Supporting Information for Publication

Synthesis of tetrahydroquinazolines from 2-aminobenzonitriles and alkylidene malonates *via* 1,4-conjugate addition and unprecedented rearrangement reaction

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General information:

All the reagents were of reagent grade (AR grade) and were used as purchased without further purification. Silica gel (60-120 mesh size) was used for column chromatography. Reactions were monitored by TLC on silica gel GF254 (0.25 mm). Melting points were recorded in an open capillary tube and are uncorrected. Fourier transform-infra red (FT-IR) spectra were recorded as neat liquid or KBr pellets. NMR spectra were recorded in $CDCl_3$ and DMSO-d6 with tetramethylsilane as the internal standard for ^1H (600 MHz, 500 MHz and 400 MHz) or ^{13}C (150 MHz, 125 MHz and 100 MHz) NMR. Chemical shifts (δ) are reported in ppm with abbreviations, s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, m = multiplet, bs = broad singlet and spin-spin coupling constants (*J*) are given in Hz. HRMS spectra were recorded using Q-TOF and micrOTOF-Q II mass spectrometer.

Synthesis of starting materials:

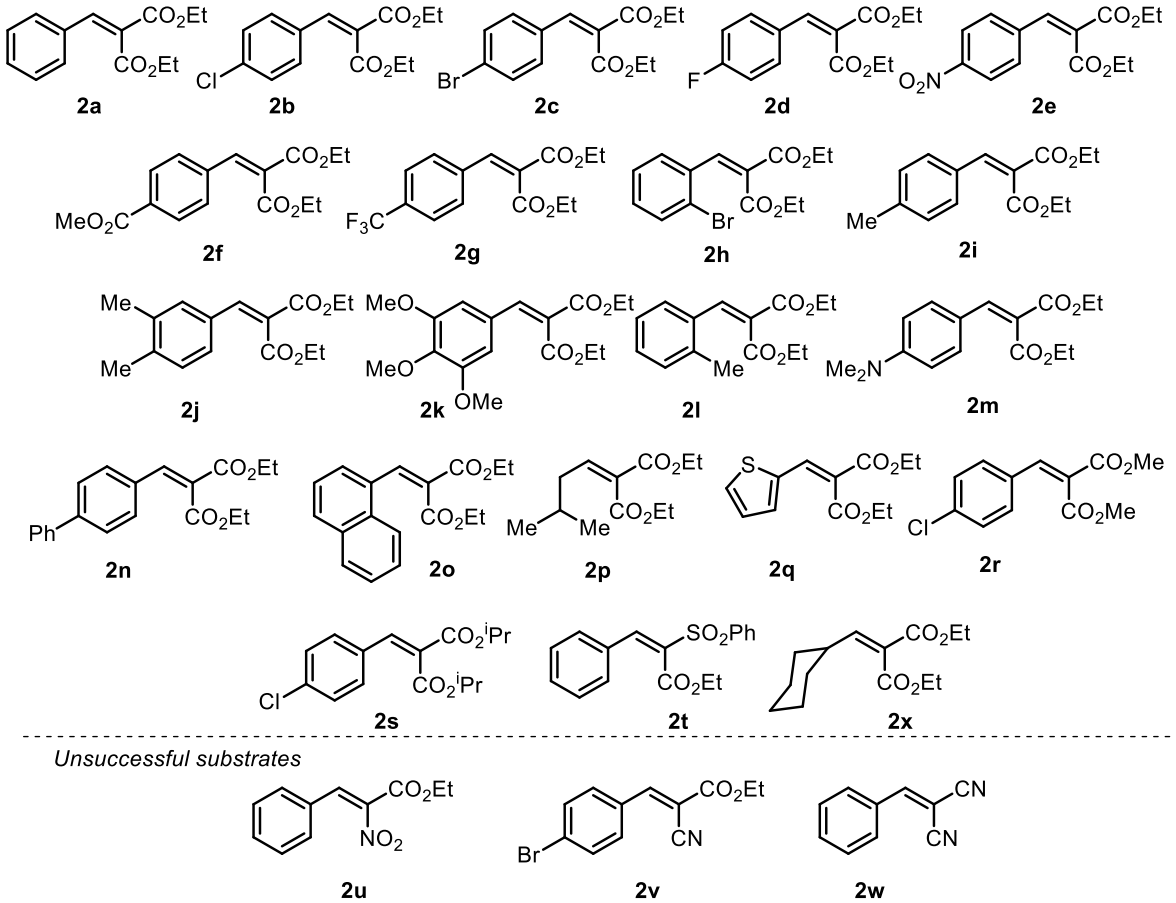


Figure S2: Alkylidene malonates employed in the reaction

All starting materials **2a-2x** were synthesized by Knoevenagel reaction from the corresponding aldehydes[1], previously reported and confirmed by comparison to the reported characterization data.[2]

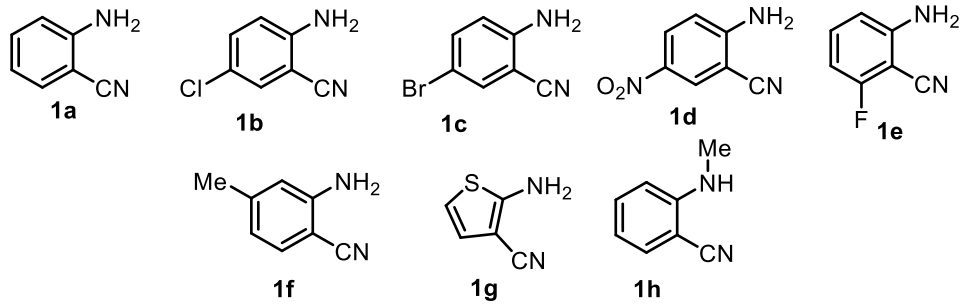
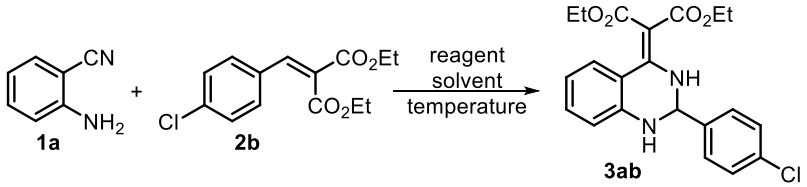


Figure S3: 2-Aminobenzonitriles employed in the reaction

Optimization Studies:

Table S3: Optimization of the reaction[a]



entry	reagent (equiv)	solvent	temp/°C	%yield[b]
1.	$SnCl_4$ (2.0)	DCM	25	52
2.	$SnCl_4$ (2.0)	DCE	25	55
3.	$SnCl_4$ (2.0)	toluene	25	20
4.	$SnCl_4$ (2.0)	THF	25	-
5.	$SnCl_4$ (2.0)	CH_3CN	25	-
6.	$SnCl_4$ (2.0)	DCE	40	65
7.	$SnCl_4$ (2.0)	DCE	80	83
8.	$SnCl_4$ (1.2)	DCE	80	86
9.	$SnCl_4$ (0.5)	DCE	80	52
10.[c]	$SnCl_4$ (1.2)	DCE	100	77
11.[d]	$SnCl_4$ (1.2)	DCE	80	46
12.	$TiCl_4$ (1.2)	DCE	25	35
13.	$AlCl_3$ (2.0)	DCE	25	-
14.	$FeCl_3$ (1.5)	DCE	80	-
15.	$InCl_3$ (0.5)	DCE	80	-
16.	$In(OTf)_3$ (0.5)	DCE	80	-
17.	$Cu(OTf)_2$ (0.5)	DCE	80	-
18.	$BF_3 \cdot OEt_2$ (1.2)	DCE	25	-
19.	TfOH (1.2)	DCE	25	-
20.	*p*-TsOH (2.0)	DCE	25	-

[a]All the reactions were carried out in (0.48 mmol) **1a**, (0.4 mmol) **2b** in 2.0 ml solvent, N_2 atmosphere, [b]Isolated yields, [c]In a sealed tube, [d]O_2 atmosphere.

In the beginning, we initiated the optimization studies by treating diethyl 2-(4-chlorobenzylidene)malonate **2b** with 2-aminobenzonitrile **1a** in the presence of 2 equiv of

$SnCl_4$ in DCM at room temperature under an inert atmosphere (Table S3, entry 1). To our delight, the reaction occurred to deliver the product diethyl 2-(2-(4-chlorophenyl)-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate **3ab** in 52% yield. Encouraged by the result, we attempted the reaction in a set of non-polar and polar solvents like DCE, toluene, THF and acetonitrile at room temperature. Similar yield was obtained with DCE (Table S3, entry 2) whereas toluene produced inferior yield (Table S3, entry 3). The reaction did not proceed at all with moderately and highly polar solvents such as THF and acetonitrile, respectively (Table S3, entries 4 and 5). However, increasing the reaction temperature to 50 °C in DCE resulted in 65% yield of **3ab** (Table S3, entry 6). Further elevating the temperature to 80 °C in DCE led to 83% yield (Table S3, entry 7). Decreasing the loading of $SnCl_4$ to 1.2 equiv and 0.5 equiv in DCE at 80 °C resulted in a synchronous yield of 86% (Table S3, entry 8) and an inferior yield of 52% (Table S3, entry 9) respectively. The reaction was performed at 100 °C in DCE in a sealed tube resulting in a decreased yield of 77% (Table S3, entry 10). When the reaction was performed with 1.2 equiv of $SnCl_4$ in DCE at 80 °C under O_2 atmosphere, it produced an inferior yield of 46% (Table S3, entry 11). The reaction was also investigated under different Lewis and Brønsted acidic conditions. It was observed that, with $TiCl_4$ (1.2 equiv) in DCE at room temperature **3ab** was formed with 35% yield (Table S3, entry 12). Other Lewis acids such as $AlCl_3$, $FeCl_3$, $InCl_3$ in DCE at 80 °C failed to give any product (Table S3, entries 13-15). Metal triflates such as indium and copper triflates and $BF_3{\cdot}OEt_2$ were also screened for the reaction but did not give any products (Table S3, entries 16-18). Brønsted acids TfOH and *p*-TsOH in DCE at room temperature were also found to be ineffective (Table S3, entries 19 and 20). Therefore, 1.2 equiv of $SnCl_4$ in DCE at 80°C are the optimum conditions for the reaction.

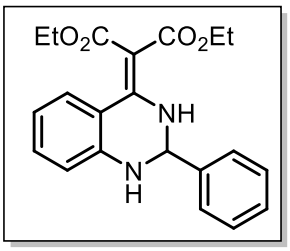
General procedure for the synthesis of 3aa-3hb:

To a solution of electron deficient alkene (0.4 mmol, 1 equiv.) and 2-aminobenzonitrile (0.48 mmol, 1.1 equiv.) in 1,2-dichloroethane (2ml) was added $SnCl_4$ (0.72 mmol, 1.2 equiv.) at 0 ^oC under nitrogen atmosphere. The reaction was then heated in an oil bath at 80 ^oC for 30 min. After completion of the reaction, the solvent was removed under reduced pressure and diluted with saturated $NaHCO_3$ solution. Then the organic layer was extracted with EtOAc (3x10 mL). The organic layer was further washed with brine solution for 2-3 times. The combined organic layers were dried over Na_2SO_4 and concentrated in rotary evaporator. The crude was subjected to column chromatography over silica gel to give the corresponding product.

Typical procedure for the synthesis of 3aa:

To a solution of diethyl 2-benzylidenemalonate (**2a**) (99 mg., 0.4 mmol) and 2-aminobenzonitrile (57 mg, 0.48 mmol) in 1,2-dichloroethane (2ml) was added $SnCl_4$ (0.06 mL, 0.48 mmol) at 0 ^oC under nitrogen atmosphere. The reaction was then heated in an oil bath at 80 ^oC for 30 min. After completion of the reaction, the solvent was removed under reduced pressure and diluted with saturated $NaHCO_3$ solution. Then the organic layer was extracted with EtOAc (3x10 mL). The organic layer was further washed with brine solution for 2-3 times. The combined organic layers were dried over Na_2SO_4 and concentrated in rotary evaporator. The crude was subjected to column chromatography over silica gel to give the corresponding product **3aa**.

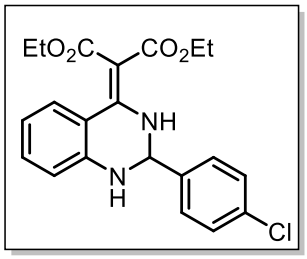
Diethyl 2-(2-phenyl-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate (3aa):



Pale yellow solid; R_f (hexane/EtOAc, 4:1) 0.50; mp 133-135 °C. Yield 102 mg, 70%; IR (KBr, neat) ν 3326, 2981, 1643, 1556, 1478, 1267, 1234, 1153, 1115, 1073, 758 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.95 (s, 1 H), 7.40 (dd, *J* = 5.9 and 3.8 Hz, 2 H), 7.33 (d, *J* = 8.1 Hz, 1 H), 7.27-7.25 (m, 3 H), 7.11 (t, *J* = 7.7 Hz, 1 H), 6.66 (t, *J* = 7.8 Hz, 1 H), 6.60 (d, *J* = 8.1 Hz , 1 H), 5.20 (d, *J* = 1.9 Hz, 1 H), 4.75 (s, 1 H), 4.06-3.95 (m, 4 H), 1.13-1.04 (m, 6 H). $^{13}C\{^1H\}$

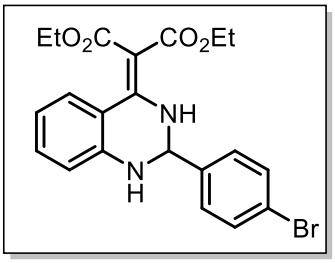
NMR (150 MHz, $CDCl_3$) δ 169.7, 169.1, 155.2, 147.3, 138.1, 132.6, 130.1, 129.3, 128.5, 127.9, 119.7, 117.2, 116.4, 89.7, 66.7, 61.1, 59.9, 14.6, 14.0. HRMS (ESI) calcd. for $C_{21}H_{23}N_2O_4$ $(M + H)^+$ 367.1652, found 367.1656.

Diethyl 2-(2-(4-chlorophenyl)-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate (3ab):



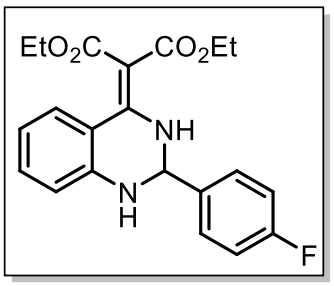
Yellow solid; R_f (hexane/EtOAc, 4:1) 0.50; mp 150-152 °C. Yield 138 mg, 86%; IR (KBr, neat) ν 3321, 2980, 1644, 1590, 1556, 1480, 1266, 1234, 1153, 1075, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1 H), 7.53-7.45 (m, 3 H), 7.38 (d, *J* = 8.4 Hz, 2 H), 7.27-7.23 (m, 1 H), 6.81 (t, *J* = 7.7 Hz, 1 H), 6.72 (d, *J* = 8.1 Hz, 1 H), 5.37 (d, *J* = 1.8 Hz, 1 H), 4.60 (s, 1 H), 4.22-4.10 (m, 4 H), 1.27-1.15 (m, 6 H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 169.7, 169.1, 154.9, 147.0, 136.8, 136.0, 132.7, 129.5, 129.3, 128.4, 119.8, 117.1, 116.5, 89.9, 65.9, 61.2, 60.0, 14.6, 14.0. HRMS (ESI) calcd. for $C_{21}H_{22}ClN_2O_4$ $(M + H)^+$ 401.1263, found 401.1285 and 403.1253.

Diethyl 2-(2-(4-bromophenyl)-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate (3ac):



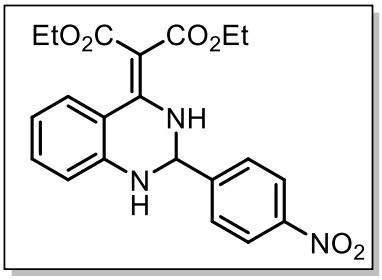
Bright yellow solid; R_f (hexane/EtOAc, 4:1) 0.50; mp 174-176 °C. Yield 129 mg, 73%; IR (KBr, neat) ν 3322, 2980, 1644, 1557, 1480, 1266, 1235, 1153, 1074, 759 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 10.06 (s, 1 H), 7.54 (d, *J* = 7.9 Hz, 2 H), 7.44 (dd, *J* = 13.5 and 7.9 Hz, 3 H), 7.25 (t, *J* = 7.7 Hz 1 H), 6.81 (t, *J* = 7.7 Hz, 1 H), 6.72 (d, *J* = 8.1 Hz, 1 H), 5.36 (d, *J* = 2.0 Hz, 1 H), 4.60 (s, 1H), 4.22-4.08 (m, 4 H), 1.26-1.15 (m, 6 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 169.7, 169.1, 154.9, 147.0, 137.4, 132.7, 132.4, 129.6, 128.4, 124.2, 119.9, 117.1, 116.5, 89.9, 66.0, 61.2, 60.0, 14.6, 14.0. HRMS (ESI) calcd. for $C_{21}H_{22}BrN_2O_4$ $(M + H)^+$ 445.0758, found 445.0768 and 447.0750.

Diethyl 2-(2-(4-fluorophenyl)-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate (3ad): Pale



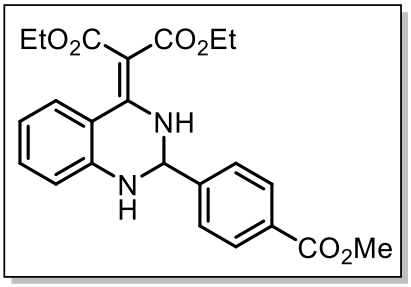
yellow solid; R_f (hexane/EtOAc, 4:1) 0.50; mp 144-146 °C. Yield 115 mg, 75%; IR (KBr, neat) ν 3328, 2983, 1690, 1567, 1453, 1266, 1212, 1155, 1073, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1 H), 7.56-7.53 (m, 2 H), 7.46 (d, *J* = 8.0 Hz, 1 H), 7.27-7.23 (m, 1 H), 7.09 (t, *J* = 8.5 Hz, 2 H), 6.81 (t, *J* = 7.7 Hz, 1 H), 6.72 (d, *J* = 8.1 Hz, 1 H), 5.37 (d, *J* = 1.8 Hz, 1 H), 4.60 (s, 1 H), 4.24-4.10 (m, 4 H), 1.26-1.15 (m, 6 H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 169.7, 169.1, 163.7 (d, *J* = 247.6 Hz), 155.0, 147.2, 134.2 (d, *J* = 3.1 Hz), 132.7, 129.9 (d, *J* = 8.3 Hz), 128.4, 119.7, 117.0, 116.4, 116.3, 116.1, 89.8, 66.0, 61.2, 60.0, 14.5, 14.0. ^{19}F NMR (470 MHz, $C_6F_6/CDCl_3$) δ -114.21 (s, -F). HRMS (ESI) calcd. for $C_{21}H_{22}FN_2O_4$ $(M + H)^+$ 385.1558, found 385.1562.

Diethyl 2-(2-(4-nitrophenyl)-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate (3ae):



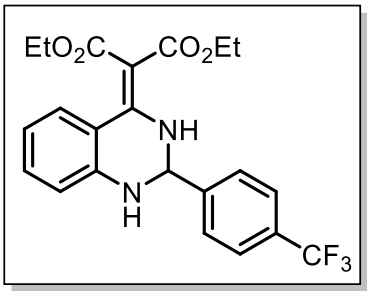
Primrose yellow solid; R_f (hexane/EtOAc,7:3) 0.40; mp 179-181 °C. Yield 148 mg, 90%; IR (KBr, neat) ν 3329, 2982, 1723, 1644, 1523, 1345, 1239, 1153, 1075, 762 cm^{-1}; ^1H NMR (400 MHz, DMSO-d6) δ 10.22 (d, *J* = 4.0 Hz, 1 H), 8.25 (d, *J* = 8.8 Hz, 2 H), 7.72 (d, *J* = 8.2 Hz, 2 H), 7.61 (s, 1 H), 7.27 (t, *J* = 7.6 Hz, 1 H), 7.21 (d, *J* = 8.0 Hz, 1 H), 6.89 (d, *J* = 8.1 Hz, 1 H), 6.68 (t, *J* = 7.6 Hz, 1 H), 5.89 (s, 1 H), 4.09-4.04 (m, 4 H), 1.13 (t, *J* = 7.1 Hz, 6 H). 13C{1H} NMR (150 MHz, DMSO-d6) δ 168.2, 153.8, 148.1, 147.5, 146.6, 132.9, 128.2, 127.4, 123.7, 118.1, 116.5, 115.3, 88.6, 62.3, 59.7, 14.0. HRMS (ESI) calcd. for $C_{21}H_{22}N_3O_6$ $(M + H)^+$ 412.1503, found 412.1526.

Diethyl 2-(2-(4-(methoxycarbonyl)phenyl)-2,3-dihydroquinazolin-4(1H)-ylidene)malonate (3af):



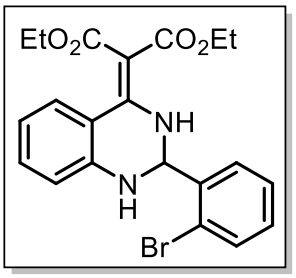
Yellow solid; R_f (hexane/EtOAc, 7:3) 0.50; mp 188-190 °C. Yield 144 mg, 85%; IR (KBr, neat) ν 3323, 2986, 1705, 1609, 1553, 1335, 1234, 1123, 1036, 759 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 10.13 (s, 1 H), 8.07 (d, *J* = 8.0 Hz, 2 H), 7.64 (d, *J* = 8.0 Hz, 2 H), 7.47 (d, *J* = 8.1 Hz, 1 H), 7.29-7.26 (m, 1 H), 6.82 (t, *J* = 7.7 Hz, 1 H), 6.75 (d, *J* = 8.0 Hz, 1 H), 5.47 (d, *J* = 1.9 Hz, 1 H), 4.56 (s, 1 H), 4.23-4.17 (m, 1 H), 4.15-4.08 (m, 3 H), 3.92 (s, 3 H), 1.25 (t, *J* = 7.1 Hz, 3 H), 1.16 (t, *J* = 7.2 Hz, 3 H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 169.6, 169.1, 166.7, 154.9, 146.8, 143.0, 132.8, 131.8, 130.5, 128.5, 128.0, 120.0, 117.2, 116.5, 90.1, 66.1, 61.3, 60.1, 52.6, 14.6, 14.0. HRMS (ESI) calcd. for $C_{23}H_{25}N_2O_6$ $(M + H)^+$ 425.1707, found 425.1725.

Diethyl 2-(2-(4-(trifluoromethyl)phenyl)-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate (3ag):



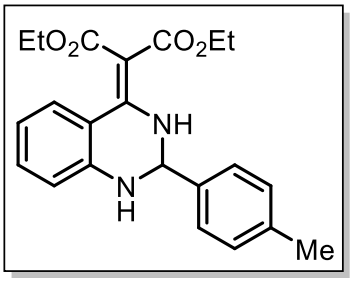
Pale yellow solid; R_f (hexane/EtOAc,7:3) 0.50; mp 145-147 °C. Yield 151 mg, 87%; IR (KBr, neat) ν 3320, 2983, 1700, 1643, 1555, 1321, 1234, 1115, 1034, 759 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 10.16 (s, 1 H), 7.71 (dd, *J* = 14.0 and 8.4 Hz, 4 H), 7.51 (dd, *J* = 8.1 and 1.4 Hz, 1 H), 7.31-7.28 (m, 1 H), 6.87-6.84 (m, 1 H), 6.76 (dd, *J* = 8.0 and 1.2 Hz, 1 H), 5.51 (d, *J* = 1.9 Hz, 1 H), 4.44 (s, 1 H), 4.26-4.10 (m, 4 H), 1.26 (t, *J* = 6.9 Hz, 3 H), 1.18 (t, *J* = 7.3 Hz, 3 H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 169.6, 169.2, 154.7, 146.7, 142.2, 132.8, 132.4 (q, *J* = 32.2 Hz), 128.5 (d, *J* = 7.7 Hz), 126.4 (q, *J* = 3.6 Hz), 124.9, 123.1, 120.3, 117.3, 116.6, 90.5, 66.1, 61.3, 60.2, 14.6, 14.1. ^{19}F NMR (470 MHz, $C_6F_6/CDCl_3$) δ -66.27 (s, $-CF_3$). HRMS (ESI) calcd. for $C_{22}H_{22}F_3N_2O_4$ $(M + H)^+$ 435.1526, found 435.1521.

Diethyl 2-(2-(2-bromophenyl)-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate (3ah):



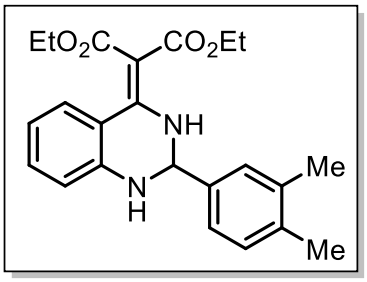
Bright yellow solid; R_f (hexane/EtOAc, 4:1) 0.50; mp 171-173 °C. Yield 158 mg, 89%; IR (KBr, neat) ν 3323, 2980, 1699, 1645, 1592, 1558, 1475, 1237, 1154, 1076, 755 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 10.28 (s, 1 H), 7.68 (dd, *J* = 7.7 and 1.8 Hz, 1 H), 7.58 (dd, *J* = 8.1 and 1.3 Hz, 1 H), 7.50 (dd, *J* = 8.1 and 1.3 Hz, 1 H), 7.35 (t, *J* = 7.6 Hz, 1 H), 7.25-7.22 (m, 2 H), 6.81 (t, *J* = 7.7 Hz, 1 H), 6.71 (d, *J* = 8.0 Hz, 1 H), 5.90 (d, *J* = 2.8 Hz, 1 H), 4.69 (s, 1 H), 4.18 (p, *J* = 7.0 Hz, 4 H), 1.29-1.17 (m, 6 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 169.7, 169.2, 155.1, 146.3, 137.6, 133.5, 132.8, 131.1, 129.2, 128.5, 128.4, 123.0, 119.9, 117.1, 116.6, 90.3, 64.8, 61.3, 60.1, 14.6, 14.1. HRMS (ESI) calcd. for $C_{21}H_{22}BrN_2O_4$ $(M + H)^+$ 445.0757, found 445.0775 and 447.0757.

Diethyl 2-(2-(*p*-tolyl)-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate (3ai):



Pale yellow solid; R_f (hexane/EtOAc, 4:1) 0.50; mp 159-161 °C. Yield 116 mg, 76%; IR (KBr, neat) ν 3326, 2982, 1643, 1585, 1550, 1479, 1268, 1238, 1153, 1074, 757 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 10.03 (s, 1 H), 7.47 (d, *J* = 8.1 Hz, 1 H), 7.43 (d, *J* = 7.8 Hz, 2 H), 7.27-7.23 (m, 1 H), 7.21 (d, *J* = 7.8 Hz, 2 H), 6.80 (t, *J* = 7.7 Hz, 1 H), 6.71 (d, *J* = 8.0 Hz, 1 H), 5.33 (d, *J* = 1.8 Hz, 1 H), 4.51 (s, 1 H), 4.21-4.11 (m, 4 H), 2.36 (s, 3 H), 1.30-1.15 (m, 6 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 169.8, 169.1, 155.3, 147.4, 140.1, 135.2, 132.6, 129.9, 128.5, 127.8, 119.6, 117.2, 116.3, 89.5, 66.5, 61.1, 59.9, 21.4, 14.6, 14.0. HRMS (ESI) calcd. for $C_{22}H_{25}N_2O_4$ $(M + H)^+$ 381.1819, found 381.1809.

Diethyl 2-(2-(3,4-dimethylphenyl)-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate (3aj):

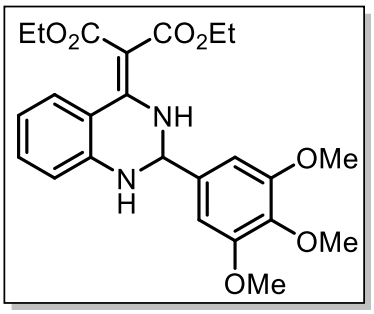


Pale yellow solid; R_f (hexane/EtOAc, 4:1) 0.50; mp 138-140 °C. Yield 108 mg, 69%; IR (KBr, neat) ν 3318, 2978, 1643, 1588, 1555, 1477, 1232, 1151, 1114, 1074, 757 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 10.00 (s, 1 H), 7.47 (d, *J* = 8.1 Hz, 1 H), 7.33 (d, *J* = 2.0 Hz, 1 H), 7.26-7.23 (m, 2 H), 7.15 (d, *J* = 7.8 Hz, 1 H), 6.79 (t, *J* = 7.7 Hz, 1

H), 6.71 (d, *J* = 8.0 Hz, 1 H), 5.29 (d, *J* = 1.7 Hz, 1 H), 4.52 (s, 1 H), 4.20-4.05 (m, 4 H), 2.27 (s, 6 H), 1.26-1.13 (m, 6 H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 169.8, 169.1, 155.4, 147.5, 138.7, 137.6, 135.5, 132.6, 130.3, 129.0, 128.5, 125.3, 119.5, 117.2, 116.3, 89.4, 66.5, 61.0, 59.9, 20.0, 19.8, 14.6, 14.0. HRMS (ESI) calcd. for $C_{23}H_{27}N_2O_4$ $(M + H)^+$ 395.1965, found 395.1982.

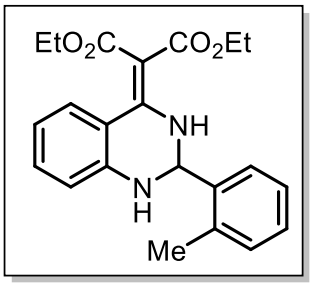
Diethyl 2-(2-(3,4,5-trimethoxyphenyl)-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate (3ak):

Pale yellow solid; R_f (hexane/EtOAc, 4:1) 0.50; mp 184-186 °C. Yield 108 mg, 59%; IR (KBr, neat) ν 3327, 2978, 1643, 1590, 1555, 1463, 1234, 1121, 1075, 761 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.99 (s, 1 H), 7.47 (d, *J* = 8.1 Hz, 1 H), 7.28 (t, *J* = 7.3 Hz, 1 H), 6.82 (t, *J* = 7.7 Hz, 1 H), 6.78-6.75 (m, 3 H), 5.30 (d, *J* = 1.7 Hz, 1 H), 4.61 (s, 1 H), 4.23-4.19 (m, 1 H), 4.16-4.07 (m, 3 H), 3.85 (d, *J* = 6.2 Hz, 9 H), 1.25 (t, *J* = 7.1 Hz, 3 H), 1.15 (t, *J* = 7.2 Hz, 3 H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 169.8, 169.1, 155.2, 153.7, 147.5, 139.0, 133.6, 132.7, 128.5, 119.7, 116.9, 116.3, 104.9, 89.5, 67.1, 61.2, 61.0, 60.0, 56.4, 14.6, 14.0. HRMS (ESI) calcd. for $C_{23}H_{27}N_2O_4$ $(M + H)^+$ 457.1969, found 457.1970.

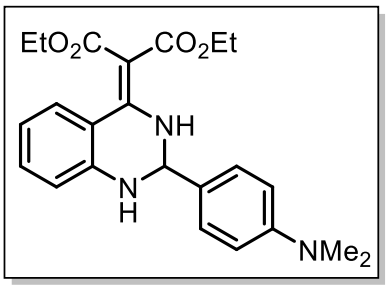


Dimethyl 2-(2-(*o*-tolyl)-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate (3al):

Yellow solid; R_f (hexane/EtOAc, 4:1) 0.50; mp 118-120 °C. Yield 91 mg, 60%; IR (KBr, neat) ν 3326, 2980, 1643, 1589, 1556, 1478, 1267, 1237, 1153, 1074, 757 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.68 (dd, *J* = 7.3 and 1.9 Hz, 1 H), 7.51 (d, *J* = 8.1 Hz, 1 H), 7.32-7.25 (m, 3 H), 7.21 (dd, *J* = 7.0 and 1.9 Hz, 1 H), 6.82 (t, *J* = 7.7 Hz, 1 H), 6.75 (d, *J* = 8.0 Hz, 1 H), 5.61 (d, *J* = 1.9 Hz, 1 H), 4.44 (s, 1 H), 4.20-4.09 (m, 4 H), 2.43 (s, 3 H), 1.26-1.16 (m, 6 H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 169.7, 169.1, 155.3, 147.9, 136.8, 135.6, 132.6, 131.4, 129.7, 128.6, 127.7, 127.0, 119.7, 117.3, 116.5, 89.8, 63.5, 61.1, 59.9, 19.3, 14.6, 14.1. HRMS (ESI) calcd. for $C_{22}H_{25}N_2O_4$ $(M + H)^+$ 381.1809, found 381.1818.

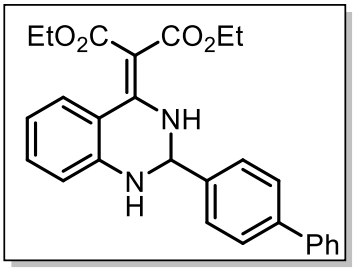


Diethyl 2-(2-(4-(dimethylamino)phenyl)-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate (3am):



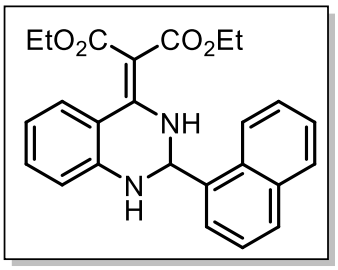
Light green solid; R_f (hexane/EtOAc,7:3) 0.50; mp 174-176 °C. Yield 103 mg, 63%; IR (KBr, neat) ν 3331, 2980, 1612, 1704, 1648, 1587, 1554, 1361, 1237, 1152, 1073, 755 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 10.00 (s, 1 H), 7.50 (d, *J* = 8.0 Hz, 1 H), 7.43 (d, *J* = 8.5 Hz, 2 H), 7.29-7.27 (m, 1 H), 6.82 (t, *J* = 7.6 Hz, 1 H), 6.75-6.72 (m, 3 H), 5.31 (d, *J* = 1.8 Hz, 1 H), 4.43 (s, 1 H), 4.22-4.08 (m, 4 H), 3.00 (s, 6 H), 1.28 (d, *J* = 8.2 Hz, 3 H), 1.17 (d, *J* = 8.0 Hz, 3 H). $^{13}C\{^1H\}$ (150 MHz, $CDCl_3$) δ 169.9, 169.1, 155.7, 151.8, 147.8, 132.5, 128.9, 128.6, 125.1, 119.4, 117.2, 116.2, 112.6, 89.1, 66.6, 61.1, 59.8, 40.7, 14.7, 14.1. HRMS (ESI) calcd. for $C_{23}H_{28}N_3O_4$ $(M + H)^+$ 410.2074, found 410.2069.

Diethyl 2-(2-([1,1'-biphenyl]-4-yl)-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate (3an):



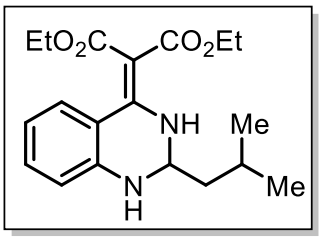
Pale yellow solid; R_f (hexane/EtOAc, 4:1) 0.40; mp 149-151 °C. Yield 129 mg, 73%; IR (KBr, neat) ν 3326, 2981, 1628, 1560, 1480, 1270, 1234, 1153, 1115, 1073, 768 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 10.13 (s, 1 H), 7.65 (s, 4 H), 7.59 (d, *J* = 7.7 Hz, 2 H), 7.51 (d, *J* = 8.1 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, 2 H), 7.38 (t, *J* = 7.4 Hz, 1 H), 7.29 (t, *J* = 7.7 Hz, 1 H), 6.84 (t, *J* = 7.7 Hz, 1 H), 6.76 (d, *J* = 8.0 Hz, 1 H), 5.45 (d, *J* = 1.9 Hz, 1 H), 4.48 (s, 1 H), 4.24-4.09 (m, 4 H), 1.28-1.16 (m, 6 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 169.8, 169.2, 155.2, 147.3, 143.3, 140.6, 137.0, 132.7, 129.1, 128.6, 128.5, 128.1, 128.0, 127.5, 119.9, 117.3, 116.4, 89.8, 66.6, 61.2, 60.0, 14.7, 14.1. HRMS (ESI) calcd. for $C_{27}H_{27}N_2O_4$ $(M + H)^+$ 443.1965, found 443.1981.

Diethyl 2-(2-(naphthalen-1-yl)-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate (3ao):



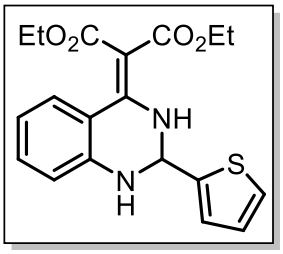
Yellow solid; R_f (hexane/EtOAc, 4:1) 0.50; mp 143-145 °C. Yield 104 mg, 63%; IR (KBr, neat) ν 3324, 2980, 1644, 1589, 1554, 1478, 1368, 1233, 1150, 1073, 762 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 10.23 (s, 1 H), 8.35 (d, *J* = 8.0 Hz, 1 H), 7.92 -7.90 (m, 2 H), 7.80 (d, *J* = 7.2 Hz, 1 H), 7.57-7.48 (m, 4 H), 7.29 (t, *J* = 7.6 Hz, 1 H), 6.85 (t, *J* = 7.7 Hz, 1 H), 6.75 (d, *J* = 8.0 Hz, 1 H), 6.07 (d, *J* = 1.9 Hz, 1 H), 4.61 (s, 1 H), 4.25-4.06 (m, 4 H), 1.23-1.19 (m, 6 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 169.8, 169.1, 155.3, 147.8, 134.4, 132.7, 132.6, 131.0, 130.7, 129.3, 128.7, 127.1, 126.5, 126.4, 125.5, 123.7, 119.8, 117.4, 116.5, 90.1, 64.6, 61.2, 59.9, 14.6, 14.1. HRMS (ESI) calcd. for $C_{25}H_{25}N_2O_4$ $(M + H)^+$ 417.1809, found 417.1827.

Diethyl 2-(2-isobutyl-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate (3ap): White solid;



R_f (hexane/EtOAc, 7:3) 0.50; mp 142-144 °C. Yield 107 mg, 77%; IR (KBr, neat) ν 3338, 2927, 1690, 1640, 1576, 1428, 1288, 1117, 1077, 787 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 10.08 (s, 1 H), 7.44-7.42 (m, 1 H), 7.25-7.22 (m, 1 H), 6.78 (t, *J* = 7.7 Hz, 1 H), 6.71 (d, *J* = 8.0 Hz, 1 H), 4.85-4.46 (m, 1 H), 4.27 (s, 1 H), 4.21-4.15 (m, 3 H), 4.09 (s, 1 H), 1.93-1.82 (m, 1 H), 1.76-1.69 (m, 1 H), 1.64-1.59 (m, 1 H), 1.34 -1.11 (m, 6 H), 0.99 (t, *J* = 7.2 Hz, 6 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 169.8, 169.3, 155.8, 147.5, 132.5, 128.5, 119.6, 117.8, 116.6, 89.2, 61.6, 61.0, 59.9, 43.5, 24.4, 23.1, 22.6, 14.6, 14.1. HRMS (ESI) calcd. for $C_{19}H_{27}N_2O_4$ $(M + H)^+$ 347.1965, found 347.1965.

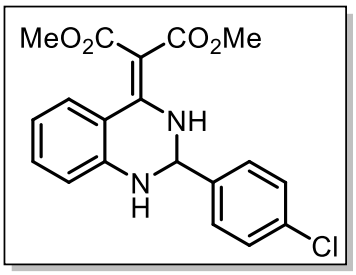
Diethyl 2-(2-(thiophen-2-yl)-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate (3aq):



Light yellow solid; R_f (hexane/EtOAc, 4:1) 0.50; mp 150-152 °C. Yield 77 mg, 52%; IR (KBr, neat) ν 3320, 2980, 1643, 1589, 1555, 1476 1422, 1236, 1150, 1071, 759 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 10.19 (s, 1 H), 7.49 (d, *J* = 8.1 Hz, 1 H), 7.36 (d, *J* = 5.1 Hz, 1 H), 7.29-7.26 (m, 1 H), 7.21 (d, *J* = 3.5 Hz, 1 H), 7.00 (t, *J* = 4.3 Hz, 1 H), 6.83 (t, *J* = 7.7 Hz, 1

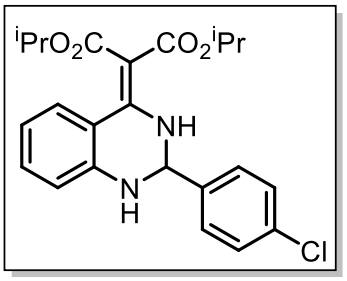
H), 6.75 (d, *J* = 8.1 Hz, 1 H), 5.73 (s, 1 H), 4.64 (s, 1 H), 4.25-4.08 (m, 4 H), 1.32-1.14 (m, 6 H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 169.6, 169.1, 154.6, 146.6, 141.4, 132.7, 128.5, 127.6, 127.5, 127.1, 120.1, 117.4, 116.6, 90.1, 62.2, 61.2, 60.1, 14.6, 14.0. HRMS (ESI) calcd. for $C_{19}H_{21}N_2O_4S$ $(M + H)^+$ 373.1217, found 373.1205.

Dimethyl 2-(2-(4-chlorophenyl)-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate (3ar):



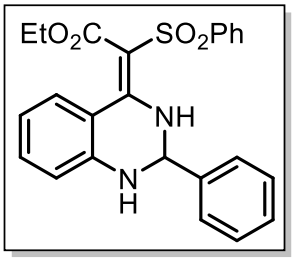
Pale yellow solid; R_f (hexane/EtOAc, 4:1) 0.50; mp 138-140 °C. Yield 124 mg, 84%; IR (KBr, neat) ν 3320, 2976, 1649, 1589, 1480, 1277, 1234, 1150, 1120, 1073, 758 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.12 (s, 1 H), 7.52 (d, *J* = 8.4 Hz, 2 H), 7.41 (dd, *J* = 8.7 and 2.4 Hz, 3 H), 7.31-7.28 (m, 1 H), 6.87-6.84 (m, 1H), 6.76 (d, *J* = 8.1 Hz, 1 H), 5.41 (d, *J* = 1.8 Hz, 1 H), 4.58 (s, 1 H), 3.67 (d, *J* = 23.0 Hz, 6 H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 170.1, 169.4, 155.6, 147.0, 136.6, 136.2, 132.9, 129.5, 129.3, 128.3, 120.0, 117.0, 116.6, 89.1, 66.0, 52.3, 51.5. HRMS (ESI) calcd. for $C_{19}H_{18}ClN_2O_4$ $(M + H)^+$ 373.0950, found 373.0969 and 375.0937.

Diisopropyl 2-(2-(4-chlorophenyl)-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate (3as):



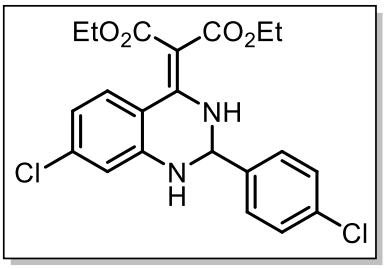
Pale yellow solid; R_f (hexane/EtOAc, 17:3) 0.50; mp 142-144 °C. Yield 77 mg, 45%; IR (KBr, neat) ν 3324, 2978, 1697, 1641, 1590, 1558, 1480, 1237, 1195, 1072, 757 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.95 (s, 1 H), 7.56 (d, *J* = 8.1 Hz, 1 H), 7.49 (d, *J* = 8.3 Hz, 2 H), 7.37 (d, *J* = 8.3 Hz, 2 H), 7.23 (t, *J* = 7.4 Hz, 1 H), 6.79 (t, *J* = 7.7 Hz, 1 H), 6.69 (d, *J* = 8.0 Hz, 1 H), 5.36 (d, *J* = 2.0 Hz, 1 H), 5.08 (p, *J* = 6.3 Hz, 1 H), 4.96 (p, *J* = 6.2 Hz, 1H), 4.52 (s, 1 H), 1.32 (d, *J* = 6.3 Hz, 3 H), 1.24 (d, *J* = 6.2 Hz, 3 H), 1.19 (dd, *J* = 12.2 and 6.3 Hz, 6 H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 169.2, 168.7, 153.7, 147.0, 137.0, 136.0, 132.6, 129.5, 129.4, 128.4, 119.8, 117.0, 116.4, 91.2, 68.5, 67.2, 66.0, 22.3, 21.9, 21.6. HRMS (ESI) calcd. for $C_{23}H_{26}ClN_2O_4$ $(M + H)^+$ 429.1576, found 429.1575 and 431.1570.

Ethyl (Z)-2-(2-phenyl-2,3-dihydroquinazolin-4(1*H*)-ylidene)-2-(phenylsulfonyl)acetate (3at):



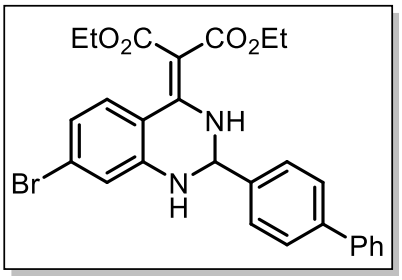
Orange gum; R_f (hexane/EtOAc, 7:3) 0.50; Yield 43 mg, 25%; IR (KBr, neat) ν 3325, 2985, 1742, 1615, 1548, 1447, 1252, 1189, 1080, 755 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 9.81 (d, *J* = 4.5 Hz, 1 H), 7.88-7.85(m, 3 H), 7.60-7.53 (m, 3 H), 7.49-7.46 (m, 2 H), 7.36-7.29 (m, 4 H), 7.03 (d, *J* = 7.9 Hz, 1 H), 6.93 (d, *J* = 8.2 Hz, 1 H), 6.61 (t, *J* = 7.6 Hz, 1 H), 5.86 (s, 1 H), 3.84-3.73 (m, 2 H), 0.85 (t, *J* = 7.0 Hz, 3 H). $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6) δ 165.7, 156.9, 147.5, 145.4, 139.5, 134.4, 131.9, 130.3, 128.7, 128.5, 128.4, 126.7, 126.2, 117.4, 116.2, 114.9, 90.8, 62.6, 59.5, 13.6. HRMS (ESI) calcd. for $C_{24}H_{23}N_2O_4S$ $(M + H)^+$ 435.1373, found 435.1386.

Diethyl 2-(2-(4-chlorophenyl)-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate (3bb):



Yellow solid; R_f (hexane/EtOAc,17:3) 0.50; mp 156-158 °C. Yield 151 mg, 87%; IR (KBr, neat) ν 3323, 2928, 1647, 1586, 1555, 1478, 1231, 1153, 1112, 1079, 825, 648 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 10.00 (s, 1 H), 7.49 (d, *J* = 8.4 Hz, 2 H), 7.44 (d, *J* = 2.2 Hz, 1 H), 7.39 (d, *J* = 8.4 Hz, 2 H), 7.20 (dd, *J* = 8.5 and 2.3 Hz, 1 H), 6.66 (d, *J* = 8.6 Hz, 1 H), 5.36 (d, *J* = 1.9 Hz, 1 H), 4.64 (s, 1 H), 4.25-4.10 (m, 4 H), 1.24 (td, *J* = 7.2 and 2.6 Hz, 6 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 153.3, 145.5, 136.5, 136.2, 132.5, 129.6, 129.3, 128.0, 124.8, 118.2, 117.7, 90.7, 66.0, 61.6, 60.2, 14.6, 14.1. HRMS (ESI) calcd. for $C_{21}H_{21}Cl_2N_2O_4$ $(M + H)^+$ 435.0873, found 435.0886 and 437.0857.

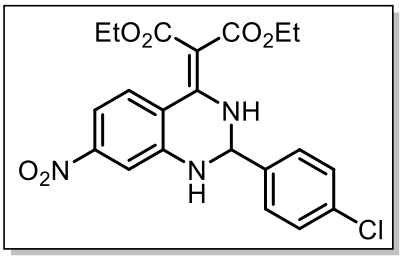
Diethyl 2-(2-([1,1'-biphenyl]-4-yl)-7-bromo-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate (3cn):



Yellow solid; R_f (hexane/EtOAc, 17:3) 0.50; mp 181-183 °C. Yield 162 mg, 78%; IR (KBr, neat) ν 3344, 2926, 1738, 1646, 1552, 1475, 1369, 1246, 1153, 1071, 765, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1 H), 7.65-7.56 (m, 7 H), 7.48-7.44 (m, 2 H), 7.40-7.37 (m, 1H), 7.35 (dd, *J* = 8.5 and 2.2 Hz, 1 H), 6.64 (d, *J* = 8.6 Hz, 1 H), 5.40 (d, *J* = 1.8 Hz, 1 H), 4.63 (s, 1 H), 4.29-4.10 (m, 4 H), 1.27-1.22 (m, 6 H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 169.3, 169.0, 153.5, 146.2, 143.4, 140.5, 136.7, 135.2, 131.1, 129.1, 128.4, 128.1, 128.0, 127.4, 118.8, 118.0, 111.6, 90.5, 66.4, 61.5, 60.2, 14.6, 14.2. HRMS (ESI) calcd. for $C_{27}H_{26}BrN_2O_4$ $(M + H)^+$ 521.1071, found 521.1076 and 523.1059.

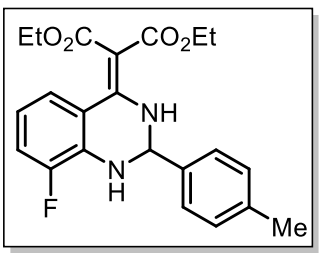
Diethyl 2-(2-(4-chlorophenyl)-7-nitro-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate (3db):

Yellow solid; R_f (hexane/EtOAc,7:3) 0.50; mp 157-159 °C. Yield 128 mg, 72%; IR (KBr, neat)



ν 3336, 2980, 1612, 1594, 1488, 1329, 1235, 1152, 1089, 829, 745 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1 H), 8.45 (d, *J* = 2.4 Hz, 1 H), 8.05 (dd, *J* = 9.0 and 2.4 Hz, 1 H), 7.47 (d, *J* = 8.6 Hz, 2 H), 7.40 (d, *J* = 8.5 Hz, 2 H), 6.69 (d, *J* = 9.0 Hz, 1 H), 5.50-5.48 (m, 2 H), 4.35-4.24 (m, 2 H), 4.21-4.09 (m, 2 H), 1.32 (t, *J* = 7.1 Hz, 3 H), 1.25 (t, *J* = 7.1 Hz, 3 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 169.4, 168.8, 151.7, 151.6, 140.1, 136.6, 135.9, 129.8, 129.2, 127.8, 125.1, 116.2, 115.2, 100.0, 65.5, 62.1, 60.5, 14.5, 14.1. HRMS (ESI) calcd. for $C_{21}H_{21}ClN_3O_6$ $(M + H)^+$ 446.1113, found 446.1131 and 448.1100.

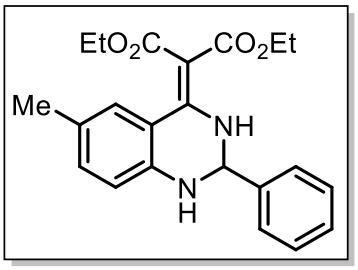
Diethyl 2-(8-fluoro-2-(p-tolyl)-2,3-dihydroquinazolin-4(1H)-ylidene)malonate (3ei):



Bright yellow solid; R_f (hexane/EtOAc, 4:1) 0.50; mp 137-139 °C. Yield 122 mg, 77%; IR (KBr, neat) ν 3333, 2978, 1707, 1645, 1565, 1311, 1234, 1125, 1033, 762 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 10.53 (s, 1 H), 7.43 (d, *J* = 8.0 Hz, 2 H), 7.24-7.22 (m, 3

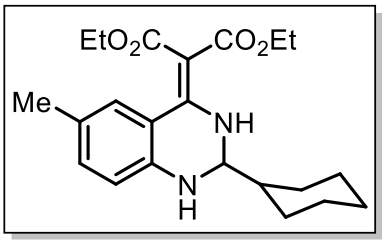
H), 6.57-6.53 (m, 2 H), 5.26 (d, *J* = 2.4 Hz, 1 H), 4.59 (s, 1 H), 4.25-4.07 (m, 4 H), 2.38 (s, 3 H), 1.26 (t, *J* = 7.1 Hz, 3 H), 1.14 (t, *J* = 7.2 Hz, 3 H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 169.9, 168.3, 161.5 (d, *J* = 251.8 Hz), 153.1, 149.8 (d, *J* = 5.5 Hz), 149.77, 140.4, 134.4, 133.2 (d, *J* = 11.1 Hz), 130.1, 127.9, 112.0 (d, *J* = 3.2 Hz), 107.8 (d, *J* = 15.5 Hz), 107.3 (d, *J* = 23.6 Hz), 91.2, 66.5, 60.5, 60.1, 21.5, 14.6, 14.2. ^{19}F NMR (470 MHz, $C_6F_6/CDCl_3$) δ -109.93 (s, -F). HRMS (ESI) calcd. for $C_{22}H_{24}FN_2O_4$ $(M + H)^+$ 399.1715, found 399.1706.

Diethyl 2-(6-methyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate (3fa):



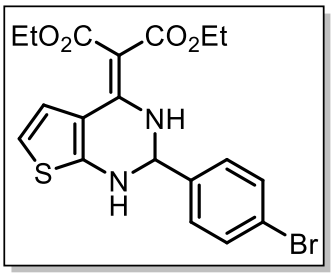
Pale yellow solid; R_f (hexane/EtOAc, 4:1) 0.50; mp 128-130 °C. Yield 126 mg, 83%; IR (KBr, neat) ν 3333, 2980, 1645, 1557, 1479, 1268, 1234, 1150, 1111, 1074, 759 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.04 (s, 1 H), 7.55-7.53 (m, 2 H), 7.42-7.40 (m, 3 H), 7.36 (d, *J* = 8.3 Hz, 1 H), 6.63 (dd, *J* = 8.2 and 1.7 Hz, 1 H), 6.52 (s, 1 H), 5.36 (d, *J* = 1.8 Hz, 1 H), 4.46 (s, 1 H), 4.22-4.11 (m, 4 H), 2.28 (s, 3 H), 1.26-1.20 (m, 6 H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 169.9, 169.2, 155.4, 147.3, 143.6, 138.3, 130.1, 129.2, 128.4, 127.9, 121.0, 116.7, 114.5, 89.1, 66.7, 61.0, 59.8, 21.8, 14.5, 14.1. HRMS (ESI) calcd. for $C_{22}H_{25}N_2O_4$ $(M + H)^+$ 381.1809, found 381.1808.

Diethyl 2-(2-cyclohexyl-6-methyl-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate (3fx):



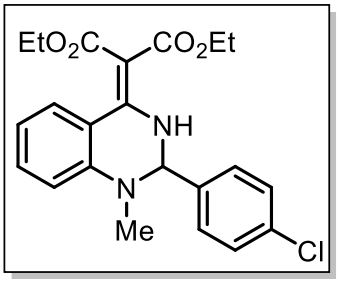
White solid; R_f (hexane/EtOAc,7:3) 0.50; mp 143-145 °C. Yield 73 mg, 47%; IR (KBr, neat) ν 3340, 2928, 1694, 1640, 1588, 1445, 1268, 1117, 1077, 787 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.20 (s, 1 H), 7.30 (d, *J* = 8.2 Hz, 1 H), 6.58 (d, *J* = 8.2 Hz, 1 H), 6.52 (s, 1 H), 4.21-4.15 (m, 4 H), 2.28 (s, 3 H), 1.93 (d, *J* = 12.9 Hz, 1 H), 1.85-1.79 (m, 3H), 1.72-1.66 (m, 2H), 1.61 (d, *J* = 5.0 Hz, 2 H), 1.29-1.17 (m, 9 H), 1.16-1.06 (m, 2 H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 170.0, 156.0, 147.3, 143.4, 128.4, 120.7, 116.8, 114.7, 88.4, 67.6, 61.0, 60.0, 41.3, 28.3, 28.2, 26.3, 25.99, 25.96, 21.8, 14.4. HRMS (ESI) calcd. for $C_{22}H_{31}N_2O_4$ $(M + H)^+$ 387.2278, found 387.2276.

Diethyl 2-(2-(4-bromophenyl)-2,3-dihydrothieno[2,3-*d*]pyrimidin-4(1*H*)-ylidene)malonate (3db):



Yellow solid; R_f (hexane/EtOAc,4:1) 0.35; mp 167-169 °C. Yield 94 mg, 52%; IR (KBr, neat) ν 3285, 2981, 1734, 1645, 1572, 1368, 1257, 1098, 1071, 737 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 9.51 (d, *J* = 2.2 Hz, 1 H), 8.38 (s, 1 H), 7.64 (d, *J* = 8.4 Hz, 2 H), 7.44 (d, *J* = 8.4 Hz, 2 H), 6.61 (d, *J* = 5.8 Hz, 1 H), 6.53 (d, *J* = 5.9 Hz, 1 H), 5.84 (s, 1 H), 4.08 (q, *J* = 7.1 Hz, 4 H), 1.17 (t, *J* = 7.1 Hz, 6 H). $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) δ 168.0, 156.7, 150.1, 139.4, 131.5, 128.9, 122.7, 122.0, 111.6, 110.0, 87.1, 64.8, 59.6, 14.0. HRMS (ESI) calcd. for $C_{19}H_{20}BrN_2O_4S$ $(M + H)^+$ 451.0322, found 451.0328 and 453.0327.

Diethyl 2-(2-(4-chlorophenyl)-1-methyl-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate (3hb):



Yellow solid; R_f (hexane/EtOAc, 4:1) 0.60; mp 150-152 °C. Yield 66 mg, 40%; IR (KBr, neat) ν 2927, 1712, 1644, 1587, 1488, 1266, 1243, 1115, 1087, 757 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 10.38 (s, 1 H), 7.49 (d, *J* = 8.3 Hz, 1 H), 7.36 (t, *J* = 7.8 Hz, 1 H), 7.30 (q, *J* = 8.6 Hz, 4 H), 6.83 (t, *J* = 7.6 Hz, 1 H), 6.78 (d, *J* = 8.3 Hz, 1 H), 5.22 (d, *J* = 3.4 Hz, 1 H), 4.16 (q, *J* = 7.1 Hz, 4 H), 2.68 (s, 3 H), 1.29-1.13 (m, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 169.7, 169.3, 155.0, 147.8, 136.6, 135.5, 133.3, 129.4, 129.2, 128.4, 119.3, 118.3, 114.4, 89.4, 71.1, 61.2, 60.1, 35.5, 14.6, 14.1. HRMS (ESI) calcd. for $C_{22}H_{24}ClN_2O_4$ $(M + H)^+$ 415.1420, found 415.1393 and 417.1429.

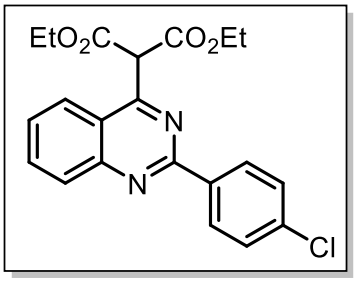
General procedure for the synthesis of 4a-4c:

To a solution of 4-Methylene substituted tetrahydroquinazoline derivative **4** (0.3 mmol, 1 equiv.) in toluene (2 mL) was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.45 mmol, 1.5 equiv.) portionwise at room temperature. The reaction mixture was stirred in an oil bath under reflux for 12 h. After completion of the reaction, the solvent was removed under

reduced pressure and diluted with saturated aqueous sodium bicarbonate solution. The mixture was extracted with DCM and the combined organic layers were washed with brine and dried over sodium sulphate. The solvent was removed under reduced pressure and the crude was purified by column chromatography over silica gel.

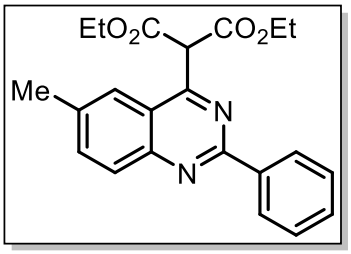
Typical procedure for the synthesis of 4a: To a solution of diethyl 2-(2-(4-chlorophenyl)-2,3-dihydroquinazolin-4(1*H*)-ylidene)malonate **3ab** (120 mg, 0.3 mmol) in toluene (2 mL) was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (102 mg, 0.45 mmol) portionwise at room temperature. The reaction mixture was stirred in an oil bath under reflux for 12 h. After completion of the reaction, the solvent was removed under reduced pressure and diluted with saturated aqueous sodium bicarbonate solution. The mixture was extracted with DCM and the combined organic layers were washed with brine and dried over sodium sulphate. The solvent was removed under reduced pressure and the crude was purified by column chromatography over silica gel to obtain the corresponding product **4a**.

Diethyl 2-(2-(4-chlorophenyl)quinazolin-4-yl)malonate (4a):



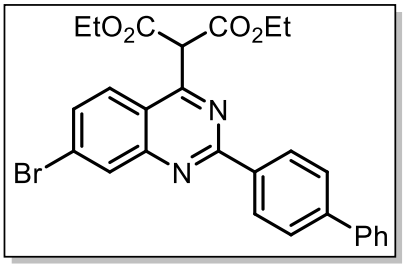
White solid; R_f (hexane/EtOAc, 4:1) 0.50; mp 140-142 °C. Yield 84 mg, 70%; IR (KBr, neat) ν 2985, 1730, 1591, 1511, 1496, 1333, 1241, 1165, 1032, 708 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.48 (d, *J* = 8.6 Hz, 2 H), 8.14-8.12 (m, 2 H), 8.09-8.04(m, 1 H), 7.79-7.75 (m, 1 H), 7.66 (d, *J* = 8.6 Hz, 2 H), 6.26 (s, 1 H), 4.30-4.23 (m, 4 H), 1.20 (t, *J* = 7.1 Hz, 6 H). $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6) δ 166.5, 163.6, 157.6, 150.3, 136.1, 135.7, 135.2, 129.7, 129.0, 128.8, 128.5, 125.0, 121.9, 61.8, 57.0, 14.0. HRMS (ESI) calcd. for $C_{21}H_{20}ClN_2O_4$ $(M + H)^+$ 399.1107, found 399.1116 and 401.1084.

Diethyl 2-(6-methyl-2-phenylquinazolin-4-yl)malonate (4b):



White solid; R_f (hexane/EtOAc, 4:1) 0.42; mp 143-145 °C. Yield 95 mg, 84%; IR (KBr, neat) ν 2982, 1737, 1598, 1549, 1496, 1348, 1245, 1173, 1031, 708 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6) δ 8.50-8.48 (m, 2 H), 8.03 (d, *J* = 8.5 Hz, 1 H), 7.92 (s, 1 H), 7.60-7.56 (m, 4 H), 6.24 (s, 1 H), 4.29-4.25 (m, 4 H), 2.58 (s, 3 H), 1.21 (t, *J* = 7.1 Hz, 6 H). $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6) δ 167.1, 163.3, 159.1, 151.1, 146.2, 137.4, 131.5, 130.8, 129.3, 128.4, 128.0, 125.1, 120.6, 62.2, 57.4, 22.1, 14.4. HRMS (ESI) calcd. for $C_{22}H_{23}N_2O_4$ $(M + H)^+$ 379.1652, found 379.1642.

Diethyl 2-(2-([1,1'-biphenyl]-4-yl)-7-bromoquinazolin-4-yl)malonate (4c):



White solid; R_f (hexane/EtOAc, 4:1) 0.4; mp 150-152 °C. Yield 118 mg, 76%; IR (KBr, neat) ν 2980, 1735, 1599, 1499, 1445, 1331, 1249, 1168, 1032, 710 cm^{-1}; ^1H NMR (600 MHz, DMSO-d6) δ 8.57 (d, *J* = 8.2 Hz, 2 H), 8.46 (d, *J* = 2.1 Hz, 1 H), 8.20 (dd, *J* = 9.0 and 2.2 Hz, 1 H), 8.08 (d, *J* = 8.9 Hz, 1 H), 7.92 (d, *J* = 8.4 Hz, 2 H), 7.80 (d, *J* = 7.2 Hz, 2 H), 7.52 (t, *J* = 7.6 Hz, 2 H), 7.43 (t, *J* = 7.4 Hz, 1 H), 6.40 (s, 1 H), 4.30 (q, *J* = 7.1 Hz, 4 H), 1.23 (t, *J* = 7.1 Hz, 6 H). $^{13}C\{^1H\}$ (150 MHz, DMSO-d6) δ 166.9, 163.3, 159.1, 149.7, 143.3, 139.7, 138.6, 135.9, 131.5, 129.6, 129.1, 128.6, 127.9, 127.6, 127.3, 123.5, 121.5, 62.3, 57.3, 14.4. HRMS (ESI) calcd. for $C_{27}H_{24}BrN_2O_4$ $(M + H)^+$ 519.0914, found 519.0929 and 521.0912.

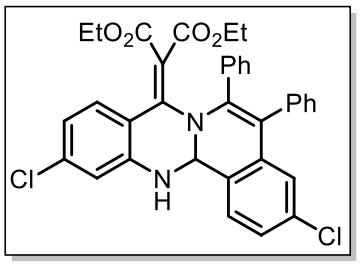
General procedure for the synthesis of 5a-5c: To an oven-dried pressure tube containing a magnetic bar was added 4-Methylene substituted tetrahydroquinazoline derivative **3** (0.2 mmol, 1 equiv.), diphenylacetylene derivative (0.4 mmol, 2 equiv.), $[Ru(p\text{-cymene})Cl_2]_2$ (0.01 mmol, 0.05 equiv.), $Cu(OAc)_2.H_2O$ (0.02 mmol, 0.1 equiv.), and ^{t}AmOH. The reaction mixture was stirred in an oil bath preheated at 120 °C for 24 h. After completion of the reaction (monitored by TLC analysis), the reaction mixture was cooled to ambient temperature, filtered through a small plug of Celite and then washed with ethyl acetate (3 × 10 mL). The solvents

were evaporated under reduced pressure and the crude material was purified using column chromatography on silica gel (n-hexane/EtOAc eluent) to give the desired product.

Typical procedure for the synthesis of 5a: To an oven-dried pressure tube containing a magnetic bar was added diethyl 2-(7-chloro-2-(4-chlorophenyl)-2,3-dihydroquinazolin-4(1H)-ylidene)malonate **3bb** (87 mg, 0.2 mmol), diphenylacetylene (71mg, 0.4 mmol), [Ru(p-cymene)Cl_2]$_2$ (6 mg, 0.01 mmol), Cu(OAc)$_2$.H_2O (4 mg, 0.02 mmol), and ^{t}AmOH (2 mL). The reactions mixture was stirred in an oil bath preheated at 120 °C for 24 h. After completion of the reaction (monitored by TLC analysis), the reaction mixture was cooled to ambient temperature, filtered through a small plug of Celite and then washed with ethyl acetate (3 × 10 mL). The solvents were evaporated under reduced pressure and the crude material was purified using column chromatography on silica gel (n-hexane/EtOAc eluent) to give the desired product **5a**.

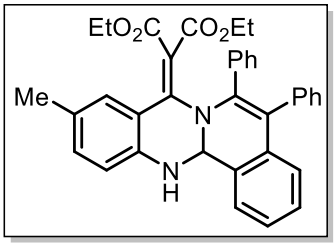
Diethyl 2-(3,11-dichloro-5,6-diphenyl-13,13a-dihydro-8*H*-isoquinolino[1,2-*b*]quinazolin-8-ylidene)malonate (5a):

Off white solid; R_f (hexane/EtOAc, 9:1) 0.50; mp 228-230 °C. Yield 62 mg, 51%; IR (KBr, neat) ν 3340, 1744, 1710, 1604, 1571, 1445, 1248, 1091, 1014, 817, 695 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 -7.54 (m, 2 H), 7.49 (d, *J* = 8.2 Hz, 1 H), 7.39-7.37 (m, 2 H), 7.30-7.24 (m, 4 H), 7.23-7.20 (m, 3 H), 7.12-7.11 (m, 3 H), 6.75 (d, *J* = 8.2 Hz, 1 H), 5.49 (s, 1 H), 4.70 (s, 1 H), 4.32-4.22 (m, 2 H), 4.20-4.14 (m, 1 H), 4.06-4.01 (m, 1 H), 1.18 (t, *J* = 7.1 Hz, 3 H), 1.07 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 168.2, 167.1, 153.7, 152.5, 143.8, 141.0, 138.7, 136.6, 134.77, 134.75, 133.0, 132.2, 132.0, 130.8, 130.6, 129.2, 128.4, 127.5, 127.4, 127.1, 126.9, 120.2, 116.6, 109.9, 68.6, 62.3, 61.8, 61.8, 14.2, 14.0. HRMS (ESI) calcd. for $C_{35}H_{29}Cl_2N_2O_4$ $(M + H)^+$ 611.1499, found 611.1509 and 613.1488.

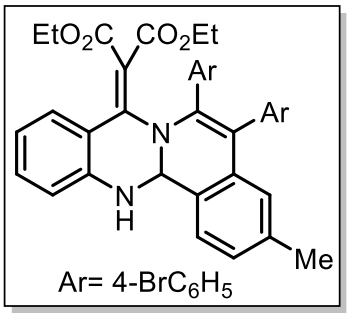


Diethyl 2-(10-methyl-5,6-diphenyl-13,13a-dihydro-8*H*-isoquinolino[1,2-*b*]quinazolin-8-ylidene)malonate (5b):

Off white solid; R_f (hexane/EtOAc, 9:1) 0.50; mp 178-180 °C. Yield 66 mg, 63%; IR (KBr, neat) ν 3346, 1739, 1707, 1621, 1577, 1446, 1256, 1095, 1024, 839, 696 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.64-7.63 (m, 2 H), 7.42-7.37 (m, 8 H), 7.35 (dd, *J* = 7.3 and 2.1 Hz, 1 H), 7.28-7.26 (m, 1 H), 7.16-7.13 (m, 3 H), 6.84 (s, 1 H), 6.65 (d, *J* = 1.3 Hz, 1 H), 5.57 (s, 1 H), 4.65 (s, 1 H), 4.38-4.32 (m, 2 H), 4.20-4.15 (m, 1 H), 4.05-4.00 (m, 1 H), 2.36 (s, 3 H), 1.27 (t, *J* = 7.1 Hz, 3 H), 1.06 (t, *J* = 7.1 Hz, 3 H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 168.5, 167.5, 153.2, 149.5, 144.3, 141.9, 140.9, 138.7, 138.2, 137.6, 131.6, 131.4, 130.9, 129.6, 129.1, 128.7, 128.5, 128.5, 128.1, 127.4, 127.3, 127.0, 115.3, 113.9, 110.6, 68.7, 62.9, 62.0, 61.5, 22.8, 14.3, 14.0. HRMS (ESI) calcd. for $C_{36}H_{33}N_2O_4$ $(M + H)^+$ 557.2435, found 557.2427.

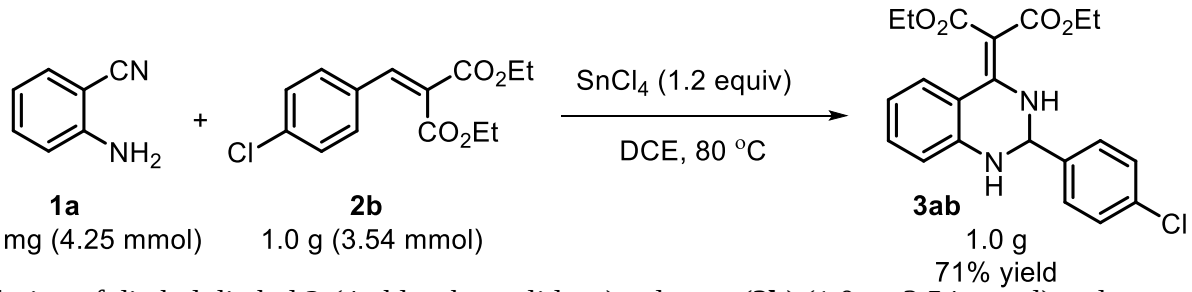


Diethyl 2-(5,6-bis(4-bromophenyl)-3-methyl-13,13a-dihydro-8*H*-isoquinolino[1,2-*b*]quinazolin-8-ylidene)malonate (5c):



Off white solid; R_f (hexane/EtOAc, 9:1) 0.50; mp 232-234 °C. Yield 81 mg, 57%; IR (KBr, neat) ν 3343, 1732, 1710, 1618, 1579, 1458, 1247, 1096, 1020, 830, 696 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.8 Hz, 2 H), 7.47 (d, *J* = 7.6 Hz, 2 H), 7.41 (t, *J* = 7.8 Hz, 1 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.23-7.17 (m, 5 H), 7.13 (d, *J* = 8.0 Hz, 1 H), 6.96 (d, *J* = 8.3 Hz, 1 H), 6.79 (d, *J* = 7.5 Hz, 1 H), 5.50 (s, 1 H), 4.70 (s, 1 H), 4.33-4.27 (m, 2 H), 4.18-4.13 (m, 1 H), 4.03-3.97 (m, 1 H), 2.39 (s, 3 H), 1.24 (t, *J* = 7.0 Hz, 3 H), 1.04 (t, *J* = 7.1 Hz, 3 H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 168.3, 167.3, 154.2, 148.0, 144.8, 139.4, 138.7, 137.2, 136.7, 135.2, 133.08, 133.05, 132.5, 132.03, 132.00, 131.8, 130.8, 129.0, 128.94, 128.91, 122.0, 121.8, 115.4, 115.3, 109.2, 68.7, 62.8, 62.1, 61.6, 21.5, 14.4, 14.0. HRMS (ESI) calcd. for $C_{36}H_{31}Br_2N_2O_4$ $(M + H)^+$ 713.0645, found 713.0648 and 715.0640.

Experimental Procedure for the Gram-Scale Reaction:



1a 502 mg (4.25 mmol)

2b 1.0 g (3.54 mmol)

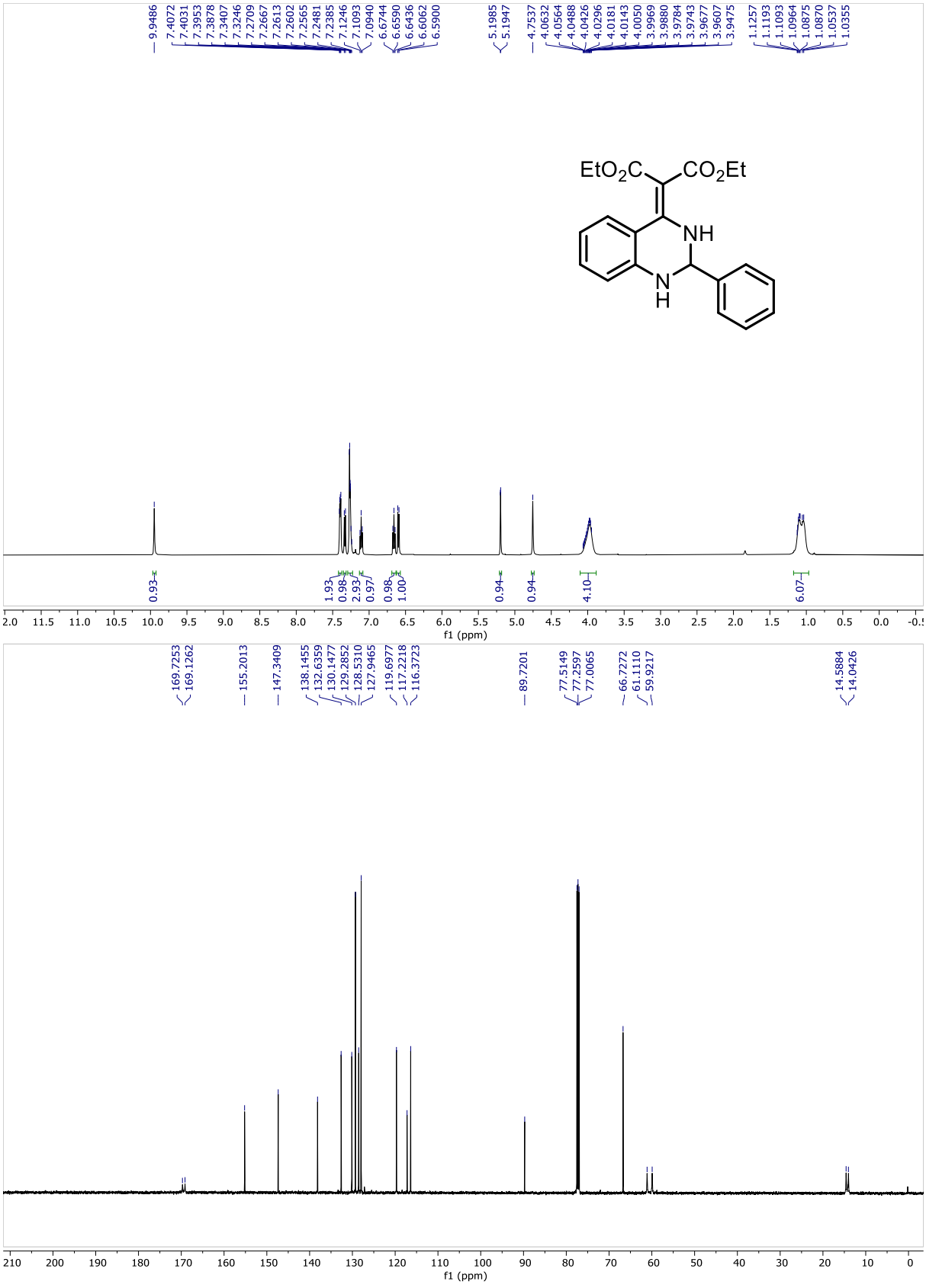
3ab 1.0 g 71% yield

To a solution of diethyl diethyl 2-(4-chlorobenzylidene)malonate (**2b**) (1.0 g., 3.54 mmol) and 2-aminobenzonitrile (502 mg, 4.25 mmol) in 1,2-dichloroethane (12 ml) was added $SnCl_4$ (0.5 mL,4.25 mmol) at 0 ^oC under nitrogen atmosphere. The reaction was then refluxed at 80 ^oC for 30 min. After completion of the reaction, the solvent was removed under reduced pressure and diluted with saturated $NaHCO_3$ solution. Then the organic layer was extracted with EtOAc (3x10 mL). The organic layer was further washed with brine solution for 2-3 times. The combined organic layers were dried over Na_2SO_4 and concentrated in rotary evaporator. The crude was subjected to column chromatography over silica gel to give the corresponding product **3ab** with 71% yield (1.0 g, yellow solid).

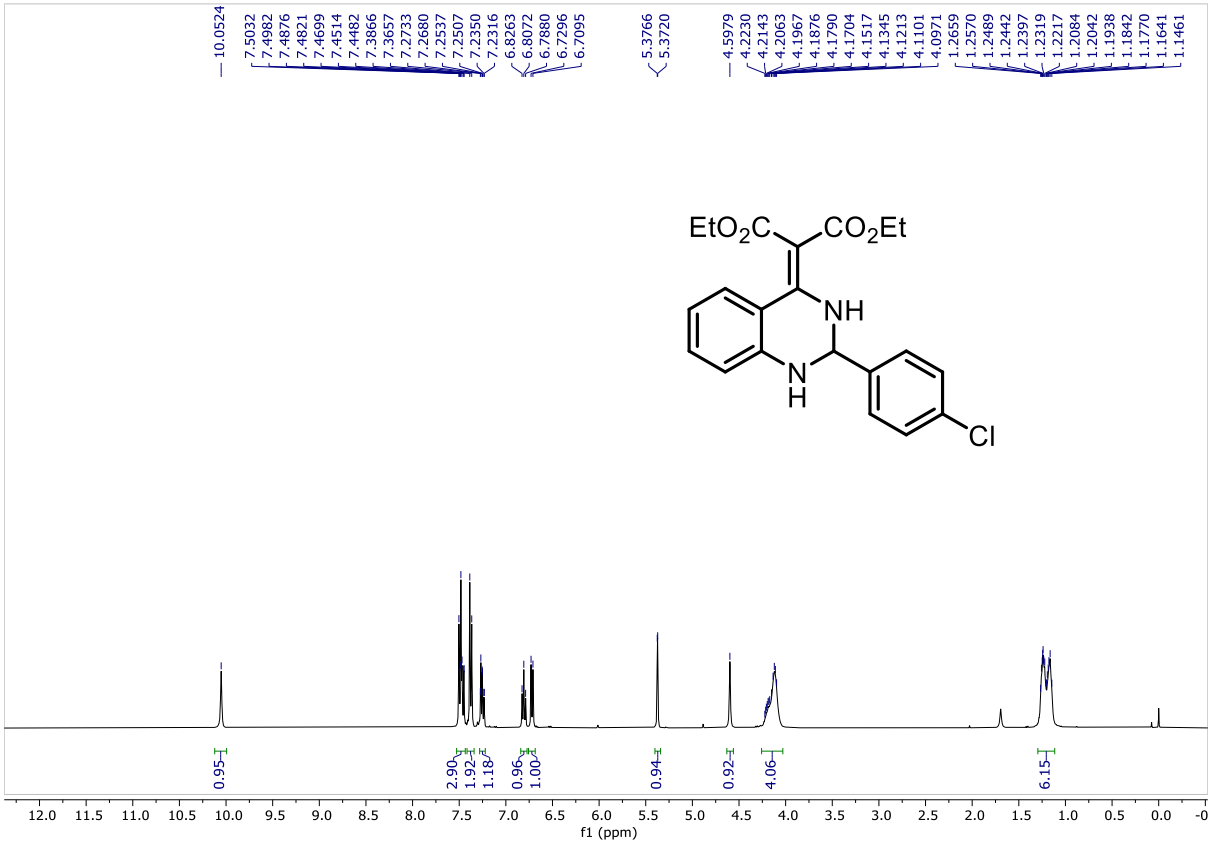
References:

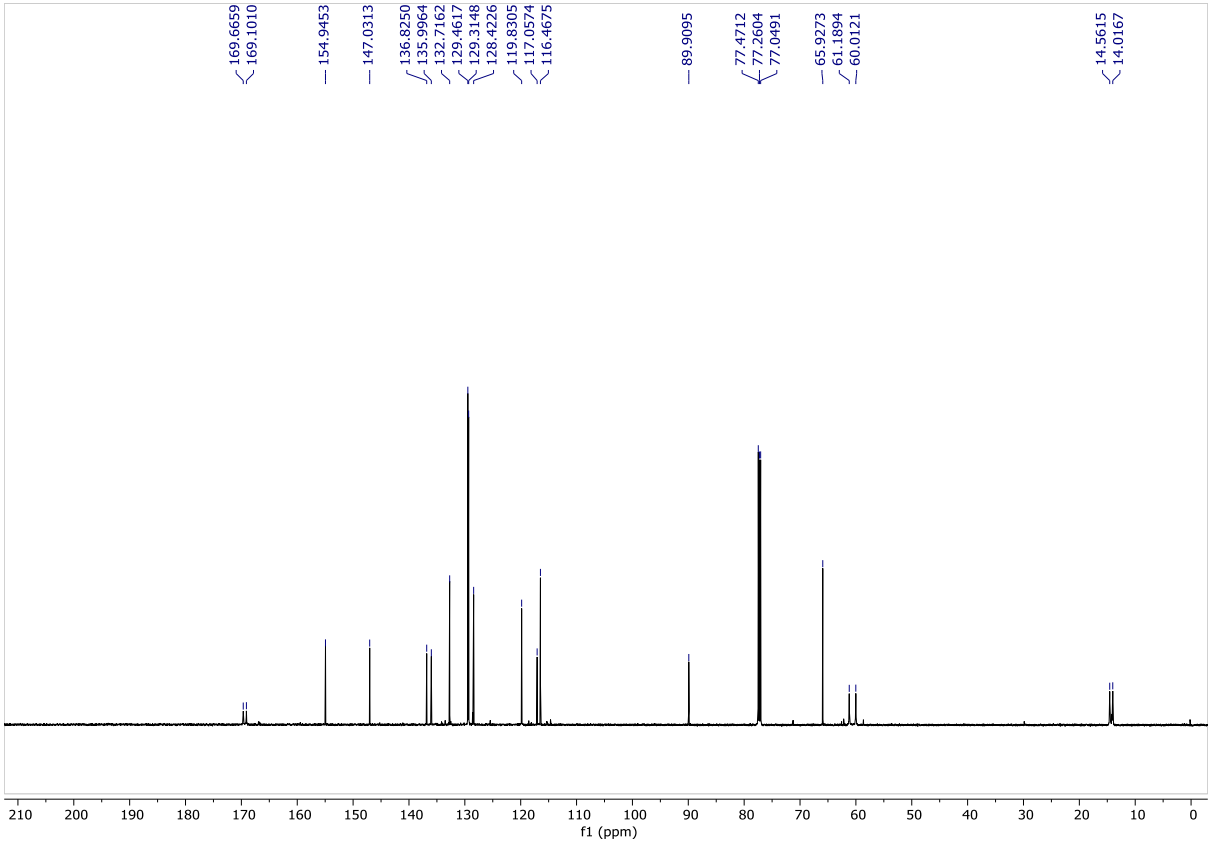
1. (a) P. Tang, Y. Y. Wei, L. Wen, H. J. Ma, Y. Yang and Y. Jiang, *J. Org. Chem.* 2022, **87**, 10890; (b) I. A. Andreev, N. K. Ratmanova, A. U. Augustin, O. A. Ivanova, I. I. Levina, V. N. Khrustalev, D. B. Werz and I. V. Trushkov, *Angew. Chem. Int. Ed.* 2021, **60**, 7927; (c) A. Sperga, A. Kazia, and J. Veliks, *Org. Biomol. Chem.* 2021, **19**, 2688; (d) A. Krech, V. Yakimchyk, T. Jarg, D. Kananovich, and M. Ošeka, *Adv. Synth. Catal.* 2024, **366**, 91; (e) S. R. Mangaonkar, and F. V. Singh, *Synthesis*. 2019, **51**, 4473.
2. (a) Y. Moussaoui and R. B. Salem, *C R Chim.* 2007, **10**, 1162; (b) J. Wang, Y. Zhou, L. Zhang, Z. Li, X. Chen and H. Liu, *Org. Lett.* 2013, **15**, 1508; (c) H. Chen, Y. Li, C. Sheng, Z. Lv, G. Dong, T. Wang, J. Liu, M. Zhang, L. Li, T. Zhang and D. Geng, *J. Med. Chem.* 2013, **56**, 685; (d) N. A. Sitte, L. Köring, P. W. Roesky and J. Paradies, *Org. Biomol. Chem.* 2020, **18**, 7321.

^{1}H ($CDCl_3$, 500 MHz) and ^{13}C{^{1}H} ($CDCl_3$, 150 MHz) spectra of compound (3aa):

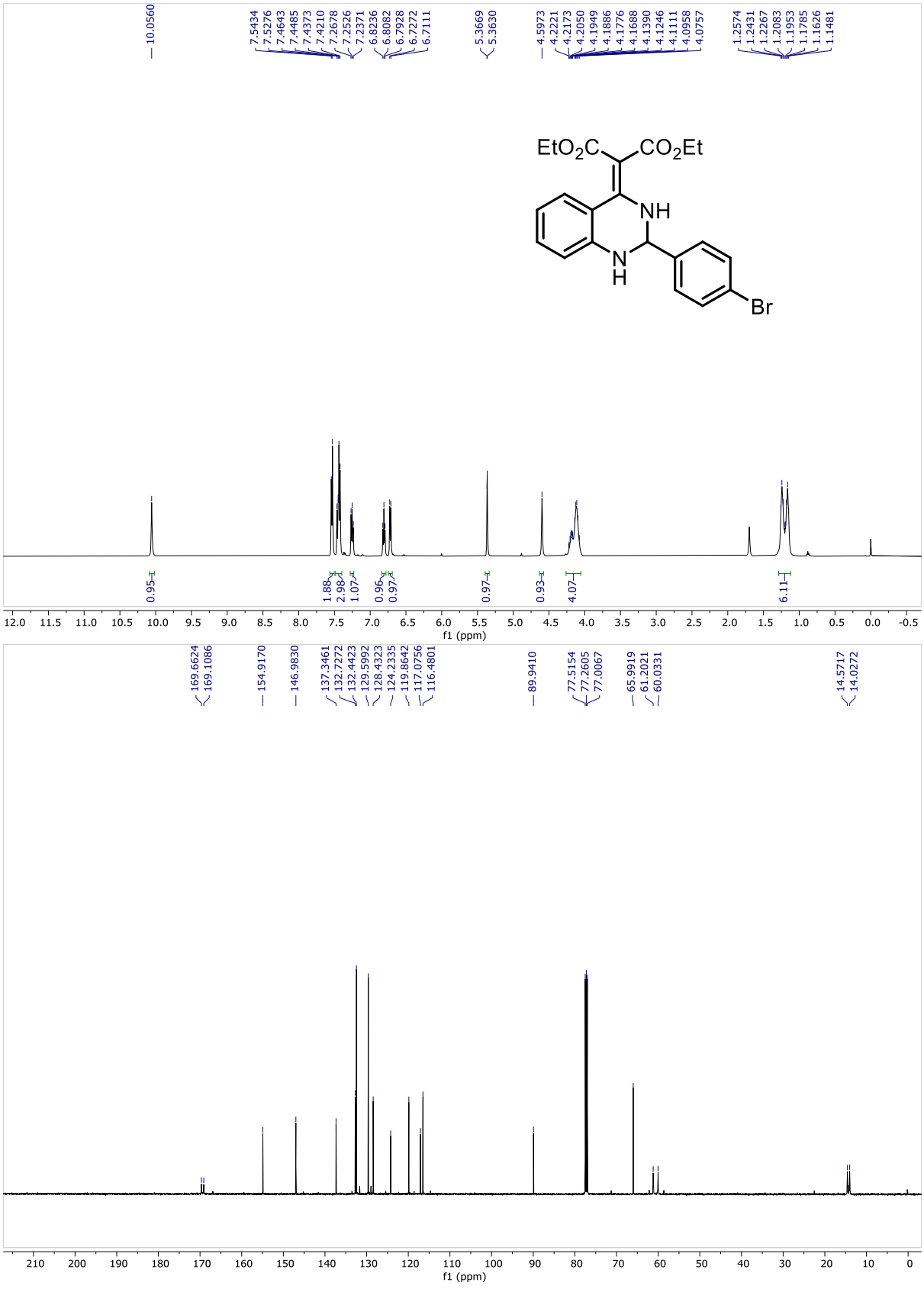


^{1}H ($CDCl_3$, 400 MHz) and ^{13}C{^{1}H} ($CDCl_3$, 150 MHz) spectra of compound (3ab):

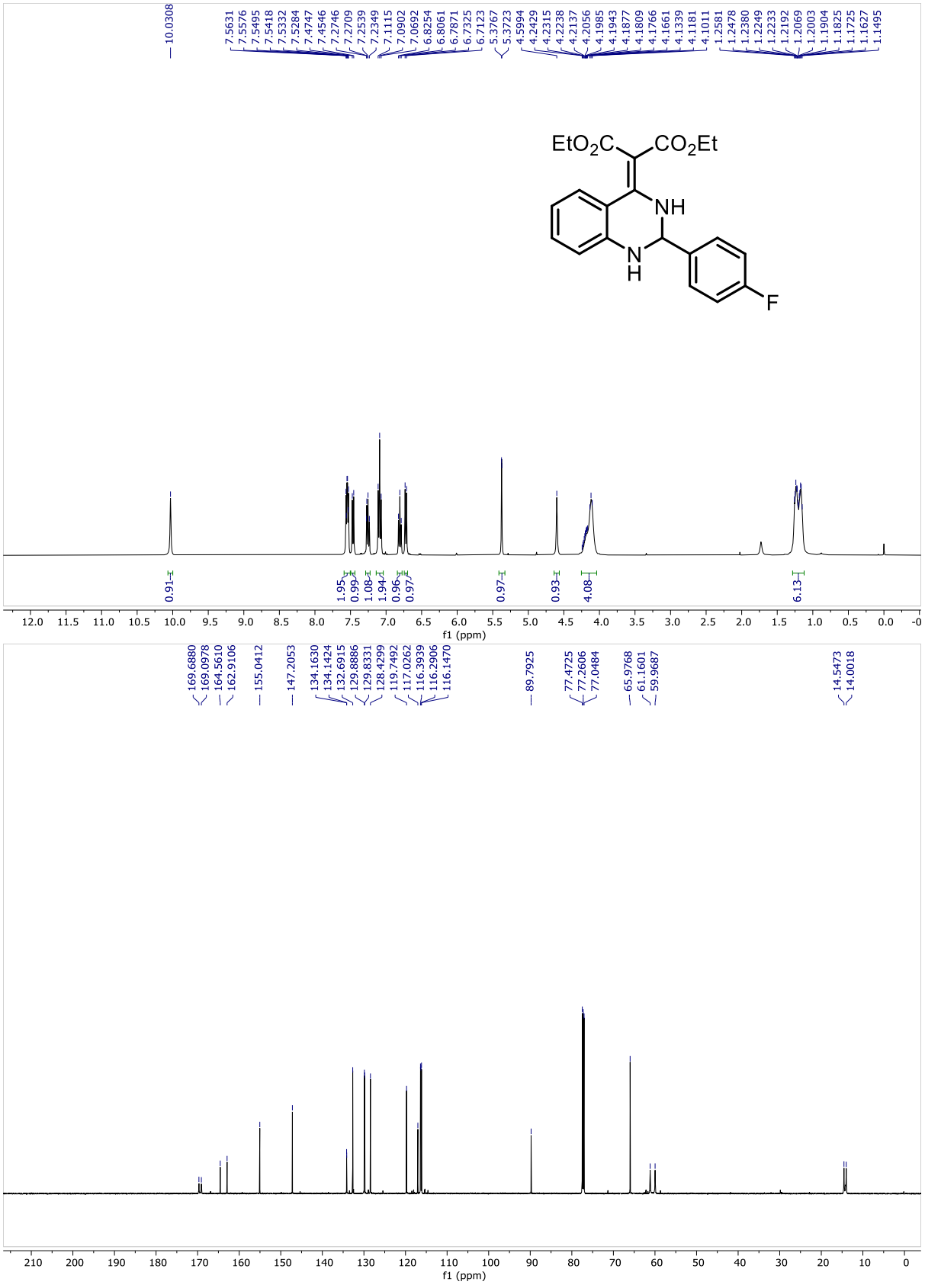




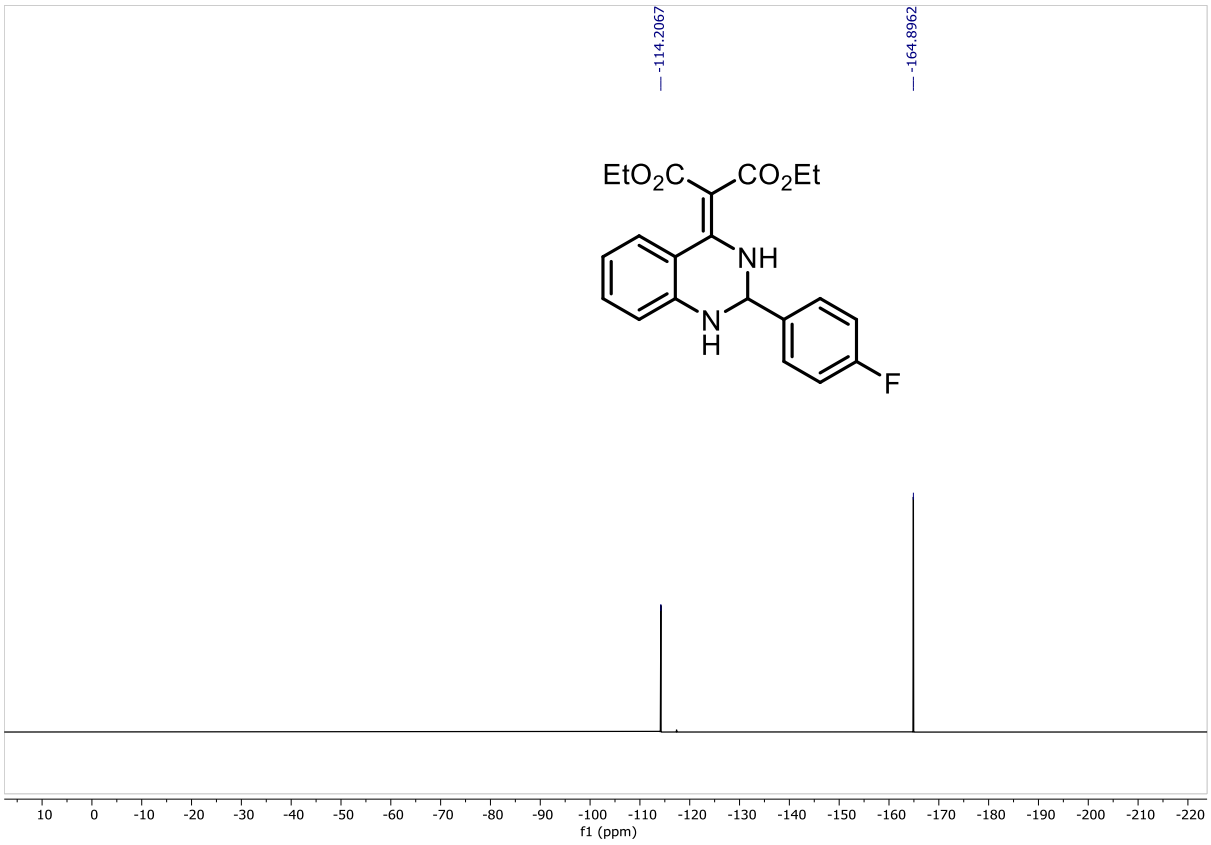
^{1}H ($CDCl_3$, 500 MHz) and ^{13}C{^{1}H} ($CDCl_3$, 125 MHz) spectra of compound (3ac):



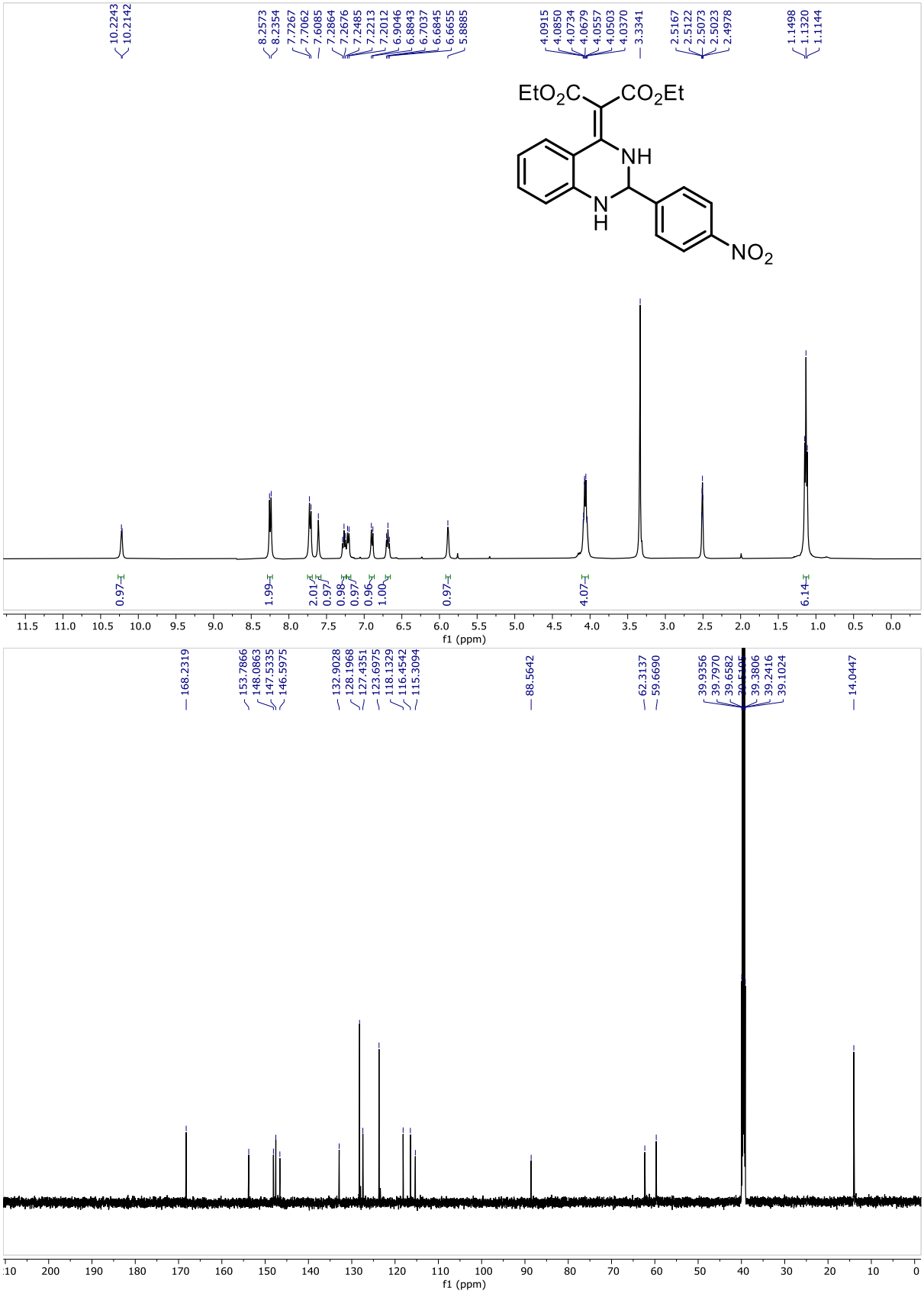
^{1}H ($CDCl_3$, 400 MHz) and ^{13}C{^{1}H} ($CDCl_3$, 150 MHz) spectra of compound (3ad):



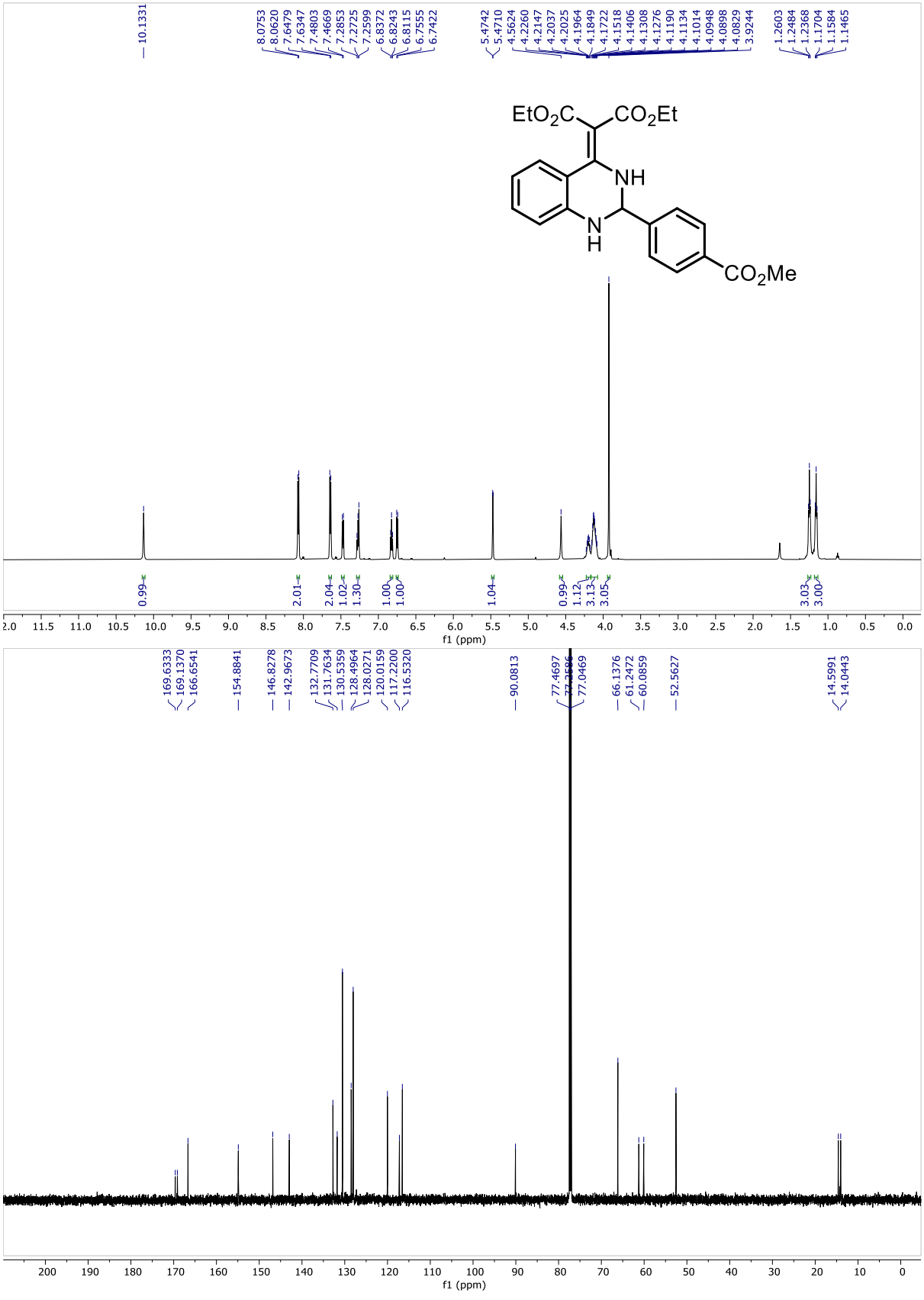
^{19}F (470 MHz, C_6F_6/$CDCl_3$) spectrum of compound (3ad):



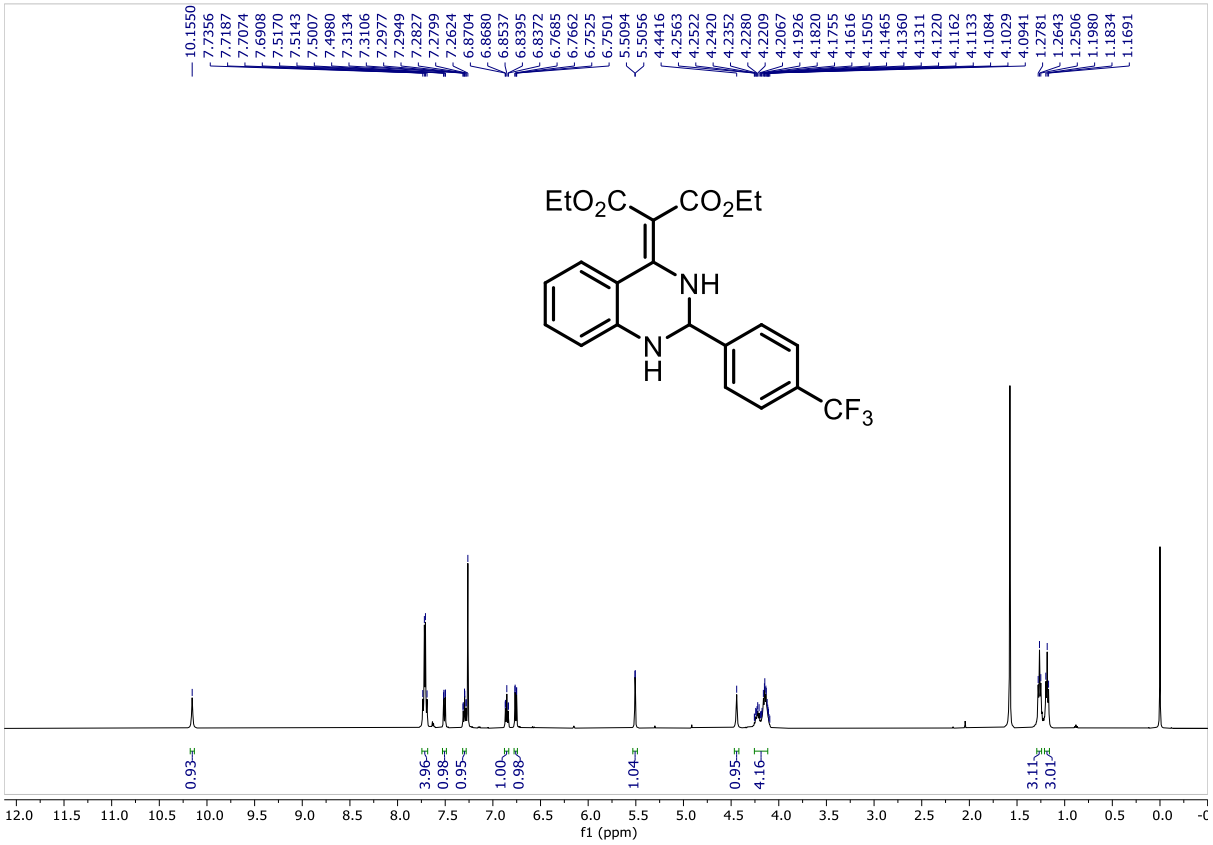
^{1}H (DMSO-d$_6$, 400 MHz) and ^{13}C{^{1}H} (DMSO-d$_6$, 150 MHz) spectra of compound (3ae):

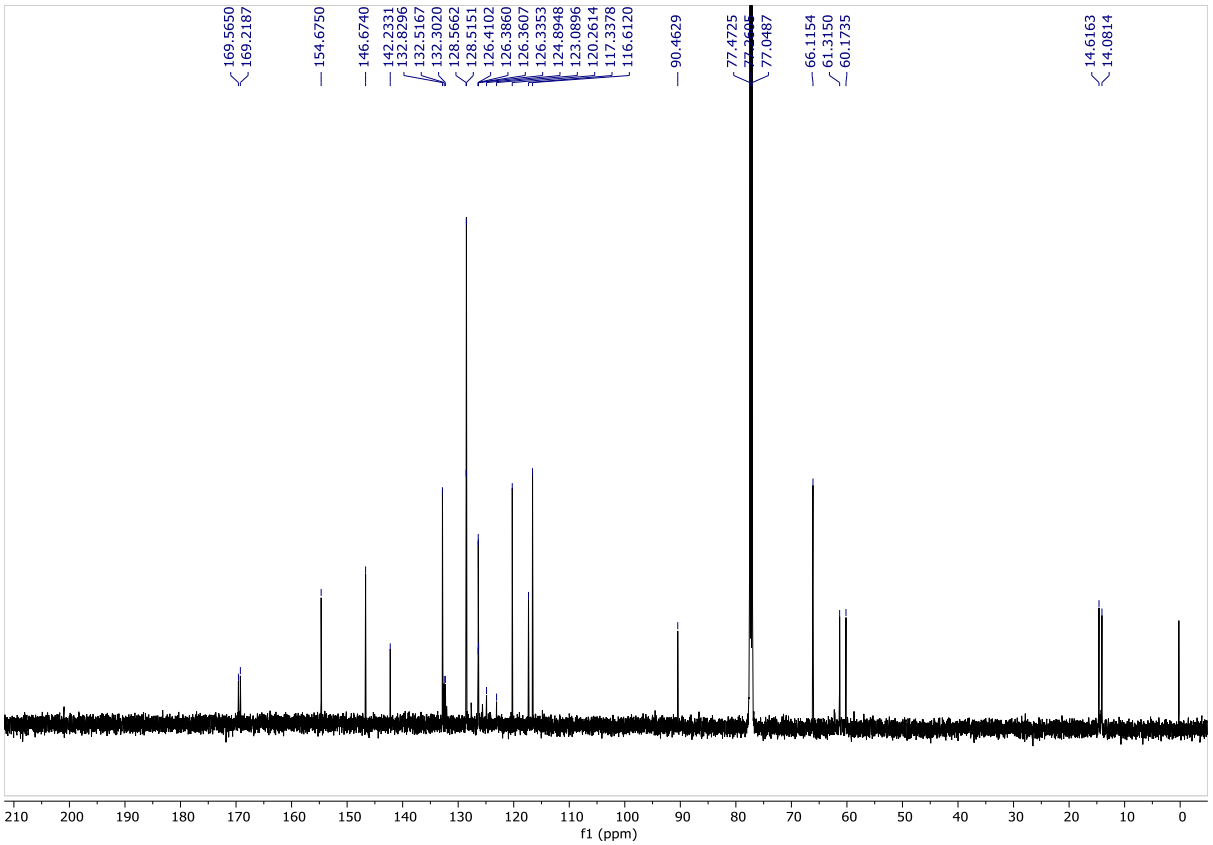


^{1}H ($CDCl_3$, 600 MHz) and ^{13}C{^{1}H} ($CDCl_3$, 150 MHz) spectra of compound (3af):

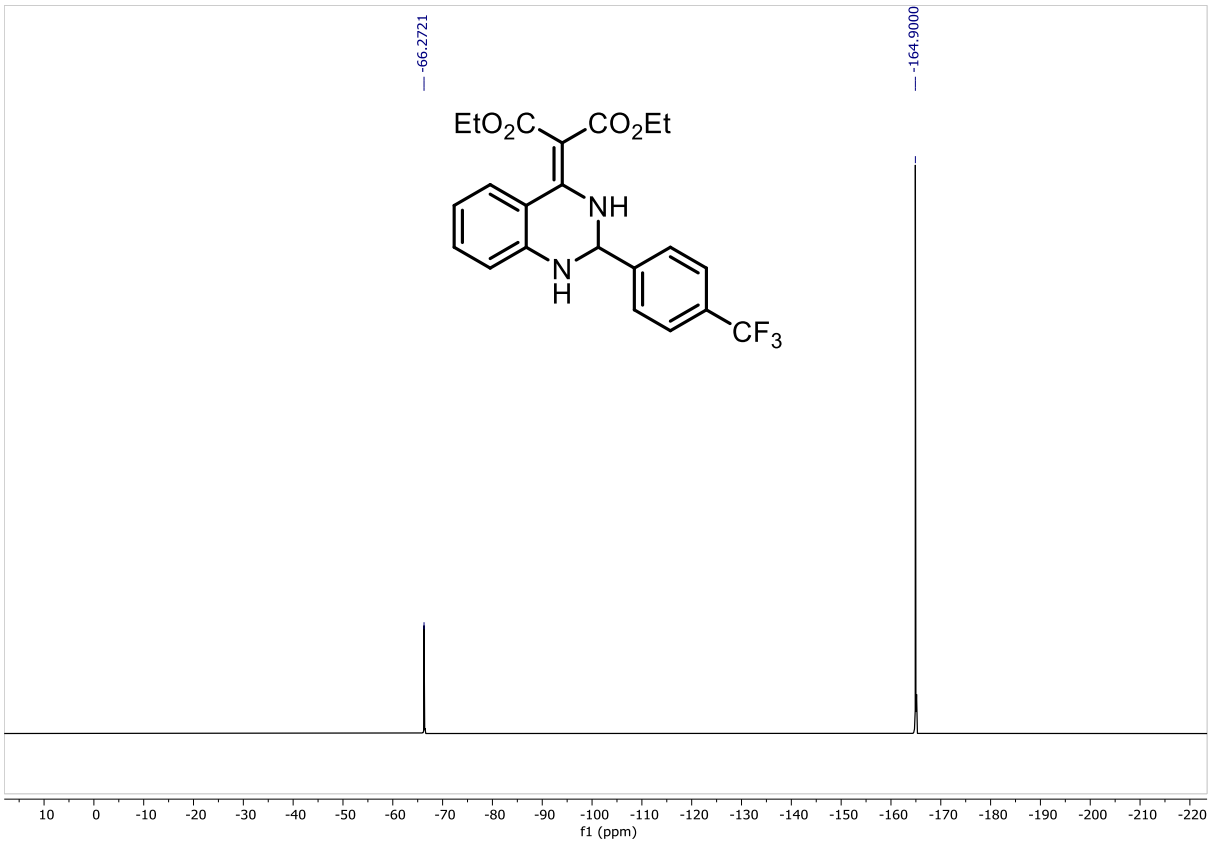


^{1}H ($CDCl_3$, 500 MHz) and ^{13}C{^{1}H} ($CDCl_3$, 150 MHz) spectra of compound (3ag):

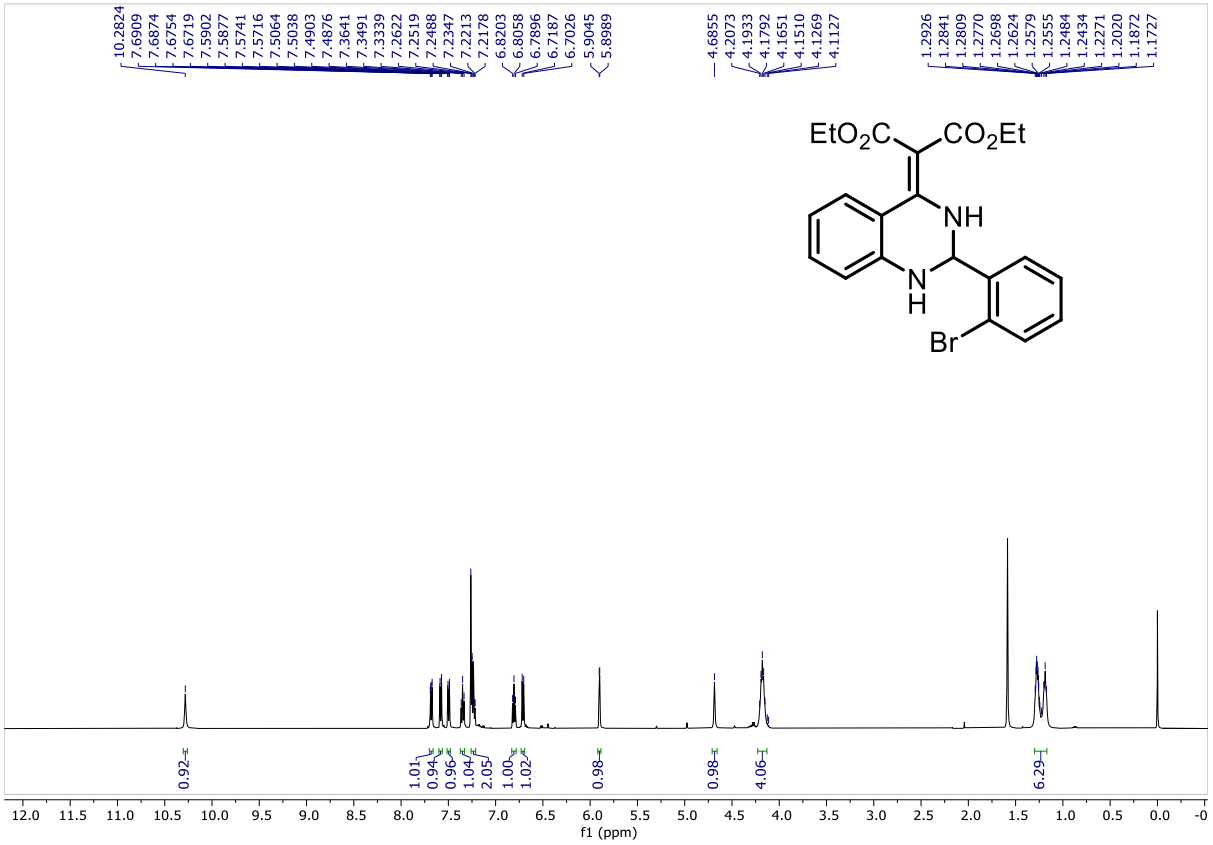


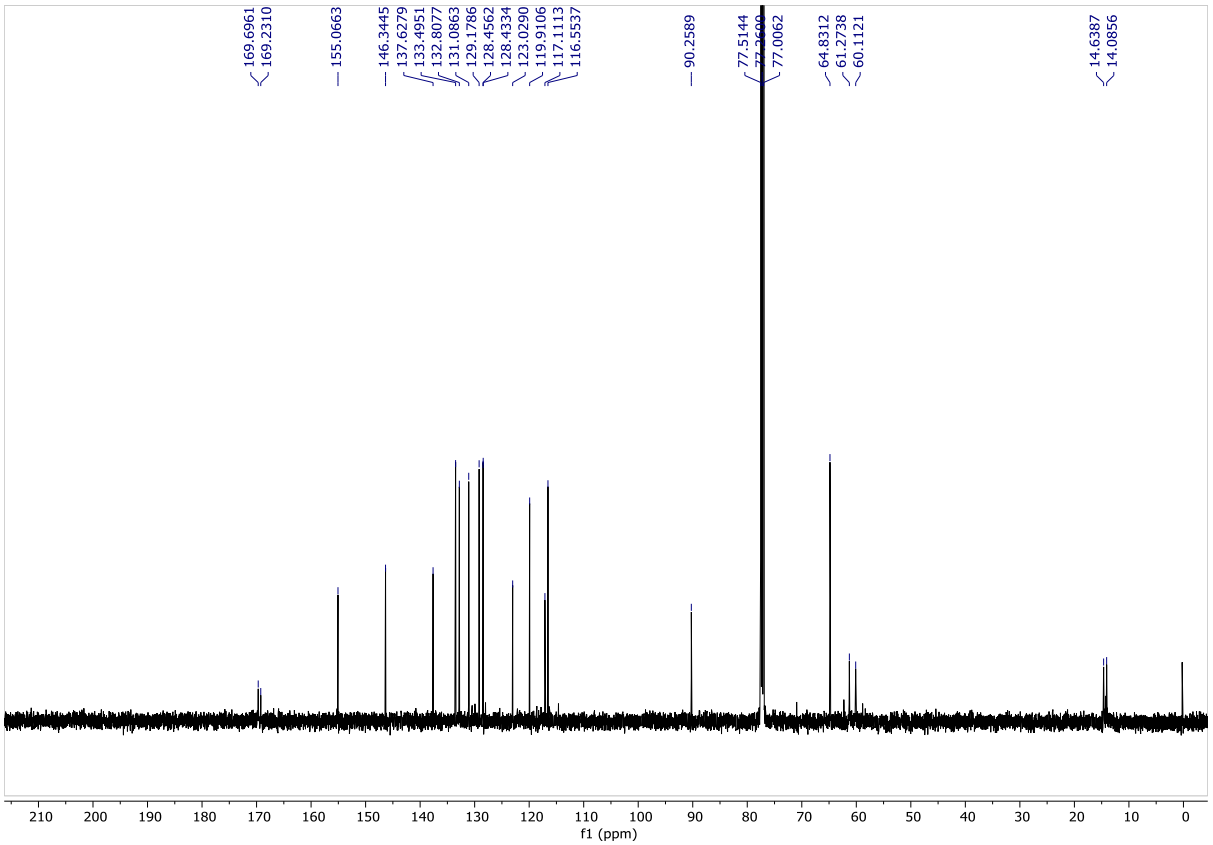


^{19}F (470 MHz, C_6F_6/$CDCl_3$) spectrum of compound (3ag):

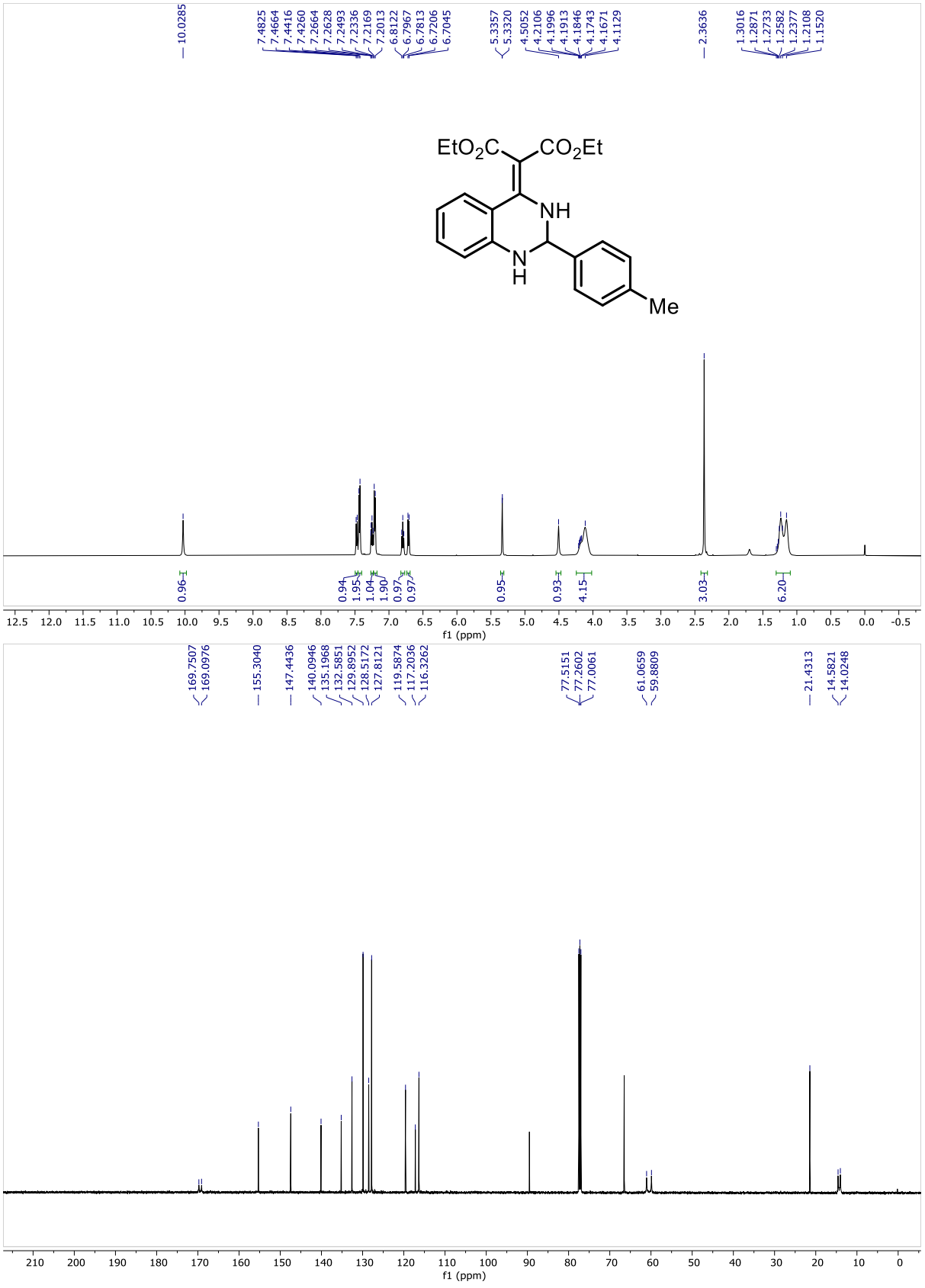


^{1}H ($CDCl_3$, 500 MHz) and ^{13}C{^{1}H} ($CDCl_3$, 125 MHz) spectra of compound (3ah):

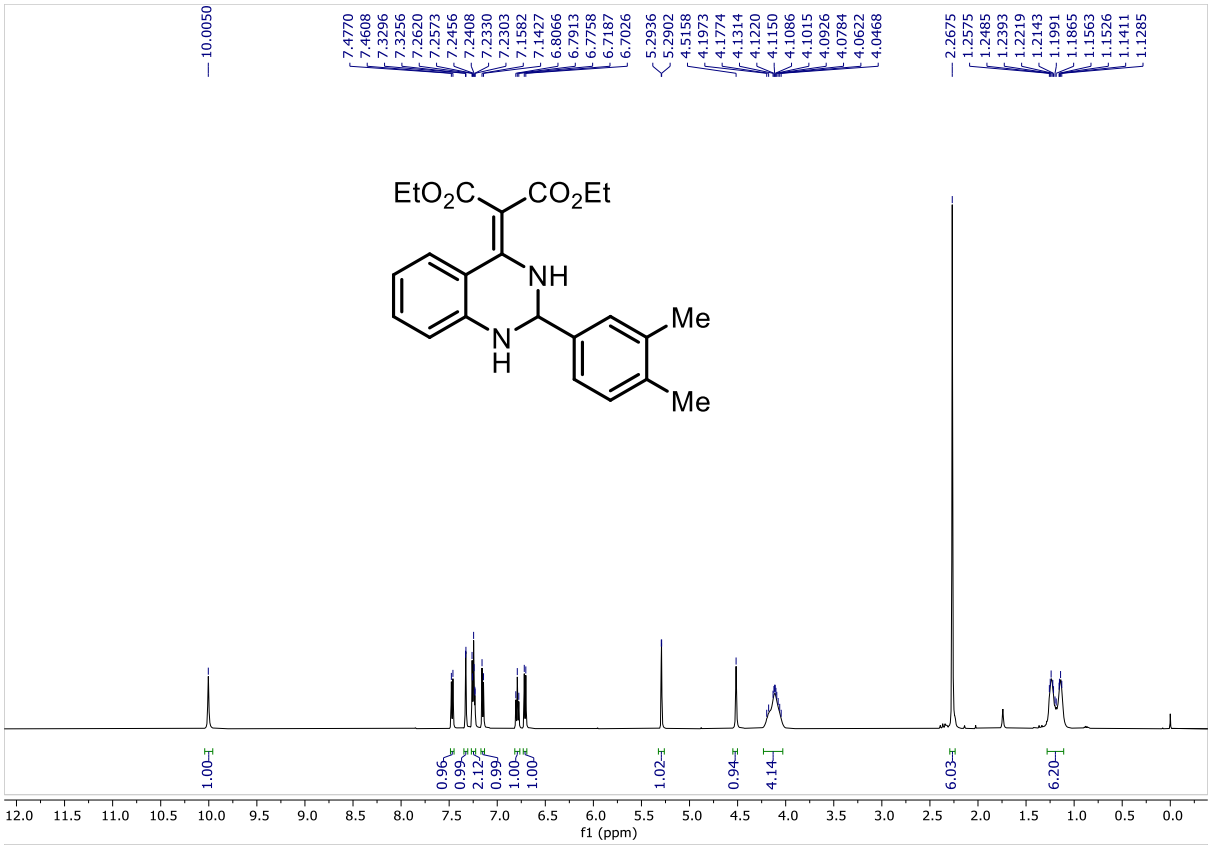


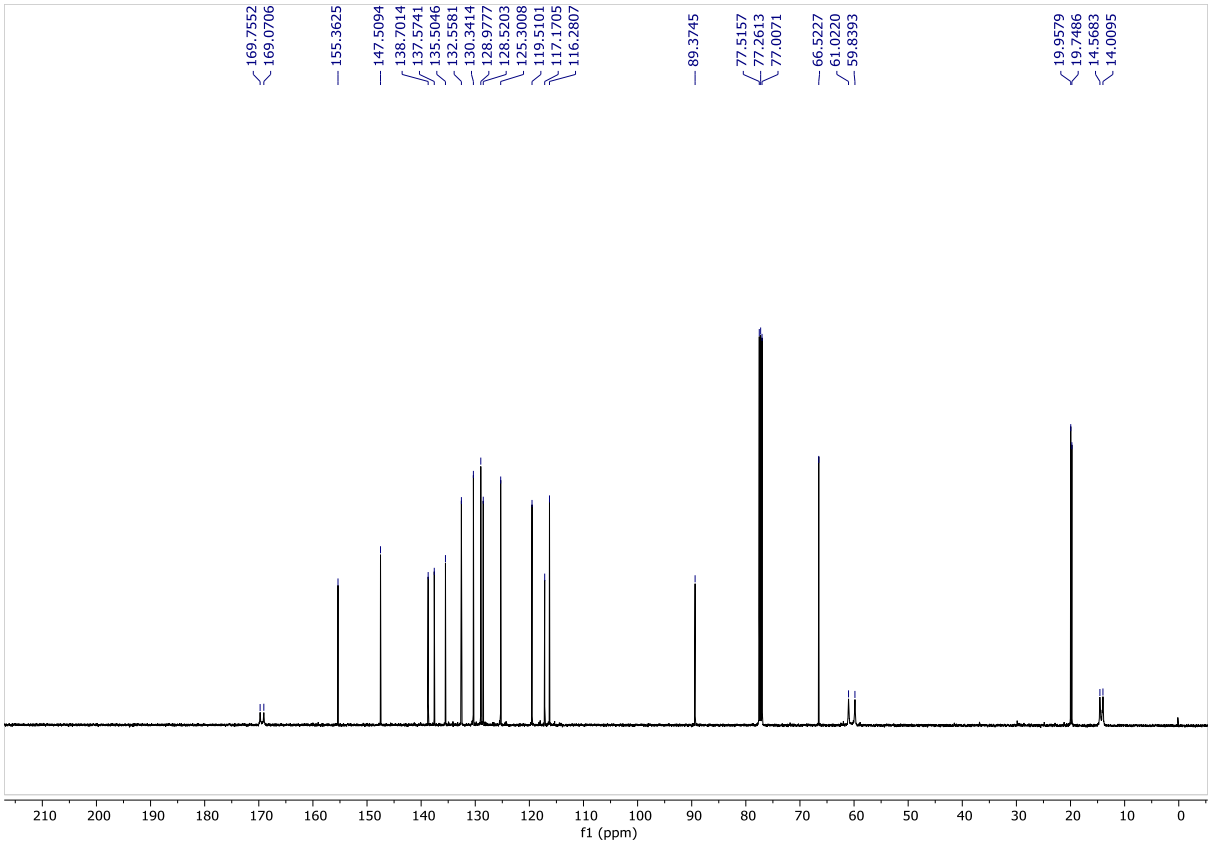


^{1}H ($CDCl_3$, 500 MHz) and ^{13}C{^{1}H} ($CDCl_3$, 125 MHz) spectra of compound (3ai):

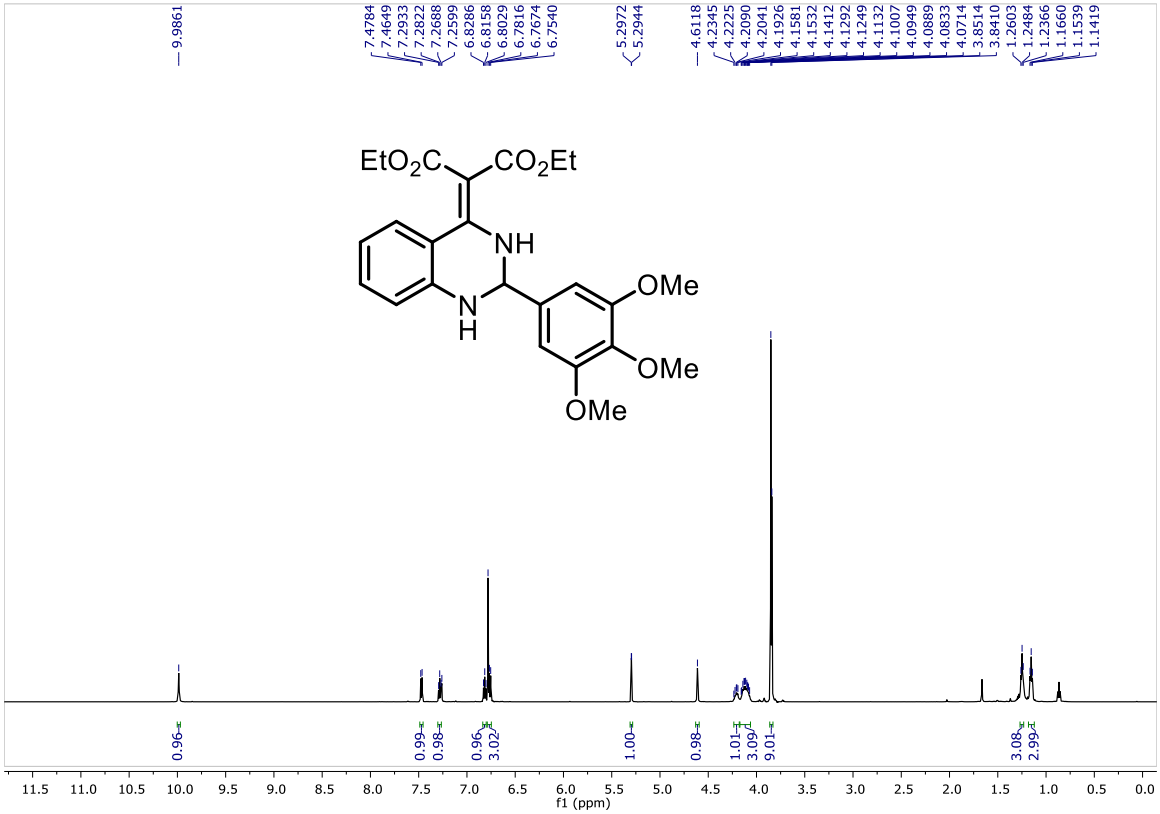


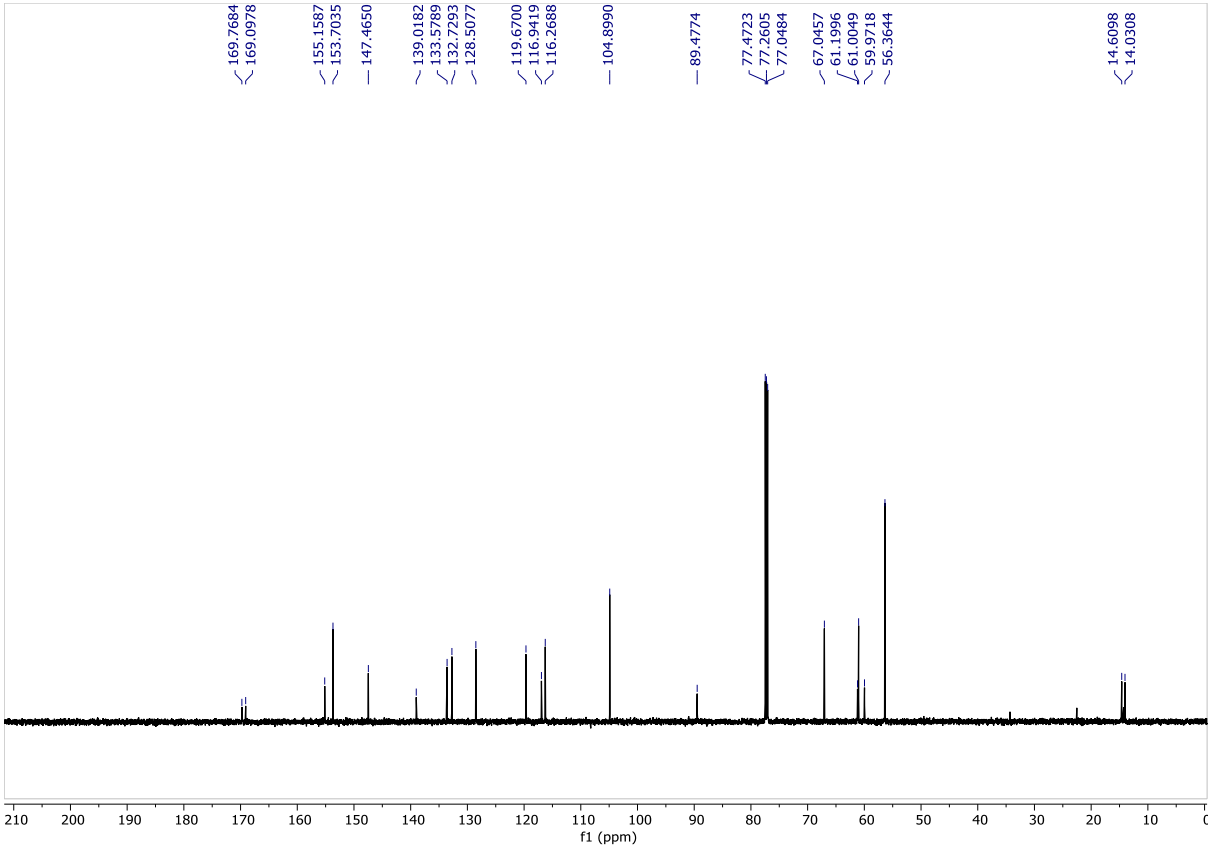
^{1}H ($CDCl_3$, 500 MHz) and ^{13}C{^{1}H} ($CDCl_3$, 125 MHz) spectra of compound (3aj):



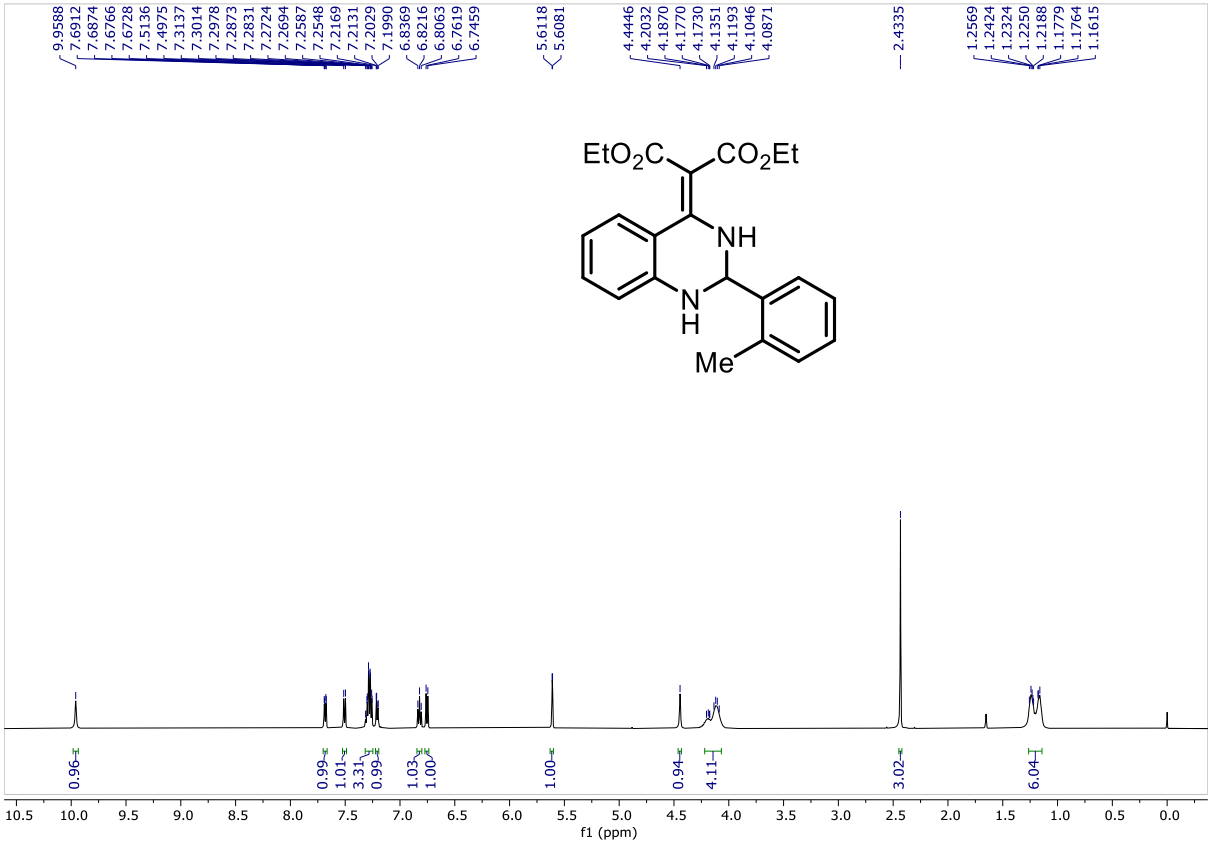


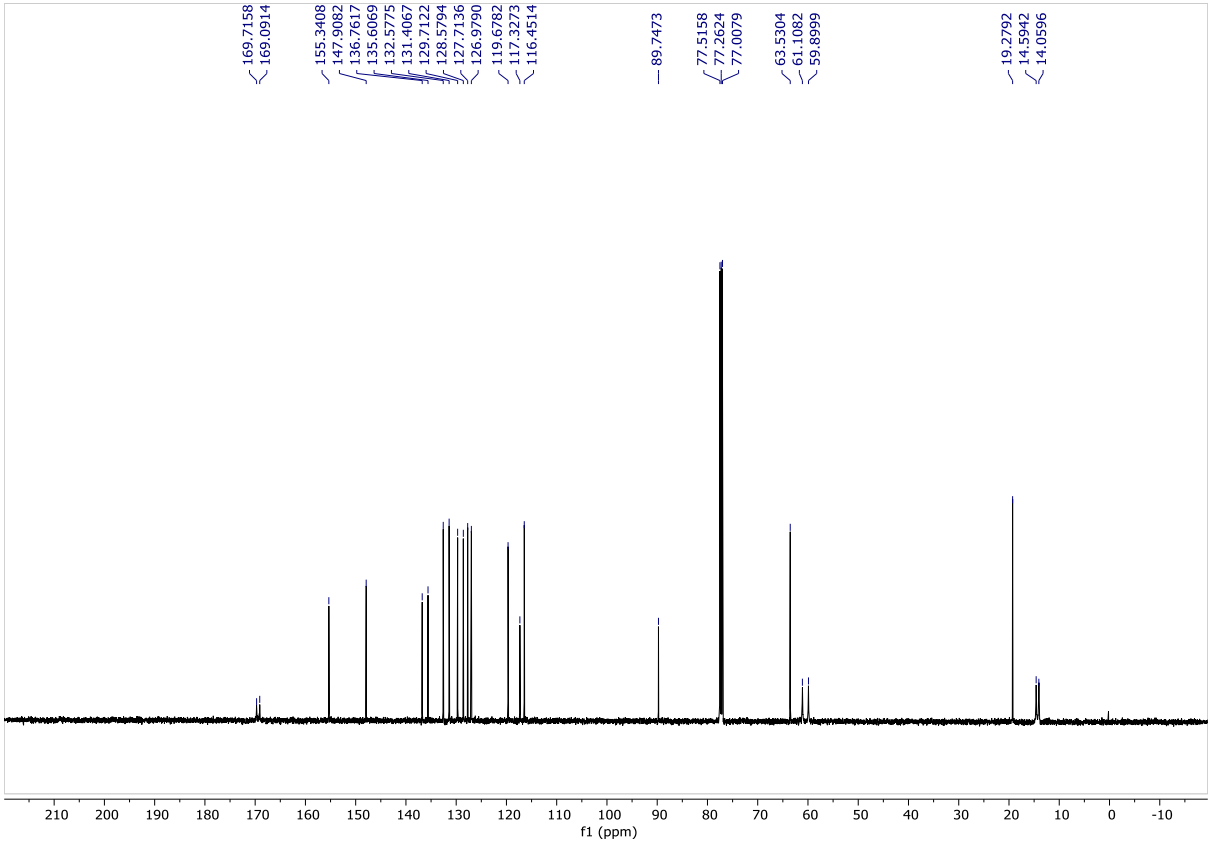
^{1}H ($CDCl_3$, 600 MHz) and $^{13}C\{^{1}H\}$ ($CDCl_3$, 150 MHz) spectra of compound (3ak):



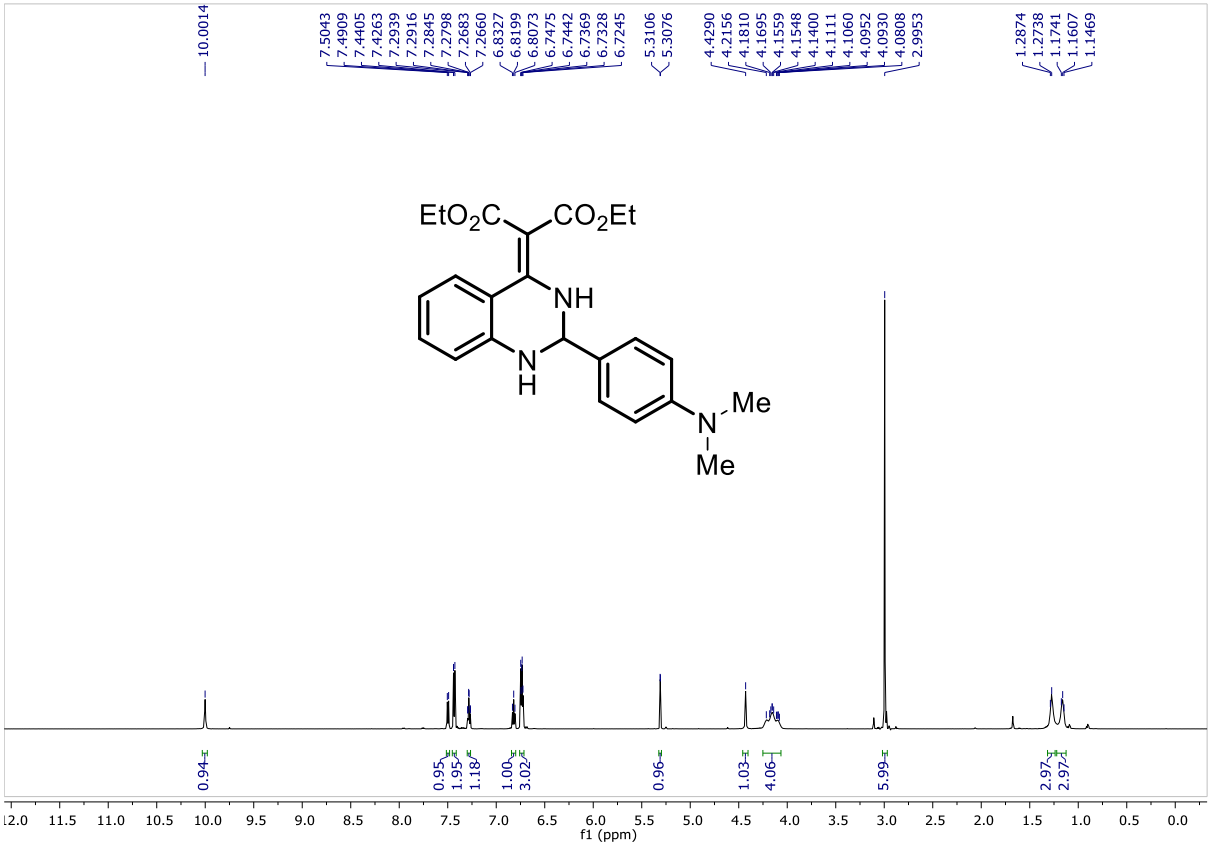


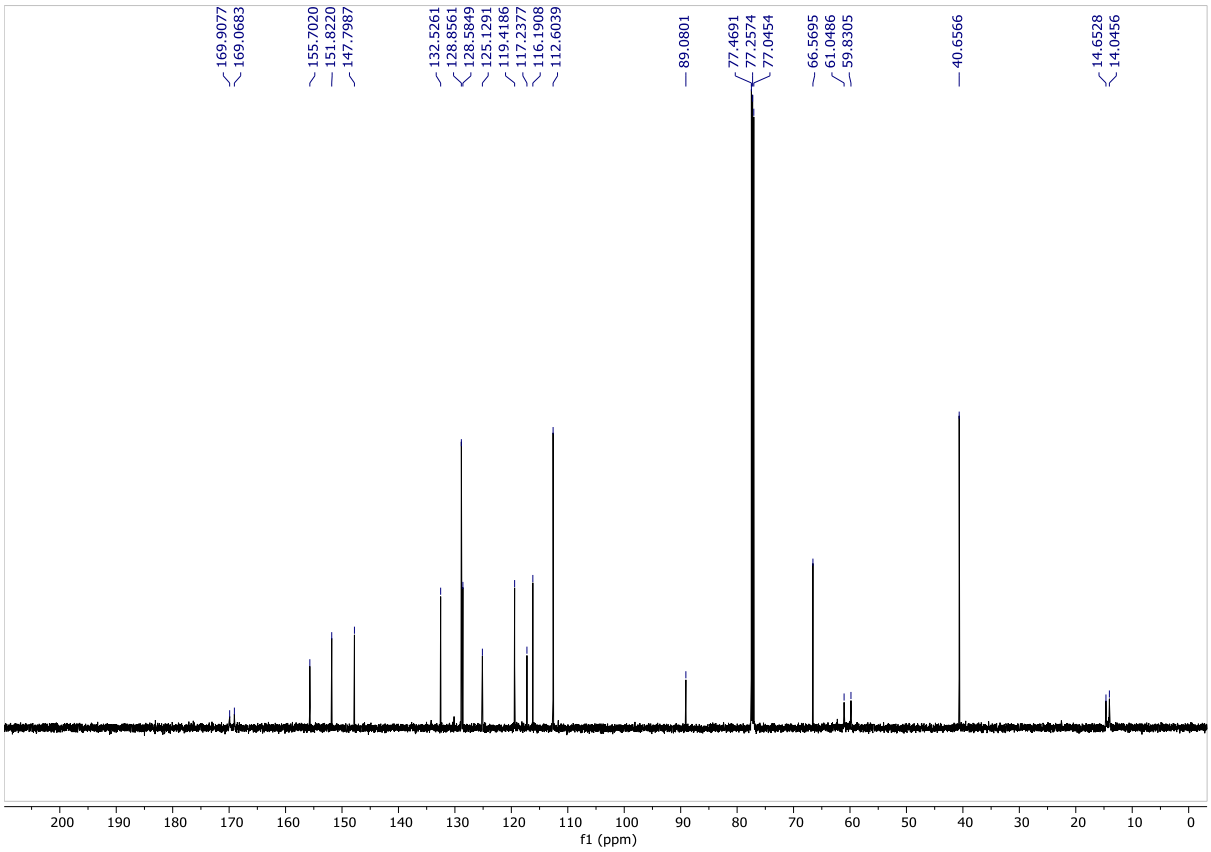
^{1}H ($CDCl_3$, 500 MHz) and ^{13}C{^{1}H} ($CDCl_3$, 125 MHz) spectra of compound (3al):



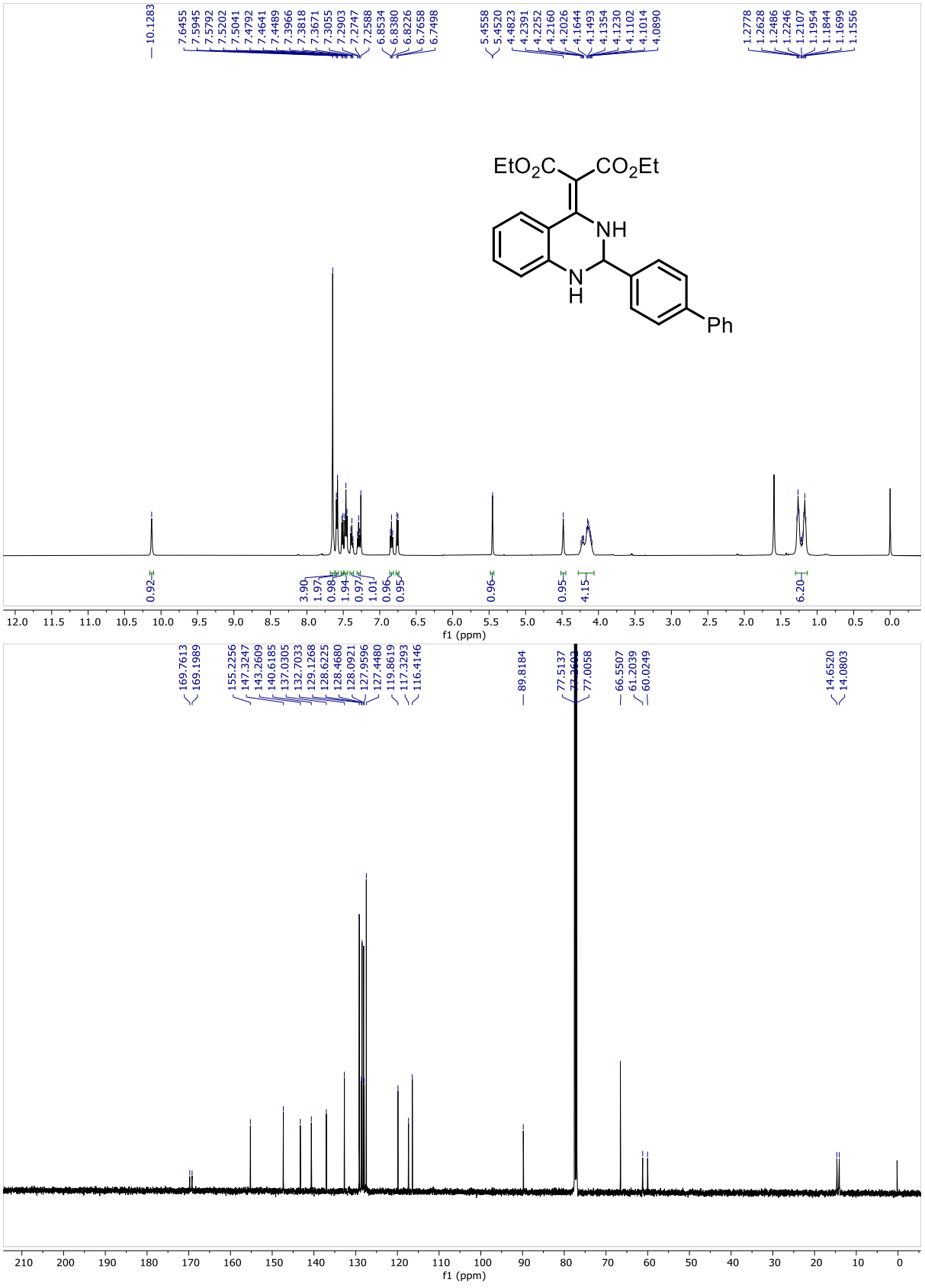


^{1}H ($CDCl_3$, 600 MHz) and ^{13}C{^{1}H} ($CDCl_3$, 150 MHz) spectra of compound (3am):

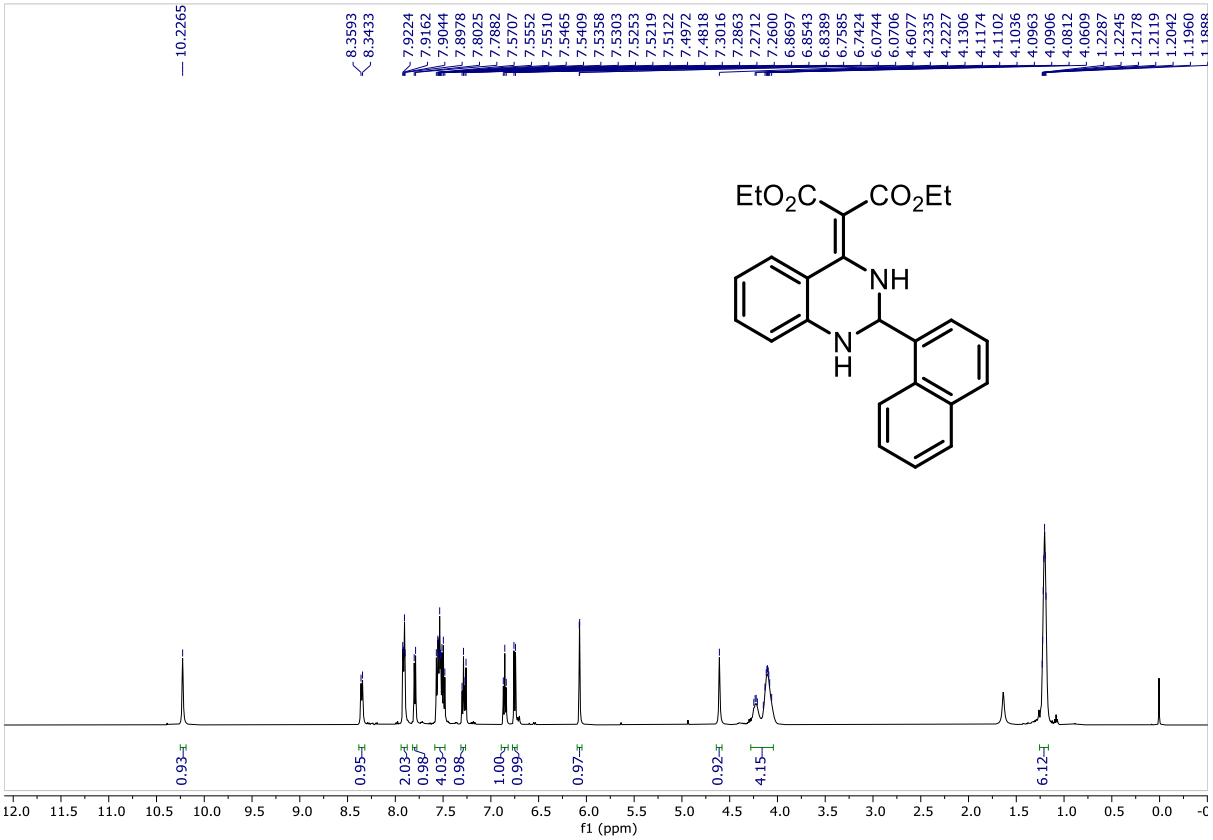


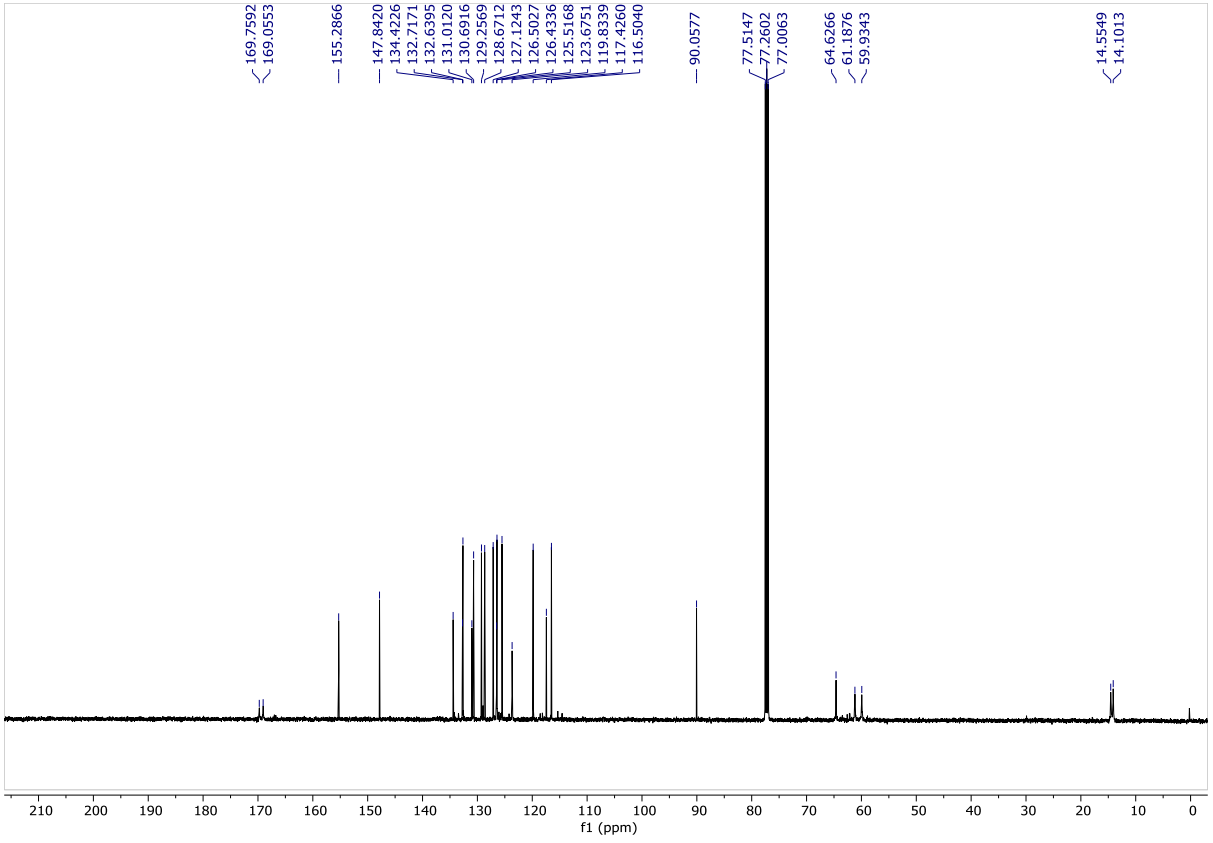


^{1}H ($CDCl_3$, 500 MHz) and ^{13}C{^{1}H} ($CDCl_3$, 125 MHz) spectra of compound (3an):

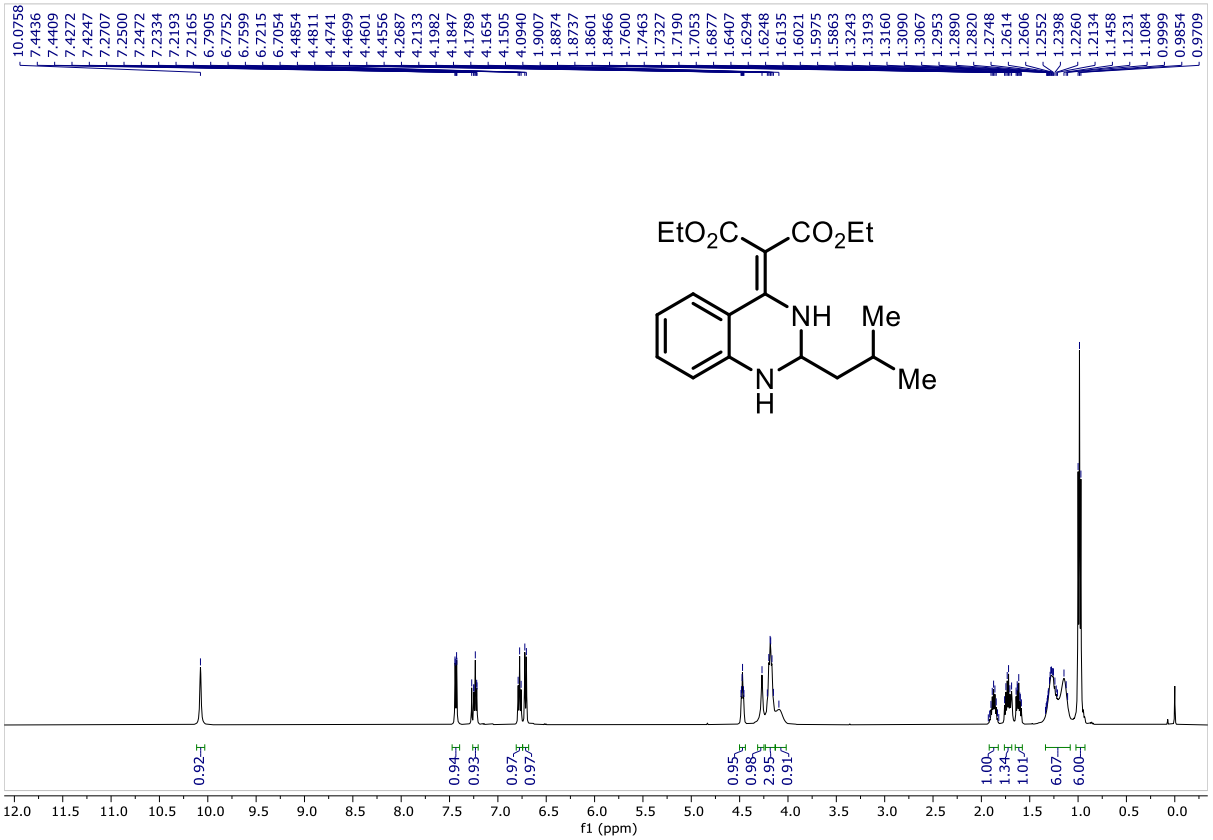


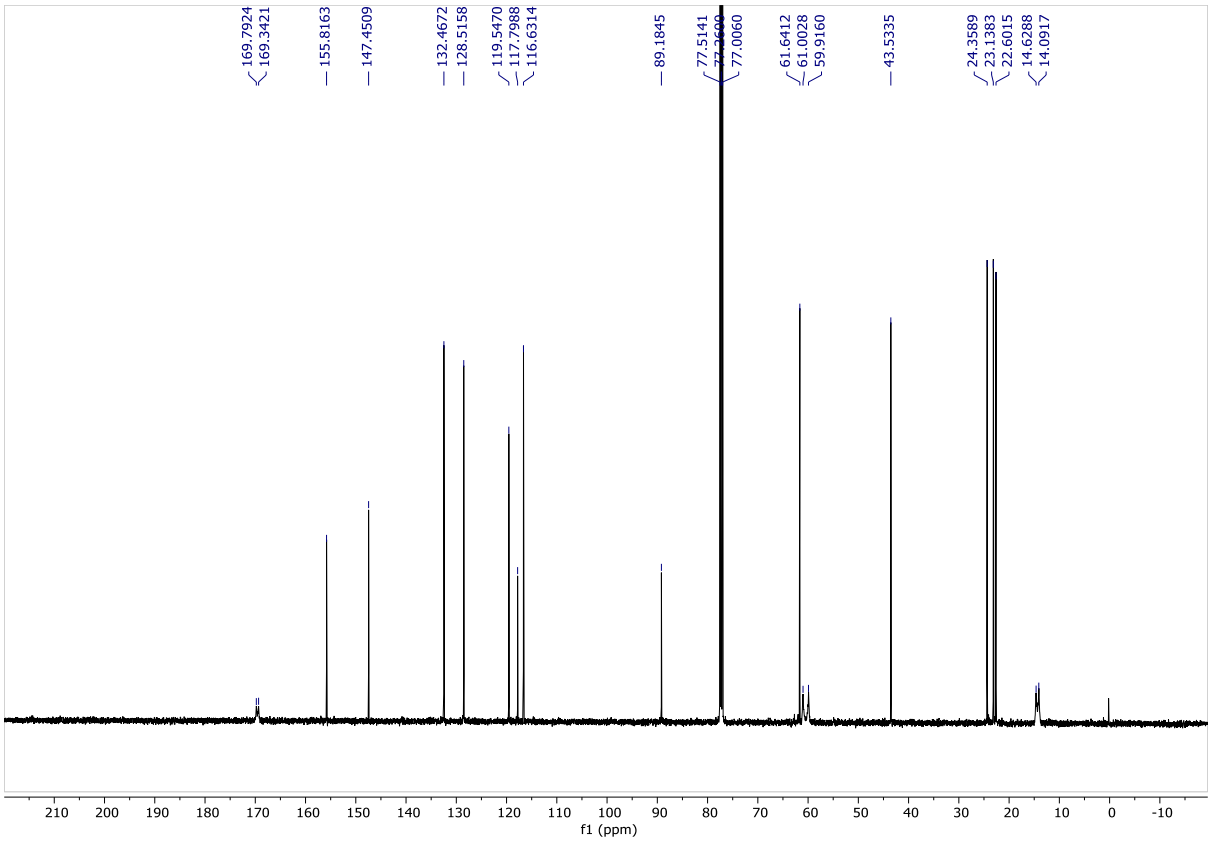
^{1}H ($CDCl_3$, 500 MHz) and ^{13}C{^{1}H} ($CDCl_3$, 125 MHz) spectra of compound (3ao):



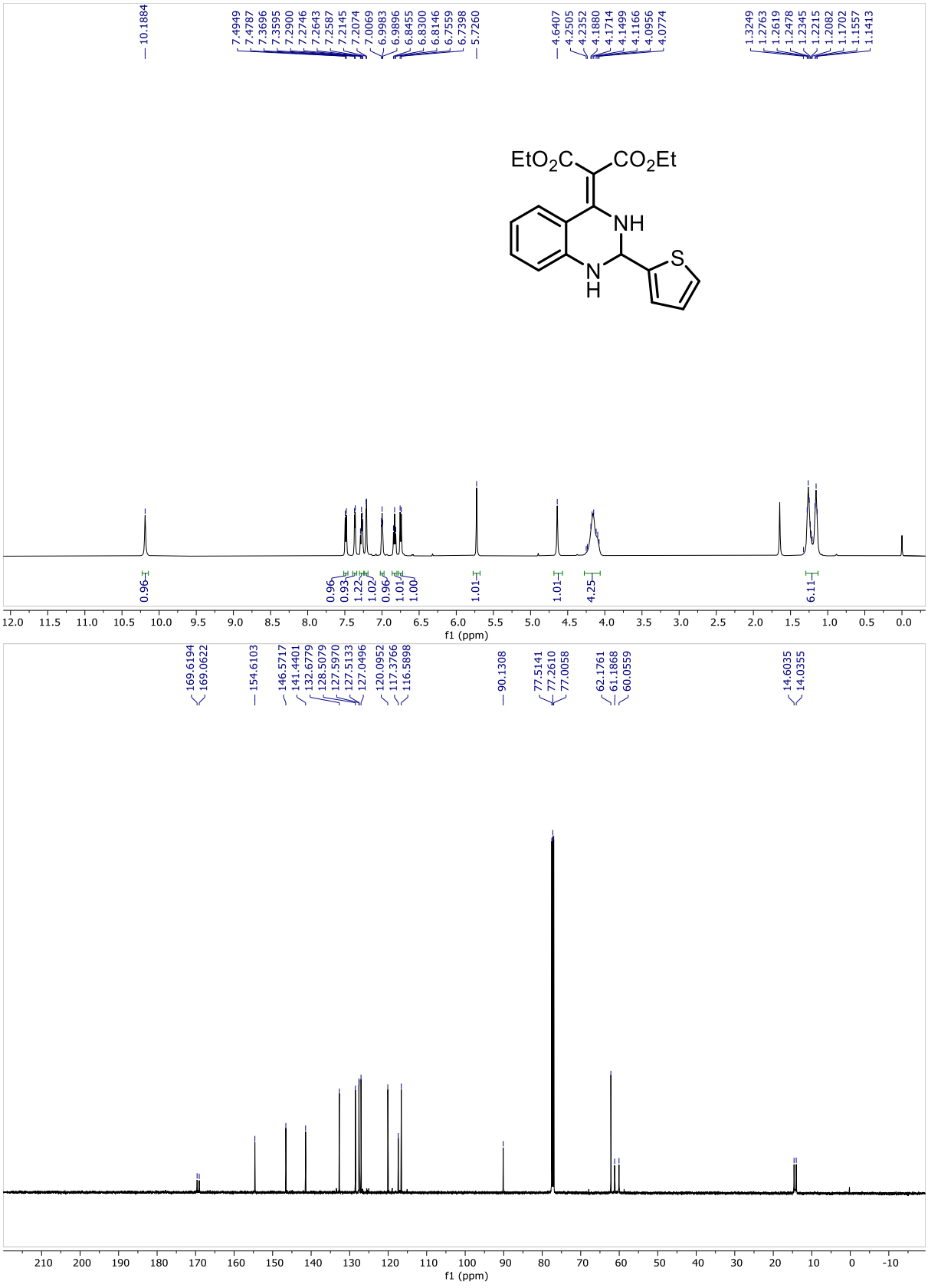


^{1}H ($CDCl_3$, 500 MHz) and ^{13}C{^{1}H} ($CDCl_3$, 125 MHz) spectra of compound (3ap):

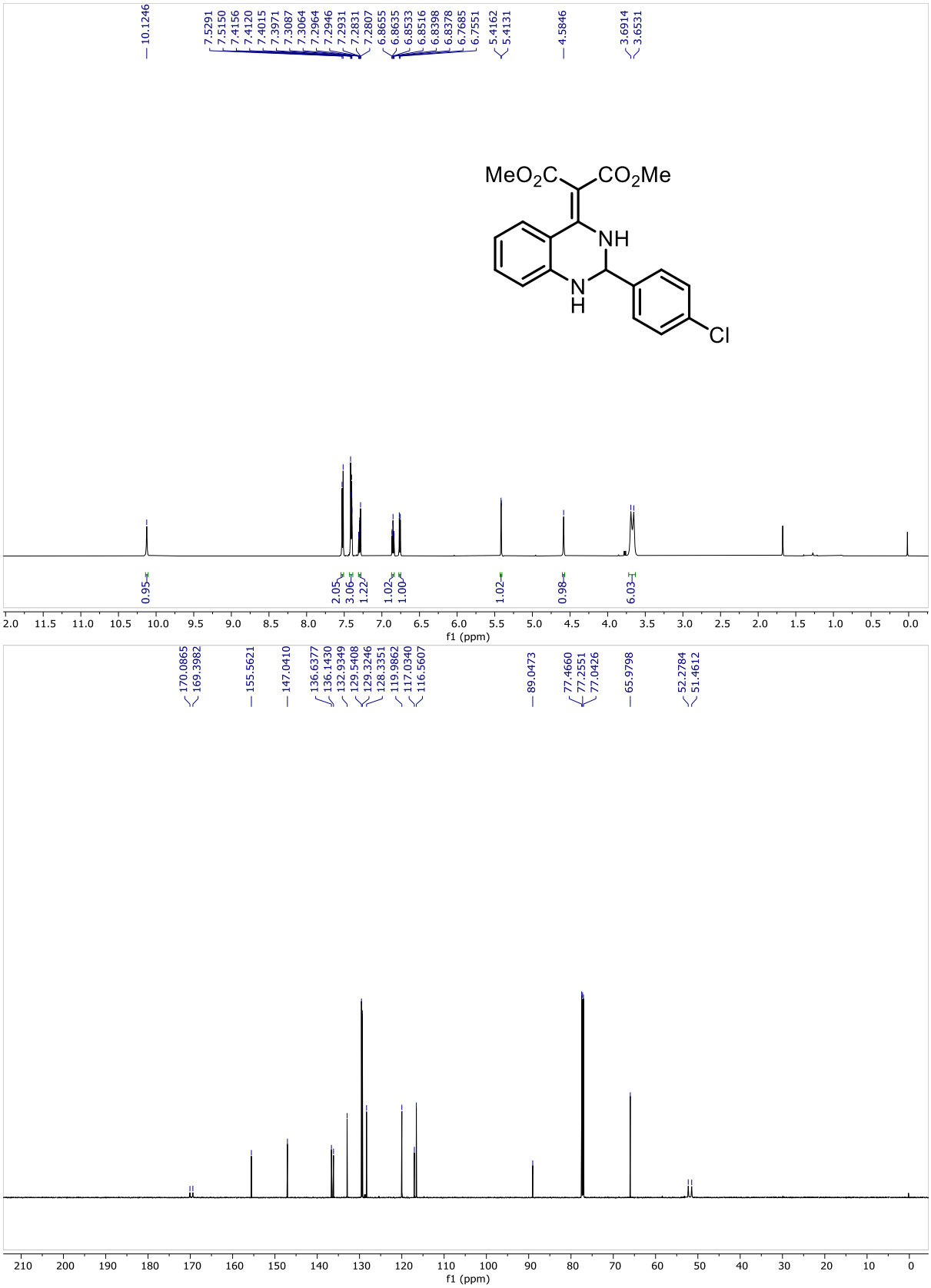




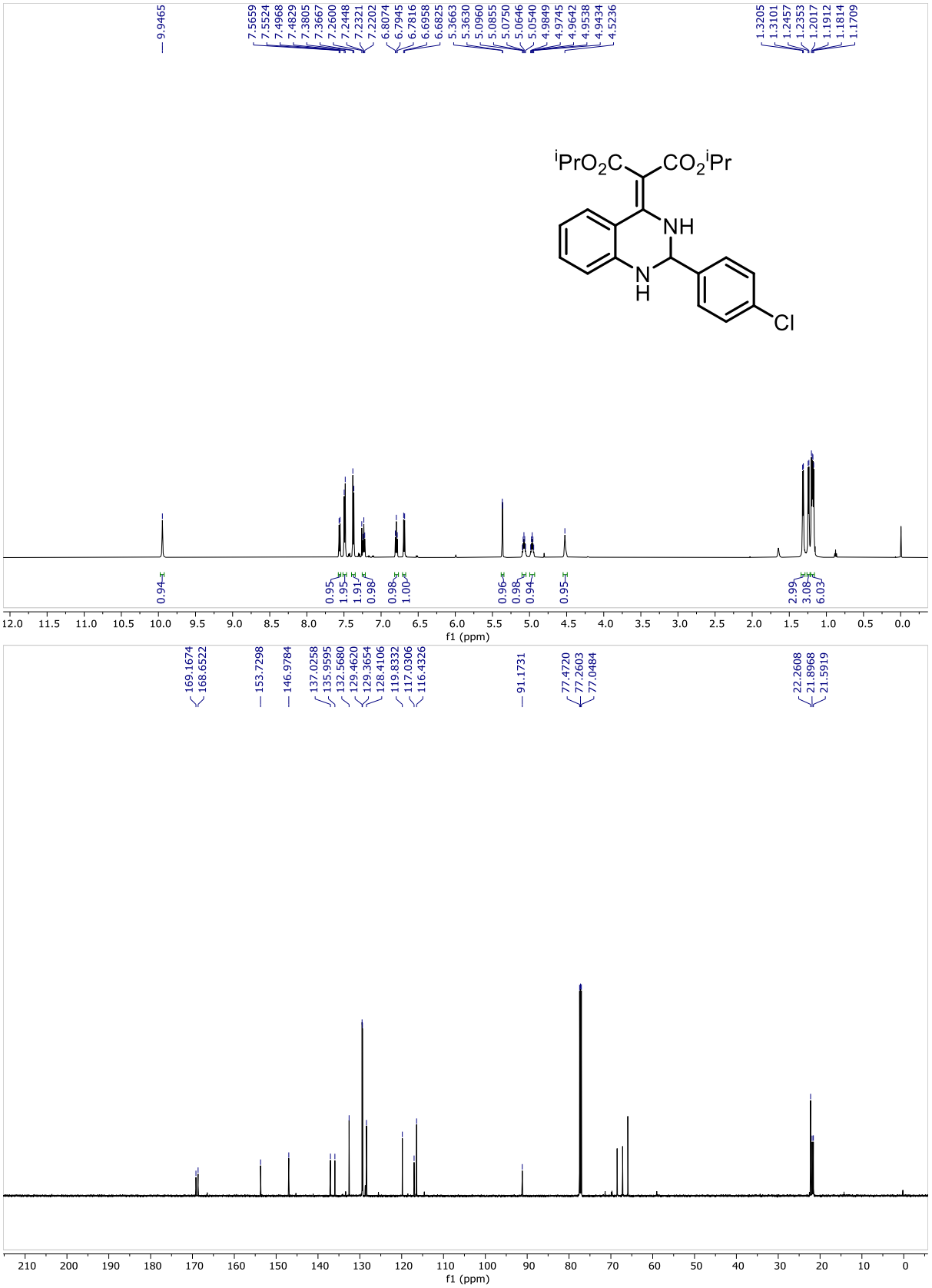
^{1}H ($CDCl_3$, 500 MHz) and ^{13}C{^{1}H} ($CDCl_3$, 125 MHz) spectra of compound (3aq):



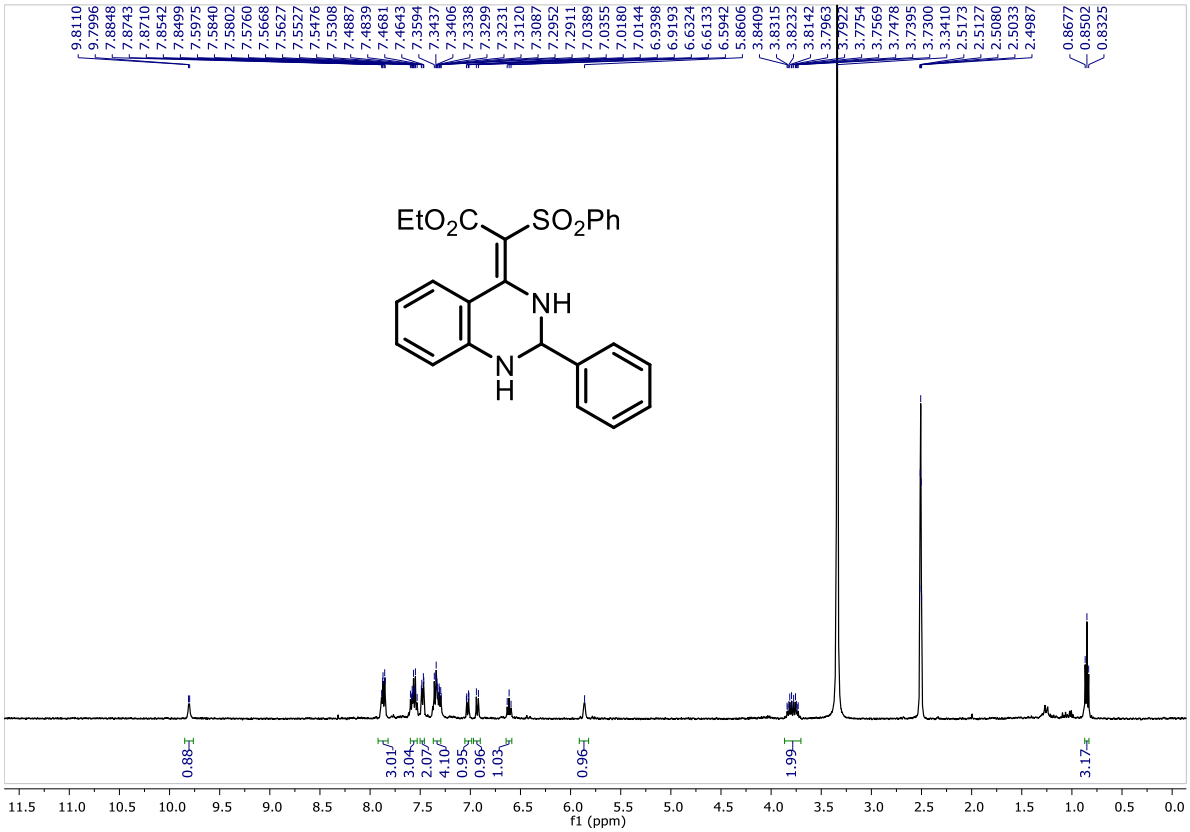
^{1}H ($CDCl_3$, 600 MHz) and $^{13}C\{^{1}H\}$ ($CDCl_3$, 150 MHz) spectra of compound (3ar):

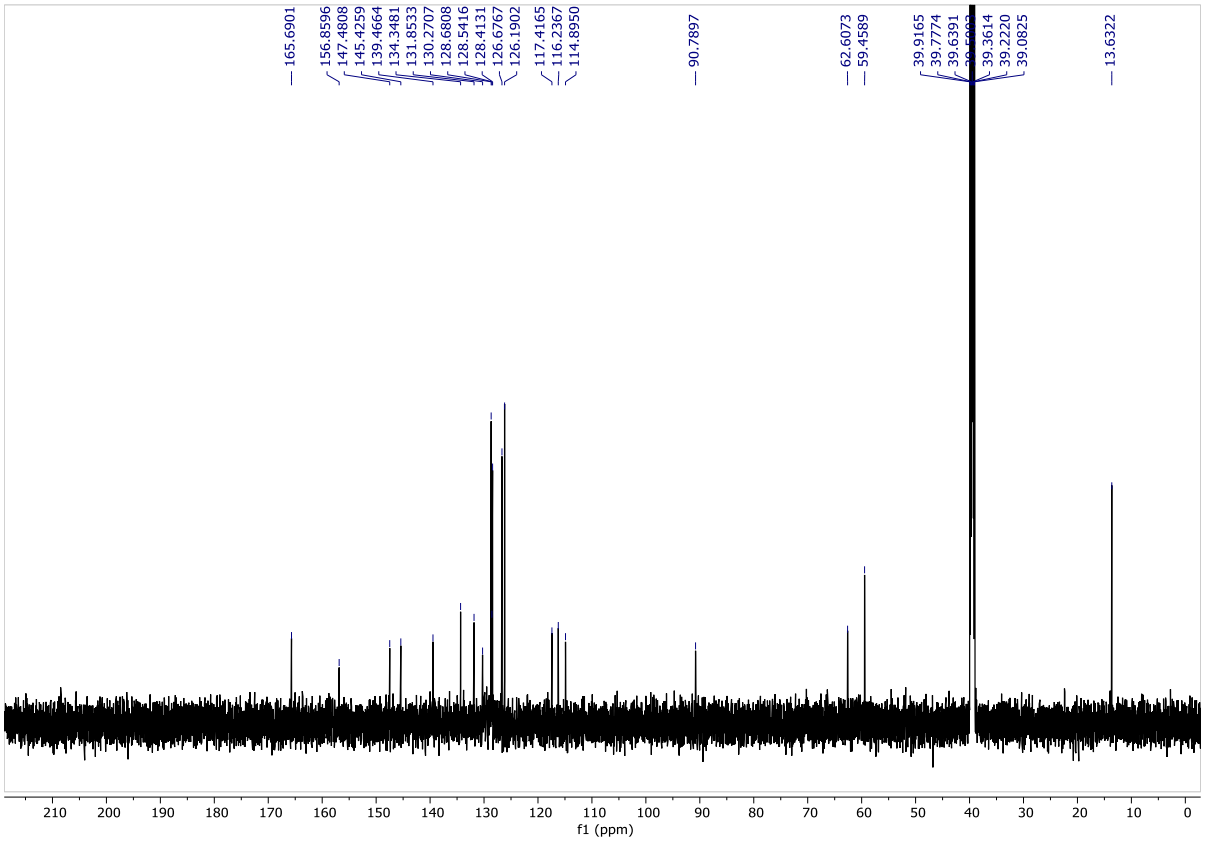


\$^{1}$H ($CDCl_3$, 600 MHz) and $^{13}C\{^{1}H\}$ ($CDCl_3$, 150 MHz) spectra of compound (3as):

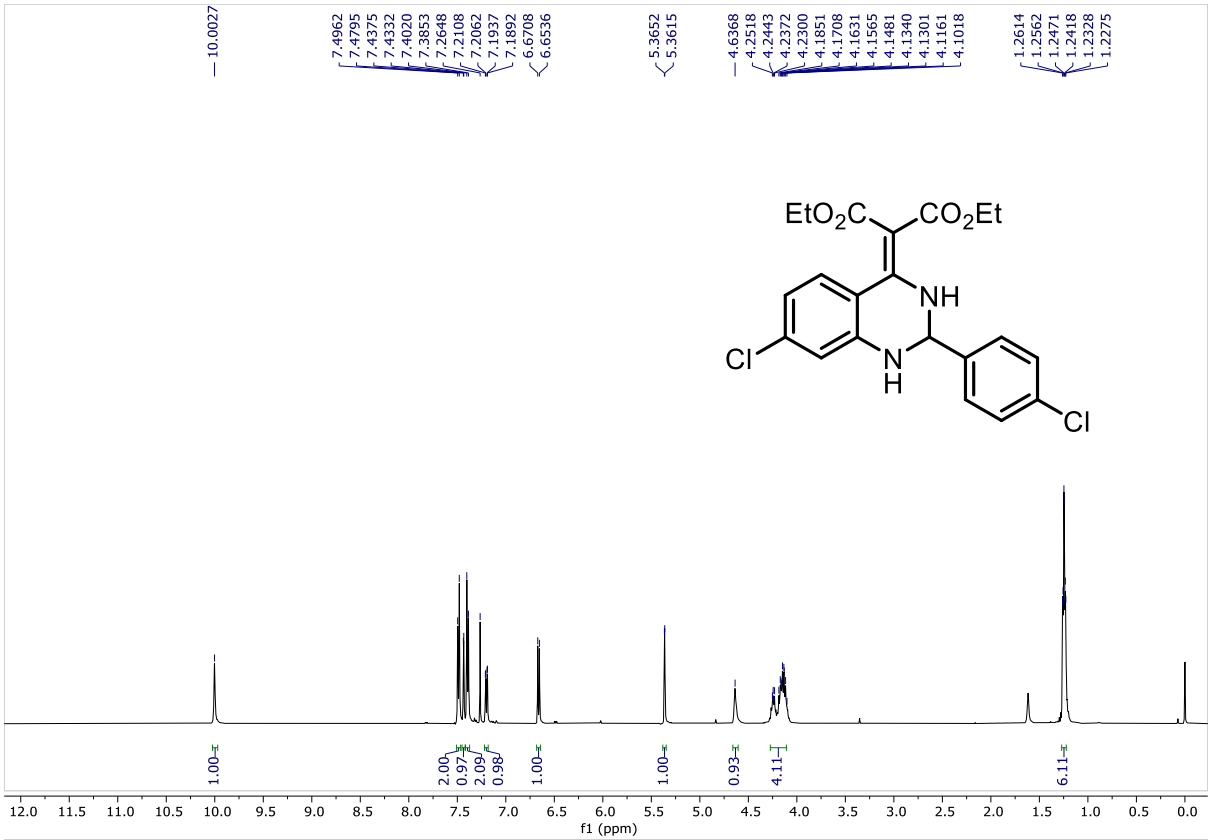


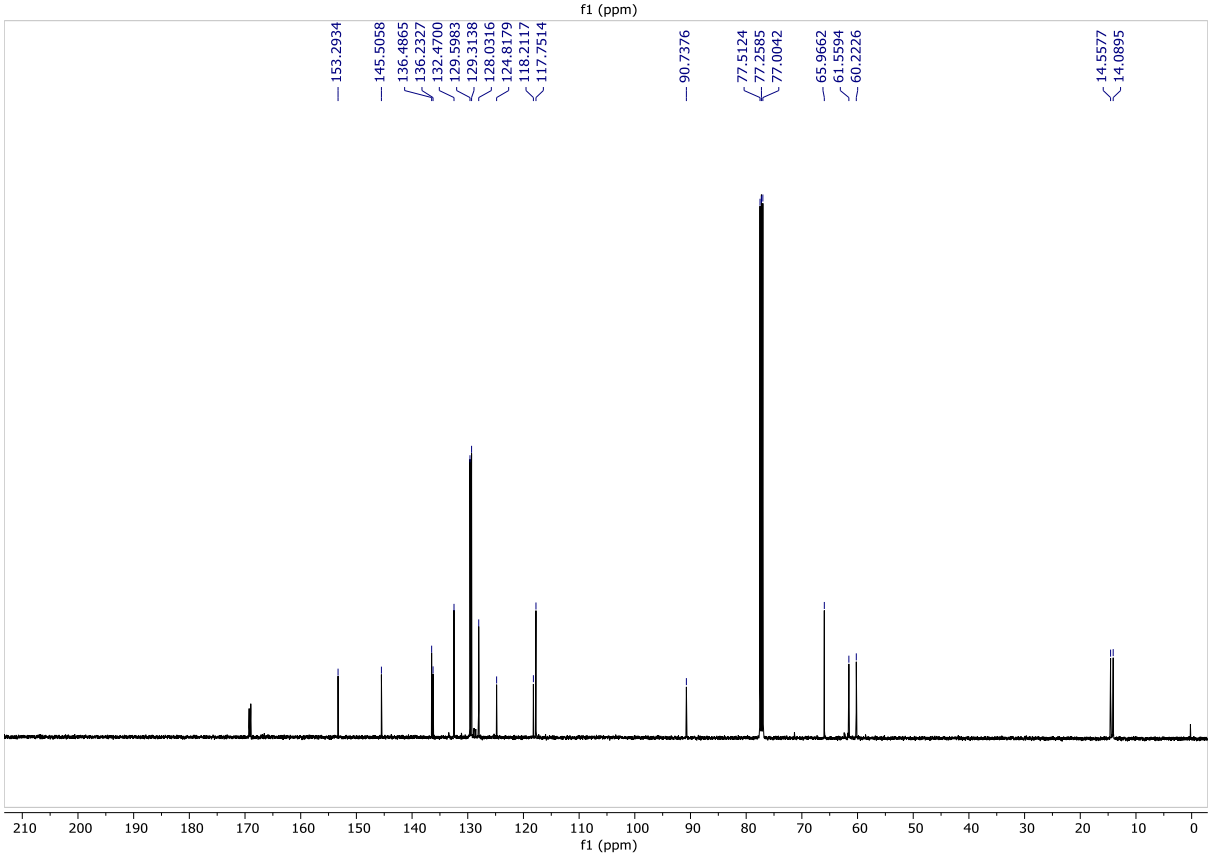
^{1}H (DMSO-d$_6$, 400 MHz) and ^{13}C{^{1}H} (DMSO-d$_6$, 150 MHz) spectra of compound (3at):



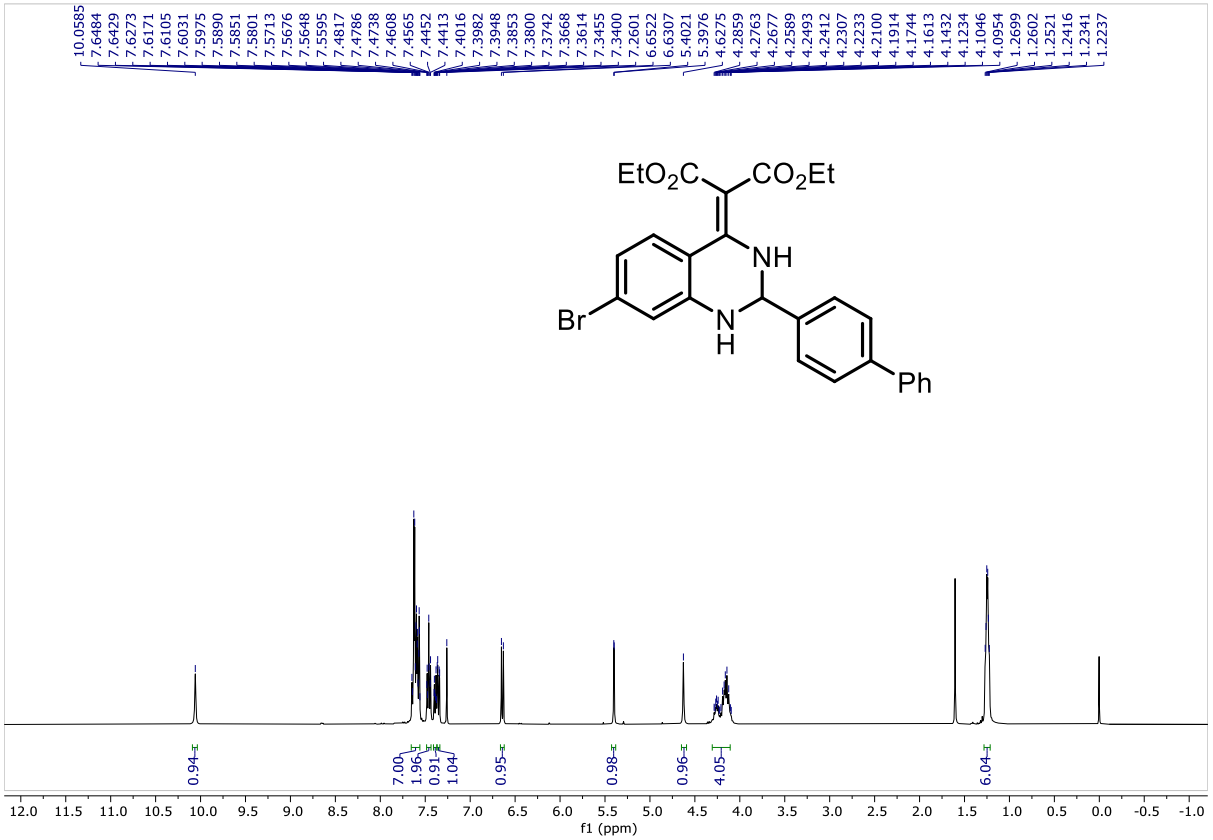


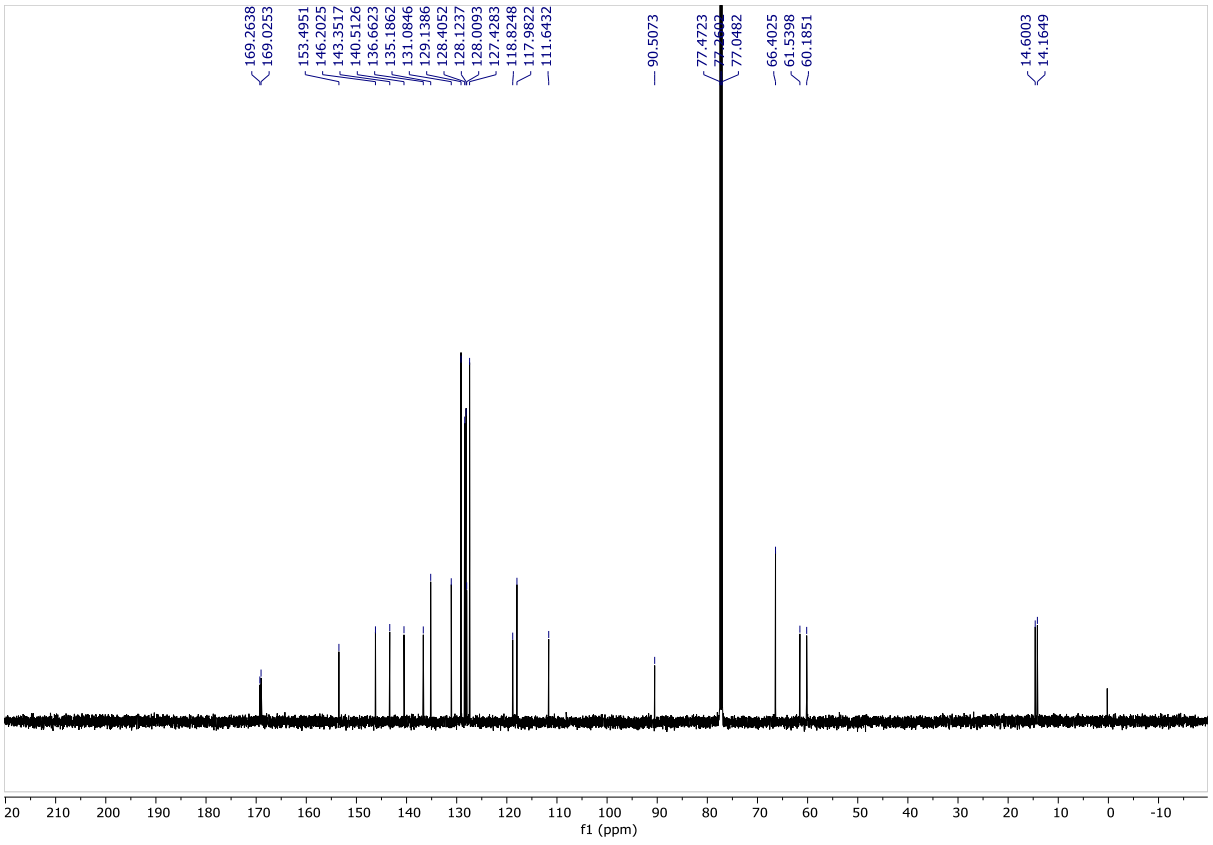
^{1}H ($CDCl_3$, 500 MHz) and ^{13}C{^{1}H} ($CDCl_3$, 125 MHz) spectra of compound (3bb):



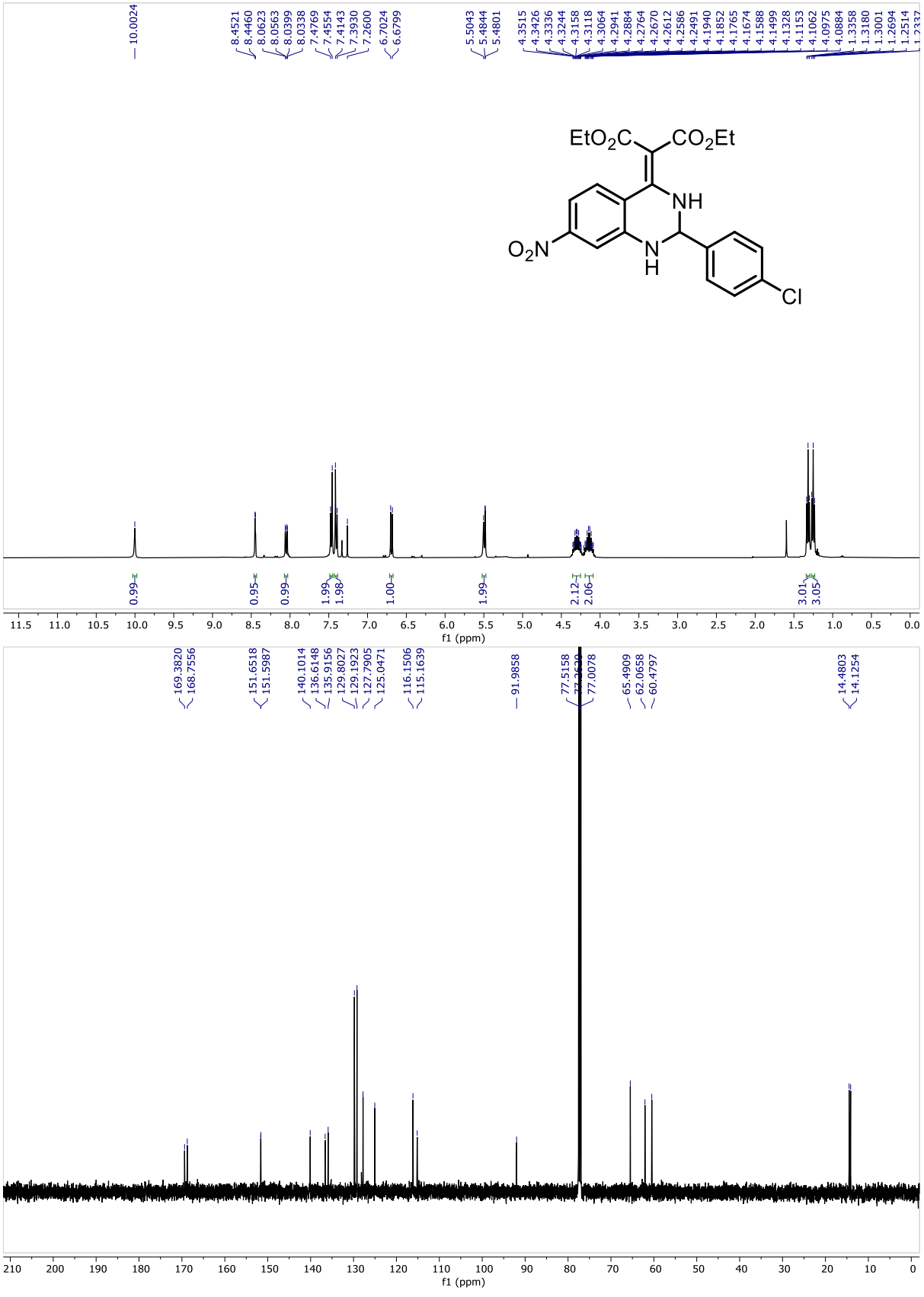


^{1}H ($CDCl_3$, 400 MHz) and ^{13}C{^{1}H} ($CDCl_3$, 150 MHz) spectra of compound (3cn):

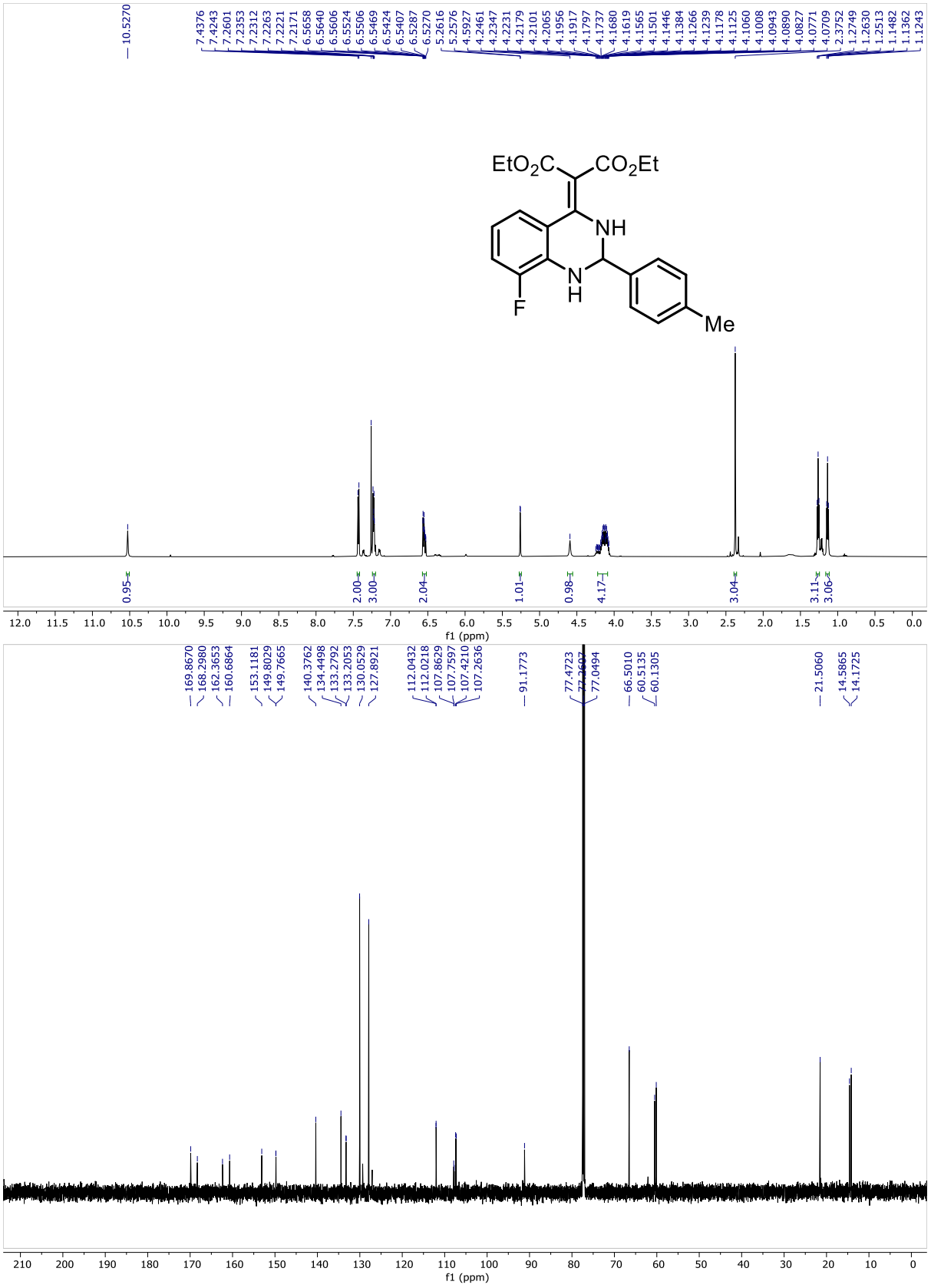




^{1}H ($CDCl_3$, 400 MHz) and $^{13}C\{^{1}H\}$ ($CDCl_3$, 125 MHz) spectra of compound (3db):

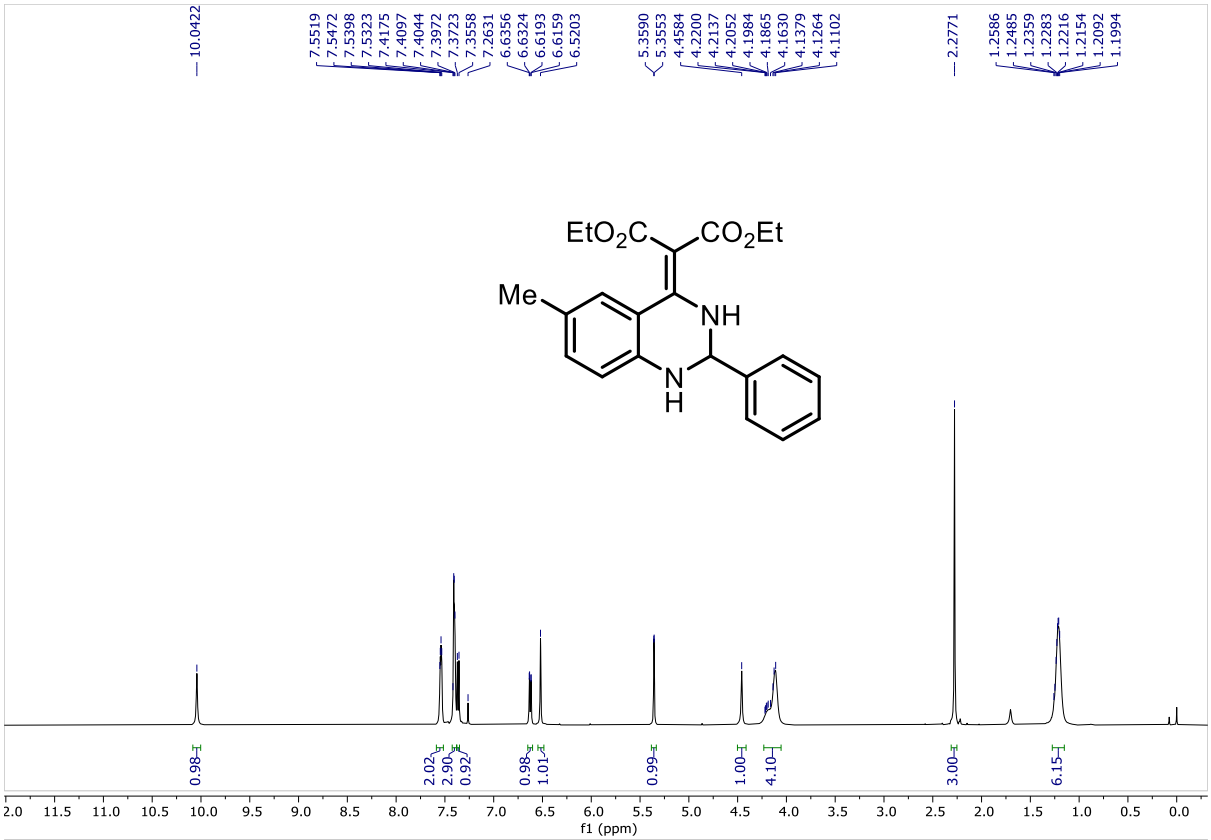


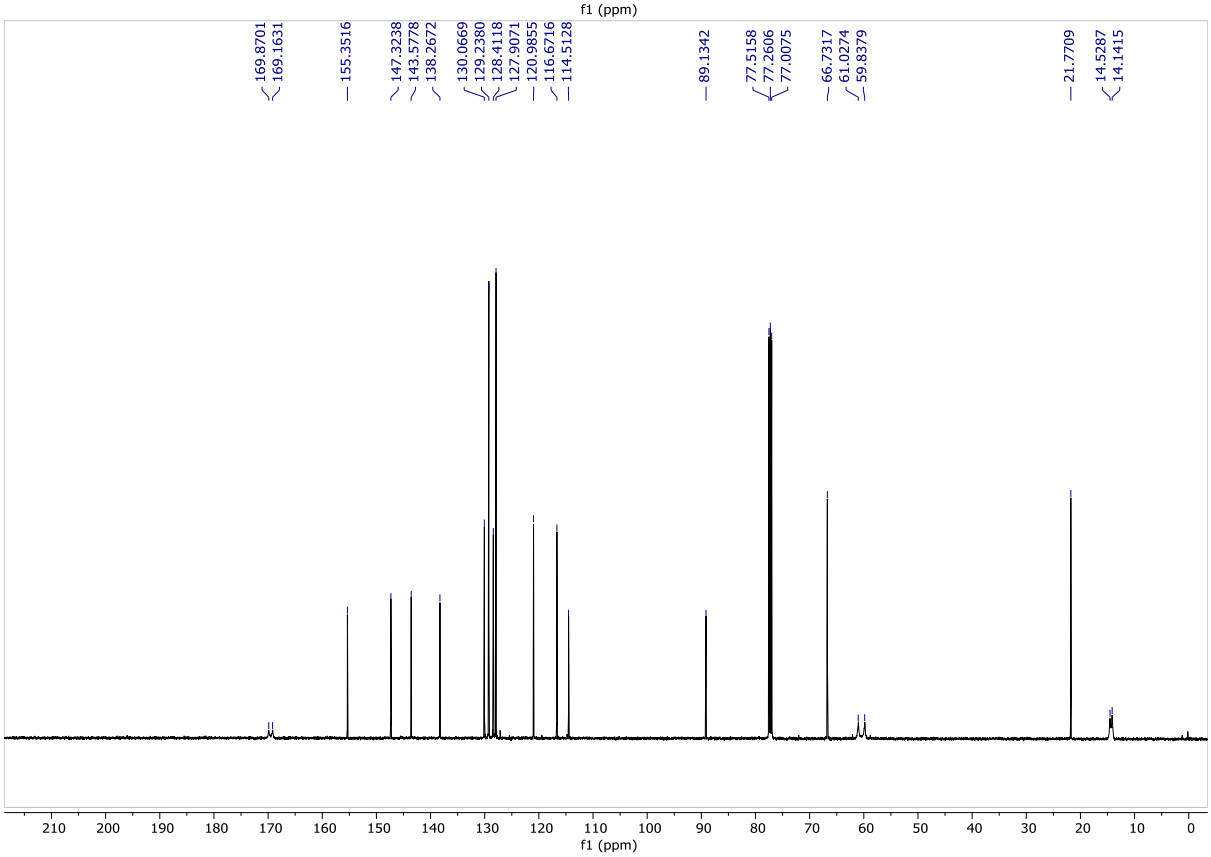
^{1}H ($CDCl_3$, 600 MHz) and ^{13}C{^{1}H} ($CDCl_3$, 150 MHz) spectra of compound (3ei):



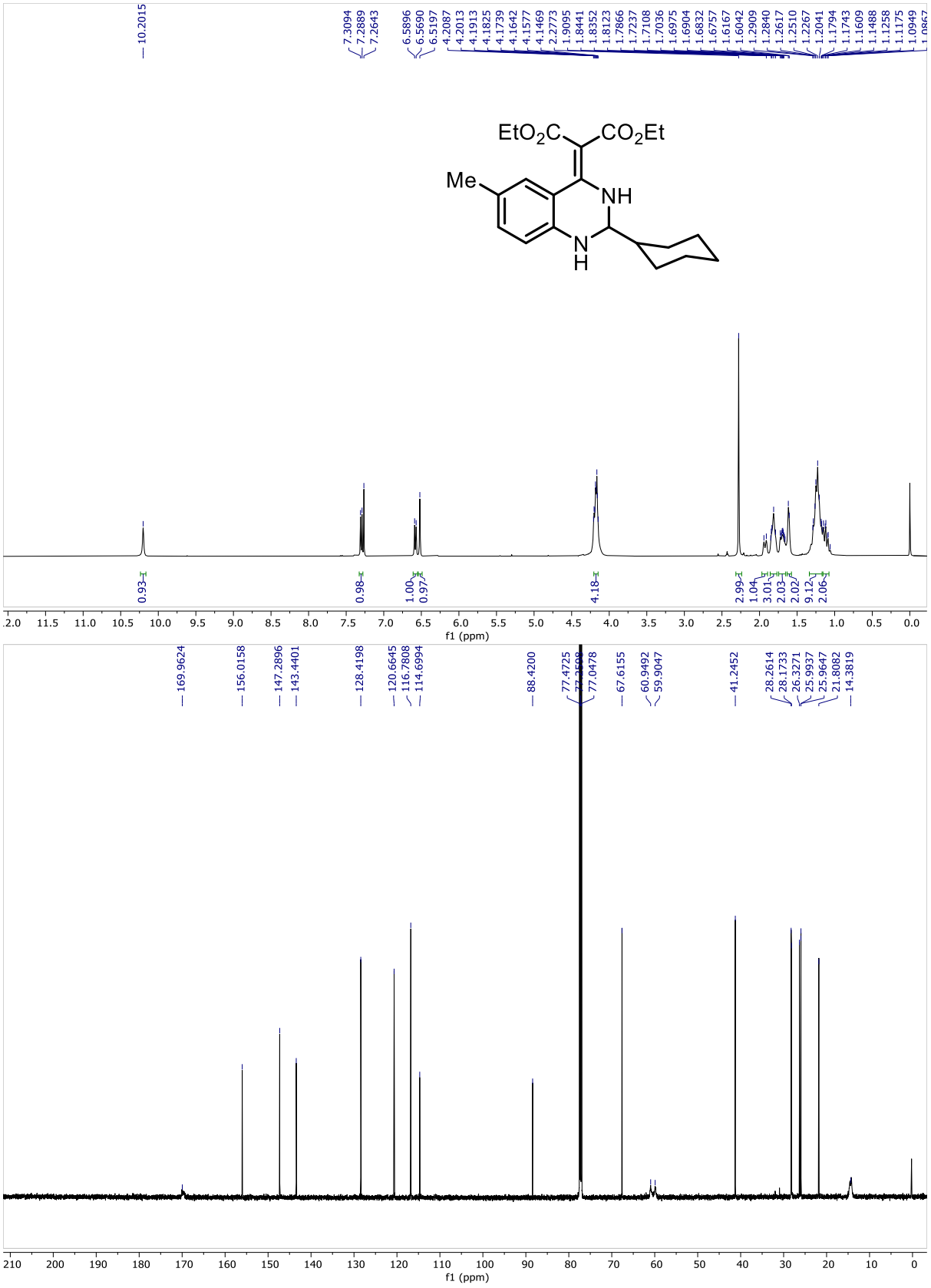
^{19}F (470 MHz, C_6F_6/$CDCl_3$) spectrum of compound (3ei):

^{1}H ($CDCl_3$, 500 MHz) and ^{13}C{^{1}H} ($CDCl_3$, 125 MHz) spectra of compound (3fa):

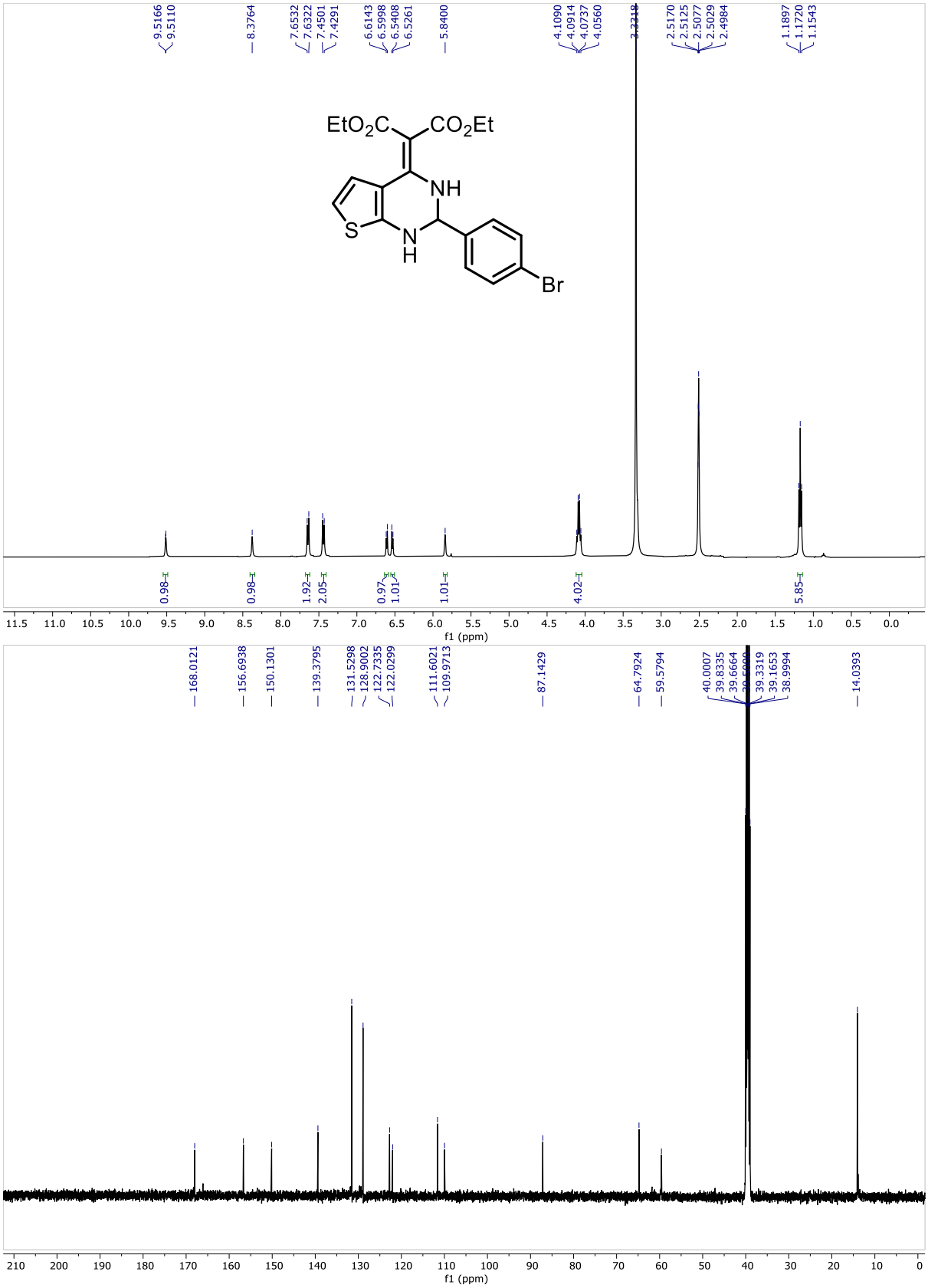




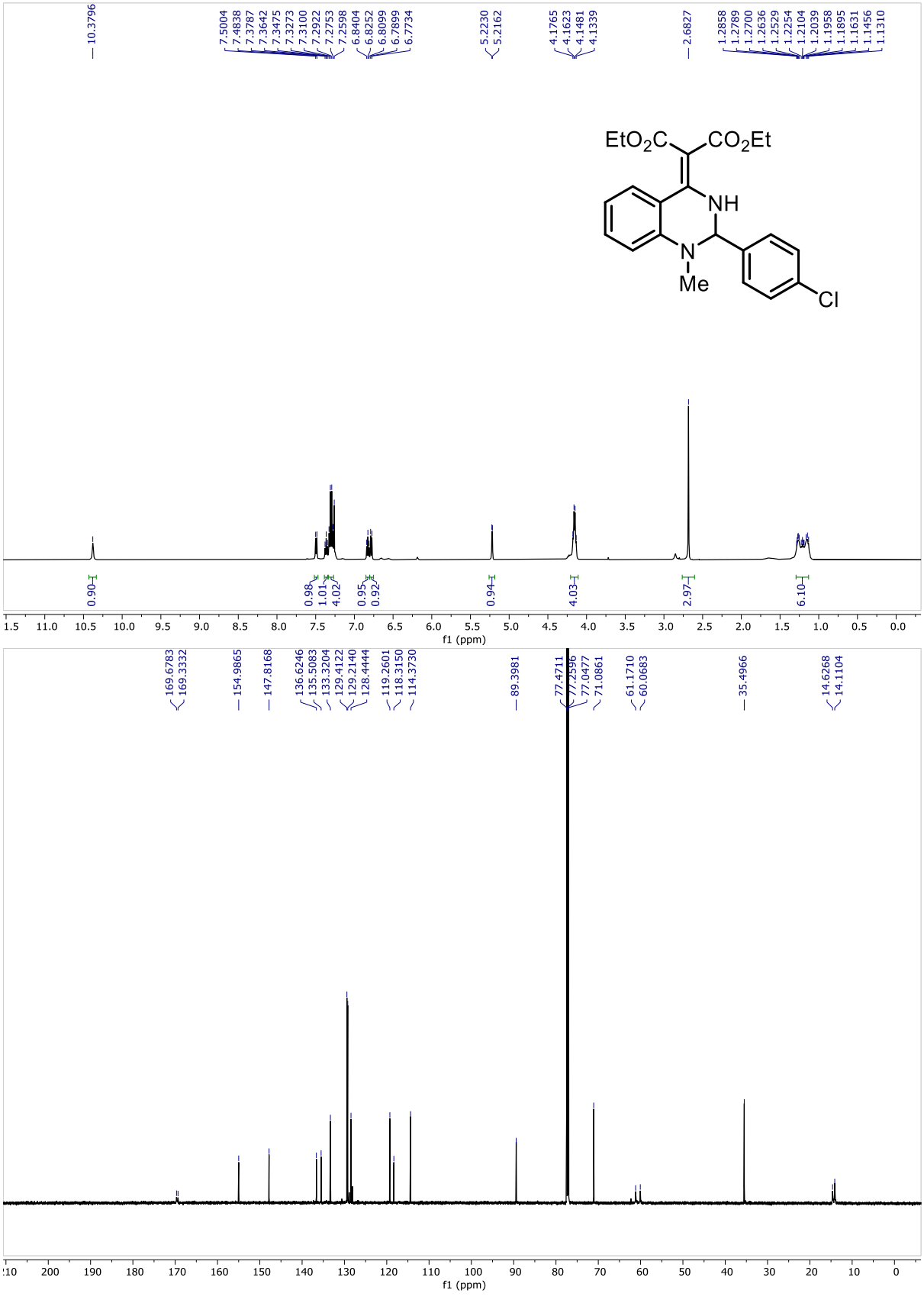
^{1}H ($CDCl_3$, 400 MHz) and ^{13}C{^{1}H} ($CDCl_3$, 150 MHz) spectra of compound (3fx):



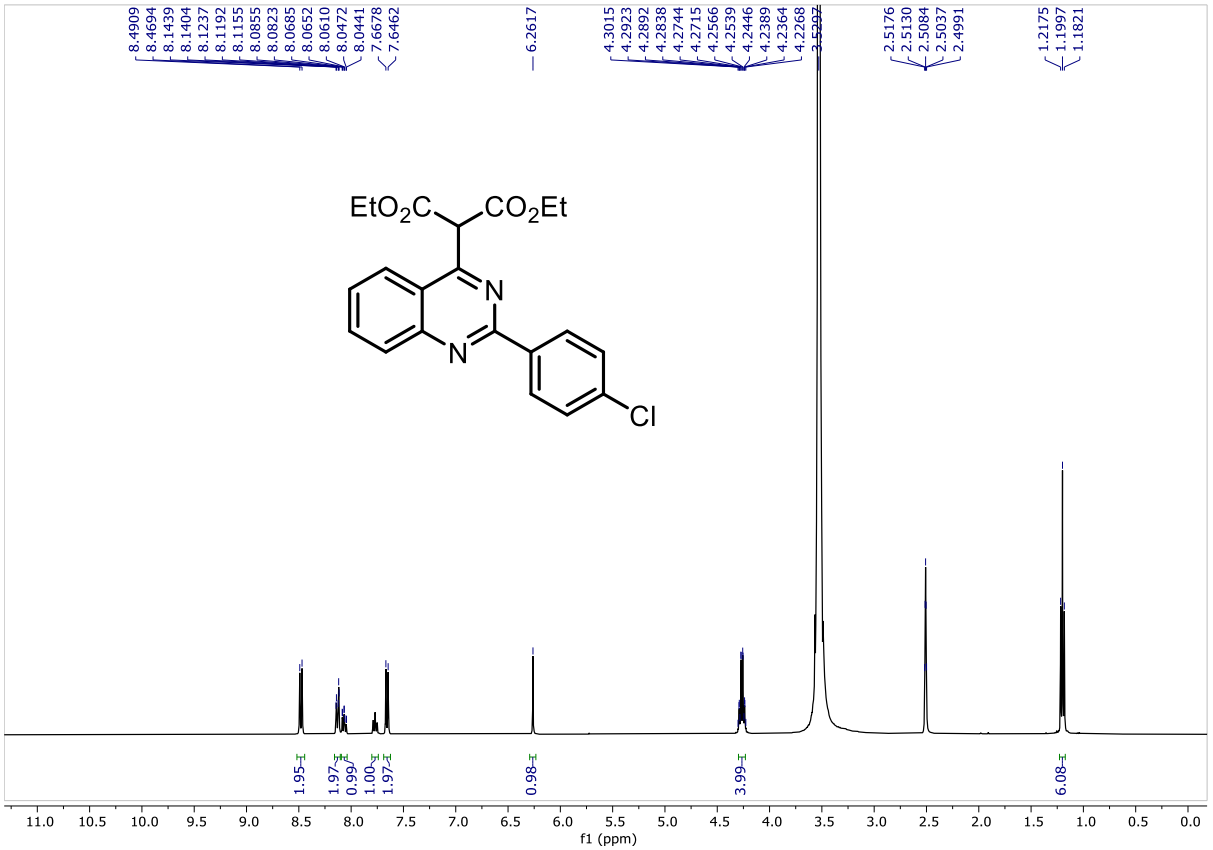
^{1}H (DMSO-d$_6$, 400 MHz) and ^{13}C{^{1}H} (DMSO-d$_6$, 125 MHz) spectra of compound (3gc):

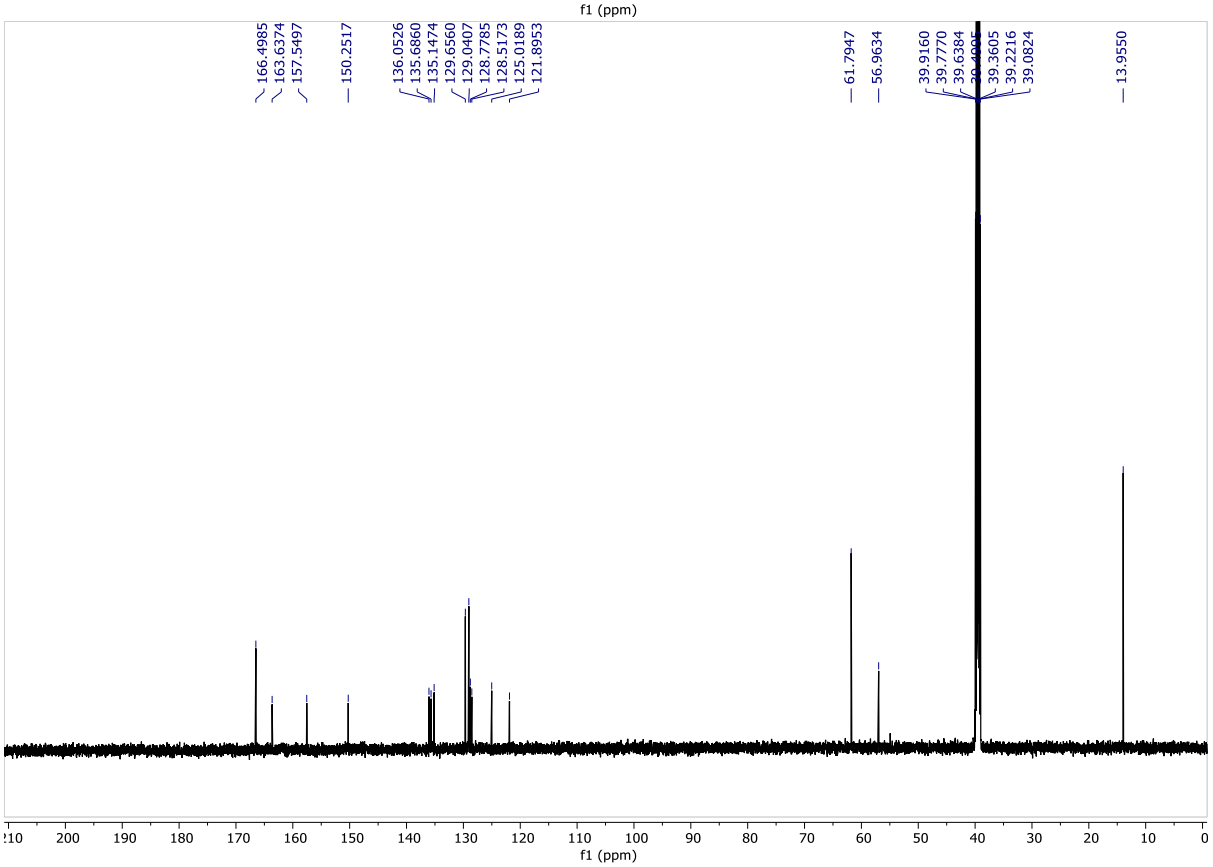


^{1}H ($CDCl_3$, 500 MHz) and ^{13}C{^{1}H} ($CDCl_3$, 150 MHz) spectra of compound (3hb):

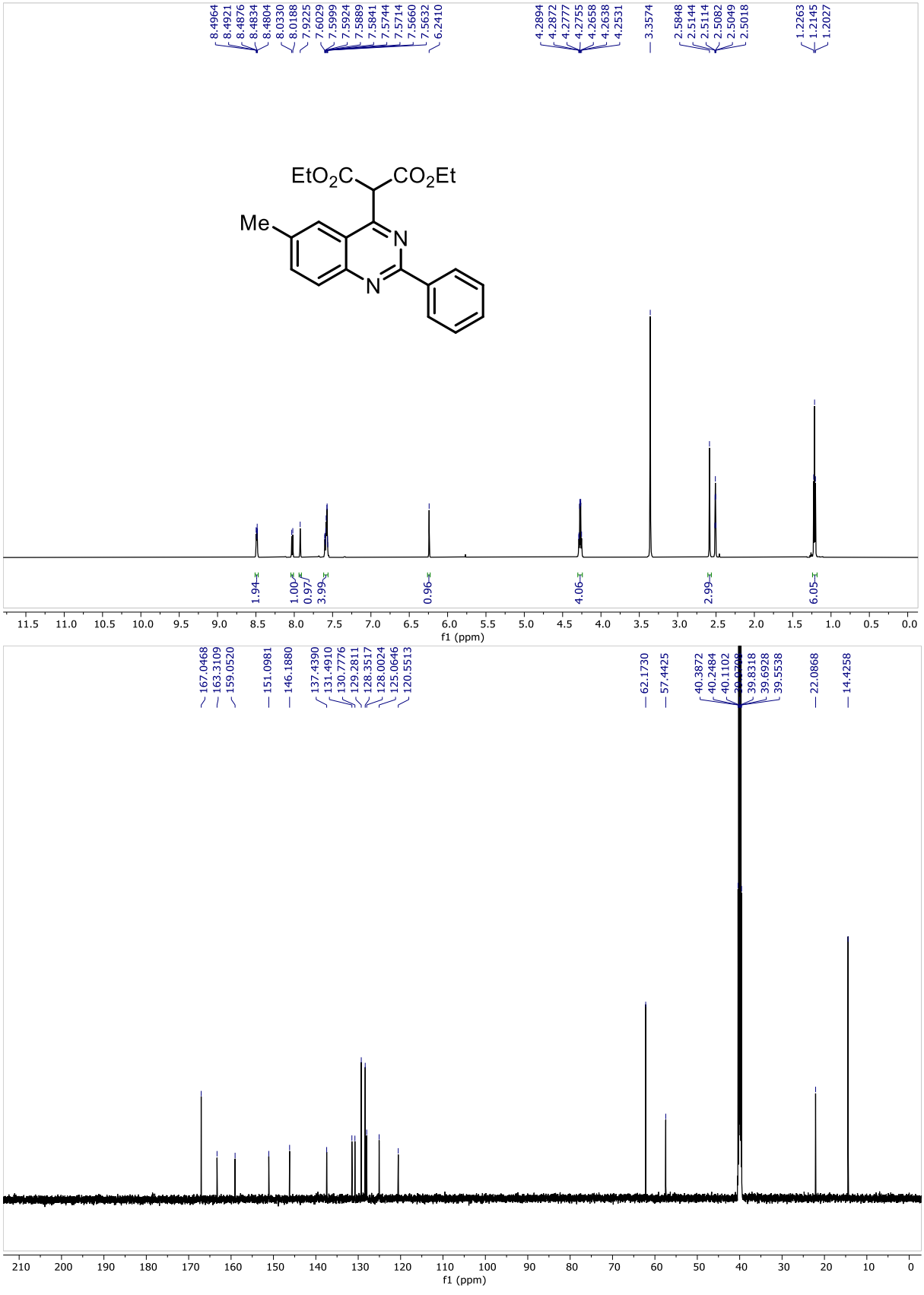


^{1}H (DMSO-d$_6$, 400 MHz) and ^{13}C{^{1}H} (DMSO-d$_6$, 150 MHz) spectra of compound (4a):

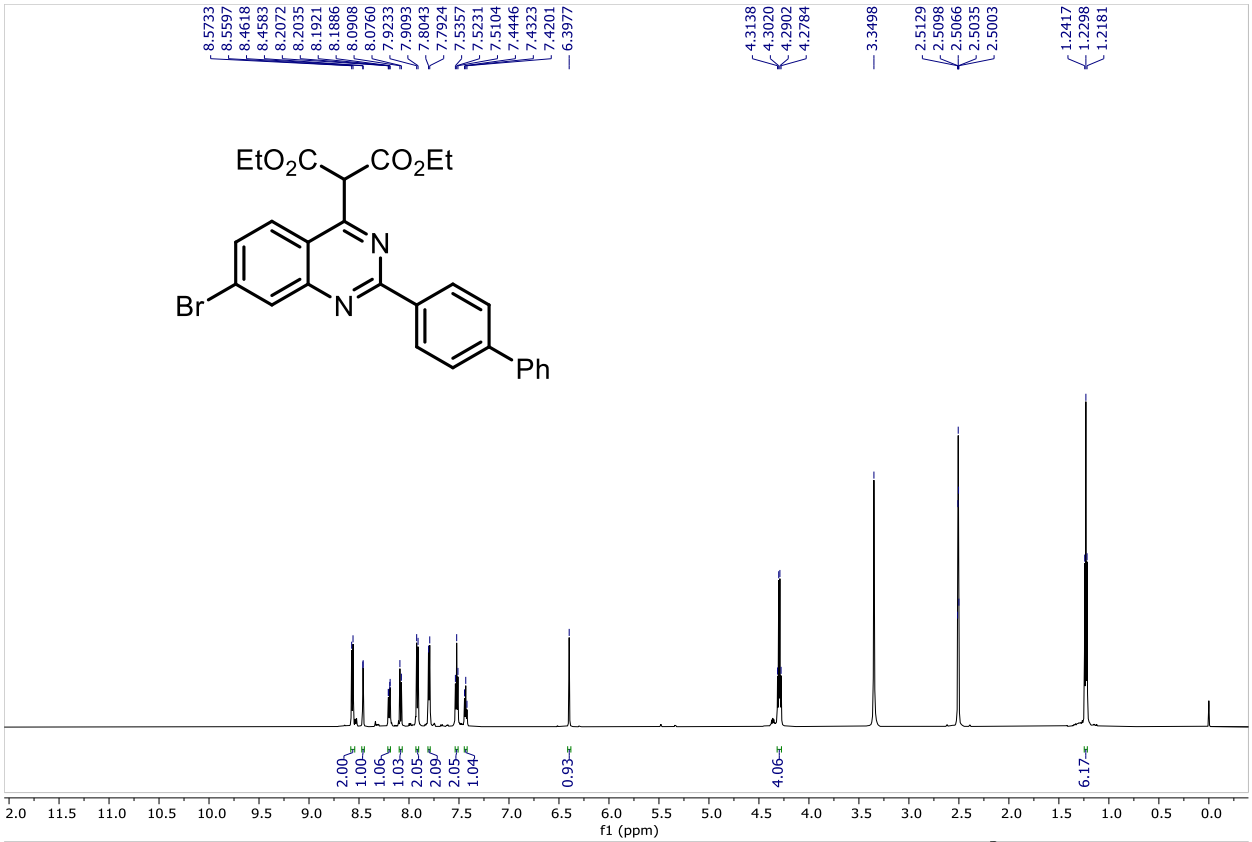


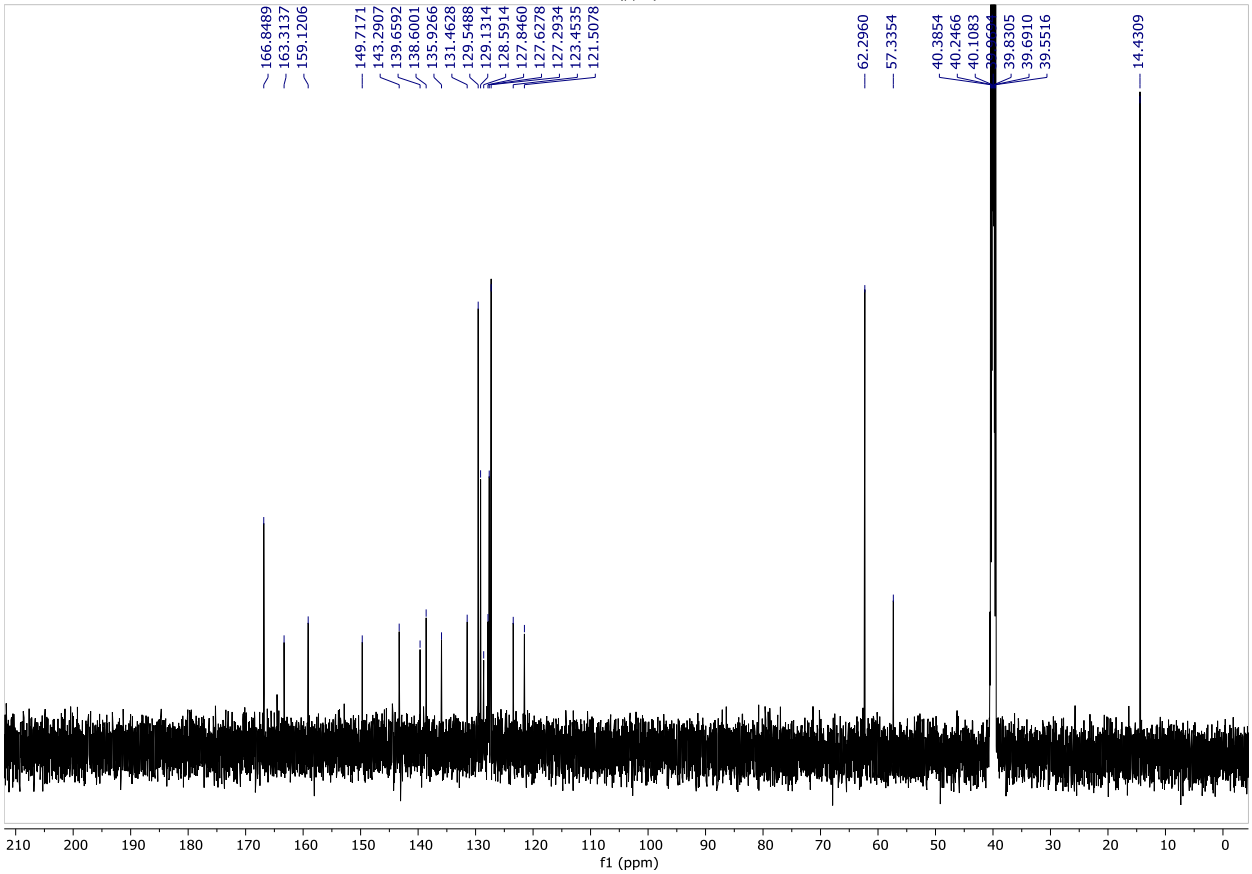


^{1}H (DMSO-d$_6$, 400 MHz) and ^{13}C{^{1}H} (DMSO-d$_6$, 150 MHz) spectra of compound (4b):

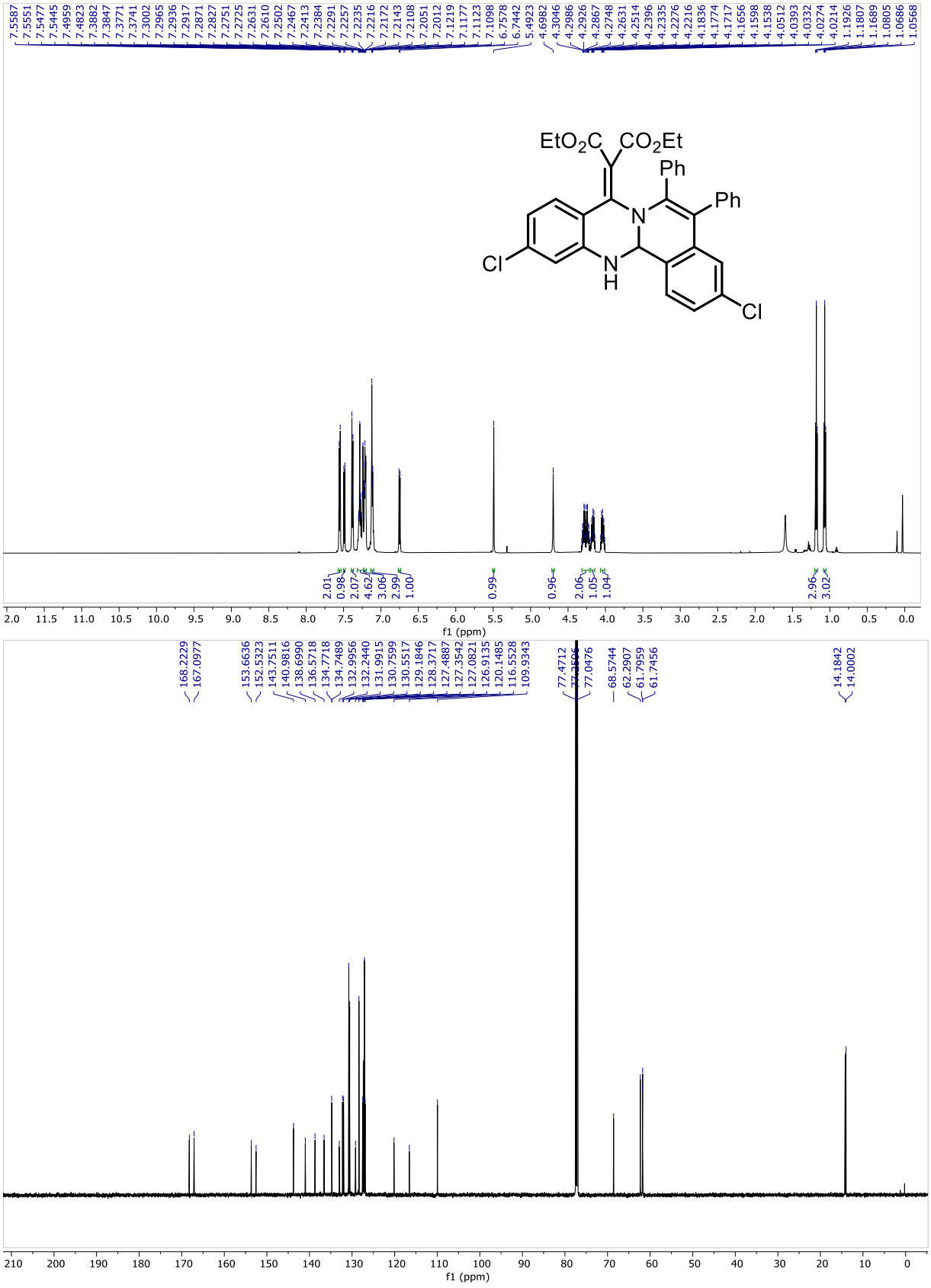


^{1}H (DMSO-d$_6$, 600 MHz) and ^{13}C{^{1}H} (DMSO-d$_6$, 150 MHz) spectra of compound (4c):

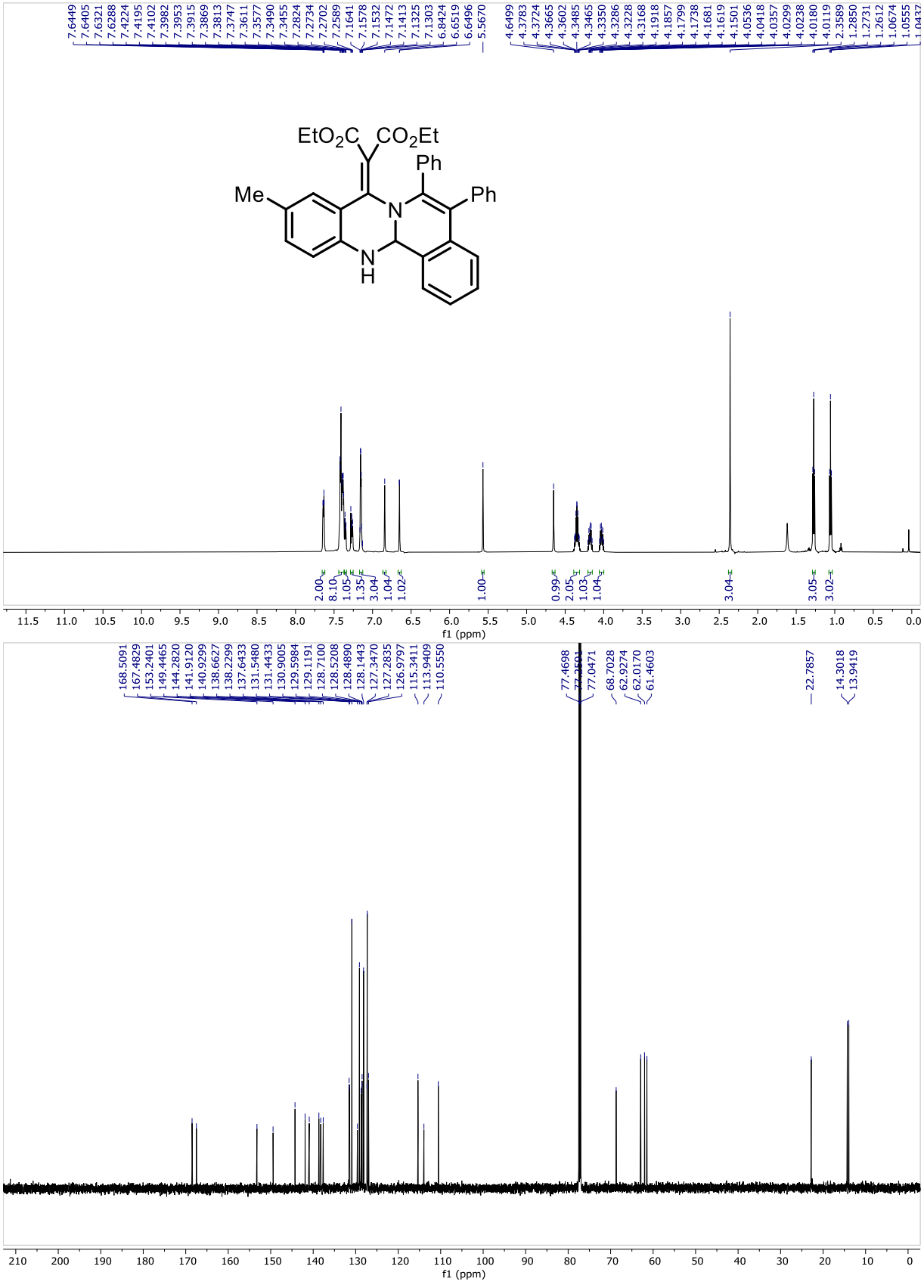




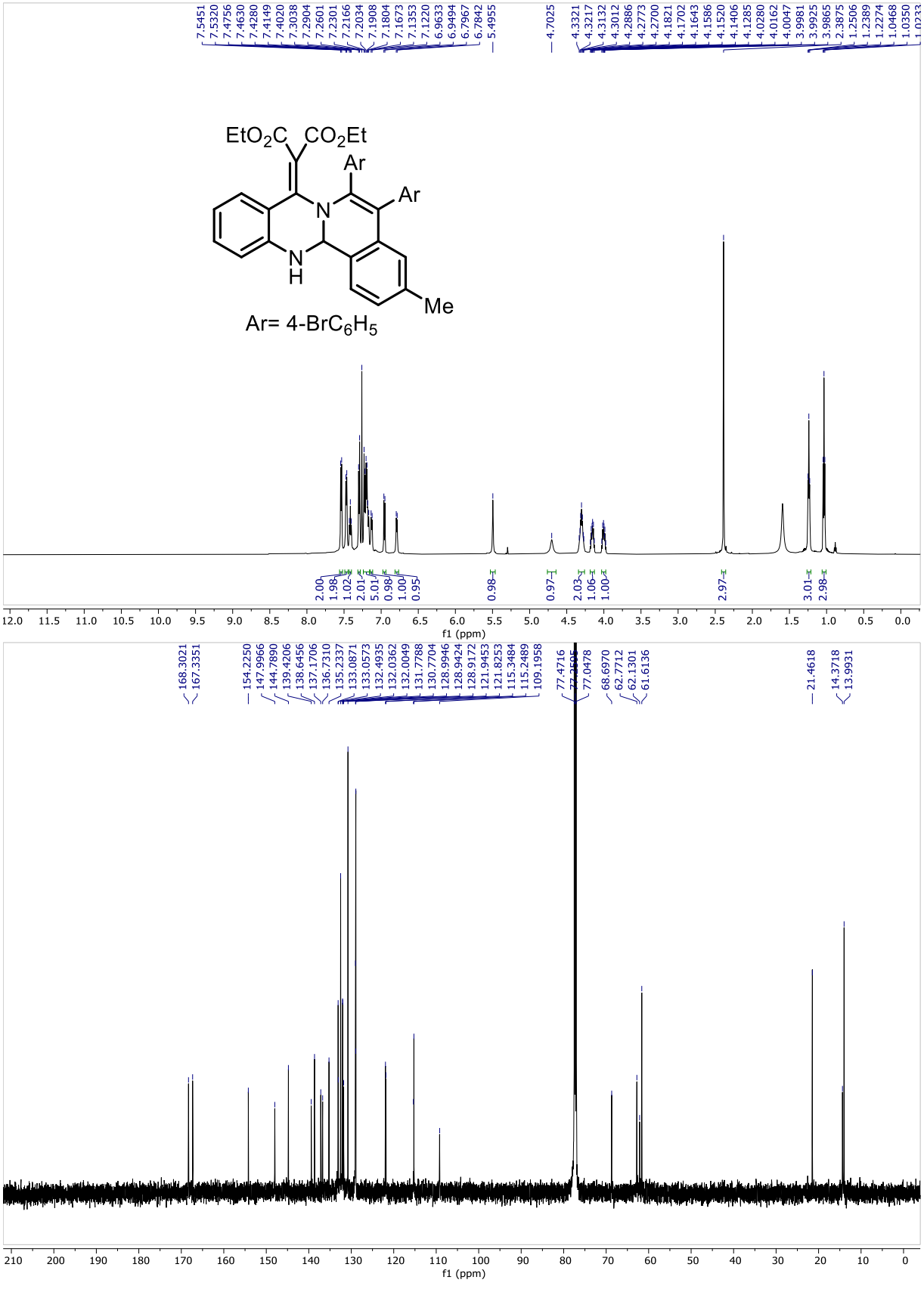
^{1}H ($CDCl_3$, 600 MHz) and $^{13}C\{^{1}H\}$ ($CDCl_3$, 150 MHz) spectra of compound (5a):



^{1}H ($CDCl_3$, 600 MHz) and ^{13}C{^{1}H} ($CDCl_3$, 150 MHz) spectra of compound (5b):



^{1}H ($CDCl_3$, 600 MHz) and ^{13}C{^{1}H} ($CDCl_3$, 150 MHz) spectra of compound (5c):



Photophysical Studies:

Photophysical studies such as UV-vis and photoluminescence were conducted on few selected compounds. The absorption λ_{max} and the emission λ_{em} spectra of the compounds were measured in 10 μM dichloromethane solution. The UV-vis and fluorescence emission spectra of these compounds (**3ab**, **3ac**, **3ah**, **3am**, **3db**, **5a**, **5b**, **5c**) are presented in Fig. 2 and their results are described in Table S58.

Table S60: UV-vis and Photoluminescence Parameters

entry	compound	λ_{max} (nm)[a]	absorbance at λ_{max}	ε (1 x 10^4 $M^{-1}cm^{-1}$)	λ_{em} (nm)[b]
1.	3ab	335	0.176	1.76	430
2.	3ac	336	0.165	1.65	430
3.	3ah	336	0.172	1.72	431
4.	3am	338	0.231	2.31	431
5.	3db	339	0.252	2.52	430
6.	5a	369	0.174	1.74	476
7.	5b	356	0.199	1.99	466
8.	5c	360	0.126	1.26	471

[a] Absorption wavelengths. [b] Emission wavelengths in DCM at a concentration of 1×10^{-5} M.

Single crystal X-ray diffraction:

Single crystals of compounds **3ar** was obtained by slow evaporation of ethyl acetate and hexane solution (1:9). Bruker APEX-II CCD diffractometer was used to collect the intensity data. The instrument is equipped with a fine focus 1.75 kW sealed tube Mo Kα radiation (λ = 0.71073 Å) at 297 K. The data acquisition was done with the APEX4 software. APEX4 software was implemented for data integration and reduction. Multi-scan empirical absorption corrections were employed to the data using the program APEX4. Structures were solved by direct methods using SHELXL-2019 and refined with full-matrix least-squares on F2 using SHELXL-2019/1.[3] Structural illustrations have been drawn with ORTEP-3 for Windows.[4] The detailed data collection and structure refinement are summarized in Table S62. CCDC-2323124 (for **3ar**), contained supplementary crystallographic data for this paper.

References:

3. G. M. Sheldrick, SHELXS-2014, Program for the crystal structure solution; University of Göttingen: Göttingen, Germany, 2014.

4. L. J. Farrugia, XRDIFF: simulation of X-ray diffraction patterns, *J. Appl. Crystallogr*. **1997**, *30*, 565.

Table S62: The crystal parameters of compound **3ar**

	CCDC 2323124
Formula	$C_{19}H_{17}ClN_2O_4$
Formula weight	366.40
T/K	297
Crystal system	Triclinic
Space group	P -1
a/Å	9.6699 (15)
b/Å	9.6753 (15)
c/Å	10.4512 (16)
α/°	76.908 (4)
β/°	71.347 (4)
γ/°	71.318 (4)
V/Å^3	869.2 (2)
Z	2
Abs. Coeff./mm^{-1}	0.248
Abs. Correction	multi-scan
GOF on F^2	1.037
Final *R* indices [$I > 2\sigma(I)$]	*R1* = 0.0369
R indices [all data]	*wR2* = 0.0927 *R1* = 0.0403 *wR2* = 0.0966

Figure S63: ORTEP diagram of compound (**3ar**) with 30% probability