

Synthesis of Amides via Palladium-Catalyzed Amidation of Aryl Halides

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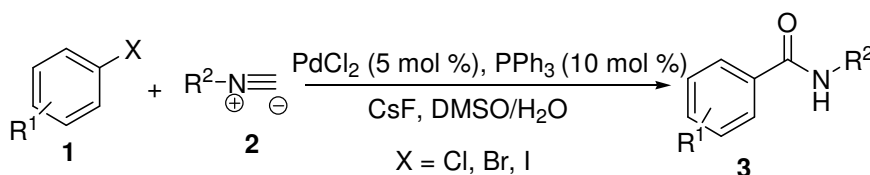
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A. General method

Melting points were measured with a BÜCHI B-545 melting point instrument and were uncorrected. ^1H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, and chloroform is solvent with TMS as the internal standard. IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker Vector 22 spectrometer. Mass spectra were recorded on a Shimadzu GCMS-QP5050A spectrometer at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). GC–MS was obtained using electron ionization. HRMS was carried out on a MAT 95XP (Thermo). TLC was performed by using commercially prepared 100–400 mesh silica gel plates (GF254) and visualization was effected at 254 nm. All the other chemicals were purchased from Aldrich Chemicals.

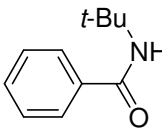
B. General procedure for the synthesis of amides

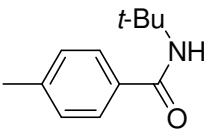
To the mixture of aryl halides (1.0 mmol), PdCl_2 (5 mol %) and PPh_3 (10 mol %) in DMSO (1.0 mL) solvent, CsF (1.0 mmol) and H_2O (0.1 mL) were added successively, stirred for five minutes at the room temperature, isocyanide (1.2 mmol) were added, then the mixture was stirred at 90 °C for 8-12 hours. Upon completion, the reaction mixture was extracted with ethyl acetate (3×10 mL), and the organic layers were combined, dried over anhydrous MgSO_4 , filtered and concentrated under reduced pressure, and the residue was separated by column chromatography (hexane/EtOAc 10:1) to give the pure product.

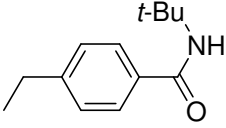


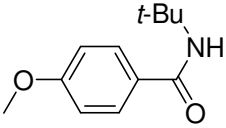
Procedure for the synthesis of *N*-(*tert*-butyl)benzamide (3aa) from bromobenzene (1a) and *tert*-butyl-isocyanide (2a). To the mixture of bromobenzene (1.0 mmol), PdCl₂ (5 mol %) and PPh₃ (10 mol %) in DMSO (1.0 mL) solvent, CsF (1.0 mmol) and H₂O (0.1 mL) were added successively, stirred for five minutes at the room temperature, *tert*-butyl-isocyanide (1.2 mmol) was added, then the mixture was stirred at 90 °C for 12 hours. Upon completion, the reaction mixture was extracted with ethyl acetate (3×10 mL), and the combined extract was dried with anhydrous MgSO₄. Solvent was removed, and the residue was separated by column chromatography to give product **3aa** in pure form.

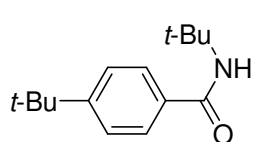
C. Analytical data for 3aa-3ya, 3ab-3ae and 3kf

 ***N*-(*tert*-butyl)benzamide (3aa)**¹
 White solid. MP = 134-136 °C. IR (KBr): 3323, 3061, 2971, 1638, 1538, 1488, 1449, 1362, 1311, 1221, 935, 875, 804, 718. ¹H NMR (400 MHz, CDCl₃) δ = 7.71 (d, *J* = 7.2 Hz, 2H), 7.48-7.38 (m, 3H), 5.96 (br. s, 1H), 1.47 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.8, 135.7, 130.8, 128.1, 126.5, 51.3, 28.3. MS (EI) *m/z*: 28, 51, 77, 105, 122, 134, 162, 177.

 ***N*-*tert*-butyl-4-methylbenzamide (3ba)**¹
 White solid. MP = 114-116 °C. IR (KBr): 3355, 3034, 2979, 2927, 1643, 1544, 1453, 1360, 1391, 1360, 1312, 1226, 957, 875, 838, 752. ¹H NMR (400 MHz, CDCl₃) δ = 7.60 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.6 Hz, 2H), 5.97 (br. s, 1H), 2.36 (s, 3H), 1.45 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.8, 141.3, 133.0, 129.0, 126.6, 51.4, 28.8, 21.3. MS (EI) *m/z*: 28, 65, 91, 119, 136, 148, 176, 191.

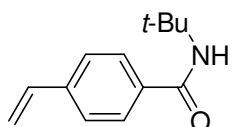
 ***N*-*tert*-butyl-4-ethylbenzamide (3ca)**
 Light yellow solid. MP = 121-123 °C. IR (KBr): 3341, 3063, 2960, 2927, 1635, 1542, 1505, 1453, 1394, 1364, 1306, 1222, 852, 768. ¹H NMR (400 MHz, CDCl₃) δ = 7.64 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 5.94 (br. s, 1H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.46 (s, 9H), 1.23 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.9, 147.6, 133.3, 127.9, 126.7, 51.4, 28.9, 28.7, 15.4. MS (EI) *m/z*: 28, 79, 105, 133, 150, 162, 190, 205. HRMS (EI) *m/z*: calcd for C₁₃H₁₉ON, 205.1467; found, 205.1463.

 ***N*-*tert*-butyl-4-methoxybenzamide (3da)**¹
 White solid. MP = 118-120 °C. IR (KBr): 3312, 3069, 2967, 2845, 1635, 1546, 1508, 1452, 1320, 1254, 1218, 1180, 878, 844, 769. ¹H NMR (400 MHz, CDCl₃) δ = 7.68 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.87 (br. s, 1H), 3.83 (s, 3H), 1.46 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.4, 161.8, 128.4, 128.2, 113.6, 55.4, 51.4, 28.9. MS (EI) *m/z*: 28, 42, 64, 77, 92, 107, 135, 151, 164, 192, 207.



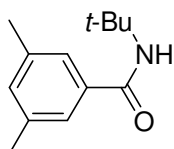
***N*-4-di-tert-butylbenzamide (3ea)²**

White solid. MP = 156-158 °C. IR (KBr): 3342, 2963, 2869, 1633, 1538, 1505, 1453, 1391, 1361, 1314, 1226, 851, 772. ¹H NMR (400 MHz, CDCl₃) δ = 7.65 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 5.96 (br. s, 1H), 1.45 (s, 9H), 1.31 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.8, 154.4, 133.0, 126.5, 125.3, 51.4, 34.8, 31.1, 28.8. MS (EI) *m/z*: 28, 41, 57, 77, 91, 118, 134, 146, 161, 178, 190, 218, 233.



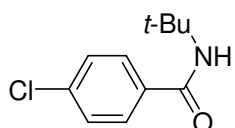
***N*-tert-butyl-4-vinylbenzamide (3fa)**

White solid. MP = 102-104 °C. IR (KBr): 3307, 3061, 2971, 2925, 1637, 1546, 1454, 1395, 1361, 1318, 1224, 909, 854, 779. ¹H NMR (400 MHz, CDCl₃) δ = 7.67 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 6.72 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.98 (br. s, 1H), 5.81 (d, *J* = 17.6 Hz, 1H), 5.33 (d, *J* = 10.8 Hz, 1H), 1.46 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.5, 140.1, 135.9, 134.9, 127.0, 126.1, 115.6, 51.5, 28.8. MS (EI) *m/z*: 28, 51, 77, 103, 131, 147, 160, 188, 203. HRMS (EI) *m/z*: calcd for C₁₃H₁₇ON, 203.1310; found, 203.1304.



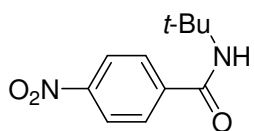
***N*-tert-butyl-3,5-dimethylbenzamide (3ga)**

White solid. MP = 116-118 °C. IR (KBr): 3359, 3030, 2959, 2924, 1647, 1548, 1451, 1368, 1395, 1363, 1318, 1221, 875, 838, 752. ¹H NMR (400 MHz, CDCl₃) δ ppm 7.31 (s, 2H), 7.09 (s, 1H), 5.91 (br. s, 1H), 2.34 (s, 6H), 1.46 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 167.3, 138.1, 135.9, 132.6, 124.4, 51.5, 28.8, 21.2. MS (EI) *m/z*: 28, 42, 57, 77, 105, 133, 150, 162, 190, 205. HRMS (EI) *m/z*: calcd for C₁₃H₁₉ON, 205.1467; found, 205.1462.



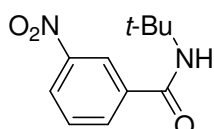
***N*-tert-butyl-4-chlorobenzamide (3ha)³**

White solid. MP = 138-140 °C. IR (KBr): 3324, 3063, 2972, 2927, 1638, 1596, 1538, 1483, 1451, 1393, 1361, 1315, 1220, 1013, 960, 846, 761. ¹H NMR (400 MHz, CDCl₃) δ ppm 7.62 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 6.04 (br. s, 1H), 1.43 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 165.8, 137.1, 134.2, 128.5, 128.1, 51.7, 28.7. MS (EI) *m/z*: 28, 41, 75, 111, 139, 156, 168, 196, 211.



***N*-tert-butyl-4-nitrobenzamide (3ia)¹**

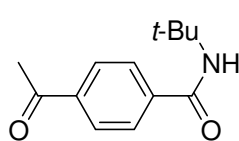
Light yellow solid. MP = 159-161 °C. IR (KBr): 3311, 3072, 2972, 2929, 1642, 1599, 1546, 1460, 1396, 1348, 1311, 1225, 866, 721. ¹H NMR (400 MHz, CDCl₃) δ ppm 8.17 (d, *J* = 8.8 Hz, 2H), 7.83 (d, *J* = 9.2 Hz, 2H), 6.23 (br. s, 1H), 1.44 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 164.9, 149.1, 141.5, 127.9, 123.5, 52.2, 28.6. MS (EI) *m/z*: 28, 41, 56, 76, 92, 104, 120, 134, 150, 167, 179, 207, 222.



***N*-tert-butyl-3-nitrobenzamide (3ja)⁴**

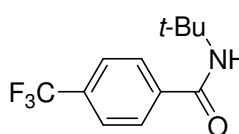
White solid. MP = 126-128 °C. IR (KBr): 3316, 3081, 2971, 2929, 1651, 1530, 1457, 1394, 1354, 1315, 1222, 919, 717. ¹H NMR (400 MHz, CDCl₃)

δ ppm 8.48 (s, 1H), 8.24 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 7.6 Hz, 1H), 7.6 (t, J = 8.0 Hz, 1H), 6.32 (br. s, 1H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 164.5, 147.9, 137.5, 133.0, 129.6, 125.5, 121.6, 52.2, 28.6. MS (EI) m/z : 28, 41, 56, 76, 92, 104, 120, 134, 150, 167, 179, 207, 222.



***N*-tert-butyl-4-acetylbenzamide (3ka)¹**

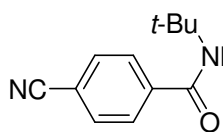
White solid. MP = 136-138 °C. IR (KBr): 3298, 3060, 2974, 2926, 1681, 1641, 1537, 1451, 1396, 1359, 1314, 1266, 1231, 959, 854, 767, 661. ^1H NMR (400 MHz, CDCl_3): δ ppm 7.91 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H), 6.14 (br. s, 1H), 2.57 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ ppm 197.4, 165.9, 139.8, 138.7, 128.3, 127.0, 51.8, 28.7, 26.7. MS (EI) m/z : 28, 43, 65, 76, 91, 104, 119, 147, 164, 176, 204, 219.



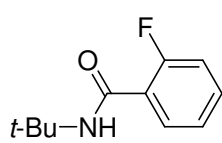
***N*-tert-butyl-4-(trifluoromethyl)benzamide (3la)¹**

White solid. MP = 153-155 °C. IR (KBr): 3272, 3073, 2979, 1637, 1547, 1452, 1398, 1327, 1223, 1157, 1122, 927, 854, 770, 677. ^1H NMR (400 MHz, CDCl_3): δ = 7.78 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 6.15 (br. s, 1H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ = 165.7, 139.2 (d, J = 0.8 Hz), 132.7 (q, J = 32.4 Hz), 127.2, 125.2 (q, J = 3.7 Hz), 123.7 (CF_3 , J = 270.8 Hz), 51.9, 28.7. MS (EI) m/z : 28, 42, 56, 75, 95, 125, 145, 173, 190, 203, 230, 245.

***N*-tert-butyl-4-cyanobenzamide (3ma)**

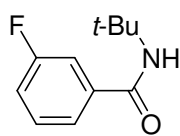


White solid. MP = 151-153 °C. IR (KBr): 3363, 3065, 2977, 2930, 2237, 1650, 1544, 1500, 1455, 1394, 1361, 1310, 1283, 1224, 864, 761. ^1H NMR (400 MHz, CDCl_3) δ ppm 7.76 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 6.29 (br. s, 1H), 1.40 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 165.0, 139.7, 132.0, 127.4, 117.9, 114.2, 51.9, 28.5. MS (EI) m/z : 28, 41, 56, 75, 102, 130, 147, 159, 171, 187, 202. HRMS (EI) m/z : calcd for $\text{C}_{12}\text{H}_{14}\text{ON}_2$, 202.1106; found, 202.1098.



***N*-tert-butyl-2-fluorobenzamide (3na)⁵**

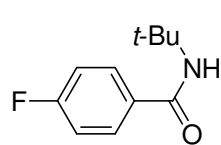
Yellow solid. MP = 33-35 °C. IR (KBr): 3462, 3320, 3072, 2970, 1665, 1531, 1465, 1366, 1308, 1225, 1097, 1033, 879, 760. ^1H NMR (400 MHz, CDCl_3) δ ppm 8.03-7.99 (m, 1H), 7.42-7.37 (m, 1H), 7.22-7.18 (m, 1H), 7.08-7.02 (m, 1H), 6.58 (br. s, 1H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 162.2 (d, J = 3.4 Hz), 160.3 (d, J = 244.5 Hz), 132.7 (d, J = 9.2 Hz), 131.7 (d, J = 2.2 Hz), 124.6 (d, J = 3.2 Hz), 122.3 (d, J = 11.7 Hz), 115.8 (d, J = 25.1 Hz), 51.6, 28.8. MS (EI) m/z : 28, 41, 56, 75, 95, 123, 140, 152, 180, 195.



***N*-tert-butyl-3-fluorobenzamide (3oa)**

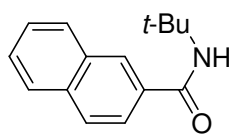
White solid. MP = 108-110 °C. IR (KBr): 3273, 3072, 2976, 2763, 1637, 1584, 1544, 1482, 1451, 1393, 1362, 1320, 1224, 935, 881, 760, 681. ^1H NMR (400 MHz, CDCl_3) δ ppm 7.45-7.38 (m, 2H), 7.36-7.30 (m, 1H), 7.14-7.09 (m, 1H), 6.04 (br. s, 1H), 1.44 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 165.5 (d, J = 2.3 Hz), 162.6 (d, J = 245.9 Hz), 138.2 (d, J = 6.6 Hz), 129.9 (d, J = 7.8 Hz), 122.1 (d, J = 3.0 Hz), 117.9 (d, J =

21.2 Hz), 114.1 (d, $J = 22.6$ Hz), 51.7, 28.7. MS (EI) m/z : 28, 41, 56, 75, 95, 123, 140, 152, 180, 195. HRMS (EI) m/z : calcd for $C_{11}H_{14}ONF$, 195.1059; found, 195.1053.



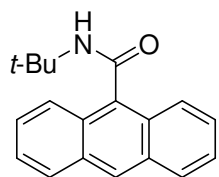
***N*-tert-butyl-4-fluorobenzamide (3pa)⁶**

White solid. MP = 126-128 °C. IR (KBr): 3314, 3076, 2967, 2927, 1643, 1549, 1502, 1457, 1394, 1361, 1318, 1292, 1228, 1156, 845, 763. ¹H NMR (400 MHz, CDCl₃) δ ppm 7.73-7.68 (m, 2H), 7.07-7.02 (m, 2H), 5.95 (br. s, 1H), 1.45 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 165.8, 164.4 (d, $J = 249.5$ Hz), 132.0 (d, $J = 3.1$ Hz), 128.9 (d, $J = 8.7$ Hz), 115.3 (d, $J = 21.7$ Hz), 51.6, 28.8. MS (EI) m/z : 28, 41, 56, 75, 95, 123, 140, 152, 180, 195.



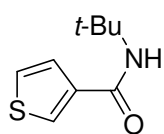
***N*-tert-butyl-2-naphthamide (3qa)**

White solid. MP = 156-158 °C. IR (KBr): 3333, 3055, 2970, 2925, 1636, 1542, 1454, 1391, 1359, 1315, 1226, 1137, 1283, 1224, 866, 828, 773, 647. ¹H NMR (400 MHz, CDCl₃) δ ppm 8.21 (s, 1H), 7.89-7.77 (m, 4H), 7.55-7.48 (m, 2H), 6.18 (br. s, 1 H), 1.52 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 167.0, 134.4, 133.1, 132.5, 128.7, 128.2, 127.6, 127.3, 126.9, 126.6, 123.5, 51.7, 28.4. MS (EI) m/z : 28, 42, 77, 101, 127, 155, 171, 184, 212, 227. HRMS (EI) m/z : calcd for $C_{15}H_{17}ON$, 227.1310; found, 227.1305.



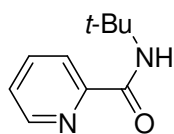
***N*-tert-butylanthracene-10-carboxamide (3ra)**

Light yellow solid. MP = 180-182 °C. IR (KBr): 3247, 3058, 2965, 2923, 1635, 1544, 1449, 1392, 1362, 1298, 1268, 1221, 881, 841, 792, 728. ¹H NMR (400 MHz, CDCl₃) δ ppm 8.44 (s, 1H), 8.12 (d, $J = 8.0$ Hz, 2H), 7.99 (d, $J = 8.0$ Hz, 2H), 7.55-7.45 (m, 4H), 5.91 (br. s, 1 H), 1.63 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 168.8, 132.8, 131.1, 128.4, 127.8, 127.8, 126.5, 125.4, 125.0, 52.5, 28.9. MS (EI) m/z : 28, 42, 57, 75, 88, 126, 151, 177, 205, 221, 277. HRMS (EI) m/z : calcd for $C_{19}H_{19}ON$, 277.1467; found, 277.1463.



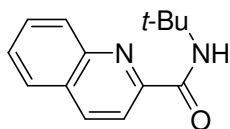
***N*-tert-butylthiophene-3-carboxamide (3sa)**

White solid. MP = 159-161 °C. IR (KBr): 3319, 3075, 2969, 1628, 1542, 1451, 1397, 1362, 1300, 1217, 843, 754. ¹H NMR (400 MHz, CDCl₃) δ ppm 7.77 (s, 1H), 7.32-7.27 (m, 2H), 5.90 (br. s, 1 H), 1.43 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 162.5, 138.8, 127.4, 126.2, 126.0, 51.5, 28.8. MS (EI) m/z : 28, 42, 57, 83, 111, 128, 134, 150, 168, 183. HRMS (EI) m/z : calcd for $C_9H_{13}ONS$, 183.0718; found, 183.0715.



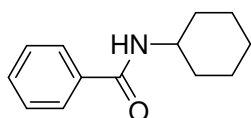
***N*-tert-butylpicolinamide (3ta)⁷**

Light yellow solid. MP = 34-36 °C. IR (KBr): 3375, 3059, 2968, 2927, 1681, 1522, 1462, 1393, 1364, 1293, 1228, 751, 700. ¹H NMR (400 MHz, CDCl₃) δ ppm 8.47 (d, $J = 4.0$ Hz, 1H), 8.13 (d, $J = 8.0$ Hz, 1H), 7.98 (br. s, 1 H), 7.81-7.76 (m, 1H), 7.37-7.34 (m, 1H), 1.46 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 163.3, 150.7, 147.6, 137.2, 125.7, 121.6, 50.8, 28.7. MS (EI) m/z : 28, 42, 51, 78, 93, 106, 123, 135, 150, 163, 178.



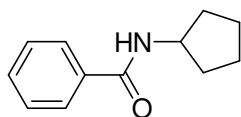
***N*-tert-butylquinoline-2-carboxamide (3ua)**

White solid. MP = 92-94 °C. IR (KBr): 3375, 3060, 2969, 2926, 1678, 1527, 1500, 1460, 1427, 1365, 1295, 1231, 1146, 957, 906, 848, 772. ¹H NMR (400 MHz, d-DMSO) δ ppm 8.59 (d, *J* = 8.4 Hz, 1H), 8.29 (br. s, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 7.6 Hz, 1H), 7.91-7.87(m, 1H), 7.76-7.72(m, 1H), 1.50 (s, 9 H). ¹³C NMR (100 MHz, d-DMSO) δ ppm 162.8, 150.4, 145.7, 137.9, 130.4, 129.1, 128.7, 128.0, 127.9, 118.0, 50.4, 28.3. MS (EI) *m/z*: 28, 42, 56, 77, 101, 128, 143, 156, 170, 185, 213, 228. HRMS (EI) *m/z*: calcd for C₁₄H₁₆ON₂, 228.1263; found, 228.1254.



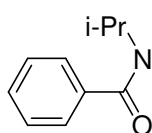
***N*-cyclohexylbenzamide (3ab)³**

White solid. MP = 152-154 °C. IR (KBr): 3313, 3245, 3073, 2928, 2853, 1629, 1538, 1450, 1332, 1293, 1152, 1081, 924, 849, 802, 754, 698. ¹H NMR (400 MHz, CDCl₃) δ ppm 7.74 (d, *J* = 7.2 Hz, 2H), 7.47-7.36 (m, 3H), 6.18 (br. s, 1H), 3.99-3.90(m, 1H), 2.01-1.11(m, 10H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 166.6, 135.0, 131.1, 128.4, 126.8, 48.6, 33.1, 25.5, 24.9. MS (EI) *m/z*: 28, 51, 77, 105, 122, 146, 160, 174, 186, 203.



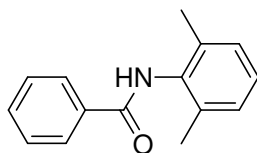
***N*-cyclopentylbenzamide (3ac)**

Light yellow solid. MP = 160-162 °C. IR (KBr): 3295, 2959, 2866, 1628, 1544, 1491, 1318, 1185, 935, 754, 701, 662. ¹H NMR (400 MHz, CDCl₃) δ ppm 7.73 (d, *J* = 7.2 Hz, 2H), 7.45-7.34 (m, 3H), 6.39 (br. s, 1H), 4.40-4.31(m, 1H), 2.07-1.43(m, 8H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 167.1, 134.8, 131.1, 128.3, 126.8, 51.6, 33.0, 23.7. MS (EI) *m/z*: 28, 51, 77, 105, 122, 144, 160, 189. HRMS (EI) *m/z*: calcd for C₁₂H₁₅ON, 189.1154; found, 189.1149.



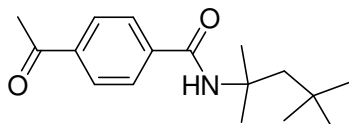
***N*-isopropylbenzamide (3ad)⁸**

Light yellow solid. MP = 101-103 °C. IR (KBr): 3299, 3064, 2972, 2929, 1633, 1542, 1492, 1461, 1352, 1289, 1169, 931, 884, 702. ¹H NMR (400 MHz, CDCl₃) δ ppm 7.74 (d, *J* = 8.4 Hz, 2H), 7.48-7.37 (m, 3H), 6.12 (br. s, 1H), 4.33-4.21(m, 1H), 1.24 (d, *J* = 6.4 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 166.7, 134.9, 131.2, 128.4, 126.8, 41.8, 22.7. MS (EI) *m/z*: 28, 51, 77, 105, 117, 148, 163.



***N*-(2,6-dimethylphenyl)benzamide (3ae)⁹**

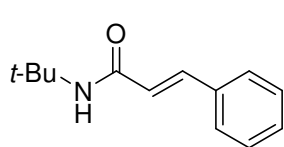
Light yellow solid. MP = 162-164 °C. IR (KBr): 3274, 2920, 1643, 1580, 1520, 1476, 1299, 1213, 932, 766, 709, 652. ¹H NMR (400 MHz, CDCl₃) δ ppm 7.92 (d, *J* = 7.6 Hz, 2H), 7.59-7.48 (m, 3H), 7.45 (br. s, 1H), 7.17-7.11(m, 3H), 2.28 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 165.9, 135.6, 134.5, 133.8, 131.8, 128.7, 128.3, 127.4, 127.2, 18.5. MS (EI) *m/z*: 28, 51, 77, 91, 105, 120, 163, 181, 209, 225, 235, 255.



4-acetyl-*N*-(2,4,4-trimethylpentan-2-yl)benzamide (3kf)

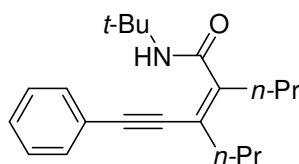
White solid. MP = 90-92 °C. IR (KBr): 3320, 2956, 1684, 1649, 1535, 1478, 1396, 1361, 1299, 1265, 1228, 1154, 959, 854, 766,

702. ^1H NMR (400 MHz, CDCl_3) δ ppm 7.94 (d, $J = 8.4$ Hz, 2H), 7.74 (d, $J = 8.4$ Hz, 2H), 6.08 (br. s, 1H), 2.58 (s, 3H), 1.85 (s, 2H), 1.51 (s, 6H), 1.02 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 197.4, 165.7, 140.1, 138.7, 128.4, 126.9, 55.8, 51.5, 31.7, 31.5, 29.2, 26.7. MS (EI) m/z : 28, 41, 65, 76, 103, 120, 148, 165, 177, 204, 221, 234, 261, 275. HRMS (EI) m/z : calcd for $\text{C}_{17}\text{H}_{25}\text{O}_2\text{N}$, 275.1885; found, 275.1868.



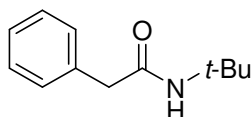
(E)-N-tert-butylcinnamamide (3va)¹⁰

White solid. MP = 144-146 °C. IR (KBr): 3294, 3066, 2969, 2927, 1721, 1660, 1621, 1548, 1452, 1392, 1346, 1284, 1220, 931, 764, 722, 686. ^1H NMR (400 MHz, CDCl_3) δ ppm 7.56 (d, $J = 15.6$ Hz, 1H), 7.46-7.44 (m, 2H), 7.33-7.29 (m, 3H), 6.42 (d, $J = 15.6$ Hz, 1H), 5.93 (br. s, 1H), 1.42 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 165.3, 140.0, 134.9, 129.3, 128.6, 127.6, 122.0, 51.4, 28.8. MS (EI) m/z : 28, 42, 58, 77, 103, 131, 146, 160, 188, 203.



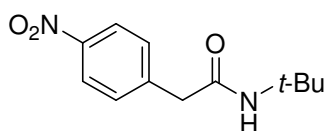
(Z)-N-tert-butyl-3-(2-phenylethynyl)-2-propylhex-2-enamide (3wa)

Yellow solid. MP = 113-115 °C. IR (KBr): 3297, 3054, 2961, 2927, 2869, 1730, 1636, 1538, 1452, 1361, 1327, 1282, 1227, 1127, 1072, 919, 877, 753, 687. ^1H NMR (400 MHz, CDCl_3) δ ppm 7.44-7.42 (m, 2H), 7.35-7.31 (m, 3H), 5.28 (br. s, 1H), 2.56-2.52 (m, 2H), 2.31-2.27 (m, 2H), 1.72-1.63 (m, 2H), 1.58-1.52 (m, 2H), 1.4(s, 9H), 1.00-0.94(m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 169.4, 144.9, 131.4, 128.3, 128.2, 123.4, 122.0, 95.1, 87.9, 51.6, 35.4, 28.8, 22.1, 21.6, 14.0, 13.8. MS (EI) m/z : 28, 41, 57, 77, 91, 115, 128, 141, 165, 181, 199, 212, 226, 254, 296, 311. HRMS (EI) m/z : calcd for $\text{C}_{21}\text{H}_{29}\text{ON}$, 311.2249; found, 311.2243.



N-tert-butyl-2-phenylacetamide (3xa)¹

White solid. MP = 113-115 °C. IR (KBr): 3100, 2925, 1769, 1638, 1491, 1371, 1312, 1177, 1132, 1033, 770, 729. ^1H NMR (400 MHz, CDCl_3) δ ppm 7.35-7.31 (m, 2H), 7.28-7.22 (m, 3H), 5.36 (br. s, 1H), 3.47 (s, 2H), 1.28 (s, 9 H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 170.2, 135.4, 129.2, 128.8, 127.0, 51.1, 44.7, 28.6. MS (EI) m/z : 28, 41, 57, 65, 92, 106, 120, 136, 176, 191.



N-tert-butyl-2-(4-nitrophenyl)acetamide (3ya):

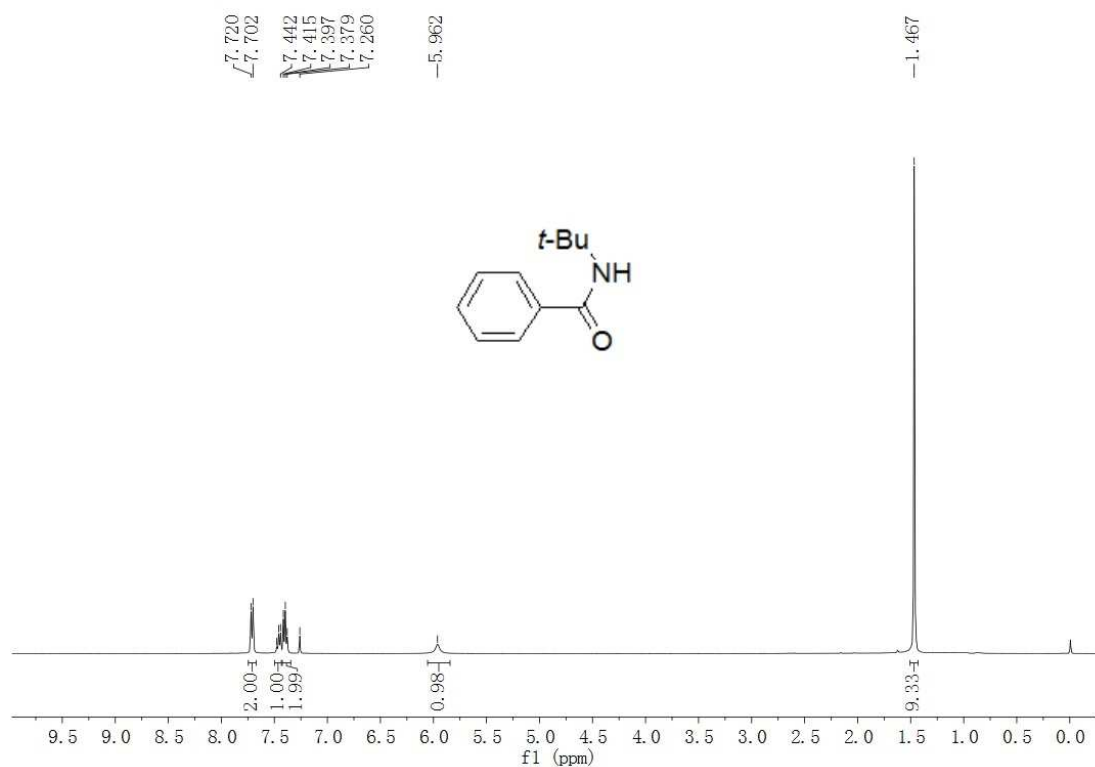
White solid. MP = 164-166 °C. IR (KBr): 3100, 2925, 1769, 1638, 1491, 1371, 1312, 1177, 1132, 1033, 770, 729. ^1H NMR (400 MHz, CDCl_3) δ ppm 8.12 (d, $J = 8.0$ Hz, 2H), 7.41 (d, $J = 8.4$ Hz, 2H), 5.72 (br. s, 1H), 3.52 (s, 2H), 1.29 (s, 9 H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 168.4, 146.8, 143.1, 130.0, 123.6, 51.5, 43.8, 28.5. MS (EI) m/z : 28, 41, 57, 78, 89, 107, 121, 137, 181, 207, 221, 236. HRMS (EI) m/z : calcd for $\text{C}_{12}\text{H}_{16}\text{O}_3\text{N}_2$, 236.1161; found, 236.1159.

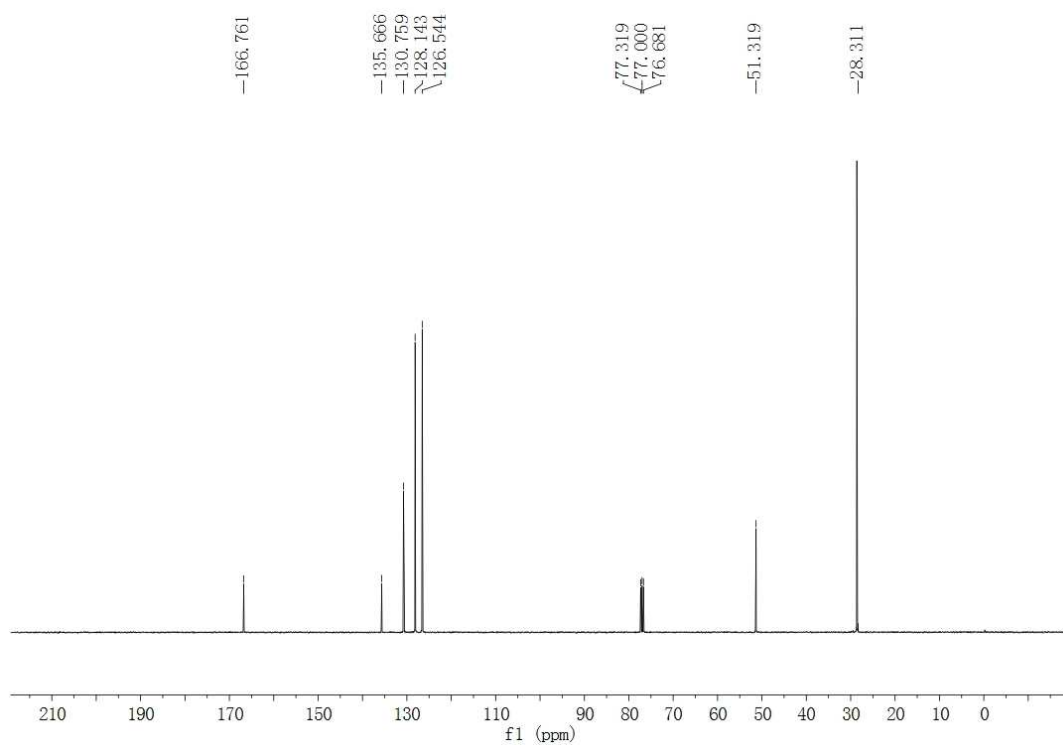
D. References

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- (5) Bellamy, E.; Bayh, O.; Hoarau, C.; Trecourt, F.; Queguiner, G.; Marsais, F. *Chem. Comm.* **2010**, *46*, 7043.
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- (7) Attila, T.; Jakab, B.; Petz, A.; Kollar, L. *Tetrahedron* **2007**, *63*, 10372.
- (8) Rolfe, A.; Probst, D. A.; Volp, K. A.; Omar, I.; Flynn, D. L.; Hanson, P. R. *J. Org. Chem.* **2008**, *73*, 8785.
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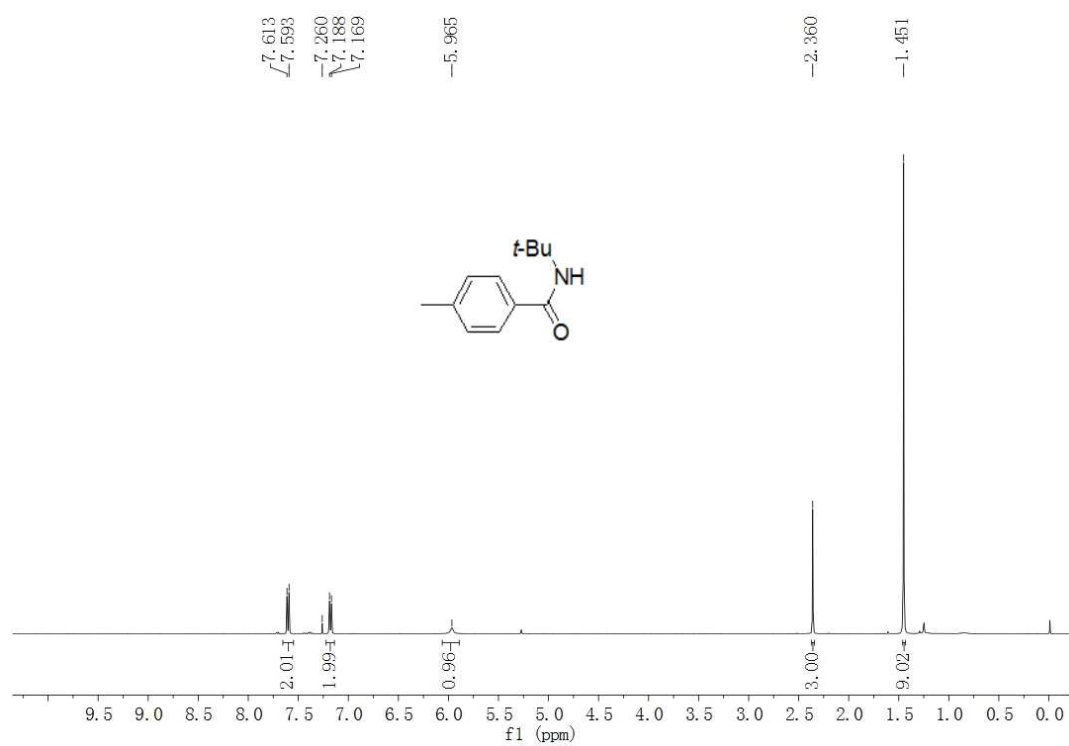
E. NMR Spectra

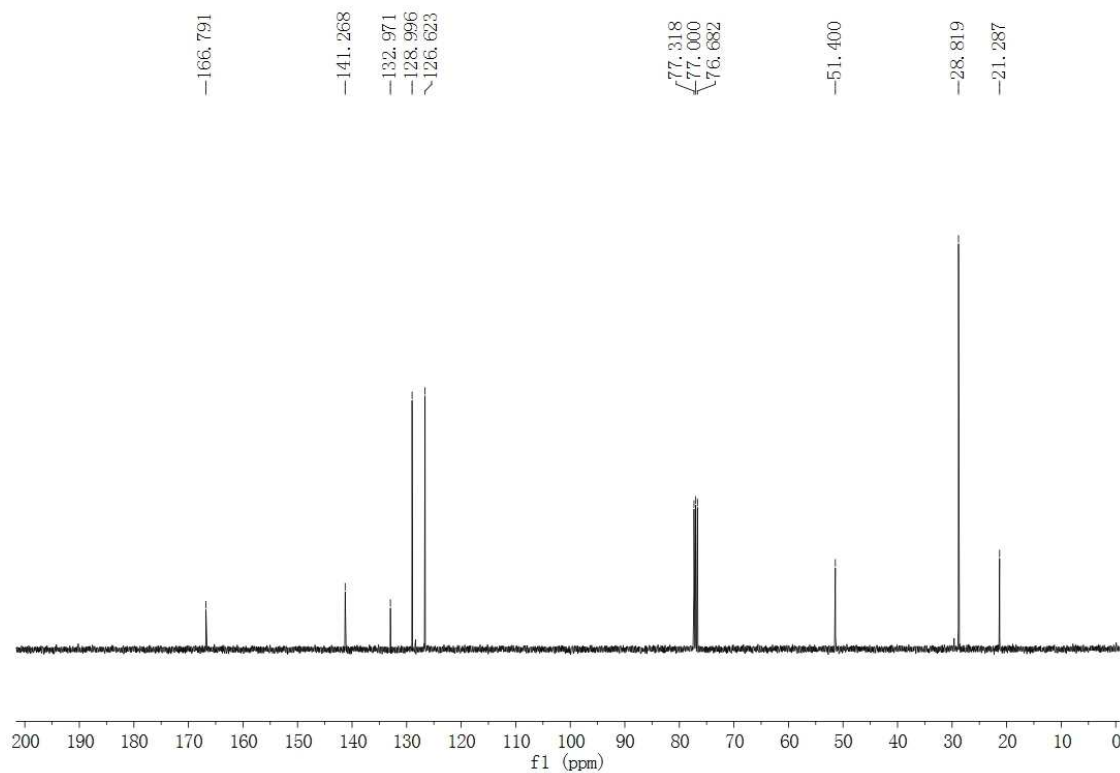
¹H NMR and ¹³C NMR of *N*-(*tert*-butyl)benzamide (3aa)



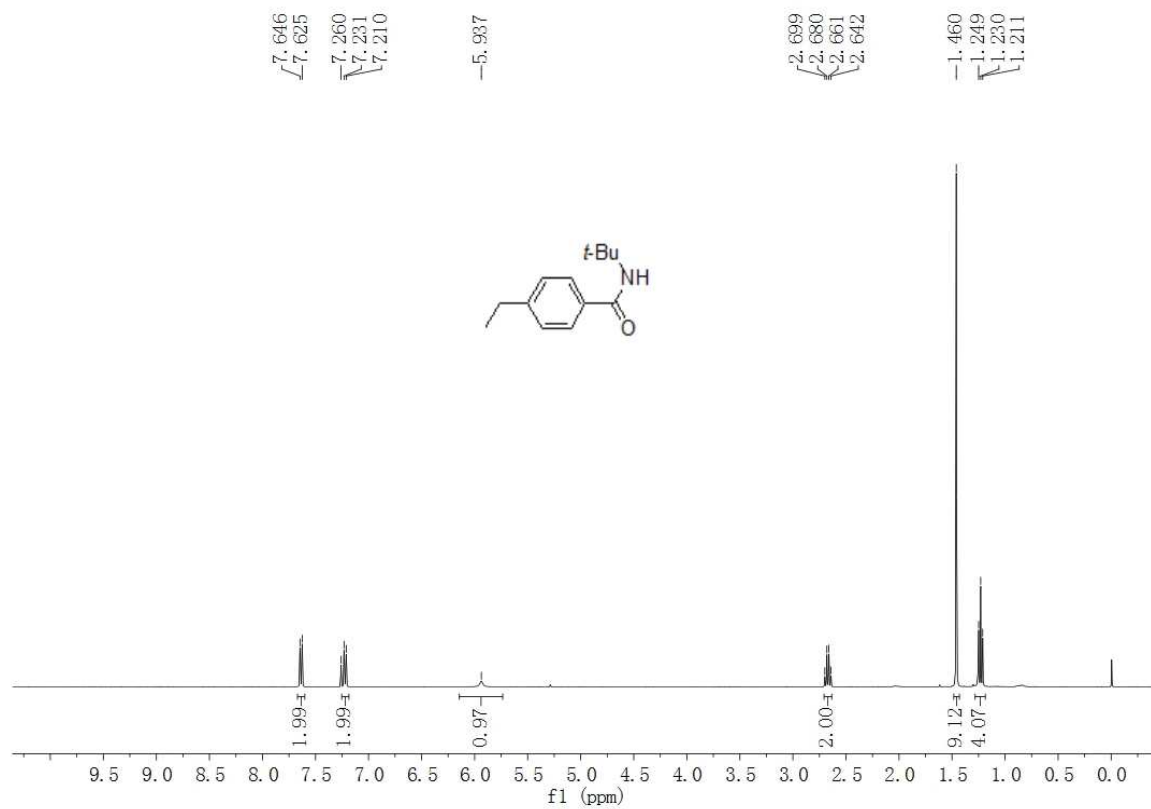


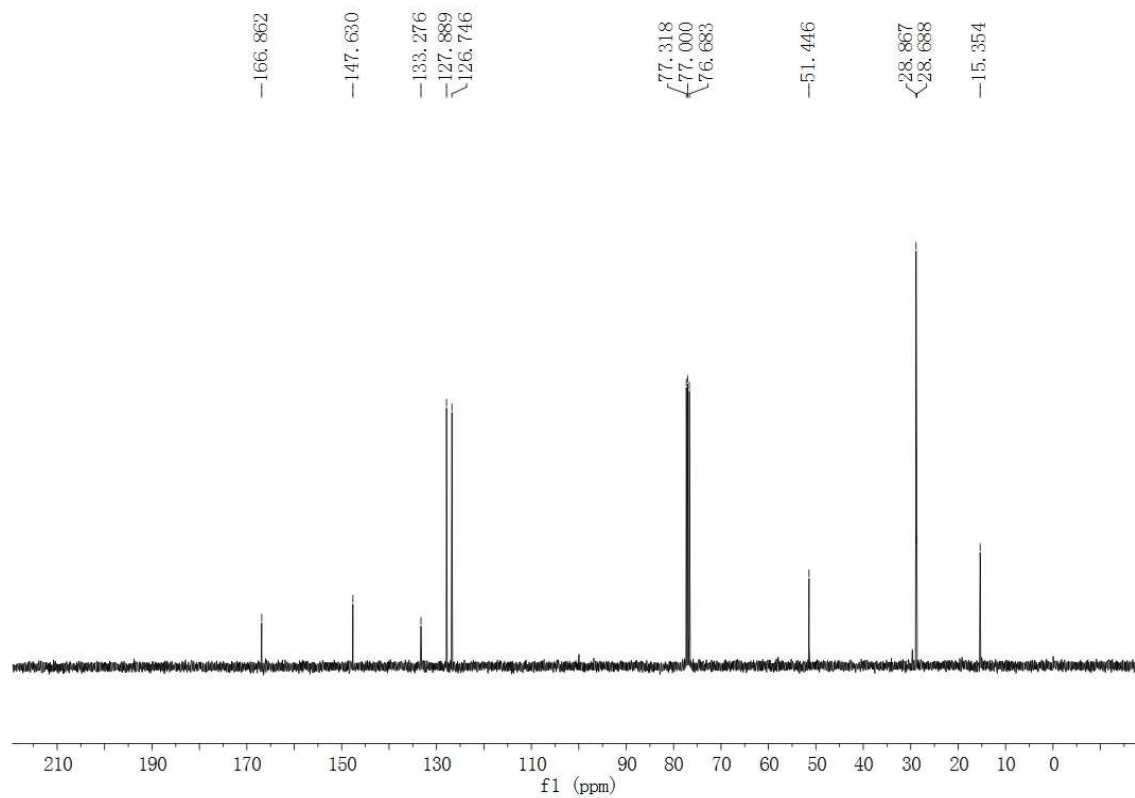
¹H NMR and ¹³C NMR of *N*-tert-butyl-4-methylbenzamide (3ba)



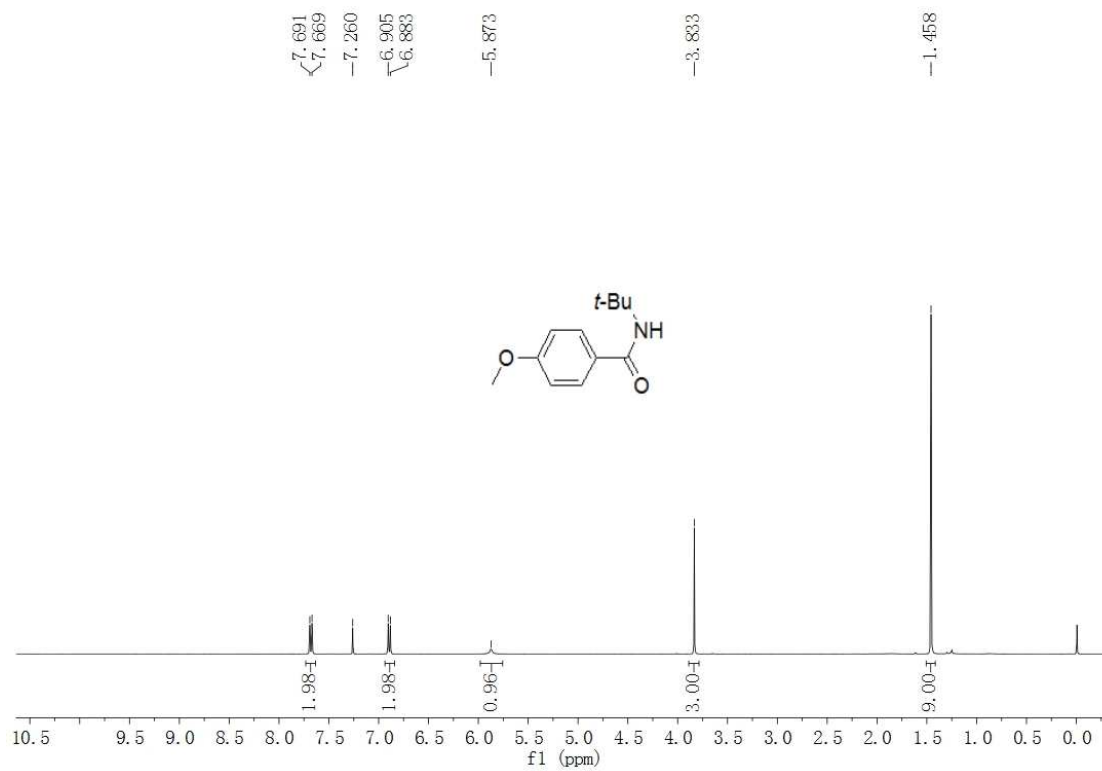


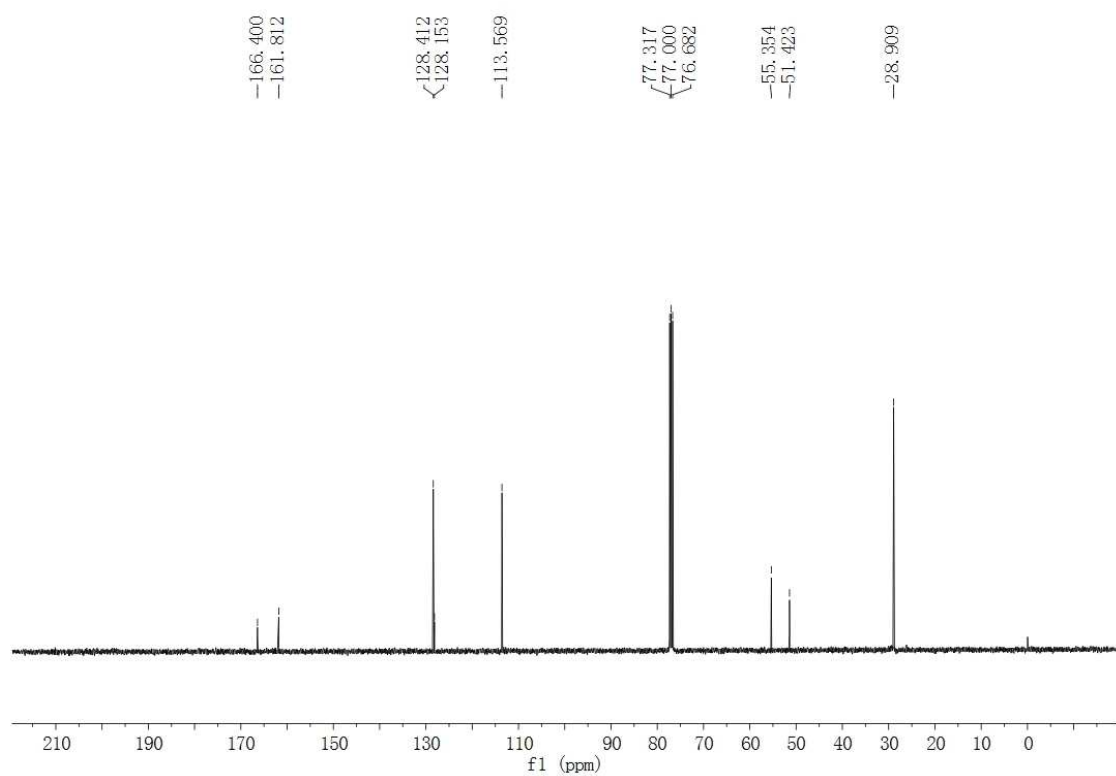
¹H NMR and ¹³C NMR of N-tert-butyl-4-ethylbenzamide (3ca)



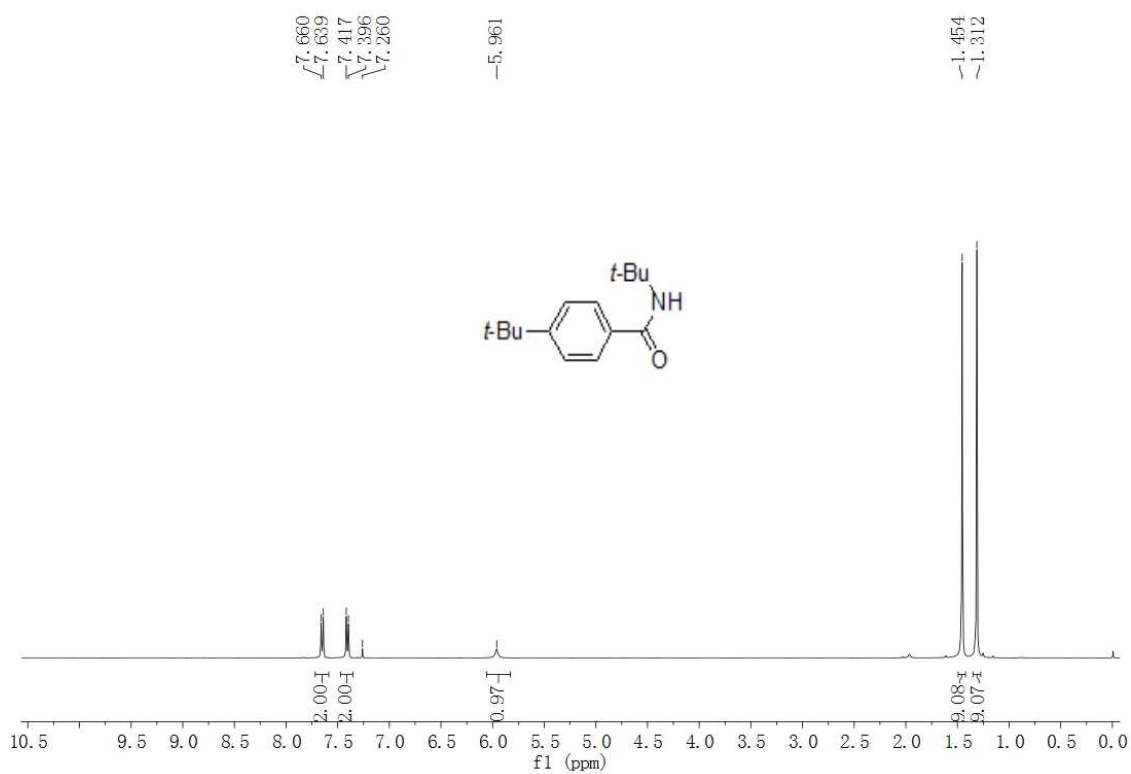


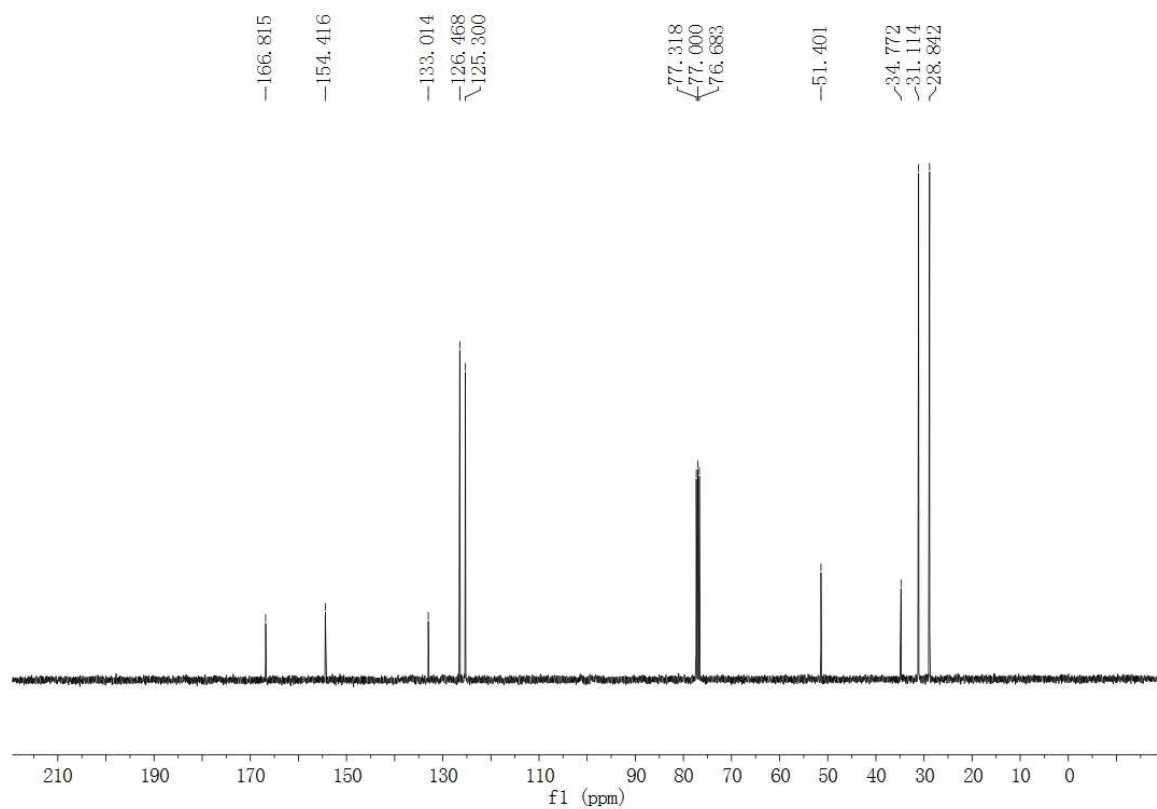
^1H NMR and ^{13}C NMR of *N*-tert-butyl-4-methoxybenzamide (3da)



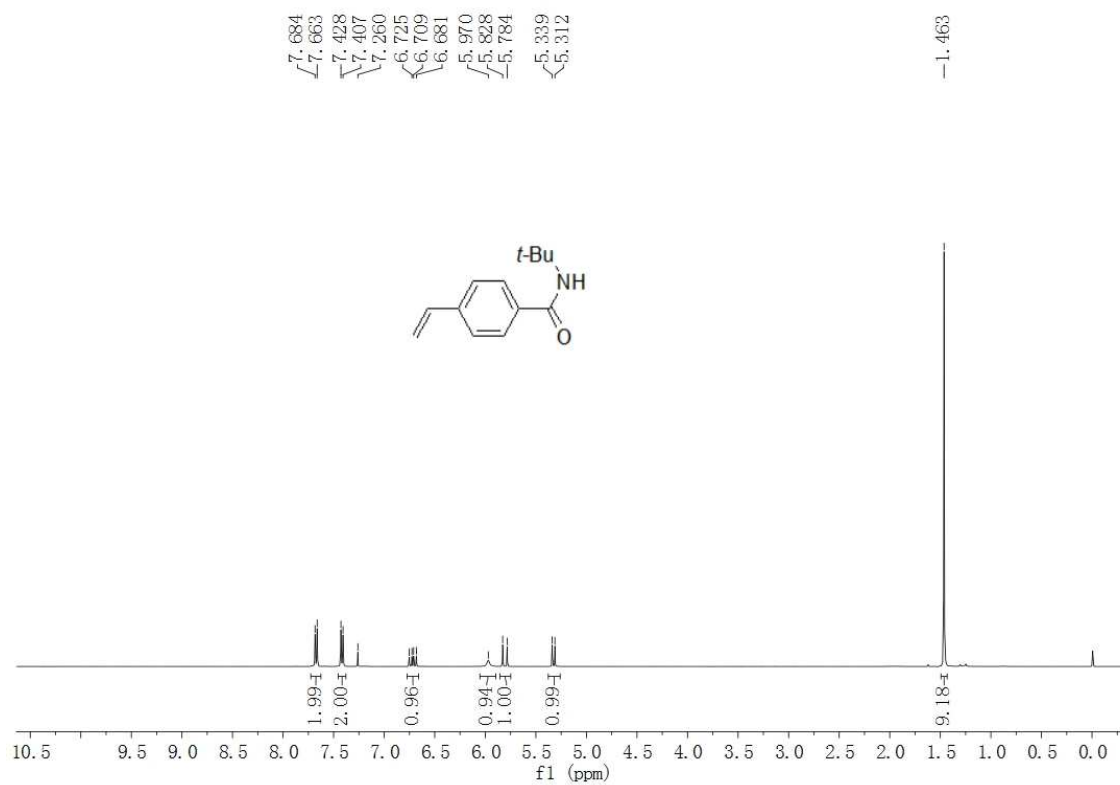


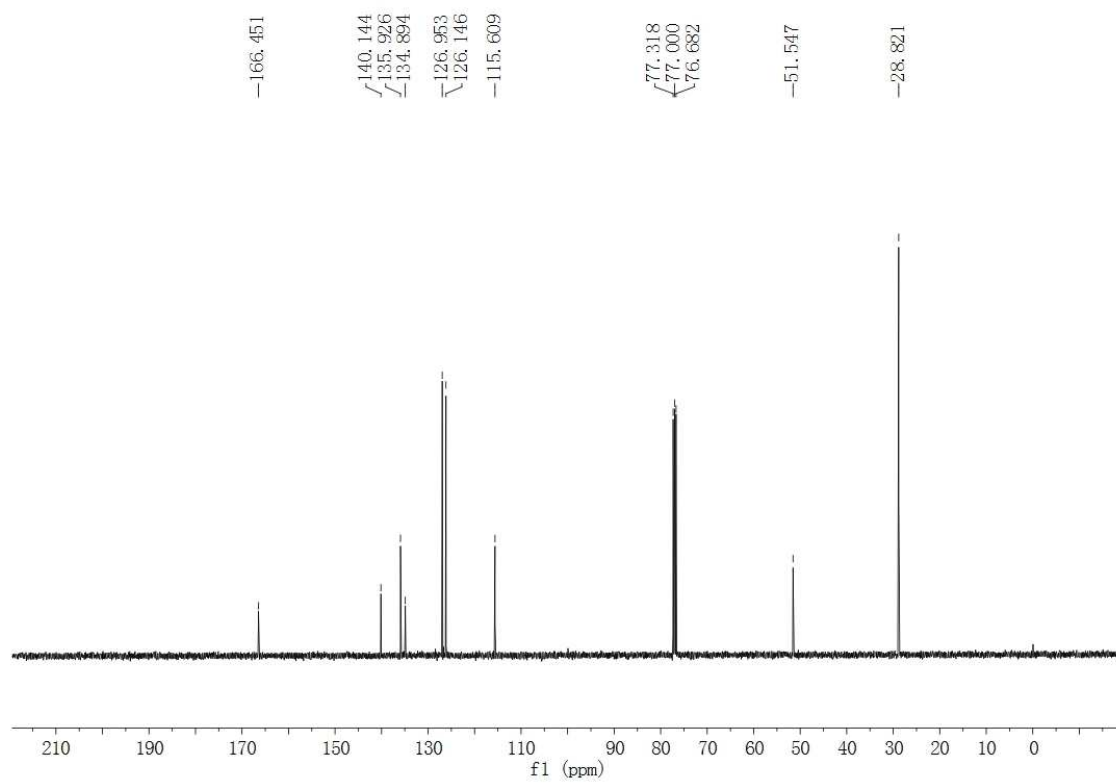
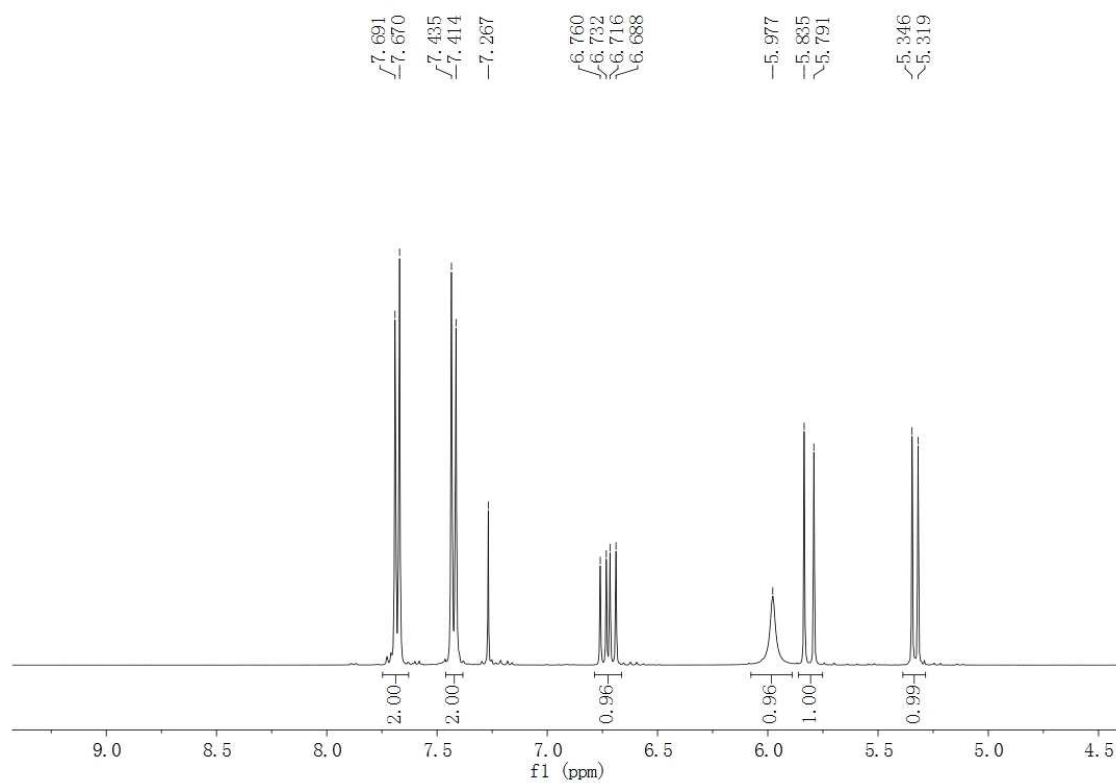
¹H NMR and ¹³C NMR of *N*-4-di-*tert*-butylbenzamide (3ea)



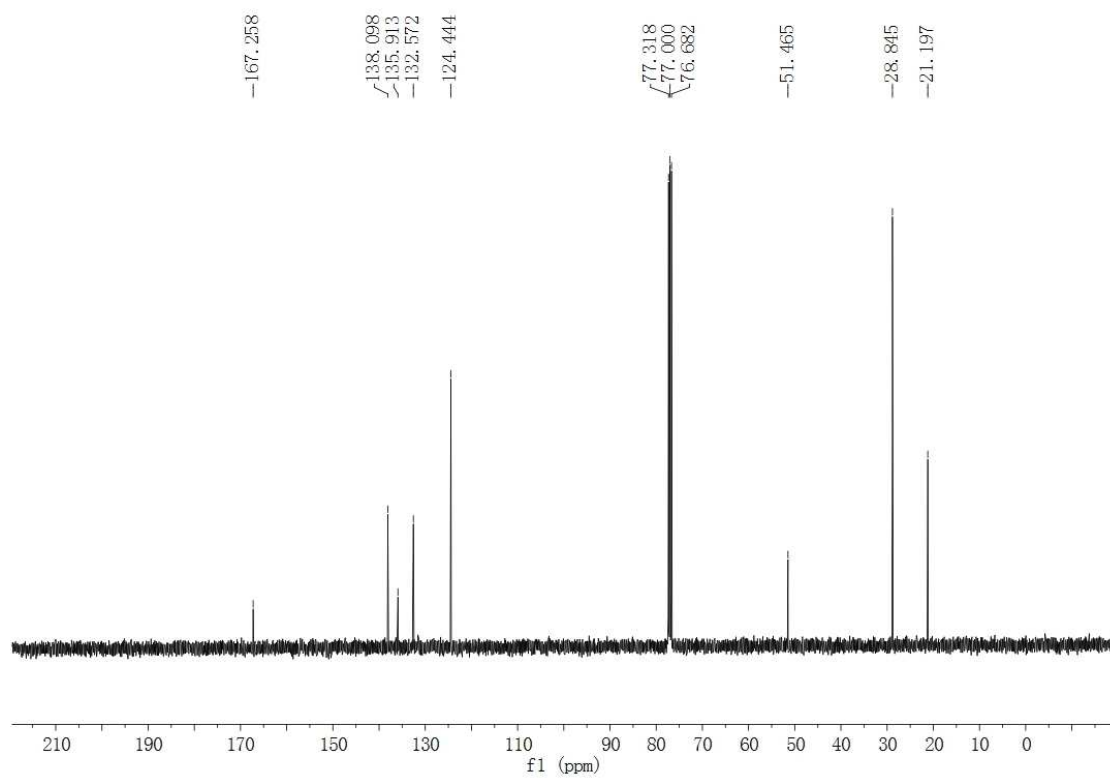
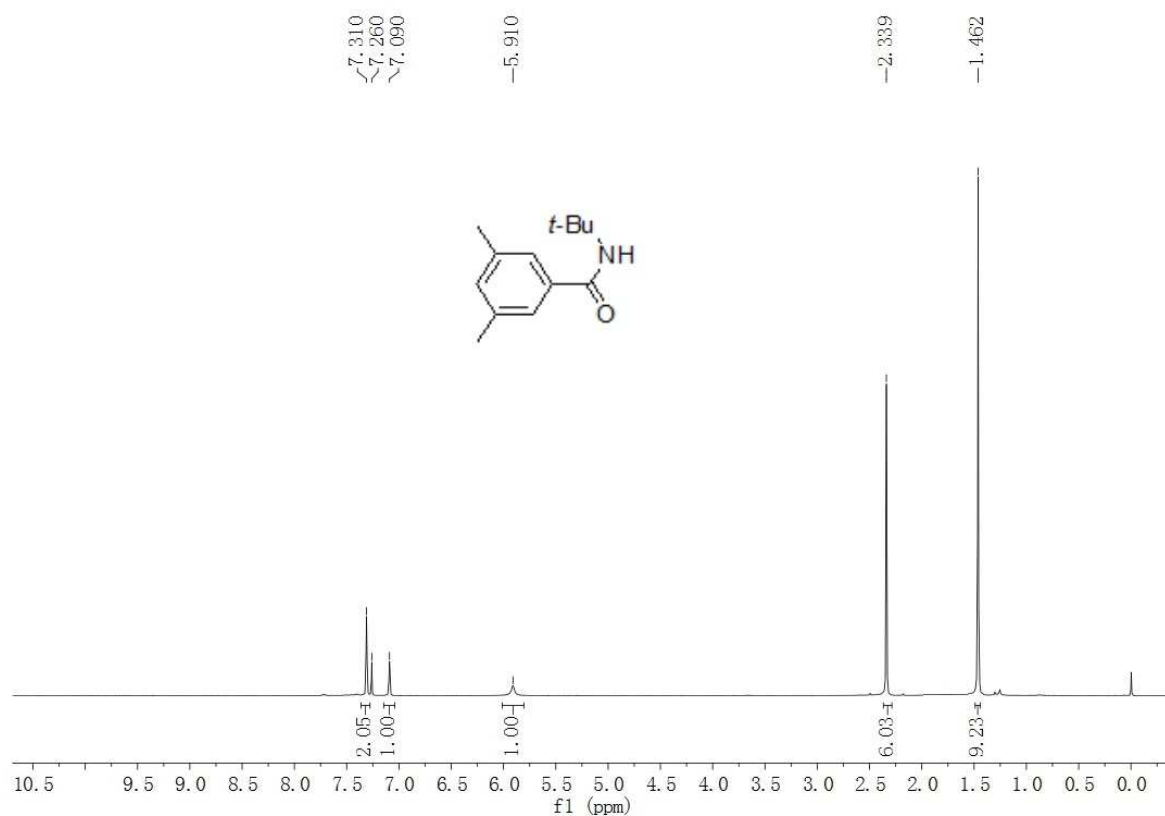


¹H NMR and ¹³C NMR of *N*-tert-butyl-4-vinylbenzamide (3fa)

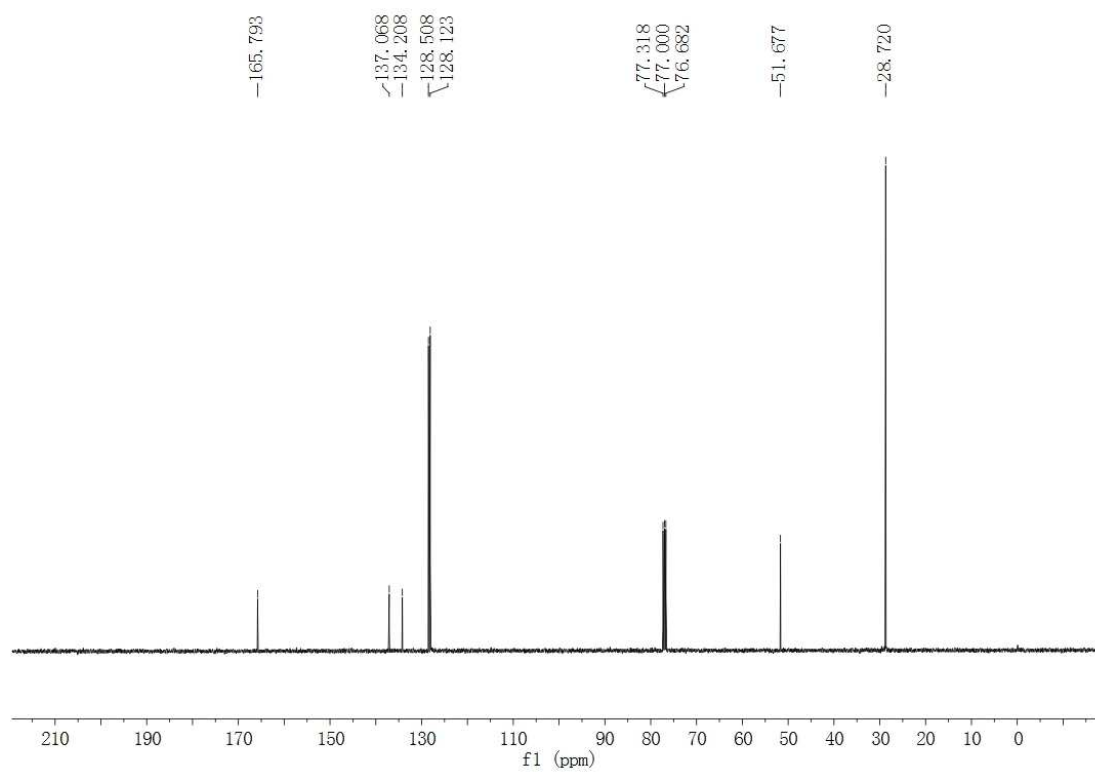
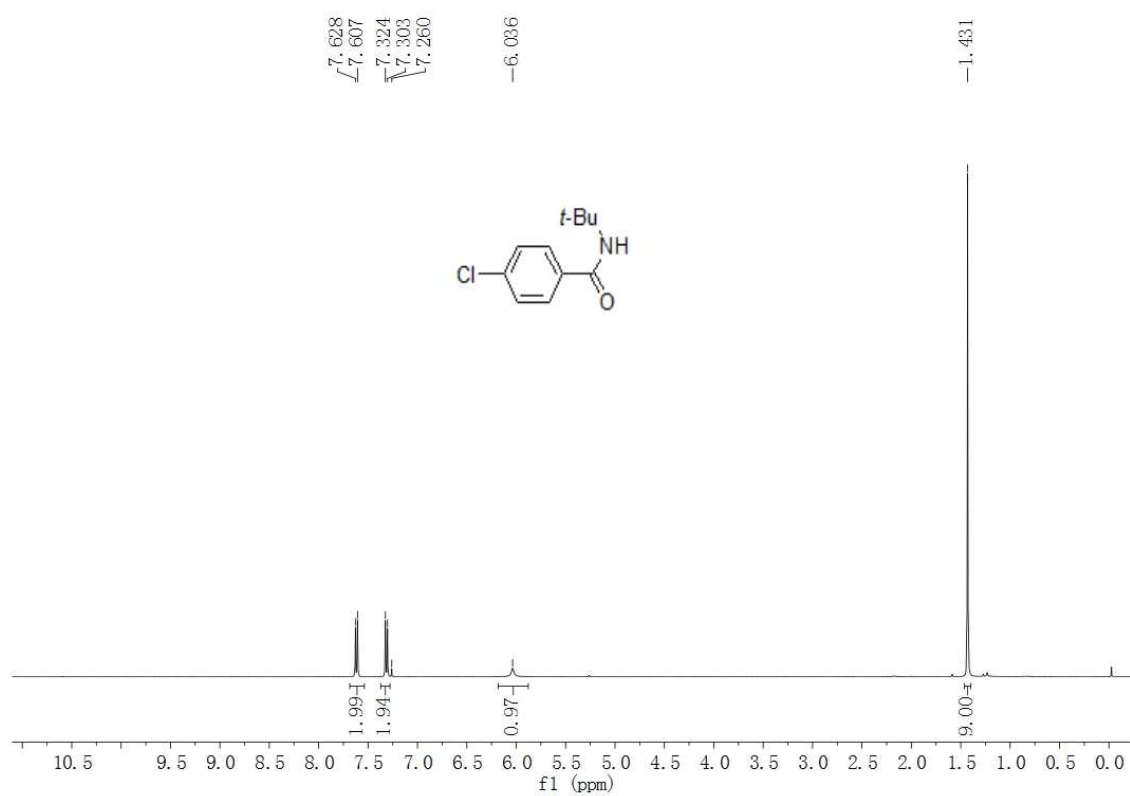




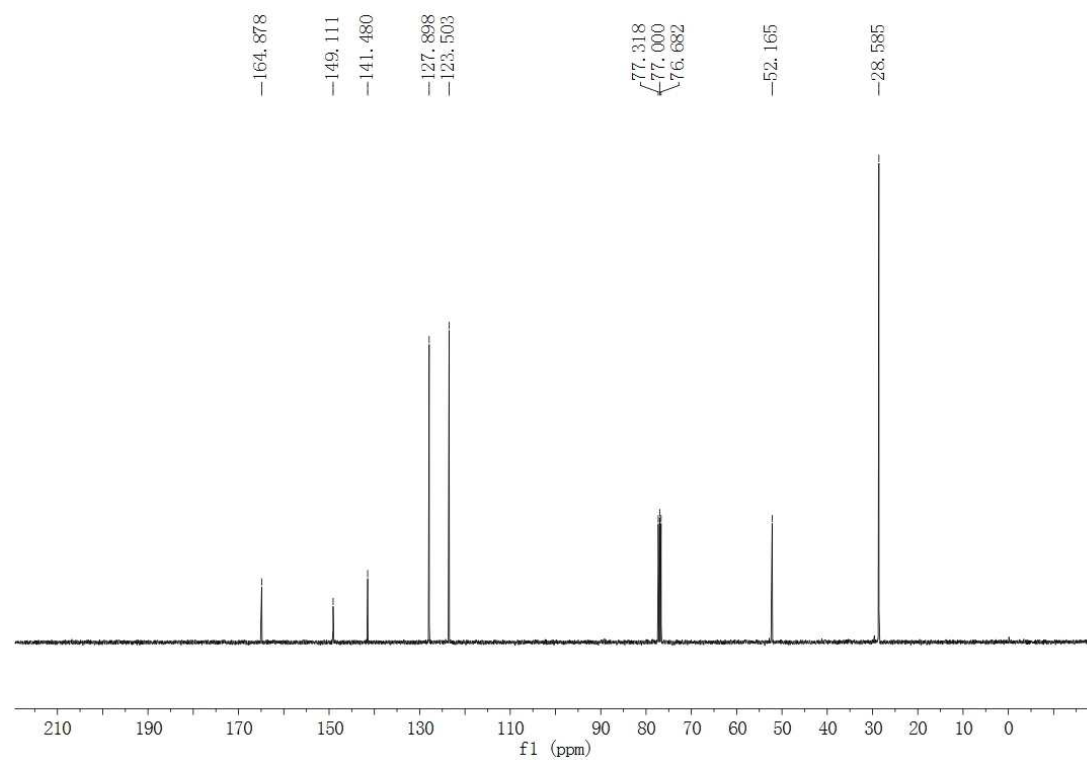
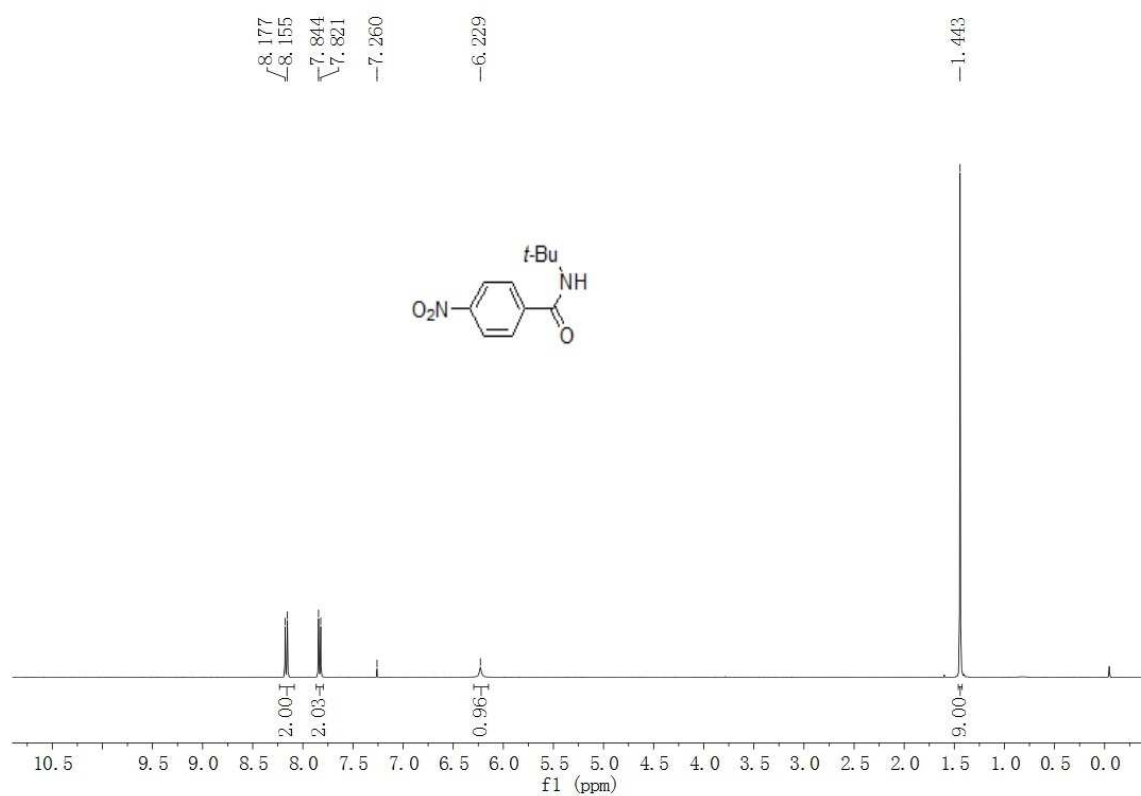
¹H NMR and ¹³C NMR of *N*-tert-butyl-3,5-dimethylbenzamide (3ga)



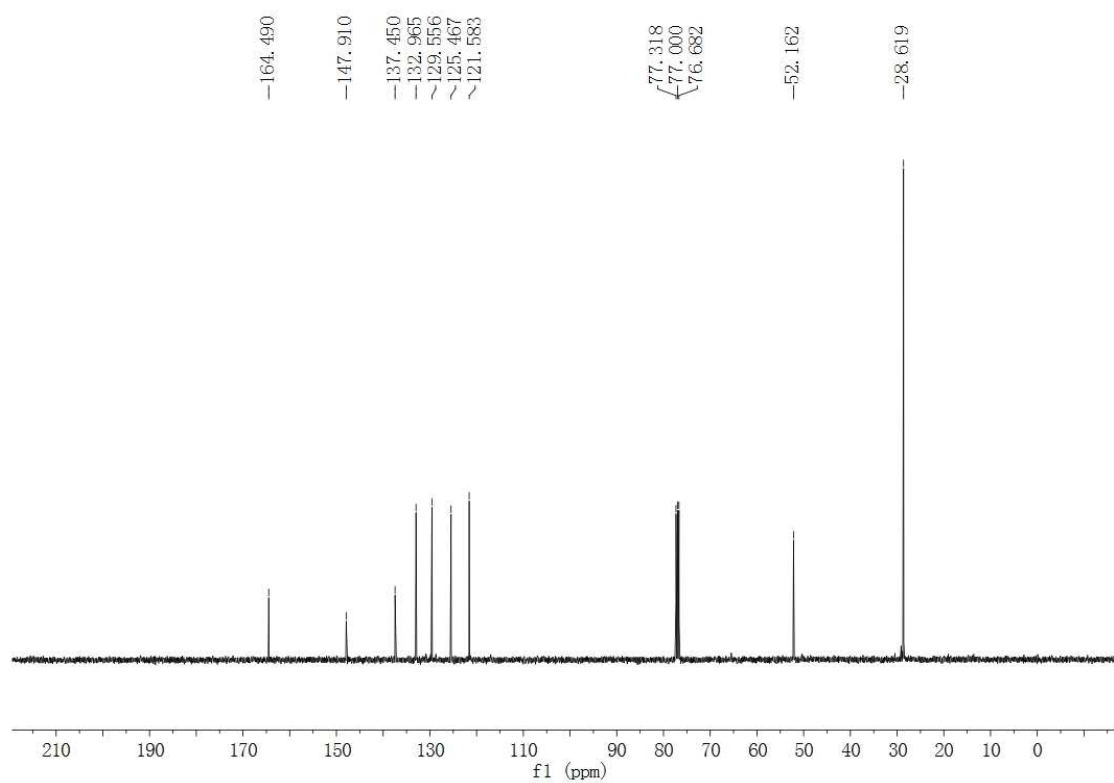
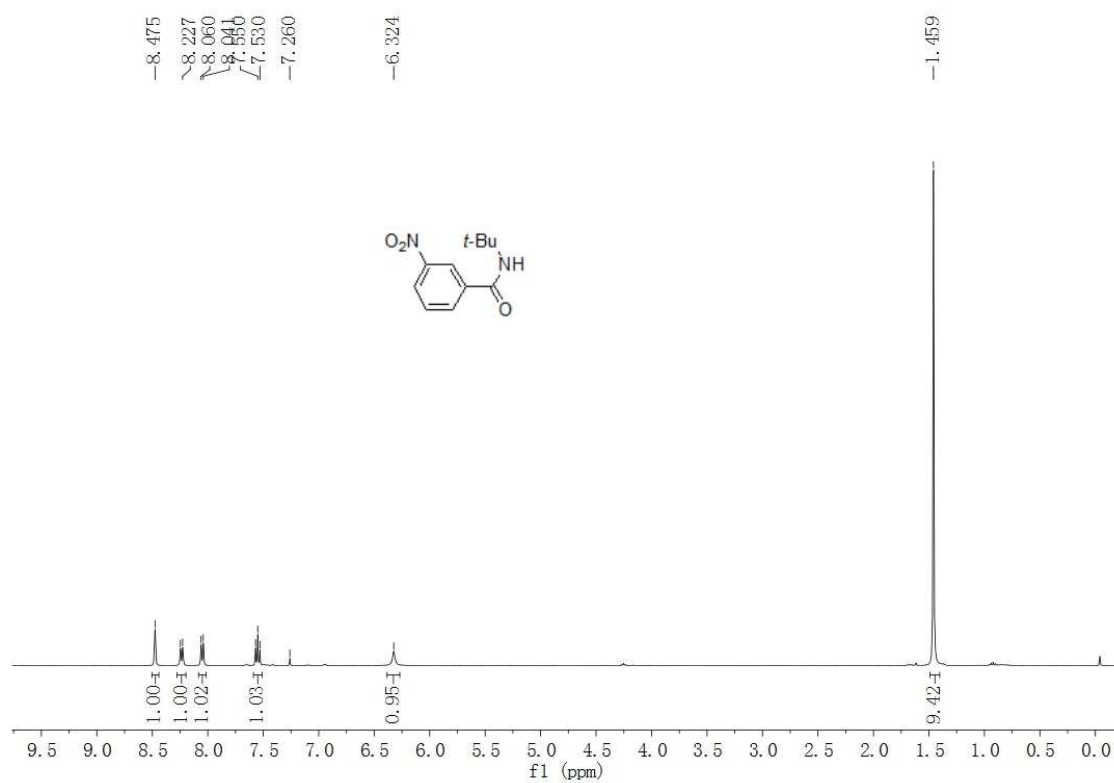
^1H NMR and ^{13}C NMR of *N*-tert-butyl-4-chlorobenzamide (3ha)



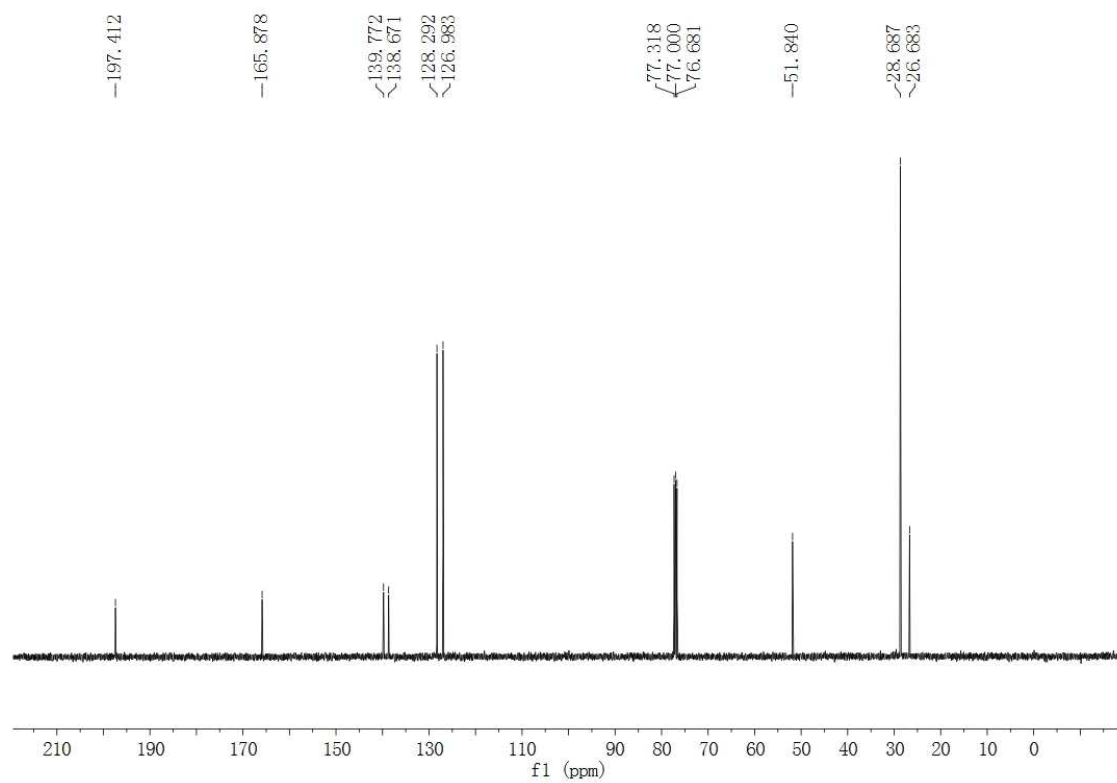
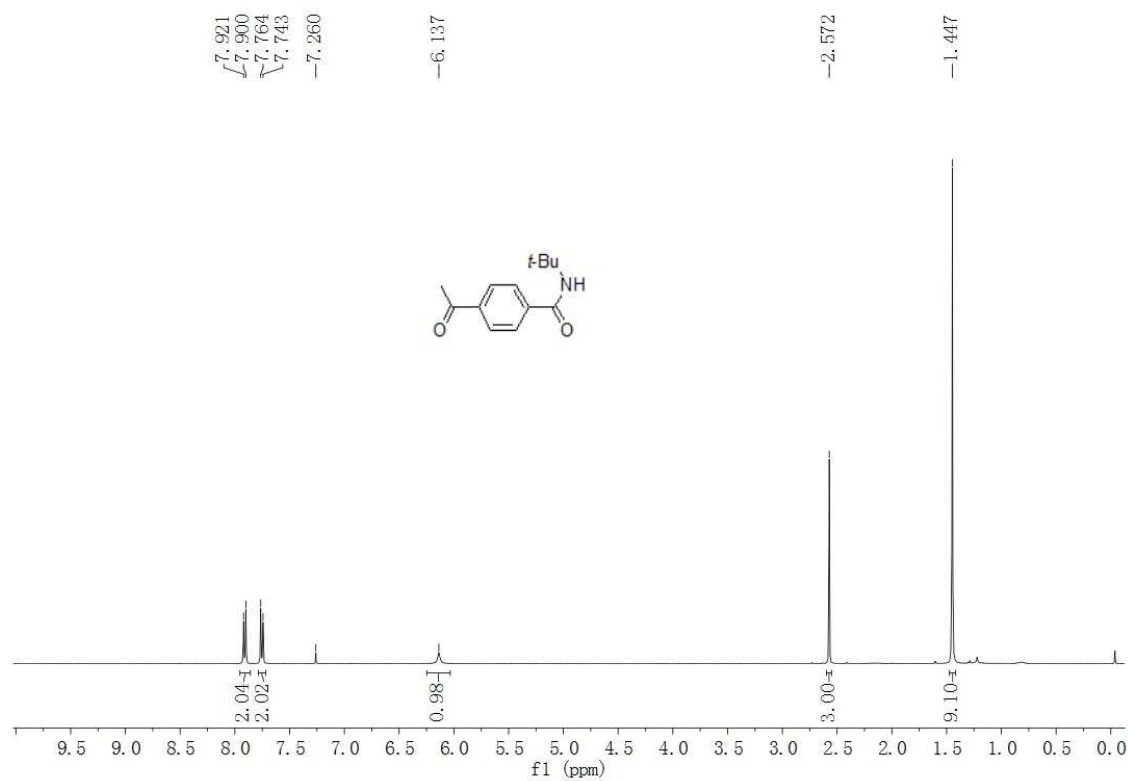
¹H NMR and ¹³C NMR of *N*-tert-butyl-4-nitrobenzamide (3ia)



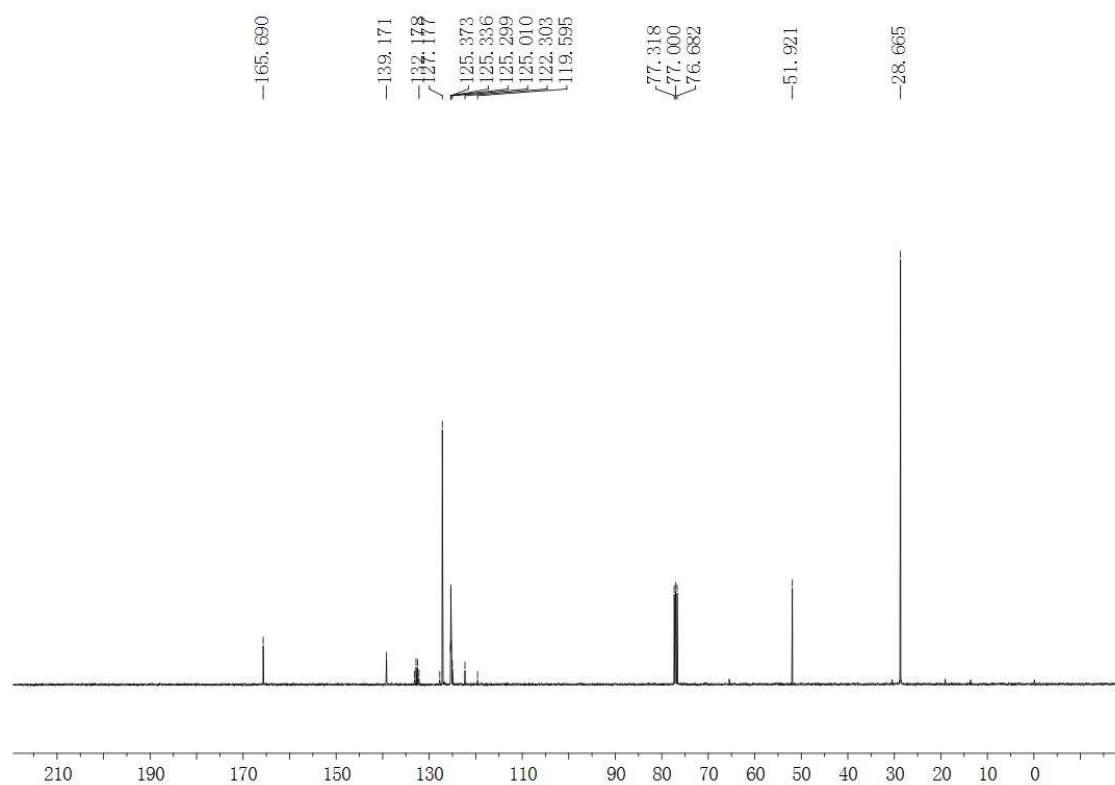
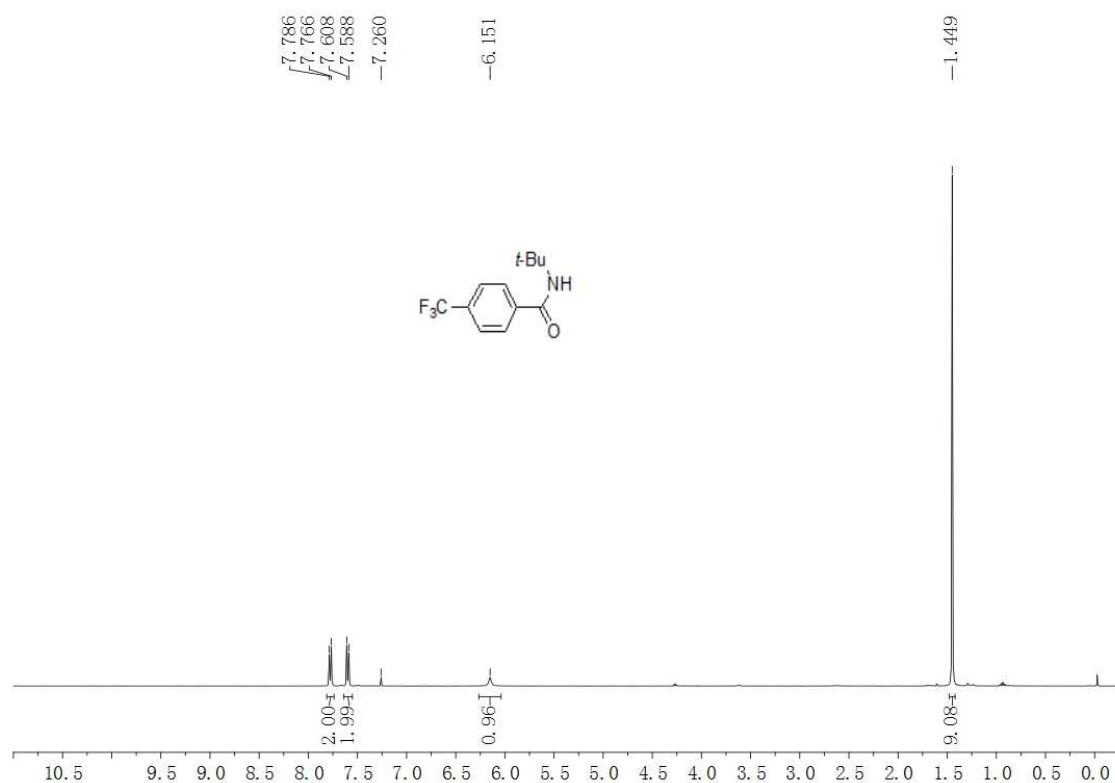
¹H NMR and ¹³C NMR of *N*-tert-butyl-3-nitrobenzamide (3ja)

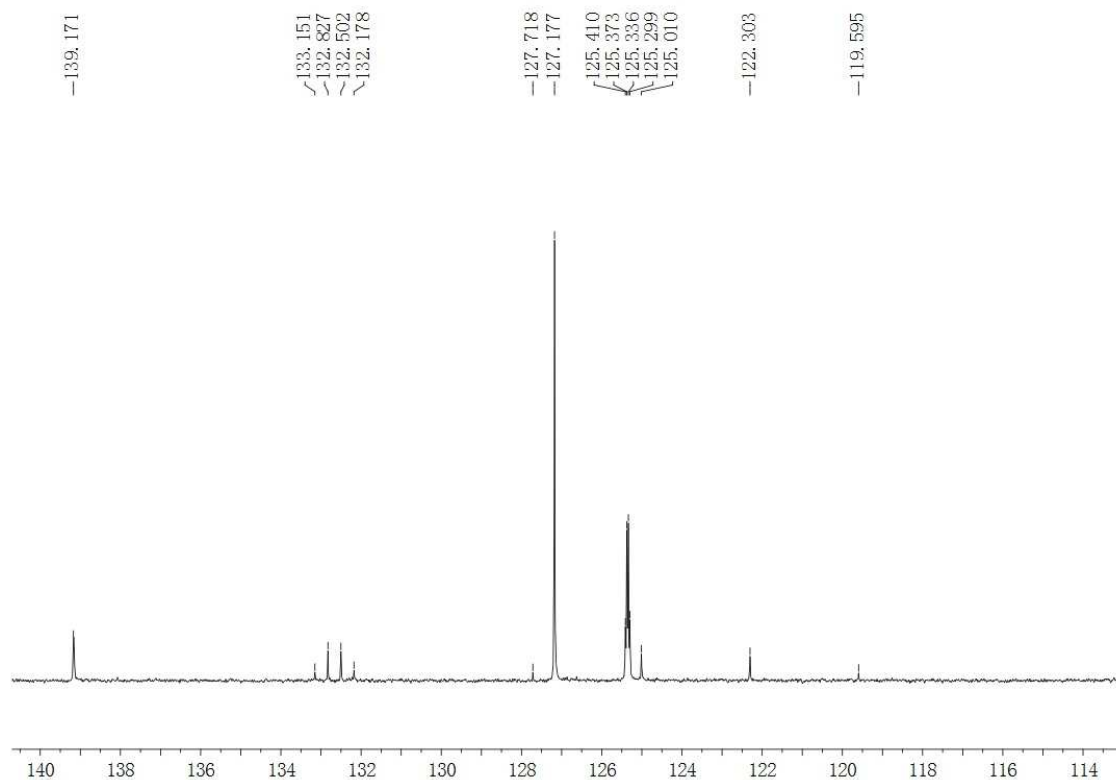


¹H NMR and ¹³C NMR of *N*-tert-butyl-4-acetylbenzamide (3ka)

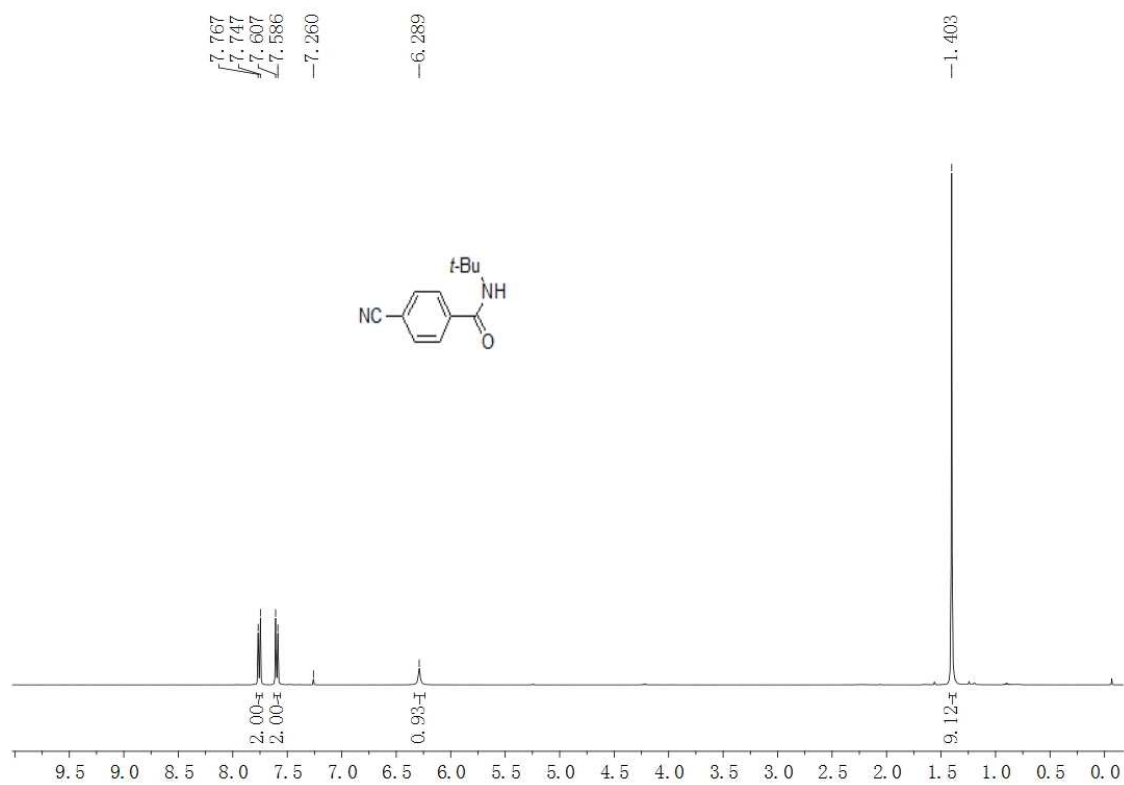


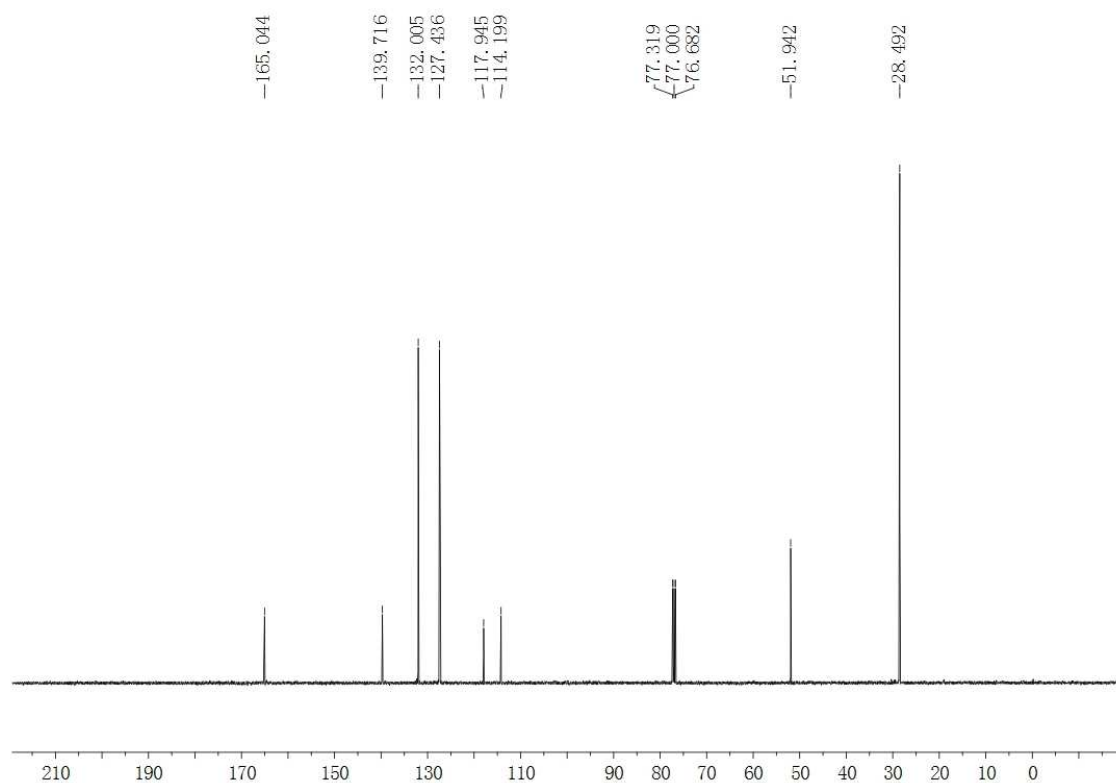
¹H NMR and ¹³C NMR of *N*-tert-butyl-4-(trifluoromethyl)benzamide (3la)



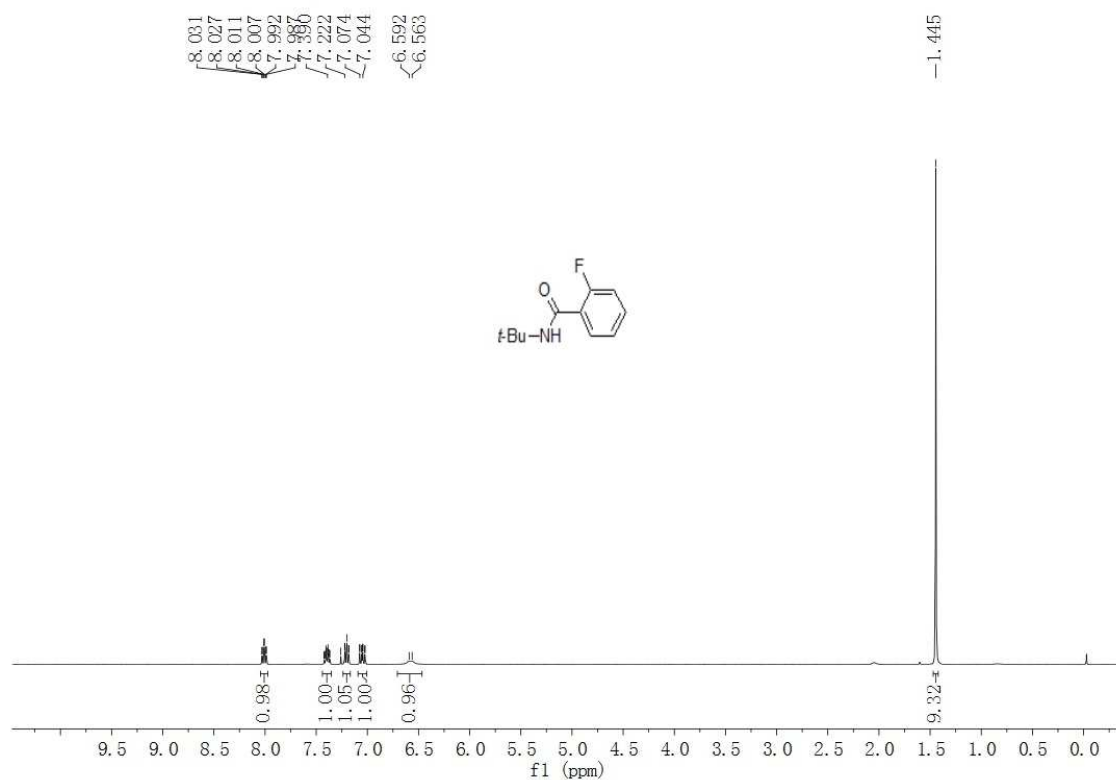


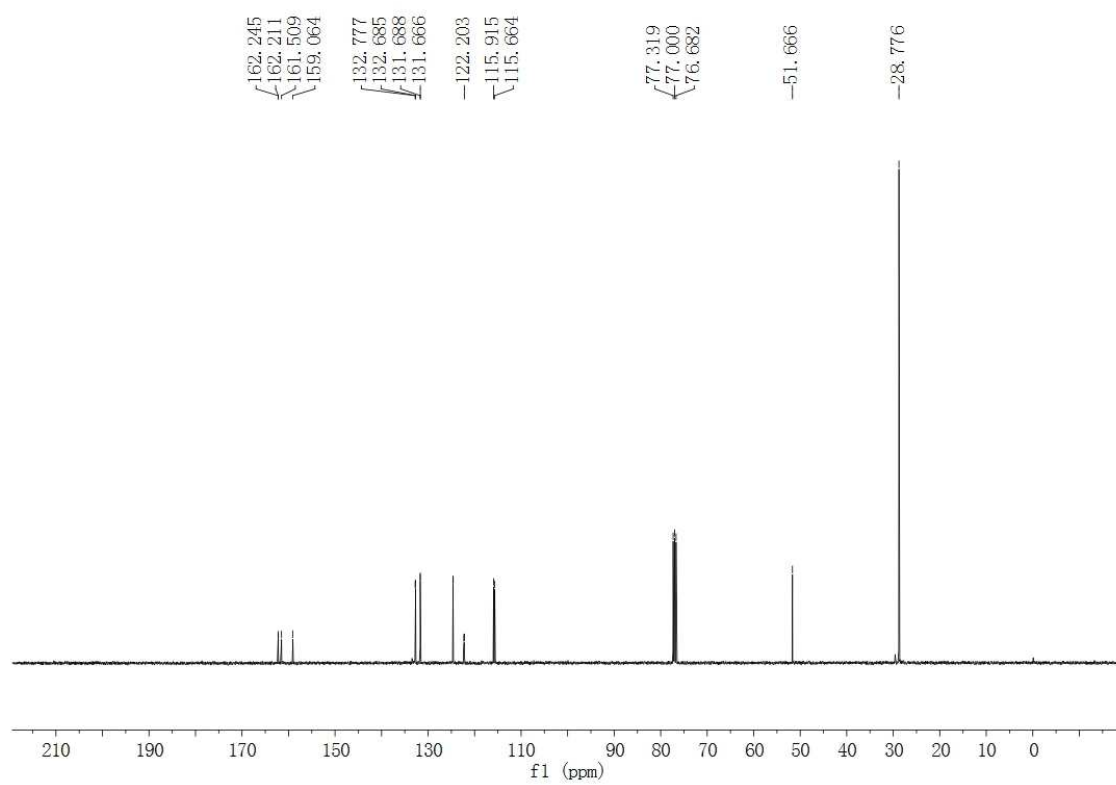
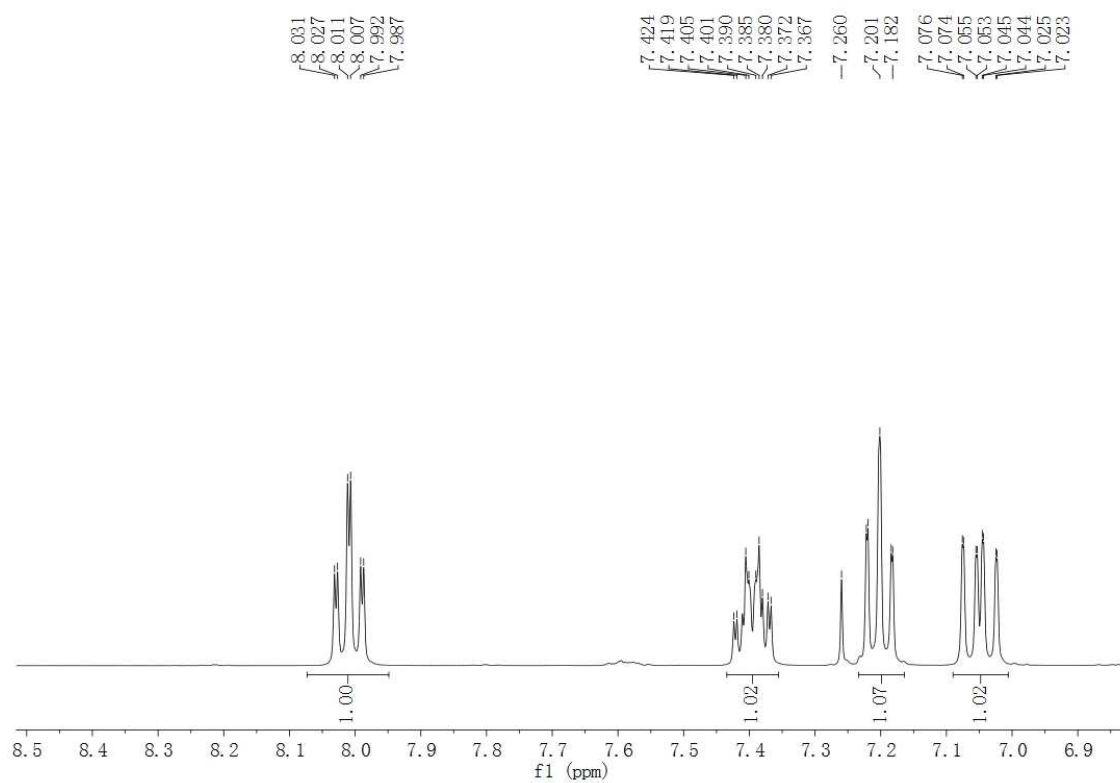
¹H NMR and ¹³C NMR of *N*-tert-butyl-4-cyanobenzamide (3ma)

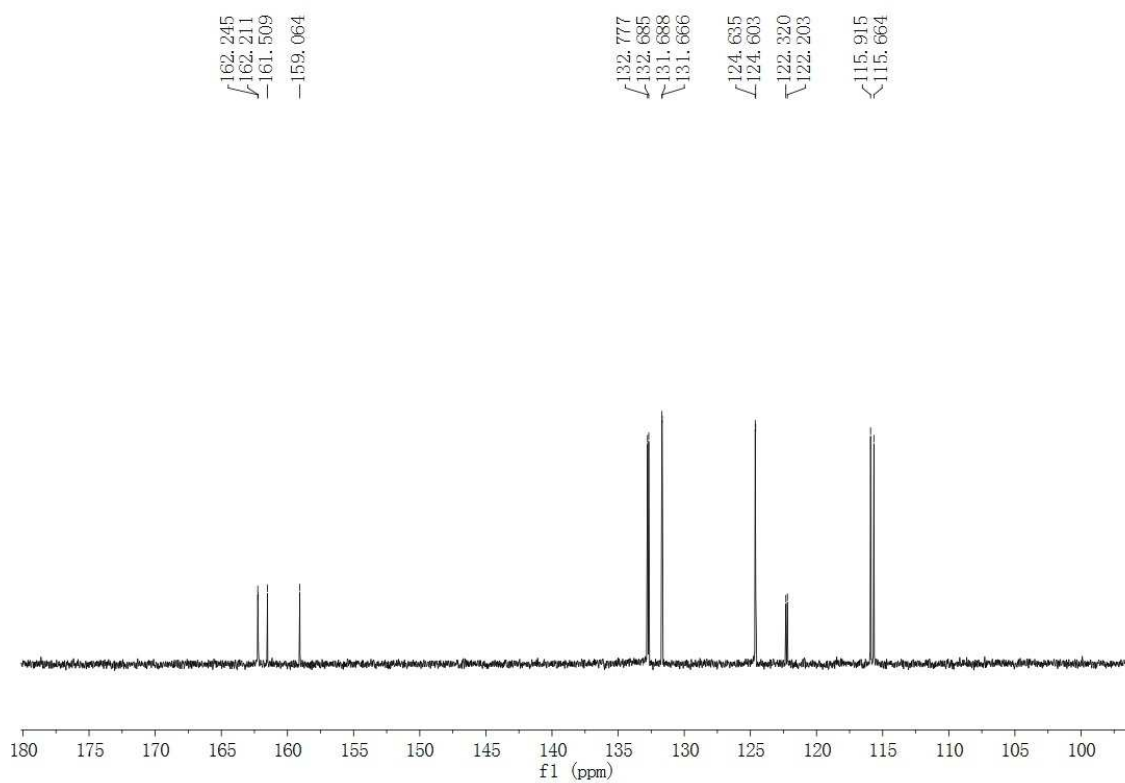




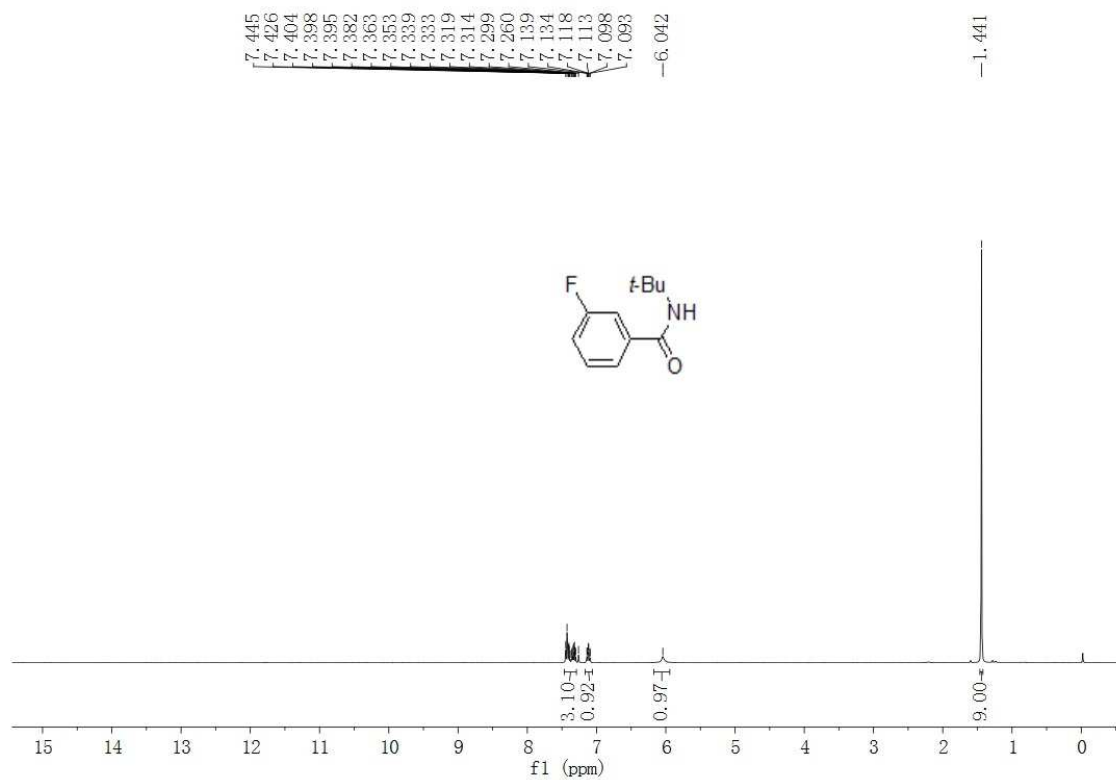
¹H NMR and ¹³C NMR of *N*-tert-butyl-2-fluorobenzamide (3na)

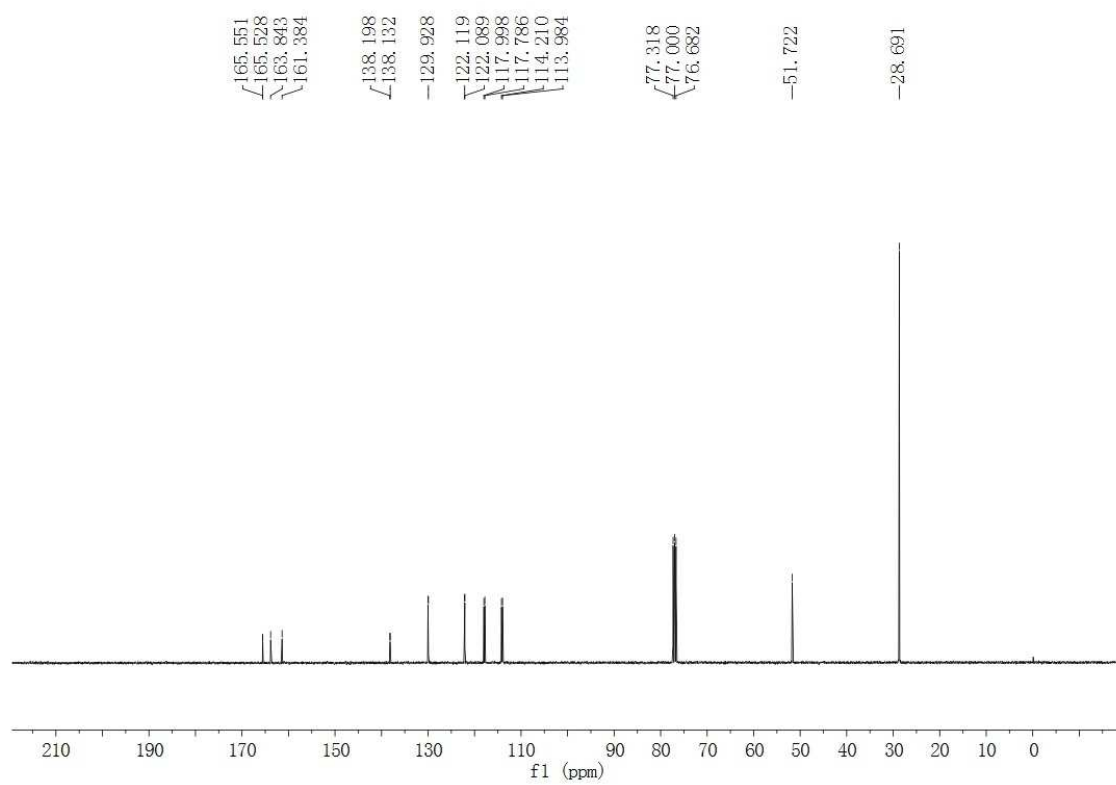
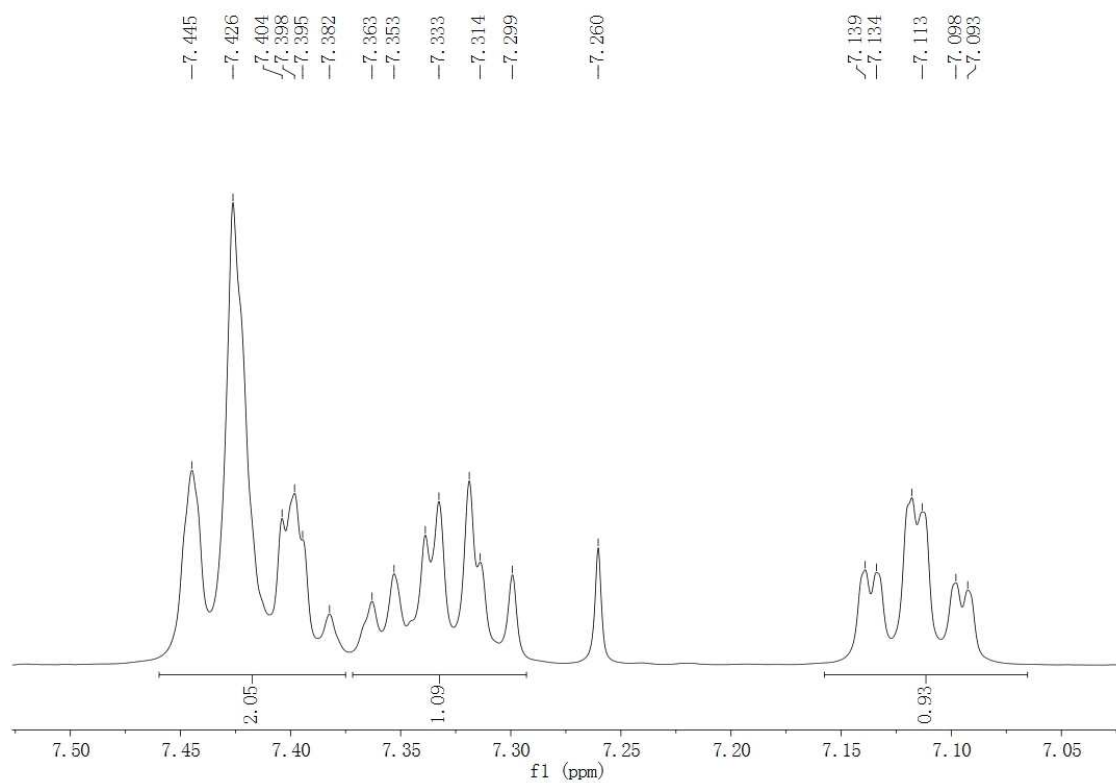


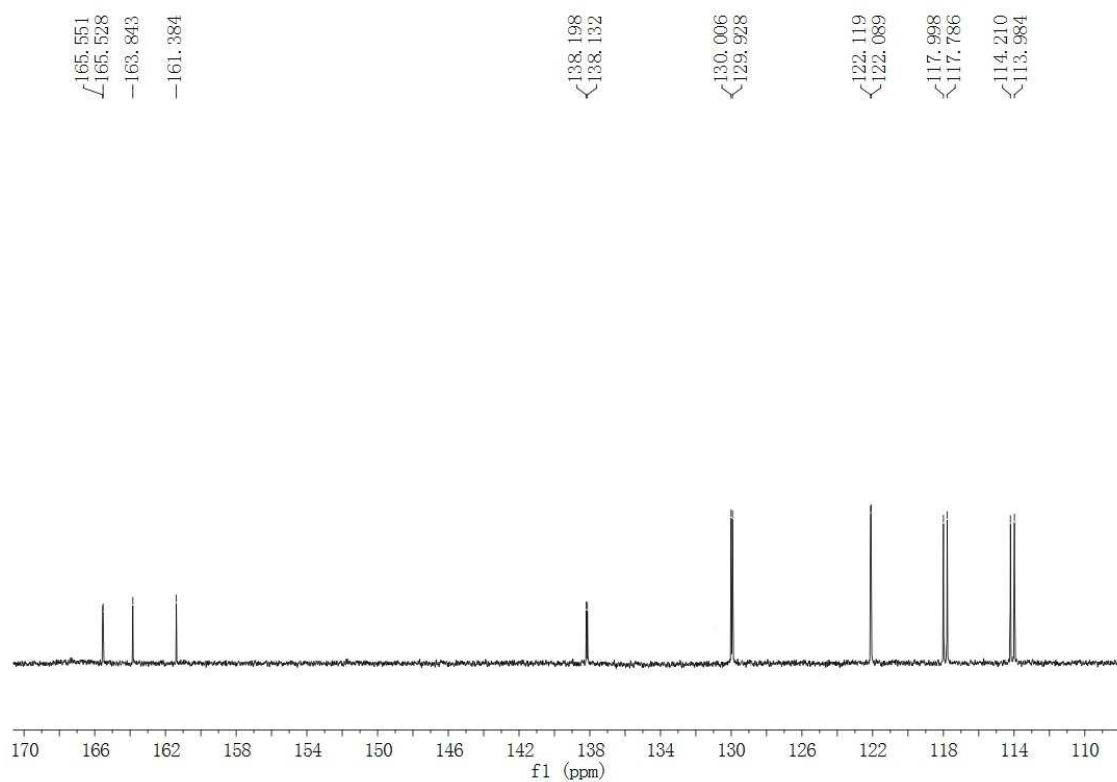




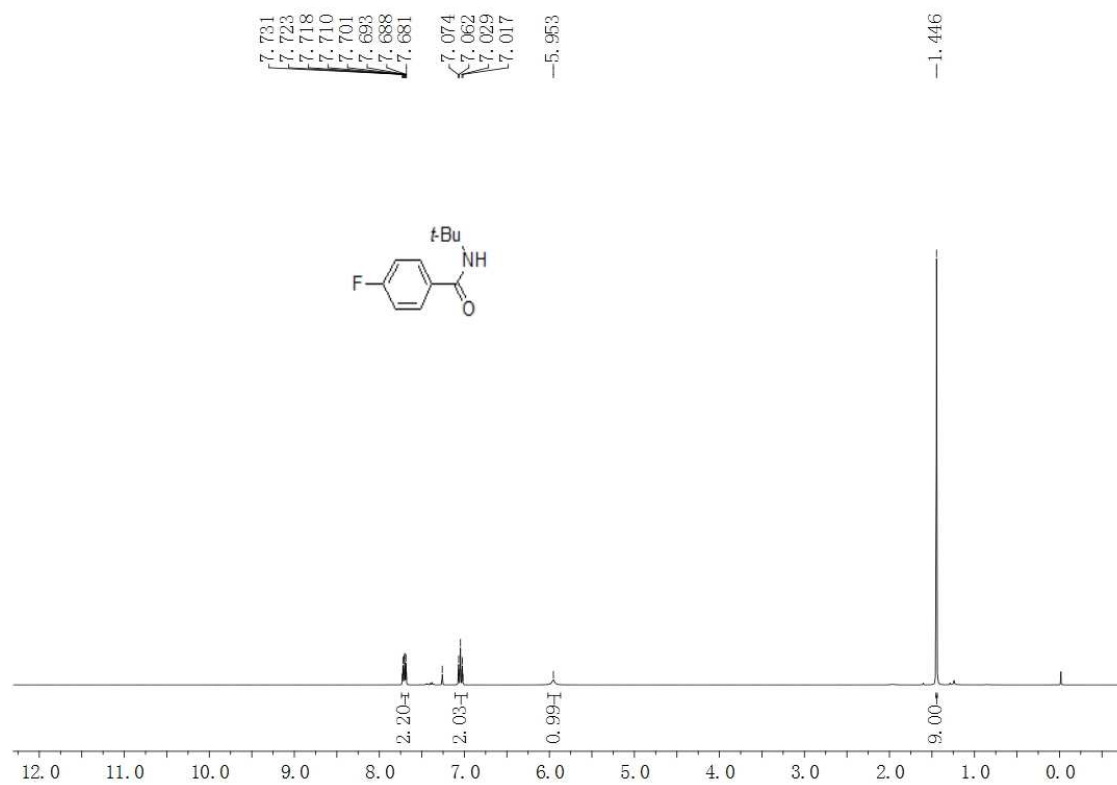
¹H NMR and ¹³C NMR of N-tert-butyl-3-fluorobenzamide (30a)

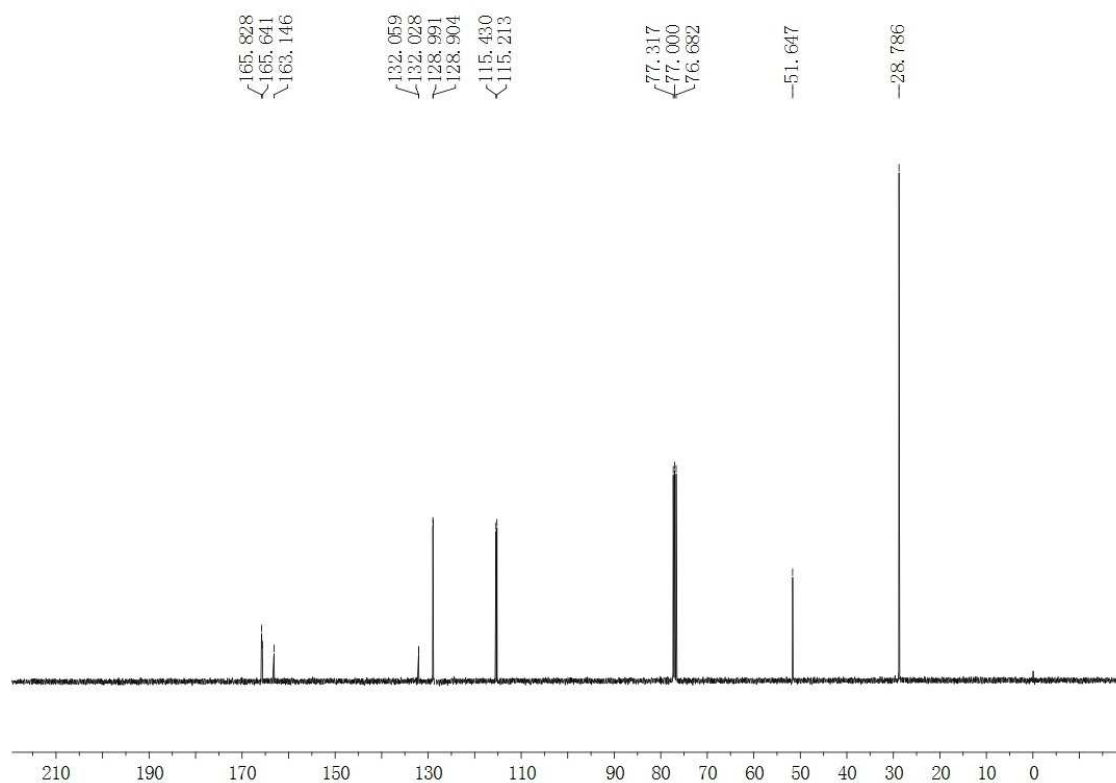




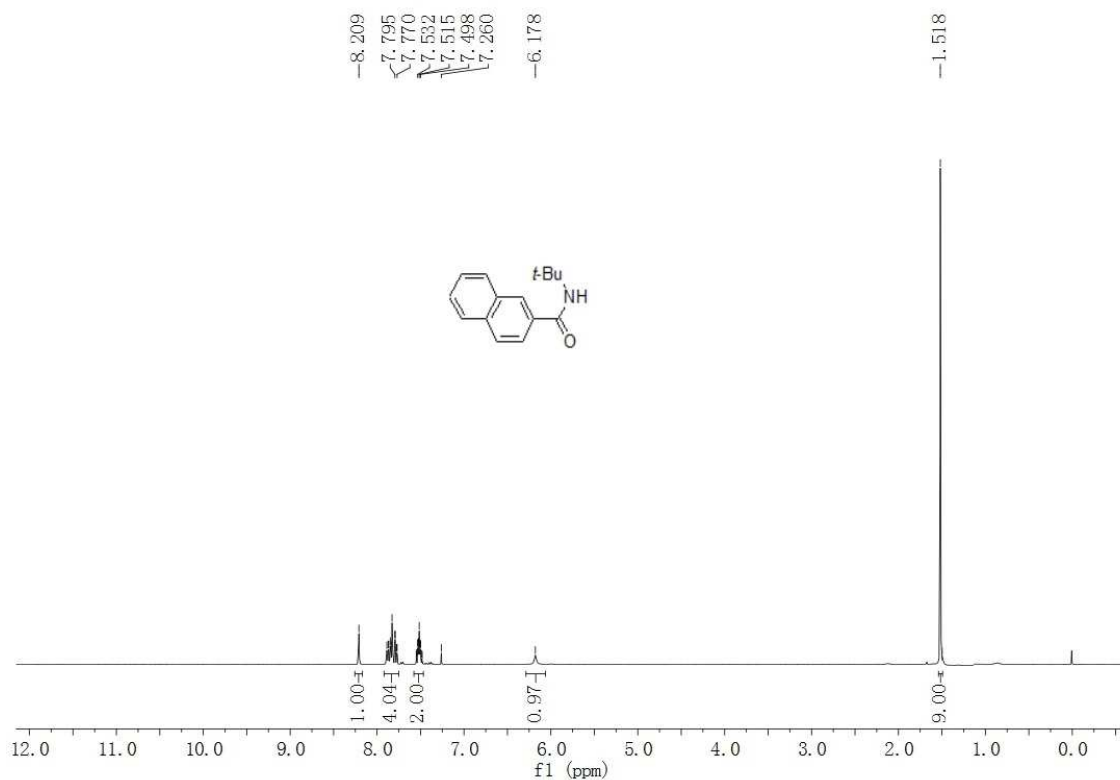


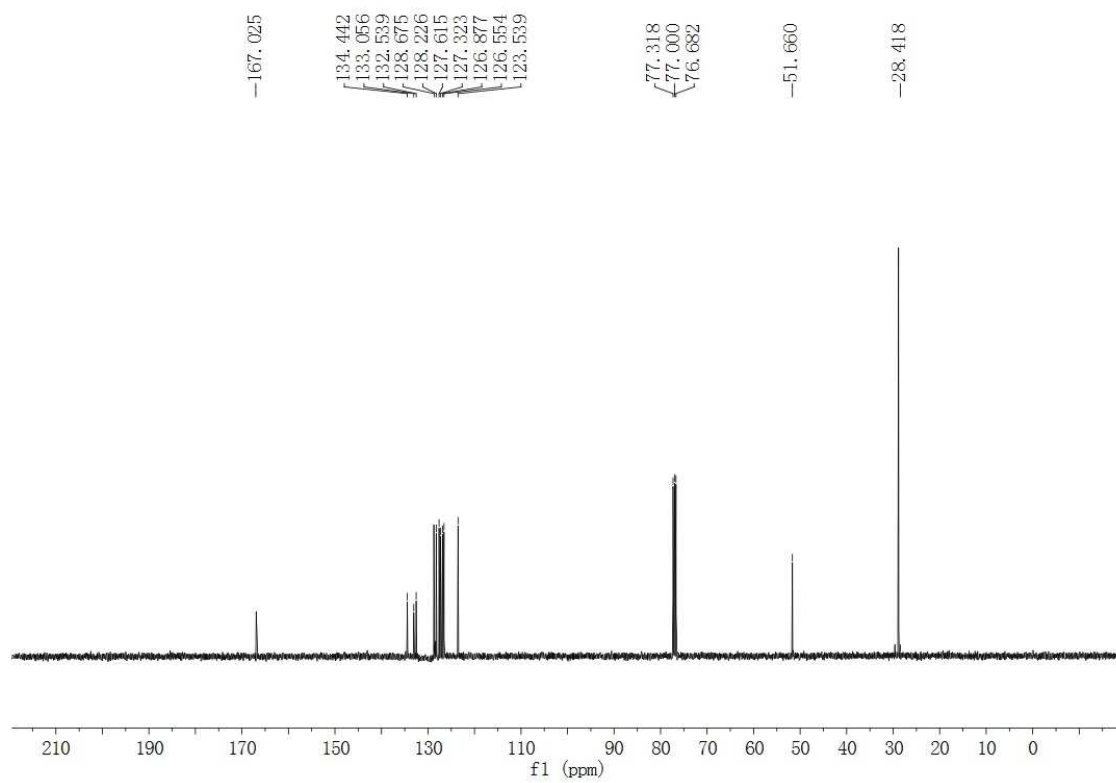
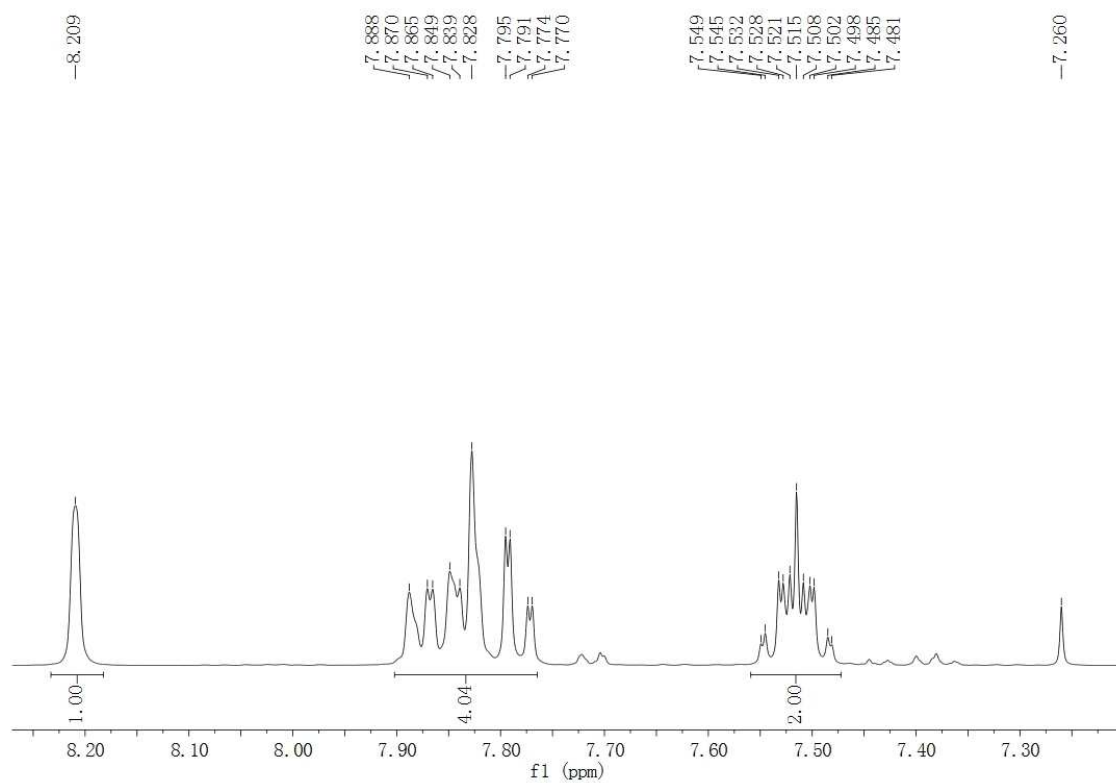
¹H NMR and ¹³C NMR of *N*-tert-butyl-4-fluorobenzamide (3pa)

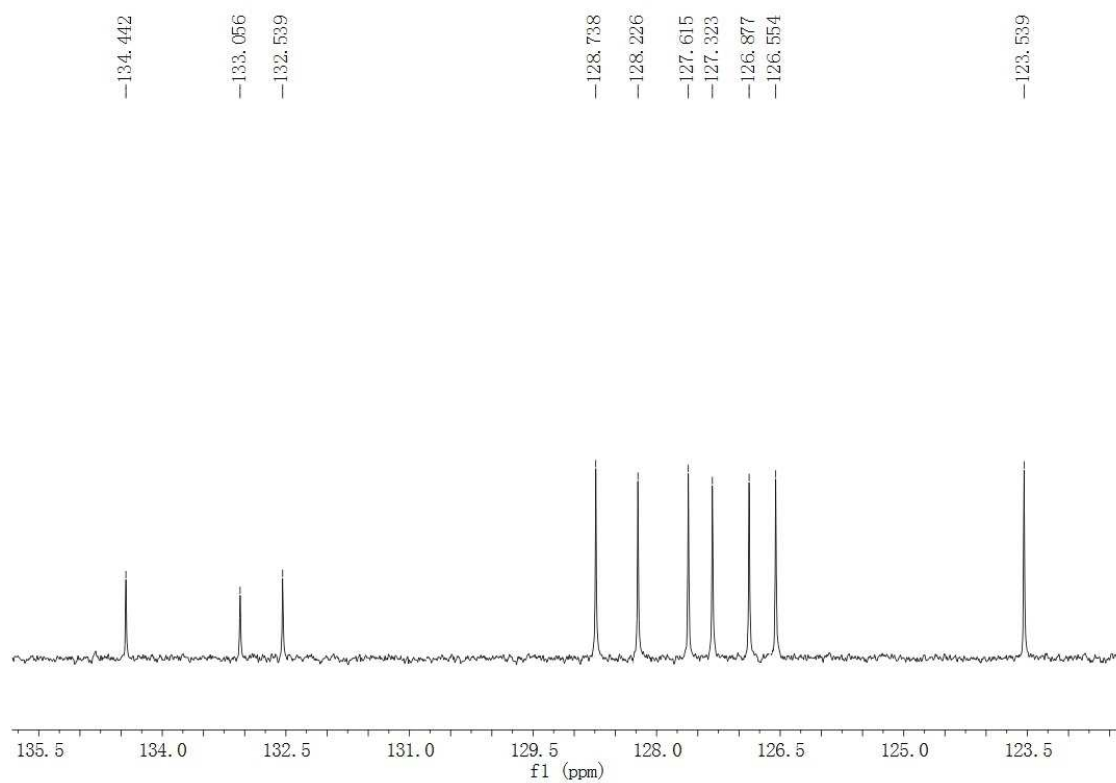




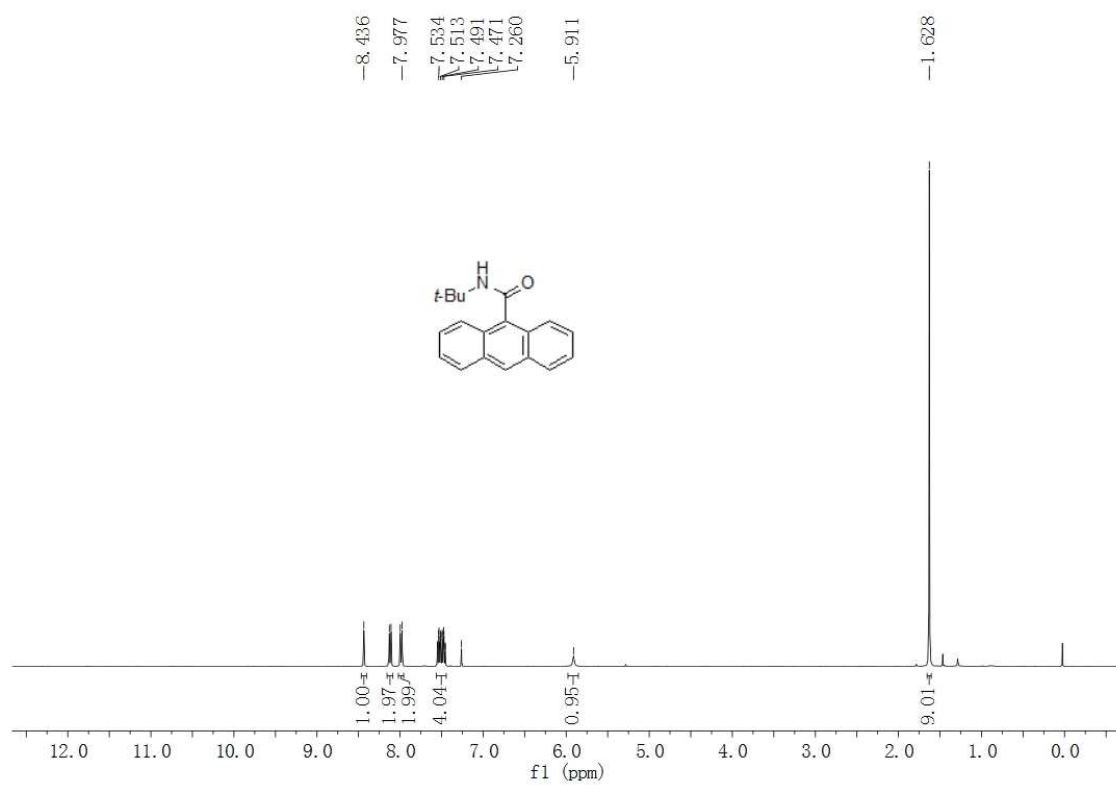
¹H NMR and ¹³C NMR of N-tert-butyl-2-naphthamide(3qa)

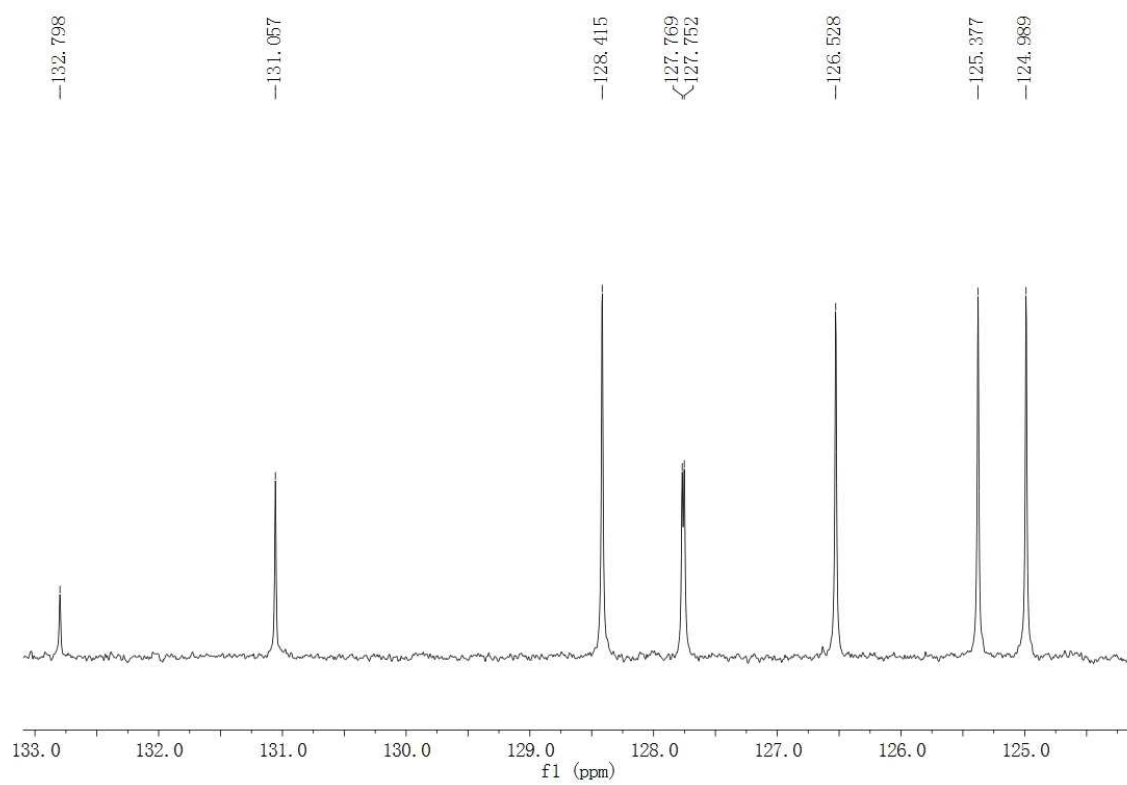
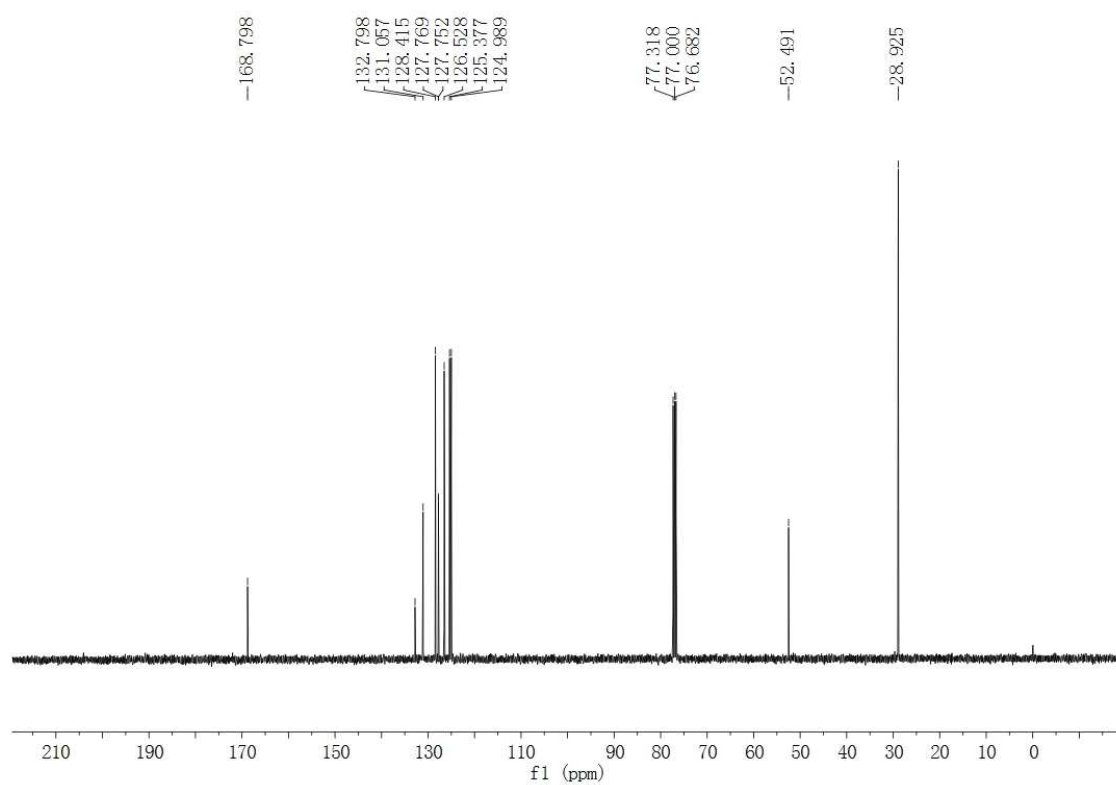




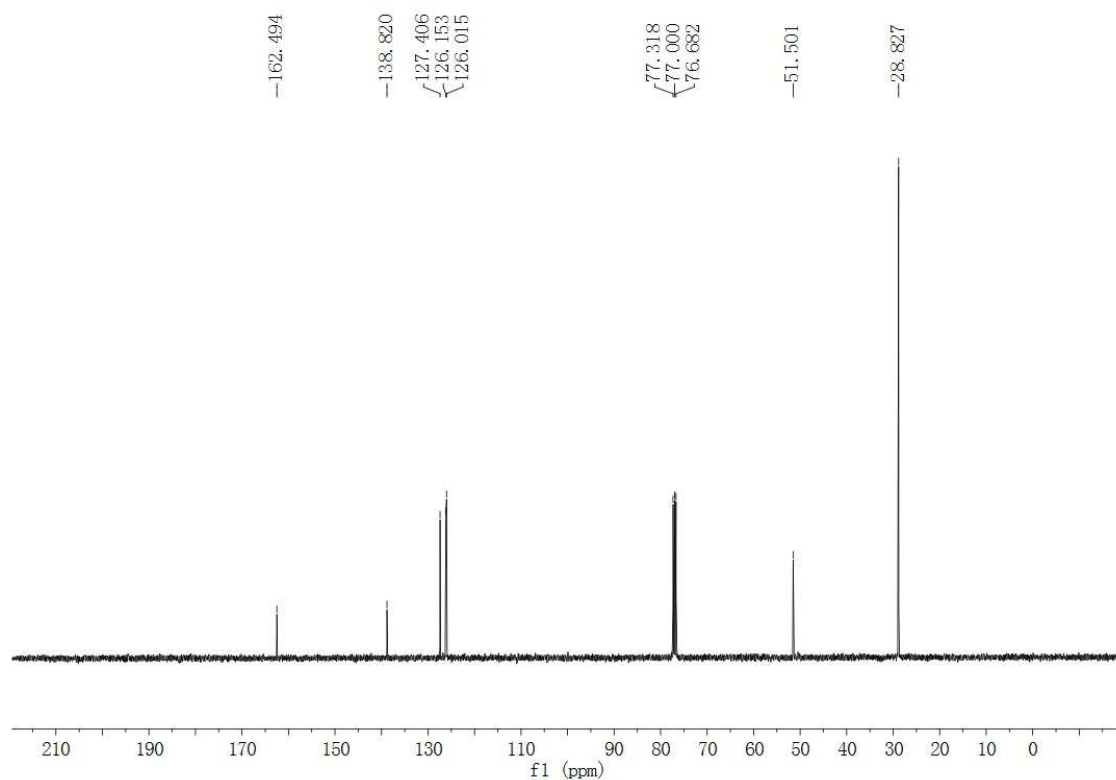
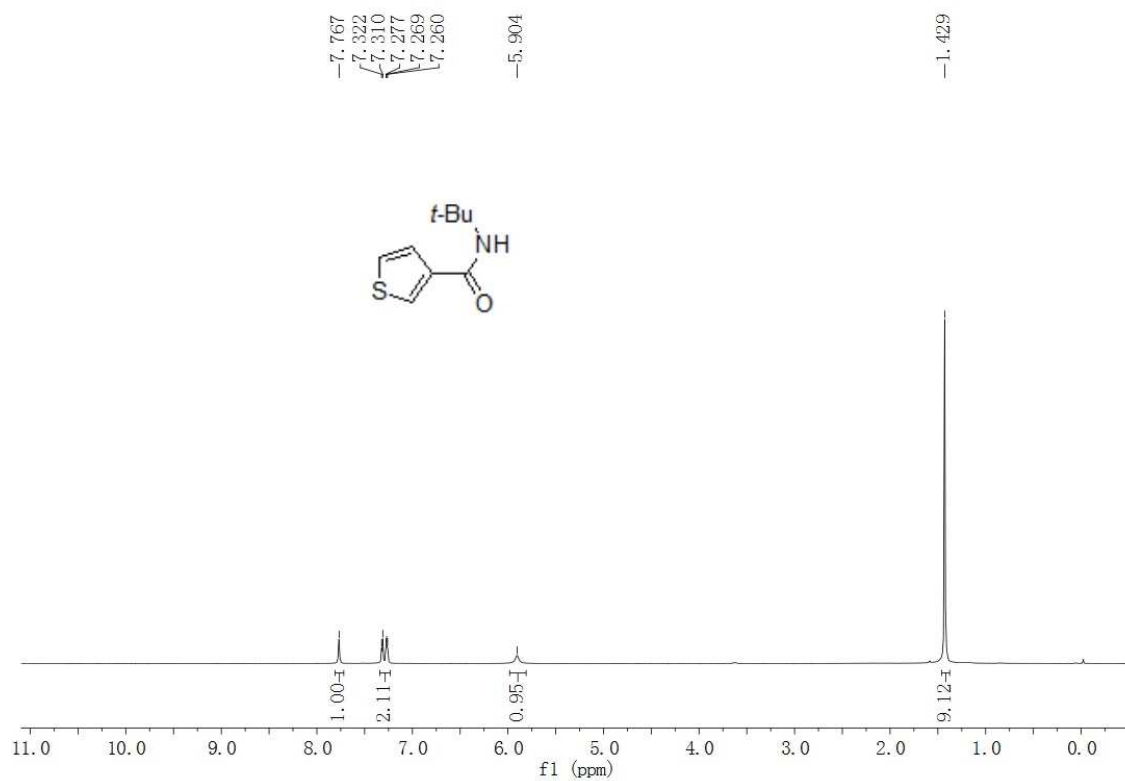


¹H NMR and ¹³C NMR of *N*-tert-butylanthracene-10-carboxamide (3ra)

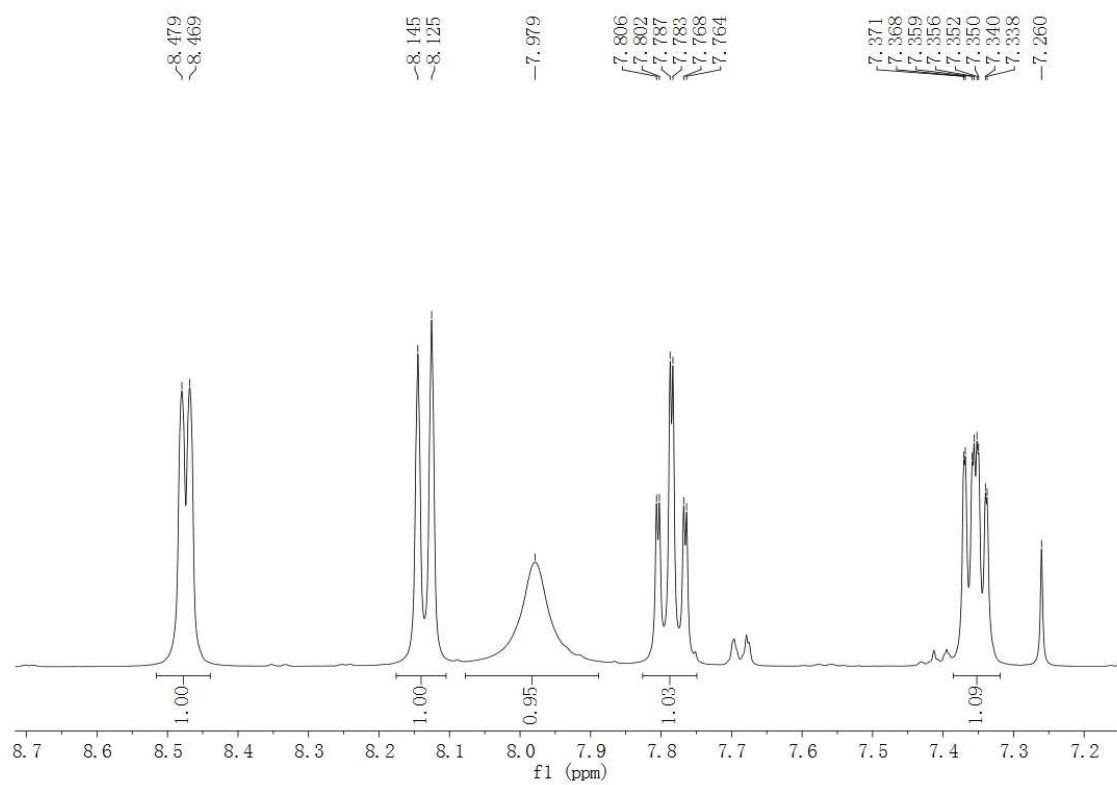
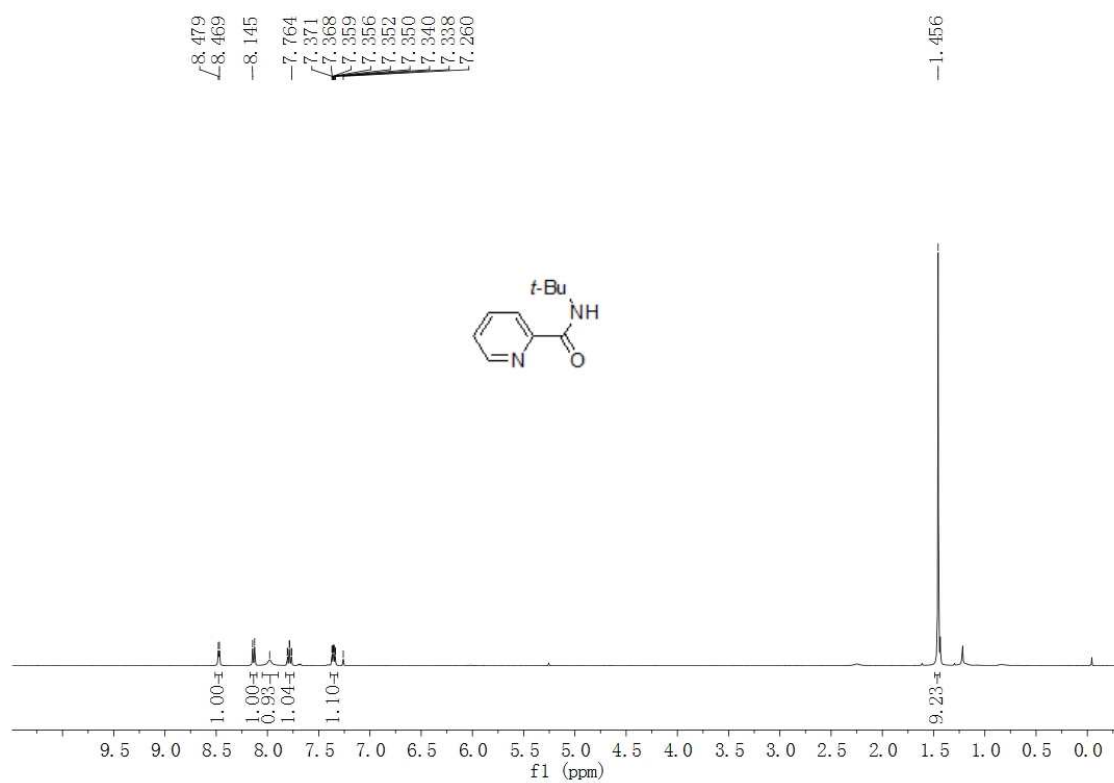


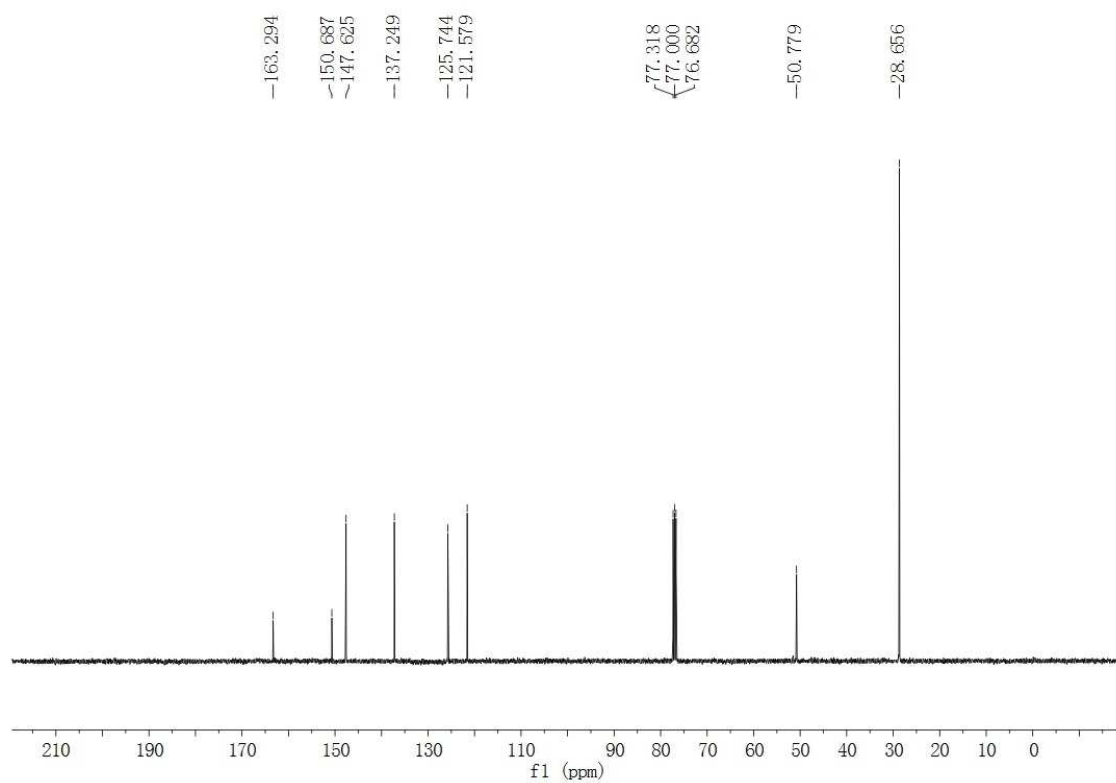


^1H NMR and ^{13}C NMR of *N*-tert-butylthiophene-3-carboxamide (3sa)

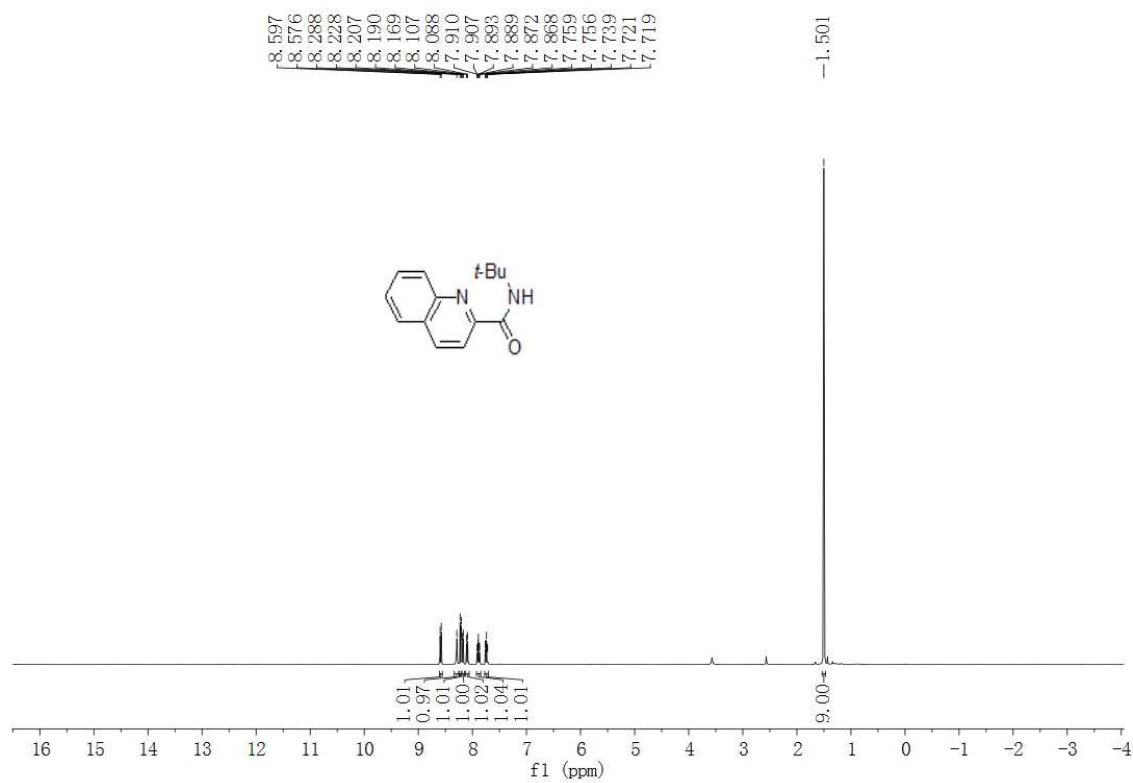


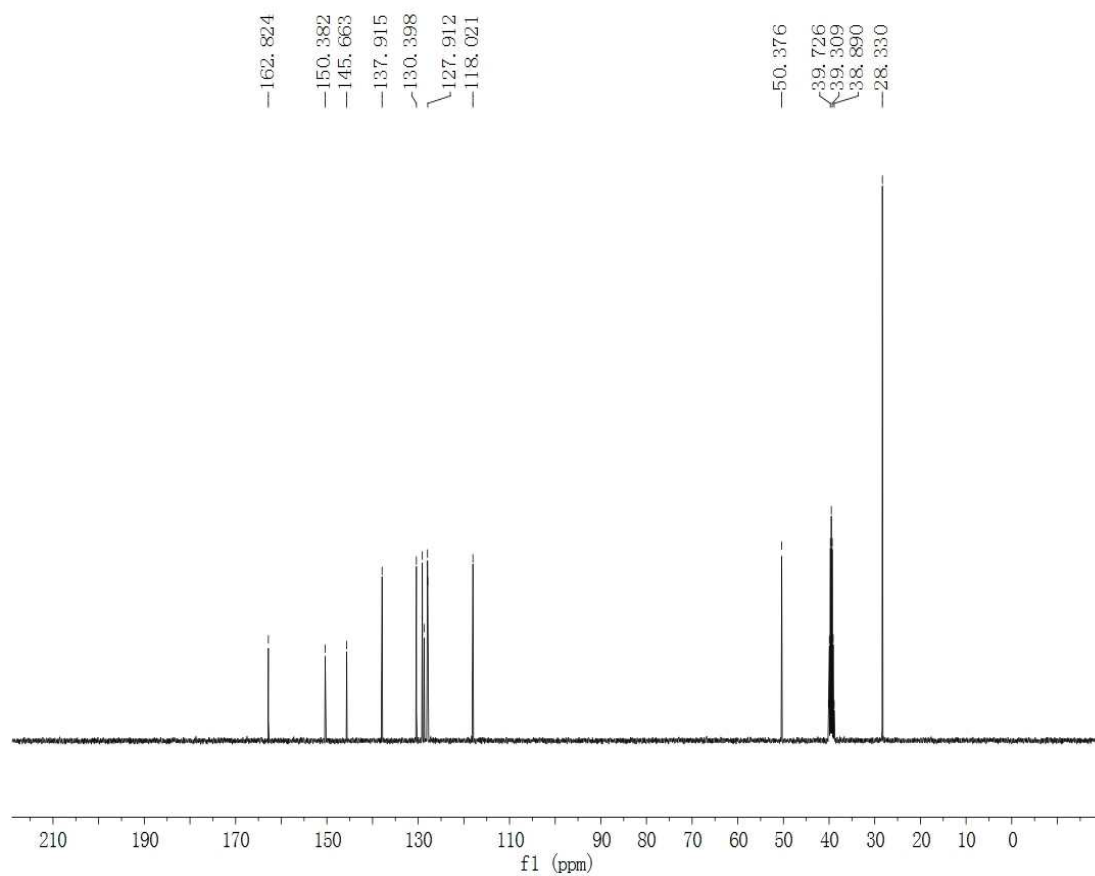
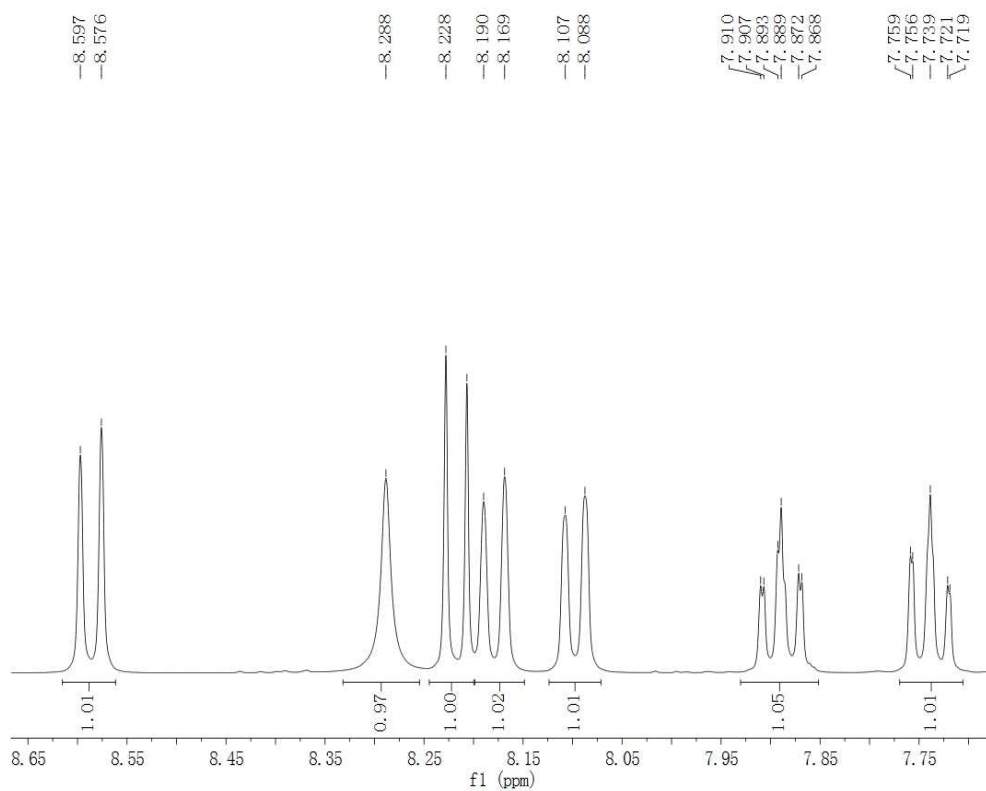
¹H NMR and ¹³C NMR of *N*-tert-butylpicolinamide (3ta)

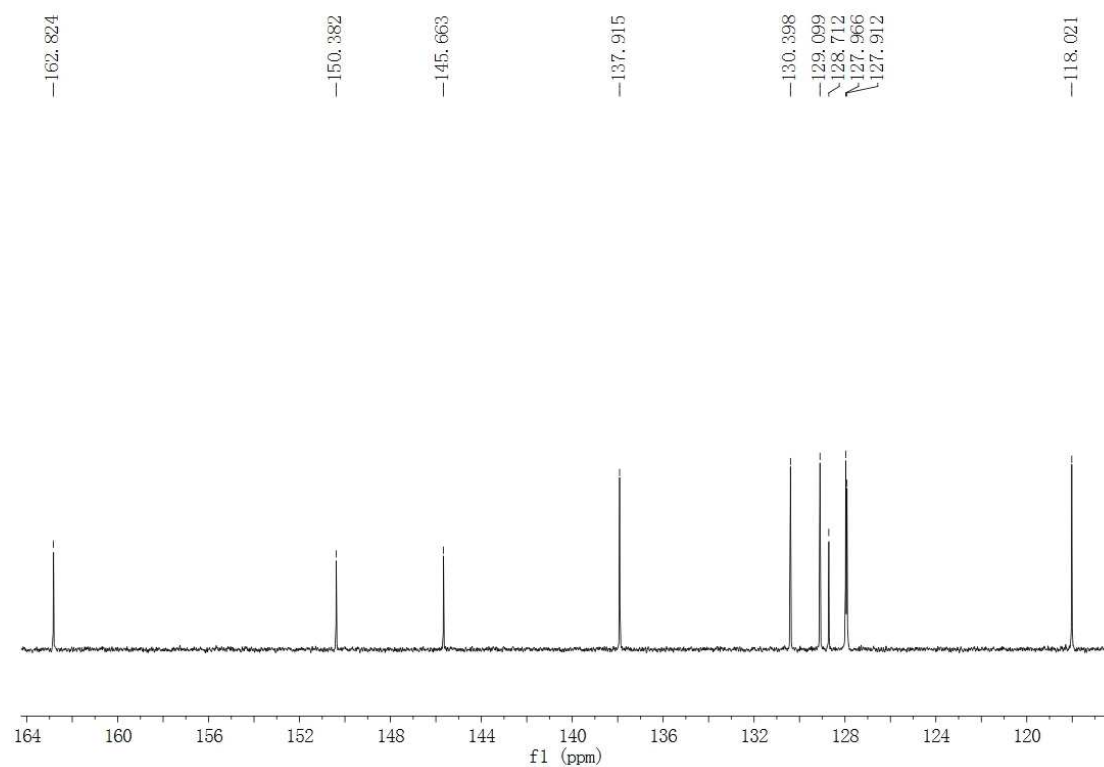




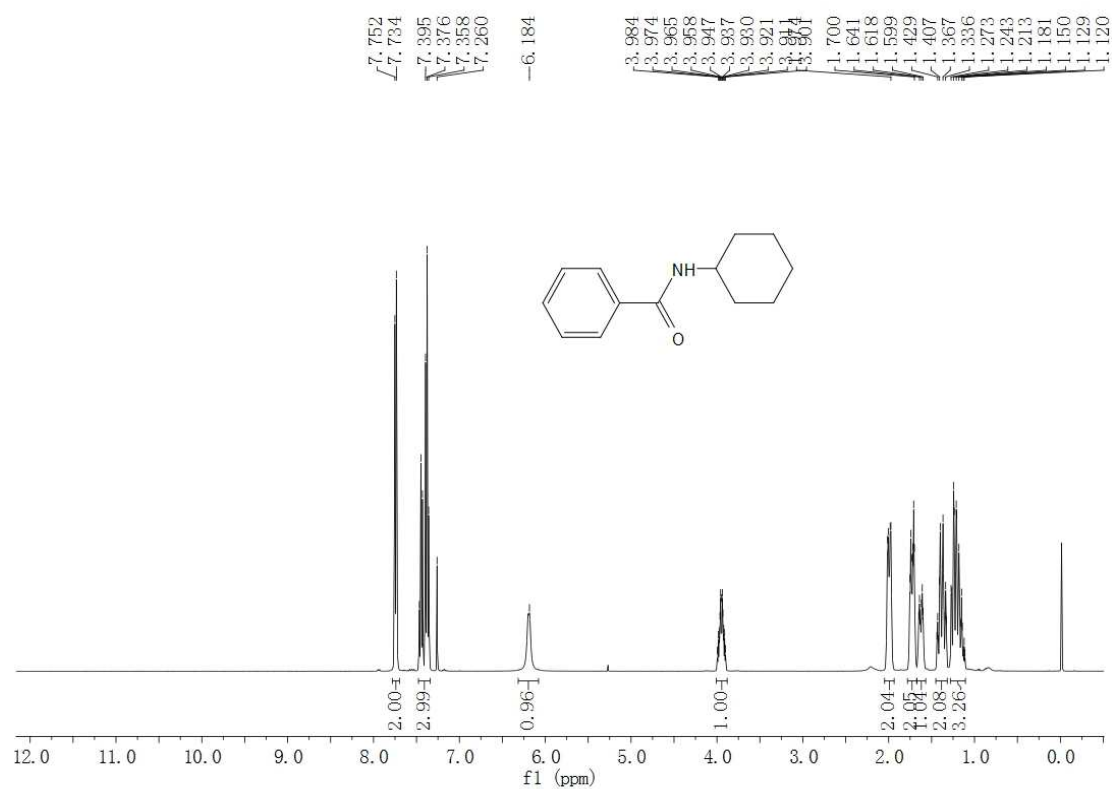
¹H NMR and ¹³C NMR of *N*-tert-butylquinoline-2-carboxamide (3ua)

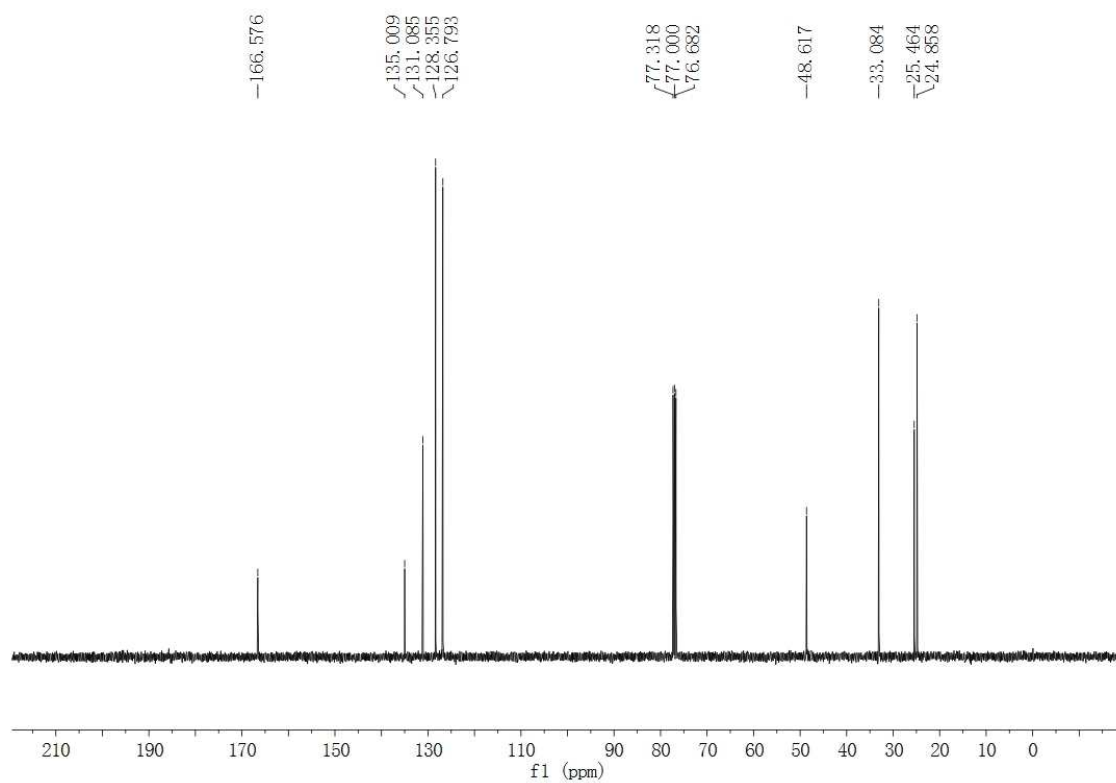




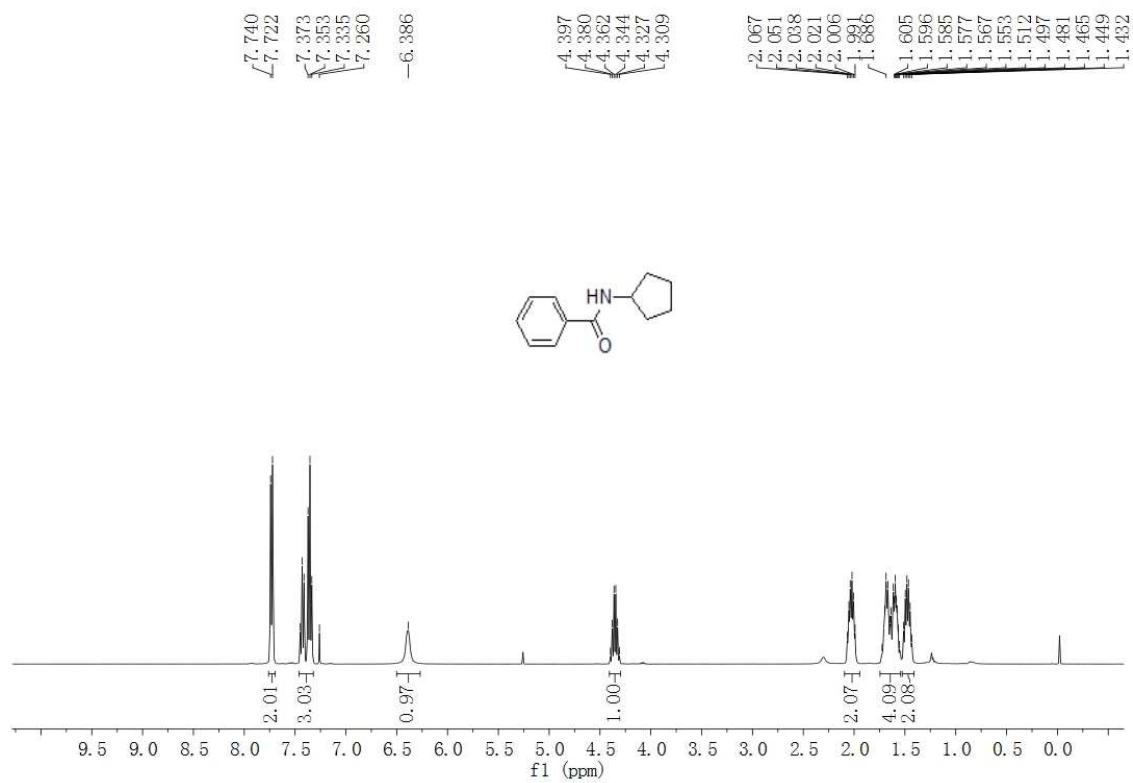


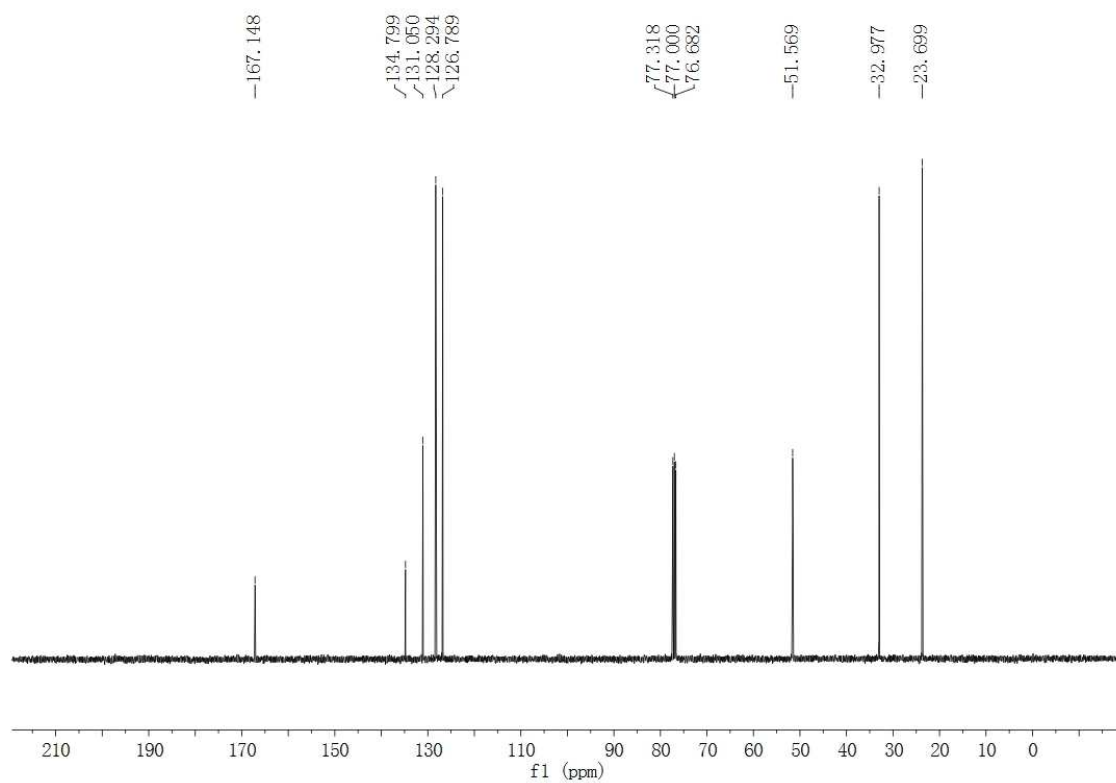
¹H NMR and ¹³C NMR of *N*-cyclohexylbenzamide (3ab)



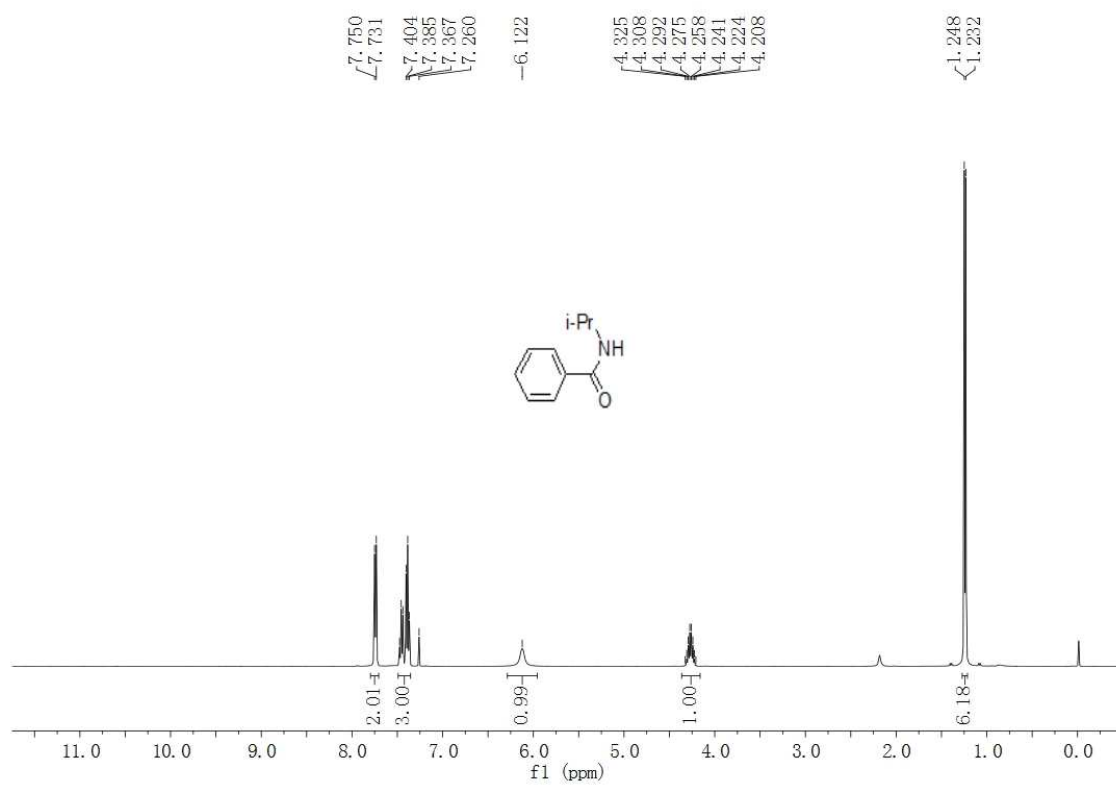


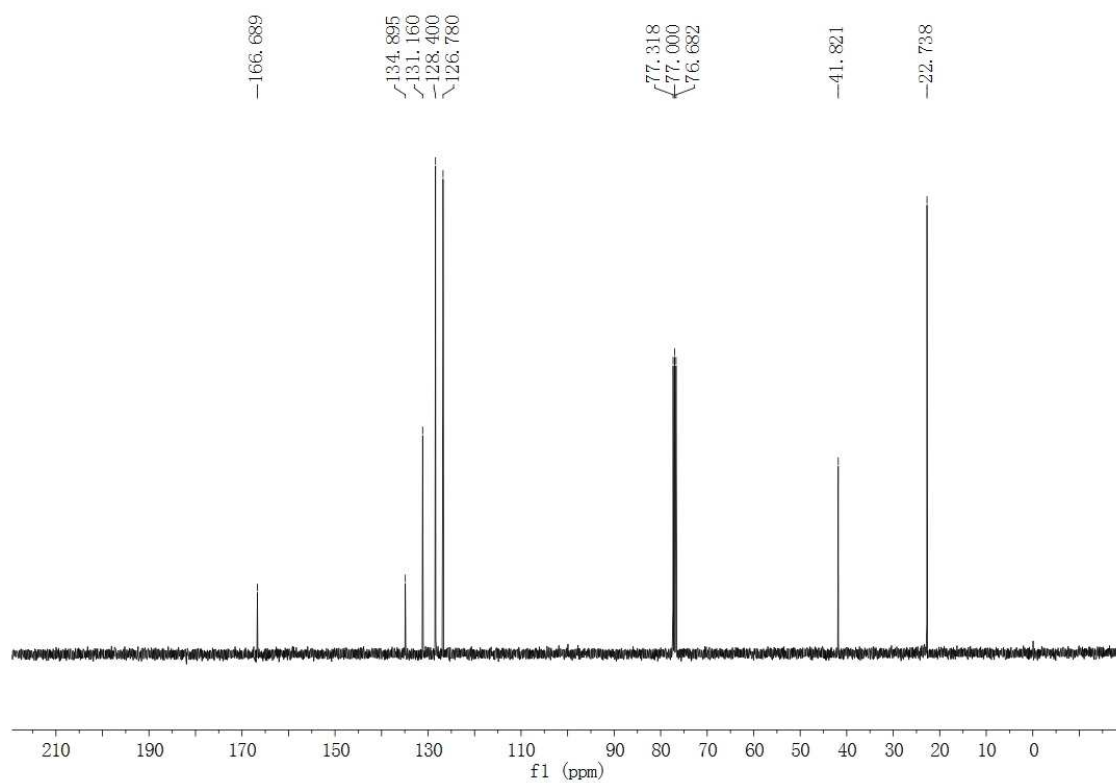
¹H NMR and ¹³C NMR of N-cyclopentylbenzamide (3ac)



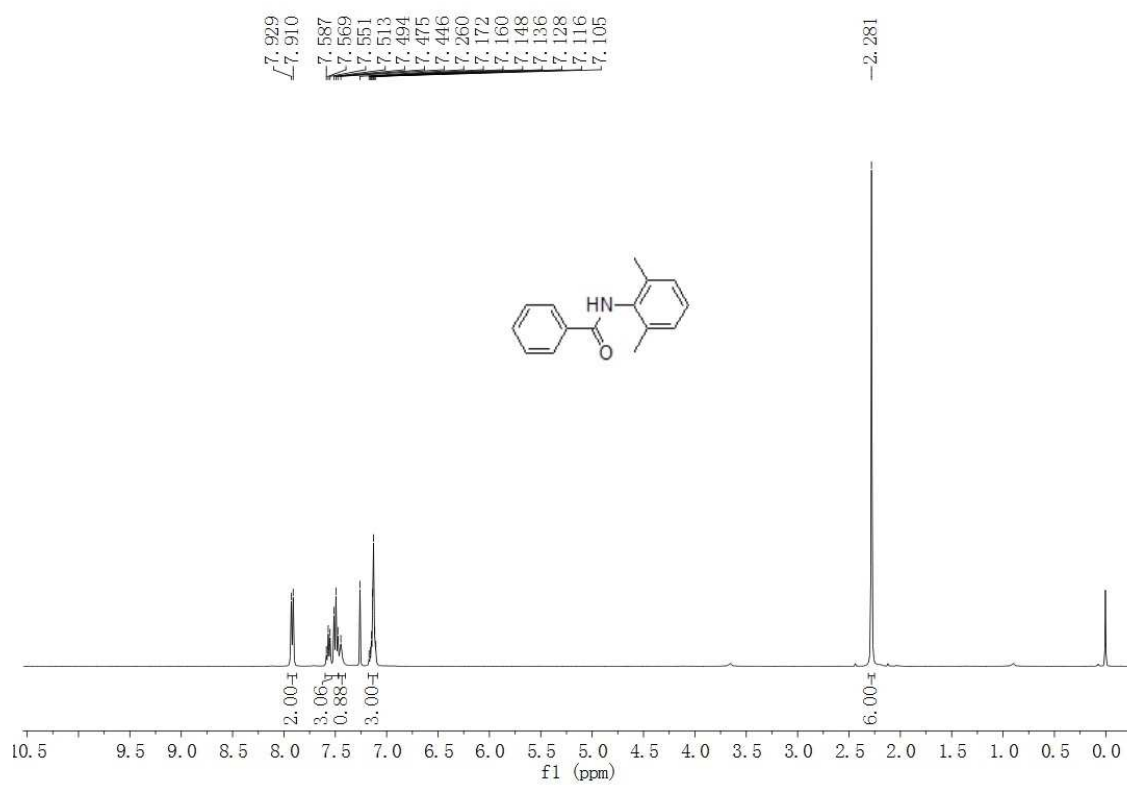


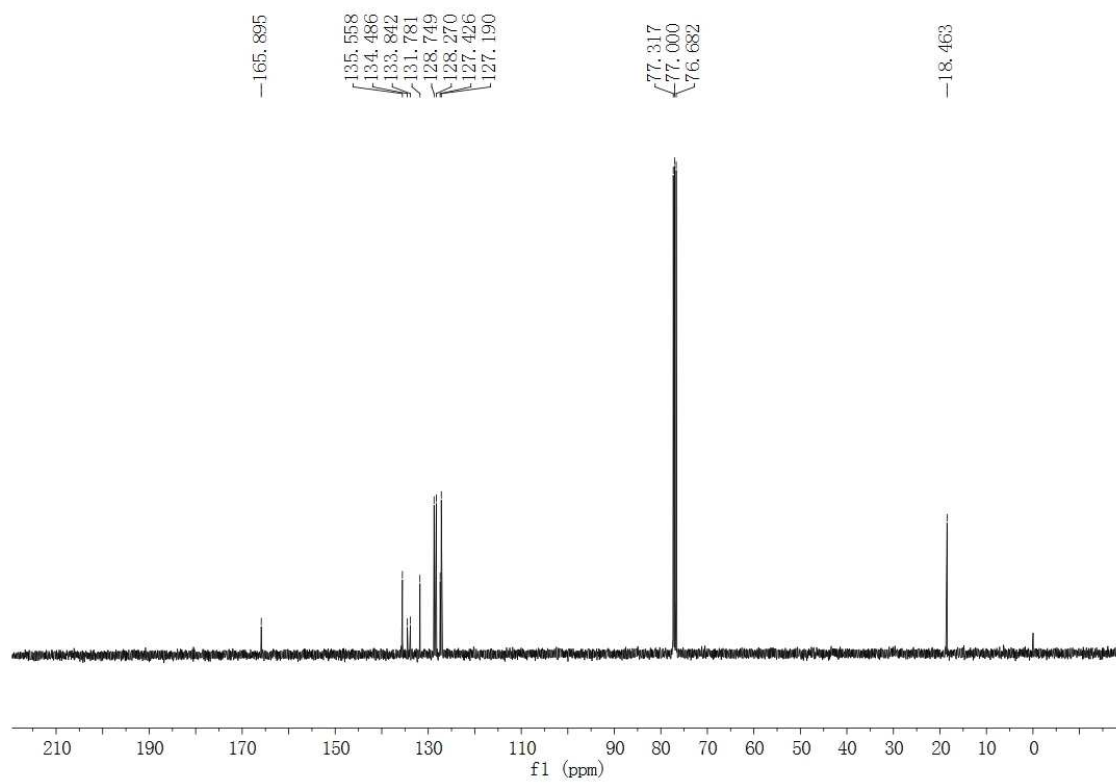
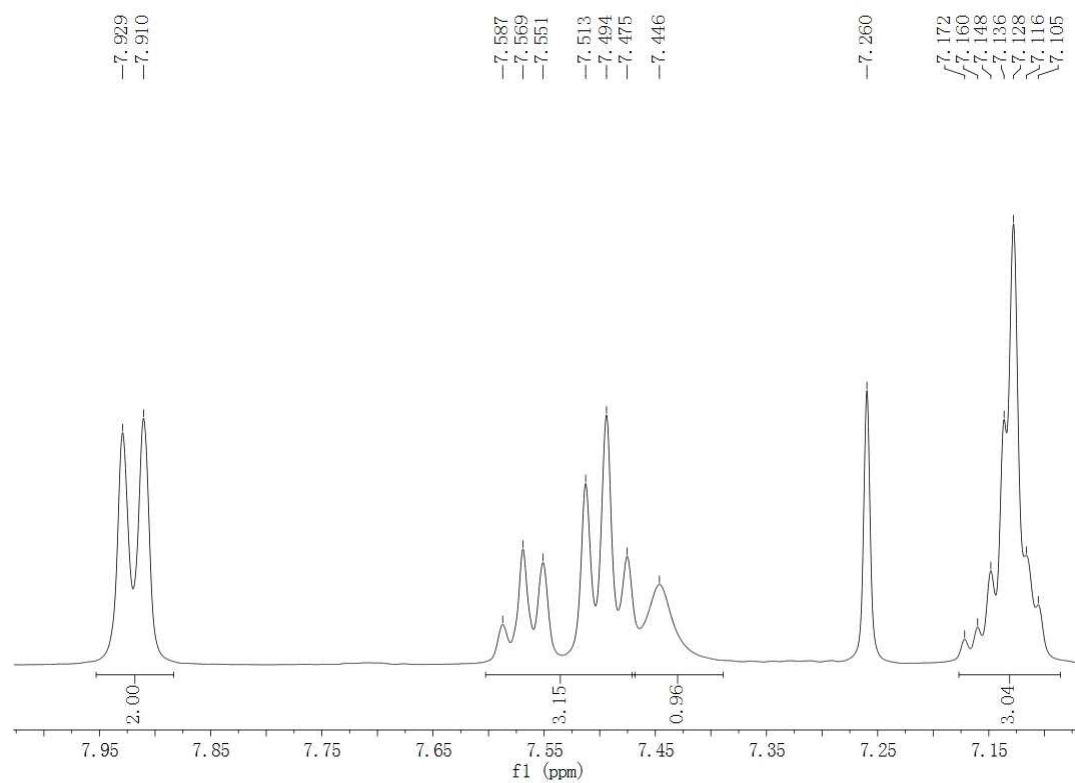
¹H NMR and ¹³C NMR of *N*-isopropylbenzamide (3ad)

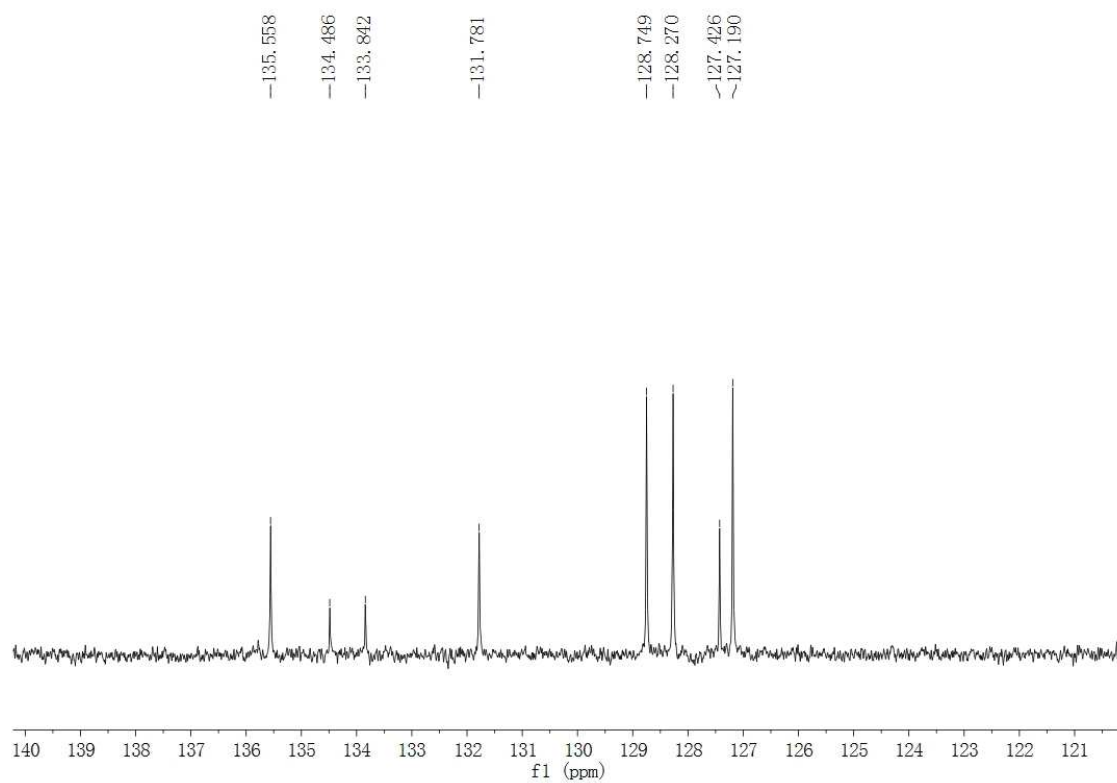




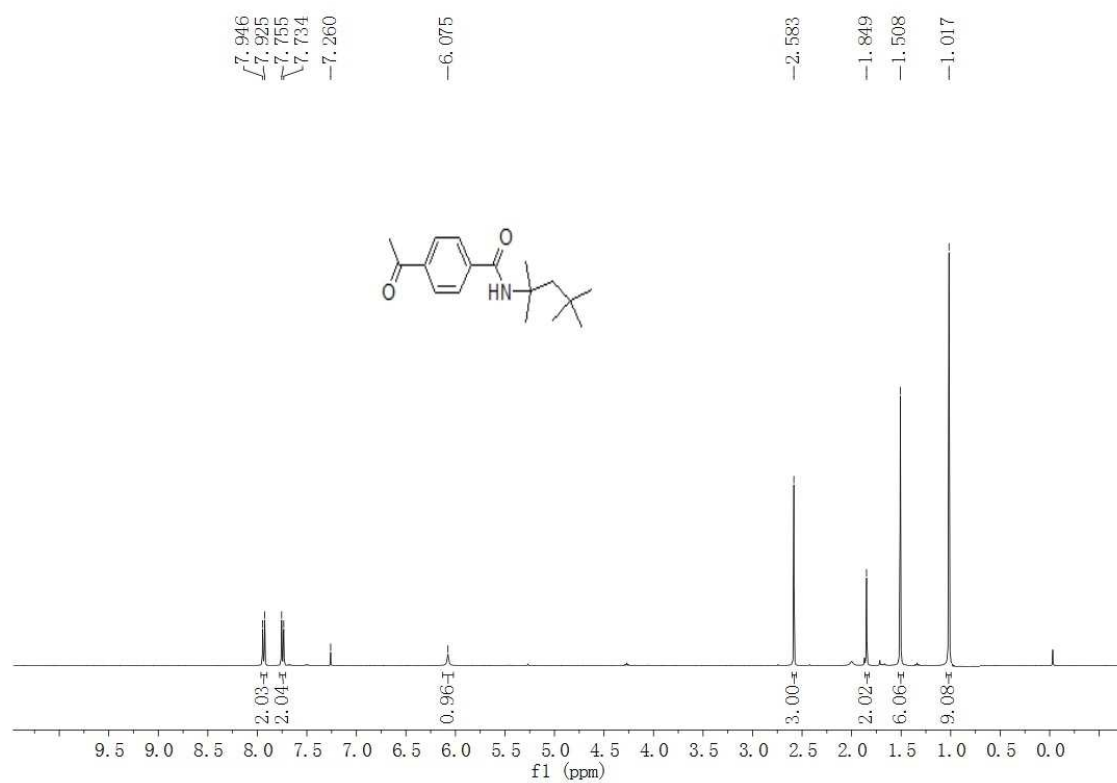
¹H NMR and ¹³C NMR of *N*-(2,6-dimethylphenyl)benzamide (3ae)

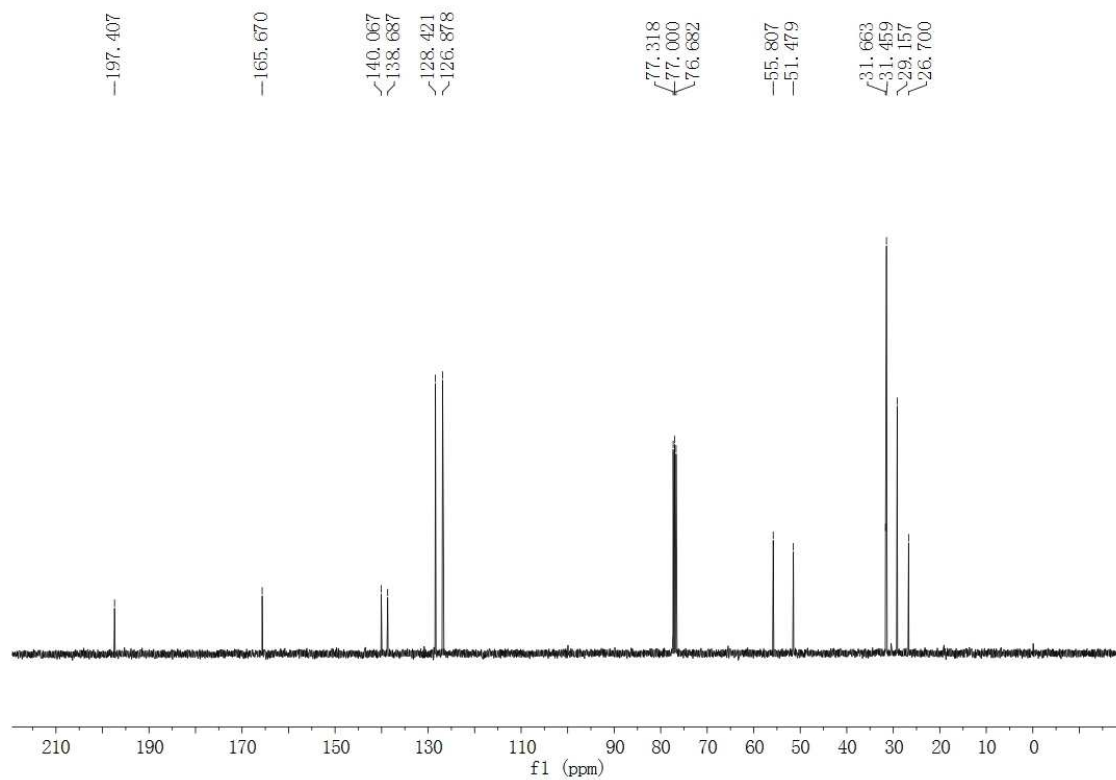




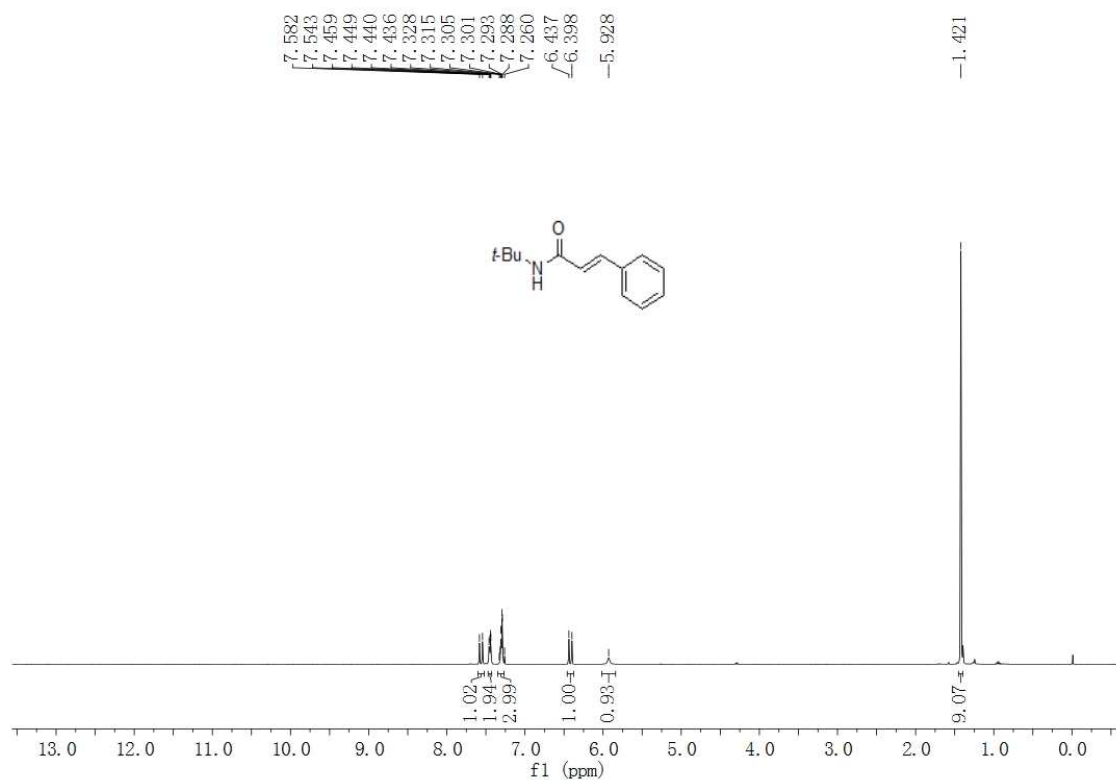


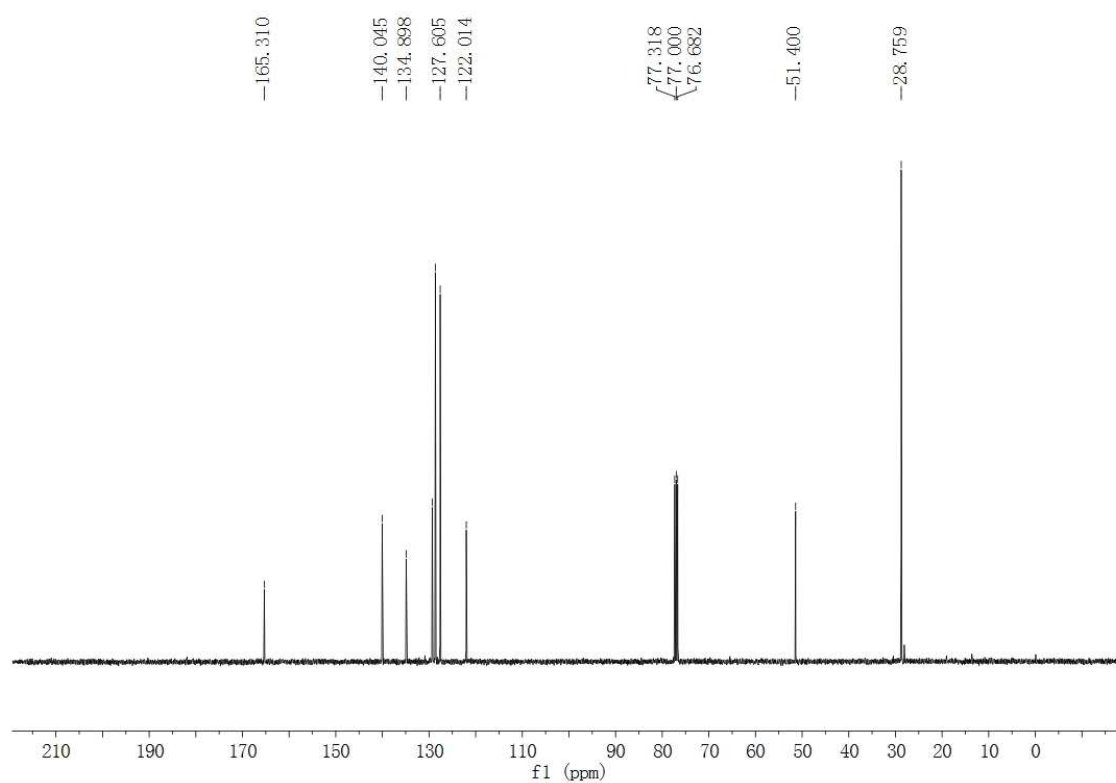
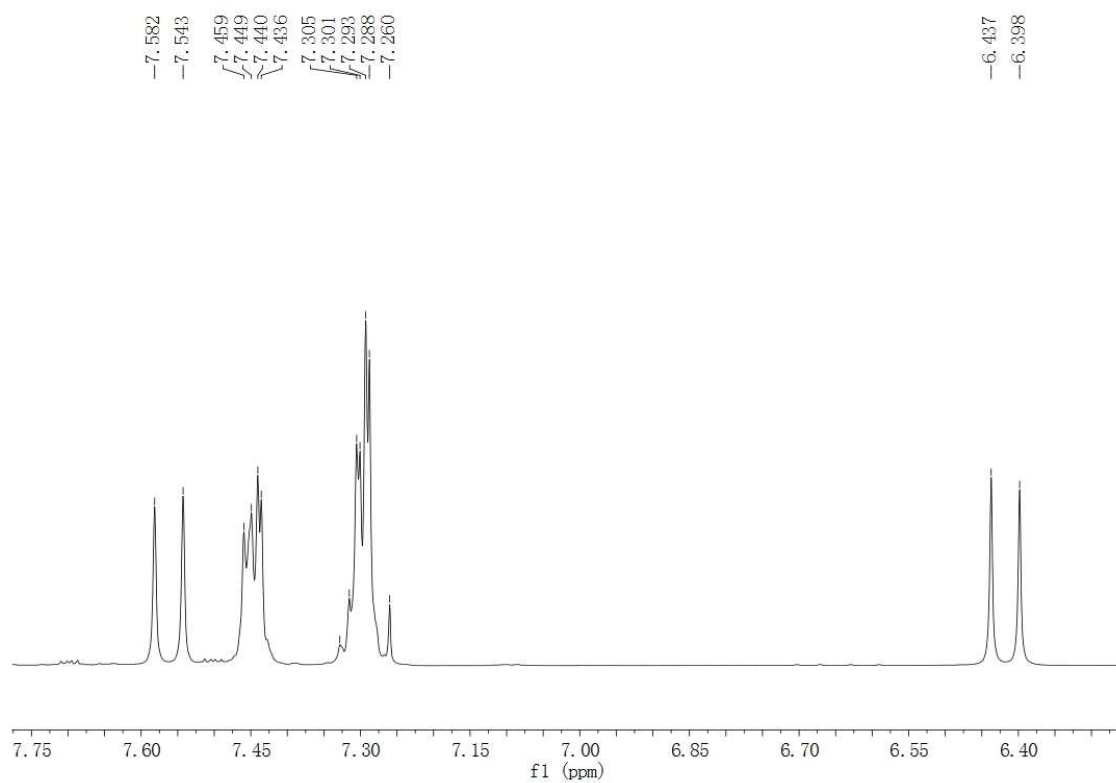
¹H NMR and ¹³C NMR of 4-acetyl-N-(2,4,4-trimethylpentan-2-yl)benzamide (3kf)

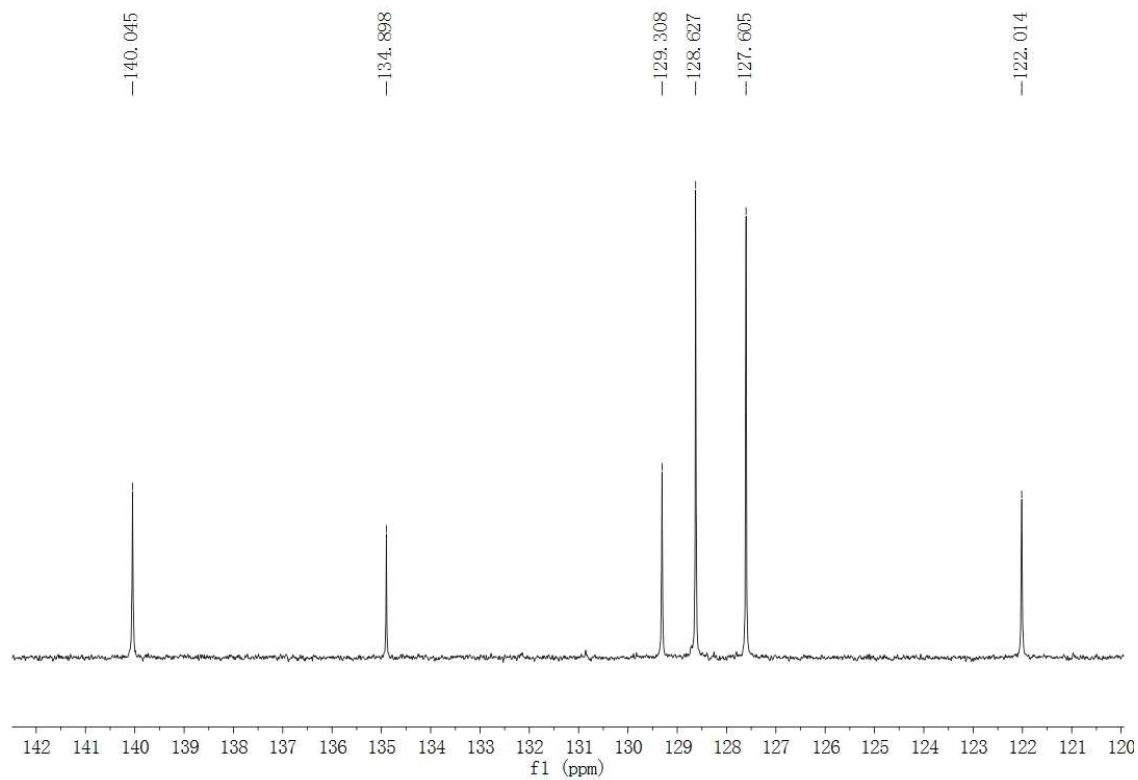




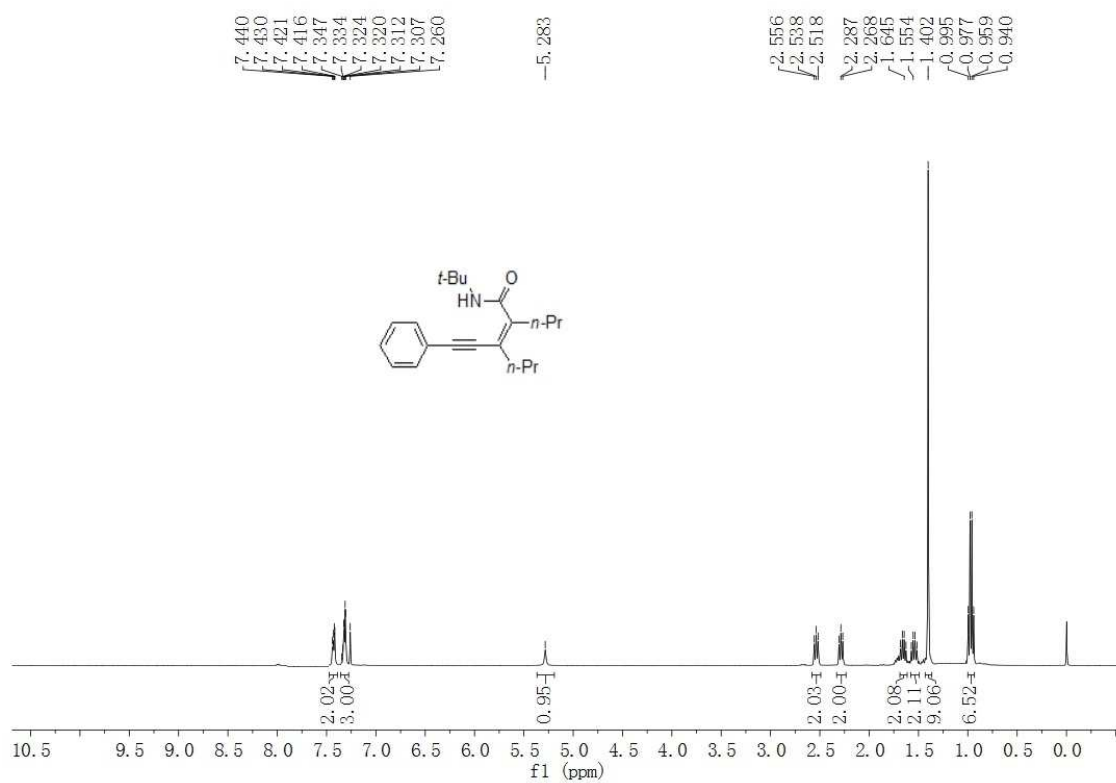
¹H NMR and ¹³C NMR of (E)-N-tert-butylcinnamamide (3va)

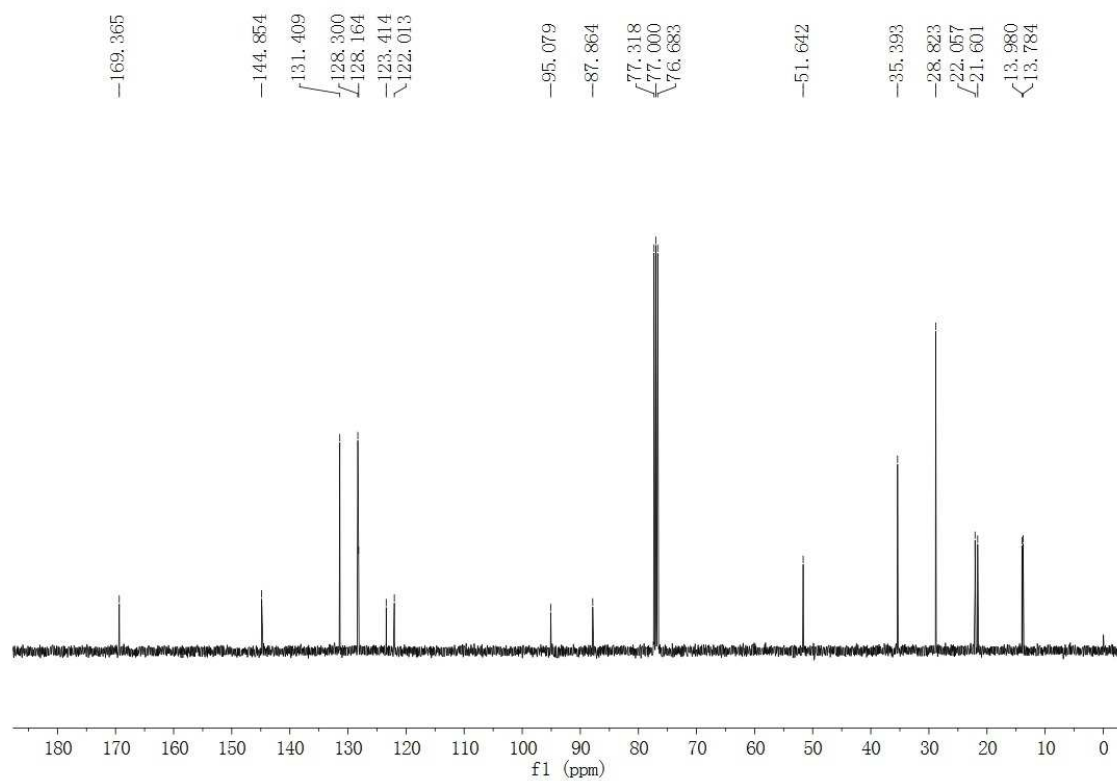
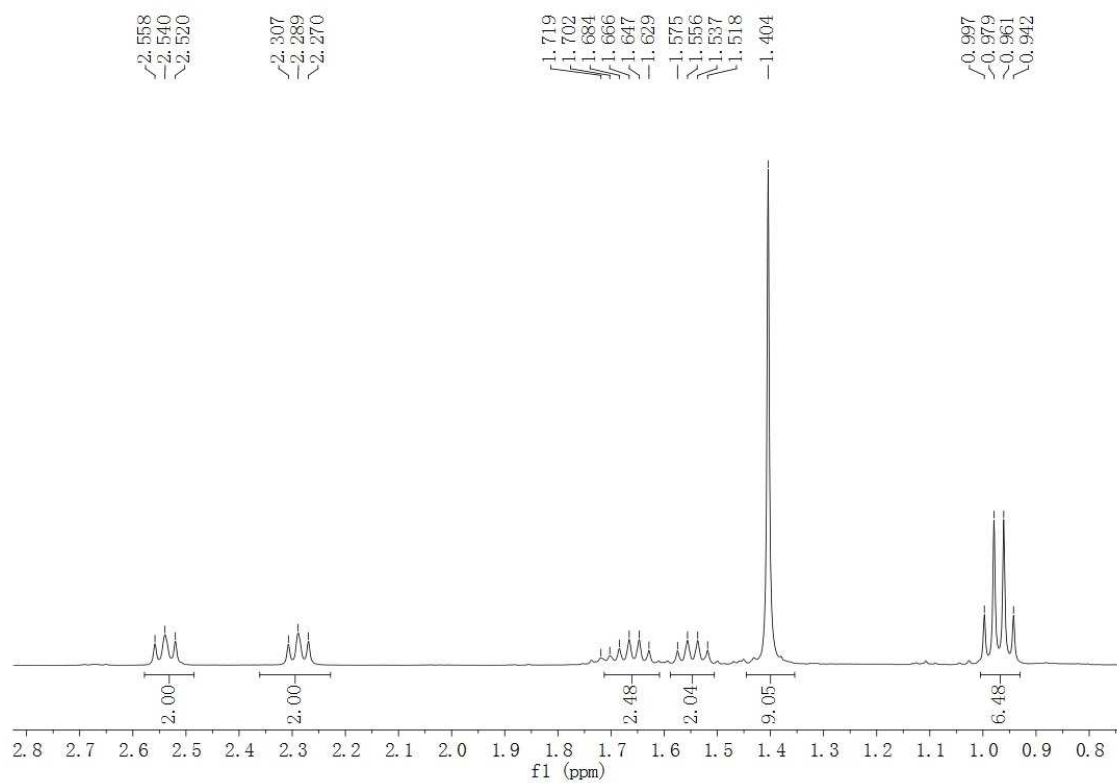




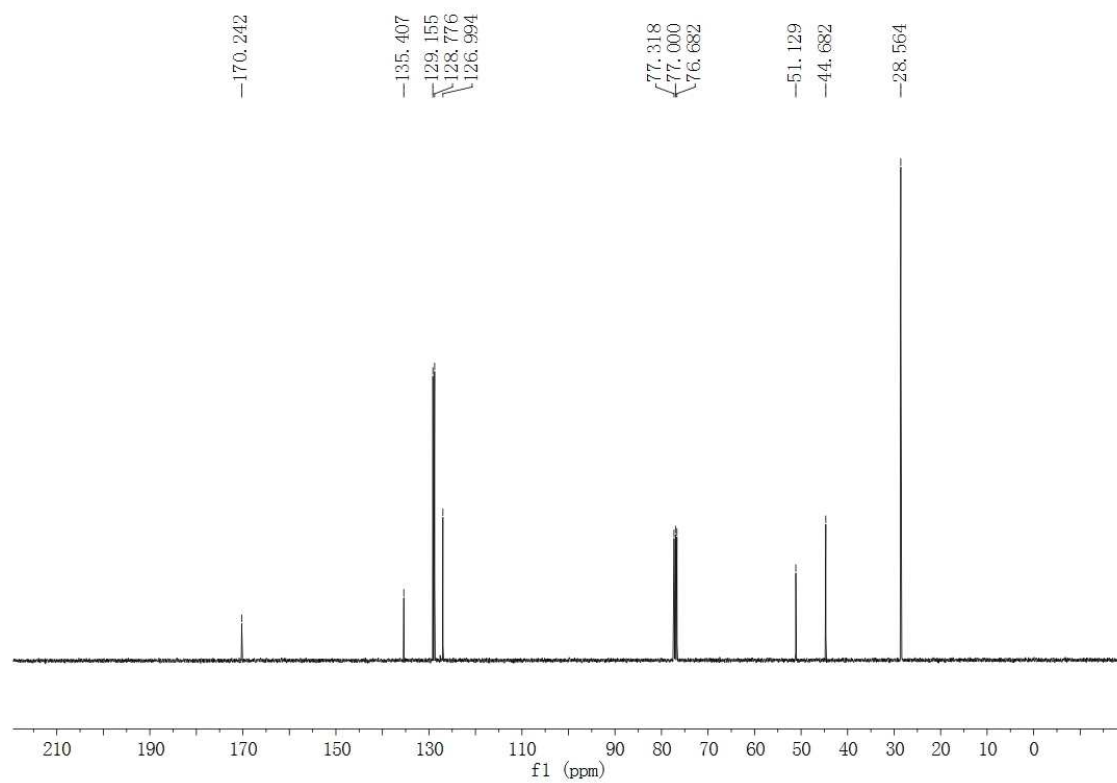
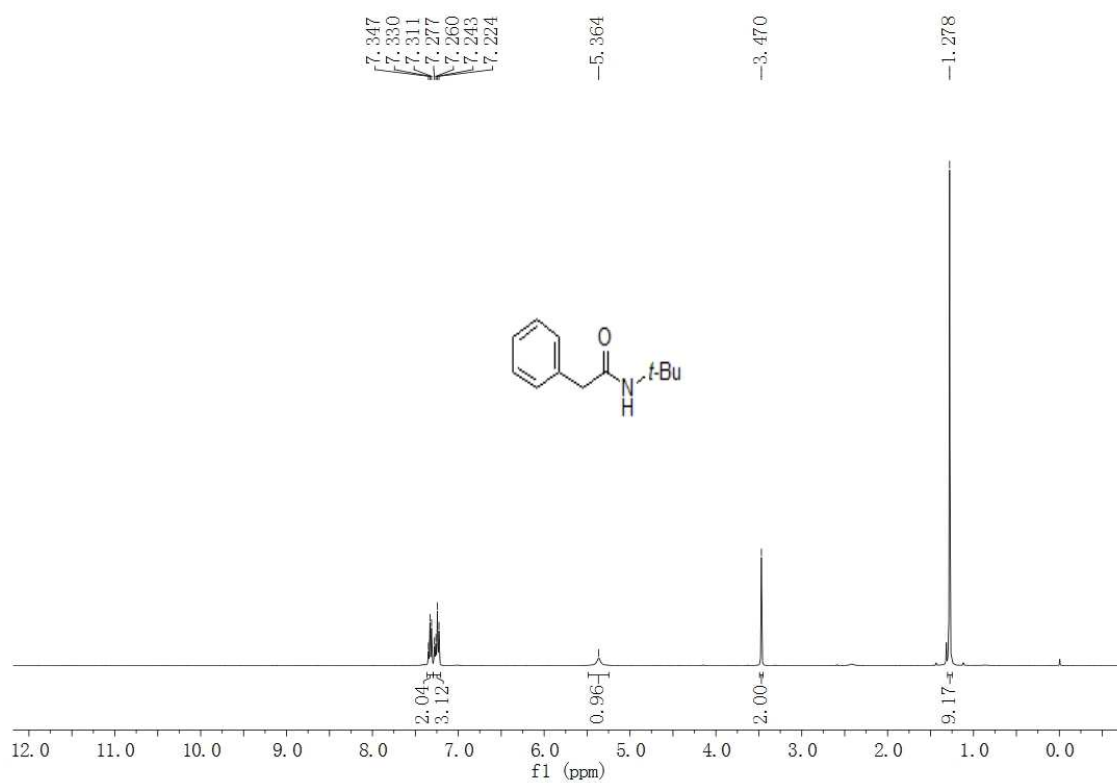


¹H NMR and ¹³C NMR of (Z)-N-tert-butyl-3-(2-phenylethynyl)-2-propylhex-2-enamide (3wa)





^1H NMR and ^{13}C NMR of *N*-tert-butyl-2-phenylacetamide (3xa)



¹H NMR and ¹³C NMR of *N*-tert-butyl-2-(4-nitrophenyl)acetamide (3ya)

