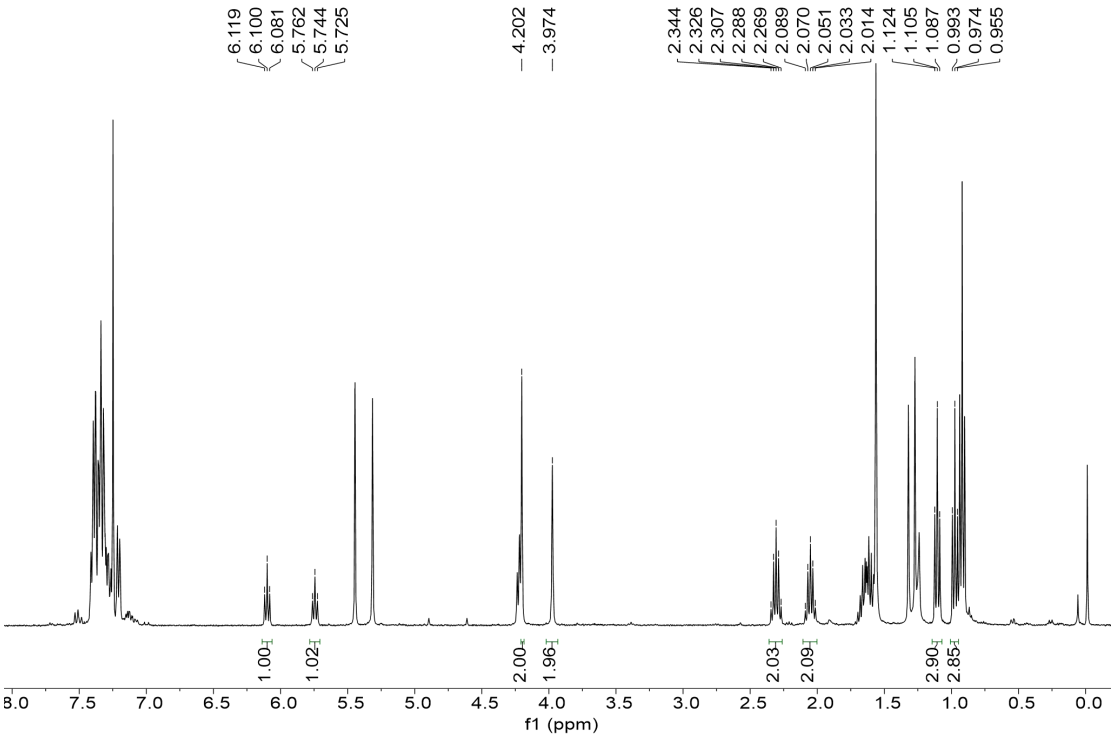
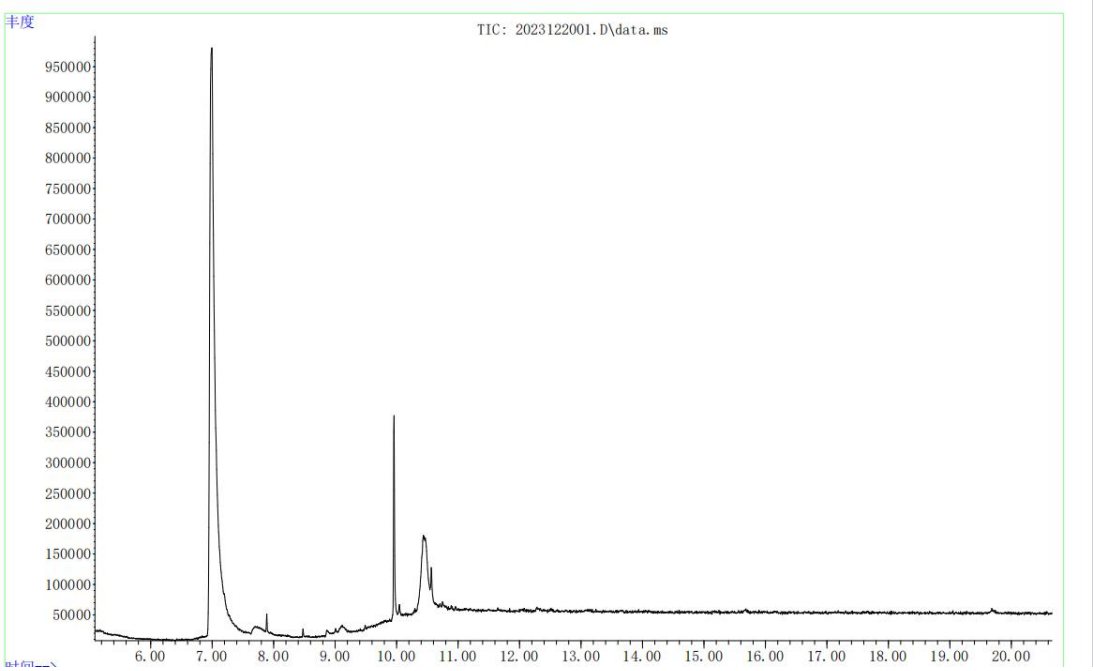


Figure S3. ^{1}H NMR spectra of compound 39



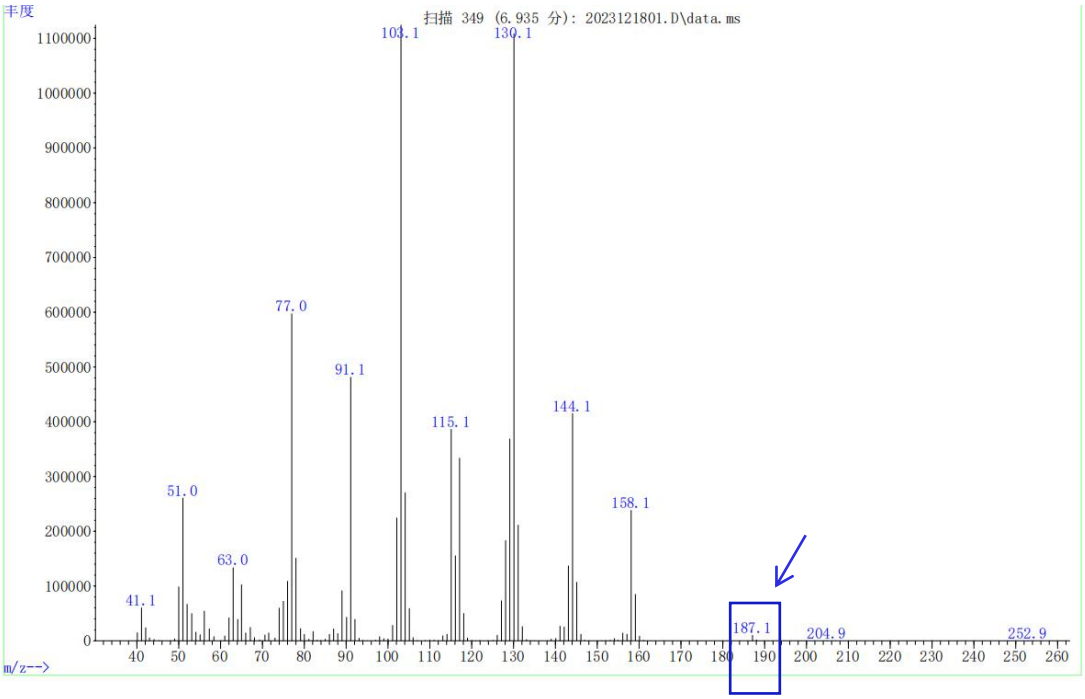
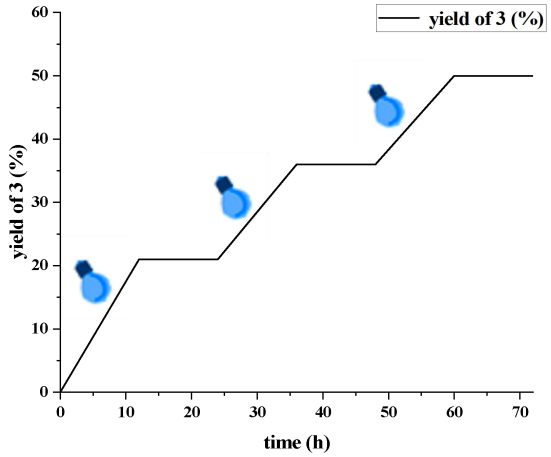


Figure S4. GC-MS spectra of compound 39

5.4. Photo-irradiation on and off experiments.



5.5. Quantum yield determination

Blue LED (λ_{max} = 415 nm) was used for measurement of quantum yield.

Determination of the light intensity at 415 nm:

According to the procedure of Yoon,[5] the photon flux of the LED (λ_{max} = 415 nm) was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (0.737 g) in H_2SO_4 (10 mL of a 0.05 M solution). A buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (5.0 mg) and sodium acetate (1.13 g) in H_2SO_4 (5.0 mL of a 0.5 M solution). Both solutions were stored in

the dark. To determine the photon flux of the LED, the ferrioxalate solution (2.0 mL) was placed in a cuvette and irradiated for 90 seconds at λ_{max} = 415 nm. After irradiation, the phenanthroline solution (0.35 mL) was added to the cuvette and the mixture was allowed to stir in the dark for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured (Figure S5). Conversion was calculated using eq 1.

$$\text{mol } Fe^{2+} = \frac{V \cdot \Delta A_{510nm}}{l \cdot \varepsilon} \qquad (1)$$

$$\text{mol } Fe^{2+} = \frac{(0.00235\text{L}) \cdot (3.70)}{(1.00\ cm) \cdot (11{,}100\ \frac{L}{mol}\ cm^{-1})} = 7.83 \times 10^{-7}\ mol$$

V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l.00 is the path length (1.00 cm), and ε is the molar absorptivity of the ferrioxalate actinometer at 510 nm (11,100 $Lmol^{-1}cm^{-1}$).

The photon flux can be calculated using eq 2.

$$\text{photon flux} = \frac{\text{mol } Fe^{2+}}{\emptyset \cdot t \cdot f} \qquad (2)$$

$$\text{photon flux} = \frac{7.83 \times 10^{-7} mol}{(1.12) \cdot (90\text{s}) \cdot (1)} = 7.77 \times 10^{-9}\ einstein/s$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.12 at λ = 415 nm), t is the irradiation time (90 s), and f is the fraction of light absorbed at 415 nm by the ferrioxalate actinometer. This value is calculated using eq 3 where A_{415} nm is the absorbance of the ferrioxalate solution at 415 nm. An absorption spectrum gave an A_{415} nm value of > 4, indicating that the fraction of absorbed light (f) is >0.9999.

$$f = 1 - 10^{-A_{415nm}} \qquad (3)$$

The photon flux was thus calculated to be 7.77 × 10^{-9} einsteins s^{-1}

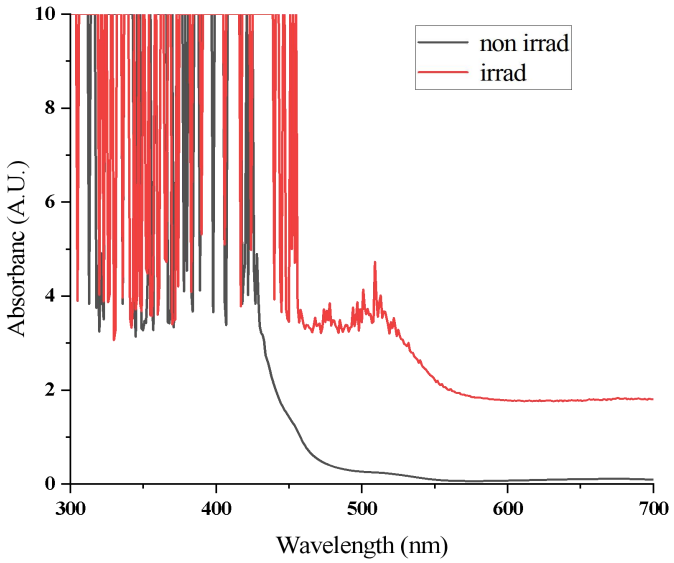
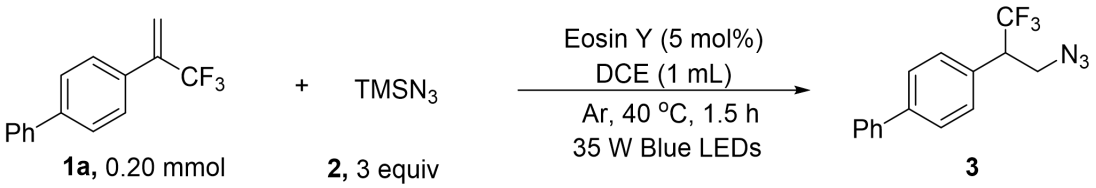


Figure S5. Absorbance of the ferrioxalate actinometer solution.

Determination of the reaction quantum yield.



1a, 0.20 mmol **2,** 3 equiv **3**

4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (49.6 mg, 0.20 mmol), $TMSN_3$ (69.1 mg, 3.0 equiv), Eosin Y (6.5 mg, 5 mol%) and DCE (1 mL) were added into a 10 mL tube successively. The tube wascharged with argon, which repeated three times. The reaction mixture was stirred at 40 ºC under the irradiation by 35 W Blue LEDs for 1.5 h (5,400 s) under blue LED irradiation (λ = 415 nm). The solvent was removed in vacuo and the yield of formed product was determined by ^{19}F NMR based on trifluorotoluene as internal standard. The yield of **3** was determined to be 4% (8.0×10^{-6} mol of **3**).

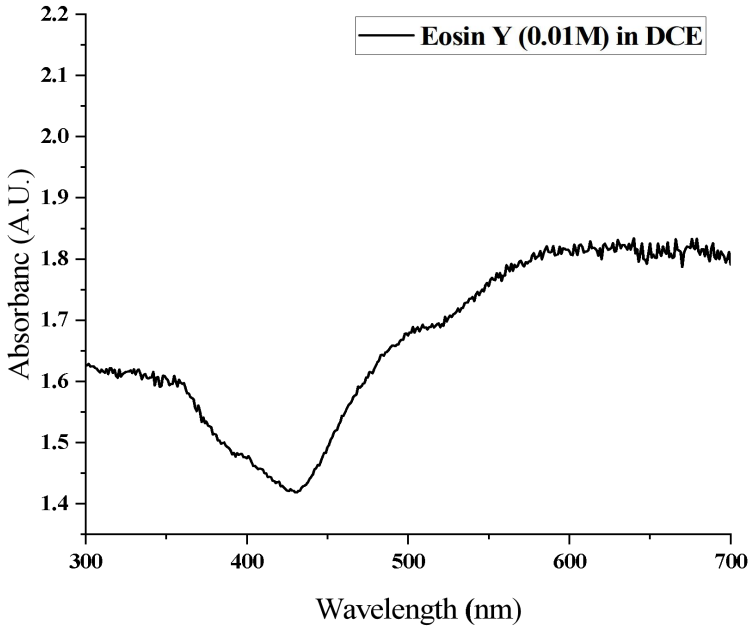


Figure S6. Absorption spectrum of Eosin Y [0.01 M] in DCE

The reaction quantum yield (Φ) was determined using eq 4 where the photon flux is 7.77×10^{-9} einsteins s^{-1} (determined by actinometry as described above), t is the reaction time (5,400 s) and f is the fraction of incident light absorbed by the catalyst, determined using eq 3. An absorption spectrum of the catalyst (0.01 M) gave an absorbance value of 1.443 at 415 nm (Figure S6), indicating that the fraction of light absorbed by the photocatalyst (f) is 0.96.

$$\emptyset = \frac{mol\ product}{flux \cdot t \cdot f} \qquad (4)$$

$$\emptyset = \frac{8.0 \times 10^{-6}\ \text{mol}}{(7.77 \times 10^{-9}\ einstein/s) \cdot (5400\ s) \cdot (0.96)} = 0.20$$

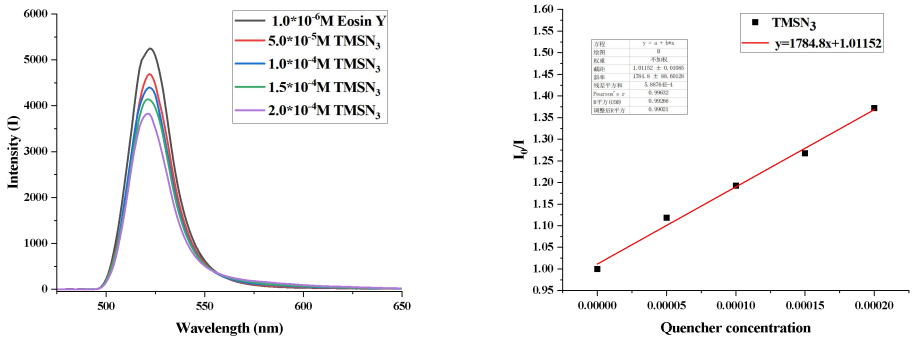
The reaction quantum yield (Φ) was calculated to be 0.20.

5.6. Stern-Volmer fluorescence quenching experiments

Formulation solution: 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (62.0 mg) was dissolved in DCE in a 25 mL volumetric flask to set the concentration to be 0.01 M. $TMSN_3$ (30.0 mg) was dissolved in DCE in a 25 mL volumetric flask to set the concentration to be 0.01 M. Dissolve the photocatalyst Eosin Y (8.8 mg) in DCE in a 25 mL volumetric flask, shake well, take out 5 mL of the solution and make up to volume with DCE in a 25 mL volumetric flask, setting the concentration to 0.1 mM.

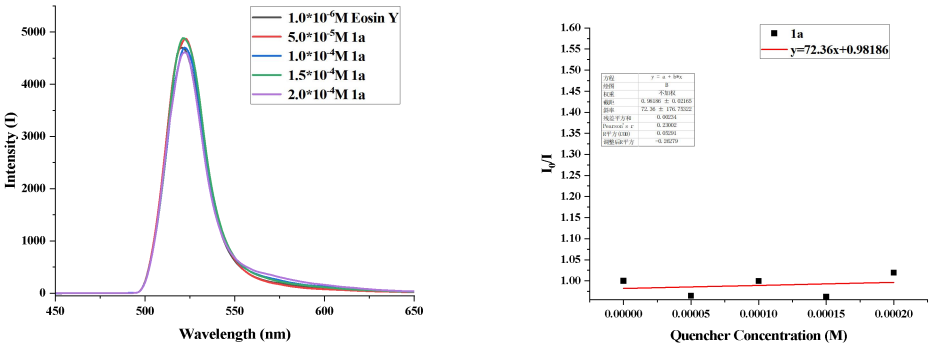
Experimental procedure: The resulting 0.1 mM solution (20 μL) was added to cuvette to obtain different concentrations of catalyst solution. This solution was then diluted to a volume of 2.0 mL by adding DCE to prepare a 1.0 μM solution. The resulting mixture was sparged with nitrogen for 3 minutes and then irradiated at 515 nm. Fluorescence emission spectra were recorded (3 trials per sample). Into this solution, 10.0 μL of a 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl solution was successively added and uniformly stirred, and the resulting irradiated at 515 nm. Fluorescence emission spectra of 0 μL, 10.0 μL, 20.0 μL, 30.0 μL and 40.0 μL fluorescence intensity. Follow this method and make changes to the amount to obtain the Stern–Volmer relationship in turn.

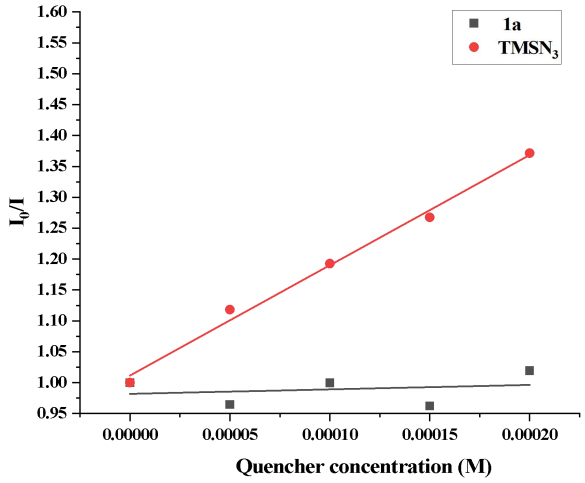
(a) Eosin Y quenched by $TMSN_3$ in DCE.



The emission intensity of the Eosin Y catalyst solution affected by the gradual increase of the amount of $TMSN_3$.

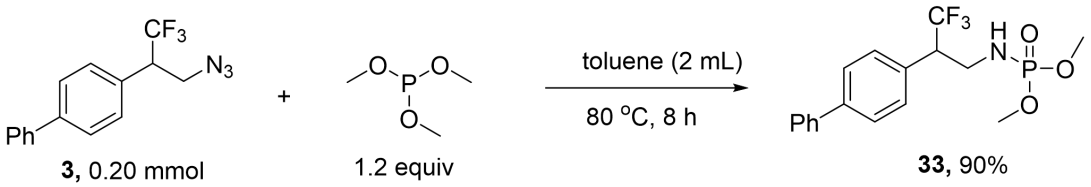
(b) Eosin Y quenched by 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (**1a**) in DCE.



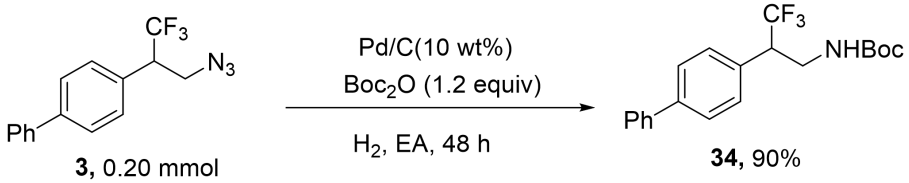


6. Selective transformations of hydroazidation product 3

(1) The reaction was carried out by modifying the literature procedure.[6] To a reaction tube was added **3** (58.2 mg, 0.20 mmol) and trimethyl phosphite (28.4 μL, 0.24 mmol) in toluene (2 mL) was heated at 80 °C with oil bath for 8 h, and then cooled to room temperature. Upon completion, the mixture was quenched with H_2O and extracted with EtOAc (3 x 20 mL). The combined organic phases were washed with brine, dried (Na_2SO_4), filtered and concentrated under reduced pressure. The crude product **33** was purified by flash column chromatography (SiO_2 200 - 300 mesh; gradient eluent: PE/EA= 2/1) to yield **33** (67.1 mg, 90%).

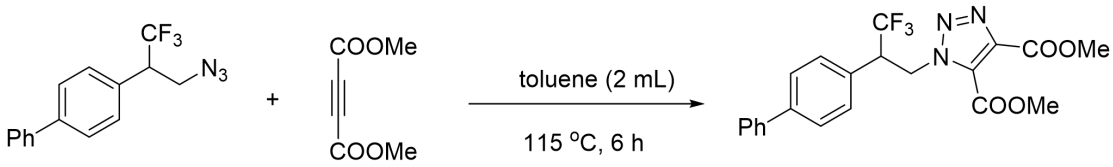


(2) The reaction was carried out by modifying the literature procedure.[6] To a reaction tube was added **3** (58.2 mg, 0.20 mmol), Boc_2O (45.0 µL, 0.20 mmol, 1.2 equiv) and 10% Pd/C (8.4 mg) were dissolved in EtOAc (2 mL), then replament of hydrogen (balloon). The resulting solution was stirred at 25 °C for 48 h. Upon completion, the mixture was quenched with H_2O and extracted with EtOAc (3 x 20 mL). The combined organic phases were washed with brine, dried (Na_2SO_4), filtered and concentrated under reduced pressure. The crude product **34** was purified by flash column chromatography (SiO_2 (200 - 300 mesh); gradient eluent: PE/EA= 15/1) to yield **34** (65.7 mg, 90%).



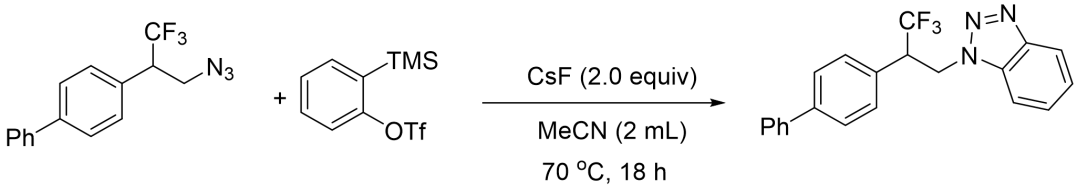
(3) The reaction was carried out by modifying the literature procedure.[7] To a reaction tube was added **3** (58.2 mg, 0.2 mmol) and dimethyl but-2-ynedioate (122.8 μL, 0.22 mmol, 1.2 equiv)

in toluene (2 mL) was heated at 115 °C with oil bath for 6 h, and then cooled to room temperature. Upon completion, the mixture was quenched with H_2O and extracted with EtOAc (3 x 20 mL). The combined organic phases were washed with brine, dried (Na_2SO_4), filtered and concentrated under reduced pressure. The crude product **35** was purified by flash column chromatography (SiO_2 (200 - 300 mesh); gradient eluent: PE/EA= 5/1) to yield **35** (68.4 mg, 79%).



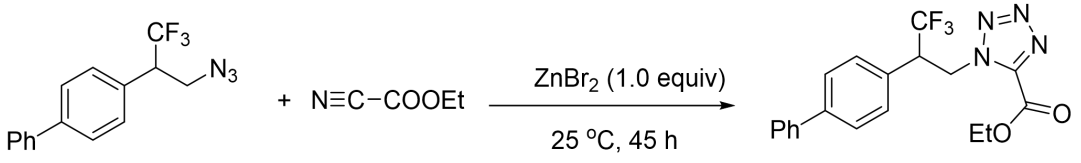
3, 0.20 mmol 1.2 equiv **35,** 79%

(4) The reaction was carried out by modifying the literature procedure.[8] To a reaction tube was added **3** (58.2 mg, 0.20 mmol), 2-(Trimethylsilyl)phenyl Triflate (71.5 mg, 0.24 mmol, 1.2 equiv) and CsF (60.4 mg, 0.40 mmol, 2.0 equiv) in MeCN (2 mL) was heated at 70 °C with oil bath for 18 h, and then cooled to room temperature. Upon completion, the mixture was quenched with H_2O and extracted with EtOAc (3 x 20 mL). The combined organic phases were washed with brine, dried (Na_2SO_4), filtered and concentrated under reduced pressure. The crude product **36** was purified by flash column chromatography (SiO_2 (200 - 300 mesh); gradient eluent: PE/EA= 5/1) to yield **36** (55.1 mg, 75%).



3, 0.20 mmol 1.2 equiv **36,** 75%

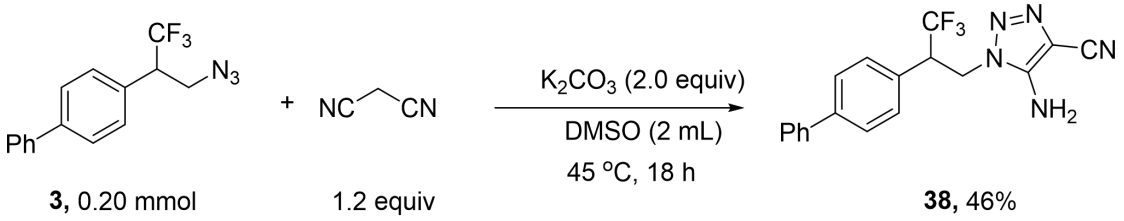
(5) The reaction was carried out by modifying the literature procedure.[9] To a reaction tube was added **3** (58.2 mg, 0.20 mmol) 13 equiv of ethyl carbonocyanidate (2.60 mmol, 0.257 g), and 1.0 equiv of $ZnBr_2$ (0.20 mmol 46.0 mg) at room temperature 25 °C for 45 h, and then cooled to room temperature. Upon completion, the mixture was quenched with H_2O and extracted with EtOAc (3 x 20 mL). The combined organic phases were washed with brine, dried (Na_2SO_4), filtered and concentrated under reduced pressure. The crude product **37** was purified by flash column chromatography (SiO_2 (200 - 300 mesh); gradient eluent: PE/EA= 5/1) to yield **37** (40.6 mg, 52%).



3, 0.20 mmol 13.0 equiv **37,** 52%

(6) The reaction was carried out by modifying the literature procedure.[10] To a reaction tube was added **3** (58.2 mg, 0.20 mmol) Malononitrile (19.8 mg, 0.30 mmol, 1.5 equiv), K_2CO_3 (55.2 mg, 0.40 mmol, 2.0 equiv) in DMSO (2 mL) was heated at 45 °C with oil bath for 6 h, and then

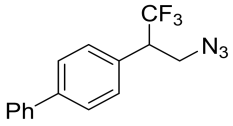
cooled to room temperature. Upon completion, the mixture was quenched with H_2O and extracted with EtOAc (3 x 20 mL). The combined organic phases were washed with brine, dried (Na_2SO_4), filtered and concentrated under reduced pressure. The crude product **38** was purified by flash column chromatography (SiO_2 (200 - 300 mesh); gradient eluent: PE/EA= 2/1) to yield **38** (33.0 mg, 46%).



3, 0.20 mmol 1.2 equiv **38,** 46%

7. Characterization data of products

4-(3-azido-1,1,1-trifluoropropan-2-yl)-1,1'-biphenyl (3)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA:200/1) to yield **3** (43.1 mg, 74%) as a white solid, mp: 82 – 86 °C.

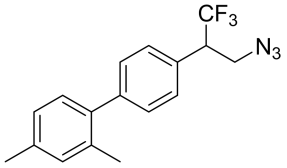
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.49 (m, 4H), 7.38 – 7.34 (m, 5H), 3.84 – 3.79 (m, 1H), 3.73 – 3.68 (m, 1H), 3.54 – 3.44 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.9, 140.2, 131.0 (d, *J* = 1.5 Hz), 129.3, 128.8, 127.7 127.6, 127.1, 125.6 (q, *J* = 280.6 Hz), 50.2 (d, *J* = 2.5 Hz), 49.8 (q, *J* = 26.8 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.28.

HRMS (APCI) m/z: $[M-N_2+H]^+$ calcd for $C_{15}H_{13}F_3N^+$ 264.0995; found 264.0991.

4'-(3-azido-1,1,1-trifluoropropan-2-yl)-2,4-dimethyl-1,1'-biphenyl (4)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 50/1) to yield **4** (32.5 mg, 51%, 71% brsm) as a colorless liquid, with 28% of starting material recovered.

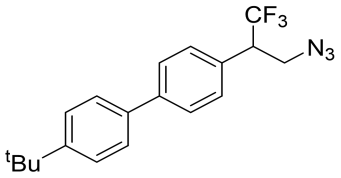
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (s, 3H), 7.14 – 7.10 (m, 2H), 7.07 – 7.05 (m, 2H), 3.90 – 3.86 (m, 1H), 3.82 – 3.77 (m, 1H), 3.63 – 3.53 (m, 1H), 2.36 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.6, 138.1, 137.2, 135.1, 131.2, 130.3 (d, *J* = 1.9 Hz), 129.9, 129.6, 128.6, 126.5, 125.6 (q, *J* = 280.6 Hz), 50.3 (d, *J* = 2.6 Hz), 49.9 (d, *J* = 26.7 Hz), 21.0, 20.3.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.24.

HRMS (APCI) m/z: $[M-N_2+H]^+$ calcd for $C_{17}H_{17}F_3N^+$ 292.1308; found 292.1303.

4-(3-azido-1,1,1-trifluoropropan-2-yl)-4'-(tert-butyl)-1,1'-biphenyl (5)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 80/1) to yield **5** (44.4 mg, 64%) as a yellow liquid.

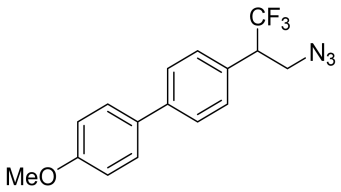
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.60 (m, 1H), 7.54 – 7.52 (m, 1H), 7.48 – 7.46 (m, 1H), 7.38 – 7.36 (m, 2H), 3.91 – 3.87 (m, 1H), 3.81 – 3.76 (m, 1H), 3.62 – 3.51 (m, 1H), 1.36 (s,9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.8, 141.8, 137.4, 130.7 (d, *J* = 1.9 Hz), 129.3, 127.6, 126.8, 125.9, 125.7 (q, *J* = 280.4 Hz), 50.3 (d, *J* = 2.5 Hz), 49.8 (q, *J* = 26.8 Hz), 34.6, 31.4.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.25.

HRMS (APCI) m/z: $[M-N_2+H]^+$ calcd for $C_{19}H_{21}F_3N^+$ 320.1621; found 320.1616.

4-(3-azido-1,1,1-trifluoropropan-2-yl)-4'-methoxy-1,1'-biphenyl (6)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 50/1) to yield **6** (37.9 mg, 59%) as a white solid, mp: 91 - 95 °C.

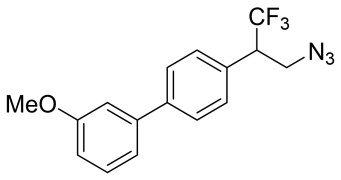
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.92 – 3.87 (m, 1H)., 3.84 (s, 3H), 3.81 – 3.76 (m, 1H)., 3.61 – 3.51 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.4, 141.5, 132.7, 130.3 (d, *J* = 1.6 Hz), 129.3, 128.1, 127.2, 125.6 (q, *J* = 280.6 Hz), 114.3, 55.3, 50.2 (d, *J* = 2.5 Hz), 49.7 (q, *J* = 26.7 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.31.

HRMS (APCI) m/z: $[M-N_2+H]^+$ calcd for $C_{16}H_{15}F_3ON^+$ 294.1100; found 294.1095.

4'-(3-azido-1,1,1-trifluoropropan-2-yl)-3-methoxy-1,1'-biphenyl (7)

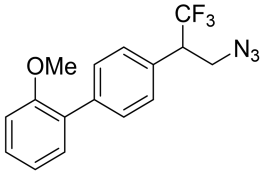


Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 50/1) to yield **7** (39.2 mg, 61%) as a yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.33 (m, 3H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.12 (s, 1H), 6.91 (dd, *J* = 8.2, 1.9 Hz, 1H), 3.91 – 3.87 (m, 1H), 3.85 (s, 3H), 3.80 – 3.75 (m, 1H), 3.62 – 3.52 (m, 1H).

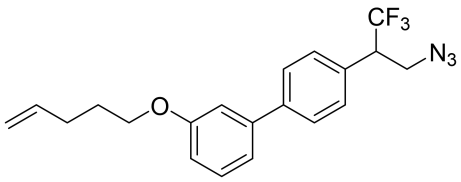
^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.0, 141.8, 141.7, 131.2 (d, *J* = 1.7 Hz), 129.8, 129.3, 127.7, 125.6 (q, *J* = 280.5 Hz), 119.6, 113.0, 112.9, 55.3, 50.2 (d, *J* = 2.5 Hz), 49.8 (q, *J* = 26.8 Hz).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.27.
HRMS (APCI) m/z: $[M-N_2+H]^+$ calcd for $C_{16}H_{15}F_3ON^+$ 294.1100; found 294.1096.

4'-(3-azido-1,1,1-trifluoropropan-2-yl)-2-methoxy-1,1'-biphenyl (8)



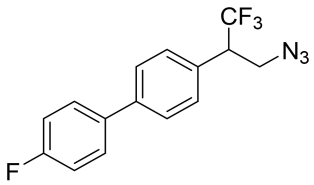
Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 50/1) to yield **8** (43.7 mg, 68%) as a yellow liquid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.56 (m, 2H), 7.35 – 7.31 (m, 4H), 7.04 – 6.97 (m, 2H), 3.92 – 3.88 (m, 1H), 3.81 – 3.76 (m, 4H), 3.61 – 3.51 (m, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.4, 139.2, 130.8, 130.5 (d, *J* = 1.7 Hz), 130.1, 129.6, 129.0, 128.5, 125.7 (q, *J* = 280.6 Hz), 120.9, 111.3, 55.5, 50.3 (d, *J* = 2.4 Hz), 49.8 (q, *J* = 26.7 Hz).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.15.
HRMS (ESI-TOF) m/z: $[M+ Na]^+$ calcd for $C_{16}H_{14}F_3N_3ONa^+$ 344.0981; found 343.0993.

4'-(3-azido-1,1,1-trifluoropropan-2-yl)-3-(pent-4-en-1-yloxy)-1,1'-biphenyl (9)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 50/1) to yield **9** (26.3 mg, 35%, 56% brsm) as a yellow liquid, with 37% of starting material recovered.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.60 (m, 2H), 7.39 – 7.33 (m, 3H), 7.17 – 7.15 (m, 1H), 7.12 (s, 1H), 6.92 – 5.89 (m, 1H), 5.92 – 5.82 (m, 1H), 5.08 (d, *J* = 17.1 Hz, 1H), 5.01 (d, *J* = 10.2 Hz, 1H), 4.03 (t, *J* = 6.4 Hz, 2H), 3.93 – 3.88 (m, 1H), 3.82 – 3.77 (m, 1H), 3.63 – 3.53 (m, 1H), 2.26 (q, *J* = 7.0 Hz, 2H), 1.91 (p, *J* = 6.7 Hz, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.4, 141.8, 141.7, 137.8, 131.1 (d, *J* = 1.6 Hz), 129.8, 129.3, 127.7, 125.6 (q, *J* = 280.5 Hz), 119.5, 115.2, 113.6, 113.5, 67.2, 50.2 (d, *J* = 2.5 Hz), 49.7 (q, *J* = 26.8 Hz), 30.1, 28.4.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.28.
HRMS (APCI) m/z: $[M-N_2+H]^+$ calcd for $C_{20}H_{21}OF_3N^+$ 348.1570; found 348.1561.

4-(3-azido-1,1,1-trifluoropropan-2-yl)-4'-fluoro-1,1'-biphenyl (10)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 250/1) to yield **10** (40.2 mg, 65%) as a yellow solid, mp: 91 - 95 ºC.

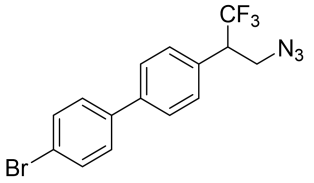
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.52 (m, 4H), 7.40 – 7.38 (m, 2H), 7.13 (t, *J* = 8.7 Hz, 2H), 3.93 – 3.89 (m, 1H), 3.82 – 3.77 (m, 1H), 3.63 – 3.53 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.6 (d, *J* = 246.9 Hz), 140.9, 136.3 (d, *J* = 3.2 Hz), 131.0, 129.4, 128.7 (d, *J* = 8.1 Hz), 127.5, 125.5 (q, *J* = 280.5 Hz), 115.7 (d, *J* = 21.5 Hz), 50.2 (d, *J* = 2.4 Hz), 49.7 (q, *J* = 26.8 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.31, -115.04.

HRMS (APCI) m/z: $[M\text{-}N_2+H]^+$ calcd for $C_{15}H_{12}F_4N^+$ 282.0900; found 282.0897.

4-(3-azido-1,1,1-trifluoropropan-2-yl)-4'-bromo-1,1'-biphenyl (11)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 250/1) to yield **11** (36.9 mg, 50%) as a yellow solid, mp: 41 - 45 ºC.

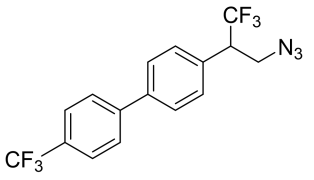
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.56 (m, 4H), 7.46 – 7.39 (m, 4H), 3.94 – 3.89 (m, 1H), 3.82 – 3.77 (m, 1H), 3.63 – 3.53 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.7, 139.1, 132.0, 131.4 (d, *J* = 1.6 Hz), 129.5, 128.7, 127.5, 125.5 (q, *J* = 280.4 Hz), 122.0, 50.2 (d, *J* = 2.3 Hz), 49.8 (q, *J* = 26.8 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.28.

HRMS (APCI) m/z: $[M\text{-}N_2+H]^+$ calcd for $C_{15}H_{12}BrF_3N^+$ 342.0100; found 342.0094.

4-(3-azido-1,1,1-trifluoropropan-2-yl)-4'-(trifluoromethyl)-1,1'-biphenyl (12)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 250/1) to yield **12** (42.4 mg, 59%) as a colorless liquid.

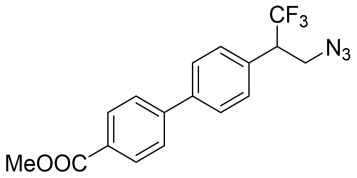
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.67 (m, 4H), 7.64 – 7.62 (m, 2H), 7.45 – 7.43 (m, 2H), 3.95 – 3.91 (m, 1H), 3.84 – 3.78 (m, 1H), 3.65 – 3.55 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.699 (d, *J* = 1.1 Hz), 140.5, 132.1 (d, *J* = 1.7 Hz), 129.7 (d, *J* = 32.6 Hz), 129.6, 127.9, 127.4, 125.8 (q, *J* = 3.7 Hz), 125.5 (q, *J* = 280.4 Hz), 124.2 (q, *J* = 272.0 Hz).50.2 (d, *J* = 2.6 Hz), 49.8 (q, *J* = 26.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.45, -68.29.

HRMS (APCI) m/z: $[M-N_2+H]^+$ calcd for $C_{16}H_{12}F_6N^+$ 332.0869; found 332.0862.

methyl 4'-(3-azido-1,1,1-trifluoropropan-2-yl)-[1,1'-biphenyl]-4-carboxylate (13)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 30/1) to yield **13** (41.2 mg, 59%) as a white solid, mp: 57 - 61 ºC.

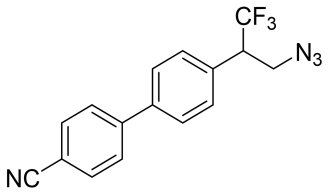
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 – 8.10 (m, 2H), 7.67 – 7.65 (m, 4H), 7.44 – 7.42 (m, 2H), 3.94 – 3.90 (m, 4H), 3.83 – 3.78 (m, 1H), 3.65 – 3.55 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.8, 144.5, 140.7, 132.0 (d, *J* = 1.5 Hz), 130.1, 129.5, 129.3, 127.8, 127.0, 125.5 (q, *J* = 280.6 Hz), 52.1, 50.1 (d, *J* = 2.6 Hz), 49.8 (q, *J* = 26.8 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.27.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{14}F_3N_3O_2Na^+$ 372.0930; found 372.0947.

4'-(3-azido-1,1,1-trifluoropropan-2-yl)-[1,1'-biphenyl]-4-carbonitrile (14)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 20/1) to yield **14** (37.3 mg, 59%) as a yellow liquid.

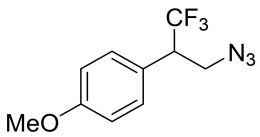
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.73 (m, 2H), 7.70 – 7.68 (m, 2H), 7.64 – 7.62 (m, 2H), 7.47 – 7.45 (m, 2H), 3.96 – 3.91 (m, 1H), 3.85 – 3.79 (m, 1H), 3.67 – 3.56 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.6, 139.8, 132.6, 132.6 (d, *J* = 1.7 Hz), 129.7, 127.8, 127.7, 125.3 (q, *J* = 280.5 Hz), 118.7, 111.3, 50.0 (d, *J* = 2.6 Hz), 49.7 (q, *J* = 26.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.24.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{11}F_3N_4Na^+$ 339.0828; found 339.0839.

1-(3-azido-1,1,1-trifluoropropan-2-yl)-4-methoxybenzene (15)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 50/1) to yield **15** (28.9 mg, 59%) as a yellow liquid.

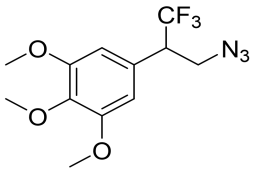
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 3.85 – 3.81 (m, 4H), 3.75 – 3.69 (m, 1H), 3.54 – 3.43 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.0, 130.0, 125.6 (q, *J* = 280.4 Hz), 123.9 (d, *J* = 1.8 Hz), 114.4, 55.2, 50.2 (q, *J* = 2.5 Hz), 49.3 (q, *J* = 26.7 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.76.

HRMS (ESI-TOF) m/z: $[M-N_3]^+$ calcd for $C_{10}H_{10}F_3O^+$ 203.0678; found 203.0681.

5-(3-azido-1,1,1-trifluoropropan-2-yl)-1,2,3-trimethoxybenzene (16)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 30/1) to yield **16** (40.9 mg, 67%) as a yellow liquid.

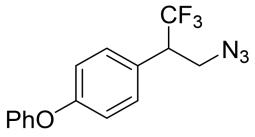
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.44 (s, 2H), 3.82 – 3.75 (m, 10H), 3.69 – 3.64 (m, 1H), 3.43 – 3.33 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.4, 138.5, 127.4 (d, *J* = 1.6 Hz), 125.5 (q, *J* = 280.4 Hz), 106.0, 60.8, 56.1, 50.3 (d, *J* = 2.4 Hz), 50.2 (q, *J* = 26.8 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.30.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{14}F_3N_3O_3Na^+$ 328.0879; found 328.0890.

1-(3-azido-1,1,1-trifluoropropan-2-yl)-4-phenoxybenzene (17)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 80/1) to yield **17** (30.7 mg, 50%) as a yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 (t, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.96 – 6.92 (m, 4H), 3.77 – 3.73 (m, 1H), 3.67 – 3.62 (m, 1H), 3.48 – 3.38 (m, 1H).

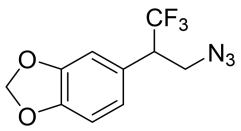
^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.1, 156.4, 130.3, 129.8, 126.3 (d, *J* = 2.1 Hz), 125.5 (q, *J* = 280.4 Hz), 123.8, 119.4, 118.7, 50.2 (d, *J* = 2.5 Hz), 49.4 (q, *J* = 26.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.56.

HRMS (APCI): m/z calcd for $C_{15}H_{13}F_3ON^+$ $(M-N_2+H)^+$: 280.0944; found: 280.0941.

HRMS (APCI) m/z: $[M-N_2+H]^+$ calcd for $C_{15}H_{13}F_3ON^+$ 280.0944; found 280.0941.

5-(3-azido-1,1,1-trifluoropropan-2-yl)benzo[d][1,3]dioxole (18)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 30/1) to yield **18** (18.1 mg, 35%) as a yellow liquid.

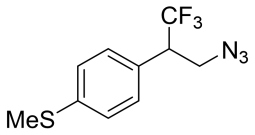
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.84 – 6.77 (m, 3H), 6.00 (s, 2H), 3.84 – 3.79 (m, 1H), 3.72 – 3.67 (m, 1H), 3.50 – 3.40 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.2, 148.1, 125.4 (q, *J* = 280.5 Hz), 125.4 (d, *J* = 1.8 Hz), 122.9, 108.7, 108.6, 101.4, 50.2 (d, *J* = 2.6 Hz), 49.7 (q, *J* = 26.8 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.69.

HRMS (APCI) m/z: $[M-N_2+H]^+$ calcd for $C_{10}H_9F_3O_2N^+$ 232.0580; found 232.0576.

(4-(3-azido-1,1,1-trifluoropropan-2-yl)phenyl)(methyl)sulfane (19)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 150/1) to yield **19** (30.3 mg, 58%) as a yellow liquid.

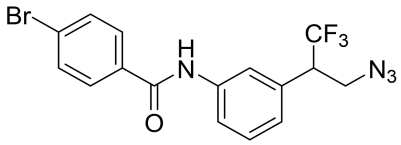
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 (t, *J* = 6.6 Hz, 4H), 3.81 – 3.76 (m, 1H), 3.69 – 3.64 (m, 1H), 3.47 – 3.37 (m, 1H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.9, 129.2, 128.4 (d, *J* = 1.2 Hz), 126.5, 125.4 (q, *J* = 280.5 Hz), 50.1 (d, *J* = 2.6 Hz), 49.5 (q, *J* = 26.8 Hz), 15.3.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.50.

HRMS (ESI-TOF) m/z: $[M-N_3]^+$ calcd for $C_{10}H_{10}F_3S^+$ 219.0450; found 219.0445.

N-(3-(3-azido-1,1,1-trifluoropropan-2-yl)phenyl)-4-bromobenzamide (20)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **20** (33.0 mg, 40%) as a white solid, mp: 118 - 122 °C.

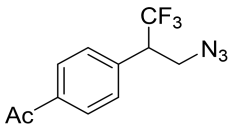
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 45.6 Hz, 1H), 7.73 – 7.70 (m, 3H), 7.63 – 7.56 (m, 3H), 7.41 – 7.36 (m, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 3.89 – 3.83 (m, 1H), 3.80 – 3.73 (m, 1H), 3.58 – 3.47 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.0, 138.3, 133.4, 133.2 (d, *J* = 1.7 Hz), 132.1, 132.0, 129.7, 128.6, 126.8, 125.4 (q, *J* = 280.7 Hz), 125.1, 120.6, 50.1, 49.9 (q, *J* = 26.8 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.16.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{12}BrF_3N_4ONa^+$ 435.0039; found 435.0055.

1-(4-(3-azido-1,1,1-trifluoropropan-2-yl)phenyl)ethan-1-one (21)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 15/1) to yield **21** (19.0 mg, 37%, 67% brsm) as a yellow liquid, with 45% of starting material recovered.

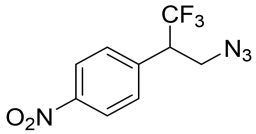
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 3.95 – 3.90 (m, 1H), 3.83 – 3.77 (m, 1H), 3.67 – 3.57 (m, 1H), 2.62 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.3, 137.5, 137.1 (d, *J* = 1.6 Hz), 129.2, 128.8, 125.2 (d, *J* = 280.6 Hz), 50.0 (q, *J* = 27.0 Hz), 49.9 (q, *J* = 2.6 Hz), 26.6.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.08.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{10}F_3N_3ONa^+$ 280.0668; found 280.0677.

1-(3-azido-1,1,1-trifluoropropan-2-yl)-4-nitrobenzene (22)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 30/1) to yield **22** (14.6 mg, 28%, 58% brsm) as a yellow liquid, with 52% of starting material recovered.

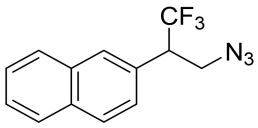
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 3.99 – 3.95 (m, 1H), 3.85 – 3.80 (m, 1H), 3.74 – 3.64 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.3, 139.1 (d, *J* = 1.7 Hz), 130.1, 124.9 (q, *J* = 280.7 Hz), 124.1, 49.85 (q, *J* = 27.3 Hz), 49.84 (d, *J* = 2.6 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -67.98.

HRMS (APCI) m/z: $[M-N_2+H]^+$ calcd for $C_9H_8F_3O_2N_2^+$ 233.0532; found 233.0530.

2-(3-azido-1,1,1-trifluoropropan-2-yl)naphthalene (23)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 200/1) to yield **23** (31.3 mg, 59%) as a yellow liquid.

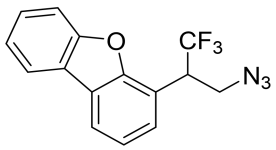
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.76 (m, 3H), 7.72 (s, 1H), 7.46 – 7.42 (m, 2H), 7.34 (d, *J* = 8.5 Hz, 1H), 3.90 – 3.85 (m, 1H), 3.81 – 3.76 (m, 1H), 3.67 – 3.57 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 133.2, 133.1, 129.4 (d, *J* = 1.7 Hz), 128.8, 128.7, 127.9, 127.7, 126.7, 126.6, 125.6 (q, *J* = 280.7 Hz), 125.6, 50.2 (d, *J* = 2.6 Hz), 50.2 (q, *J* = 26.8 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.05.

HRMS (APCI) m/z: $[M-N_2+H]^+$ calcd for $C_{13}H_{11}F_3N^+$ 238.0838; found 238.0834.

2-(3-(1,1-difluoro-4-(4-methoxyphenyl)but-1-en-2-yl)phenyl)isoindoline-1,3-dione (24)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 200/1) to yield **24** (28.7 mg, 47%) as a yellow liquid.

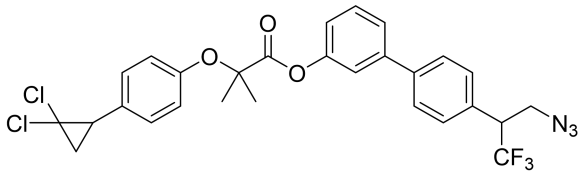
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.88 (m, 2H), 7.54 – 7.52 (m, 1H), 7.44 – 7.38 (m, 2H), 7.34 – 7.28 (m, 2H), 4.35 – 4.24 (m, 1H), 3.96 – 3.94 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.0, 154.8, 127.6, 126.3, 125.6 (q, *J* = 280.6 Hz), 124.7, 124.0, 123.1, 123.1, 121.2, 120.8, 116.2 (d, *J* = 1.8 Hz), 111.8, 49.5 (d, *J* = 2.4 Hz), 43.9 (q, *J* = 27.6 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -67.92.

HRMS (APCI) m/z: $[M-N_2+H]^+$ calcd for $C_{15}H_{11}F_3ON^+$ 278.0787; found 278.0783.

4'-(3-azido-1,1,1-trifluoropropan-2-yl)-[1,1'-biphenyl]-3-yl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate (28)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 8/1) to yield **28** (68.1 mg, 58%) as a yellow oil.

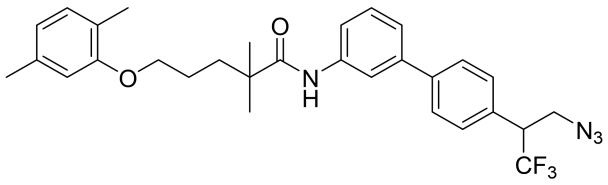
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.54 (m, 2H), 7.45 – 7.38 (m, 4H), 7.24 – 7.16 (m, 3H), 6.98 – 6.95 (m, 3H), 3.92 – 3.88 (m, 1H), 3.81 – 3.78 (m, 1H), 3.63 – 3.53 (m, 1H), 2.85 (dd, *J* = 10.3, 8.7 Hz, 1H), 1.94 (dd, *J* = 10.6, 7.5 Hz, 1H), 1.80 – 1.76 (m, 7H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.8, 155.0, 150.9, 141.8, 140.7, 131.5 (d, *J* = 1.5 Hz), 129.82, 129.81, 129.4, 128.4, 127.7, 125.5 (q, *J* = 280.5 Hz), 124.8, 120.4, 120.0, 118.5, 79.3, 60.8, 50.1 (d, *J* = 2.6 Hz), 49.7 (q, *J* = 26.8 Hz), 34.7, 25.7, 25.4 (d, *J* = 2.3 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.22.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{28}H_{24}Cl_2F_3N_3O_3Na^+$ 600.1039; found 600.1050.

N-(4'-(3-azido-1,1,1-trifluoropropan-2-yl)-[1,1'-biphenyl]-3-yl)-5-(2,5-dimethylphenoxy)-2,2-dimethylpentanamide (29)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **29** (34.4 mg, 32%) as a white solid, mp: 91 - 95 °C.

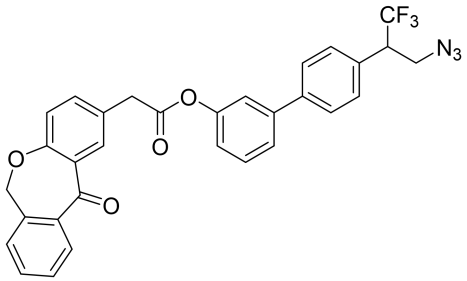
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (s, 1H), 7.61 – 7.59 (m, 2H), 7.48 – 7.46 (m, 2H), 7.40 – 7.32 (m, 4H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 6.61 (s, 1H), 3.95 (s, 2H), 3.92 – 3.88 (m, 1H), 3.81 – 3.76 (m, 1H), 3.62 – 3.52 (m, 1H), 2.27 (s, 3H), 2.17 (s, 3H), 1.84 (s, 4H), 1.36 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.8, 156.7, 141.4, 141.1, 138.3, 136.5, 131.2 (d, *J* = 1.5 Hz), 130.3, 129.3, 129.2, 127.7, 125.5 (q, *J* = 280.6 Hz), 123.4, 122.9, 120.8, 119.1, 118.9, 112.2, 67.8, 50.2 (d, *J* = 2.4 Hz), 49.7 (q, *J* = 26.8 Hz), 42.8, 37.6, 25.6, 25.1, 21.3, 15.8.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.29.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{30}H_{33}F_3N_4O_2Na^+$ 561.2448; found 561.2455.

4'-(3-azido-1,1,1-trifluoropropan-2-yl)-[1,1'-biphenyl]-3-yl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (30)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 8/1) to yield **30** (43.4 mg, 39%) as a yellow oil.

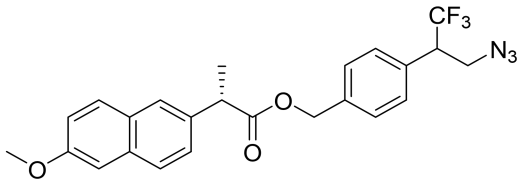
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 2.1 Hz, 1H), 7.91 – 7.89 (m, 1H), 7.59 – 7.52 (m, 4H), 7.49 – 7.42 (m, 3H), 7.39 – 7.35 (m, 3H), 7.30 (s, 1H), 7.10 – 7.06 (m, 2H), 5.19 (s, 2H), 3.91 – 3.87 (m, 3H), 3.81 – 3.75 (m, 1H), 3.62 – 3.52 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.7, 169.8, 160.6, 151.0, 141.7, 140.7, 140.3, 136.2, 135.4, 132.7, 132.5, 131.4 (d, *J* = 1.2 Hz), 129.7, 129.4, 129.3, 129.2, 127.8, 127.7, 127.1, 125.5 (d, *J* = 280.4 Hz), 125.2, 124.6, 121.2, 120.6, 120.1, 73.5, 50.1 (d, *J* = 2.3 Hz), 49.7 (q, *J* = 26.7 Hz), 40.2.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.24.

HRMS (APCI) m/z: $[M+H]^+$ calcd for $C_{31}H_{23}O_4F_3N_3^+$ 558.1635; found 558.1625.

4-(3-azido-1,1,1-trifluoropropan-2-yl)benzyl (2S)-2-(6-methoxynaphthalen-2-yl)propanoate (31)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 8/1) to yield **31** (27.4 mg, 30%) as a yellow liquid.

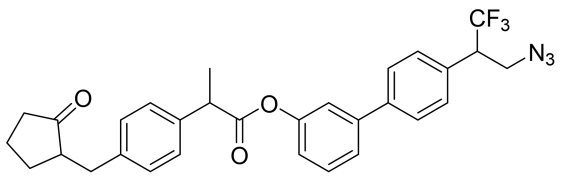
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.64 (m, 3H), 7.39 – 7.37 (m, 1H), 7.26 – 7.20 (m, 4H), 7.15 – 7.11 (m, 2H), 5.15 – 5.08 (m, 2H), 3.94 – 3.88 (m, 4H), 3.85 – 3.81 (m, 1H), 3.72 – 3.67 (m, 1H), 3.54 – 3.44 (m, 1H), 1.59 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.3, 157.6, 136.8, 135.3, 133.6, 131.8 (d, *J* = 1.6 Hz), 129.2, 128.9, 128.8, 128.3, 127.1, 126.1 (d, *J* = 1.5 Hz), 125.9, 125.4 (q, *J* = 280.5 Hz), 118.9, 105.5, 65.6, 55.2, 50.1 (d, *J* = 2.4 Hz), 49.7 (q, *J* = 26.7 Hz), 45.3, 18.4.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.29.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{24}H_{22}F_3N_3O_3Na^+$ 480.1505; found 480.1527.

4'-(3-azido-1,1,1-trifluoropropan-2-yl)-[1,1'-biphenyl]-3-yl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate (32)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 100/1) to yield **32** (41.7 mg, 39%) as a yellow oil.

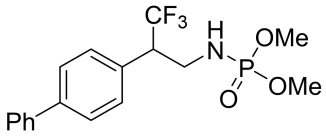
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.56 (m, 2H), 7.42 – 7.37 (m, 4H), 7.34 – 7.32 (m, 2H), 7.21 – 7.17 (m, 3H), 7.02 – 7.99 (m, 1H), 3.96 (q, *J* = 7.1 Hz, 1H), 3.92 – 3.88 (m, 1H), 3.81 – 3.76 (m, 1H), 3.63 – 3.52 (m, 1H), 3.15 (dd, *J* = 13.9, 4.0 Hz, 1H), 2.54 (dd, *J* = 13.8, 9.6 Hz, 1H), 2.39 – 2.31 (m, 2H), 2.16 – 2.06 (m, 2H), 1.99 – 1.92 (m, 1H), 1.77 – 1.68 (m, 1H), 1.62 (d, *J* = 7.2 Hz, 3H), 1.59 – 1.51 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.0, 151.2, 141.7, 140.8, 139.1, 137.7, 131.4, 129.6, 129.31, 129.30, 127.7, 127.5, 125.5 (d, *J* = 280.2 Hz), 124.4, 120.5, 120.1, 50.9, 50.1 (d, *J* = 2.6 Hz), 49.7 (q, *J* = 26.8 Hz), 45.2, 38.1, 35.1, 29.1, 20.4, 18.4.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.28.

HRMS (APCI) m/z: $[M-N_2+H]^+$ calcd for $C_{30}H_{29}O_3F_3N^+$ 508.2094; found 508.2088.

dimethyl (2-([1,1'-biphenyl]-4-yl)-3,3,3-trifluoropropyl)phosphoramidate (33)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 1/1) to yield **33** (67.1 mg, 90%) as a white solid, mp: 68 - 72 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.55 (m, 4H), 7.45 – 7.42 (m, 2H), 7.37 – 7.33 (m, 3H), 3.66 (d, *J* = 11.1 Hz, 3H), 3.61 – 3.49 (m, 5H), 3.43 – 3.33 (m, 1H), 2.88 – 2.82 (m, 1H).

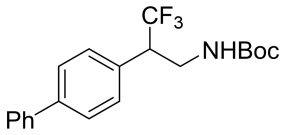
^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.7, 140.1, 131.2 (d, *J* = 2.0 Hz), 129.4, 128.8, 127.6, 127.5, 127.0, 125.9 (q, *J* = 280.9 Hz), 53.0 (dd, *J* = 13.7, 5.6 Hz), 51.2 (qd, *J* = 25.9, 5.1 Hz), 40.6.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.25.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 10.70.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{19}F_3NO_3PNa^+$ 396.0947; found 396.0958.

tert-butyl (2-([1,1'-biphenyl]-4-yl)-3,3,3-trifluoropropyl)carbamate (34)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 2/1) to yield **34** (65.7 mg, 90%) as a white solid, mp: 89 - 93 °C.

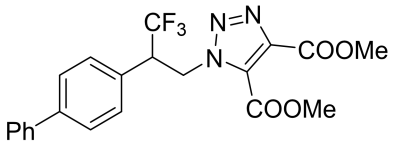
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.56 (m, 4H), 7.45 – 7.42 (m, 2H), 7.37 – 7.35 (m, 3H), 4.64 (s, 1H), 3.89 – 3.84 (m, 1H), 3.71 – 3.65 (m, 1H), 3.55 – 3.48 (m, 1H), 1.40 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.6, 141.5, 140.3, 131.8, 129.4, 128.8, 127.6, 127.6, 127.1, 126.2 (q, *J* = 280.6 Hz), 79.9, 49.5 (q, *J* = 25.4 Hz), 40.2, 28.3.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.06.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{20}H_{22}F_3NO_2Na^+$ 388.1495; found 388.1506.

dimethyl 1-(2-([1,1'-biphenyl]-4-yl)-3,3,3-trifluoropropyl)-1H-1,2,3-triazole-4,5-dicarboxylate (35)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 5/1) to yield **35** (68.4 mg, 79%) as a yellow liquid.

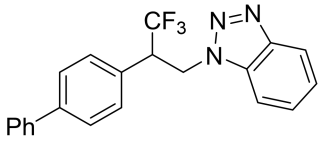
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.53 (m, 4H), 7.45 – 7.41 (m, 2H), 7.37 – 7.33 (m, 1H), 7.29 – 7.27 (m, 2H), 5.21 (qd, *J* = 13.9, 7.7 Hz, 2H), 4.25 – 4.14 (m, 1H), 3.92 (s, 3H), 3.87 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.0, 158.5, 142.0, 139.8, 130.1, 129.2, 129.0, 128.7, 127.71, 127.70, 127.63, 126.9, 125.2 (q, *J* = 280.5 Hz), 53.3, 52.6, 50.2 (q, *J* = 27.6 Hz), 49.0 (d, *J* = 2.7 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.09.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{21}H_{18}F_3N_3O_4Na^+$ 456.1142; found 456.1154.

1-(2-([1,1'-biphenyl]-4-yl)-3,3,3-trifluoropropyl)-1H-benzo[d][1,2,3]triazole (36)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 5/1) to yield **36** (55.1 mg, 75%) as a white solid, mp: 105 - 109 °C.

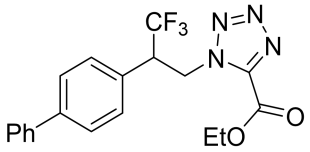
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.3 Hz, 1H), 7.49 – 7.46 (m, 4H), 7.42 – 7.25 (m, 8H), 5.27 (dd, *J* = 14.3, 5.5 Hz, 1H), 5.04 (dd, *J* = 14.3, 9.2 Hz, 1H), 4.30 – 4.19 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.6, 141.9, 139.9, 133.0, 130.2 (d, *J* = 1.3 Hz), 129.0, 128.7, 127.6, 127.6, 127.5, 126.9, 123.9, 125.6 (q, *J* = 280.3 Hz), 120.0, 108.7, 50.2 (q, *J* = 26.9 Hz), 47.5 (d, *J* = 2.8 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.05.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{21}H_{16}F_3N_3Na^+$ 390.1189; found 390.1193.

ethyl 1-(2-([1,1'-biphenyl]-4-yl)-3,3,3-trifluoropropyl)-1H-tetrazole-5-carboxylate (37)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 5/1) to yield **37** (40.6 mg, 52%) as a white solid, mp: 75 - 79 °C.

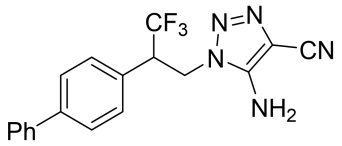
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.53 (m, 4H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.38 – 7.35 (m, 1H), 7.31 – 7.29 (m, 2H), 5.41 – 5.30 (m, 2H), 4.53 – 4.41 (m, 2H), 4.28 – 4.17 (m, 1H), 1.41 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.3, 145.8, 142.3, 139.7, 129.2, 128.8, 128.6, 127.8, 127.7, 127.0, 125.2 (q, *J* = 280.5 Hz), 63.8, 49.9 (q, *J* = 27.6 Hz), 48.0 (d, *J* = 2.8 Hz), 13.8.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -68.15.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{17}F_3N_4O_2Na^+$ 413.1196; found 413.1203.

1-(2-([1,1'-biphenyl]-4-yl)-3,3,3-trifluoropropyl)-5-amino-1H-1,2,3-triazole-4-carbonitrile (38)



Prepared according to standard conditions. Purification by thin layer chromatography was performed (PE/EA: 2/1) to yield **38** (33.0 mg, 46%) as a white solid, mp: 189 - 193 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.71 – 7.68 (m, 4H), 7.57 – 7.55 (m, 2H), 7.47 (t, J = 7.6 Hz, 2H), 7.40 – 7.36 (m, 1H), 7.21 (s, 2H), 4.93 – 4.88 (m, 1H), 4.84 – 4.78 (m, 1H), 4.54 – 4.43 (m, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 148.3, 140.6, 139.2, 130.4, 129.9, 129.0, 127.8, 126.9, 126.7, 125.9 (q, J = 280.7 Hz), 113.5, 100.9, 47.0 (q, J = 26.8, 26.1 Hz), 44.1.

^{19}F NMR (376 MHz, DMSO-d_6) δ -67.17.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{14}F_3N_5Na^+$ 380.1094; found 380.1102.

8. References

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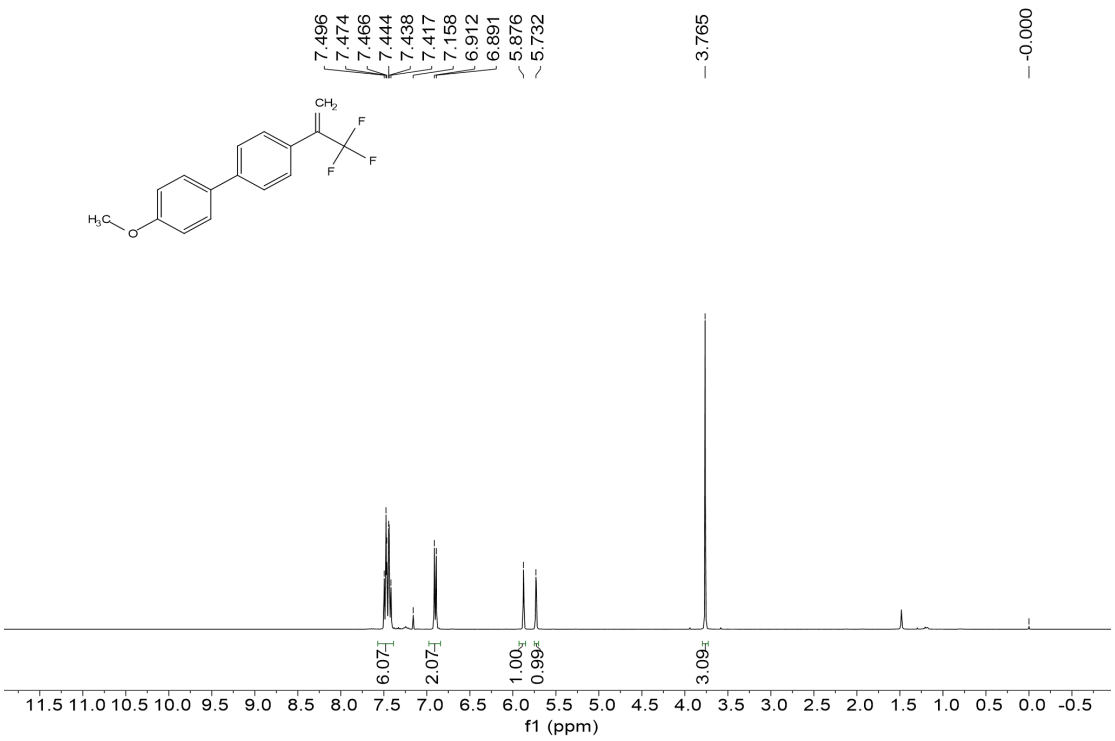
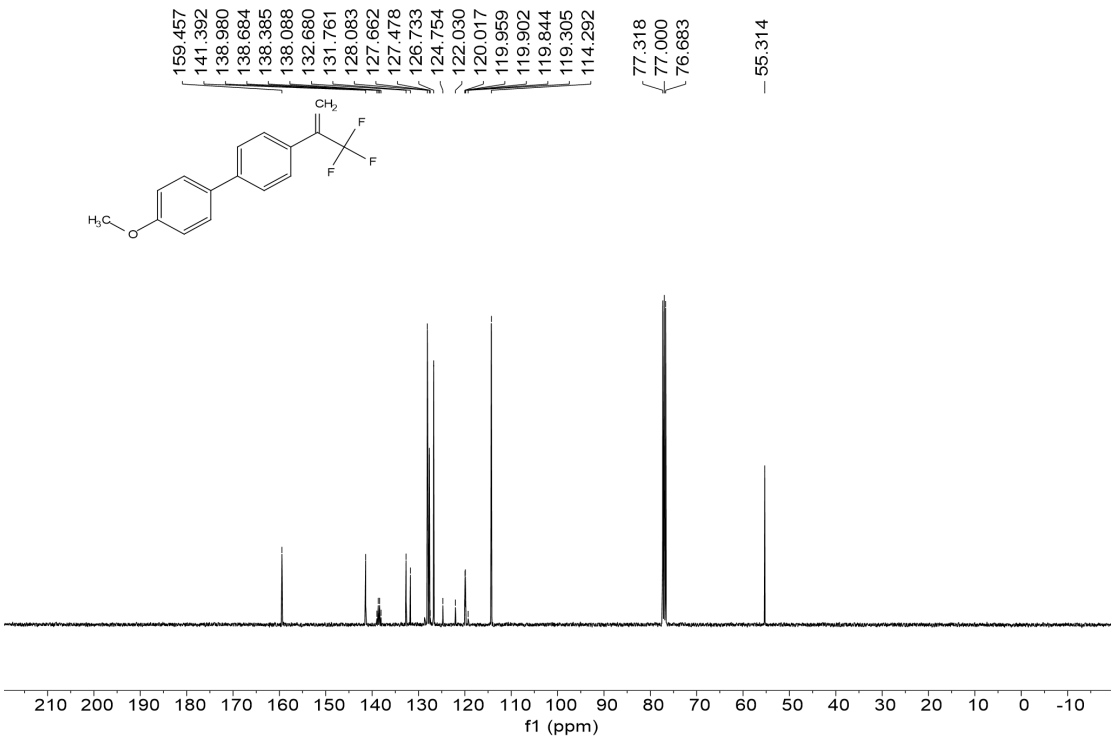
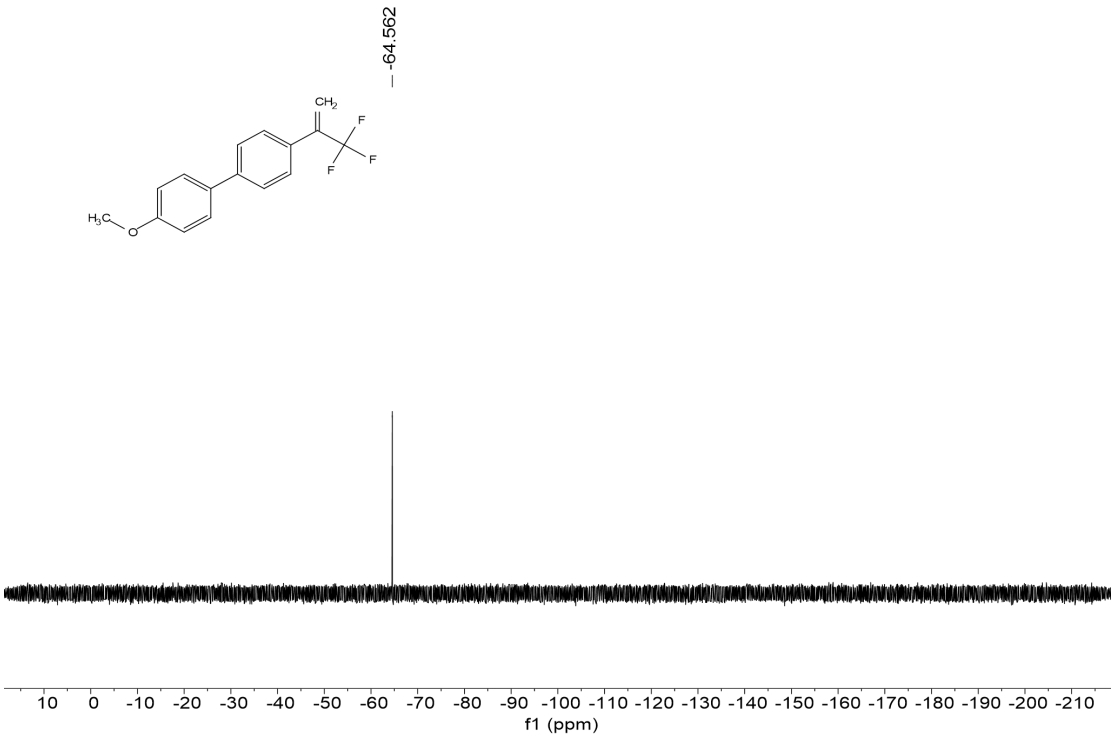
9. NMR spectra

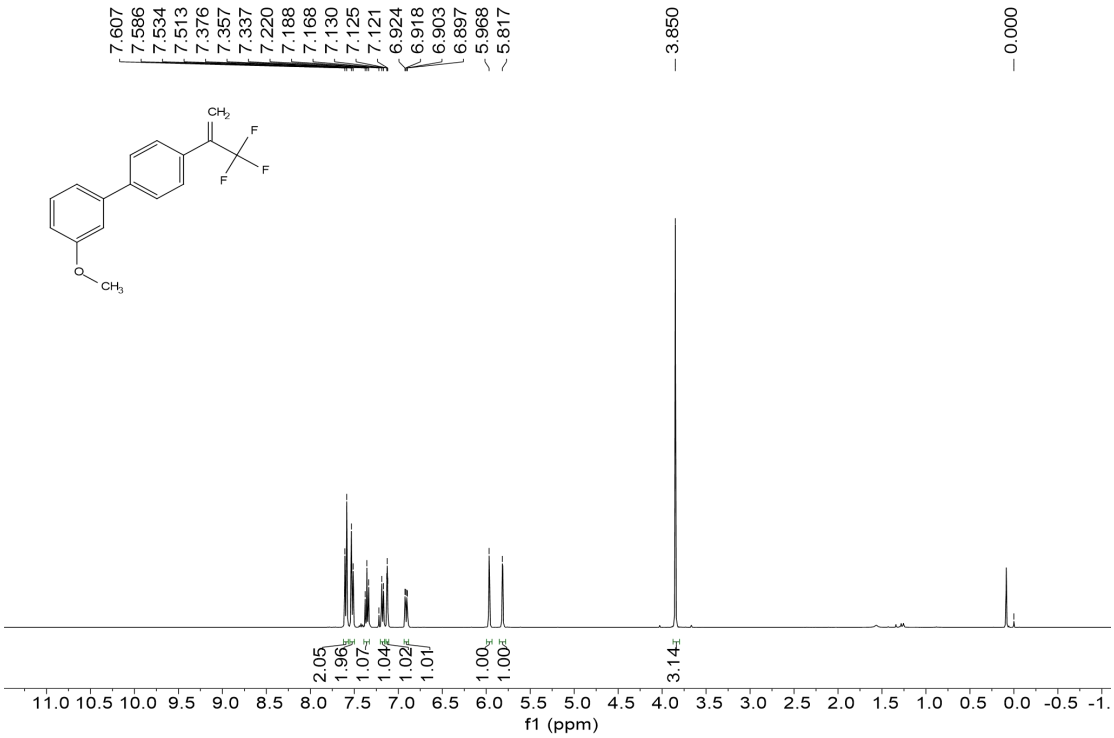
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **1l**

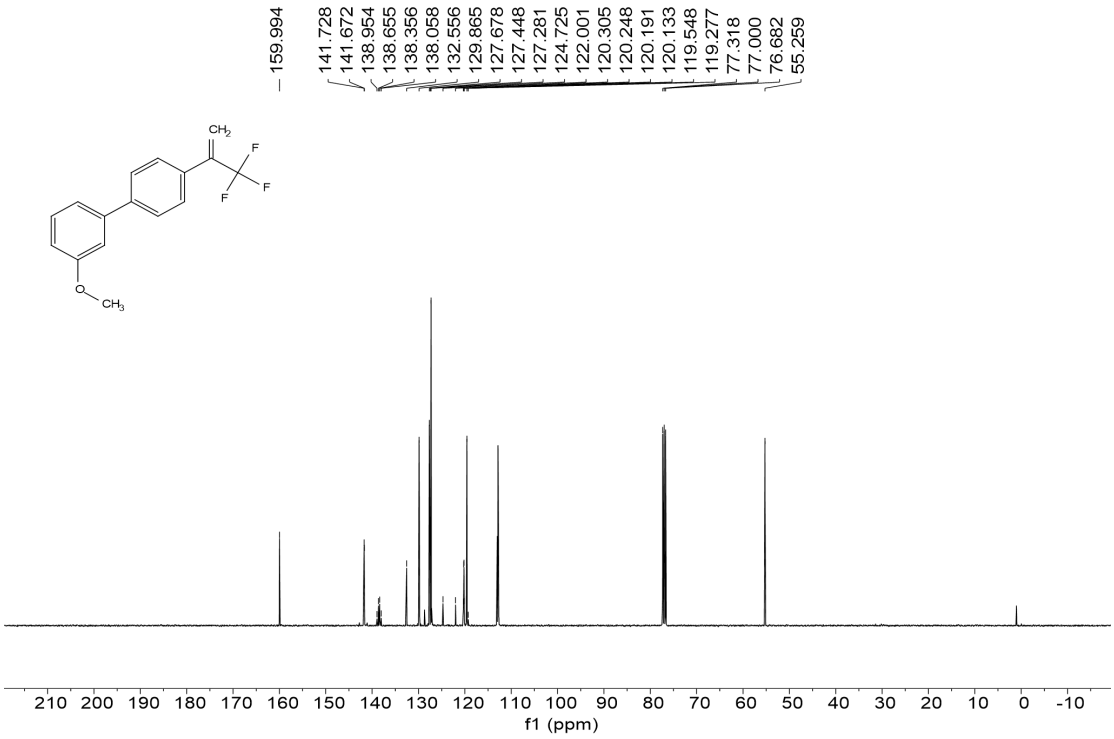






^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **1m**

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141.672
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138.655
138.356
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132.556
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127.678
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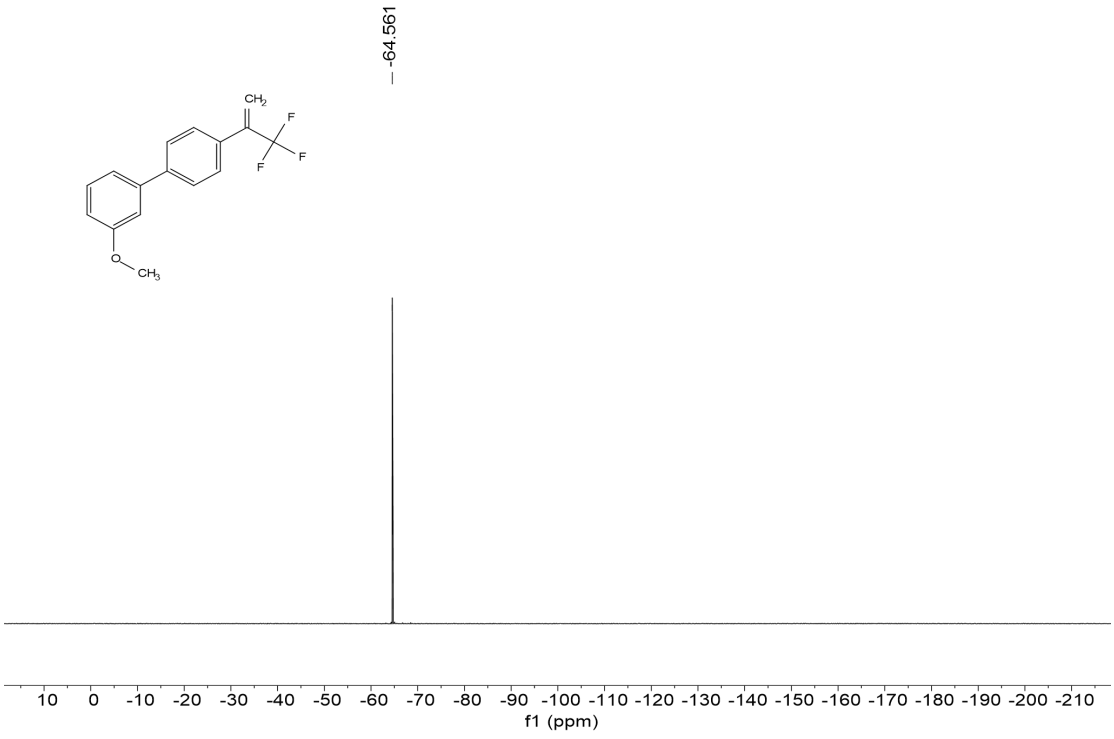
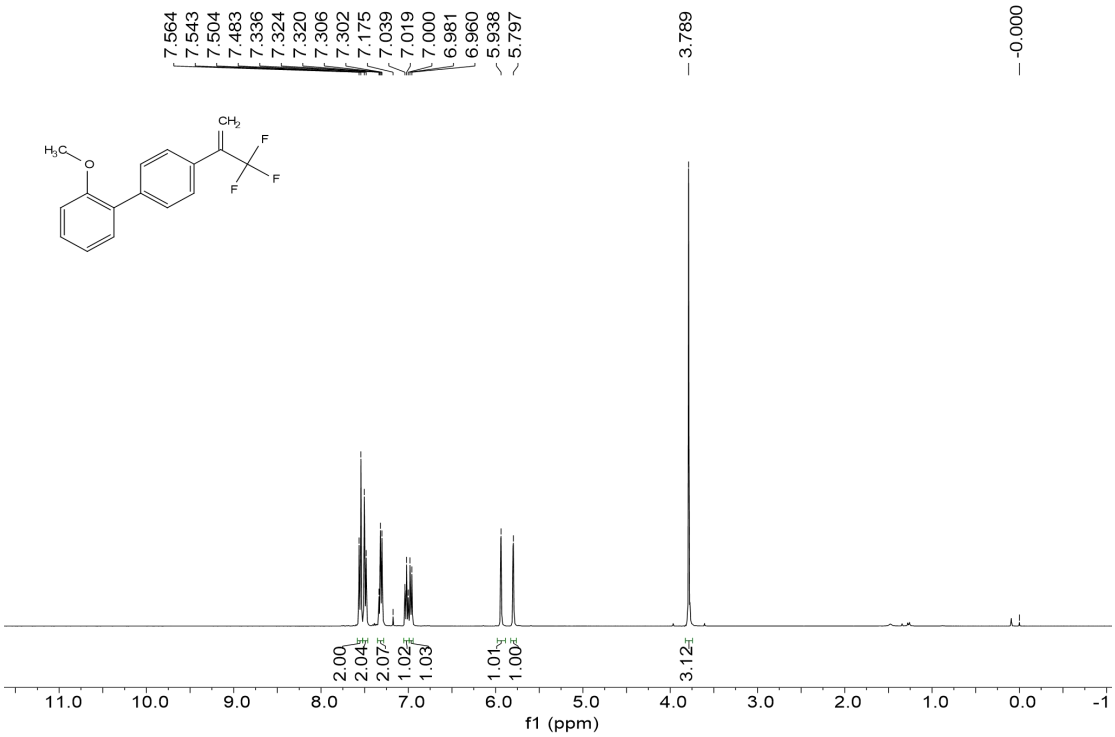
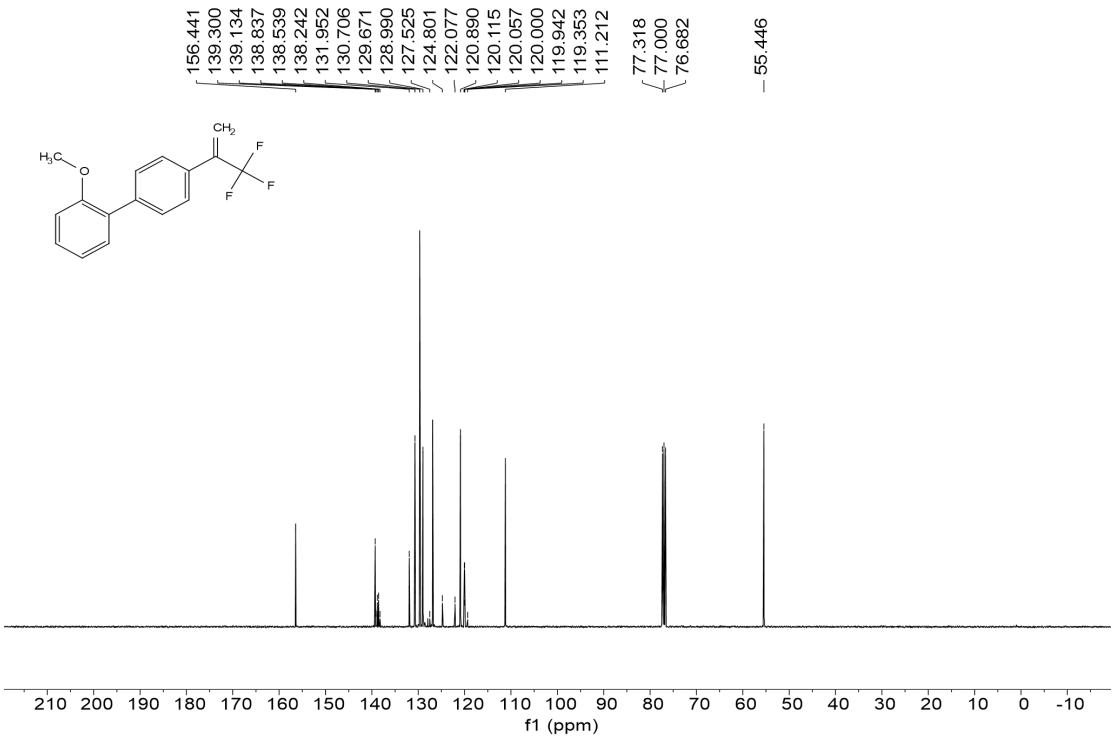
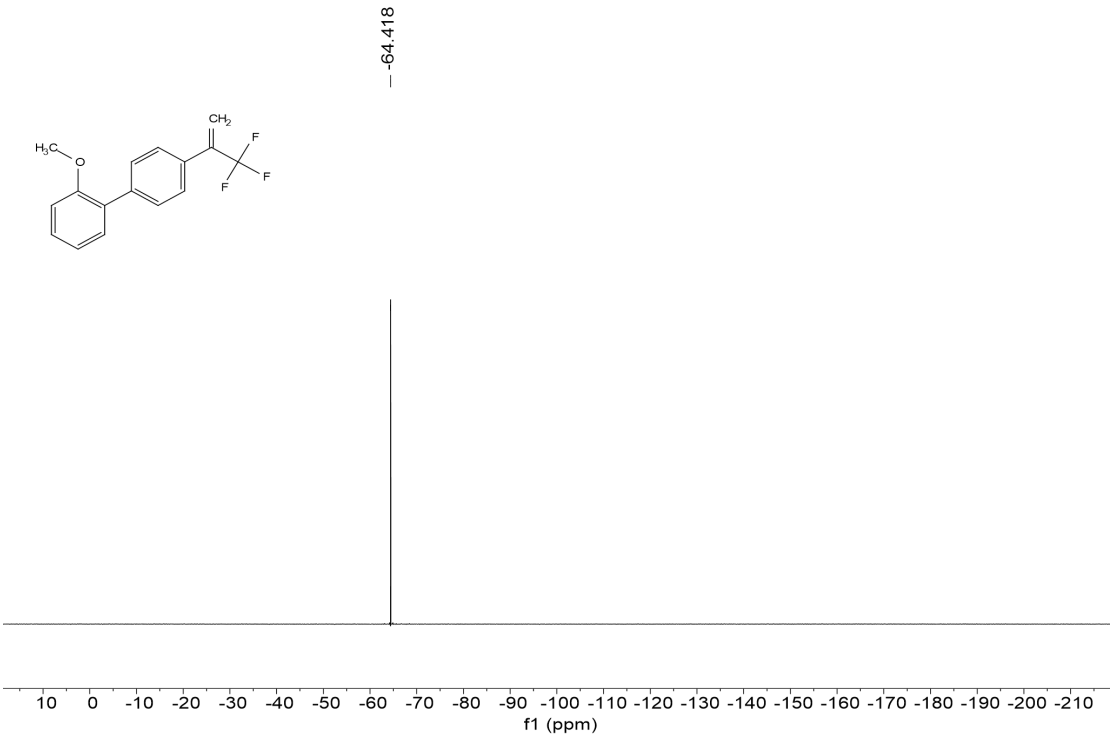
124.725
122.001
120.305
120.248
120.191
120.133
119.548
119.277
77.318
77.000
76.682
55.259
CH2
F
F
F
O
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-64.561
CH2
F
F
F
O
CH3
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)

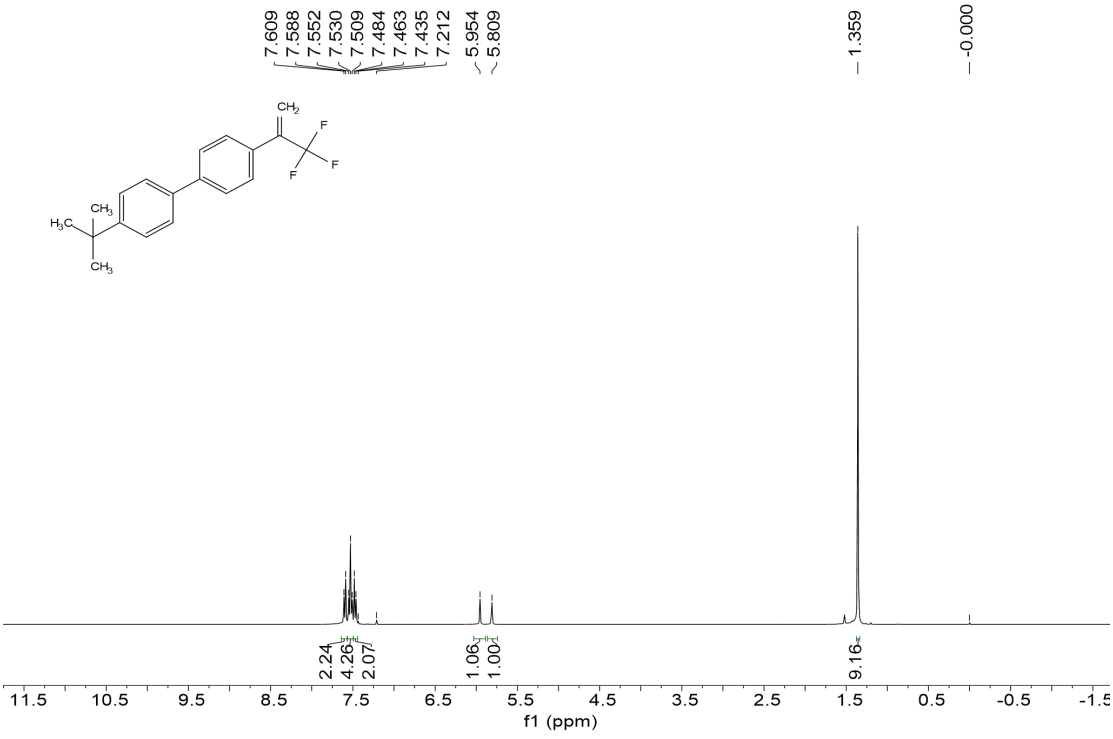
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **1n**

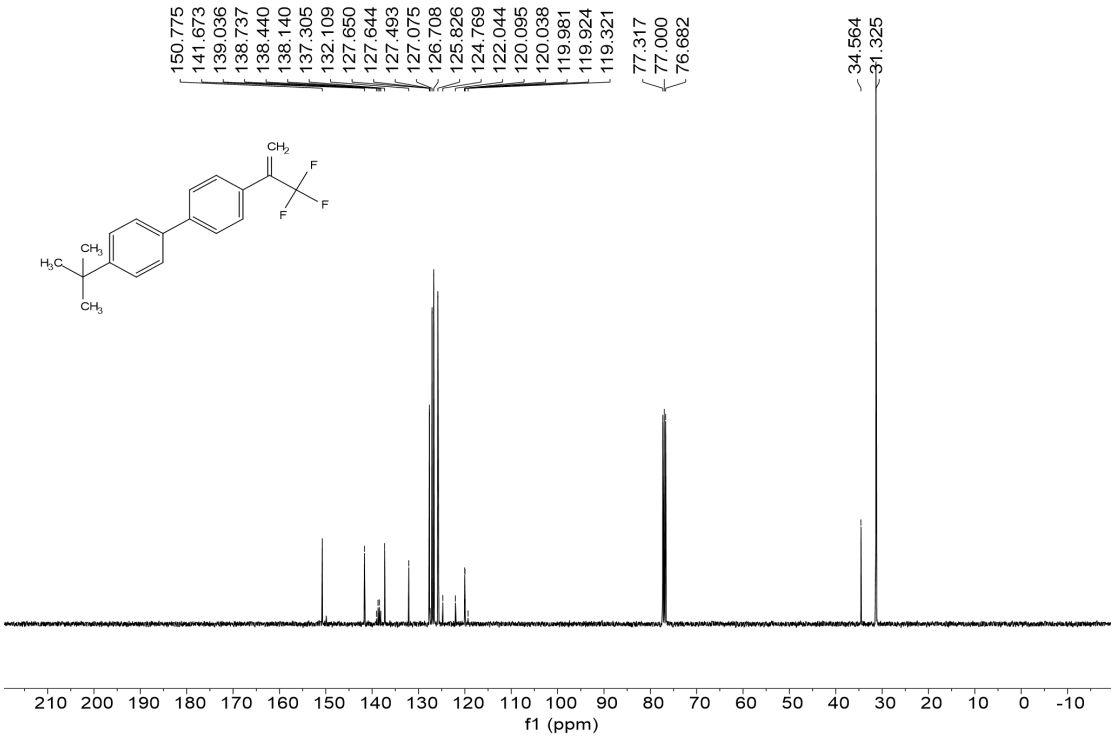






^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **1o**

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127.644
127.493
127.075
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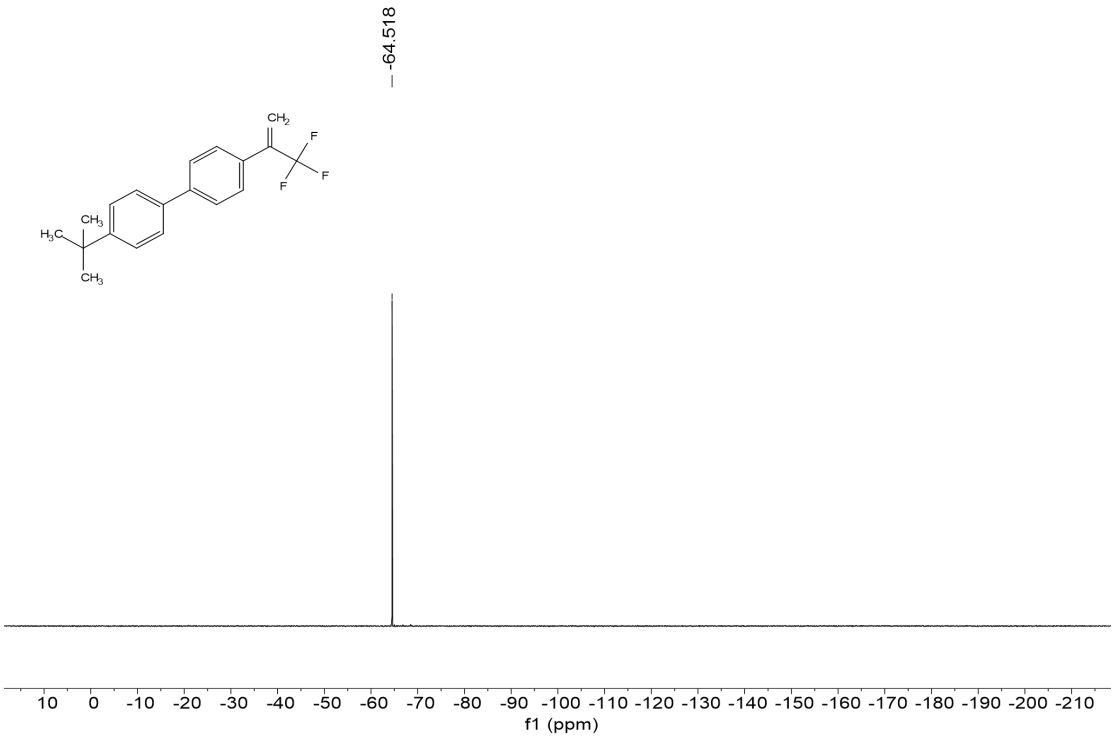
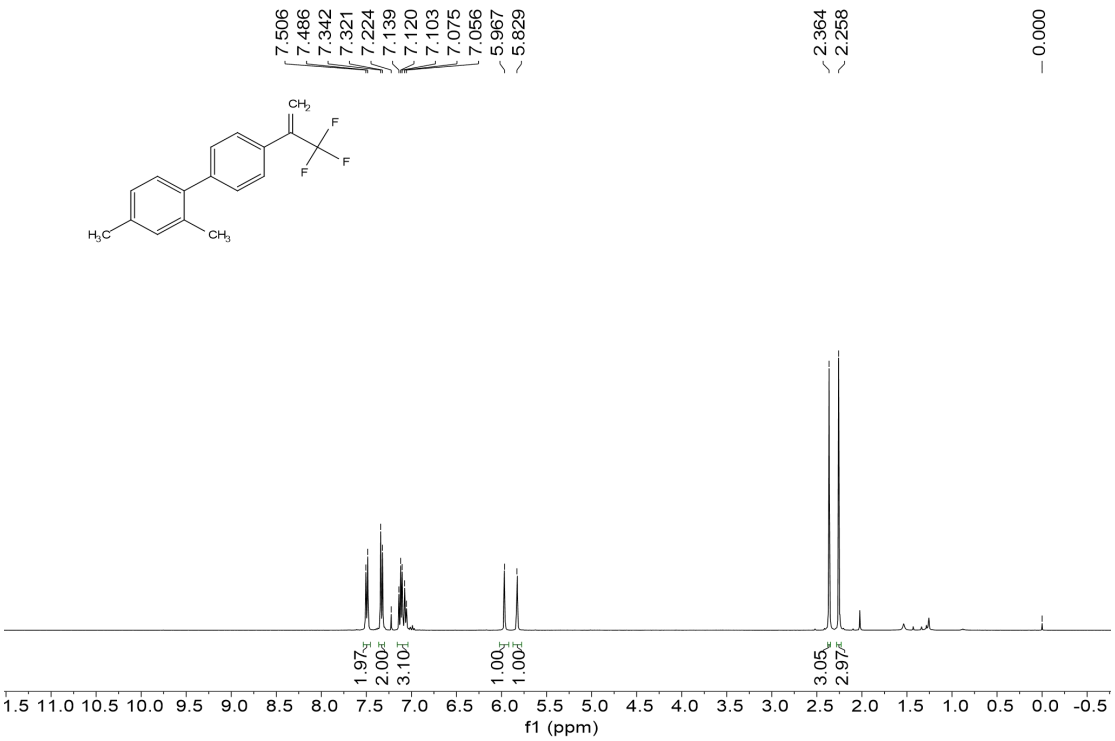
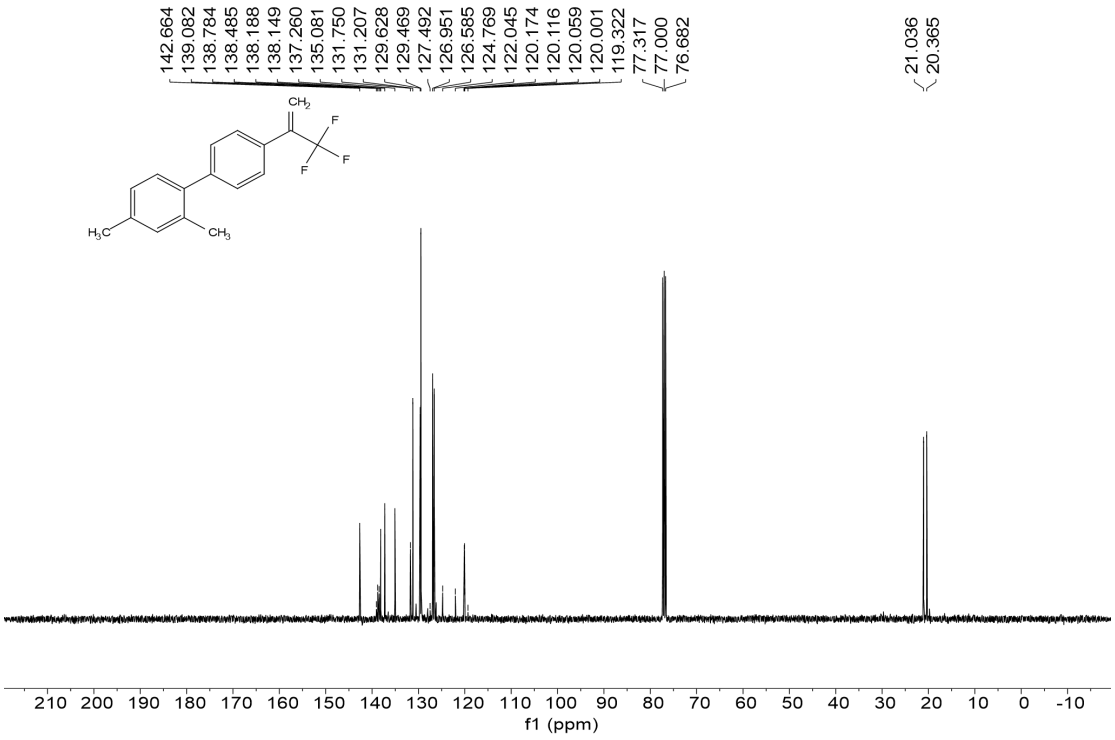
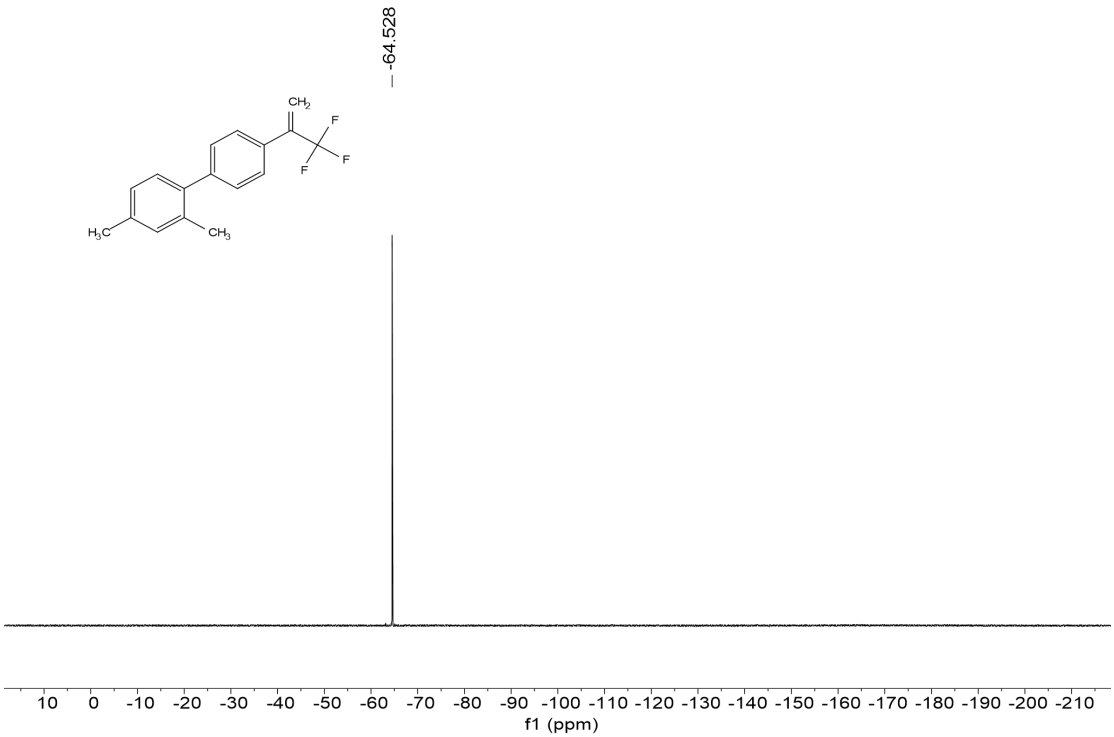
125.826
124.769
122.044
120.095
120.038
119.981
119.924
119.321
77.317
77.000
76.682
34.564
31.325
CH2
F
F
F
CH3
H3C
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-64.518
CH2
F
F
F
CH3
H3C
CH3
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)

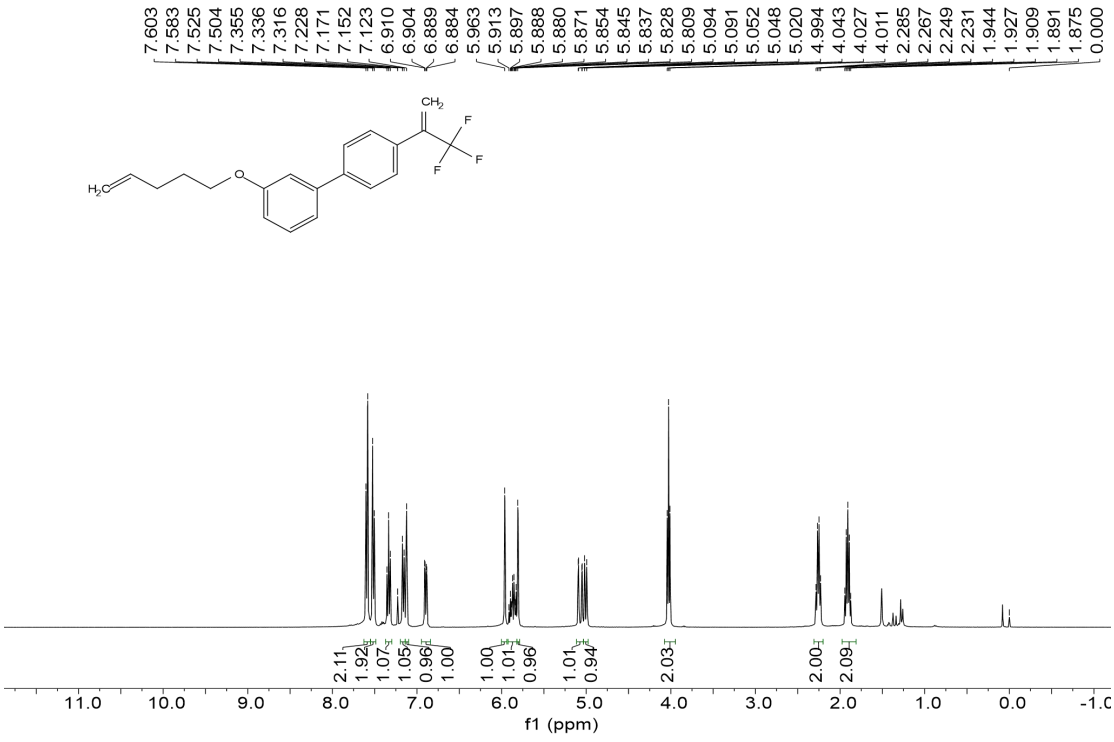
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **1p**

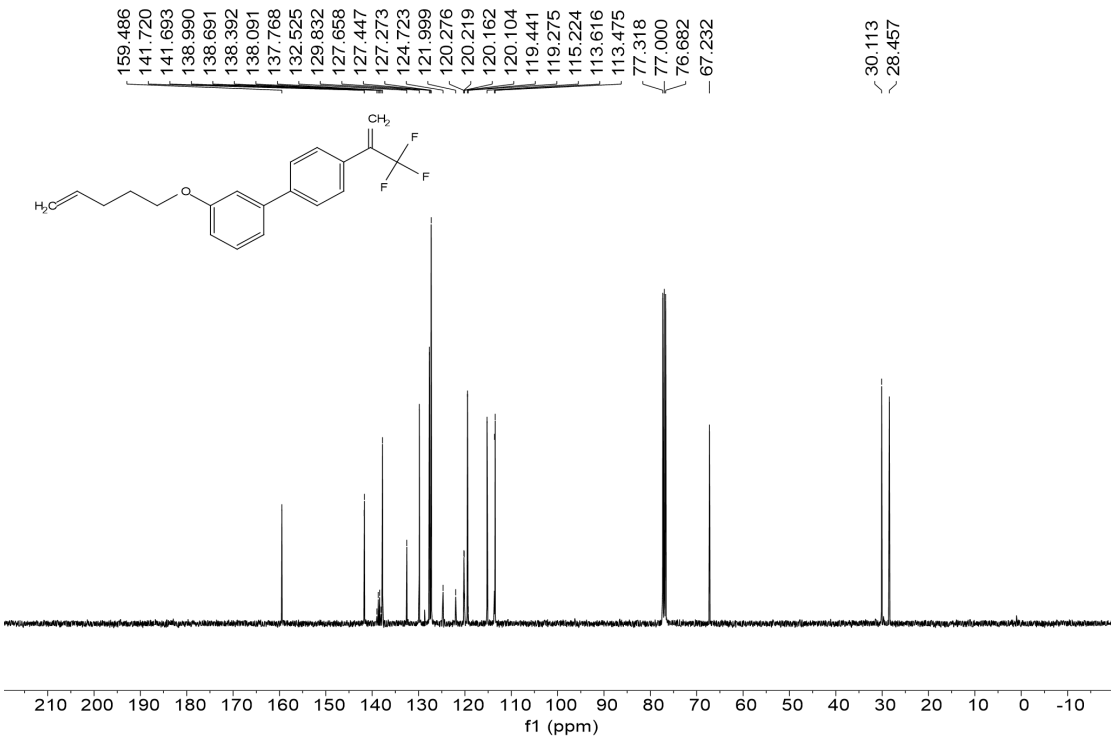






^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **1q**

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138.091
137.768
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127.447
127.273
124.723
121.999
120.276
120.219
120.162
120.104
119.441
119.275
115.224
113.616
113.475
77.318
77.000
76.682
67.232
30.113
28.457
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F
F
H2C
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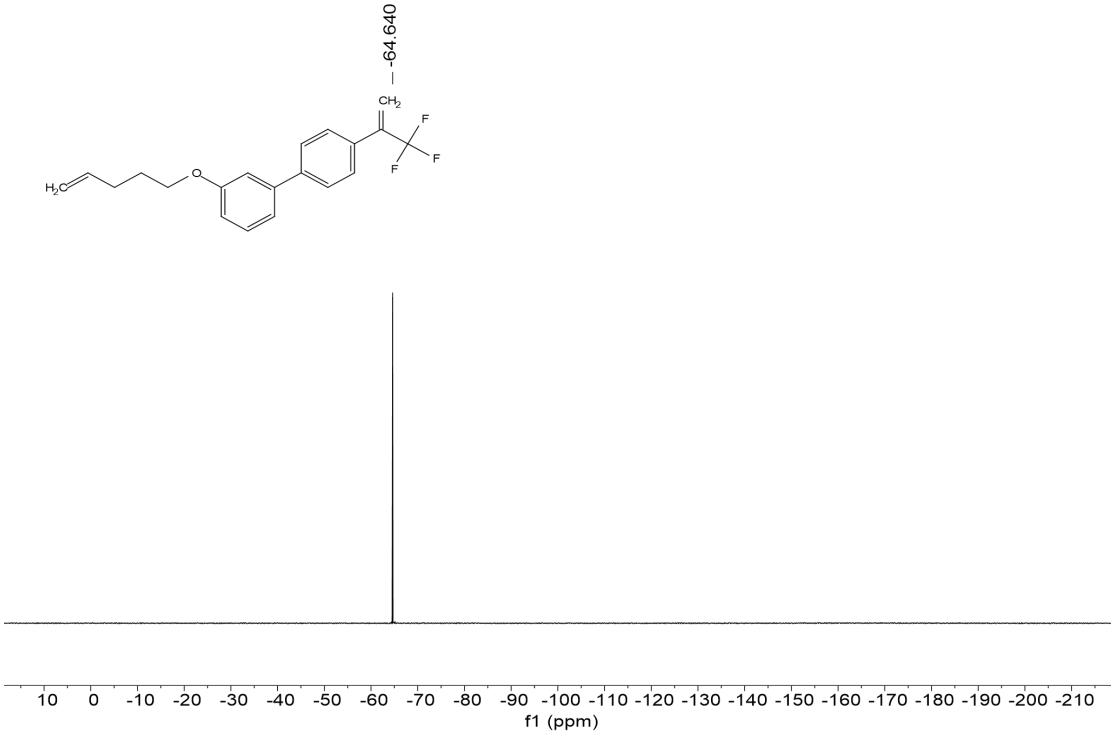
f1 (ppm)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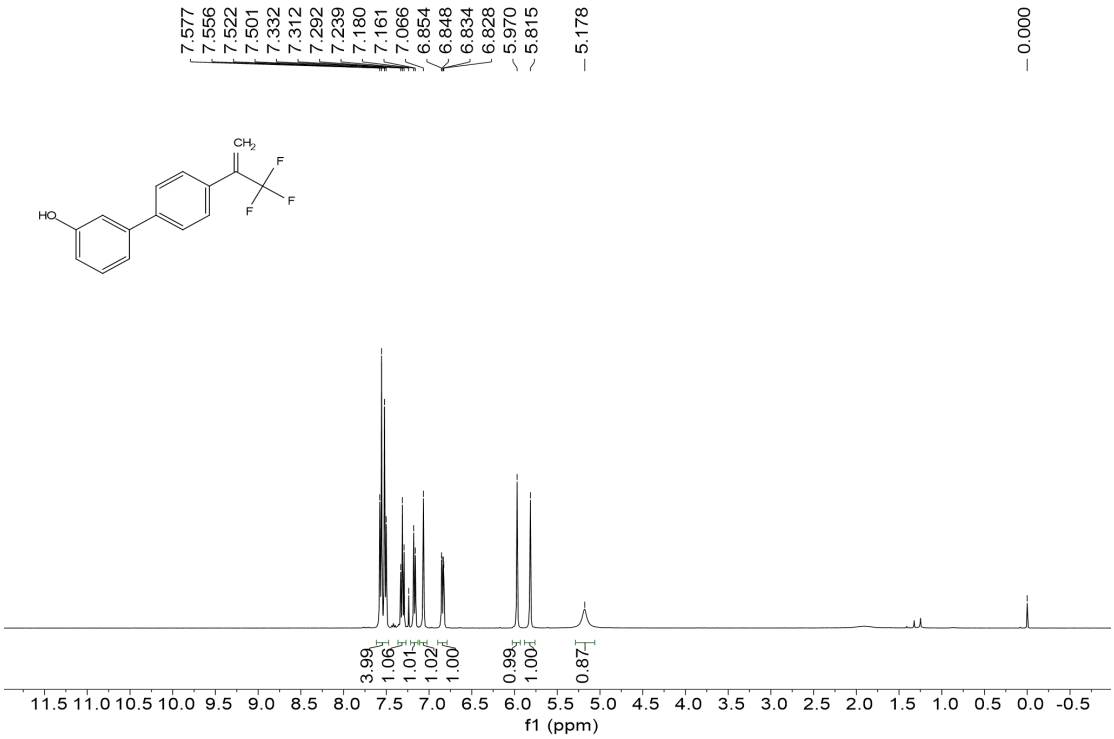
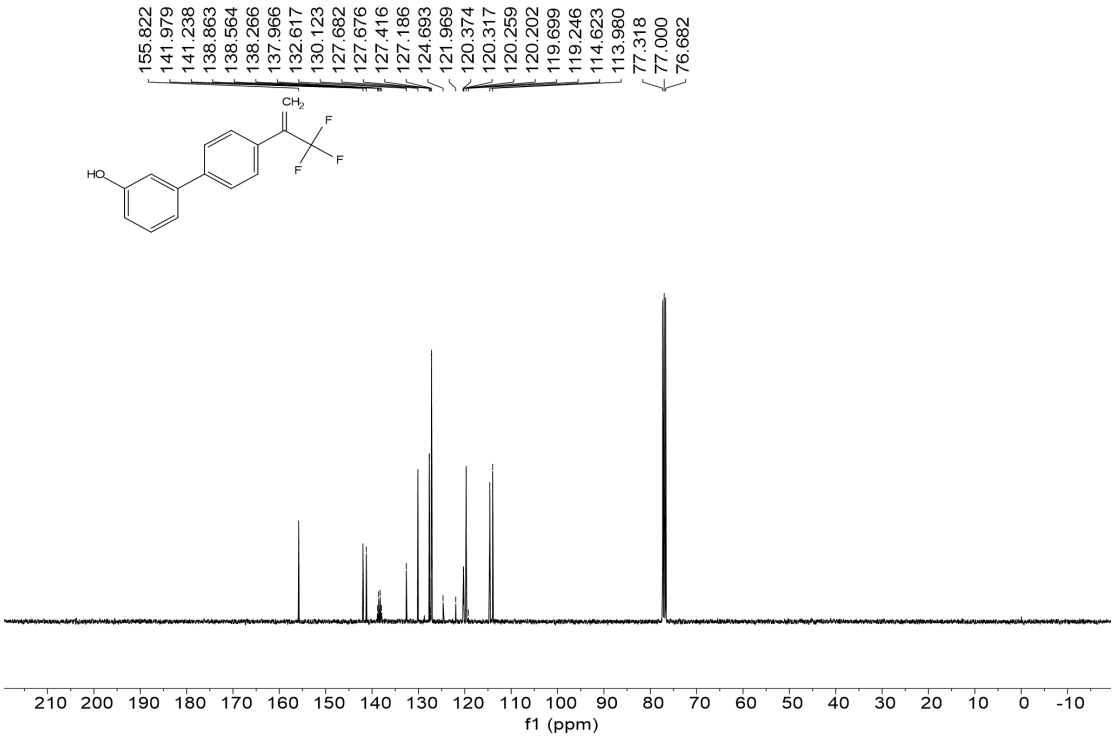
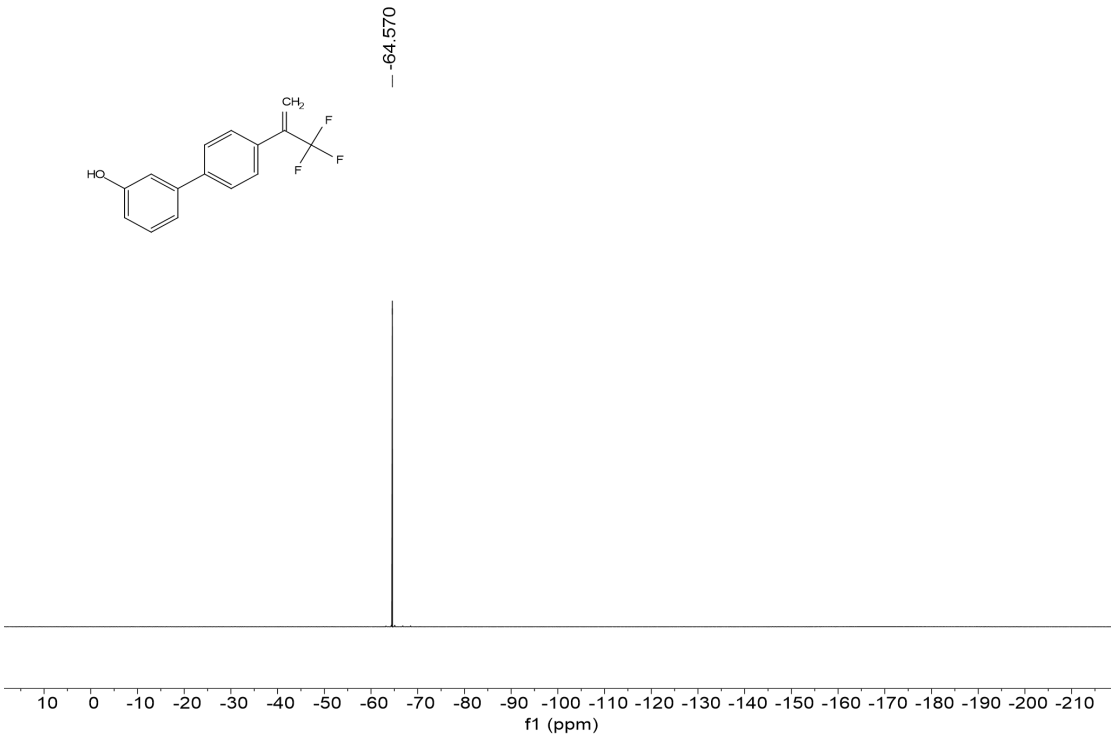
CH2
F
F
F
H2C
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

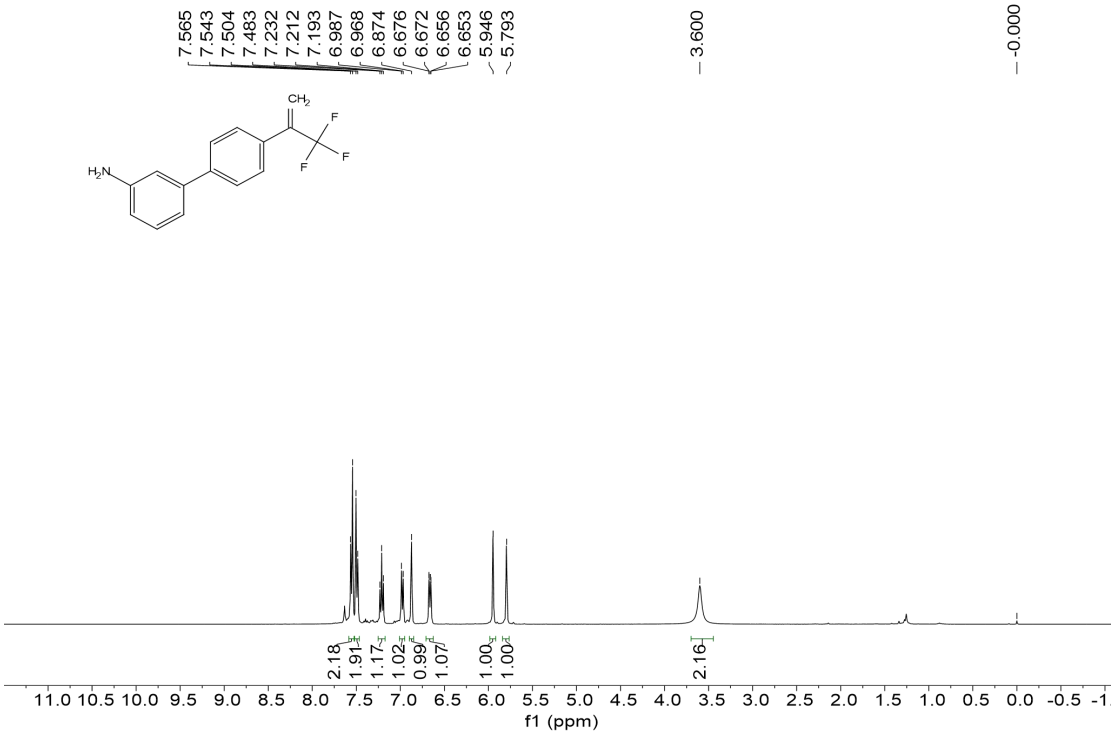
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **S2**

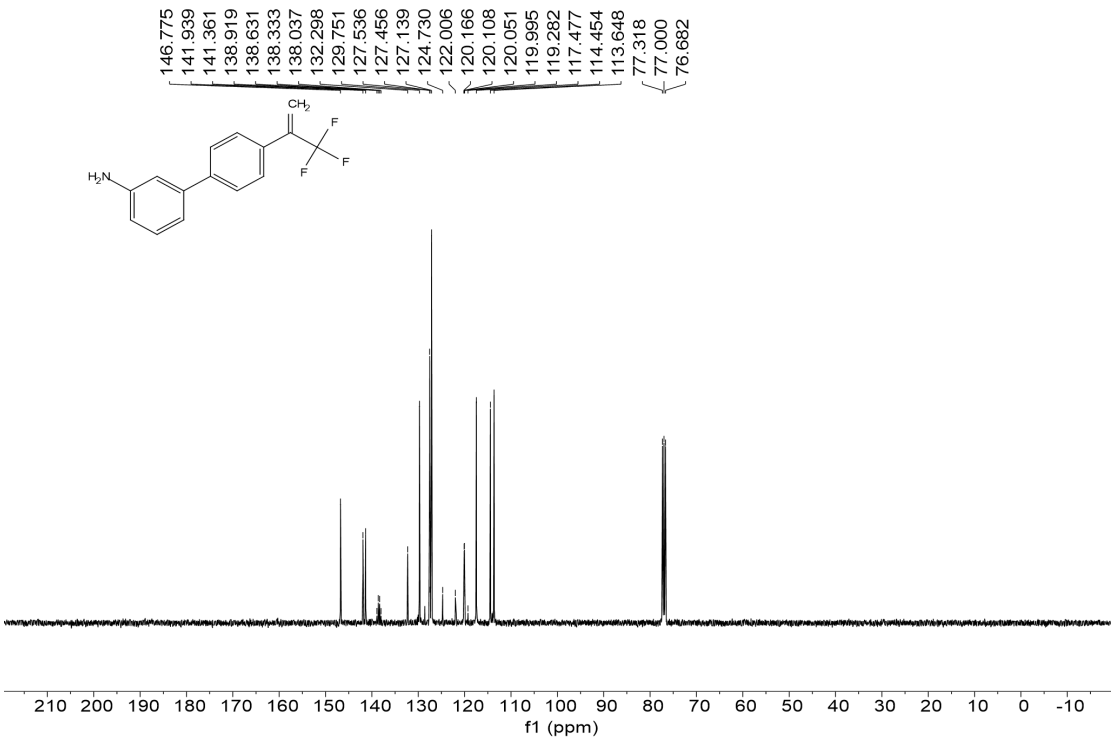






^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **S3**

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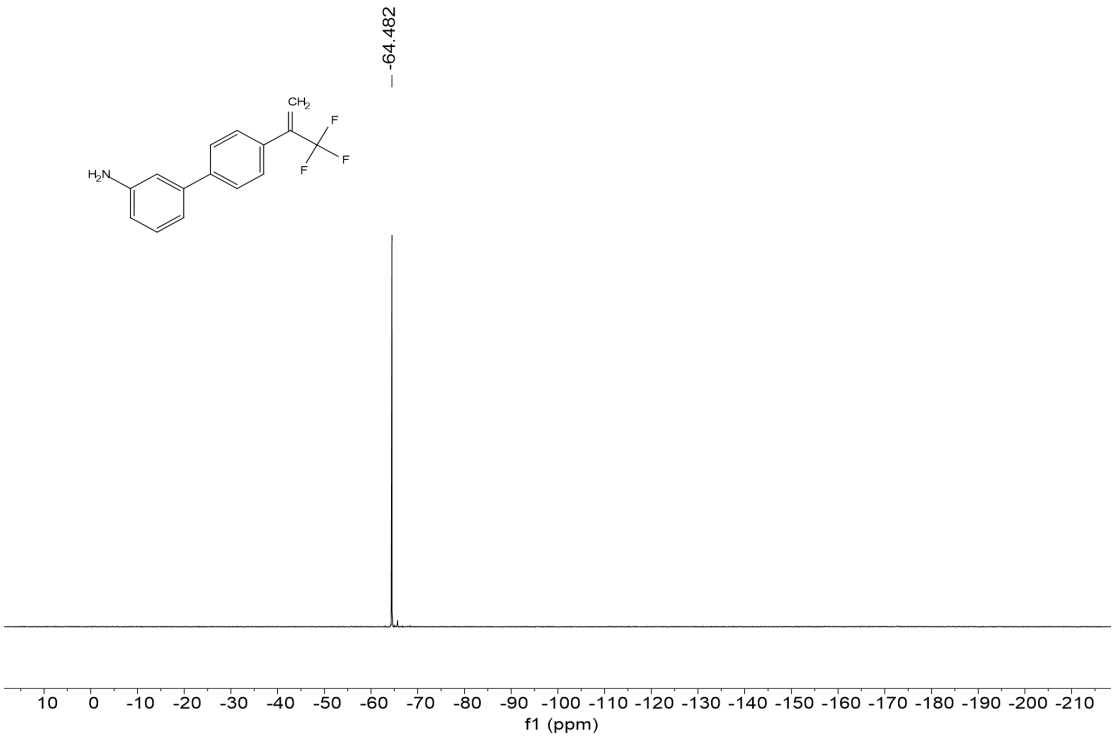
127.139
124.730
122.006
120.166
120.108
120.051
119.995
119.282
117.477
114.454
113.648
77.318
77.000
76.682
CH2
F
F
F
H2N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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CH2
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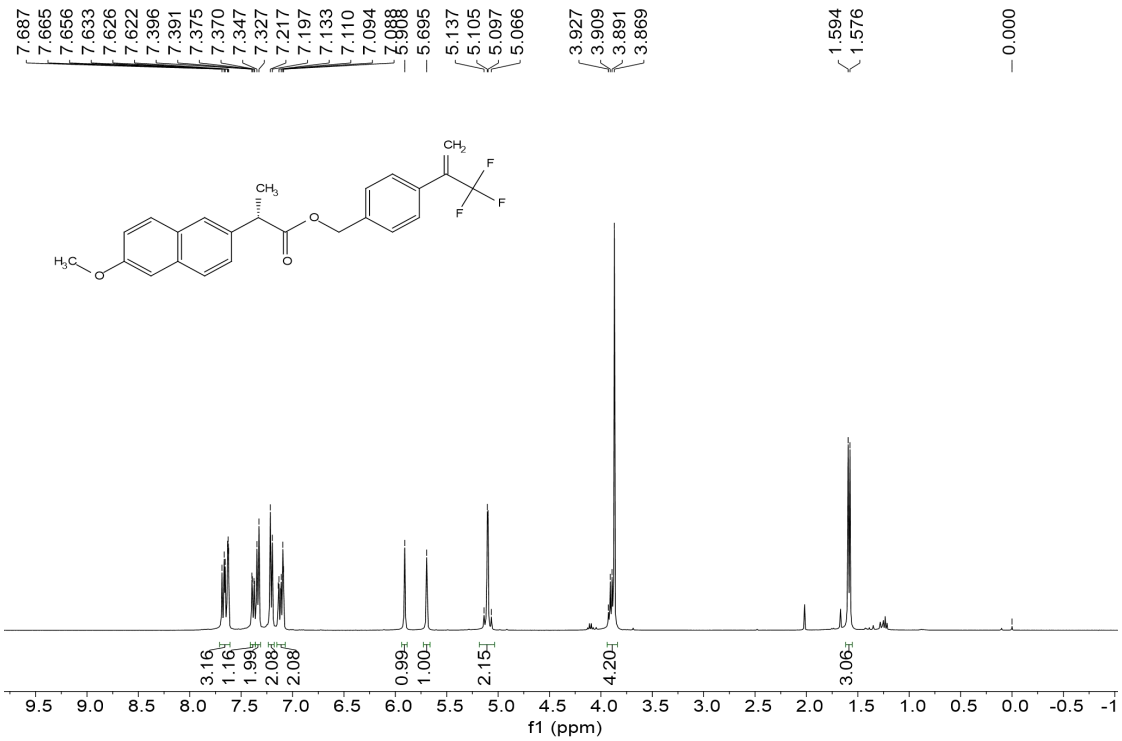
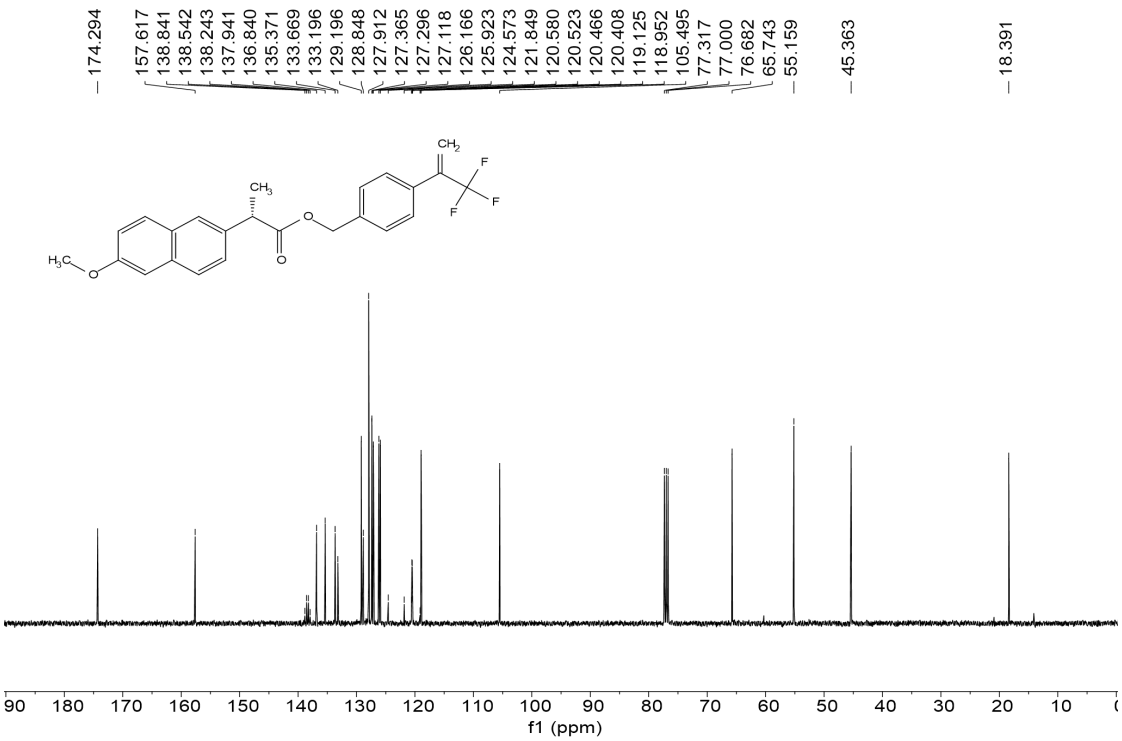
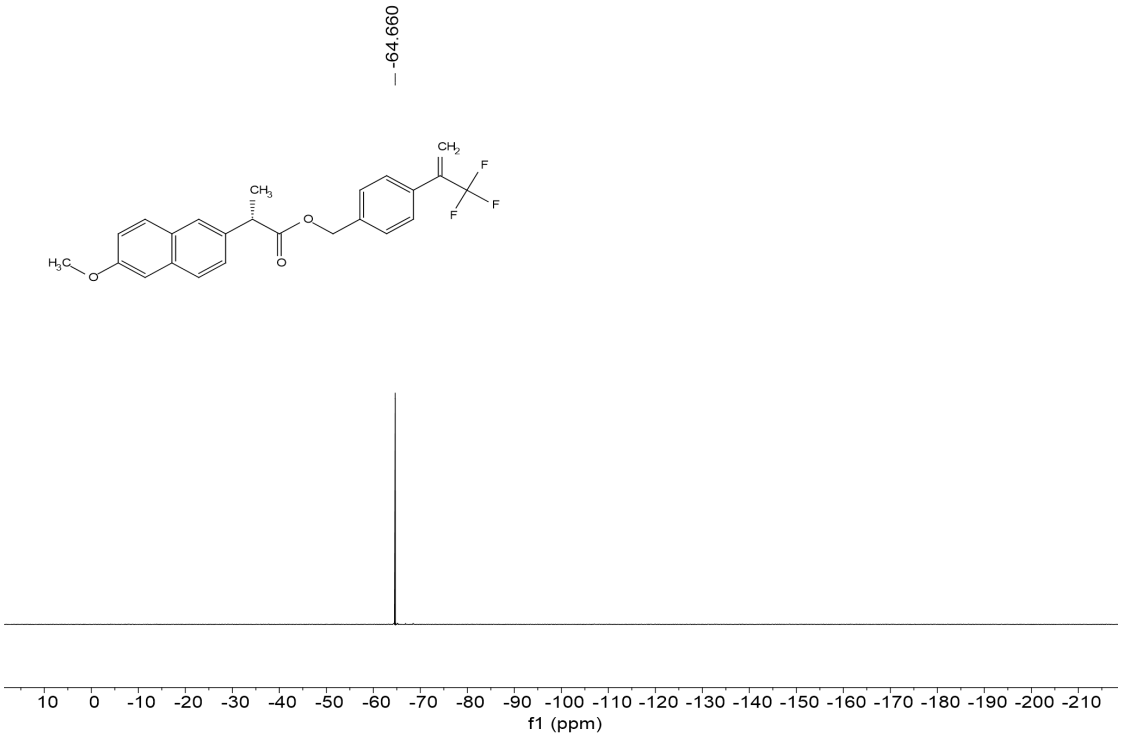
F
F
H2N
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

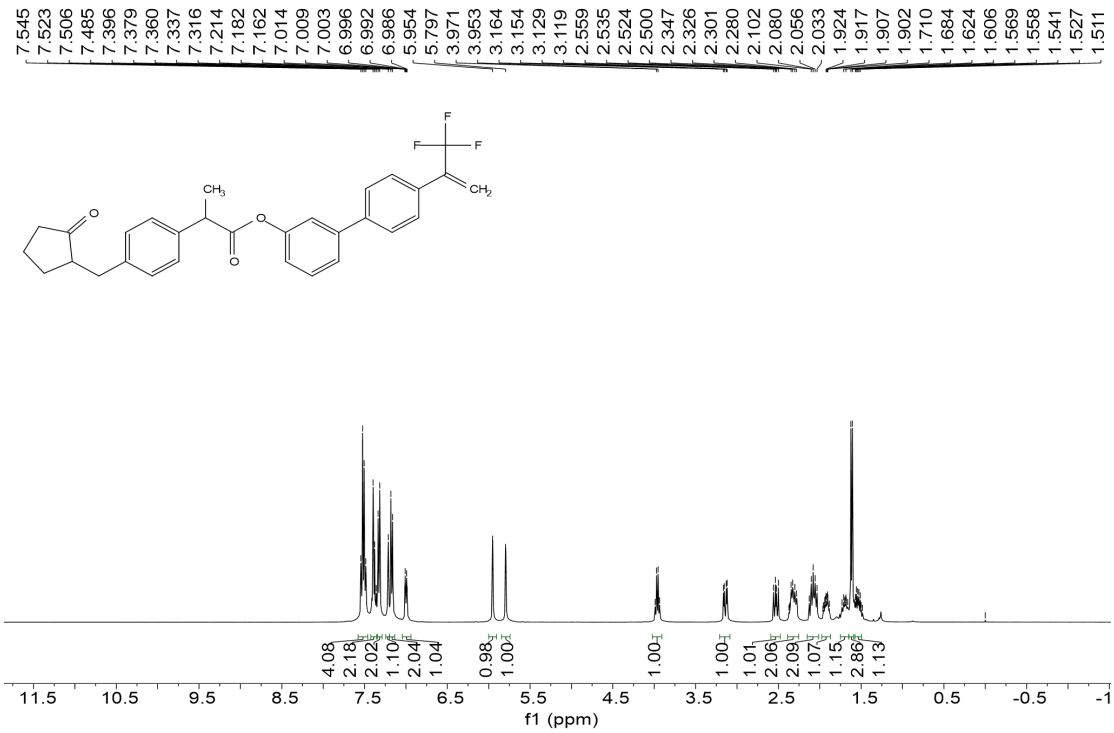
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **1w**

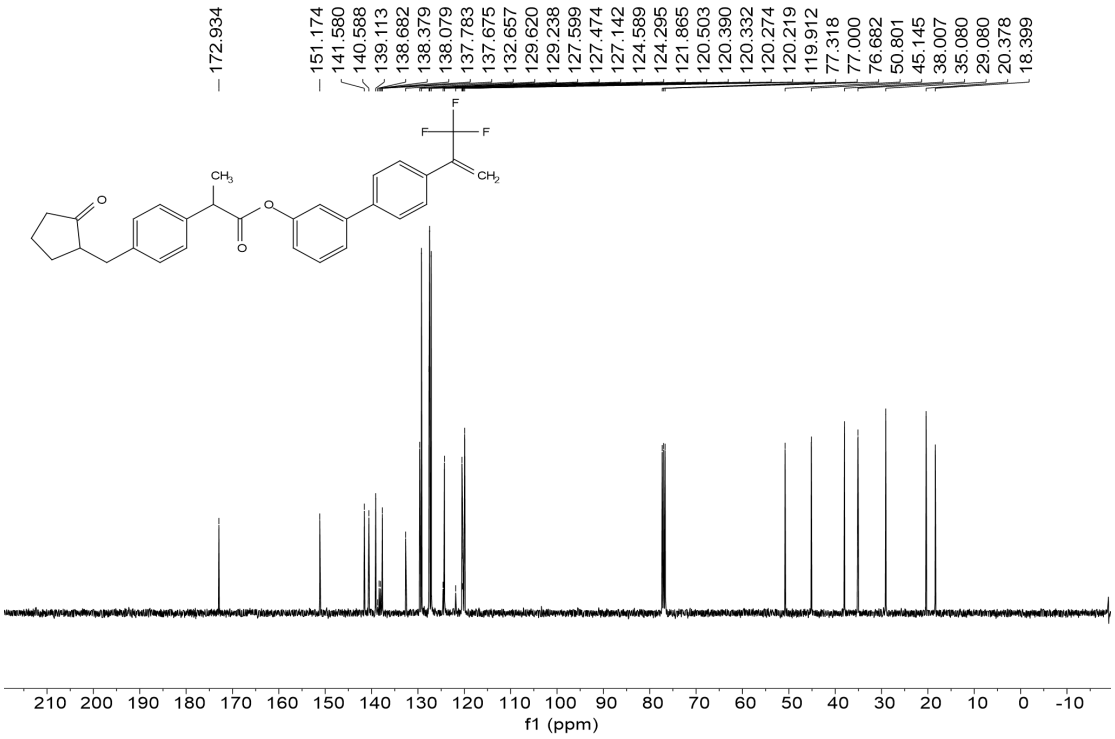






^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **1x**

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139.113
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137.675
132.657
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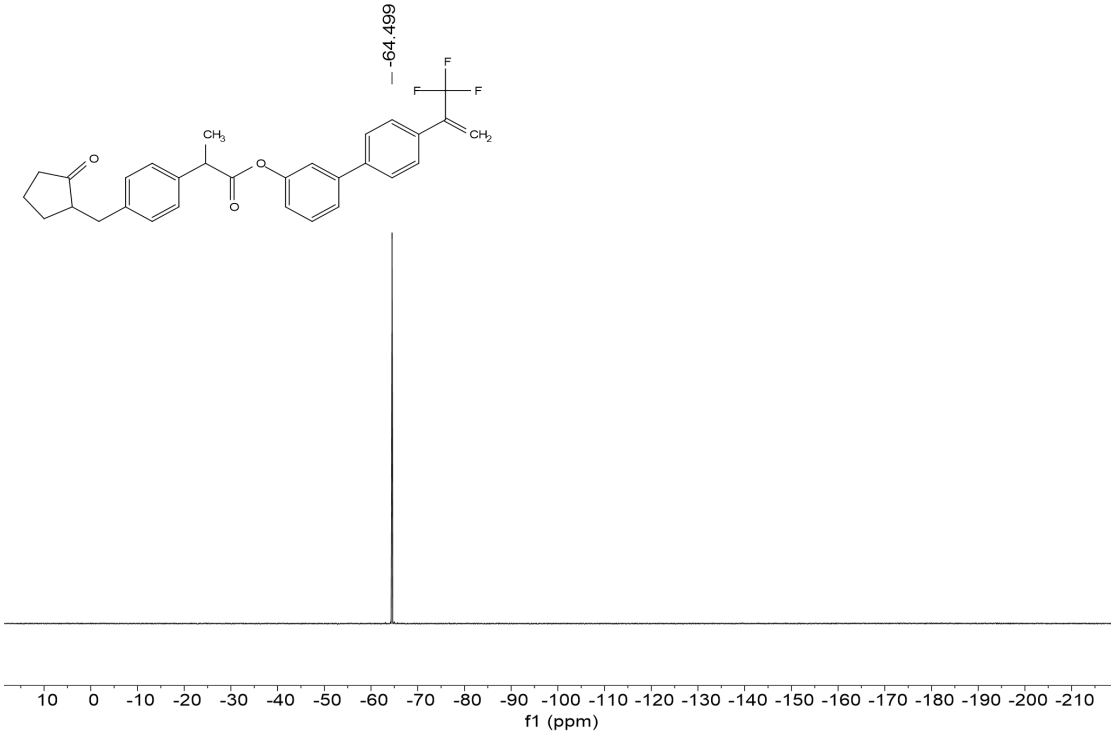
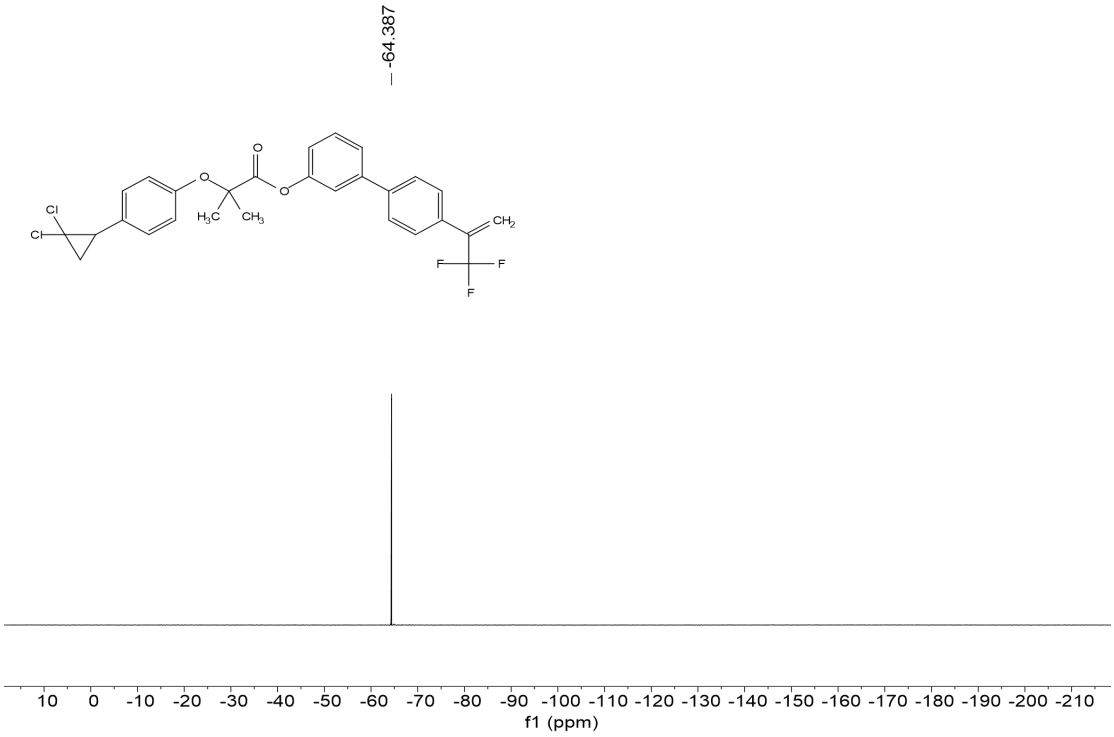
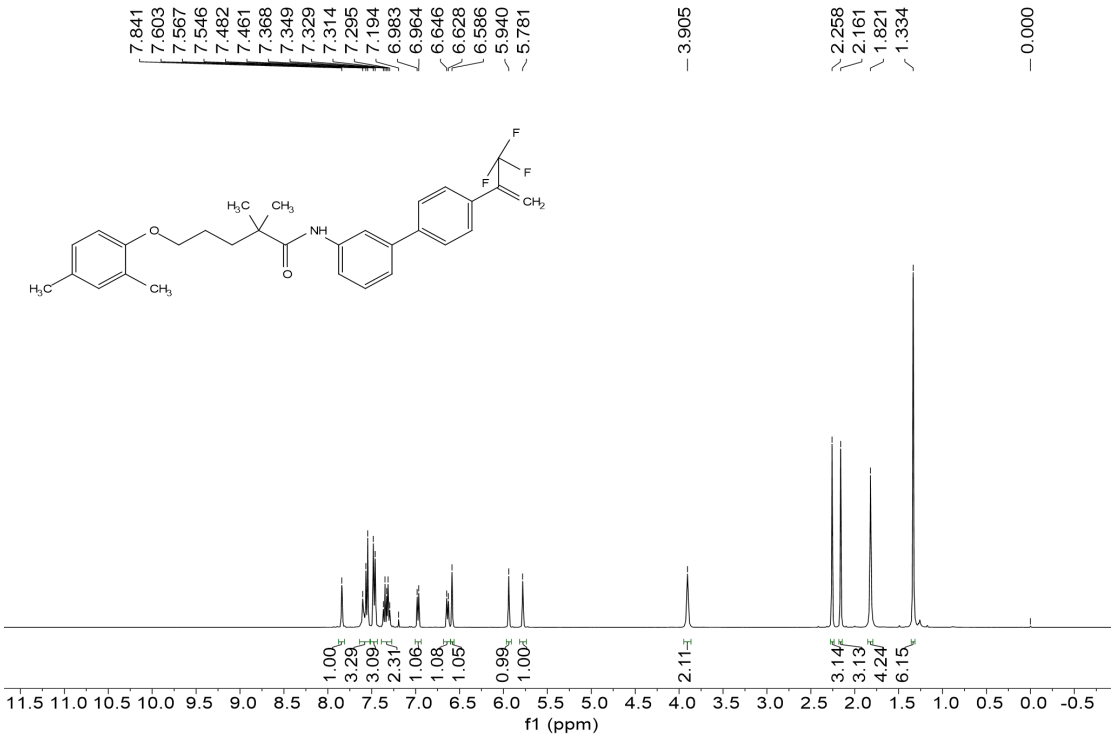
129.238
127.599
127.474
127.142
124.589
124.295
121.865
120.503
120.390
120.332
120.274
120.219
119.912
77.318
77.000
76.682
50.801
45.145
38.007
35.080
29.080
20.378
18.399
F
F
F
CH3
CH2
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

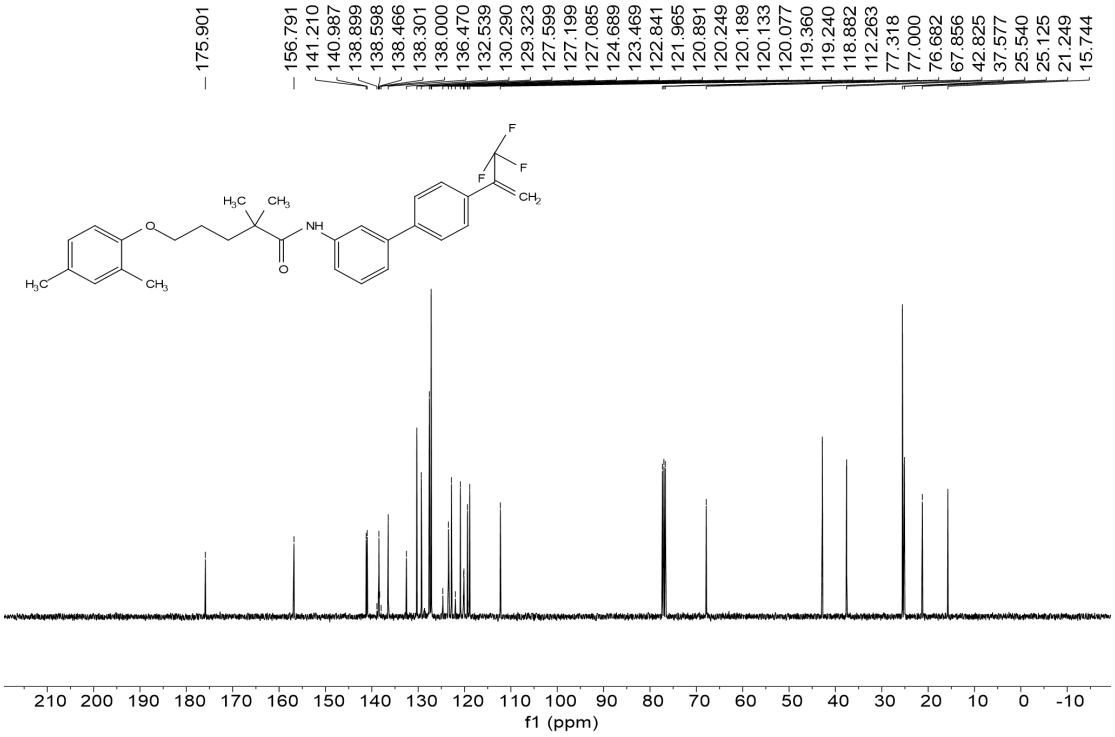

-64.499
F
F
F
CH3
CH2
O
O
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

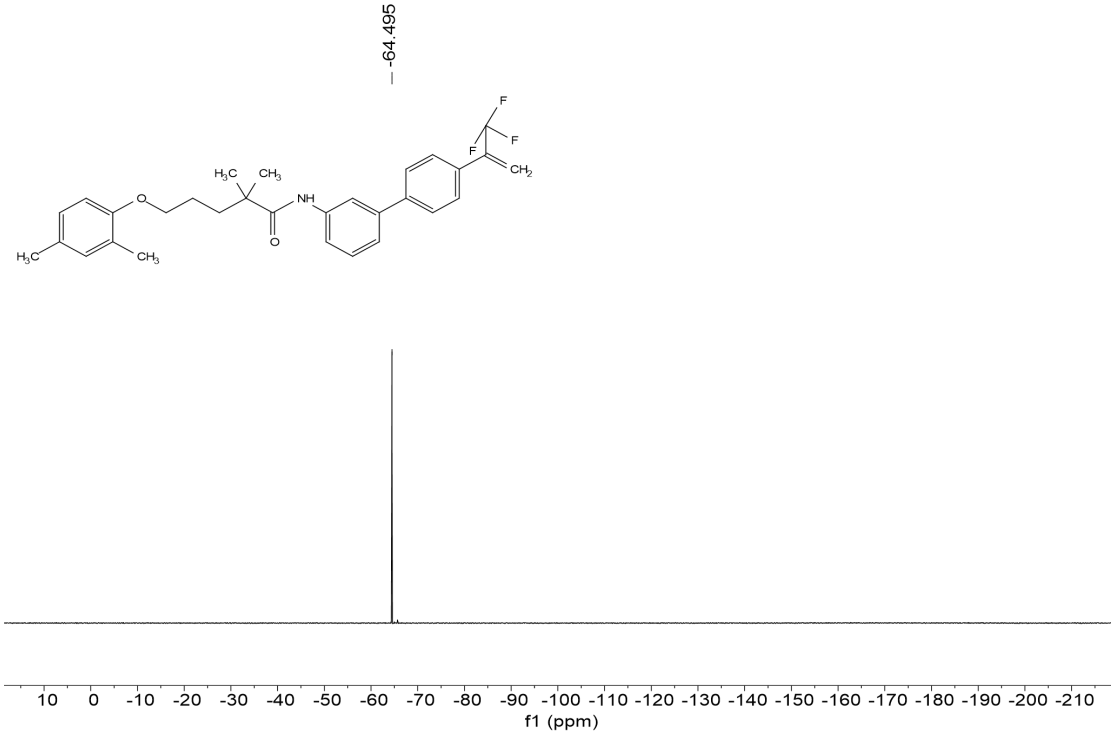
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **1y**



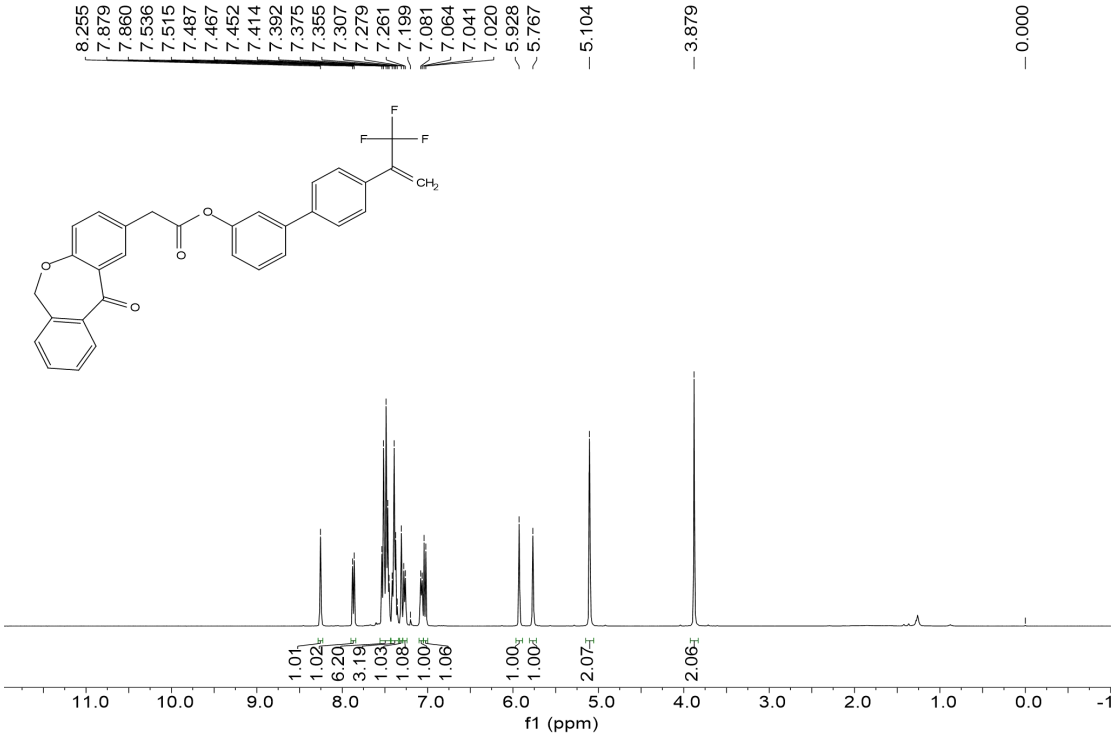
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **1z**

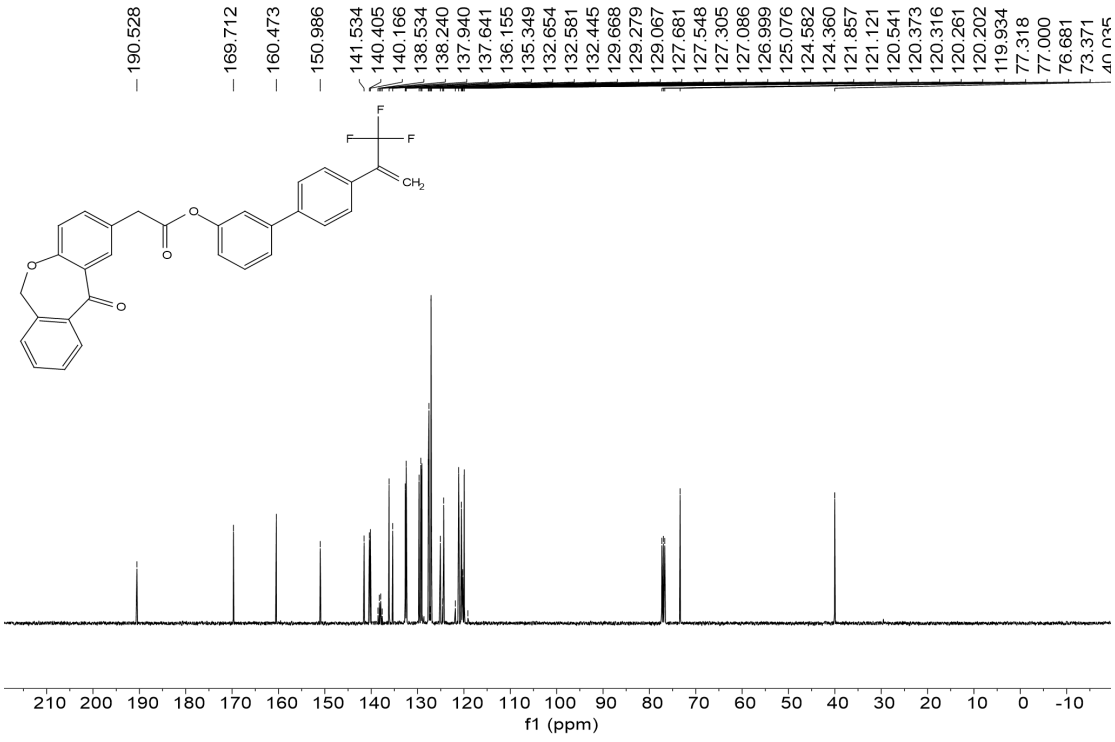


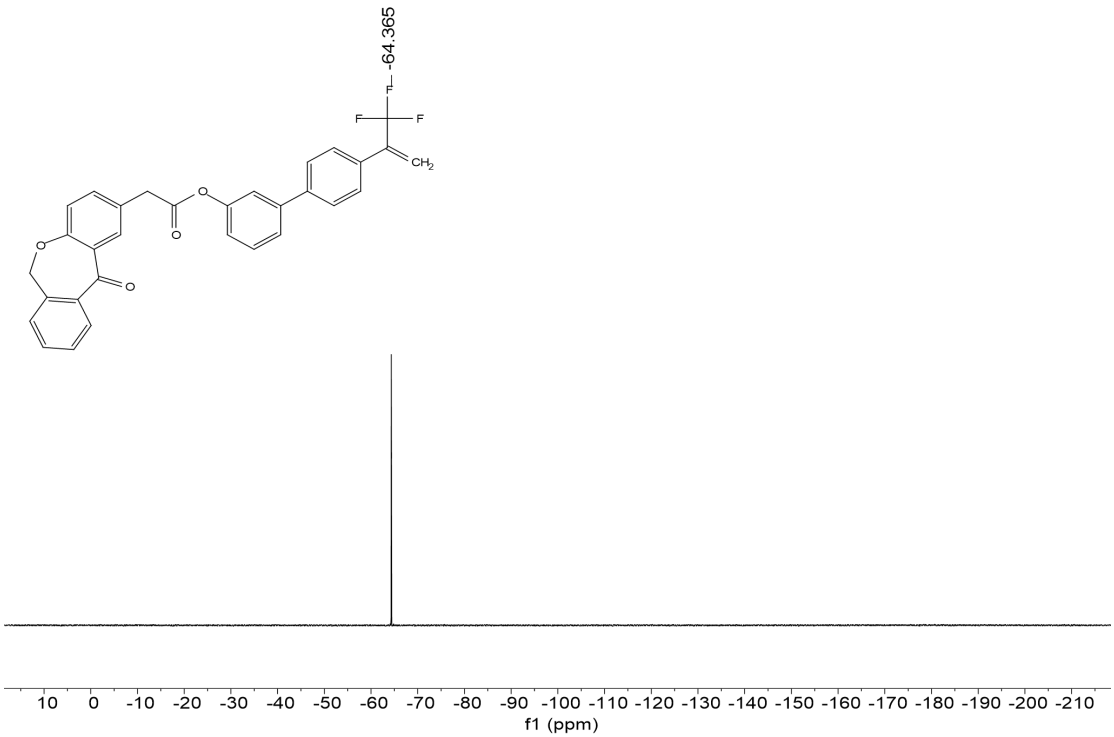

175.901
156.791
141.210
140.987
138.899
138.598
138.466
138.301
138.000
136.470
132.539
130.290
129.323
127.599
127.199
127.085
124.689
123.469
122.841
121.965
120.891
120.249
120.189
120.133
120.077
119.360
119.240
118.882
112.263
77.318
77.000
76.682
67.856
42.825
37.577
25.540
25.125
21.249
15.744
F
F
F
CH2
H3C
CH3
NH
O
O
H3C
CH3
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)


-64.495
F
F
F
CH2
H3C
CH3
NH
O
O
H3C
CH3
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)

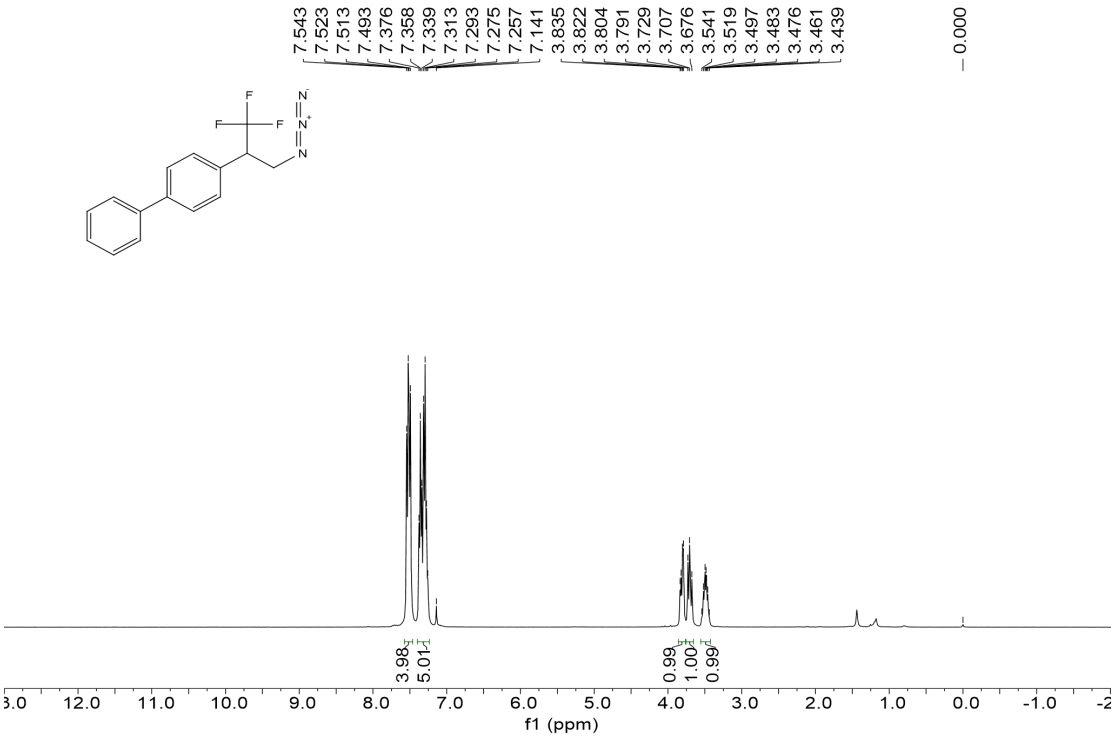
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **1za**

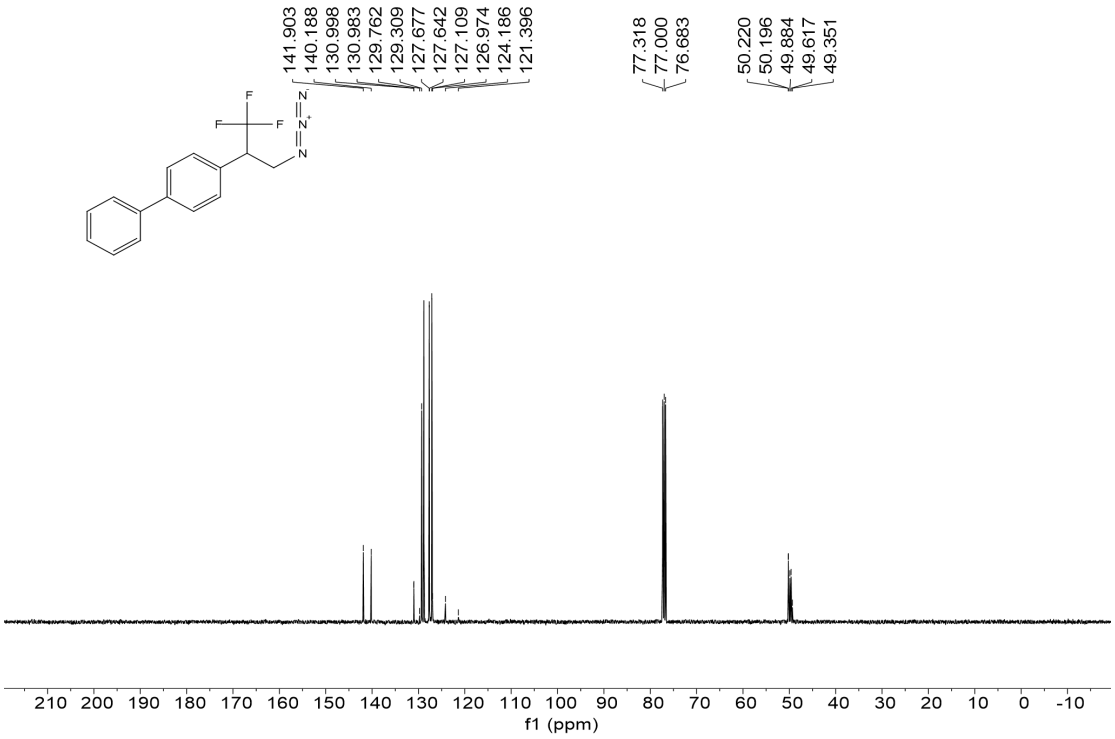


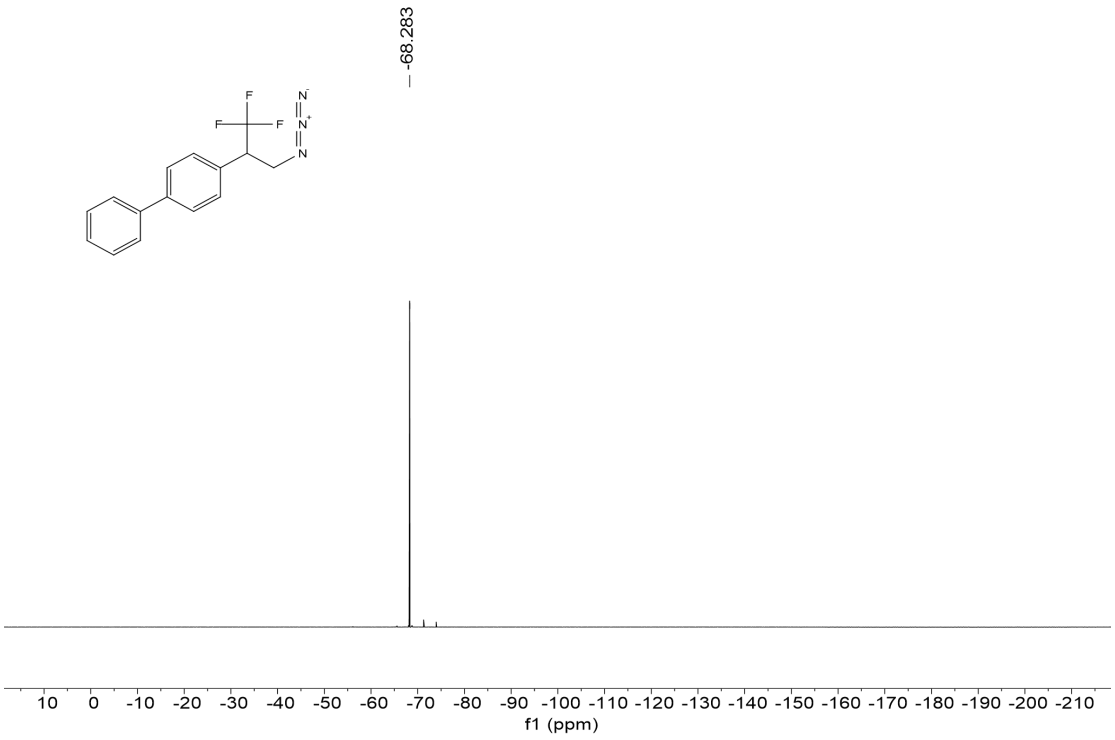




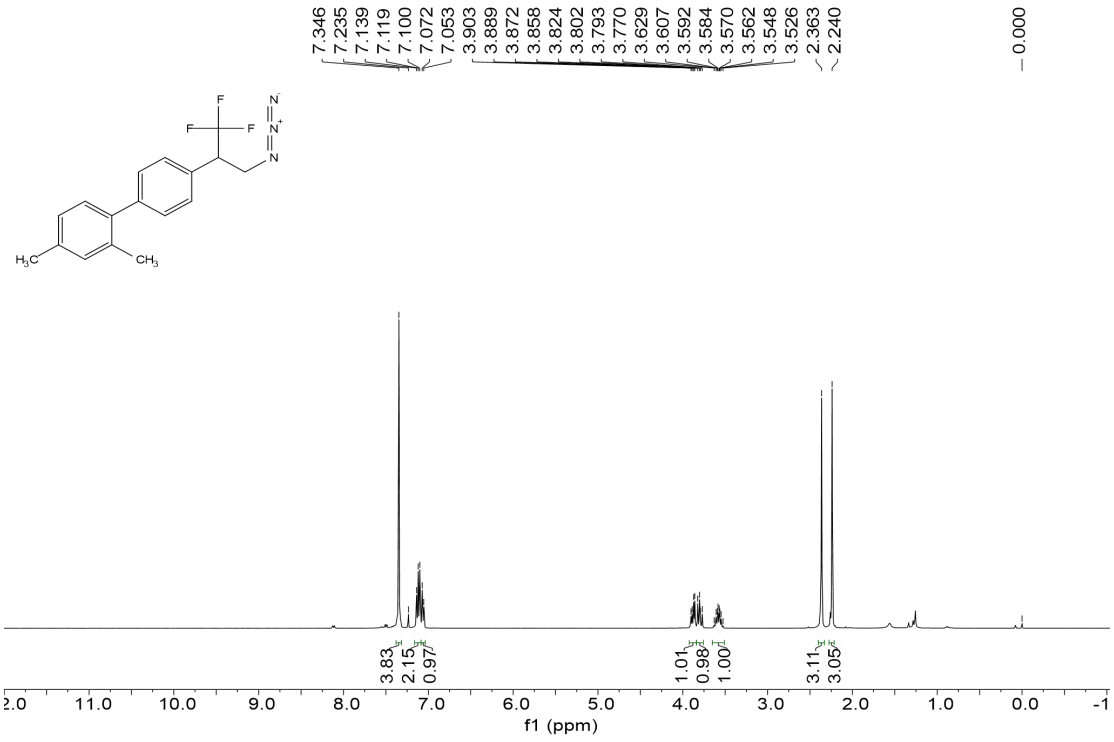
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **3**

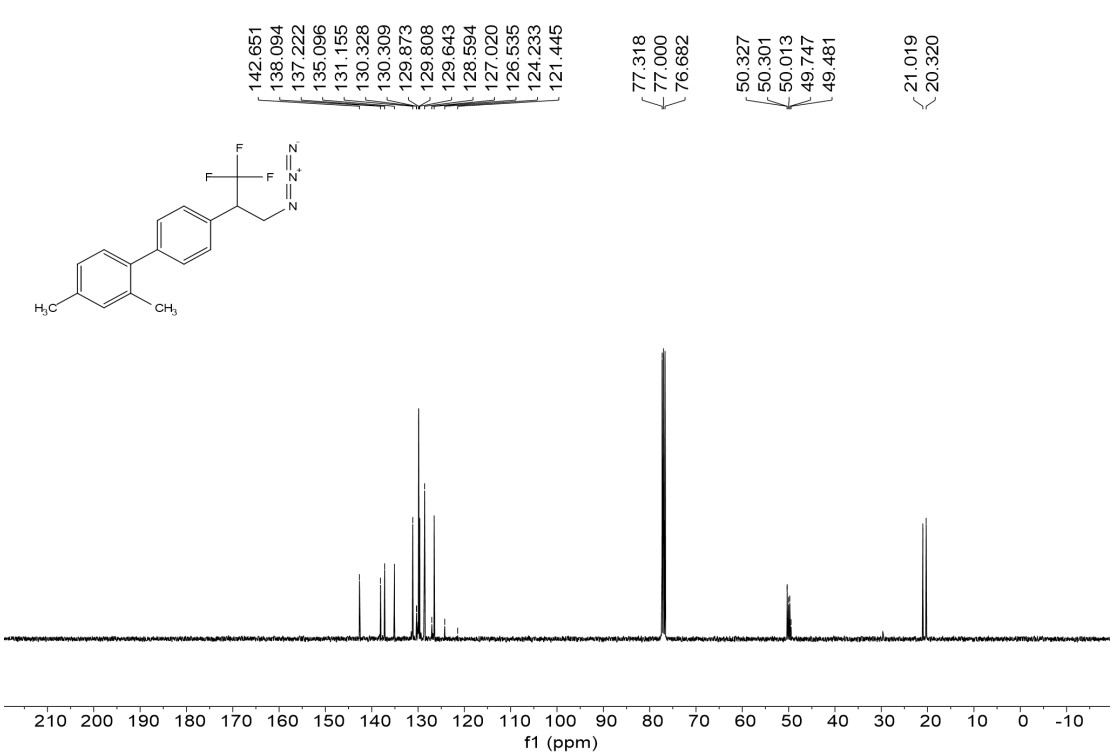


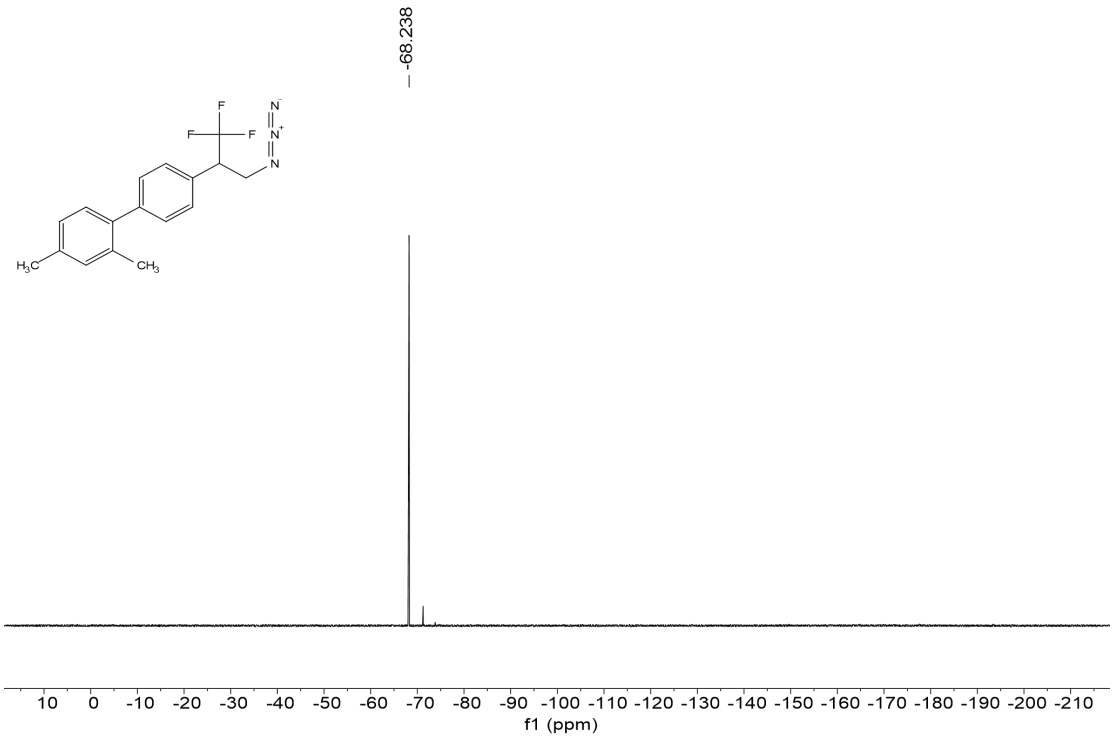

141.903
140.188
130.998
130.983
129.762
129.309
127.677
127.642
127.109
126.974
124.186
121.396
77.318
77.000
76.683
50.220
50.196
49.884
49.617
49.351
F
F
F
N
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-68.283
F
F
F
N
N
N
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)

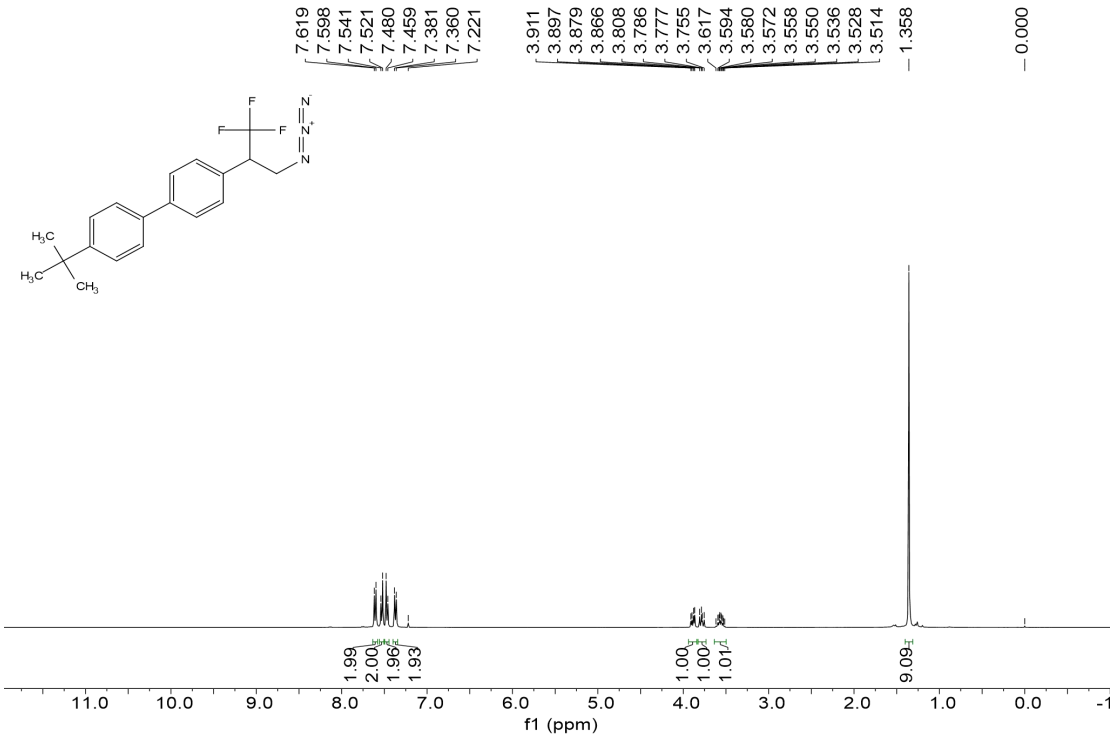
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **4**

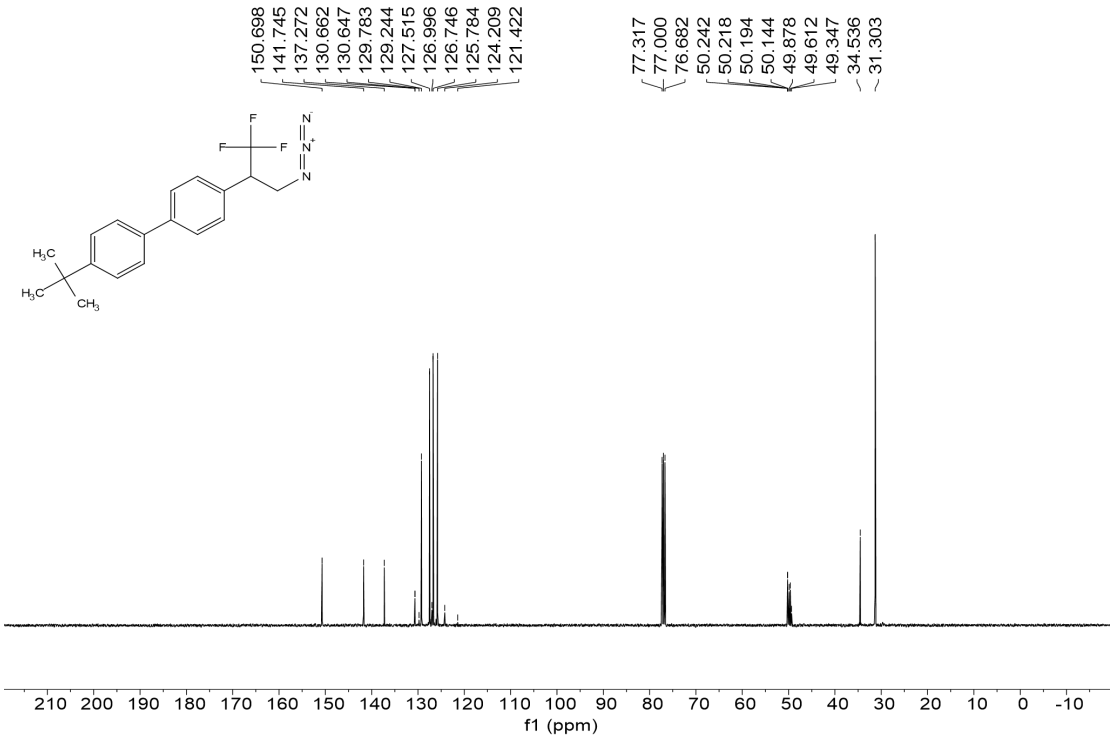


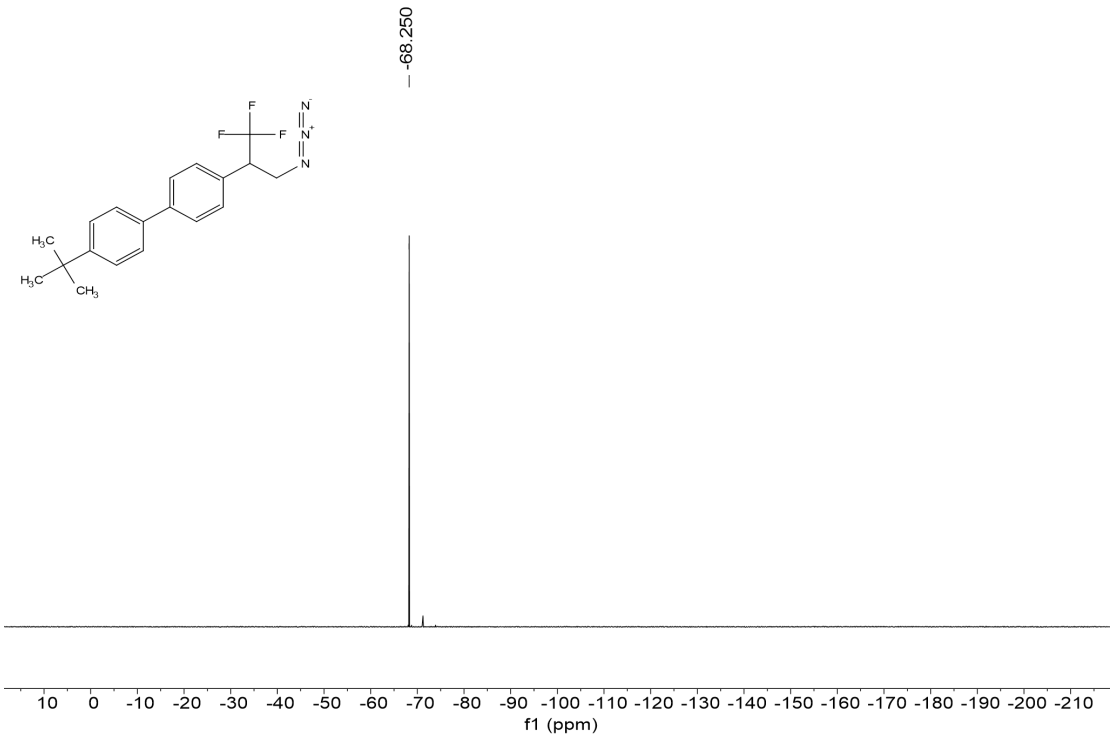




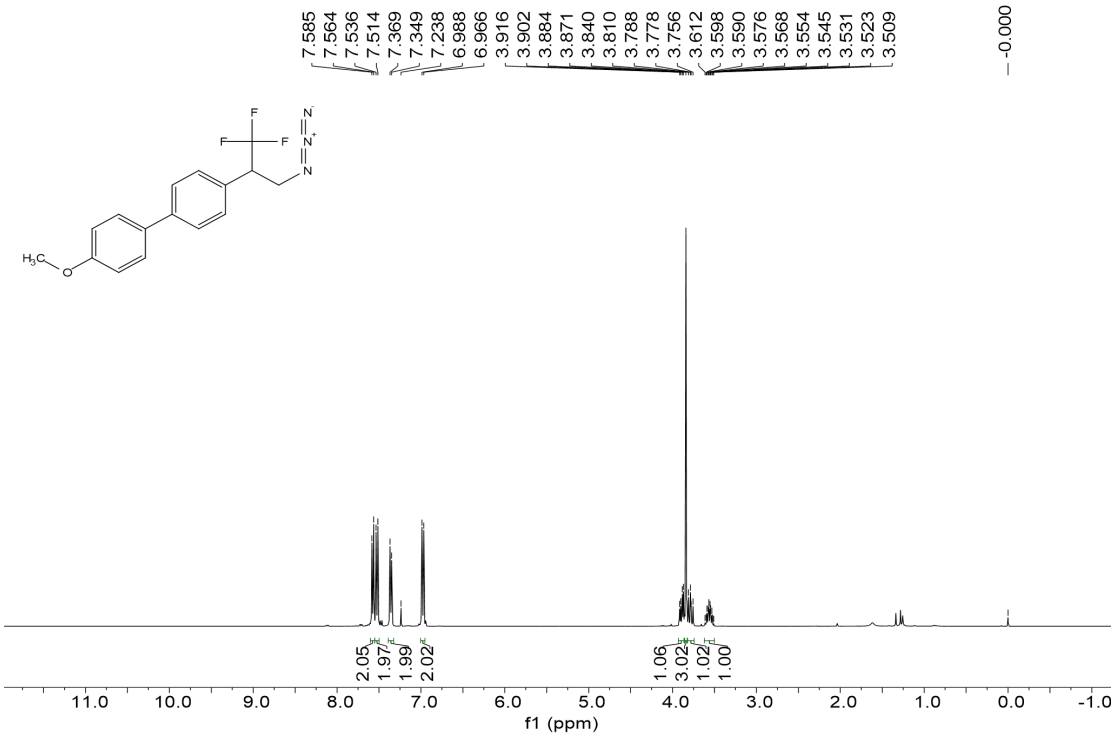
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **5**

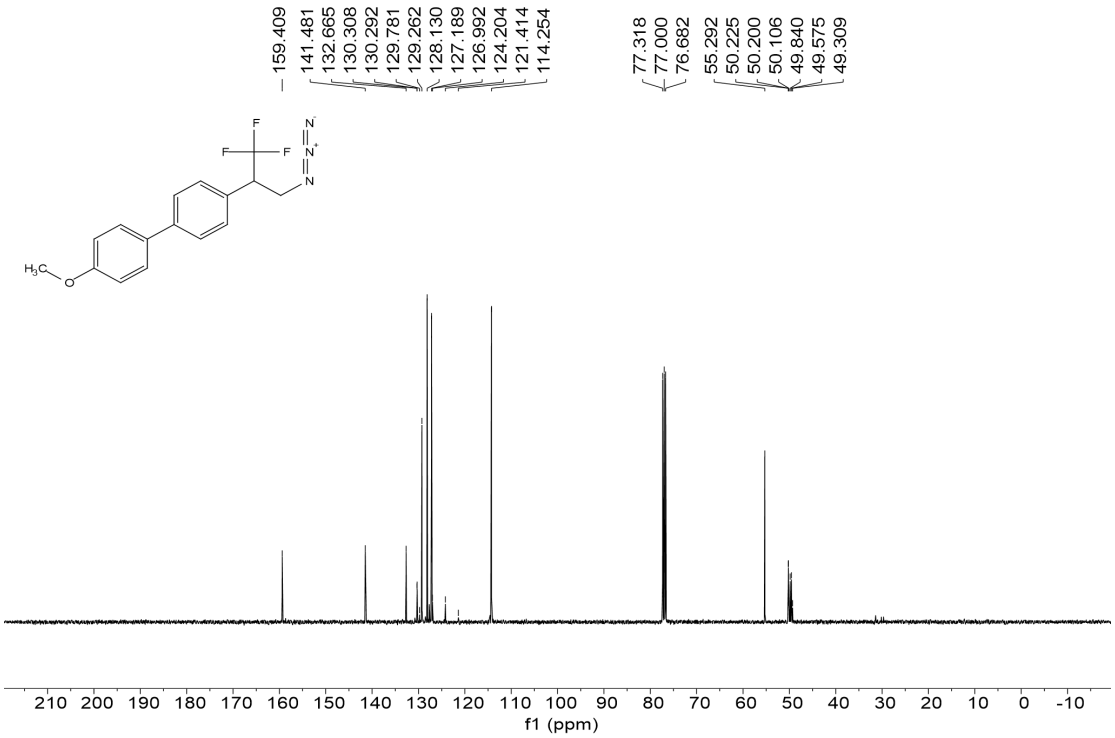



150.698
141.745
137.272
130.662
130.647
129.783
129.244
127.515
126.996
126.746
125.784
124.209
121.422
77.317
77.000
76.682
50.242
50.218
50.194
50.144
49.878
49.612
49.347
34.536
31.303
F
F
F
N
N
N
H3C
H3C
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

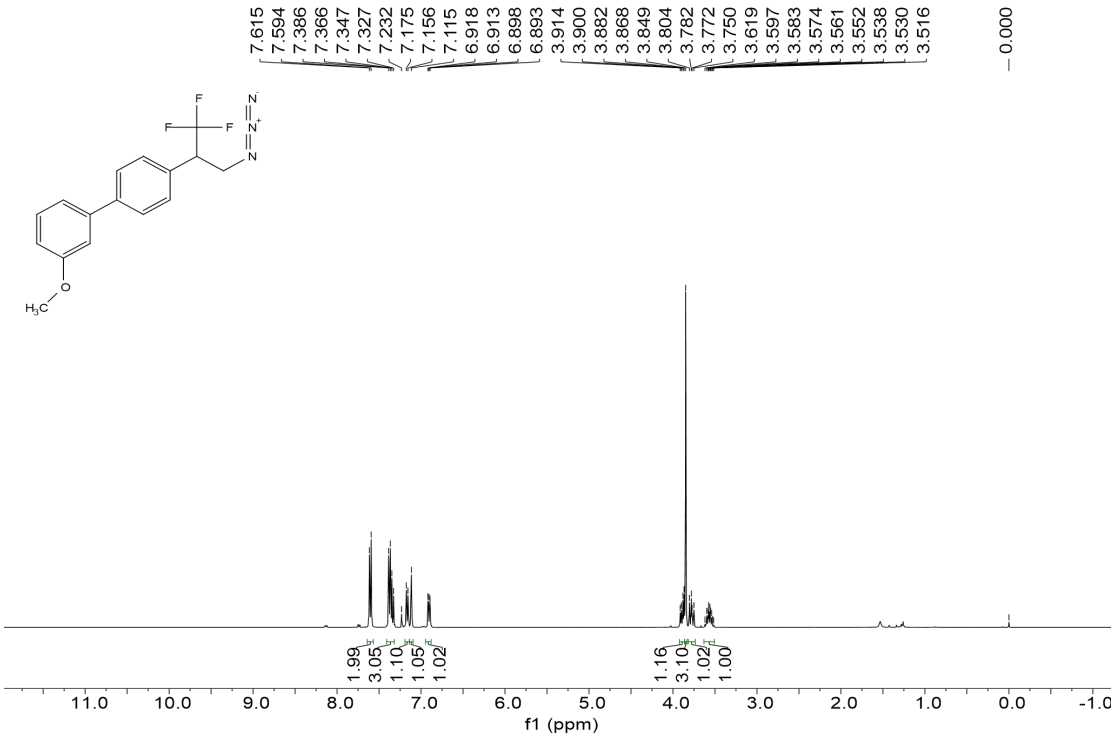

-68.250
F
F
F
N
N
N
H3C
H3C
CH3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

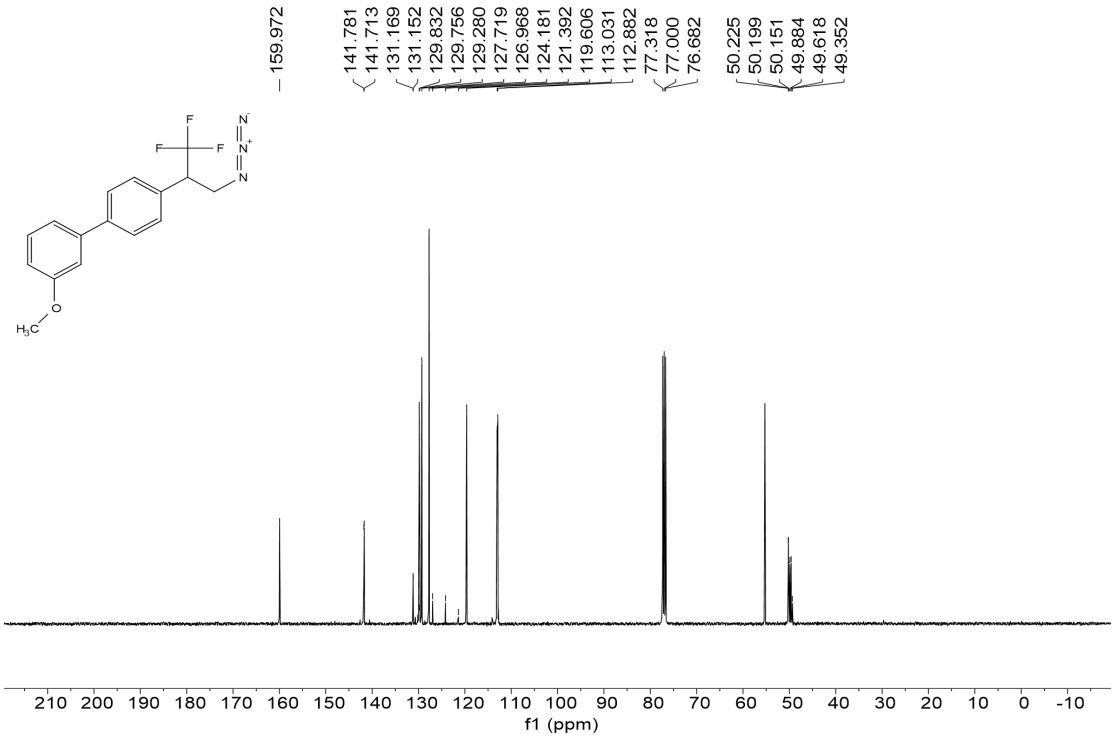
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **6**

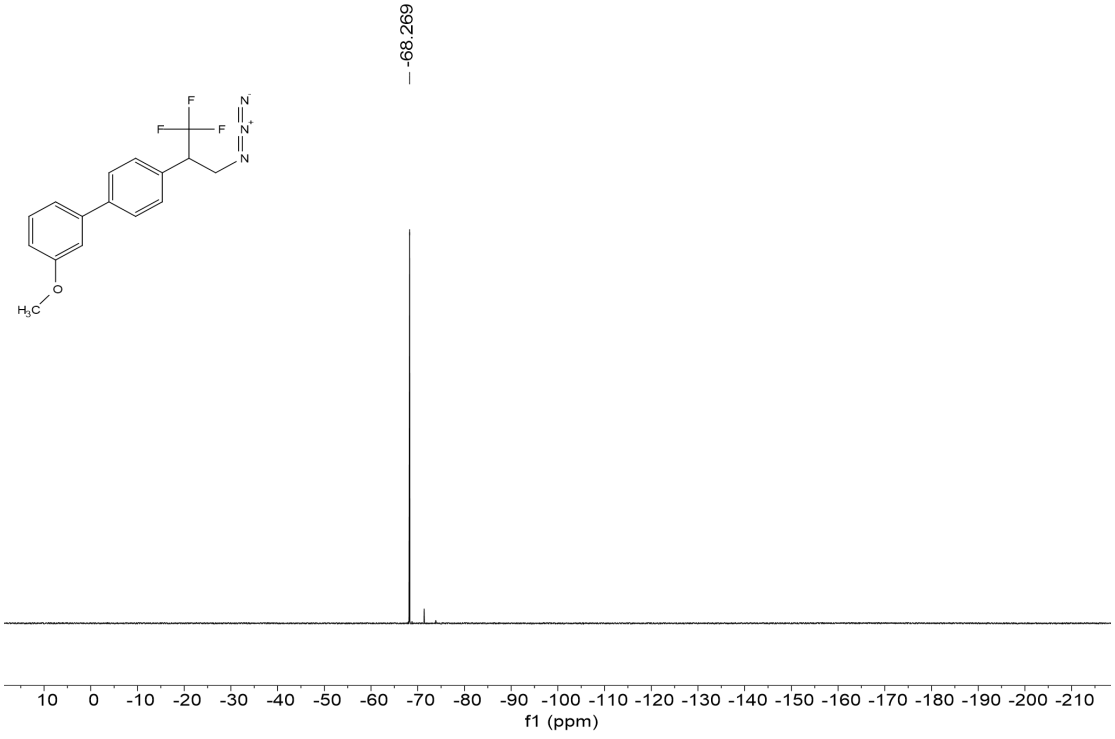




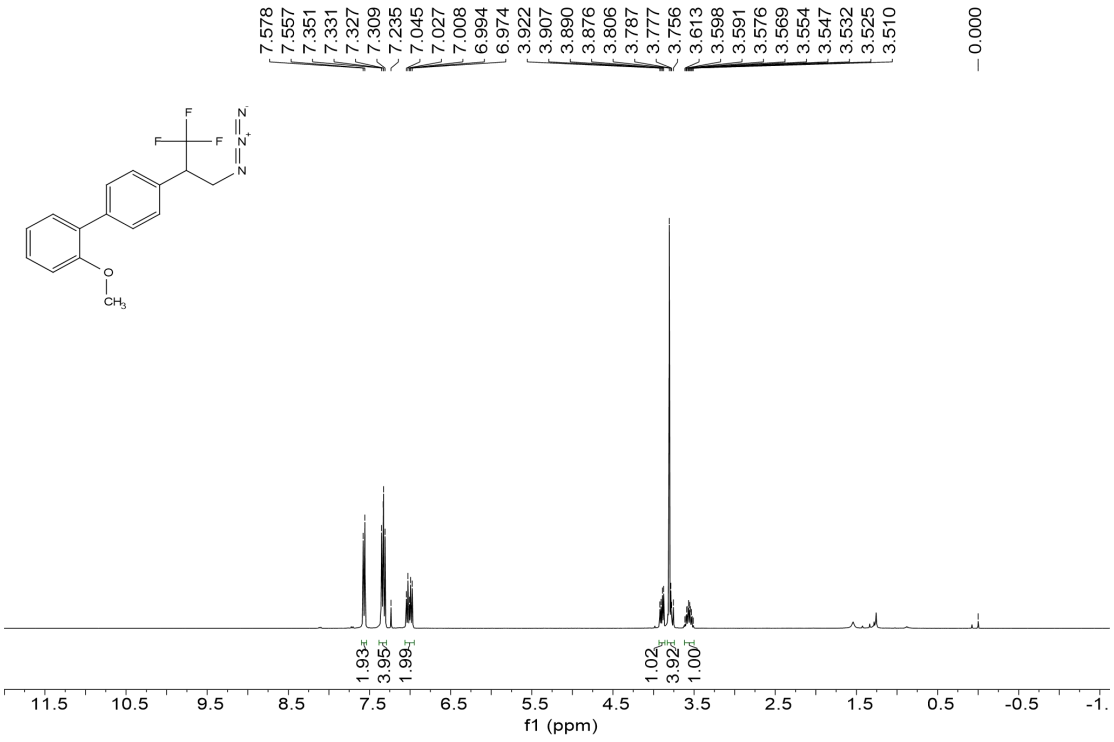
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **7**

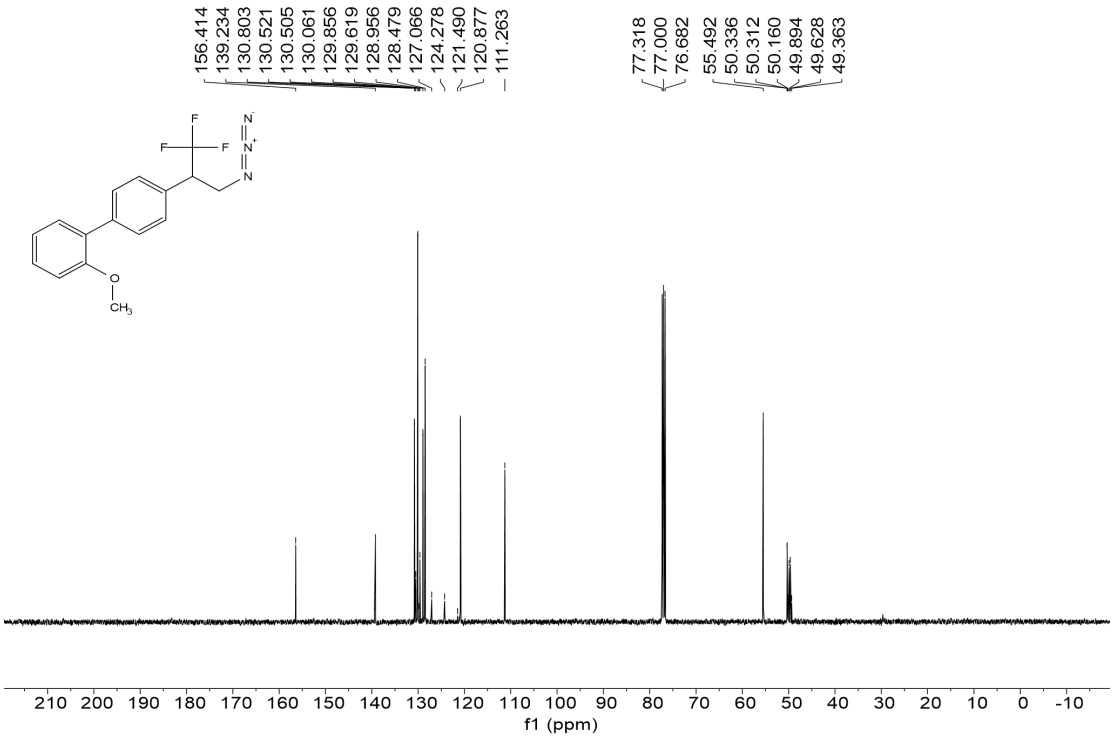


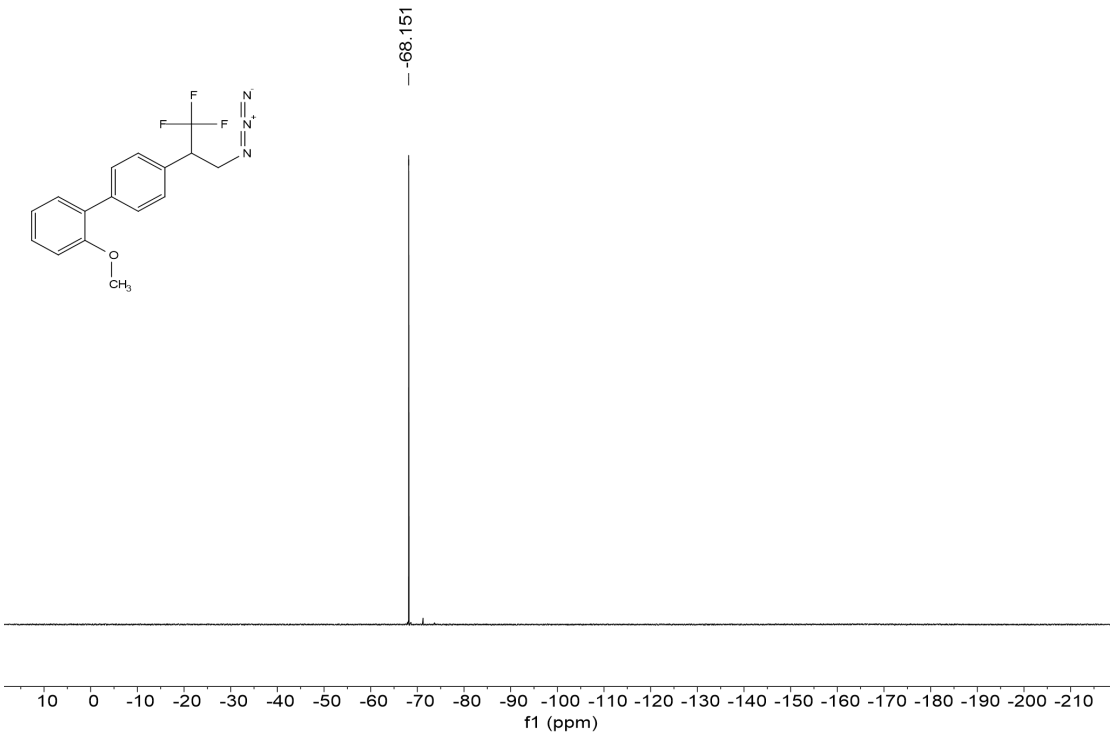

159.972
141.781
141.713
131.169
131.152
129.832
129.756
129.280
127.719
126.968
124.181
121.392
119.606
113.031
112.882
77.318
77.000
76.682
50.225
50.199
50.151
49.884
49.618
49.352
F
F
F
N
N
N
O
H3C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-68.269
F
F
F
N
N
N
O
H3C
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)

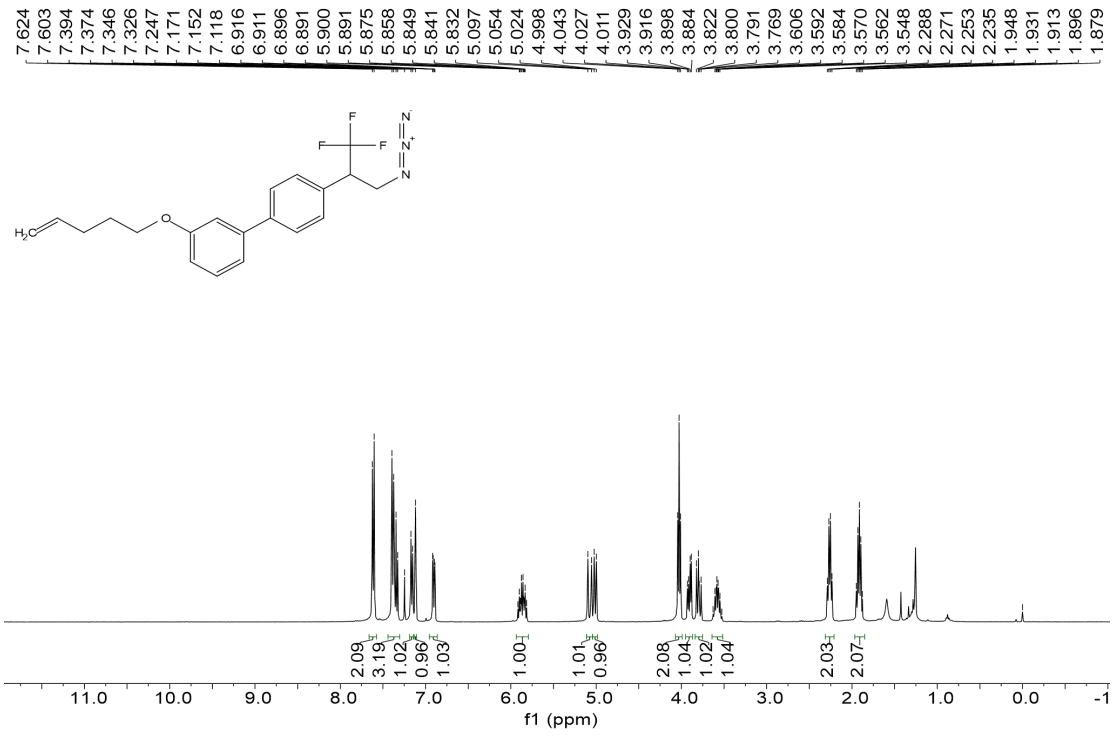
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **8**

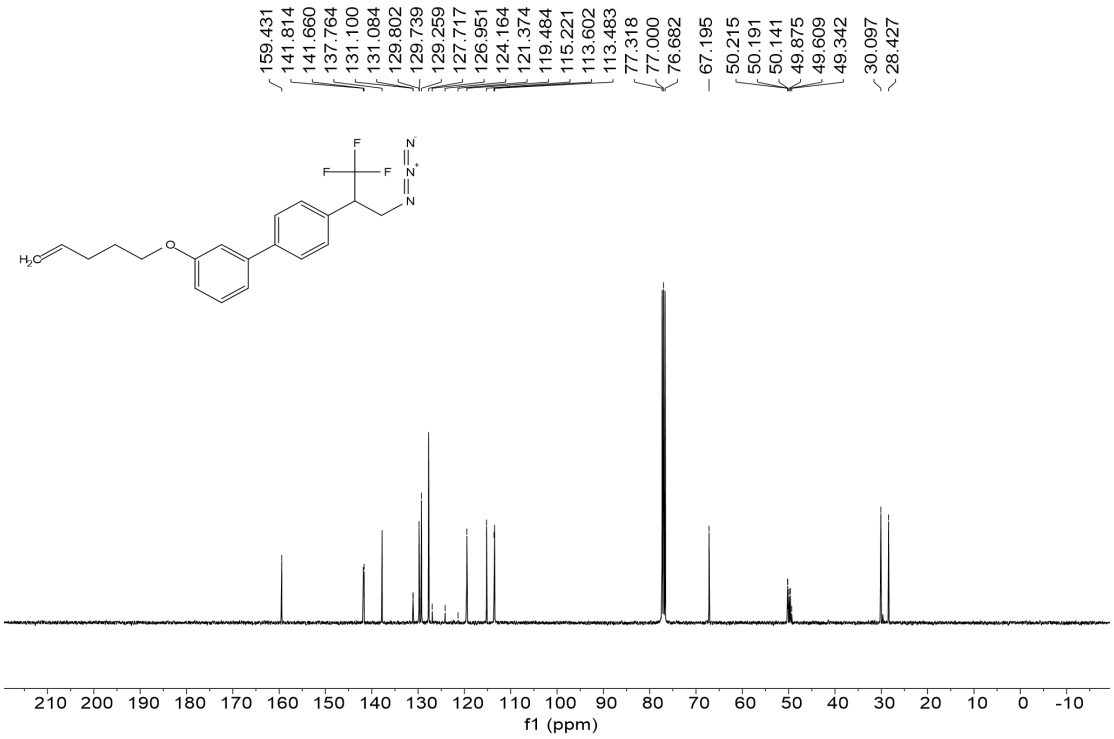


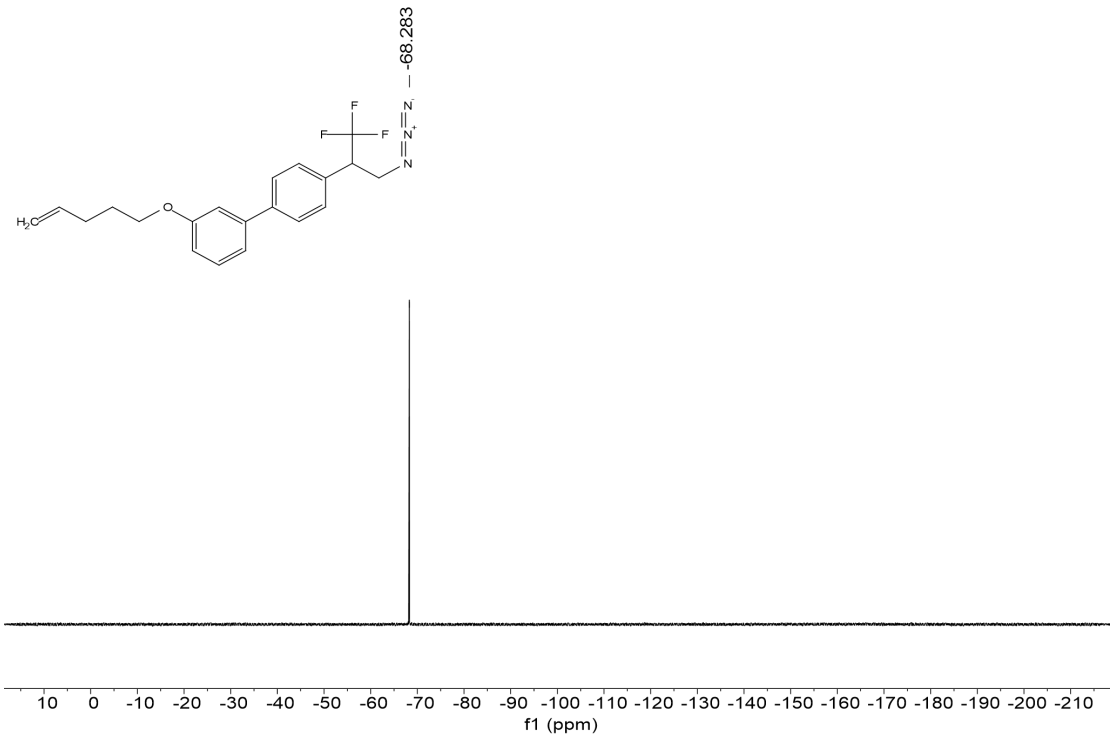




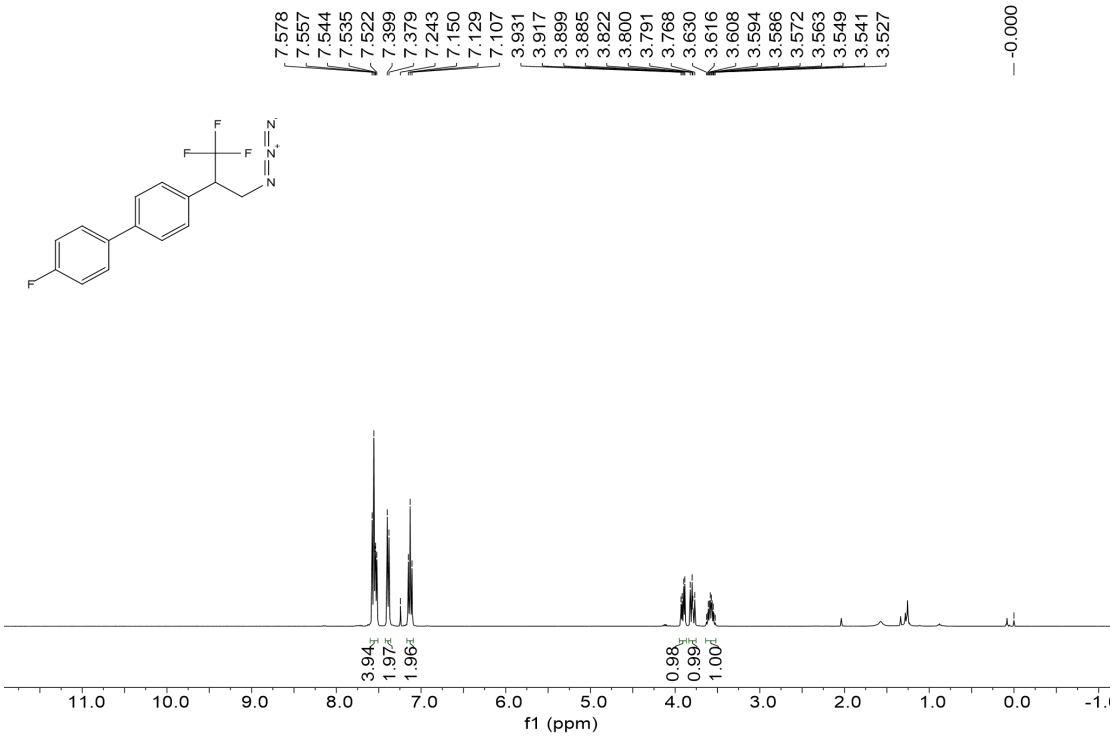
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **9**

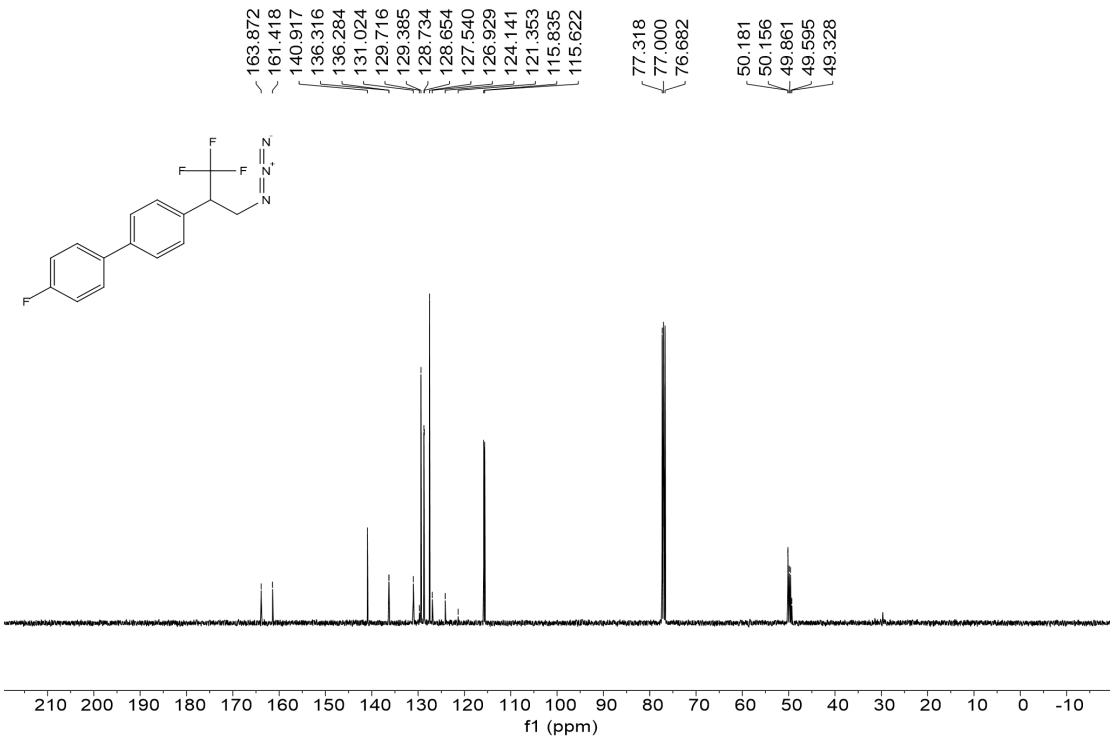


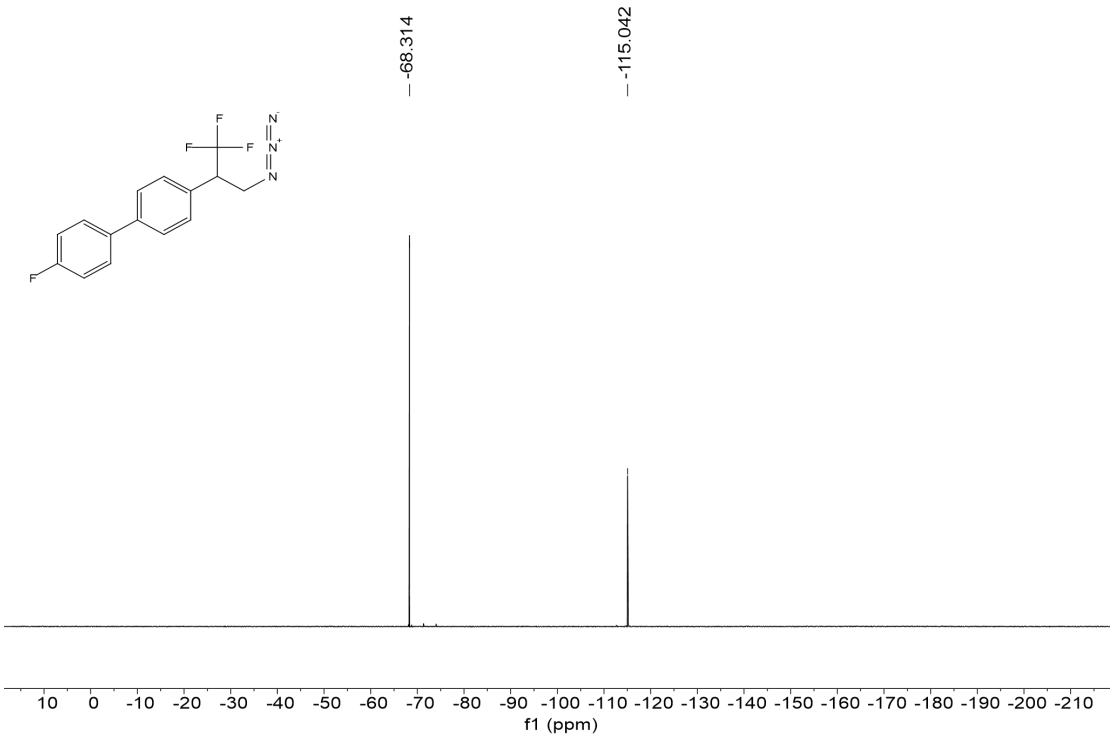

159.431
141.814
141.660
137.764
131.100
131.084
129.802
129.739
129.259
127.717
126.951
124.164
121.374
119.484
115.221
113.602
113.483
77.318
77.000
76.682
67.195
50.215
50.191
50.141
49.875
49.609
49.342
30.097
28.427
F
F
F
N
N
N
O
H2C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-68.283
F
F
F
N
N
N
O
H2C
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)

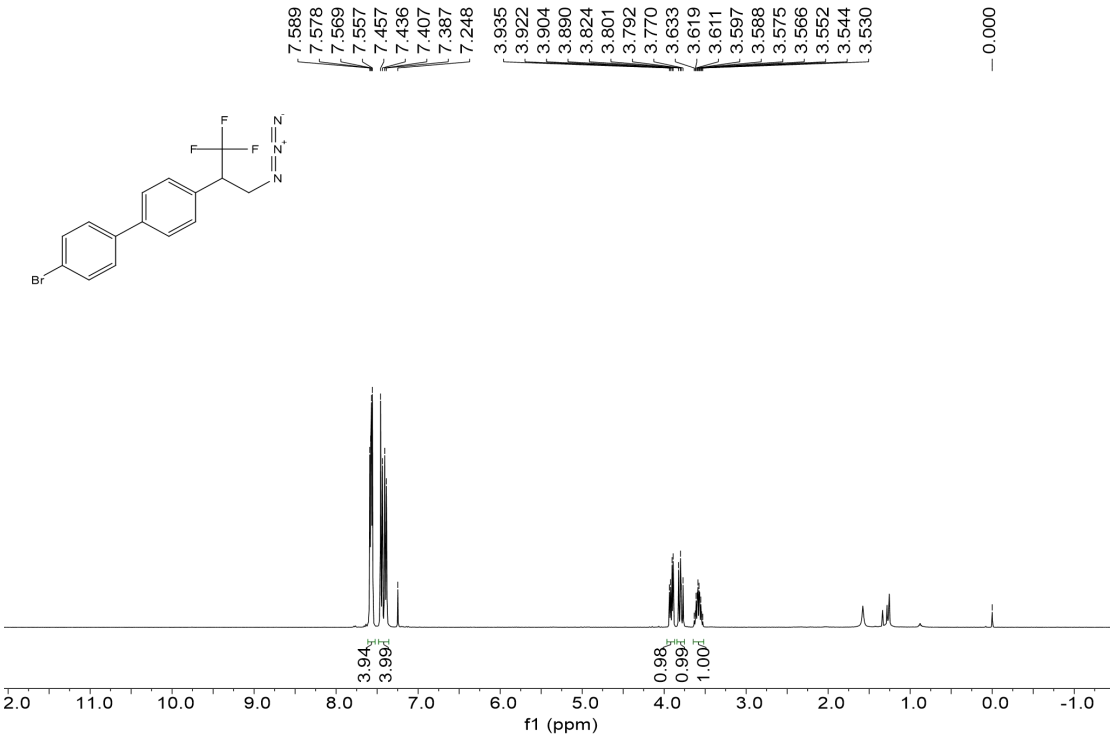
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **10**

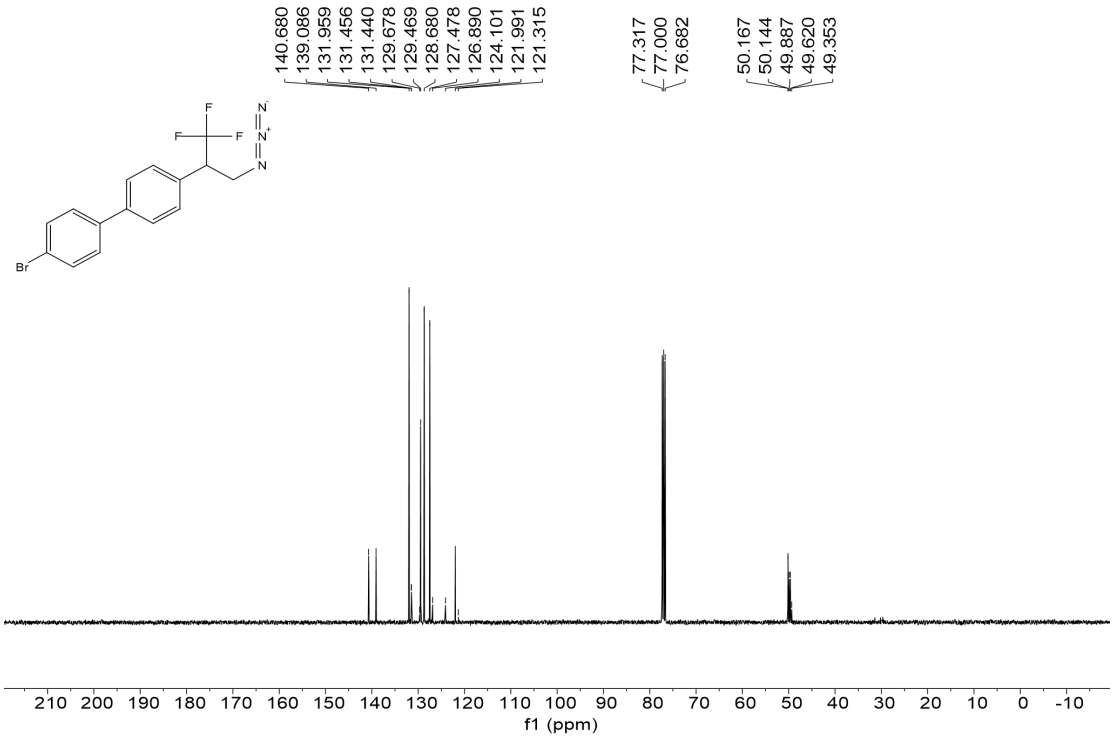


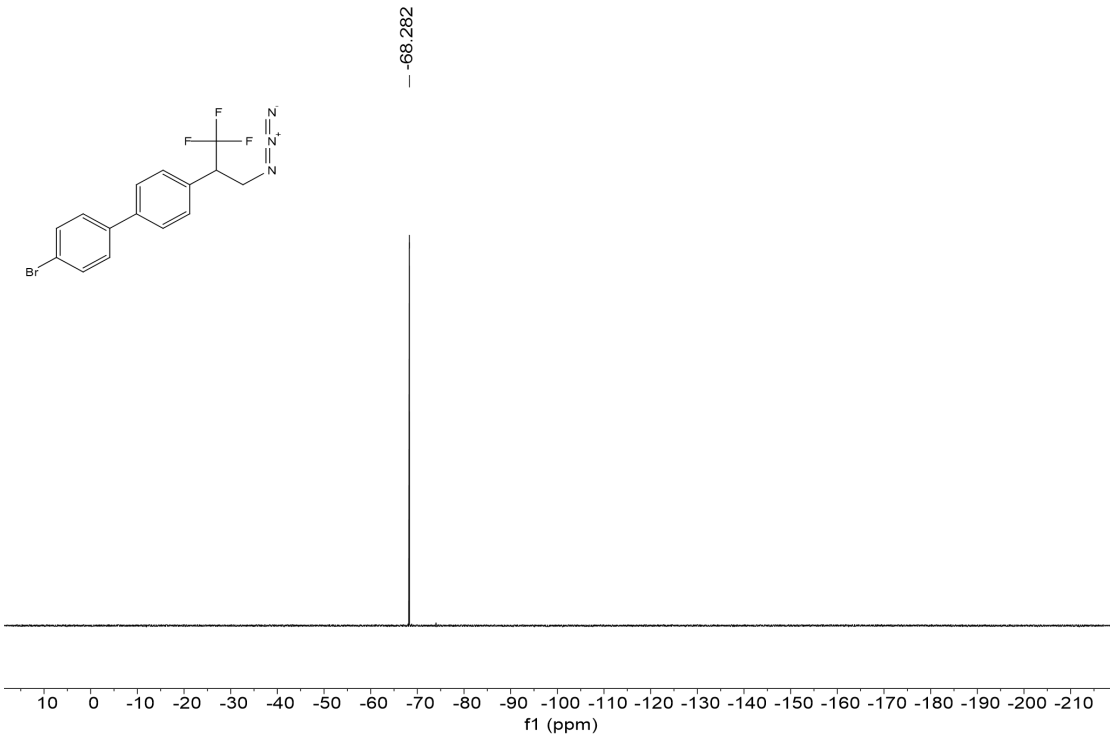




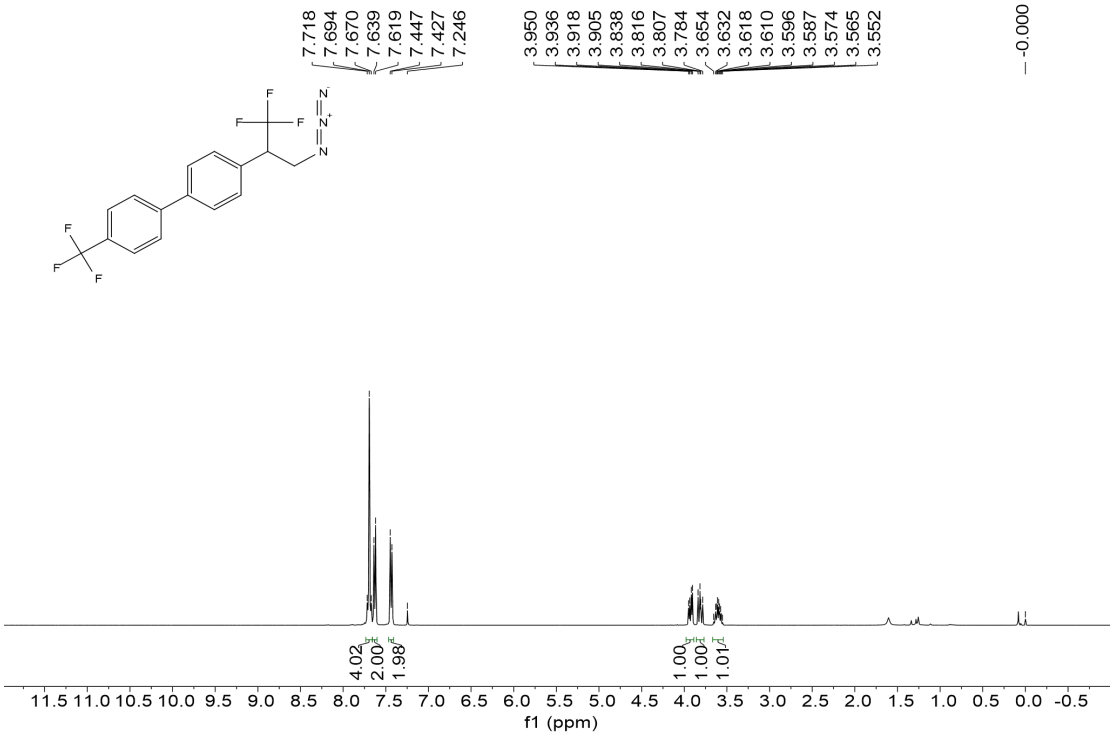
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **11**

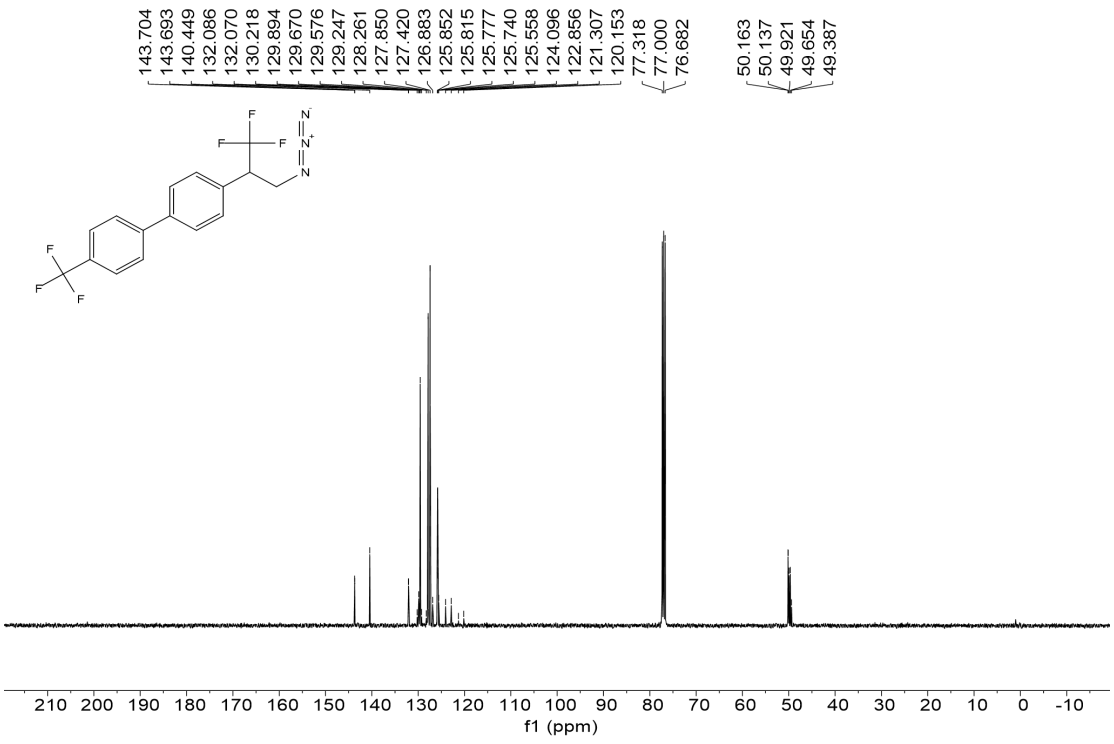


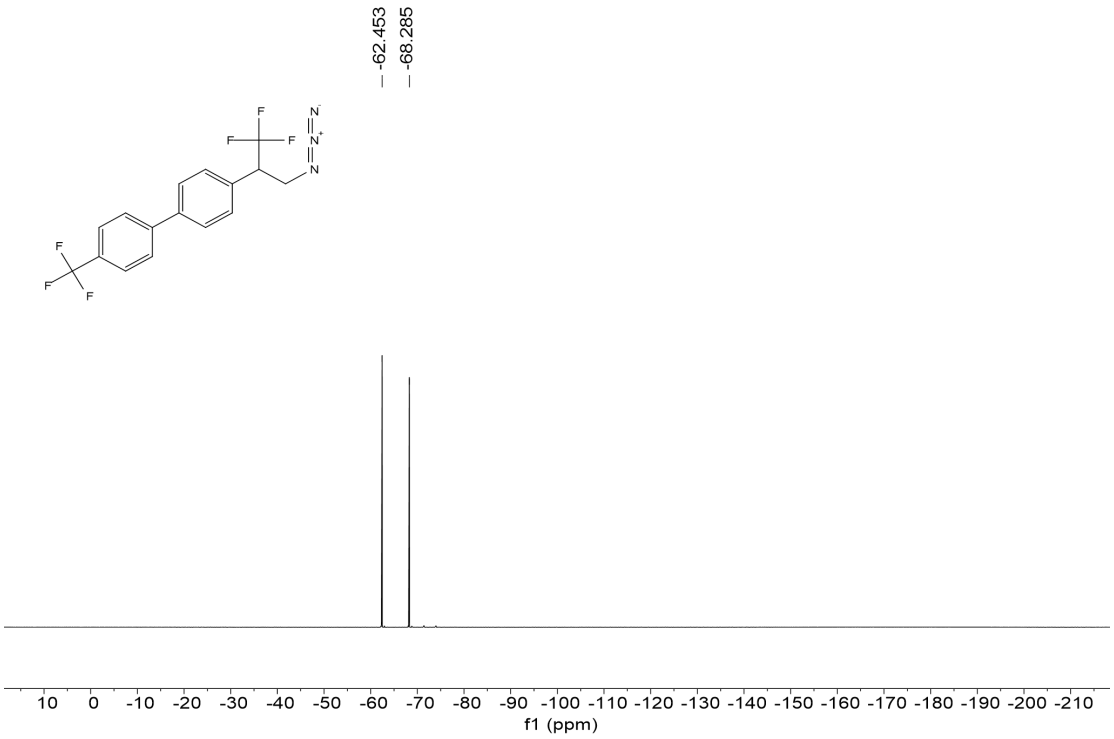

140.680
139.086
131.959
131.456
131.440
129.678
129.469
128.680
127.478
126.890
124.101
121.991
121.315
77.317
77.000
76.682
50.167
50.144
49.887
49.620
49.353
F
F
F
N
N
N
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-68.282
F
F
F
N
N
N
Br
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)

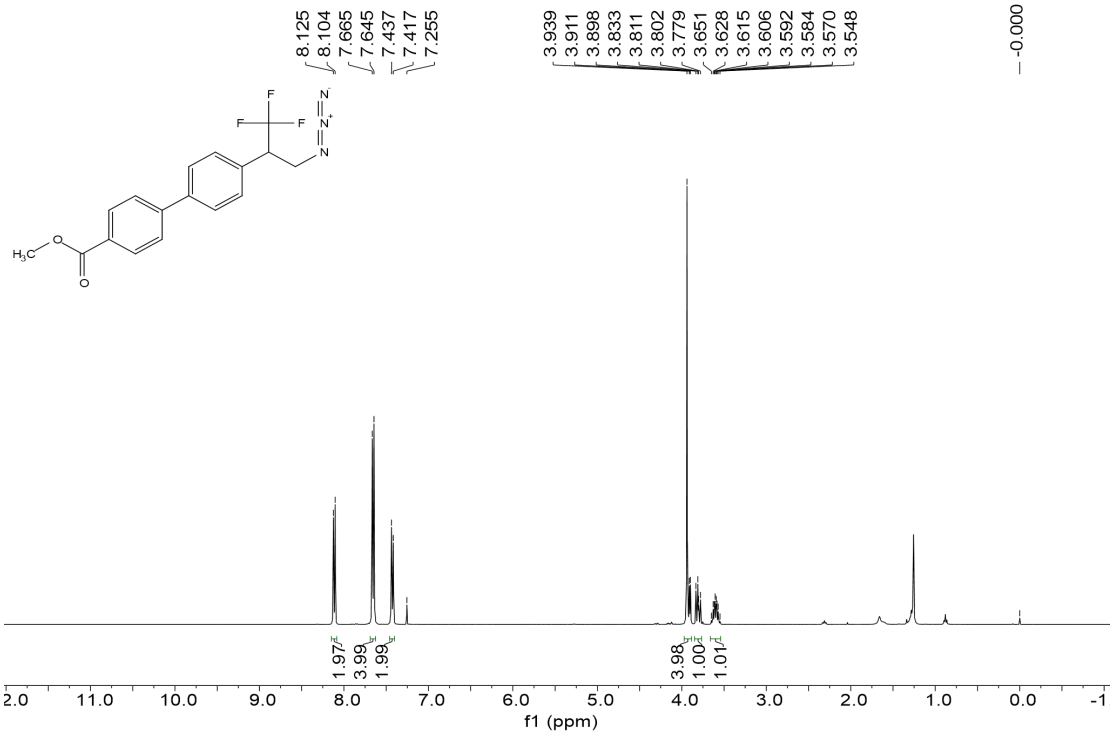
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **12**

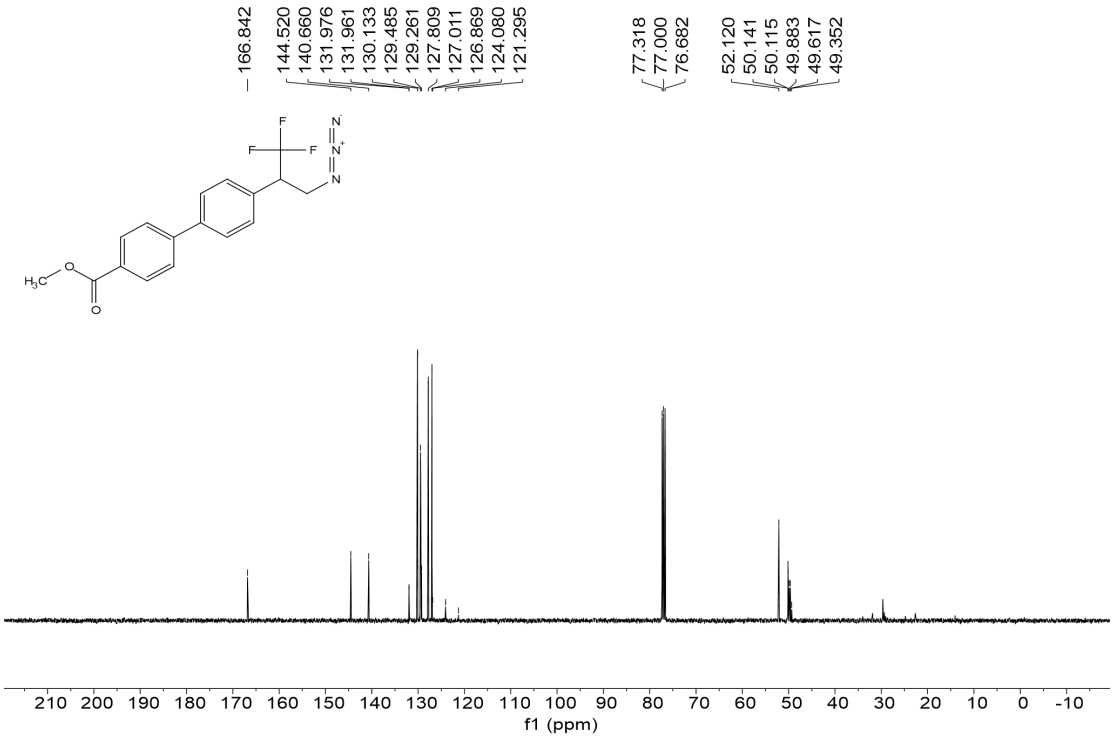






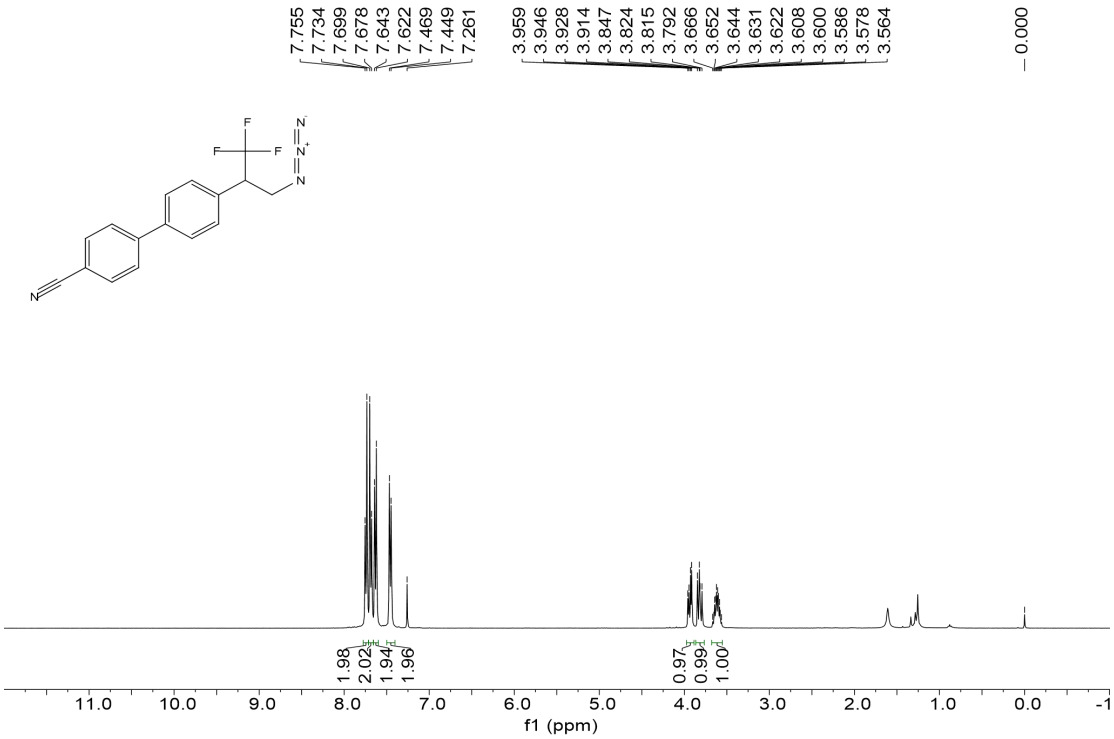
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **13**

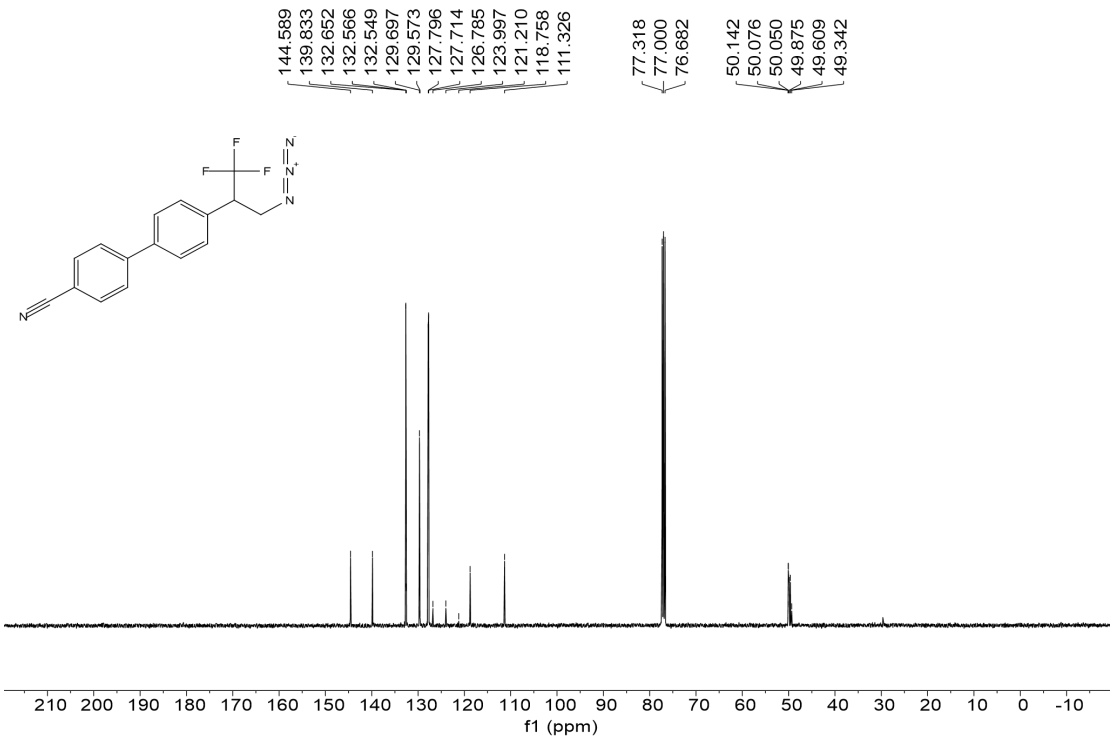


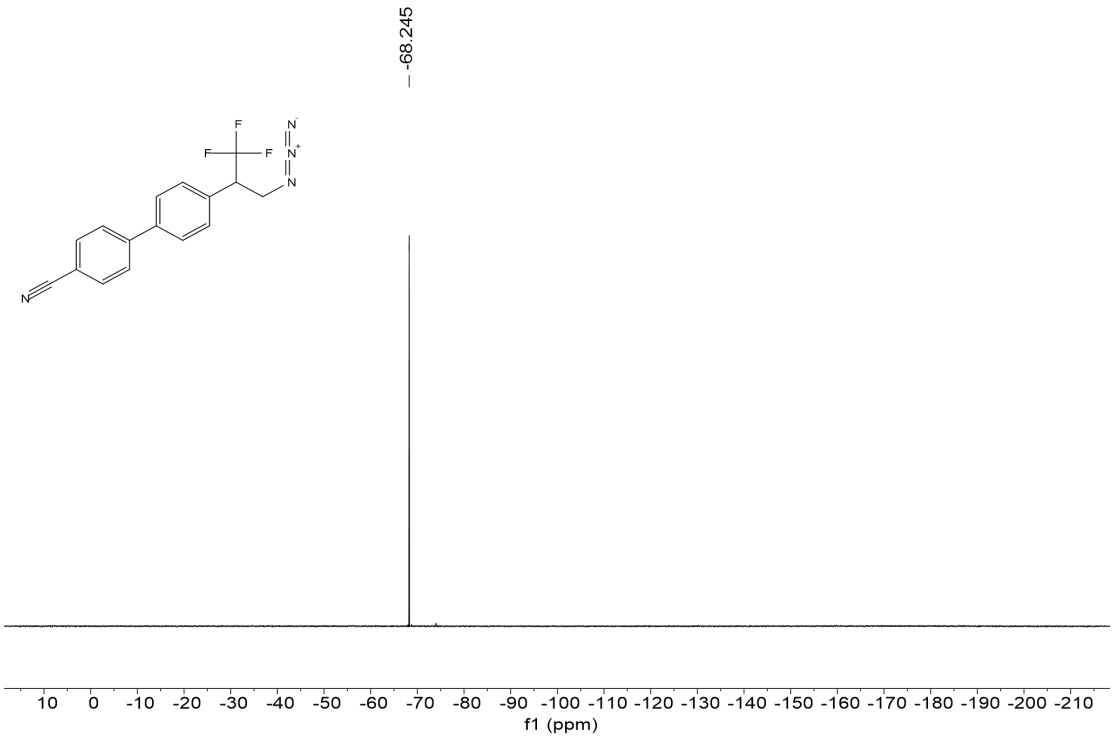

166.842
144.520
140.660
131.976
131.961
130.133
129.485
129.261
127.809
127.011
126.869
124.080
121.295
77.318
77.000
76.682
52.120
50.141
50.115
49.883
49.617
49.352
F
F
F
N
N
N
O
O
H3C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-68.269
F
F
F
N
N
N
O
O
H3C
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)

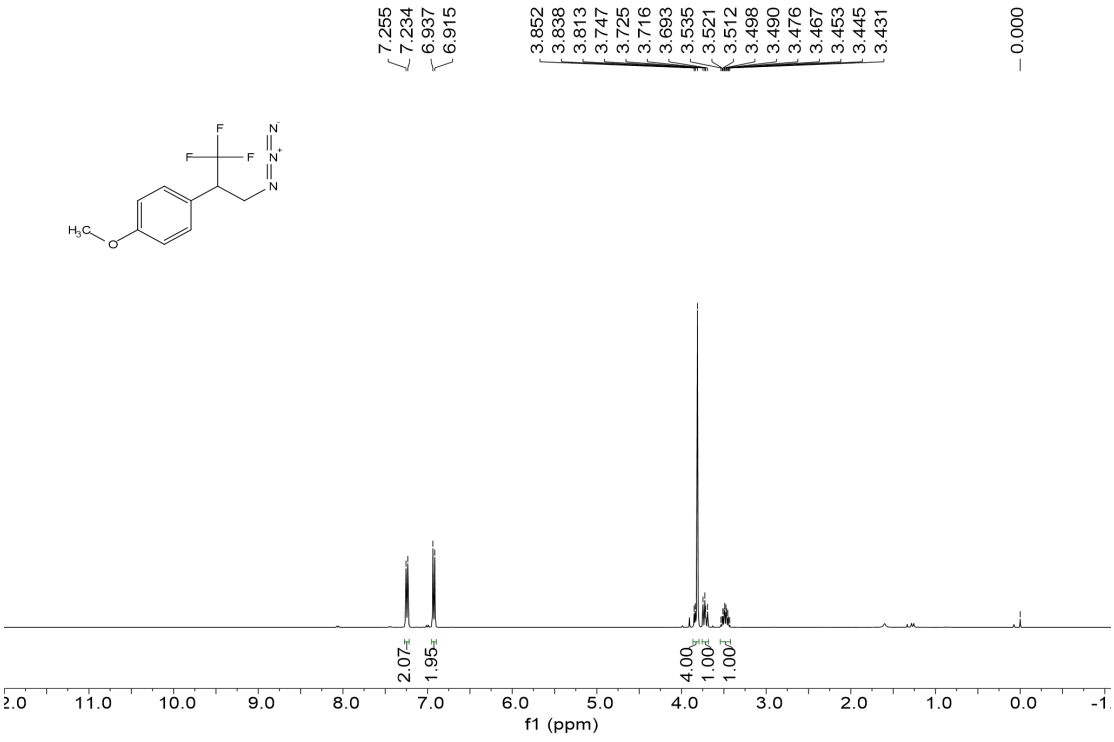
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **14**

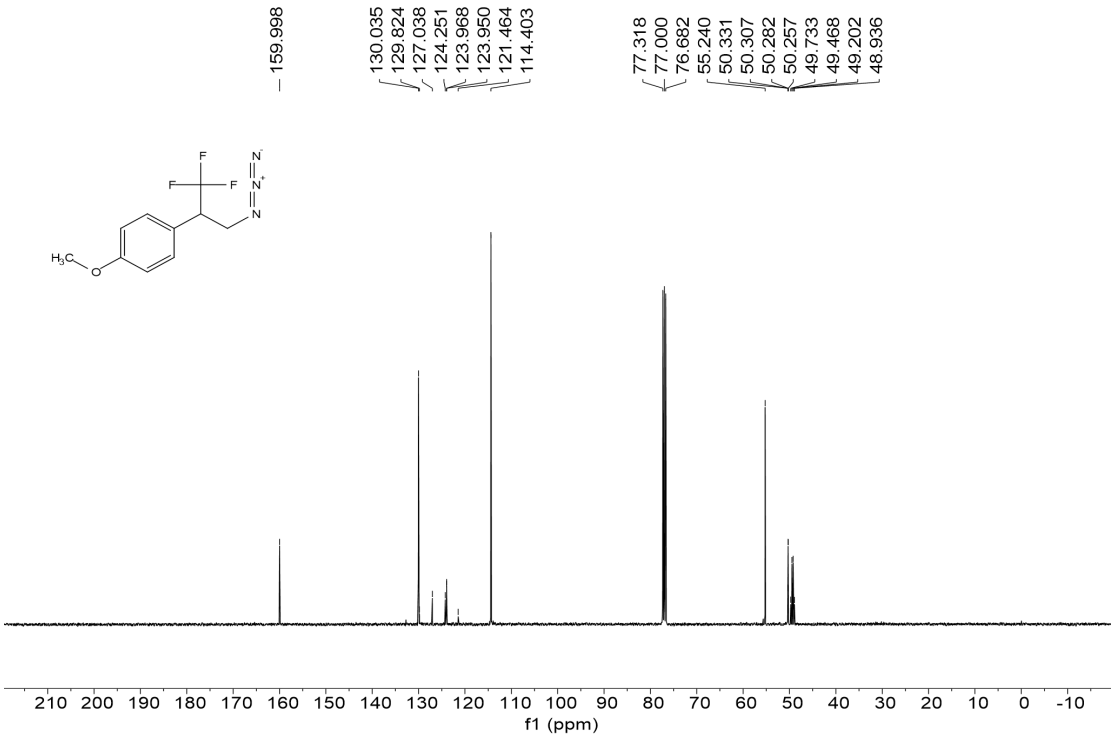


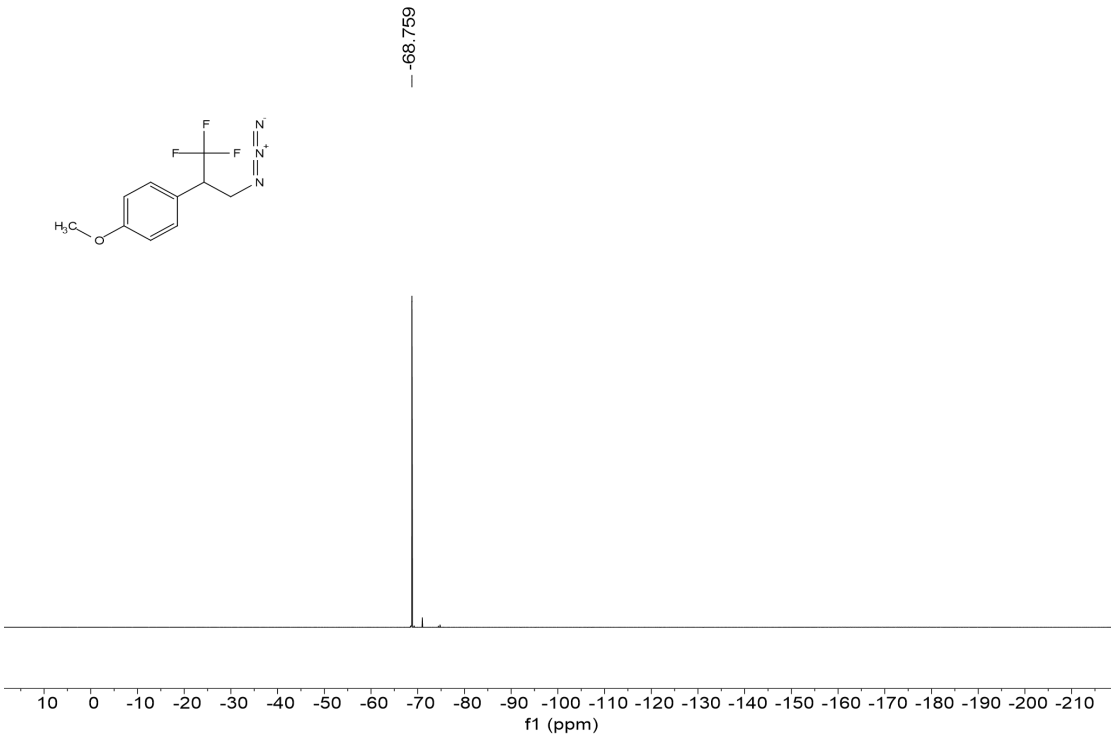




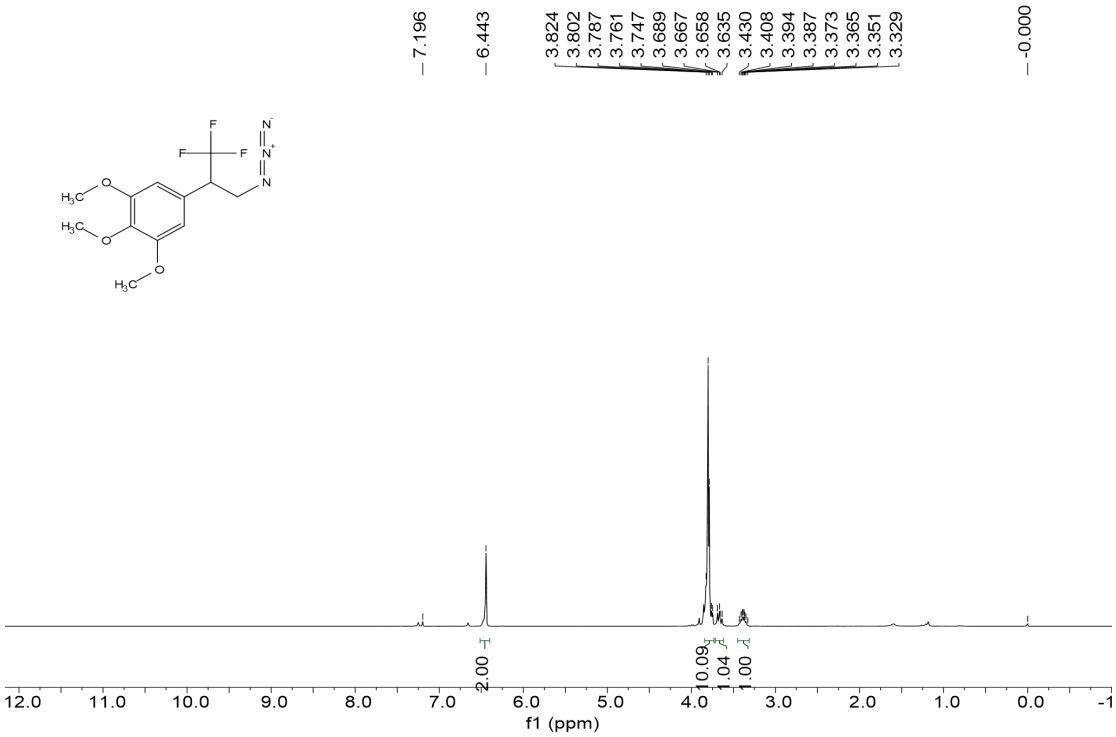
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **15**

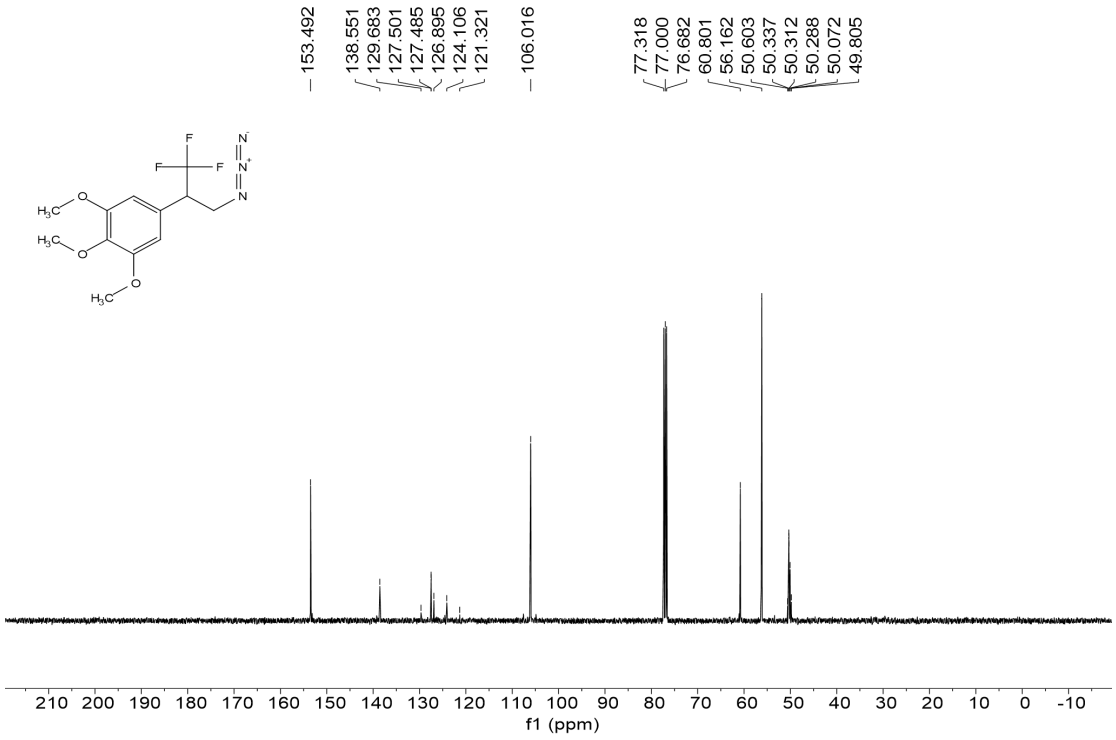


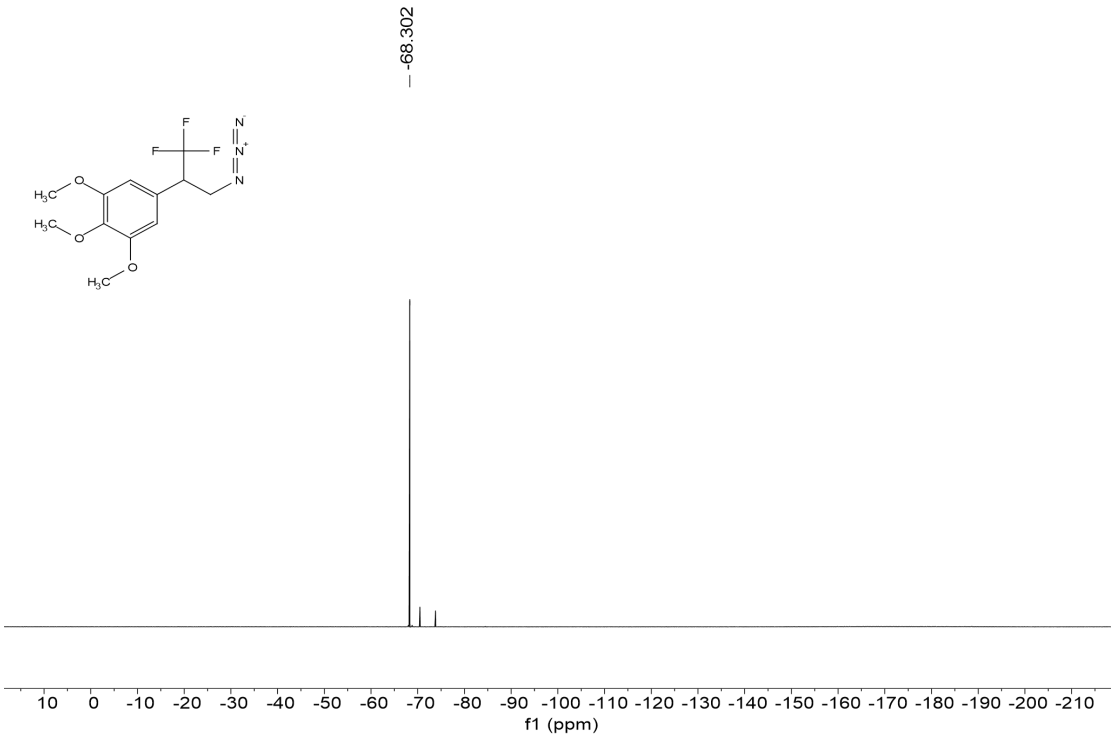

159.998
130.035
129.824
127.038
124.251
123.968
123.950
121.464
114.403
77.318
77.000
76.682
55.240
50.331
50.307
50.282
50.257
49.733
49.468
49.202
48.936
F
F
F
N
N
N
H3C
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-68.759
F
F
F
N
N
N
H3C
O
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)

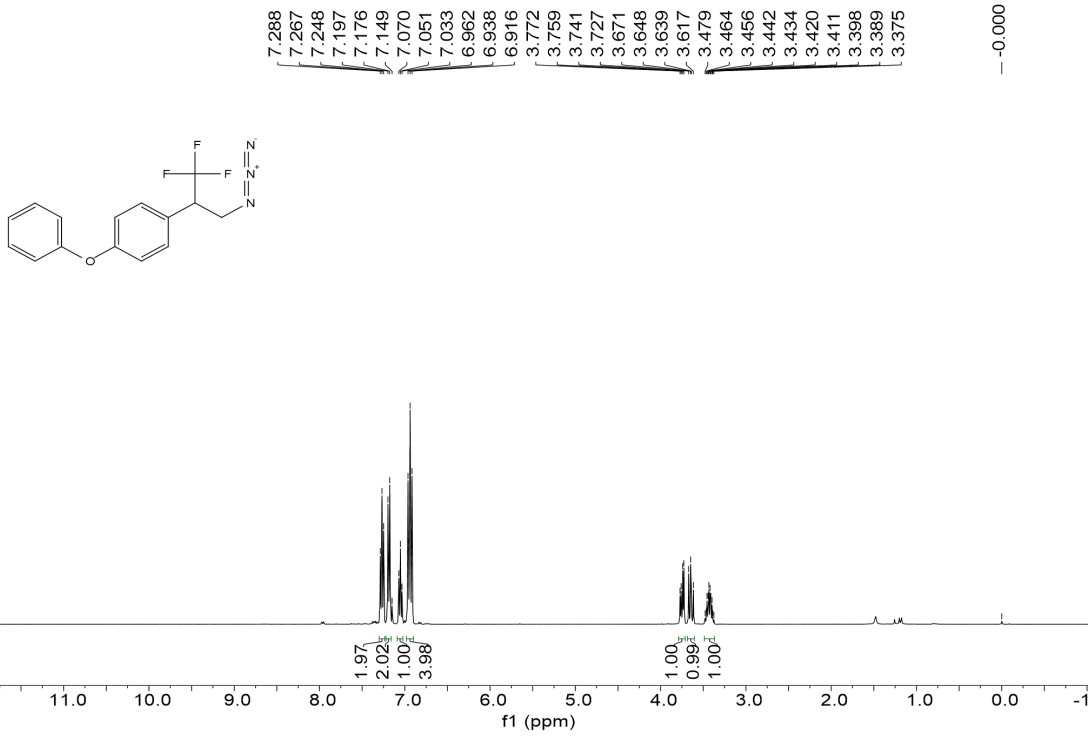
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **16**

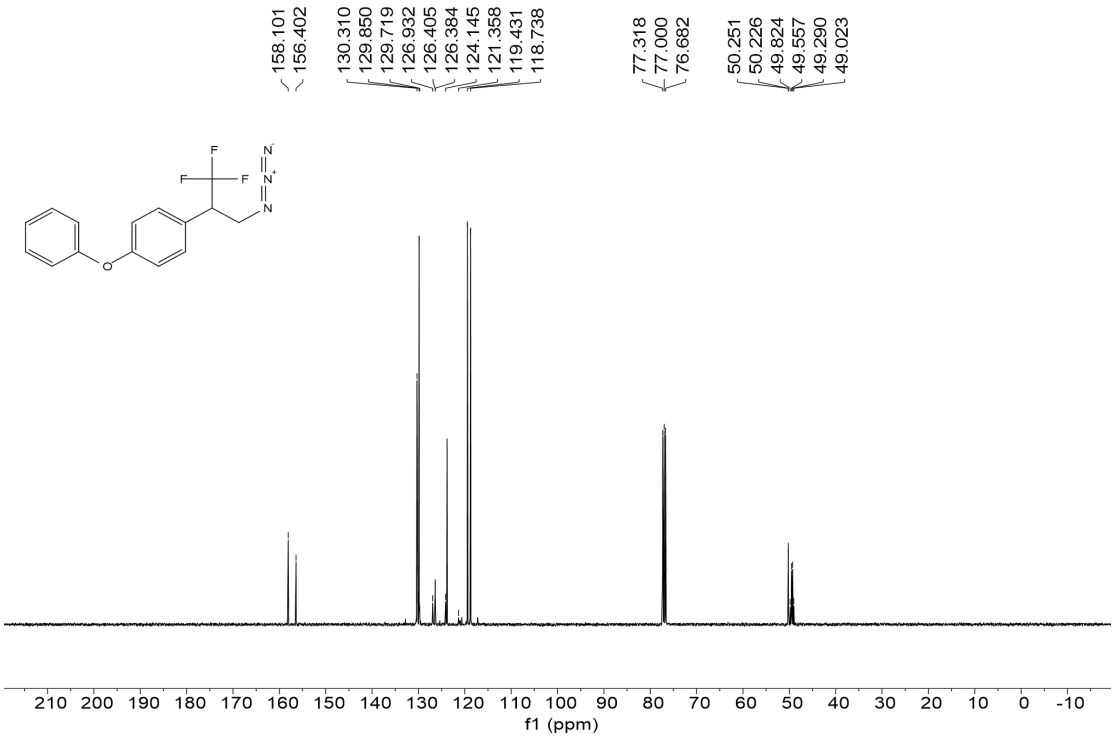


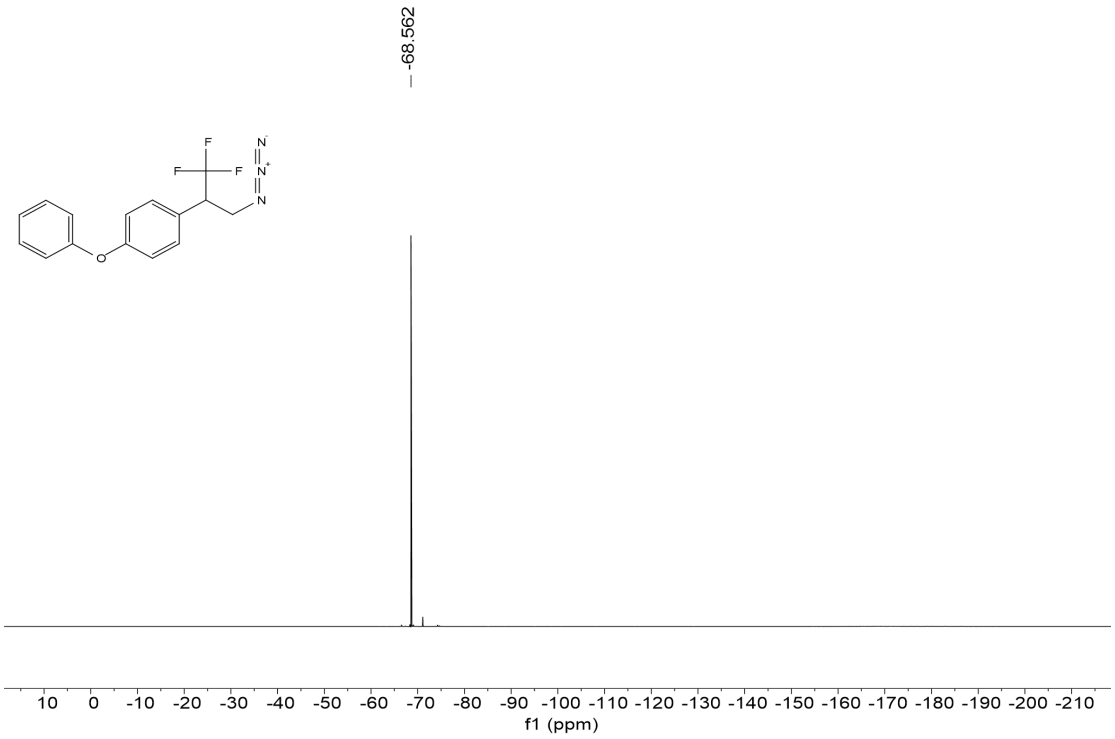




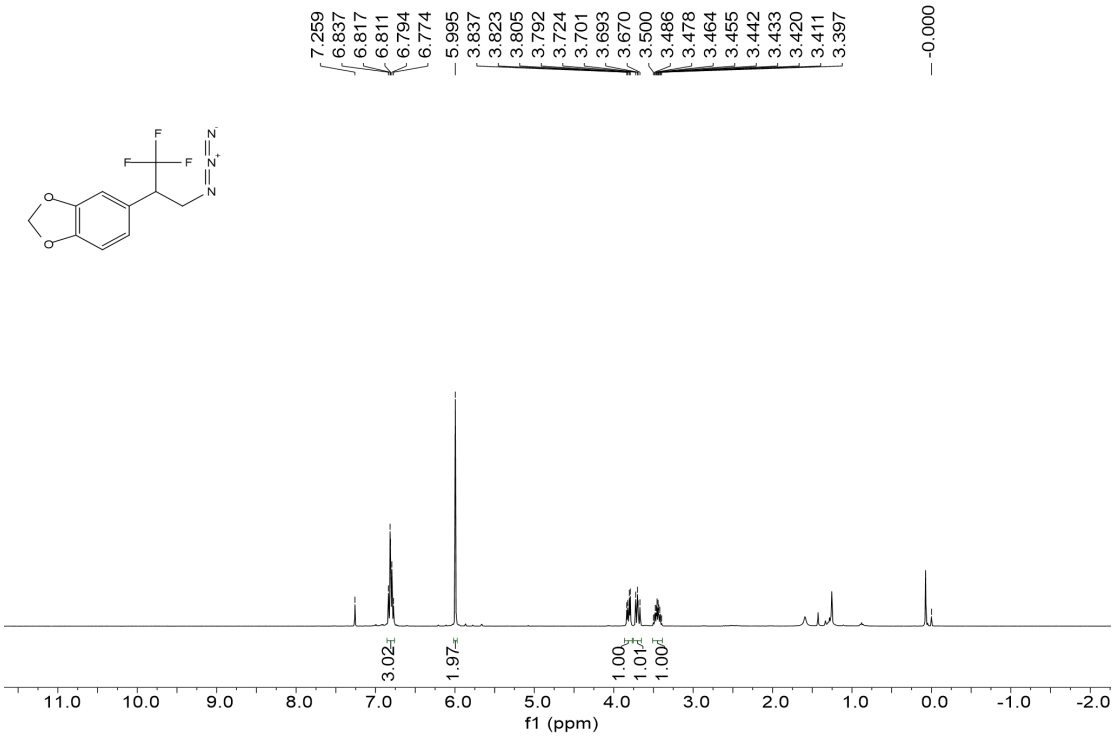
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **17**

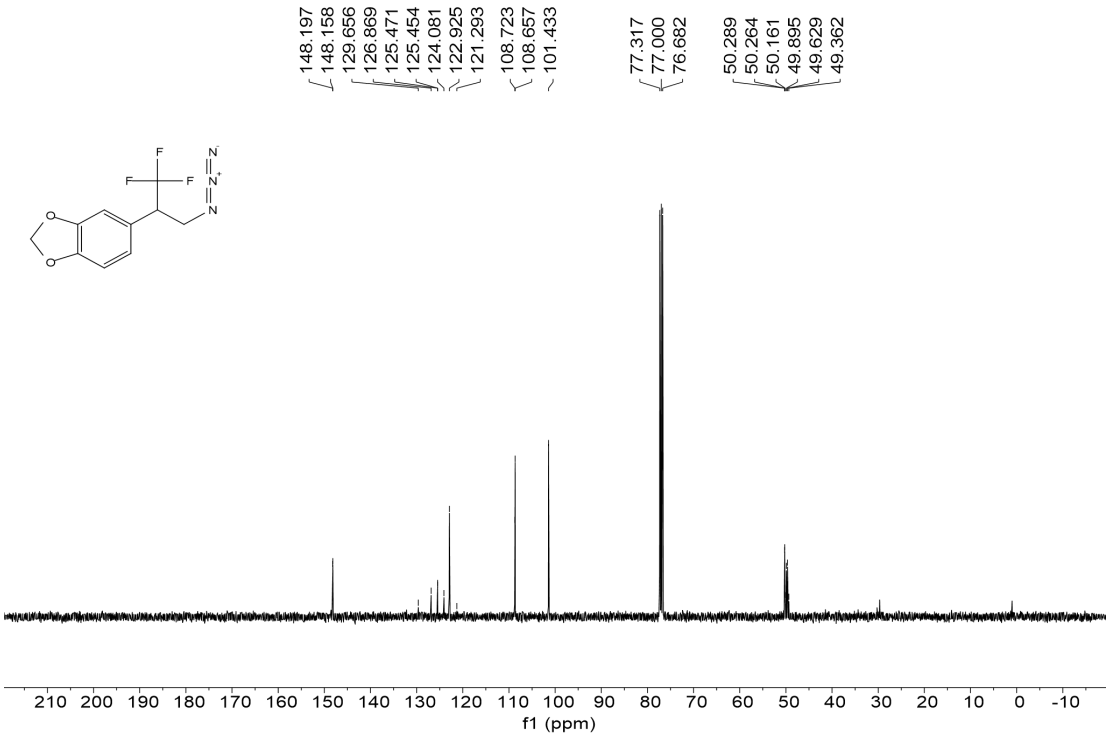


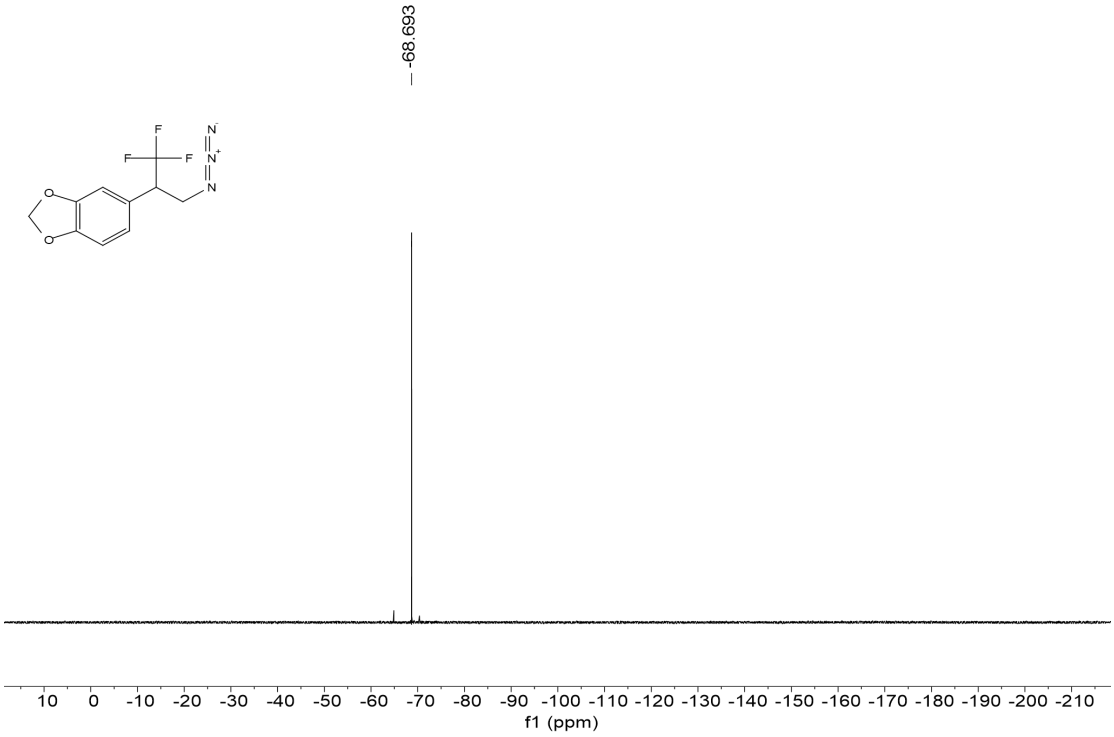

158.101
156.402
130.310
129.850
129.719
126.932
126.405
126.384
124.145
121.358
119.431
118.738
77.318
77.000
76.682
50.251
50.226
49.824
49.557
49.290
49.023
F
F
F
N
N
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-68.562
F
F
F
N
N
N
O
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)

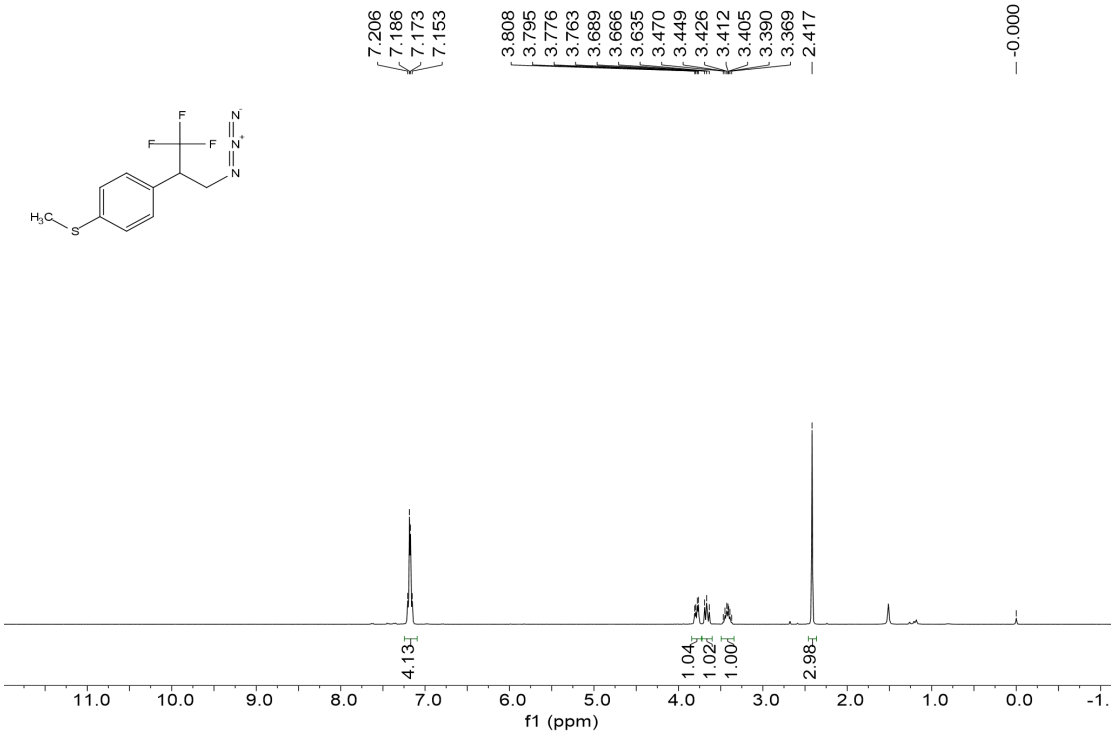
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **18**

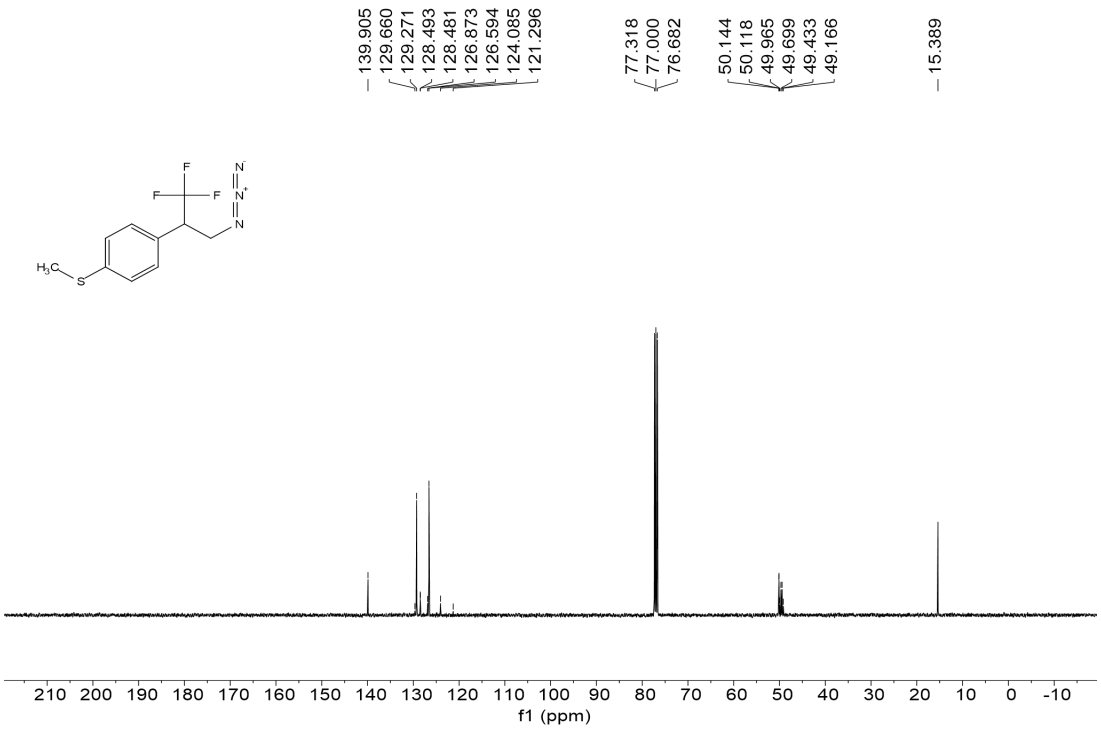


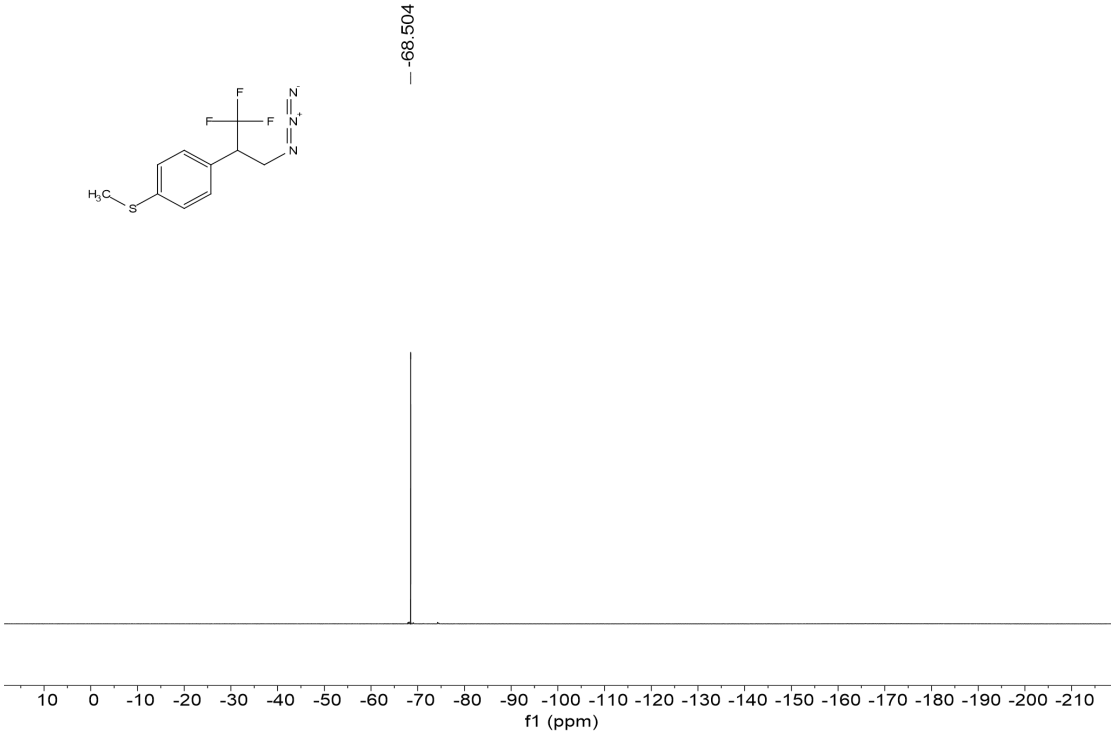




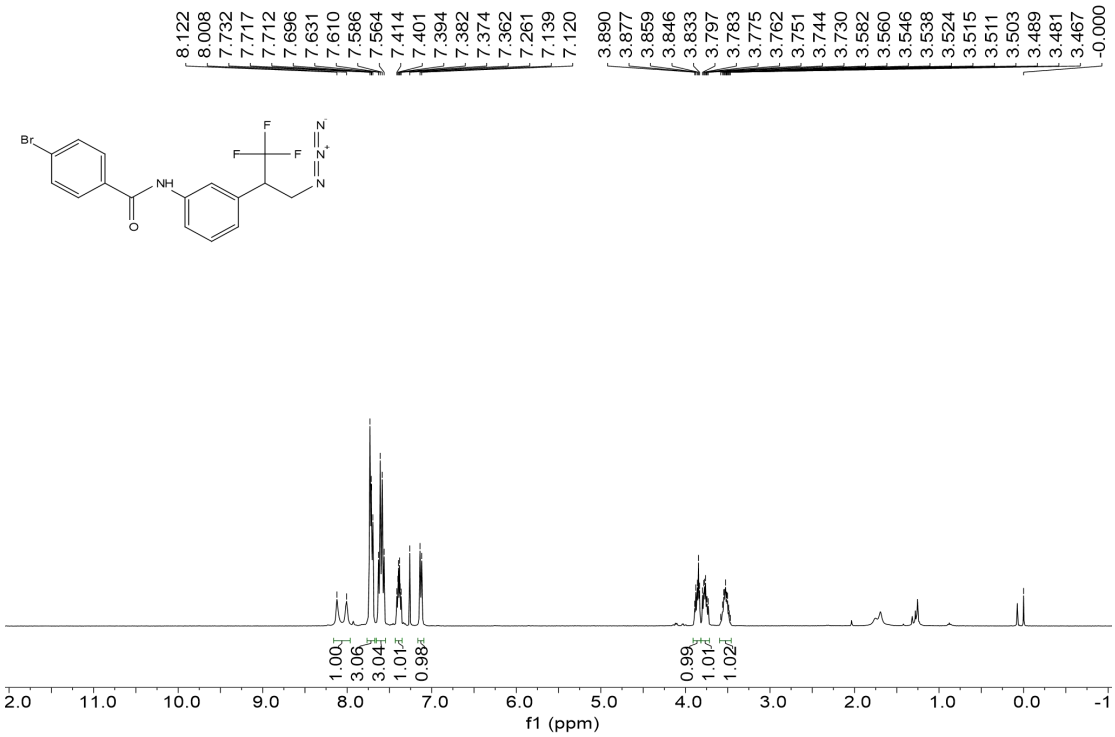
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **19**

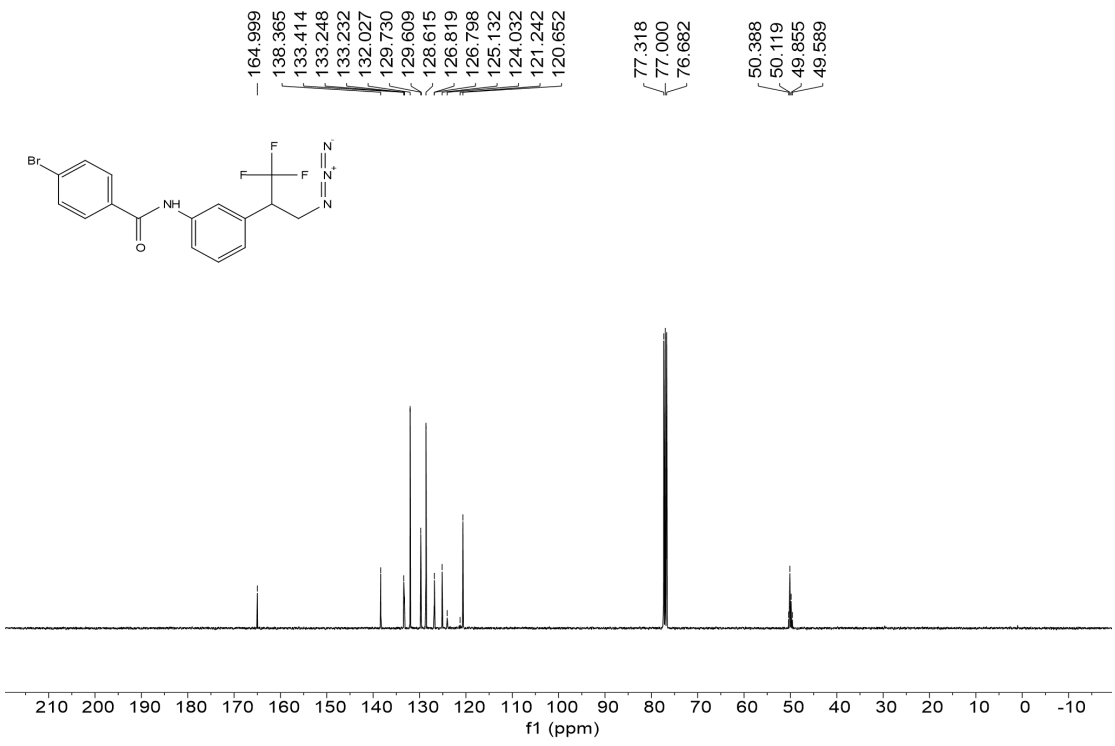


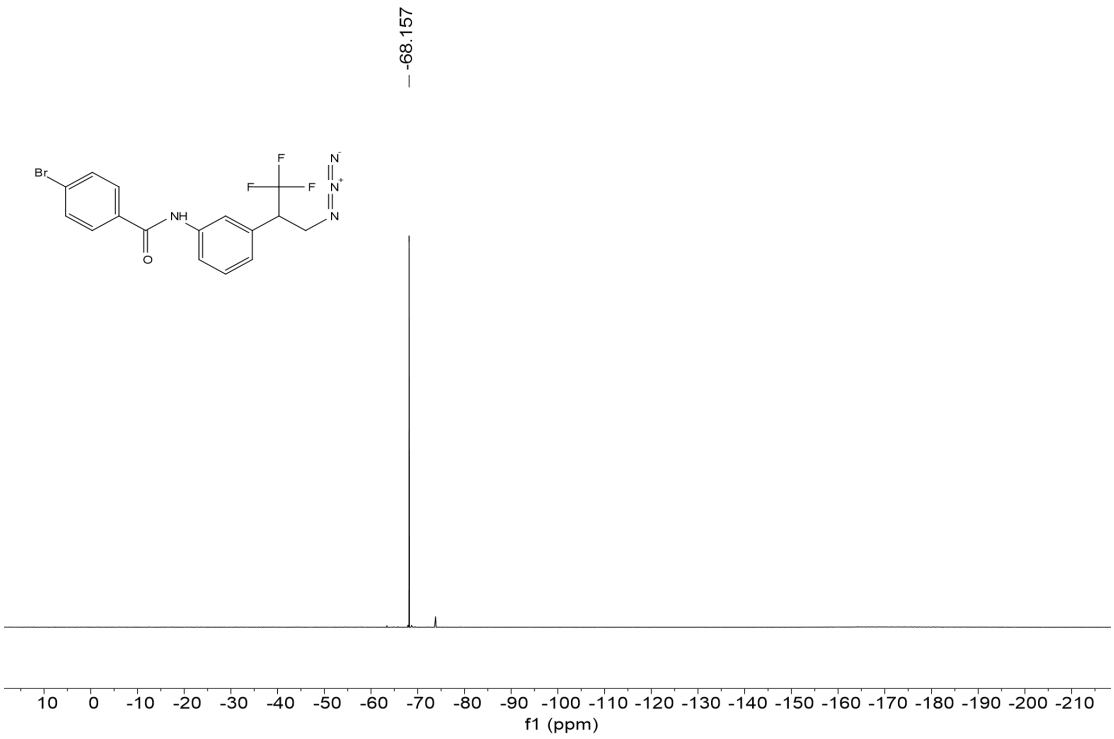

139.905
129.660
129.271
128.493
128.481
126.873
126.594
124.085
121.296
77.318
77.000
76.682
50.144
50.118
49.965
49.699
49.433
49.166
15.389
F
F
F
N
N
N
H3C
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-68.504
F
F
F
N
N
N
H3C
S
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)

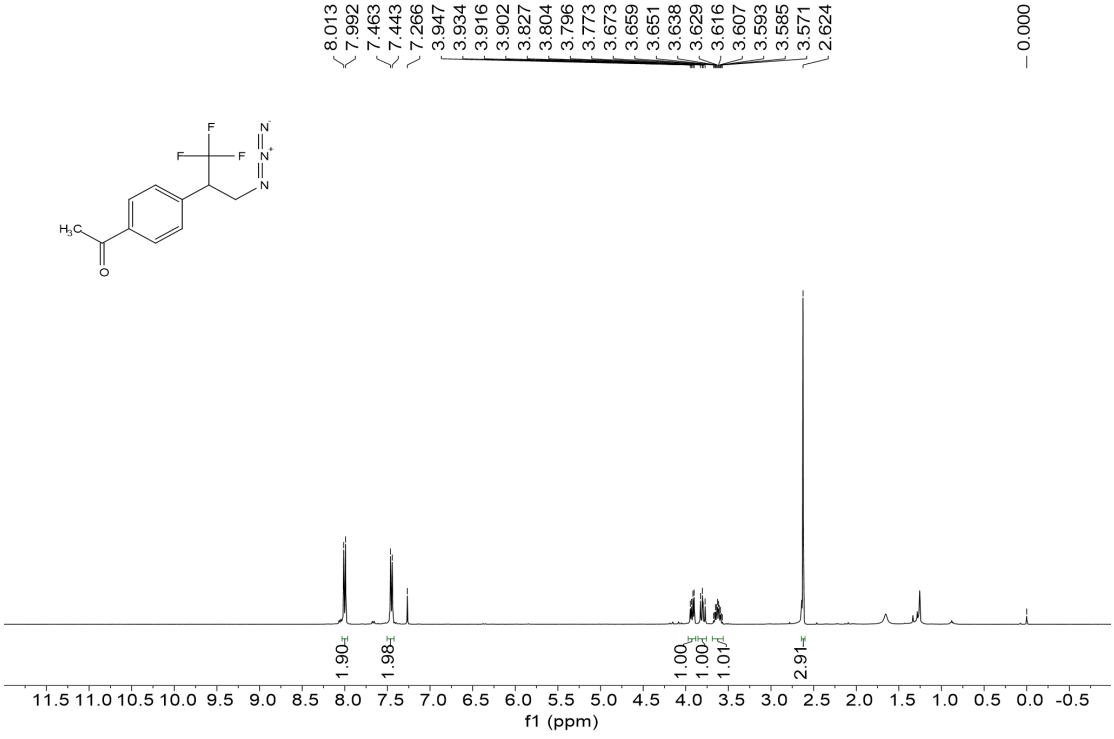
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **20**

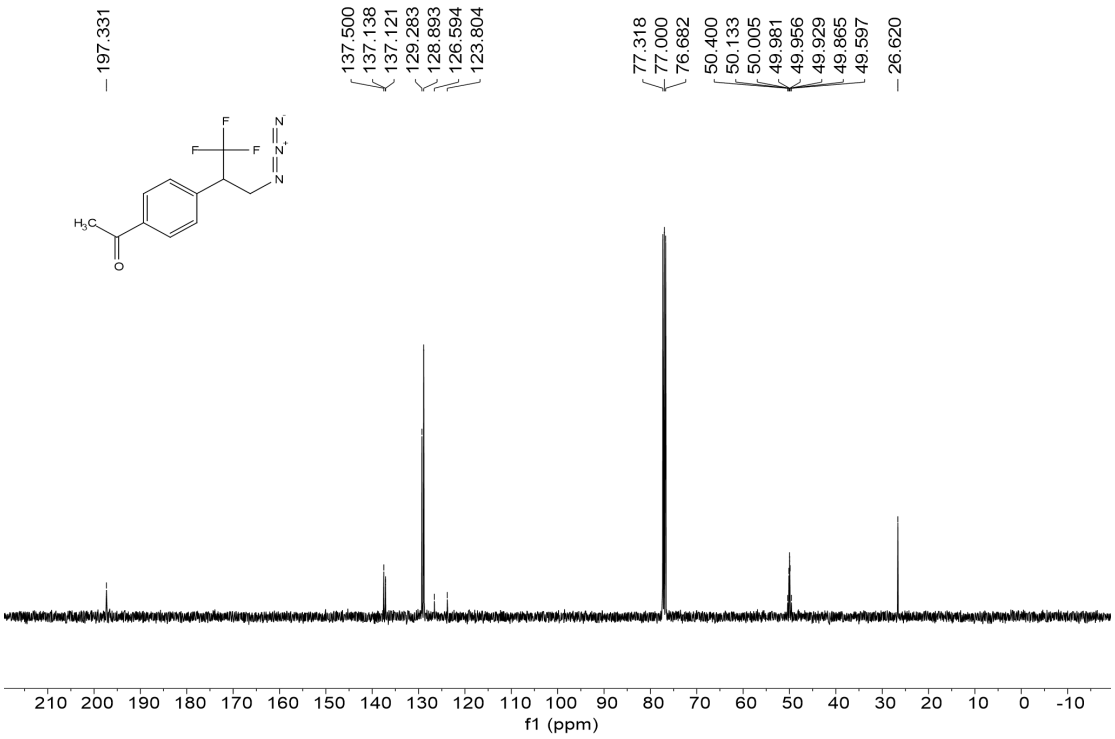


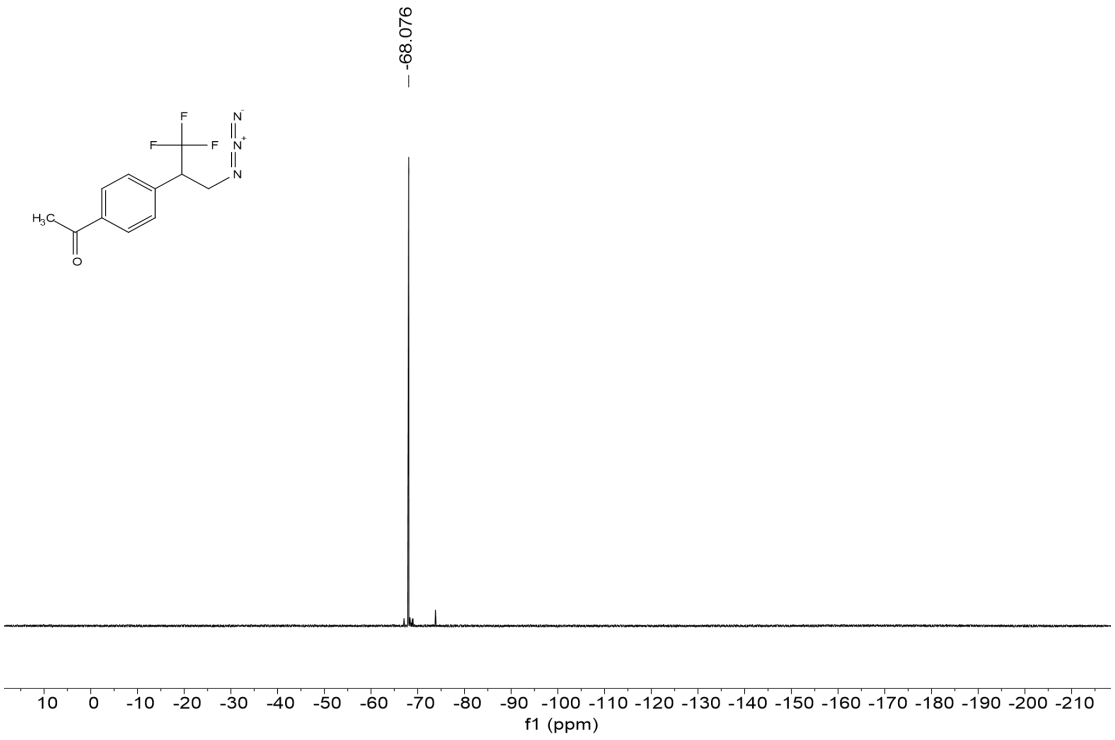




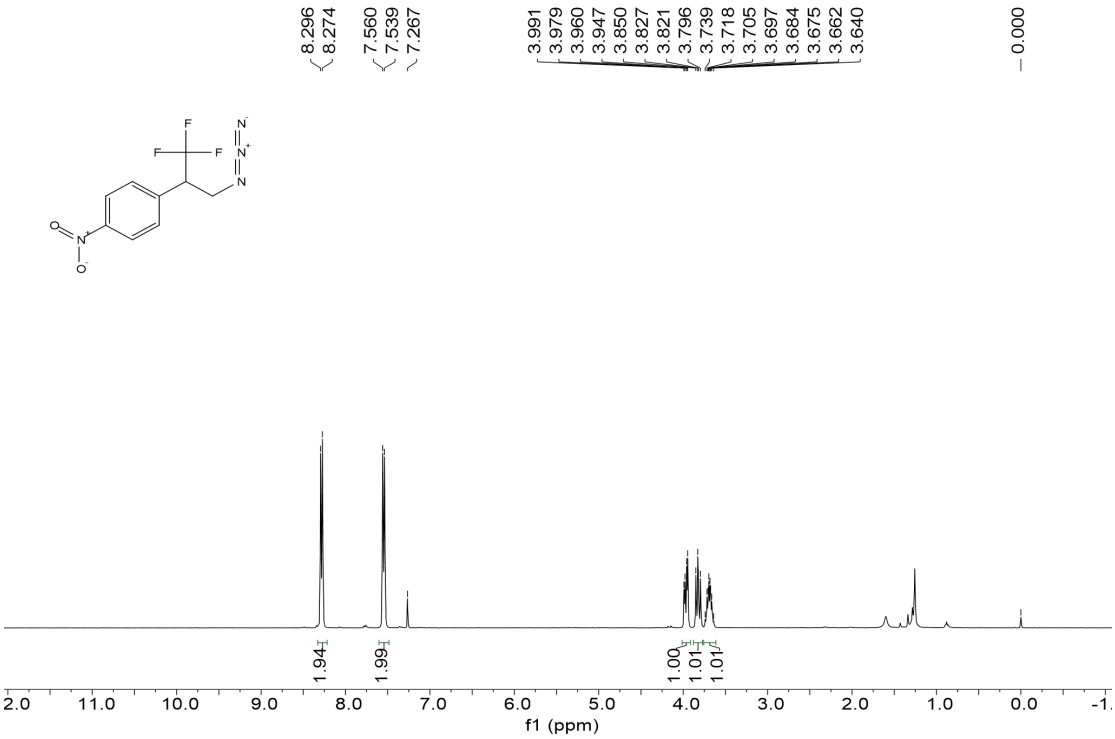
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **21**

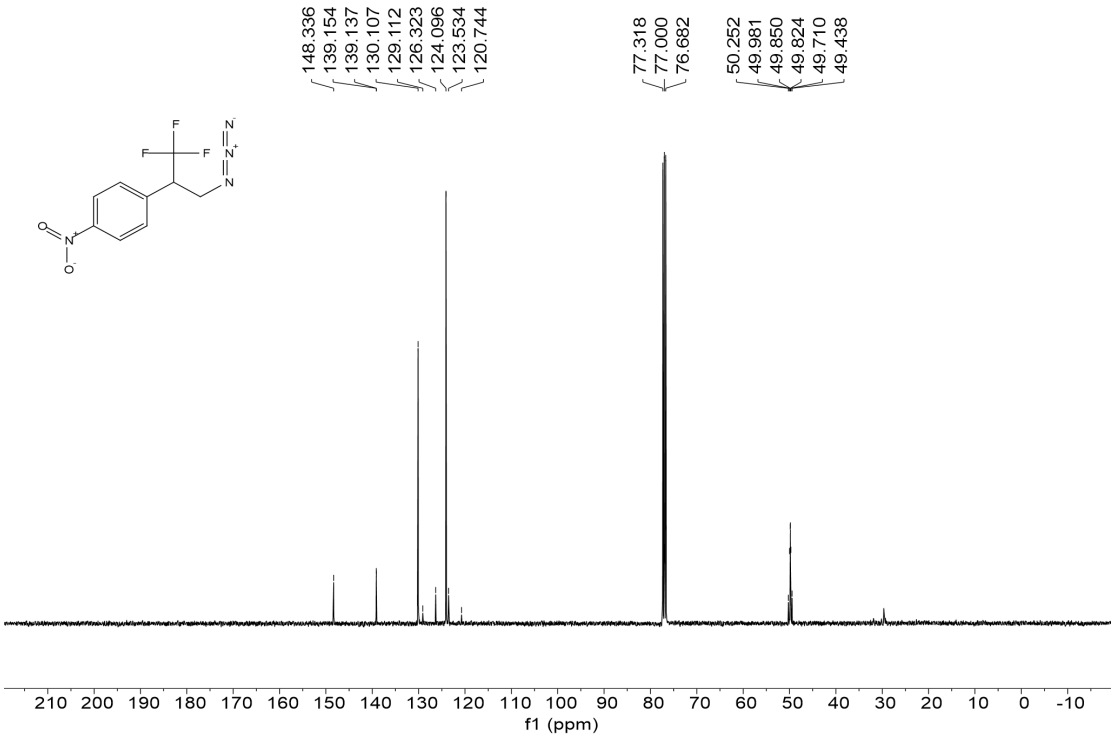


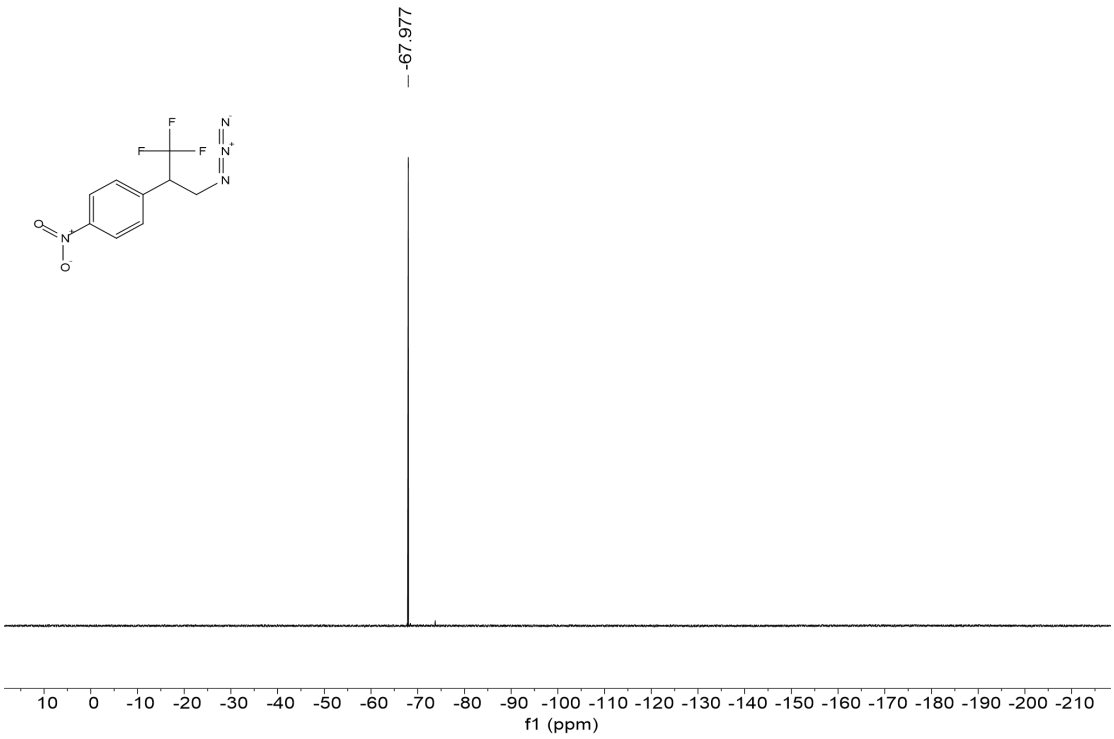

197.331
137.500
137.138
137.121
129.283
128.893
126.594
123.804
77.318
77.000
76.682
50.400
50.133
50.005
49.981
49.956
49.929
49.865
49.597
26.620
F
F
F
N
N
N
H3C
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-68.076
F
F
F
N
N
N
H3C
O
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)

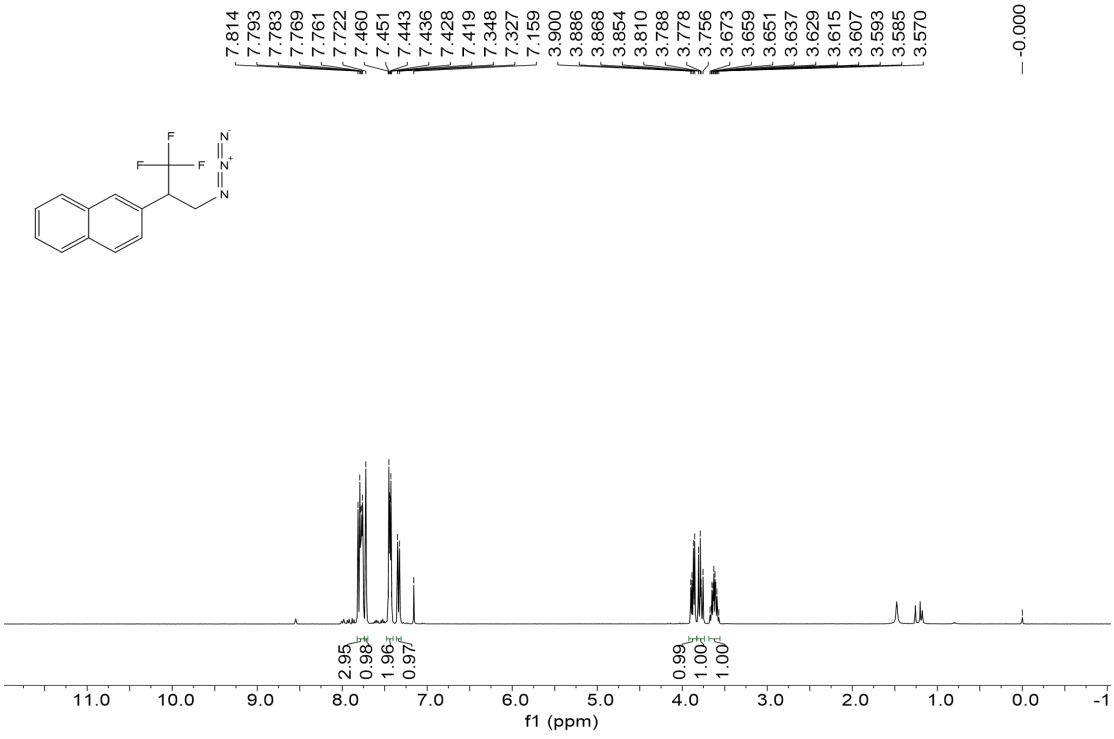
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **22**

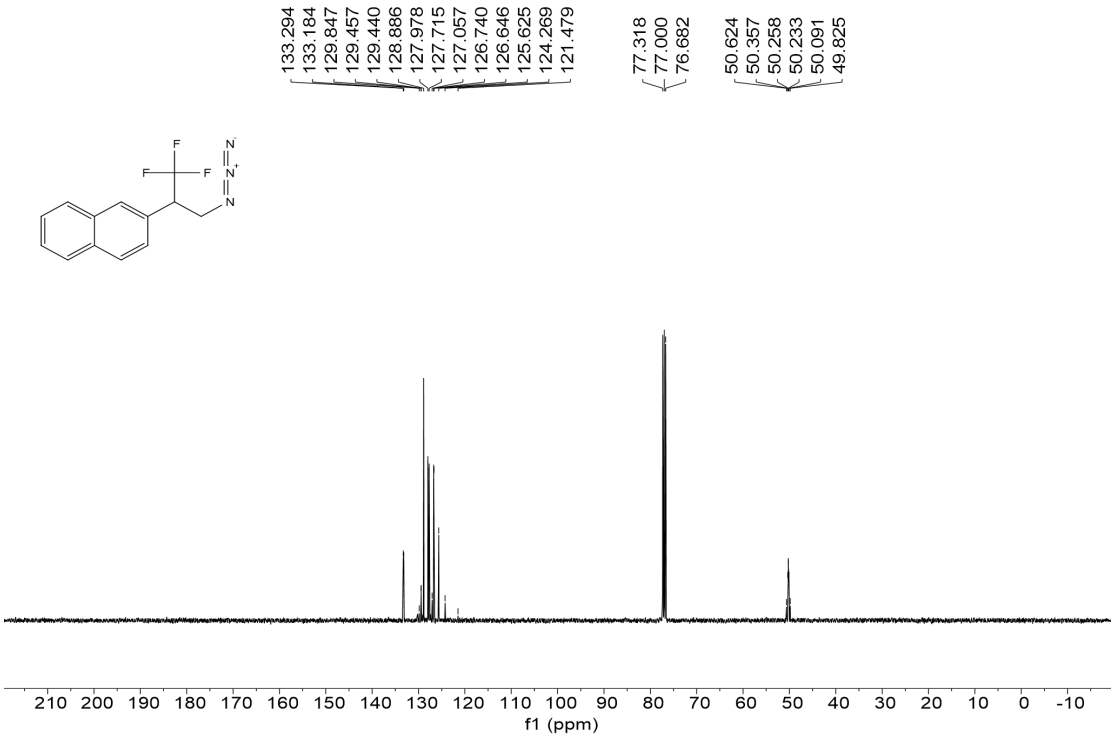


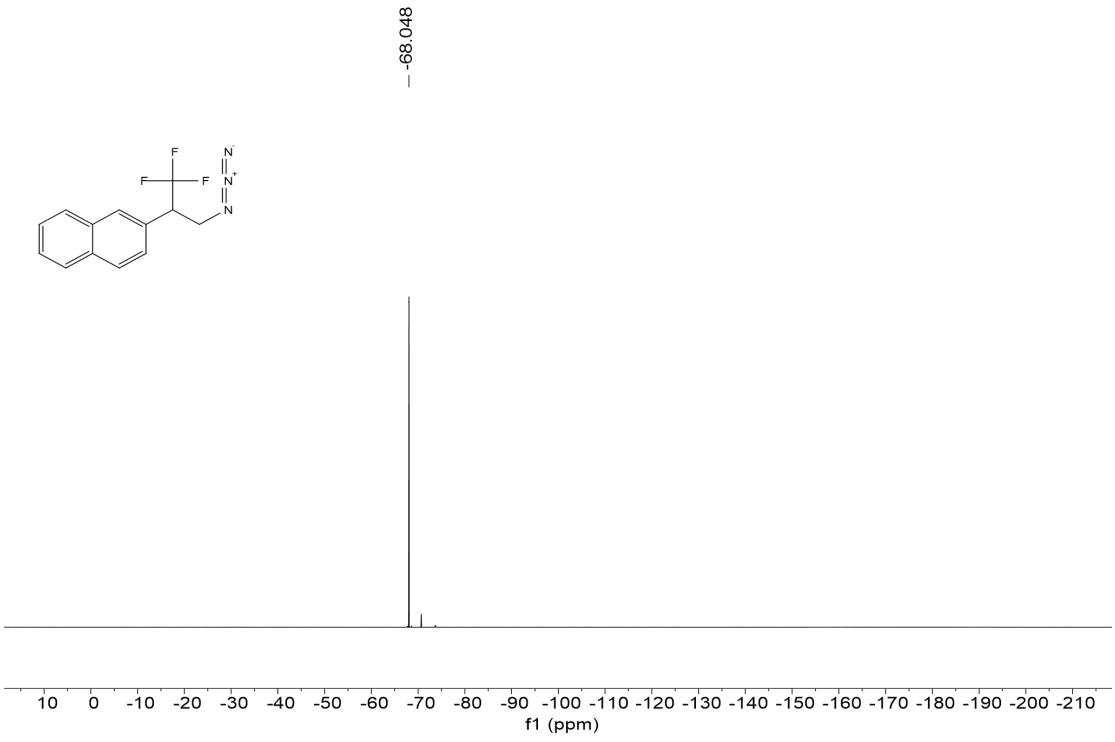




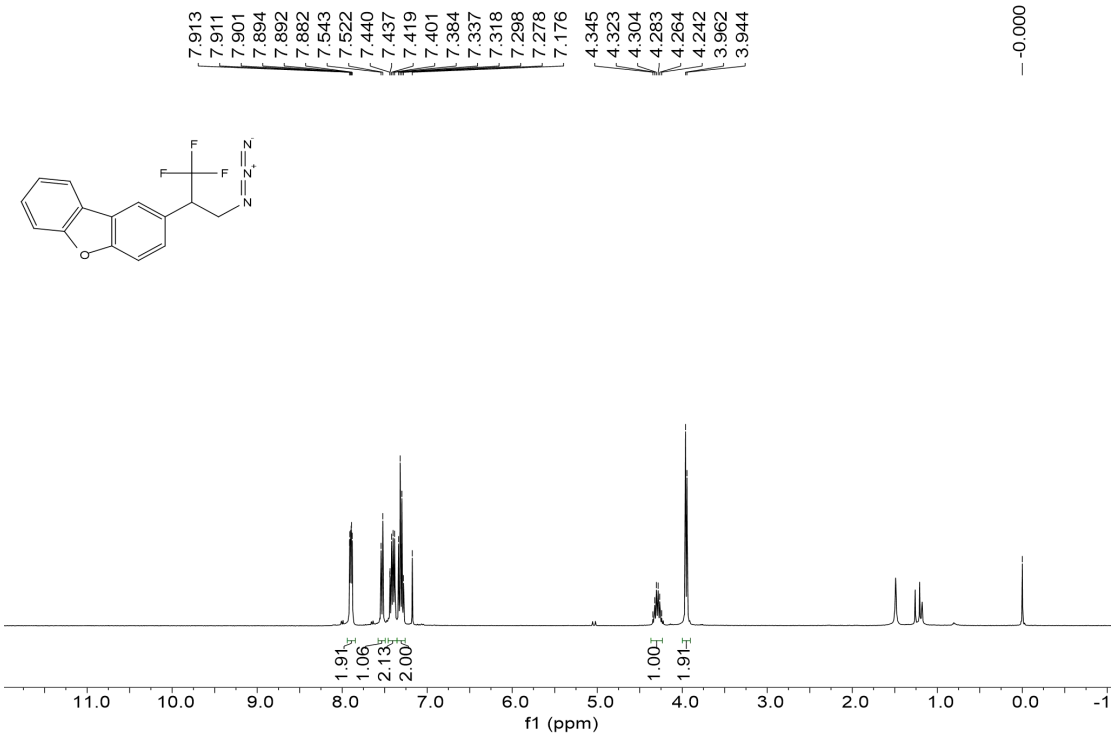
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **23**

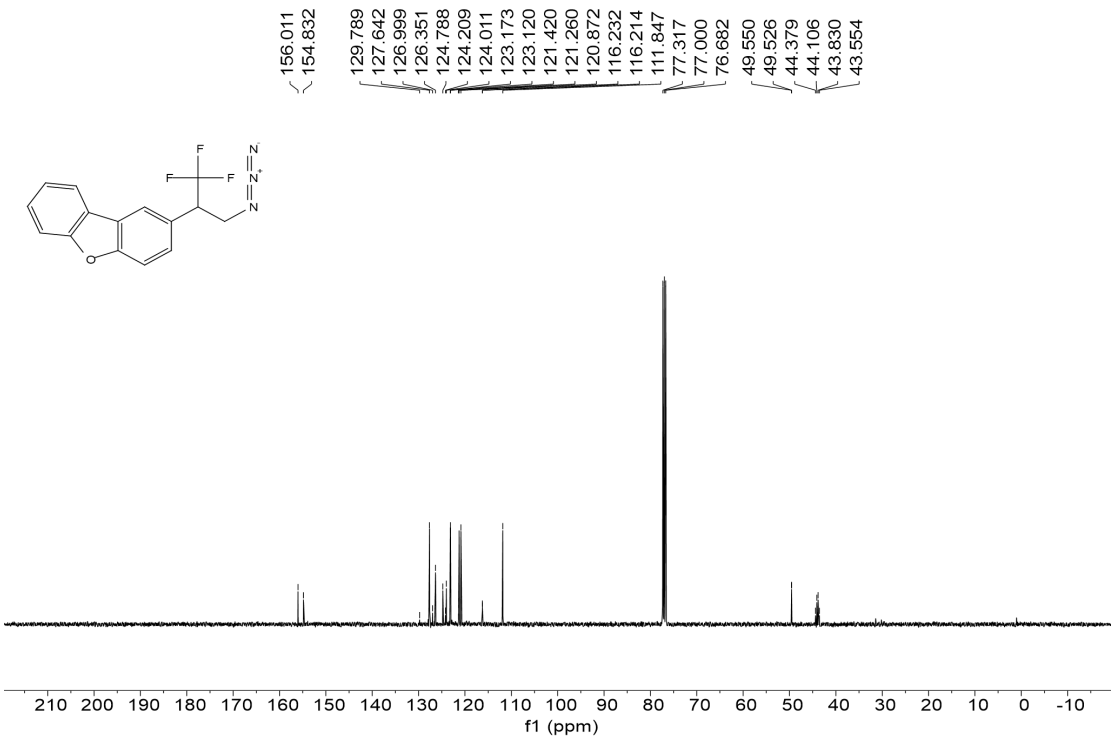


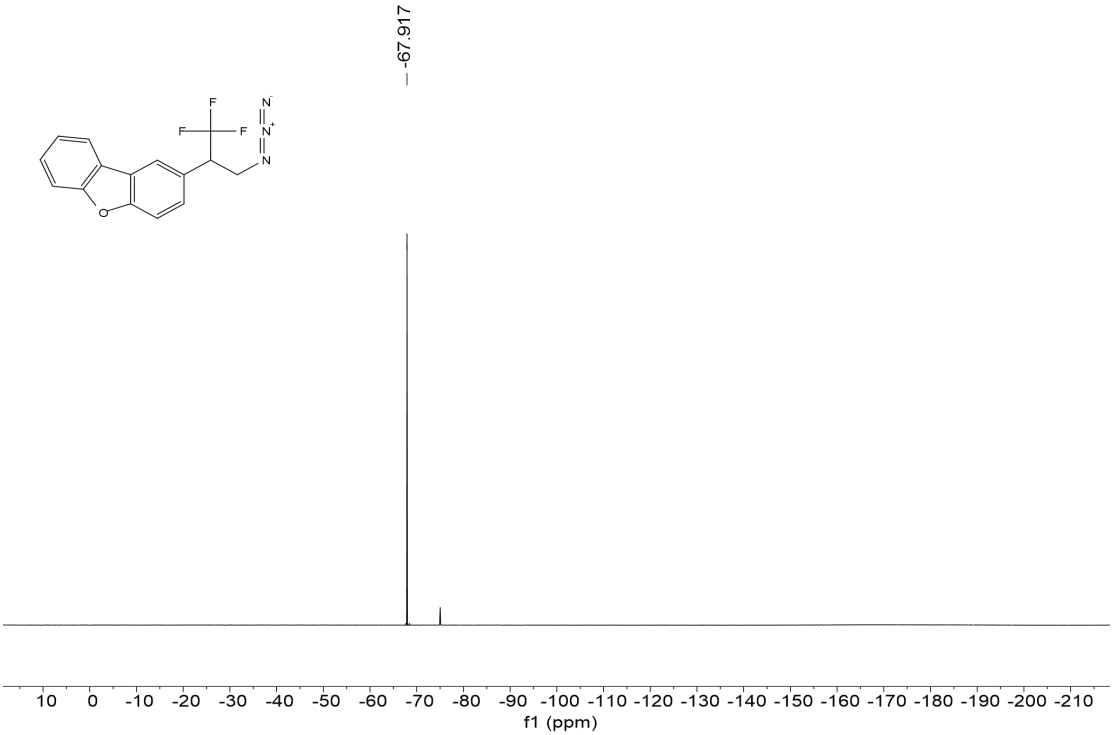

133.294
133.184
129.847
129.457
129.440
128.886
127.978
127.715
127.057
126.740
126.646
125.625
124.269
121.479
77.318
77.000
76.682
50.624
50.357
50.258
50.233
50.091
49.825
F
F
F
N
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-68.048
F
F
F
N
N
N
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)

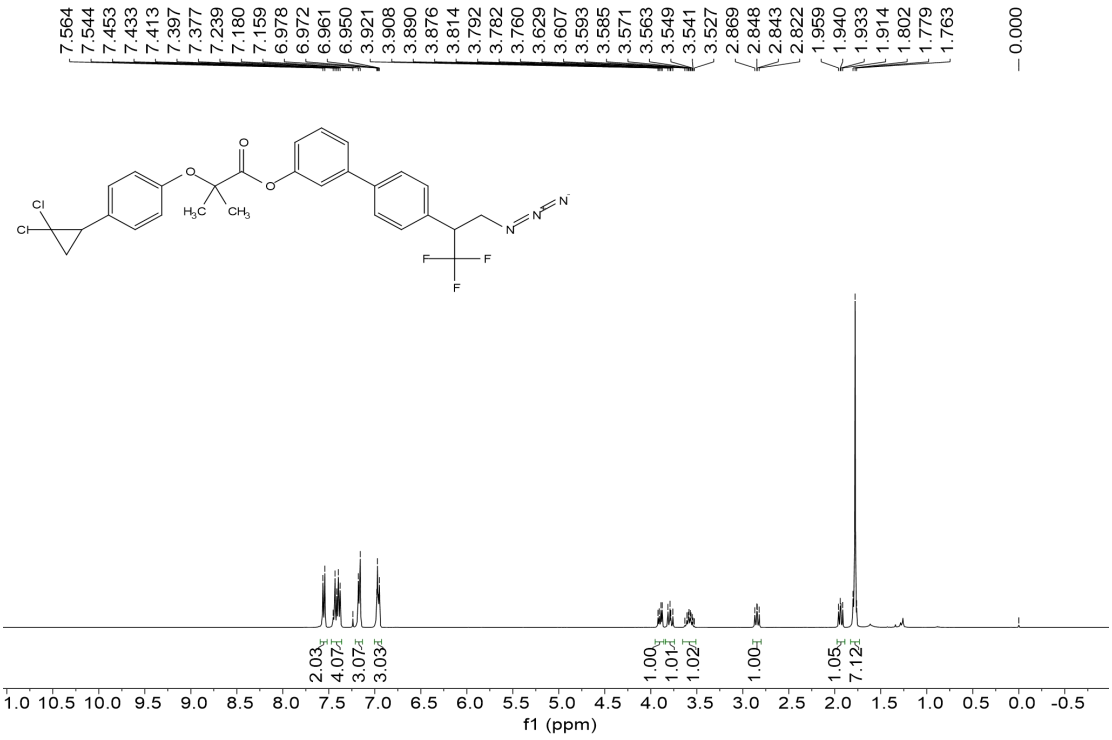
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **24**

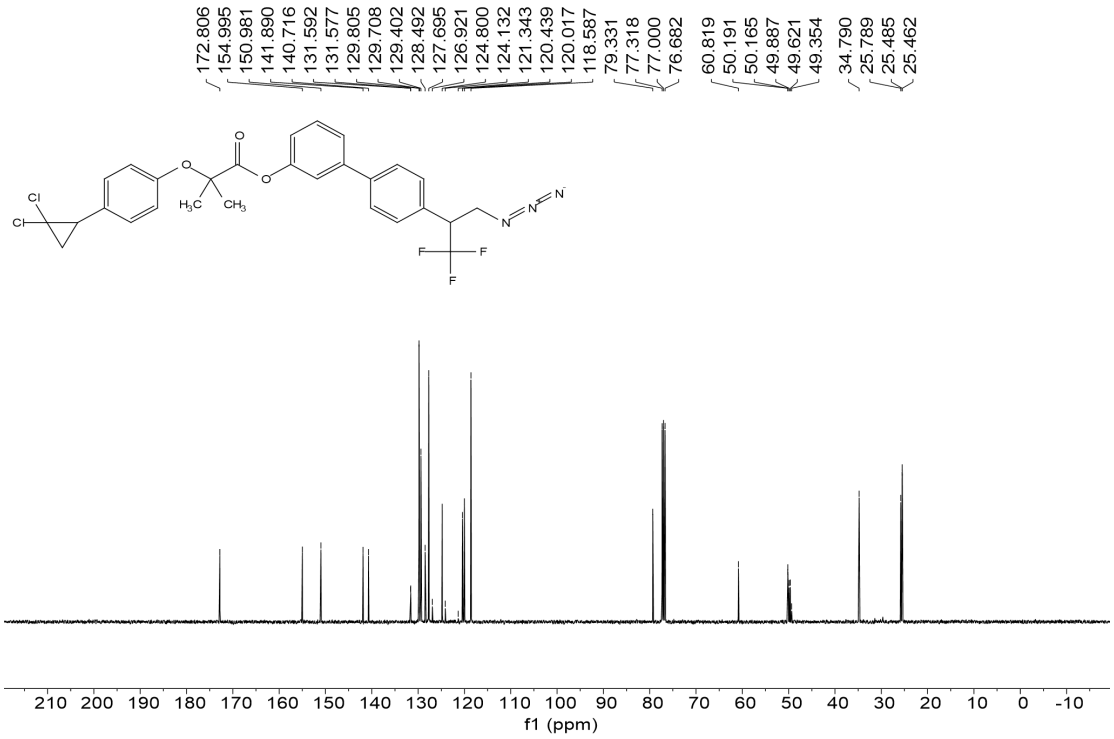


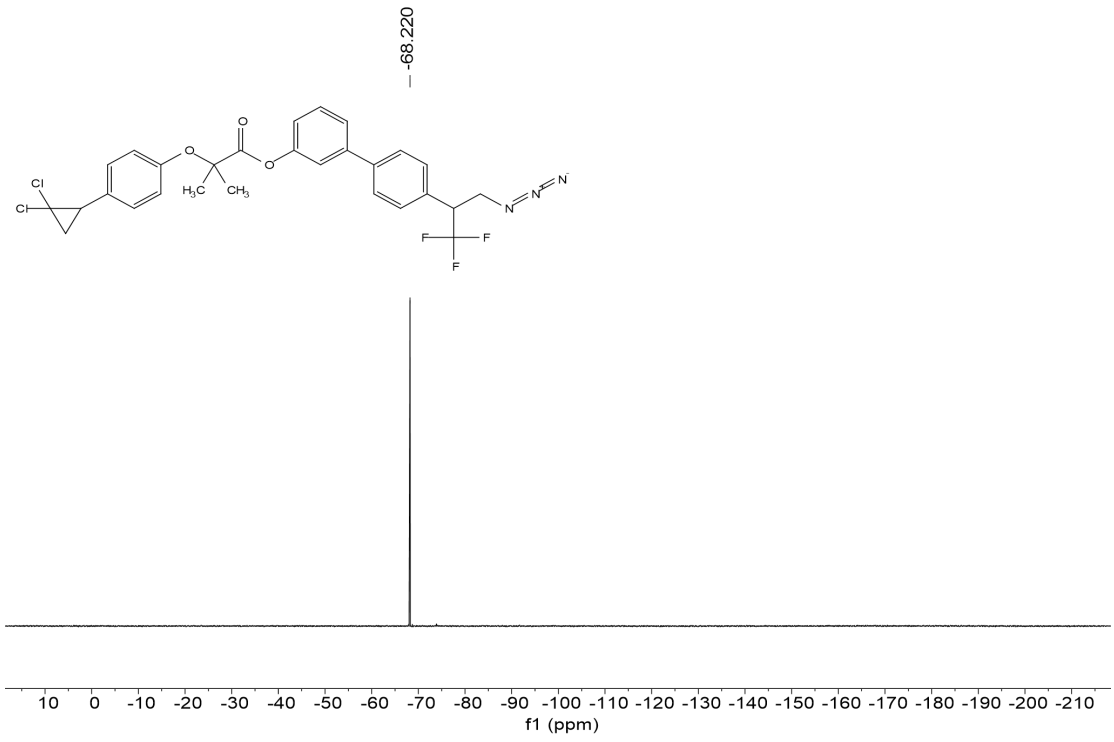




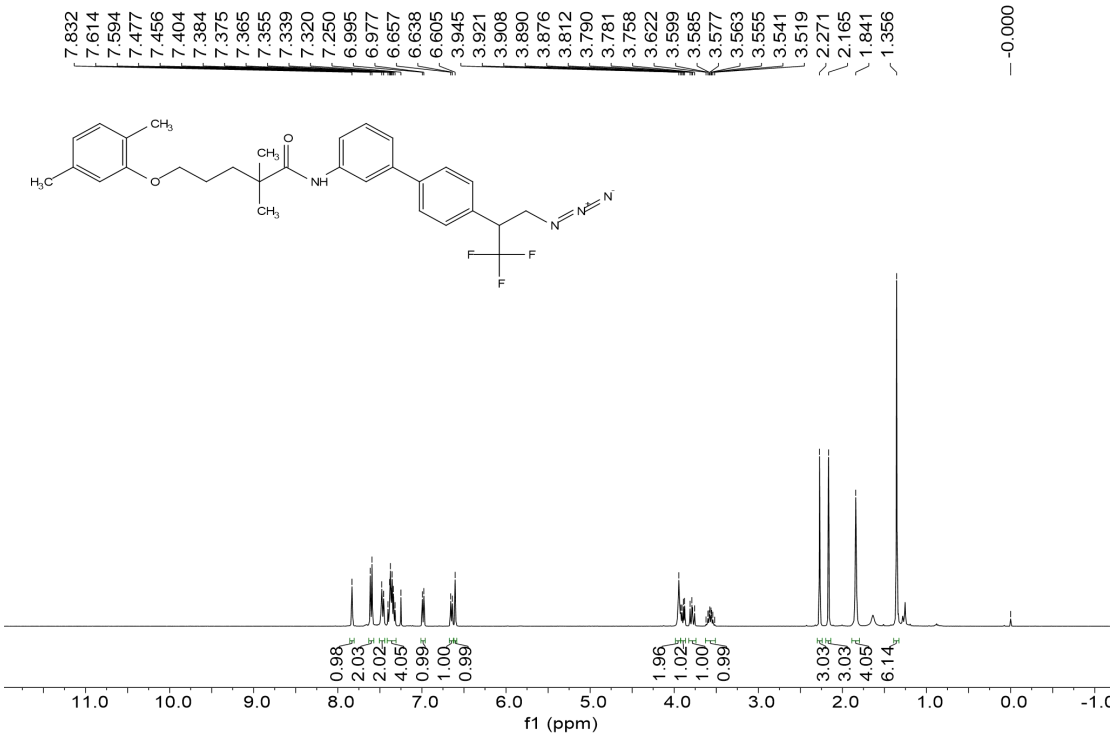
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **28**

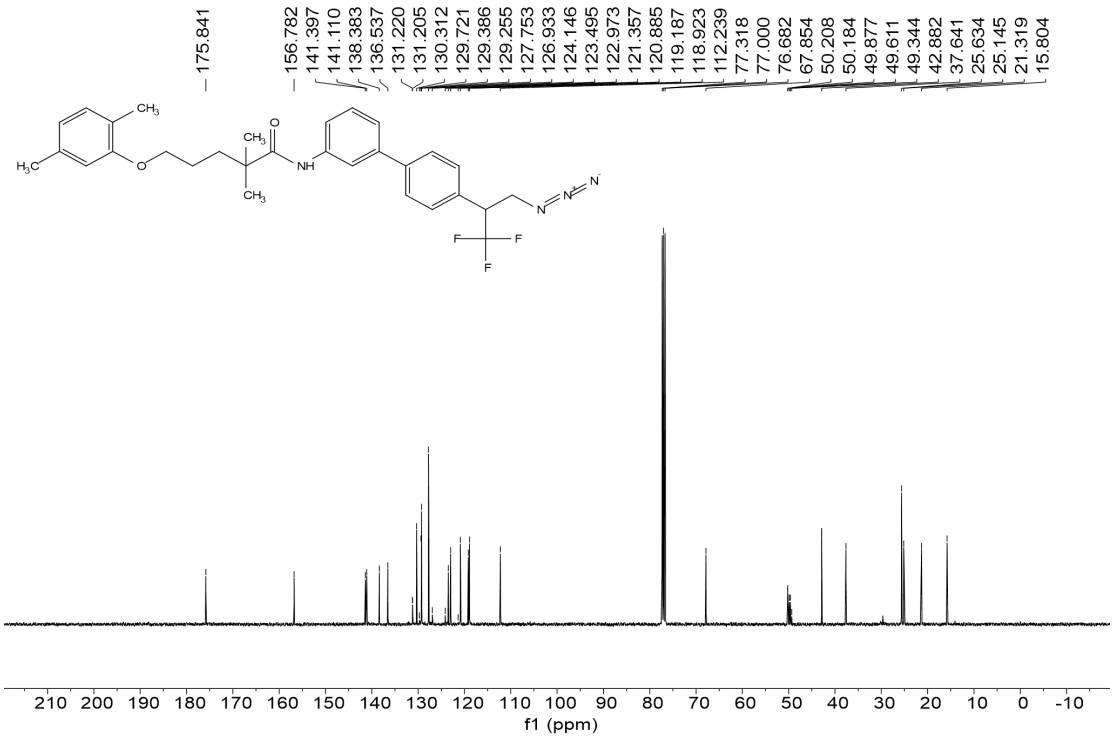


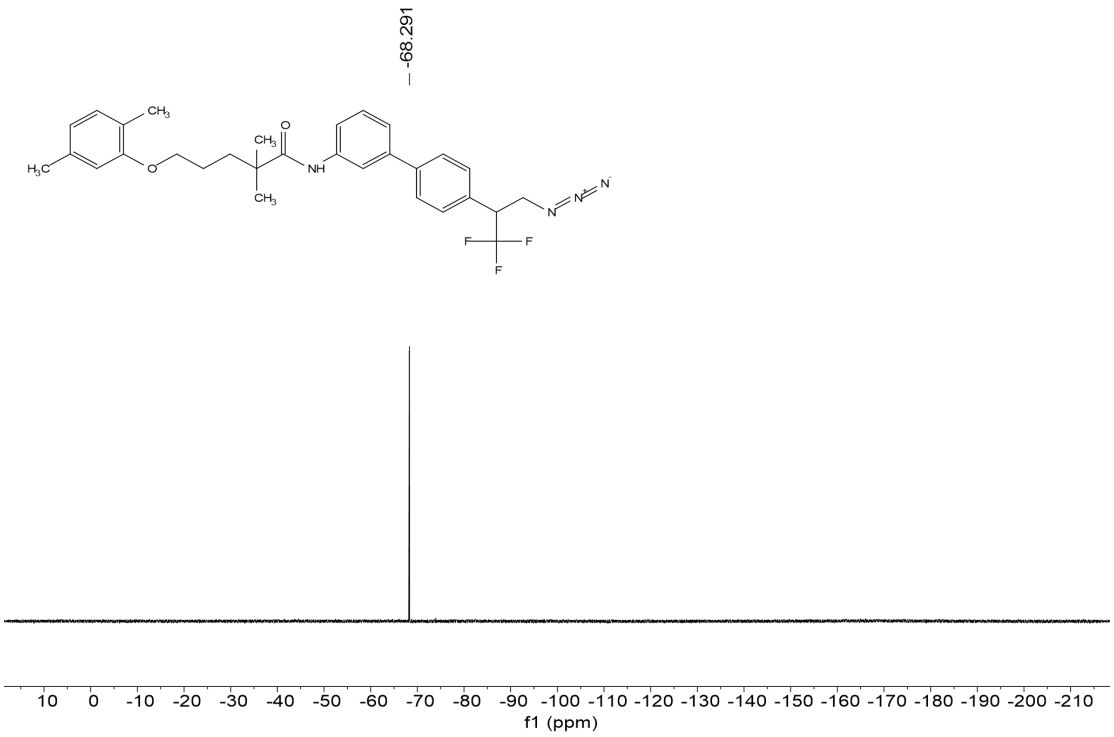

172.806
154.995
150.981
141.890
140.716
131.592
131.577
129.805
129.708
129.402
128.492
127.695
126.921
124.800
124.132
121.343
120.439
120.017
118.587
79.331
77.318
77.000
76.682
60.819
50.191
50.165
49.887
49.621
49.354
34.790
25.789
25.485
25.462
Cl
Cl
O
O
O
H3C
CH3
N
N
N
F
F
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-68.220
Cl
Cl
O
O
O
H3C
CH3
N
N
N
F
F
F
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)

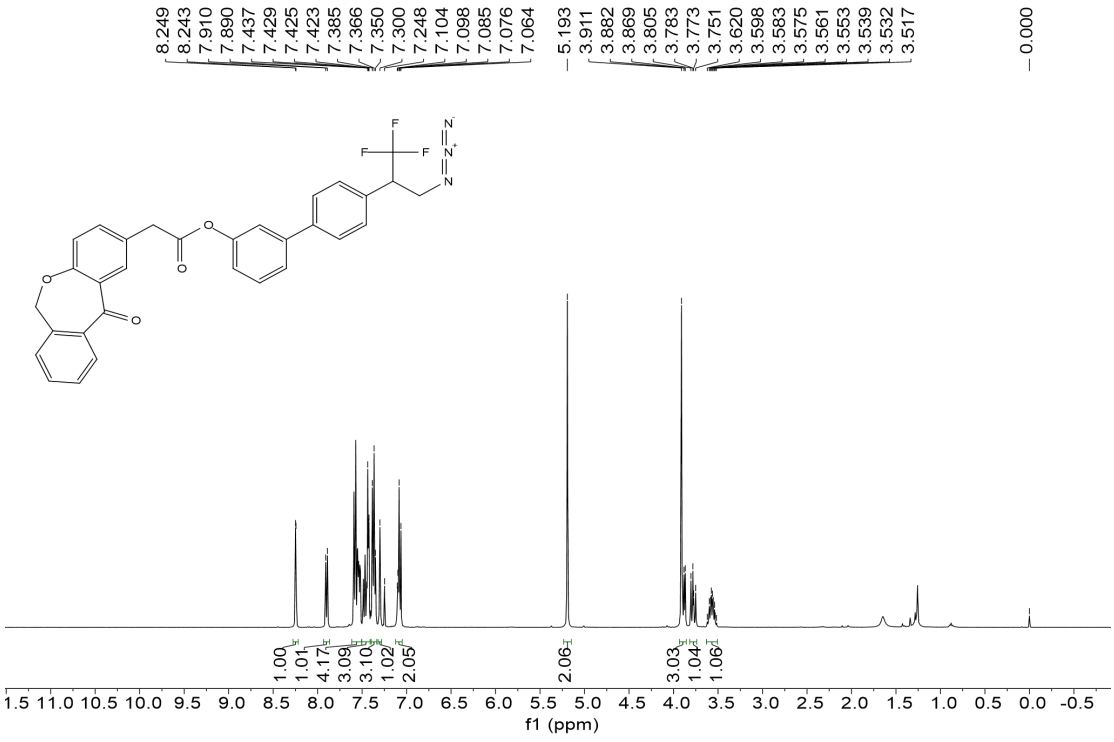
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **29**

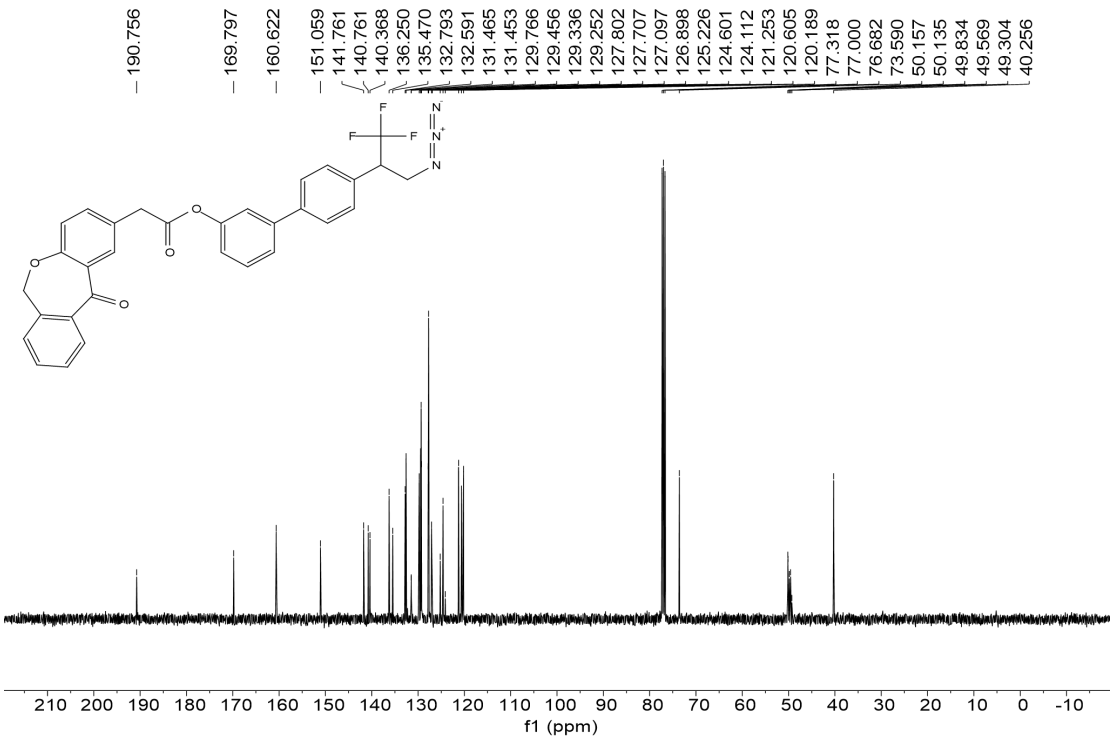


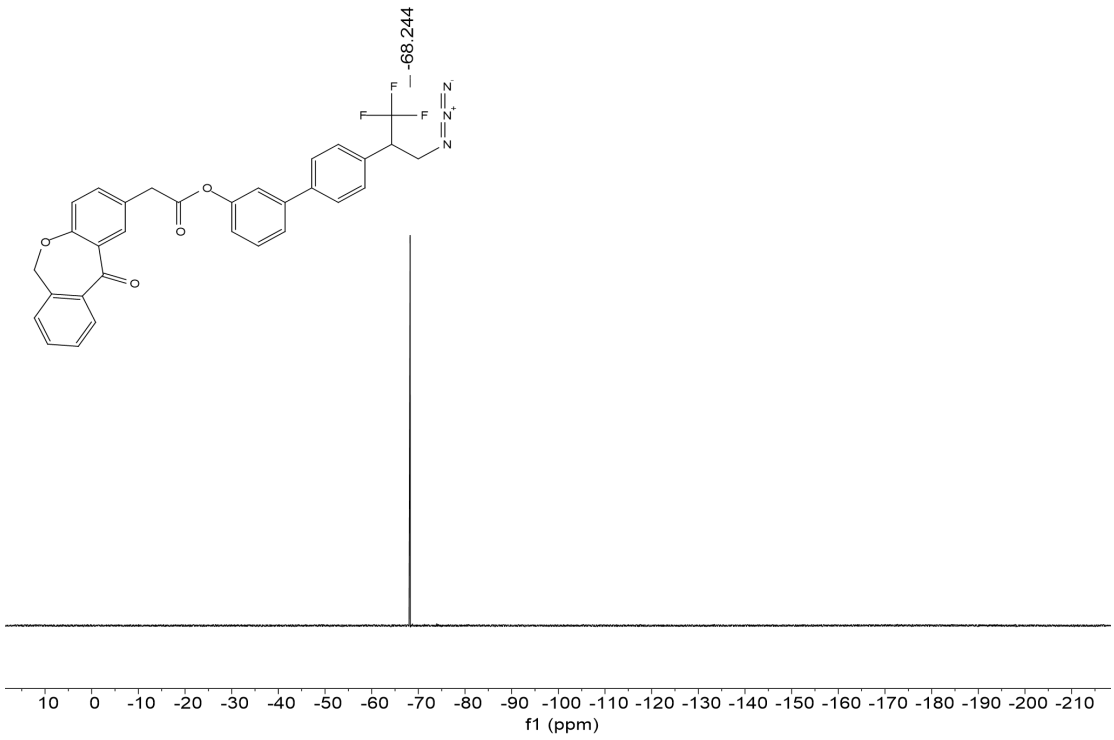




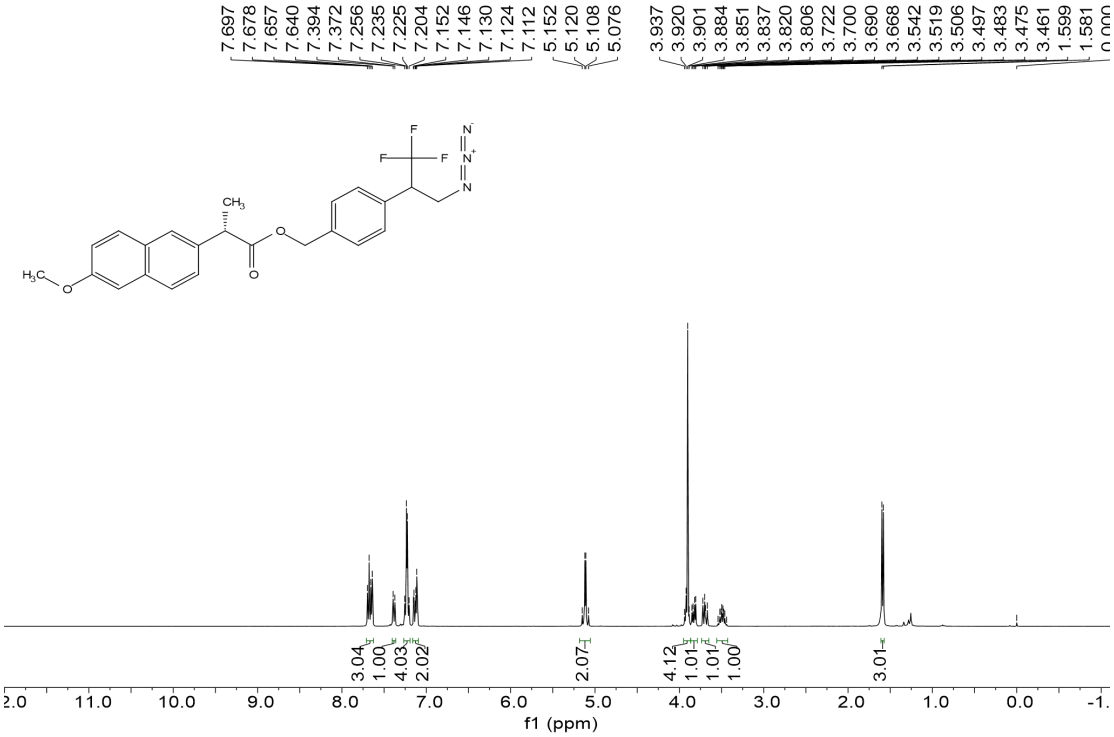
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **30**

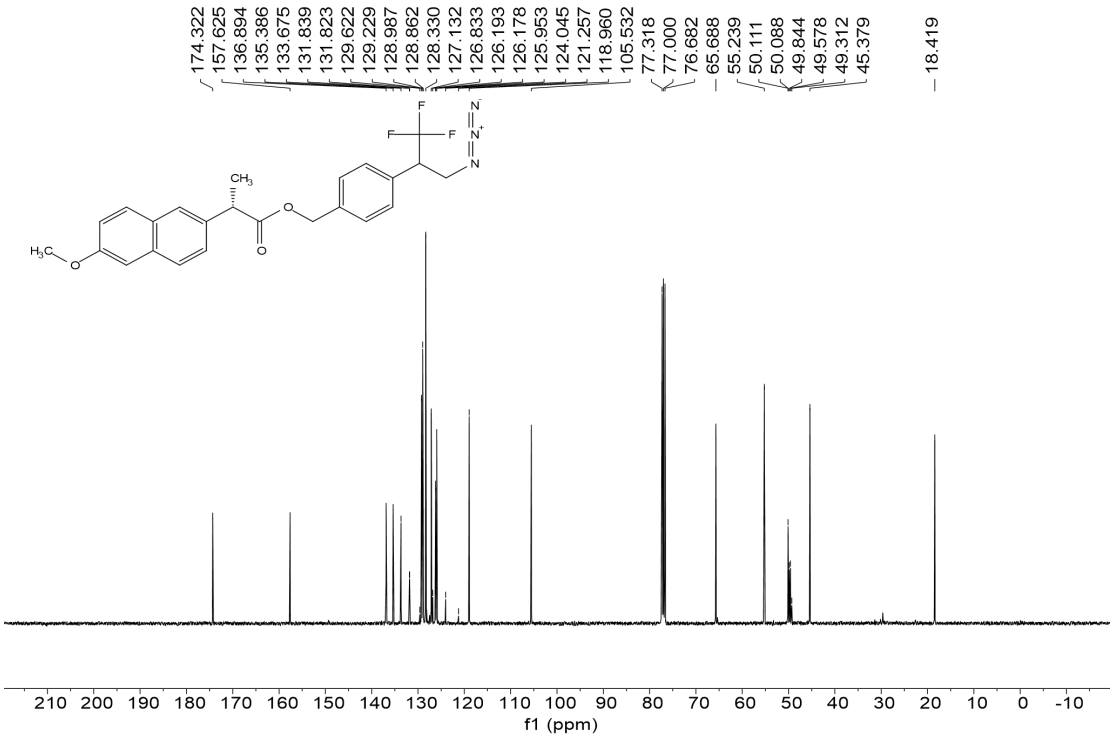


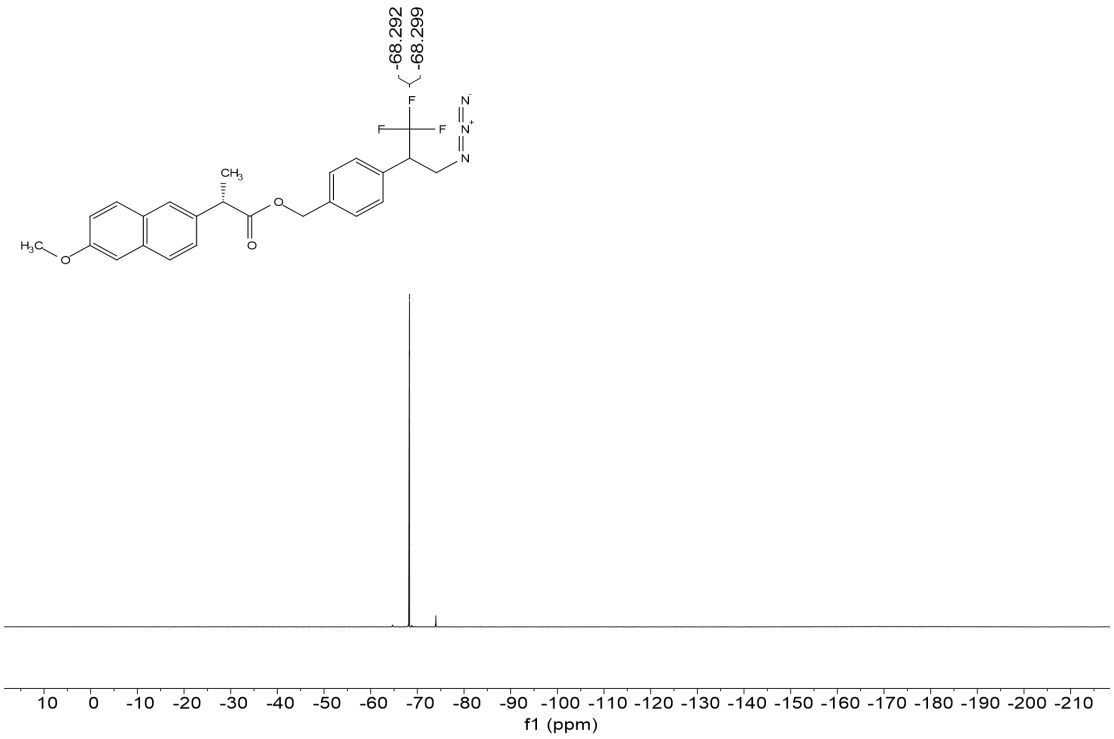

190.756
169.797
160.622
151.059
141.761
140.761
140.368
136.250
135.470
132.793
132.591
131.465
131.453
129.766
129.456
129.336
129.252
127.802
127.707
127.097
126.898
125.226
124.601
124.112
121.253
120.605
120.189
77.318
77.000
76.682
73.590
50.157
50.135
49.834
49.569
49.304
40.256
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-68.244
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)

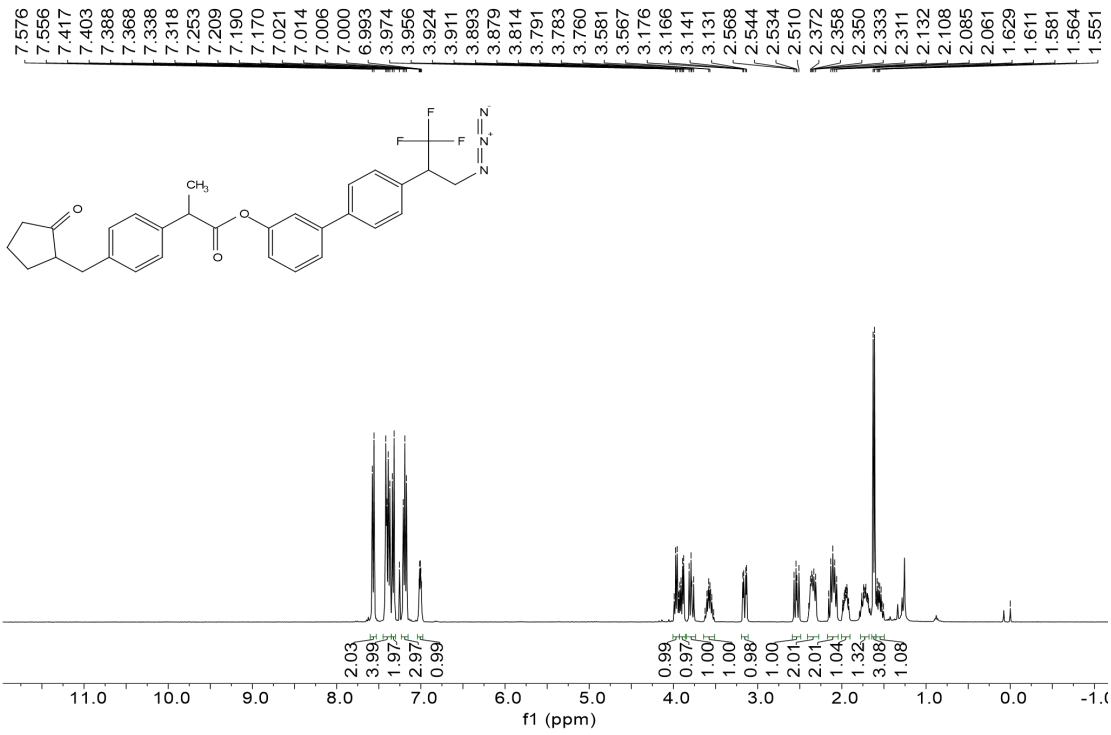
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **31**

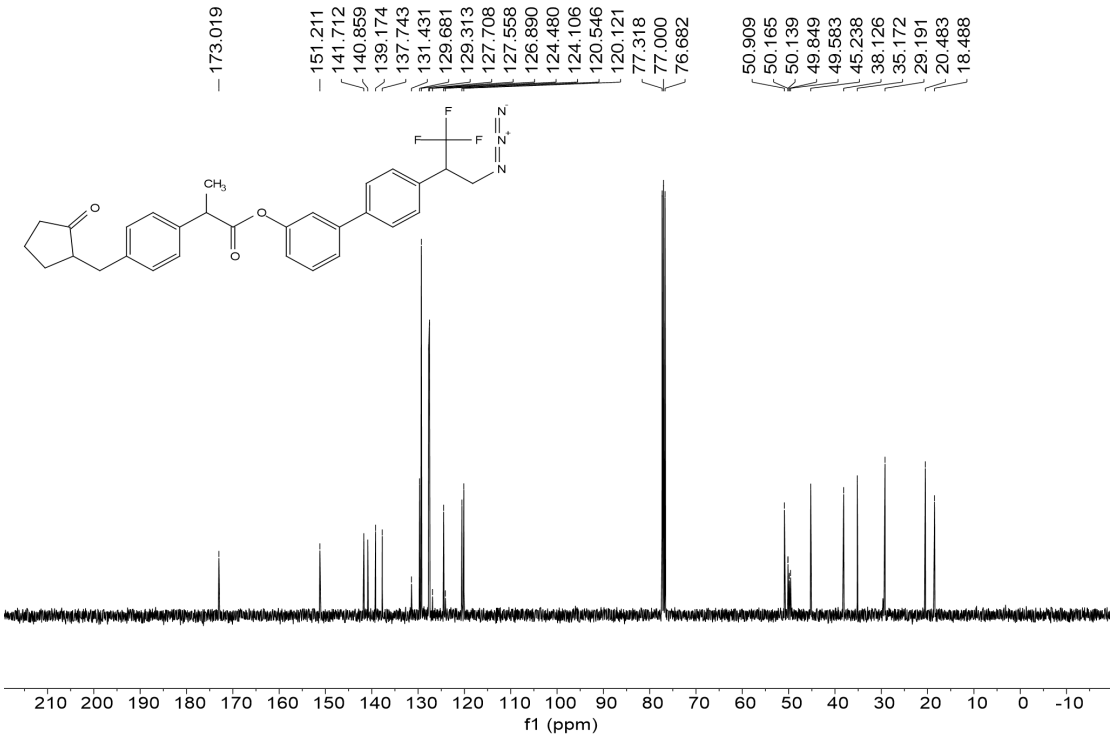


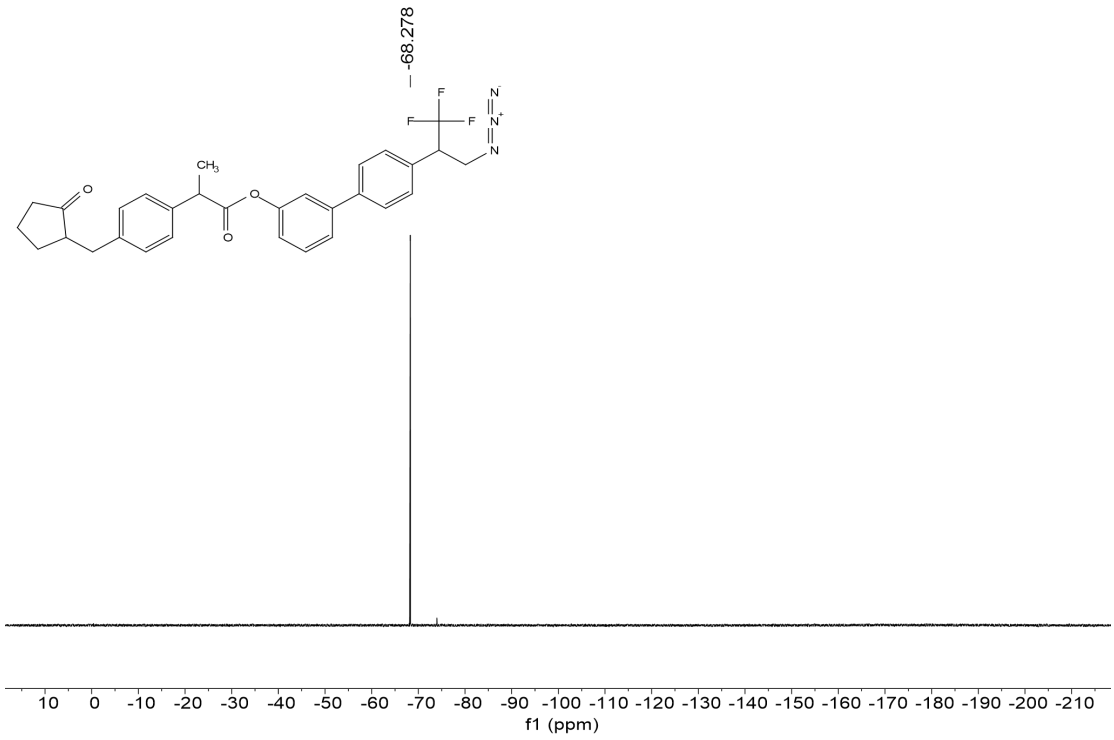




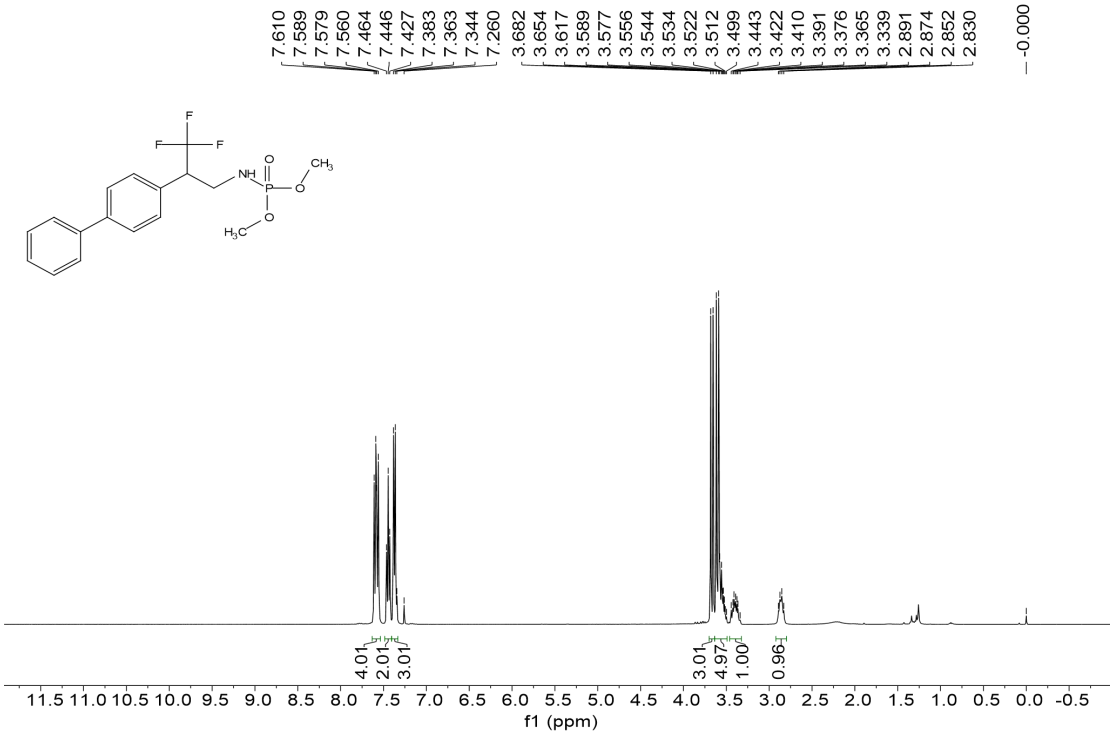
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **32**

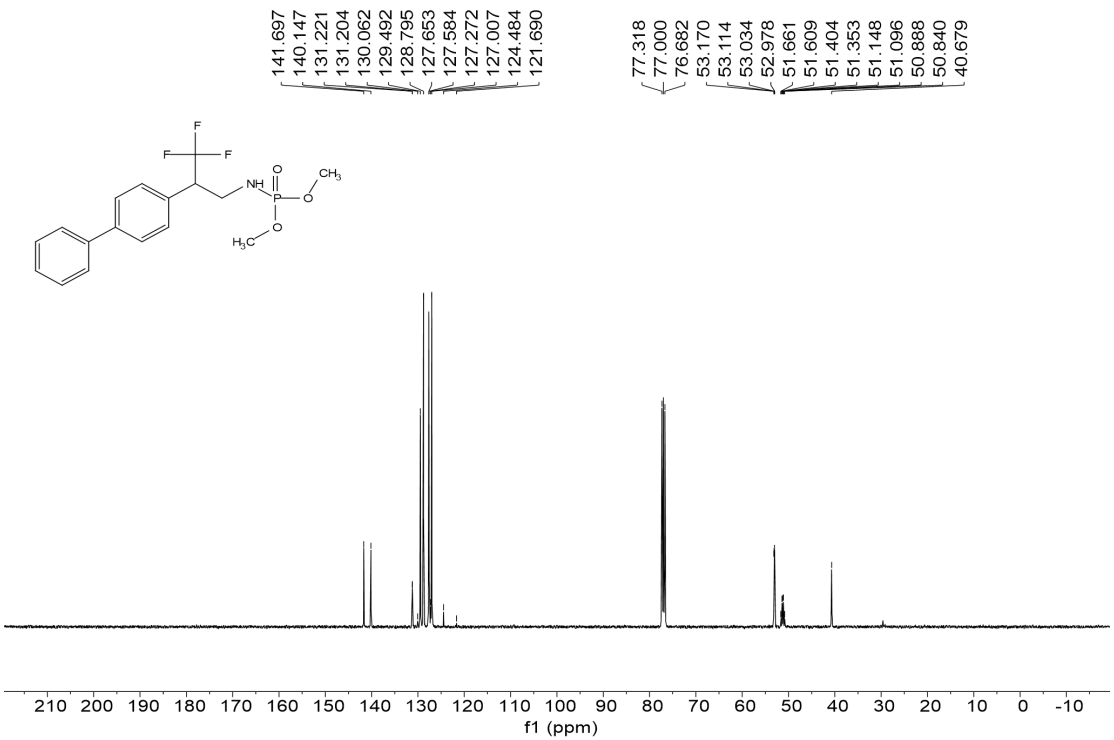



173.019
151.211
141.712
140.859
139.174
137.743
131.431
129.681
129.313
127.708
127.558
126.890
124.480
124.106
120.546
120.121
77.318
77.000
76.682
50.909
50.165
50.139
49.849
49.583
45.238
38.126
35.172
29.191
20.483
18.488
F
F
F
N
N
N
CH3
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

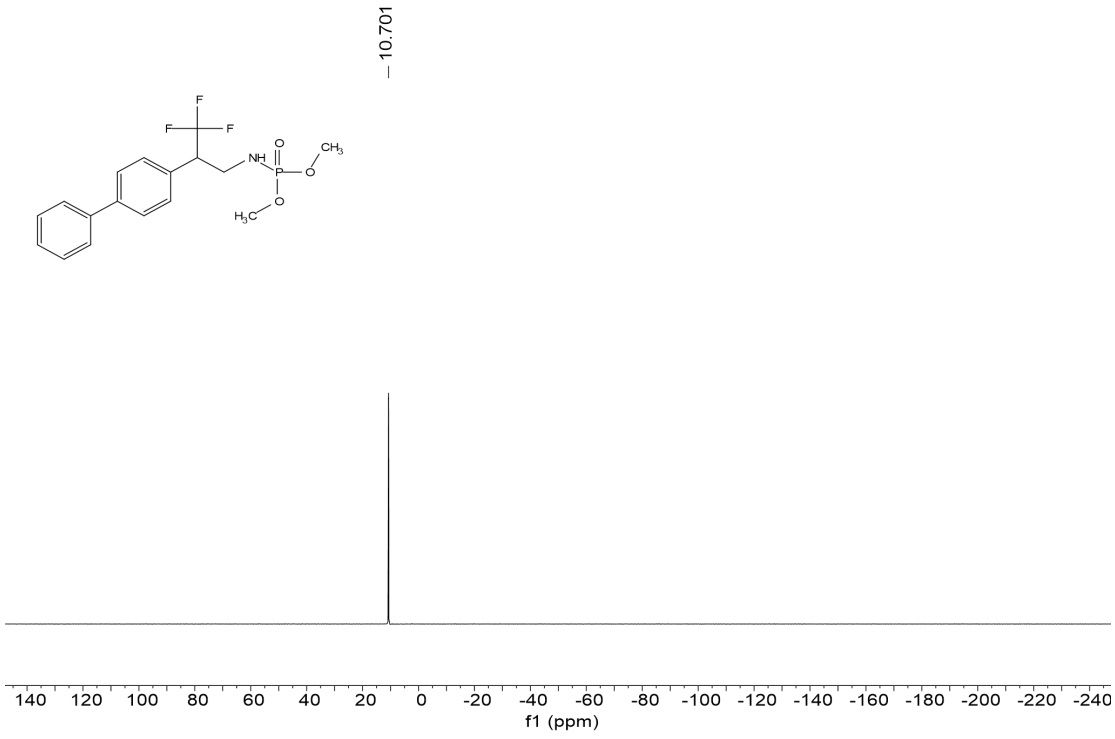

-68.278
F
F
F
N
N
N
CH3
O
O
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$), ^{19}F (376 MHz, $CDCl_3$) and ^{31}P (162 MHz, $CDCl_3$) spectrum of compound **33**

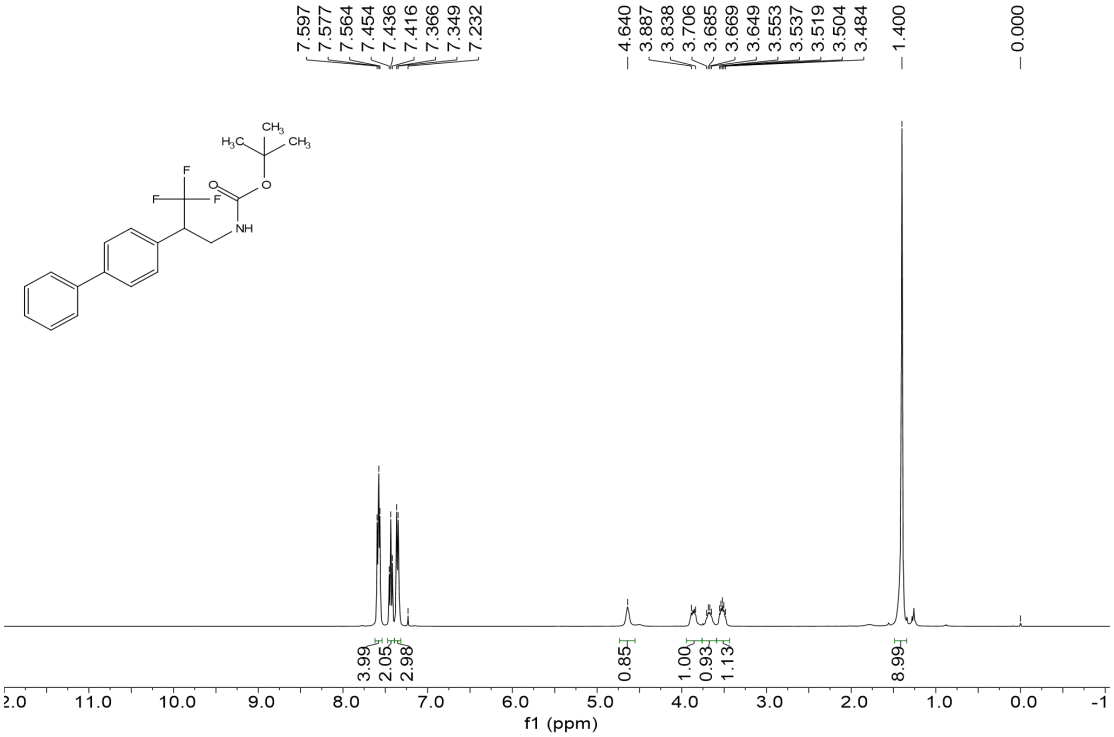


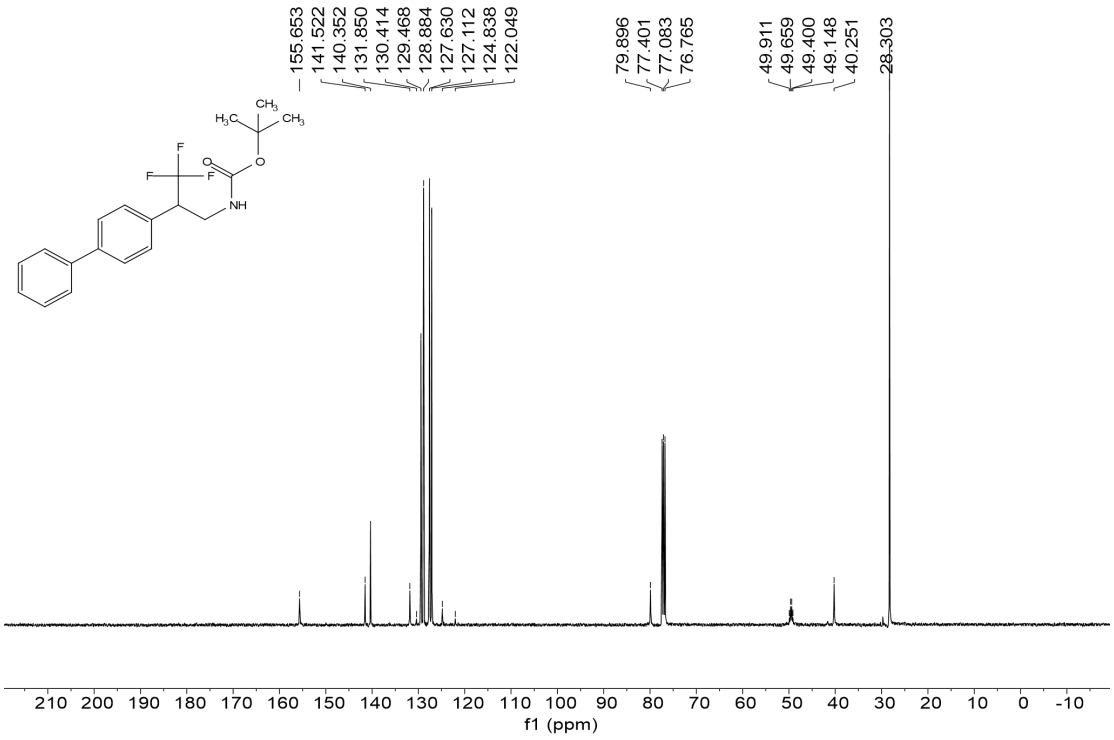



-68.246
F
F
F
NH
O
P
O
O
CH3
H3C
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

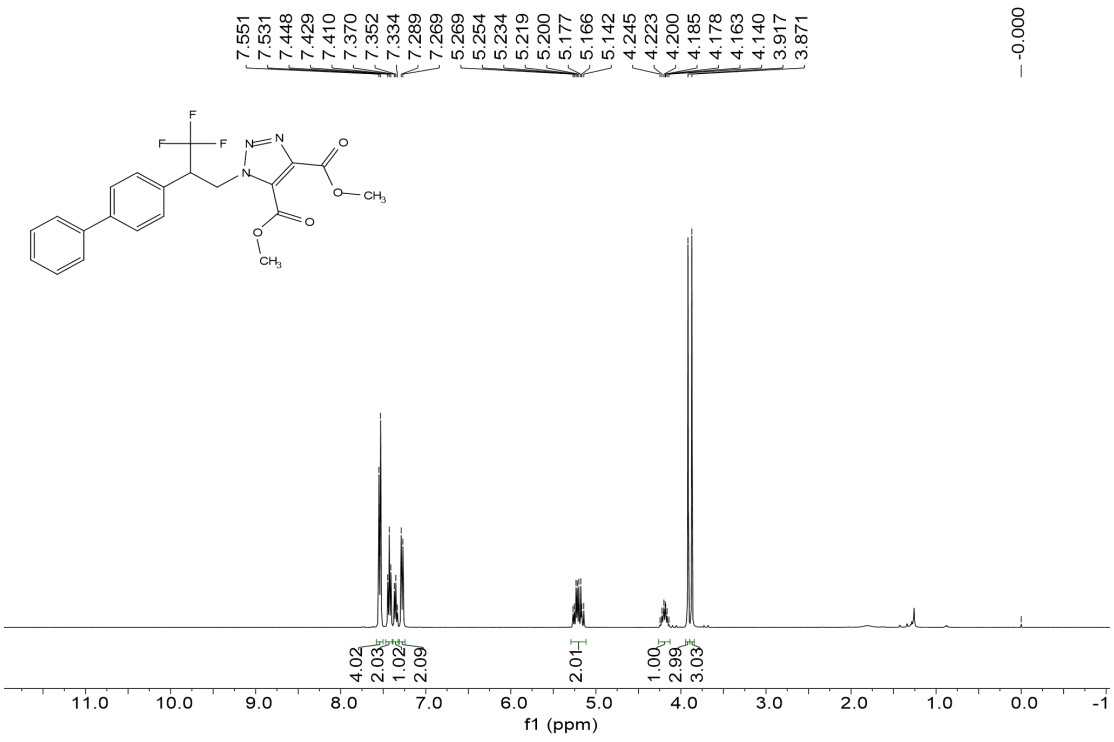

10.701
F
F
F
NH
O
P
O
O
CH3
H3C
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

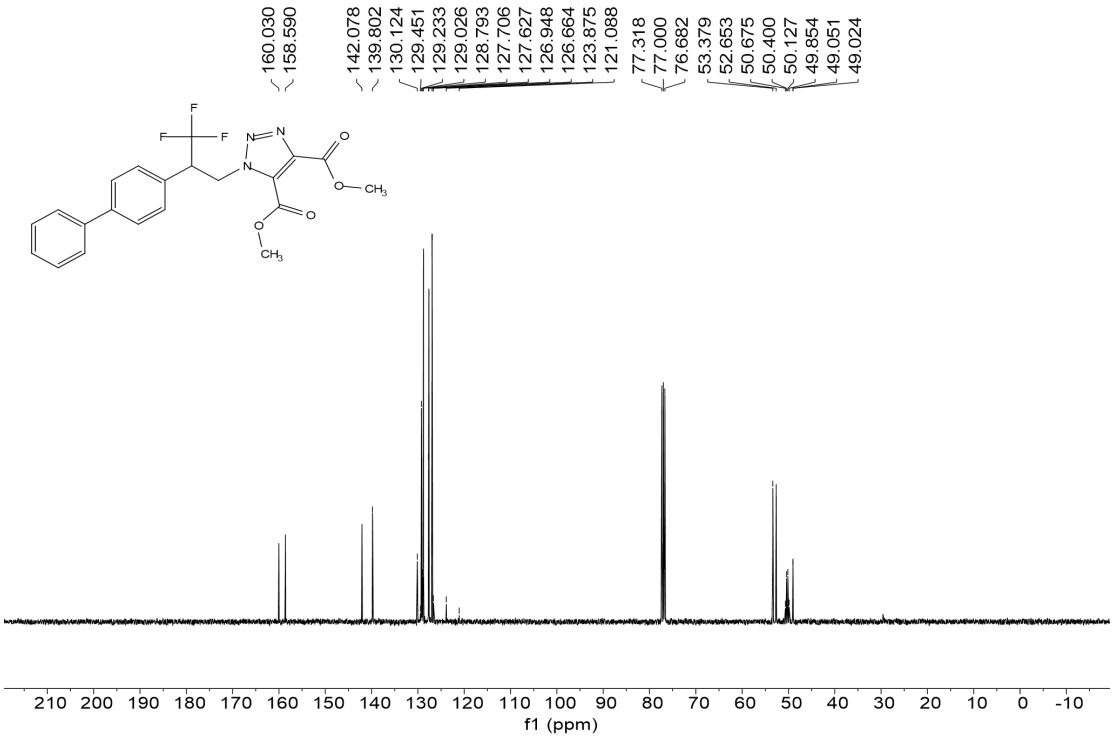
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **34**

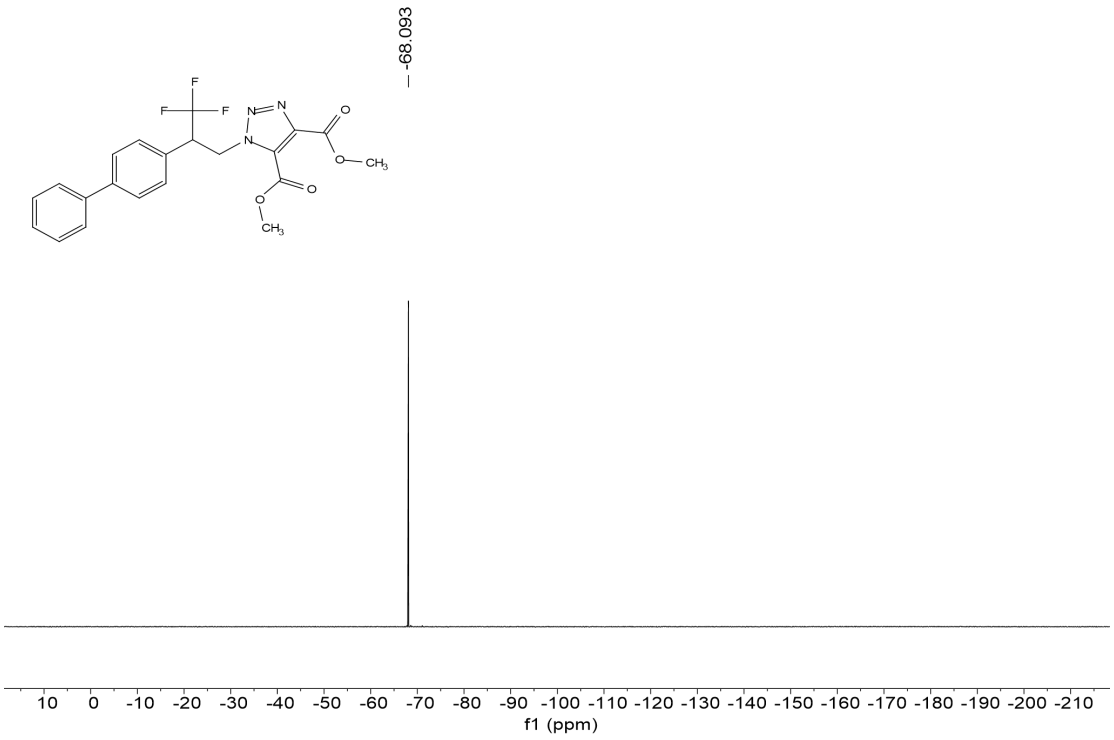




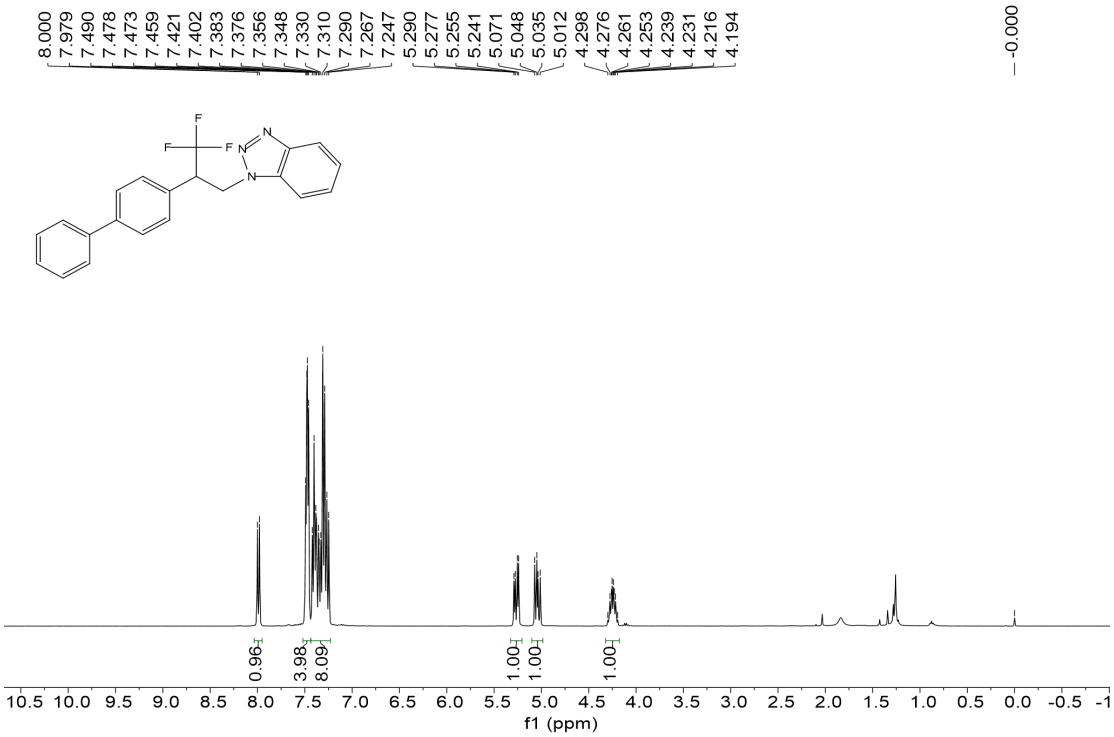
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **35**

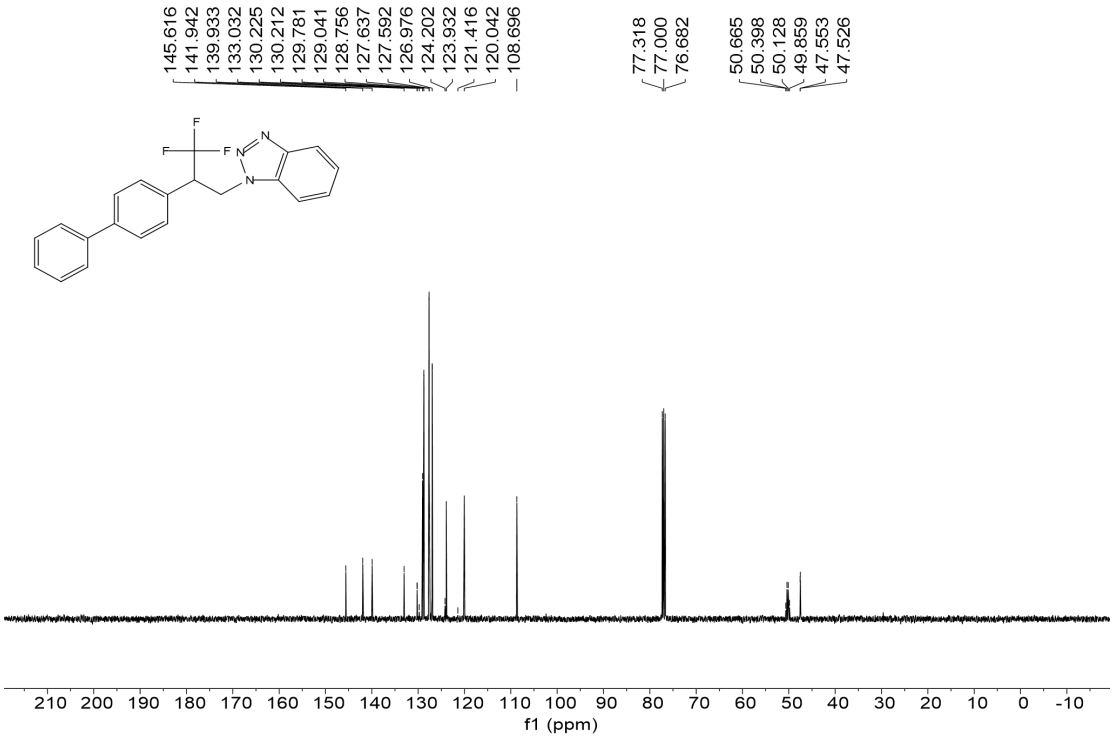


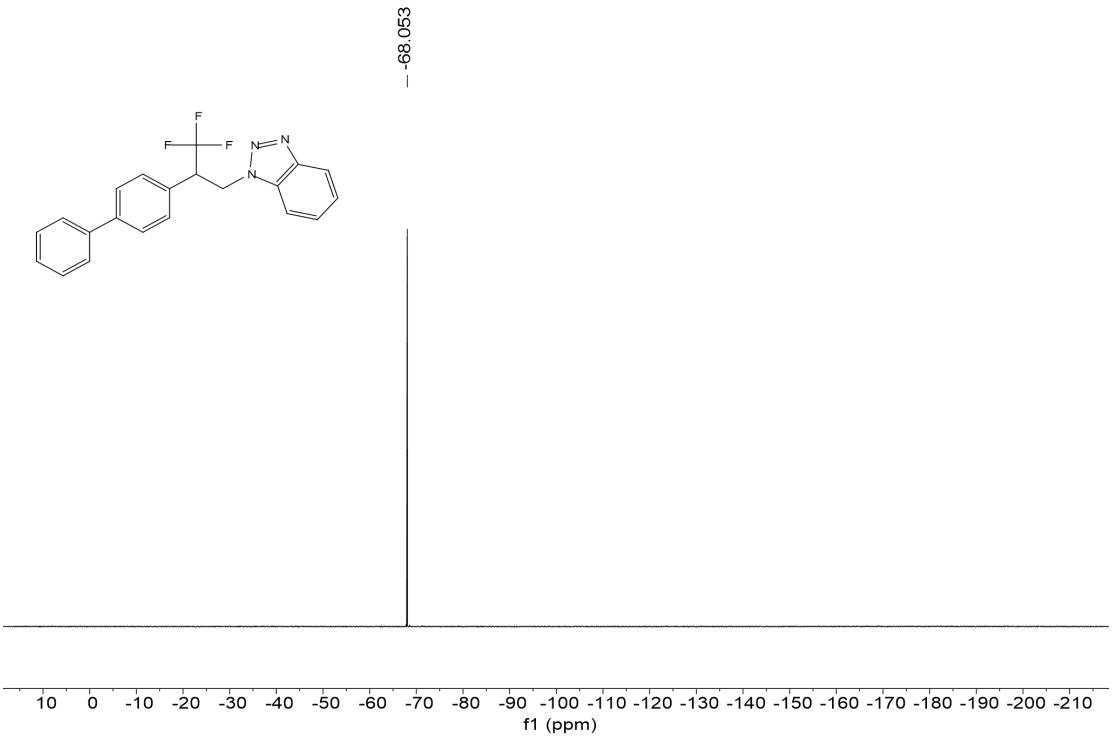

160.030
158.590
142.078
139.802
130.124
129.451
129.233
129.026
128.793
127.706
127.627
126.948
126.664
123.875
121.088
77.318
77.000
76.682
53.379
52.653
50.675
50.400
50.127
49.854
49.051
49.024
F
F
F
N
N
N
O
O
O
CH3
O
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-68.093
F
F
F
N
N
N
O
O
O
CH3
O
CH3
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)

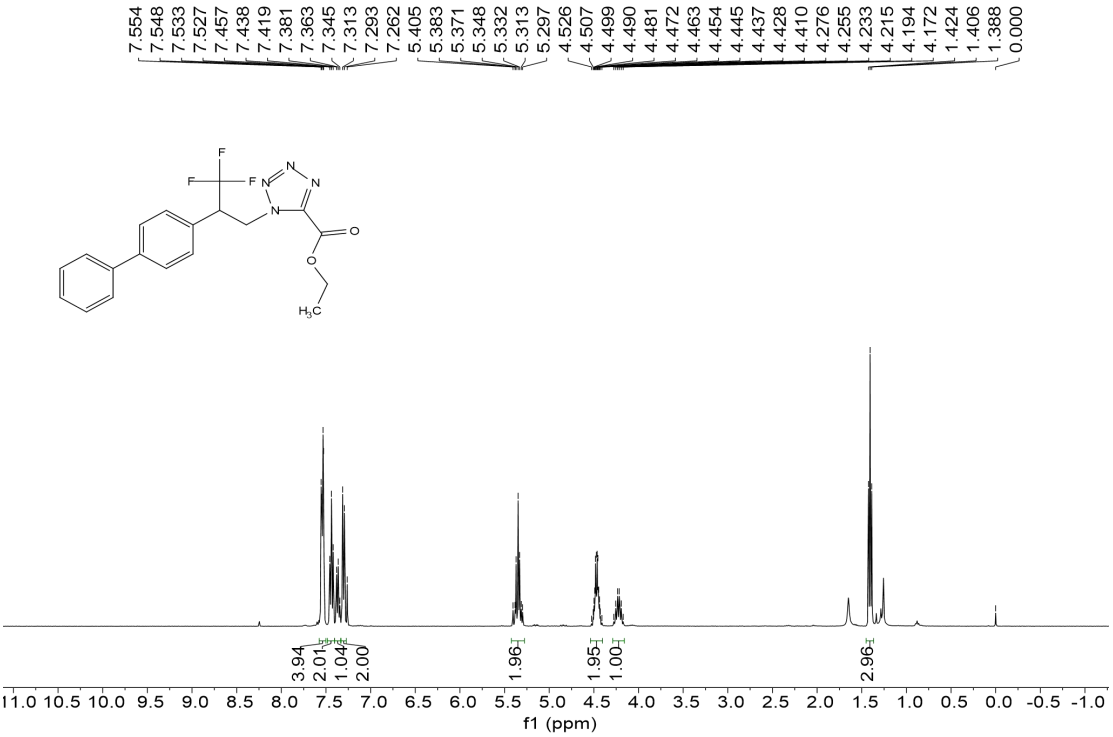
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$) and ^{19}F (376 MHz, $CDCl_3$) NMR spectrum of compound **36**

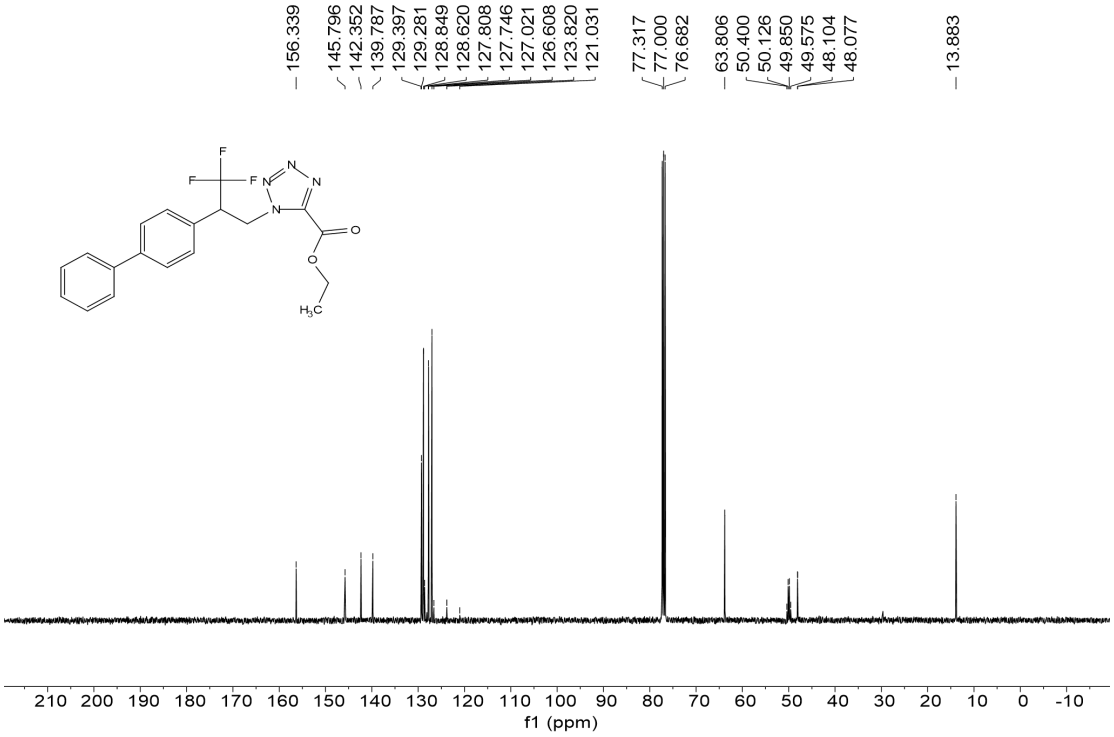


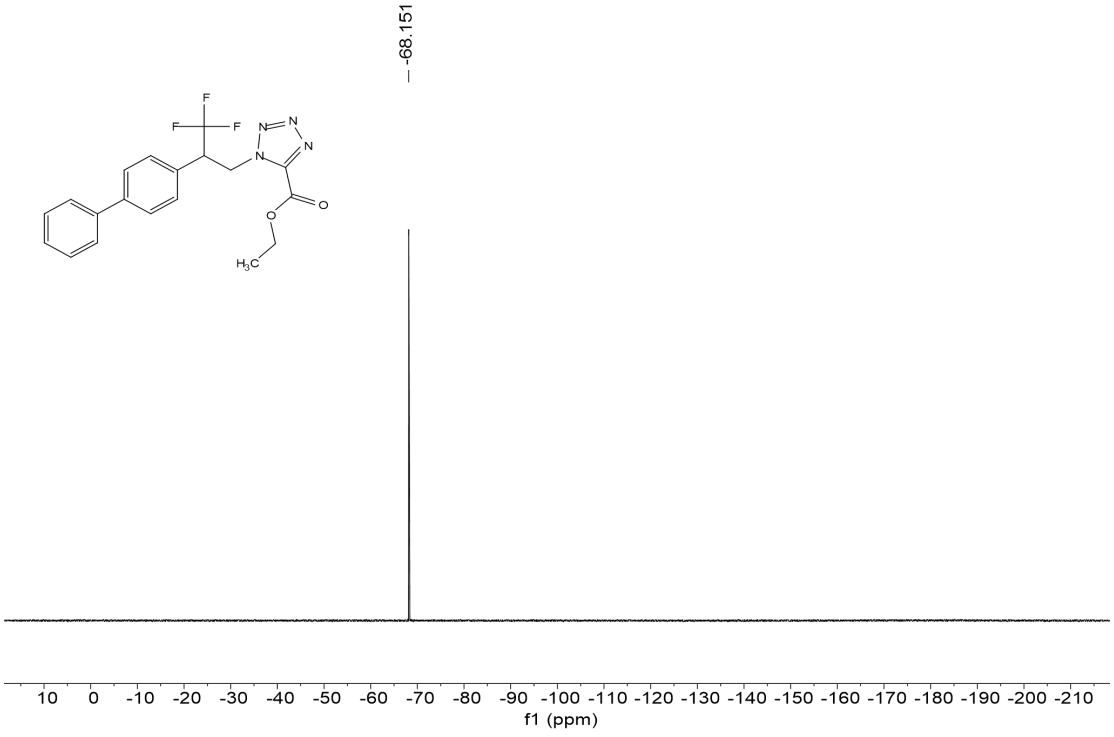


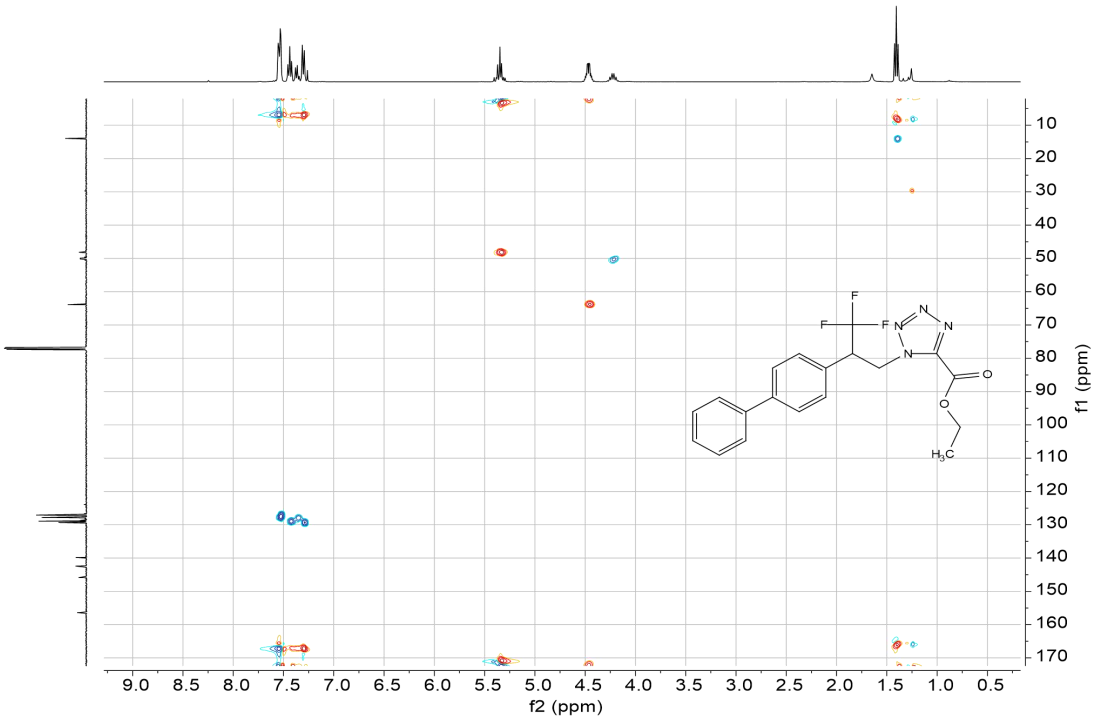


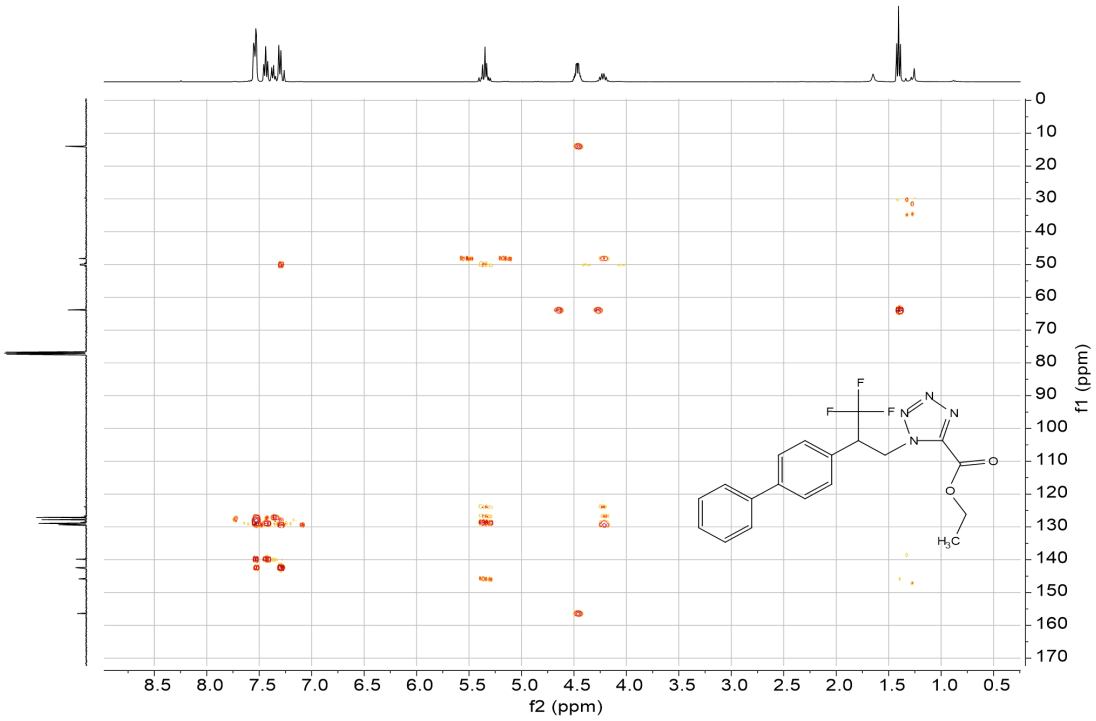
^{1}H (400 MHz, $CDCl_3$), ^{13}C (101 MHz, $CDCl_3$), ^{19}F (376 MHz, $CDCl_3$), HSQC (400 MHz, 101 MHz, $CDCl_3$) and HMBC (400 MHz, 101 MHz, $CDCl_3$) NMR spectrum of compound **37**



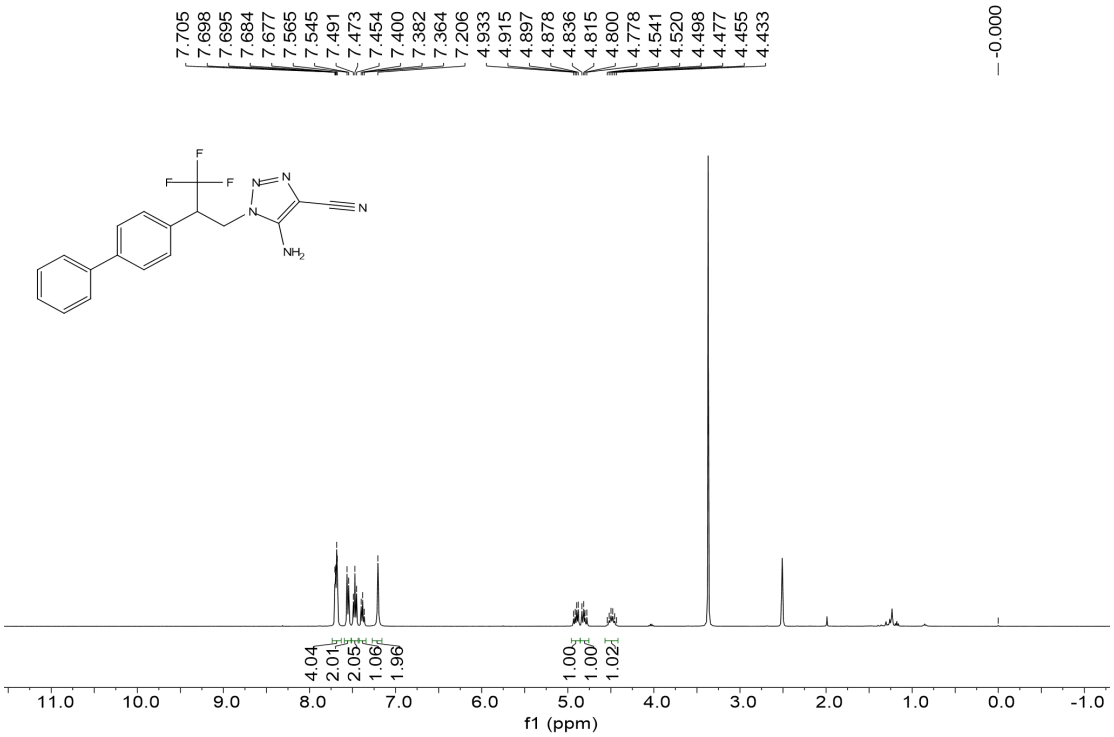

156.339
145.796
142.352
139.787
129.397
129.281
128.849
128.620
127.808
127.746
127.021
126.608
123.820
121.031
77.317
77.000
76.682
63.806
50.400
50.126
49.850
49.575
48.104
48.077
13.883
F
F
F
N
N
N
N
O
O
H3C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

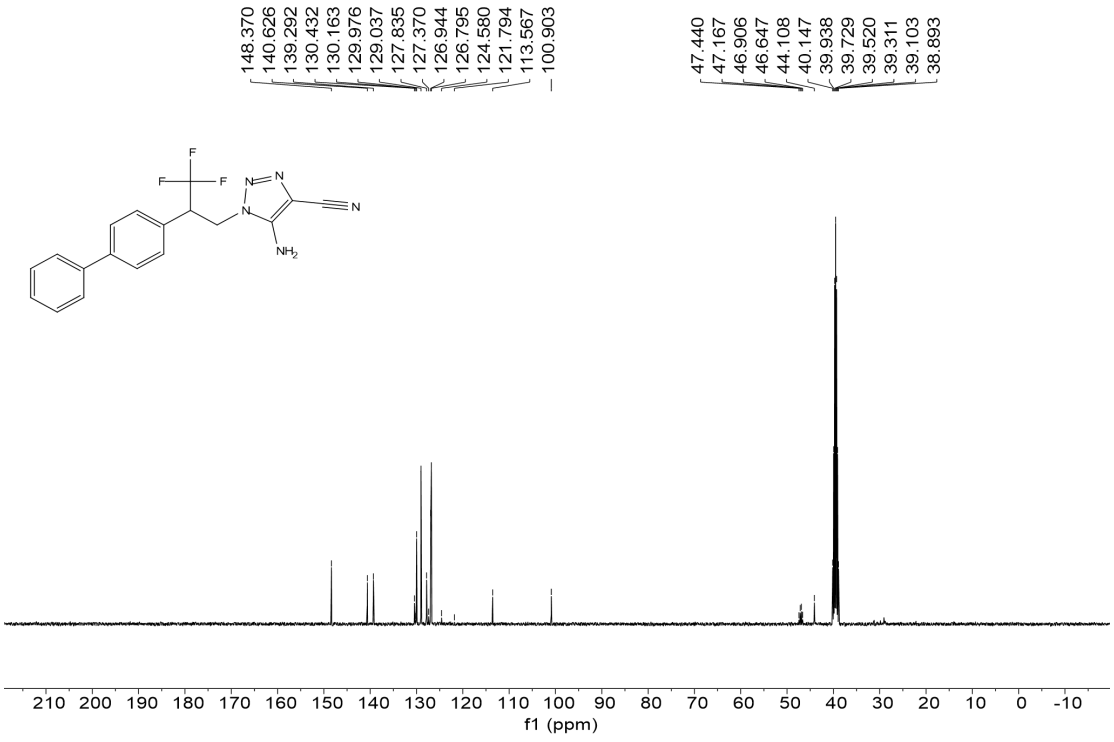

-68.151
F
F
F
N
N
N
N
O
O
H3C
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

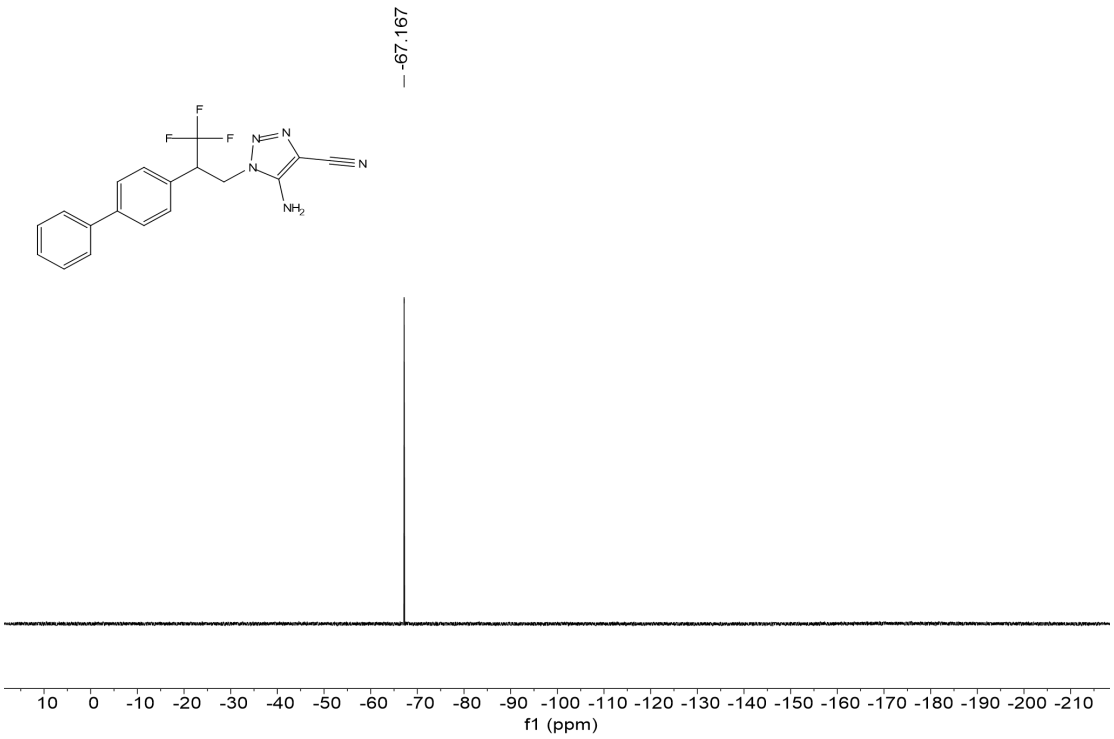

f2 (ppm)
f1 (ppm)


f2 (ppm)
f1 (ppm)

^{1}H (400 MHz, DMSO), ^{13}C (101 MHz, DMSO) and ^{19}F (376 MHz, DMSO) NMR spectrum of compound **38**






-67.167
F
F
F
N
N
N
N
NH2
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)