Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Three-Component Reaction of Phosphorus Ylides with Isocyanates: Facile Synthesis of 2-Amino-3-Carboxylate-4-Quinolones

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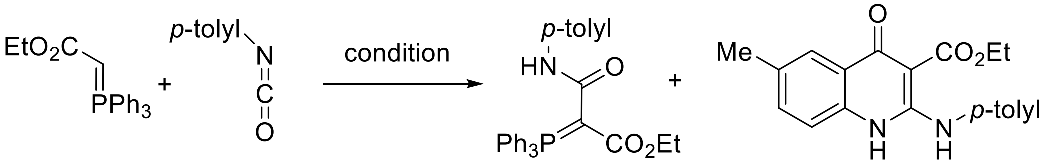
1. General Information

Unless otherwise noted, all reactions were carried out in nitrogen atmosphere under anhydrous conditions using screw cap sealed tube. Solvents were purified prior to use according to standard procedures. All other reagents were purchased from commercial sources and used without further purification. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV 400 spectrometer operating at 400 MHz for ^1H, and 100 MHz for ^{13}C. Chemical shifts are reported in parts per million (ppm) with respect to tetramethylsilane (TMS, $\delta = 0$). Peak multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, br = broad signal. High-resolution ESI mass spectra were acquired with a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer. IR data were obtained on a Nicolet iS10 FT-IR spectrometer. Melting points were measured for all amorphous compounds on an SGW® X-4B apparatus and uncorrected. All reactions were monitored by thin layer chromatography (TLC) and visualized by UV irradiation or stained with potassium permanganate. X-ray crystallographic analysis was performed at Bruker D8 Quest. Column chromatography was performed on silica gel (200–300 mesh) using a mixture of petroleum ether (b.p. 60–90 ºC)/ethyl acetate as eluent.

2. Optimization of Reaction Conditions

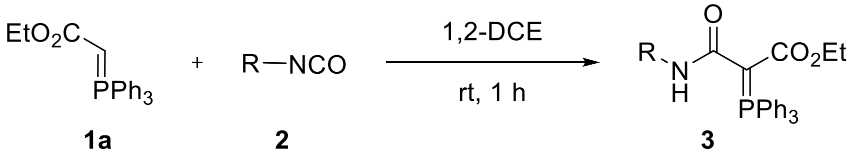
Table S1. Optimization of Reaction Conditions[a]



entry	solvent	temperature	time	yield of **3a**[b]	yield of **4a**[b]
1	1,4-dioxane	100 °C	36 h	8%	68%
2	CH_3CN	100 °C	36 h	12%	47%
3	***1,2-DCE***	***100 °C***	***36 h***	***trace***	***74%***
4	DMSO	100 °C	36 h	10%	51%
5	THF	reflux	36 h	19%	54%
6	DMF	100 °C	36 h	56%	trace
7	benzene	reflux	36 h	14%	61%
8	toluene	100 °C	36 h	11%	55%
9	1,2-DCE	rt	12 h	96%	trace
10	1,2-DCE	40 °C	24 h	92%	trace
11	1,2-DCE	60 °C	36 h	60%	11%
12	1,2-DCE	80 °C	36 h	16%	54%

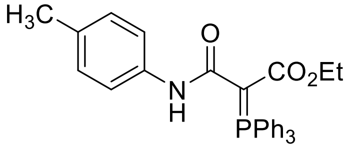
[a] Reaction conditions: P-ylide **1a** (0.50 mmol) and isocyanate **2a** (1.0 mmol) were stirred in the specified solvent (3.0 mL) at the indicated temperature under N_2 atmosphere. [b] Yield of isolated product.

3. General Procedure for the Synthesis of P-Ylides 3



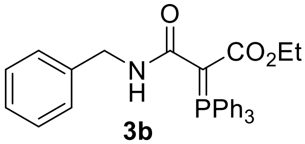
General procedure: Under N_2 atmosphere, to a solution of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (1.0 mmol) in 1,2-dichloroethane (3 mL) was added isocyanate **2** (1.0 mmol) (isocyanates **2c**–**k** were synthesized as previously described[1]) and the mixture was stirred at ambient temperature for 1 h. The solvent was removed by rotary evaporation under reduced pressure and the residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether) to yield **3**.

4. Analytical Data for Compounds 3



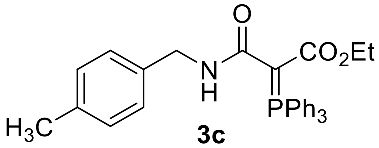
3a

3a[2]: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (348 mg, 1.0 mmol) and 1-isocyanato-4-methylbenzene (133 mg, 1.0 mmol) provided **3a** as white solid, in 462 mg, 96% yield, m. p: 175–177 ^{o}C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.88 (br s, 1H), 7.74–7.68 (m, 6H), 7.53–7.48 (m, 3H), 7.45–7.37 (m, 6H), 7.39 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 3.69 (q, J = 7.1 Hz, 2H), 2.23 (s, 3H), 0.53 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 170.1 (d, $J_{P\text{-}C}$ = 12.7 Hz), 168.0 (d, $J_{P\text{-}C}$ = 9.5 Hz), 137.4 (d, $J_{P\text{-}C}$ = 1.8 Hz), 133.2 (d, $J_{P\text{-}C}$ = 9.7 Hz), 131.4 (d, $J_{P\text{-}C}$ = 3.0 Hz), 130.9, 128.9, 128.3 (d, $J_{P\text{-}C}$ = 12.6 Hz), 127.5 (d, $J_{P\text{-}C}$ = 94.9 Hz), 119.3, 58.16, 56.6 (d, $J_{P\text{-}C}$ = 128.0 Hz), 20.6, 13.5. IR ν_{max} (neat): 2978, 1641, 1618, 1581, 1518, 1438, 1365, 1291, 1251, 1222, 1095, 814, 775, 736, 707, 685, 556, 513, 498, 432 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{29}NO_3P$ [M+H]$^+$: 482.1879, found: 482.1880.



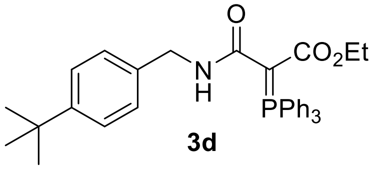
3b

3b: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (348 mg, 1.0 mmol) and (isocyanatomethyl)benzene (133 mg, 1.0 mmol) provided **3b** as white solid, in 462 mg, 96% yield, m. p: 77–79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (t, *J* = 5.8 Hz, 1H), 7.71–7.66 (m, 6H), 7.51–7.47 (m, 3H), 7.44–7.39 (m, 6H), 7.31–7.28 (m, 4H), 7.21–7.16 (m, 1H), 4.42 (d, *J* = 5.8 Hz, 2H), 3.65 (q, *J* = 7.1 Hz, 2H), 0.49 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9 (d, $J_{P\text{-}C}$ = 12.9 Hz), 169.7 (d, $J_{P\text{-}C}$ = 9.0 Hz), 140.5, 133.2 (d, $J_{P\text{-}C}$ = 9.8 Hz), 131.3 (d, $J_{P\text{-}C}$ = 3.0 Hz), 128.3, 128.2, 128.1 (d, $J_{P\text{-}C}$ = 4.2 Hz), 127.5, 126.8 (d, $J_{P\text{-}C}$ = 90.6 Hz), 57.8, 55.1 (d, $J_{P\text{-}C}$ = 128.3 Hz), 42.77 (d, $J_{P\text{-}C}$ = 1.7 Hz), 13.5. IR v_{max} (neat): 3329, 2977, 1616, 1510, 1435, 1368, 1312, 1156, 1098, 776, 752, 690, 511, 484 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{29}NO_3P$ $[M+H]^+$: 482.1879, found: 482.1874.



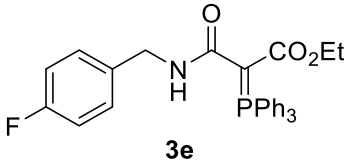
3c

3c: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (348 mg, 1.0 mmol) and 1-(isocyanatomethyl)-4-methylbenzene (147 mg, 1.0 mmol) provided **3c** as white solid, in 450 mg, 91% yield, m. p: 119–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (t, *J* = 5.7 Hz, 1H), 7.71–7.66 (m, 6H), 7.52–7.48 (m, 3H), 7.44–7.40 (m, 6H), 7.19 (d, *J* = 7.7 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 2H), 4.38 (d, *J* = 5.7 Hz, 2H), 3.64 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 0.48 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9 (d, $J_{P\text{-}C}$ = 13.1 Hz), 169.7 (d, $J_{P\text{-}C}$ = 9.0 Hz), 137.5, 135.8, 133.2 (d, $J_{P\text{-}C}$ = 9.8 Hz), 131.3 (d, $J_{P\text{-}C}$ = 2.9 Hz), 128.8, 128.2 (d, $J_{P\text{-}C}$ = 12.5 Hz), 127.5, 127.3 (d, $J_{P\text{-}C}$ = 11.9 Hz), 57.8, 55.0 (d, $J_{P\text{-}C}$ = 128.4 Hz), 42.5 (d, $J_{P\text{-}C}$ = 1.7 Hz), 21.0, 13.5. IR v_{max} (neat): 3352, 1622, 1593, 1515, 1436, 1405, 1364, 1309, 1297, 1285, 1163, 1141, 1093, 1038, 824, 796, 774, 747, 719, 688, 624, 582, 547, 513, 480, 452 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{31}NO_3P$ $[M+H]^+$: 496.2036, found: 496.2032.



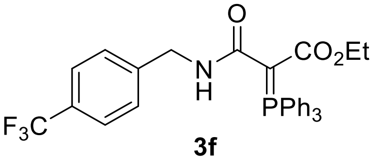
3d

3d: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (348 mg, 1.0 mmol) and 1-(tert-butyl)-4-(isocyanatomethyl)benzene (189 mg, 1.0 mmol) provided **3d** as white solid, in 500 mg, 93% yield, m. p: 53–55 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (t, *J* = 5.7 Hz, 1H), 7.71–7.66 (m, 6H), 7.50–7.48 (m, 3H), 7.44–7.40 (m, 6H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 4.39 (d, *J* = 5.7 Hz, 2H), 3.64 (q, *J* = 7.1 Hz, 2H), 1.31 (s, 9H), 0.48 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8 (d, $J_{P\text{-}C}$ = 12.9 Hz), 169.6 (d, $J_{P\text{-}C}$ = 9.1 Hz), 149.1, 137.4, 133.2 (d, $J_{P\text{-}C}$ = 9.8 Hz), 131.3 (d, $J_{P\text{-}C}$ = 3.1 Hz), 128.2 (d, $J_{P\text{-}C}$ = 12.5 Hz), 127.4, 127.2 (d, $J_{P\text{-}C}$ = 16.0 Hz),125.0, 57.8, 55.0 (d, $J_{P\text{-}C}$ = 128.4 Hz), 42.5 (d, $J_{P\text{-}C}$ = 1.7 Hz), 34.3, 31.3, 13.5. IR ν_{max} (neat): 2960, 1624, 1582, 1513, 1436, 1366, 1300, 1166, 1095, 806, 777, 746, 690, 554, 518, 486 cm^{-1}. HRMS (ESI) calcd for $C_{34}H_{37}NO_3P$ $[M+H]^+$: 538.2505, found: 538.2503.



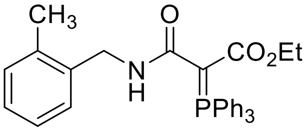
3e

3e: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (348 mg, 1.0 mmol) and 1-fluoro-4-(isocyanatomethyl)benzene (151 mg, 1.0 mmol) provided **3e** as white solid, in 449 mg, 90% yield, m. p: 103–105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (t, *J* = 6.1 Hz, 1H), 7.71–7.63 (m, 6H), 7.54–7.49 (m, 3H), 7.46–7.41 (m, 6H), 7.24–7.22 (m, 2H), 6.96–6.92 (m, 2H), 4.37 (d, *J* = 6.1 Hz, 2H), 3.64 (q, *J* = 7.1 Hz, 2H), 0.48 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0 (d, $J_{P\text{-}C}$ = 12.8 Hz), 169.8 (d, $J_{P\text{-}C}$ = 9.0 Hz), 161.6 (d, $J_{F\text{-}C}$ = 242.0 Hz), 136.4 (d, $J_{F\text{-}C}$ = 3.0 Hz), 133.2 (d, $J_{P\text{-}C}$ = 9.7 Hz), 131.4 (d, $J_{P\text{-}C}$ = 3.0 Hz), 129.1 (d, $J_{F\text{-}C}$ = 7.9 Hz), 128.3 (d, $J_{F\text{-}C}$ = 12.0 Hz), 127.7 (d, $J_{P\text{-}C}$ = 94.8 Hz), 114.8 (d, $J_{F\text{-}C}$ = 22.0 Hz), 57.9, 55.1 (d, $J_{P\text{-}C}$ = 128.1 Hz), 42.0 (d, $J_{P\text{-}C}$ = 1.7 Hz), 13.5. IR ν_{max} (neat): 3325, 1618, 1581, 1504, 1435, 1410, 1389, 1368, 1311, 1292, 1215, 1151, 1098, 1038, 831, 812, 779, 753, 722, 690, 647, 579, 546, 451, cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{28}FNO_3P$ [M+H]$^+$: 500.1785, found: 500.1783.



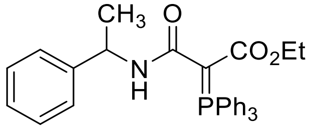
3f

3f: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (348 mg, 1.0 mmol) and 1-(isocyanatomethyl)-4-(trifluoromethyl)benzene (201 mg, 1.0 mmol) provided **3f** as white solid, in 500 mg, 91% yield, m. p: 137–139 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.11 (t, *J* = 6.2 Hz, 1H), 7.71–7.65 (m, 6H), 7.52–7.49 (m, 3H), 7.45–7.42 (m, 6H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H).4.46 (d, *J* = 6.2 Hz, 2H), 3.66 (q, *J* = 7.1 Hz, 2H), 0.50 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 170.1 (d, $J_{P\text{-}C}$ = 9.0 Hz), 169.9 (d, $J_{P\text{-}C}$ = 9.4 Hz), 133.2 (d, $J_{P\text{-}C}$ = 9.7 Hz), 131.4 (d, $J_{F\text{-}C}$ = 2.0 Hz), 127.3 (q, $J_{F\text{-}C}$ = 304.0 Hz), 128.3 (d, $J_{P\text{-}C}$ = 12.6 Hz), 127.5 (d, $J_{P\text{-}C}$ = 95.0 Hz), 124.9 (q, $J_{F\text{-}C}$ = 11.0 Hz), 122.9, 57.9, 55.2 (d, $J_{P\text{-}C}$ = 127.9 Hz), 42.3 (d, $J_{P\text{-}C}$ = 1.7 Hz), 13.5. IR ν_{max} (neat): 2929, 1626, 1582, 1521, 1438, 1415, 1368, 1319, 1303, 1165, 1103, 1062, 1015, 893, 778, 752, 718, 691, 628, 564, 509, 458, 424 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{28}F_3NO_3P$ [M+H]$^+$: 550.1753, found: 550.1755.



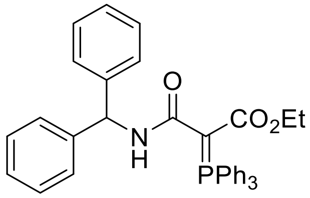
3g

3g: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (348 mg, 1.0 mmol) and 1-(isocyanatomethyl)-2-methylbenzene (147 mg, 1.0 mmol) provided **3g** as white solid, in 478 mg, 96% yield, m. p: 122–125 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.88 (t, *J* = 5.6 Hz,1H), 7.71–7.66 (m, 6H), 7.53–7.49 (m, 3H), 7.46–7.42 (m, 6H), 7.37–7.35 (m, 1H), 7.19–7.12 (m, 3H), 4.45 (d, *J* = 5.6 Hz, 2H), 3.68 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 0.51 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 169.8 (d, $J_{P\text{-}C}$ = 13.1 Hz), 169.5 (d, $J_{P\text{-}C}$ = 8.9 Hz), 137.9, 135.9, 133.1 (d, $J_{P\text{-}C}$ = 9.8 Hz), 131.2 (d, $J_{P\text{-}C}$ = 3.0 Hz), 129.8, 128.1 (d, $J_{P\text{-}C}$ = 12.5 Hz), 128.2, 127.1 (d, $J_{P\text{-}C}$ = 120.4 Hz), 127.2, 125.6, 57.8, 55.0 (d, $J_{P\text{-}C}$ = 128.3 Hz), 40.7 (d, $J_{P\text{-}C}$ = 1.8 Hz), 18.9, 13.4. IR ν_{max} (neat): 2898, 1621, 1587, 1518, 1484, 1460, 1436, 1409, 1367, 1308, 1165, 1100, 1027, 998, 751, 719, 691, 642, 562, 511, 492, 429 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{31}NO_3P$ [M+H]$^+$: 496.2036, found: 496.2034.



3h

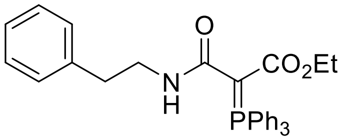
3h: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (348 mg, 1.0 mmol) and (1-isocyanatoethyl)benzene (147 mg, 1.0 mmol) provided **3h** as white solid, in 450 mg, 91% yield, m. p: 157–159 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.02 (d, *J* = 8.2 Hz, 1H), 7.66–7.60 (m, 6H), 7.50–7.45 (m, 3H), 7.41–7.35 (m, 8H), 7.31–7.27 (m, 2H), 7.21–7.17 (m, 1H), 5.05 (quint, *J* = 8.2 Hz, 1H), 3.73–3.60 (m, 2H), 1.46 (d, *J* = 6.9 Hz, 3H), 0.50 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 170.0 (d, J_{P-C} = 13.3 Hz), 169.2 (d, J_{P-C} = 8.7 Hz), 145.7, 133.2 (d, J_{P-C} = 9.8 Hz), 131.2 (d, J_{P-C} = 3.0 Hz), 128.3, 128.2 (d, J_{P-C} = 12.5 Hz), 128.1, 126.8 (d, J_{P-C} = 122.2 Hz), 126.1, 57.8, 55.3 (d, J_{P-C} = 128.4 Hz), 47.9 (d, J_{P-C} = 1.7 Hz), 23.3, 13.5. IR ν_{max} (neat): 3306, 2979, 1622, 1602, 1509, 1435, 1366, 1300, 1273, 1104, 1090, 1070, 1025, 998, 777, 746, 689, 621, 598, 562, 541, 514, 495, 460, 435 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{31}NO_3P$ [M+H]$^+$: 496.2036, found: 496.2031.



3i

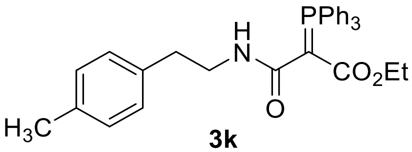
3i: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (348 mg, 1.0 mmol) and (isocyanatomethylene)dibenzene (209 mg, 1.0 mmol) provided **3i** as white solid, in 546 mg, 98% yield, m. p: 191–193 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.50 (d, *J* = 8.7 Hz, 1H), 7.66–7.60 (m, 6H), 7.50–7.45 (m, 3H), 7.40–7.35 (m, 6H), 7.34–7.31 (m, 4H), 7.29–7.24 (m, 4H), 7.21–7.17 (m, 2H), 6.23 (d, *J* = 8.7 Hz, 1H), 3.67 (q, *J* = 7.1 Hz, 2H), 0.49 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 170.0 (d, J_{P-C} = 13.1 Hz), 169.2 (d, J_{P-C} = 8.8

Hz), 143.6, 133.2 (d, $J_{P\text{-}C}$ = 9.8 Hz), 131.3 (d, $J_{P\text{-}C}$ = 3.0 Hz), 128.3, 128.1 (d, $J_{P\text{-}C}$ = 2.9 Hz), 127.4, 126.8 (d, $J_{P\text{-}C}$ = 81.1 Hz), 57.9, 56.1 (d, $J_{P\text{-}C}$ = 1.7 Hz), 55.4 (d, $J_{P\text{-}C}$ = 128.3 Hz), 13.5. IR ν_{max} (neat): 3300, 1618, 1578, 1492, 1434, 1395, 1369, 1309, 1186, 1114, 1096, 1027, 998, 774, 747, 703, 689, 641, 579, 543, 521, 507, 467, 420 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{33}NO_3P$ [M+H]$^+$: 558.2192, found: 558.2191.



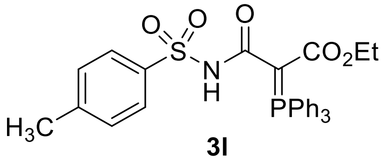
3j

3j: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (348 mg, 1.0 mmol) and (2-isocyanatoethyl)benzene (147 mg, 1.0 mmol) provided **3j** as white solid, in 466 mg, 94% yield, m. p: 86–88 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (t, *J* = 5.9 Hz, 1H), 7.68–7.63 (m, 6H), 7.52–7.47 (m, 3H), 7.44–7.39 (m, 6H), 7.25–7.17 (m, 5H), 3.64 (q, *J* = 7.1 Hz, 2H), 3.47 (q, *J* = 7.1 Hz, 2H), 2.80 (t, *J* = 7.1 Hz, 2H), 0.50 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9 (d, $J_{P\text{-}C}$ = 5.0 Hz), 169.8 (d, $J_{P\text{-}C}$ = 9.3 Hz), 140.0, 133.1 (d, $J_{P\text{-}C}$ = 9.7 Hz), 131.3 (d, $J_{P\text{-}C}$ = 2.9 Hz), 128.8, 128.3, 128.2 (d, $J_{P\text{-}C}$ = 12.5 Hz), 128.1, 126.6 (d, $J_{P\text{-}C}$ = 165.6 Hz), 57.8, 55.0 (d, $J_{P\text{-}C}$ = 128.4 Hz), 40.2, 36.7, 13.5. IR ν_{max} (neat): 2979, 1622, 1577, 1521, 1436, 1367, 1303, 1093, 1029, 778, 749, 689, 553, 514, 414 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{31}NO_3P$ [M+H]$^+$: 496.2036, found: 496.2030.



3k

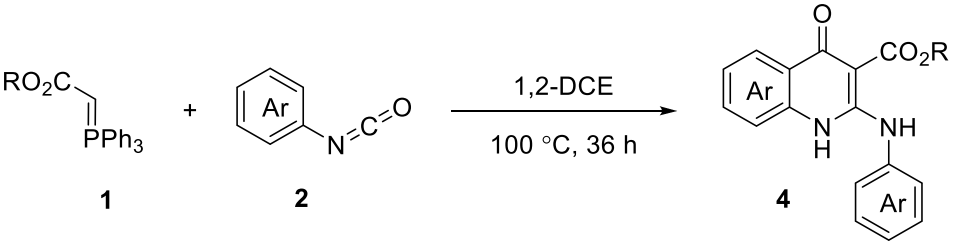
3k: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (348 mg, 1.0 mmol) and 1-(2-isocyanatoethyl)-4-methylbenzene (161 mg, 1.0 mmol) provided **3k** as white solid, in 470 mg, 92% yield, m. p: 120–122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (t, *J* = 5.4 Hz, 1H), 7.69–7.63 (m, 6H), 7.50–7.47 (m, 3H), 7.44–7.39 (m, 6H), 7.11–7.04 (m, 3H), 7.00 (s, 1H), 3.64 (q, *J* = 7.1 Hz, 2H), 3.46–3.41 (m, 2H), 2.76 (t, *J* = 7.4 Hz, 2H), 2.30 (s, 3H), 0.50 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9 (d, $J_{P\text{-}C}$ = 2.0 Hz), 169.8 (d, $J_{P\text{-}C}$ = 8.8 Hz), 136.9, 135.1, 133.2 (d, $J_{P\text{-}C}$ = 9.8 Hz), 131.3 (d, $J_{P\text{-}C}$ = 2.9 Hz), 128.8, 128.6, 127.9 (d, $J_{P\text{-}C}$ = 93.0 Hz), 128.2 (d, $J_{P\text{-}C}$ = 12.5 Hz), 57.8, 55.0 (d, $J_{P\text{-}C}$ = 128.4 Hz), 40.4, 36.3, 21.0, 13.6. IR ν_{max} (neat): 2976, 1625, 1585, 1525, 1504, 1483, 1437, 1393, 1369, 1303, 1217, 1161, 1093, 872, 844, 809, 777, 751, 706, 690, 639, 567, 543, 509, 464 cm^{-1}. HRMS (ESI) calcd for $C_{32}H_{33}NO_3P$ [M+H]$^+$: 510.2192, found: 510.2192.



3l

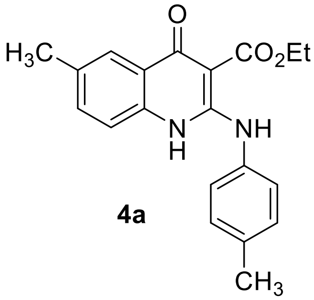
3l: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (348 mg, 1.0 mmol) and 4-methylbenzenesulfonyl isocyanate (197 mg, 1.0 mmol) provided **3l** as white solid, in 545 mg, 100% yield, m. p: 176–179 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 11.87 (br s, 1H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.52–7.47 (m, 9H), 7.39–7.33 (m, 6H), 7.19 (d, *J* = 8.3 Hz, 2H), 3.67 (q, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 0.49 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 169.8 (d, $J_{P\text{-}C}$ = 11.4 Hz), 166.1 (d, $J_{P\text{-}C}$ = 10.7 Hz), 142.7, 137.8, 133.1 (d, $J_{P\text{-}C}$ = 9.9 Hz), 131.8 (d, $J_{P\text{-}C}$ = 3.0 Hz), 128.8, 128.4 (d, $J_{P\text{-}C}$ = 12.7 Hz), 127.8, 125.4 (d, $J_{P\text{-}C}$ = 94.6 Hz), 58.8, 57.6 (d, $J_{P\text{-}C}$ = 123.0 Hz), 21.5, 13.3. IR ν_{max} (neat): 2989, 1614, 1414, 1367, 1340, 1308, 1155, 1130, 1090, 1032, 876, 824, 812, 778, 751, 739, 706, 687, 657, 571, 537, 521, 503, 481, 423 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{29}NO_5PS$ [M+H]$^+$: 546.1499, found: 546.1498.

5. General Procedure for the Synthesis of 2-Amino-3-Carboxylate-4-Quinolones 4



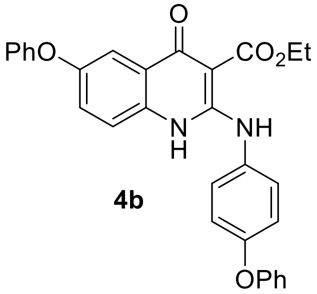
Under N_2 atmosphere, to a solution of P-ylide **1** (0.50 mmol) in 1,2-dichloroethane (3 mL) was added isocyanate **2** (1.0 mmol). The mixture was stirred at 100 °C for 36 h. Then, the reaction mixture was cooled to ambient temperature. The solvent was removed by rotary evaporation under reduced pressure and the residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether) to yield **4**.

6. Analytical Data for Compounds 4



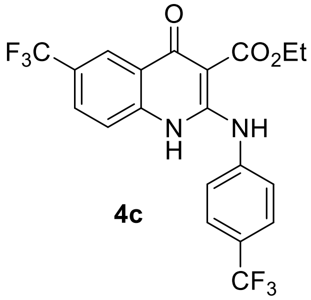
4a

4a: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol) and 1-isocyanato-4-methylbenzene **2a** (197 mg, 1.0 mmol) provided **4a** as yellow solid, in 124 mg, 74% yield, m. p: 222–224 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.69 (br s, 1H), 10.60 (br s, 1H), 7.80 (s, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.28 (m, 4H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 2.34 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.6, 169.6, 153.3, 135.2, 135.1, 134.3, 132.7, 132.0, 130.3, 124.9, 124.2, 123.9, 117.4, 93.3, 59.6, 20.6, 20.9, 14.3. IR v_{max} (neat): 2956, 1632, 1578, 1514, 1434, 1365, 1281, 1200, 1148, 1096, 1018, 807, 742, 665, 556, 541, 520, 489 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{21}N_2O_3$ $[M+H]^+$: 337.1547, found: 337.1540.



4b

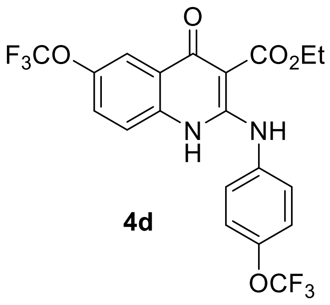
4b: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol) and 1-isocyanato-4-phenoxybenzene **2b** (211 mg, 1.0 mmol) provided **4b** as yellow solid, in 118 mg, 48% yield, m. p: 157–159 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 10.82 (br s, 1H), 10.59 (br s, 1H), 7.58 (d, *J* = 8.9 Hz, 1H), 7.47–7.39 (m, 7H), 7.31 (dd, *J* = 8.9, 2.8 Hz, 1H), 7.20–7.16 (m, 2H), 7.11–7.03 (m, 6H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 172.9, 169.4, 156.7, 156.6, 154.7, 153.4, 152.7, 133.3, 132.2, 130.1, 126.5, 125.2, 123.7, 123.6, 123.5, 119.8, 119.6, 118.8, 118.7, 112.9, 93.1, 59.7, 14.3. IR v_{max} (neat): 2977, 1632, 1582, 1524, 1503, 1485, 1368, 1303, 1280, 1217, 1161, 1095, 1051, 872, 844, 807, 768, 742, 706, 688, 566, 523, 506, 428 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{25}N_2O_5$ [M+H]$^+$: 493.1758, found: 493.1762.



4c

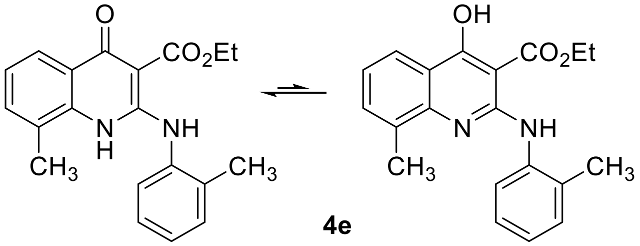
4c: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol) and 1-isocyanato-4-(trifluoromethyl)benzene **2c** (187 mg, 1.0 mmol) provided **4c** as yellow solid, in 144 mg, 65% yield, m. p: 124–126 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 12.79 (br s, 1H), 9.54 (br s, 1H), 8.36 (s, 1H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.76 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 2H), 4.59 (q, *J* = 7.1 Hz, 2H), 1.58 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 169.8, 169.3, 152.6, 142.6, 129.0 (q, J_{F-C} = 10.0 Hz), 128.2

127.1, 126.1 (q, $J_{F\text{-}C}$ = 12.0 Hz), 124.2 (q, $J_{F\text{-}C}$ = 289.1 Hz), 125.1, 124.8, 122.9, 122.8, 121.9 (q, $J_{F\text{-}C}$ = 13.1 Hz), 116.9, 93.6, 63.5, 14.1. IR v_{max} (neat): 3392, 1660, 1635, 1597, 1547, 1443, 1415, 1316, 1257, 1150, 1110, 1064, 1011, 950, 908, 870, 850, 834, 730, 609, 525, 414 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{15}F_6N_2O_3$ [M+H]$^+$: 445.0982, found: 445.0974.



4d

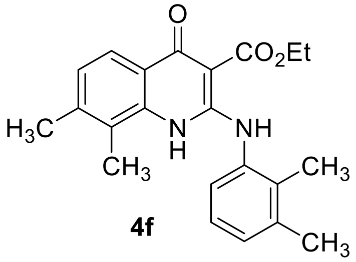
4d: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol) and 1-isocyanato-4-(trifluoromethoxy)benzene **2d** (203 mg, 1.0 mmol) provided **4d** as yellow solid, in 125 mg, 52% yield, m. p: 167–169 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 11.30 (br s, 1H), 10.46 (s, 1H), 7.86 (s, 1H), 7.63 (d, *J* = 8.6 Hz, 1H), 7.58–7.53 (m, 3H), 7.42 (d, *J* = 8.6 Hz, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d$_6$) δ ^{13}C NMR 168.6, 152.8, 145.3 (q, $J_{F\text{-}C}$ = 14.0 Hz), 143.9, 136.9, 125.2, 125.0 (q, $J_{F\text{-}C}$ = 10.1 Hz), 122.7 (q, $J_{F\text{-}C}$ = 259.2 Hz), 122.36, 117.6 (q, $J_{F\text{-}C}$ = 258.0 Hz), 116.5, 99.5, 95.1, 60.1, 14.16. IR v_{max} (neat): 2968, 1656, 1583, 1508, 1449, 1352, 1239, 1191, 1160, 1016, 919, 832, 800, 665, 597, 571, 541, 474 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{15}F_6N_2O_5$ [M+H]$^+$: 447.0880, found: 447.0873.



4e

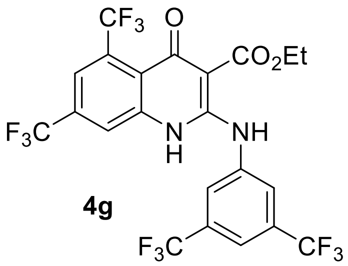
4e: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol) and 1-isocyanato-2-methylbenzene **2e** (133 mg, 1.0 mmol) provided **4e** as yellow solid, in 113 mg, 67% yield,

m. p: 84–86 °C; existing as a pair of tautomers (keto : enol = 1 : 0.3). ^{1}H NMR (400 MHz, $CDCl_3$) keto: δ 11.26 (br s, 1H), 8.19 (d, *J* = 6.2 Hz, 1H), 7.61 (br s, 1H), 7.44 (d, *J* = 6.2 Hz, 1H), 7.40–7.38 (m, 3H), 7.30–7.26 (m, 1H), 7.16–7.11 (m, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 2.03 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H); enol: δ 12.83 (br s, 1H), 9.06 (br s, 1H), 8.70 (d, *J* = 8.0 Hz, 1H), 7.98–7.96 (m, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.26–7.21 (m, 2H), 7.01 (td, *J* = 7.4, 1.0 Hz, 2H), 4.64 (q, *J* = 7.2 Hz, 2H), 2.57 (s, 3H), 2.38 (s, 3H), 1.54 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) keto: δ 175.4, 170.7, 154.2, 135.7, 134.2, 132.8, 132.3, 128.5, 127.8, 126.5, 125.2, 124.3, 123.1, 122.0, 91.9, 60.5, 17.8, 15.3, 14.4; enol: δ 170.2, 169.9, 150.8, 148.2, 138.6, 134.4, 133.3, 133.1, 130.0, 127.5, 126.1, 122.5, 121.8, 121.2, 116.0, 92.5, 62.8, 18.5, 18.0, 14.5. IR ν_{max} (neat): 3421, 1622, 1577, 1544, 1467, 1393, 1373, 1306, 1237, 1178, 1156, 1071, 1027, 870, 780, 752, 569, 541, 454 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{21}N_2O_3$ $[M+H]^+$: 337.1547, found: 337.1536.



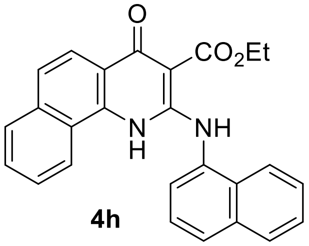
4f

4f: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol) and 1-isocyanato-2,3-dimethylbenzene **2f** (147 mg, 1.0 mmol) provided **4f** as yellow solid, in 131 mg, 72% yield, m. p: 116–118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.21 (br s, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 7.67 (br s, 1H), 7.28–7.24 (m, 3H), 7.03 (d, *J* = 8.2 Hz, 1H), 4.44 (q, *J* = 7.0 Hz, 2H), 2.38 (s, 3H), 2.30 (s, 3H), 2.24 (s, 3H), 1.87 (s, 3H), 1.49 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 170.7, 154.4, 140.3, 139.8, 134.3, 134.1, 132.9, 130.0, 127.0, 125.4, 124.3, 122.4, 119.9, 91.3, 60.4, 20.5, 14.4, 14.1, 11.3. IR ν_{max} (neat): 3416, 2921, 1621, 1600, 1581, 1536, 1462, 1369, 1297, 1239, 1218, 1183, 1165, 1092, 1019, 882, 866, 794, 777, 714, 593, 573, 538, 455 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{25}N_2O_3$ $[M+H]^+$: 365.1859, found: 365.1851.



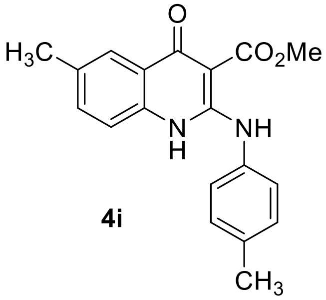
4g

4g: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol) and 1-isocyanato-3,5-bis(trifluoromethyl)benzene **2g** (255 mg, 1.0 mmol) provided **4g** as yellow solid, in 175 mg, 60% yield, m. p: 79–81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.48 (br s, 1H), 9.71 (br s, 1H), 8.30 (s, 2H), 8.03 (s, 1H), 7.90 (s, 1H), 7.61 (s, 1H), 4.73 (q, *J* = 7.1 Hz, 2H), 1.64 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 168.9, 152.2, 150.1, 140.5, 133.6, 133.3, 132.1 (q, $J_{F\text{-}C}$ = 99.1 Hz), 129.2 (d, $J_{F\text{-}C}$ = 3.2 Hz), 128.6, 128.2, 124.6, 121.9, 120.49 (d, $J_{F\text{-}C}$ = 4.1 Hz), 116.5 (septet, $J_{F\text{-}C}$ = 22.1 Hz), 115.3, 94.9, 64.3, 14.2. IR ν_{max} (neat): 3392, 1663, 1590, 1562, 1473, 1377, 1272, 1272, 1121, 998, 947, 882, 850, 773, 725, 701, 681, 613, 539, 452 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{13}F_{12}N_2O_3$ [M+H]$^+$: 581.0729, found: 581.0729.



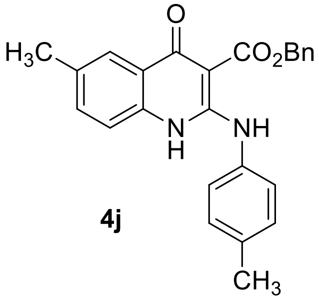
4h

4h: Following the general procedure, the reaction of ethyl 2-(triphenylphosphoranylidene)acetate **1a** (174 mg, 0.50 mmol) and 1-isocyanatonaphthalene **2h** (169 mg, 1.0 mmol) provided **4h** as yellow solid, in 160 mg, 78% yield, m. p: 105–107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.65 (br s, 1H), 9.73 (br s, 1H), 8.80 (d, *J* = 8.2 Hz, 1H), 8.64 (d, *J* = 7.8 Hz, 1H), 8.09–8.07 (m, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.92–7.90 (m, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.63–7.57 (m, 2H), 7.53–7.47 (m, 4H), 4.61 (q, *J* = 7.2 Hz, 2H), 1.54 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 168.8, 152.7, 148.5, 135.8, 135.1, 134.3, 130.0, 128.8, 128.7, 127.5, 126.2, 125.8, 125.7, 125.7, 125.6, 123.6, 122.9, 121.2, 119.8, 119.5, 112.1, 92.9, 63.0, 14.4. IR v_{max} (neat): 3428, 2975, 1618, 1577, 1540, 1503, 1446, 1404, 1369, 1301, 1273, 1245, 1162, 1092, 1021, 881, 865, 832, 816, 798, 780, 762, 694, 653, 629, 567, 534, 487, 451 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{21}N_2O_3$ $[M+H]^+$: 409.1546, found: 409.1538.



4i

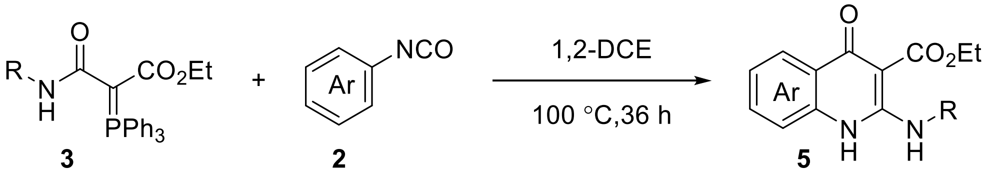
4i: Following the general procedure, the reaction of methyl 2-(triphenylphosphoranylidene)acetate **1b** (167 mg, 0.50 mmol) and 1-isocyanato-4-methylbenzene **2a** (133 mg, 1.0 mmol) provided **4i** as yellow solid, in 97 mg, 60% yield, m. p: 229–231 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.18 (br s, 1H), 8.81 (br s, 1H), 8.03 (s, 1H), 7.66–7.60 (m, 1H), 7.53 (d, *J* = 6.3 Hz, 1H), 7.45 (d, *J* = 6.3 Hz, 1H), 7.27–7.23 (m, 1H), 7.16 (s, 2H), 3.82 (s, 3H), 2.40 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 170.9, 154.4, 137.4, 134.1, 133.0, 132.3, 132.0, 131.9, 131.8, 130.8, 128.4, 128.3, 126.4, 125.8, 124.0, 115.8, 92.0, 51.4, 20.9, 20.8. IR v_{max} (neat): 2913, 1645, 1573, 1512, 1433, 1308, 1281, 1203, 1094, 974, 828, 807, 783, 745, 720, 694, 588, 539, 519, 490 cm^{-1}. HRMS (ESI) calcd for $C_{19}H_{19}N_2O_3$ $[M+H]^+$: 323.1391, found: 323.1380.



4j

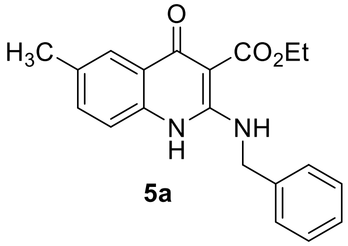
4j: Following the general procedure, the reaction of benzyl 2-(triphenylphosphoranylidene)acetate **1c** (205 mg, 0.50 mmol) and 1-isocyanato-4-methylbenzene **2a** (133 mg, 1.0 mmol) provided **4j** as yellow solid, in 120 mg, 60% yield, m. p: 206–208 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.92 (br s, 1H), 9.16 (br s, 1H), 7.97 (s, 1H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.30–7.20 (m, 5H), 7.08–7.06 (m, 4H), 5.33 (s, 2H), 2.38 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 154.1, 136.3, 133.2, 132.8, 130.4, 128.3, 127.6, 125.9, 125.2, 92.1, 65.9, 20.9, 20.8. IR v_{max} (neat): 2947, 1642, 1578, 1495, 1430, 1397, 1379, 1341, 1277, 1194, 1151, 1094, 973, 903, 834, 807, 769, 696, 662, 601, 543, 521, 490, 454 cm^{-1}. HRMS (ESI) calcd for $C_{25}H_{23}N_2O_3$ $[M+H]^+$: 399.1703, found: 399.1710.

7. General Procedure for the Synthesis of 2-Amino-3-Carboxylate-4-Quinolones 5



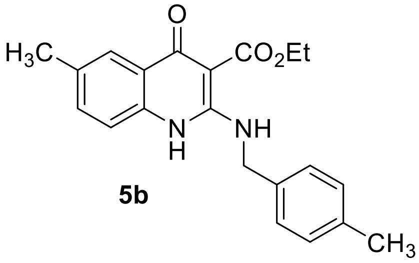
Under N_2 atmosphere, to a solution of P-ylide **3** (0.50 mmol) in 1,2-dichloroethane (3 mL) was added isocyanate **2** (0.50 mmol). The mixture was stirred at 100 °C for 36 h. Then, the reaction mixture was cooled to ambient temperature. The solvent was removed by rotary evaporation under reduced pressure and the residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether) to yield **5**.

8. Analytical Data for Compounds 5



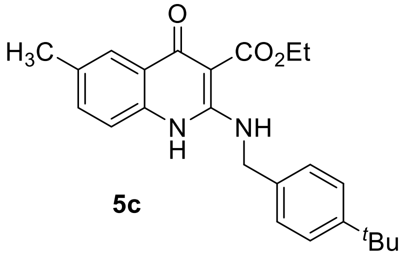
5a

5a: Following the general procedure, the reaction of ethyl 3-(benzylamino)-3-oxo-2-(triphenylphosphoranylidene)propanoate **3b** (240 mg, 0.50 mmol) and 1-isocyanato-4-methylbenzene **2a** (66 mg, 0.50 mmol) provided **5a** as yellow solid, in 138 mg, 64% yield, m. p: 209–211 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 10.46 (br s, 1H), 9.77 (t, *J* = 4.0 Hz, 1H), 7.78 (s, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.41 (d, *J* = 4.4 Hz, 4H), 7.37–7.31 (m, 2H), 4.72 (d, *J* = 5.6 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 173.2, 169.9, 155.4, 137.3, 135.2, 132.7, 131.8, 128.8, 128.2, 127.6, 127.4, 127.2, 125.2, 123.6, 116.7, 90.9, 59.2, 45.0, 20.6, 14.4. IR v_{max} (neat): 2979, 1642, 1606, 1576, 1531, 1494, 1423, 1328, 1306, 1280, 1224, 1140, 1109, 1077, 1051, 1027, 957, 912, 821, 807, 767, 718, 673, 641, 581, 561, 537, 484, 455, 429 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{21}N_2O_3$ [M+H]$^+$: 337.1546, found: 337.1552.



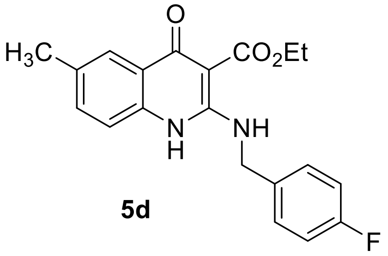
5b

5b: Following the general procedure, the reaction of ethyl 3-((4-methylbenzyl)amino)-3-oxo-2-(triphenylphosphoranylidene)propanoate **3c** (248 mg, 0.50 mmol) and 1-isocyanato-4-methylbenzene **2a** (66 mg, 0.50 mmol) provided **5b** as yellow solid, in 146 mg, 83% yield, m. p: 214–216 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.40 (br s, 1H), 9.70 (t, *J* = 5.2 Hz, 1H), 7.77 (s, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.35 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 4.65 (d, *J* = 5.2 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 2.30 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.2, 169.9, 155.3, 136.9, 135.2, 134.1, 132.7, 131.8, 129.4, 127.5, 125.2, 123.6, 116.7, 90.9, 59.2, 44.9, 20.7, 20.6, 14.40. IR v_{max} (neat): 2986, 1648, 1596, 1571, 1526, 1444, 1380, 1282, 1220, 1169, 1131, 1102, 1045, 1009, 821, 809, 768, 746, 709, 674, 556, 543, 480, 435 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{23}N_2O_3$ [M+H]$^+$: 351.1703, found: 351.1700.



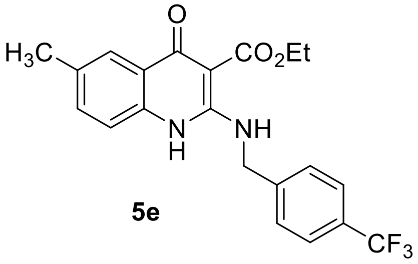
5c

5c: Following the general procedure, the reaction of ethyl 3-((4-(tert-butyl)benzyl)amino)-3-oxo-2-(triphenylphosphoranylidene)propanoate **3d** (269 mg, 0.50 mmol) and 1-isocyanato-4-methylbenzene **2a** (66 mg, 0.50 mmol) provided **5c** as yellow solid, in 165 mg, 84% yield, m. p: 197–199 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.47 (br s, 1H), 9.75 (t, *J* = 4.0 Hz, 1H), 7.79 (s, 1H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.36–7.32 (m, 3H), 4.67 (d, *J* = 4.9 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 1.27 (s, 9H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.2, 169.9, 155.4, 150.1, 135.2, 134.1, 132.6, 131.8, 127.2, 125.6, 125.2, 123.6, 116.7, 90.8, 59.1, 44.8, 34.2, 31.1, 20.6, 14.4. IR v_{max} (neat): 2960, 1624, 1582, 1513, 1436, 1366, 1300, 1166, 1095, 806, 777, 746, 690, 554, 518, 486 cm^{-1}. HRMS (ESI) calcd for $C_{24}H_{29}N_2O_3$ [M+H]$^+$: 393.2172, found: 393.2167.



5d

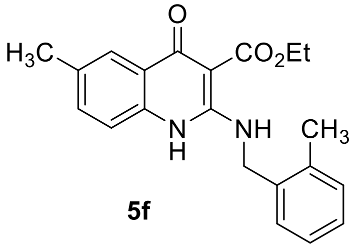
5d: Following the general procedure, the reaction of ethyl 3-((4-fluorobenzyl)amino)-3-oxo-2-(triphenylphosphoranylidene)propanoate **3e** (250 mg, 0.50 mmol) and 1-isocyanato-4-methylbenzene **2a** (66 mg, 0.50 mmol) provided **5d** as yellow solid, in 100 mg, 56% yield, m. p: 195–197 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 10.46 (br s, 1H), 9.74 (t, *J* = 5.8 Hz, 1H), 7.77 (s, 1H), 7.48–7.44 (m, 3H), 7.35 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.26–7.21 (m, 2H), 4.70 (d, *J* = 5.8 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 173.2, 169.9, 161.6 (d, $J_{F\text{-}C}$ = 242.0 Hz), 155.3, 135.2, 133.6, 132.7, 131.9, 129.6 (d, $J_{F\text{-}C}$ = 8.3 Hz), 125.1, 123.7, 116.7, 115.6 (d, $J_{F\text{-}C}$ = 21.2 Hz), 91.0, 59.2, 44.2, 20.6, 14.4. IR v_{max} (neat): 2976, 1642, 1601, 1582, 1538, 1508, 1425, 1328, 1305, 1281, 1226, 1138, 1111, 1094, 1053, 1027, 956, 902, 830, 802, 768, 735, 674, 643, 567, 540, 498, 454 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{20}FN_2O_3$ [M+H]$^+$: 335.1452, found: 335.1447.



5e

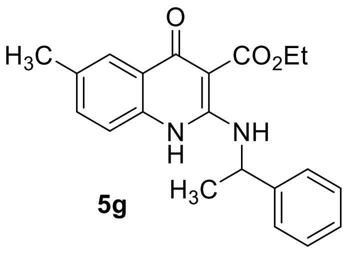
5e: Following the general procedure, the reaction of ethyl 3-oxo-3-((4-(trifluoromethyl)benzyl)amino)-2-(triphenylphosphoranylidene)propanoate **3f** (275 mg, 0.50 mmol) and 1-isocyanato-4-methylbenzene **2a** (66 mg, 0.50 mmol) provided **5e** as yellow solid, in 102 mg, 50% yield, m. p: 194–196 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ

10.47 (br s, 1H), 9.84 (t, J = 6.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 3H), 7.59 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.3 Hz, 1H), 7.34 (dd, J = 8.3, 1.4 Hz, 1H), 4.86 (d, J = 6.0 Hz, 2H), 4.18 (q, J = 7.1 Hz, 2H), 2.33 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 173.2, 169.9, 155.4, 142.6, 135.2, 132.3 (d, $J_{F\text{-}C}$ = 78.0 Hz), 127.3 (q, $J_{F\text{-}C}$ = 259.2 Hz), 125.6 (q, $J_{F\text{-}C}$ = 8.3 Hz), 125.1, 123.7, 122.9, 116.7, 91.2, 59.2, 44.3, 20.6, 14.4. IR ν_{max} (neat): 2957, 1649, 1602, 1569, 1525, 1428, 1369, 1322, 1281, 1223, 1162, 1125, 1105, 1066, 1017, 954, 902, 820, 808, 716, 676, 638, 591, 566, 543, 518, 470, 439 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{20}F_3N_2O_3$ [M+H]$^+$: 405.1420, found: 405.1420.



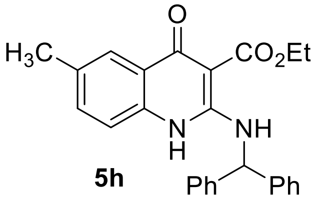
5f

5f: Following the general procedure, the reaction of ethyl 3-((2-methylbenzyl)amino)-3-oxo-2-(triphenylphosphoranylidene)propanoate **3g** (248 mg, 0.50 mmol) and 1-isocyanato-4-methylbenzene **2a** (66 mg, 0.50 mmol) provided **5f** as yellow solid, in 124 mg, 71% yield, m. p: 179–181 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 10.45 (br s, 1H), 9.65 (t, J = 5.4 Hz, 1H), 7.78 (s, 1H), 7.48 (d, J = 8.3 Hz, 1H), 7.37 (d, J = 8.3 Hz, 1H), 7.32 (d, J = 6.7 Hz, 1H), 7.26–7.21 (m, 3H), 4.68 (d, J = 5.4 Hz, 2H), 4.15 (q, J = 7.1 Hz, 2H), 3.35 (s, 3H), 2.34 (s, 3H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 173.1, 170.0, 155.5, 136.1, 135.2, 135.1, 132.7, 131.8, 130.5, 127.8, 127.5, 126.3, 125.2, 123.7, 116.7, 90.8, 59.2, 43.5, 20.6, 18.6, 14.3. IR ν_{max} (neat): 2974, 1651, 1600, 1571, 1528, 1443, 1424, 1331, 1280, 1222, 1171, 1136, 1096, 1051, 954, 824, 810, 770, 745, 730, 673, 558, 542, 469, 427 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{23}N_2O_3$ [M+H]$^+$: 351.1703, found: 351.1700.

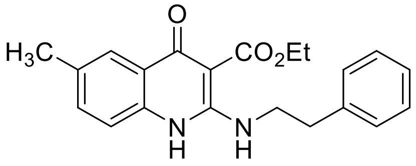


5g

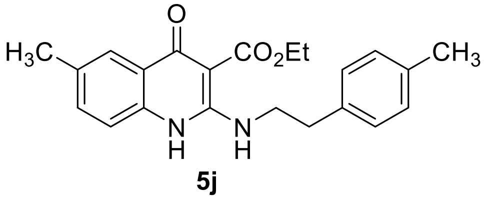
5g: Following the general procedure, the reaction of ethyl 3-oxo-3-((1-phenylethyl)amino)-2-(triphenylphosphoranylidene)propanoate **3h** (248 mg, 0.50 mmol) and 1-isocyanato-4-methylbenzene **2a** (66 mg, 0.50 mmol) provided **5g** as yellow solid, in 53 mg, 30% yield, m. p: 214–216 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 10.63 (br s, 1H), 9.90 (d, *J* = 8.3 Hz, 1H), 7.76 (s, 1H), 7.46–7.27 (m, 7H), 5.39–5.35 (m, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.33 (s, 3H), 1.57 (d, *J* = 6.5 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 172.9, 170.0, 154.6, 142.8, 133.0, 132.1, 128.8, 128.2, 127.5, 125.7, 125.0, 122.9, 116.8, 91.3, 59.6, 50.1, 23.4, 20.6, 14.3. IR ν_{max} (neat): 2973, 1646, 1605, 1574, 1532, 1493, 1439, 1376, 1345, 1307, 1280, 1228, 1202, 1142, 1107, 1084, 1023, 957, 871, 822, 807, 771, 724, 697, 682, 589, 561, 537, 460 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{23}N_2O_3$ [M+H]$^+$: 351.1703, found: 351.1700.


5h

5h: Following the general procedure, the reaction of ethyl 3-(benzhydrylamino)-3-oxo-2-(triphenylphosphoranylidene)propanoate **3i** (279 mg, 0.50 mmol) and 1-isocyanato-4-methylbenzene **2a** (66 mg, 0.50 mmol) provided **5h** as yellow solid, in 145 mg, 70% yield, m. p: 249–251 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 10.54 (br s, 1H), 10.48 (d, *J* = 8.8 Hz, 1H), 8.32 (s, 1H), 7.76 (s, 1H), 7.42–7.28 (m, 11H), 6.53 (d, *J* = 8.8 Hz, 1H), 4.22 (q, *J* = 7.0 Hz, 2H), 2.32 (s, 3H), 1.26 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d$_6$) 173.3, 170.4, 154.9, 141.2, 134.9, 132.8, 132.1, 129.0, 127.7, 126.7, 125.2, 123.7, 116.6, 91.3, 79.2, 59.5, 58.2, 20.6, 14.3. IR ν_{max} (neat): 2979, 1649, 1600, 1570, 1526, 1439, 1311, 1281, 1221, 1134, 1104, 1027, 825, 810, 738, 697, 607, 564, 543, 470, 438 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{25}N_2O_3$ [M+H]$^+$: 413.1859, found: 413.1852.

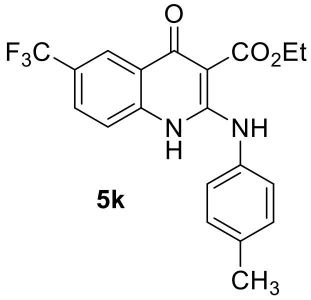

5i

5i: Following the general procedure, the reaction of ethyl 3-oxo-3-(phenethylamino)-2-(triphenylphosphoranylidene)propanoate **3j** (248 mg, 0.50 mmol) and 1-isocyanato-4-methylbenzene **2a** (66 mg, 0.50 mmol) provided **5i** as yellow solid, in 97 mg, 55% yield, m. p: 224–226 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 10.28 (br s, 1H), 9.49 (t, *J* = 5.2 Hz, 1H), 7.76 (s, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.33–7.24 (m, 6H), 4.15 (q, *J* = 7.0 Hz, 2H), 3.67 (dd, *J* = 12.2, 6.6 Hz, 2H), 2.96 (t, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 1.23 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 173.1, 169.9, 155.3, 138.5, 135.3, 132.6, 131.7, 128.9, 128.4, 126.5, 125.1, 123.6, 116.7, 90.7, 59.1, 42.9, 34.6, 20.7, 14.4. IR ν_{max} (neat): 2973, 1646, 1601, 1573, 1527, 1497, 1446, 1390, 1364, 1322, 1280, 1223, 1196, 1167, 1132, 1104, 1052, 955, 809, 752, 697, 677, 558, 541, 469 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{23}N_2O_3$ [M+H]$^+$: 351.1703, found: 351.1700.



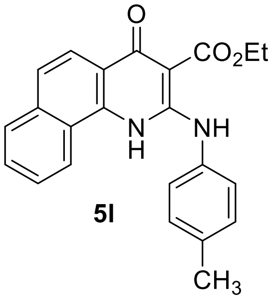
5j

5j: Following the general procedure, the reaction of ethyl 3-((4-methylphenethyl)amino)-3-oxo-2-(triphenylphosphoranylidene)propanoate **3k** (255 mg, 0.50 mmol) and 1-isocyanato-4-methylbenzene **2a** (66 mg, 0.50 mmol) provided **5j** as yellow solid, in 114 mg, 62% yield, m. p: 173–175 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 10.26 (br s, 1H), 9.45 (t, *J* = 5.2 Hz, 1H), 7.76 (s, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.20 (d, *J* = 7.7 Hz, 2H), 7.11 (d, *J* = 7.7 Hz, 2H), 4.15 (q, *J* = 7.0, 2H), 3.65 (q, *J* = 6.9 Hz, 2H), 2.90 (t, *J* = 6.9 Hz, 2H), 2.33 (s, 3H), 2.26 (s, 3H), 1.23 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 173.2, 169.9, 155.3, 135.4, 135.4, 135.3, 132.6, 131.7, 128.9, 128.7, 125.1, 123.6, 116.7, 90.7, 59.1, 43.0, 34.1, 20.6, 14.4. IR ν_{max} (neat): 2918, 1648, 1604, 1573, 1513, 1461, 1390, 1366, 1324, 1282, 1222, 1136, 1105, 808, 694, 674, 597, 560, 541, 512, 488, 463 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{25}N_2O_3$ [M+H]$^+$: 365.1859, found: 365.1856.



5k

5k: Following the general procedure, the reaction of ethyl 3-oxo-3-(p-tolylamino)-2-(triphenylphosphoranylidene)propanoate **3a** (241 mg, 0.50 mmol) and 1-isocyanato-4-(trifluoromethyl)benzene **2c** (93 mg, 0.50 mmol) provided **5k** as yellow solid, in 125 mg, 64% yield, m. p: 195–197 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 11.05 (br s, 1H), 10.79 (br s, 1H), 8.26 (s, 1H), 7.84 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.32–7.27 (m, 4H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 169.2, 154.2, 135.7 (q, $J_{F\text{-}C}$ = 10.0 Hz), 133.8, 130.3, 129.7, 128.0 (q, $J_{F\text{-}C}$ = 47.2 Hz), 123.8 (q, $J_{F\text{-}C}$ = 270.1 Hz), 124.7, 122.6, 118.9, 93.6, 59.9, 20.6, 14.3. IR ν_{max} (neat): 2971, 1632, 1582, 1515, 1443, 1369, 1316, 1279, 1248, 1211, 1151, 1105, 1066, 1019, 923, 835, 808, 775, 747, 721, 664, 612, 537, 506, 482, 421 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{18}F_3N_2O_3$ [M+H]$^+$: 391.1264, found: 391.1254.

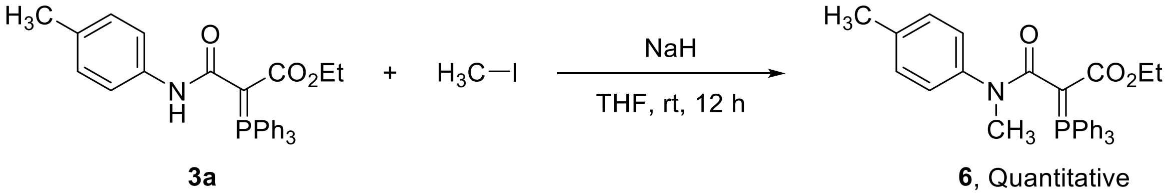


5l

5l: Following the general procedure, the reaction of ethyl 3-oxo-3-(p-tolylamino)-2-(triphenylphosphoranylidene)propanoate **3a** (241 mg, 0.50 mmol) and 1-isocyanatonaphthalene **2h** (84 mg, 0.50 mmol) provided **5l** as yellow solid, in 126 mg, 67% yield, m. p: 92–94 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 12.68 (br s, 1H), 9.21 (br s, 1H), 8.96–8.93 (m, 1H), 7.97–7.94 (m, 1H), 7.80–7.78 (m, 1H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.64–7.57 (m, 2H), 7.51–7.47 (m, 1H), 7.24–7.21 (m, 2H), 4.51 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.52 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 170.0, 168.8, 152.1, 148.6, 137.4, 135.8, 132.1, 130.0, 129.2, 128.8, 127.5, 126.2, 125.7, 122.7, 120.8, 120.7, 119.8, 111.9, 92.4, 62.7, 20.9, 14.1. IR ν_{max} (neat): 3408, 2919, 1617, 1588, 1537, 1509, 1448, 1397, 1368, 1302, 1251, 1205, 1169, 1104, 1068, 1026, 839, 800, 788, 752, 656, 600, 571, 502, 453, 427 cm^{-1}. HRMS (ESI) calcd for $C_{23}H_{21}N_2O_3$ $[M+H]^+$: 373.1546, found: 373.1540.

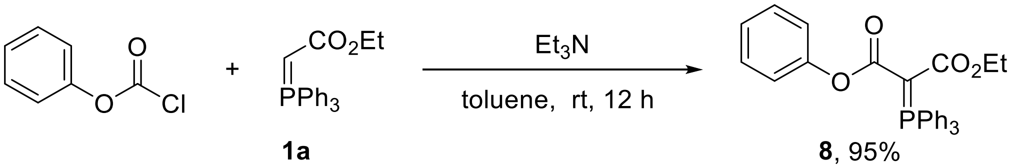
9. Synthesis of Compounds 6 and 8

Synthesis of Compound **6**:



To a solution of P-ylide (**3a**, 241 mg, 0.50 mmol) in THF (2 mL, 0.2 M) were added MeI (78 mg, 0.55 mmol) and NaH (60% dispersion in mineral oil, 24 mg, 1.0 mmol) under N_2 atmosphere. The reaction mixture was stirred at room temperature for 12 hours. After the reaction was completed, the reaction mixture was poured into water and then the product was extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether) to give the product **6** (250 mg, quantitative) as a white solid, m. p: 183–185 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.66 (m, 6H), 7.63–7.49 (m, 3H), 7.44–7.39 (m, 6H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.99 (d, *J* = 8.2 Hz, 2H), 3.79 (q, *J* = 7.1 Hz, 2H), 3.32 (s, 3H), 2.34 (s, 3H), 0.84 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4 (d, $J_{P\text{-}C}$ = 13.0 Hz), 166.9 (d, $J_{P\text{-}C}$ = 11.2 Hz), 143.7, 134.7, 133.5 (d, $J_{P\text{-}C}$ = 9.9 Hz), 131.6 (d, $J_{P\text{-}C}$ = 2.9 Hz), 128.8, 128.3 (d, $J_{P\text{-}C}$ = 12.4 Hz), 126.7 (d, $J_{P\text{-}C}$ = 93.8 Hz), 57.8, 51.9 (d, $J_{P\text{-}C}$ = 122.2 Hz), 38.9, 20.9, 14.4. IR ν_{max} (neat): 2922, 1628, 1601, 1511, 1481, 1436, 1361, 1303, 1266, 1156, 1103, 1073, 1034, 998, 825, 759, 744, 713, 691, 618, 580, 548, 518, 496 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{31}NO_3P$ $[M+H]^+$: 496.2037, found: 496.2032.

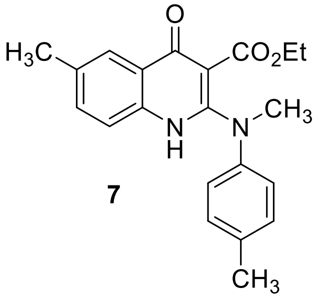
Synthesis of Compound **8**[3]:



A solution of phenyl chloroformate (156 mg, 1.0 mmol) in dry toluene (2 mL) is added slowly to a suspension of ethyl 2-(triphenylphosphoranylidene)acetate (**1a**, 348 mg, 1.0 mmol) and trimethylamine (101 mg, 1.0 mmol) in toluene (2 mL) at room temperature. After 12 h the reaction mixture extracted with ethyl acetate, dried over $MgSO_4$, and concentrated in vacuo. Recrystallization of the residue from CH_2Cl_2/petroleum ether to give the product **8** (445 mg, 95%) as colourless crystals, m. p: 66–68 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (m, 6H), 7.67–7.63 (m, 3H), 7.49–7.45 (m, 6H), 7.15–7.11 (m, 2H), 7.00–6.96 (m, 1H), 6.67–6.63 (m, 2H), 3.89 (q, J = 7.1 Hz, 2H), 0.88 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8 (d, $J_{P\text{-}C}$ = 13.0 Hz), 165.6 (d, $J_{P\text{-}C}$ = 13.1 Hz), 151.1, 133.3 (d, $J_{P\text{-}C}$ = 9.8 Hz), 131.9 (d, $J_{P\text{-}C}$ = 3.0 Hz), 128.6 (d, $J_{P\text{-}C}$ = 12.5 Hz), 128.6, 126.3 (d, $J_{P\text{-}C}$ = 94.2 Hz), 124.1, 121.8, 58.9, 53.4 (d, $J_{P\text{-}C}$ = 121.3 Hz), 14.0. IR ν_{max} (neat): 1716, 1643, 1590, 1484, 1437, 1297, 1201, 1160, 1102, 1038, 998, 957, 749, 720, 688, 559, 541, 517 cm^{-1}. HRMS (ESI) calcd for $C_{29}H_{26}O_4P$ [M+H]$^+$: 469.1564, found: 469.1558.

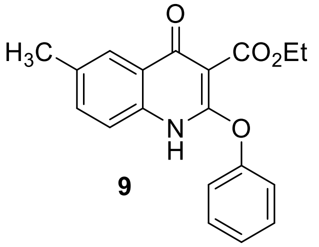
10. Synthesis of Compounds 7, 9, and 11

The synthesis of compounds **7**, **9**, and **11** follows the general procedure for the synthesis of 2-amino-3-carboxylate-4-quinolones **5**.



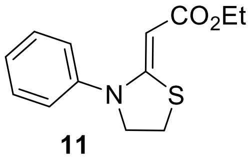
7

7: Following the general procedure, the reaction of ethyl 3-(methyl(p-tolyl)amino)-3-oxo-2-(triphenylphosphoranylidene)propanoate **6** (248 mg, 0.50 mmol) and 1-isocyanato-4-methylbenzene **2a** (66 mg, 0.50 mmol) provided **7** as yellow solid, in 88 mg, 50% yield, m. p: 214–216 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.78 (br s, 1H), 7.84 (s, 1H), 7.48 (s, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.80 (d, *J* = 8.1 Hz, 2H), 3.71 (q, *J* = 7.1 Hz, 2H), 3.30 (s, 3H), 2.40 (s, 3H), 2.22 (s, 3H), 0.98 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.5, 165.3, 151.7, 143.5, 136.8, 133.4, 132.8, 130.0, 129.3, 124.2, 117.9, 109.8, 79.2, 59.8, 20.7, 20.2, 13.7. IR ν_{max} (neat): 2920, 1715, 1628, 1571, 1542, 1509, 1491, 1369, 1349, 1267, 1163, 1096, 1037, 954, 825, 721, 647, 614, 592, 560, 541, 468 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{23}N_2O_3$ [M+H]$^+$: 351.1704, found: 351.1701.



9

9: Following the general procedure, the reaction of 1-ethyl 3-phenyl 2-(triphenylphosphoranylidene)malonate **8** (234 mg, 0.50 mmol) and 1-isocyanato-4-methylbenzene **2a** (66 mg, 0.50 mmol) provided **9** as yellow solid, in 82 mg, 51% yield, m. p: 95–97 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 13.48 (br s, 1H), 8.01 (s, 1H), 7.53–7.47 (m, 2H), 7.43–7.39 (m, 2H), 7.22–7.18 (m, 3H), 4.47 (q, *J* = 7.1 Hz, 2H), 2.50 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 171.1, 170.3, 158.4, 154.3, 145.6, 134.8, 134.3, 129.2, 127.2, 123.9, 122.5, 120.9, 118.3, 95.6, 62.1, 21.3, 14.0. IR ν_{max} (neat): 2978, 1719, 1650, 1570, 1510, 1490, 1418, 1373, 1314, 1281, 1204, 1085, 1022, 926, 820, 767, 690, 647, 547, 496, 450 cm^{-1}. HRMS (ESI) calcd for $C_{19}H_{18}NO_4$ $[M+H]^+$: 324.1231, found: 324.1227.

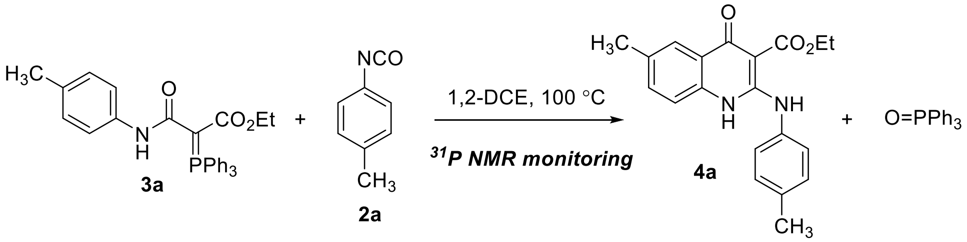


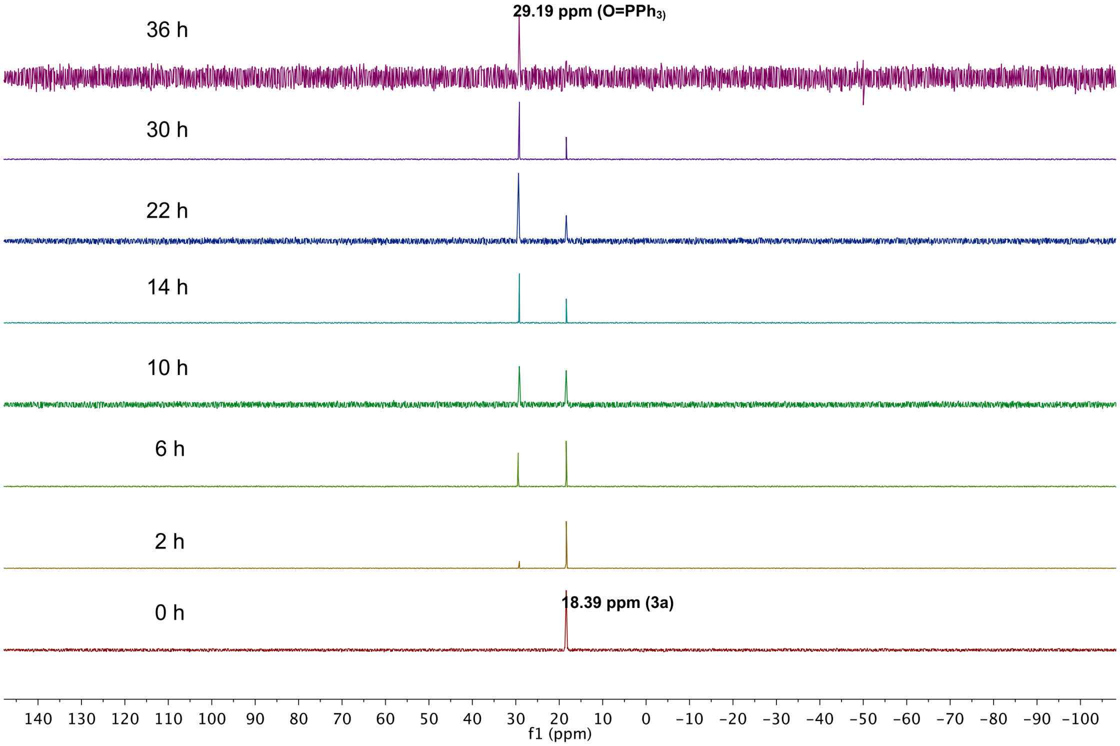
11

11: Following the general procedure, the reaction of ethyl 3-(phenylamino)-3-thioxo-2-(triphenylphosphoranylidene)propanoate **10** (242 mg, 0.50 mmol) and 1-isocyanato-4-methylbenzene **2a** (66 mg, 0.50 mmol) provided **11** as yellow solid, in 52 mg, 42% yield, m. p: 45–47 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44–7.40 (m, 2H), 7.29–7.23 (m, 3H), 4.99 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.97 (t, *J* = 7.0 Hz, 2H), 3.18 (t, *J* = 7.0 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 163.7, 141.5, 129.6, 126.8, 125.3, 82.7, 59.0, 56.0, 27.6, 14.5. IR ν_{max} (neat): 2976, 1736, 1666, 1595, 1536, 1491, 1368, 1304, 1263, 1198, 1170, 1129, 1039, 767, 694, 545, 520 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_{16}NO_2S$ $[M+H]^+$: 250.0897, found: 250.0889.

11. NMR Tracking Experiments

Under N_2 atmosphere, to a solution of P-ylide **3a** (241 mg, 0.50 mmol) in 1,2-dichloroethane (3 mL) was added isocyanate **2a** (66 mg, 0.50 mmol) and the mixture was stirred at 100 °C. The reaction was monitored by ^{31}P NMR measurement as shown below. At different time intervals (0 h, 2 h, 6 h, 10 h, 14 h, 22 h, 30 h, 36 h), 100 μL of reaction mixture was collected and evaporated. The residue was then dissolved in $CDCl_3$ and subjected to ^{31}P NMR measurement. It was found only two peaks appeared at δ 18.39 and δ 29.19 ppm corresponding to **3a** and $O{=}PPh_3$, respectively. The absence of any other ^{31}P NMR signals might imply the Wittig process occurring in the tandem sequence.





12. X-ray Crystallographic Data

3a: Single crystal of compound **3a** was obtained by recrystallization from mixed solvents of dichloromethane and hexane. The structure is shown in Figure S1. CIF file of **3a** can be obtained from the Cambridge Crystallographic Data Center using deposition number CCDC: 1964343.

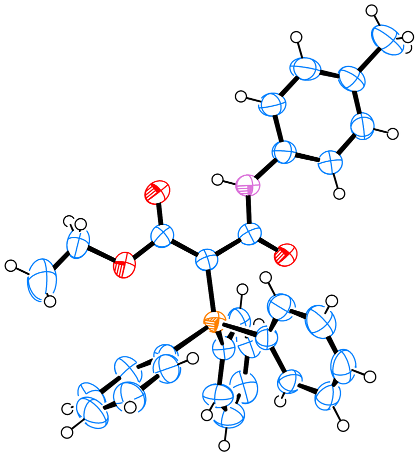


Figure S1. X-ray Single Crystal Structure of **3a**

4a: Single crystal of compound **4a** was obtained by recrystallization from mixed solvents of dichloromethane and hexane. The structure is shown in Figure S2. CIF file of **4a** can be obtained from the Cambridge Crystallographic Data Center using deposition number CCDC: 1963704.

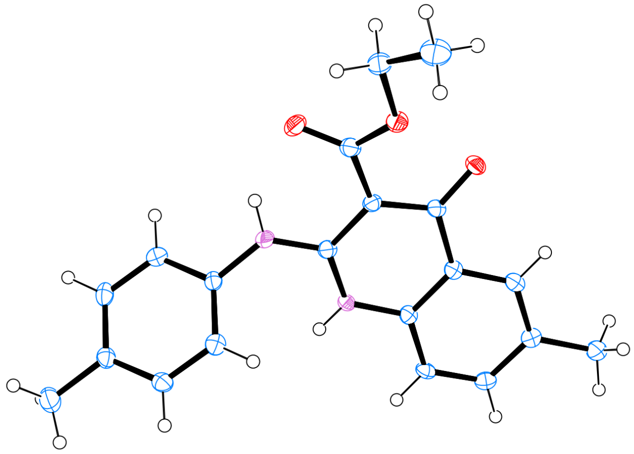


Figure S2. X-ray Single Crystal Structure of **4a**

5a: Single crystal of compound **5a** was obtained by recrystallization from mixed solvents of dichloromethane and hexane. The structure is shown in Figure S3. CIF file of **5a** can be obtained from the Cambridge Crystallographic Data Center using deposition number CCDC: 1963707.

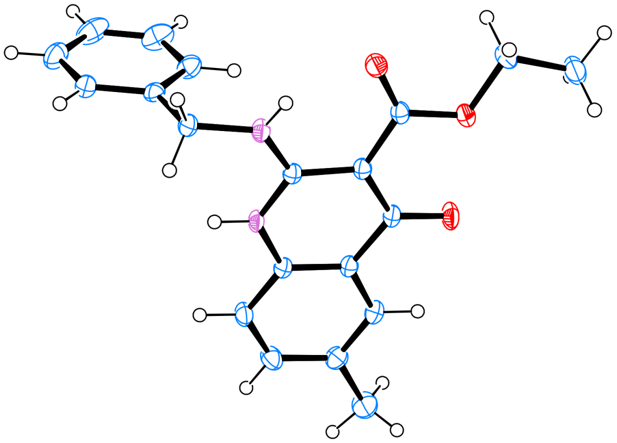


Figure S3. X-ray Single Crystal Structure of **5a**

11: Single crystal of compound **11** was obtained by recrystallization from mixed solvents of dichloromethane and hexane. The structure is shown in Figure S4. CIF file of **11** can be obtained from the Cambridge Crystallographic Data Center using deposition number CCDC: 1969290.

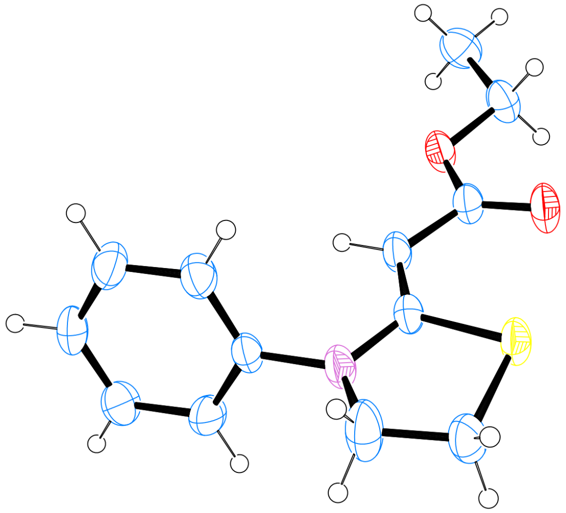


Figure S4. X-ray Single Crystal Structure of **11**

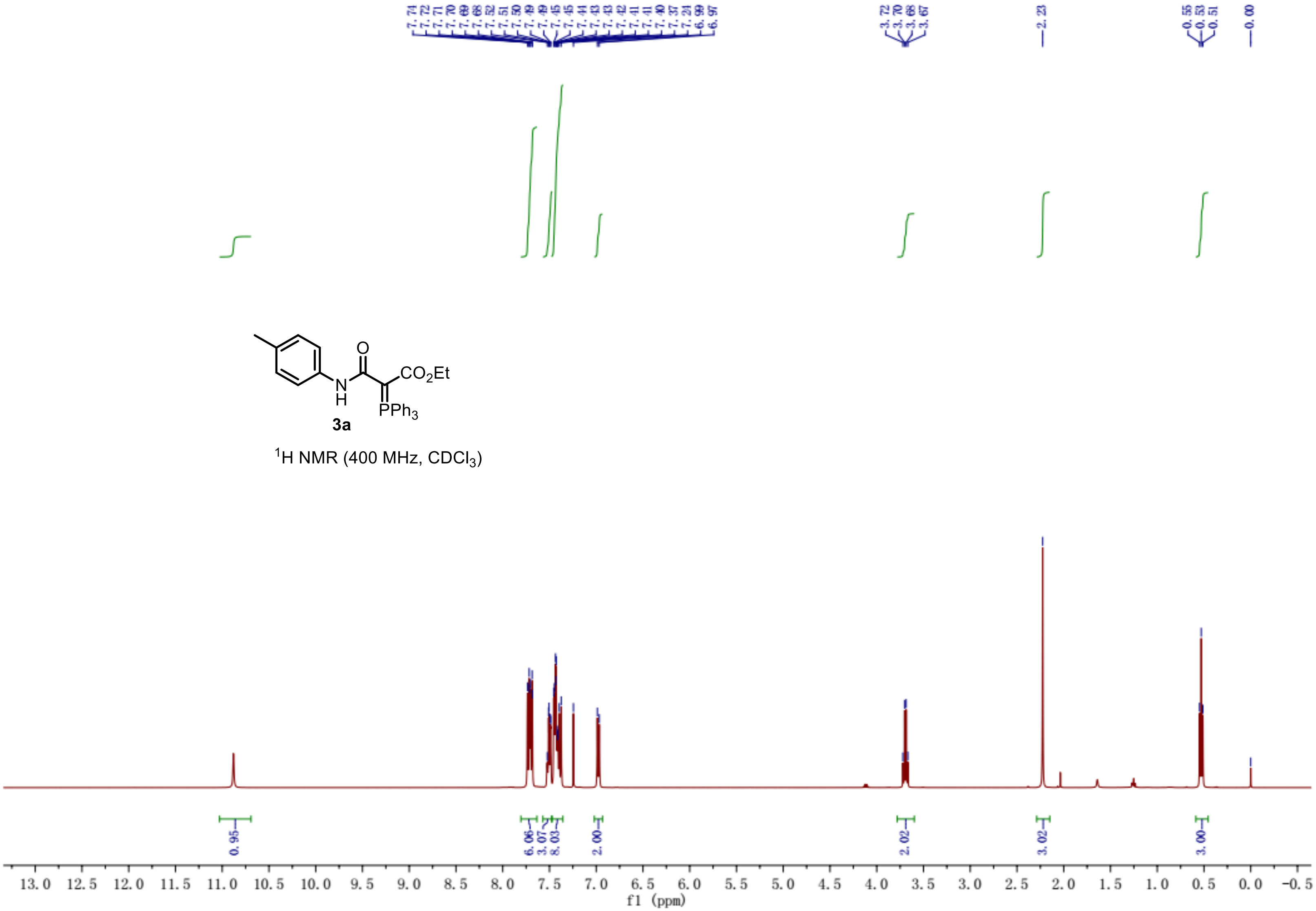
13. References

1. a) D. Z. Liu, Z. Tian, Z. H. Yan, L. X. Wu, Y. Ma, Q. Wang, W. Liu, H. G. Zhou and C. Yang, *Bioorg. Med. Chem*. 2013, **21**, 2960. b) J.-N. Chen, X.-F. Wang, T. Li, D.-W. Wu, X.-B. Fu, G.-J. Zhang, X.-C. Shen and H.-S. Wang, *Eur. J. Med. Chem*. 2016, **107**, 12.

2. P-ylide **3a** is a known compound yet with incomplete characterization, see: R. A. Aitken, N. A. Al-Awadi, G. Dawson, O. El-Dusouqi, K. Kaul and A. Kumar, *Int. J. Chem. Kinet*. 2006, **39**, 6.

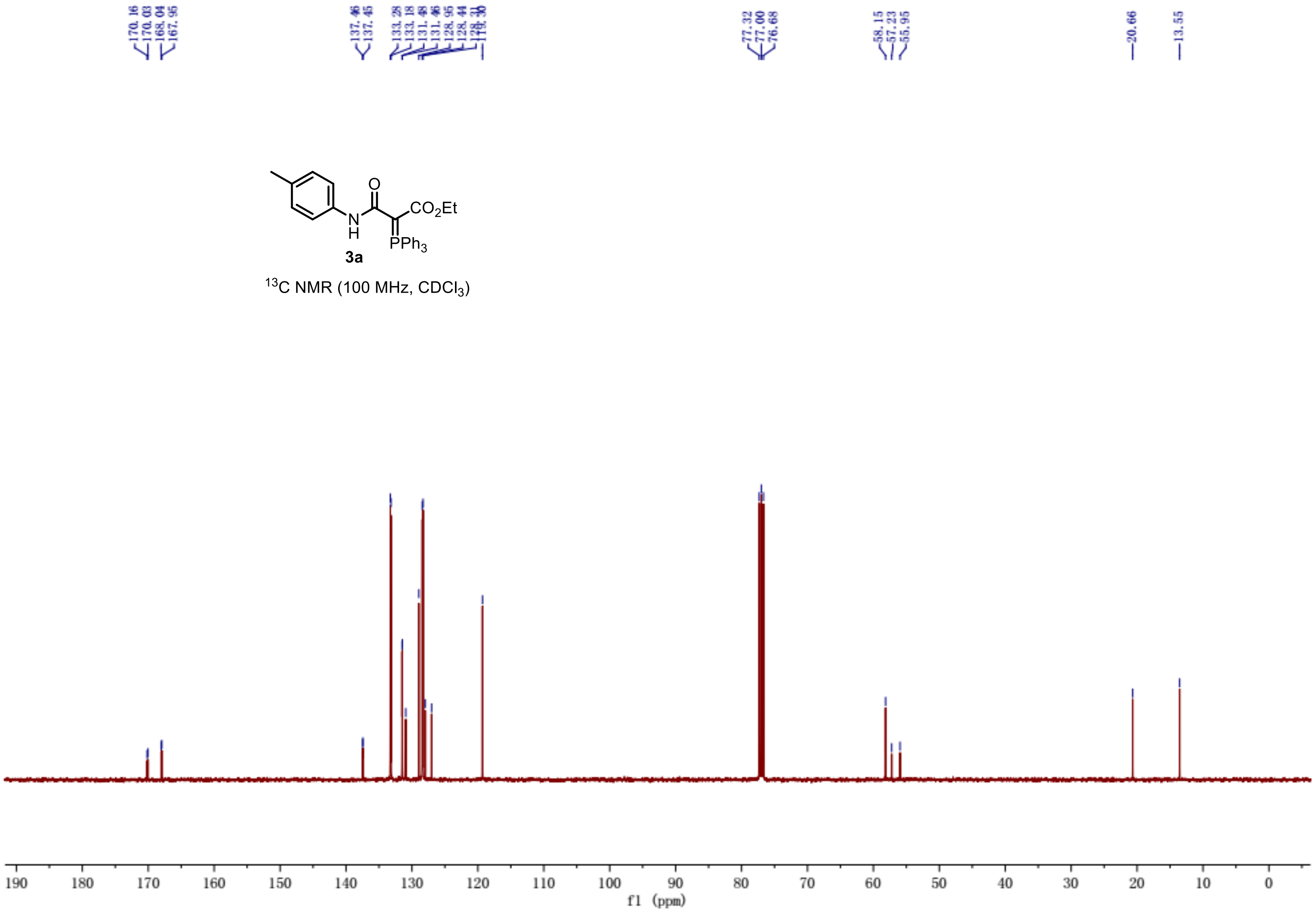
3. R. A. Aitken and S. Seth, *Synlett*, 1990, 211.

14. ^{1}H and ^{13}C NMR Spectra Copies



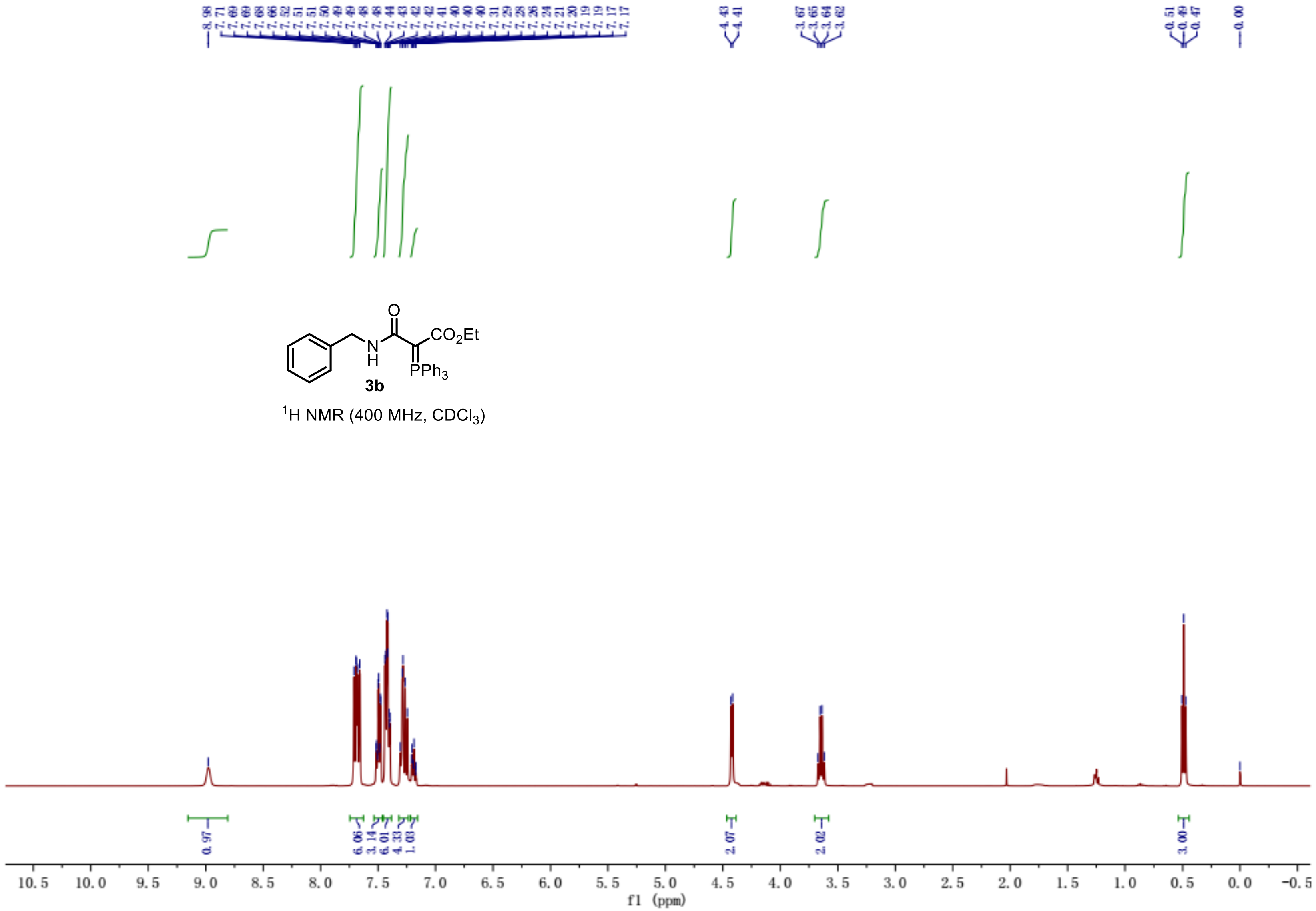
3a

^{1}H NMR (400 MHz, $CDCl_3$)



3a

^{13}C NMR (100 MHz, $CDCl_3$)



3b

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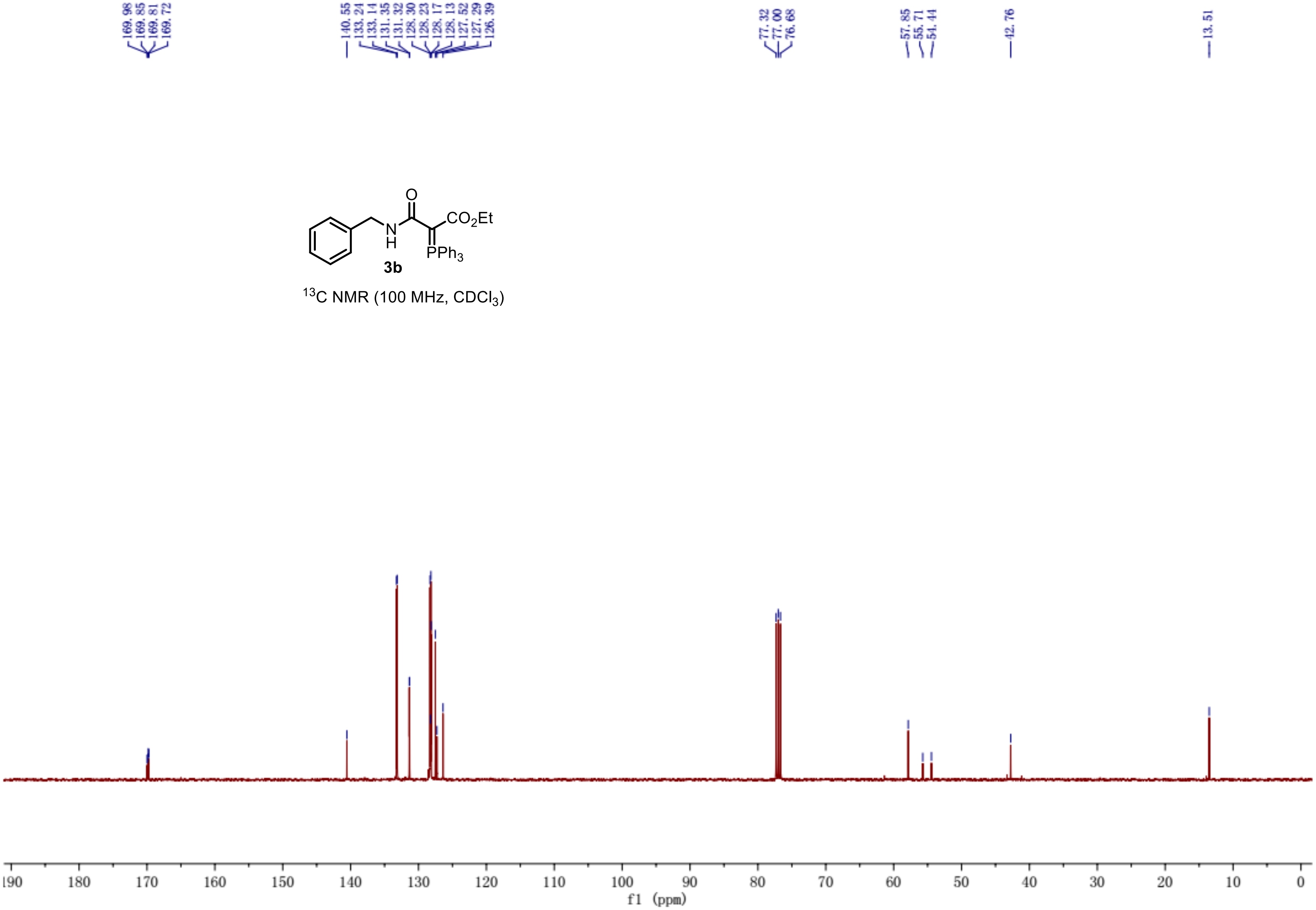
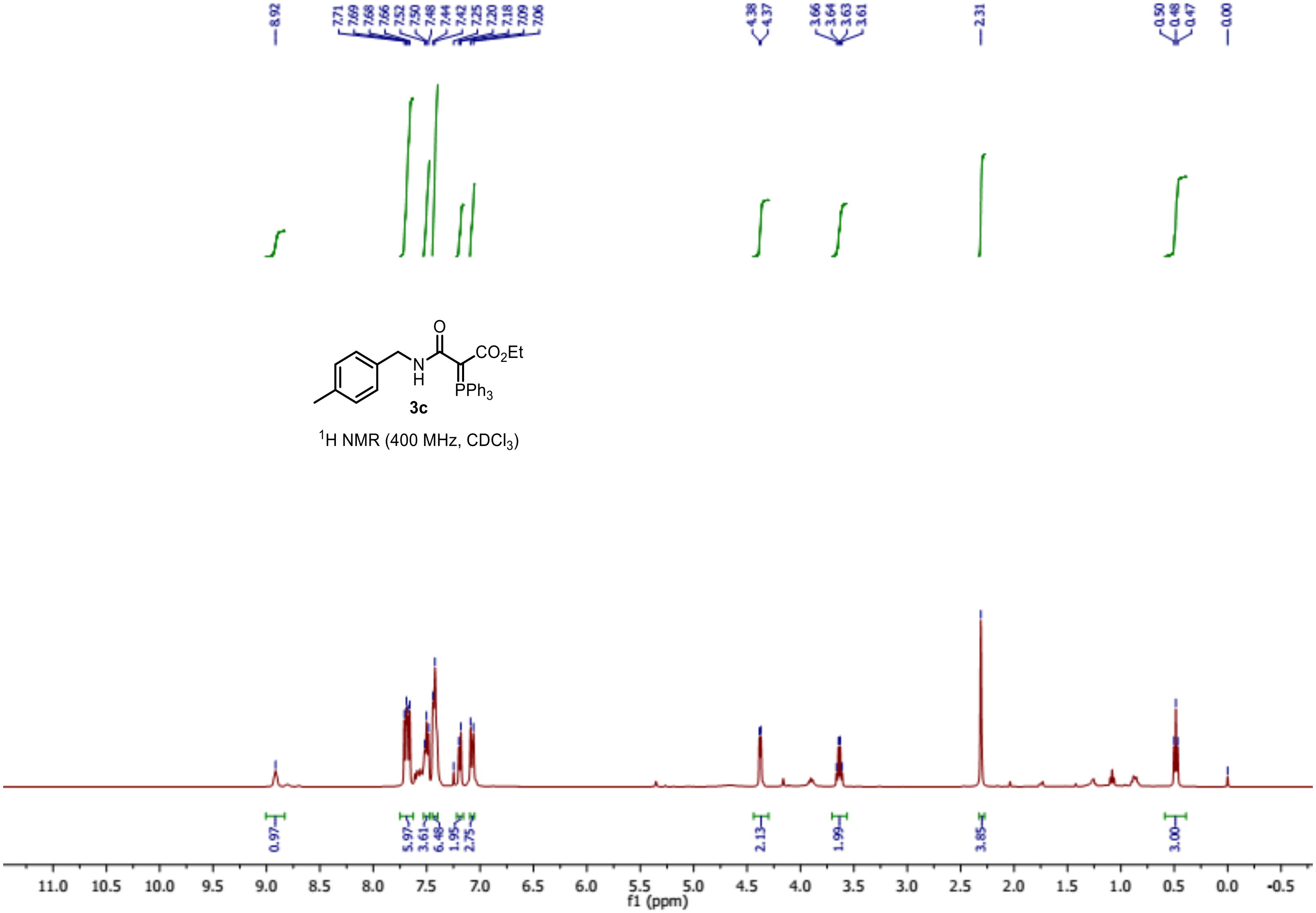


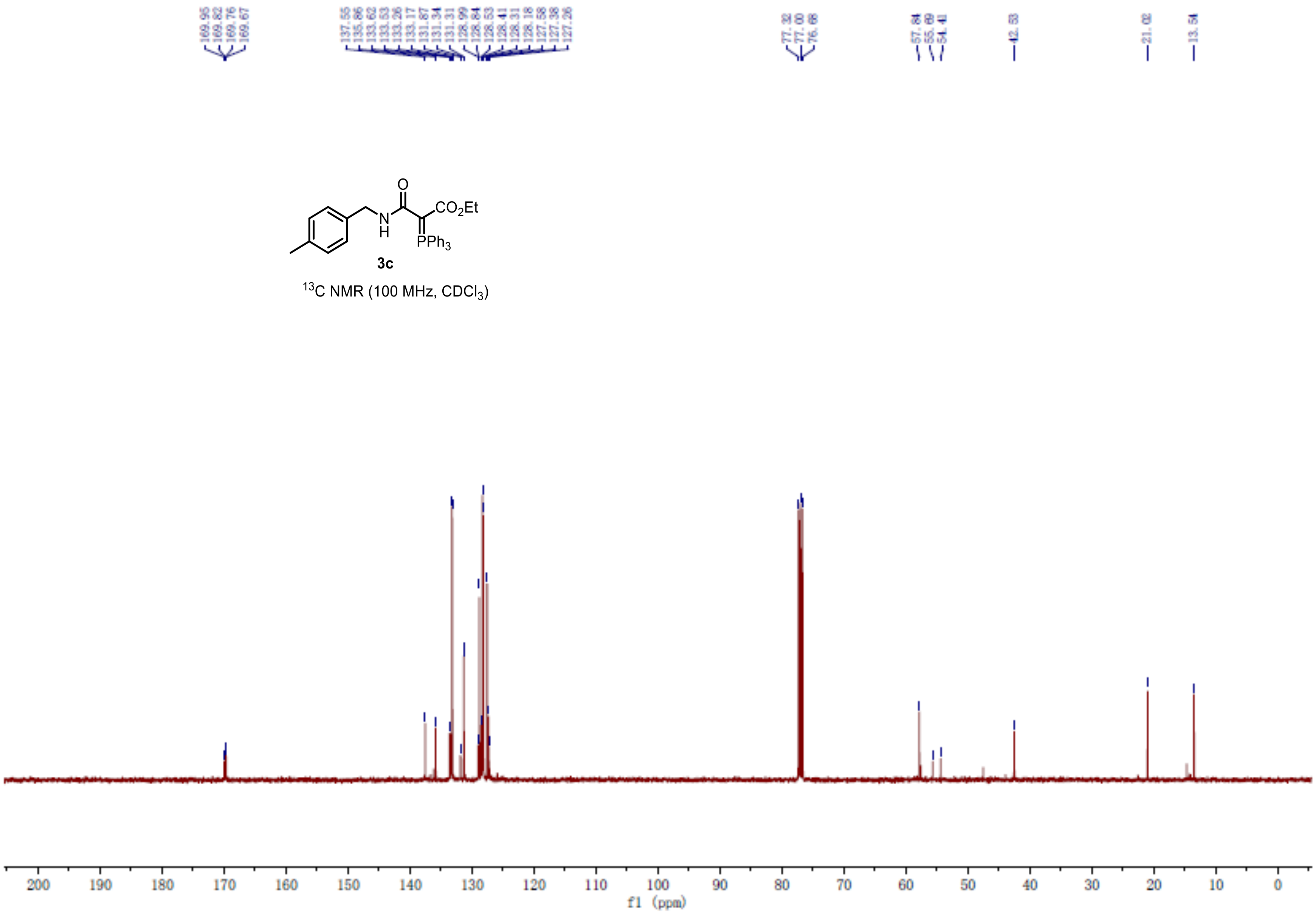
3b

^{13}C NMR (100 MHz, $CDCl_3$)



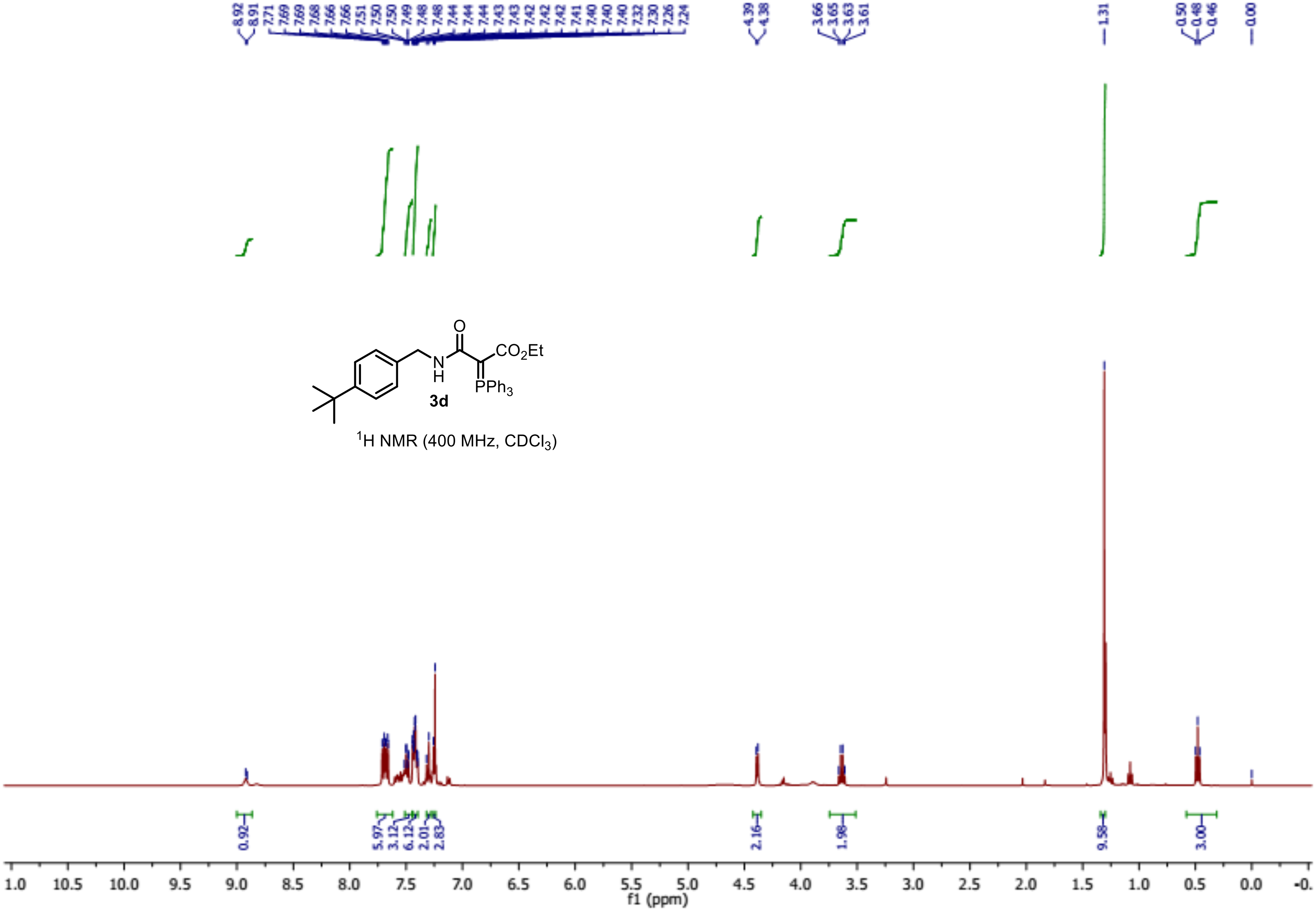
3c

^{1}H NMR (400 MHz, CDCl$_3$)



3c

^{13}C NMR (100 MHz, CDCl$_3$)



3d

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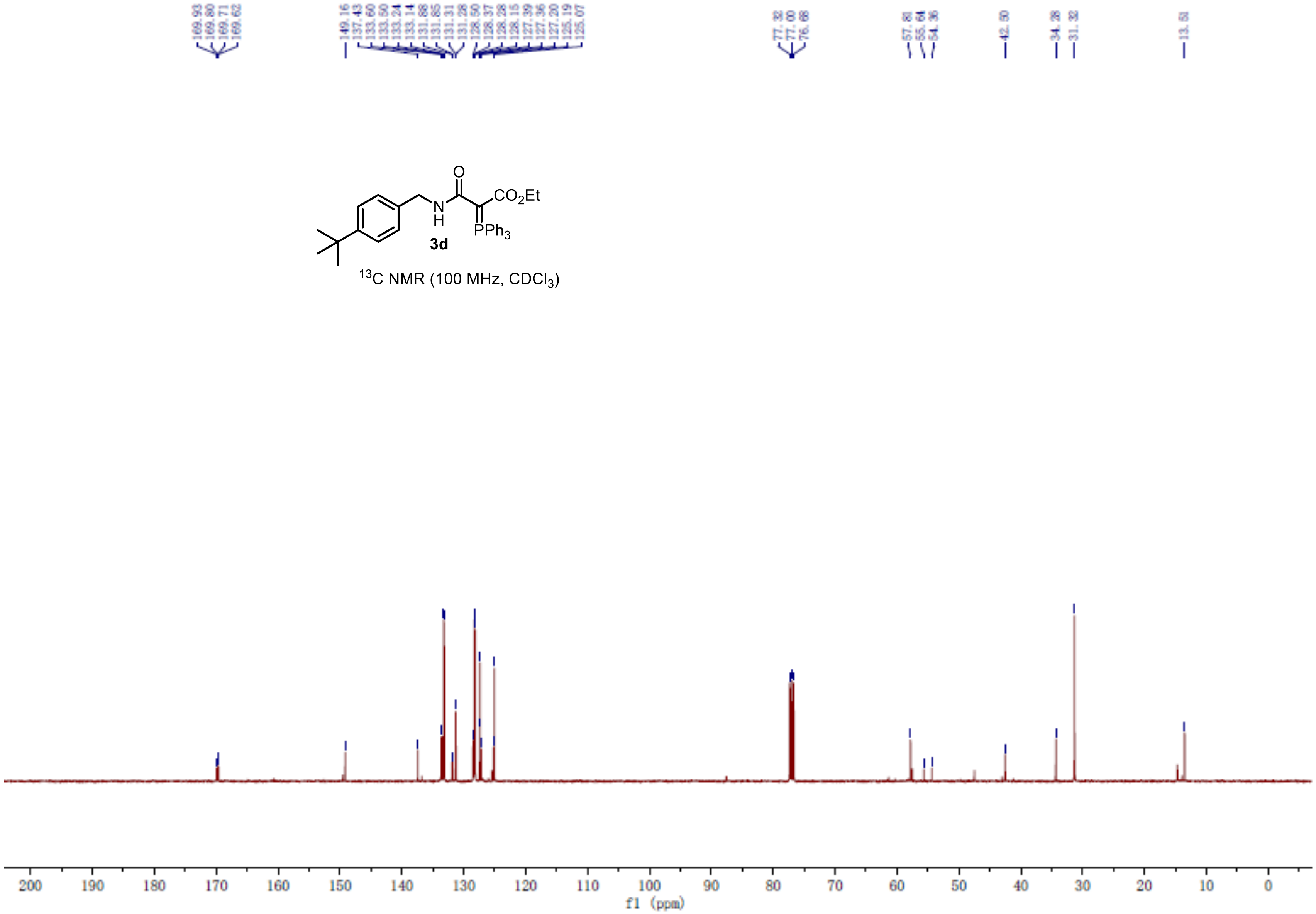
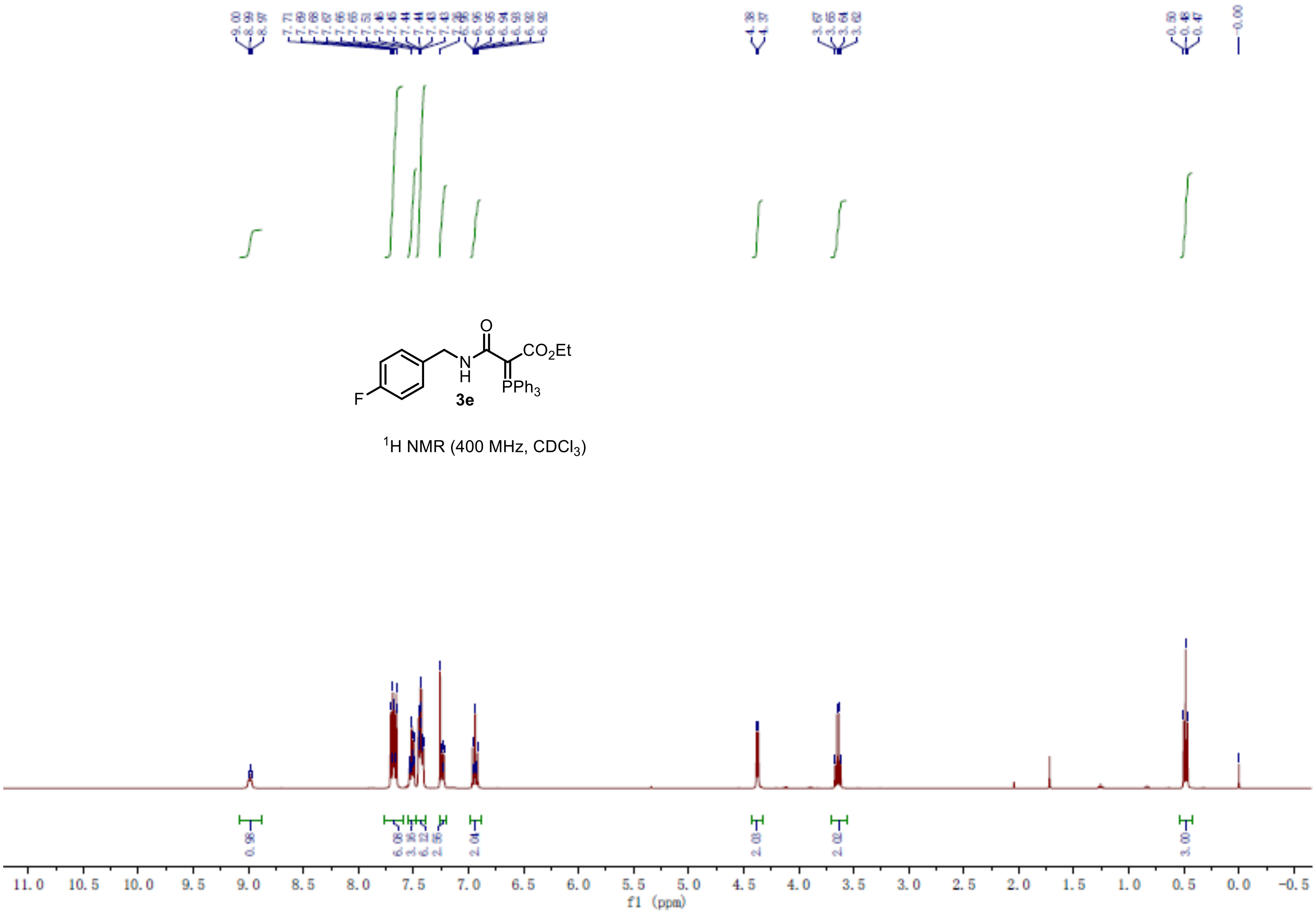
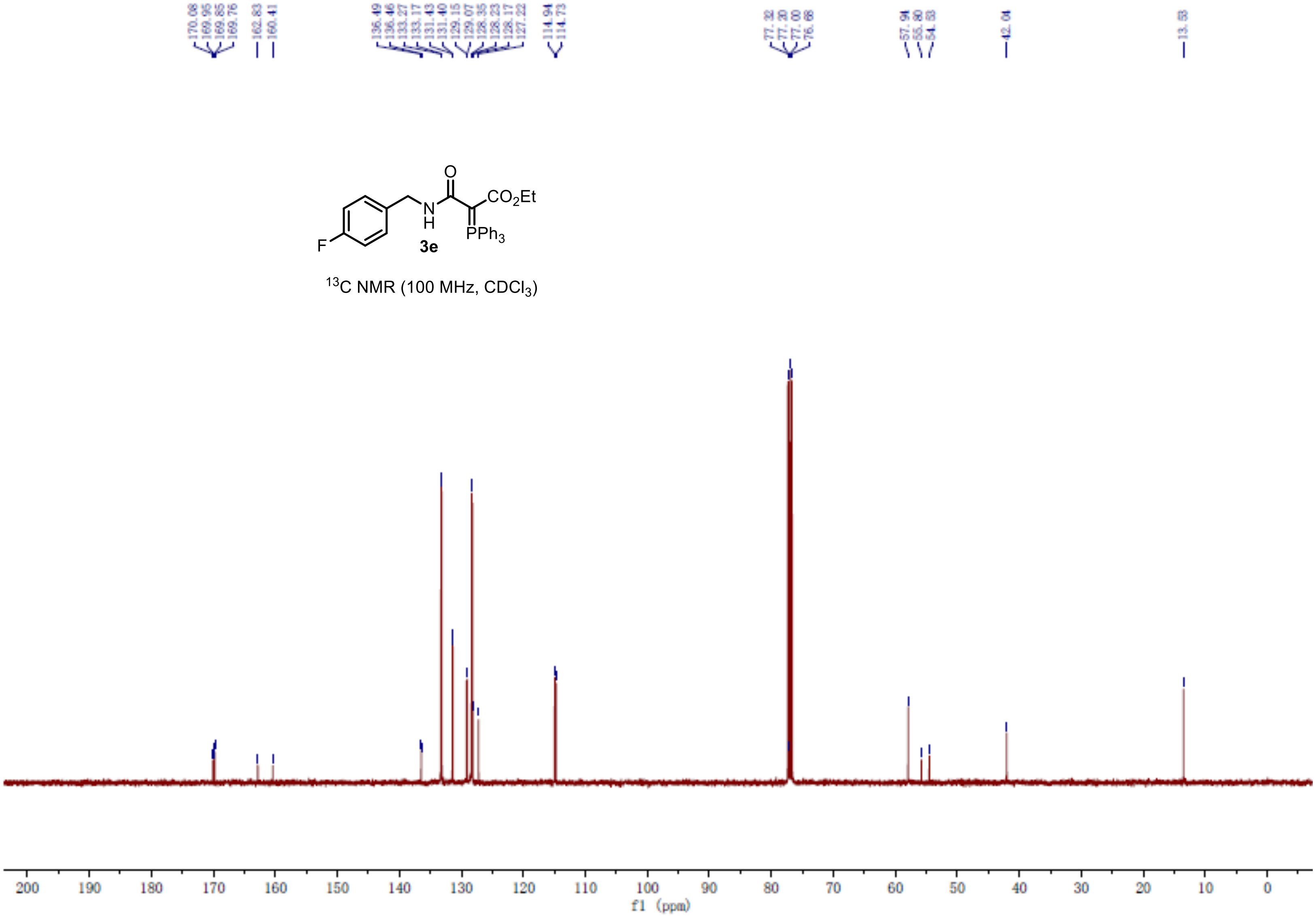


3d

^{13}C NMR (100 MHz, CDCl$_3$)

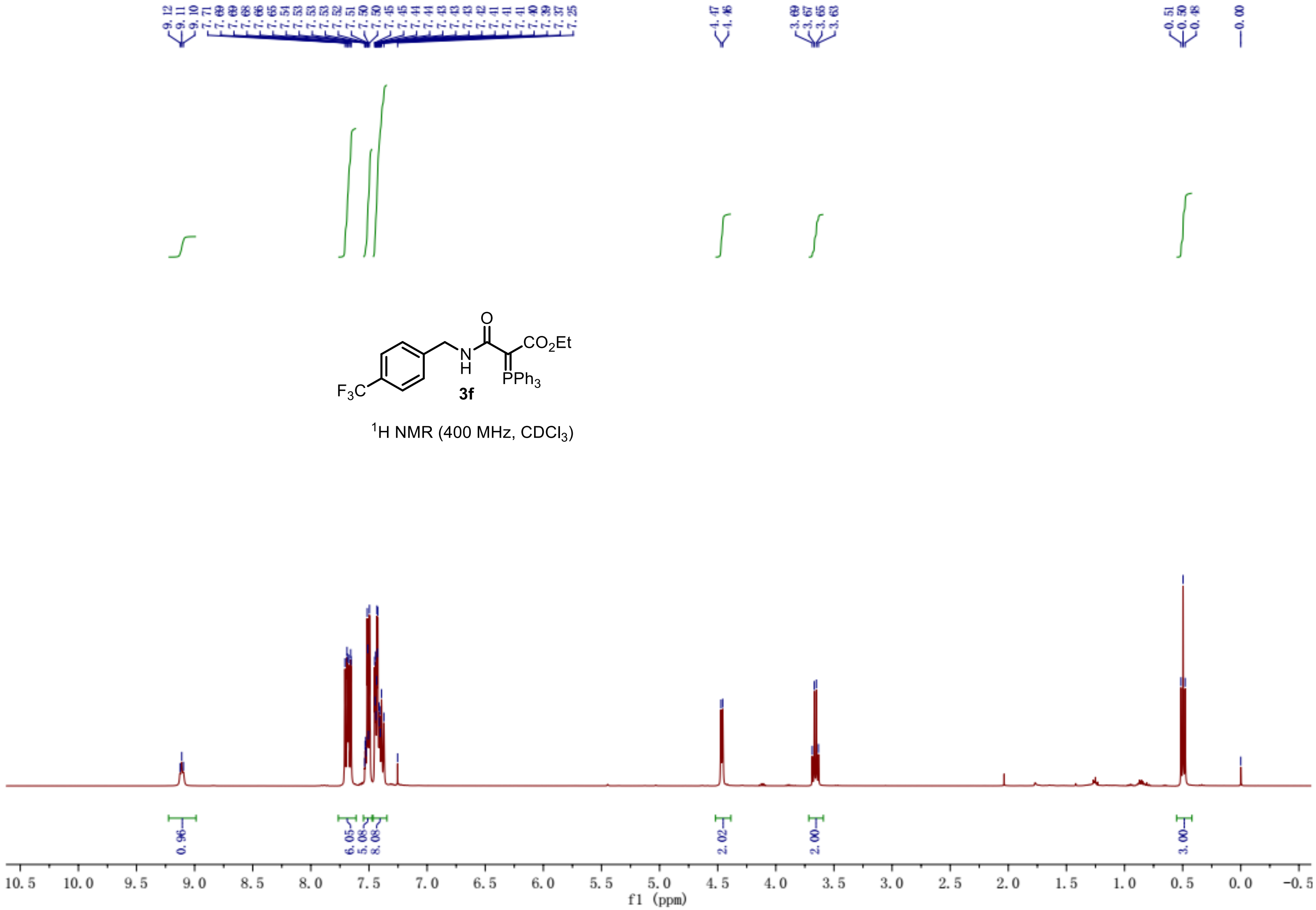


^1H NMR (400 MHz, $CDCl_3$)



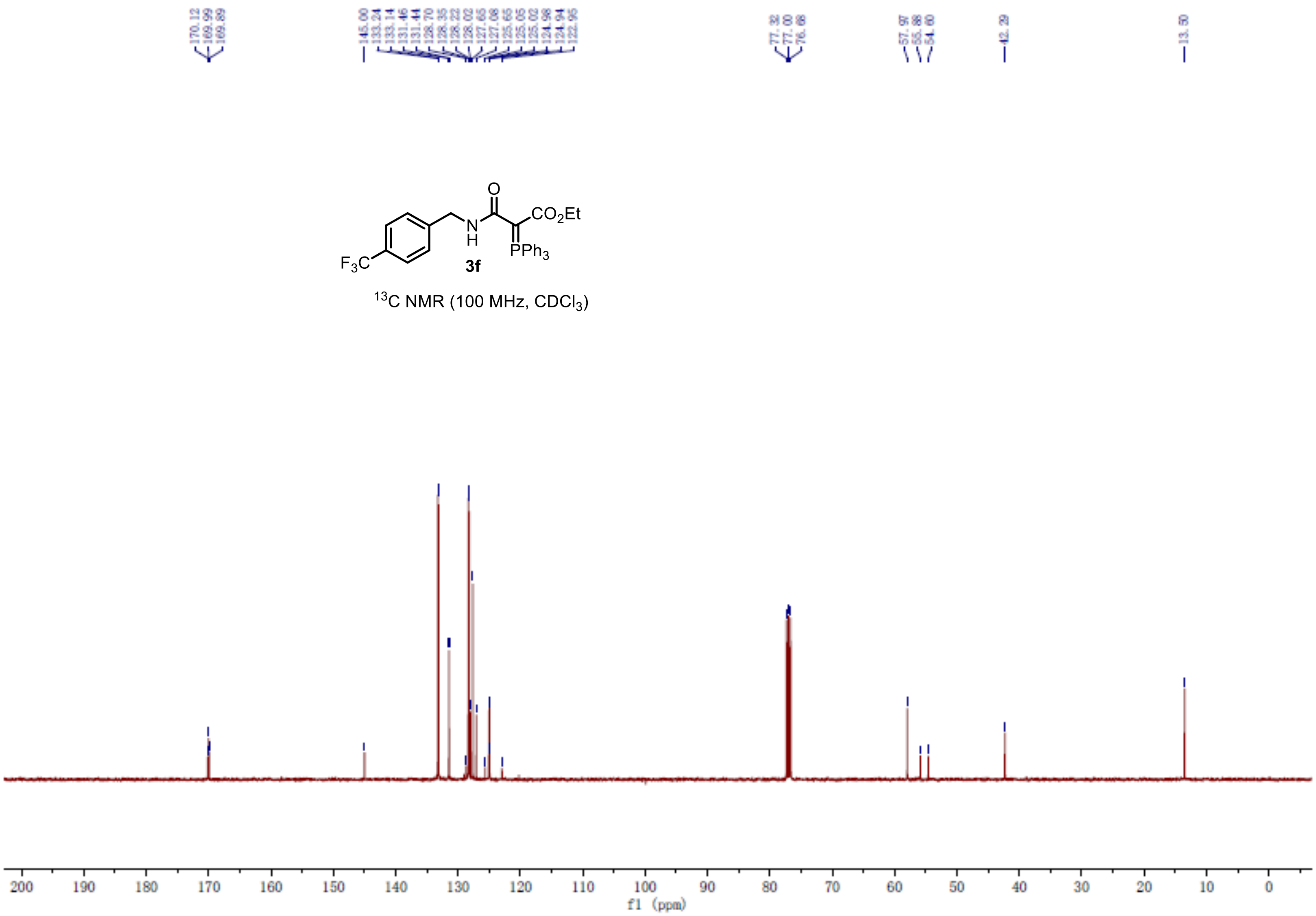
3e

^{13}C NMR (100 MHz, $CDCl_3$)



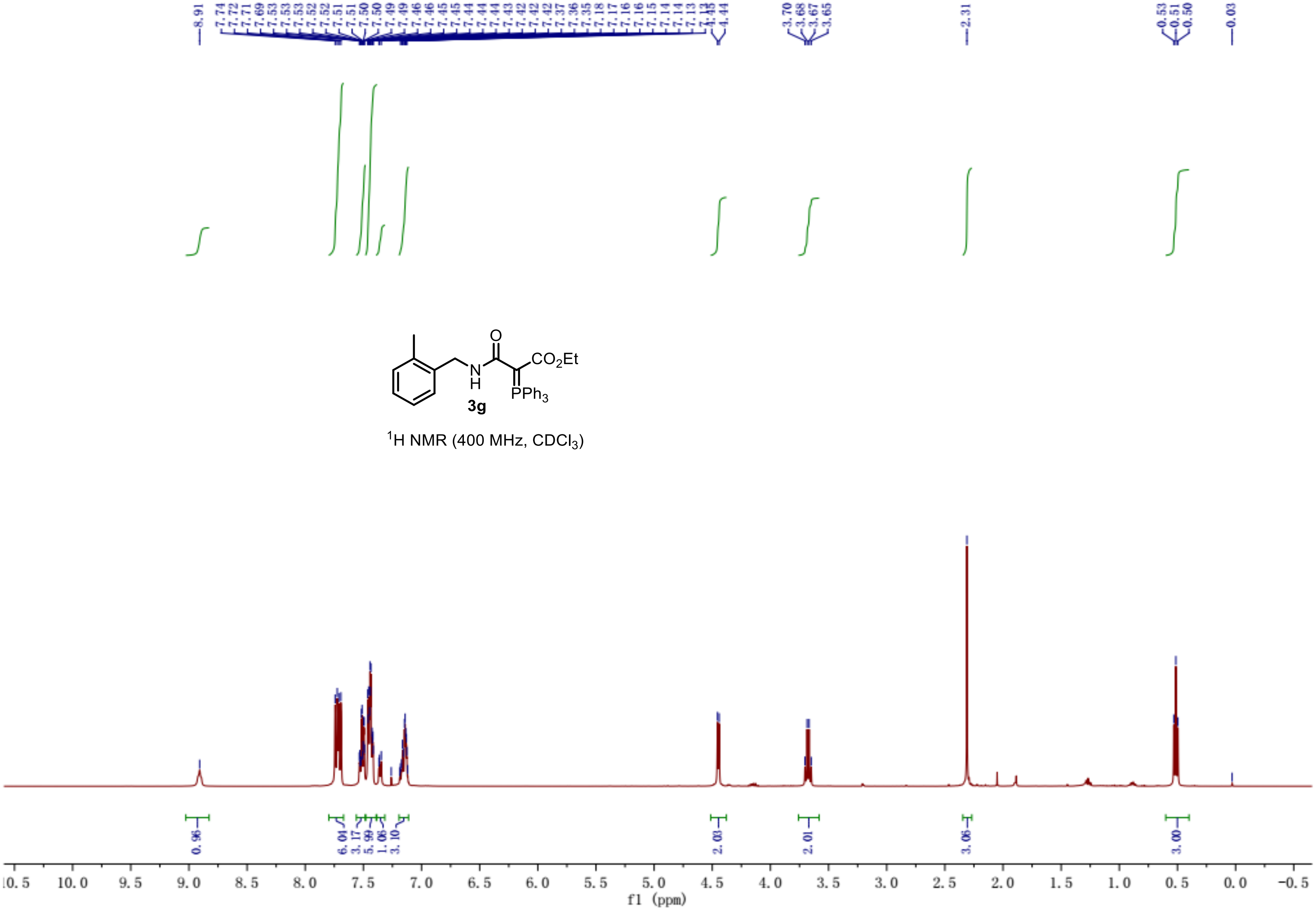
3f

^{1}H NMR (400 MHz, CDCl$_3$)



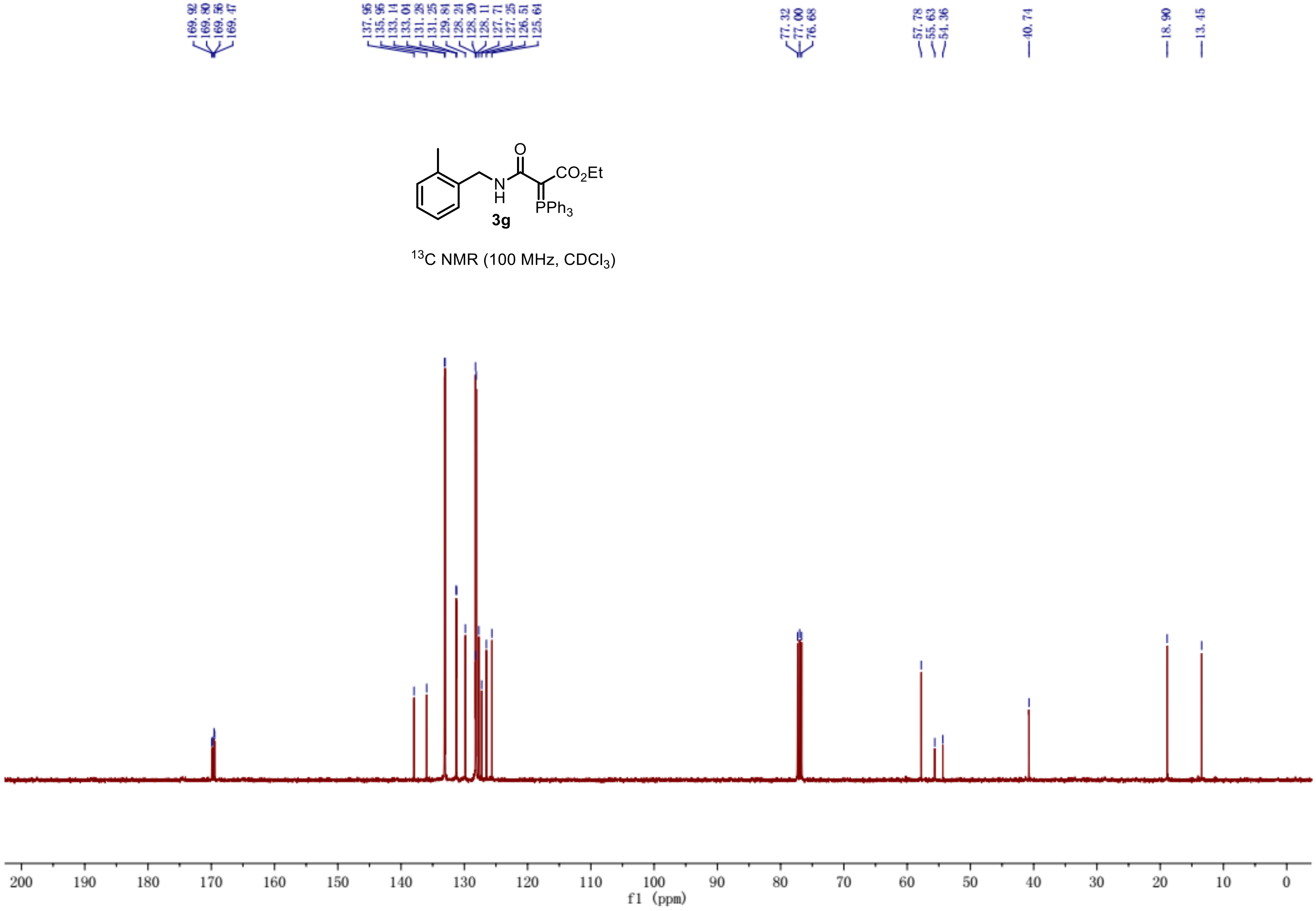
3f

^{13}C NMR (100 MHz, $CDCl_3$)



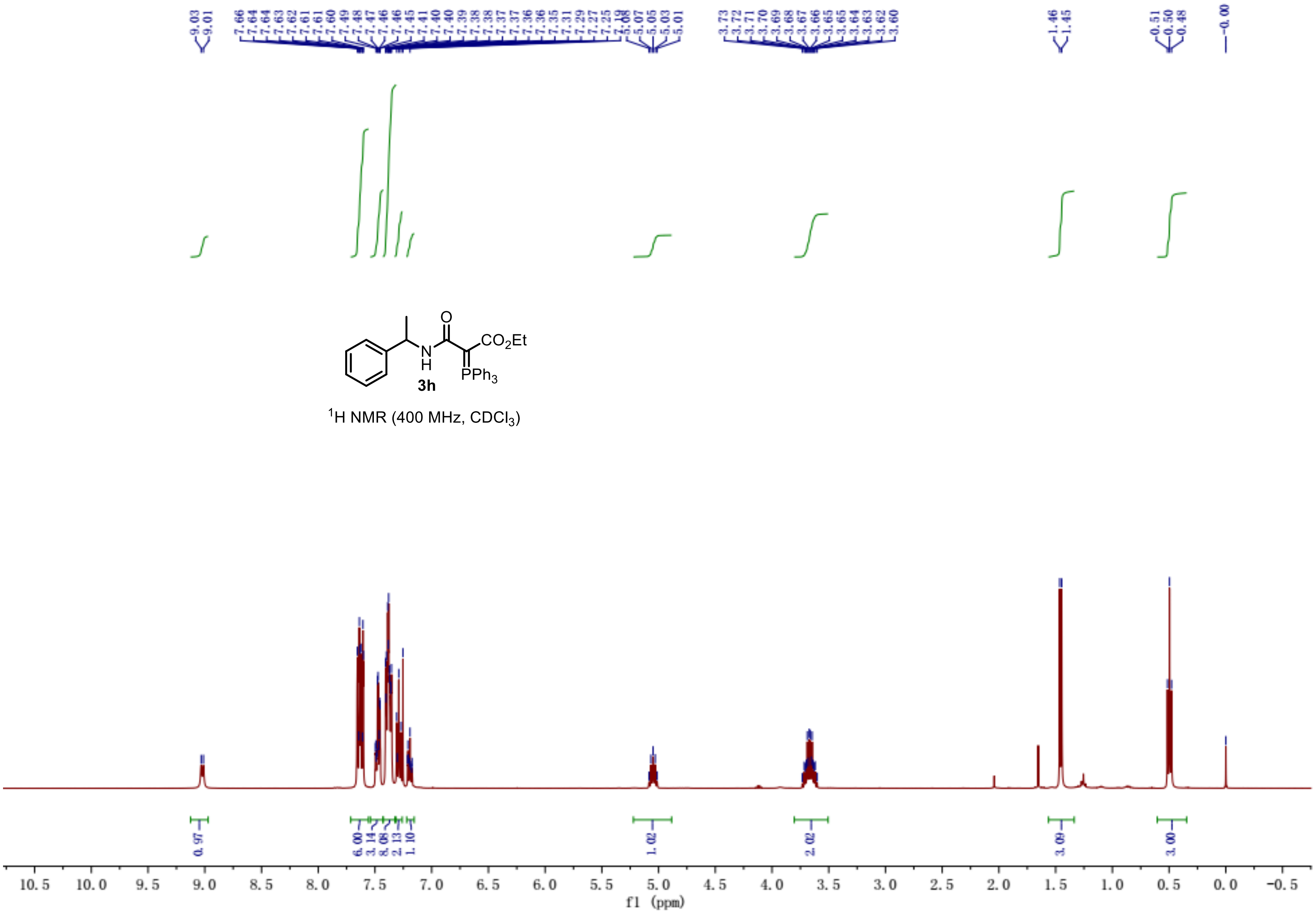
3g

^{1}H NMR (400 MHz, CDCl$_3$)



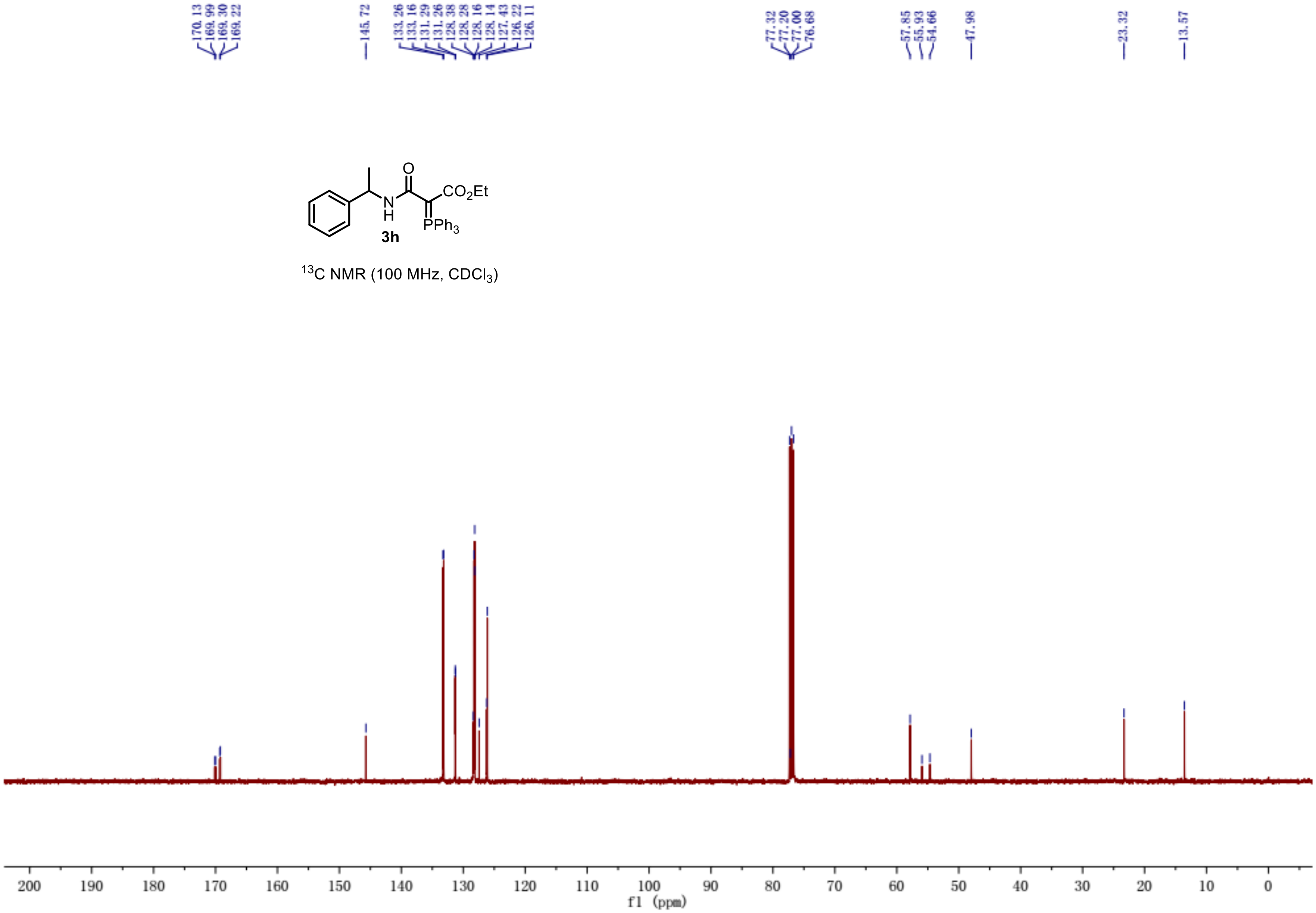
3g

^{13}C NMR (100 MHz, CDCl$_3$)



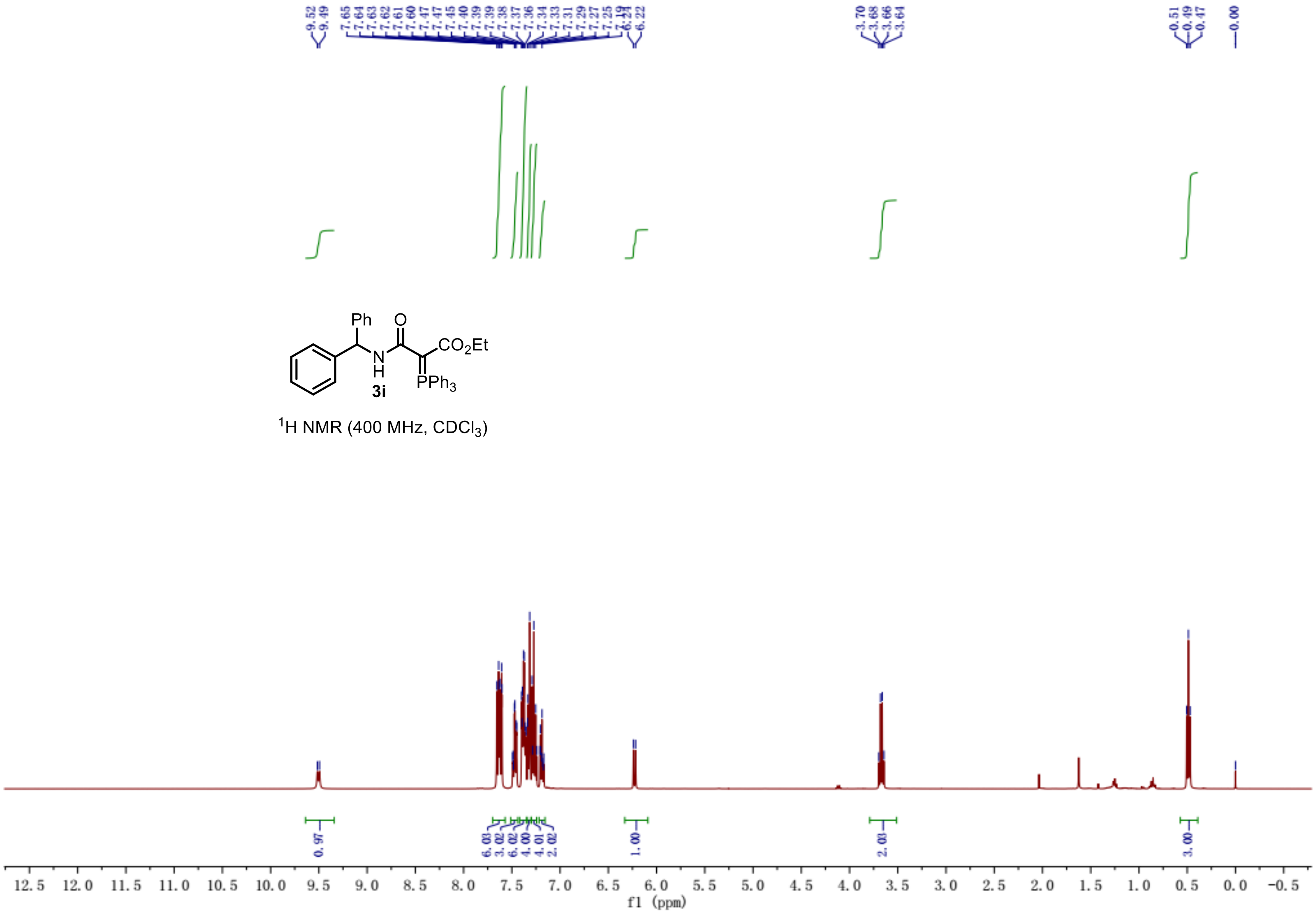
3h

^{1}H NMR (400 MHz, CDCl$_3$)



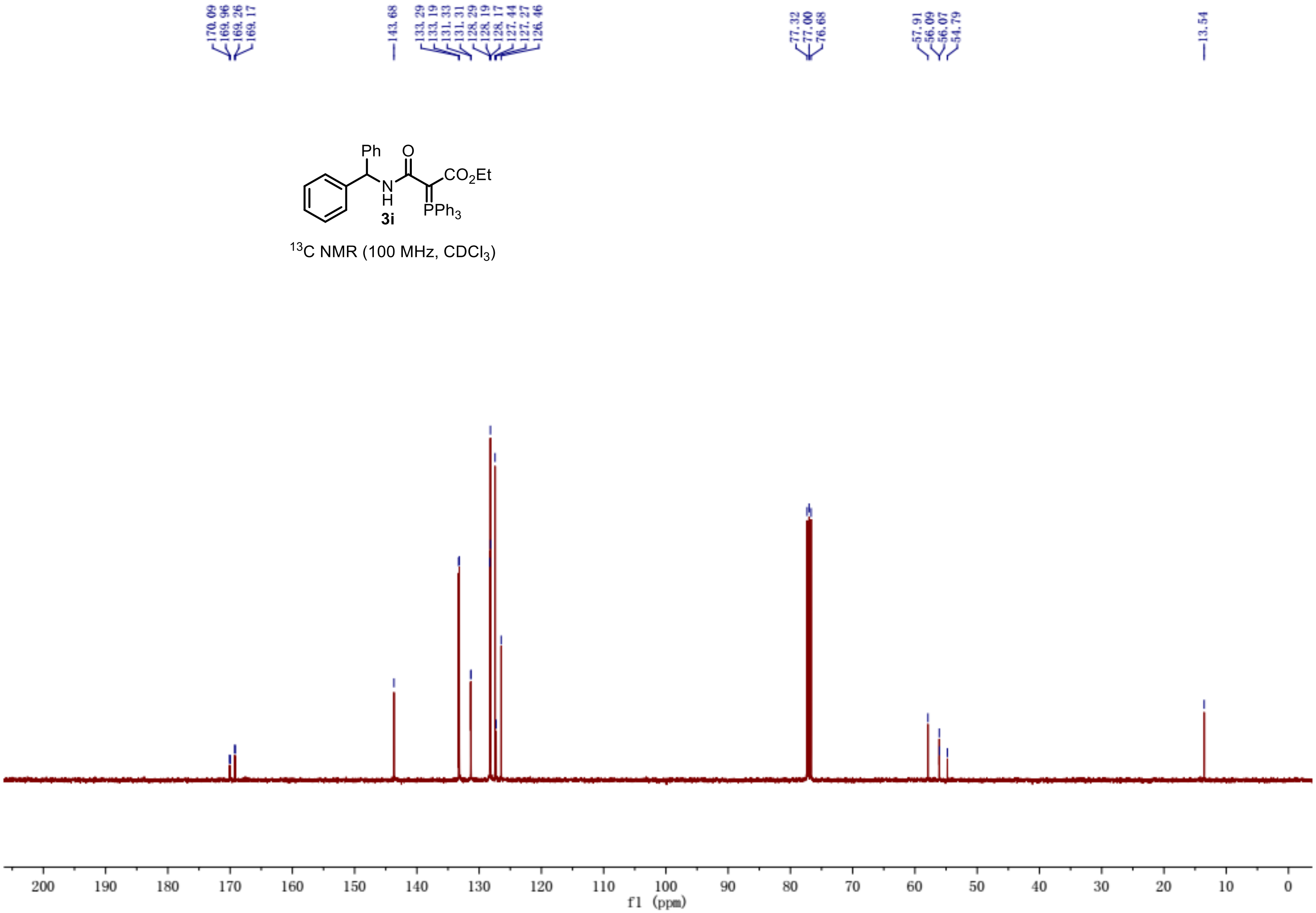
3h

^{13}C NMR (100 MHz, CDCl$_3$)



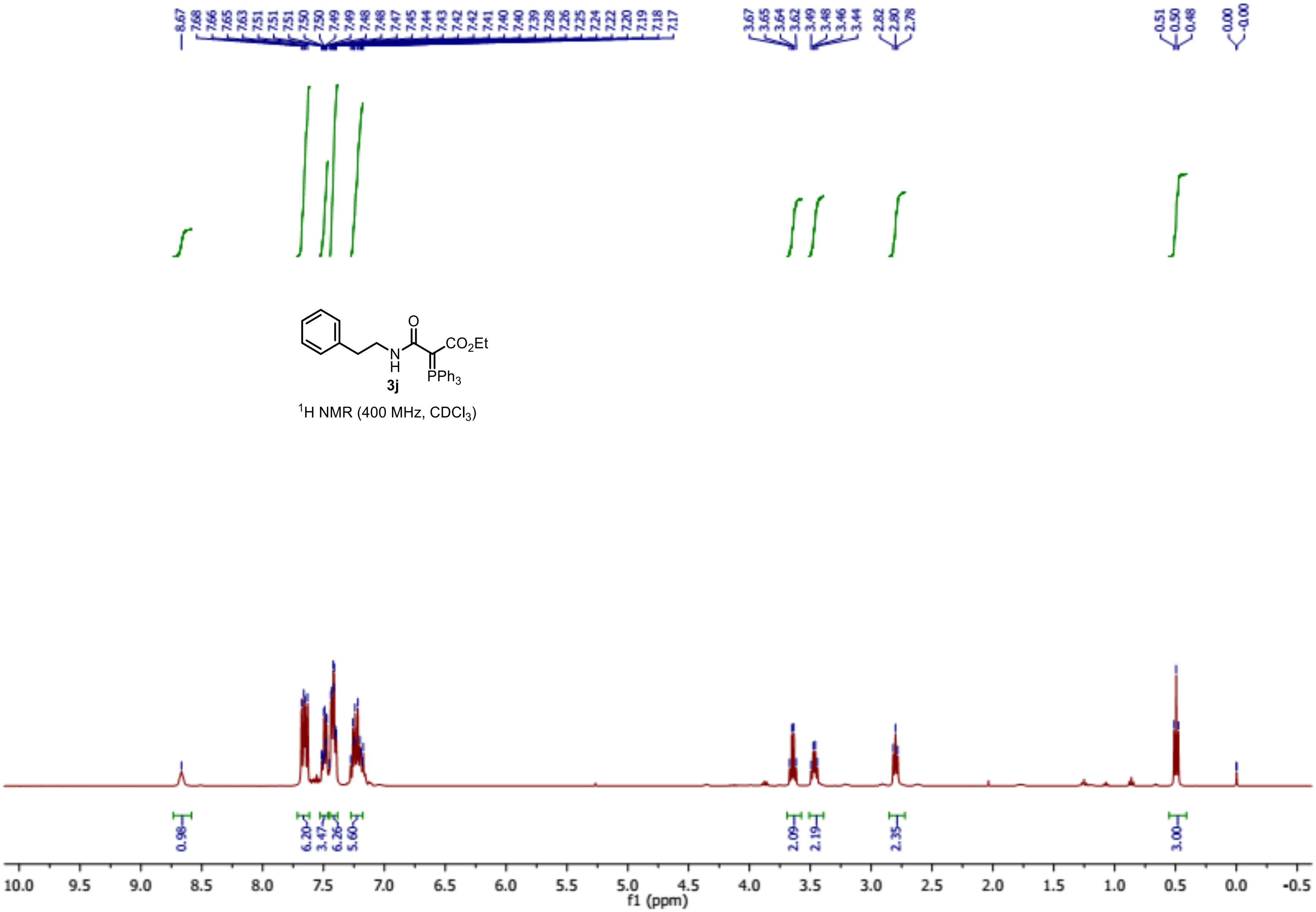
3i

^{1}H NMR (400 MHz, $CDCl_3$)



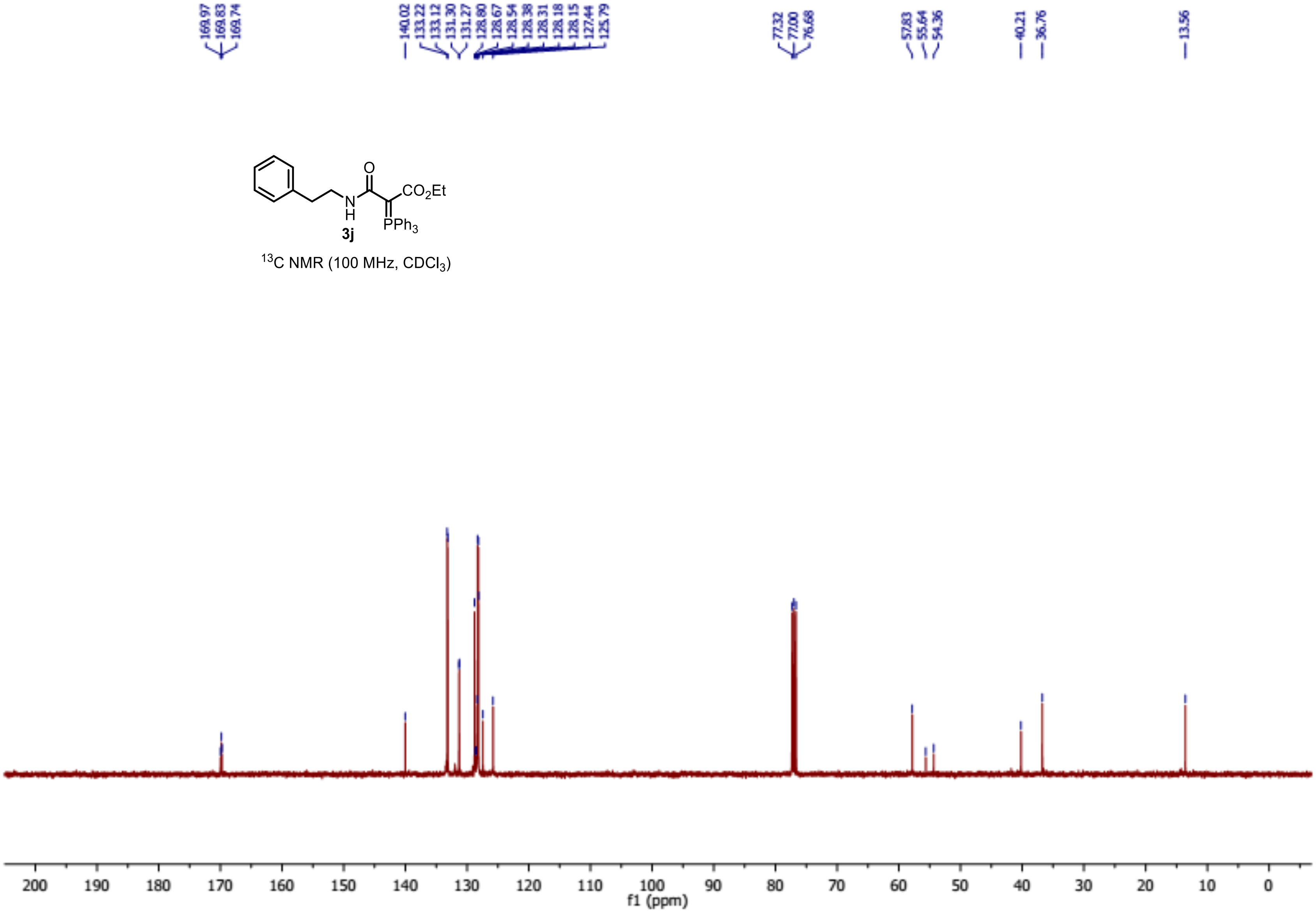
3i

^{13}C NMR (100 MHz, CDCl$_3$)



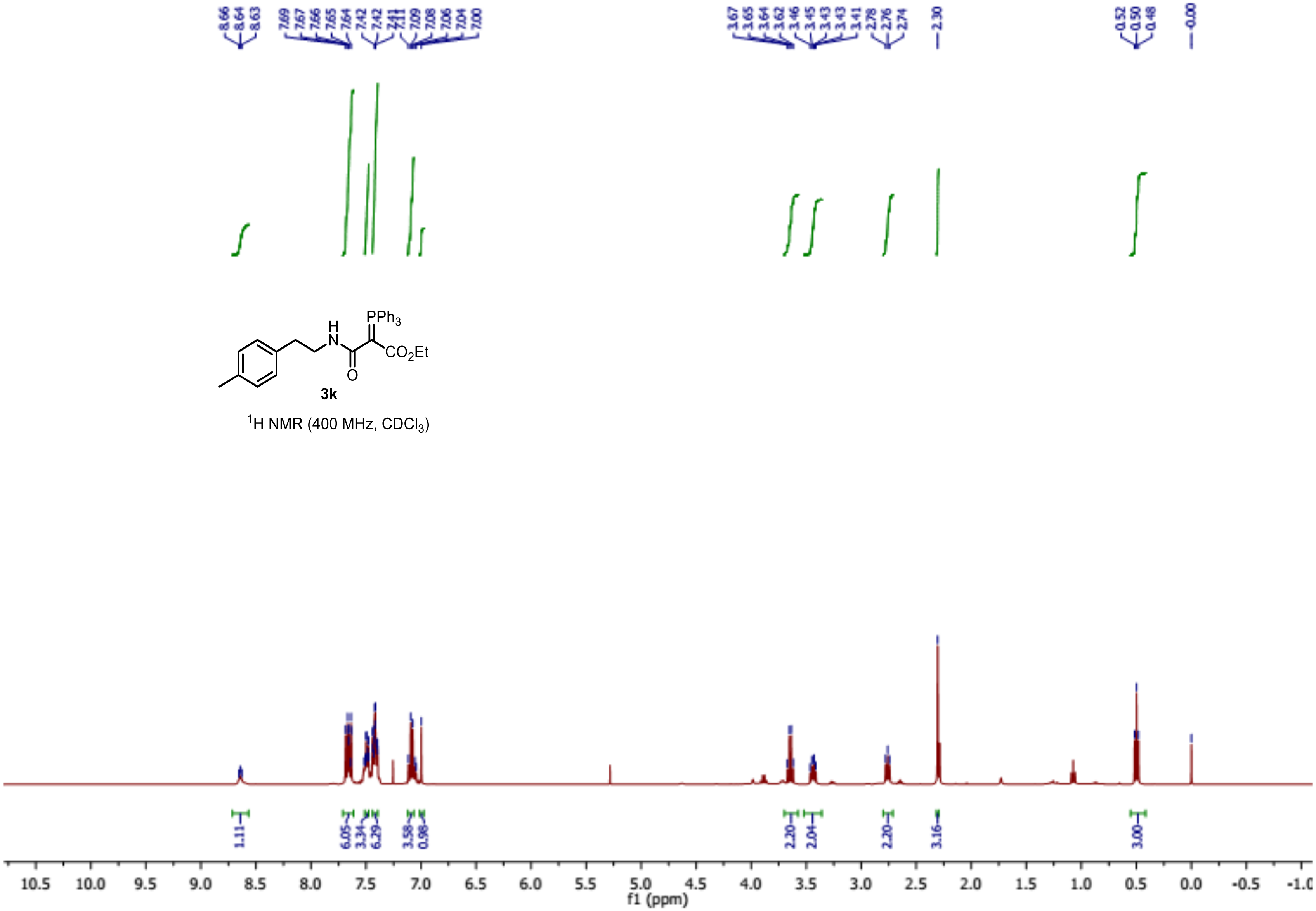
3j

^{1}H NMR (400 MHz, CDCl$_3$)



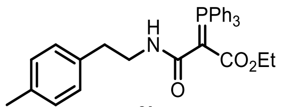
3j

^{13}C NMR (100 MHz, CDCl$_3$)



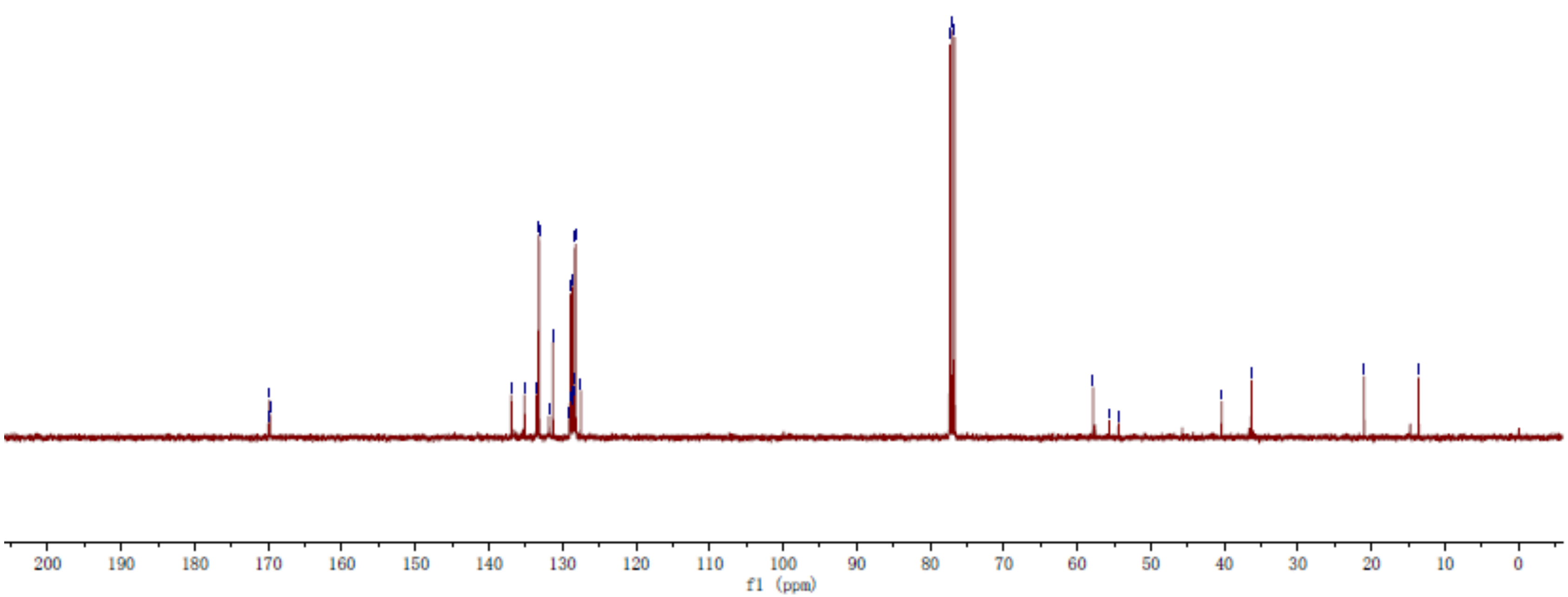
3k

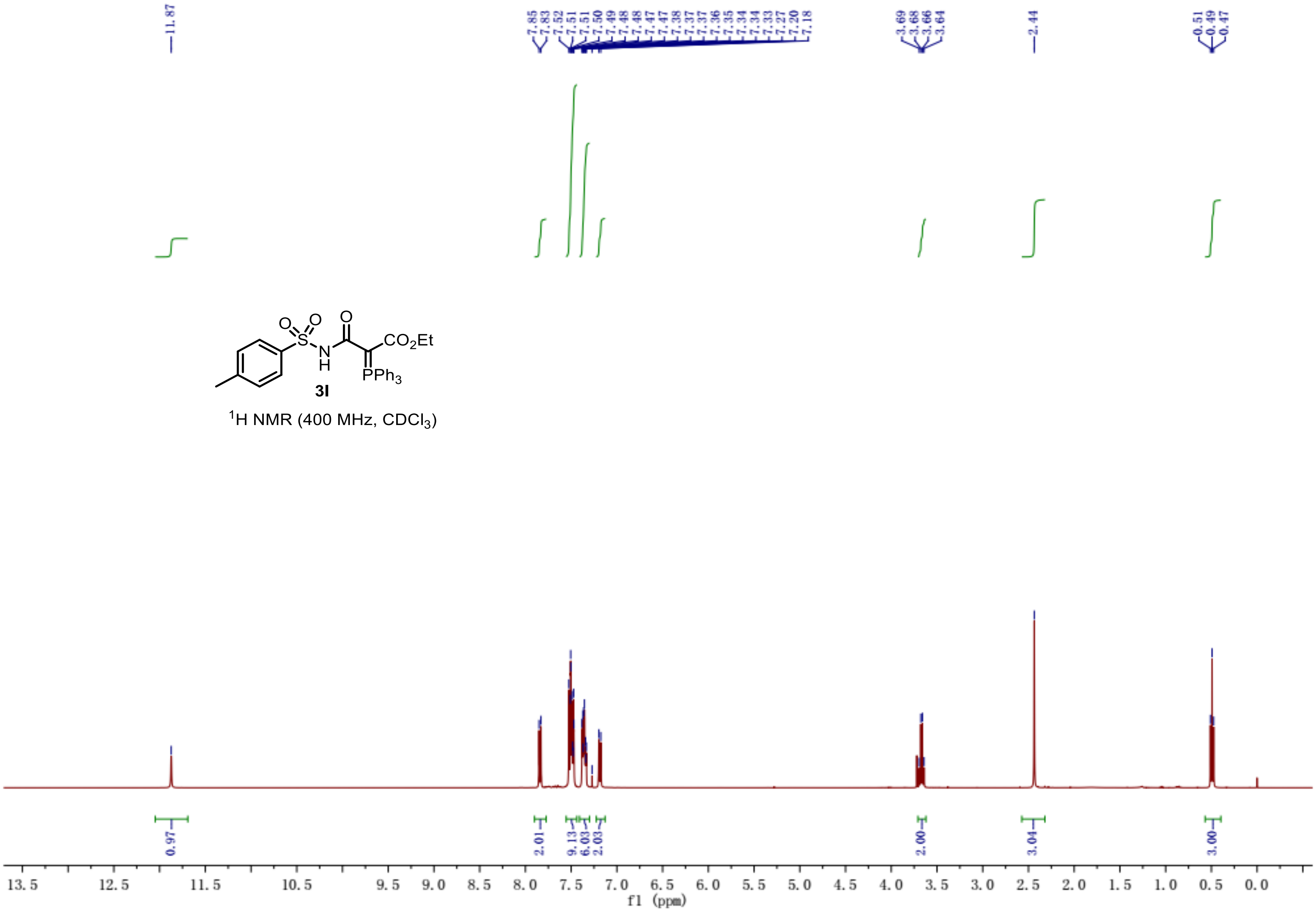
^{1}H NMR (400 MHz, CDCl$_3$)



3k

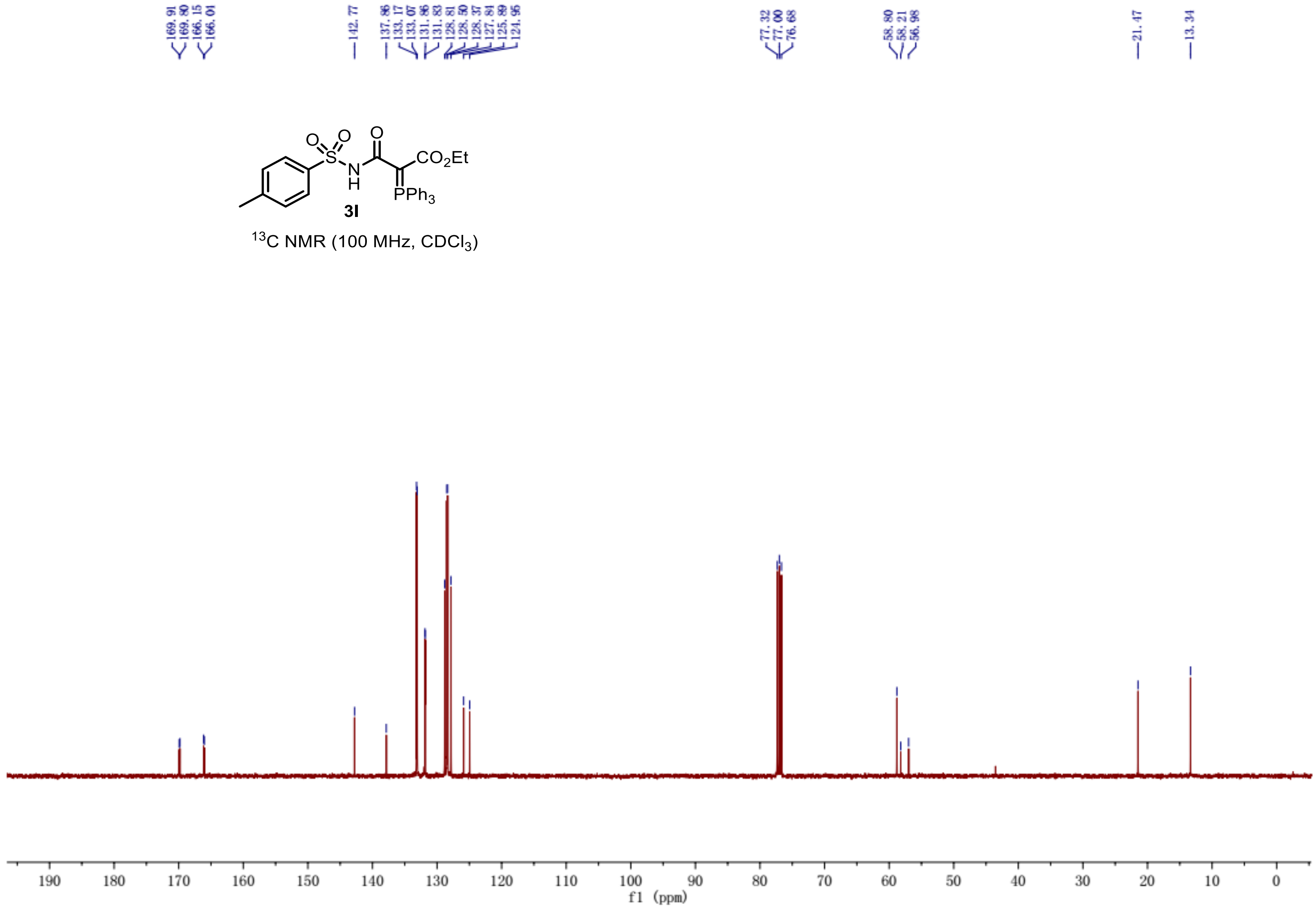
^{13}C NMR (100 MHz, CDCl$_3$)





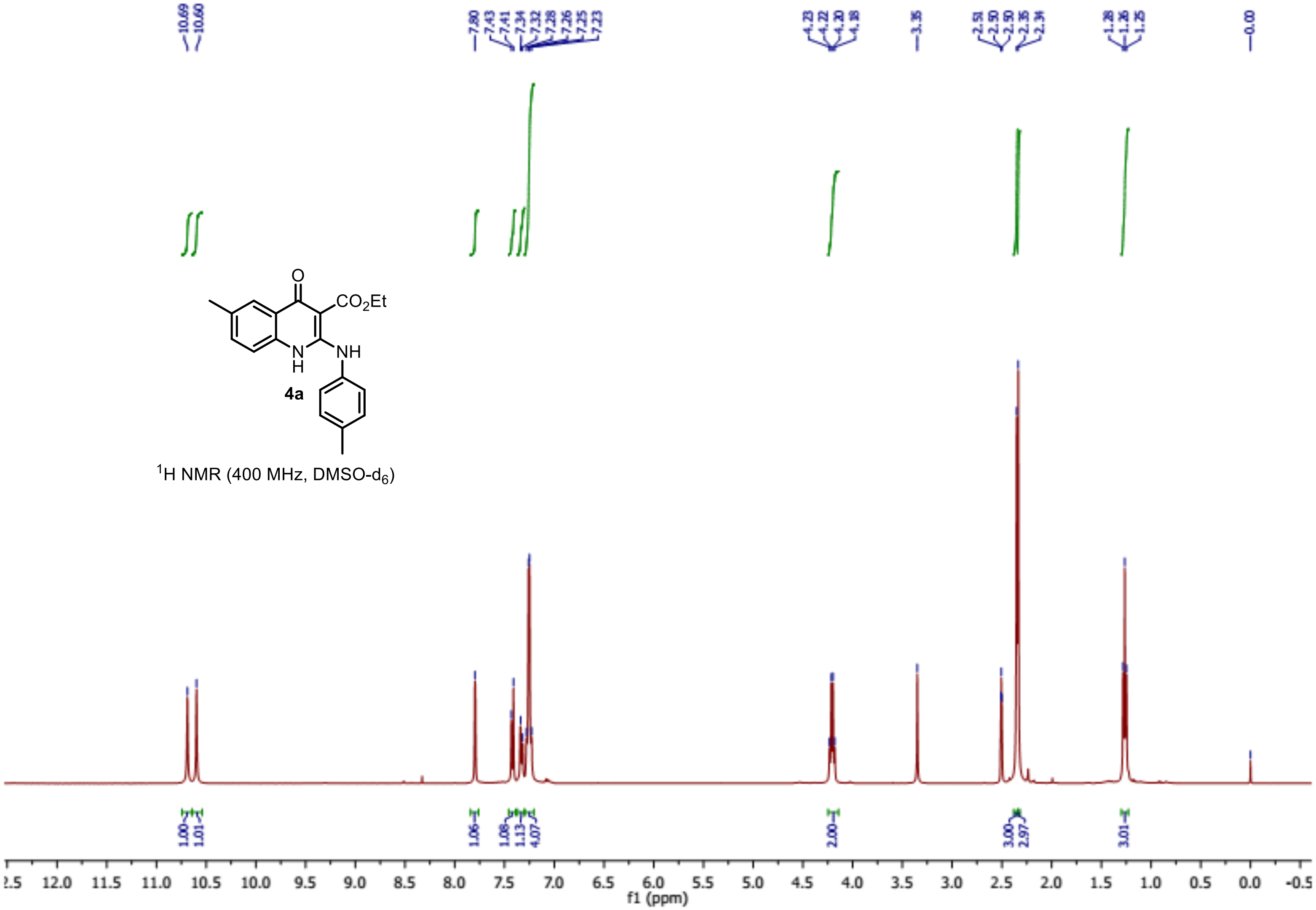
3l

^{1}H NMR (400 MHz, CDCl$_3$)



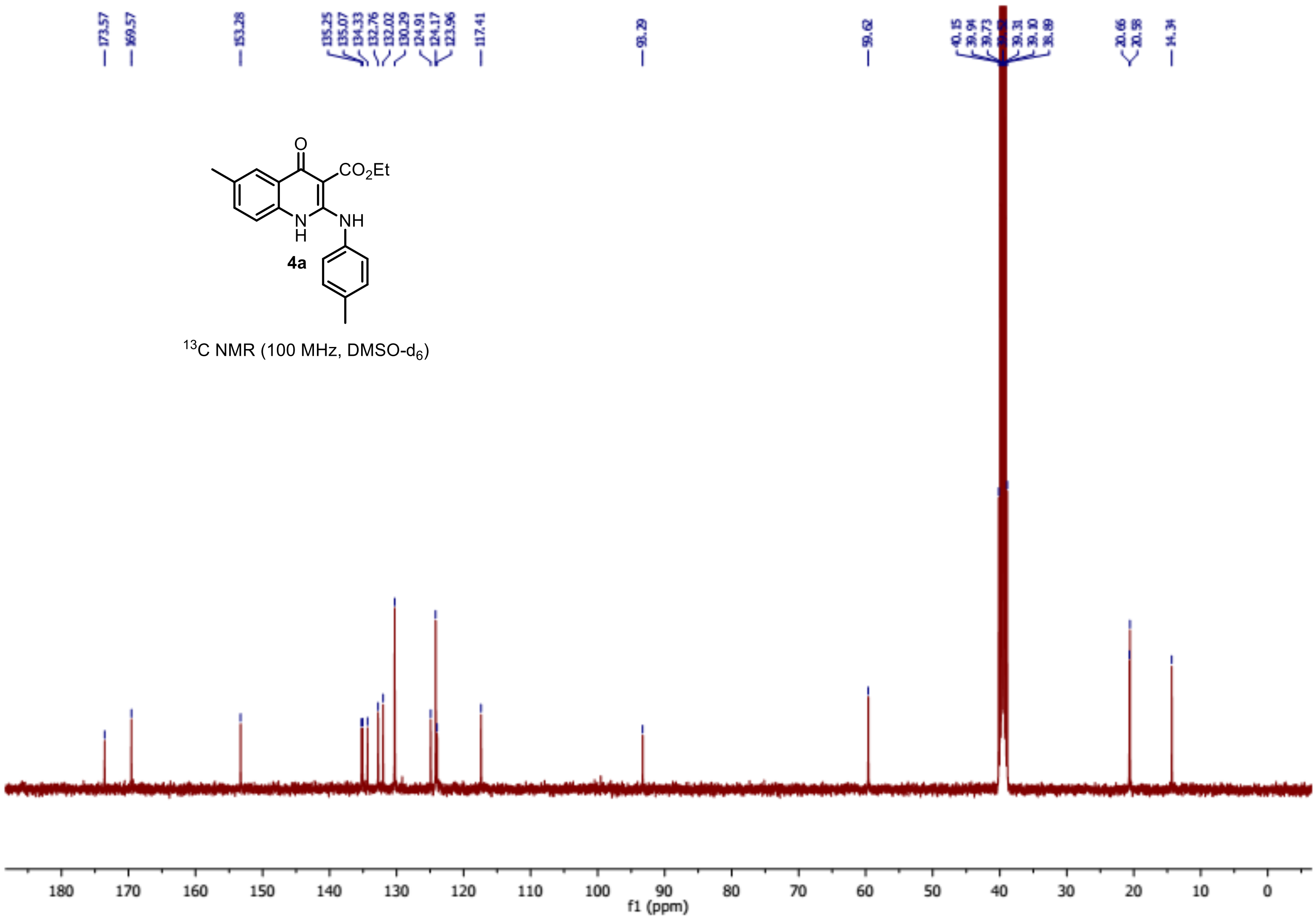
3l

^{13}C NMR (100 MHz, CDCl$_3$)



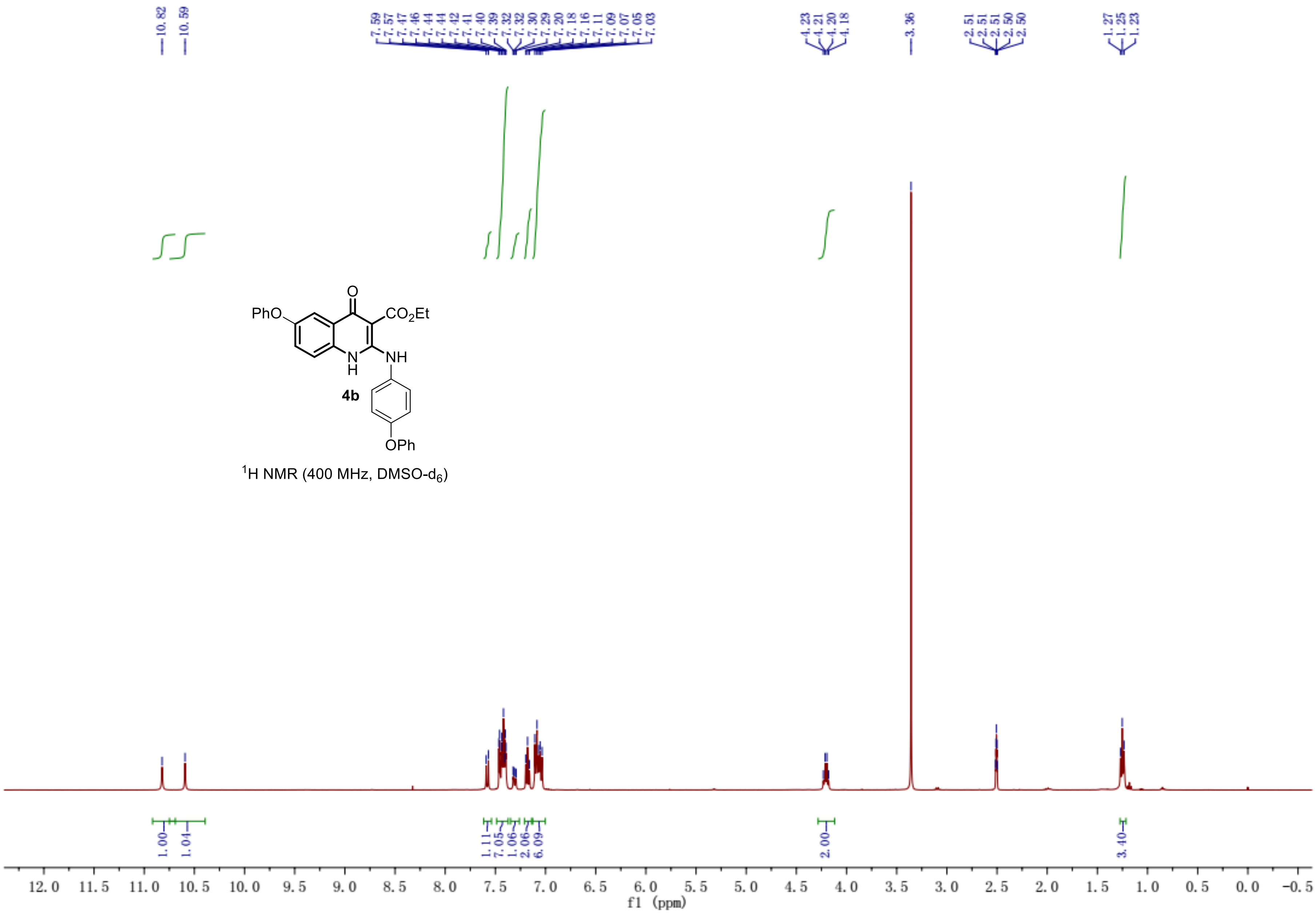
4a

^1H NMR (400 MHz, DMSO-d_6)

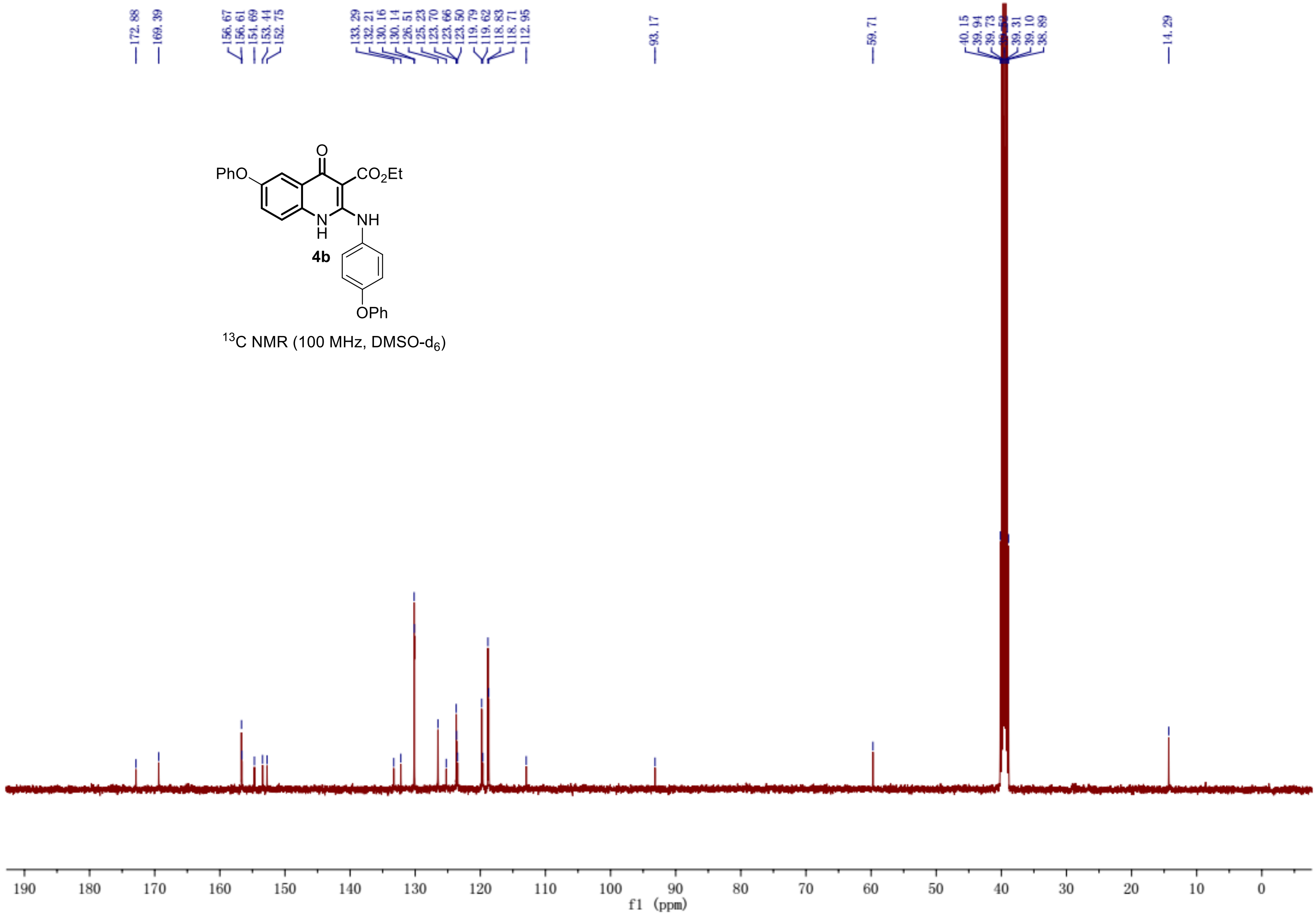


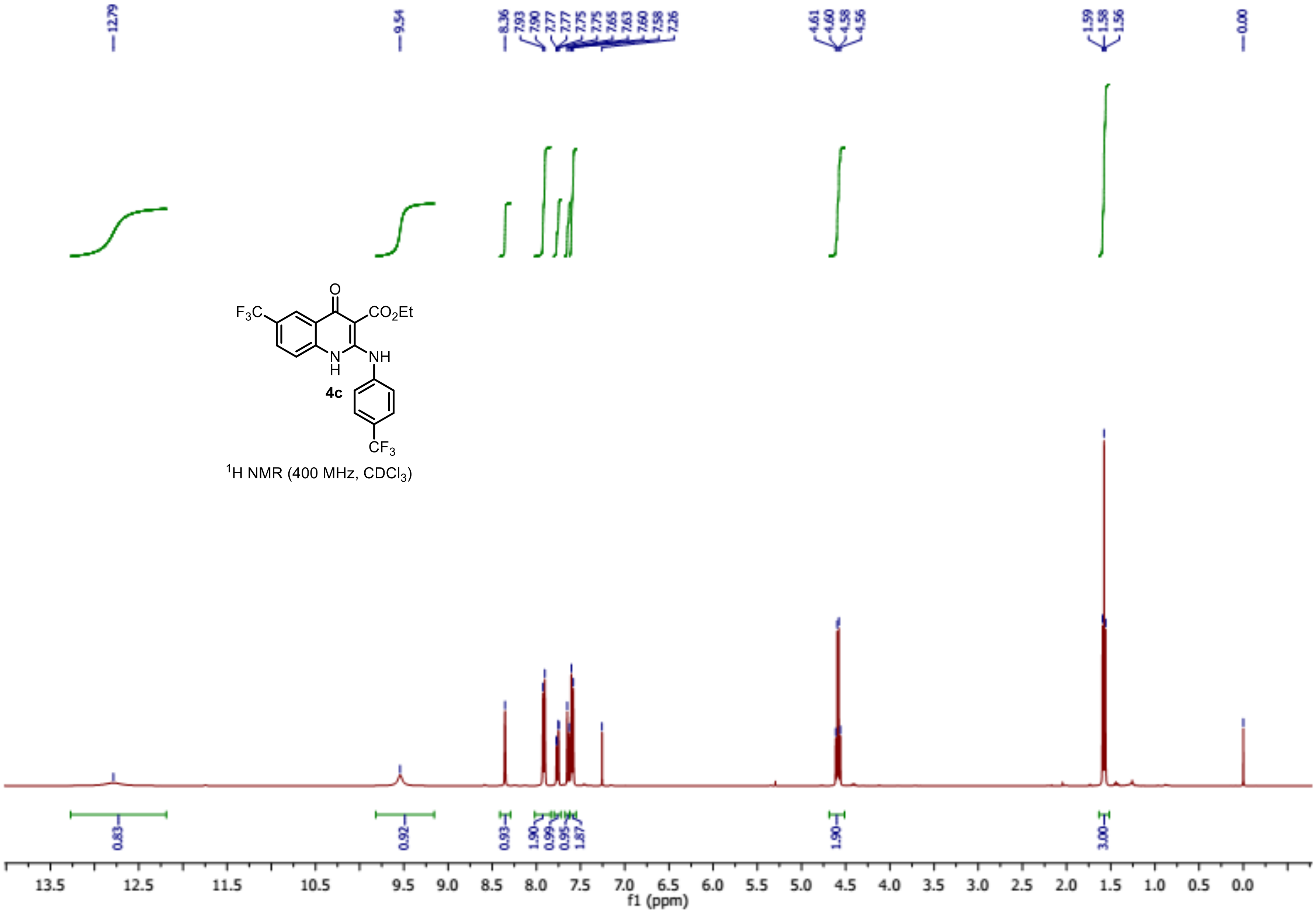
4a

^{13}C NMR (100 MHz, DMSO-d$_6$)



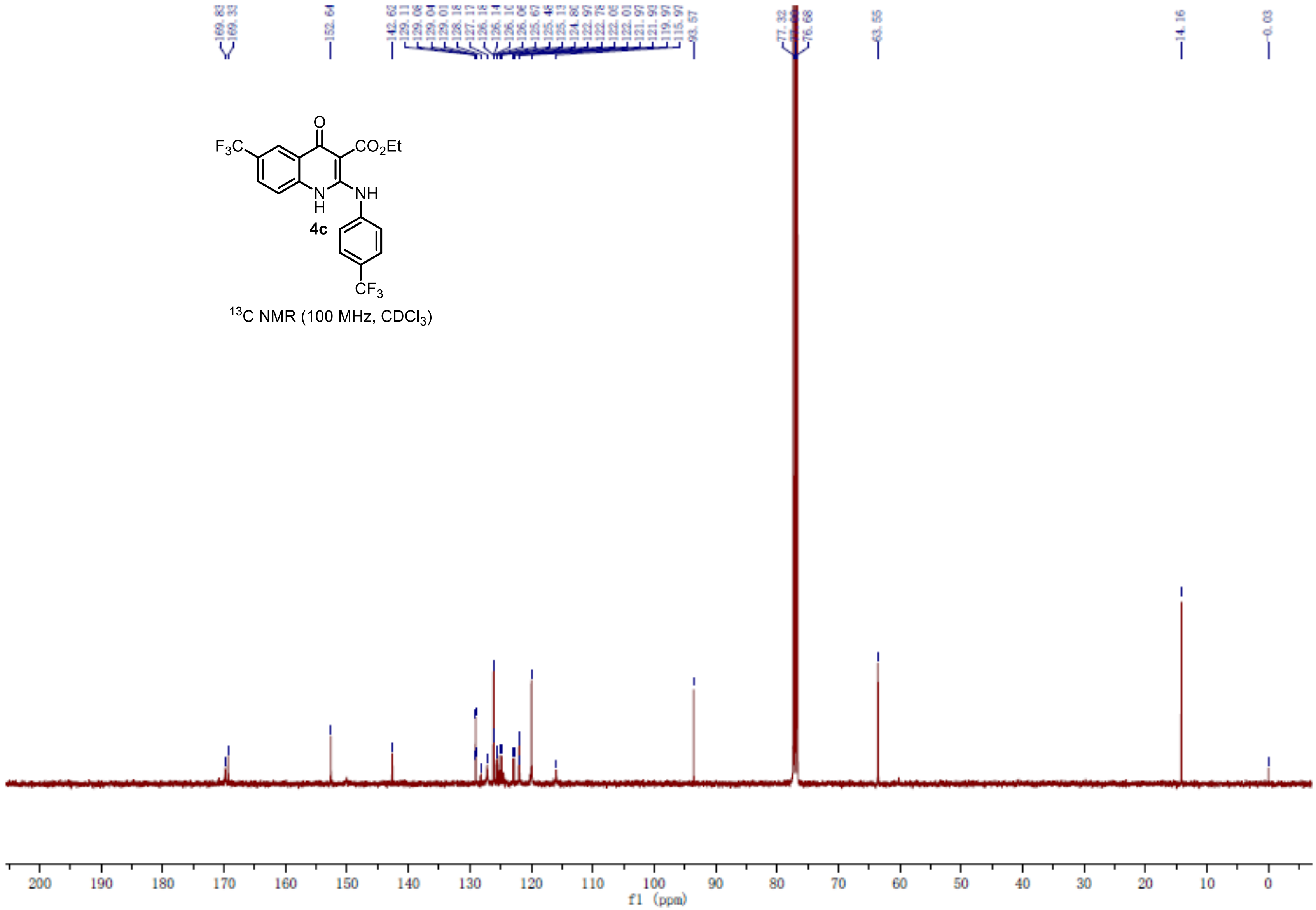
^{1}H NMR (400 MHz, DMSO-d_6)


172. 88
169. 39
156. 67
156. 61
154. 69
153. 44
152. 75
133. 29
132. 21
130. 16
130. 14
126. 51
125. 23
123. 70
123. 66
123. 50
119. 79
119. 62
118. 83
118. 71
112. 95
93. 17
59. 71
40. 15
39. 94
39. 73
39. 52
39. 31
39. 10
38. 89
14. 29
PhO
O
CO2Et
N
H
NH
OPh
4b
13C NMR (100 MHz, DMSO-d6)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



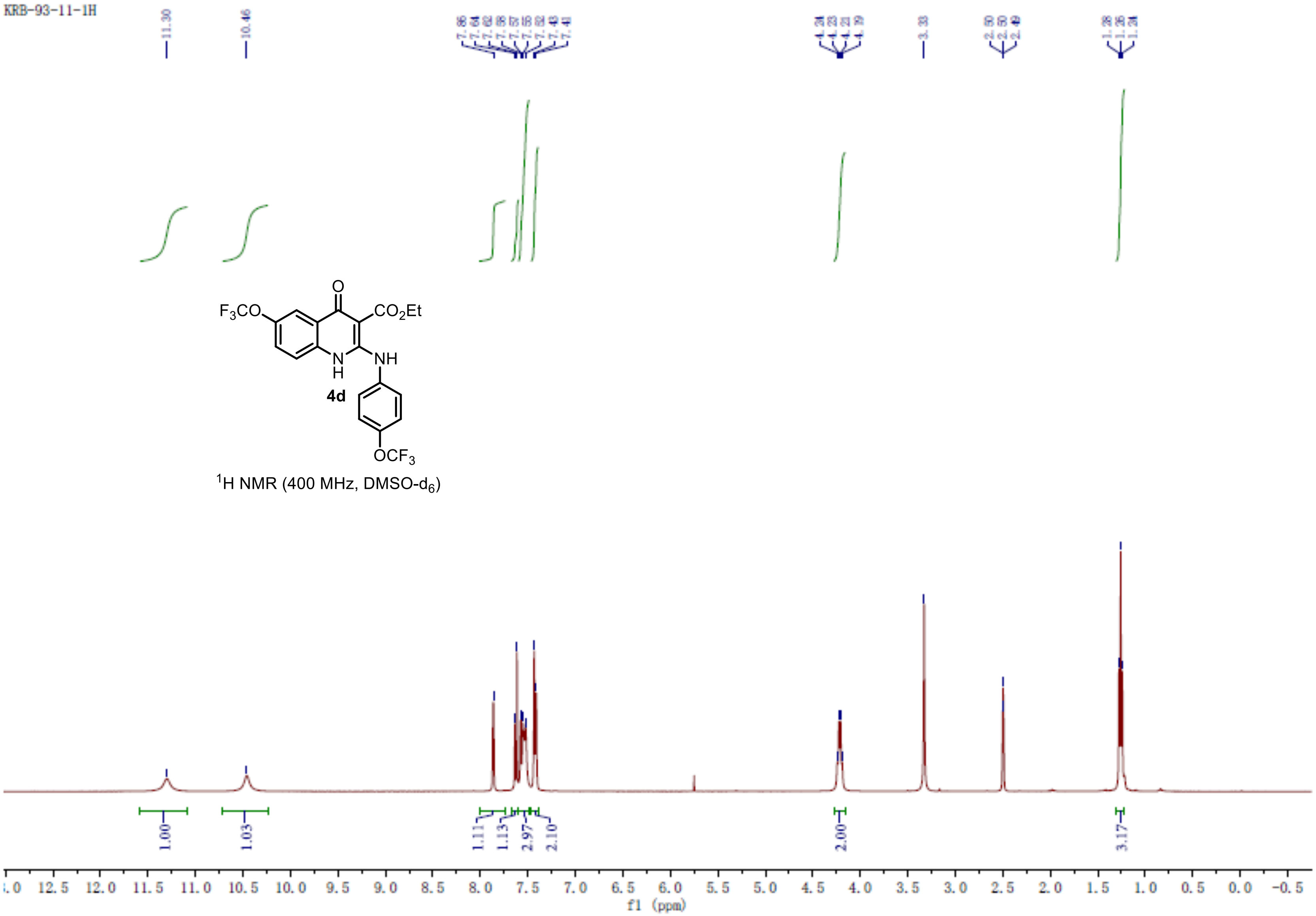
4c

^{1}H NMR (400 MHz, $CDCl_3$)



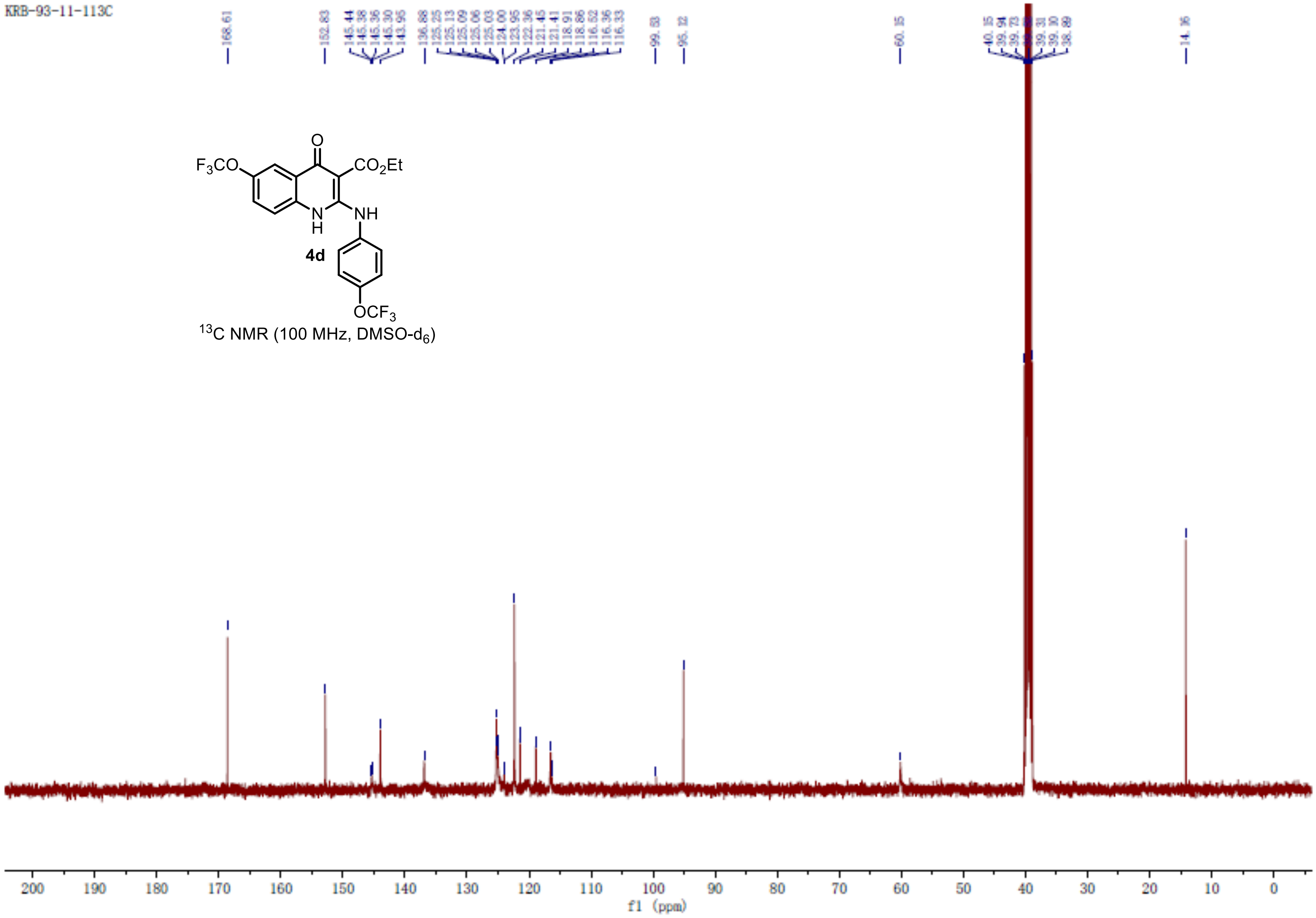
4c

^{13}C NMR (100 MHz, CDCl$_3$)

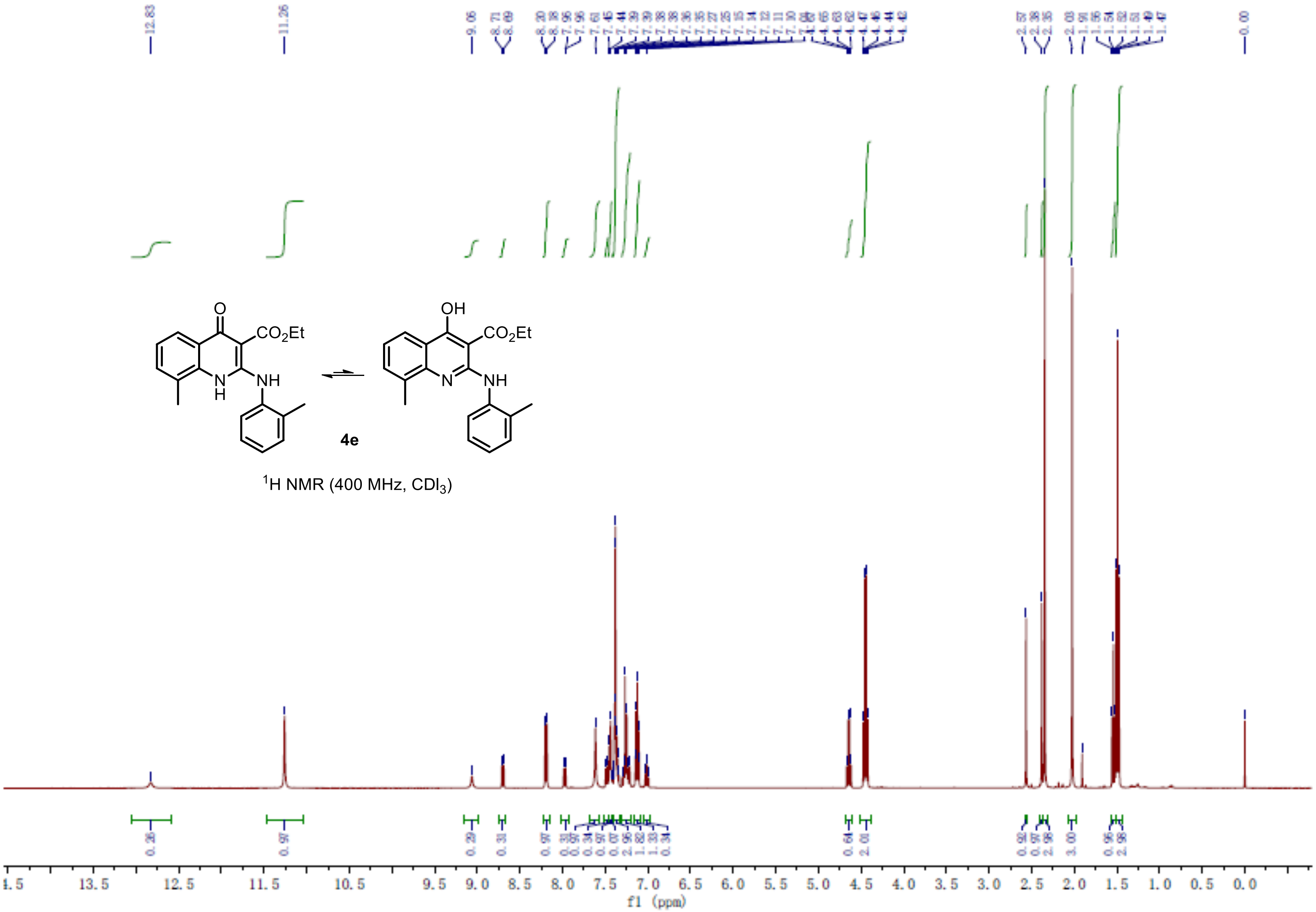


4d

^{1}H NMR (400 MHz, DMSO-d_6)

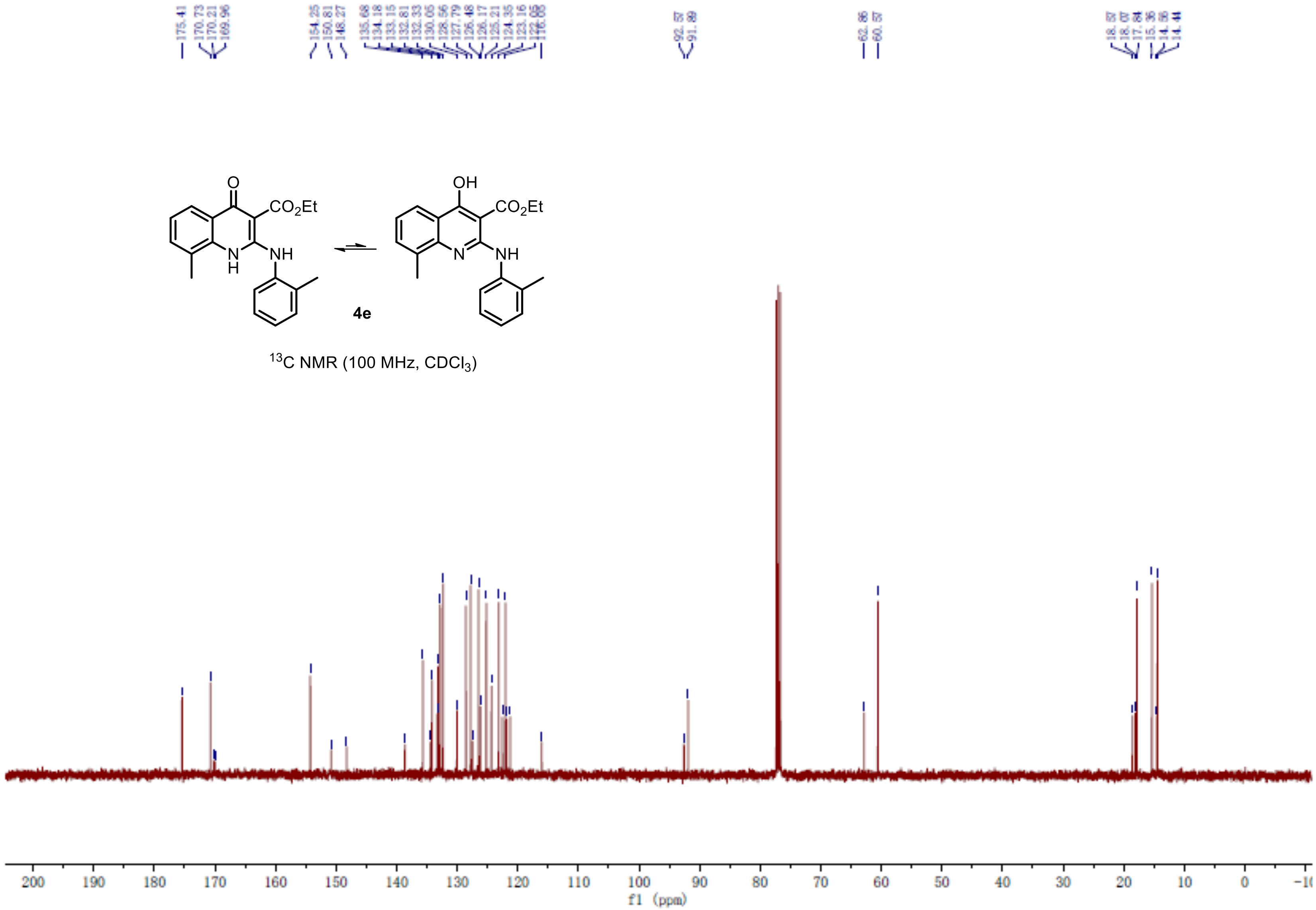


^{13}C NMR (100 MHz, DMSO-d_6)



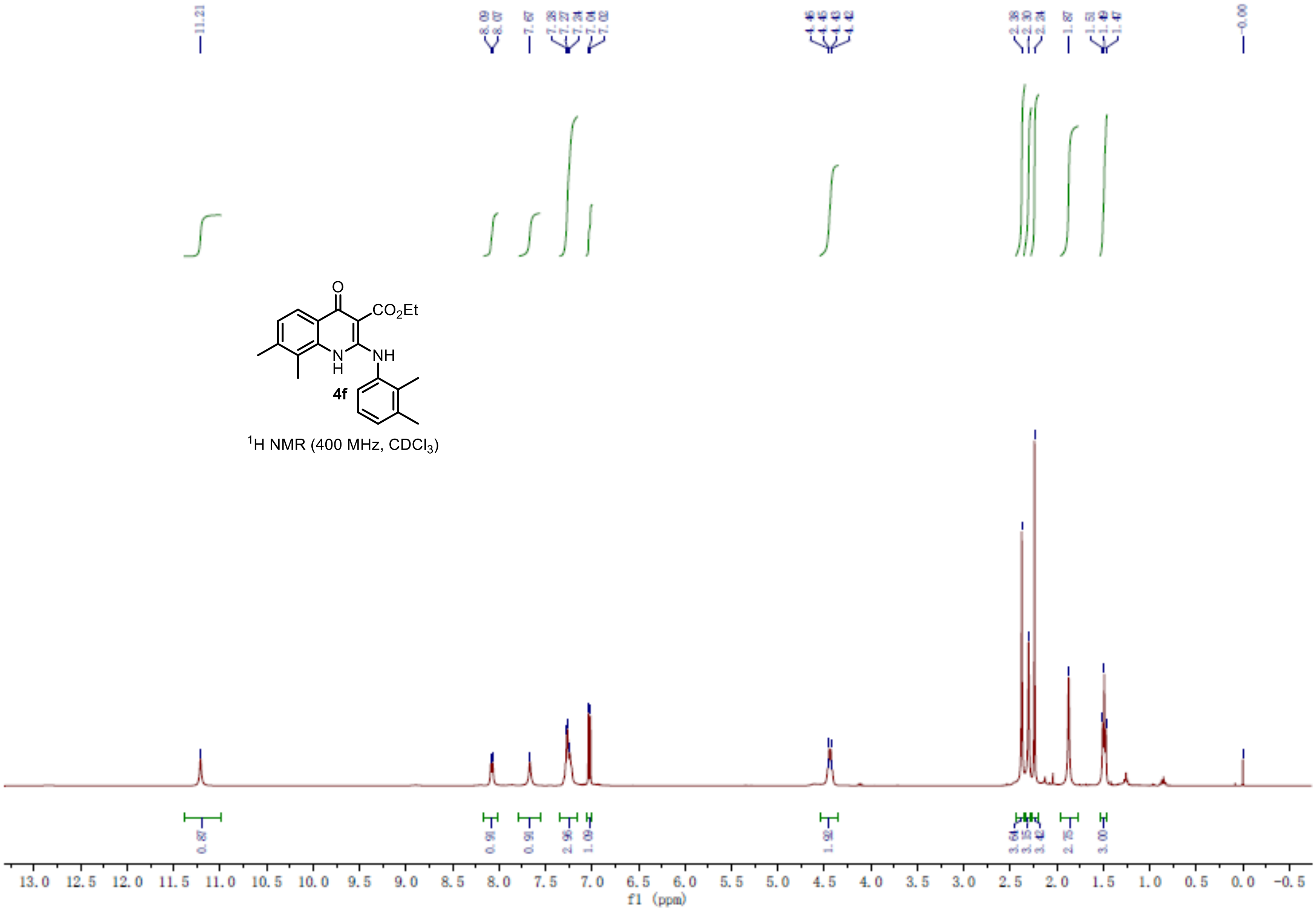
4e

^{1}H NMR (400 MHz, CDI$_3$)



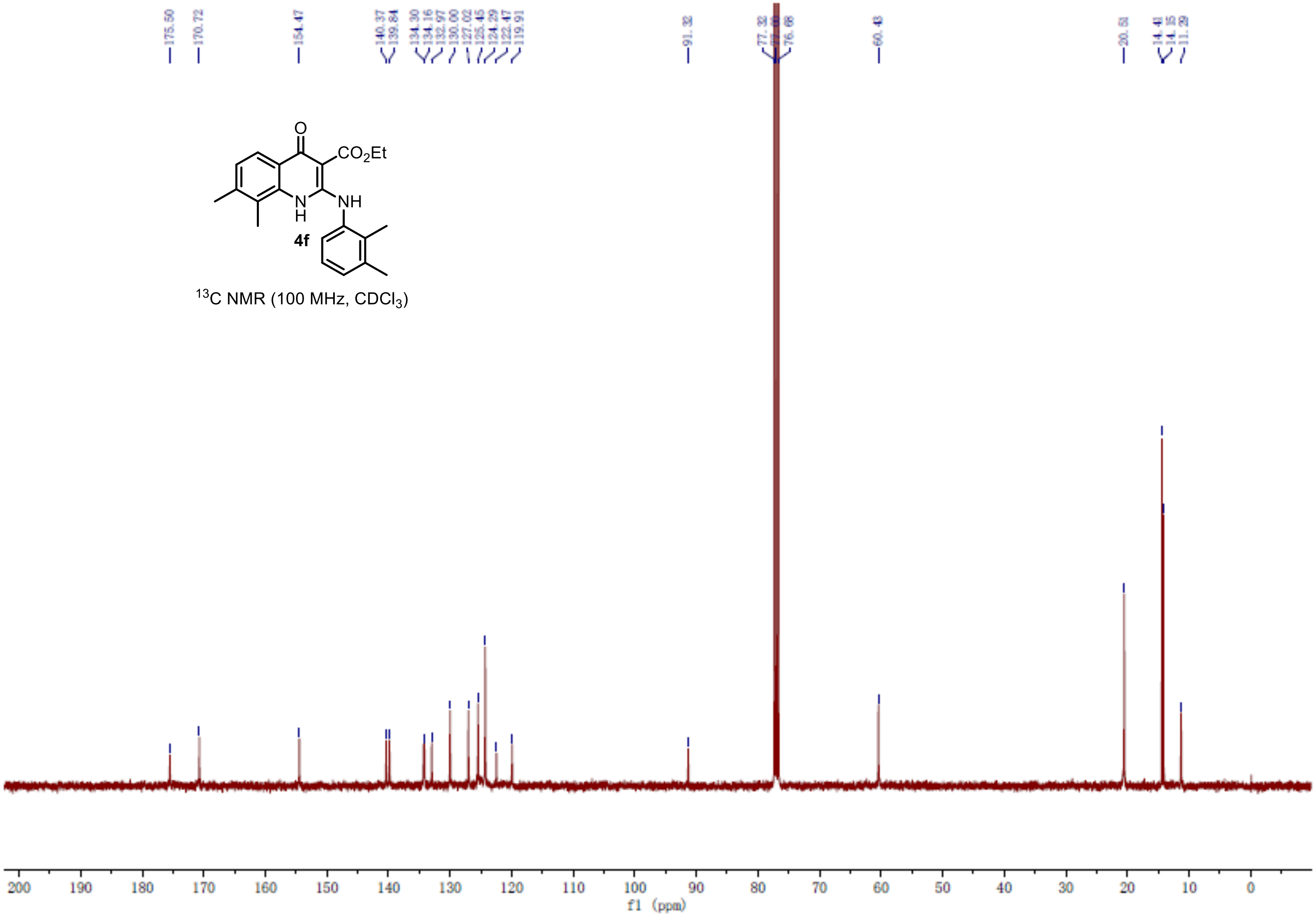
4e

^{13}C NMR (100 MHz, CDCl$_3$)

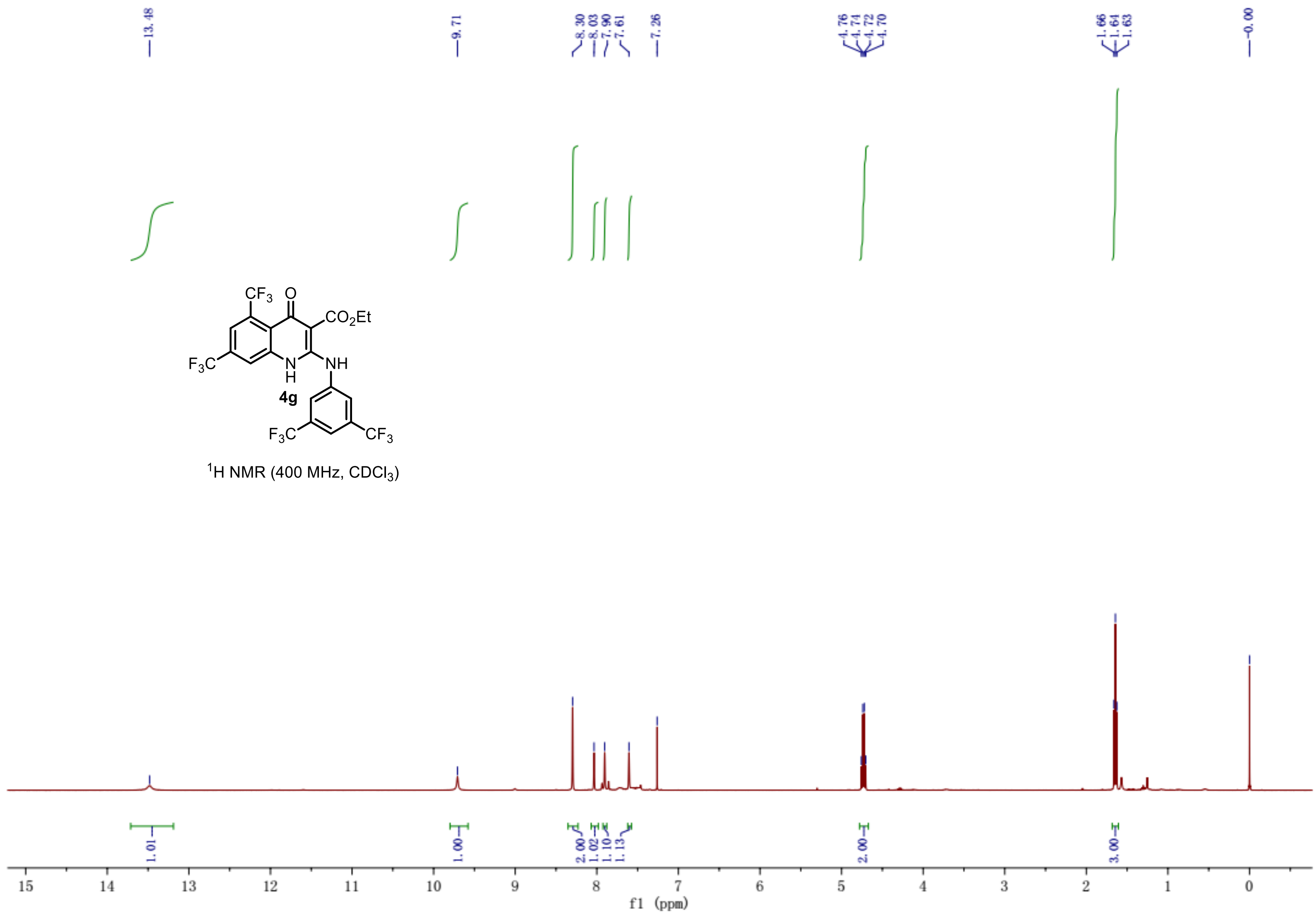


4f

^{1}H NMR (400 MHz, $CDCl_3$)

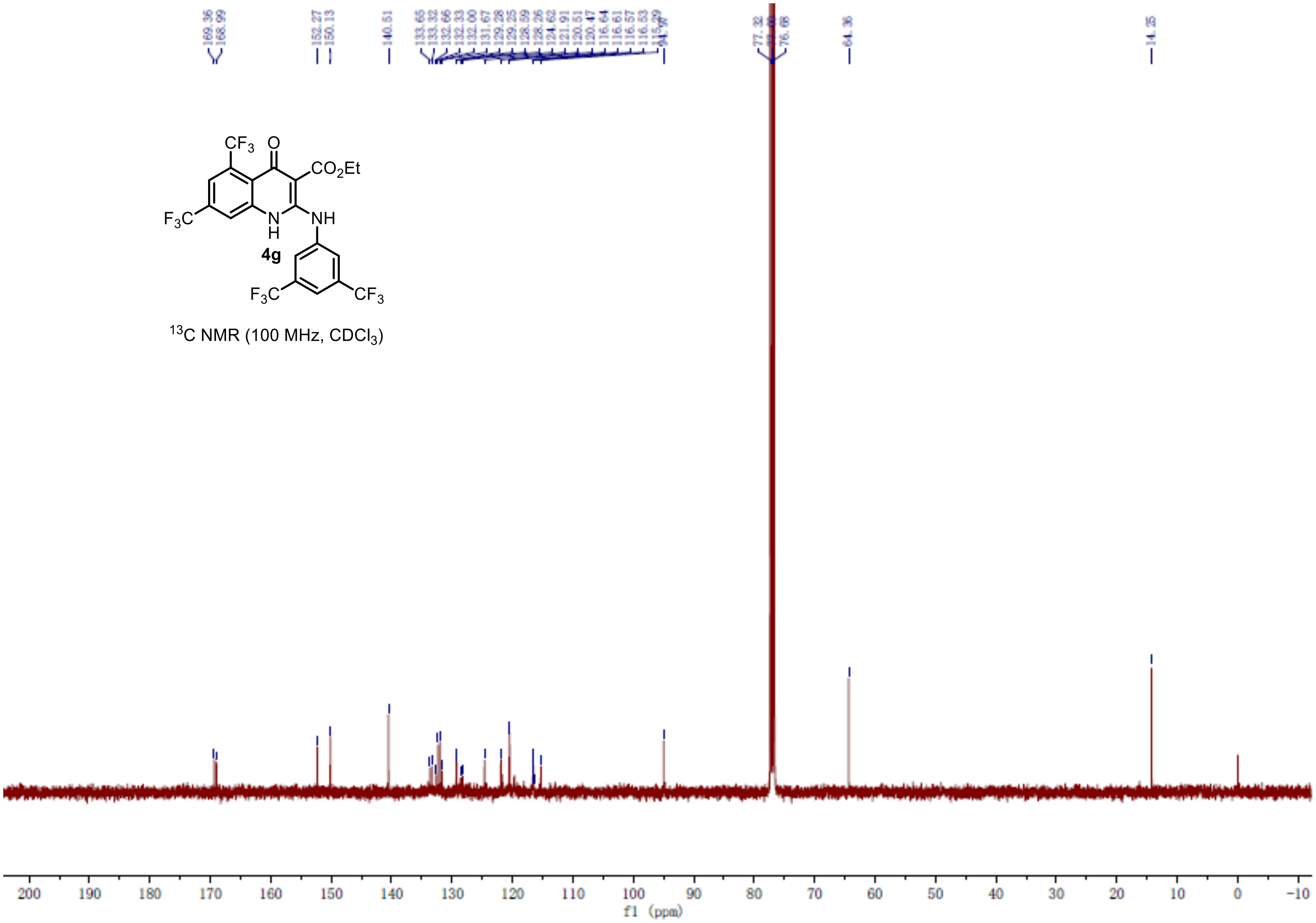


^{13}C NMR (100 MHz, CDCl$_3$)



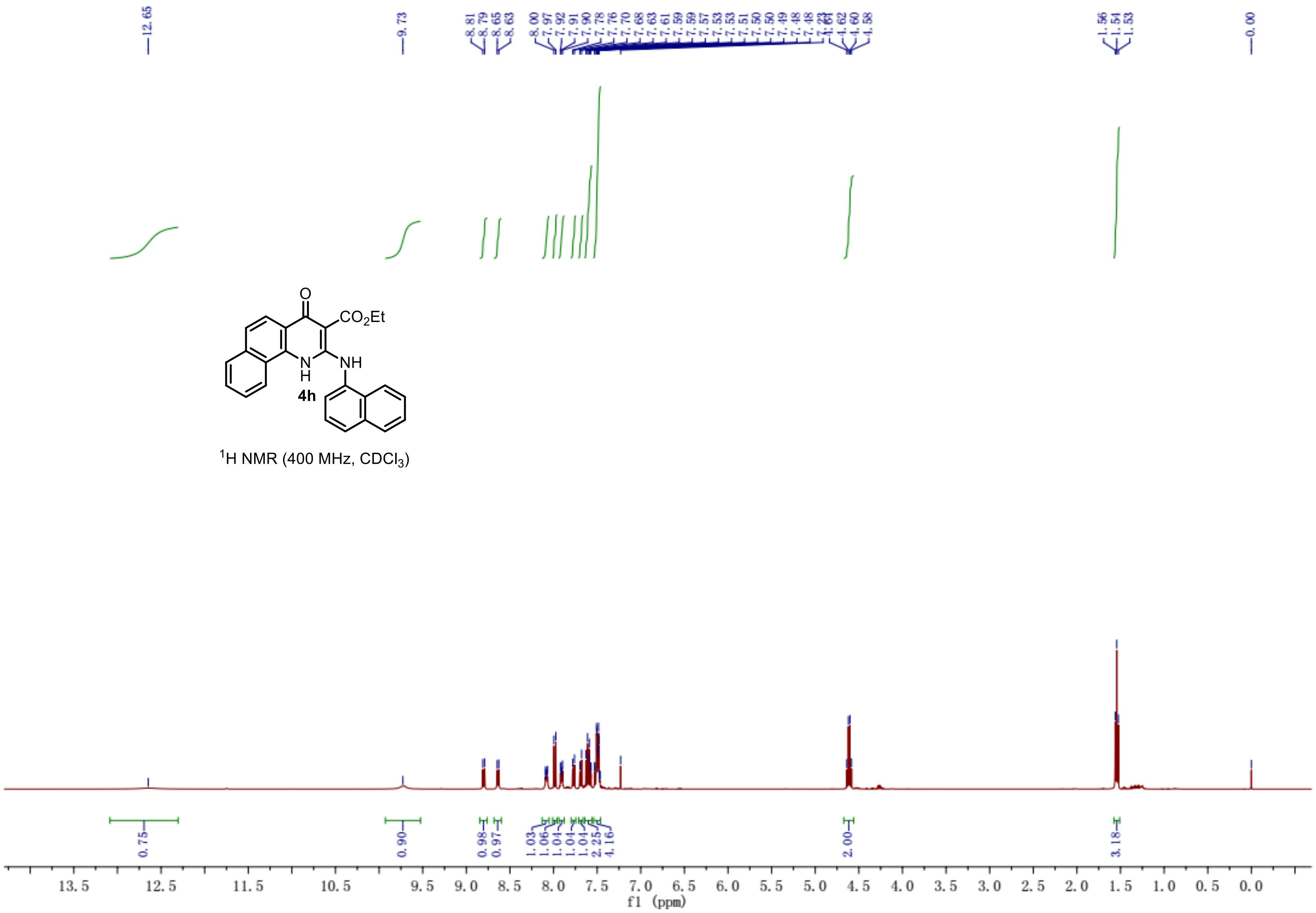
4g

^{1}H NMR (400 MHz, CDCl$_3$)



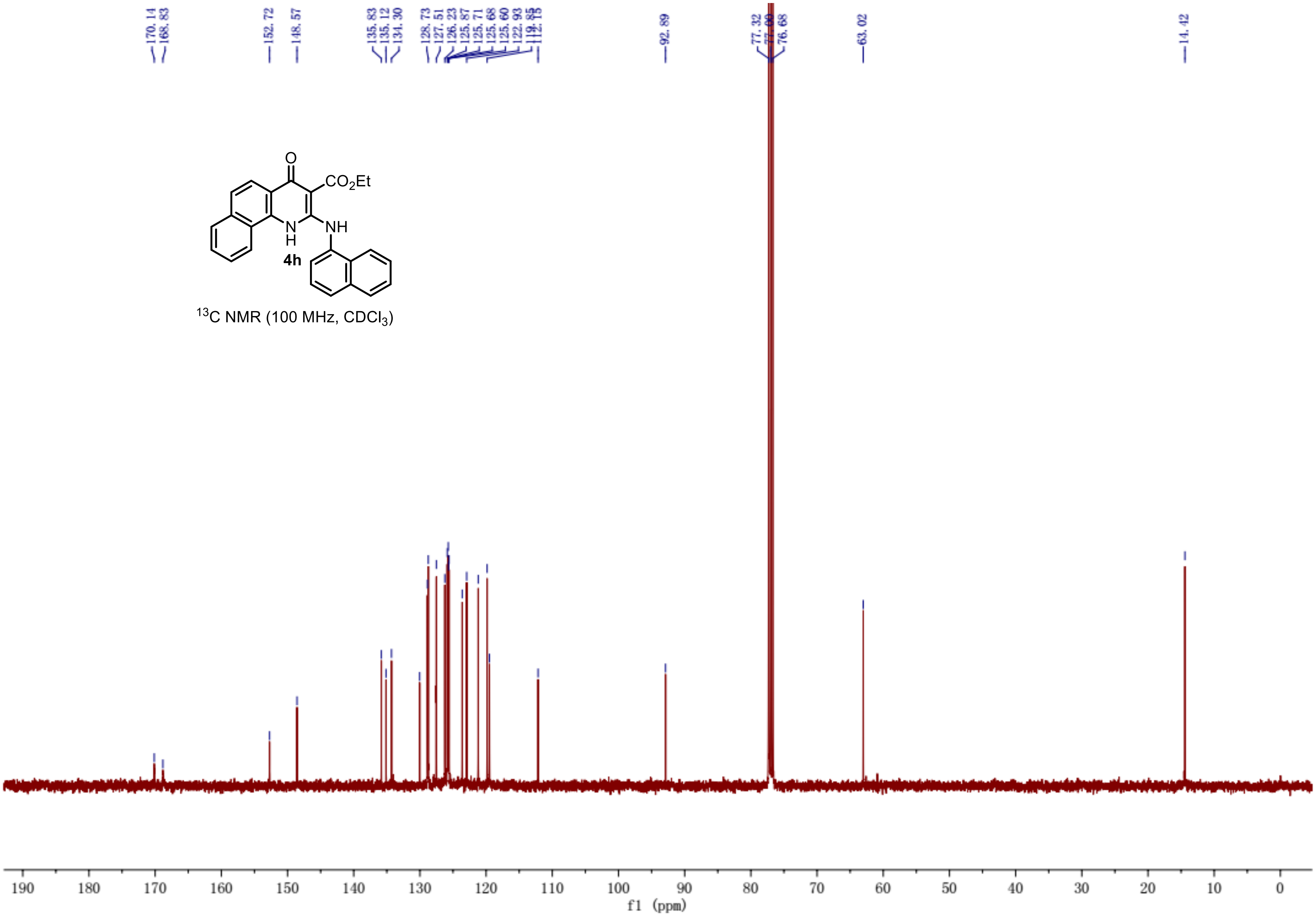
4g

^{13}C NMR (100 MHz, CDCl$_3$)

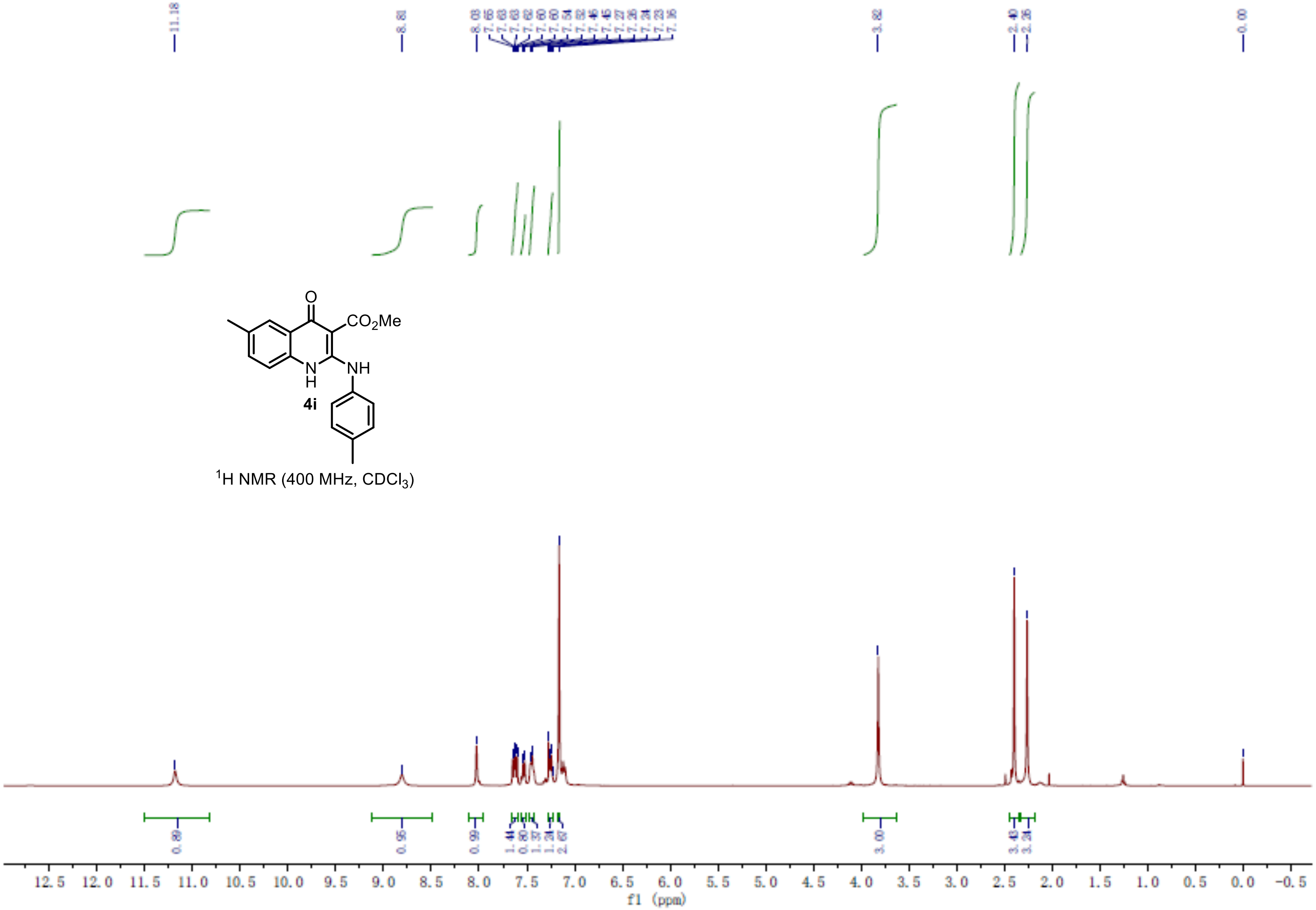


4h

^{1}H NMR (400 MHz, CDCl$_3$)

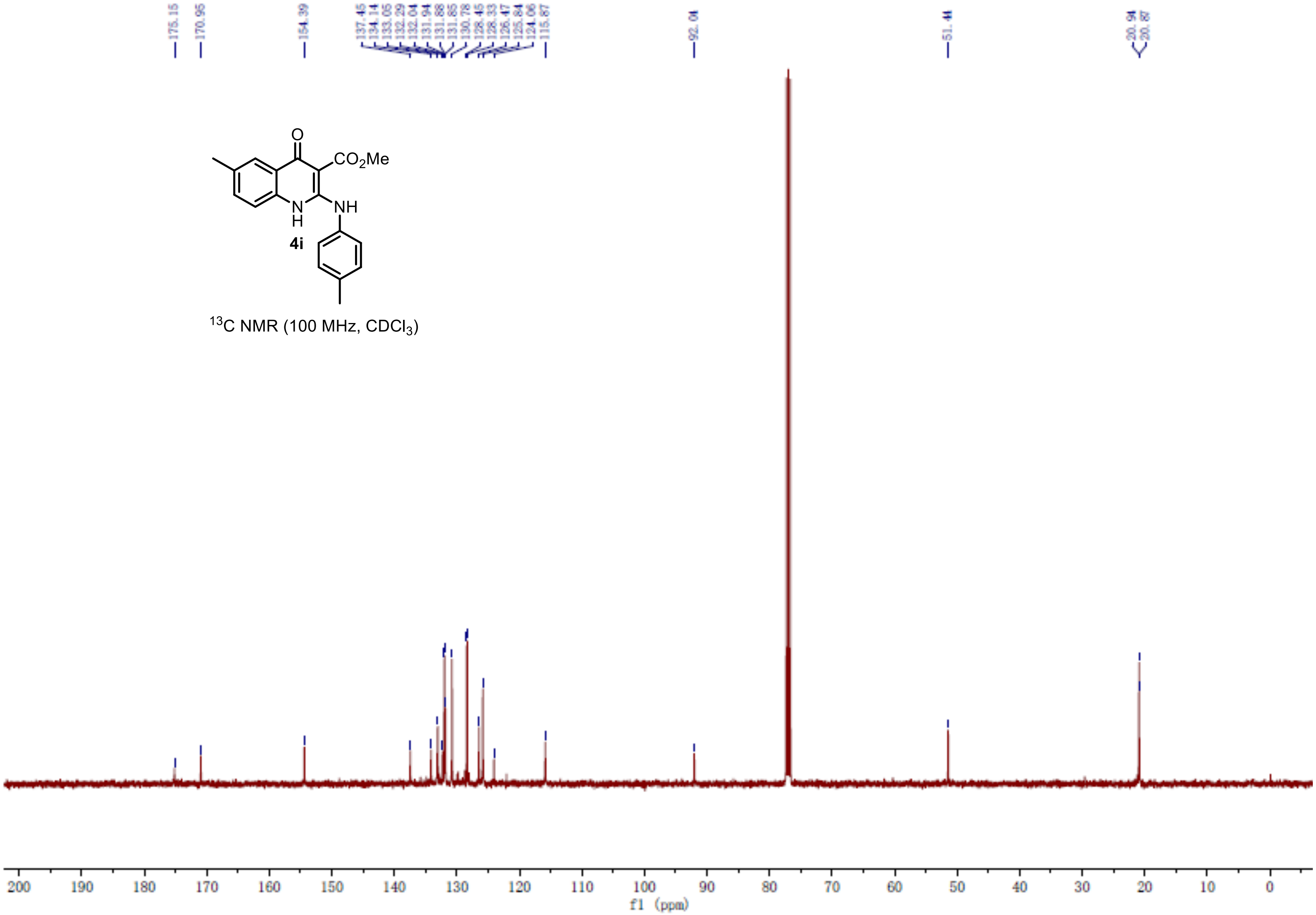


^{13}C NMR (100 MHz, CDCl$_3$)



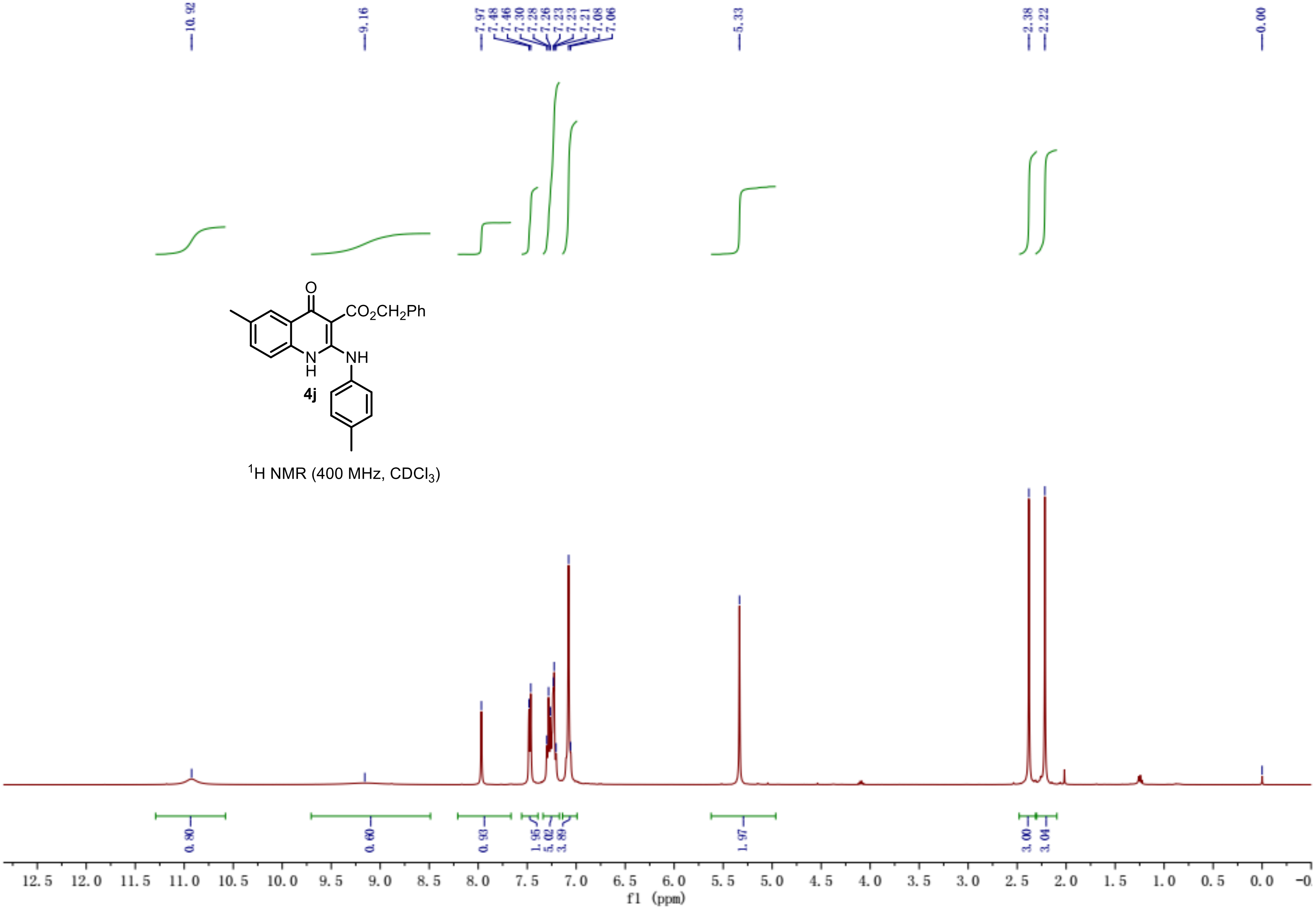
4i

^{1}H NMR (400 MHz, CDCl$_3$)



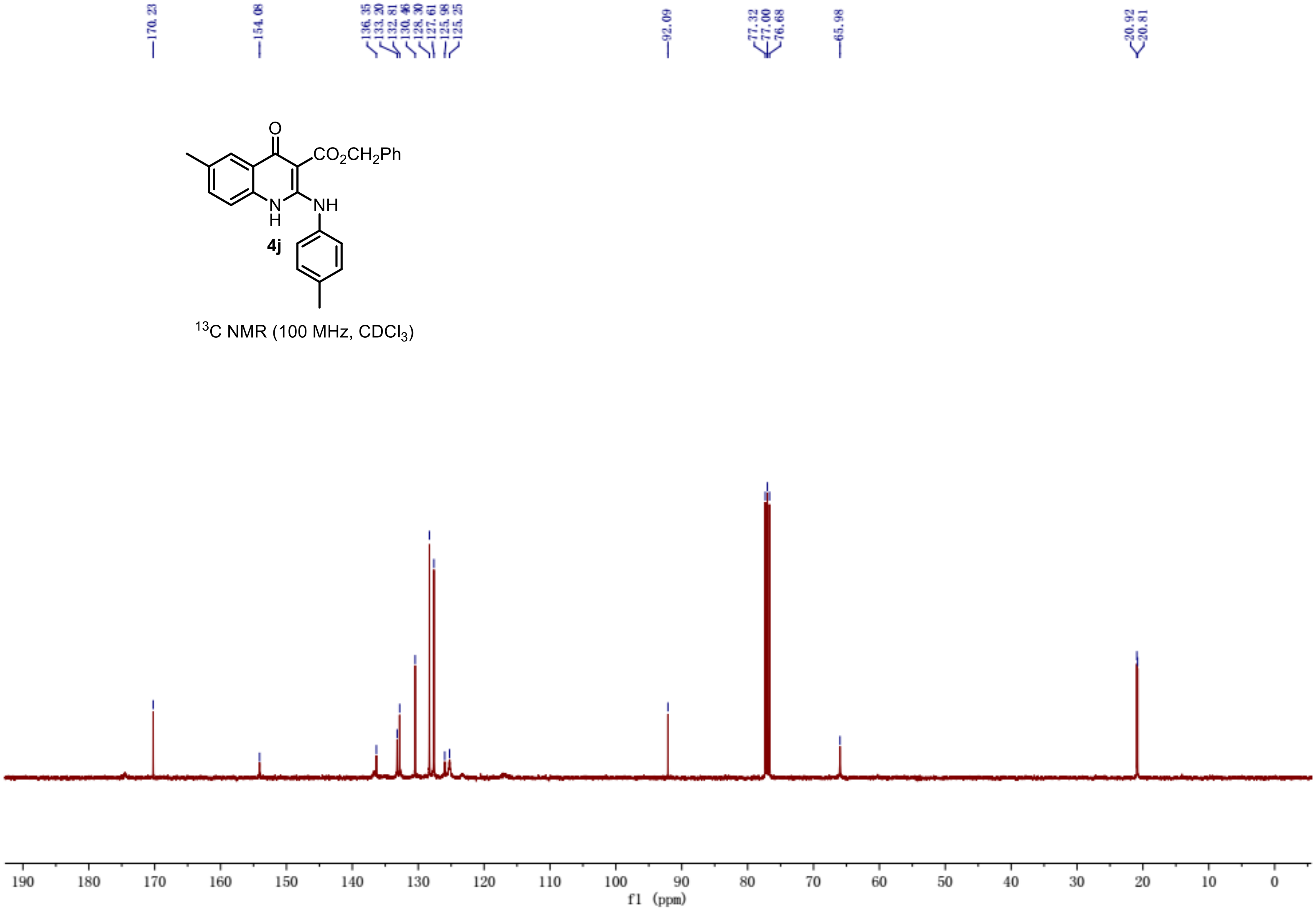
4i

^{13}C NMR (100 MHz, CDCl$_3$)



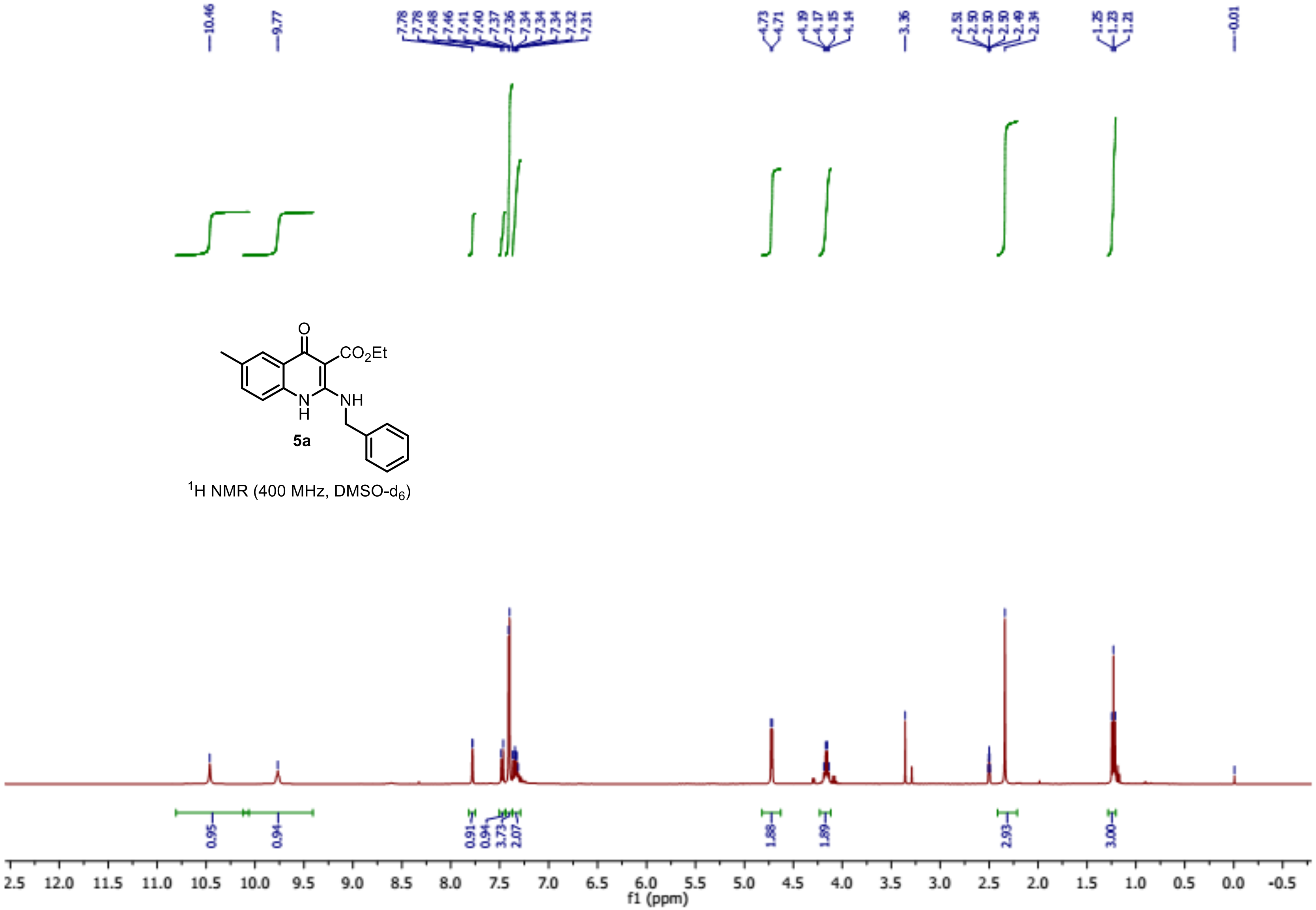
4j

^{1}H NMR (400 MHz, CDCl$_3$)



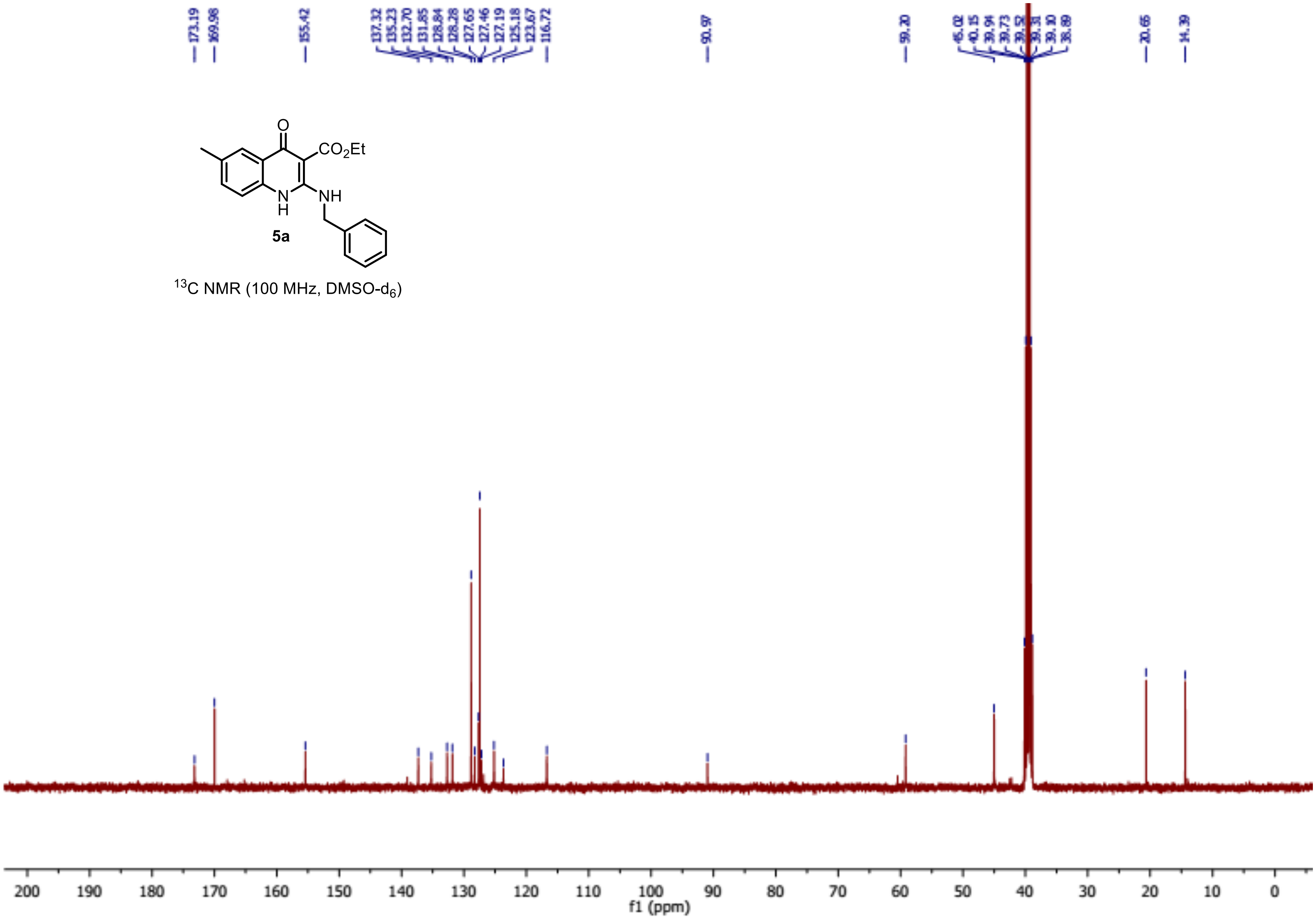
4j

^{13}C NMR (100 MHz, $CDCl_3$)



5a

^{1}H NMR (400 MHz, DMSO-d$_6$)

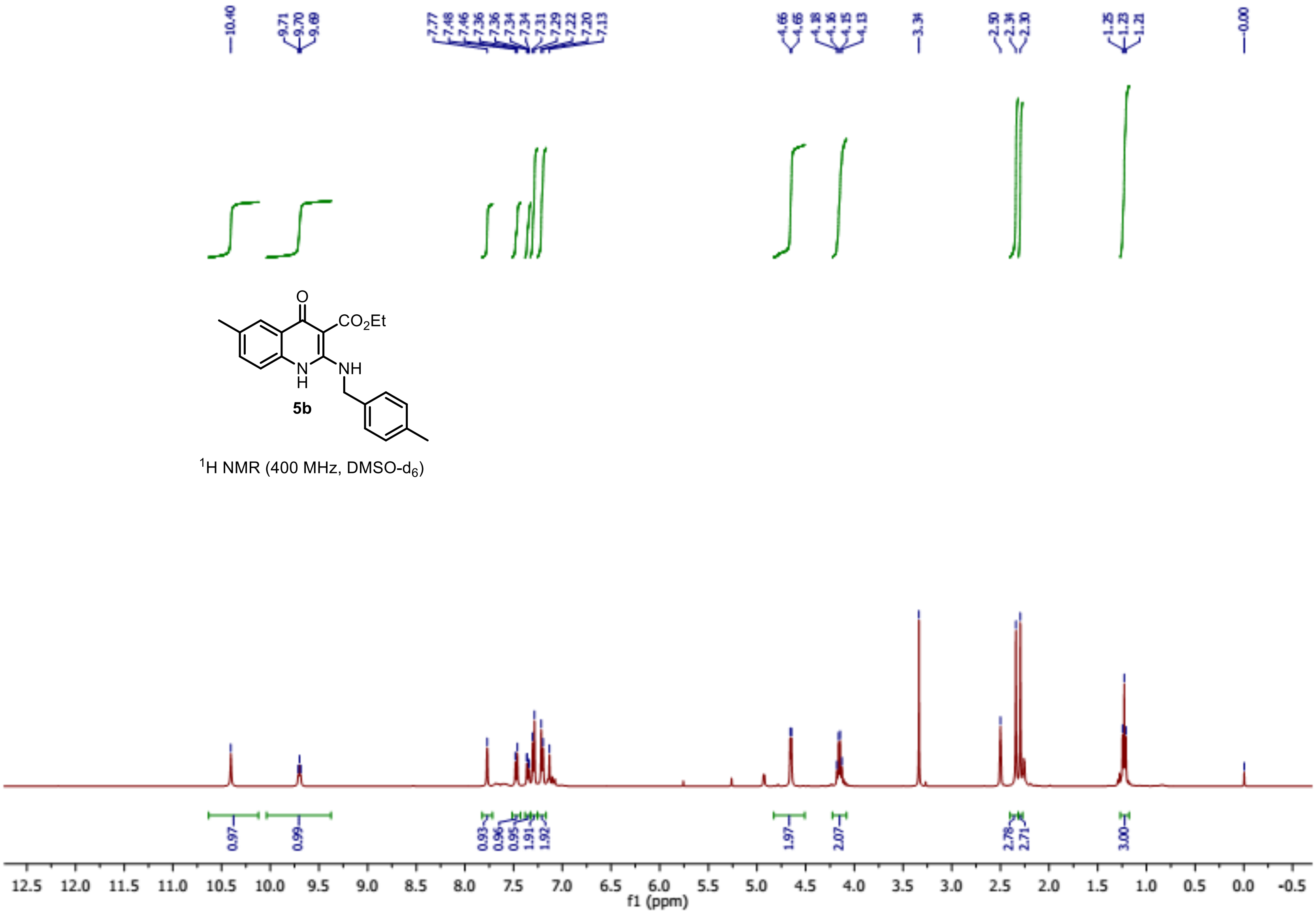


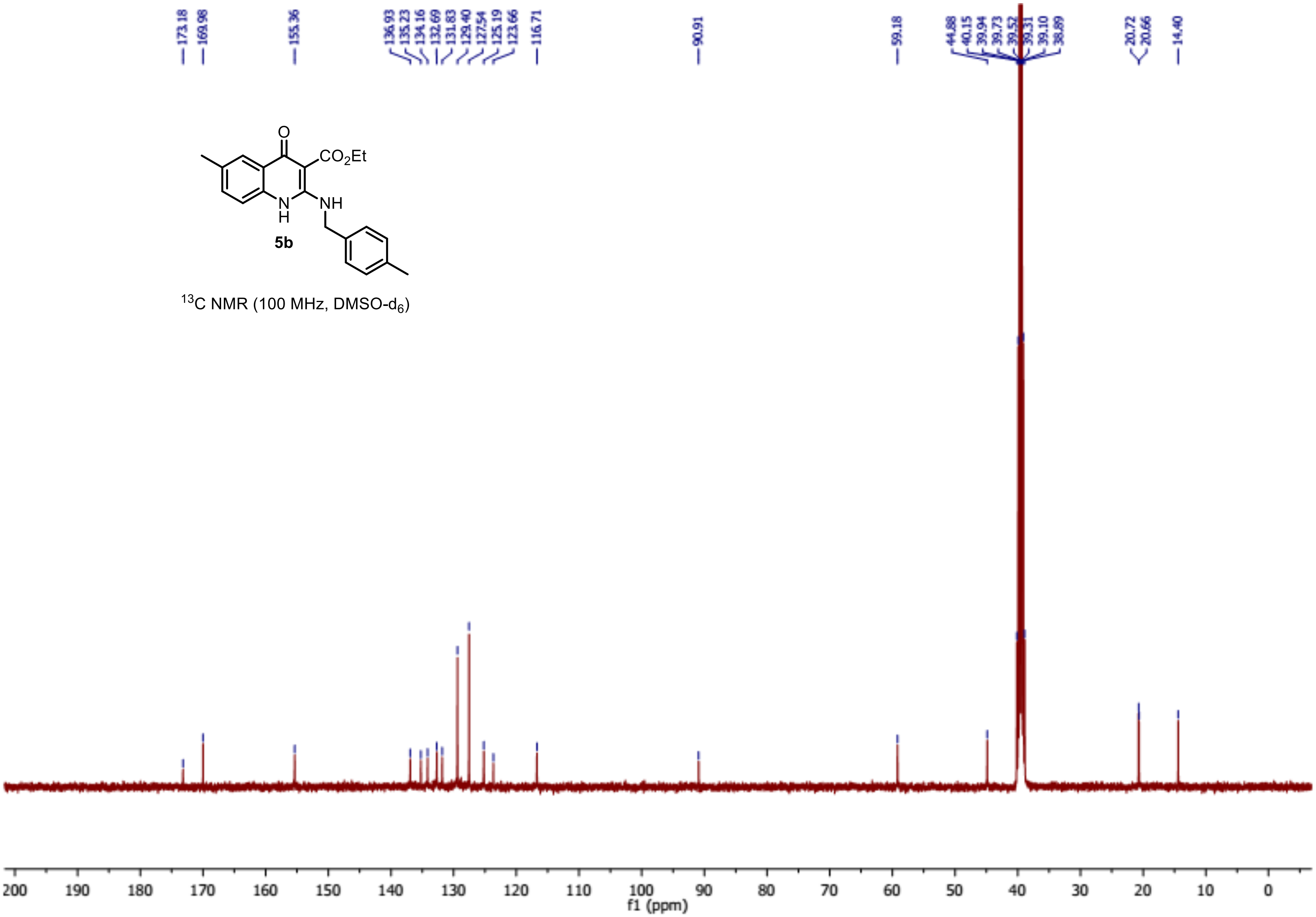
5a

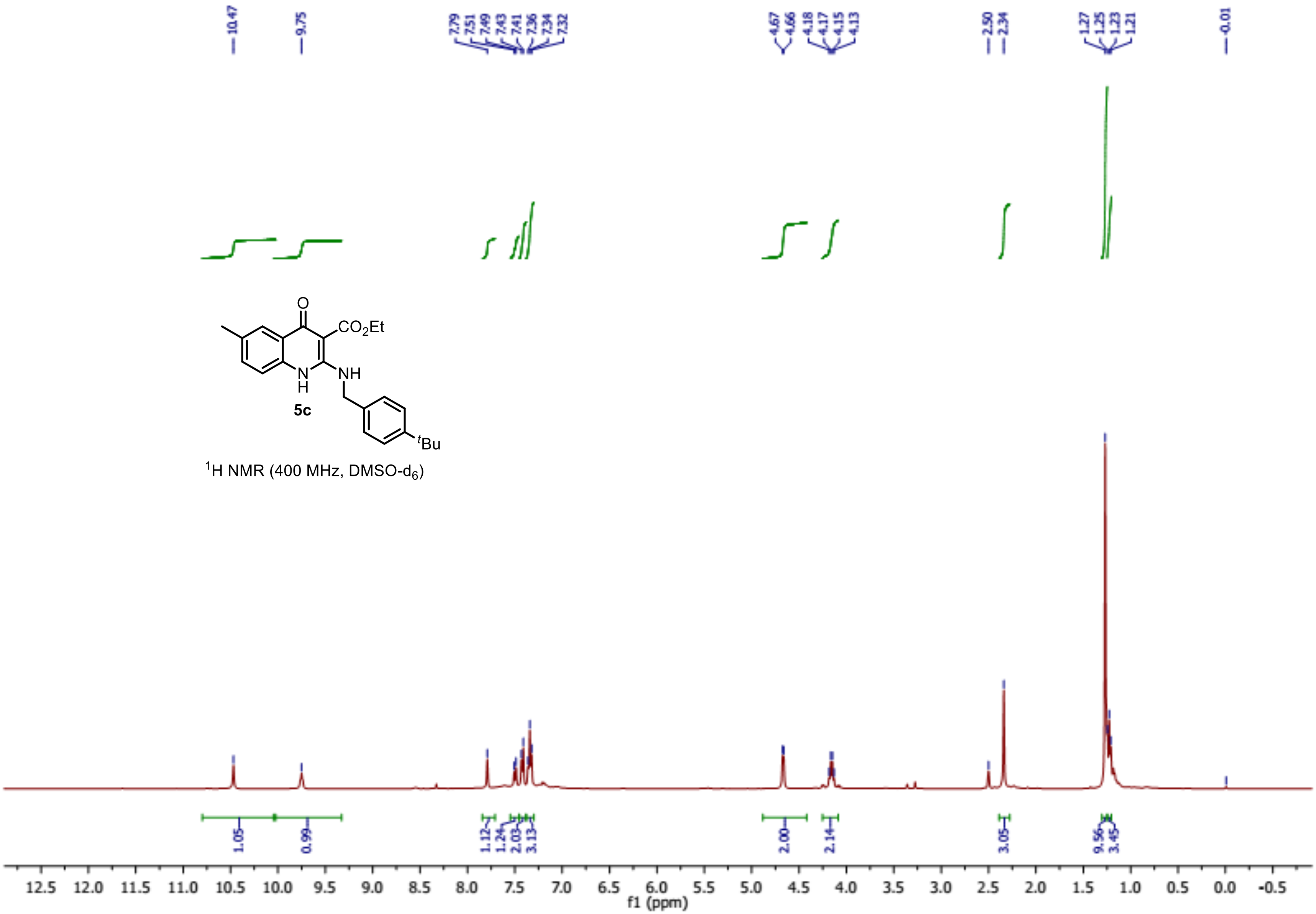
^{13}C NMR (100 MHz, DMSO-d_6)

5b

^{1}H NMR (400 MHz, DMSO-d_6)

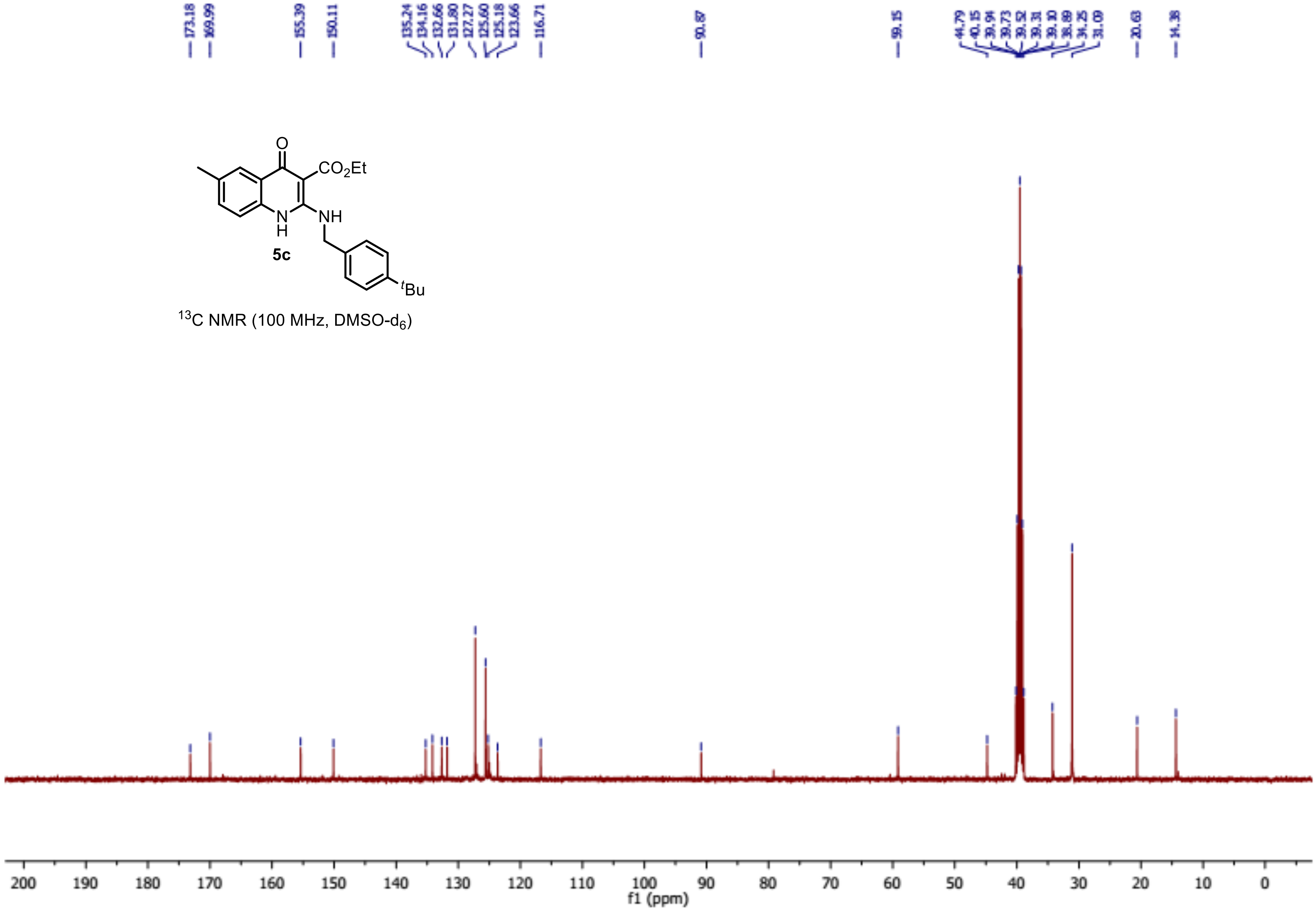



173.18
169.98
155.36
136.93
135.23
134.16
132.69
131.83
129.40
127.54
125.19
123.66
116.71
90.91
59.18
44.88
40.15
39.94
39.73
39.52
39.31
39.10
38.89
20.72
20.66
14.40
O
CO_2Et
N
H
NH
5b
^{13}C NMR (100 MHz, DMSO-d_6)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



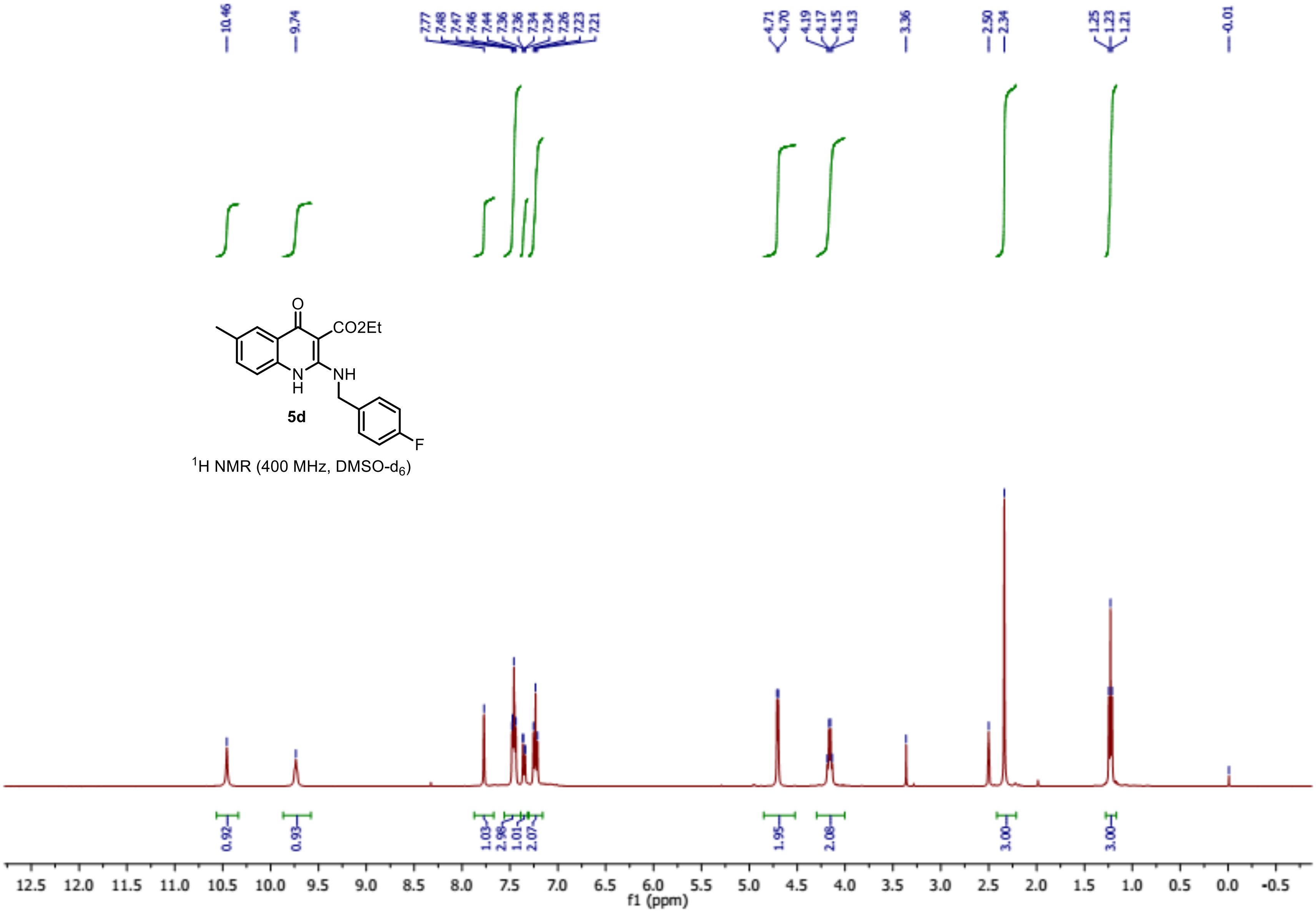
5c

^{1}H NMR (400 MHz, DMSO-d$_6$)



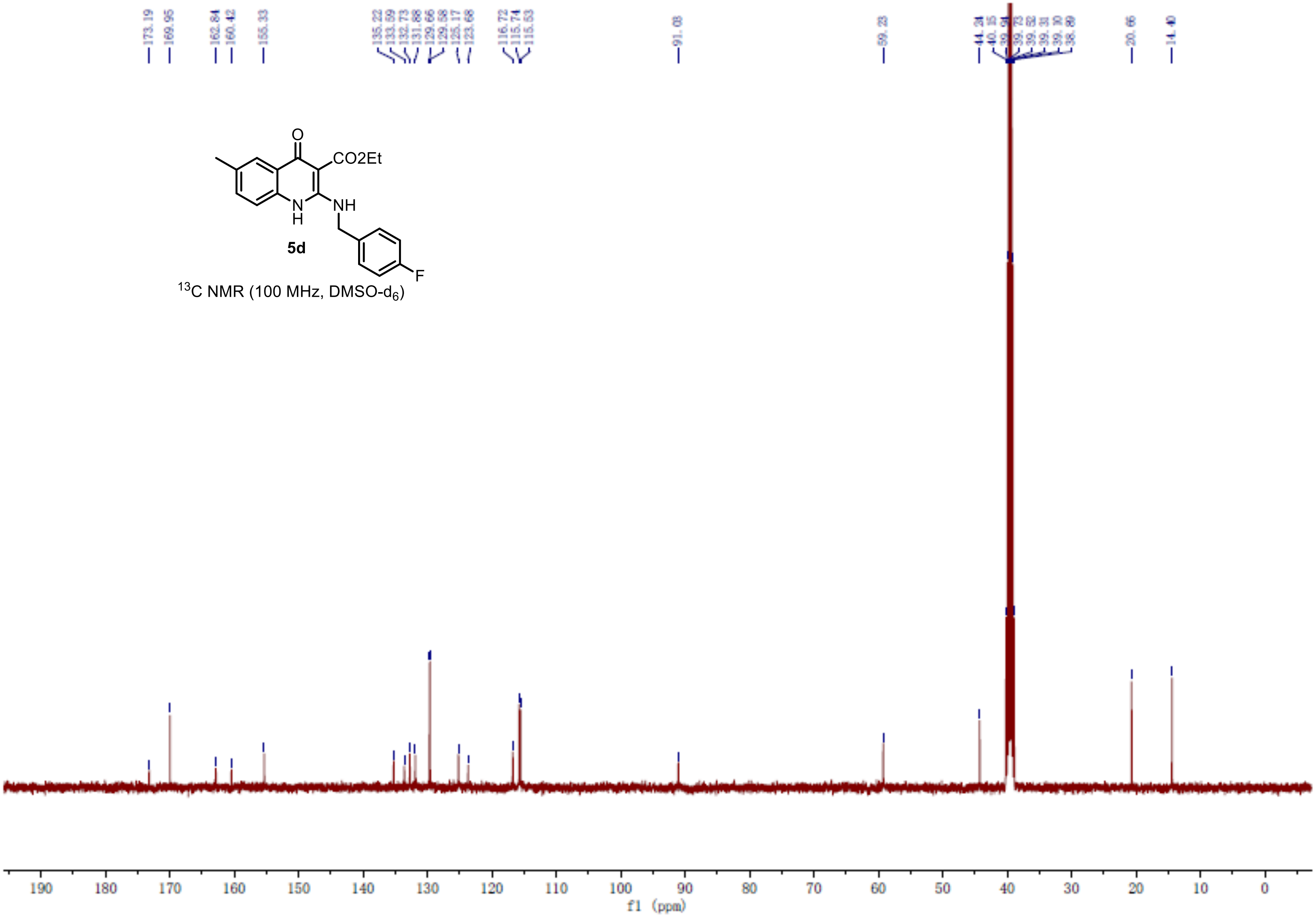
5c

^{13}C NMR (100 MHz, DMSO-d_6)



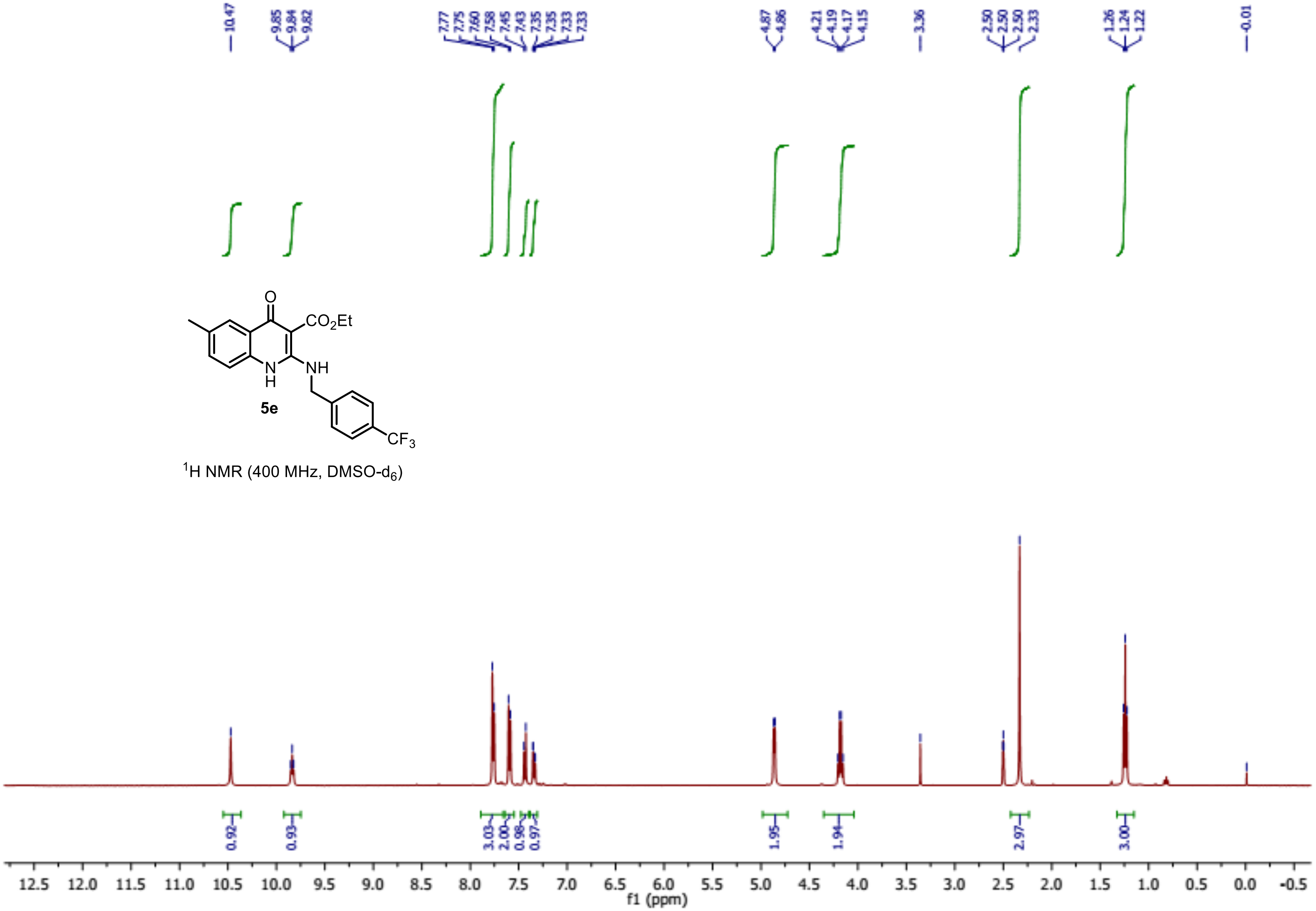
5d

^{1}H NMR (400 MHz, DMSO-d$_6$)



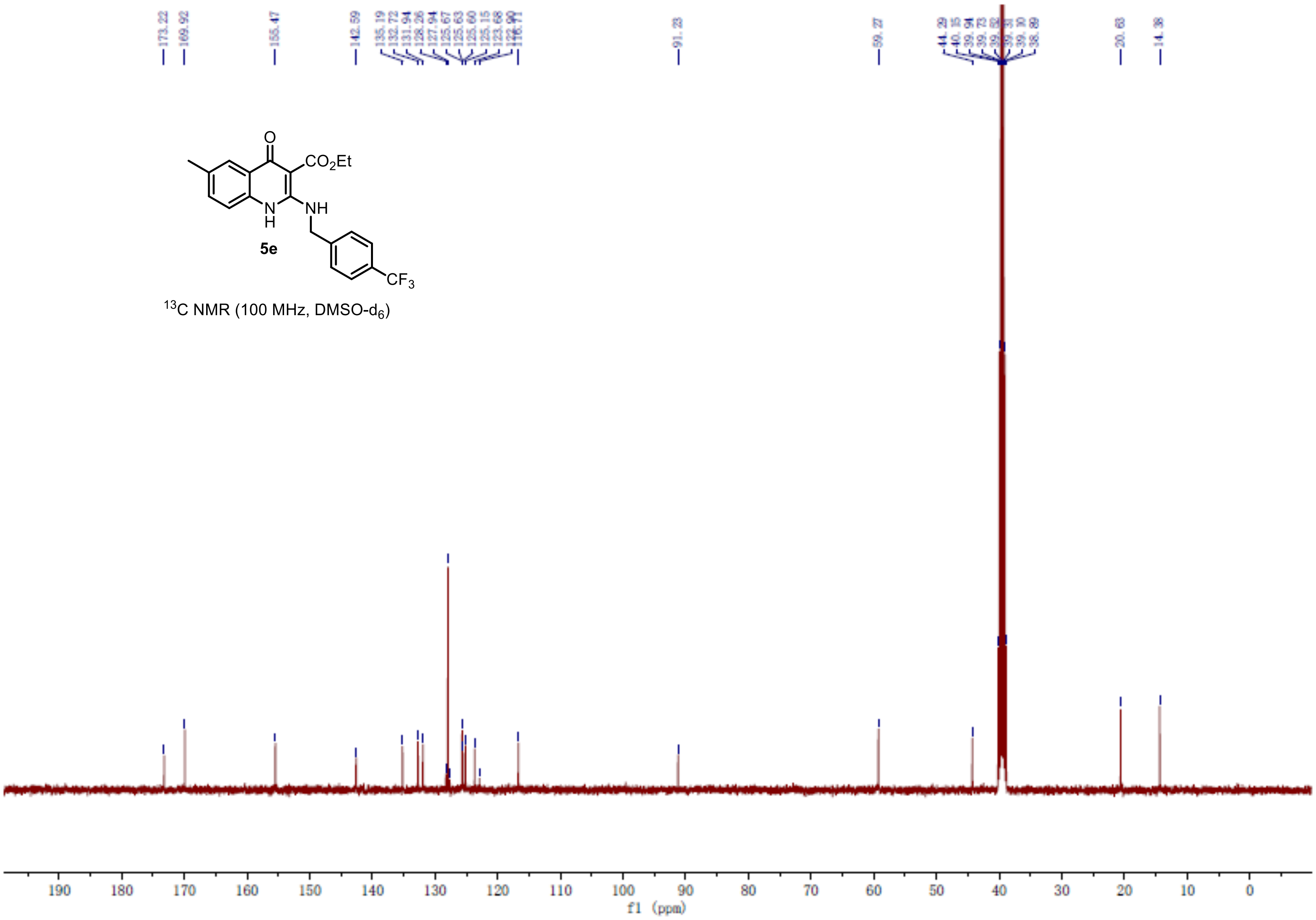
5d

^{13}C NMR (100 MHz, DMSO-d_6)



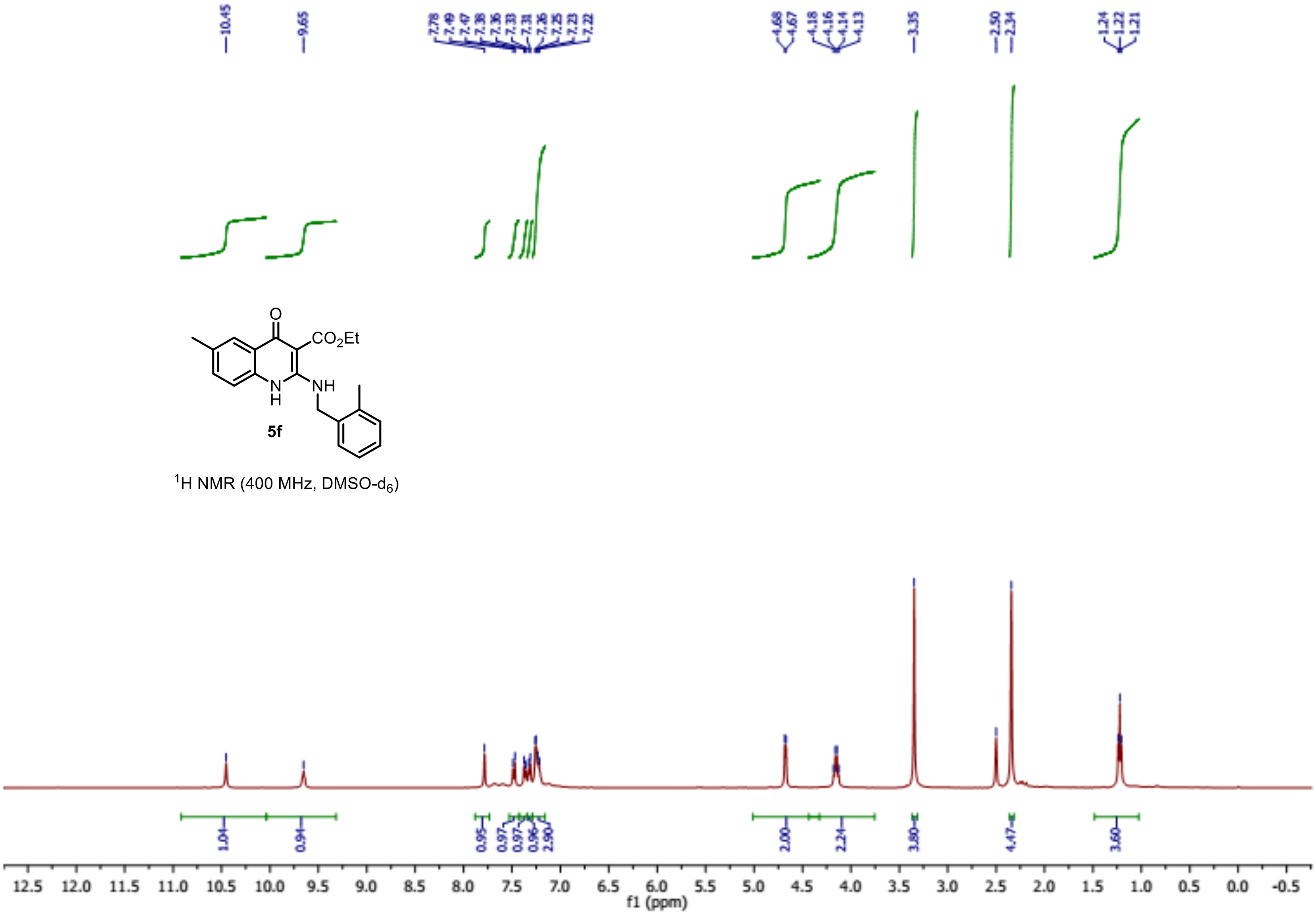
5e

^{1}H NMR (400 MHz, DMSO-d_6)



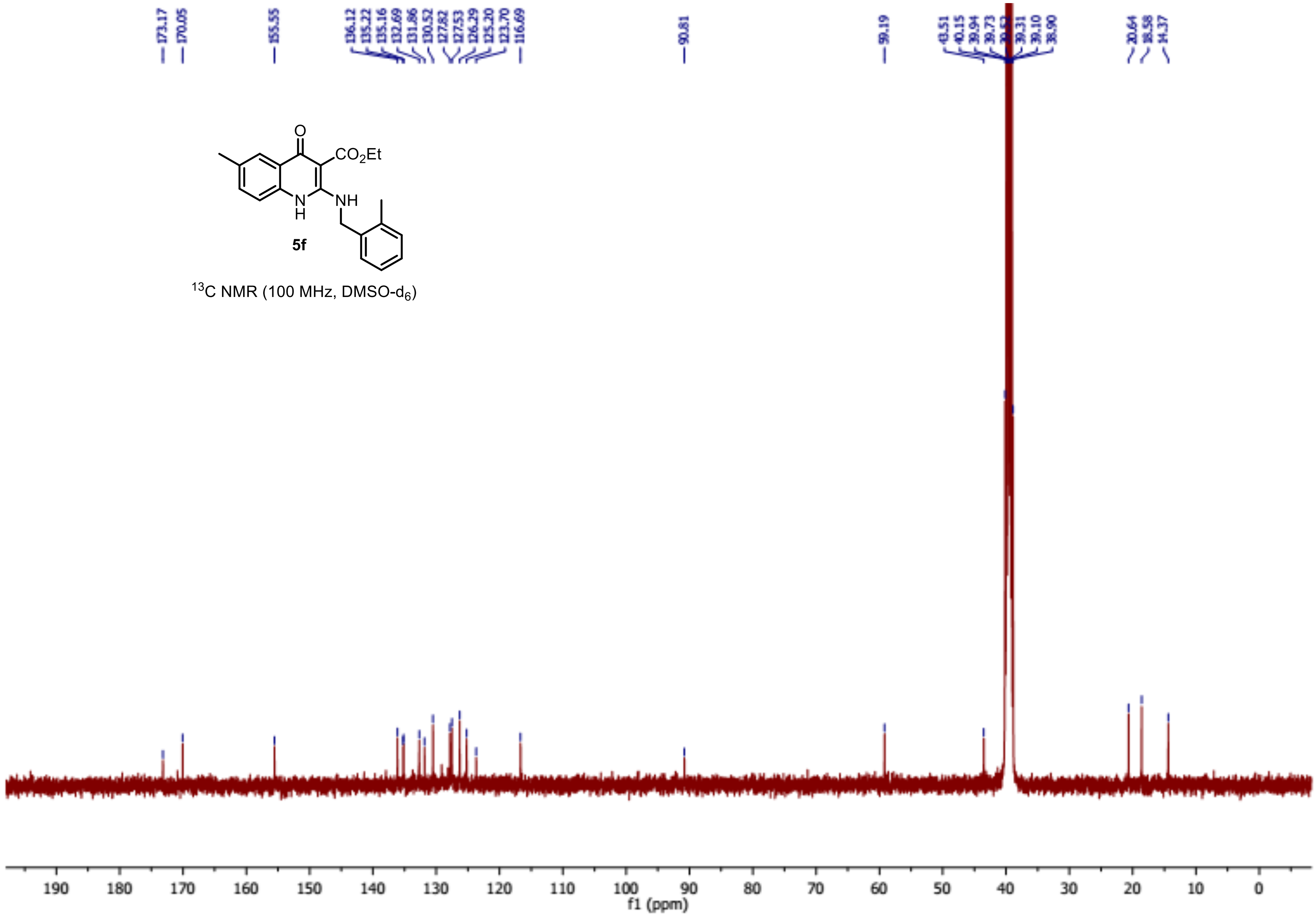
5e

^{13}C NMR (100 MHz, DMSO-d_6)



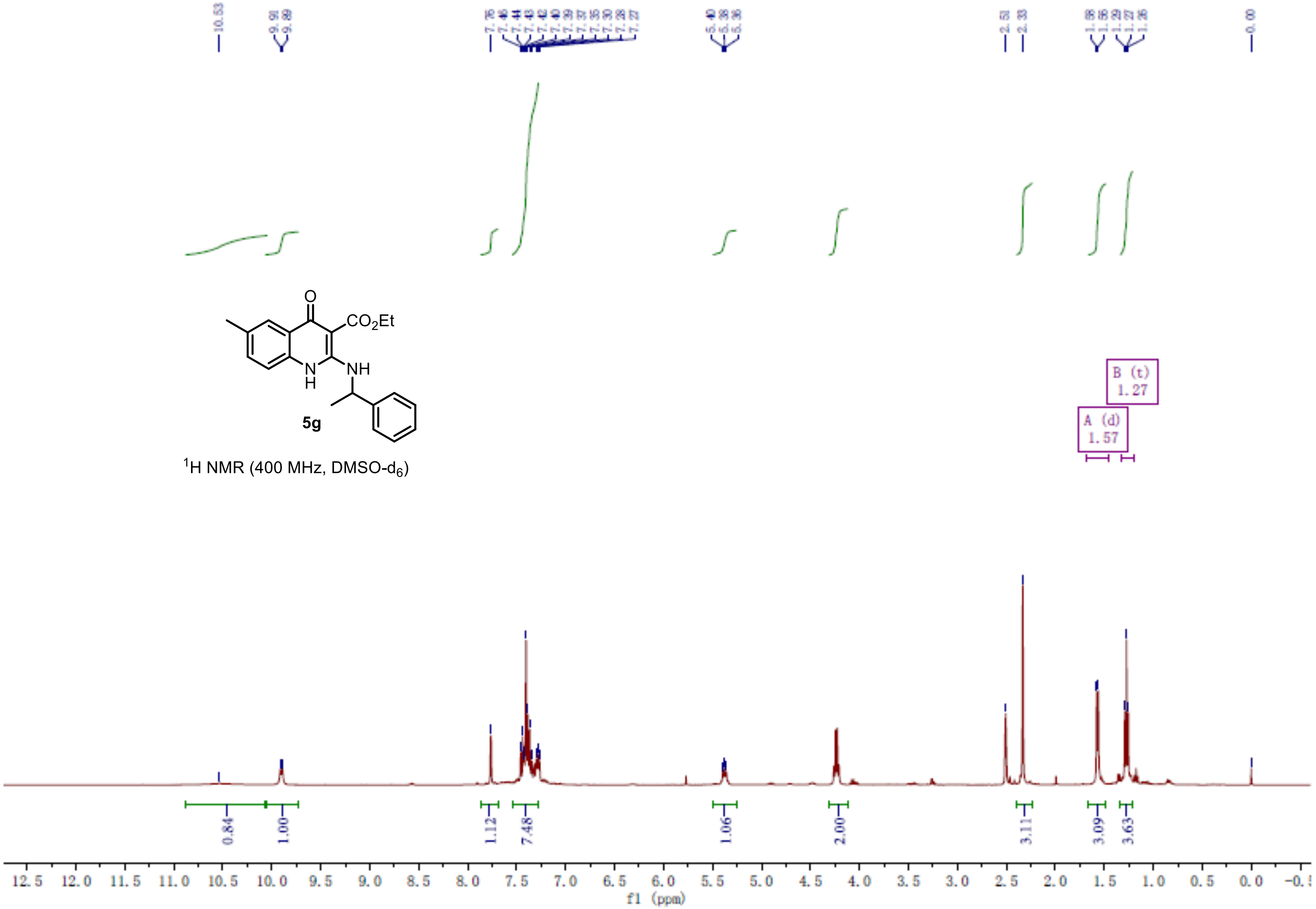
5f

^{1}H NMR (400 MHz, DMSO-d_6)



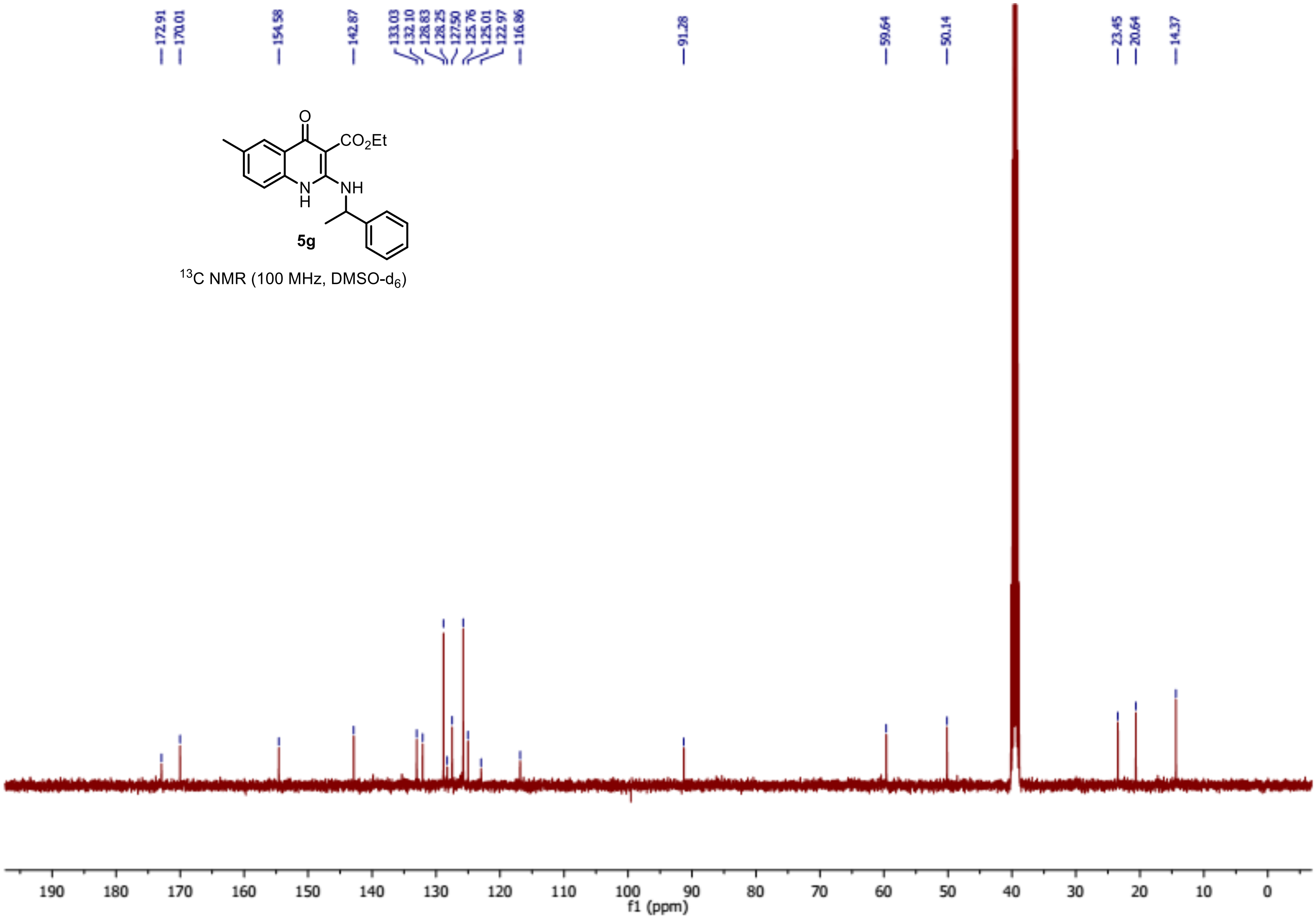
5f

^{13}C NMR (100 MHz, DMSO-d$_6$)



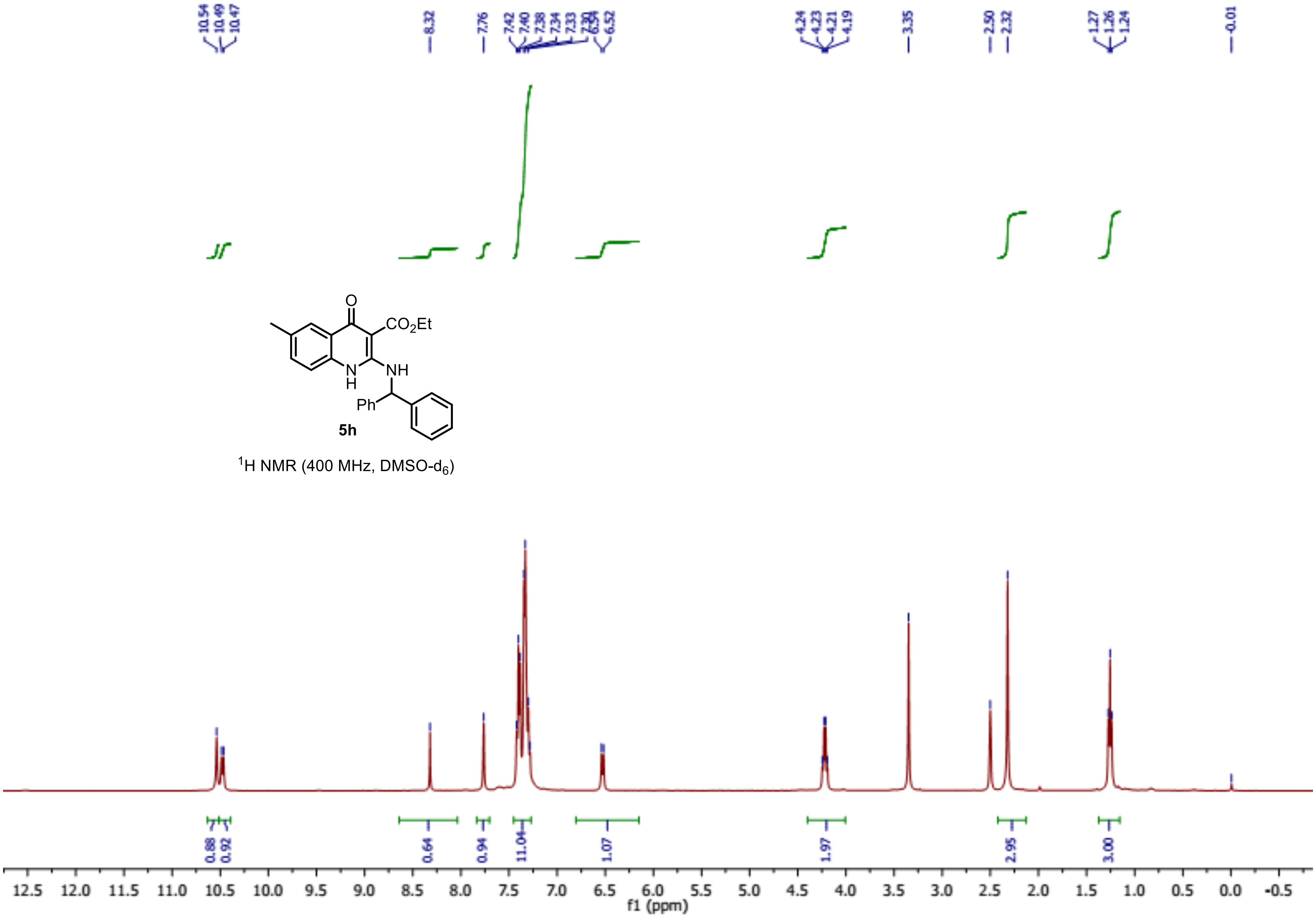
5g

^{1}H NMR (400 MHz, DMSO-d$_6$)



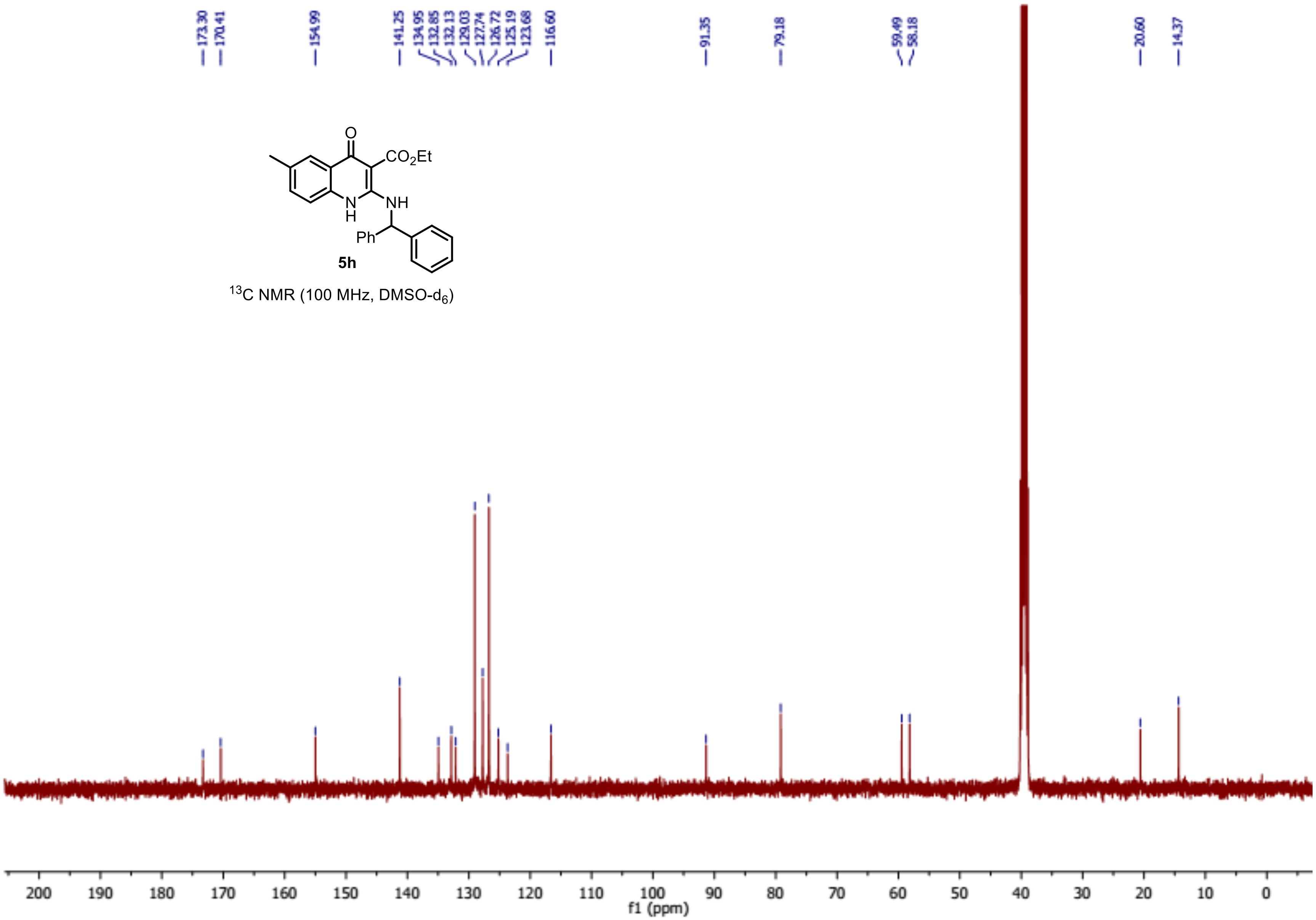
5g

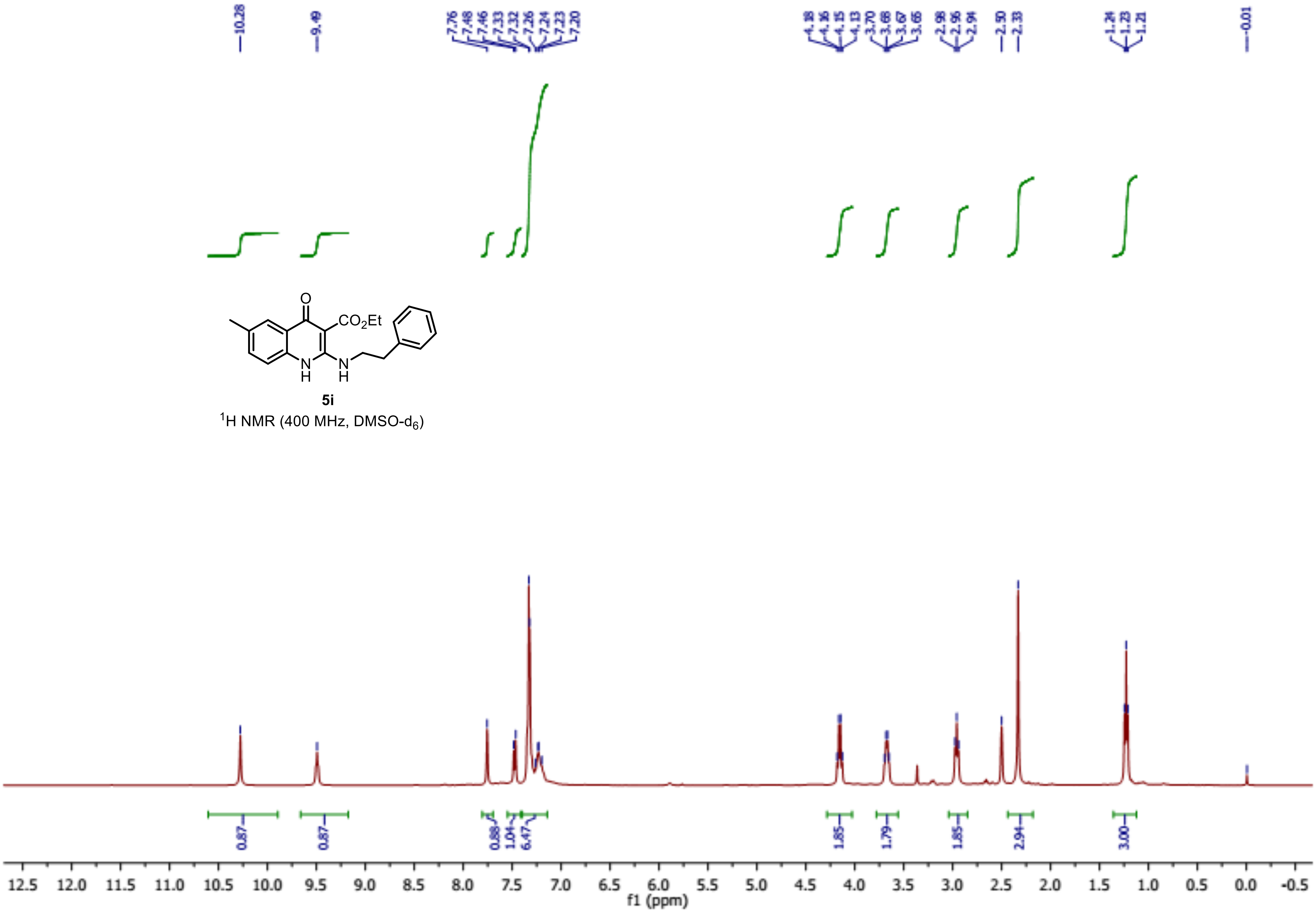
^{13}C NMR (100 MHz, DMSO-d_6)



5h

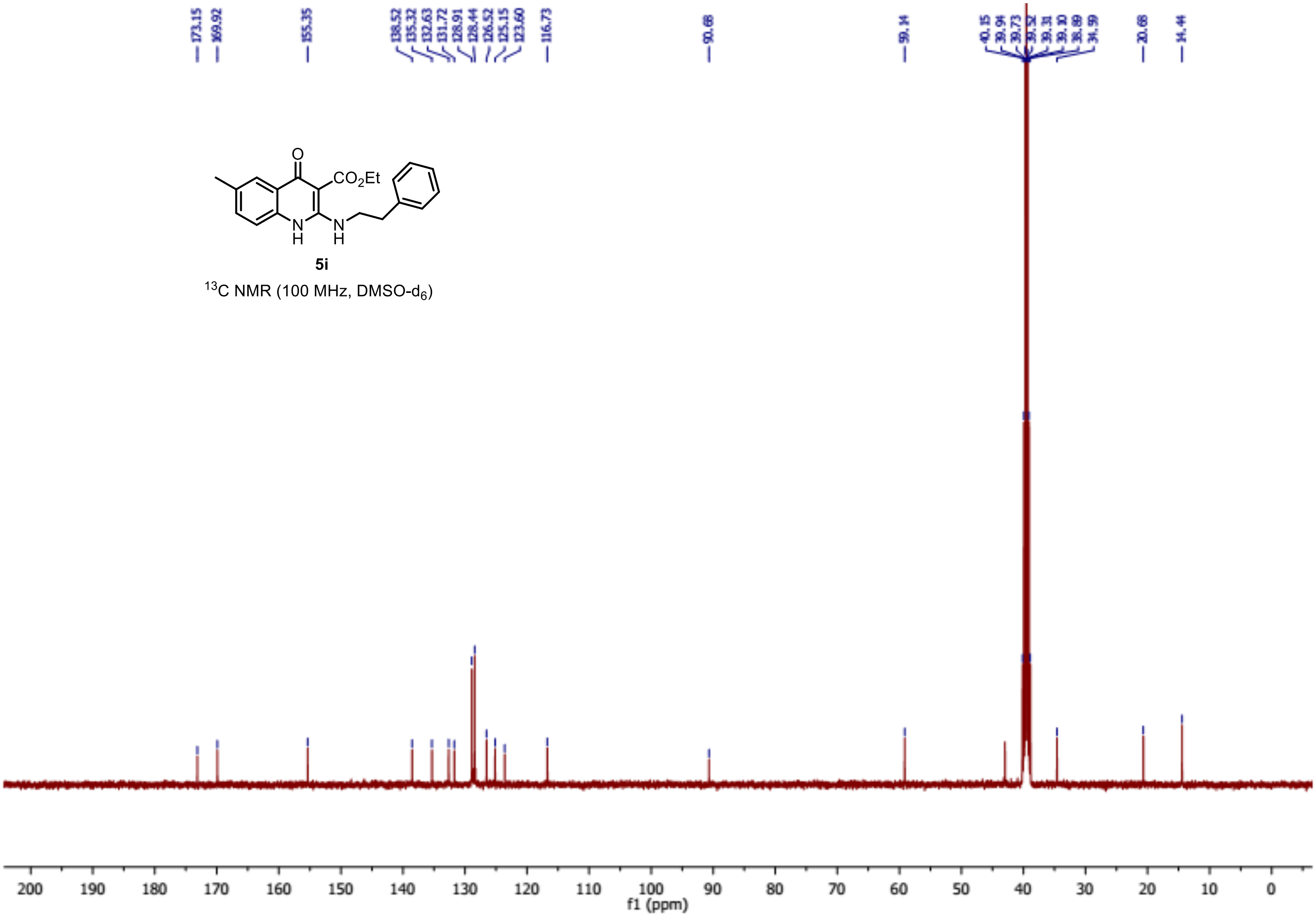
^{1}H NMR (400 MHz, DMSO-d_6)


173.30
170.41
154.99
141.25
134.95
132.85
132.13
129.03
127.74
126.72
125.19
123.68
116.60
91.35
79.18
59.49
58.18
20.60
14.37
O
CO_2Et
N
H
NH
Ph
5h
^{13}C NMR (100 MHz, DMSO-d_6)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



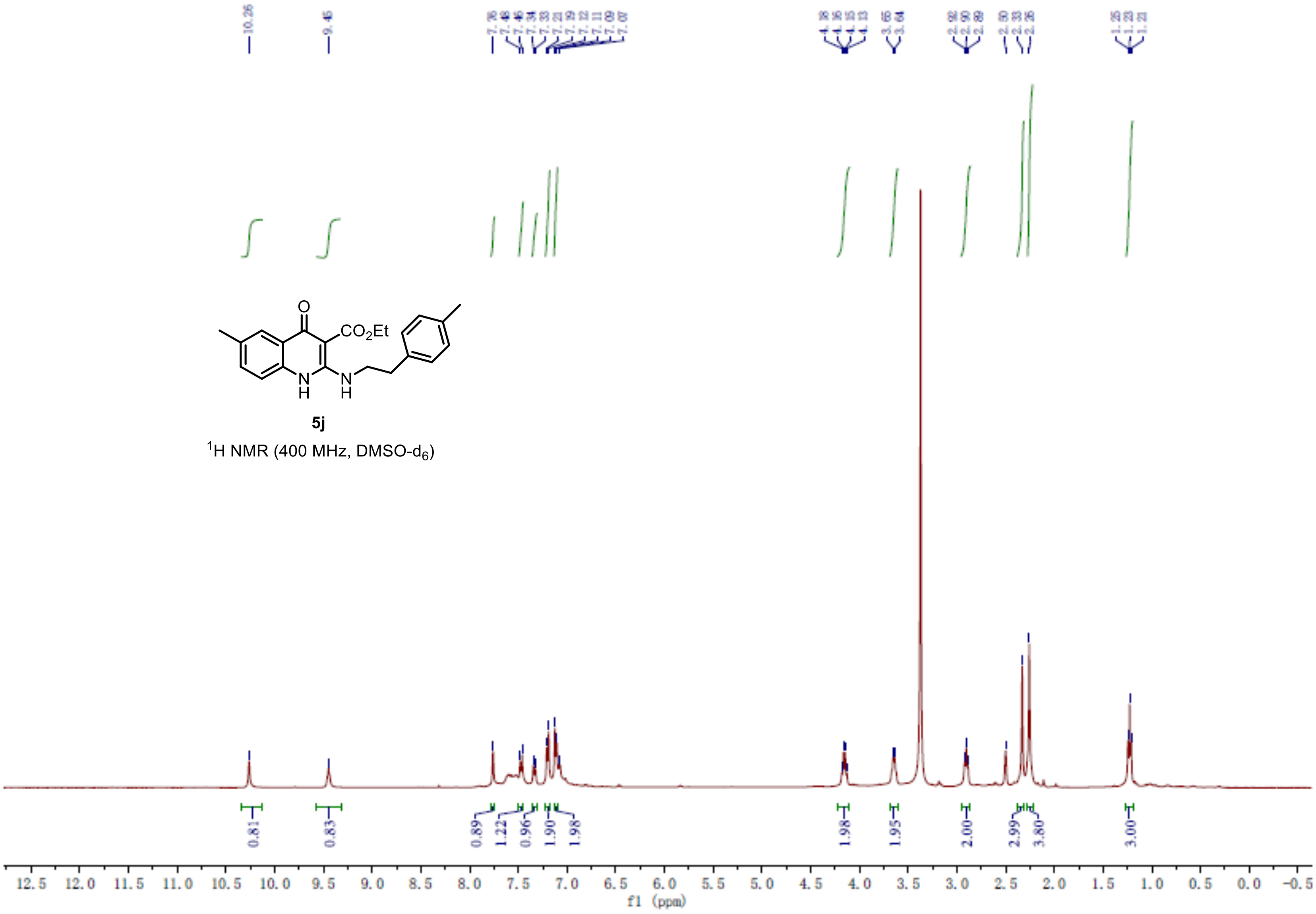
5i

^{1}H NMR (400 MHz, DMSO-d_6)



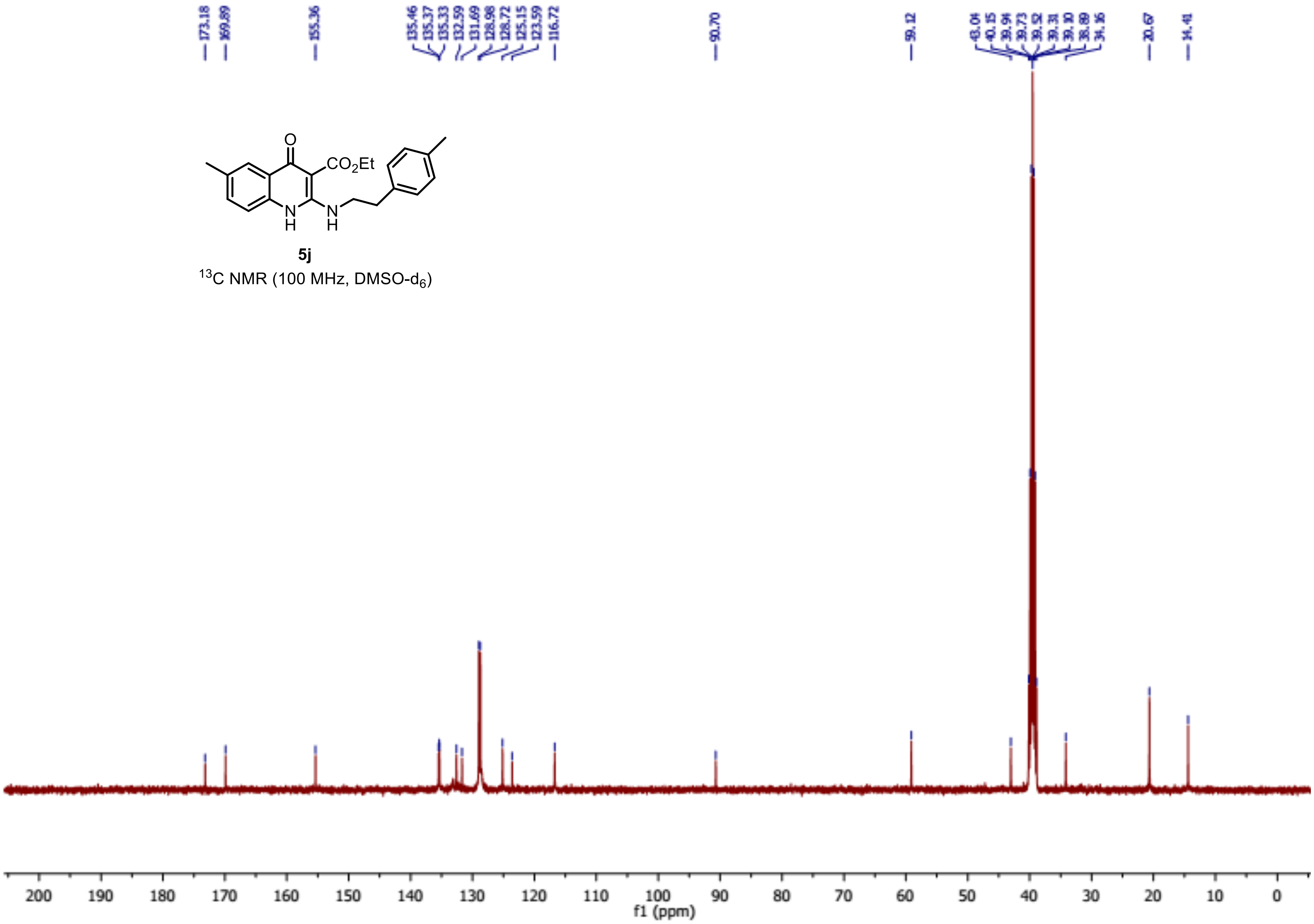
5i

^{13}C NMR (100 MHz, DMSO-d_6)



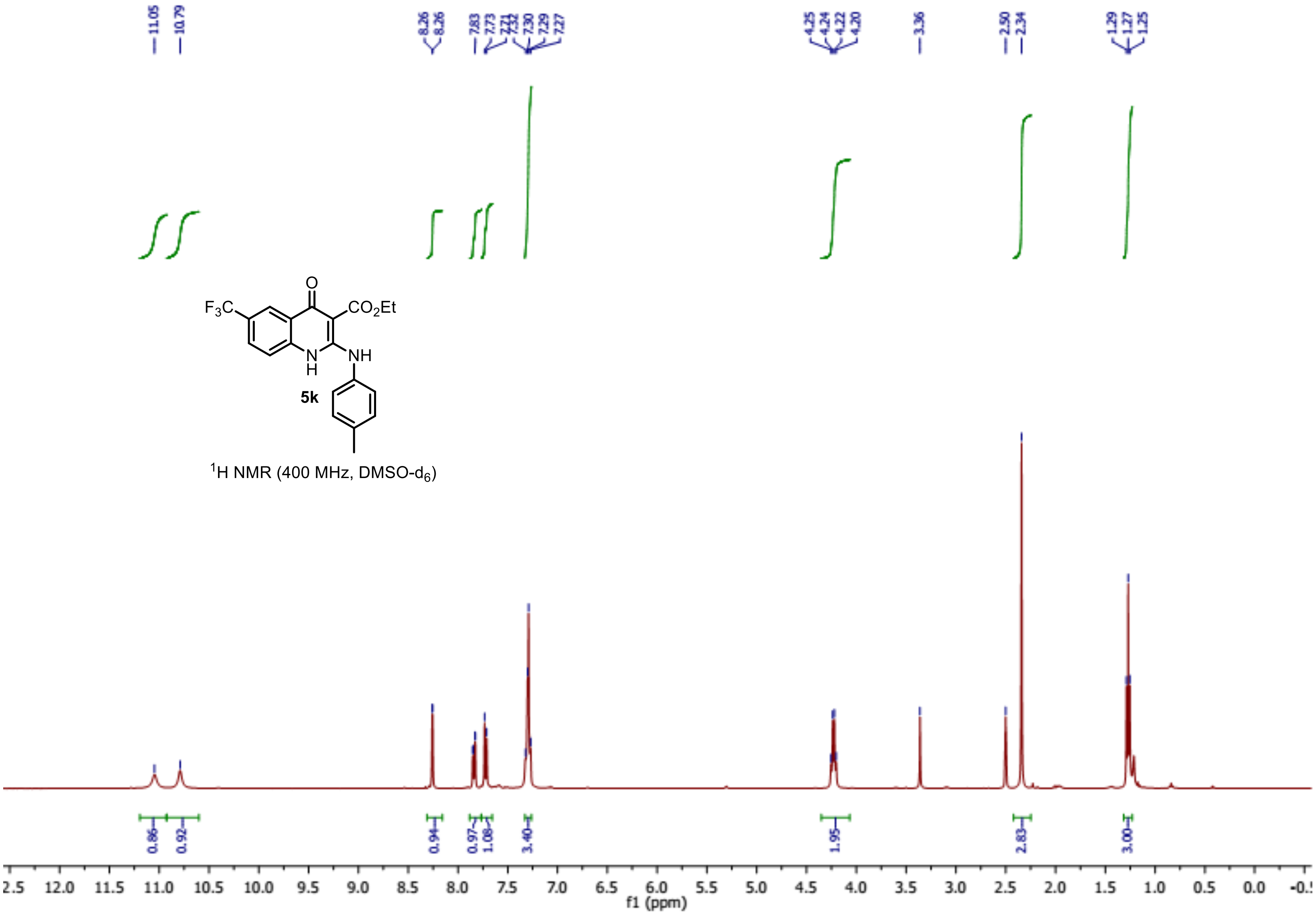
5j

^{1}H NMR (400 MHz, DMSO-d$_6$)



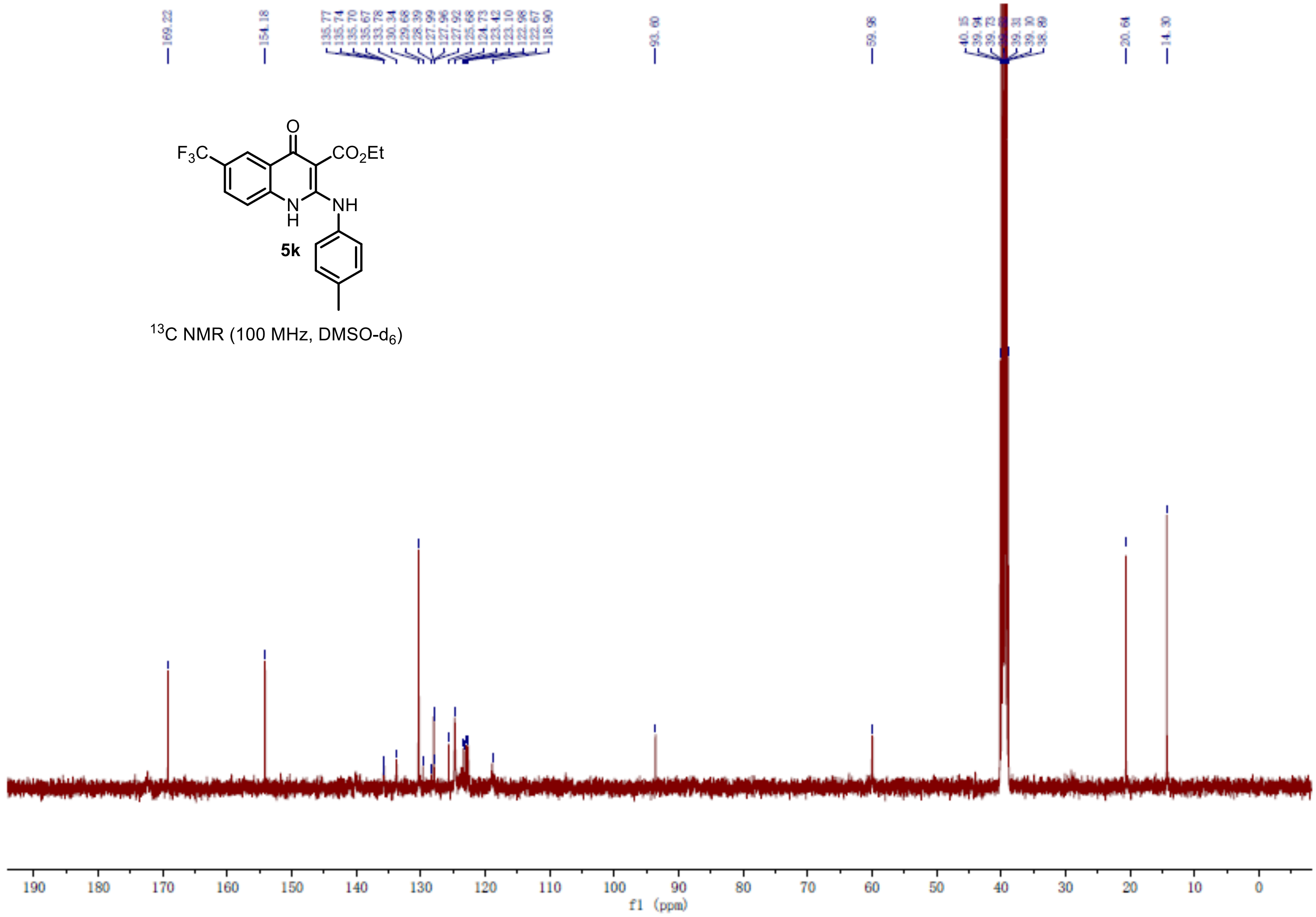
5j

^{13}C NMR (100 MHz, DMSO-d_6)



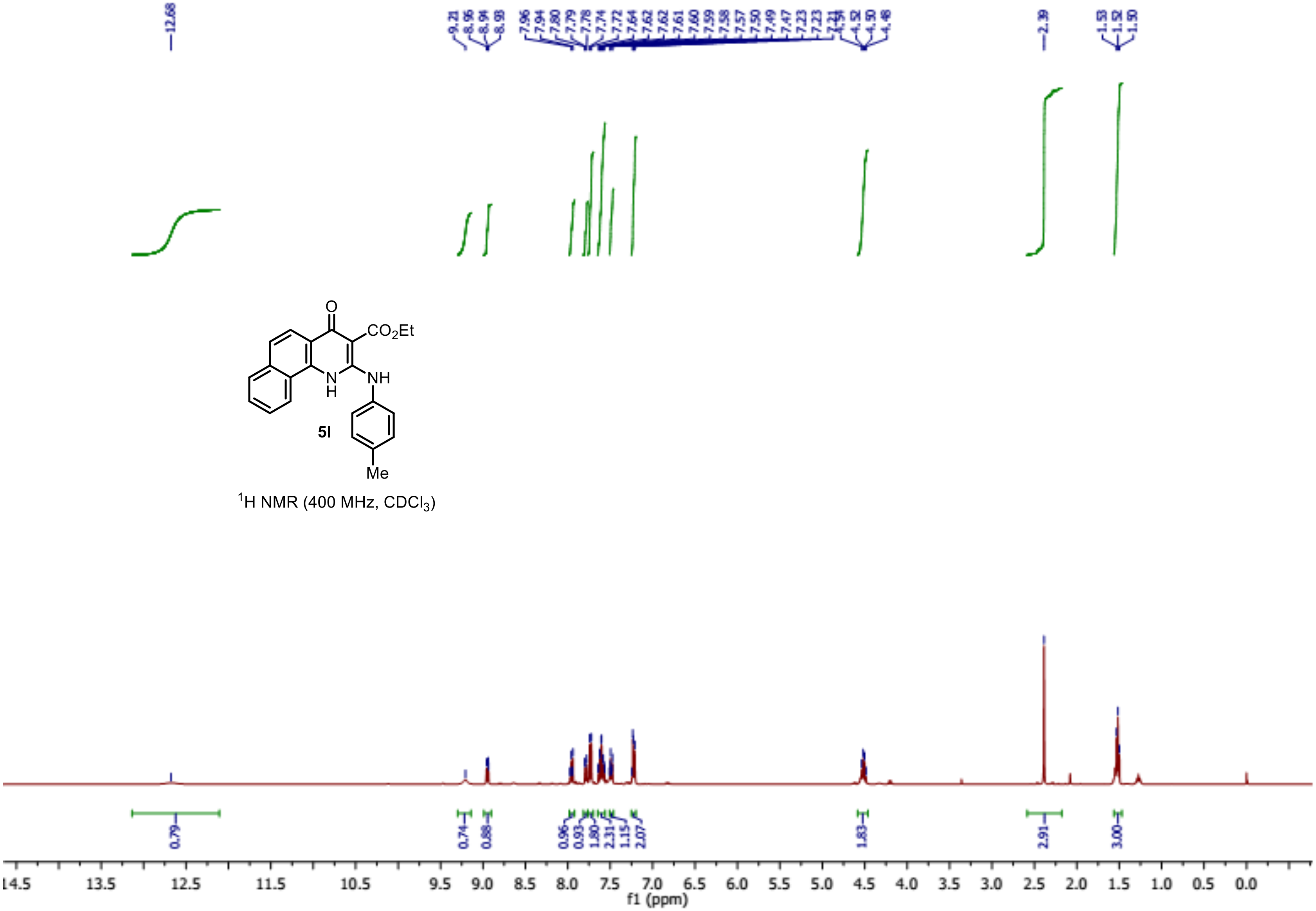
5k

^{1}H NMR (400 MHz, DMSO-d$_6$)



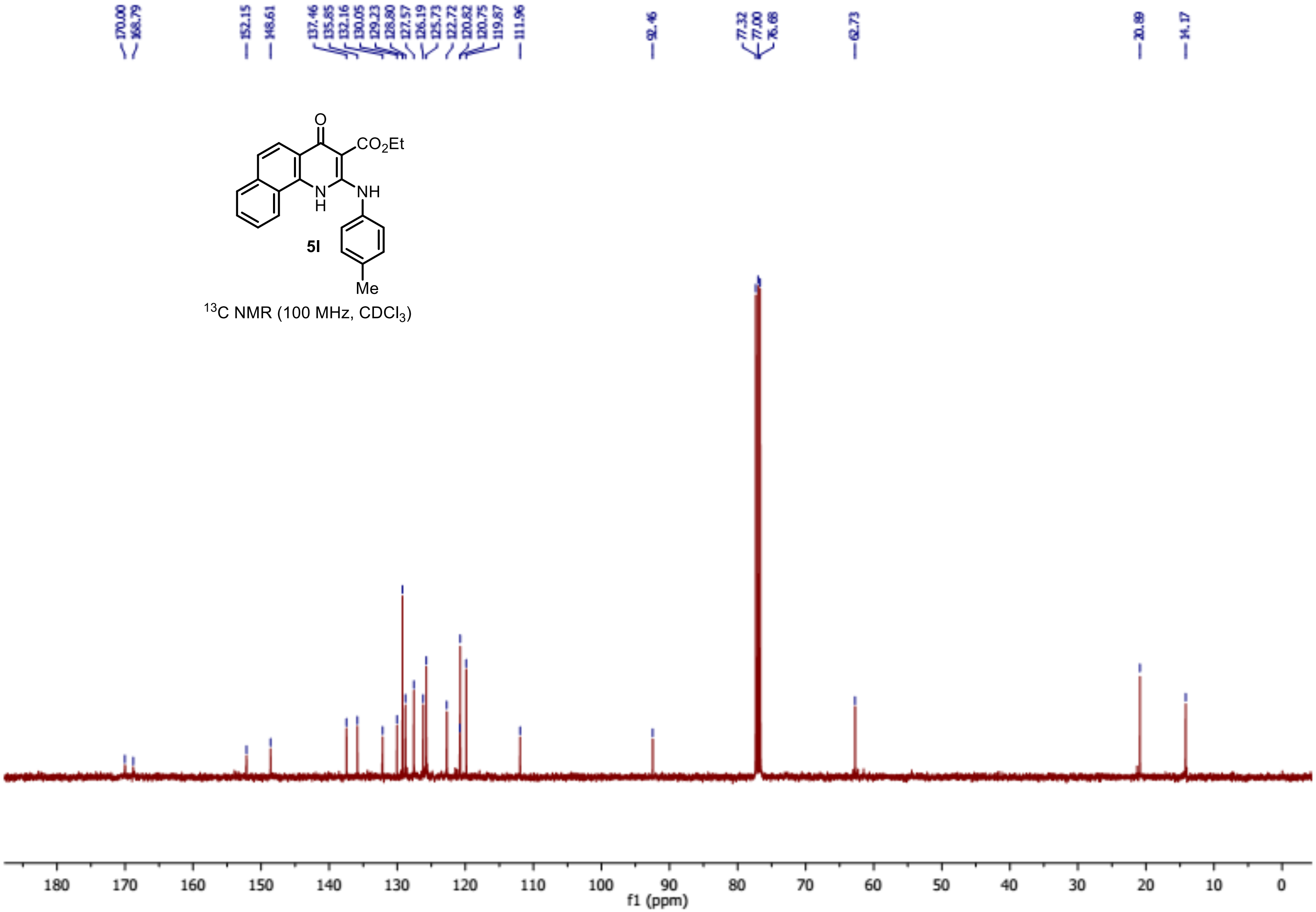
5k

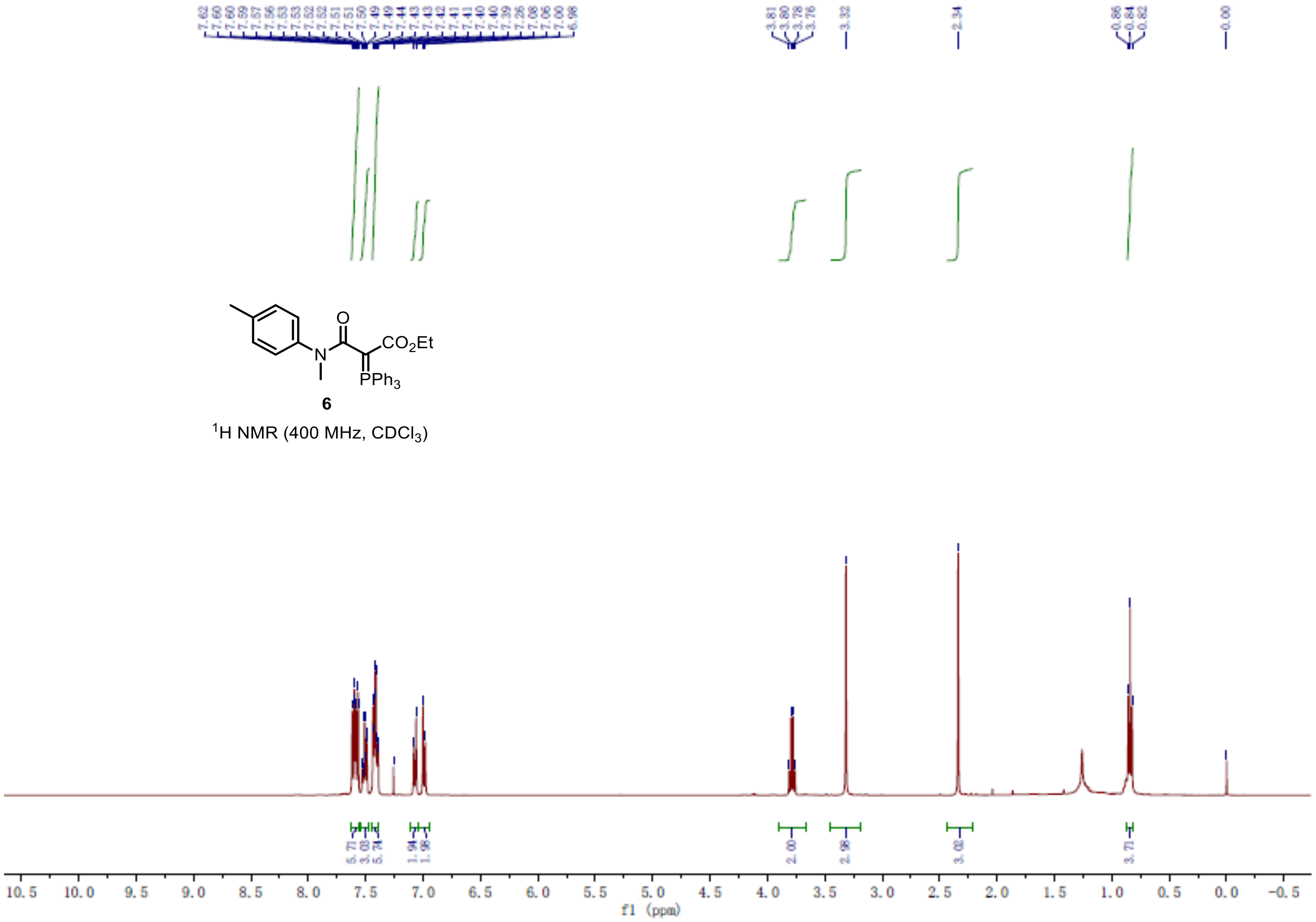
^{13}C NMR (100 MHz, DMSO-d_6)



5l

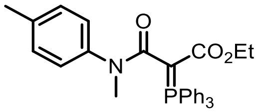
^{1}H NMR (400 MHz, $CDCl_3$)


170.00
168.79
152.15
148.61
137.46
135.85
132.16
130.05
129.23
128.80
127.57
126.19
125.73
122.72
120.82
120.75
119.87
111.96
92.46
77.32
77.00
76.68
62.73
20.89
14.17
O
CO_2Et
N
H
NH
5l
Me
^{13}C NMR (100 MHz, $CDCl_3$)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



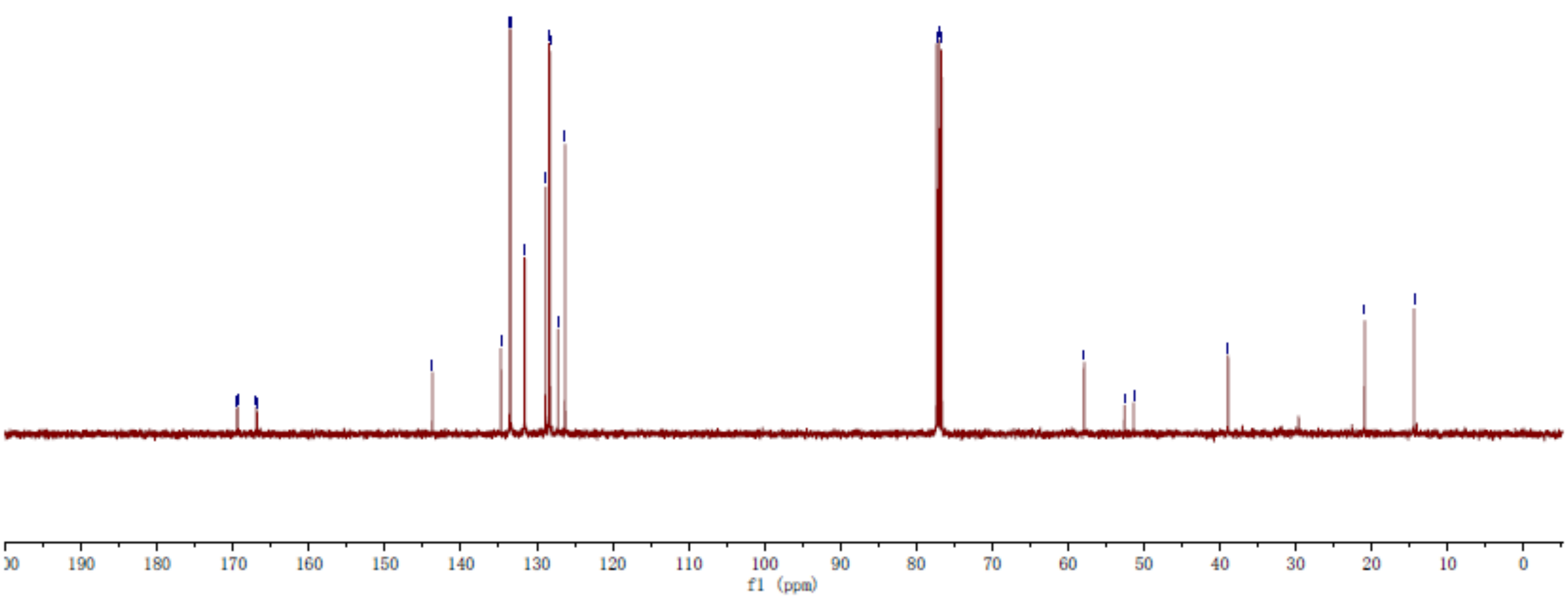
6

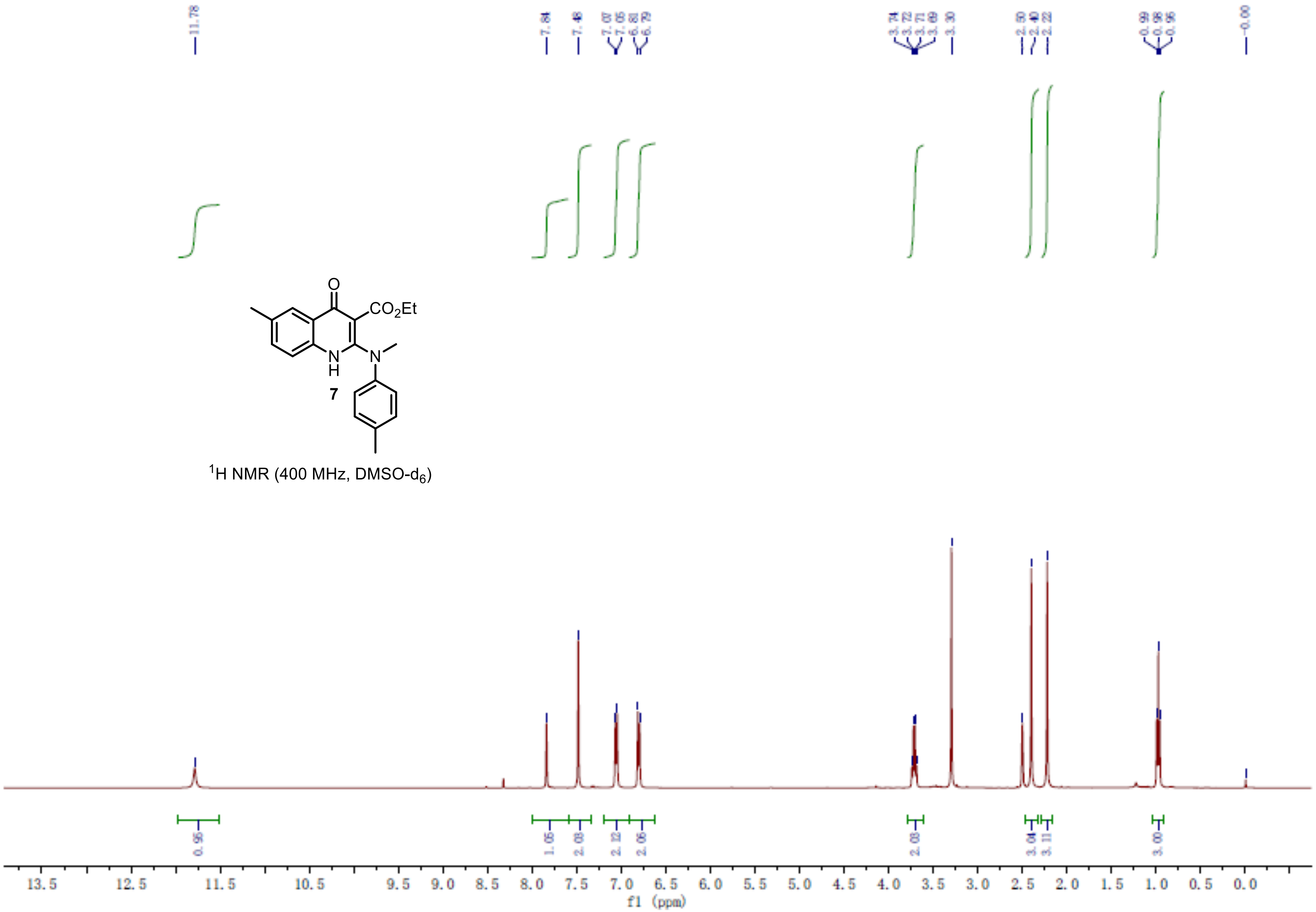
^{1}H NMR (400 MHz, CDCl$_3$)



6

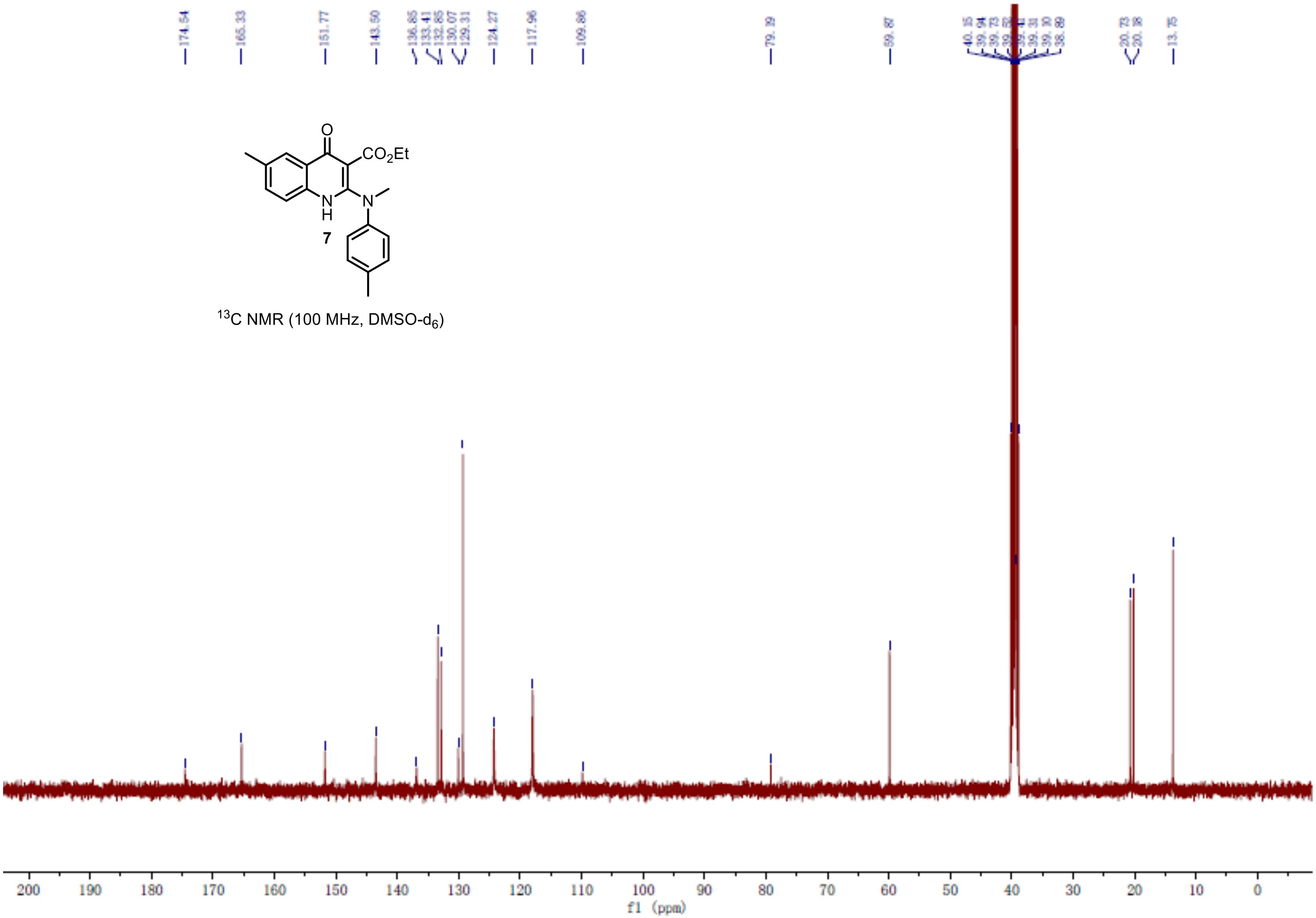
^{13}C NMR (100 MHz, $CDCl_3$)





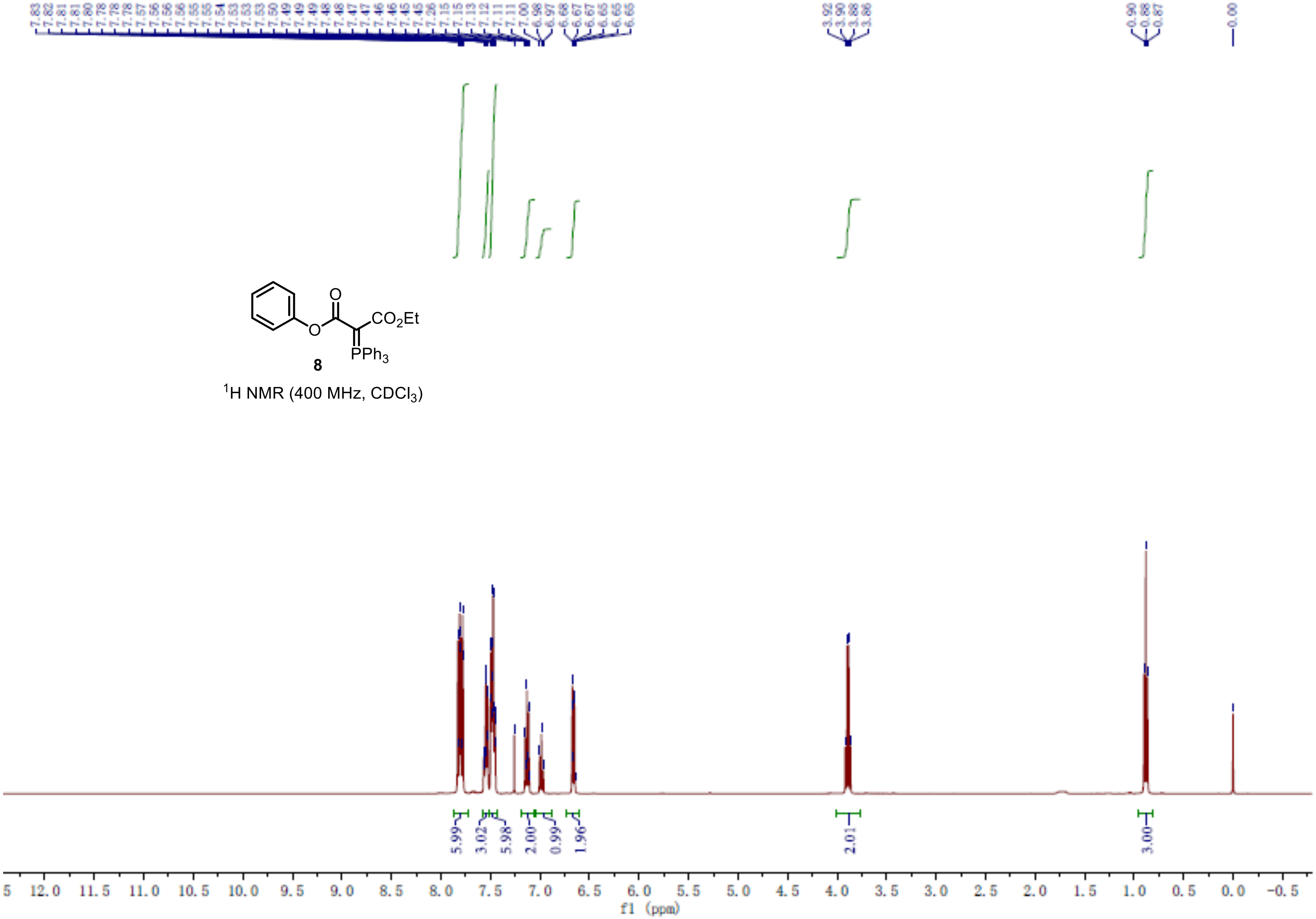
7

^{1}H NMR (400 MHz, DMSO-d_6)



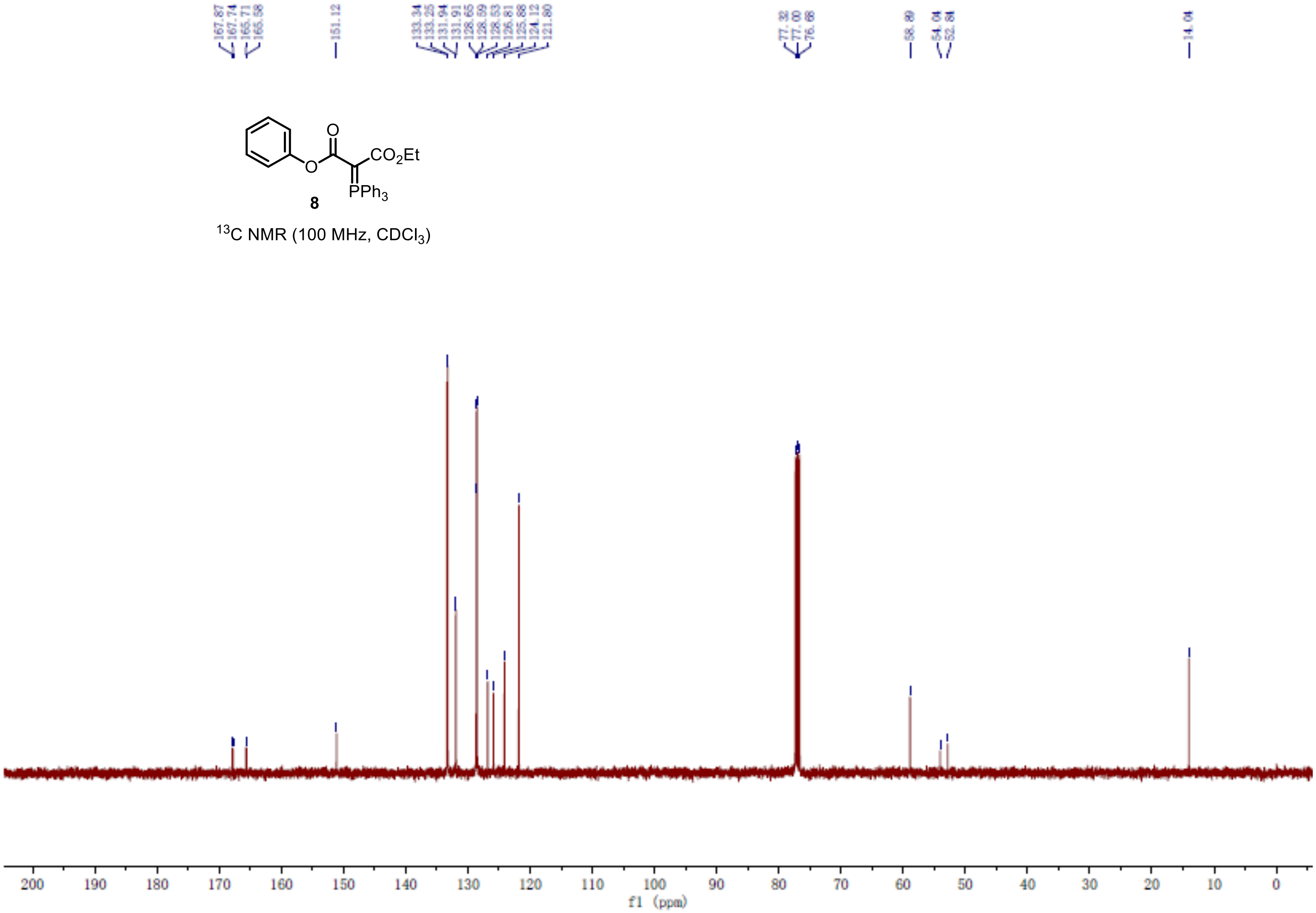
7

^{13}C NMR (100 MHz, DMSO-d_6)



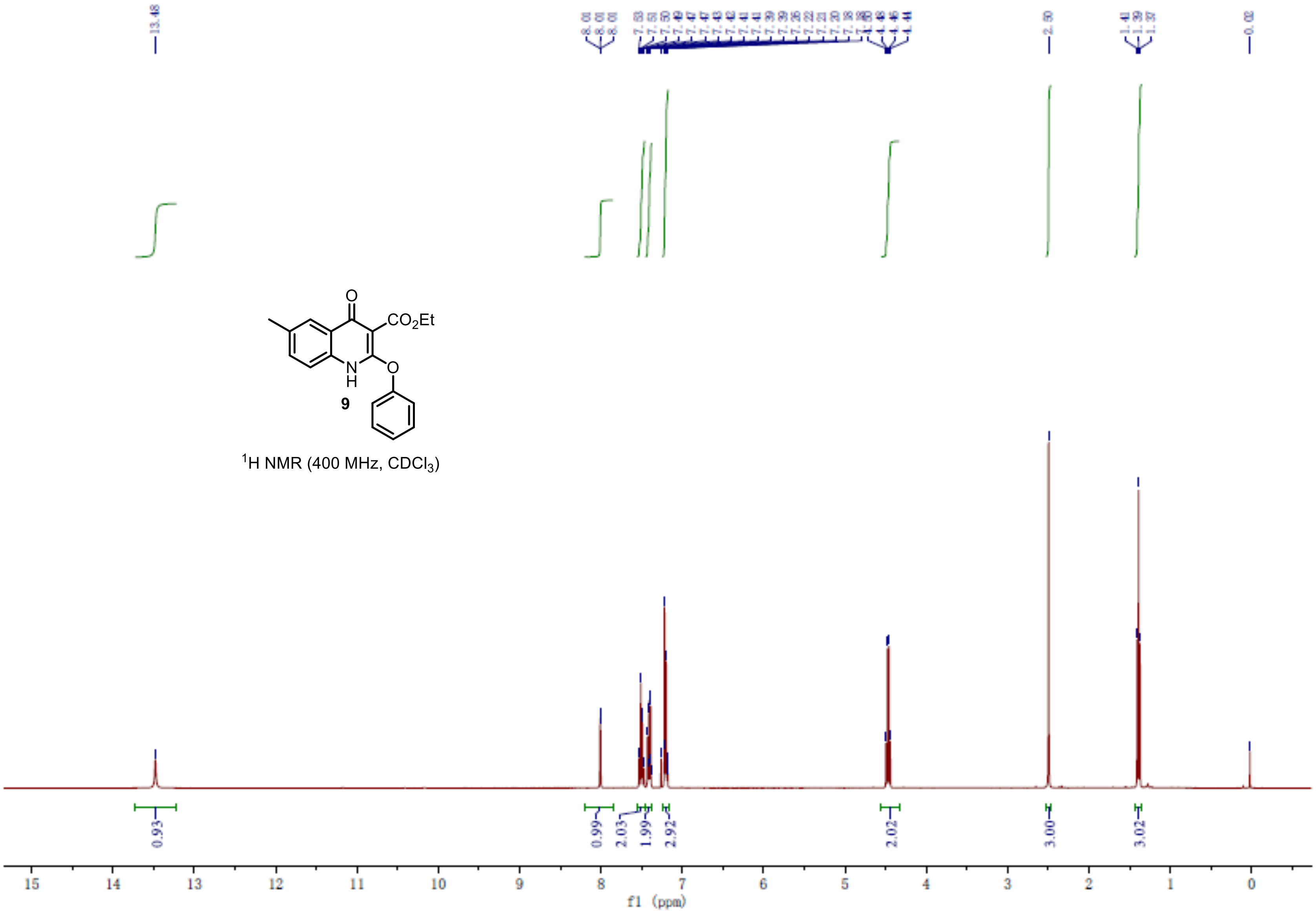
8

^{1}H NMR (400 MHz, CDCl$_3$)



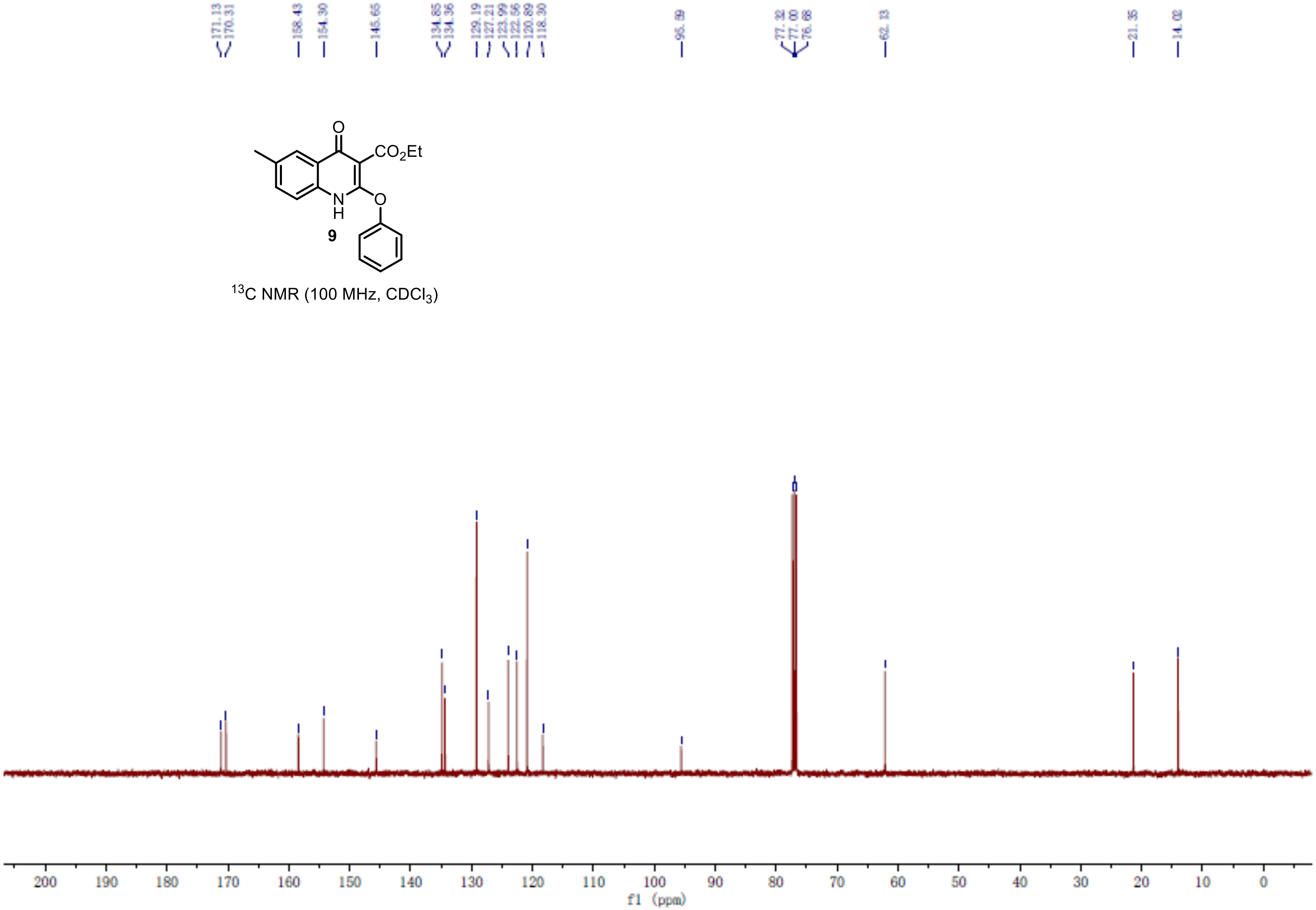
8

^{13}C NMR (100 MHz, $CDCl_3$)



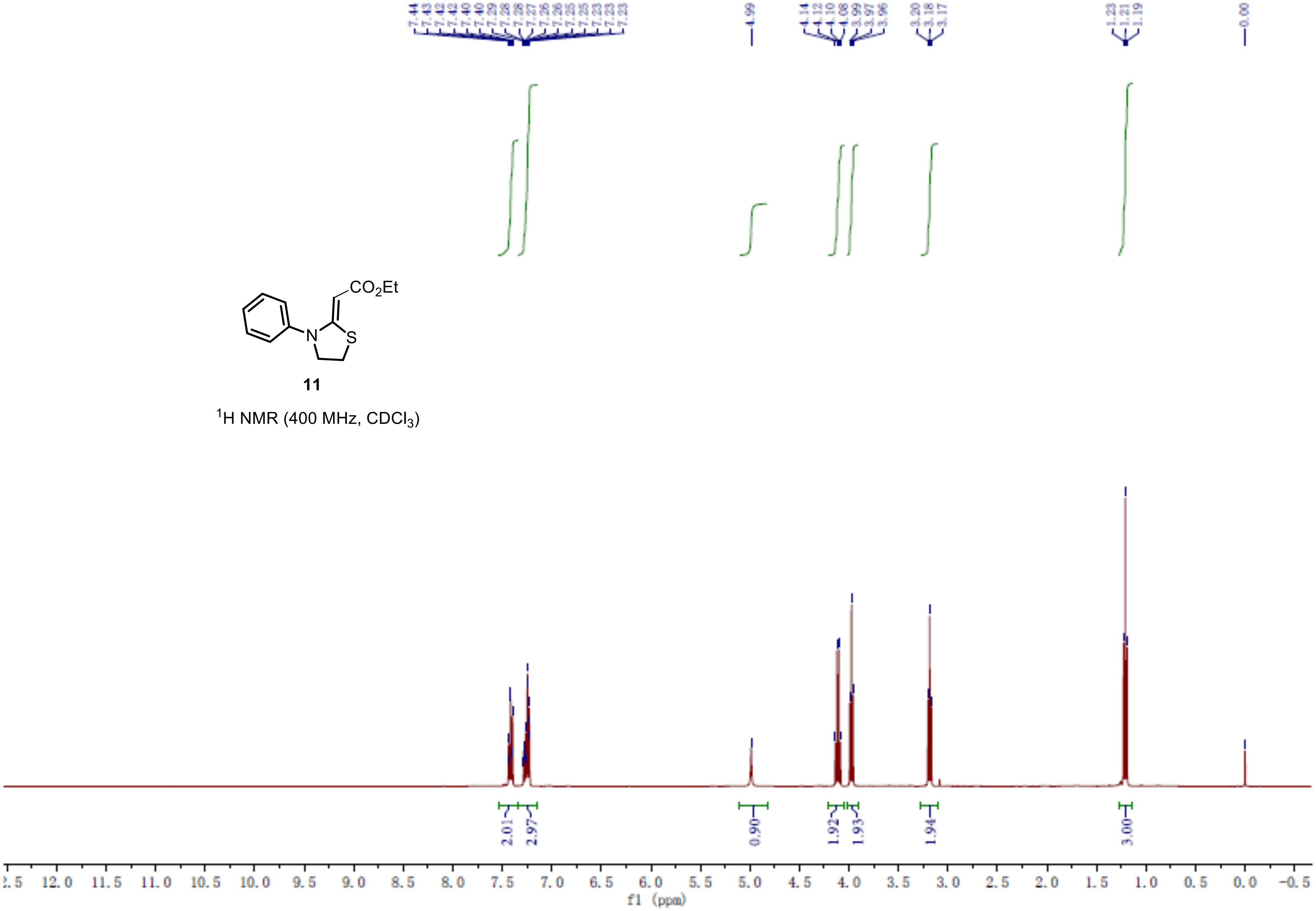
9

^{1}H NMR (400 MHz, $CDCl_3$)



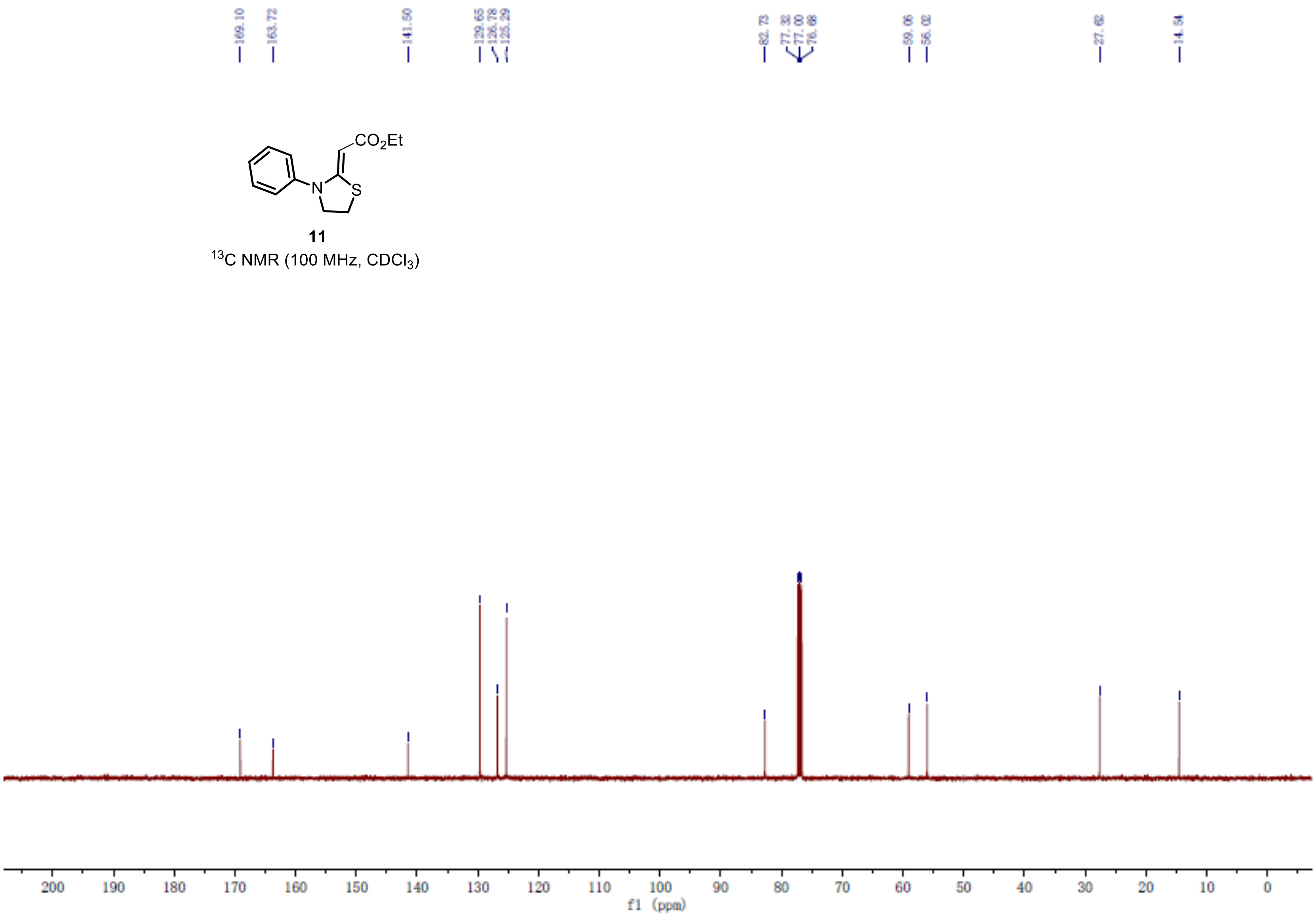
9

^{13}C NMR (100 MHz, $CDCl_3$)



11

^{1}H NMR (400 MHz, CDCl$_3$)



11

^{13}C NMR (100 MHz, $CDCl_3$)