Supporting information *for*

Lossen Rearrangement by Rh(III)-Catalyzed C-H Activation/Annulation of Aryl Hydroxamates with Alkynes: Access to Quinolone-containing Amino Acid Derivatives

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Contents

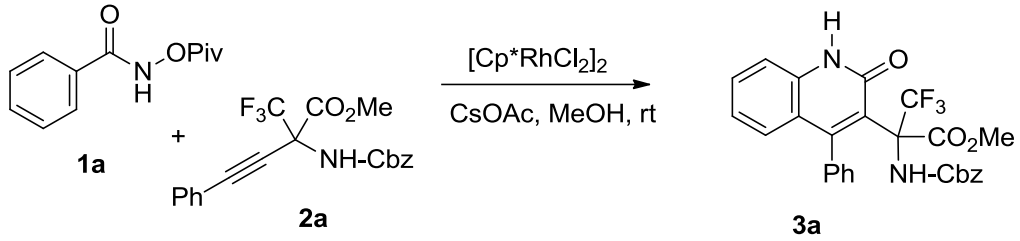
General information

All solvents used in reactions were freshly distilled from appropriate drying agents before use. All other reagents were distilled as necessary. The corresponding starting acetylenes were easily synthesized *via* the previously described protocol.[1] 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. Chromatography was carried out using Merck silica gel (Kieselgel 60, 0.063-0.200 mm) and petroleum ether/ethyl acetate as an eluent. The NMR spectra were obtained with Bruker AV-300, AV-400 and AV-500 spectrometers operating at 300, 400, and 500 MHz, respectively, for ^{1}H (TMS reference), at 101 and 126 for ^{13}C $\{^{1}H\}$, and at 282 and 376 MHz for ^{19}F ($CCl^{3}F$ reference).

[1] a) G. T. Shchetnikov, A. S. Peregudov, S. N. Osipov, *Synlett*, **2007**, 136-140; b) D. Sémeril, J. Le Notre, C. Bruneau, P.H. Dixneuf, A.F. Kolomiets, S.N. Osipov, *New J. Chem.*, **2001**, *25*(1), 16-18.

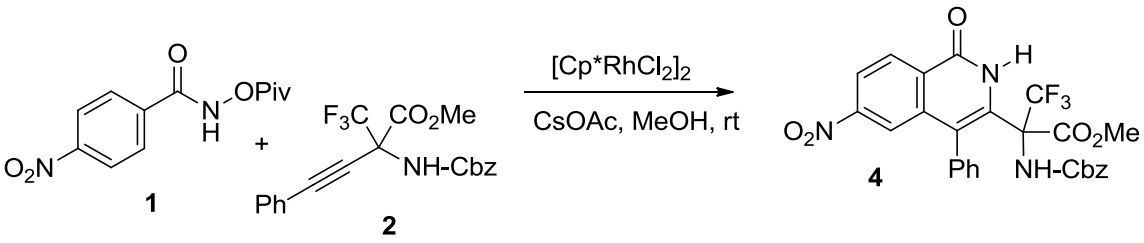
General procedures.

A. General procedure for C-H activation/annulation of aryl hydroxamates with acetylenes *via* Lossen rearrangement.



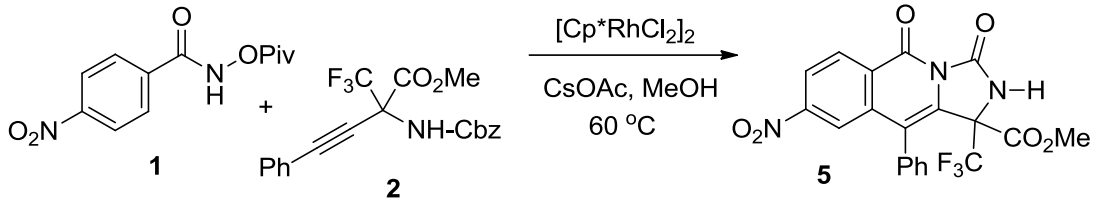
A dried 10 mL Schlenk tube equipped with a magnetic stirring bar was charged with a corresponding acetylene (0.1 g, 0.3 mmol, 1 equiv.), MeOH (3 mL), corresponding aryl hydroxamate (0.07 g, 0.3 mmol, 1 equiv.), $[Cp^*RhCl_2]_2$ (4.7 mg, 7.6 μmol, 3 mol.%) and CsOAc (0.09 g, 0.5 mmol, 2 equiv.) under Ar. The reaction mixture was stirred at room temperature for 2.5-3 h until the completion of the reaction monitored by TLC ^{19}F NMR. Then water (7 mL) was added to a residue and the aqueous mixture was extracted with ethyl acetate (3 x 7 mL). The organic layer was dried over $MgSO_4$, filtered and evaporated to dryness. The residue was purified by recrystallization (eluent petroleum ether/ethyl acetate) to give the desired product.

B. General procedure for C-H activation/annulation of aryl hydroxamates with acetylenes.



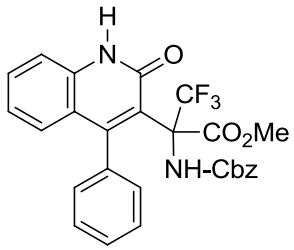
A dried 10 mL Schlenk tube equipped with a magnetic stirring bar was charged with a corresponding acetylene (0.1 g, 0.3 mmol, 1 equiv.), MeOH (3 mL), corresponding aryl hydroxamate (0.07 g, 0.3 mmol, 1 equiv.), $[Cp^*RhCl_2]_2$ (4.7 mg, 7.6 μmol, 3 mol.%) and CsOAc (0.1 g, 0.5 mmol, 2 equiv.) under Ar. The reaction mixture was stirred at room temperature overnight until the completion of the reaction monitored by TLC ^{19}F NMR. Then water (7 mL) was added to a residue and the aqueous mixture was extracted with ethyl acetate (3 x 7 mL). The organic layer was dried over $MgSO_4$, filtered and evaporated to dryness. The residue was purified by recrystallization or column chromatography (eluent petroleum ether/ethyl acetate) to give the desired product.

C. General procedure for C-H activation/annulation of aryl hydroxamates with acetylenes followed by the cascade cyclization.

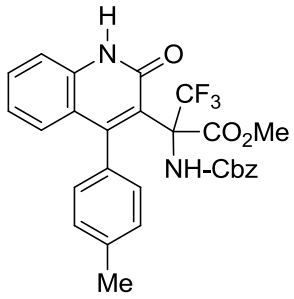


A dried 10 mL Schlenk tube equipped with a magnetic stirring bar was charged with a corresponding acetylene (0.1 g, 0.3 mmol, 1 equiv.), MeOH (3 mL), corresponding aryl hydroxamate (0.07 g, 0.3 mmol, 1 equiv.), $[Cp^*RhCl_2]_2$ (4.7 mg, 7.6 μmol, 3 mol.%) and CsOAc (0.1 g, 0.5 mmol, 2 equiv.) under Ar. The reaction mixture was stirred at 60°C overnight until the completion of the reaction monitored by TLC ^{19}F NMR. Then water (7 mL) was added to a residue and the aqueous mixture was extracted with ethyl acetate (3 x 7 mL). The organic layer was dried over $MgSO_4$, filtered and evaporated to dryness. The residue was purified by recrystallization or column chromatography (eluent petroleum ether/ethyl acetate) to give the desired product.

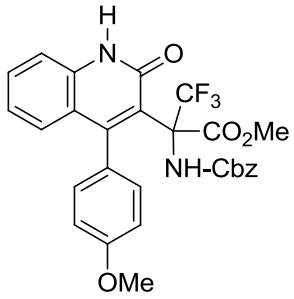
Characterization Data for the products



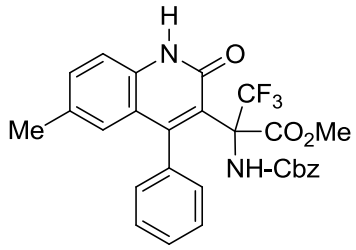
Methyl 2-(((benzyloxy)carbonyl)amino)-3,3,3-trifluoro-2-(2-oxo-4-phenyl-1,2-dihydroquinolin-3-yl)propanoate (3a). Was synthesized according to the general procedure A. Yield 73% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 166–168°C. ^1H NMR (DMSO-d_6, 500 MHz): δ 12.73 (s, 1H), 10.34 (br. s, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.54 - 7.44 (m, 4H), 7.39 - 7.30 (m, 5H), 7.25 (d, J = 6.5 Hz, 1H), 7.10 - 7.07 (m, 2H), 6.41 (d, J = 8.3 Hz, 1H), 5.04 (d, J = 12.7 Hz, 1H), 5.00 (d, J = 12.7 Hz, 1H), 3.30 (s, 3H). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 126 MHz): δ 164.0, 162.5, 154.7, 153.9, 137.7, 136.8, 133.3, 132.8, 130.6, 129.3, 128.8, 128.5, 128.4, 128.3, 128.2, 127.8, 124.4 (q, J = 290.4 Hz), 123.3, 121.4, 115.6, 67.5 (q, J = 29.0 Hz), 66.4, 52.8. ^{19}F NMR (DMSO-d_6, 376 MHz): δ -72.66 (s, 3F). Anal. Calcd for $C_{27}H_{21}F_3N_2O_5$: C, 63.53; H, 4.15; N, 5.49. Found: C, 63.67; H, 4.41; N, 5.21.



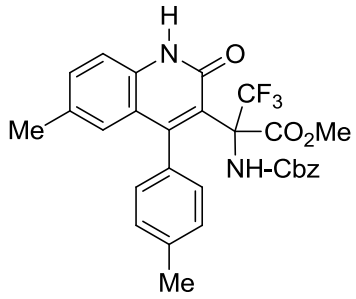
Methyl 2-(benzyloxycarbonylamino)-3,3,3-trifluoro-2-(2-oxo-4-*p*-tolyl-1,2-dihydroquinolin-3-yl)propanoate (3b). Was synthesized according to the general procedure A. Yield 50% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 161-163°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 12.59 (s, 1H), 7.39 - 7.30 (m, 10H), 7.08 (d, *J* = 8.2 Hz, 1H), 7.02 (t, *J* = 7.7 Hz, 1H), 6.66 (d, *J* = 7.7 Hz, 1H), 5.09 (d, *J* = 12.5 Hz, 1H), 5.04 (d, *J* = 12.3 Hz, 1H), 3.56 (s, 3H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 165.0, 163.6, 155.6, 154.1, 139.1, 137.2, 136.2, 132.3, 130.6, 130.4, 130.1, 128.8, 128.7, 128.5, 128.0, 127.9, 124.1 (q, *J* = 288.5 Hz), 123.2, 122.3, 119.9, 115.6, 67.4 (q, *J* = 27.9 Hz), 66.9, 52.9, 21.4. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -72.78 (s, 3F). Anal. Calcd for $C_{28}H_{23}F_3N_2O_5$: C, 64.12; H, 4.42; N, 5.34. Found: C, 64.07; H, 4.47; N, 5.33.



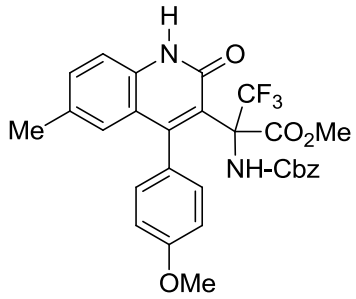
Methyl 2-(benzyloxycarbonylamino)-3,3,3-trifluoro-2-(4-(4-methoxyphenyl)-2-oxo-1,2-dihydroquinolin-3-yl)propanoate (3c). Was synthesized according to the general procedure A. Yield 66% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 222-224°C. ^{1}H NMR (acetone-d_6, 400 MHz): δ 11.52 (s, 1H), 10.39 (br. s, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.40 - 7.33 (m, 5H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.15 - 7.06 (m, 4H), 6.61 (d, *J* = 8.4 Hz, 1H), 5.08 (d, *J* = 12.5 Hz, 1H), 5.03 (d, *J* = 12.5 Hz, 1H), 3.93 (s, 3H), 3.41 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 165.0, 163.7, 159.9, 155.5, 154.1, 137.1, 136.2, 132.3, 131.9, 131.6, 128.7, 128.5, 128.0, 127.9, 125.5, 124.1 (q, *J* = 289.7 Hz), 123.3, 122.6, 120.0, 115.6, 113.6, 113.2, 67.5 (q, *J* = 30.3 Hz), 66.9, 55.4, 53.1. ^{19}F NMR (acetone-d_6, 376 MHz): δ -73.66 (s, 3F). Anal. Calcd for $C_{28}H_{23}F_3N_2O_6$: C, 62.22; H, 4.29; N, 5.18. Found: C, 62.04; H, 4.27; N, 5.04.



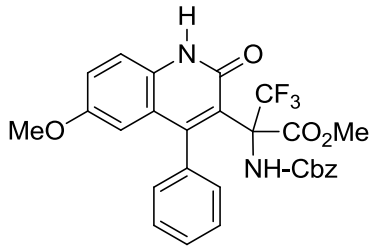
Methyl 2-(((benzyloxy)carbonyl)amino)-3,3,3-trifluoro-2-(6-methyl-2-oxo-4-phenyl-1,2-dihydroquinolin-3-yl)propanoate (3d). Was synthesized according to the general procedure A. Yield 71% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 195–197°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 12.82 (s, 1H), 7.48 (s, 3H), 7.31 - 7.22 (m, 7H), 7.13 (s, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 6.28 (s, 1H), 5.08 (d, *J* = 12.2 Hz, 1H), 5.02 (d, *J* = 12.2 Hz, 1H), 3.44 (s, 3H), 2.13 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$,101 MHz): δ 164.9, 163.5, 155.2, 154.1, 136.2, 135.1, 133.9, 133.5, 132.8, 130.6, 130.4, 128.9, 128.4, 127.9, 127.8, 127.4, 124.1 (q, *J* = 287.7 Hz), 122.0, 118.8, 115.4, 67.5 (q, *J* = 29.0 Hz), 66.9, 52.9, 21.2. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -72.73 (s, 3F). Anal. Calcd for $C_{28}H_{23}F_3N_2O_5$: C, 64.12; H, 4.42; N, 5.34. Found: C, 63.89; H, 4.61; N, 5.33.



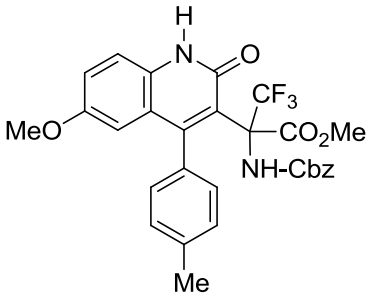
Methyl 2-(benzyloxycarbonylamino)-3,3,3-trifluoro-2-(6-methyl-2-oxo-4-*p*-tolyl-1,2-dihydroquinolin-3-yl)propanoate (3e). Was synthesized according to the general procedure A. Yield 70% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 230-231°C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 12.63 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.40 - 7.29 (m, 8H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.23 (s, 1H), 5.02 (d, *J* = 12.8 Hz, 1H), 4.98 (d, *J* = 12.3 Hz, 1H), 3.32 (s, 3H), 2.41 (s, 3H), 2.12 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 164.9, 163.5, 155.4, 154.1, 138.9, 136.3, 135.3, 133.9, 132.8, 130.6, 130.4, 130.2, 128.8, 128.5, 128.3, 128.1, 127.9, 127.8, 124.2 (q, *J* = 288.0 Hz), 122.2, 119.3, 115.5, 67.5 (q, *J* = 30.0 Hz), 66.9, 52.9, 21.4, 21.2. ^{19}F NMR (DMSO-d_6, 376 MHz): δ -72.12 (s, 3F). Anal. Calcd for $C_{29}H_{25}F_3N_2O_5$: C, 64.68; H 4.68; N 5.20. Found: C, 64.41; H, 4.78; N, 5.24.



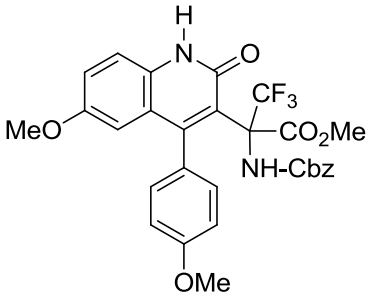
Methyl 2-(benzyloxycarbonylamino)-3,3,3-trifluoro-2-(4-(4-methoxyphenyl)-6-methyl-2-oxo-1,2-dihydroquinolin-3-yl)propanoate (3f). Was synthesized according to the general procedure A. Yield 69% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 268-269°C. ^{1}H NMR (DMSO-*d*$_6$, 500 MHz): δ 12.63 (s, 1H), 10.42 (br. s, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.38 - 7.30 (m, 6H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 1H), 6.26 (s, 1H), 5.03 (d, *J* = 13.2 Hz, 1H), 4.99 (d, *J* = 12.6 Hz, 1H), 3.85 (s, 3H), 3.34 (s, 3H), 2.13 (s, 3H). ^{13}C{^{1}H} NMR (DMSO-*d*$_6$, 126 MHz): δ 164.2, 162.4, 159.7, 154.7, 153.9, 136.9, 135.9, 134.1, 132.3, 132.1, 131.9, 128.9, 128.5, 128.2, 127.8, 126.9, 125.5, 124.5 (q, *J* = 288.6 Hz), 121.8, 119.1, 115.7, 113.6, 67.6 (q, *J* = 29.2 Hz), 66.5, 55.7, 52.9, 21.3. ^{19}F NMR (DMSO-*d*$_6$, 376 MHz): δ -72.26 (s, 3F). Anal. Calcd for $C_{29}H_{25}F_3N_2O_6$: C, 62.81; H, 4.54; N, 5.05. Found: C, 62.90; H, 4.62; N, 5.09.



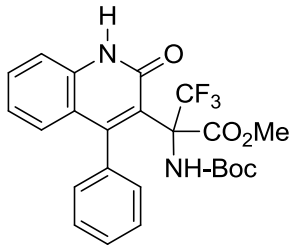
Methyl 2-(benzyloxycarbonylamino)-3,3,3-trifluoro-2-(6-methoxy-2-oxo-4-phenyl-1,2-dihydroquinolin-3-yl)propanoate (3g). Was synthesized according to the general procedure A. Yield 84% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 146-148°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 13.01 (s, 1H), 9.70 (br. s, 1H), 7.52 - 7.51 (m, 3H), 7.39 - 7.31 (m, 7H), 7.18 (s, 1H), 6.93 (d, *J* = 8.8 Hz, 1H), 5.95 (s, 1H), 5.11 (d, *J* = 11.7 Hz, 1H), 5.07 (d, *J* = 13.1 Hz, 1H), 3.51 (s, 3H), 3.48 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 164.9, 163.3, 155.4, 154.8, 154.2, 136.3, 133.8, 131.9, 130.6, 130.4, 129.1, 128.5, 128.2, 128.1, 127.9, 127.5, 124.2 (q, *J* = 280.3 Hz), 122.9, 121.9, 119.4, 116.9, 109.9, 67.7 (q, *J* = 29.5 Hz), 66.9, 55.3, 52.9. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -72.63 (s, 3F). Anal. Calcd for $C_{28}H_{23}F_3N_2O_6$: C, 62.22; H, 4.29; N, 5.18. Found: C, 62.15; H, 4.28; N, 5.13.



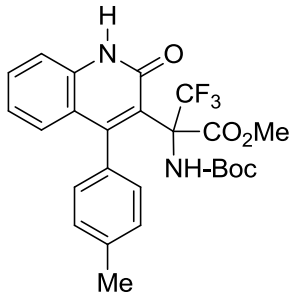
Methyl 2-(benzyloxycarbonylamino)-3,3,3-trifluoro-2-(6-methoxy-2-oxo-4-*p*-tolyl-1,2-dihydroquinolin-3-yl)propanoate (3h). Was synthesized according to the general procedure A. Yield 79% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 169-171°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 12.82 (s, 1H), 7.37 - 7.30 (m, 8H), 7.26 (s, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 6.97 (dd, *J* = 8.9, 2.7 Hz, 1H), 6.05 (d, *J* = 2.7 Hz, 1H), 5.10 (d, *J* = 12.4 Hz, 1H), 5.05 (d, *J* = 12.3 Hz, 1H), 3.55 (s, 3H), 3.54 (s, 3H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 164.9, 163.1, 155.3, 154.9, 154.1, 139.0, 136.3, 132.0, 130.6, 130.4, 130.1, 128.8, 128.5, 128.4, 128.0, 127.8, 124.1 (q, *J* = 288.6 Hz), 123.1, 121.6, 119.9, 116.8, 110.3, 67.5 (q, *J* = 30.5 Hz), 66.9, 55.4, 52.9, 21,4. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -72.80 (s, 3F). Anal. Calcd for $C_{29}H_{25}F_3N_2O_6$: C, 62.81; H, 4.54; N, 5.05. Found: C, 63.04; H, 4.57; N, 4.95.



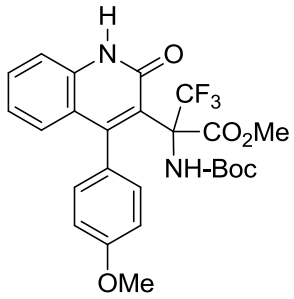
Methyl 2-(benzyloxycarbonylamino)-3,3,3-trifluoro-2-(6-methoxy-4-(4-methoxyphenyl)-2-oxo-1,2-dihydroquinolin-3-yl)propanoate (3i). Was synthesized according to the general procedure A. Yield 83% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 202-205°C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 12.64 (s, 1H), 10.55 (br. s, 1H), 7.42 - 7.29 (m, 7H), 7.14 (d, *J* = 8.8 Hz, 1H), 7.09 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.04 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.00 (dd, *J* = 8.3, 1.6 Hz, 1H), 5.85 (s, 1H), 5.03 (d, *J* = 12.5 Hz, 1H), 4.99 (d, *J* = 12.5 Hz, 1H), 3.84 (s, 3H), 3.50 (s, 3H), 3.32 (s, 3H). ^{13}C{^{1}H} NMR (DMSO-d_6, 126 MHz): δ 164.1, 162.1, 159.8, 154.9, 154.3, 153.9, 136.9, 132.4, 132.1, 132.0, 128.9, 128.5, 128.2, 125.6, 124.5 (q, *J* = 288.6 Hz), 122.7, 121.4, 119.5, 117.1, 113.6, 110.8, 67.5 (q, *J* = 26.5 Hz), 66.5, 55.7, 55.6, 52.9. ^{19}F NMR (DMSO-d_6, 376 MHz): δ -72.26 (s, 3F). Anal. Calcd for $C_{29}H_{25}F_3N_2O_7$: C, 61.05; H, 4.42; N, 4.91. Found: C, 60.94; H, 4.49; N, 4.87.



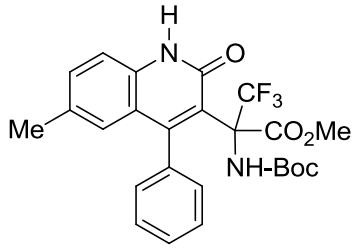
Methyl 2-(*tert*-butoxycarbonylamino)-3,3,3-trifluoro-2-(2-oxo-4-phenyl-1,2-dihydroquinolin-3-yl)propanoate (3j). Was synthesized according to the general procedure A. Yield 77% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 210-212ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 13.23 (s, 1H), 7.60 - 7.52 (m, 5H), 7.42 (s, 1H), 7.21 (s, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 3.54 (s, 3H), 1.43 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 164.9, 163.6, 155.1, 153.3, 137.2, 133.7, 132.1, 130.5, 130.1, 128.9, 128.6, 128.1, 127.6, 124.2 (q, *J* = 289.0 Hz), 123.2, 122.1, 119.9, 115.6, 80.0, 67.2 (q, *J* = 29.7 Hz), 52.7, 28.2. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -73.02 (s, 3F). Anal. Calcd for $C_{24}H_{23}F_3N_2O_5$: C, 60.50; H, 4.87; N, 5.88. Found: C, 60.17; H, 4.81; N, 5.69.



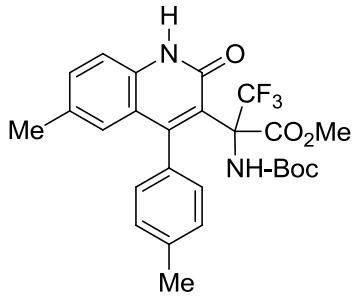
Methyl 2-(*tert*-butoxycarbonylamino)-3,3,3-trifluoro-2-(2-oxo-4-*p*-tolyl-1,2-dihydroquinolin-3-yl)propanoate (3k). Was synthesized according to the general procedure A. Yield 58% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 154-156ºC. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 12.61 (s, 1H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.36 - 7.31 (m, 2H), 7.13 - 7.06 (m, 2H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.44 (d, *J* = 8.4 Hz, 1H), 3.33 (s, 3H), 2.42 (s, 3H), 1.33 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 165.1, 163.5, 155.3, 153.2, 138.9, 137.2, 132.1, 130.7, 130.3, 129.9, 128.8, 128.7, 128.5, 124.3 (q, *J* = 285.4 Hz), 123.1, 122.3, 120.3, 115.6, 79.9, 67.1 (q, *J* = 31.1 Hz), 52.8, 28.2, 21.4. ^{19}F NMR (DMSO-d_6, 376 MHz): δ -72.53 (s, 3F). Anal. Calcd for $C_{25}H_{25}F_3N_2O_5$: C, 61.22; H, 5.14; N, 5.71. Found: C, 59.89; H, 5.21; N, 5.47.



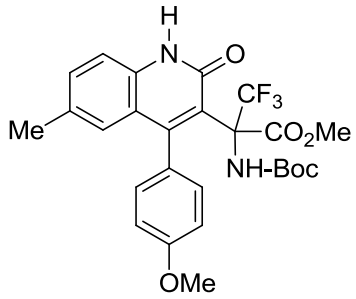
Methyl 2-(*tert*-butoxycarbonylamino)-3,3,3-trifluoro-2-(4-(4-methoxyphenyl)-2-oxo-1,2-dihydroquinolin-3-yl)propanoate (3l). Was synthesized according to the general procedure A. Yield 70% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 221-223ºC. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 13.09 (s, 1H), 7.57 (s, 1H), 7.52 (s, 1H), 7.33 (s, 1H), 7.07 (s, 4H), 6.72 (s, 1H), 3.94 (s, 3H), 3.59 (s, 3H), 1.44 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 165.1, 163.7, 159.9, 155.3, 153.3, 137.2, 132.1, 131.9, 131.5, 128.7, 125.6, 124.3 (q, *J* = 287.7 Hz), 123.2, 122.6, 120.4, 115.6, 113.6, 113.2, 80.0, 67.2 (q, *J* = 28.4 Hz), 55.4, 52.8, 28.2. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -72.53 (s, 3F). Anal. Calcd for $C_{25}H_{25}F_3N_2O_6$: C, 59.29; H, 4.98; N, 5.53. Found: C, 58.99; H, 4.82; N, 5.52.



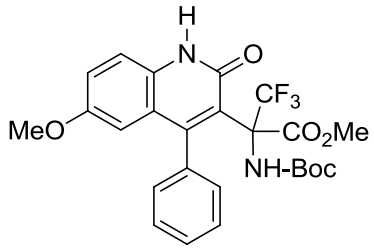
Methyl 2-(*tert*-butoxycarbonylamino)-3,3,3-trifluoro-2-(6-methyl-2-oxo-4-phenyl-1,2-dihydroquinolin-3-yl)propanoate (3m). Was synthesized according to the general procedure A. Yield 78% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 165-167ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 12.81 (s, 1H), 7.55 - 7.53 (m, 3H), 7.40 (s, 1H), 7.38 (s, 2H), 7.19 (s, 1H), 6.37 (s, 1H), 3.52 (s, 3H), 2.22 (s, 3H), 1.43 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 165.1, 163.5, 154.8, 153.3, 135.4, 133.8, 133.7, 132.8, 130.6, 130.2, 128.9, 128.1, 127.9, 127.6, 124.3 (q, *J* = 289.1 Hz), 122.1, 119.6, 115.5, 79.9, 67.2 (q, *J* = 27.7 Hz), 52.7, 28.2, 21.3. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -73.04 (s, 3F). Anal. Calcd for $C_{25}H_{25}F_3N_2O_5$: C, 61.22; H, 5.14; N, 5.71. Found: C, 61.21; H, 5.37; N, 5.77.



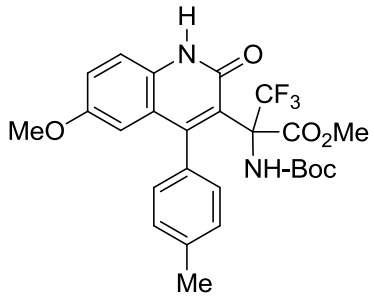
Methyl 2-(*tert*-butoxycarbonylamino)-3,3,3-trifluoro-2-(6-methyl-2-oxo-4-*p*-tolyl-1,2-dihydroquinolin-3-yl)propanoate (3n).Was synthesized according to the general procedure A. Yield 90% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 134-136ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 13.02 (s, 1H), 7.41 - 7.34 (m, 4H), 7.26 (s, 1H), 7.09 (s, 1H), 6.43 (s, 1H), 3.56 (s, 3H), 2.51 (s, 3H), 2.24 (s, 3H), 1.42 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 165.1, 163.3, 155.0, 153.2, 138.8, 135.3, 133.6, 132.7, 130.7, 130.3, 129.9, 128.8, 128.4, 127.9, 124.2 (q, *J* = 290.0 Hz), 122.2, 119.9, 115.4, 79.8, 67.1 (q, *J* = 30.4 Hz), 52.7, 28.2, 21.4, 21.3. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -73.22 (s, 3F). Anal. Calcd for $C_{26}H_{27}F_3N_2O_5$: C, 61.90; H, 5.39; N, 5.55. Found: C, 61.92; H, 5.32; N, 5.38.



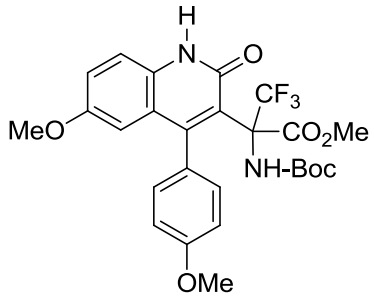
Methyl 2-(*tert*-butoxycarbonylamino)-3,3,3-trifluoro-2-(4-(4-methoxyphenyl)-6-methyl-2-oxo-1,2-dihydroquinolin-3-yl)propanoate (3o). Was synthesized according to the general procedure A. Yield 83% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 162-164ºC. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 13.05 (s, 1H), 7.40 (q, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 7.3 Hz, 1H), 7.09 (s, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.45 (s, 1H), 3.95 (s, 3H), 3.57 (s, 3H), 2.25 (s, 3H), 1.43 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 165.1, 163.5, 159.8, 155.0, 153.4, 135.3, 133.6, 132.8, 131.9, 131.5, 127.9, 125.7, 124.3 (q, *J* = 290.0 Hz), 122.5, 120.1, 115.5, 113.5, 113.1, 79.9, 67.2 (q, *J* = 25.8 Hz), 55.4, 52.8, 28.2, 21.3. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -72.58 (s, 3F, CF_3). Anal. Calcd for $C_{26}H_{27}F_3N_2O_6$: C, 60.00; H, 5.23; N, 5.38. Found: C, 60.13; H, 5.33; N, 5.11.



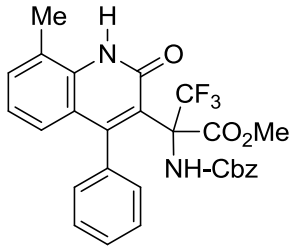
Methyl 2-(*tert*-butoxycarbonylamino)-3,3,3-trifluoro-2-(6-methoxy-2-oxo-4-phenyl-1,2-dihydroquinolin-3-yl)propanoate (3p). Was synthesized according to the general procedure A. Yield 64% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 158-160ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 12.98 (s, 1H), 7.56 - 7.51 (m, 3H), 7.44 - 7.40 (m, 2H), 7.21 (dd, *J* = 9.0, 2.7 Hz, 2H), 5.98 (s, 1H), 3.53 (s, 3H), 3.50 (s, 3H), 1.43 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 165.1, 163.2, 155.3, 154.6, 153.4, 133.9, 132.1, 130.6, 130.2, 129.0, 128.2, 127.6, 124.3 (q, *J* = 289.0 Hz), 122.9, 121.9, 119.9, 116.9, 109.7, 80.1, 67.3 (q, *J* = 29.1 Hz), 55.2, 52.7, 28.2. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -73.07 (s, 3F). Anal. Calcd for $C_{25}H_{25}F_3N_2O_6$: C, 59.29; H, 4.98; N, 5.53. Found: C, 59.54; H, 4.80; N, 5.21.



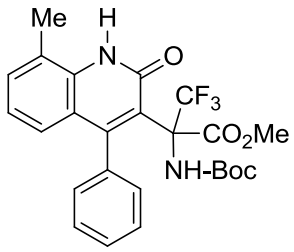
Methyl 2-(*tert*-butoxycarbonylamino)-3,3,3-trifluoro-2-(6-methoxy-2-oxo-4-*p*-tolyl-1,2-dihydroquinolin-3-yl)propanoate (3q). Was synthesized according to the general procedure A. Yield 85% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 149-151ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 12.95 (s, 1H), 7.43 (d, *J* = 8.7 Hz, 1H), 7.34, (d, *J* = 7.4 Hz, 2H), 7.27 (s, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 7.0 Hz, 1H), 6.07 (s, 1H), 3.57 (s, 3H), 3.54 (s, 3H), 2.49 (s, 3H), 1.42 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 165.1, 163.1, 155.2, 154.7, 153.3, 138.9, 132.1, 130.8, 130.3, 129.9, 128.9, 128.4, 124.2 (q, *J* = 289.0 Hz), 123.1, 121.6, 120.4, 116.9, 110.1, 79.9, 67.2 (q, *J* = 31.4 Hz), 55.3, 52.7, 28.2, 21.4.^{19}F NMR ($CDCl_3$, 376 MHz): δ -73.11 (s, 3F). Anal. Calcd for $C_{26}H_{27}F_3N_2O_6$: C, 60.00; H, 5.23; N, 5.38. Found: C, 59.77; H, 5.11; N, 5.04.



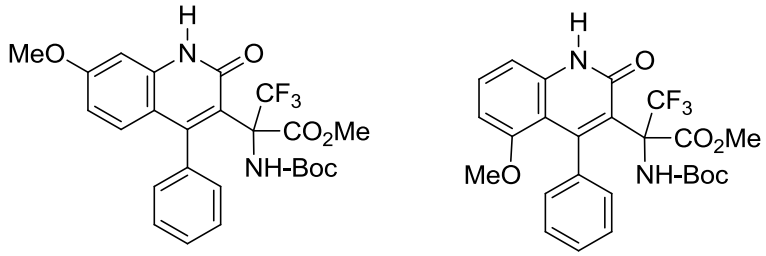
Methyl 2-(*tert*-butoxycarbonylamino)-3,3,3-trifluoro-2-(6-methoxy-4-(4-methoxyphenyl)-2-oxo-1,2-dihydroquinolin-3-yl)propanoate (3r). Was synthesized according to the general procedure A. Yield 84% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 153-156ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 12.90 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 8.7 Hz, 1H), 7.09 - 7.04 (m, 3H), 6.08 (s, 1H), 3.93 (s, 3H), 3.57 (s, 3H), 3.55 (s, 3H), 1.43 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 165.1, 163.2, 159.9, 155.3, 154.7, 153.4, 132.1, 131.9, 131.5, 125.8, 124.3 (q, *J* = 288.8 Hz), 123.4, 121.7, 120.6, 116.9, 113.6, 113.2, 109.9, 79.9, 67.3 (q, *J* = 29.4 Hz), 55.4, 52.8, 28.2. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -73.06 (s, 3F). Anal. Calcd for $C_{26}H_{27}F_3N_2O_7$: C, 58.21; H, 5.07; N, 5.22. Found: C, 58.39; H, 5.31; N, 5.39.



Methyl 2-(((benzyloxy)carbonyl)amino)-3,3,3-trifluoro-2-(8-methyl-2-oxo-4-phenyl-1,2-dihydroquinolin-3-yl)propanoate (3s). Was synthesized according to the general procedure A. Yield 55% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 203–205°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.70 (s, 1H), 9.54 (br. s, 1H), 7.52 - 7.49 (m, 3H), 7.39 - 7.27 (m, 7H), 7.16 (s, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.44 (d, *J* = 8.3 Hz, 1H), 5.09 (d, *J* = 12.3 Hz, 1H), 5.05 (d, *J* = 12.3 Hz, 1H), 3.45 (s, 3H), 2.51 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 164.8, 162.9, 155.6, 154.2, 136.2, 135.7, 133.9, 133.2, 130.7, 130.5, 128.8, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.2, 127.0, 124.1 (q, *J* = 288.8 Hz), 123.4, 122.7, 122.1, 119.2, 67.5 (q, *J* = 29.7 Hz), 66.9, 52.9, 17.1. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -72.61 (s, 3F). Anal. Calcd for $C_{28}H_{23}F_3N_2O_5$: C, 64.12; H, 4.42; N, 5.34. Found: C, 63.89; H, 4.57; N, 5.38.

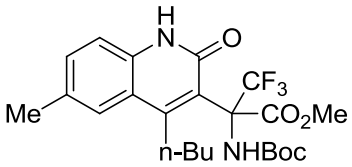


Methyl 2-((*tert*-butoxycarbonyl)amino)-3,3,3-trifluoro-2-(8-methyl-2-oxo-4-phenyl-1,2-dihydroquinolin-3-yl)propanoate (3t). Was synthesized according to the general procedure A. Yield 73% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 213–215°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.74 (s, 1H), 8.78 (br. s, 1H), 7.52-7.51 (m, 3H), 7.41 - 7.39 (m, 2H), 7.17 (s, 1H), 6.96 (t, *J* = 7.8 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 3.48 (s, 3H), 2.64 (s, 3H), 1.40 (s, 9H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 164.8, 162.9, 155.4, 153.3, 135.8, 134.1, 133.1, 130.6, 130.3, 128.8, 127.9, 127.3, 126.9, 124.2 (q, *J* = 289.0 Hz), 123.5, 122.6, 122.1, 119.9, 80.0, 67.2 (q, *J* = 29.3 Hz), 52.7, 28.2, 17.2. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -72.82 (s, 3F). Anal. Calcd for $C_{25}H_{25}F_3N_2O_5$: C, 61.22; H, 5.14; N, 5.71. Found: C, 60.05; H, 5.19; N, 5.63.

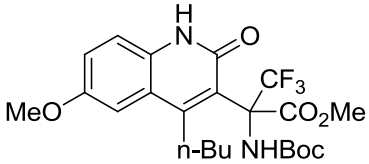


Methyl 2-(*tert*-butoxycarbonylamino)-3,3,3-trifluoro-2-(5-methoxy-2-oxo-4-phenyl-1,2-dihydroquinolin-3-yl)propanoate (3ua) and methyl 2-(*tert*-butoxycarbonylamino)-3,3,3-trifluoro-2-(7-methoxy-2-oxo-4-phenyl-1,2-dihydroquinolin-3-yl)propanoate (3ub). Was synthesized according to the general procedure A. Yield 61% as an off-white solid containing an inseparable 3:2 regioisomers mixture (eluent petroleum ether/ethyl acetate = 3/1). M.p. (mixture of regioisomers) 167-186ºC. **Major isomer** (**3ua**): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 13.71 (s, 1H), 7.46 - 7.39 (m, 5H), 7.19 (s, 1H), 7.14 (d, *J* = 8.2 Hz, 1H), 6.49 (d, *J* = 8.1 Hz, 1H), 4.00 (s, 3H), 3.54 (s, 3H), 1.41 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 165.1, 164.0, 158.4, 154.8, 153.3, 139.6, 137.1, 134.2, 130.4, 130.0, 128.9, 128.1, 127.3, 124.4 (q, *J* = 288.7 Hz), 116.2, 111.6, 105.4, 79.9, 66.9 (q, *J* = 31.4 Hz), 55.9, 52.7, 28.2. ^{19}F NMR ($CDCl_3$, 282 MHz): δ -73.34 (s, 3F). Anal. Calcd for $C_{25}H_{25}F_3N_2O_6$: C, 59.29; H, 4.98; N, 5.53. Found: C, 59.31; H, 4.77; N, 5.23.

Minor isomer (**3ub**): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 13.19 (s, 1H), 7.53 - 7.49 (m, 4H), 7.31 (s, 1H), 7.02 (s, 1H), 6.64 (d, *J* = 9.1 Hz, 1H) 6.52 (d, *J* = 8.1 Hz, 1H), 3.70 (s, 3H), 3.23 (s, 3H), 1.34 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 165.0, 163.2, 162.5, 153.9, 152.7, 139.3, 137.1, 133.1, 129.8, 129.5, 128.9, 128.1, 127.7, 127.3, 124.2 (q, *J* = 289.3 Hz), 114.1, 108.9, 96.8, 79.9, 66.9 (q, *J* = 31.4 Hz), 56.2, 52.7, 28.1. ^{19}F NMR ($CDCl_3$, 282 MHz): δ -73.34 (s, 3F). Anal. Calcd for $C_{25}H_{25}F_3N_2O_6$: C, 59.29; H, 4.98; N, 5.53. Found: C, 59.31; H, 4.77; N, 5.23.

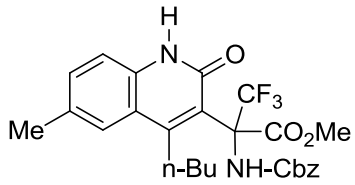


Methyl 2-(*tert*-butoxycarbonylamino)-2-(4-butyl-6-methyl-2-oxo-1,2-dihydroquinolin-3-yl)-3,3,3-trifluoropropanoate (3v). Was synthesized according to the general procedure A. Yield 73% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 211-212 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 12.84 (s, 1H), 10.67 (br. s, 1H), 7.60 (s, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 3.92 (s, 3H), 3.17 (s, 1H), 3.05 (s, 1H), 2.49 (s, 1H), 1.57 (s, 4H), 1.51 (s, 9H), 1.05-1.02 (m, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 167.5, 164.1, 156.6, 154.0, 135.4, 133.3, 132.8, 130.1, 125.6, 124.7 (q, *J* = 288.9 Hz), 119.8, 116.2, 80.1, 67.3 (q, *J* = 28.3 Hz), 53.1, 31.9, 29.7, 28.3, 23.3, 21.6, 13.8. ^{19}F NMR ($CDCl_3$, 282 MHz): δ -74.44 (s, 3F). Anal. Calcd for $C_{23}H_{29}F_3N_2O_5$: C, 58.72; H, 6.21; N, 5.95. Found: C, 58.67; H, 6.23; N, 5.90.

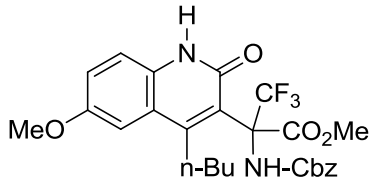


Methyl 2-(tert-butoxycarbonylamino)-2-(4-butyl-6-methoxy-2-oxo-1,2-dihydroquinolin-3-yl)-3,3,3-trifluoropropanoate (3w). Was synthesized according to the general procedure A. Yield 75% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 220-221 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 12.86 (s, 1H), 10.78 (br.s, 1H), 7.40 (d, *J* = 8.9 Hz, 1H), 7.25 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.21 (s, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 3.18 (s, 1H), 3.03 (s, 1H), 1.59 (s, 4H), 1.50 (s, 9H), 1.05-1.03 (s, 3H).

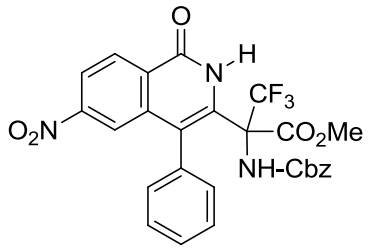
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz): δ 167.5, 163.7, 156.0, 155.5, 154.0, 132.1, 131.2, 124.7 (q, *J* = 288.3 Hz), 121.5, 120.6, 117.6, 107.5, 80.1, 67.3 (q, *J* = 30.1 Hz), 55.6, 53.2, 31.3, 29.9, 28.3, 23.3, 13.8. ^{19}F NMR ($CDCl_3$, 282 MHz): δ -74.44 (s, 3F). Anal. Calcd for $C_{23}H_{29}F_3N_2O_6$: C, 56.78; H, 6.01; N, 5.76. Found: C, 56.75; H, 6.04; N, 5.74.



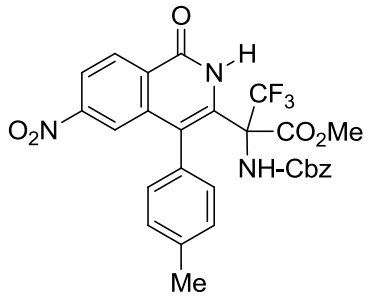
Methyl 2-(((benzyloxy)carbonyl)amino)-2-(4-butyl-6-methyl-2-oxo-1,2-dihydroquinolin-3-yl)-3,3,3-trifluoropropanoate (3x). Was synthesized according to the general procedure A. Yield 68% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 173-175°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 12.93 (s, 1H), 11.39 (br.s, 1H), 7.54 - 7.20 (m, 7H), 6.82 (s, 1H), 5.16 (s, 2H), 3.94 (s, 3H), 3.21-2.95 (m, 2H), 2.4 (s, 3H), 1.56 (s, 4H), 1.03 (s, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$,126 MHz): δ 167.2, 164.3, 156.8, 154.7, 136.3, 135.2, 133.5, 132.9, 128.5, 128.2, 128.1, 125.5, 124.6 (q, *J* = 288.0 Hz), 119.7, 116.2, 67.6 (q, *J* = 30.7 Hz), 67.1, 53.4, 31.8, 29.9, 23.3, 21.5, 13.8. ^{19}F NMR ($CDCl_3$, 282 MHz): δ -74.07 (s, 3F). Anal. Calcd for $C_{26}H_{27}F_3N_2O_5$: C, 61.90; H, 5.39; N, 5.55. Found: C, 61.86; H, 5.38; N, 5.59.



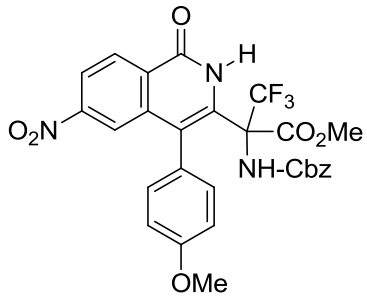
Methyl 2-(((benzyloxy)carbonyl)amino)-2-(4-butyl-6-methoxy-2-oxo-1,2-dihydroquinolin-3-yl)-3,3,3-trifluoropropanoate (3y). Was synthesized according to the general procedure A. Yield 72% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 196-198°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 12.92 (s, 1H), 11.36 (br.s, 1H), 7.38 - 7.34 (m, 5H), 7.25 (s, 1H), 7.16 (s, 1H), 6.81 (d, *J* = 8.8 Hz, 1H), 5.19 (d, *J* = 12.5 Hz, 1H), 5.14 (d, *J* = 12.2 Hz, 1H), 3.93 (s, 3H), 3.84 (s, 3H), 3.12 (s, 1H), 2.99 (s, 1H), 1.58 (s, 4H), 1.03 (s, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$,126 MHz): δ 167.2, 164.3, 156.8, 154.7, 136.3, 135.2, 133.5, 132.9, 128.5, 128.2, 128.1, 125.5, 124.6 (q, *J* = 288.0 Hz), 119.7, 116.2, 67.6 (q, *J* = 30.7 Hz), 67.1, 53.4, 31.8, 29.9, 23.3, 21.5, 13.8. ^{19}F NMR ($CDCl_3$, 282 MHz): δ -73.98 (s, 3F). Anal. Calcd for $C_{26}H_{27}F_3N_2O_6$: C, 60.00; H, 5.23; N, 5.38. Found: C, 60.04; H, 5.21; N, 5.29.



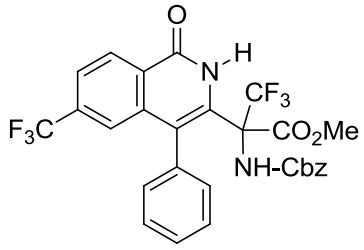
Methyl 2-(((benzyloxy)carbonyl)amino)-3,3,3-trifluoro-2-(6-nitro-1-oxo-4-phenyl-1,2-dihydroisoquinolin-3-yl)propanoate (4a). Was synthesized according to the general procedure B. Yield 51% as a light yellow solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 189–190°C. ^{1}H NMR (acetone-*d*$_6$, 400 MHz): δ 11.38 (br. s, 1H), 8.60 (d, *J* = 8.9 Hz, 1H), 8.40 (d, *J* = 9.0 Hz, 1H), 7.75 (s, 1H), 7.58 - 7.53 (m, 4H), 7.38 - 7.33 (m, 6H), 7.15 (d, *J* = 7.0 Hz, 1H), 5.13 (d, *J* = 12.0 Hz, 1H), 5.08 (d, *J* = 12.1 Hz, 1H), 3.53 (s, 3H). ^{13}C{^{1}H} NMR (acetone-*d*$_6$, 126 MHz): δ 164.4, 159.0, 153.7, 149.7, 140.1, 136.3, 132.8, 131.9, 131.8, 131.7, 128.9, 128.5, 128.4, 128.3, 128.2, 123.7 (q, *J* = 292.9 Hz), 121.6, 121.3, 66.8, 66.7 (q, *J* = 28.1 Hz), 53.1. ^{19}F NMR (acetone-*d*$_6$, 376 MHz) δ -72.26 (s, 3F). Anal. Calcd for $C_{27}H_{20}F_3N_3O_7$: C, 58.38; H, 3.63; N, 7.56; Found: C, 58.59; H, 3.59; N, 7.38.



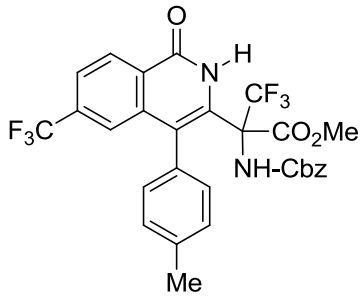
Methyl 2-(benzyloxycarbonylamino)-3,3,3-trifluoro-2-(6-nitro-1-oxo-4-*p*-tolyl-1,2-dihydroisoquinolin-3-yl)propanoate (4b). Was synthesized according to the general procedure B. Yield 50% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 168-170°C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.63 (d, *J* = 8.7 Hz, 1H), 8.27 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.69 (s, 1H), 7.33 (br. s, 4H), 7.29 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.86 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.01 (s, 1H), 5.11 (s, 2H), 3.70 (s, 3H), 2.46 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 163.8, 160.1, 153.4, 150.5, 139.9, 139.8, 135.3, 131.4, 131.1, 130.7, 130.0, 129.6, 129.5, 129.2, 128.7, 128.6, 128.5, 128.4, 127.0, 122.9 (q, *J* = 291.1 Hz), 121.7, 121.4, 119.2, 67.8, 66.2 (q, *J* = 28.8 Hz), 54.9, 21.5. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -69.02 (s, 3F). Anal. Calcd for $C_{28}H_{22}F_3N_3O_7$: C, 59.05; H, 3.89; N, 7.38. Found: C, 59.31; H, 3.92; N, 7.45.



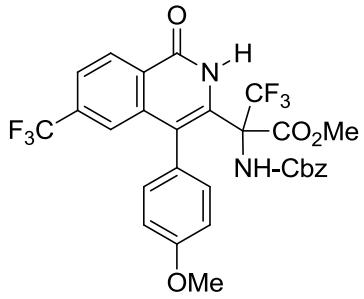
Methyl 2-(benzyloxycarbonylamino)-3,3,3-trifluoro-2-(4-(4-methoxyphenyl)-6-nitro-1-oxo-1,2-dihydroisoquinolin-3-yl)propanoate (4c). Was synthesized according to the general procedure B. Yield 57% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 276-279°C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.63 (s, 1H), 8.29 (s, 1H), 7.72 (s, 1H), 7.33 (s, 5H), 7.00 - 6.87 (m, 4H), 6.07 (s, 1H), 5.12 (s, 2H), 3.90 (s, 3H), 3.70 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 163.7, 160.4, 160.1, 153.4, 150.5, 140.0, 135.3, 132.9, 132.2, 131.5, 129.6, 129.3, 128.7, 128.6, 128.5, 123.2, 122.9 (q, *J* = 290.0 Hz), 121.6, 121.4, 118.9, 114.8, 114.3, 67.8, 66.3 (q, *J* = 29.2 Hz), 55.4, 54.9. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -68.99 (s, 3F). Anal. Calcd for $C_{28}H_{22}F_3N_3O_8$: C, 57.44; H, 3.79; N, 7.18. Found: C, 57.23; H, 3.61; N, 6.98.



Methyl 2-(benzyloxycarbonylamino)-3,3,3-trifluoro-2-(1-oxo-4-phenyl-6-(trifluoromethyl)-1,2-dihydroisoquinolin-3-yl)propanoate (4d). Was synthesized according to the general procedure B. Yield 56% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 256-258°C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.60 (d, *J* = 8.3 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.51 - 7.46 (m, 2H), 7.40 - 7.36 (m, 2H), 7.31 (br. s, 3H), 7.05 - 7.03 (m, 2H), 6.97 (d, *J* = 7.3 Hz, 1H), 6.00 (s, 1H), 5.11 (s, 2H), 3.68 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 163.9, 160.6, 153.4, 138.9, 135.3, 134.3 (q, *J* = 32.6 Hz), 132.0, 131.6, 130.9, 130.2, 129.4, 129.1, 128.7, 128.6, 128.6, 128.5, 128.5, 127.8, 123.9 (q, *J* = 3.2 Hz), 123.4 (q, *J* = 273.1 Hz), 123.3 (q, *J* = 4.0 Hz), 122.9 (q, *J* = 290.7 Hz), 119.1, 67.8, 66.3 (q, *J* = 28.8 Hz), 54.8. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -61.96 (s, 3F), -71.26 (s, 3F). Anal. Calcd for $C_{28}H_{20}F_6N_2O_5$: C, 58.14; H, 3.48; N, 4.84. Found: C, 58.34; H, 3.37; N, 4.71.

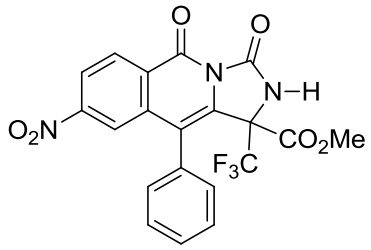


Methyl 2-(benzyloxycarbonylamino)-3,3,3-trifluoro-2-(1-oxo-4-*p*-tolyl-6-(trifluoromethyl)-1,2-dihydroisoquinolin-3-yl)propanoate (4e). Was synthesized according to the general procedure B. Yield 37% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 176-178°C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.59 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.39 - 7.26 (m, 6H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.09 (s, 1H), 6.92 (d, *J* = 7.2 Hz, 1H), 6.85 (d, *J* = 6.2 Hz, 1H), 6.04 (s, 1H), 5.11 (s, 2H), 3.68 (s, 3H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 163.9, 160.8, 153.4, 139.5, 139.2, 135.3, 134.3 (q, *J* = 32.1 Hz), 131.5, 130.9, 130.2, 129.8, 129.4, 128.8, 128.6, 128.5, 128.5, 128.4, 127.8, 123.8 (m), 123.5 (q, *J* = 273.6 Hz), 123.4 (q, *J* = 3.5 Hz), 123.0 (q, *J* = 291.3 Hz), 119.3, 67.7, 66.3 (q, *J* = 28.6 Hz), 54.8, 21.4. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -63.10 (s, 3F), -69.04 (s, 3F). Anal. Calcd for $C_{29}H_{22}F_6N_2O_5$: C, 58.79; H, 3.74; N, 4.73. Found: C, 58.49; H, 3.64; N, 4.79.

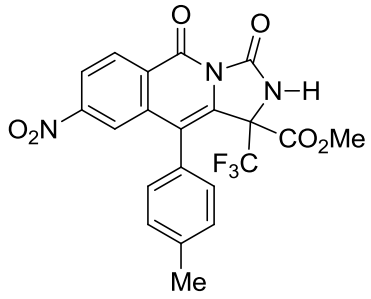


Methyl 2-(benzyloxycarbonylamino)-3,3,3-trifluoro-2-(4-(4-methoxyphenyl)-1-oxo-6-(trifluoromethyl)-1,2-dihydroisoquinolin-3-yl)propanoate (4f). Was synthesized according to the general procedure B. Yield 40% as a white solid (eluent petroleum ether/ethyl acetate = 3/1). M.p. 125-128°C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.58 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.39 - 7.28 (m, 4H), 7.11 (s, 1H), 6.97 (d, *J* = 8.5 Hz, 2H), 6.86 (s, 2H), 6.12 (s, 1H), 5.12 (s, 2H), 3.88 (s, 3H), 3.68 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 163.8, 160.6, 160.2, 153.4, 139.3, 135.3, 134.3 (q, *J* = 32.6 Hz), 133.0, 132.3, 130.6, 128.6, 128.5, 128.5, 128.4, 127.8, 123.8 - 123.8 (m), 123.6, 123.5 (q, *J* = 273.3 Hz), 123.4 - 123.3 (m), 123.0 (q, *J* = 290.4 Hz), 119.0, 114.6, 114.0, 67.7, 66.3 (q, *J* = 28.6 Hz), 55.3, 54.8.

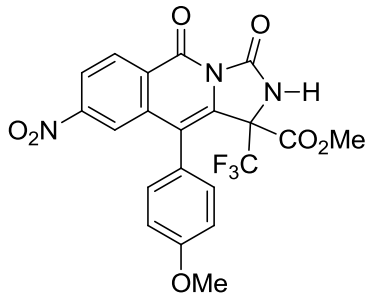
^{19}F NMR ($CDCl_3$, 376 MHz): δ -63.10 (s, 3F), -69.00 (s, 3F). Anal. Calcd for $C_{29}H_{22}F_6N_2O_6$: C, 57.24; H, 3.64; N, 4.60. Found: C, 57.13; H, 3.51; N, 4.49.



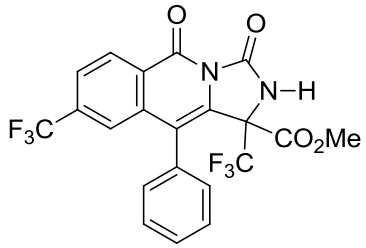
Methyl 8-nitro-3,5-dioxo-10-phenyl-1-(trifluoromethyl)-1,2,3,5-tetrahydroimidazo[1,5-b]isoquinoline-1-carboxylate (5a). Was synthesized according to the general procedure C. Yield 30% as a white solid (eluent petroleum ether/ethyl acetate = 2/1). M.p. 230–232°C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 10.67 (s, 1H), 8.61 (d, J = 8.6 Hz, 1H), 8.40 (d, J = 9.6 Hz, 1H), 7.59 (s, 4H), 7.40 (s, 1H), 7.11 (s, 1H), 3.78 (s, 3H).^{13}C{^{1}H} NMR (DMSO-d_6, 126 MHz): δ 163.8, 157.2, 151.6, 151.0, 138.4, 132.3, 131.0, 130.6, 130.5, 130.1, 130.0, 129.7, 129.5, 129.4, 123.2, 122.3 (q, J = 285.4 Hz), 121.4, 118.0, 65.2 (q, J = 30.5 Hz), 54.8. ^{19}F NMR (DMSO-d_6, 376 MHz): δ -72.30 (s, 3F). Anal. Calcd for $C_{20}H_{12}F_3N_3O_6$: C, 53.70; H, 2.70; N, 9.39; Found: C, 53.81; H, 3.03; N, 9.33.



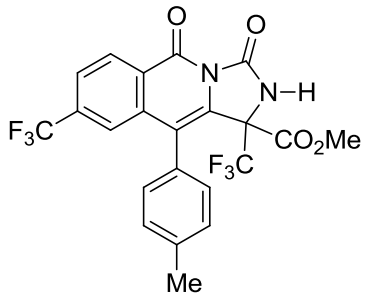
Methyl 8-nitro-3,5-dioxo-10-*p*-tolyl-1-(trifluoromethyl)-1,2,3,5-tetrahydroimidazo[1,5-b]isoquinoline-1-carboxylate (5b). Was synthesized according to the general procedure C. Yield 36% as a white solid (eluent petroleum ether/ethyl acetate = 2/1). M.p. 267-270°C. ^{1}H NMR (acetone-d_6, 400 MHz): δ 9.22 (s, 1H), 8.69 (d, J = 8.9 Hz, 1H), 8.44 (dd, J = 8.6, 2.3 Hz, 1H), 7.79 (s, 1H), 7.48 - 7.42 (m, 2H), 7.37 (d, J = 7.9 Hz, 1H), 7.12 (d, J = 7.7 Hz, 1H), 3.84 (s, 3H), 2.48 (s, 3H). ^{13}C{^{1}H} NMR (DMSO-d_6, 126 MHz): δ 163.8, 157.2, 155.3, 151.7, 151.0, 139.5, 138.5, 132.1, 130.9, 130.6, 130.0, 129.9, 129.8, 127.5, 123.1, 122.4 (q, J = 288.7 Hz), 121.4, 117.9, 65.2 (q, J = 31.4 Hz), 54.7, 21.4. ^{19}F NMR (acetone-d_6, 376 MHz): δ -73.53 (s, 3F). Anal. Calcd for $C_{21}H_{14}F_3N_3O_6$: C, 54.67; H, 3.06; N, 9.11. Found: C, 54.29; H, 2.96; N, 8.91.



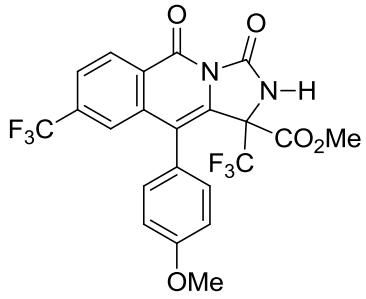
Methyl 10-(4-methoxyphenyl)-8-nitro-3,5-dioxo-1-(trifluoromethyl)-1,2,3,5-tetrahydroimidazo[1,5-b]isoquinoline-1-carboxylate (5c). Was synthesized according to the general procedure C. Yield 41% as a white solid (eluent petroleum ether/ethyl acetate = 2/1). M.p. 289-291°C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 10.67 (s, 1H), 8.60 (d, J = 8.8 Hz, 1H), 8.41 (d, J = 9.0 Hz, 1H), 7.64 (s, 1H), 7.32 (s, 1H), 7.17 - 7.11 (m, 2H), 7.01 (d, J = 7.9 Hz, 1H), 3.87 (s, 3H), 3.79 (s, 3H). ^{13}C{^{1}H} NMR (DMSO-d_6, 126 MHz): δ 163.8, 160.3, 157.2, 151.7, 151.1, 138.8, 133.7, 131.4, 130.9, 130.6, 130.1, 123.1, 122.4 (q, J = 286.5 Hz), 122.2, 121.4, 117.8, 115.1, 114.6, 65.2 (q, J = 32.3 Hz), 55.7, 54.8. ^{19}F NMR (DMSO-d_6, 376 MHz): δ -72.35 (s, 3F). Anal. Calcd for $C_{21}H_{14}F_3N_3O_7$: C, 52.84; H, 2.96; N, 8.80. Found: C, 52.74; H, 2.71; N, 8.53.



Methyl 3,5-dioxo-10-phenyl-1,8-bis(trifluoromethyl)-1,2,3,5-tetrahydroimidazo[1,5-b]isoquinoline-1-carboxylate (5d). Was synthesized according to the general procedure C. Yield 40% as a white solid (eluent petroleum ether/ethyl acetate = 2/1). M.p. 264-266°C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 10.63 (s, 1H), 8.59 (d, J = 8.3 Hz, 1H), 8.02 (dd, J = 8.4, 1.7 Hz, 1H), 7.59 - 7.55 (m, 3H), 7.39 (d, J = 6.4 Hz, 1H), 7.11 - 7.09 (m, 1H), 7.07 (s, 1H), 3.76 (s, 3H). ^{13}C{^{1}H} NMR (DMSO-d_6, 126 MHz): δ 163.8, 157.4, 151.8, 137.9, 133.9 (q, J = 32.1 Hz), 132.3, 130.6, 130.0, 129.9, 129.9, 129.5, 129.4, 129.3, 129.2, 125.5 - 125.4 (m), 123.7 (q, J = 273.0 Hz), 123.0 (q, J = 4.2 Hz), 122.4 (q, J = 285.8 Hz), 117.9, 65.2 (q, J = 31.0 Hz), 54.7. ^{19}F NMR (DMSO-d_6, 376 MHz): δ -62.10 (s, 3F), -72.37 (s, 3F). Anal. Calcd for $C_{21}H_{12}F_6N_2O_4$: C, 53.63; H, 2.57; N, 5.96. Found: C, 53.31; H, 2.44; N, 5.85.

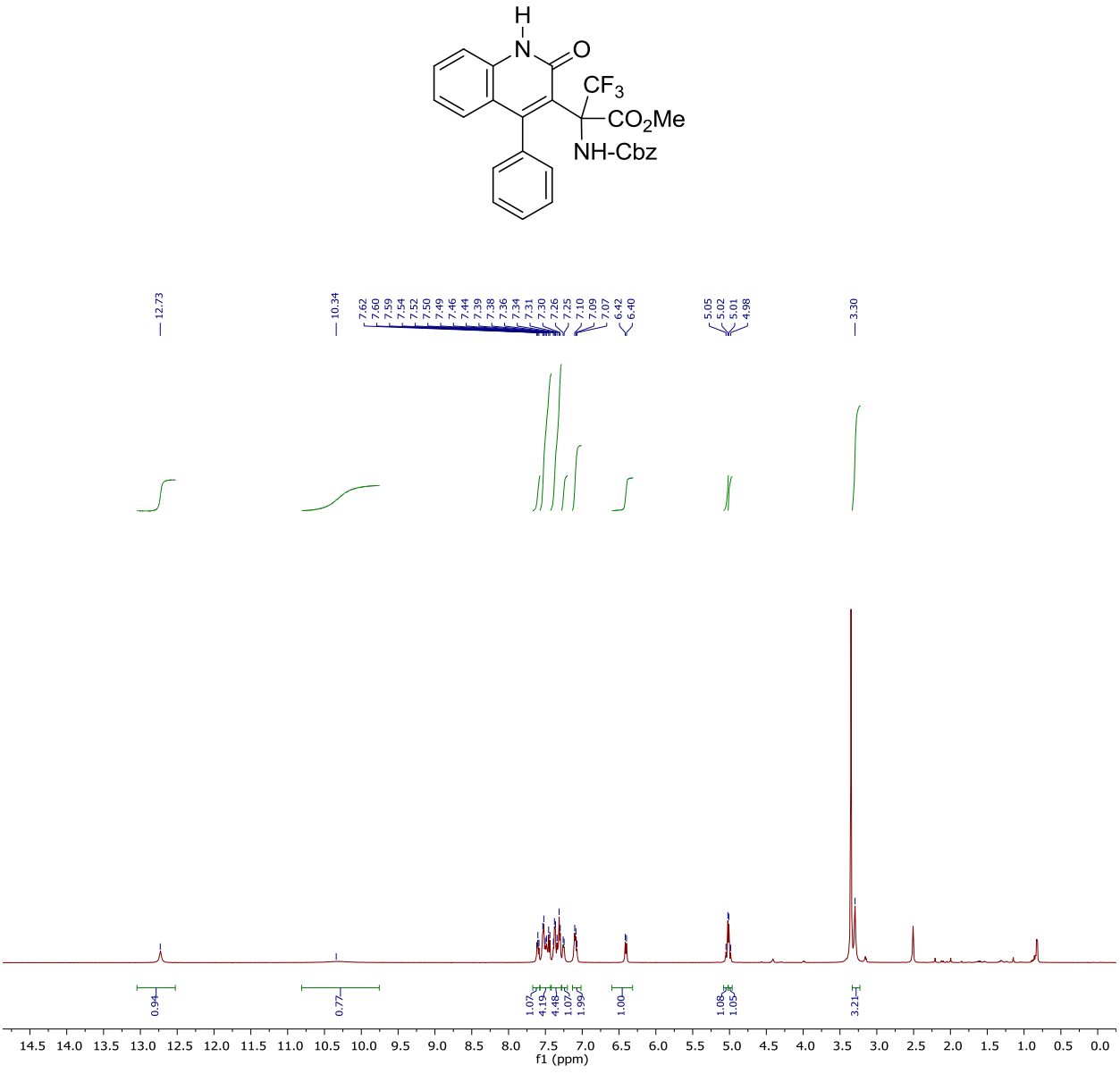


Methyl 3,5-dioxo-10-*p*-tolyl-1,8-bis(trifluoromethyl)-1,2,3,5-tetrahydroimidazo[1,5-b]isoquinoline-1-carboxylate (5e). Was synthesized according to the general procedure C. Yield 41% as a white solid (eluent petroleum ether/ethyl acetate = 2/1). M.p. 244-246°C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 10.62 (s, 1H), 8.58 (d, *J* = 8.3 Hz, 1H), 8.01 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.39 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.35 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.26 (d, *J* = 7.8 Hz, 1H), 7.10 (s, 1H), 6.97 (dd, *J* = 7.7, 1.9 Hz, 1H), 3.76 (s, 3H), 2.42 (s, 3H). ^{13}C{^{1}H} NMR (DMSO-d_6, 126 MHz): δ 163.8, 157.4, 151.8, 139.4, 138.0, 133.9 (q, *J* = 32.2 Hz), 132.2, 130.0, 129.9, 129.9, 129.8, 129.4, 128.8, 127.6, 125.4 - 125.3 (m), 124.6 (q, *J* = 278.3 Hz), 123.8 (q, *J* = 273.2 Hz), 123.1 (q, *J* = 3.9 Hz), 117.9, 65.2 (q, *J* = 31.2 Hz), 54.7, 21.4. ^{19}F NMR (DMSO-d_6, 376 MHz): δ -63.22 (s, 3F), -72.73 (s, 3F). Anal. Calcd for $C_{22}H_{14}F_6N_2O_4$: C, 54.55; H, 2.91; N, 5.78. Found: C, 54.31; H, 2.78; N, 5.59.

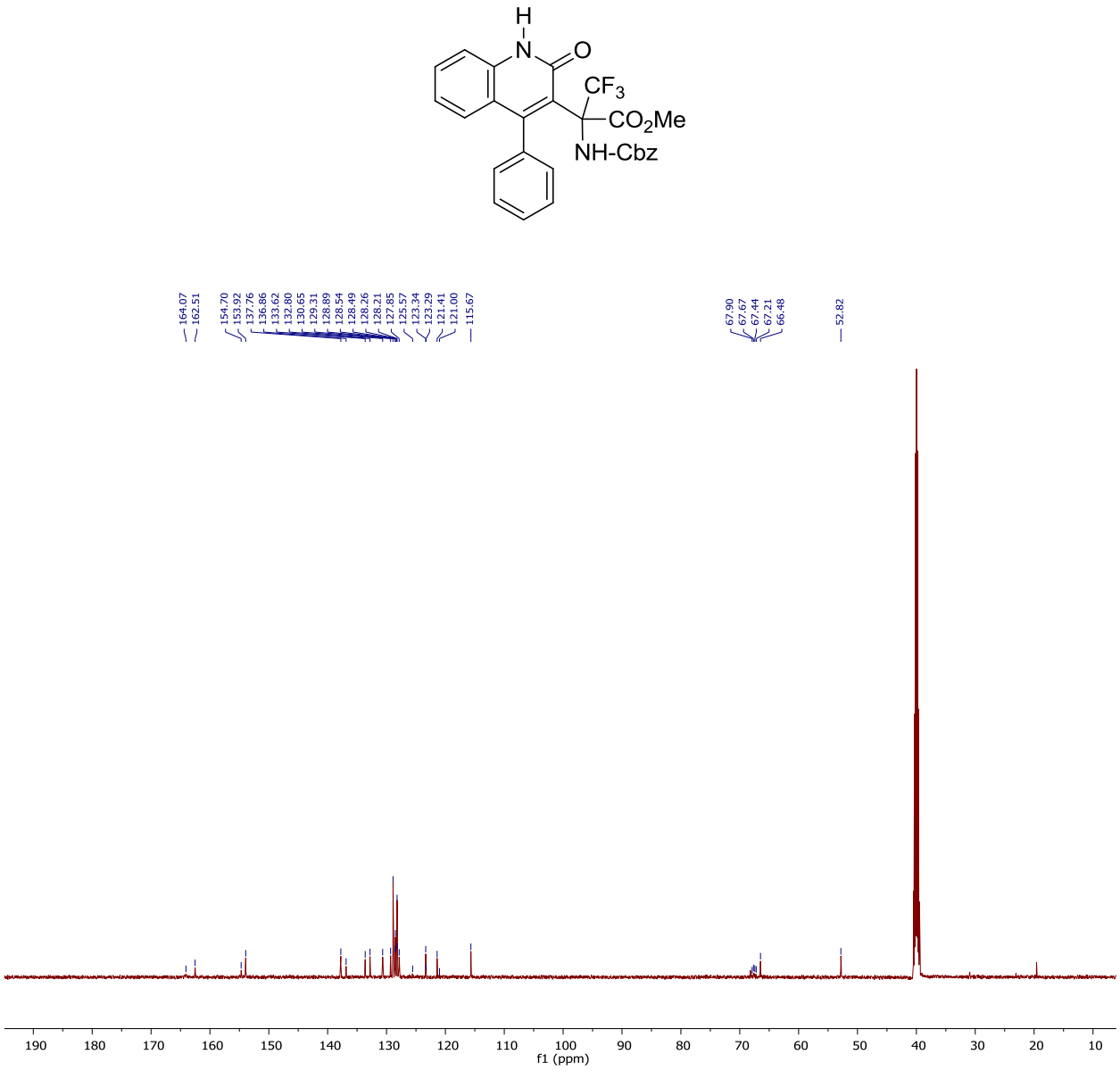


Methyl 10-(4-methoxyphenyl)-3,5-dioxo-1,8-bis(trifluoromethyl)-1,2,3,5-tetrahydroimidazo[1,5-b]isoquinoline-1-carboxylate (5f). Was synthesized according to the general procedure C. Yield 25% as a white solid (eluent petroleum ether/ethyl acetate = 2/1). M.p. 243-245°C. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 10.66 (s, 1H), 8.62 (d, *J* = 8.2 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.19 - 7.11 (m, 3H), 7.04 (d, *J* = 8.1 Hz, 1H), 3.89 (s, 3H), 3.81 (s, 3H). ^{13}C{^{1}H} NMR (DMSO-d_6, 126 MHz): δ 163.8, 160.2, 157.5, 151.8, 138.3, 133.9 (q, *J* = 32.2 Hz), 133.6, 131.3, 129.9, 129.8, 129.6, 128.8, 125.4 - 125.3 (m), 123.8 (q, *J* = 273.1 Hz), 123.1 - 123.0 (m), 122.5 (q, *J* = 285.9 Hz), 117.8, 114.9, 114.5, 65.2 (q, *J* = 20.9 Hz), 55.7, 54.7. ^{19}F NMR (DMSO-d_6, 376 MHz): δ -61.99 (s, 3F), -72.39 (s, 3F). Anal. Calcd for $C_{22}H_{14}F_6N_2O_5$: C, 52.81; H, 2.82; N, 5.60. Found: C, 53.01; H, 2.75; N, 5.43.

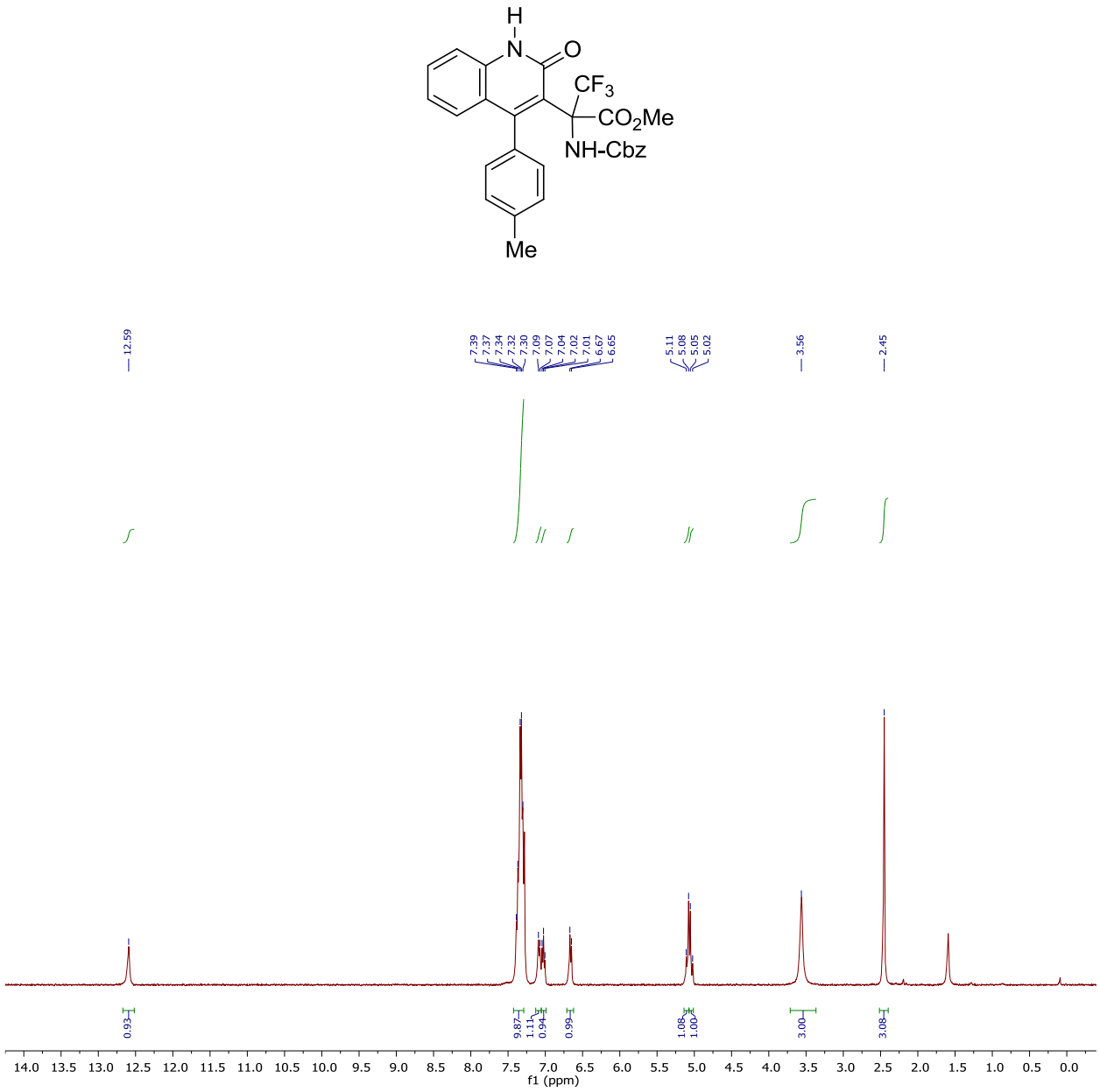
^{1}H and ^{13}C NMR Spectra of Compounds



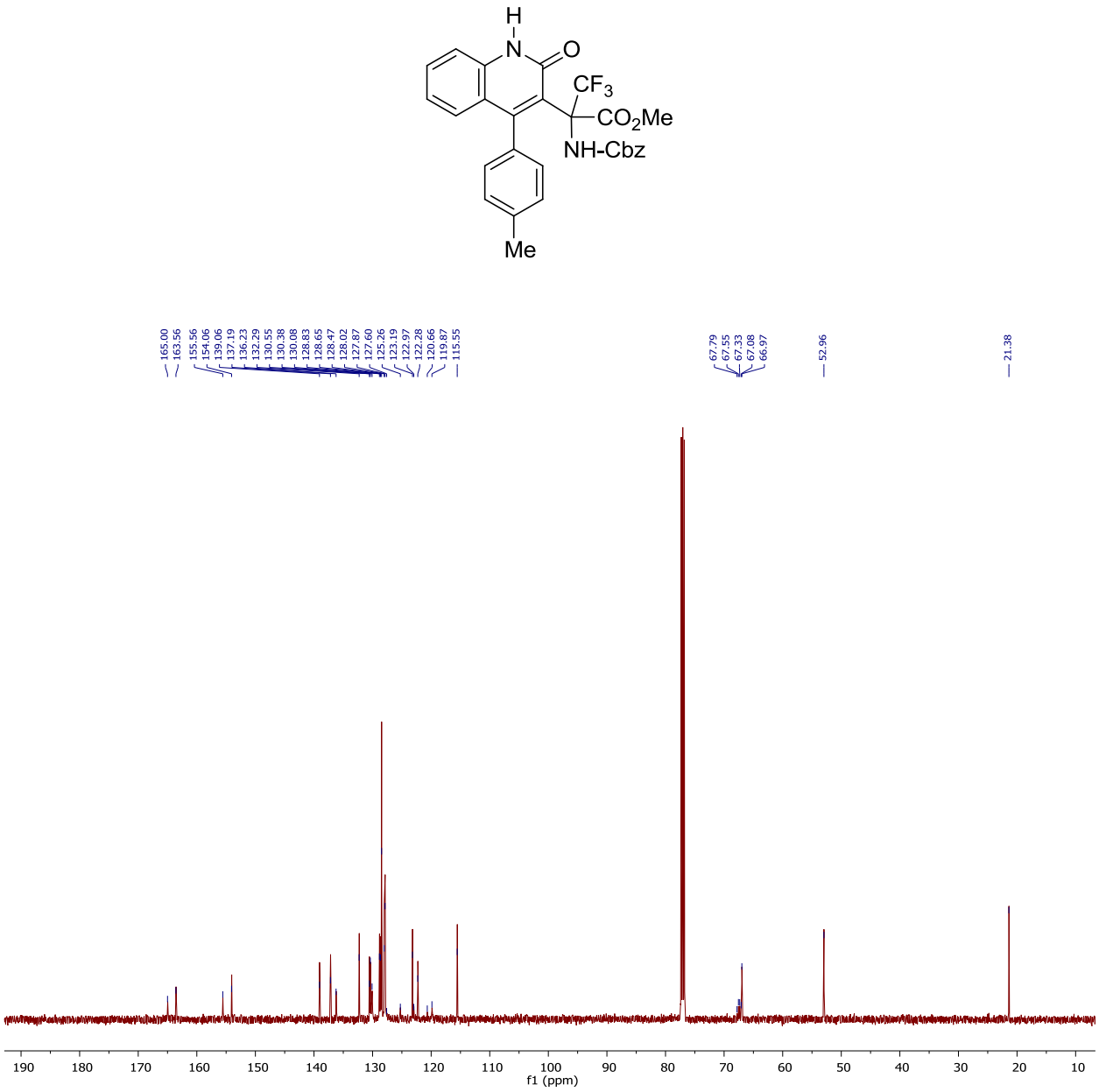
^{1}H NMR spectrum of compound **3a** in DMSO-d_6



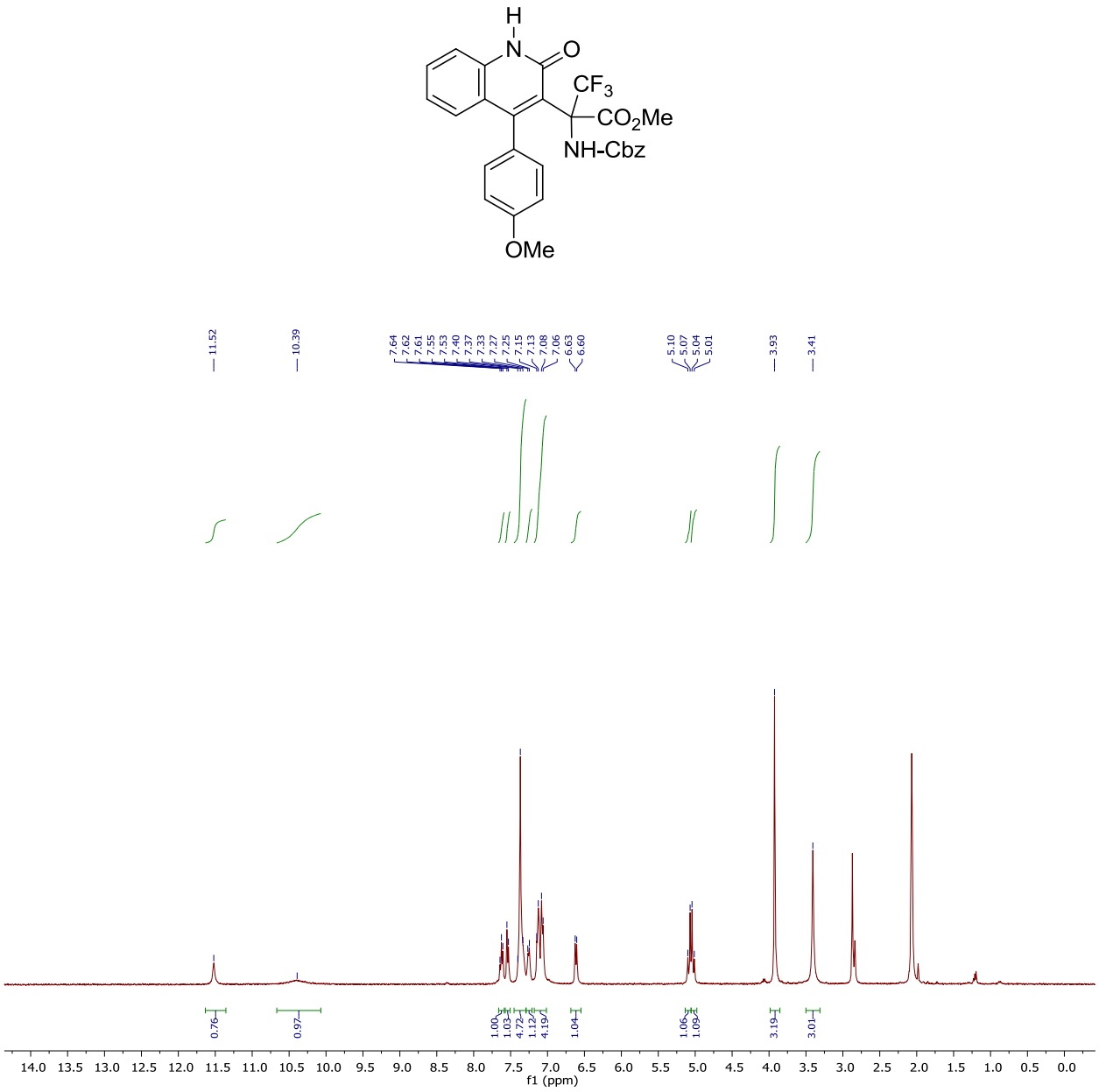
^{13}C NMR spectrum of compound **3a** in DMSO-d_6



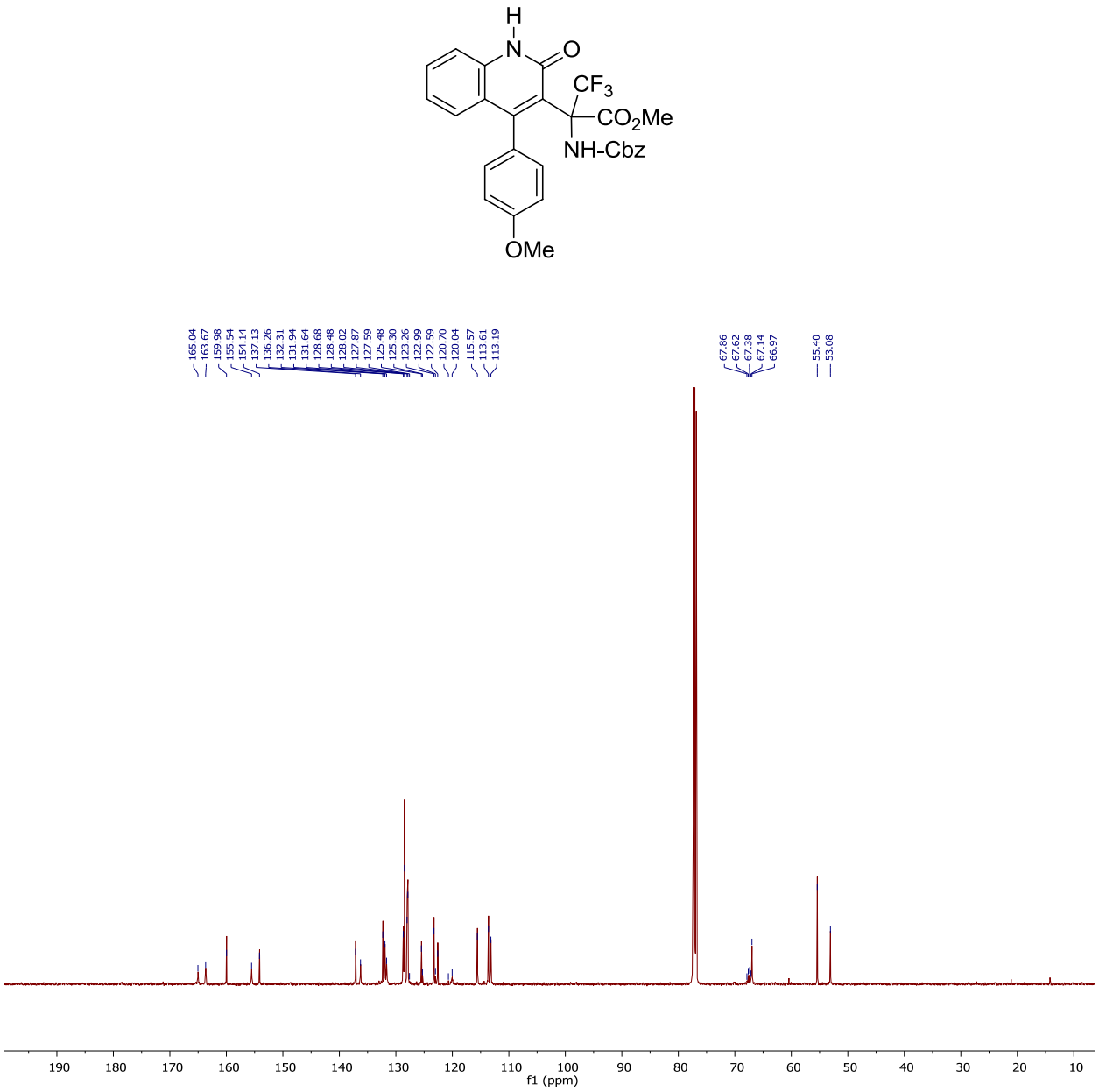
^{1}H NMR spectrum of compound **3b** in $CDCl_3$



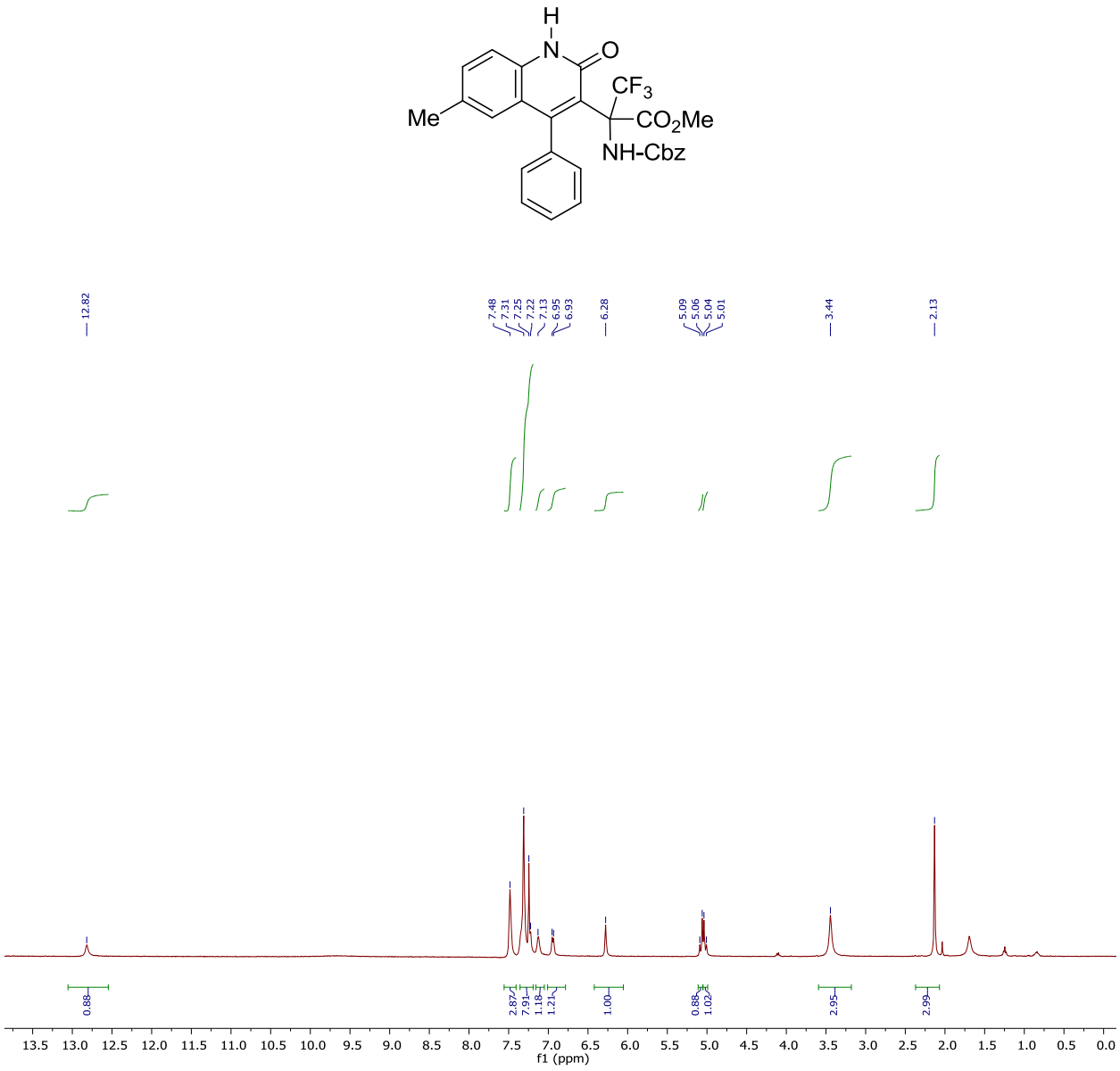
^{13}C NMR spectrum of compound **3b** in $CDCl_3$



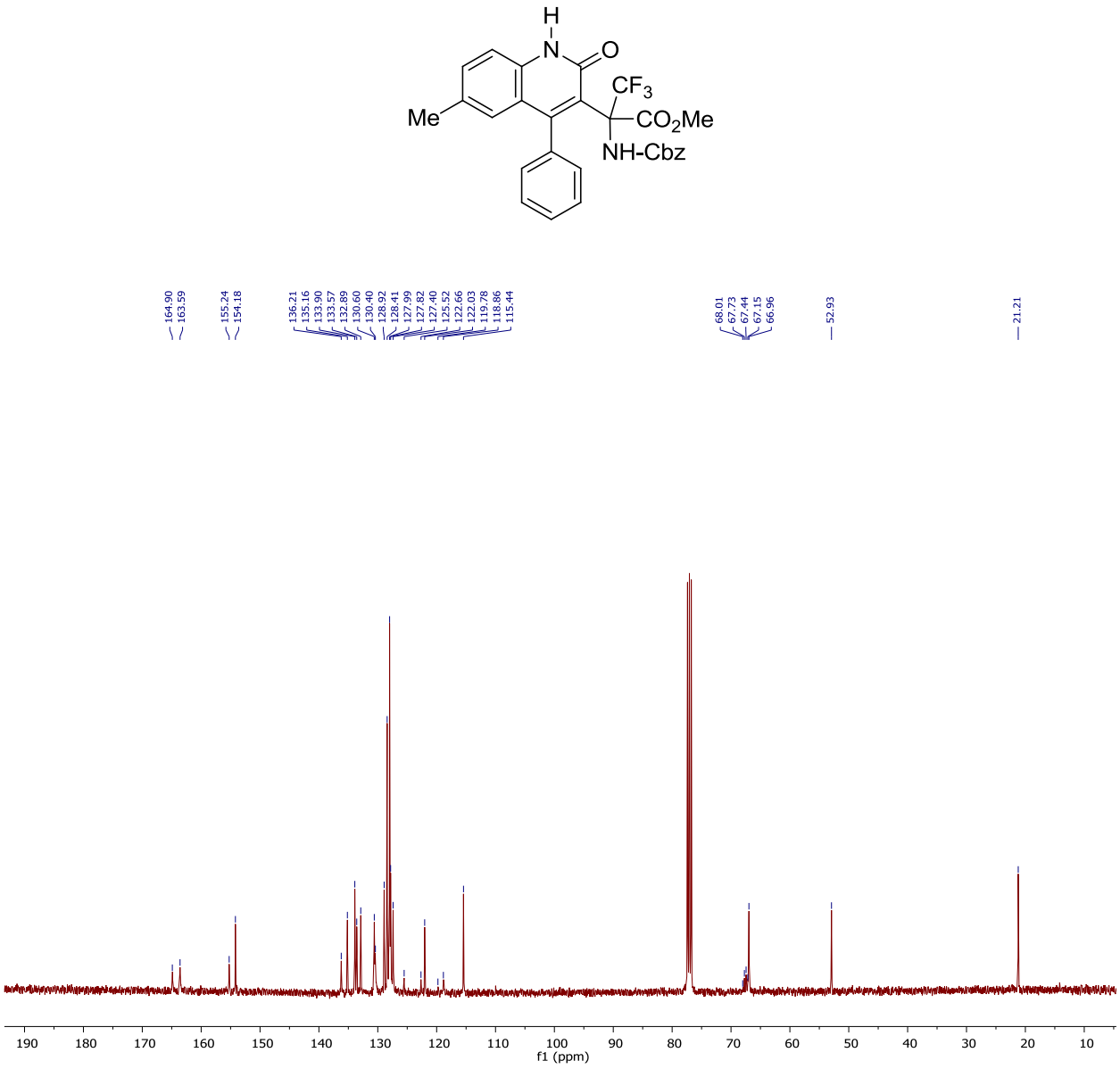
^{1}H NMR spectrum of compound **3c** in acetone-d_6



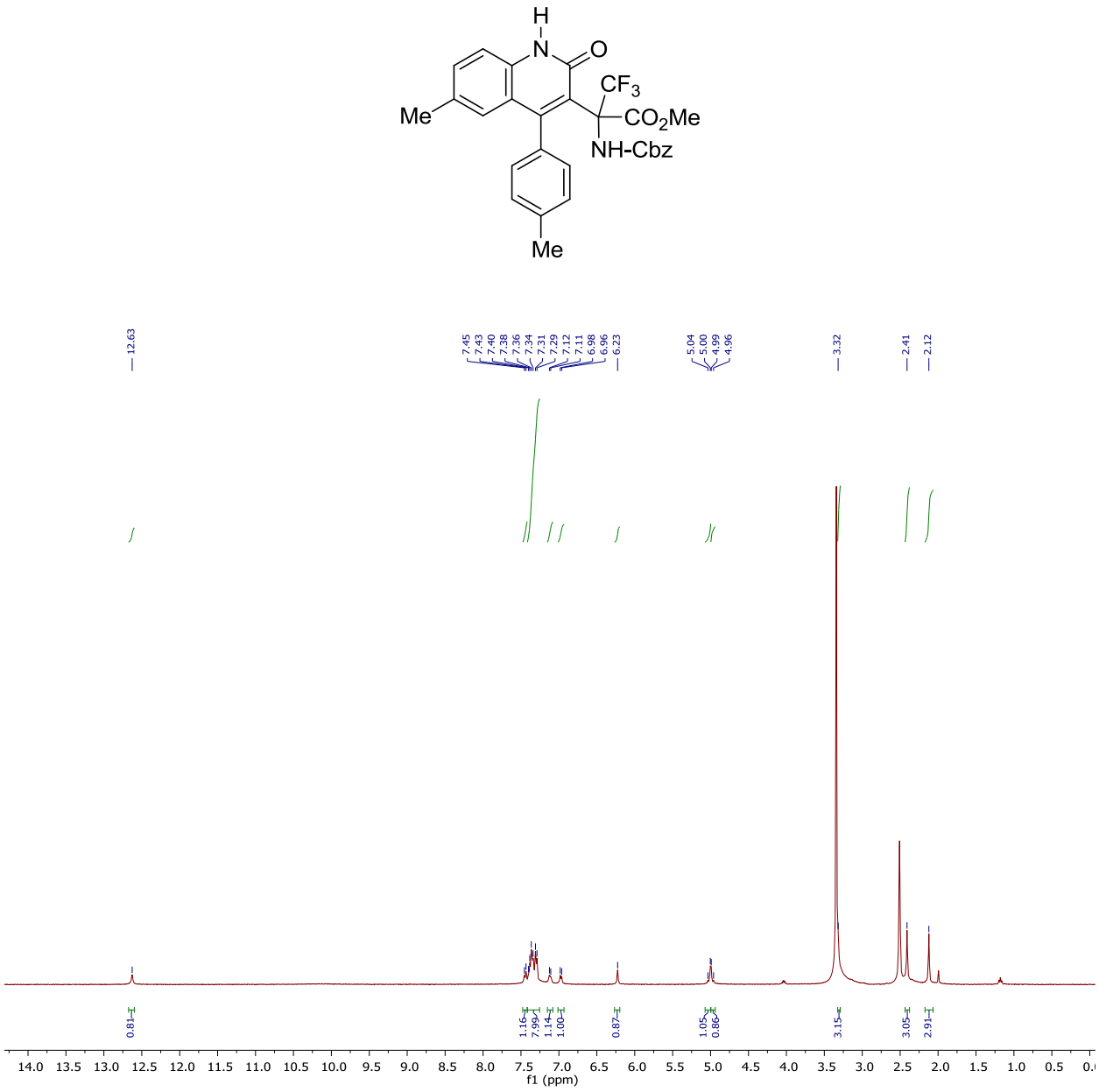
^{13}C NMR spectrum of compound **3c** in $CDCl_3$



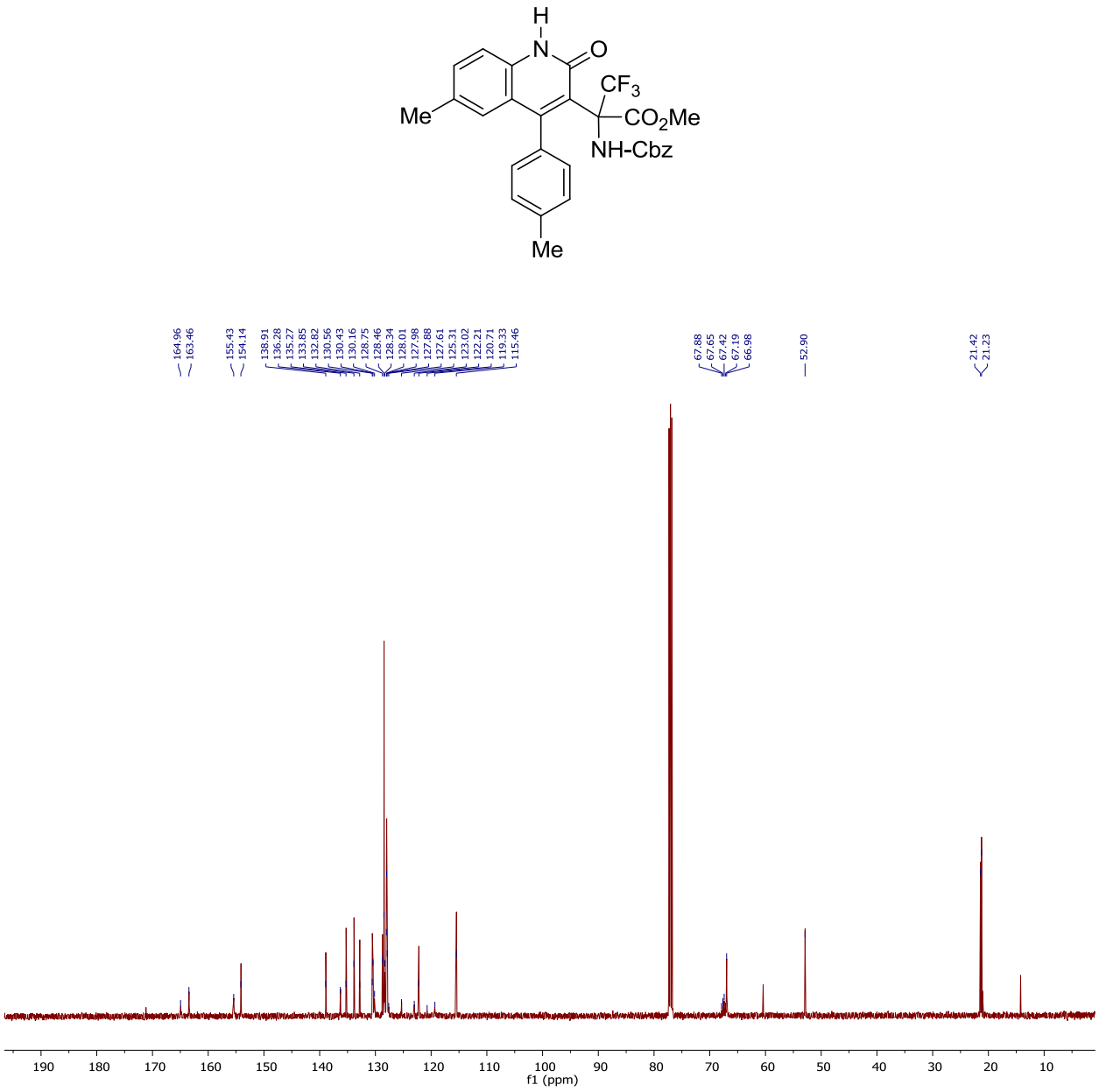
^{1}H NMR spectrum of compound **3d** in $CDCl_3$



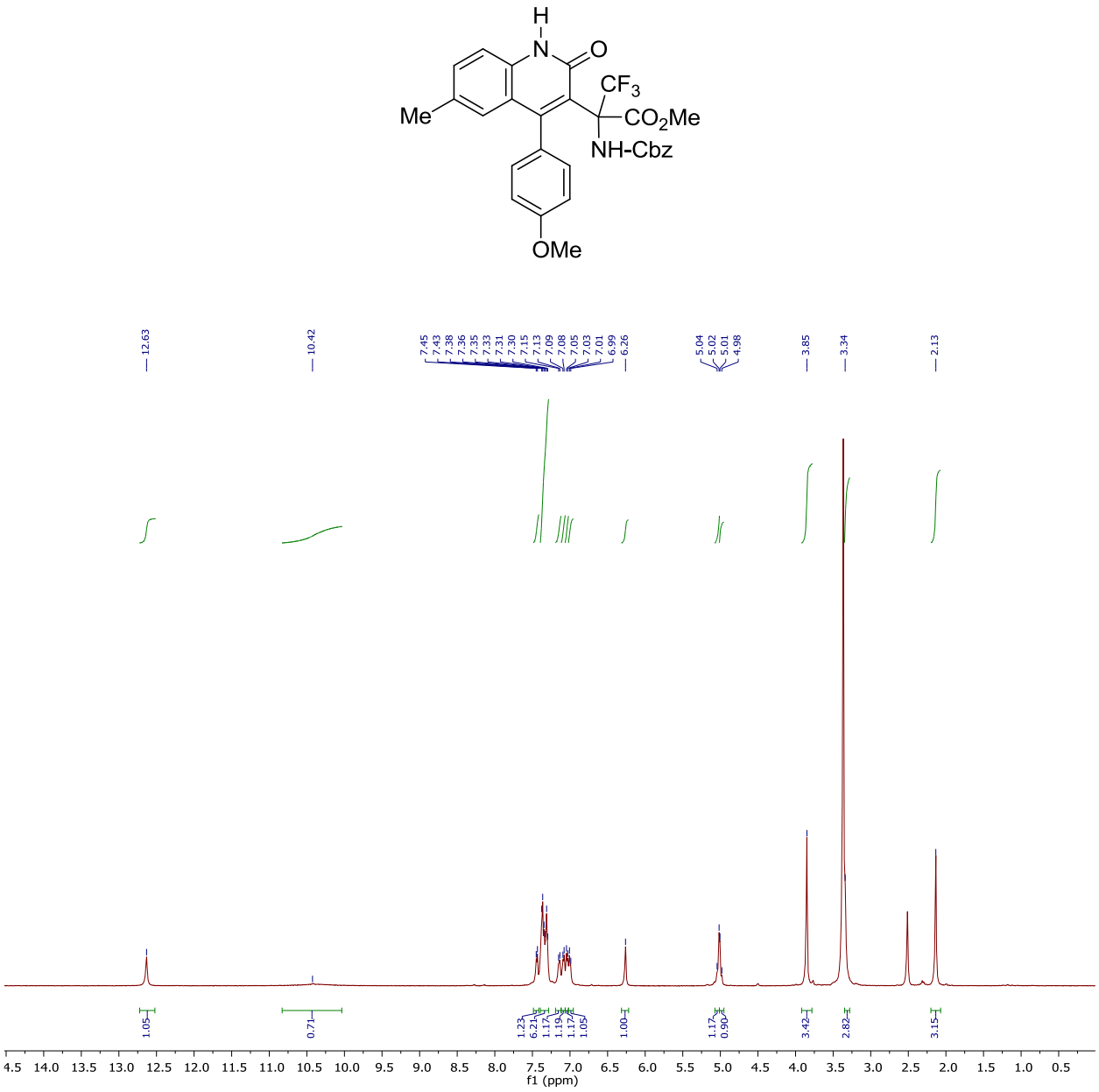
^{13}C NMR spectrum of compound **3d** in $CDCl_3$



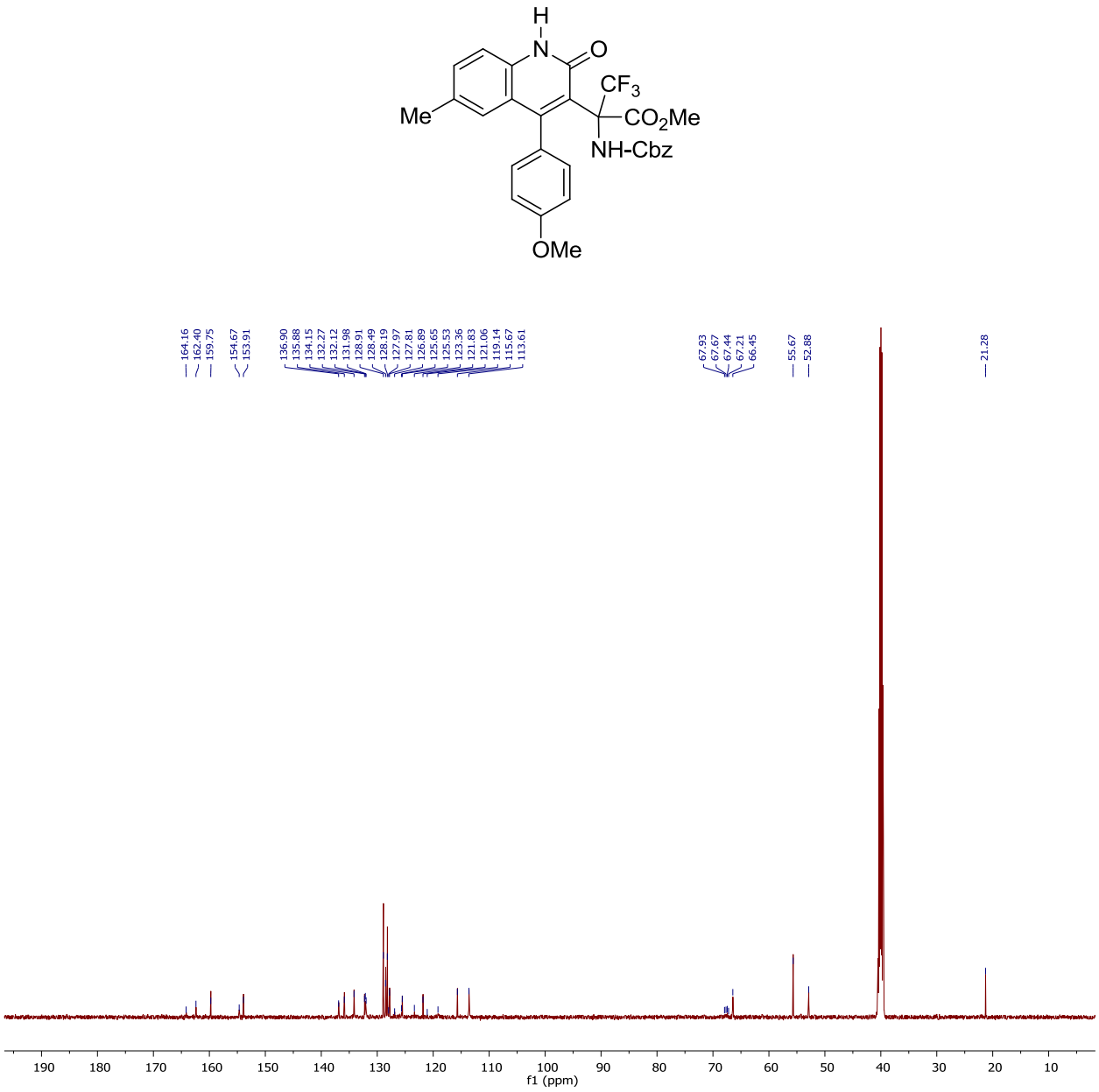
^{1}H NMR spectrum of compound **3e** in DMSO-d_6



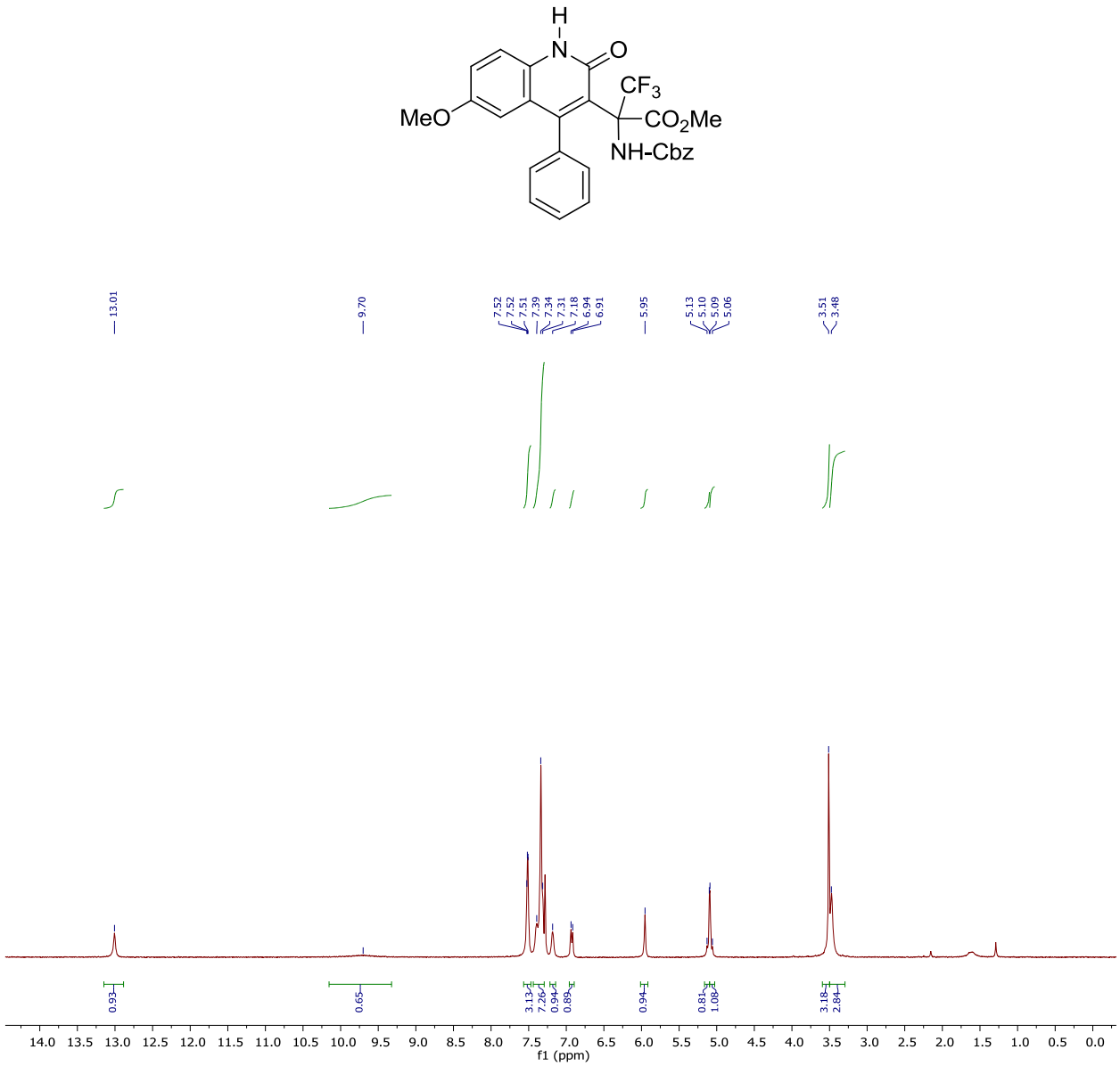
^{13}C NMR spectrum of compound **3e** in $CDCl_3$



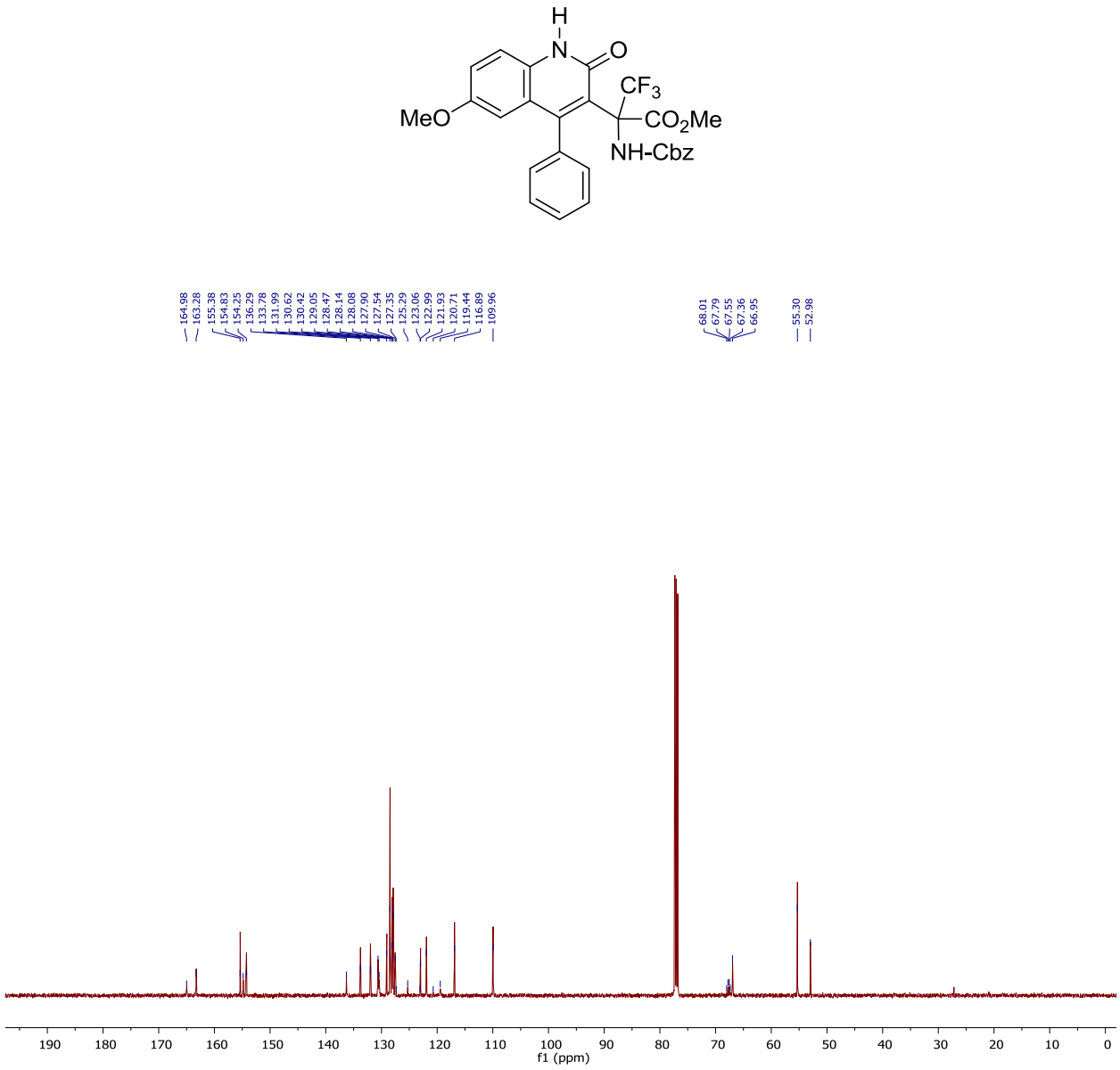
^{1}H NMR spectrum of compound **3f** in DMSO-*d*$_6$



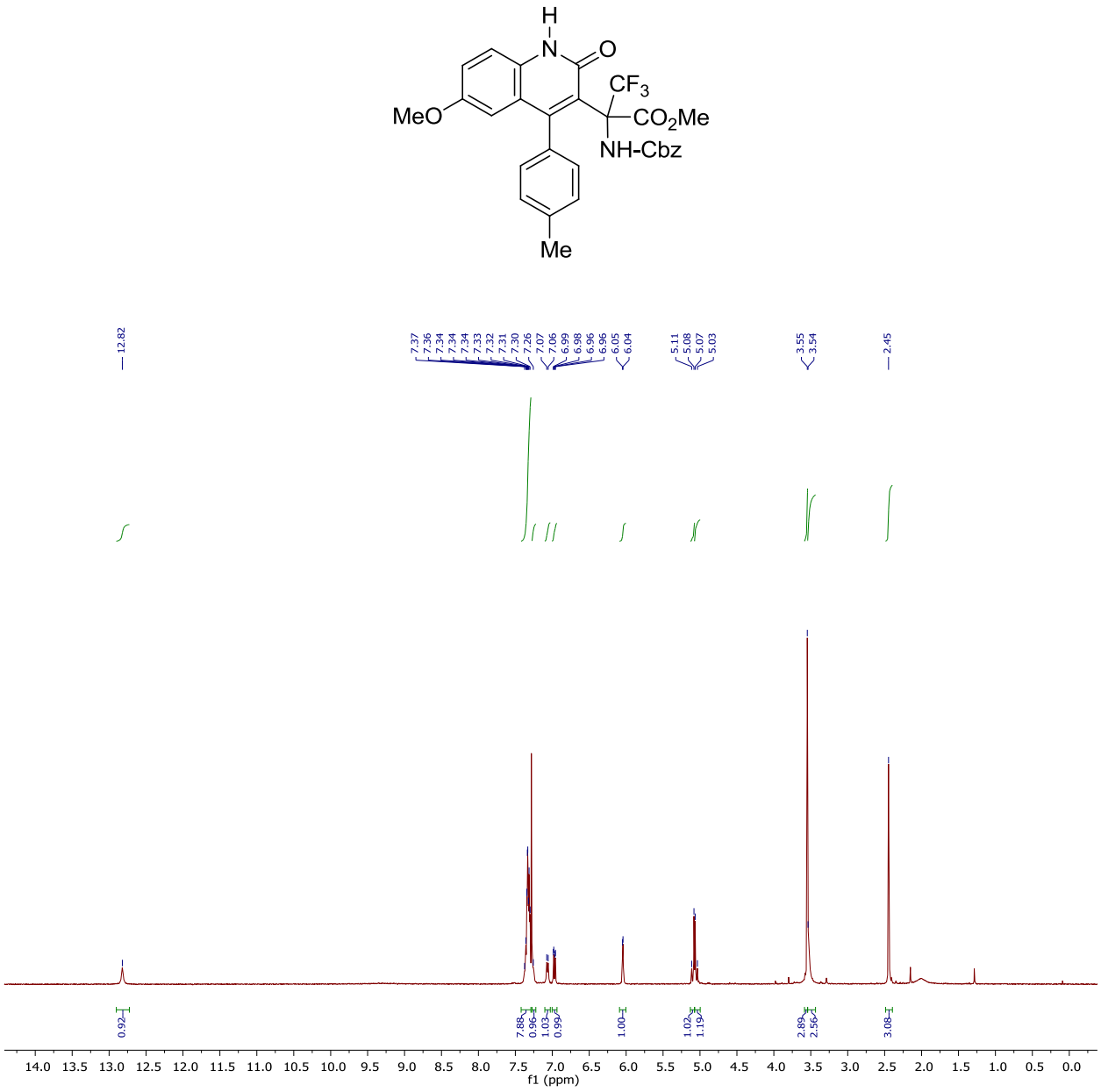
^{13}C NMR spectrum of compound **3f** in DMSO-d_6



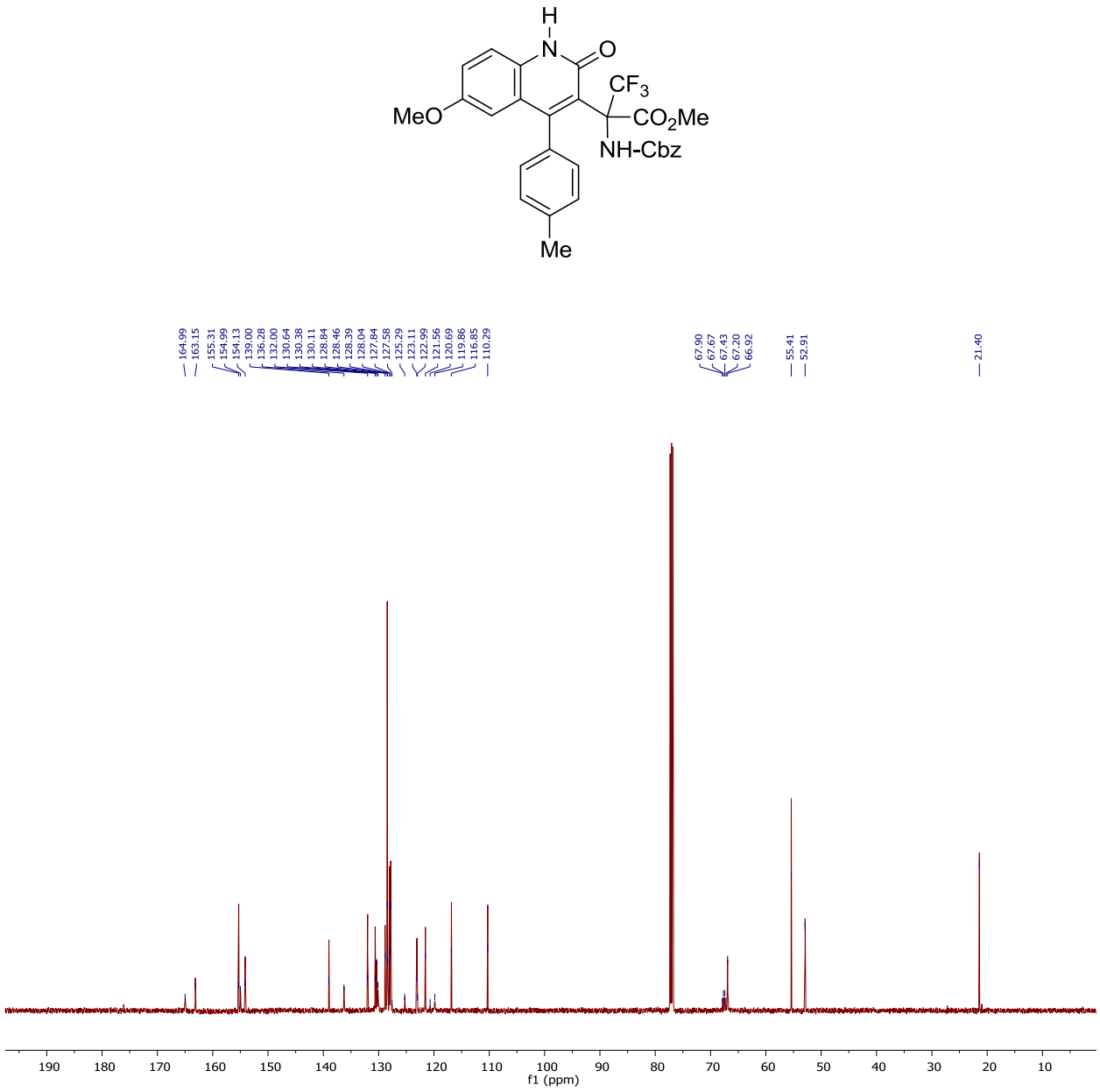
^{1}H NMR spectrum of compound **3g** in $CDCl_3$



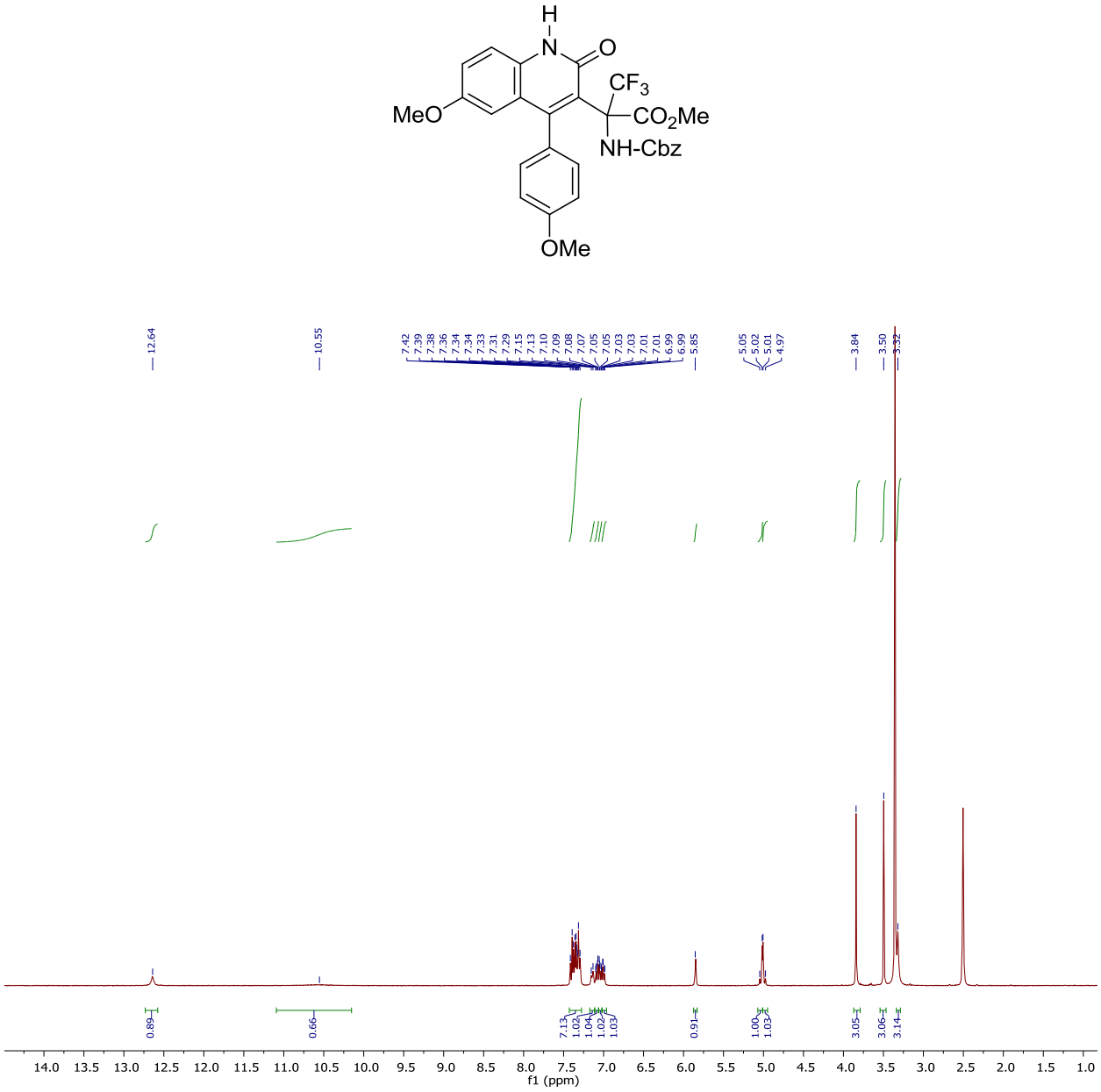
^{13}C NMR spectrum of compound **3g** in $CDCl_3$



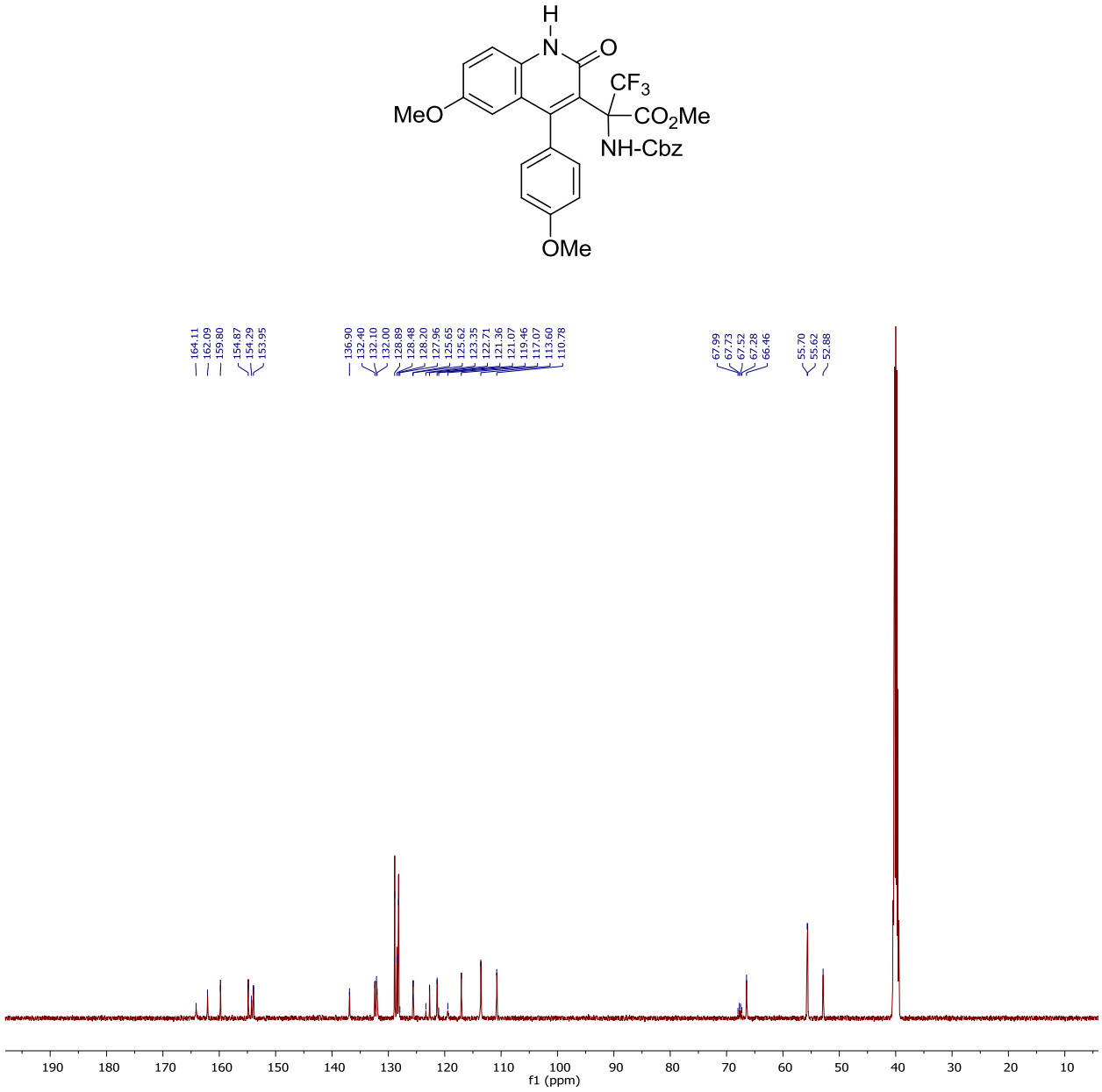
^{1}H NMR spectrum of compound **3h** in $CDCl_3$



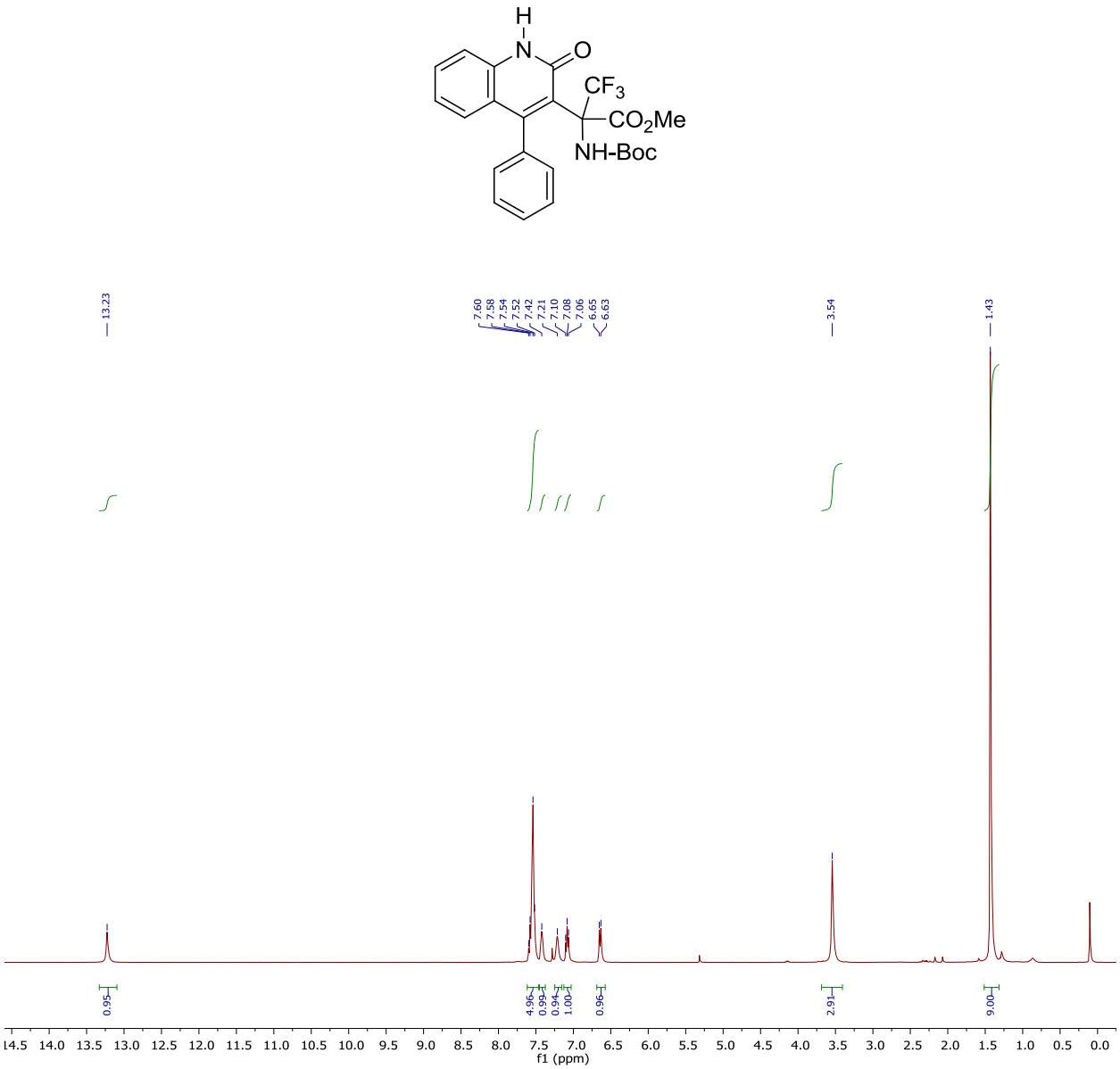
^{13}C NMR spectrum of compound **3h** in $CDCl_3$



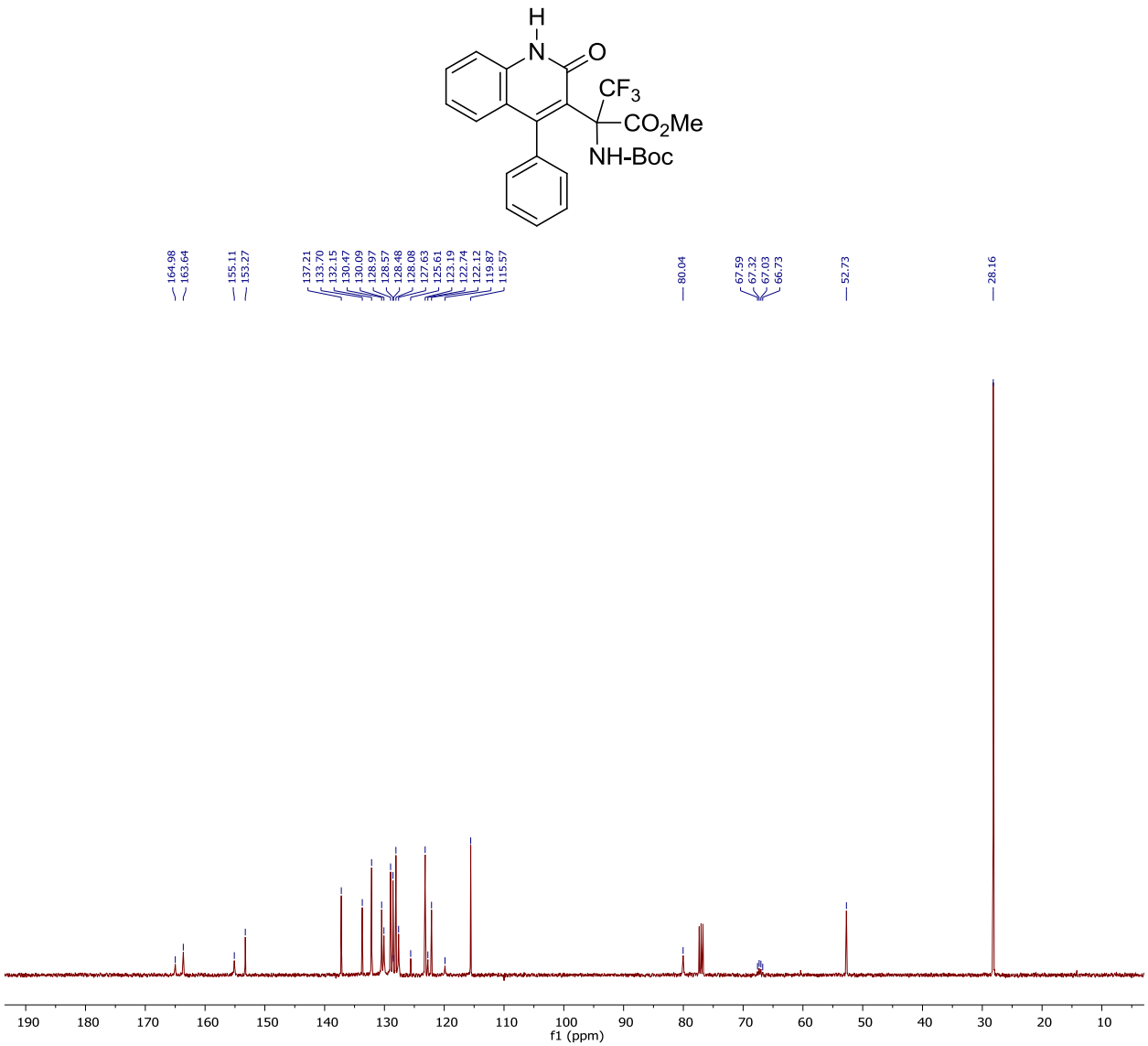
^{1}H NMR spectrum of compound **3i** in DMSO-d_6



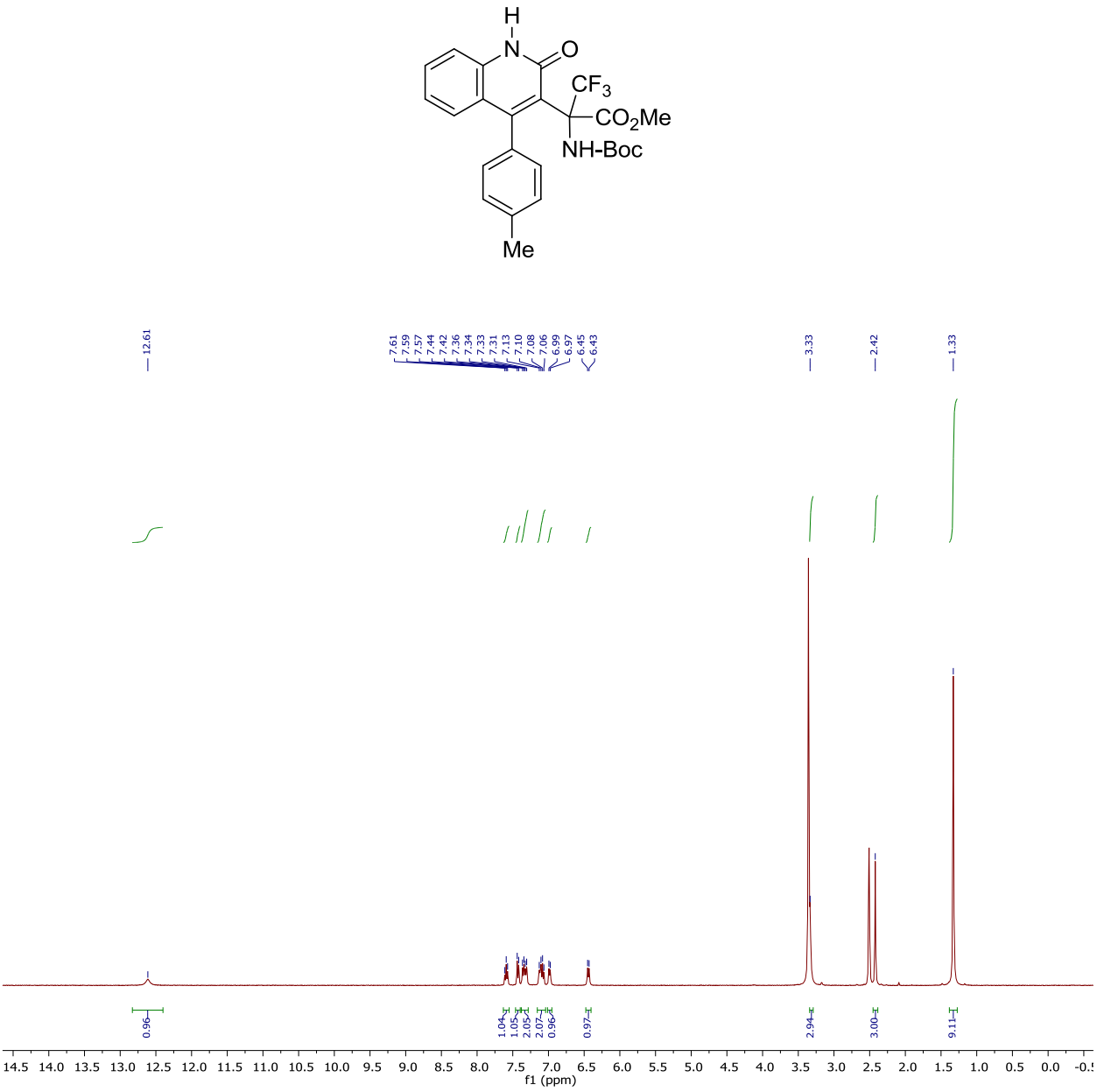
^{13}C NMR spectrum of compound **3i** in DMSO-d_6



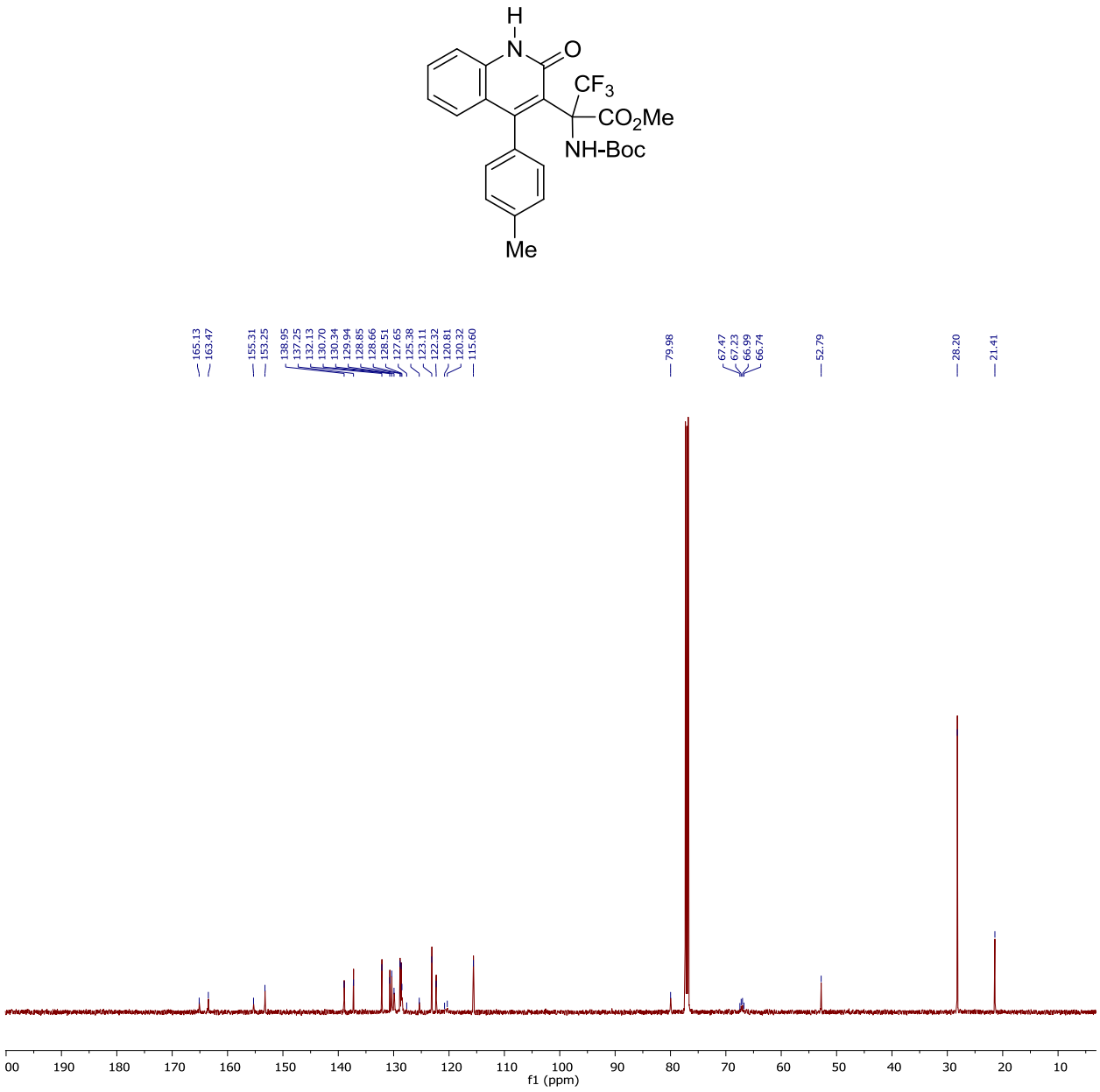
^{1}H NMR spectrum of compound **3j** in $CDCl_3$



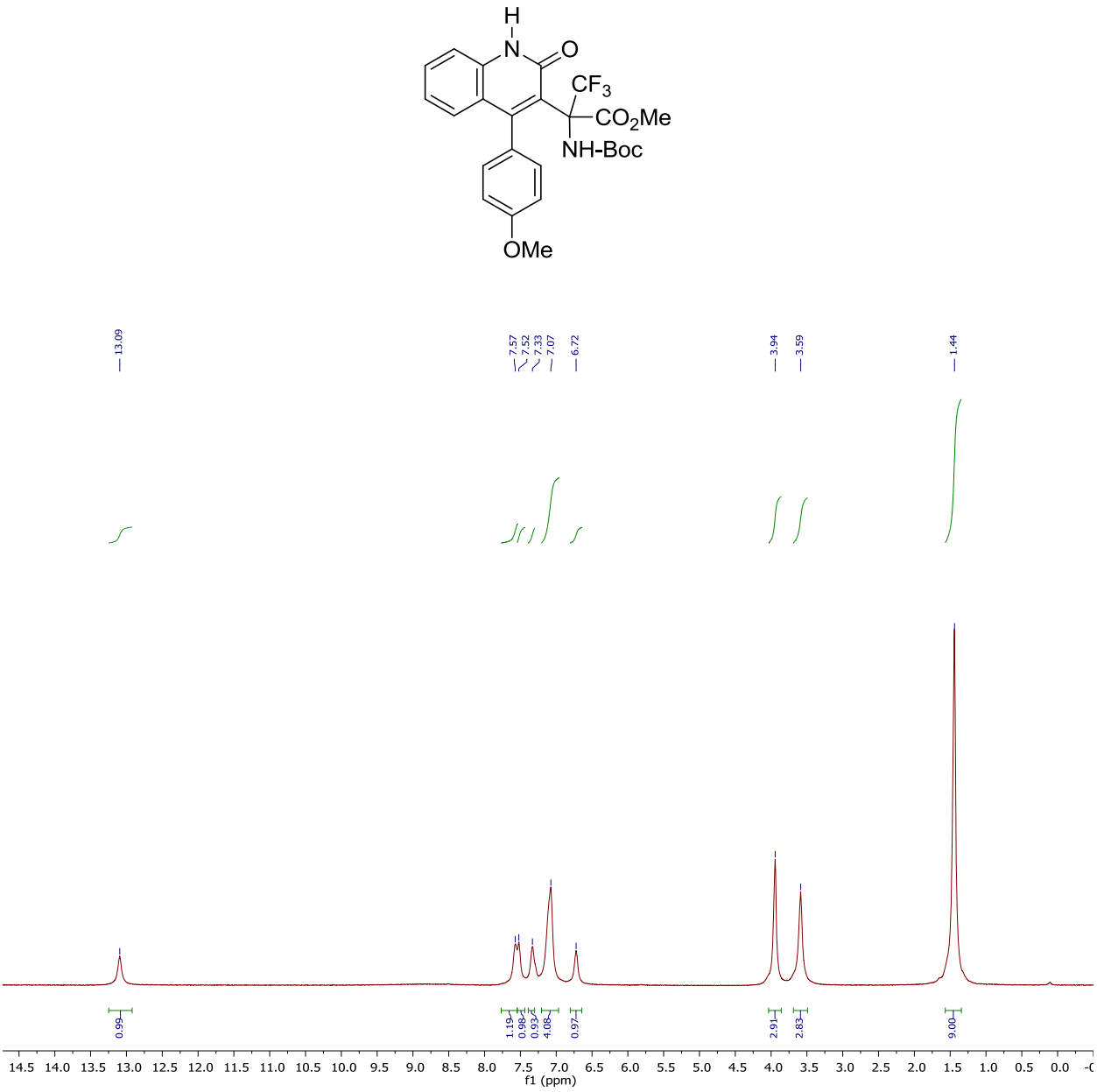
^{13}C NMR spectrum of compound **3j** in $CDCl_3$



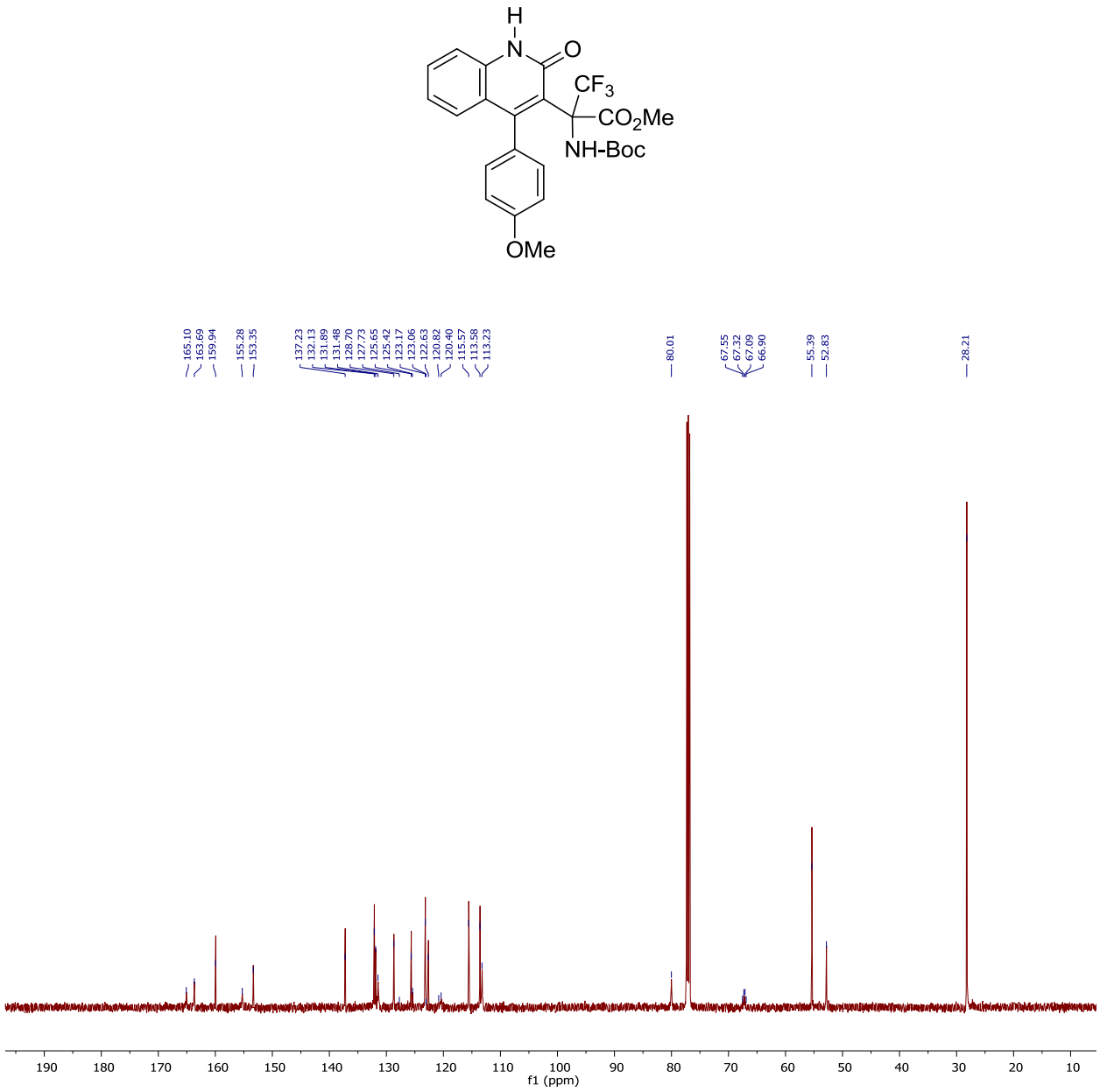
^{1}H NMR spectrum of compound **3k** in DMSO-d_6



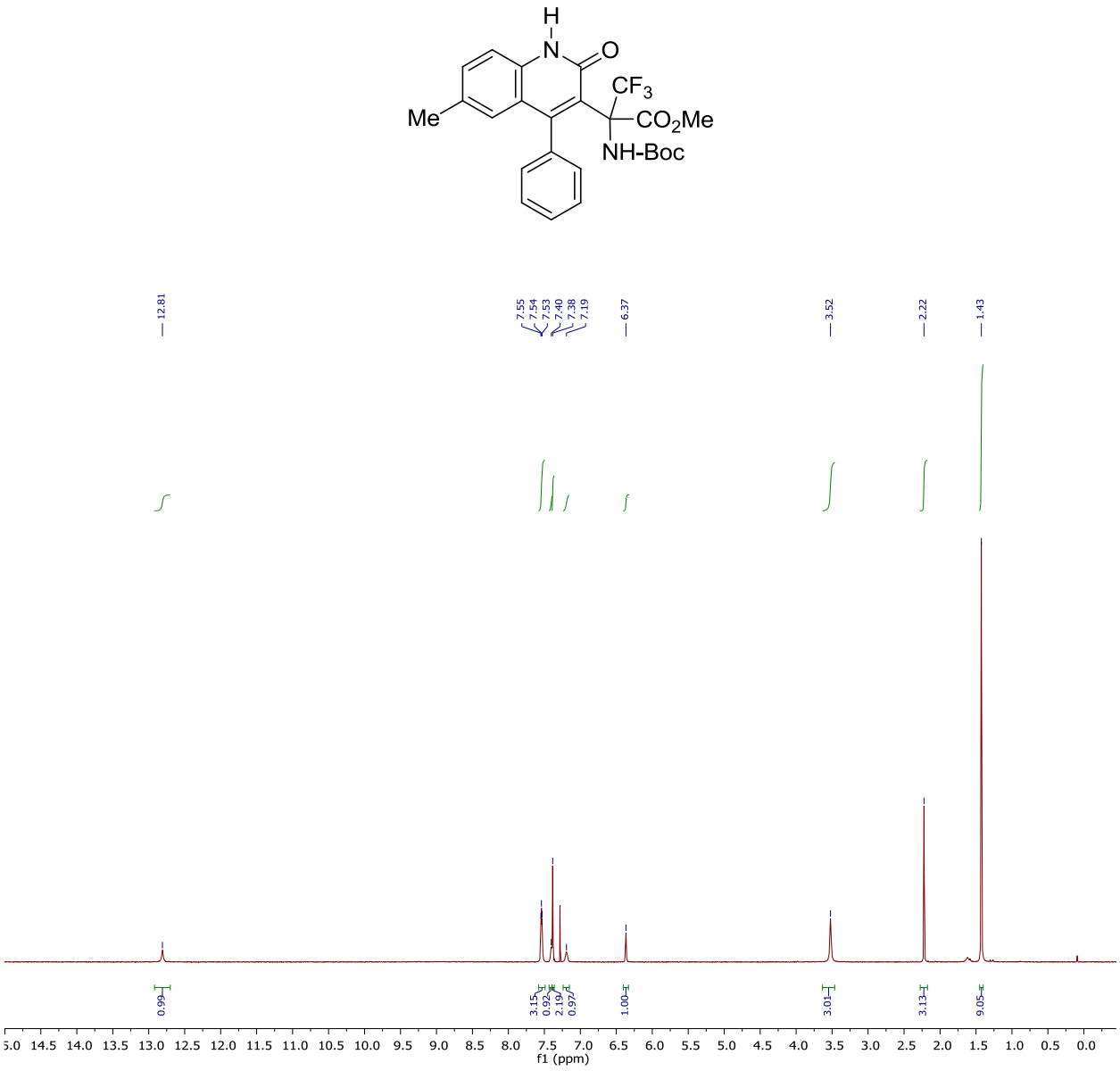
^{13}C NMR spectrum of compound **3k** in $CDCl_3$



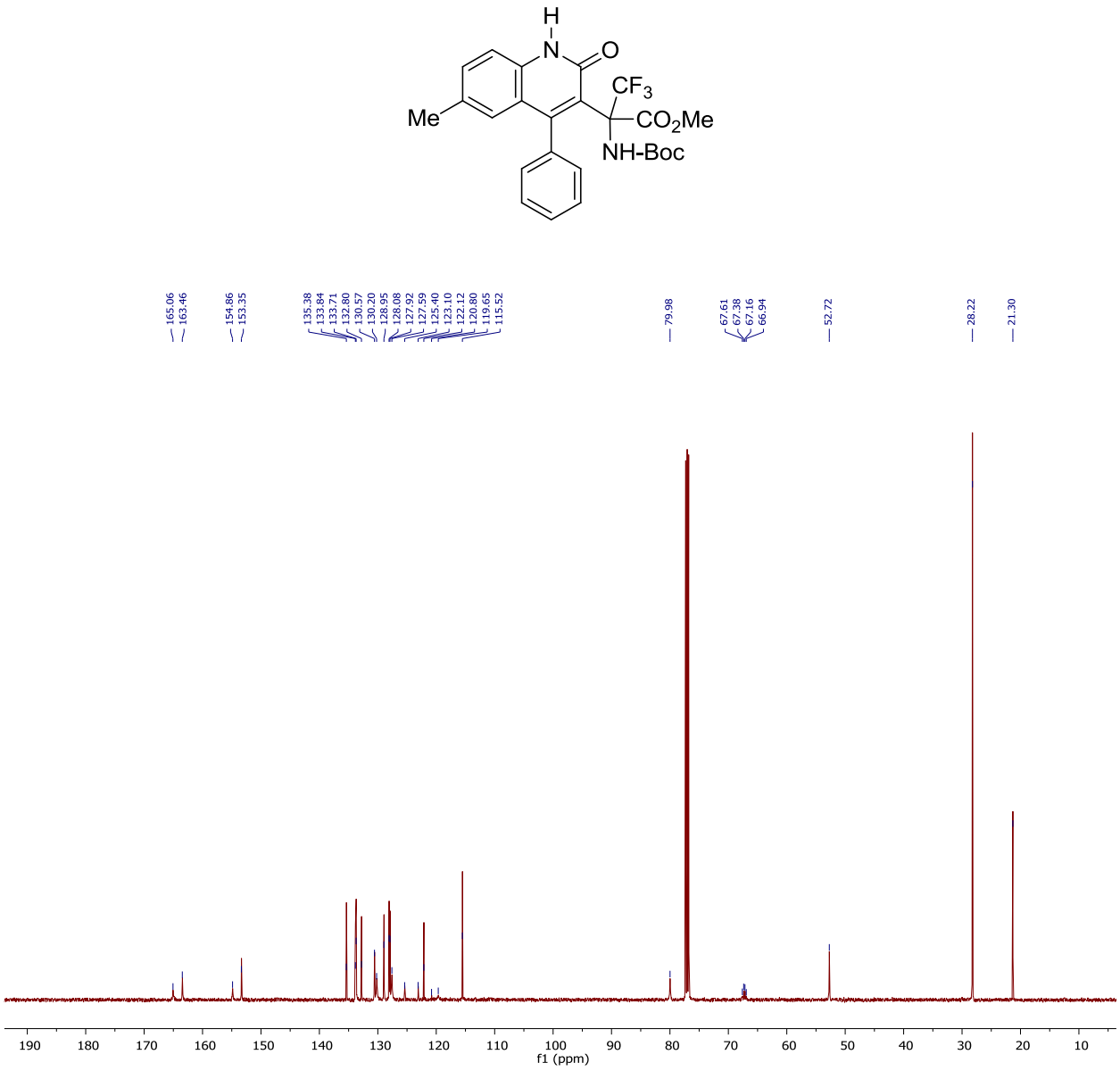
^{1}H NMR spectrum of compound **3l** in $CDCl_3$



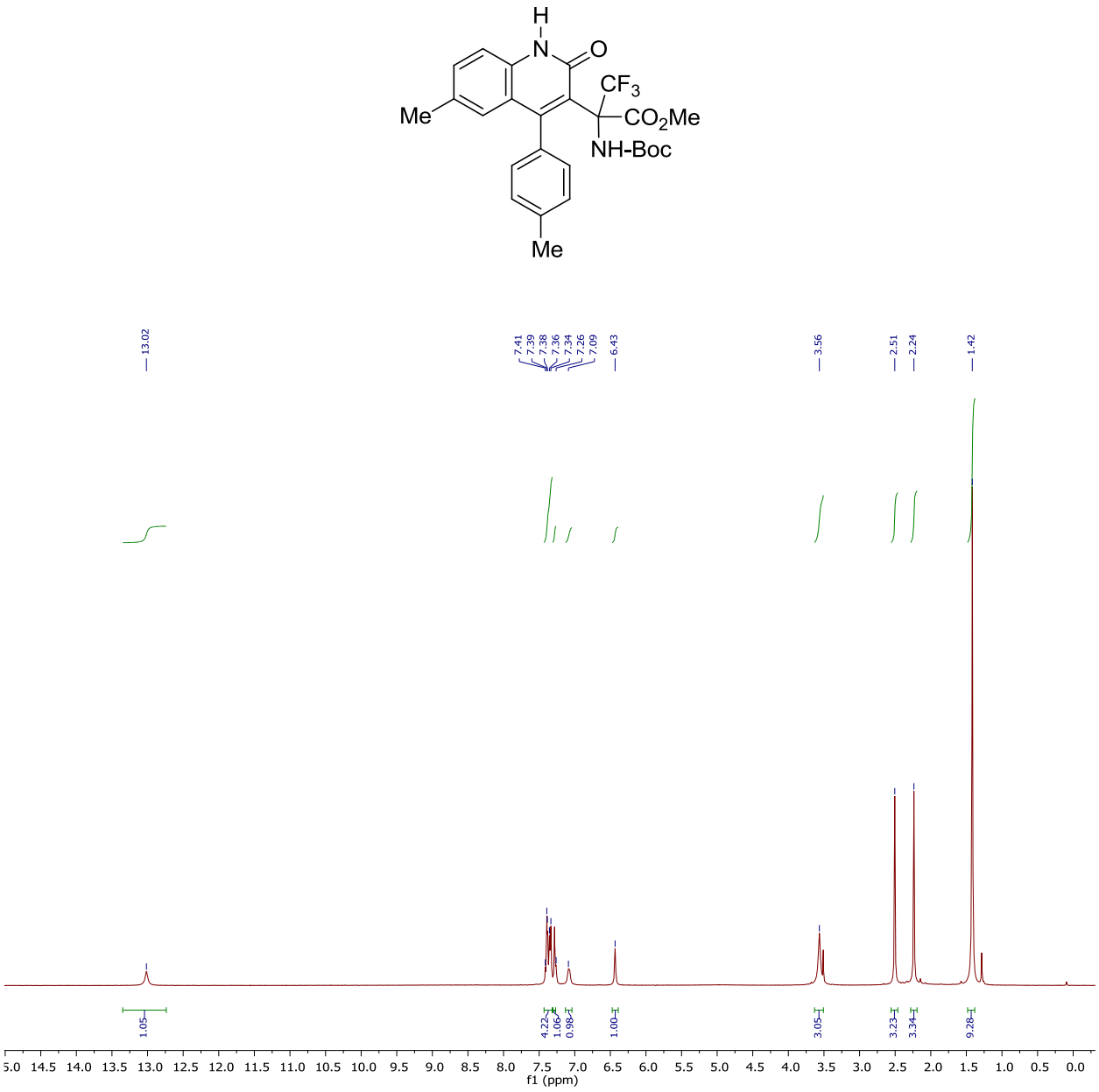
^{13}C NMR spectrum of compound **3l** in $CDCl_3$



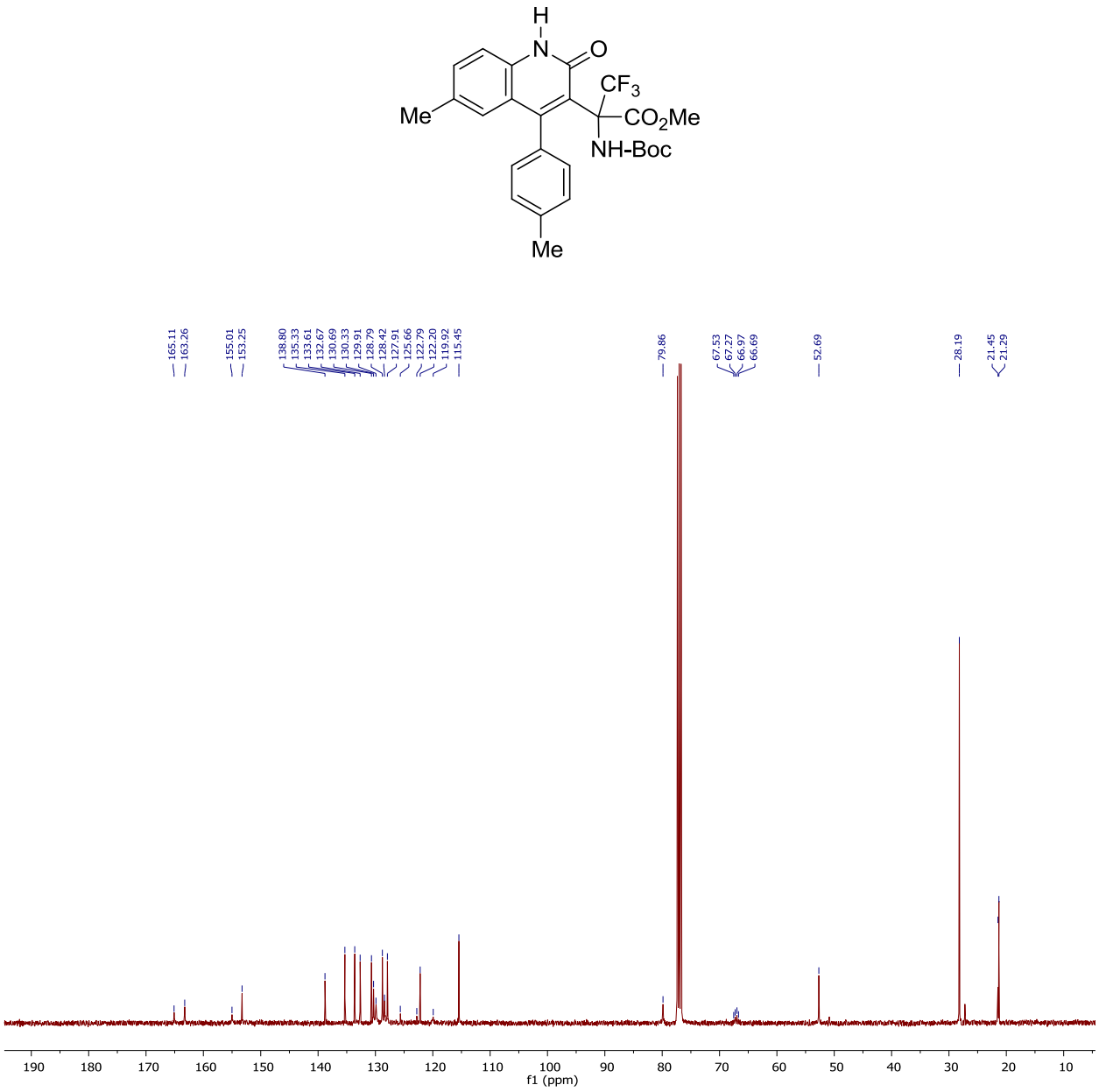
^{1}H NMR spectrum of compound **3m** in $CDCl_3$



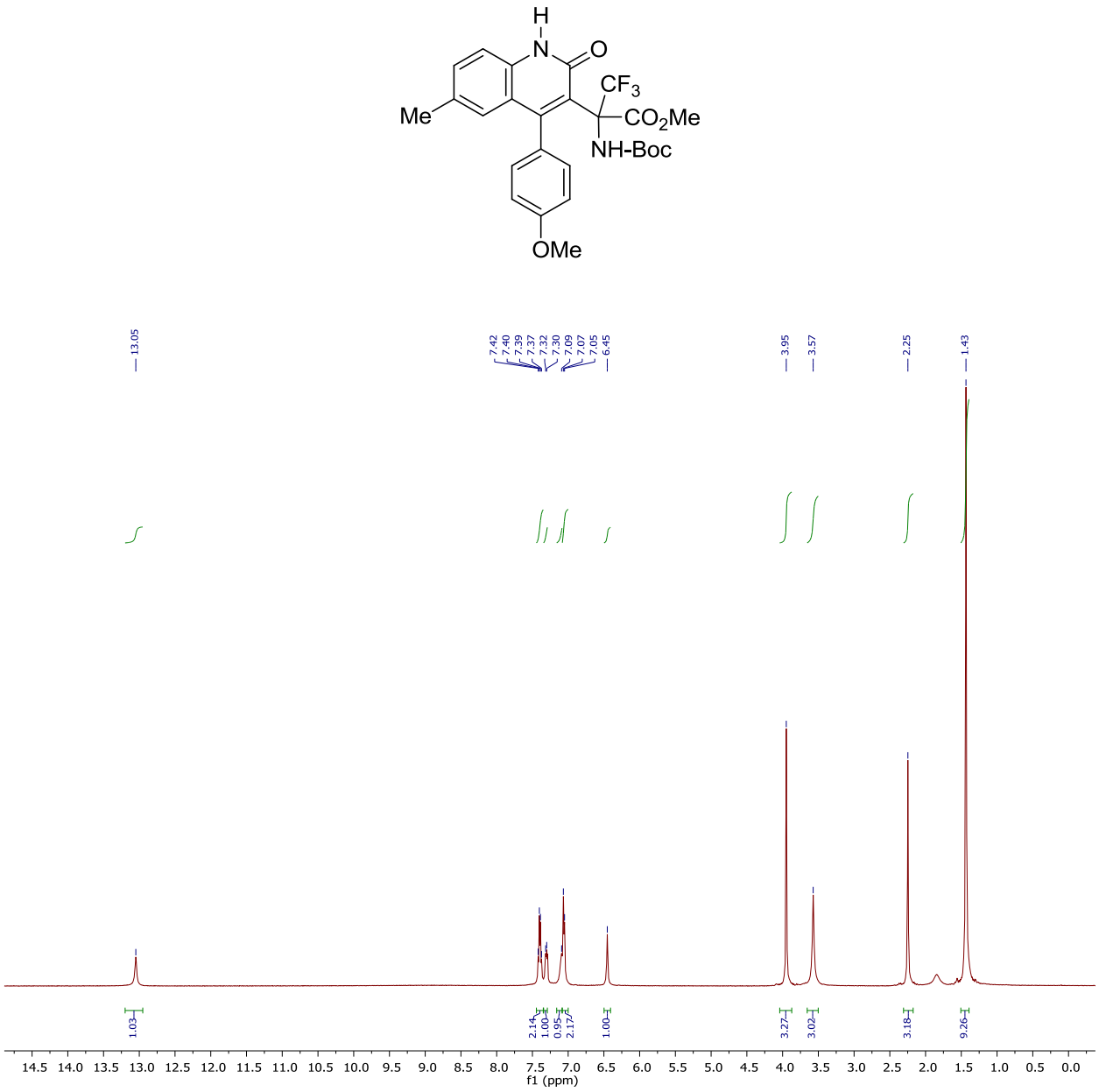
^{13}C NMR spectrum of compound **3m** in $CDCl_3$



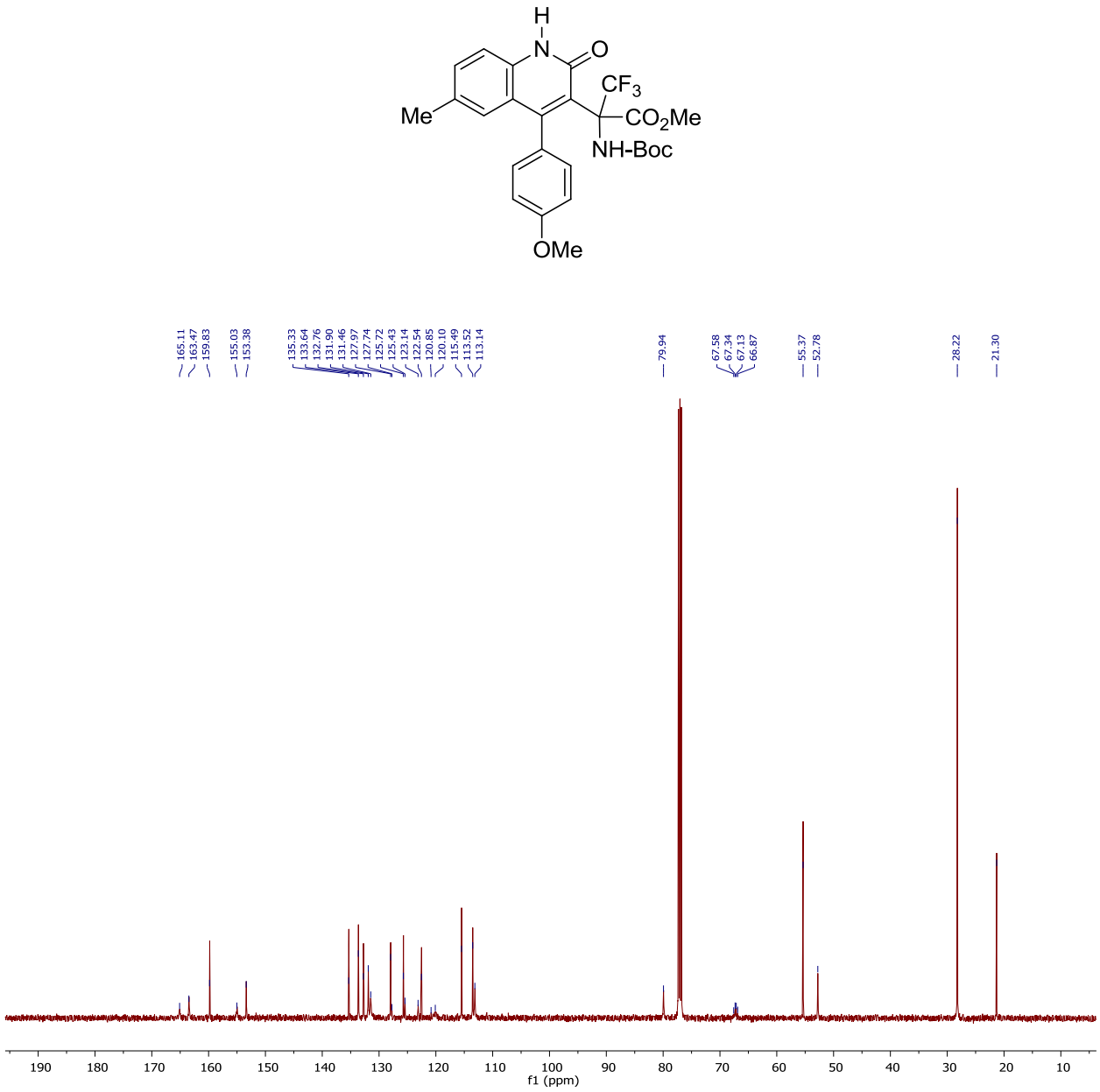
^{1}H NMR spectrum of compound **3n** in $CDCl_3$



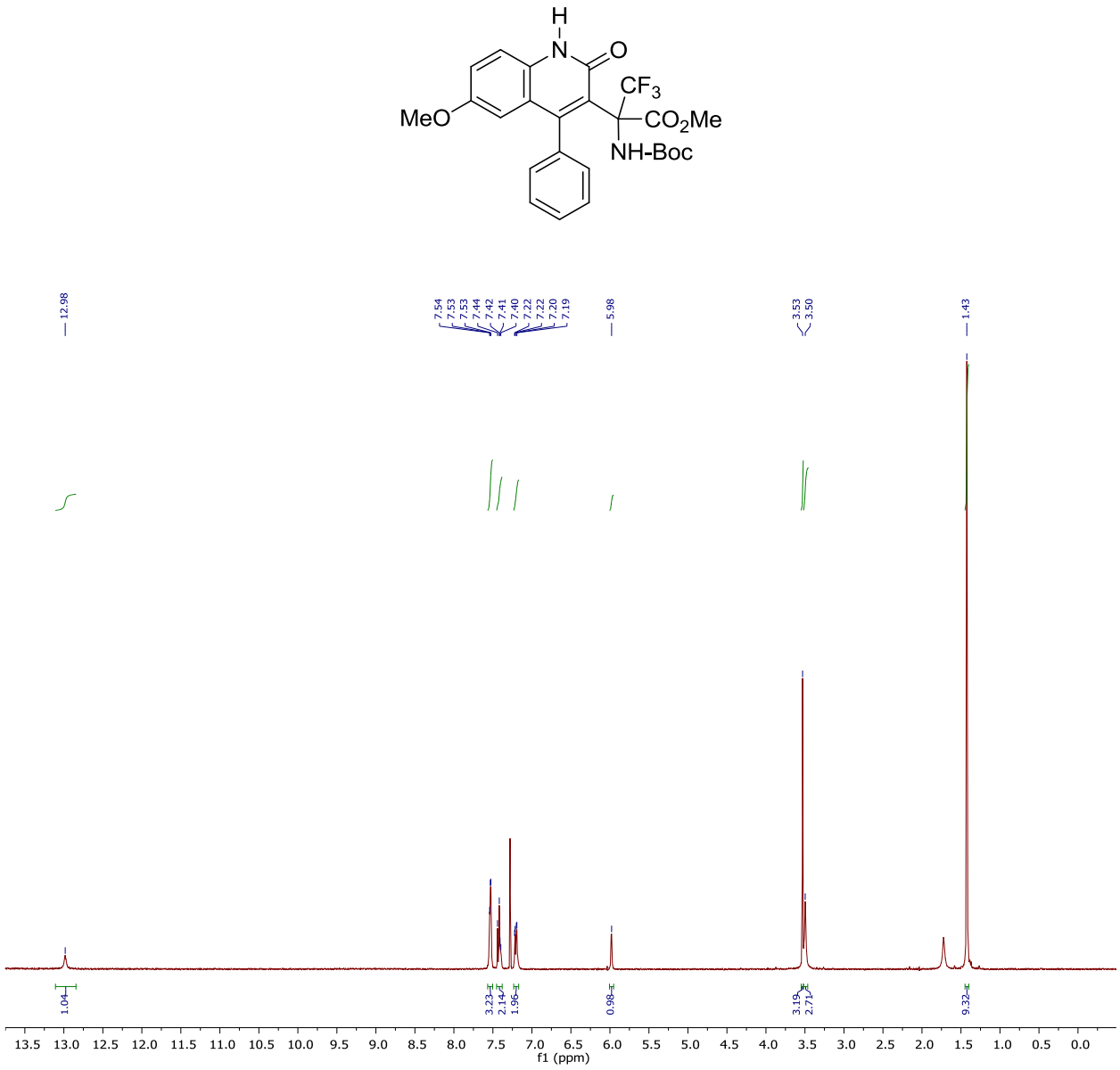
^{13}C NMR spectrum of compound **3n** in $CDCl_3$



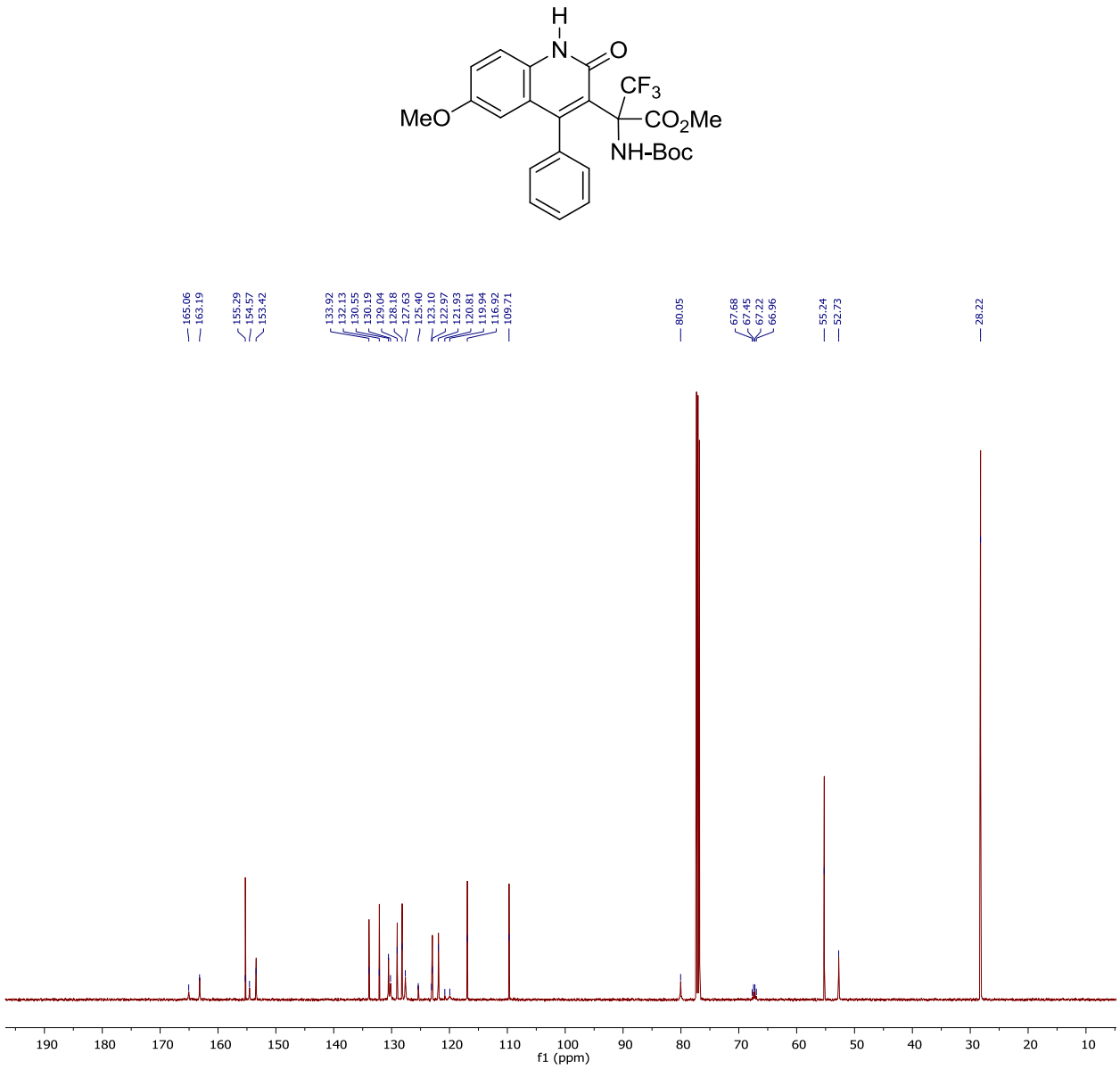
^{1}H NMR spectrum of compound **3o** in $CDCl_3$



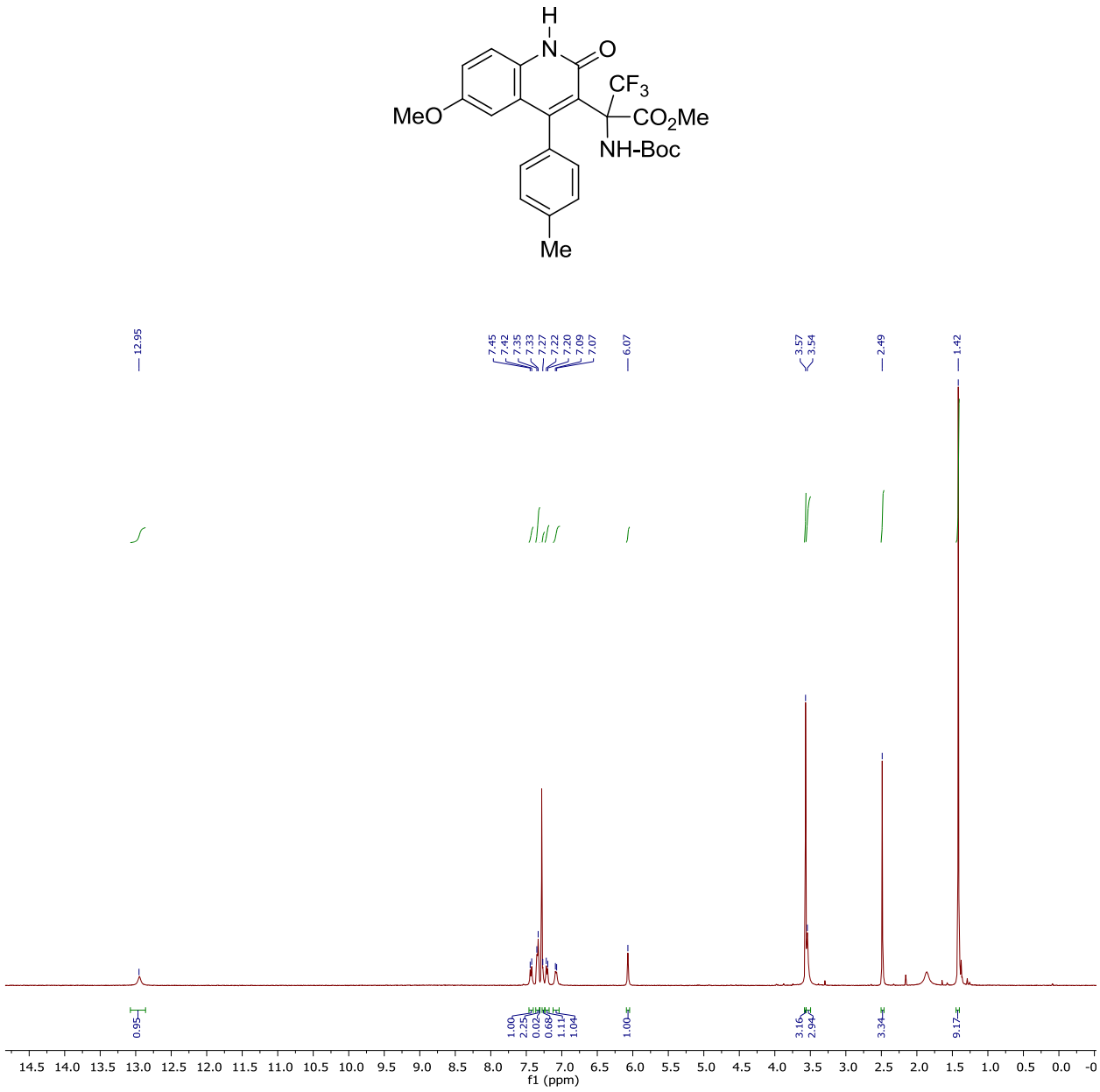
^{13}C NMR spectrum of compound **3o** in $CDCl_3$



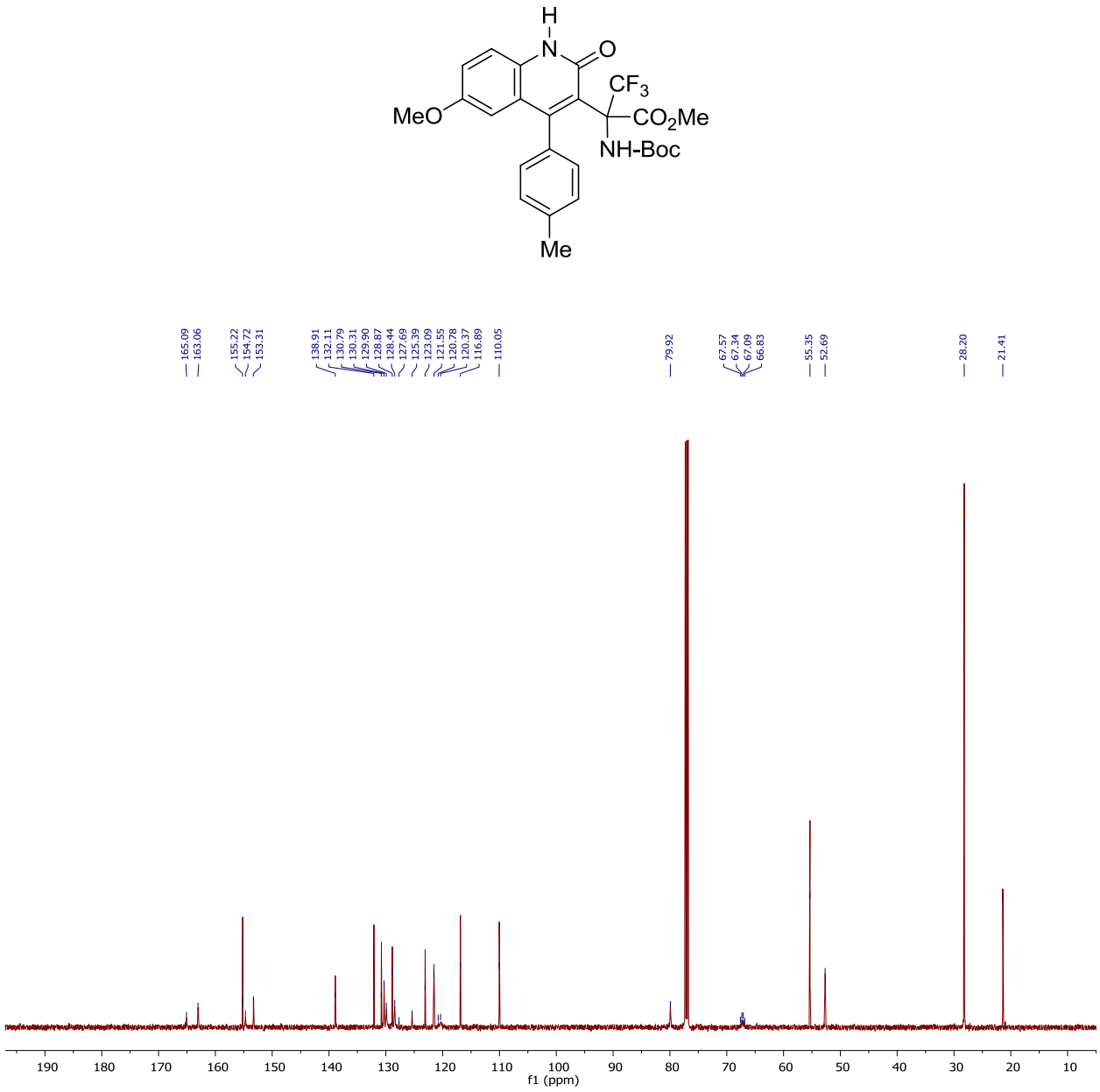
^{1}H NMR spectrum of compound **3p** in $CDCl_3$



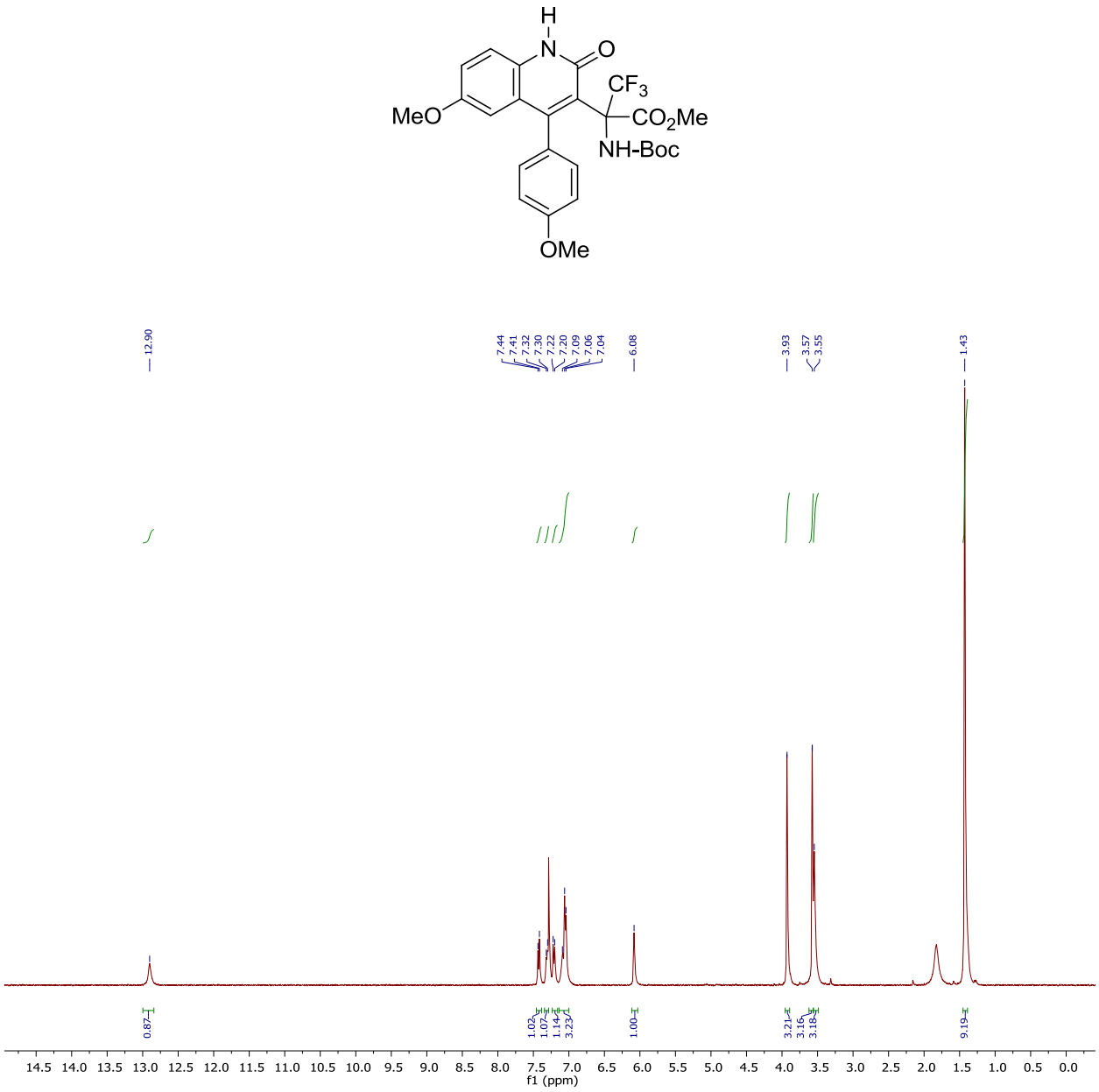
^{13}C NMR spectrum of compound **3p** in $CDCl_3$



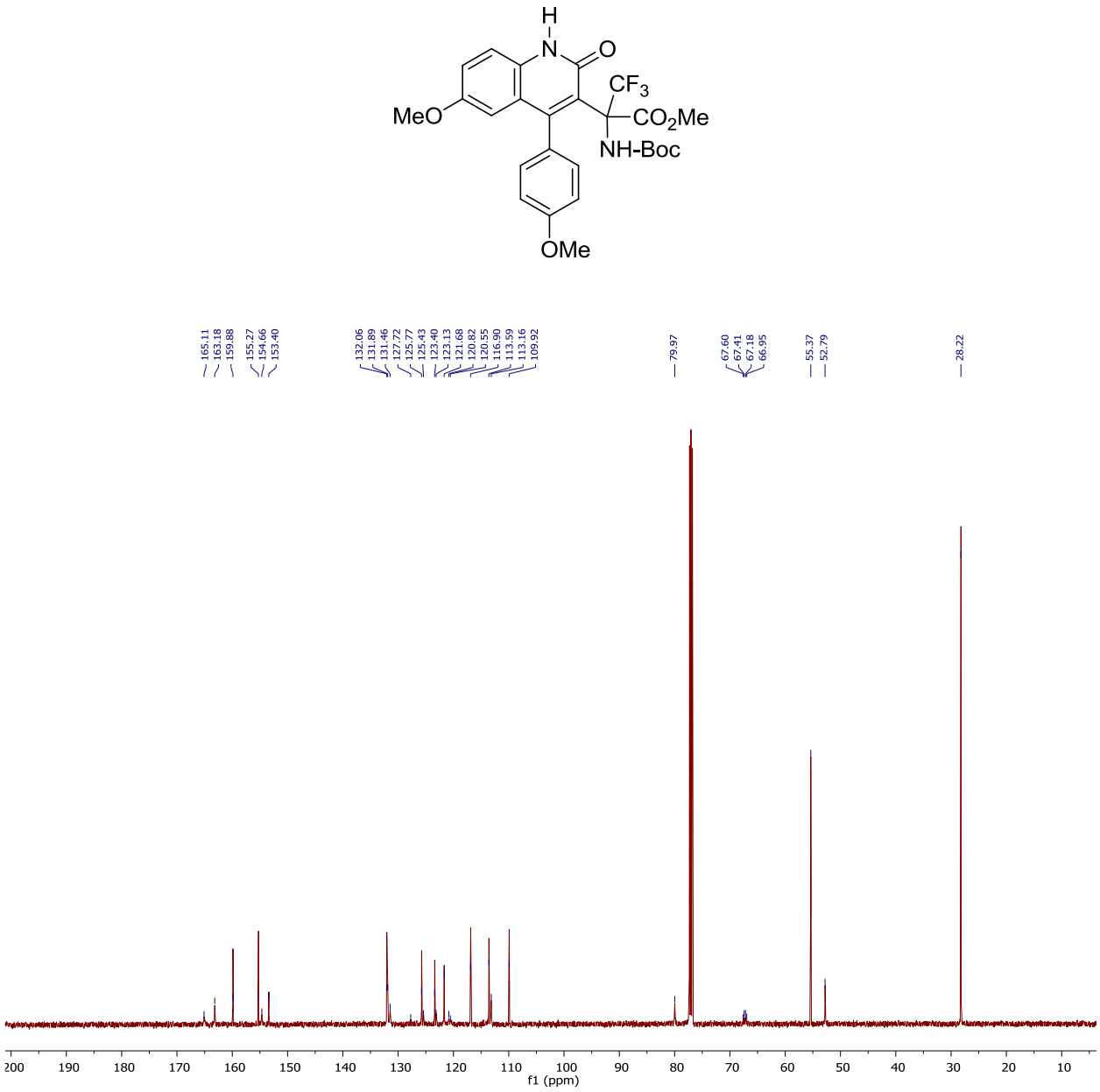
^{1}H NMR spectrum of compound **3q** in $CDCl_3$



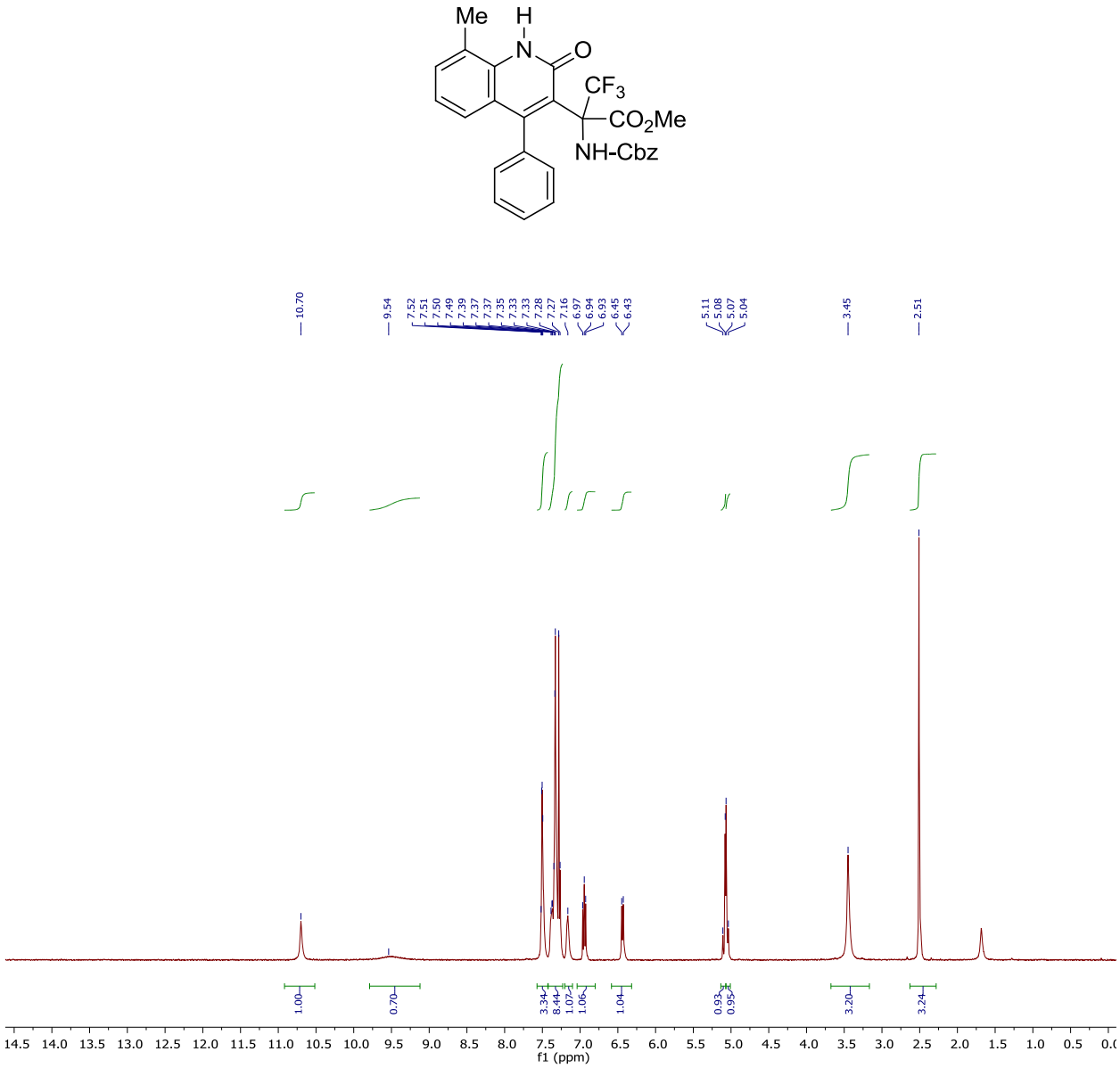
^{13}C NMR spectrum of compound **3q** in $CDCl_3$



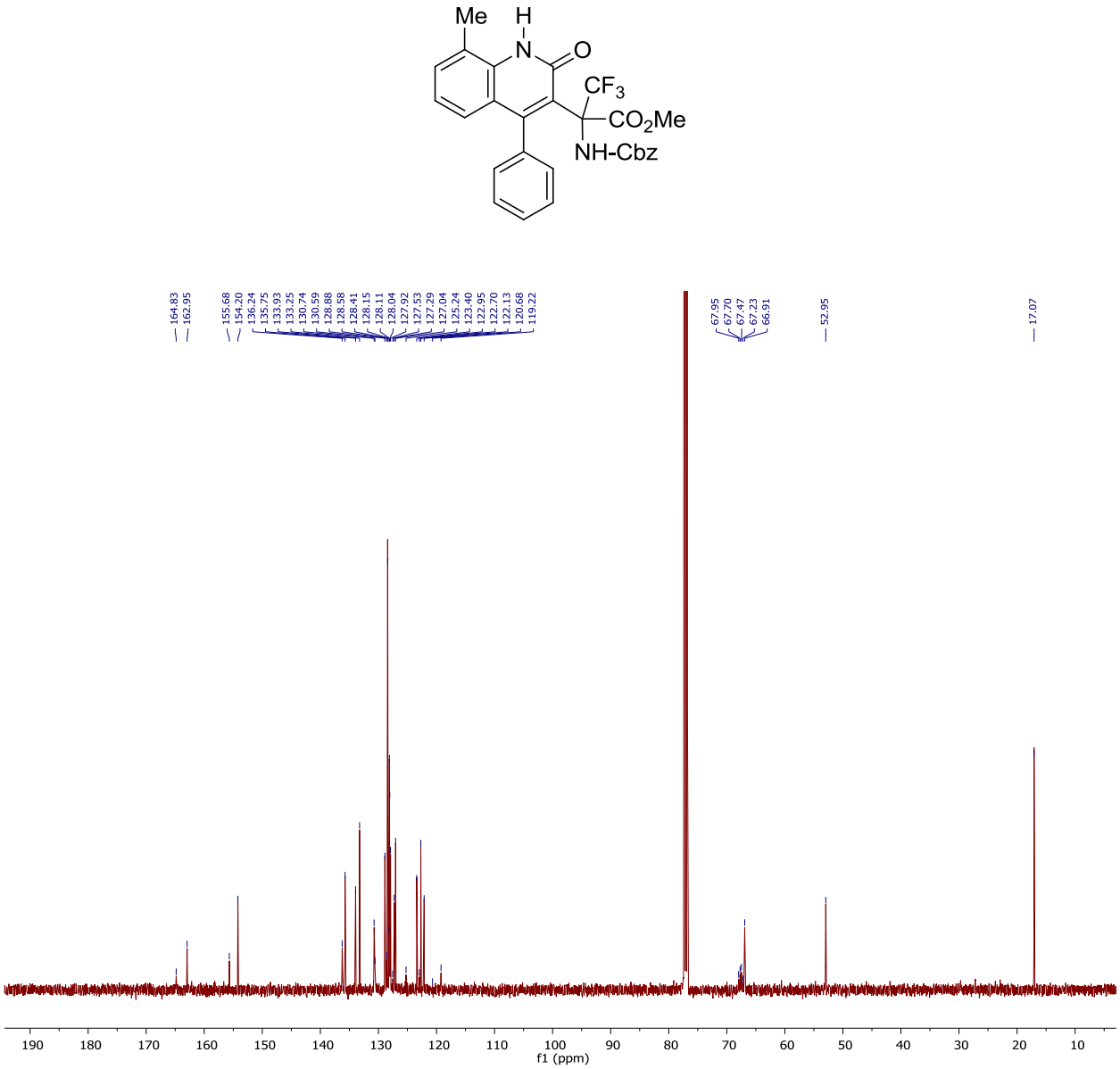
^{1}H NMR spectrum of compound **3r** in $CDCl_3$



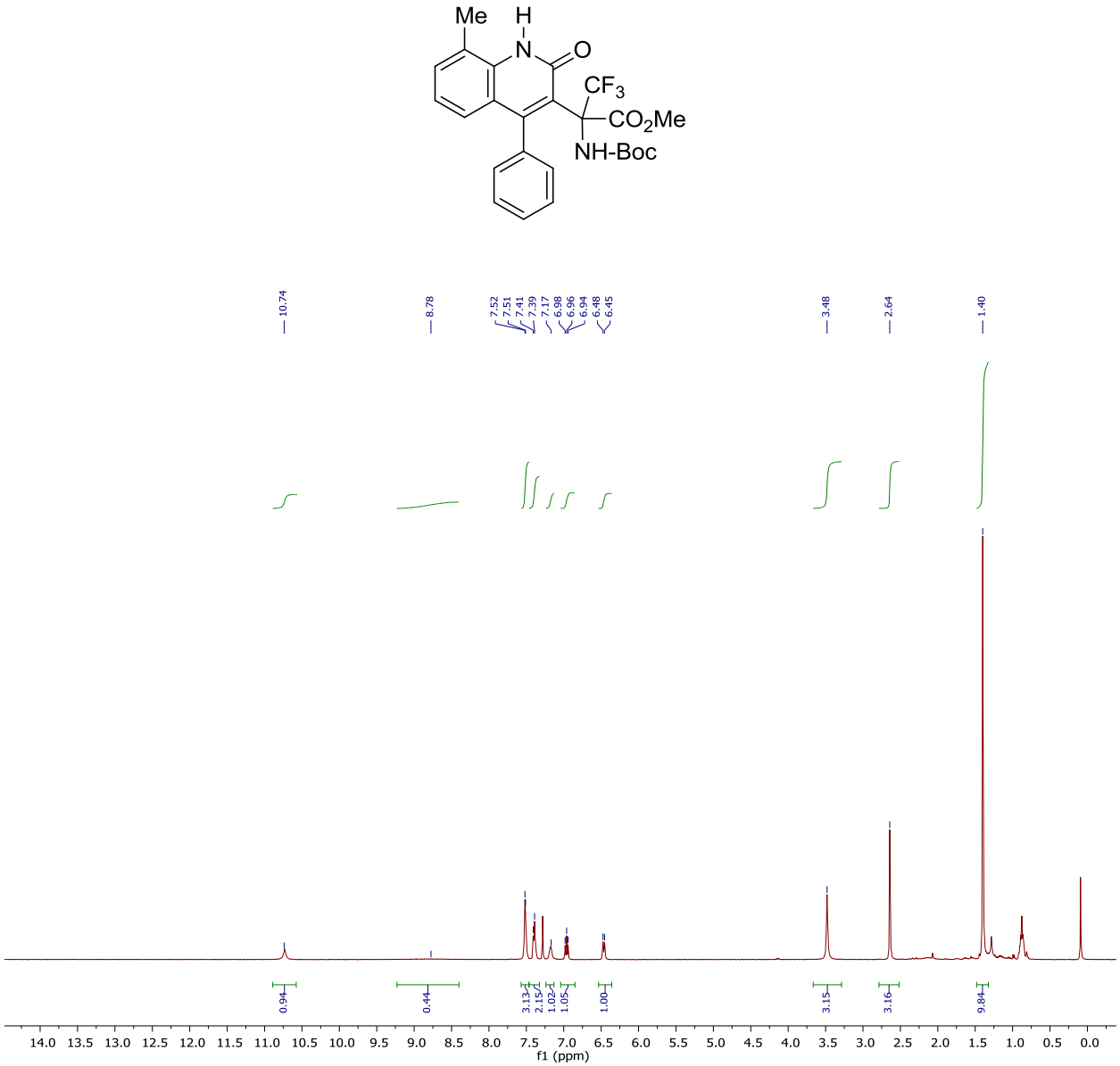
^{13}C NMR spectrum of compound **3r** in $CDCl_3$



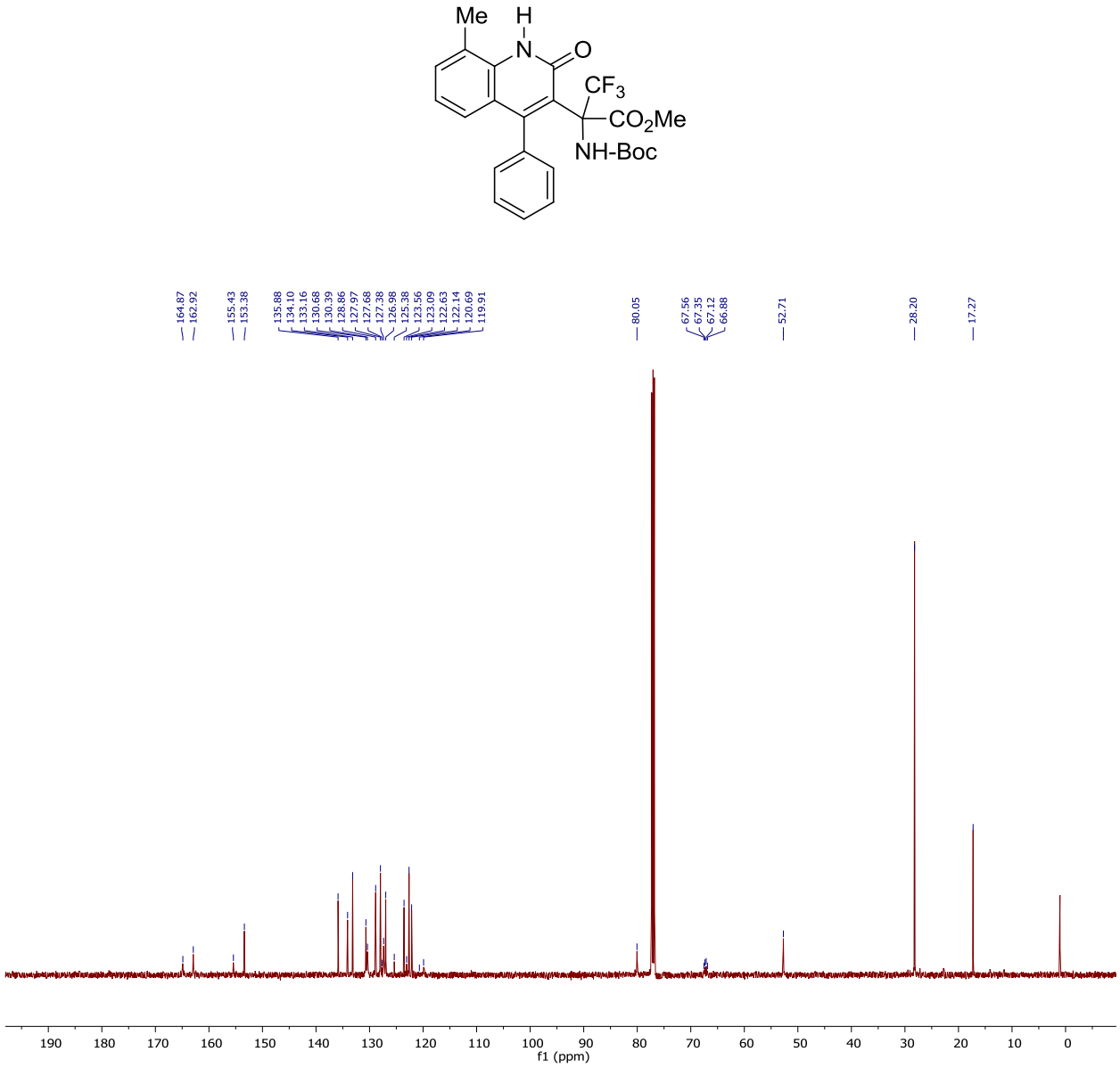
^{1}H NMR spectrum of compound **3s** in $CDCl_3$



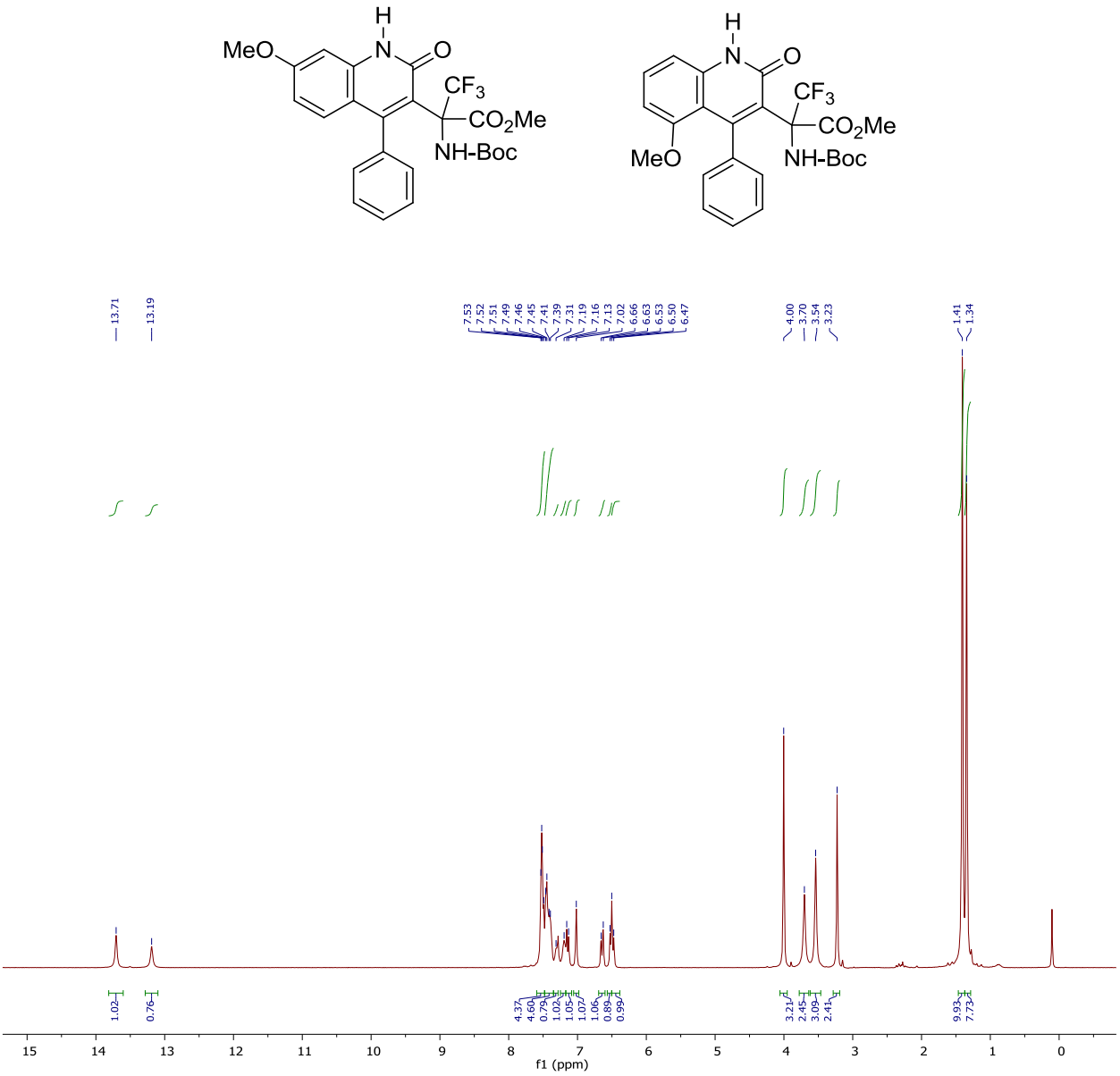
^{13}C NMR spectrum of compound **3s** in $CDCl_3$



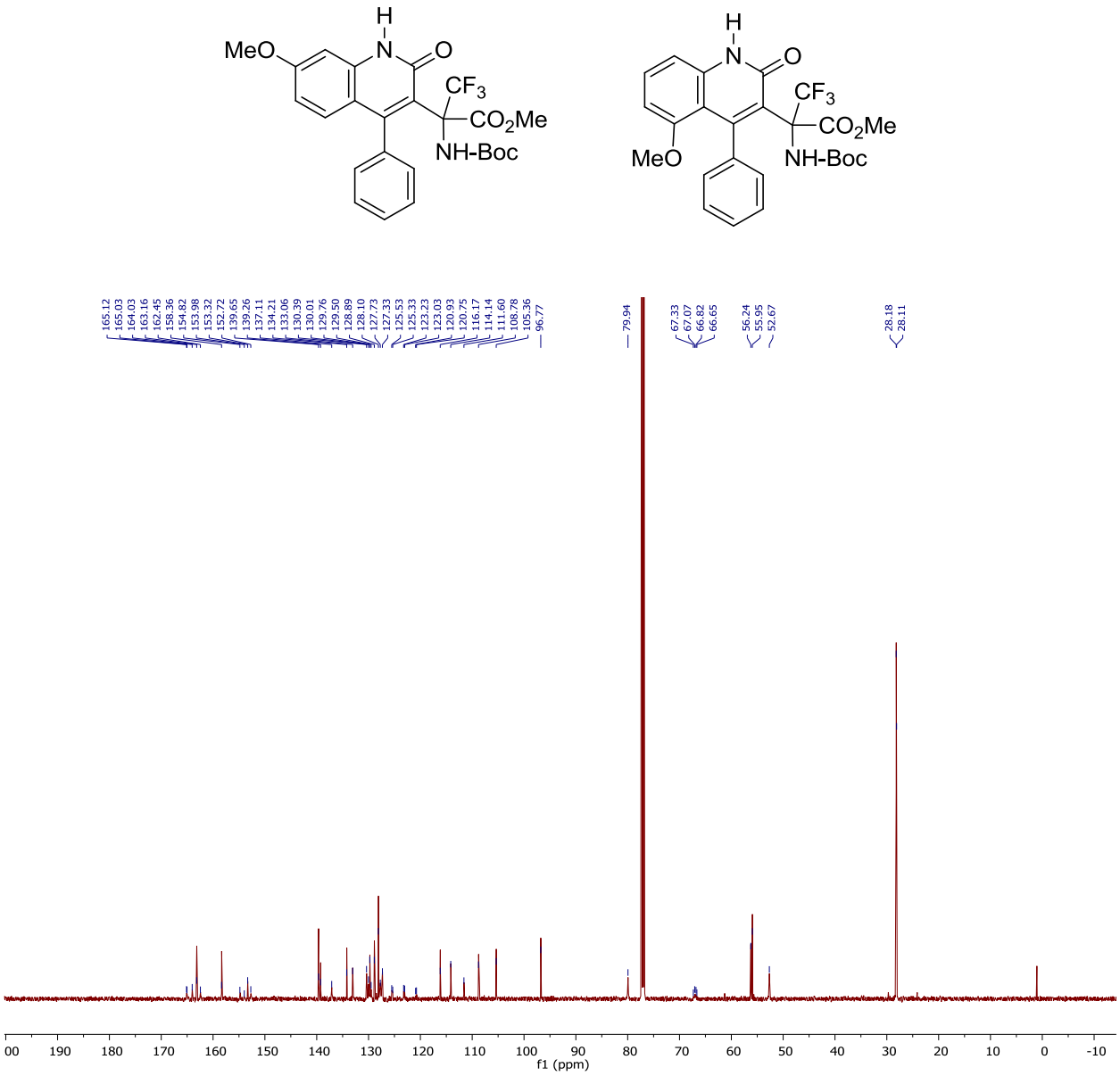
^{1}H NMR spectrum of compound **3t** in $CDCl_3$



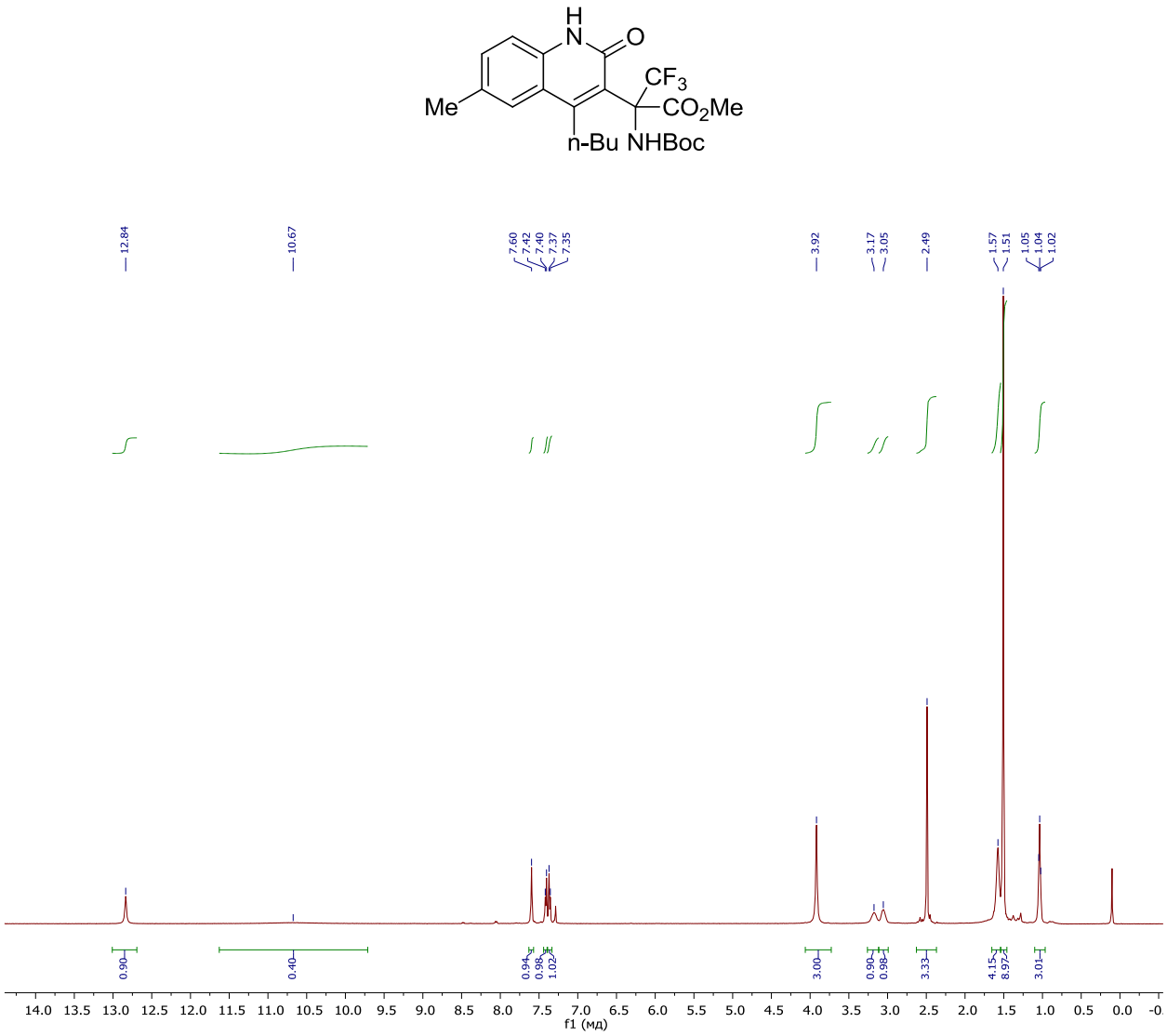
^{13}C NMR spectrum of compound **3t** in $CDCl_3$



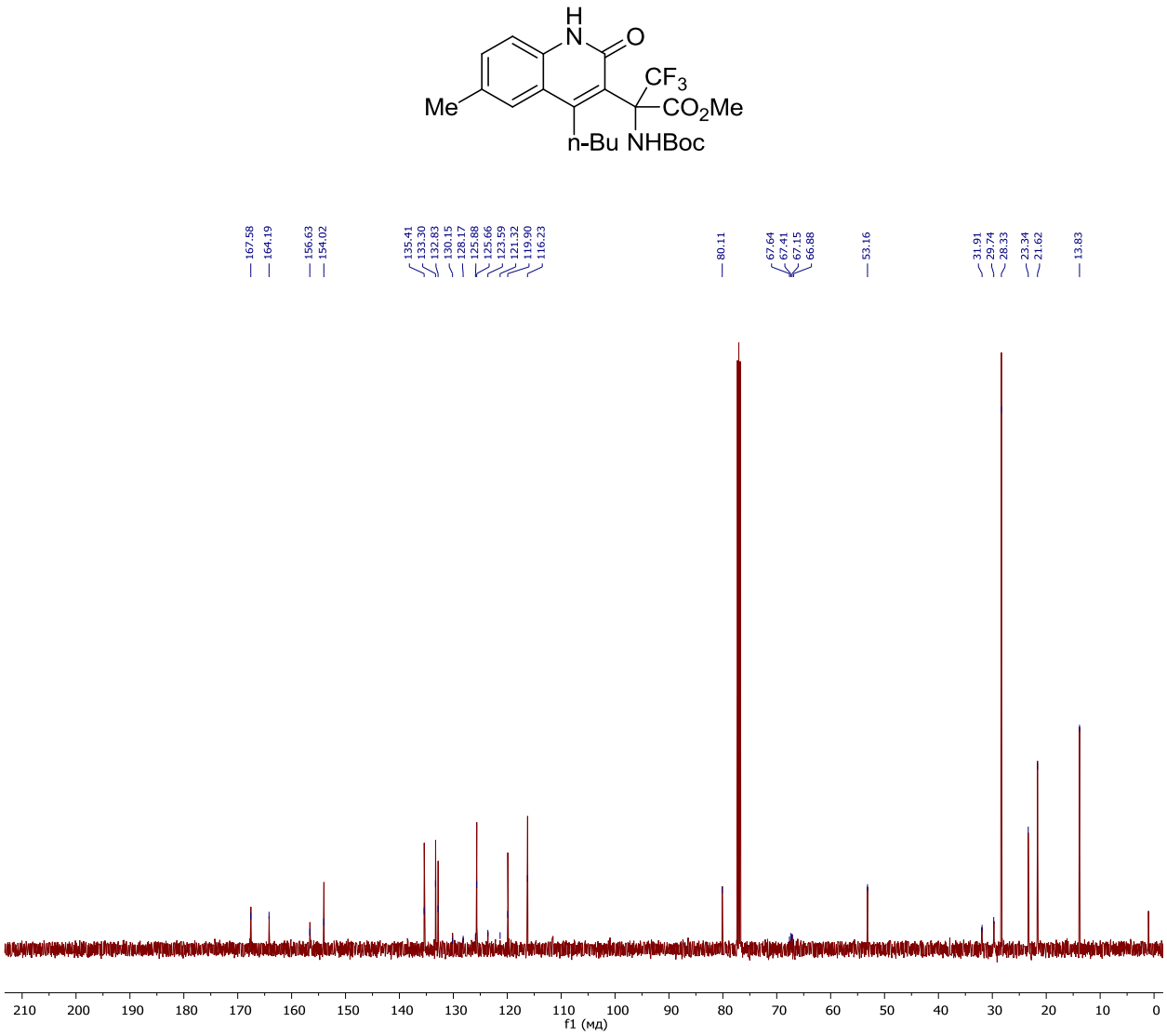
^{1}H NMR spectrum of compound **3ua** and **3ub** in $CDCl_3$



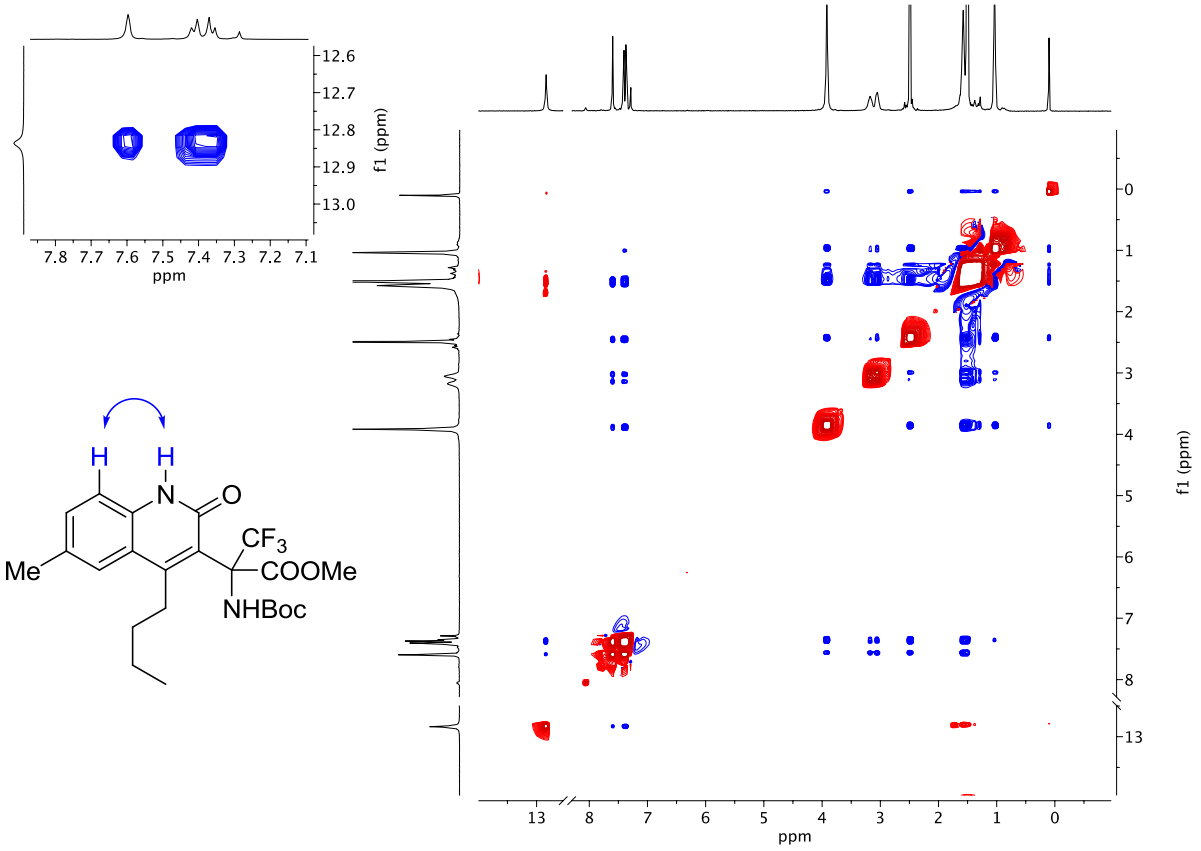
^{13}C NMR spectrum of compound **3ua** and **3ub** in $CDCl_3$



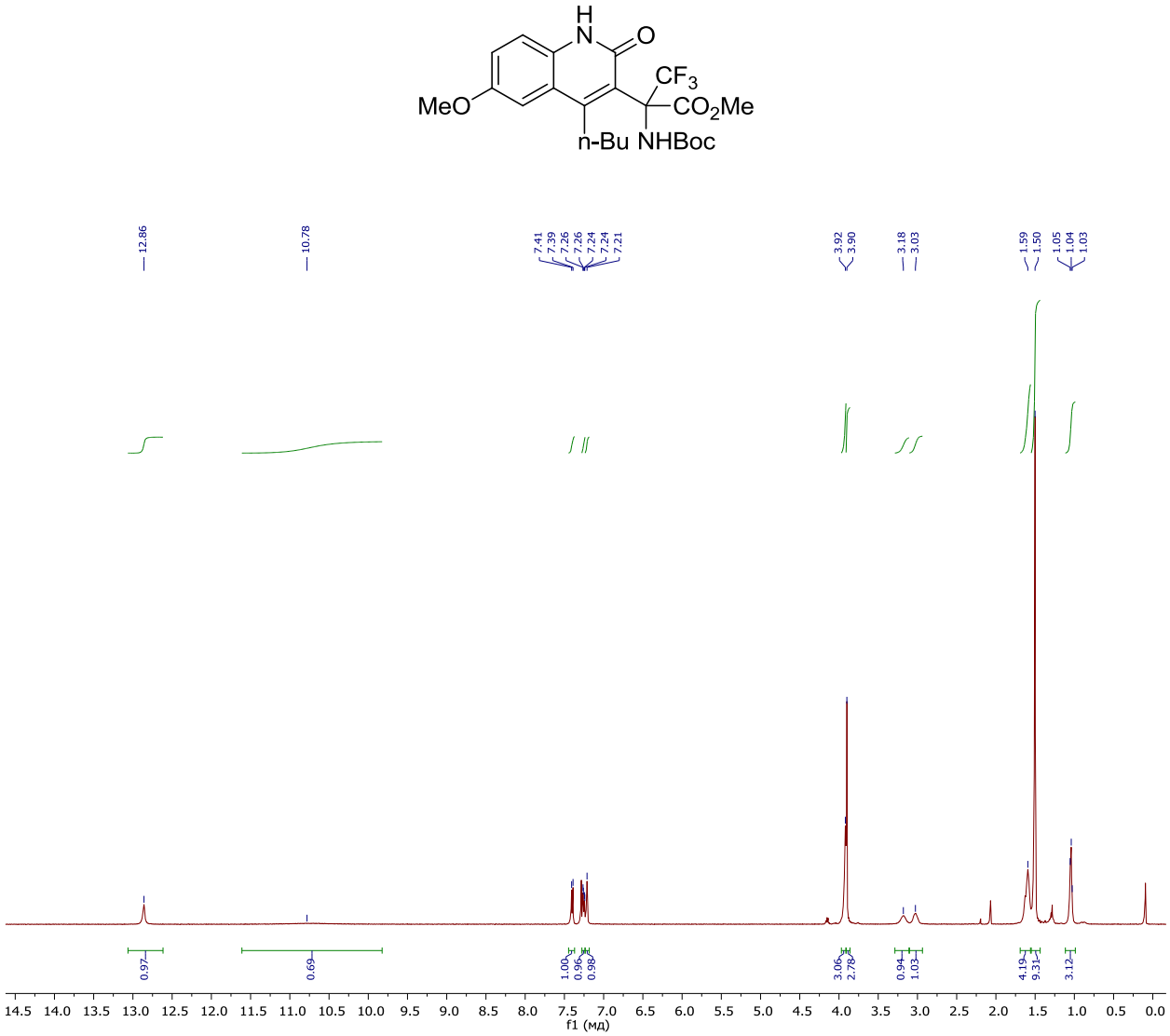
^{1}H NMR spectrum of compound **3v** in $CDCl_3$



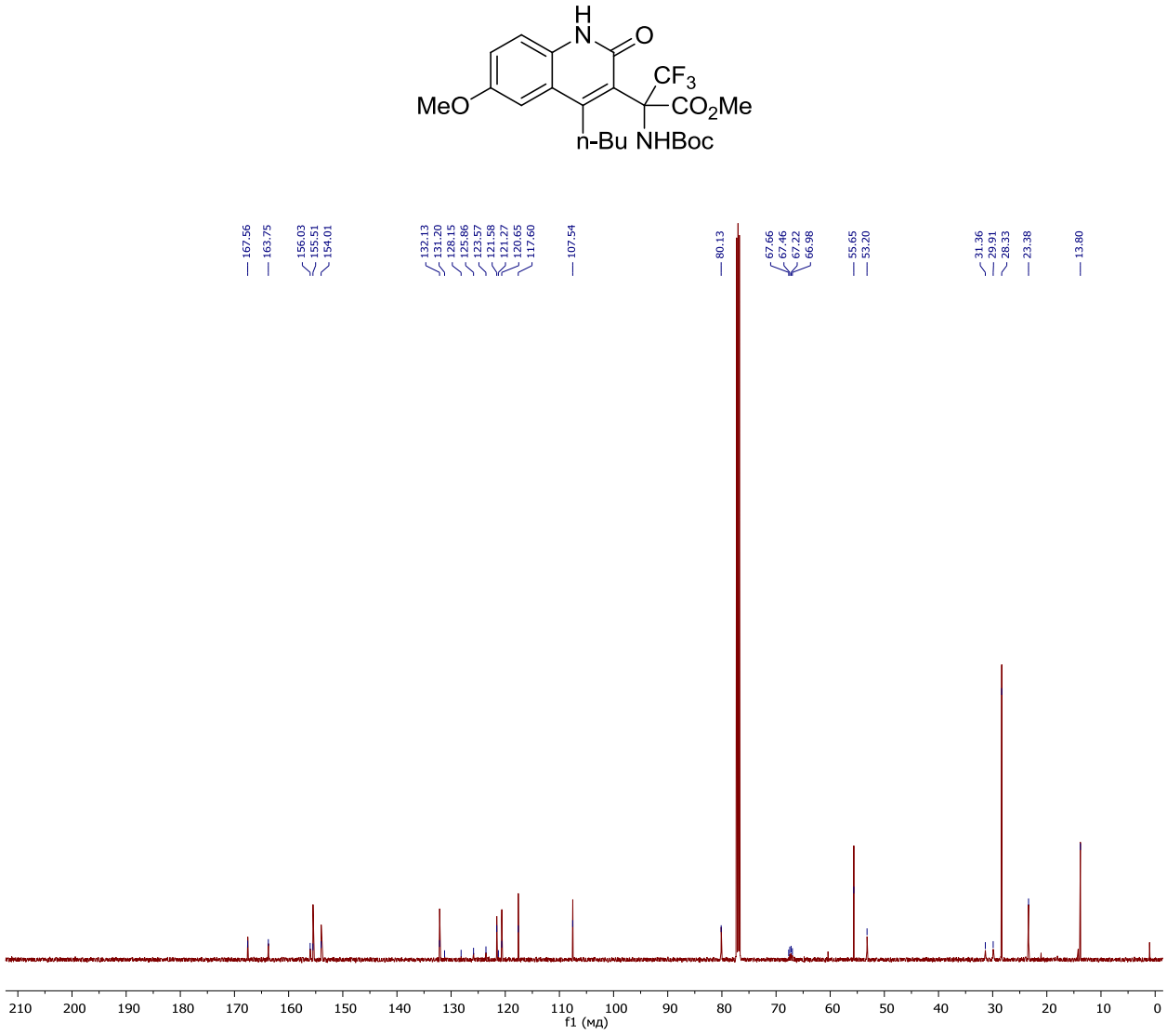
^{13}C NMR spectrum of compound **3v** in $CDCl_3$



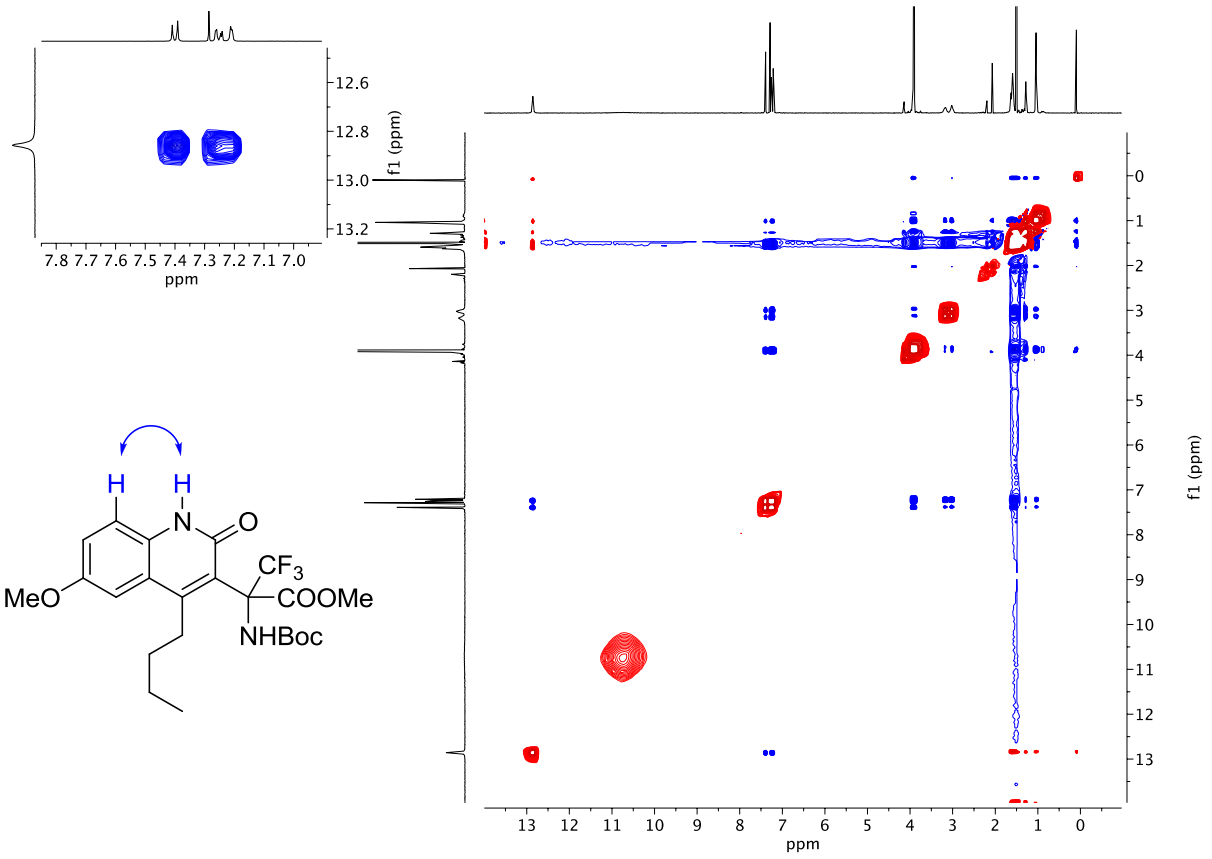
^{1}H-^{1}H NOESY NMR spectrum of compound **3v** in $CDCl_3$



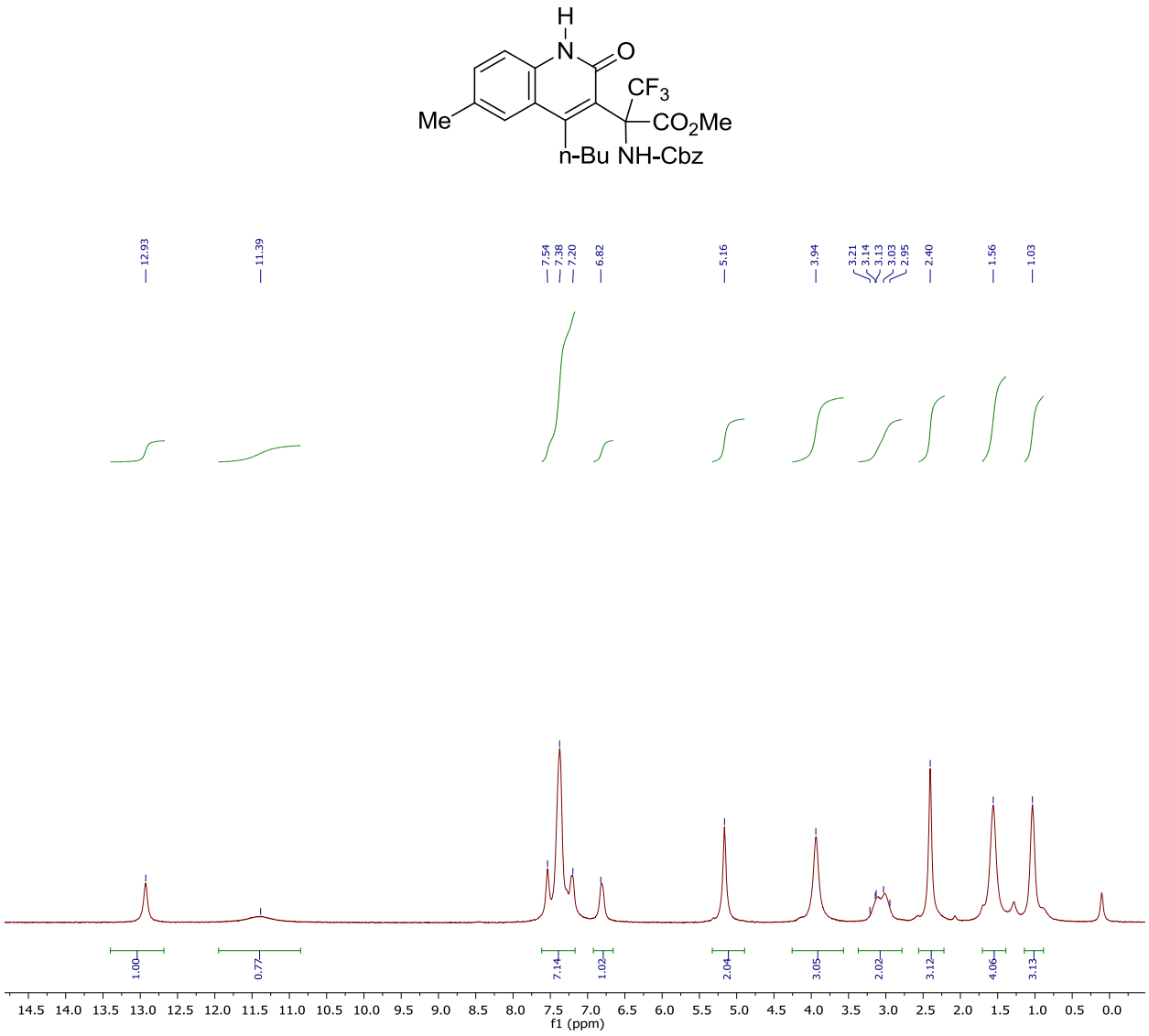
^{1}H NMR spectrum of compound **3w** in $CDCl_3$



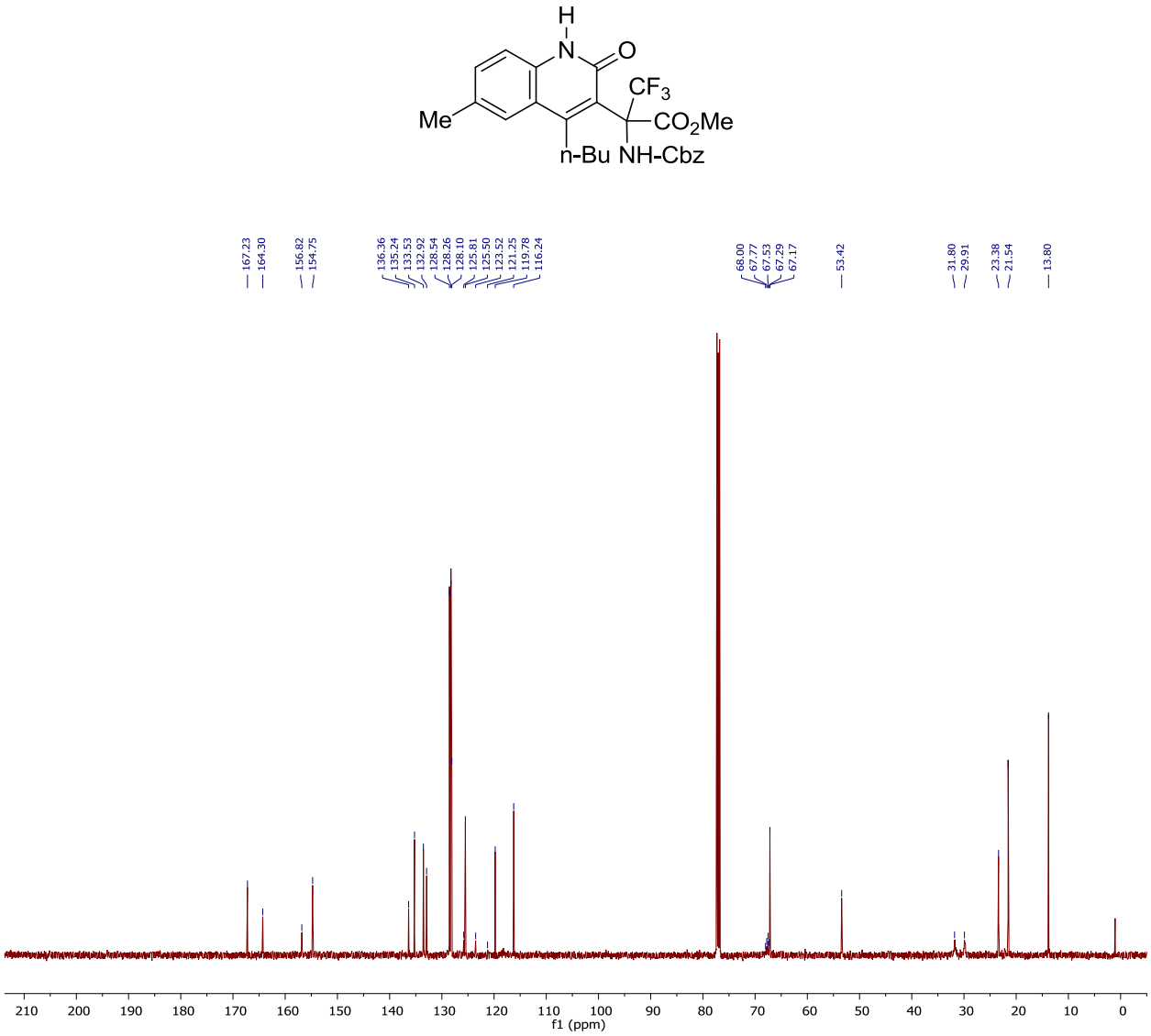
^{13}C NMR spectrum of compound **3w** in $CDCl_3$



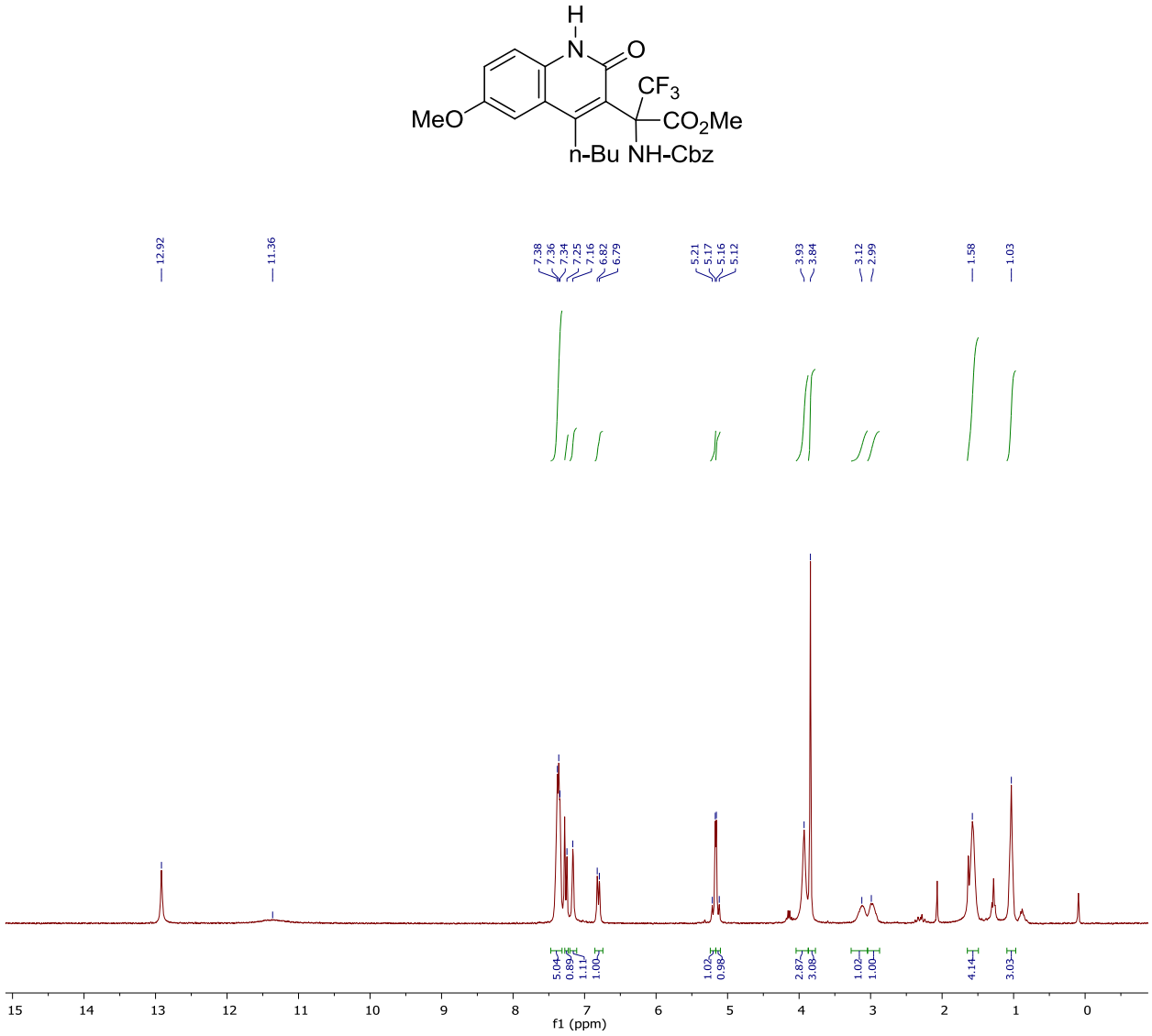
^{1}H-^{1}H NOESY NMR spectrum of compound **3w** in $CDCl_3$



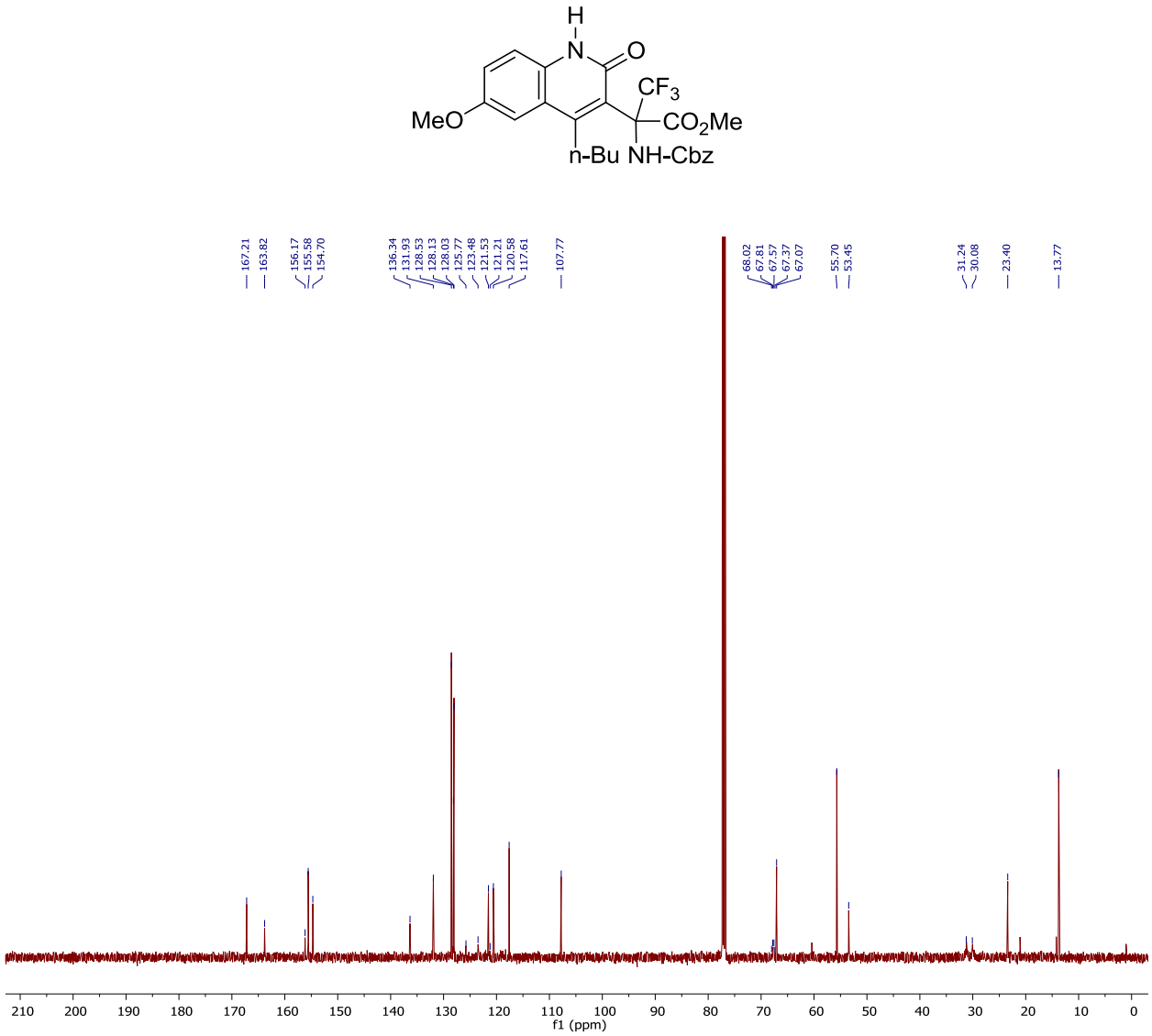
^{1}H NMR spectrum of compound **3x** in $CDCl_3$



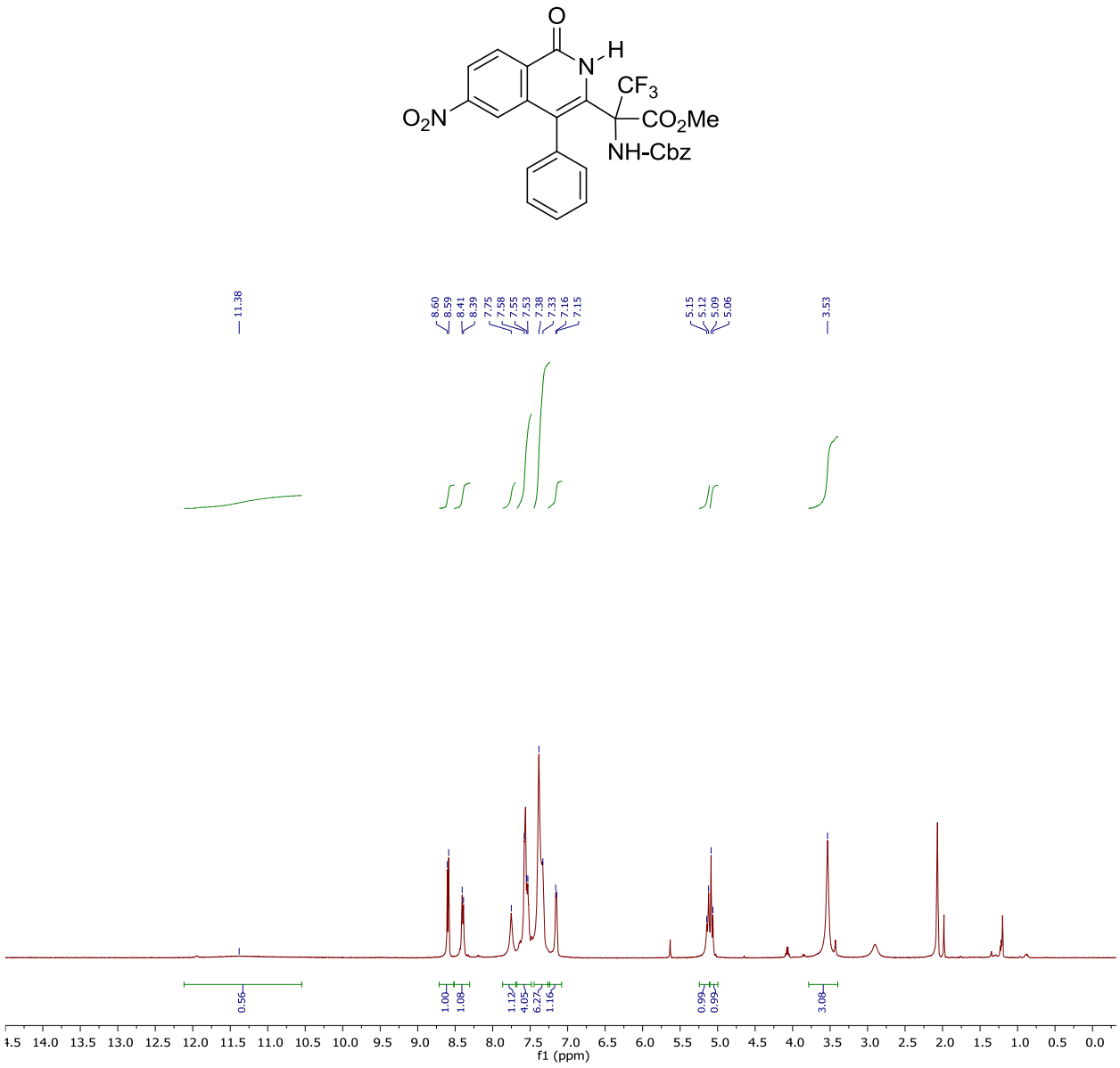
^{13}C NMR spectrum of compound **3x** in $CDCl_3$



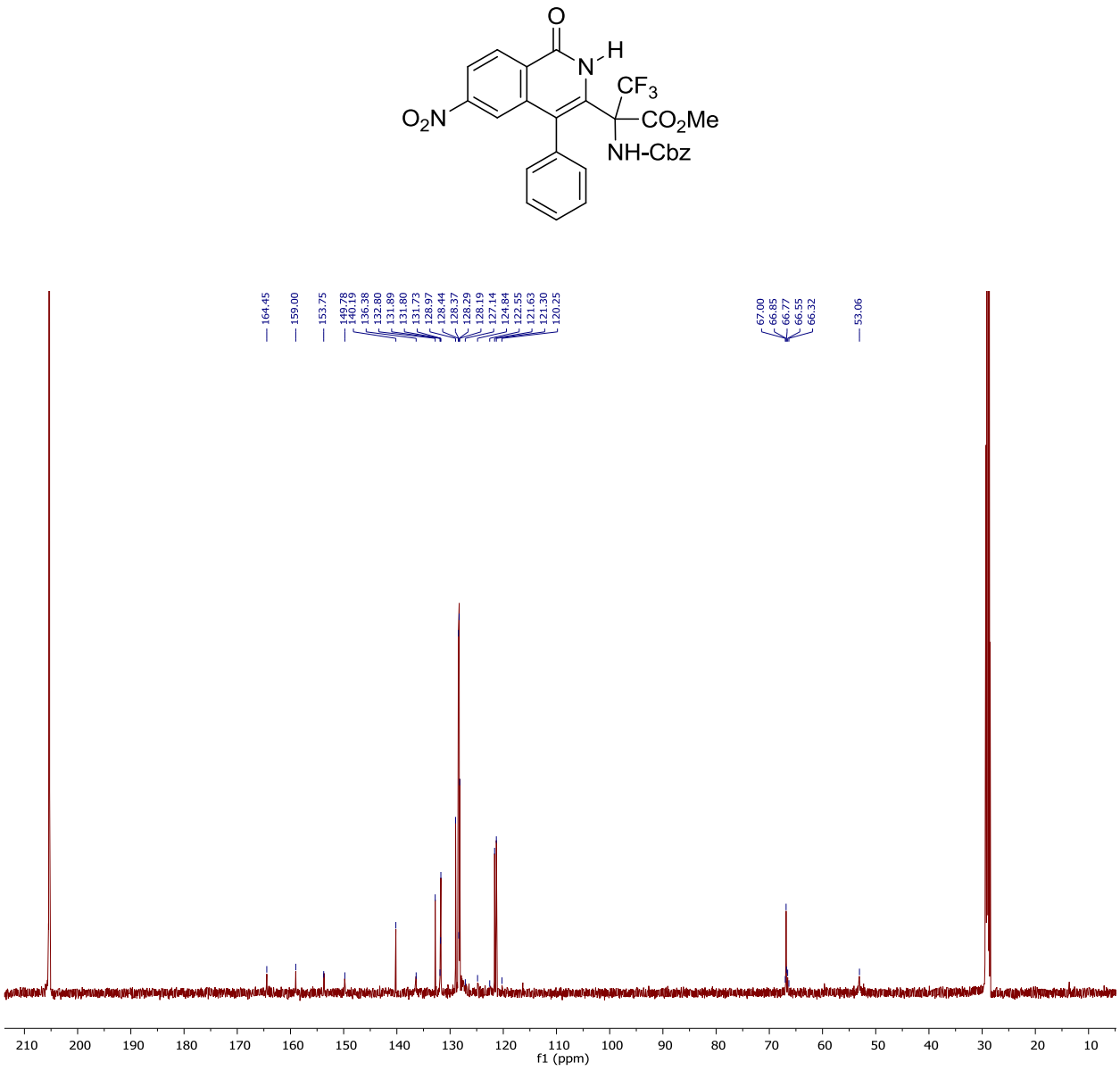
^{1}H NMR spectrum of compound **3y** in $CDCl_3$



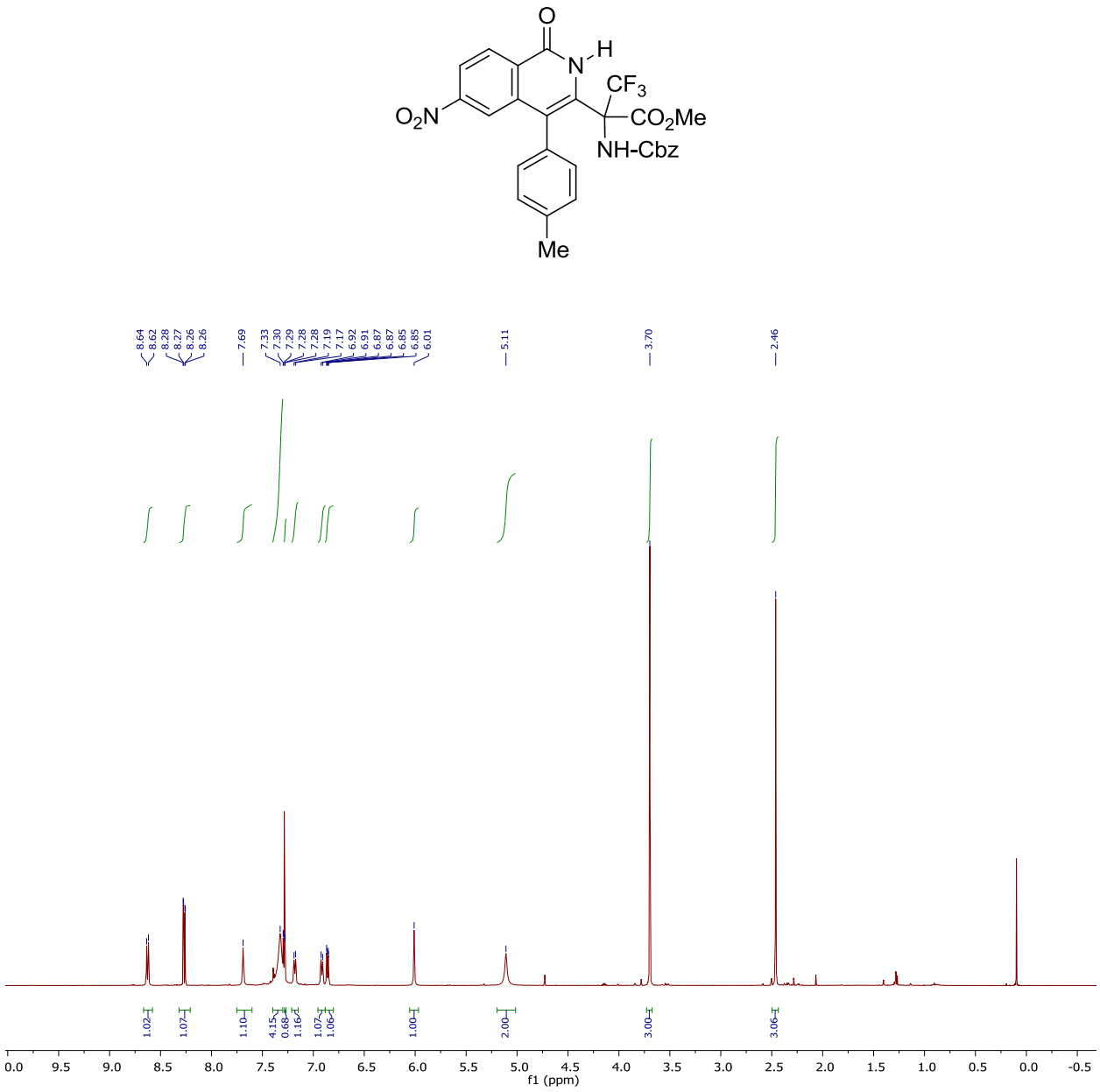
^{13}C NMR spectrum of compound **3y** in $CDCl_3$



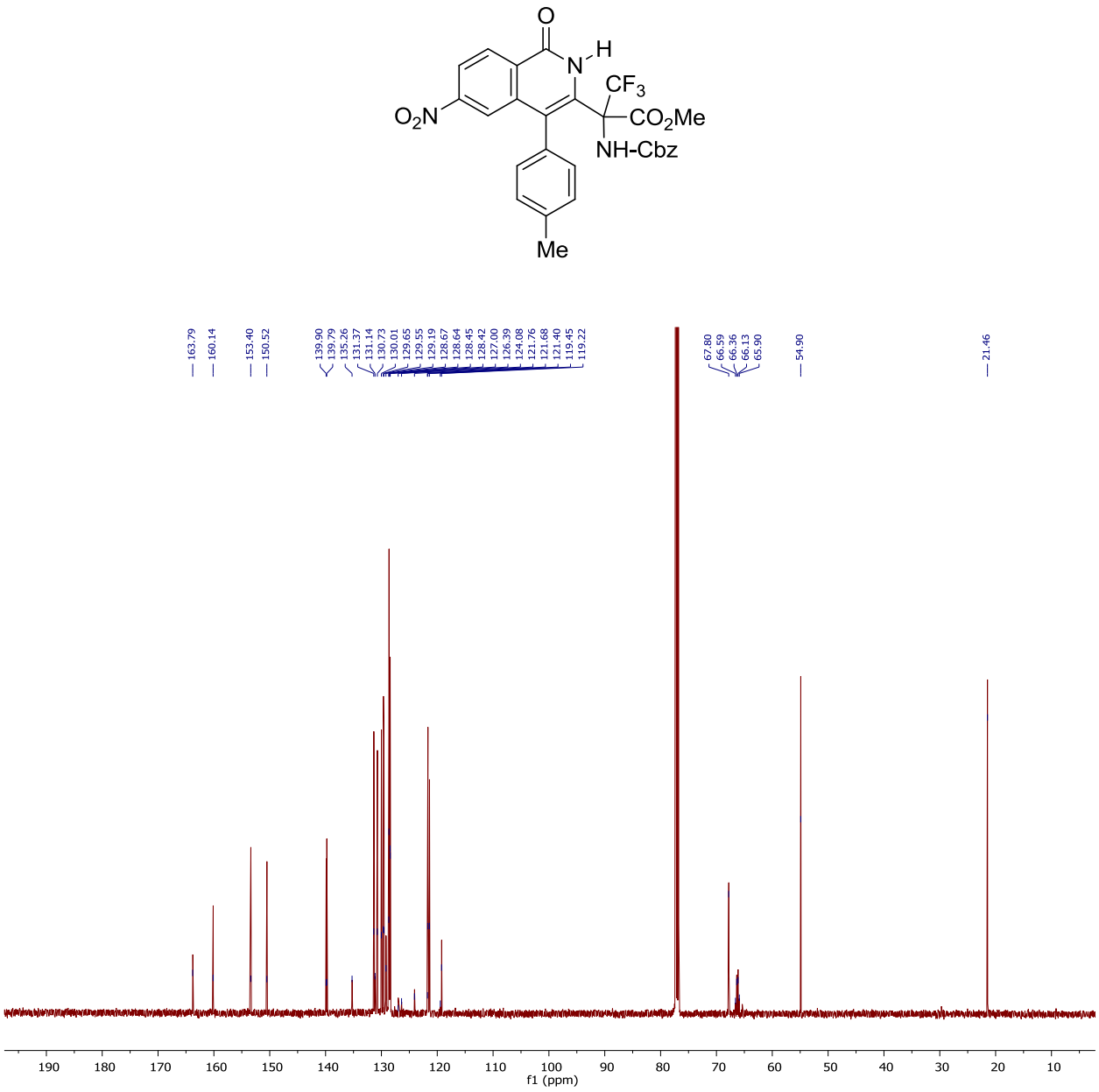
^{1}H NMR spectrum of compound **4a** in acetone-d_6



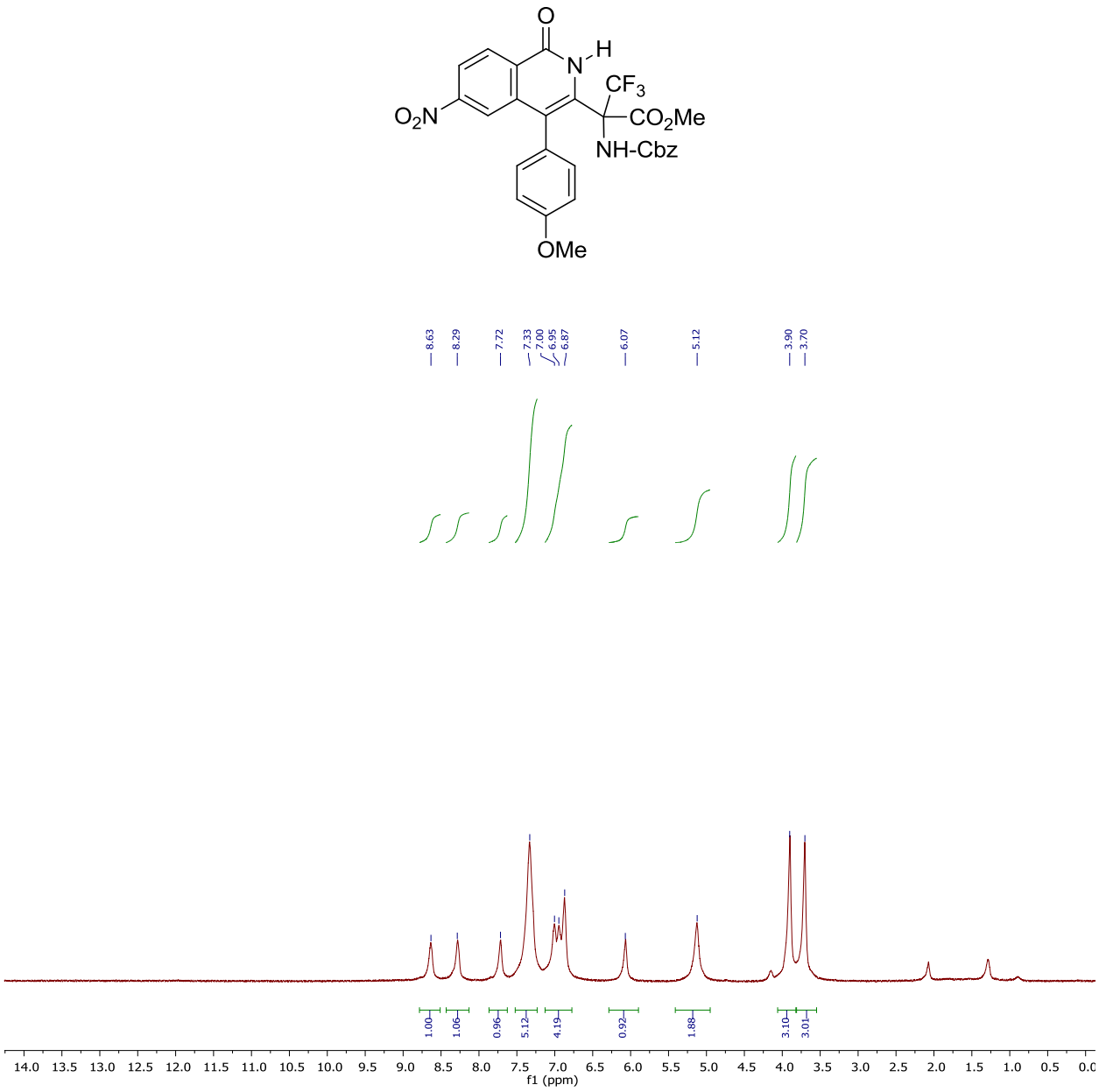
^{13}C NMR spectrum of compound **4a** in acetone-d_6



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



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



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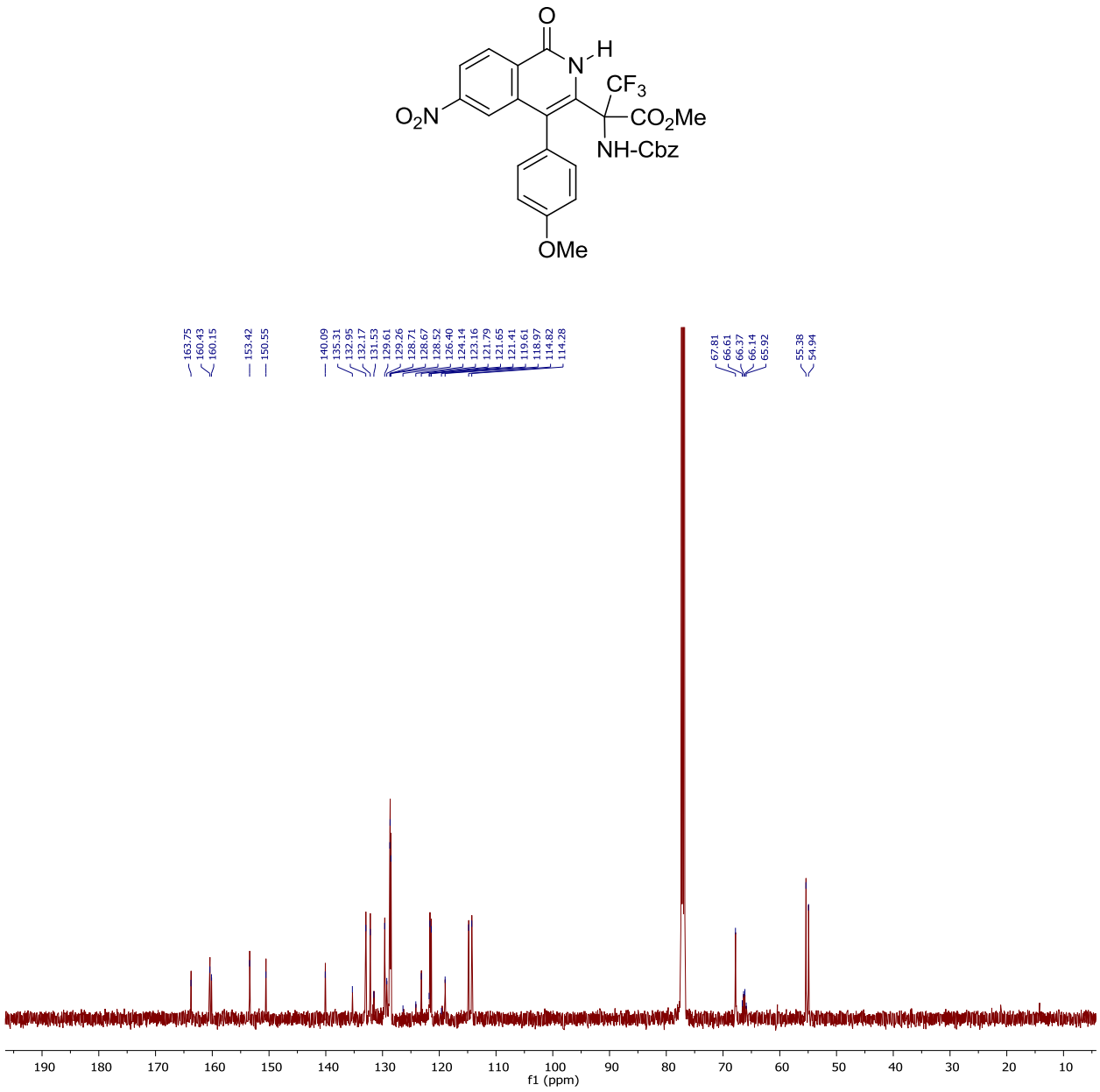
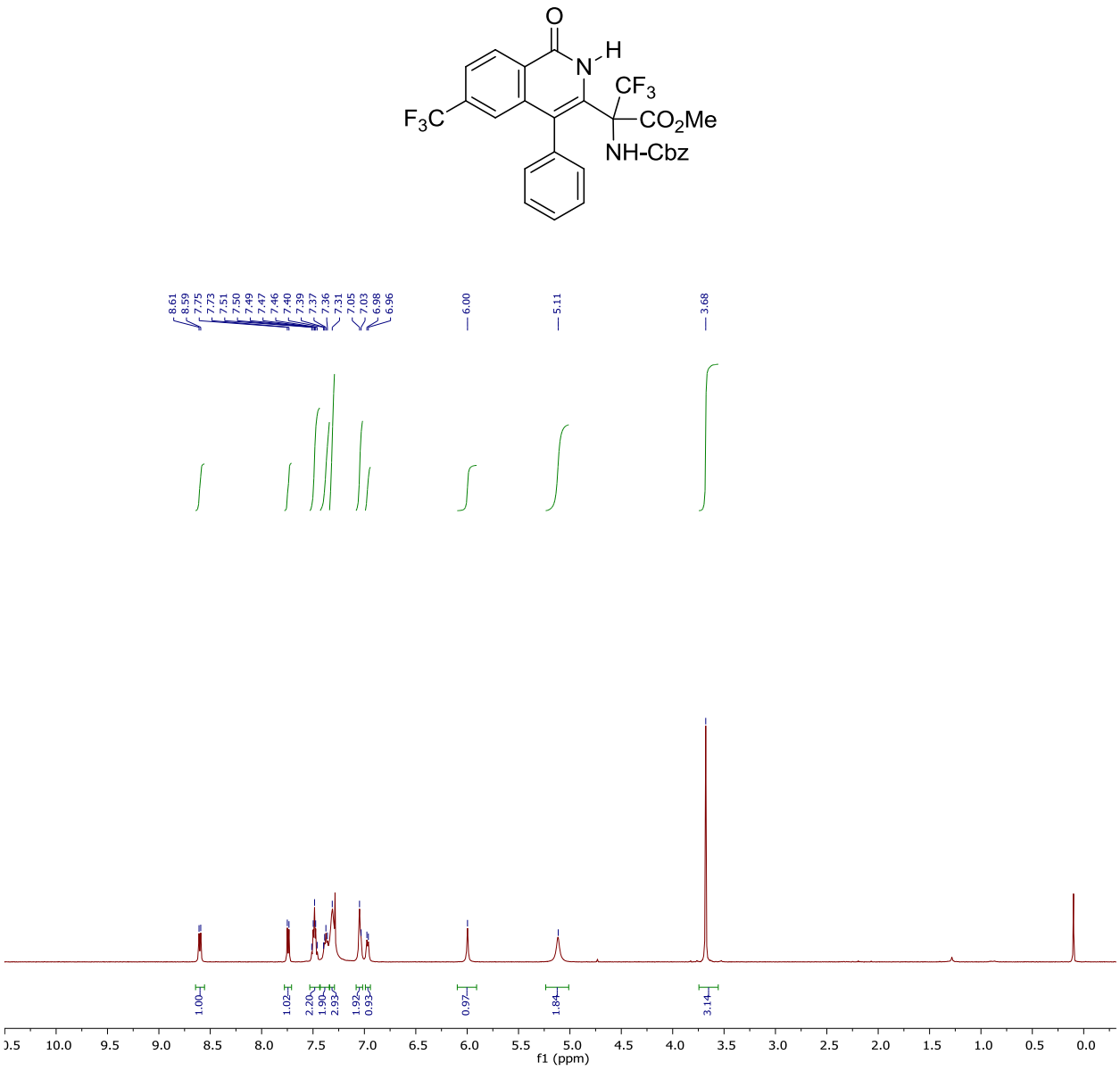


^{13}C NMR spectrum of compound **4c** in $CDCl_3$



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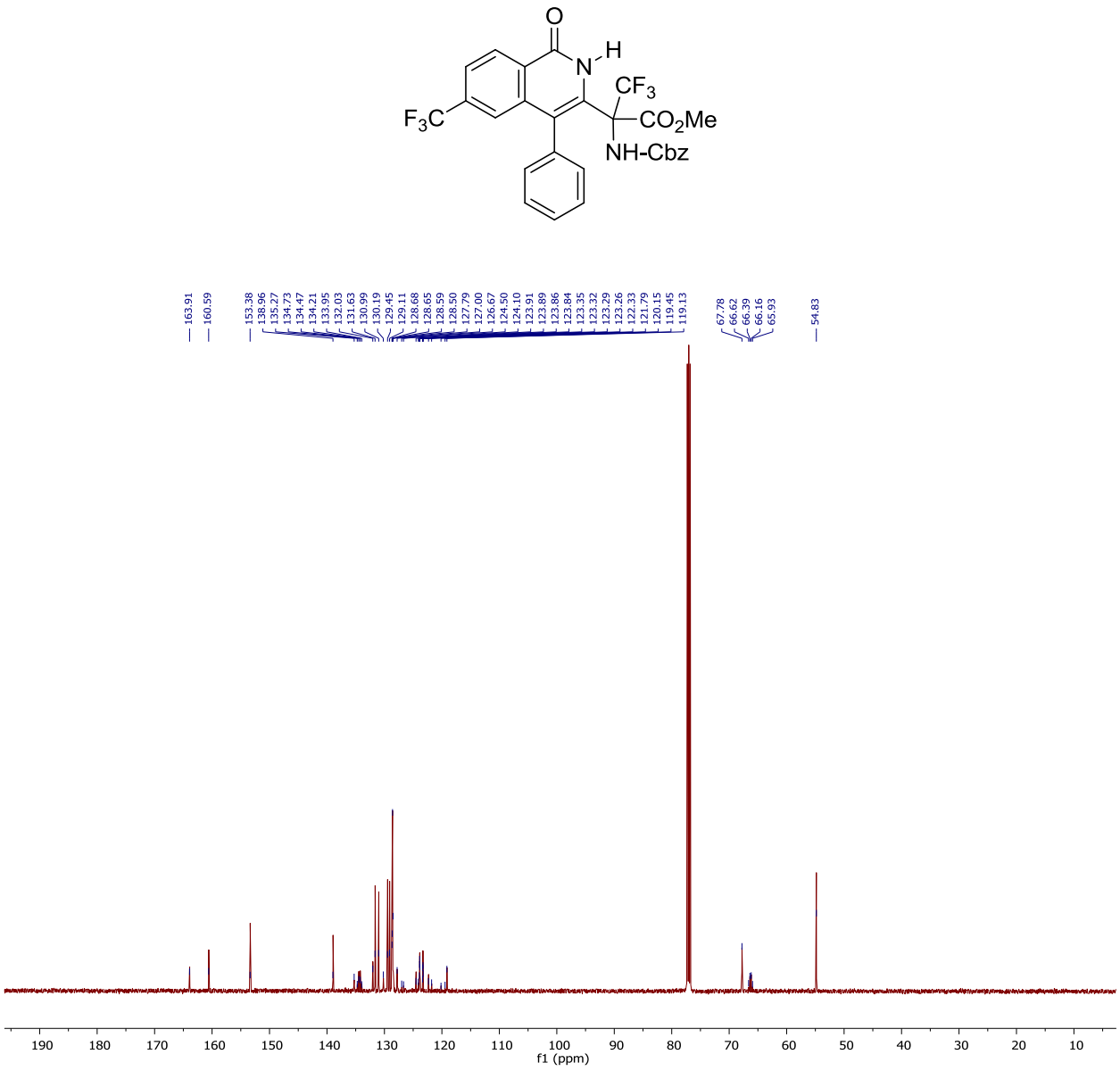
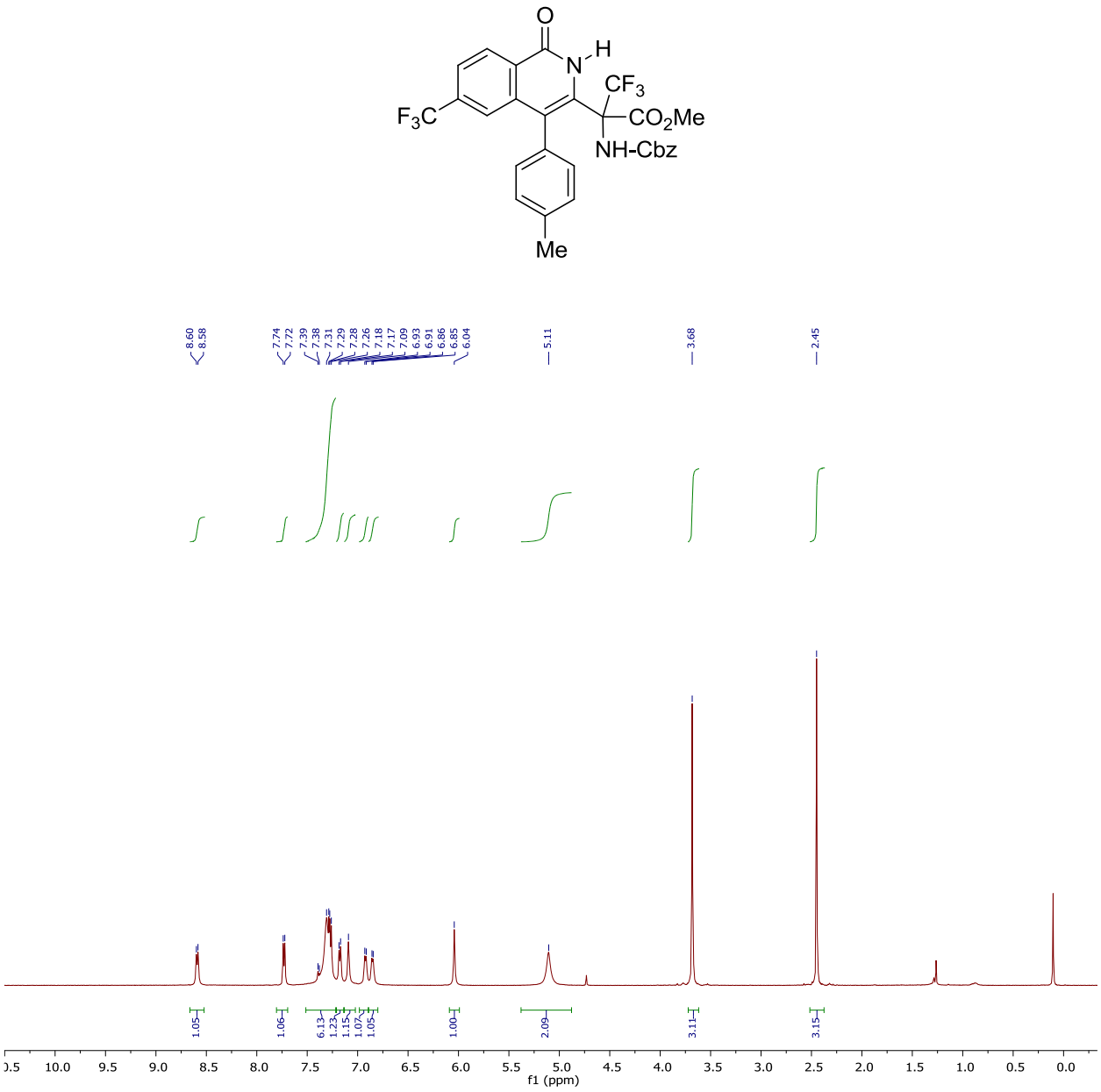
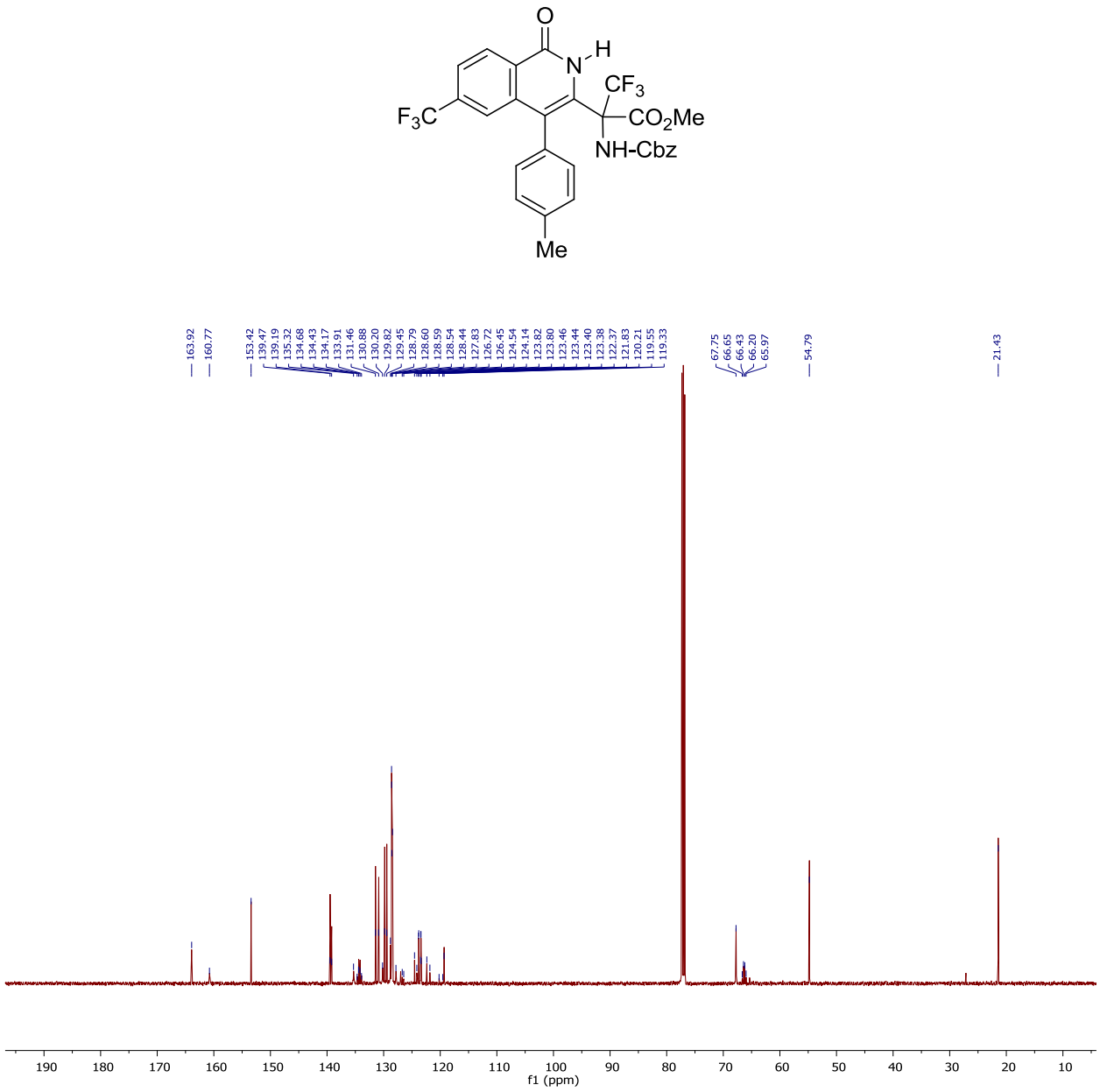


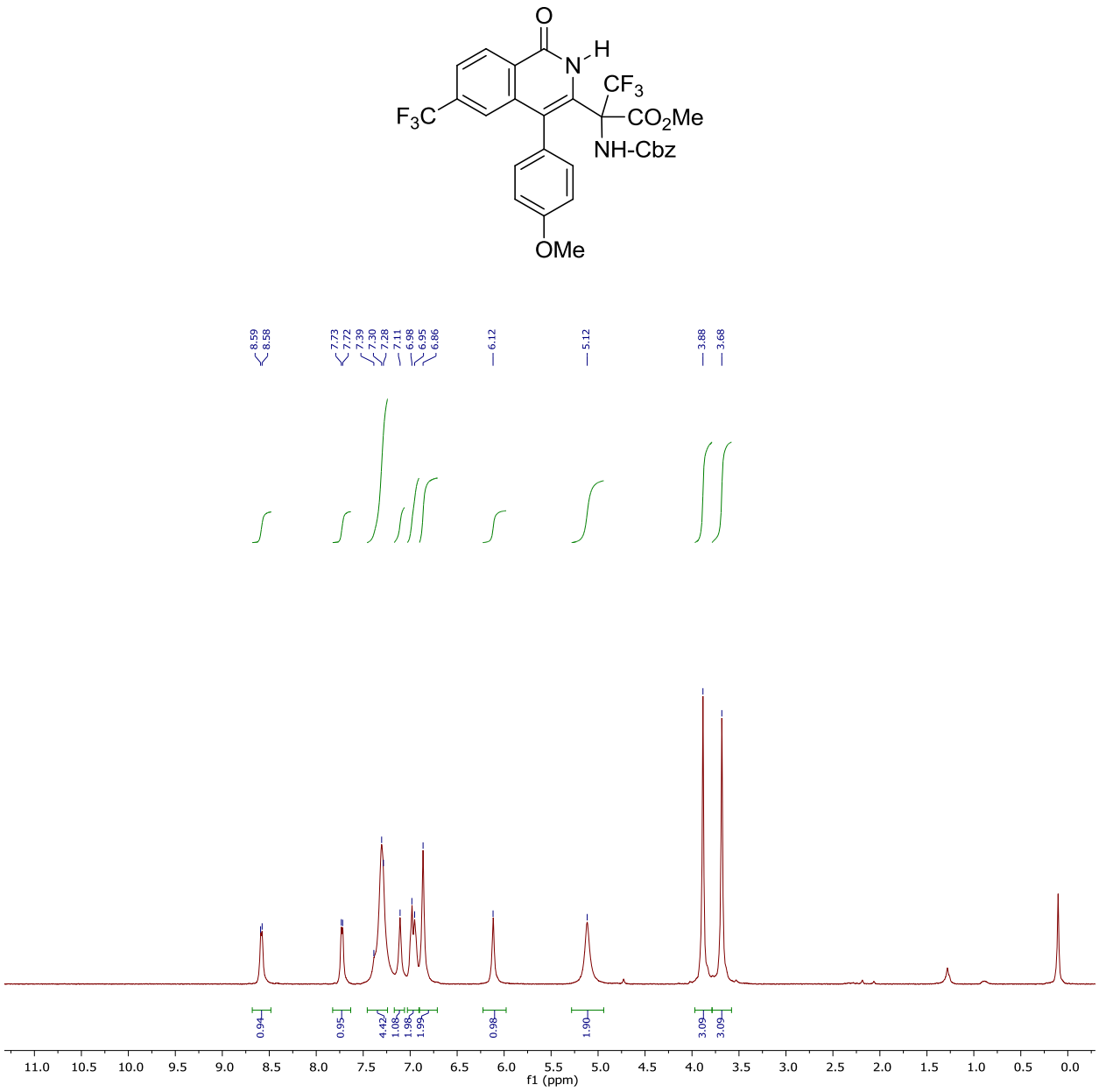
^{13}C NMR spectrum of compound **4d** in $CDCl_3$



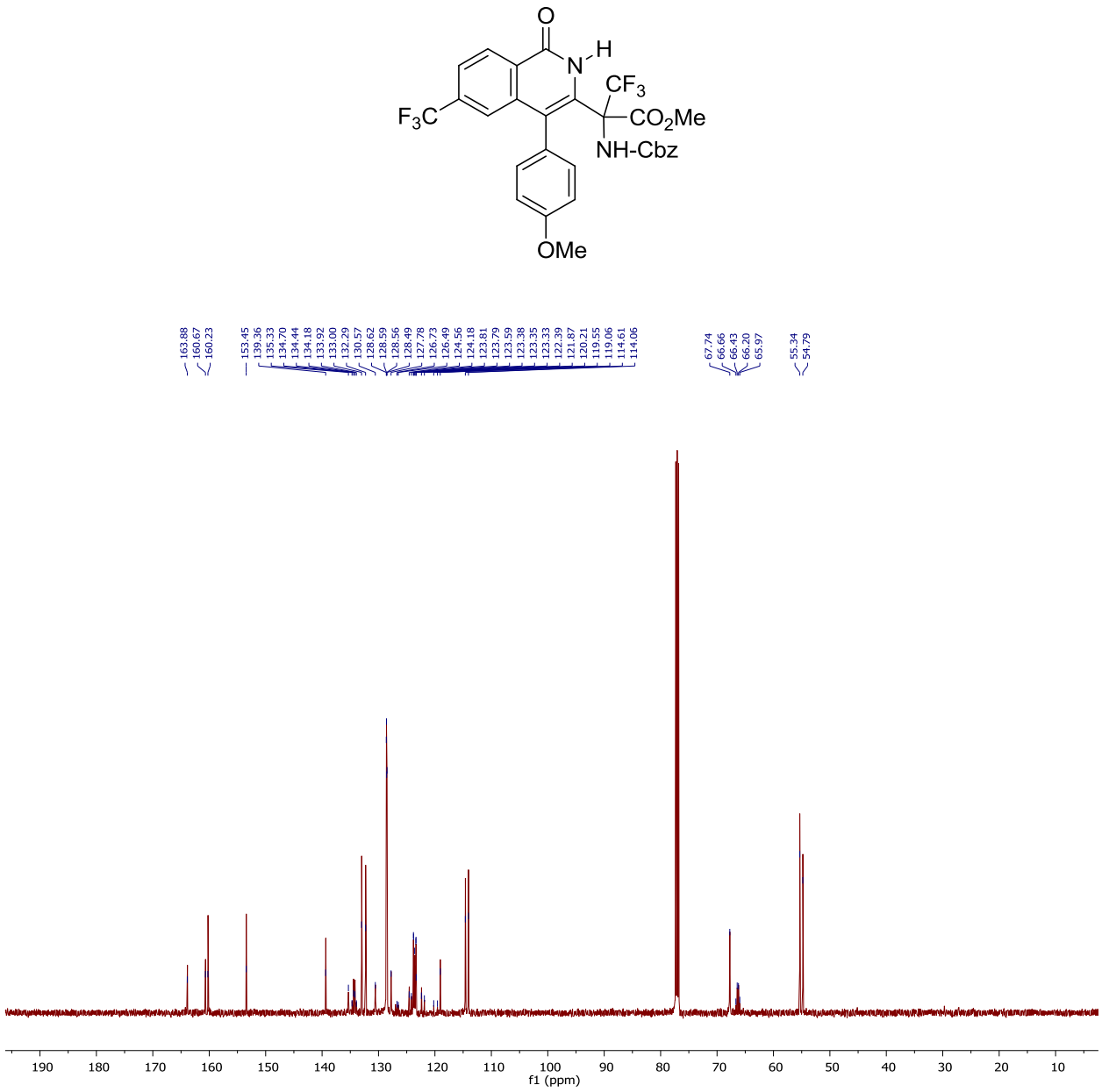
^{1}H NMR spectrum of compound **4e** in $CDCl_3$



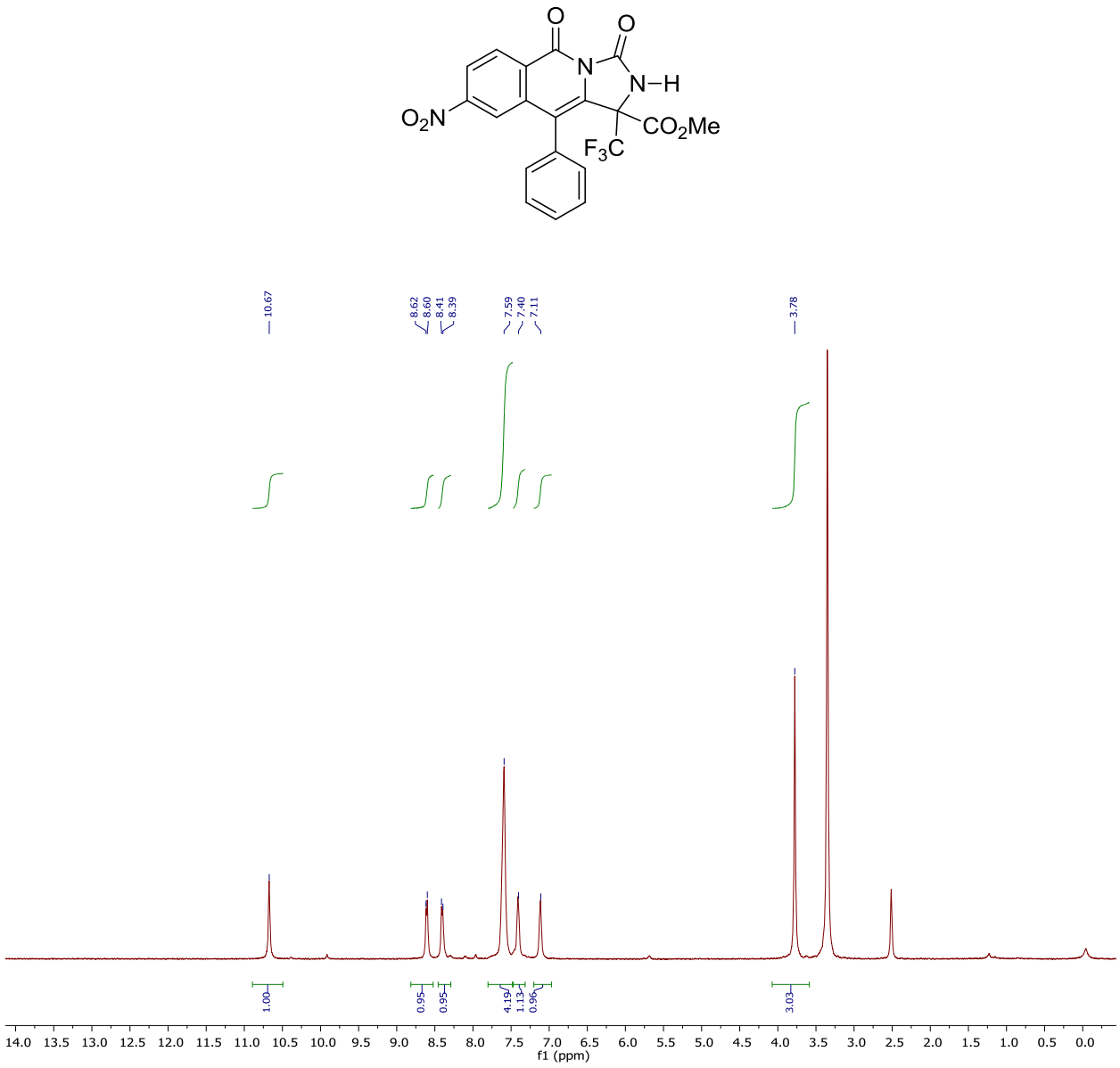
^{13}C NMR spectrum of compound **4e** in $CDCl_3$



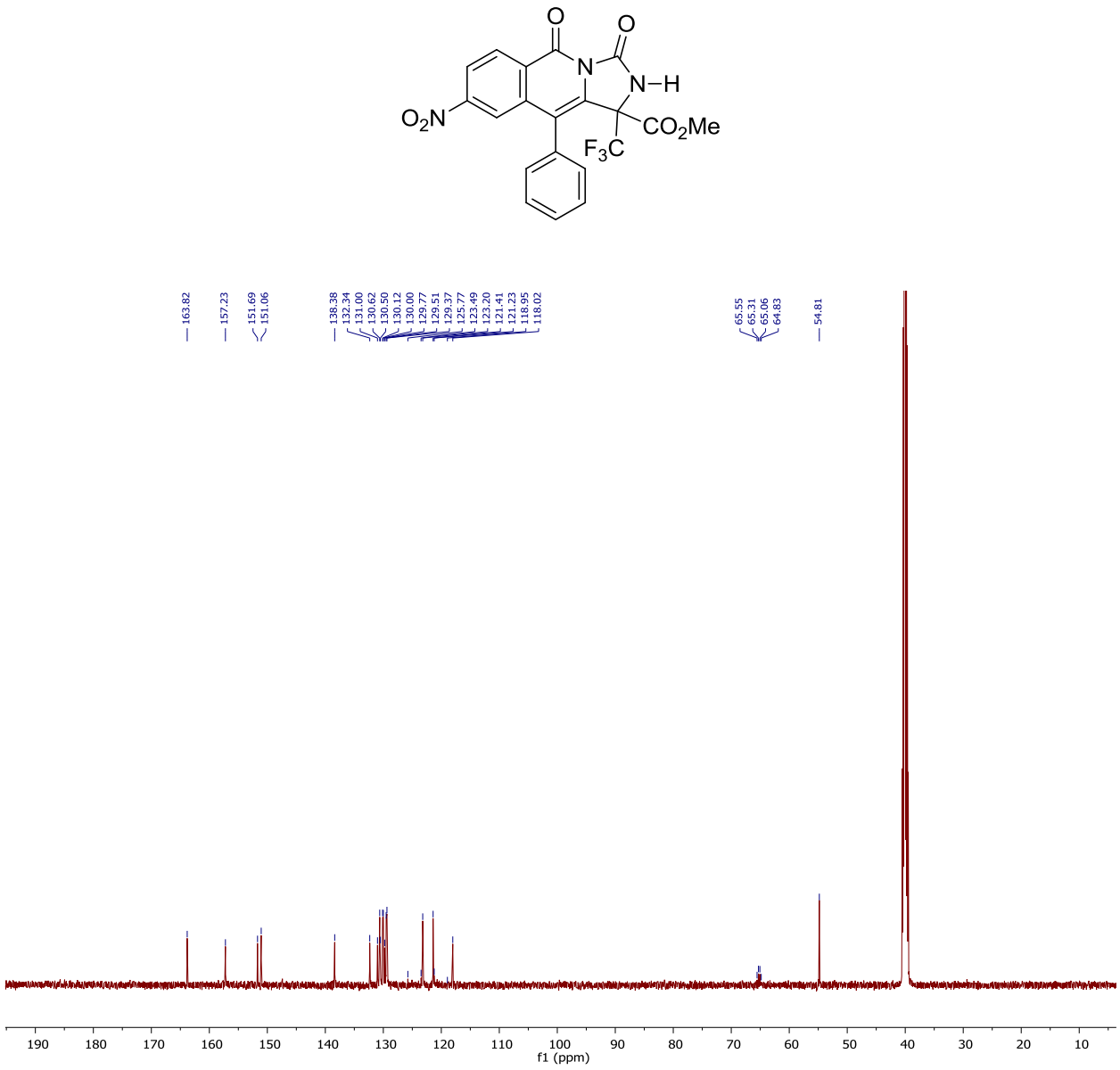
^{1}H NMR spectrum of compound **4f** in $CDCl_3$



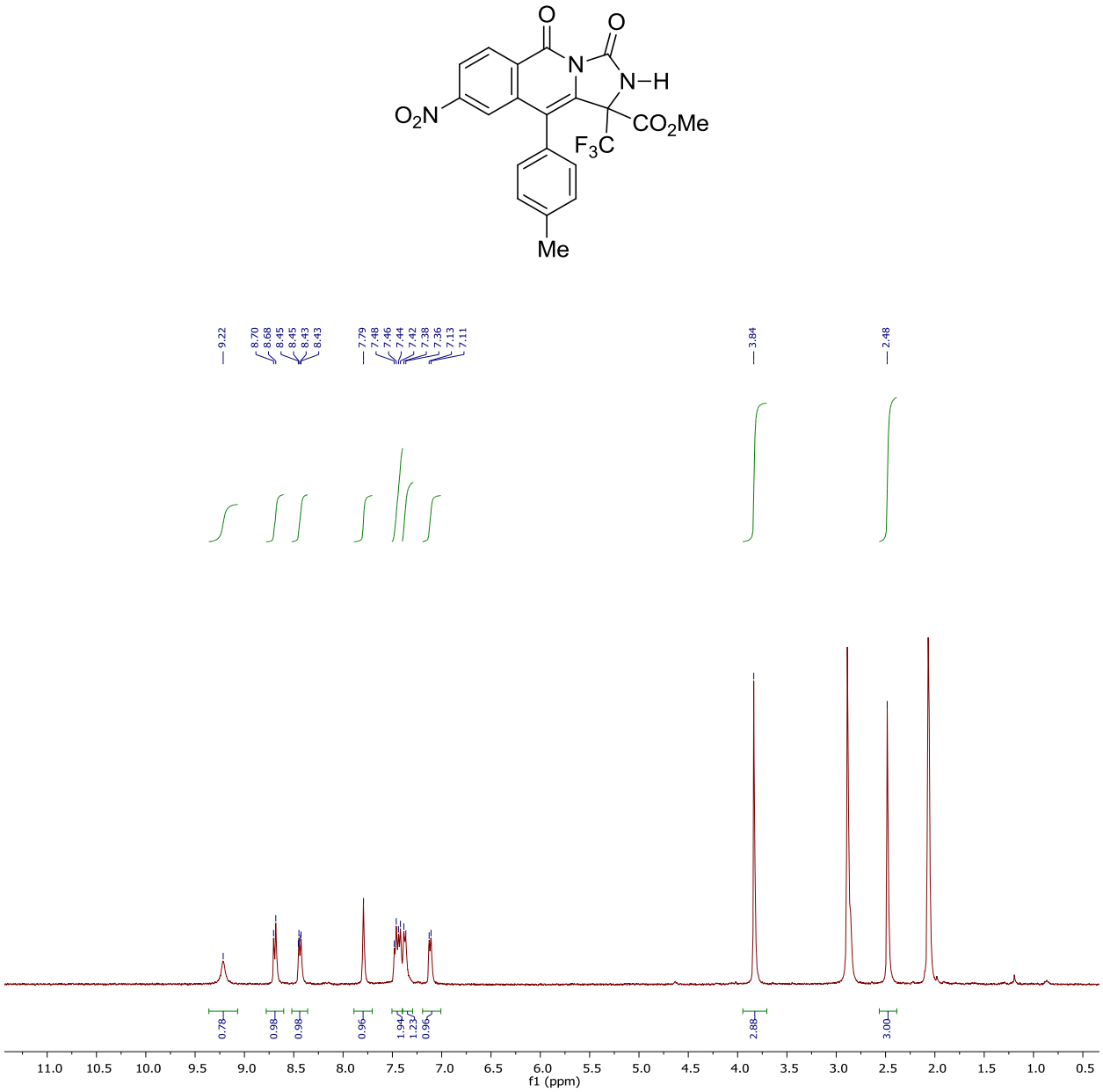
^{13}C NMR spectrum of compound **4f** in $CDCl_3$



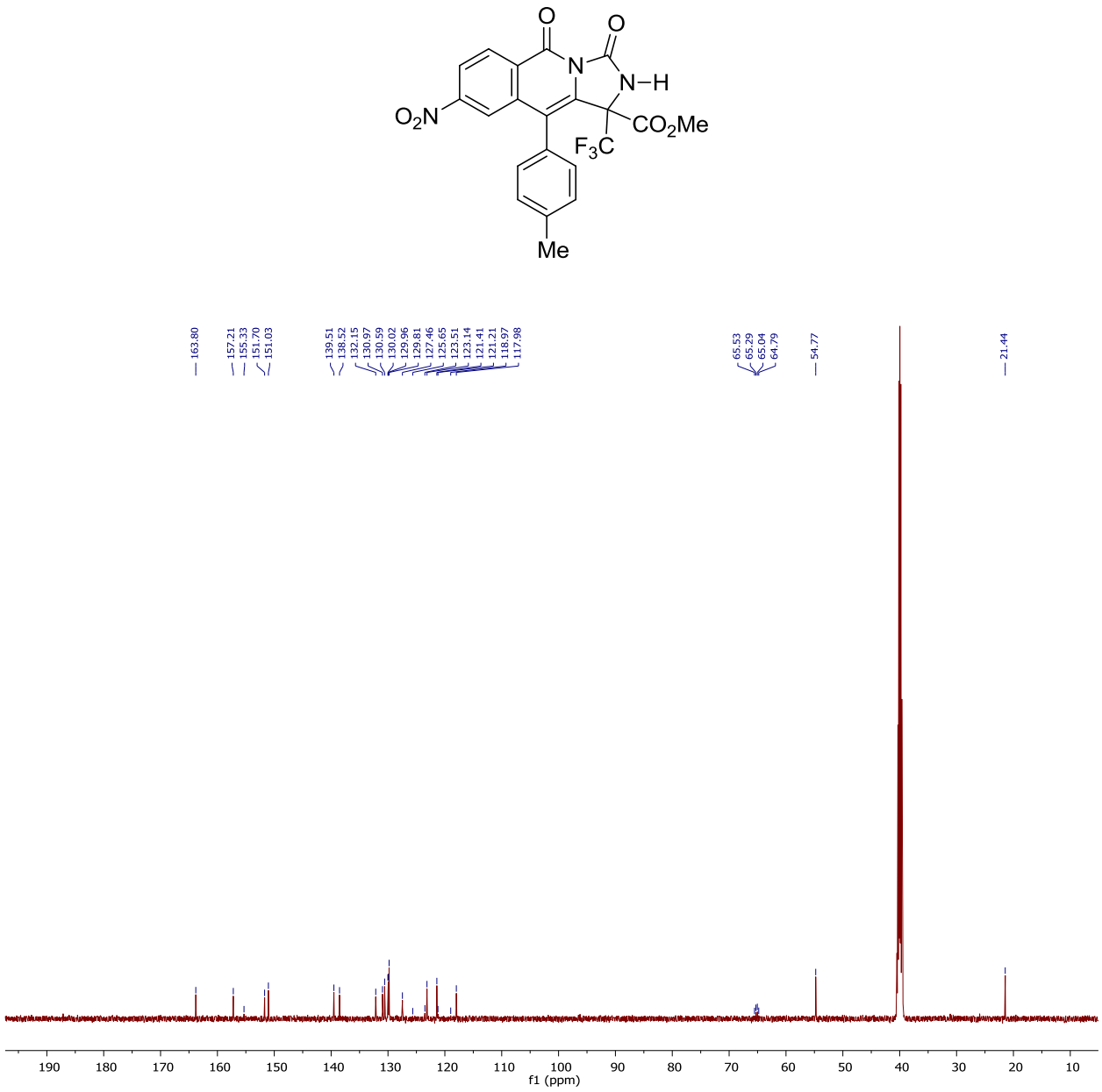
^{1}H NMR spectrum of compound **5a** in DMSO-*d*$_6$



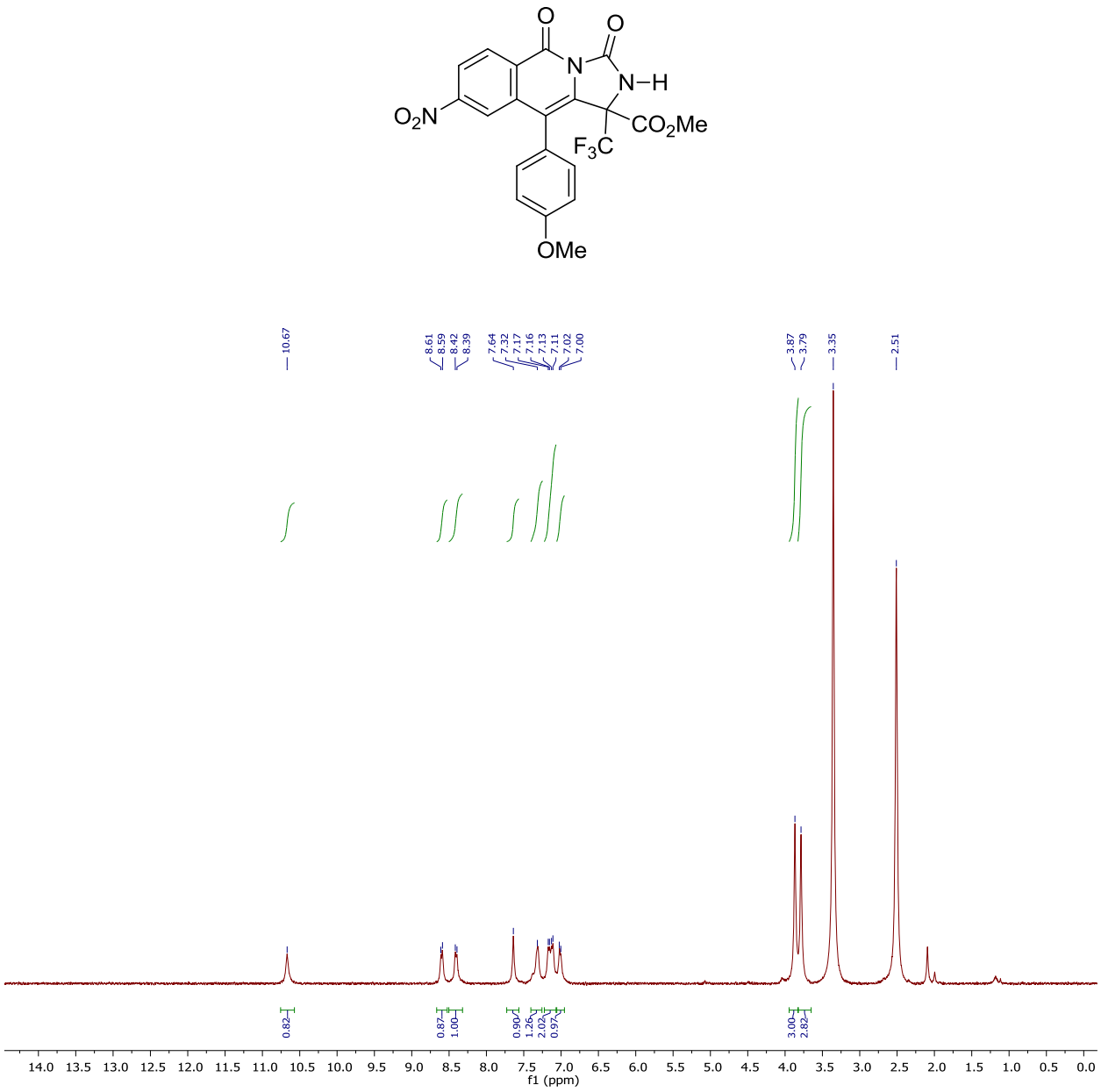
^{13}C NMR spectrum of compound **5a** in DMSO-d_6



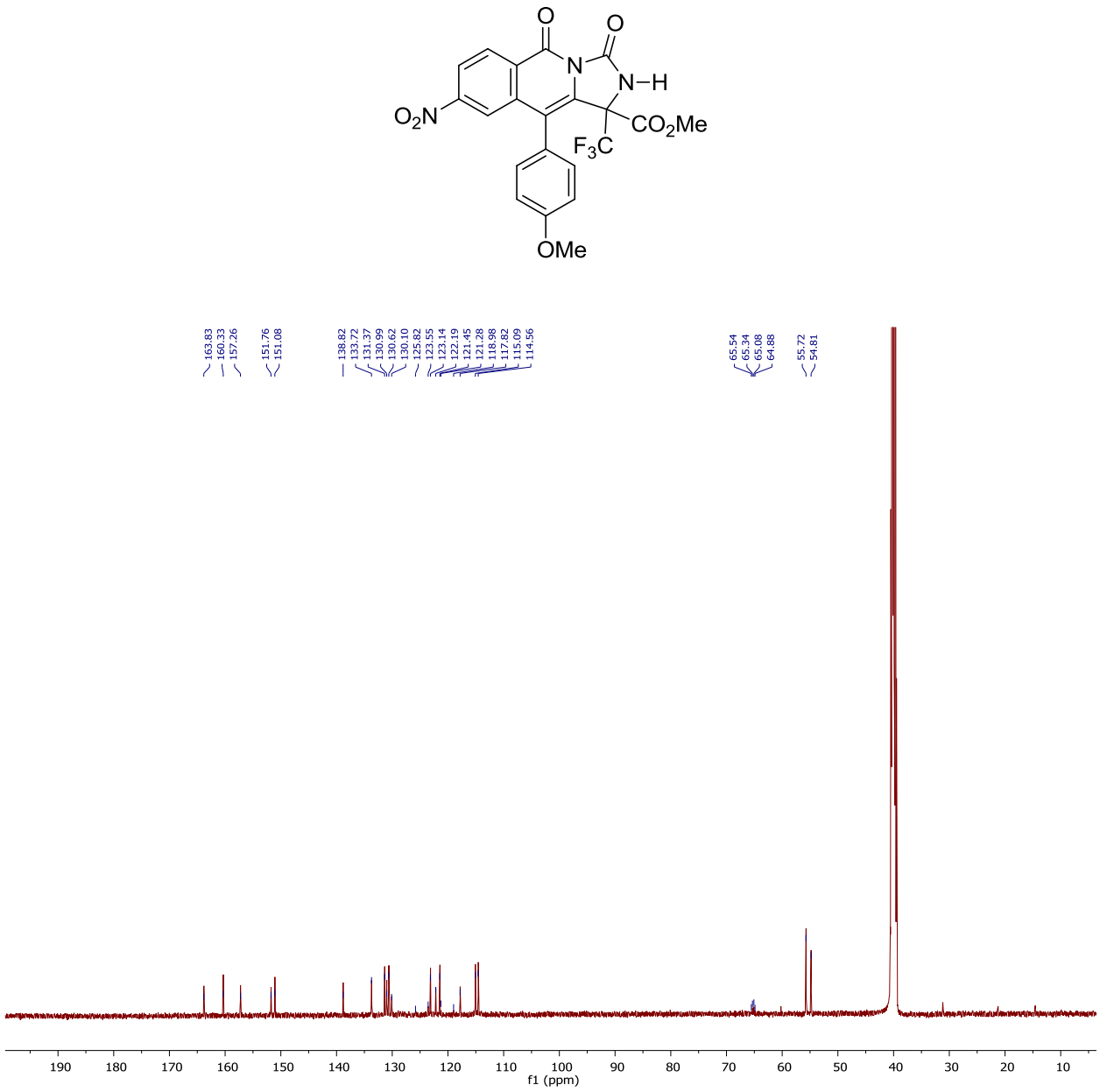
^{1}H NMR spectrum of compound **5b** in acetone-d_6



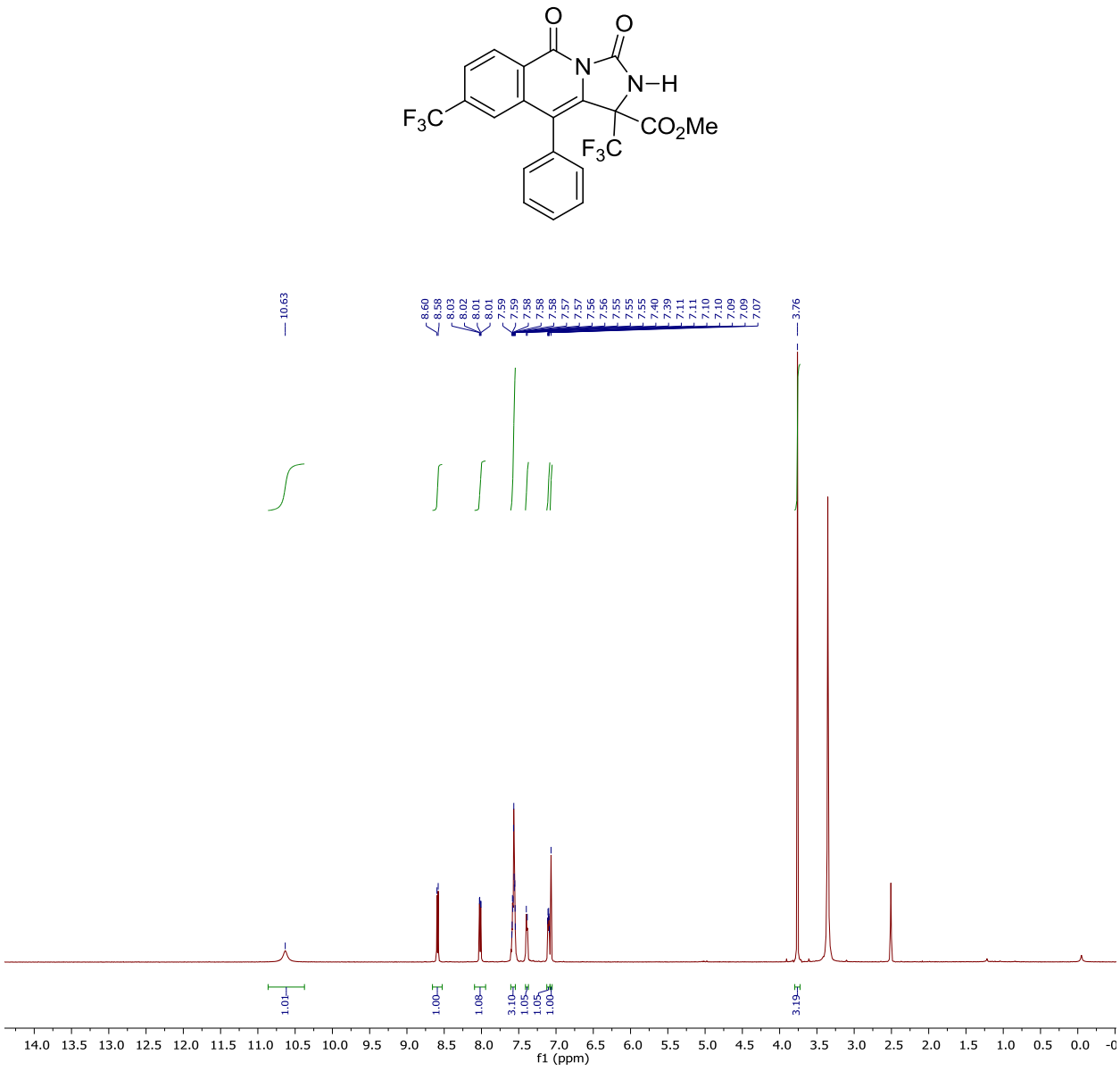
^{13}C NMR spectrum of compound **5b** in DMSO-d_6



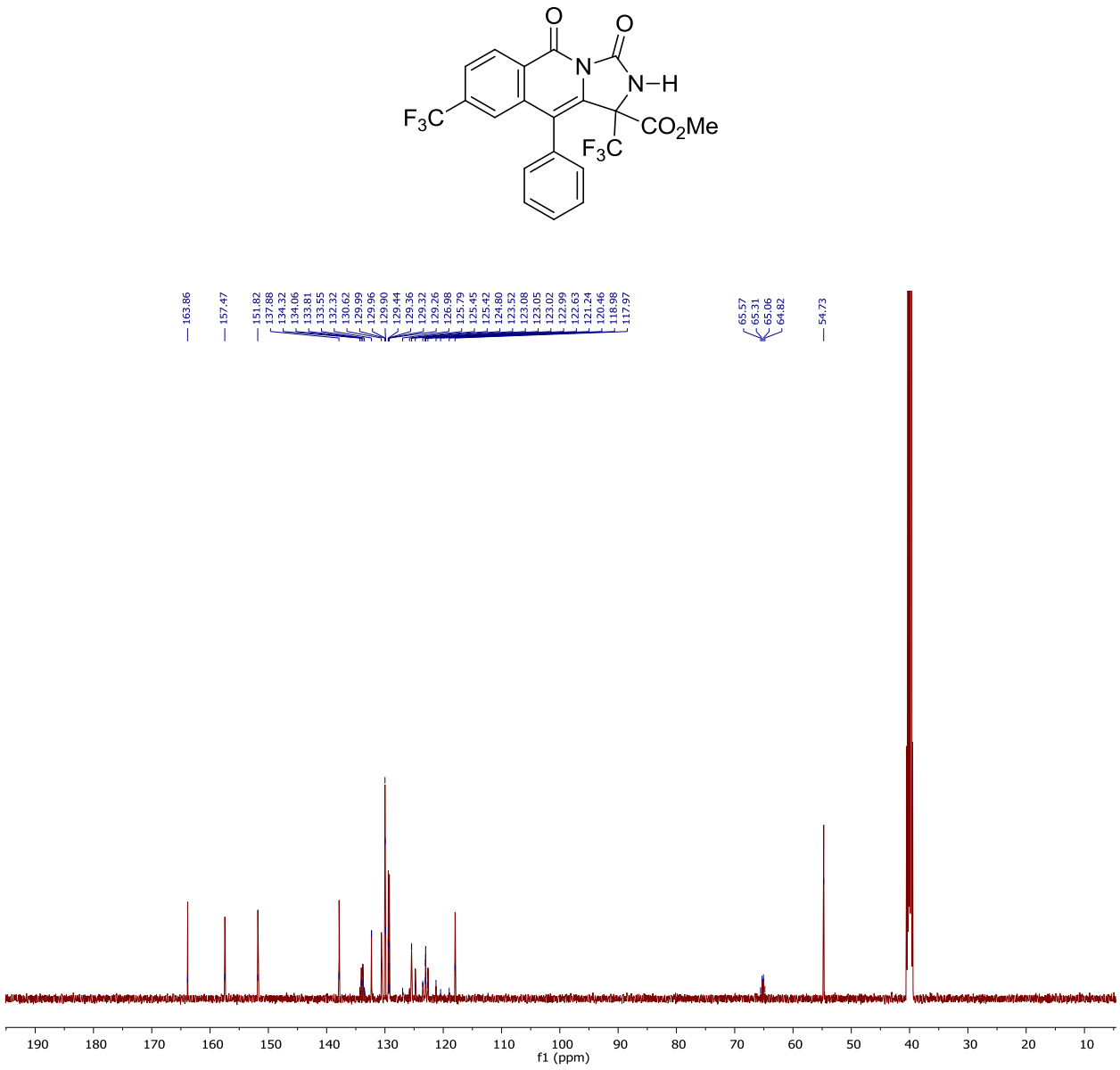
^{1}H NMR spectrum of compound **5c** in DMSO-d_6



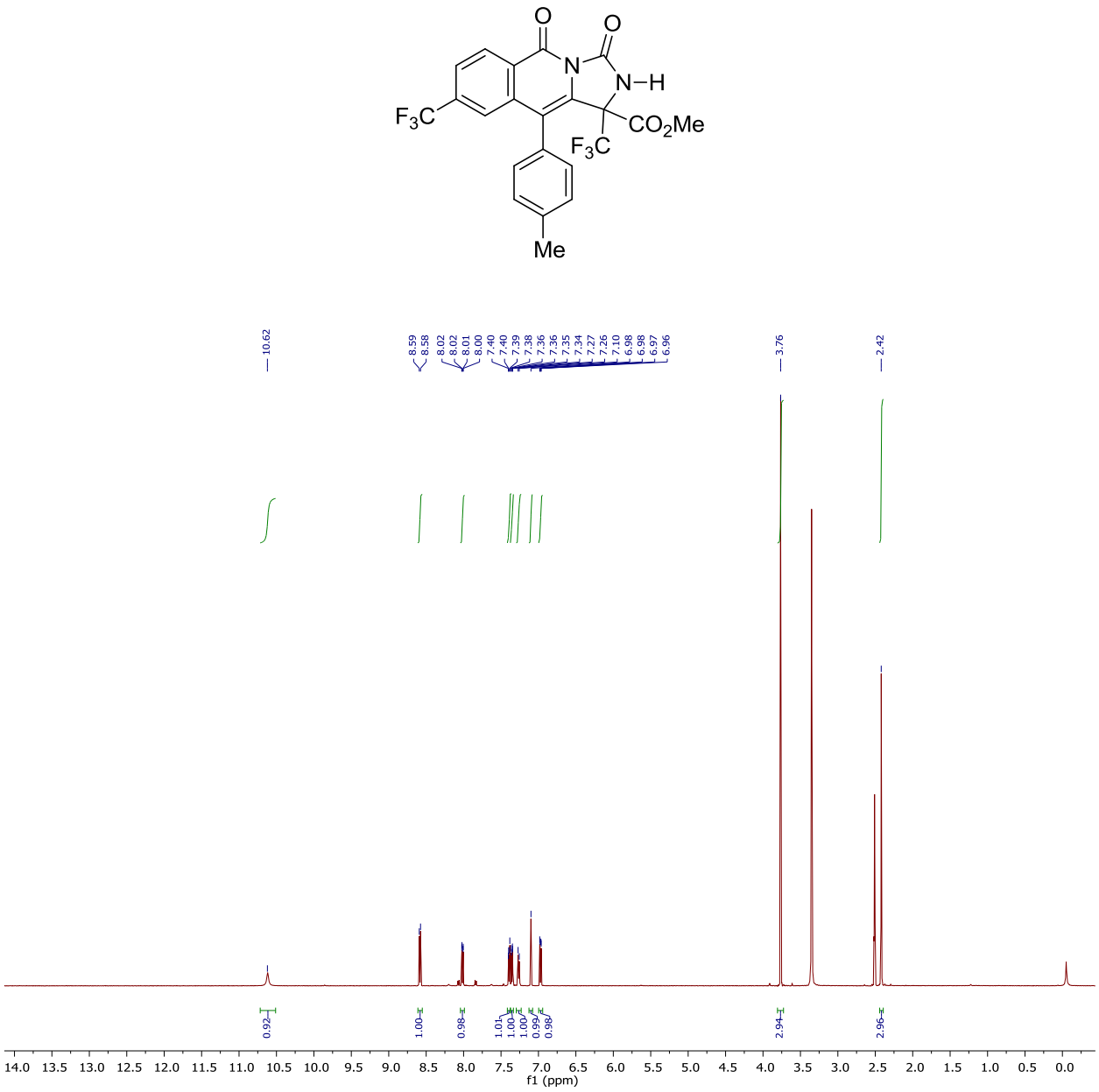
^{13}C NMR spectrum of compound **5c** in DMSO-*d*$_6$



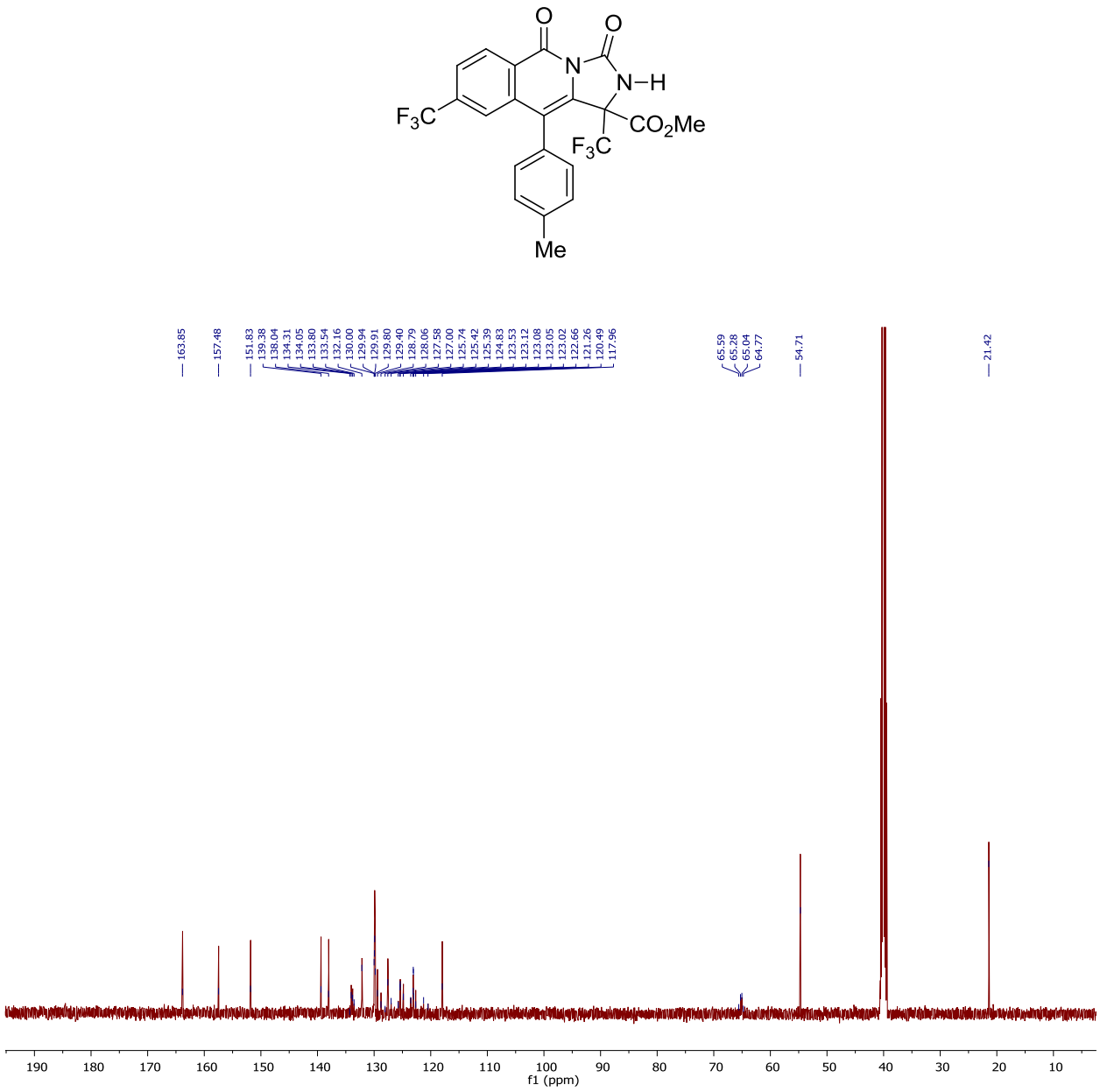
^{1}H NMR spectrum of compound **5d** in DMSO-d_6



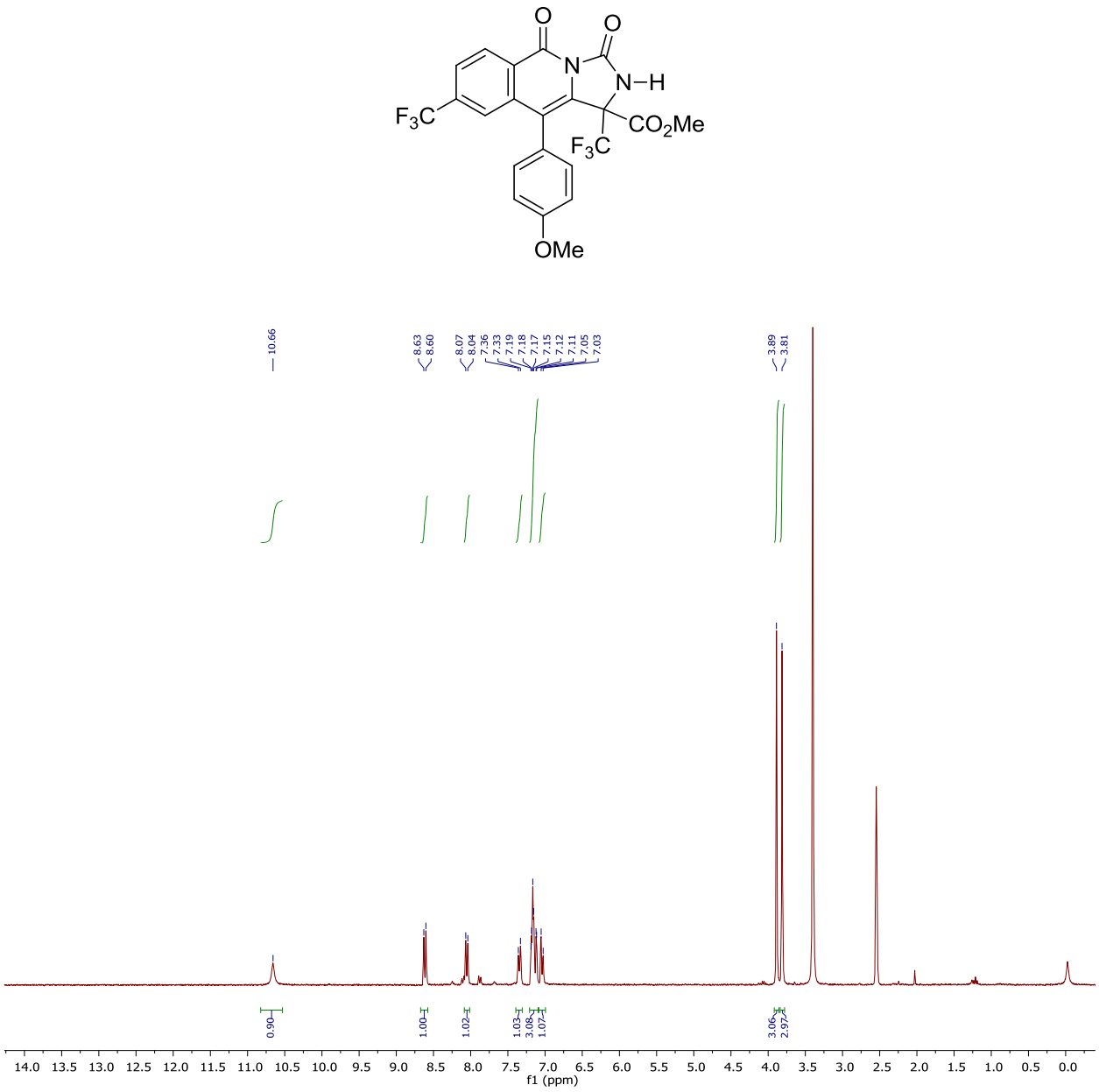
^{13}C NMR spectrum of compound **5d** in DMSO-d_6



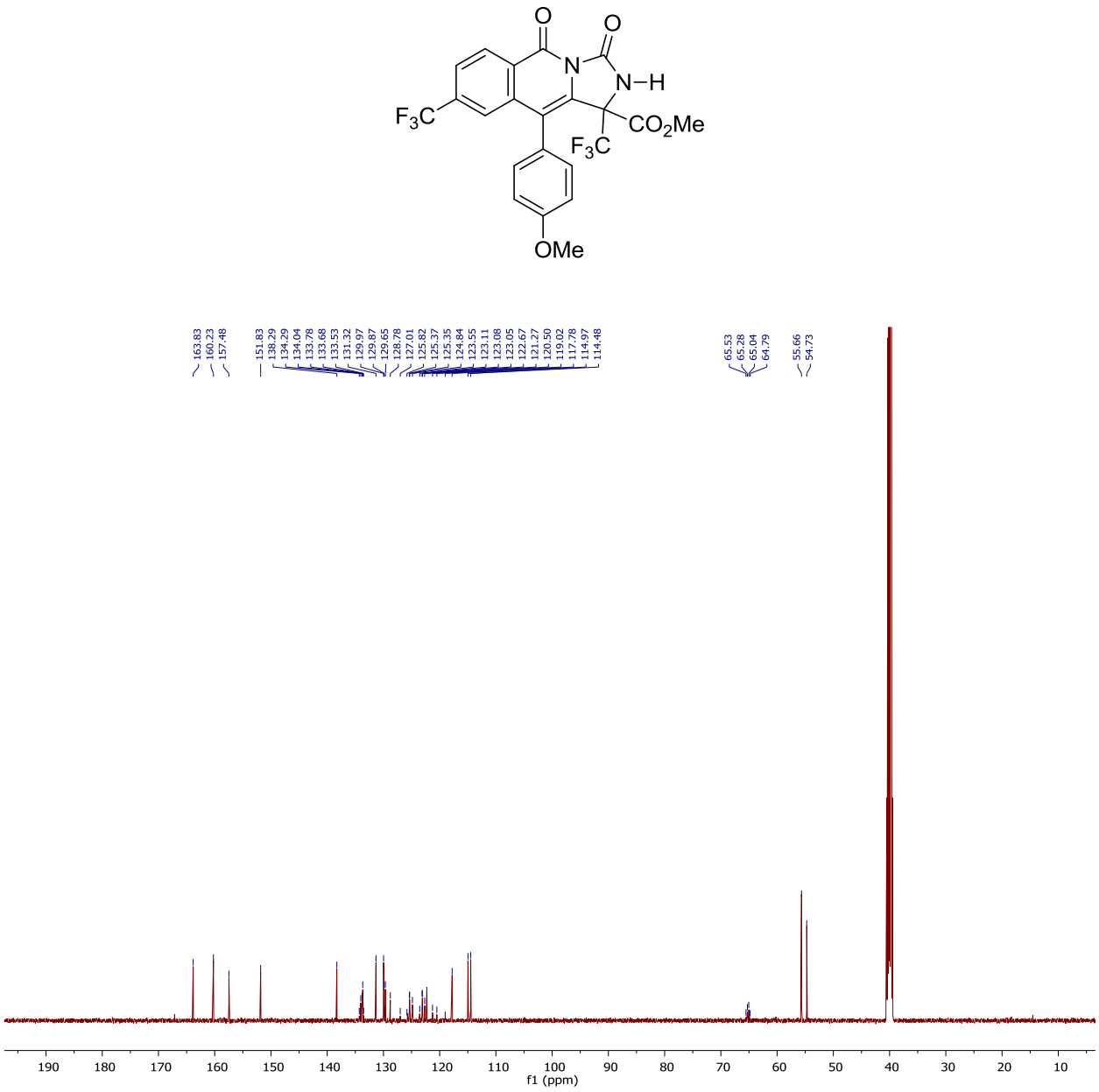
^{1}H NMR spectrum of compound **5e** in DMSO-d_6



^{13}C NMR spectrum of compound **5e** in DMSO-*d*$_6$



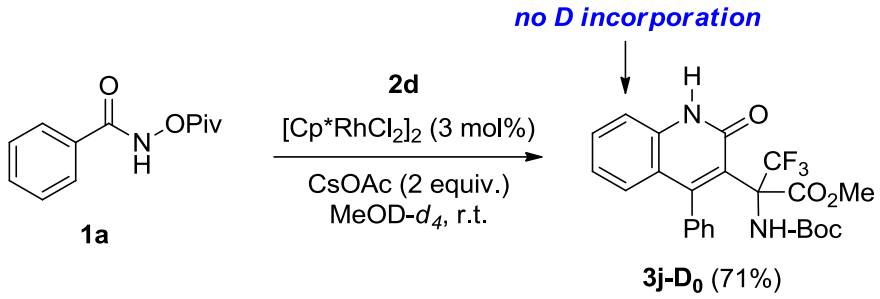
^{1}H NMR spectrum of compound **5f** in DMSO-d_6



^{13}C NMR spectrum of compound **5f** in DMSO-d_6

Mechanism studies

Reversibility of C-H activation step in the presence of acetylene 2a.



Compound **3j** was synthesized according to the general procedure A using methanol-d_4 instead of MeOH. The degree of the deuterium incorporation in isoquinolinone **3j-D0** was determined by ^{1}H NMR (Fig.1).

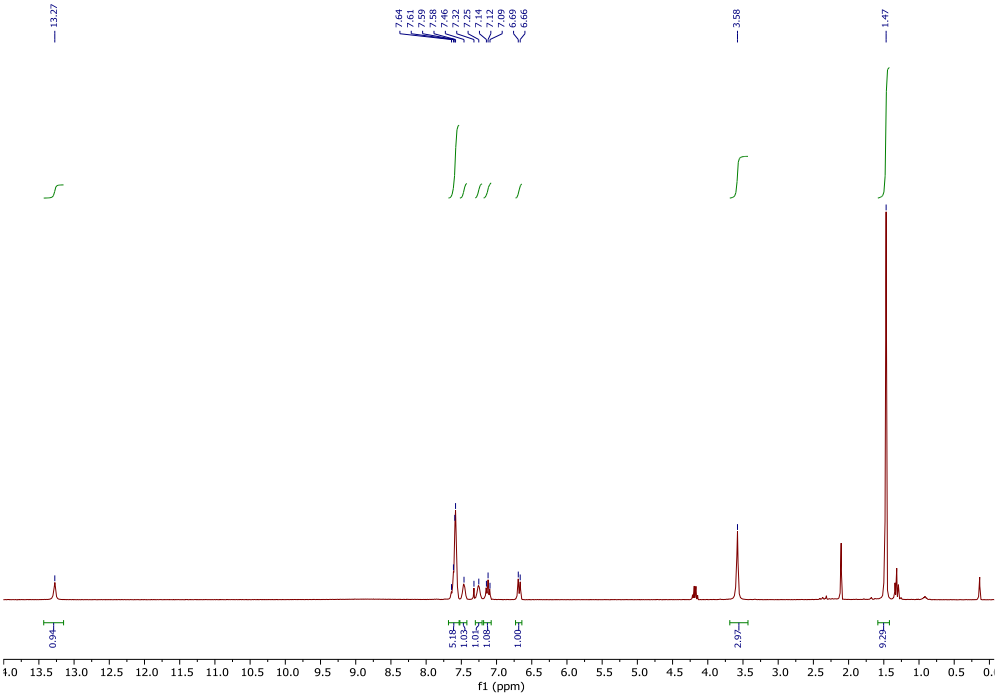
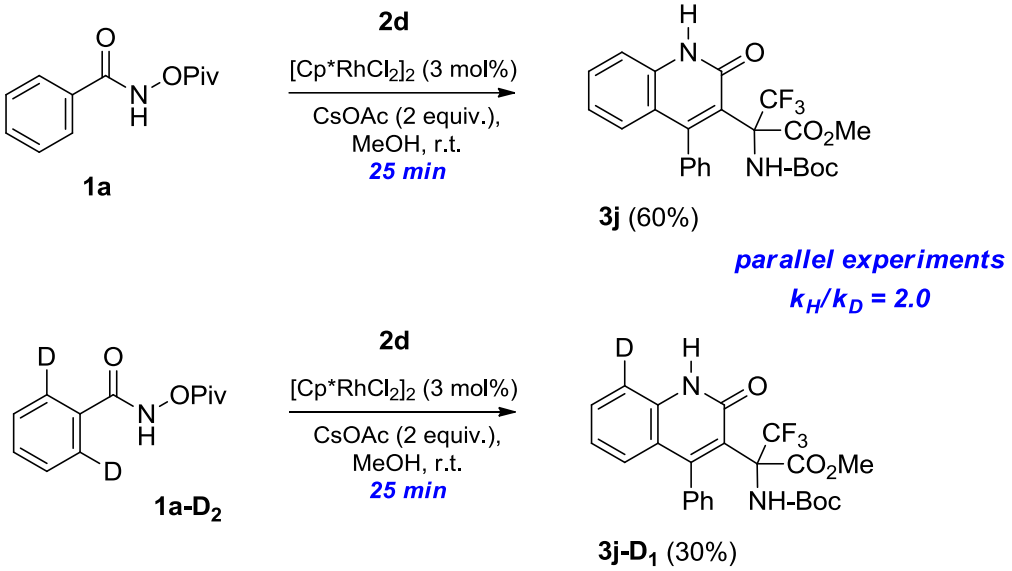


Fig. 1. The ^{1}H NMR spectra obtained from the reversibility of C-H bond activation experiment

Kinetic isotope effect study.



Procedure: Two separate dried screw cap reaction tubes (10 mL) equipped with magnetic stirring bars were charged with methanol (1.0 mL) and acetylene **2d** (10 mg, 0.03 mmol) under Ar. Then the corresponding aryl hydroxamates **1a** (6 mg, 0.03 mmol) and **1a-D₂** (6.2 mg, 0.03 mmol), $[Cp^*RhCl_2]_2$ (0.5 mg, 0.8 μmol), and CsOAc (0.11 g, 0.06 mmol) were added in each of them. The reaction tubes were capped and stirred at room temperature for 25 min. Then the solvent was evaporated under reduced pressure and ^{19}F NMR spectra were obtained for the resulting residues. The corresponding yields were determined by integrating trifluoromethyl groups and the value k_H/k_D was calculated using the ratio of the corresponding yields (Fig.2). The KIE value is found to be $k_H/k_D = 2.0$ indicating that the C-H bond cleavage might well not occur during the rate-determining step.

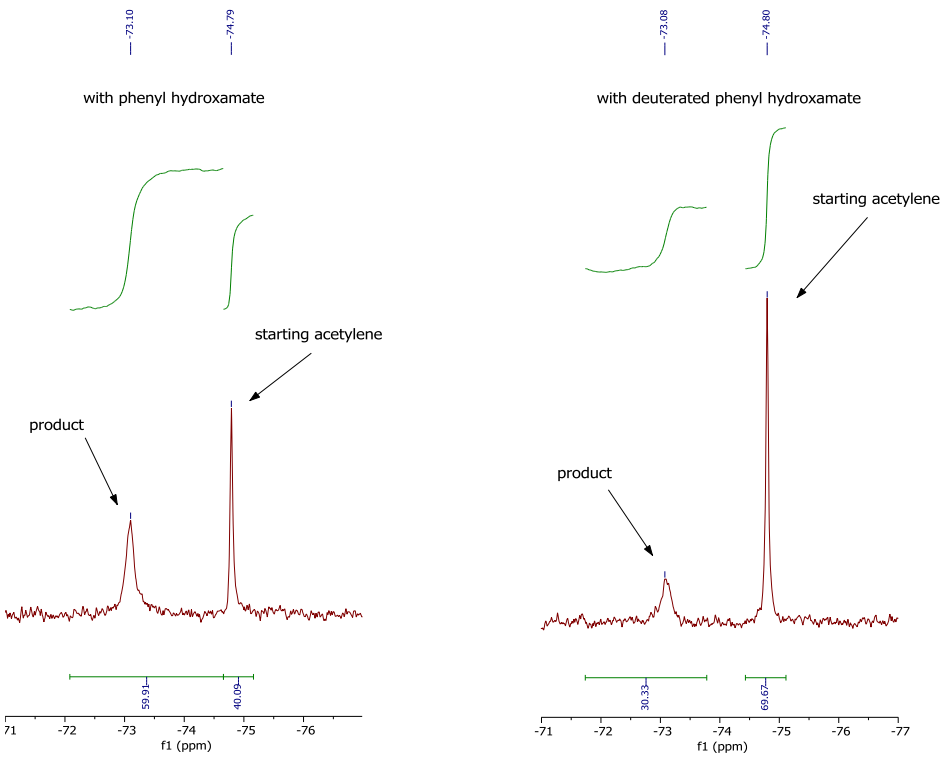
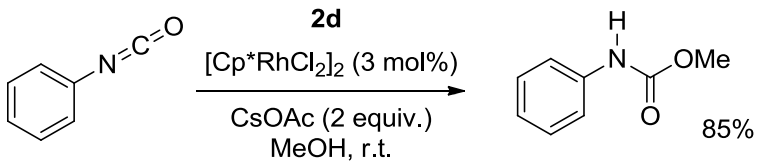


Fig. **2** ^{19}F NMR spectra of the products obtained from KIE experiment.

A control experiment for Lossen rearrangement with phenyl isocyanate



Procedure:

A dried 10 mL Schlenk tube equipped with a magnetic stirring bar was charged with acetylene **2d** (120 mg, 0.3 mmol 1 equiv.), MeOH (2.4 mL), phenyl isocyanate (40 mg, 0.3 mmol, 1 equiv.), $[Cp^*RhCl_2]_2$ (6.0 mg, 10 μmol, 3 mol%) and CsOAc (129 mg, 0.7 mmol, 2 equiv.) under Ar. The reaction mixture was stirred at room temperature for 2.5 – 3 hours with monitoring its composition by TLC and ^{19}F NMR. Then the solvent was evaporated under reduced pressure, and the residue was column-chromatographed to isolate the starting acetylene and methyl phenyl carbamate.

Scale up synthesis of 3a

A dried 50 mL Schlenk tube equipped with a magnetic stirrer was charged with acetylene **2a** (1.0 g, 2.5 mmol, 1 equiv.), MeOH (15 mL), aryl hydroxamate **1a** (0.56 g, 2.5 mmol, 1 equiv.), $[Cp^*RhCl_2]_2$ (0.05 g, 0.08 mmol, 3 mol%) and CsOAc (1.0 g, 5.1 mmol, 2 equiv.) under Ar. The reaction mixture was stirred at room temperature for 2.5-3 h until the completion of the reaction monitored by TLC. Then water (25 mL) was added to a residue and the aqueous mixture was extracted with ethyl acetate (3 x 15 mL). The organic layer was dried over $MgSO_4$, filtered from the drying agent, and evaporated to dryness. The residue was purified by recrystallization (eluent petroleum ether/ethyl acetate) to give 0.84 g (75% yield) of the analytically pure product.

X-ray Diffraction Study

X-Ray structure analysis of **3a**, **3d**, **5c**: Bruker AXS SMART 1000, CCD - detector $\lambda(MoK_\alpha)$ = 0.71073Å, graphite monochromator, ω - scanning, T=150.

The structure was solved by direct method and refined by full - matrix least squares method for F^2 with anisotropic parameters for all non - hydrogen atoms. All calculations were performed with the use of the SHELXTL PLUS program packages.[1-4]

1. SMART (control) and SAINT (integration) Software, Version 5.0, Bruker AXS Inc., Madison, WI, 1997.
2. SAINT: Area - Detector Integration Sofware. Bruker: Madison, 603 Wisconsin, USA, 2012.
3. Sheldrick G.M. SADABS. Program for scaling and Correction of Area Detector Data, University of Göttingen, 1997.
4. G.M .Sheldrick, *Acta Crystallogr. C*. **2015**, *71*, 3. doi.org/10.1107/S2053229614024218.

Special details

3d: Solvate molecular of CH_2Cl_2

Hydrogen bonding (N(2)…O(10) 2.771Å, N(5)…O(4) 2.816Å) fig. S1

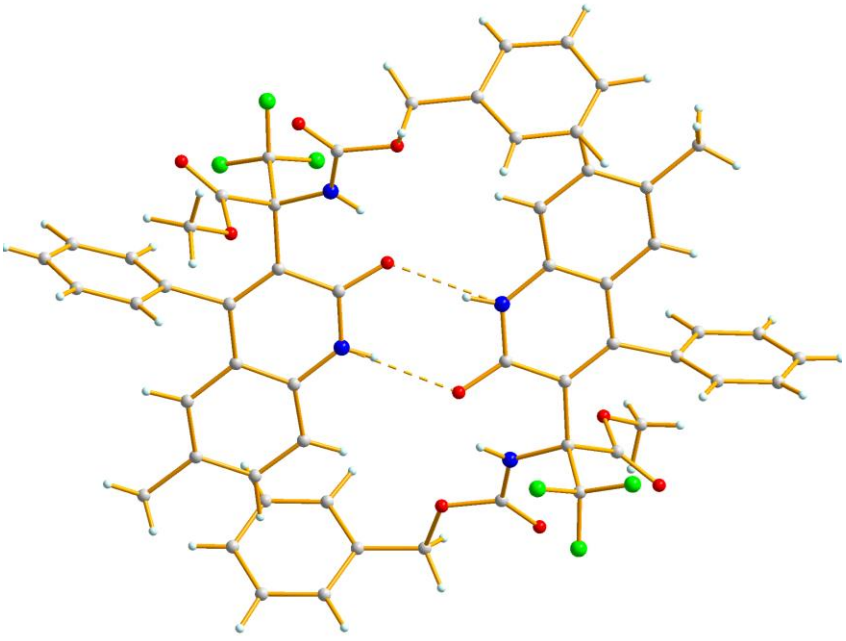


Fig S. Hydrogen bonding in the crystals of **3d**

Table S1. Crystal Data and Structure Refinement for Compounds **3a, 3d, 5c**

	3a	**3d**	**5c**
CCDC	2097694	2097695	2097693
empirical formula	$C_{27}H_{21}F_3N_2O_5$	$C_{58}H_{49}Cl_4F_6N_4O_{10}$	$C_{21}H_{14}F_3N_3O_7$
f.w.	510.46	1217.81	477.35
colour	colourless	colourless	colourless
temp (K)	150(2)	150(2)	150(2)
crystal system	orthorhombic	monoclinic	monoclinic
space group	Pbca	P2(1)/c	C2/c
unit cell dimensions (Å,deg)	a = 15.718(2)	a = 10.8152(8)	a = 18.8139(12)
	b = 13.4294(19)	b = 16.2213(11)	b = 13.3867(6)
	c = 24.950(3)	c = 32.017(2)	c = 15.4997(9)
	α = 90	α = 90	α = 90
	β = 90	β = 93.774(2)	β = 100.572(3)
	γ = 90	γ = 90	γ = 90
V(Å^3)	5266.6(12)	5604.7(7)	3837.4(4)
Z	8	4	8
d(calculated) (Mg/m^3)	1.288	1.443	1.652
abs coeff (mm^{-1})	0.103	0.294	0.144
F(000)	2112	2508	1952
cryst size (mm)	0.18 x 0.16 x 0.14	0.22 x 0.20 x 0.18	0.200 x 0.180 x 0.160
θ range for data collection (deg).	2.155 to 24.999	2.207 to 27.999	2.185 to 27.999
index ranges	- 18<=h<=18, - 13<=k<=15, - 29<=l<=29	- 14<=h<=14, - 21<=k<=21, - 42<=l<=42	- 24<=h<=24, - 17<=k<=17, - 20<=l<=19
reflns collected	4597	13521	4329
independent reflns	2363 [R(int) = 0.1125]	8156 [R(int) = 0.0718]	2879 [R(int) = 0.0683]
data / restraints / params	2363 / 0 / 399	8156 / 0 / 927	2879 / 0 / 363
goodness - of - fit on F^2	1.008	1.004	1.050
[a]final R indices [I>2sigma(I)]	R1 = 0.0870, wR2 = 0.2044	R1 = 0.0760, wR2 = 0.1813	R1 = 0.0537, wR2 = 0.1057
[a]R indices (all data)	R1 = 0.1609, wR2 = 0.2534	R1 = 0.1291, wR2 = 0.2095	R1 = 0.0940, wR2 = 0.1195
[b]largest diff. peak and hole(e.A^{-3})	0.861 and - 0.208	0.537 and - 0.739	0.288 and - 0.282

[a] $R_1 = \Sigma \big| |F_o| - |F_c| \big| / \Sigma |F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$

[b] In all structures the largest diff. peak is observed in the vicinity of heavy atom

Table S2. Bond lengths [Å] and angles [°] for **3a**.

F1 - C1	1.334(6)	F2 - C1	1.331(6)
F3 - C1	1.334(6)	O1 - C3	1.307(6)
O1 - C4	1.435(8)	O2 - C3	1.200(6)
O3 - C5	1.211(6)	O4 - C5	1.355(6)
O4 - C6	1.461(7)	O5 - C14	1.248(5)
N1 - C5	1.343(6)	N1 - C2	1.464(6)
N2 - C14	1.350(6)	N2 - C15	1.363(6)
C1 - C2	1.541(7)	C2 - C13	1.544(7)
C2 - C3	1.550(7)	C6 - C7	1.513(9)
C7 - C12	1.360(9)	C7 - C8	1.393(10)
C8 - C9	1.483(11)	C9 - C10	1.246(10)
C10 - C11	1.362(10)	C11 - C12	1.408(9)
C13 - C21	1.381(6)	C13 - C14	1.472(6)
C15 - C20	1.397(6)	C15 - C16	1.405(6)
C16 - C17	1.357(7)	C17 - C18	1.389(7)
C18 - C19	1.369(7)	C19 - C20	1.401(6)
C20 - C21	1.442(6)	C21 - C22	1.489(6)
C22 - C27	1.388(7)	C22 - C23	1.391(7)
C23 - C24	1.387(7)	C24 - C25	1.363(9)
C25 - C26	1.357(9)	C26 - C27	1.392(7)

C3 - O1 - C4	113.0(5)	C5 - O4 - C6	114.9(4)
C5 - N1 - C2	125.8(4)	C14 - N2 - C15	125.9(4)
F2 - C1 - F3	106.2(4)	F2 - C1 - F1	107.5(4)
F3 - C1 - F1	106.5(4)	F2 - C1 - C2	112.8(4)
F3 - C1 - C2	110.8(4)	F1 - C1 - C2	112.7(4)
N1 - C2 - C1	107.2(4)	N1 - C2 - C13	110.4(3)
C1 - C2 - C13	108.2(4)	N1 - C2 - C3	108.1(4)
C1 - C2 - C3	108.2(4)	C13 - C2 - C3	114.5(4)
O2 - C3 - O1	126.9(5)	O2 - C3 - C2	123.5(5)
O1 - C3 - C2	109.7(4)	O3 - C5 - N1	125.8(5)
O3 - C5 - O4	125.7(5)	N1 - C5 - O4	108.4(4)
O4 - C6 - C7	107.8(5)	C12 - C7 - C8	118.4(7)
C12 - C7 - C6	120.2(7)	C8 - C7 - C6	121.4(7)
C7 - C8 - C9	119.7(7)	C10 - C9 - C8	117.6(8)
C9 - C10 - C11	125.1(8)	C10 - C11 - C12	119.3(7)
C7 - C12 - C11	119.9(7)	C21 - C13 - C14	118.9(4)
C21 - C13 - C2	124.7(4)	C14 - C13 - C2	116.3(4)
O5 - C14 - N2	117.5(4)	O5 - C14 - C13	125.7(4)
N2 - C14 - C13	116.8(4)	N2 - C15 - C20	118.3(4)
N2 - C15 - C16	120.1(4)	C20 - C15 - C16	121.6(4)
C17 - C16 - C15	119.3(4)	C16 - C17 - C18	120.6(5)
C19 - C18 - C17	119.9(5)	C18 - C19 - C20	121.9(5)
C15 - C20 - C19	116.7(4)	C15 - C20 - C21	119.3(4)

C19 - C20 - C21	124.0(4)	C13 - C21 - C20	120.4(4)
C13 - C21 - C22	125.3(4)	C20 - C21 - C22	114.3(4)
C27 - C22 - C23	118.6(5)	C27 - C22 - C21	121.7(5)
C23 - C22 - C21	119.0(4)	C24 - C23 - C22	120.3(5)
C25 - C24 - C23	120.2(6)	C26 - C25 - C24	120.4(6)
C25 - C26 - C27	120.5(6)	C22 - C27 - C26	119.9(6)

Table S3. Bond lengths [Å] and angles [°] for **3d**

Cl1 - C57	1.766(6)	Cl2 - C57	1.745(6)
Cl3 - C58	1.718(6)	Cl4 - C58	1.739(5)
F1 - C2	1.348(4)	F2 - C2	1.337(4)
F3 - C2	1.336(4)	F4 - C30	1.332(4)
F5 - C30	1.340(4)	F6 - C30	1.338(4)
O1 - C3	1.321(4)	O1 - C4	1.443(4)
O2 - C3	1.196(4)	O3 - C5	1.346(4)
O3 - C6	1.454(4)	O4 - C5	1.209(4)
O5 - C14	1.254(4)	O6 - C31	1.330(4)
O6 - C32	1.457(4)	O7 - C31	1.189(4)
O8 - C33	1.359(4)	O8 - C34	1.472(5)
O9 - C33	1.200(4)	O10 - C42	1.258(4)
N1 - C5	1.363(4)	N1 - C1	1.454(4)
N2 - C14	1.352(4)	N2 - C15	1.368(4)
N3 - C33	1.355(5)	N3 - C29	1.454(4)
N4 - C42	1.348(4)	N4 - C43	1.369(4)
C1 - C2	1.545(5)	C1 - C3	1.549(4)
C1 - C13	1.554(4)	C6 - C7	1.494(5)
C7 - C12	1.388(5)	C7 - C8	1.391(5)
C8 - C9	1.389(6)	C9 - C10	1.383(6)
C10 - C11	1.377(6)	C11 - C12	1.379(6)
C13 - C22	1.374(4)	C13 - C14	1.475(4)
C15 - C21	1.392(4)	C15 - C16	1.414(5)
C16 - C17	1.367(5)	C17 - C18	1.402(5)
C18 - C20	1.380(5)	C18 - C19	1.504(5)
C20 - C21	1.402(5)	C21 - C22	1.462(4)
C22 - C23	1.500(4)	C23 - C28	1.392(5)
C23 - C24	1.396(5)	C24 - C25	1.379(5)
C25 - C26	1.377(5)	C26 - C27	1.379(5)
C27 - C28	1.388(5)	C29 - C30	1.542(5)
C29 - C41	1.560(4)	C29 - C31	1.564(5)
C34 - C35	1.466(7)	C35 - C40	1.382(6)
C35 - C36	1.440(7)	C36 - C37	1.369(8)
C37 - C38	1.352(8)	C38 - C39	1.334(8)
C39 - C40	1.358(7)	C41 - C50	1.369(5)
C41 - C42	1.472(4)	C43 - C49	1.395(4)
C43 - C44	1.402(5)	C44 - C45	1.372(5)
C45 - C46	1.400(5)	C46 - C48	1.384(5)
C46 - C47	1.508(5)	C48 - C49	1.413(5)
C49 - C50	1.459(5)	C50 - C51	1.507(4)
C51 - C56	1.391(5)	C51 - C52	1.392(5)
C52 - C53	1.388(5)	C53 - C54	1.368(6)
C54 - C55	1.387(6)	C55 - C56	1.374(5)

C3 - O1 - C4	114.7(3)	C5 - O3 - C6	114.6(3)
C31 - O6 - C32	115.5(3)	C33 - O8 - C34	114.4(3)
C5 - N1 - C1	125.4(3)	C14 - N2 - C15	125.5(3)
C33 - N3 - C29	125.8(3)	C42 - N4 - C43	126.5(3)
N1 - C1 - C2	107.8(3)	N1 - C1 - C3	107.9(3)
C2 - C1 - C3	108.6(2)	N1 - C1 - C13	109.4(2)
C2 - C1 - C13	109.6(3)	C3 - C1 - C13	113.4(3)
F3 - C2 - F2	107.3(2)	F3 - C2 - F1	106.2(3)
F2 - C2 - F1	106.0(3)	F3 - C2 - C1	112.7(3)
F2 - C2 - C1	113.4(3)	F1 - C2 - C1	110.8(3)
O2 - C3 - O1	126.5(3)	O2 - C3 - C1	124.6(3)
O1 - C3 - C1	108.9(3)	O4 - C5 - O3	124.9(3)
O4 - C5 - N1	127.4(3)	O3 - C5 - N1	107.6(3)
O3 - C6 - C7	106.6(3)	C12 - C7 - C8	118.6(4)
C12 - C7 - C6	120.1(3)	C8 - C7 - C6	121.3(4)
C9 - C8 - C7	120.7(4)	C10 - C9 - C8	119.5(4)
C11 - C10 - C9	120.3(4)	C10 - C11 - C12	120.1(4)
C11 - C12 - C7	120.8(4)	C22 - C13 - C14	118.5(3)
C22 - C13 - C1	124.5(3)	C14 - C13 - C1	117.0(3)
O5 - C14 - N2	117.5(3)	O5 - C14 - C13	125.3(3)
N2 - C14 - C13	117.2(3)	N2 - C15 - C21	119.1(3)
N2 - C15 - C16	120.1(3)	C21 - C15 - C16	120.9(3)
C17 - C16 - C15	119.0(3)	C16 - C17 - C18	121.8(3)
C20 - C18 - C17	118.2(3)	C20 - C18 - C19	121.1(4)
C17 - C18 - C19	120.7(4)	C18 - C20 - C21	122.2(3)
C15 - C21 - C20	118.0(3)	C15 - C21 - C22	118.4(3)
C20 - C21 - C22	123.7(3)	C13 - C22 - C21	121.0(3)
C13 - C22 - C23	126.4(3)	C21 - C22 - C23	112.6(3)
C28 - C23 - C24	119.3(3)	C28 - C23 - C22	120.0(3)
C24 - C23 - C22	119.3(3)	C25 - C24 - C23	119.6(3)
C26 - C25 - C24	121.2(3)	C25 - C26 - C27	119.5(3)
C26 - C27 - C28	120.4(3)	C27 - C28 - C23	120.0(3)
N3 - C29 - C30	106.6(3)	N3 - C29 - C41	109.4(3)
C30 - C29 - C41	109.7(3)	N3 - C29 - C31	107.8(3)
C30 - C29 - C31	109.1(3)	C41 - C29 - C31	114.0(3)
F4 - C30 - F6	106.7(3)	F4 - C30 - F5	106.3(3)
F6 - C30 - F5	106.6(3)	F4 - C30 - C29	112.8(3)
F6 - C30 - C29	113.7(3)	F5 - C30 - C29	110.3(3)
O7 - C31 - O6	127.5(3)	O7 - C31 - C29	124.8(3)
O6 - C31 - C29	107.8(3)	O9 - C33 - N3	127.5(4)
O9 - C33 - O8	124.6(4)	N3 - C33 - O8	107.9(3)
C35 - C34 - O8	107.0(4)	C40 - C35 - C36	116.0(4)
C40 - C35 - C34	123.6(5)	C36 - C35 - C34	120.4(5)
C37 - C36 - C35	119.4(5)	C38 - C37 - C36	121.3(5)

C39 - C38 - C37	120.1(5)	C38 - C39 - C40	121.5(5)
C39 - C40 - C35	121.7(5)	C50 - C41 - C42	119.1(3)
C50 - C41 - C29	123.9(3)	C42 - C41 - C29	116.9(3)
O10 - C42 - N4	117.6(3)	O10 - C42 - C41	126.0(3)
N4 - C42 - C41	116.5(3)	N4 - C43 - C49	118.3(3)
N4 - C43 - C44	120.2(3)	C49 - C43 - C44	121.5(3)
C45 - C44 - C43	118.9(3)	C44 - C45 - C46	121.6(3)
C48 - C46 - C45	118.7(3)	C48 - C46 - C47	121.5(3)
C45 - C46 - C47	119.7(3)	C46 - C48 - C49	121.5(3)
C43 - C49 - C48	117.7(3)	C43 - C49 - C50	118.5(3)
C48 - C49 - C50	123.8(3)	C41 - C50 - C49	121.0(3)
C41 - C50 - C51	124.9(3)	C49 - C50 - C51	114.1(3)
C56 - C51 - C52	119.2(3)	C56 - C51 - C50	120.0(3)
C52 - C51 - C50	120.3(3)	C53 - C52 - C51	119.4(4)
C54 - C53 - C52	120.8(4)	C53 - C54 - C55	119.9(4)
C56 - C55 - C54	120.0(4)	C55 - C56 - C51	120.5(4)
Cl2 - C57 - Cl1	113.1(3)	Cl3 - C58 - Cl4	112.7(3)

Table S4. Bond lengths [Å] and angles [°] for **5c**.

F(1) - C(8)	1.340(3)	F(2) - C(8)	1.328(3)
F(3) - C(8)	1.323(3)	O(1) - N(1)	1.215(2)
O(2) - N(1)	1.213(2)	O(3) - C(5)	1.208(3)
O(4) - C(6)	1.203(2)	O(5) - C(9)	1.194(3)
O(6) - C(9)	1.317(3)	O(6) - C(11)	1.447(3)
O(7) - C(17)	1.359(2)	O(7) - C(18)	1.437(3)
N(1) - C(1)	1.476(3)	N(2) - C(5)	1.405(3)
N(2) - C(12)	1.410(2)	N(2) - C(6)	1.420(3)
N(3) - C(6)	1.353(3)	N(3) - C(7)	1.443(3)
C(1) - C(21)	1.368(3)	C(1) - C(2)	1.383(3)
C(2) - C(3)	1.372(3)	C(3) - C(4)	1.400(3)
C(4) - C(10)	1.407(3)	C(4) - C(5)	1.467(3)
C(7) - C(12)	1.521(3)	C(7) - C(8)	1.536(3)
C(7) - C(9)	1.549(3)	C(10) - C(21)	1.402(3)
C(10) - C(13)	1.458(3)	C(12) - C(13)	1.332(3)
C(13) - C(14)	1.496(3)	C(14) - C(15)	1.380(3)
C(14) - C(20)	1.395(3)	C(15) - C(16)	1.389(3)
C(16) - C(17)	1.380(3)	C(17) - C(19)	1.393(3)
C(19) - C(20)	1.373(3)		

C(9) - O(6) - C(11)	116.1(2)	C(17) - O(7) - C(18)	117.90(19)
O(2) - N(1) - O(1)	123.8(2)	O(2) - N(1) - C(1)	118.42(19)
O(1) - N(1) - C(1)	117.77(19)	C(5) - N(2) - C(12)	123.84(18)
C(5) - N(2) - C(6)	125.05(17)	C(12) - N(2) - C(6)	110.94(17)
C(6) - N(3) - C(7)	114.1(2)	C(21) - C(1) - C(2)	123.9(2)
C(21) - C(1) - N(1)	118.5(2)	C(2) - C(1) - N(1)	117.6(2)
C(3) - C(2) - C(1)	117.9(2)	C(2) - C(3) - C(4)	120.5(2)
C(3) - C(4) - C(10)	120.5(2)	C(3) - C(4) - C(5)	117.23(19)
C(10) - C(4) - C(5)	122.25(19)	O(3) - C(5) - N(2)	122.2(2)
O(3) - C(5) - C(4)	124.5(2)	N(2) - C(5) - C(4)	113.31(17)
O(4) - C(6) - N(3)	127.4(2)	O(4) - C(6) - N(2)	126.64(19)
N(3) - C(6) - N(2)	105.97(18)	N(3) - C(7) - C(12)	101.54(16)
N(3) - C(7) - C(8)	107.17(18)	C(12) - C(7) - C(8)	110.68(18)
N(3) - C(7) - C(9)	109.51(17)	C(12) - C(7) - C(9)	112.91(18)
C(8) - C(7) - C(9)	114.12(17)	F(3) - C(8) - F(2)	108.28(18)
F(3) - C(8) - F(1)	107.00(19)	F(2) - C(8) - F(1)	106.67(19)
F(3) - C(8) - C(7)	114.10(19)	F(2) - C(8) - C(7)	111.35(19)
F(1) - C(8) - C(7)	109.09(17)	O(5) - C(9) - O(6)	126.8(2)
O(5) - C(9) - C(7)	121.72(18)	O(6) - C(9) - C(7)	111.42(18)
C(21) - C(10) - C(4)	118.6(2)	C(21) - C(10) - C(13)	121.29(19)
C(4) - C(10) - C(13)	120.1(2)	C(13) - C(12) - N(2)	123.11(19)
C(13) - C(12) - C(7)	130.92(18)	N(2) - C(12) - C(7)	105.95(18)
C(12) - C(13) - C(10)	117.34(18)	C(12) - C(13) - C(14)	122.74(19)
C(10) - C(13) - C(14)	119.88(19)	C(15) - C(14) - C(20)	118.3(2)
C(15) - C(14) - C(13)	119.82(19)	C(20) - C(14) - C(13)	121.80(19)
C(14) - C(15) - C(16)	121.7(2)	C(17) - C(16) - C(15)	119.5(2)
O(7) - C(17) - C(16)	124.5(2)	O(7) - C(17) - C(19)	116.2(2)
C(16) - C(17) - C(19)	119.3(2)	C(20) - C(19) - C(17)	120.8(2)
C(19) - C(20) - C(14)	120.5(2)	C(1) - C(21) - C(10)	118.6(2)

Computational details

The DFT calculations were performed by Gaussian 09 program.[1] Geometry optimizations were done without any restrictions with the M11L functional[2] applying 6-31G(d,p) basis set for all atoms except Rh, which was described by SDD[3] basis set supplied with ECP[4] for core electrons. Optimizations were performed in methanol described by SMD[5] solvation model (ε = 32.613). The nature of all the stationary points on the potential energy surfaces was confirmed by vibrational analysis. Transition state (TS) structures showed only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the Intrinsic Reaction Coordinate (IRC) method.[6]
NBO analysis of charges was performed with the NBO Pro 6.0 program.[7]

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Table S5. XYZ coordinates of all optimized species and their energies in Ha

INT1-Me, E = -2712.00708280, H= -2711.147555, G=-2711.295138

7	-0.578538000	-2.081597000	1.367812000
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6	-3.725886000	-2.868931000	1.429160000
1	-3.429795000	-3.633173000	2.156360000
6	-4.924675000	-2.984703000	0.757054000
1	-5.574269000	-3.847290000	0.941425000
6	-5.322615000	-1.996259000	-0.139385000
6	-4.486875000	-0.905846000	-0.326848000
1	-4.812001000	-0.113472000	-1.011834000
6	-3.249860000	-0.780665000	0.311677000
6	1.208262000	-2.239535000	-2.071392000
6	0.263519000	-3.201354000	-1.687770000
6	-1.043625000	-2.665353000	-1.985323000
6	-0.880220000	-1.387136000	-2.586473000
6	0.509859000	-1.087164000	-2.596572000
45	-0.102554000	-1.315539000	-0.519240000
6	-1.652517000	-1.705953000	2.062619000
8	-1.710559000	-1.436547000	3.251663000
6	-1.106705000	0.447569000	-0.008797000
6	1.153879000	0.074840000	-3.242725000
1	1.349947000	-0.138073000	-4.308316000
1	0.528019000	0.977106000	-3.197397000
1	2.122758000	0.321823000	-2.781722000
6	2.671659000	-2.299079000	-1.895874000
1	3.164644000	-2.538729000	-2.852867000
1	3.080673000	-1.328954000	-1.565644000
1	2.977976000	-3.062396000	-1.166269000
6	0.504409000	-4.527204000	-1.084996000
1	0.380322000	-5.332549000	-1.828763000
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6	-2.294321000	-3.433355000	-1.858790000
1	-2.357620000	-4.166964000	-2.681320000
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1	-3.187997000	-2.798160000	-1.916023000
6	-1.945475000	-0.545953000	-3.163159000
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1	-1.686771000	0.522406000	-3.127893000
8	0.558371000	-2.040165000	2.286573000
6	1.593642000	-1.483760000	1.768632000
8	1.584620000	-0.968422000	0.659015000
6	2.855953000	-1.559042000	2.588694000
6	-6.607542000	-2.113067000	-0.877757000
1	-7.442438000	-2.363293000	-0.204921000
1	-6.864032000	-1.181883000	-1.402770000
1	-6.566795000	-2.915670000	-1.632638000
6	3.883390000	-0.628477000	1.974507000
1	3.528621000	0.415289000	1.952914000
1	4.807359000	-0.659279000	2.572545000
1	4.139673000	-0.921696000	0.941981000
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1	1.827286000	-1.846650000	4.490277000
1	3.489042000	-1.225254000	4.615894000
1	2.175773000	-0.143244000	4.097224000
6	3.335676000	-3.001461000	2.513625000
1	3.511177000	-3.314528000	1.470213000
1	4.287941000	-3.100303000	3.057620000
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6	-2.450336000	0.460869000	0.148852000
6	-0.292628000	1.752645000	0.145091000
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6	5.532677000	0.627372000	-1.750507000
6	6.256645000	1.631177000	0.302060000
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6	7.222436000	0.646783000	0.440891000
1	6.154237000	2.412911000	1.062779000
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8	1.818131000	3.653856000	-0.612892000
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8	-0.775966000	2.971847000	-1.858641000
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6	-1.569654000	5.111831000	-0.602562000
1	-2.286400000	4.901284000	-1.407746000
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1	-0.665449000	5.573851000	-1.026505000
6	-3.332288000	1.668137000	0.172860000
6	-3.680718000	2.310230000	-1.012969000
6	-3.938014000	2.088569000	1.354964000
6	-4.567190000	3.375297000	-1.009808000
6	-4.806346000	3.163908000	1.362176000
6	-5.119339000	3.816863000	0.179753000
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1	-3.710826000	1.564343000	2.289158000
1	-4.827434000	3.865761000	-1.953067000
1	-5.254111000	3.493078000	2.304950000
1	-5.812219000	4.663579000	0.185128000

TS-Los-Me, E=-2711.98783548, H=-2711.131692, G=-2711.279895, v_i=-374 cm^{-1}

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6	0.526675000	-1.280494000	-2.420249000
45	-0.354747000	-1.449032000	-0.409695000

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6	-0.089401000	1.616845000	0.287585000
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1	4.591942000	3.037369000	0.082407000
6	5.677025000	1.414916000	-0.816710000
6	5.588453000	0.083884000	-1.206831000
6	6.927766000	1.957495000	-0.550270000
6	6.732708000	-0.688338000	-1.321309000
1	4.609876000	-0.360104000	-1.423514000
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6	-4.650263000	-0.831980000	-0.175667000
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1	2.078477000	-0.636822000	3.779198000
6	4.086091000	-2.934973000	2.155856000
1	4.382920000	-3.144617000	1.113813000
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6	5.501731000	0.890374000	-1.800376000
6	6.277207000	1.896917000	0.231919000
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9	0.085262000	0.989810000	2.462464000
9	0.523730000	3.025226000	2.074471000
8	3.074824000	1.877312000	-0.499955000
6	1.892800000	2.448810000	-0.341822000
8	1.683428000	3.633422000	-0.446736000
6	-0.812580000	2.943603000	-0.557178000
8	-0.757866000	2.937779000	-1.752935000
8	-1.237606000	3.941161000	0.169924000
6	-1.553795000	5.110432000	-0.559717000
1	-2.252237000	4.893411000	-1.379317000
1	-2.012746000	5.795593000	0.160435000
1	-0.632867000	5.552627000	-0.969085000
6	-3.413350000	1.681676000	0.186799000
6	-3.707082000	2.353256000	-0.996856000
6	-4.073463000	2.073887000	1.349251000
6	-4.588582000	3.422764000	-1.007159000
6	-4.939711000	3.150688000	1.344050000
6	-5.194329000	3.836090000	0.165937000
1	-3.237716000	2.027365000	-1.931147000
1	-3.891111000	1.527424000	2.280242000
1	-4.803999000	3.937179000	-1.948879000
1	-5.431187000	3.455858000	2.273051000
1	-5.884333000	4.685138000	0.161043000

INT1-NO2, E=-2877.11605477, H=-2876.279046, G=-2876.429632

7	-0.456794000	-2.021061000	1.459930000
6	-2.717475000	-1.488470000	1.314813000
6	-3.591401000	-2.534311000	1.585436000
1	-3.288436000	-3.317729000	2.286212000
6	-4.835828000	-2.587613000	0.997223000
1	-5.529224000	-3.403645000	1.201445000
6	-5.185073000	-1.552545000	0.147116000
6	-4.340191000	-0.494203000	-0.128129000
1	-4.678197000	0.300276000	-0.797374000
6	-3.069178000	-0.454148000	0.437129000
6	1.139307000	-2.359530000	-2.053504000
6	0.108990000	-3.208238000	-1.627394000
6	-1.143779000	-2.541315000	-1.896848000
6	-0.862879000	-1.293821000	-2.517913000
6	0.550220000	-1.141349000	-2.566843000
45	-0.017556000	-1.290051000	-0.473853000
6	-1.450579000	-1.425492000	2.119802000
8	-1.448465000	-0.953277000	3.241451000
6	-2.183976000	0.715052000	0.221008000
6	-0.848617000	0.575041000	0.043455000
6	1.293097000	-0.054090000	-3.235335000
1	1.446619000	-0.293926000	-4.302039000
1	0.758787000	0.904885000	-3.186937000
1	2.289876000	0.099891000	-2.794318000
6	2.592001000	-2.580235000	-1.933020000
1	3.015627000	-2.870486000	-2.908900000
1	3.120718000	-1.663003000	-1.621154000
1	2.838656000	-3.376211000	-1.216182000
6	0.227805000	-4.539070000	-1.000719000
1	-0.002314000	-5.342775000	-1.720084000
1	1.239712000	-4.723932000	-0.613628000
1	-0.475862000	-4.654462000	-0.161299000
6	-2.462545000	-3.177685000	-1.743924000
1	-2.620357000	-3.889912000	-2.572496000
1	-2.539411000	-3.756855000	-0.812270000
1	-3.287084000	-2.454400000	-1.778470000
6	-1.850587000	-0.351935000	-3.074521000
1	-2.062309000	-0.610399000	-4.125885000
1	-2.808132000	-0.382412000	-2.534930000
1	-1.482327000	0.683809000	-3.060508000
8	0.705069000	-1.996733000	2.342209000
6	0.072722000	1.810999000	0.146120000
7	1.363631000	1.472394000	-0.349865000
6	4.658325000	2.294543000	-1.070198000
1	1.652768000	0.513768000	-0.234782000
1	4.600227000	2.711526000	-2.091096000
1	4.799979000	3.125575000	-0.360261000
6	5.719687000	1.258569000	-0.934353000
6	5.744527000	0.185289000	-1.819438000
6	6.610264000	1.280551000	0.128881000
6	6.644876000	-0.849602000	-1.642169000
1	5.040354000	0.163524000	-2.660514000
6	7.520030000	0.249304000	0.302556000
1	6.585417000	2.117218000	0.835649000
6	7.534993000	-0.818128000	-0.578886000
1	6.657498000	-1.688289000	-2.344645000
1	8.221759000	0.277320000	1.141358000

1	8.249324000	-1.634817000	-0.439051000
6	1.759237000	-1.533652000	1.769265000
8	1.750426000	-1.074469000	0.636012000
6	3.036046000	-1.657640000	2.560340000
7	-6.475187000	-1.578019000	-0.471960000
6	0.265665000	2.133514000	1.643634000
9	-0.826167000	2.490729000	2.269713000
9	0.731138000	1.057407000	2.260990000
9	1.162134000	3.082438000	1.826134000
8	3.455637000	1.604750000	-0.778784000
6	2.357256000	2.326499000	-0.617203000
8	2.286242000	3.525411000	-0.718279000
6	-0.371335000	3.029979000	-0.673500000
8	-0.370745000	3.024278000	-1.870429000
8	-0.696895000	4.047852000	0.075375000
6	-0.989959000	5.238108000	-0.631467000
1	-1.715933000	5.056970000	-1.435315000
1	-1.405610000	5.929400000	0.108871000
1	-0.064041000	5.651848000	-1.058144000
6	4.099213000	-0.807821000	1.892476000
1	3.803727000	0.253573000	1.847637000
1	5.034765000	-0.874605000	2.469066000
1	4.311429000	-1.146646000	0.864049000
6	2.805658000	-1.212384000	3.991860000
1	2.044236000	-1.825104000	4.496601000
1	3.744627000	-1.307283000	4.558289000
1	2.487562000	-0.159330000	4.042754000
6	3.425948000	-3.128143000	2.515010000
1	3.543184000	-3.482033000	1.476574000
1	4.390639000	-3.267150000	3.027205000
1	2.678835000	-3.763793000	3.014158000
6	-2.972919000	1.984590000	0.225701000
6	-3.311383000	2.608207000	-0.972791000
6	-3.513547000	2.482819000	1.409172000
6	-4.122985000	3.731314000	-0.981889000
6	-4.306768000	3.614880000	1.402089000
6	-4.609244000	4.247846000	0.206192000
1	-2.933175000	2.201996000	-1.917115000
1	-3.296154000	1.973137000	2.353645000
1	-4.376579000	4.207545000	-1.934048000
1	-4.704742000	4.004234000	2.344131000
1	-5.242873000	5.139681000	0.200635000
8	-6.768495000	-0.682493000	-1.231301000
8	-7.216872000	-2.497466000	-0.208395000

TS-Los-NO2, E=-2877.09003715, H=-2876.257037, G=-2876.407550, v_i=-457 cm^{-1}

7	-1.004318000	-2.091355000	1.213997000
6	-2.842244000	-1.547308000	1.184145000
6	-3.711501000	-2.621849000	1.350685000
1	-3.400353000	-3.478918000	1.953200000
6	-4.961619000	-2.578591000	0.782177000
1	-5.675512000	-3.392713000	0.906479000
6	-5.279549000	-1.457764000	0.030759000
6	-4.412033000	-0.399867000	-0.168786000
1	-4.738379000	0.449647000	-0.772372000
6	-3.133582000	-0.434002000	0.377927000
6	1.239349000	-2.310253000	-1.918674000
6	0.212623000	-3.211431000	-1.572240000
6	-1.035587000	-2.593757000	-1.932608000
6	-0.763548000	-1.316335000	-2.497937000
6	0.648723000	-1.117143000	-2.463738000
45	-0.082729000	-1.325878000	-0.393810000
6	-1.607135000	-1.472906000	2.149616000
8	-1.576747000	-1.055654000	3.269011000
6	-2.209811000	0.708284000	0.232337000
6	-0.868903000	0.552876000	0.093106000
6	1.386006000	-0.012164000	-3.108196000
1	1.539571000	-0.234823000	-4.178581000
1	0.845106000	0.941966000	-3.046346000
1	2.380631000	0.139770000	-2.664448000
6	2.685697000	-2.497594000	-1.712585000
1	3.150575000	-2.874802000	-2.638800000
1	3.191223000	-1.549825000	-1.465456000
1	2.906236000	-3.223737000	-0.916822000
6	0.362980000	-4.542152000	-0.950338000
1	0.379619000	-5.342375000	-1.709183000
1	1.295060000	-4.619463000	-0.371560000
1	-0.468642000	-4.766962000	-0.265749000
6	-2.356708000	-3.233015000	-1.816027000
1	-2.526369000	-3.889976000	-2.685976000
1	-2.433764000	-3.867077000	-0.920587000
1	-3.175740000	-2.500386000	-1.798902000
6	-1.752843000	-0.398673000	-3.093382000
1	-1.928045000	-0.664568000	-4.149539000
1	-2.727465000	-0.447737000	-2.584555000
1	-1.407033000	0.644654000	-3.071114000
8	0.923126000	-2.546282000	2.304539000
6	0.070264000	1.765872000	0.237635000
7	1.372074000	1.411824000	-0.220019000
6	4.616969000	2.352777000	-1.028067000
1	1.679289000	0.469000000	-0.012066000
1	4.496706000	2.800019000	-2.030382000
1	4.756254000	3.165987000	-0.297134000
6	5.728110000	1.363127000	-0.976453000
6	5.798853000	0.355863000	-1.933403000
6	6.633701000	1.364266000	0.074596000
6	6.759484000	-0.634681000	-1.838453000
1	5.084984000	0.351504000	-2.766414000
6	7.603144000	0.378427000	0.166034000
1	6.573953000	2.150371000	0.835353000
6	7.663767000	-0.623915000	-0.787021000
1	6.808557000	-1.422142000	-2.596351000
1	8.316273000	0.390294000	0.995555000
1	8.425806000	-1.405468000	-0.713152000
6	1.762721000	-1.794298000	1.818652000
8	1.593296000	-1.077803000	0.794970000
6	3.146477000	-1.707199000	2.476091000
7	-6.574957000	-1.395853000	-0.585920000
6	0.218672000	2.087595000	1.741735000
9	-0.883116000	2.486517000	2.325931000
9	0.623913000	1.003326000	2.380048000
9	1.137665000	3.009987000	1.944302000
8	3.455127000	1.606808000	-0.707403000
6	2.336837000	2.287706000	-0.520288000
8	2.226570000	3.484022000	-0.631950000
6	-0.345314000	2.985683000	-0.599881000
8	-0.349700000	2.959591000	-1.796012000
8	-0.652096000	4.016883000	0.136854000
6	-0.912883000	5.207593000	-0.581811000
1	-1.635091000	5.036617000	-1.391084000
1	-1.319686000	5.913409000	0.149624000
1	0.026392000	5.596765000	-1.002682000
6	4.040733000	-0.713860000	1.766686000
1	3.609672000	0.300844000	1.769796000
1	5.017703000	-0.661168000	2.276685000

1	4.230685000	-0.998865000	0.717523000
6	2.943858000	-1.288352000	3.920344000
1	2.305276000	-2.001303000	4.463203000
1	3.914295000	-1.237263000	4.440239000
1	2.477219000	-0.292080000	3.992536000
6	3.756601000	-3.096221000	2.421478000
1	3.886666000	-3.442374000	1.381403000
1	4.752035000	-3.093418000	2.894651000
1	3.131785000	-3.833483000	2.948615000
6	-2.972797000	1.995914000	0.221582000
6	-3.278829000	2.614947000	-0.987526000
6	-3.522866000	2.509336000	1.393317000
6	-4.066833000	3.754050000	-1.016834000
6	-4.290842000	3.658548000	1.365225000
6	-4.559644000	4.289176000	0.160500000
1	-2.894750000	2.191374000	-1.921752000
1	-3.334873000	2.000727000	2.343988000
1	-4.295736000	4.228609000	-1.975836000
1	-4.696961000	4.061477000	2.297831000
1	-5.173665000	5.194240000	0.138863000
8	-6.837651000	-0.435615000	-1.271013000
8	-7.340108000	-2.310057000	-0.387554000

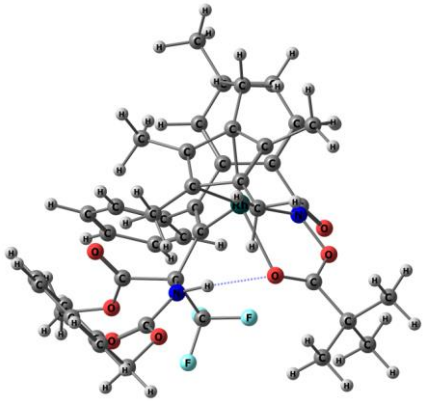
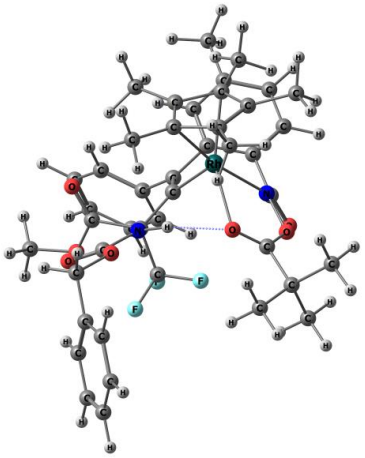
INT2-NO2, E=-2877.17096893, H=-2876.334366, G=-2876.484455

7	-1.402147000	-1.760562000	1.311611000
6	-2.750517000	-1.622614000	0.974698000
6	-3.625551000	-2.669128000	1.217452000
1	-3.255297000	-3.568486000	1.715701000
6	-4.938623000	-2.575223000	0.815577000
1	-5.643135000	-3.388148000	0.991690000
6	-5.332213000	-1.415652000	0.171572000
6	-4.471212000	-0.356960000	-0.053253000
1	-4.851707000	0.540424000	-0.544600000
6	-3.139384000	-0.431890000	0.339265000
6	1.051285000	-2.426616000	-1.956130000
6	-0.107236000	-3.165851000	-1.718878000
6	-1.238675000	-2.334479000	-2.074158000
6	-0.759267000	-1.096518000	-2.552823000
6	0.664613000	-1.107093000	-2.416811000
45	-0.162874000	-1.275466000	-0.433254000
6	-0.924318000	-1.980303000	2.409774000
8	-0.383999000	-2.150701000	3.409662000
6	-2.241627000	0.734992000	0.217758000
6	-0.899646000	0.596253000	0.080051000
6	1.602072000	-0.093213000	-2.935862000
1	1.838369000	-0.306719000	-3.993521000
1	1.186763000	0.923194000	-2.889327000
1	2.556625000	-0.094496000	-2.386988000
6	2.452716000	-2.843507000	-1.767995000
1	2.928968000	-3.007084000	-2.749348000
1	3.047486000	-2.062218000	-1.265232000
1	2.544231000	-3.772756000	-1.190844000
6	-0.232046000	-4.547373000	-1.215591000
1	-0.640570000	-5.213346000	-1.994365000
1	0.731761000	-4.962726000	-0.894372000
1	-0.923353000	-4.606268000	-0.358074000
6	-2.627876000	-2.820704000	-2.132581000
1	-2.779267000	-3.359280000	-3.084396000
1	-2.854410000	-3.535609000	-1.328804000
1	-3.366578000	-2.008109000	-2.101348000
6	-1.574431000	-0.023506000	-3.149571000
1	-1.695326000	-0.203435000	-4.231388000
1	-2.585109000	0.018003000	-2.715562000
1	-1.110094000	0.964913000	-3.030104000
8	1.413874000	-3.263271000	1.346809000
6	0.044668000	1.791396000	0.289282000
7	1.363456000	1.429570000	-0.117521000
6	4.599463000	2.498212000	-0.819402000
1	1.652810000	0.475220000	0.079157000
1	4.480752000	2.995578000	-1.797776000
1	4.684748000	3.275863000	-0.042790000
6	5.756525000	1.562142000	-0.794365000
6	5.909039000	0.625406000	-1.811298000
6	6.632159000	1.543091000	0.281712000
6	6.920134000	-0.316424000	-1.750438000
1	5.219619000	0.638475000	-2.664125000
6	7.651160000	0.605937000	0.340065000
1	6.509205000	2.273652000	1.088783000
6	7.792716000	-0.327248000	-0.672748000
1	7.032749000	-1.049371000	-2.554784000
1	8.339490000	0.600964000	1.190431000
1	8.593419000	-1.071226000	-0.624734000
6	1.951686000	-2.164649000	1.375111000
8	1.447752000	-1.102552000	0.886428000
6	3.289169000	-1.983989000	2.100050000
7	-6.685512000	-1.301714000	-0.271914000
6	0.129480000	2.082391000	1.805247000
9	-0.986875000	2.504256000	2.346212000
9	0.472050000	0.977953000	2.445551000
9	1.062812000	2.975307000	2.069411000
8	3.462266000	1.687647000	-0.567340000
6	2.322738000	2.326126000	-0.370656000
8	2.188551000	3.524216000	-0.440453000
6	-0.323962000	3.033634000	-0.536760000
8	-0.284802000	3.036128000	-1.732983000
8	-0.662238000	4.049317000	0.209587000
6	-0.903492000	5.251284000	-0.495208000
1	-1.601649000	5.093190000	-1.328155000
1	-1.333638000	5.943999000	0.235585000
1	0.046382000	5.650264000	-0.881960000
6	4.056911000	-0.790680000	1.573408000
1	3.512221000	0.154267000	1.728048000
1	5.027120000	-0.704206000	2.092455000
1	4.270380000	-0.884860000	0.493357000
6	2.955718000	-1.773742000	3.568469000
1	2.411177000	-2.636215000	3.986190000
1	3.878561000	-1.641835000	4.157505000
1	2.334424000	-0.874025000	3.716061000
6	4.115339000	-3.242669000	1.934985000
1	4.347661000	-3.438825000	0.874069000
1	5.074555000	-3.143323000	2.469162000
1	3.597926000	-4.127929000	2.332761000
6	-3.010987000	2.016715000	0.242245000
6	-3.271915000	2.694823000	-0.945382000
6	-3.611714000	2.475141000	1.412792000
6	-4.064268000	3.831940000	-0.953090000
6	-4.387140000	3.619216000	1.408852000
6	-4.610939000	4.306675000	0.225858000
1	-2.848580000	2.320273000	-1.883322000
1	-3.457212000	1.926251000	2.347258000
1	-4.256237000	4.350826000	-1.897276000
1	-4.832454000	3.975662000	2.342636000
1	-5.230225000	5.208483000	0.222342000
8	-7.017895000	-0.295099000	-0.856261000
8	-7.440887000	-2.219903000	-0.043790000

Analysis of possible conformers was done by semi-empirical quantum mechanical methods GFNn-xTB realized as XTB software package using **C**onformer-**R**otamer **E**nsemble **S**ampling **T**ool (CREST). The program was run with the NCI option for non-covalent interactions considerations, solvent (methanol) was introduced by ALPB model.

Almost all conformers of intermediate **B** (see proposed mechanism on Scheme 5) with Ph-C≡C- moiety possess hydrogen bond between NH proton and the pivalate oxygen (Table S6). Introducing of CH_2 group between the triple bond and the quaternary amino acid carbon (H-C≡C-***CH₂***-amino acid*) greatly disrupts the structure of the reaction center. Only one conformer (with low occupancy - 16.6%) features NH...O hydrogen bond, whereas all others have another mode of the pivalate coordination, which replaced by the substrate CO_2Me group (Table S7). This coordination mode should completely block Lossen rearrangement, whereas NH...O hydrogen bond in (Ph-C≡C)-containing ligand favors the Lossen pathway.

Table S6. Conformers of intermediate **B** (see Scheme 5 in manuscript).

Most favored isomer of **B** ΔG_{rel} = 0.00 kcal/mol Occupancy = 40.3%	
ΔG_{rel} = 0.09 kcal/mol Occupancy = 23.7%	

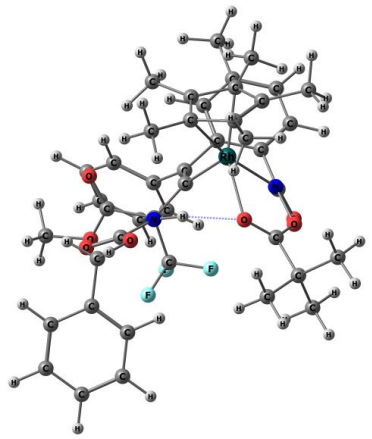
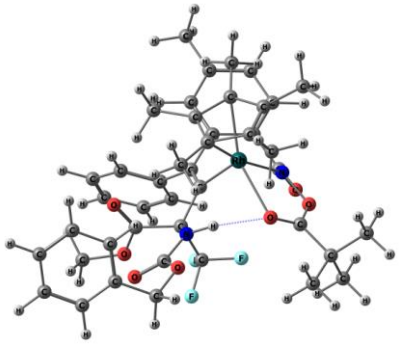
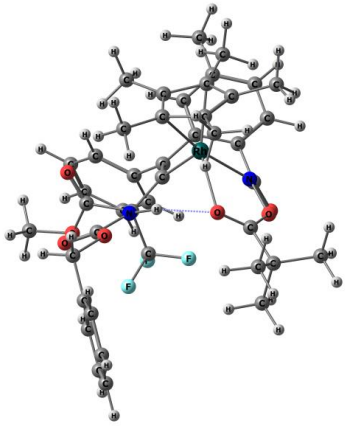
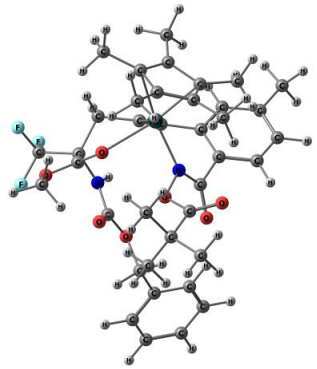
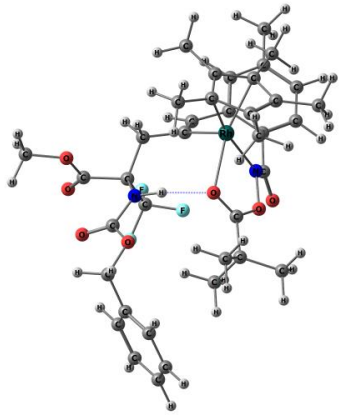
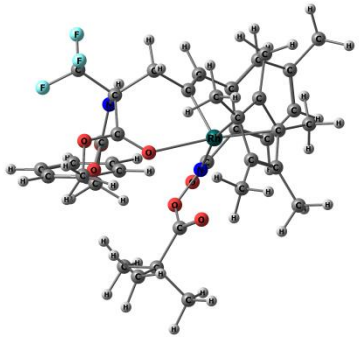
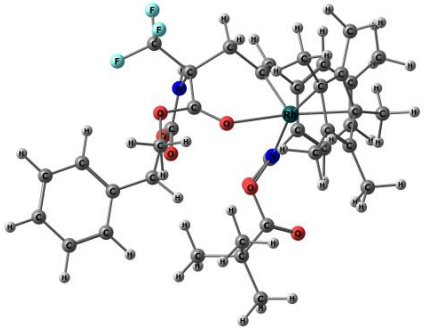
ΔG_{rel} = 0.42 kcal/mol Occupancy = 8.1%	
ΔG_{rel} = 0.39 kcal/mol Occupancy = 5.2%	
ΔG_{rel} = 0.15 kcal/mol Occupancy = 5.0%	

Table S7. Conformers of H-C≡C-***CH₂***-amino acid (homologue of **B**)* sorted by occupancy.

Most favored isomer Pivalate uncoordinated from Rh, CO_2Me group take its place. ΔG_{rel} = 0.00 kcal/mol Occupancy = 31.3%	
The only isomer with hydrogen bond ΔG_{rel} = +0.43 kcal/mol Occupancy = 16.6%	
Pivalate uncoordinated from Rh, CO_2Me group take its place. ΔG_{rel} = 0.29 kcal/mol Occupancy = 15.8%	
Pivalate uncoordinated from Rh, CO_2Me group take its place. ΔG_{rel} = 0.30 kcal/mol Occupancy = 6.9%	

*See: D.V. Vorobyeva, D.A. Petropavlovskikh, I.A. Godovikov, S.E. Nefedov, S.N. Osipov, *Eur. J. Org. Chem.* **2021**, 1883.