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Catalyst-Free Visible-Light-Induced Decarboxylative Amination of Glycine Derivatives with Azo Compounds

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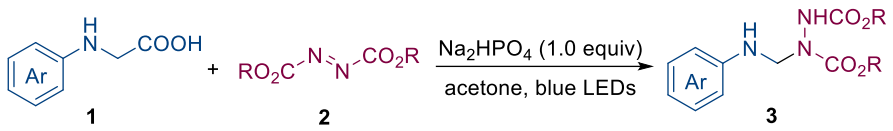
1. General methods

Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry nitrogen atmosphere. All solvents were purified and dried according to standard methods prior to use.

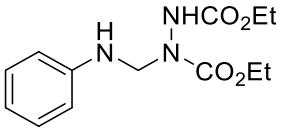
^{1}H and ^{13}C NMR spectra were recorded on a Bruker instrument (600 MHz, 400 MHz, 150 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). HRMS were obtained on an Agilent qtof 6540 LC-MS (ESI) mass spectrometer with the use of quadrupole analyzer. Fourier Transform Infrared spectra were recorded on a Nicolet iS50 FT-IR spectrophotometer. Melting points (M.p.) were determined in open capillaries without further correction.

Substrates **1** were synthesized according to the literature procedures.[1] Substrates **2** were purchased from Energy-chemical, solvents were purchased from Aladdin, and used without further purification.

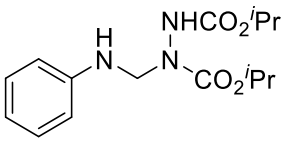
2. General procedure for visible-light-induced decarboxylative amination of glycine derivatives with azo compounds



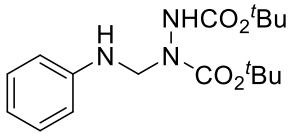
To a flame-dried sealed tube were added **1** (0.3 mmol, 1.0 equiv), **2** (0.6 mmol, 2.0 equiv), Na_2HPO_4 (1.0 equiv) and acetone (3 mL). The reaction mixture was degassed via freeze-pump-thaw for 3 cycles. After the reaction mixture was thoroughly degassed, the vial was sealed and positioned approximately 2~3 cm from 30 W blue LEDs. Then the reaction mixture was stirred at room temperature for the indicated time (monitored by TLC) under nitrogen atmosphere. Afterwards, the reaction mixture was concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 3/1) to afford the desired products **3**. The analytical data of the products **3a**-**3s** are summarized below.



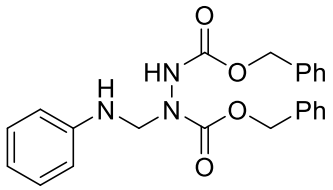
3a, yellow liquid, 42.6 mg, 76% yield. ^{1}H NMR (600 MHz, DMSO-d_6, 110 ℃) δ 8.92 (br s, 1H), 7.10 (br s, 2H), 6.74 (br s, 2H), 6.63 (br s, 1H), 5.95 (br s, 1H), 4.82 (s, 2H), 4.14-4.06 (m, 4H), 1.23-1.17 (m, 6H). ^{13}C NMR (150 MHz, DMSO-d_6, 110 ℃) δ 155.4, 155.2, 146.5, 128.0, 116.6, 112.6, 61.0, 60.2, 13.8. IR (thin film): νmax (cm^{-1}) = 3402, 1720, 1682, 1604, 1520, 1429, 1386, 1231, 1163, 1107, 1064, 1000, 857, 745, 691, 516. HRMS (ESI) calcd for $C_{13}H_{20}N_3O_4$ $[M+H]^+$: 282.1454. Found: 282.1447.



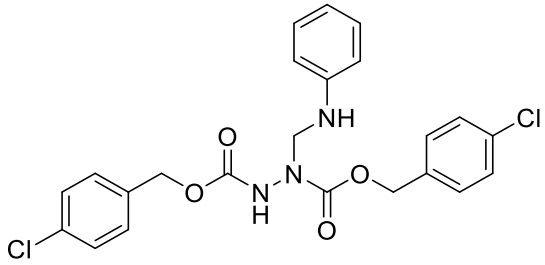
3b, yellow liquid, 66.1 mg, 71% yield. Two rotamers were observed by NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-6.40 (m, 5H), 4.95-4.61 (m, 4H), 1.82-0.88 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 145.5, 129.2, 118.7, 113.5, 70.0, 58.7, 21.9, 21.8. IR (thin film): νmax (cm^{-1}) = 2980, 1695, 1604, 1500, 1414, 1374, 1245, 1180, 1105, 1044, 912, 752, 694. HRMS (ESI) calcd for $C_{15}H_{24}N_3O_4$ $[M+H]^+$: 310.1767. Found: 310.1760.



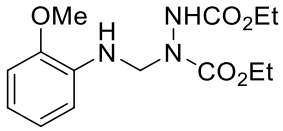
3c, yellow liquid, 85.9 mg, 85% yield. Two rotamers were observed by NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-6.29 (m, 5H), 4.90-4.64 (m, 2H), 1.46 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 145.7, 129.2, 118.4, 113.5, 81.3, 58.4, 28.1, 27.9. IR (thin film): νmax (cm^{-1}) = 2980, 1695, 1604, 1500, 1414, 1374, 1245, 1180, 1105, 1044, 912, 752, 694. HRMS (ESI) calcd for $C_{17}H_{28}N_3O_4$ $[M+H]^+$: 338.2080. Found: 338.2073.



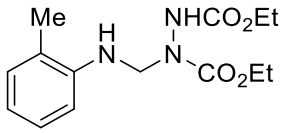
3d, white solid, 76.7 mg, 63% yield. m.p. = 139.5-142.5 °C. Two rotamers were observed by NMR. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.36-7.05 (m, 12H), 6.71-6.54 (m, 3H), 5.75-5.05 (m, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.9, 151.6, 146.8, 136.4, 135.2, 128.9, 128.5, 128.4, 128.0, 127.8, 127.8, 127.3, 116.9, 112.6, 68.6, 66.1. IR (thin film): νmax (cm^{-1}) = 3406, 3250, 3033, 1715, 1679, 1606, 1522, 1498, 1429, 1366, 1256, 1109, 1057, 967, 890, 747, 730, 691, 524. HRMS (ESI) calcd for $C_{23}H_{24}N_3O_4$ $[M+H]^+$: 406.1767. Found: 406.1757.



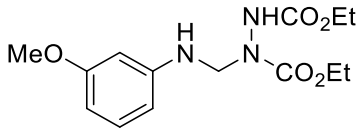
3e, white solid, 112.7 mg, 79% yield. m.p. = 97.5-102.0 °C. Two rotamers were observed by NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-6.60 (m, 13H), 5.18-4.53 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 145.1, 134.3, 133.8, 129.5, 129.3, 128.7, 119.0, 113.5, 66.9, 58.9. IR (thin film): νmax (cm^{-1}) = 3409, 3288, 1717, 1697, 1604, 1493, 1425, 1401, 1271, 1243, 1159, 1096, 1016, 895, 807, 749, 693, 544, 405. HRMS (ESI) calcd for $C_{23}H_{22}Cl_2N_3O_4$ $[M+H]^+$: 474.0987. Found: 474.0986.



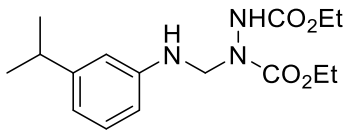
3f, yellow liquid, 47.6 mg, 51% yield. Two rotamers were observed by NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86-6.39 (m, 5H), 5.11-4.16 (m, 7H), 3.83 (s, 3H), 1.37-1.26 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 147.0, 135.1, 121.2, 118.1, 111.1, 109.9, 62.1, 57.8, 55.4, 14.4, 14.3. IR (thin film): νmax (cm^{-1}) = 2987, 2901, 1703, 1602, 1514, 1461, 1411, 1381, 1342, 1221, 1175, 1116, 1066, 1053, 740. HRMS (ESI) calcd for $C_{14}H_{22}N_3O_5$ $[M+H]^+$: 312.1559. Found: 312.1557.



3g, yellow liquid, 52.6 mg, 59% yield. Two rotamers were observed by NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-6.49 (m, 4H), 5.02-3.66 (m, 6H), 2.32-1.85 (m, 3H), 1.66-0.88 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 143.4, 130.4, 127.1, 122.5, 118.4, 110.9, 62.1, 58.6, 17.4, 14.4, 14.3. IR (thin film): νmax (cm^{-1}) = 2987, 2901, 1703, 1514, 1409, 1394, 1380, 1242, 1167, 1152, 1066, 1056, 1028, 750. HRMS (ESI) calcd for $C_{14}H_{22}N_3O_4$ $[M+H]^+$: 296.1610. Found: 296.1614.

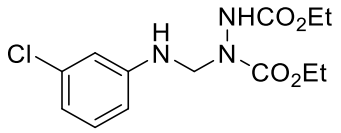


3h, yellow liquid, 47.1 mg, 50% yield. Two rotamers were observed by NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10-6.32 (m, 4H), 4.94-3.57 (m, 9H), 1.26 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 155.9, 146.9, 130.0, 106.4, 104.2, 99.2, 62.1, 58.5, 55.0, 14.4, 14.3. IR (thin film): νmax (cm^{-1}) = 3239, 2989, 1741, 1693, 1529, 1482, 1229, 1162, 1065, 1020, 782, 758, 731, 688, 648, 593. HRMS (ESI) calcd for $C_{14}H_{22}N_3O_5$ $[M+H]^+$: 312.1559. Found: 312.1559.

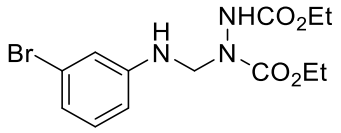


3i, yellow liquid, 47.0 mg, 48% yield. Two rotamers were observed by NMR. ^{1}H NMR

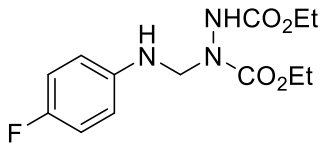
(400 MHz, $CDCl_3$) δ 7.13-6.44 (m, 4H), 4.97-4.17 (m, 6H), 2.86-2.78 (m, 1H), 1.42-1.21 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 150.3, 145.4, 129.2, 117.1, 111.8, 111.0, 62.2, 58.6, 34.2, 34.0, 23.9, 14.4, 14.3. IR (thin film): νmax (cm^{-1}) = 2968, 2901, 1703, 1607, 1593, 1480, 1467, 1409, 1394, 1381, 1230, 1196, 1172, 1151, 1066. HRMS (ESI) calcd for $C_{16}H_{26}N_3O_4$ $[M+H]^+$: 324.1923. Found: 324.1924.



3j, yellow liquid, 66.2 mg, 70% yield. Two rotamers were observed by NMR. ^1H NMR (400 MHz, $CDCl_3$) δ 7.10-6.59 (m, 4H), 4.94-4.14 (m, 6H), 1.38-1.18 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 146.8, 135.0, 130.3, 118.6, 113.4, 111.7, 62.3, 58.6, 14.4, 14.3. IR (thin film): νmax (cm^{-1}) = 3387, 3295, 2985, 1696, 1601, 1515, 1480, 1377, 1224, 1151, 1066, 1019, 987, 866, 845, 762, 682, 591, 525, 442. HRMS (ESI) calcd for $C_{13}H_{19}ClN_3O_4$ $[M+H]^+$: 316.1064. Found:316.1065.

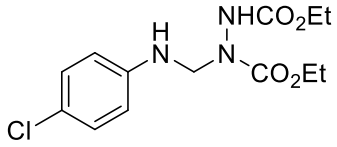


3k, yellow liquid, 66.2 mg, 65% yield. Two rotamers were observed by NMR. ^1H NMR (400 MHz, $CDCl_3$) δ 7.04-6.64 (m, 4H), 4.93-4.08 (m, 6H), 1.94-1.14 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 147.0, 130.5, 123.1, 121.5, 116.3, 112.06, 62.2, 58.50, 14.4, 14.3. IR (thin film): νmax (cm^{-1}) = 3385, 3294, 2987, 2901, 1696, 1600, 1514, 1377, 1224, 1066, 984, 840, 761, 681, 664, 525, 437. HRMS (ESI) calcd for $C_{13}H_{19}BrN_3O_4$ $[M+H]^+$: 360.0559. Found:360.0560.

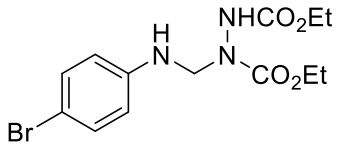


3l, yellow liquid, 64.8 mg, 72% yield. Two rotamers were observed by NMR. ^1H NMR (400 MHz, $CDCl_3$) δ 6.92-6.65 (m, 4H), 4.92-3.66 (m, 6H), 1.42-1.23 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 156.0, 155.3, 141.7, 115.8, 115.6, 114.6, 62.6, 62.2, 59.2, 14.4, 14.3. ^{19}F NMR (375 MHz, $CDCl_3$) δ -126.4. IR (thin film): νmax (cm^{-1}) = 3675, 3403, 3281, 2901, 2989, 1716, 1680, 1509, 1428, 1387, 1220, 1160, 1112, 1065,

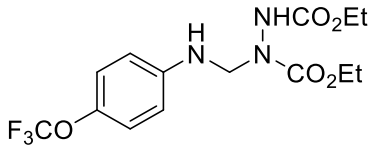
1001, 859, 825, 769, 508. HRMS (ESI) calcd for $C_{13}H_{19}FN_3O_4$ $[M+H]^+$: 300.1360. Found: 300.1363.



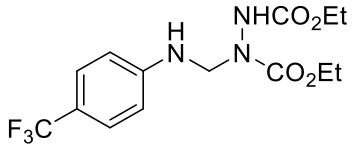
3m, yellow liquid, 64.4 mg, 68% yield. Two rotamers were observed by NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-6.65 (m, 4H), 4.91-4.14 (m, 6H), 1.94-1.14 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 144.1, 129.0, 123.3, 114.7, 62.6, 62.2, 58.7, 14.4, 14.3. IR (thin film): νmax (cm^{-1}) = 3675, 3394, 3286, 2979, 2901, 1712, 1680, 1519, 1493, 1437, 1381, 1235, 1165, 1088, 1066, 1007, 906, 816, 764, 729, 629, 532, 504. HRMS (ESI) calcd for $C_{13}H_{19}ClN_3O_4$ $[M+H]^+$: 316.1064. Found: 316.1064.



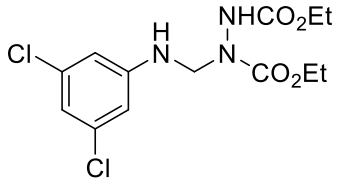
3n, yellow liquid, 73.6 mg, 68% yield. Two rotamers were observed by NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-6.58 (m, 4H), 4.91-4.11 (m, 6H), 1.42-1.14 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 144.6, 131.9, 115.2, 110.4, 62.6, 62.2, 58.5, 14.4, 14.3. IR (thin film): νmax (cm^{-1}) = 3394, 3287, 2978, 1711, 1680, 1597, 1517, 1489, 1437, 1381, 1235, 1157, 1096, 1074, 1007, 906, 814, 764, 730, 526, 501. HRMS (ESI) calcd for $C_{13}H_{19}{}^{79}BrN_3O_4$ $[M+H]^+$: 360.0559. Found: 360.0562.



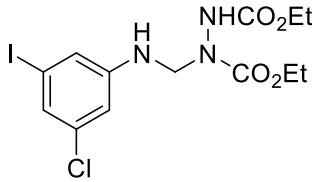
3o, yellow liquid, 74.4 mg, 68% yield. Two rotamers were observed by NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09-6.69 (m, 4H), 4.94-3.66 (m, 6H), 1.42-1.14 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 144.4, 141.4, 122.4, 121.9, 119.3, 114.0, 62.7, 62.3, 58.8, 14.4, 14.3. ^{19}F NMR (375 MHz, $CDCl_3$) δ -58.5. IR (thin film): νmax (cm^{-1}) = 3675, 3397, 3281, 2988, 2901, 1718, 1678, 1525, 1270, 1221, 1152, 1118, 1093, 991, 838, 817, 767, 545. HRMS (ESI) calcd for $C_{14}H_{19}F_3N_3O_5$ $[M+H]^+$: 366.1277. Found: 366.1278.



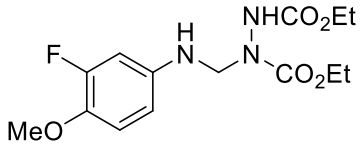
3p, yellow liquid, 52.1 mg, 50% yield. Two rotamers were observed by NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-6.77 (m, 4H), 4.99-4.18 (m, 6H), 1.34-1.23 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 155.2, 152.2, 148.4, 126.6, 126.5, 126.0, 123.3, 120.1, 112.8, 64.1, 62.5, 62.3, 58.1, 14.3, 14.0. ^{19}F NMR (375 MHz, $CDCl_3$) δ -61.3. IR (thin film): νmax (cm^{-1}) = 2988, 2901, 1712, 1616, 1536, 1408, 1382, 1321, 1250, 1189, 1161, 1104, 1066, 830. HRMS (ESI) calcd for $C_{14}H_{19}F_3N_3O_4$ $[M+H]^+$: 350.1328. Found: 350.1329.



3q, yellow liquid, 55.9 mg, 53% yield. Two rotamers were observed by NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-6.67 (m, 3H), 5.18-4.19 (m, 6H), 1.38-1.13 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 140.5, 128.9, 127.7, 122.9, 120.0, 113.2, 62.8, 62.3, 57.8, 14.4. IR (thin film): νmax (cm^{-1}) = 2988, 2901, 1702, 1508, 1410, 1394, 1381, 1228, 1163, 1066, 1028, 867. HRMS (ESI) calcd for $C_{13}H_{18}Cl_2N_3O_4$ $[M+H]^+$: 350.0674. Found: 350.0675.

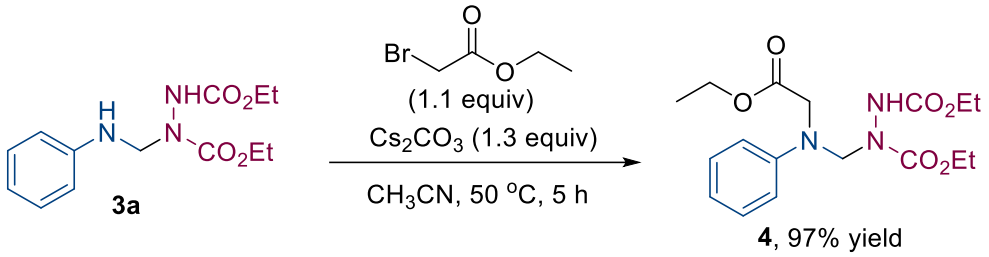


3r, yellow liquid, 94.2 mg, 71% yield. Two rotamers were observed by NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-6.79 (m, 3H), 5.00-4.14 (m, 6H), 1.85-1.12 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 143.9, 138.0, 129.2, 123.6, 112.3, 85.0, 62.8, 62.3, 58.4, 14.4. IR (thin film): νmax (cm^{-1}) = 2987, 2901, 1705, 1651, 1504, 1465, 1445, 1409, 1379, 1221, 1163, 1058, 869, 761, 731. HRMS (ESI) calcd for $C_{13}H_{18}ClIN_3O_4$ $[M+H]^+$: 442.0031. Found: 442.0016.

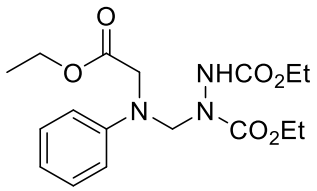


3s, brown liquid, 92.3 mg, 93% yield. Two rotamers were observed by NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88-6.42 (m, 3H), 4.88-3.66 (m, 9H), 1.38-1.22 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 155.9, 154.4, 152.0, 140.3, 115.6, 108.7, 102.6, 62.6, 62.1, 59.3, 57.2, 14.3, 14.3. ^{19}F NMR (375 MHz, $CDCl_3$) δ -133.3. IR (thin film): νmax (cm^{-1}) = 2988, 1694, 1520, 1221, 1187, 1172, 1058, 1027, 759, 595, 449, 404. HRMS (ESI) calcd for $C_{14}H_{21}FN_3O_5$ $[M+H]^+$: 330.1465. Found: 330.1462.

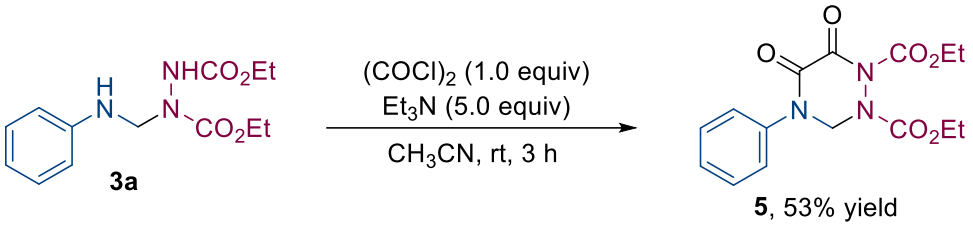
3. Transformations of product 3a



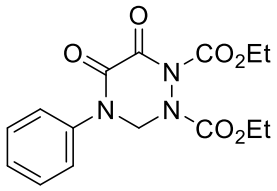
To a solution of **3a** (28.13 mg, 0.1 mmol) in CH_3CN (2 mL) were added ethyl 2-bromoacetate (18.37 mg, 0.11 mmol) and Cs_2CO_3 (42.36 mg, 0.13 mmol) under air atmosphere. The reaction mixture was stirred at 50 °C for 5 h. After the reaction was complete (monitored by TLC), the suspension was filtered and washed with ethyl acetate. Then the filtrate was concentrated by rotary evaporation and the residue was purified by silica gel column chromatography (PE/EtOAc = 5/1) to afford the desired product **4**.



4, yellow liquid, 35.5 mg, 97% yield. Two rotamers were observed by NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-6.68 (m, 5H), 5.39-5.10 (m, 1H) 4.72-3.31 (m, 10H), 1.30-1.13 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 155.5, 155.4, 145.3, 129.2, 123.8, 118.6, 113.6, 113.5, 62.9, 62.4, 61.5, 61.4, 57.6, 53.5, 29.6, 14.5, 14.3, 14.1. IR (thin film): νmax (cm^{-1}) = 2988, 2915, 2848, 1713, 1604, 1409, 1394, 1378, 1331, 1303, 1249, 1057, 761. HRMS (ESI) calcd for $C_{17}H_{26}N_3O_6$ $[M+H]^+$: 368.1822. Found: 368.1814.



To a solution of **3a** (63.6 mg, 0.36 mmol) in CH_3CN (7 mL) were added oxalyl chloride (45.17 mg, 0.36 mmol) and triethylamine (180 mg, 1.78 mmol) under air. The reaction mixture was stirred at 50 °C for 5 h. After the reaction was complete (monitored by TLC). Then the filtrate was concentrated by rotary evaporation and the residue was purified by silica gel column chromatography (PE/EtOAc = 2/1) to afford the desired product **5**.



5, yellow liquid, 63.6 mg, 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.43 (m, 2H), 7.38-7.35 (m, 3H), 5.67 (d, *J* = 13.2 Hz, 1H), 5.33 (d, *J* = 13.2 Hz, 1H), 4.44-4.30 (m, 4H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.32 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 154.0, 153.9, 149.6, 137.1, 129.6, 128.2, 125.0, 64.8, 64.8, 63.0, 14.1, 14.0. IR (thin film): νmax (cm^{-1}) = 1795, 1743, 1695, 1493, 1370, 1210, 1080, 1021, 847, 761, 730, 695, 503, 420, 411. HRMS (ESI) calcd for $C_{15}H_{18}N_3O_6$ $[M+H]^+$: 336.1196. Found: 336.1189.

4. UV/Vis absorption spectra

UV/vis absorption spectra based on **1a** (0.01 M in acetone), **2a** (0.01 M in acetone) , the mixture of **1a** and **2a** (**1a**:**2a** = 1:1, 0.01 M in acetone) and the mixture of **1a** , **2a** and Na_2HPO_4 (**1a**:**2a**:Na_2HPO_4 = 1:1:1, 0.01 M in acetone) were recorded respectively in 1 cm path quartz cuvettes using Pgeneral TU-1901 UV/Vis spectrometer.

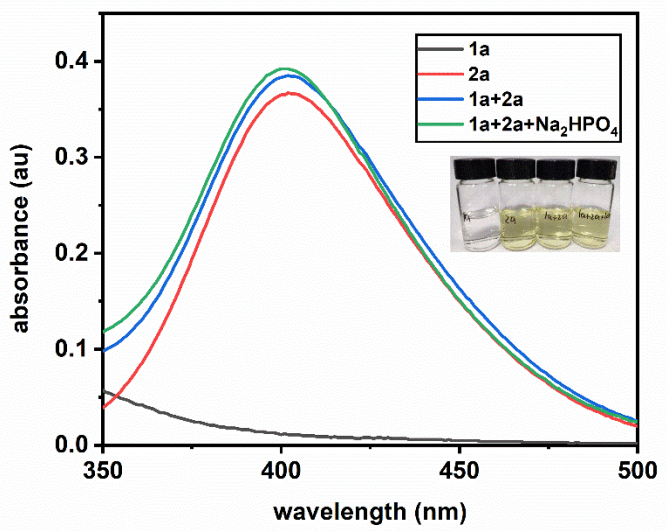


Figure S1. UV/vis spectra of **1a**, **2a**, the mixture of **1a** and **2a**, and the mixture of **1a**, **2a** and Na_2HPO_4.

5. Emission spectra of the LED lamps

The following spectra were recorded on EVERFINE Corporation HAAS-2000_VIS_V2 High-precision fast spectroradiometer. The forward current of the LEDs is 25 mA. Electroluminescence (EL) measurements of the LED lamps were carried out at room temperature using Everfine HAAS-2000. For the light collection, the LEDs were placed inside a 30 cm-diameter integrating sphere coupled to a high accuracy array spectroradiometer (wavelength accuracy <0.3 nm) and a programmable test power LED300E.

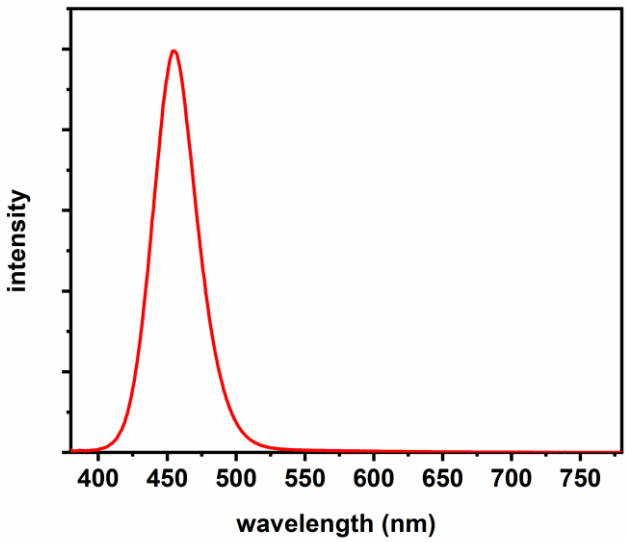


Figure S2. Emission spectra of the blue LEDs lamp.

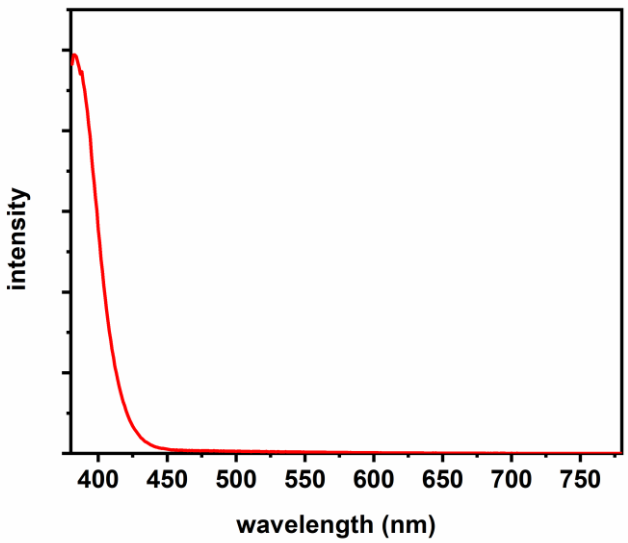


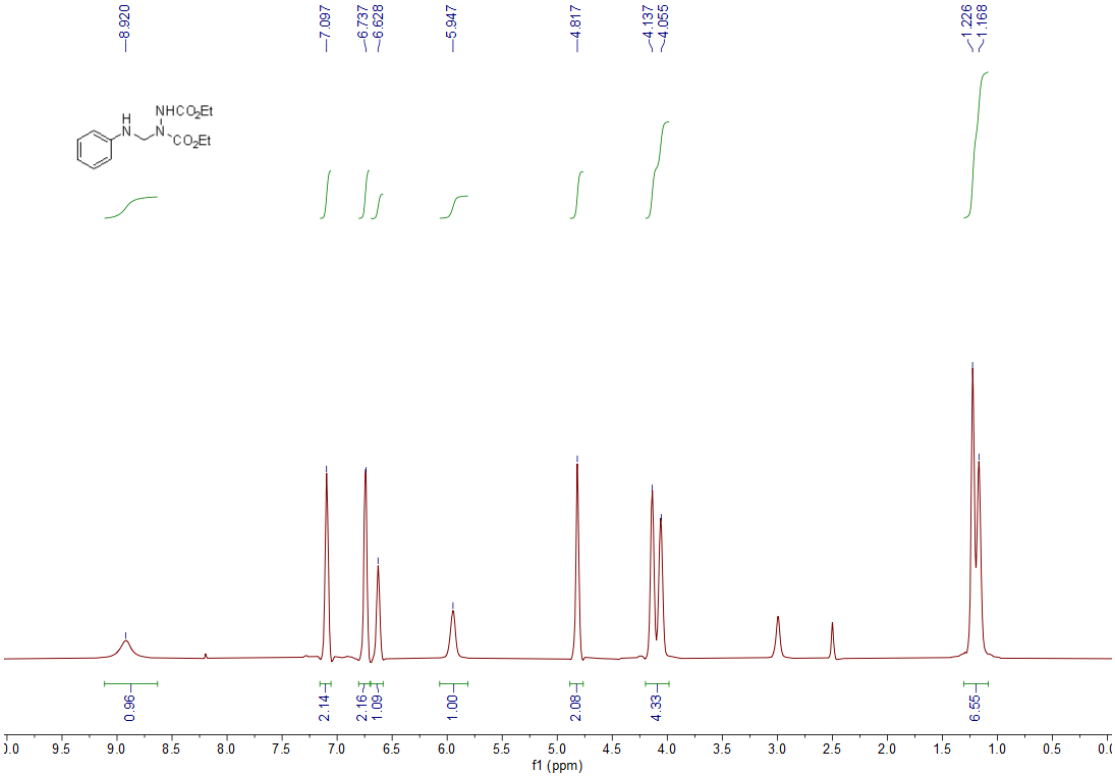
Figure S3. Emission spectra of the purple LEDs lamp.

6. References

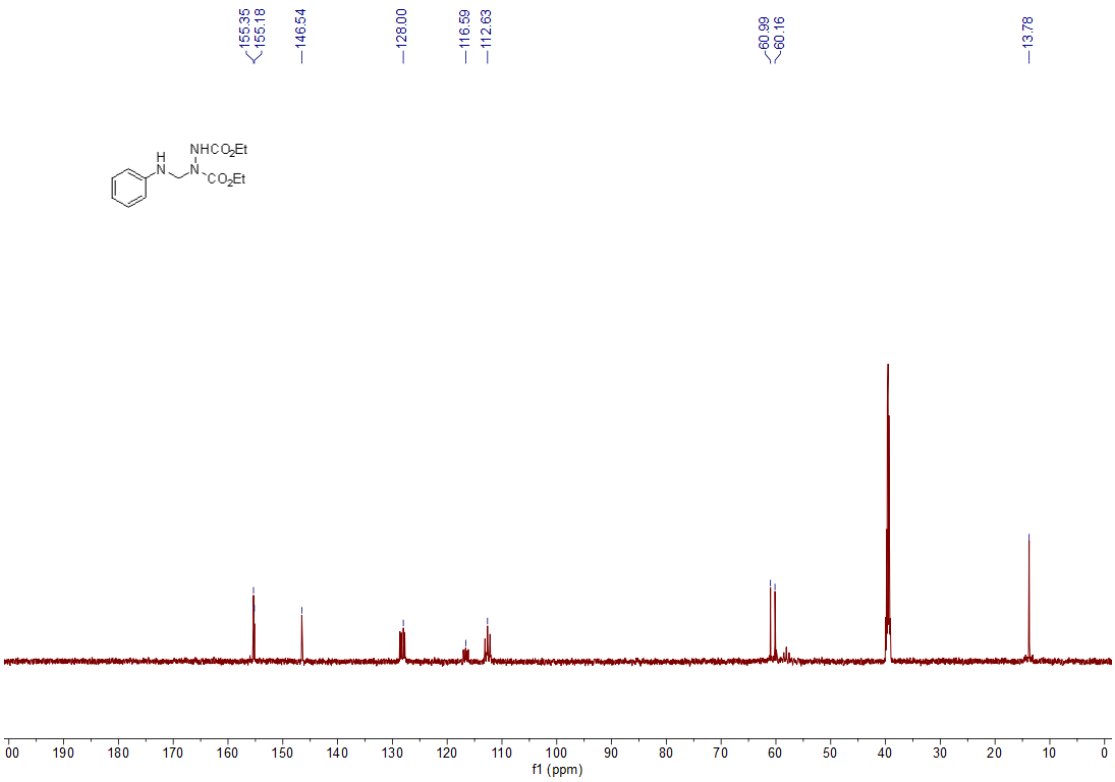
[1] (a) Z. Yao, X. Wu, X. Zhang, Q. Xiong, S. Jiang and Z. Yu, Synthesis and evaluation of photo-activatable β-diarylsydnone-l-alanines for fluorogenic photo-click cyclization of peptides. *Org. Biomol. Chem.*, 2019, **17**, 6777-6781; (b) N. Pe´try, T. Vanderbeeken, A. Malher, Y. Bringer, P. Retailleau, X. Bantreil and F. Lamaty, Mechanosynthesis of sydnone-containing coordination complexes, *Chem. Commun.*, 2019, **55**, 9495-9498.

7. Copies of NMR spectra

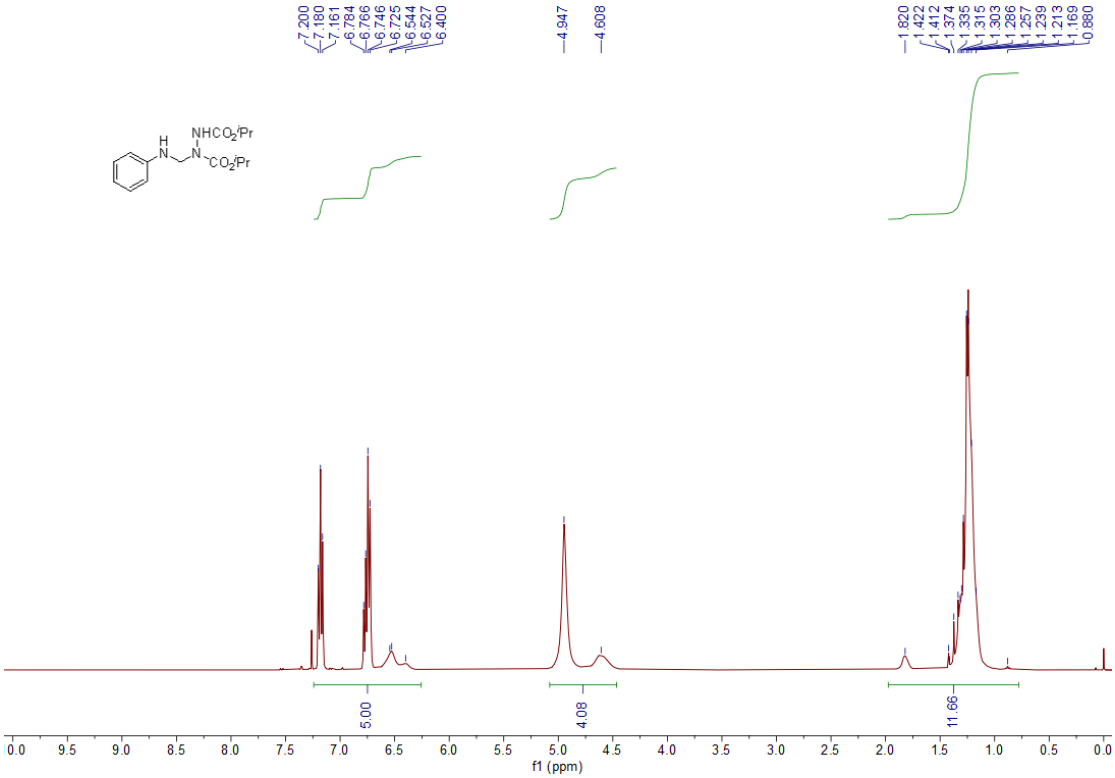
^{1}H NMR Spectrum of **3a**



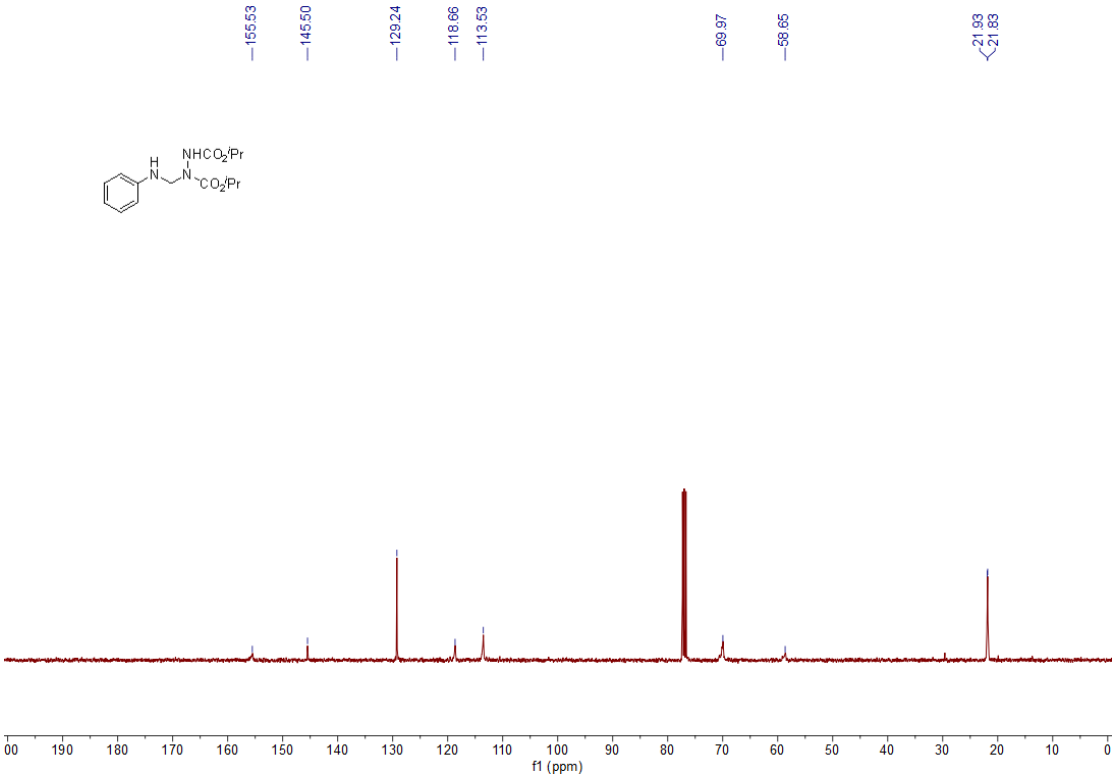
^{13}C NMR Spectrum of **3a**



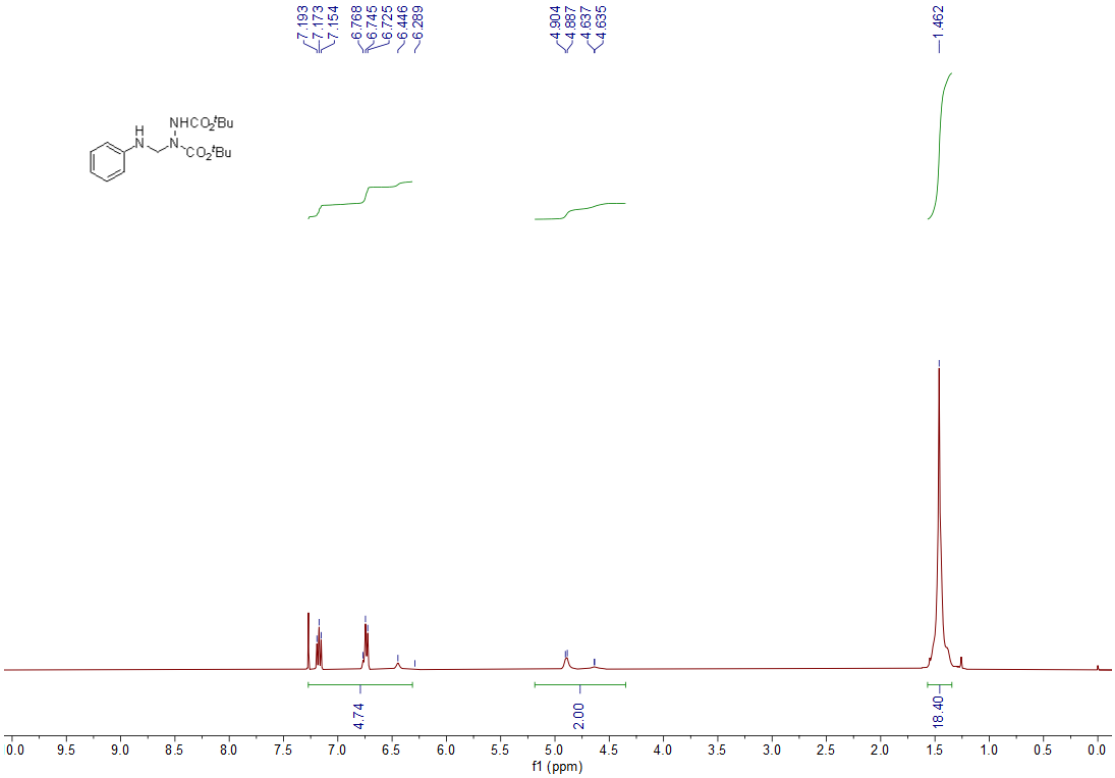
^{1}H NMR Spectrum of **3b**



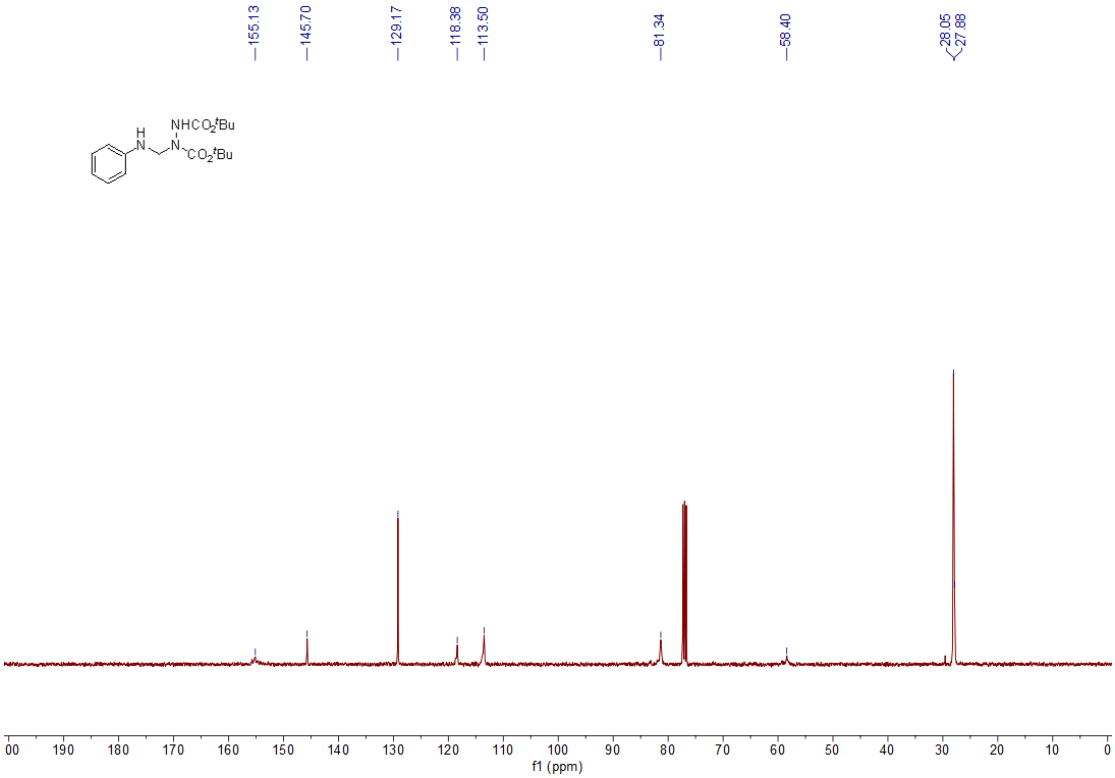
^{13}C NMR Spectrum of **3b**



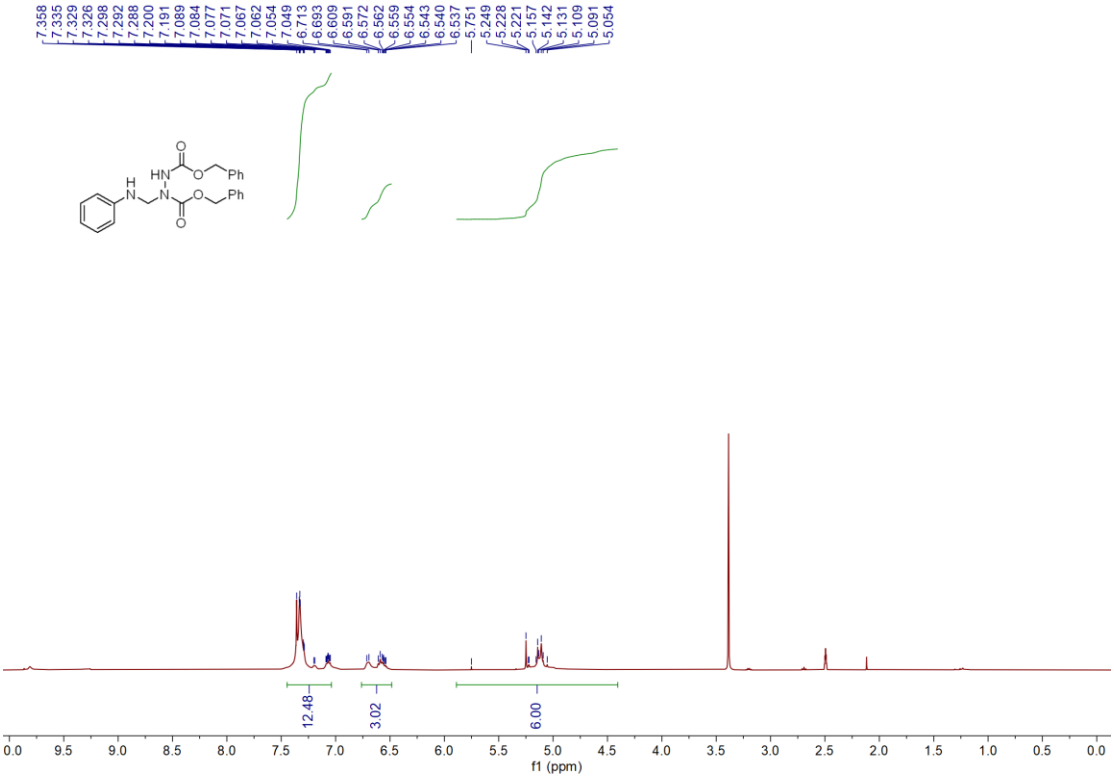
^{1}H NMR Spectrum of **3c**



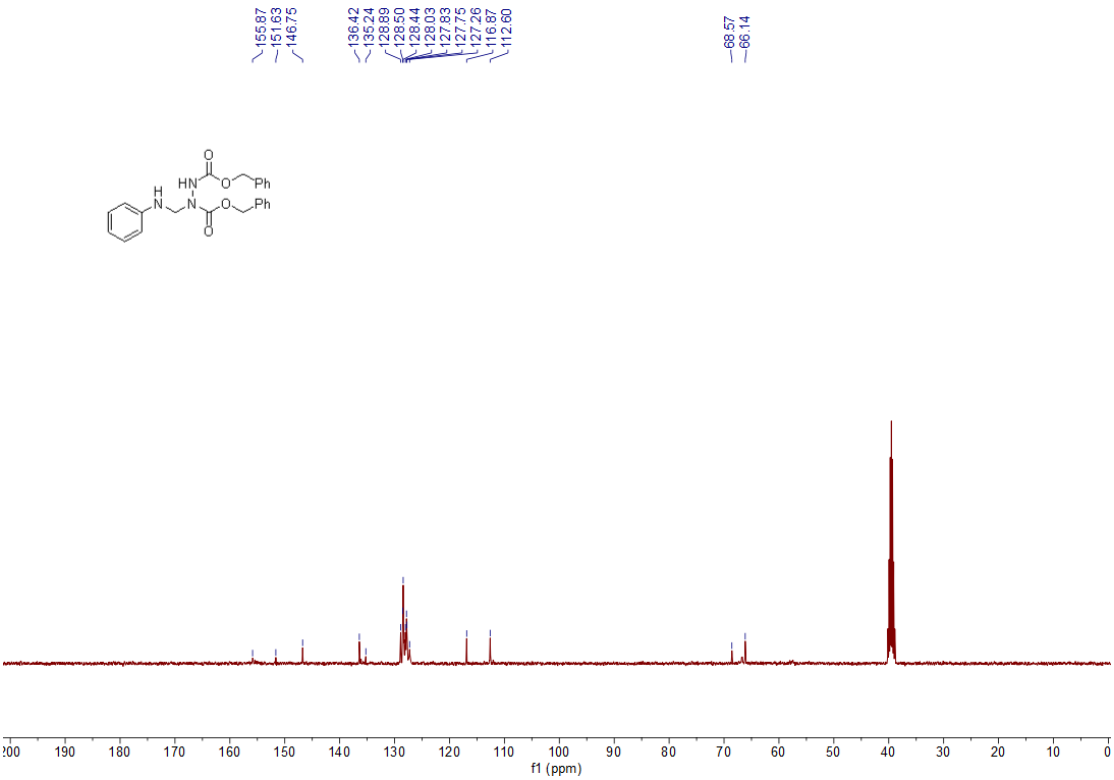
^{13}C NMR Spectrum of **3c**



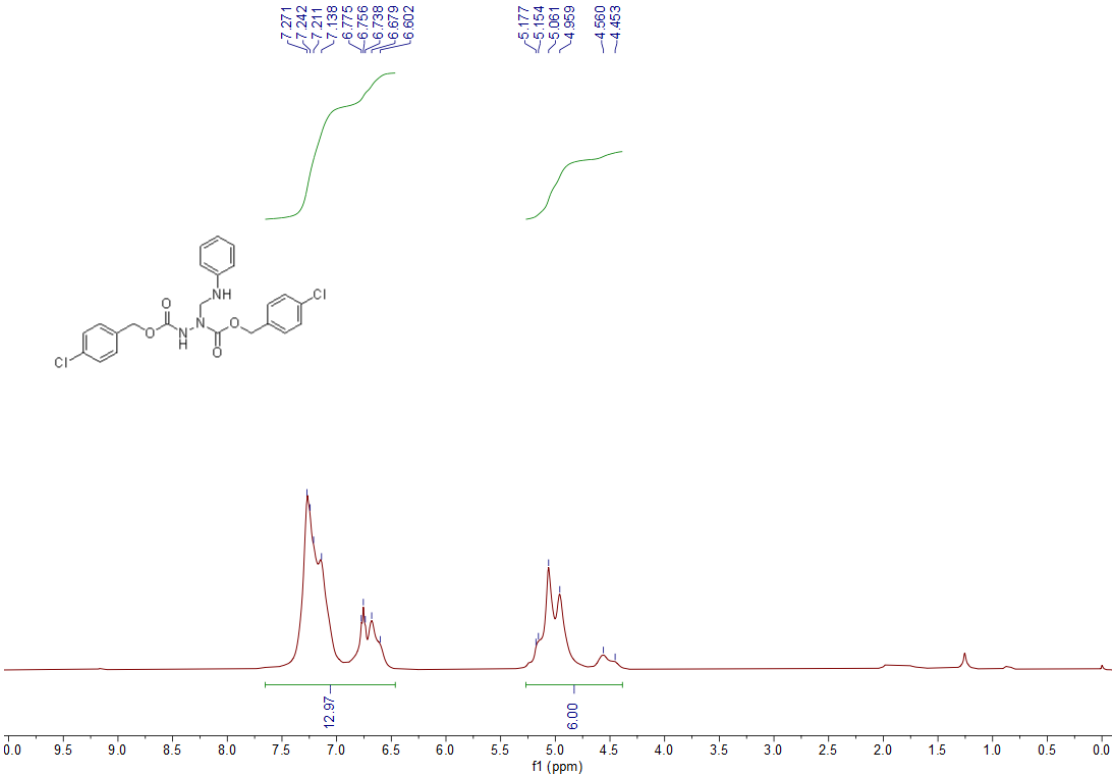
^{1}H NMR Spectrum of **3d**



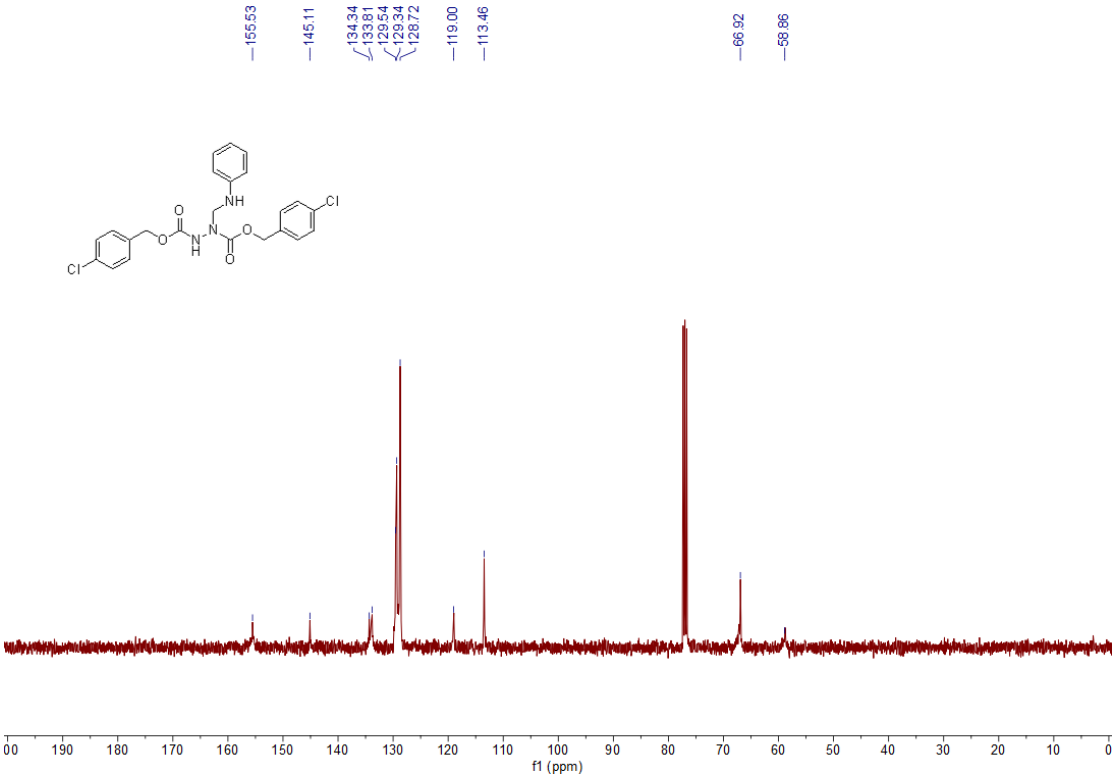
^{13}C NMR Spectrum of **3d**



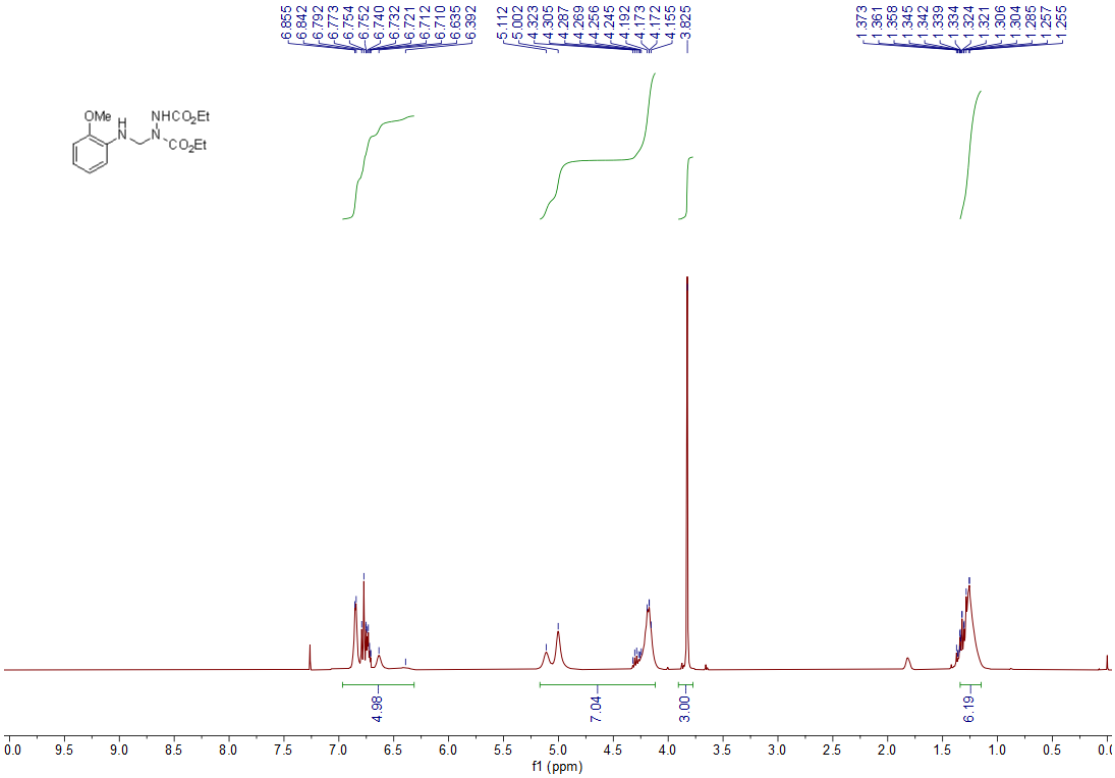
^{1}H NMR Spectrum of **3e**



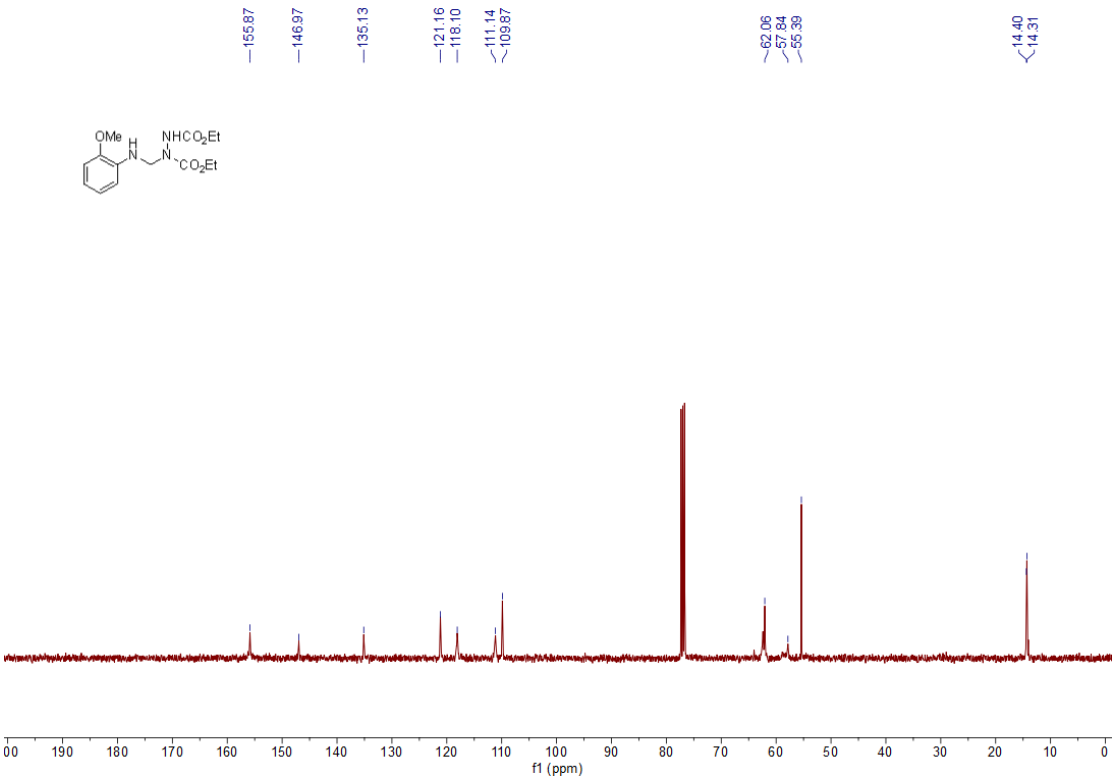
^{13}C NMR Spectrum of **3e**



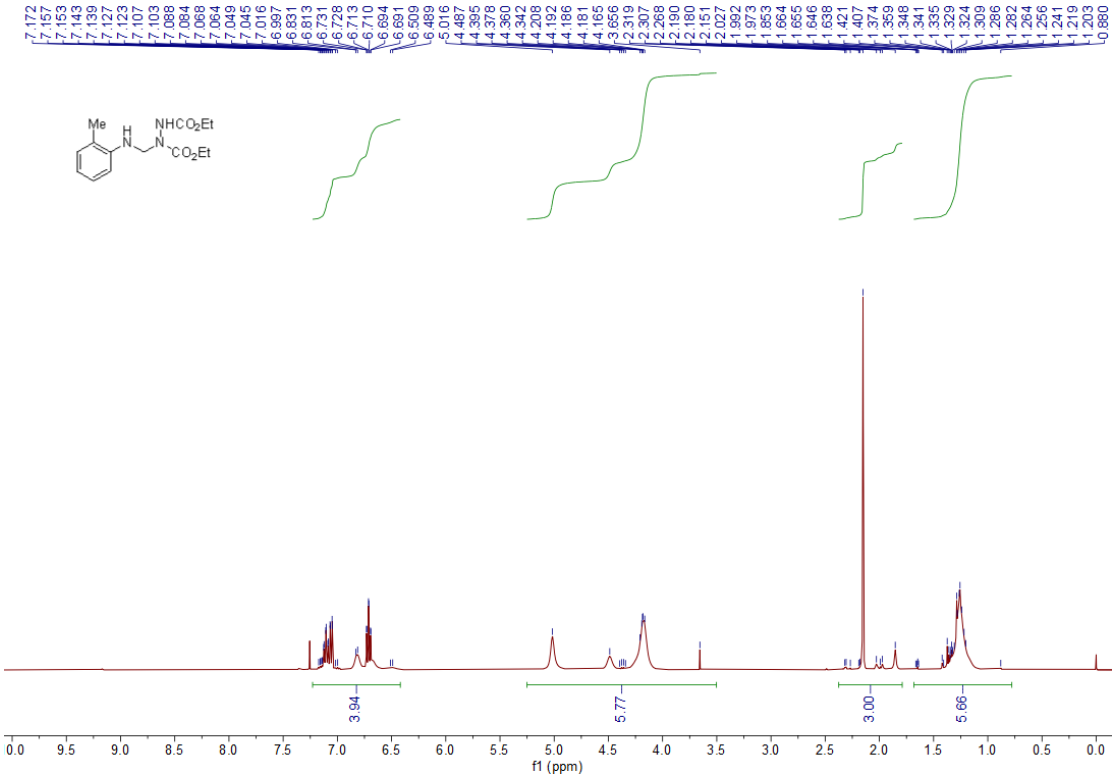
^{1}H NMR Spectrum of **3f**



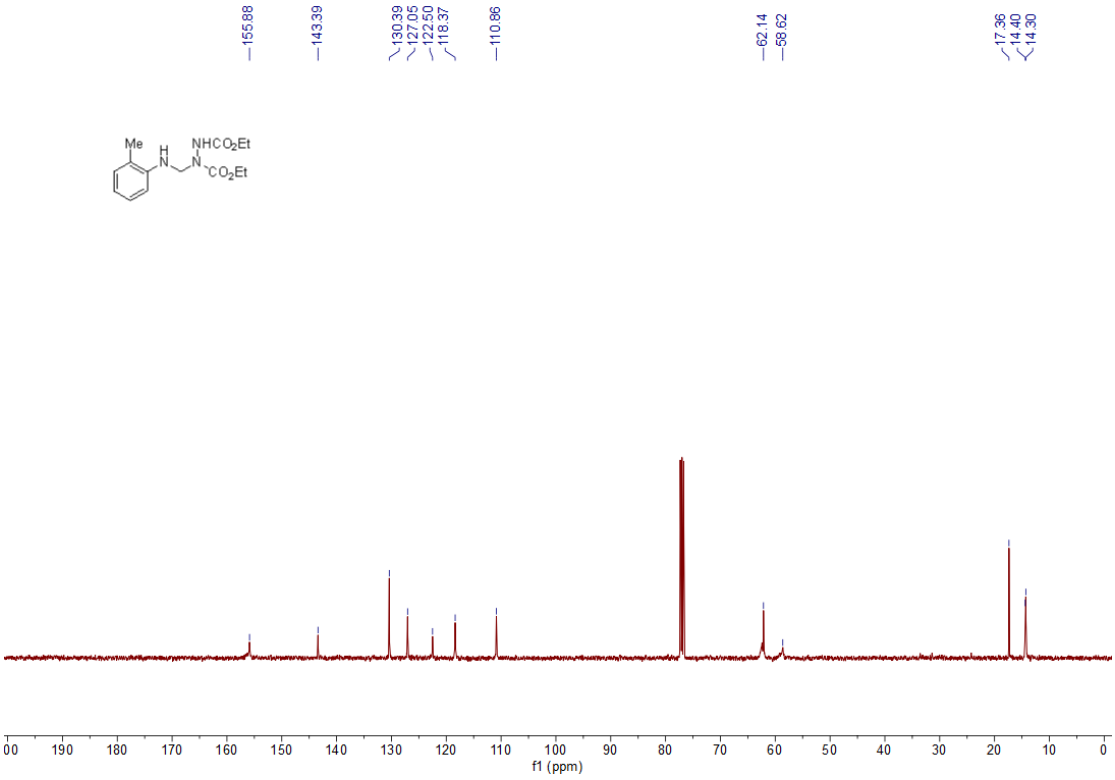
^{13}C NMR Spectrum of **3f**



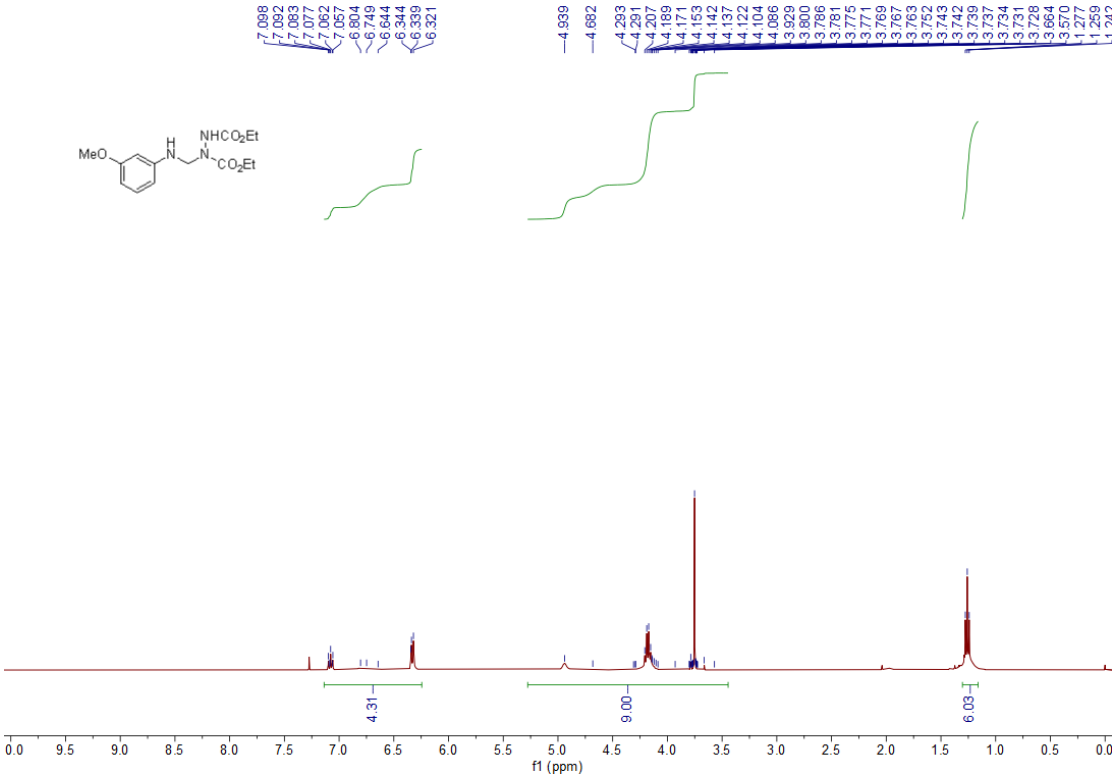
^{1}H NMR Spectrum of **3g**



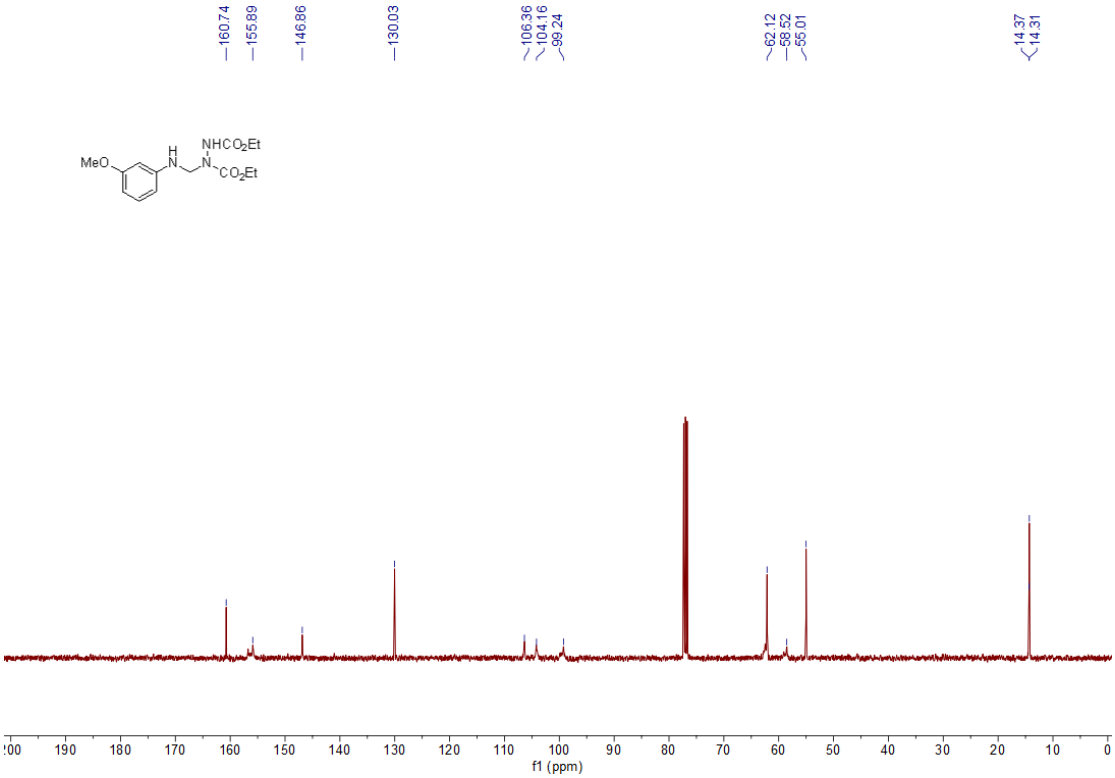
^{13}C NMR Spectrum of **3g**



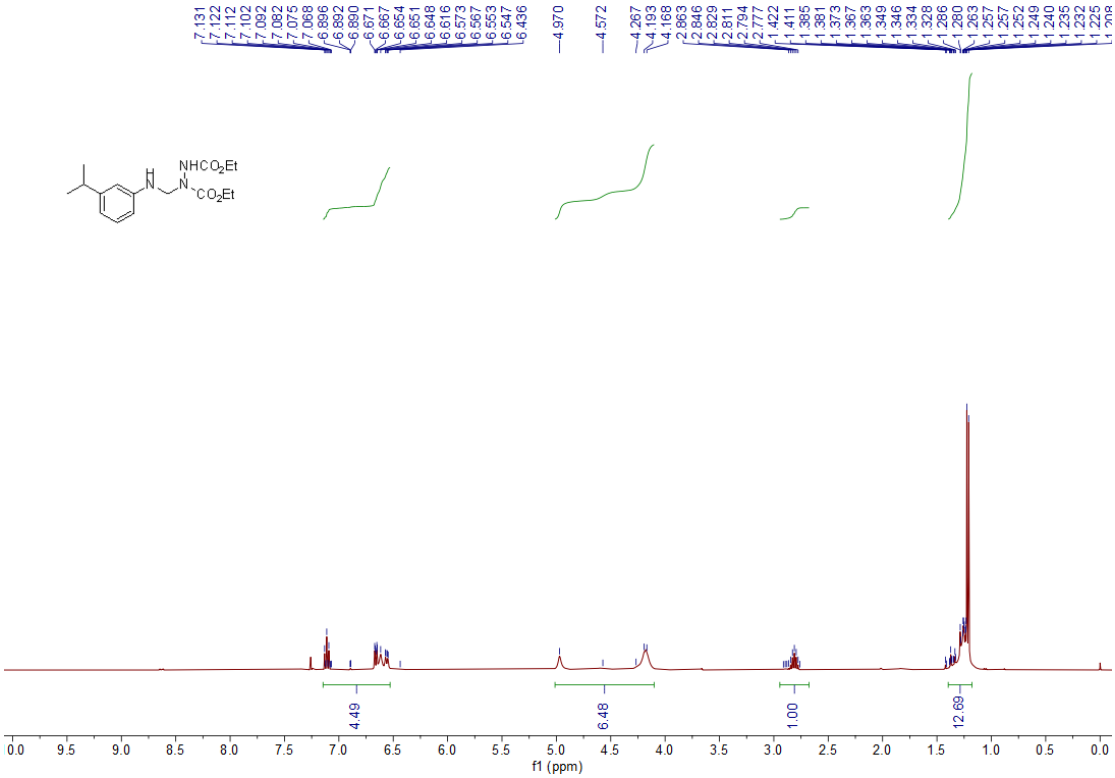
^{1}H NMR Spectrum of **3h**



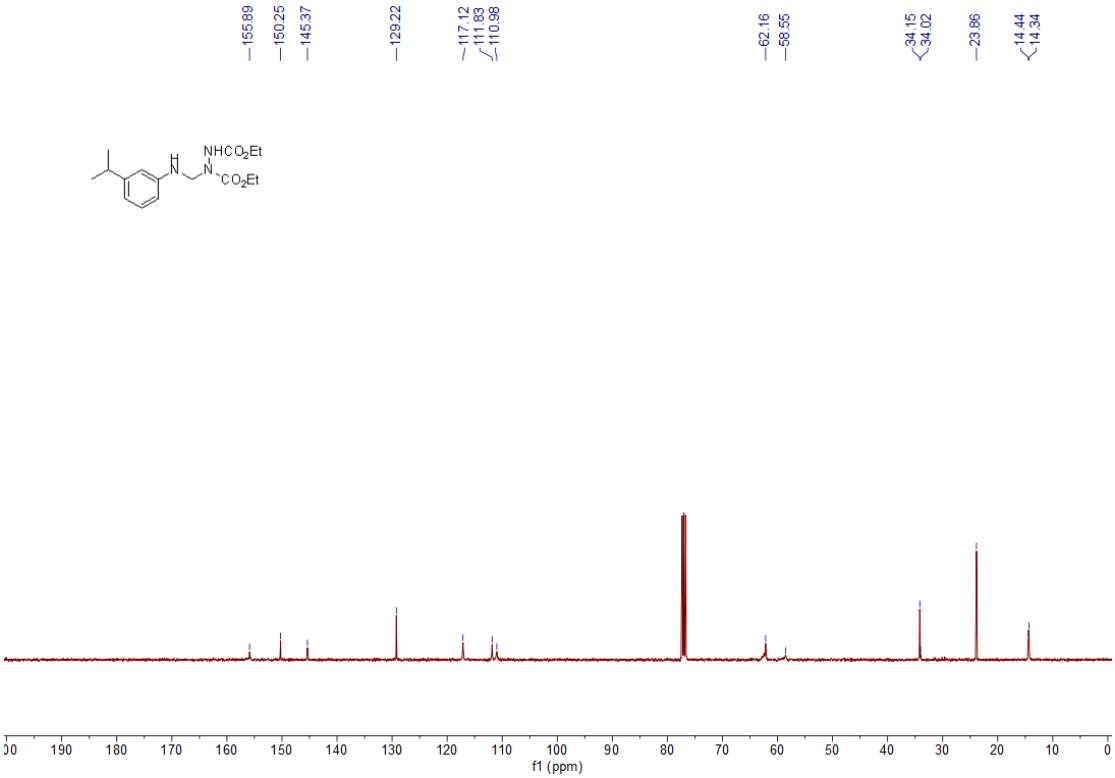
^{13}C NMR Spectrum of **3h**



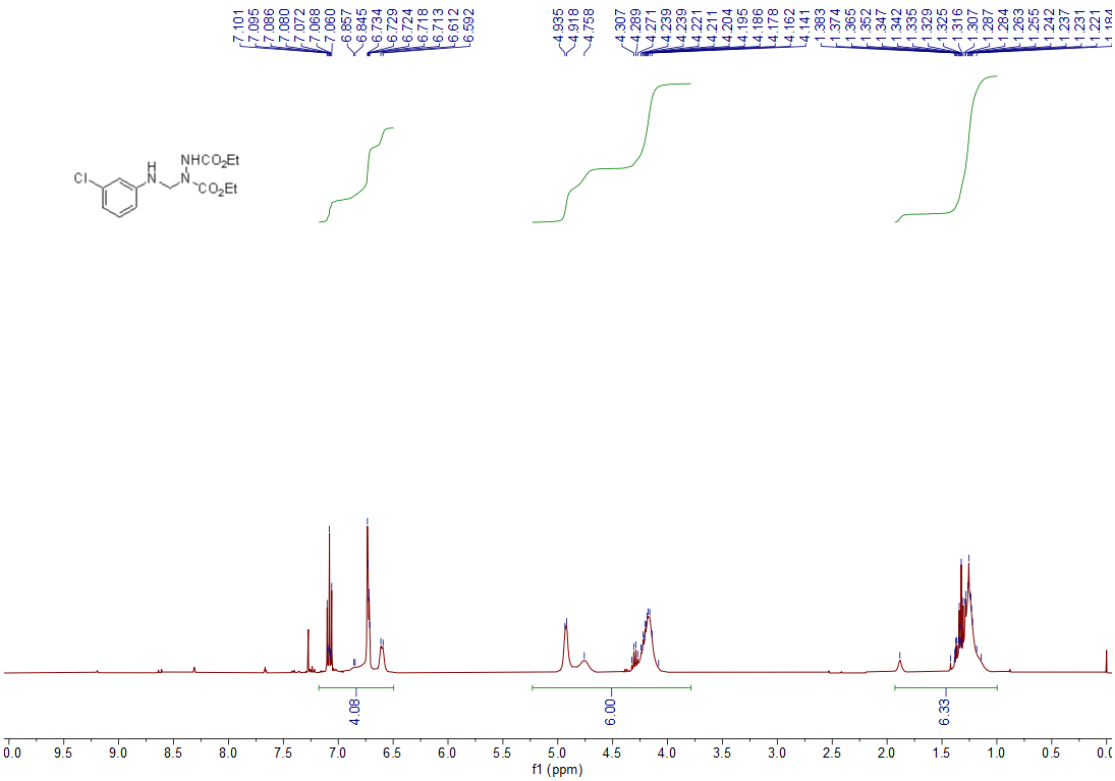
^{1}H NMR Spectrum of **3i**



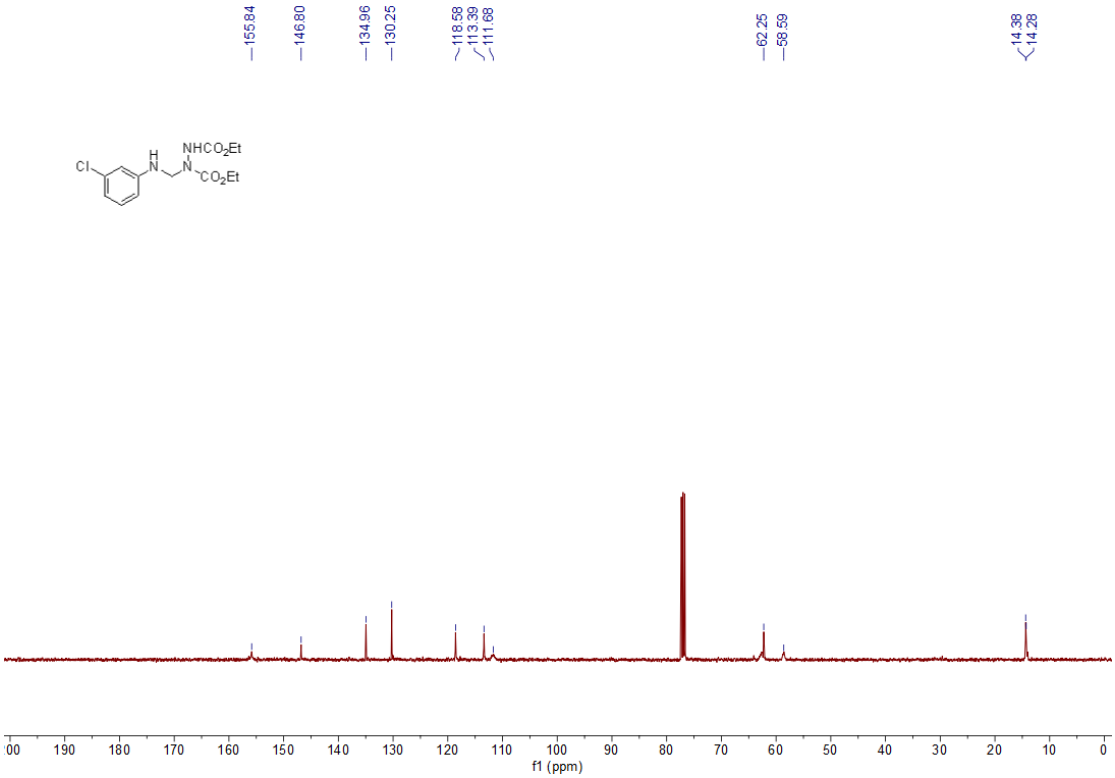
^{13}C NMR Spectrum of **3i**



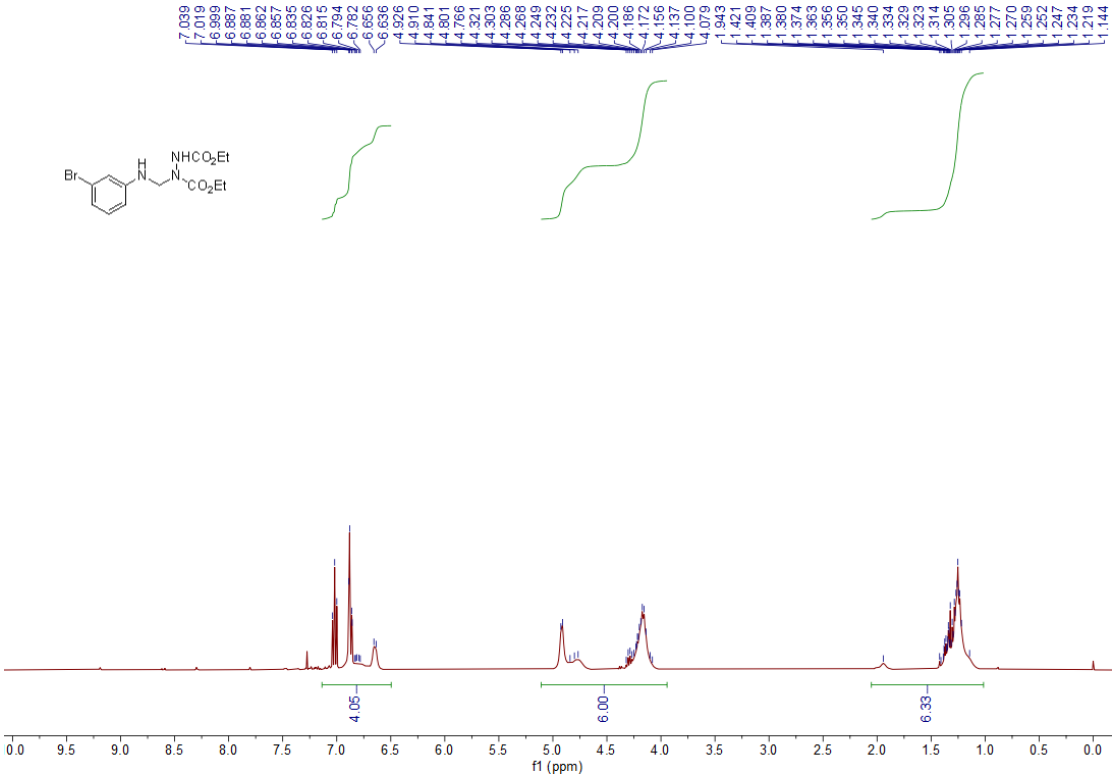
^{1}H NMR Spectrum of **3j**



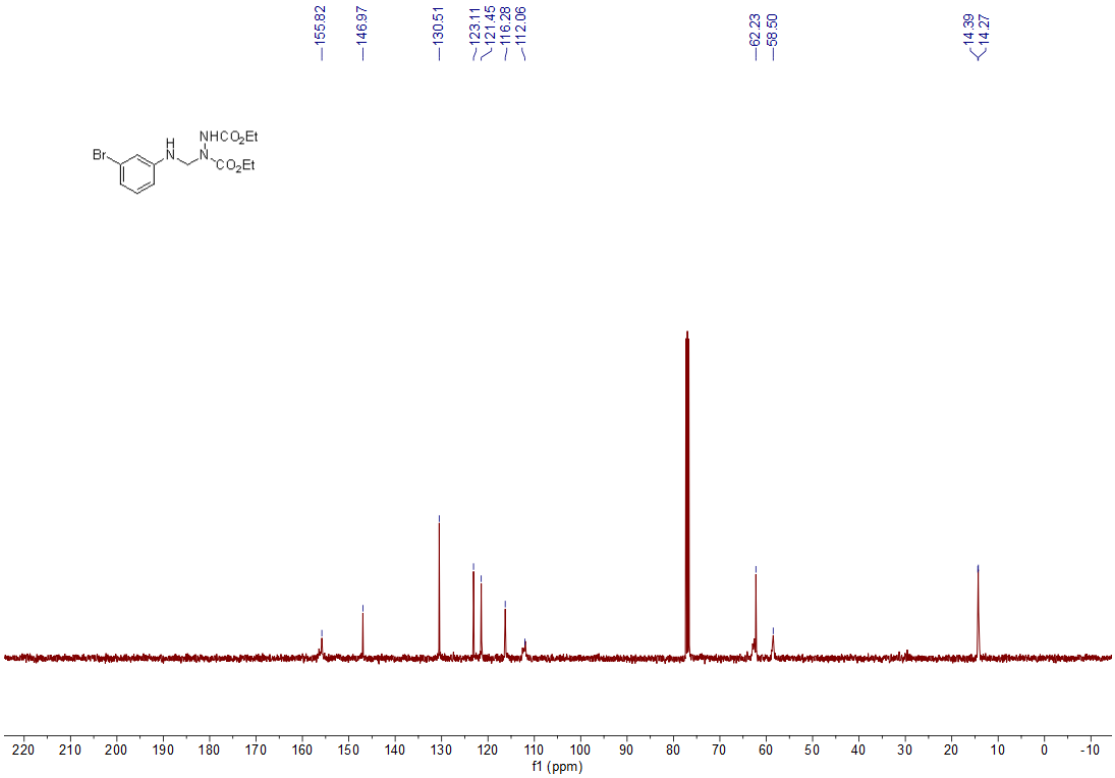
^{13}C NMR Spectrum of **3j**



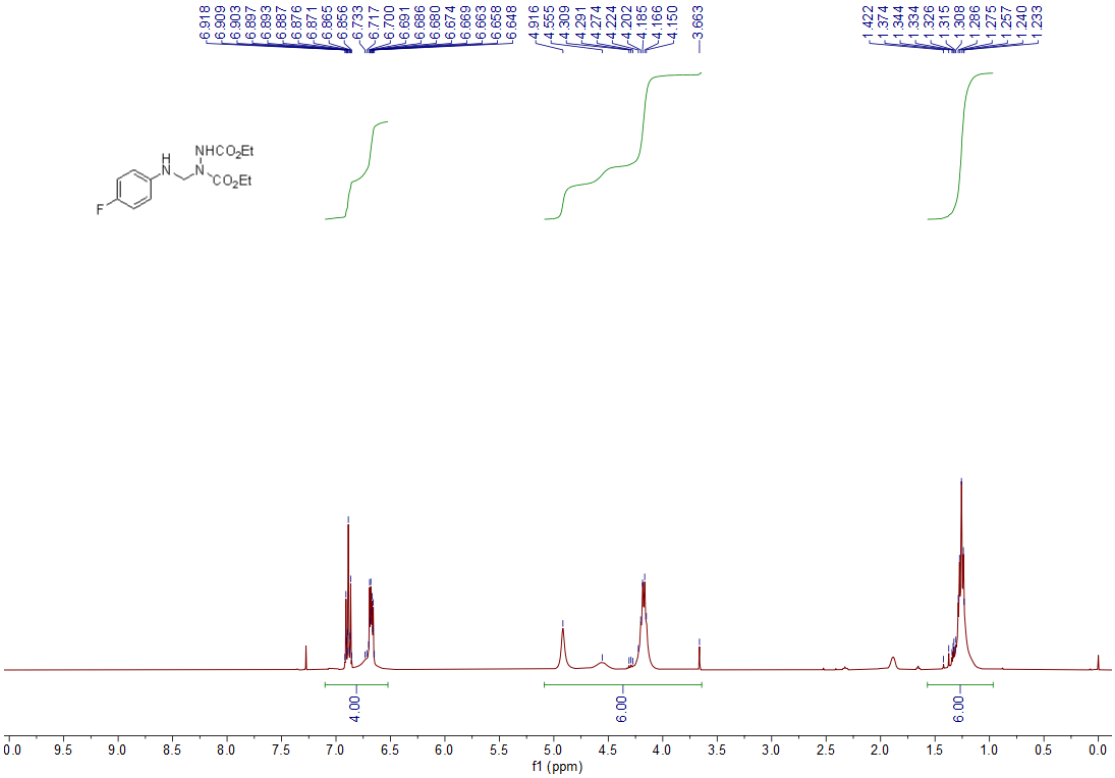
^{1}H NMR Spectrum of **3k**



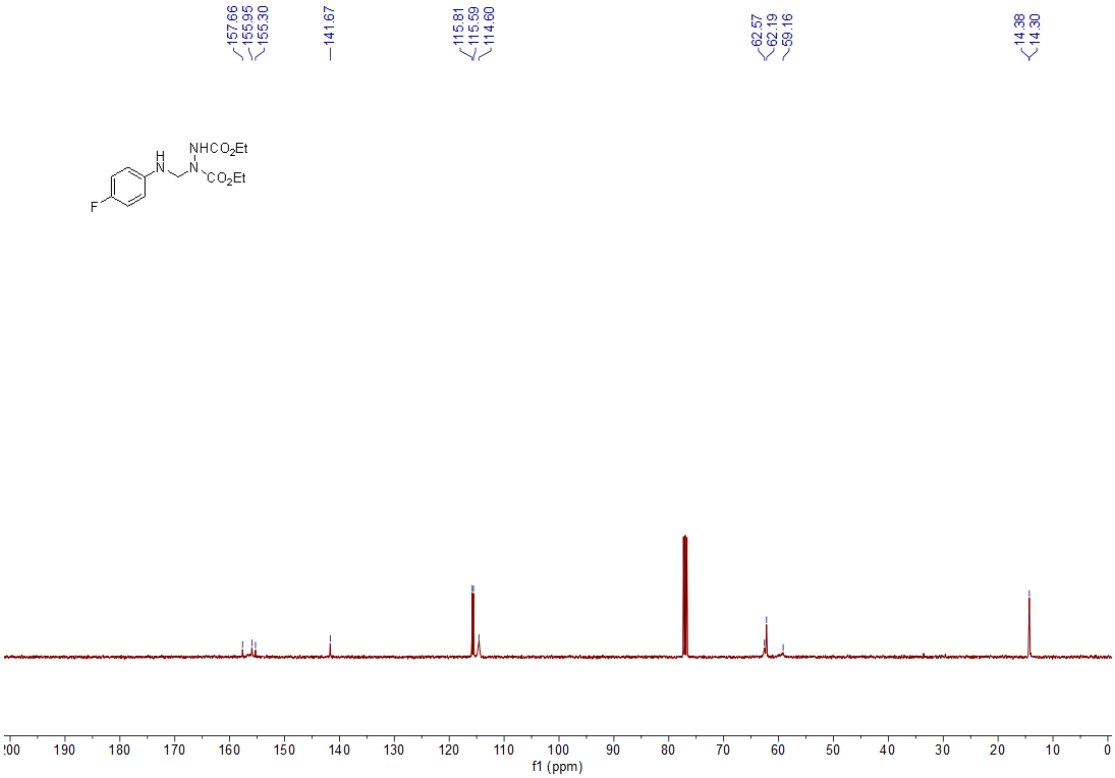
^{13}C NMR Spectrum of **3k**



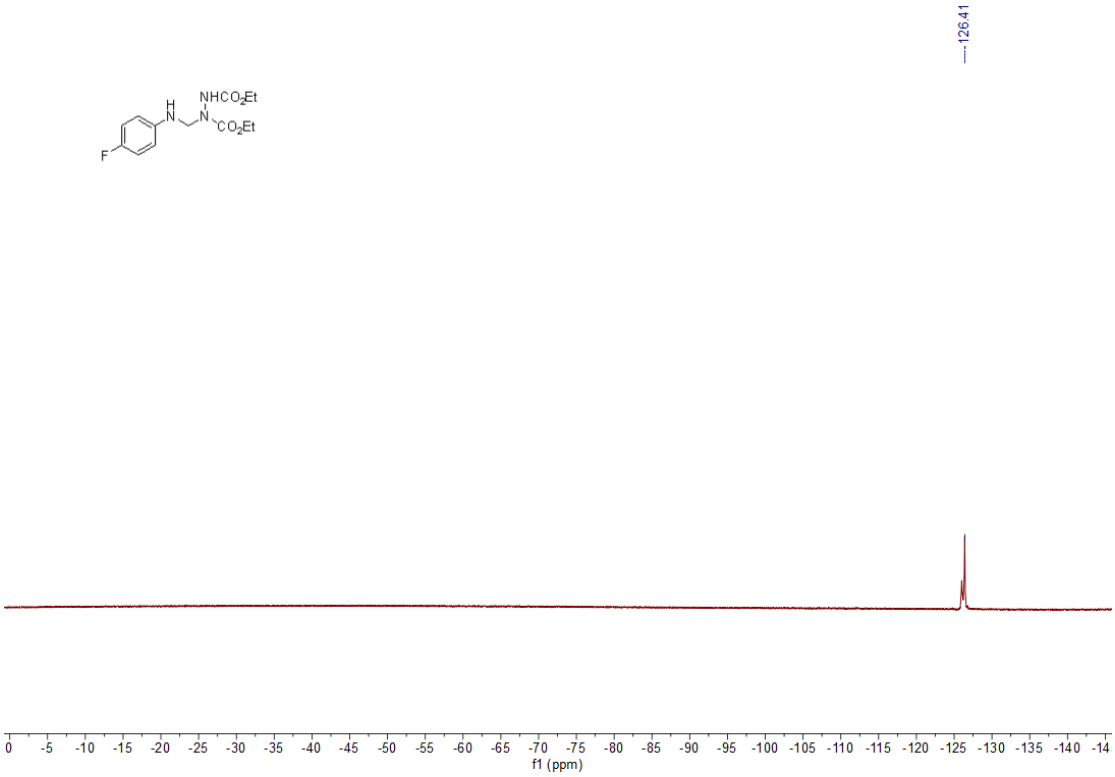
^{1}H NMR Spectrum of **3l**



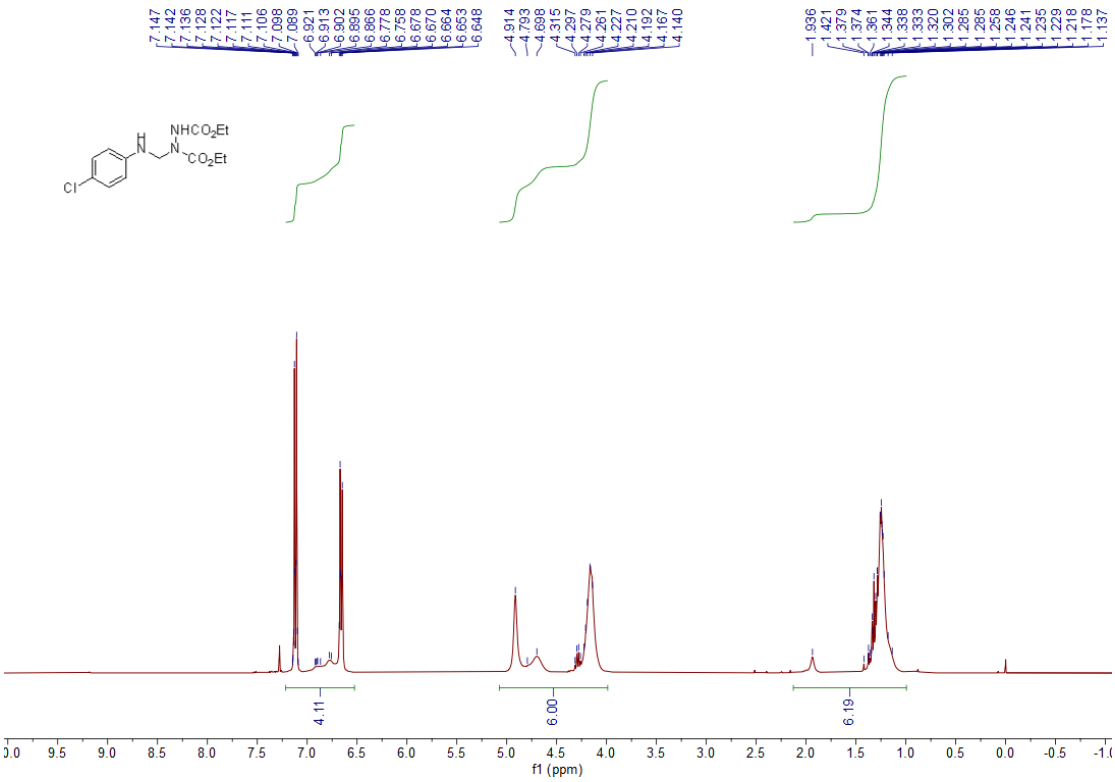
^{13}C NMR Spectrum of **3l**



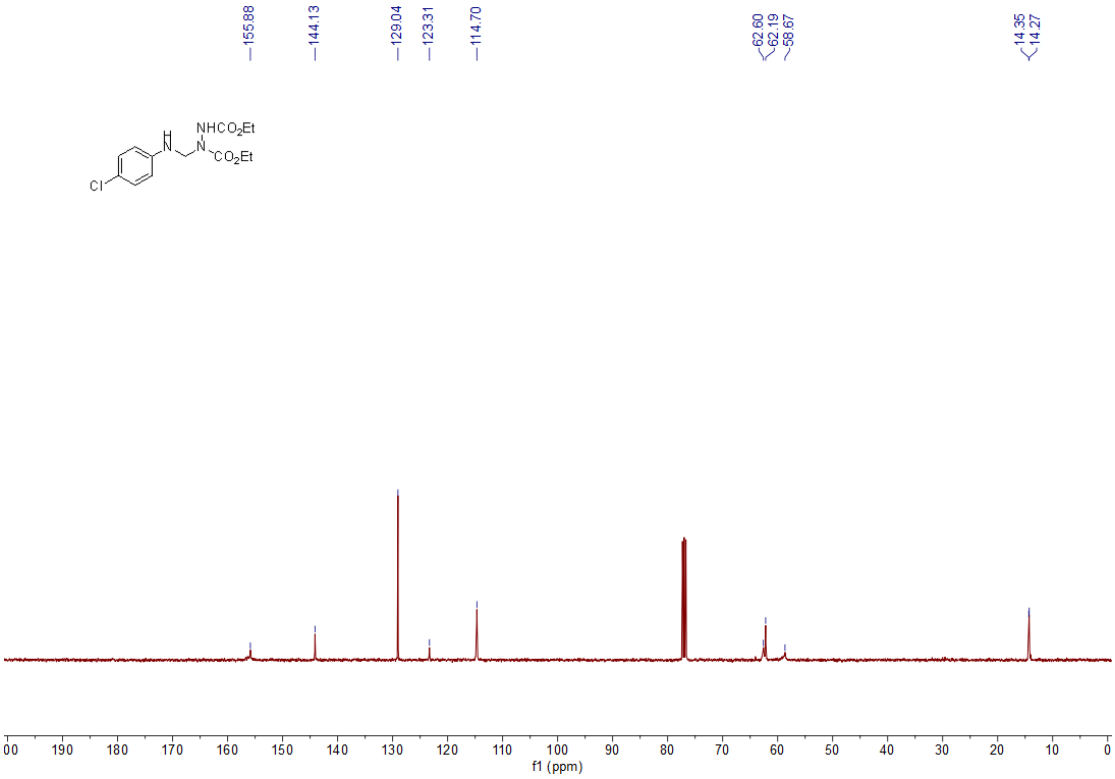
^{19}F NMR Spectrum of **3l**



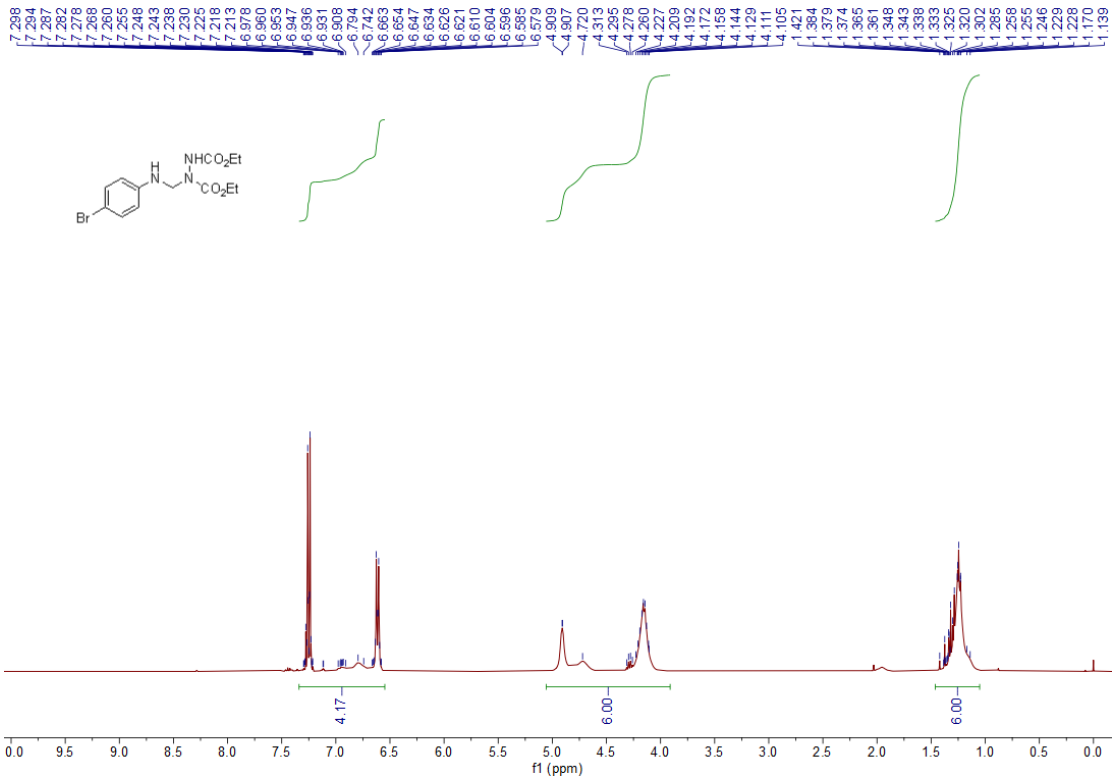
^{1}H NMR Spectrum of **3m**



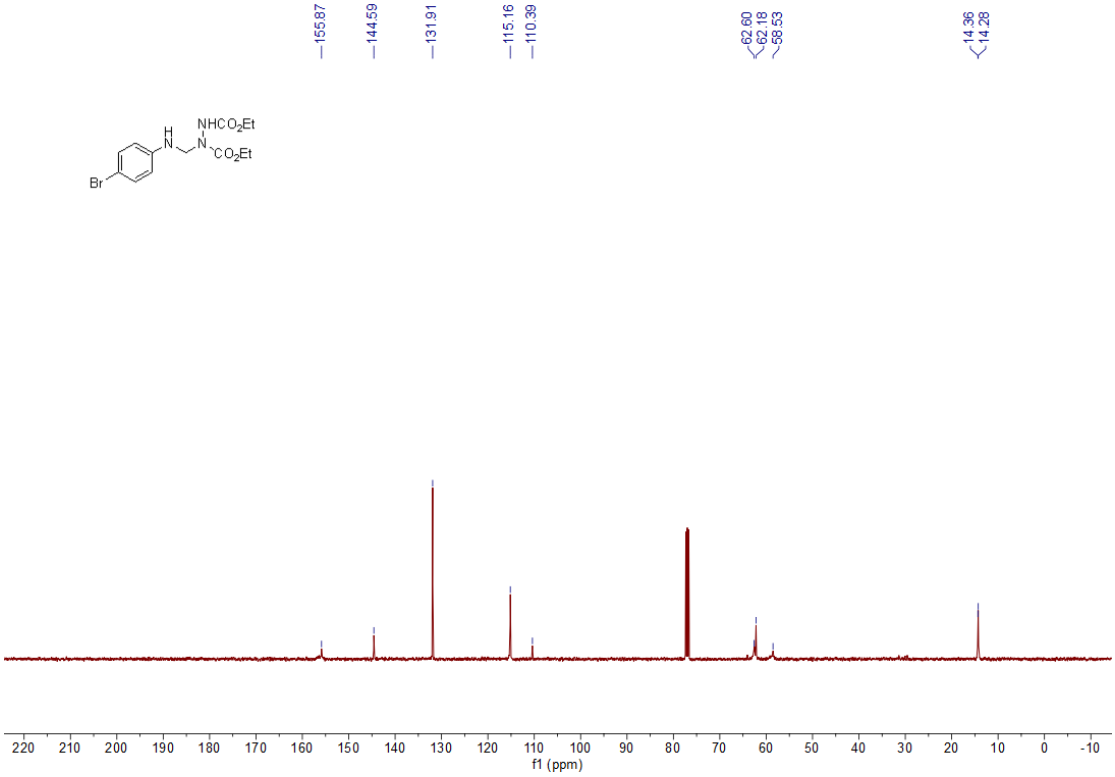
^{13}C NMR Spectrum of **3m**



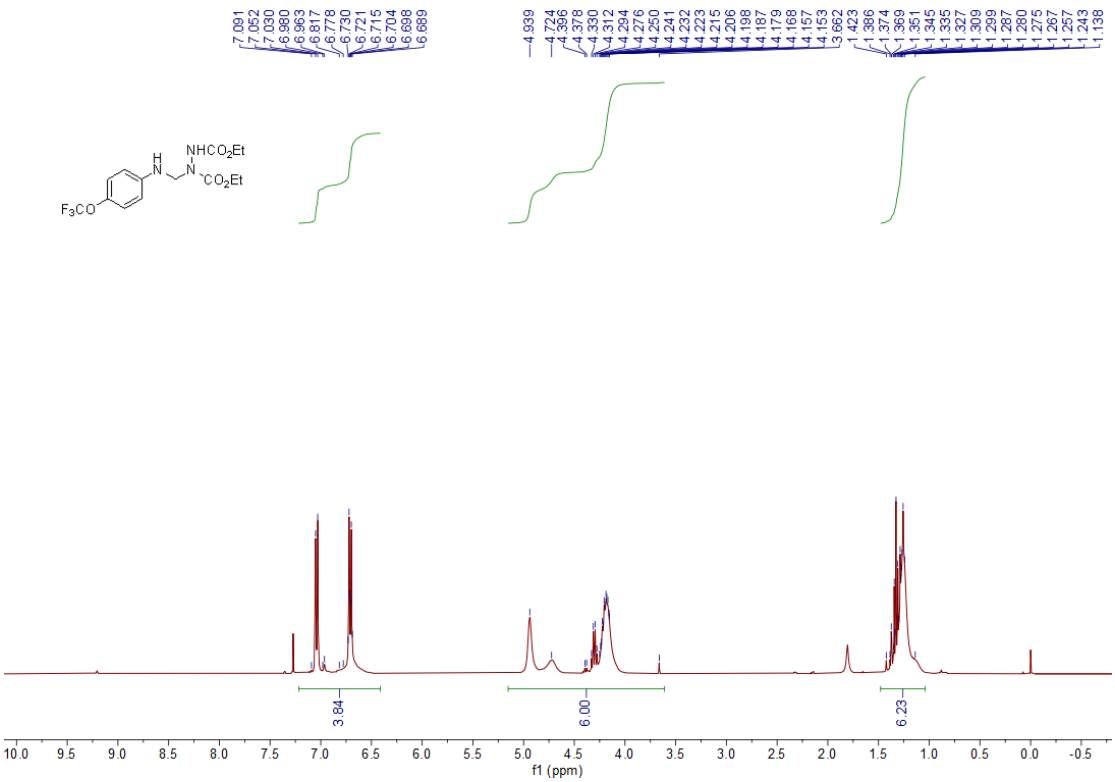
^{1}H NMR Spectrum of **3n**



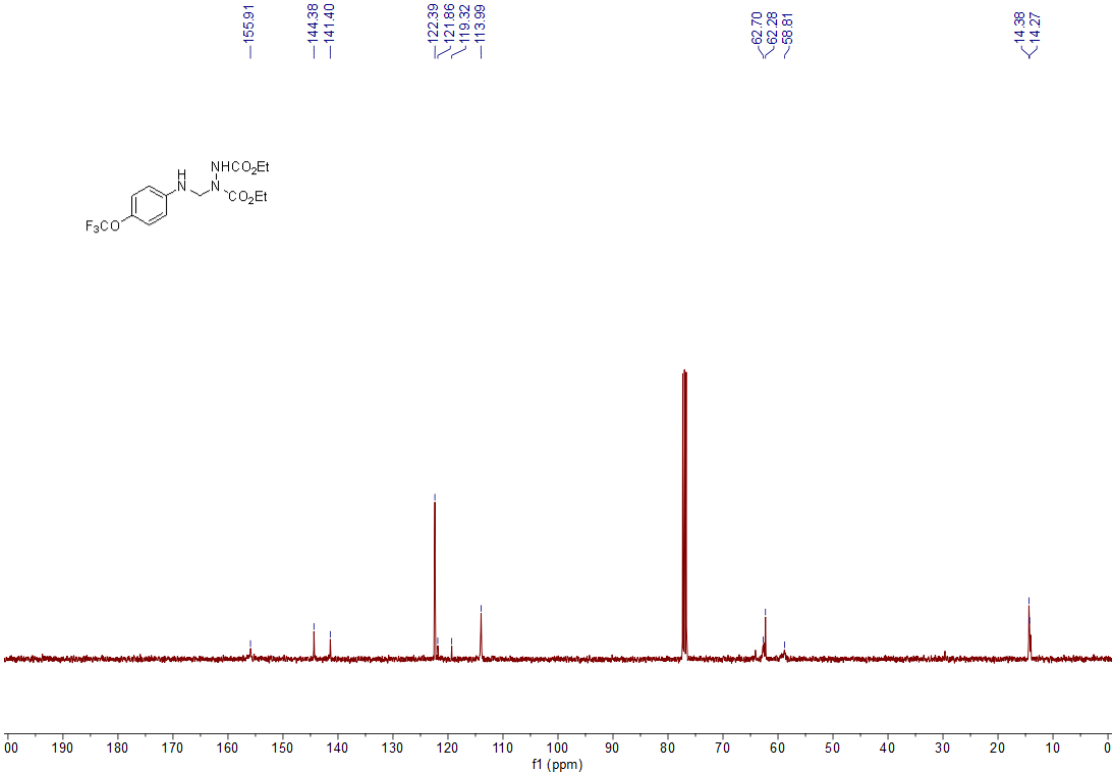
^{13}C NMR Spectrum of **3n**



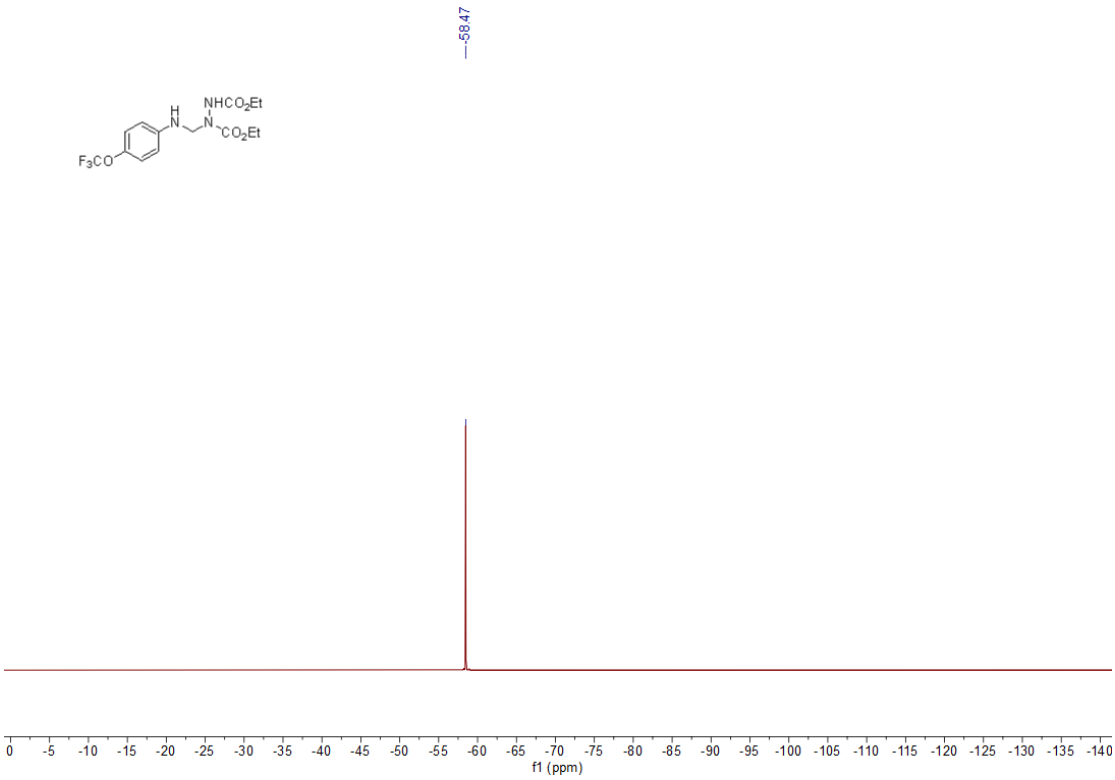
^{1}H NMR Spectrum of **3o**



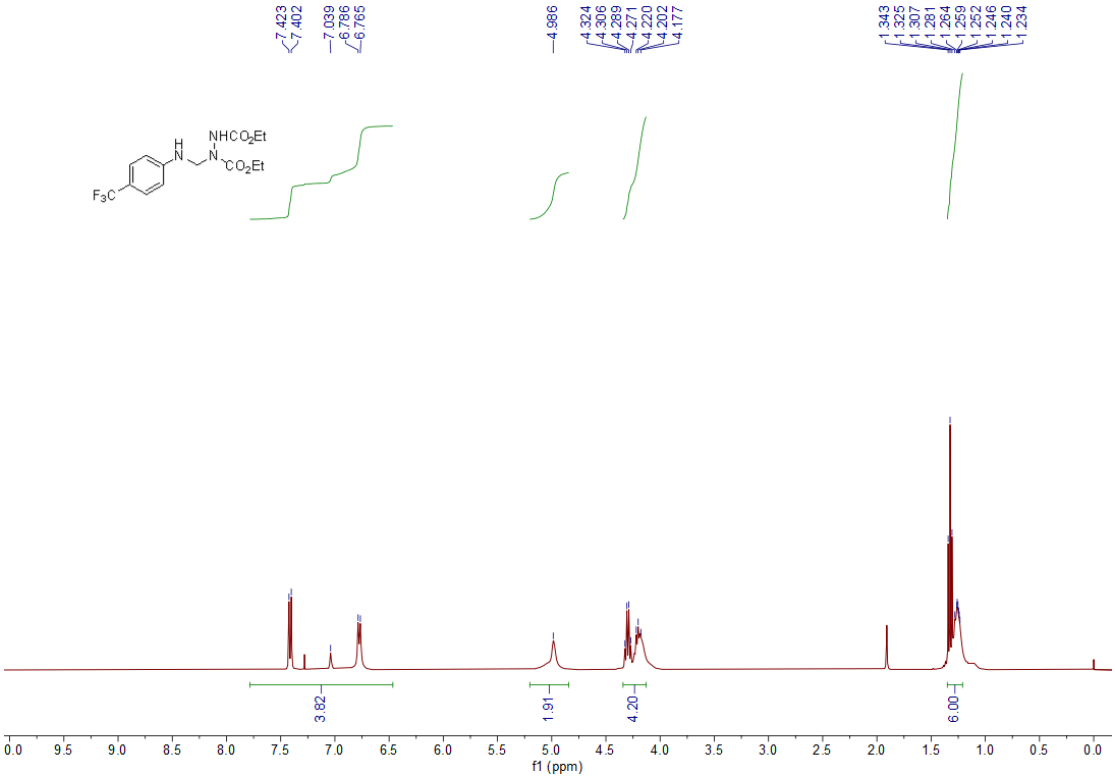
^{13}C NMR Spectrum of **3o**



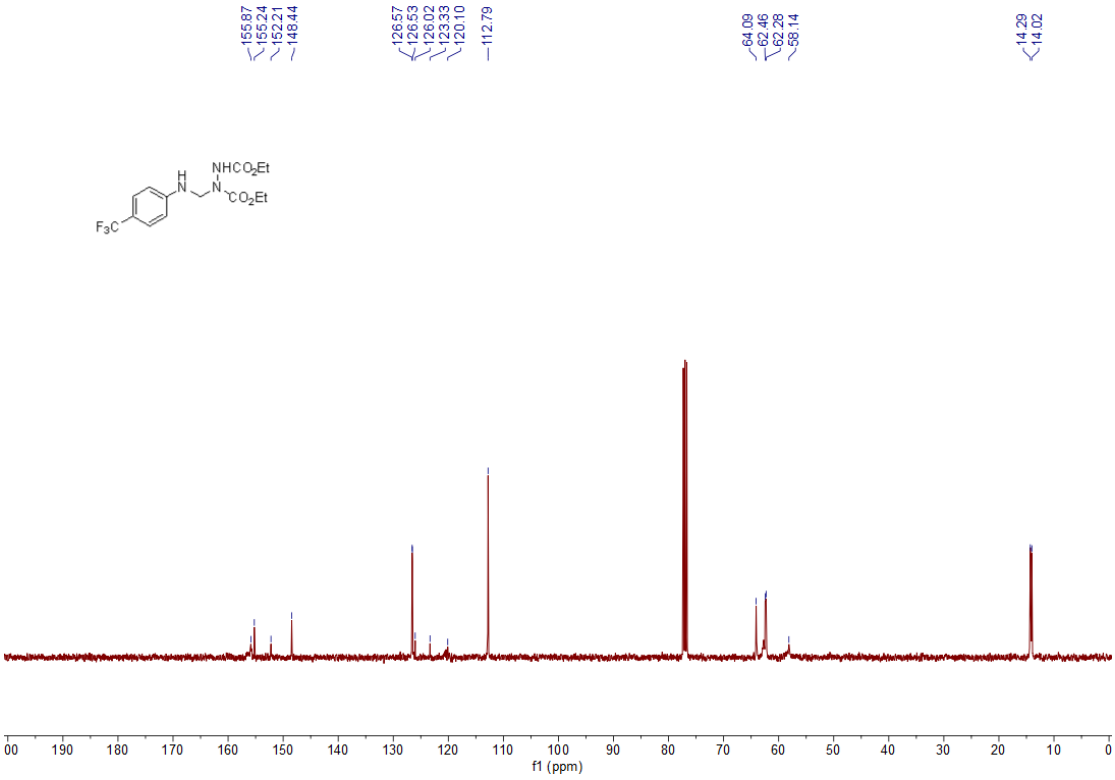
^{19}F NMR Spectrum of **3o**



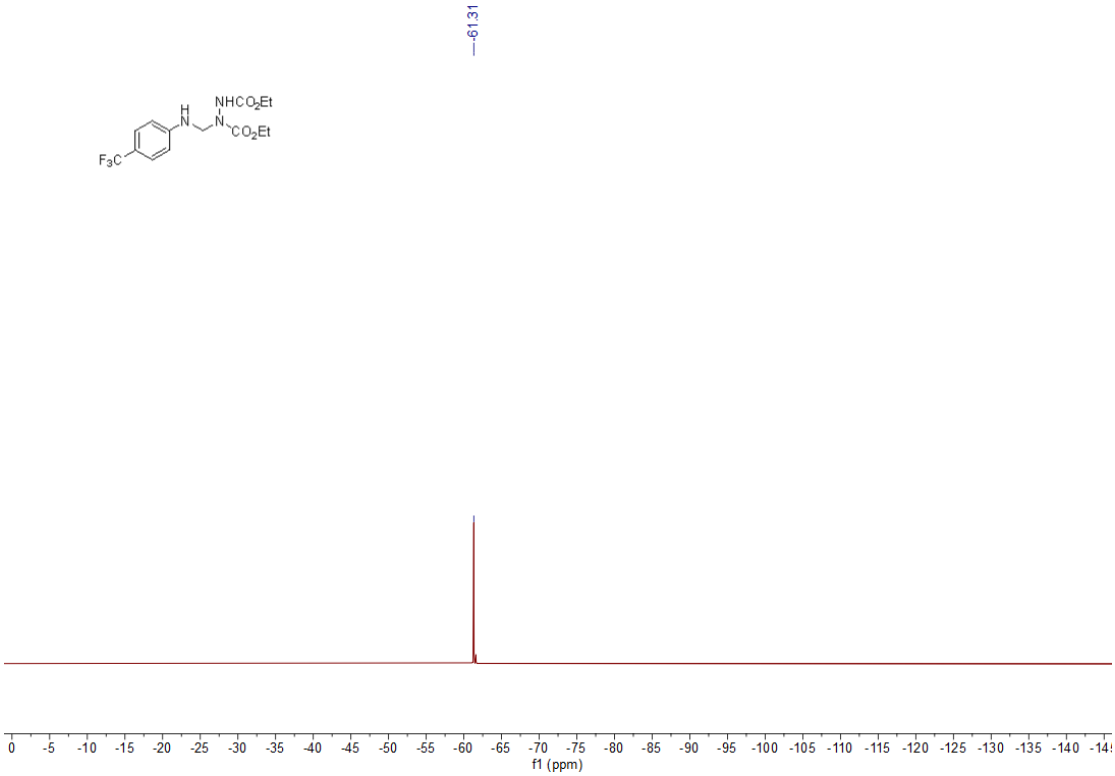
^{1}H NMR Spectrum of **3p**



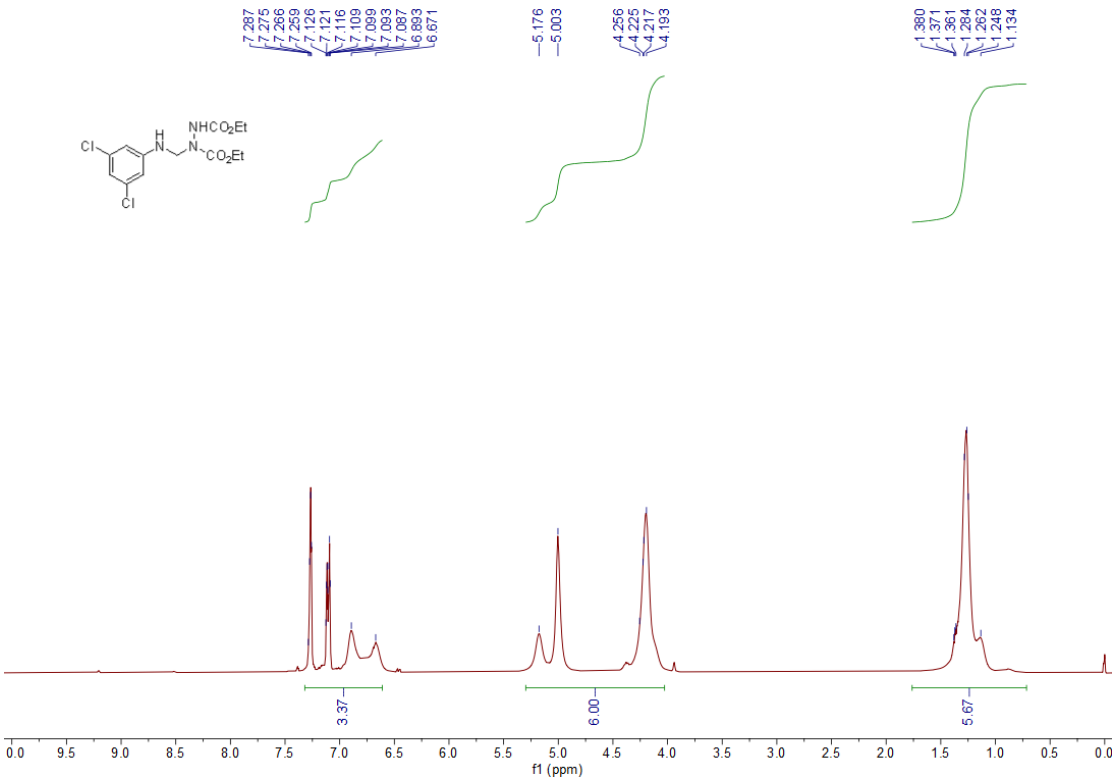
^{13}C NMR Spectrum of **3p**



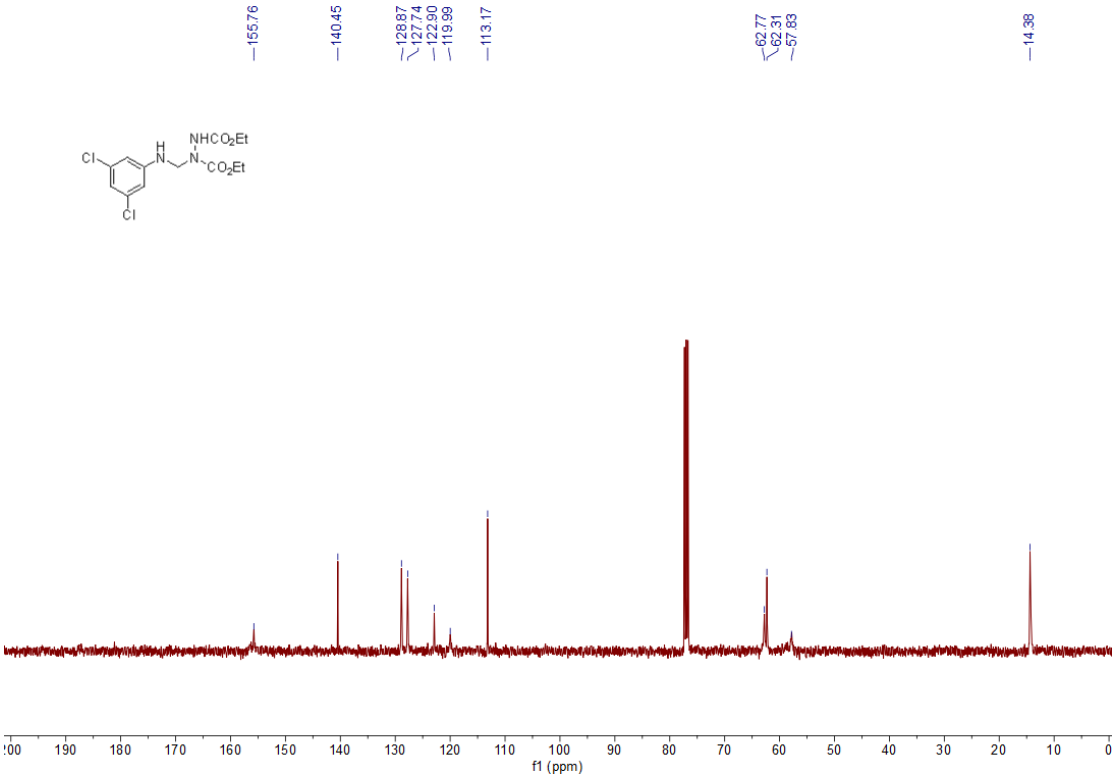
^{19}F NMR Spectrum of **3p**



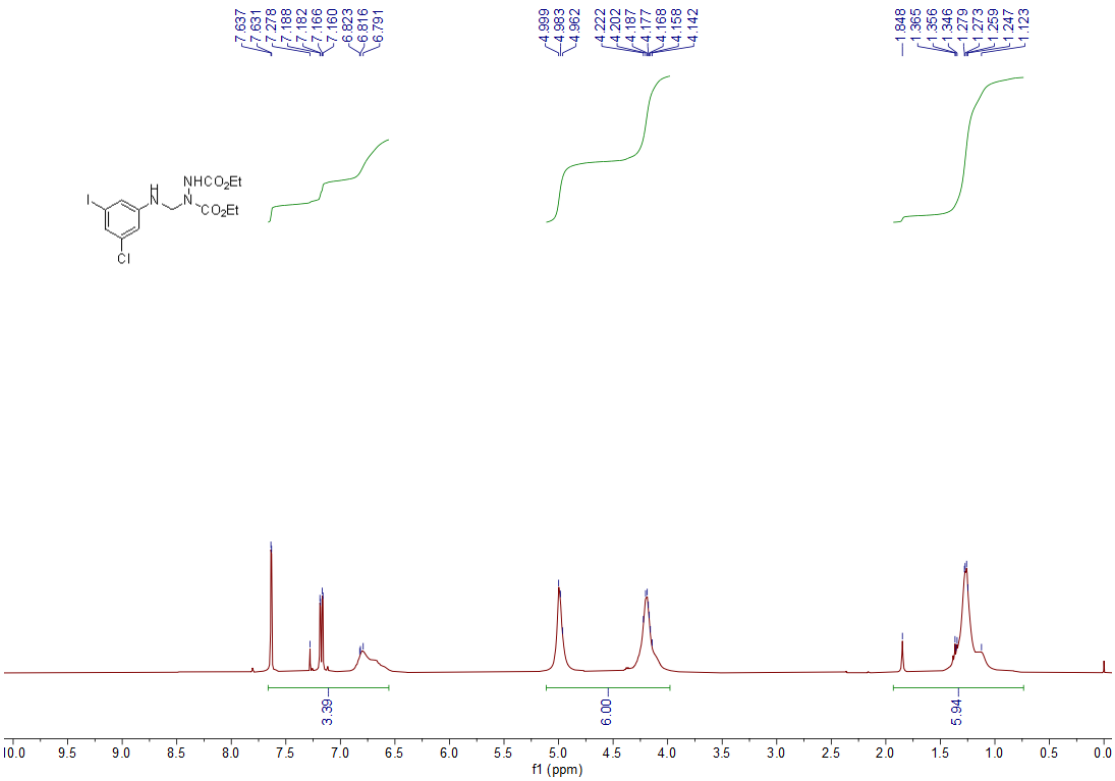
^{1}H NMR Spectrum of **3q**



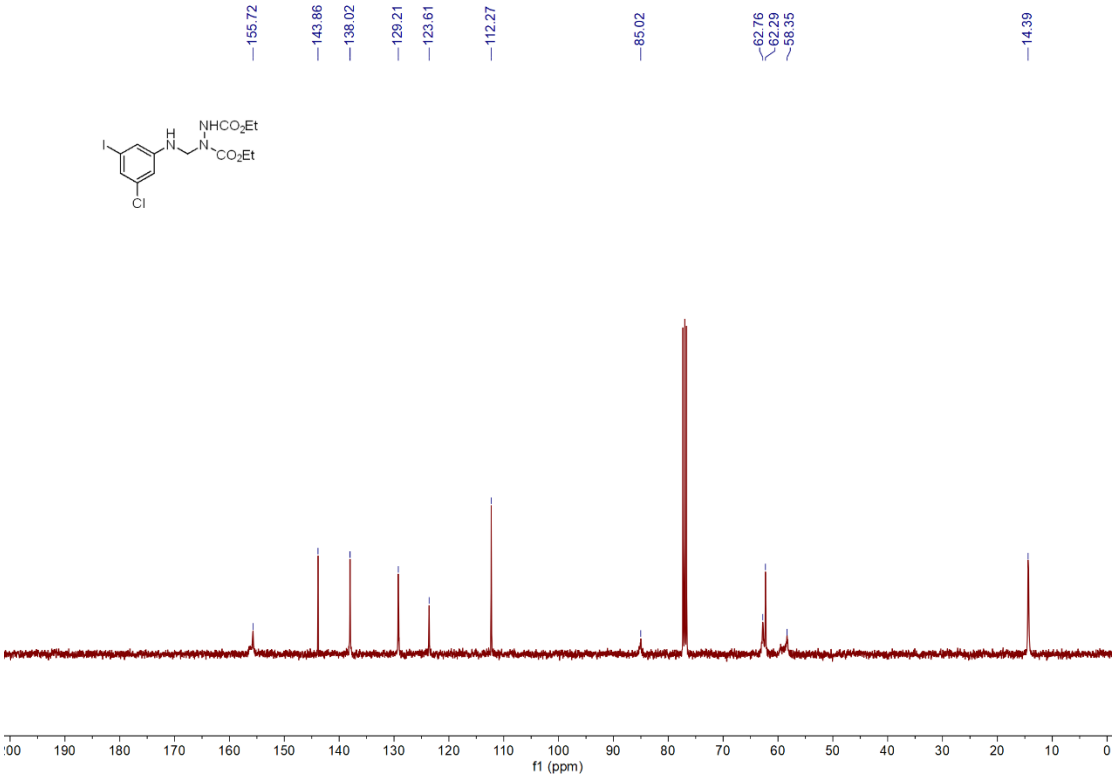
^{13}C NMR Spectrum of **3q**



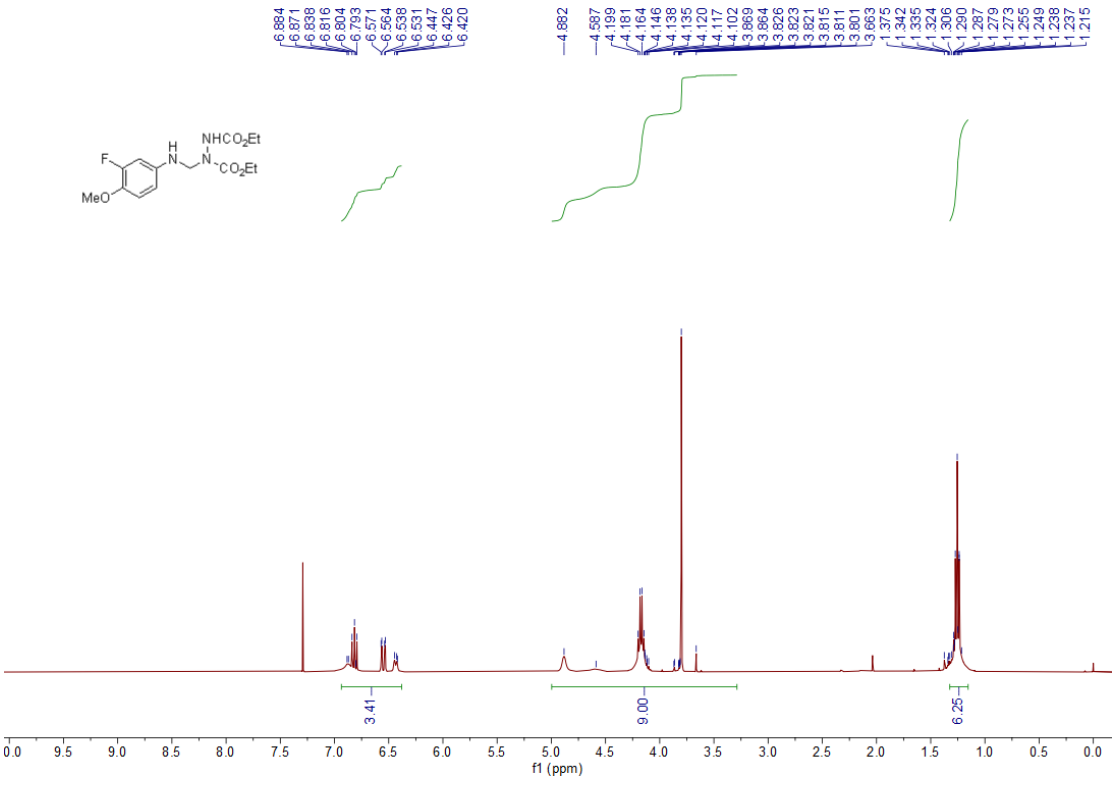
^{1}H NMR Spectrum of **3r**



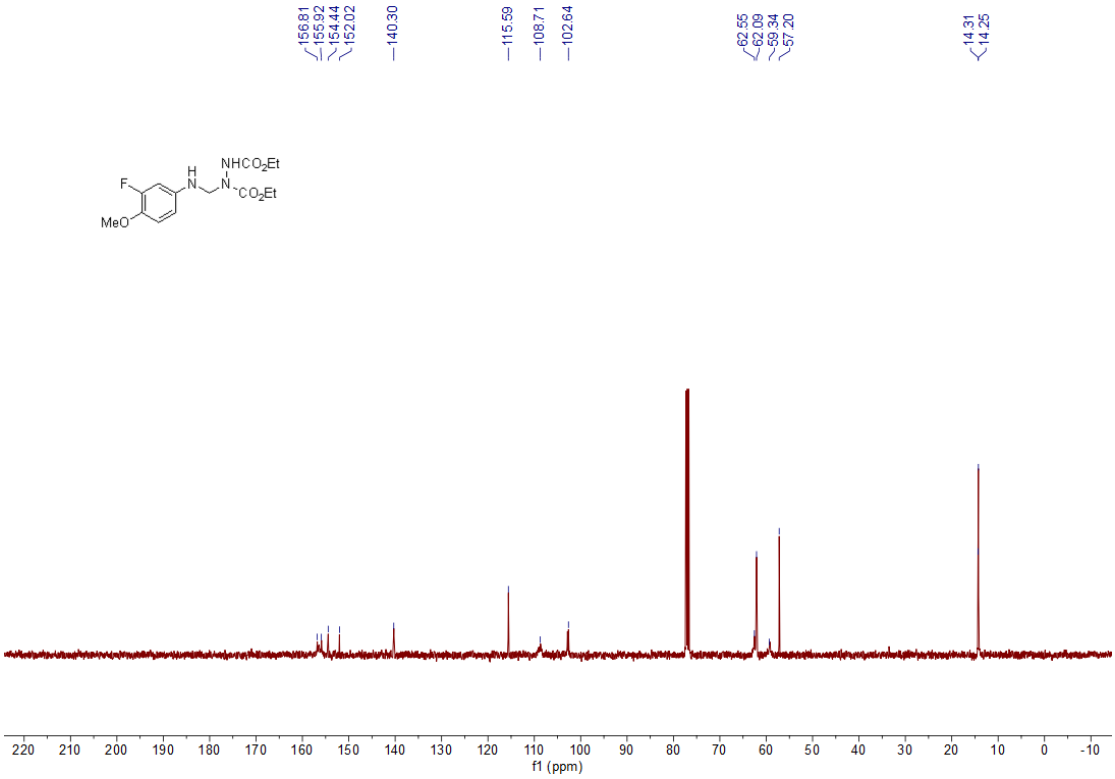
^{13}C NMR Spectrum of **3r**



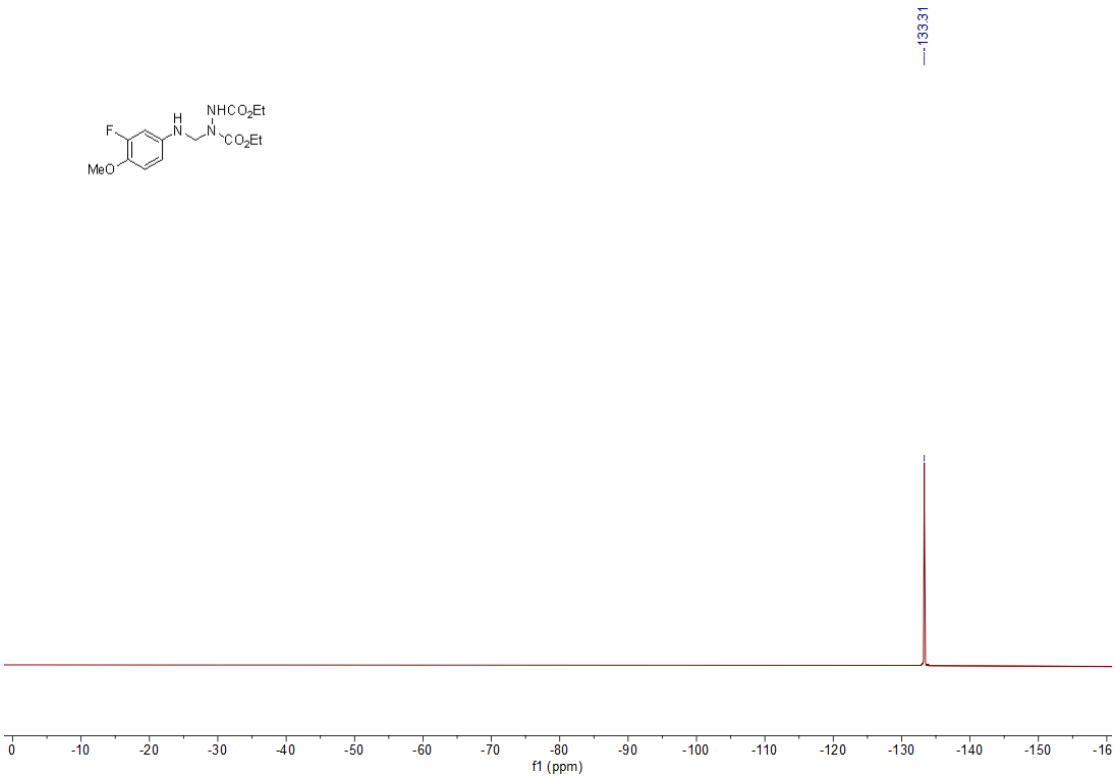
^{1}H NMR Spectrum of **3s**



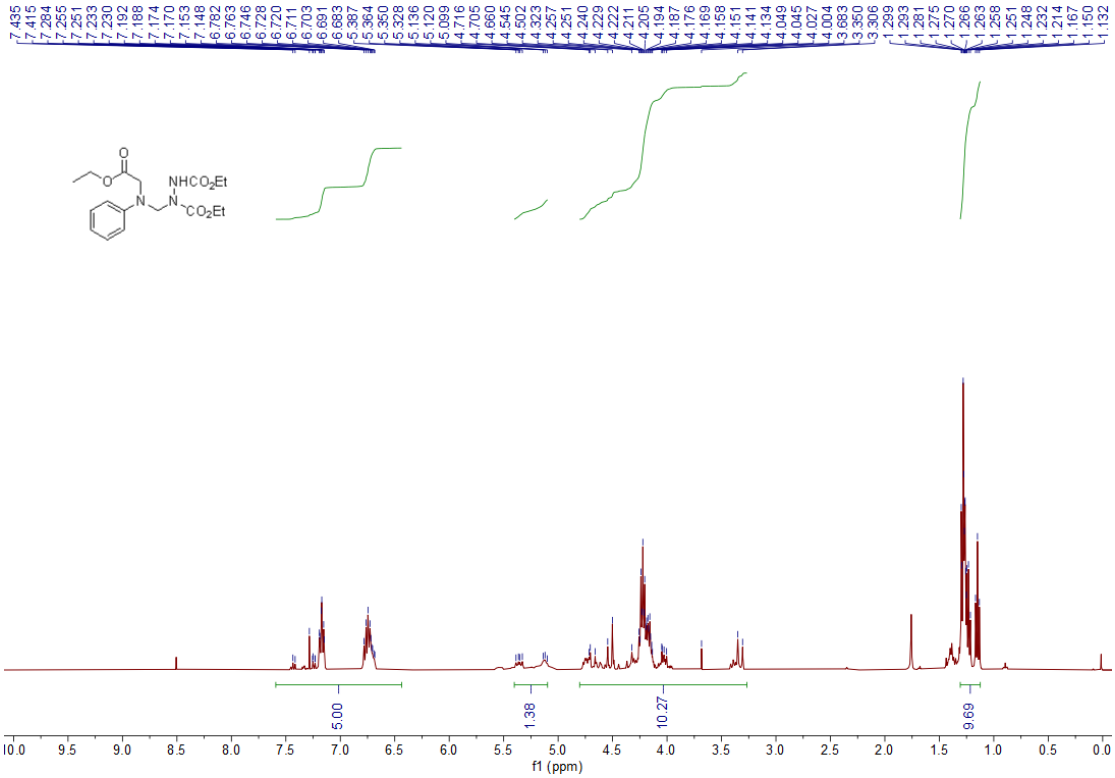
^{13}C NMR Spectrum of **3s**



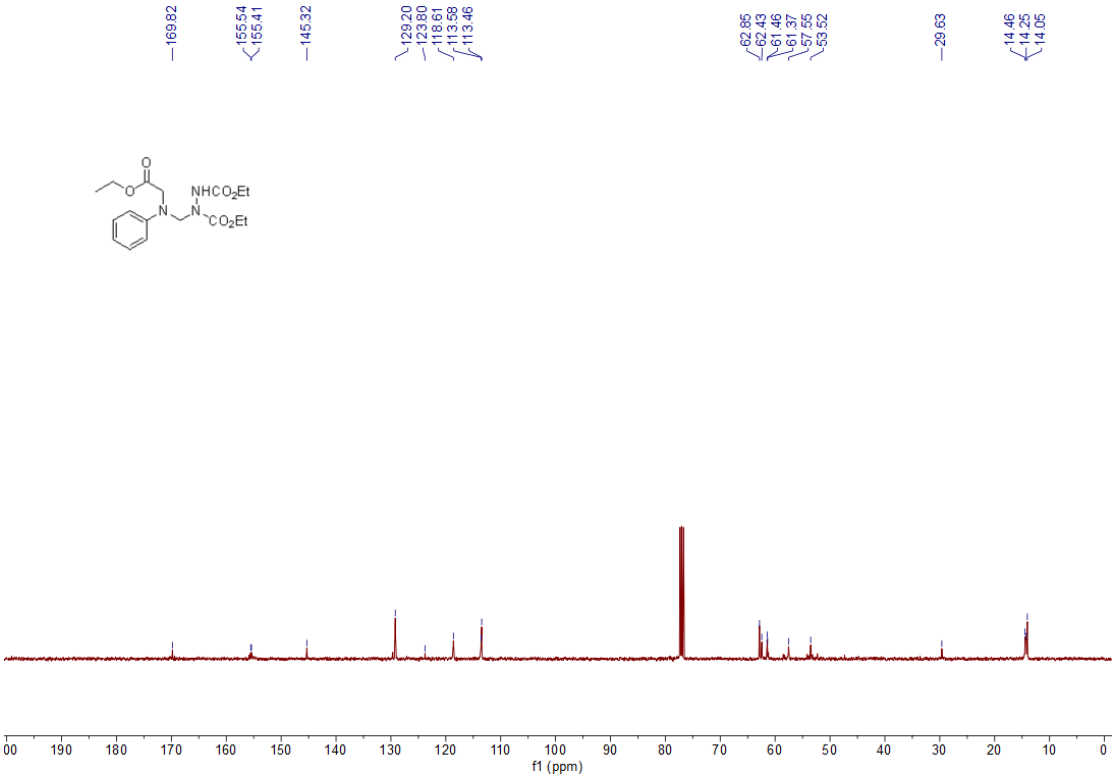
^{19}F NMR Spectrum of **3s**



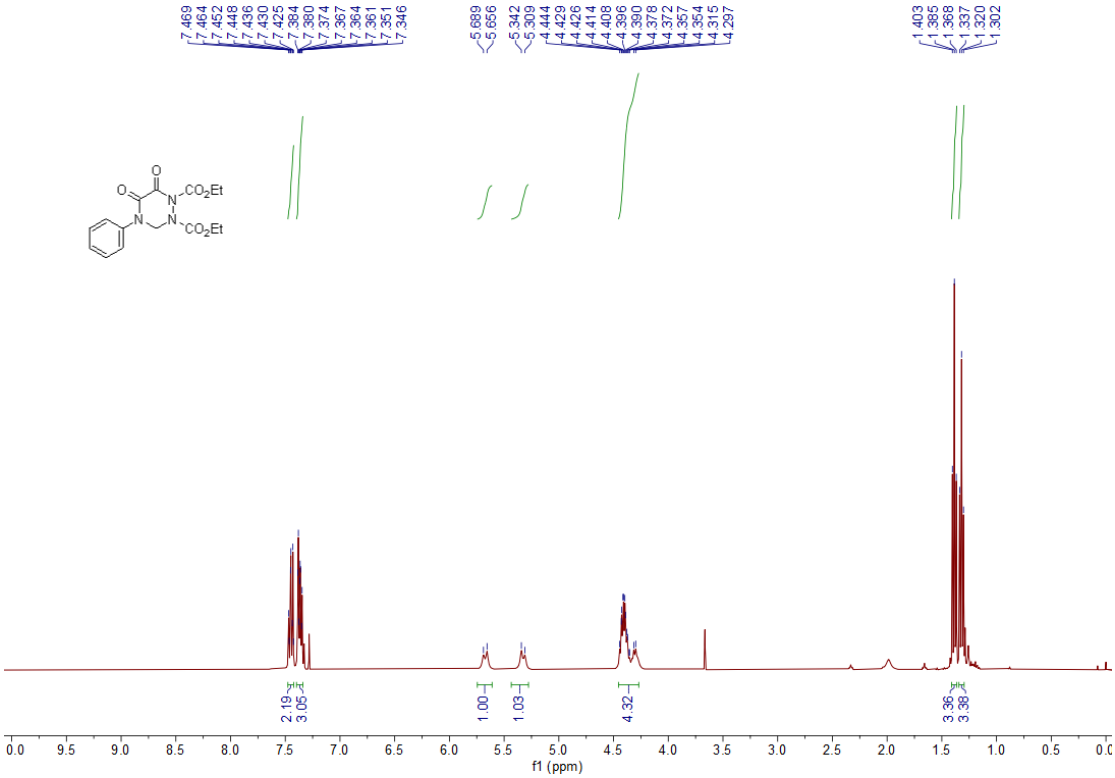
^{1}H NMR Spectrum of **4**



^{13}C NMR Spectrum of **4**



^{1}H NMR Spectrum of **5**



^{13}C NMR Spectrum of **5**