Supporting Information

Trifluoromethyl-Substituted Sulfonium Ylide: Rh-Catalyzed Carbenoid Addition to Trifluoromethylthioether

Yafei Liu, Xinxin Shao, Panpan Zhang, Long Lu* and Qilong Shen*

Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032

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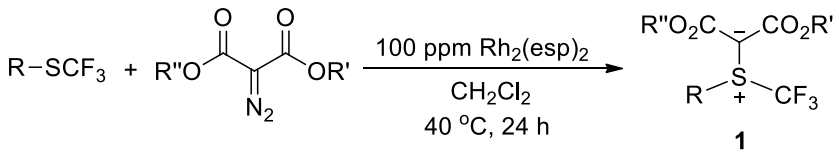
General Information

All solvents were purified by standard method. ^{1}H NMR spectra were recorded on a 500 MHz, 400 MHz or 300 MHz. ^{19}F NMR were recorded on a 376 MHz or 282 MHz spectrometer. ^{13}C NMR spectra were recorded on a Bruker AM400 spectrometer and Agilent 400 or 500 MHz spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as inter standard. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Flash column chromatograph was carried out using 300-400 mesh silica gel at medium pressure. Elemental analysis was conducted on the VARIO EL III. X-ray structure was obtained on BRUKER SMART APEX CCD.

Alkyl trifluoromethylthioethers were prepared according to a modified procedure reported by Yagupolskii[1] and aryl trifluoromethylthioethers were prepared according to a procedure reported by Shen and coworkers.[2] Phenyltrifluoromethylthioether and all other reagents were received from commercial sources. Solvents were freshly dried and degassed according to the purification handbook *Purification of Laboratory Chemicals* before using.

General Procedure for Rh Catalyzed Addition of Diazomalonate with Trifluoromethylthioether



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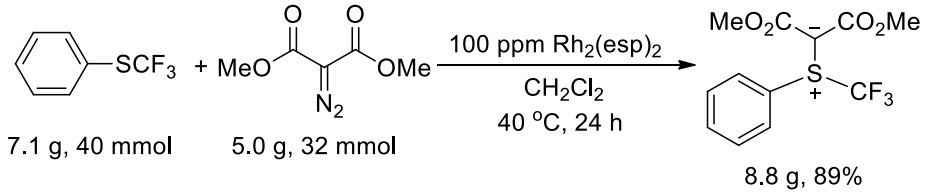
$RSCF_3$ (0.50 mmol, 1.0 equiv), $Rh_2(esp)_2$ (1.5 mL from stock solution A, 0.01 mol%) were placed into an oven-dried Schlenk tube that was equipped with a stirring bar under N_2. Diazomalonate (0.40 mmol, 0.8 equiv) was added. The tube was quickly sealed with a rubber stopper. The reaction was stirred at 40 ^oC for 24 h. The mixture was cooled to room temperature, then concentrated in *vacuo*. The product was purified by flash chromatography.

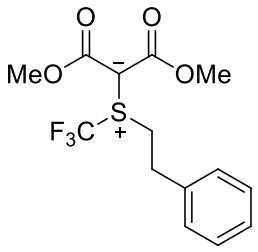
Stock solution A (2.67×10^{-2} M). 4.0 mg of $Rh_2(esp)_2$ was dissolved in 15 mL CH_2Cl_2. 2.0 mL of the above solution was diluted to 20.0 mL with CH_2Cl_2. The resulting solution was stirred at room temperature for one minute before use.

General Procedure for Formation of 1i on 8 g Scale



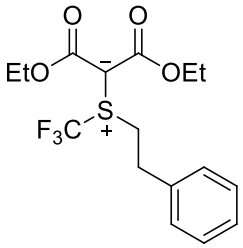
$PhSCF_3$ (7.13 g, 40 mmol), $Rh_2(esp)_2$ (3.0 mg, 0.01 mol%) and 120 mL CH_2Cl_2 were placed into an oven-dried Schlenk tube that was equipped with a stirring bar under N_2. Dimethyl diazomalonate (5.0 g, 32 mmol) was added slowly. The tube was quickly sealed with a rubber stopper. The reaction was stirred at 40 ^oC for 24 h. The mixture was cooled to room temperature. The mixture was then concentrated in *vacuo*. The product was purified by flash chromatography to give Trifluoromethyl-phenyl bis(carbomethoxy) methylide **1i** as a white solid (8.8 g, 89% yield).

Trifluoromethyl-(phenylethyl) bis(carbomethoxy) methylide 1a



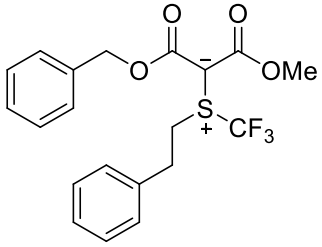
White solid (113 mg, 84%). Mp: 77-78 ^{o}C. Eluent: ethyl acetate/petroleum ether = 1/1 (R_f = 0.7). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.37 – 7.28 (m, 3 H), 7.19 (dd, *J* = 5.1, 3.1 Hz, 2 H), 4.62 (ddd, *J* = 11.7, 8.7, 5.0 Hz, 1 H), 3.75 (s, 6 H), 3.45 (dt, *J* = 11.7, 8.3 Hz, 1 H), 3.14 – 3.03 (m, 1 H), 2.93 (dt, *J* = 14.3, 8.5 Hz, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -55.7 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 166.16, 136.24, 129.05, 128.61, 127.66, 123.52 (q, *J* = 333.7 Hz), 51.64, 51.51, 40.38, 29.77 ppm. IR (KBr): ν = 3064, 3031, 2973, 2934, 1675, 1604, 1523, 1499, 1444, 1432, 1331, 1246, 1222, 1182, 1153, 1085, 966, 940, 922, 871, 794, 774, 748, 738, 695, 646, 569, 555 cm^{-1}. MS (ESI): 336.9 (M^++H). HRMS (ESI): Calculated for $C_{14}H_{15}O_4SF_3Na$: 359.0543 (M^+ +Na), Found: 395.0535.

Trifluoromethyl-(phenylethyl) bis(carboethoxy) methylide 1b



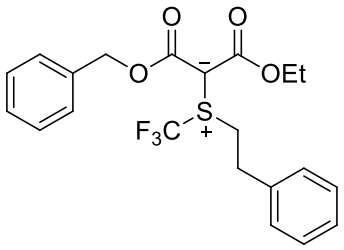
Colorless oil (122 mg, 84%). Eluent: ethyl acetate/petroleum ether = 1/1 (R_f = 0.6). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.32 (dt, *J* = 13.6, 6.8 Hz, 3 H), 7.19 (d, *J* = 6.8 Hz, 2 H), 4.61 (m, 1 H), 4.21 (d, *J* = 6.5 Hz, 4 H), 3.41 (m, 1 H), 3.20 – 3.03 (m, 1 H), 2.99 – 2.84 (m, 1 H), 1.29 (s, 6 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -56.0 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 165.75, 136.36, 129.04, 128.60, 127.60, 123.58 (q, *J* = 334.1 Hz), 60.21, 51.64, 40.47, 29.71, 14.43 ppm. IR (KBr): ν = 2981, 1729, 1696, 1654, 1498, 1456, 1391, 1369, 1305, 1235, 1184, 1097, 1019, 774, 749, 701 cm^{-1}. MS (ESI): 364.9 (M^++H). HRMS (ESI): Calculated for $C_{16}H_{20}O_4SF_3$: 365.1025 (M^++H), Found: 365.1034.

Trifluoromethyl-(phenylethyl) carbomethoxy carbobenzyloxy methylide 1c



Pale yellow oil (116 mg, 35%). Eluent: ethyl acetate/petroleum ether = 1/1 (R_f = 0.6). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.53 – 7.19 (m, 8 H), 7.12 (s, 2 H), 5.21 (s, 2 H), 4.60 (m, 1 H), 3.77 (s, 3 H), 3.41 (m, 1 H), 3.03 (m, 1 H), 2.98 – 2.76 (m, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -55.8 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 166.34, 165.17, 136.67, 136.14, 129.00, 128.54, 128.41, 127.77, 127.73, 127.58, 123.49 (q, *J* = 333.8 Hz), 65.81, 51.63, 51.56, 40.34, 29.66 ppm. IR (KBr): ν = 3064, 3030, 2950, 1731, 1698, 1662, 1605, 1498, 1456, 1435, 1378, 1309, 1235, 1186, 1142, 1097, 1029, 979, 909, 772, 749, 699, 652, 584 cm^{-1}. MS (ESI): 413.0 (M^++H). HRMS (ESI): Calculated for $C_{20}H_{20}O_4SF_3$: 413.1024 (M^++H), Found: 413.1029.

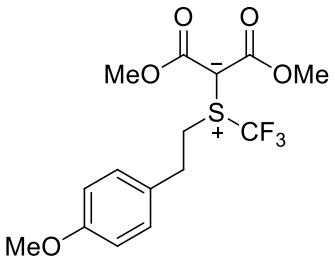
Trifluoromethyl-(phenylethyl) carboethoxy carbobenzyloxy methylide 1d



Colorless oil (86 mg, 25%). Eluent: ethyl acetate/petroleum ether = 1/1 (R_f = 0.7). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.36 (dd, *J* = 15.6, 8.5 Hz, 3 H), 7.32 – 7.22 (m, 5 H), 7.13 (d, *J* = 5.3 Hz, 2 H), 5.22 (s, 2 H), 4.59 (m, 1 H), 4.23 (d, *J* = 6.8 Hz, 2 H), 3.40 (m, 1 H), 3.04 (m, 1 H), 2.97 – 2.73 (m, 1 H), 1.38 – 1.12 (m, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -55.9 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 165.77, 165.44, 136.69, 136.24, 129.02, 128.56, 128.39, 127.74, 127.72, 127.58, 123.54 (d, *J* = 333.9 Hz), 65.87, 60.35, 51.87, 40.37, 29.68, 14.44 ppm. IR (KBr): ν = 3064, 3031, 2980, 1731, 1698, 1655, 1586, 1498, 1456, 1376, 1301, 1230, 1142, 1096,

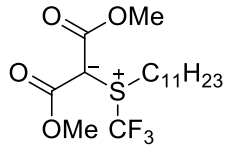
1029, 910, 859, 772, 749, 698, 653, 599, 583 cm^{-1}. MS (ESI): 427.0 (M^++H). HRMS (ESI): Calculated for $C_{21}H_{22}O_4SF_3$: 427.1180 (M^++H), Found: 427.1185.

Trifluoromethyl-(4-methoxyphenyl)ethyl bis(carbomethoxy) methylide 1e



White solid (129 mg, 88%). Mp: 72-73 ^oC. Eluent: ethyl acetate/petroleum ether = 1/1 (R_f = 0.5). ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.14 – 7.04 (m, 2 H), 6.94 – 6.81 (m, 2 H), 4.58 (ddd, *J* = 11.7, 8.5, 4.9 Hz, 1 H), 3.80 (s, 3 H), 3.74 (s, 6 H), 3.40 (dt, *J* = 11.6, 8.3 Hz, 1 H), 3.15 – 2.95 (m, 1 H), 2.87 (dt, *J* = 14.5, 8.4 Hz, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -55.7 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 166.18, 159.06, 129.71, 128.14, 123.54 (q, *J* = 333.7 Hz), 114.42, 55.29, 51.63, 51.50, 40.73, 28.93 ppm. IR (KBr): ν = 3062, 3029, 2975, 2936, 1689, 1654, 1612, 1515, 1437, 1319, 1282, 1237, 1205, 1184, 1149, 1086, 1037, 964, 829, 773, 744, 687 cm^{-1}. MS (ESI): 388.9 (M^++Na). HRMS (ESI): Calculated for $C_{15}H_{18}O_5SF_3$: 367.0817 (M^++H), Found: 367.0822.

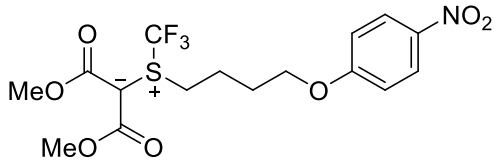
Trifluoromethyl-undecyl bis(carbomethoxy) methylide 1f



White solid (136 mg, 88%). Mp: 59-61 ^oC. Eluent: ethyl acetate/petroleum ether = 1/1 (R_f = 0.8). ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 4.22 (ddd, *J* = 11.9, 9.0, 5.3 Hz, 1 H), 3.73 (s, 6 H), 3.26 (ddd, *J* = 11.9, 8.6, 7.4 Hz, 1 H), 1.82 – 1.56 (m, 2 H), 1.53 – 1.36 (m, 2 H), 1.35 – 1.19 (m, 14 H), 0.87 (t, *J* = 6.8 Hz, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -55.8 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 166.20, 123.49 (q, *J* = 333.2 Hz), 52.18, 51.47, 38.98, 31.82, 29.45, 29.36, 29.23, 29.12, 28.77, 28.04, 23.65, 22.61, 14.05 ppm. IR (KBr): ν = 3011, 2951, 2921, 2850, 1687, 1660, 1467, 1439, 1325, 1241, 1207, 1183, 1112, 1081, 1013, 967, 864, 799, 774, 750, 725,

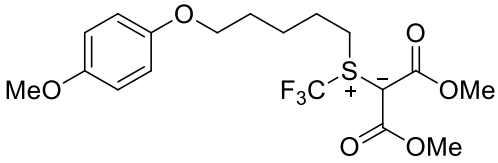
555, 508, 493, 476, 466, 430 cm^{-1}. MS (ESI): 409.0 (M^++Na). HRMS (ESI): Calculated for $C_{17}H_{29}O_4SNaF_3$: 409.1639 (M^++H), Found: 409.1631.

Trifluoromethyl-(4-(4-nitrophenoxy)butyl) bis(carbomethoxy) methylide 1g



Pale yellow solid (120 mg, 71%). Mp: 91-93 ^oC. Eluent: ethyl acetate/petroleum ether = 1/2 (R_f = 0.1). ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.19 (d, *J* = 9.2 Hz, 2 H), 6.93 (d, *J* = 9.3 Hz, 2 H), 4.40 (ddd, *J* = 12.6, 8.0, 4.5 Hz, 1 H), 4.09 (t, *J* = 5.1 Hz, 2 H), 3.72 (s, 6 H), 3.36 (dt, *J* = 11.8, 7.6 Hz, 1 H), 1.97 (ddd, *J* = 17.9, 13.3, 7.5 Hz, 4 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -55.7 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 166.17, 163.40, 141.74, 125.94, 114.34, 123.45 (q, *J* = 333.5 Hz), 67.38, 51.90, 51.58, 38.41, 27.41, 20.85 ppm. IR (KBr): ν = 3014, 2948, 2878, 2845, 1693, 1654, 1609, 1593, 1513, 1498, 1479, 1439, 1396, 1346, 1328, 1267, 1244, 1226, 1209, 1190, 1106, 1075, 1037, 1001, 966, 864, 844, 808, 775, 751, 714, 691, 654, 554, 536 489 cm^{-1}. MS (ESI): 425.9 (M^++H). HRMS (ESI): Calculated for $C_{16}H_{19}O_7SNF_3$: 426.0819 (M^++H), Found: 426.0829.

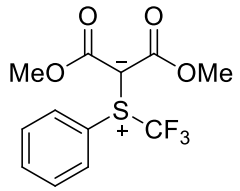
Trifluoromethyl-(5-(4-methoxyphenoxy)pentyl) bis(carbomethoxy) methylide 1h



White solid (136 mg, 80%). Eluent: ethyl acetate/petroleum ether = 1/1 (R_f = 0.5). Mp: 69-72 ^oC. ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 6.86 – 6.76 (m, 4 H), 4.29 (ddd, *J* = 12.0, 8.9, 5.2 Hz, 1 H), 3.91 (t, *J* = 6.0 Hz, 2 H), 3.77 (s, 3 H), 3.74 (s, 6 H), 3.30 (ddd, *J* = 11.9, 8.6, 7.2 Hz, 1 H), 1.90 – 1.73 (m, 4 H), 1.73 – 1.61 (m, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -55.7 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 166.19, 153.85, 152.87, 123.47 (q, *J* = 333.4 Hz), 115.33, 114.64, 67.66 , 55.69, 52.08, 51.51, 38.78, 28.56, 24.92, 23.51 ppm. IR (KBr): ν = 3013, 2996, 2944, 2908, 2872, 2829, 1687, 1657, 1592, 1514, 1466, 1440, 1398, 1330, 1243, 1208, 1184, 1108, 1080, 1048, 1015, 1001, 967, 828, 807, 775, 749, 705, 552, 522 cm^{-1}. MS (ESI): 424.9

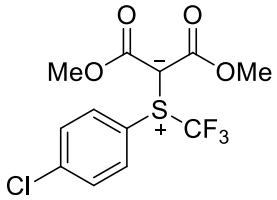
(M^++H). HRMS (ESI): Calculated for $C_{18}H_{24}O_6SF_3$: 425.1232 (M^++H), Found: 425.1240.

Trifluoromethyl-phenyl bis(carbomethoxy) methylide 1i



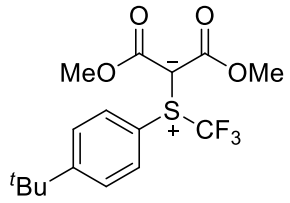
White solid (113 mg, 92%). Mp: 65-67 ^oC. Eluent: ethyl acetate/petroleum ether = 1/2 (R_f = 0.6). ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.72 (d, *J* = 7.7 Hz, 2 H), 7.63 (t, *J* = 7.3 Hz, 1 H), 7.57 (t, *J* = 7.4 Hz, 2 H), 3.74 (s, 6 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -51.1 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 165.74, 132.84, 130.19, 128.47, 125.78, 123.69 (q, *J* = 333.1 Hz), 54.16, 51.63 ppm. IR (KBr): ν = 3528, 3065, 2995, 2952, 2843, 1736, 1705, 1667, 1579, 1477, 1436, 1301, 1243, 1182, 1077, 1023, 999, 965, 921, 821, 772, 750, 696, 684, 564, 517 cm^{-1}. MS (ESI): 308.9 (M^++H). HRMS (ESI): Calculated for $C_{12}H_{12}O_4SF_3$: 309.0399 (M^++H), Found: 309.0403.

Trifluoromethyl-((4-chloro)-phenyl) bis(carbomethoxy) methylide 1j



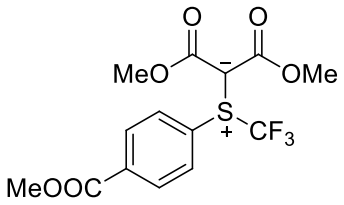
Pink solid (97 mg, 71%). Mp: 85-87 ^oC. Eluent: ethyl acetate/petroleum ether = 1/2 (R_f = 0.6). ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.68 (d, *J* = 8.6 Hz, 2 H), 7.54 (d, *J* = 8.9 Hz, 2 H), 3.74 (s, 6 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -51.1 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 165.58, 139.87, 130.49, 130.08, 124.12, 123.55 (q, *J* = 333.6 Hz), 54.35, 51.72 ppm. IR (KBr): ν = 3090, 2994, 2952, 2843, 2251, 1736, 1702, 1667, 1572, 1478, 1395, 1316, 1184, 1081, 1009, 965, 918, 821, 772, 739, 647, 577, 519 cm^{-1}. MS (ESI): 342.7 (M^++H). HRMS (ESI): Calculated for $C_{12}H_{11}O_4ClSF_3$: 343.0010 (M^++H), Found: 343.0013.

Trifluoromethyl-(4-*tert*-butylphenyl) bis(carbomethoxy) methylide 1k



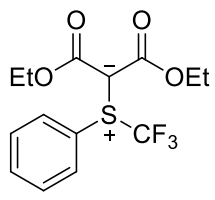
Colorless oil (118 mg, 81%). Eluent: ethyl acetate/petroleum ether = 1/2 (R_f = 0.6).^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.64 (d, *J* = 8.6 Hz, 2 H), 7.54 (d, *J* = 8.8 Hz, 2 H), 3.72 (s, 6 H), 1.31 (s, 9 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -51.5 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) 165.77, 156.95, 128.62, 127.27, 122.10, 123.66 (d, *J* = 332.8 Hz), 54.59, 51.51, 35.10, 30.89 ppm. IR (KBr): ν = 2960, 2873, 2251, 1735, 1706, 1670, 1590, 1490, 1435, 1401, 1309, 1241, 1183, 1084, 1009, 966, 919, 830, 772, 734, 647, 598, 562 cm^{-1}. MS (ESI): 365.0 (M^++H). HRMS (ESI): Calculated for $C_{16}H_{20}O_4SF_3$: 365.1024 (M^++H), Found: 365.1029.

Trifluoromethyl-(4-carbomethoxy-phenyl) bis(carbomethoxy) methylide 1l



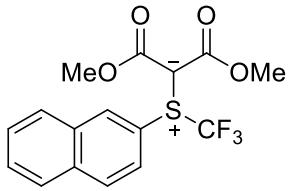
White solid (124 mg, 85%). Mp: 103-104 ^{o}C. Eluent: ethyl acetate/petroleum ether = 1/2 (R_f = 0.5).^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.20 (d, *J* = 8.8 Hz, 2 H), 7.74 (d, *J* = 8.3 Hz, 2 H), 3.95 (s, 3 H), 3.73 (s, 6 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -50.5 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 165.43, 165.13, 134.01, 131.04, 130.26, 127.95, 123.54 (q, *J* = 334.2 Hz), 53.41, 52.73, 51.71 ppm. IR (KBr): ν = 2998, 2954, 2845, 2252, 1732, 1671, 1596, 1436, 1400, 1317, 1282, 1244, 1187, 1084, 1013, 964, 916, 854, 773, 761, 733, 686, 647, 571 cm^{-1}. MS (ESI): 366.9 (M^++H). HRMS (ESI): Calculated for $C_{14}H_{14}O_6SF_3$: 367.0453 (M^++H), Found: 367.0448.

Trifluoromethyl-phenyl bis(carboethoxy) methylide 1m



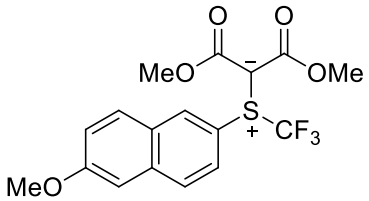
Colorless oil (156 mg, 58%). Eluent: ethyl acetate/petroleum ether = 1/2 (R_f = 0.7). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.63 (d, *J* = 7.7 Hz, 2 H), 7.58 – 7.44 (m, 3 H), 4.12 (q, *J* = 7.1 Hz, 4 H), 1.16 (t, *J* = 7.1 Hz, 6 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -51.3 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 165.24, 132.58, 130.03, 128.12, 126.04, 123.71 (q, *J* = 333.6 Hz), 60.31, 53.84, 14.27 ppm. IR (KBr): ν = 3065, 2982, 2905, 1776, 1701, 1654, 1579, 1532, 1478, 1446, 1391, 1369, 1299, 1234, 1179, 1085, 1022, 999, 920, 863, 838, 772, 749, 695, 684, 613, 564, 522 cm^{-1}. MS (ESI): 337.0 (M^++H). HRMS (ESI): Calculated for $C_{14}H_{16}O_4SF_3$: 337.0714 (M^++H), Found: 337.0716.

Trifluoromethyl-(naphthalen-2-yl) bis(carbomethoxy) methylide 1n



Pink solid (103 mg, 72%). Mp: 132-133 ^{o}C. Eluent: ethyl acetate/petroleum ether = 1/2 (R_f = 0.6).^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.21 (s, 1 H), 8.01 (d, *J* = 8.9 Hz, 1 H), 7.92 (d, *J* = 8.1 Hz, 2 H), 7.75 (d, *J* = 8.9 Hz, 1 H), 7.71 – 7.55 (m, 2 H), 3.76 (s, 6 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -50.9 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) 165.78, 134.66, 132.84, 130.41, 130.08, 129.27, 128.76, 127.96, 125.44, 123.78 (q, *J* = 333.2 Hz), 123.13, 122.62, 54.53, 51.64 ppm. IR (KBr): ν = 3063, 2960, 1694, 1674, 1589, 1504, 1439, 1353, 1314, 1238, 1218, 1178, 1129, 1089, 1051, 958, 888, 862, 809, 769, 760, 745, 639, 623, 559 cm^{-1}. MS (ESI): 358.9 (M^++H). HRMS (ESI): Calculated for $C_{16}H_{14}O_4SF_3$: 359.0556 (M^++H), Found: 359.0559.

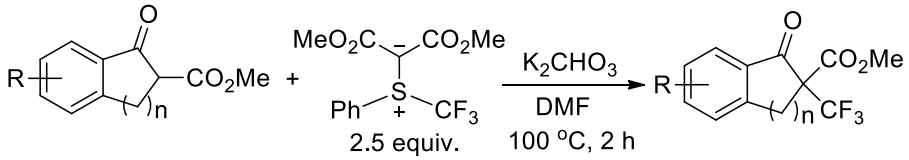
Trifluoromethyl-((6-methoxynaphthalen)-2-yl) bis(carbomethoxy) methylide 1o



Pale yellow solid (110 mg, 71%). Mp: 123-125 ^{o}C. Eluent: ethyl acetate/petroleum ether = 1/2 (R_f = 0.6). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.15 (s, 1 H), 7.88

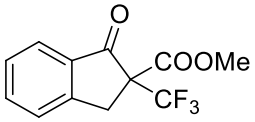
(d, *J* = 8.9 Hz, 1 H), 7.81 (d, *J* = 9.0 Hz, 1 H), 7.76 (d, *J* = 9.8 Hz, 1 H), 7.27 (dd, *J* = 8.8, 2.7 Hz, 1 H), 7.17 (d, *J* = 2.3 Hz, 1 H), 3.95 (s, 3 H), 3.76 (s, 6 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -51.4 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 165.91, 160.28, 136.63, 130.43, 130.35, 129.00, 123.80 (q, *J* = 333.0 Hz), 128.31, 124.32, 120.99, 119.69, 105.75, 99.95, 55.52, 55.32, 51.62 ppm. IR (KBr): ν = 2951, 2843, 2251, 1729, 1697, 1625, 1593, 1502, 1436, 1393, 1317, 1269, 1243, 1218, 1184, 1083, 1029, 965, 911, 853, 813, 773, 732, 647, 575 cm^{-1}. MS (ESI): 388.9 (M^++H). HRMS (ESI): Calculated for $C_{17}H_{16}O_5SF_3$: 389.0661 (M^++H), Found: 389.0665.

General Procedure for Trifluoromethylation of β-Ketoester



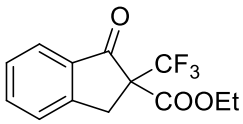
β-ketoester (0.50 mmol, 1.0 equiv), K_2CO_3 (83 mg, 0.6 mmol, 1.2 equiv), and reagent **1i** (385 mg, 1.25 mmol, 2.5 equiv) were placed into an oven-dried Schlenk tube that was equipped with a stirring bar under N_2. The tube was quickly sealed with a rubber stopper and 3.0 mL of freshly distilled DMF was added. The reaction was stirred at 100 ^oC for 2 h. The mixture was cooled to room temperature, and 20 mL of distilled water and 20 mL of Et_2O was added and the organic phase was separated. The aqueous phase was extracted with Et_2O (5 x 10 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The product was purified by flash chromatography on silica gel or further purified by preparation HPLC.

Methyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate[3] 2a



Pale yellow solid (63 mg, 48%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.5).^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.84 (d, *J* = 7.7 Hz, 1 H), 7.70 (t, *J* = 7.8 Hz, 1 H), 7.53 (d, *J* = 7.7 Hz, 1 H), 7.47 (t, *J* = 7.5 Hz, 1 H), 3.78 (s, 3 H), 3.74 (d, *J* = 17.8 Hz, 1 H), 3.60 (d, *J* = 17.8 Hz, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -69.4 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 192.83, 165.61, 151.64, 136.28, 134.35, 128.50, 126.30, 125.59, 123.47 (q, *J* = 281.6 Hz), 62.99 (q, *J* = 26.3 Hz), 53.55, 34.16 ppm.

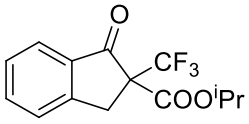
Ethyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate[3] 2b



Pale yellow solid (83 mg, 61%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.81 (d, *J* = 7.8 Hz, 1 H), 7.68 (t, *J* = 7.5 Hz, 1 H), 7.52 (d, *J* = 8.3 Hz, 1 H), 7.44 (t, *J* = 7.5 Hz, 1 H), 4.22 (q, *J* = 7.1 Hz,

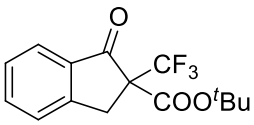
2 H), 3.72 (d, *J* = 17.7 Hz, 1 H), 3.58 (d, *J* = 17.7 Hz, 1 H), 1.21 (t, *J* = 7.1 Hz, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -69.3 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 192.97, 165.06, 151.65, 136.19, 134.30, 128.39, 126.26, 125.38, 123.48 (q, *J* = 281.6 Hz), 63.01 (q, *J* = 26.0 Hz), 62.71, 34.08, 13.71 ppm.

Isopropyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate[3] 2c



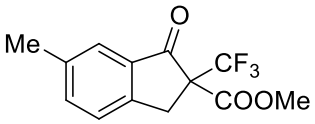
White solid (91 mg, 64%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.84 (d, *J* = 7.8 Hz, 1 H), 7.69 (t, *J* = 7.1 Hz, 1 H), 7.53 (d, *J* = 7.8 Hz, 1 H), 7.46 (t, *J* = 7.5 Hz, 1 H), 5.10 (hept, *J* = 6.0 Hz, 1 H), 3.71 (d, *J* = 17.6 Hz, 1 H), 3.58 (d, *J* = 17.7 Hz, 1 H), 1.23 (d, *J* = 6.3 Hz, 6 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -69.2 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 193.05, 164.64, 151.69, 136.11, 134.48, 128.40, 126.24, 125.49, 123.54 (q, *J* = 281.5 Hz), 70.86, 63.24 (d, *J* = 25.8 Hz), 34.15, 21.36, 21.28 ppm.

***tert*-Butyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate[3] 2d**



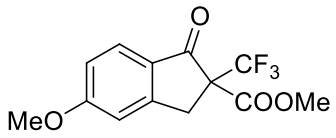
White solid (74 mg, 49%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.83 (d, *J* = 7.8 Hz, 1 H), 7.67 (t, *J* = 7.5 Hz, 1 H), 7.52 (d, *J* = 7.8 Hz, 1 H), 7.44 (t, *J* = 7.5 Hz, 1 H), 3.68 (d, *J* = 17.7 Hz, 1 H), 3.56 (d, *J* = 17.6 Hz, 1 H), 1.42 (s, 9 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -69.1 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 193.39, 164.04, 151.67, 135.98, 134.61, 128.31, 126.20, 125.38, 123.58 (q, *J* = 281.3 Hz), 84.27, 63.81 (q, *J* = 25.8 Hz), 34.24, 27.65 ppm.

Methyl 6-methyl-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxyl -ate [5] 2e



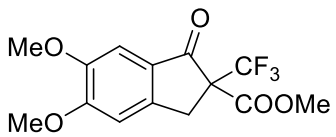
Yellow solid (67 mg, 48%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.63 (s, 1 H), 7.51 (d, *J* = 8.7 Hz, 1 H), 7.41 (d, *J* = 7.9 Hz, 1 H), 3.77 (s, 3 H), 3.68 (d, *J* = 17.6 Hz, 1 H), 3.54 (d, *J* = 17.6 Hz, 1 H), 2.42 (s, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -69.4 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 192.91, 165.75, 149.14, 138.74, 137.63, 134.57, 125.97, 125.42, 123.55 (q, *J* = 281.5 Hz), 63.32 (q, *J* = 26.1 Hz), 53.52, 33.86, 21.04 ppm. IR (KBr): ν = 2960, 1760, 1725, 1618, 1586, 1497, 1436, 1384, 1313, 1280, 1224, 1248, 1186, 1160, 1125, 1084, 1046, 966, 945, 878, 823, 792, 758, 734, 693, 657, 502 cm^{-1}. MS (ESI): 272.9 (M^++H). HRMS (ESI): Calculated for $C_{13}H_{12}O_3F_3$: 273.07 (M^++H), Found: 273.0733.

Methyl 5-methoxy-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-indene-2-carboxyl -ate[4] 2f



White solid (108 mg, 75%). Eluent: ethyl acetate/petroleum ether = 1/8 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.75 (d, *J* = 8.6 Hz, 1 H), 6.97 (dd, *J* = 8.6, 2.2 Hz, 1 H), 6.93 (d, 1 H), 3.91 (s, 3 H), 3.77 (s, 3 H), 3.68 (d, *J* = 17.8 Hz, 1 H), 3.51 (d, *J* = 17.8 Hz, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -69.5 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 190.71, 166.53, 165.81, 154.86, 136.00, 127.28, 123.57 (q, *J* = 281.5 Hz), 116.70, 109.35, 63.27 (q, *J* = 26.1 Hz), 55.86, 53.45, 34.00 ppm.

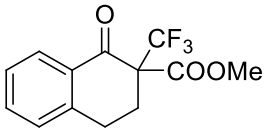
Methyl 5,6-dimethoxy-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2 –carboxylate[3] 2g



White solid (111 mg, 70%). Eluent: ethyl acetate/petroleum ether = 1/7 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.19 (s, 1 H), 6.91 (s, 1 H), 3.98 (s, 3 H), 3.90 (s, 3 H), 3.77 (s, 3 H), 3.62 (d, *J* = 17.5 Hz, 1 H), 3.47 (d, *J* = 17.5 Hz, 1 H); ^{19}F

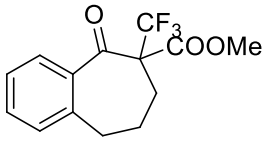
NMR (375 MHz, $CDCl_3$) δ -69.4 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 191.15, 165.84, 156.78, 150.21, 147.57, 127.06, 123.56 (q, *J* = 281.5 Hz), 106.94, 105.28, 63.30 (q, *J* = 26.0 Hz), 56.42, 56.14, 53.43, 33.78 ppm.

Methyl 1-oxo-2-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate[3] 2h



White solid (78 mg, 57%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.5). ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.10 (d, *J* = 8.8 Hz, 1 H), 7.53 (td, *J* = 7.5, 1.3 Hz, 1 H), 7.36 (t, *J* = 7.6 Hz, 1 H), 7.25 (d, *J* = 8.5 Hz, 1 H), 3.75 (s, 3 H), 3.02 (dd, *J* = 8.4, 3.9 Hz, 2 H), 2.82 (dt, *J* = 13.6, 4.0 Hz, 1 H), 2.47 (dt, *J* = 13.6, 8.5 Hz, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -68.8 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 186.97, 165.77, 142.07, 134.32, 131.33, 128.69, 128.38, 127.26, 123.77 (q, *J* = 284.1 Hz), 61.93 (q, *J* = 24.2 Hz), 53.57, 27.68, 25.02 ppm.

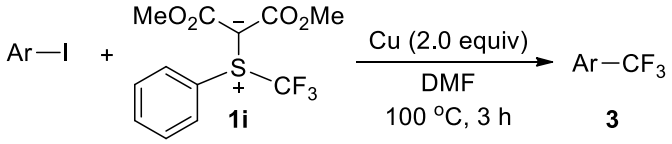
Methyl 5-oxo-6-(trifluoromethyl)-6,7,8,9-tetrahydro-5H-benzo[7]annulene-6 -carboxylate[5] 2i



White solid (70 mg, 49%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.5). ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.47 (d, *J* = 7.6 Hz, 1 H), 7.40 (t, *J* = 7.2 Hz, 1 H), 7.30 (t, *J* = 7.5 Hz, 1 H), 7.14 (d, *J* = 7.5 Hz, 1 H), 3.69 (s, 3 H), 2.96 (ddd, *J* = 14.7, 9.0, 5.4 Hz, 1 H), 2.85 (dt, *J* = 15.5, 5.9 Hz, 1 H), 2.56 (ddd, *J* = 14.0, 6.9, 5.4 Hz, 1 H), 2.21 (ddd, *J* = 13.8, 8.2, 5.4 Hz, 1 H), 2.11 – 1.90 (m, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -67.5 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 197.15, 166.16, 138.71, 137.80, 131.97, 129.10, 129.04, 126.82, 123.79 (q, *J* = 285.1 Hz), 66.14 (q, *J* = 23.2 Hz), 53.30, 31.72, 27.59, 22.44 ppm. IR (KBr): ν = 2956, 2875, 1751, 1699, 1599, 1484, 1449, 1361, 1264, 1199, 1164, 1119, 1075, 1026, 1012, 992,

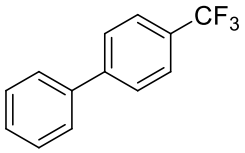
954, 884, 855, 839, 821, 797, 772, 748, 734, 651, 630 cm^{-1}. MS (ESI): 286.9 (M^++H). HRMS (ESI): Calculated for $C_{14}H_{14}O_3F_3$: 287.09 (M^++H), Found: 287.0890.

General Procedure for Trifluoromethylation of Aryl Iodides



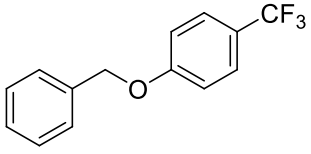
Aryl iodide (0.50 mmol, 1.0 equiv), Cu (64 mg, 1.0 mmol, 2.0 equiv), and reagent **1i** (539 mg, 1.75 mmol, 3.5 equiv) were placed into an oven-dried Schlenk tube that was equipped with a stirring bar under N_2. The tube was quickly sealed with a rubber stopper and 5.0 mL of freshly distilled DMF was added. The reaction was stirred at 100 ^{o}C for 3 h. The mixture was cooled to room temperature, and 20 mL of distilled water and 20 mL of Et_2O was added and the organic phase was separated. The aqueous phase was extracted with Et_2O (5 x 10 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The product was purified by flash chromatography on silica gel or further purified by Kugelrohr distillation.

4-(Trifluoromethyl)biphenyl[6] 3a



White solid (104 mg, 94%). Eluent: petroleum ether (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.70 (s, 4 H), 7.61 (d, *J* = 7.2 Hz, 2 H), 7.49 (t, *J* = 7.4 Hz, 2 H), 7.42 (t, *J* = 6.7 Hz, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -62.4 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 144.69, 139.74, 129.30 (q, *J* = 32.5 Hz), 128.97, 128.17, 127.40, 127.26. 125.69 (q, *J* = 3.8 Hz). 124.24 (q, *J* = 262.2 Hz) ppm.

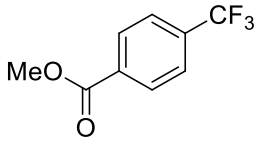
1-(Benzyloxy)-4-(trifluoromethyl)benzene[6] 3b



White solid (95 mg, 75%). Eluent: petroleum ether (R_f = 0.9). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.55 (d, *J* = 8.9 Hz, 2 H), 7.42 (q, *J* = 8.0 Hz, 4 H), 7.36 – 7.30 (m, *J* = 8.0 Hz, 1 H), 7.04 (d, *J* = 8.8 Hz, 2 H), 5.11 (s, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -61.5 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 161.12, 136.17, 128.70,

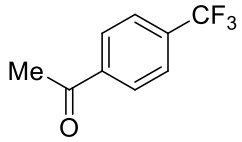
128.24, 127.44, 126.91 (q, *J* = 3.8 Hz), 124.40 (q, *J* = 271.0 Hz), 123.1(q, *J* = 32.9 Hz), 114.81, 70.13 ppm.

Methyl 4-(trifluoromethyl)benzoate[7] 3c



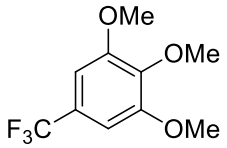
Colorless liquid (86 mg, 84%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.16 (d, *J* = 8.1 Hz, 2 H), 7.71 (d, *J* = 8.2 Hz, 2 H), 3.96 (s, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -63.2 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 165.87, 134.45 (q, *J* = 32.7 Hz), 133.36, 129.98, 125.41 (q, *J* = 3.6 Hz), 123.63 (q, *J* = 272.8 Hz), 52.51 ppm.

1-(4-(Trifluoromethyl)phenyl)ethanone[6] 3d



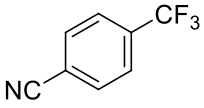
White solid (74 mg, 79%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.06 (d, *J* = 8.1 Hz, 2 H), 7.73 (d, *J* = 8.2 Hz, 2 H), 2.64 (s, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -63.2 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$, 293 K, TMS) δ 196.97, 139.63, 134.40 (q, *J* = 32.7 Hz), 128.60, 125.66 (q, *J* = 3.8 Hz), 123.57 (q, *J* = 272.7 Hz), 26.78 ppm.

1,2,3-Trimethoxy-5-(trifluoromethyl)benzene[8] 3e



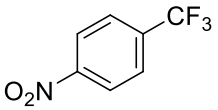
White solid (89 mg, 75%). Eluent: petroleum ether (R_f = 0.6). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 6.83 (s, 2 H), 3.90 (s, 6 H), 3.88 (s, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -62.1 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 153.38, 140.55, 125.70 (q, *J* = 32.6 Hz), 124.03 (q, *J* = 271.9 Hz), 102.50 (q, *J* = 3.8 Hz), 60.89, 56.26 ppm.

4-(Trifluoromethyl)benzonitrile[7] 3f



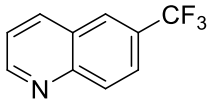
White solid (74 mg, 87%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.81 (d, *J* = 8.3 Hz, 2 H), 7.76 (d, *J* = 8.3 Hz, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -63.6 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 134.56 (q, *J* = 33.4 Hz), 132.67, 126.18 (q, *J* = 3.7 Hz), 123.02 (q, *J* = 273.0 Hz), 117.43, 116.04 ppm.

1-Nitro-4-(trifluoromethyl)benzene[6] 3g



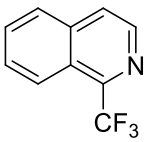
White solid (86 mg, 90%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.37 (d, *J* = 8.5 Hz, 2 H), 7.85 (d, *J* = 8.5 Hz, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -63.2 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 150.01, 136.10 (q, *J* = 33.4 Hz), 126.78 (q, *J* = 3.7 Hz), 124.09, 122.9 (q, *J* = 273.1 Hz) ppm.

6-(Trifluoromethyl)quinolone[7] 3h



White solid (72 mg, 72%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.95 (d, *J* = 4.0 Hz, 1 H), 8.14 (d, *J* = 8.5 Hz, 2 H), 8.04 (s, 1 H), 7.80 (d, *J* = 8.8 Hz, 1 H), 7.41 (dd, *J* = 8.3, 4.2 Hz, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -62.4 (s, 3 F); ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 152.31, 148.95, 136.66, 130.55, 128.24 (q, *J* = 32.6 Hz), 127.01, 125.63 (q, *J* = 4.4 Hz), 124.93 (q, *J* = 3.0 Hz), 123.84 (q, *J* = 272.3 Hz), 122.10 ppm.

1-(Trifluoromethyl)isoquinoline[8] 3i



White solid (69 mg, 70%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.58 (d, *J* = 5.5 Hz, 1 H), 8.30 (d, *J* = 8.5 Hz, 1 H), 7.92 (d, *J* = 8.1 Hz, 1 H), 7.84 (d, *J* = 5.6 Hz, 1 H), δ 7.74 (dt, *J* = 15.4, 7.0 Hz, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -63.0 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ

146.42 (q, J = 33.2 Hz), 140.76, 137.14, 130.90, 128.84, 127.52, 124.63 (q, J = 2.9 Hz), 124.59, 124.55, 122.24 (q, J = 276.2 Hz) ppm.

Reference

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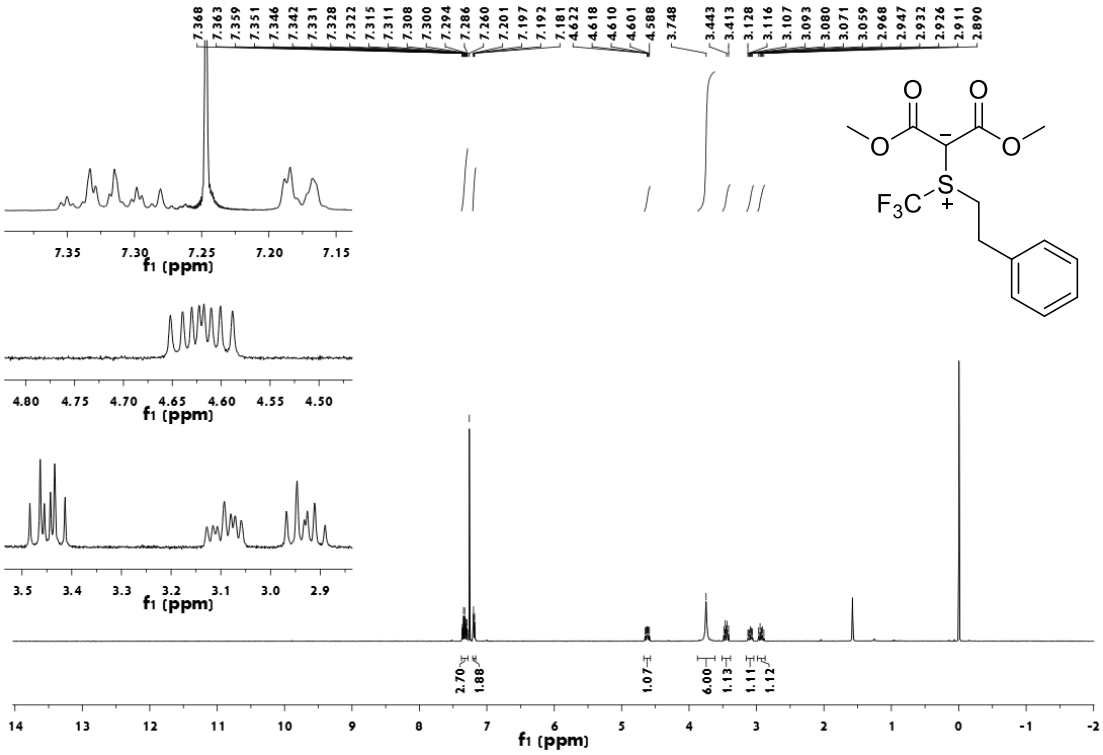
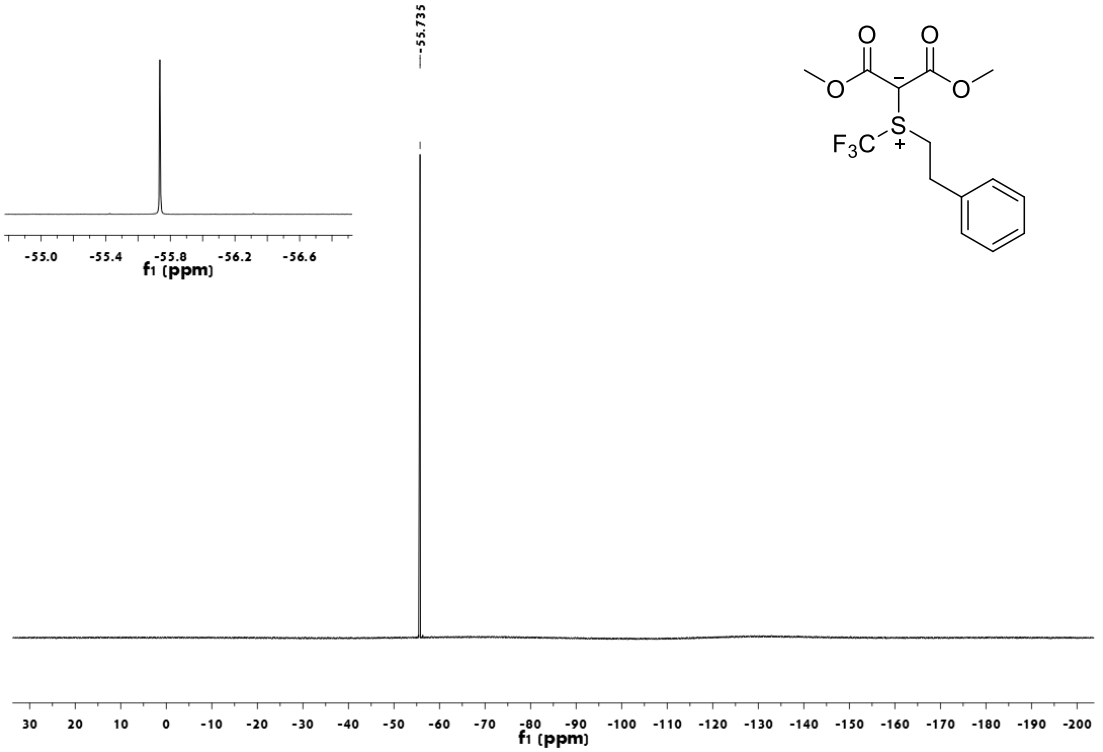
^{1}H NMR spectrum of trifluoromethyl-(phenylethyl) bis(carbomethoxy) methylide 1a



^{19}F NMR spectrum of trifluoromethyl-(phenylethyl) bis(carbomethoxy) methylide 1a



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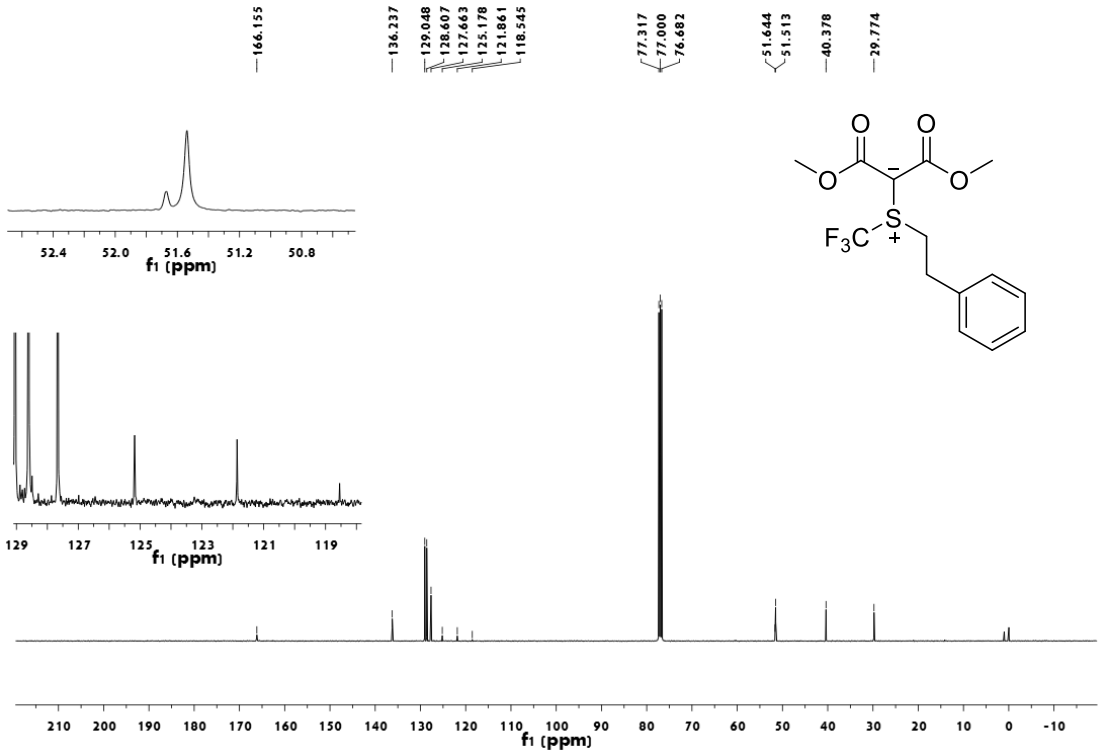
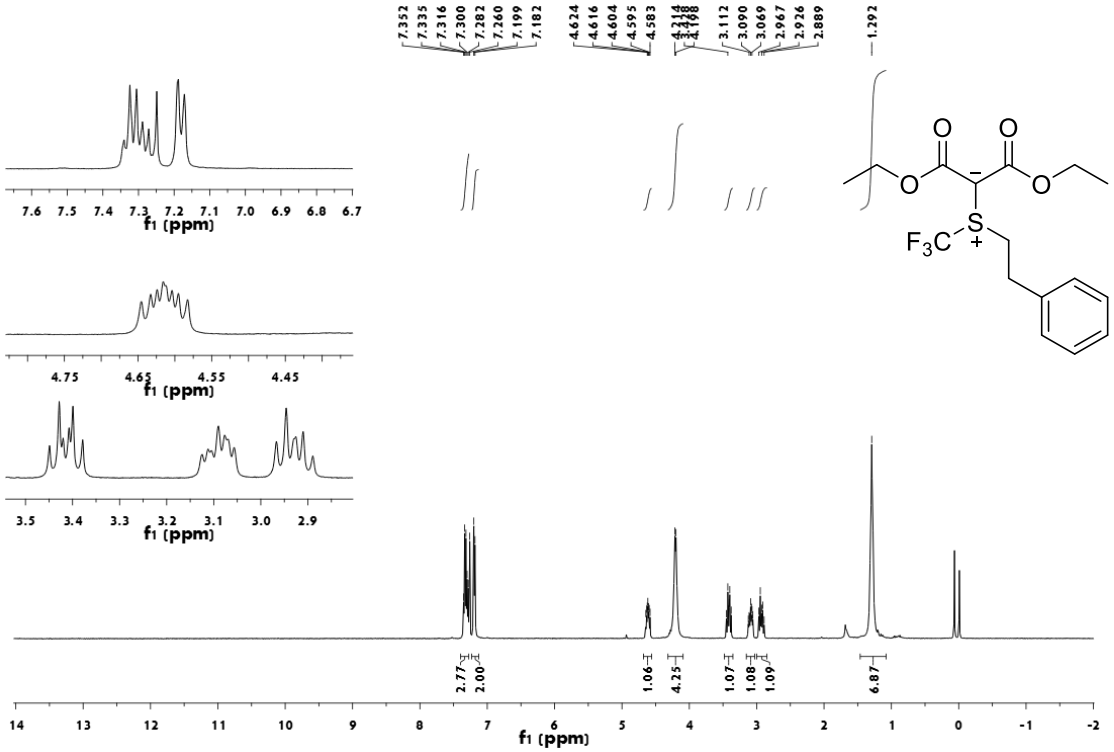
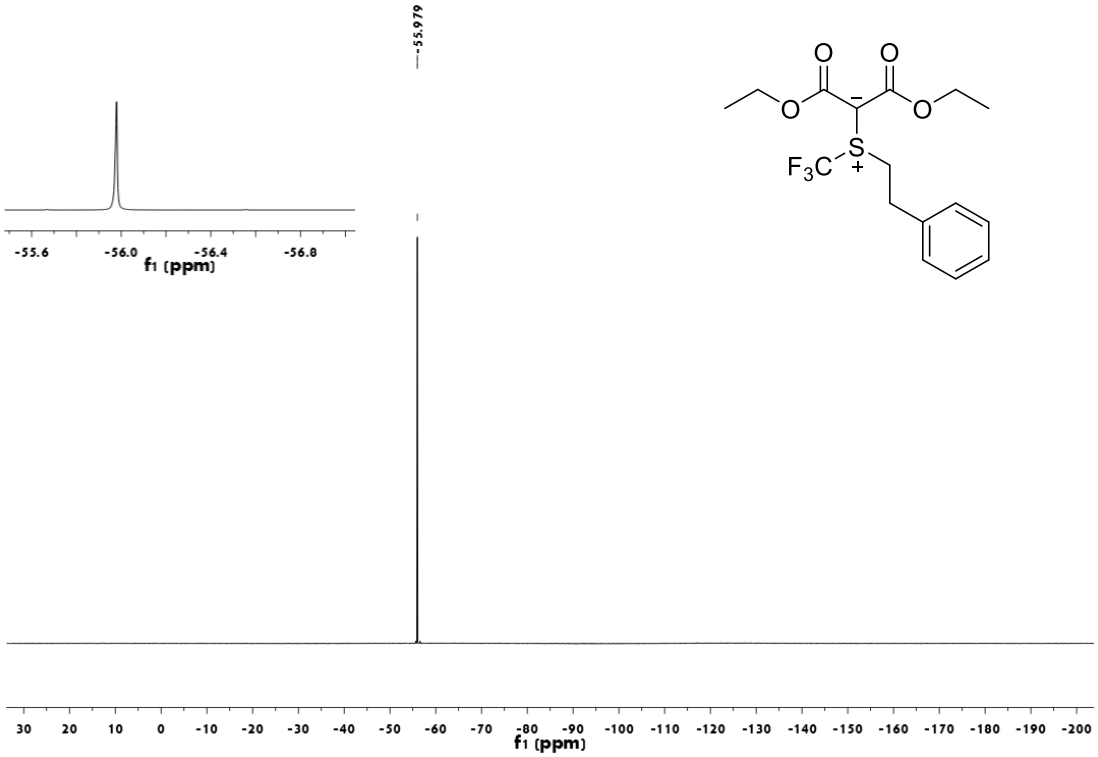


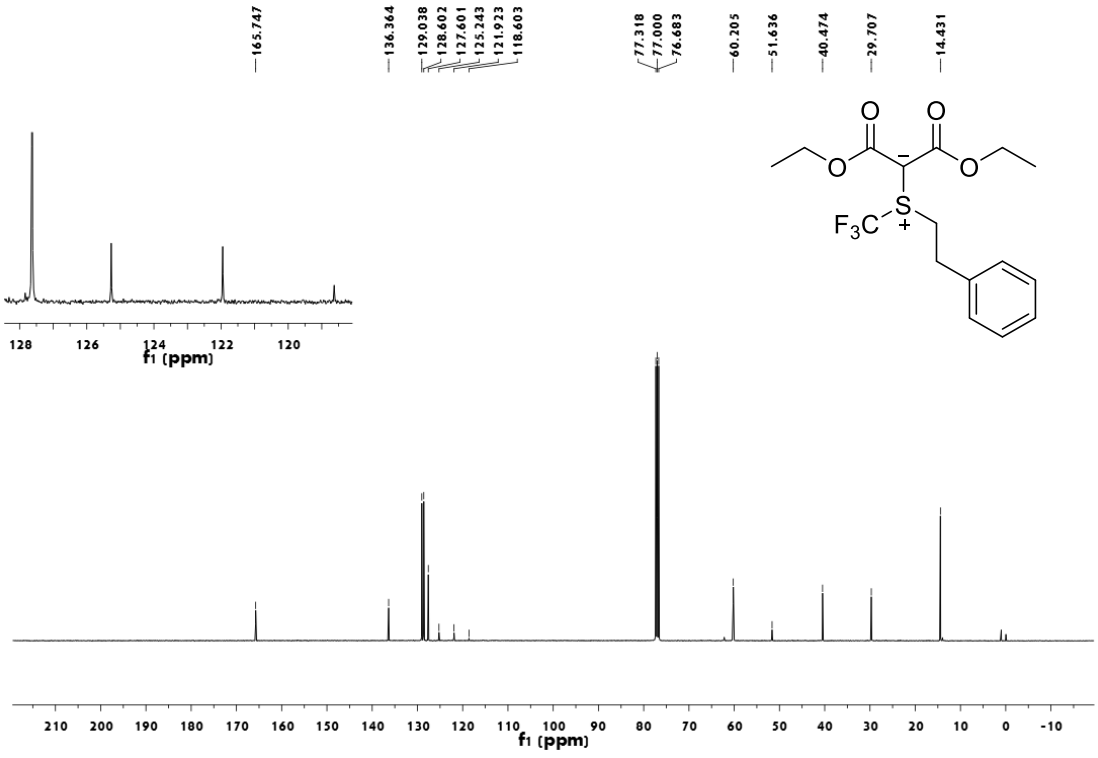
^{1}H NMR spectrum of trifluoromethyl-(phenylethyl) bis(carboethoxy) methylide 1b



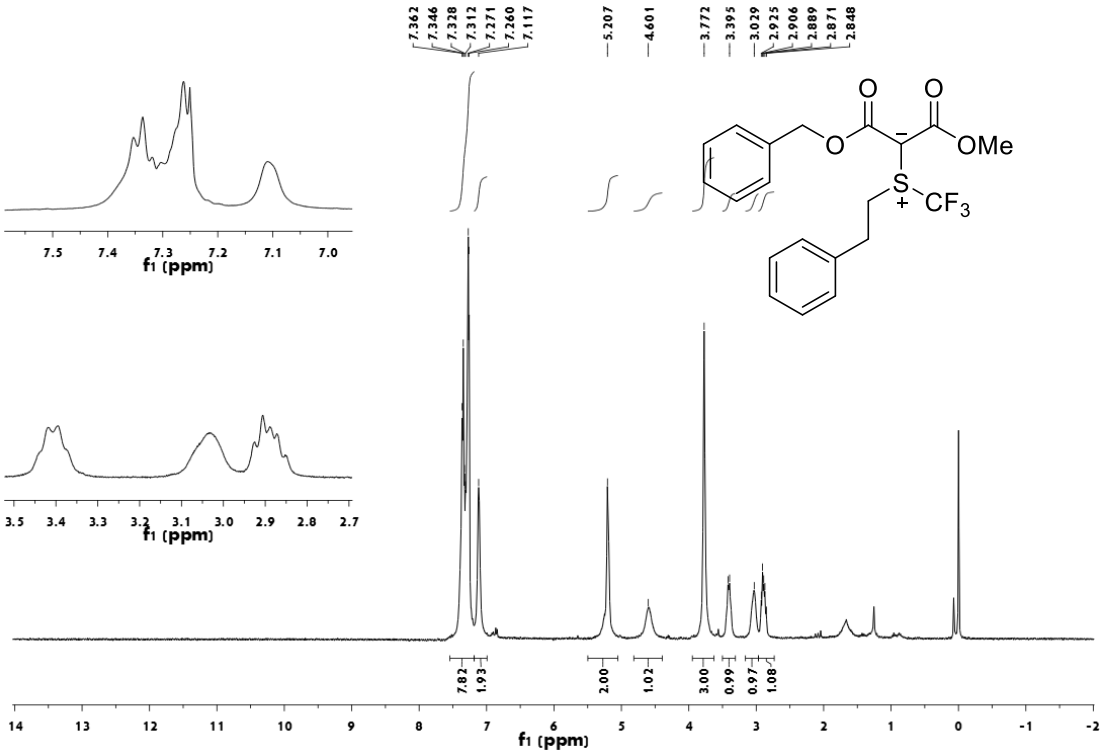
^{19}F NMR spectrum of trifluoromethyl-(phenylethyl) bis(carboethoxy) methylide 1b



^{13}C NMR spectrum of Trifluoromethyl-(phenylethyl) bis(carboethoxy) methylide 1b



^{1}H NMR spectrum of trifluoromethyl-(phenylethyl) carbomethoxy carbobenzyloxy methylide 1c



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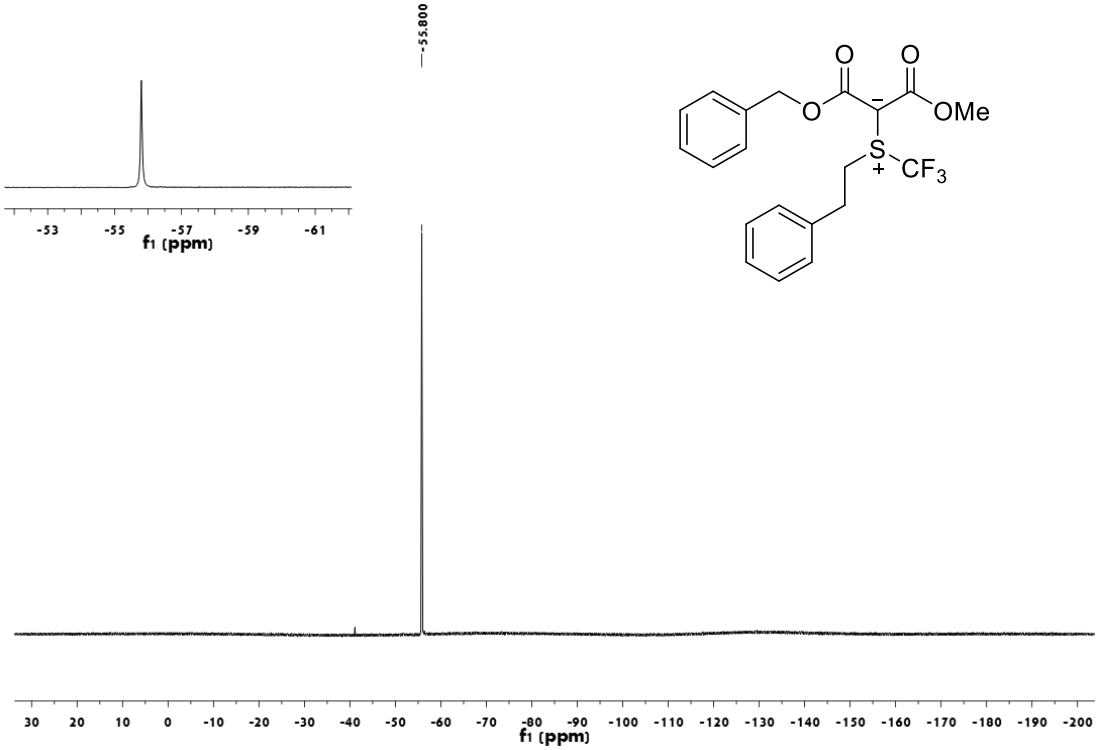

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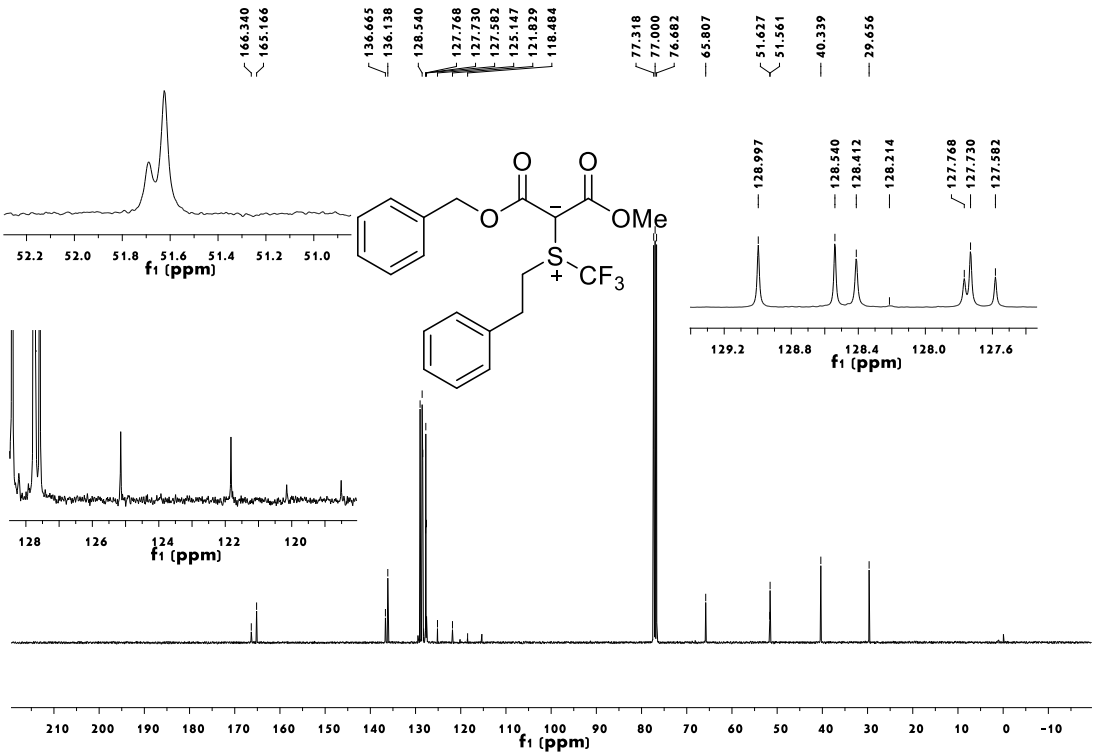
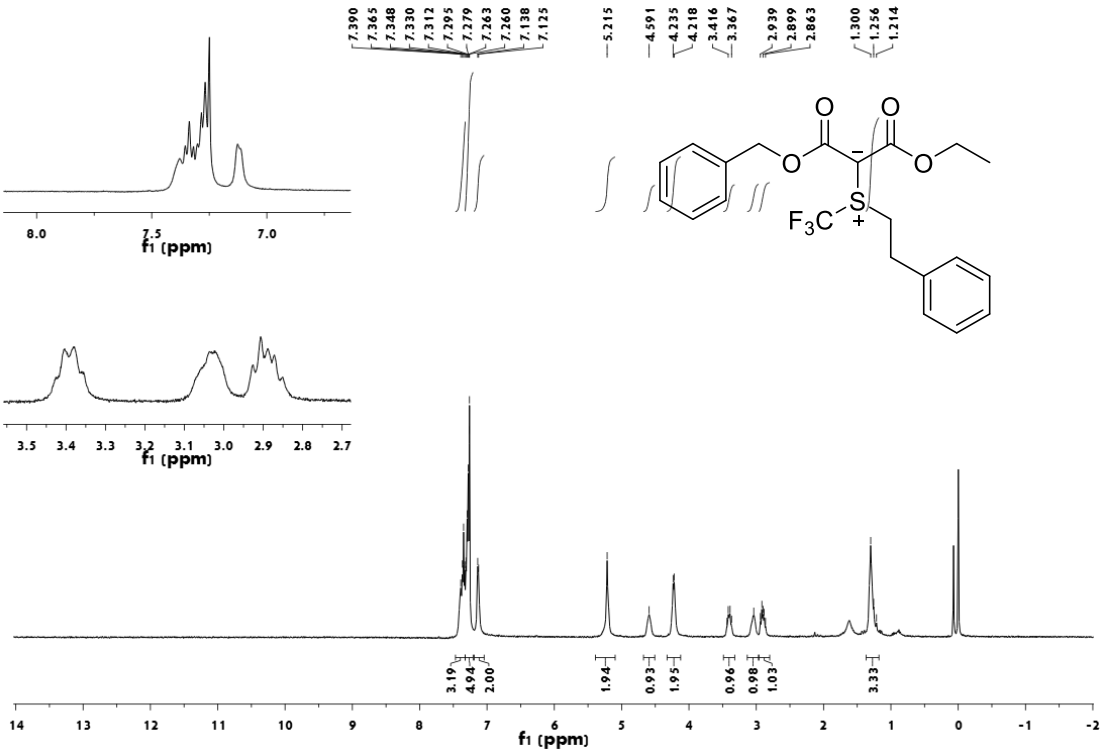
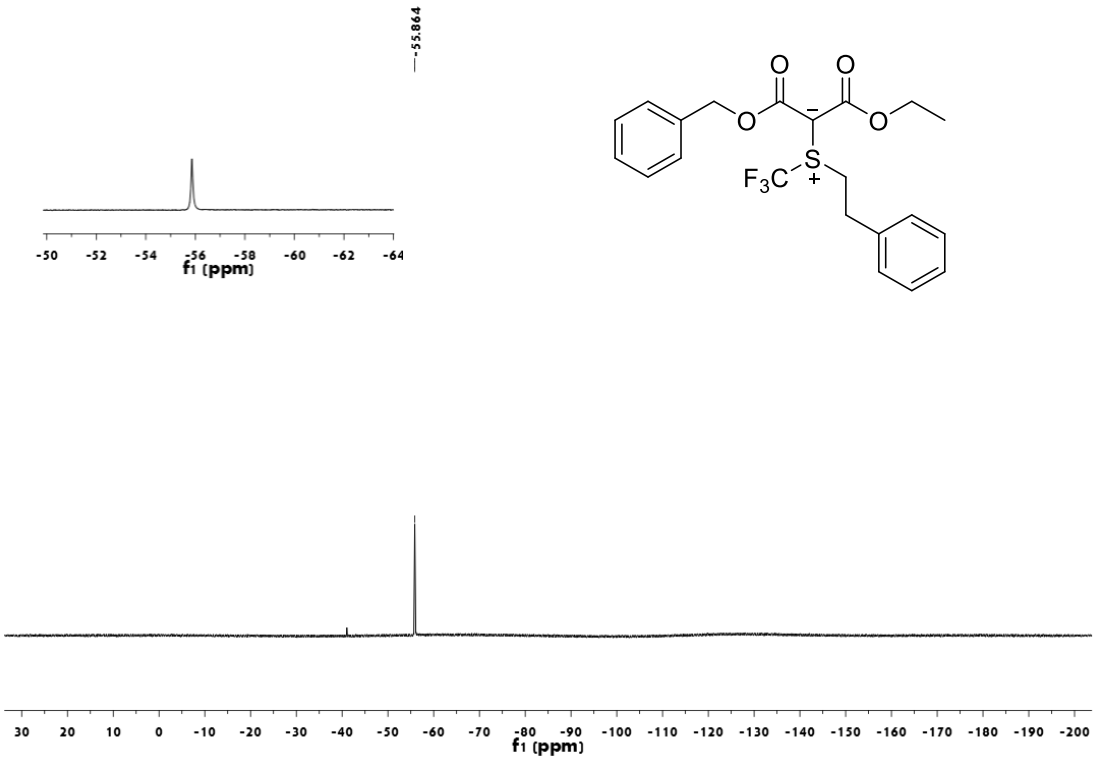


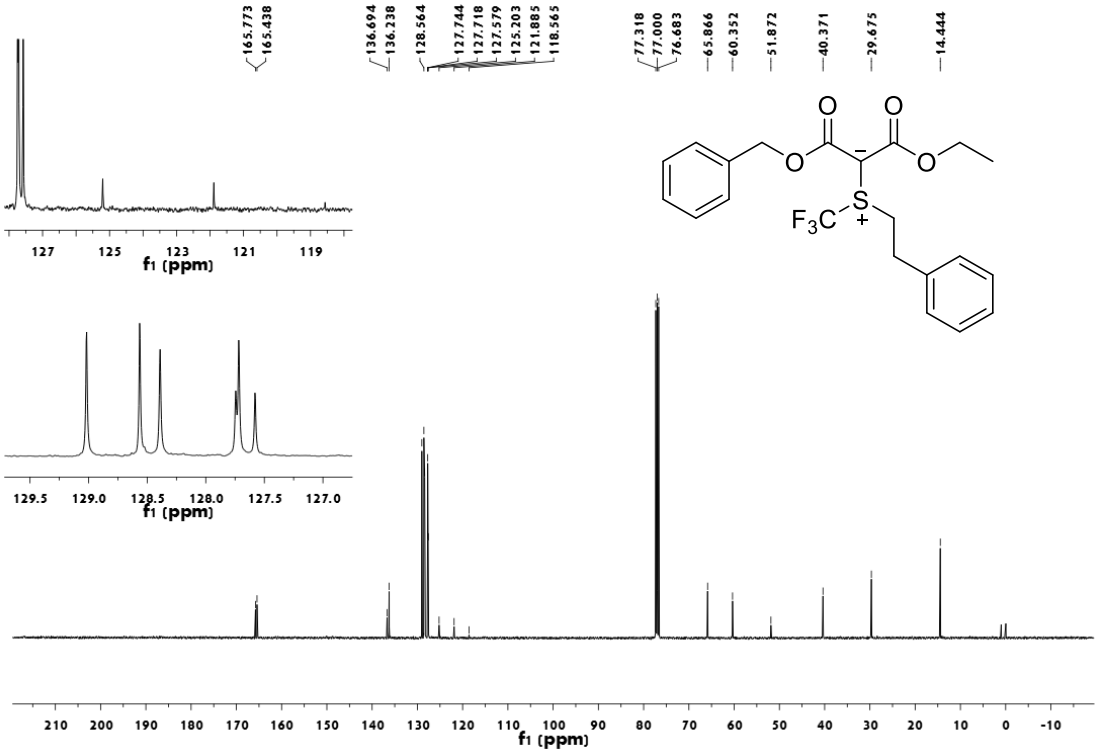
^{1}H NMR spectrum of trifluoromethyl-(phenylethyl) carboethoxy carbobenzyloxy methylide 1d



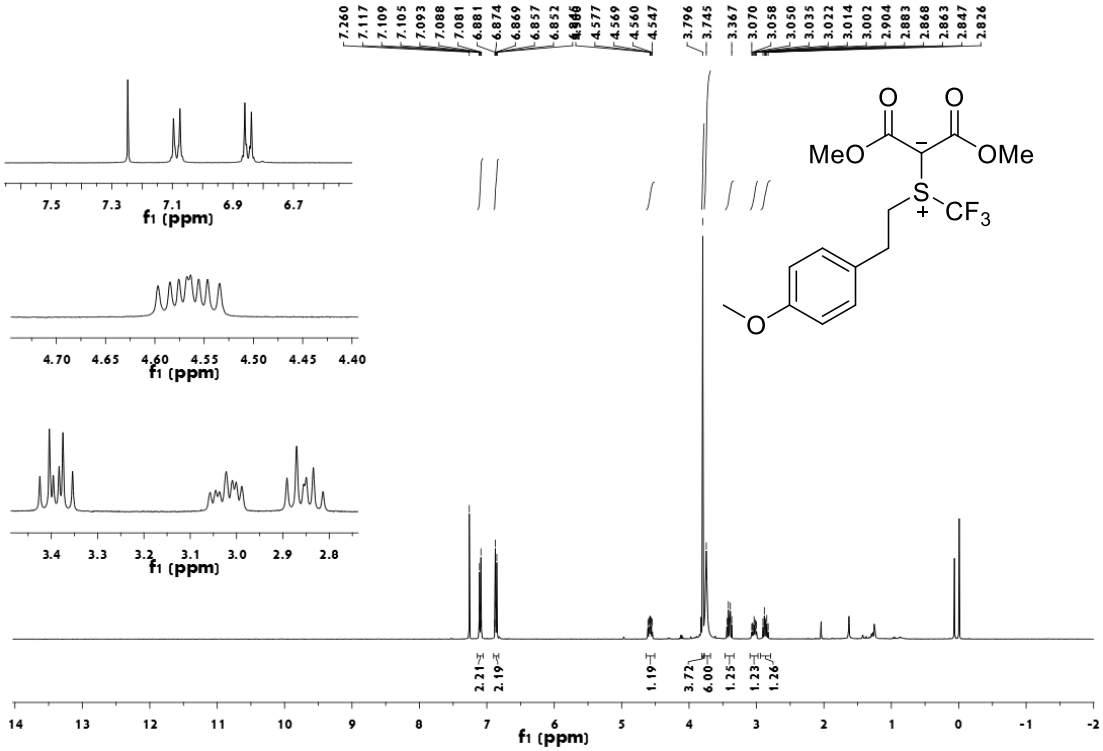
^{19}F NMR spectrum of trifluoromethyl-(phenylethyl) carboethoxy carbobenzyloxy methylide 1d



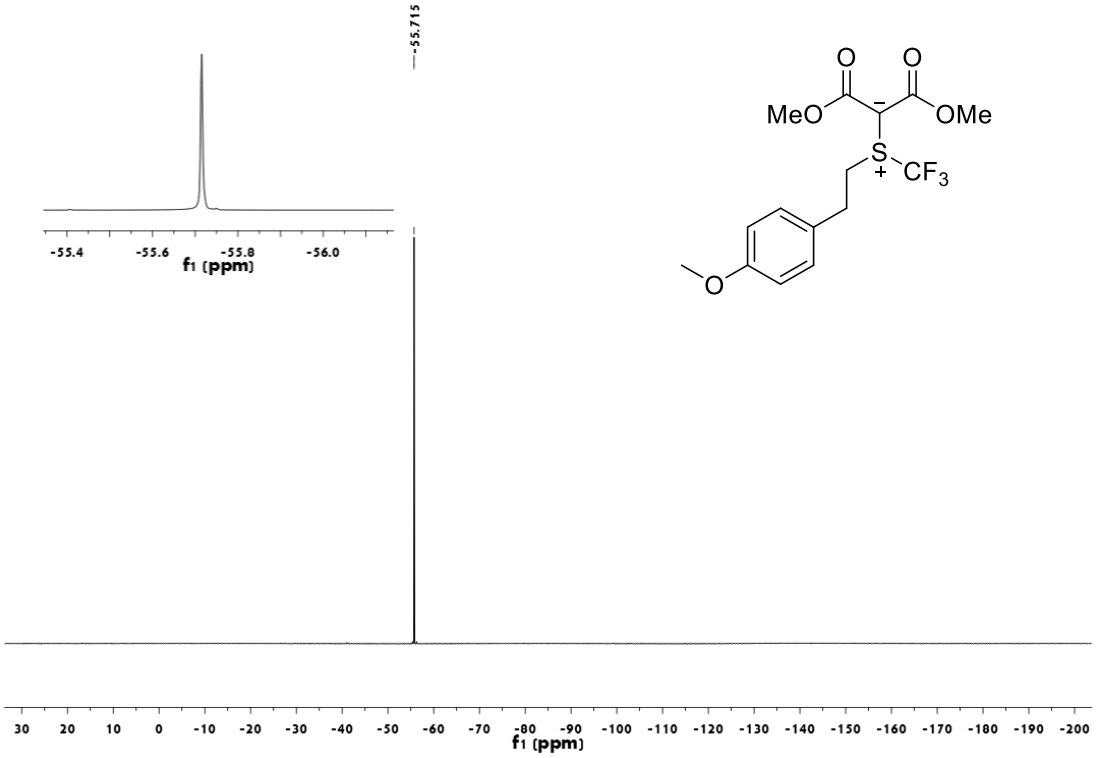
^{13}C NMR spectrum of trifluoromethyl-(phenylethyl) carboethoxy carbobenzyloxy methylide 1d



^{1}H NMR spectrum of trifluoromethyl-(4-methoxyphenyl)ethyl bis(carbomethoxy) methylide 1e



^{19}F NMR spectrum of trifluoromethyl-(4-methoxyphenyl)ethyl bis(carbomethoxy) methylide 1e



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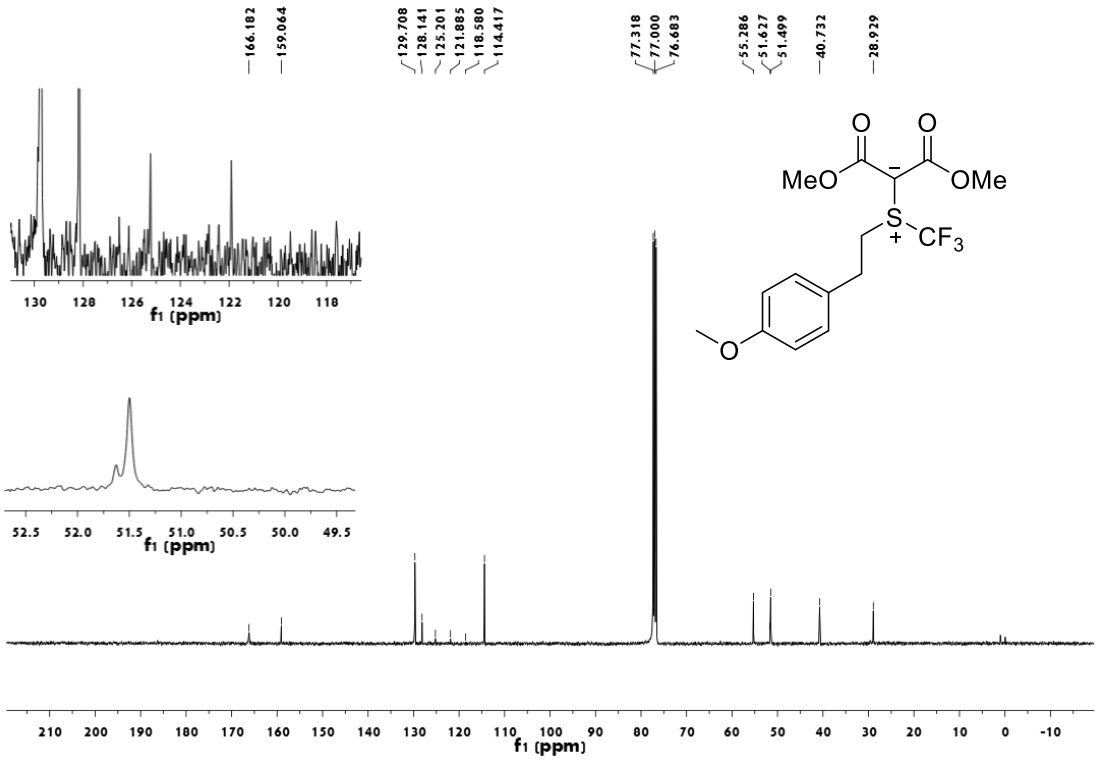
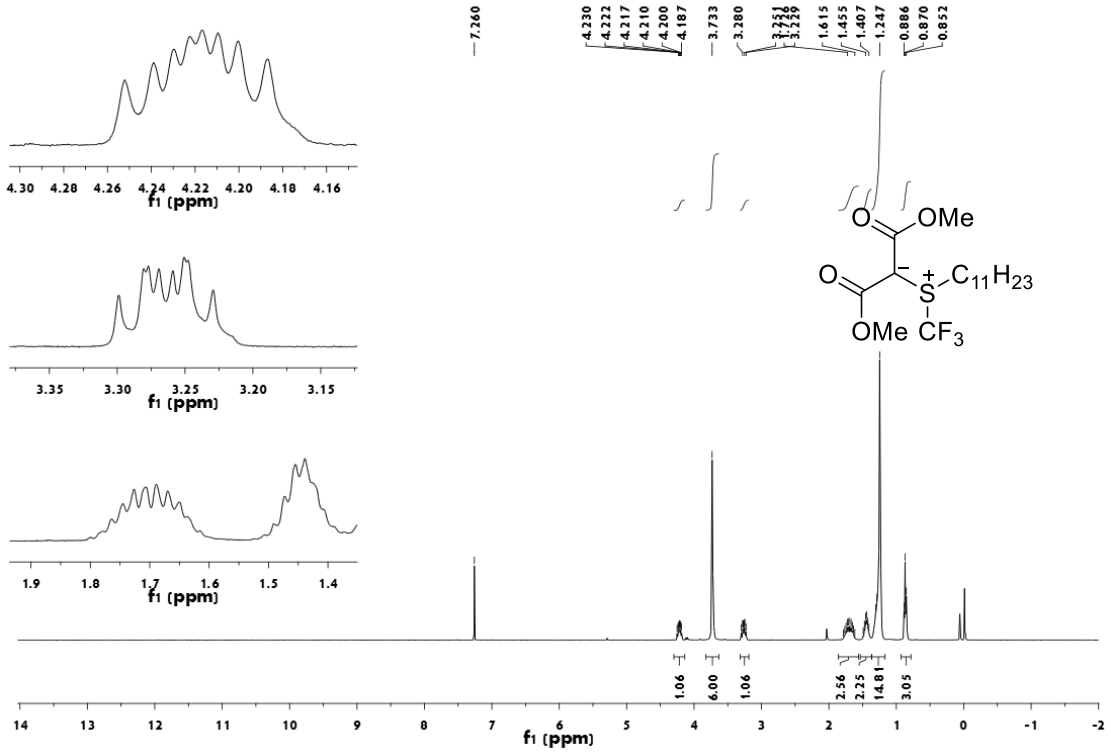
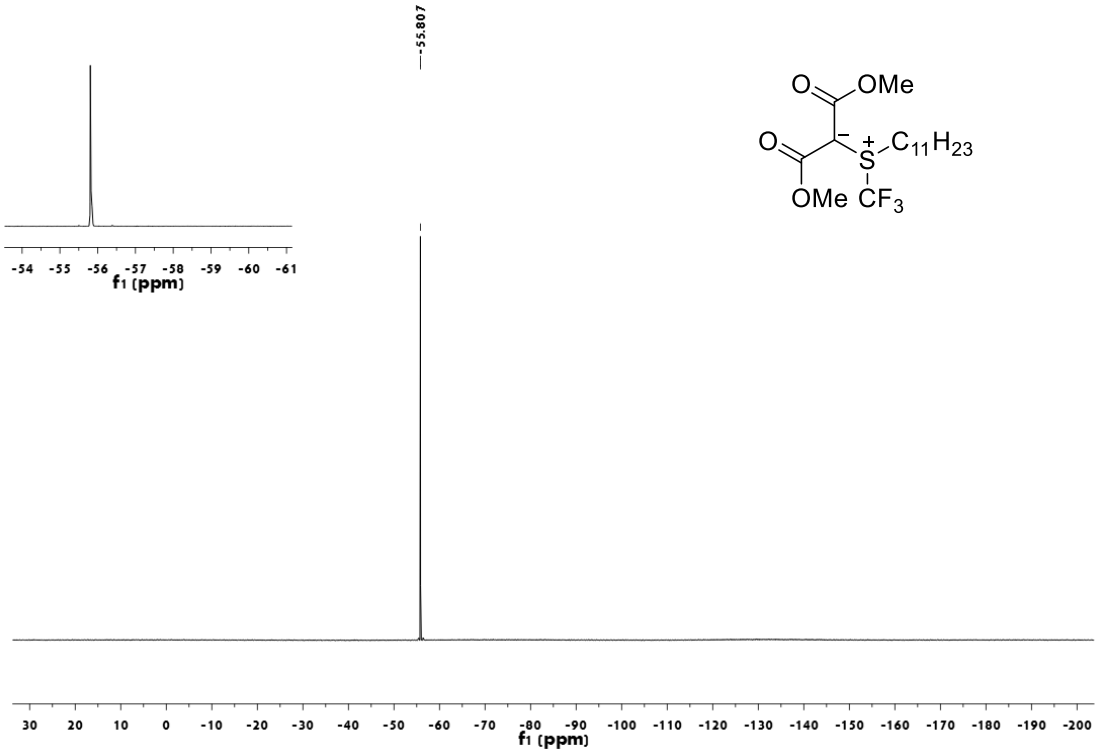


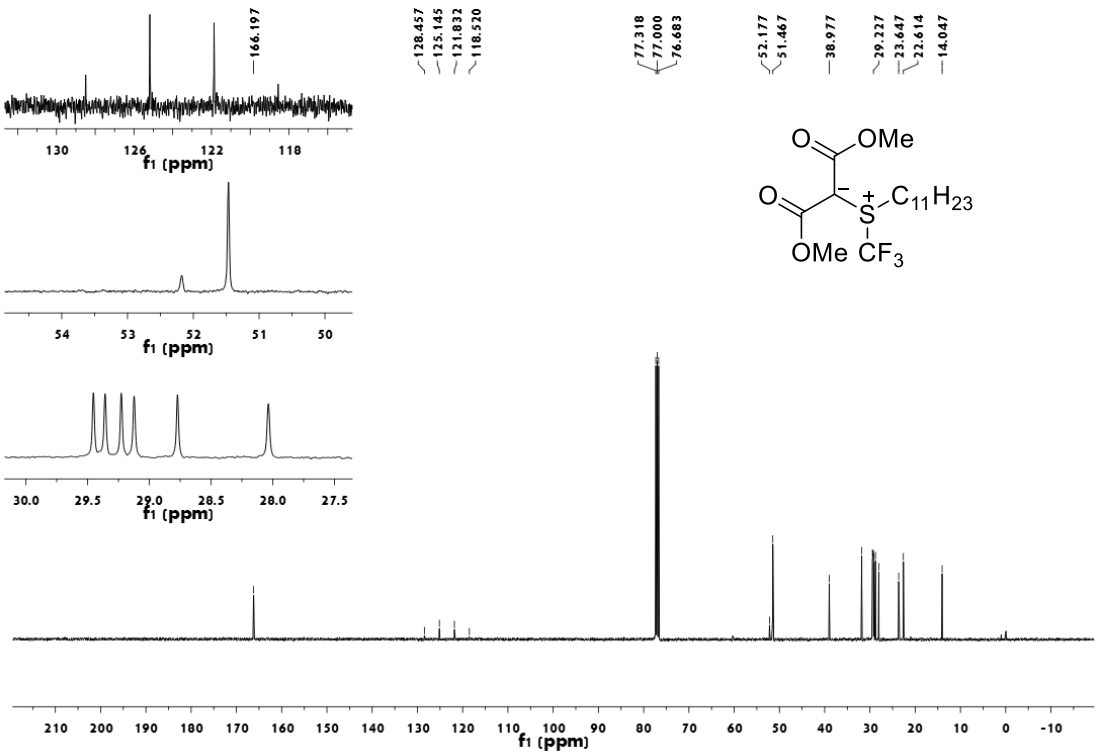
^{1}H NMR spectrum of trifluoromethyl-undecyl bis(carbomethoxy) methylide 1f



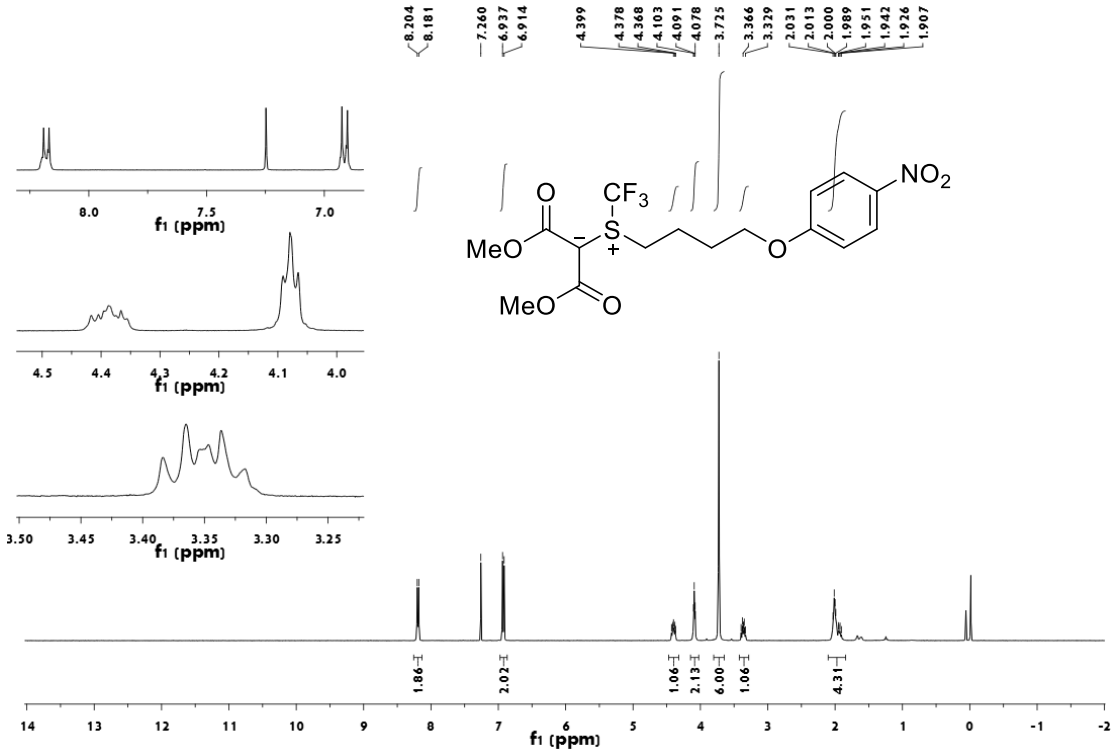
^{19}F NMR spectrum of trifluoromethyl-undecyl bis(carbomethoxy) methylide 1f



^{13}C NMR spectrum of trifluoromethyl-undecyl bis(carbomethoxy) methylide 1f



^{1}H NMR spectrum of trifluoromethyl-(4-(4-nitrophenoxy)butyl) bis(carbomethoxy) methylide 1g



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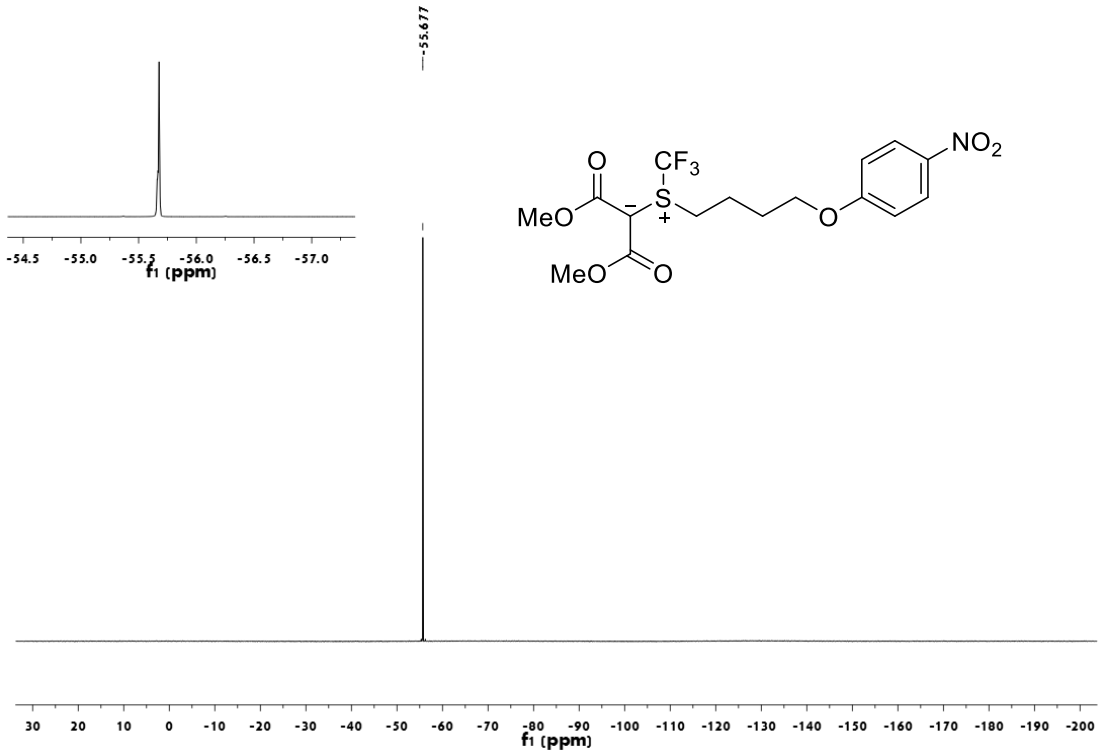
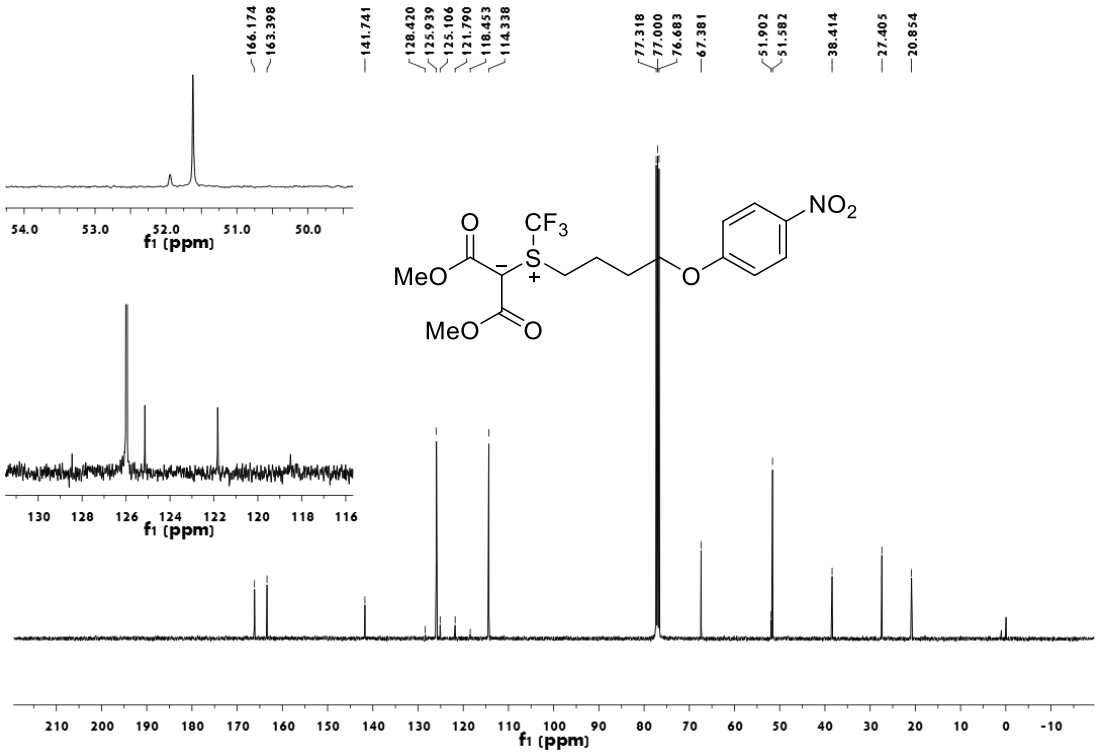
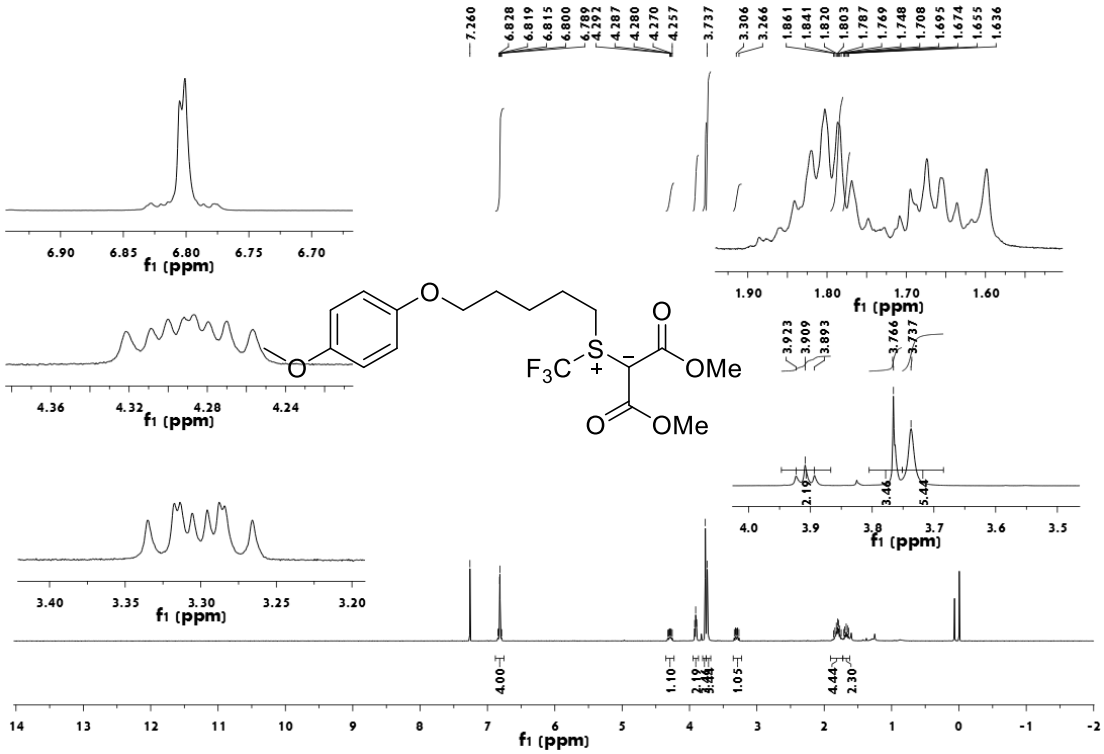


^{13}C NMR spectrum of trifluoromethyl-(4-(4-nitrophenoxy)butyl) bis(carbomethoxy) methylide 1g



^{1}H NMR spectrum of trifluoromethyl-(5-(4-methoxyphenoxy)pentyl) bis(carbomethoxy) methylide 1h



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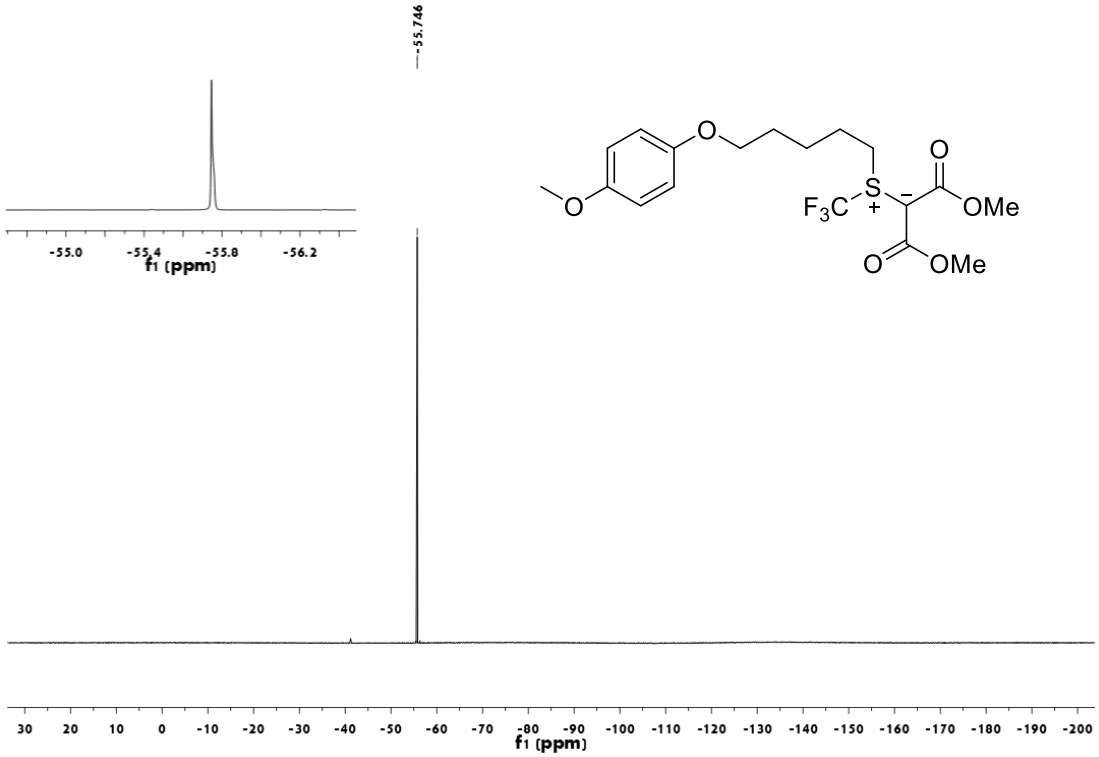
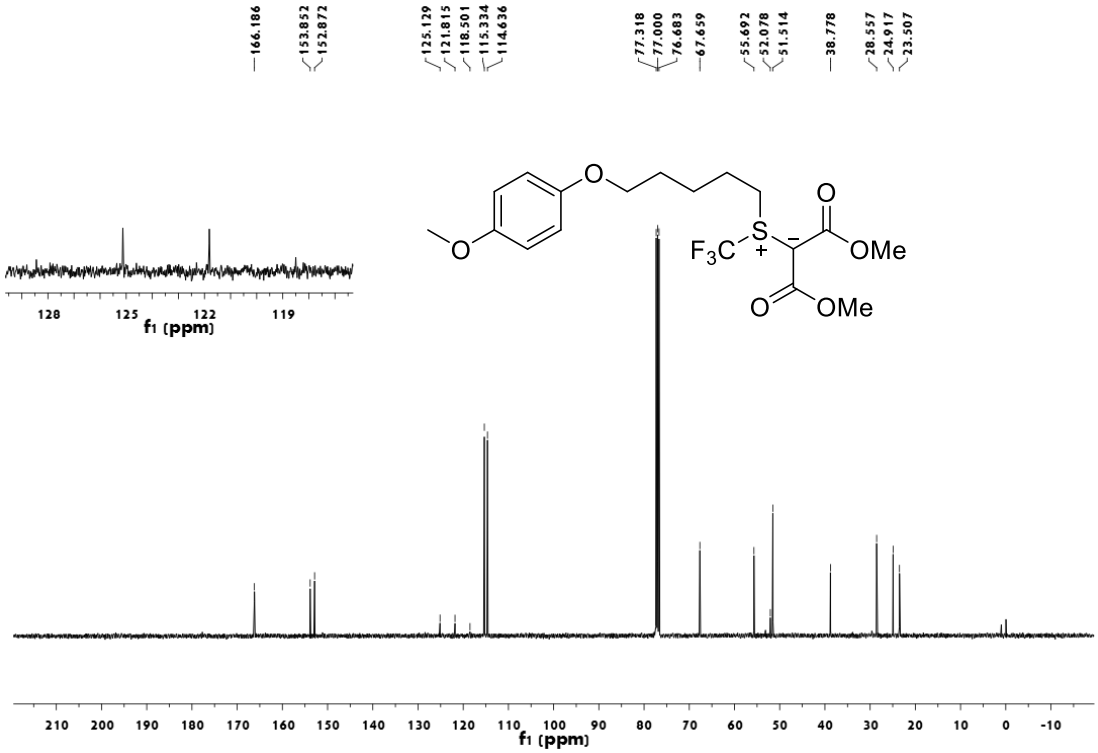
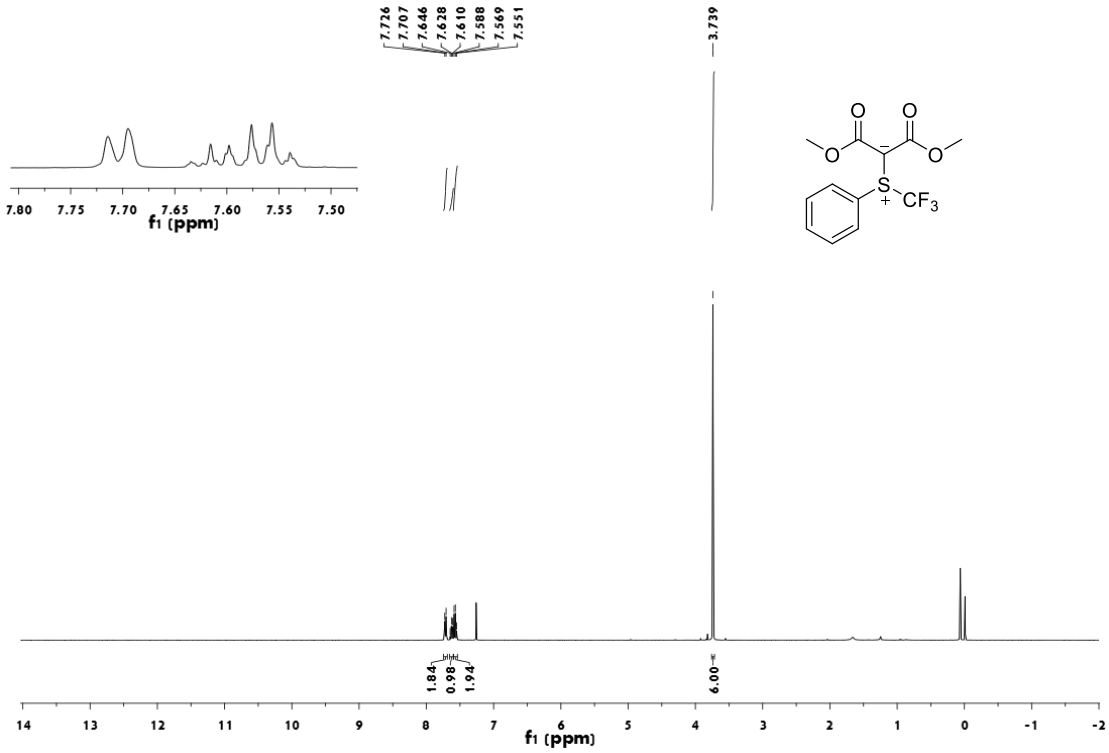


^{13}C NMR spectrum of trifluoromethyl-(5-(4-methoxyphenoxy)pentyl) bis(carbomethoxy) methylide 1h



^{1}H NMR spectrum of trifluoromethyl-phenyl bis(carbomethoxy) methylide 1i



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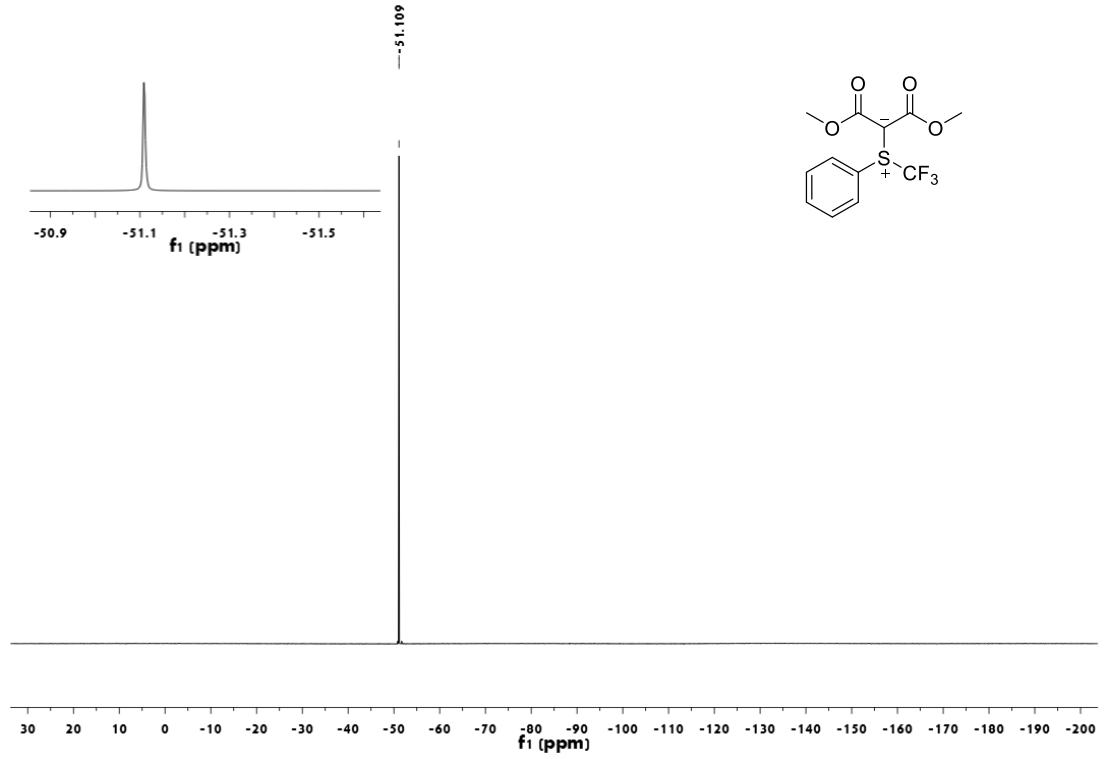
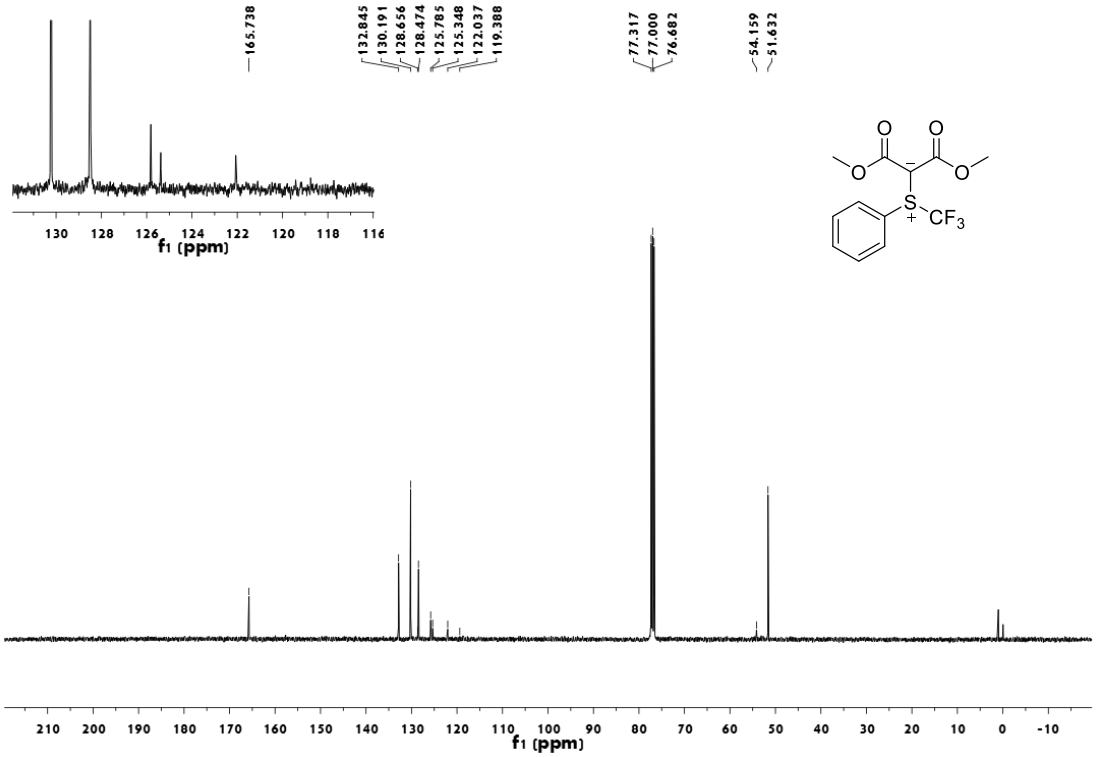
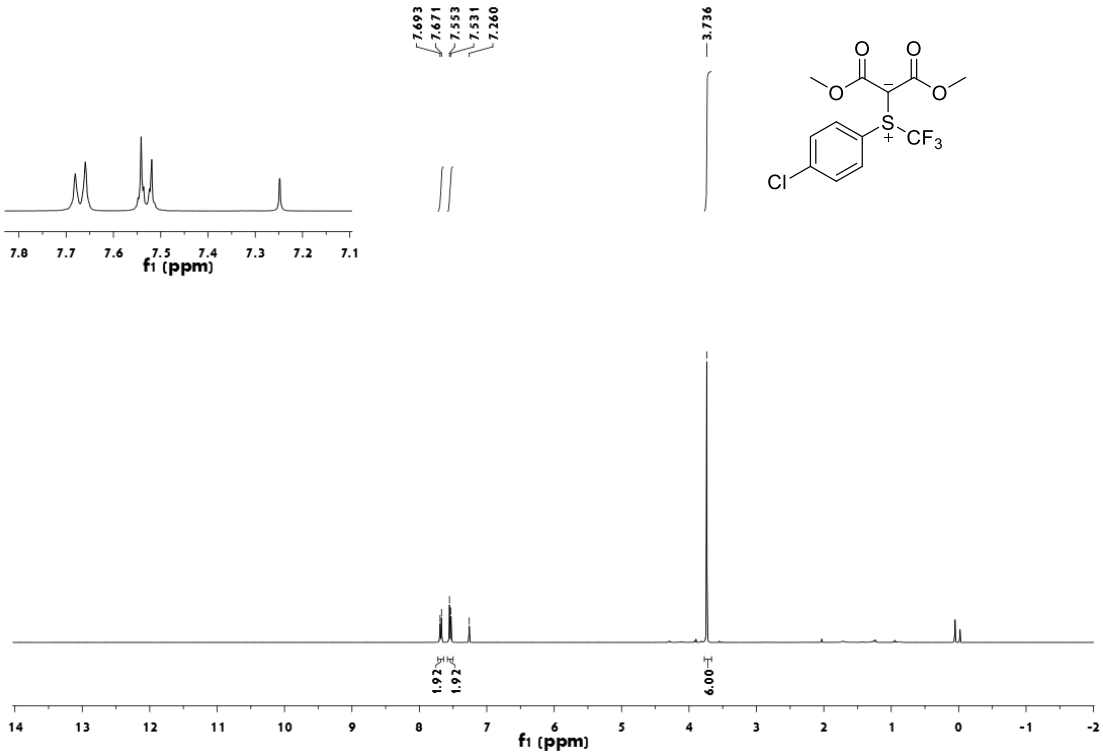


^{13}C NMR spectrum of trifluoromethyl-phenyl bis(carbomethoxy) methylide 1i



^{1}H NMR spectrum of trifluoromethyl-((4-chloro)-phenyl) bis(carbomethoxy) methylide 1j



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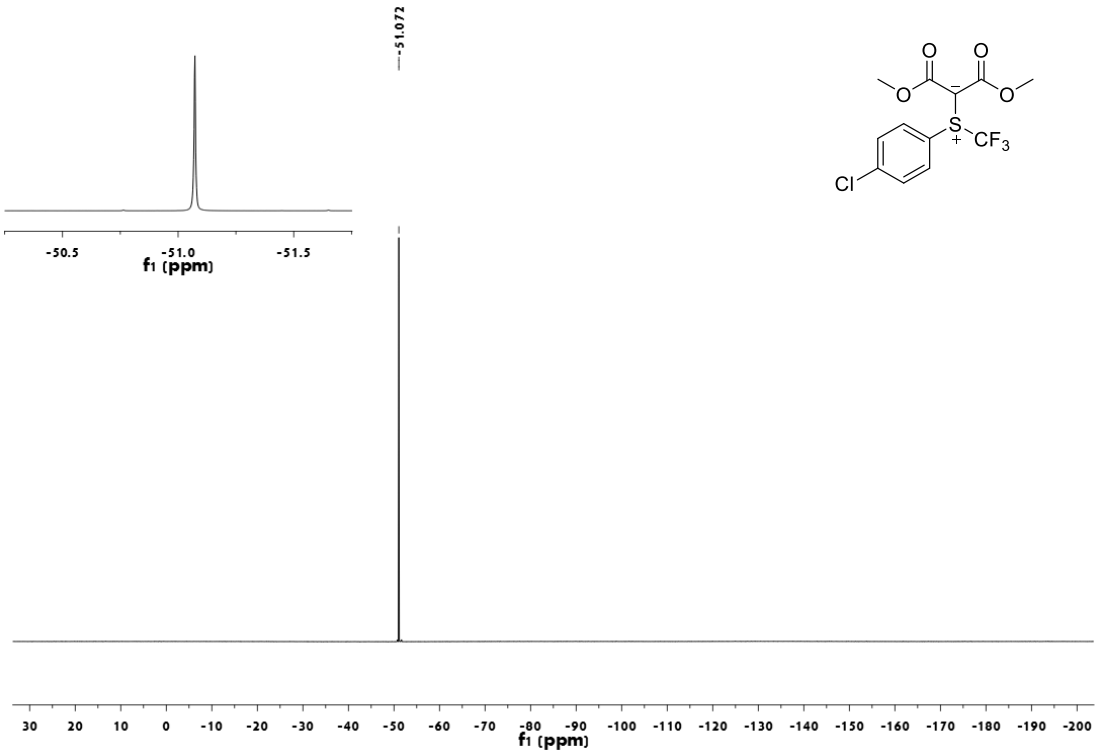
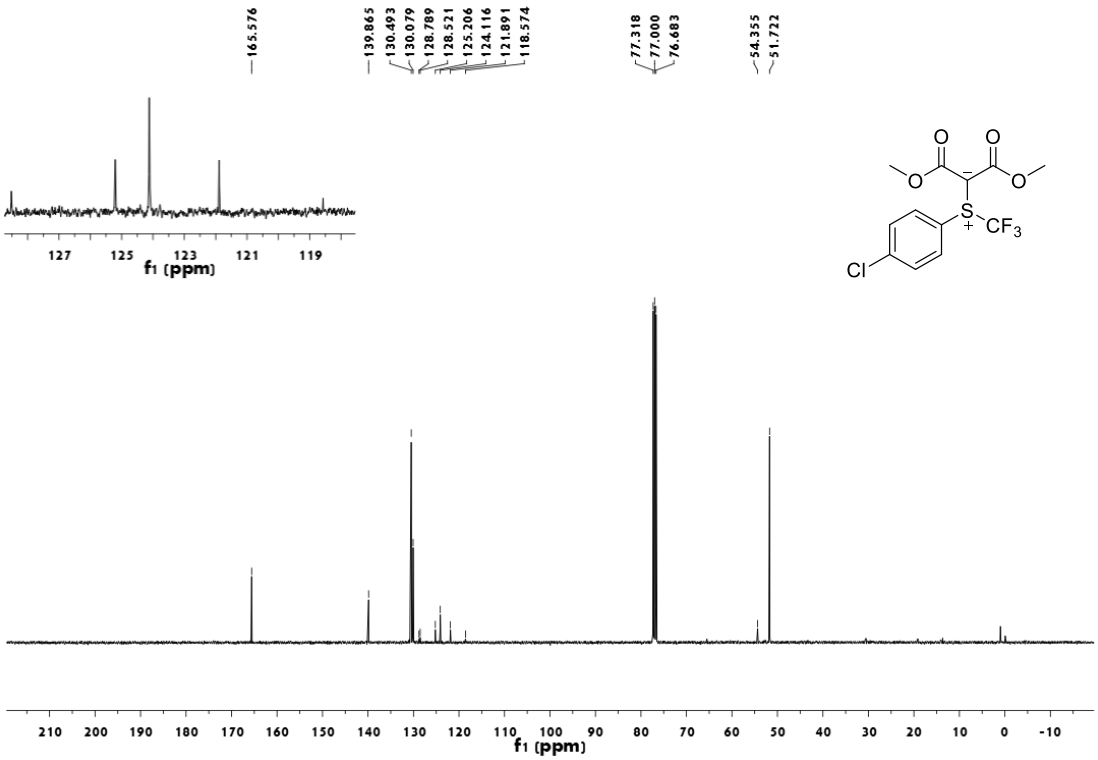
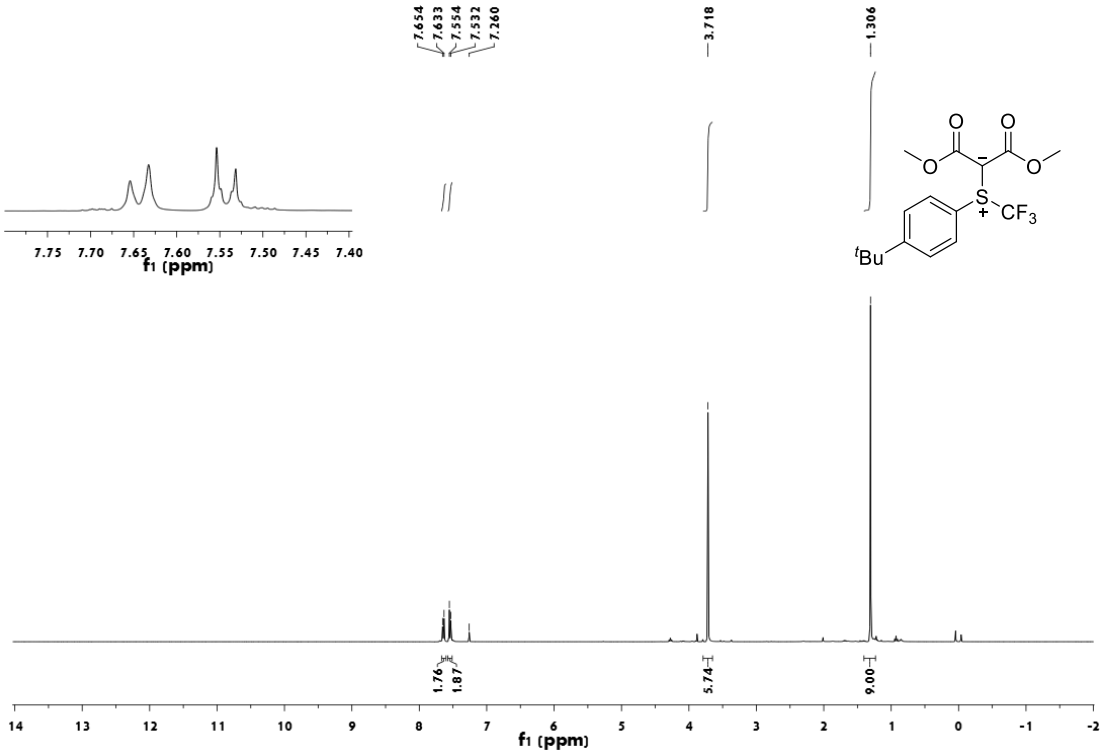


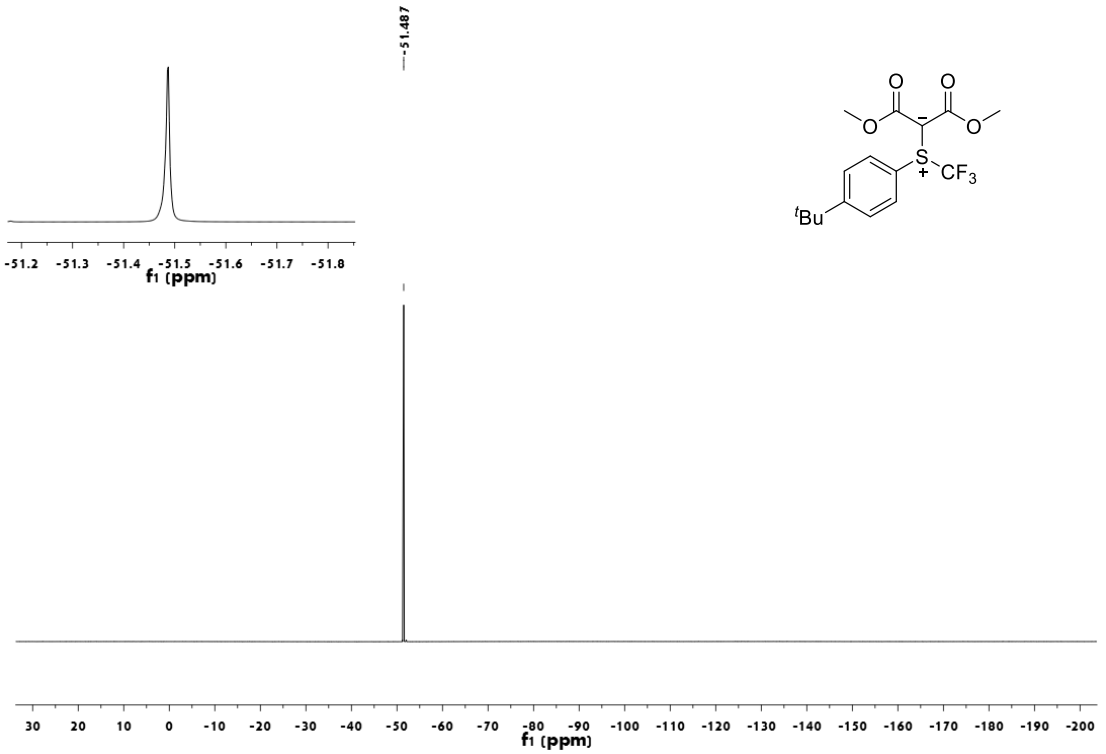
^{13}C NMR spectrum of trifluoromethyl-((4-chloro)-phenyl) bis(carbomethoxy) methylide 1j



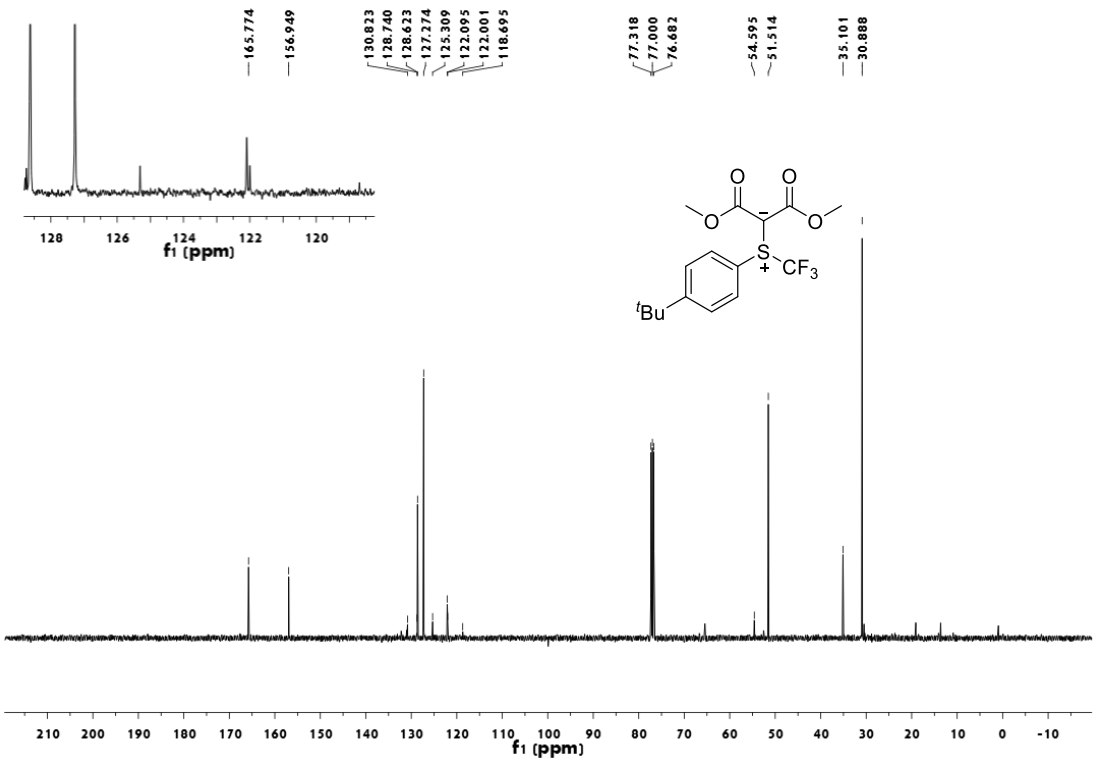
^{1}H NMR spectrum of trifluoromethyl-(4-*tert*-butylphenyl) bis(carbomethoxy) methylide 1k



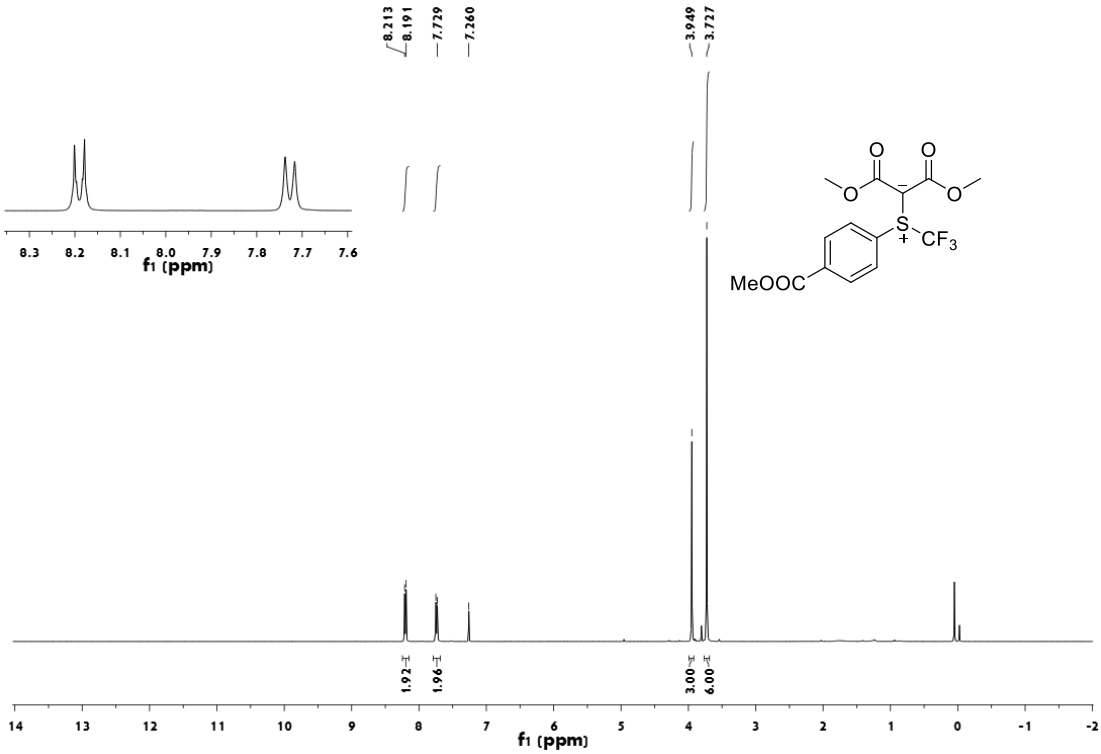
^{19}F NMR spectrum of trifluoromethyl-(4-*tert*-butylphenyl) bis(carbomethoxy) methylide 1k



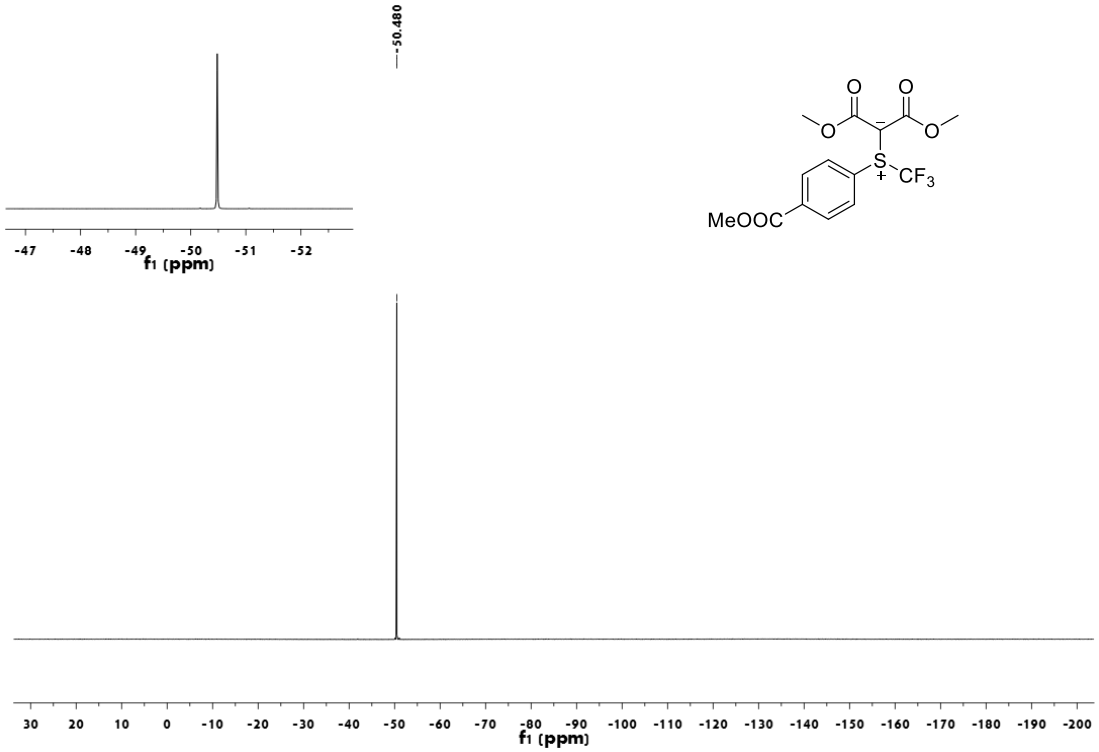
^{13}C NMR spectrum of trifluoromethyl-(4-*tert*-butylphenyl) bis(carbomethoxy) methylide 1k



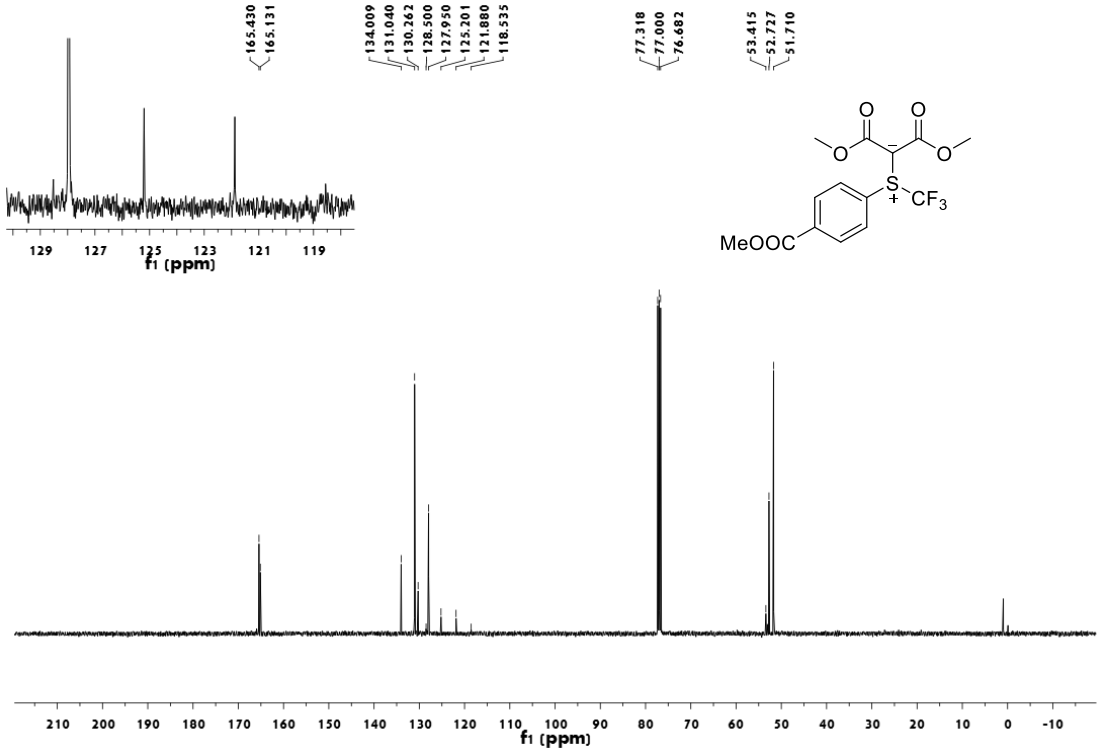
^{1}H NMR spectrum of trifluoromethyl-(4-carbomethoxy-phenyl) bis(carbomethoxy) methylide 1l



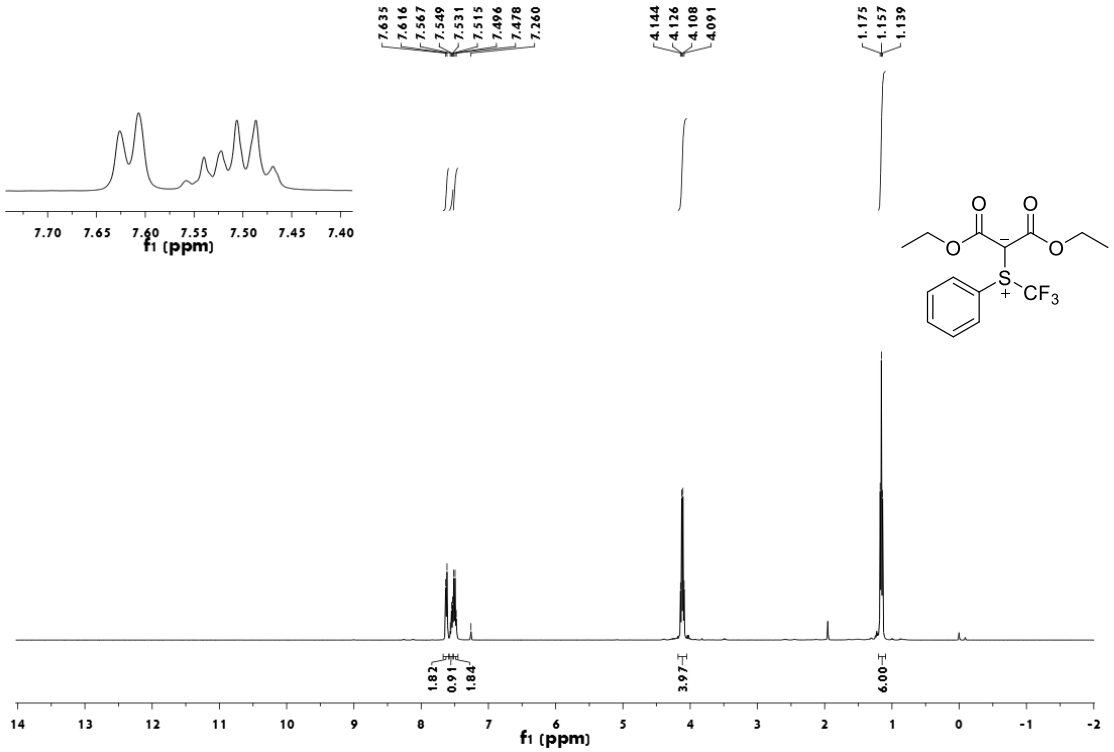
^{19}F NMR spectrum of trifluoromethyl-(4-carbomethoxy-phenyl) bis(carbomethoxy) methylide 1l



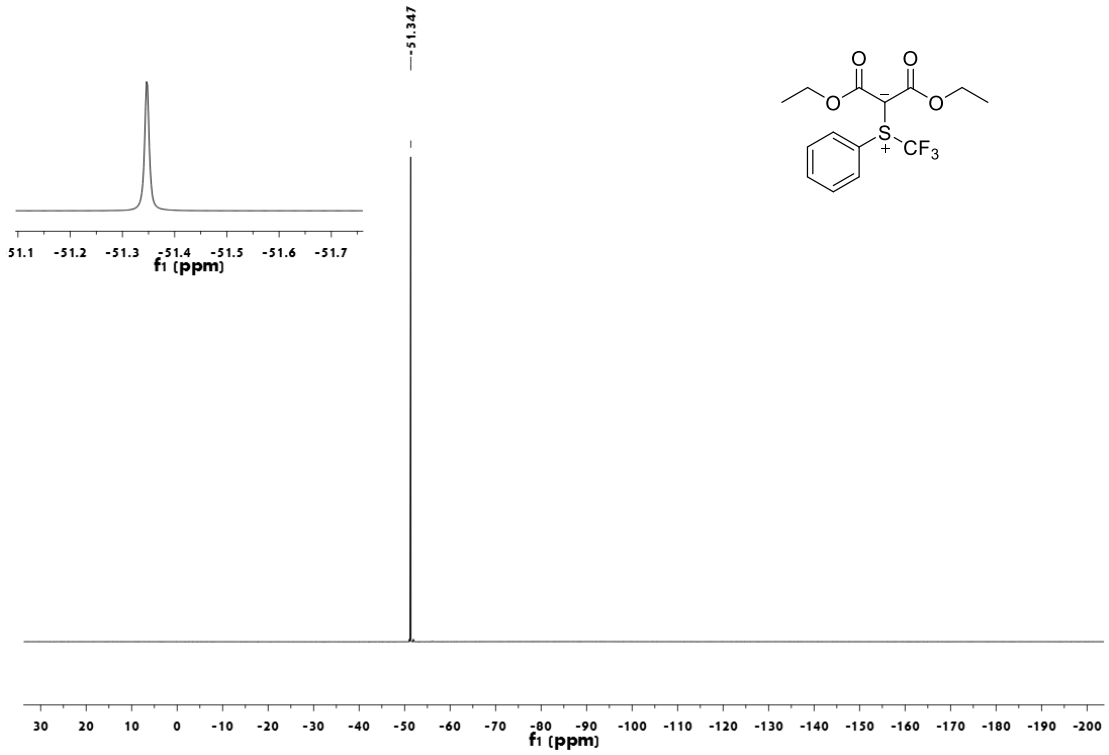
^{13}C NMR spectrum of trifluoromethyl-(4-carbomethoxy-phenyl) bis(carbomethoxy) methylide 1l



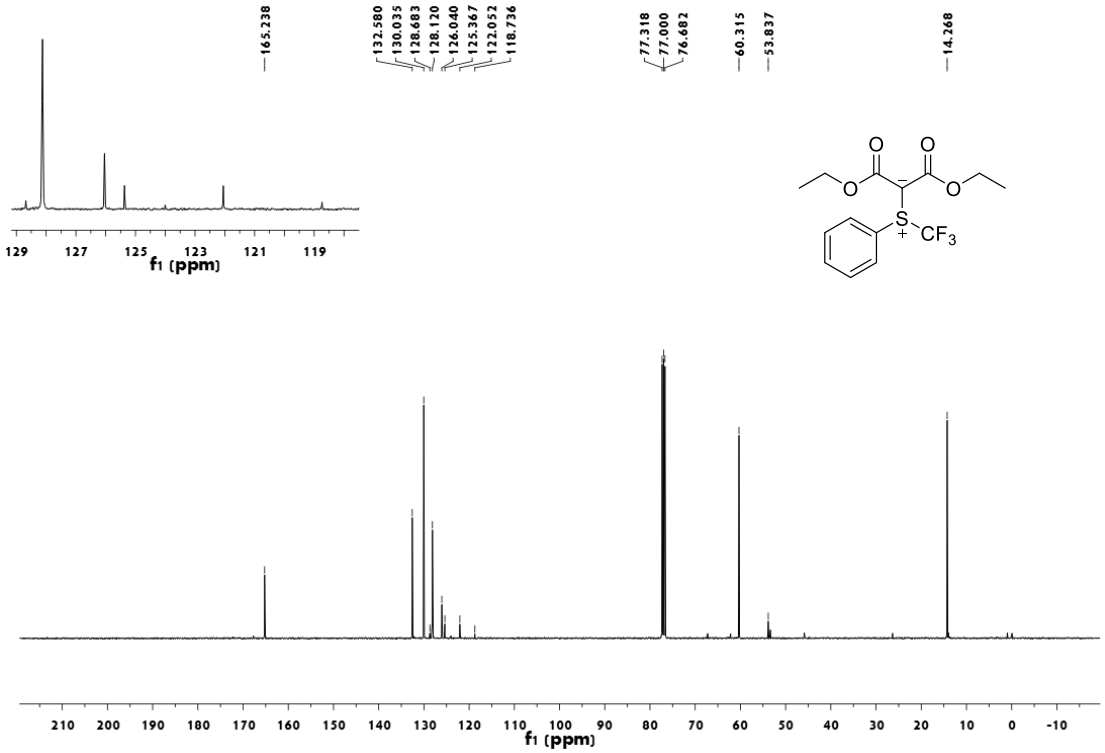
^{1}H NMR spectrum of trifluoromethyl-phenyl bis(carboethoxy) methylide1m



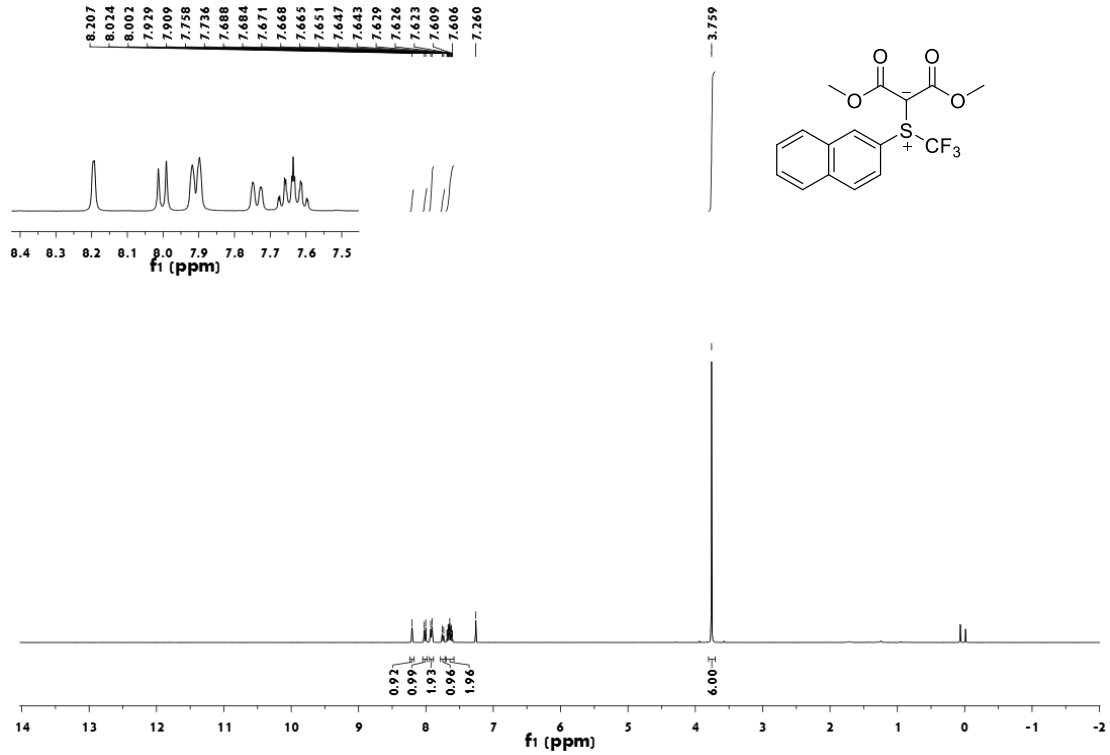
^{19}F NMR spectrum of trifluoromethyl-phenyl bis(carboethoxy) methylide 1m



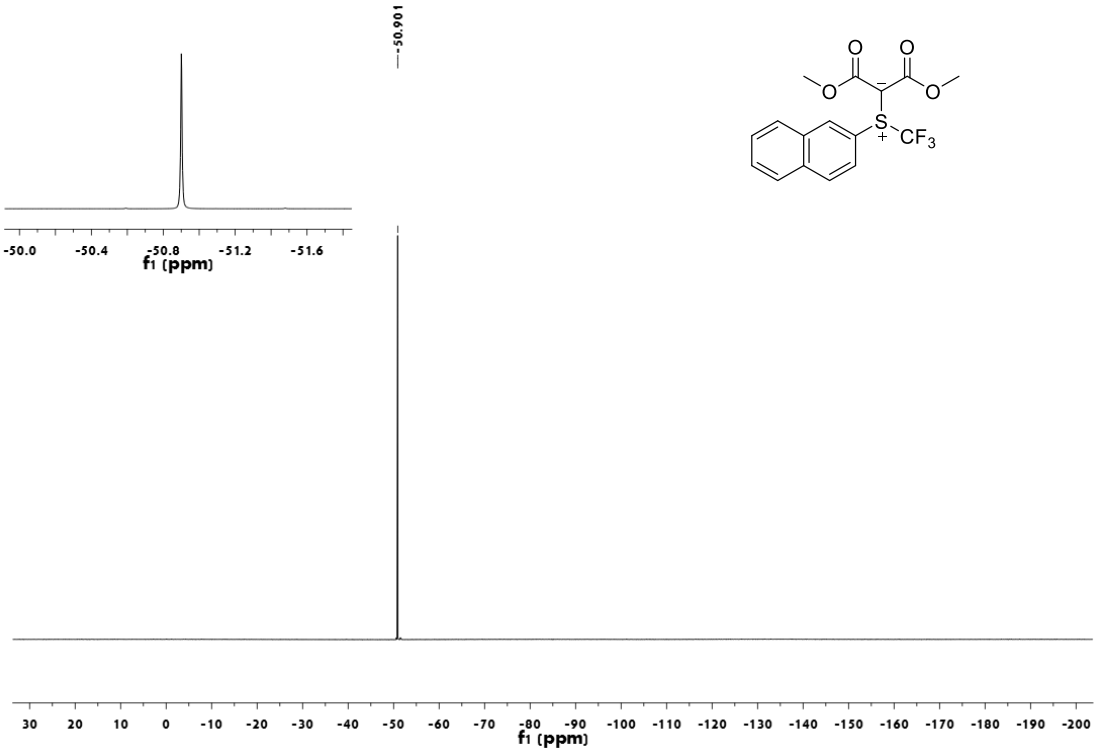
^{13}C NMR spectrum of trifluoromethyl-phenyl bis(carboethoxy) methylide 1m



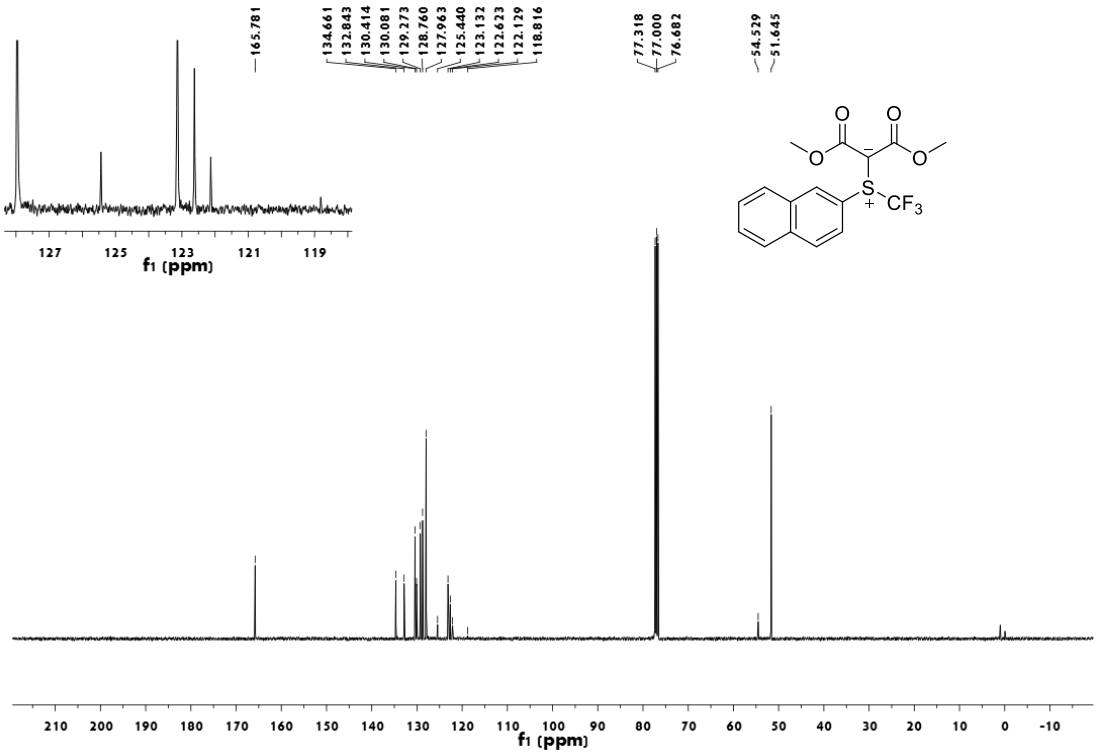
^{1}H NMR spectrum of trifluoromethyl-(naphthalen-2-yl) bis(carbomethoxy) methylide 1n



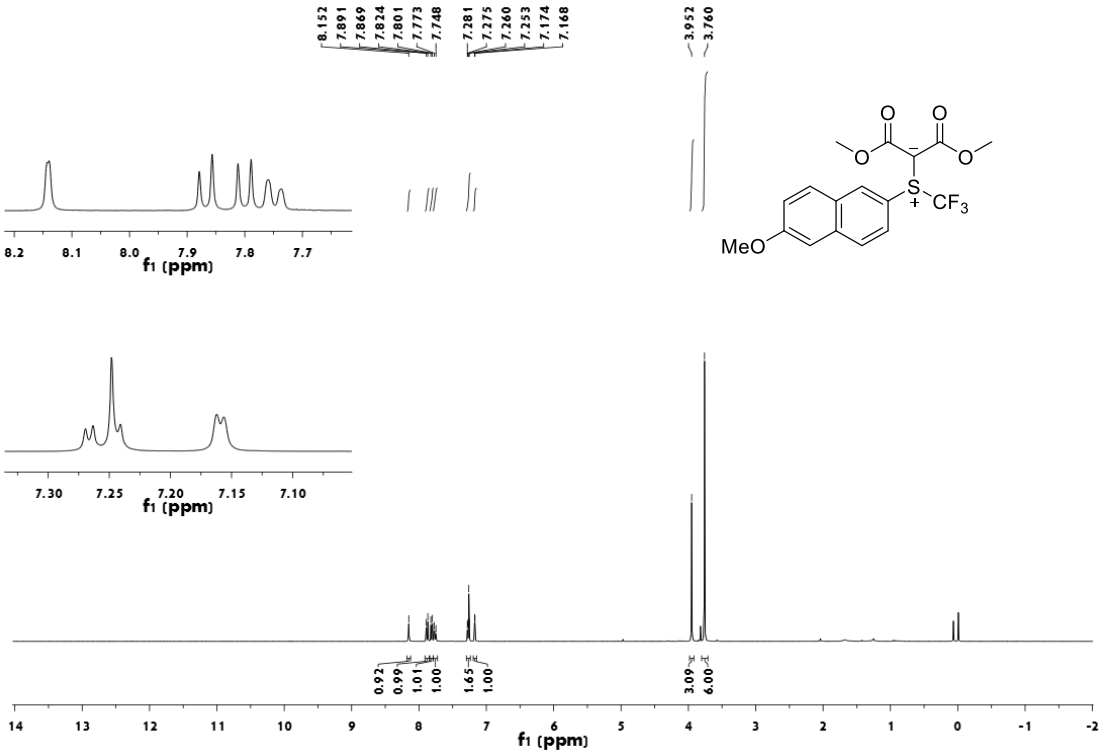
^{19}F NMR spectrum of trifluoromethyl-(naphthalen-2-yl) bis(carbomethoxy) methylide 1n



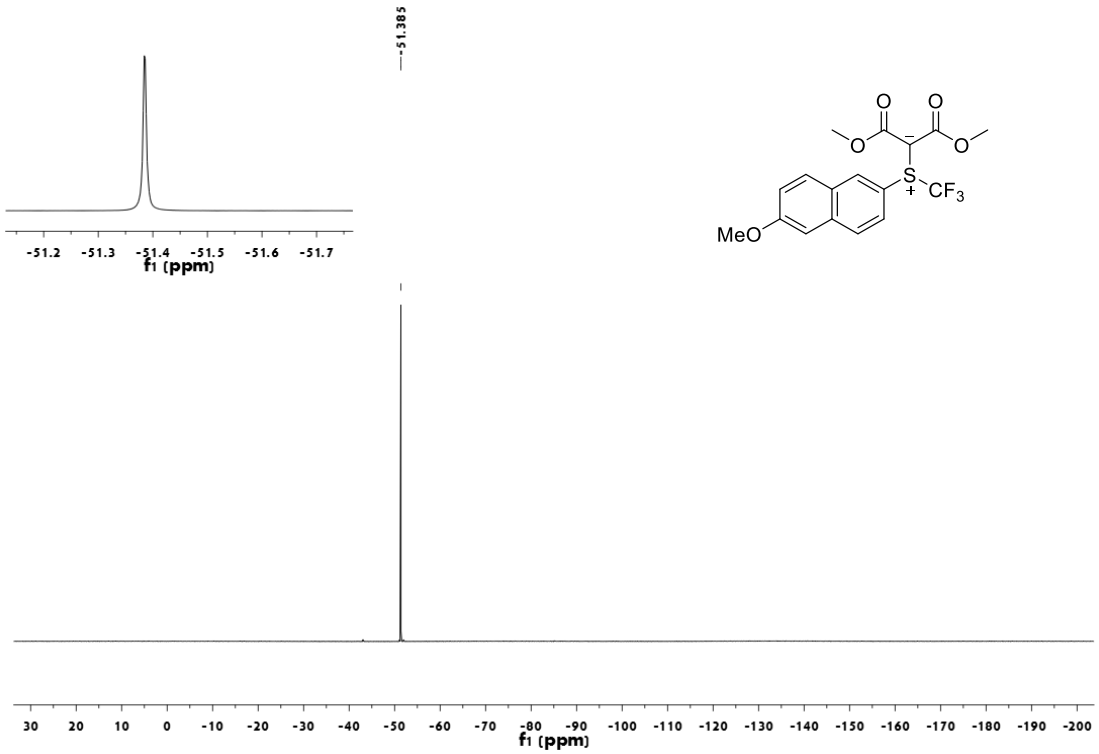
^{13}C NMR spectrum of trifluoromethyl-(naphthalen-2-yl) bis(carbomethoxy) methylide 1n



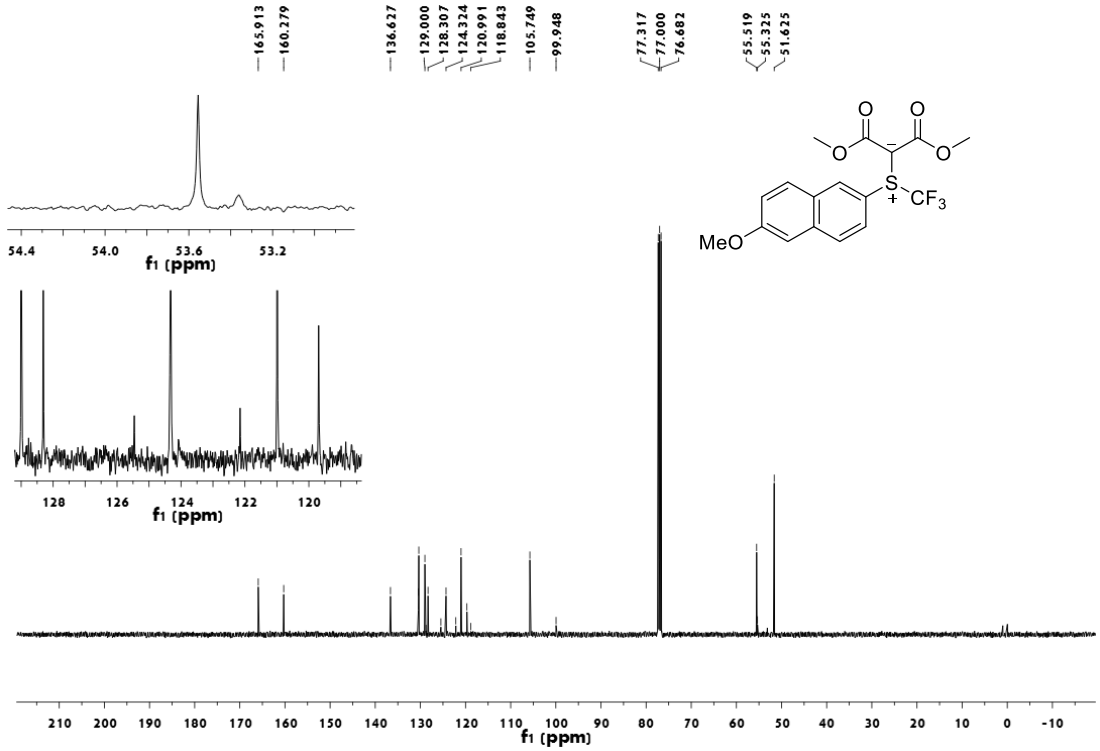
^{1}H NMR spectrum of trifluoromethyl-((6-methoxynaphthalen)-2-yl) bis(carbomethoxy) methylide 1o



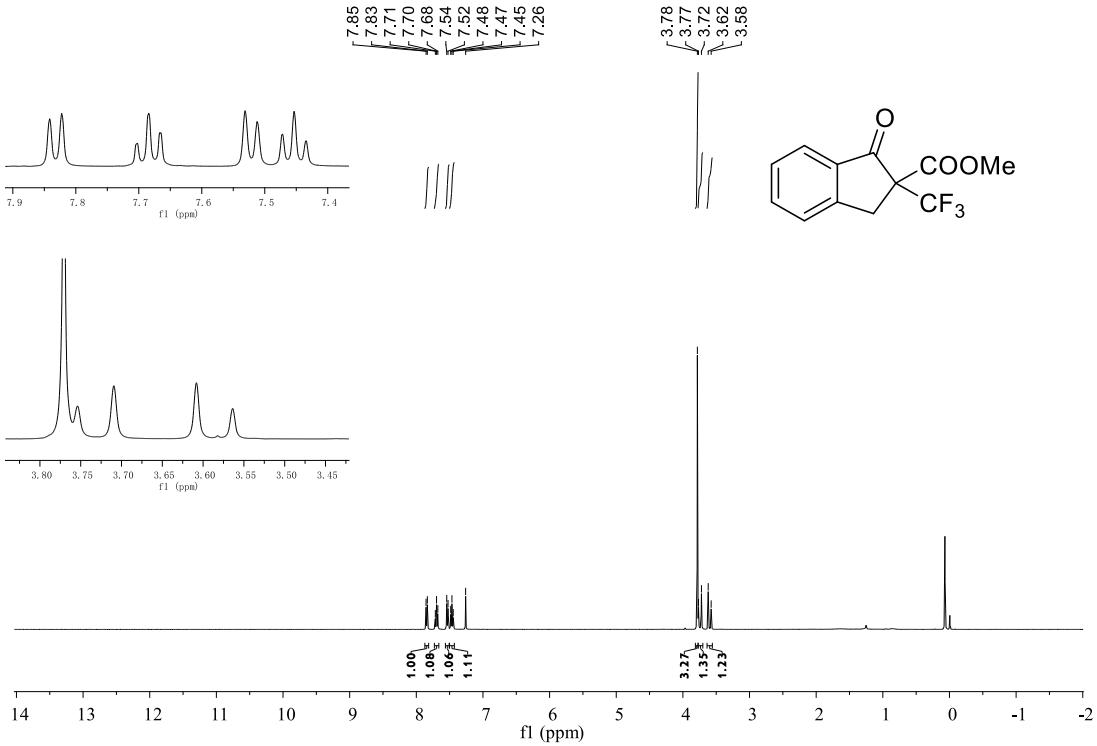
^{19}F NMR spectrum of trifluoromethyl-((6-methoxynaphthalen)-2-yl) bis(carbomethoxy) methylide 1o



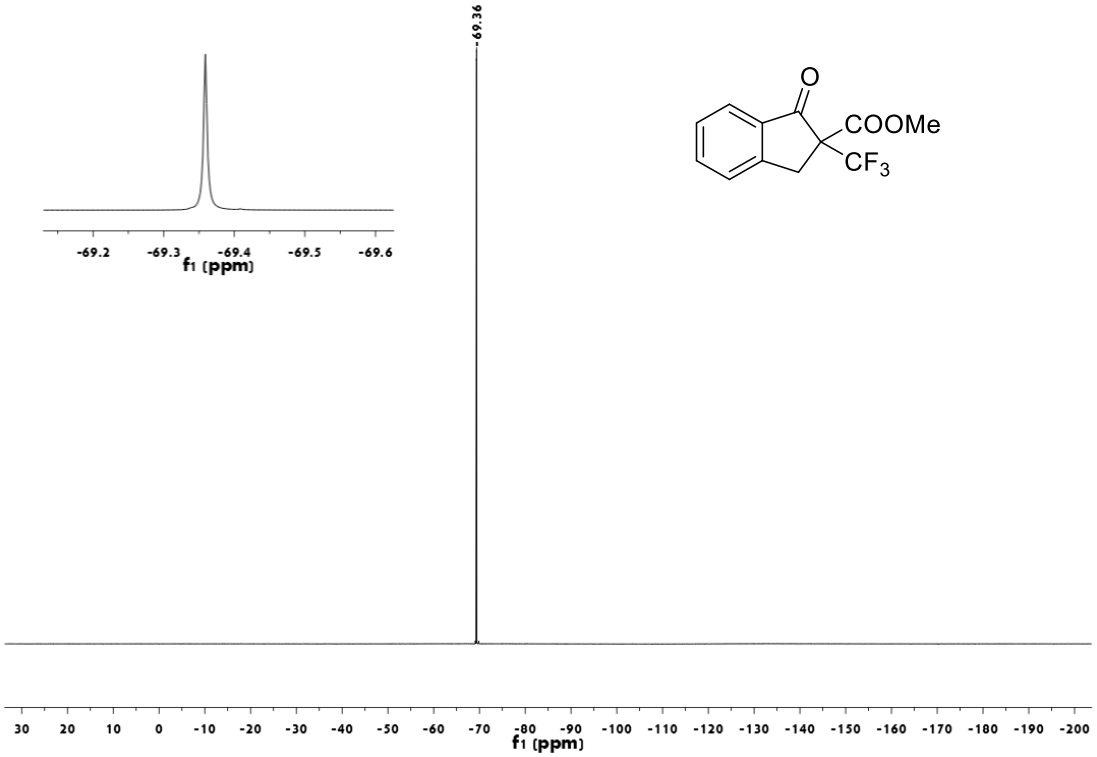
^{13}C NMR spectrum of trifluoromethyl-((6-methoxynaphthalen)-2-yl) bis(carbomethoxy) methylide 1o



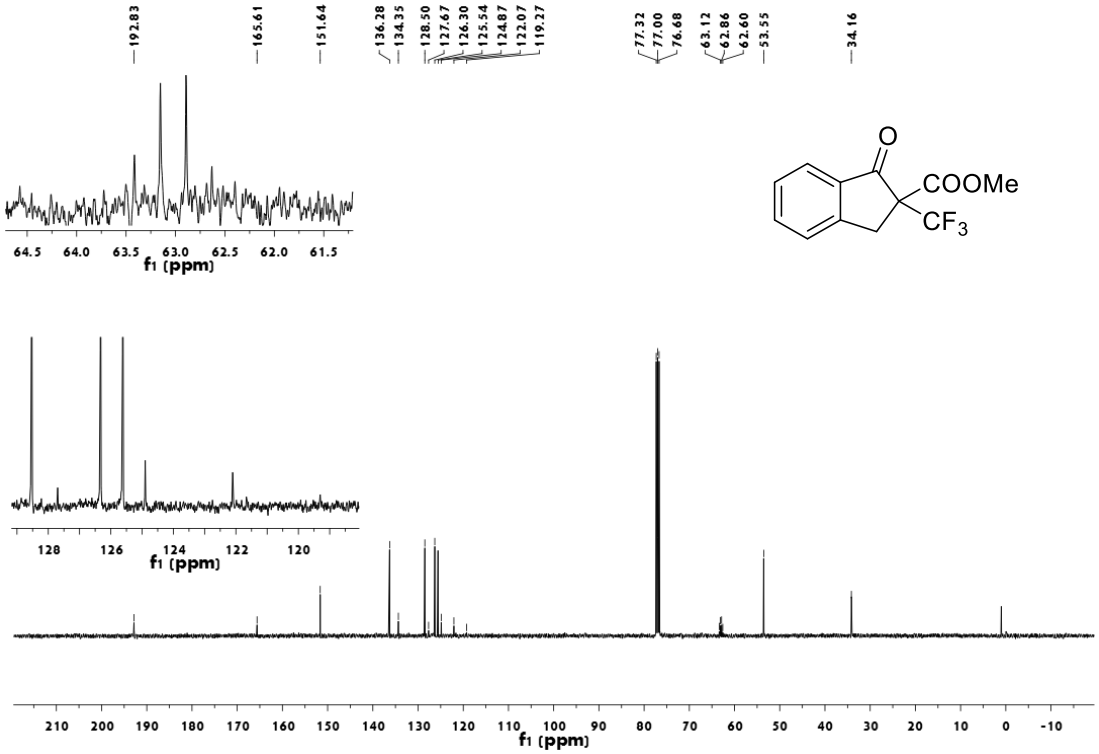
^{1}H NMR spectrum of methyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2a



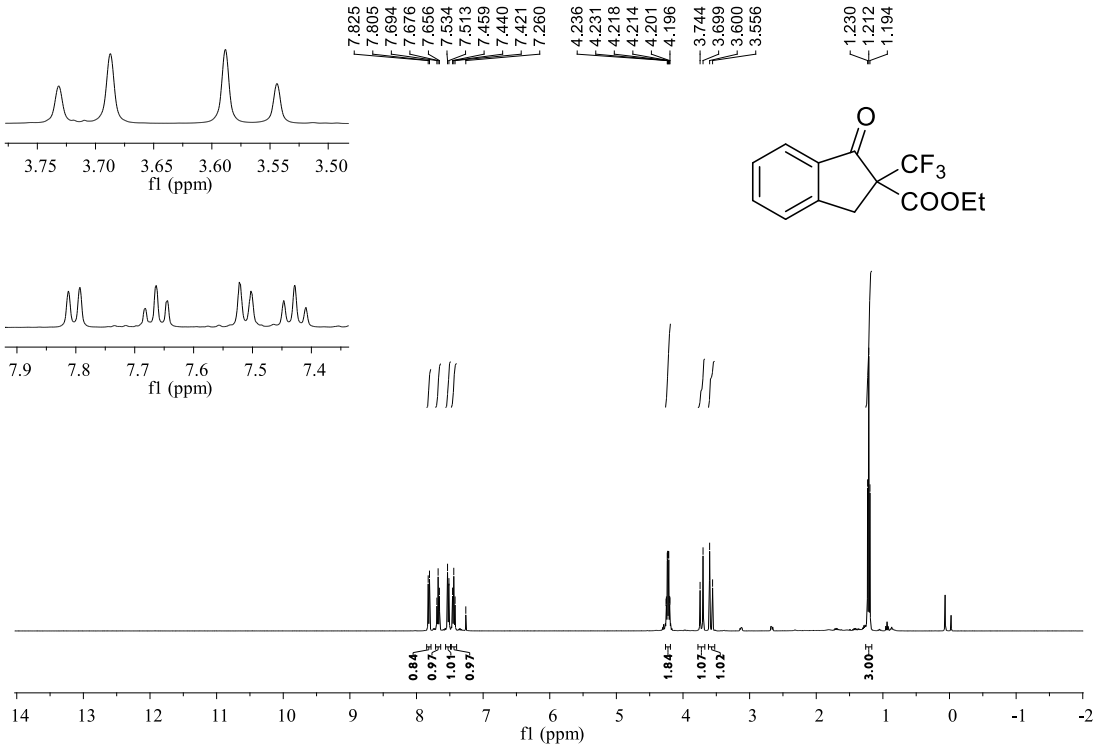
^{19}F NMR spectrum of Methyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2a



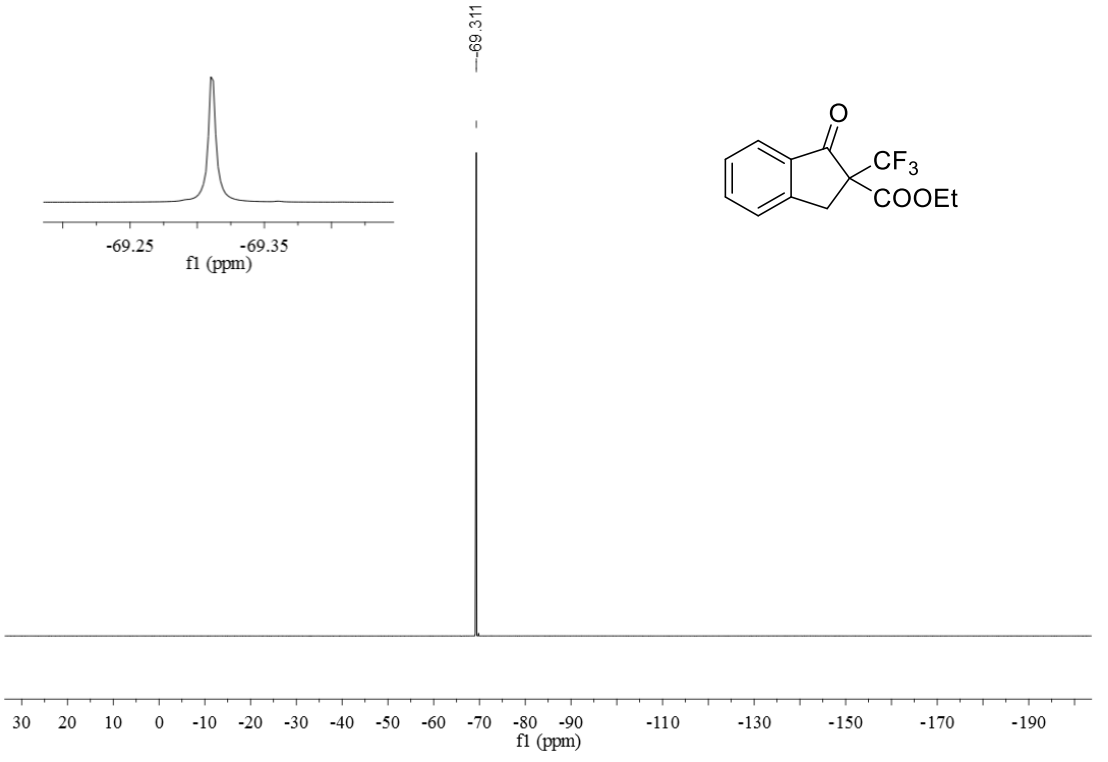
^{13}C NMR spectrum of methyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2a



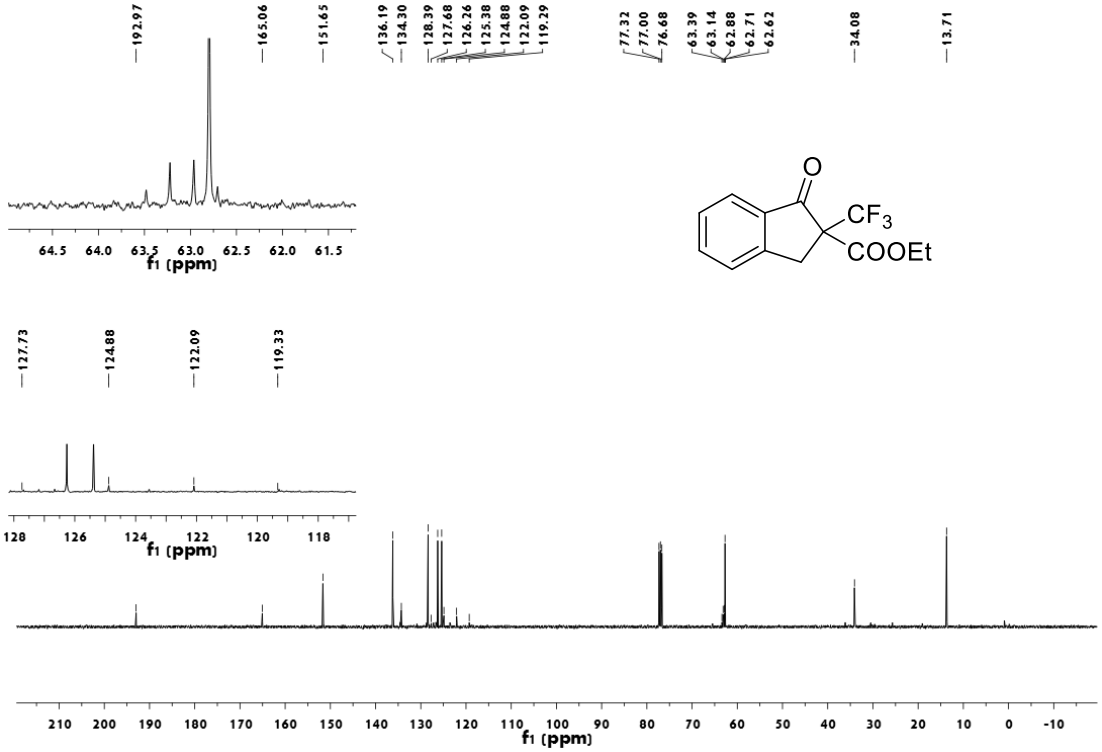
^{1}H NMR spectrum of ethyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2b



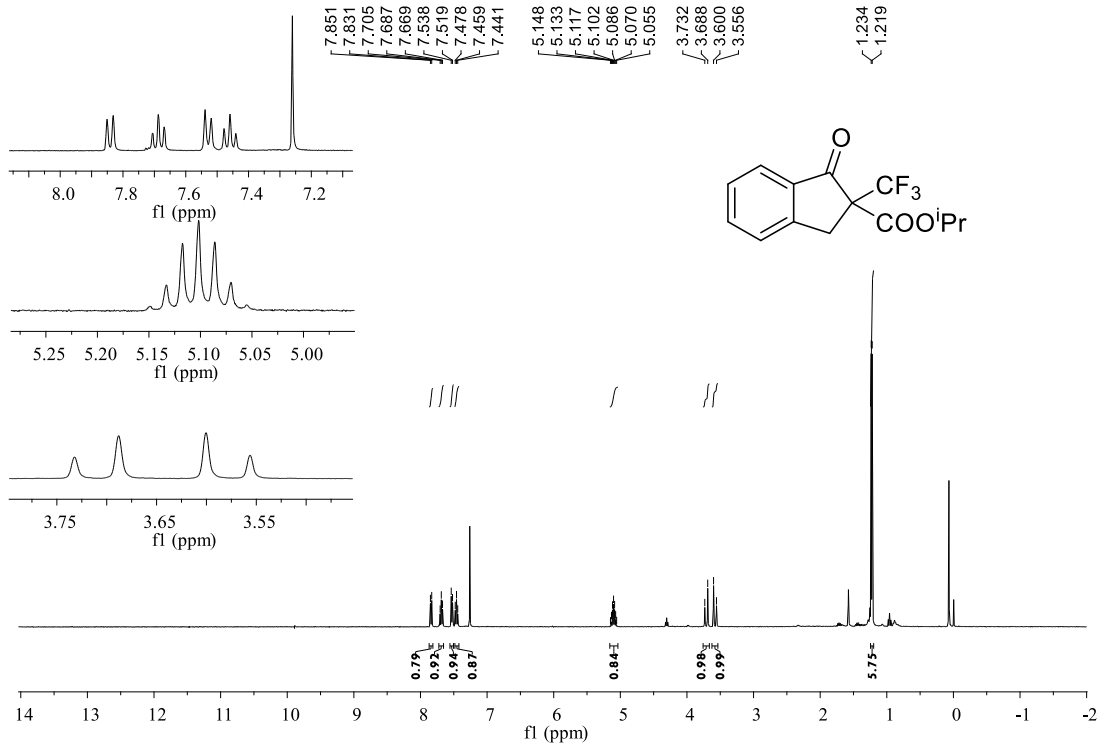
^{19}F NMR spectrum of ethyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2b



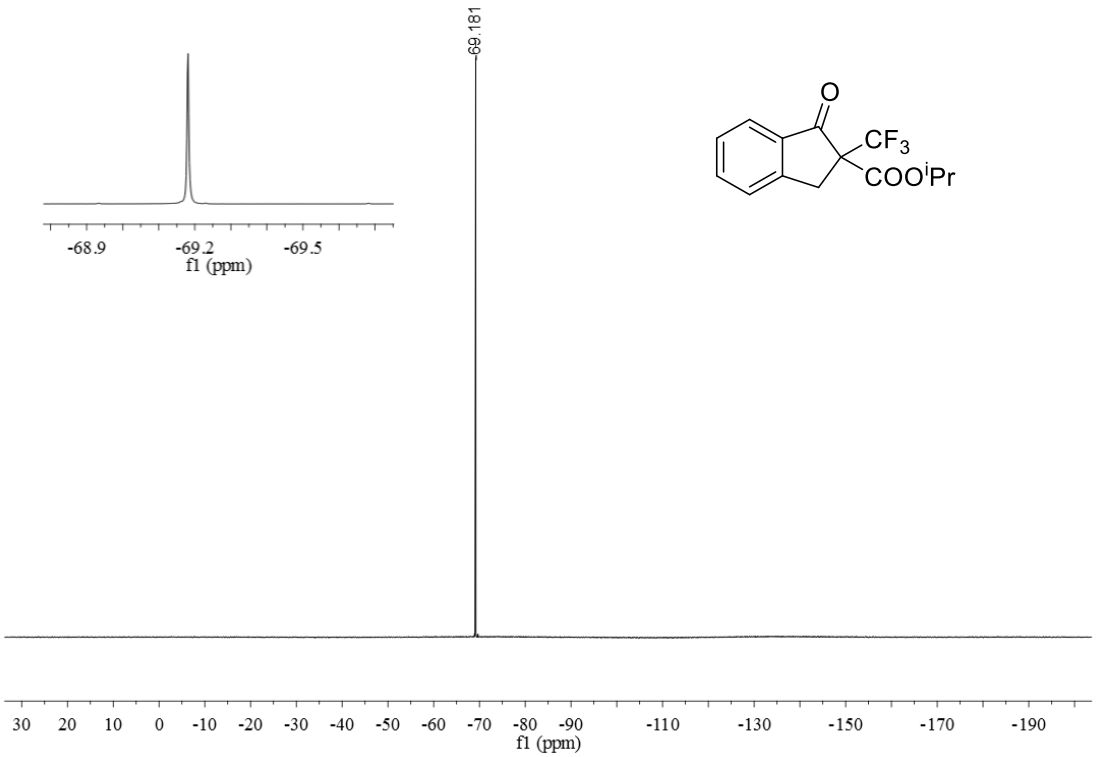
^{13}C NMR spectrum of ethyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2b



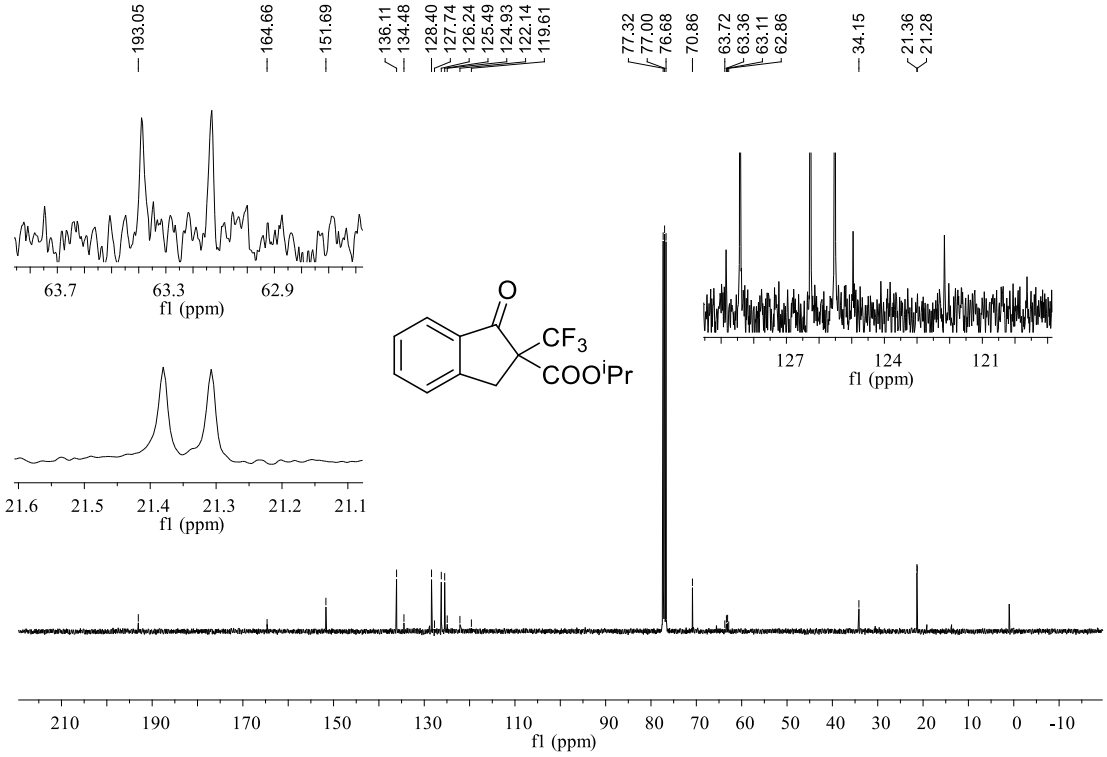
^{1}H NMR spectrum of isopropyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2c



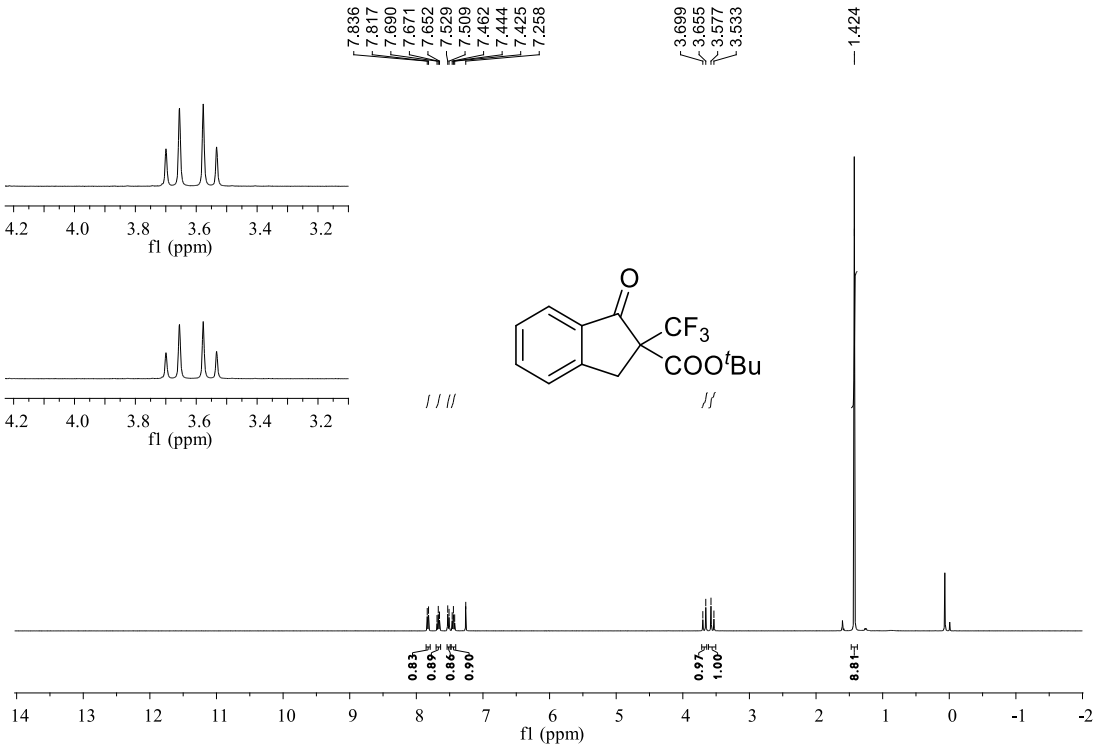
^{19}F NMR spectrum of isopropyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2c



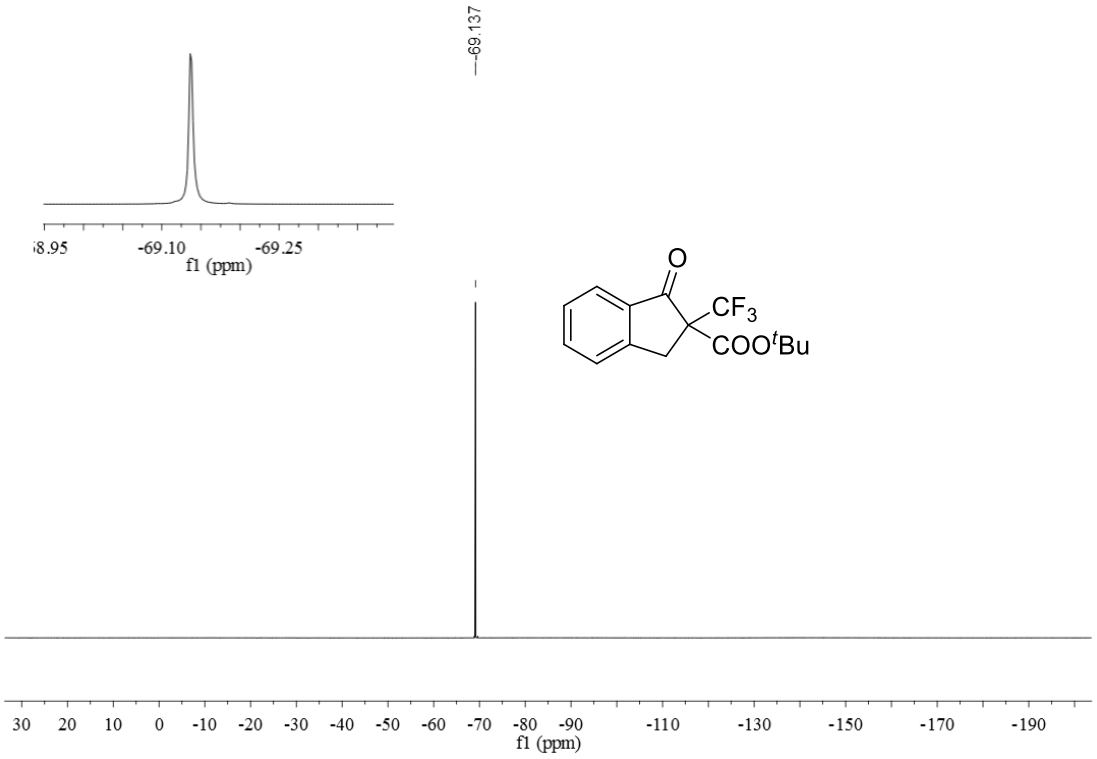
^{13}C NMR spectrum of isopropyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2c



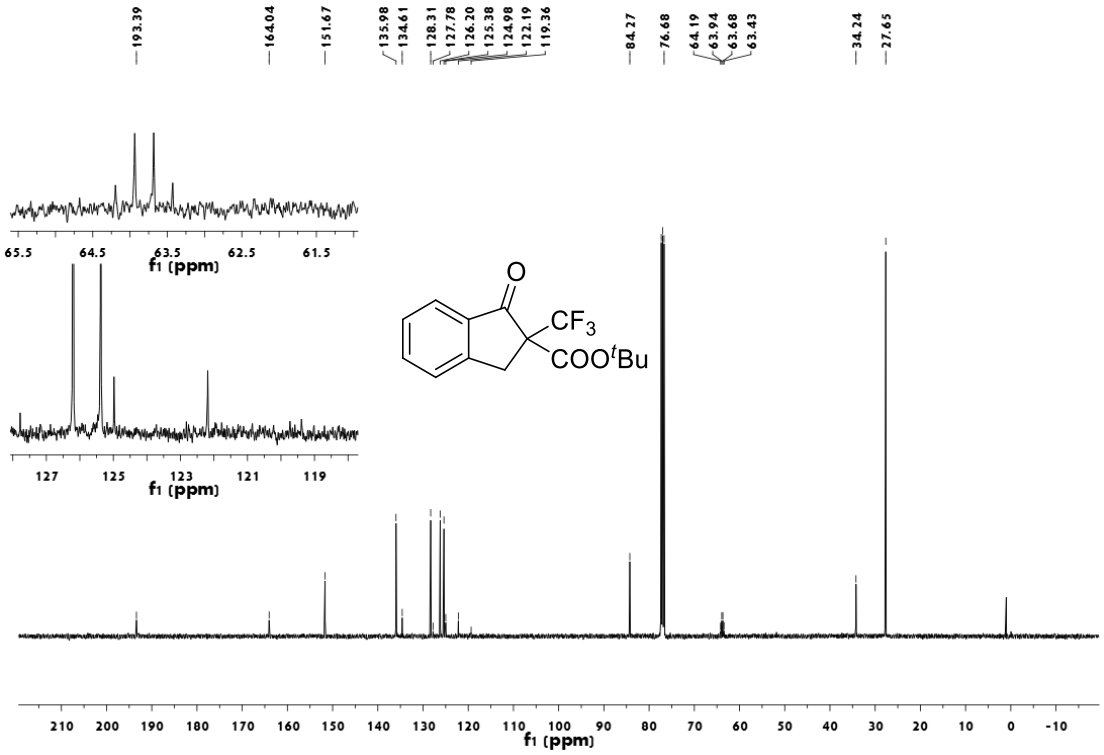
^{1}H NMR spectrum of *tert*-butyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2d



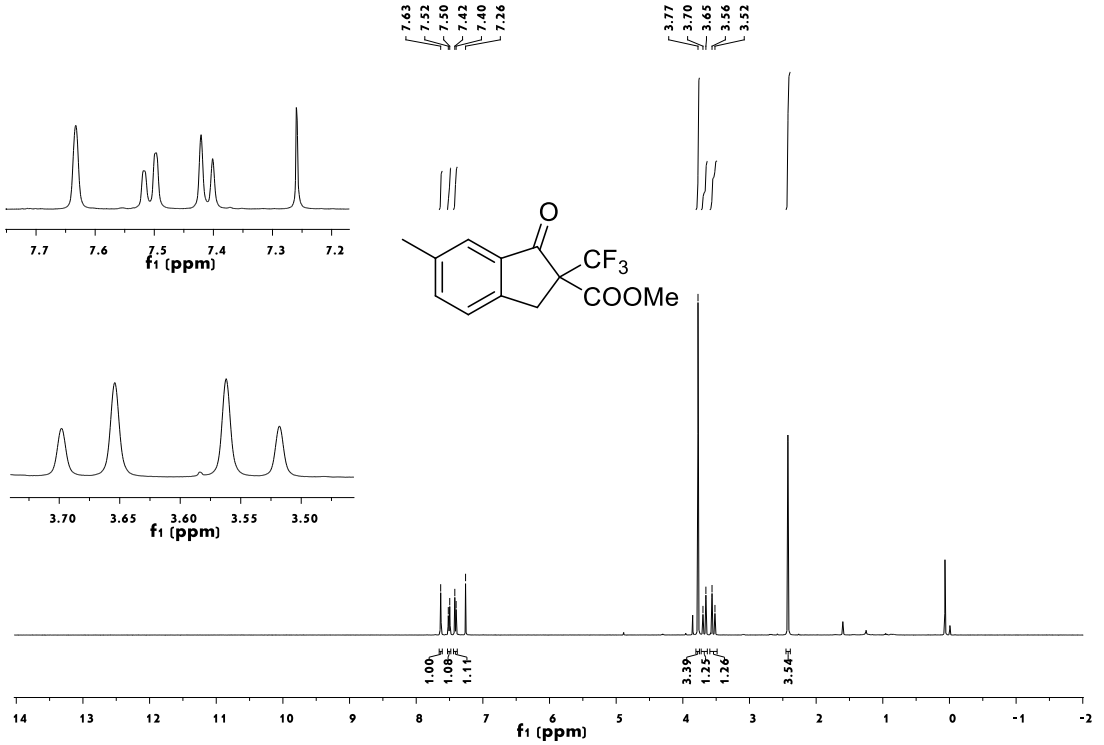
^{19}F NMR spectrum of *tert*-butyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2d



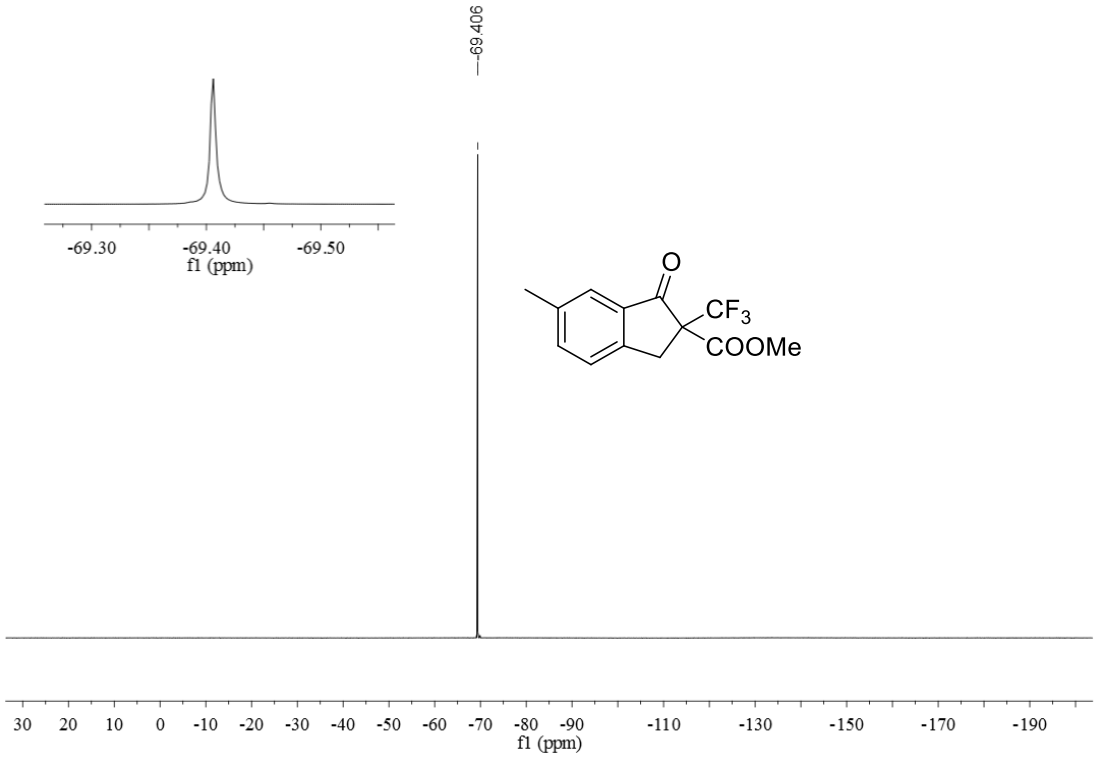
^{13}C NMR spectrum of *tert*-butyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2d



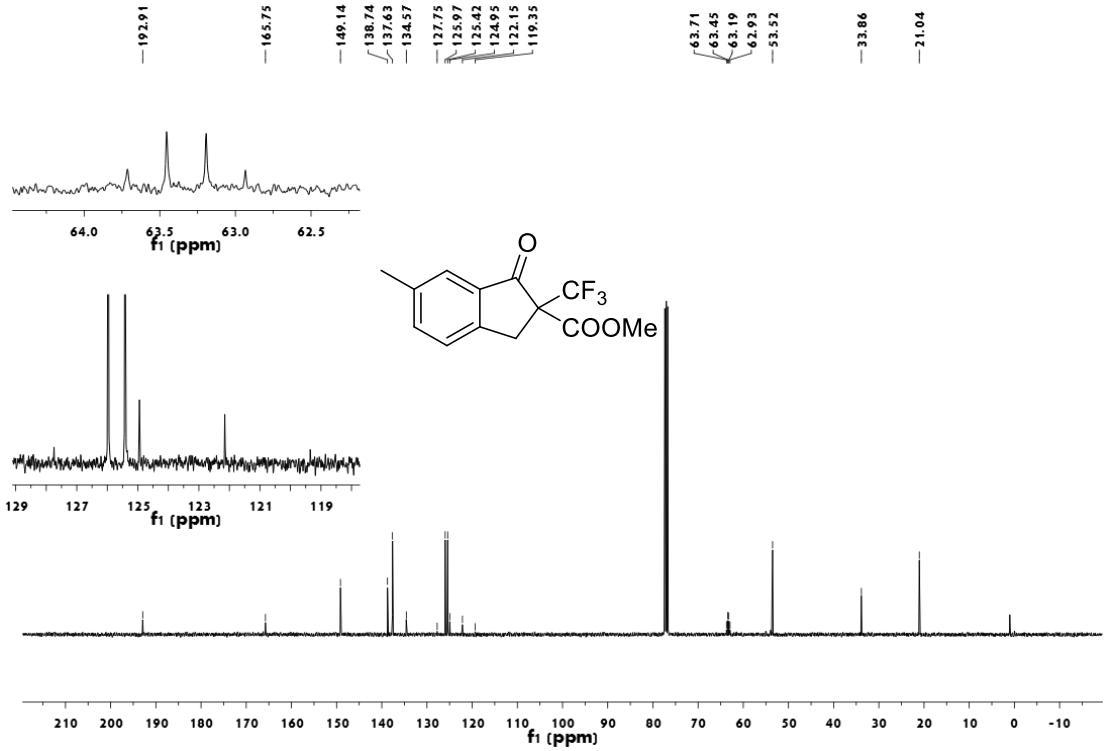
^{1}H NMR spectrum of methyl 6-methyl-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-indene-2-carboxylate 2e



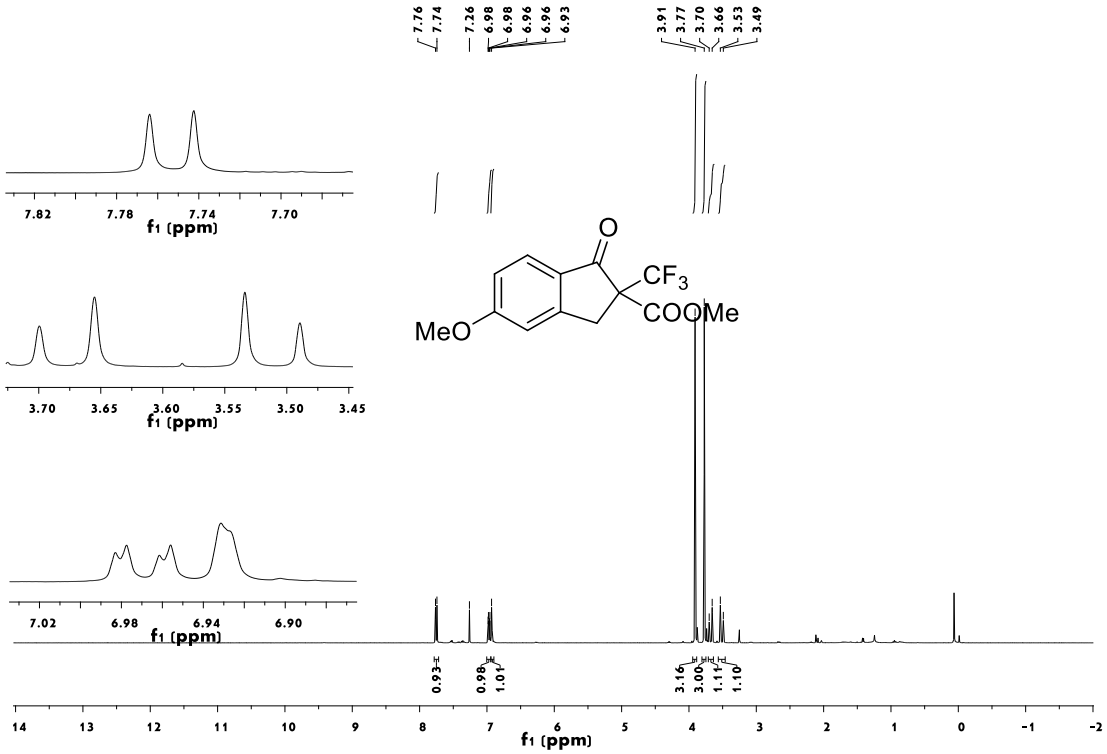
^{19}F NMR spectrum of methyl 6-methyl-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2e



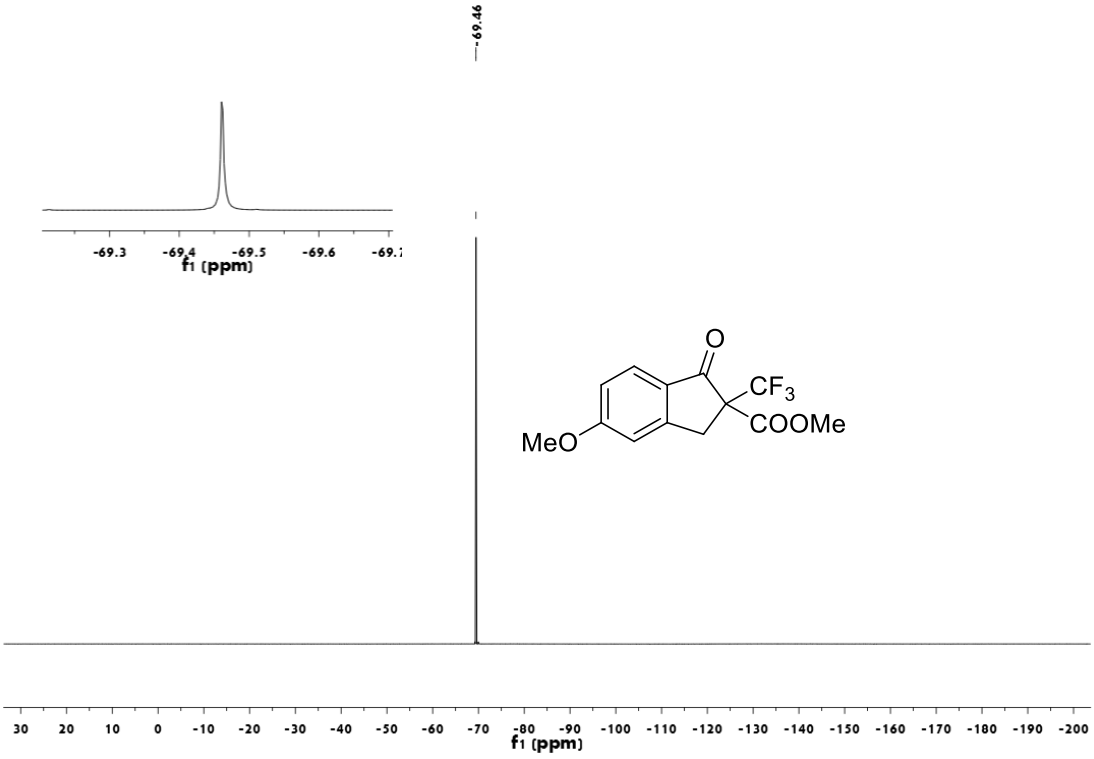
^{13}C NMR spectrum of methyl 6-methyl-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2e



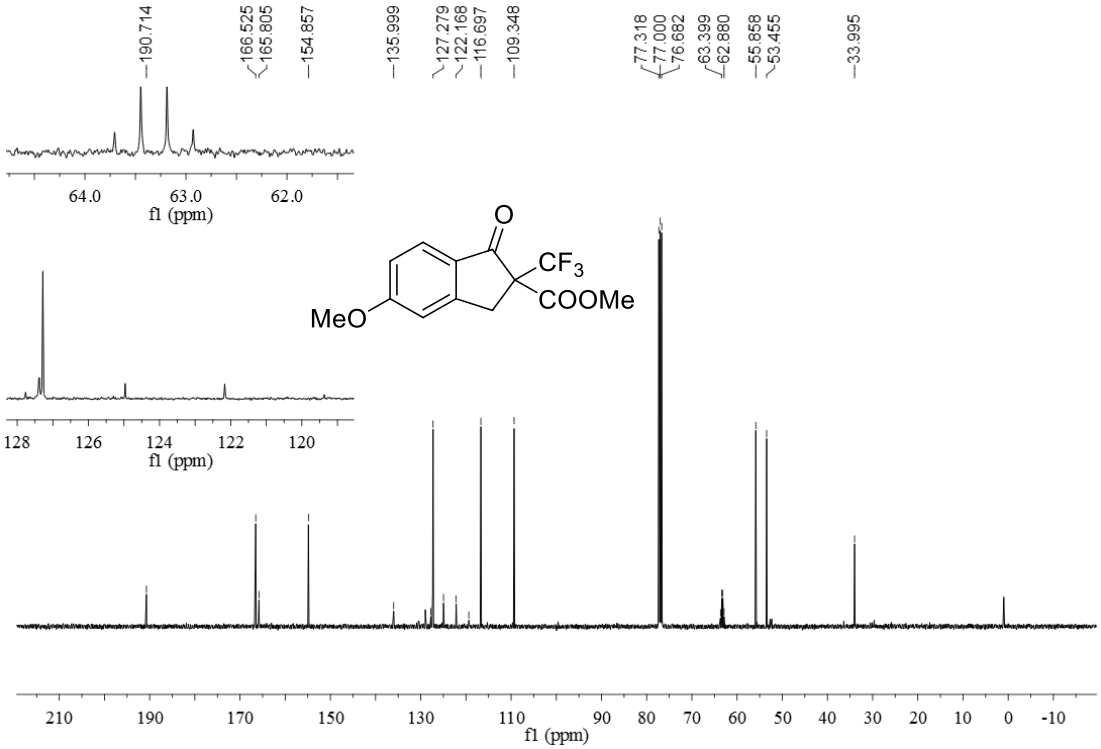
^{1}H NMR spectrum of methyl 5-methoxy-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2f



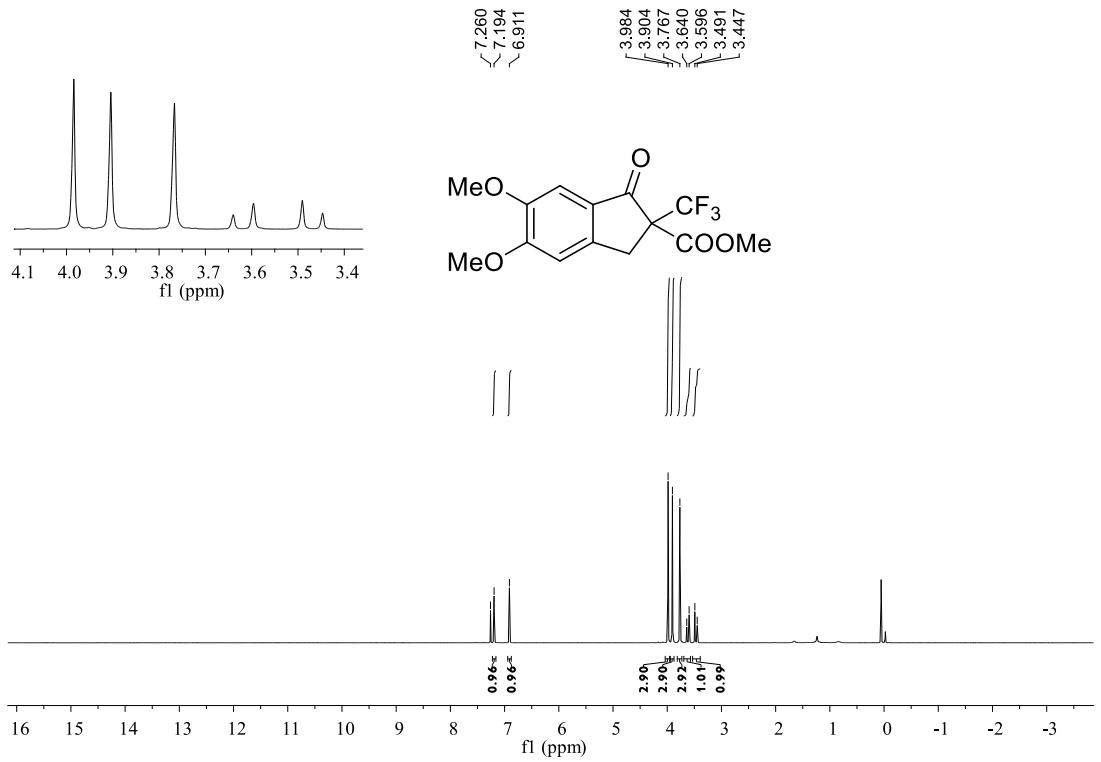
^{19}F NMR spectrum of methyl 5-methoxy-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2f



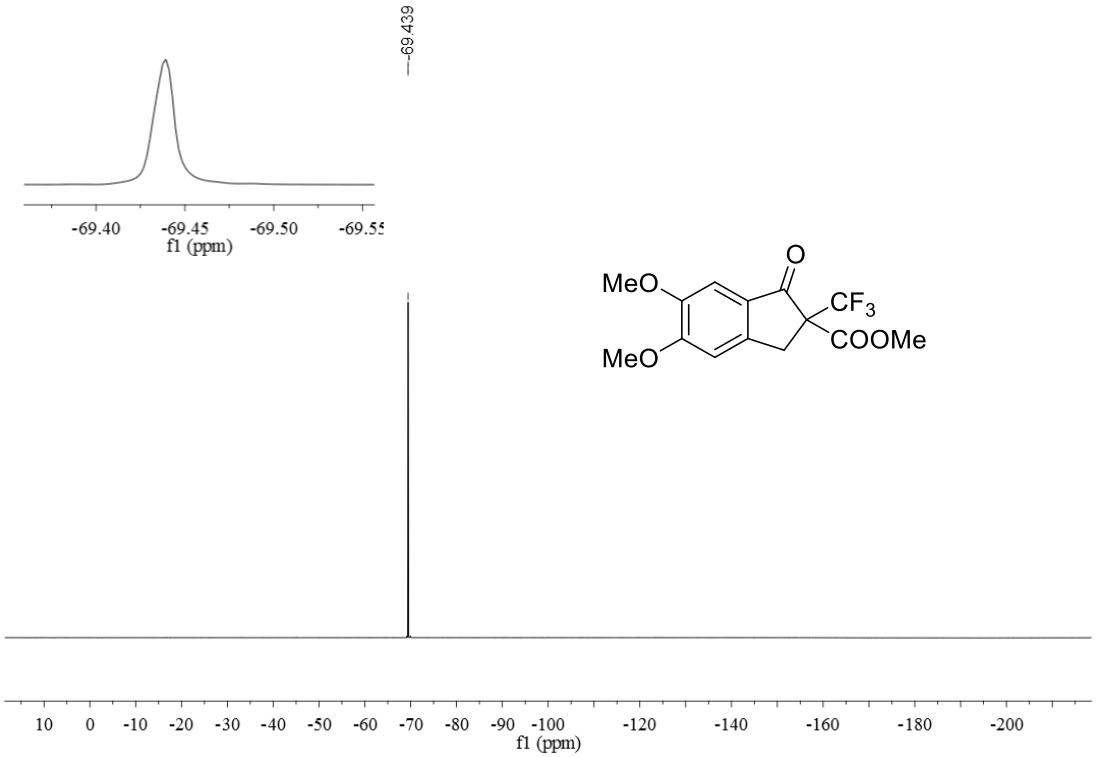
^{13}C NMR spectrum of methyl 5-methoxy-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2f



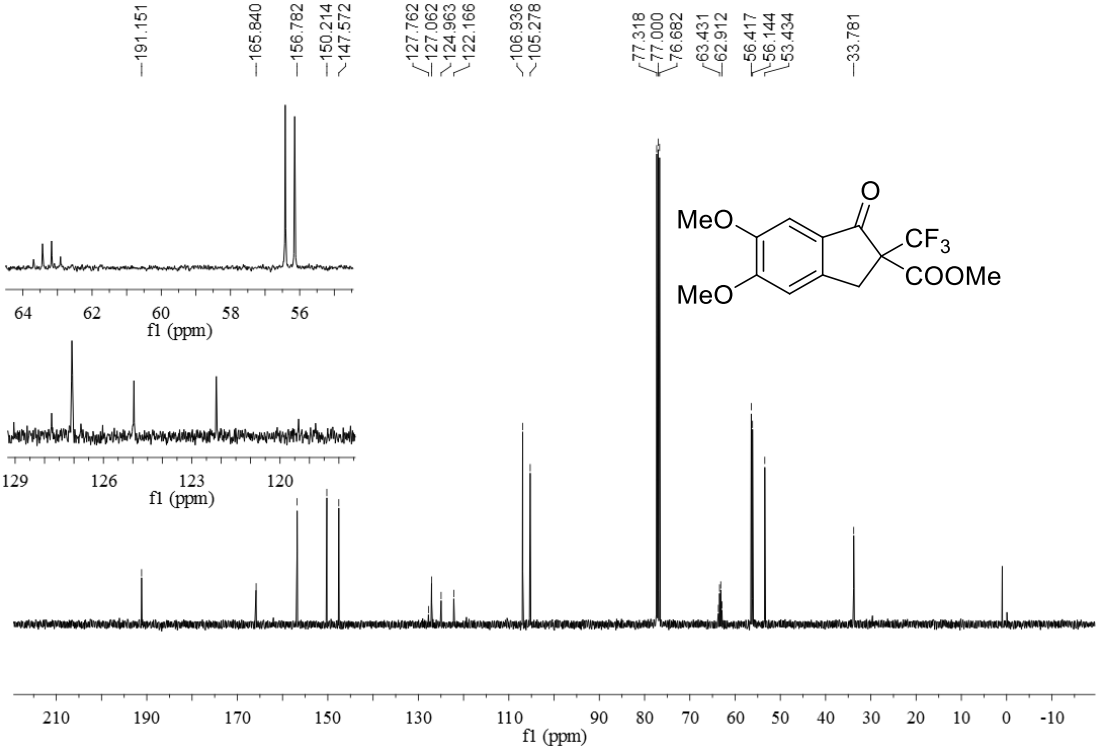
^{1}H NMR spectrum of methyl 5,6-dimethoxy -1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2g



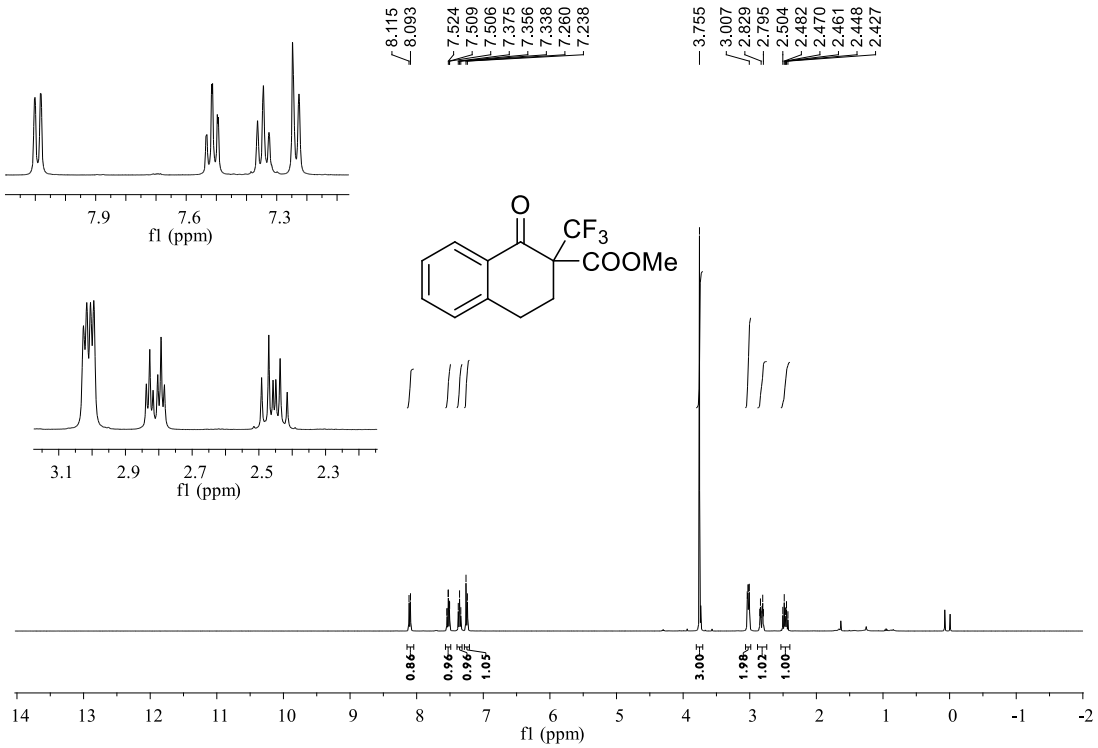
^{19}F NMR spectrum of methyl 5,6-dimethoxy -1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2g



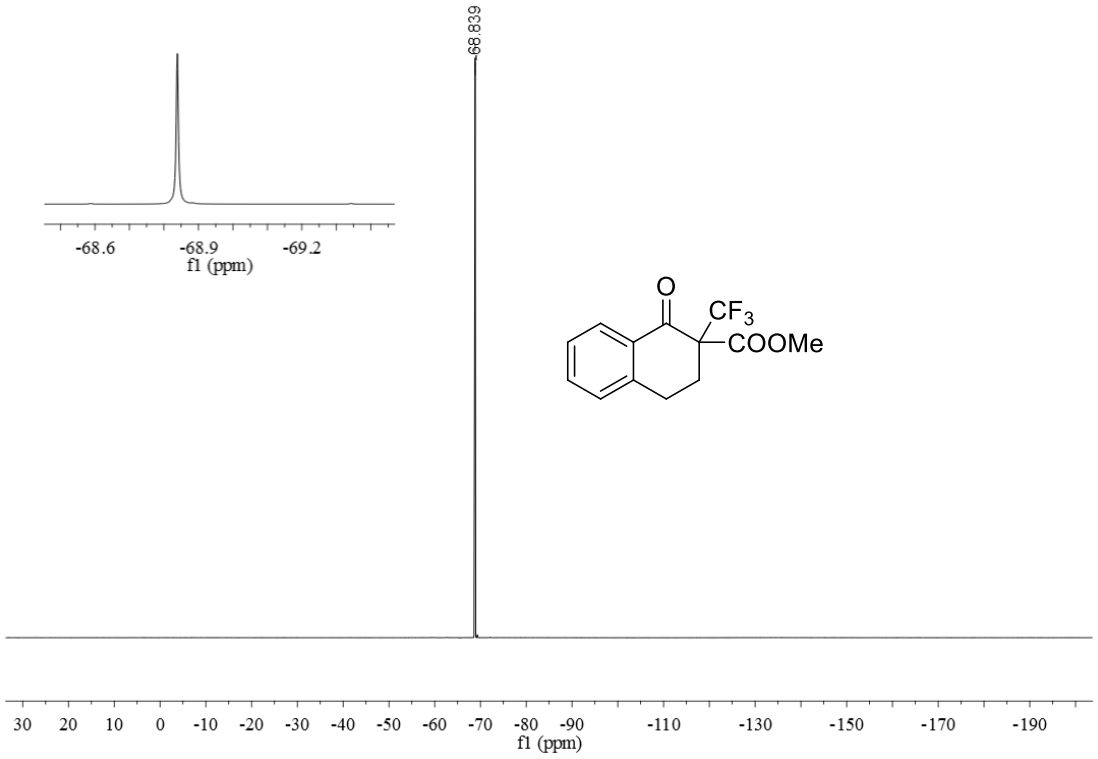
^{13}C NMR spectrum of methyl 5,6-dimethoxy -1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2g



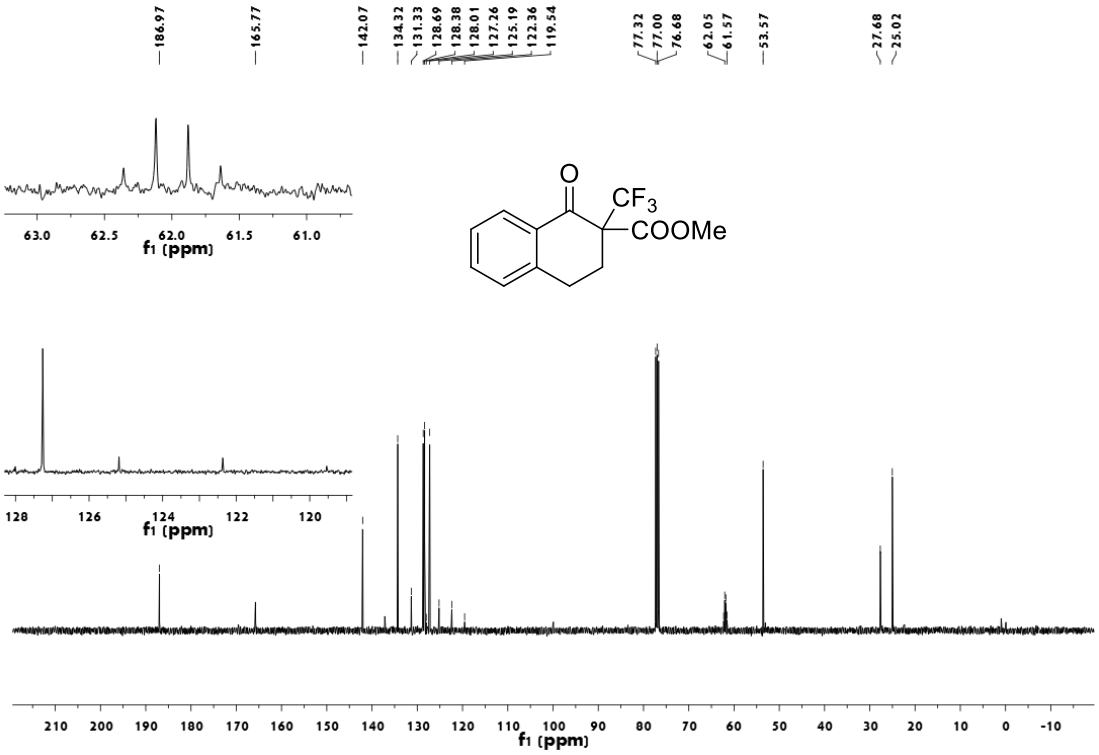
^{1}H NMR spectrum of methyl 1-oxo-2-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate 2h



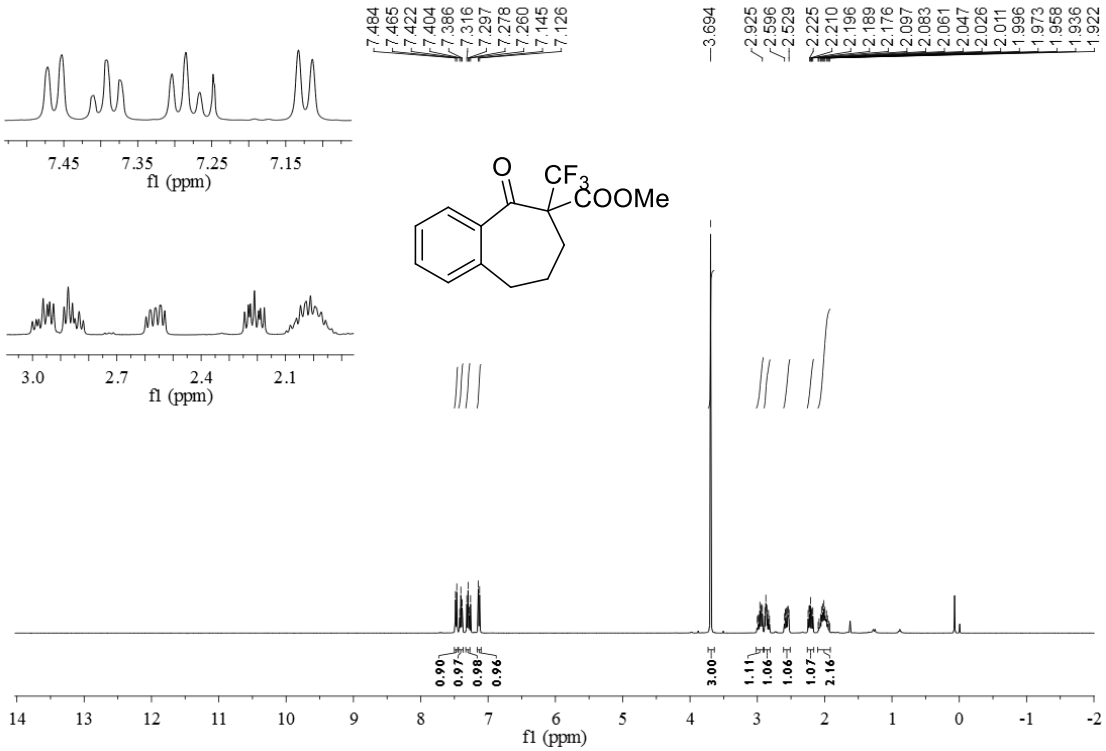
^{19}F NMR spectrum of methyl 1-oxo-2-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate 2h



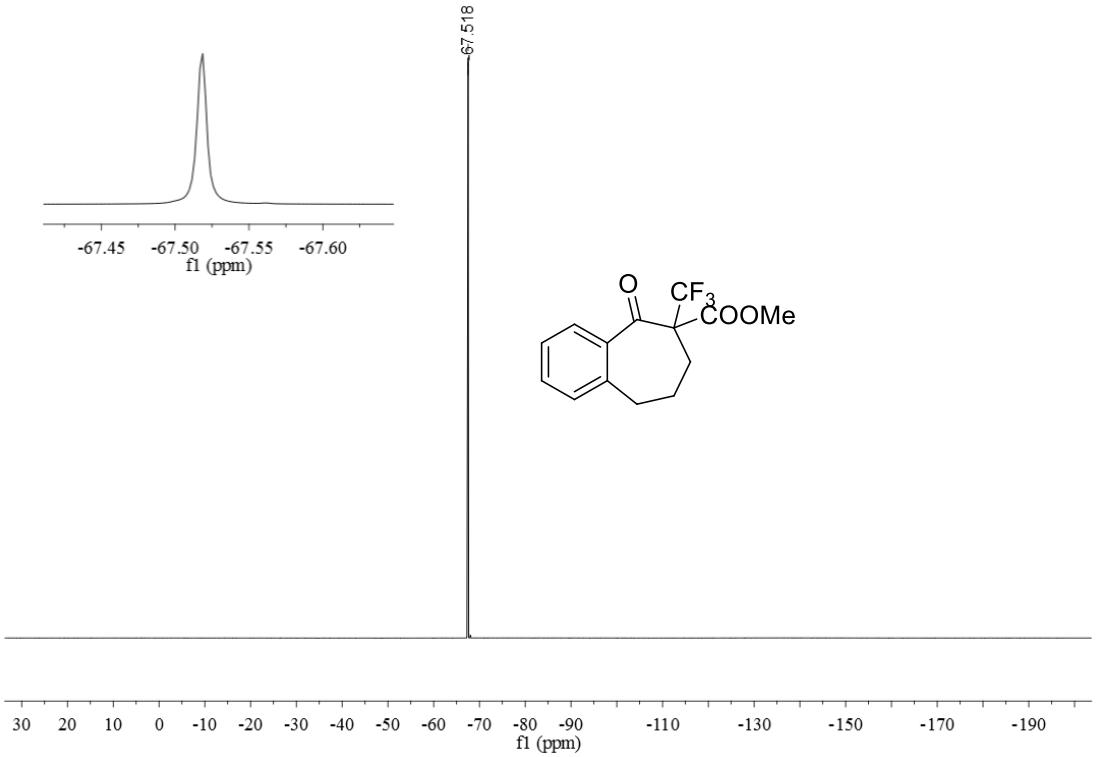
^{13}C NMR spectrum of methyl 1-oxo-2-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate 2h



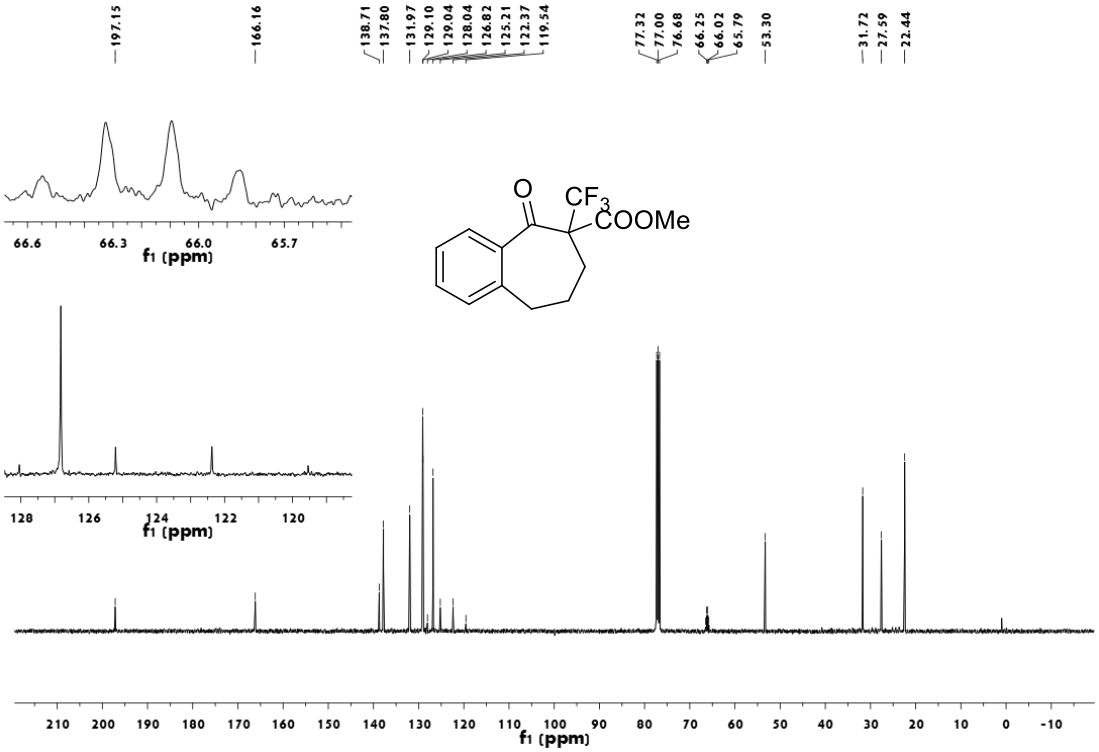
^{1}H NMR spectrum of methyl 5-oxo-6-(trifluoromethyl)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene-6-carboxylate 2i



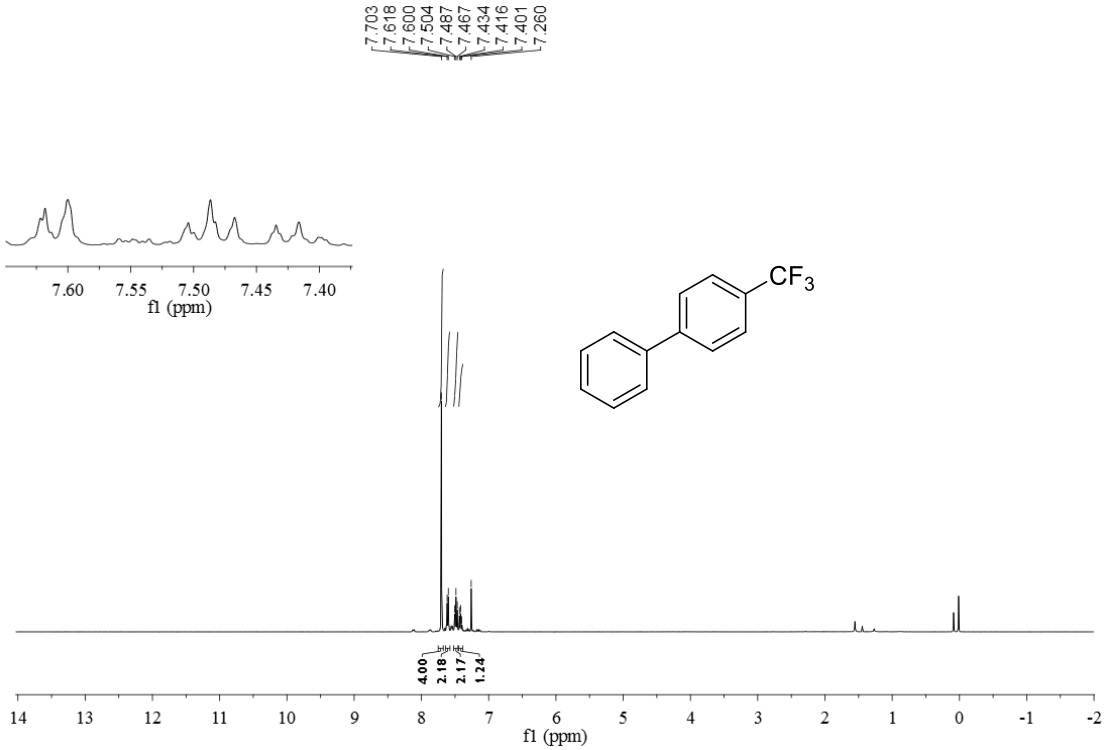
^{19}F NMR spectrum of methyl 5-oxo -6-(trifluoromethyl)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene-6-carboxylate 2i



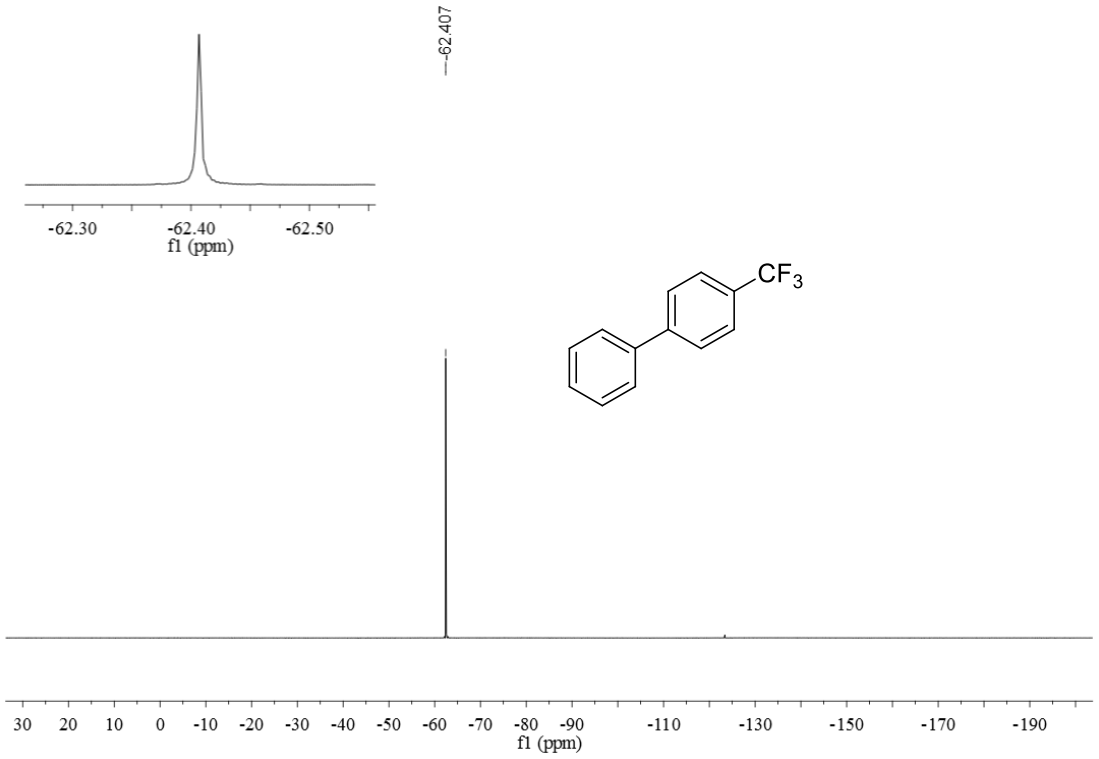
^{13}C NMR spectrum of methyl 5-oxo -6-(trifluoromethyl)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene-6-carboxylate 2i



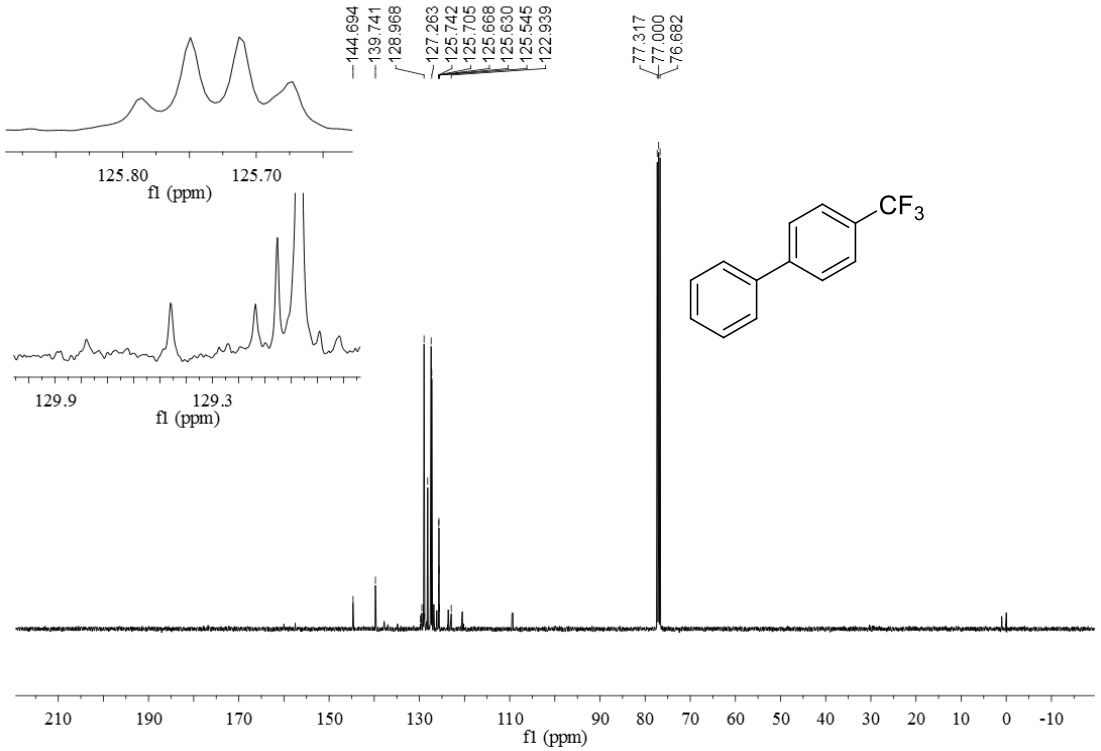
^{1}H NMR spectrum of 4-(trifluoromethyl)biphenyl 3a



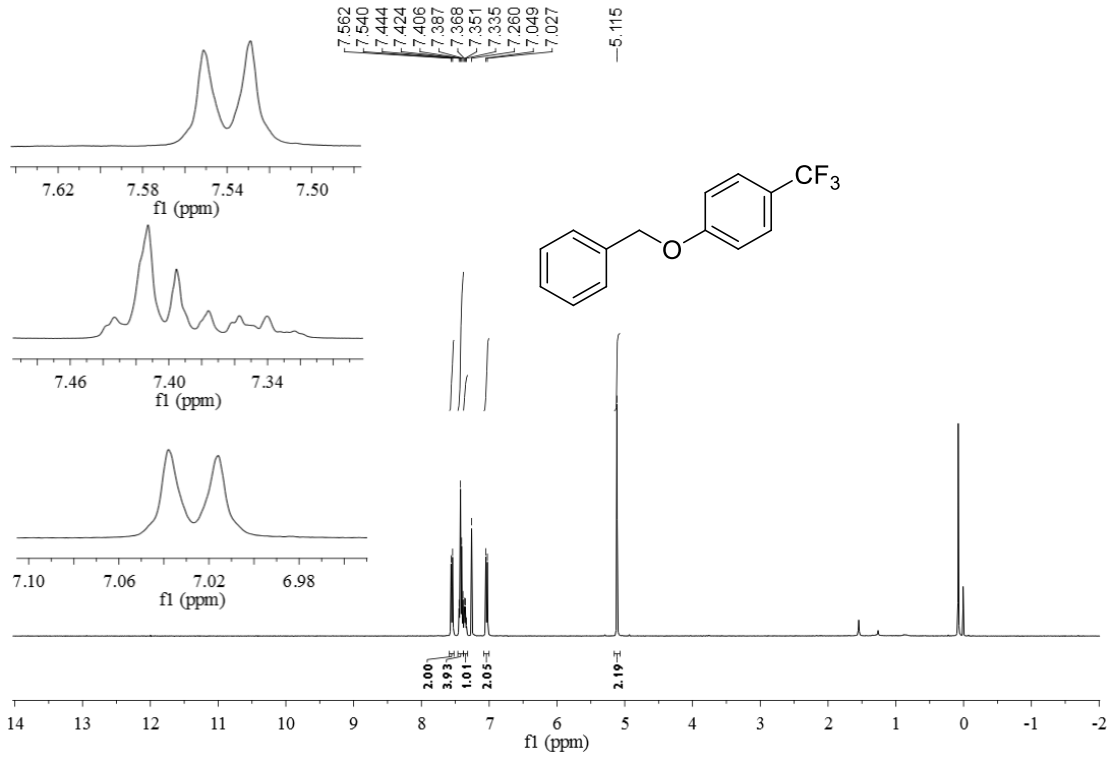
^{19}F NMR spectrum of 4-(trifluoromethyl)biphenyl 3a



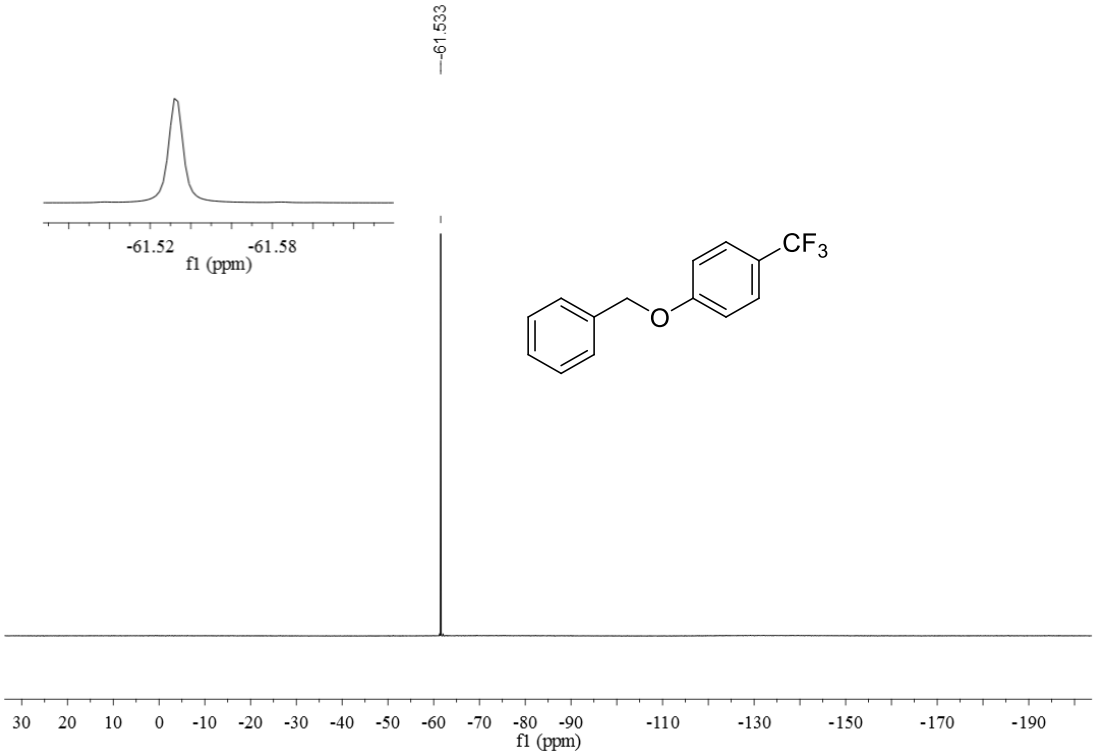
^{13}C NMR spectrum of 4-(trifluoromethyl)biphenyl 3a



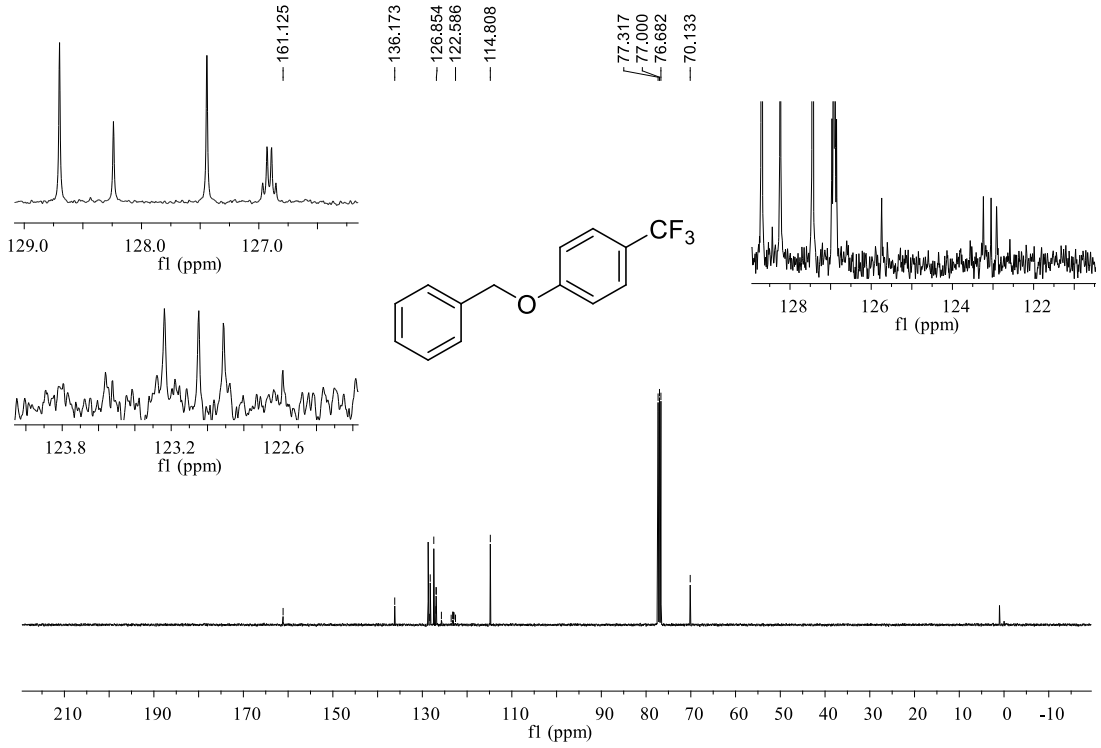
^{1}H NMR spectrum of 1-(benzyloxy)-4-(trifluoromethyl)benzene 3b



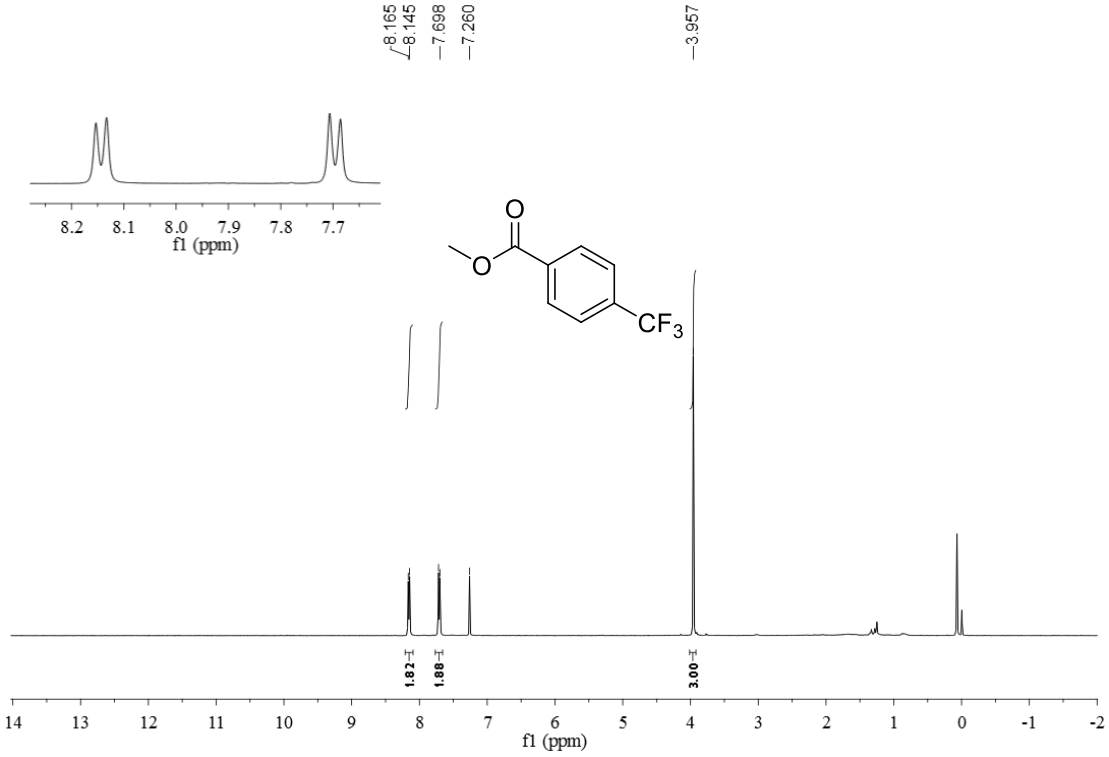
^{19}F NMR spectrum of 1-(benzyloxy)-4-(trifluoromethyl)benzene 3b



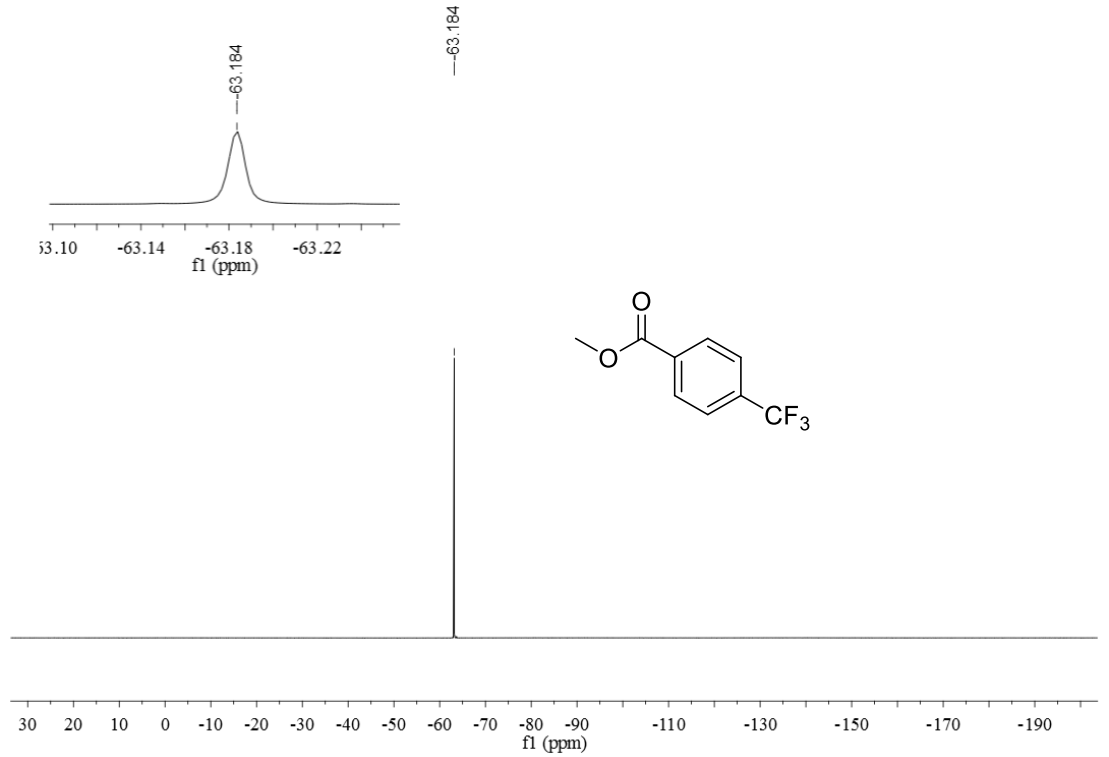
^{13}C NMR spectrum of 1-(benzyloxy)-4-(trifluoromethyl)benzene 3b



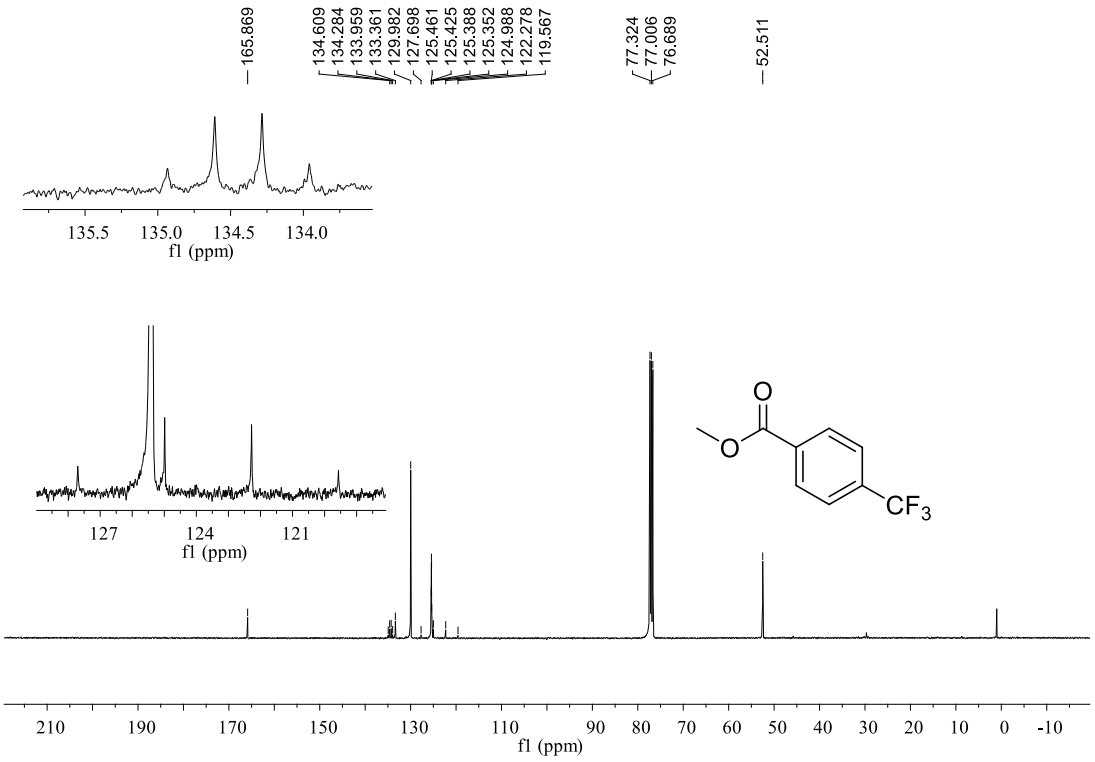
^{1}H NMR spectrum of methyl 4-(trifluoromethyl)benzoate 3c



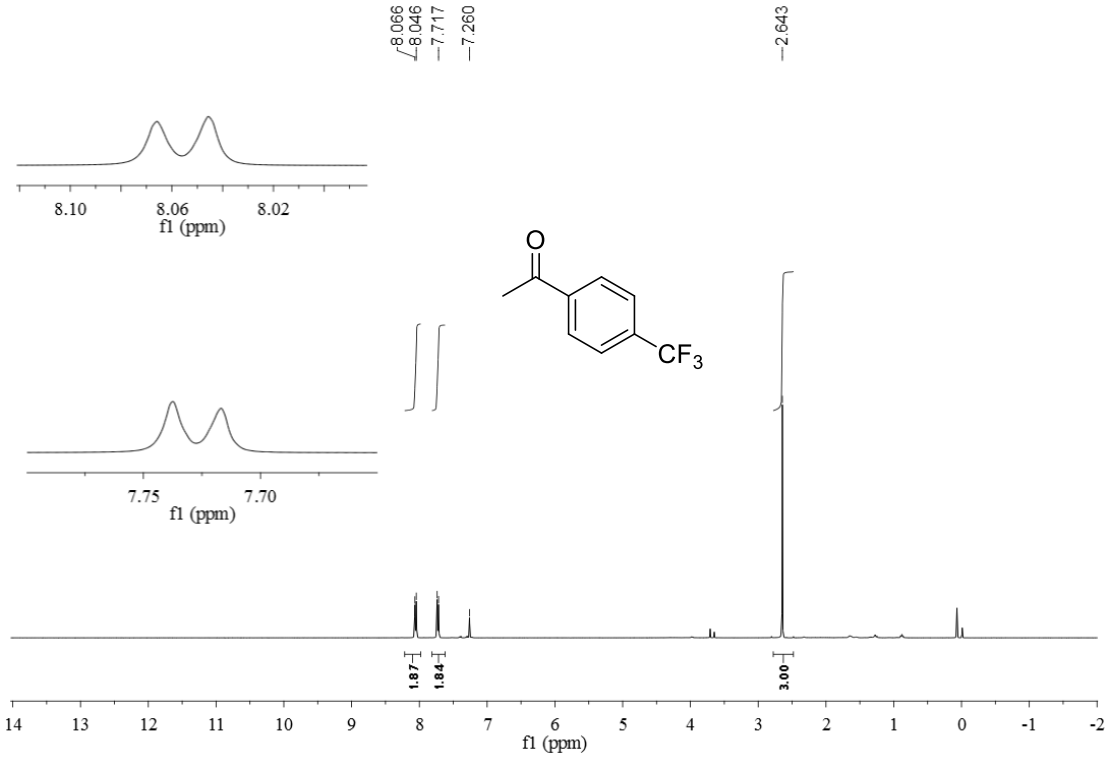
^{19}F NMR spectrum of methyl 4-(trifluoromethyl)benzoate 3c



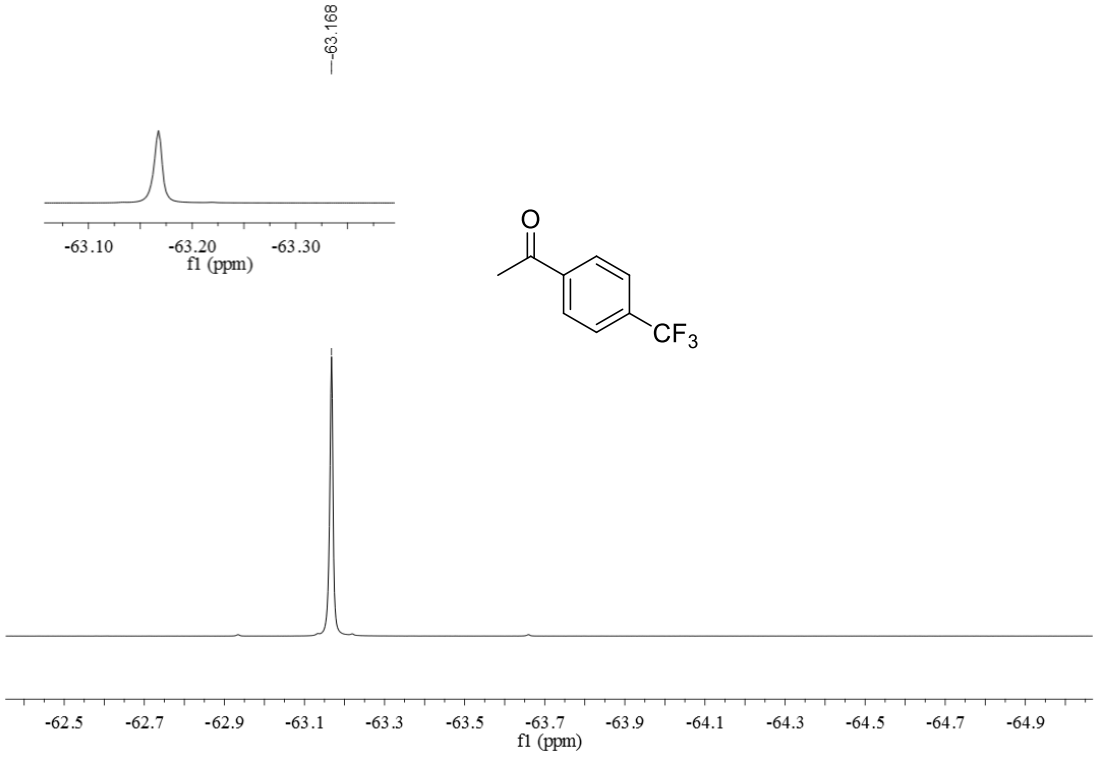
^{13}C NMR spectrum of methyl 4-(Trifluoromethyl)benzoate 3c



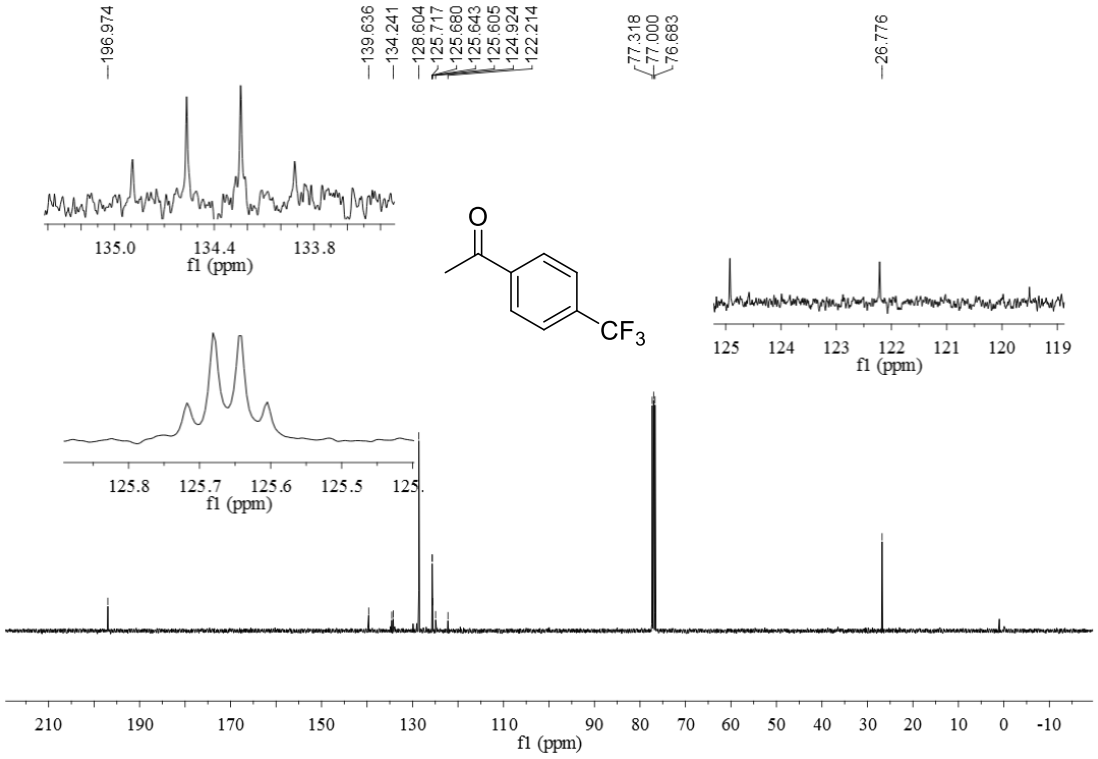
^{1}H NMR spectrum of 1-(4-(trifluoromethyl)phenyl)ethanone 3d



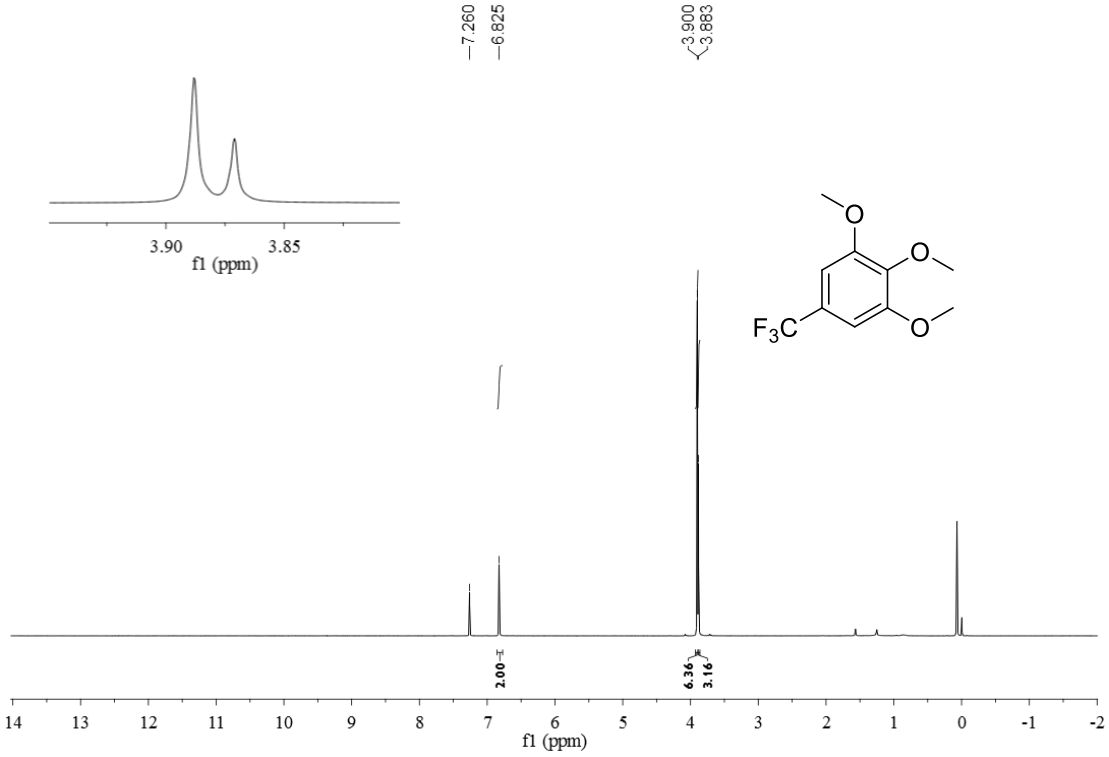
^{19}F NMR spectrum of 1-(4-(trifluoromethyl)phenyl)ethanone 3d



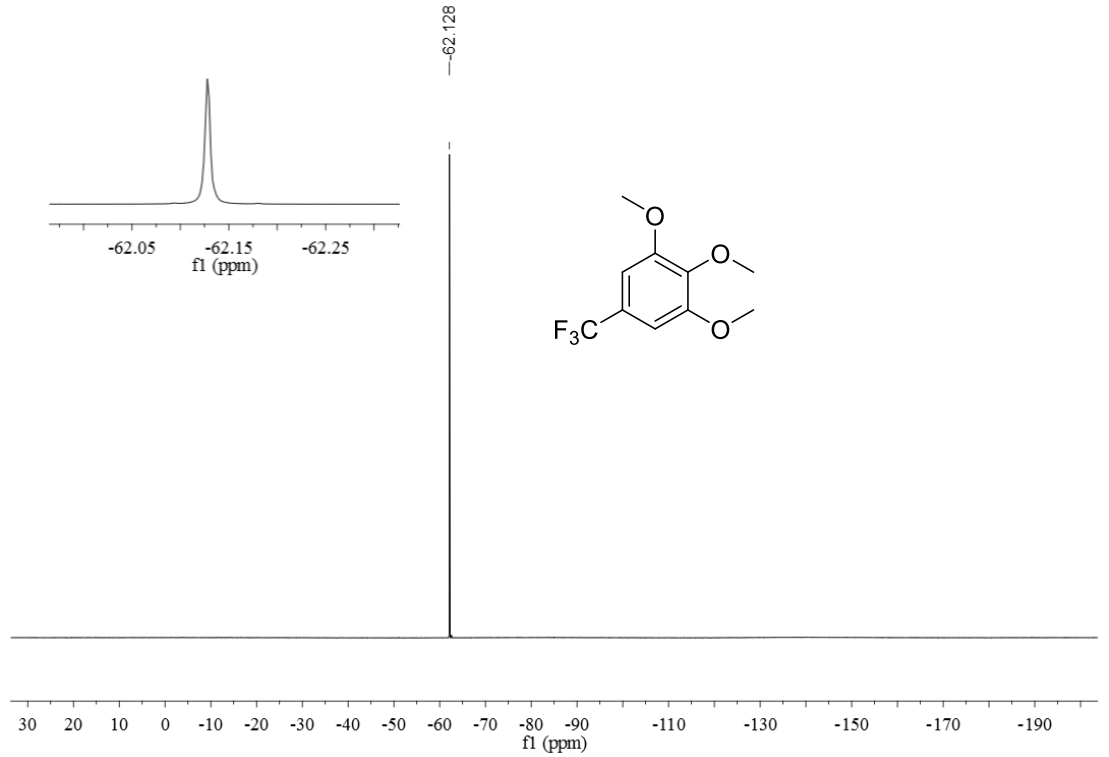
^{13}C NMR spectrum of 1-(4-(trifluoromethyl)phenyl)ethanone 3d



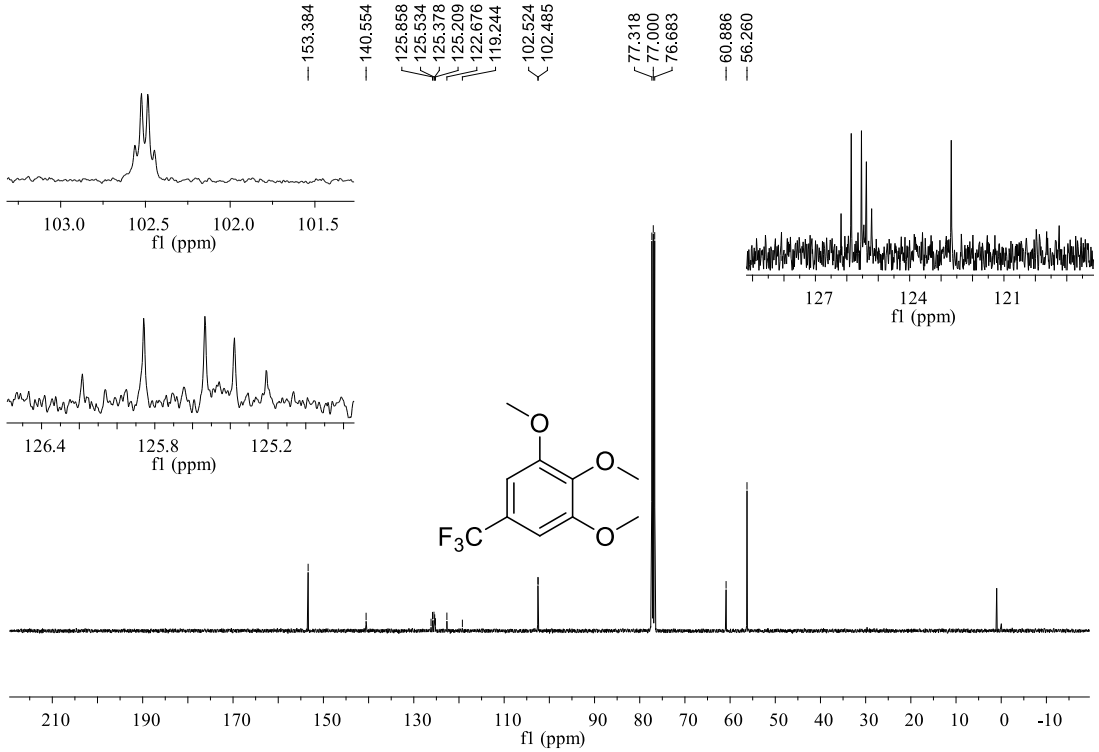
^{1}H NMR spectrum of 1,2,3-trimethoxy-5-(trifluoromethyl)benzene 3e



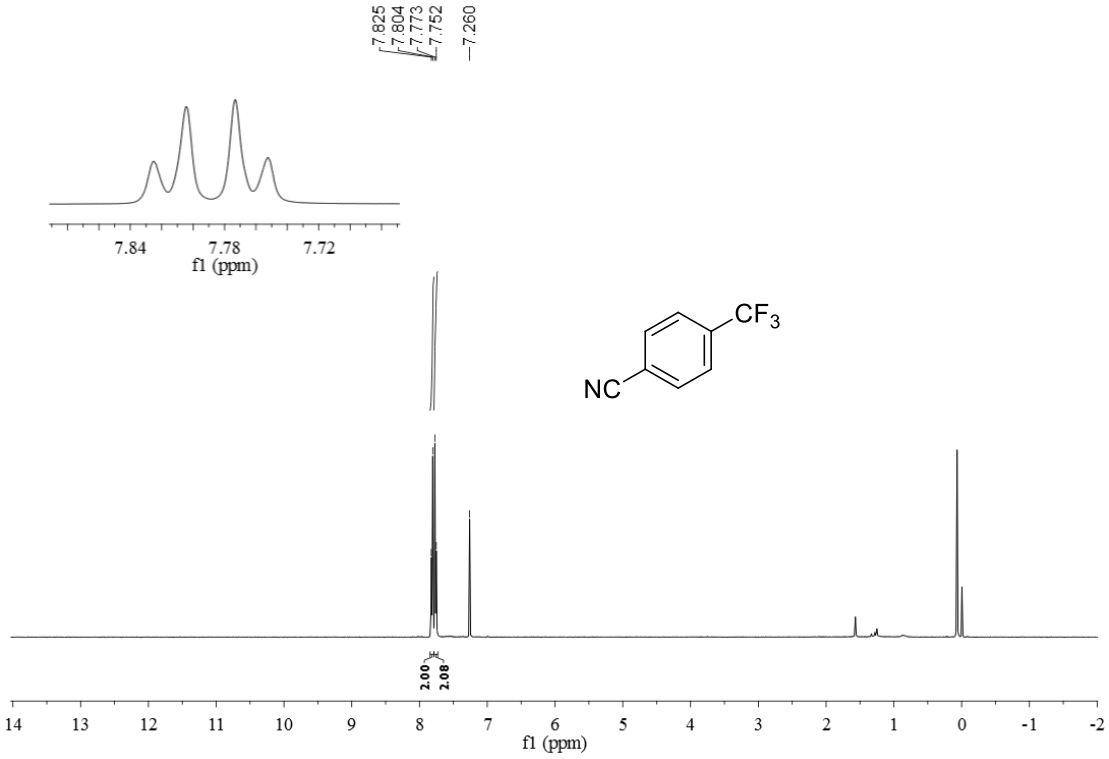
^{19}F NMR spectrum of 1,2,3-trimethoxy-5-(trifluoromethyl)benzene 3e



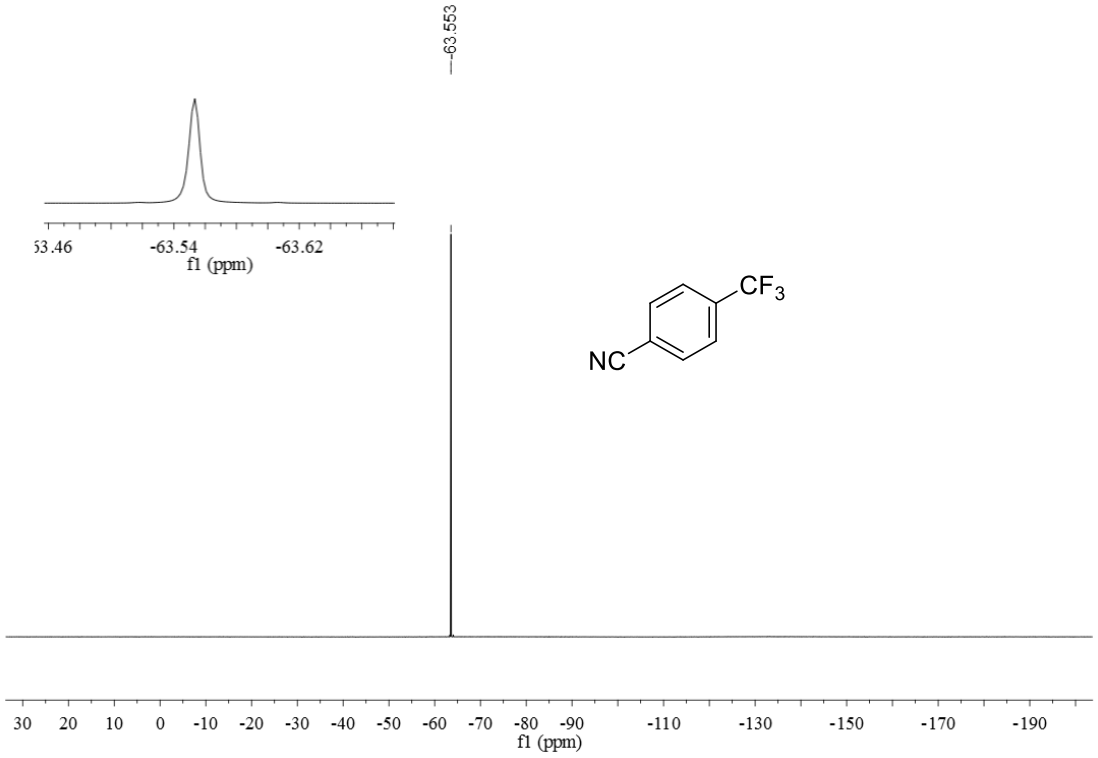
^{13}C NMR spectrum of 1,2,3-trimethoxy-5-(trifluoromethyl)benzene 3e



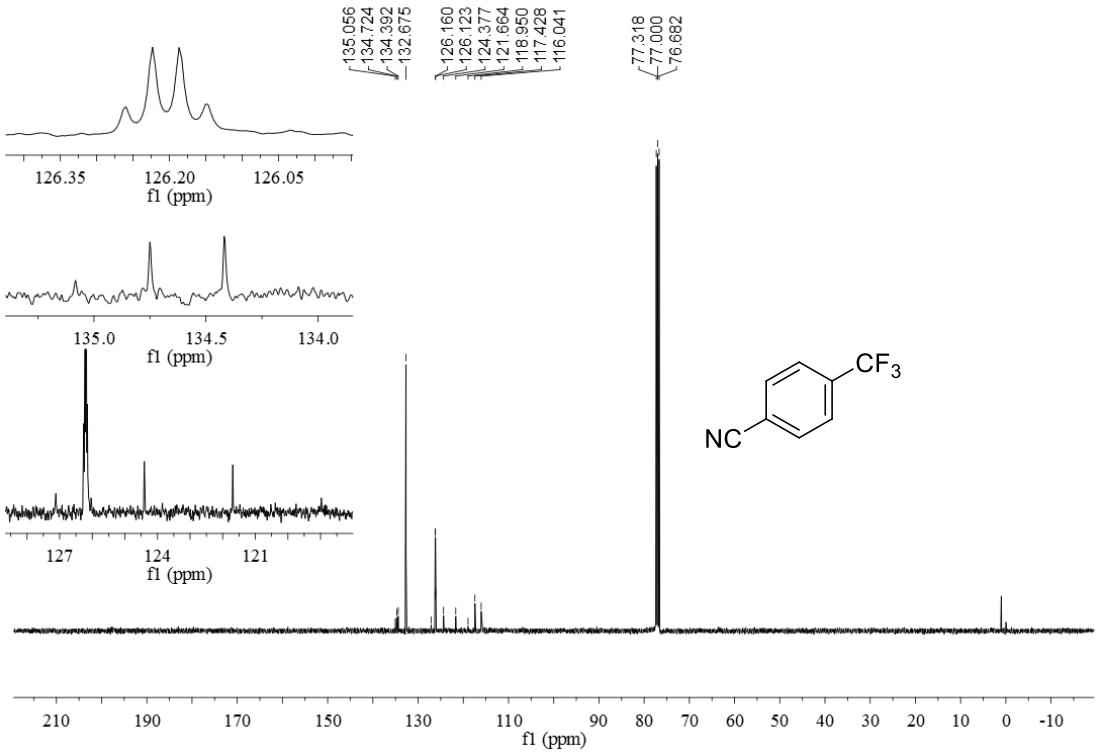
^{1}H NMR spectrum of 4-(trifluoromethyl)benzonitrile 3f



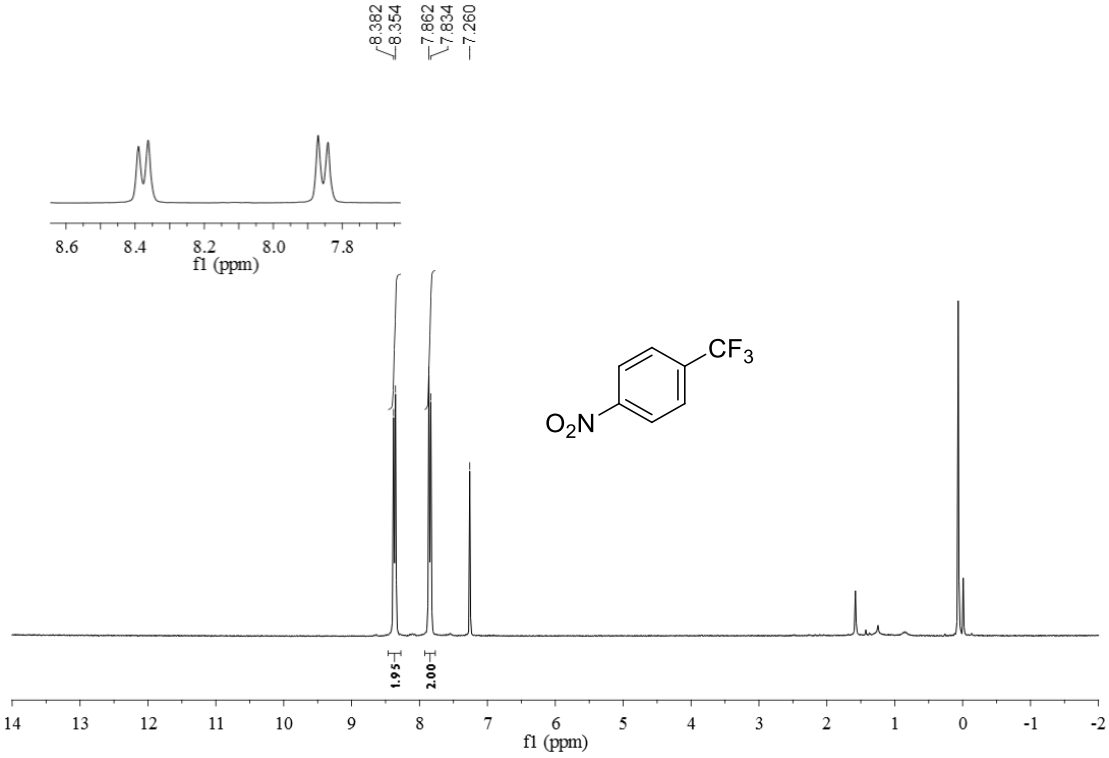
^{19}F NMR spectrum of 4-(trifluoromethyl)benzonitrile 3f



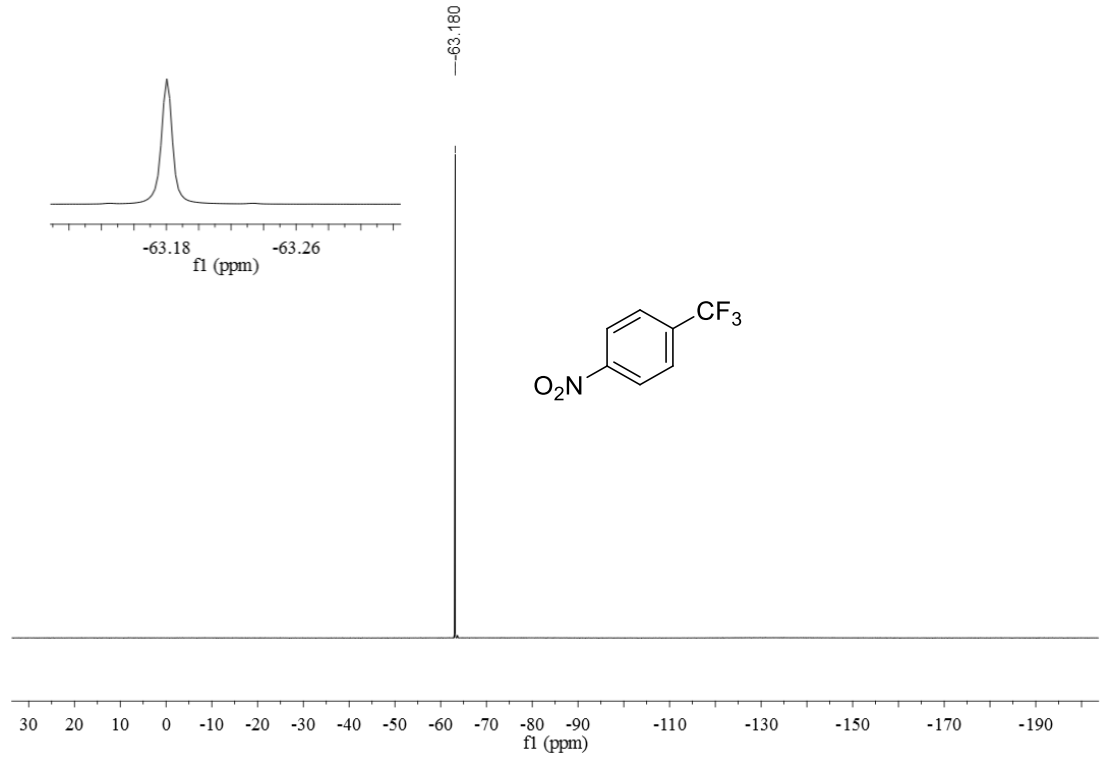
^{13}C NMR spectrum of 4-(trifluoromethyl)benzonitrile 3f



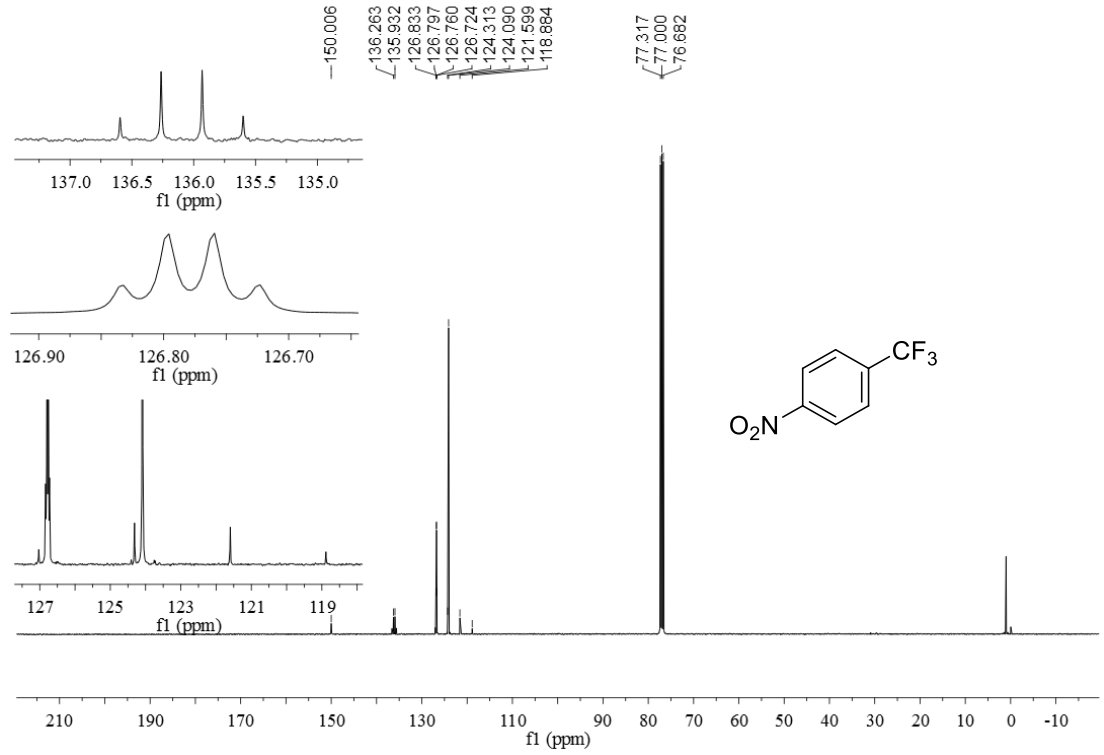
^{1}H NMR spectrum of 1-nitro-4-(trifluoromethyl)benzene 3g



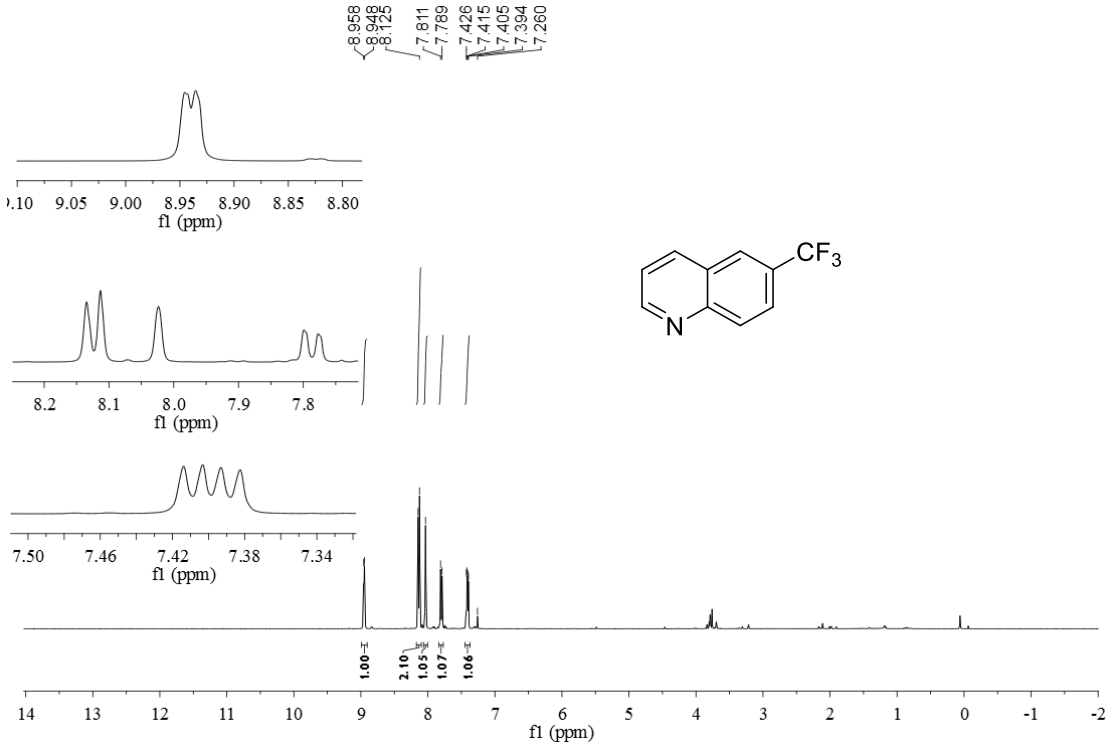
^{19}F NMR spectrum of 1-nitro-4-(trifluoromethyl)benzene 3g



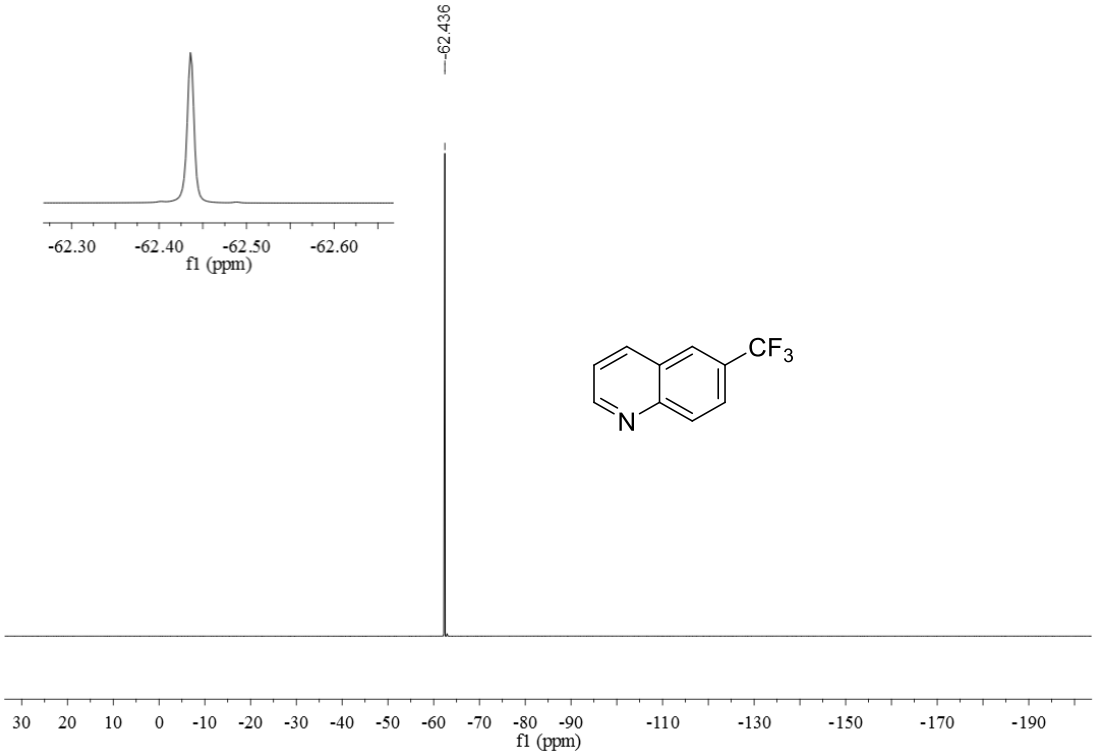
^{13}C NMR spectrum of 1-nitro-4-(trifluoromethyl)benzene 3g



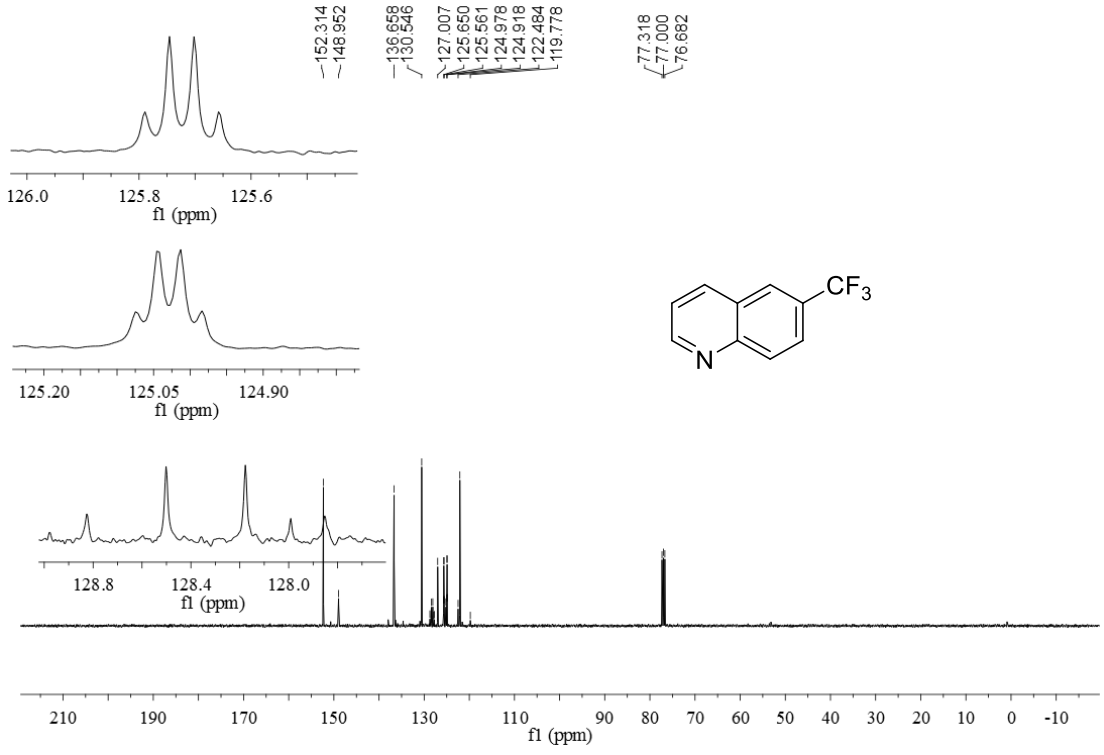
^{1}H NMR spectrum of 6-(trifluoromethyl)quinolone 3h



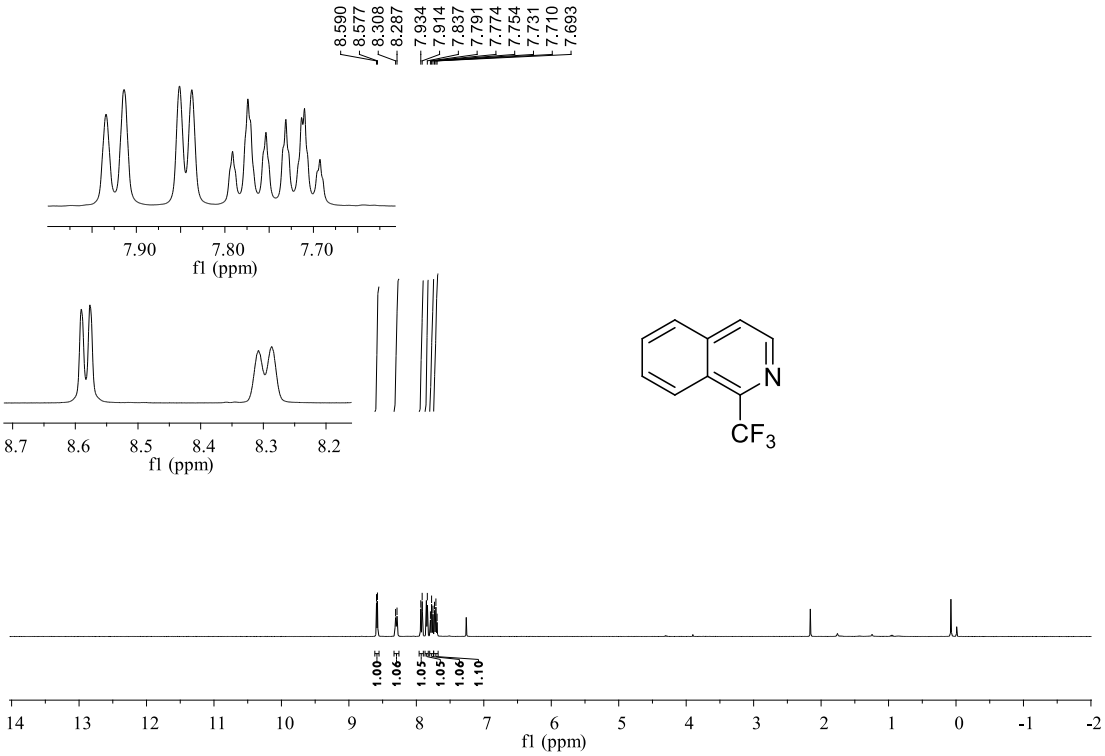
^{19}F NMR spectrum of 6-(trifluoromethyl)quinolone 3h



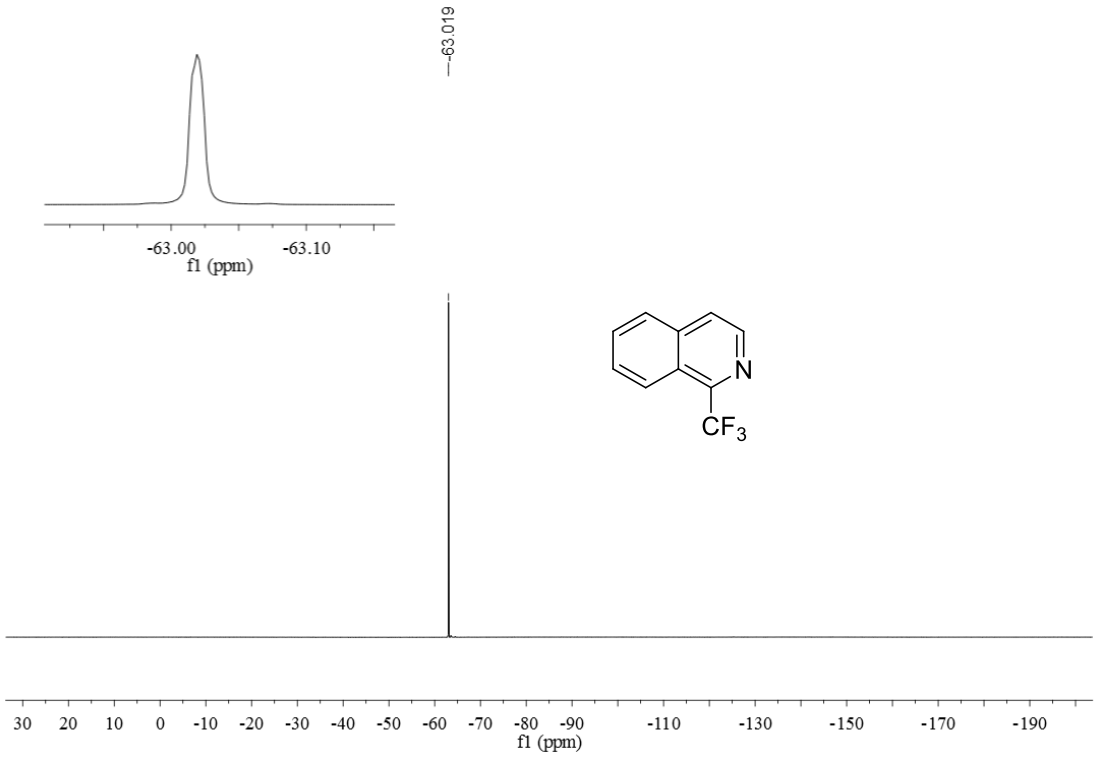
^{13}C NMR spectrum of 6-(trifluoromethyl)quinolone 3h



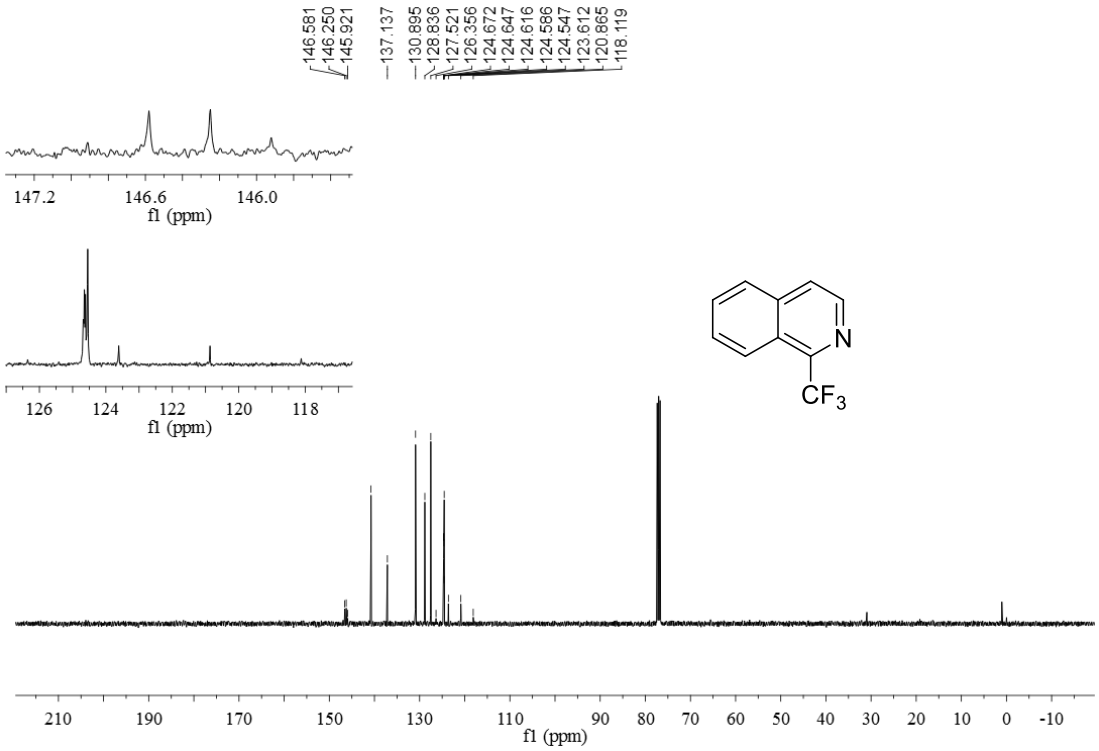
^{1}H NMR spectrum of 1-(trifluoromethyl)isoquinoline 3i



^{19}F NMR spectrum of 1-(trifluoromethyl)isoquinoline 3i



^{13}C NMR spectrum of 1-(trifluoromethyl)isoquinoline 3i



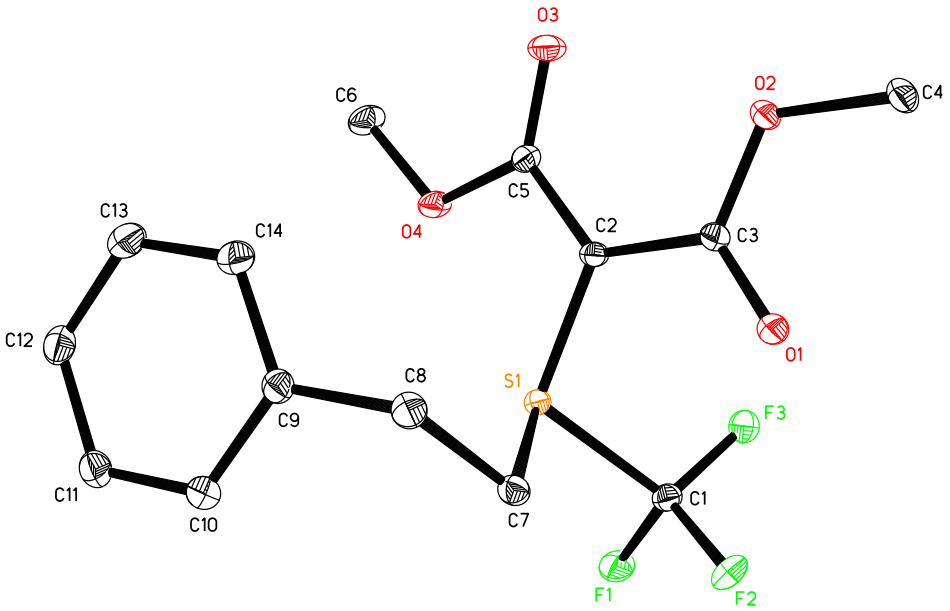


Figure S1. X-ray structure of compound 1i. ORTEP drawing at 50% probability

Table S1. Crystal data and structure refinement for mo_dm14643_0m.

Identification code	mo_dm14643_0m	
Empirical formula	C14 H15 F3 O4 S	
Formula weight	336.32	
Temperature	130 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 5.4571(5) Å	α= 90 °.
	b = 34.890(3) Å	β= 96.378(2) °.
	c = 7.6271(7) Å	γ = 90 °.
Volume	1443.2(2) $Å^3$	
Z	4	
Density (calculated)	1.548 Mg/m^3	
Absorption coefficient	0.274 mm^{-1}	
F(000)	696	
Crystal size	0.3 x 0.25 x 0.2 mm^3	
Theta range for data collection	1.167 to 30.573 °.	
Index ranges	-7<=h<=7, -49<=k<=49, -10<=l<=7	
Reflections collected	14482	
Independent reflections	4407 [R(int) = 0.0256]	
Completeness to theta = 25.242 °	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.6880	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4407 / 0 / 201	
Goodness-of-fit on F^2	1.184	
Final R indices [I>2sigma(I)]	R1 = 0.0446, wR2 = 0.1210	
R indices (all data)	R1 = 0.0530, wR2 = 0.1316	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.453 and -0.383 e.$Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for mo_dm14643_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	4778(1)	950(1)	2825(1)	15(1)
F(1)	6898(2)	435(1)	1035(2)	26(1)
F(2)	3058(2)	317(1)	1063(2)	25(1)
F(3)	5569(2)	210(1)	3385(2)	23(1)
O(1)	602(2)	542(1)	4056(2)	21(1)
O(2)	1576(2)	659(1)	6948(2)	20(1)
O(3)	5244(3)	1183(1)	7774(2)	27(1)
O(4)	7534(2)	1311(1)	5571(2)	22(1)
C(1)	5054(3)	442(1)	2034(2)	18(1)
C(2)	4028(3)	931(1)	4923(2)	16(1)
C(3)	1920(3)	698(1)	5245(2)	16(1)
C(4)	-385(3)	398(1)	7272(2)	21(1)
C(5)	5584(3)	1143(1)	6237(2)	17(1)
C(6)	9072(4)	1547(1)	6778(3)	27(1)
C(7)	2104(3)	1093(1)	1318(2)	18(1)
C(8)	1246(3)	1488(1)	1874(2)	21(1)
C(9)	3208(3)	1794(1)	1941(2)	19(1)
C(10)	4322(4)	1889(1)	440(2)	23(1)
C(11)	6144(4)	2168(1)	507(3)	26(1)
C(12)	6895(4)	2355(1)	2079(3)	26(1)
C(13)	5816(4)	2264(1)	3581(3)	30(1)
C(14)	3986(4)	1985(1)	3507(3)	27(1)

Table S3. Bond lengths [Å] and angles [°] for mo_dm14643_0m.

S(1)-C(1)	1.8819(18)
S(1)-C(2)	1.6963(16)
S(1)-C(7)	1.8246(17)
F(1)-C(1)	1.328(2)
F(2)-C(1)	1.321(2)
F(3)-C(1)	1.315(2)
O(1)-C(3)	1.221(2)
O(2)-C(3)	1.3394(19)
O(2)-C(4)	1.448(2)
O(3)-C(5)	1.215(2)
O(4)-C(5)	1.361(2)
O(4)-C(6)	1.435(2)
C(2)-C(3)	1.451(2)
C(2)-C(5)	1.443(2)
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(7)-C(8)	1.529(2)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(8)-C(9)	1.509(3)
C(9)-C(10)	1.394(2)
C(9)-C(14)	1.393(3)
C(10)-H(10)	0.9500
C(10)-C(11)	1.388(3)
C(11)-H(11)	0.9500
C(11)-C(12)	1.387(3)
C(12)-H(12)	0.9500
C(12)-C(13)	1.382(3)
C(13)-H(13)	0.9500
C(13)-C(14)	1.390(3)

C(14)-H(14)	0.9500
C(2)-S(1)-C(1)	107.65(8)
C(2)-S(1)-C(7)	110.17(8)
C(7)-S(1)-C(1)	98.24(8)
C(3)-O(2)-C(4)	114.51(13)
C(5)-O(4)-C(6)	115.68(14)
F(1)-C(1)-S(1)	107.07(12)
F(2)-C(1)-S(1)	113.52(12)
F(2)-C(1)-F(1)	107.61(14)
F(3)-C(1)-S(1)	110.16(11)
F(3)-C(1)-F(1)	109.20(14)
F(3)-C(1)-F(2)	109.15(14)
C(3)-C(2)-S(1)	117.35(12)
C(5)-C(2)-S(1)	116.78(12)
C(5)-C(2)-C(3)	125.85(14)
O(1)-C(3)-O(2)	122.74(15)
O(1)-C(3)-C(2)	122.43(15)
O(2)-C(3)-C(2)	114.81(14)
O(2)-C(4)-H(4A)	109.5
O(2)-C(4)-H(4B)	109.5
O(2)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
O(3)-C(5)-O(4)	121.32(15)
O(3)-C(5)-C(2)	126.00(16)
O(4)-C(5)-C(2)	112.66(14)
O(4)-C(6)-H(6A)	109.5
O(4)-C(6)-H(6B)	109.5
O(4)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
S(1)-C(7)-H(7A)	110.0
S(1)-C(7)-H(7B)	110.0
H(7A)-C(7)-H(7B)	108.3
C(8)-C(7)-S(1)	108.69(12)

C(8)-C(7)-H(7A)	110.0
C(8)-C(7)-H(7B)	110.0
C(7)-C(8)-H(8A)	108.7
C(7)-C(8)-H(8B)	108.7
H(8A)-C(8)-H(8B)	107.6
C(9)-C(8)-C(7)	114.13(14)
C(9)-C(8)-H(8A)	108.7
C(9)-C(8)-H(8B)	108.7
C(10)-C(9)-C(8)	120.82(16)
C(14)-C(9)-C(8)	121.03(16)
C(14)-C(9)-C(10)	118.14(17)
C(9)-C(10)-H(10)	119.6
C(11)-C(10)-C(9)	120.77(17)
C(11)-C(10)-H(10)	119.6
C(10)-C(11)-H(11)	119.9
C(12)-C(11)-C(10)	120.28(18)
C(12)-C(11)-H(11)	119.9
C(11)-C(12)-H(12)	120.2
C(13)-C(12)-C(11)	119.69(18)
C(13)-C(12)-H(12)	120.2
C(12)-C(13)-H(13)	120.1
C(12)-C(13)-C(14)	119.88(19)
C(14)-C(13)-H(13)	120.1
C(9)-C(14)-H(14)	119.4
C(13)-C(14)-C(9)	121.24(18)
C(13)-C(14)-H(14)	119.4

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for mo_dm14643_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	16(1)	16(1)	14(1)	-1(1)	3(1)	-3(1)
F(1)	27(1)	29(1)	25(1)	-8(1)	13(1)	-2(1)
F(2)	25(1)	22(1)	27(1)	-9(1)	-2(1)	-3(1)
F(3)	28(1)	18(1)	23(1)	1(1)	3(1)	1(1)
O(1)	23(1)	23(1)	16(1)	-1(1)	3(1)	-7(1)
O(2)	21(1)	23(1)	15(1)	0(1)	4(1)	-7(1)
O(3)	28(1)	35(1)	17(1)	-9(1)	7(1)	-11(1)
O(4)	19(1)	29(1)	18(1)	-7(1)	4(1)	-9(1)
C(1)	19(1)	19(1)	17(1)	-3(1)	3(1)	-2(1)
C(2)	17(1)	18(1)	12(1)	-2(1)	3(1)	-2(1)
C(3)	17(1)	17(1)	15(1)	0(1)	4(1)	0(1)
C(4)	20(1)	24(1)	19(1)	2(1)	6(1)	-5(1)
C(5)	16(1)	17(1)	17(1)	-2(1)	2(1)	-1(1)
C(6)	23(1)	33(1)	25(1)	-11(1)	3(1)	-10(1)
C(7)	19(1)	20(1)	15(1)	2(1)	0(1)	-1(1)
C(8)	21(1)	20(1)	22(1)	0(1)	4(1)	1(1)
C(9)	21(1)	17(1)	21(1)	1(1)	4(1)	3(1)
C(10)	27(1)	22(1)	19(1)	0(1)	3(1)	0(1)
C(11)	31(1)	22(1)	25(1)	3(1)	7(1)	-2(1)
C(12)	29(1)	19(1)	31(1)	-1(1)	5(1)	-2(1)
C(13)	38(1)	26(1)	27(1)	-7(1)	6(1)	-6(1)
C(14)	34(1)	25(1)	24(1)	-5(1)	10(1)	-3(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for mo_dm14643_0m.

	x	y	z	U(eq)
H(4A)	-1951	491	6669	31
H(4B)	-501	383	8543	31
H(4C)	-29	143	6823	31
H(6A)	8043	1690	7524	40
H(6B)	9995	1727	6114	40
H(6C)	10230	1385	7521	40
H(7A)	2549	1104	96	21
H(7B)	759	904	1357	21
H(8A)	-175	1569	1037	25
H(8B)	668	1466	3055	25
H(10)	3827	1761	-642	27
H(11)	6880	2230	-527	31
H(12)	8145	2545	2124	31
H(13)	6324	2391	4661	36
H(14)	3252	1924	4545	32

Table S6. Torsion angles [°] for mo_dm14643_0m.

S(1)-C(2)-C(3)-O(1)	-5.4(2)
S(1)-C(2)-C(3)-O(2)	172.88(12)
S(1)-C(2)-C(5)-O(3)	174.99(16)
S(1)-C(2)-C(5)-O(4)	-3.4(2)
S(1)-C(7)-C(8)-C(9)	56.88(17)
C(1)-S(1)-C(2)-C(3)	-52.19(15)
C(1)-S(1)-C(2)-C(5)	126.50(13)
C(1)-S(1)-C(7)-C(8)	171.78(12)
C(2)-S(1)-C(1)-F(1)	-143.17(11)
C(2)-S(1)-C(1)-F(2)	98.23(13)
C(2)-S(1)-C(1)-F(3)	-24.53(14)
C(2)-S(1)-C(7)-C(8)	59.47(13)
C(3)-C(2)-C(5)-O(3)	-6.5(3)
C(3)-C(2)-C(5)-O(4)	175.12(16)
C(4)-O(2)-C(3)-O(1)	3.8(2)
C(4)-O(2)-C(3)-C(2)	-174.47(15)
C(5)-C(2)-C(3)-O(1)	176.05(16)
C(5)-C(2)-C(3)-O(2)	-5.7(2)
C(6)-O(4)-C(5)-O(3)	-2.4(3)
C(6)-O(4)-C(5)-C(2)	176.11(16)
C(7)-S(1)-C(1)-F(1)	102.52(12)
C(7)-S(1)-C(1)-F(2)	-16.09(14)
C(7)-S(1)-C(1)-F(3)	-138.84(12)
C(7)-S(1)-C(2)-C(3)	53.90(15)
C(7)-S(1)-C(2)-C(5)	-127.42(13)
C(7)-C(8)-C(9)-C(10)	59.4(2)
C(7)-C(8)-C(9)-C(14)	-119.49(19)
C(8)-C(9)-C(10)-C(11)	-179.30(17)
C(8)-C(9)-C(14)-C(13)	179.10(19)
C(9)-C(10)-C(11)-C(12)	0.3(3)
C(10)-C(9)-C(14)-C(13)	0.1(3)
C(10)-C(11)-C(12)-C(13)	-0.2(3)
C(11)-C(12)-C(13)-C(14)	0.0(3)
C(12)-C(13)-C(14)-C(9)	0.0(3)
C(14)-C(9)-C(10)-C(11)	-0.3(3)