Supporting information *for*

Pd(II)-Catalyzed Regioselective Hydroarylation of Allenyl-containing α-Amino Acid Derivatives with Aryl Boronic Acids

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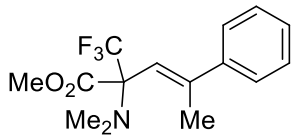
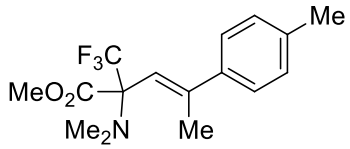
General information

All solvents used in reactions were freshly distilled from appropriate drying agents before use. All other reagents were distilled as necessary. Analytical TLC was performed with Merck silica gel 60 F 254 plates; visualization was accomplished with UV light or spraying with $Ce(SO_4)_2$ solution in 5% H_2SO_4. NMR spectra were obtained with Bruker AV-300, AV-500 and Inova-400 spectrometers operating at 400 and 500 MHz, respectively, for ^{1}H (TMS reference), at 101 and 126 MHz for ^{13}C, at 282 and 376 MHz for ^{19}F (CCl_3F reference). High-resolution mass spectra (HRMS) were recorded on a LCMS-9030 device (Shimadzu, Japan) by electrospray ionization mass spectrometry (ESI-MS). Electrospray ionization (ESI) mass spectra (MS) were obtained from acetonitrile solution.

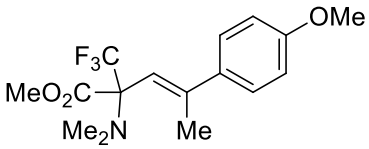
General procedure for hydroarylation of allenes with arylboronic acids. A dried 10 mL Schlenk tube equipped with a magnetic stirrer was charged with a corresponding allene (0.44 mmol, 1.0 equiv.), 1,4-dioxane (2 mL), corresponding aryl boronic acid (1.1 equiv.), $Pd(OAc)_2$ (1 mg, 4 μmol, 1 mol%), dppf (2.5 mg, 4 μmol, 1 mol%) and K_3PO_4 (0.047 g, 0.22 mmol, 0.5 equiv.) under Ar. The reaction mixture was stirred at 50°C for 1-3 h until the completion of the reaction monitored by TLC and ^{19}F NMR. The heterogeneous mixture was passed through a short layer of celite, which was additionally washed with a CH_2Cl_2. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (gradient elution: petroleum ether/dichloromethane = 5:1, petroleum ether/ethyl acetate = 20:1) to give the desired product.



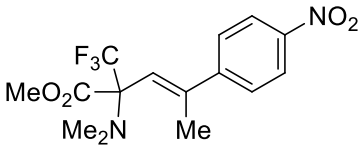
(*E*)-Methyl 2-(dimethylamino)-4-phenyl-2-(trifluoromethyl)pent-3-enoate (3a). Yield 81% (109.3 mg) as a pale yellow thick oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.29 (m, 5H, Ar), 5.78 (s, 1H, CH), 3.81 (s, 3H, OCH_3), 2.55 (s, 6H, $N(CH_3)_2$), 2.23 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 145.1, 143.5, 128.3, 127.8, 126.2 (q, J = 296.9 Hz, *C*F_3), 125.9, 119.7, 73.6 (q, J = 24.0 Hz, >*C*<), 52.5, 40.0, 16.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.75 (s, 3F, CF_3). HRMS (ESI): *m/z* calcd. for $C_{15}H_{19}F_3NO_2$ $[M+H]^+$ 302.1362, found 302.1369.



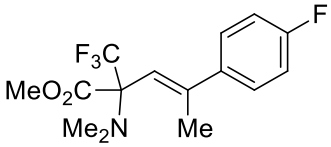
(*E*)-Methyl 2-(dimethylamino)-4-*p*-tolyl-2-(trifluoromethyl)pent-3-enoate (3b) Yield 83% (95.6 mg) as a thick pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.0 Hz, 2H, Ar), 7.14 (d, J = 8.0 Hz, 2H, Ar), 5.76 (s, 1H, CH), 3.80 (s, 3H, OCH_3), 2.54 (s, 6H, $N(CH_3)_2$), 2.34 (s, 3H, CH_3), 2.21 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 144.9, 140.6, 137.7, 128.9, 126.2 (q, J = 296.9 Hz, *C*F_3), 125.8, 118.9, 73.6 (q, J = 23.8 Hz, >*C*<), 52.6, 40.0, 21.0, 16.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.78 (s, 3F, CF_3). HRMS (ESI): *m/z* calcd. for $C_{16}H_{21}F_3NO_2$ $[M+H]^+$ 316.1519, found 316.1525.



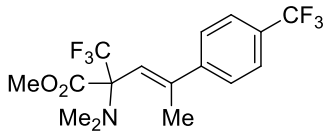
(*E*)-Methyl 2-(dimethylamino)-4-(4-methoxyphenyl)-2-(trifluoromethyl)pent-3-enoate (3c). Yield 68% (100.9 mg) as a pale yellow thick oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.8 Hz, 2H, Ar), 6.85 (d, J = 8.8 Hz, 2H, Ar), 5.71 (s, 1H, CH), 3.80 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 2.54 (s, 6H, $N(CH_3)_2$), 2.19 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 159.4, 144.4, 135.8, 127.0, 126.2 (q, J = 297.0 Hz, *C*F_3), 118.2, 113.6, 73.6 (q, J = 23.8 Hz, >*C*<), 55.2, 52.5, 39.9, 16.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.77 (s, 3F, CF_3). HRMS (ESI): *m/z* calcd. for $C_{16}H_{21}F_3NO_3$ $[M+H]^+$ 332.1468, found 332.1470.



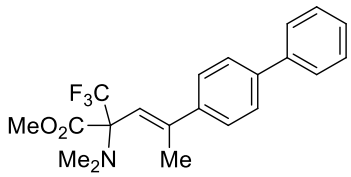
(*E*)-Methyl 2-(dimethylamino)-4-(4-nitrophenyl)-2-(trifluoromethyl)pent-3-enoate (3d). Yield 86% (65.9 mg) as a yellow solid. M.p. 60-62. ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.8 Hz, 2H, Ar), 7.50 (d, J = 8.8 Hz, 2H, Ar), 5.86 (s, 1H, CH), 3.81 (s, 3H, OCH_3), 2.53 (s, 6H, $N(CH_3)_2$), 2.26 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 149.8, 147.3, 143.6, 126.9, 125.8 (q, J = 296.7 Hz, *C*F_3), 123.6, 123.0, 73.7 (q, J = 24.2 Hz, >*C*<), 52.7, 40.0, 16.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.70 (s, 3F, CF_3). HRMS (ESI): *m/z* calcd. for $C_{15}H_{18}F_3N_2O_4$ $[M+H]^+$ 347.1213, found 347.1219.



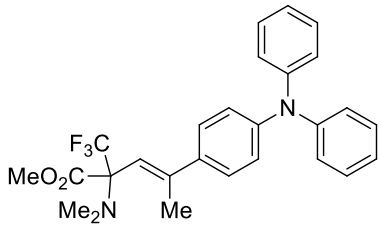
(*E*)-Methyl 2-(dimethylamino)-4-(4-fluorophenyl)-2-(trifluoromethyl)pent-3-enoate (3e). Yield 70% (88.4 mg) as a pale yellow thick oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.32 (m, 2H, Ar), 7.00 (t, J = 8.8 Hz, 2H, Ar), 5.71 (s, 1H, CH), 3.80 (s, 3H, OCH_3), 2.53 (s, 6H, $N(CH_3)_2$), 2.20 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 162.5 (d, J = 248.0 Hz), 144.2, 139.5, 127.6 (d, J = 8.1 Hz), 126.1 (q, J = 296.8 Hz, CF_3), 119.7, 115.1 (d, J = 21.5 Hz), 73.6 (q, J = 24.2 Hz, >*C*<), 52.5, 39.9, 17.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.79 (s, 3F, CF_3), -114.53 (s, 1F, F). HRMS (ESI): *m/z* calcd. for $C_{15}H_{18}F_4NO_2$ $[M+H]^+$ 320.1268, found 320.1274.



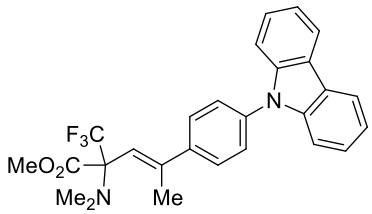
(*E*)-Methyl 2-(dimethylamino)-2-(trifluoromethyl)-4-(4-(trifluoromethyl)phenyl)pent-3-enoate (3f). Yield 79% (93.1 mg) as a pale yellow thick oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.0 Hz, 2H, Ar), 7.47 (d, J = 8.0 Hz, 2H, Ar), 5.81 (s, 1H, CH), 3.81 (s, 3H, OCH_3), 2.54 (s, 6H, $N(CH_3)_2$), 2.25 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 147.0, 144.1, 129.8 (q, J = 32.7 Hz, >*C*<), 126.3, 126.0 (q, J = 296.6 Hz, *C*F_3), 125.3 (q, J = 3.6 Hz), 124.0 (q, J = 272.9 Hz, *C*F_3), 121.6, 73.6 (q, J = 24.3 Hz, >*C*<), 52.6, 40.0, 16.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.63 (s, 3F, CF_3), -66.78 (s, 3F, CF_3). HRMS (ESI): *m/z* calcd. for $C_{16}H_{18}F_6NO_2$ $[M+H]^+$ 370.1236, found 370.1244.



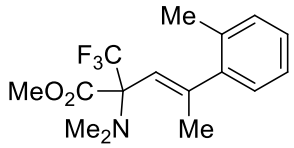
(*E*)-Methyl 4-(biphenyl-4-yl)-2-(dimethylamino)-2-(trifluoromethyl)pent-3-enoate (3g). Yield 83% (100.1 mg) as a white solid. M.p. 81-83 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 4H, Ar), 7.50 – 7.44 (m, 4H, Ar), 7.38 – 7.35 (m, 1H, Ar), 5.88 (s, 1H, CH), 3.84 (s, 3H, OCH_3), 2.59 (s, 6H, $N(CH_3)_2$), 2.29 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 144.6, 142.3, 140.8, 140.5, 128.8, 127.4, 127.1, 127.0, 126.4, 126.2 (q, J = 296.9 Hz, *C*F_3), 119.7, 73.7 (q, J = 23.3 Hz, >*C*<), 52.6, 40.0, 16.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.66 (s, 3F, CF_3). HRMS (ESI): *m/z* calcd. for $C_{21}H_{23}F_3NO_2$ $[M+H]^+$ 378.1675, found 378.1678.



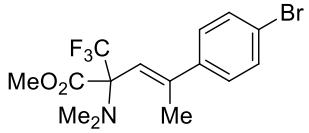
(*E*)-Methyl 2-(dimethylamino)-4-(4-(diphenylamino)phenyl)-2-(trifluoromethyl)pent-3-enoate (3h). Yield 77% (99.8 mg) as a pale yellow thick oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 6H, Ar), 7.10 (d, J = 7.7 Hz, 4H, Ar), 7.05 – 7.01 (m, 4H, Ar), 5.79 (s, 1H, CH), 3.81 (s, 3H, OCH_3), 2.56 (s, 6H, $N(CH_3)_2$), 2.23 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 147.7, 147.5, 144.3, 137.0, 129.2, 126.7, 126.3 (q, J = 297.1 Hz, *C*F_3), 124.4, 123.1, 123.0, 118.3, 73.7 (q, J = 23.6 Hz, >*C*<), 52.6, 40.0, 16.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.66 (s, 3F, CF_3). HRMS (ESI): *m/z* calcd. for $C_{27}H_{27}F_3N_2O_2$ $[M]^{+\bullet}$ 468.2025, found 468.2026.



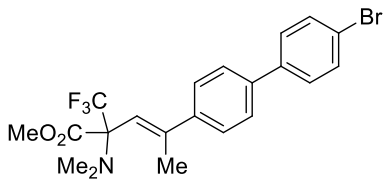
(*E*)-Methyl 4-(4-(9*H*-carbazol-9-yl)phenyl)-2-(dimethylamino)-2-(trifluoromethyl)pent-3-enoate (3i). Yield 85% (100.3 mg) as a pale yellow thick oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 7.6 Hz, 2H, Ar), 7.64 (d, J = 8.4 Hz, 2H, Ar), 7.55 (d, J = 8.4 Hz, 2H, Ar), 7.43 – 7.40 (m, 4H, Ar), 7.32 – 7.29 (m, 2H, Ar), 5.95 (s, 1H, CH), 3.87 (s, 3H, OCH_3), 2.63 (s, 6H, $N(CH_3)_2$), 2.36 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 144.4, 142.4, 140.7, 137.3, 127.4, 126.8, 126.2 (q, J = 297.0 Hz, *C*F_3), 125.9, 123.4, 120.4, 120.3, 120.0, 109.7, 73.7 (q, J = 23.9 Hz, >*C*<), 52.7, 40.1, 16.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.60 (s, 3F, CF_3). HRMS (ESI): *m/z* calcd. for $C_{27}H_{26}F_3N_2O_2$ $[M+H]^+$ 467.1941, found 467.1938.



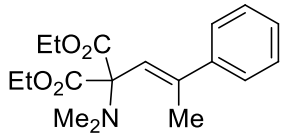
(*E*)-Methyl 2-(dimethylamino)-4-(o-tolyl)-2-(trifluoromethyl)pent-3-enoate (3j). The reaction time is 8 hours. Yield 51% (54.1 mg) as a pale-yellow thick oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.14 (m, 3H, Ar), 7.06 (d, J = 7.0 Hz, 1H, Ar), 5.41 (s, 1H, CH), 3.85 (s, 3H, OCH_3), 2.60 (s, 6H, $N(CH_3)_2$), 2.26 (s, 3H, CH_3), 2.09 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 146.8, 145.1, 134.4, 130.4, 127.5, 127.3, 126.2 (q, J = 294.9 Hz, *C*F_3), 125.8, 121.5, 73.6 (q, J = 24.8 Hz, >*C*<), 52.6, 40.3, 19.5, 19.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.96 (s, 3F, CF_3). HRMS (ESI): *m/z* calcd. for $C_{16}H_{21}F_3NO_2$ $[M+H]^+$ 316.1519, found 316.1517.



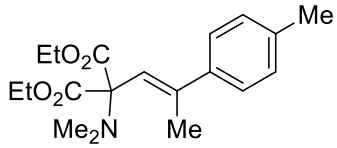
(*E*)-Methyl 4-(4-bromophenyl)-2-(dimethylamino)-2-(trifluoromethyl)pent-3-enoate (3k). Yield 61% (81.9 mg) as a pale yellow thick oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.5 Hz, 2H, Ar), 7.23 (d, J = 8.6 Hz, 2H, Ar), 5.74 (s, 1H, CH), 3.80 (s, 3H, OCH_3), 2.52 (s, 6H, $N(CH_3)_2$), 2.19 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 144.1, 142.3, 131.4, 127.6, 126.0 (q, J = 296.8 Hz, *C*F_3), 121.8, 120.2, 73.6 (q, J = 23.9 Hz, >*C*<), 52.6, 40.0, 16.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.76 (s, 3F, CF_3). HRMS (ESI): *m/z* calcd. for. $C_{15}H_{18}BrF_3NO_2$ $[M+H]^+$ 380.0468, found 380.0467.



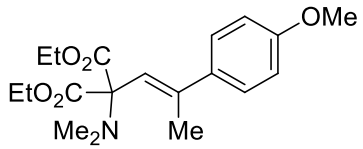
(*E*)-Methyl 4-(4'-bromobiphenyl-4-yl)-2-(dimethylamino)-2-(trifluoromethyl)pent-3-enoate (3l). Yield 14% (22 mg) as a white solid. M.p. 69-71 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 5.55 (m, 4H, Ar), 7.50 – 7.47 (m, 4H, Ar), 5.87 (s, 1H, CH), 3.85 (s, 3H, OCH_3), 2.59 (s, 6H, $N(CH_3)_2$), 2.29 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 144.5, 142.7, 139.5, 139.4, 131.9, 128.6, 126.8, 126.5, 126.2 (q, J = 296.2 Hz, CF_3), 121.7, 120.0, 73.7 (q, J = 23.9 Hz, >*C*<), 52.6, 40.0, 16.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.65 (s, 3F, CF_3). HRMS (ESI): *m/z* calcd. for. $C_{21}H_{22}BrF_3NO_2$ $[M+H]^+$ 456.0781, found 456.0789.



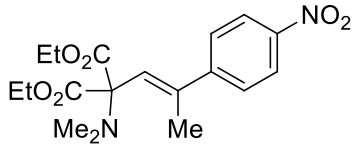
(*E*)-Diethyl 2-(dimethylamino)-2-(2-phenylprop-1-enyl)malonate (4a). Yield 64% (57.1 mg) as a pale yellow thick oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.39 (m, 2H, Ar), 7.33 – 2.29 (m, 2H, Ar), 7.27 – 7.23 (m, 1H, Ar), 6.13 (s, 1H, CH), 4.24 (q, J = 7.1 Hz, 4H, $2OCH_2$), 2.40 (s, 6H, $N(CH_3)_2$), 2.17 (s, 3H, CH_3), 1.26 (t, J = 7.1 Hz, 6H, $2CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 143.6, 142.2, 128.2, 127.4, 125.9, 123.7, 74.9, 61.1, 40.5, 16.8, 14.2. HRMS (ESI): *m/z* calcd. for $C_{18}H_{26}NO_4$ $[M+H]^+$ 320.1856, found 320.1850.



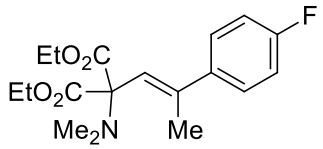
(*E*)-Diethyl 2-(dimethylamino)-2-(2-*p*-tolylprop-1-enyl)malonate (4b). Yield 61% (68.6 mg) as a pale yellow thick oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.1 Hz, 2H, Ar), 7.12 (d, J = 8.1 Hz, 2H, Ar), 6.11 (s, 1H, CH), 4.24 (q, J = 7.1 Hz, 4H, $2OCH_2$), 2.40 (s, 6H, $N(CH_3)_2$), 2.33 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 1.26 (t, J = 7.1 Hz, 6H, $2CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 142.0, 140.7, 137.2, 128.8, 125.7, 122.9, 74.9, 61.0, 40.4, 21.0, 16.7, 14.2. HRMS (ESI): *m/z* calcd. for $C_{19}H_{28}NO_4$ $[M+H]^+$ 334.2013, found 334.2015.



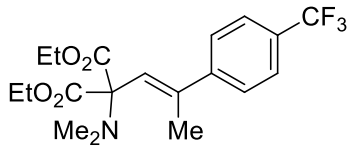
(*E*)-Diethyl 2-(dimethylamino)-2-(2-(4-methoxyphenyl)prop-1-enyl)malonate (4c). Yield 44% (53.2 mg) as a pale yellow thick oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.8 Hz, 2H, Ar), 6.83 (d, J = 8.8 Hz, 2H, Ar), 6.06 (s, 1H, CH), 4.23 (q, J = 7.1 Hz, 4H, $2OCH_2$), 3.78 (s, 3H, OCH_3), 2.39 (s, 6H, $N(CH_3)_2$), 2.13 (s, 3H, CH_3), 1.25 (t, J = 7.1 Hz, 6H, $2CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 159.1, 141.5, 136.0, 126.9, 122.1, 113.5, 74.9, 61.0, 55.2, 40.4, 16.7, 14.2. HRMS (ESI): *m/z* calcd. for $C_{19}H_{28}NO_5$ $[M+H]^+$ 350.1962, found 350.1967.



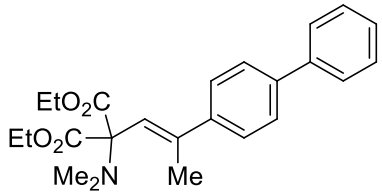
(*E*)-Diethyl 2-(dimethylamino)-2-(2-(4-nitrophenyl)prop-1-enyl)malonate (4d). Yield 51% (51.2 mg) as a pale yellow thick oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.8 Hz, 2H, Ar), 7.51 (d, J = 8.7 Hz, 2H, Ar), 6.26 (s, 1H, CH), 4.24 (q, J = 7.1 Hz, 4H, $2OCH_2$), 2.38 (s, 6H, $N(CH_3)_2$), 2.20 (s, 3H, CH_3), 1.25 (t, J = 7.1 Hz, 6H, $2CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 149.9, 147.0, 140.6, 127.2, 126.6, 123.5, 74.9, 61.3, 40.4, 16.5, 14.2. HRMS (ESI): *m/z* calcd. for $C_{18}H_{25}N_2O_6$ $[M+H]^+$ 365.1707, found 365.1711.



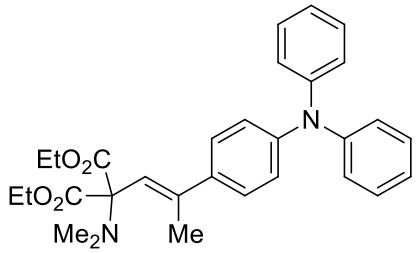
(*E*)-Diethyl 2-(dimethylamino)-2-(2-(4-fluorophenyl)prop-1-enyl)malonate (4e). Yield 68% (74.7 mg) as a pale yellow thick oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 2H, Ar), 6.97 (t, J = 8.5 Hz, 2H, Ar), 6.07 (s, 1H, CH), 4.23 (q, J = 7.1 Hz, 4H, $2OCH_2$), 2.38 (s, 6H, $N(CH_3)_2$), 2.14 (s, 3H, CH_3), 1.24 (t, J = 7.1 Hz, 6H, $2CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 162.3 (d, J = 247.4 Hz), 141.3, 139.6, 127.5 (d, J = 8.1 Hz), 123.6, 114.9 (d, J = 21.4 Hz), 74.8, 61.1, 40.4, 16.9, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.22 (s, 1F, F). HRMS (ESI): *m/z* calcd. for $C_{18}H_{25}FNO_4$ $[M+H]^+$ 338.1762, found 338.1765.



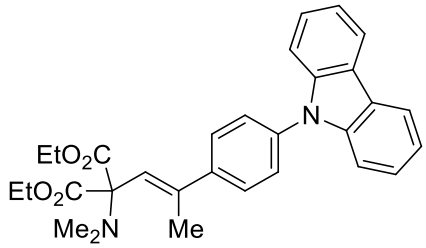
(*E*)-Diethyl 2-(dimethylamino)-2-(2-(4-(trifluoromethyl)phenyl)prop-1-enyl)malonate (4f). Yield 55% (54.7 mg) as a pale yellow thick oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.4 Hz, 2H, Ar), 7.48 (d, J = 8.4 Hz, 2H, Ar), 6.19 (s, 1H, CH), 4.24 (q, J = 7.1 Hz, 4H, $2OCH_2$), 2.39 (s, 6H, $N(CH_3)_2$), 2.18 (s, 3H, CH_3), 1.25 (t, J = 7.1 Hz, 6H, $2CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 147.0, 141.2, 129.4 (q, J = 32.4 Hz), 126.2, 125.6, 125.2 (q, J = 3.6 Hz), 124.1 (q, J = 273 Hz, CF_3), 74.8, 61.2, 40.4, 16.6, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.57 (s, 3F, CF_3). HRMS (ESI): *m/z* calcd. for $C_{19}H_{25}F_3NO_4$ $[M+H]^+$ 388.1730, found 388.1724.



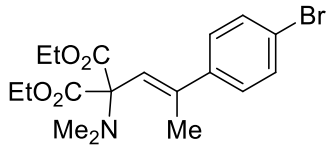
(*E*)-Diethyl 2-(2-(biphenyl-4-yl)prop-1-enyl)-2-(dimethylamino)malonate (4g). Yield 75% (95.1 mg) as a pale yellow thick oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.50 (m, 6H, Ar), 7.43 (t, J = 7.6 Hz, 2H, Ar), 7.36 – 7.32 (m, 1H, Ar), 6.24 (s, 1H, CH), 4.27 (q, J = 7.1 Hz, 4H, $2OCH_2$), 2.44 (s, 6H, $N(CH_3)_2$), 2.24 (s, 3H, CH_3), 1.29 (t, J = 7.1 Hz, 6H, $2CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 142.4, 141.7, 140.6, 140.3, 128.7, 127.3, 127.0, 126.9, 126.3, 123.7, 74.9, 61.1, 40.5, 16.7, 14.2. HRMS (ESI): *m/z* calcd. for $C_{24}H_{30}NO_4$ $[M+H]^+$ 396.2169, found 396.2172.



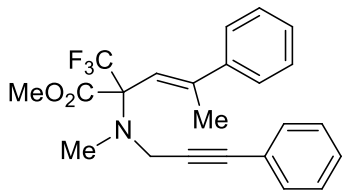
(*E*)-Diethyl 2-(dimethylamino)-2-(2-(4-(diphenylamino)phenyl)prop-1-enyl)malonate (4h). Yield 64% (69.5 mg) as a pale yellow thick oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.29 (m, 2H, Ar), 7.25 – 7.21 (m, 4H, Ar), 7.09 – 7.07 (m, 4H, Ar), 7.02 – 6.98 (m, 4H, Ar), 6.12 (s, 1H, CH), 4.25 (q, J = 7.1 Hz, 4H, $2OCH_2$), 2.40 (s, 6H, $N(CH_3)_2$), 2.15 (s, 3H, CH_3), 1.27 (t, J = 7.1 Hz, 6H, $2CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 147.5, 147.2, 141.4, 137.4, 129.2, 126.6, 124.2, 123.3, 122.8, 122.3, 74.9, 61.1, 40.5, 16.6, 14.2. HRMS (ESI): *m/z* calcd. for $C_{30}H_{34}N_2NaO_4$ $[M+Na]^+$ 509.2411, found 509.2418.



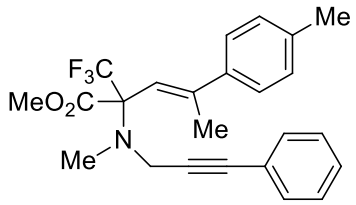
(*E*)-Diethyl 2-(2-(4-(9*H*-carbazol-9-yl)phenyl)prop-1-enyl)-2-(dimethylamino)malonate (4i). Yield 62% (69.8 mg) as a yellow solid. M.p. 130-132ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 7.7 Hz, 2H, Ar), 7.66 (d, J = 8.4 Hz, 2H, Ar), 7.53 (d, J = 8.4 Hz, 2H, Ar), 7.44 – 7.39 (m, 4H, Ar), 7.31 – 7.27 (m, 2H, Ar), 6.32 (s, 1H, CH), 4.31 (q, J = 7.1 Hz, 4H, $2OCH_2$), 2.48 (s, 6H, $N(CH_3)_2$), 2.31 (s, 3H, CH_3), 1.32 (t, J = 7.1 Hz, 6H, $2CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 142.6, 141.5, 140.8, 136.9, 127.3, 126.7, 125.9, 124.4, 123.3, 120.2, 119.9, 109.7, 74.9, 61.2, 40.5, 16.8, 14.3. HRMS (ESI): *m/z* calcd. for $C_{30}H_{33}N_2O_4$ $[M+H]^+$ 485.2435, found 485.2440.



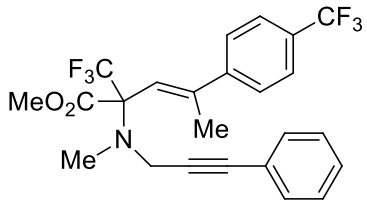
(*E*)-Diethyl 2-(2-(4-bromophenyl)prop-1-enyl)-2-(dimethylamino)malonate (4j). Yield 47% (49.6 mg) as a pale yellow thick oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.5 Hz, 2H, Ar), 7.25 (d, J = 8.5 Hz, 2H, Ar), 6.11 (s, 1H, CH), 4.24 (q, J = 7.1 Hz, 4H, $2OCH_2$), 2.38 (s, 6H, $N(CH_3)_2$), 2.14 (s, 3H, CH_3), 1.25 (t, J = 7.1 Hz, 6H, $2CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 142.4, 141.2, 132.3, 131.2, 127.5, 124.2, 74.8, 61.2, 40.4, 16.6, 14.2. HRMS (ESI): *m/z* calcd. for $C_{18}H_{25}BrNO_4$ $[M+H]^+$ 398.0961, found 398.0961.



(*E*)-Methyl 2-(methyl(3-phenylprop-2-ynyl)amino)-4-phenyl-2-(trifluoromethyl)pent-3-enoate (6a). Yield 80% (39.4 mg) as a pale yellow thick oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 4H, Ar), 7.37 – 7.29 (m, 6H, Ar), 5.83 (s, 1H, CH), 3.96 (d, J = 17.2 Hz, 1H, CH_2), 3.82 (s, 3H, OCH_3), 3.78 (d, J = 17.2 Hz, 1H, CH_2), 2.75 (s, 3H, $N(CH_3)$), 2.36 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 146.6, 143.3, 131.6, 128.3, 128.2, 128.0, 127.9, 126.0, 125.9 (q, J = 296.3 Hz, CF_3), 123.3, 118.9, 86.5, 83.5, 73.5 (q, J = 24.3 Hz, >*C*<), 52.8, 42.4, 36.9, 17.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.91 (s, 3F, CF_3). HRMS (ESI): *m/z* calcd. for $C_{23}H_{23}F_3NO_2$ $[M+H]^+$ 402.1675, found 402.1674.

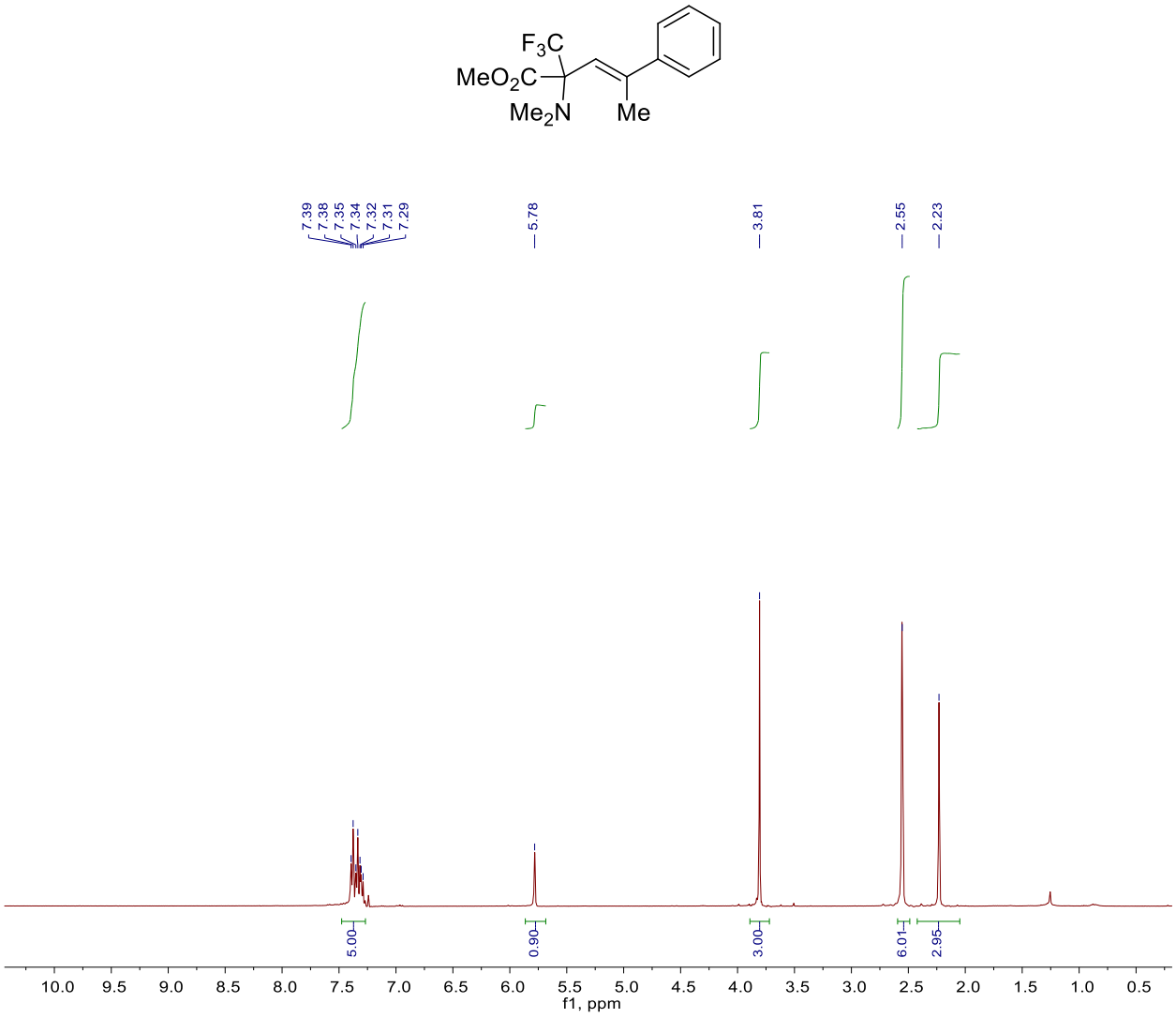


(*E*)-Methyl 2-(methyl(3-phenylprop-2-ynyl)amino)-4-*p*-tolyl-2-(trifluoromethyl)pent-3-enoate (6b). Yield 67% (63.2 mg) as a thick pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.43 (m, 2H, Ar), 7.33 – 7.29 (m, 5H, Ar), 7.17 – 7.16 (m, 2H, Ar), 5.81 (s, 1H, CH), 3.96 (d, J = 16.8 Hz, 1H, CH_2), 3.82 (s, 3H, OCH_3), 3.78 (d, J = 16.4 Hz, 1H, CH_2), 2.75 (s, 3H, $N(CH_3)$), 2.36 (s, 3H, CH_3), 2.34 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 146.3, 140.4, 137.9, 131.6, 129.0, 128.2, 127.9, 126.0 (q, J = 296.1 Hz, CF_3), 125.8, 123.3, 118.2, 86.5, 83.5, 73.5 (q, J = 24.8 Hz, >*C*<), 52.7, 42.3, 36.9, 21.0, 17.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.92 (s, 3F, CF_3). HRMS (ESI): *m/z* calcd. for $C_{24}H_{25}F_3NO_2$ $[M+H]^+$ 416.1832, found 416.1841.

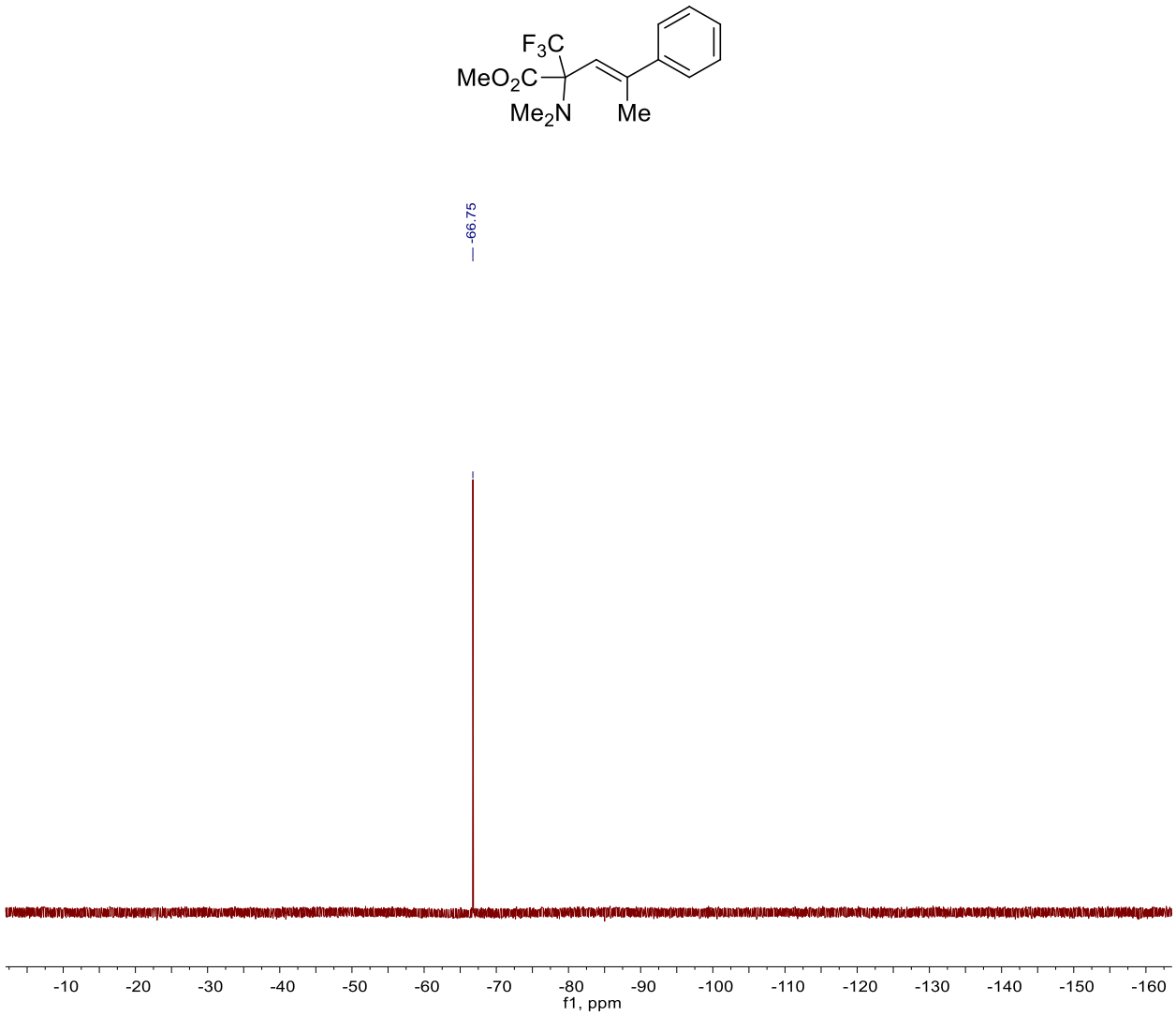


(*E*)-Methyl 2-(methyl(3-phenylprop-2-ynyl)amino)-2-(trifluoromethyl)-4-(4-(trifluoromethyl)phenyl)pent-3-enoate (6c). Yield 71% (75.0 mg) as a pale yellow thick oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.3 Hz, 2H, Ar), 7.50 (d, J = 8.2 Hz, 2H, Ar), 7.44 – 7.41 (m, 2H, Ar), 7.30 – 7.29 (m, 3H, Ar), 5.86 (s, 1H, CH), 3.92 (d, J = 17.1 Hz, 1H, CH_2), 3.83 (s, 3H, OCH_3), 3.77 (d, J = 16.4 Hz, 1H, CH_2), 2.75 (s, 3H, $N(CH_3)$), 2.38 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 146.8, 145.5, 131.5, 129.7 (q, J = 32.2 Hz, >*C*<), 128.2, 128.0, 126.4, 126.3 (q, J = 256.8 Hz, CF_3), 125.8 (q, J = 295.9 Hz, CF_3), 125.3 (q, J = 3.6 Hz), 123.2, 120.9, 86.1, 83.7, 73.5 (q, J = 24.9 Hz, >*C*<), 52.8, 42.5, 36.9, 17.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.60 (s, 3F, CF_3), -66.92 (s, 3F, CF_3). HRMS (ESI): *m/z* calcd. for $C_{24}H_{22}F_6NO_2$ $[M+H]^+$ 470.1549, found 470.1538.

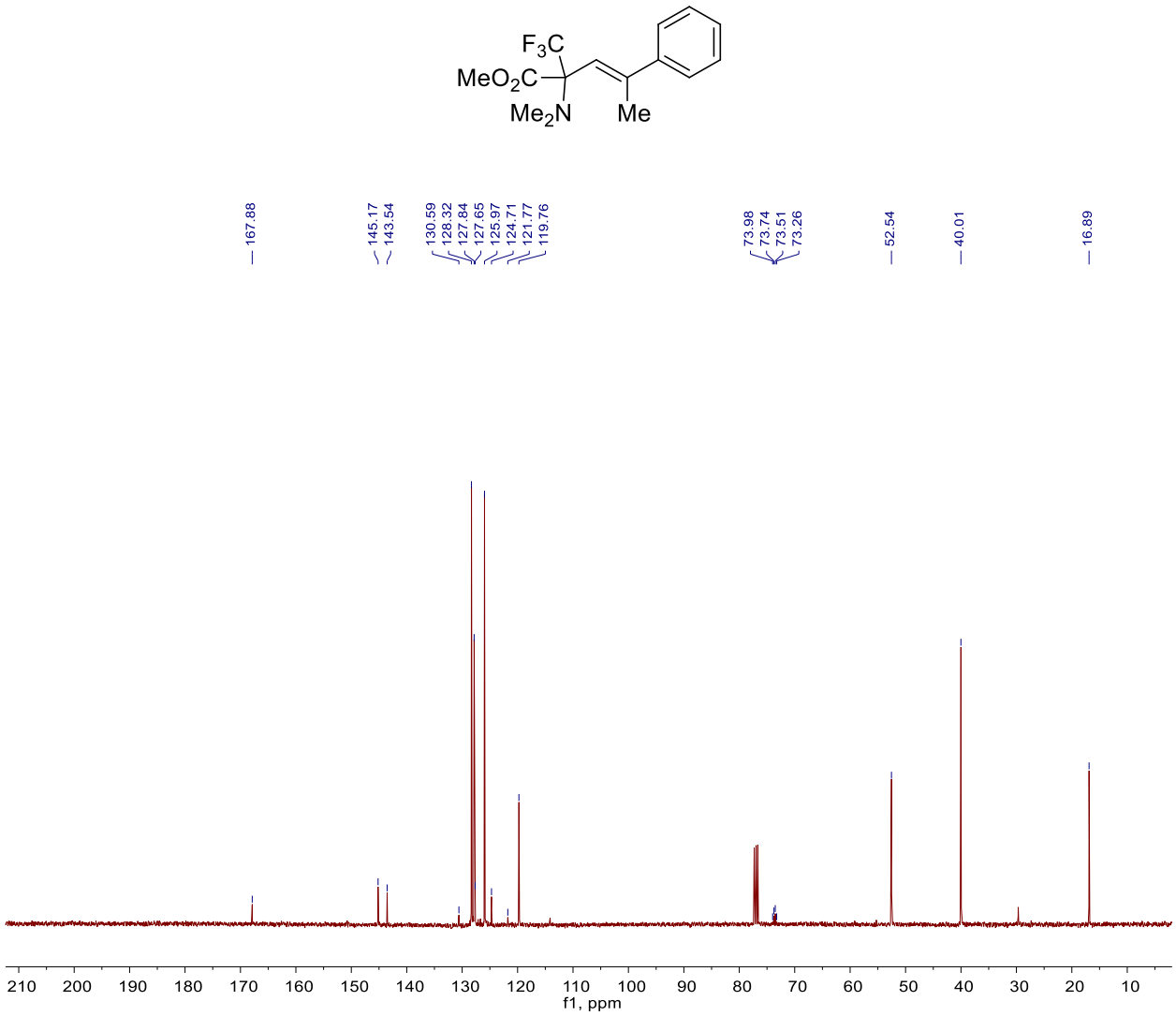
^{1}H NMR, ^{19}F NMR and ^{13}C NMR Spectra.



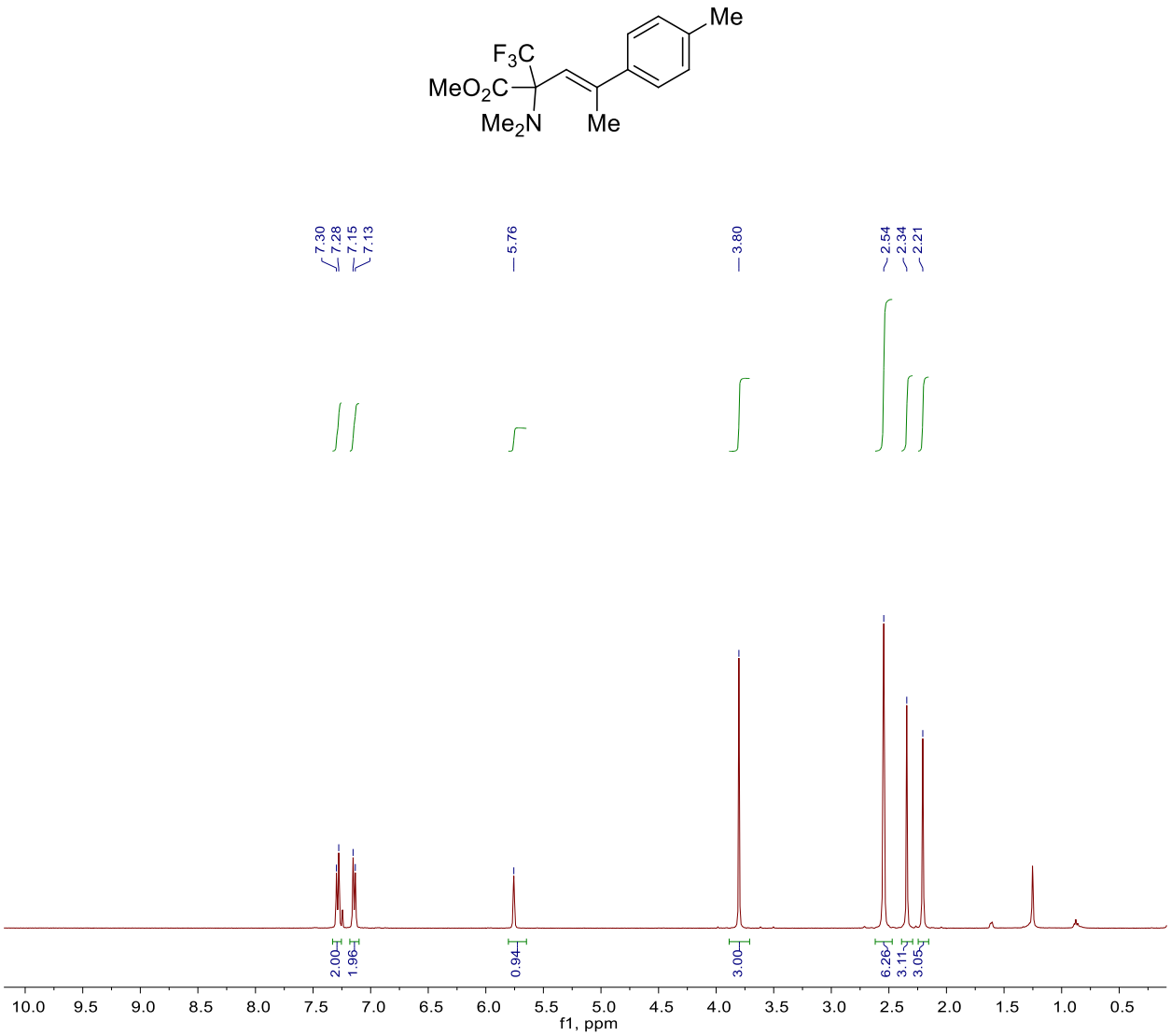
^{1}H spectrum of **3a** in $CDCl_3$



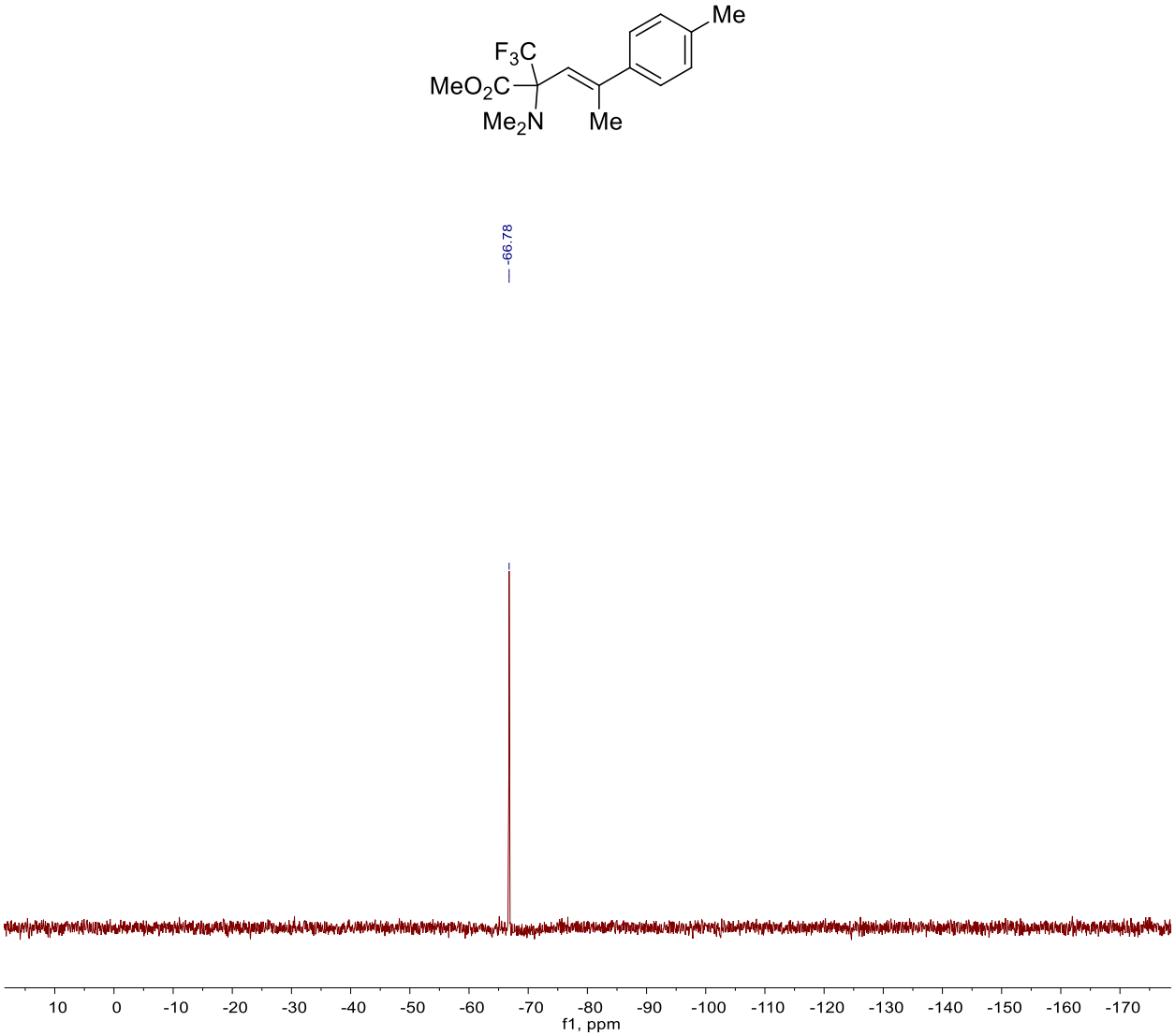
^{19}F spectrum of **3a** in $CDCl_3$



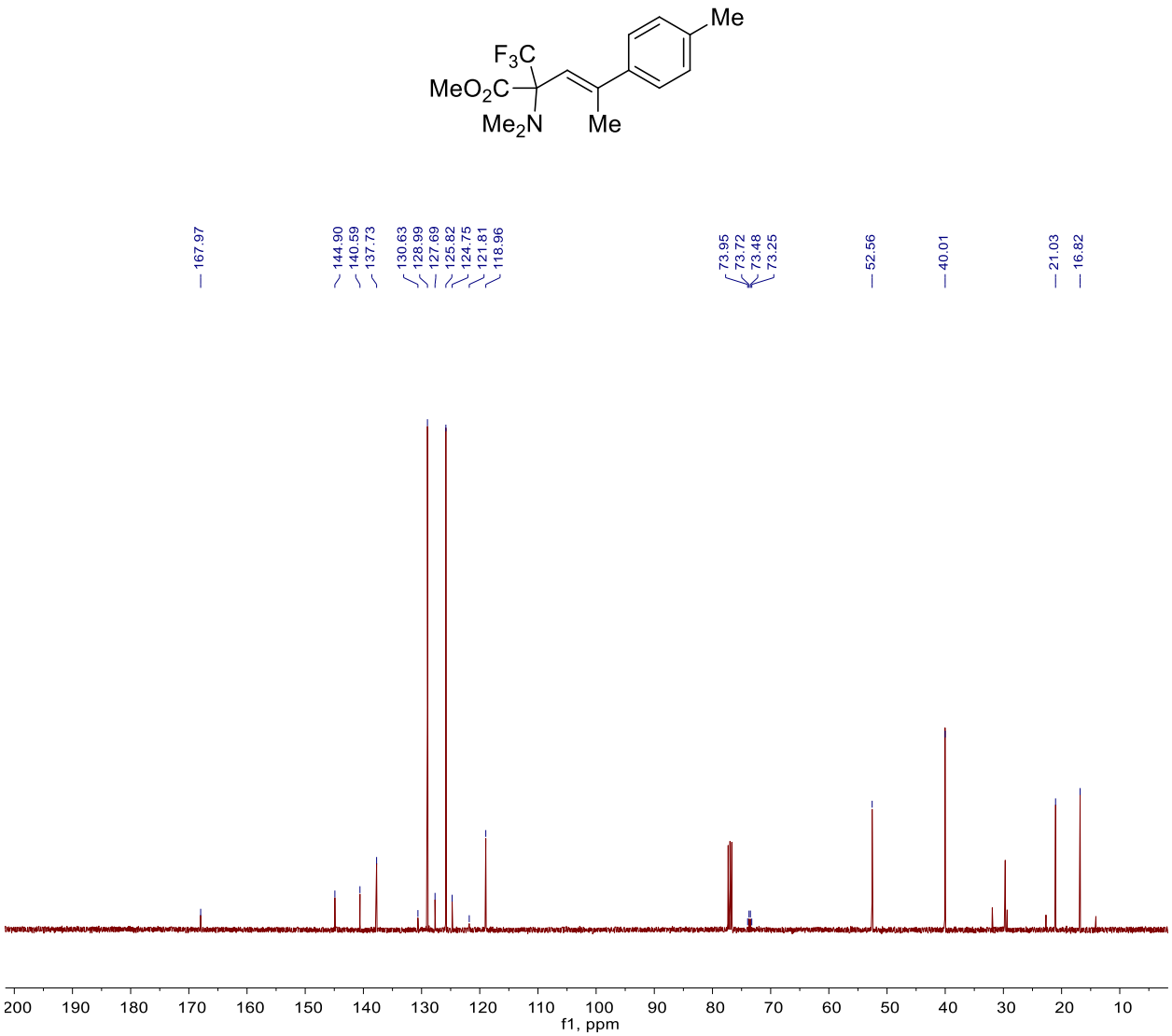
^{13}C spectrum of **3a** in $CDCl_3$



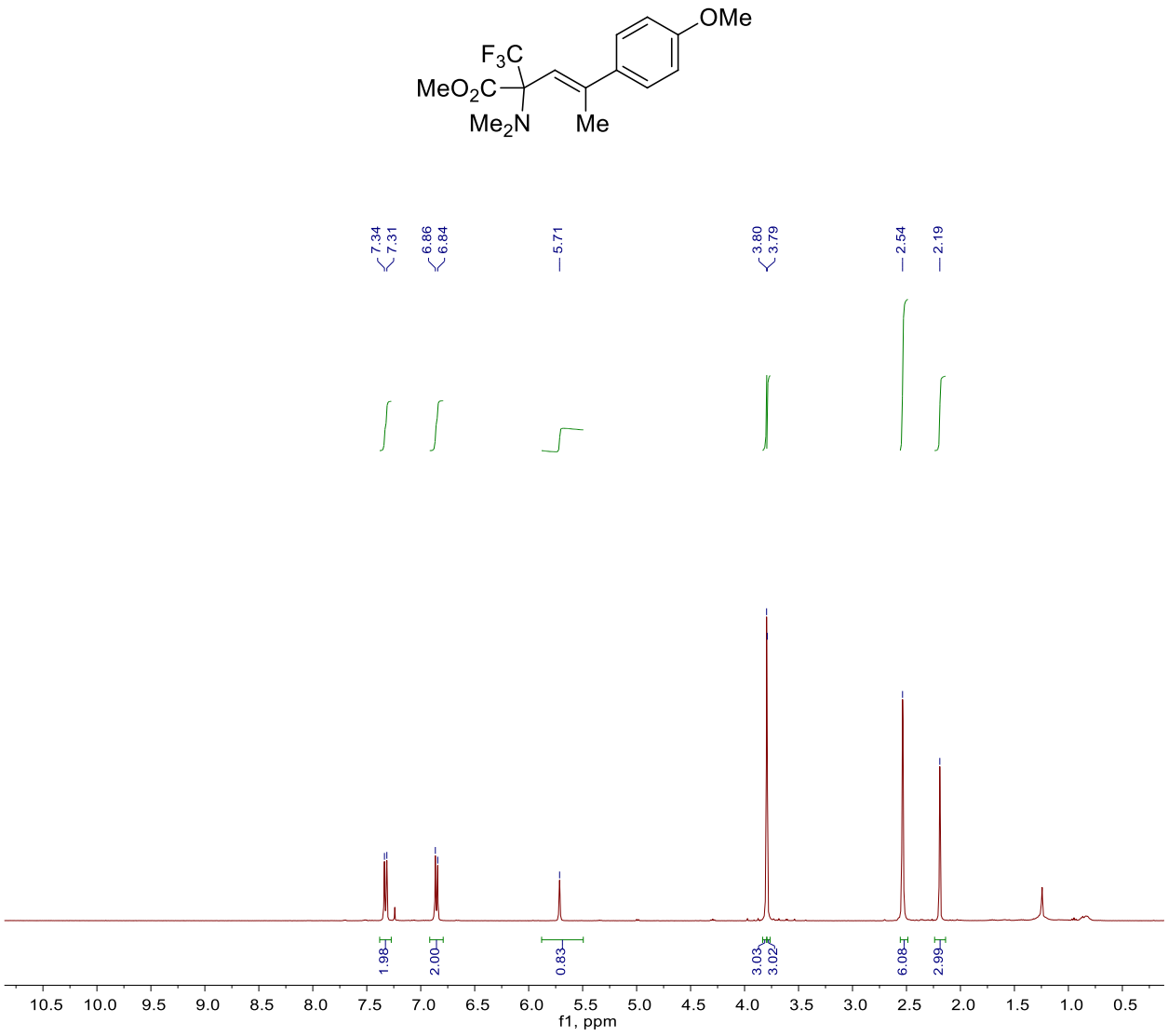
^{1}H spectrum of **3b** in $CDCl_3$



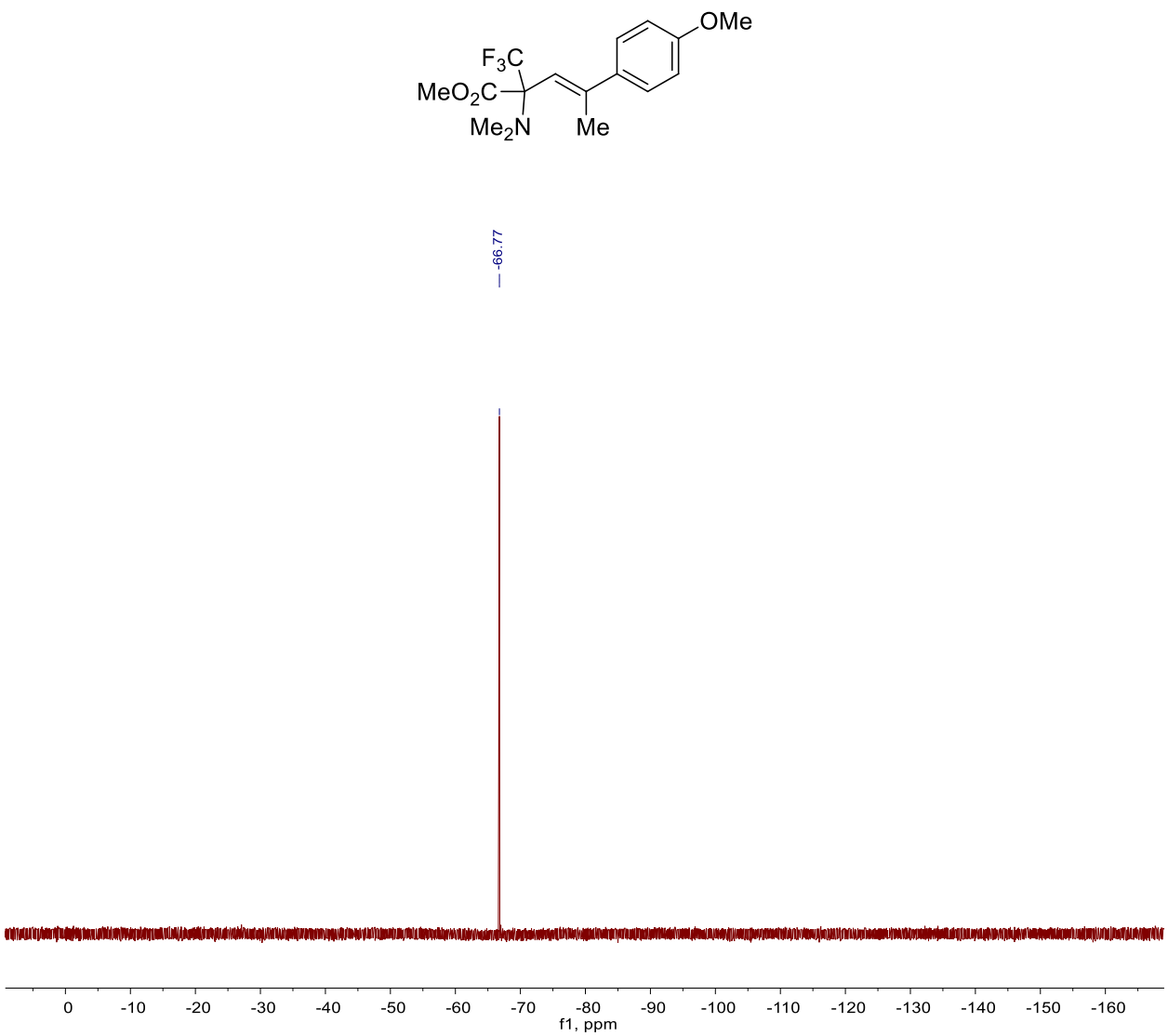
^{19}F spectrum of **3b** in $CDCl_3$



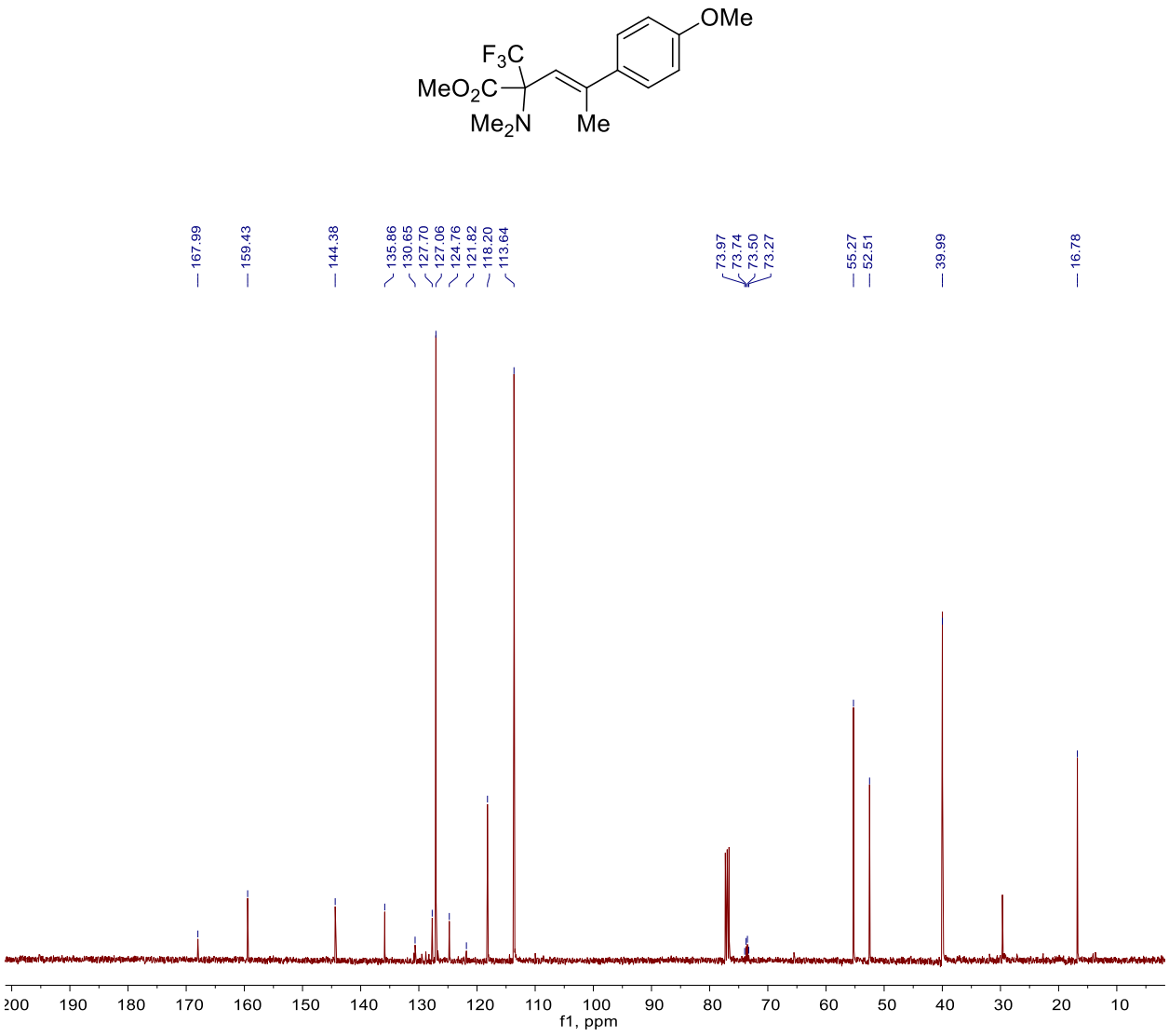
^{13}C spectrum of **3b** in $CDCl_3$



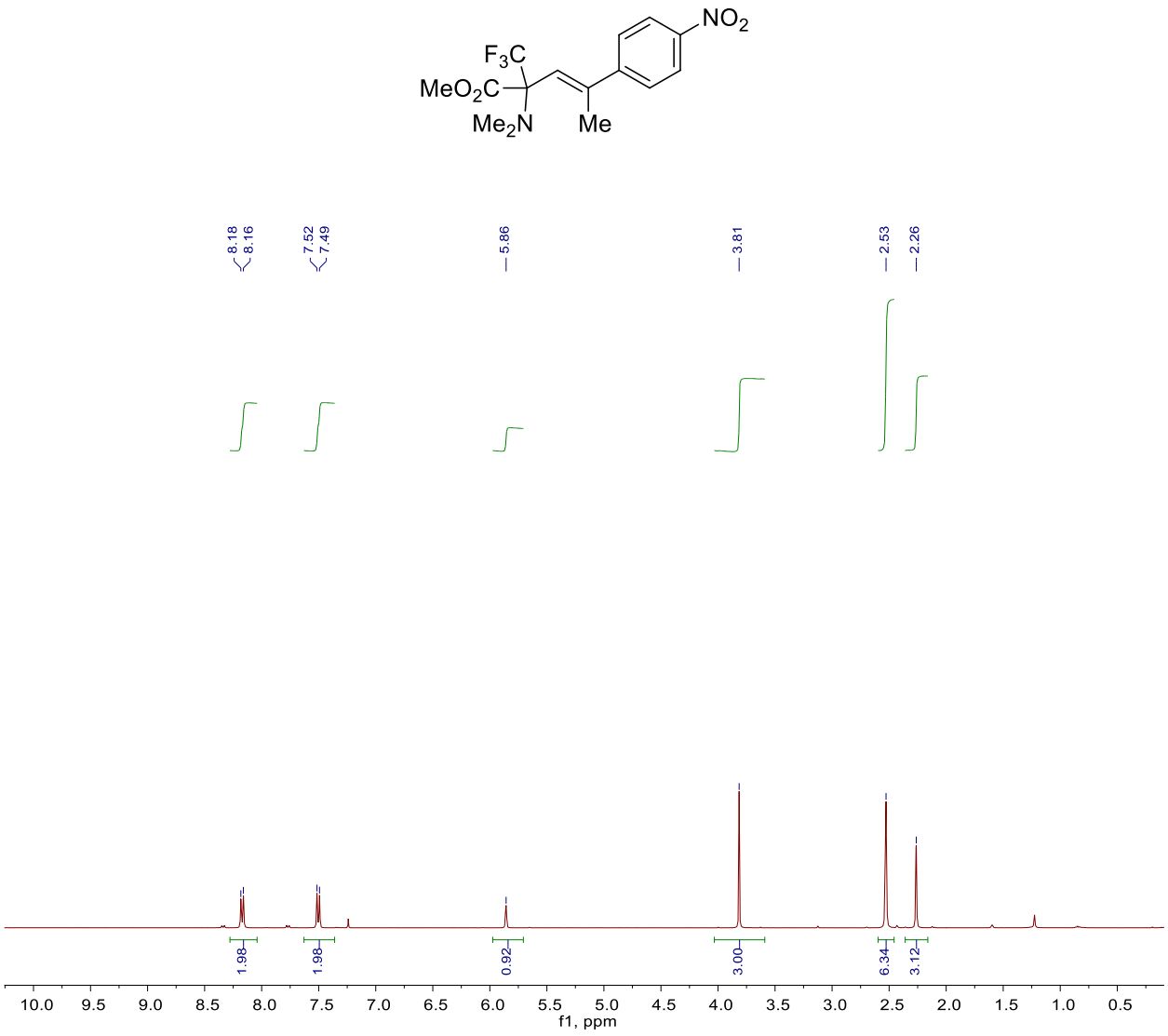
^{1}H spectrum of **3c** in $CDCl_3$



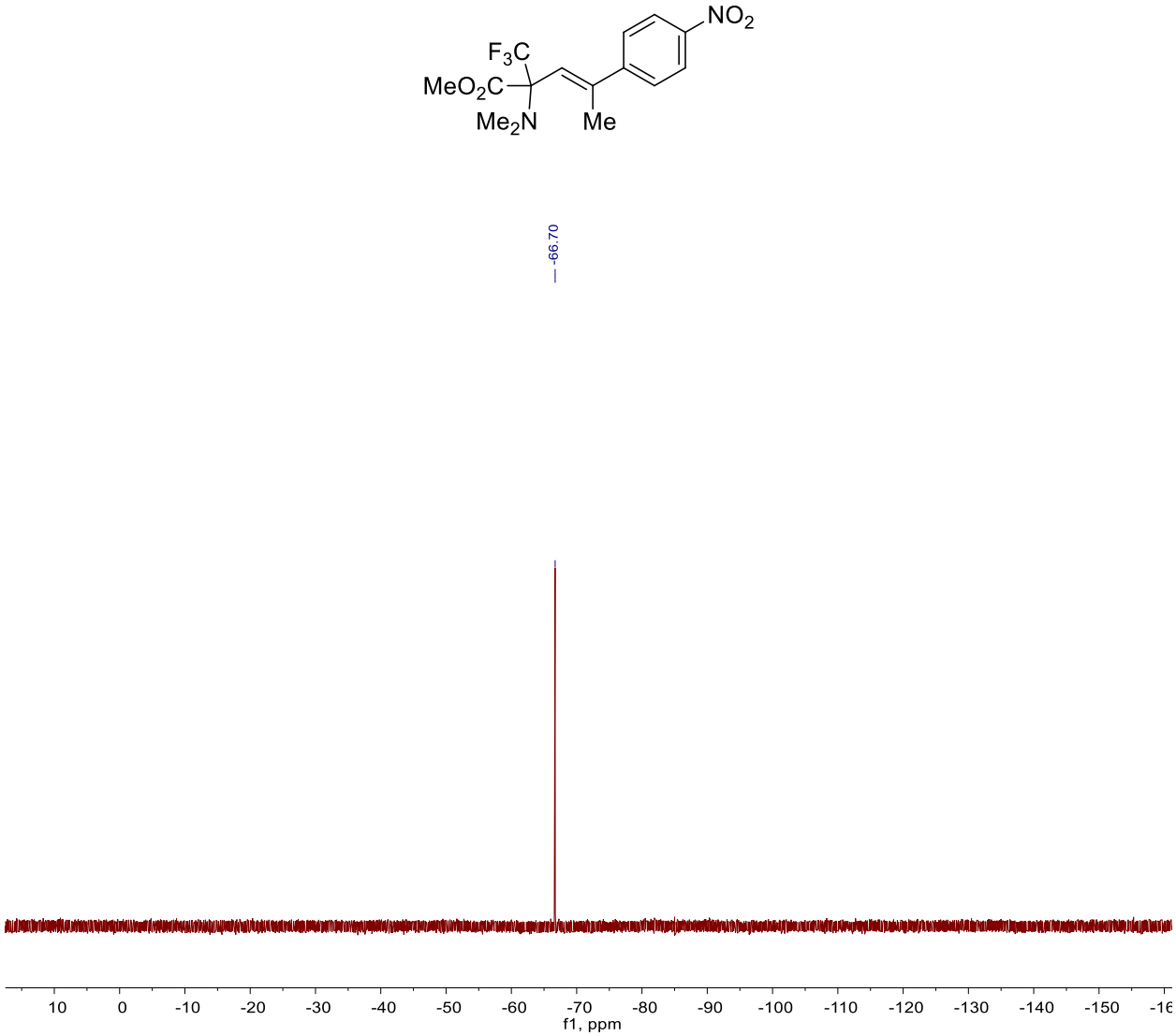
^{19}F spectrum of **3c** in $CDCl_3$



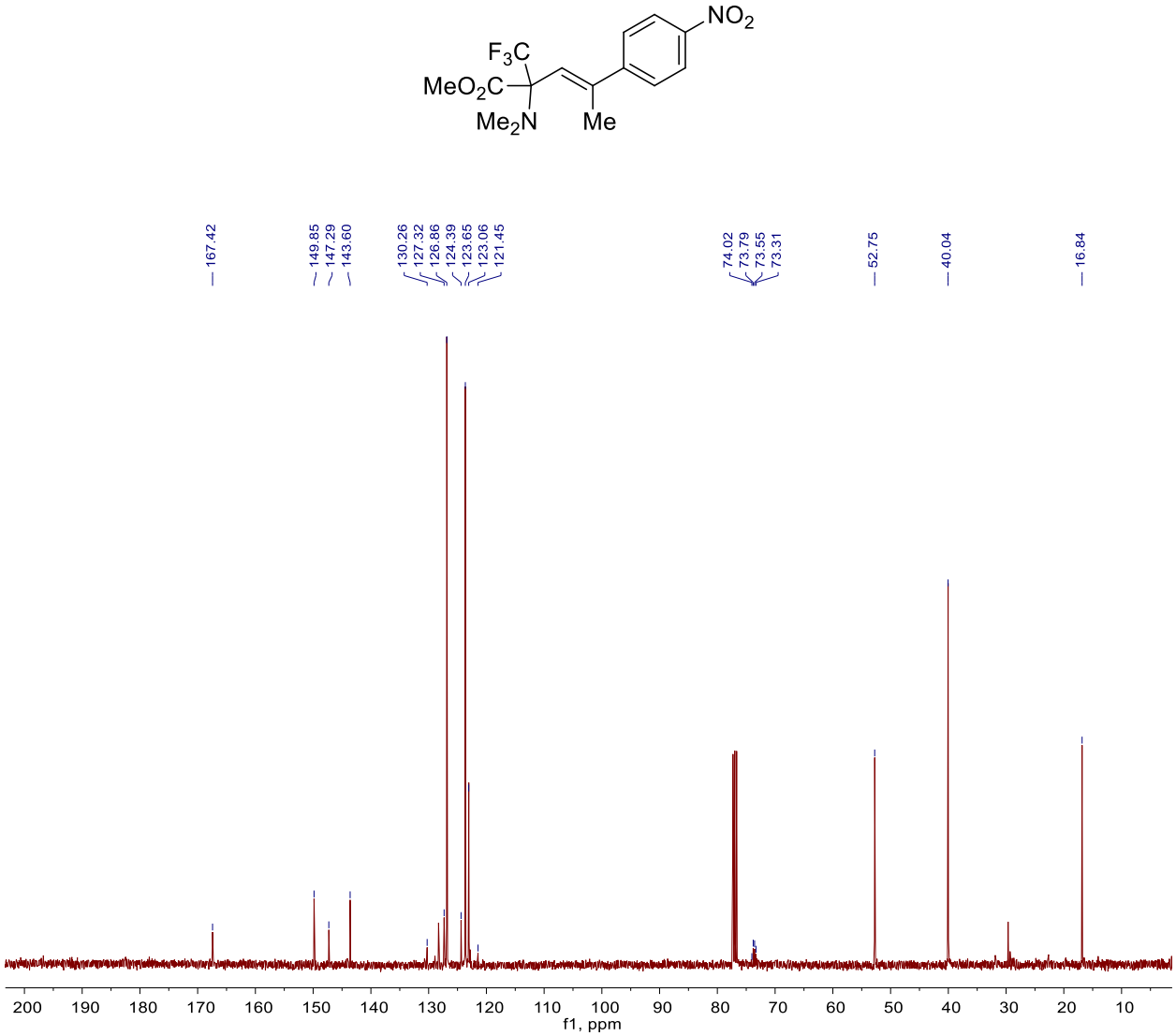
^{13}C spectrum of **3c** in $CDCl_3$



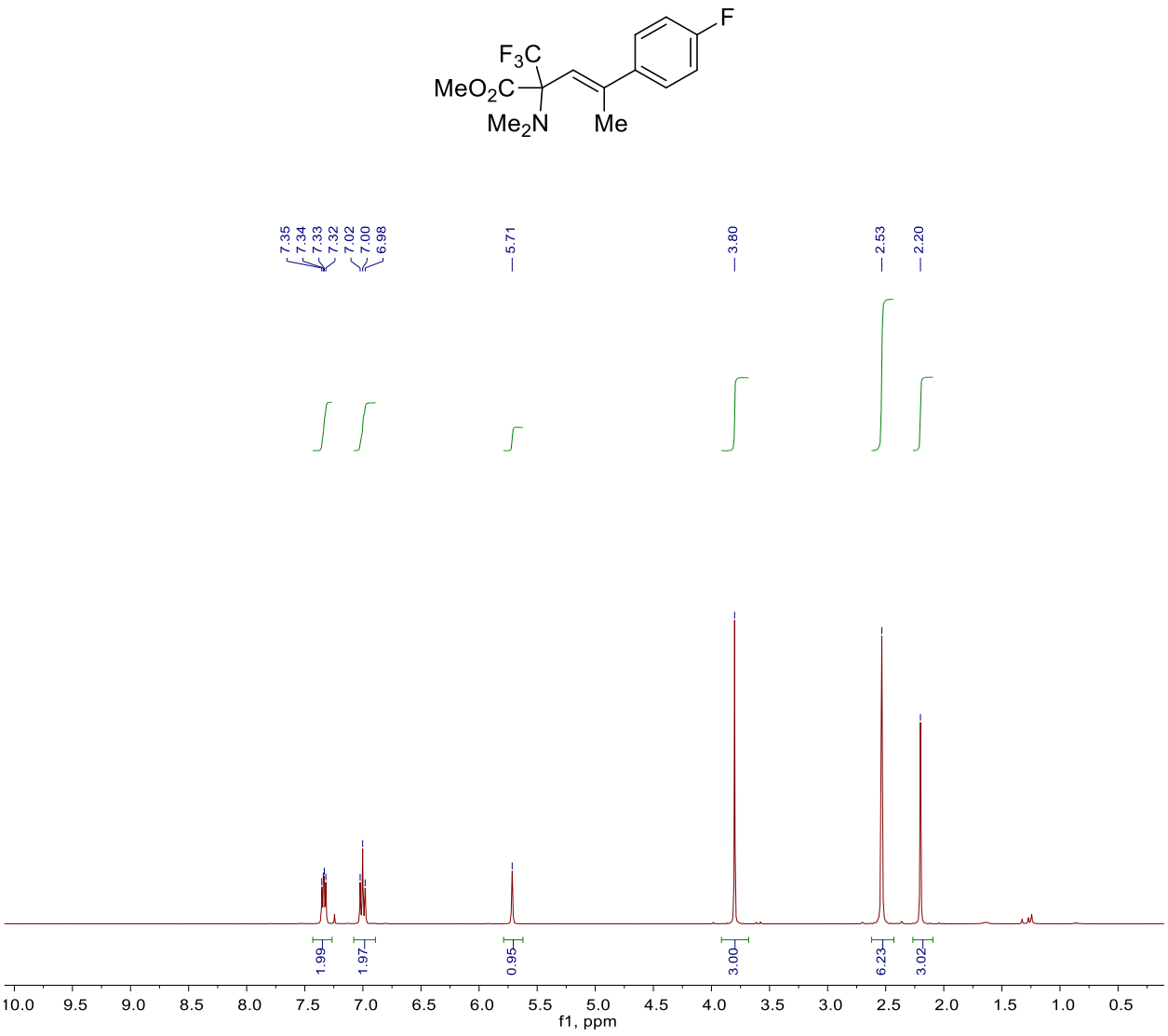
^{1}H spectrum of **3d** in $CDCl_3$



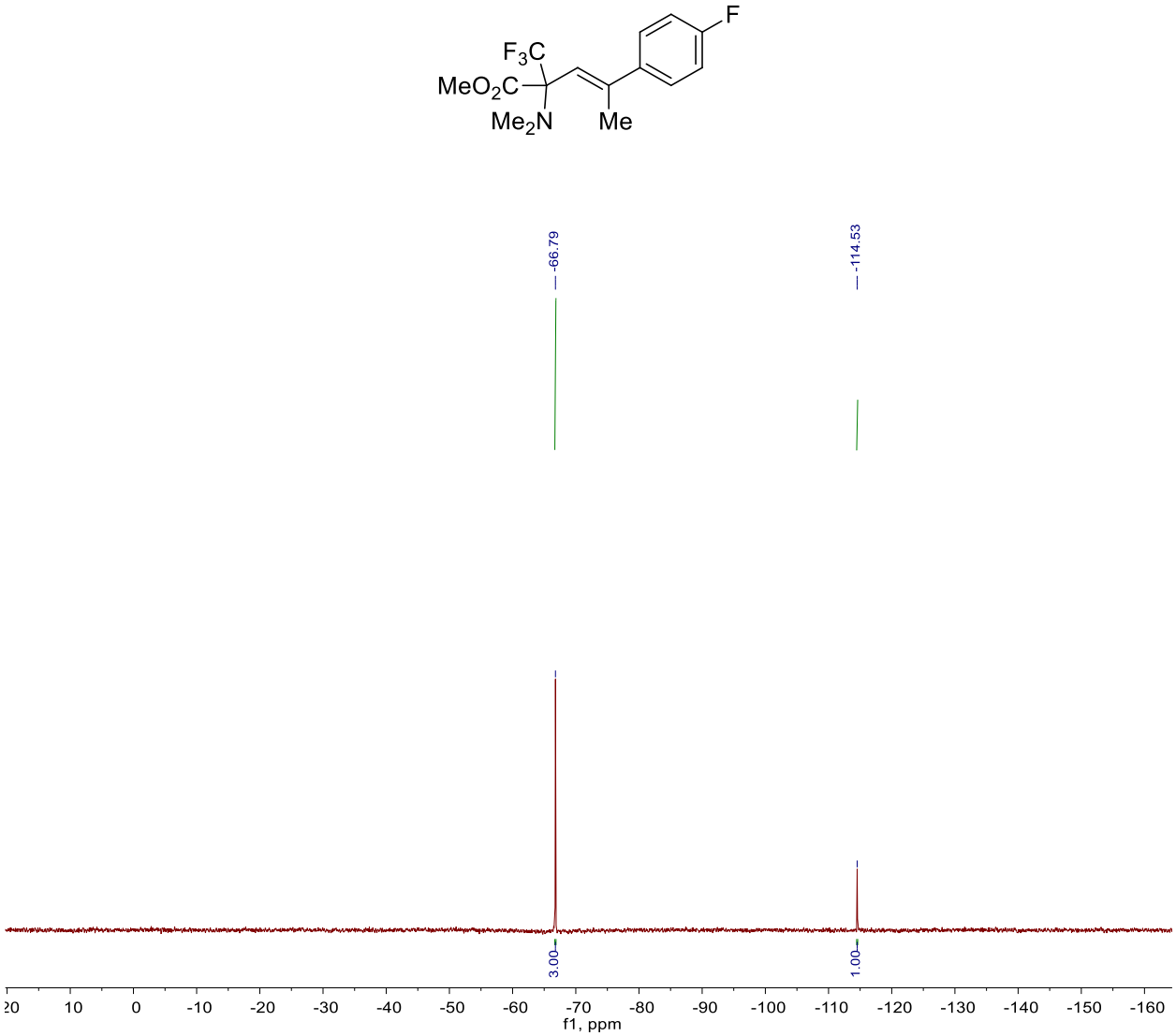
^{19}F spectrum of **3d** in $CDCl_3$



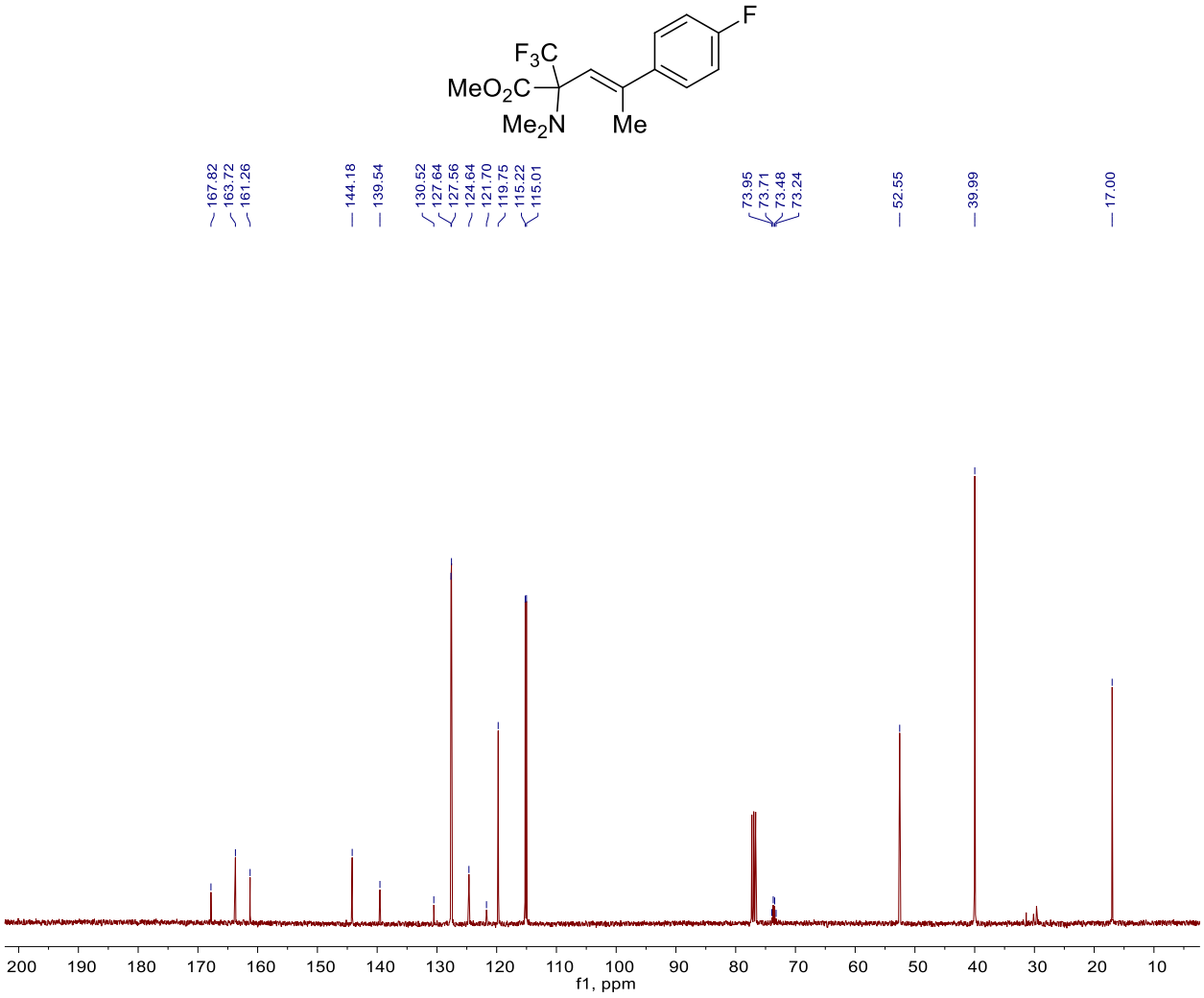
^{13}C spectrum of **3d** in $CDCl_3$



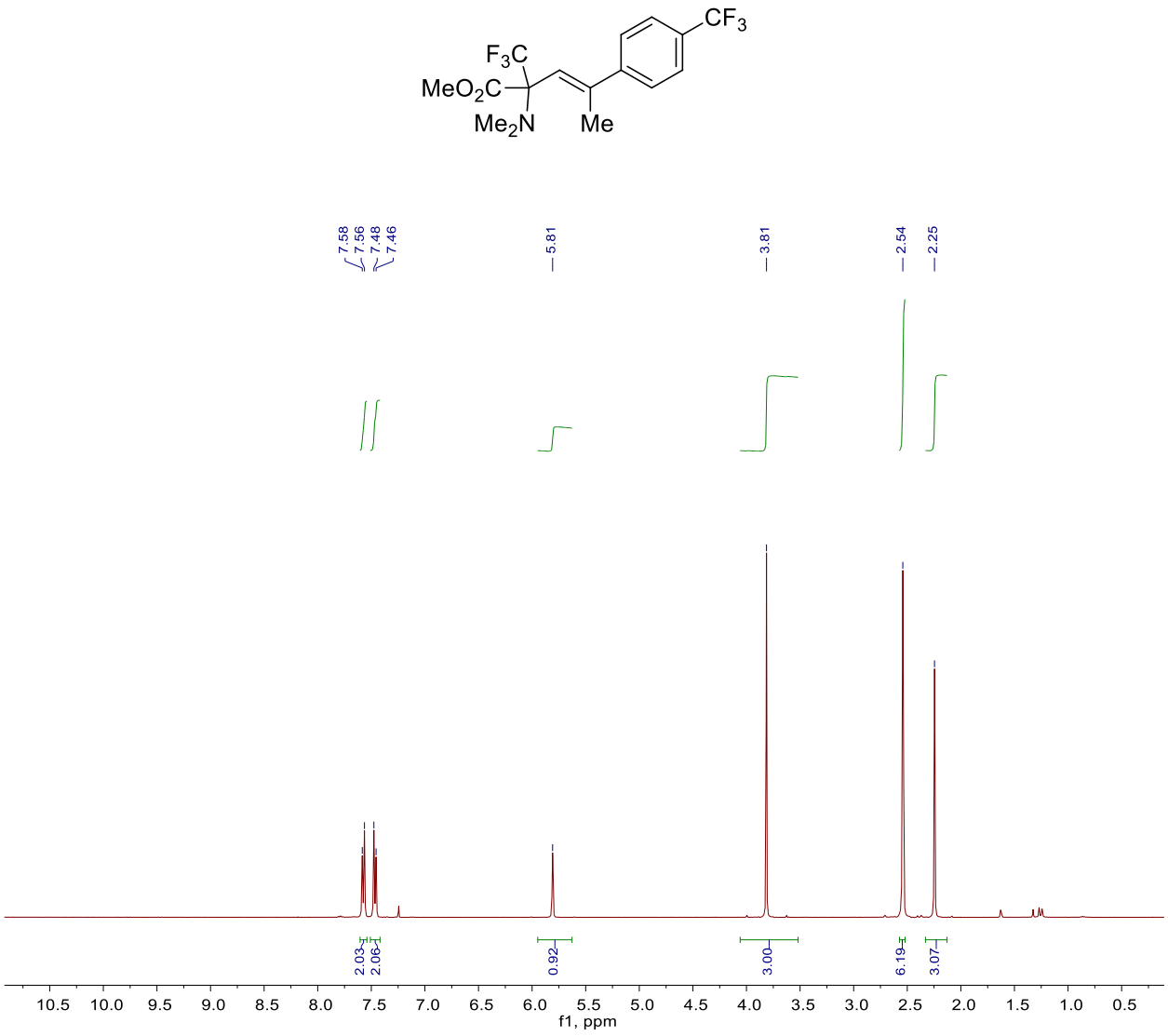
^{1}H spectrum of **3e** in $CDCl_3$



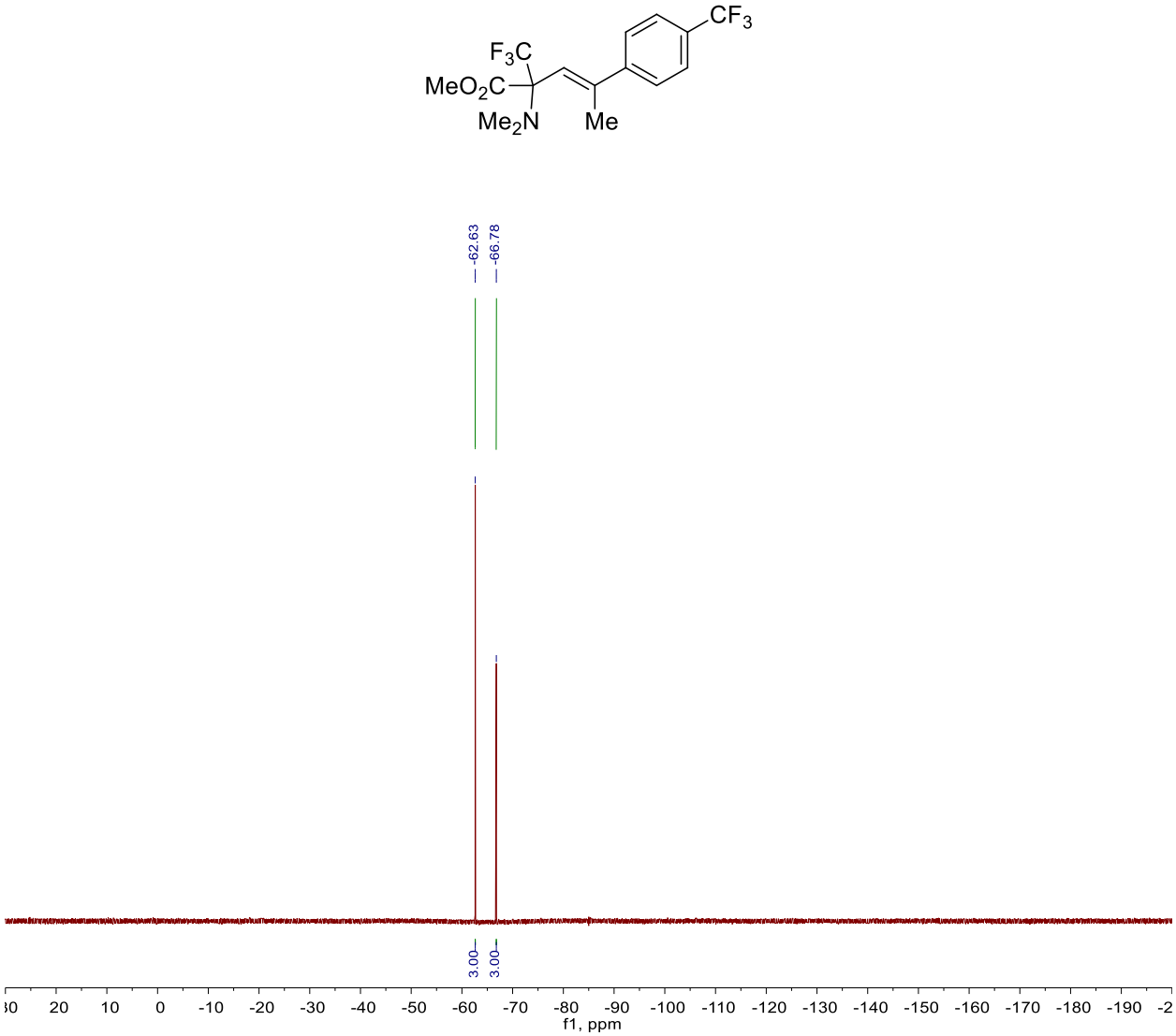
^{19}F spectrum of **3e** in $CDCl_3$



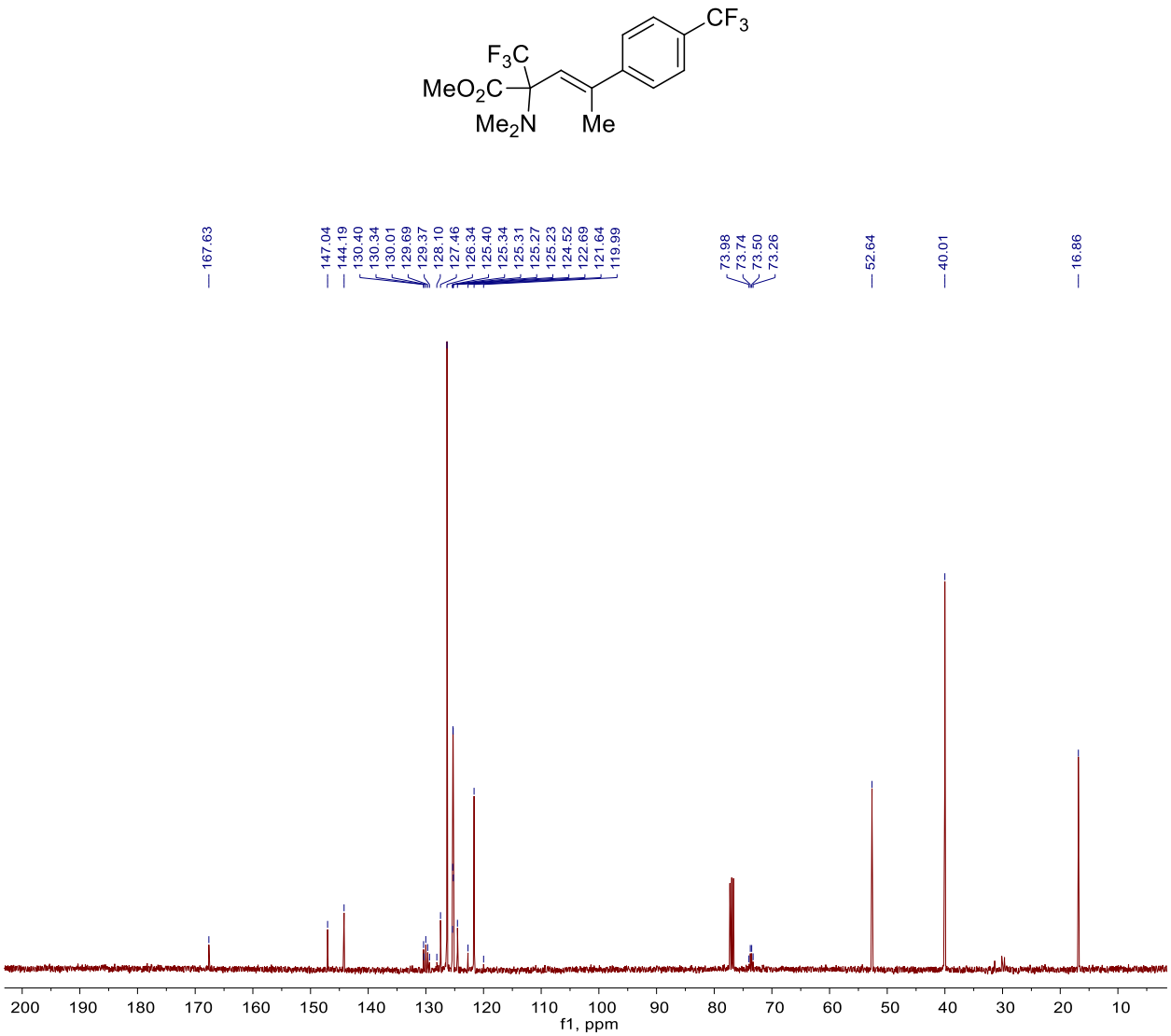
^{13}C spectrum of **3e** in $CDCl_3$



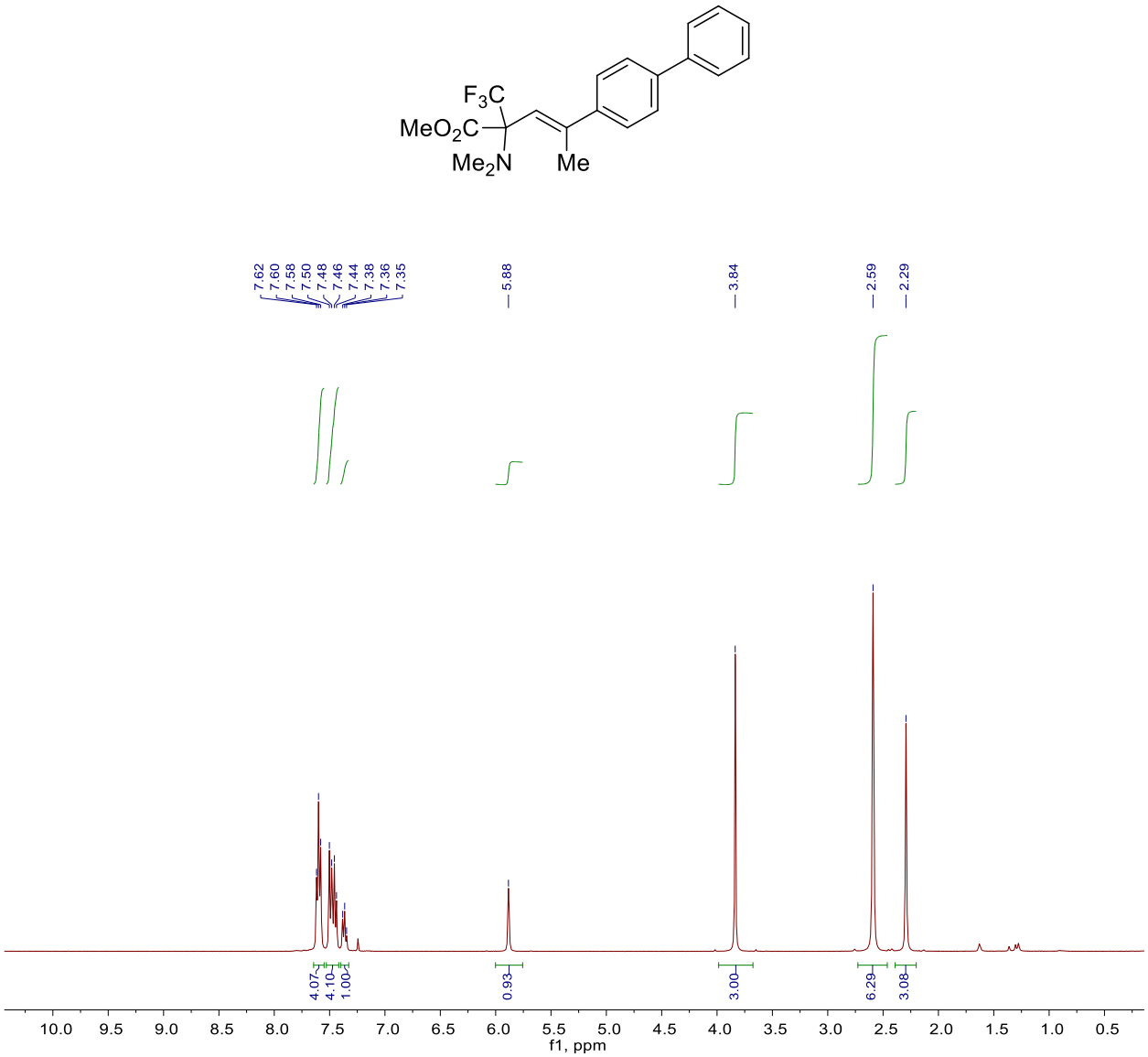
^{1}H spectrum of **3f** in $CDCl_3$



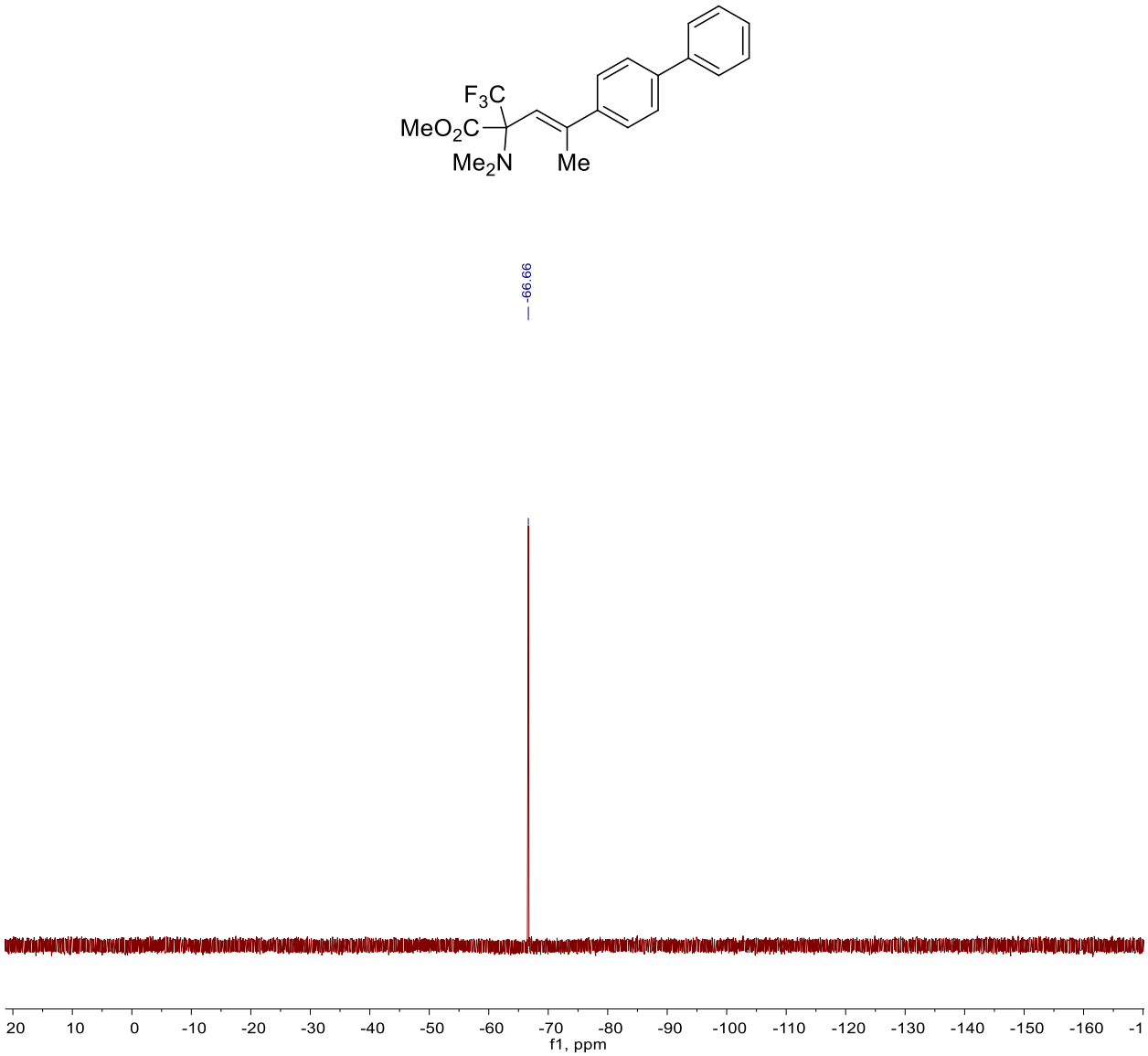
^{19}F spectrum of **3f** in $CDCl_3$



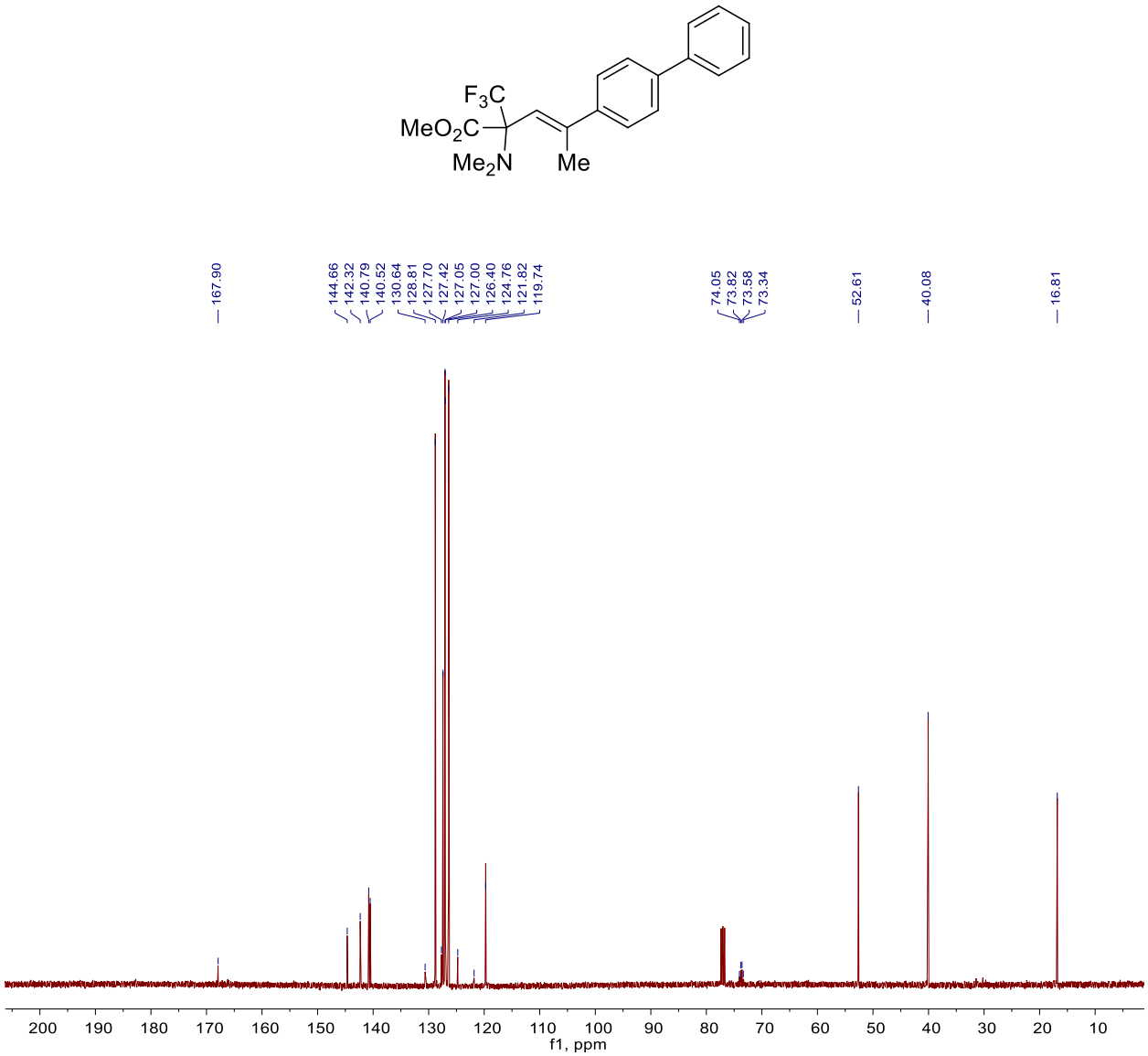
^{13}C spectrum of **3f** in $CDCl_3$



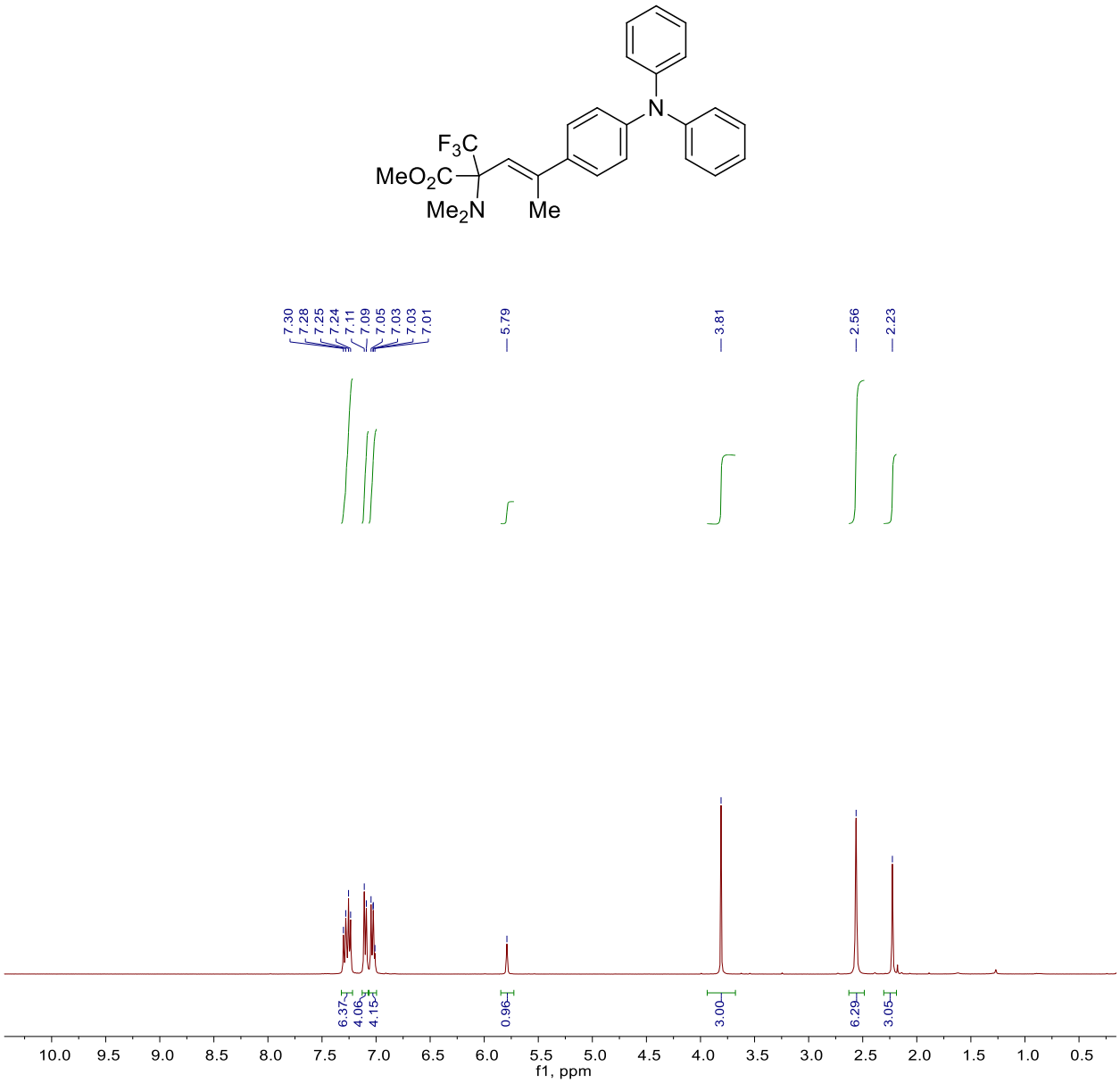
^{1}H spectrum of **3g** in $CDCl_3$



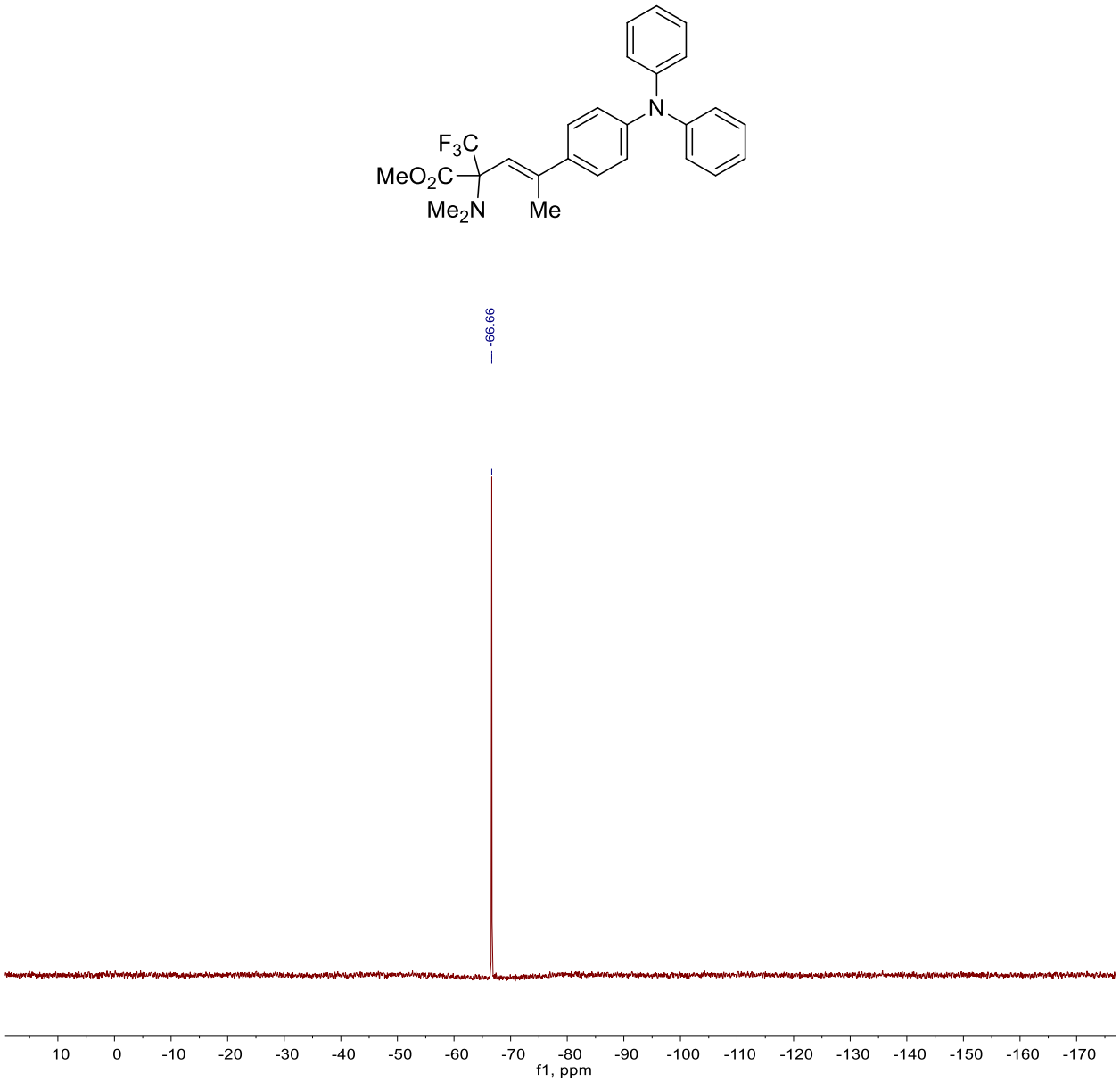
^{19}F spectrum of **3g** in $CDCl_3$



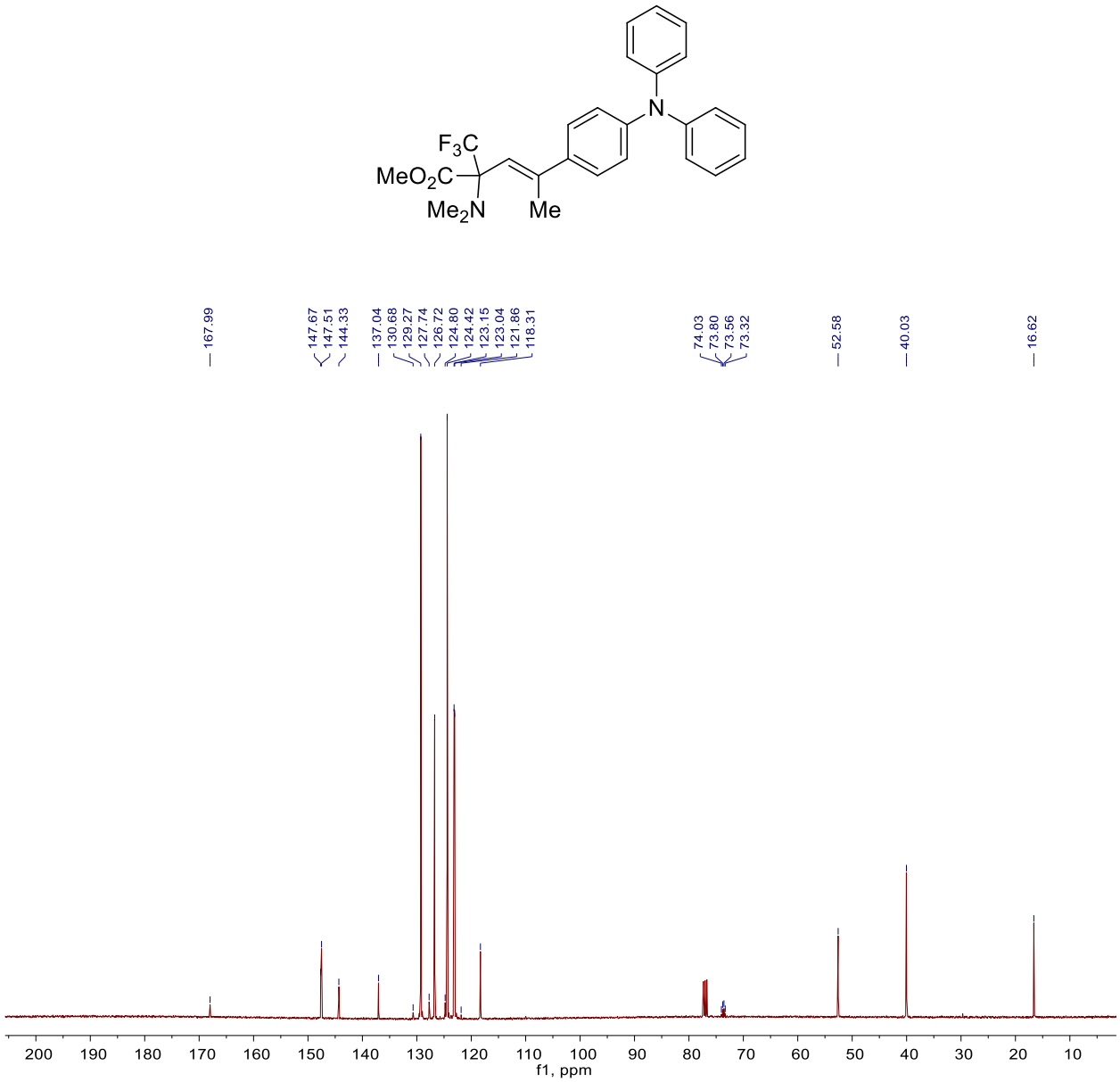
^{13}C spectrum of **3g** in $CDCl_3$



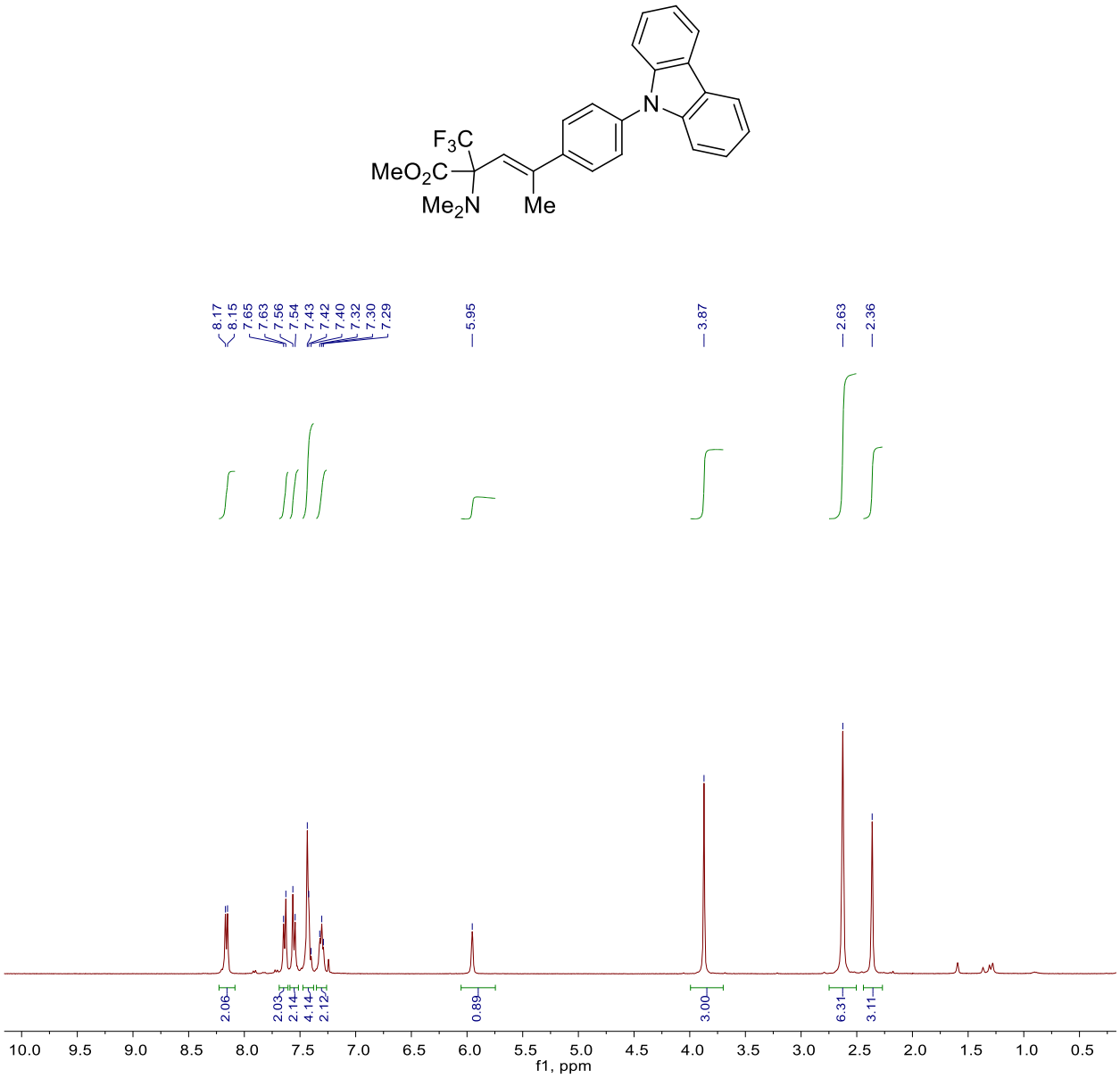
^{1}H spectrum of **3h** in $CDCl_3$



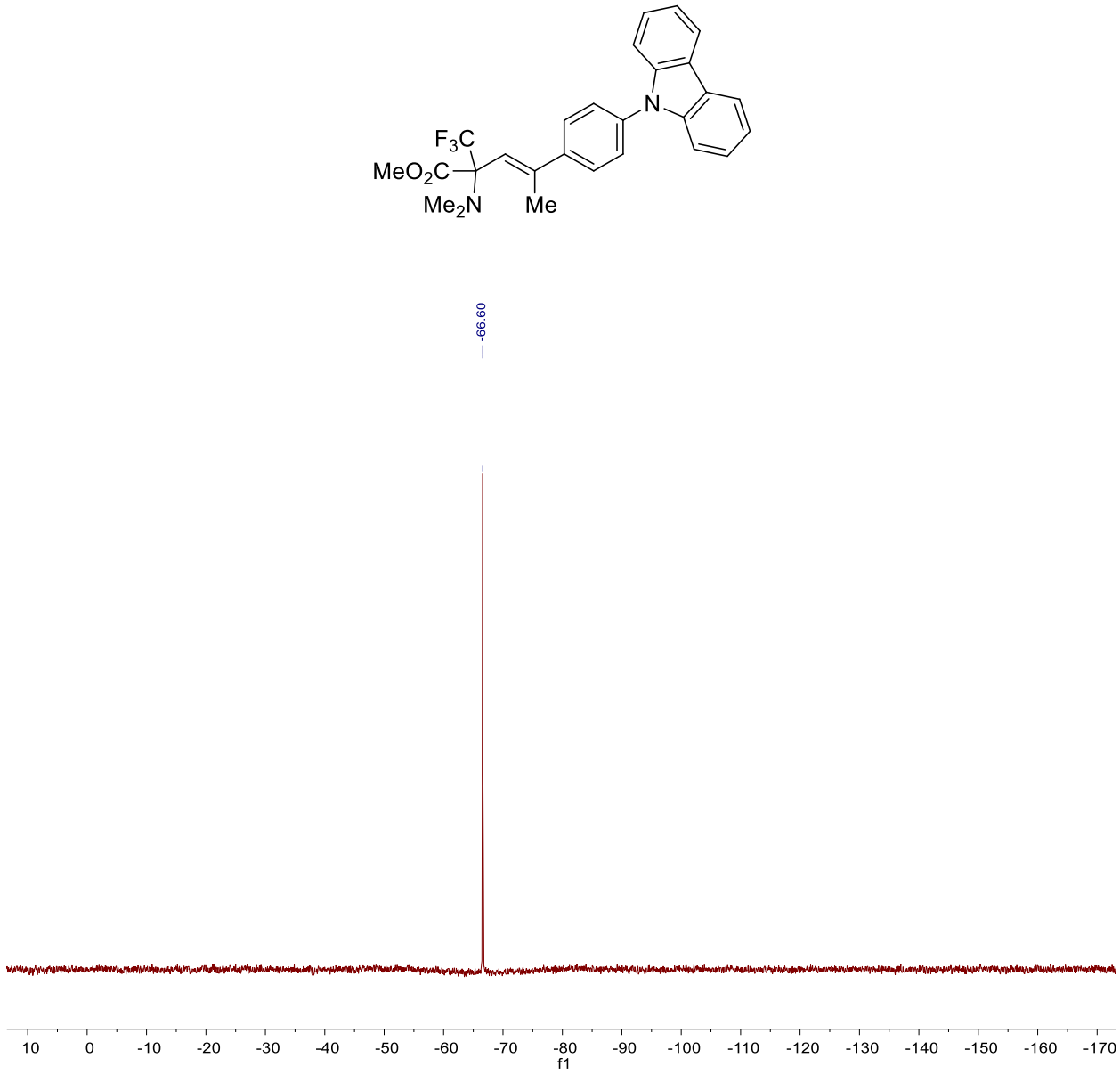
^{19}F spectrum of **3h** in $CDCl_3$



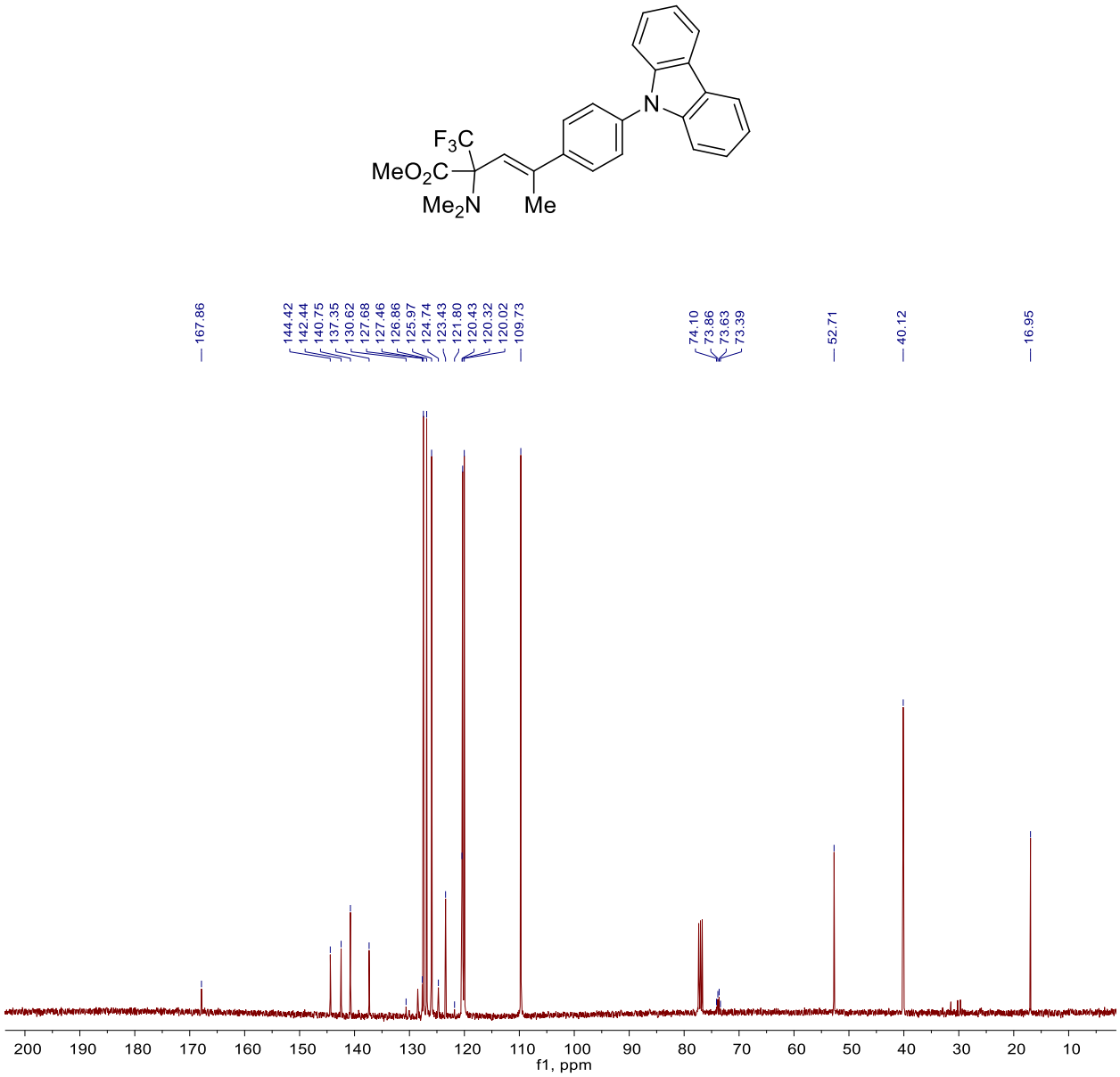
^{13}C spectrum of **3h** in $CDCl_3$



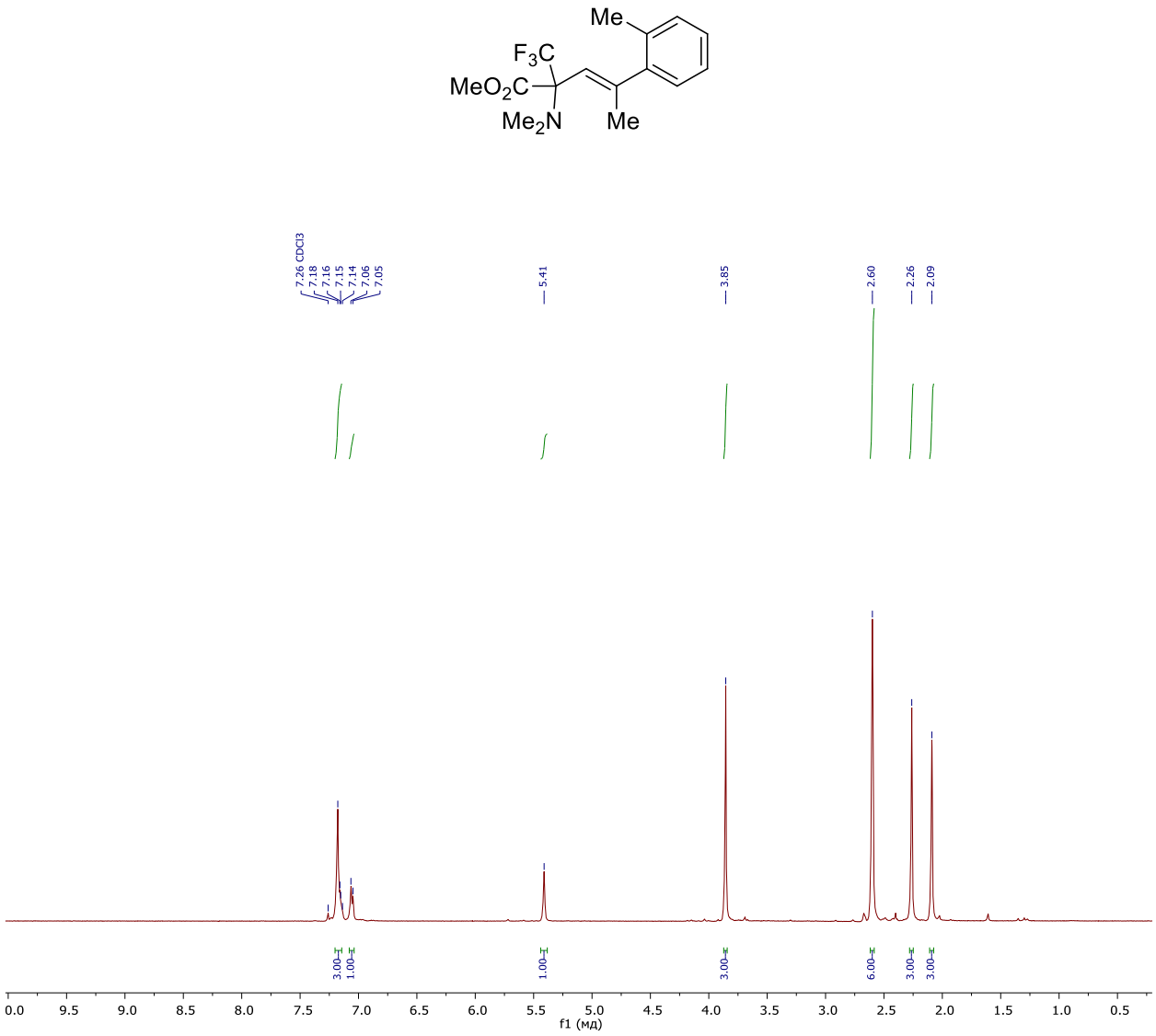
^{1}H spectrum of **3i** in $CDCl_3$



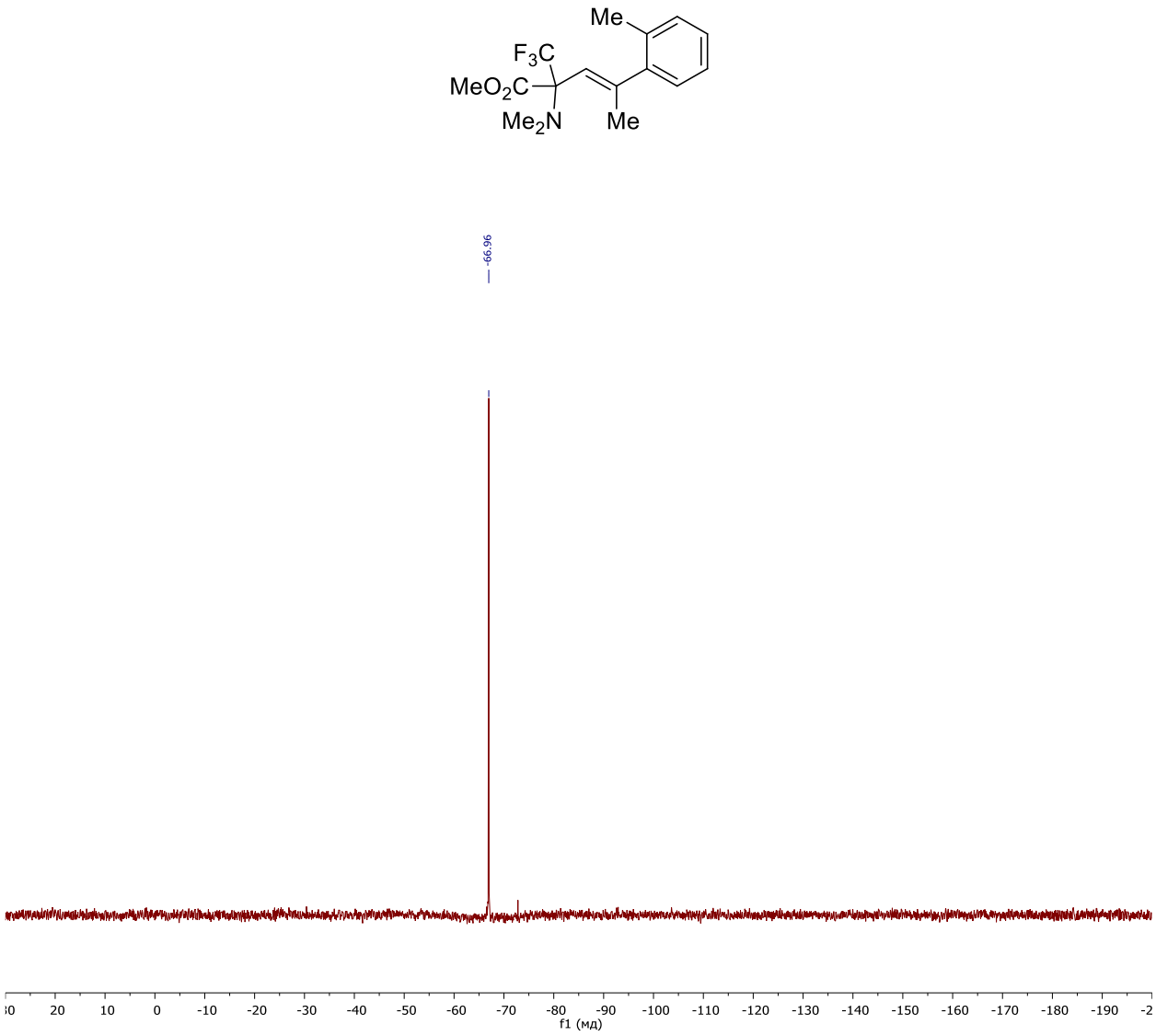
^{19}F spectrum of **3i** in $CDCl_3$



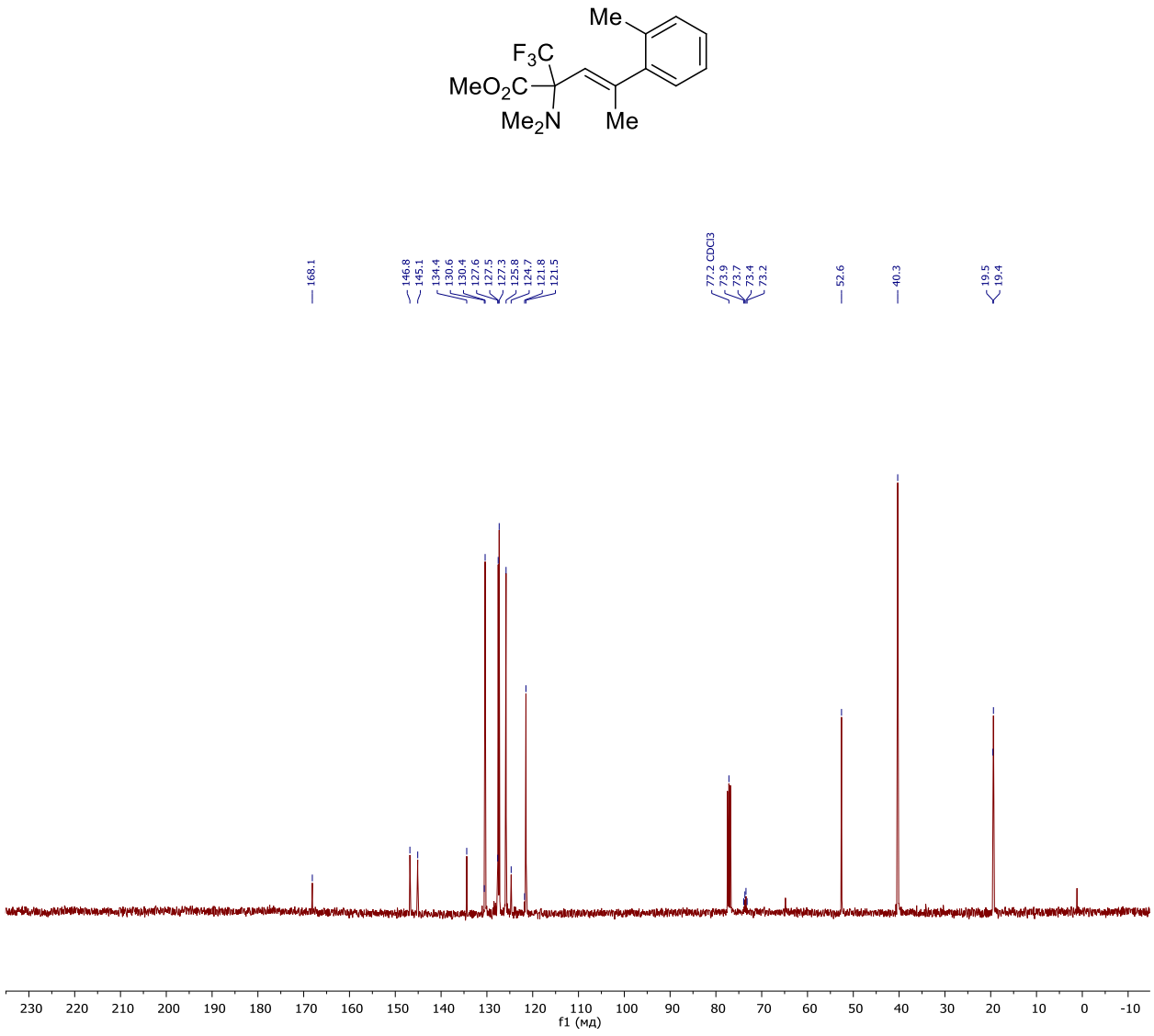
^{13}C spectrum of **3i** in $CDCl_3$



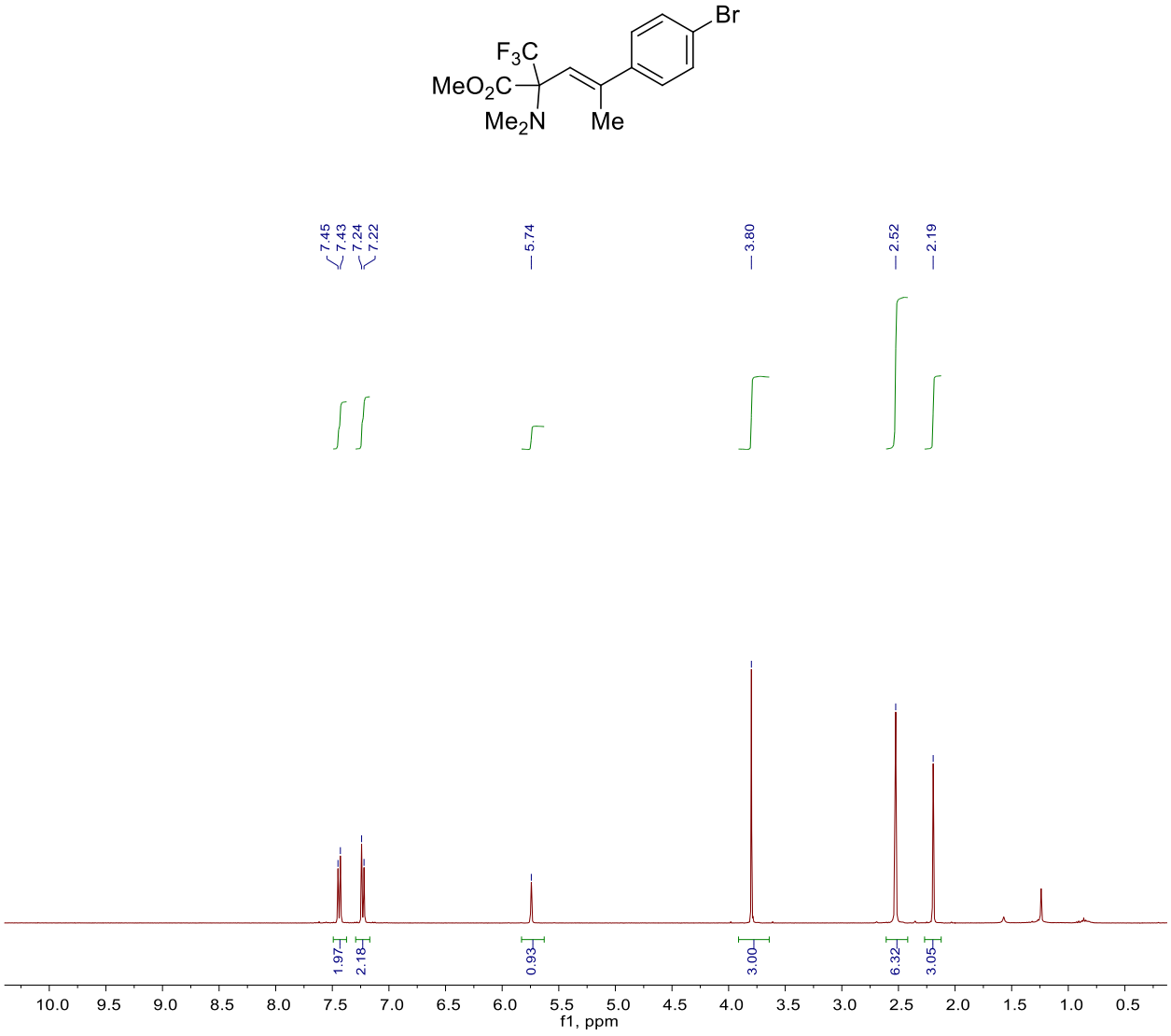
^{1}H spectrum of **3j** in $CDCl_3$



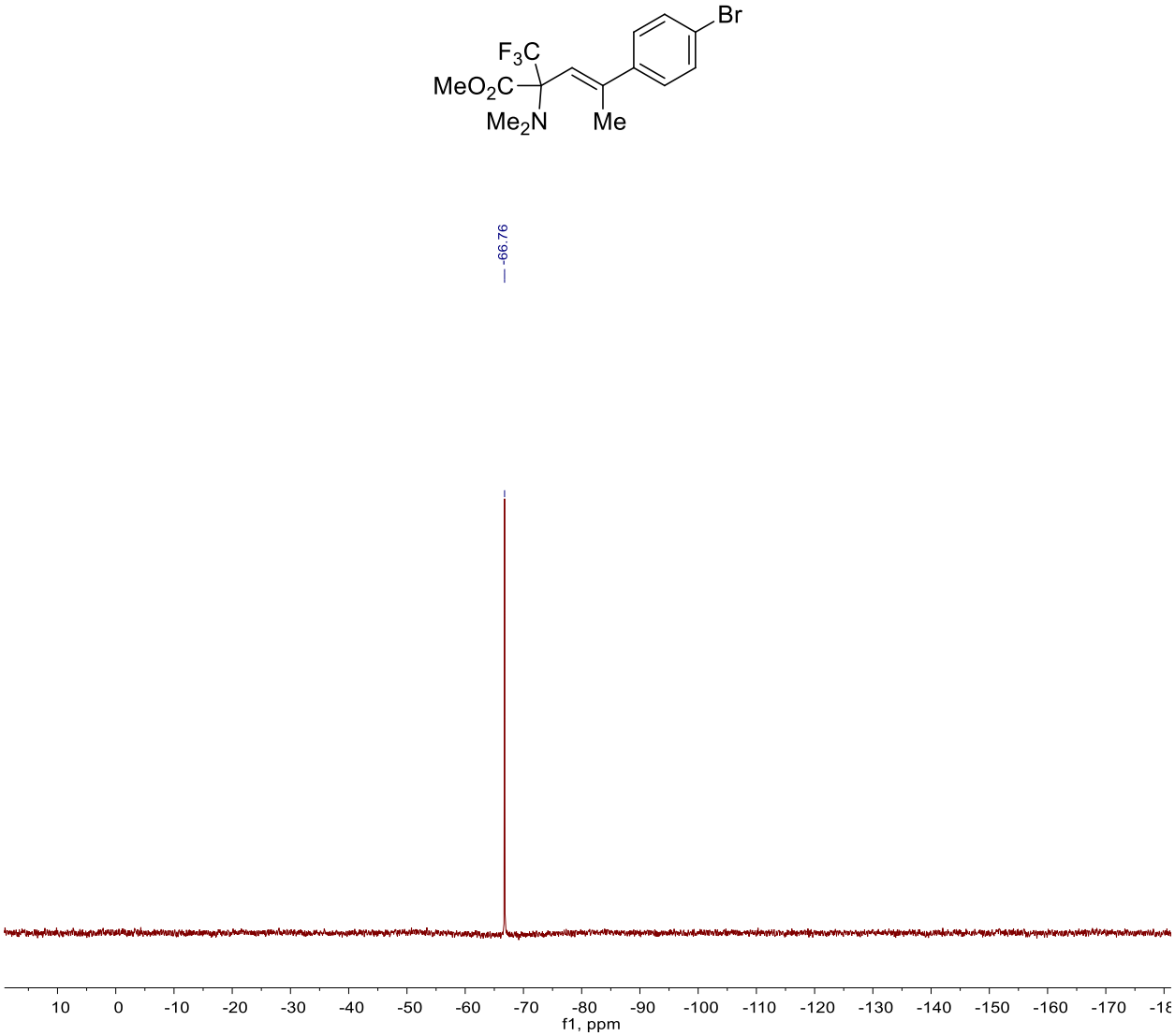
^{19}F spectrum of **3j** in $CDCl_3$



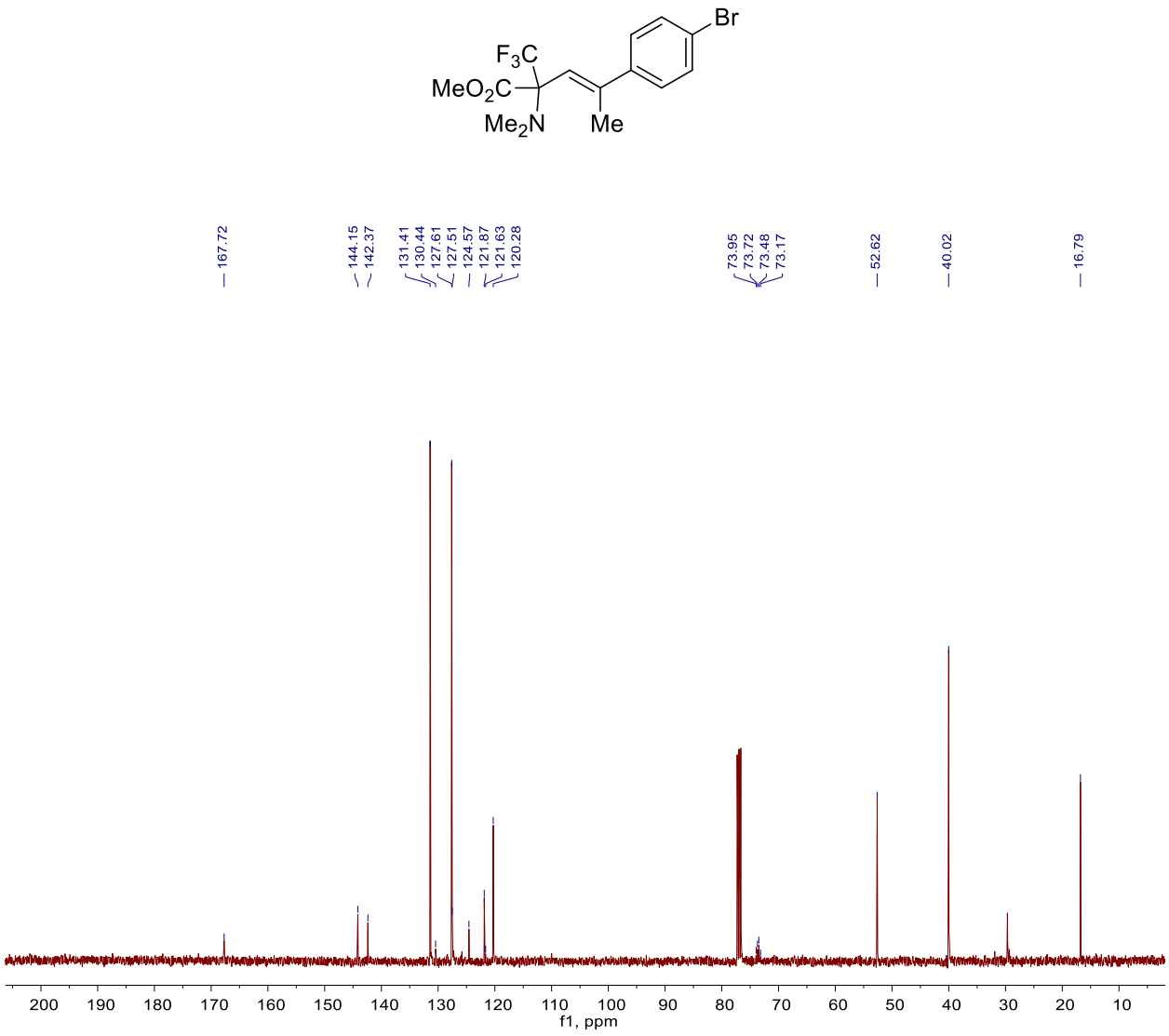
^{13}C spectrum of **3j** in $CDCl_3$



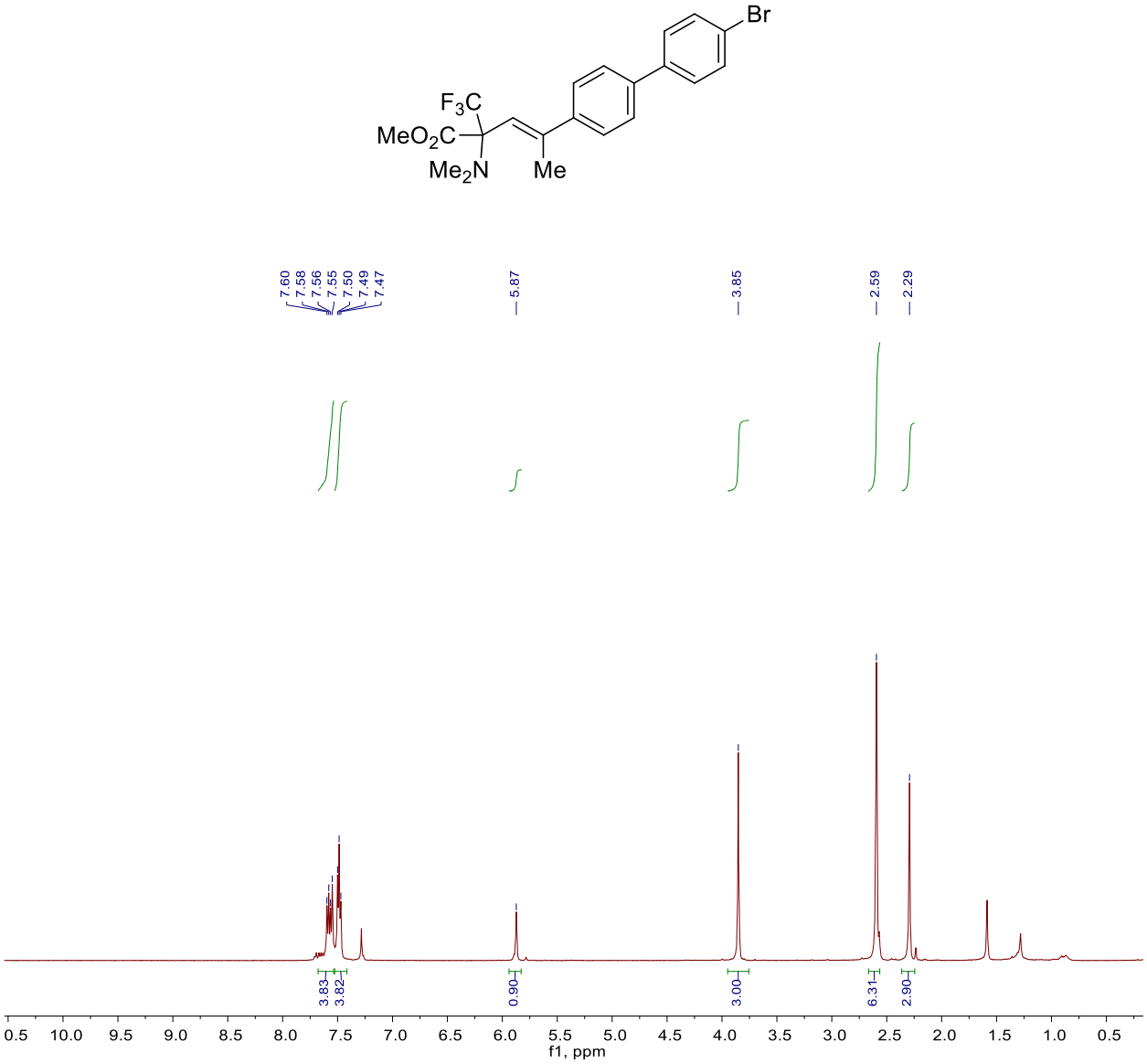
^{1}H spectrum of **3k** in $CDCl_3$



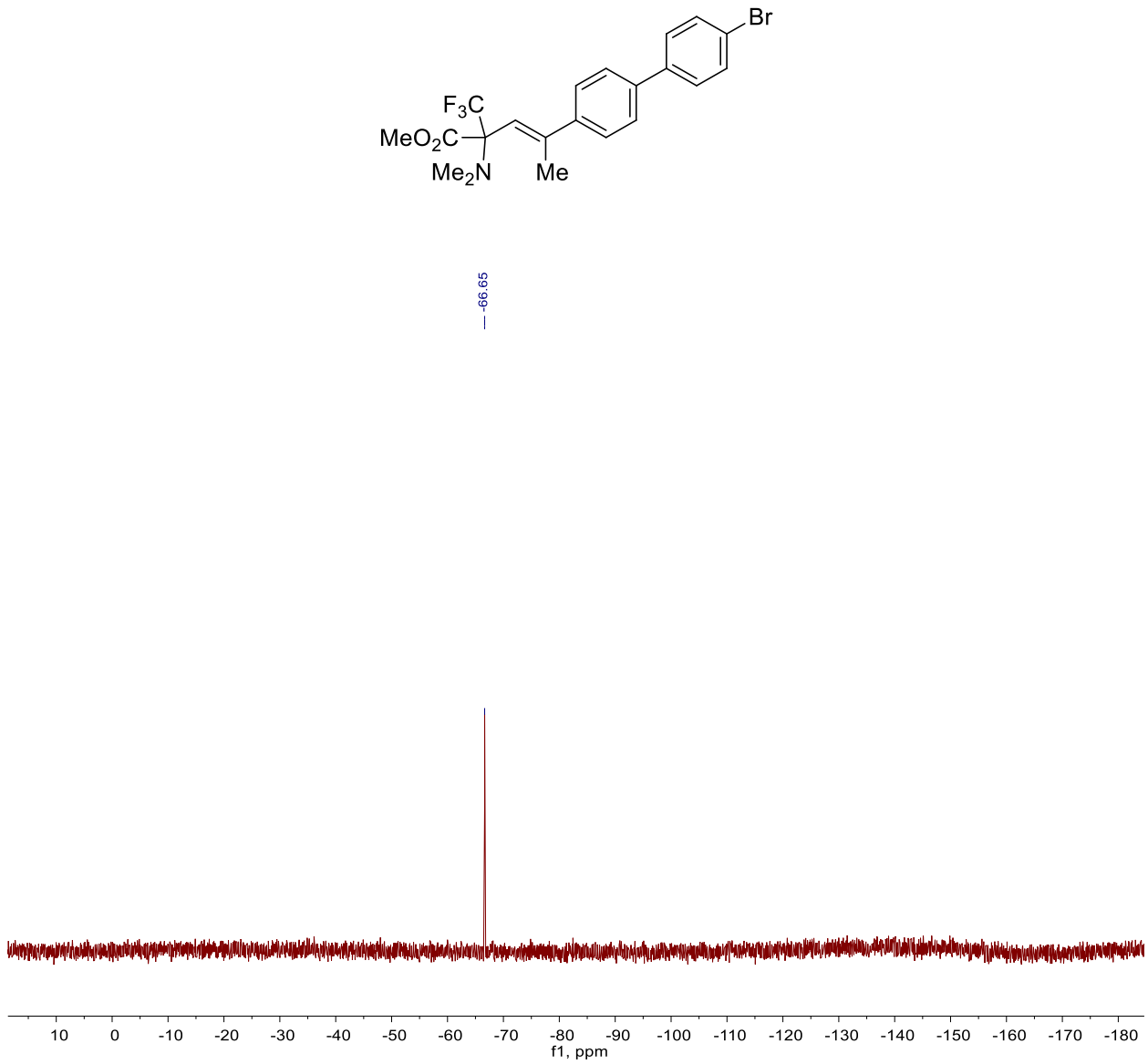
^{19}F spectrum of **3k** in $CDCl_3$



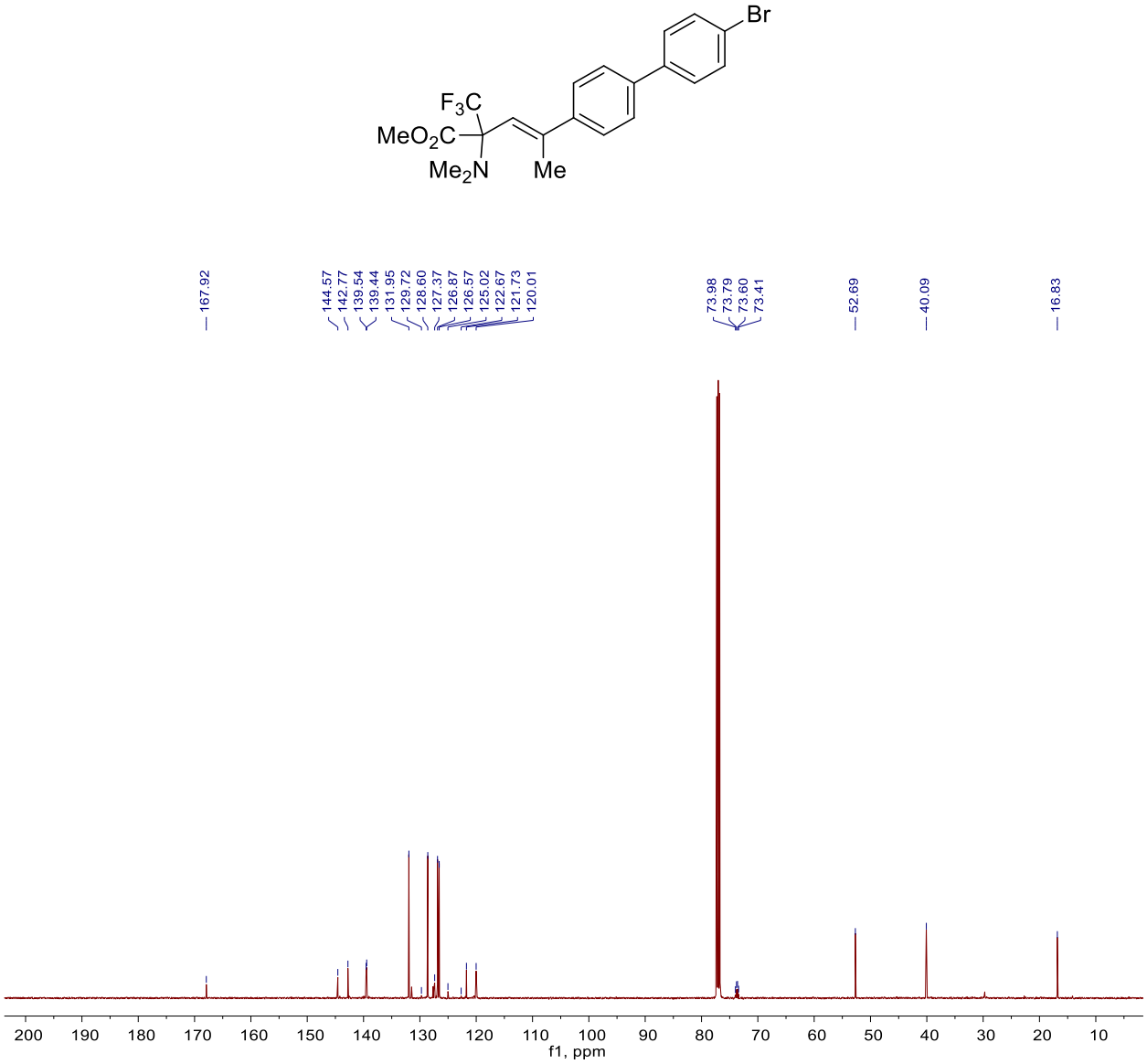
^{13}C spectrum of **3k** in $CDCl_3$



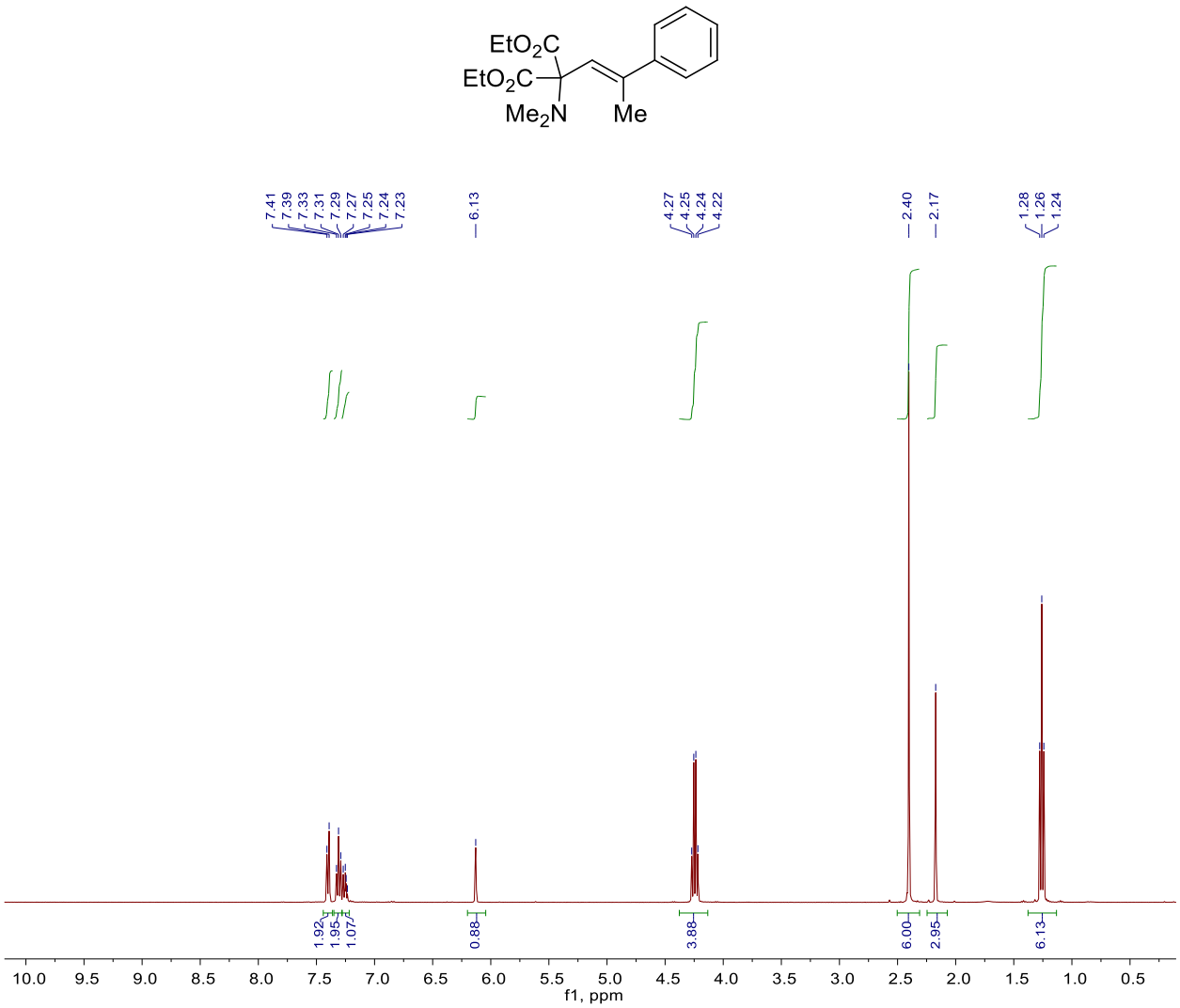
^{1}H spectrum of **3l** in $CDCl_3$



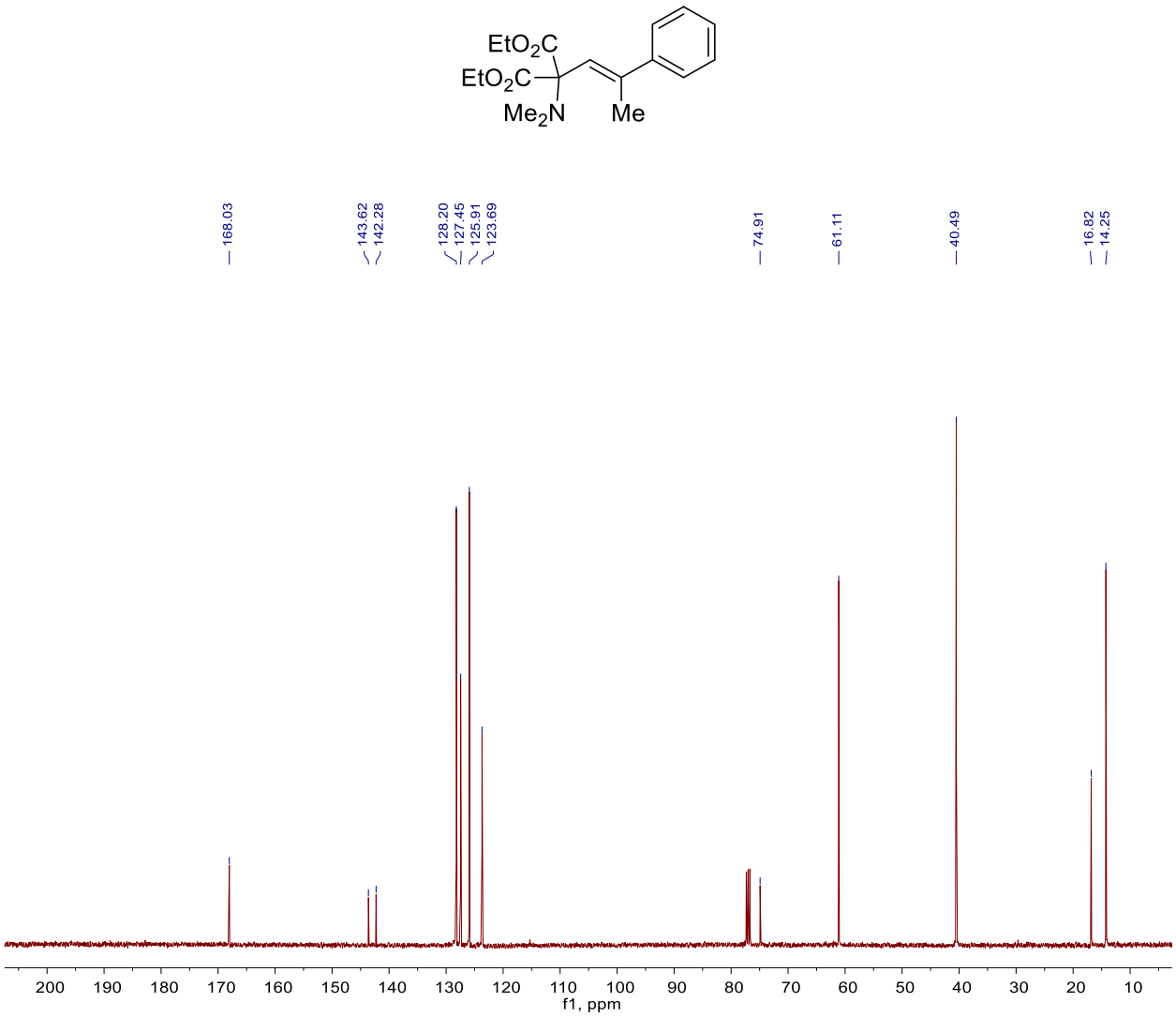
^{19}F spectrum of **3l** in $CDCl_3$



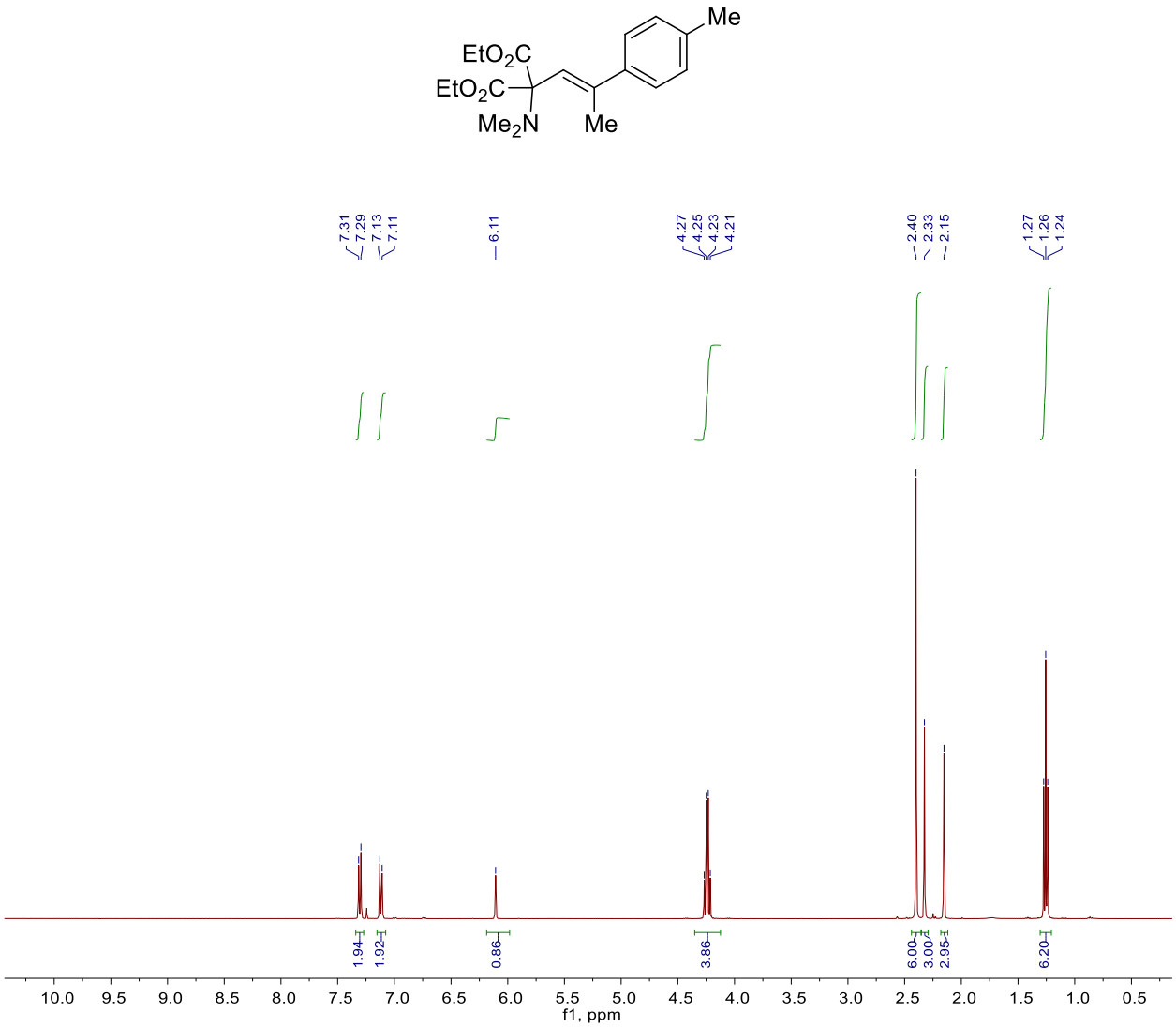
^{13}C spectrum of **3l** in $CDCl_3$



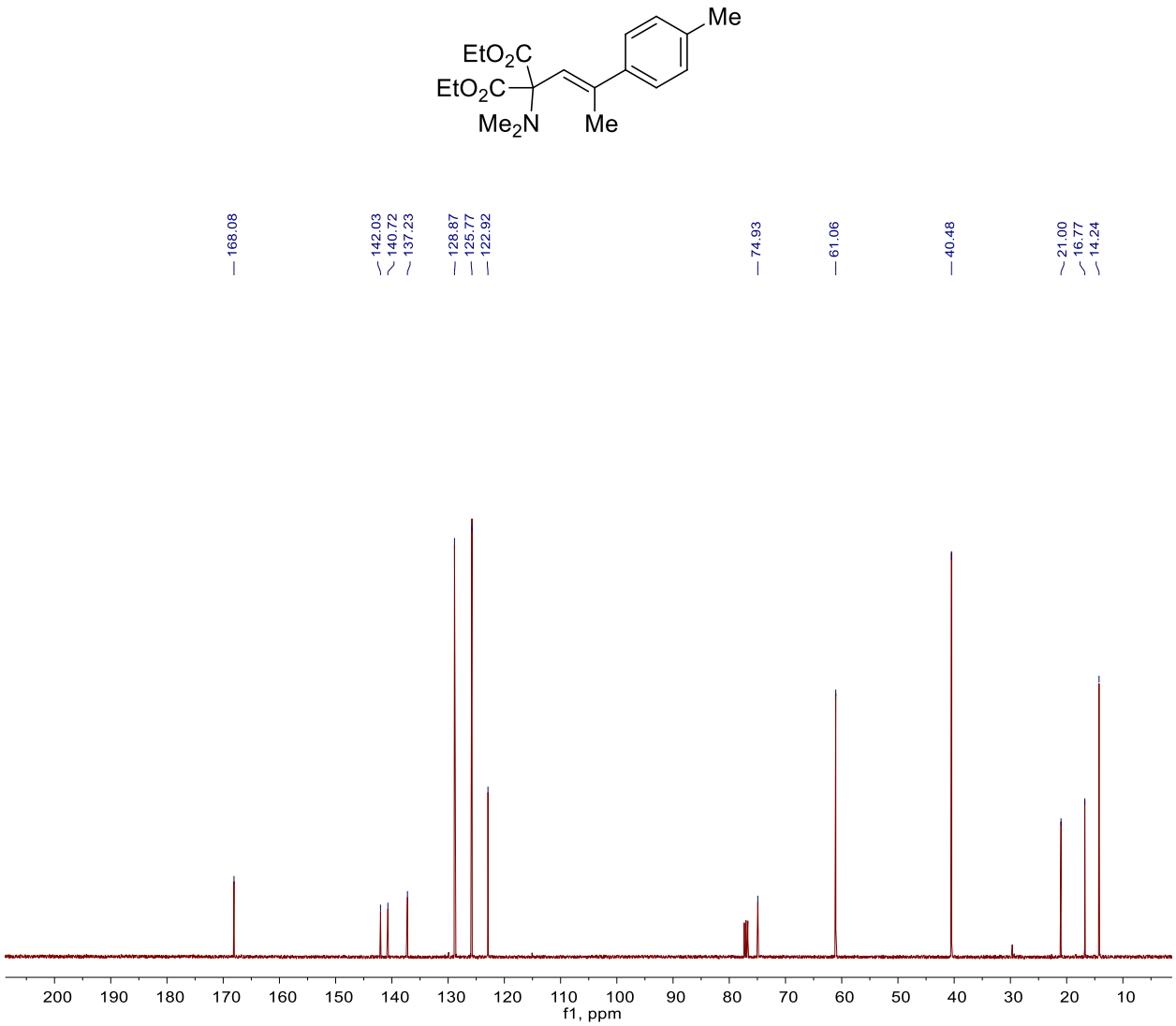
^{1}H spectrum of **4a** in $CDCl_3$



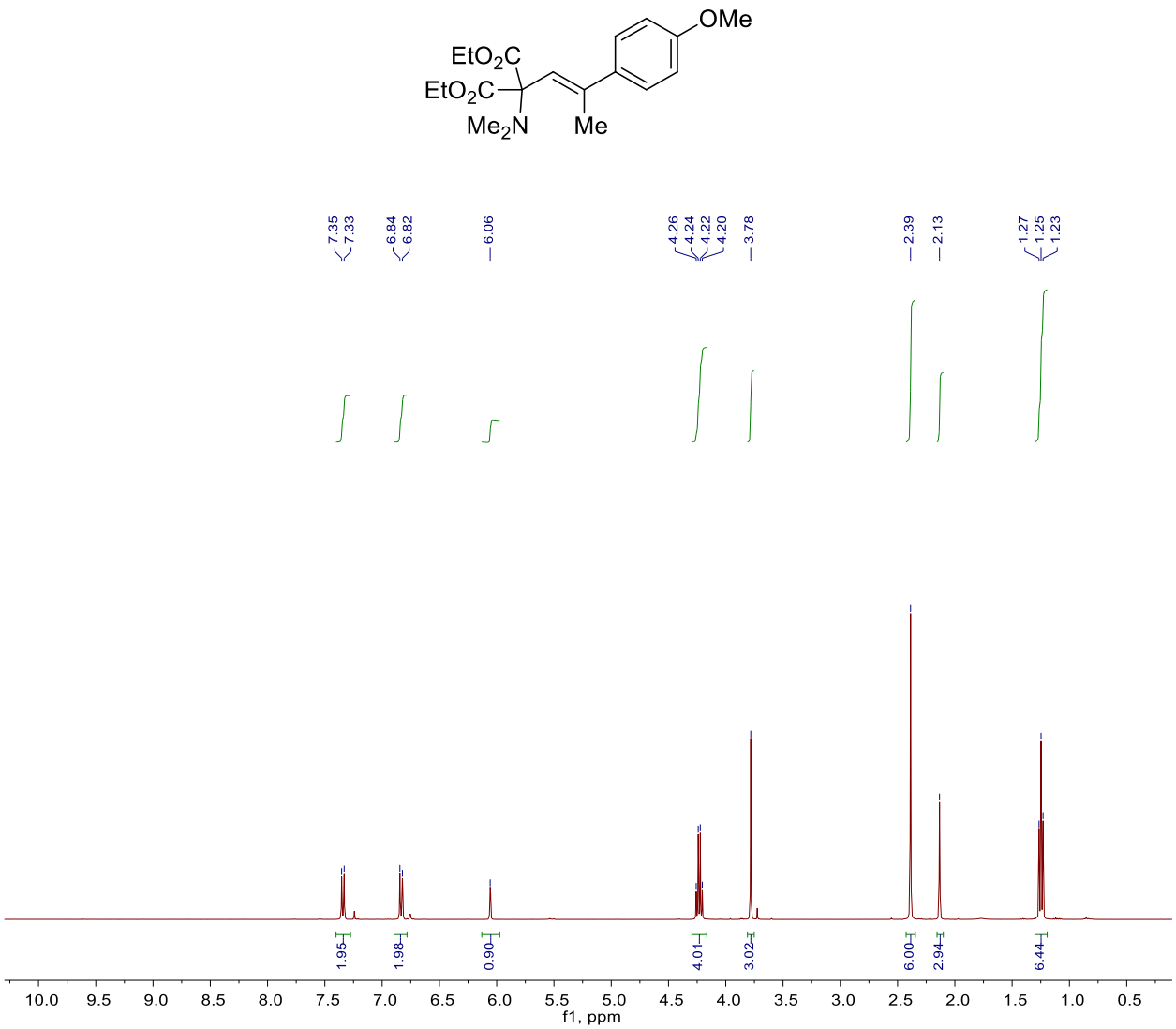
^{13}C spectrum of **4a** in $CDCl_3$



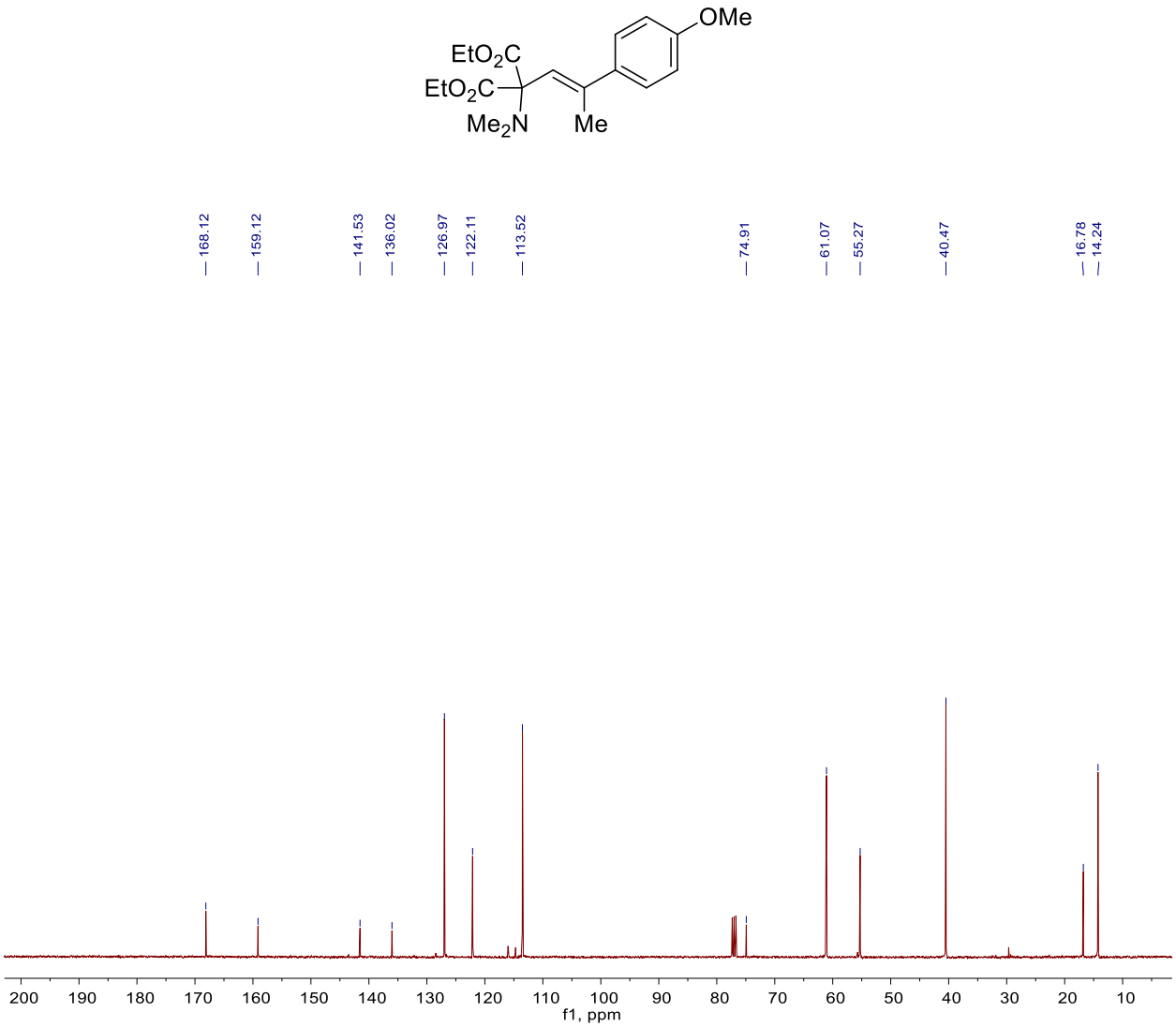
^{1}H spectrum of **4b** in $CDCl_3$



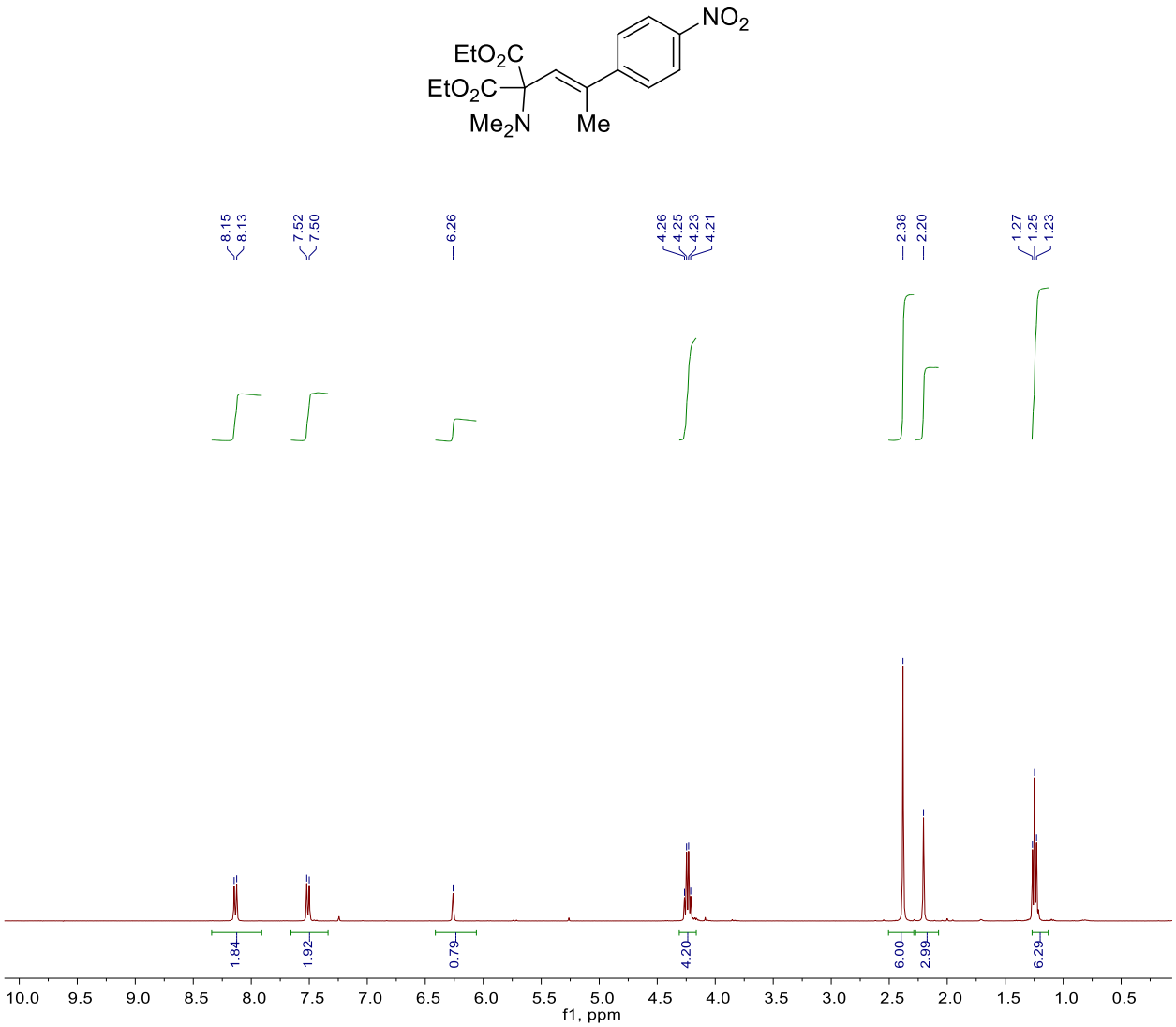
^{13}C spectrum of **4b** in $CDCl_3$



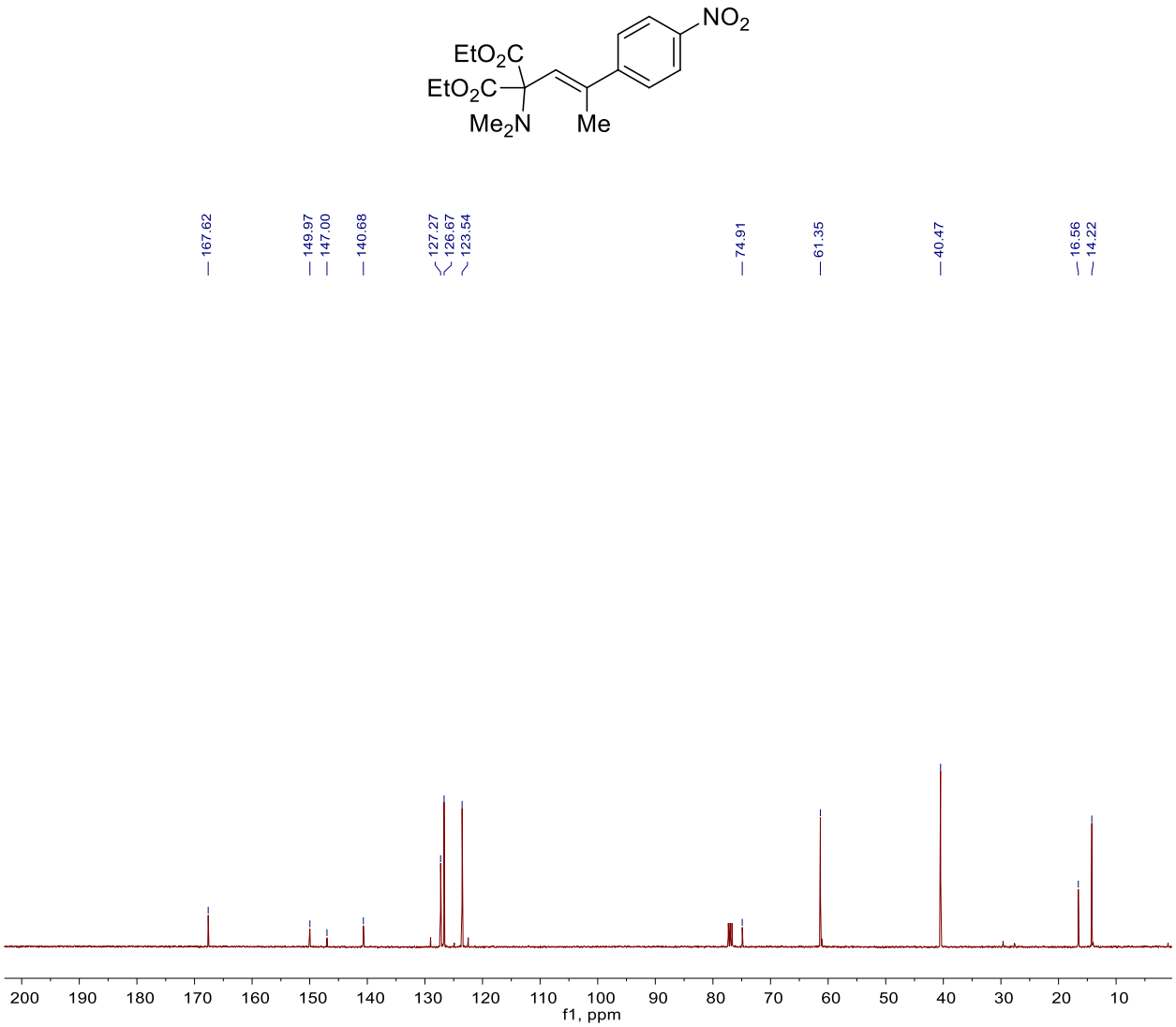
^{1}H spectrum of **4c** in $CDCl_3$



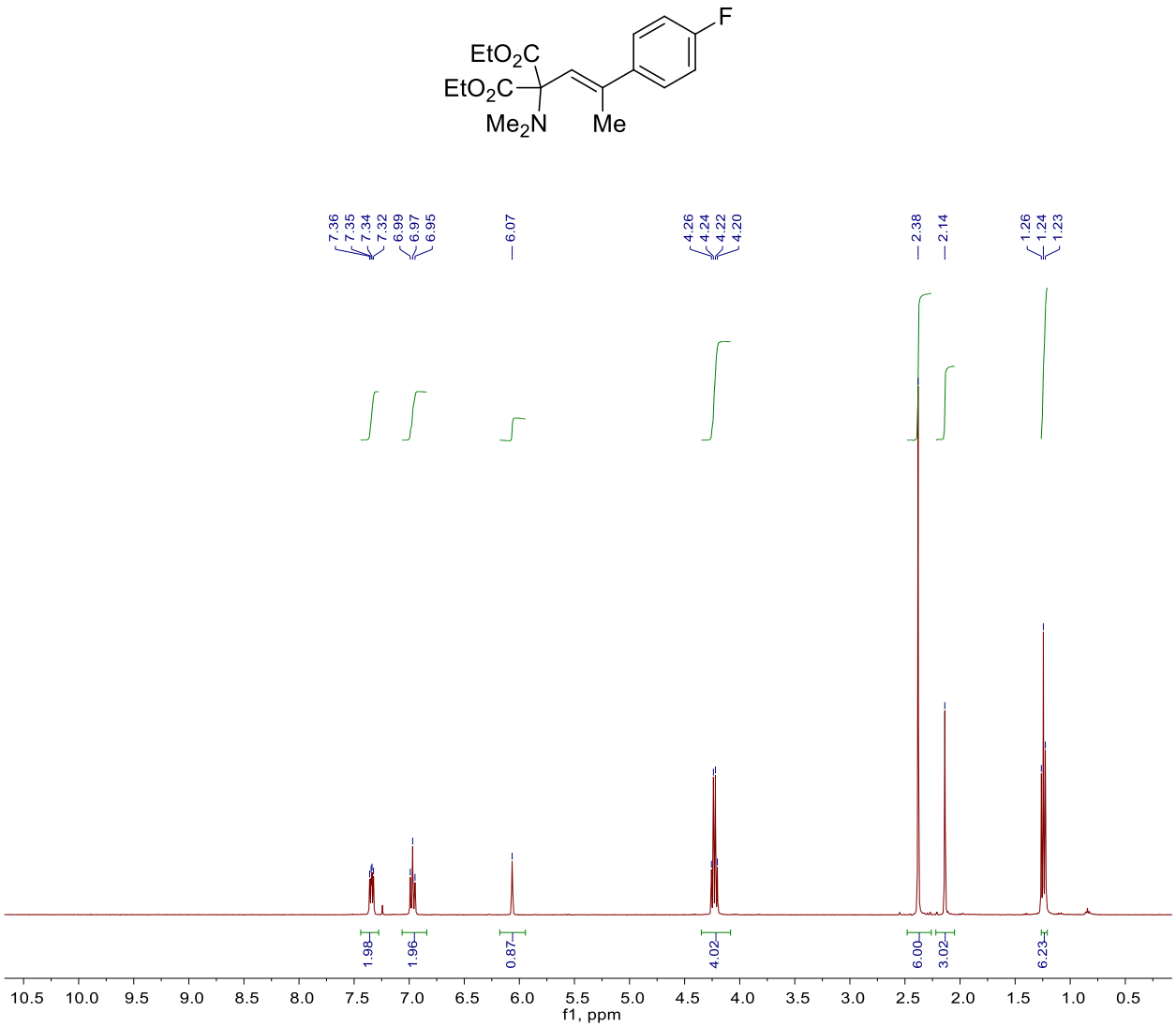
^{13}C spectrum of **4c** in $CDCl_3$



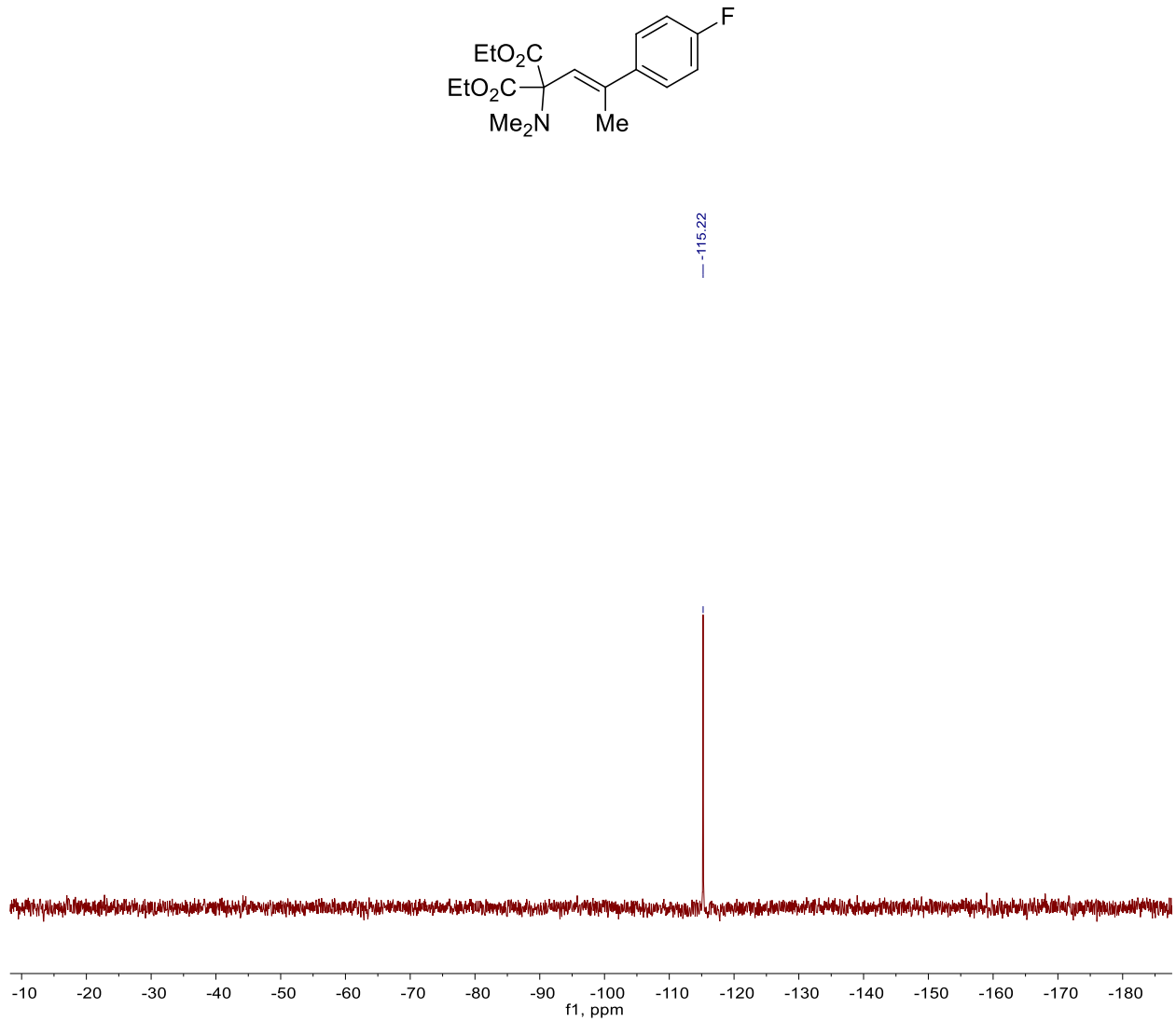
^{1}H spectrum of **4d** in $CDCl_3$



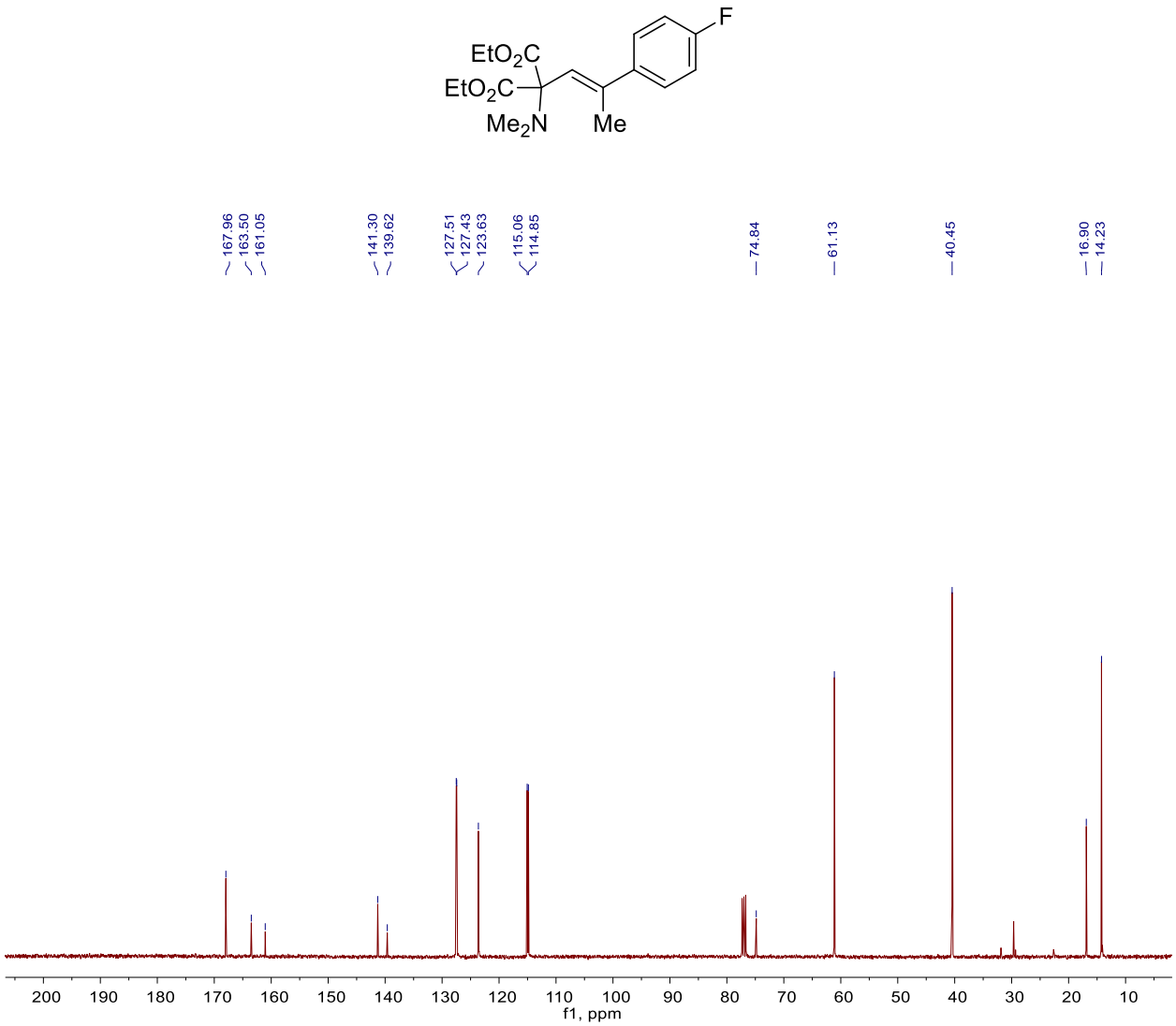
^{13}C spectrum of **4d** in $CDCl_3$



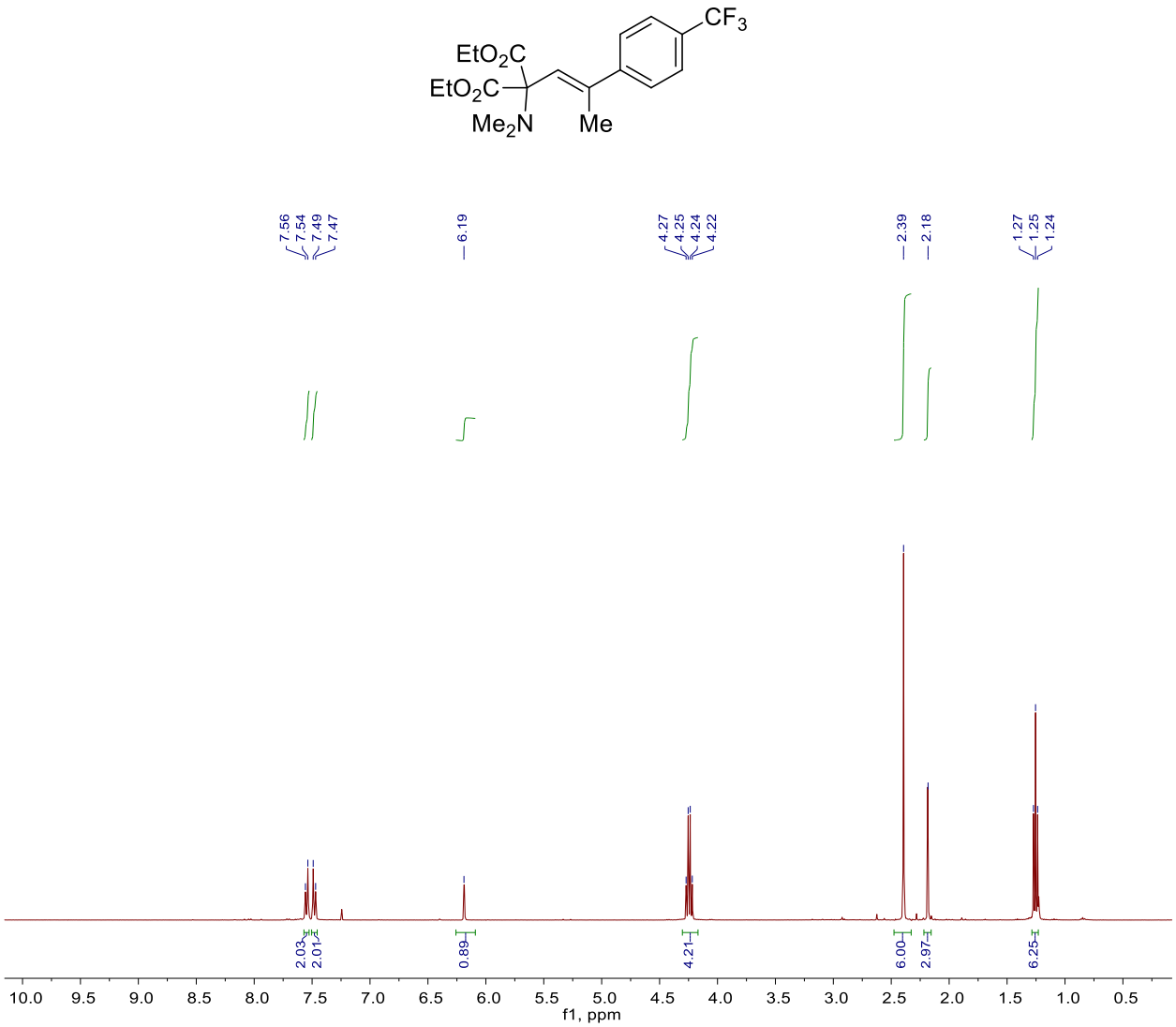
^{1}H spectrum of **4e** in $CDCl_3$



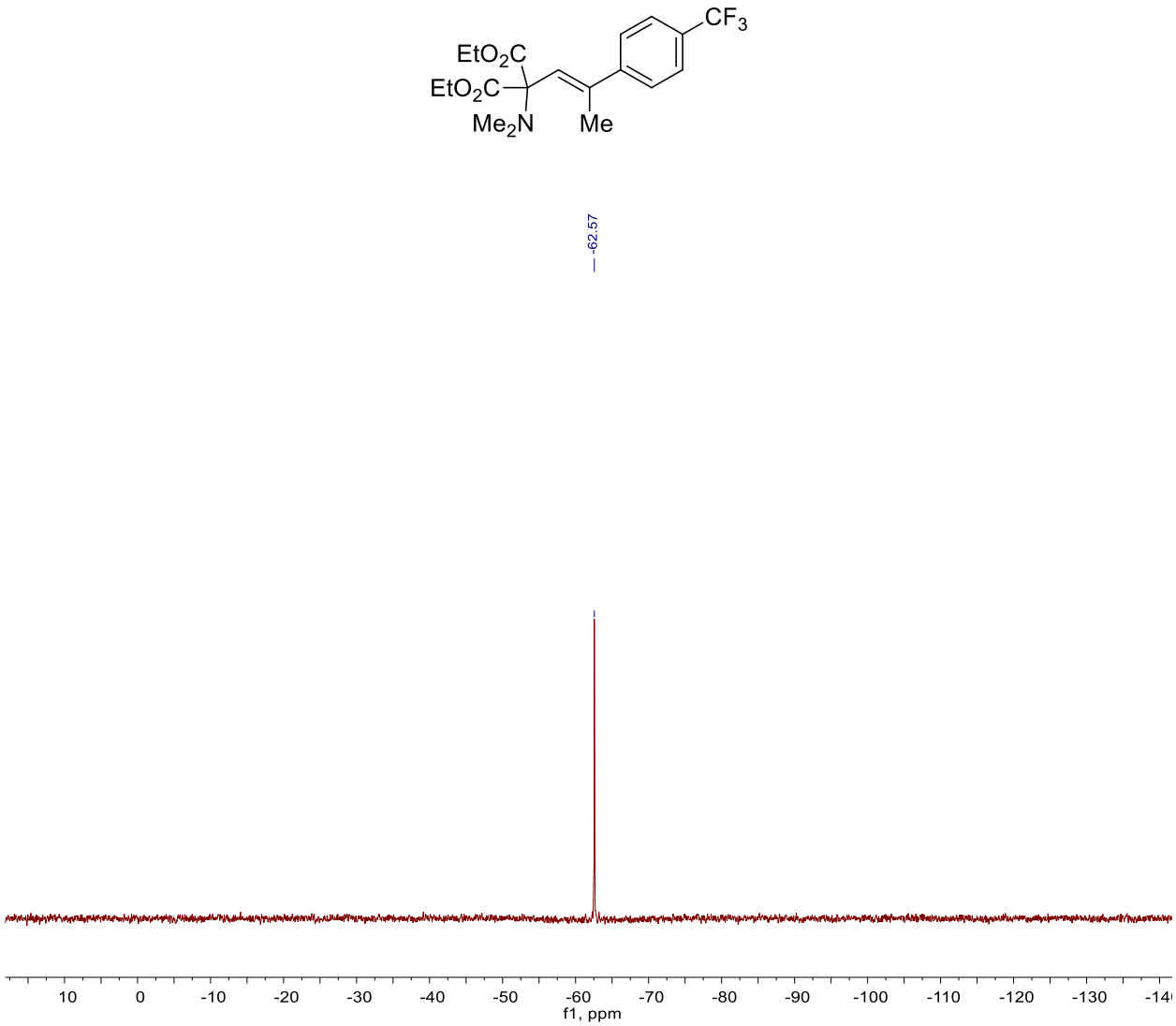
^{19}F spectrum of **4e** in $CDCl_3$



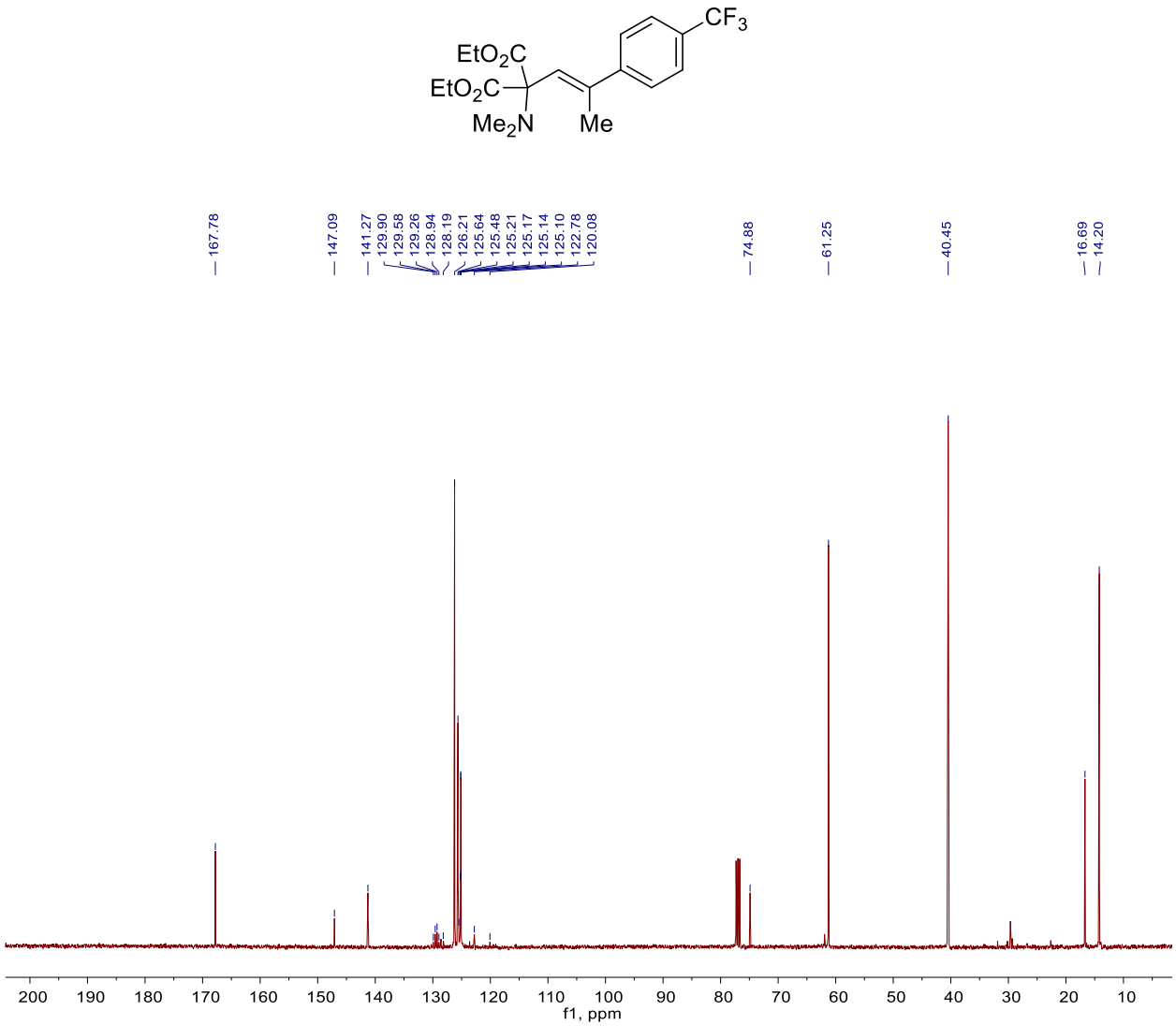
^{13}C spectrum of **4e** in $CDCl_3$



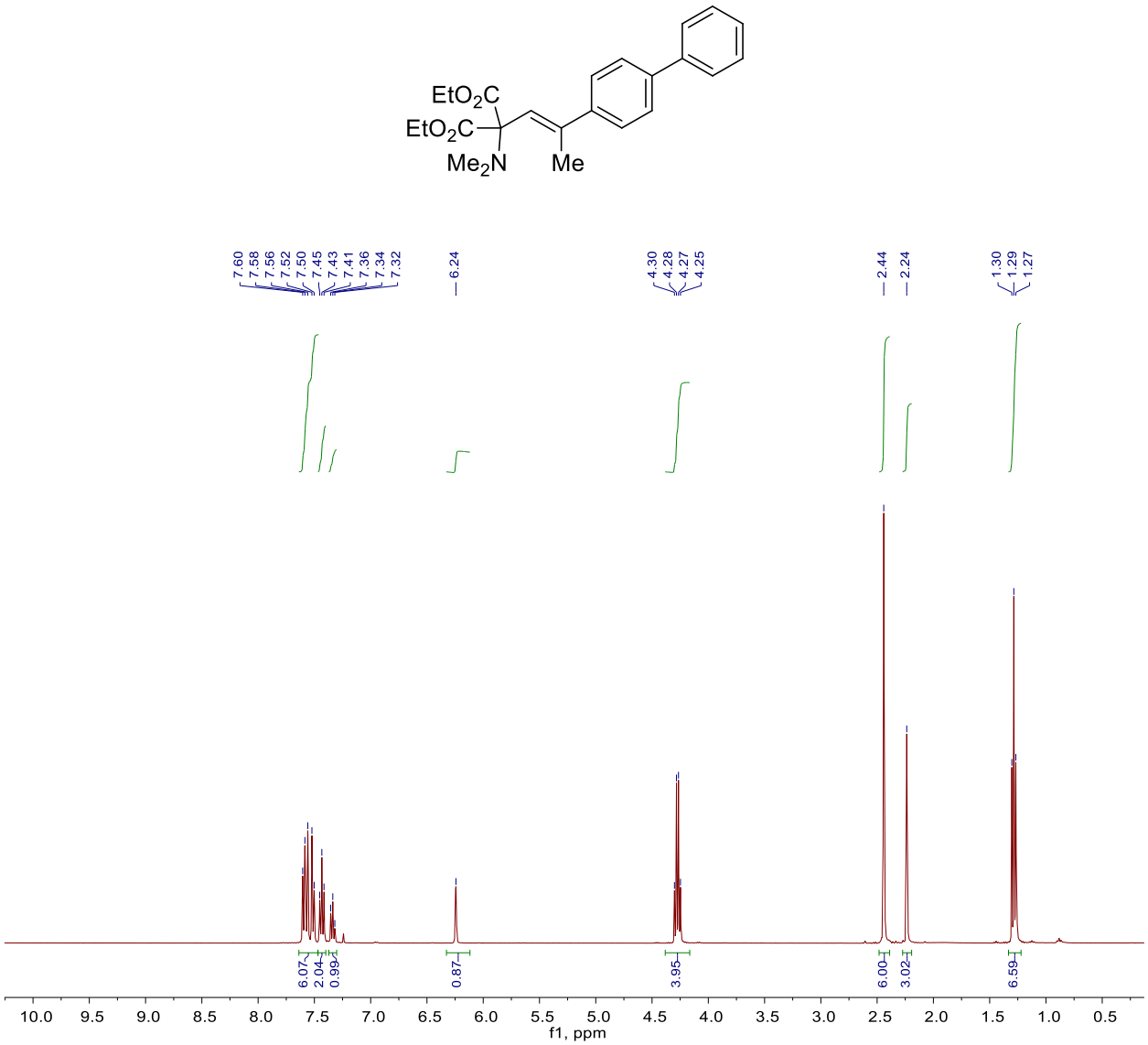
^{1}H spectrum of **4f** in $CDCl_3$



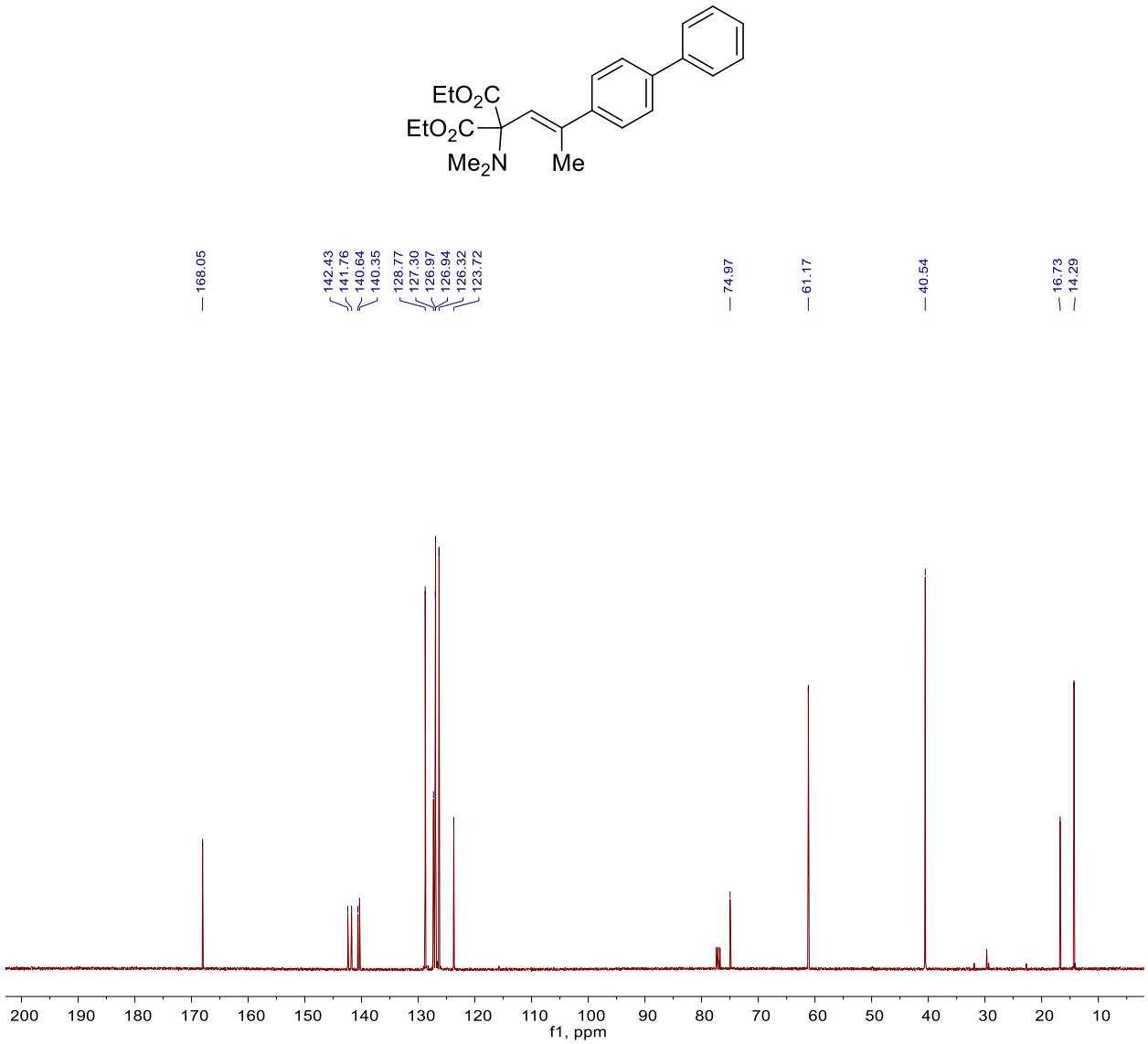
^{19}F spectrum of **4f** in $CDCl_3$



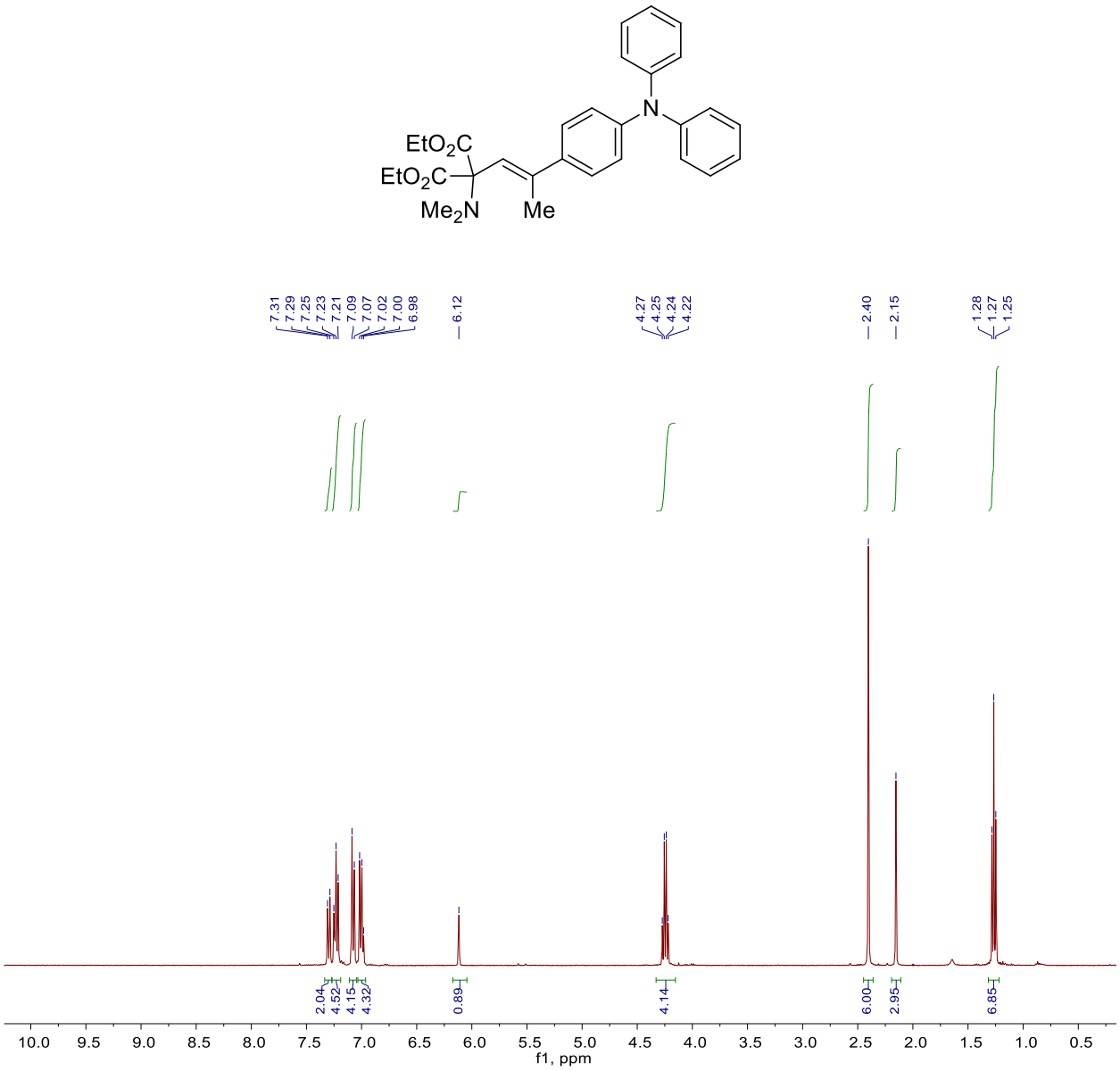
^{13}C spectrum of **4f** in $CDCl_3$



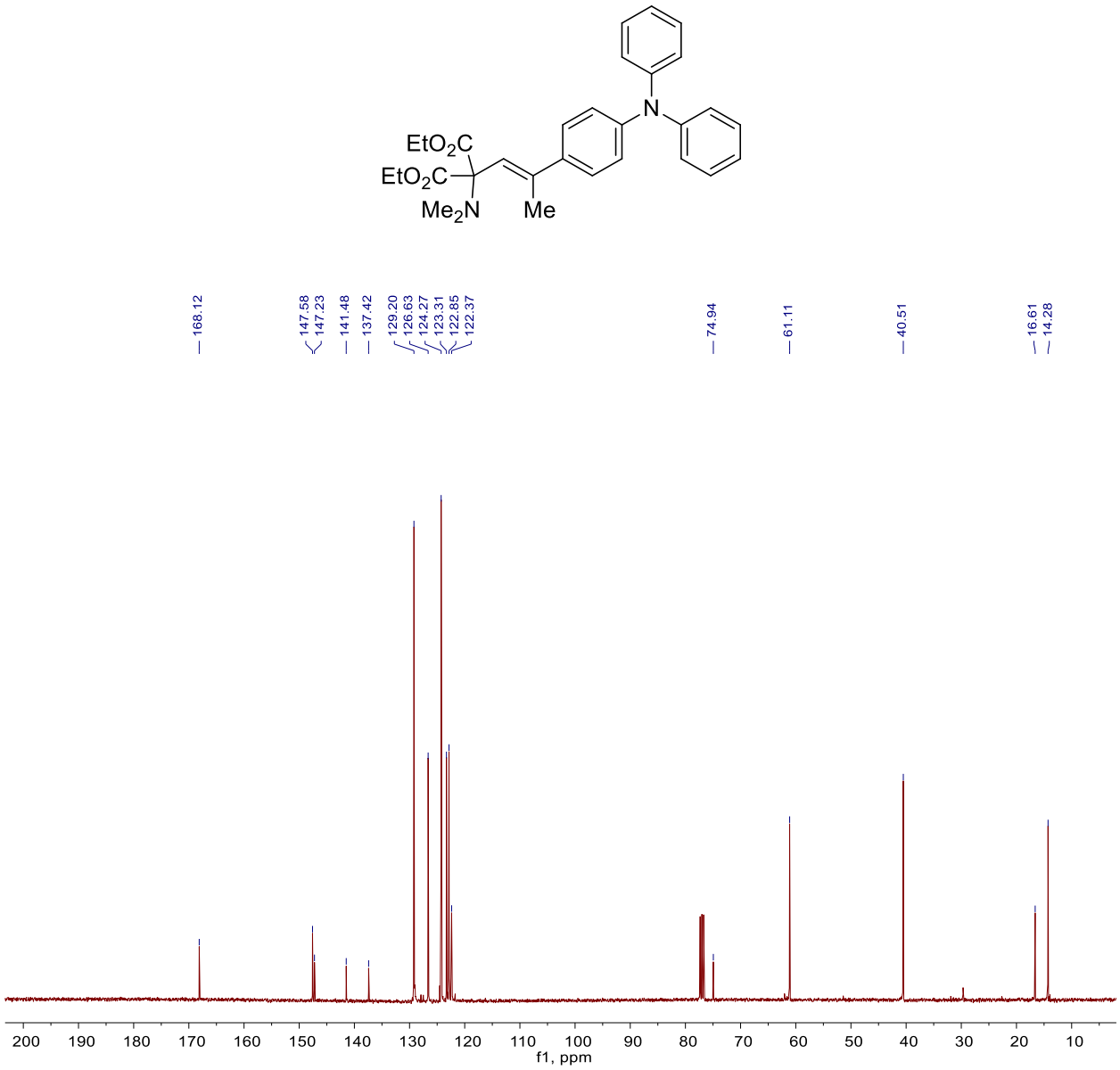
^{1}H spectrum of **4g** in $CDCl_3$



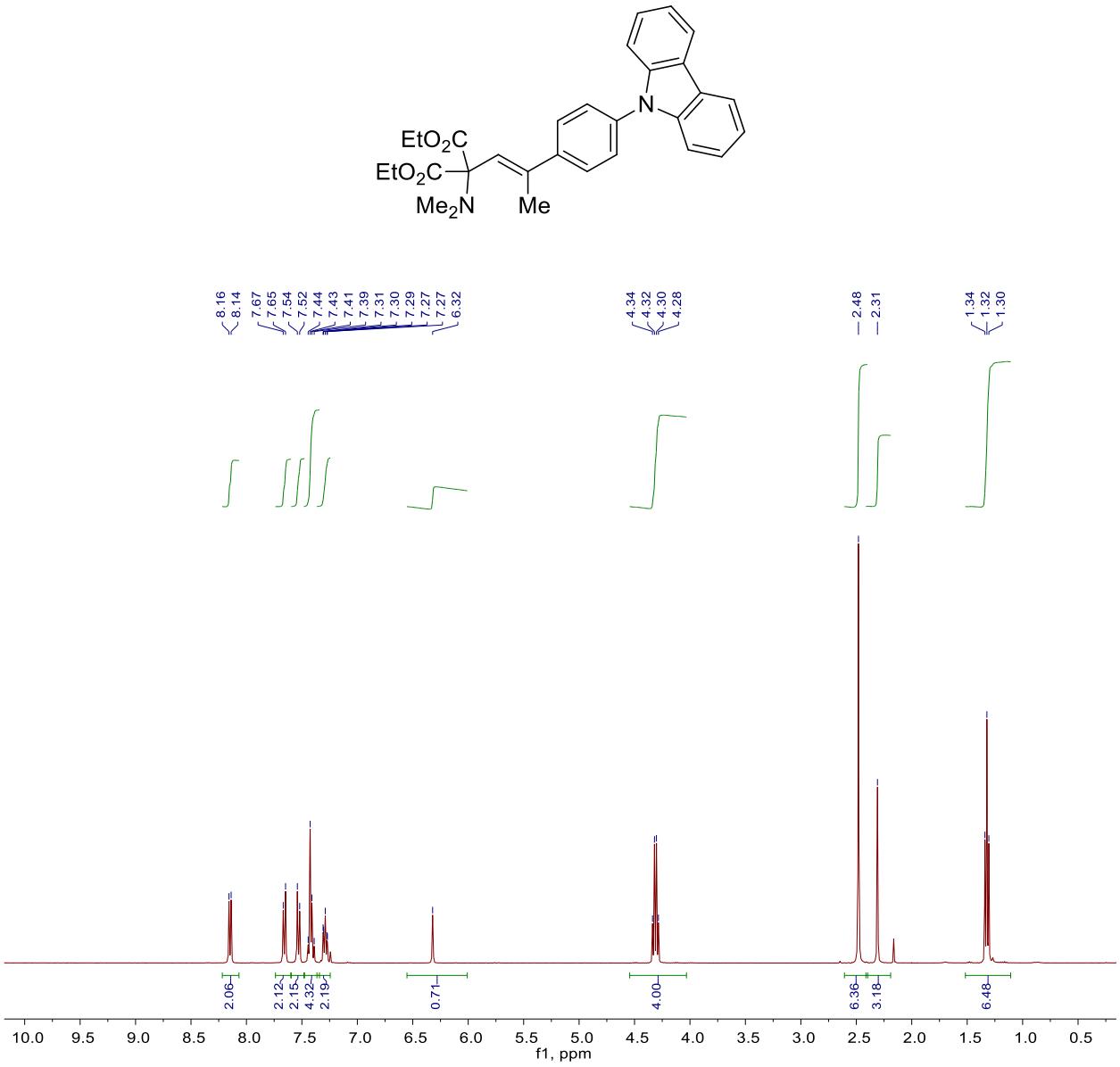
^{13}C spectrum of **4g** in $CDCl_3$



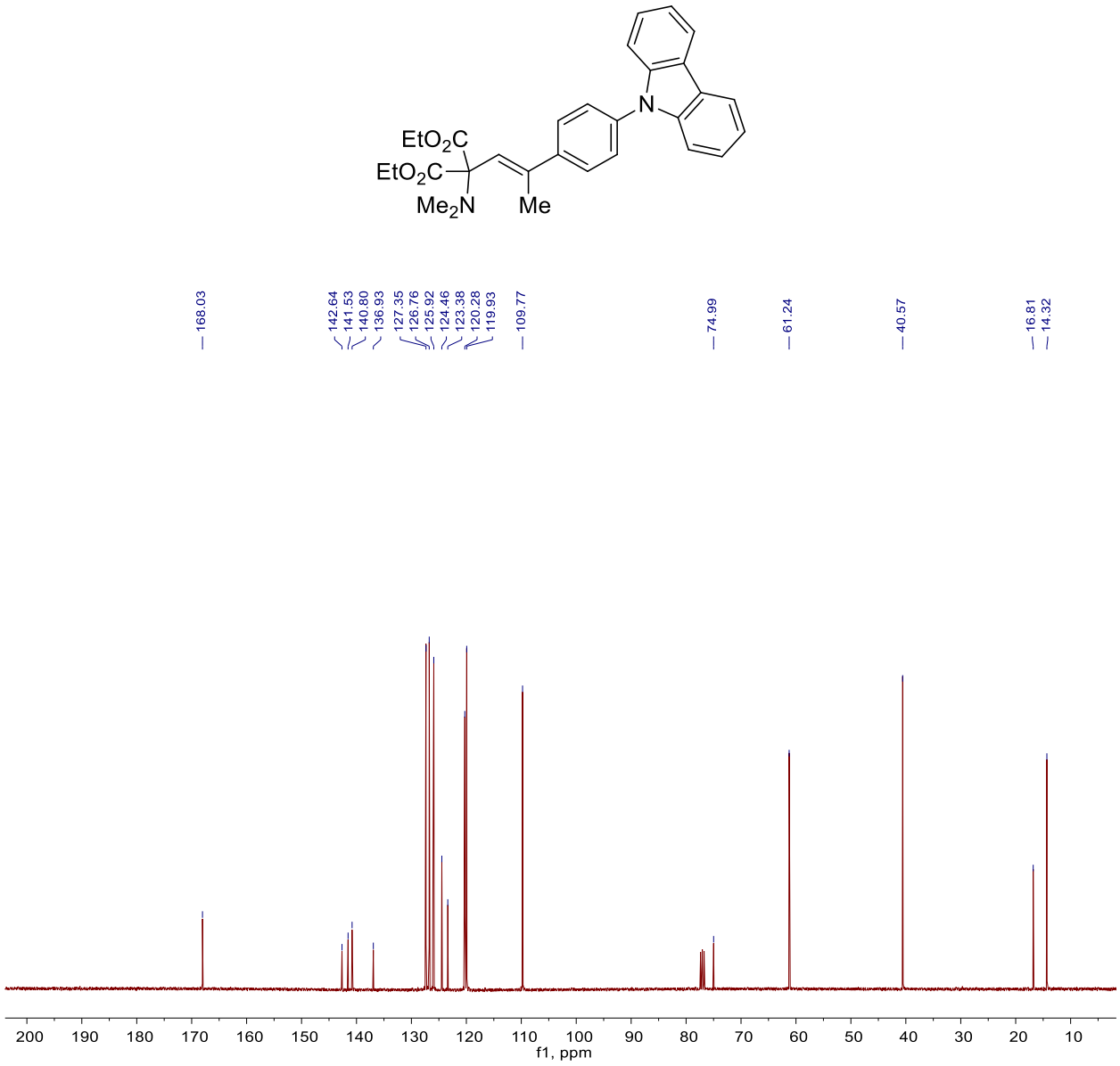
^{1}H spectrum of **4h** in $CDCl_3$



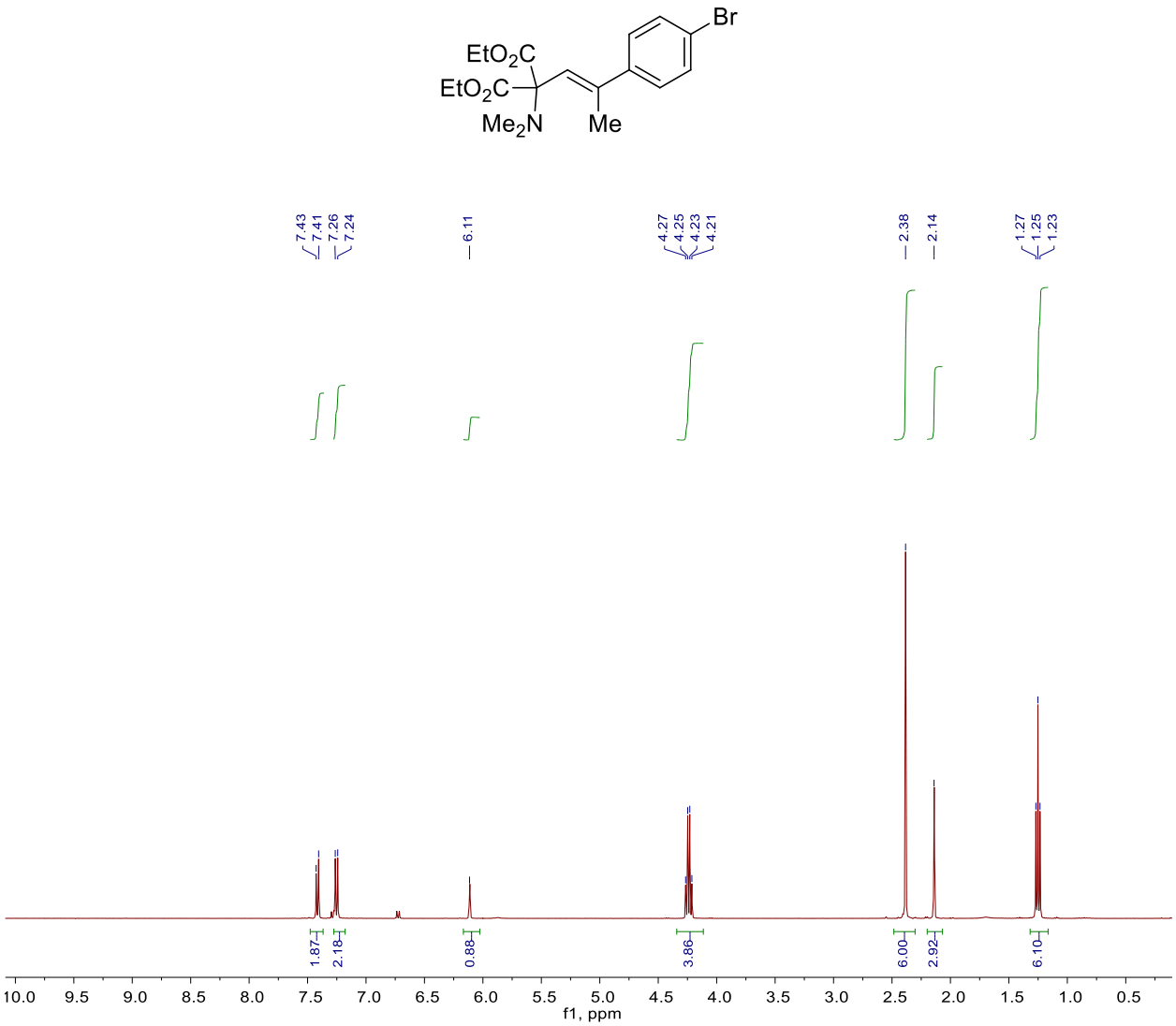
^{13}C spectrum of **4h** in $CDCl_3$



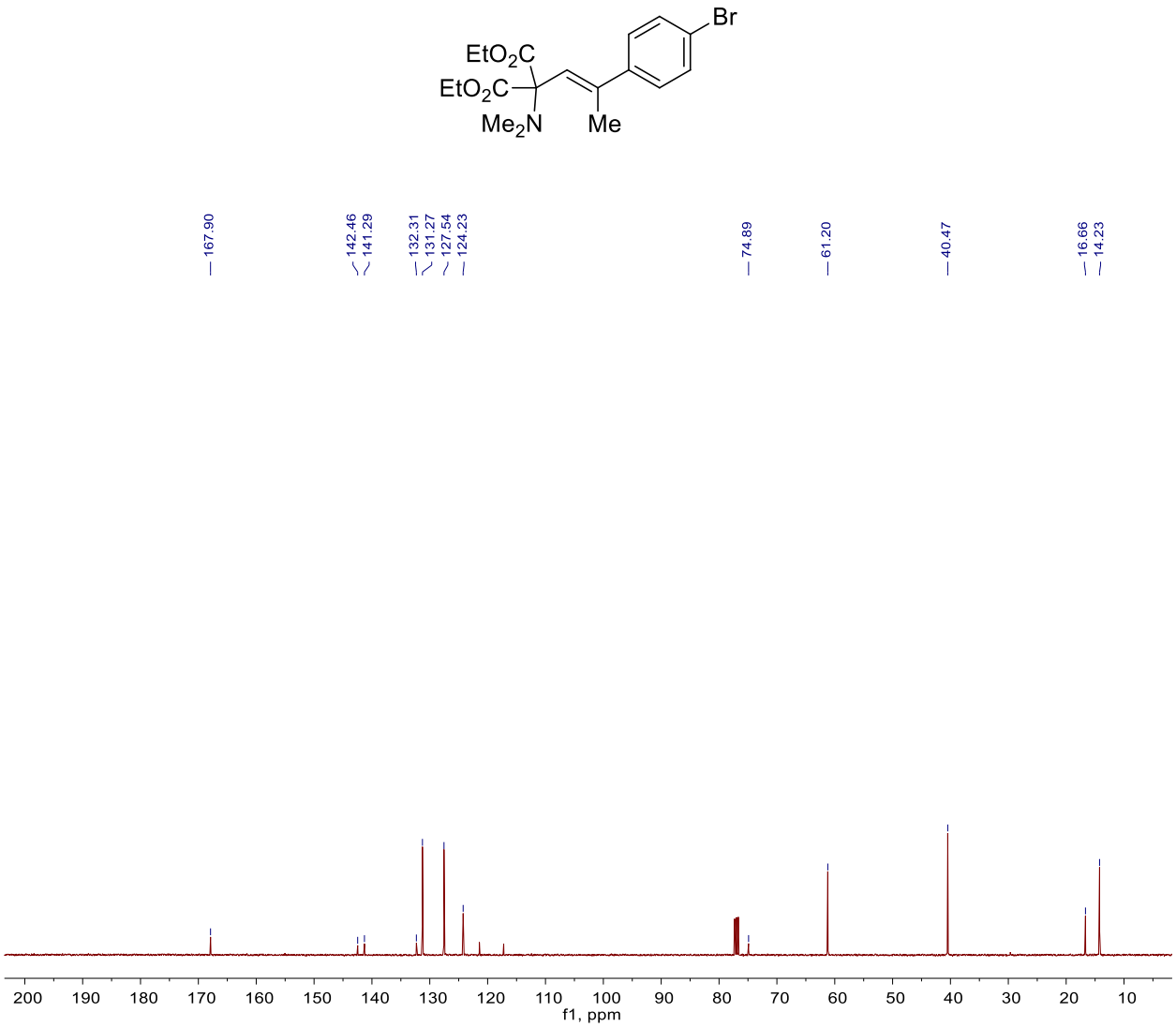
^{1}H spectrum of **4i** in $CDCl_3$



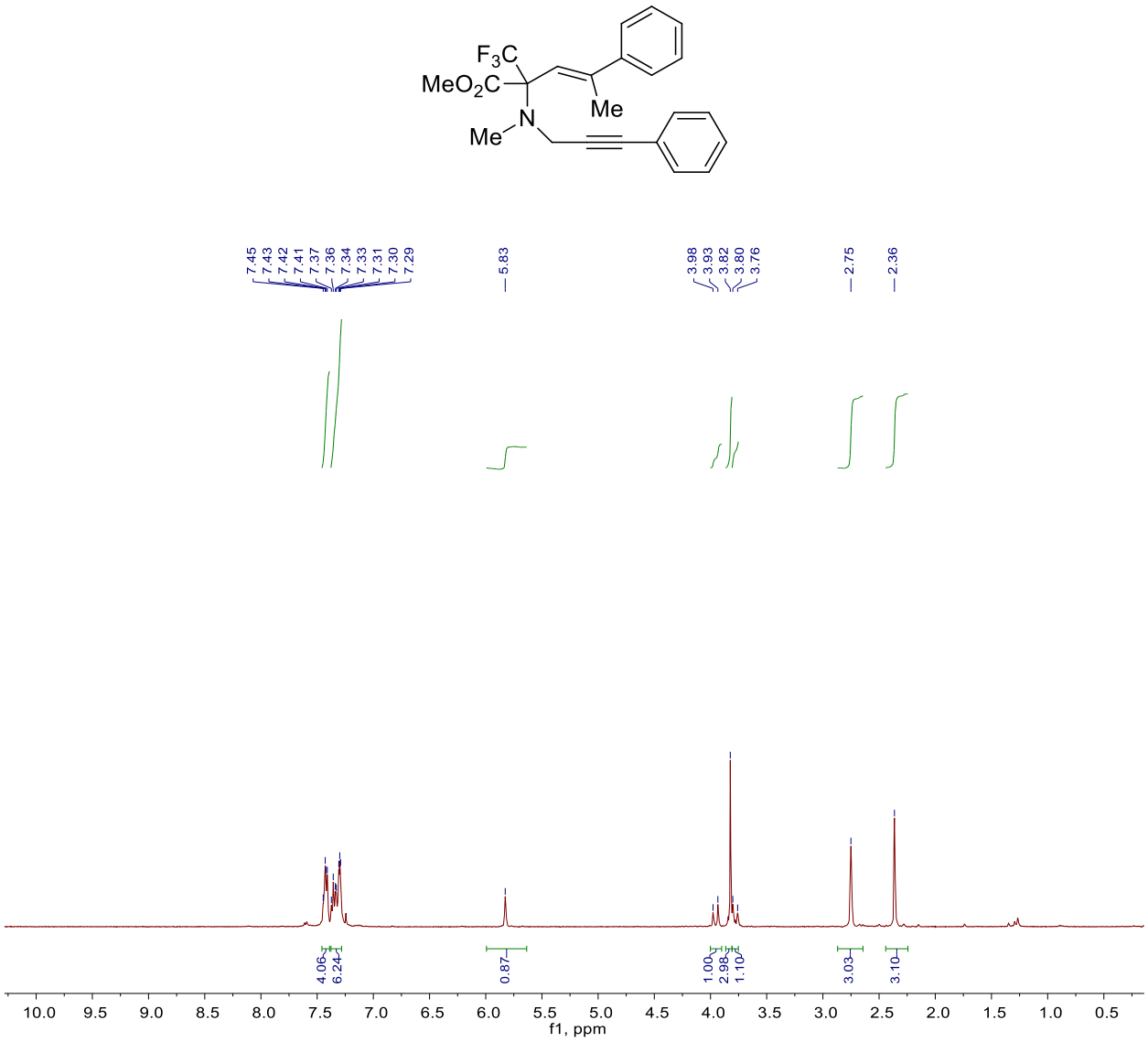
^{13}C spectrum of **4i** in $CDCl_3$



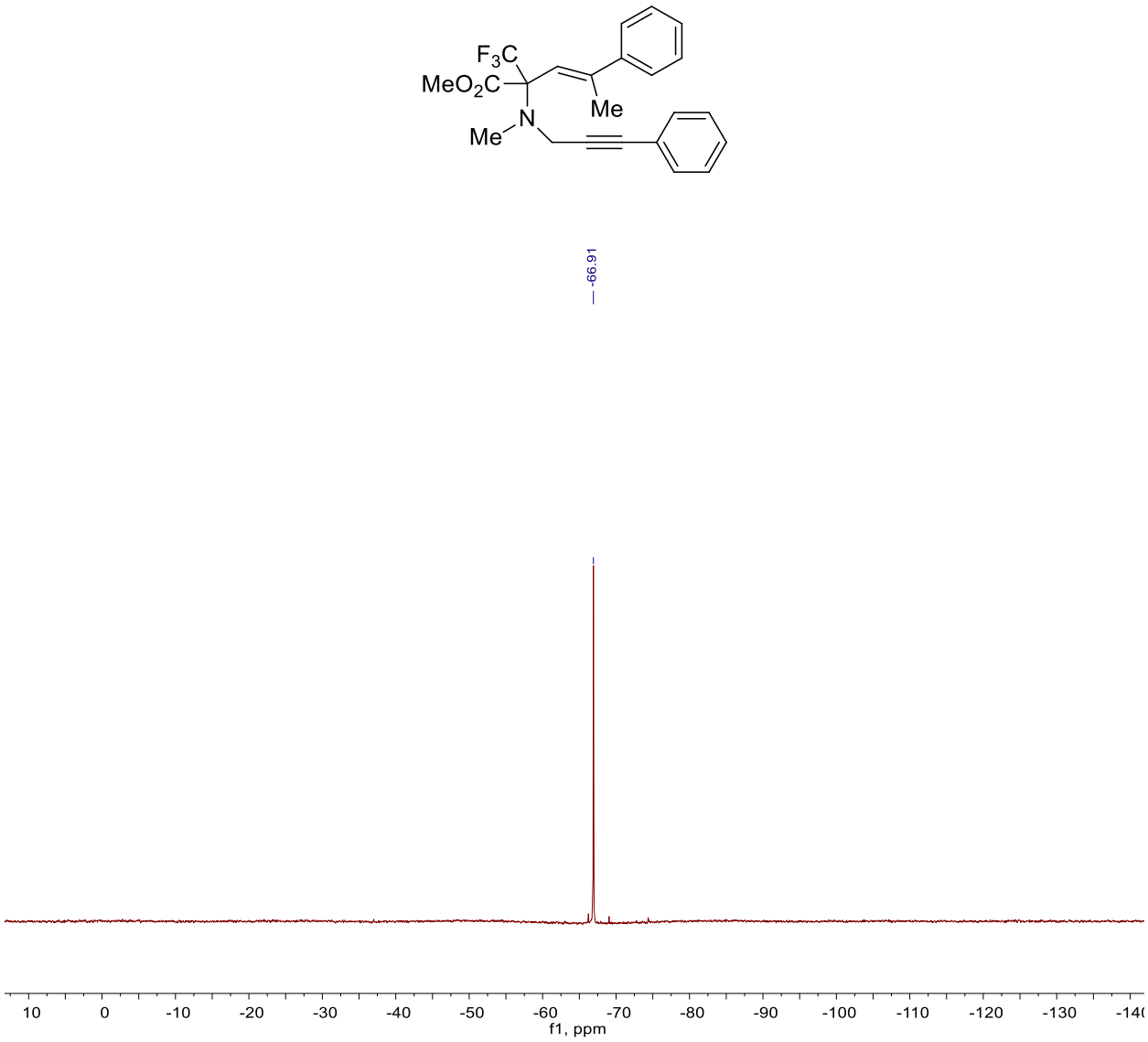
^{1}H spectrum of **4j** in $CDCl_3$



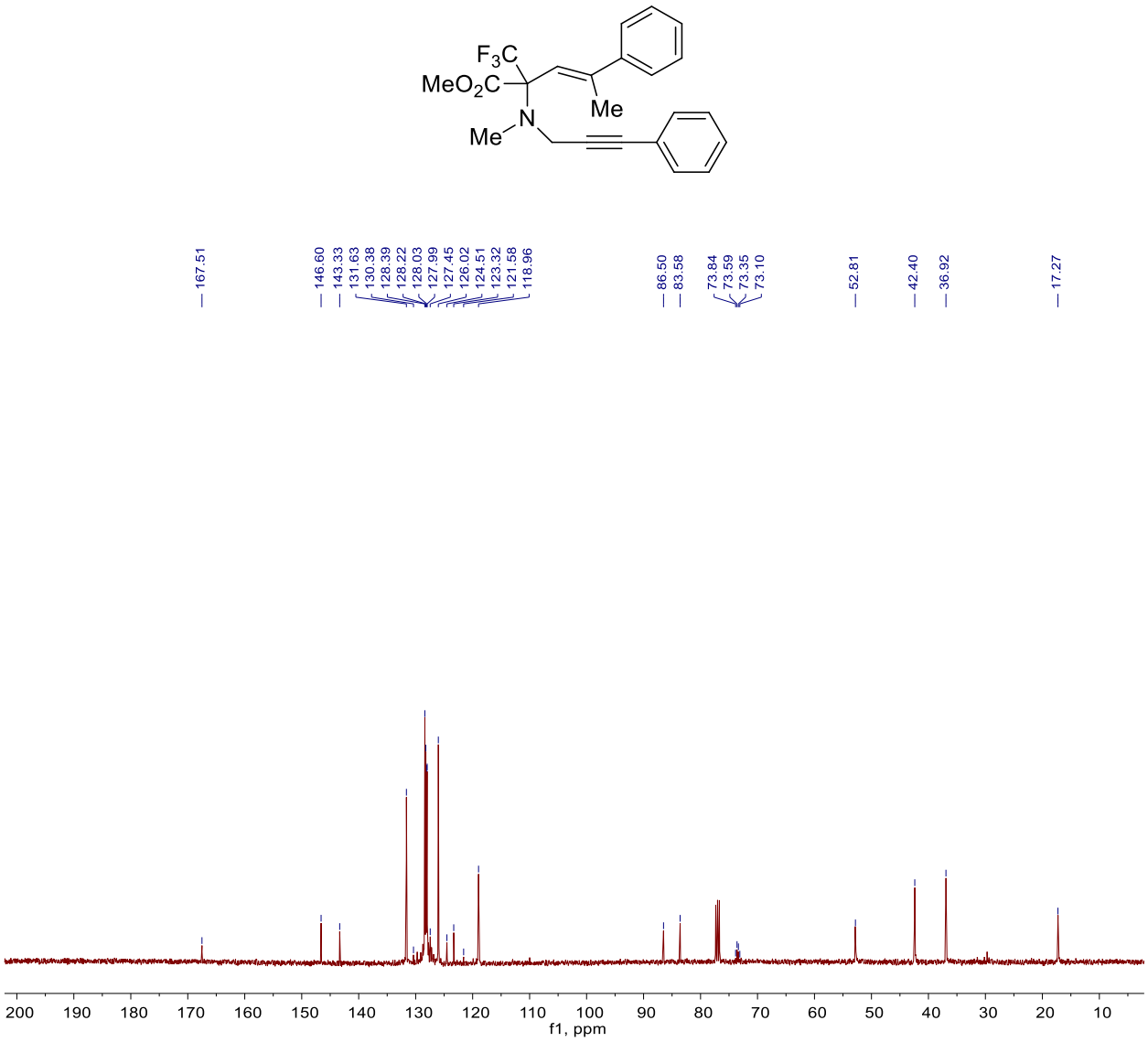
^{13}C spectrum of **4j** in $CDCl_3$



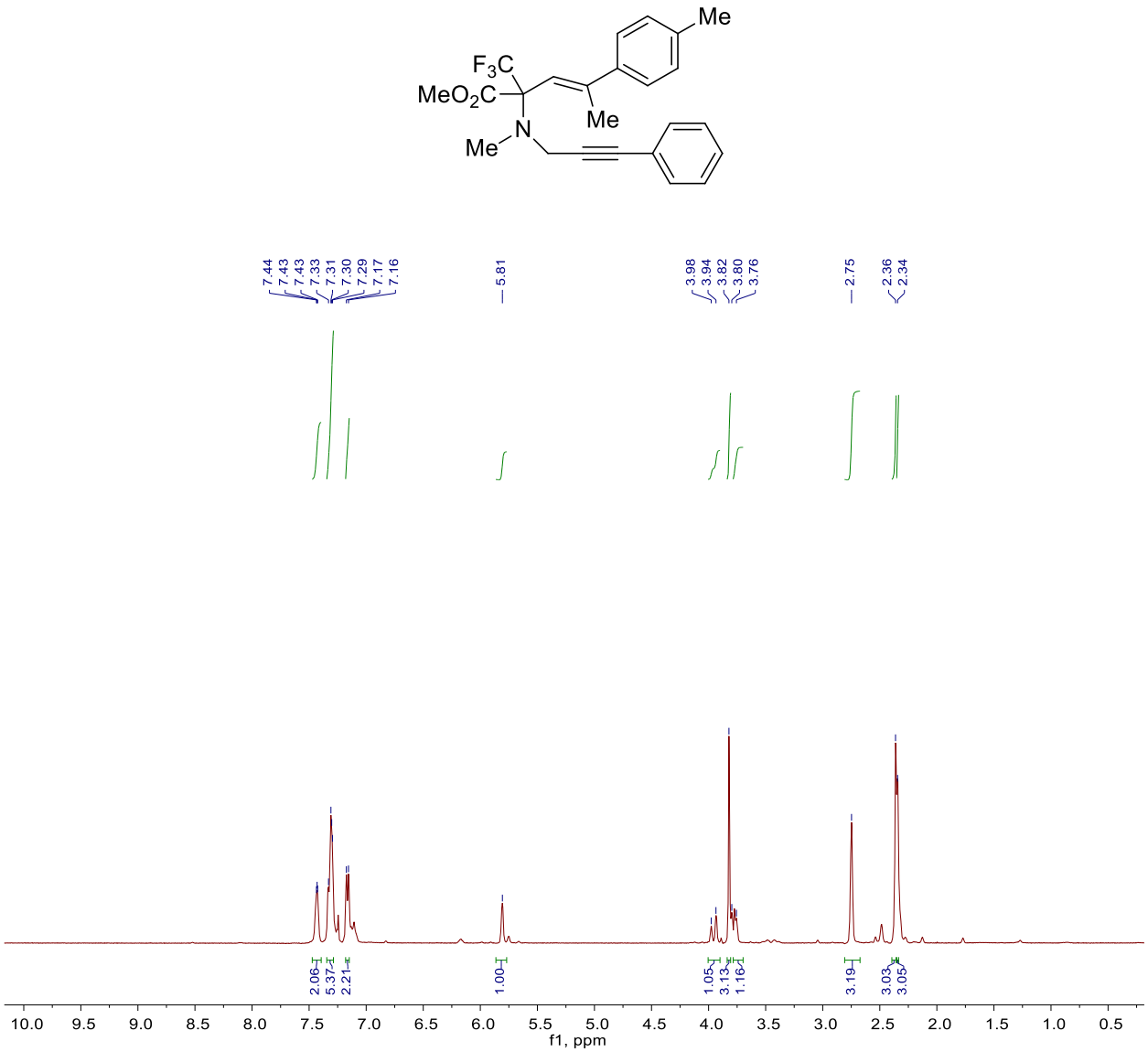
^{1}H spectrum of **6a** in $CDCl_3$



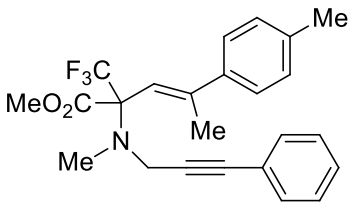
^{19}F spectrum of **6a** in $CDCl_3$

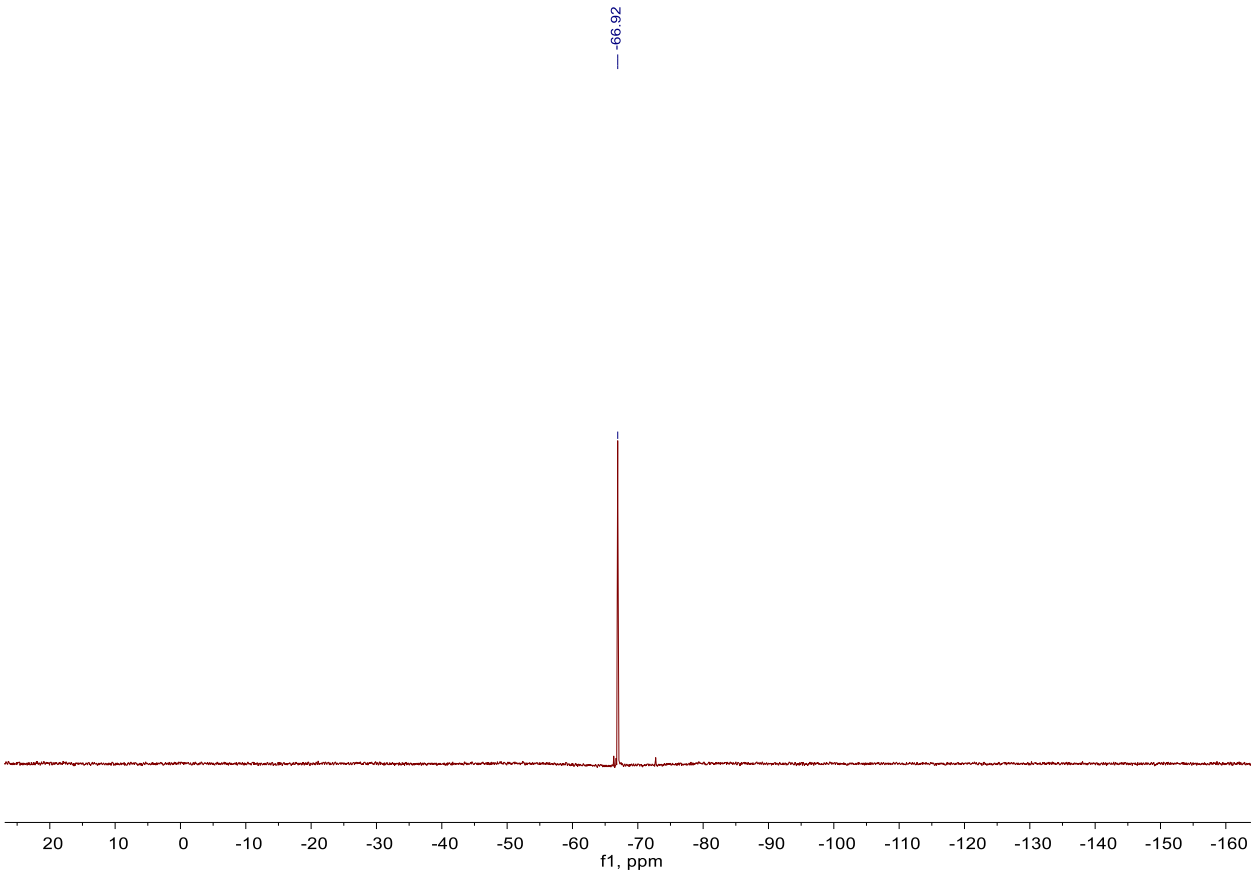


^{13}C spectrum of **6a** in $CDCl_3$

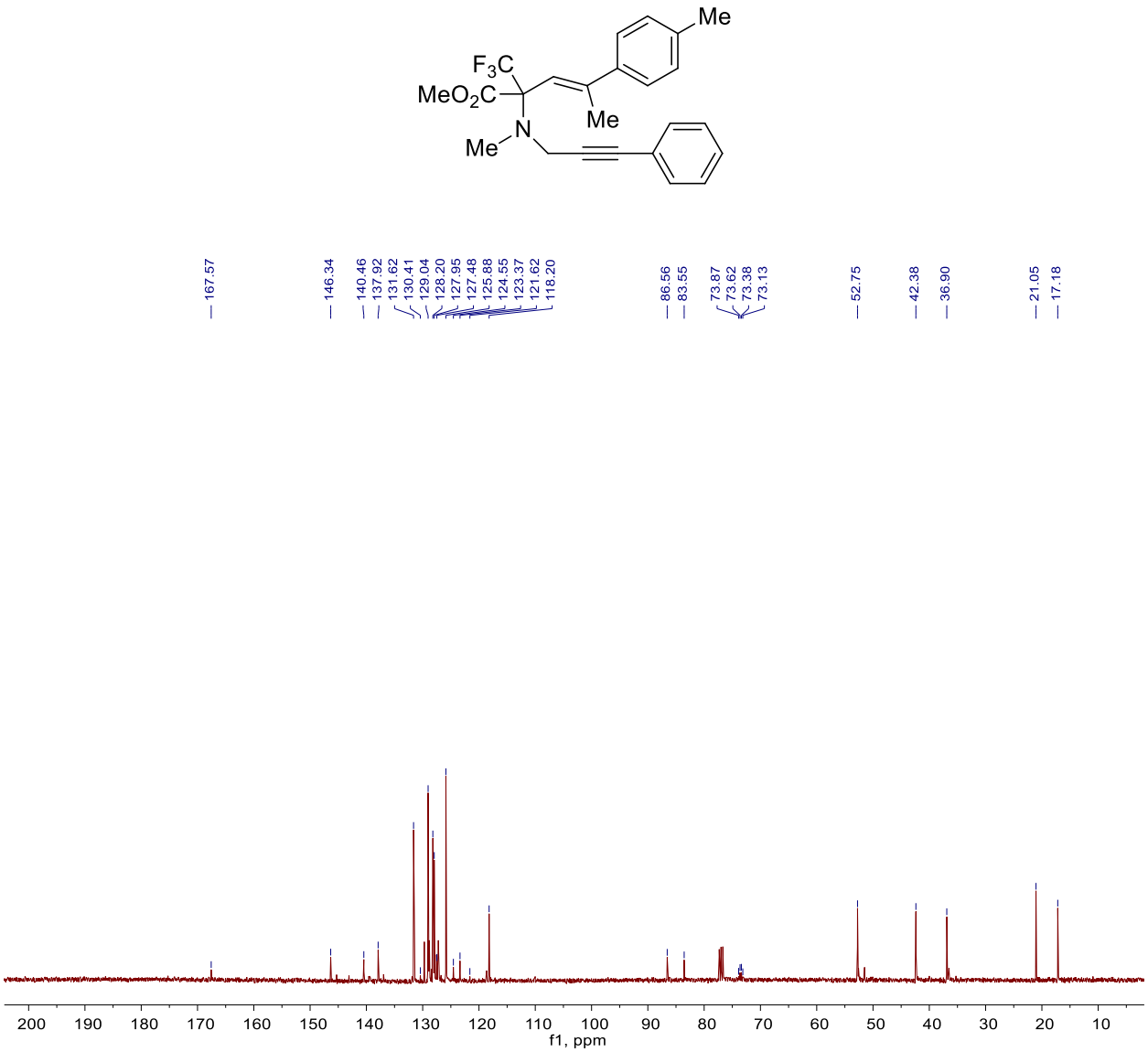


^{1}H spectrum of **6b** in $CDCl_3$

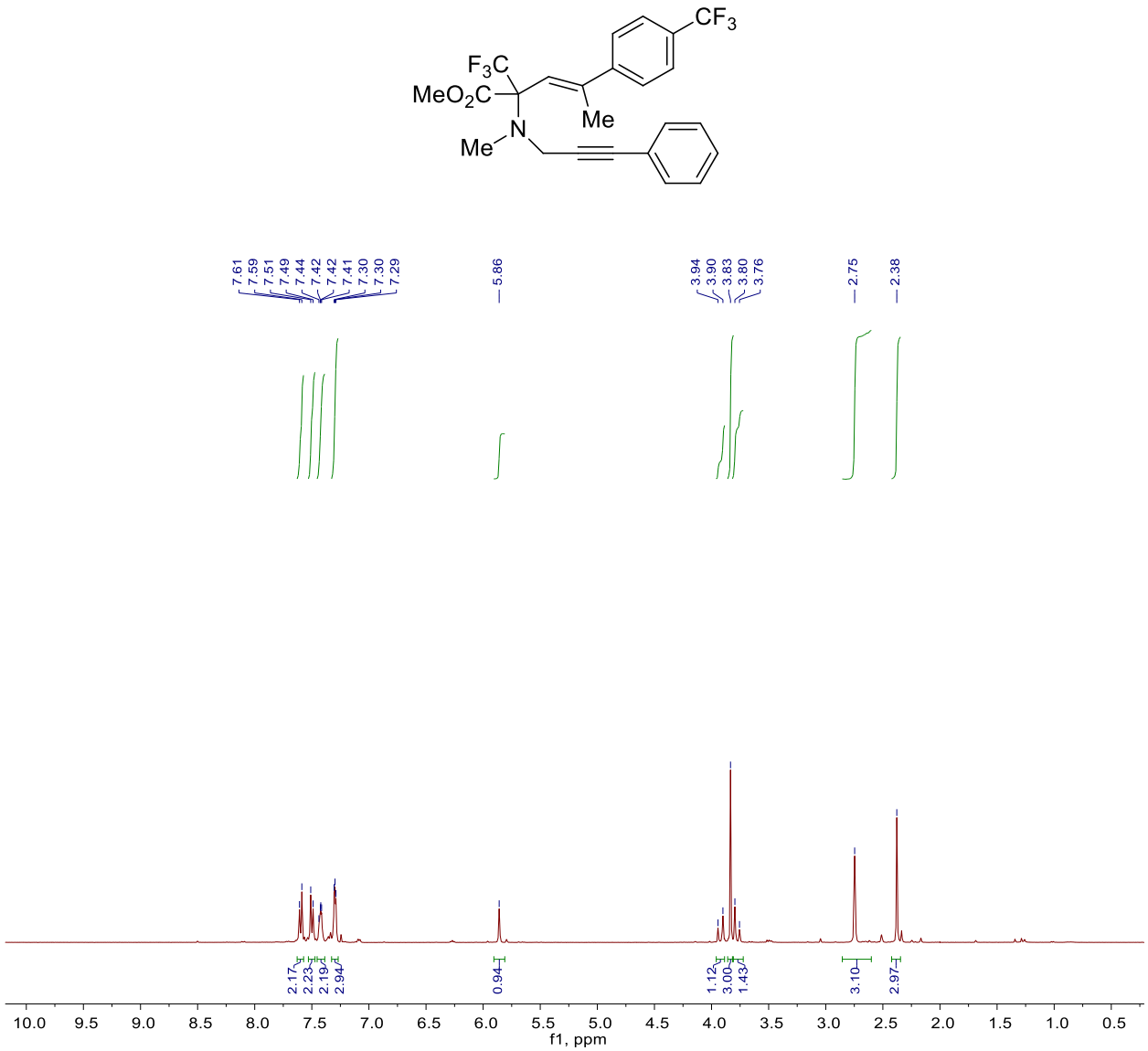




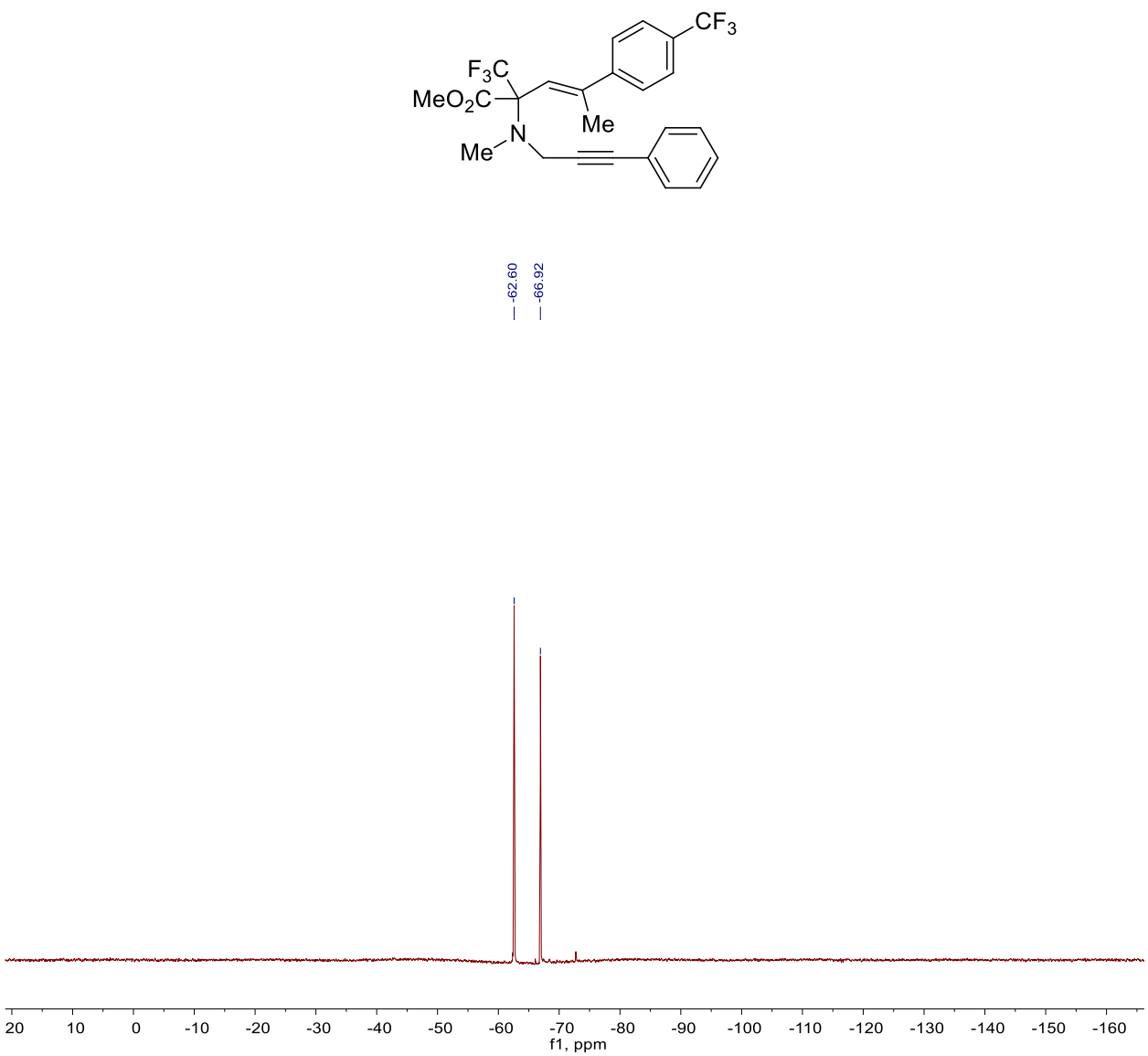
^{19}F spectrum of **6b** in $CDCl_3$



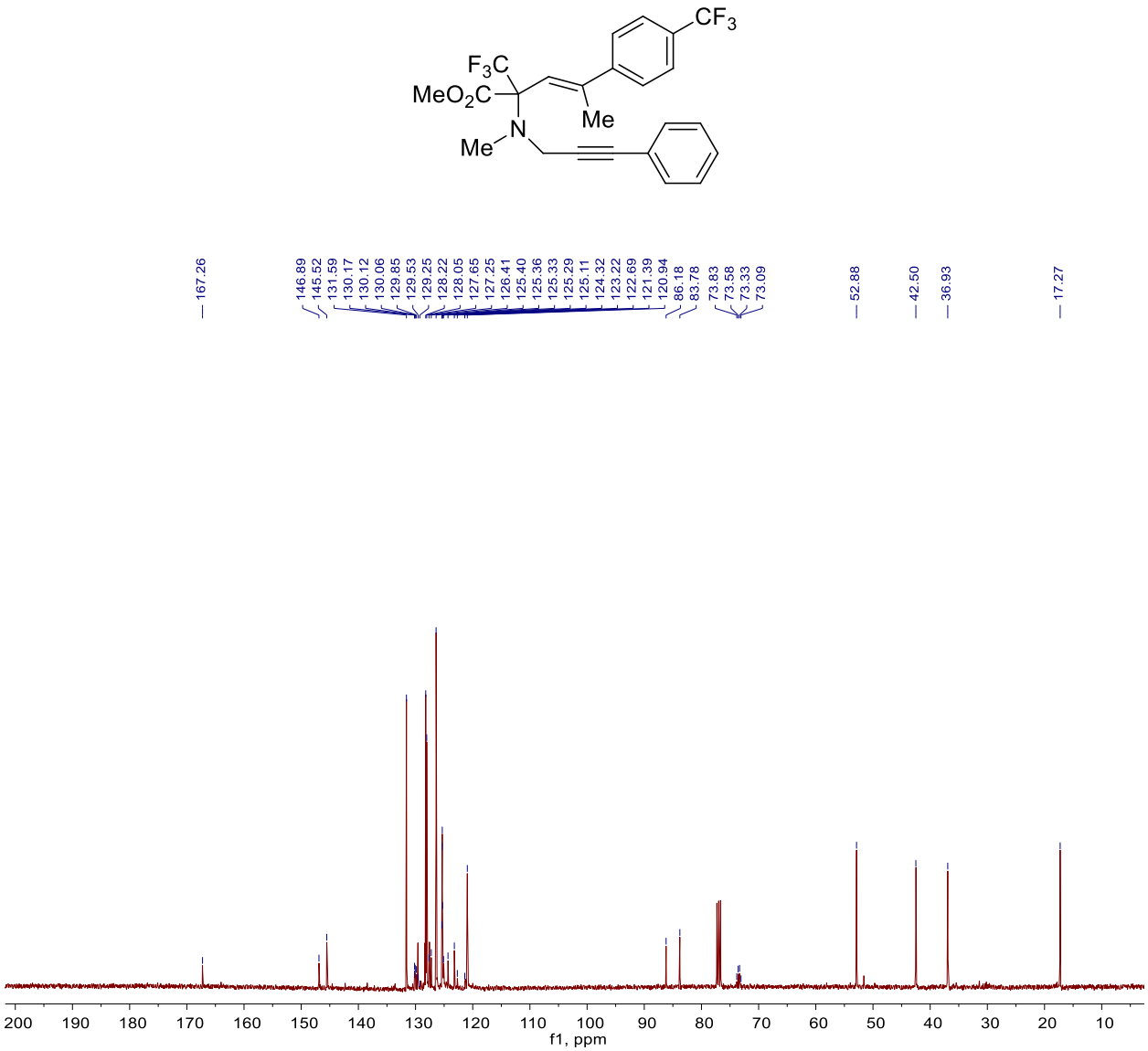
^{13}C spectrum of **6b** in $CDCl_3$



^{1}H spectrum of **6c** in $CDCl_3$



^{19}F spectrum of **6b** in $CDCl_3$



^{13}C spectrum of **6c** in $CDCl_3$

X-ray crystallography data of 4i

Table S1. Crystal data and structure refinement for 4i (CCDC 2442651)

Empirical formula	$C_{30}H_{32}N_2O_4$
Formula weight	484.57
Temperature/K	120
Crystal system	triclinic
Space group	P-1
a/Å	9.531(10)
b/Å	11.853(14)
c/Å	12.147(14)
α/°	70.51(3)
β/°	74.23(3)
γ/°	85.57(4)
Volume/Å3	1245(2)
Z	2
ρcalcg/cm3	1.293
μ/mm-1	0.086
F(000)	516.0
Crystal size/mm3	0.29 × 0.24 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.686 to 51.998
Index ranges	-11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -14 ≤ l ≤ 14
Reflections collected	10579
Independent reflections	4820 [Rint = 0.1473, Rsigma = 0.3111]
Data/restraints/parameters	4820/0/330
Goodness-of-fit on F2	0.857
Final R indexes [I>=2σ (I)]	R1 = 0.0976, wR2 = 0.2165
Final R indexes [all data]	R1 = 0.2045, wR2 = 0.2875
Largest diff. peak/hole / e Å-3	0.36/-0.42