Silver-Mediated Methoxycarbonyl-tetrafluoroethylation of Arenes

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SUPPORTING INFORMATION

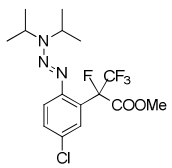
General. NMR spectra were recorded on a *Bruker* AM 400, a *Bruker* Avance 300 or a *Bruker* DRX 500 spectrometer as solutions. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to residual solvent peaks. All coupling constants (*J*) are absolute values and are expressed in Hertz (Hz). The description of signals includes: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, dq = doublet of quartets, dd = doublet of doublet and bs = broad singlet. The spectra were analyzed according to first order. – MS (EI) (electron impact mass spectrometry) and MS (FAB) (fast atom bombardment mass spectroscopy) were performed by using a *Finnigan* MAT 95 (70 eV). IR (infrared spectroscopy) was recorded on a FT-IR *Bruker alpha*. Solvents, reagents and chemicals were purchased from *Aldrich*, *ABCR* and *Acros*. All solvents, reagents and chemicals were used as purchased unless stated otherwise.

A: Methoxycarbonyltetrafluoroethylation of triazenes

General procedure for the methoxycarbonyltetrafluoroethylation of triazenes:

A vial equipped with a septum and a stirring bar was charged with 202 mg (1.60 mmol, 4.00 equiv.) of AgF and 0.40 mmol of the triazenes. The reaction vessel was closed and 0.17 mL (225 mg, 1.60 mmol, 4.00 equiv.) methyl 2,3,3-trifluoroacrylate (MTA) was added via syringe under argon atmosphere. The suspension was heated to 100 °C and was stirred for 16 hours at 100 °C. Afterwards, the solution was cooled to room temperature and 5 mL of ethyl acetate were added. The solution was poured into a flask and the vial was extracted another two times. Finally, the solvent was removed in vacuum and the crude product was purified by flash column chromatography.

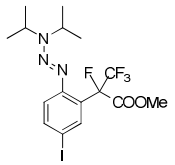
(*E*)-Methyl 2-(5-chloro-2-(3,3-diisopropyltriaz-1-en-1-yl)phenyl)-2,3,3,3-tetrafluoropropanoate (2a)



The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 50:1) as a colorless liquid. 54 mg (35%). R_f = 0.20 (cyclohexane/ethyl acetate = 50:1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (d, ^3J = 6.8 Hz, 3 H, CH_3), 1.20 (d, ^3J = 6.8 Hz, 3 H, CH_3), 1.35–1.39 (m, 6 H, CH_3), 3.74 (s, 3 H, OCH_3), 3.98 (sept, ^3J = 6.6 Hz, 1 H, C*H*), 5.10 (sept, ^3J = 6.8 Hz, 1 H, C*H*), 7.35 (dd, ^3J = 8.8 Hz, ^4J = 2.3 Hz, 1 H, Ar-*H*-4), 7.49 (dd, ^3J = 8.8 Hz, ^5J = 1.0 Hz, 1 H, Ar-*H*-3), 7.59 (bs, 1 H, Ar-*H*-6) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.2, 23.97, 24.03, 47.0, 48.6, 53.0, 91.5 (dq, ^1J = 193.2 Hz, ^2J = 31.8 Hz), 117.7, 121.3 (dq, ^1J = 285.8 Hz, ^2J = 29.8 Hz), 125.5 (d, ^2J = 21.0 Hz), 127.0 (d, ^3J = 13.7 Hz), 129.7, 130.9, 147.3 (d, ^3J = 3.3 Hz), 163.8 (d, ^2J = 22.3 Hz) ppm. – ^{19}F NMR (367 MHz, $CDCl_3$): δ = –75.9 (d, ^3J = 7.9 Hz, 3 F, CF_3), –164.3 (q, ^3J = 7.9 Hz, 1 F, C*F*) ppm. – IR (film): $\tilde{\nu}$ = 2978 (w), 1763 (m), 1472 (w), 1395 (m), 1367 (m), 1296 (m), 1257 (m), 1232 (m), 1204 (s), 1173 (s), 1127 (m), 1094 (s), 1062 (m), 1038 (s),

988 (m), 921 (w), 883 (w), 857 (vw), 828 (m), 810 (w), 773 (w), 755 (m), 741 (m), 715 (m), 699 (w), 652 (w), 642 (w), 590 (w), 574 (w) cm^{-1}. – MS (EI), *m/z* (%): 397 (17) [M^+], 297 (9) [M^+–$C_6H_{14}N$], 269 (34) [M^+–$C_6H_{14}N_3$], 100 (100) [$C_6H_{14}N$]. – HRMS ($C_{16}H_{20}ClN_3O_2F_4$ [M^+]): calcd. 397.1180; found 397.1182.

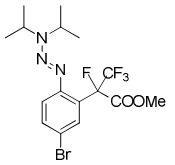
(*E*)-Methyl 2-(2-(3,3-diisopropyltriaz-1-en-1-yl)-5-iodophenyl)-2,3,3,3-tetrafluoropropanoate (2b)



The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 50:1) as a yellow solid. 63 mg (32%). R_f = 0.18 (cyclohexane/ethyl acetate = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (d, ^3J = 6.6 Hz, 3 H, CH_3), 1.20 (d, ^3J = 6.8 Hz, 3 H, CH_3), 1.34–1.40 (m, 6 H, CH_3), 3.73 (s, 3 H, OCH_3), 3.97 (sept, ^3J = 6.6 Hz, 1 H, C*H*), 5.10 (sept, ^3J = 6.8 Hz, 1 H, C*H*), 7.29 (d, ^3J = 8.6 Hz, 1 H, Ar-*H*-3), 7.69 (dd, ^3J = 8.6 Hz, ^4J = 1.9 Hz, 1 H, Ar-*H*-4), 7.90 (bs, 1 H, Ar-*H*-6) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.2, 23.98, 24.03, 47.1, 48.7, 53.0, 87.7, 91.4 (dq, ^1J = 193.0 Hz, ^2J = 31.9 Hz), 118.2, 121.7 (dq, ^1J = 286.0 Hz, ^2J = 29.9 Hz), 125.5 (d, ^2J = 20.7 Hz), 135.6 (d, ^3J = 14.7 Hz), 139.7, 148.4 (d, ^3J = 3.2 Hz), 163.8 (d, ^2J = 22.2 Hz) ppm. – ^{19}F NMR (367 MHz, $CDCl_3$): δ = –75.9 (d, ^3J = 8.0 Hz, 3 F, CF_3), 164.6 (m, 1 F, C*F*) ppm. – IR (film): $\tilde{\nu}$= 2976 (w), 1757 (m), 1467 (w), 1417 (m), 1390 (m), 1367 (m), 1295 (m), 1260 (m), 1234 (m), 1210 (m), 1174 (m), 1130 (m), 1096 (m), 1081 (m), 1055 (m), 1027 (m), 977 (m), 921 (w), 881 (w), 856 (w), 825 (m), 807 (w), 751 (w), 740 (m), 715 (w), 683 (w), 644 (w), 605 (vw), 586 (w), 553 (w), 527 (w), 484 (w), 443 (w) cm^{-1}. – MS (FAB), *m/z* (%): 490 (57) [M^++H], 389 (15) [M^+–$C_6H_{14}N$], 361 (21)[M^+–$C_6H_{14}N_3$], 100 (100) [$C_6H_{14}N$]. – HRMS ($C_{16}H_{21}F_4IN_3O_2$ [M^++H]): calcd. 490.0615; found 490.0618.

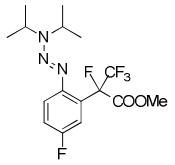
(*E*)-Methyl 2-(5-bromo-2-(3,3-diisopropyltriaz-1-en-1-yl)phenyl)-2,3,3,3-tetrafluoropropanoate (2c)



The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 20:1) as an orange solid. 93 mg (53%). R_f = 0.25 (cyclohexane/ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (d, ^3J = 6.8 Hz, 3 H, CH_3), 1.20 (d, ^3J = 6.8 Hz, 3 H, CH_3), 1.35–1.39 (m, 6 H, *CH*$_3$), 3.74 (s, 3 H, OCH_3), 3.98 (sept, ^3J = 6.6 Hz, 1 H, C*H*), 5.10 (sept, ^3J = 6.8 Hz, 1 H, C*H*), 7.42 (dd, ^3J = 8.7 Hz, ^5J = 1.0 Hz, 1 H, Ar-*H*-3), 7.50 (dd, ^3J = 8.7 Hz, ^4J = 2.2 Hz, 1 H, Ar-*H*-4), 7.73 (bs, 1 H, Ar-*H*-6) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.2, 23.97, 24.03, 47.1, 48.7, 53.0, 91.5 (dq, ^1J = 193.2 Hz, ^2J = 31.8 Hz), 117.3, 118.0, 121.4 (dq, ^1J = 286.0 Hz, ^2J = 29.8 Hz), 125.8 (d, ^2J = 21.0 Hz), 129.8 (d, ^3J = 14.8 Hz), 133.9, 147.3 (d, ^3J = 3.1 Hz), 163.8 (d, ^2J = 22.2 Hz) ppm. – ^{19}F NMR (367 MHz, $CDCl_3$): δ = –75.9 (d, ^3J = 8.0 Hz, 3 F, CF_3), –164.4 (m, 1 F, C*F*) ppm. – IR (film): $\tilde{\nu}$= 2976 (w), 2929 (w), 1757 (m), 1468 (w), 1418 (m), 1392 (m), 1367 (m), 1294 (m), 1261 (m), 1232 (m), 1210 (m), 1174 (s), 1132 (m), 1085 (m), 1056 (m), 1027 (s), 981 (m), 920 (w), 879 (m), 857 (w), 825 (m), 809 (w), 751 (m), 740 (m), 715 (m), 688 (w), 646 (w), 605 (w), 587 (w) cm^{-1} – MS (EI), *m/z* (%): 441 (10) [M^+], 313 (15)[M^+–$C_6H_{14}N_3$], 100 (100) [$C_6H_{14}N$]. – HRMS ($C_{16}H_{20}F_4BrN_3O_2$ [M^+]): calcd. 441.0675; found 441.0676.

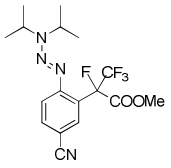
(*E*)-Methyl 2-(2-(3,3-diisopropyltriaz-1-en-1-yl)-5-fluorophenyl)-2,3,3,3-tetrafluoropropanoate (2d)



The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 50:1) as a yellow oil. 62 mg (41%). R_f = 0.35 (cyclohexane/ethyl acetate = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (d, ^3J = 6.8 Hz, 3 H, CH_3), 1.20 (d, ^3J = 6.8 Hz, 3 H, CH_3), 1.32–1.42 (m, 6 H, CH_3), 3.74 (s, 3 H, OCH_3), 3.98 (sept, ^3J = 6.6 Hz, 1 H, C*H*), 5.09 (sept, ^3J = 6.8 Hz, 1 H, C*H*), 7.08–7.15 (m, 1 H, Ar-*H*-4), 7.31–7.35 (m, 1 H, Ar-*H*-3), 7.44 (dd,^3J = 8.9 Hz, ^4J = 5.3 Hz, 1 H, Ar-*H*-6) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.3, 24.0, 24.1, 46.9, 48.4, 53.0, 91.5 (dq, ^1J = 193.1 Hz, ^2J = 31.3 Hz), 113.9 (dd, ^2J = 25.8 Hz, ^3J = 13.9 Hz), 117.8 (d, ^3J = 8.1 Hz), 117.9 (d, ^2J = 24.7 Hz), 121.4 (q, ^1J = 285.7 Hz, ^2J = 29.8 Hz), 125.5 (dd, ^2J = 21.1 Hz, ^3J = 7.6 Hz), 145.2, 159.7 (dd, ^1J = 243.7 Hz, ^4J = 1.1 Hz), 163.8 (d, ^2J = 22.4 Hz) ppm. – ^{19}F NMR (367 MHz, $CDCl_3$): δ = –75.9 (d, ^3J = 8.0 Hz, 3 F, CF_3), –118.0 (s, 1 F, Ar-*F*), –163.9 (m, 1 F, C*F*) ppm. – IR (ATR): $\tilde{\nu}$= 2979 (w), 1763 (m), 1609 (vw), 1487 (m), 1435 (m), 1406 (m), 1383 (w),

1369 (m), 1298 (m), 1277 (m), 1254 (m), 1208 (s), 1155 (s), 1096 (m), 1068 (m), 1038 (m), 1007 (m), 920 (w), 867 (w), 826 (m), 794 (m), 758 (w), 729 (w), 715 (w), 663 (w), 650 (w), 606 (w), 568 (w), 551 (w), 489 (w), 445 (w), 429 (w) cm^{-1}. – MS (EI), *m/z* (%): 381 (16) [M^+], 281 (12) [M^+–$C_6H_{14}N$], 253 (31) [M^+–$C_6H_{14}N_3$], 100 (100) [$C_6H_{14}N$]. – HRMS ($C_{16}H_{20}F_5N_3O_2$ [M^+]): calcd. 381.1476; found 381.1475.

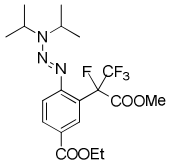


(*E*)-Methyl 2-(5-cyano-2-(3,3-diisopropyltriaz-1-en-1-yl)phenyl)-2,3,3,3-tetrafluoropropanoate (2e)

The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 10:1) as an orange solid. 28 mg (18%). R_f = 0.15 (cyclohexane/ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19 (d, ^3J = 6.8 Hz, 3 H, CH_3), 1.23 (d, ^3J = 6.8 Hz, 3 H, CH_3), 1.38–1.41 (m, 6 H, CH_3), 3.73 (s, 3 H, OCH_3), 4.02 (sept, ^3J = 6.6 Hz, 1 H, C*H*), 5.16 (sept, ^3J = 6.8 Hz, 1 H, C*H*), 7.59 (bs, 2 H, Ar-*H*-3, Ar-*H*-4), 7.90 (bs, 1 H, Ar-*H*-6) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.2, 23.96, 24.01, 48.1, 49.4, 53.1, 91.4 (dq, ^1J = 194.0 Hz, ^2J = 32.2 Hz), 107.2, 117.0, 118.9, 121.2 (dq, ^1J = 286.0 Hz, ^2J = 29.9 Hz), 125.0 (d, ^2J = 21.1 Hz), 131.7 (d, ^3J = 13.8 Hz), 134.3, 152.0 (d, ^3J = 3.0 Hz), 163.4 (d, ^2J = 22.5 Hz) ppm. – ^{19}F NMR (367 MHz, $CDCl_3$): δ = –75.8 (d, ^3J = 8.0 Hz, 3 F, CF_3), –164.8 (m, 1 F, C*F*) ppm. – IR (ATR): $\tilde{\nu}$ = 2979 (w), 2225 (w), 1763 (m), 1604 (w), 1484 (w), 1419 (m), 1392 (m), 1367 (s), 1297 (m), 1239 (s), 1206 (s); 1154 (s), 1128 (m), 1095 (s), 1067 (m), 1028 (s), 1002 (m), 899 (s), 839 (m), 823 (w), 786 (w), 760 (w), 746 (w), 717 (w), 665 (w), 592 (w), 577 (w), 559 (w), 474 (w) cm^{-1}. – MS (EI), *m/z* (%): 388 (34) [M^+], 288 (9) [M^+–$C_6H_{14}N$], 260 (45) [M^+–$C_6H_{14}N_3$], 100 (100) [$C_6H_{14}N$]. – HRMS ($C_{17}H_{20}F_4N_4O_2$ [M^+]): calcd. 388.1522; found 388.1523.

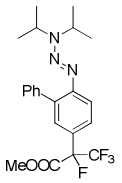
(*E*)-Methyl 2-(2-(3,3-diisopropyltriaz-1-en-1-yl)-5-ethoxycarbonylphenyl)-2,3,3,3-tetrafluoropropanoate (2f)



The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 10:1) as a brownish solid. 51 mg (29%). R_f = 0.20 (cyclohexane/ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19 (d, ^3J = 6.8 Hz, 3 H, CH_3), 1.22 (d, ^3J = 6.8 Hz, 3 H, CH_3), 1.38–1.41 (m, 9 H, 2xCH_3, CH_2CH_3), 3.73 (s, 3 H, OCH_3), 4.02 (sept, ^3J = 6.6 Hz, 1 H, C*H*), 4.38 (m, 2 H, OCH_2), 5.17 (sept, ^3J = 6.8 Hz, 1 H, C*H*), 7.59 (d, ^3J = 8.6 Hz, 1 H, Ar-*H*-3), 8.07 (dd, ^3J = 8.6 Hz, ^4J = 1.9 Hz, 1 H, Ar-*H*-4), 8.32 (bs, 1 H, Ar-*H*-6) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.4, 19.3, 24.0, 24.1, 47.5, 49.0, 52.9, 61.0, 116.1, 124.1 (d, ^2J = 20.8 Hz), 126.1, 129.0 (d, ^3J = 12.9 Hz), 132.2, 152.1 (d, ^3J = 3.0 Hz), 164.1 (d, ^2J = 22.5 Hz), 165.9 ppm. – ^{19}F NMR (367 MHz, $CDCl_3$): δ = –75.8 (d, ^3J = 8.0 Hz, 3 F, CF_3), –164.1 (m, 1 F, C*F*) ppm. – IR (ATR): $\tilde{\nu}$ = 2980 (w), 1763 (m), 1714 (m), 1605 (w), 1395 (m), 1381 (m), 1365 (m), 1297 (m), 1248 (s), 1207 (s), 1170 (s), 1094 (s), 1064 (s), 1024 (s), 911 (m), 849 (w), 804 (w), 774 (m), 757 (w), 741 (m), 716 (m), 688 (w), 650 (w), 588 (w), 537 (w), 442 (m) cm^{-1}. – MS (EI), *m/z* (%): 435 (5) [M^+], 307 (10) [M^+–$C_6H_{14}N_3$], 59 (100) [$C_6H_{14}N$]. – HRMS ($C_{19}H_{25}F_4N_3O_4$ [M^+]): calcd. 435.1781; found 435.1780.

(*E*)-Methyl 2-(3-phenyl-4-(3,3-diisopropyltriaz-1-en-1-yl)phenyl)-2,3,3,3-tetrafluoropropanoate (2g)

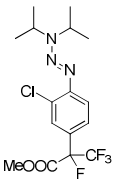


The product was obtained as a 10:1 mixture of *para*- and *ortho* methoxycarbonyltetrafluoroethylated product after flash column chromatography (cyclohexane/ethyl acetate = 50:1) as a yellow oil. 81 mg (46%). R_f = 0.25 (cyclohexane/ethyl acetate = 50:1). The spectra were solved for the main isomer (*para*).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.09–1.14 (m, 6 H, CH_3), 1.36–1.37 (m, 6 H, CH_3), 3.92 (s, 3 H, OCH_3), 3.99 (bs, 1 H, C*H*), 4.93 (bs, 1 H, C*H*), 7.31–7.40 (m, 3 H, Ph-*H*-3', Ph-*H*-4', Ph-*H*-5'), 7.48–7.50 (m, 2 H, Ph-*H*-2', Ph-*H*-6'), 7.54–7.56 (m, 2 H, Ar-*H*-5, Ar-*H*-6), 7.62 (s, 1 H, Ar-*H*-2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.3, 23.8, 46.8, 49.5, 53.7, 92.7 (dq, ^1J = 201.5 Hz, ^2J = 32.2 Hz), 117.7, 121.5 (dq, ^1J = 285.2 Hz, ^2J = 30.3 Hz), 125.09 (d, ^3J = 9.0 Hz), 125.10 (d, ^2J = 22.8 Hz), 126.7, 127.5, 127.8 (d, ^3J = 9.7 Hz), 130.4, 136.1, 139.6, 150.4, 164.6 (d, ^2J = 24.1 Hz) ppm. – ^{19}F NMR (367 MHz, $CDCl_3$): δ = –77.0 (d, ^3J = 7.9 Hz, 3 F, CF_3), –171.7 (q, ^3J = 7.9 Hz, 1 F, C*F*) ppm. –

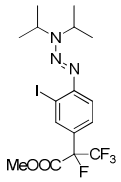
IR (film): $\tilde{\nu}$= 2976 (m), 2934 (w), 1759 (s), 1600 (w), 1480 (m), 1420 (m), 1399 (s), 1382 (m), 1366 (m), 1256 (s), 1226 (m), 1203 (s), 1180 (s), 1156 (m), 1108 (m), 1035 (m), 972 (m), 915 (vw), 898 (w), 834 (w), 809 (w), 789 (w), 773 (w), 728 (w), 699 (m), 652 (vw), 593 (vw), 570 (vw), 552 (w) cm^{-1}. – MS (EI), *m/z* (%): 439 (68) [M^+], 339 (10) [M^+–$C_6H_{14}N$], 311 (82) [M^+–$C_6H_{14}N_3$], 100 (100) [$C_6H_{14}N$]. – HRMS ($C_{22}H_{25}O_2N_3F_4$ [M^+]): calcd. 439.1882; found 439.1881.

(*E*)-Methyl 2-(3-chloro-4-(3,3-diisopropyltriaz-1-en-1-yl)phenyl)-2,3,3,3-tetrafluoropropanoate (2h)



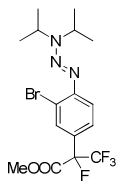
The product was obtained as a 6.4:1 mixture of *para*- and *ortho* methoxycarbonyltetrafluoroethylated product after flash column chromatography (cyclohexane/ethyl acetate = 50:1) as a yellow oil. 90 mg (57%). R_f = 0.15 (cyclohexane/ethyl acetate = 50:1). The spectra were solved for the main isomer (*para*). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.30 (d, ^3J = 6.8 Hz, 6 H, CH_3), 1.39 (d, ^3J = 6.6 Hz, 6 H, CH_3), 3.92 (s, 3 H, OCH_3), 4.07 (sept, ^3J = 6.6 Hz, 1 H, CH), 5.21 (sept, ^3J = 6.8 Hz, 1 H, C*H*), 7.44 (dd, ^3J = 8.6 Hz, ^4J = 1.7 Hz, 1 H, Ar-*H*-6), 7.49 (d, ^3J = 8.6 Hz, 1 H, Ar-*H*-5), 7.65 (d, ^4J = 1.7 Hz, 1 H, Ar-*H*-2) ppm.– ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.9, 23.7, 47.7, 50.3, 53.8, 92.0 (dq, ^1J = 202.8 Hz, ^2J = 32.5 Hz), 118.2, 121.0 (dq, ^1J = 285.4 Hz, ^2J = 29.8 Hz), 124.4 (d, ^3J = 8.8 Hz), 125.5 (d, ^2J = 22.0 Hz), 127.4 (d, ^3J = 9.9 Hz), 129.4, 149.7, 164.2 (d, ^2J = 23.9 Hz) ppm. – ^{19}F NMR (367 MHz, $CDCl_3$): δ = –77.2 (d, ^3J = 7.7 Hz, 3 F, CF_3), –172.2 (m, 1 F, C*F*) ppm. – IR (film): $\tilde{\nu}$= 2977 (m), 2936 (w), 1760 (m), 1598 (w), 1561 (vw), 1485 (m), 1468 (m), 1414 (s), 1393 (m), 1368 (m), 1289 (m), 1233 (s), 1188 (s), 1158 (m), 1100 (m), 1060 (m), 1039 (m), 983 (m), 923 (w), 886 (w), 832 (w), 808 (w), 783 (w), 752 (w), 722 (w), 685 (w), 644 (w), 594 (w), 535 (w) cm^{-1}. – MS (EI), *m/z* (%): 397 (24) [M^+], 297 (17) [M^+–$C_6H_{14}N$], 269 (50) [M^+–$C_6H_{14}N_3$], 100 (100). – HRMS ($C_{16}H_{20}N_3O_2F_4$ [M^+]): calcd. 397.1180; found 397.1183.

(*E*)-Methyl 2-(4-(3,3-diisopropyltriaz-1-en-1-yl)-3-iodophenyl)-2,3,3,3-tetrafluoropropanoate (2i)



The product was obtained as a 5.6:1 mixture of *para*- and *ortho* methoxycarbonyltetrafluoroethylated product after flash column chromatography (cyclohexane/ethyl acetate = 50:1) as a yellow oil. 98 mg (50%). R_f = 0.28 (cyclohexane/ethyl acetate = 50:1). The spectra were solved for the main isomer (*para*). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.33 (d, ^3J = 6.8 Hz, 6 H, CH_3), 1.39 (d, ^3J = 6.6 Hz, 6 H, CH_3), 3.92 (s, 3H, OCH_3), 4.07 (sept, ^3J = 6.6 Hz, 1 H, C*H*), 5.19 (sept, ^3J = 6.8 Hz, 1 H, C*H*), 7.39 (d, ^3J = 8.6 Hz, 1 H, Ar-*H*-5), 7.53 (dd, ^3J = 8.6 Hz, ^4J = 1.5 Hz, 1 H, Ar-*H*-6), 8.07 (bs, 1 H, Ar-*H*-2) ppm. –^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.9, 23.7, 48.2, 50.4, 53.8, 91.7 (dq, ^1J = 202.8 Hz, ^2J = 32.4 Hz), 96.2 (d, ^4J = 1.1 Hz), 116.9, 121.1 (dq,^1J = 285.4 Hz, ^2J = 30.0 Hz), 126.0 (d, ^3J = 7.9 Hz), 126.2 (d, ^2J = 21.6 Hz), 136.1 (d, ^3J = 10.2 Hz), 152.6, 164.2 (d, ^2J = 23.9 Hz) ppm. – ^{19}F NMR (367 MHz, $CDCl_3$): δ = –77.1 (d, ^3J = 7.9 Hz, 3 F, CF_3), –172.1 (m, 1 F, C*F*) ppm. – IR (film) : $\tilde{\nu}$= 2976 (w), 2935 (w), 1760 (m), 1591 (vw), 1474 (w), 1410 (m), 1380 (m), 1367 (m), 1286 (m), 1230 (s), 1186 (s), 1157 (m), 1128 (m), 1106 (m), 1040 (m), 971 (w), 888 (vw), 832 (w), 804 (w), 769 (vw), 751 (w), 713 (vw), 693 (vw), 668 (vw), 642 (vw), 589 (vw), 561 (vw) cm^{-1}. – MS (FAB), *m/z* (%): 490 (69) [M^++H], 489 (20) [M^+–$C_6H_{14}N$], 361 (55) [M^+–$C_6H_{14}N_3$], 100 (100). – HRMS ($C_{16}H_{21}IN_3O_2F_4$ [M^++H]): calcd. 490.0614; found 490.0613.

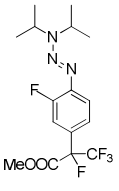
(*E*)-Methyl 2-(3-bromo-4-(3,3-diisopropyltriaz-1-en-1-yl)phenyl)-2,3,3,3-tetrafluoropropanoate (2j)



The product was obtained as a 5.6:1 mixture of *para*- and *ortho* methoxycarbonyltetrafluoroethylated product after flash column chromatography (cyclohexane/ethyl acetate = 50:1) as a yellow oil. 79 mg (45%). R_f = 0.30 (cyclohexane/ethyl acetate = 50:1). The spectra were solved for the main isomere (*para*). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (d, ^3J = 6.8 Hz, 6 H, CH_3), 1.39 (d, ^3J = 6.6 Hz, 6 H, CH_3), 3.92 (s, 3 H, OCH_3), 4.07 (sept, ^3J = 6.6 Hz, 1 H, C*H*), 5.18 (sept, ^3J = 6.8 Hz, 1 H, C*H*), 7.46 (d, ^3J = 8.7 Hz, 1 H, Ar-*H*-5), 7.49 (dd, ^3J = 8.7 Hz, ^4J = 1.6 Hz, 1 H, Ar-*H*-6), 7.83 (d, ^4J = 1.6 Hz, 1 H, Ar-*H*-2) ppm. –^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.9, 23.6, 48.0, 50.4, 53.8, 91.9 (dq, ^1J = 202.8 Hz, ^2J = 32.4 Hz), 118.0 (d, ^4J = 0.9 Hz), 119.7 (d, ^4J = 1.3 Hz), 121.1 (dq, ^1J = 285.4 Hz, ^2J = 30.0 Hz), 125.0

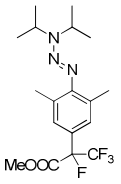
(d, ^3J = 9.8 Hz), 125.8 (d, ^2J = 22.0 Hz), 130.4 (d, ^3J = 10.2 Hz), 150.7 (d, ^5J = 1.1 Hz), 164.2 (d, ^2J= 23.8 Hz) ppm. –^{19}F NMR (367 MHz, $CDCl_3$): δ = –77.1 (d, ^3J = 7.9 Hz, 3 F, CF_3), –172.1 (m, 1 F, C*F*) ppm. – IR (film) : $\tilde{\nu}$= 2977 (w), 1760 (m), 1596 (vw), 1468 (w), 1412 (m), 1391 (w), 1368 (w), 1288 (m), 1232 (m), 1188 (m), 1158 (w), 1107 (w), 1038 (w), 976 (w), 886 (vw), 832 (vw), 805 (vw), 773 (vw), 751 (vw), 716 (vw), 674 (vw) cm^{-1}. – MS (FAB), *m/z* (%): 442 (10) [M^++H], 341 (8) [M^+–$C_6H_{14}N$], 313 (13) [M^+–$C_6H_{14}N_3$], 100 (100). – HRMS ($C_{16}H_{21}BrN_3O_2F_4$ [M^++H]): calcd. 442.0753; found 442.0756.

(*E*)-Methyl 2-(4-(3,3-diisopropyltriaz-1-en-1-yl)-3-fluorophenyl)-2,3,3,3-tetrafluoropropanoate (2k)



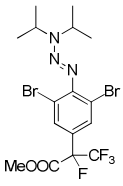
The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 50:1) as a yellow oil. 75 mg (49%). R_f = 0.20 (cyclohexane/ethyl acetate = 50:1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (d, ^3J = 6.6 Hz, 6 H, CH_3), 1.39 (d, ^3J = 6.5 Hz, 6 H, CH_3), 3.92 (s, 3 H, OCH_3), 4.04 (sept, ^3J = 6.5 Hz, 1 H, C*H*), 5.33 (sept, ^3J = 6.6 Hz, 1 H, C*H*), 7.32–7.34 (m, 1 H, Ar-*H*-2), 7.36–7.40 (m, 1 H, Ar-*H*-6), 7.50–7.54 (m, 1 H, Ar-*H*-5) ppm. –^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 23.8, 46.8, 49.6, 91.6 (dq, ^1J = 203.9 Hz, ^2J = 32.4 Hz), 114.2 (dd, ^2J = 24.0 Hz, ^3J = 10.0 Hz), 119.1, 121.0 (dq, ^1J = 285.4 Hz, ^2J = 30.0 Hz), 121.4, 125.5 (dd, ^2J = 22.3 Hz, ^3J = 7.5 Hz), 141.6 (d, ^2J = 7.2 Hz), 155.8 (dd, ^1J = 250.1 Hz, ^4J = 1.9 Hz), 164.2 (d, ^2J = 23.9 Hz) ppm. –^{19}F NMR (367 MHz, $CDCl_3$): δ = –77.2 (d, ^3J = 7.9 Hz, 3 F, CF_3), –126.5 (s, 1 F, Ar-*F*), –171.8 (m, 1 F, C*F*) ppm. – IR (ATR): $\tilde{\nu}$= 2977 (w), 1758 (m), 1578 (vw), 1498 (vw), 1433 (m), 1398 (m), 1366 (m), 1253 (s), 1198 (s), 1157 (m), 1123 (m), 1104 (m), 1032 (m), 993 (m), 869 (w), 826 (w), 797 (m), 753(w), 739 (w), 698 (w), 647 (w), 604 (w), 533 (w) cm^{-1}. – MS (EI), *m/z* (%): 381 (15) [M^+], 281 (27) [M^+–$C_6H_{14}N$], 253 (51) [M^+–$C_6H_{14}N_3$], 58 (100). – HRMS ($C_{16}H_{20}O_2N_3F_5$ [M^+]): calcd. 381.1475; found 381.1473.

(*E*)-Methyl 2-(4-(3,3-diisopropyltriaz-1-en-1-yl)-3,5-dimethylphenyl)-2,3,3,3-tetrafluoropropanoate (2l)



The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 5:1) as a yellow oil. 47 mg (30%). R_f = 0.68 (cyclohexane/ethyl acetate = 5:1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.53 (bs, 12 H, CH_3), 2.46 (s, 6 H, Ar-CH_3), 4.14 (s, 3 H, OCH_3), 4.23 (bs, 1 H, C*H*), 5.40 (bs, 1 H, C*H*), 7.49 (s, 2 H, Ar-*H*-2, Ar-*H*-6) ppm.– ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 19.2, 23.7, 45.7, 48.9, 53.6, 92.6 (dq, ^1J = 201.3 Hz, ^2J = 32.0 Hz), 121.4 (dq, ^1J = 285.1 Hz, ^2J = 30.2 Hz), 124.3 (d, ^2J = 21.5 Hz), 125.4 (d, ^3J = 9.2 Hz), 130.9, 151.5, 164.7 (d, ^2J = 23.9 Hz) ppm. – ^{19}F NMR (367 MHz, $CDCl_3$): δ = –77.0 (d, ^3J = 7.7 Hz, 3 F, CF_3),–171.9 (q, ^3J = 7.7 Hz, 1 F, C*F*) ppm. – IR (ATR): $\tilde{\nu}$= 2972 (w), 2916 (w), 2848 (w), 1758 (m), 1467 (w), 1434 (m), 1399 (w), 1365 (w), 1263 (m), 1224 (m), 1200 (m), 1153 (m), 1115 (m), 1057 (m), 1027 (m), 983 (w), 874 (w), 793 (w), 748 (w), 719 (w), 672 (w), 553 (vw) cm^{-1}. –MS (EI), *m/z* (%): 391 (14) [M^+], 263 (100) [M+–$C_6H_{14}N_3$]. – HRMS ($C_{18}H_{25}O_2N_3F_4$ [M^+]): calcd. 391.1882; found 391.1884.

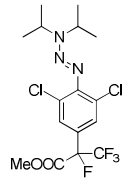
(*E*)-Methyl 2-(3,5-dibromo-4-(3,3-diisopropyltriaz-1-en-1-yl)phenyl)-2,3,3,3-tetrafluoropropanoate (2m)



The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 50:1) as a white solid. 78 mg (38%). R_f = 0.30 (cyclohexane/ethyl acetate = 50:1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (d, ^3J = 6.8 Hz, 6 H, CH_3), 1.37 (d, ^3J = 6.6 Hz, 6 H, CH_3), 3.94 (s, 3 H, OCH_3), 4.06 (sept, ^3J = 6.6 Hz, 1 H, C*H*), 5.13 (sept, ^3J = 6.8 Hz, 1 H, C*H*), 7.80 (s, 2 H, Ar-*H*-2, Ar-*H*-6) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.0, 23.7, 47.2, 50.0, 54.1, 91.1 (dq, ^1J = 204.9 Hz, ^2J = 32.8 Hz), 118.3, 120.9 (dq, ^1J = 285.5 Hz, ^2J = 29.5 Hz), 126.8 (d, ^3J = 22.4 Hz), 129.6 (d, ^3J = 9.5 Hz), 150.8, 163.9 (d, ^2J = 23.8 Hz) ppm. – ^{19}F NMR (367 MHz, $CDCl_3$): δ = –77.1 (bs, 3 F, CF_3), –172.8 (bs, 1 F, C*F*) ppm. – IR (film): $\tilde{\nu}$= 3074 (vw), 2977 (w), 1758 (s), 1537 (w), 1464 (w), 1438 (w), 1402 (s), 1369 (m), 1281 (s), 1229 (s), 1209 (s), 1185 (s), 1155 (s), 1131 (m), 1112 (m), 1097 (m), 1035 (s), 990 (m), 919 (w), 882 (m), 811 (w), 784 (w), 740 (m), 731 (s), 662 (m), 604 (w), 566 (w), 527 (w), 500 (w) cm^{-1}. – MS (EI), *m/z* (%): 521 (17)

[M^+], 421 (15) [M^+–$C_6H_{14}N$], 393 (38) [M^+–$C_6H_{14}N_3$], 100 (100) [$C_6H_{14}N$]. – HRMS ($C_{16}H_{19}O_2Br_2N_3F_4$ [M^+]): calcd. 518.9780; found 518.9782.

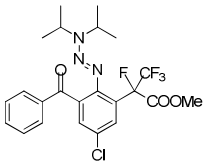
(*E*)-Methyl 2-(3,5-dichloro-4-(3,3-diisopropyltriaz-1-en-1-yl)phenyl)-2,3,3,3-tetrafluoropropanoate (2n)



The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 60:1) as a colorless oil. 59 mg (38%). R_f = 0.30 (cyclohexane/ethyl acetate = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 (d, ^3J = 6.8 Hz, 6 H, CH_3), 1.35 (d, ^3J = 6.6 Hz, 6H, CH_3), 3.94 (s, 3 H, OCH_3), 4.05 (sept, ^3J = 6.6 Hz, 1 H, C*H*), 5.16 (sept, ^3J = 6.8 Hz, 1 H, C*H*), 7.58 (s, 2 H, Ar-*H*-2, Ar-*H*-6) ppm. –^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.9, 23.6, 47.1, 49.9, 54.1, 91.4 (dq, ^1J = 205.0 Hz, ^2J = 32.9 Hz), 120.9 (dq, ^1J = 285.6 Hz, ^2J = 29.5 Hz), 125.89 (d, ^2J = 22.4 Hz), 125.90 (d, ^3J = 9.5 Hz), 129.2 (d, ^4J = 1.5 Hz), 148.6, 163.7 (d, ^2J = 23.8 Hz) ppm. – ^{19}F NMR (367 MHz, $CDCl_3$): δ = –77.1 (d, ^3J = 7.8 Hz, 3 F, CF_3), –172.9 (m, 1 F, C*F*) ppm. – IR (film): $\tilde{\nu}$= 3443 (vw), 2976 (w), 2928 (w), 1760 (w), 1548 (vw), 1409 (w), 1367 (w), 1295 (w), 1233 (w), 1200 (w), 1125 (w), 1043 (w), 1001 (vw), 875 (vw), 802 (vw), 754 (vw), 735 (vw) cm^{-1}. – MS (EI), *m/z* (%): 431 (12) [M^+], 331 (17) [M^+–$C_6H_{14}N$], 303 (19) [M+–$C_6H_{14}N_3$], 100 (100) [$C_6H_{14}N$]. – HRMS ($C_{16}H_{19}O_2Cl_2N_3F_4$ [M^+]): calcd. 431.0790; found 431.0793.

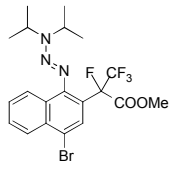
(*E*)-Methyl 2-(3-benzoyl-5-chloro-2-(3,3-diisopropyltriaz-1-en-1-yl)phenyl)-2,3,3,3-tetrafluoropropanoate (2o)



The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 50:1) as a yellow solid. 42 mg (21%). R_f = 0.25 (cyclohexane/ethyl acetate = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83 (d, ^3J = 6.8 Hz, 3 H, CH_3), 0.91–0.94 (m, 6 H, CH_3), 0.97 (d, ^3J = 6.8 Hz, 3 H, CH_3), 3.70 (sept, ^3J = 6.6 Hz, 1 H, C*H*), 3.79 (s, 3 H, OCH_3), 4.82 (sept, ^3J = 6.8 Hz, 1 H, C*H*), 7.32–7.37 (m, 2 H, Ar-*H*-3', Ar-*H*-5'), 7.42 (d, ^3J = 2.3 Hz, 1 H, Ar-*H*-6), 7.48 (t, ^3J = 7.4 Hz, 1 H, Ar-*H*-4'), 7.68 (d, ^3J = 7.4 Hz, 2 H, Ar-*H*-2', Ar-*H*-6'), 7.74 (d, ^4J = 1.6 Hz, 1 H, Ar-*H*-4) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.9, 19.0, 23.0, 23.1, 47.6, 49.4, 53.0, 91.3 (dq, ^1J = 194.1 Hz, ^2J = 32.1 Hz), 121.2 (dq, ^1J = 285.8 Hz, ^2J = 29.7 Hz), 126.5 (d, ^2J = 21.2 Hz), 128.2, 128.6 (d, ^3J = 14.4 Hz), 129.9, 130.0, 131.0, 132.2, 133.1, 135.8, 147.0 (d, ^3J = 3.0 Hz), 163.4 (d, ^3J = 22.1 Hz), 194.4 ppm. – ^{19}F NMR (367 MHz, $CDCl_3$): δ = –75.7 (d, ^3J = 7.9 Hz, 3 F, CF_3), –164.0 (m, 1 F, C*F*) ppm. – IR (film): $\tilde{\nu}$= 3066 (w), 2979 (m), 1767 (m), 1668 (m), 1597 (m), 1410 (m), 1211 (m), 1100 (m), 1054 (m), 1032 (m), 963 (m), 923 (w), 884 (m), 861 (w), 804 (m), 786 (w), 759 (m), 696 (m), 658 (m), 579 (w), 539 (w), 460 (w) cm^{-1}. – MS (EI), *m/z* (%): 501 (6) [M^+], 373 (7) [M^+–$C_6H_{14}N_3$] 100 (100) [$C_6H_{14}N$]. – HRMS ($C_{23}H_{24}ClF_4N_3O_3$ [M^+]): calcd. 501.1442; found 501.1445.

(*E*)-Methyl 2-(4-bromo-1-(3,3-diisopropyltriaz-1-en-1-yl)naphthalen-2-yl)-2,3,3,3-tetrafluoropropanoate (2p)



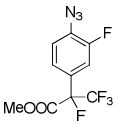
The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 50:1) as a red oil. 88 mg (45%). R_f = 0.18 (cyclohexane/ethyl acetate = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26–1.32 (m, 9 H, CH_3), 1.40 (d, ^3J = 6.6 Hz, 3 H, CH_3), 3.79 (s, 3 H, OCH_3), 4.05 (sept, ^3J = 6.6 Hz, 1 H, C*H*), 5.38 (sept, ^3J = 6.8 Hz, 1 H, C*H*), 7.47–7.52 (m, 1 H, Ar-*H*-7), 7.61–7.67 (m, 1 H, Ar-*H*-6), 7.90 (d, ^3J = 8.6 Hz, 1 H, Ar-*H*-8), 8.02 (s, 1 H, Ar-*H*-3), 8.27 (d, ^3J = 8.5 Hz, 1 H, Ar-*H*-5) ppm. – ^{13}C NMR (100°MHz, $CDCl_3$): δ = 19.3, 19.6, 23.6, 23.9, 45.8, 48.5, 53.1, 91.5 (dq, ^1J = 192.7 Hz, ^2J = 31.8 Hz), 118.4, 120.5 (d, ^2J = 22.0 Hz), 121.4 (dq, ^1J = 285.6 Hz, ^2J = 30.1 Hz), 126.1, 126.5, 126.8 (d, ^3J = 15.2 Hz), 127.2, 128.0, 128.3, 133.8, 147.3 (d, ^3J = 3.6 Hz), 164.1 (d, ^2J = 22.0 Hz) ppm. – ^{19}F NMR (367 MHz, $CDCl_3$): δ = –75.9 (d, ^3J = 8.0 Hz, 3 F, CF_3), –163.1 (m, 1 F, C*F*) ppm. – IR (ATR): $\tilde{\nu}$= 2977 (w), 1761 (m), 1585 (vw), 1421 (m), 1404 (m), 1353 (m), 1321 (w), 1295 (m), 1257 (m), 1205 (s), 1175 (s), 1155 (s), 1108 (m), 1093 (m), 1073 (m), 1036 (s), 931 (m), 880 (w), 838 (w), 798 (w), 746 (m), 729 (m), 672 (w), 635 (w), 583

(w), 557 (w), 534 (w), 502 (w), 453 (w) cm^{-1}. – MS (EI), *m/z* (%): 491 (1) [M^+], 363 (1) [M+–$C_6H_{14}N_3$], 84 (100). – HRMS ($C_{20}H_{22}BrO_2N_3F_4$ [M^+]): calcd. 491.0831; found 491.0835.

B: Transformations of the triazene moiety

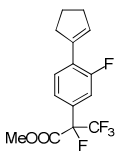
Methyl 2-(4-azido-3-fluorophenyl)-2,3,3,3-tetrafluoropropanoate (3)



A vial equipped with a septum and a stirring bar was charged with the triazene **2k** (50 mg, 0.131 mmol). The reaction vessel was closed and abs. dichloromethane (1 mL) was added *via* syringe under argon atmosphere. The solution was cooled down to 0 °C and 0.09 mL of TMS-N_3 (75.6 mg, 0.66 mmol, 5.00 equiv.) and 0.10 mL of TFA (149 mg, 1.31 mmol, 1.00 equiv.) were added *via* syringe. After 1 h stirring at room temperature the solvent was reduced under vacuum. The pure compound could be obtained after flash column chromatography (cyclohexane/ethyl acetate = 50:1) as a slightly yellow oil. 34 mg (87%). R_f = 0.25 (cyclohexane/ethyl acetate = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.93 (s, 3 H, OC*H*$_3$), 7.10–7.17 (m, 1 H, Ar-*H*-5), 7.41–7.47 (m, 2 H, Ar-*H*-2, Ar-*H*-6) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 54.1, 91.5 (ddq, ^1J = 204.3 Hz, ^2J = 32.9 Hz, ^4J = 1.3 Hz), 114.8 (dd, ^2J = 22.7 Hz, ^3J = 10.3 Hz), 120.8 (dq, ^1J = 285.5 Hz, ^2J = 29.5 Hz), 121.4, 122.4 (dd, ^3J = 9.5 Hz, ^4J = 3.1 Hz), 126.8 (dd, ^2J = 22.7 Hz, ^3J = 22.7 Hz), 130.6 (d, ^2J = 10.9 Hz), 154.6 (dd, ^1J = 250.9 Hz, ^4J = 2.1 Hz), 163.7 (d, ^2J = 23.7 Hz) ppm. – ^{19}F NMR (367 MHz, $CDCl_3$): δ = –77.3 (d, ^3J = 7.8 Hz, 3 F, C*F*$_3$), –123.9 (s, 1 F, Ar-*F*), –172.7 (m, 1 F, C*F*) ppm. – IR (film): $\tilde{\nu}$ = 2442 (vw), 3085 (vw), 2963 (w), 2927 (w), 2854 (w), 2415 (vw), 2258 (vw), 2136 (m), 2102 (m), 1760 (m), 1618 (w), 1584 (w), 1510 (m), 1470 (w), 1434 (m), 1299 (m), 1205 (m), 1171 (m), 1096 (m), 1039 (m), 998 (w), 945 (vw), 924 (vw), 876 (w), 820 (w), 799 (w), 753 (w), 702 (w), 664 (vw) cm^{-1}. – MS (EI), *m/z* (%): 295 (10) [M^+], 267 (12) [M^+–N_2], 59 (100) [COOMe]. – HRMS ($C_{10}H_6O_2N_3F_5$ [M^+]): calcd. 295.0380; found 295.0382.

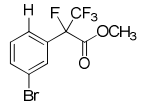
Methyl 2-(4-(cyclopent-1-en-1-yl)-3-fluorophenyl)-2,3,3,3-tetrafluoropropanoate (4)



A vial equipped with a septum and a stirring bar was charged with the triazene **2k** (60 mg, 0.157 mmol). The reaction vessel was closed and 1 mL of dichloromethane was added via syringe under argon atmosphere. Then, 0.048 mL (71.8 mg, 0.630 mmol, 4.00 equiv.) trifluoroacetic acid was added and the solution stirred for 20 min at room temperature. The vial was opened and 3.5 mg (0.0157 mmol, 0.10 equiv.) $Pd(OAc)_2$ and 0.111 mL (86 mg, 8.00 equiv.) cyclopenten were added. The vial was closed and the solution was stirred for another 16 h at 45 °C. Afterwards, the solvent was removed in vacuum and the crude product was purified by flash column chromatography (cyclohexane/ethyl acetate = 50:1) and **4** could be obtained as a brownish oil. 39 mg (93%). R_f = 0.35 (cyclohexane/ethyl acetate = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.99 (quint, ^3J = 7.5 Hz, 2 H, C*H*$_2$), 2.55–2.60 (m, 2 H, C*H*$_2$), 2.71–2.76 (m, 2 H, C*H*$_2$), 3.93 (s, 3 H, OC*H*$_3$), 6.44–6.46 (m, 1 H, *C*H), 7.34–7.41 (m, 3 H, Ar-*H*) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.7, 34.0, 34.3, 53.9, 91.8 (ddq, ^1J = 203.4 Hz, ^2J = 32.4 Hz, ^4J = 1.4 Hz), 113.6 (dd, ^2J = 27.0 Hz, ^3J = 9.4 Hz), 120.8 (dq, ^1J = 285.4 Hz, ^2J = 29.7 Hz), 121.1 (dd, ^3J = 9.5 Hz, ^4J = 2.3 Hz), 127.2 (d, ^2J = 12.6 Hz), 128.7 (dd, ^2J = 22.4 Hz, ^3J = 22.3 Hz), 129.0 (d, ^4J = 5.1 Hz), 133.8 (d, ^3J = 10.4 Hz), 135.8 (d, ^3J = 3.4 Hz), 160.3 (dd, ^1J = 251.9 Hz, ^4J = 2.1 Hz), 164.0 (^2J = 23.8 Hz) ppm. – ^{19}F NMR (367 MHz, $CDCl_3$): δ = –77.2 (d, ^3J = 7.5 Hz, 3 F, C*F*$_3$), –110.2 (s, 1 F, Ar-*F*), –172.8 (m, 1 F, C*F*) ppm. – IR (ATR): $\tilde{\nu}$ = 2959 (vw), 1758 (m), 1693 (w), 1620 (vw), 1574 (vw), 1505 (vw), 1438 (w), 1420 (w), 1259 (m), 1195 (s), 1167 (m), 1108 (m), 1064 (w), 1037 (m), 1000 (m), 922 (w), 868 (w), 828 (w), 796 (m), 752 (m), 702 (w), 652 (w), 568 (vw), 530 (w), 447 (vw) cm^{-1}. – MS (EI), *m/z* (%): 320 (100) [M^+], 261 (34) [M^+–COOMe]. – HRMS ($C_{15}H_{13}O_2F_5$ [M^+]): calcd. 320.0835; found 320.0838.

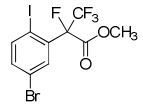
Methyl 2-(3-bromophenyl)-2,3,3,3-tetrafluoropropanoate (5)



A vial equipped with a septum and a stirring bar was charged with the triazene **2c** (50 mg, 0.11 mmol). The reaction vessel was closed and abs. dimethoxyethane (1 mL)

was added *via* syringe under argon atmosphere. Then 0.015 mL (17 mg, 0.12 mmol, 1.10 equiv.) BF_3*OEt_2 was added and the solution was stirred for 16 h at room temperature. The solution was concentrated in vacuum. The pure product could be obtained after flash column chromatography (cyclohexane/ethyl acetate = 50:1) as a yellowish oil. 13 mg (38%). R_f = 0.70 (cyclohexane/ethyl acetate = 50:1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.93 (s, 3 H, OC*H*$_3$), 7.34 (t, ^3J = 8.0 Hz, 1 H, Ar-*H*-5), 7.58–7.65 (m, 2 H, Ar-*H*-4, Ar-*H*-6), 7.80 (s, 1 H, Ar-*H*-2) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 54.1, 91.5 (dq, ^1J = 204.4 Hz, ^2J = 32.5 Hz), 121.0 (dq, ^1J = 285.5 Hz, ^2J = 29.4 Hz), 122.9 (d, ^4J = 2.1 Hz), 124.3 (d, ^3J = 9.5 Hz), 128.7 (d, ^3J = 10.6 Hz), 130.3, 131.4 (d, ^2J = 21.9 Hz), 133.7, 163.9 (d, ^2J = 23.9 Hz) ppm. – ^{19}F NMR (367 MHz, $CDCl_3$): δ = –77.1 (d, ^3J = 7.6 Hz, 3 F, C*F*$_3$), –173.5 (m, 1 F, C*F*) ppm. – IR (film): $\tilde{\nu}$= 2923 (vw), 2852 (vw), 1760 (vw), 1571 (vw), 1439 (vw), 1296 (vw), 1189 (w), 1117 (vw), 1038 (vw), 787 (vw), 737 (vw), 668 (vw), 636 (vw), 455 (vw) cm^{-1}. – MS (EI), *m/z* (%): 313 (66) [M$^+$], 254 (58) [M$^+$–COOMe], 204 (100) [M$^+$–CF_2COOMe]. – HRMS ($C_{10}H_7BrO_2F_4$ [M$^+$]): calcd. 313.9565; found 313.9565.

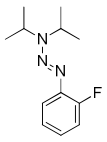
Methyl 2-(5-bromo-2-iodophenyl)-2,3,3,3-tetrafluoropropanoate (6)



A vial equipped with a septum and a stirring bar was charged with the triazene **2c** (50 mg, 0.11 mmol). The reaction vessel was closed and abs. dichloromethane (1 mL) was added *via* syringe under argon atmosphere. Then 0.097 mL (136 mg, 0.68 mmol, 6.00 equiv.) of TMS-I was added and the solution was heated to 100 °C for 6 h. Then, the solution was cooled to room temperature and concentrated in vacuum. The pure product could be obtained after flash column chromatography (cyclohexane/ethyl acetate = 20:1) as a white solid. 33 mg (66%). R_f = 0.20 (cyclohexane/ethyl acetate = 20:1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.93 (s, 3 H, OC*H*$_3$), 7.27 (dd, ^3J = 8.4 Hz, ^4J = 2.3 Hz, 1 H, Ar-*H*-4), 7.71 (s, 1 H, Ar-*H*-6), 7.84 (d, ^3J = 8.4 Hz, 1 H, Ar-*H*-3) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 54.3, 91.2 (d, ^3J = 3.0 Hz), 121.1 (dq, ^1J = 287.3 Hz, ^2J = 29.5 Hz), 122.6, 132.3 (dq, ^3J = 11.0 Hz, ^4J = 2.7 Hz), 134.8, 134.9 (d, ^2J = 20.5 Hz), 143.8, 163.0 (d, ^2J = 23.6 Hz) ppm. – ^{19}F NMR (367 MHz, $CDCl_3$): δ = –73.6 (d, ^3J = 9.0 Hz, 3 F, C*F*$_3$), –159.2 (q, ^3J = 9.0 Hz, 1 F, C*F*) ppm. – IR (ATR): $\tilde{\nu}$= 2956 (vw), 1758 (w), 1458 (vw), 1437 (vw), 1375 (vw), 1295 (w), 1260 (w), 1178 (m), 1033 (m), 968 (m), 807 (w), 760 (w), 741 (w), 716 (w), 682 (w), 637 (vw), 549 (vw), 433 (w) cm^{-1}. – MS (EI), *m/z* (%): 439 (32) [M$^+$], 380 (10) [M$^+$–COOMe], 313 (100) [M$^+$–I]. – HRMS ($C_{10}H_6BrIO_2F_4$ [M$^+$]): calcd. 439.8532; found 439.8532.

C: Synthesis of Flurbiperfluoroprofen (9)

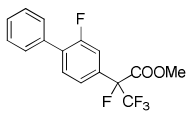
(*E*)-1-(2-Fluorophenyl)-3,3-diisopropyltriaz-1-ene (1k)



A flask equipped with a septum and a stirring bar was charged with 2.00 g (18.0 mmol, 1.00 eq.) of 2-fluoroaniline. The flask was closed and THF (5 mL) was added via a syringe under argon atmosphere. The solution was cooled down to –20 °C and then 3.42 mL BF_3*OEt_2 (27.0 mmol, 3.83 g, 1.50 eq.) was added. Afterwards, 3.63 mL isoamyl nitrite (27.0 mmol, 3.26 g, 1.50 eq.) was slowly added under vigorous stirring. It was stirred for 2 h at this temperature. The precipitate was then filtered off and washed with ice-cold diethyl ether. Without further isolation, the precipitate was then poured with acetonitrile into a freshly prepared flask containing 7.64 mL diisopropylamine (54.0 mmol, 5.47 g, 3.00 eq.) and a 9:1 mixture of THF/pyridine (altogether 10 mL) at –20 °C. The solution was stirred under slow warming to room temperature for 16 h. Afterwards, the reaction was quenched with sat. NH_4Cl-solution. The aqueous phase was extracted with ethyl acetate two times and then the organic layer was dried over MgSO4. Finally, the solvent was removed in vacuum and the pure product could be obtained after flash column chromatography (cyclohexane/ ethyl acetate = 25:1) as an orange solid. 3.70 g (92%). R_f = 0.63 (cyclohexane/ethyl acetate = 25:1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (bs, 6 H, C*H*$_3$), 1.37 (bs, 6 H, C*H*$_3$), 4.02 (bs, 1 H, C*H*), 5.33 (bs, 1 H, C*H*), 7.02–7.11 (m, 3 H, Ar-*H*), 7.43–7.48 (m, 1 H, Ar-*H*) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.3 (bs), 23.9 (bs), 46.1 (bs), 49.0 (bs), 116.1 (d, ^2J = 20.0 Hz), 119.0 (d, ^4J = 2.0 Hz), 123.9 (d, ^3J = 3.7 Hz), 125.2 (d, ^3J = 7.7 Hz), 139.8 (d, ^2J = 7.4 Hz), 156.3 (d, ^2J = 248.5 Hz) ppm. – ^{19}F NMR (367 MHz, $CDCl_3$): δ = –128.6 (s, 1 F, *C*F) ppm. – IR (ATR): $\tilde{\nu}$= 2975 (w), 2934 (w), 1582 (w), 1486 (m),

1454 (w), 1399 (m), 1369 (m), 1267 (m), 1232 (m), 1209 (m), 1182 (w), 1148 (m), 1103 (m), 1027 (m), 933 (w), 914 (w), 888 (w), 854 (vw), 817 (m), 748 (m), 730 (m), 631 (w), 588 (w), 564 (w), 528 (w), 503 (w), 471 (w), 426 (vw) cm^{-1}. – MS (EI), *m/z* (%): 223 (23) [M^+], 123 (69) [M^+–$C_6H_{14}N$], 95 (100) [M^+–$C_6H_{14}N_3$]. – HRMS ($C_{12}H_{18}N_3F$ [M^+]): calcd. 223.1484; found 223.1485.

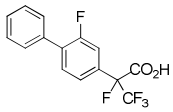
Methyl 2,3,3,3-tetrafluoro-2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (8)



A vial equipped with a septum and a stirring bar was charged with the triazene **2k** (200 mg, 0.525 mmol). The reaction vessel was closed and 6 mL of benzene was added via syringe under argon atmosphere. Afterwards, 0.040 mL (59.8 mg, 0.525 mmol, 1.00 equiv.) trifluoroacetic acid was added and the solution stirred for 16 h at 80 °C. Then, the solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by flash column chromatography (cyclohexane/ethyl acetate = 25:1) and **8** could be obtained as a colourless liquid (101 mg, 59%). R_f = 0.25 (cyclohexane/ethyl acetate = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.96 (s, 3 H, OC*H*$_3$), 7.39–7.56 (m, 8 H, Ar-*H*) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 54.1, 91.7 (dq, ^1J = 203.9 Hz, ^2J = 32.6 Hz), 114.1 (dd, ^2J = 26.8 Hz, ^3J = 10.0 Hz), 120.8 (dq, ^1J = 285.5 Hz, ^2J = 29.6 Hz), 121.6, 128.4, 128.6, 128.9 (d, ^4J = 2.4 Hz), 130.1 (dd, ^2J = 22.4 Hz, ^3J = 7.9 Hz), 131.2 (d, ^3J = 2.6 Hz), 131.4 (d, ^2J = 13.5 Hz), 134.5, 159.5 (dd, ^1J = 249.5 Hz), 163.9 (d, ^2J = 23.8 Hz) ppm. – ^{19}F NMR (367 MHz, $CDCl_3$): δ = –77.0 (d, ^3J = 7.9 Hz, 3 F, C*F*$_3$), –115.7 (s, 1 F, Ar-*F*), –172.8 (m, 1 F, C*F*) ppm. – IR (film): $\tilde{\nu}$= 3444 (w), 3035 (w), 2960 (vw), 2927 (vw), 2131 (vw), 1760 (m), 1604 (vw), 1584 (vw), 1564 (vw), 1517 (vw), 1485 (w), 1439 (w), 1415 (w), 1288 (m), 1203 (m), 1170 (m), 1138 (w), 1112 (w), 1041 (w), 1011 (w), 867 (w), 832 (vw), 798 (w), 769 (w), 752 (w), 723 (vw), 697 (w), 639 (vw), 574 (vw) cm^{-1}. – MS (EI), *m/z* (%): 330 (98) [M^+], 271 (100) [M^+–$COOCH_3$]. – HRMS ($C_{16}H_{11}O_2F_5$ [M^+]): calcd. 330.0679; found 330.0681.

2,3,3,3-Tetrafluoro-2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoic acid (9)



A flask equipped with a septum and a stirring bar was charged with **8** (101 mg, 0.306 mmol). Then, methanolic KOH (7 mL, 0.80 mmol/mL) was added. The reaction vessel was closed and the solution was stirred for 16 h at room temperature. Afterwards, the solvent was removed in vacuum and the residue was solved in water. The water phase was first washed with diethyl ether and then acidified with 2M HCl. Then, the water phase was extracted with ethyl acetate and dried over $MgSO_4$. The solvent was removed in vacuum and the product was obtained as a white solid. 86 mg (89%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.59 (m, 8 H, Ar-*H*), 10.48 (s, 1 H, COO*H*) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 91.5 (dq, ^1J = 201.6 Hz, ^2J = 34.3 Hz), 114.1 (dd, ^2J = 27.0 Hz, ^3J = 10.2 Hz), 120.7 (dq, ^1J = 285.6 Hz, ^2J = 29.3 Hz), 121.6 (dd, ^3J = 9.5 Hz, ^4J = 3.0 Hz), 128.4, 128.6, 128.9 (d, ^4J = 2.9 Hz), 129.4 (dd, ^2J = 22.2 Hz, ^3J = 8.0 Hz), 131.3 (d, ^3J = 3.2 Hz),131.7 (d, ^2J = 13.5 Hz), 134.4, 159.5 (dd, ^1J = 249.8 Hz, ^4J = 2.0 Hz), 168.3 (d, ^2J = 25.1 Hz) ppm. – ^{19}F NMR (367 MHz, $CDCl_3$): δ = –76.8 (d, ^3J = 7.4 Hz, 3 F, C*F*$_3$), –115.4 (s, 1 F, Ar-*F*), –172.6 (m, 1 F, C*F*) ppm. – IR (ATR): $\tilde{\nu}$= 2923 (w), 1753 (m), 1581 (w), 1561 (vw), 1514 (vw), 1483 (w), 1405 (w) 1286 (m), 1265 (m), 1203 (s), 1167 (m), 1137 (m), 1114 (m), 1075 (w), 1020 (w), 995 (m), 864 (m), 833 (m), 767 (m), 726 (m), 692 (m), 644 (w), 572 (w), 548 (w), 525 (w), 497 (w), 456 (w), 419 (vw) cm^{-1}. – MS (EI), *m/z* (%): 316 (30) [M^+], 271 (51) [M^+–COOH], 84 (100).– HRMS ($C_{15}H_9O_2F_5$ [M^+]): calcd. 316.0522; found 316.0524.

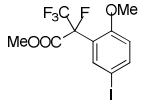
D: Methoxycarbonyltetrafluoroethylation of anisoles

General procedure for the methoxycarbonyltetrafluoroethylation of anisoles:

A vial equipped with a septum and a stirring bar was charged with 202 mg (1.60 mmol, 4.00 equiv.) of AgF and 0.40 mmol of the anisole derivatives. The reaction vessel was closed and 0.17 mL (225 mg, 1.60 mmol, 4.00 equiv.) methyl 2,3,3-tifluoroacrylate (MTA) was added via syringe under argon atmosphere. The suspension was heated to 100 °C and was stirred for 16 hours at 100 °C. Afterwards,

the solution was cooled to room temperature and 5 mL of ethyl acetate were added. The solution was poured into a flask and the vial was extracted another two times. Finally, the solvent was removed in vacuum and the crude product was purified by flash column chromatography.

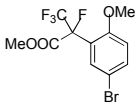
Methyl 2,3,3,3-tetrafluoro-2-(5-iodo-2-methoxyphenyl)propanoate (11a)



The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 10:1) as a colorless oil. 66 mg (42%). R_f = 0.15 (cyclohexane/ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.79 (s, 3 H, COOCH_3), 3.86 (s, 3 H, OCH_3), 6.73 (dd, ^3J = 8.7 Hz, ^5J = 0.9 Hz, 1 H, Ar-*H*-3), 7.75 (dd, ^3J = 8.7 Hz, ^4J = 2.0 Hz, 1 H, Ar-*H*-4), 7.82 (bs, 1 H, Ar-*H*-6) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 53.4, 55.1, 82.8, 90.3 (dq, ^1J = 196.7 Hz, ^2J = 32.8 Hz), 114.0, 121.1 (dq, ^1J = 285.6 Hz, ^2J = 30.0 Hz), 121.8 (d, ^2J = 21.4 Hz), 136.7 (d, ^3J = 11.1 Hz), 140.8, 156.7 (d, ^3J = 4.2 Hz), 164.0 (d, ^2J = 23.0 Hz) ppm. – ^{19}F NMR (367 MHz, $CDCl_3$): δ = –76.1 (d, ^3J = 8.6 Hz, 3 F, CF_3), –164.6 (m, 1 F, C*F*) ppm. – IR (film): $\tilde{\nu}$ = 2956 (w), 2848 (w), 1770 (s), 1592 (m), 1488 (s), 1462 (m), 1439 (m), 1396 (w), 1285 (s), 1179 (s), 1144 (m), 1090 (m), 1068 (m), 1040 (s), 977 (m), 922 (w), 890 (w), 814 (m), 793 (w), 758 (w), 741 (w), 711 (w), 659 (w), 640 (w), 614 (m), 538 (w) cm^{-1}. – MS (EI), *m/z* (%): 391 (60) [M$^+$], 332 (36) [M$^+$–COOMe], 158 (100). – HRMS ($C_{11}H_9O_3IF_4$ [M$^+$]): calcd. 391.9532; found 391.9531.

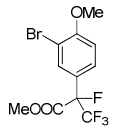
Methyl 2-(5-bromo-2-methoxyphenyl)-2,3,3,3-tetrafluoropropanoate (11b)



The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 5:1) as a colorless oil. 46 mg (33%). R_f = 0.13 (cyclohexane/ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.79 (s, 3 H, COOCH_3), 3.86 (s, 3 H, OCH_3), 6.83 (d, ^3J = 8.8 Hz, 1 H, Ar-*H*-3), 7.55 (dd, ^3J = 8.8 Hz, ^5J = 2.4 Hz, 1 H, Ar-*H*-4), 7.67 (bs, 1 H, Ar-*H*-6) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 53.4, 56.3, 90.5 (dq, ^1J = 196.8 Hz, ^2J = 32.8 Hz), 113.2, 113.6, 121.1 (dq, ^1J = 285.7 Hz, ^2J = 30.0 Hz), 121.5 (d, ^3J = 21.4 Hz), 130.9 (d, ^3J = 11.2 Hz), 134.8, 155.9 (d, ^3J = 4.3 Hz), 164.0 (d, ^2J = 22.9 Hz) ppm. – ^{19}F NMR (367 MHz, $CDCl_3$): δ = –76.0 (d, ^3J = 8.6 Hz, 3 F, CF_3), –164.3 (m, 1 F, C*F*) ppm. – IR (film): $\tilde{\nu}$ = 3011 (w), 2958 (w), 2850 (w), 1771 (m), 1597 (w), 1491 (m), 1463 (w), 1439 (m), 1402 (w), 1270 (m), 1180 (m), 1096 (m), 1070 (m), 1040 (m), 1024 (m), 983 (w), 969 (w), 922 (w), 889 (w), 815 (w), 795 (w), 759 (w), 741 (w), 710 (w), 661 (w), 643 (w), 625 (w), 548 (vw) cm^{-1}. – MS (EI), *m/z* (%): 344 (100) [M$^+$], 285 (36) [M$^+$–COOMe]. – HRMS ($C_{11}H_9BrO_3F_4$ [M$^+$]): calcd. 343.9671; found 343.9674.

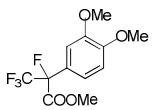
Methyl 2-(3-bromo-4-methoxyphenyl)-2,3,3,3-tetrafluoropropanoate (11c)



The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 5:1) as a colorless oil. 35 mg (25%). R_f = 0.23 (cyclohexane/ethyl acetate = 10:1).

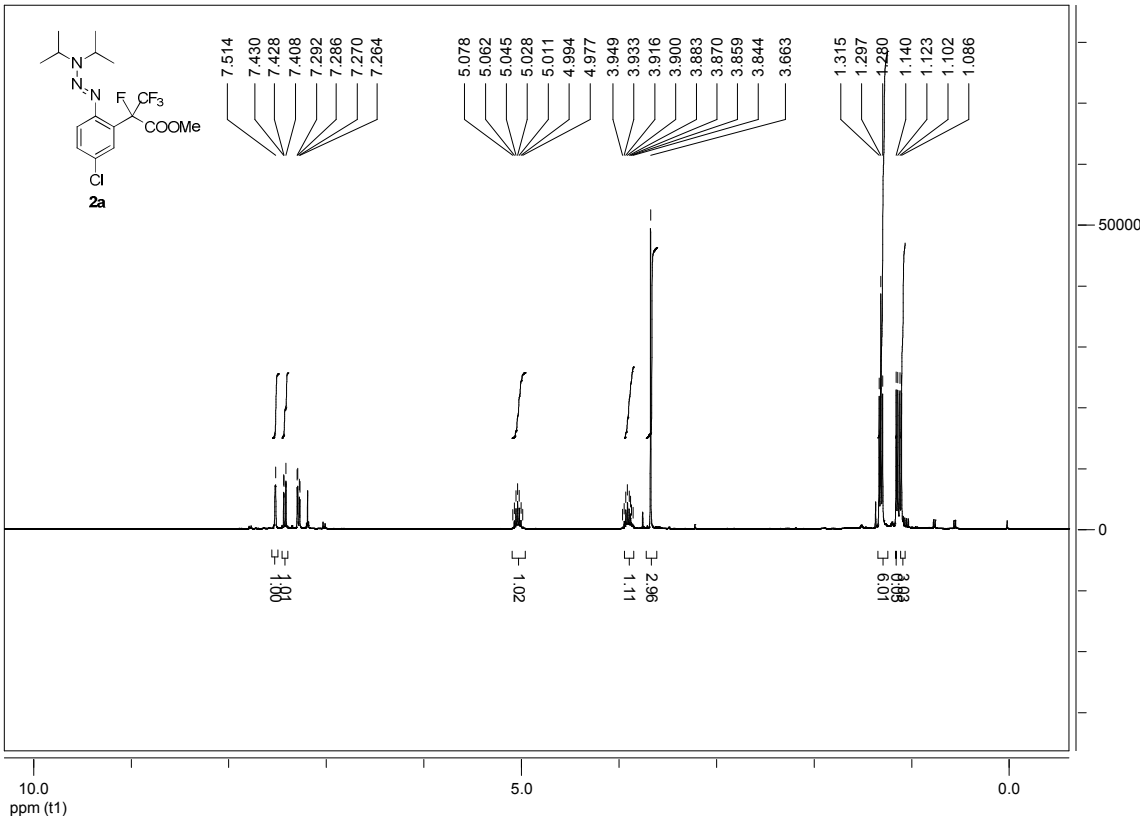
^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.93 (s, 3 H, OCH_3), 3.94 (s, 3 H, OCH_3), 6.94 (d, ^3J = 8.7 Hz, 1 H, Ar-*H*-5), 7.56 (dd, ^3J = 8.7 Hz, ^4J = 2.2 Hz, 1 H, Ar-*H*-6), 7.81 (d, ^3J = 2.2 Hz, 1 H, Ar-*H*-2) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 53.9, 56.4, 91.5 (dq, ^1J = 202.9 Hz, ^2J = 32.4 Hz), 111.6, 112.1, 122.5 (d, ^2J = 22.6 Hz), 121.1 (dq, ^1J = 285.5 Hz, ^2J = 30.1 Hz), 126.3 (d, ^3J = 9.4 Hz), 130.7 (d, ^3J = 10.1 Hz), 157.5, 164.1 (d, ^2J = 23.5 Hz) ppm. – ^{19}F NMR (367 MHz, $CDCl_3$): δ = –77.2 (d, ^3J = 7.7 Hz, 3 F, CF_3), –171.8 (m, 1 F, C*F*) ppm. – IR (film): $\tilde{\nu}$ = 3486 (vw), 3016 (w), 2962 (w), 2851 (w), 1759 (m), 1604 (w), 1502 (m), 1462 (m), 1441 (m), 1404 (w), 1265 (m), 1186 (m), 1111 (m), 1059 (m), 1038 (m), 978 (w), 889 (w), 815 (w), 797 (w), 753 (w), 704 (w), 673 (w), 628 (w), 602 (w), 542 (vw) cm^{-1}. – MS (EI), *m/z* (%): 344 (45) [M$^+$], 285 (72) [M$^+$–COOMe], 59 (100). – HRMS ($C_{11}H_9BrO_3F_4$ [M$^+$]): calcd. 343.9671; found 343.9669.

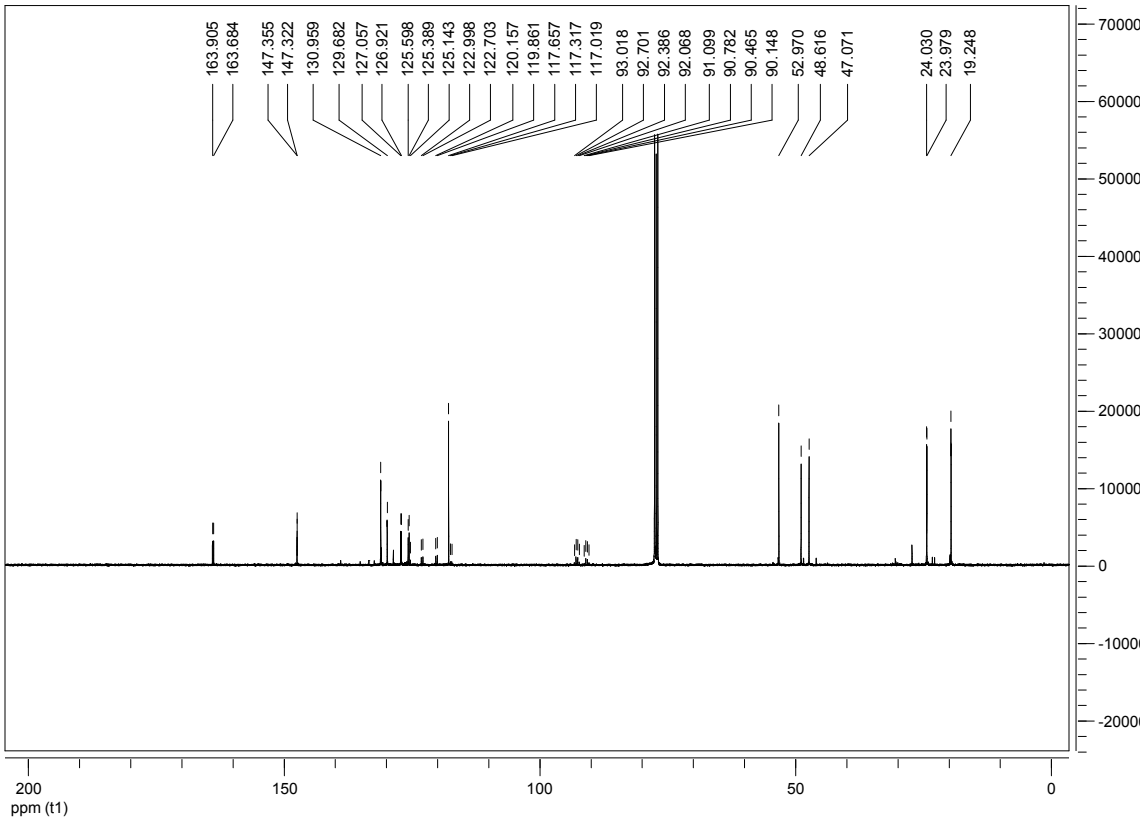
Methyl 2-(3,4-dimethoxyphenyl)-2,3,3,3-tetrafluoropropanoate (11d)



The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 5:1) as a colorless oil. 34 mg (29%). R_f = 0.08 (cyclohexane/ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.89 (s, 3 H, OCH_3), 3.90 (s, 3 H, OCH_3), 3.91 (s, 3 H, COOCH_3), 6.91 (d, ^3J = 8.5 Hz, 1 H, Ar-*H*-5), 7.12 (d, ^5J = 1.9 Hz, 1 H, Ar-*H*-2), 7.17 (dd, ^3J = 8.5 Hz, ^5J = 1.9 Hz, 1 H, Ar-*H*-6) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 53.7, 55.9, 56.0, 92.2 (dq, ^1J = 202.2 Hz, ^2J = 32.3 Hz), 108.5 (d, ^3J = 10.2 Hz), 110.9, 118.6 (d, ^3J = 9.7 Hz), 121.1 (dq, ^1J = 285.2 Hz, ^2J = 30.0 Hz), 121.4 (d, ^2J = 22.1 Hz), 149.1 (d, ^4J = 1.4 Hz), 150.7 (d, ^5J = 1.4 Hz), 164.5 (d, ^2J = 23.8 Hz) ppm. – ^{19}F NMR (367 MHz, $CDCl_3$): δ = –77.7 (d, ^3J = 7.7 Hz, 3 F, CF_3), –171.4 (m, 1 F, C*F*) ppm. – IR (film): $\tilde{\nu}$ = 3452 (w), 3009 (m), 2962 (m), 2843 (m), 2605 (w), 2035 (vw), 1758 (m), 1605 (m), 1520 (m), 1442 (m), 1418 (m), 1266 (s), 1205 (m), 1168 (m), 1151 (m), 1121 (m), 1027 (m), 993 (m), 944 (w), 919 (w), 856 (m), 812 (m), 798 (m), 770 (m), 751 (m), 694 (m), 614 (w), 546 (w), 488 (vw) cm^{-1}. – MS (EI), *m/z* (%): 296 (45) [M$^+$], 237 (100) [M$^+$–COOMe]. – HRMS ($C_{12}H_{12}O_4F_4$ [M$^+$]): calcd. 296.0672; found 296.0673.

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147.322
130.959
129.682
127.057
126.921
125.598
125.389
125.143
122.998
122.703
120.157
119.861
117.657
117.317
117.019
93.018
92.701
92.386
92.068
91.099
90.782
90.465
90.148
52.970
48.616
47.071
24.030
23.979
19.248
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60000
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40000
30000
20000
10000
0
-10000
-20000
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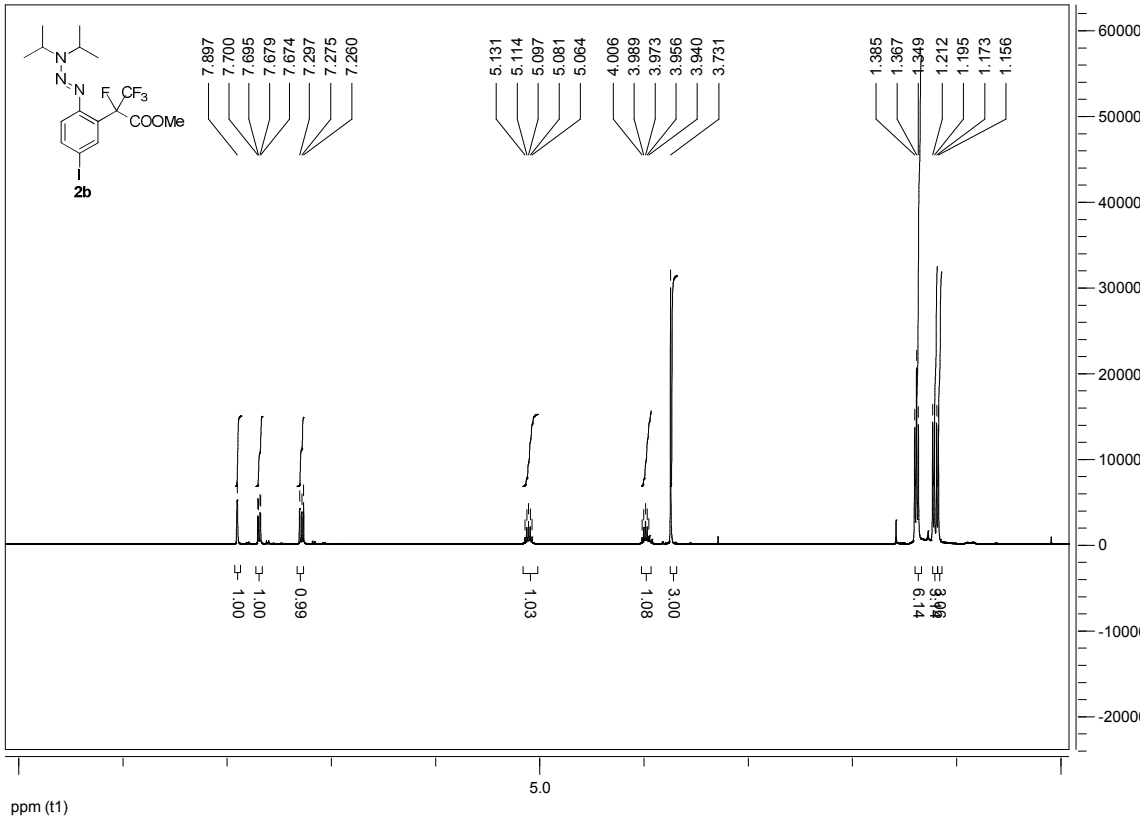
150
100
50
0
ppm (t1)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CF3
COOMe
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7.700
7.695
7.679
7.674
7.297
7.275
7.260
5.131
5.114
5.097
5.081
5.064
4.006
3.989
3.973
3.956
3.940
3.731
1.385
1.367
1.349
1.212
1.195
1.173
1.156
1.00
1.00
0.99
1.03
1.08
3.00
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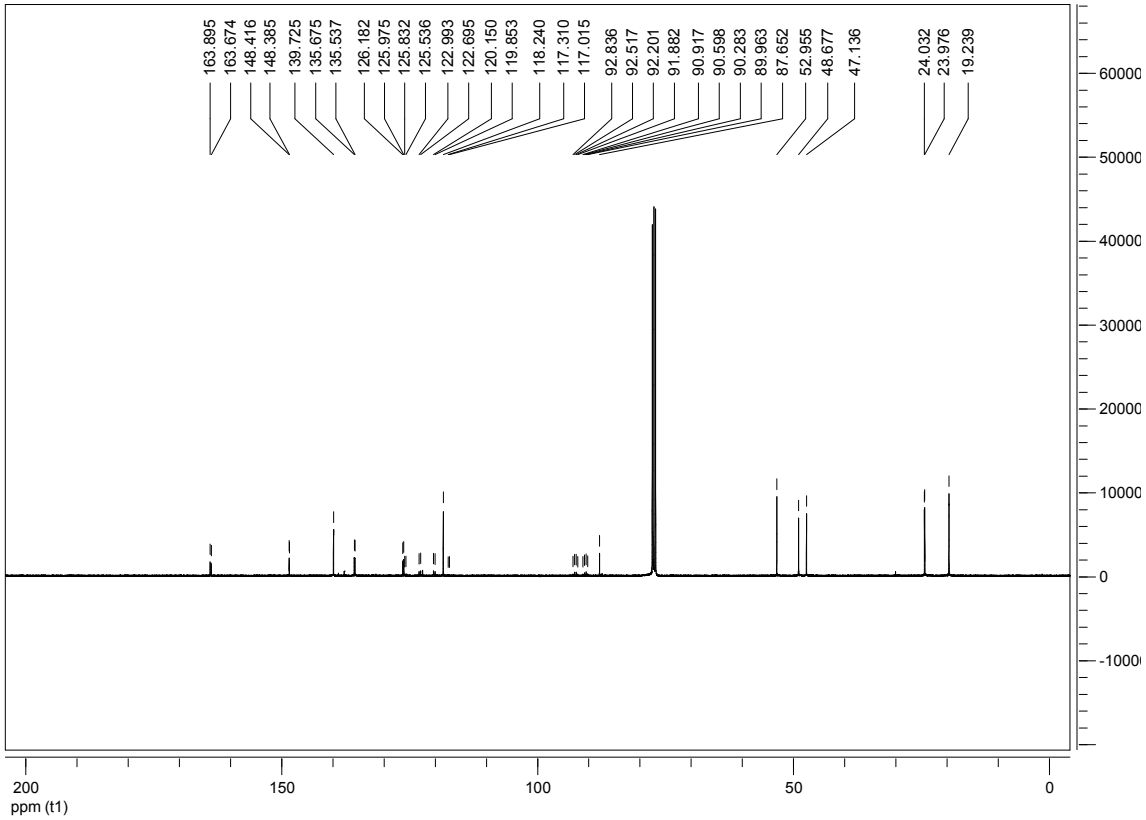
50000
40000
30000
20000
10000
0
-10000
-20000
5.0
ppm (t1)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135.675
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125.536
122.993
122.695
120.150
119.853
118.240
117.310
117.015
92.836
92.517
92.201
91.882
90.917
90.598
90.283
89.963
87.652
52.955
48.677
47.136
24.032
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20000
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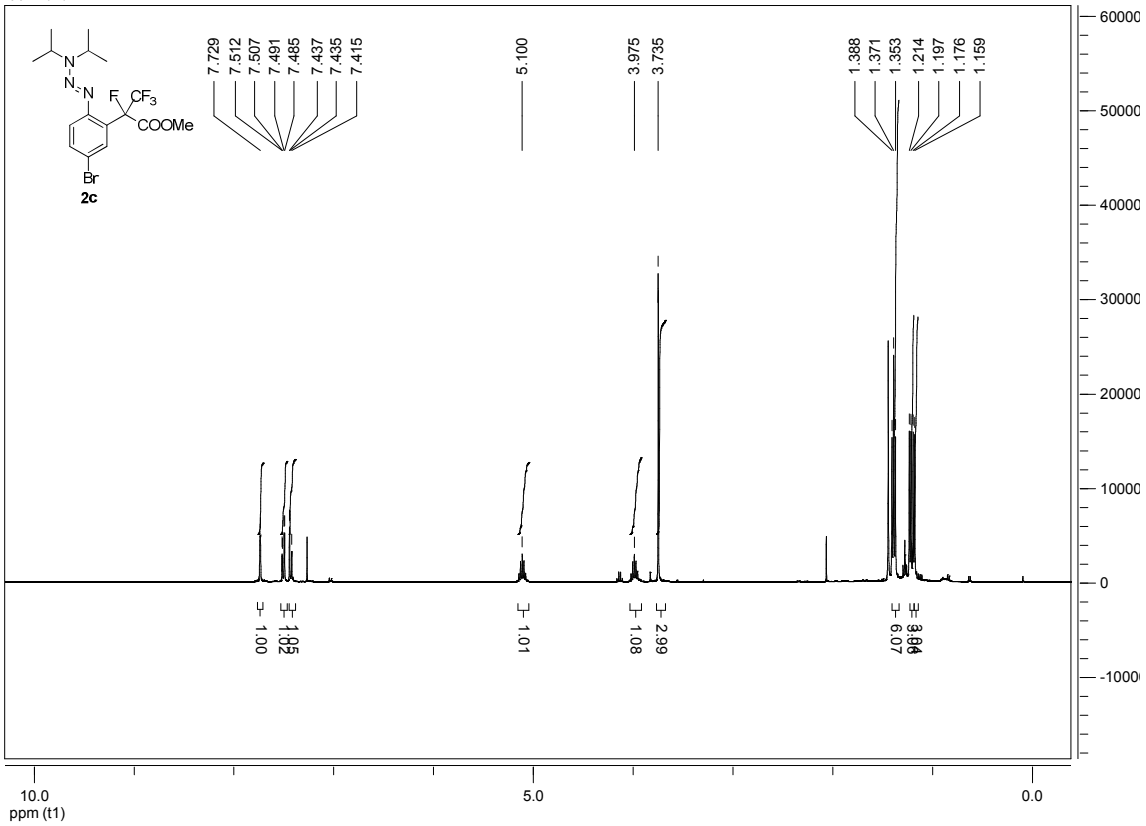
50
0
ppm (t1)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COOMe
Br
2c
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7.507
7.491
7.485
7.437
7.435
7.415
5.100
3.975
3.735
1.388
1.371
1.353
1.214
1.197
1.176
1.159
1.00
1.01
1.08
2.99
9.07
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50000
40000
30000
20000
10000
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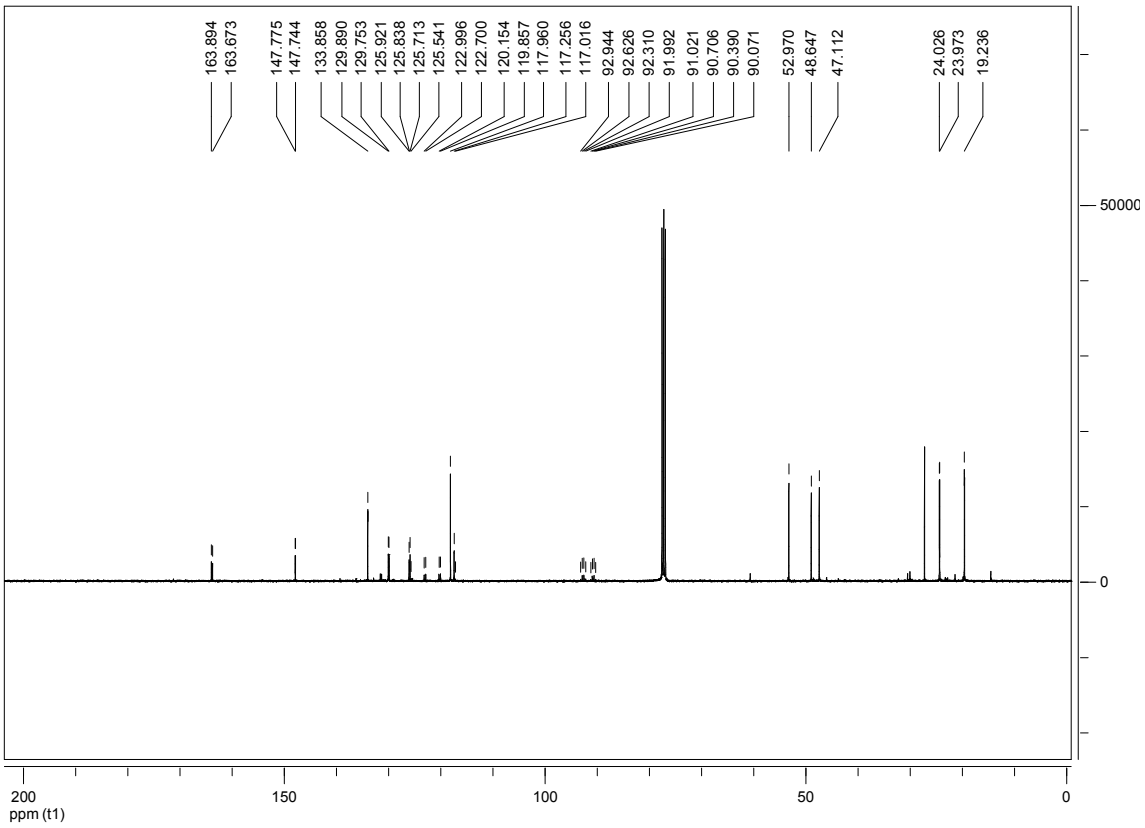
-10000
10.0
5.0
0.0
ppm (t1)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125.713
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122.700
120.154
119.857
117.960
117.256
117.016
92.944
92.626
92.310
91.992
91.021
90.706
90.390
90.071
52.970
48.647
47.112
24.026
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150
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50
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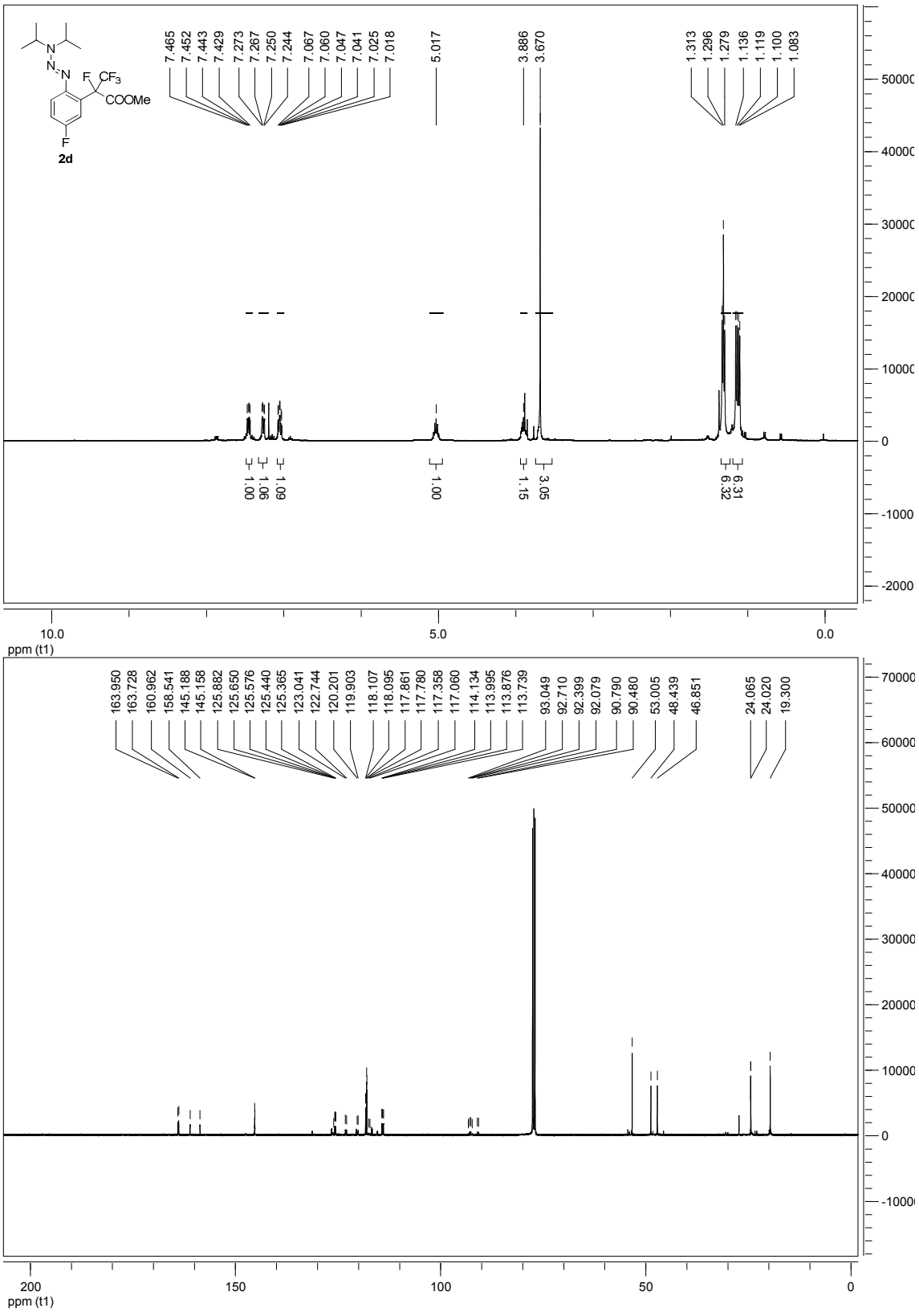
ppm (t1)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7.244
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7.060
7.047
7.041
7.025
7.018
5.017
3.886
3.670
1.313
1.296
1.279
1.136
1.119
1.100
1.083
1.00
1.06
1.09
1.00
1.15
3.05
6.32
1.31
10.0
5.0
0.0
ppm (t1)
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158.541
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145.158
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125.650
125.576
125.440
125.365
123.041
122.744
120.201
119.903
118.107
118.095
117.861
117.780
117.358
117.060
114.134
113.995
113.876
113.739
93.049
92.710
92.399
92.079
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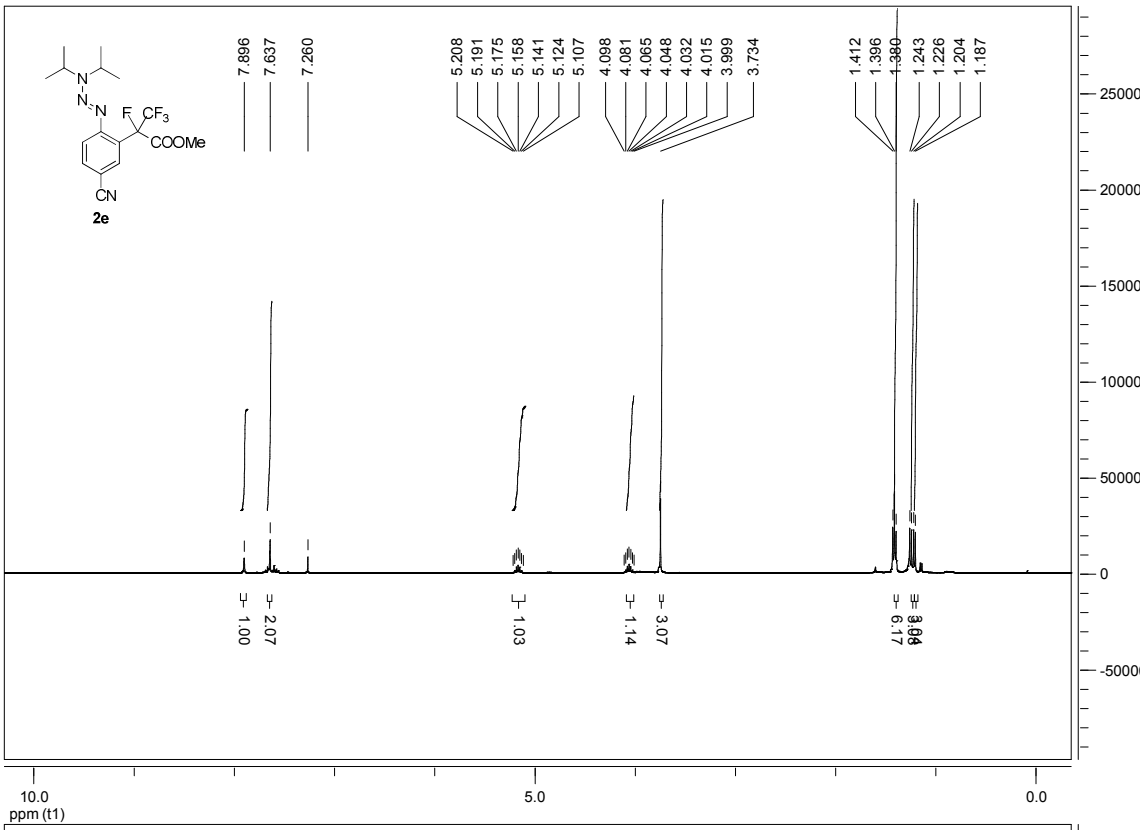
50
0
ppm (t1)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5.191
5.175
5.158
5.141
5.124
5.107
4.098
4.081
4.065
4.048
4.032
4.015
3.999
3.734
1.412
1.396
1.380
1.243
1.226
1.204
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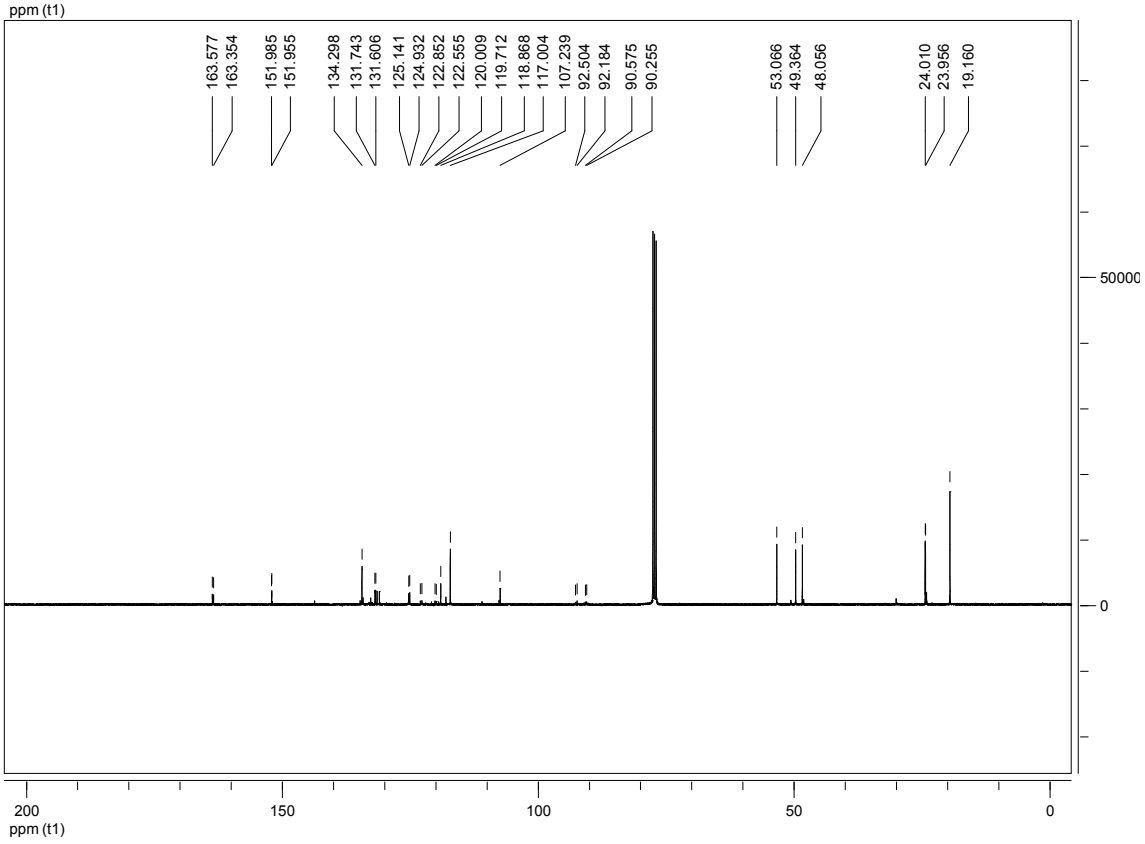
1.03
1.14
3.07
6.17
10.0
5.0
0.0
ppm (t1)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119.712
118.868
117.004
107.239
92.504
92.184
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90.255
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24.010
23.956
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50
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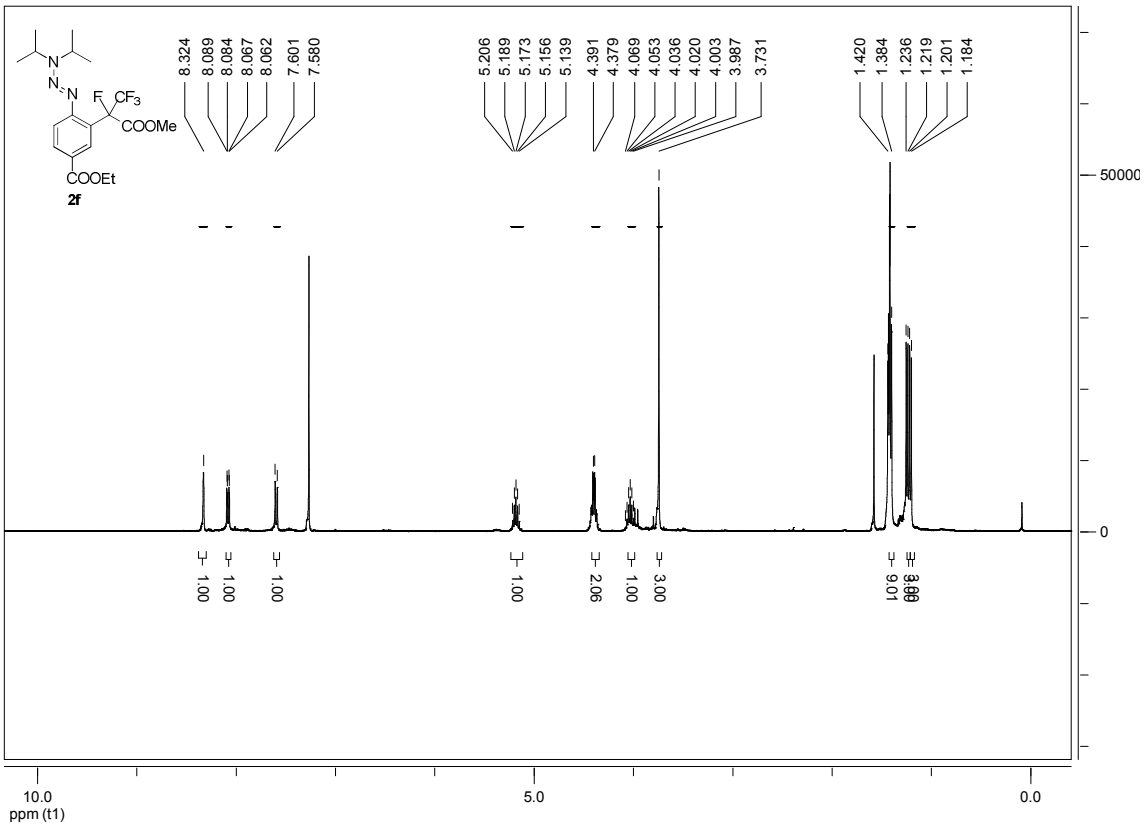
ppm (t1)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5.206
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4.379
4.069
4.053
4.036
4.020
4.003
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3.731
1.420
1.384
1.236
1.219
1.201
1.184
COOEt
2f
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1.00
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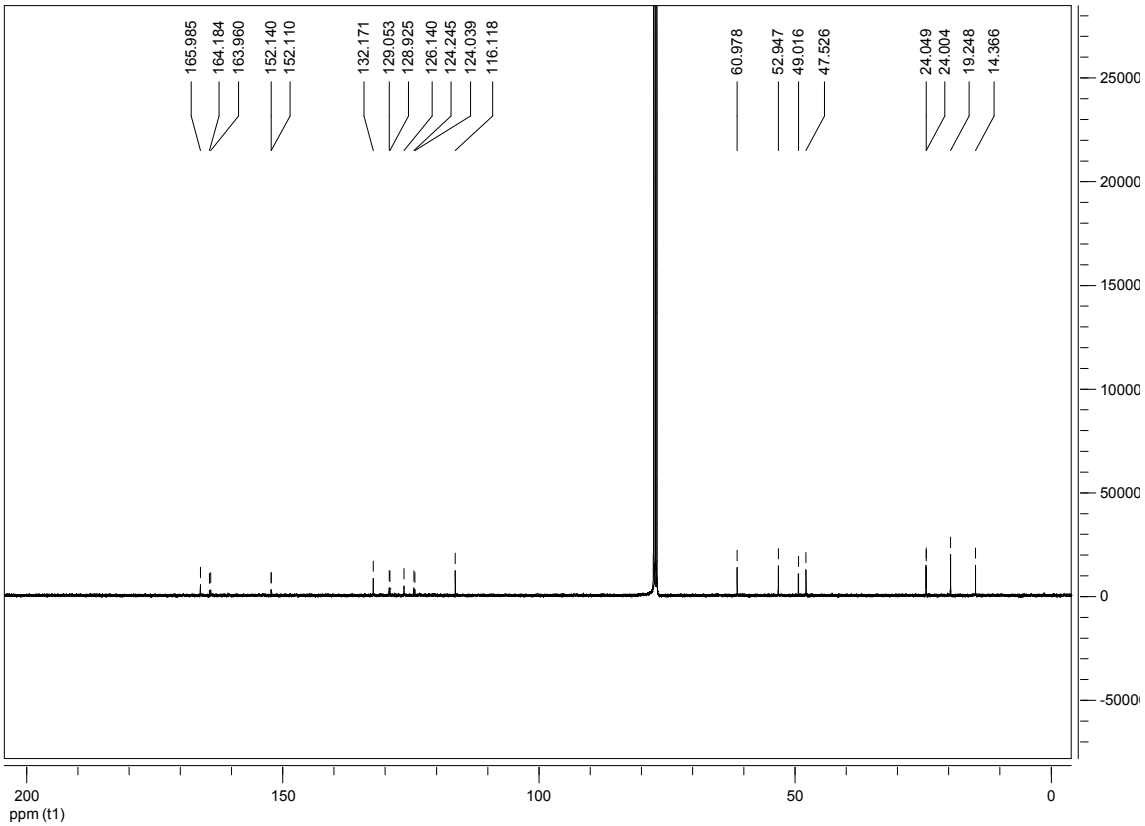
ppm (t1)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163.960
152.140
152.110
132.171
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128.925
126.140
124.245
124.039
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60.978
52.947
49.016
47.526
24.049
24.004
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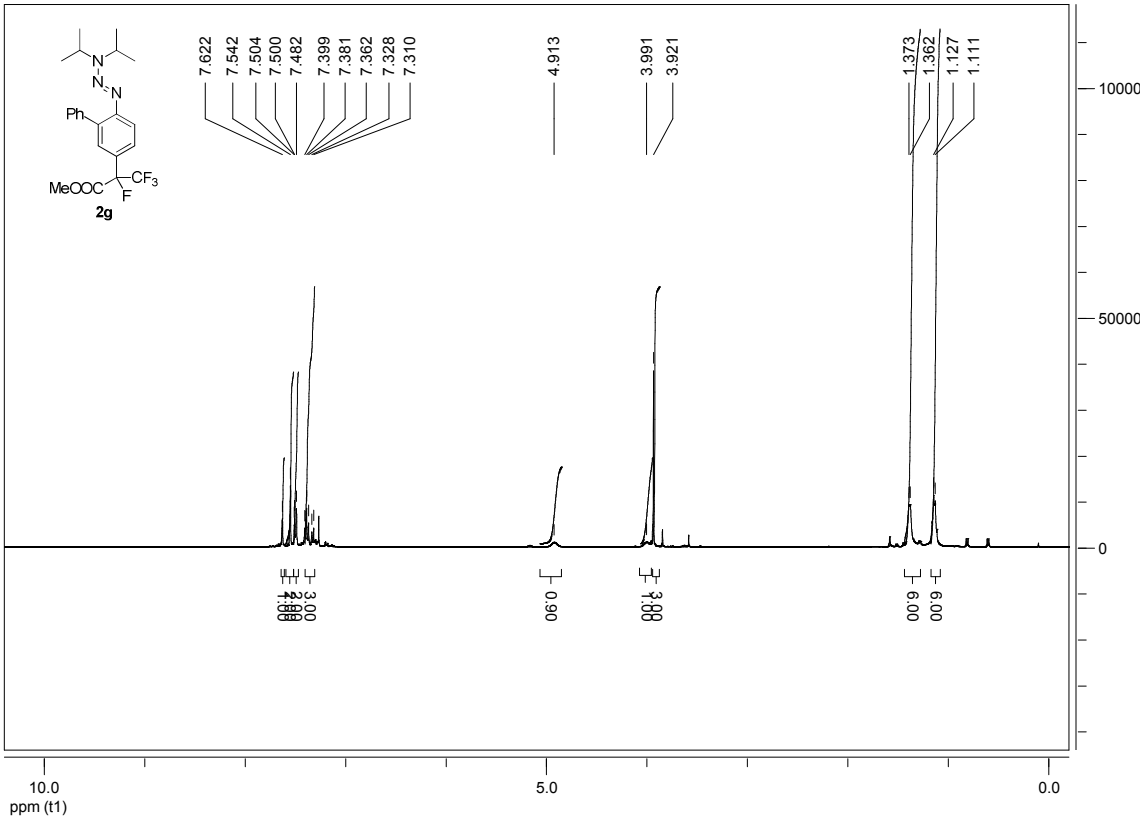
200
150
100
50
0
ppm (t1)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7.399
7.381
7.362
7.328
7.310
4.913
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3.921
1.373
1.362
1.127
1.111
Ph
MeOOC
CF3
F
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1.00
6.00
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10.0
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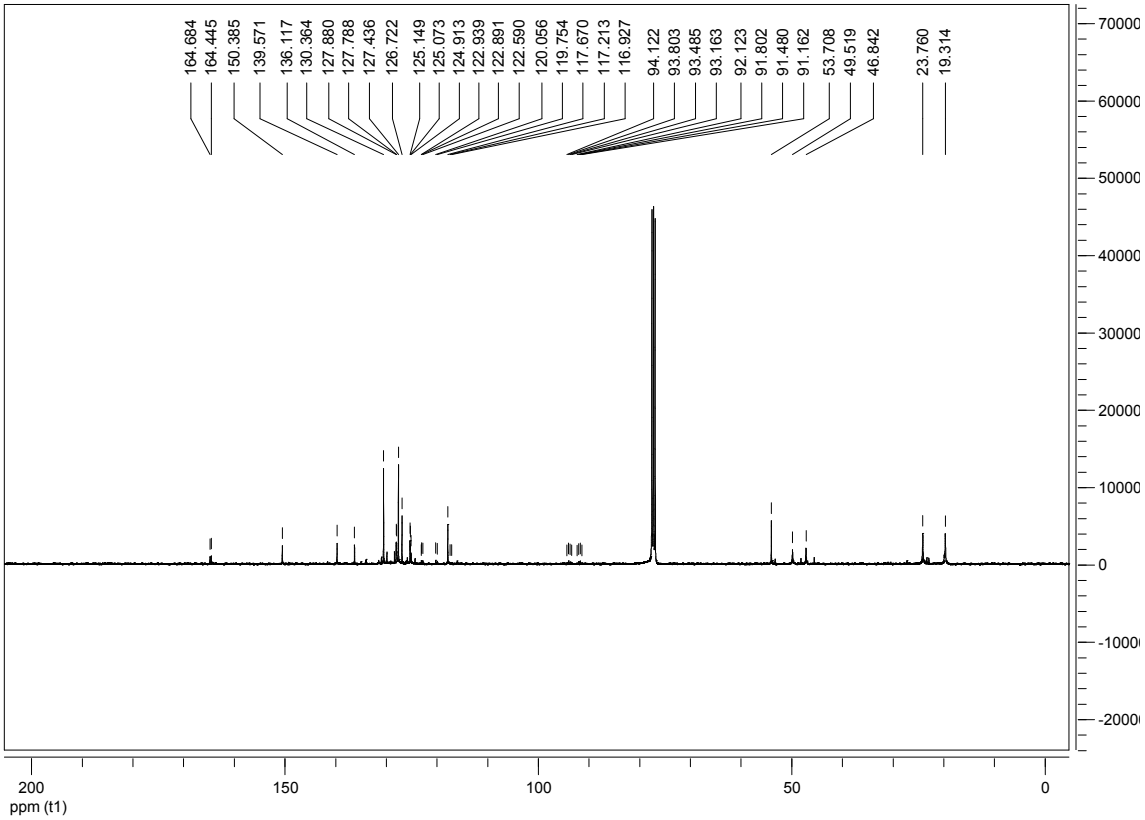
ppm (t1)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127.788
127.436
126.722
125.149
125.073
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122.939
122.891
122.590
120.056
119.754
117.670
117.213
116.927
94.122
93.803
93.485
93.163
92.123
91.802
91.480
91.162
53.708
49.519
46.842
23.760
19.314
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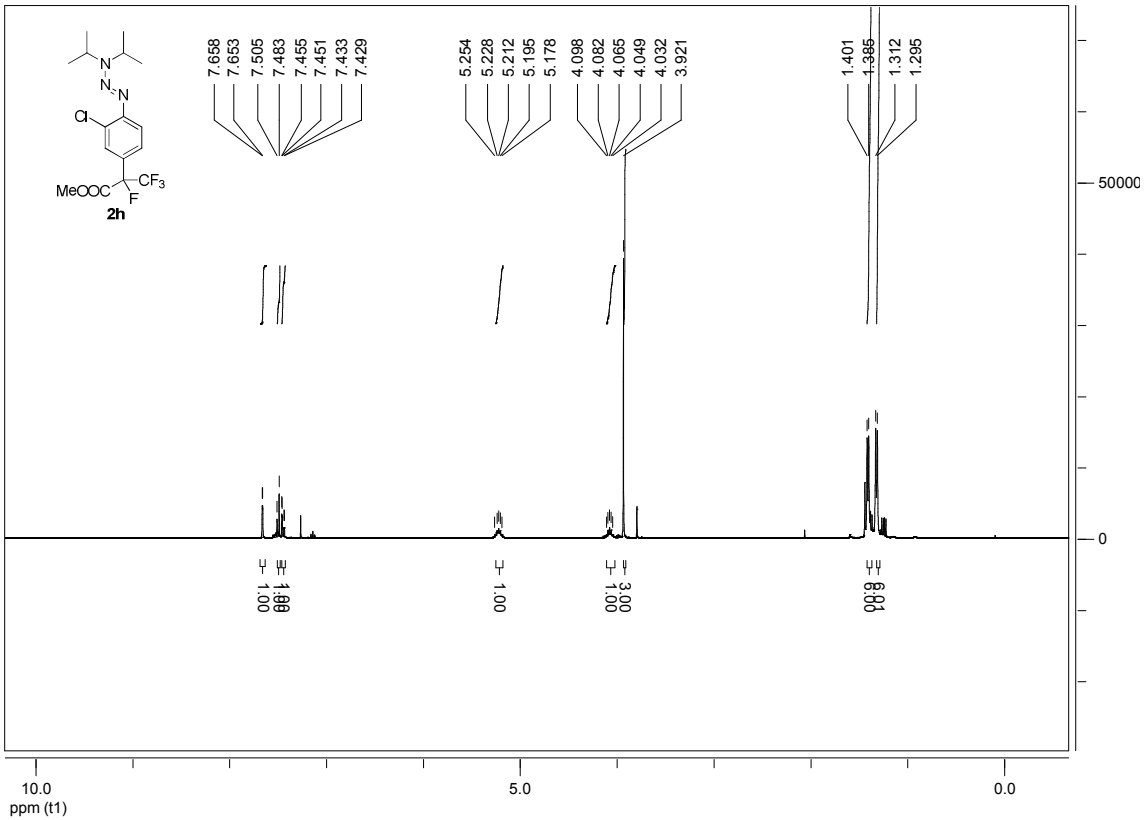
200
150
100
50
0
ppm (t1)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7.483
7.455
7.451
7.433
7.429
5.254
5.228
5.212
5.195
5.178
4.098
4.082
4.065
4.049
4.032
3.921
1.401
1.385
1.312
1.295
Cl
N
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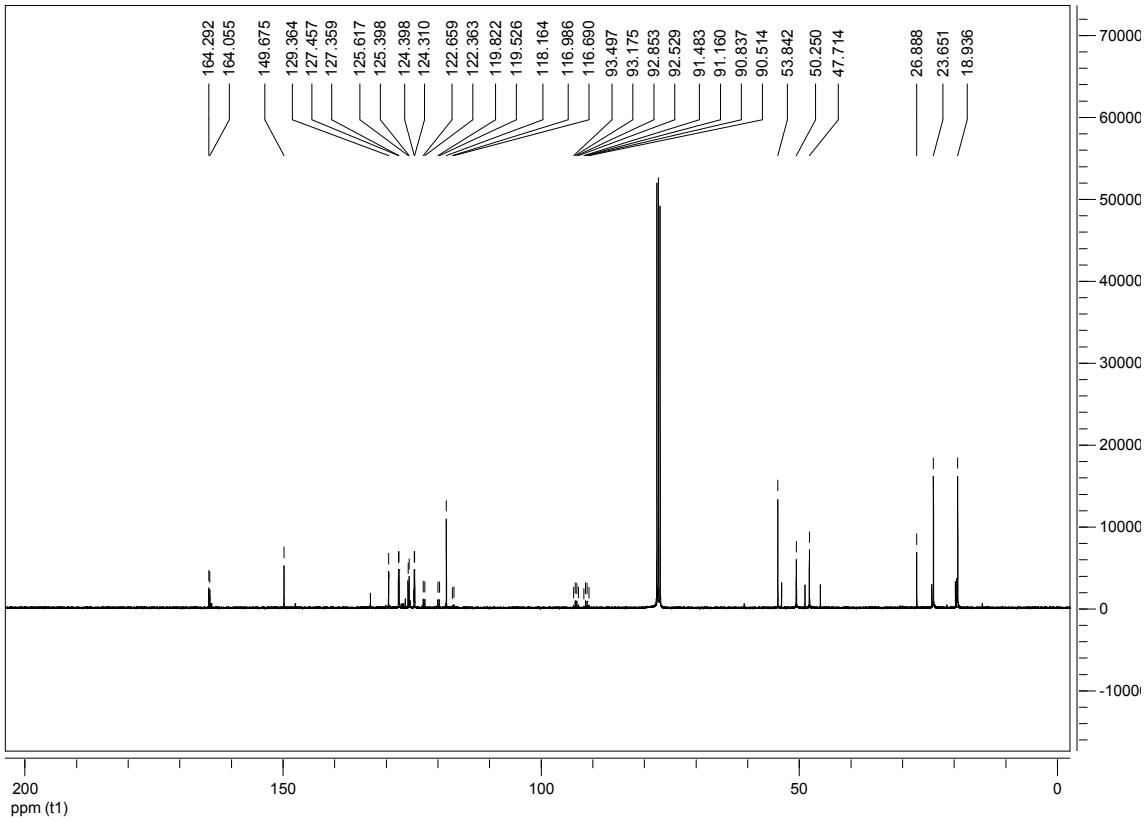
3.00
6.01
10.0
5.0
0.0
ppm (t1)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127.359
125.617
125.398
124.398
124.310
122.659
122.363
119.822
119.526
118.164
116.986
116.690
93.497
93.175
92.853
92.529
91.483
91.160
90.837
90.514
53.842
50.250
47.714
26.888
23.651
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40000
30000
20000
10000
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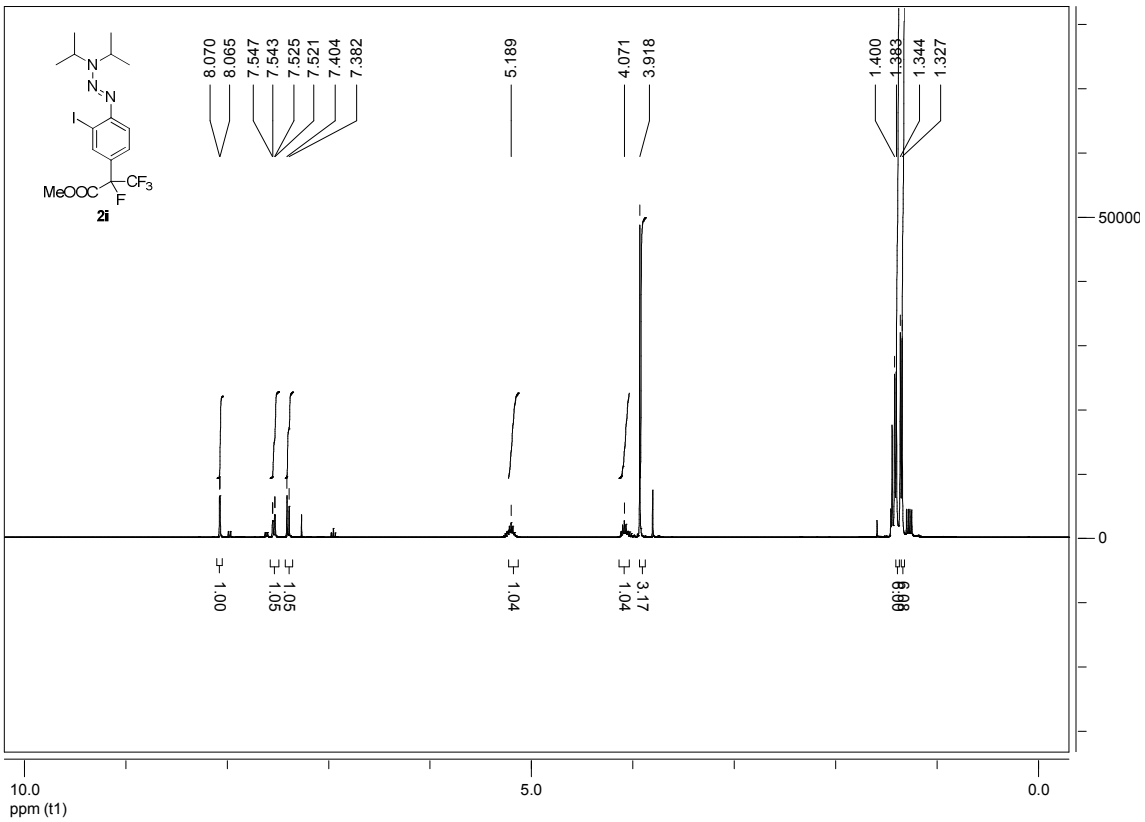
200
150
100
50
0
ppm (t1)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8.065
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7.543
7.525
7.521
7.404
7.382
5.189
4.071
3.918
1.400
1.383
1.344
1.327
MeOOC
CF3
F
2i
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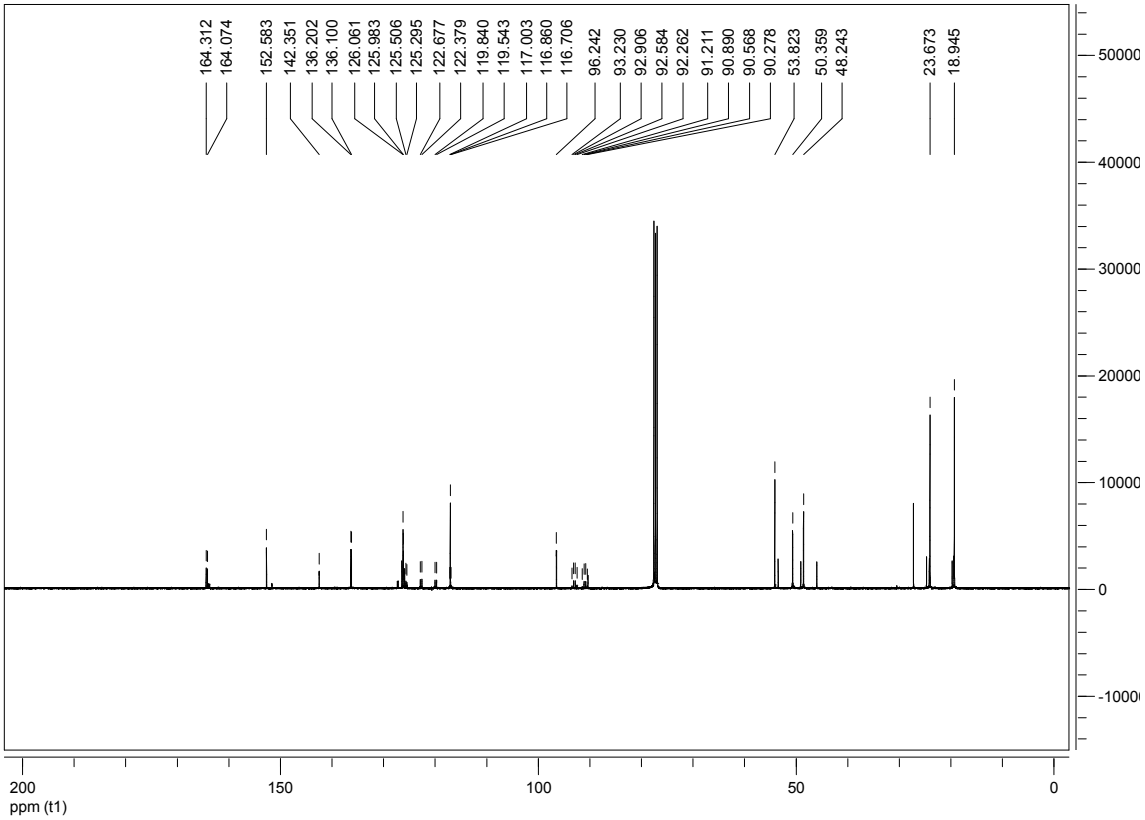
1.05
1.05
1.04
3.17
1.04
9.08
10.0
5.0
0.0
ppm (t1)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164.074
152.583
142.351
136.202
136.100
126.061
125.983
125.506
125.295
122.677
122.379
119.840
119.543
117.003
116.860
116.706
96.242
93.230
92.906
92.584
92.262
91.211
90.890
90.568
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53.823
50.359
48.243
23.673
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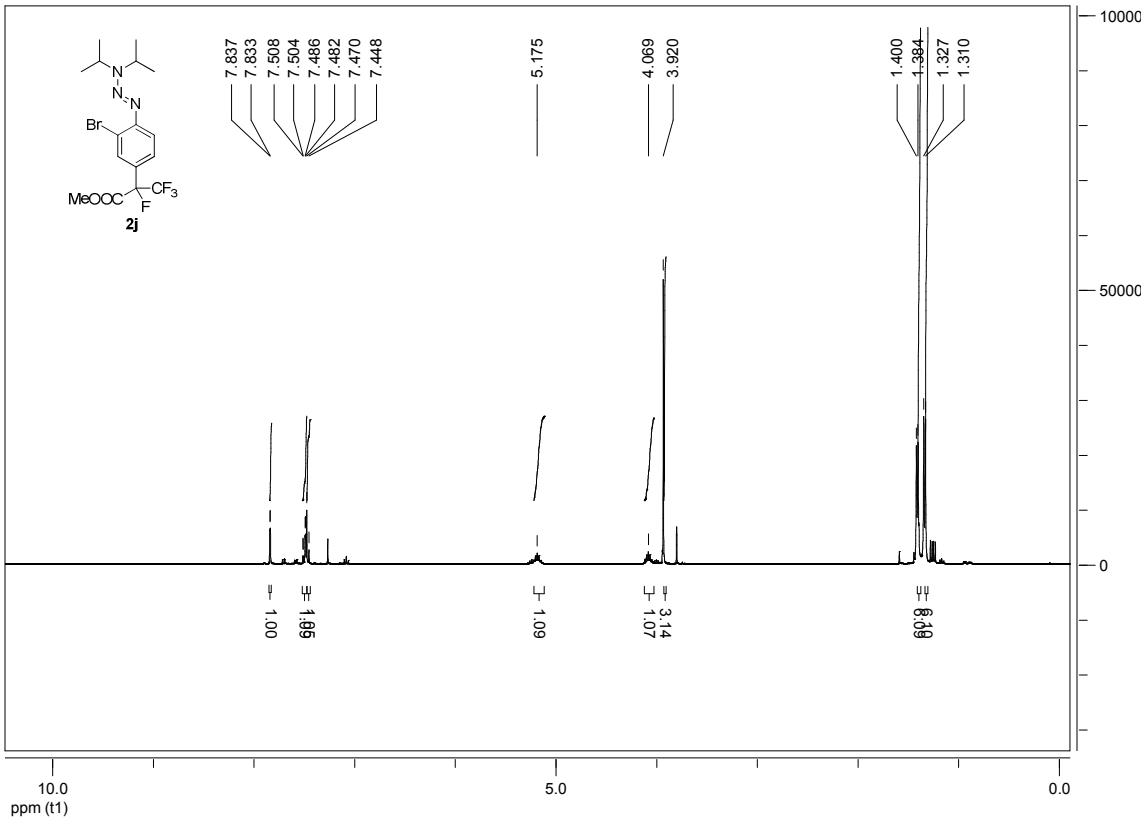
200
150
100
50
0
ppm (t1)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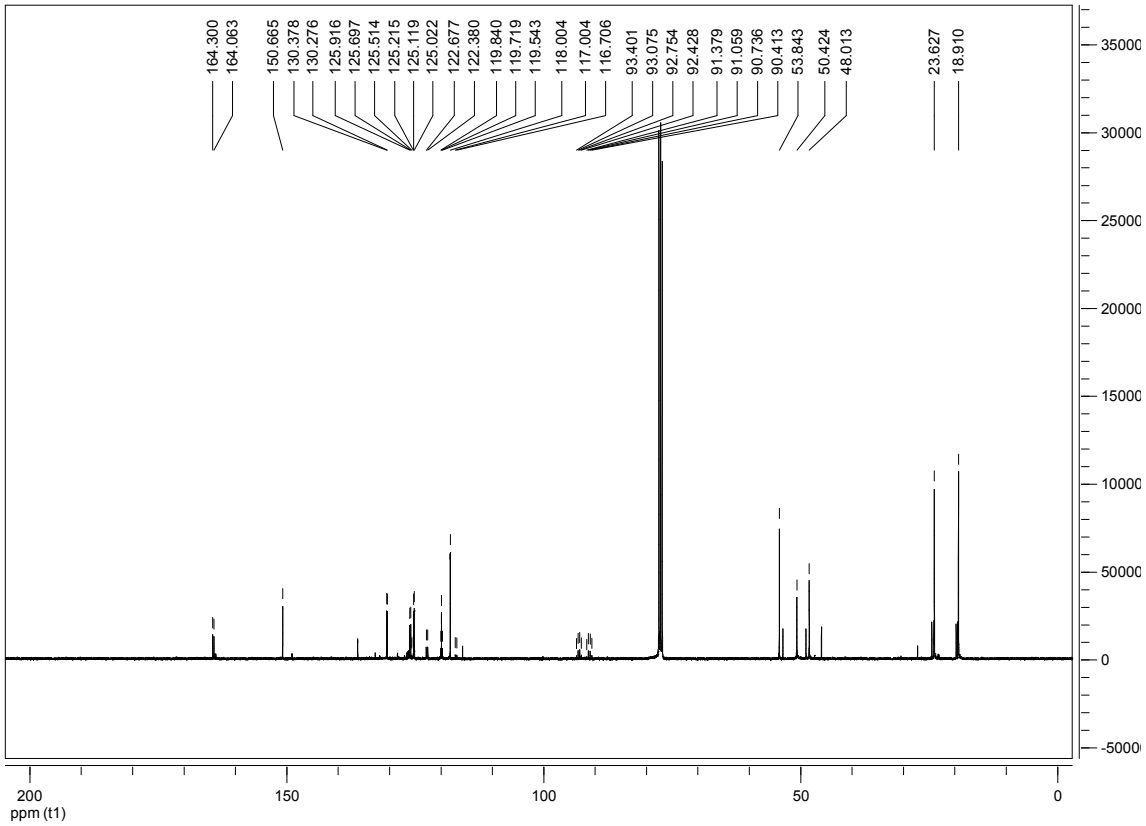
7.504
7.486
7.482
7.470
7.448
5.175
4.069
3.920
1.400
1.384
1.327
1.310
1.00
1.95
1.09
3.14
1.07
6.09
10.0
5.0
0.0
ppm (t1)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125.514
125.215
125.119
125.022
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122.380
119.840
119.719
119.543
118.004
117.004
116.706
93.401
93.075
92.754
92.428
91.379
91.059
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48.013
23.627
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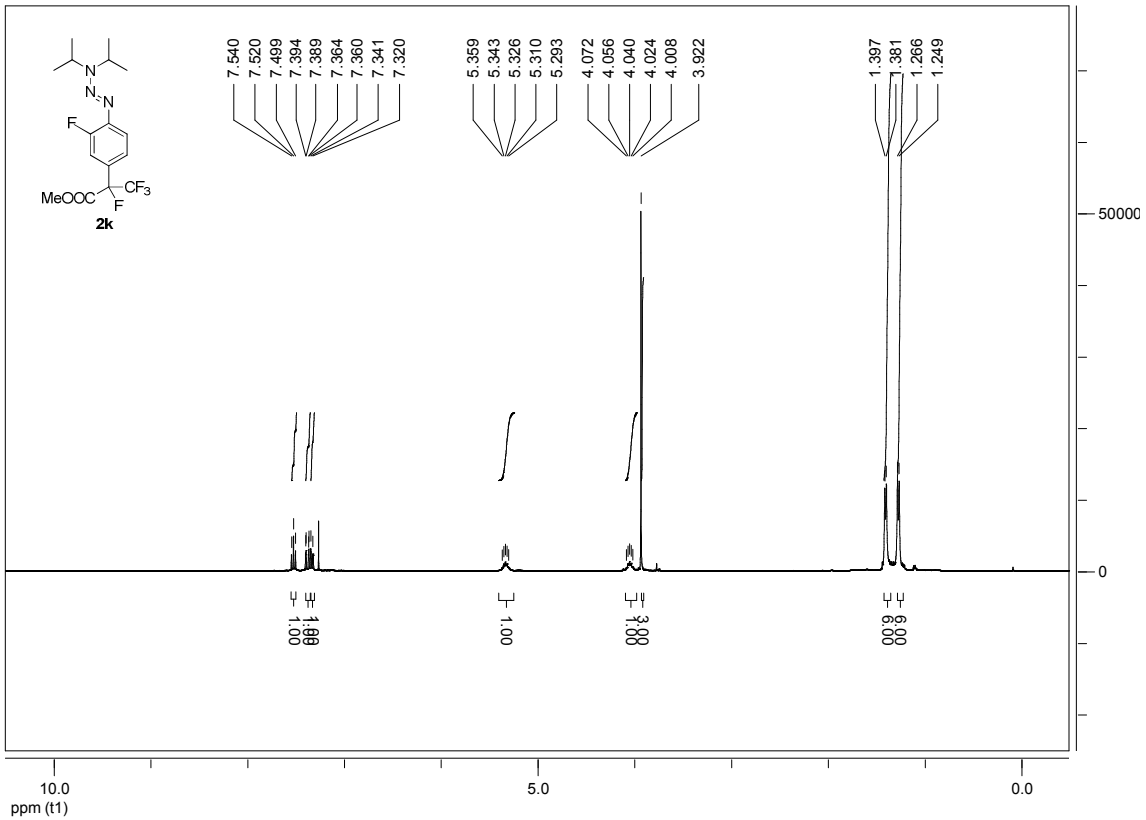
50
0
ppm (t1)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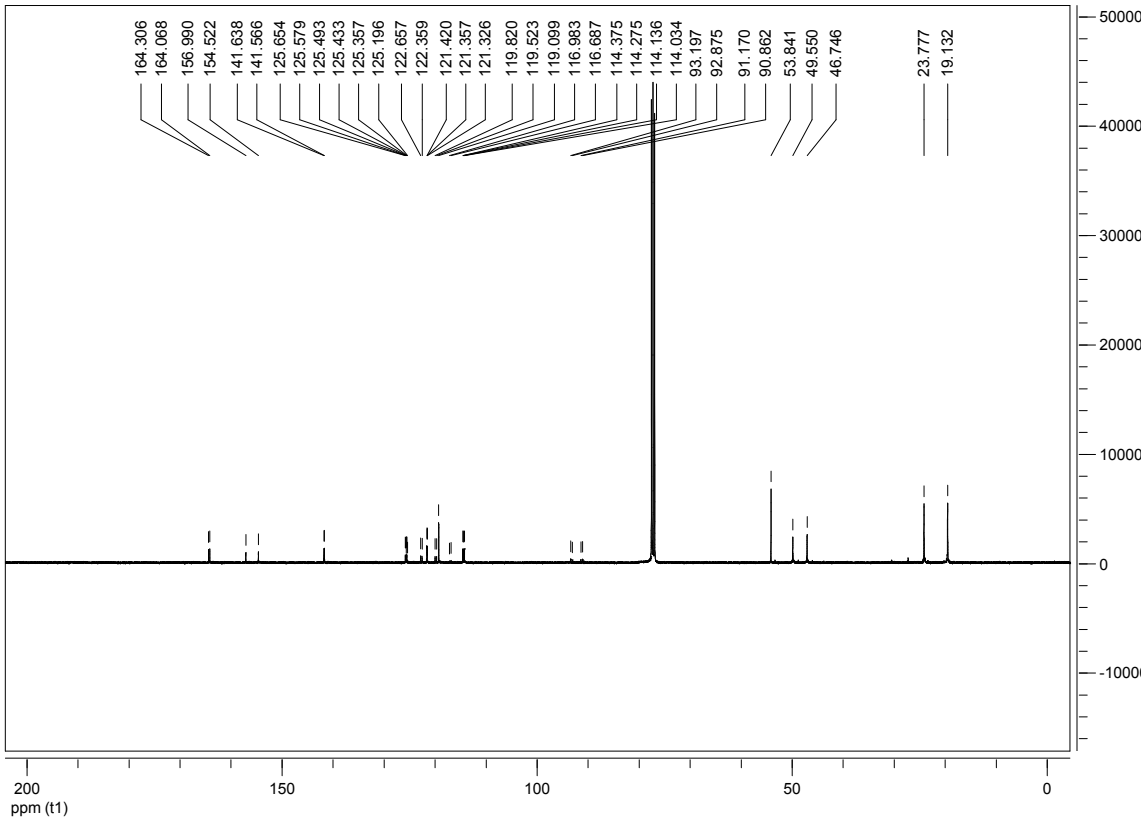
7.520
7.499
7.394
7.389
7.364
7.360
7.341
7.320
5.359
5.343
5.326
5.310
5.293
4.072
4.056
4.040
4.024
4.008
3.922
1.397
1.381
1.266
1.249
MeOOC
CF3
F
2k
50000
0
10.0
5.0
0.0
ppm (t1)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164.068
156.990
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125.579
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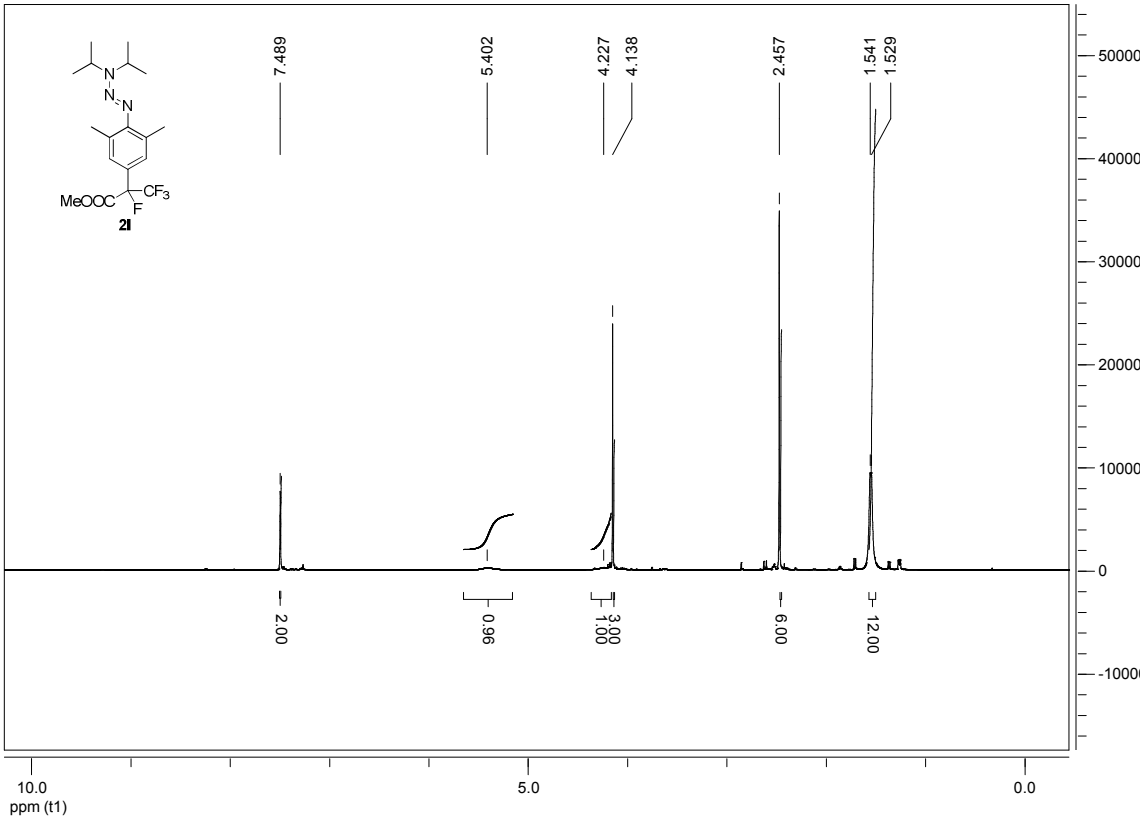
125.433
125.357
125.196
122.657
122.359
121.420
121.357
121.326
119.820
119.523
119.099
116.983
116.687
114.375
114.275
114.136
114.034
93.197
92.875
91.170
90.862
53.841
49.550
46.746
23.777
19.132
50000
40000
30000
20000
10000
0
-10000
200
150
100
50
0
ppm (t1)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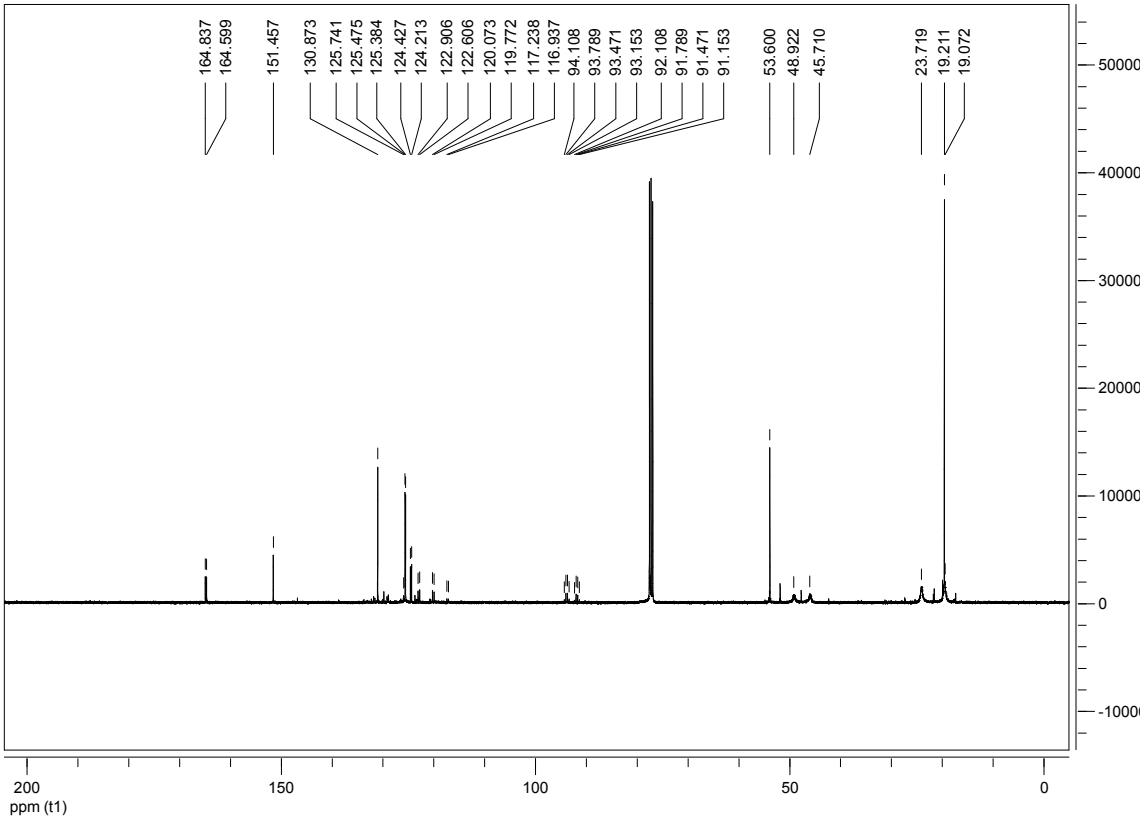
4.227
4.138
2.457
1.541
1.529
2.00
0.96
3.00
1.00
6.00
12.00
10.0
5.0
0.0
ppm (t1)
MeOOC
CF3
F
2l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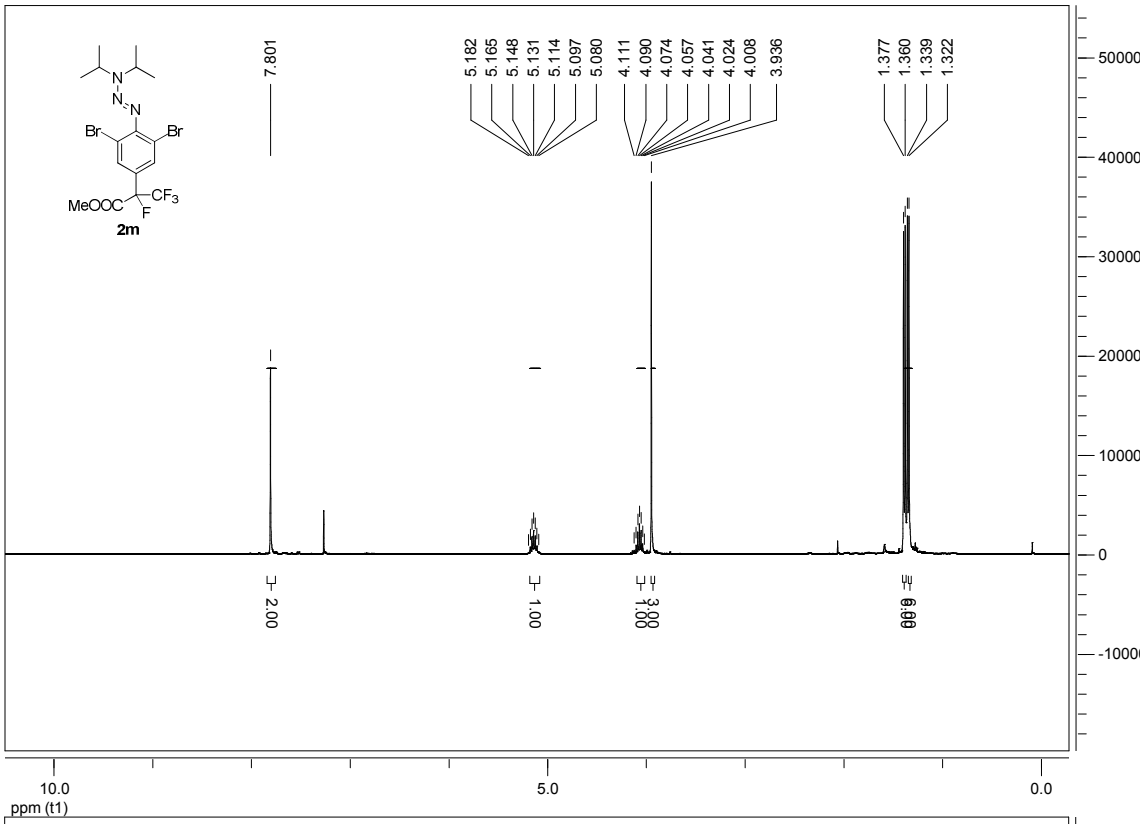
164.599
151.457
130.873
125.741
125.475
125.384
124.427
124.213
122.906
122.606
120.073
119.772
117.238
116.937
94.108
93.789
93.471
93.153
92.108
91.789
91.471
91.153
53.600
48.922
45.710
23.719
19.211
19.072
200
150
100
50
0
ppm (t1)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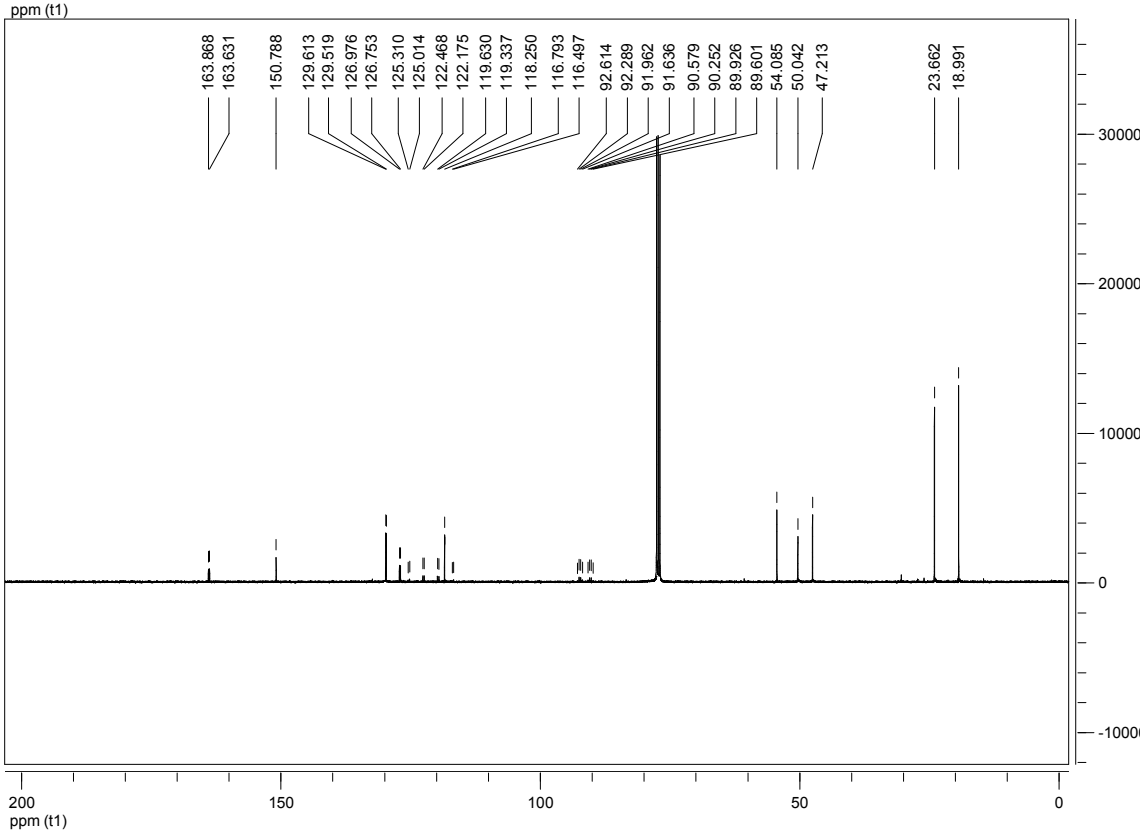
5.182
5.165
5.148
5.131
5.114
5.097
5.080
4.111
4.090
4.074
4.057
4.041
4.024
4.008
3.936
1.377
1.360
1.339
1.322
2.00
1.00
3.00
6.00
10.0
5.0
0.0
ppm (t1)
Br
Br
MeOOC
CF3
F
2m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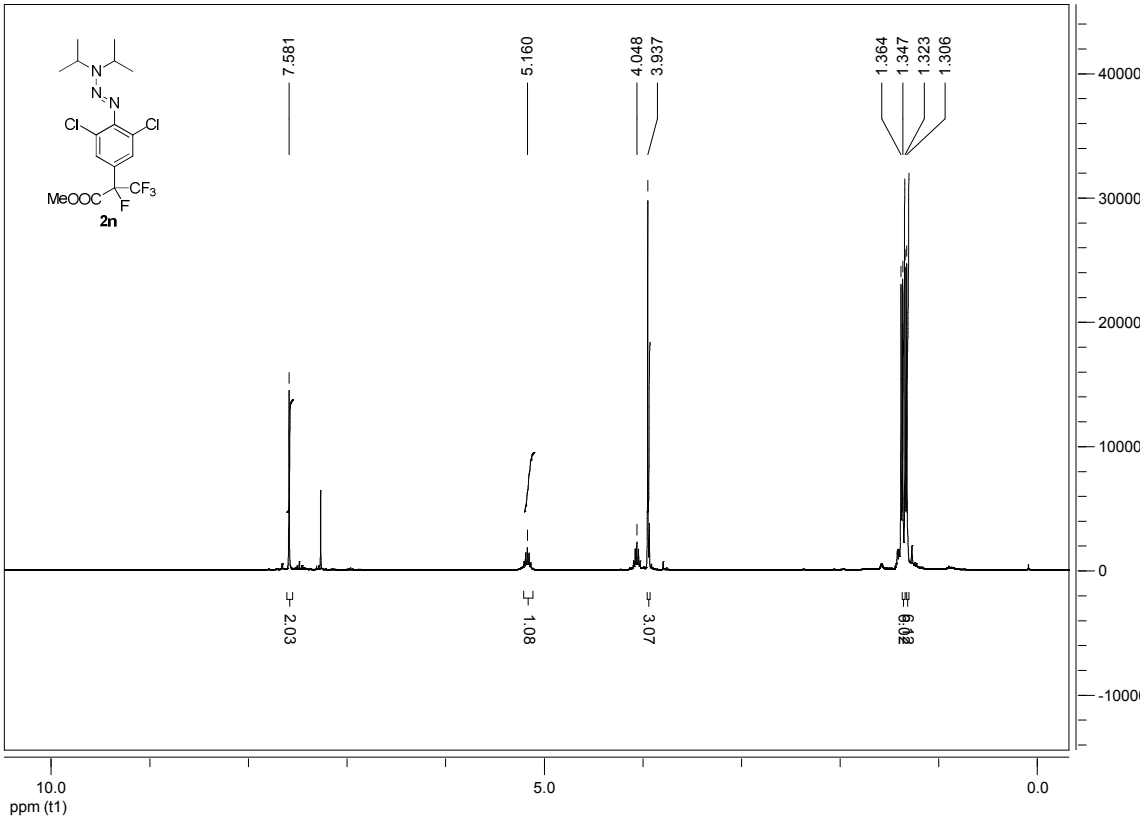
150.788
129.613
129.519
126.976
126.753
125.310
125.014
122.468
122.175
119.630
119.337
118.250
116.793
116.497
92.614
92.289
91.962
91.636
90.579
90.252
89.926
89.601
54.085
50.042
47.213
23.662
18.991
200
150
100
50
0
ppm (t1)


7.581
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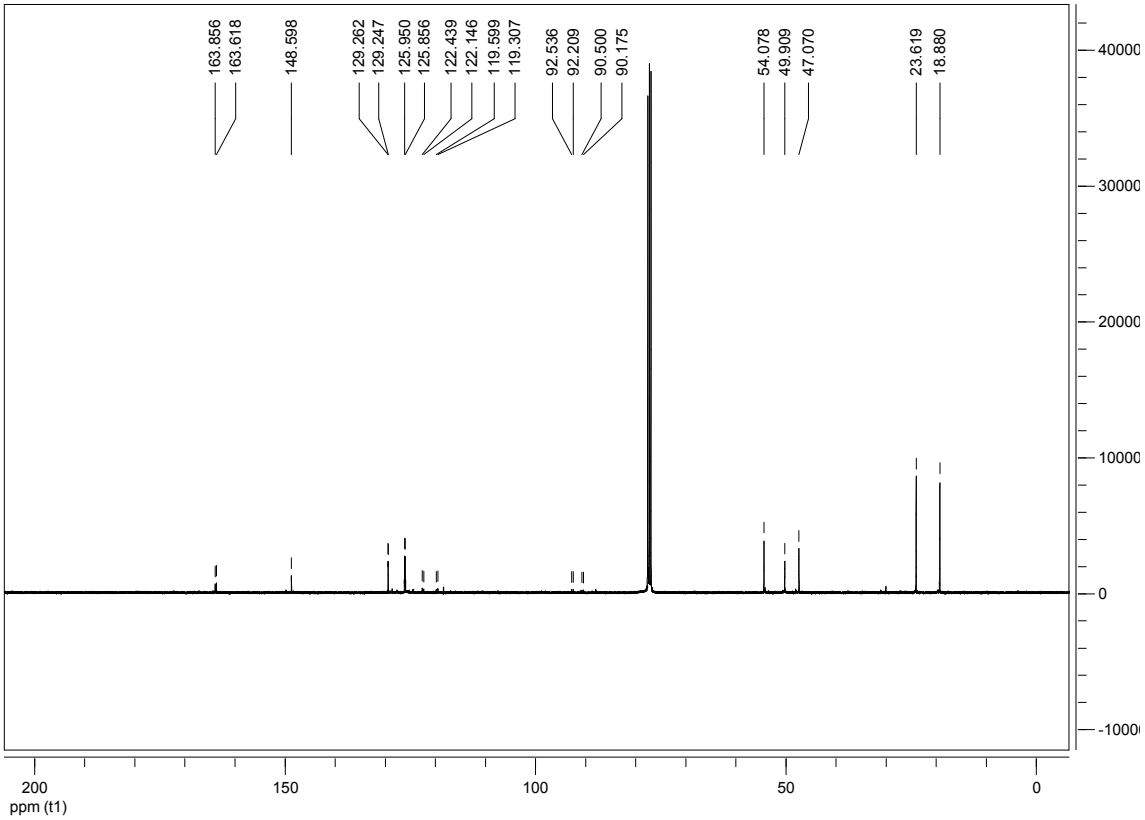
4.048
3.937
1.364
1.347
1.323
1.306
2.03
1.08
3.07
6.02
MeOOC
CF3
F
Cl
Cl
2n
10.0
5.0
0.0
ppm (t1)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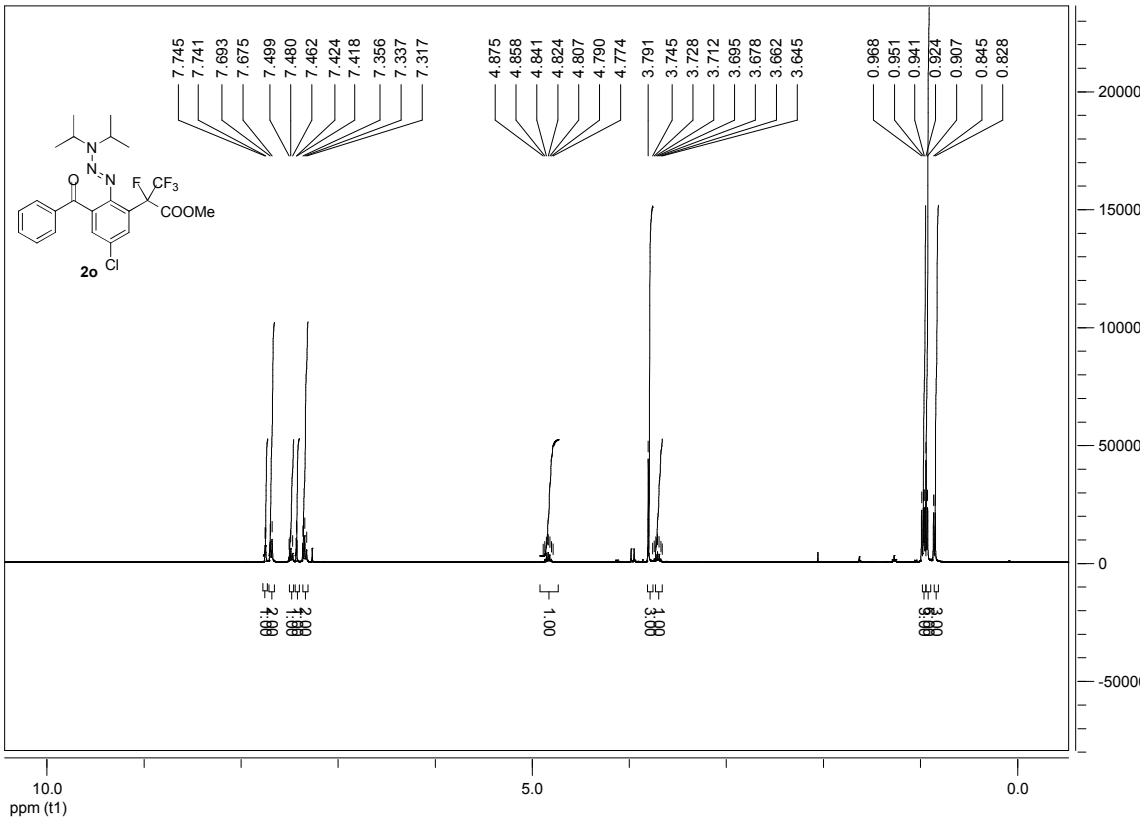
163.618
148.598
129.262
129.247
125.950
125.856
122.439
122.146
119.599
119.307
92.536
92.209
90.500
90.175
54.078
49.909
47.070
23.619
18.880
200
150
100
50
0
ppm (t1)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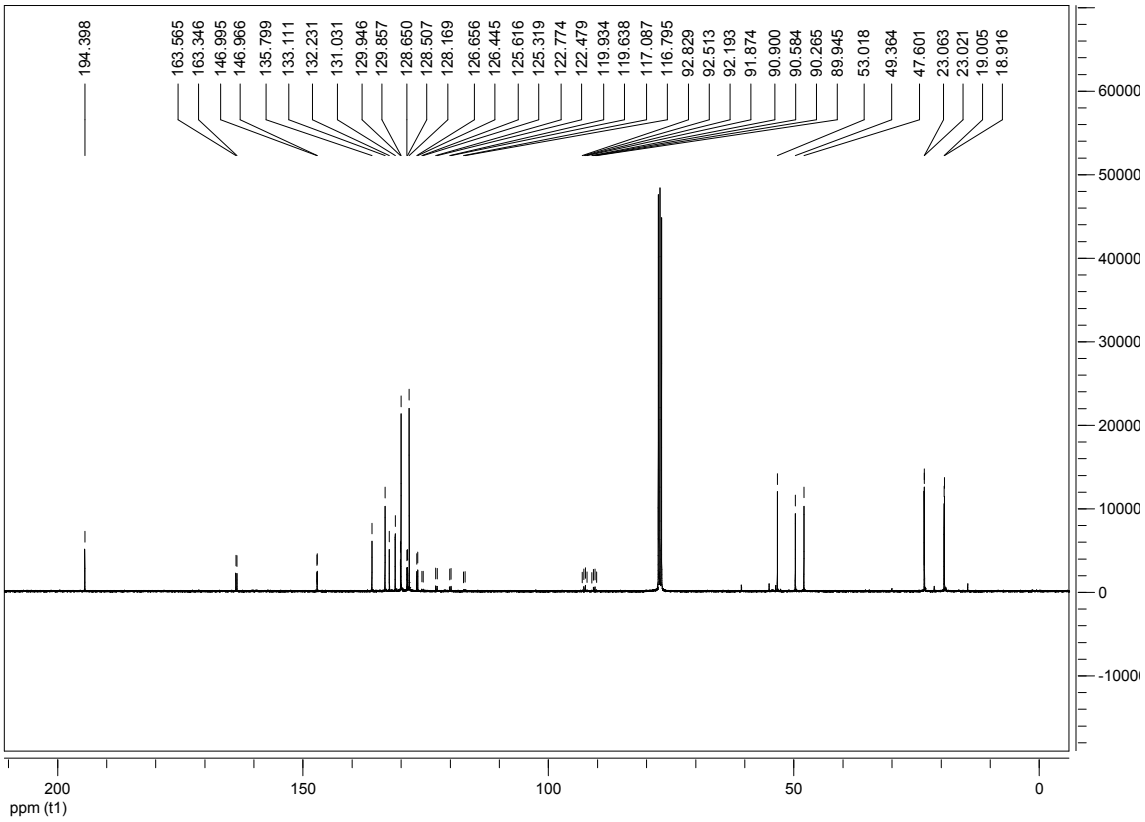
7.741
7.693
7.675
7.499
7.480
7.462
7.424
7.418
7.356
7.337
7.317
4.875
4.858
4.841
4.824
4.807
4.790
4.774
3.791
3.745
3.728
3.712
3.695
3.678
3.662
3.645
0.968
0.951
0.941
0.924
0.907
0.845
0.828
2o
ppm (t1)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163.346
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146.966
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132.231
131.031
129.946
129.857
128.650
128.507
128.169
126.656
126.445
125.616
125.319
122.774
122.479
119.934
119.638
117.087
116.795
92.829
92.513
92.193
91.874
90.900
90.584
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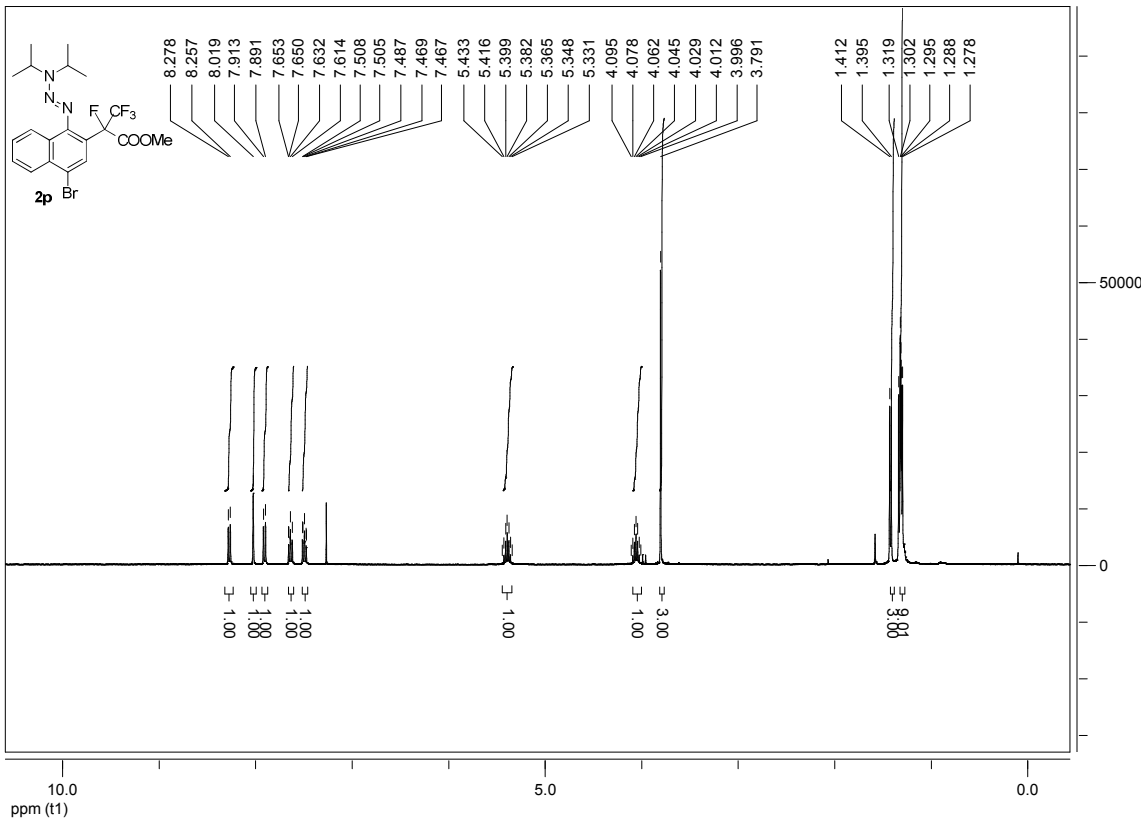
89.945
53.018
49.364
47.601
23.063
23.021
19.005
18.916
ppm (t1)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8.019
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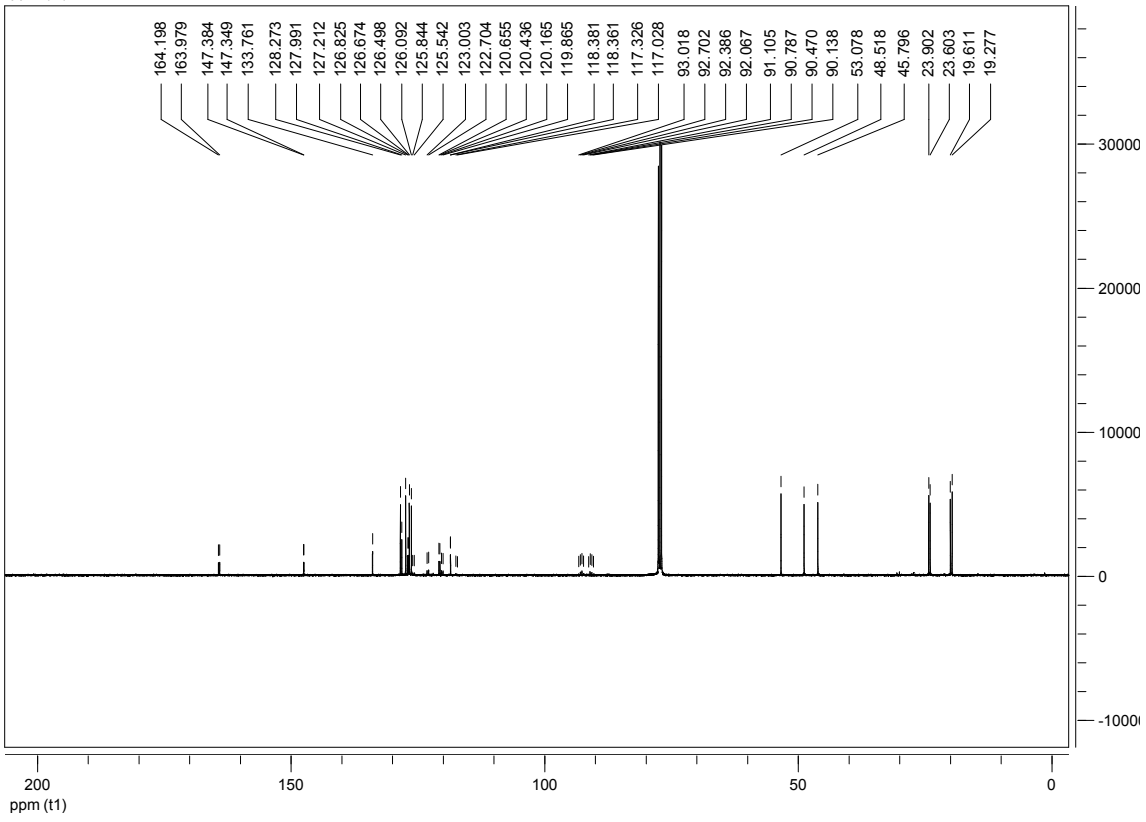
7.891
7.653
7.650
7.632
7.614
7.508
7.505
7.487
7.469
7.467
5.433
5.416
5.399
5.382
5.365
5.348
5.331
4.095
4.078
4.062
4.045
4.029
4.012
3.996
3.791
1.412
1.395
1.319
1.302
1.295
1.288
1.278
F
CF3
COOMe
2p
Br
1.00
1.00
1.00
1.00
1.00
3.00
9.00
9.01
50000
0
10.0
5.0
0.0
ppm (t1)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126.092
125.844
125.542
123.003
122.704
120.655
120.436
120.165
119.865
118.381
118.361
117.326
117.028
93.018
92.702
92.386
92.067
91.105
90.787
90.470
90.138
53.078
48.518
45.796
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19.277
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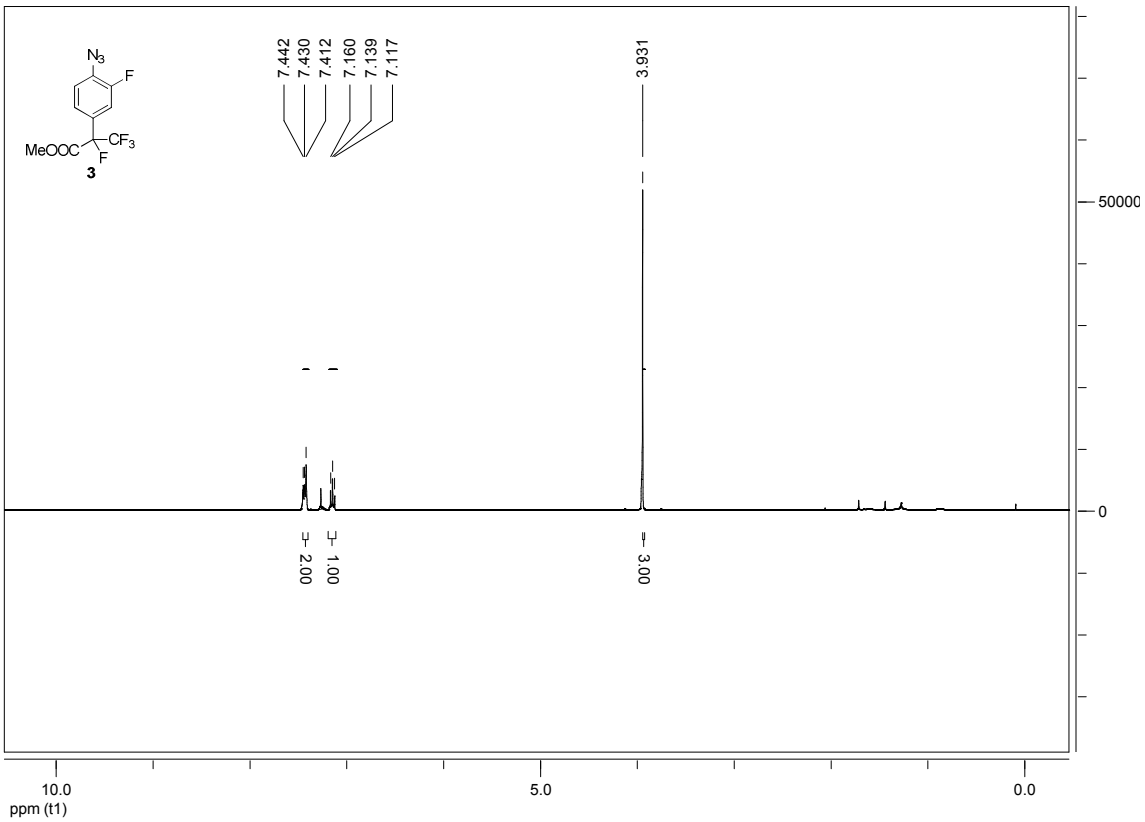
20000
10000
0
-10000
200
150
100
50
0
ppm (t1)


N3
F
MeOOC
CF3
F
3
7.442
7.430
7.412
7.160
7.139
7.117
3.931
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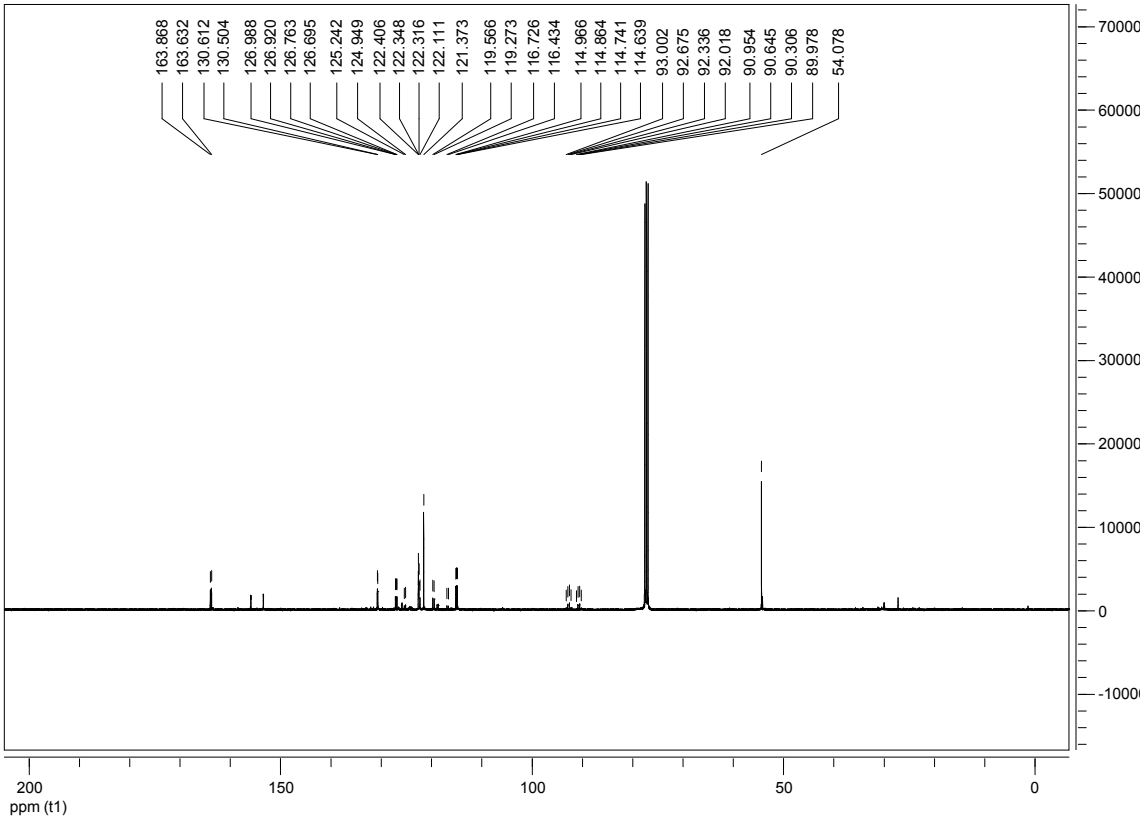
1.00
3.00
50000
0
10.0
5.0
0.0
ppm (t1)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126.988
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126.695
125.242
124.949
122.406
122.348
122.316
122.111
121.373
119.566
119.273
116.726
116.434
114.966
114.864
114.741
114.639
93.002
92.675
92.336
92.018
90.954
90.645
90.306
89.978
54.078
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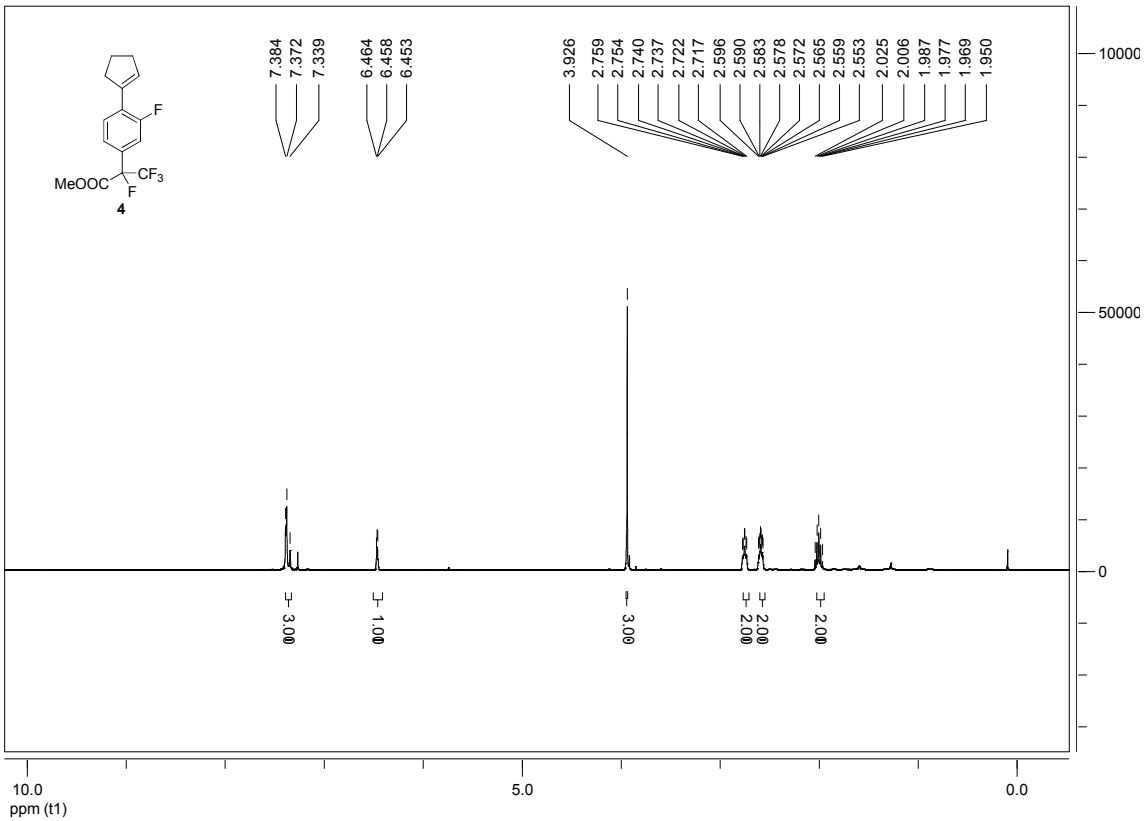
60000
50000
40000
30000
20000
10000
0
-10000
200
150
100
50
0
ppm (t1)


7.384
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7.339
6.464
6.458
6.453
3.926
2.759
2.754
2.740
2.737
2.722
2.717
2.596
2.590
2.583
2.578
2.572
2.565
2.559
2.553
2.025
2.006
1.987
1.977
1.969
1.950
F
MeOOC
CF3
F
4
3.00
1.00
3.00
2.00
2.00
2.00
10000
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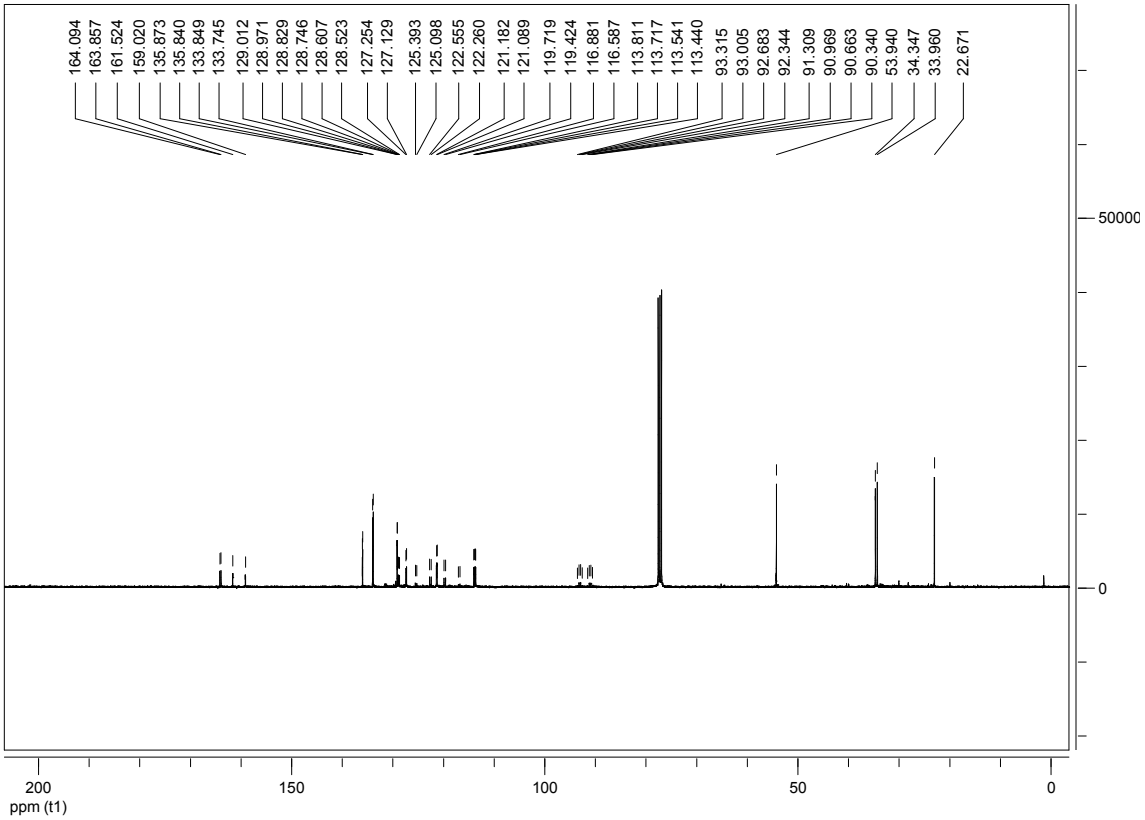
10.0
5.0
0.0
ppm (t1)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133.745
129.012
128.971
128.829
128.746
128.607
128.523
127.254
127.129
125.393
125.098
122.555
122.260
121.182
121.089
119.719
119.424
116.881
116.587
113.811
113.717
113.541
113.440
93.315
93.005
92.683
92.344
91.309
90.969
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34.347
33.960
22.671
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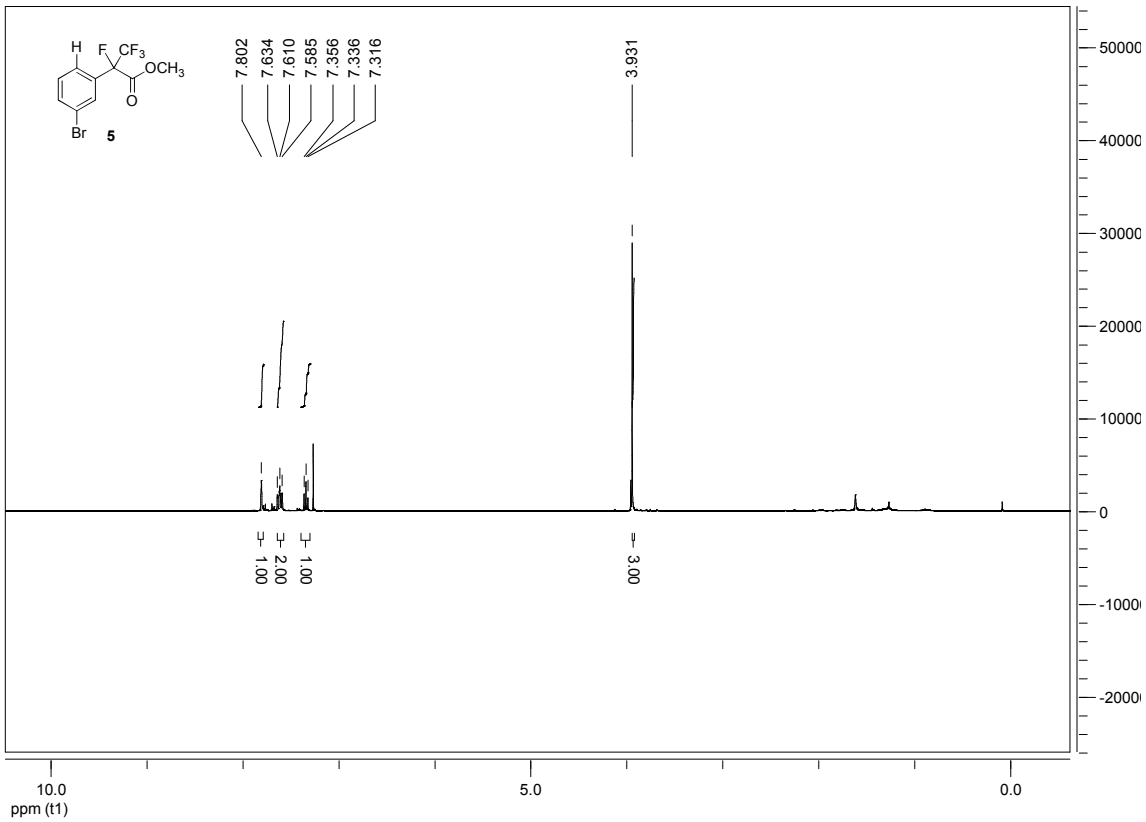
200
150
100
50
0
ppm (t1)


H
F
CF3
OCH3
O
Br
5
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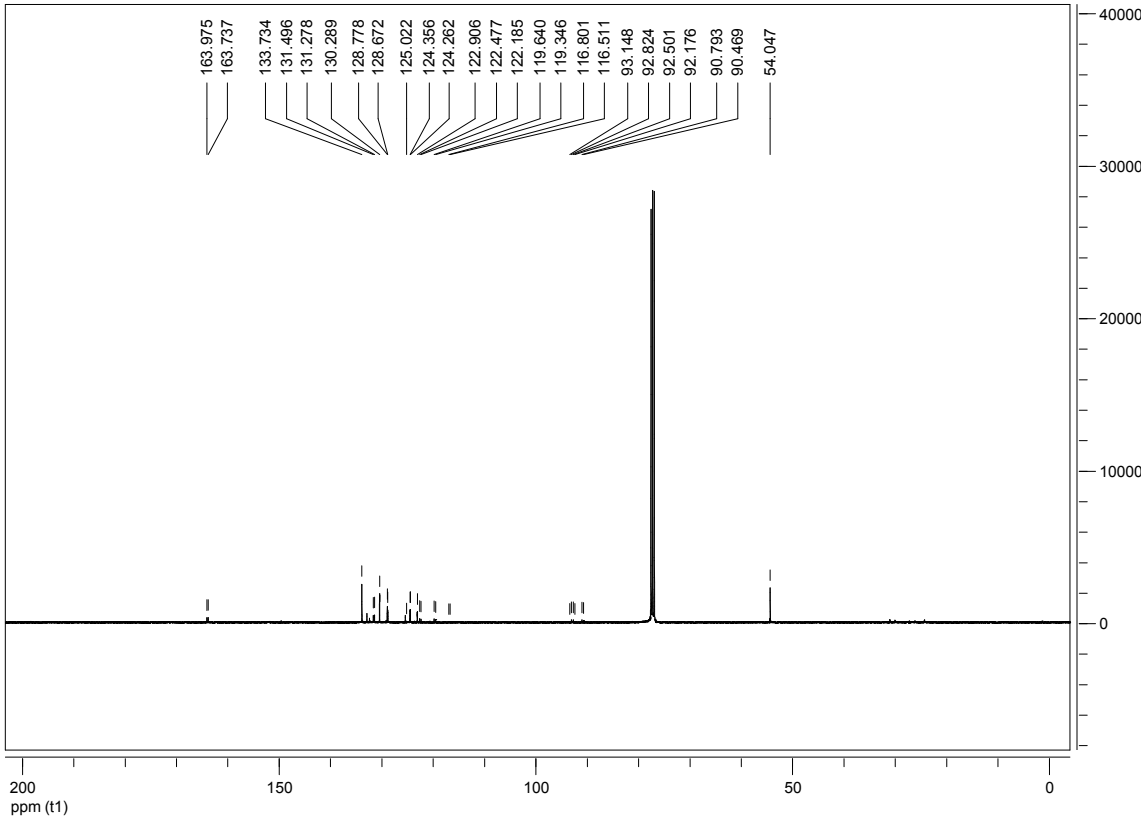
7.634
7.610
7.585
7.356
7.336
7.316
3.931
1.00
2.00
1.00
3.00
50000
40000
30000
20000
10000
0
-10000
-20000
10.0
5.0
0.0
ppm (t1)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131.496
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128.672
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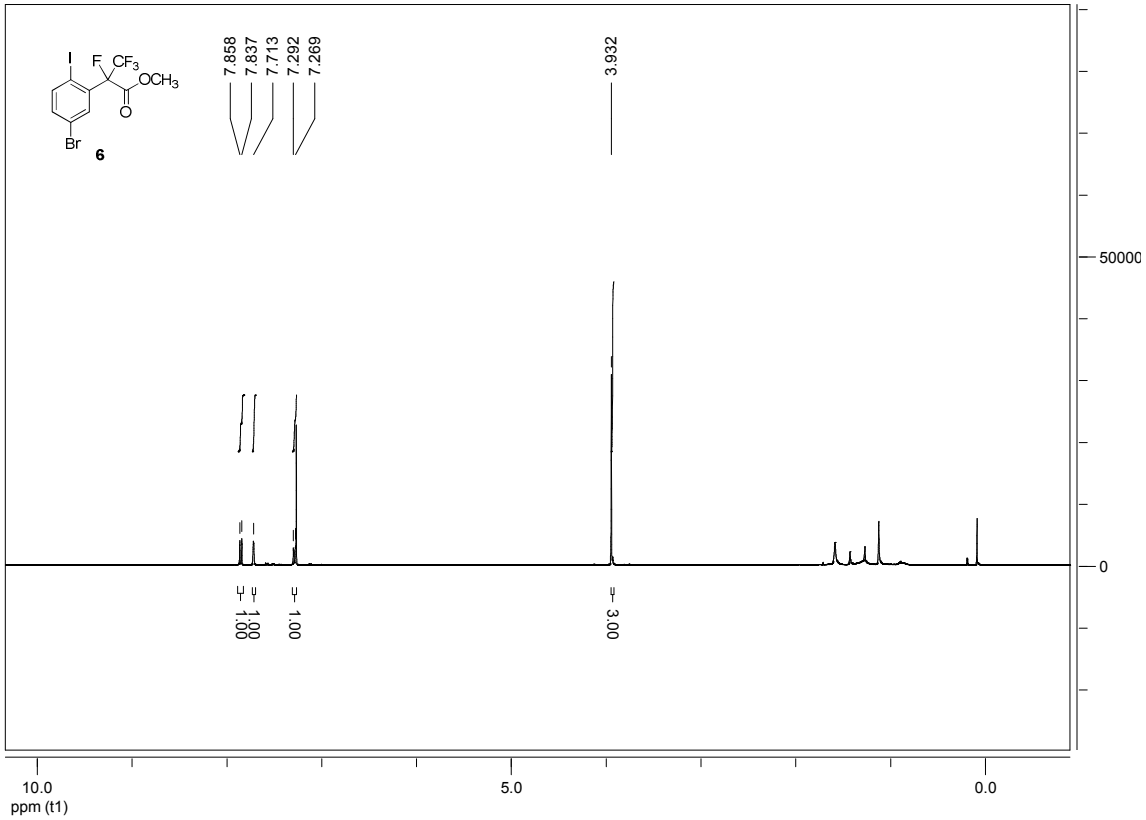
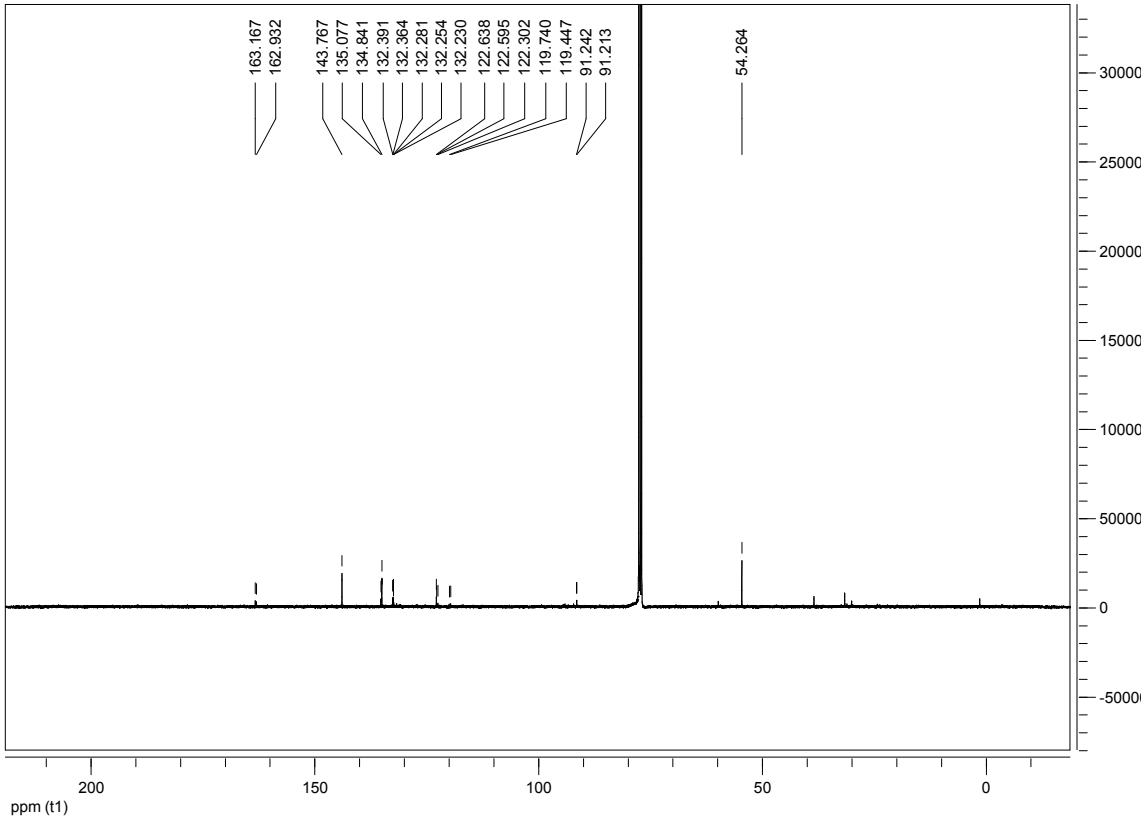
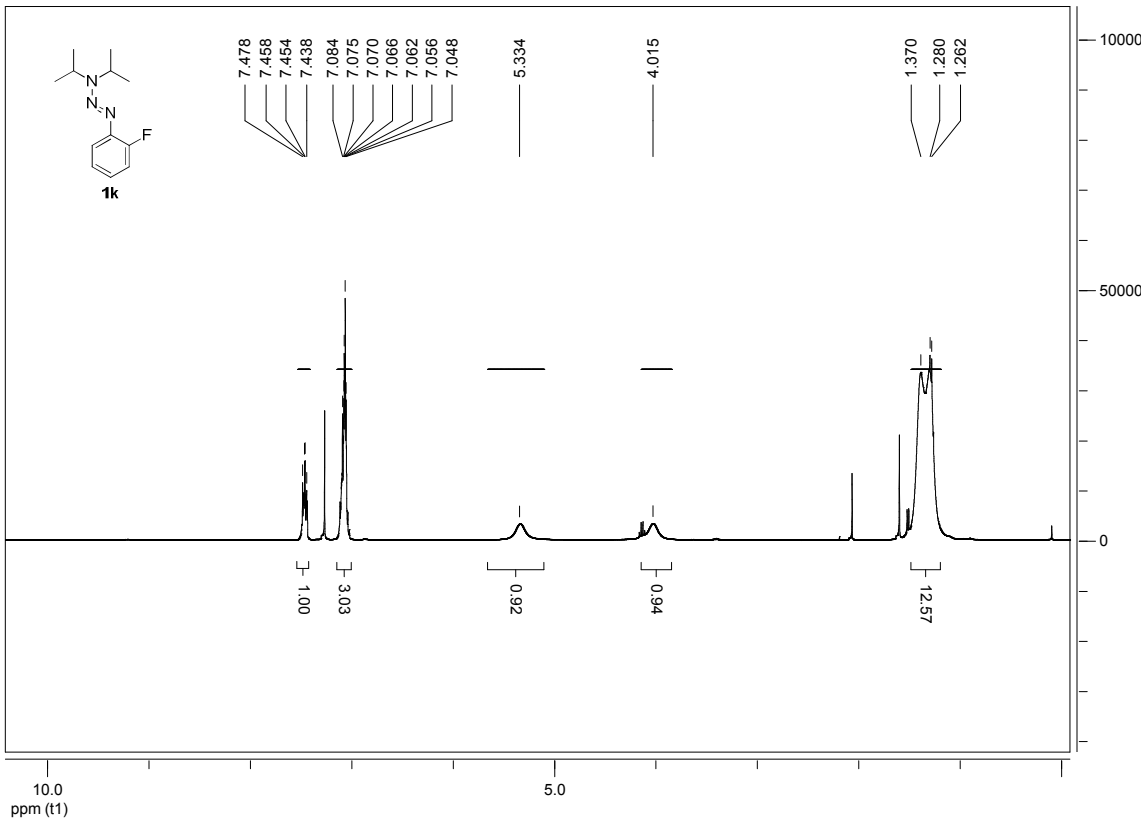
124.356
124.262
122.906
122.477
122.185
119.640
119.346
116.801
116.511
93.148
92.824
92.501
92.176
90.793
90.469
54.047
40000
30000
20000
10000
0
200
150
100
50
0
ppm (t1)


I
F
CF3
OCH3
O
Br
6
7.858
7.837
7.713
7.292
7.269
3.932
1.00
1.00
1.00
3.00
50000
0
10.0
5.0
0.0
ppm (t1)


163.167
162.932
143.767
135.077
134.841
132.391
132.364
132.281
132.254
132.230
122.638
122.595
122.302
119.740
119.447
91.242
91.213
54.264
30000
25000
20000
15000
10000
50000
0
-5000
200
150
100
50
0
ppm (t1)


1k
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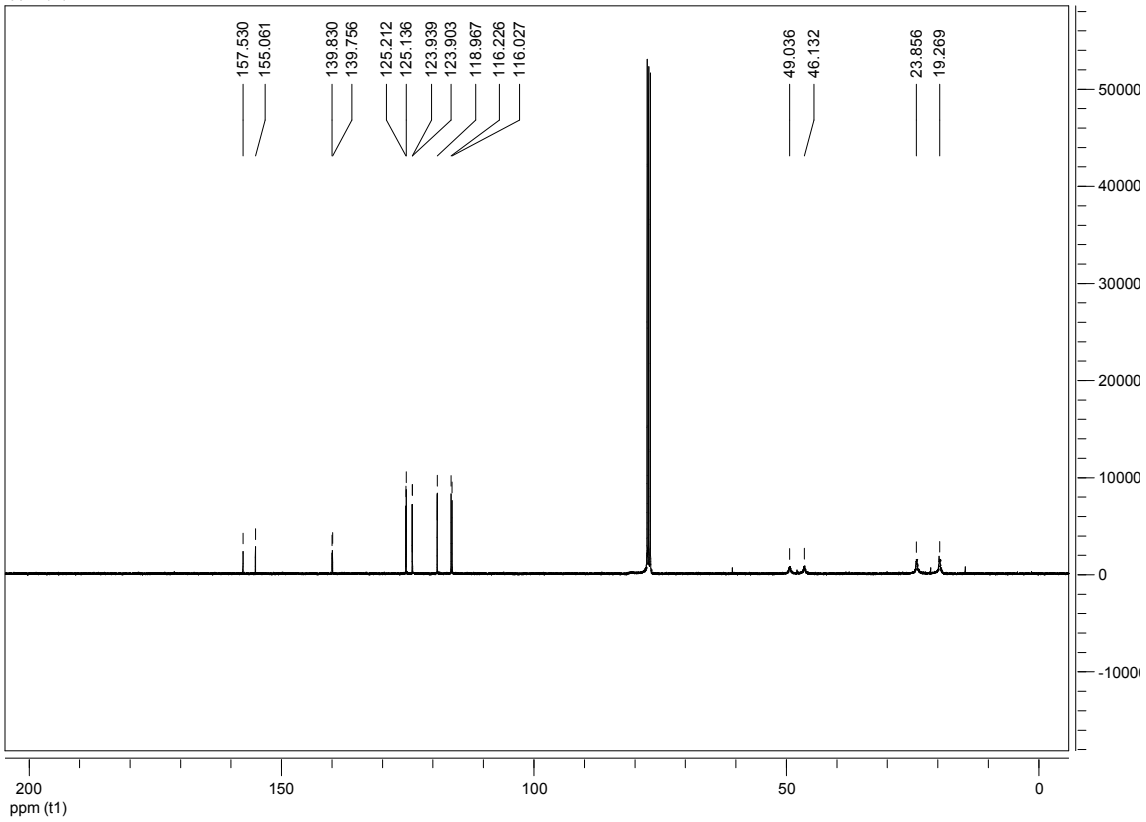
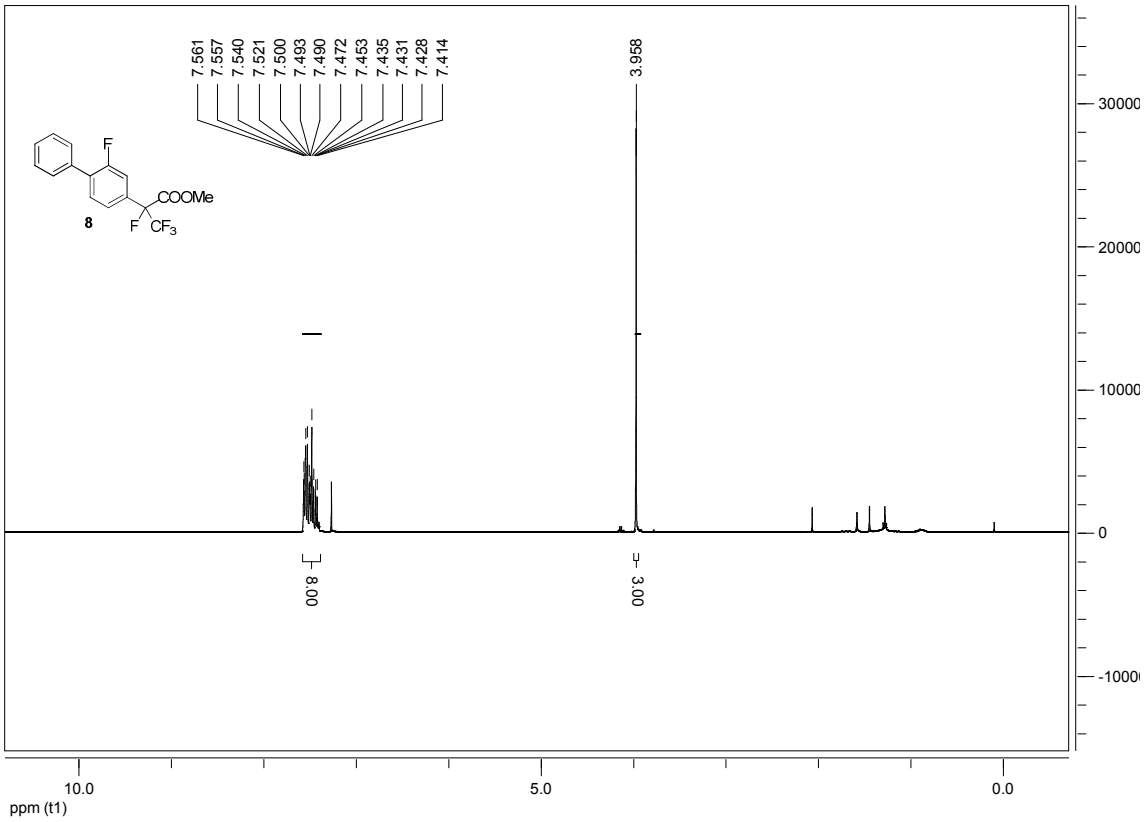
7.458
7.454
7.438
7.084
7.075
7.070
7.066
7.062
7.056
7.048
5.334
4.015
1.370
1.280
1.262
1.00
3.03
0.92
0.94
12.57
10.0
5.0
ppm (t1)


157.530
155.061
139.830
139.756
125.212
125.136
123.939
123.903
118.967
116.226
116.027
49.036
46.132
23.856
19.269
200
150
100
50
0
ppm (t1)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7.557
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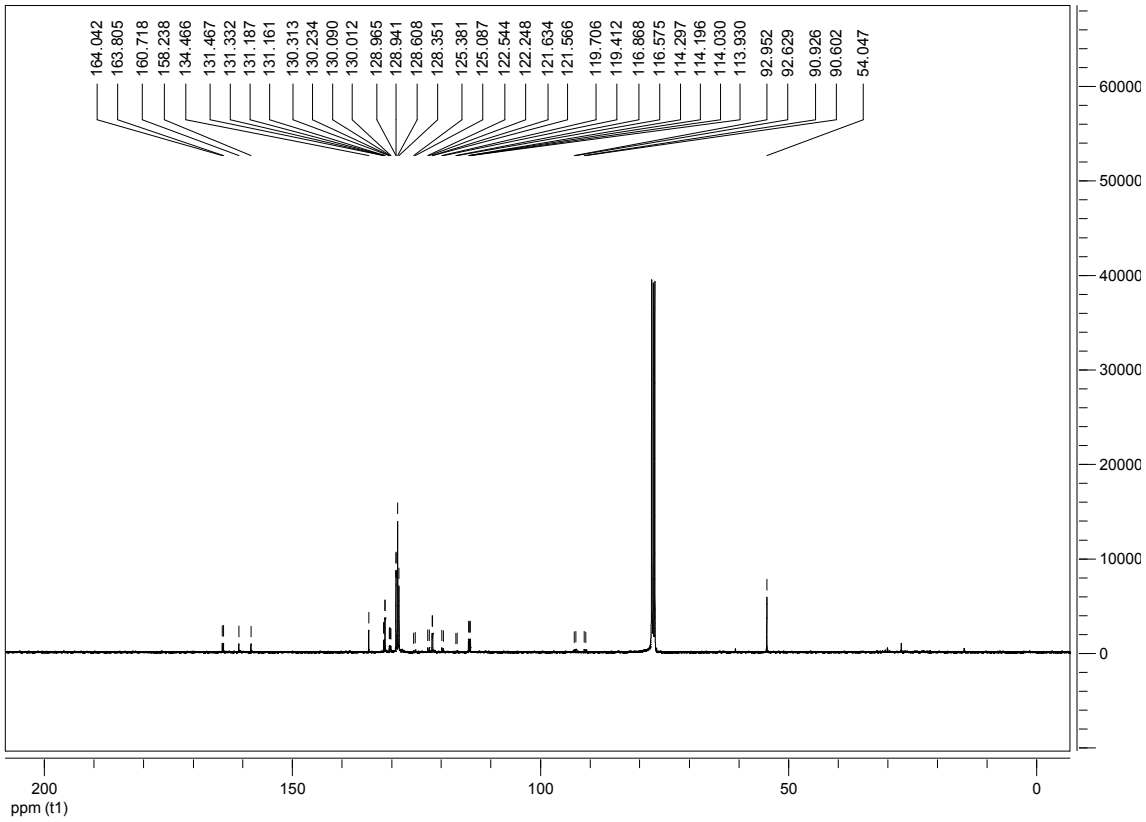
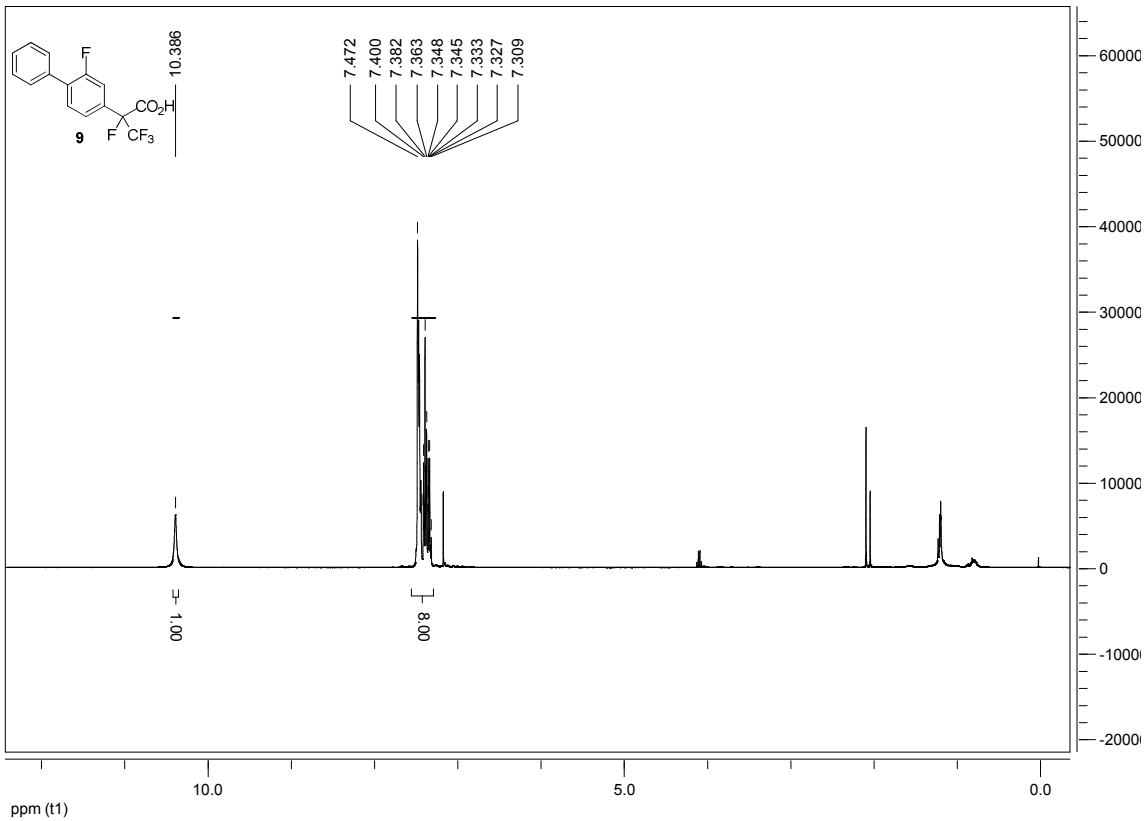
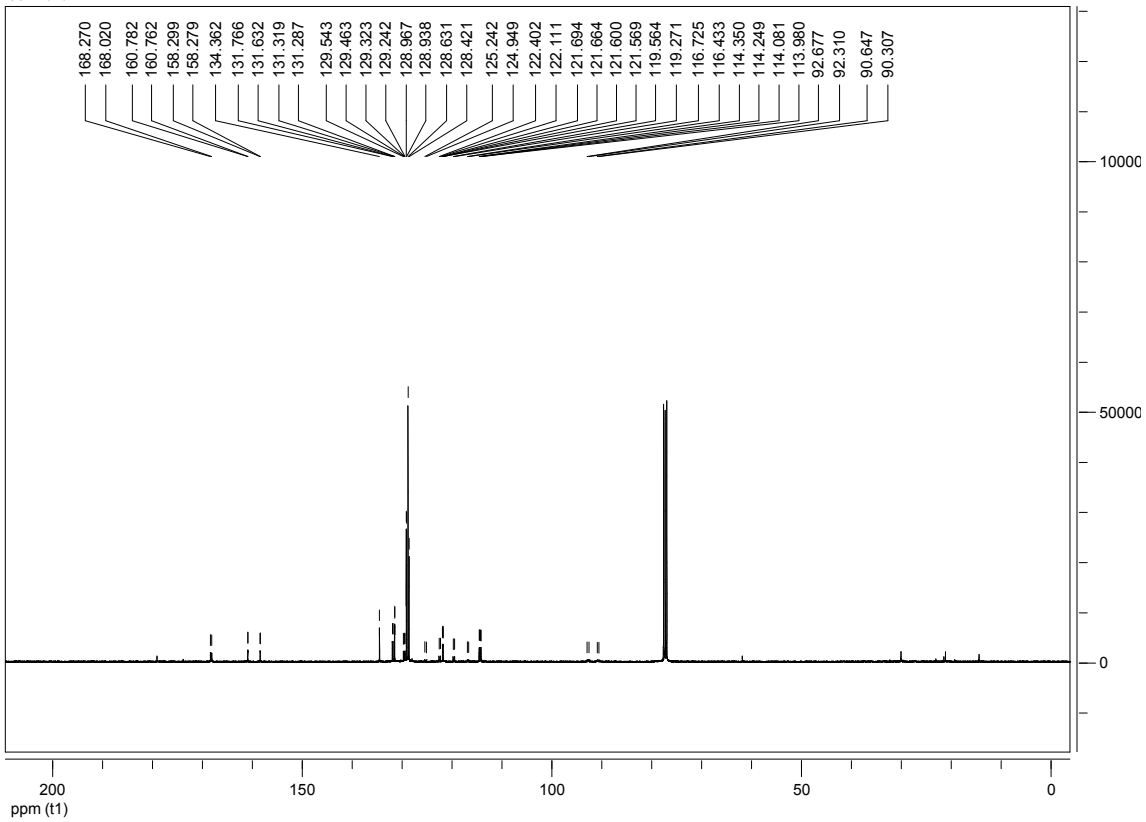
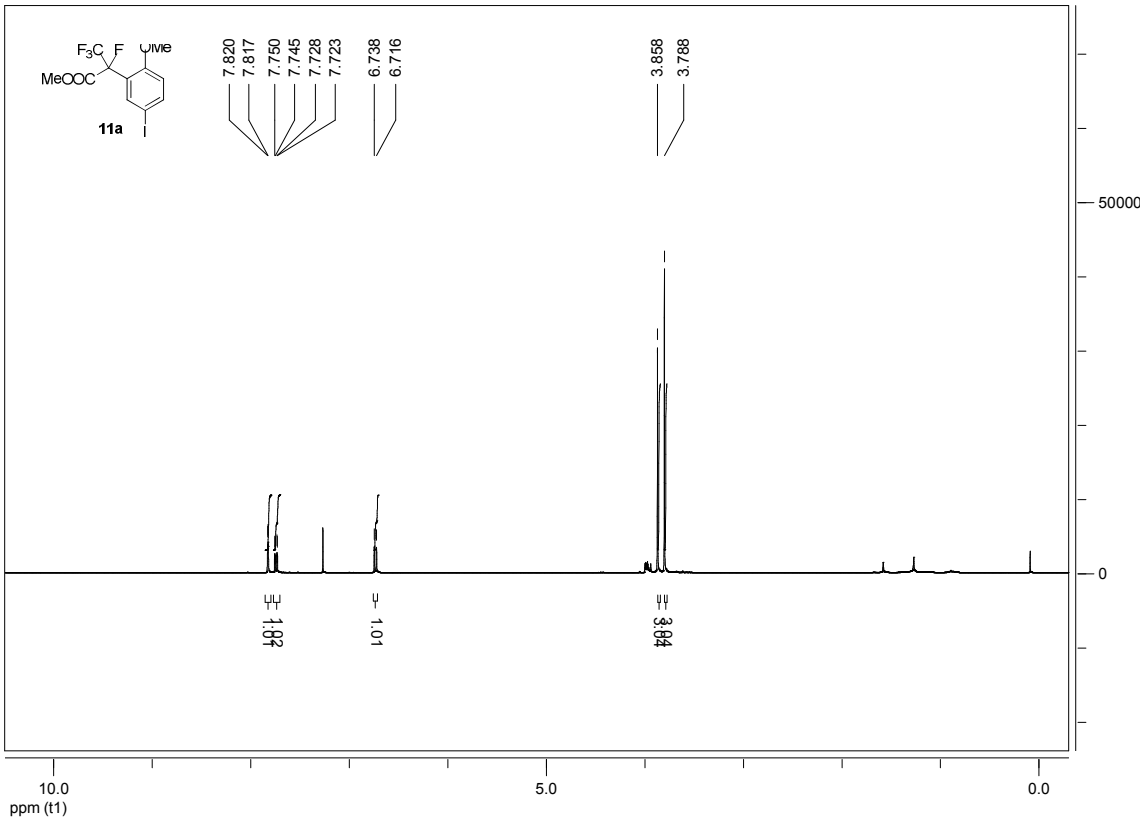
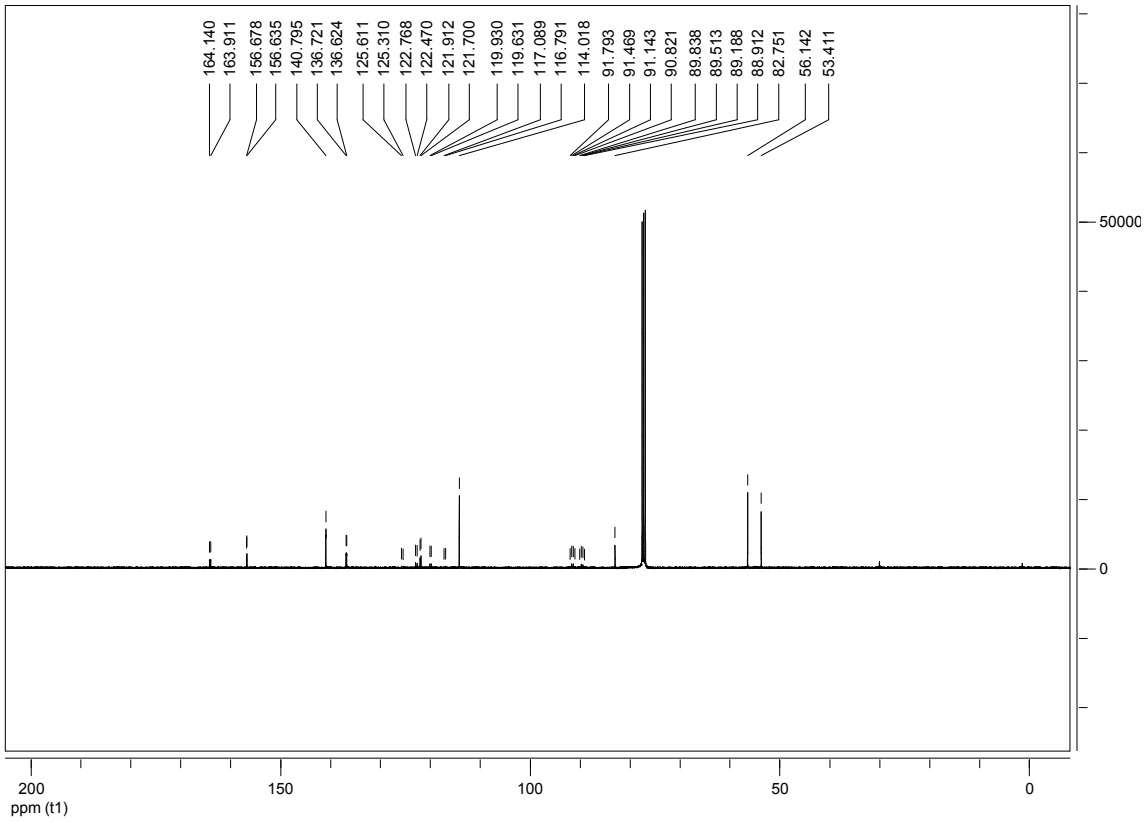
7.521
7.500
7.493
7.490
7.472
7.453
7.435
7.431
7.428
7.414
3.958
F
COOMe
F CF3
8
8.00
3.00
30000
20000
10000
0
-10000
10.0
5.0
0.0
ppm (t1)

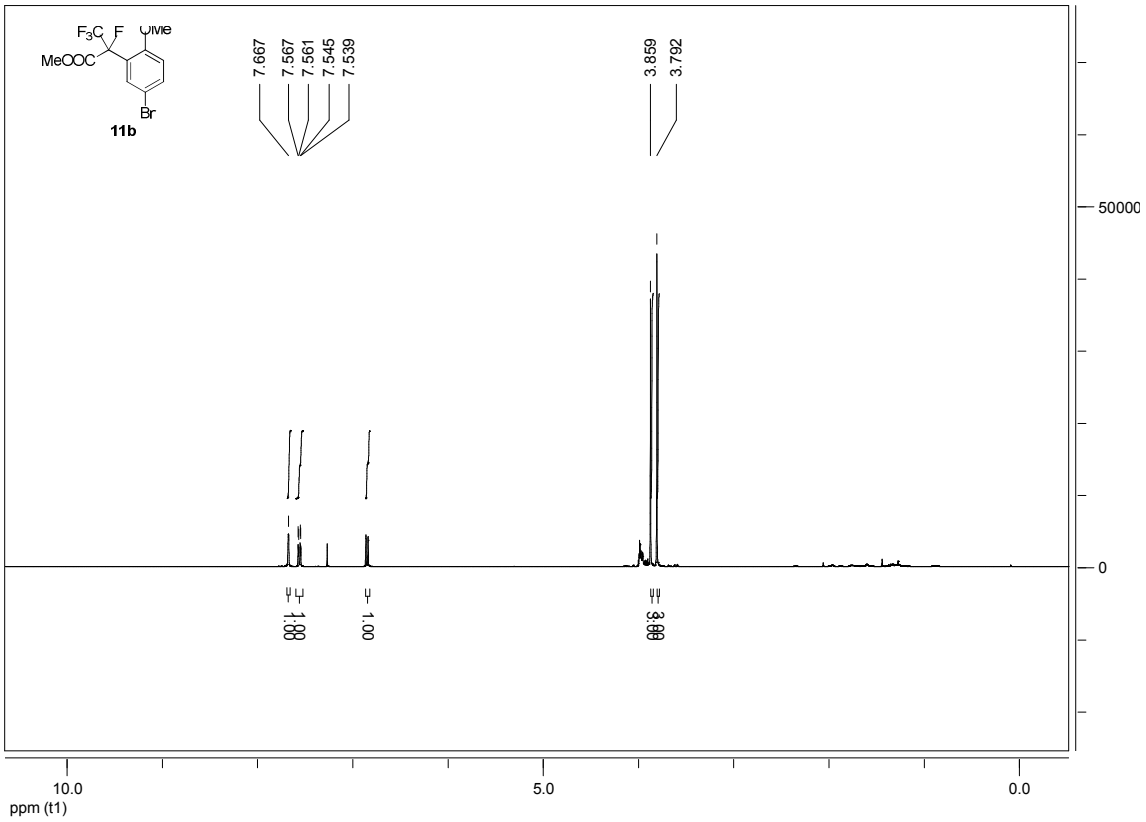

164.042
163.805
160.718
158.238
134.466
131.467
131.332
131.187
131.161
130.313
130.234
130.090
130.012
128.965
128.941
128.608
128.351
125.381
125.087
122.544
122.248
121.634
121.566
119.706
119.412
116.868
116.575
114.297
114.196
114.030
113.930
92.952
92.629
90.926
90.602
54.047
60000
50000
40000
30000
20000
10000
0
200
150
100
50
0
ppm (t1)

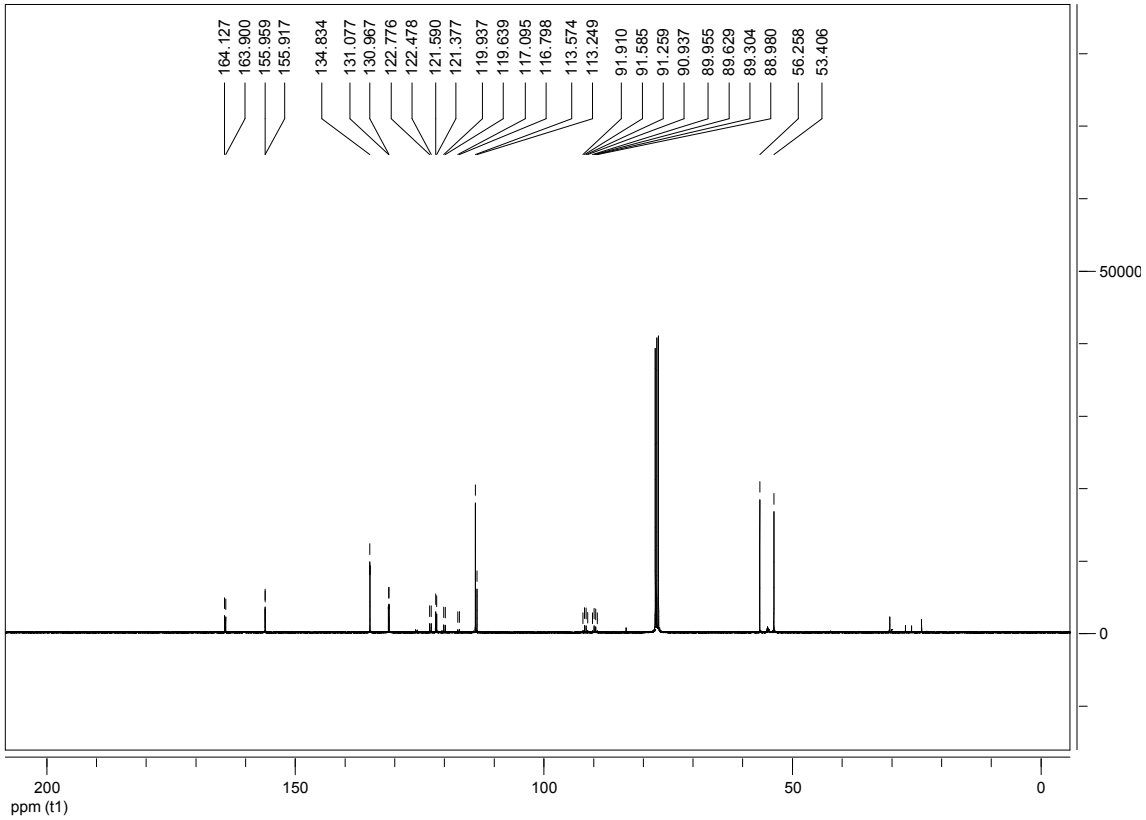

F
CO2H
F CF3
9
10.386
7.472
7.400
7.382
7.363
7.348
7.345
7.333
7.327
7.309
1.00
8.00
60000
50000
40000
30000
20000
10000
0
-10000
-20000
10.0
5.0
0.0
ppm (t1)

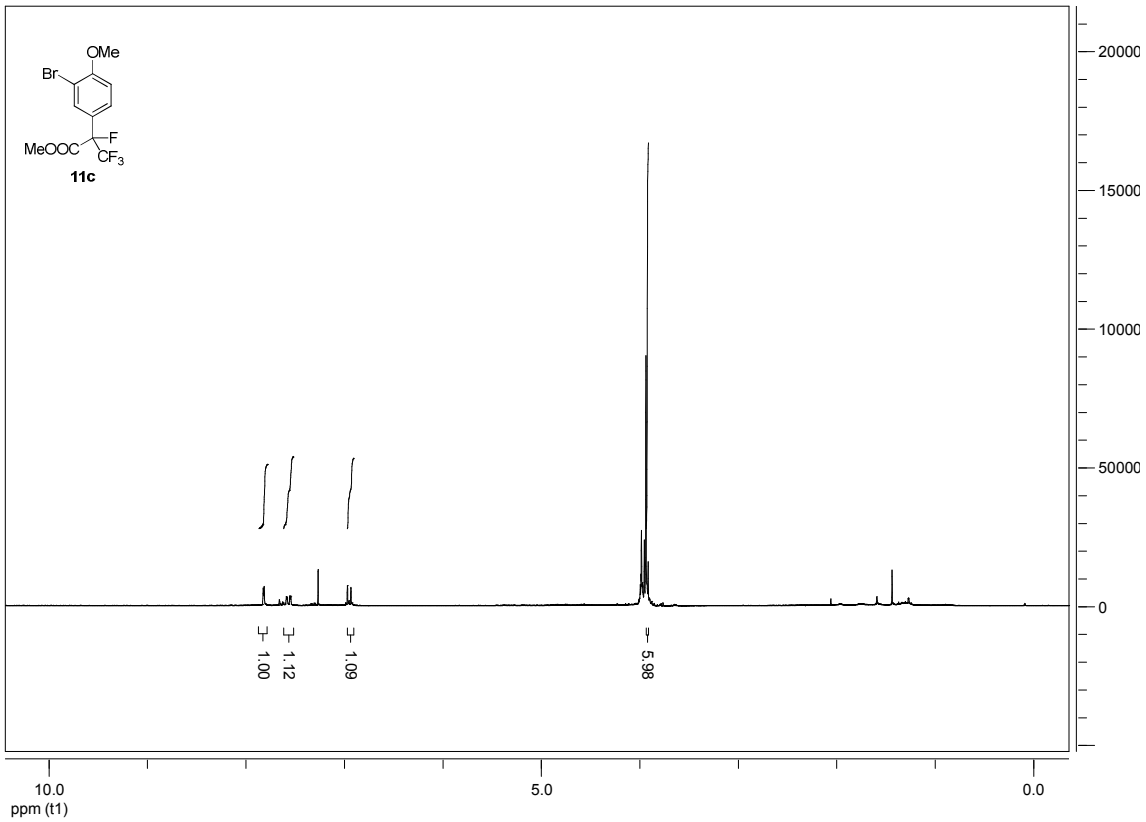

168.270
168.020
160.782
160.762
158.299
158.279
134.362
131.766
131.632
131.319
131.287
129.543
129.463
129.323
129.242
128.967
128.938
128.631
128.421
125.242
124.949
122.402
122.111
121.694
121.664
121.600
121.569
119.564
119.271
116.725
116.433
114.350
114.249
114.081
113.980
92.677
92.310
90.647
90.307
10000
50000
0
200
150
100
50
0
ppm (t1)

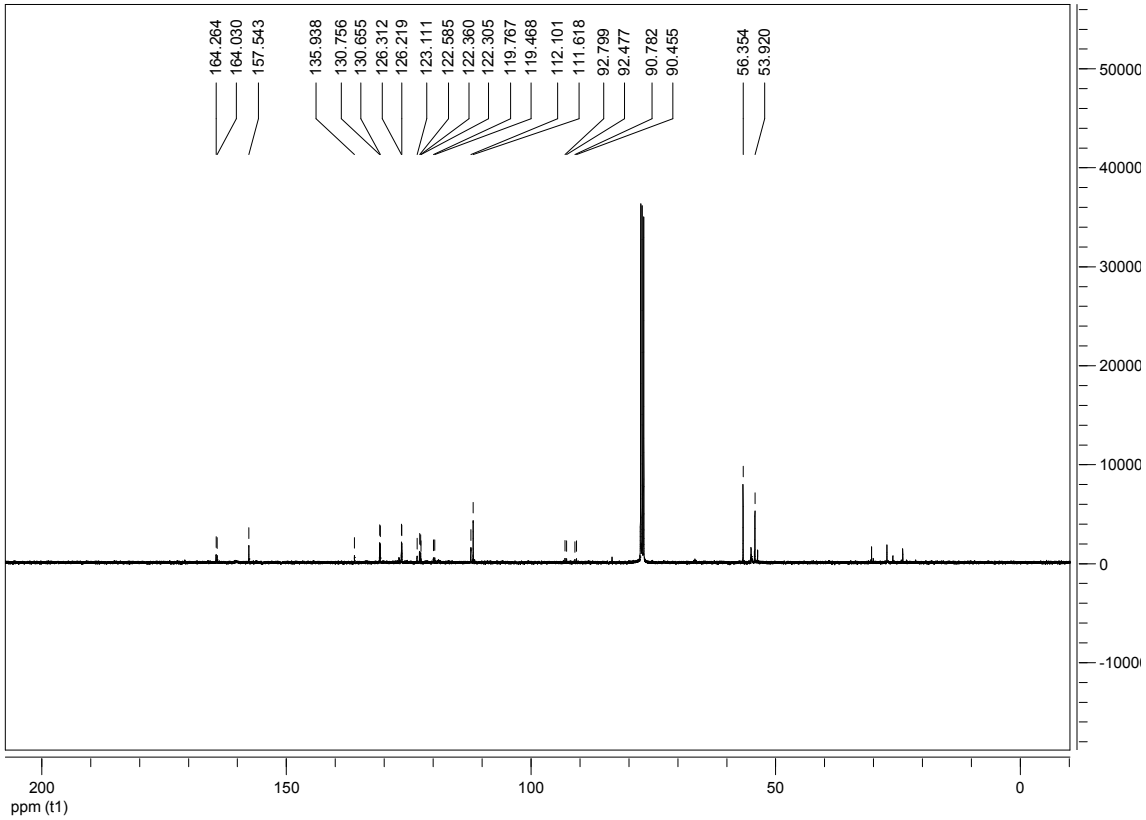

F3C F OMe
MeOOC
I
11a
7.820
7.817
7.750
7.745
7.728
7.723
6.738
6.716
3.858
3.788
50000
0
2.04
1.01
3.04
10.0
5.0
0.0
ppm (t1)

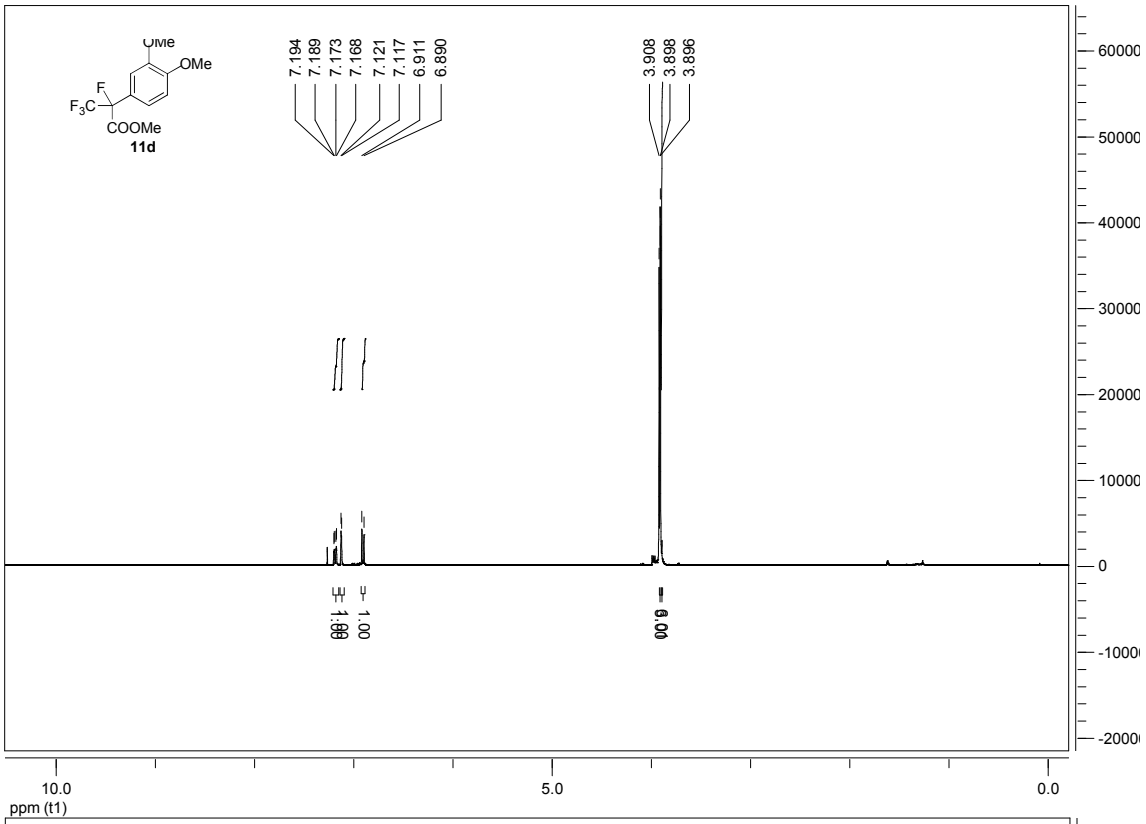

164.140
163.911
156.678
156.635
140.795
136.721
136.624
125.611
125.310
122.768
122.470
121.912
121.700
119.930
119.631
117.089
116.791
114.018
91.793
91.469
91.143
90.821
89.838
89.513
89.188
88.912
82.751
56.142
53.411
50000
0
200
150
100
50
0
ppm (t1)

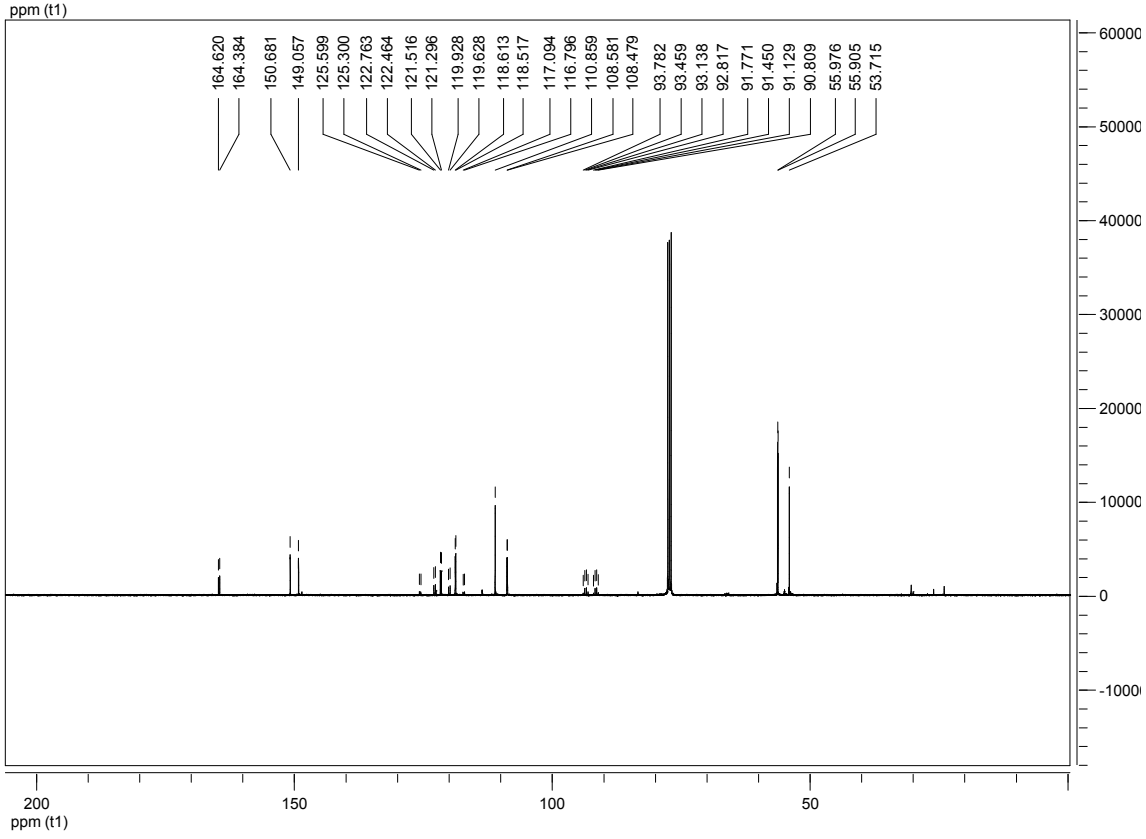

F3C F OMe
MeOOC
Br
11b
7.667
7.567
7.561
7.545
7.539
3.859
3.792
1.00
1.00
3.00
50000
0
10.0
5.0
0.0
ppm (t1)


164.127
163.900
155.959
155.917
134.834
131.077
130.967
122.776
122.478
121.590
121.377
119.937
119.639
117.095
116.798
113.574
113.249
91.910
91.585
91.259
90.937
89.955
89.629
89.304
88.980
56.258
53.406
50000
0
200
150
100
50
0
ppm (t1)


OMe
Br
MeOOC
F
CF3
11c
1.00
1.12
1.09
5.98
10.0
5.0
0.0
ppm (t1)


164.264
164.030
157.543
135.938
130.756
130.655
126.312
126.219
123.111
122.585
122.360
122.305
119.767
119.468
112.101
111.618
92.799
92.477
90.782
90.455
56.354
53.920
200
150
100
50
0
ppm (t1)


OMe
OMe
F
F3C
COOMe
11d
7.194
7.189
7.173
7.168
7.121
7.117
6.911
6.890
3.908
3.898
3.896
1.00
1.00
10.0
5.0
0.0
ppm (t1)


164.620
164.384
150.681
149.057
125.599
125.300
122.763
122.464
121.516
121.296
119.928
119.628
118.613
118.517
117.094
116.796
110.859
108.581
108.479
93.782
93.459
93.138
92.817
91.771
91.450
91.129
90.809
55.976
55.905
53.715
200
150
100
50
ppm (t1)