Supporting information

Aryne-involved α-C(sp^3)−H arylation of 4-aminopyrazolones *via* two distinct systems: dual phase-transfer catalysis and ultraviolet photochemistry

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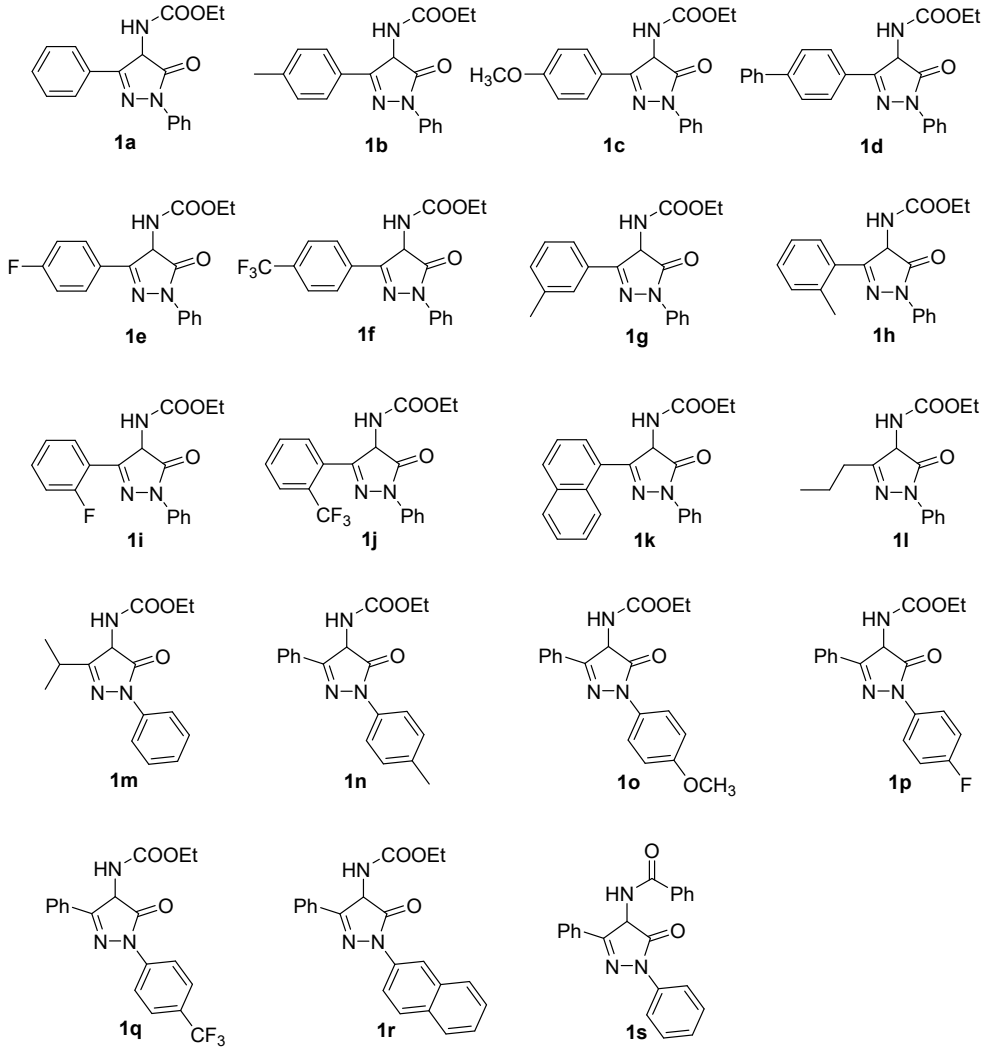
1. Substrates and their preparations

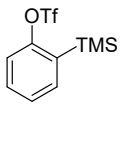
1.1 4-Aminopyrazolones

4-Aminopyrazolones (**1a-s**) were prepared according to the procedure we reported.[1]

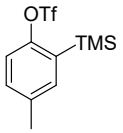


1.2 Kobayashi aryne precursors

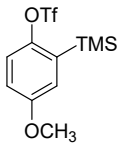
Compounds **2a** and **2f** were purchased from Bidepharm. Compounds **2b-e** were prepared according to the reported procedure.[2]



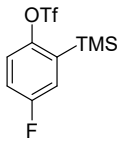
2a



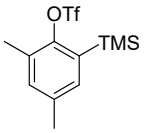
2b



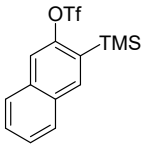
2c



2d



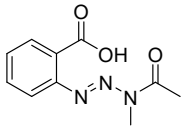
2e



2f

1.3 *ortho*-(*N*-Acetyl-*N*-alkyltriazeno)benzoic acid

Compounds **4** was prepared according to the reported procedure.[3]



4

2. Triaminocyclopropenium salts and their preparations

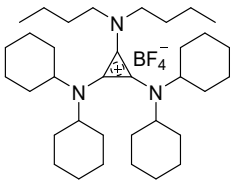
2.1 Procedures for the synthesis of triaminocyclopropenium salts **C1-7**

Triaminocyclopropenium salts **C1-7** were prepared according to the procedures we reported.[4]

2.2 Procedure for the synthesis of triaminocyclopropenium salt **C8**

Dibutylamino bis(dicyclohexylamino) cyclopropenium chloride **C3** (0.50 g, 0.9 mmol) was dissolved in dichloromethane (45 mL). The solution was washed with an aqueous solution of sodium tetrafluoroborate (5%, m/V, 10 mL) six times. The organic phase was dried over anhydrous sodium sulfate, filtered, and concentrated to afford **C8** as a white solid (0.48 g, 79% yield).

Dibutylamino bis(dicyclohexylamino) cyclopropenium tetrafluoroborate (C8)

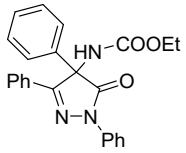


White solid; 0.48 g, 79% yield; M.P.: 161.9-162.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.50−3.42 (m, 4H), 3.40−3.28 (m, 4H), 1.98−1.82 (m, 17H), 1.76−1.53 (m, 17H), 1.43−1.28 (m, 12H), 1.23−1.13 (m, 4H), 0.97 (t, J = 7.3 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 119.5, 119.3, 60.6, 51.7, 32.1, 30.9, 25.7, 24.7, 19.6, 13.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -153.93. FTIR (cm^{-1}): 2936, 2862, 1629, 1599, 1494, 1454, 1371, 1346, 1156, 1093, 1052, 988, 829, 758. HRMS (ESI-TOF) *m/z*: $[M]^+$ Calcd for $C_{35}H_{62}N_3$ 524.4938; Found 524.4957.

3. General procedure for the dual phase-transfer catalysis

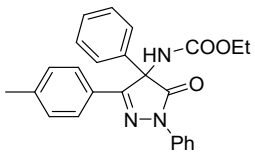
4-Aminopyrazolone **1** (0.1 mmol), dibutylamino bis(dicyclohexylamino) cyclopropenium chloride **C3** (11.2 mg, 20 mol%), CsF (45.6 mg, 0.3 mmol) and CsOH (50.4 mg, 0.3 mmol) were added to a reaction tube sequentially. The reaction tube was then evacuated and backfilled with argon, and this operation was repeated 4 times. Under the argon ambience, ultra-dry THF (2 mL) and Kobayashi aryne precursor **2** (0.3 mmol) were injected into the tube using a syringe. The mixture was stirred at 25℃ for 15 h. After that, the resulting mixture was diluted with dichloromethane, filtered through a pad of silica gel, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford product **3**.

Ethyl (5-oxo-1,3,4-triphenyl-4,5-dihydro-1H-pyrazol-4-yl)carbamate (3a)



Purified by column chromatography on silica gel (using petroleum ether : EtOAc = 6 : 1 as an eluent); white solid; 33.5 mg, 84% yield; M.P.: 145.9-146.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−7.95 (m, 2H), 7.86−7.80 (m, 2H), 7.56−7.49 (m, 2H), 7.44−7.33 (m, 8H), 7.18 (t, *J* = 7.4 Hz, 1H), 5.96 (s, 1H), 4.12−3.93 (m, 2H), 1.20-1.01 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.5, 156.4, 154.7, 138.3, 134.1, 130.6, 129.8, 129.7, 129.7, 128.9, 128.8, 127.1, 125.9, 125.3, 119.2, 68.3, 62.1, 14.3. FTIR (cm^{-1}): 3242, 3132, 2984, 2922, 1730, 1717, 1631, 1597, 1501, 1490, 1478, 1450, 1377, 1343, 1321, 1300, 1235, 1154, 1109, 767, 689. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{22}N_3O_3$ 400.1656; Found 400.1664.

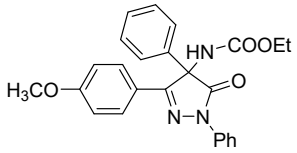
Ethyl (5-oxo-1,4-diphenyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-4-yl)carbamate (3b)



Purified by column chromatography on silica gel (using petroleum ether : EtOAc = 6 : 1 as an eluent); white solid; 37.9 mg, 92% yield; M.P.: 155.2-155.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−7.95 (m, 2H), 7.75−7.69 (m, 2H), 7.55−7.49 (m, 2H), 7.42−7.34 (m, 5H), 7.21−7.13 (m, 3H), 5.91 (s, 1H), 4.12−3.94 (m, 2H), 2.36 (s, 3H), 1.22-1.02 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.4, 156.5, 154.7, 141.0, 138.4, 134.2,

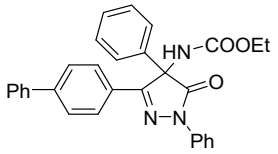
129.7, 129.7, 129.5, 128.8, 127.1, 126.9, 126.0, 125.2, 119.1, 68.3, 62.1, 21.6, 14.3. FTIR (cm^{-1}): 3394, 2981, 2964, 1724, 1710, 1634, 1595, 1491, 1380, 1349, 1316, 1299, 1258, 1143, 817, 759, 691. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{24}N_3O_3$ 414.1812; Found 414.1815.

Ethyl (3-(4-((λ^1-oxidaneyl)-λ^5-methyl)phenyl)-5-oxo-1,4-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)carbamate (3c)



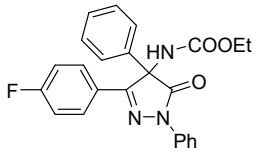
Purified by column chromatography on silica gel (using petroleum ether : EtOAc = 6 : 1 as an eluent); white solid; 39.1 mg, 91% yield; M.P.: 152.1-152.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01−7.94 (m, 2H), 7.81−7.74 (m, 2H), 7.56−7.49 (m, 2H), 7.42−7.32 (m, 5H), 7.17 (t, *J* = 7.4 Hz, 1H), 6.92−6.84 (m, 2H), 5.95 (s, 1H), 4.10−3.94 (m, 2H), 3.81 (s, 3H), 1.21-1.01 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.3, 161.4, 156.2, 154.7, 138.4, 134.3, 129.7, 129.6, 128.8, 128.8, 126.0, 125.2, 122.3, 119.1, 114.3, 68.3, 62.1, 55.4, 14.3. FTIR (cm^{-1}): 3293, 3133, 2977, 2971, 1719, 1707, 1631, 1594, 1517, 1498, 1490, 1376, 1348, 1324, 1318, 1264, 1147, 1096, 826, 759, 689. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{24}N_3O_4$ 430.1761; Found 430.1762.

Ethyl (3-([1,1'-biphenyl]-4-yl)-5-oxo-1,4-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)carbamate (3d)



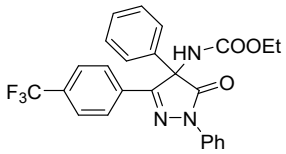
Purified by column chromatography on silica gel (using petroleum ether : EtOAc = 6 : 1 as an eluent); white solid; 38.5 mg, 81% yield; M.P.: 178.5-179.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04−7.96 (m, 2H), 7.94−7.87 (m, 2H), 7.64−7.53 (m, 6H), 7.47−7.32 (m, 8H), 7.19 (t, *J* = 7.3 Hz, 1H), 5.98 (s, 1H), 4.16−3.95 (m, 2H), 1.22-1.03 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.5, 156.2, 154.7, 143.2, 140.1, 138.3, 134.1, 129.8, 129.8, 129.0, 128.9, 128.5, 128.0, 127.5, 127.4, 127.1, 126.0, 125.4, 119.2, 68.3, 62.2, 14.3. FTIR (cm^{-1}): 3338, 2983, 1726, 1712, 1630, 1597, 1518, 1495, 1384, 1349, 1319, 1258, 1156, 1063, 841, 759, 696. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{30}H_{26}N_3O_3$ 476.1969; Found 476.1976.

Ethyl (3-(4-fluorophenyl)-5-oxo-1,4-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)carbamate (3e)



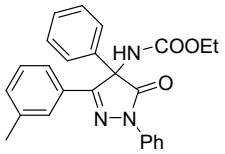
Purified by column chromatography on silica gel (using petroleum ether : EtOAc = 6 : 1 as an eluent); white solid; 37.5 mg, 90% yield; M.P.: 203.0-203.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98−7.93 (m, 2H), 7.87−7.80 (m, 2H), 7.54−7.47 (m, 2H), 7.43−7.34 (m, 5H), 7.22−7.15 (m, 1H), 7.10−7.01 (m, 2H), 6.00 (s, 1H), 4.14−3.95 (m, 2H), 1.21-1.02 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.4, 164.0 (d, J = 253.5 Hz), 155.6, 154.7, 138.2, 133.8, 129.9, 129.8, 129.2, 129.1, 128.9, 125.9, 125.4, 119.1, 116.0 (d, J = 22.2 Hz), 68.2, 62.2, 14.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -108.71. FTIR (cm^{-1}): 3295, 2994, 1712, 1629, 1596, 1518, 1501, 1384, 1316, 1258, 1230, 1156, 1096, 1061, 833, 759, 692. HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ Calcd for $C_{24}H_{21}FN_3O_3$ 418.1561; Found 418.1568.

Ethyl (5-oxo-1,4-diphenyl-3-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrazol-4-yl)carbamate (3f)



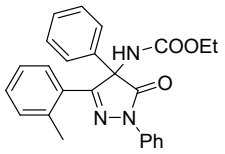
Purified by column chromatography on silica gel (using petroleum ether : EtOAc = 6 : 1 as an eluent); white solid; 29.4 mg, 63% yield; M.P.: 142.2-142.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−7.91 (m, 4H), 7.63 (d, J = 8.4 Hz, 2H), 7.52−7.45 (m, 2H), 7.45−7.35 (m, 5H), 7.21 (t, J = 7.4 Hz, 1H), 6.01 (s, 1H), 4.15−3.95 (m, 2H), 1.22-1.04 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.5, 155.1, 154.7, 138.0, 133.5, 132.9, 132.0 (q, J = 33.3 Hz), 130.0, 129.9, 128.9, 127.2, 125.8, 125.8, 125.7, 123.8 (d, J = 273.7 Hz), 119.2, 68.0, 62.3, 14.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.93. FTIR (cm^{-1}): 3348, 2982, 1712, 1632, 1601, 1496, 1448, 1377, 1351, 1320, 1258, 1166, 1126, 1060, 1017, 845, 753, 691. HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ Calcd for $C_{25}H_{21}F_3N_3O_3$ 468.1530; Found 468.1532.

Ethyl (5-oxo-1,4-diphenyl-3-(m-tolyl)-4,5-dihydro-1H-pyrazol-4-yl)carbamate (3g)



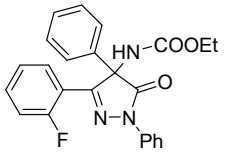
Purified by column chromatography on silica gel (using petroleum ether : EtOAc = 6 : 1 as an eluent); white solid; 37.6 mg, 91% yield; M.P.: 173.5-174.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01−7.94 (m, 2H), 7.76 (s, 1H), 7.57−7.46 (m, 3H), 7.42−7.33 (m, 5H), 7.27−7.15 (m, 3H), 5.92 (s, 1H), 4.14−3.94 (m, 2H), 2.35 (s, 3H), 1.22-1.02 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.5, 156.6, 154.7, 138.6, 138.3, 134.2, 131.5, 129.8, 129.7, 129.6, 128.8, 128.6, 127.4, 126.0, 125.3, 124.4, 119.2, 68.3, 62.1, 21.5, 14.3. FTIR (cm^{-1}): 3405, 3173, 2989, 2935, 1737, 1716, 1633, 1596, 1492, 1378, 1348, 1323, 1305, 1287, 1246, 1145, 1063, 785, 767, 710, 694. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{24}N_3O_3$ 414.1812; Found 414.1812.

Ethyl (5-oxo-1,4-diphenyl-3-(o-tolyl)-4,5-dihydro-1H-pyrazol-4-yl)carbamate (3h)



Purified by column chromatography on silica gel (using petroleum ether : EtOAc = 6 : 1 as an eluent); pink solid; 21.1 mg, 51% yield; M.P.: 169.2-169.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−7.94 (m, 2H), 7.48−7.17 (m, 11H), 7.09 (t, J = 7.5 Hz, 1H), 5.82 (s, 1H), 4.14−3.97 (m, 2H), 2.64 (s, 3H), 1.23-1.03 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.2, 157.7, 154.9, 139.6, 138.4, 134.2, 132.3, 129.7, 129.7, 129.2, 128.9, 128.2, 128.2, 125.8, 125.5, 125.2, 119.0, 69.8, 62.1, 23.1, 14.3. FTIR (cm^{-1}): 3392, 3179, 2966, 1725, 1709, 1633, 1596, 1490, 1378, 1349, 1263, 1155, 1062, 775, 756, 692. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{24}N_3O_3$ 414.1812; Found 414.1817.

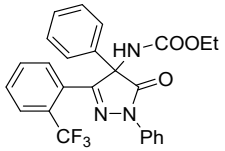
Ethyl (3-(2-fluorophenyl)-5-oxo-1,4-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)carbamate (3i)



Purified by column chromatography on silica gel (using petroleum ether : EtOAc = 6 : 1 as an eluent); white solid; 20.1 mg, 48% yield; M.P.: 157.6-158.1 °C. ^{1}H NMR (400

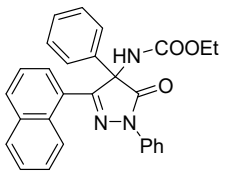
MHz, $CDCl_3$) δ 8.30−8.16 (m, 1H), 7.96 (d, *J* = 7.9 Hz, 2H), 7.55−7.46 (m, 2H), 7.45−7.32 (m, 6H), 7.29−7.14 (m, 2H), 7.10−6.97 (m, 1H), 5.87 (s, 1H), 4.16−3.95 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 3H). 13C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.8, 160.0 (d, *J* = 254.5 Hz), 154.9, 153.5, 138.2, 134.1, 132.5, 129.6, 129.4, 128.9, 125.4, 125.1, 124.8, 124.8, 119.2, 117.5, 117.0 (d, *J* = 23.2 Hz), 69.0, 62.0, 14.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -108.06. FTIR (cm^{-1}): 3404, 3189, 2993, 1730, 1709, 1631, 1614, 1600, 1494, 1446, 1379, 1350, 1316, 1261, 1225, 1179, 1149, 1066, 1018, 777, 760, 686. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{21}FN_3O_3$ 418.1561; Found 418.1569.

Ethyl (5-oxo-1,4-diphenyl-3-(2-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrazol-4-yl)carbamate (3j)



Purified by column chromatography on silica gel (using petroleum ether : EtOAc = 6 : 1 as an eluent); white solid; 18.7 mg, 40% yield; M.P.: 168.5-168.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03−7.97 (m, 2H), 7.87−7.77 (m, 1H), 7.58−7.48 (m, 3H), 7.45−7.27 (m, 7H), 7.24−7.19 (m, 1H), 5.87 (s, 1H), 4.21−4.01 (m, 2H), 1.31-1.12 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.3, 155.0, 153.9, 138.1, 133.6, 132.4, 131.5, 130.1, 130.0, 129.8, 129.6, 129.4, 129.0, 128.0, 125.9, 125.6, 123.5 (d, *J* = 274.7 Hz), 119.0, 70.1, 62.4, 14.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -58.28. FTIR (cm^{-1}): 3292, 3159, 2992, 1731, 1714, 1633, 1597, 1505, 1488, 1445, 1381, 1347, 1327, 1307, 1257, 1162, 1142, 1117, 1075, 1034, 770, 762, 688. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{21}F_3N_3O_3$ 468.1530; Found 468.1530.

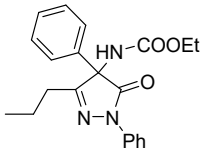
Ethyl (3-(naphthalen-1-yl)-5-oxo-1,4-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)carbamate (3k)



Purified by column chromatography on silica gel (using petroleum ether : EtOAc = 6 : 1 as an eluent); yellow solid; 38.2 mg, 85% yield; M.P.: 79.4-79.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15−8.98 (m, 1H), 8.05 (d, *J* = 7.9 Hz, 2H), 7.93−7.81 (m, 2H), 7.66−7.39 (m, 7H), 7.38−7.27 (m, 4H), 7.27−7.17 (m, 1H), 5.93 (s, 1H), 4.13−3.89 (m,

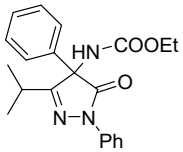
2H), 1.16-0.98 (m, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 171.2, 157.5, 155.0, 138.4, 134.4, 131.5, 131.2, 129.8, 129.0, 128.7, 128.1, 127.7, 126.6, 126.4, 126.0, 125.8, 125.5, 124.5, 119.2, 70.3, 62.1, 14.3. FTIR (cm^{-1}): 3404, 3322, 2978, 1735, 1714, 1691, 1628, 1596, 1498, 1448, 1375, 1347, 1331, 1298, 1261, 1250, 1151, 1129, 1098, 1064, 1025, 805, 773, 694. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{28}H_{24}N_3O_3$ 450.1812; Found 450.1818.

Ethyl (5-oxo-1,4-diphenyl-3-propyl-4,5-dihydro-1H-pyrazol-4-yl)carbamate (3l)



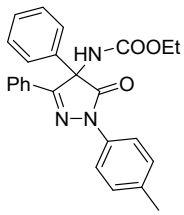
Purified by column chromatography on silica gel (using petroleum ether : EtOAc = 6 : 1 as an eluent); white solid; 34.3 mg, 94% yield; M.P.: 119.7-120.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96−7.89 (m, 2H), 7.44−7.34 (m, 7H), 7.20−7.13 (m, 1H), 5.70 (s, 1H), 4.19−4.05 (m, 2H), 2.49−2.29 (m, 2H), 1.89−1.69 (m, 2H), 1.30−1.12 (m, 3H), 1.01 (t, J = 7.4 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 171.9, 162.5, 154.9, 138.3, 133.8, 129.7, 129.6, 128.8, 125.4, 125.1, 119.0, 69.5, 62.1, 29.9, 18.6, 14.4, 14.0. FTIR (cm^{-1}): 3391, 3278, 2964, 1720, 1704, 1631, 1596, 1493, 1460, 1450, 1382, 1352, 1260, 1156, 1094, 1066, 1050, 759, 692. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{24}N_3O_3$ 366.1812; Found 366.1819.

Ethyl (3-isopropyl-5-oxo-1,4-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)carbamate (3m)



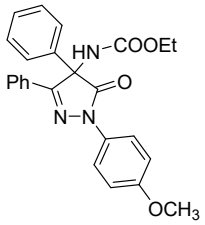
Purified by column chromatography on silica gel (using petroleum ether : EtOAc = 6 : 1 as an eluent); white solid; 32.1 mg, 88% yield; M.P.: 135.4-136.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.8 Hz, 2H), 7.45−7.33 (m, 7H), 7.16 (t, J = 7.4 Hz, 1H), 5.76 (s, 1H), 4.22−4.03 (m, 2H), 2.78−2.67 (m, 1H), 1.34-1.09 (m, 9H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 171.8, 166.4, 154.9, 138.3, 133.7, 129.7, 129.5, 128.8, 125.2, 125.1, 119.0, 69.7, 62.1, 28.5, 20.9, 14.4. FTIR (cm^{-1}): 3405, 3276, 2972, 1707, 1631, 1600, 1492, 1379, 1349, 1264, 1148, 1084, 1062, 759, 693. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{24}N_3O_3$ 366.1812; Found 366.1817.

Ethyl (5-oxo-3,4-diphenyl-1-(p-tolyl)-4,5-dihydro-1H-pyrazol-4-yl)carbamate (3n)



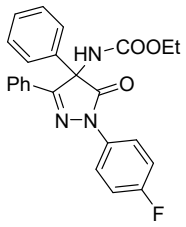
Purified by column chromatography on silica gel (using petroleum ether : EtOAc = 6 : 1 as an eluent); white solid; 37.6 mg, 91% yield; M.P.: 174.2-174.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.78 (m, 4H), 7.55−7.49 (m, 2H), 7.41−7.33 (m, 6H), 7.19 (d, *J* = 8.4 Hz, 2H), 5.93 (s, 1H), 4.11−3.94 (m, 2H), 2.33 (s, 3H), 1.20-1.01 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.4, 156.3, 154.7, 137.0, 135.9, 135.0, 134.2, 130.5, 129.7, 129.7, 129.4, 128.8, 127.1, 125.9, 119.3, 68.2, 62.1, 21.0, 14.3. FTIR (cm^{-1}): 3285, 2994, 2978, 1707, 1631, 1612, 1512, 1494, 1448, 1385, 1349, 1301, 1261, 1184, 1159, 1096, 1057, 812, 766, 693. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{24}N_3O_3$ 414.1812; Found 414.1816.

Ethyl (1-(4-methoxyphenyl)-5-oxo-3,4-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)carbamate (3o)



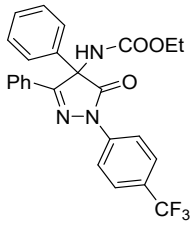
Purified by column chromatography on silica gel (using petroleum ether : EtOAc = 6 : 1 as an eluent); white solid; 38.2 mg, 89% yield; M.P.: 152.9-153.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87−7.78 (m, 4H), 7.55−7.49 (m, 2H), 7.43−7.33 (m, 6H), 6.95−6.88 (m, 2H), 5.93 (s, 1H), 4.11−3.95 (m, 2H), 3.79 (s, 3H), 1.22-1.03 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.3, 157.3, 156.2, 154.7, 134.2, 131.7, 130.5, 129.7, 129.7, 128.8, 127.0, 125.9, 121.1, 114.0, 111.7, 68.1, 62.1, 55.5, 14.3. FTIR (cm^{-1}): 3400, 3339, 2985, 1721, 1703, 1632, 1603, 1511, 1496, 1444, 1381, 1352, 1299, 1250, 1174, 1158, 1116, 1096, 1063, 1034, 832, 768, 688. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{24}N_3O_4$ 430.1761; Found 430.1764.

Ethyl (1-(4-fluorophenyl)-5-oxo-3,4-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)carbamate (3p)



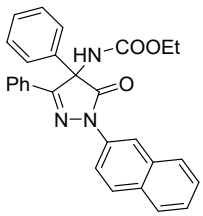
Purified by column chromatography on silica gel (using petroleum ether : EtOAc = 6 : 1 as an eluent); white solid; 26.7 mg, 64% yield; M.P.: 160.3-160.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98−7.90 (m, 2H), 7.85−7.78 (m, 2H), 7.56−7.48 (m, 2H), 7.45−7.34 (m, 6H), 7.12−7.03 (m, 2H), 5.95 (s, 1H), 4.12−3.93 (m, 2H), 1.21-1.03 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.4, 160.1 (d, J = 245.4 Hz), 156.6, 154.8, 134.5, 134.0, 130.7, 129.9, 129.7, 129.5, 128.8, 127.1, 126.0, 121.0, 115.5 (d, J = 22.2 Hz), 68.2, 62.1, 14.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -116.89. FTIR (cm^{-1}): 3317, 2984, 2935, 1712, 1631, 1600, 1591, 1509, 1496, 1446, 1385, 1350, 1321, 1301, 1262, 1231, 1221, 1187, 1163, 1155, 1059, 1011, 838, 762, 688. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{21}FN_3O_3$ 418.1561; Found 418.1568.

Ethyl (5-oxo-3,4-diphenyl-1-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrazol-4-yl)carbamate (3q)



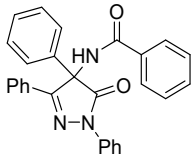
Purified by column chromatography on silica gel (using petroleum ether : EtOAc = 6 : 1 as an eluent); white solid; 24.3 mg, 52% yield; M.P.: 170.2-170.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19−8.13 (m, 2H), 7.88−7.80 (m, 2H), 7.64 (d, J = 8.6 Hz, 2H), 7.56−7.49 (m, 2H), 7.47−7.35 (m, 6H), 5.97 (s, 1H), 4.11-3.95 (m, 2H), 1.22-1.04 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.7, 157.5, 154.7, 141.0, 133.7, 130.9, 130.0, 129.8, 129.3, 128.9, 127.2, 126.8 (q, J = 33.7 Hz), 126.1, 125.9, 124.1 (d, J = 272.7 Hz), 118.5, 68.4, 62.2, 14.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.10. FTIR (cm^{-1}): 3383, 3176, 2987, 1738, 1724, 1631, 1614, 1518, 1509, 1498, 1446, 1387, 1352, 1324, 1297, 1255, 1223, 1173, 1153, 1057, 1016, 844, 762, 688. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{21}F_3N_3O_3$ 468.1530; Found 468.1538.

Ethyl (1-(naphthalen-2-yl)-5-oxo-3,4-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)carbamate (3r)



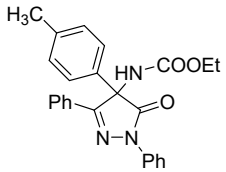
Purified by column chromatography on silica gel (using petroleum ether : EtOAc = 6 : 1 as an eluent); white solid; 26.1 mg, 58% yield; M.P.: 163.7-164.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 1.9 Hz, 1H), 8.17 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.91−7.77 (m, 5H), 7.60−7.53 (m, 2H), 7.48−7.34 (m, 8H), 5.98 (s, 1H), 4.14−3.95 (m, 2H), 1.22-1.01 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.7, 156.6, 154.8, 135.9, 134.1, 133.5, 131.2, 130.7, 129.9, 129.8, 129.6, 128.8, 128.7, 128.1, 127.6, 127.2, 126.5, 126.0, 125.4, 118.7, 116.5, 68.4, 62.2, 14.3. FTIR (cm^{-1}): 3313, 2984, 1731, 1701, 1633, 1599, 1511, 1494, 1471, 1446, 1393, 1351, 1324, 1262, 1149, 1126, 1068, 1024, 813, 758, 693. HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ Calcd for $C_{28}H_{24}N_3O_3$ 450.1812; Found 450.1811.

N-(5-oxo-1,3,4-triphenyl-4,5-dihydro-1H-pyrazol-4-yl)benzamide (3s)



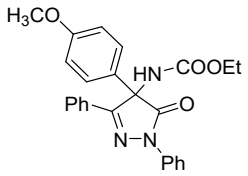
Purified by column chromatography on silica gel (using petroleum ether : EtOAc = 6 : 1 as an eluent); white solid; 38.3 mg, 89% yield; M.P.: 204.6-205.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03−7.96 (m, 2H), 7.89−7.83 (m, 2H), 7.78−7.72 (m, 2H), 7.64−7.57 (m, 2H), 7.50−7.44 (m, 1H), 7.43−7.30 (m, 10H), 7.21−7.14 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.0, 166.6, 155.4, 138.4, 134.3, 132.4, 132.2, 130.5, 130.0, 129.8, 128.8, 128.8, 128.7, 127.4, 127.2, 127.1, 126.2, 125.4, 119.3, 68.1. FTIR (cm^{-1}): 3363, 3173, 2955, 2929, 1720, 1711, 1661, 1631, 1598, 1516, 1485, 1448, 1383, 1349, 1325, 1286, 1161, 1153, 1071, 771, 753, 694. HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ Calcd for $C_{28}H_{22}N_3O_2$ 432.1707; Found 432.1712.

Ethyl (5-oxo-1,3-diphenyl-4-(p-tolyl)-4,5-dihydro-1H-pyrazol-4-yl)carbamate (3t)



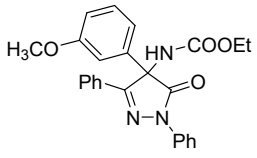
Purified by column chromatography on silica gel (using petroleum ether : EtOAc = 6 : 1 as an eluent); white solid; 26.8 mg, 65% yield; M.P.: 130.9-131.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03−7.94 (m, 2H), 7.86−7.77 (m, 2H), 7.44−7.35 (m, 6H), 7.29−7.14 (m, 4H), 5.82 (s, 1H), 4.13−3.95 (m, 2H), 2.33 (s, 3H), 1.22-1.04 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.5, 156.5, 154.6, 139.8, 138.3, 134.0, 130.4, 129.5, 128.8, 127.1, 126.2, 125.7, 125.3, 122.9, 119.1, 68.2, 62.1, 21.6, 14.3. FTIR (cm^{-1}): 3400, 3254, 3141, 2980, 2924, 1718, 1631, 1594, 1490, 1381, 1349, 1321, 1151, 1098, 1066, 838, 768, 688. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{24}N_3O_3$ 414.1812; Found 414.1819.

Ethyl (4-(4-methoxyphenyl)-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)carbamate (3u)



Purified by column chromatography on silica gel (using petroleum ether : EtOAc = 6 : 1 as an eluent); white solid; 16.3 mg, 38% yield; M.P.: 159.1-159.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01−7.95 (m, 2H), 7.87−7.82 (m, 2H), 7.48−7.36 (m, 7H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.93−6.86 (m, 2H), 5.74 (s, 1H), 4.11−3.96 (m, 2H), 3.78 (s, 3H), 1.22-1.50 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.2, 160.5, 152.4, 138.3, 135.4, 130.7, 129.6, 128.8, 128.7, 127.1, 125.3, 119.2, 118.0, 115.1, 111.7, 62.1, 55.4, 37.8, 14.2. FTIR (cm^{-1}): 3383, 2966, 2927, 1734, 1717, 1630, 1597, 1508, 1499, 1490, 1456, 1379, 1349, 1322, 1251, 1180, 1149, 1109, 1061, 1021, 823, 763, 690. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{24}N_3O_4$ 430.1761; Found 430.1763.

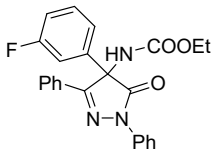
Ethyl (4-(3-methoxyphenyl)-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)carbamate (3v)



Purified by column chromatography on silica gel (using petroleum ether : EtOAc = 6 : 1 as an eluent); white solid; 16.2 mg, 38% yield; M.P.: 174.8-174.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01−7.95 (m, 2H), 7.85−7.79 (m, 2H), 7.45−7.36 (m, 5H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.11−7.05 (m, 2H), 6.95−6.89 (m, 1H), 5.79 (s,

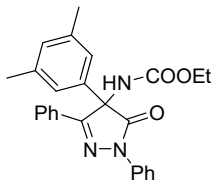
1H), 4.12−3.96 (m, 2H), 3.76 (s, 3H), 1.23-1.06 (m, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 171.7, 160.6, 153.8, 138.3, 136.0, 130.5, 129.8, 128.8, 128.8, 127.4, 127.1, 126.0, 125.2, 122.8, 119.1, 117.9, 115.0, 67.6, 62.0, 55.4, 14.3. FTIR (cm^{-1}): 3383, 2967, 2928, 1718, 1631, 1598, 1508, 1498, 1489, 1459, 1381, 1350, 1322, 1251, 1177, 1147, 1110, 1061, 1017, 796, 762, 699, 693. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{24}N_3O_4$ 430.1761; Found 430.1763.

Ethyl (4-(3-fluorophenyl)-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)carbamate (3w)



Purified by column chromatography on silica gel (using petroleum ether : EtOAc = 6 : 1 as an eluent); white solid; 23.7 mg, 57% yield; M.P.: 126.9-127.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01−7.93 (m, 2H), 7.86−7.78 (m, 2H), 7.57−7.50 (m, 1H), 7.47−7.16 (m, 8H), 7.10−7.04 (m, 1H), 5.87 (s, 1H), 4.13−3.95 (m, 2H), 1.21-1.01 (m, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 171.1 (d, J = 42.4 Hz), 163.3 (dd, J = 251.5 Hz, J = 21.2 Hz), 156.1, 154.6, 138.2, 138.1, 136.3 (d, J = 8.1 Hz), 131.4, 131.3, 130.7, 130.0 (d, J = 3.3 Hz), 129.4 (d, J = 17.2 Hz) 128.9, 128.2 (d, J = 9.1 Hz), 127.0, 125.5, 125.5, 121.6 (d, J = 3.0 Hz), 119.1, 117.1, 116.9, 116.6, 113.6, 113.3, 67.8 (d, J = 28.3 Hz), 62.3, 14.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ -109.66. FTIR (cm^{-1}): 3389, 3324, 2987, 1724, 1703, 1631, 1600, 1500, 1476, 1455, 1383, 1344, 1322, 1262, 1234, 1183, 1157, 1068, 1024, 848, 751, 684. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{21}FN_3O_3$ 418.1561; Found 418.1565.

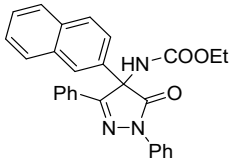
Ethyl (4-(3,5-dimethylphenyl)-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)carbamate (3x)



Purified by column chromatography on silica gel (using petroleum ether : EtOAc = 6 : 1 as an eluent); white solid; 23.1 mg, 54% yield; M.P.: 147.9-148.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−7.95 (m, 2H), 7.81−7.75 (m, 2H), 7.44−7.34 (m, 5H), 7.23−7.16 (m, 2H), 7.09 (s, 1H), 6.95−6.89 (m, 1H), 5.75 (s, 1H), 4.07−3.96 (m, 2H), 2.75 (s, 3H),

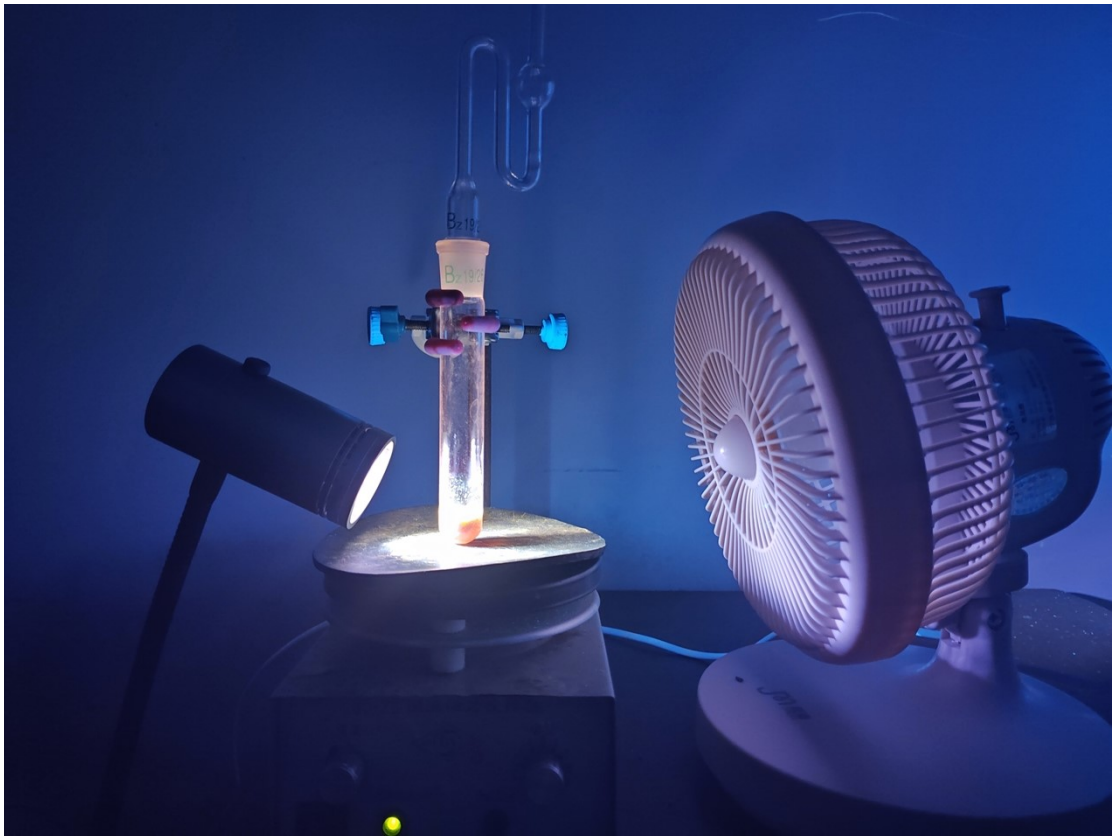
2.28 (s, 3H), 1.07 (t, J = 6.6 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 171.6, 156.4, 154.1, 139.5, 138.3, 137.2, 134.9, 130.4, 129.9, 128.8, 127.7, 127.5, 127.2, 125.2, 119.2, 69.0, 62.0, 21.2, 20.8, 14.2. FTIR (cm^{-1}): 3249, 3136, 2973, 2918, 1734, 1711, 1598, 1495, 1446, 1412, 1375, 1325, 1286, 1243, 1145, 1098, 1062, 1026, 882, 757, 689. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{26}H_{25}N_3NaO_3$ 450.1788; Found 450.1790.

Ethyl (4-(naphthalen-2-yl)-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)carbamate (3y)



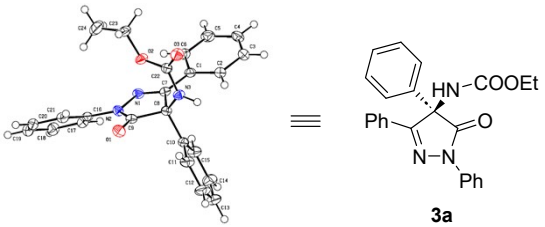
Purified by column chromatography on silica gel (using petroleum ether : EtOAc = 6 : 1 as an eluent); white solid; 33.2 mg, 74% yield; M.P.: 165.5-166.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02−7.95 (m, 3H), 7.88−7.82 (m, 3H), 7.81−7.73 (m, 2H), 7.62 (dd, J = 8.7, 2.0 Hz, 1H), 7.52−7.44 (m, 2H), 7.42−7.32 (m, 5H), 7.17 (t, J = 7.3 Hz, 1H), 6.14 (s, 1H), 4.13−3.95 (m, 2H), 1.23-1.02 (m, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 171.5, 156.8, 154.8, 138.3, 133.6, 133.3, 131.2, 130.7, 129.9, 129.7, 128.9, 128.6, 128.5, 127.7, 127.3, 127.2, 127.0, 125.7, 125.4, 122.8, 119.2, 68.5, 62.2, 14.3. FTIR (cm^{-1}): 3305, 2994, 2980, 1720, 1704, 1599, 1511, 1494, 1479, 1450, 1382, 1317, 1285, 1264, 1243, 1184, 1155, 1085, 1063, 1030, 860, 810, 780, 753, 682. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{28}H_{23}N_3NaO_3$ 472.1632; Found 472.1633.

4. Reaction device for the ultraviolet photochemistry



5. Crystallographic information for compound 3a

The single crystal of compound **3a** was obtained from petroleum ether/dichloromethane mixed solvent system.



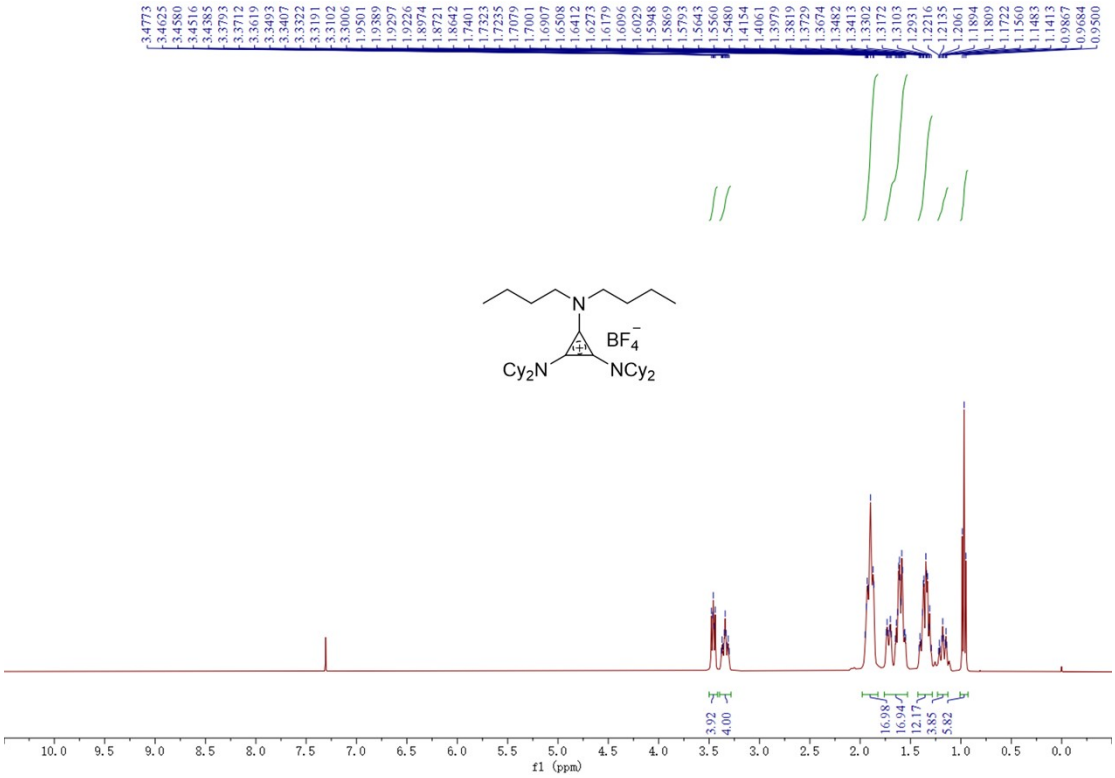
3a

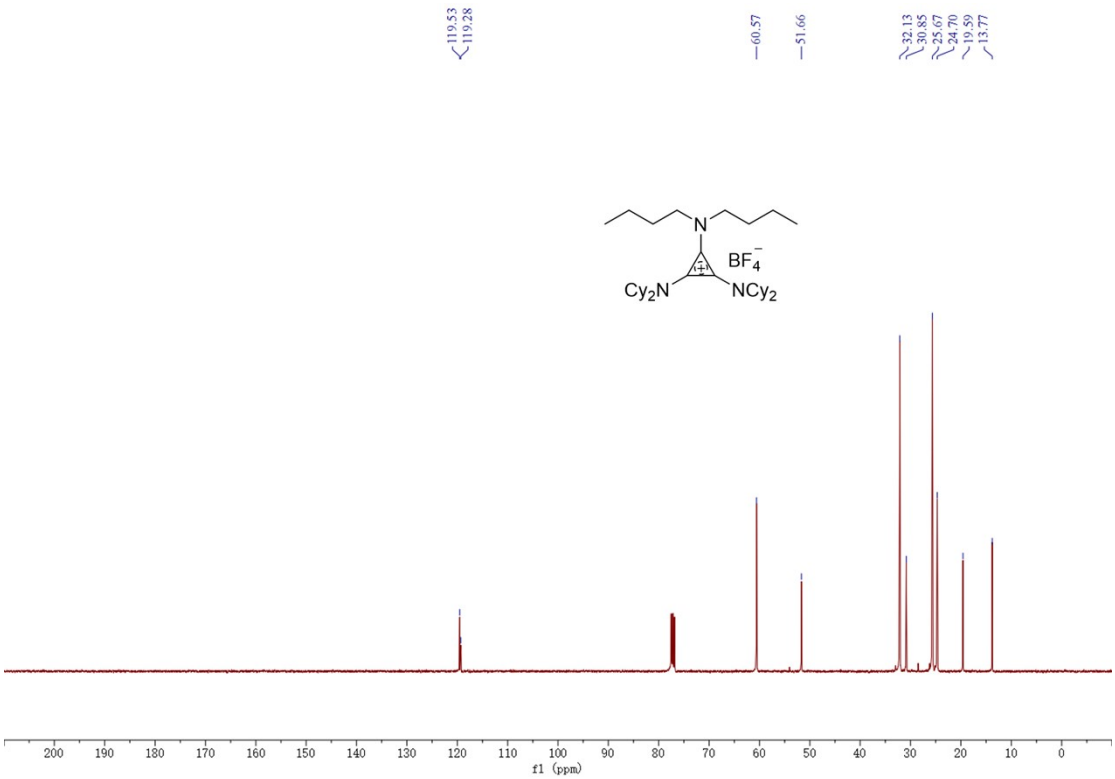
(The ellipsoid contour is drawn at 30% probability level)

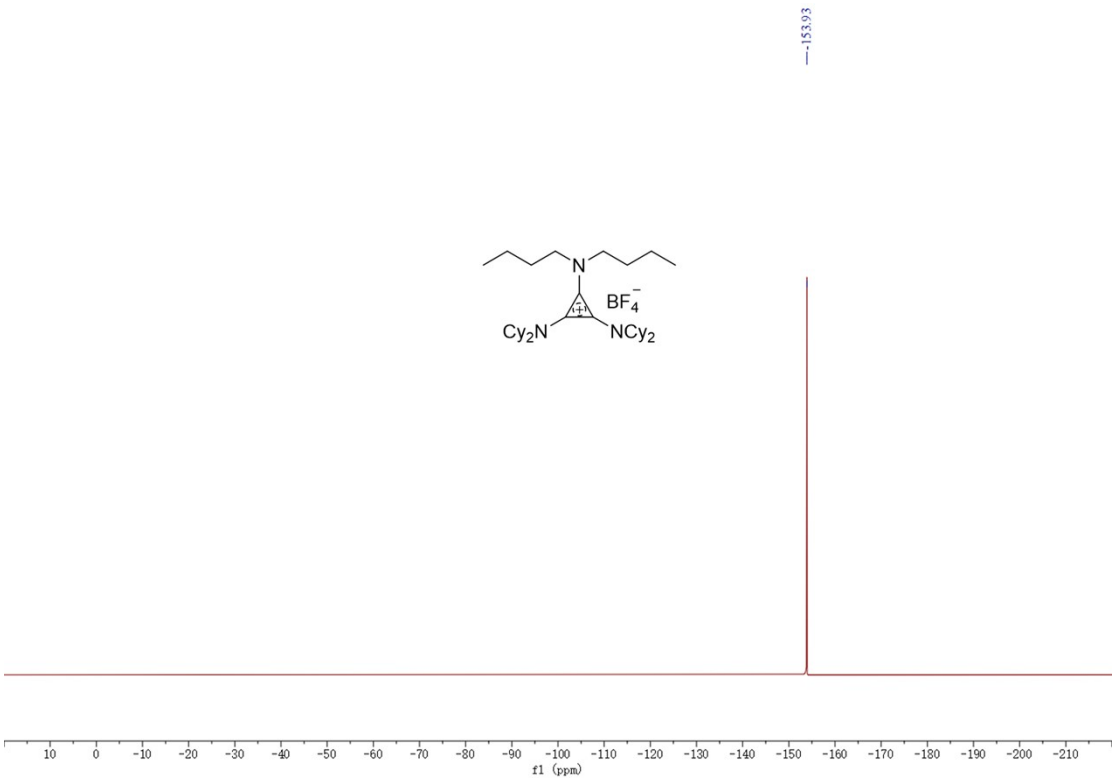
Identification code	**3a**
CCDC number	2421824
Empirical formula	$C_{24}H_{21}N_3O_3$
Formula weight	399.44
Temperature/K	127(30)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.2783(3)
b/Å	13.2651(4)
c/Å	17.3247(5)
α/°	90
β/°	101.723(3)
γ/°	90
Volume/Å^3	2087.81(11)
Z	4
ρ_{calc}g/cm^3	1.271
μ/mm^{-1}	0.690
F(000)	840.0
Crystal size/mm^3	0.16 × 0.13 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.462 to 146.02
Index ranges	-11 ≤ h ≤ 11, -15 ≤ k ≤ 16, -14 ≤ l ≤ 21
Reflections collected	14210
Independent reflections	4048 [R_{int} = 0.0471, R_{sigma} = 0.0379]
Data/restraints/parameters	4048/0/277
Goodness-of-fit on F^2	1.081
Final R indexes [I>=2σ (I)]	R_1 = 0.0458, wR_2 = 0.1498
Final R indexes [all data]	R_1 = 0.0512, wR_2 = 0.1599
Largest diff. peak/hole/e Å^{-3}	0.39/-0.30

6. NMR spectra

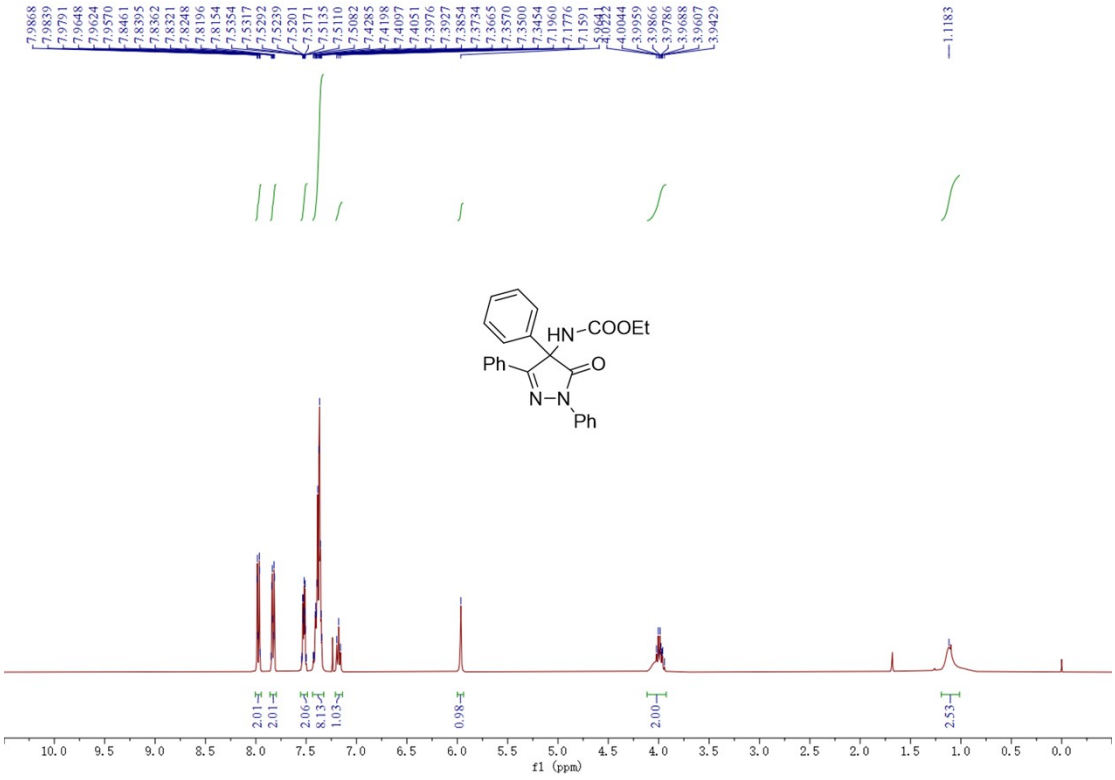
^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR Spectra for C8

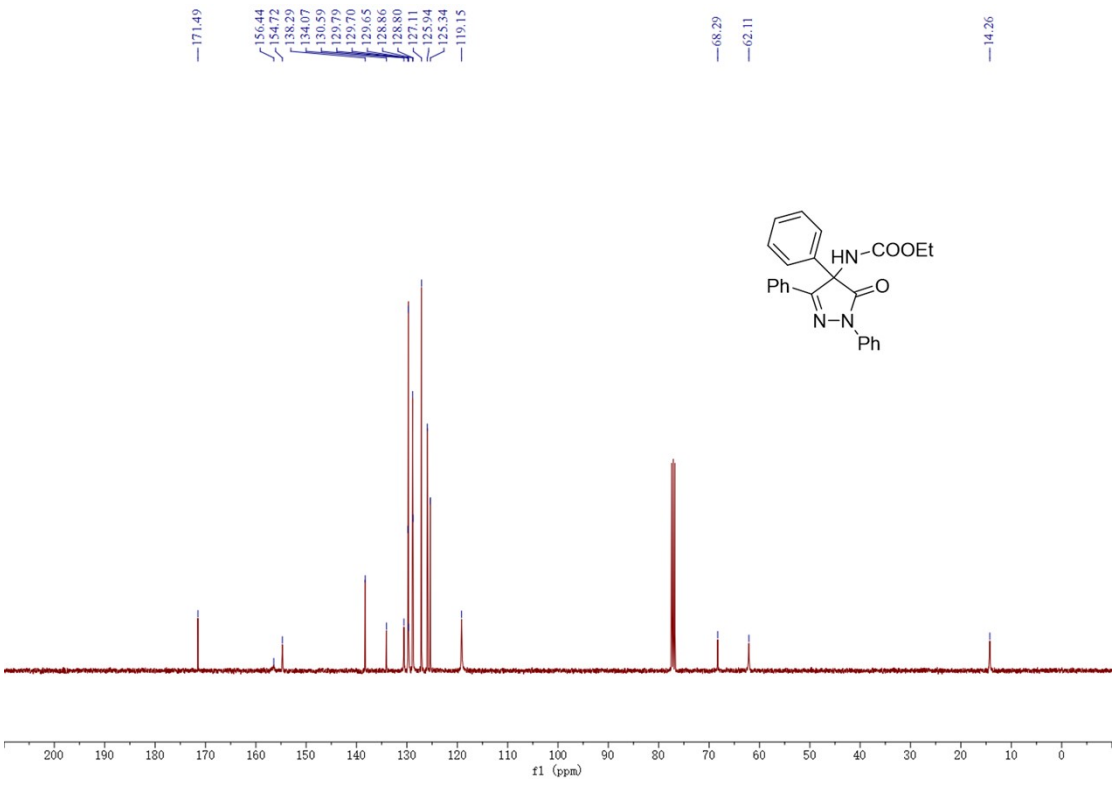




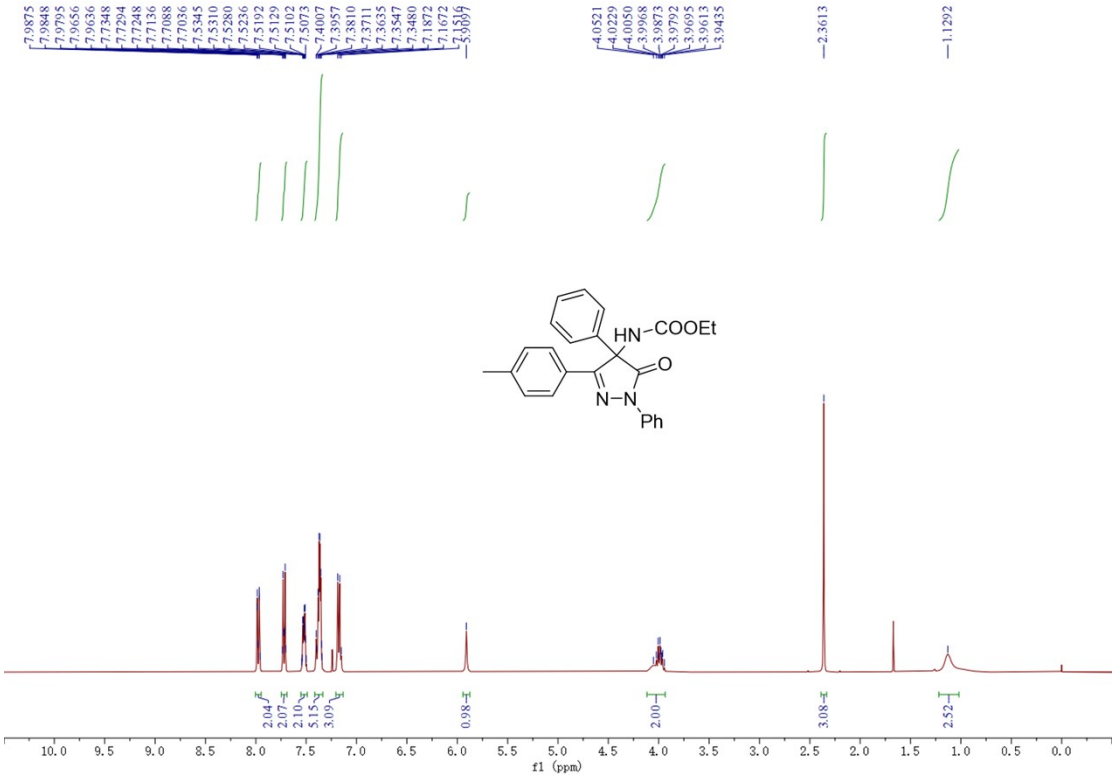

-153.93
N
BF4−
Cy2N
NCy2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

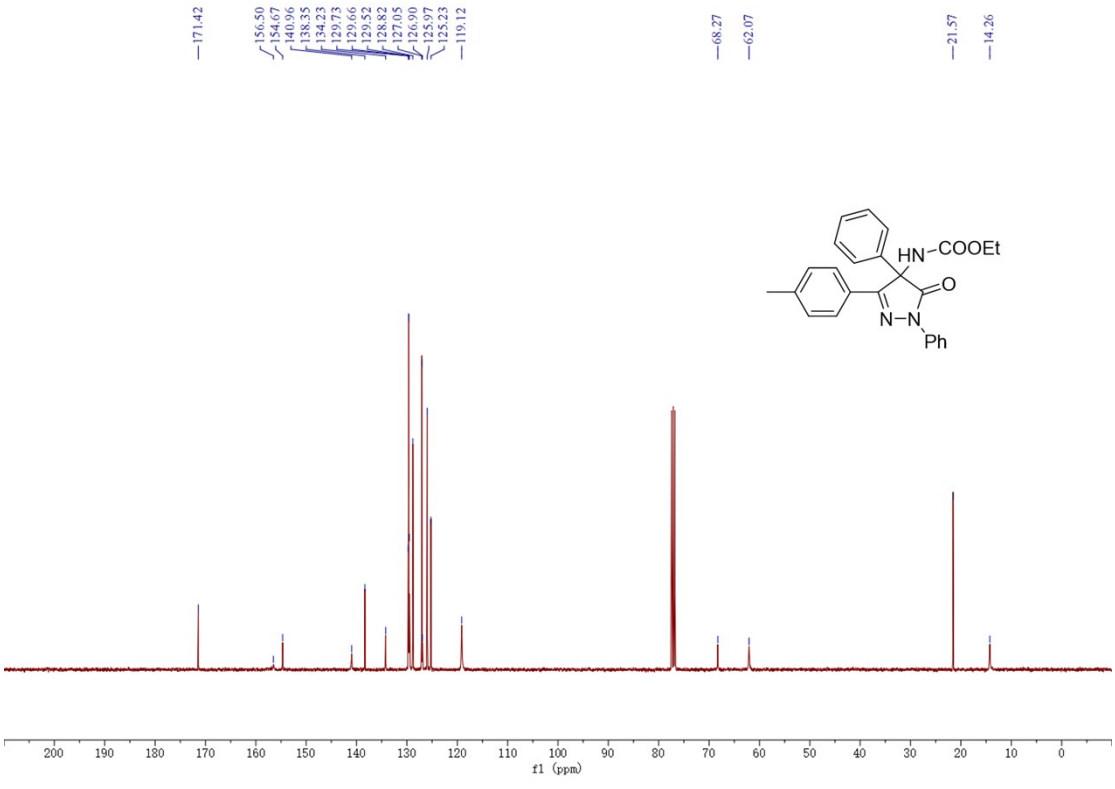
^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra for 3a



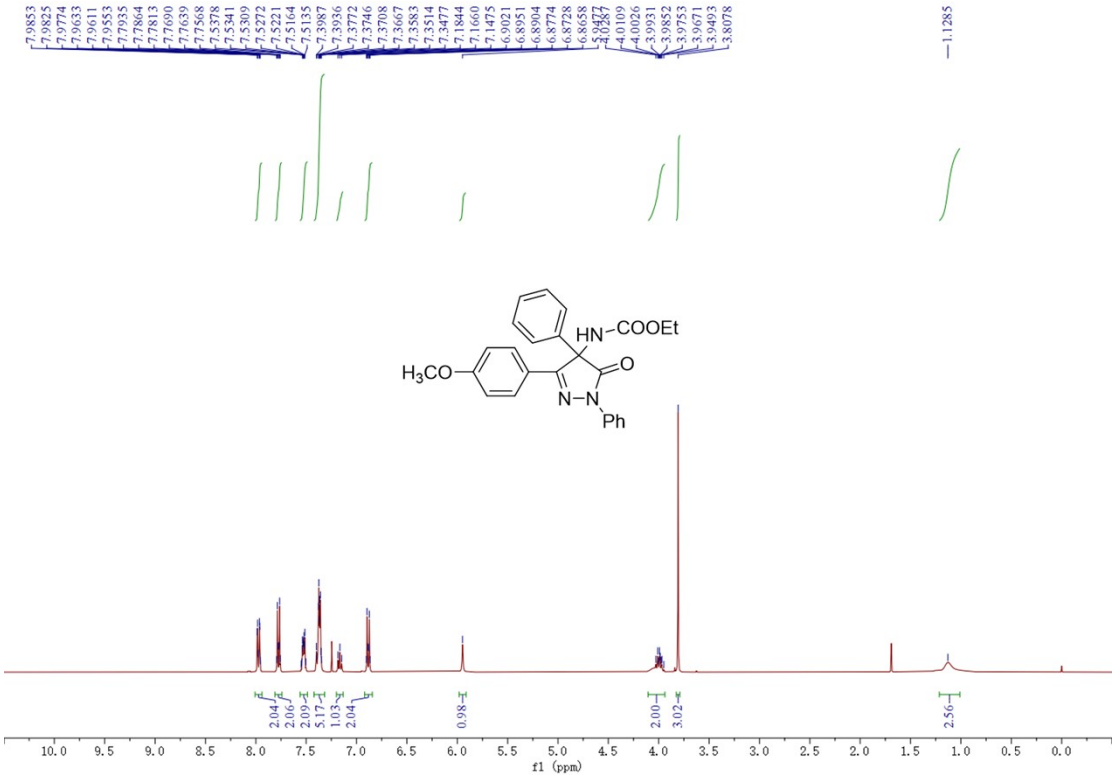


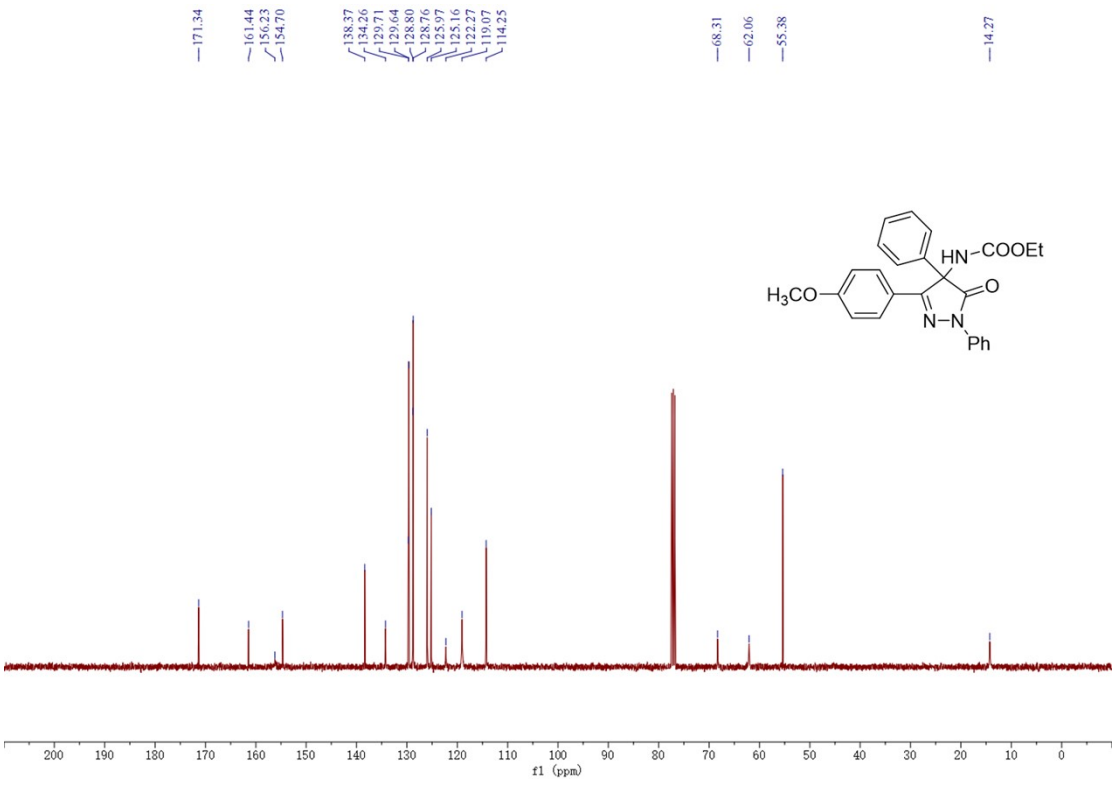
^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra for 3b



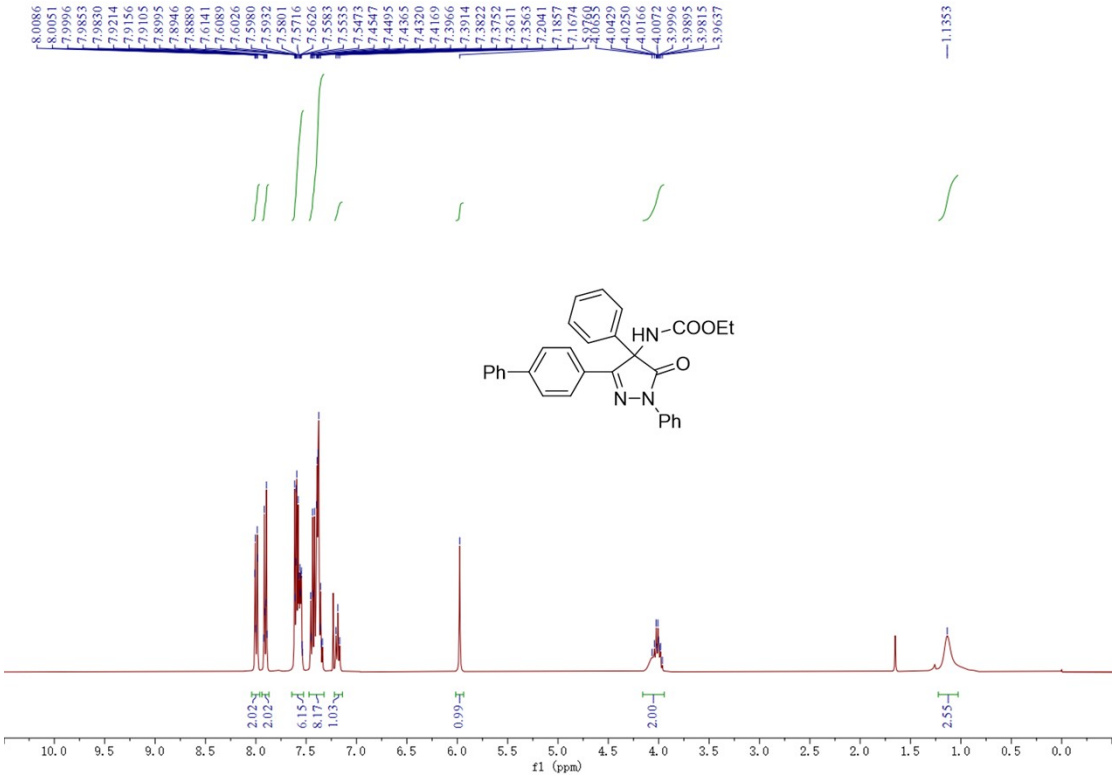


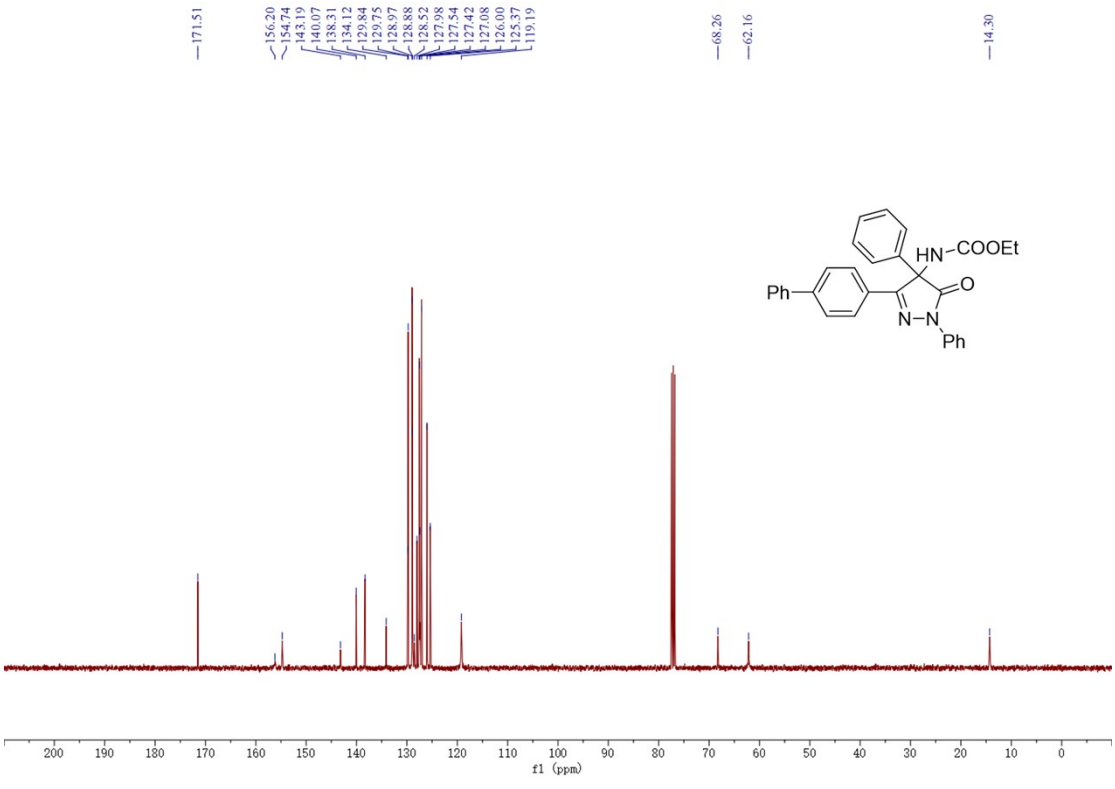
^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra for 3c



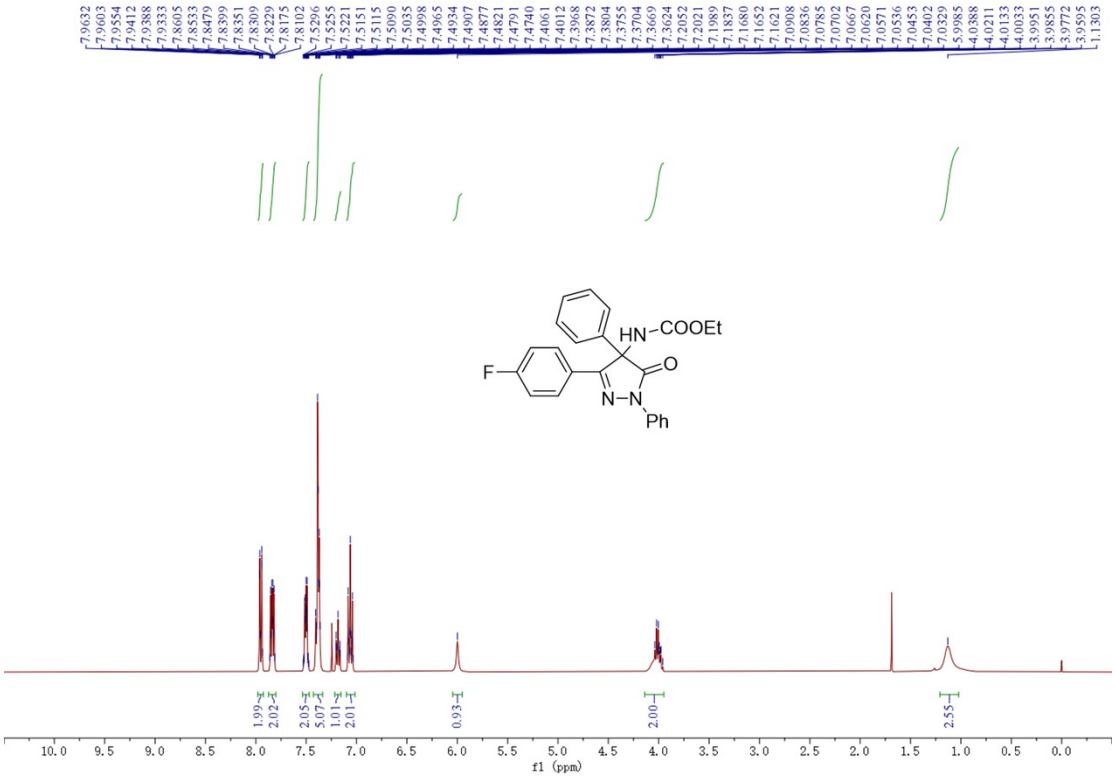


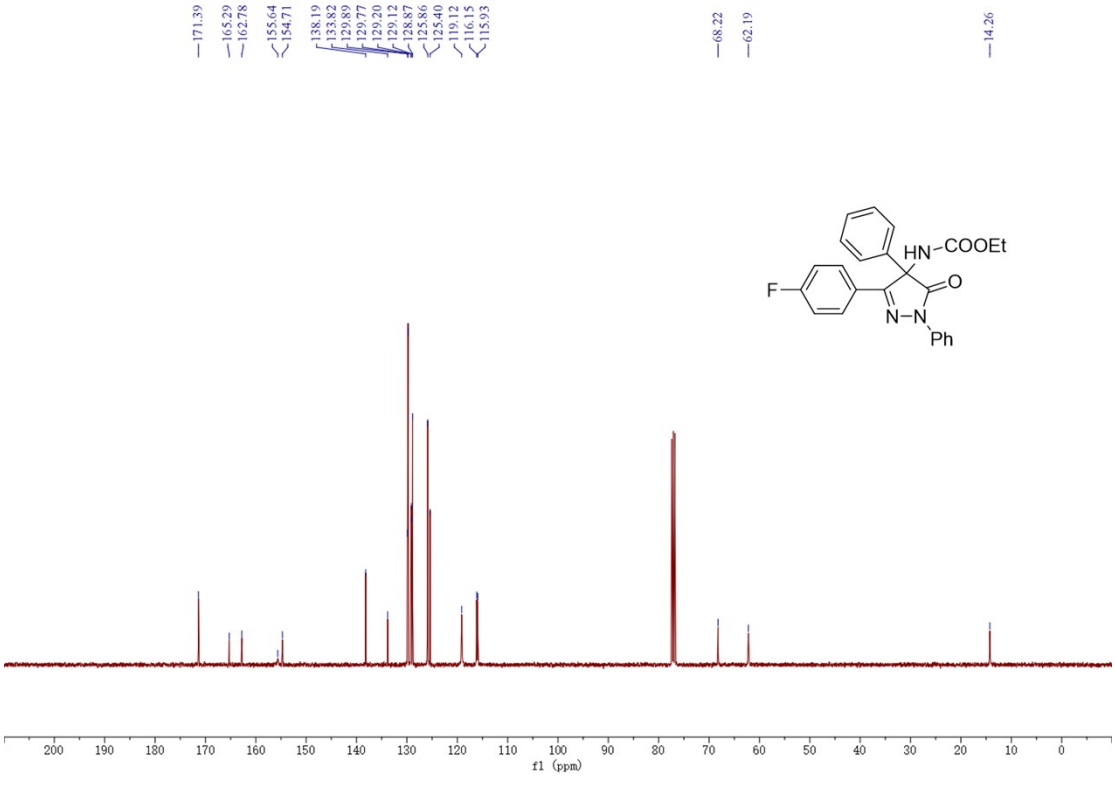
^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra for 3d

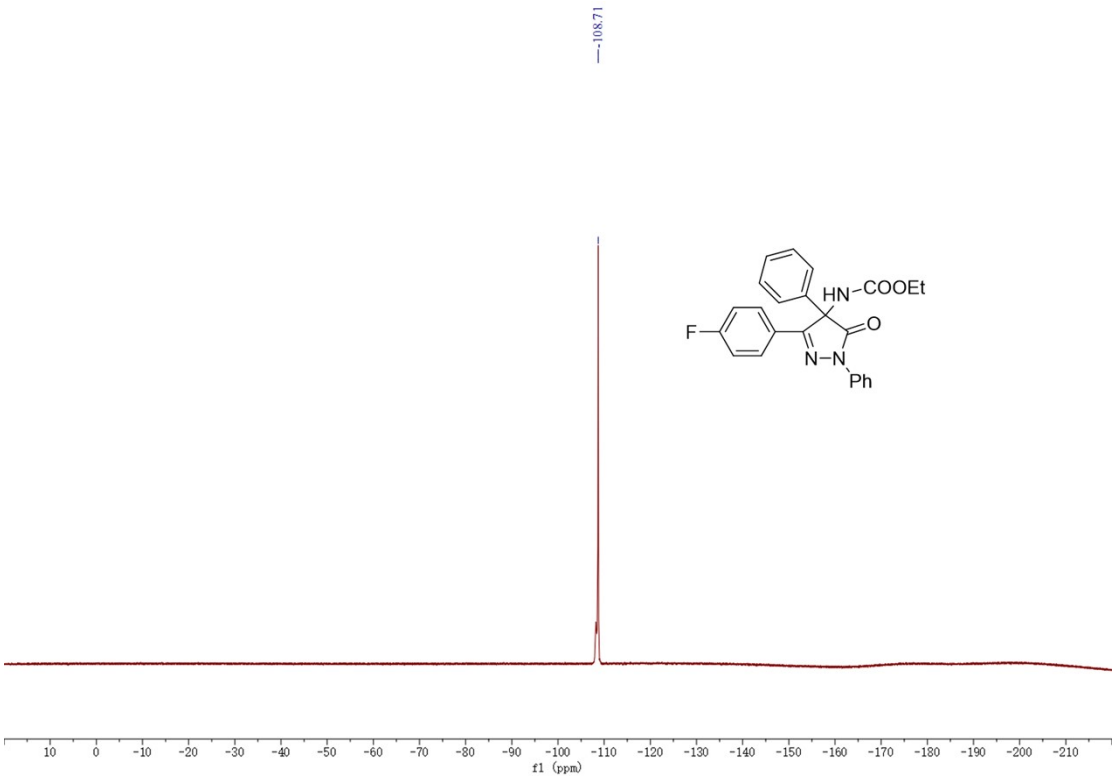




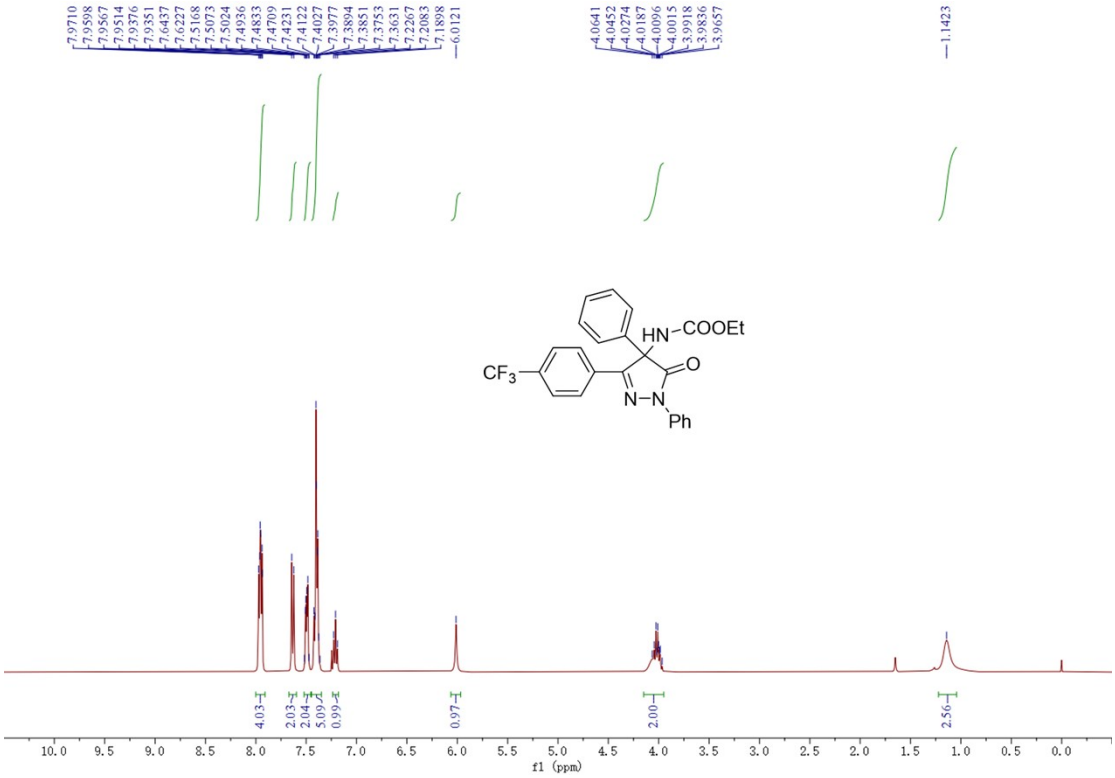
^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR Spectra for 3e

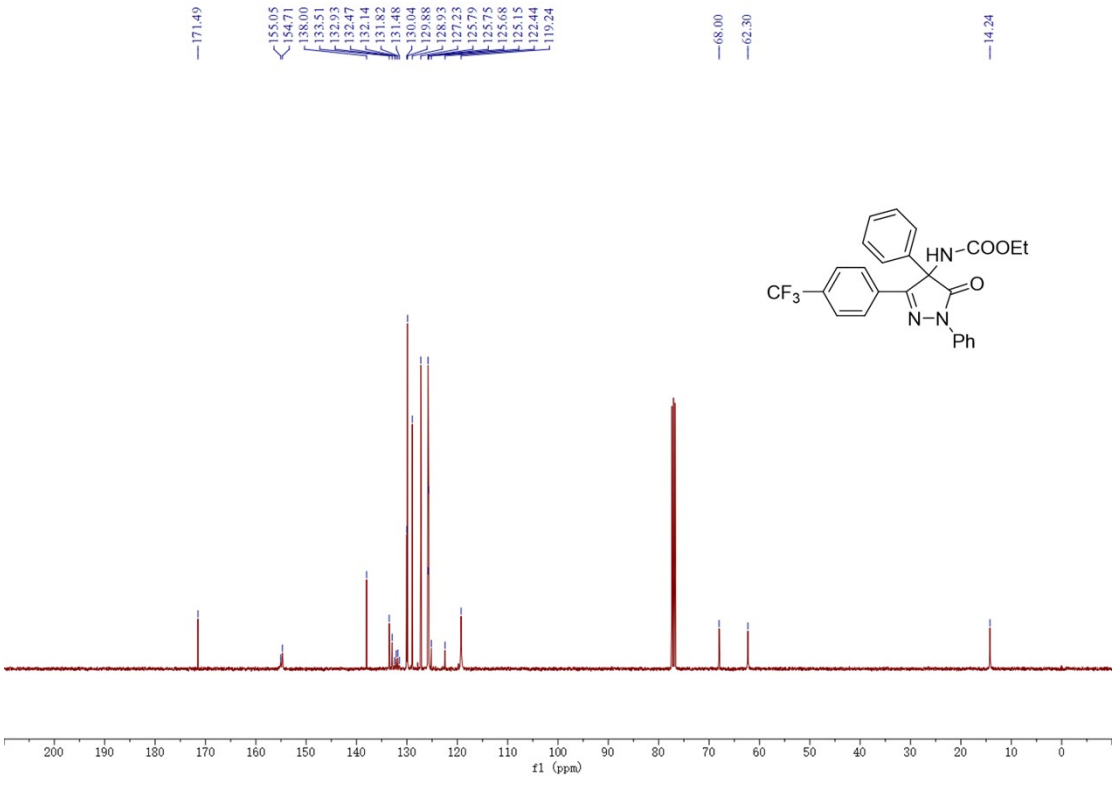


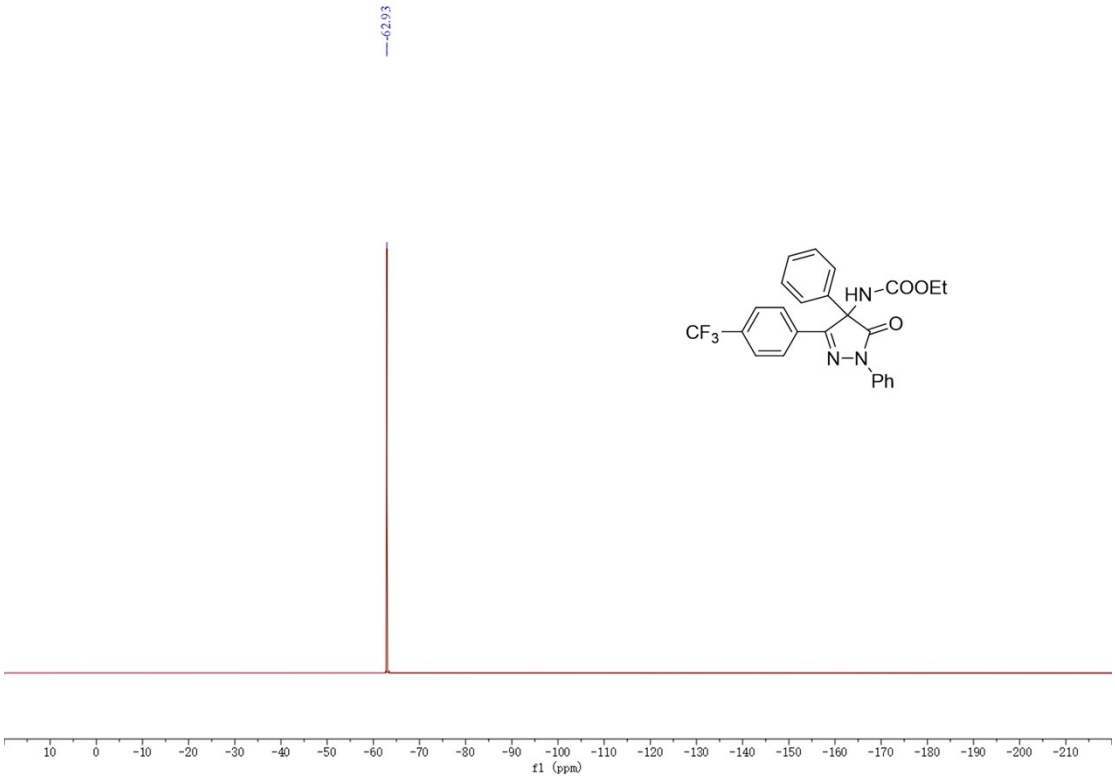



-108.71
HN
COOEt
O
F
N
N
Ph
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR Spectra for 3f






-62.93
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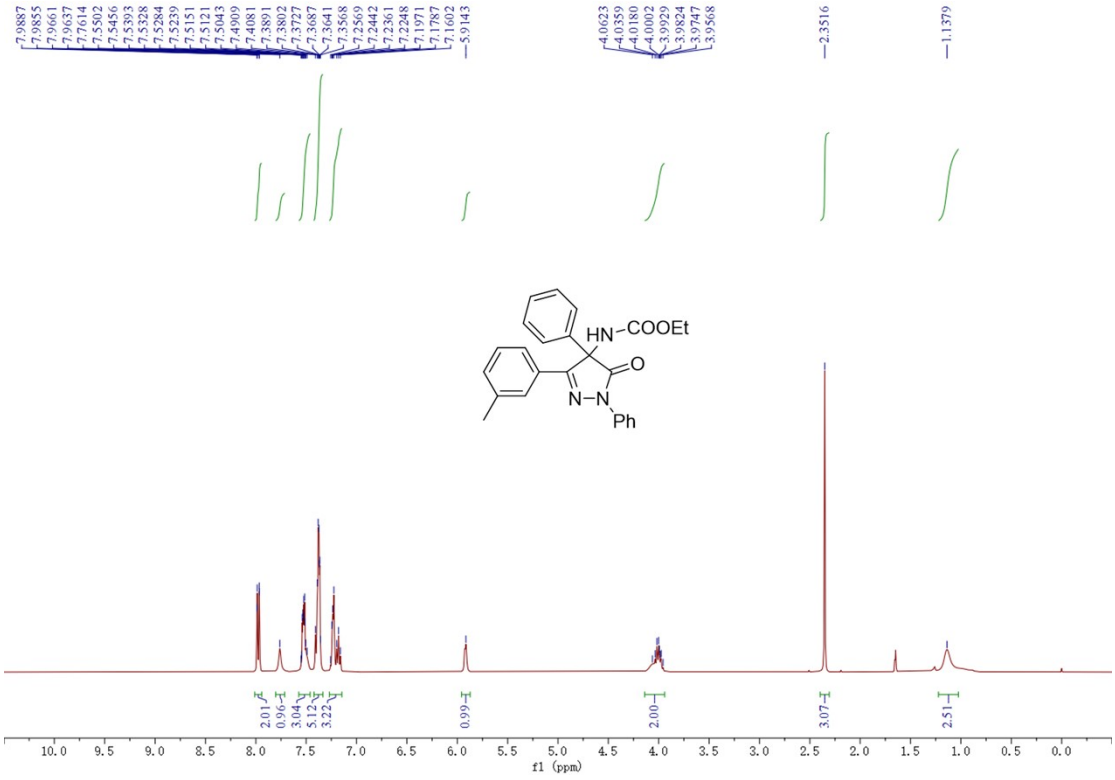
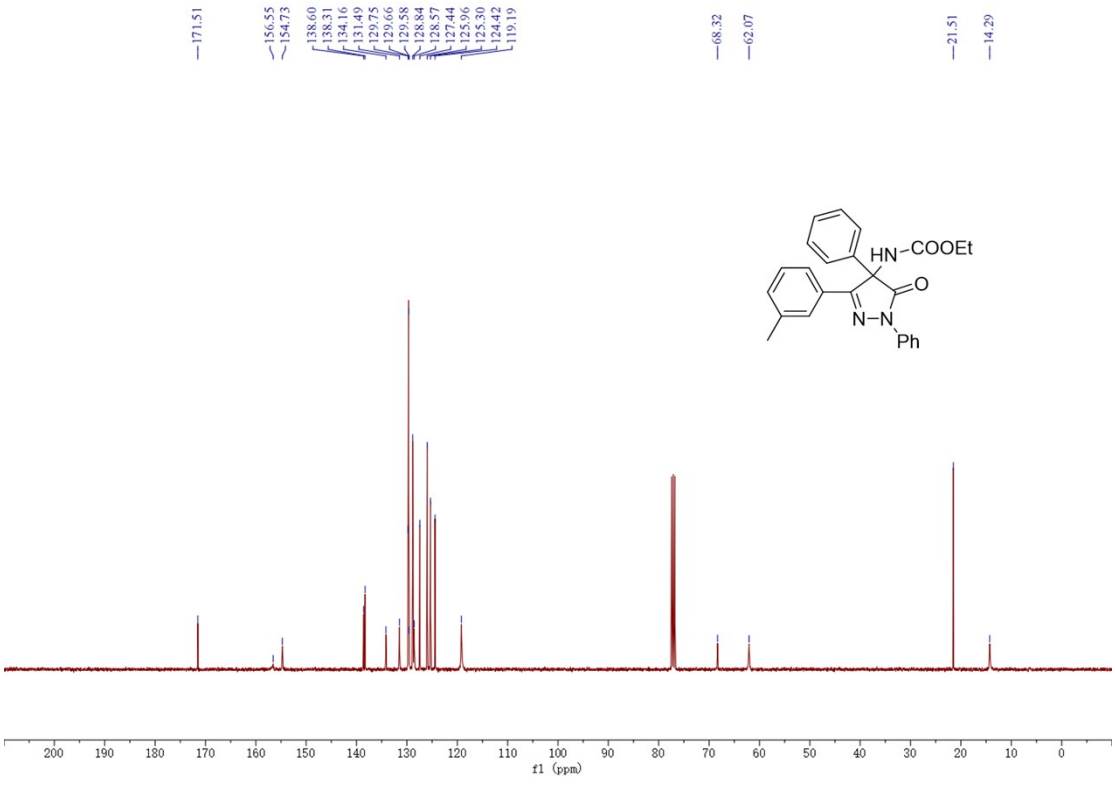
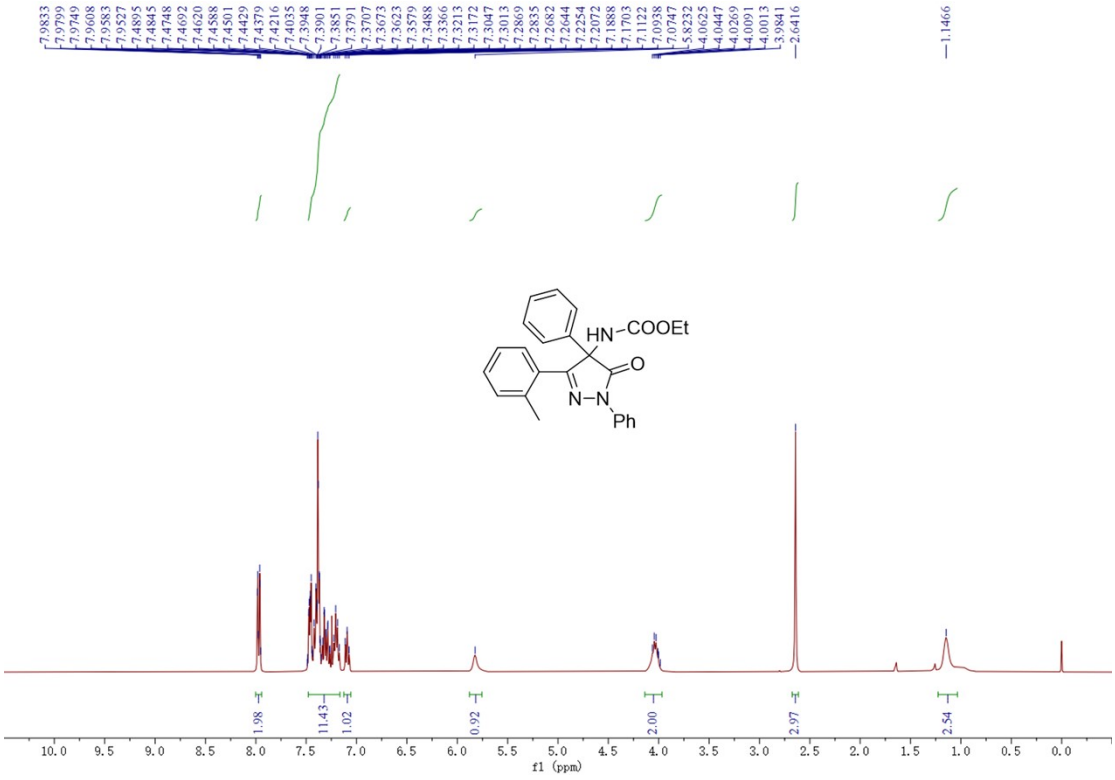
O
CF3
N–N
Ph
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

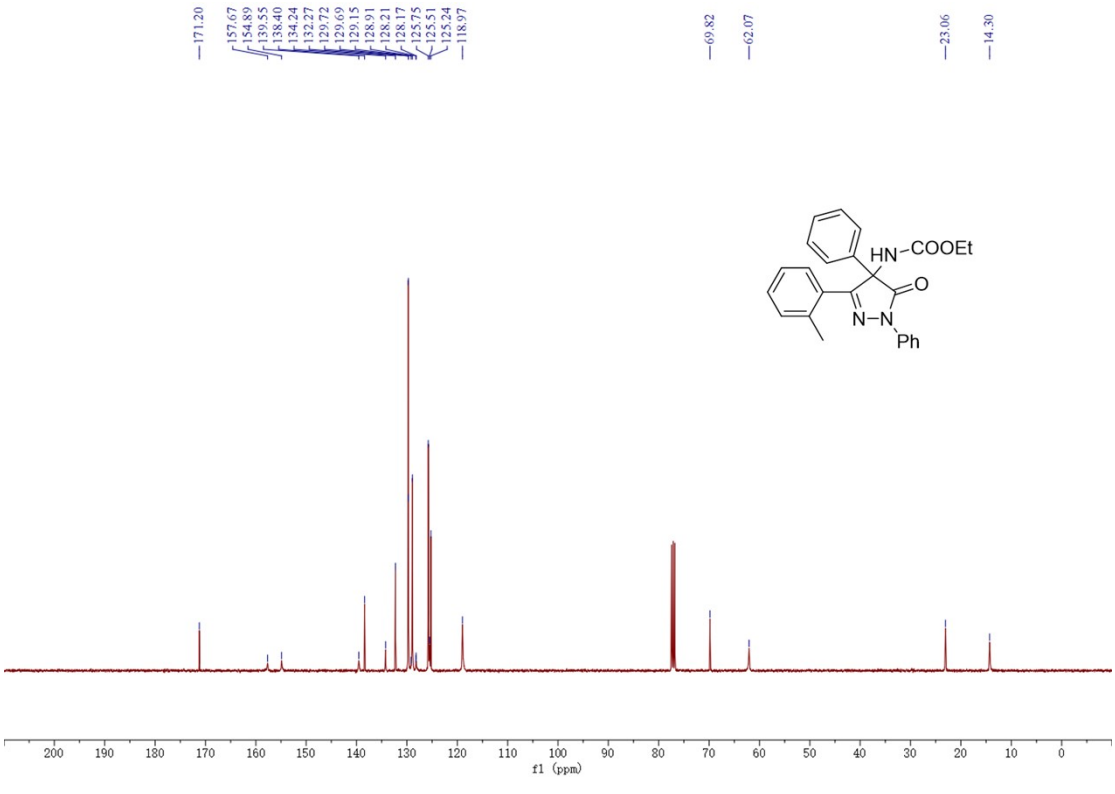
^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra for 3g



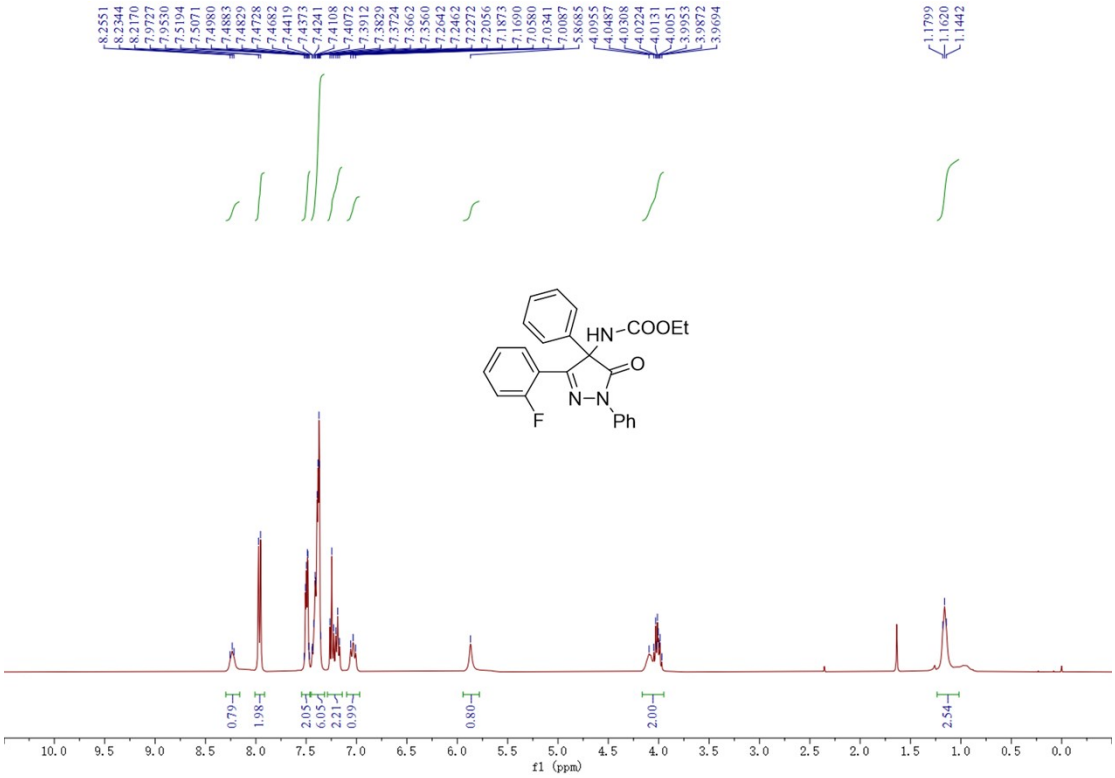


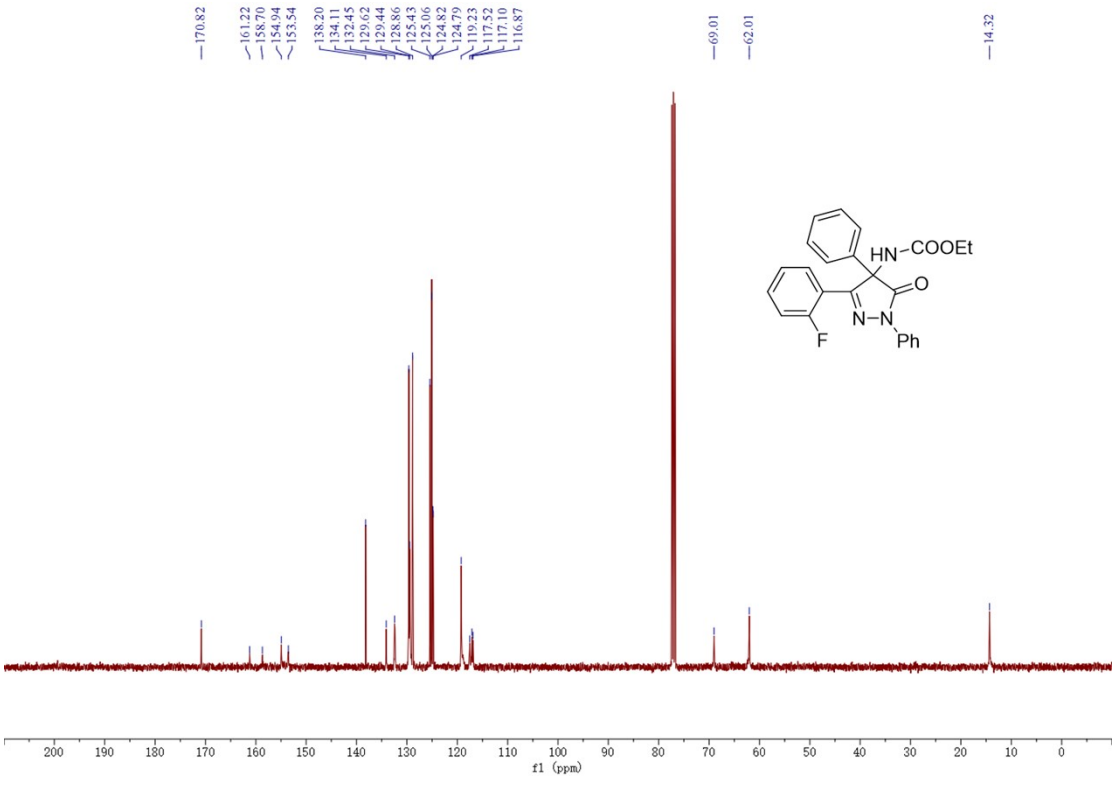
^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra for 3h

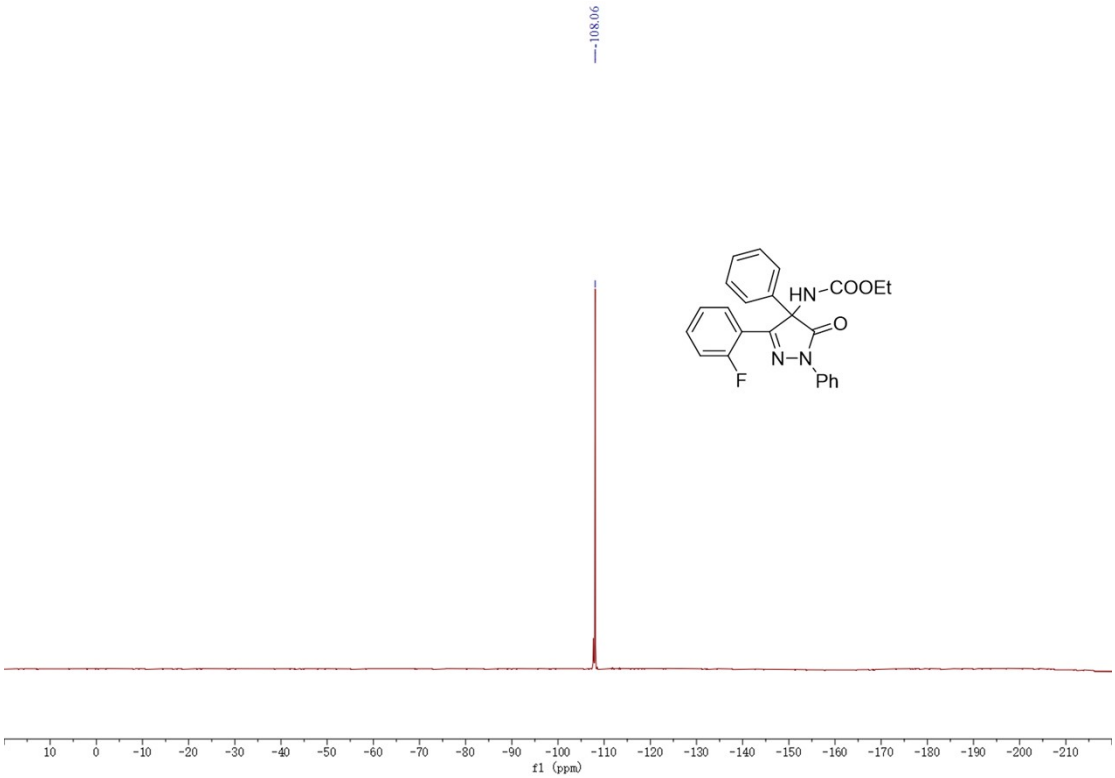




^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR Spectra for 3i






-108.06
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COOEt
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Ph
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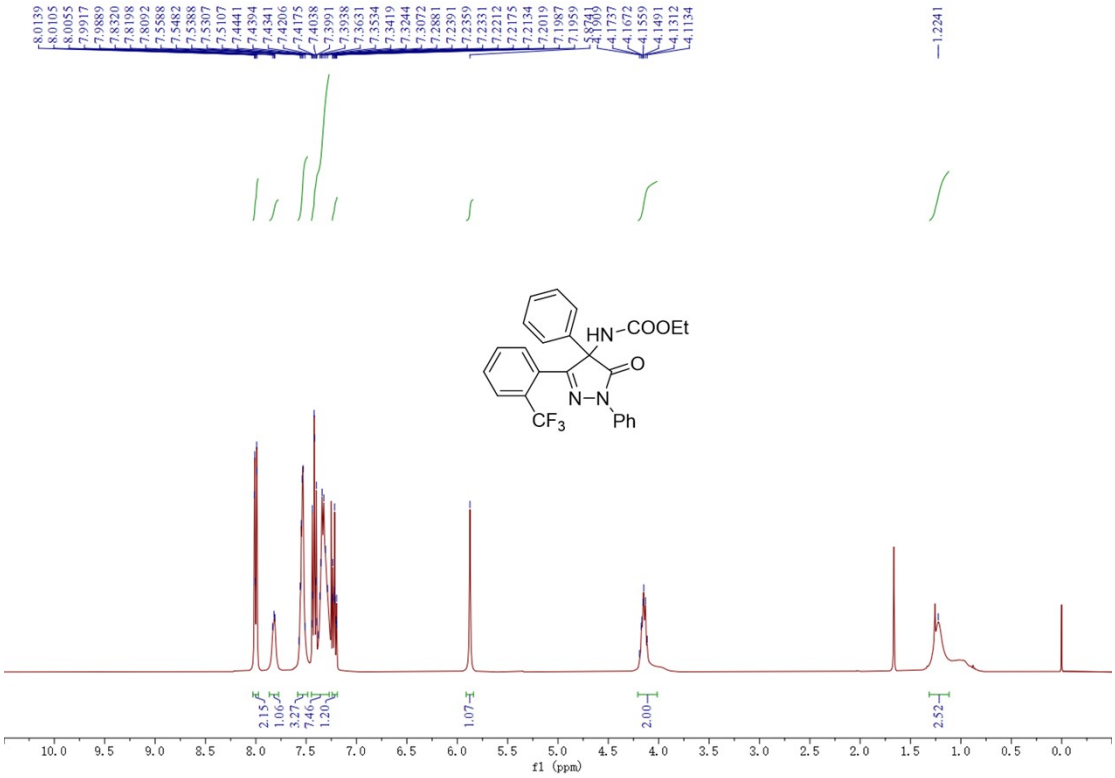
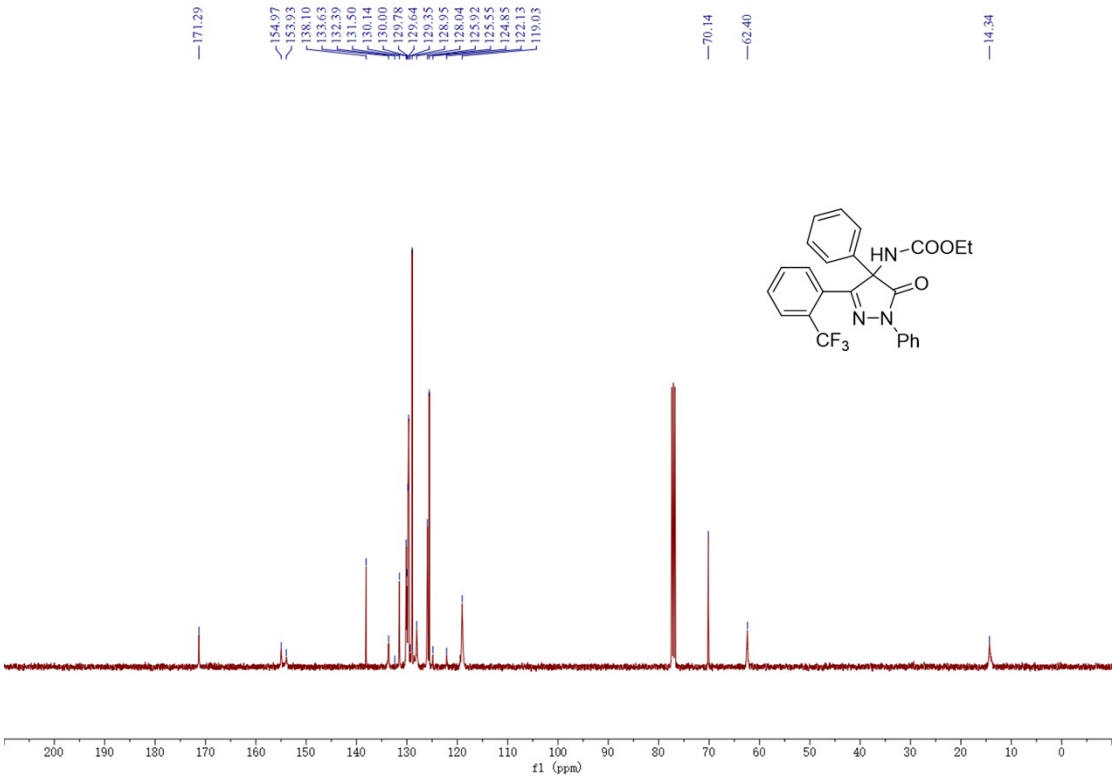
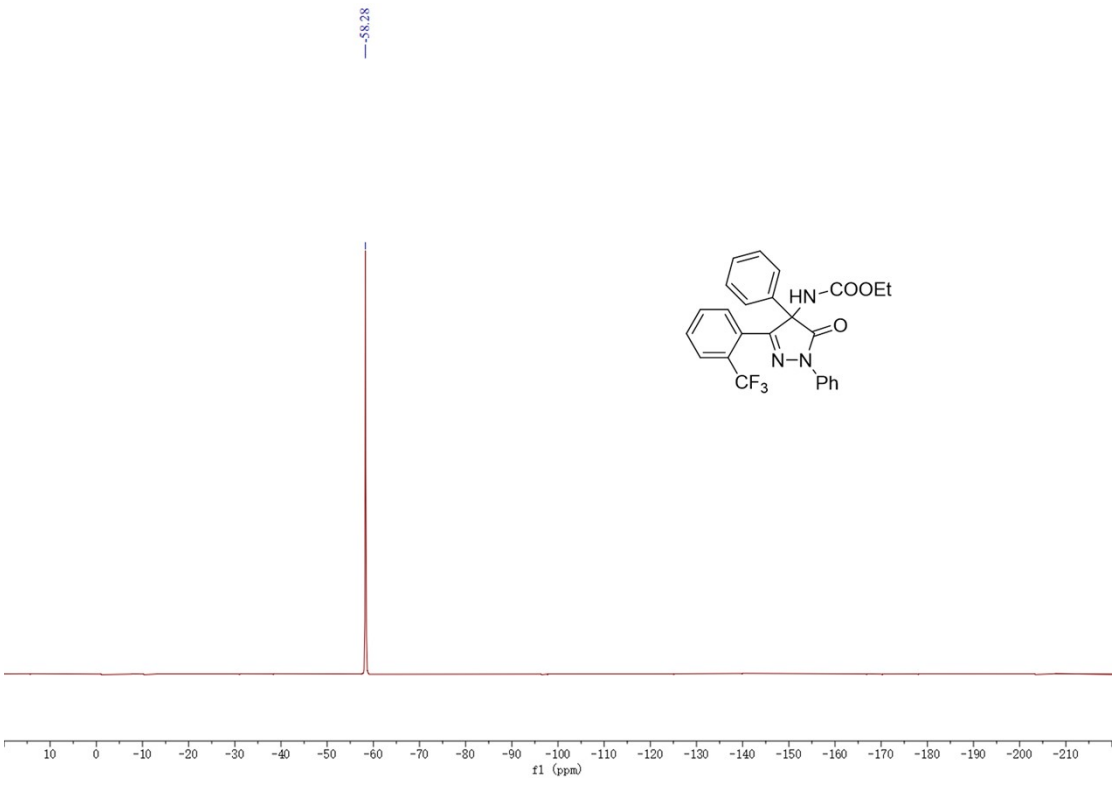
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR Spectra for 3j



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N
Ph
CF3
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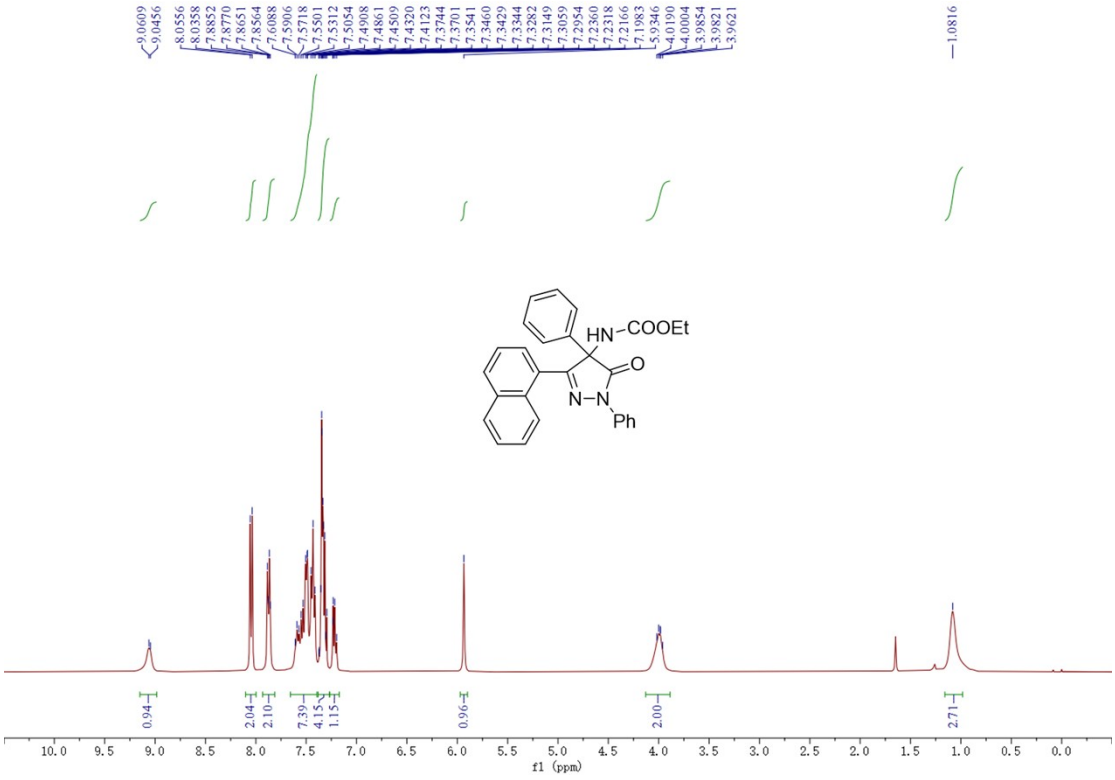
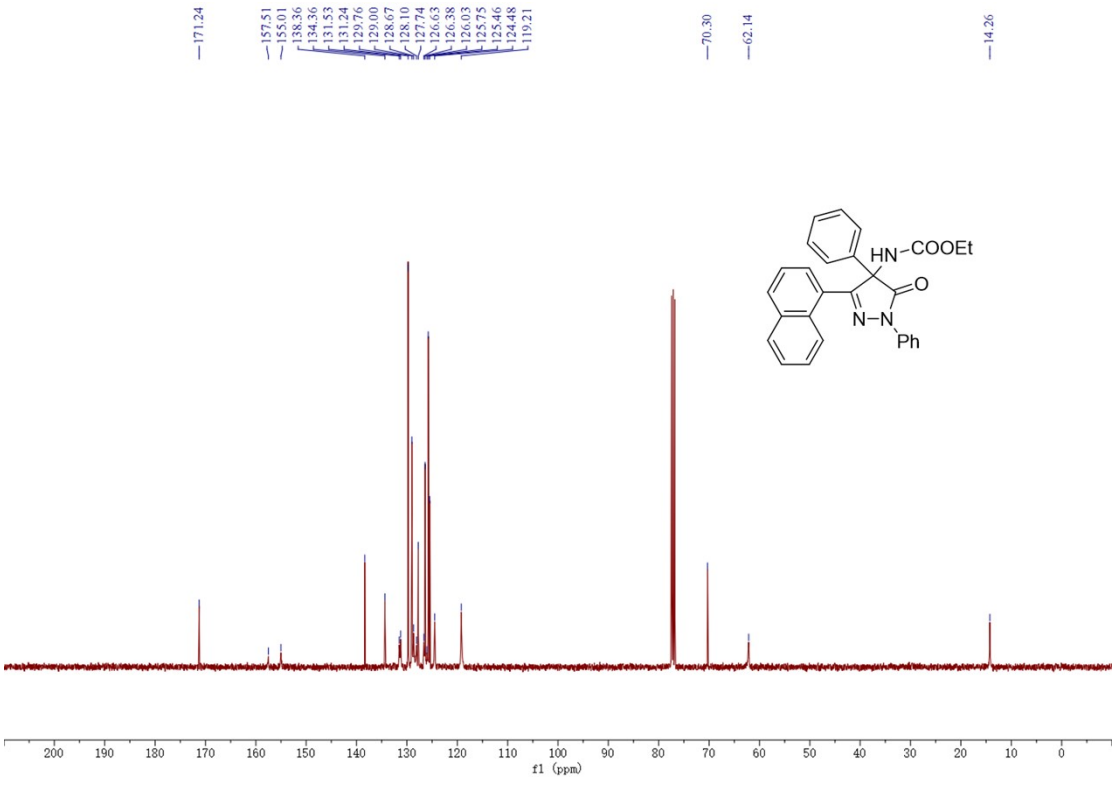
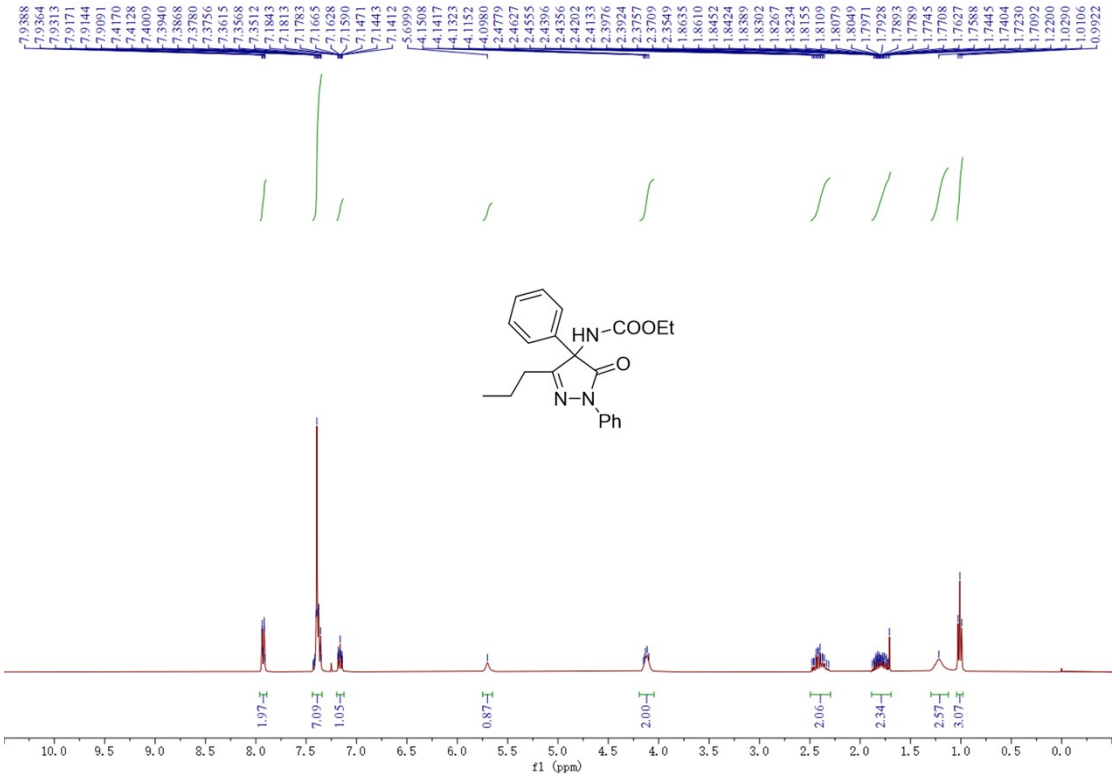
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

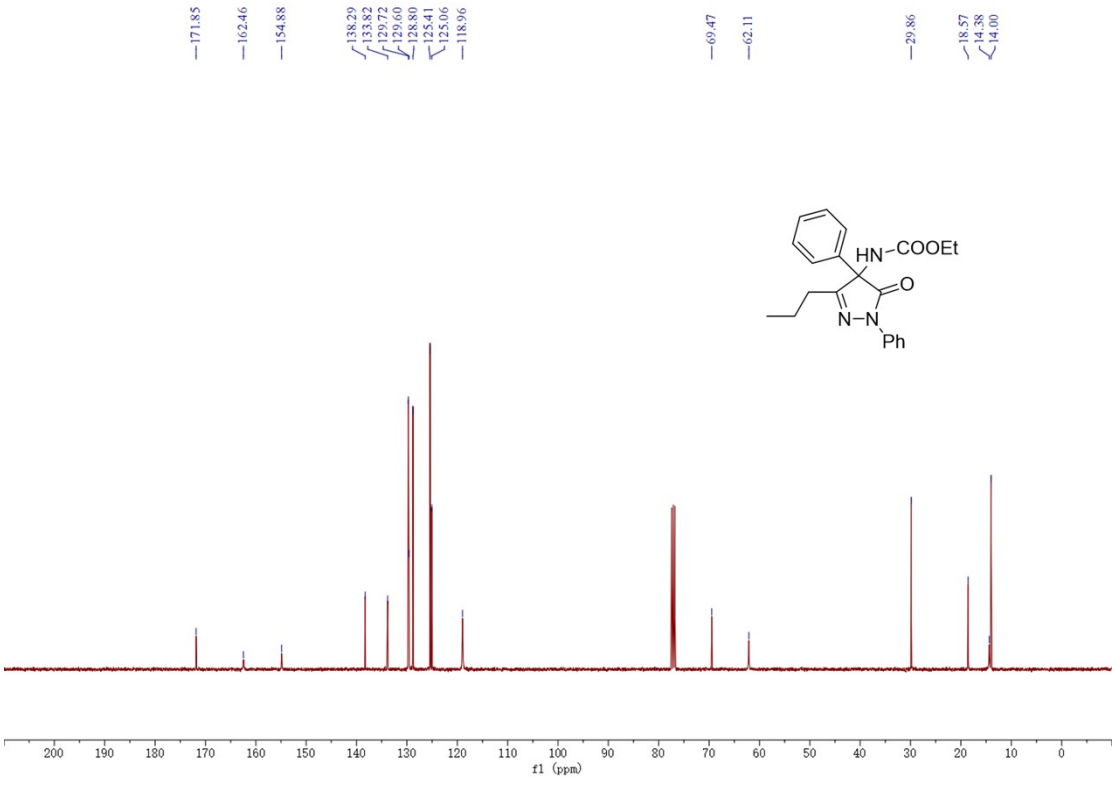
^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra for 3k



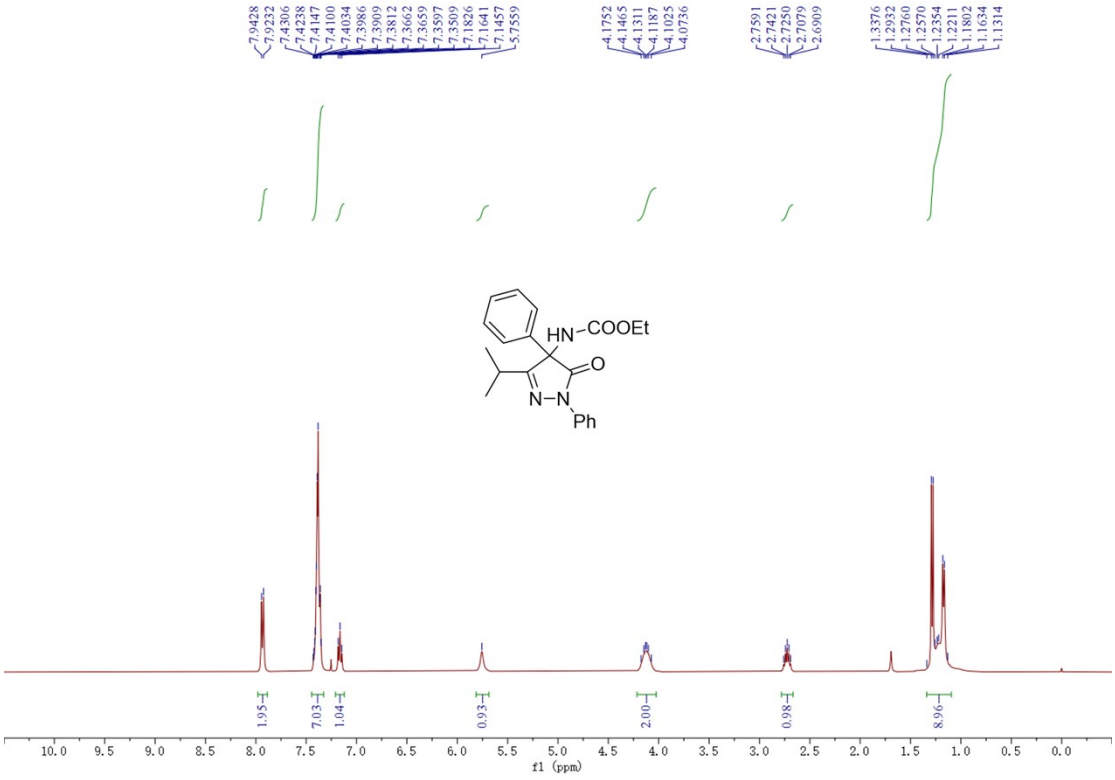


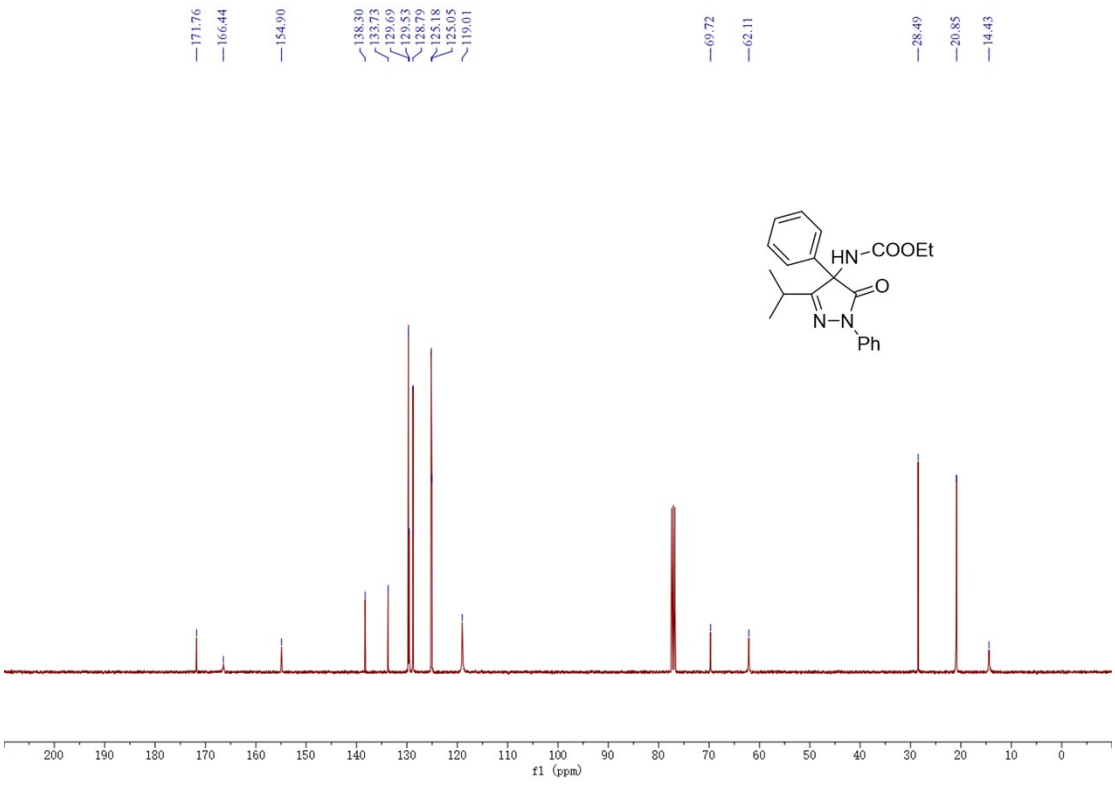
^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra for 3l



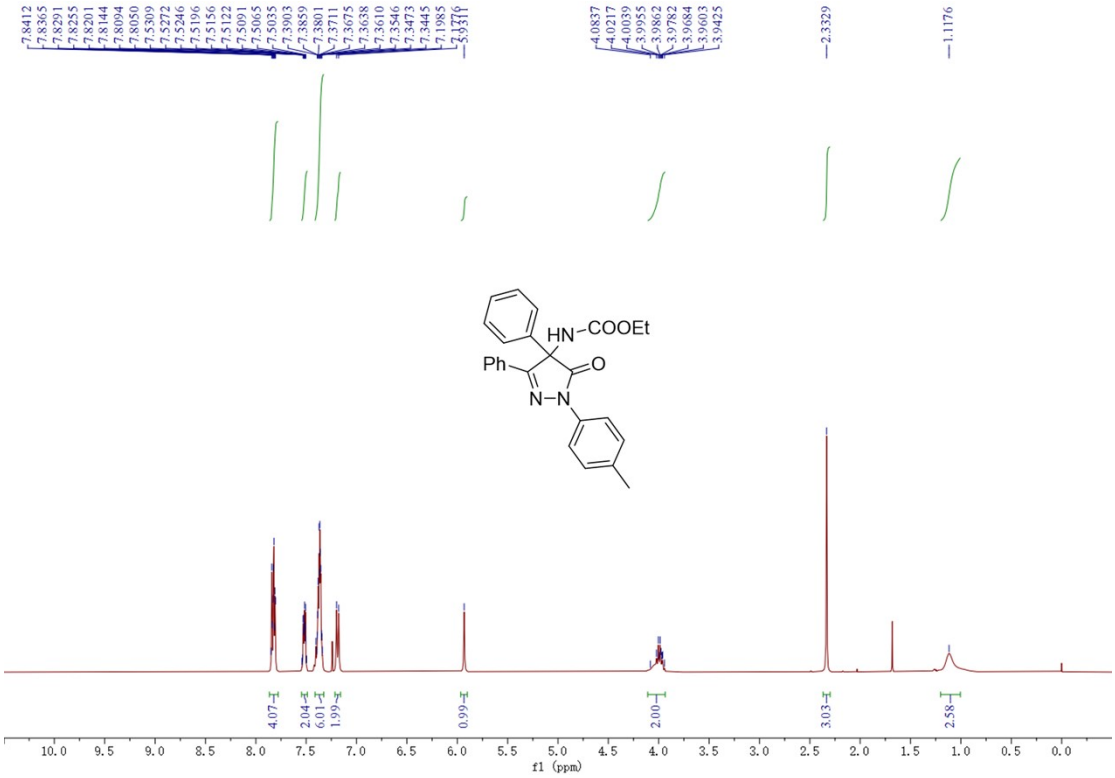


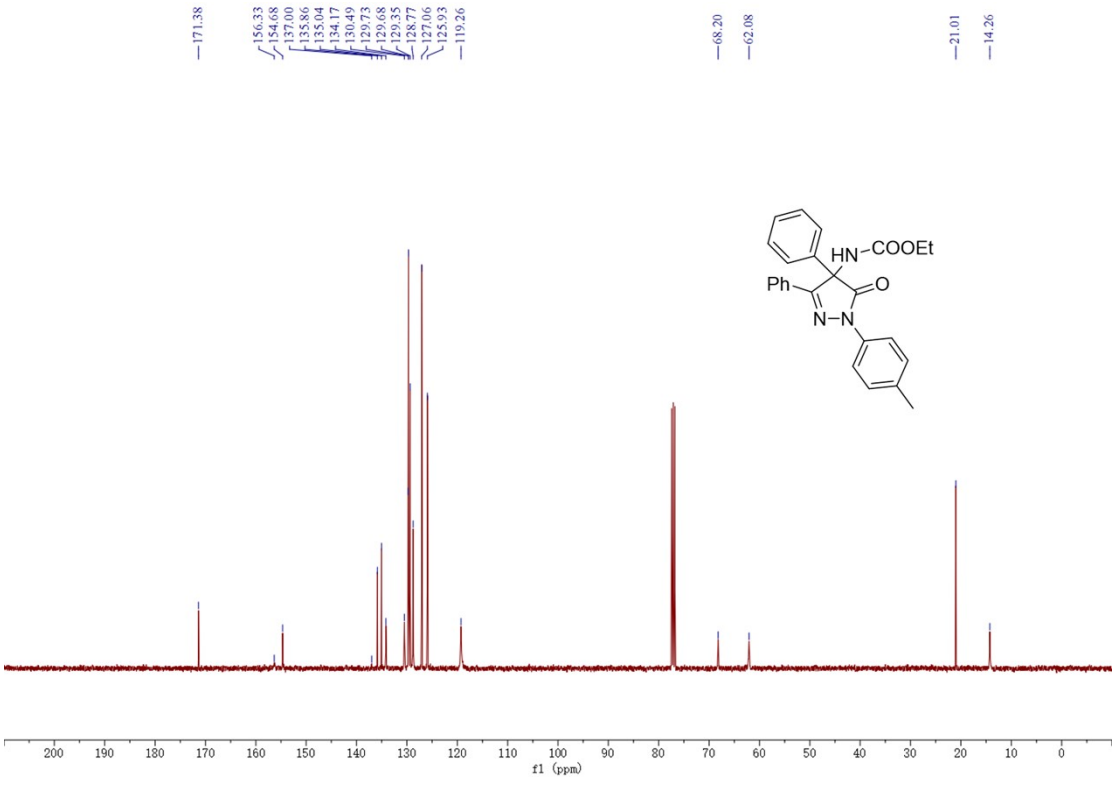
^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra for 3m



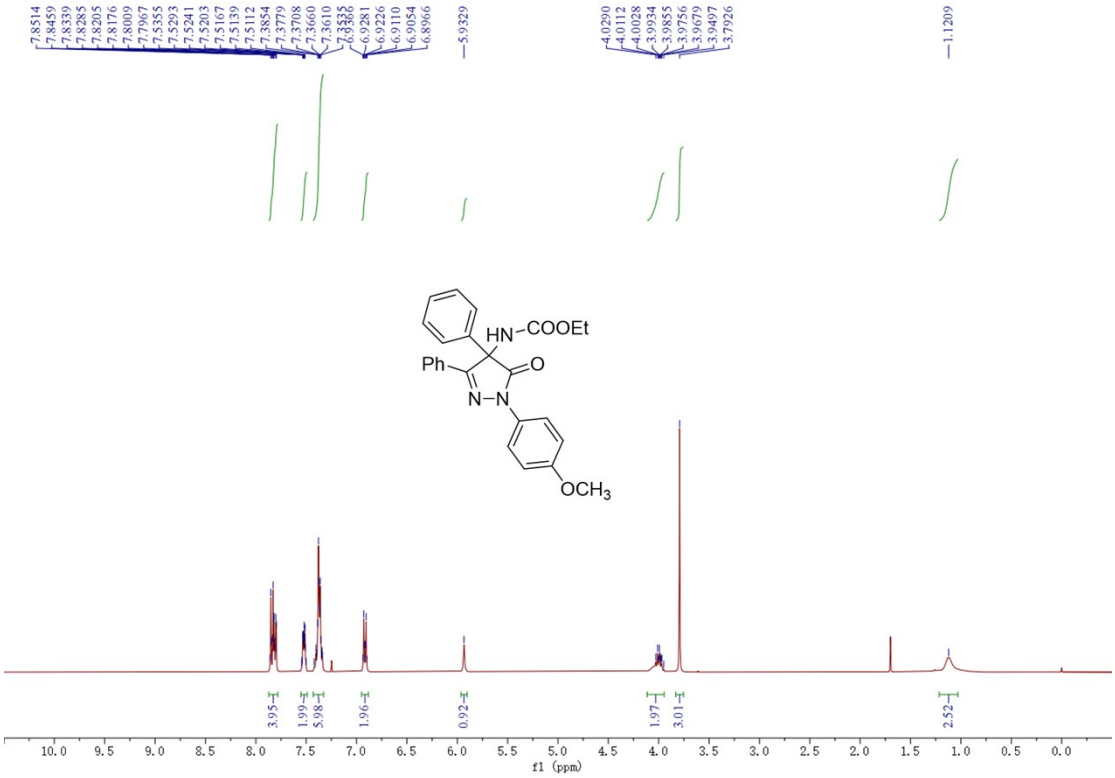


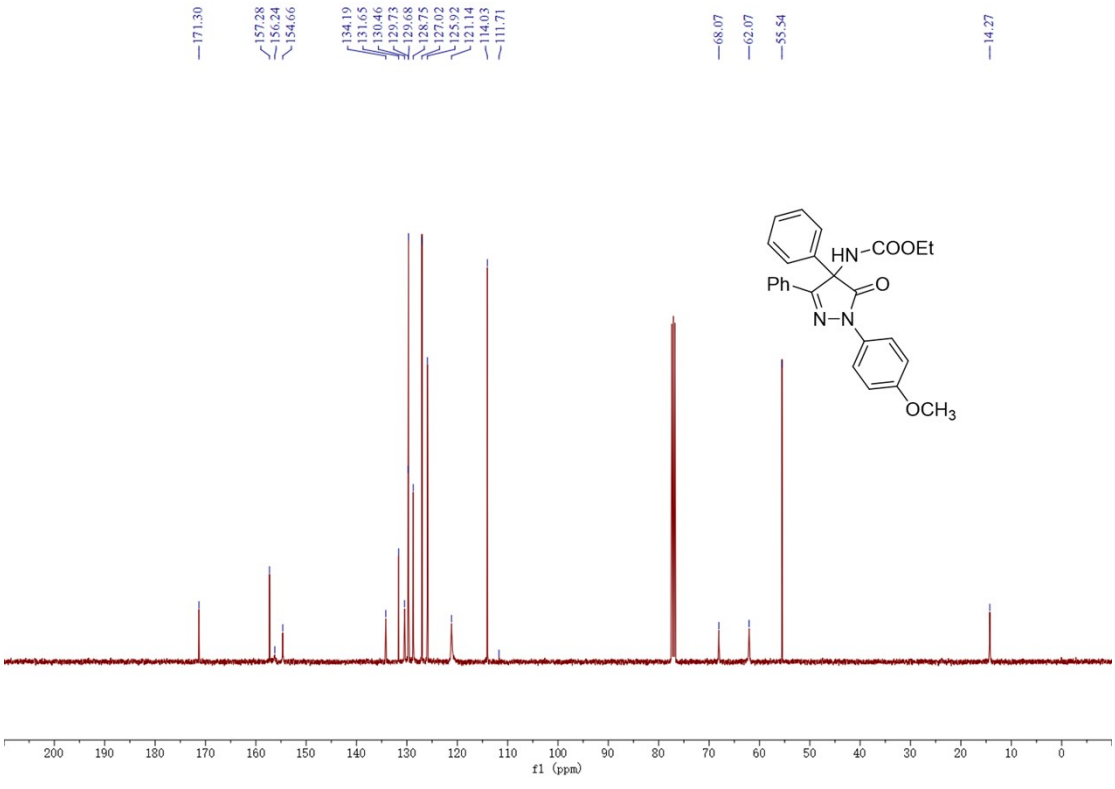
^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra for 3n



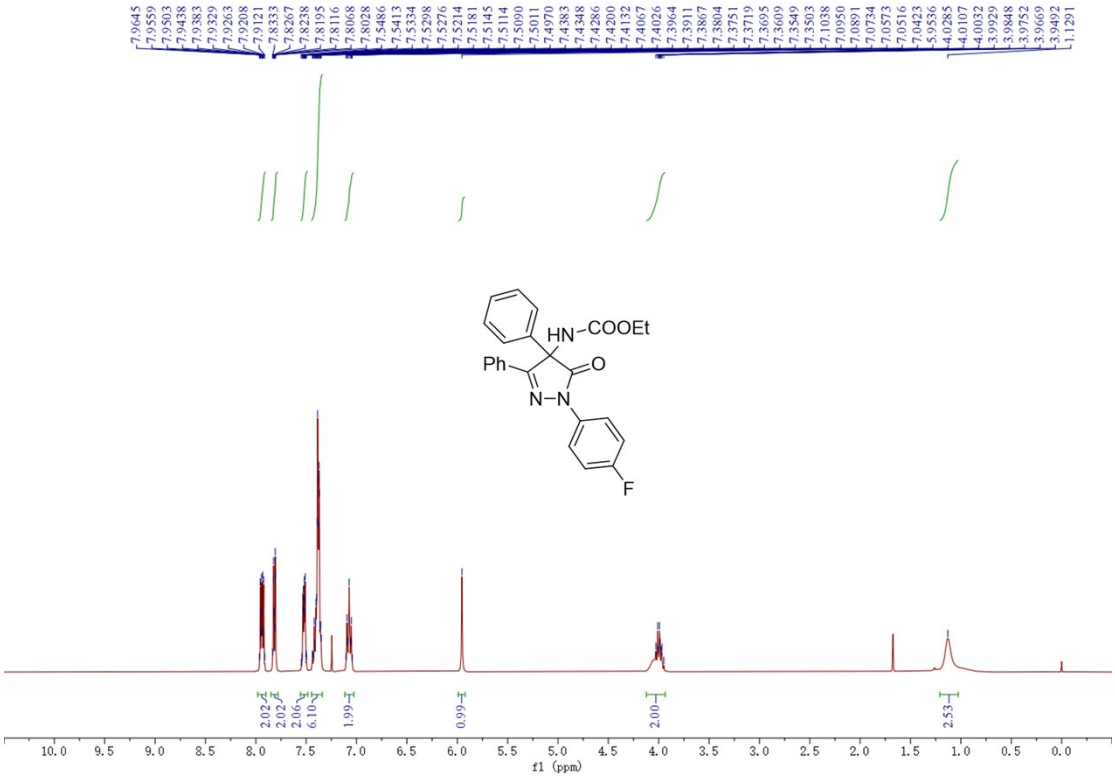


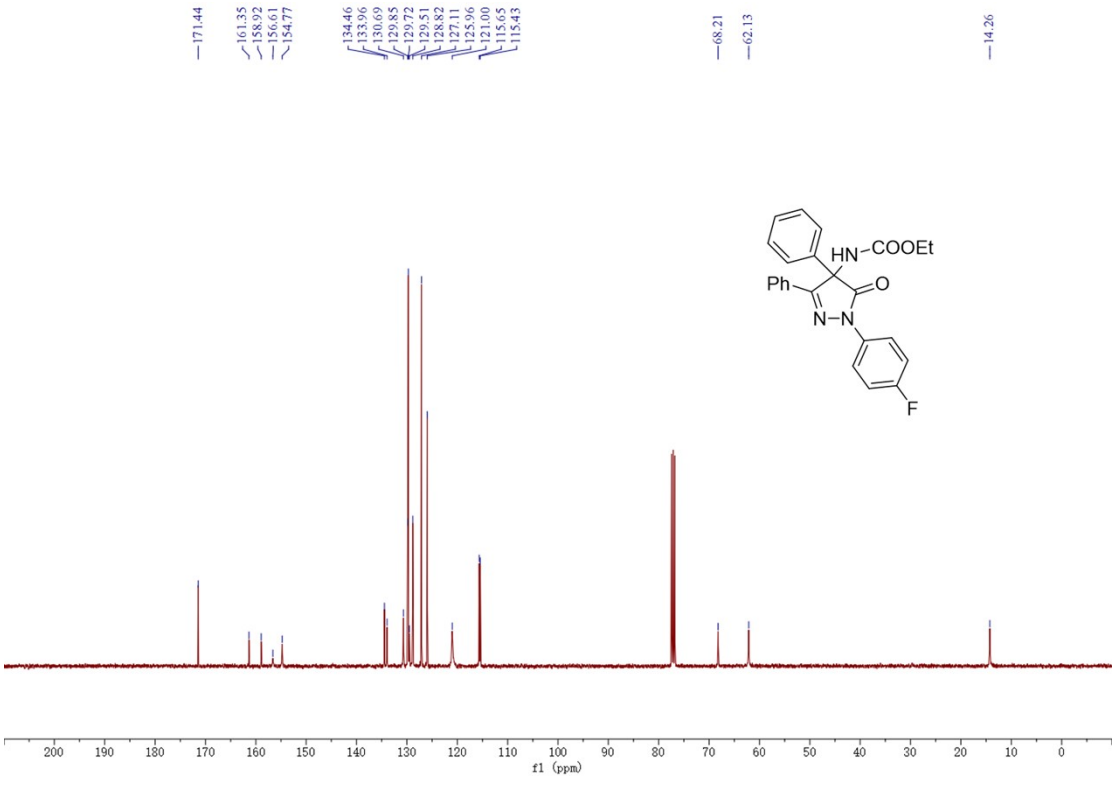
^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra for 3o

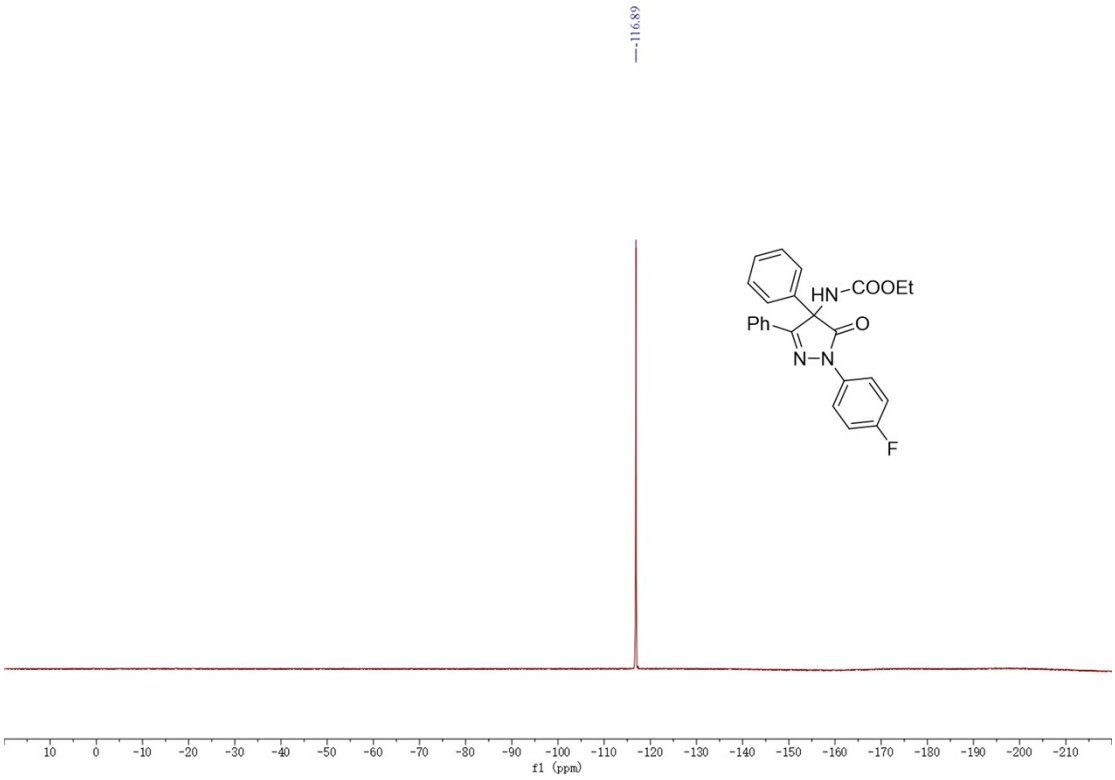




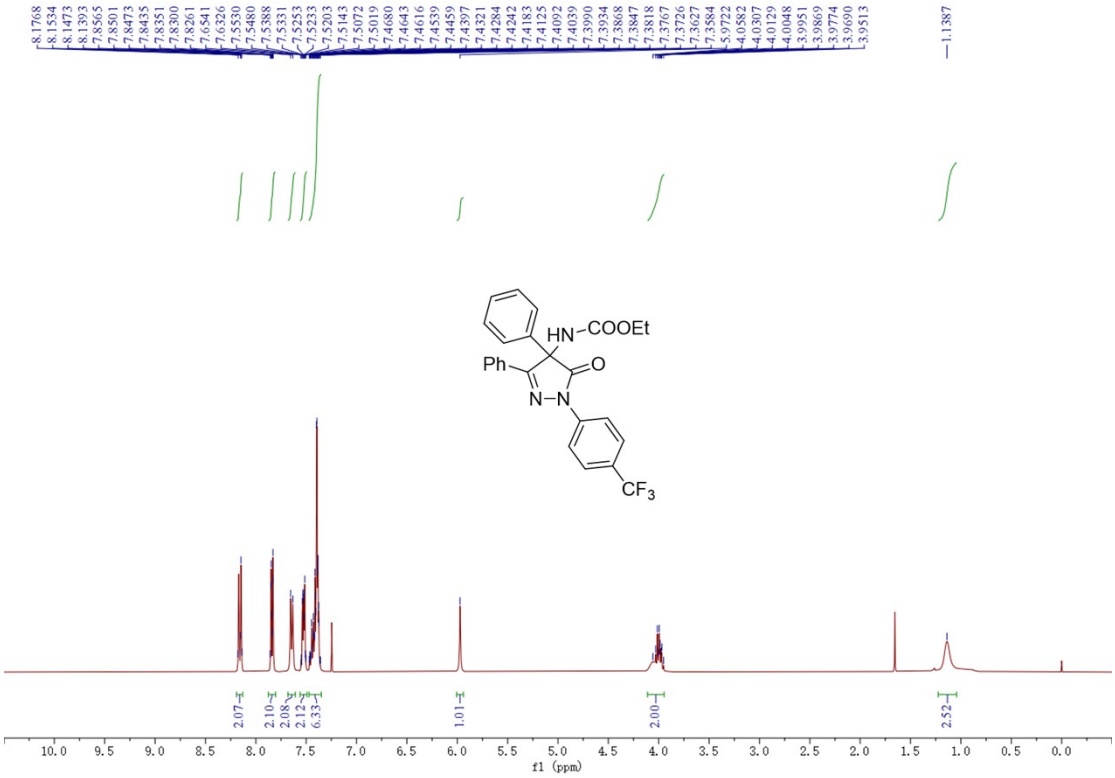
^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR Spectra for 3p

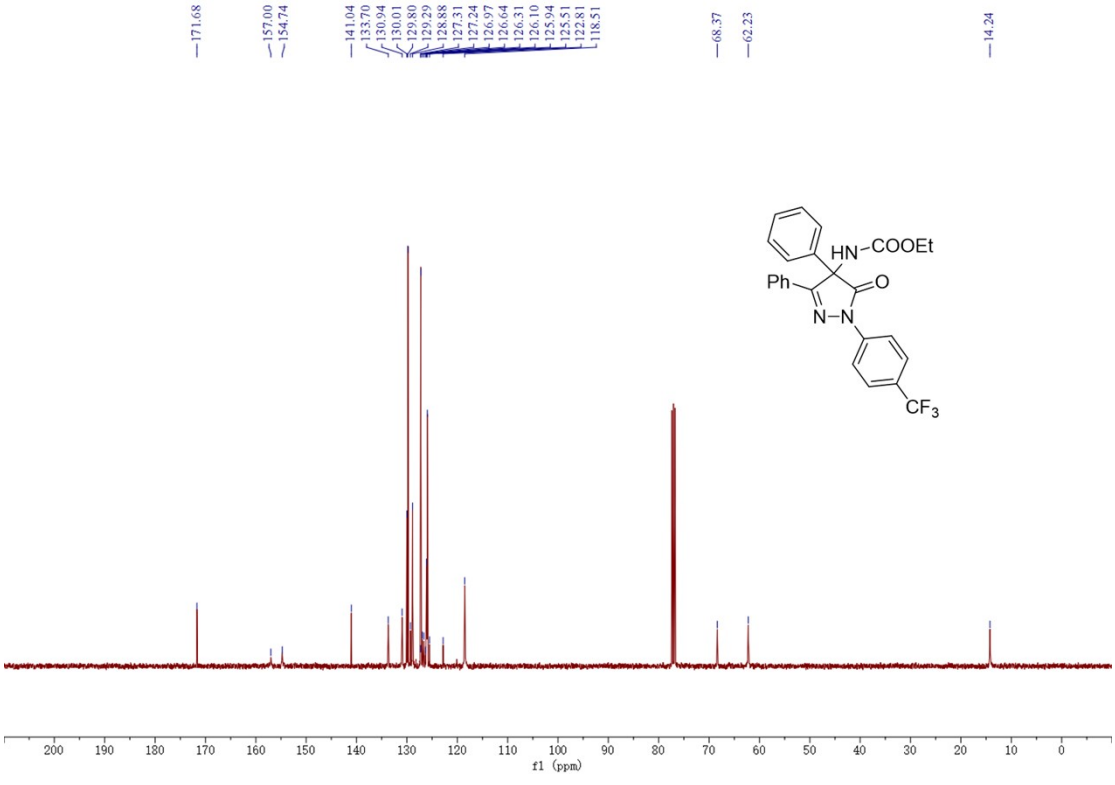


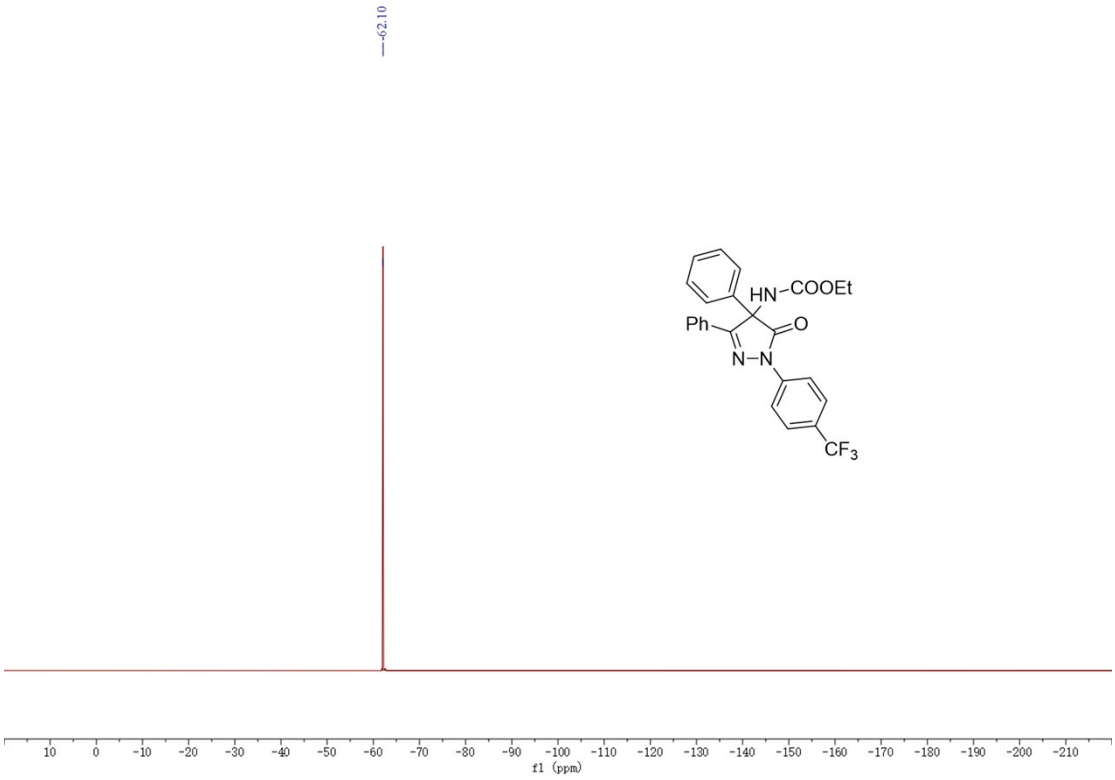



-116.89
HN–COOEt
Ph
O
N–N
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR Spectra for 3q



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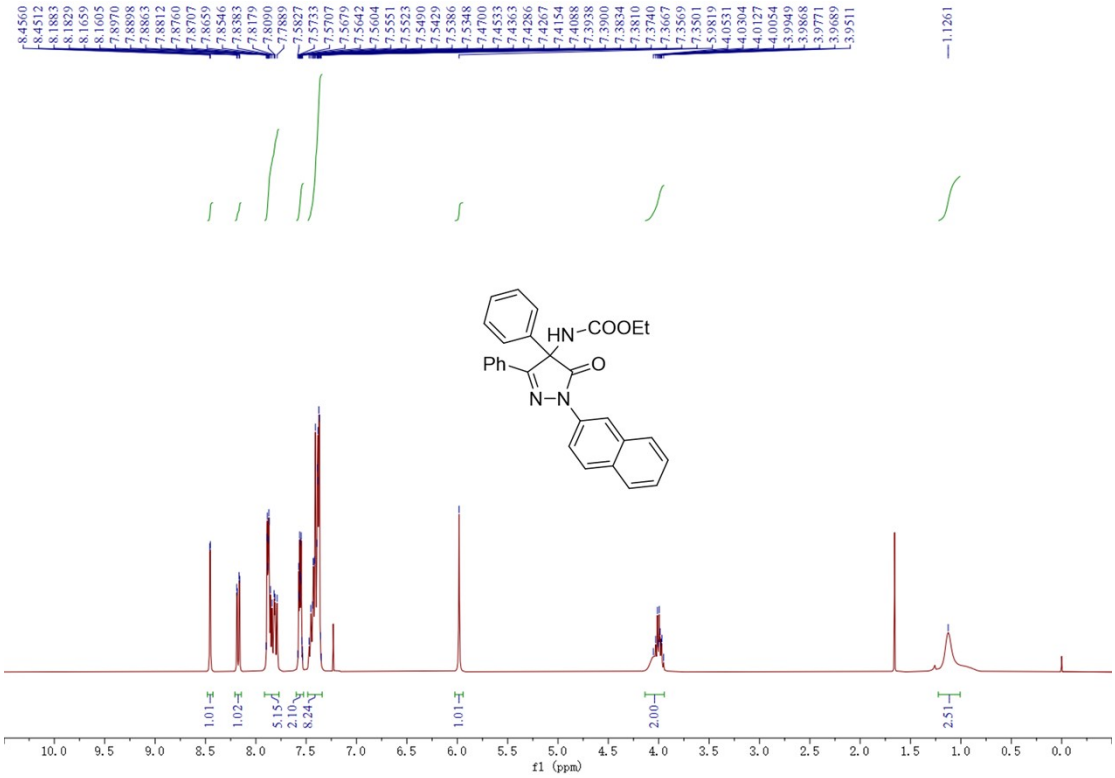
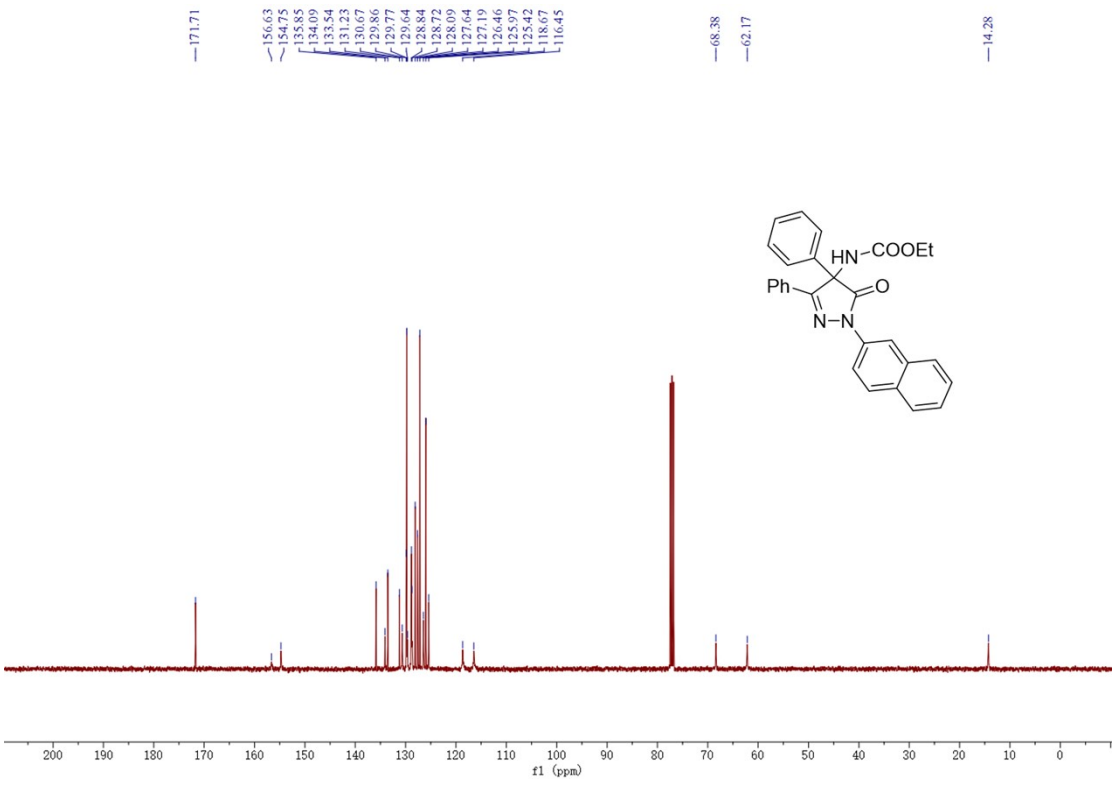
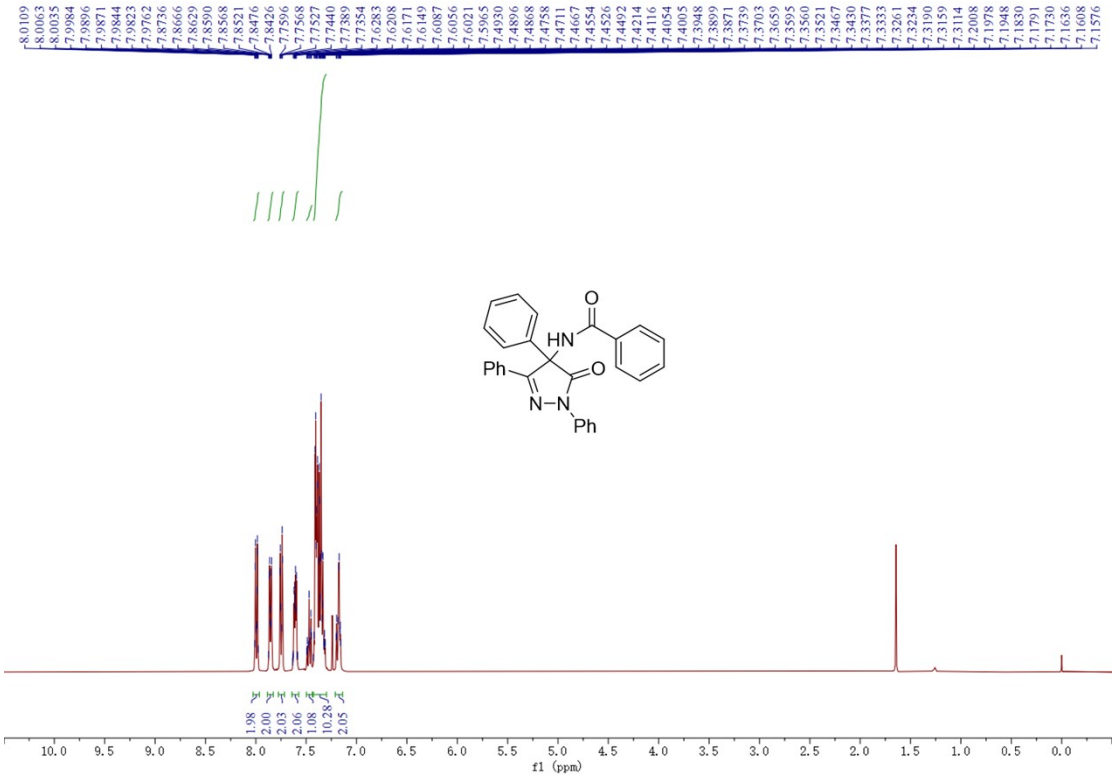
COOEt
Ph
O
N
N
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

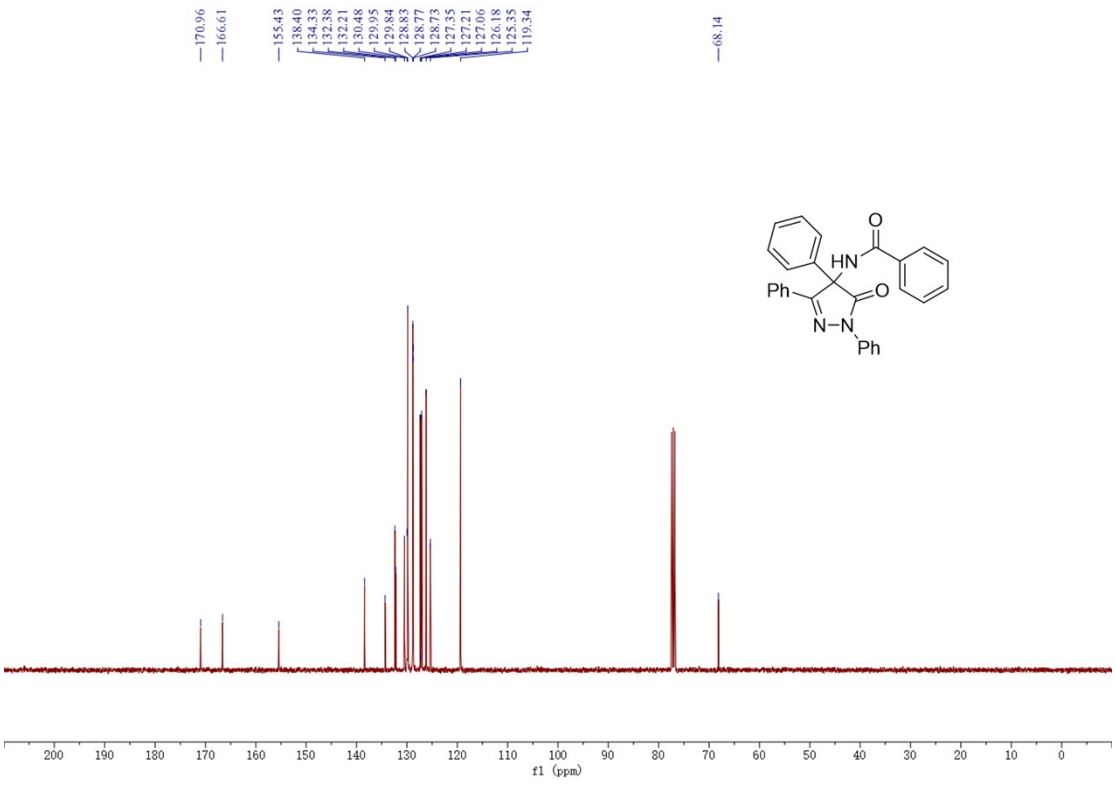
^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra for 3r



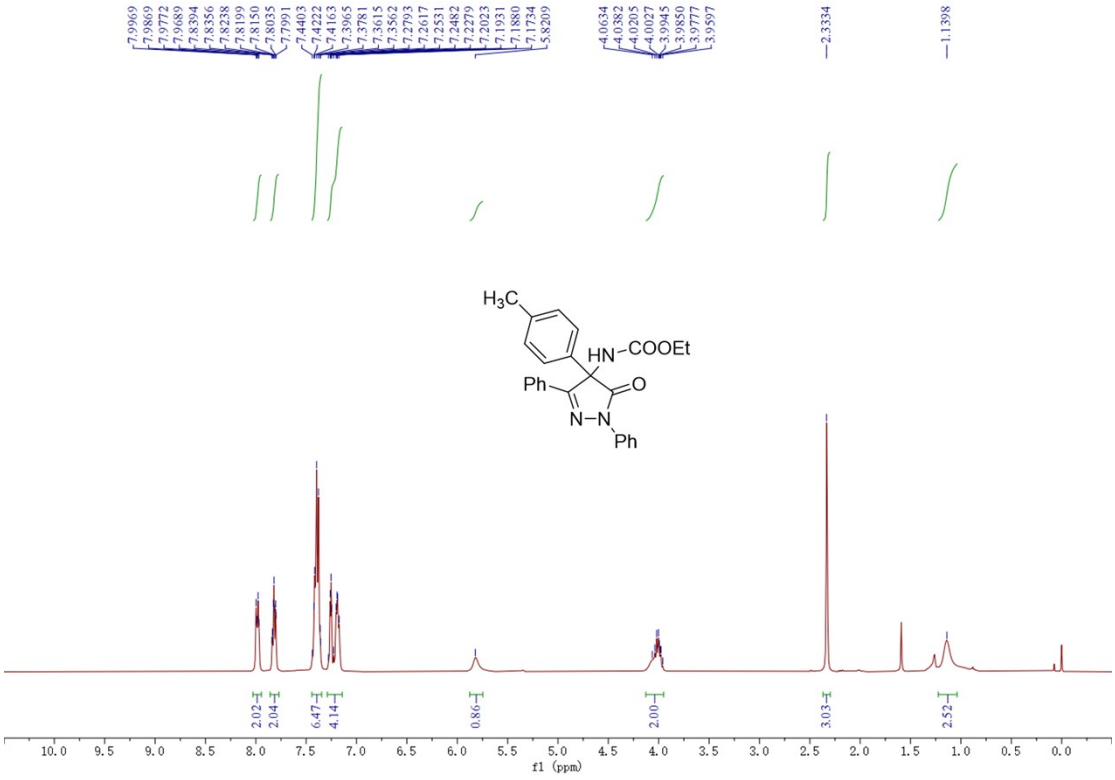


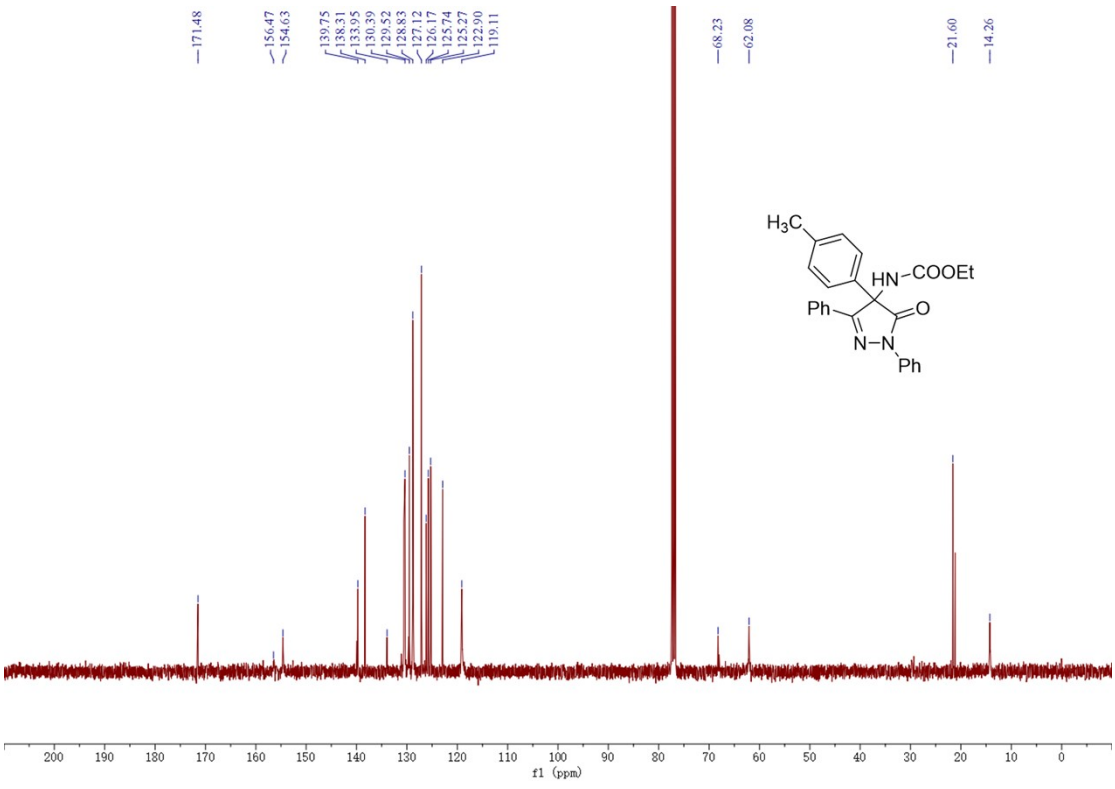
^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra for 3s



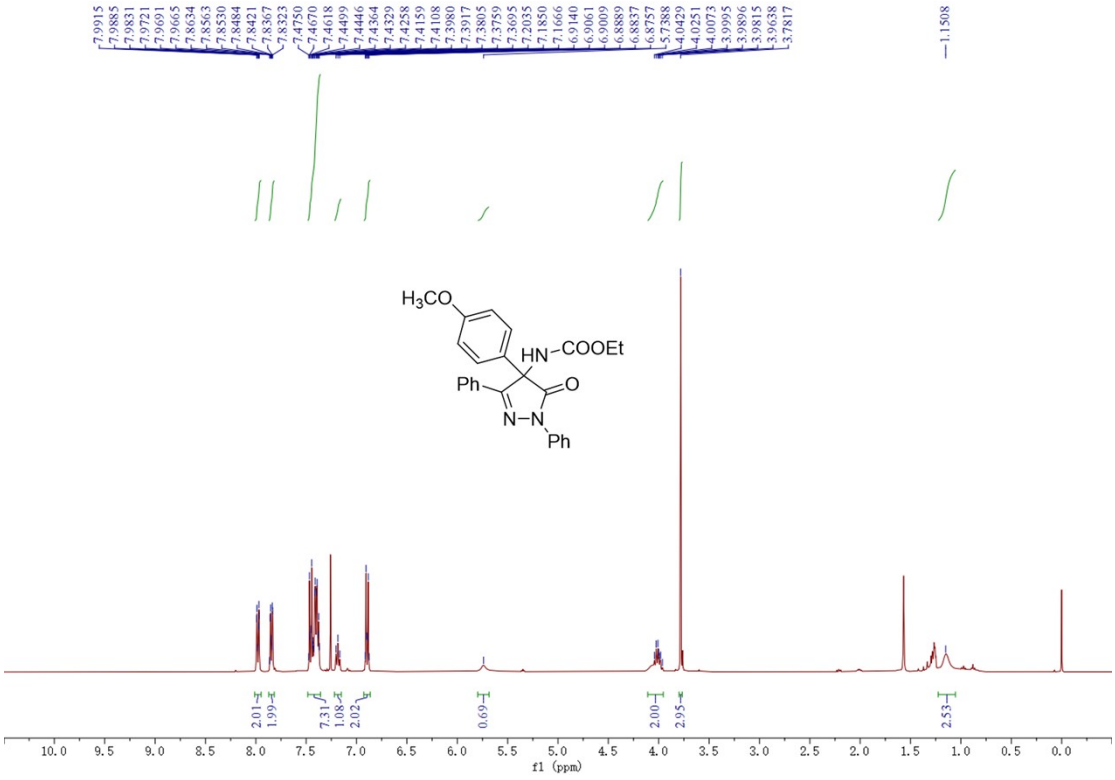


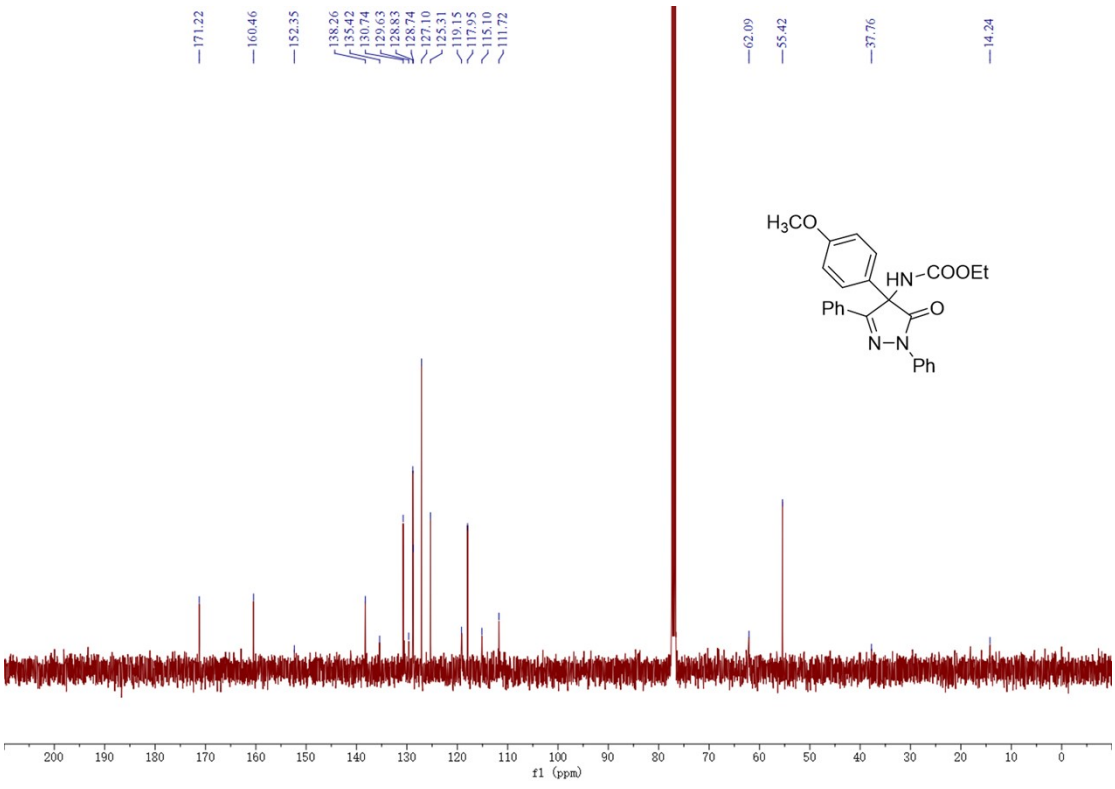
^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra for 3t



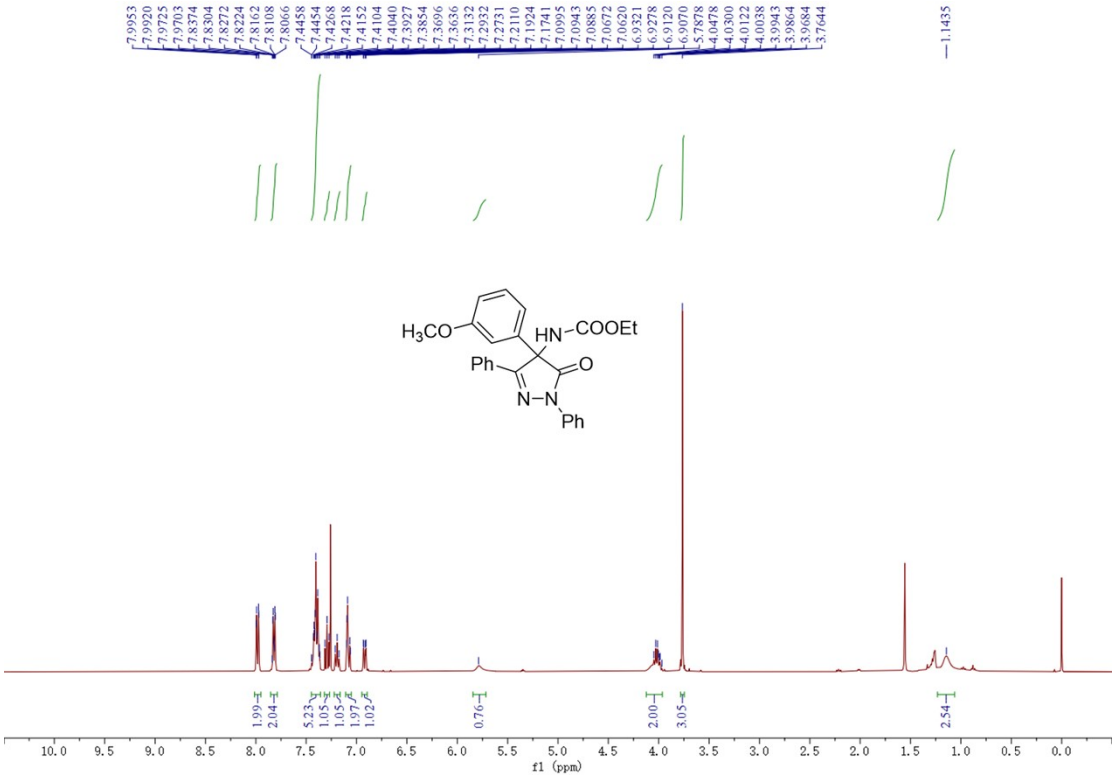


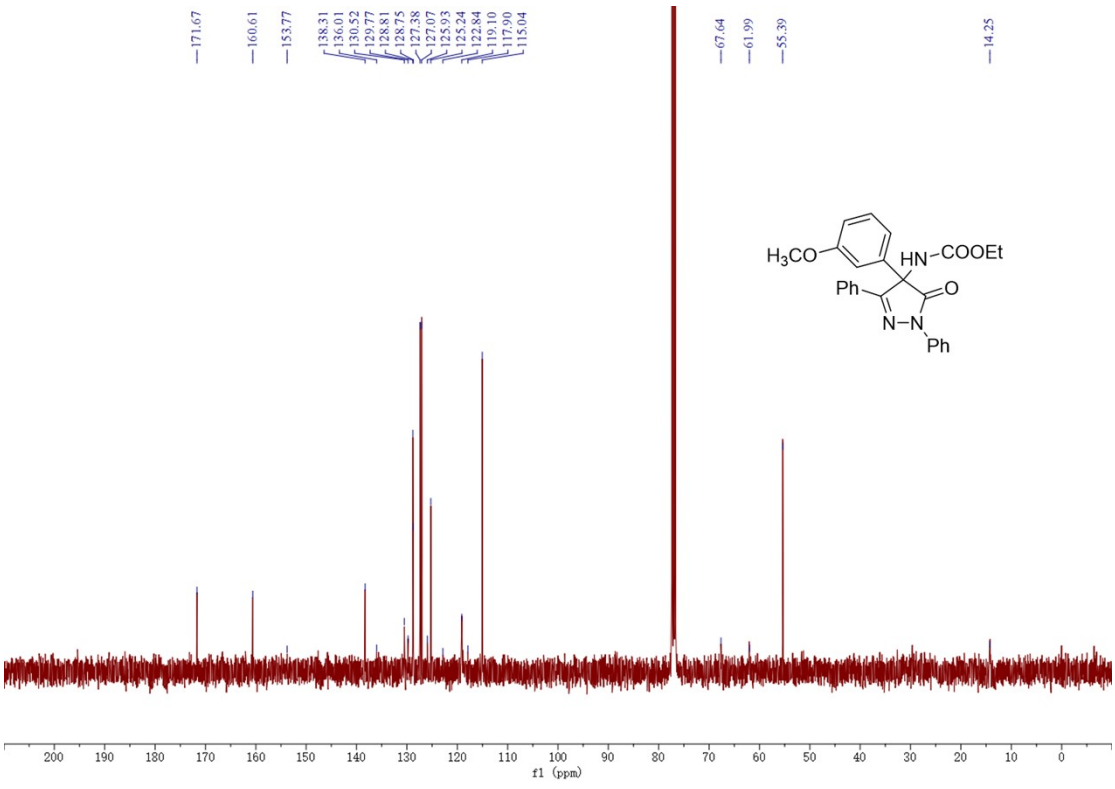
^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra for 3u



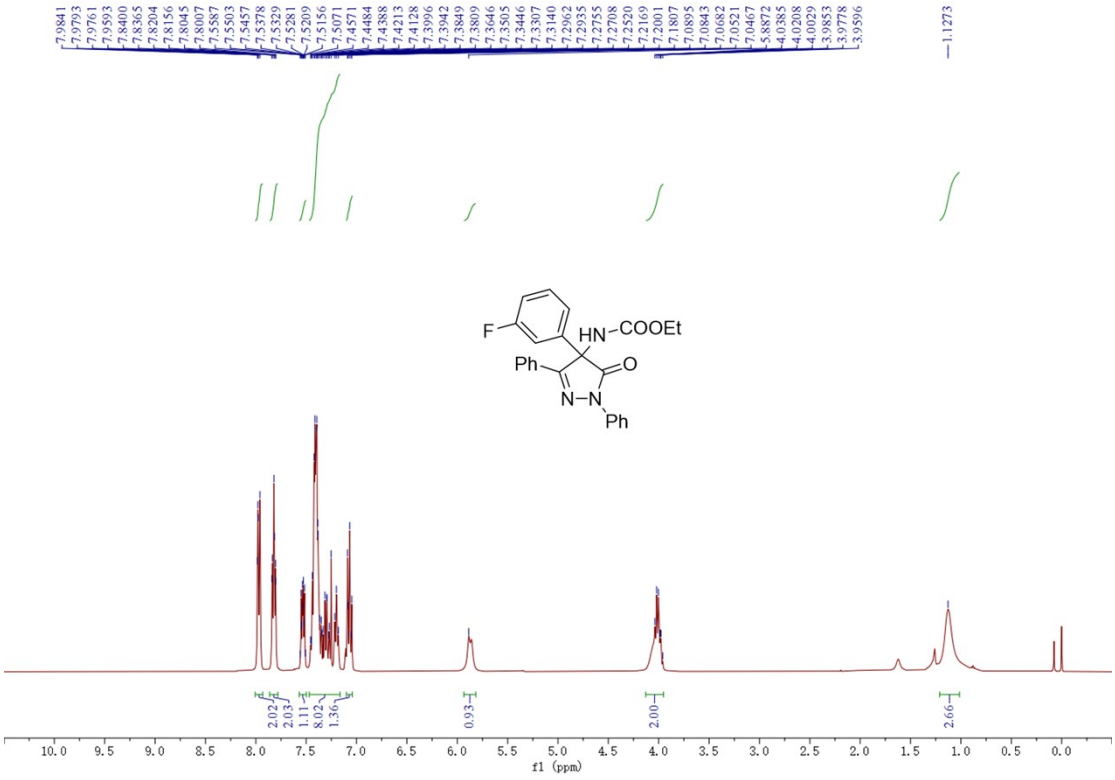


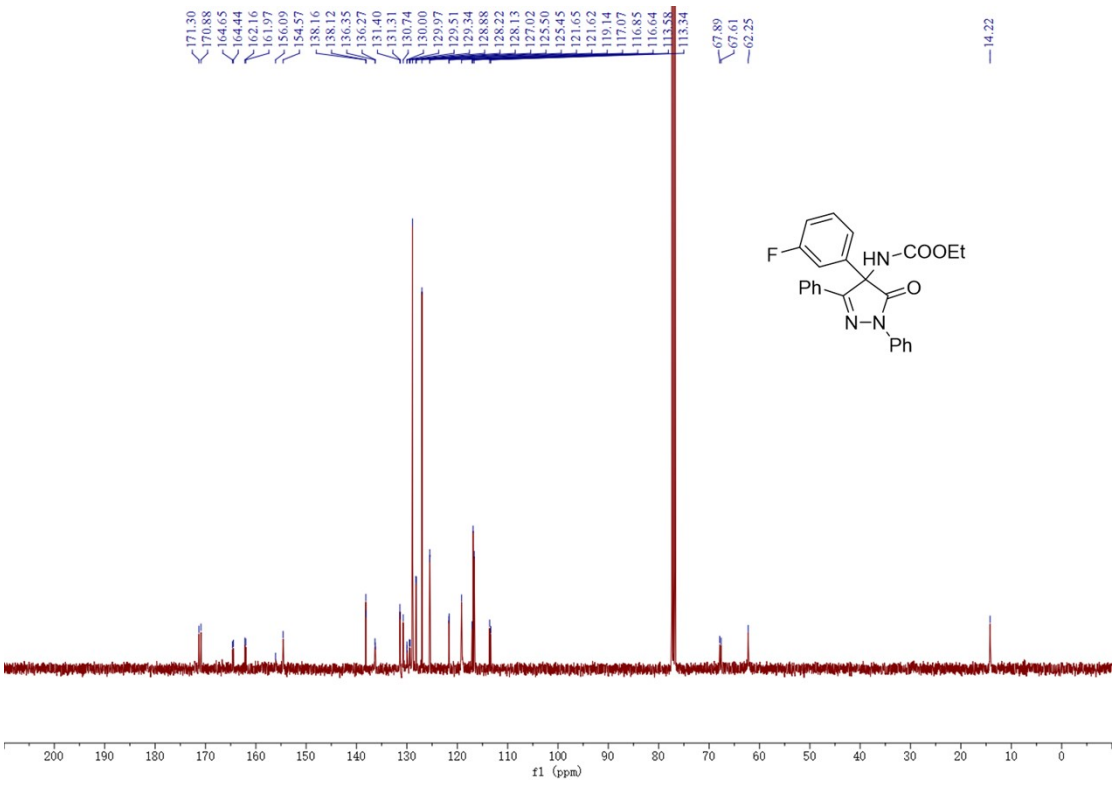
^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra for 3v

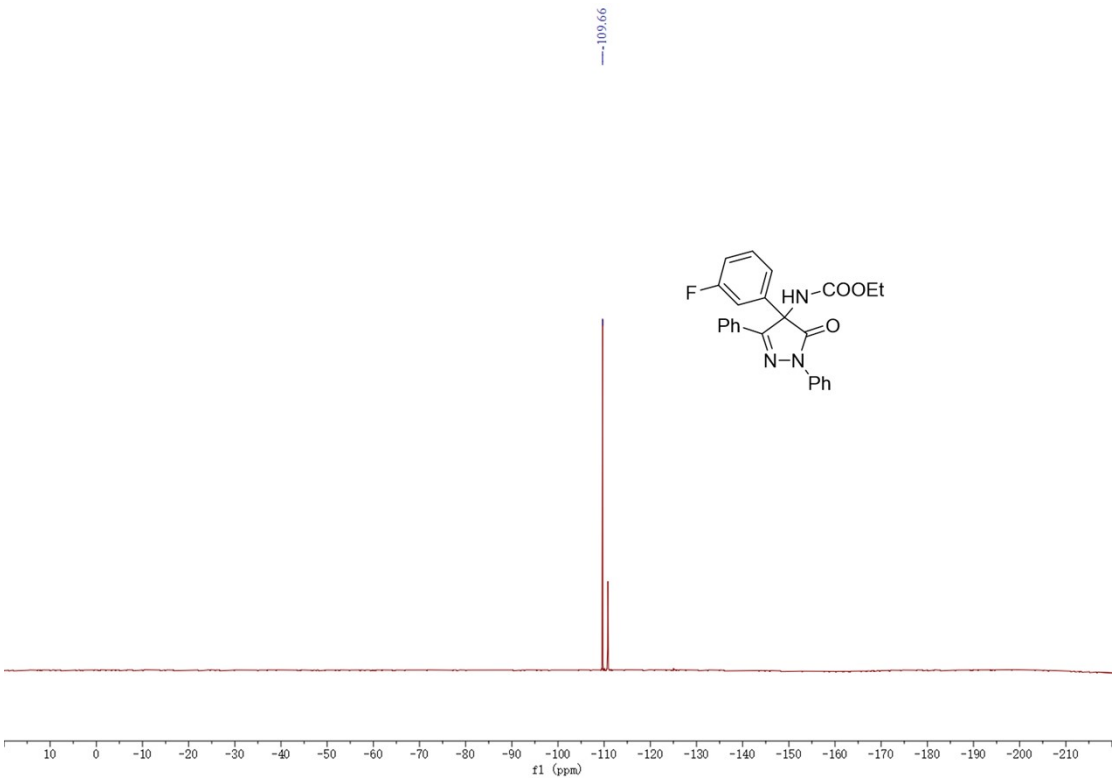




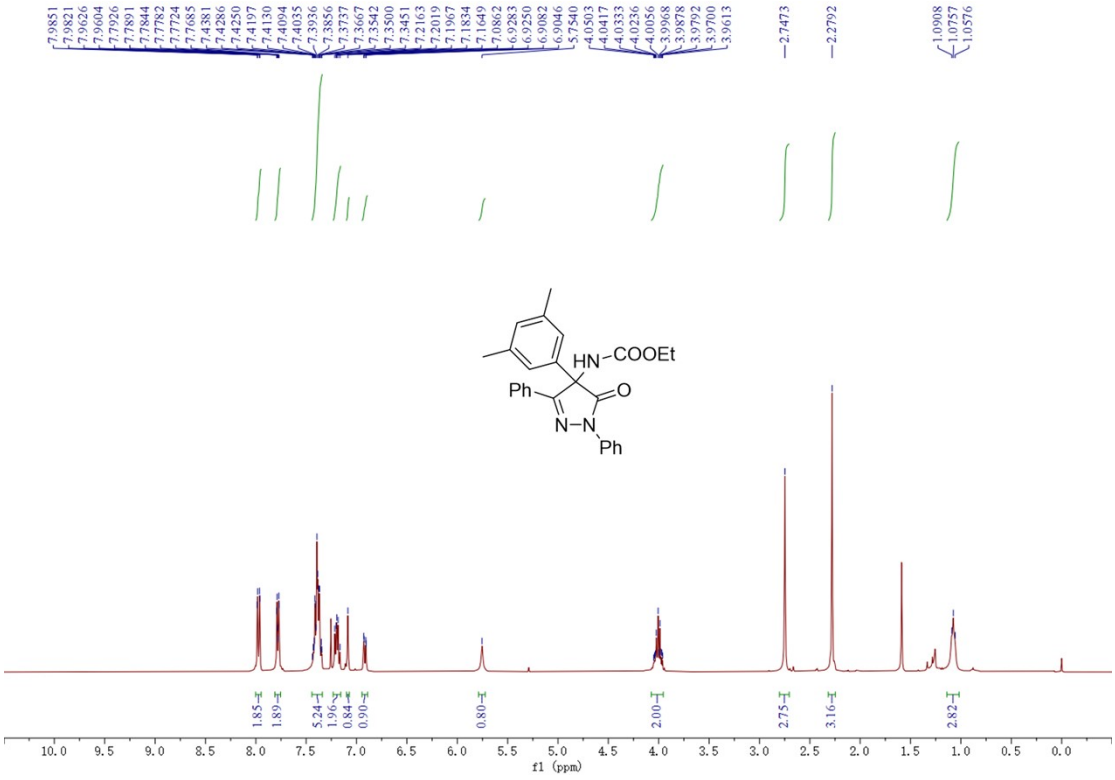
^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR Spectra for 3w

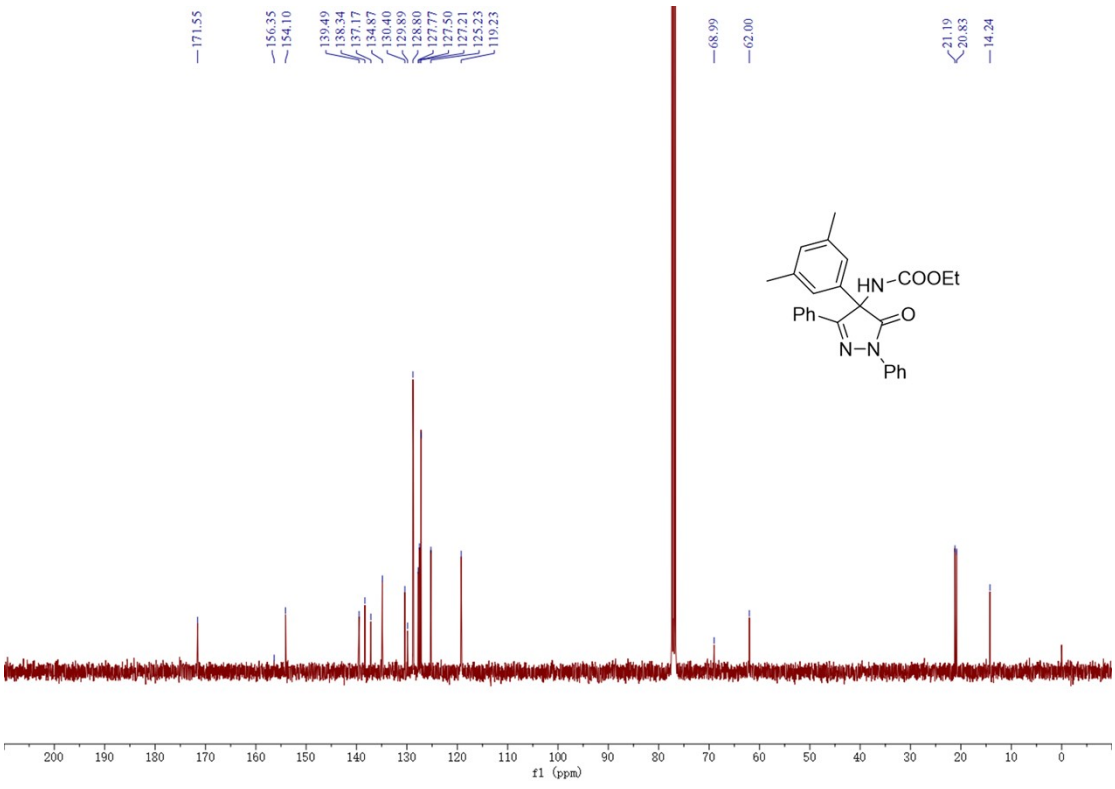




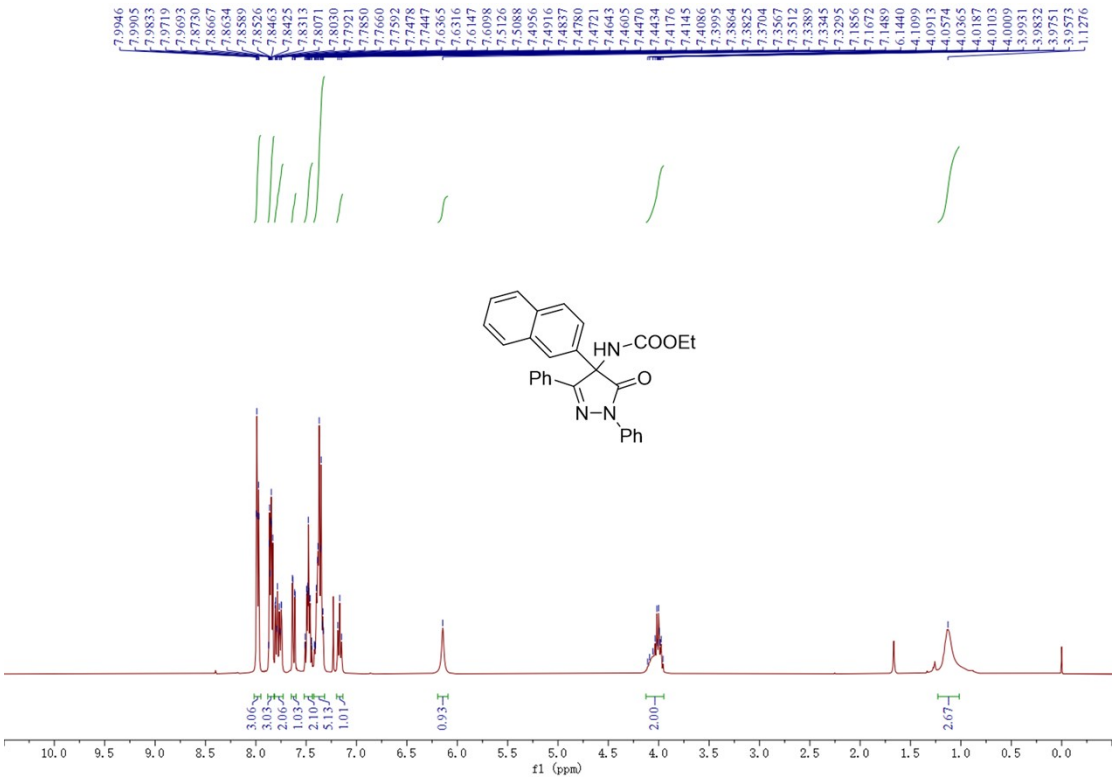

-109.66
F
HN
COOEt
Ph
O
N
N
Ph
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

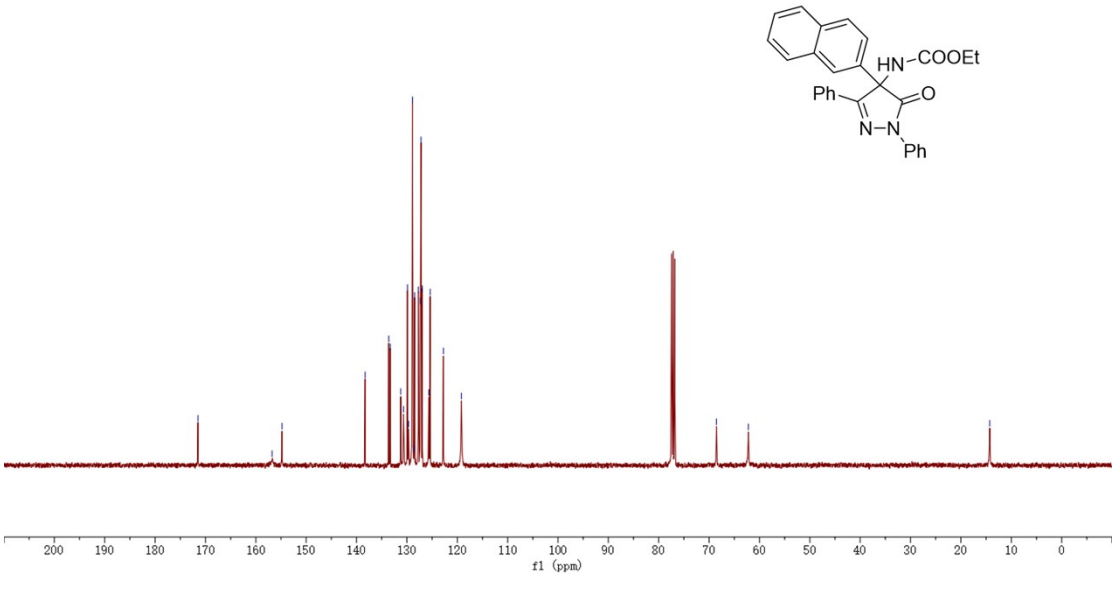
^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra for 3x



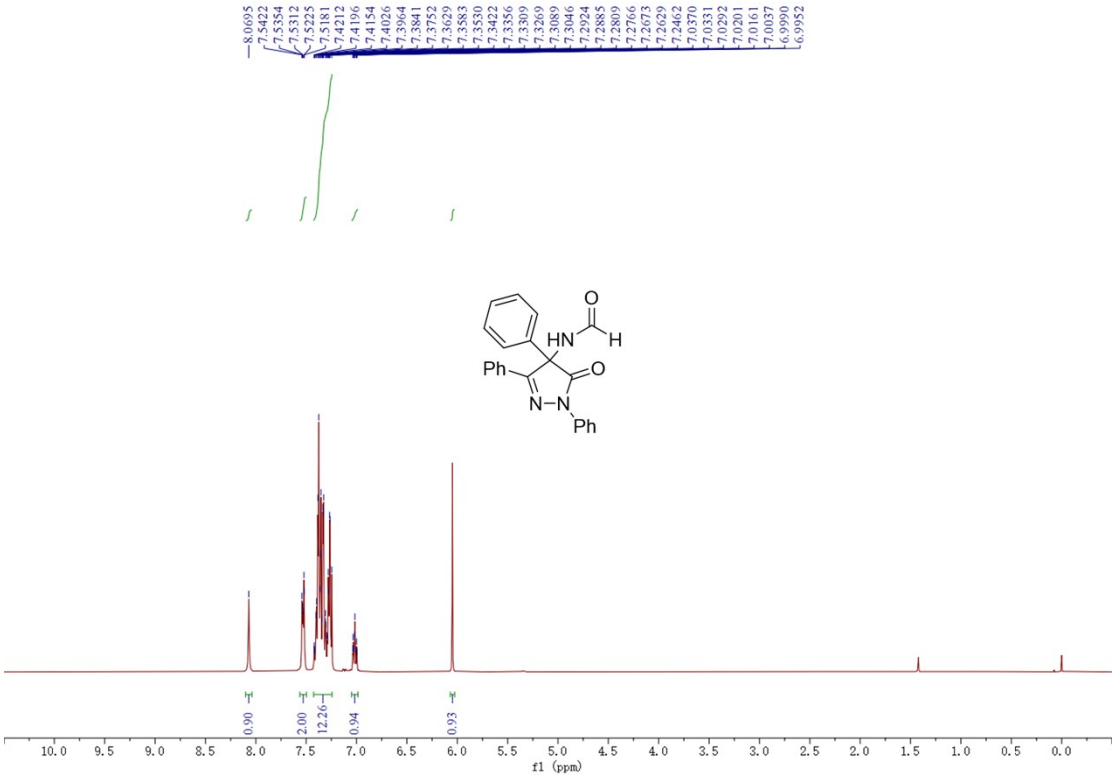


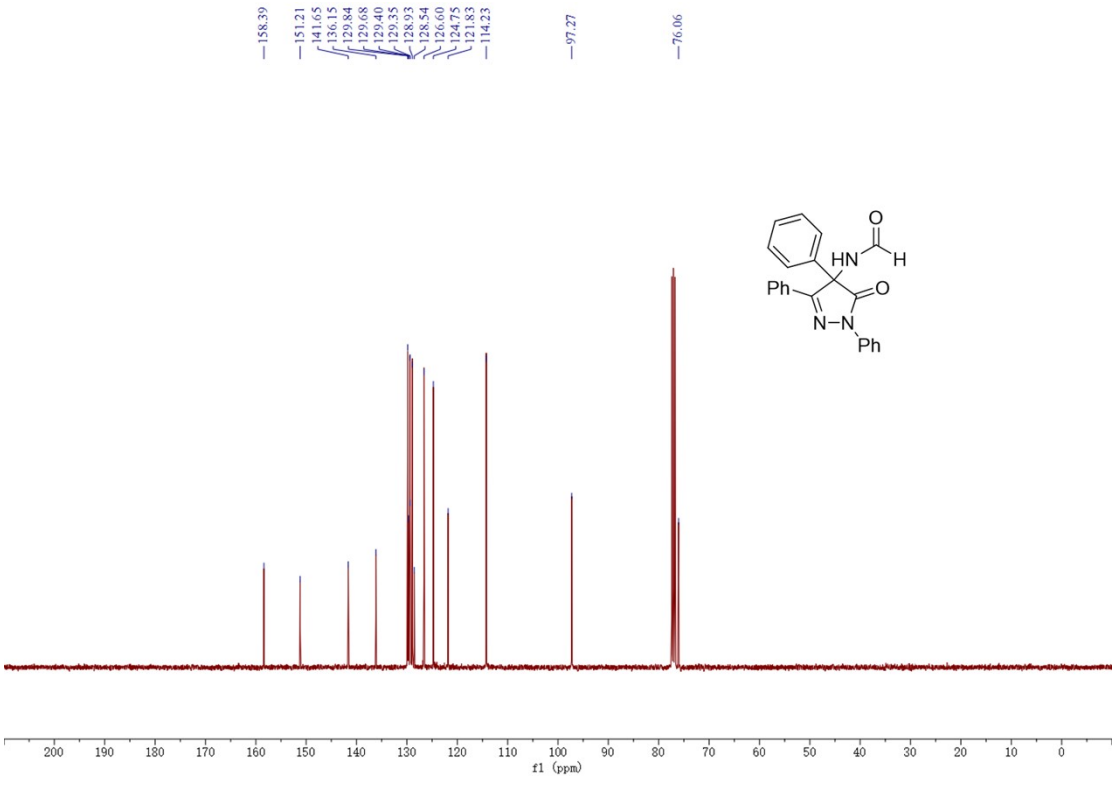
^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra for 3y



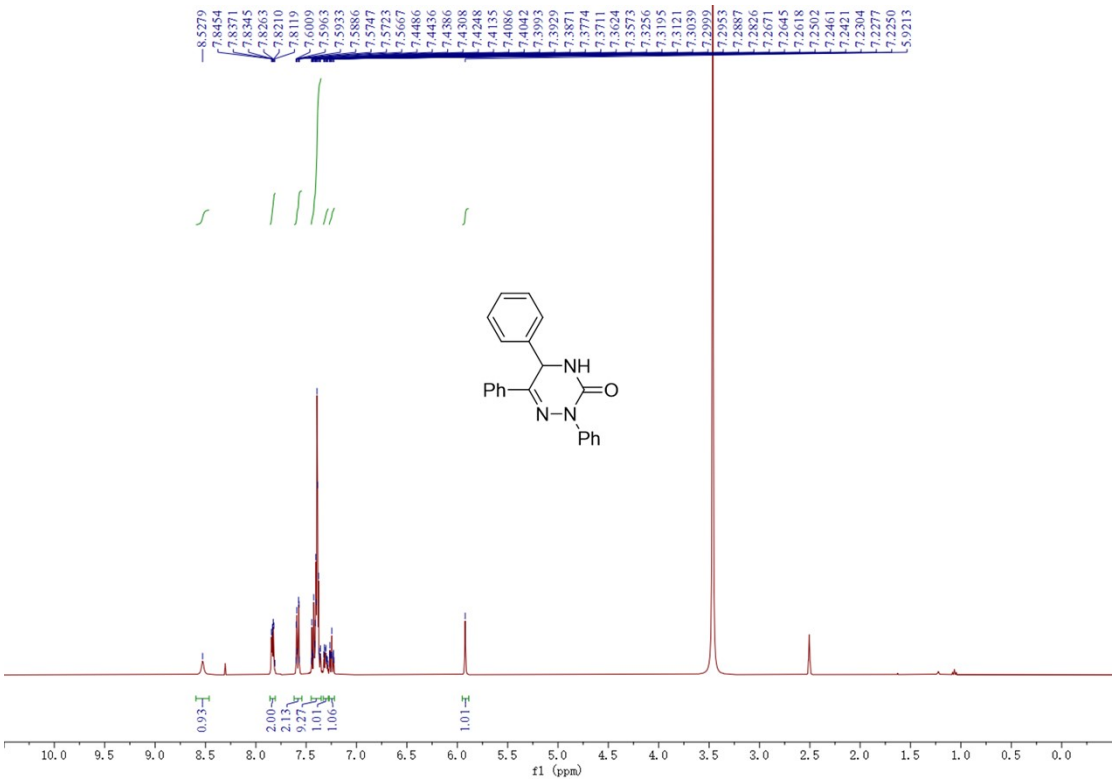


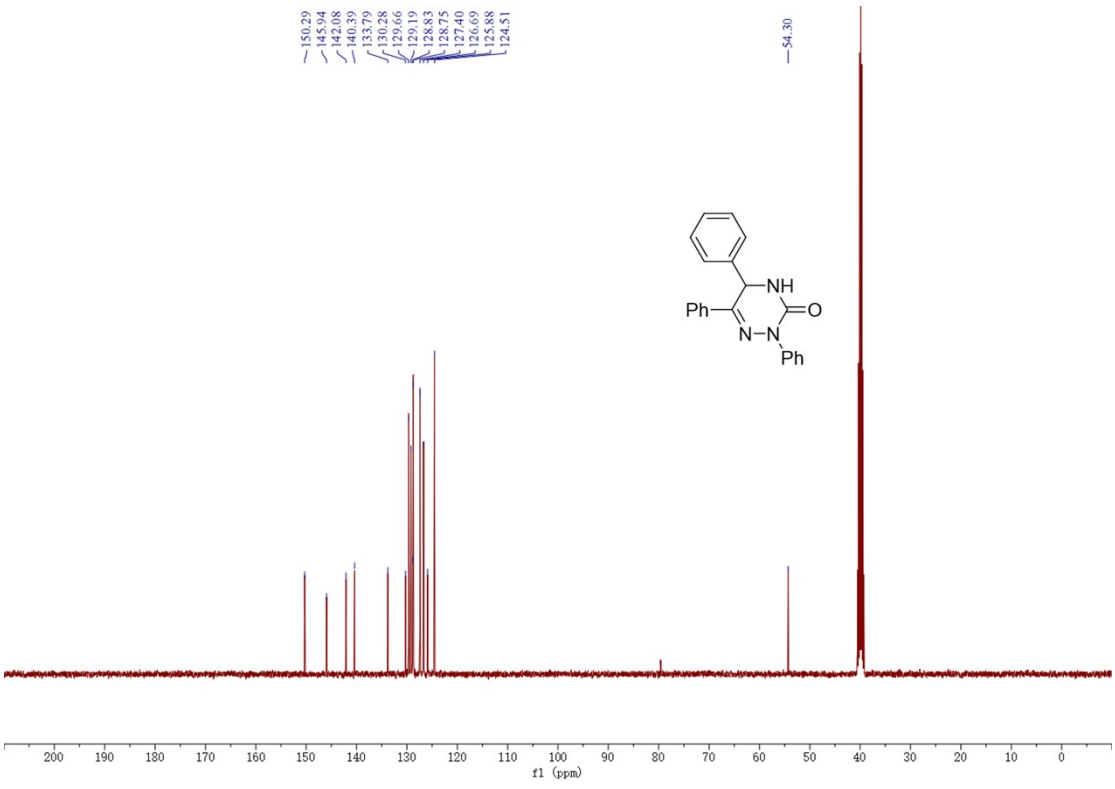
^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra for 5





^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra for 6





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[3] (a) H. Khan, D. Barman and S. Sen, *J. Org. Chem.*, 2024, **89**, 6257−6262. (b) C. Bracken, A. S. Batsanov and M. Baumann, *SynOpen*, 2021, **5**, 29−35. (c) A. W. Gann, J. W. Amoroso, V. J. Einck, W. P. Rice, J. J. Chambers and N. A. Scgnarr, *Org. Lett.*, 2014, **16**, 2003−2005.

[4] L. Chen and L.-H. Ran, *ChemistrySelect*, 2024, **9**, e202404878.