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Transition metal-free *N*-fluoroalkylation of amines using cyanurate activated fluoroalcohols

Outline

1. Experimental

1.1. General procedure for the synthesis of 2,4,6-tris(2,2,2-trifluoroethoxy)-1,3,5-triazine (TTFET)

Into a canonical flask (100 mL), a mixture of 2,2,2-trifluoroethanol (33.0 mmol, 2.376 mL), and sodium hydride (36.3 mmol, 0.871 g) was stirred in THF (30 mL) for 1.50 h at room temperature. Then cyanuric chloride (10.0 mmol, 1.84 g) was added and the reaction media was refluxed for 5 h. The reaction was then allowed to cool down to room temperature. The precipitate was filtered, washed with THF and dried in vacuum to afford the product TTFET as white solid.

1.2. General procedure for the synthesis of *N*-trifluoroethylated amine derivatives

To a solution of TTFET (1.0 mmol or 0.6 mmol) in THF or DMF (3 mL) was added amine (1.0 mmol) at room temperature or 100 °C. The reaction mixture was stirred until the reaction was complete. Then the reaction mixture was filtered, eluting with EtOAc (3 x 5 mL), and the filtrate was concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc, to afford the pure product.

1.3. One pot procedure for the synthesis of *N*-trifluoroethylated amine derivatives

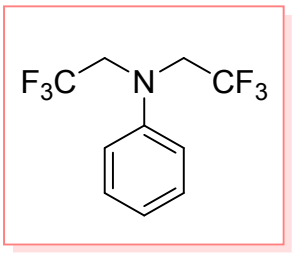
Into a canonical flask (25 mL), a mixture of 2,2,2-trifluoroethanol (3.0 mmol, 0.216 mL), and sodium hydride (3.3 mmol, 0.079 g) was stirred in THF (5 mL) for 1.50 h at room temperature. Then cyanuric chloride (1.0 mmol, 0.184 g) was added to the reaction media and let stirring continue for another 5 h. After that, amine (1.0 mmol) was added to the flask and the mixture was stirred until the reaction was complete. Then the reaction mixture was filtered, eluting with EtOAc (3 x 5 mL), and the filtrate was concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc, to afford the desired product.

1.4. General procedure for the synthesis of *N*-fluoroalkylated anilines

The procedure is same as the procedure of the synthesis of *N*-trifluoroethylated amine derivatives, just fluoroalcohols were used instead of 2,2,2-trifluoroethanol.

2. Spectral data for synthesized compounds

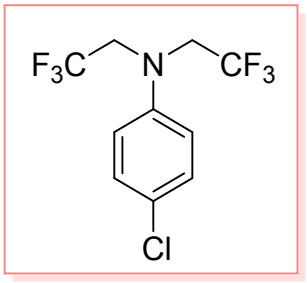
2.1. *N,N*-bis(2,2,2-trifluoroethyl)aniline (2a)



To a solution of TTFET (1.0 mmol) in THF (3 mL) was added aniline (1.0 mmol, 0.09 mL) at room temperature. The reaction mixture was stirred for 6 h. Then the reaction mixture was filtered, eluting with EtOAc (3 x 5 mL), and the filtrate was concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc20:5 (v/v), to afford the title compound.

Yield: 90%. Orange solid. M.p. 88-90 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.55 (d, *J* = 6.0 Hz, 2H), 7.41 (dd, *J* = 9.0, 6.0 Hz, 2H), 7.21 (t, *J* = 9.0 Hz, 1H), 4.80 (q, *J* = 9.0 Hz, 4H). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ (ppm) 147.7, 129.1, 126.6 (q, *J* = 278.6 Hz), 125.1, 121.4, 63.5 (q, *J* = 40.0 Hz). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -73.59 (d, *J* = 62.1 Hz). IR (KBr): 3249, 2918, 2857, 1611, 1444, 1277, 1172, 1133, 1124, 960, 810, 729. Anal. calcd. for $C_{10}H_9F_6N$ (257.18): C 46.70, H 3.53, N 5.45. Found: C 46.63, H 3.47, N 5.37.

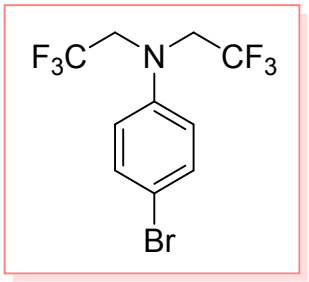
2.2. 4-Chloro-*N,N*-bis(2,2,2-trifluoroethyl)aniline (2b)



To a solution of TTFET (1.0 mmol) in DMF (3 mL) was added 4-chloro aniline (1.0 mmol, 0.128 g) at 100 °C. The reaction mixture was stirred for 10 h.Then the reaction mixture was cooled down to room temperature and 30 ml of EtOAc, 30 ml of water were added. After separation of the organic layer from water, the aqueous phases were extracted with EtOAc (2 x 15 ml) again. The combined organic layers were then dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc 20:7 (v/v), to afford the title compound.

Yield: 85%. Pale yellow solid. M.p. 129-131 ^{o}C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.48 (d, *J* = 9.0 Hz, 2H), 7.36 (d, *J* = 9.0 Hz, 2H), 4.80 (q, *J* = 9.0 Hz, 4H). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ (ppm) 148.7, 132.2 (q, *J* = 277.1 Hz), 129.2, 124.5, 122.7, 63.4 (q, *J* = 41.5 Hz). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -73.58 (d, *J* = 50.8 Hz). IR (KBr): 3290, 3200, 2922, 2852, 1614, 1418, 1313, 1269, 1258, 1177, 1114, 1014, 962, 867, 829, 811, 767, 679. Anal. calcd. for $C_{10}H_8ClF_6N$ (291.62): C 41.19, H 2.77, N 4.80. Found: C 41.11, H 2.71, N 4.72.

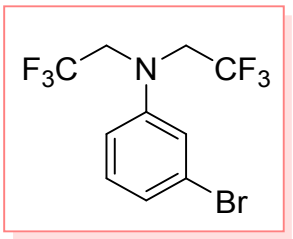
2.3. 4-Bromo-*N,N*-bis(2,2,2-trifluoroethyl)aniline (2c)



To a solution of TTFET (1.0 mmol) in DMF (3 mL) was added 4-bromo aniline (1.0 mmol, 0.172 g) at 100 °C. The reaction mixture was stirred for 8 h.Then the reaction mixture was cooled down to room temperature and 30 ml of EtOAc, 30 ml of water were added. After separation of the organic layer from water, the aqueous phases were extracted with EtOAc (2 x 15 ml) again. The combined organic layers were then dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc 20:5 (v/v), to afford the title compound.

Yield: 88%. Orange solid. M.p. 114-116 ^oC. ^1H-NMR (250 MHz, $CDCl_3$) δ (ppm) 7.52 - 7.39 (m, 4H), 4.82 - 4.70 (m, 4H). ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ (ppm) 146.3, 132.1, 123.0, 118.7 (q, *J* = 260.6 Hz), 117.6, 63.1 (q, *J* = 39.4 Hz). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -73.47 ~ -73.65 (m). IR (KBr): 2920, 2852, 1742, 1608, 1582, 1544, 1490, 1418, 1270, 1239, 1169, 1076, 1011, 961, 858, 825, 811, 719, 669, 606. Anal. calcd. for $C_{10}H_8BrF_6N$ (336.08): C 35.74, H 2.40, N 4.17. Found: C 35.65, H 2.35, N 4.11.

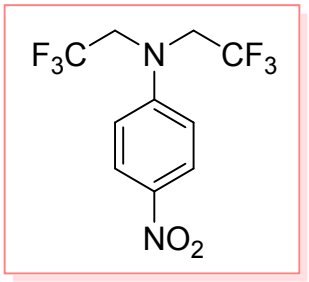
2.4. 3-Bromo-*N,N*-bis(2,2,2-trifluoroethyl)aniline (2d)



To a solution of TTFET (1.0 mmol) in DMF (3 mL) was added 3-bromo aniline (1.0 mmol, 0.11 mL) at 100 °C. The reaction mixture was stirred for 8 h.Then the reaction mixture was cooled down to room temperature and 30 ml of EtOAc, 30 ml of water were added. After separation of the organic layer from water, the aqueous phases were extracted with EtOAc (2 x 15 ml) again. The combined organic layers were then dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc 20:7 (v/v), to afford the title compound.

Yield: 86%. Yellow oil. ^1H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.45 (d, *J* = 6.0 Hz, 1H), 7.34 - 7.20 (m, 3H), 4.89 - 4.77 (m, 4H).^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -73.51 ~ -73.67 (m). IR (KBr): 3408, 3272, 3144, 2973, 2930, 2857, 1608, 1583, 1423, 1397, 1270, 1170, 1133, 998, 960, 858, 814, 778, 679, 612, 596. Anal. calcd. for $C_{10}H_8BrF_6N$ (336.08): C 35.74, H 2.40, N 4.17. Found: C 35.68, H 2.33, N 4.09.

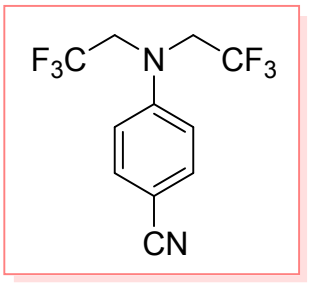
2.5. 4-Nitro-*N,N*-bis(2,2,2-trifluoroethyl)aniline (2e)



To a solution of TTFET (1.0 mmol) in DMF (3 mL) was added 4-nitro aniline (1.0 mmol, 0.138 g) at 100 °C. The reaction mixture was stirred for 12 h.Then the reaction mixture was cooled down to room temperature and 30 ml of EtOAc, 30 ml of water were added. After separation of the organic layer from water, the aqueous phases were extracted with EtOAc (2 x 15 ml) again. The combined organic layers were then dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc 20:8 (v/v), to afford the title compound.

Yield: 76%. Yellow solid. M.p. 145-147 °C. ^{1}H-NMR (250 MHz, $CDCl_3$) δ (ppm) 8.27 (d, *J* = 10.0 Hz, 2H), 7.78 (d, *J* = 10.0 Hz, 2H), 4.82 (q, *J* = 10.0 Hz, 4H). ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ (ppm) 154.1, 142.8, 125.1, 121.9 (q, *J* = 278.1 Hz), 120.1, 63.7 (q, *J* = 43.8 Hz). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -73.52 (s). IR (KBr): 3372, 3068, 2928, 2853, 1578, 1420, 1382, 1335, 1266, 1236, 1181, 1113, 1015, 963, 861, 837, 812, 752, 681. Anal. calcd. for $C_{10}H_8F_6N_2O_2$ (302.18): C 39.75, H 2.67, N 9.27. Found: C 39.68, H 2.60, N 9.21.

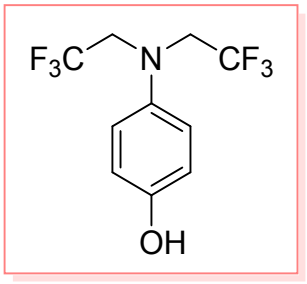
2.6. 4-Cyano-*N,N*-bis(2,2,2-trifluoroethyl)aniline (2f)



To a solution of TTFET (1.0 mmol) in DMF (3 mL) was added 4-aminobenzonitrile (1.0 mmol, 0.118 g) at 100 °C. The reaction mixture was stirred for 12 h.Then the reaction mixture was cooled down to room temperature and 30 ml of EtOAc, 30 ml of water were added. After separation of the organic layer from water, the aqueous phases were extracted with EtOAc (2 x 15 ml) again. The combined organic layers were then dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc 20:5 (v/v), to afford the title compound.

Yield: 78%. White solid. M.p. 132-134 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.76 - 7.68 (m, 4H), 4.83 (q, *J* = 9.0 Hz, 4H). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -73.54 (s). IR (KBr): 2948, 2919, 2851, 2229, 1594, 1416, 1262, 1175, 1118, 1018, 964, 869, 838, 814, 607, 592. Anal. calcd. for $C_{11}H_8F_6N_2$ (282.19): C 46.82, H 2.86, N 9.93. Found: C 46.75, H 2.80, N 9.84.

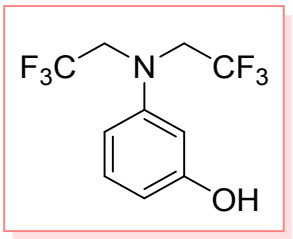
2.7. 4-Hydroxy-*N,N*-bis(2,2,2-trifluoroethyl)aniline (2g)



To a solution of TTFET (1.0 mmol) in THF (3 mL) was added 4-aminophenol (1.0 mmol, 0.109 g) at room temperature. The reaction mixture was stirred for 6 h. Then the reaction mixture was filtered, eluting with EtOAc (3 x 5 mL), and the filtrate was concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc 20:10 (v/v), to afford the title compound.

Yield: 90%. white solid. M.p. 273-275 °C. ^{1}H-NMR (250 MHz, $CDCl_3$) δ (ppm) 7.32 (d, *J* = 7.5 Hz, 2H), 7.23 - 7.21 (m, 1H), 6.86 (d, *J* = 7.5 Hz, 2H), 4.79 - 4.72 (m, 4H).^{13}C-NMR (75.5 MHz, DMSO-d_6) δ (ppm) 154.6, 129.6, 123.9 (q, *J* = 277.8 Hz), 123.8, 115.6, 62.9 (q, *J* = 37.0 Hz).^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -73.53 (s). IR (KBr): 3432, 2921, 2852, 1731, 1626, 1447, 1239, 1082, 878, 670. Anal. calcd. for $C_{10}H_9F_6NO$ (273.18): C 43.97, H 3.32, N 5.13. Found: C 43.91, H 3.24, N 5.04.

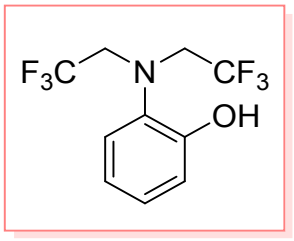
2.8. 3-Hydroxy-*N,N*-bis(2,2,2-trifluoroethyl)aniline (2h)



To a solution of TTFET (1.0 mmol) in THF (3 mL) was added 3-aminophenol (1.0 mmol, 0.109 g) at room temperature. The reaction mixture was stirred for 6 h. Then the reaction mixture was filtered, eluting with EtOAc (3 x 5 mL), and the filtrate was concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc 20:5 (v/v), to afford the title compound.

Yield: 91%. Yellow solid. M.p. 199-201 °C. ^{1}H-NMR (250 MHz, $CDCl_3$) δ (ppm) 7.31 (s, 1H),7.17 - 7.10 (m, 2H), 6.90 - 6.86 (m, 1H), 6.62 - 6.57 (m, 1H), 4.72 (q, *J* = 10.0 Hz, 4H). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -73.57 (d, *J* = 62.1 Hz). IR (KBr): 3430, 3240, 2966, 2926, 2854, 1558, 1496, 1424, 1394, 1271, 1167, 1109, 961, 859, 848, 806, 773, 680, 600. Anal. calcd. for $C_{10}H_9F_6NO$ (273.18): C 43.97, H 3.32, N 5.13. Found: C 43.90, H 3.24, N 5.02.

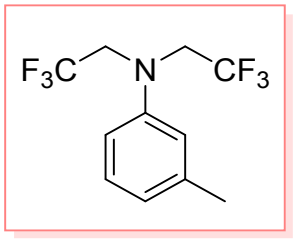
2.9. 2-Hydroxy-*N,N*-bis(2,2,2-trifluoroethyl)aniline (2i)



To a solution of TTFET (1.0 mmol) in THF (3 mL) was added 2-aminophenol (1.0 mmol, 0.109 g) at room temperature. The reaction mixture was stirred for 6 h. Then the reaction mixture was filtered, eluting with EtOAc (3 x 5 mL), and the filtrate was concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc 20:7 (v/v), to afford the title compound.

Yield: 85%. Orange solid. M.p. 191-193 ºC. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.67 (s, 1H), 7.60 (d, *J* = 9.0 Hz, 1H), 7.14 (dd, *J* = 9.0, 6.0 Hz, 1H), 7.04 - 6.93 (m, 2H), 4.82 (q, *J* = 9.0 Hz, 4H).^{13}C-NMR (75.5 MHz, DMSO-d_6) δ (ppm) 150.9, 139.6, 128.5 (q, *J* = 276.3 Hz), 125.0, 119.3, 116.2, 63.0 (q, *J* = 34.7 Hz).^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -73.58 (td, *J* = 42.4, 8.5 Hz). IR (KBr): 3404, 3354, 2922, 2853, 1567, 1439, 1271, 1174, 1122, 961, 864, 808, 751, 604. Anal. calcd. for $C_{10}H_9F_6NO$ (273.18): C 43.97, H 3.32, N 5.13. Found: C 43.91, H 3.24, N 5.01.

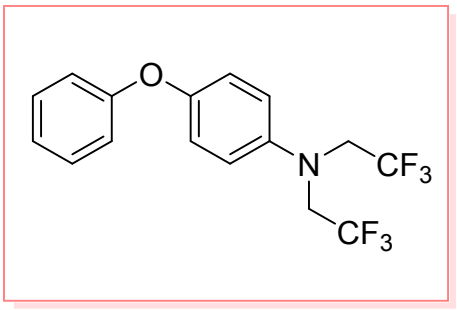
2.10. 3-Methyl-*N,N*-bis(2,2,2-trifluoroethyl)aniline (2j)



To a solution of TTFET (1.0 mmol) in DMF (3 mL) was added *m*-toluidine (1.0 mmol, 0.11 mL) at 100 °C. The reaction mixture was stirred for 6 h.Then the reaction mixture was cooled down to room temperature and 30 ml of EtOAc, 30 ml of water were added. After separation of the organic layer from water, the aqueous phases were extracted with EtOAc (2 x 15 ml) again. The combined organic layers were then dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc 20:8 (v/v), to afford the title compound.

Yield: 92%. Pink solid. M.p. 92-94 ºC. ^{1}H-NMR (250 MHz, $CDCl_3$) δ (ppm) 7.34 - 7.10 (m, 4H), 4.73 - 4.61 (m, 4H), 2.27 (s, 3H). ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ (ppm) 150.7, 139.9, 128.6, 124.0, 122.9 (q, *J* = 260.6 Hz), 121.6, 118.2, 63.1 (q, *J* = 42.5 Hz), 29.7. ^{19}FNMR (282.4 MHz, $CDCl_3$) δ (ppm) -73.56 (s). IR (KBr): 3280, 3135, 2968, 2922, 2851, 1593, 1418, 1398, 1266, 1236, 1162, 1122, 962, 852, 814, 782, 724, 689, 610. Anal. calcd. for $C_{11}H_{11}F_6N$ (271.21): C 48.72, H 4.09, N 5.16. Found: C 48.64, H 4.00, N 5.08.

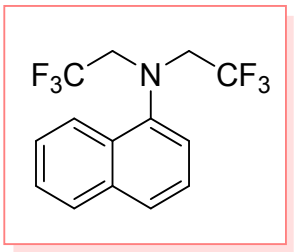
2.11. 4-*N,N*-bis(2,2,2-trifluoroethyl)aminodiphenylether (2k)



To a solution of TTFET (1.0 mmol) in THF (3 mL) was added 4-phenoxyaniline (1.0 mmol, 0.185 g) at room temperature. The reaction mixture was stirred for 8 h. Then the reaction mixture was filtered, eluting with EtOAc (3 x 5 mL), and the filtrate was concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc 20:4 (v/v), to afford the title compound.

Yield: 90%. Pale yellow solid. M.p. 108 - 110 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.48 (d, *J* = 9.0 Hz, 2H), 7.37 (dd, *J* = 9.0, 6.0 Hz, 2H), 7.14 (t, *J* = 9.0 Hz, 1H), 7.05 (d, *J* = 6.0 Hz, 4H), 4.79 (s, 4H). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ (ppm) 157.1, 150.3, 141.7, 129.8, 126.8 (q, *J* = 279.4 Hz), 123.4, 123.4, 119.3, 118.8, 63.3 (q, *J* = 41.5 Hz). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -73.58 (d, *J* = 53.6 Hz).IR (KBr): 3256, 2918, 2851, 1625, 1522, 1438, 1279, 1261, 1245, 1164, 1111, 1018, 962, 882, 856, 814, 759, 677. Anal. calcd. for $C_{16}H_{13}F_6NO$ (349.28): C 55.02, H 3.75, N 4.01. Found: C 54.94, H 3.67, N 3.96.

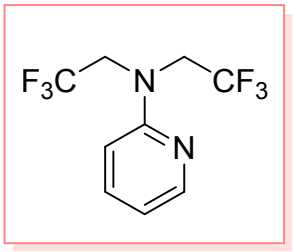
2.12. *N,N*-bis(2,2,2-trifluoroethyl)naphthalene-1-amine (2l)



To a solution of TTFET (1.0 mmol) in DMF (3 mL) was added 1-naphthyl amine (1.0 mmol, 0.143 g) at 100 °C. The reaction mixture was stirred for 10 h.Then the reaction mixture was cooled down to room temperature and 30 ml of EtOAc, 30 ml of water were added. After separation of the organic layer from water, the aqueous phases were extracted with EtOAc (2 x 15 ml) again. The combined organic layers were then dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc 20:1 (v/v), to afford the title compound.

Yield: 88%. Yellow solid. M.p. 136-138 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.98 - 7.76 (m, 7H), 4.14 (q, *J* = 9.0 Hz, 4H). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -73.47 (s). IR (KBr): 2922, 2852, 1717, 1635, 1456, 1158, 1065, 606, 592. Anal. calcd. for $C_{14}H_{11}F_6N$ (307.24): C 54.73, H 3.61, N 4.56. Found: C 54.64, H 3.55, N 4.51.

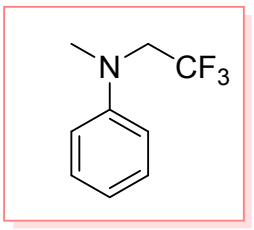
2.13. 2-*N,N*-bis(2,2,2-trifluoroethyl)aminopyridine (2m)



To a solution of TTFET (1.0 mmol) in DMF (3 mL) was added 2-amino pyridine (1.0 mmol, 0.094 g) at 100 °C. The reaction mixture was stirred for 12 h.Then the reaction mixture was cooled down to room temperature and 30 ml of EtOAc, 30 ml of water were added. After separation of the organic layer from water, the aqueous phases were extracted with EtOAc (2 x 15 ml) again. The combined organic layers were then dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc 20:9 (v/v), to afford the title compound.

Yield: 70%. White solid. M.p. 187-189 ºC. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.64 (s, 1H), 8.31 (s, 1H), 7.82 (dd, *J* = 9.0, 6.0 Hz, 1H), 7.12 (s, 1H), 4.84 (q, *J* = 9.0 Hz, 4H). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -73.55 (s). IR (KBr): 3123, 2972, 2930, 1603, 1582, 1540, 1428, 1396, 1374, 1310, 1266, 1232, 1166, 1134, 1098, 1056, 996, 960, 855, 813, 779, 761, 696, 628, 609. Anal. calcd. for $C_9H_8F_6N_2$ (258.17): C 41.87, H 3.12, N 10.85. Found: C 41.80, H 3.05, N 10.77.

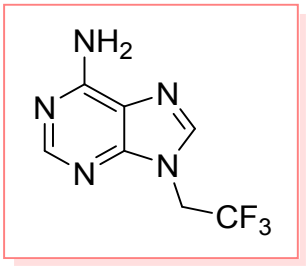
2.14. *N*-(2,2,2-trifluoroethyl)-*N*-methyl aniline (2n) [1]



To a solution of TTFET (1.0 mmol) in DMF (3 mL) was added *N*-methyl aniline (1.0 mmol, 0.11 mL) at 100 °C. The reaction mixture was stirred for 6 h.Then the reaction mixture was cooled down to room temperature and 30 ml of EtOAc, 30 ml of water were added. After separation of the organic layer from water, the aqueous phases were extracted with EtOAc (2 x 15 ml) again. The combined organic layers were then dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc 20:4 (v/v), to afford the title compound.

Yield: 92%. Pale yellow oil.^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.36 - 7.28 (m, 5H), 4.52 - 4.49 (m, 2H), 3.56 (s, 3H). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -73.63 (s). IR (KBr): 2919, 2851, 2527, 2135, 1715, 1632, 1448, 1271, 1091, 892, 720, 666. Anal. calcd. for $C_9H_{10}F_3N$ (189.18): C 57.14, H 5.33, N 7.40. Found: C 57.06, H 5.24, N 7.32.

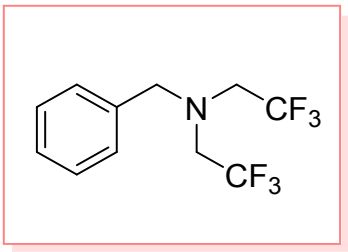
2.15. 9-(2,2,2-trifluoroethyl)adenine (2o)



To a solution of TTFET (1.0 mmol) in DMF (3 mL) was added adenine(1.0 mmol, 0.135 g) at 100 °C. The reaction mixture was stirred for 12 h.Then the reaction mixture was cooled down to room temperature and 30 ml of EtOAc, 30 ml of water were added. After separation of the organic layer from water, the aqueous phases were extracted with EtOAc (2 x 15 ml) again. The combined organic layers were then dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with EtOAc/EtOH 20:2 (v/v), to afford the title compound.

Yield: 67%. White solid. M.p. 371-373 ^oC. ^1H-NMR (300 MHz, DMSO-d_6) δ (ppm) 8.56 (s, 1H), 8.37 (s, 1H), 4.96 (q, *J* = 9.0 Hz, 2H), 1.10 (s, 2H). ^{19}F NMR (282.4 MHz, DMSO-d_6) δ (ppm) -67.67 (s). IR (KBr): 3415, 3188, 2922, 2846, 1606, 1479, 1374, 1311, 1278, 1166, 1138, 959, 878, 856, 804, 604. Anal. calcd. for $C_7H_6F_3N_5$ (217.16): C 38.72, H 2.79, N 32.25. Found: C 38.66, H 2.72, N 32.18.

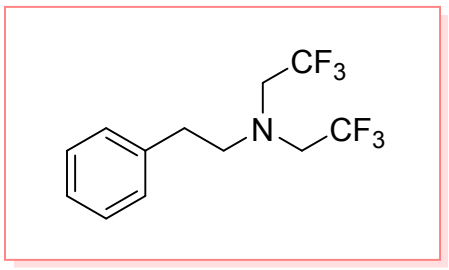
2.16. Benzyl-*N,N*-bis(2,2,2-trifluoroethyl)amine (2p)



To a solution of TTFET (1.0 mmol) in DMF (3 mL) was added benzyl amine(1.0 mmol, 0.11 mL) at 100 °C. The reaction mixture was stirred for 7 h.Then the reaction mixture was cooled down to room temperature and 30 ml of EtOAc, 30 ml of water were added. After separation of the organic layer from water, the aqueous phases were extracted with EtOAc (2 x 15 ml) again. The combined organic layers were then dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc 20:7 (v/v), to afford the title compound.

Yield: 87%. White solid. M.p. 153-155 ^oC. ^1H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.35 - 7.28 (m, 5H), 4.75 - 4.63 (m, 4H), 3.15 (s, 2H). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -73.63 (s). IR (KBr): 3262, 3114, 3031, 2966, 1599, 1570, 1520, 1404, 1359, 1266, 1248, 1172, 1092, 1061, 1019, 958, 854, 807, 736, 720, 698, 610. Anal. calcd. for $C_{11}H_{11}F_6N$ (271.21): C 48.72, H 4.09, N 5.16. Found: C 48.63, H 4.01, N 5.08.

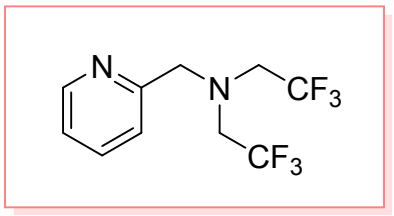
2-Phenylethyl-*N,N*-bis(2,2,2-trifluoroethyl)amine (2q)



To a solution of TTFET (1.0 mmol) in DMF (3 mL) was added 2-phenylethylamine (1.0 mmol, 0.126 mL) at 100 °C. The reaction mixture was stirred for 8 h. Then the reaction mixture was cooled down to room temperature and 30 ml of EtOAc, 30 ml of water were added. After separation of the organic layer from water, the aqueous phases were extracted with EtOAc (2 x 15 ml) again. The combined organic layers were then dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc20:3 (v/v), to afford the title compound.

Yield: 89%. Yellow oil.^{1}H-NMR (250 MHz, $CDCl_3$) δ (ppm) 7.31 – 7.27 (m, 2H), 7.23 – 7.16 (m, 3H), 4.70 – 4.44 (m, 8H). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -73.69 (d, *J* = 45.2 Hz). IR (KBr): 2980, 2840, 2516, 2123, 1606, 1440, 1273, 1250, 1168, 962, 900, 871, 816, 686. Anal. calcd. for $C_{12}H_{13}F_6N$ (285.23): C 50.53, H 4.59, N 4.91. Found: C 50.46, H 4.51, N 4.85.

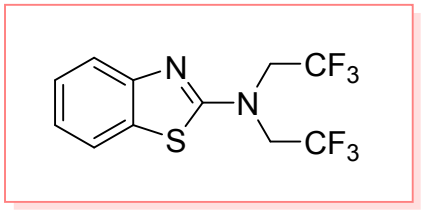
2-*N,N*-bis(2,2,2-trifluoroethyl)(aminomethyl) pyridine (2r)



To a solution of TTFET (1.0 mmol) in DMF (3 mL) was added 2-(aminomethyl) pyridine (1.0 mmol, 0.102 mL) at 100 °C. The reaction mixture was stirred for 8 h. Then the reaction mixture was cooled down to room temperature and 30 ml of EtOAc, 30 ml of water were added. After separation of the organic layer from water, the aqueous phases were extracted with EtOAc (2 x 15 ml) again. The combined organic layers were then dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc20:8(v/v), to afford the title compound.

Yield: 84%. Yellow oil.^{1}H-NMR (250 MHz, $CDCl_3$) δ (ppm) 8.60 – 8.57 (m, 1H), 8.25 – 8.21 (m, 1H), 7.92 – 7.85 (m, 1H), 7.53 – 7.48 (m, 1H), 5.43 (s, 2H), 4.82 (q, *J* = 10.0 Hz, 4H). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -73.66 (d, *J* = 50.8 Hz). IR (KBr): 3025, 2947, 1616, 1433, 1273, 1171, 1000, 960, 912, 857, 839, 816, 765, 750, 720, 702, 596. Anal. calcd. for $C_{10}H_{10}F_6N_2$ (272.19): C 44.13, H 3.70, N 10.29. Found: C 44.05, H 3.62, N 10.22.

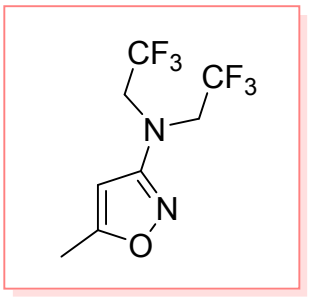
2-*N,N*-bis(2,2,2-trifluoroethyl)aminobenzothiazole (2s)



To a solution of TTFET (1.0 mmol) in DMF (3 mL) was added 2-aminobenzothiazole (1.0 mmol, 0.150 g) at 100 °C. The reaction mixture was stirred for 10 h. Then the reaction mixture was cooled down to room temperature and 30 ml of EtOAc, 30 ml of water were added. After separation of the organic layer from water, the aqueous phases were extracted with EtOAc (2 x 15 ml) again. The combined organic layers were then dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc20:6(v/v), to afford the title compound.

Yield: 86%. Yellow solid.M.p. 176-178 °C.^{1}H-NMR (250 MHz, $CDCl_3$) δ (ppm) 7.85 (d, *J* = 10.0 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.51 - 7.49 (m, 2H), 4.82 (q, *J* = 10.0 Hz, 4H). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -73.49 (s). IR (KBr): 2925, 2856, 1719, 1597, 1464, 1269, 1198, 1169, 1132, 962, 810, 751, 596. Anal. calcd. for $C_{11}H_8F_6N_2S$ (314.25): C 42.04, H 2.57, N 8.91. Found: C 41.97, H 2.51, N 8.83.

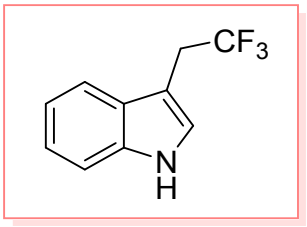
5-Methyl-*N,N*-bis(2,2,2-trifluoroethyl)isoxazole-3-amine (2t)



To a solution of TTFET (1.0 mmol) in DMF (3 mL) was added 3-amino-5-methylisoxazole (1.0 mmol, 0.098 g) at 100 °C. The reaction mixture was stirred for 7 h. Then the reaction mixture was cooled down to room temperature and 30 ml of EtOAc, 30 ml of water were added. After separation of the organic layer from water, the aqueous phases were extracted with EtOAc (2 x 15 ml) again. The combined organic layers were then dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc20:5(v/v), to afford the title compound.

Yield: 87%. Yellow solid.M.p. 119-121 °C.^{1}H-NMR (250 MHz, $CDCl_3$) δ (ppm) 6.69 (s, 1H), 4.74 (q, *J* = 10.0 Hz, 4H), 2.39 (s, 3H). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -73.55 (s). IR (KBr): 2959, 2925, 2854, 1583, 1430, 1270, 1165, 1117, 959, 937, 872, 814, 687, 596. Anal. calcd. for $C_8H_8F_6N_2O$ (262.16): C 36.65, H 3.08, N 10.69. Found: C 36.58, H 3.01, N 10.62.

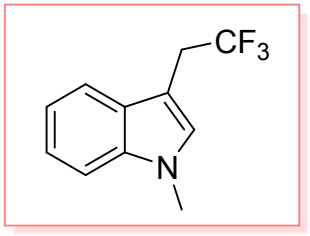
2.17. 3-(2,2,2-Trifluoroethyl)-1*H*-indole (2u) [2]



To a solution of TTFET (1.0 mmol) in DMF (3 mL) was added indole(1.0 mmol, 0.117 g) at 100 °C. The reaction mixture was stirred for 12 h.Then the reaction mixture was cooled down to room temperature and 30 ml of EtOAc, 30 ml of water were added. After separation of the organic layer from water, the aqueous phases were extracted with EtOAc (2 x 15 ml) again. The combined organic layers were then dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc 20:7 (v/v), to afford the title compound.

Yield: 65%. Brownish red solid. M.p. 55-57 °C. ^{1}H-NMR (250 MHz, $CDCl_3$) δ (ppm) 7.92 (s, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 2H), 6.95 (s, 1H), 4.26 - 4.25 (m, 2H). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -63.00 (s). IR (KBr): 3400, 3056, 2955, 2852, 1709, 1612, 1459, 1378, 1340, 1214, 1153, 1126, 1021, 894, 823, 742, 703. Anal. calcd. for $C_{10}H_8F_3N$ (199.18): C 60.30, H 4.05, N 7.03. Found: C 60.23, H 4.00, N 6.95.

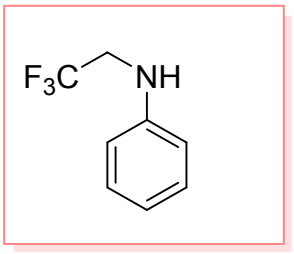
1-Methyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (2v)[2]



To a solution of TTFET (1.0 mmol) in DMF (3 mL) was added 1-methylindole (1.0 mmol, 0.125 mL) at 100 °C. The reaction mixture was stirred for 12 h. Then the reaction mixture was cooled down to room temperature and 30 ml of EtOAc, 30 ml of water were added. After separation of the organic layer from water, the aqueous phases were extracted with EtOAc (2 x 15 ml) again. The combined organic layers were then dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc20:3(v/v), to afford the title compound.

Yield: 74%. Yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.74 - 7.60 (m, 4H), 6.93 (s, 1H), 4.14 (q, *J* = 9.0 Hz, 2H), 3.91 (s, 3H). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -63.89 (s). IR (KBr): 2926, 2857, 2512, 2133, 1627, 1392, 1098, 878, 673, 605. Anal. calcd. for $C_{11}H_{10}F_3N$ (213.20): C 61.97, H 4.73, N 6.57. Found: C 61.91, H 4.65, N 6.49.

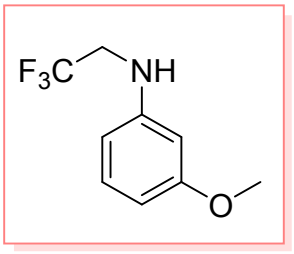
2.18. *N*-(2,2,2-Trifluoroethyl)aniline (3a) [3]



To a solution of TTFET (0.6 mmol) in THF (3 mL) was added aniline (1.0 mmol, 0.09 mL) at room temperature. The reaction mixture was stirred for 6 h. Then the reaction mixture was filtered, eluting with EtOAc (3 x 5 mL), and the filtrate was concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc 20:5 (v/v), to afford the title compound.

Yield: 79%. Yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.52 (d, *J* = 7.5 Hz, 2H), 7.27 (dd, *J* = 10.0, 7.5 Hz, 2H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.85 (s, 1H), 4.68 (q, *J* = 10.0 Hz, 2H). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -73.57 (s). IR (KBr): 3283, 2919, 2851, 1594, 1558, 1418, 1398, 1266, 1237, 1162, 1089, 1066, 962, 860, 814, 755, 723, 689, 610. Anal. calcd. for $C_8H_8F_3N$ (175.15): C 54.86, H 4.60, N 8.00. Found: C 54.79, H 4.52, N 7.91.

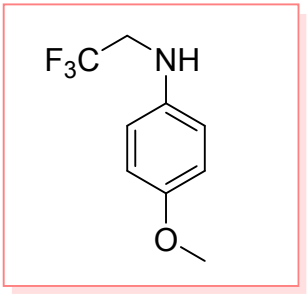
2.19. 3-Methoxy-*N*-(2,2,2-trifluoroethyl)aniline (3b) [1]



To a solution of TTFET (0.6 mmol) in DMF (3 mL) was added *m*-anisidine (1.0 mmol, 0.11 mL) at 100 °C. The reaction mixture was stirred for 8 h.Then the reaction mixture was cooled down to room temperature and 30 ml of EtOAc, 30 ml of water were added. After separation of the organic layer from water, the aqueous phases were extracted with EtOAc (2 x 15 ml) again. The combined organic layers were then dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc 20:5 (v/v), to afford the title compound.

Yield: 72%. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.43 (s, 1H), 7.24 - 7.21 (m, 1H), 7.04 (d, *J* = 9.0 Hz, 1H), 6.98 (s, 1H), 6.64 (d, *J* = 9.0 Hz, 1H), 4.76 (q, *J* = 9.0 Hz, 2H), 3.83 (s, 3H).^{13}C-NMR (75.5 MHz, $CDCl_3$) δ (ppm) 160.1, 139.8, 129.5, 119.0 (q, *J* = 273.3 Hz), 112.2, 108.8, 105.9, 62.5 (q, *J* = 37.0 Hz), 55.2.^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -73.56 (t, *J* = 8.5 Hz). IR (KBr): 3286, 3137, 2926, 1595, 1418, 1374, 1269, 1204, 1161, 1120, 1074, 1026, 962, 868, 856, 806, 766, 607. Anal. calcd. for $C_9H_{10}F_3NO$ (205.18): C 52.68, H 4.91, N 6.83. Found: C 52.61, H 4.83, N 6.74.

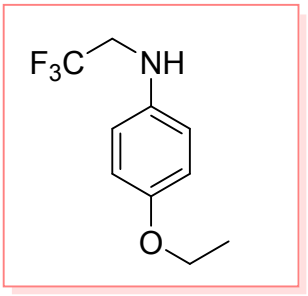
2.20. 4-Methoxy-*N*-(2,2,2-trifluoroethyl)aniline (3c) [3]



To a solution of TTFET (0.6 mmol) in THF (3 mL) was added *p*-anisidine (1.0 mmol, 0.123 g) at room temperature. The reaction mixture was stirred for 5 h. Then the reaction mixture was filtered, eluting with EtOAc (3 x 5 mL), and the filtrate was concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc 20:7 (v/v), to afford the title compound.

Yield: 75%. Pale yellow oil.^{1}H-NMR (250 MHz, $CDCl_3$) δ (ppm) 7.47 - 7.43 (m, 2H), 6.90 - 6.85 (m, 3H), 4.78 - 4.67 (m, 2H), 3.79 (s, 3H). ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ (ppm) 149.2, 138.3, 124.3 (q, *J* = 276.2 Hz), 114.0, 58.0 (q, *J* = 33.1 Hz), 55.5. ^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -73.47 (s). IR (KBr): 3258, 3132, 3033, 2952, 2924, 2850, 1611, 1592, 1558, 1516, 1406, 1366, 1253, 1230, 1180, 1154, 1121, 1075, 1037, 1016, 957, 825, 805, 780, 756, 729. Anal. calcd. for $C_9H_{10}F_3NO$ (205.18): C 52.68, H 4.91, N 6.83. Found: C 52.59, H 4.84, N 6.75.

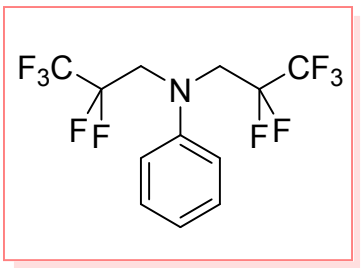
2.21. 4-Ethoxy-*N*-(2,2,2-trifluoroethyl)aniline (3d)



To a solution of TTFET (0.6 mmol) in THF (3 mL) was added 4-ethoxy aniline (1.0 mmol, 0.13 mL) at room temperature. The reaction mixture was stirred for 7 h. Then the reaction mixture was filtered, eluting with EtOAc (3 x 5 mL), and the filtrate was concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc 20:4 (v/v), to afford the title compound.

Yield: 76%. Yellow solid. M.p. 128-130 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.37 (d, *J* = 10.0 Hz, 2H), 6.83 - 6.76 (m, 3H), 4.66 (q, *J* = 10.0 Hz, 2H), 3.95 (q, *J* = 7.5 Hz, 2H), 1.34 (t, *J* = 7.5 Hz, 3H). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -73.49 (s). IR (KBr): 3284, 3138, 2926, 2854, 1592, 1558, 1510,1407, 1259, 1242, 1166, 1120, 1076, 1051, 1026, 962, 926, 866, 826, 805, 710, 600. Anal. calcd. for $C_{10}H_{12}F_3NO$ (219.20): C 54.79, H 5.52, N 6.39. Found: C 54.71, H 5.44, N 6.31.

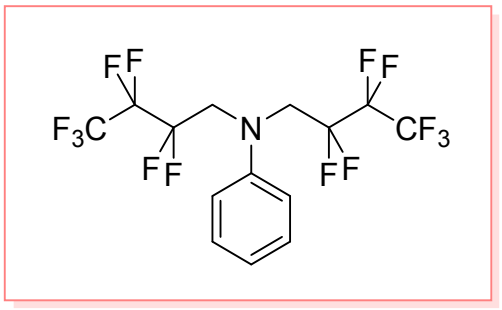
2.22. *N,N*-bis(2,2,3,3,3-pentafluoropropyl)aniline (4a)



Into a canonical flask (25 mL), a mixture of 2,2,3,3,3-pentafluoro-1-propanol (3.0 mmol, 0.3 mL), and sodium hydride (3.3 mmol, 0.079 g) was stirred in THF (5 mL) for 1.50 h at room temperature. Then cyanuric chloride (1.0 mmol, 0.184 g) was added and the reaction media was refluxed for 5 h. The reaction was then allowed to cool down to room temperature. The precipitate was filtered, washed with THF and dried in vacuum to afford the product 2,4,6-tris(2,2,3,3,3-pentafluoropropoxy)-1,3,5-triazine as white solid.
To a solution of 2,4,6-tris(2,2,3,3,3-pentafluoropropoxy)-1,3,5-triazine (1.0 mmol) in THF (3 mL) was added aniline (1.0 mmol, 0.09 mL) at 50 °C. The reaction mixture was stirred for 12 h.The reaction was then allowed to cool down to room temperature.Then the reaction mixture was filtered, eluting with EtOAc (3 x 5 mL), and the filtrate was concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc20:5 (v/v), to afford the title compound.

Yield: 72%. Yellow solid. M.p. 147-149 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.53 (d, *J* = 9.0 Hz, 2H), 7.40 (t, *J* = 9.0 Hz, 2H), 7.21 (t, *J* = 9.0 Hz, 1H), 4.89 (t, *J* = 15.0 Hz, 4H). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -83.66 (s), -123.44 _ -123.59 (m). IR (KBr): 2952, 2918, 2844, 1627, 1457, 1362, 1204, 1162, 1100, 1050, 998, 973, 809, 720, 677. Anal. calcd. for $C_{12}H_9F_{10}N$ (357.20): C 40.35, H 2.54, N 3.92. Found: C 40.28, H 2.46, N 3.85.

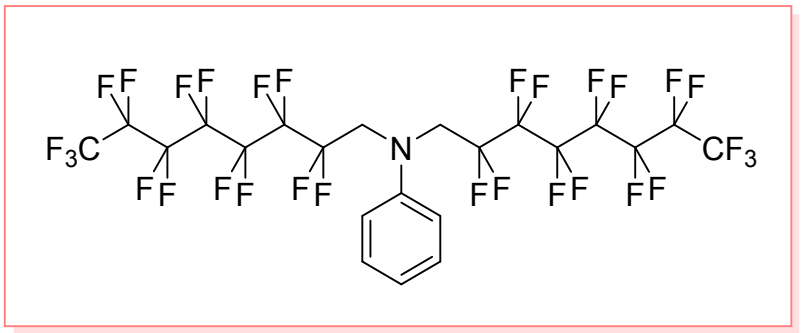
2.23. *N,N*-bis(2,2,3,3,4,4,4-heptafluorobutyl)aniline (4b)



Into a canonical flask (25 ml), a mixture of 2,2,3,3,4,4,4-heptafluoro-1-butanol (3.0 mmol, 0.36 ml), and sodium hydride (3.3 mmol, 0.079 g) was stirred in THF (5 ml) for 1.50 h at room temperature. Then cyanuric chloride (1.0 mmol, 0.184 g)was added and the reaction media was refluxed for 5 h. The reaction was then allowed to cool down to room temperature. The precipitate was filtered, washed with THF and dried in vacuum to afford the product 2,4,6-tris(2,2,3,3,4,4,4-heptafluorobutoxy)-1,3,5-triazine as white solid.
To a solution of 2,4,6-tris(2,2,3,3,4,4,4-heptafluorobutoxy)-1,3,5-triazine (1.0 mmol) in THF (3 mL) was added aniline (1.0 mmol, 0.09 mL) at 50°C. The reaction mixture was stirred for 12 h.The reaction was then allowed to cool down to room temperature. Then the reaction mixture was filtered, eluting with EtOAc (3 x 5 mL), and the filtrate was concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc20:5 (v/v), to afford the title compound.

Yield: 71%. Yellow solid. M.p. 63-65 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.53 (d, *J* = 9.0 Hz, 2H), 7.40 (dd, *J* = 9.0, 6.0 Hz, 2H), 7.21 (t, *J* = 9.0 Hz, 1H), 4.93 (t, *J* = 12.0 Hz, 4H). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -80.79 (s), -120.54 (s), -127.54 ~ -127.65 (m). IR (KBr): 3275, 2955, 2924, 2846, 1611, 1593, 1437, 1347, 1230, 1184, 1123, 1020, 956, 912, 842, 808, 749, 689. Anal. calcd. for $C_{14}H_9F_{14}N$ (457.21): C 36.78, H 1.98, N 3.06. Found: C 36.69, H 1.91, N 2.97.

2.24. *N,N*-bis(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)aniline (4c)

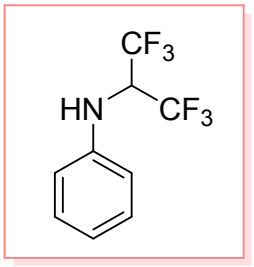


Into a canonical flask (25 ml), a mixture of 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-octanol (3.0 mmol, 1.2 g), and sodium hydride (3.3 mmol, 0.079 g) were stirred in THF (5 ml) for 1.50 h at room temperature. Then cyanuric chloride (1.0 mmol, 0.184 g)was added and the reaction media was refluxed for 5 h. The reaction was then allowed to cool down to room temperature. The precipitate was filtered, washed with THF and dried in vacuum to afford the product 2,4,6-tris(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctoxy)-1,3,5-triazine as white solid.
To a solution of 2,4,6-tris(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctoxy)-1,3,5-triazine (1.0 mmol) in DMF (3 mL) was added aniline (1.0 mmol, 0.09 mL) at 100 °C. The reaction mixture was stirred for 18 h.Then the reaction mixture was cooled down to room temperature and 30 ml of EtOAc, 30 ml of water were added. After separation of the organic layer from water, the aqueous phases were extracted with EtOAc (2 x 15 ml) again. The combined organic layers were then dried over anhydrous Na_2SO_4, filtered and

concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc 20:3 (v/v), to afford the title compound.

Yield: 65%. Yellow solid. M.p. 109-111 ºC. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.53 (d, *J* = 6.0 Hz, 2H), 7.40 (dd, *J* = 9.0, 6.0 Hz, 2H), 7.21 (t, *J* = 9.0 Hz, 1H), 4.95 (t, *J* = 12.0 Hz, 4H). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -80.70 (s), -119.47 (s), -121.94 (s), -122.73 (s), -123.28 (s), -126.14 (s).IR (KBr): 3310, 3137, 2979, 1633, 1601, 1451, 1424, 1358, 1330, 1312, 1234, 1205, 1146, 1107, 1033, 1008, 949, 884, 810, 755, 722, 702, 666. Anal. calcd. for $C_{22}H_9F_{30}N$ (857.27): C 30.82, H 1.06, N 1.63. Found: C 30.75, H 1.01, N 1.55.

2.25. *N*-(1,1,1,3,3,3-hexafluoropropyl)aniline (4d)

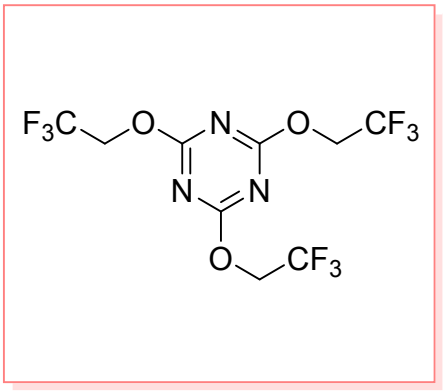


Into a canonical flask (25 ml), a mixture of 1,1,1,3,3,3-hexafluoro-2-propanol (3.0 mmol, 0.3 ml), and sodium hydride (3.3 mmol, 0.079 g) were stirred in THF (5 ml) for 1.50 h at room temperature. Then cyanuric chloride (1.0 mmol, 0.184 g)was added and the reaction media was refluxed for 5 h. The reaction was then allowed to cool down to room temperature. The precipitate was filtered, washed with THF and dried in vacuum to afford the product 2,4,6-tris(1,1,1,3,3,3-hexafluoro-2-propoxy)-1,3,5-triazine as pale yellow solid.

To a solution of 2,4,6-tris(1,1,1,3,3,3-hexafluoro-2-propoxy)-1,3,5-triazine (0.6 mmol) in DMF (3 mL) was added aniline (1.0 mmol, 0.09 mL) at 100 °C. The reaction mixture was stirred for 10 h.Then the reaction mixture was cooled down to room temperature and 30 ml of EtOAc, 30 ml of water were added. After separation of the organic layer from water, the aqueous phases were extracted with EtOAc (2 x 15 ml) again. The combined organic layers were then dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography, eluting with hexane/EtOAc 20:2 (v/v), to afford the title compound.

Yield: 68%. Pale yellow solid. M.p. 154-156 ºC. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.59 (d, *J* = 6.0 Hz, 2H), 7.36 (dd, *J* = 9.0, 6.0 Hz, 2H), 7.14 - 7.09 (m, 2H), 6.35 (sep, *J* = 6.0 Hz, 1H). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ (ppm) -72.99 (s).IR (KBr): 3442, 3048, 2966, 2846, 1617, 1544, 1428, 1261, 1230, 1130, 1108, 912, 856, 804, 756, 691. Anal. calcd. for $C_9H_7F_6N$ (243.15): C 44.46, H 2.90, N 5.76. Found: C 44.37, H 2.82, N 5.68.

2.26. 2,4,6-tris(2,2,2-trifluoroethoxy)-1,3,5-triazine (TTFET)



Yield: 90%. White solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 4.04 (q, *J* = 7.5 Hz).^{13}C-NMR (75.5 MHz, $CDCl_3$) δ (ppm) 167.6, 117.6 (q, *J* = 277.8 Hz), 59.4 (q, *J* = 37.8 Hz). IR (KBr): 2919, 2851, 1592, 1526, 1425, 1266, 1238, 1163, 1024, 962, 809, 754, 678.Anal. calcd. for $C_9H_6F_9N_3O_3$ (375.15): C 28.81, H 1.61, N 11.20. Found: C 28.73, H 1.54, N 11.13.

3. References

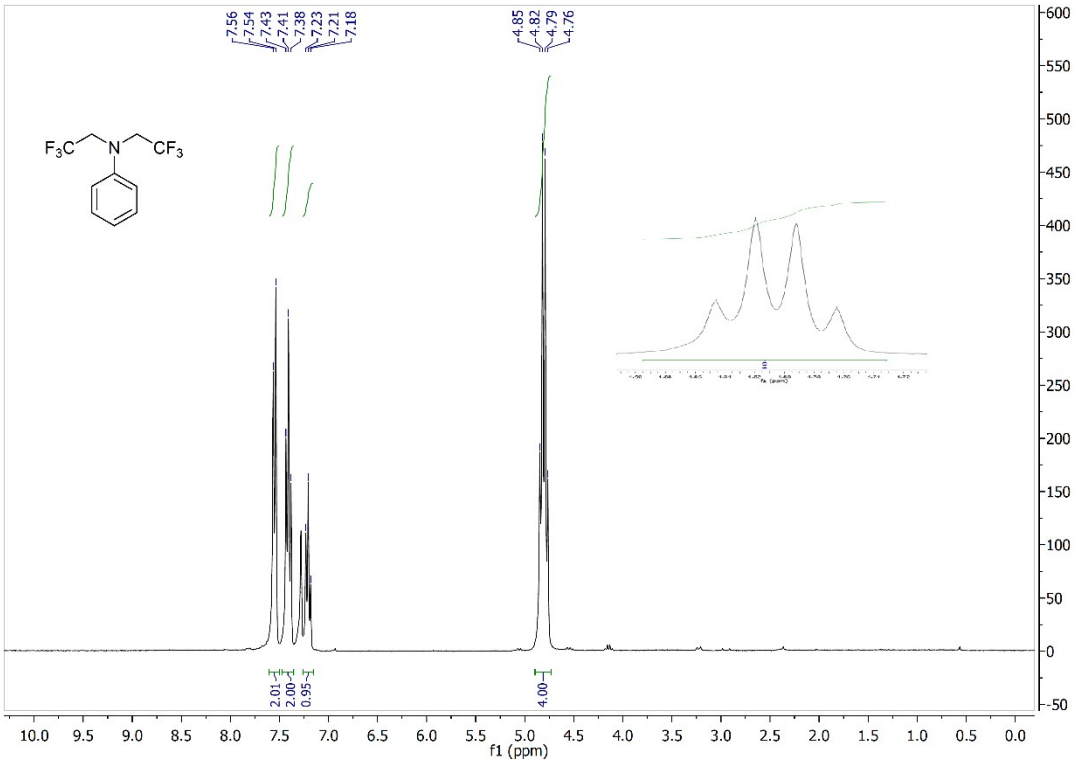
[1] H. Mimura, K. Kawada, T. Yamashita, T. Sakamoto, Y. Kikugawa, *J. Fluor. Chem.* **2010**, *131*, 477-486.

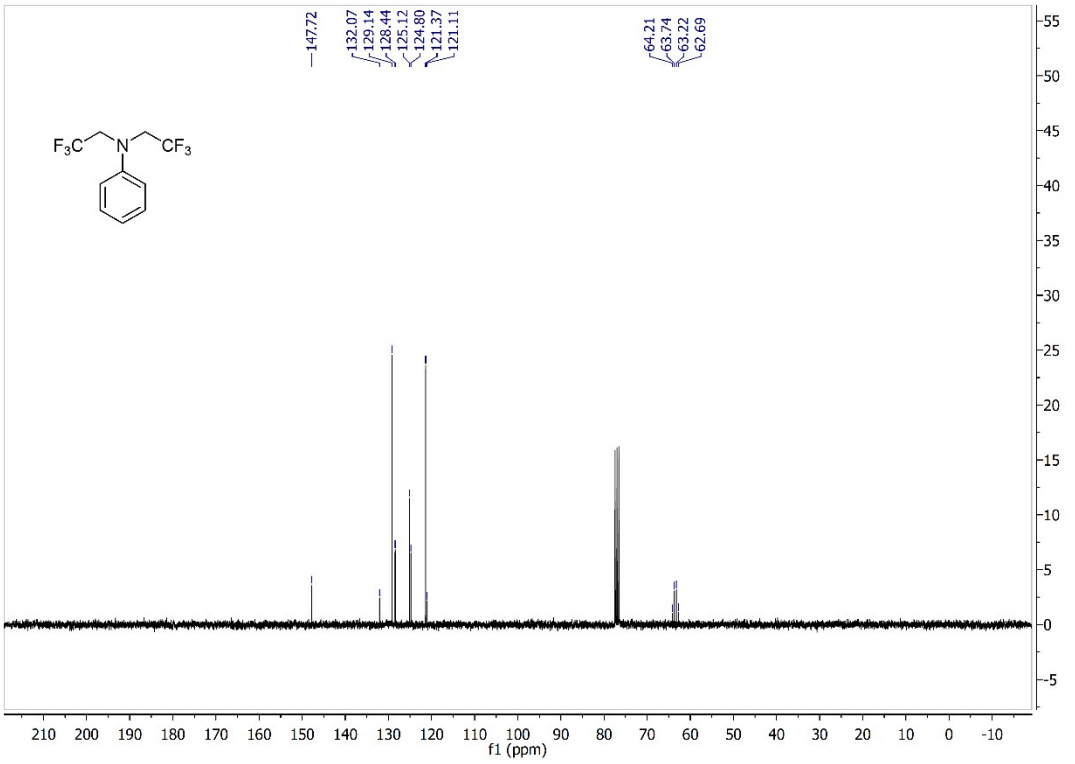
[2] G. L. Tolnai, A. Szekely, Z. Mako, T. Gati, J. Daru, T. Bihari, A. Stirling and Z. Novak, *Chem. Commun.* **2015**, *51*, 4488-4491.

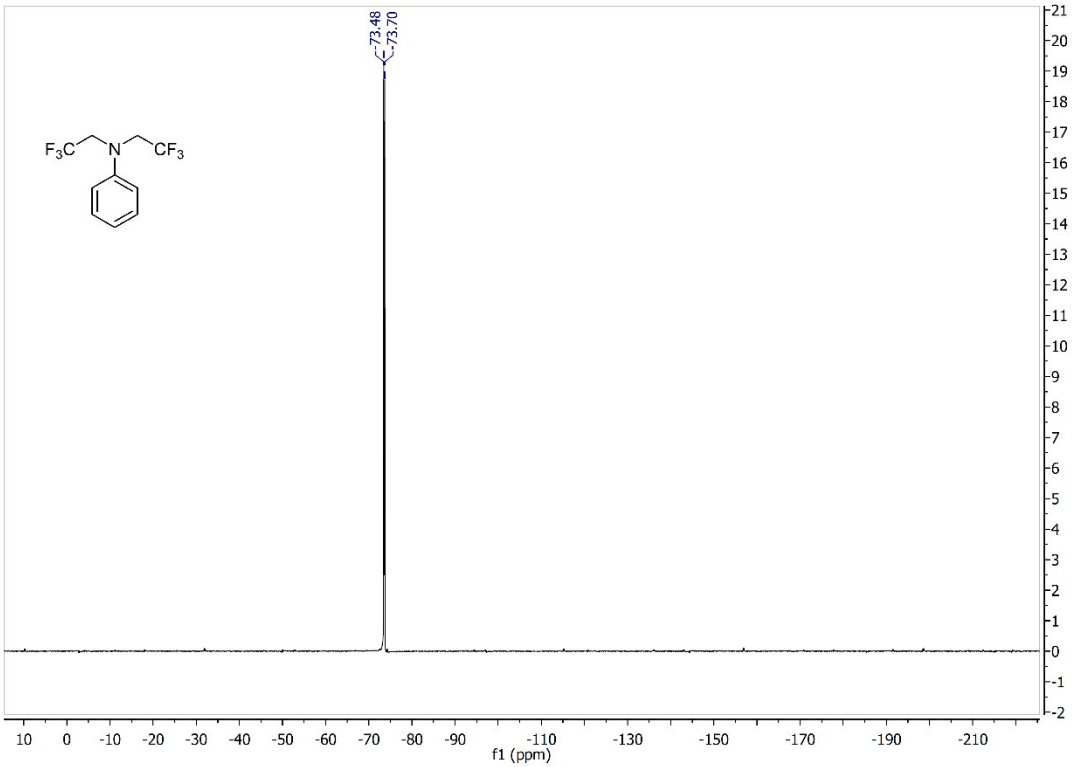
[3] H. Luo, G. Wu, Y. Zhang, J. Wang, *Angew. Chem. Int. Ed.* **2015**, *54*, 14503-14507.

4. Copy of FT-IR, ^{1}HNMR, ^{13}CNMR and ^{19}FNMR of synthesized compounds

N,N-bis(2,2,2-trifluoroethyl)aniline (2a)



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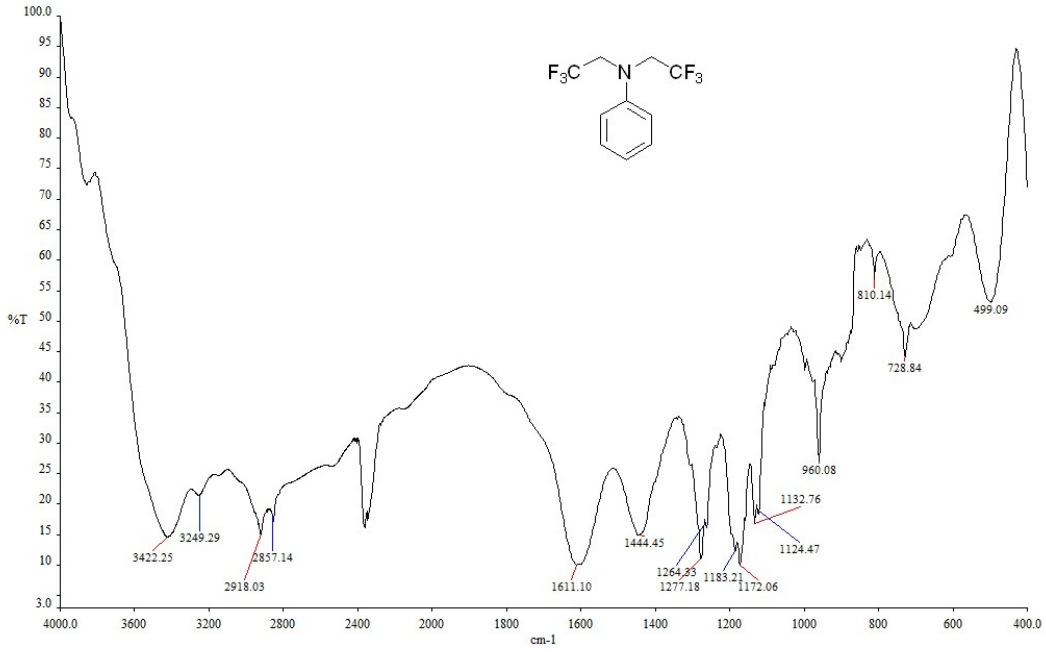
-73.70
F3C
N
CF3
f1 (ppm)


F3C
N
CF3
%T
cm-1
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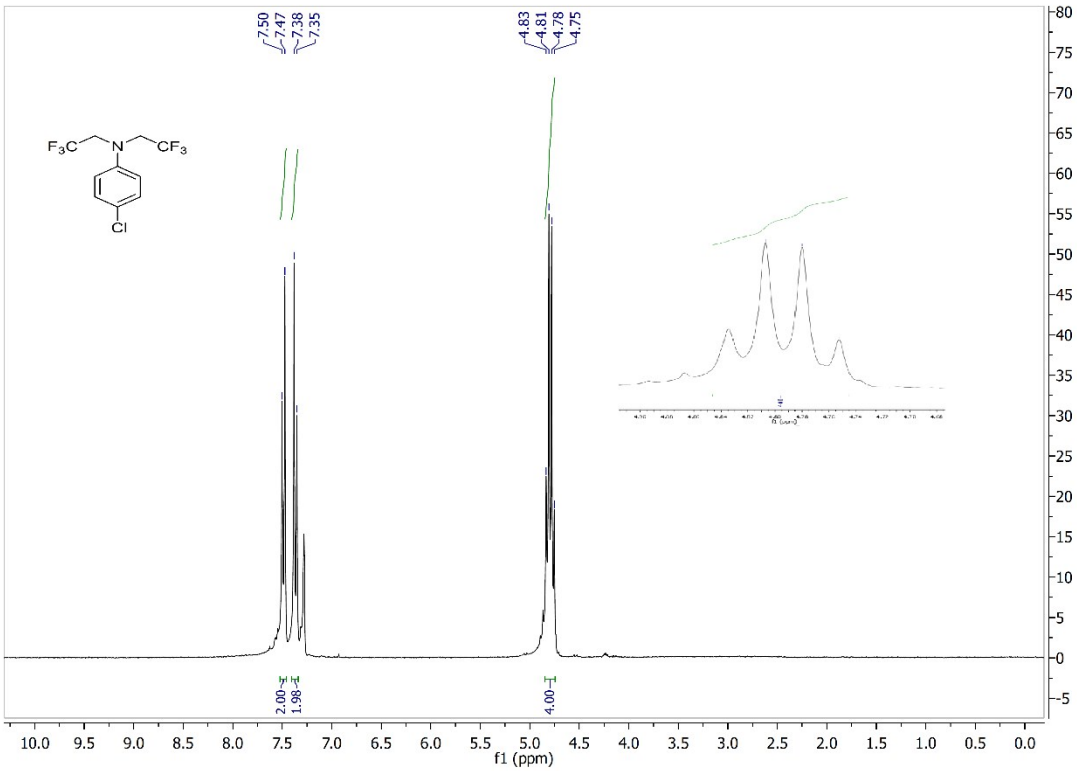
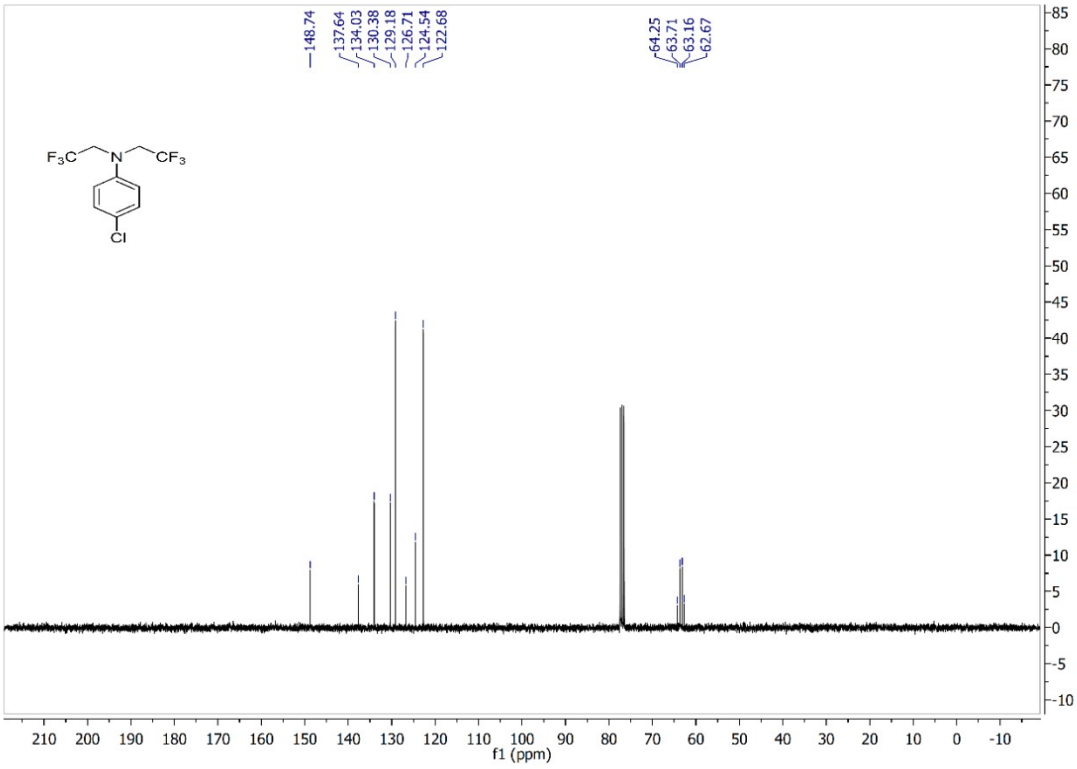
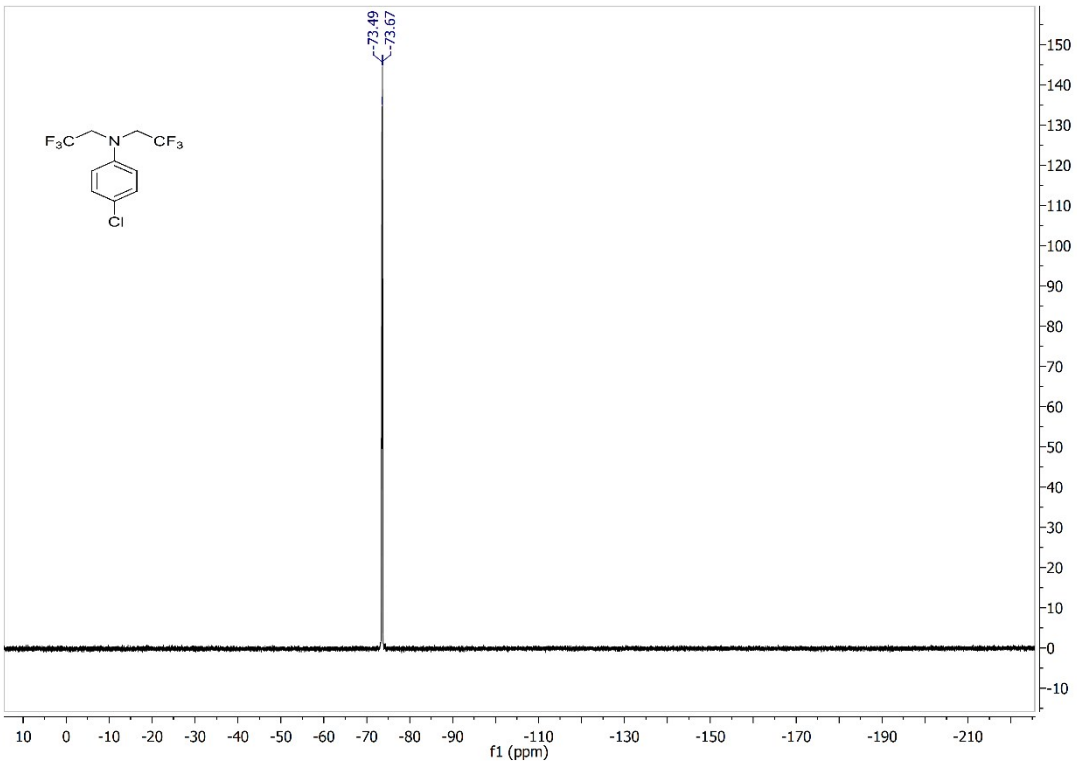
3249.29
2918.03
2857.14
1611.10
1444.45
1277.18
1264.33
1183.21
1172.06
1132.76
1124.47
960.08
810.14
728.84
499.09

4-Chloro-*N,N*-bis(2,2,2-trifluoroethyl)aniline (2b)



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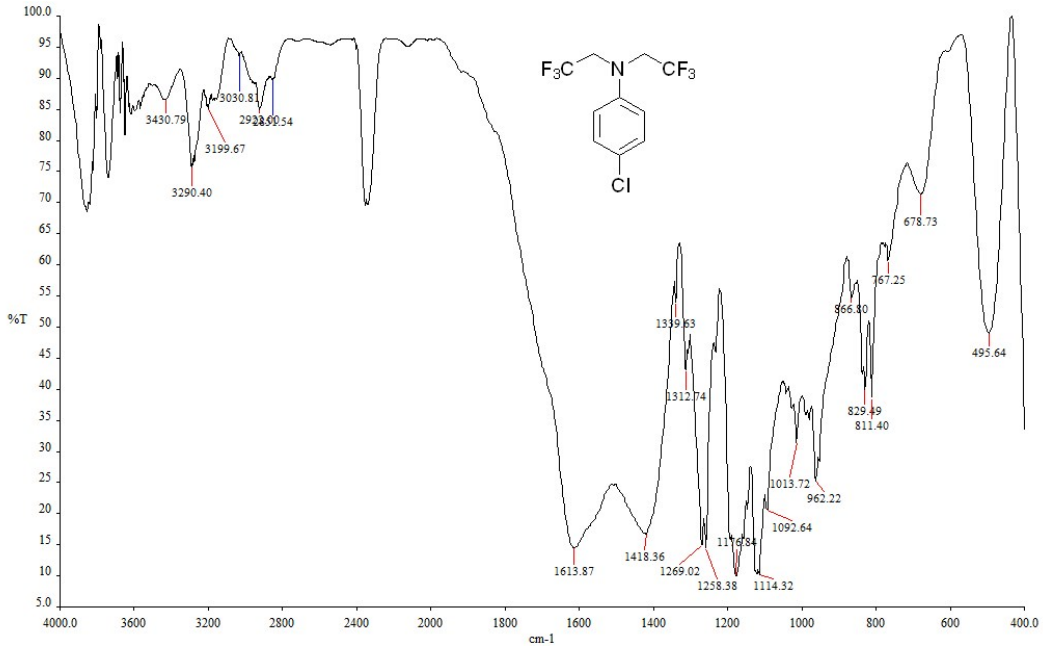
-73.67
F3C
N
CF3
Cl
f1 (ppm)


%T
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3030.81
3199.67
3290.40
1613.87
1418.36
1339.63
1312.74
1269.02
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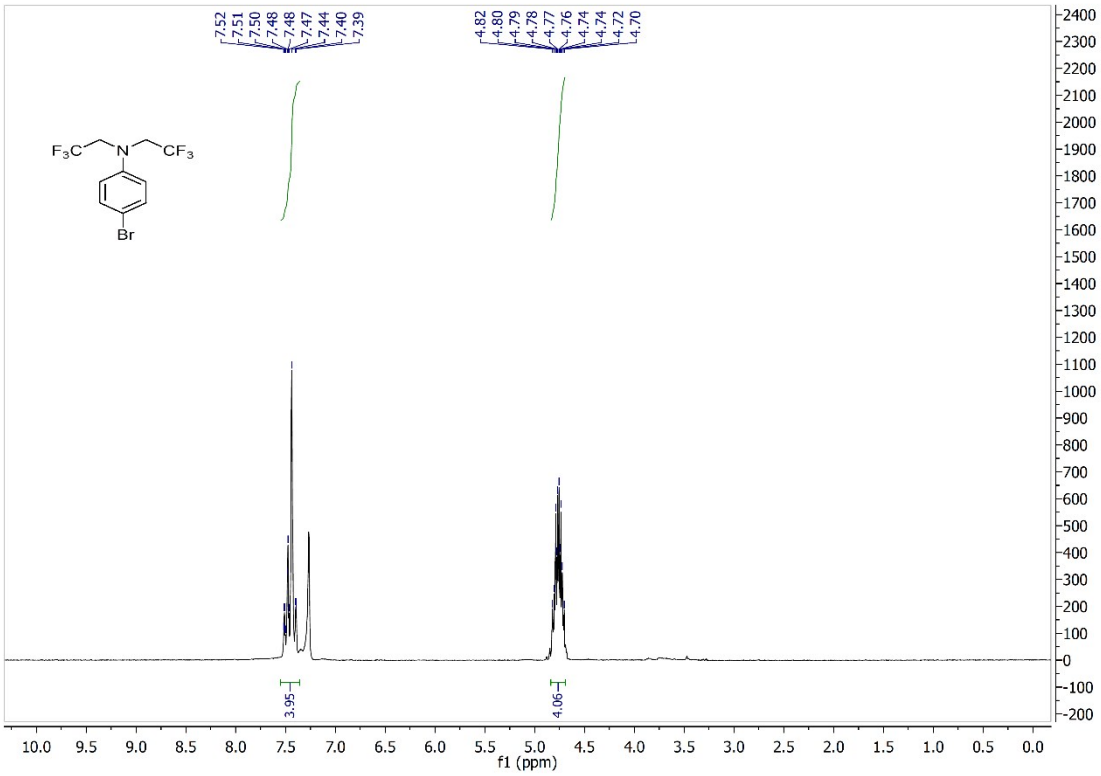
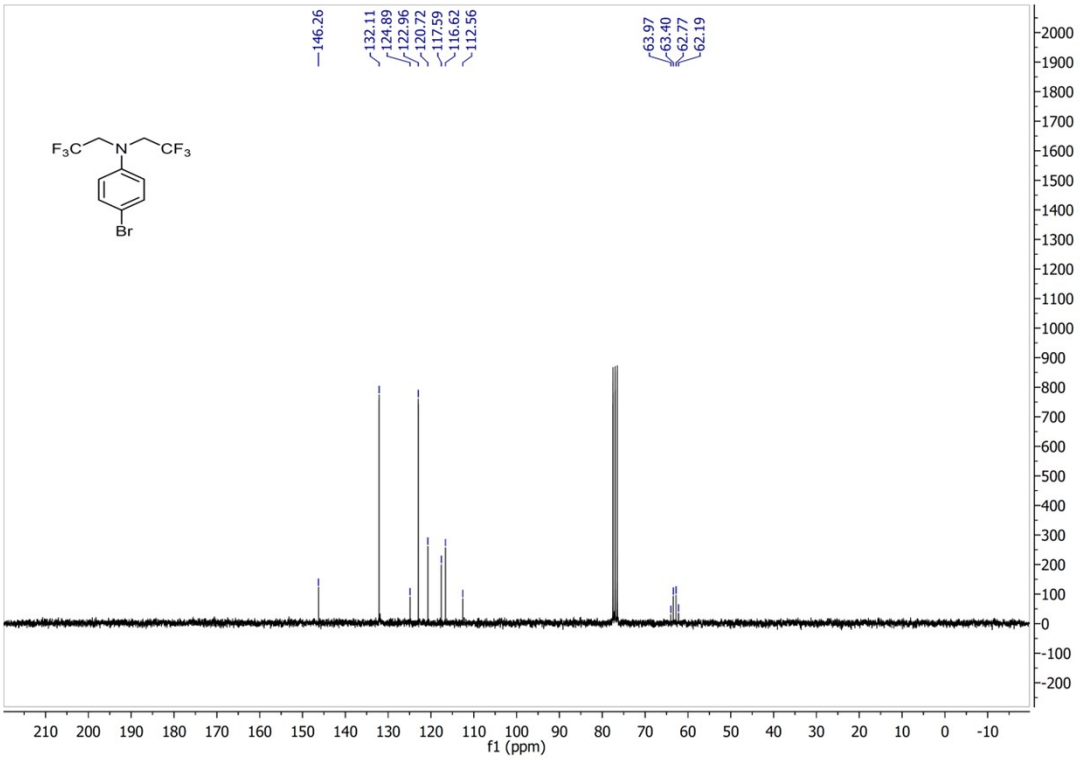
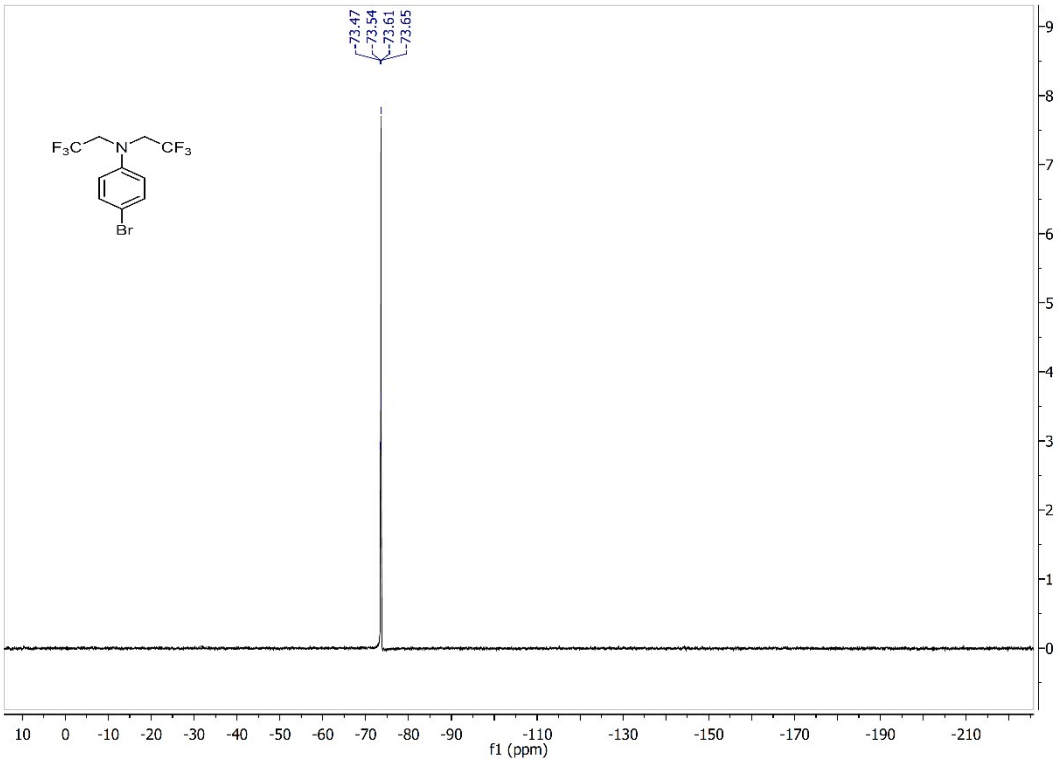
1114.32
1092.64
1013.72
962.22
866.30
829.49
811.40
767.25
678.73
495.64
F3C
N
CF3
Cl
cm-1

4-Bromo-*N,N*-bis(2,2,2-trifluoroethyl)aniline (2c)



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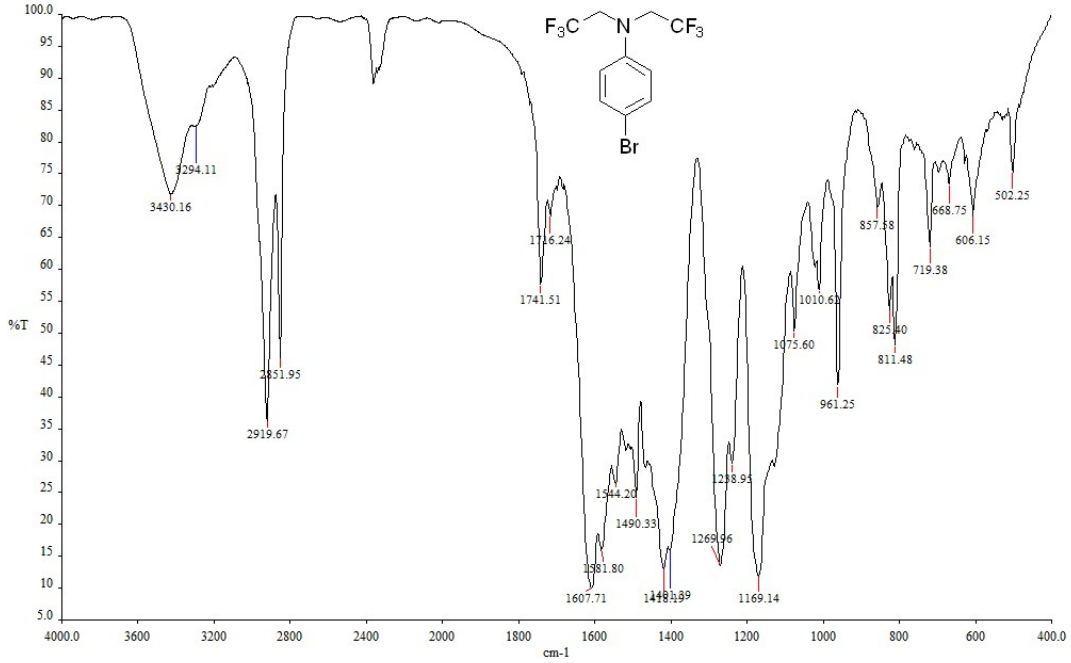
-73.61
-73.65
F3C
N
CF3
Br
f1 (ppm)


F3C
N
CF3
Br
%T
cm-1
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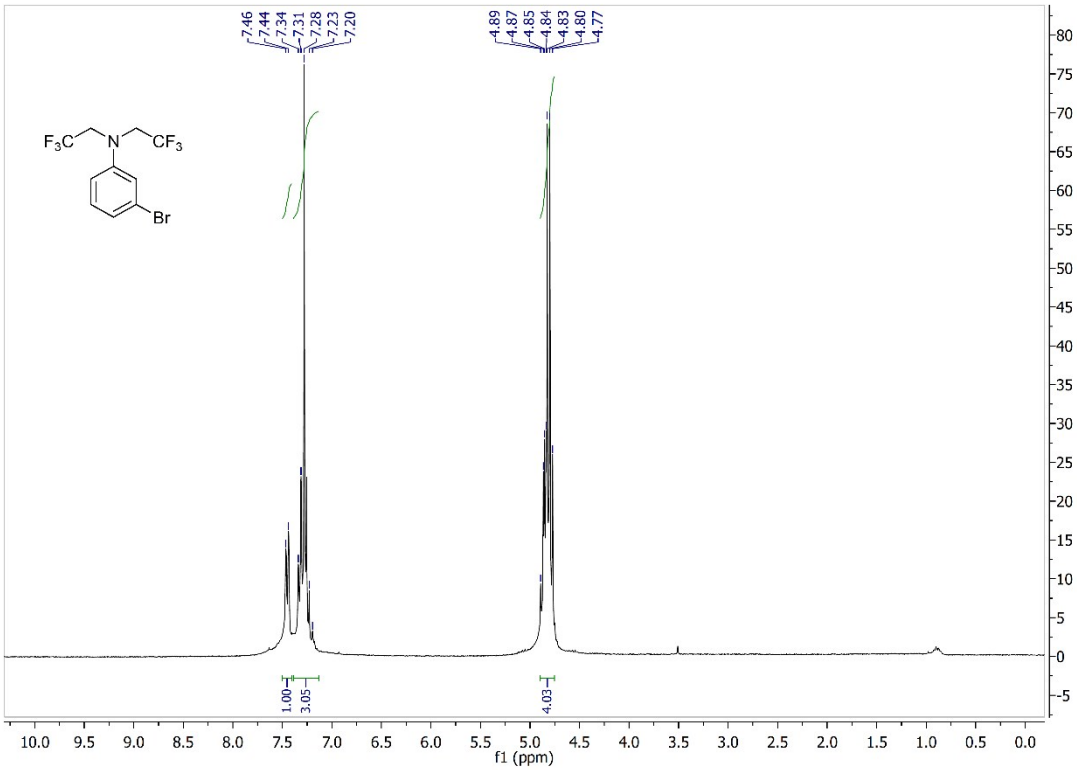
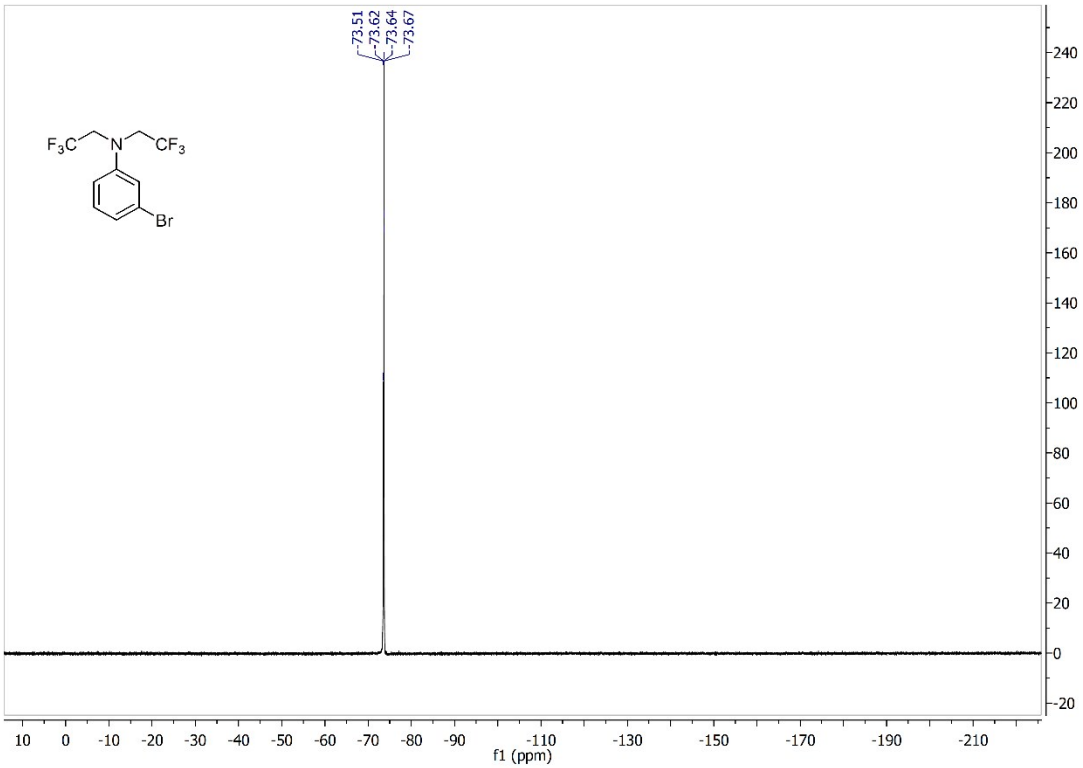
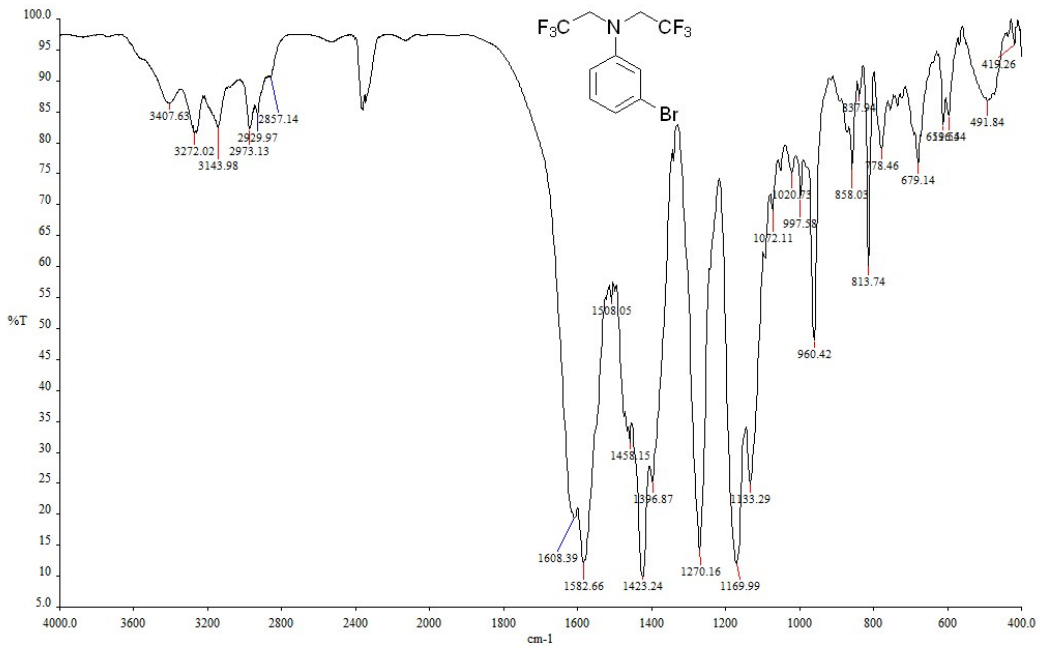
1607.71
1581.80
1544.20
1490.33
1269.96
1238.95
1169.14
1075.60
1010.62
961.25
857.58
825.40
811.48
719.38
668.75
606.15
502.25

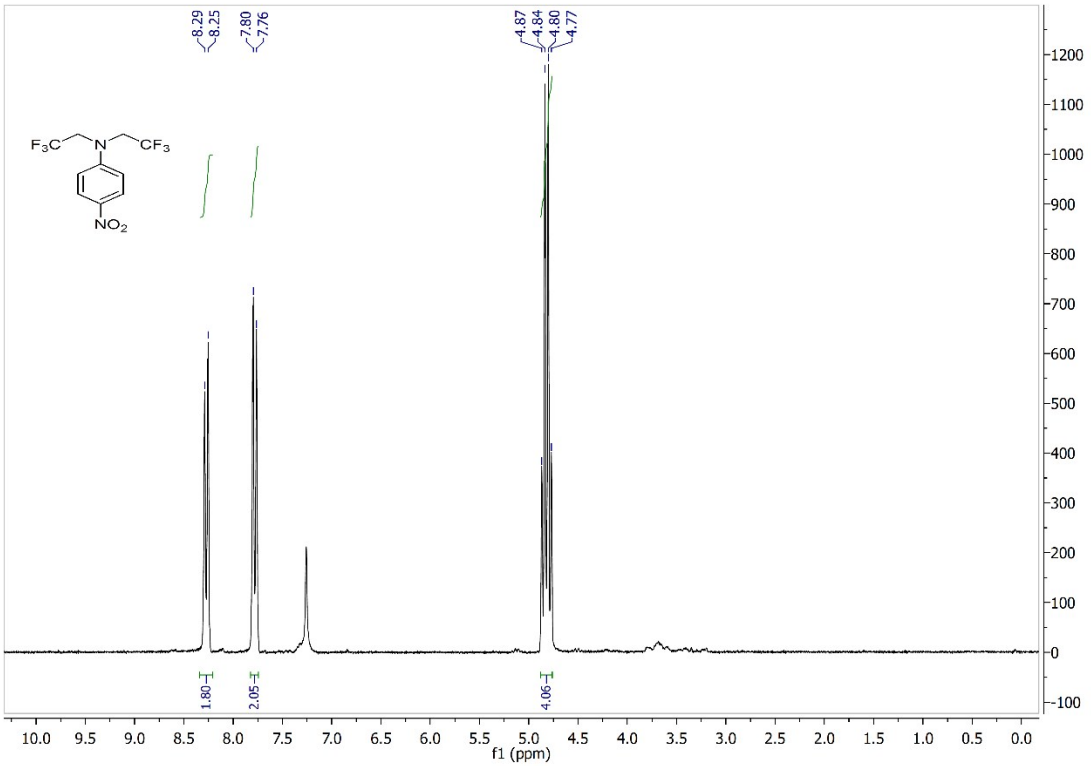
3-Bromo-*N,N*-bis(2,2,2-trifluoroethyl)aniline (2d)

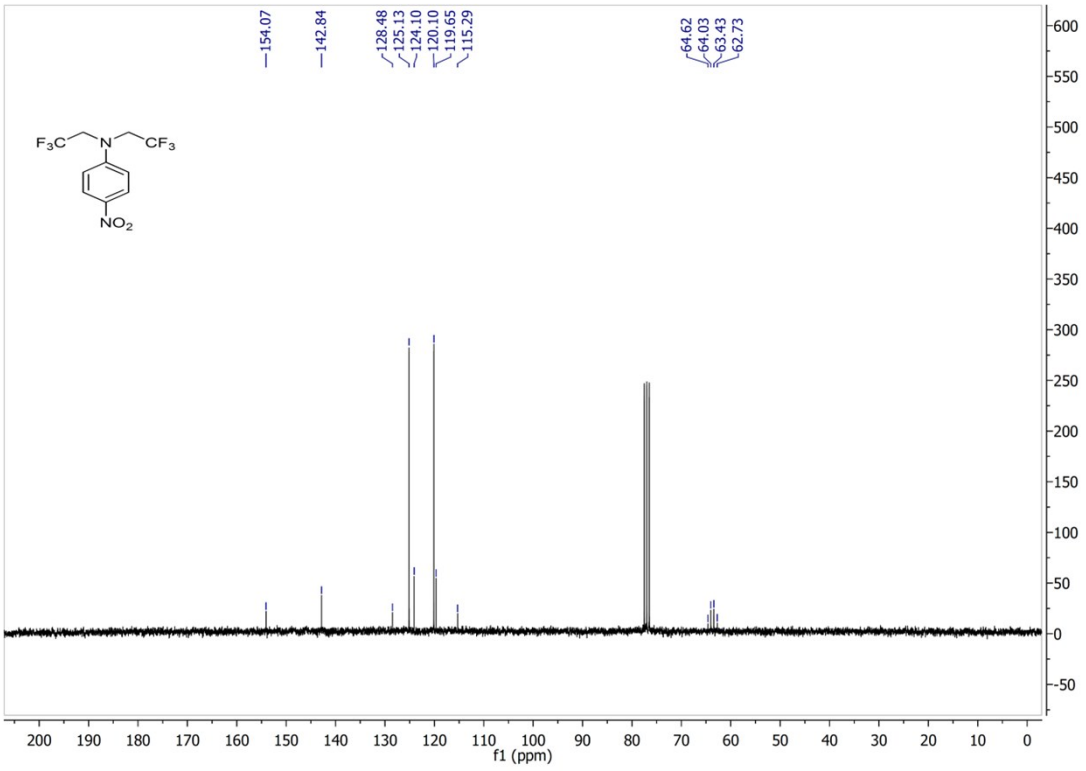






4-Nitro-*N,N*-bis(2,2,2-trifluoroethyl)aniline (2e)

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125.13
124.10
120.10
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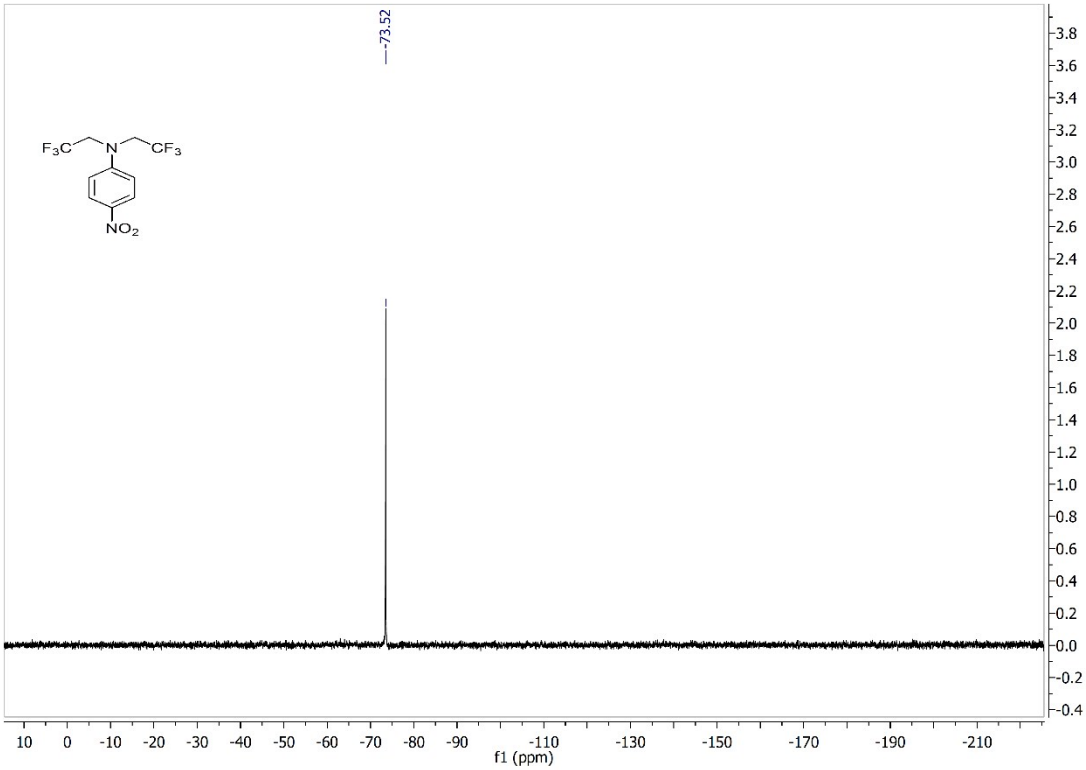
62.73
F3C
N
CF3
NO2
f1 (ppm)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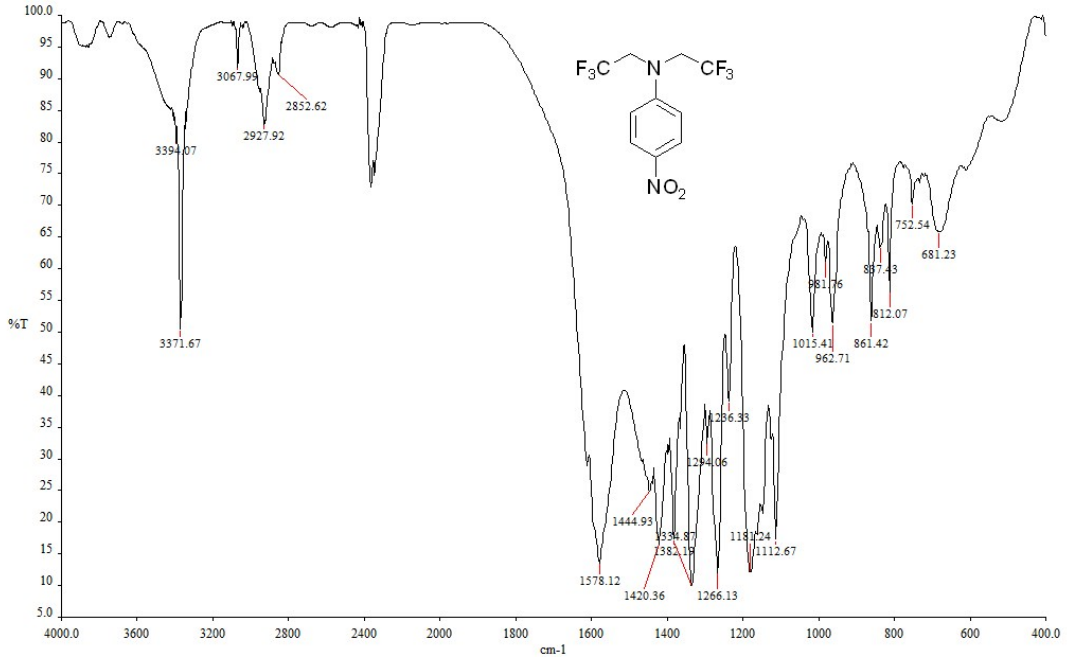
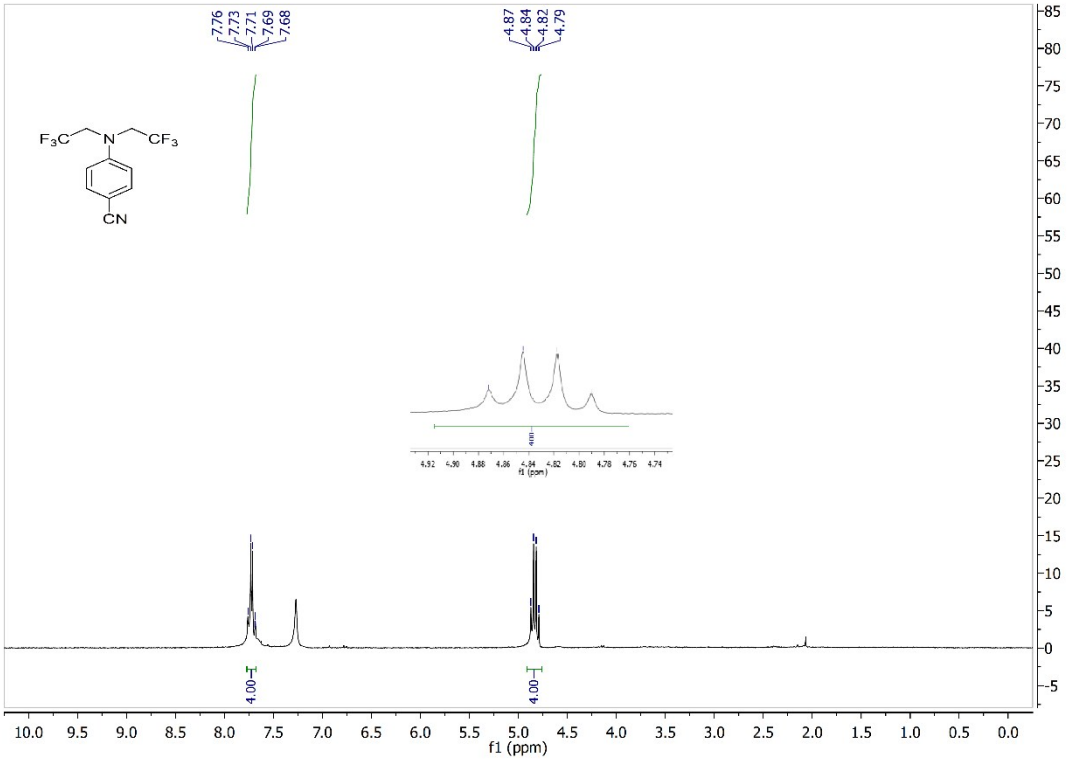
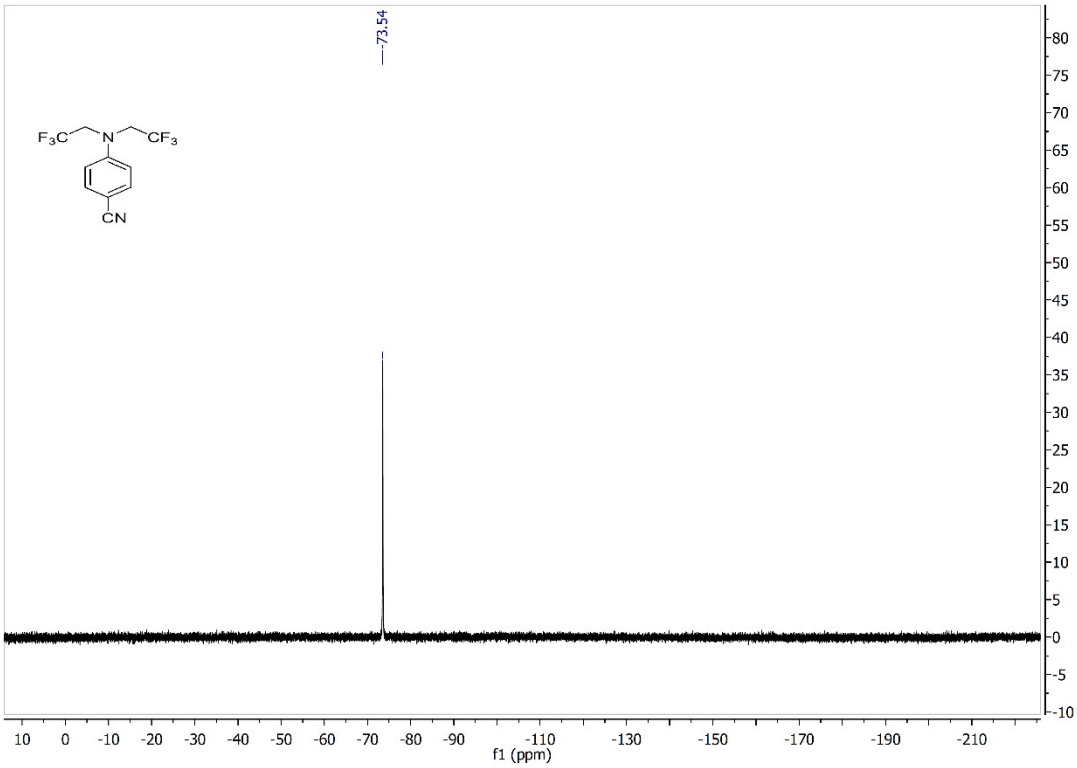
NO2
f1 (ppm)



4-Cyano-*N,N*-bis(2,2,2-trifluoroethyl)aniline (2f)

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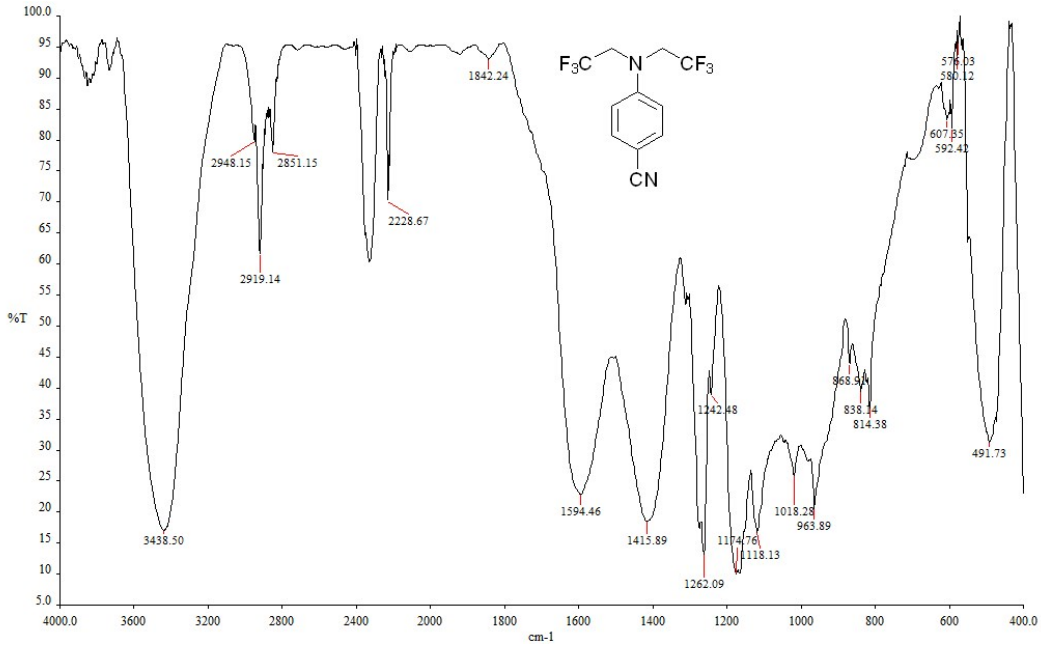
F3C
N
CF3
CN
f1 (ppm)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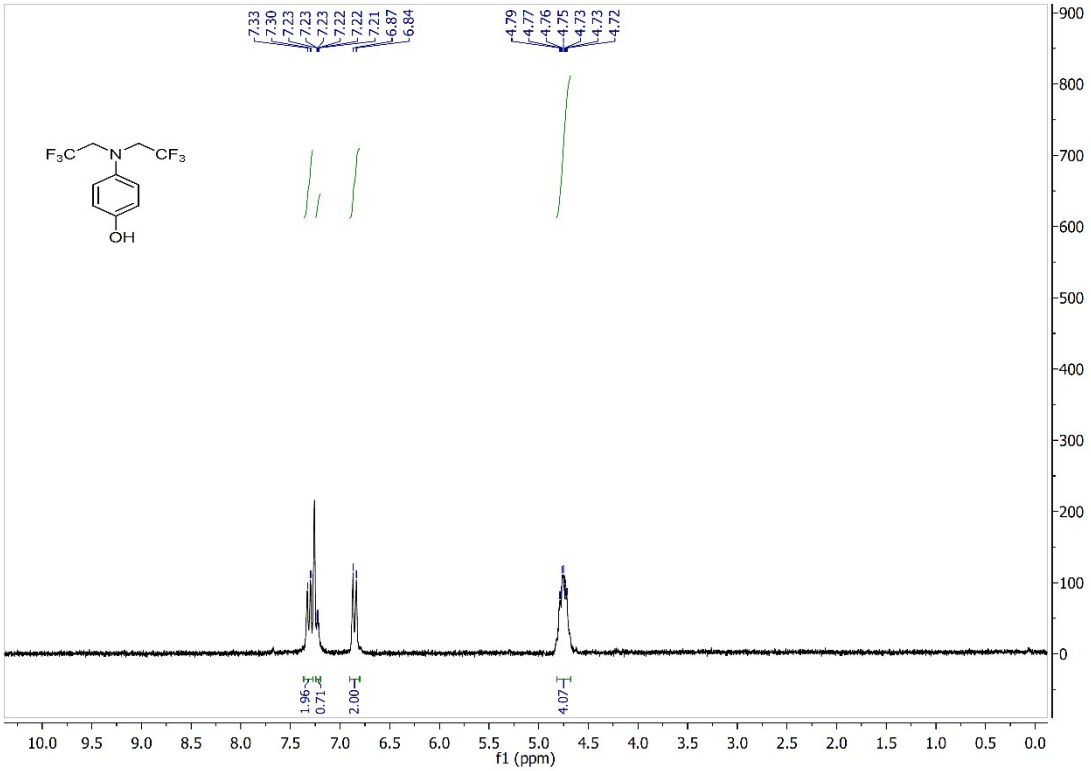
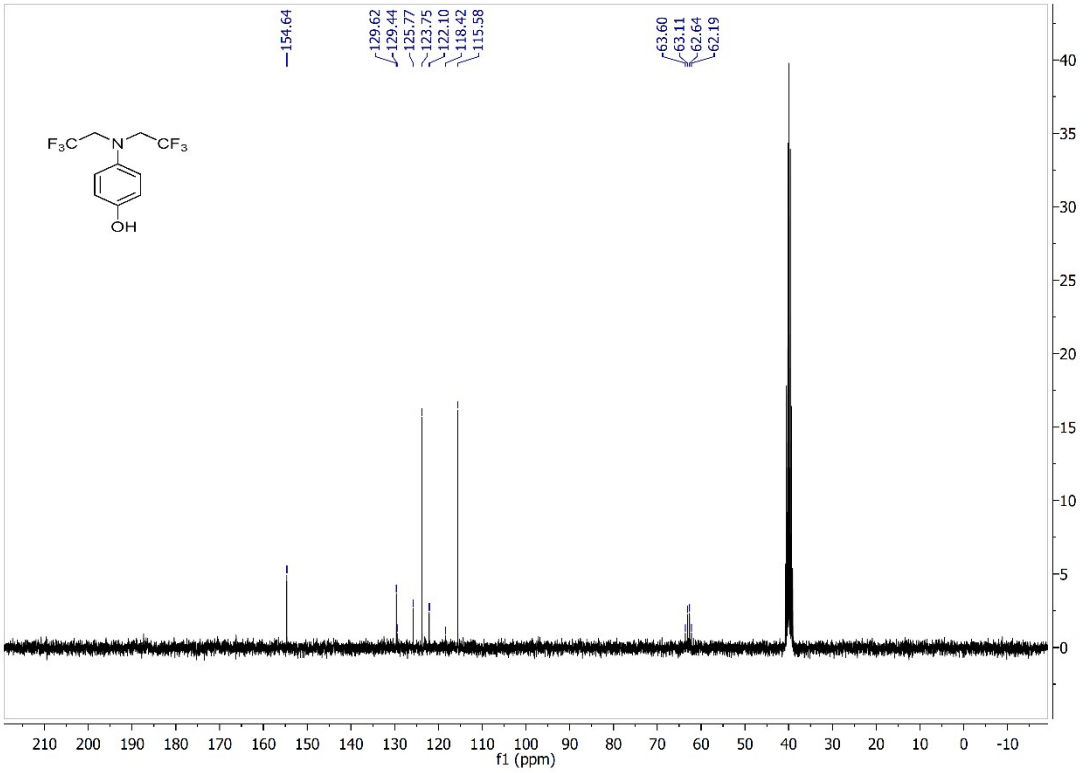
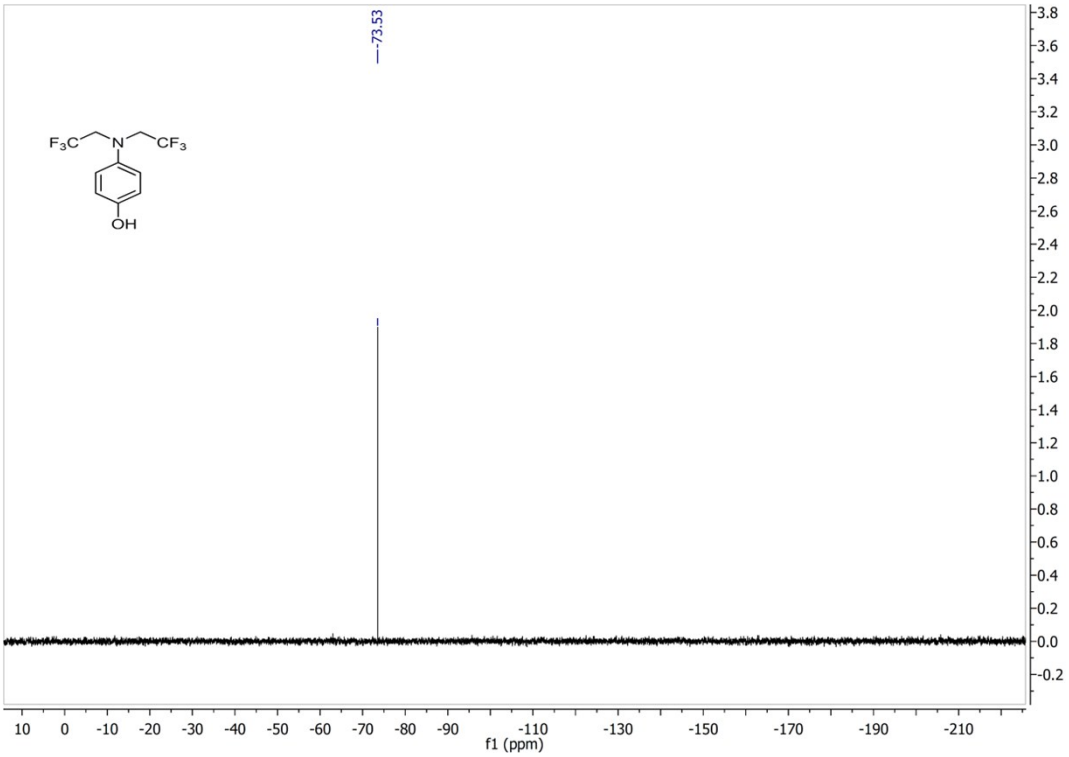
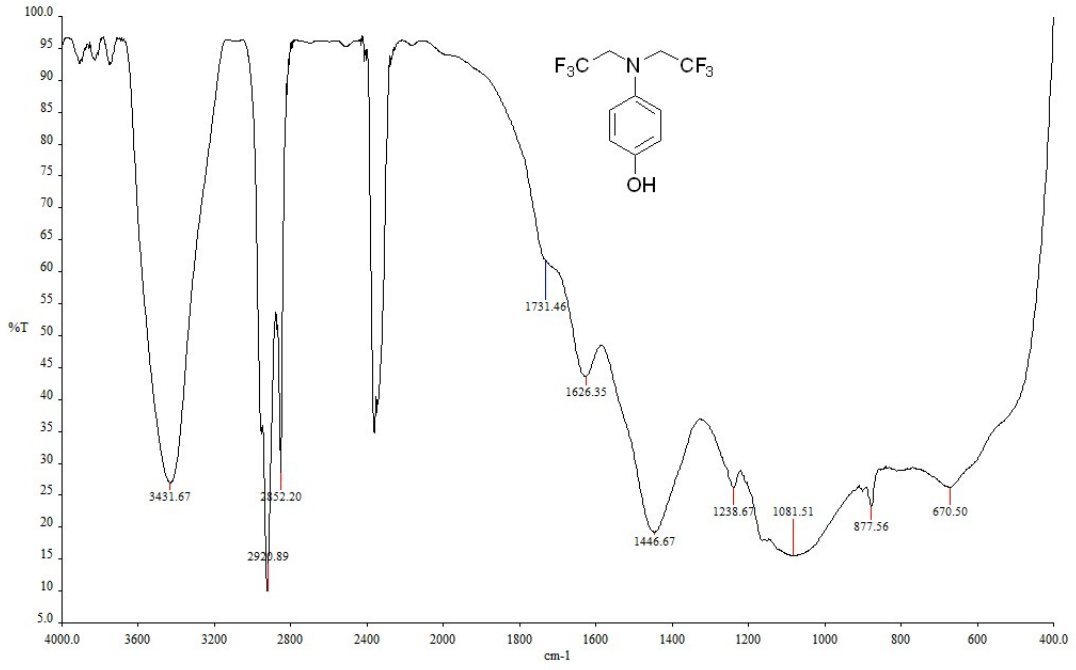
1174.76
1118.13
1018.28
963.89
838.14
814.38
607.85
592.42
580.12
491.73
F3C
N
CF3
CN

4-Hydroxy-*N,N*-bis(2,2,2-trifluoroethyl)aniline (2g)

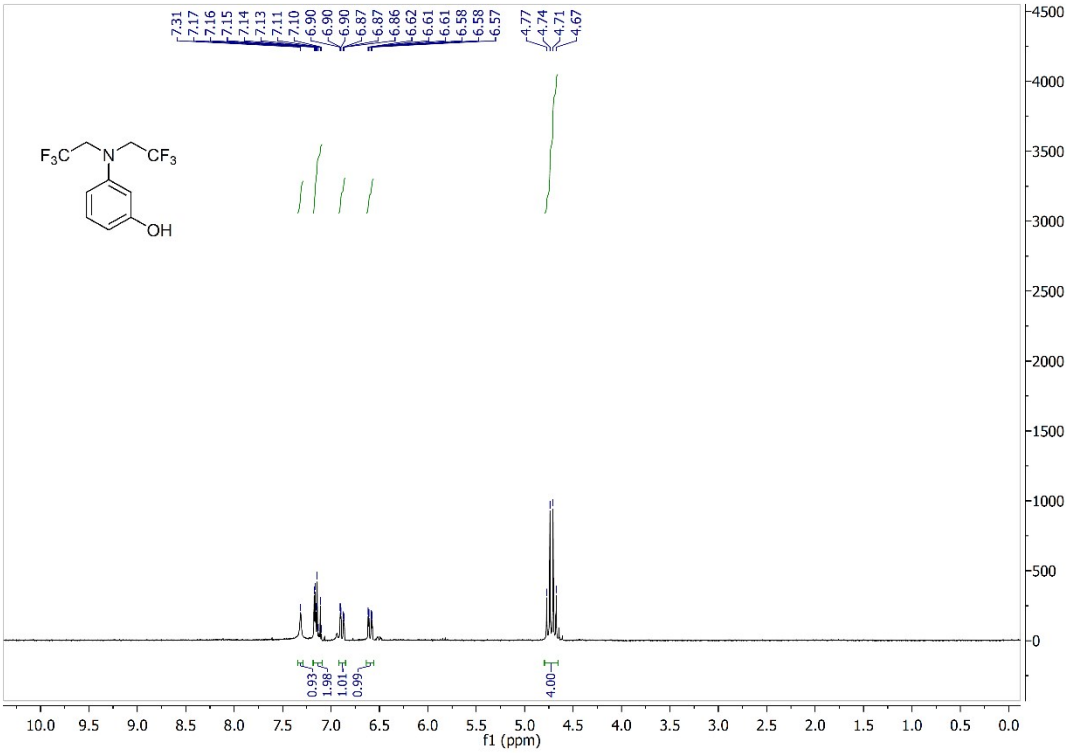


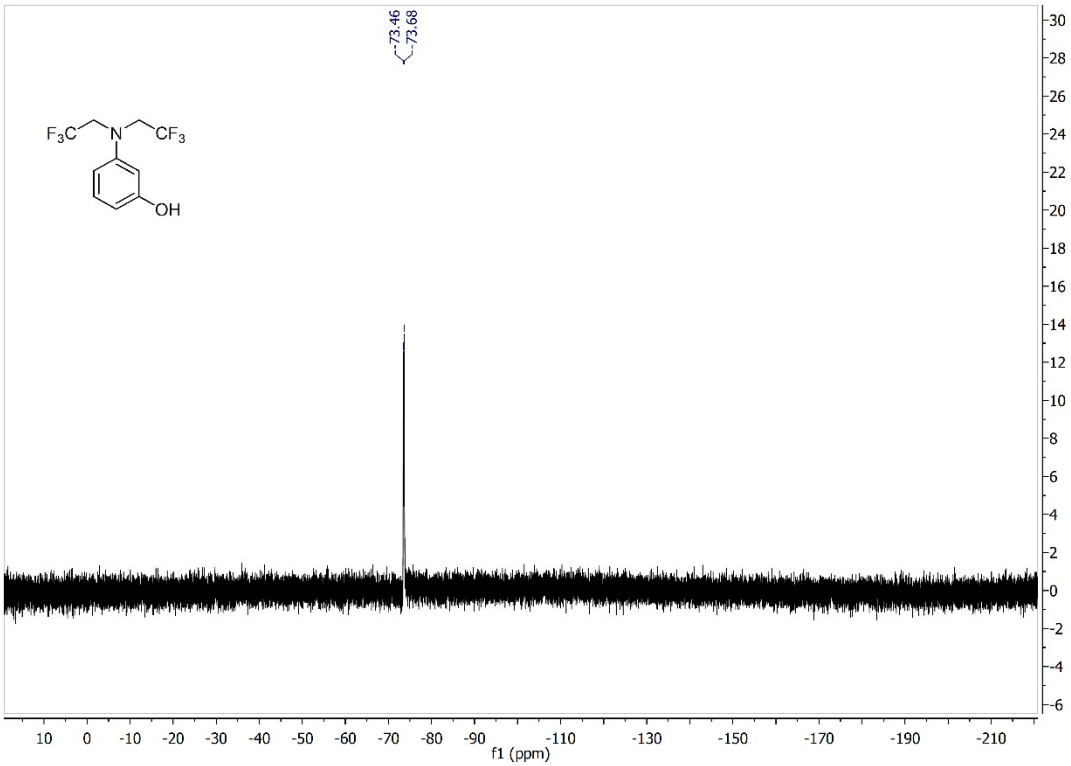


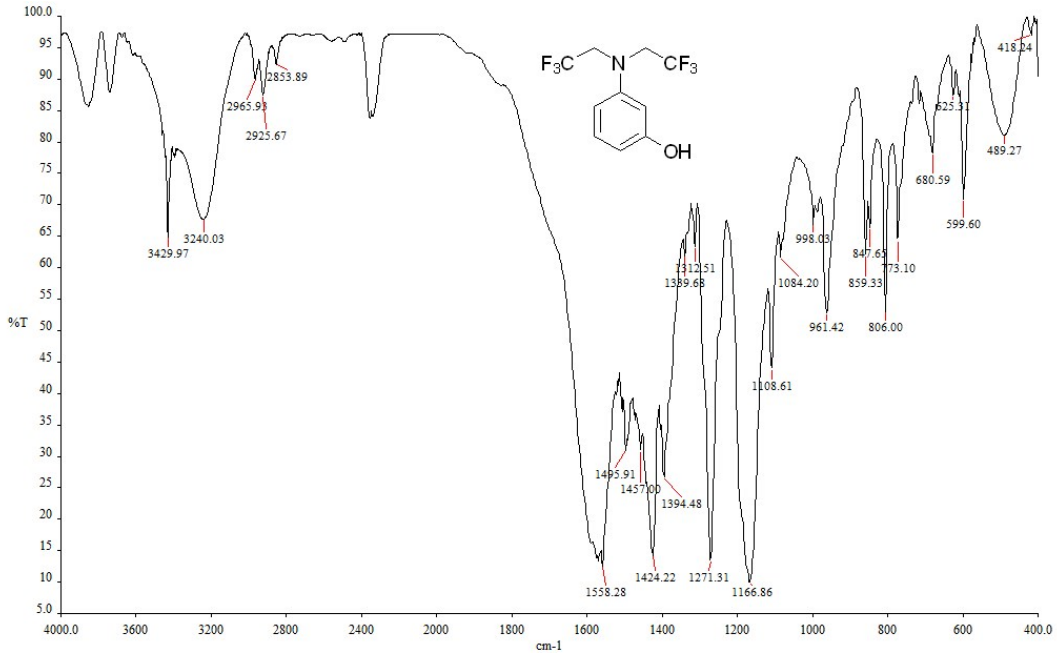

-73.53
F3C
N
CF3
OH
f1 (ppm)


%T
3431.67
2922.89
2852.20
1731.46
1626.35
1446.67
1238.67
1081.51
877.56
670.50
cm-1

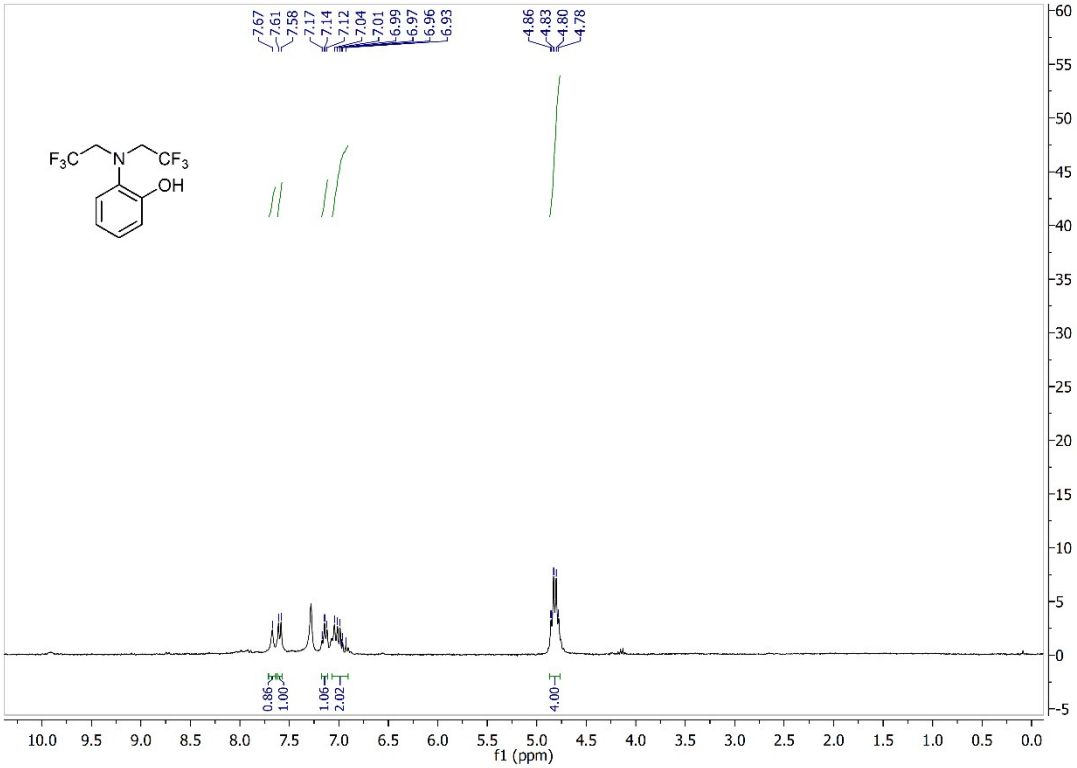
3-Hydroxy-*N,N*-bis(2,2,2-trifluoroethyl)aniline (2h)

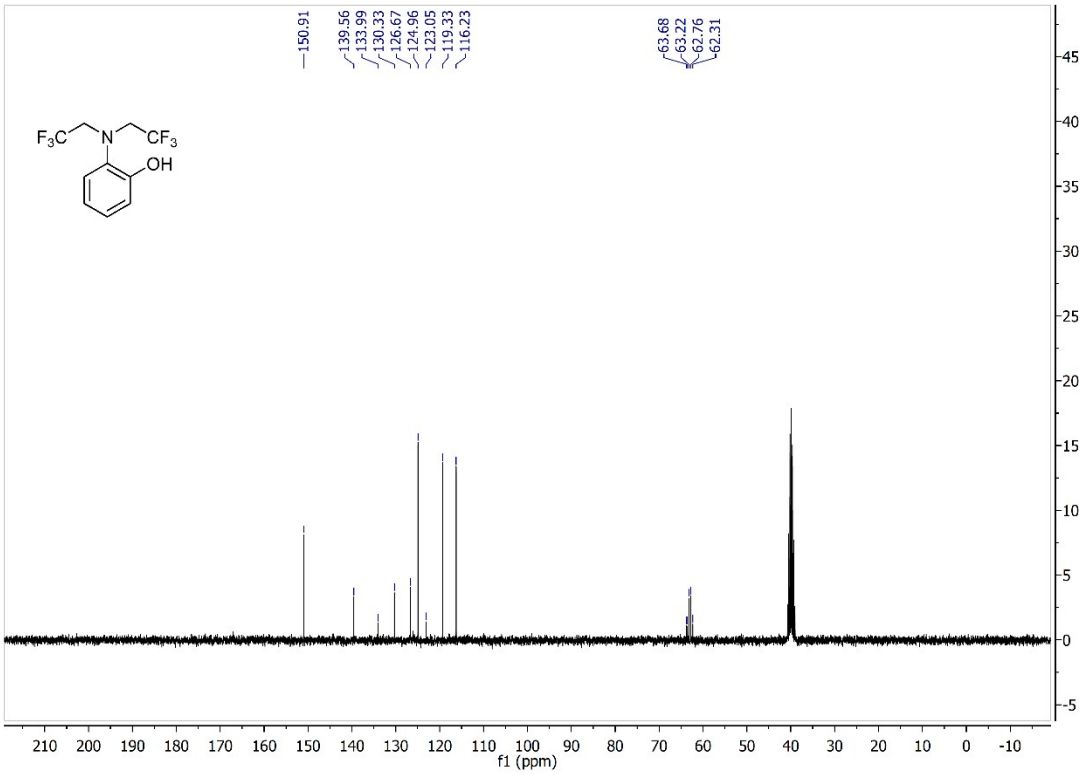


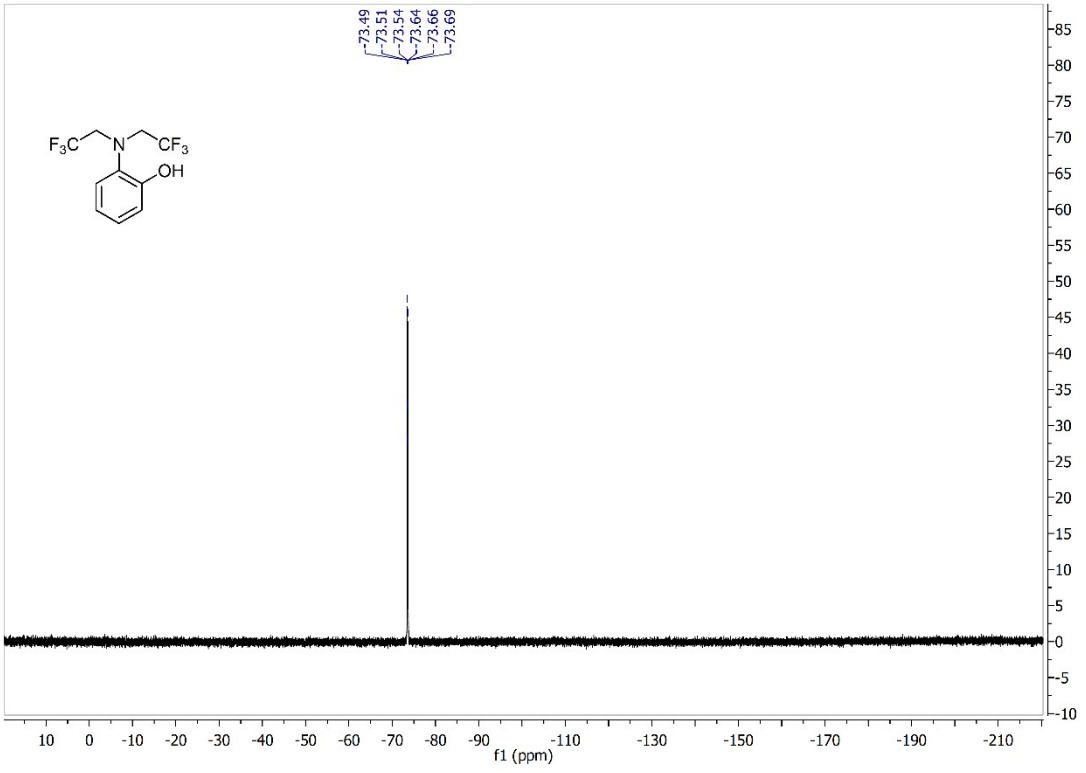


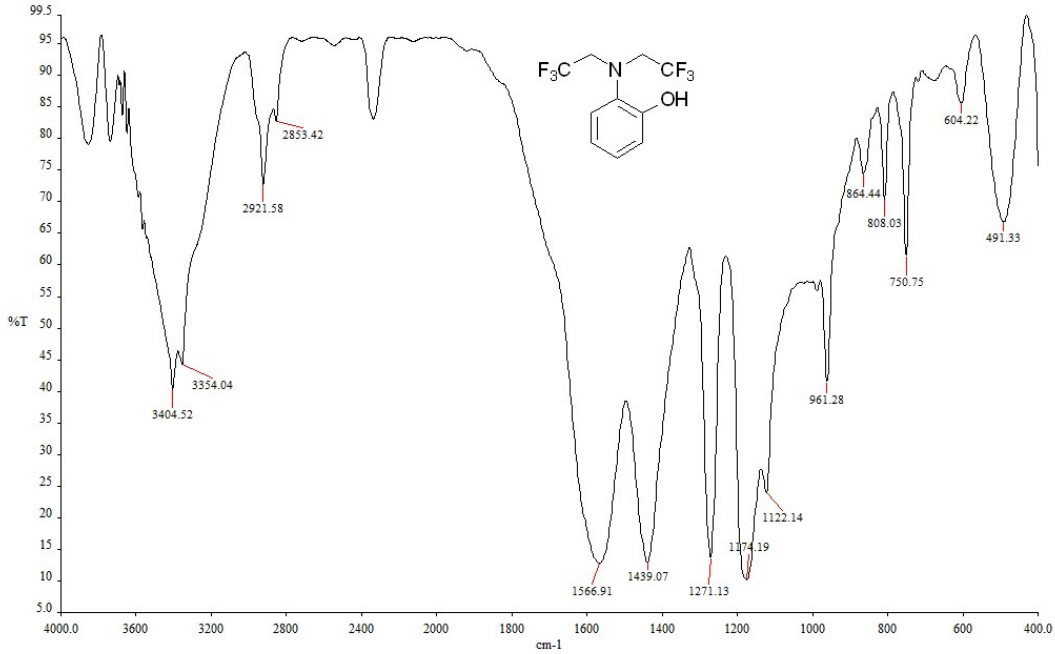


2-Hydroxy-*N,N*-bis(2,2,2-trifluoroethyl)aniline (2i)

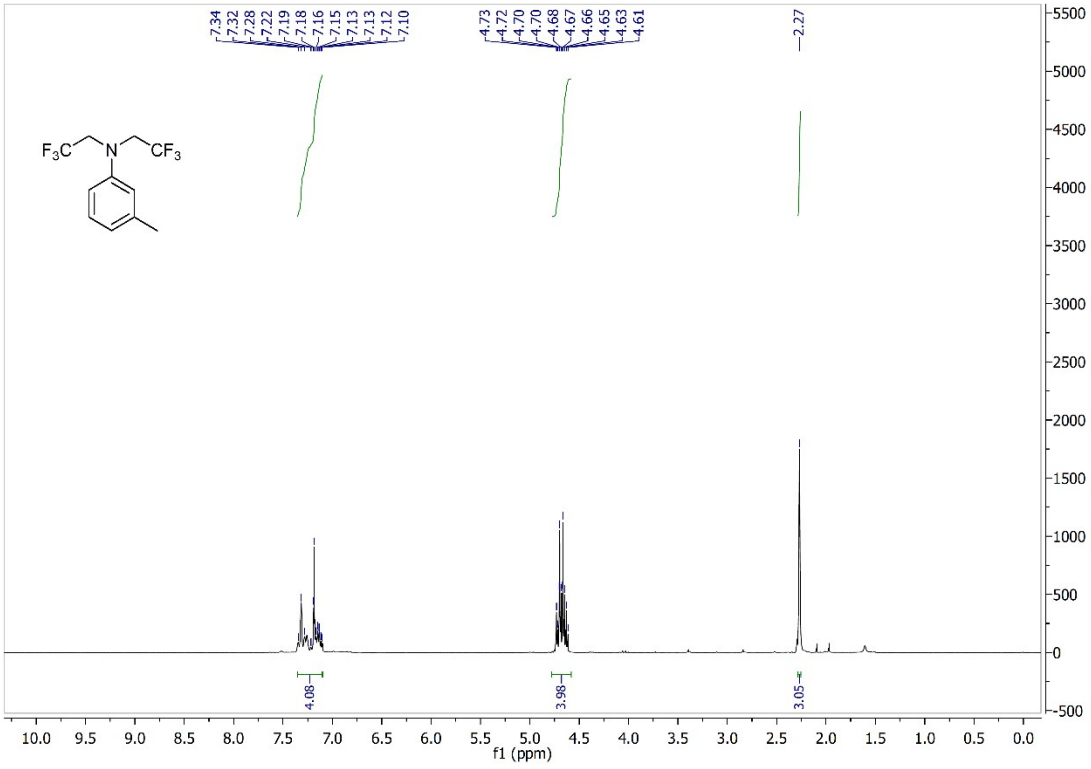


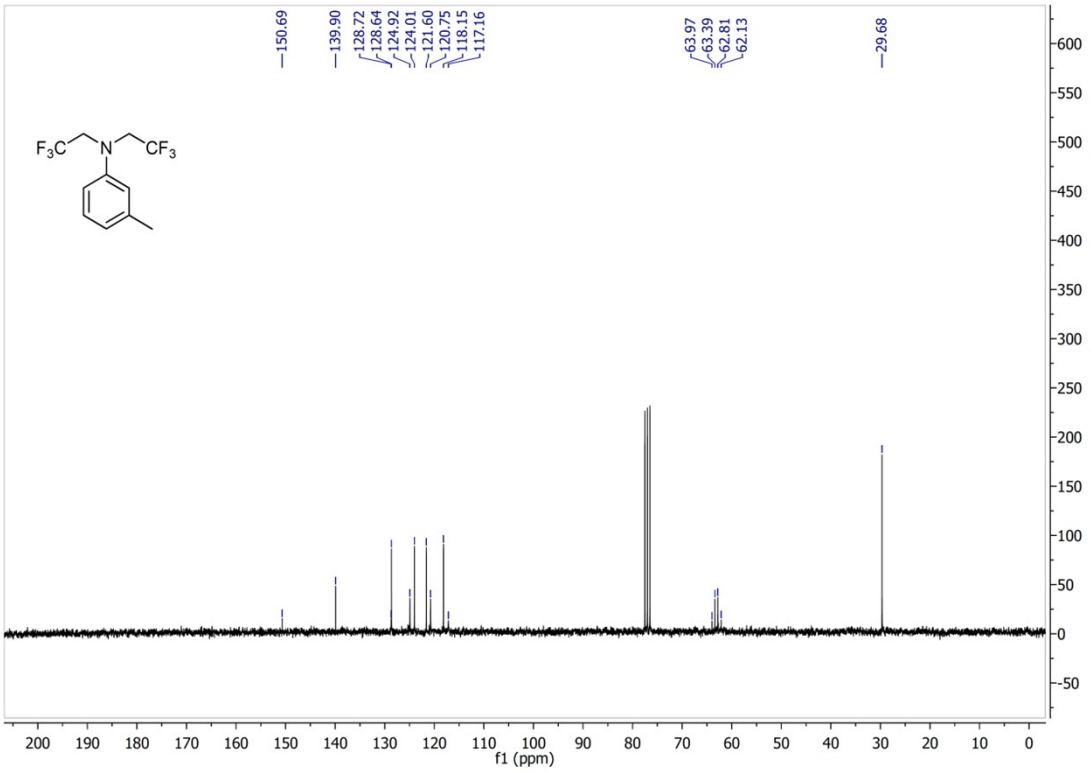

150.91
139.56
133.99
130.33
126.67
124.96
123.05
119.33
116.23
63.68
63.22
62.76
62.31
F3C
N
CF3
OH
f1 (ppm)

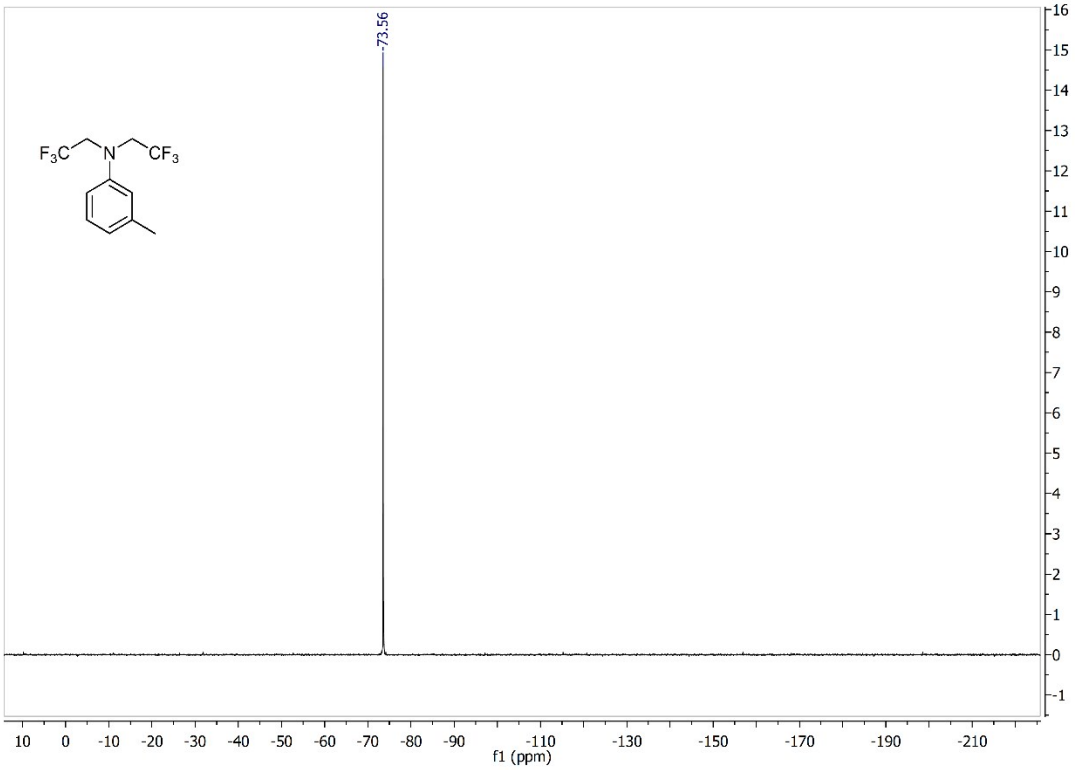

-73.49
-73.51
-73.54
-73.64
-73.66
-73.69
F3C
N
CF3
OH
f1 (ppm)

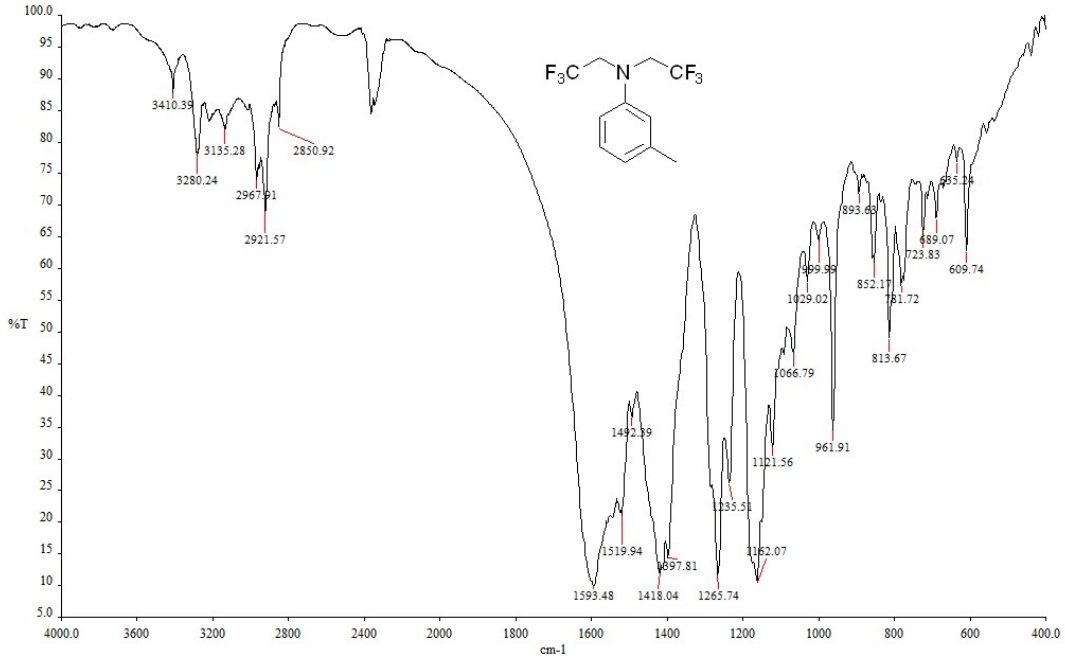


3-Methyl-*N,N*-bis(2,2,2-trifluoroethyl)aniline (2j)

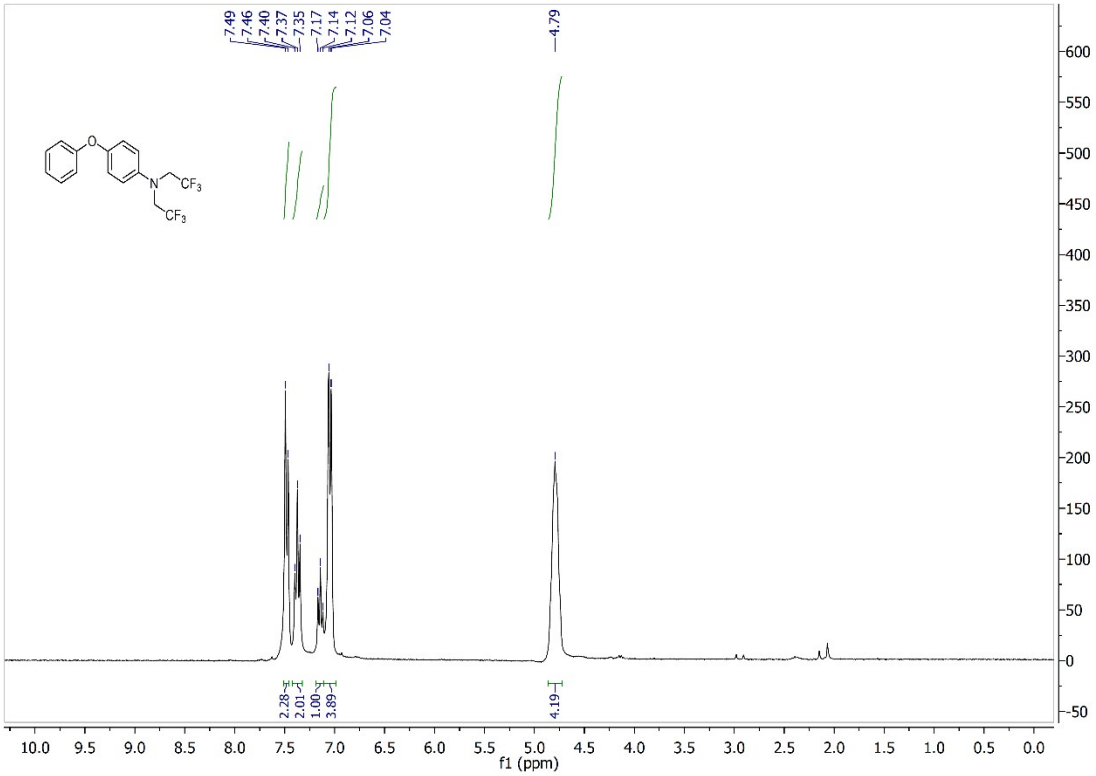


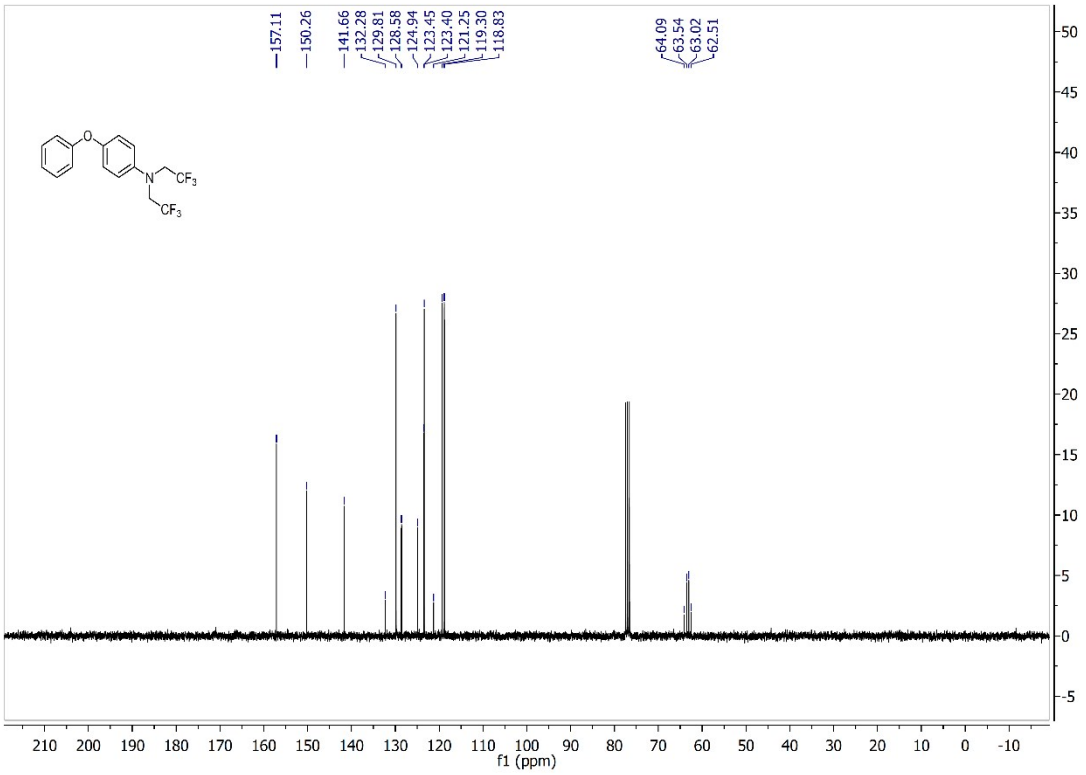

150.69
139.90
128.72
128.64
124.92
124.01
121.60
120.75
118.15
117.16
63.97
63.39
62.81
62.13
29.68
F3C
N
CF3
f1 (ppm)

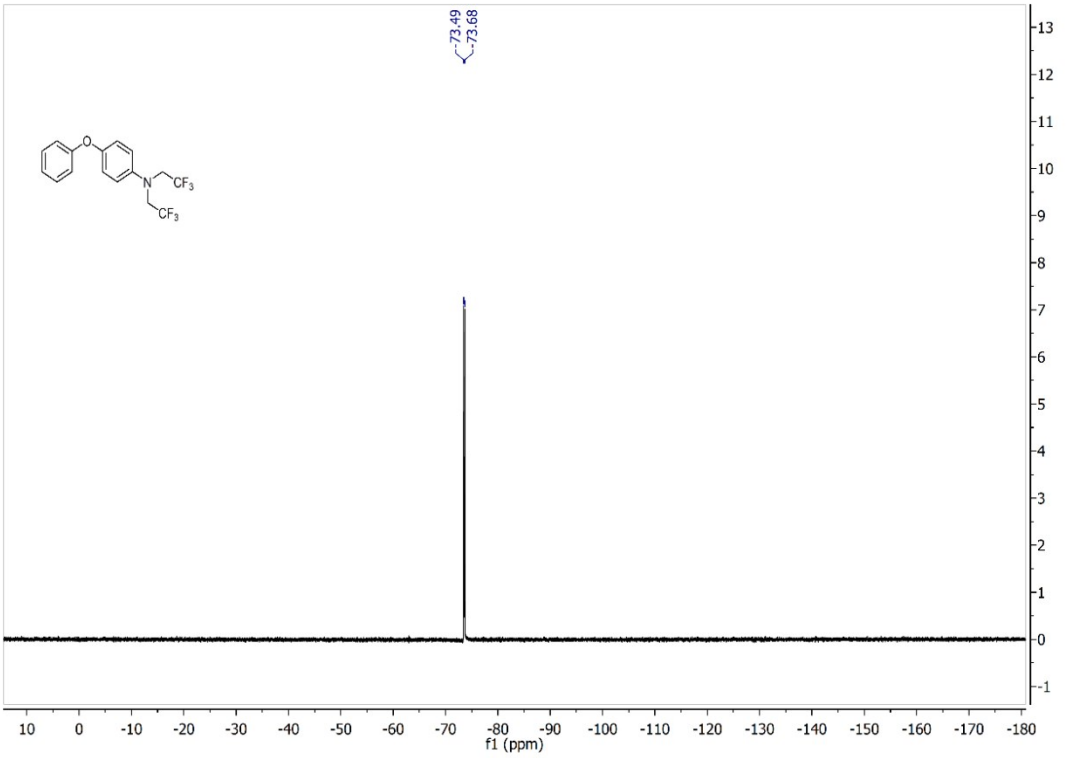

-73.56
F3C
N
CF3
f1 (ppm)

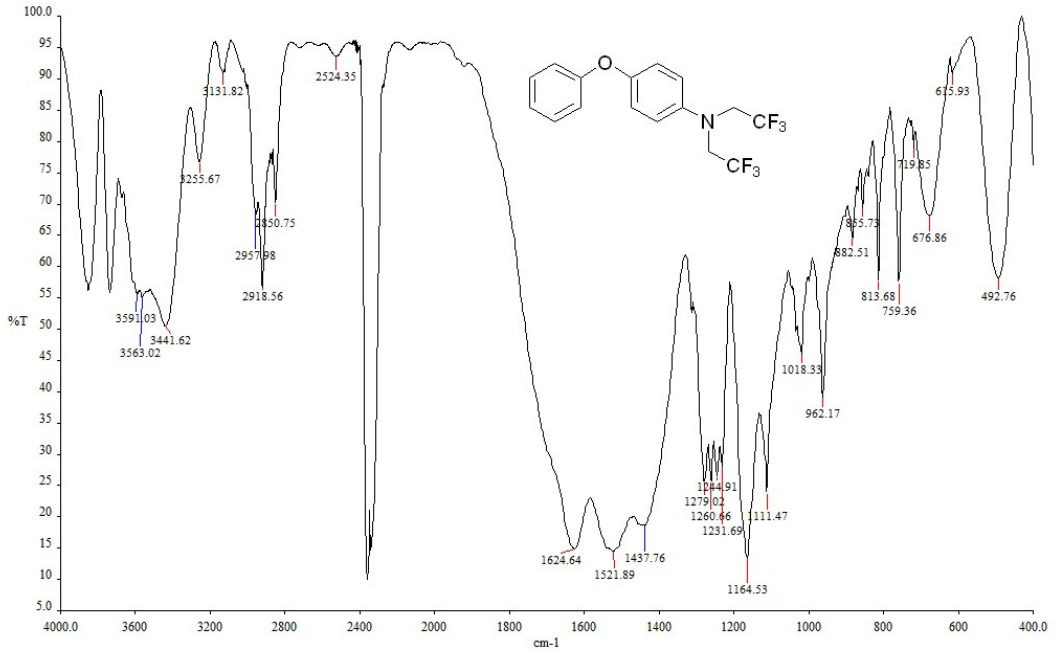


4-*N*,*N*-bis(2,2,2-trifluoroethyl)aminodiphenylether (2k)

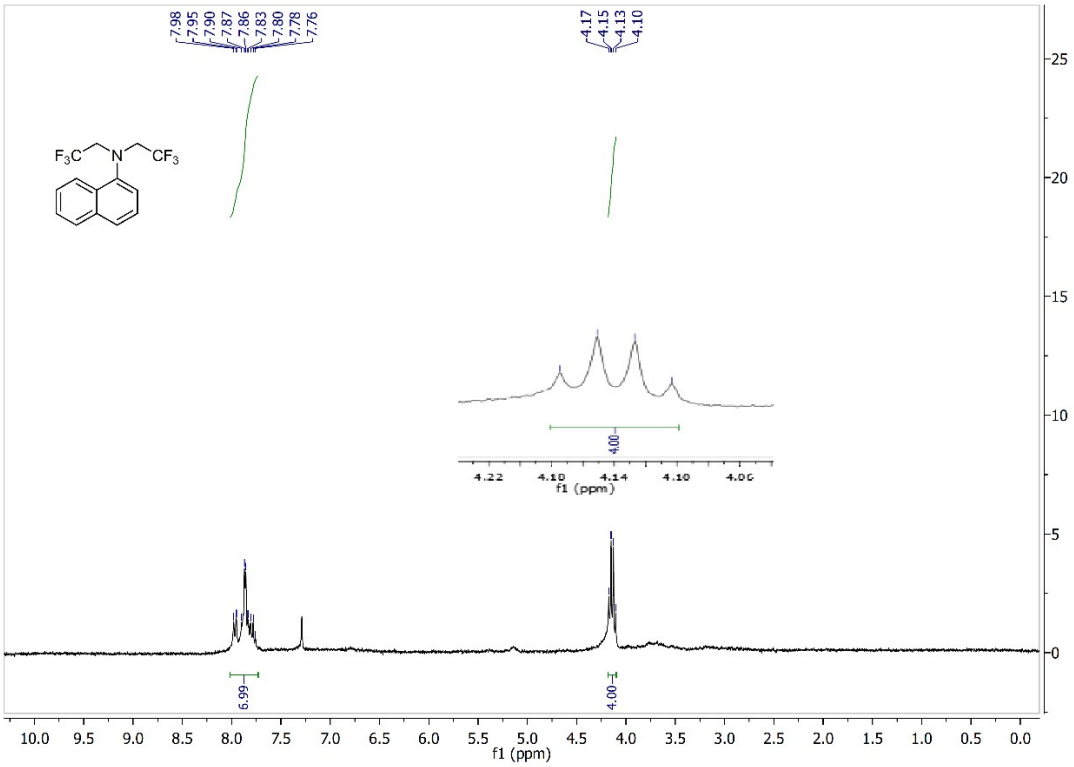


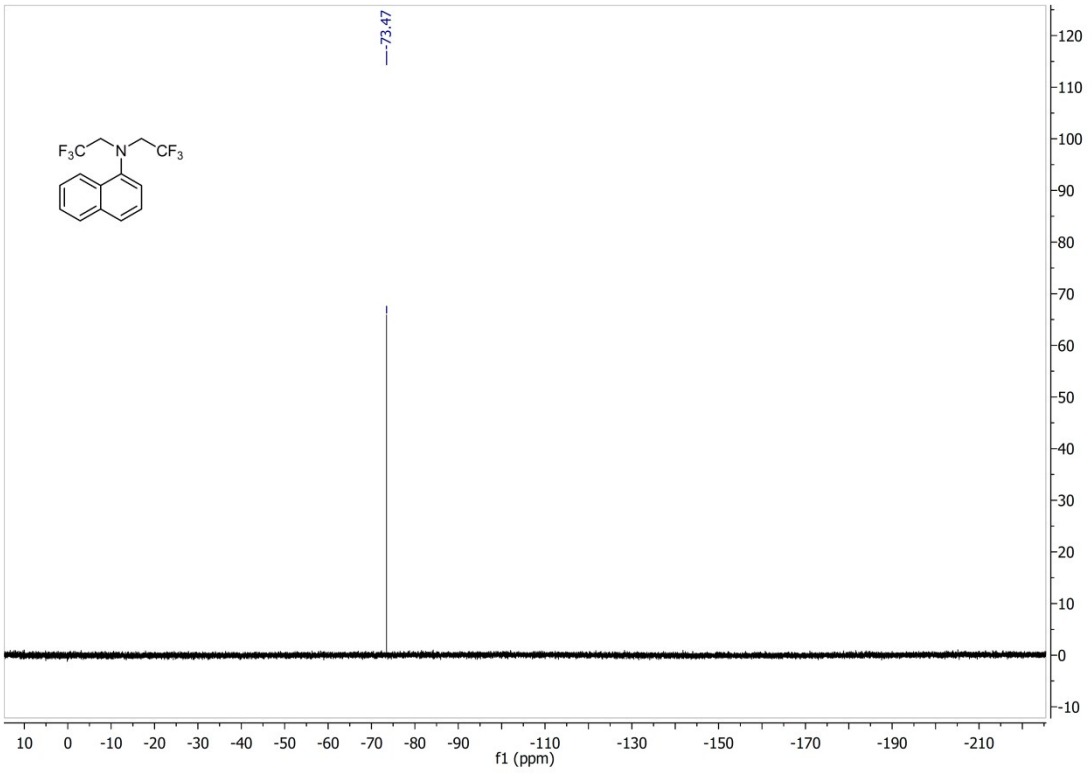

157.11
150.26
141.66
132.28
129.81
128.58
124.94
123.45
123.40
121.25
119.30
118.83
64.09
63.54
63.02
62.51
O
N
CF3
CF3
f1 (ppm)

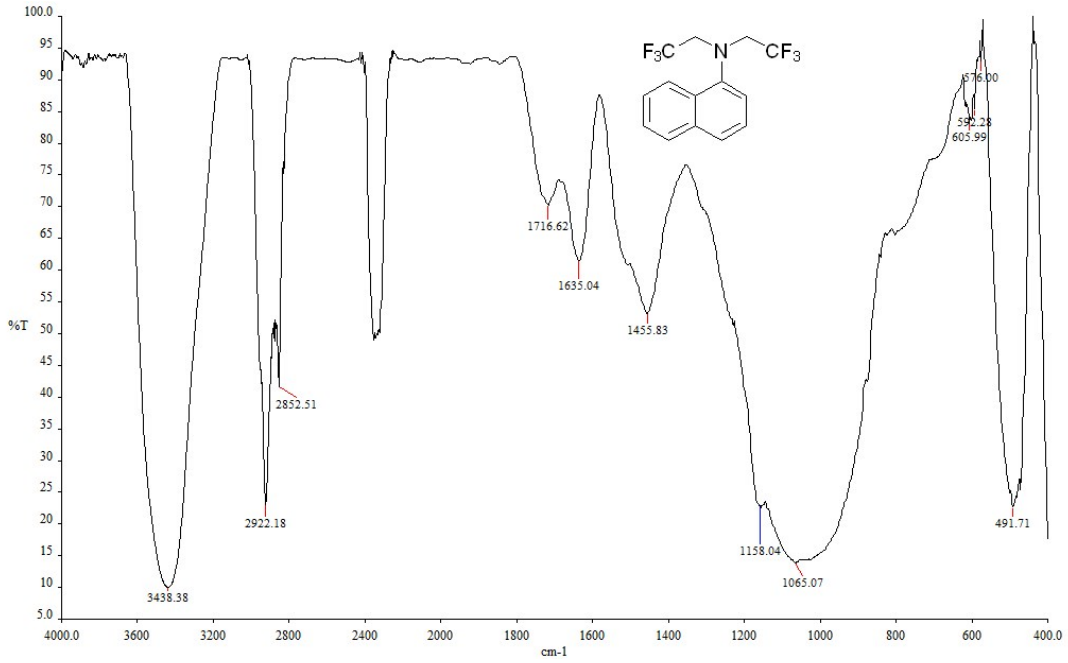

73.49
73.68
O
N
CF3
CF3
f1 (ppm)



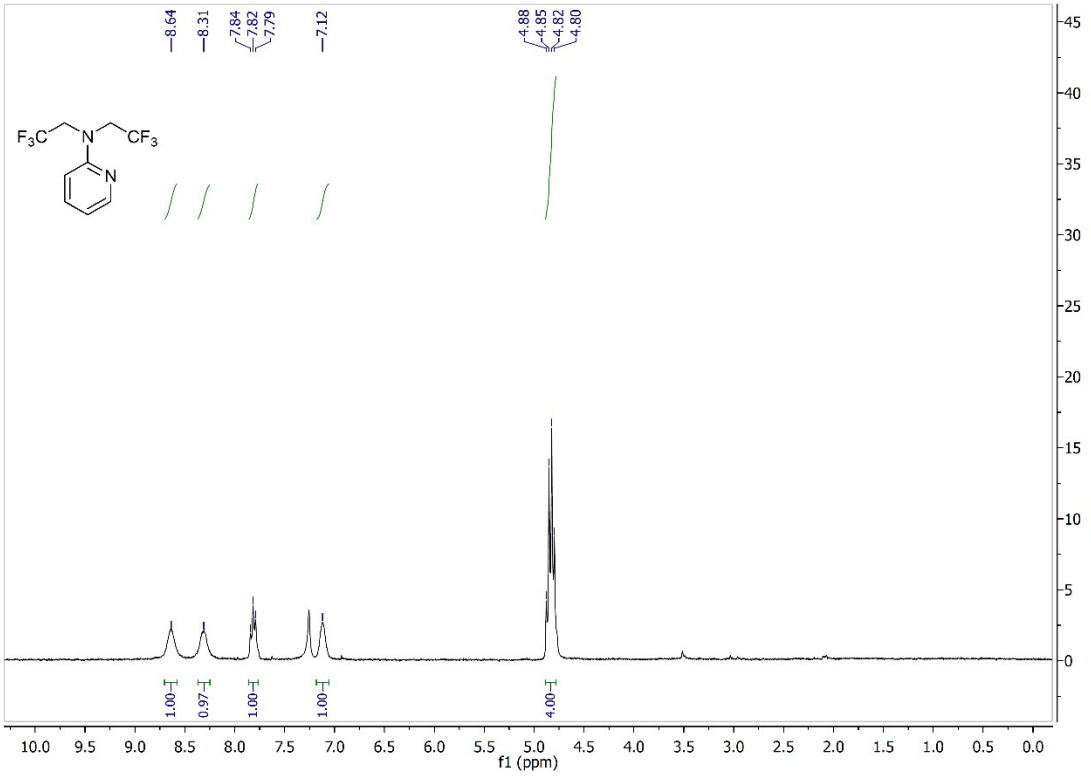
N,N-bis(2,2,2-trifluoroethyl)naphthalene-1-amine (2l)

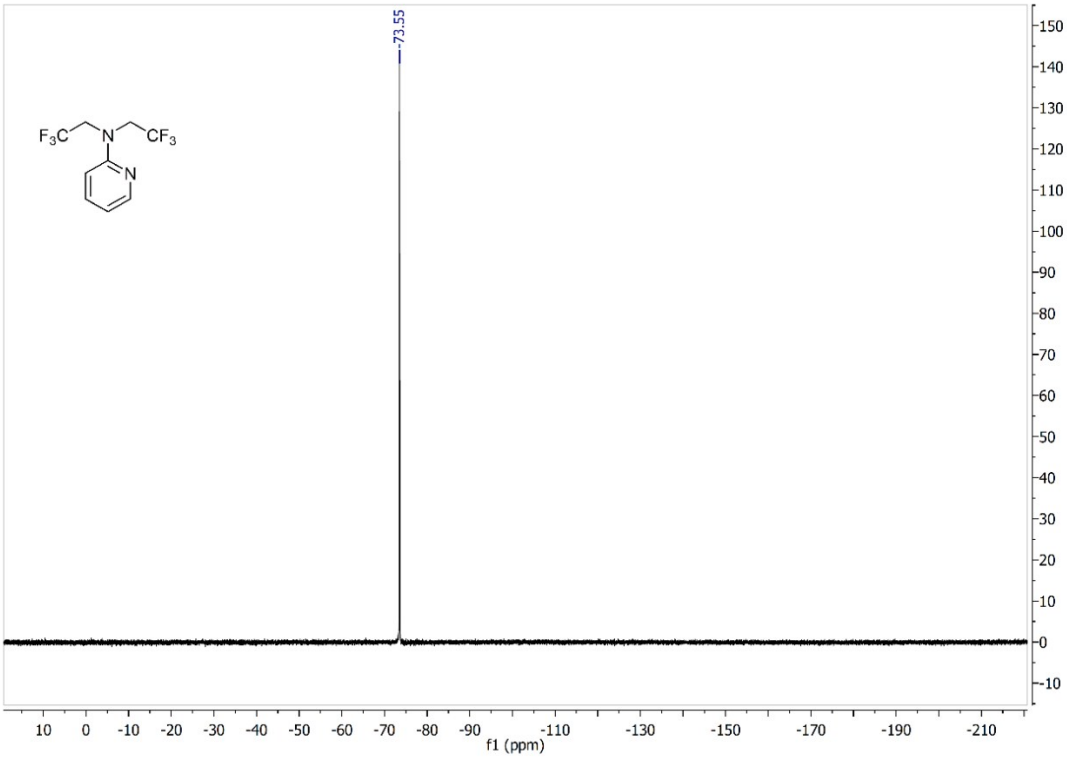


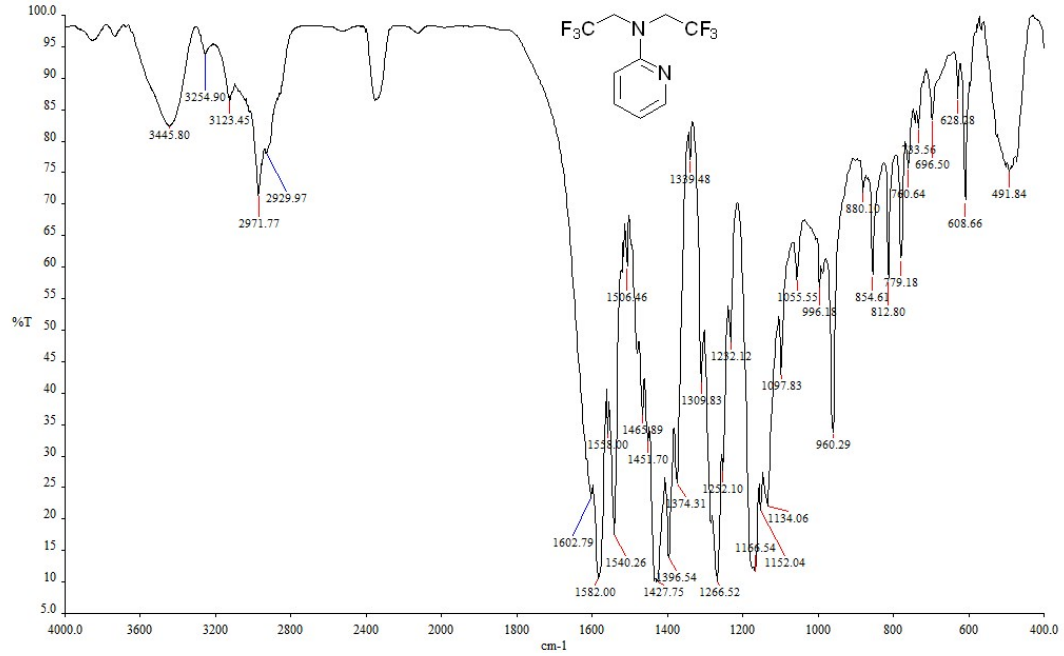

-73.47
F3C
N
CF3
f1 (ppm)


%T
cm-1
3438.38
2922.18
2852.51
1716.62
1635.04
1455.83
1158.04
1065.07
605.99
491.71
F3C
N
CF3

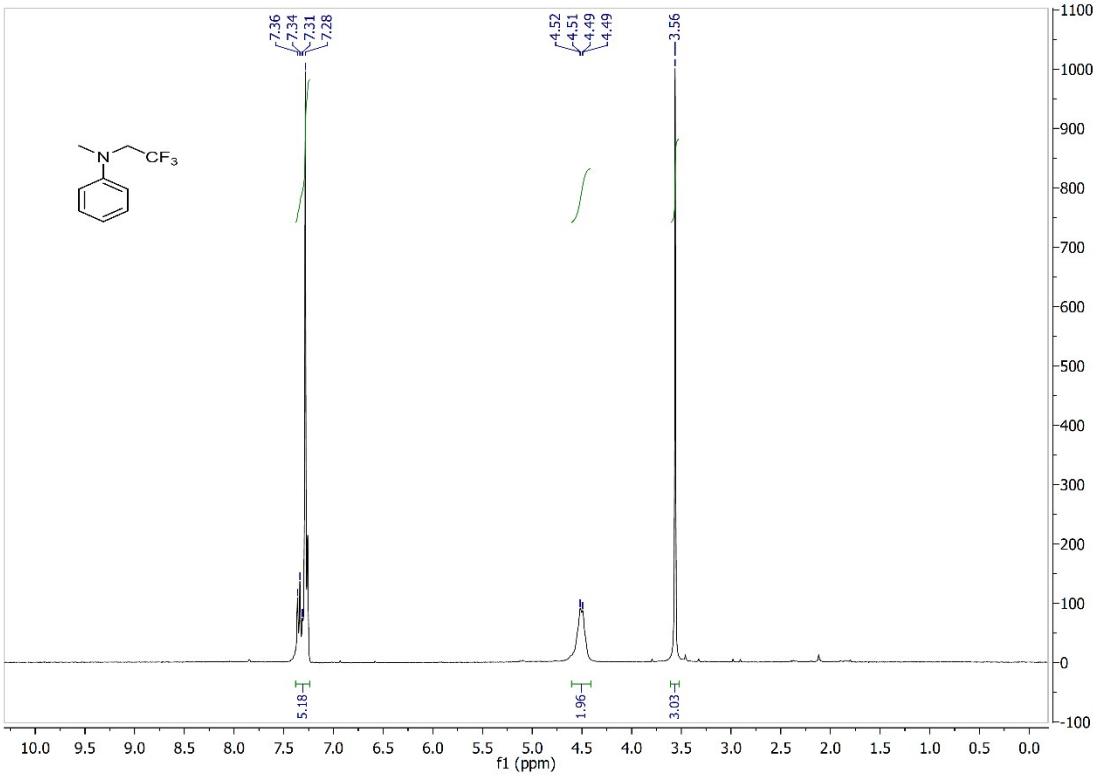
2-*N,N*-bis(2,2,2-trifluoroethyl)aminopyridine (2m)

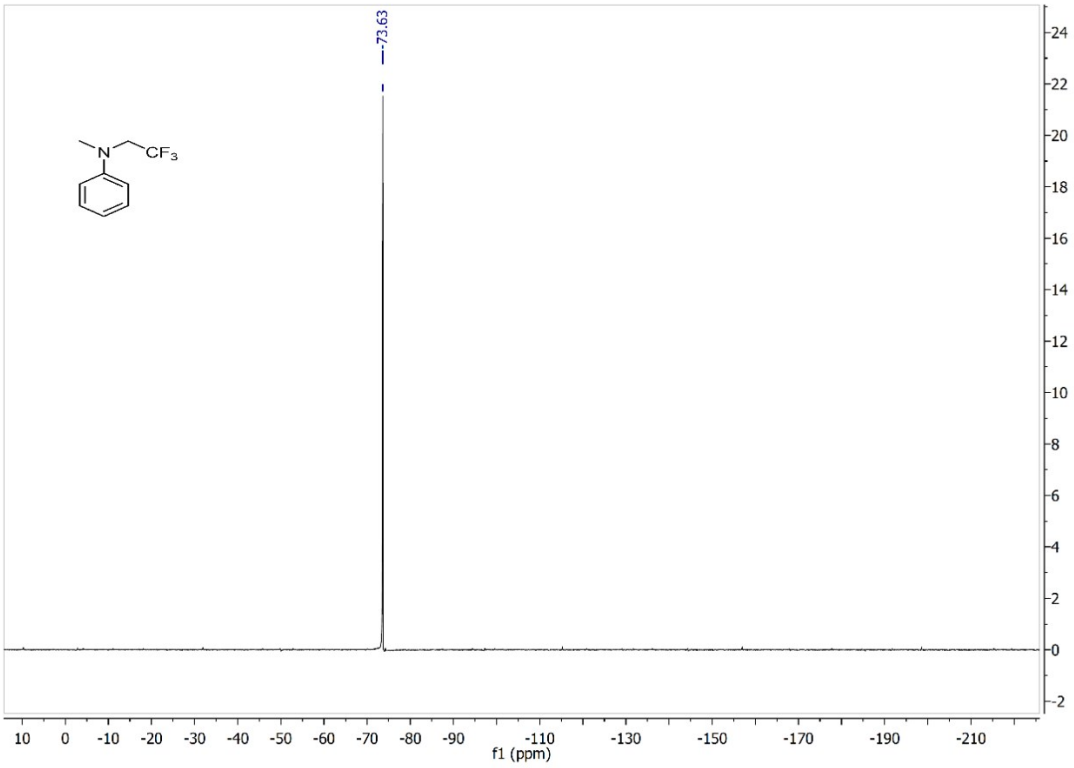


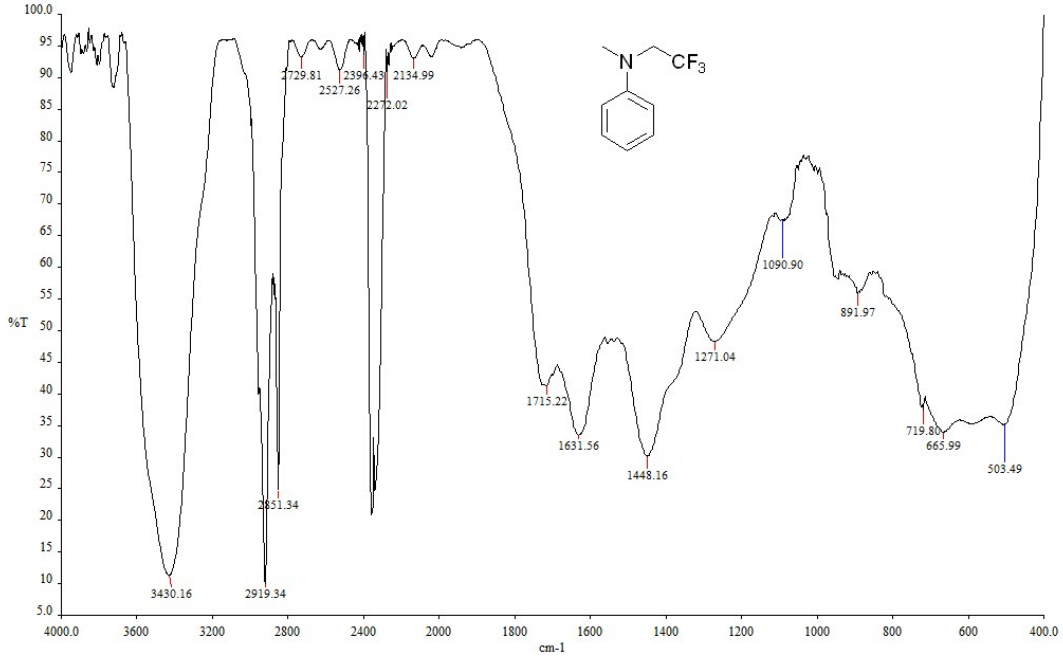




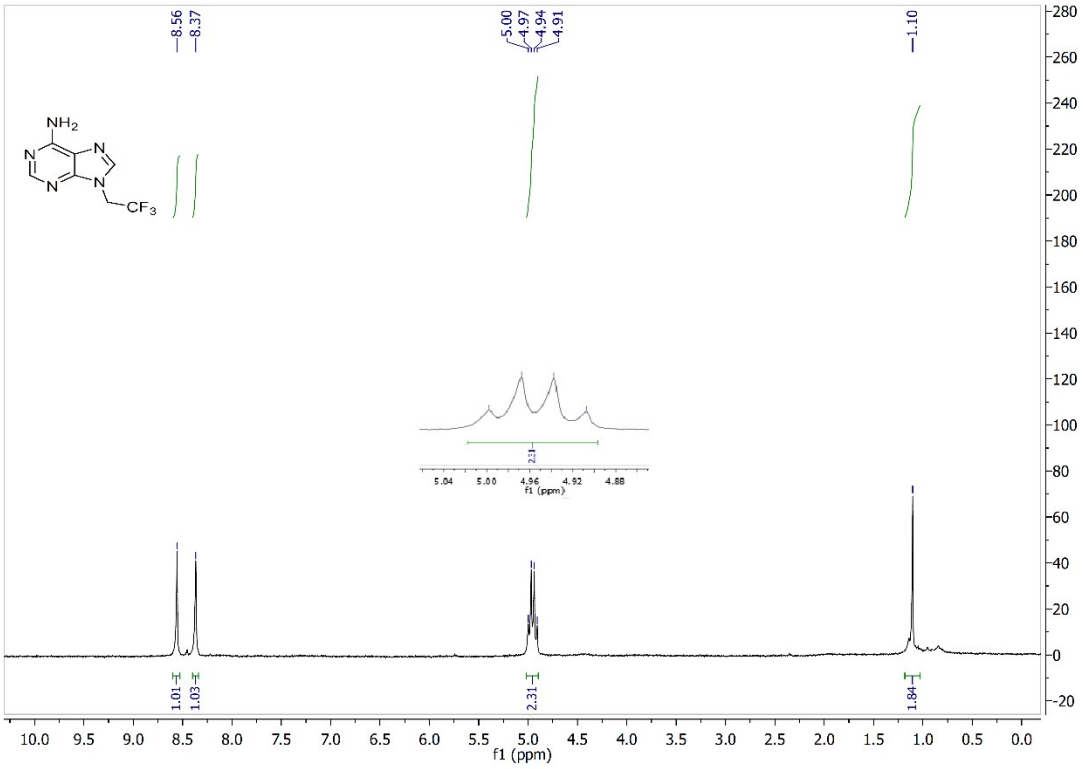
N-(2,2,2-trifluoroethyl)-*N*-methyl aniline (2n)

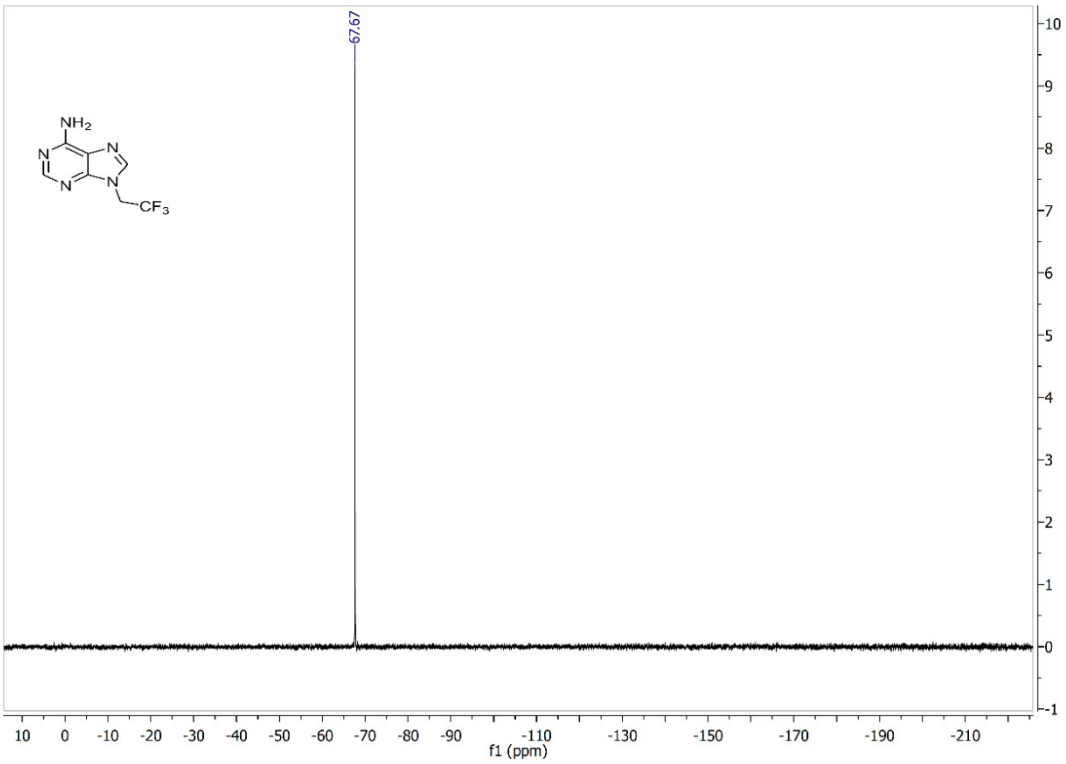


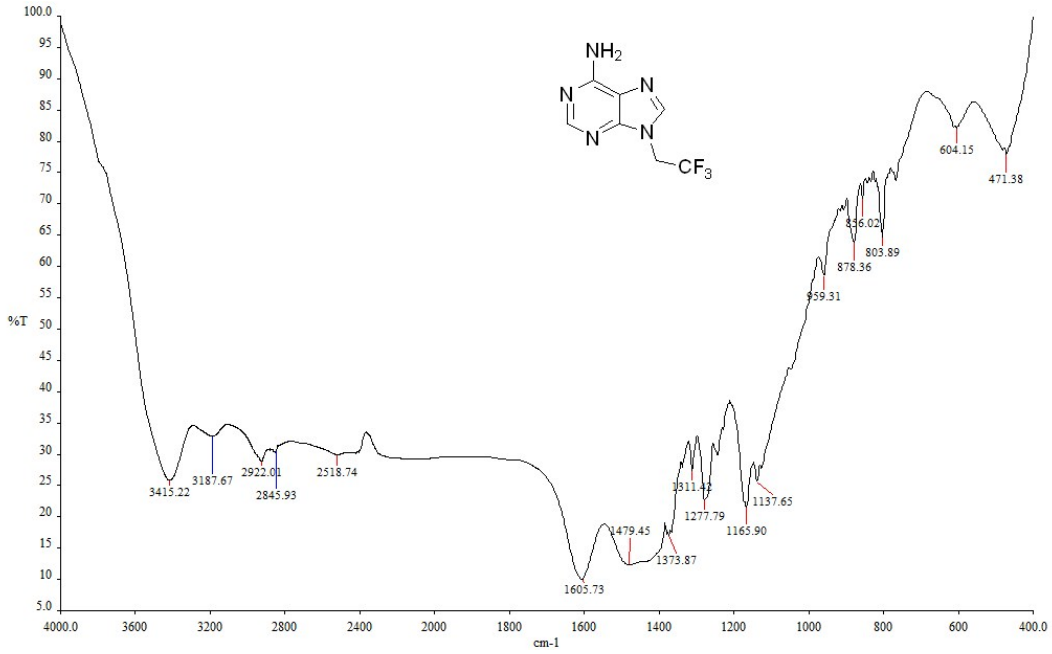

-73.63
N
CF3
24
22
20
18
16
14
12
10
8
6
4
2
0
-2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)


%T
100.0
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5.0
4000.0 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600 400.0
cm-1
3430.16
2919.34
2851.34
2729.81
2527.26
2396.43
2272.02
2134.99
1715.22
1631.56
1448.16
1271.04
1090.90
891.97
719.80
665.99
503.49
N
CF3

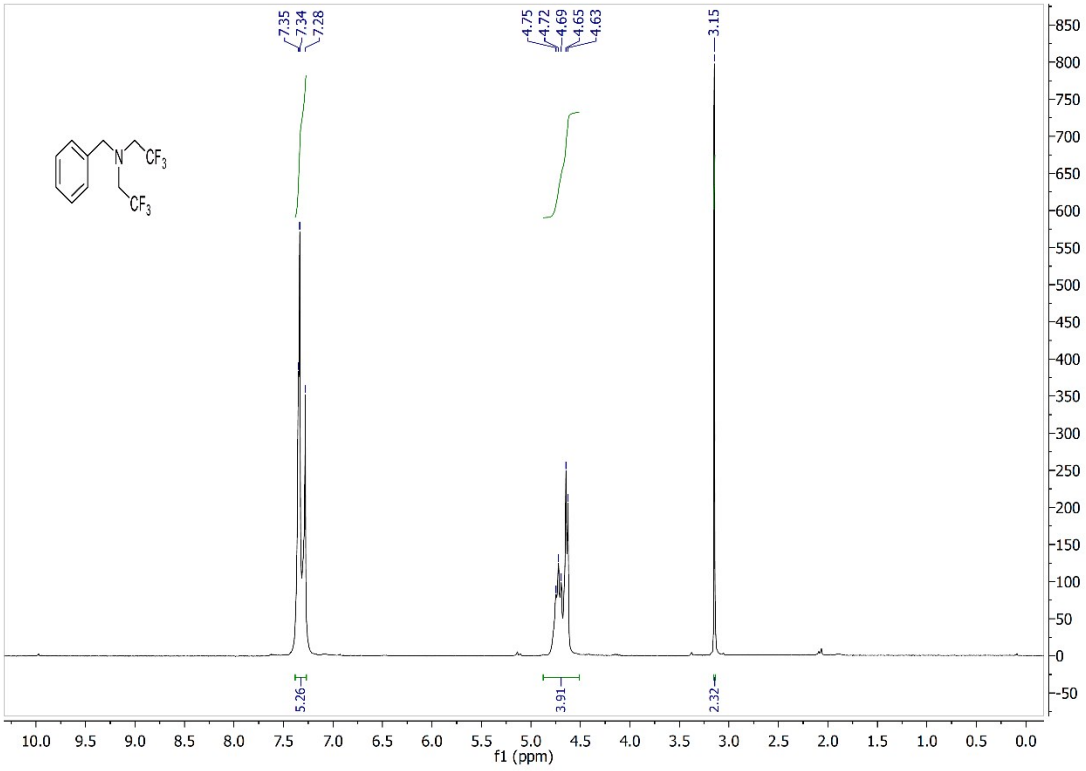
9-(2,2,2-trifluoroethyl)adenine (2o)

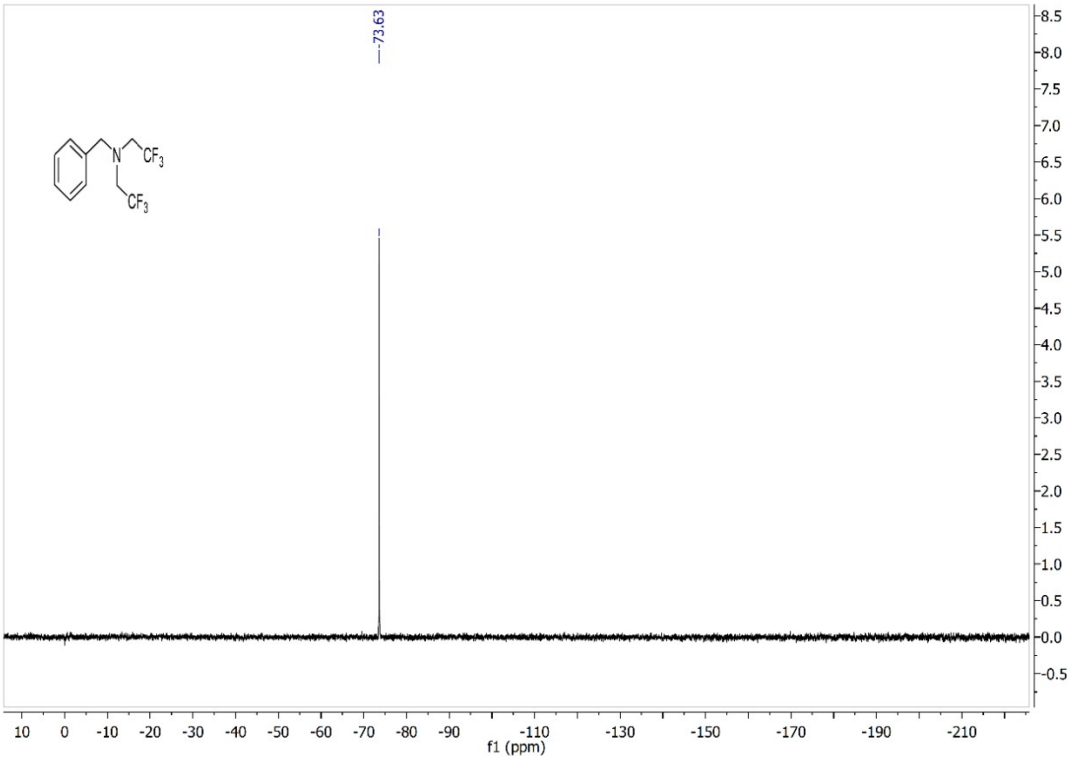


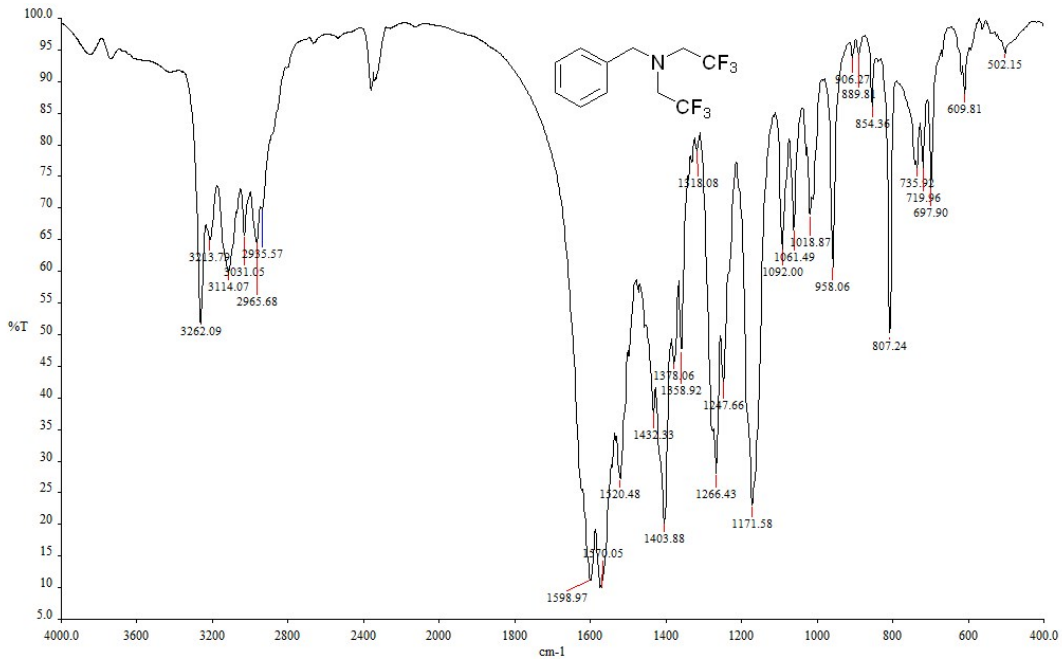




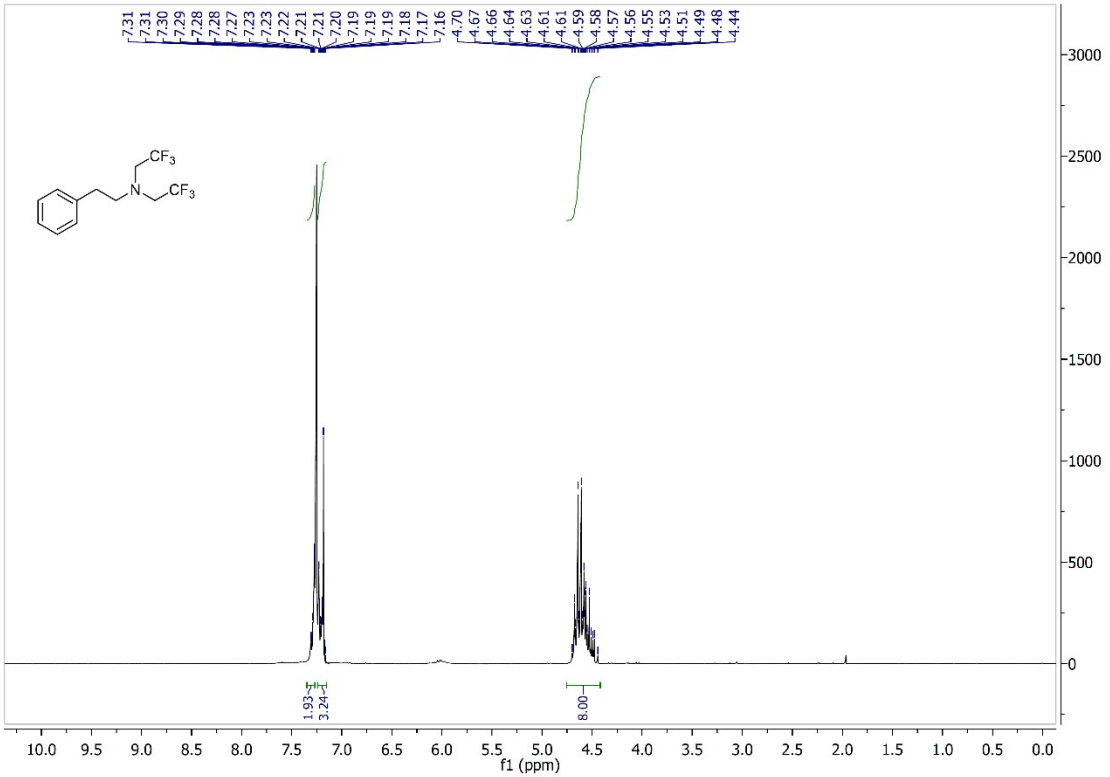
Benzyl-*N,N*-bis(2,2,2-trifluoroethyl)amine (2p)

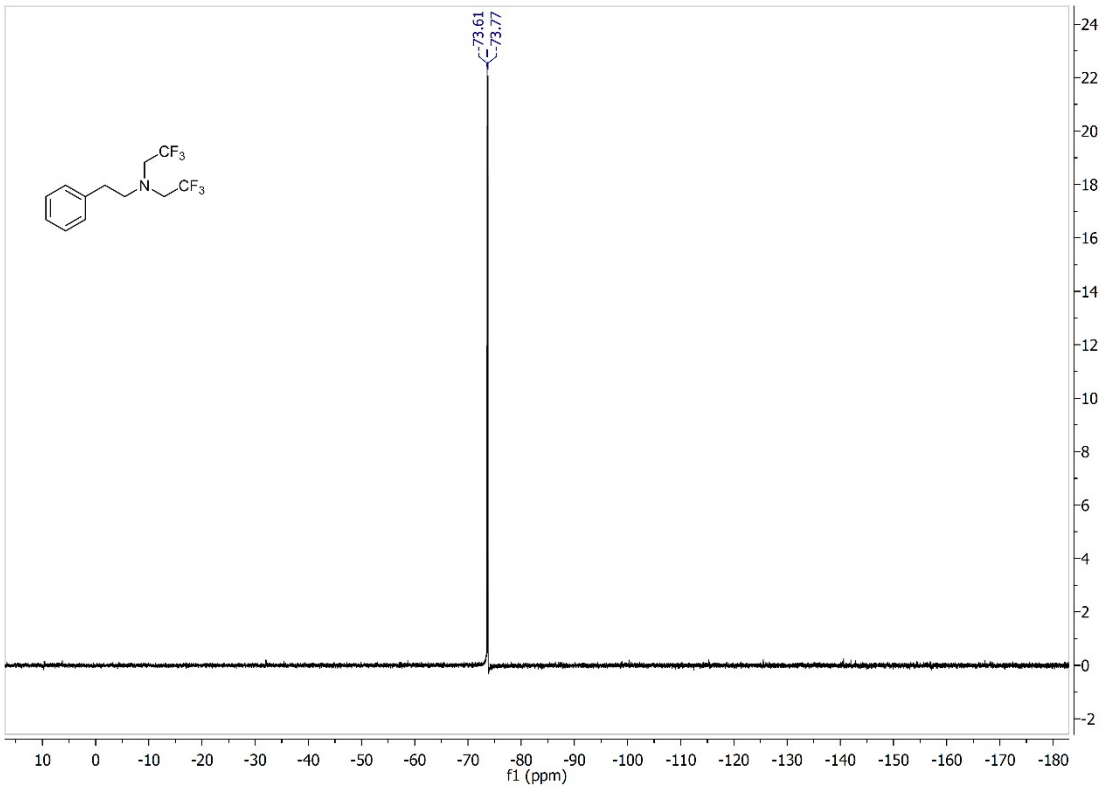


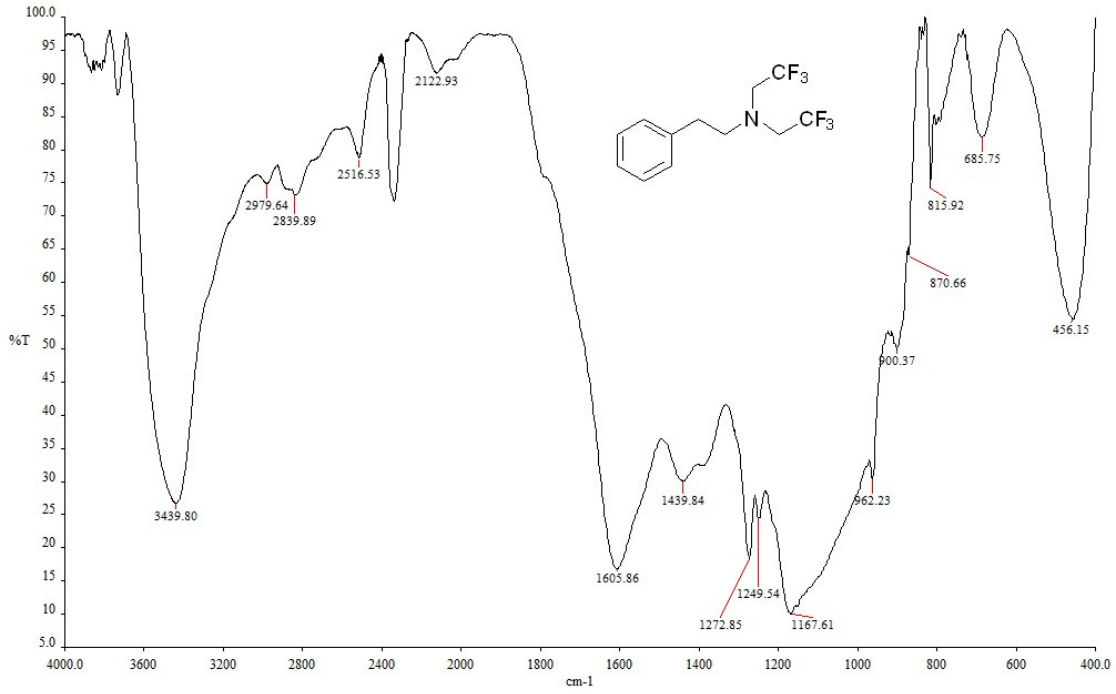

-73.63
N
CF3
CF3
f1 (ppm)


%T
cm-1
3262.09
3213.79
3114.07
3031.05
2965.68
2935.57
1598.97
1570.05
1520.48
1432.33
1403.88
1378.06
1358.92
1318.08
1266.43
1247.66
1171.58
1092.00
1061.49
1018.87
958.06
906.27
889.81
854.36
807.24
735.92
719.96
697.90
609.81
502.15

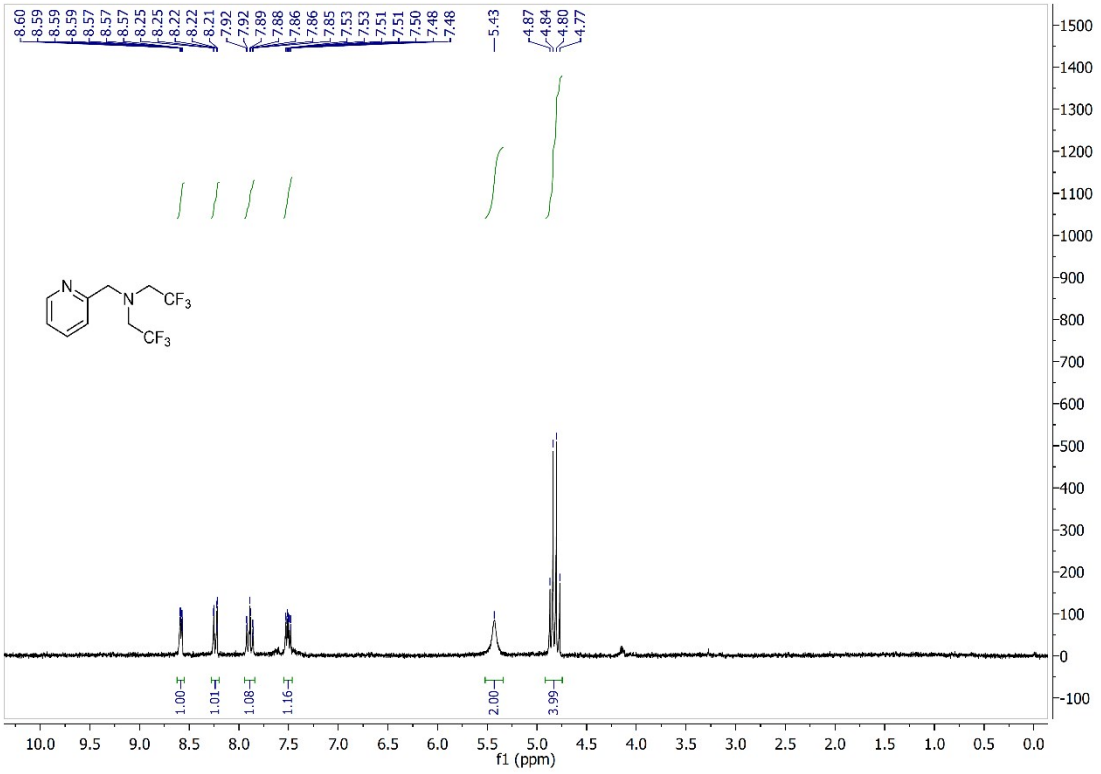
2-Phenylethyl-*N,N*-bis(2,2,2-trifluoroethyl)amine (2q)

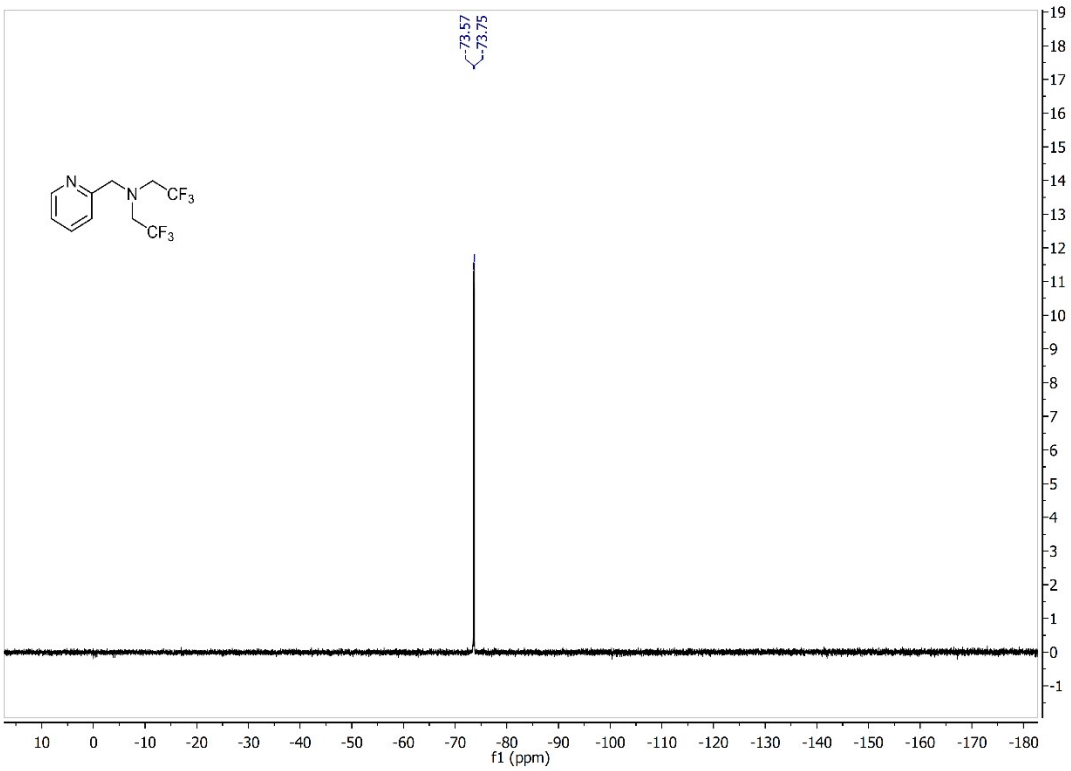


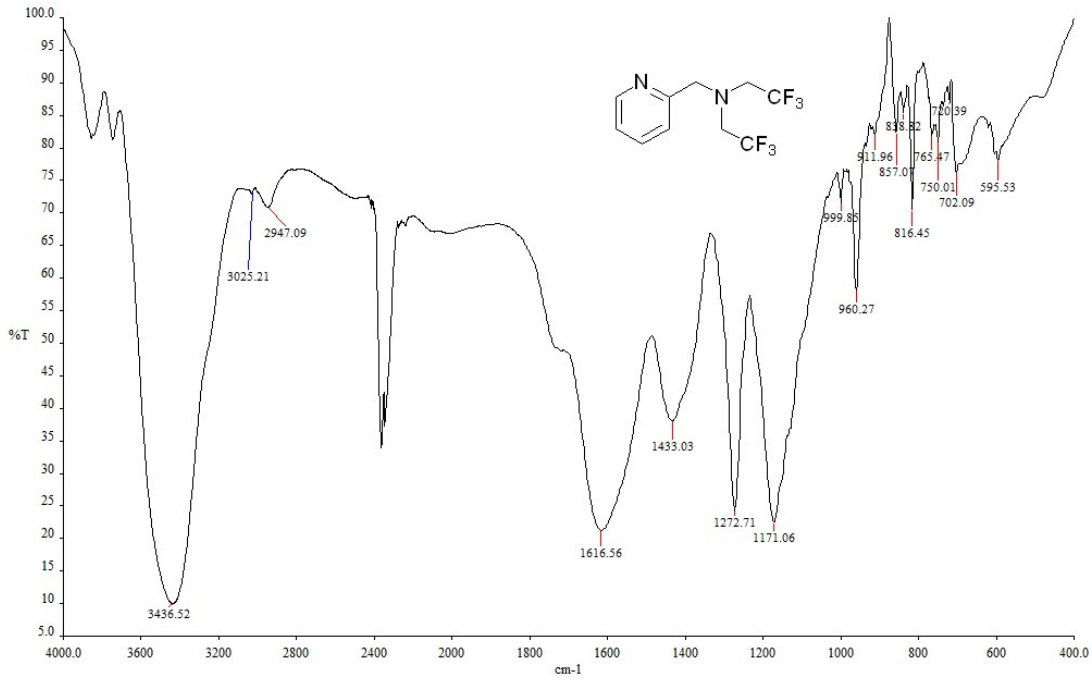




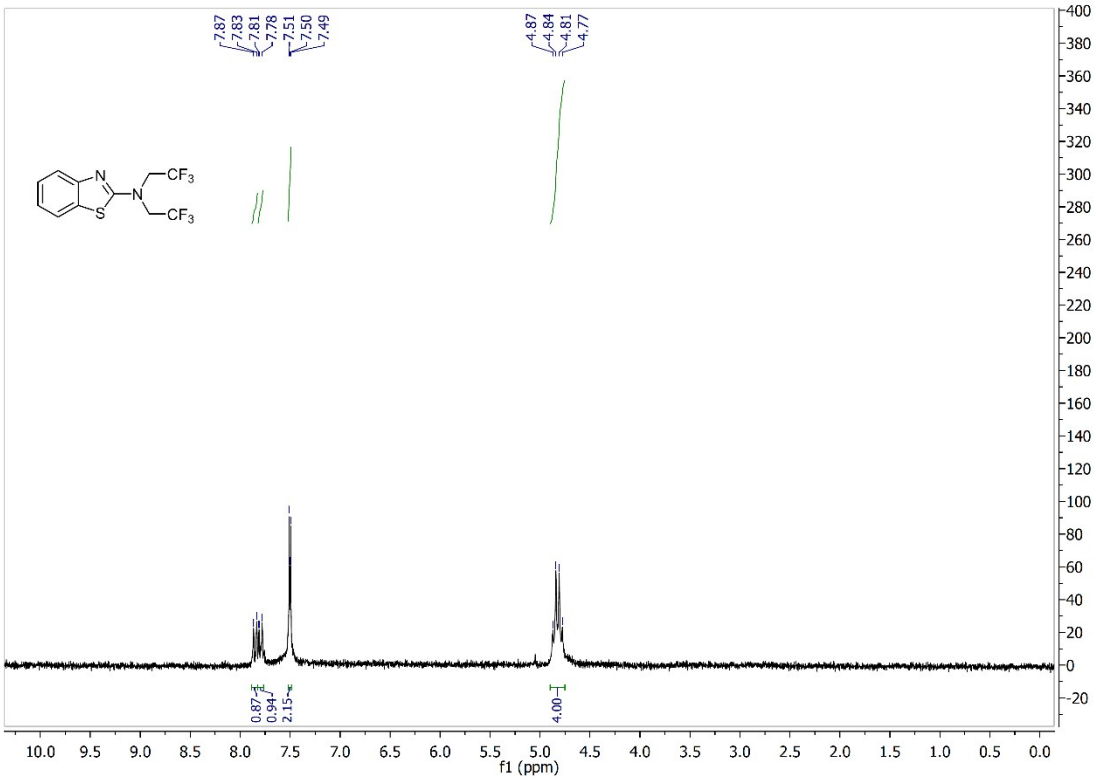
2-*N,N*-bis(2,2,2-trifluoroethyl)(aminomethyl) pyridine (2r)

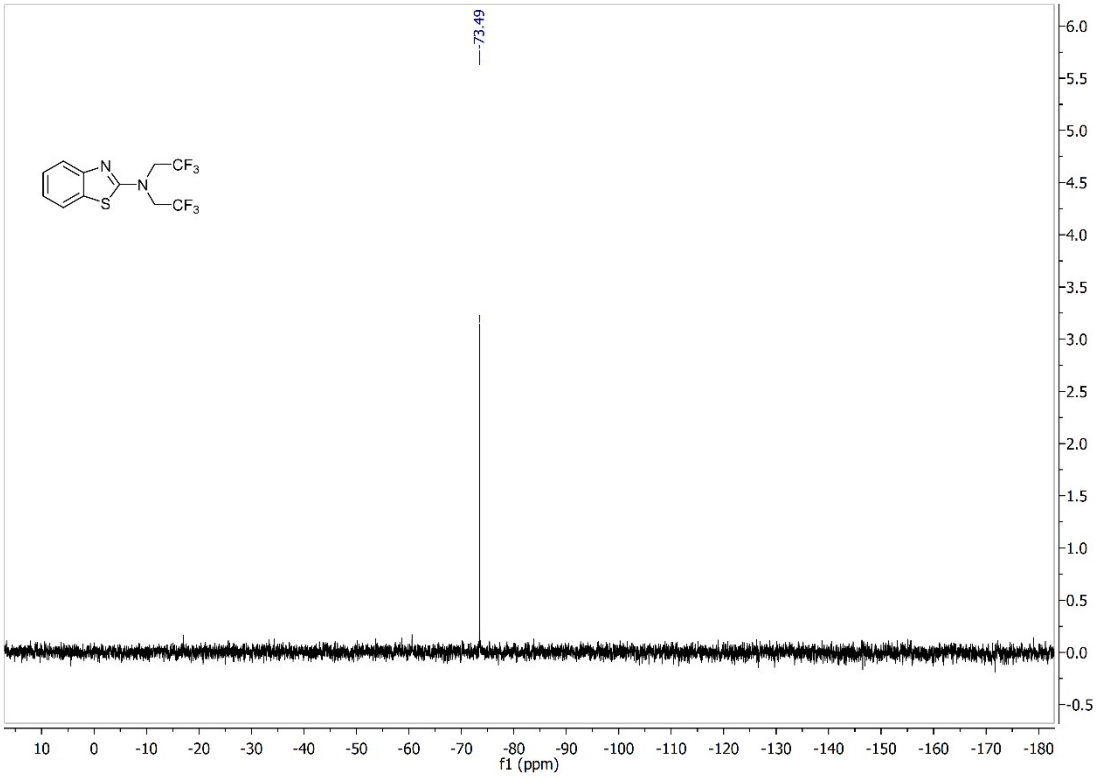


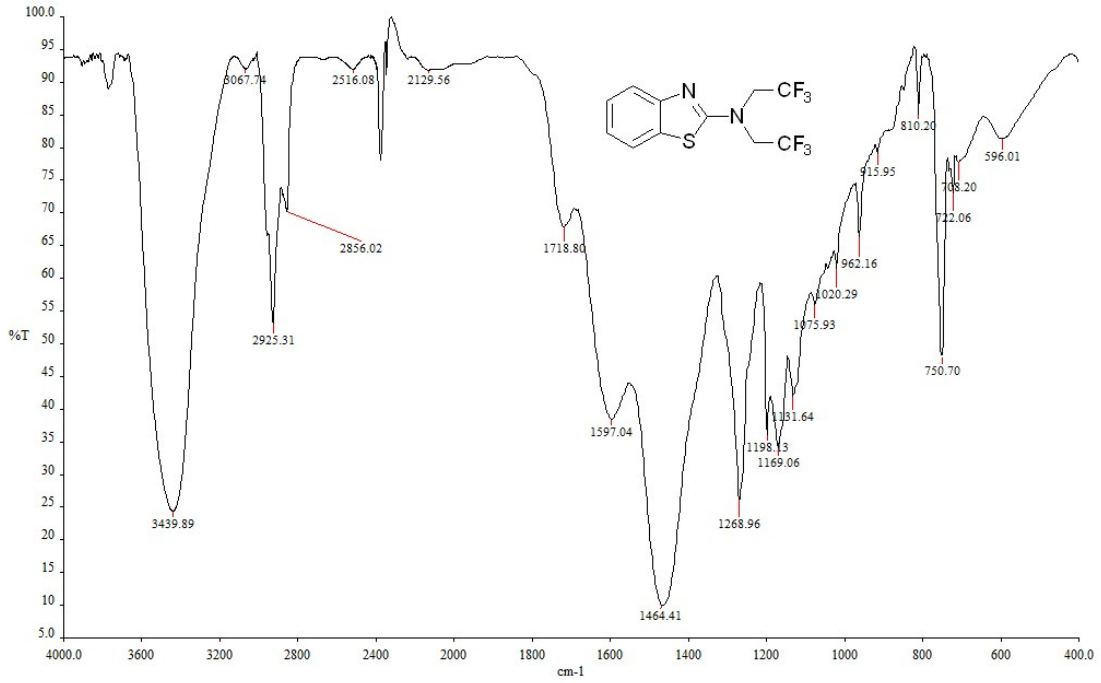




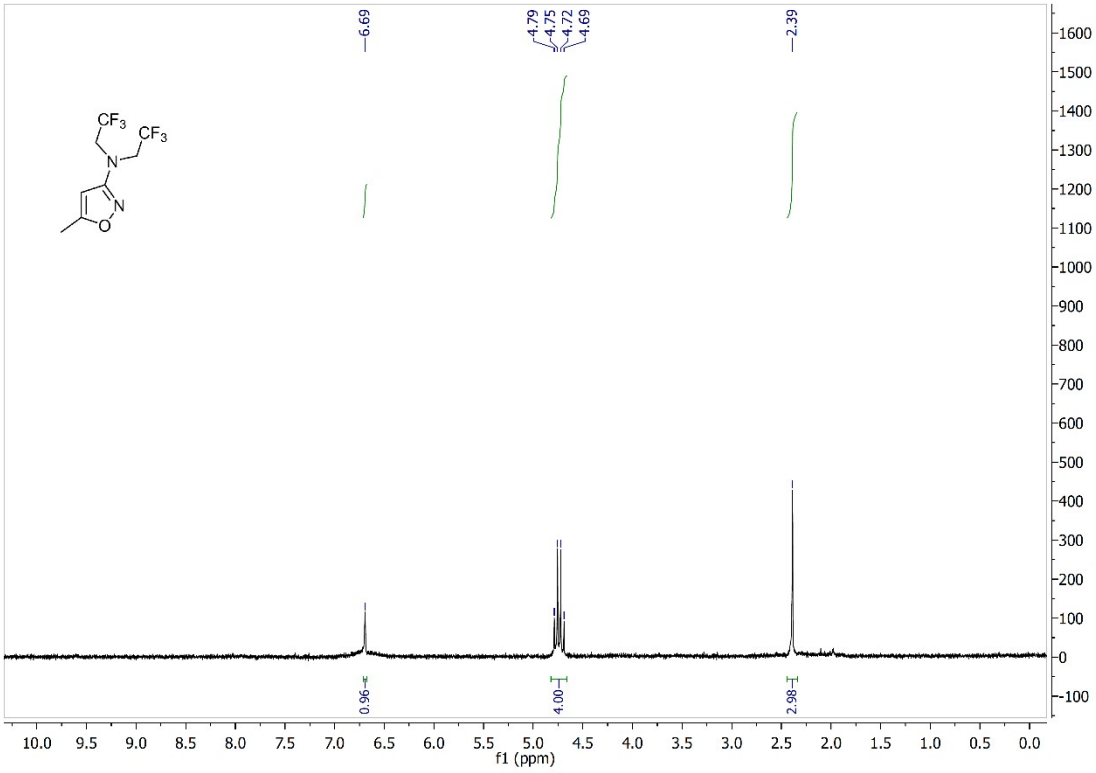
2-*N,N*-bis(2,2,2-trifluoroethyl)aminobenzothiazole (2s)

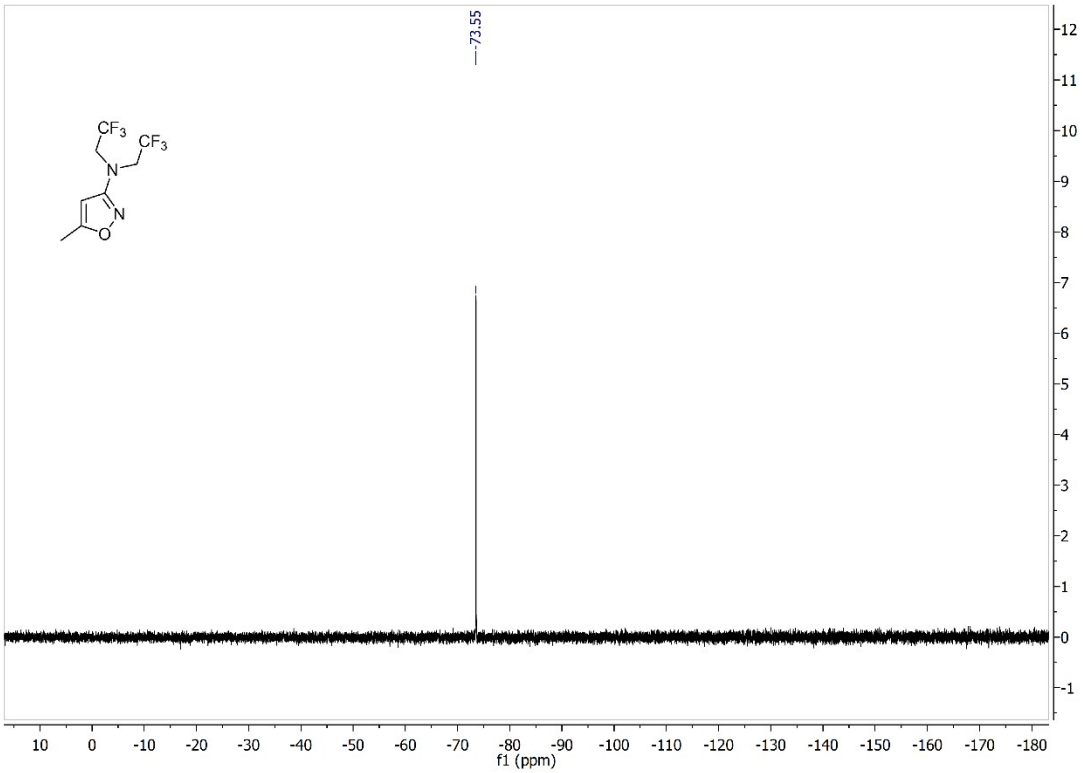

7.87
7.83
7.81
7.78
7.51
7.50
7.49
4.87
4.84
4.81
4.77
N
S
N
CF3
CF3
0.87
0.94
2.15
4.00
f1 (ppm)

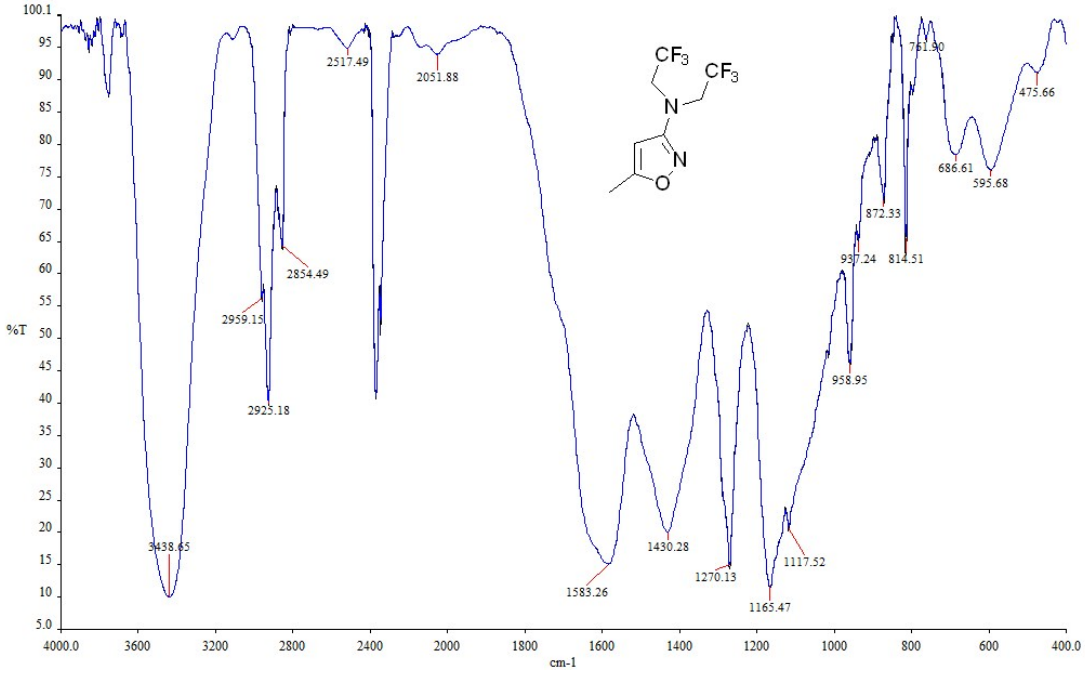

-73.49
N
S
N
CF3
CF3
f1 (ppm)



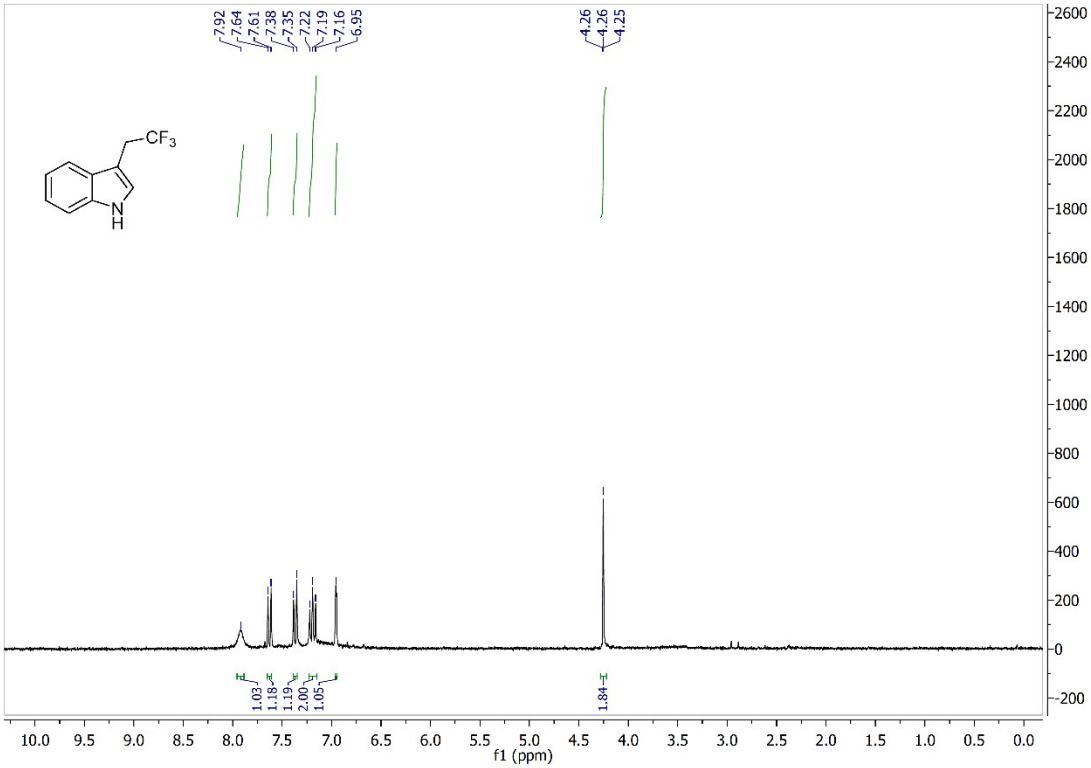
5-Methyl-*N*,*N*-bis(2,2,2-trifluoroethyl)isoxazole-3-amine (2t)

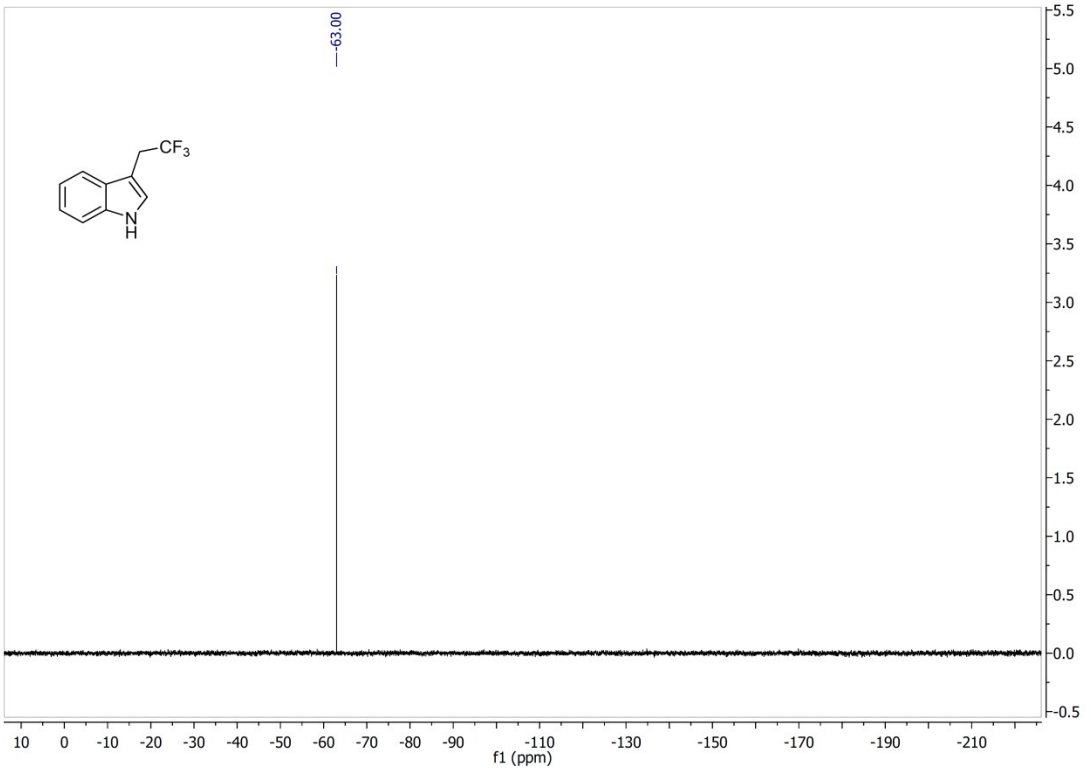


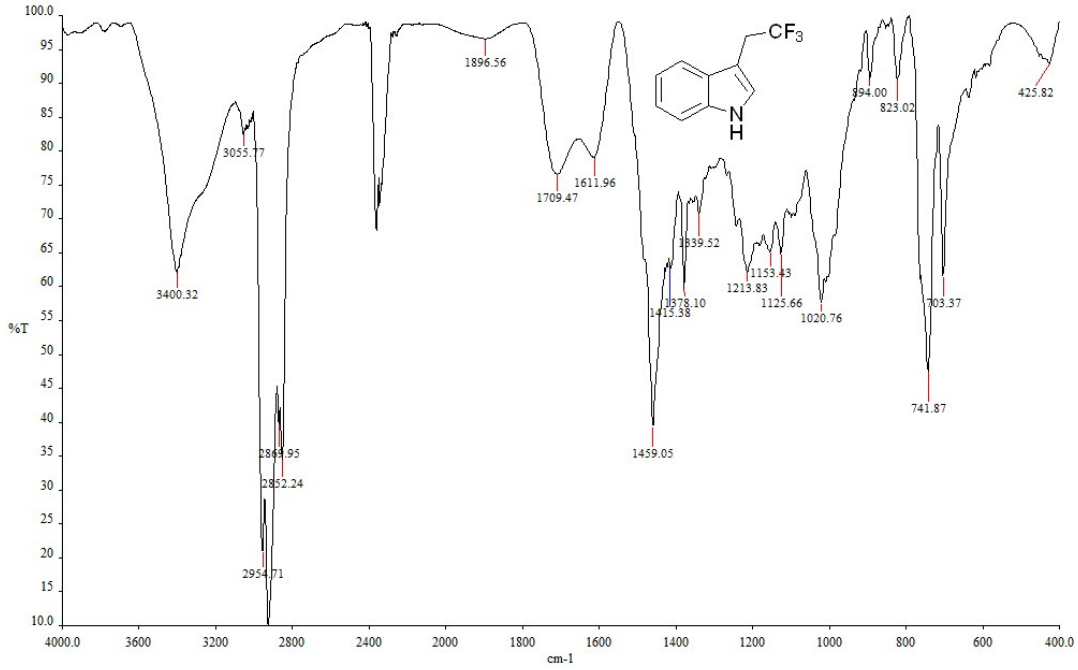

-73.55
CF3
CF3
N
O
N
f1 (ppm)


CF3
CF3
N
O
N
%T
cm-1
3438.65
2959.15
2925.18
2854.49
2517.49
2051.88
1583.26
1430.28
1270.13
1165.47
1117.52
958.95
937.24
872.33
814.51
761.90
686.61
595.68
475.66

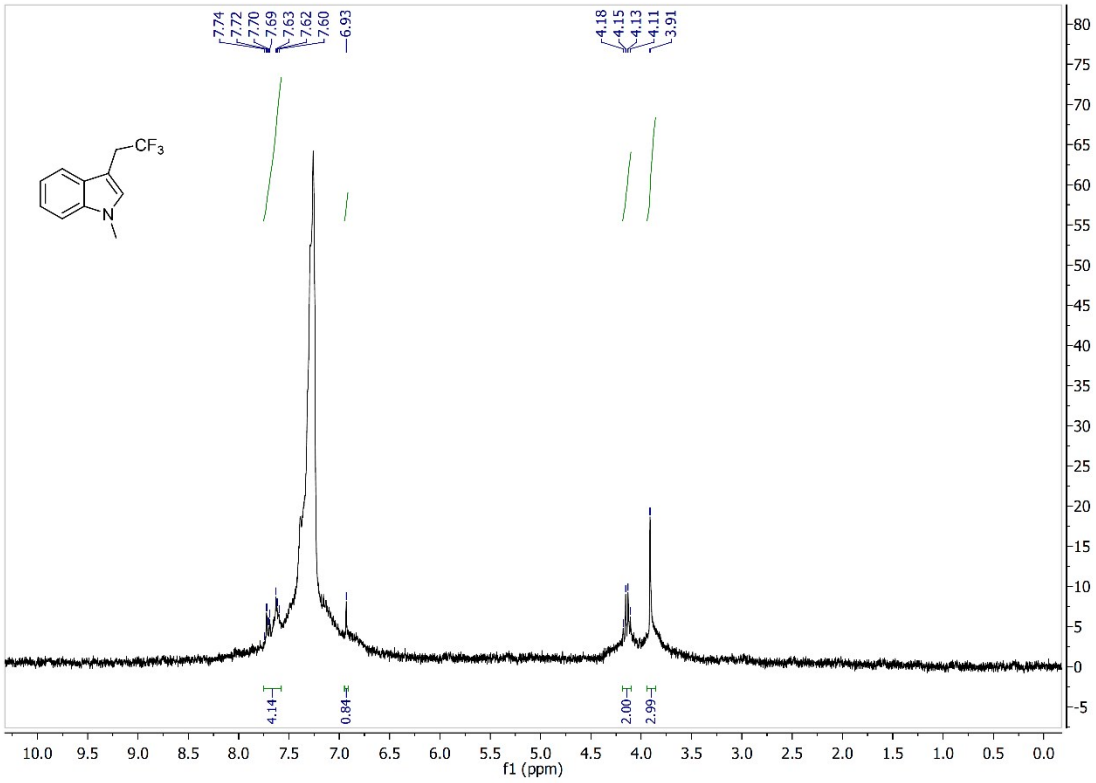
3-(2,2,2-Trifluoroethyl)-1*H*-indole (2u)

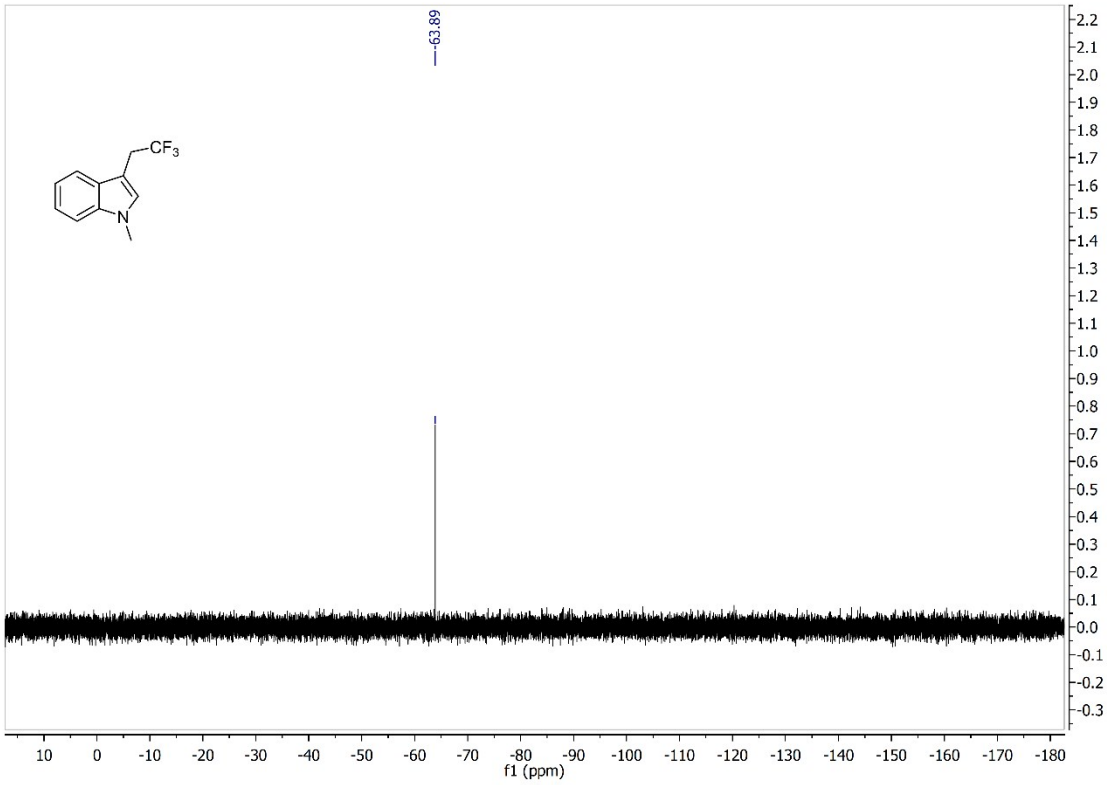


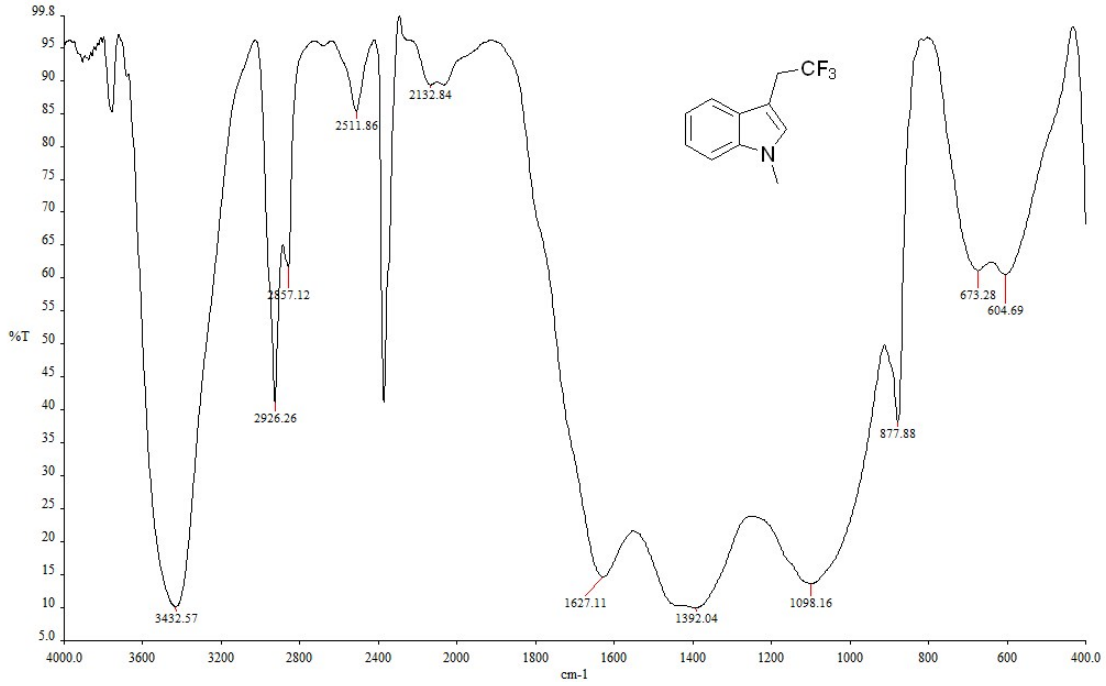




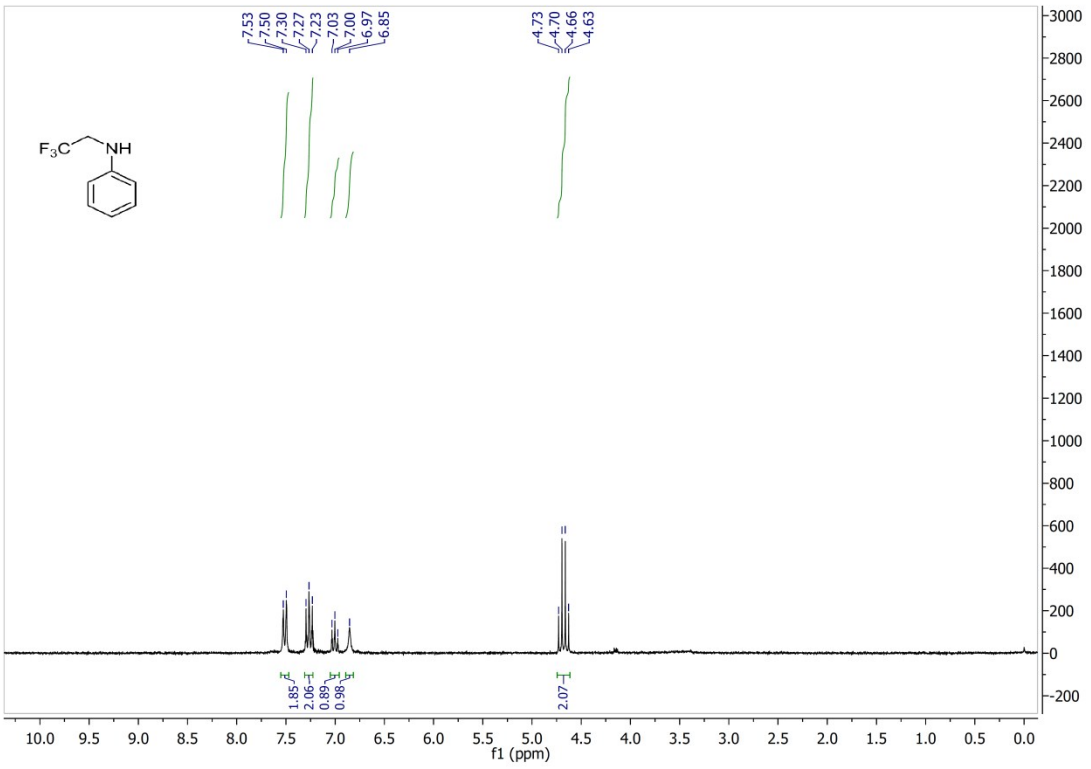
1-Methyl-3-(2,2,2-trifluoroethyl)-1*H*-indole (2v)

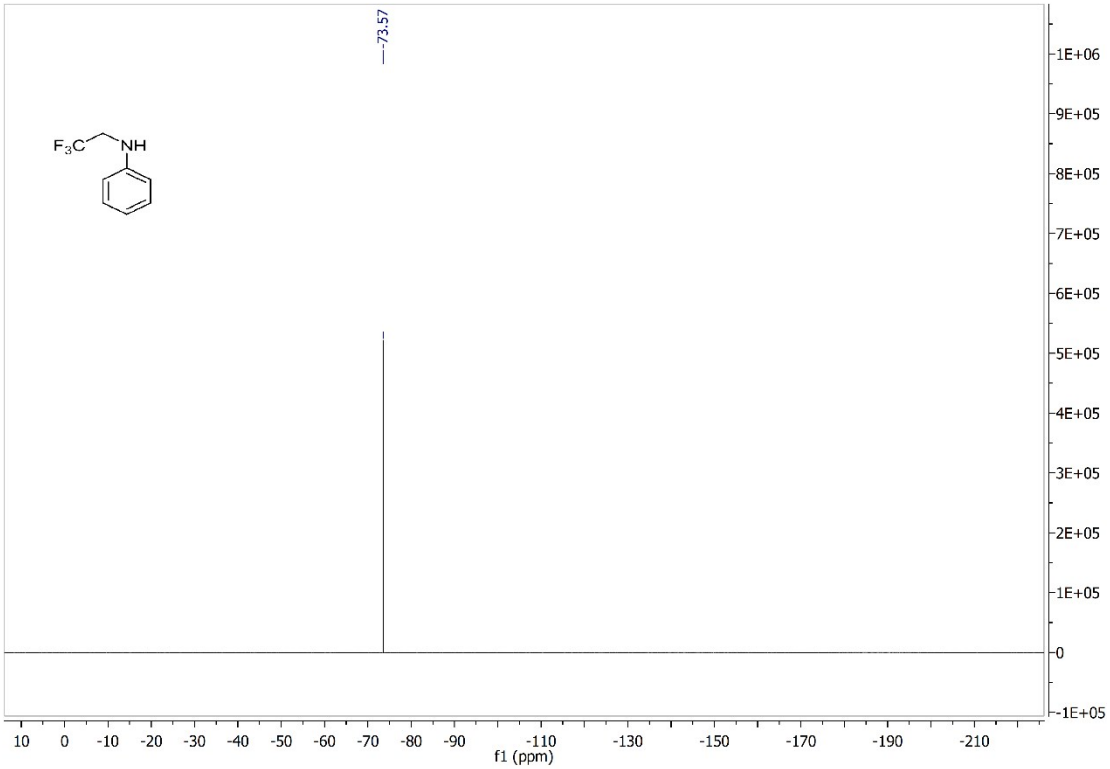


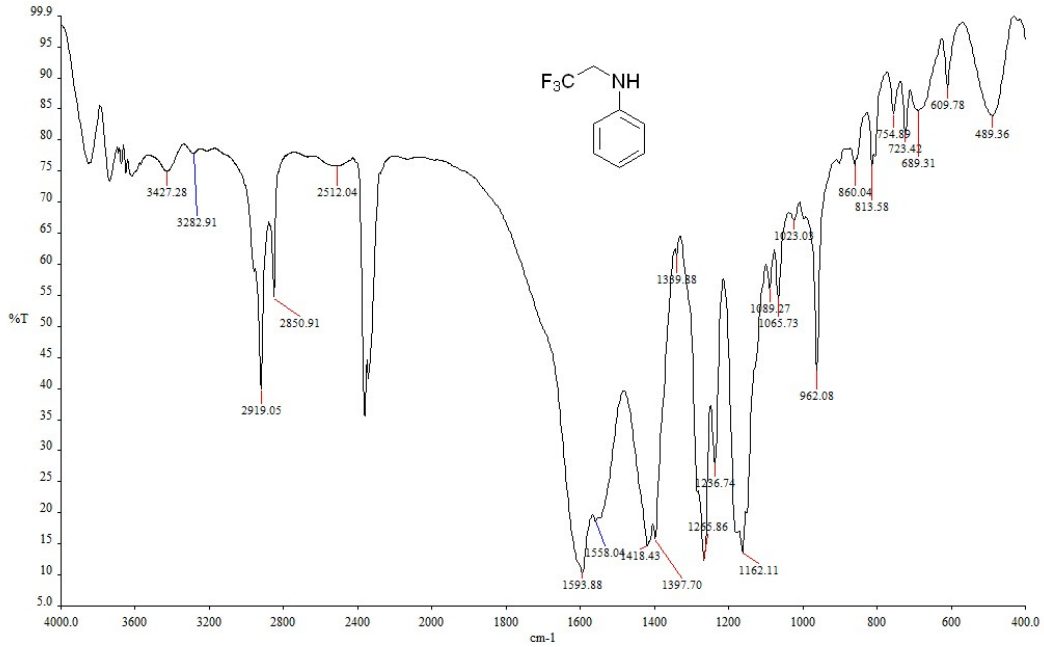

-63.89
CF3
N
f1 (ppm)


%T
3432.57
2926.26
2857.12
2511.86
2132.84
1627.11
1392.04
1098.16
877.88
673.28
604.69
CF3
N
cm-1

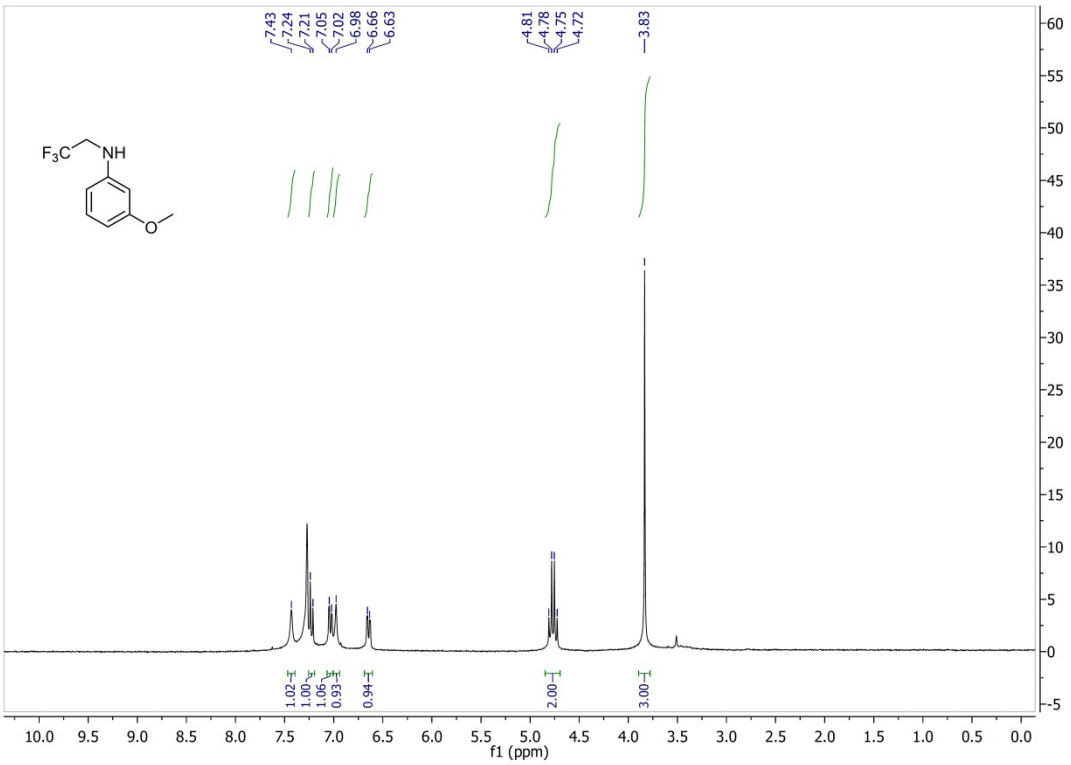
N-(2,2,2-Trifluoroethyl)aniline (3a)

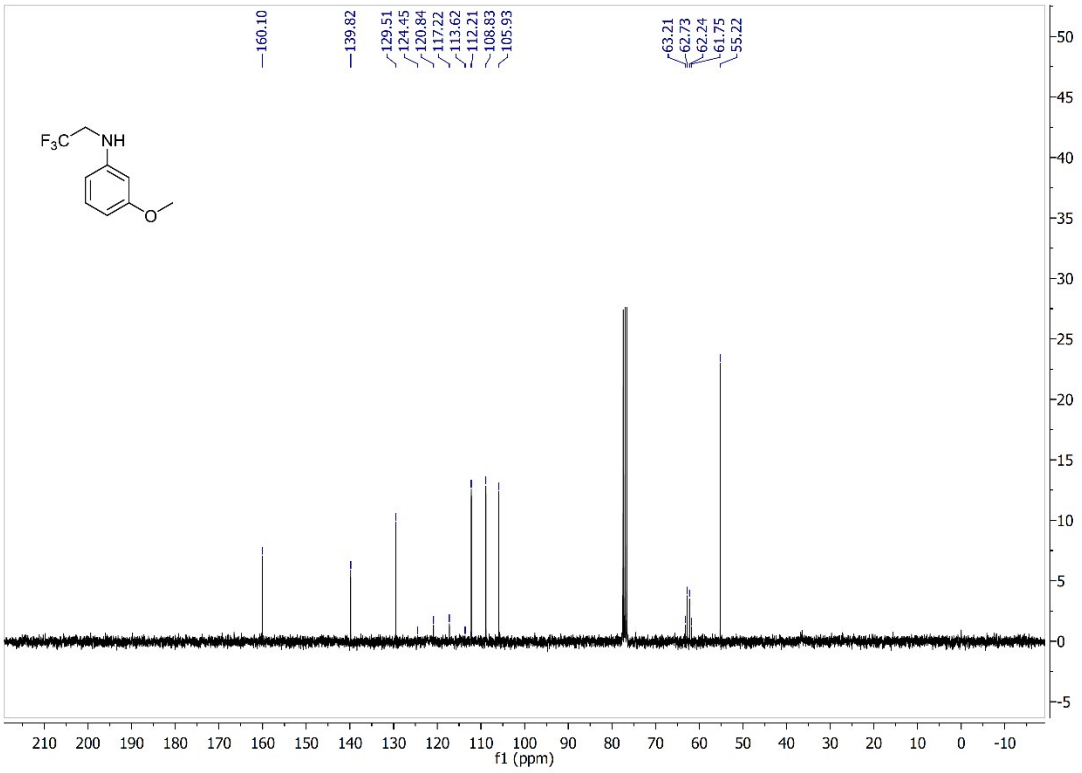


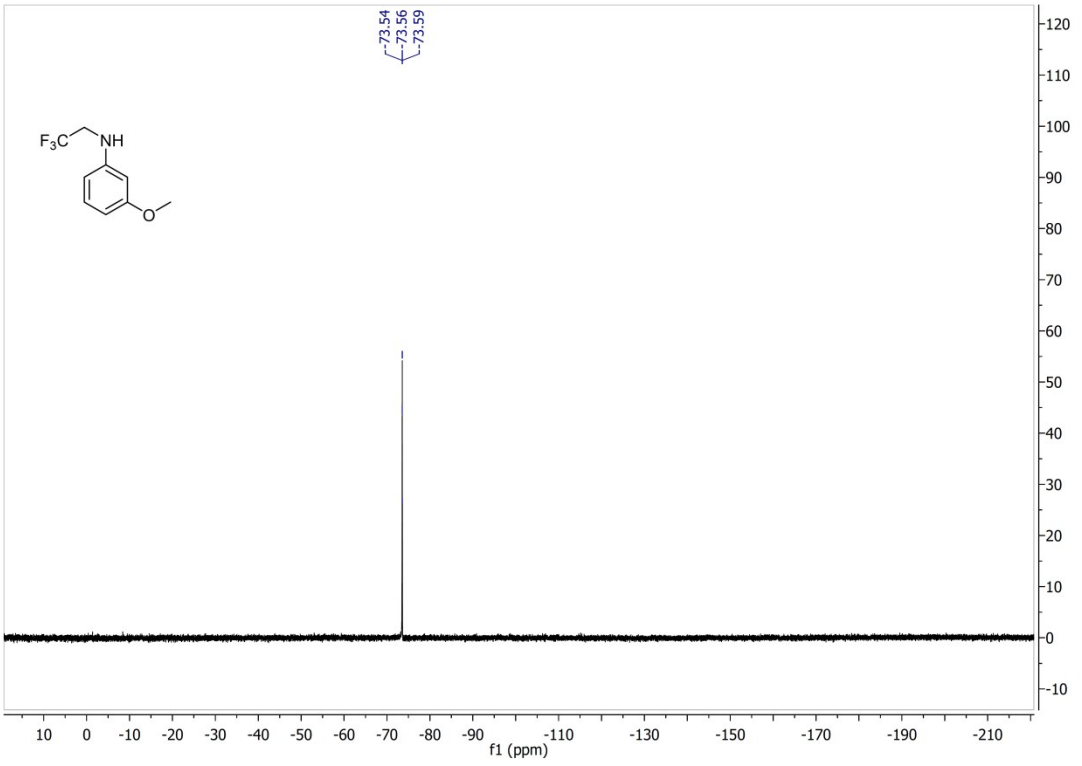


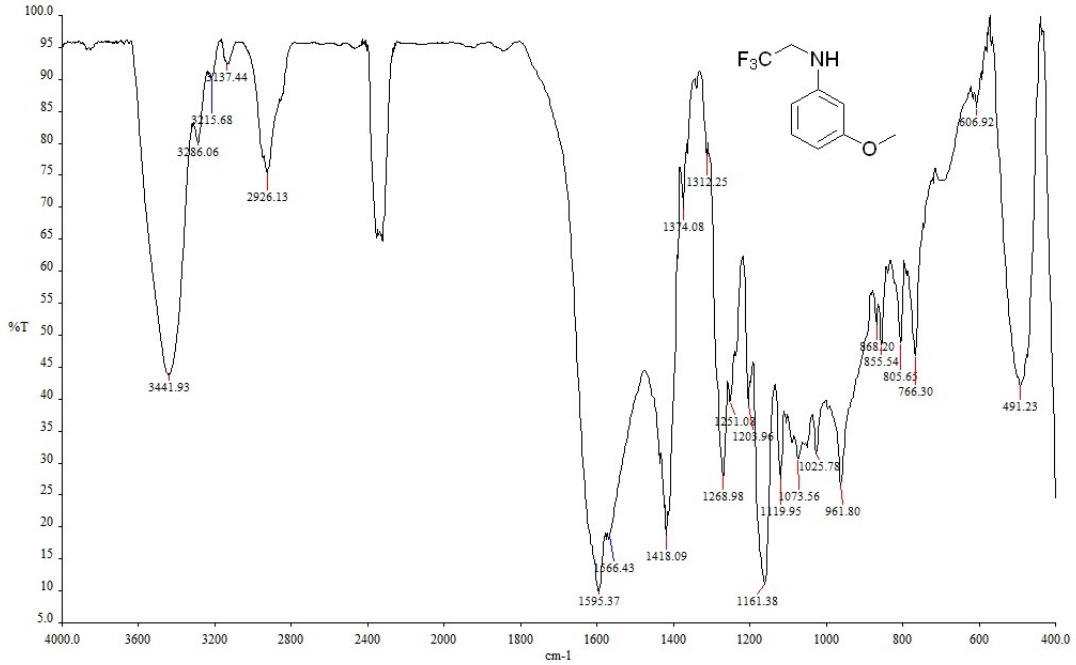


3-Methoxy-*N*-(2,2,2-trifluoroethyl)aniline (3b)

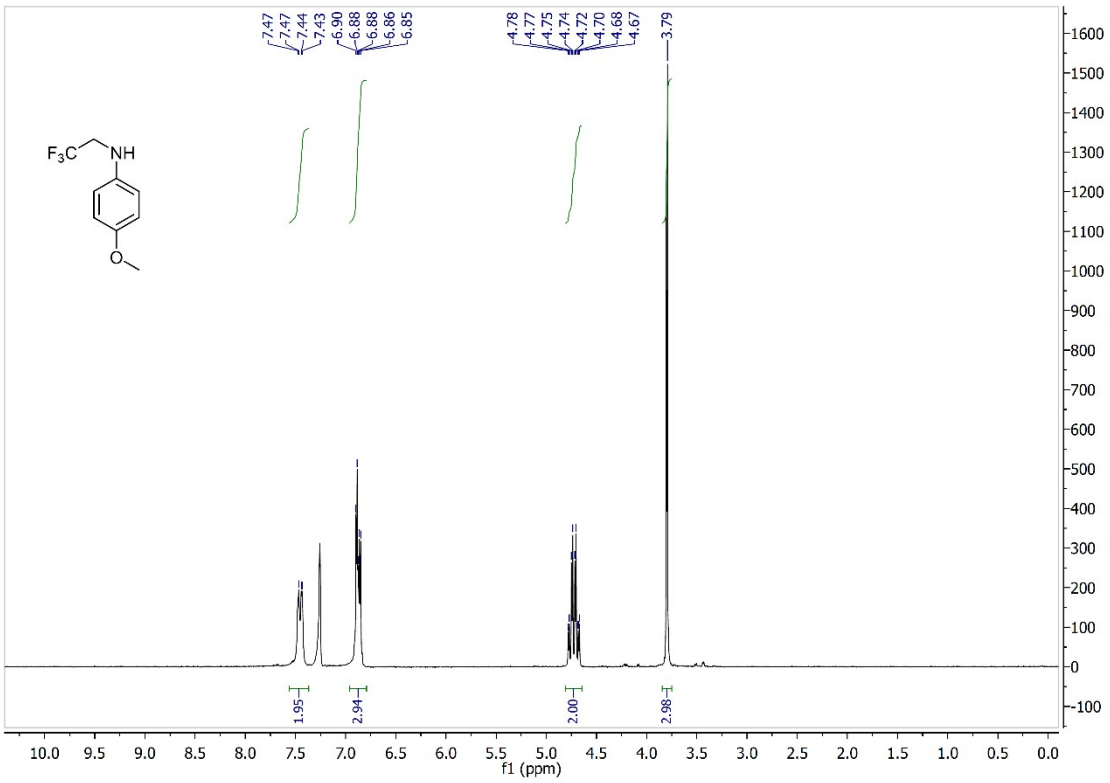


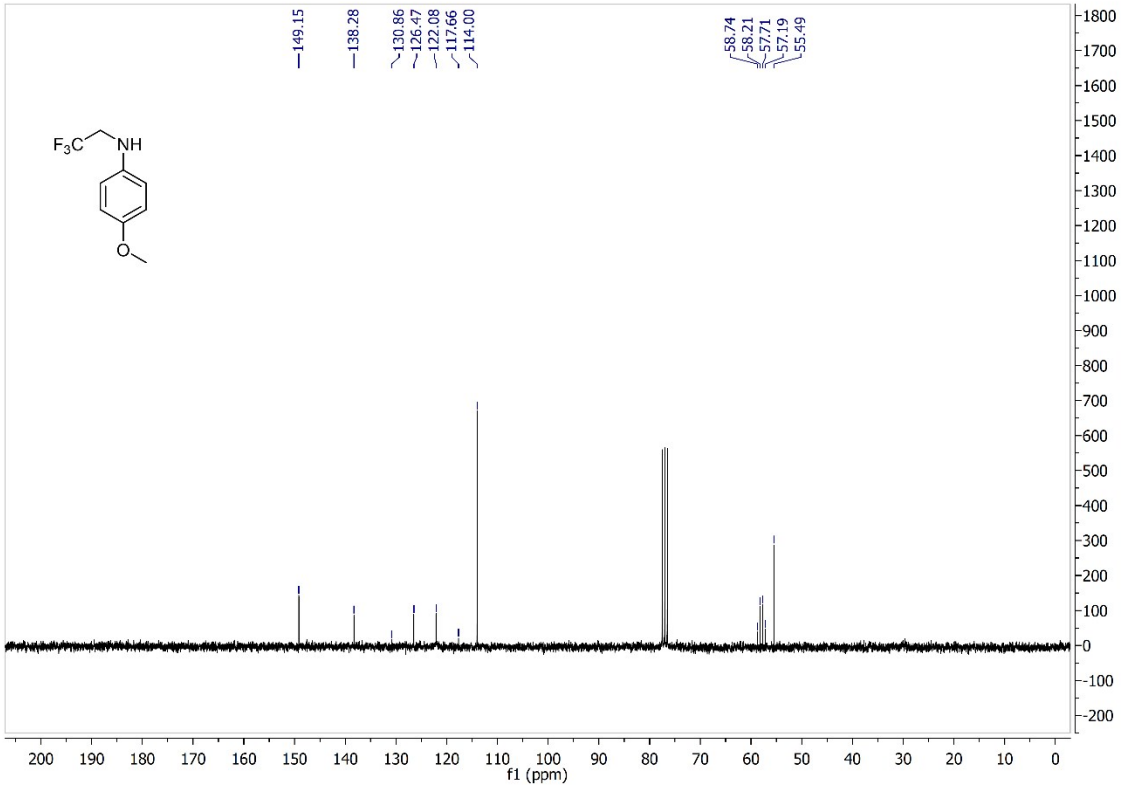

160.10
139.82
129.51
124.45
120.84
117.22
113.62
112.21
108.83
105.93
63.21
62.73
62.24
61.75
55.22
F3C
NH
O
f1 (ppm)

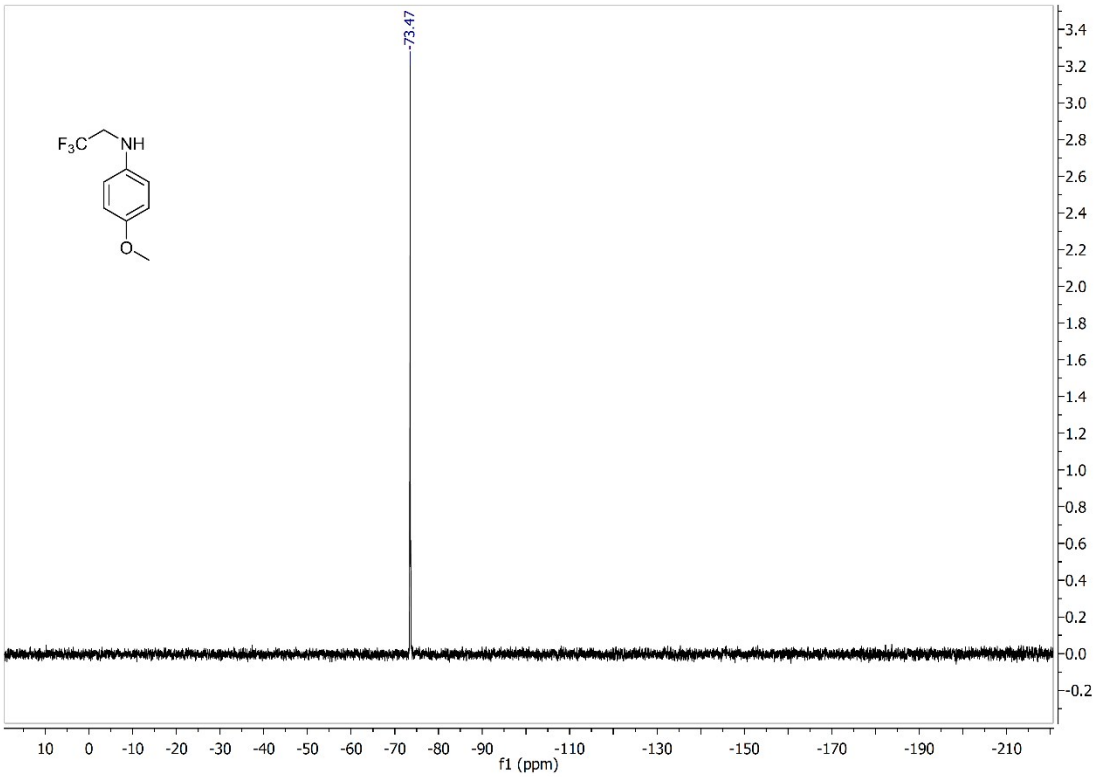

-73.54
-73.56
-73.59
F3C
NH
O
f1 (ppm)

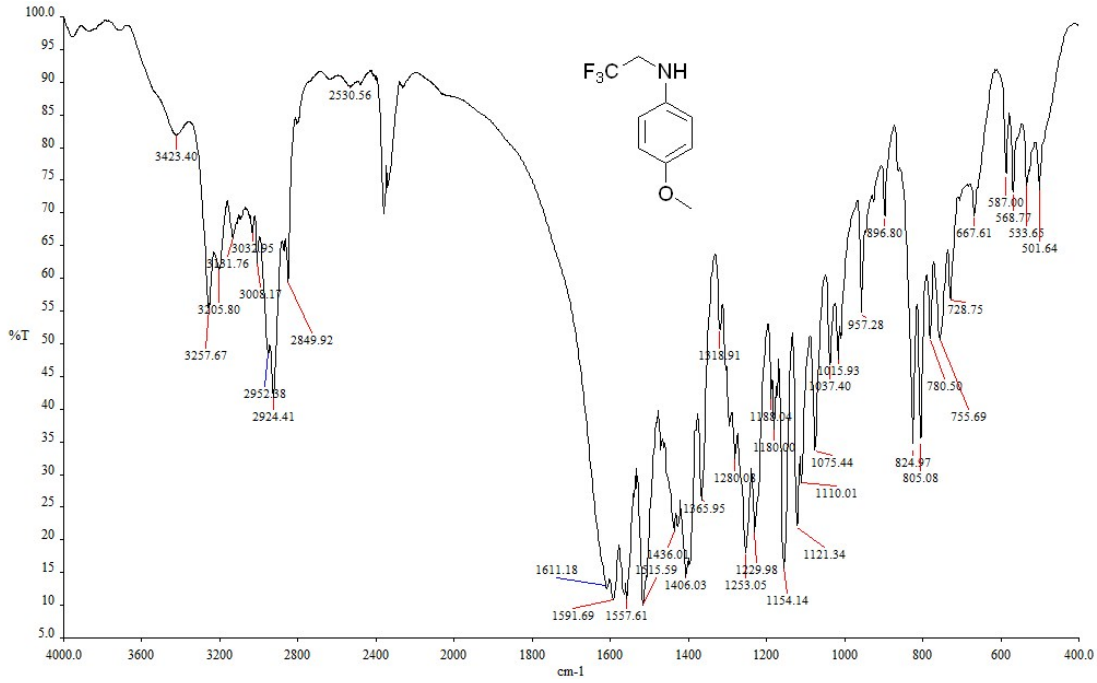


4-Methoxy-*N*-(2,2,2-trifluoroethyl)aniline (3c)

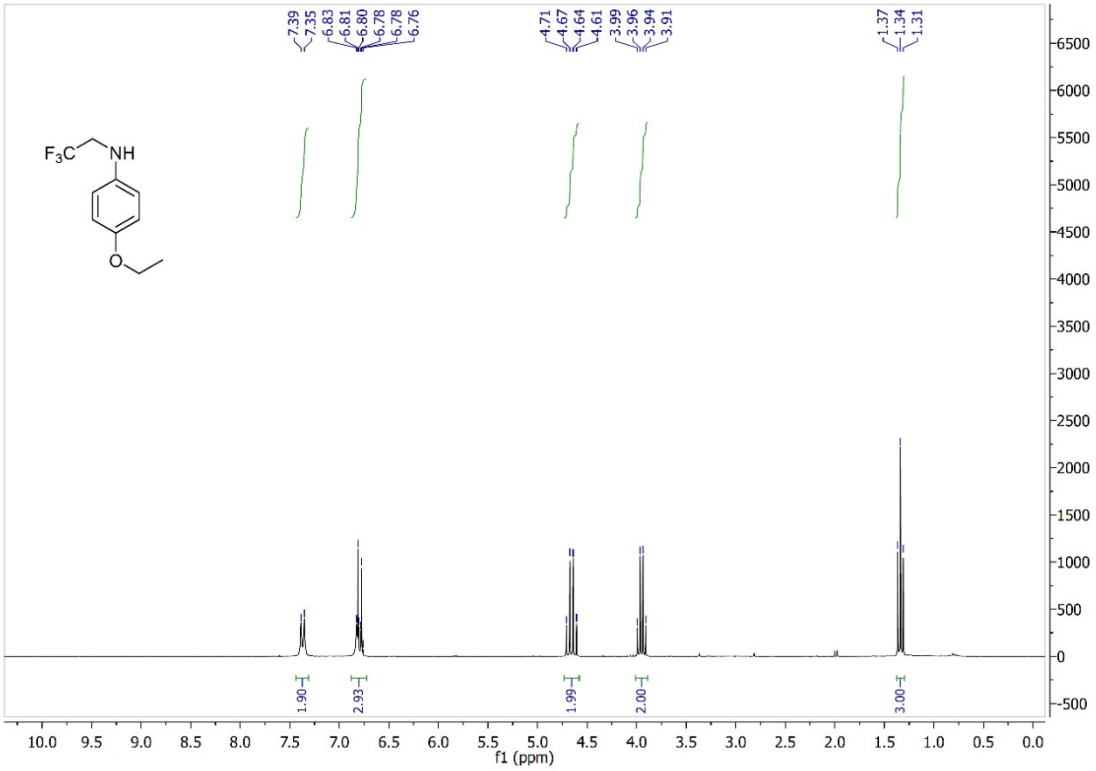


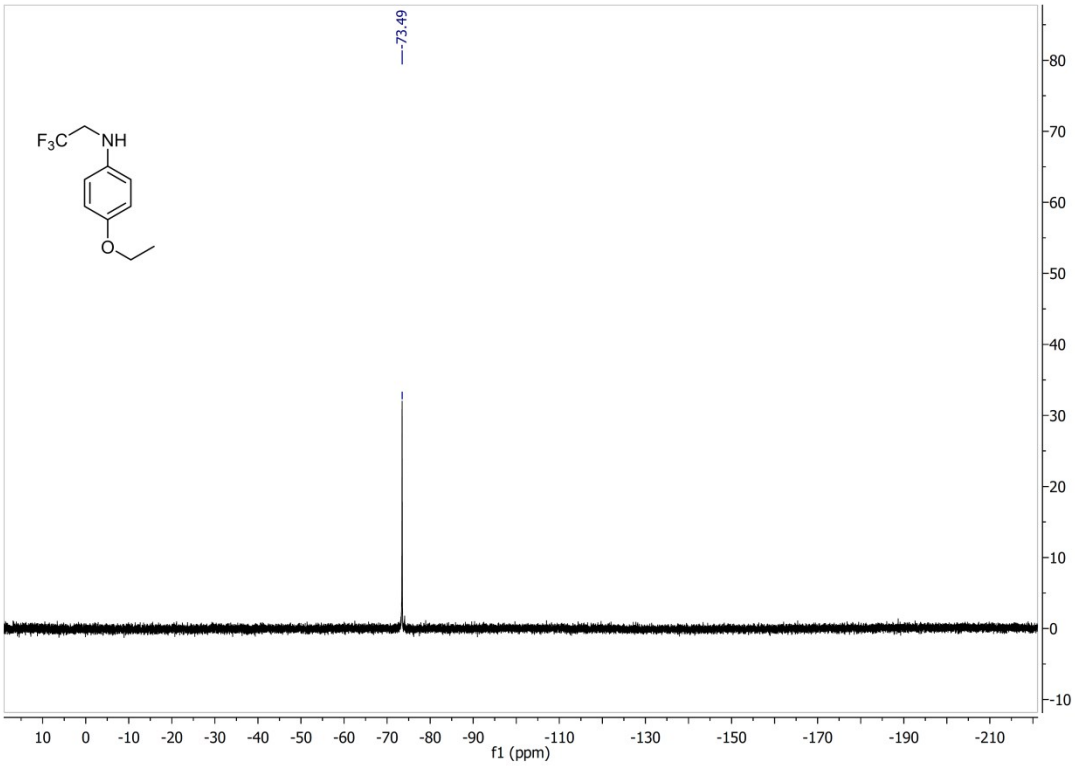

149.15
138.28
130.86
126.47
122.08
117.66
114.00
58.74
58.21
57.71
57.19
55.49
F3C
NH
O
f1 (ppm)

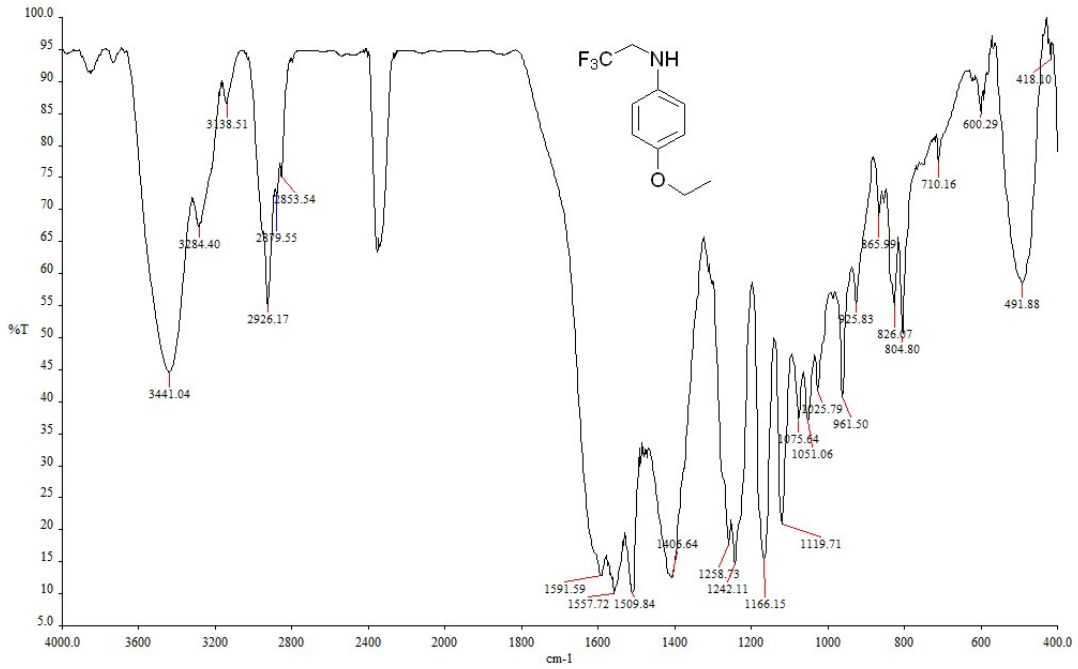

-73.47
F3C
NH
O
f1 (ppm)



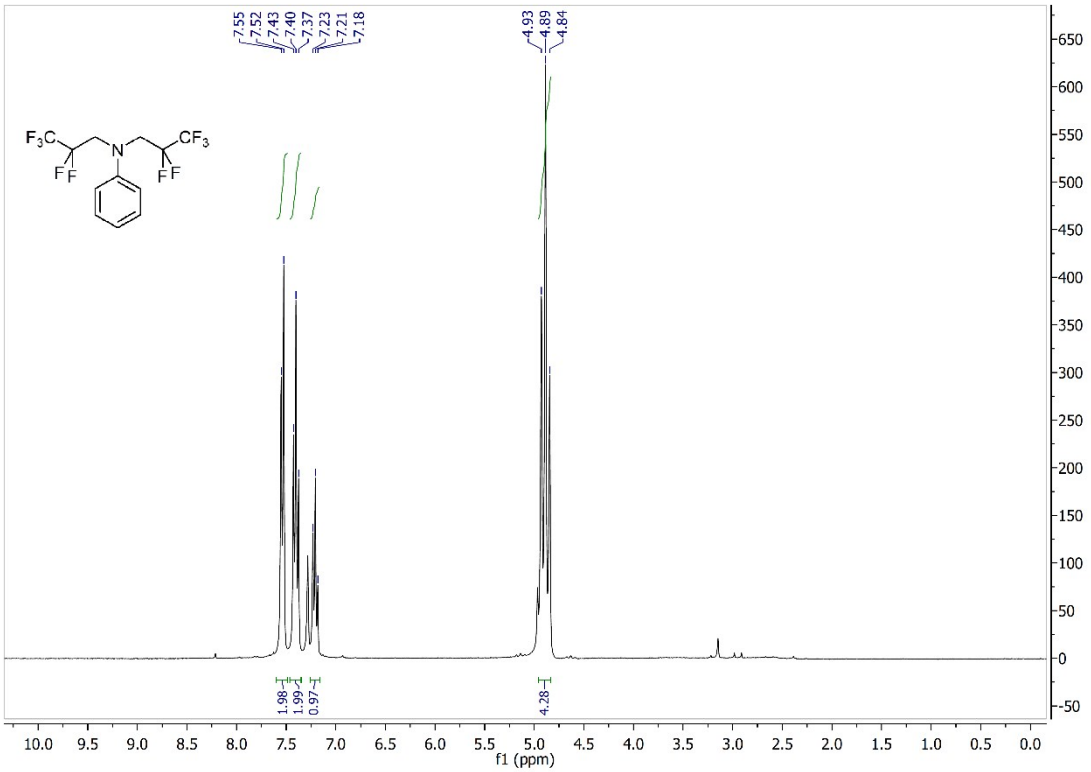
4-Ethoxy-*N*-(2,2,2-trifluoroethyl)aniline (3d)

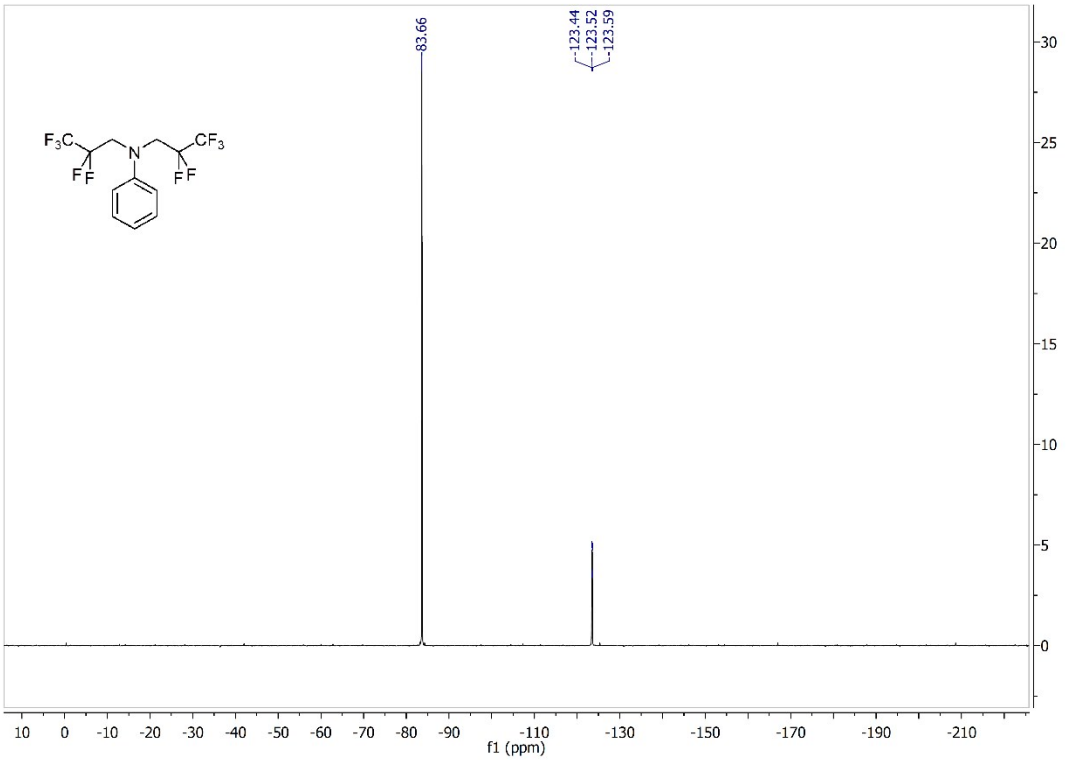


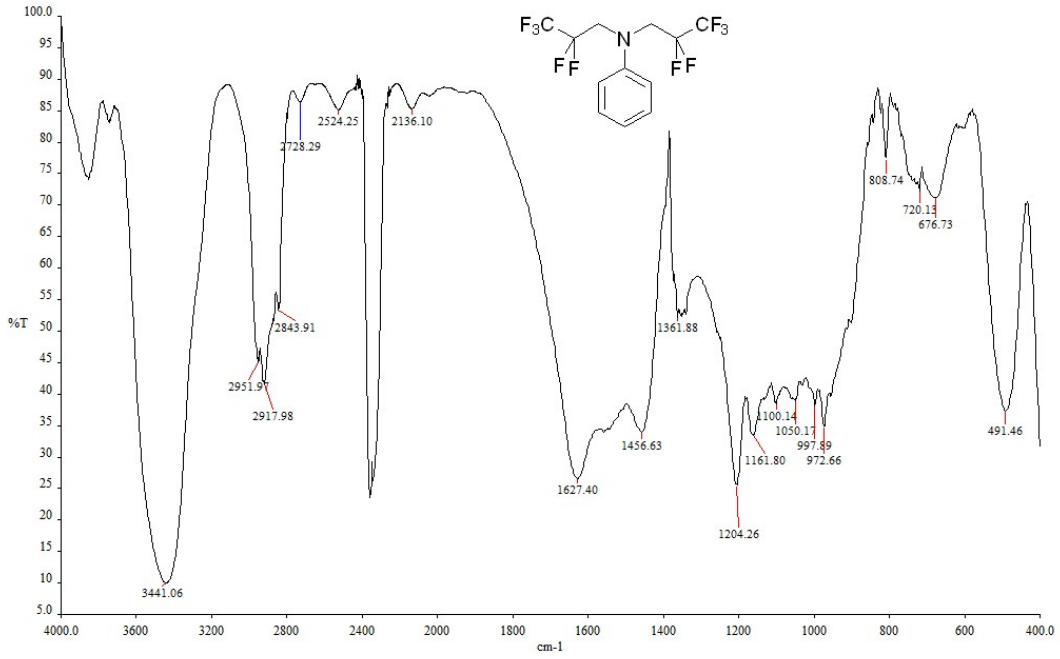

-73.49
F3C
NH
O
f1 (ppm)


%T
cm-1
F3C
NH
O
3441.04
3284.40
3138.51
2926.17
2853.54
2879.55
1591.59
1557.72
1509.84
1406.64
1258.73
1242.11
1166.15
1119.71
1075.64
1051.06
1025.79
961.50
925.83
865.99
826.07
804.80
710.16
600.29
491.88
418.10

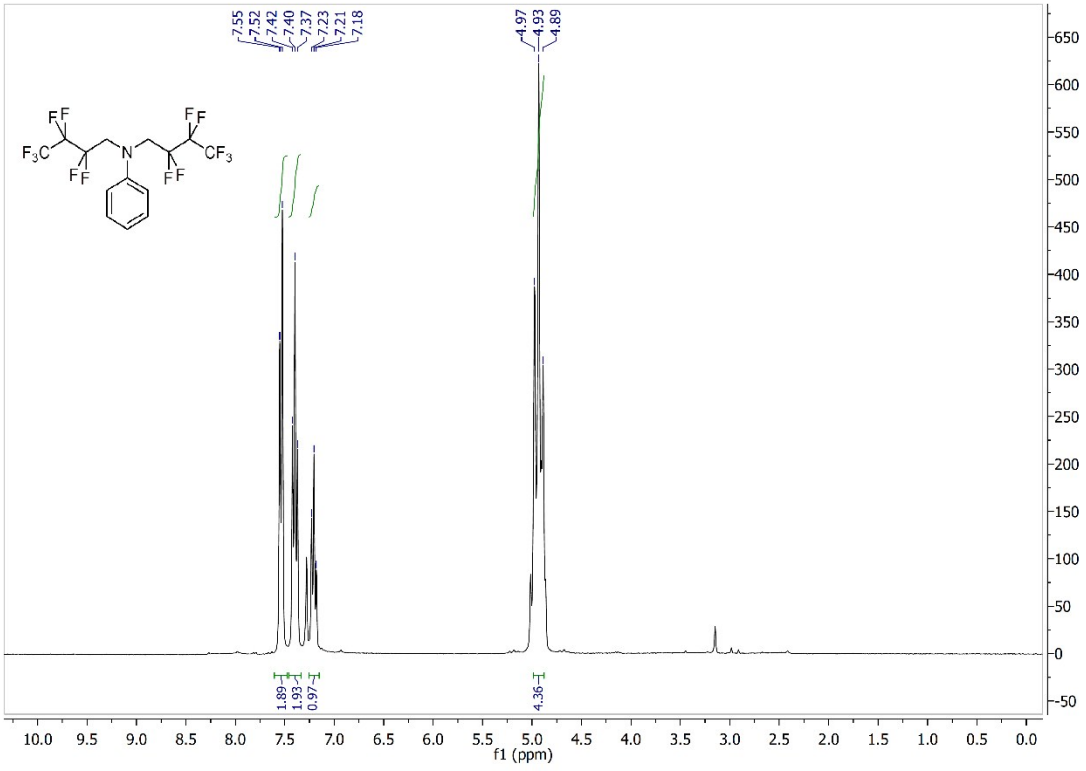
N,N-bis(2,2,3,3,3-pentafluoropropyl)aniline (4a)

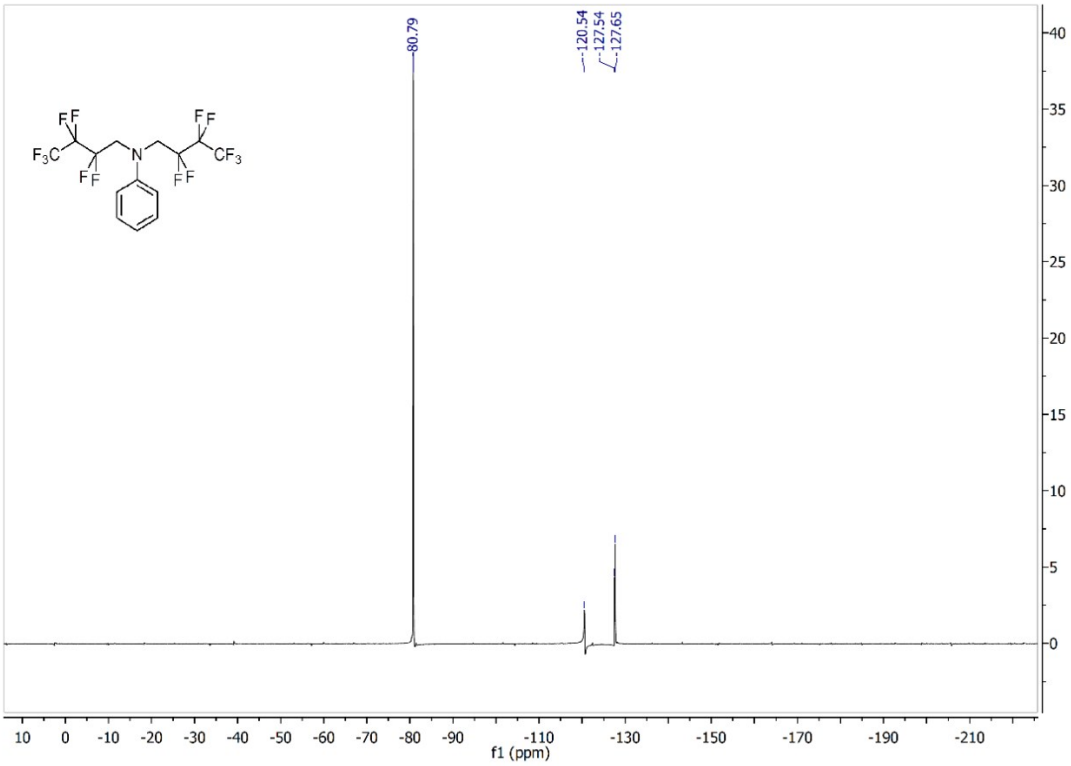


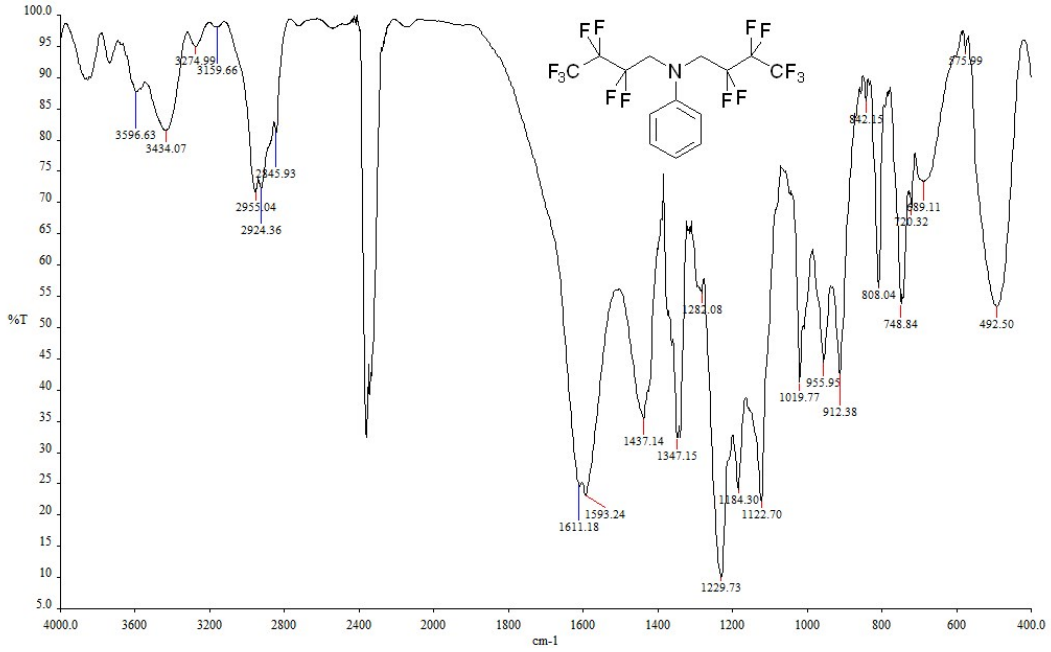




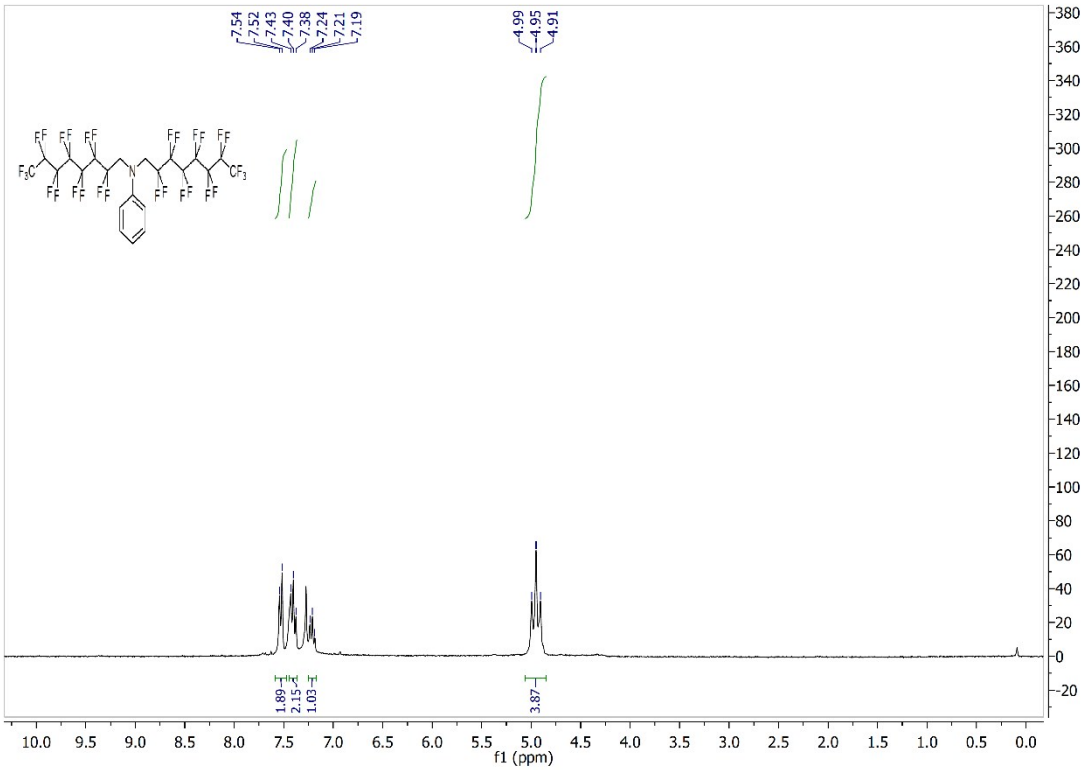
N,N-bis(2,2,3,3,4,4,4-heptafluorobutyl)aniline (4b)

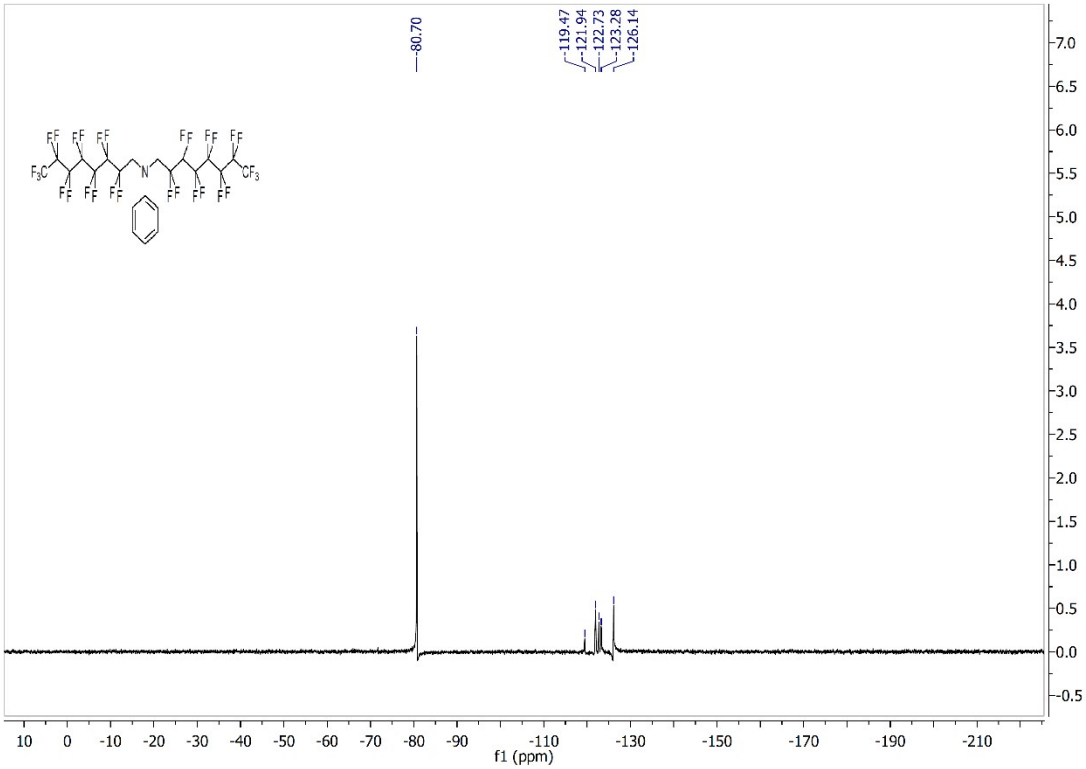


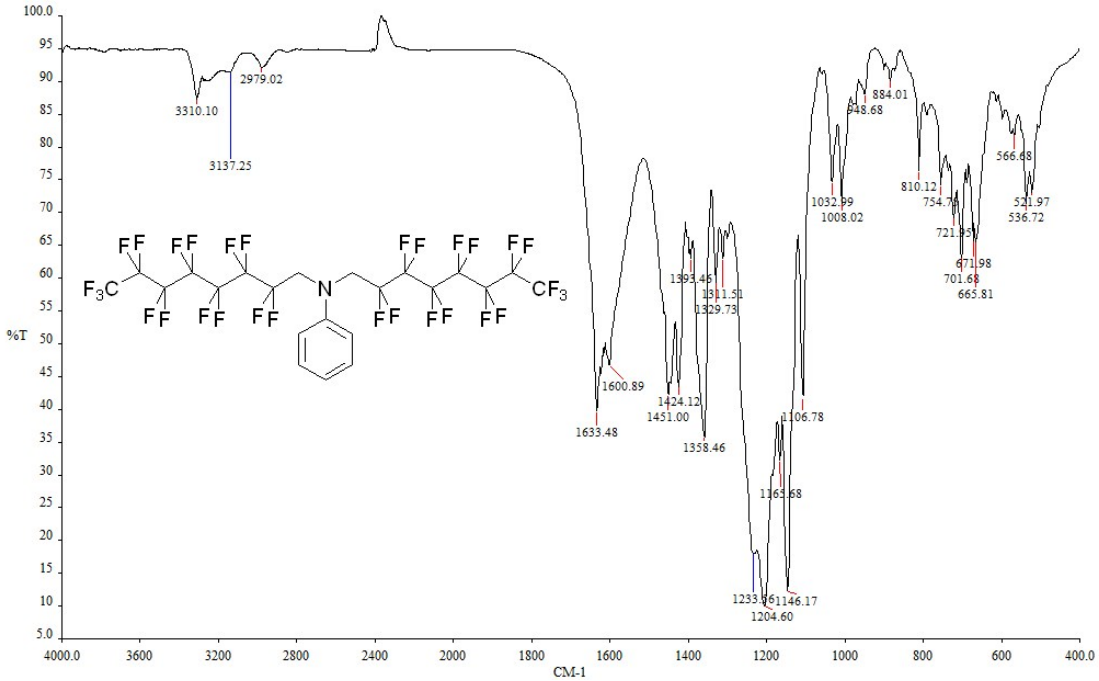

80.79
-120.54
-127.54
-127.65
f1 (ppm)


%T
cm-1
3596.63
3434.07
3274.99
3159.66
2955.04
2924.36
2845.93
1611.18
1593.24
1437.14
1347.15
1282.08
1229.73
1184.30
1122.70
1019.77
955.95
912.38
842.15
808.04
748.84
720.32
689.11
575.99
492.50

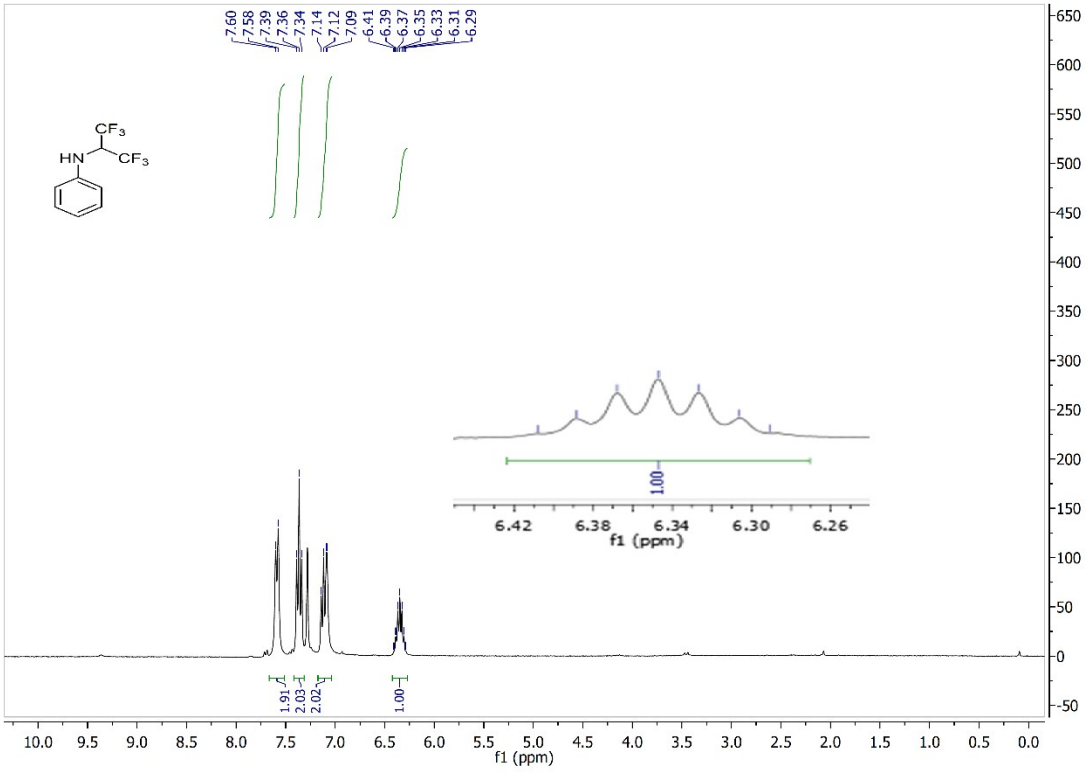
N,N-bis(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)aniline (4c)

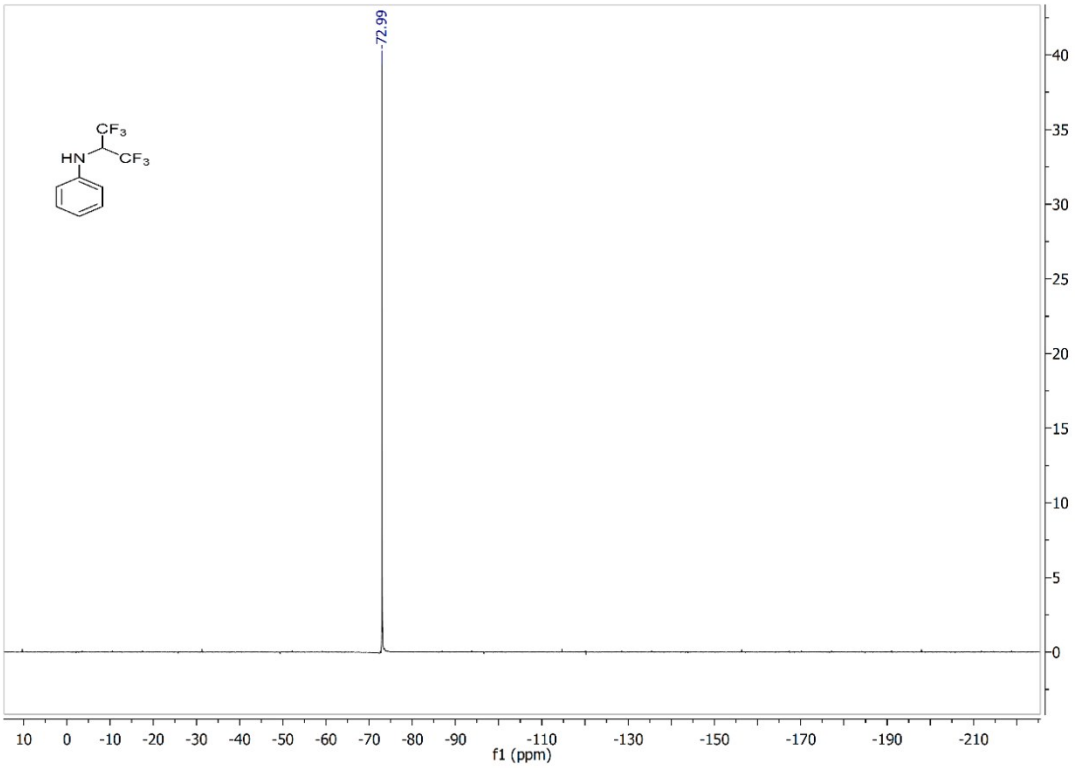


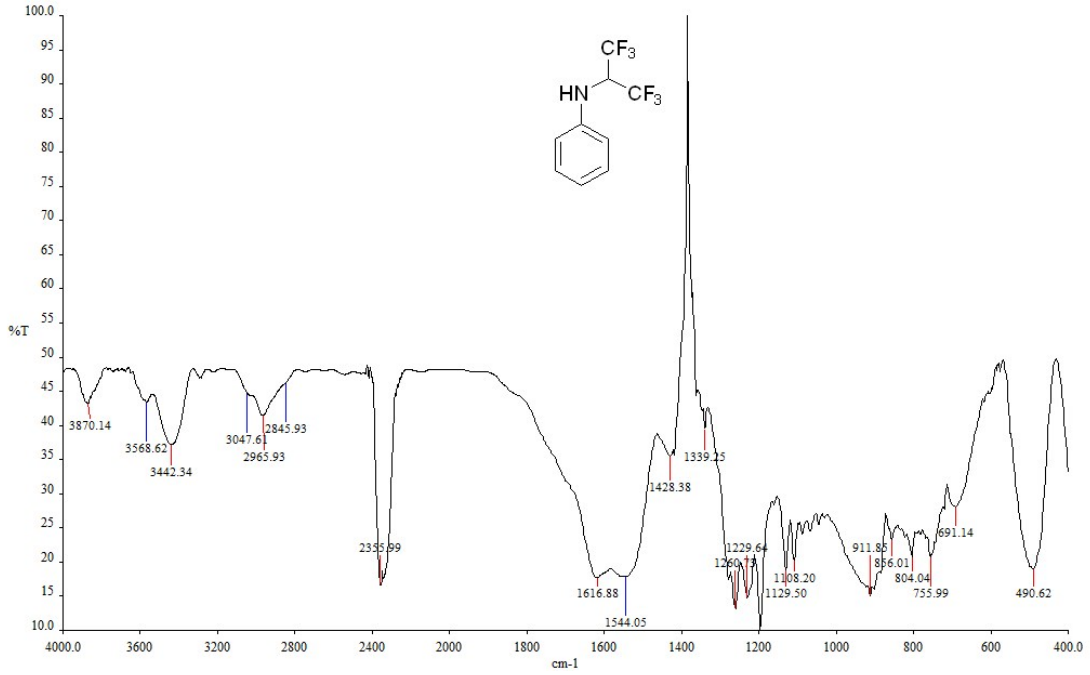




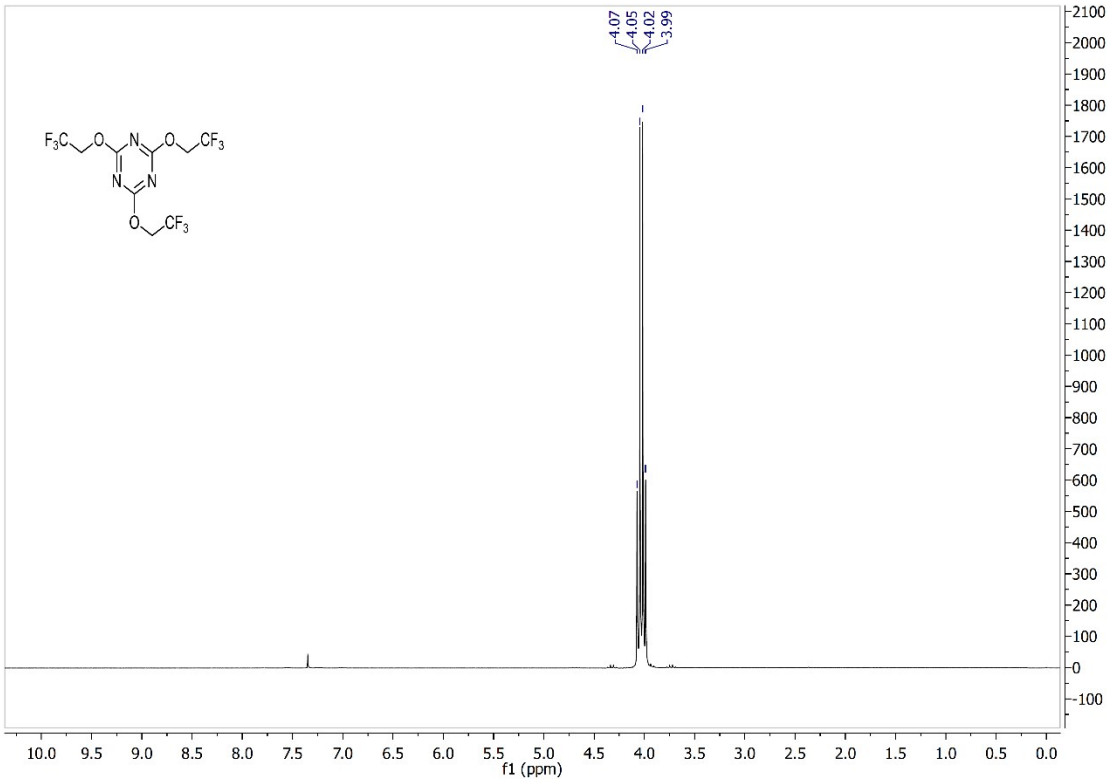
N-(1,1,1,3,3,3-hexafluoropropyl)aniline (4d)

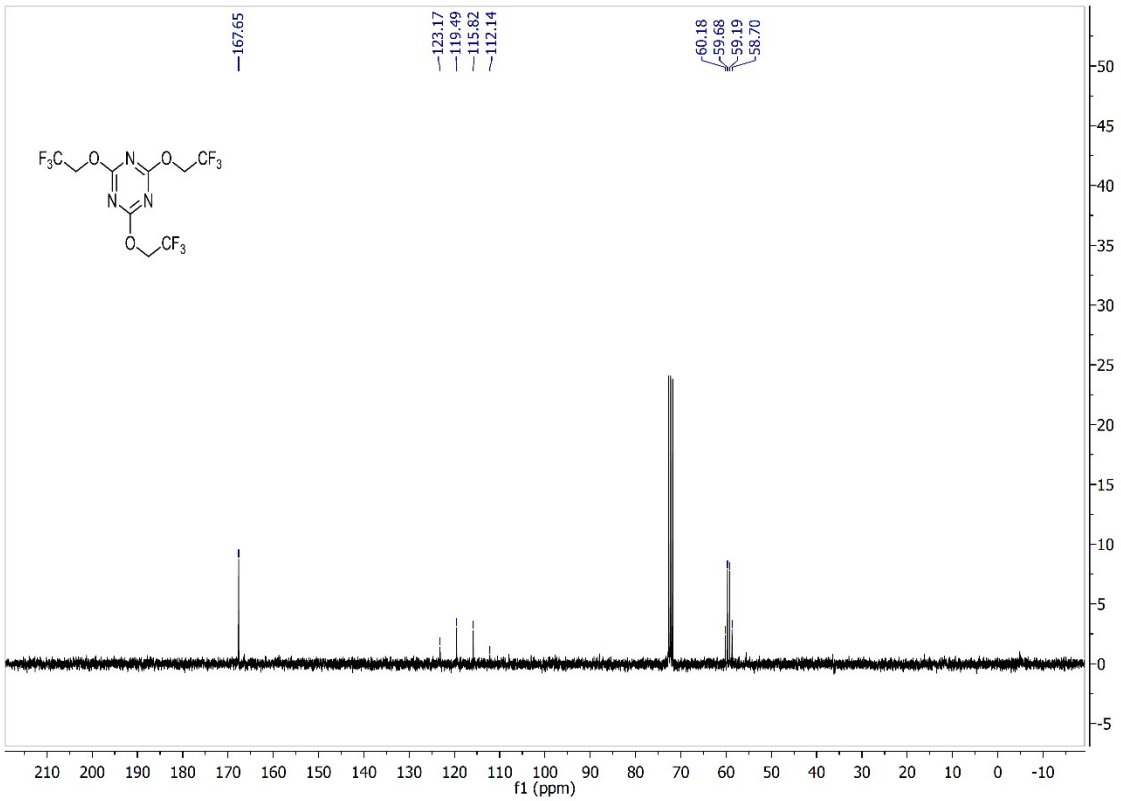


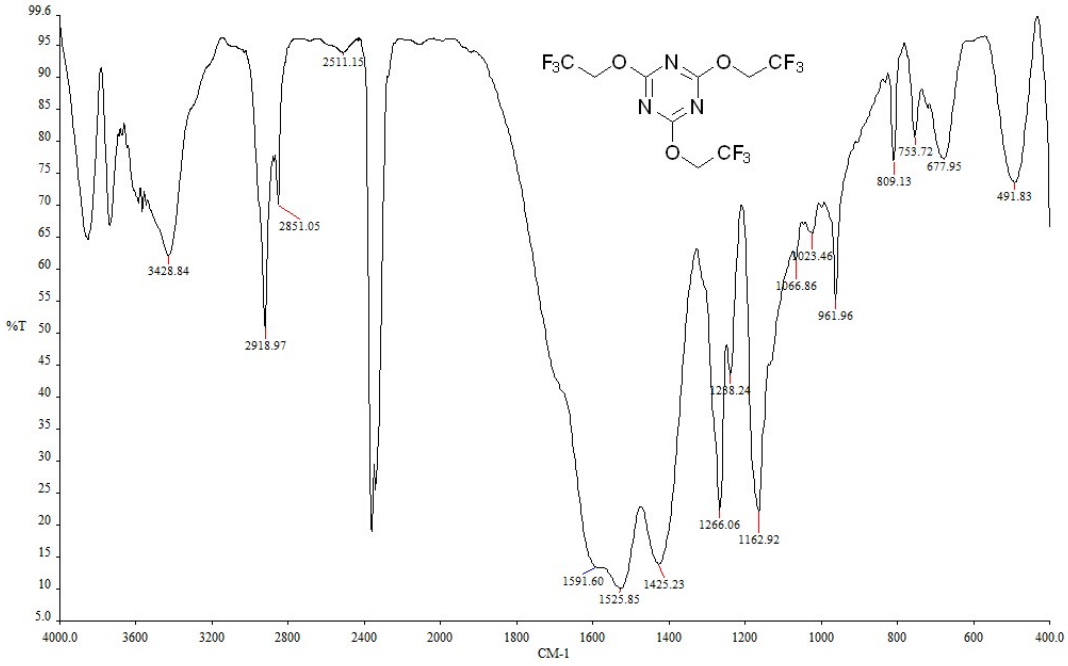

-72.99
CF3
HN
CF3
40
35
30
25
20
15
10
5
0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)


CF3
HN
CF3
%T
100.0
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10.0
3870.14
3568.62
3442.34
3047.61
2965.93
2845.93
2355.99
1616.88
1544.05
1428.38
1339.25
1229.64
1260.13
1129.50
1108.20
911.85
856.01
804.04
755.99
691.14
490.62
4000.0 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600 400.0
cm-1

2,4,6-tris(2,2,2-trifluoroethoxy)-1,3,5-triazine (TTFET)






%T
CM-1
3428.84
2918.97
2851.05
2511.15
1591.60
1525.85
1425.23
1266.06
1238.24
1162.92
1066.86
1023.46
961.96
809.13
753.72
677.95
491.83
F3C
O
N
O
CF3
N
N
O
CF3