Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Visible light driven, nickel-catalyzed aryl esterification using a triplet photosensitizer thioxanthen-9-one

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Table of Contents

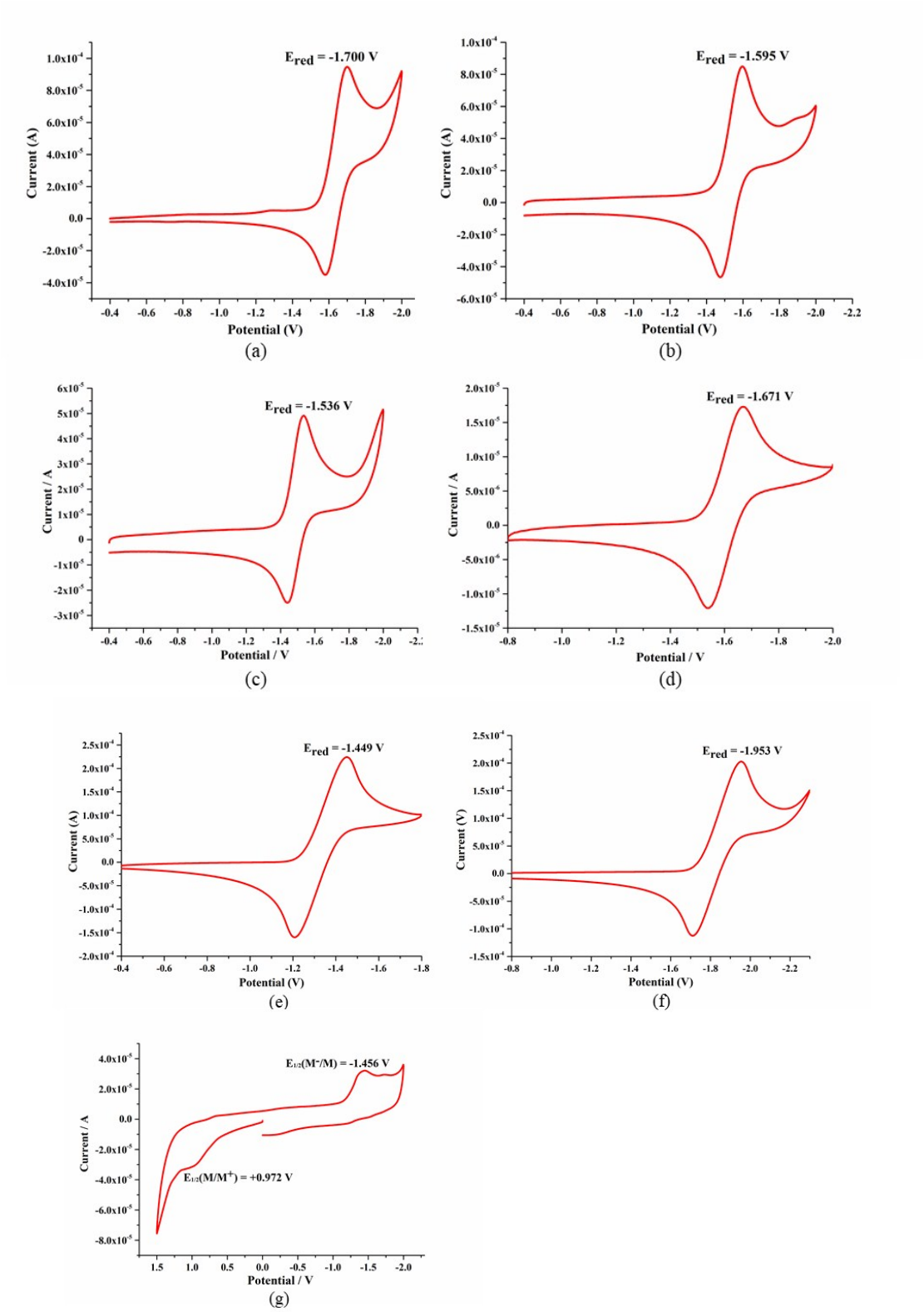


Fig. S1 Cyclic voltammograms of TXO (a), Cl-TXO (b), CF_3-TXO (c), XO (d), FLN (e), BPHO (f) (nBu_4NPF_6/MeCN electrolyte) and **4** (g) (nBu_4NPF_6/DMSO electrolyte) at 100 mV/s scan rate. Working electrode: glassy carbon electrode tip (3 mm diameter); Counter electrode: platinum wire; Reference electrode: Saturated Calomel Electrode (SCE).

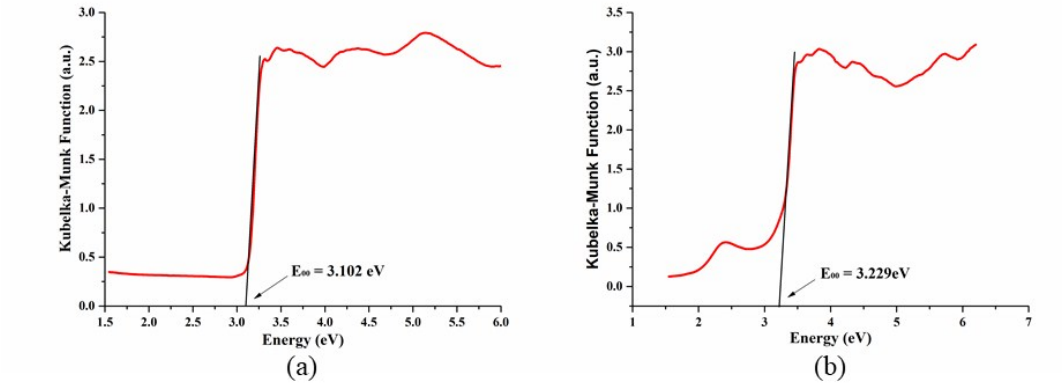
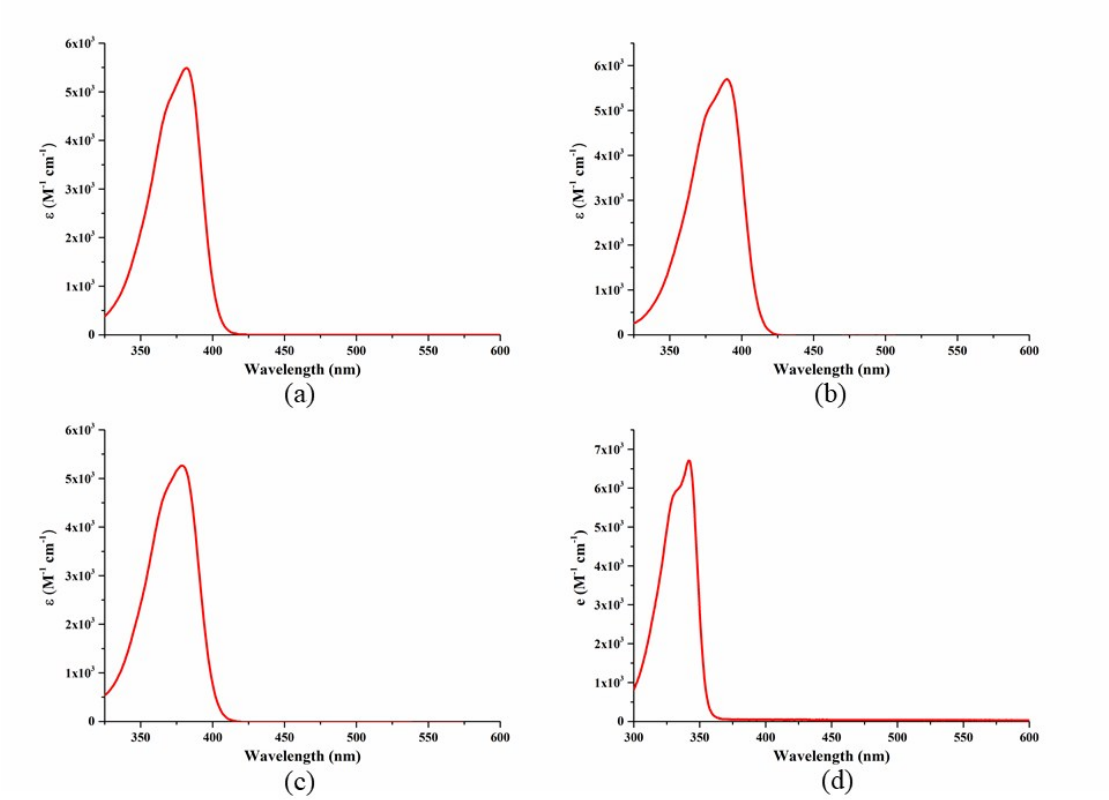


Fig. S2 Solid-state diffusion-reflection spectra of BPHO (a), XO (b) derived from diffuse reflectance data at ambient temperature.

Table S1 Electrochemical Properties of TXO, Cl-TXO, CF_3-TXO, XO, FLN and BPHO.

	E_{red} (V)	E_{00} (V)	E_{red}* (V)
TXO	-1.700	2.980	1.280
CF_3-TXO	-1.536	2.952	1.416
Cl-TXO	-1.595	2.925	1.330
FLN	-1.499	2.451	0.952
XO	-1.671	3.229	1.558
BPHO	-1.953	3.102	1.149



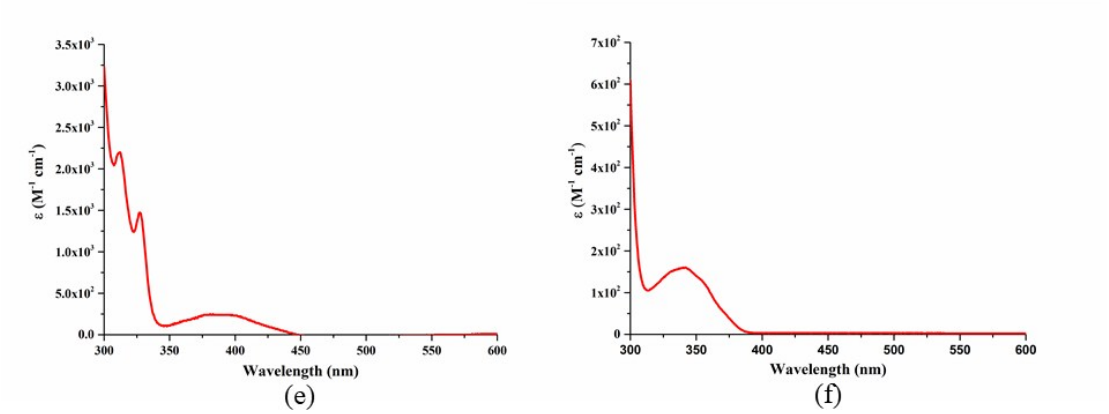
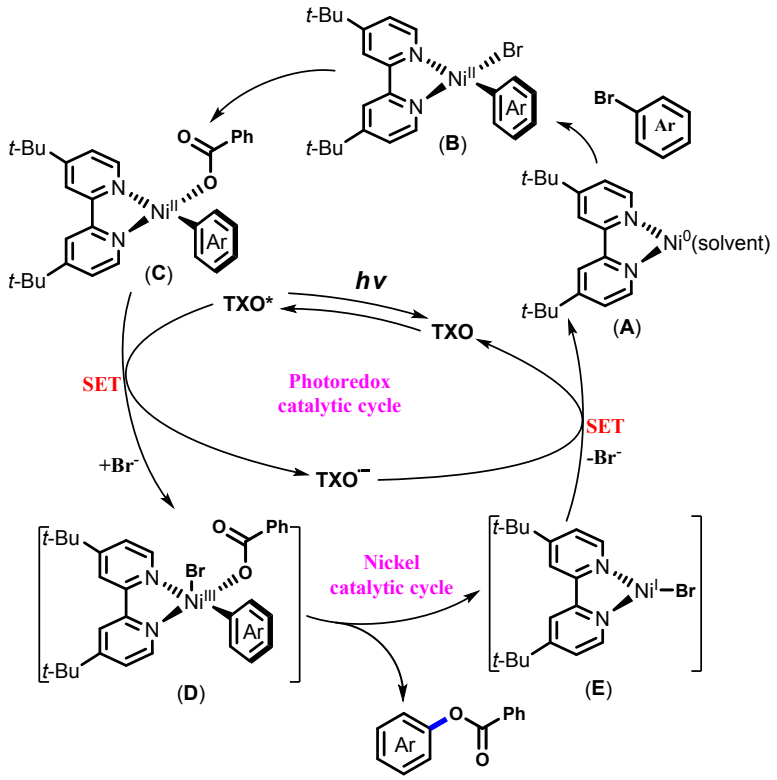


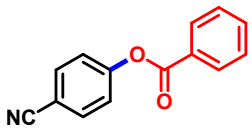
Fig. S3 UV-Vis absorption spectra of TXO (a), Cl-TXO (b), CF_3-TXO (c), XO (d), FLN (e) and BPHO (f) in DMSO (1×10^{-4} mol L^{-1}).



Scheme S1 The nickel and photoredox cycles would merge via a SET between the Ni(II) complex **C** and the oxidizing photoexcited *TXO to generate the critical Ni(III) species **D** and the reduced **TXO**$^{\bullet-}$.

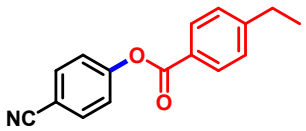
^{1}H and ^{13}C NMR data of products

4-cynaophenyl benzoate (3aa)[S1]



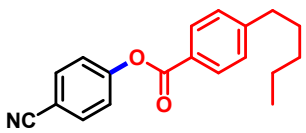
Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and benzoic acid (0.4 mmol). The crude product was purified by preparative thin-layer chromatography (TLC), using ether/ethyl acetate (EtOAc) with 100/1 (v/v) as an eluent, to yield the white solid of **3aa**. Yield: 41.0 mg (92%). M.P. = 92.2-92.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.19 (d, *J* = 7.7 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 164.5, 154.4, 134.3, 133.9, 130.4, 129.0, 128.8, 123.1, 118.4, 110.0. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{14}H_9NO_2Na^+$ 246.0525; Found 246.0498.

4-cyanophenyl 4-ethylbenzoate (3ab)[S2]



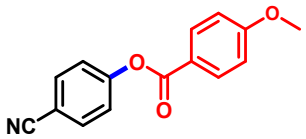
Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 4-ethylbenzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid of **3ab**. Yield: 46.2 mg (92%). M.P. = 60.3-60.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.10 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.42-7.31 (m, 4H), 2.76 (q, *J* = 7.5 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 164.5, 154.5, 151.5, 133.9, 130.6, 128.5, 126.2, 123.1, 118.5, 110.0, 29.3, 15.4. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{16}H_{13}NO_2Na^+$ 274.0838; Found 274.0864.

4-cyanophenyl 4-pentylbenzoate (3ac)[S2]



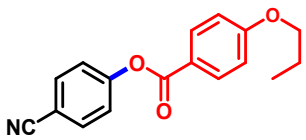
Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 4-pentylbenzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid **3ac**. Yield: 53.3 mg (91%). M.P. = 58.1-58.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.10 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.5 Hz, 2H), 7.35 (t, J = 8.9 Hz, 4H), 2.71 (t, J = 7.7 Hz, 2H), 1.67 (dd, J = 14.2, 7.3 Hz, 2H), 1.34 (d, J = 3.2 Hz, 4H), 0.90 (t, J = 6.5, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 164.6, 154.6, 150.3, 133.9, 130.6, 129.0, 126.2, 123.1, 118.5, 109.9, 36.3, 31.6, 30.9, 22.7, 14.2. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{19}H_{19}NO_2Na^+$ 316.1308; Found 316.1343.

4-cyanophenyl 4-methoxybenzoate (3ad)[S3]



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 4-methoxybenzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid **3ad**. Yield: 47.1 mg (93%). M.P. = 109.2-109.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.13 (d, J = 8.8 Hz, 2H), 7.72 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 164.5, 164.1, 154.6, 133.8, 132.6, 123.1, 120.9, 118.5, 114.2, 109.7, 55.7. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{15}H_{11}NO_3Na^+$ 276.0631; Found 276.0663.

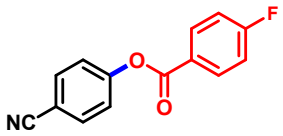
(4-cyanophenyl) 4-propoxybenzoate (3ae)



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 4-propoxybenzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid **3ae**. Yield: 51.7 mg (92%). M.P. = 99.8-100.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.6 Hz, 2H), 7.72 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.6 Hz, 2H), 4.01 (t, J = 6.5 Hz, 2H), 1.92-1.80 (m, 2H), 1.06 (d, J = 14.8

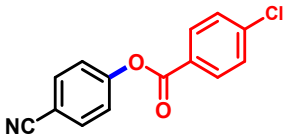
Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.1, 154.6, 133.8, 132.6, 123.1, 120.7, 118.5, 114.6, 109.7, 70.0, 29.9, 22.6, 10.6. IR (KBr disk) 2963, 2926, 2882, 2232, 1720, 1603, 1576, 1511, 1498, 1473, 1421 1301, 1260, 1205, 1167, 1063, 1040, 1008, 880, 847, 764, 696, 554 cm^{-1}. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{17}H_{15}NO_3Na^+$ 304.0944; Found 304.0930.

4-cyanophenyl 4-fluorobenzoate (3af)[S4]



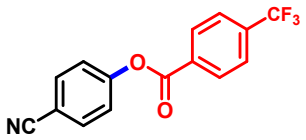
Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 4-fluorobenzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/ethyl acetate (EtOAc) = 100/1 (v/v) as an eluent, to yield the white solid **3af**. Yield: 43.9 mg (91%). M.P. = 99.1-99.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.22 (dd, *J* = 7.2, 5.9 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.21 (t, *J* = 8.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 166.6 (d, *J* = 256.7 Hz), 163.5, 154.2, 133.9, 133.1 (d, *J* = 10.6 Hz), 125.5 (d, *J* = 3.0 Hz), 123.0, 118.4, 116.3 (d, *J* = 22.7 Hz), 110.1. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{14}H_8FNO_2Na^+$ 264.0431; Found 264.0432.

4-cyanophenyl 4-chlorobenzoate (3ag)[S3]



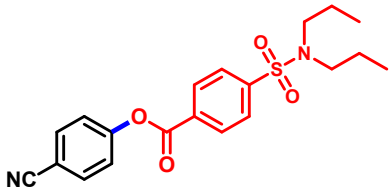
Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 4-chlorobenzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid of **3ag**. Yield: 45.2 mg (88%). M.P. = 113.4-113.9°C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.12 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 163.7, 154.2, 141.0, 133.9, 131.8, 129.4, 127.3, 123.0, 118.4, 110.2. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{14}H_8FNO_2Na^+$ 280.0136; Found 280.0123.

4-trifluoromethylphenyl 4-cyanobenzoate (3ah)[S5]



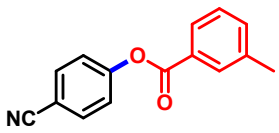
Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 4-(trifluoromethyl)benzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid of **3ah**. Yield: 43.7 mg (75%). M.P. = 124.7-125.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.32 (d, J = 8.0 Hz, 2H), 7.79 (dd, J = 15.5, 8.3 Hz, 4H), 7.40 (d, J = 8.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 163.3, 154.0, 135.8 (q, J = 32.9 Hz), 134.0, 132.1, 130.9, 126.0, 124.5 (q, J = 273.3 Hz), 122.9, 118.3, 110.5. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{15}H_8F_3NO_2Na^+$ 314.0399; Found 314.0382.

4-cyanophenyl 4-(N,N-dipropylsulfamoyl)benzoate (3ai)



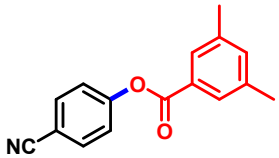
Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 4-(N,N-dipropylsulfamoyl)benzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid of **3ai**. Yield: 47.1 mg (61%). M.P. = 104.5-105.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.30 (d, J = 8.2 Hz, 2H), 7.96 (d, J = 8.3 Hz, 2H), 7.76 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 3.19-3.07 (m, 4H), 1.64-1.48 (m, 4H), 0.88 (t, J = 7.3 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 163.2, 154.0, 145.7, 135.8, 134.0, 132.1, 131.1, 127.5, 122.9, 118.3, 110.5, 50.1, 22.1, 11.3. IR (KBr disk) 2963, 2974, 2873, 2225, 1741, 1599, 1498, 1465, 1399, 1342, 1293, 1257, 1218, 1181, 1168, 1158, 1090, 1074, 1012, 988, 857, 798, 748, 722, 600, 571, 553 cm^{-1}. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{20}H_{22}N_2O_4SNa^+$ 409.1192; Found 409.1170.

4-cyanophenyl 3-methylbenzoate (3aj)



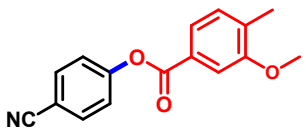
Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 3-methylbenzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid of **3aj**. Yield: 41.7 mg (88%). M.P. = 81.1-81.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 164.6, 154.5, 138.8, 135.1, 133.9, 130.9, 128.8, 128.7, 127.6, 123.1, 118.4, 109.9, 21.4. IR (KBr disk) 2960, 2922, 2230, 1729, 1600, 1584, 1500, 1410, 1384, 1277, 1212, 1186, 1166, 1086, 901, 865, 813, 797, 732, 681, 553, 534, 496 cm^{-1}. HRMS (QTOF-MS) *m/z* m/z [M + Na]$^+$ Calcd for $C_{15}H_{11}NO_2Na^+$ 260.0682; Found 260.0679.

4-cyanophenyl 3,5-dimethylbenzoate (3ak)



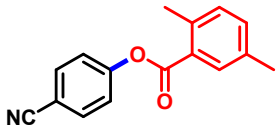
Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 3,5-dimethylbenzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid of **3ak**. Yield: 45.2 mg (90%). M.P. = 123.5-124.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.80 (s, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.30 (s, 1H), 2.41 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 164.8, 154.6, 138.7, 136.0, 133.9, 128.7, 128.2, 123.1, 118.5, 109.9, 21.4. IR (KBr disk) 2962, 2920, 2229, 1726, 1611, 1599, 1504, 1458, 1408, 1378, 1311, 1261, 1192, 1184, 1163, 1020, 911, 863, 802, 754, 673, 545 cm^{-1}. HRMS (QTOF-MS) *m/z* [M + Na]$^+$ Calcd for $C_{16}H_{13}NO_2Na^+$ 274.0838; Found 274.0862.

4-cyanophenyl 3-methoxy-4-methylbenzoate (3al)



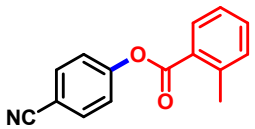
Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 3-methoxy-4-methylbenzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid of **3al**. Yield: 47.5 mg (89%). M.P. = 108.8-109.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.74 (t, *J* = 6.9, 3H), 7.58 (s, 1H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 3.92 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 164.6, 158.0, 154.5, 134.4, 133.8, 130.9, 127.4, 123.1, 122.9, 118.5, 111.0, 109.9, 55.7, 16.8. IR (KBr disk) 2992, 2230, 1740, 1603, 1584, 1505, 1465, 1454, 1411, 1373, 1292, 1278, 1224, 1169, 1138, 1083, 1035, 916, 881, 859, 799, 723, 574 cm^{-1}. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{16}H_{13}NO_3Na^+$ 290.0788; Found 290.0782.

4-cyanophenyl 2,5-dimethylbenzoate (3am)



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 2,5-dimethylbenzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid of **3am**. Yield: 42.2 mg (84%). M.P. = 83.0-84.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.96 (s, 1H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.39-7.30 (m, 3H), 7.22 (d, *J* = 7.7 Hz, 1H), 2.61 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 165.0, 154.5, 138.8, 135.9, 134.3, 133.8, 132.3, 131.8, 127.4, 123.2, 118.5, 109.8, 21.7, 21.0. IR (KBr disk) 298, 2228, 1735, 1600, 1569, 1496, 1410, 1382, 1302, 1289, 1253, 1213, 1181, 1170, 1158, 1041, 990, 916, 857, 822, 801, 768, 677, 548, 513 cm^{-1}. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{16}H_{13}NO_2Na^+$ 274.0838; Found 274.0832.

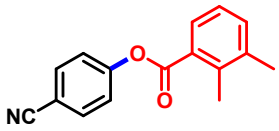
4-cyanophenyl 2-methylbenzoate (3an)



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 2-methylbenzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1

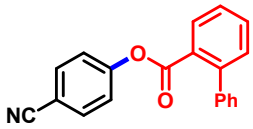
(v/v) as an eluent, to yield the white solid of **3an**. Yield: 43.1 mg (91%). M.P. = 82.3-83.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.16 (d, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 4H), 2.67 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 164.9, 154.5, 142.0, 133.9, 133.5, 132.4, 131.5, 127.7, 126.3, 123.2, 118.5, 109.9, 22.2. IR (KBr disk) 2962, 2924, 2852, 2229, 1741, 1603, 1577, 1499, 1458, 1411, 1382, 1288, 1261, 1217, 1169, 1140, 1097, 1042, 874, 802, 732, 687, 663, 547 cm^{-1}. HRMS (QTOF-MS) *m/z* [M + Na]$^{+}$ Calcd for $C_{15}H_{11}NO_2Na^{+}$ 260.0682; Found 260.0673.

4-cyanophenyl 2,3-dimethylbenzoate (3ao)



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 2,3-dimethylbenzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid of **3ao**. Yield: 44.2 mg (88%). M.P. = 96.5-97.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.91 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.23 (dd, *J* = 13.6, 5.8 Hz, 1H), 2.54 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 165.8, 154.5, 139.5, 138.7, 134.7, 133.9, 128.8, 128.7, 125.6, 123.2, 118.5, 109.8, 20.8, 16.9. IR (KBr disk) 2920, 2231, 1735, 1603, 1584, 1505, 1458, 1384, 1296, 1296, 1260, 1245, 1220, 1198, 1174, 1128, 1092, 1017, 893, 861, 833, 817, 803, 777, 748, 623, 554 cm^{-1}. HRMS (QTOF-MS) *m/z* [M + Na]$^{+}$ Calcd for $C_{16}H_{13}NO_2Na^{+}$ 274.0838; Found 274.0839.

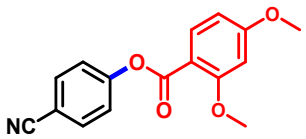
4-cyanophenyl [1,1'-biphenyl]-2-carboxylate (3ap)



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and [1,1'-biphenyl]-2-carboxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid of **3ap**. Yield: 43.7 mg (73%).

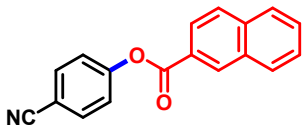
M.P. = 115.1-116.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.69-7.56 (m, 3H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.45 (dd, *J* = 13.6, 6.7 Hz, 3H), 7.40 (d, *J* = 6.9 Hz, 3H), 6.95 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 166.3, 154.0, 143.3, 141.3, 133.6, 132.5, 131.1, 130.6, 129.5, 128.6, 128.5, 127.7, 127.6, 122.5, 118.4, 109.7. IR (KBr disk) 2924, 2226, 1720, 1596, 1494, 1275, 1237, 1200, 1157, 1113, 1085, 1075, 1039, 1011, 889, 816, 773, 747, 700, 652, 552 cm^{-1}. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{20}H_{13}NO_2Na^+$ 322.0838; Found 322.0849.

4-cyanophenyl 2,4-dimethoxybenzoate (3aq)



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 2,4-dimethoxybenzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid of **3aq**. Yield: 45.8 mg (81%). M.P. = 135.6-136.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.05 (d, *J* = 8.7 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 6.56 (dd, *J* = 13.5, 4.7 Hz, 2H), 3.92 (s, 3H), 3.89 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 165.7, 162.8, 162.7, 154.7, 134.9, 133.7, 123.3, 118.7, 110.3 109.4, 105.2, 99.2, 56.2, 55.8. IR (KBr disk) 2956, 2924, 2848, 2227, 1751, 1617, 1601, 1573, 1508, 1495, 1473, 1453, 1444, 1306, 1270, 1247, 1215, 1187, 1168, 1156, 1044, 1018, 860, 824, 754, 683, 648, 623, 548 cm^{-1}. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{16}H_{13}NO_4Na^+$ 306.0737; Found 306.0732.

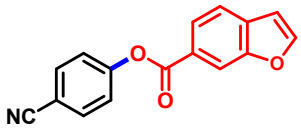
4-cyanophenyl 2-naphthoate (3ar)



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 2-naphthoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid of **3ar**. Yield: 36.0 mg (66%). M.P. = 134.4.135.1 °C. ^{1}H

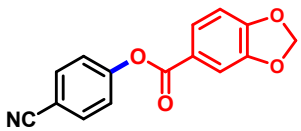
NMR (400 MHz, $CDCl_3$, ppm) δ 8.79 (s, 1H), 8.17 (d, *J* = 8.6 Hz, 1H), 8.04-7.91 (m, 3H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.67 (t, *J* = 7.3 Hz, 1H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 164.7, 154.6, 136.3, 134.0, 132.7, 132.5, 129.8, 129.2, 128.9, 128.1, 127.3, 126.0, 125.5, 123.2, 118.5, 110.1. IR (KBr disk) 2955, 2924, 2852, 2230, 1734, 1629, 1599, 1498, 1463, 1377, 1290, 1277, 1216, 1193, 1167, 1132, 1075, 1018, 949, 890, 874, 860, 825, 817, 799, 776, 764, 551 cm^{-1}. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{18}H_{11}NO_2Na^+$ 296.0682; Found 296.0726.

4-cyanophenyl benzofuran-6-carboxylate (3as)



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and benzofuran-6-carboxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid of **3as**. Yield: 36.8 mg (70%). M.P. = 128.7-129.2 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.35 (s, 1H), 8.09 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 1.6 Hz, 1H), 7.73 (t, *J* = 8.8 Hz, 3H), 7.39 (d, *J* = 8.5 Hz, 2H), 6.89 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 164.7, 154.5, 148.9, 133.9, 133.1, 124.9, 124.8, 123.1, 121.5, 118.5, 114.0, 109.9, 107.2. IR (KBr disk) 2958, 2924, 2852, 2228, 1736, 1621, 1602, 1527, 1497, 1484, 1433, 1409, 1294, 1222, 1212, 1166, 1109, 1054, 1043, 1026, 930, 891, 865, 829, 811, 777, 733, 549 cm^{-1}. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{16}H_9NO_3Na^+$ 286.0475; Found 286.0484.

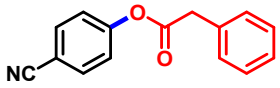
4-cyanophenyl benzo[*d*][1,3]dioxole-5-carboxylate (3at)



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and benzo[*d*][1,3]dioxole-5-carboxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid of **3at**. Yield: 39.5 mg (74%). M.P. = 157.8-158.5 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.80 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* =

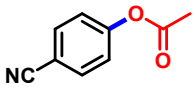
8.5 Hz, 2H), 7.57 (s, 1H), 7.34 (d, J = 8.5 Hz, 2H), 6.91 (d, J = 8.2 Hz, 1H), 6.09 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 163.8, 154.5, 152.9, 148.3, 133.9, 126.7, 123.1, 122.6, 118.5, 110.1, 109.9, 108.5, 102.3. IR (KBr disk) 2963, 2232, 1732, 1604, 1496, 1445, 1408, 1367, 1262, 1234, 1214, 1099, 1023, 927, 917, 864, 800, 749, 703, 549 cm^{-1}. HRMS (QTOF-MS) *m/z* [M + Na]$^+$ Calcd for $C_{15}H_9NO_4Na^+$ 290.0424; Found 290.0470.

4-cyanophenyl 2-phenylacetate (3au)[S6]



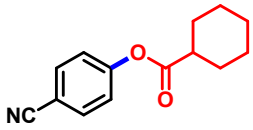
Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 2-phenylacetic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as aneluent, to yield the colorless oil of **3au**. Yield: 38.4 mg (81%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.67 (d, J = 8.4 Hz, 2H), 7.43-7.30 (m, 5H), 7.21 (d, J = 8.4 Hz, 2H), 3.88 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 169.4, 154.2, 133.9, 132.9, 129.5, 129.1, 127.9, 122.8, 118.4, 110.1, 41.6. HRMS (QTOF-MS) *m/z* [M + Na]$^+$ Calcd for $C_{15}H_{11}NO_2Na^+$ 260.0682; Found 260.0692.

4-cyanophenyl acetate (3av)[S7]



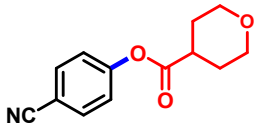
Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and acetic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid of **3av**. Yield: 24.8 mg (77%). M.P. = 56.5-57.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.69 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 8.5 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 168.7, 154.1, 133.9, 122.9, 118.4, 109.9, 21.3. HRMS (QTOF-MS) *m/z* [M + Na]$^+$ Calcd for $C_9H_7NO_2Na^+$ 184.0368; Found 184.0366.

4-cyanophenyl cyclohexanecarboxylate (3aw)



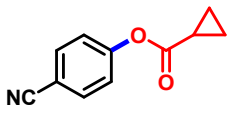
Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and cyclohexanecarboxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as aneluent, to yield the white solid of **3aw**. Yield: 36.6 mg (80%). M.P. = 37.5-38.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.67 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 2.62-2.51 (m, 1H), 2.05 (d, J = 11.9 Hz, 2H), 1.88-1.76 (m, 2H), 1.69 (d, J = 10.4 Hz, 1H), 1.64-1.50 (m, 2H), 1.40-1.24 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 173.8, 154.4, 133.8, 122.9, 118.5, 109.7, 43.3, 29.0, 25.8, 25.4. IR (KBr disk) 2937, 2859, 2233, 1751, 1602, 1499, 1454, 1410, 1312, 1247, 1212, 1192, 1166, 1152, 1120, 1018, 997, 923, 889, 863, 843, 549 cm^{-1}. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{14}H_{15}NO_2Na^+$ 252.0985; Found 252.0971.

4-cyanophenyl tetrahydro-2H-pyran-4-carboxylate (3ax)



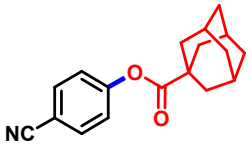
Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and tetrahydro-2H-pyran-4-carboxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid of **3ax**. Yield: 37.4 mg (81%). M.P. = 49.6-50.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.68 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 8.5 Hz, 2H), 4.02 (d, J = 11.6 Hz, 2H), 3.50 (t, J = 10.5 Hz, 2H), 2.82 (ddd, J = 14.9, 10.6, 3.9 Hz, 1H), 1.98 (t, J = 10.0, 2H), 1.94-1.83 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 172.3, 154.1, 133.8, 122.8, 118.3, 109.9, 67.0, 40.4, 28.6. IR (KBr disk) 2959, 2850, 2231, 1755, 1600, 1500, 1447, 1411, 1388, 1320, 1278, 1241, 1168, 1151, 1125, 1090, 1023, 984, 937, 8772, 853, 821, 782, 563, 551 cm^{-1}. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{13}H_{13}NO_3Na^+$ 254.0788; Found 254.0783.

4-cyanophenyl cyclopropanecarboxylate (3ay)[S8]



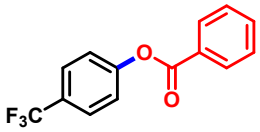
Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and cyclopropanecarboxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid of **3ay**. Yield: 30.7 mg (82%). M.P. = 50.1-51.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.68 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 1.91-1.80 (m, 1H), 1.23-1.15 (m, 2H), 1.11-1.03 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 172.8, 154.3, 133.8, 122.9, 118.5, 109.7, 13.2, 9.9. HRMS (QTOF-MS) $[M + Na]^+$ Calcd for $C_{11}H_9NO_2Na^+$ 210.0525; Found 210.0494.

4-cyanophenyl 1-Adamantanecarboxylate (3az)



Following the General Procedure with 4-bromobenzonitrile (0.2 mmol) and 1-Adamantanecarboxylic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid of **3az**. Yield: 47.2 mg (84%). M.P. = 109.5-110.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.67 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 2.09 (s, 3H), 2.04 (s, 6H), 1.81-1.71 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 175.5, 154.7, 133.7, 122.9, 118.5, 109.6, 41.4, 38.8, 36.5, 28.0. IR (KBr disk) 2923, 2906, 2854, 2229, 1753, 1604, 1507, 1452, 1343, 1203, 1177, 1169, 1098, 1036, 1022, 974, 900, 861, 789, 729, 665, 549 cm^{-1}. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{18}H_{19}NO_2Na^+$ 304.1308; Found 304.1295.

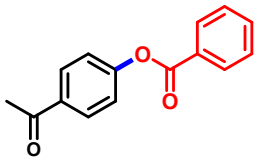
4-(trifluoromethyl)phenyl benzoate (3ba)[S9]



Following the General Procedure with 1-bromo-4-(trifluoromethyl)benzene (0.2 mmol) and benzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc

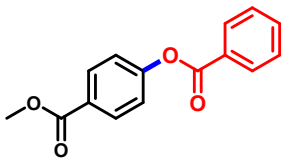
with 100/1 (v/v) as an eluent, to yield the colorless solid of **3ba**. Yield: 48.4 mg (91%). M.P. = 107.6-108.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.22 (d, J = 7.6 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 7.4 Hz, 1H), 7.54 (t, J = 7.6 Hz, 2H), 7.36 (d, J = 8.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 164.9, 153.7, 134.2, 130.5, 129.2, 128.9, 128.4 (q, J = 31.7 Hz), 127.1 (q, J = 4.53 Hz), 124.1 (q, J = 271.8 Hz), 122.5. HRMS (QTOF-MS) $[M + Na]^+$ Calcd for $C_{14}H_9F_3O_2Na^+$ 289.0446; Found 289.0427.

4-acetylphenyl benzoate (3ca)[S9]



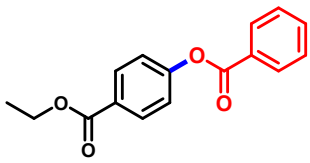
Following the General Procedure with 4-bromoacetophenone (0.2 mmol) and benzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the colorless solid of **3ca**. Yield: 41.3 mg (86%). M.P. = 133.1-133.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.21 (d, J = 7.6 Hz, 2H), 8.05 (d, J = 8.4 Hz, 2H), 7.66 (t, J = 7.3 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 2.63 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 197.0, 164.8, 154.9, 135.0, 134.1, 130.4, 130.2, 129.2, 128.7, 122.1, 26.8. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{15}H_{12}O_3Na^+$ 263.0673; Found 263.0678.

methyl 4-(benzoyloxy)benzoate (3da)[S9]



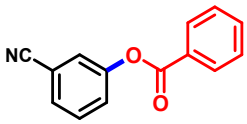
Following the General Procedure with methyl 4-bromobenzoate (0.2 mmol) and benzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the colorless solid of **3da**. Yield: 43.5 mg (85%). M.P. = 130.4-131.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.21 (d, J = 7.5 Hz, 2H), 8.13 (d, J = 8.6 Hz, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.7 Hz, 2H), 7.31 (d, J = 8.6 Hz, 2H), 3.93 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 166.6, 164.9, 154.8, 134.1, 131.4, 130.5, 129.3, 128.9, 128.0, 122.0, 52.4. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{15}H_{12}O_4Na^+$ 279.0627; Found 279.0609.

ethyl 4-(benzoyloxy)benzoate (3ea)[S10]



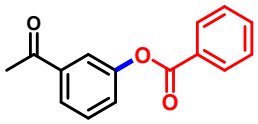
Following the General Procedure with ethyl 4-bromobenzoate (0.2 mmol) and benzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the colorless solid of **3ea**. Yield: 46.4 mg (86%). M.P. = 80.7-81.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.21 (d, J = 7.7 Hz, 2H), 8.14 (d, J = 8.4 Hz, 2H), 7.66 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.5 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 4.40 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 166.1, 164.9, 154.8, 134.1, 131.4, 130.5, 129.4, 128.9, 128.4, 121.9, 77.4, 77.2, 77.0, 61.3, 14.6. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{16}H_{14}O_4Na^+$ 293.0784; Found 293.0755.

3-cyanophenyl benzoate (3fa)[S11]



Following the General Procedure with 3-bromobenzonitrile (0.2 mmol) and benzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid of **3fa**. Yield: 30.8 mg (69%). M.P. = 86.5-87.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.19 (d, J = 7.6 Hz, 2H), 7.68 (t, J = 7.2 Hz, 1H), 7.53 (dt, J = 13.0, 7.7 Hz, 5H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 164.8, 151.3, 134.4, 130.7, 130.5, 129.9, 129.0, 128.9, 127.0, 125.8, 118.1, 113.8. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{14}H_9O_2Na^+$ 246.0525; Found 246.0498.

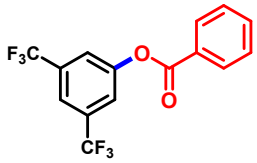
3-acetylphenyl benzoate (3ga)[S12]



Following the General Procedure with 3-bromoacetophenone (0.2 mmol) and benzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v)

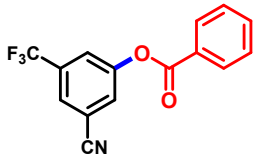
as an eluent, to yield the colorless solid of **3ga**. Yield: 30.2 mg (63%). M.P. = 47.1-47.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.22 (d, *J* = 7.5 Hz, 2H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.81 (s, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.54 (dt, *J* = 12.7, 6.5 Hz, 3H), 7.45 (d, *J* =8.0 Hz, 1H), 2.63 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 197.2, 165.2, 151.4, 138.8, 134.1, 130.4, 130.0, 129.4, 128.9, 126.8, 126.0, 26.9. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{15}H_{12}O_3Na^+$ 263.0678; Found 263.0672.

3,5-bis(trifluoromethyl)phenyl benzoate (3ha)[S9]



Following the General Procedure with the corresponding 3,5-bis(trifluoromethyl)bromobenzene (0.2 mmol) and benzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the colorless oil of **3ha**. Yield: 58.1 mg (87%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.21 (d, *J* = 7.7 Hz, 2H), 7.81 (s, 1H), 7.74 (s, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 164.5, 151.7, 134.6, 133.2 (q, *J* = 33.2 Hz), 130.6, 129.1, 128.5, 123.02 (q, *J* = 273.3 Hz), 122.92 (q, *J* = 3.0 Hz), 119.96 (p, *J* = 3.02 Hz). HRMS (QTOF-MS) *m/z* m/z $[M + Na]^+$ Calcd for $C_{15}H_8F_6O_2Na^+$ 357.0320; Found 357.0323.

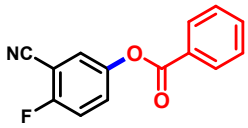
3-cyano-5-(trifluoromethyl)phenyl benzoate (3ia)



Following the General Procedure with 3-bromo-5-(trifluoromethyl)benzonitrile (0.2 mmol) and benzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the colorless oil of **3ia**. Yield: 48.3 mg (83%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.19 (d, *J* = 7.6 Hz, 2H), 7.82 (s, 1H), 7.78 (s, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 164.3, 151.7, 134.8, 133.6 (q, *J* = 34.4 Hz), 130.6, 129.1, 129.1, 128.2, 126.4 (q, *J* = 3.0 Hz), 124.0 (q, *J* = 4.5 Hz), 122.61 (q, *J* =

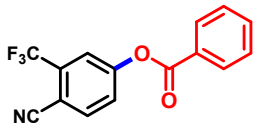
273.3 Hz), 116.7, 114.8. IR (KBr disk): 2963, 2925, 2230, 1746, 1600, 1444, 1347, 1315, 1261, 1226, 1179, 1139, 1102, 1079, 1058, 1025, 953, 894, 878, 801, 718, 707, 696, 640, 585 cm^{-1}. HRMS (QTOF-MS) *m/z* m/z $[M + Na]^+$ Calcd for $C_{15}H_8F_3NO_2Na^+$ 314.0399; Found 314.0341.

3-cyano-4-fluorophenyl benzoate (3ja)



Following the General Procedure with 5-bromo-2-fluorobenzonitrile (0.2 mmol) and benzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the colorless solid of **3ja**. Yield: 34.7 mg (72%). M.P. = 131.9-132.7 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.18 (d, *J* = 7.6 Hz, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.54 (dd, *J* = 9.6, 5.6 Hz, 3H), 7.51-7.44 (m, 1H), 7.30 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 164.8, 161.8, 160.0, 134.5, 130.5, 129.0 (d, *J* = 7.55 Hz), 129.0, 128.6, 126.7, 117.7 (d, *J* = 21.1 Hz), 113.3, 102.5 (d, *J* = 18.1 Hz). IR (KBr disk) 2956, 2924, 2852, 2239, 1724, 1618, 1499, 1454, 1378, 1265, 1211, 1194, 1178, 1072, 1059, 1024, 913, 820, 786, 699, 677, 491. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{14}H_8FNO_2Na^+$ 264.0431; Found 264.0576.

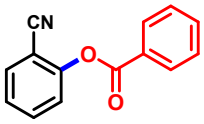
4-cyano-3-(trifluoromethyl)phenyl benzoate (3ka)



Following the General Procedure with 4-bromo-2-(trifluoromethyl)benzonitrile (0.2 mmol) and benzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid of **3ka**. Yield: 43.1 mg (74%). M.P. = 130.8-131.4 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.19 (d, *J* = 7.6 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.77-7.67 (m, 2H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 164.1, 154.3, 136.5, 135.0, 134.8, 130.6, 129.1, 128.3, 126.0, 122.0 (q, *J* = 274.8 Hz), 121.2 (q, *J* = 4.7 Hz), 115.2, 107.5. IR (KBr disk) 2957, 2923, 2852 2229, 1746, 1614, 1599, 1499, 1452, 1430, 1319, 1313, 1262, 1249, 1205, 1182, 1172, 1141, 1124, 1050, 1023, 924, 909,

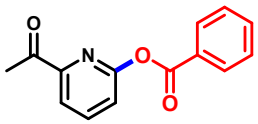
709, 558 cm^{-1}. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{15}H_8F_3NO_2Na^+$ 314.0399; Found 314.0330.

2-cyanophenyl benzoate (3la)[S13]



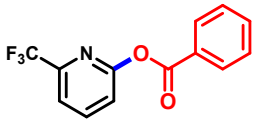
Following the General Procedure with 2-bromobenzonitrile (0.2 mmol) and benzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid of **3la**. Yield: 11.6 mg (26%) for 24 h or 29.0 mg (65%) for 48 h. M.P. = 91.8-92.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.26 (d, *J* = 7.6 Hz, 2H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 2H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 164.2, 152.8, 134.5, 134.3, 133.6, 130.8, 129.0, 128.6, 126.5, 123.5, 115.4, 107.3. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{14}H_9O_2Na^+$ 246.0525; Found 246.0499.

6-acetylpyridin-2-yl benzoate (3ma)



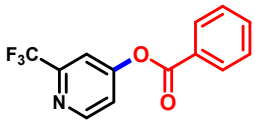
Following the General Procedure with 2-bromo-6-acetylpyridine (0.2 mmol) and benzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the colorless oil of **3ma**. Yield: 36.2 mg (75%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.25 (d, *J* = 7.6 Hz, 2H), 8.05-7.93 (m, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 7.7 Hz, 1H), 2.69 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 199.2, 165.0, 157.5, 152.9, 140.5, 134.3, 130.6, 129.0, 128.9, 120.8, 120.2, 26.0. IR (KBr disk) 2959, 2923, 2851, 1738, 1694, 1599, 1588, 1571, 1447, 1384, 1357, 1270, 1249, 1214, 1178, 1081, 1061, 1023, 996, 871, 799, 709, 582 cm^{-1}. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{14}H_{11}NO_3Na^+$ 264.0631; Found 264.0638.

6-(trifluoromethyl)pyridin-2-yl benzoate (3na)



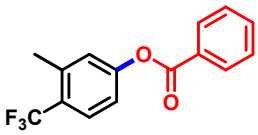
Following the General Procedure with 2-bromo-6-(trifluoromethyl)pyridine (0.2 mmol) and benzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the colorless solid of **3na**. Yield: 40.6 mg (76%). M.P. = 87.8-88.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.15 (d, J = 7.7 Hz, 2H), 7.94 (t, J = 7.8 Hz, 1H), 7.58 (dd, J = 6.9, 4.2 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.36 (d, J = 8.2 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 164.6, 158.3, 147.5 (q, J = 35.7 Hz), 141.1, 134.4, 130.7, 128.9, 128.6, 121.1 (q, J = 273.3 Hz), 120.4, 118.9 (q, J = 3.0 Hz). IR (KBr disk) 2957, 2925, 2853, 1747, 1600, 1463, 1437, 1384, 1344, 1263, 1222, 1192, 1178, 1145, 1123, 1079, 1057, 1024, 996, 903, 801, 707 cm^{-1}. HRMS (QTOF-MS) *m/z* [M + Na]$^{+}$ Calcd for $C_{13}H_8F_3NO_2Na^{+}$ 290.0399; Found 290.0389.

2-(trifluoromethyl)pyridin-4-yl benzoate (3oa)[S9]



Following the General Procedure with 4-bromo-2-(trifluoromethyl)pyridine (0.2 mmol) and benzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the colorless oil of **3oa**. Yield: 42.2 mg (79%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.78 (d, J = 5.3 Hz, 1H), 8.19 (d, J = 7.6 Hz, 2H), 7.69 (dd, J = 14.0, 6.5 Hz, 2H), 7.55 (t, J = 7.7 Hz, 2H), 7.47 (d, J = 4.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 163.7, 159.0, 152.0, 150.33 (q, J = 35.2 Hz), 134.7, 130.6, 129.1, 128.3, 121.3 (q, J = 274.8 Hz), 119.8, 114.7 (q, J = 2.6 Hz). HRMS (QTOF-MS) *m/z* [M + Na]$^{+}$ Calcd for $C_{13}H_8F_3NO_2Na^{+}$ 290.0399; Found 290.0363.

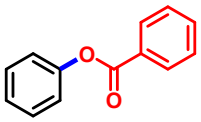
3-methyl-4-(trifluoromethyl)phenyl benzoate (3pa)



Following the General Procedure with 4-bromo-2-methylbenzotrifluoride (0.2 mmol) and benzoic

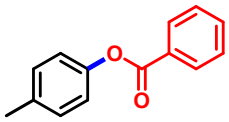
acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the colorless oil of **3pa**. Yield: 31.4 mg (56%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.20 (d, J = 7.6 Hz, 2H), 7.67 (t, J = 9.1 Hz, 2H), 7.53 (t, J = 7.6 Hz, 2H), 7.15 (d, J = 13.4 Hz, 2H), 2.52 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 165.0, 153.4, 139.1, 134.1, 130.5, 129.3, 128.9, 127.6 (q, J = 5.6 Hz), 126.8 (q, J = 30.2 Hz), 125.3, 124.5 (q, J = 273.3 Hz), 119.3, 19.6. IR (KBr disk) 2957, 2914, 2853, 1743, 1618, 1453, 1315, 1261, 1231, 1176, 1152, 1117, 1082, 1066, 1042, 1025, 706 cm^{-1}. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{13}H_8F_3NO_2Na^+$ 303.0603; Found 303.0582.

Phenyl benzoate (3qa)[S14]



Following the General Procedure with iodobenzene (0.2 mmol) and benzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid of **3qa**. Yield: 17.4 mg (44%). M.P. = 70.5-71.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.22 (d, J = 7.5 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.44 (t, J = 7.8 Hz, 2H), 7.29 (d, J = 7.4 Hz, 1H), 7.22 (d, J = 7.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 165.4, 151.2, 133.8, 130.4, 129.8, 129.71, 128.8, 126.1, 121.9. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{13}H_{10}O_2Na^+$ 221.0573; Found 221.0586.

***p*-tolyl benzoate (3ra)**[S15]



Following the General Procedure with 1-iodo-4-methylbenzene (0.2 mmol) and benzoic acid (0.4 mmol). The crude product was purified by preparative TLC, using ether/EtOAc with 100/1 (v/v) as an eluent, to yield the white solid of **3ra**. Yield: 13.6 mg (32%). M.P. = 71.6-72.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.20 (d, J = 7.6 Hz, 2H), 7.63 (t, J = 7.3 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.27–7.18 (m, 2H), 7.09 (d, J = 8.2 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 165.6, 148.9, 135.7, 133.9, 130.4, 130.2, 129.9, 128.7, 121.5, 21.1. HRMS (QTOF-MS) *m/z* $[M + Na]^+$ Calcd for $C_{14}H_{12}O_2Na^+$ 235.0729; Found 235.0778.

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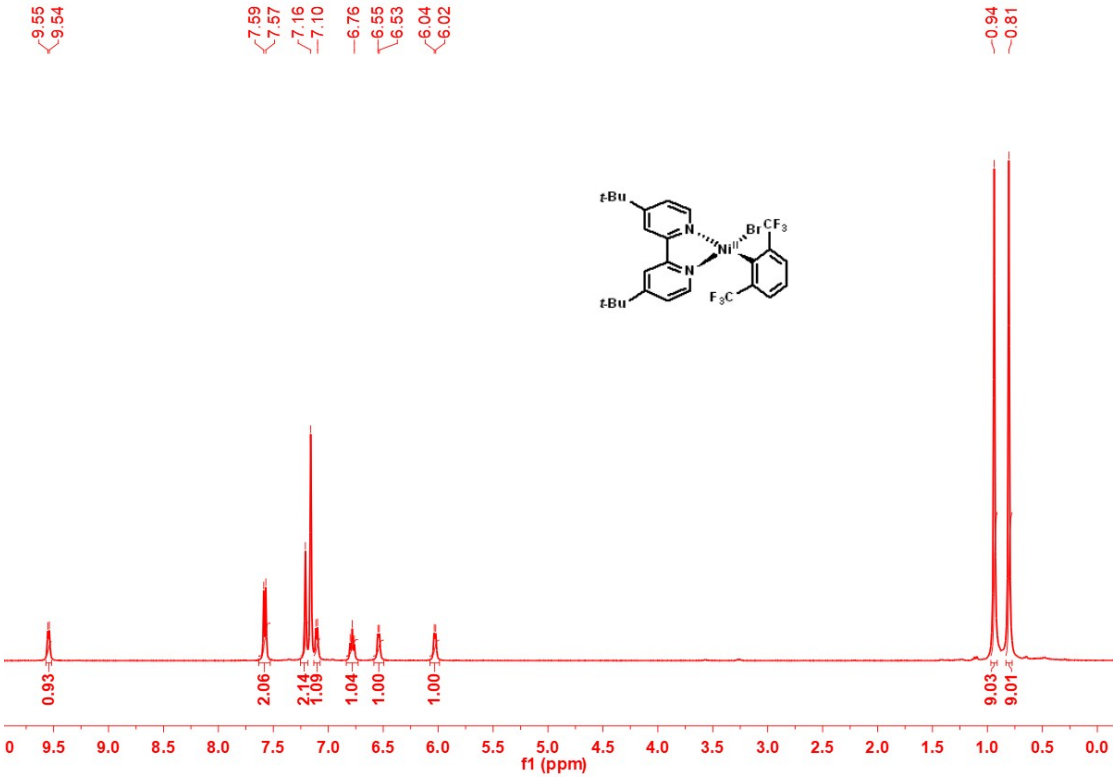
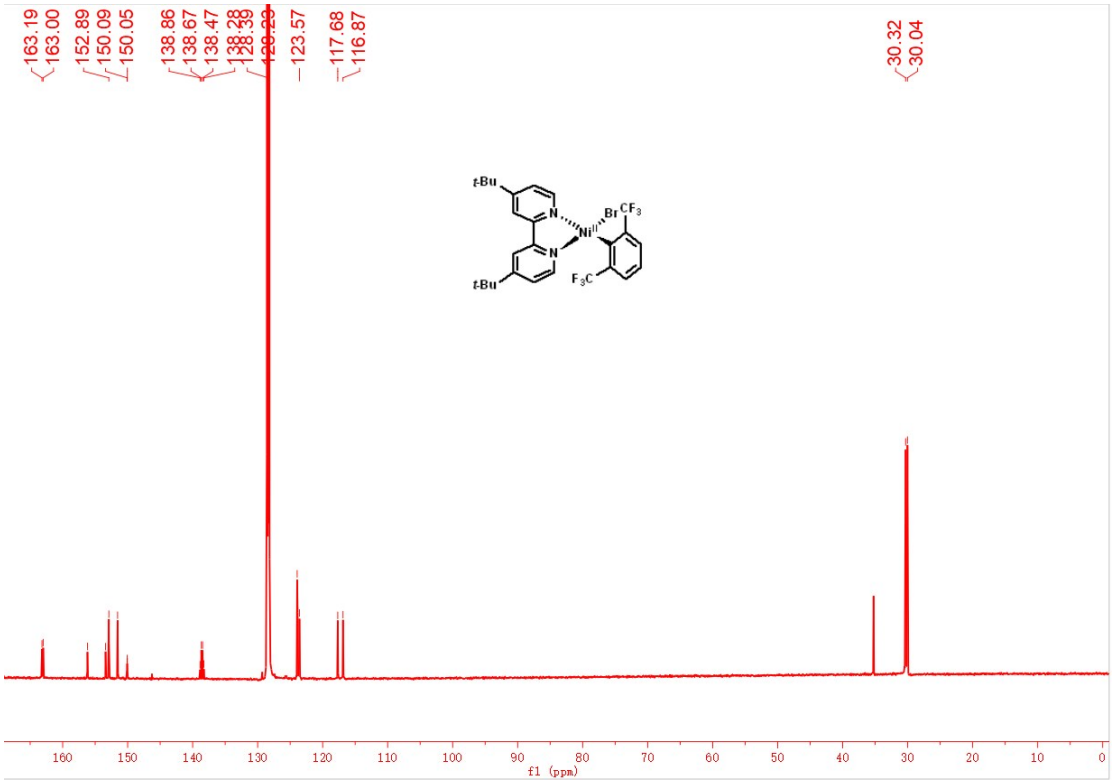
NMR spectra

Fig. S4. The ^{1}H, ^{13}C and ^{19}F NMR spectra for (dtbbpy)-2,6-bis(trifluoromethyl)phenylnickel(II) bromide





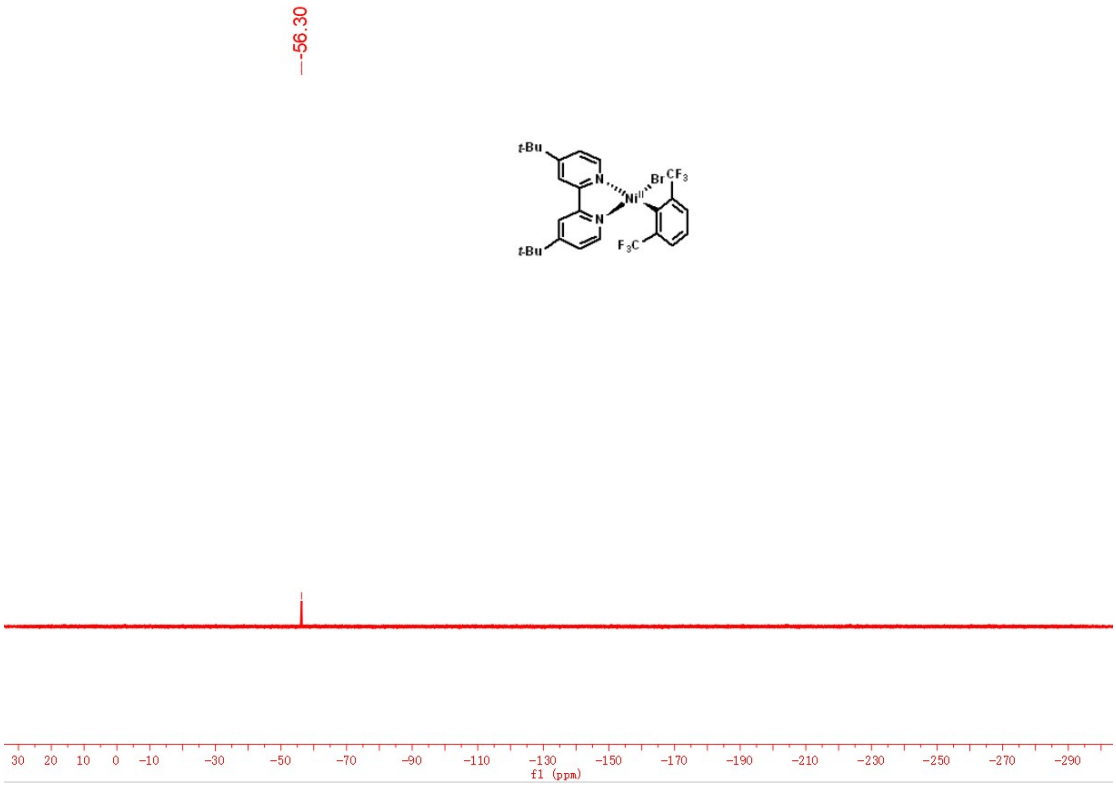
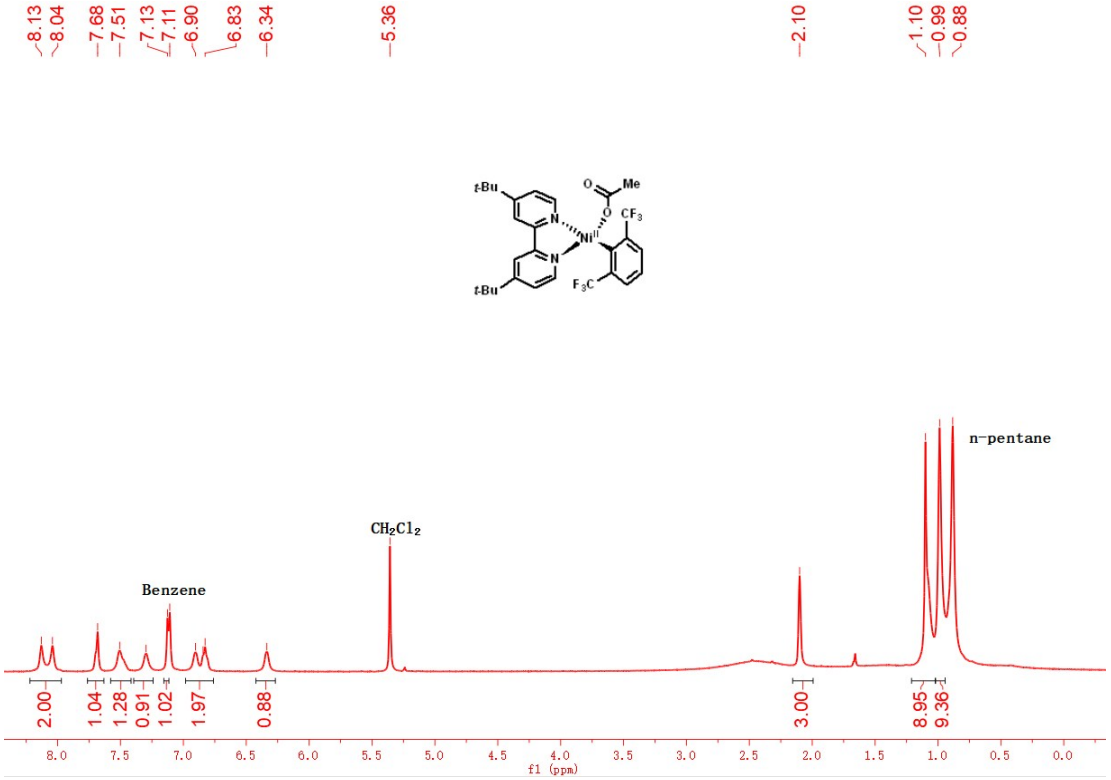

-56.30
t-Bu
t-Bu
N
N
Ni
Br
CF3
F3C
30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290
f1 (ppm)

Fig. S5 The ^{1}H and ^{19}F NMR spectra for (dtbbpy)-2,6-bis(trifluoromethyl)phenylnickel(II) acetate (**4**)



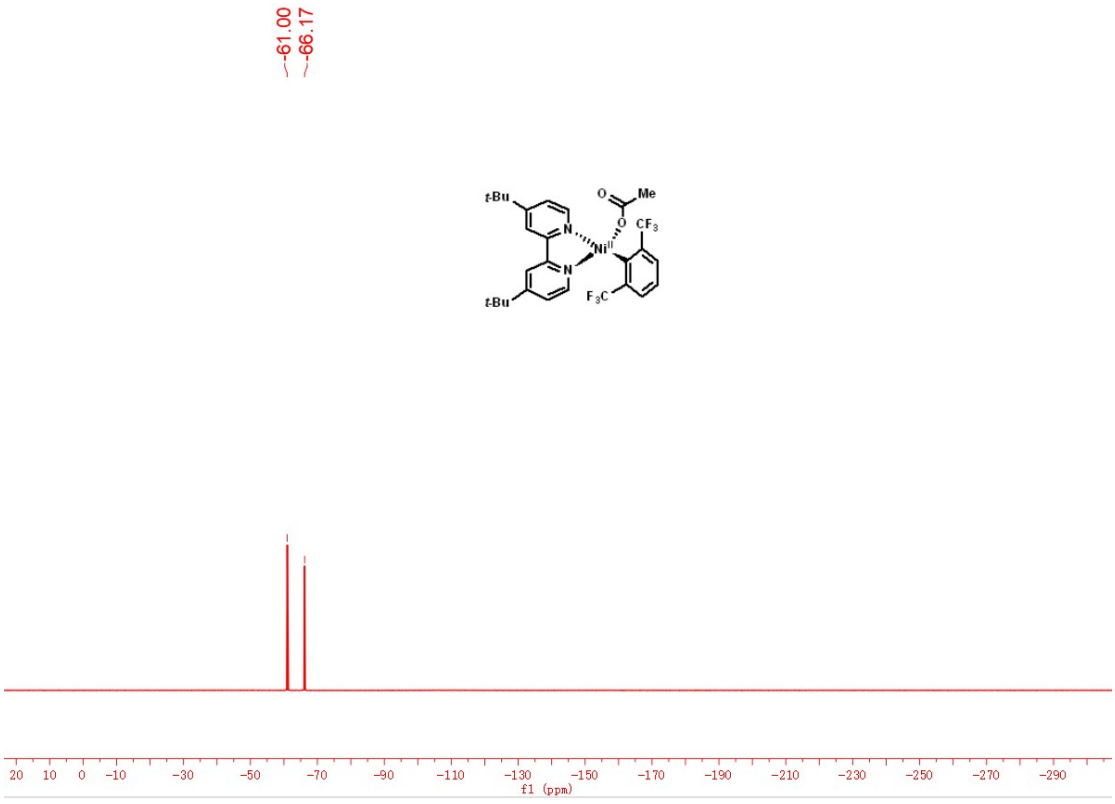


Fig. S6 The ^{1}H and ^{13}C NMR spectra for 4-cynaophenyl benzoate (**3aa**)

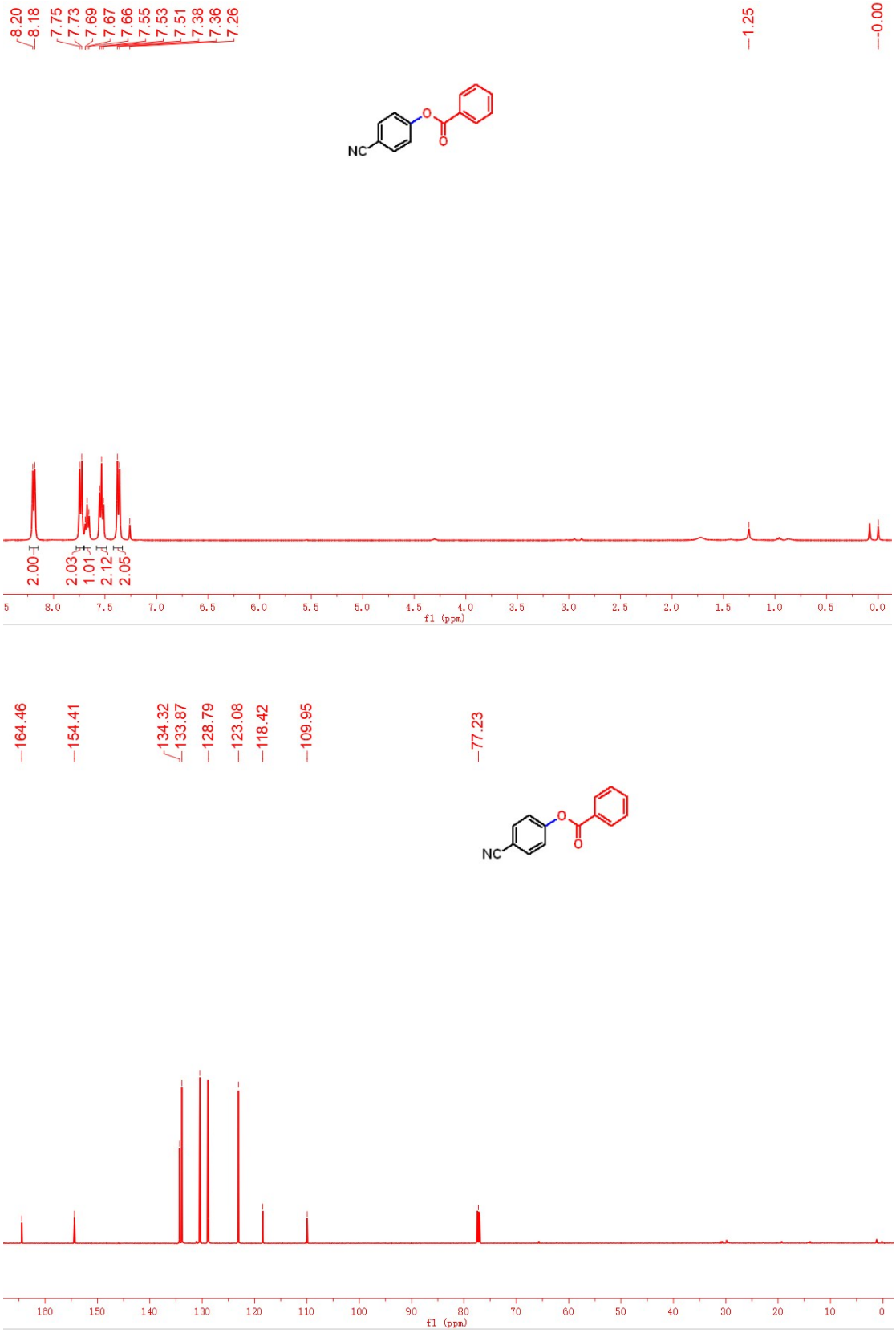


Fig. S7 The ^{1}H and ^{13}C NMR spectra for 4-cyanophenyl 4-ethylbenzoate (**3ab**)

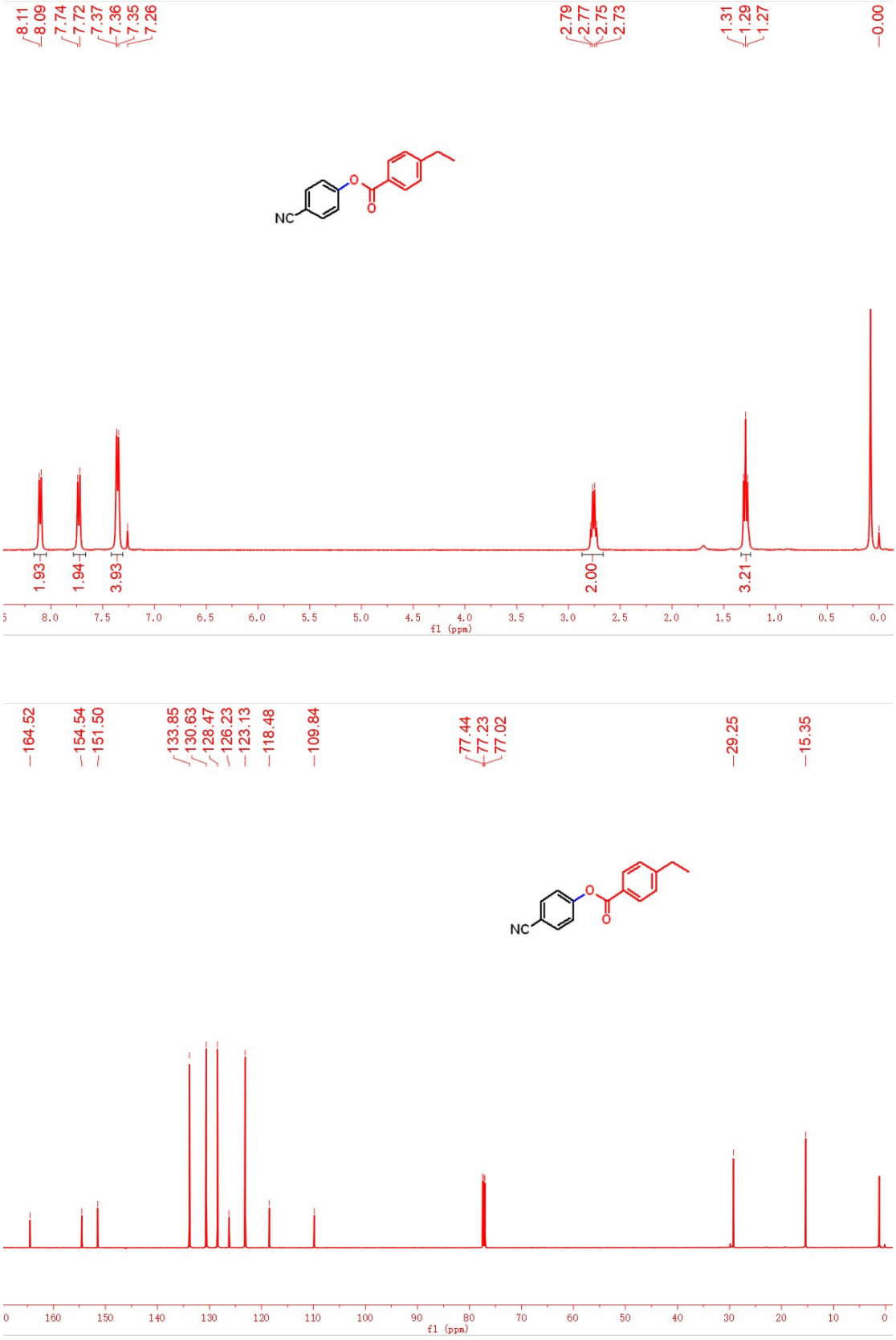


Fig. S8 The ^{1}H and ^{13}C NMR spectra for 4-cyanophenyl 4-pentylbenzoate (**3ac**)

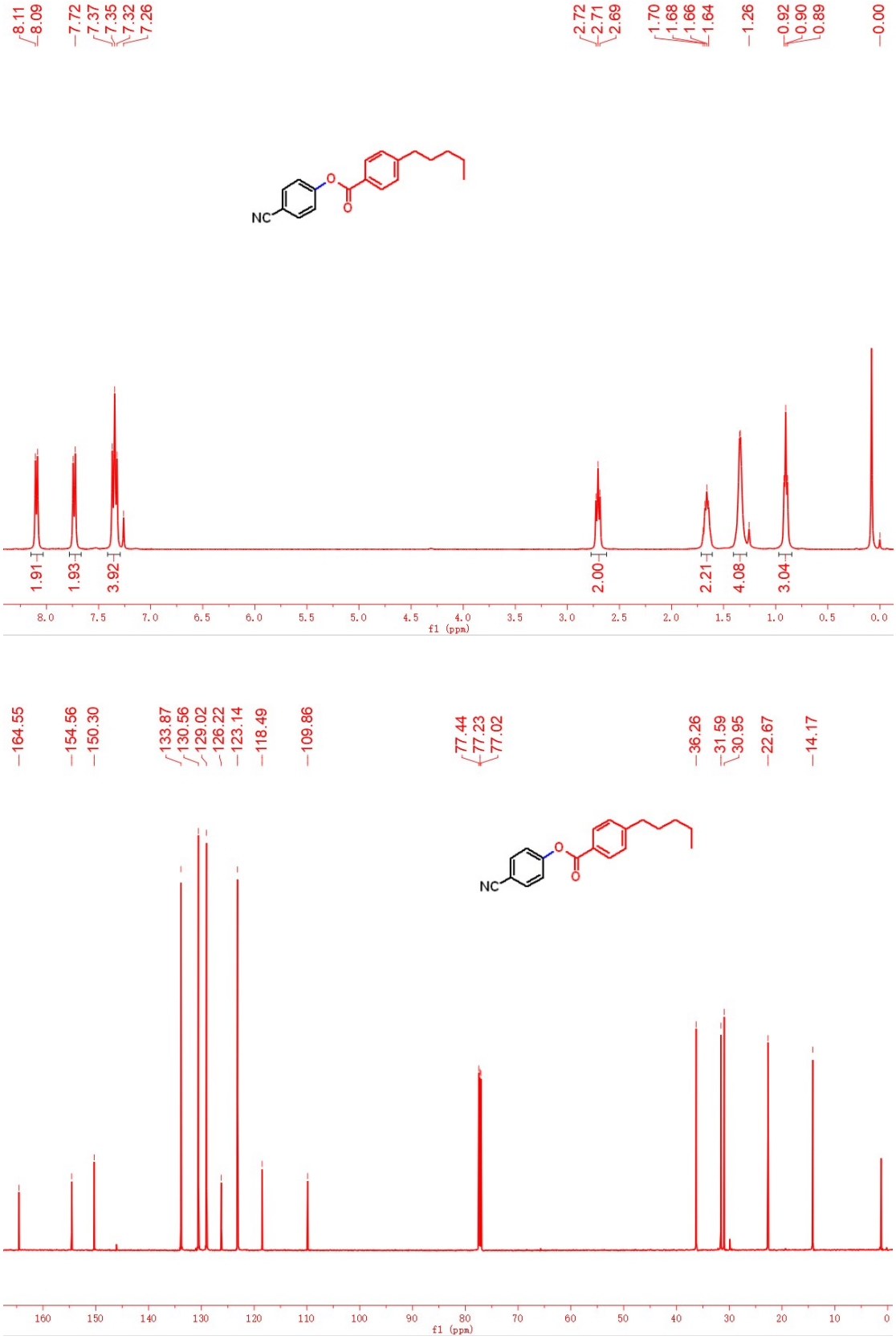


Fig. S9 The ^{1}H and ^{13}C NMR spectra for 4-cyanophenyl 4-methoxybenzoate (**3ad**)

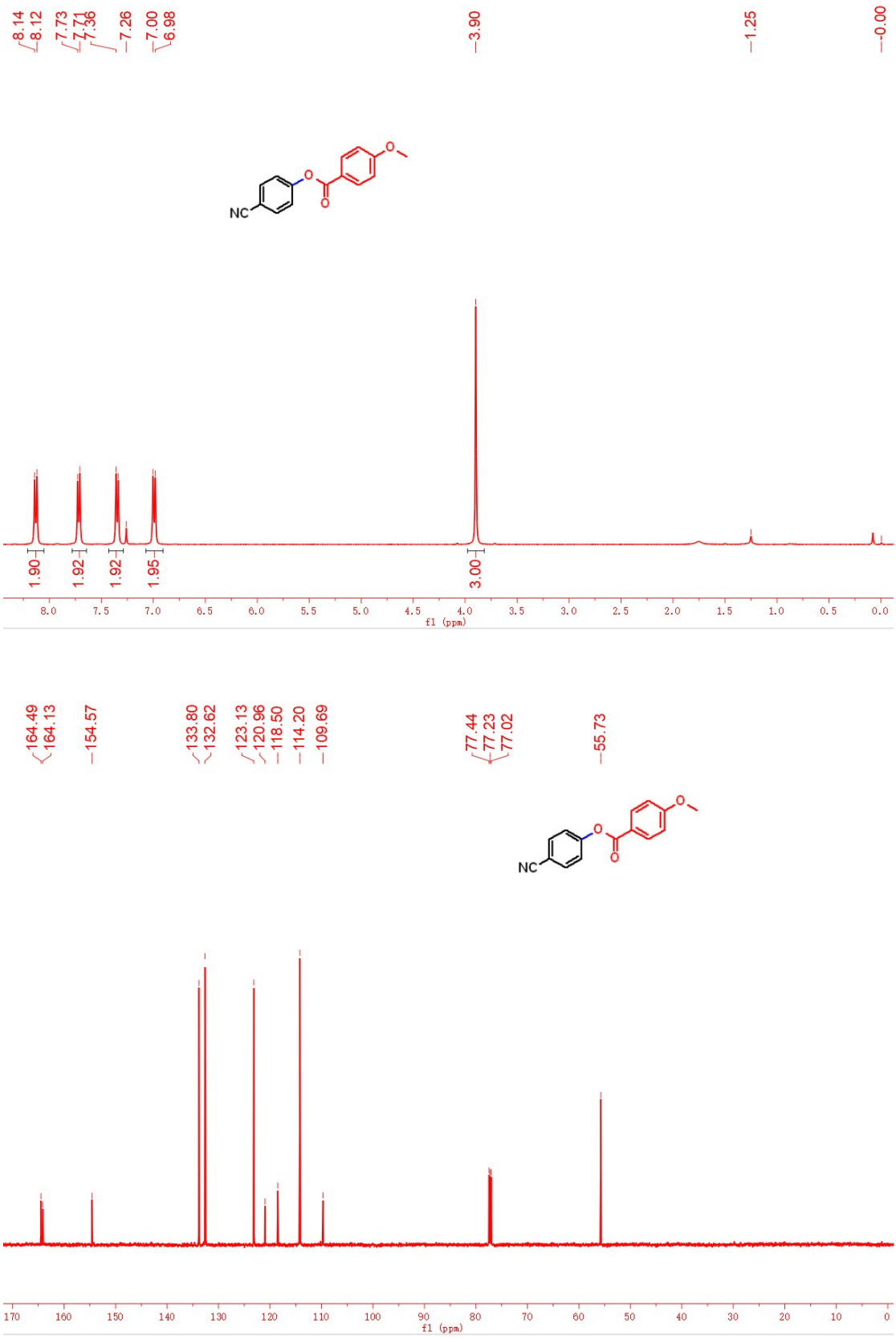


Fig. S10 The ^{1}H and ^{13}C NMR spectra for (4-cyanophenyl) 4-propoxybenzoate (**3ae**)

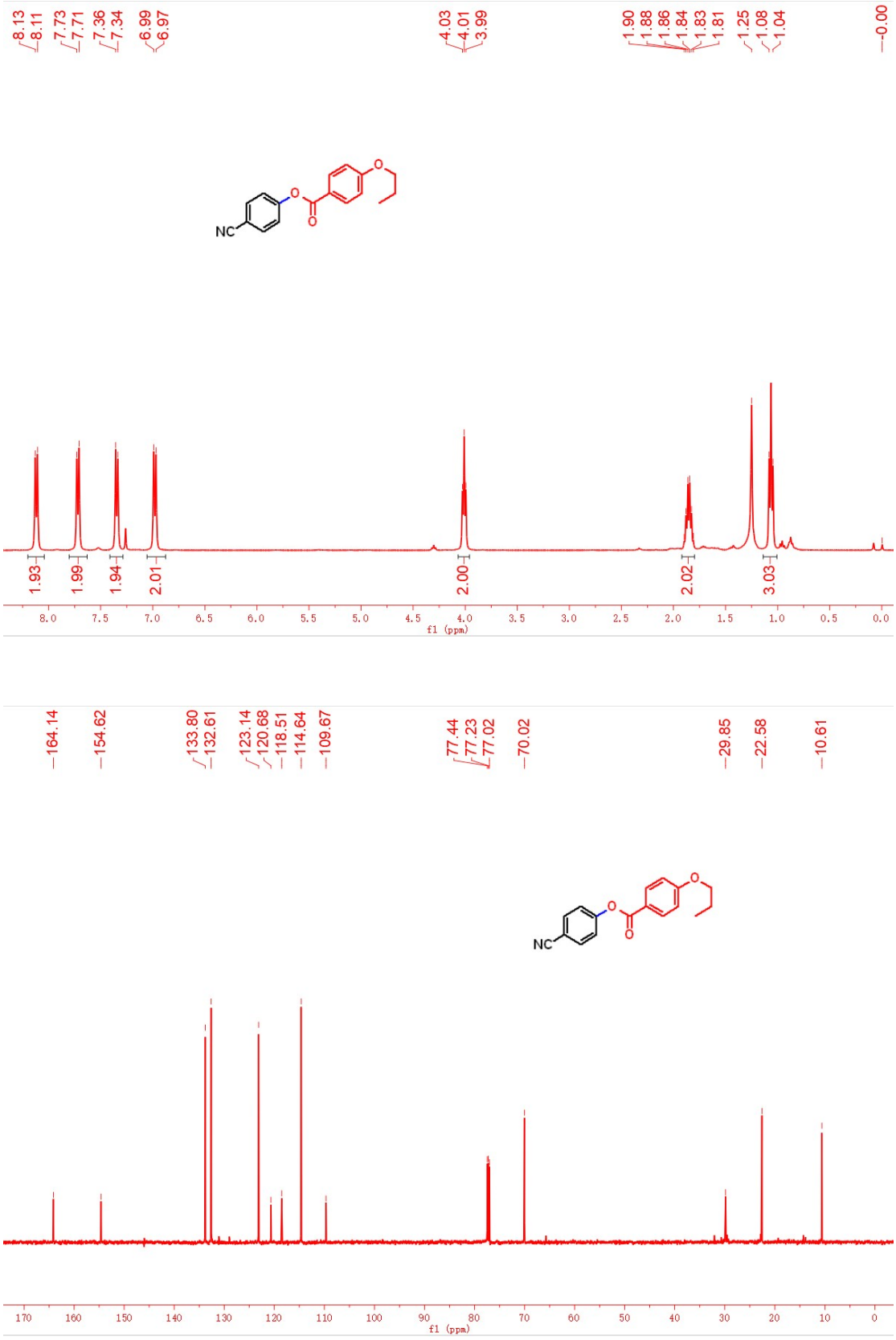
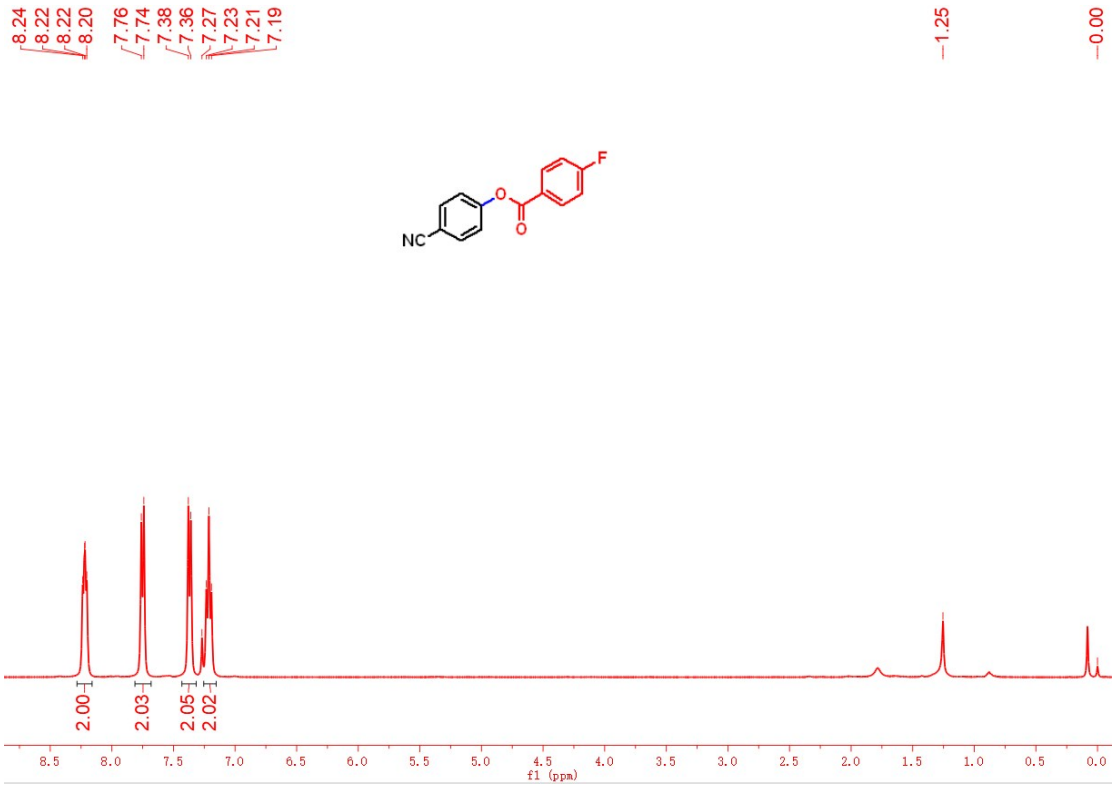


Fig. S11 The ^{1}H and ^{13}C NMR spectra for 4-fluorbenzoesaeure-4'-cyanophenylester (**3af**)



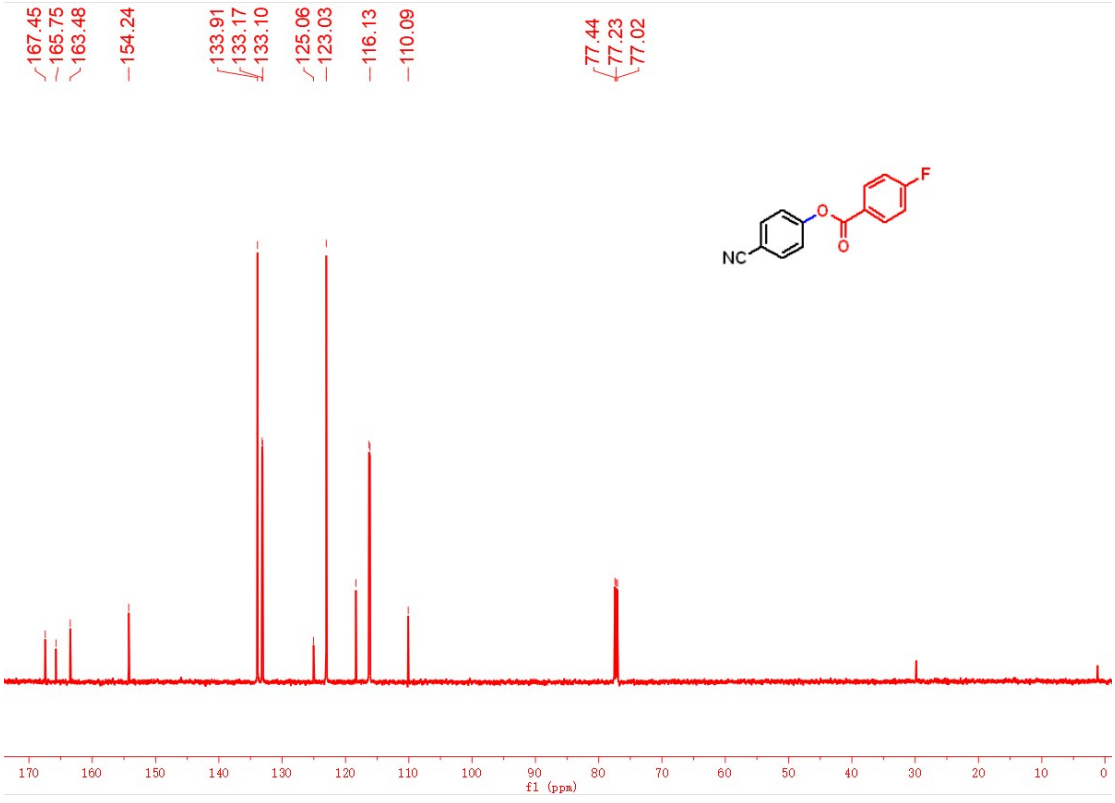
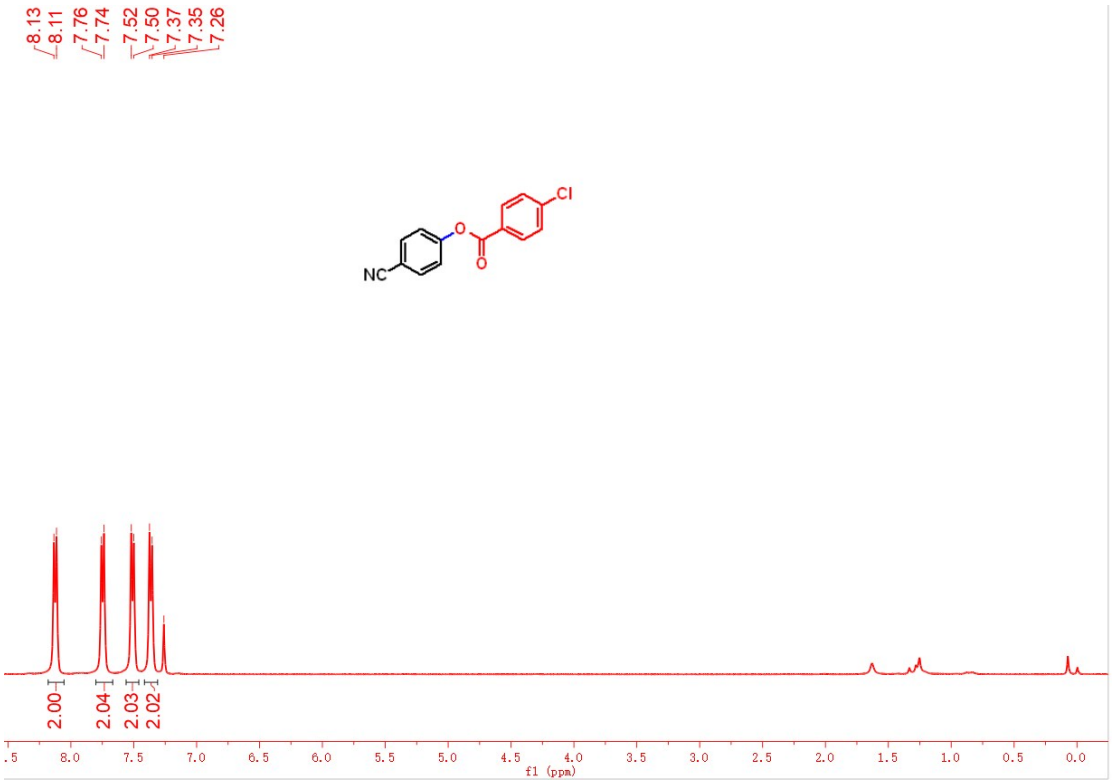


Fig. S12 The ^{1}H and ^{13}C NMR spectra for 4-cyanophenyl 4-chlorobenzoate (**3ag**)



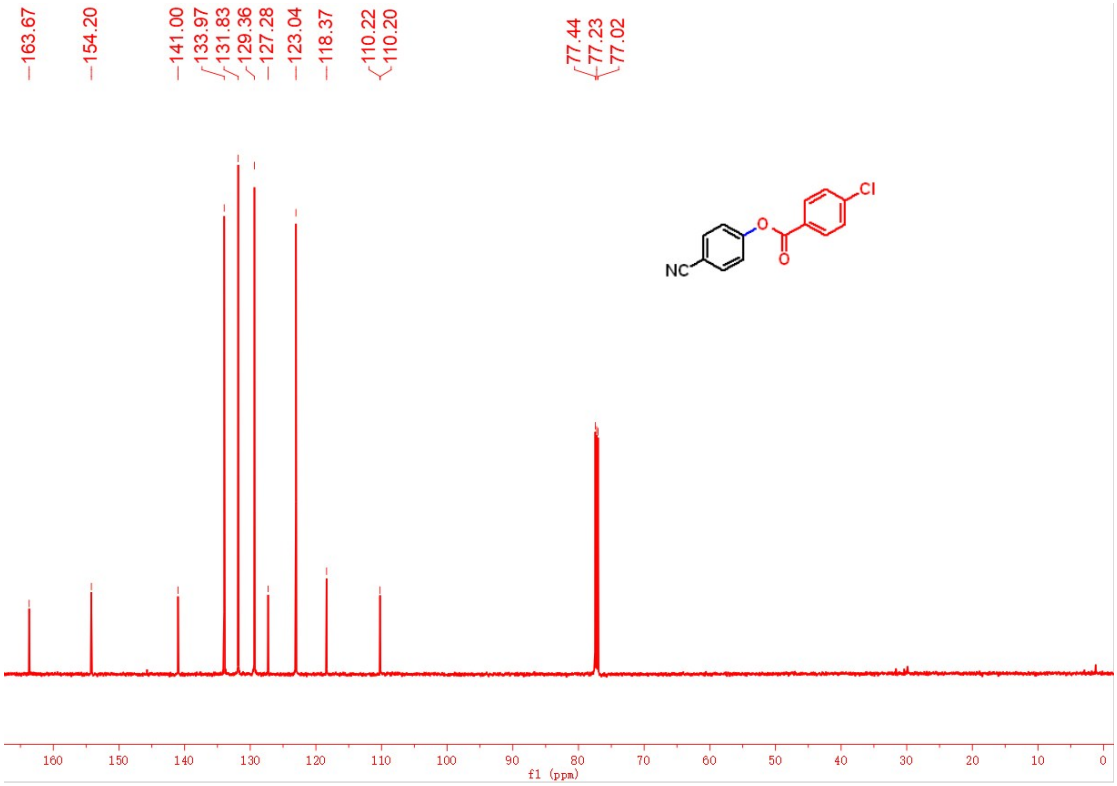


Fig. S13 The ^{1}H and ^{13}C NMR spectra for 4-trifluoromethylphenyl 4-cyanobenzoate (**3ah**)

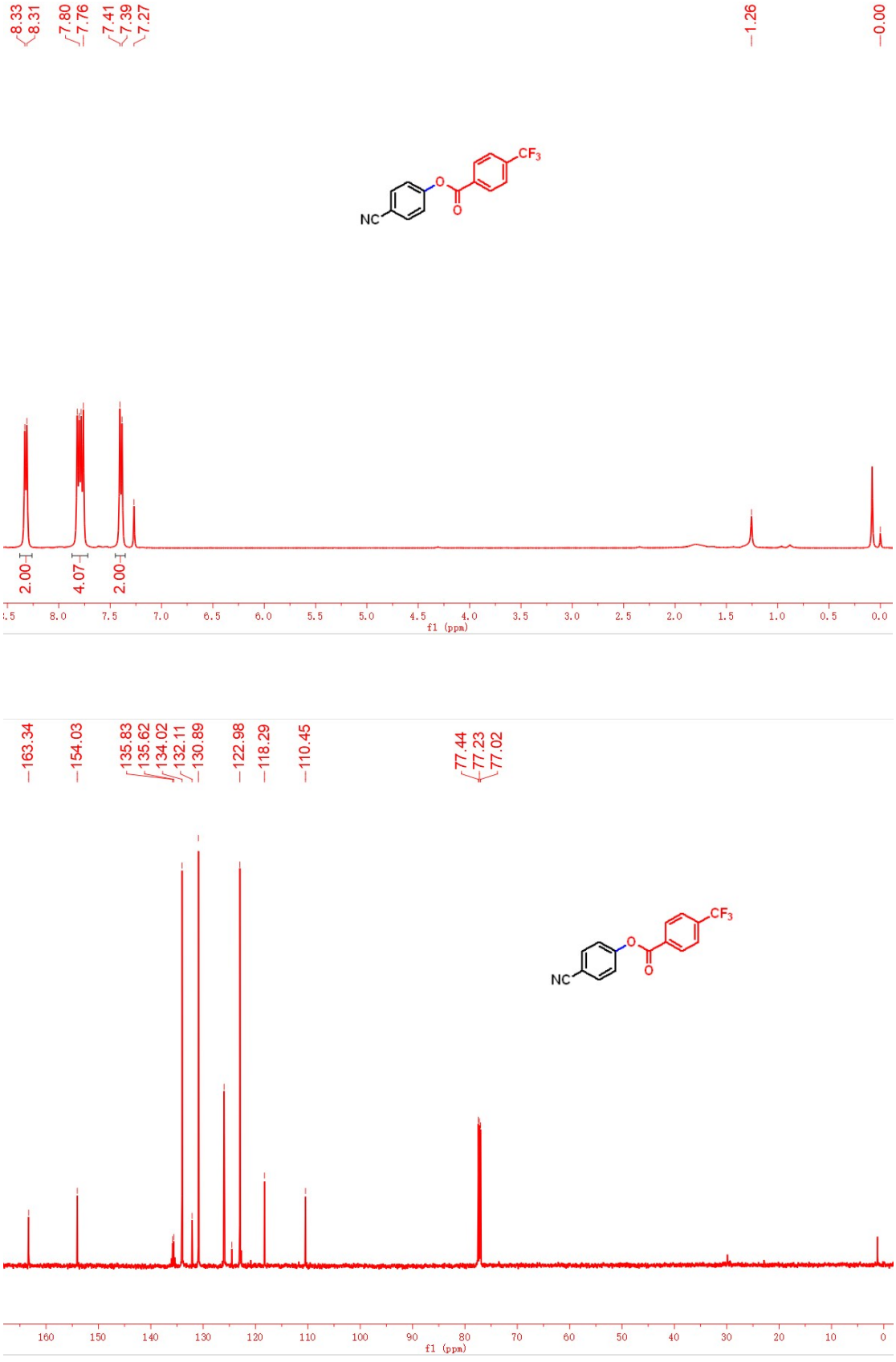
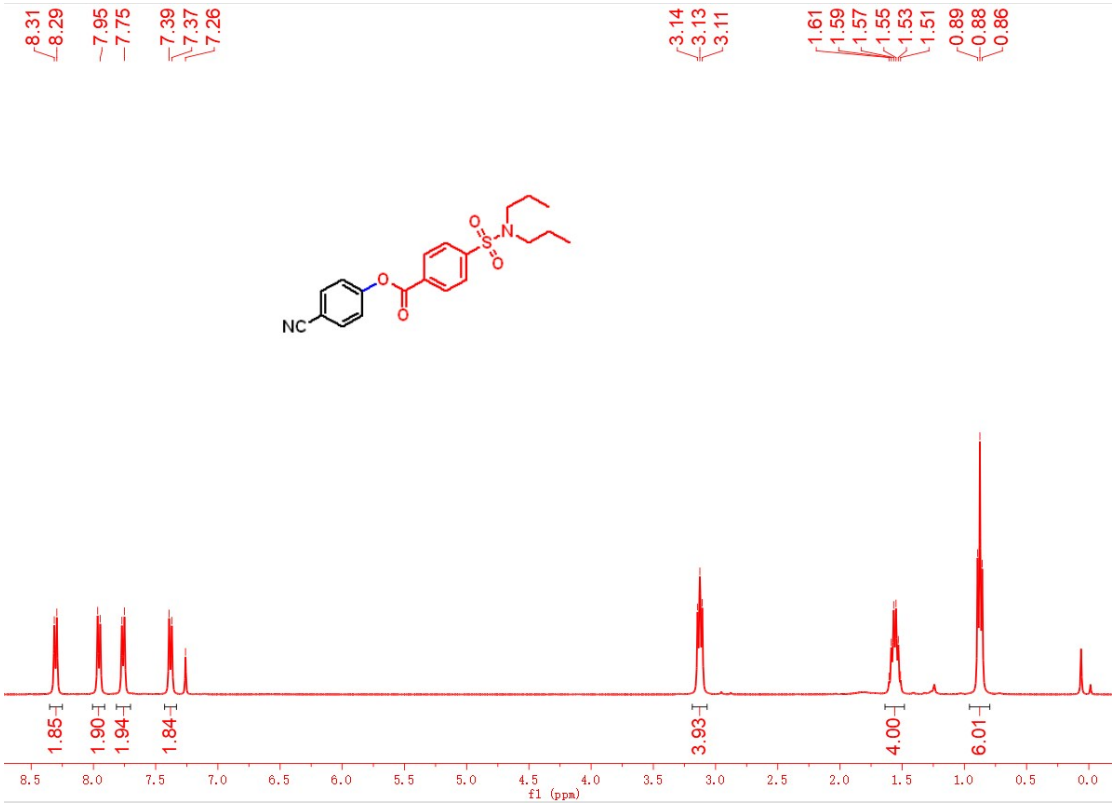


Fig. S14 The ^{1}H and ^{13}C NMR spectra for 4-cyanophenyl 4-(N,N-dipropylsulfamoyl)benzoate (**3ai**)



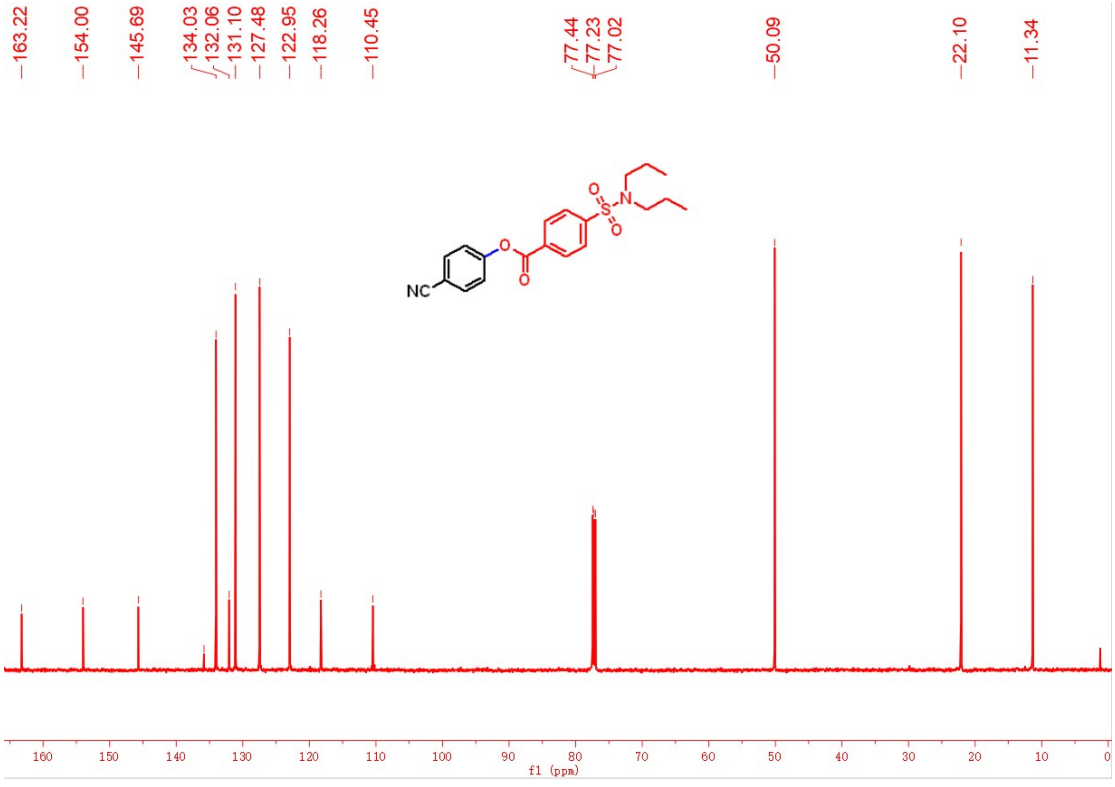


Fig. S15 The ^{1}H and ^{13}C NMR spectra for 4-cyanophenyl 3-methylbenzoate (**3aj**)

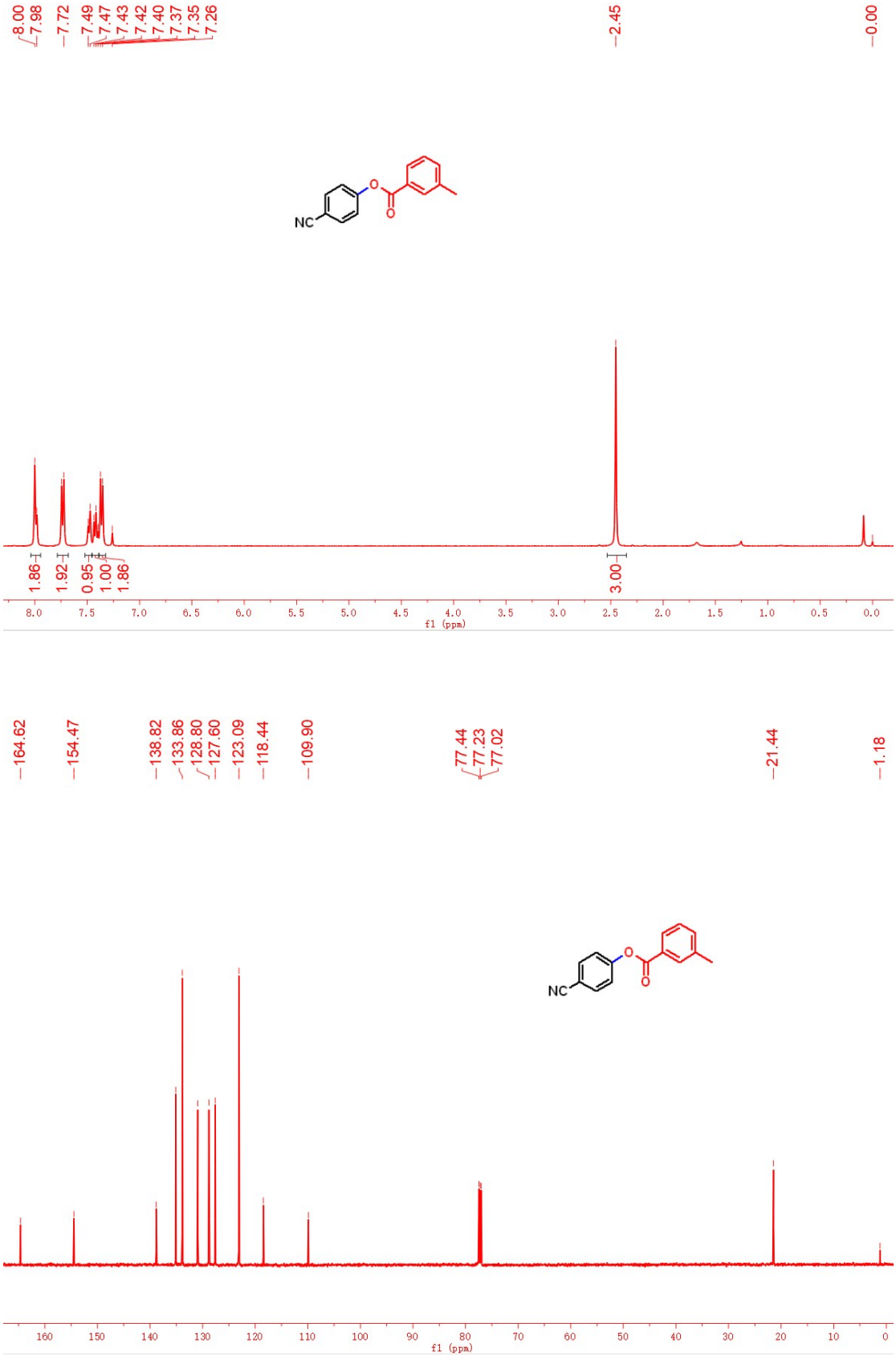
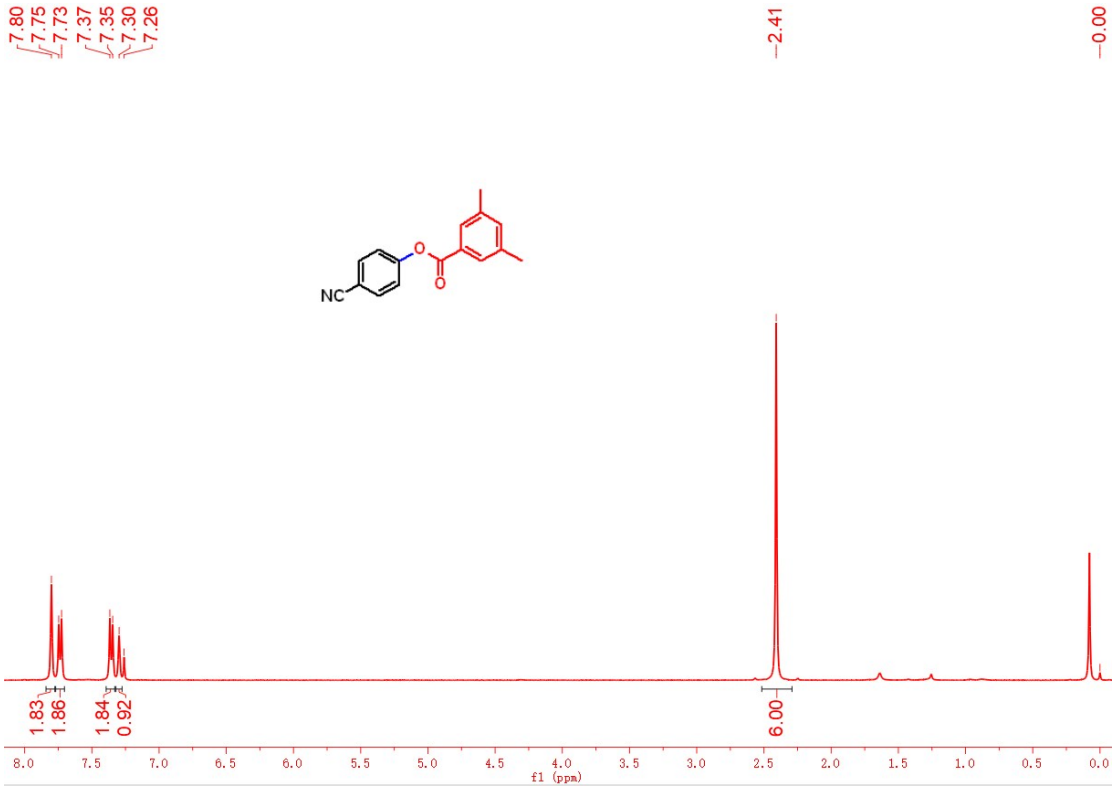


Fig. S16 The ^{1}H and ^{13}C NMR spectra for 4-cyanophenyl 3,5-dimethylbenzoate (**3ak**)



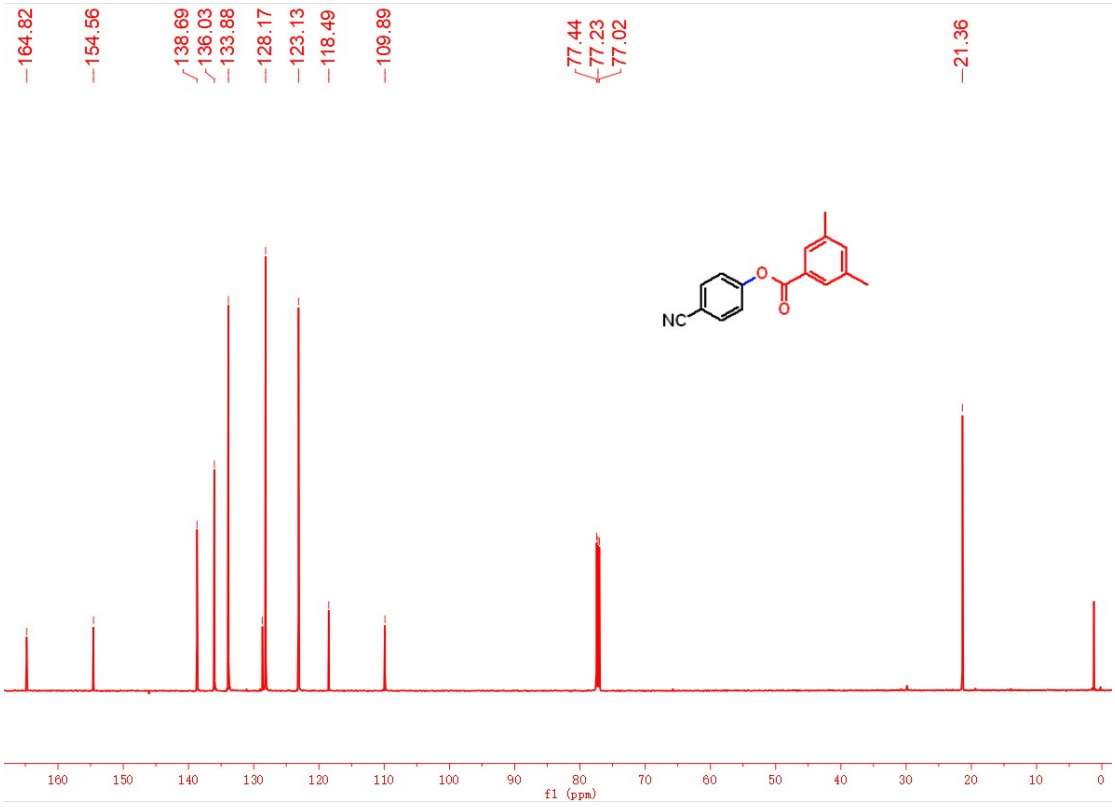


Fig. S17 The ^{1}H and ^{13}C NMR spectra for 4-cyanophenyl 3-methoxy-4-methylbenzoate (**3al**)

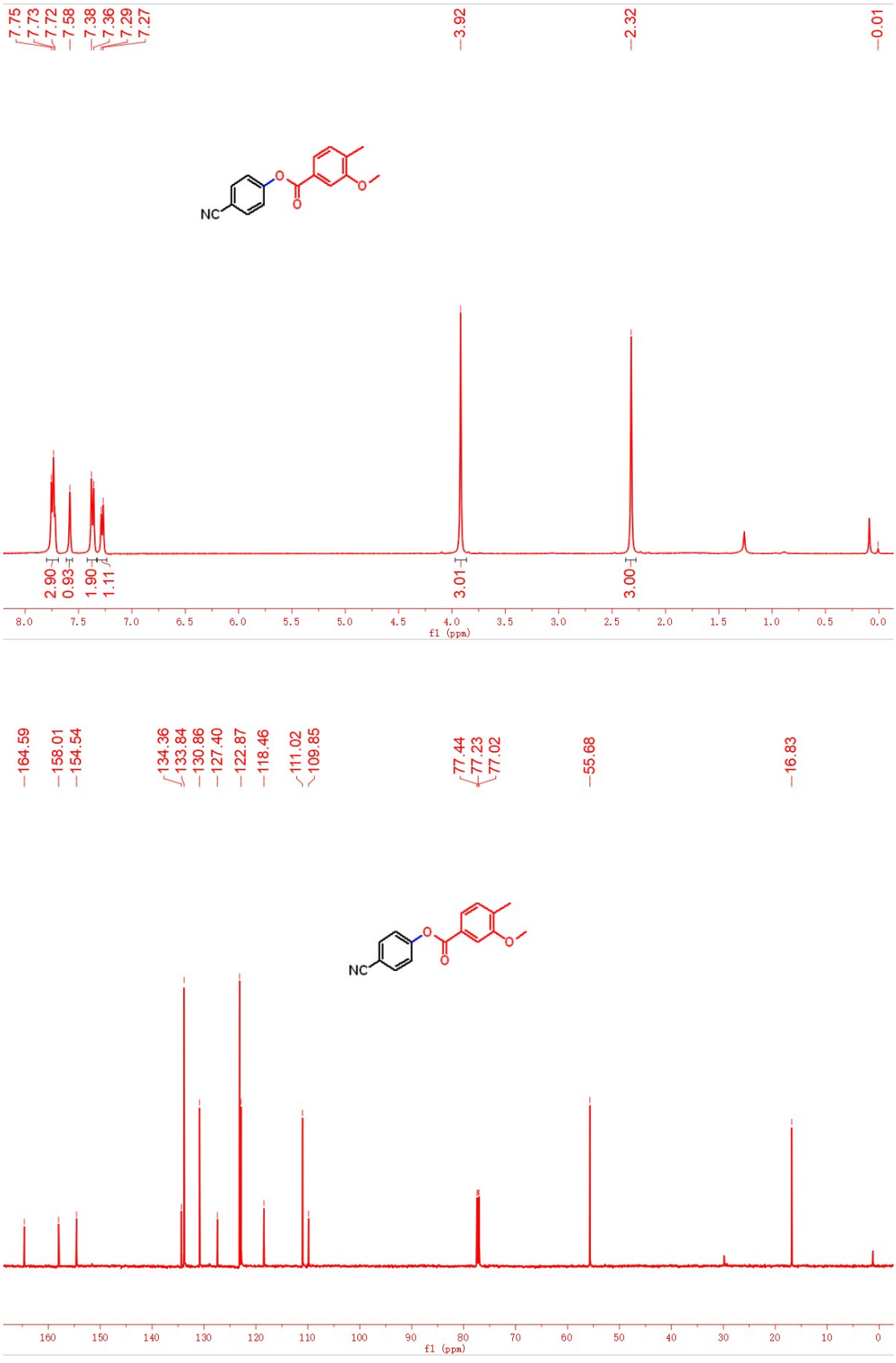
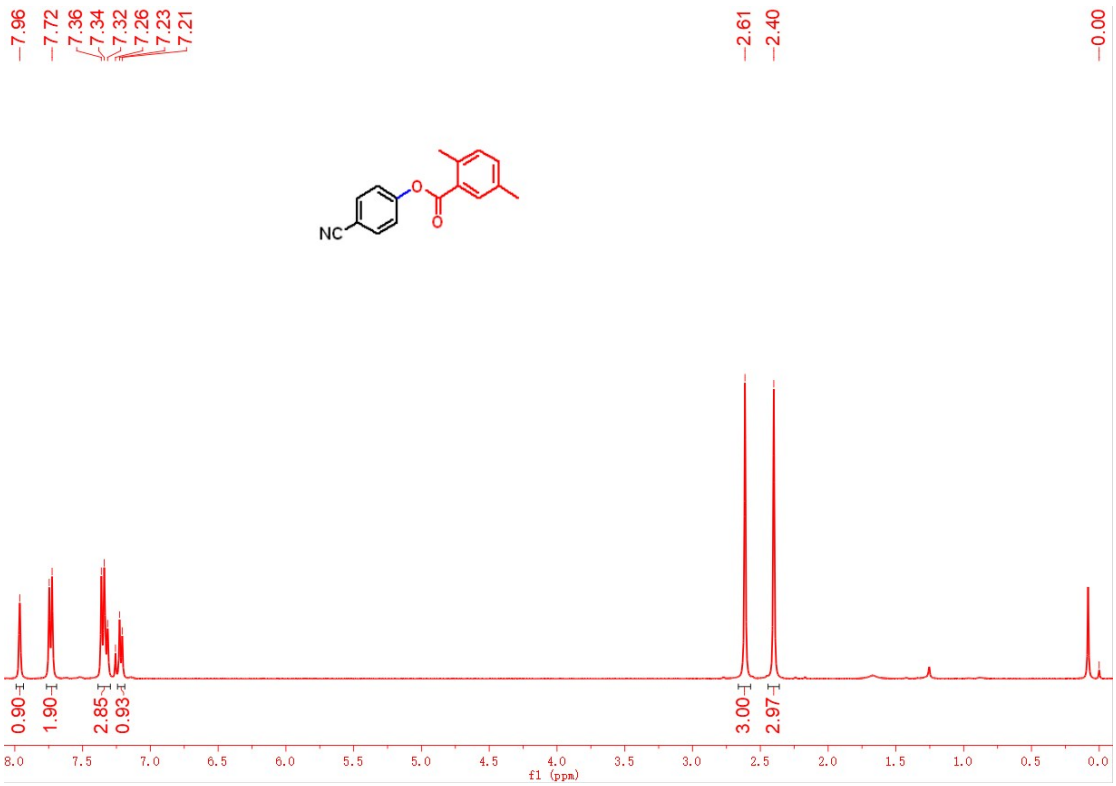


Fig. S18 The ^{1}H and ^{13}C NMR spectra for 4-cyanophenyl 2,5-dimethylbenzoate (**3am**)



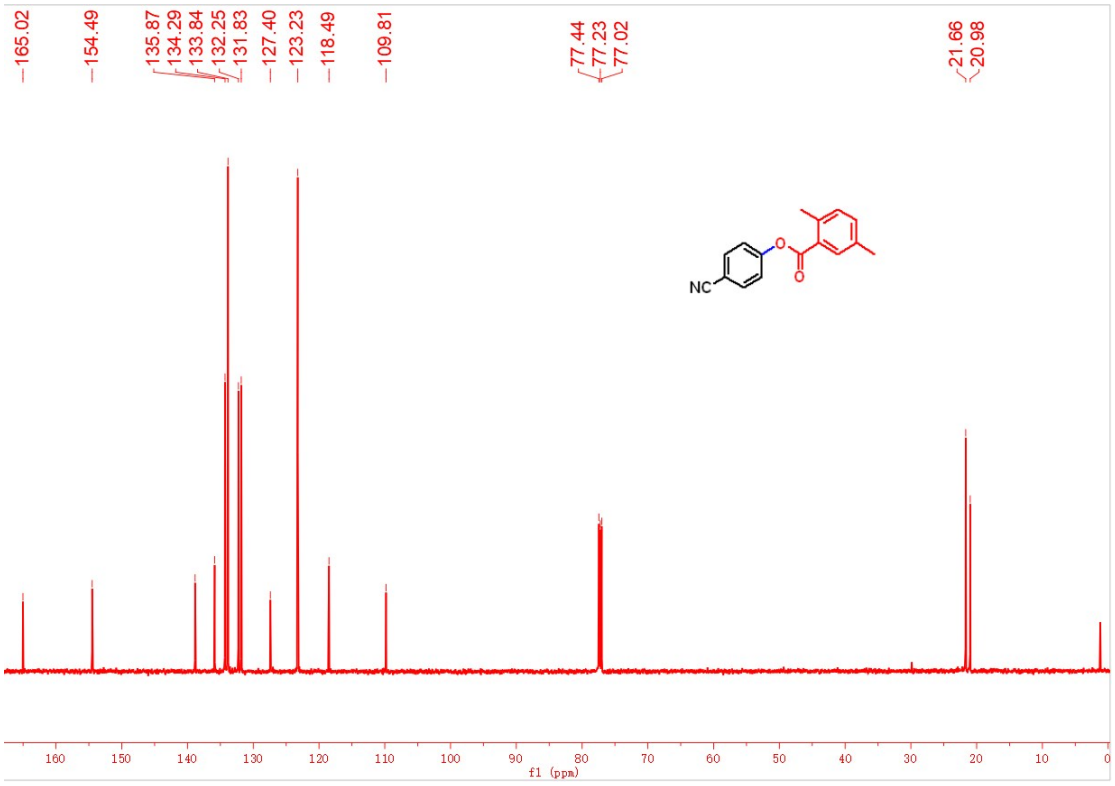
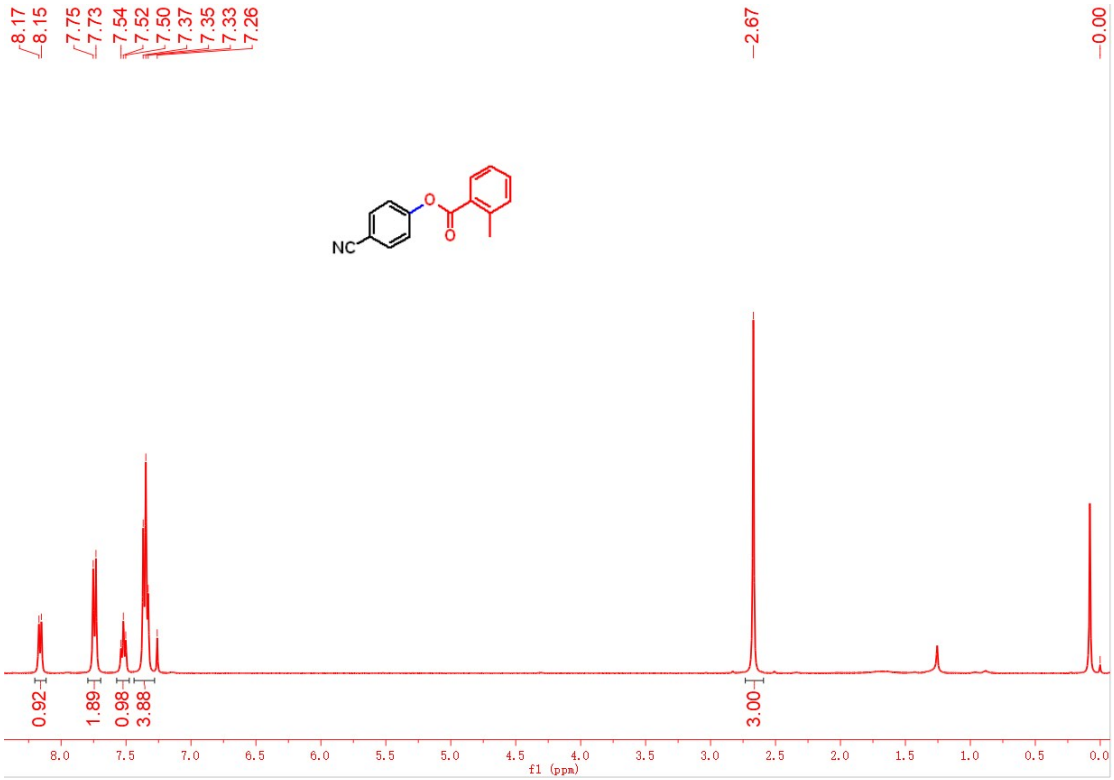


Fig. S19 The ^{1}H and ^{13}C NMR spectra for 4-cyanophenyl 2-methylbenzoate (**3an**)



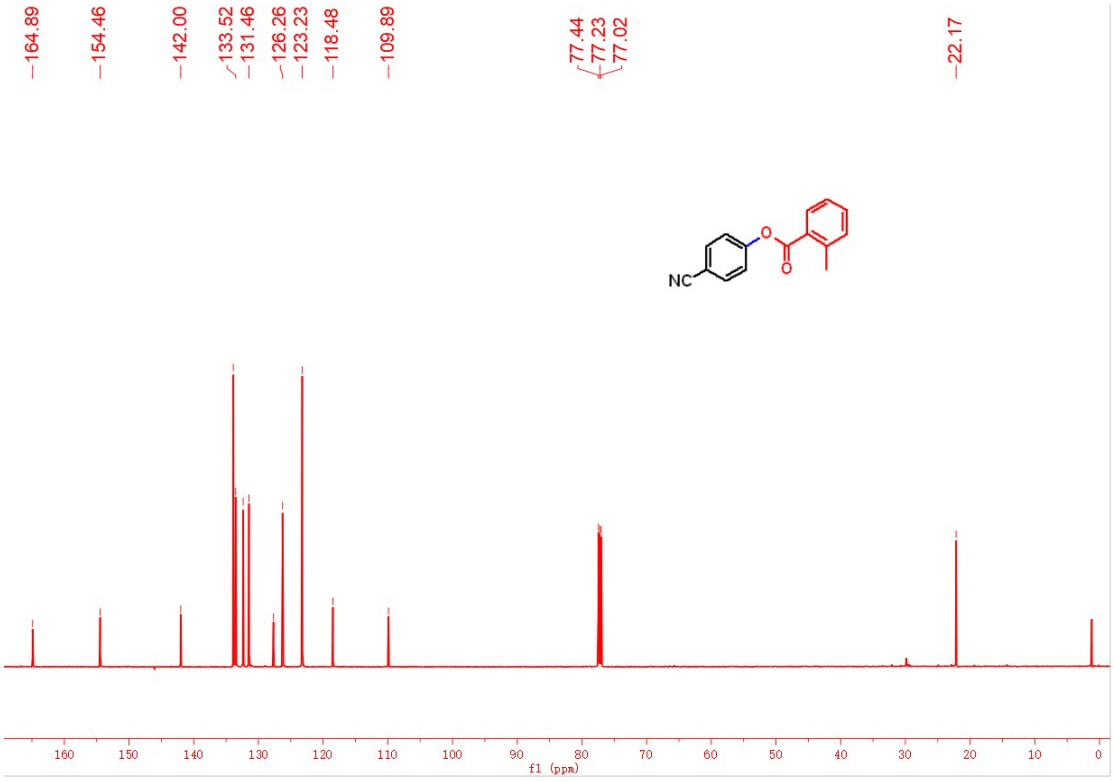
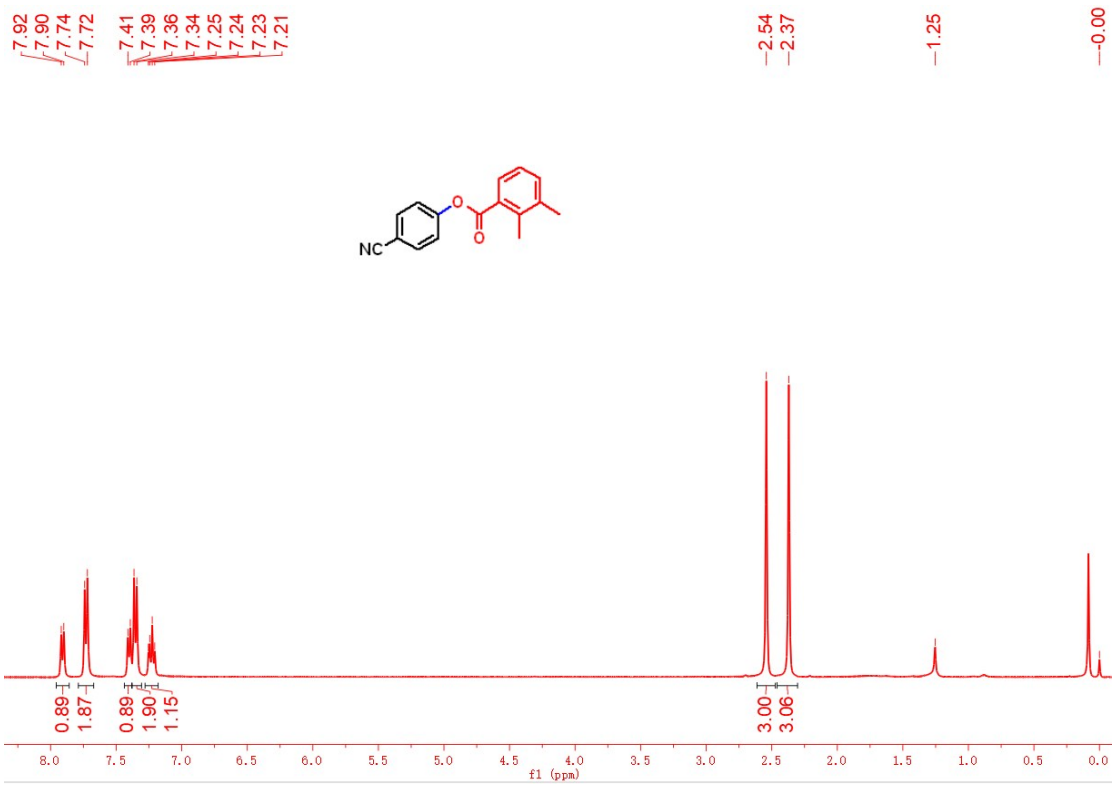


Fig. S20 The ^{1}H and ^{13}C NMR spectra for 4-cyanophenyl 2,3-dimethylbenzoate (**3ao**)



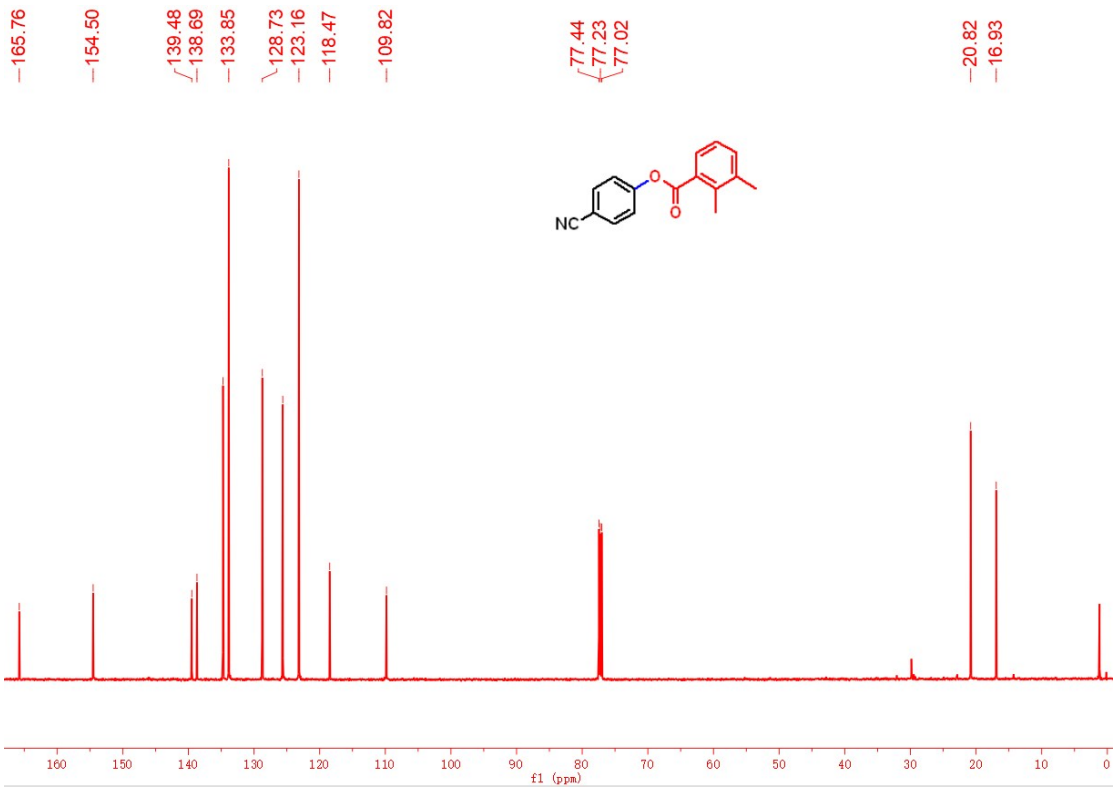


Fig. S21 The ^{1}H and ^{13}C NMR spectra for 4-cyanophenyl [1,1'-biphenyl]-2-carboxylate (**3ap**)

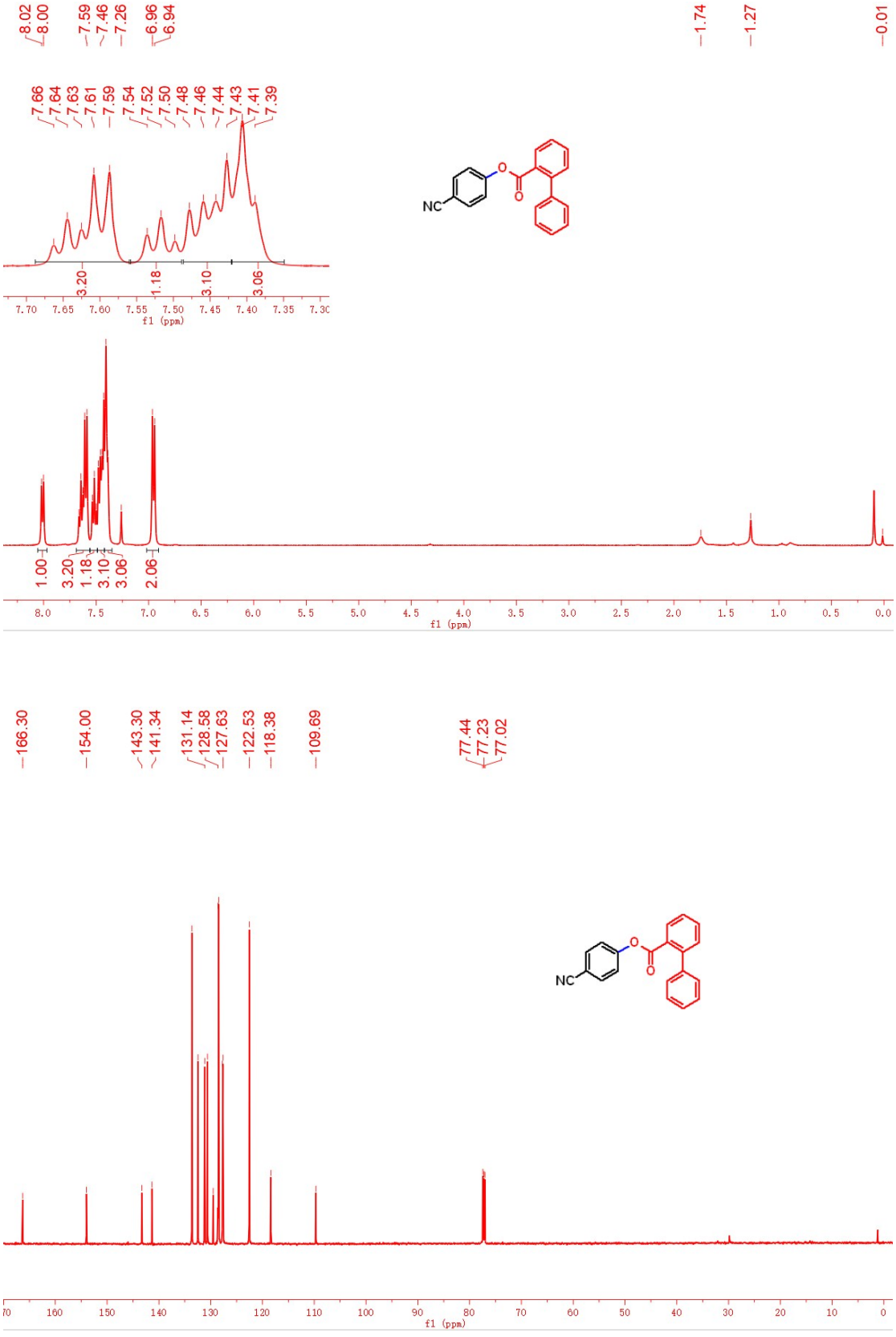
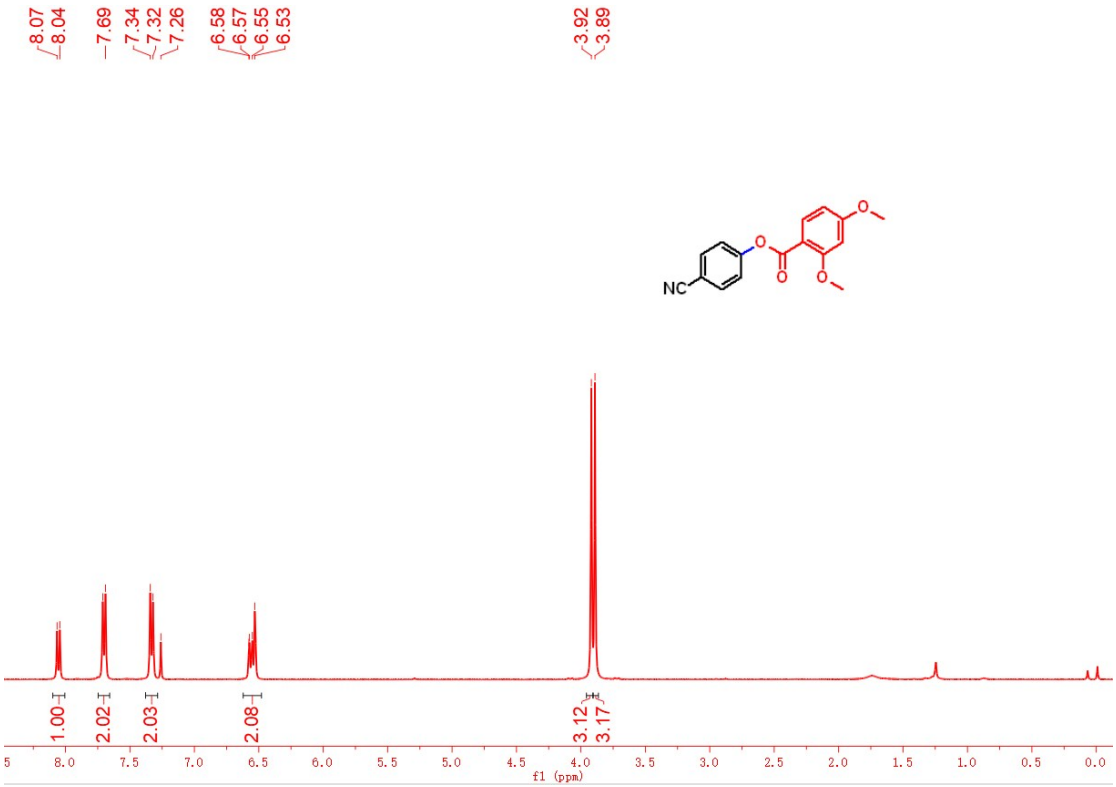


Fig. S22 The ^{1}H and ^{13}C NMR spectra for 4-cyanophenyl 2,4-dimethoxybenzoate (**3aq**)



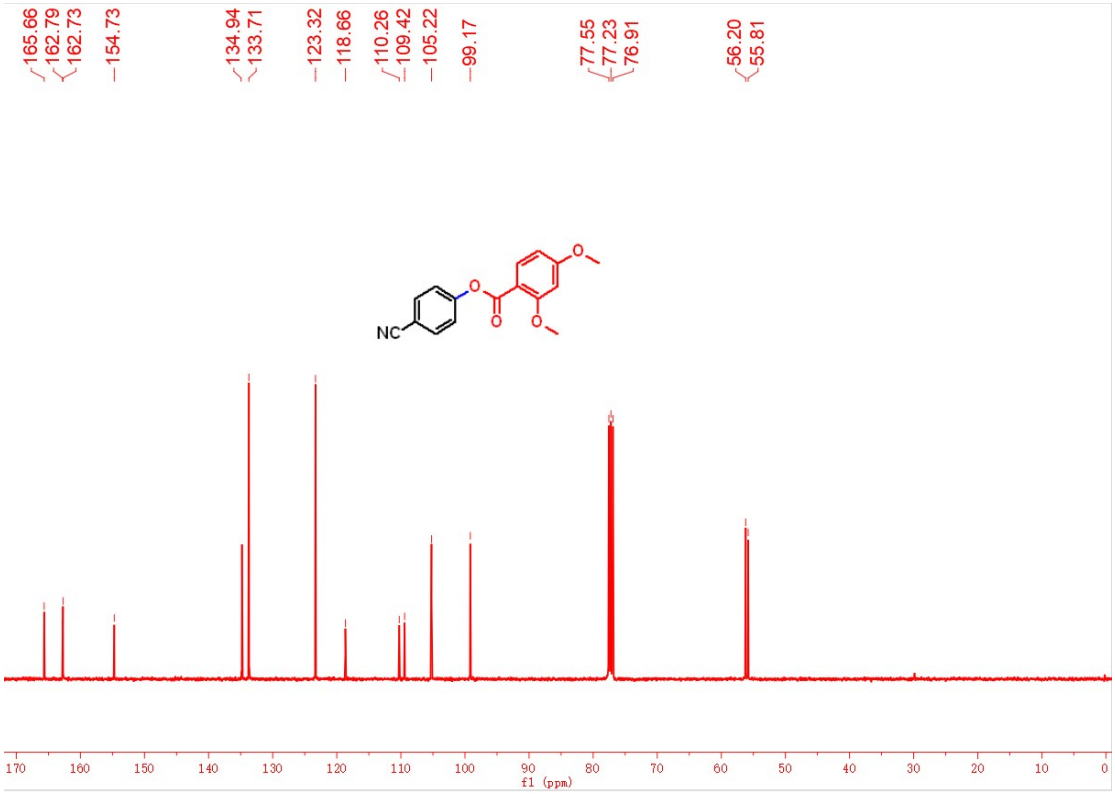
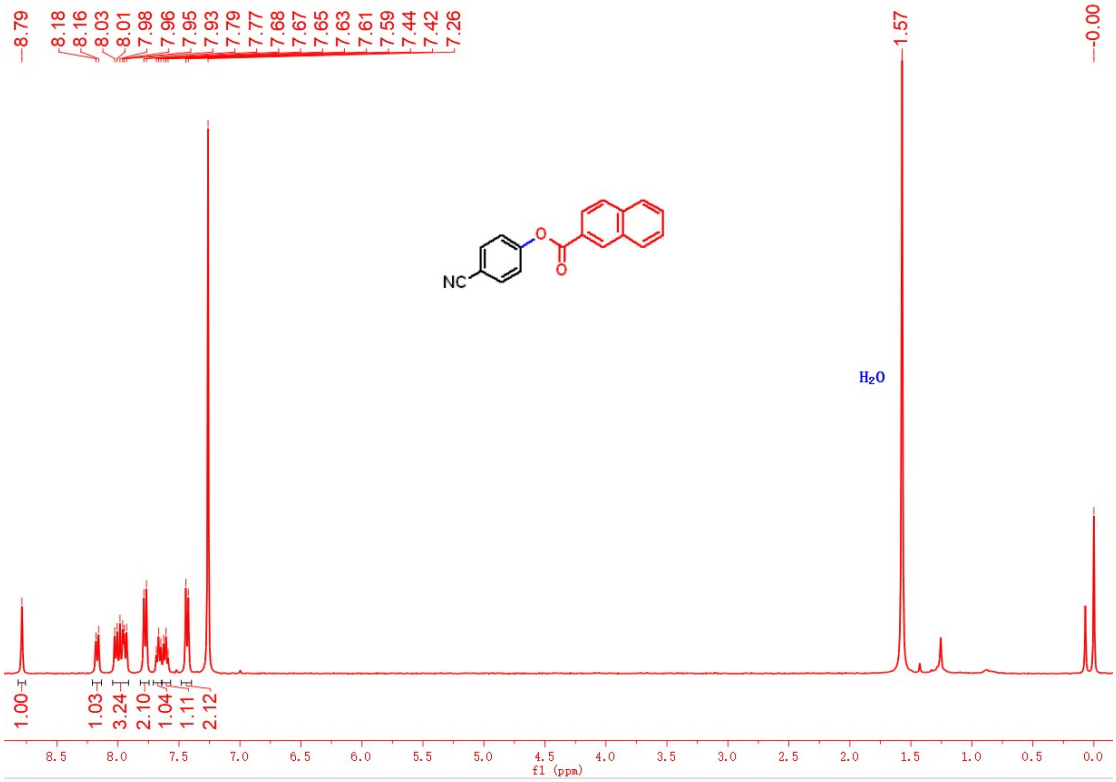


Fig. S23 The ^{1}H and ^{13}C NMR spectra for 4-cyanophenyl 2-naphthoate (**3ar**)



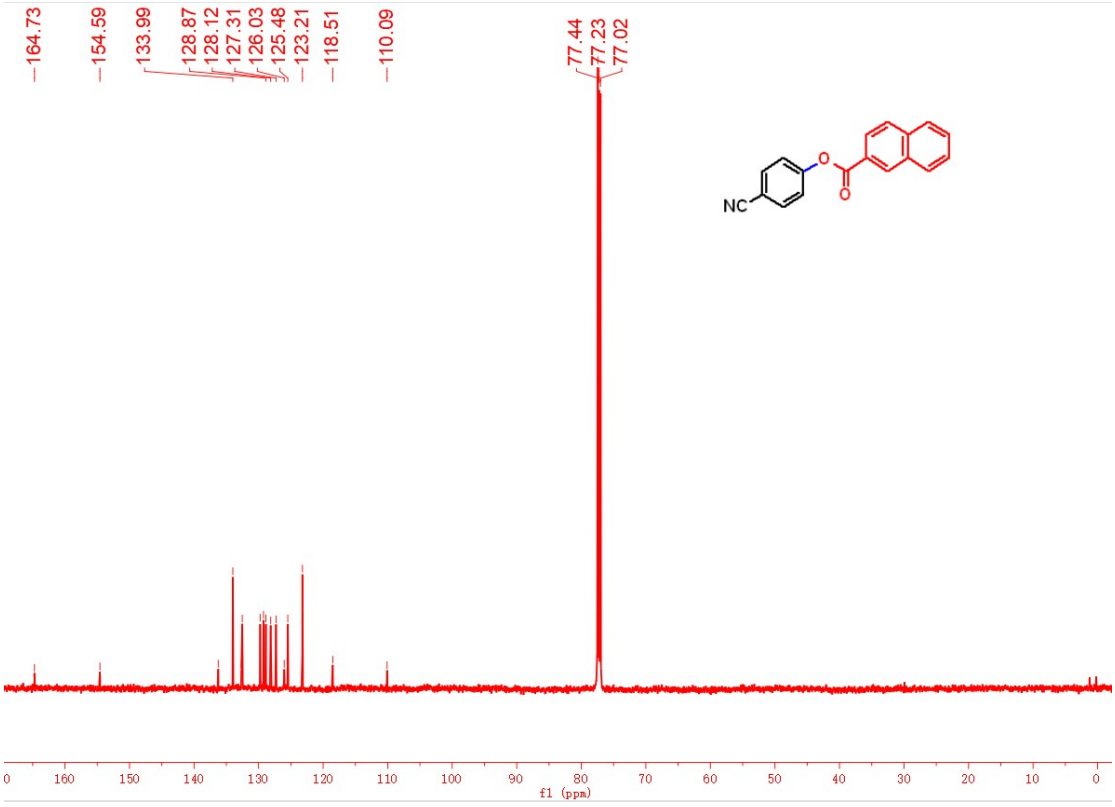
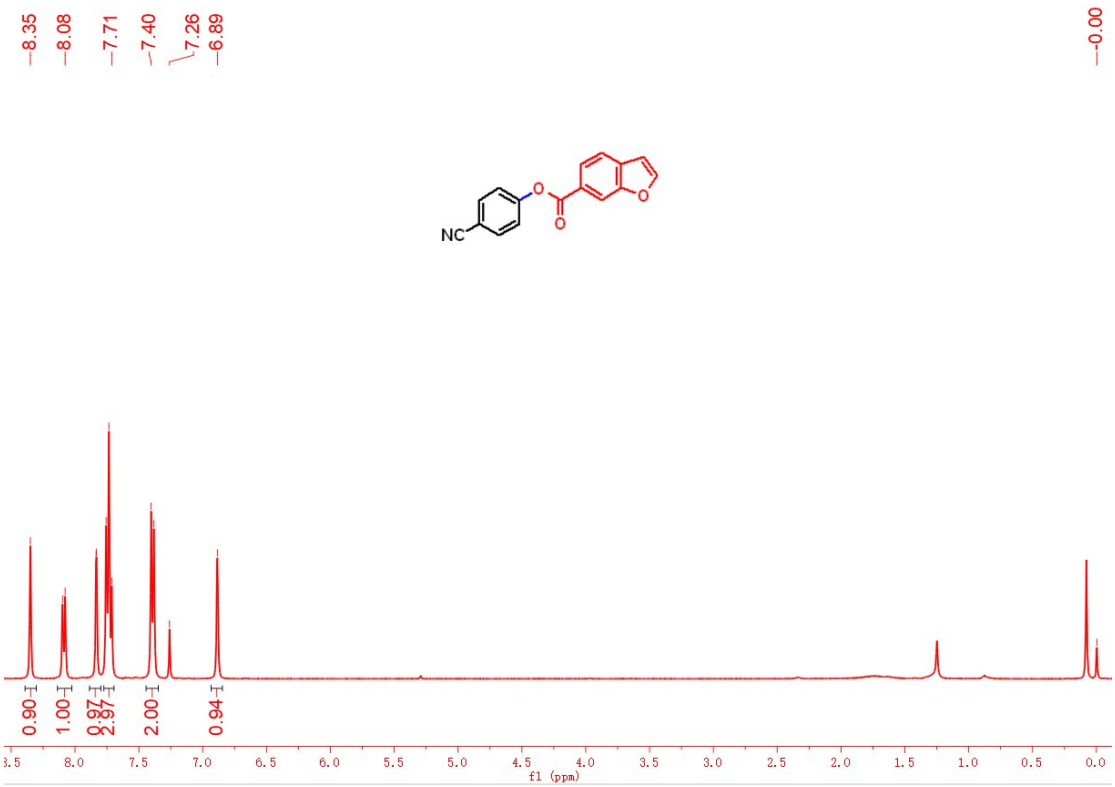


Fig. S24 The ^{1}H and ^{13}C NMR spectra for 4-cyanophenyl benzofuran-6-carboxylate (**3as**)



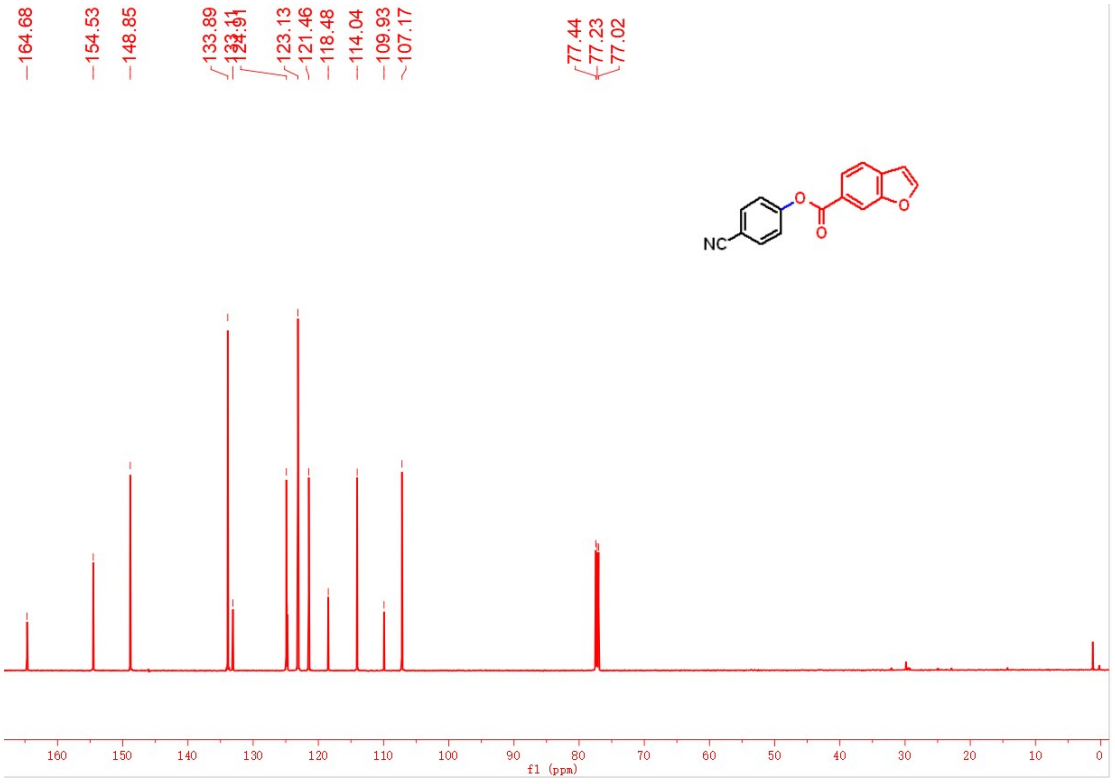
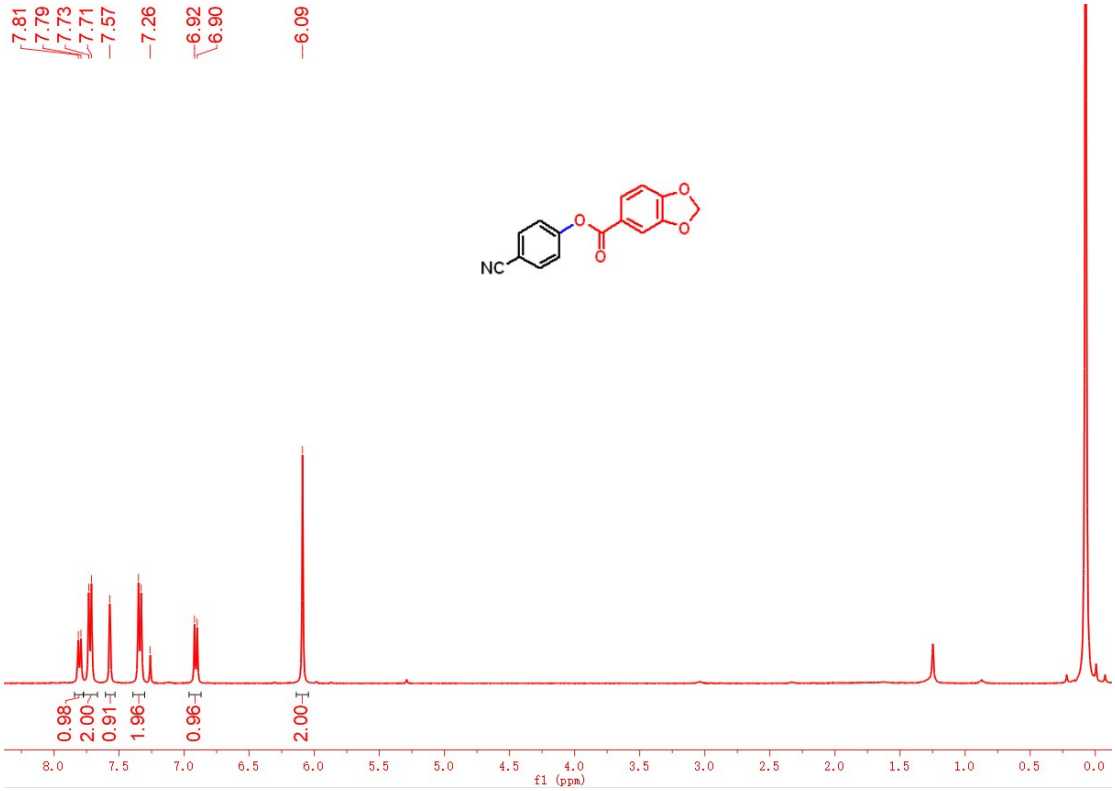


Fig. S25 The ^{1}H and ^{13}C NMR spectra for 4-cyanophenyl benzo[*d*][1,3]dioxole-5-carboxylate (**3at**)



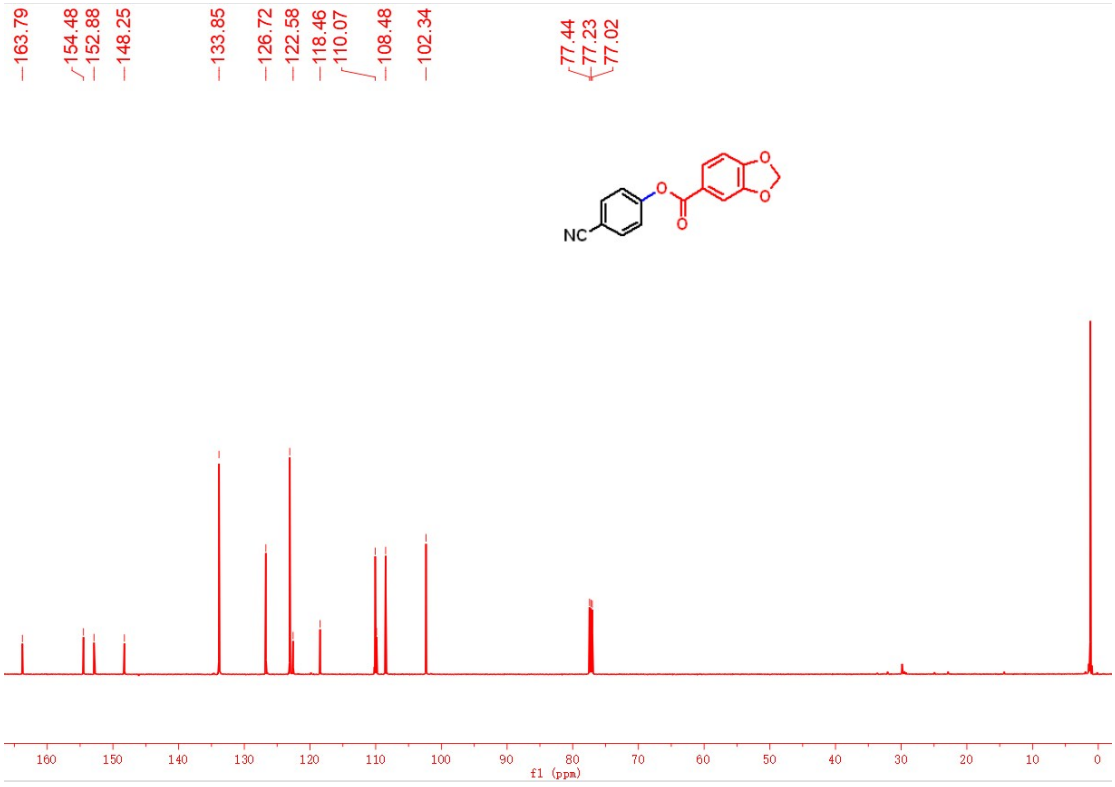


Fig. S26 The ^{1}H and ^{13}C NMR spectra for 4-cyanophenyl 2-phenylacetate (**3au**)

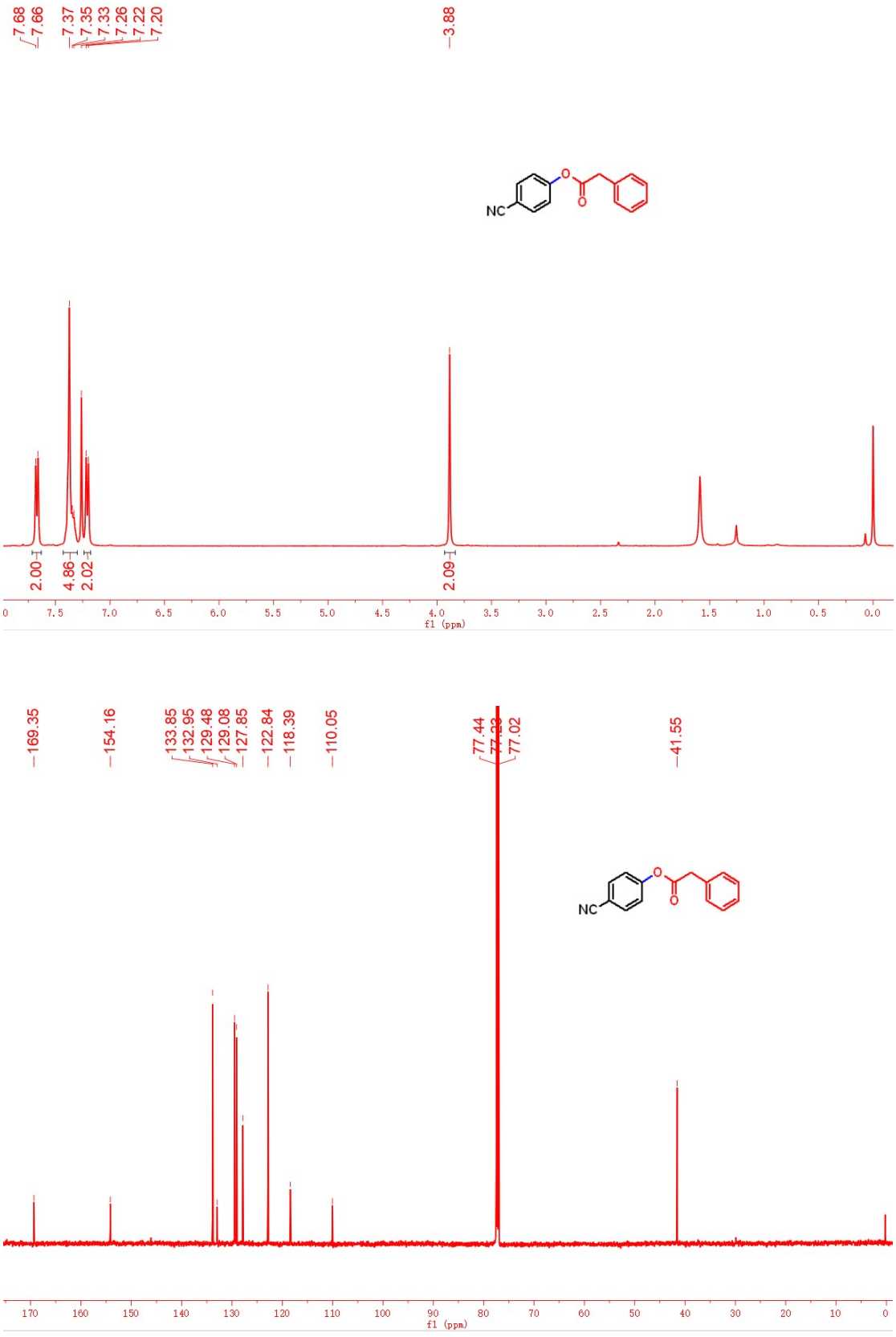


Fig. S27 The ^{1}H and ^{13}C NMR spectra for 4-cyanophenyl acetate (**3av**)

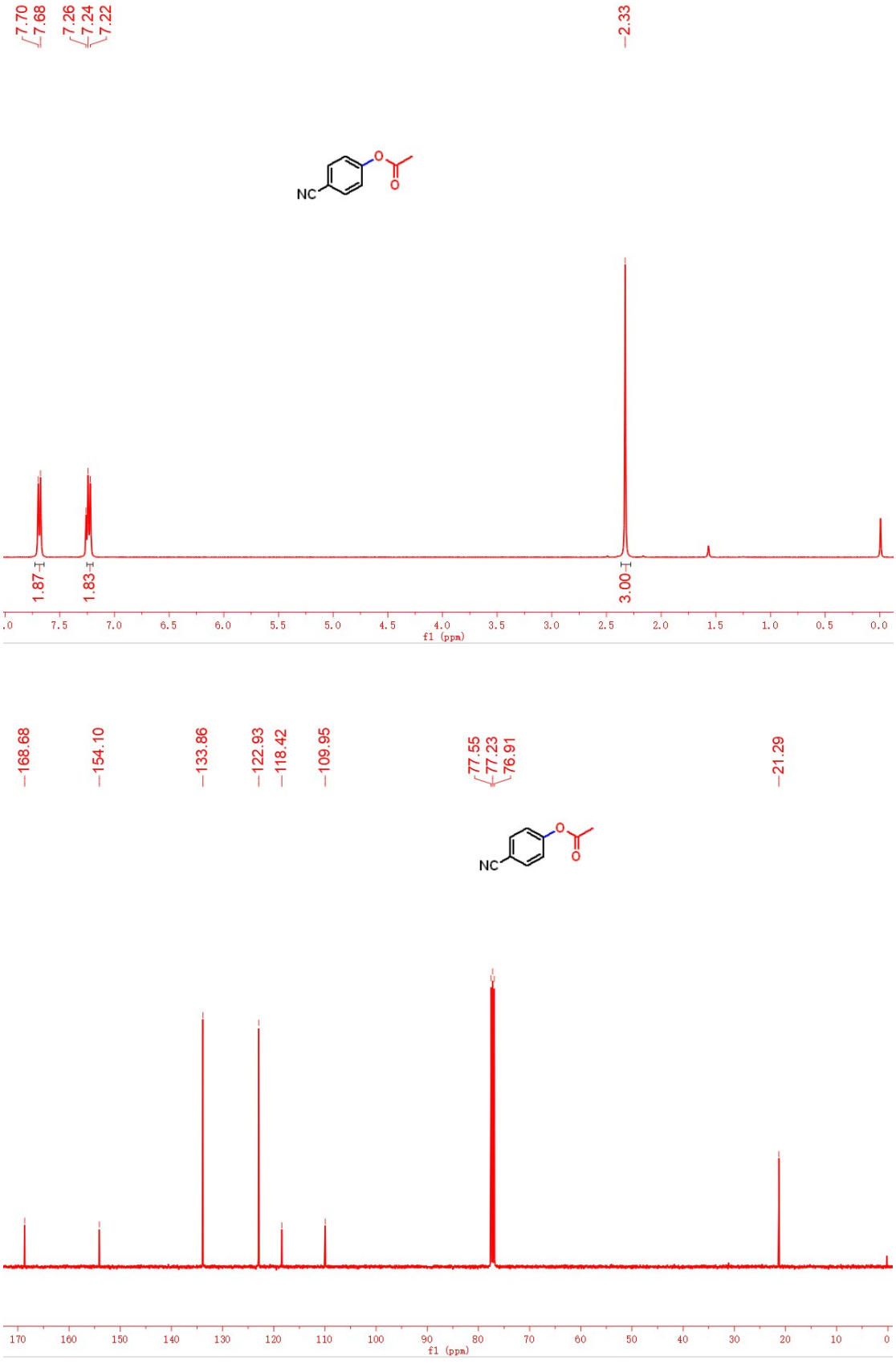


Fig. S28 The ^{1}H and ^{13}C NMR spectra for 4-cyanophenyl cyclohexanecarboxylate (**3aw**)

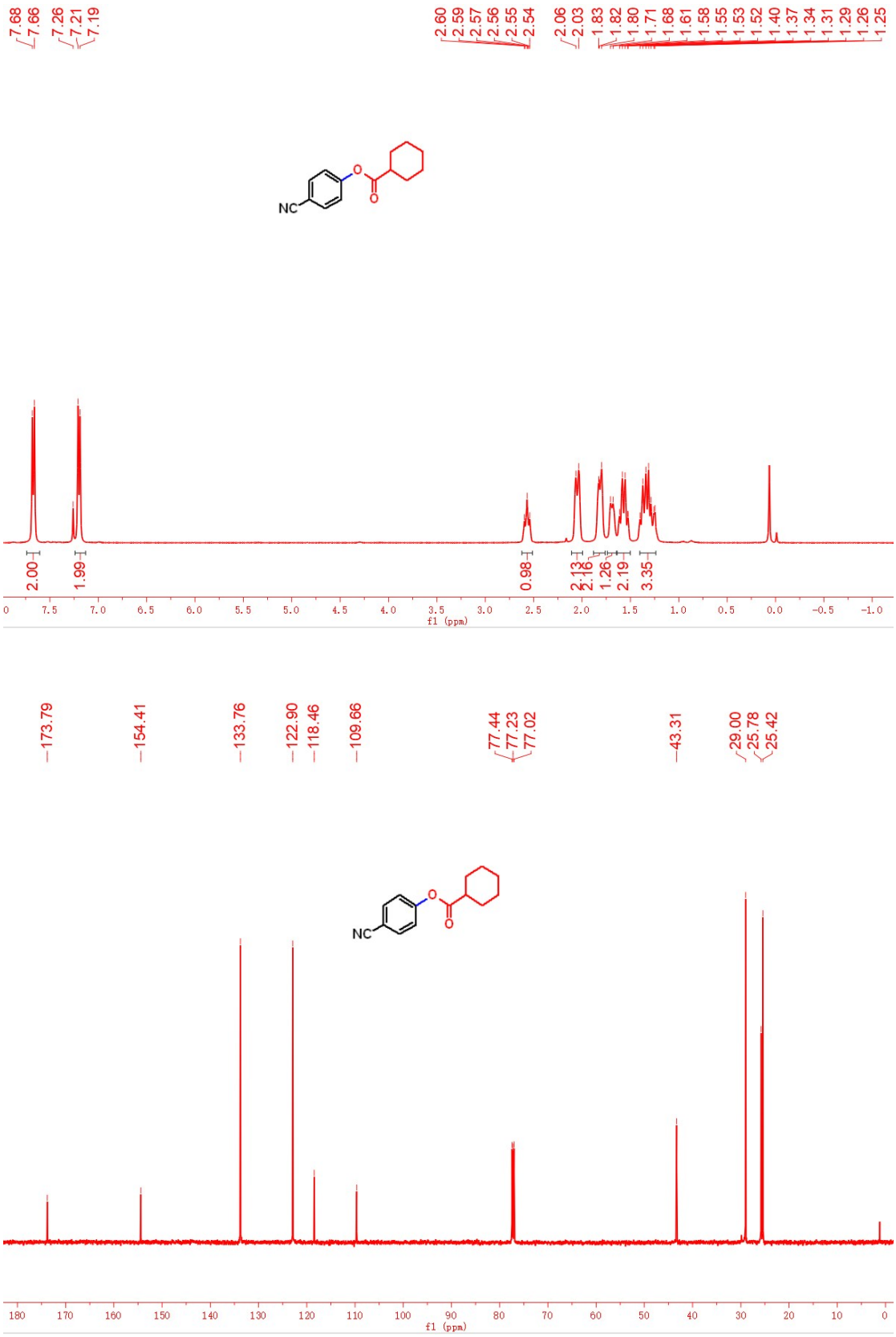


Fig. S29 The ^{1}H and ^{13}C NMR spectra for 4-cyanophenyl tetrahydro-2H-pyran-4-carboxylate (**3ax**)

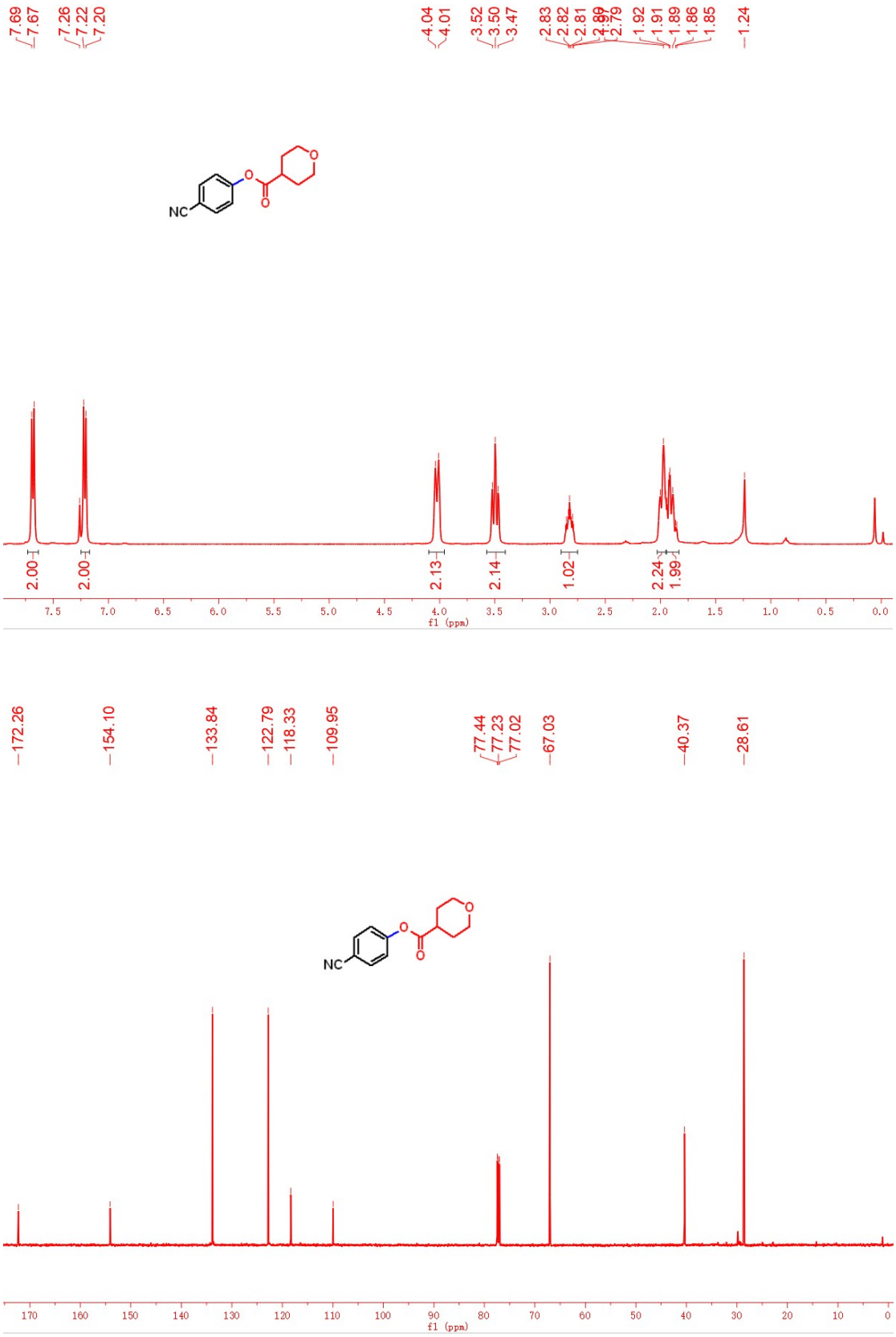


Fig. S30 The ^{1}H and ^{13}C NMR spectra for 4-cyanophenyl cyclopropanecarboxylate (**3ay**)

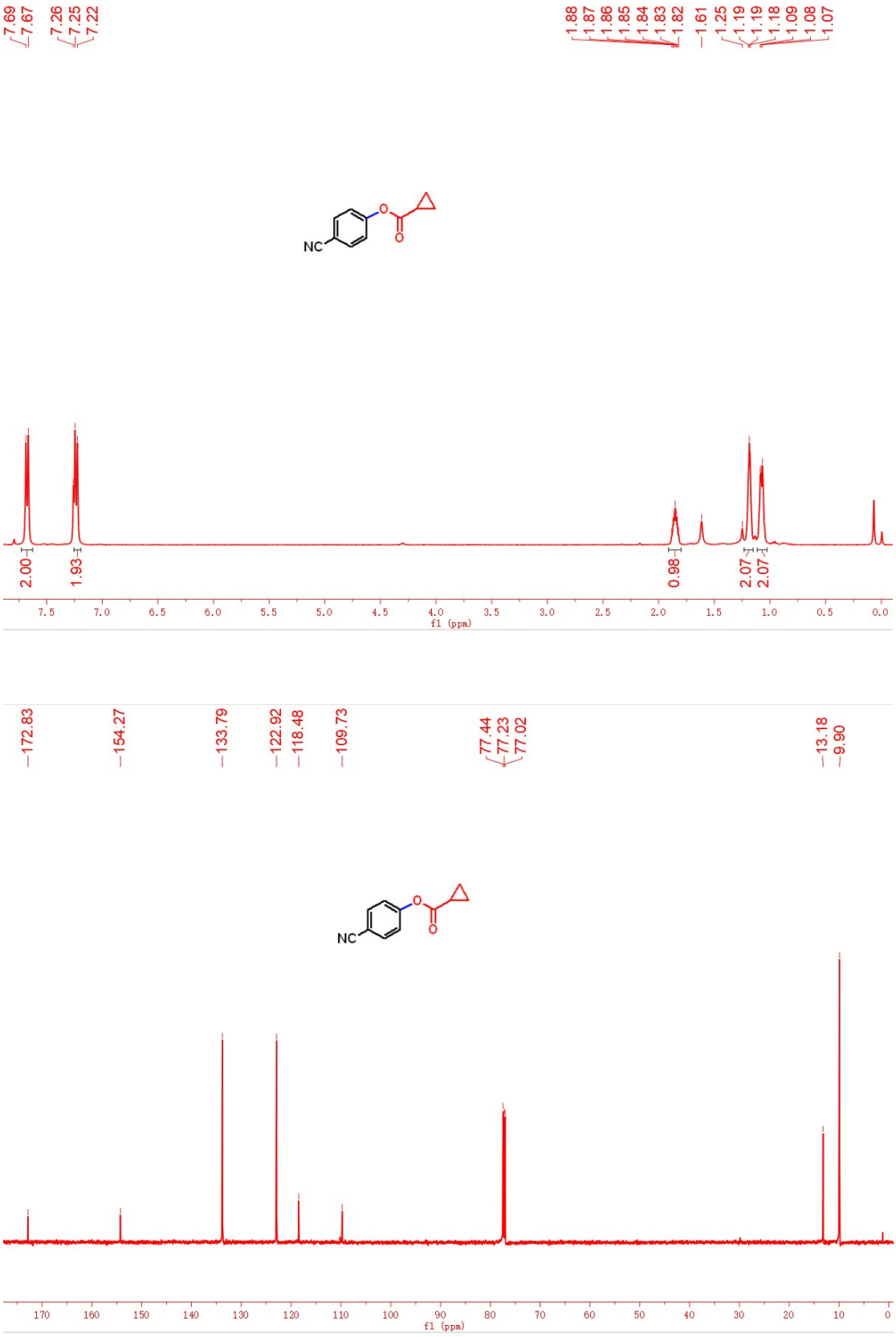


Fig. S31 The ^{1}H and ^{13}C NMR spectra for 4-cyanophenyl 1-Adamantanecarboxylate (**3az**)

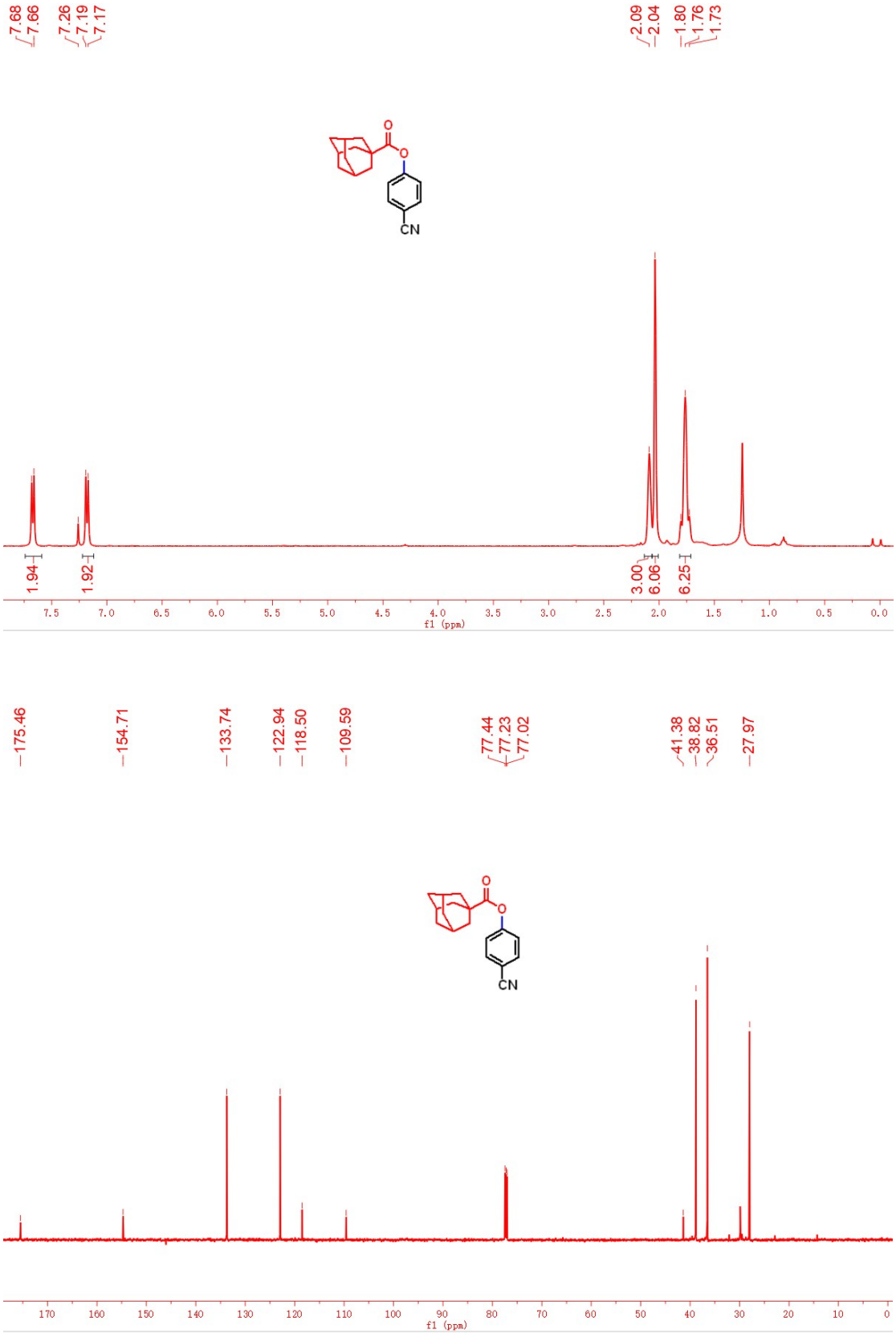
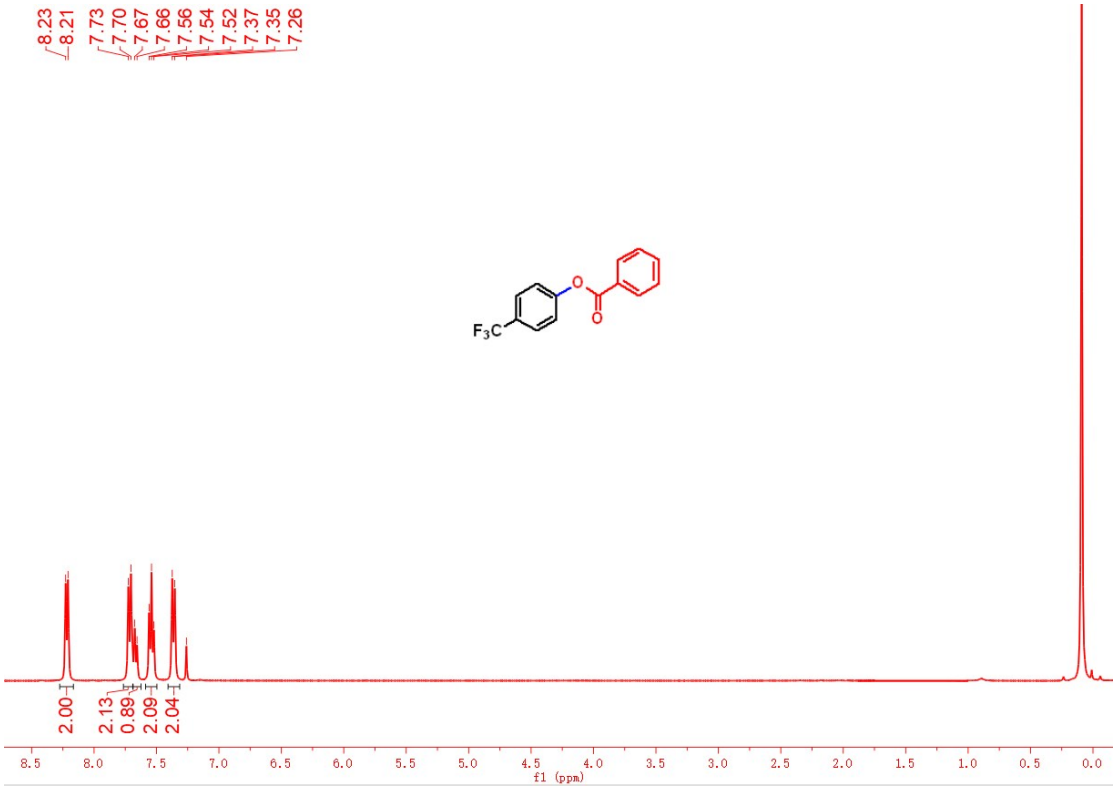


Fig. S32 The ^{1}H and ^{13}C NMR spectra for 4-(trifluoromethyl)phenyl benzoate (**3ba**)



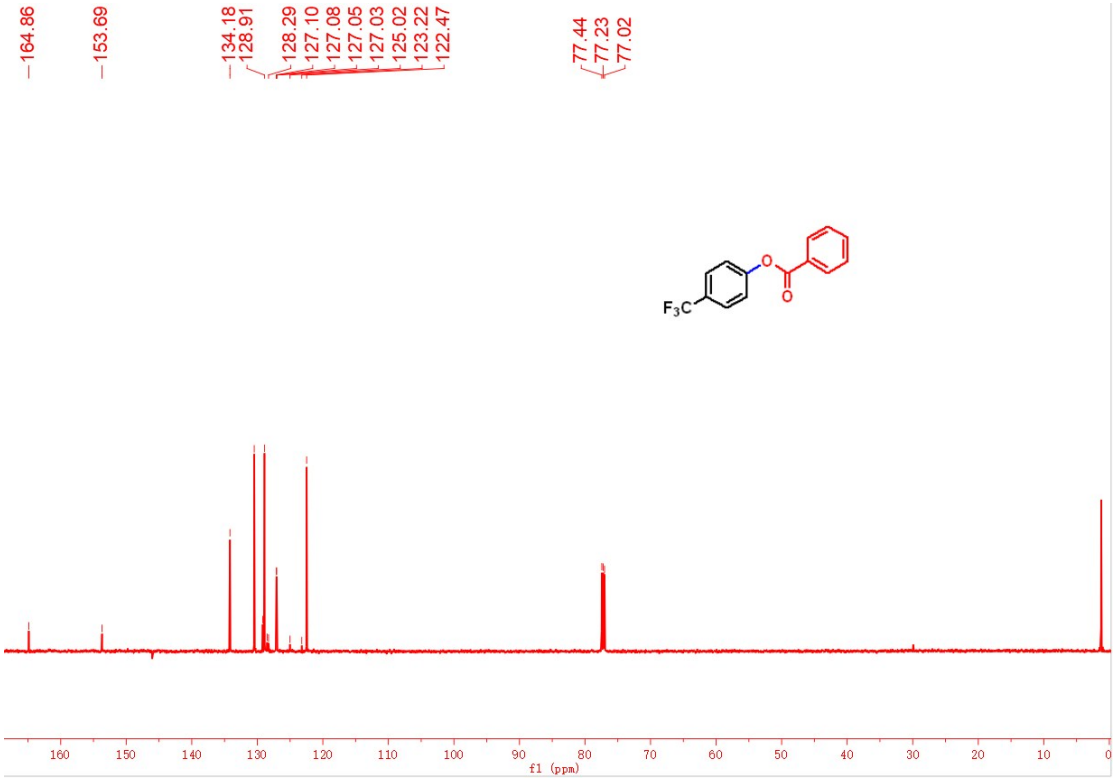
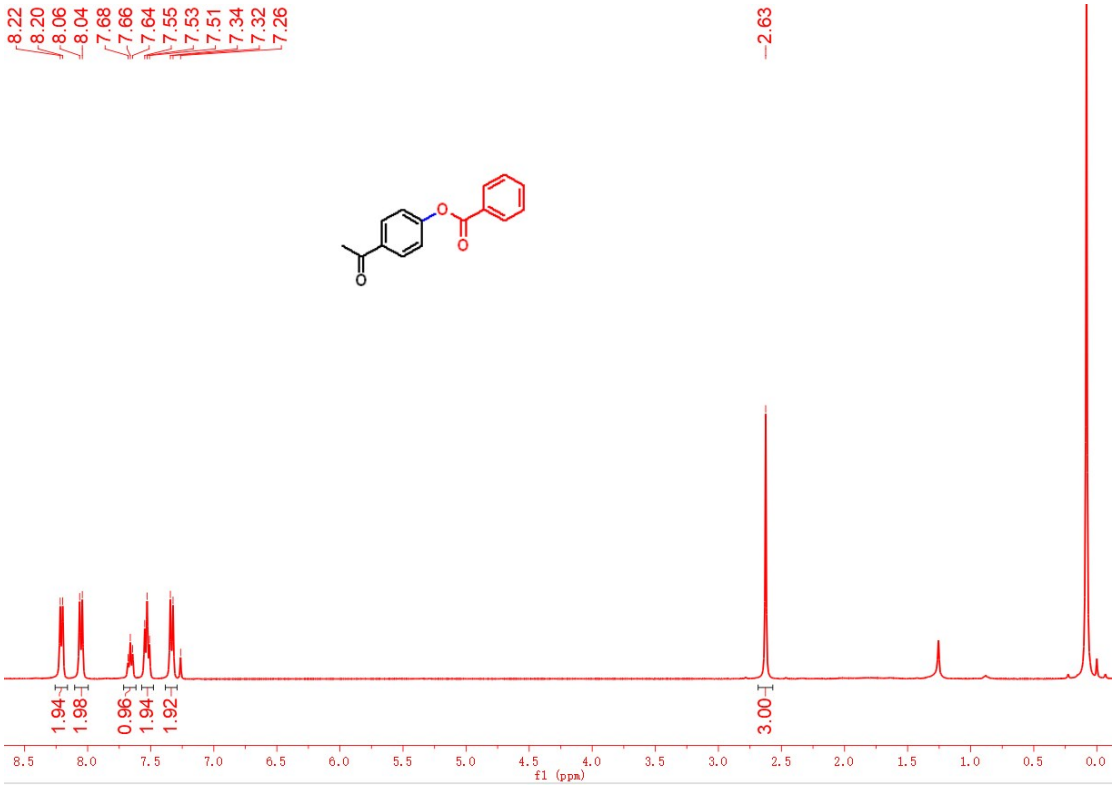


Fig. S33 The ^{1}H and ^{13}C NMR spectra for 4-acetylphenyl benzoate (**3ca**)



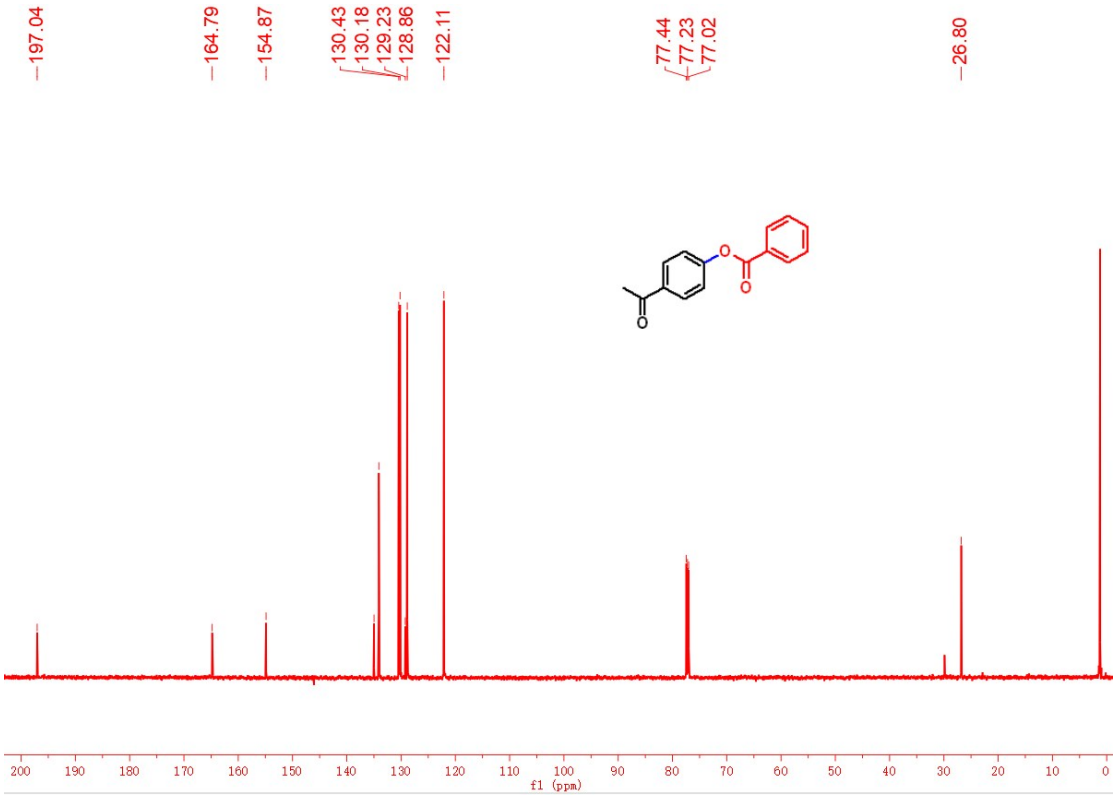
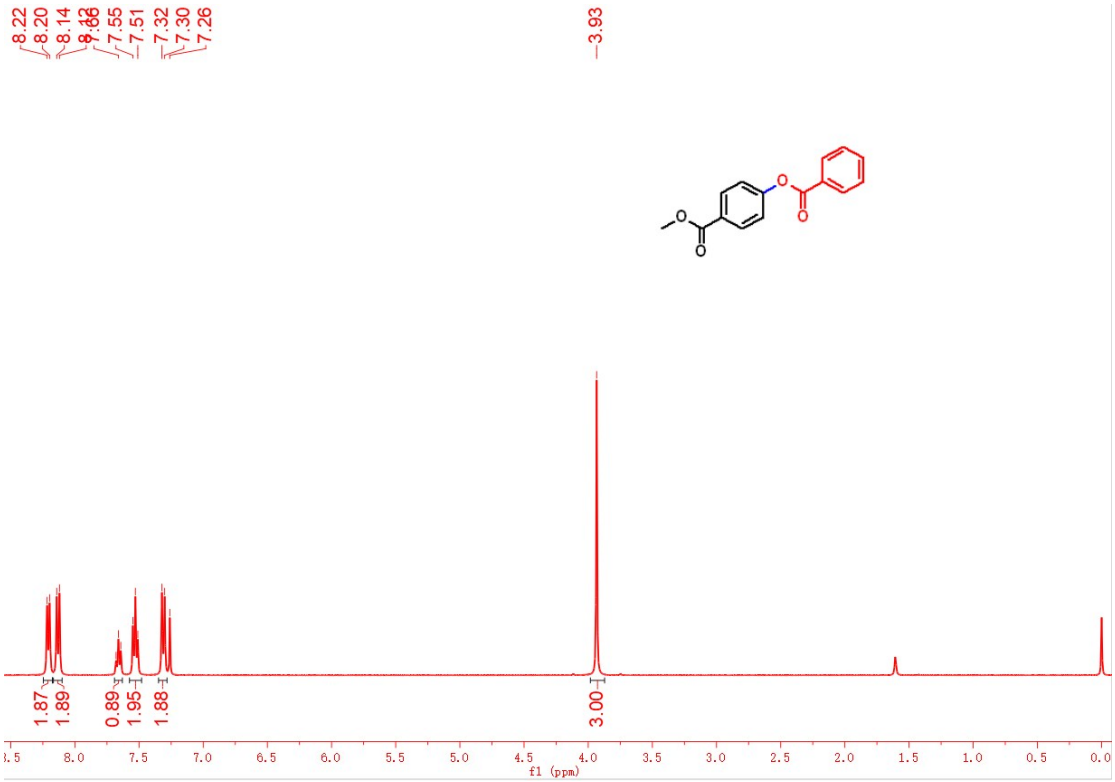


Fig. S34 The ^{1}H and ^{13}C NMR spectra for methyl 4-(benzoyloxy)benzoate (**3da**)



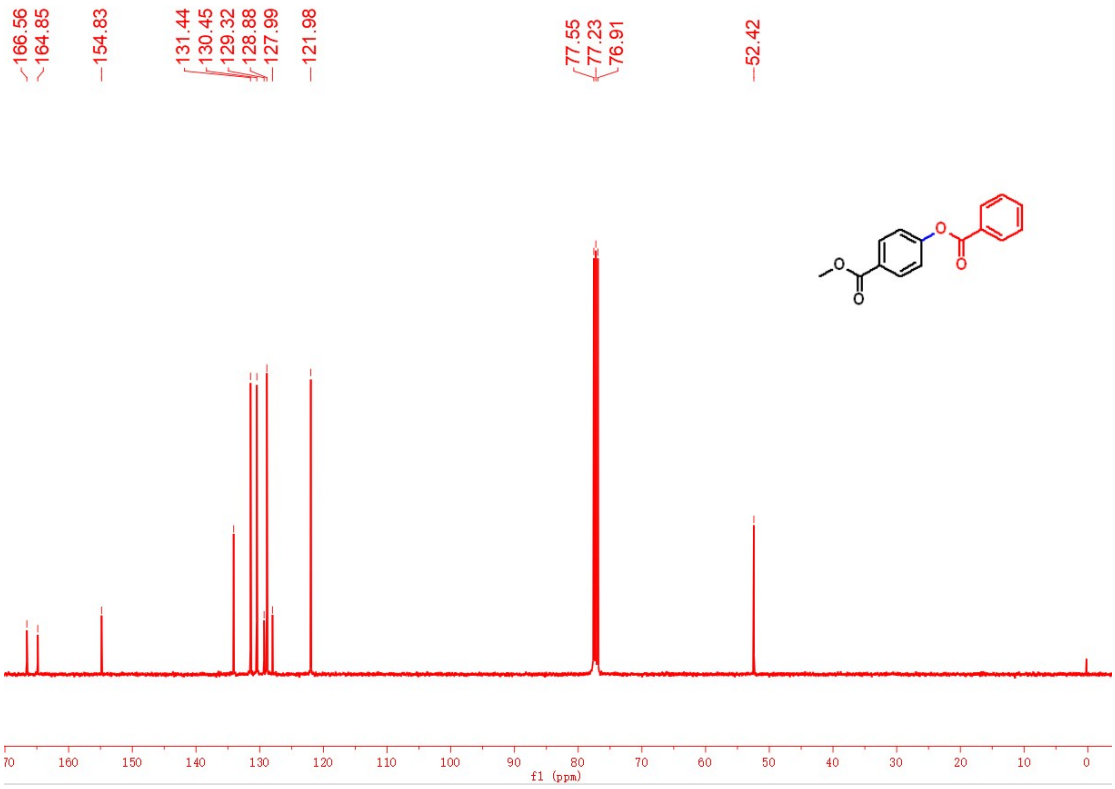
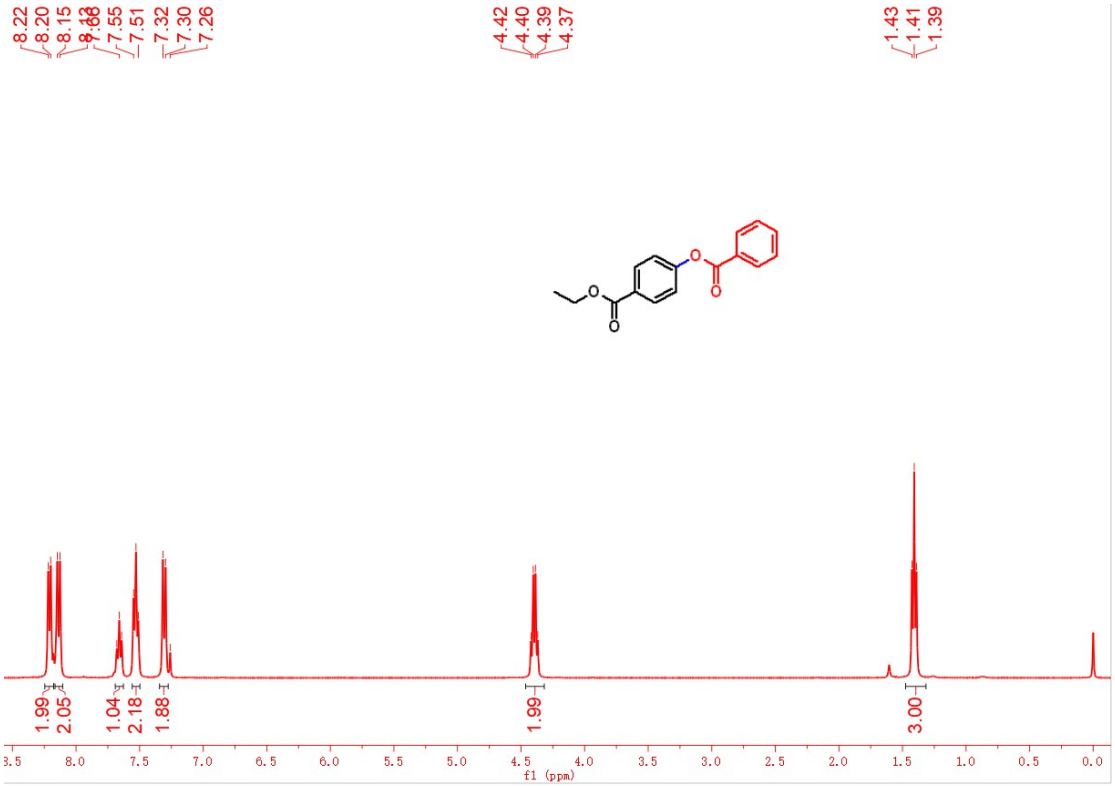


Fig. S35 The ^{1}H and ^{13}C NMR spectra for ethyl 4-(benzoyloxy)benzoate (**3ea**)



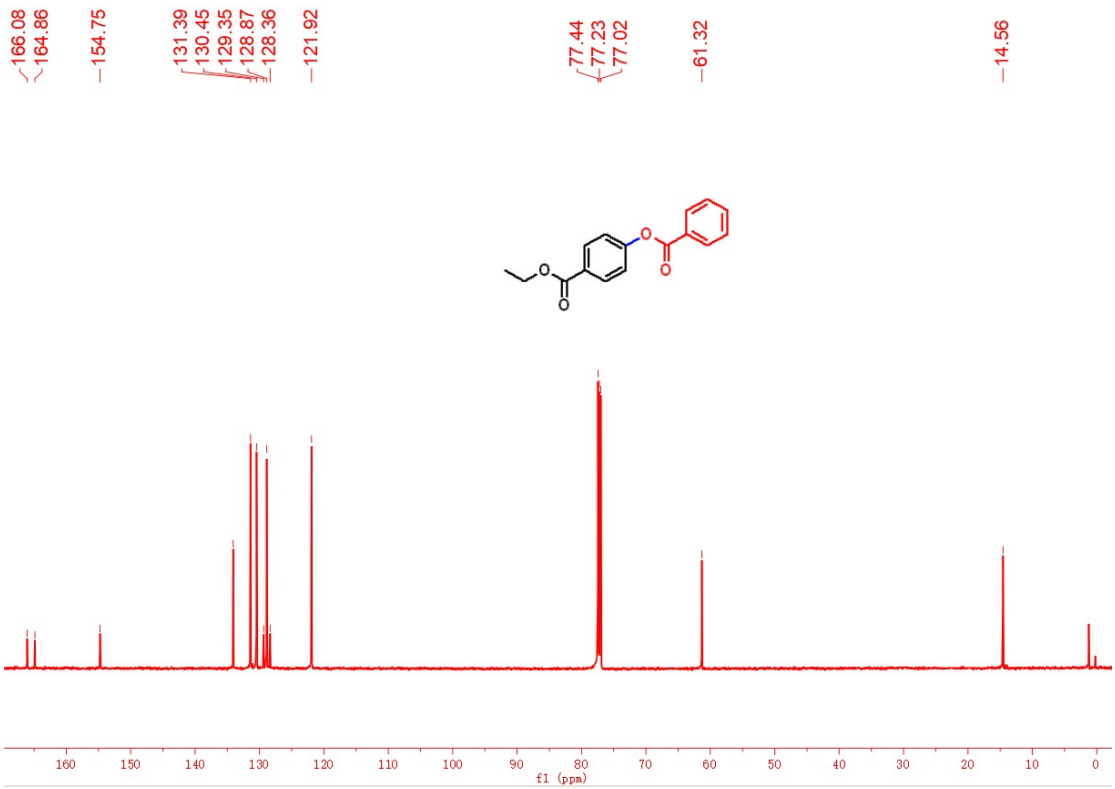


Fig. S36 The ^{1}H and ^{13}C NMR spectra for 3-cyanophenyl benzoate (**3fa**)

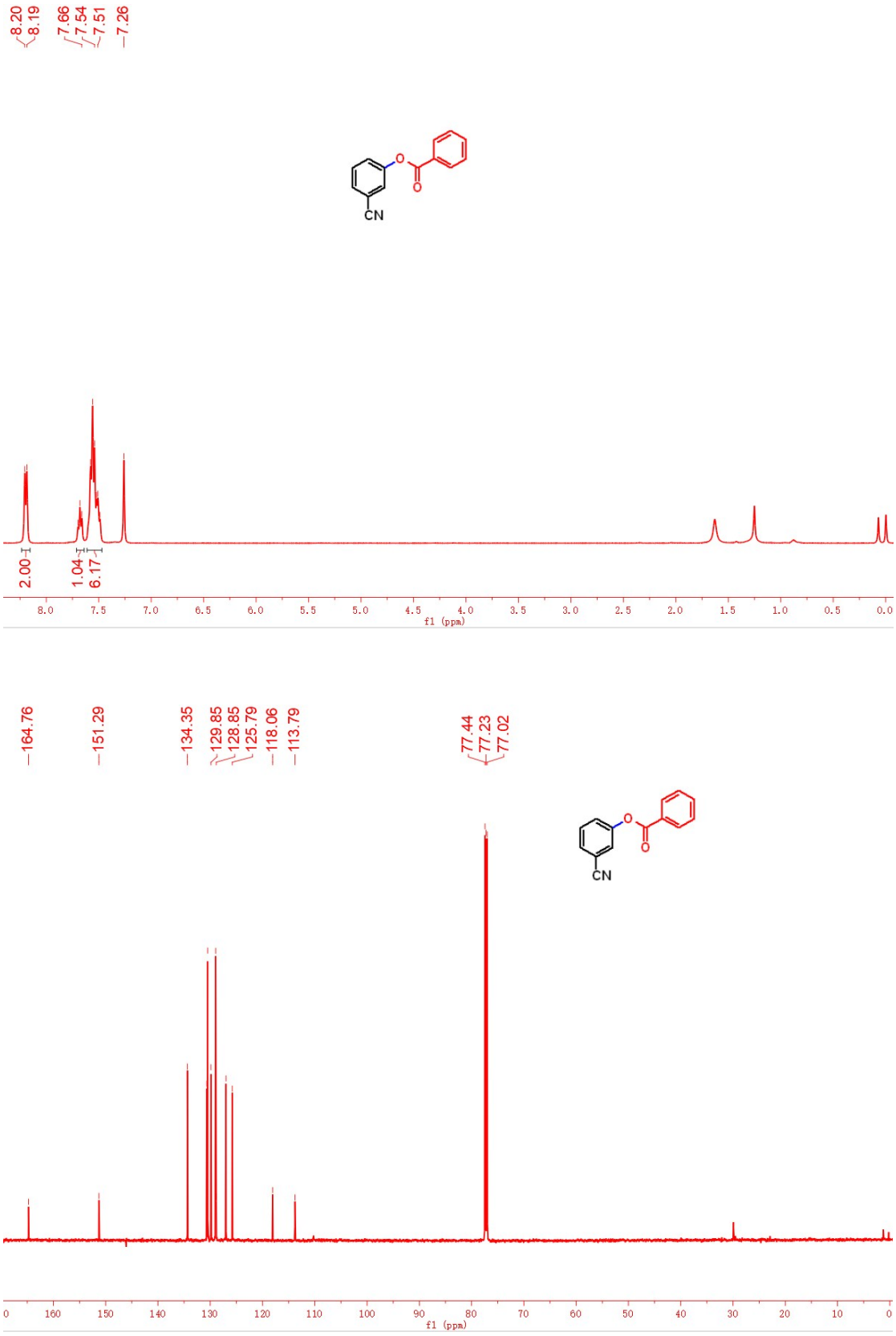


Fig. S37 The ^{1}H and ^{13}C NMR spectra for 3-acetylphenyl benzoate (**3ga**)

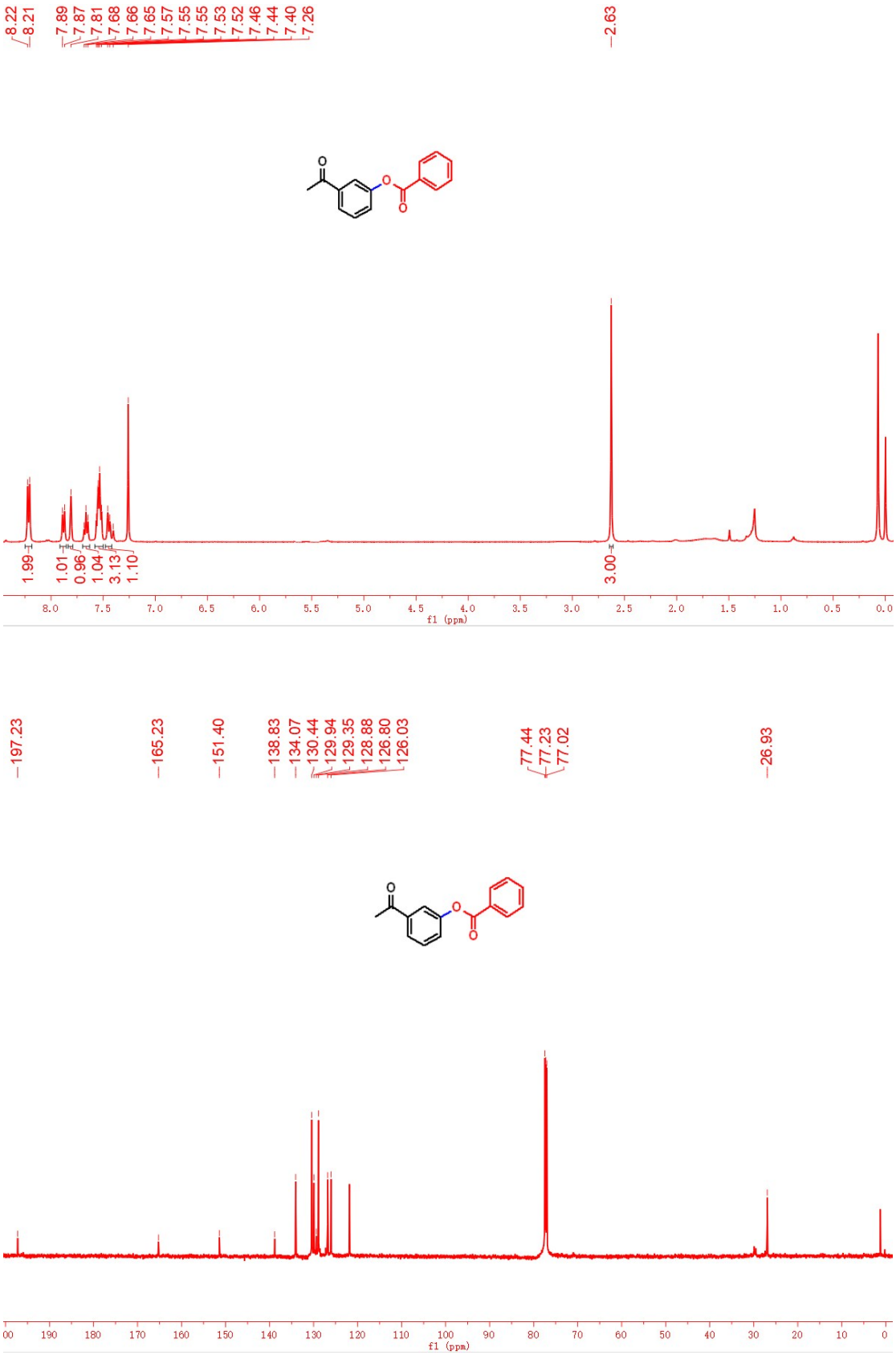


Fig. S38 The ^{1}H and ^{13}C NMR spectra for 3,5-bis(trifluoromethyl)phenyl benzoate (**3ha**)

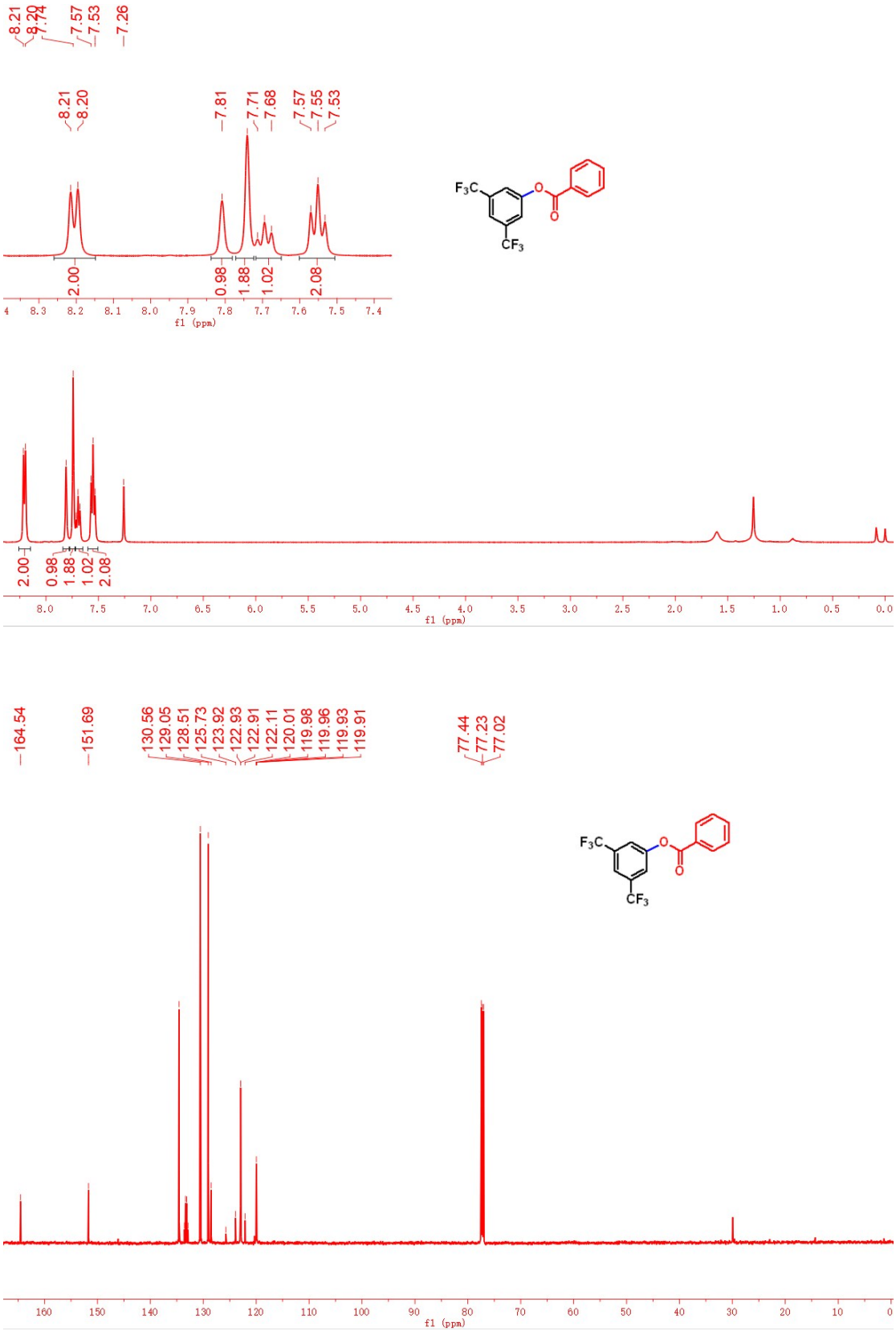


Fig. S39 The ^{1}H and ^{13}C NMR spectra for 3-cyano-5-(trifluoromethyl)phenyl benzoate (**3ia**)

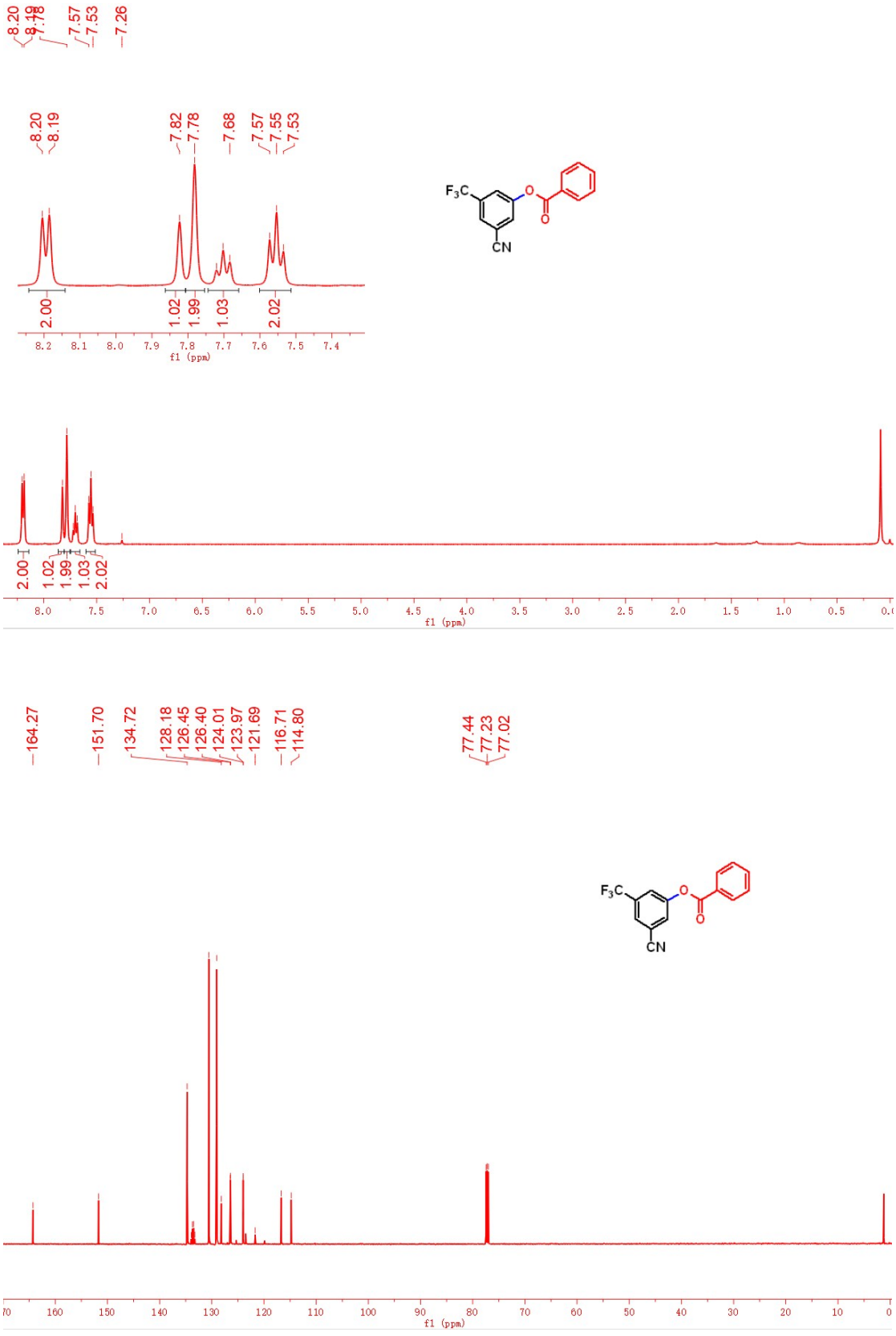


Fig. S40 The ^{1}H and ^{13}C NMR spectra for 3-cyano-4-fluorophenyl benzoate (**3ja**)

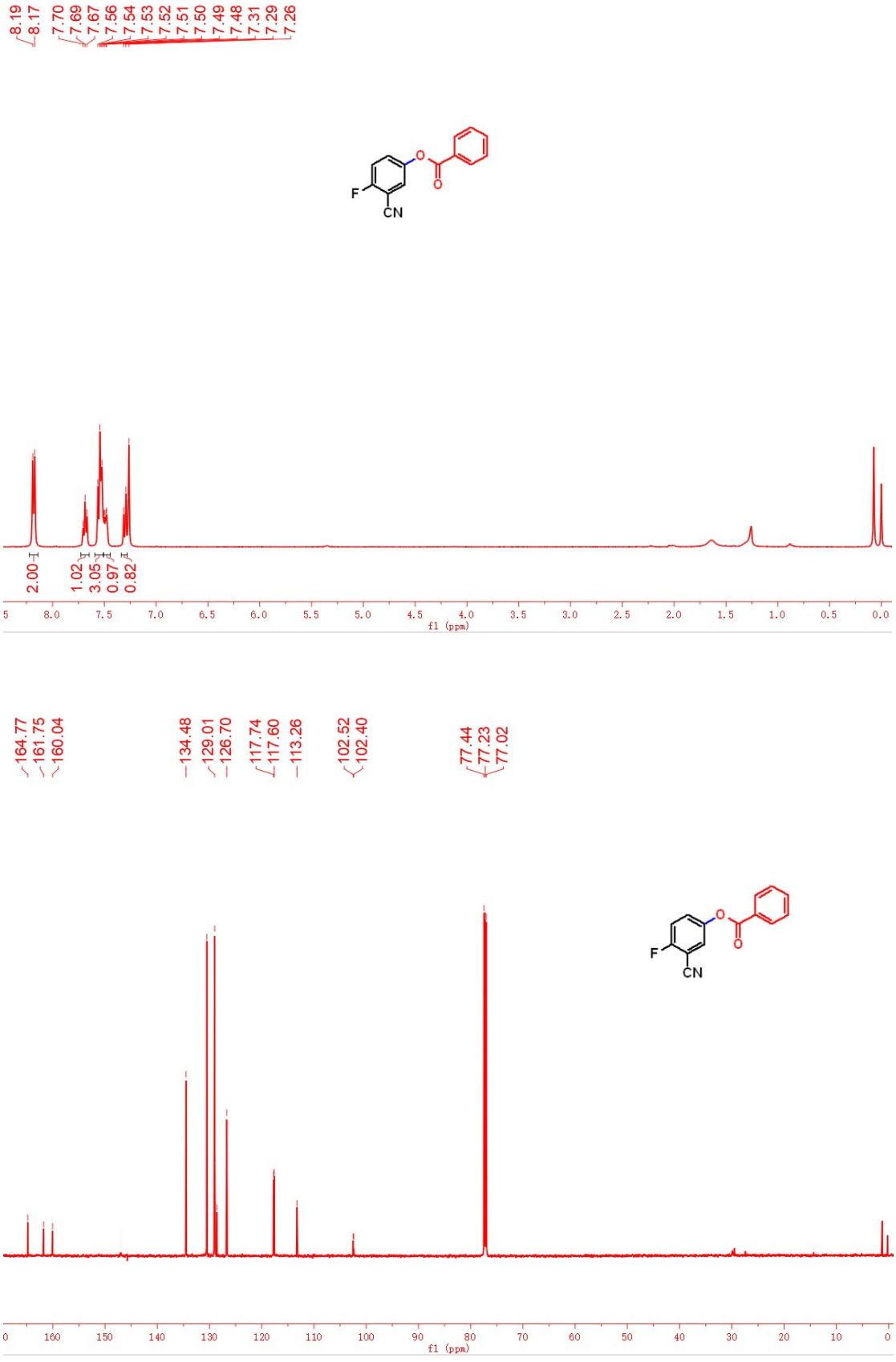


Fig. S41 The ^{1}H and ^{13}C NMR spectra for 4-cyano-3-(trifluoromethyl)phenyl benzoate (**3ka**)

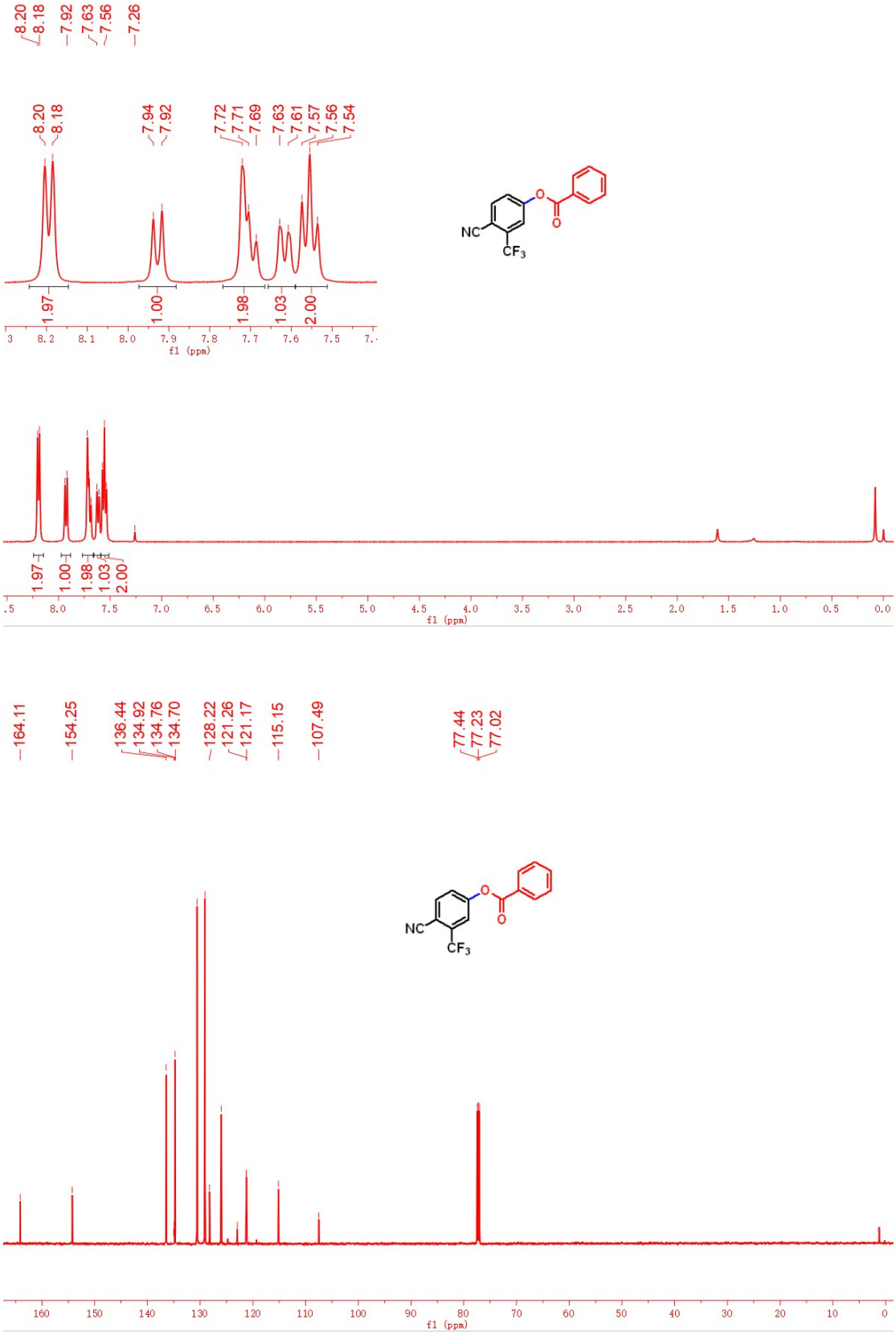


Fig. S42 The ^{1}H and ^{13}C NMR spectra for 2-cyanophenyl benzoate (**3la**)

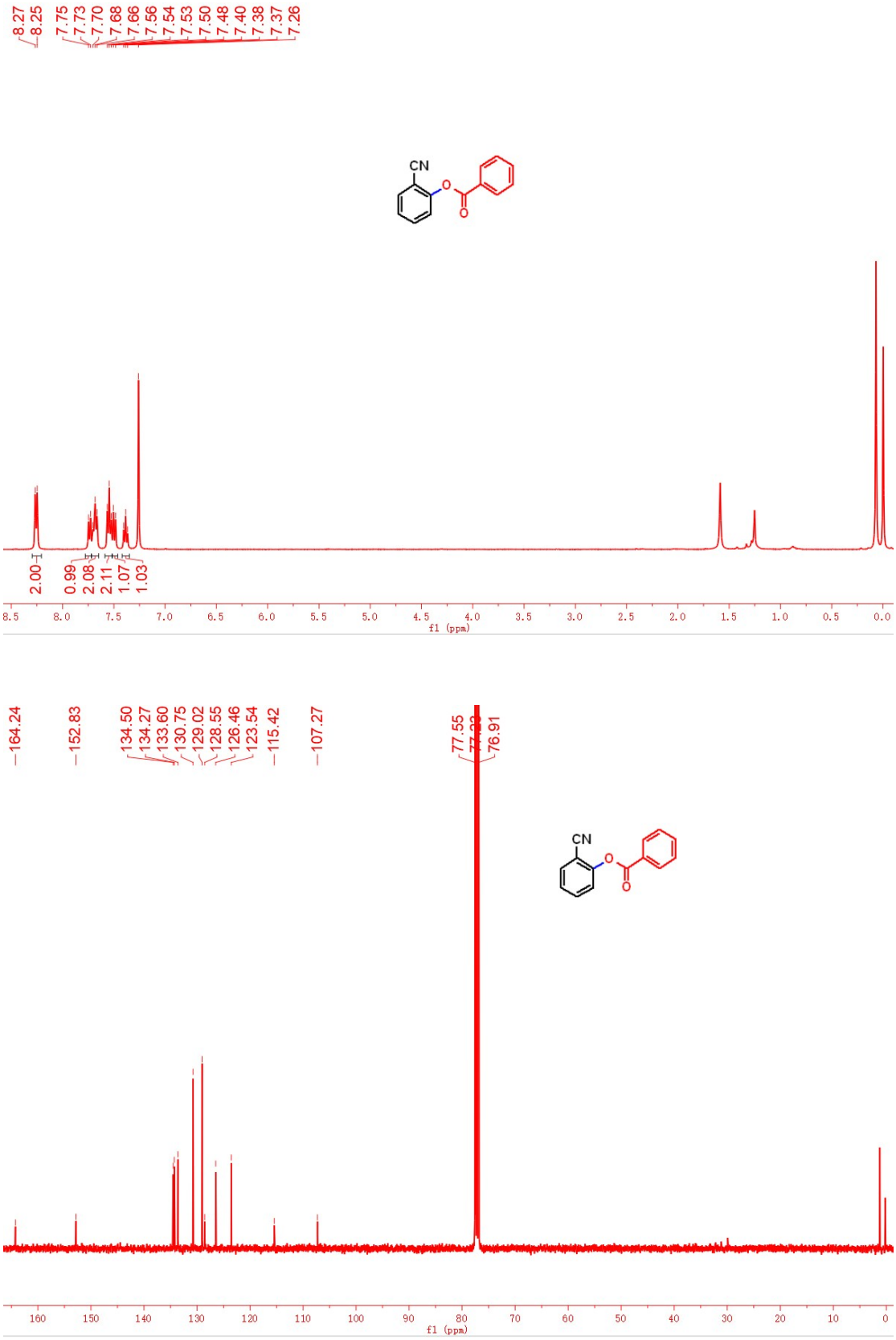


Fig. S43 The ^{1}H and ^{13}C NMR spectra for 6-acetylpyridin-2-yl benzoate (**3ma**)

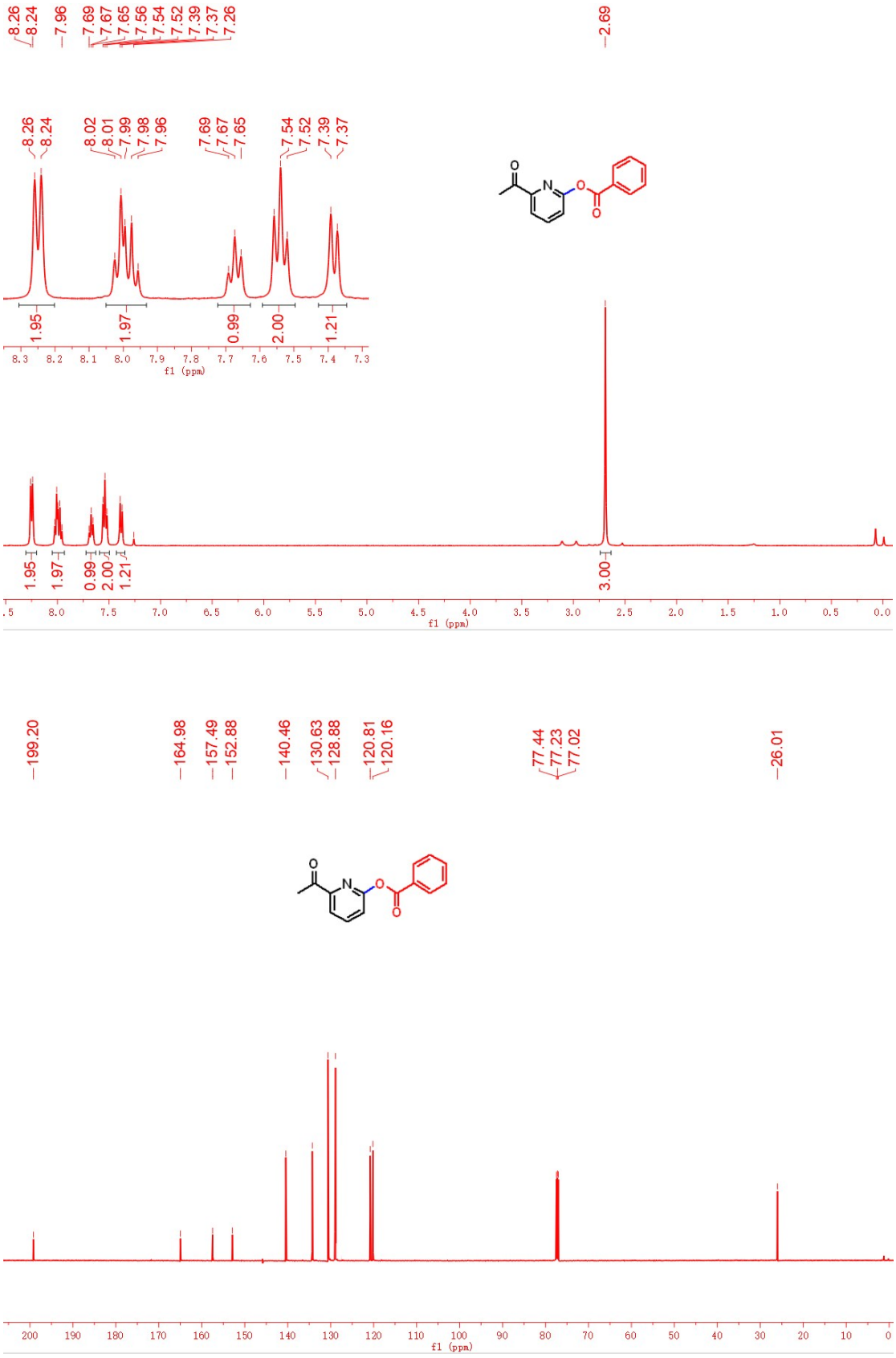


Fig. S44 The ^{1}H and ^{13}C NMR spectra for 6-(trifluoromethyl)pyridin-2-yl benzoate (**3na**)

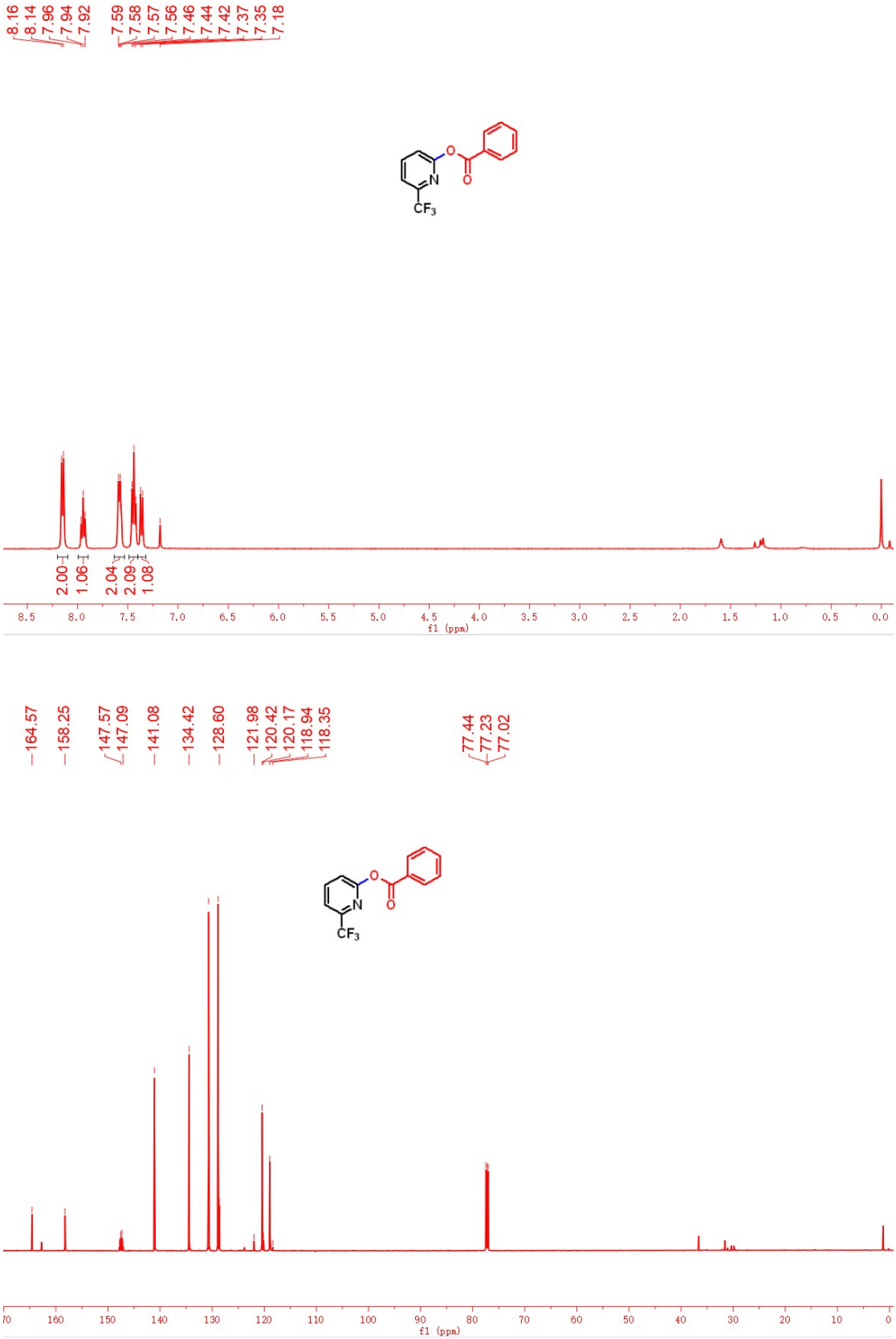


Fig. S45 The ^{1}H and ^{13}C NMR spectra for 2-(trifluoromethyl)pyridin-4-yl benzoate (**3oa**)

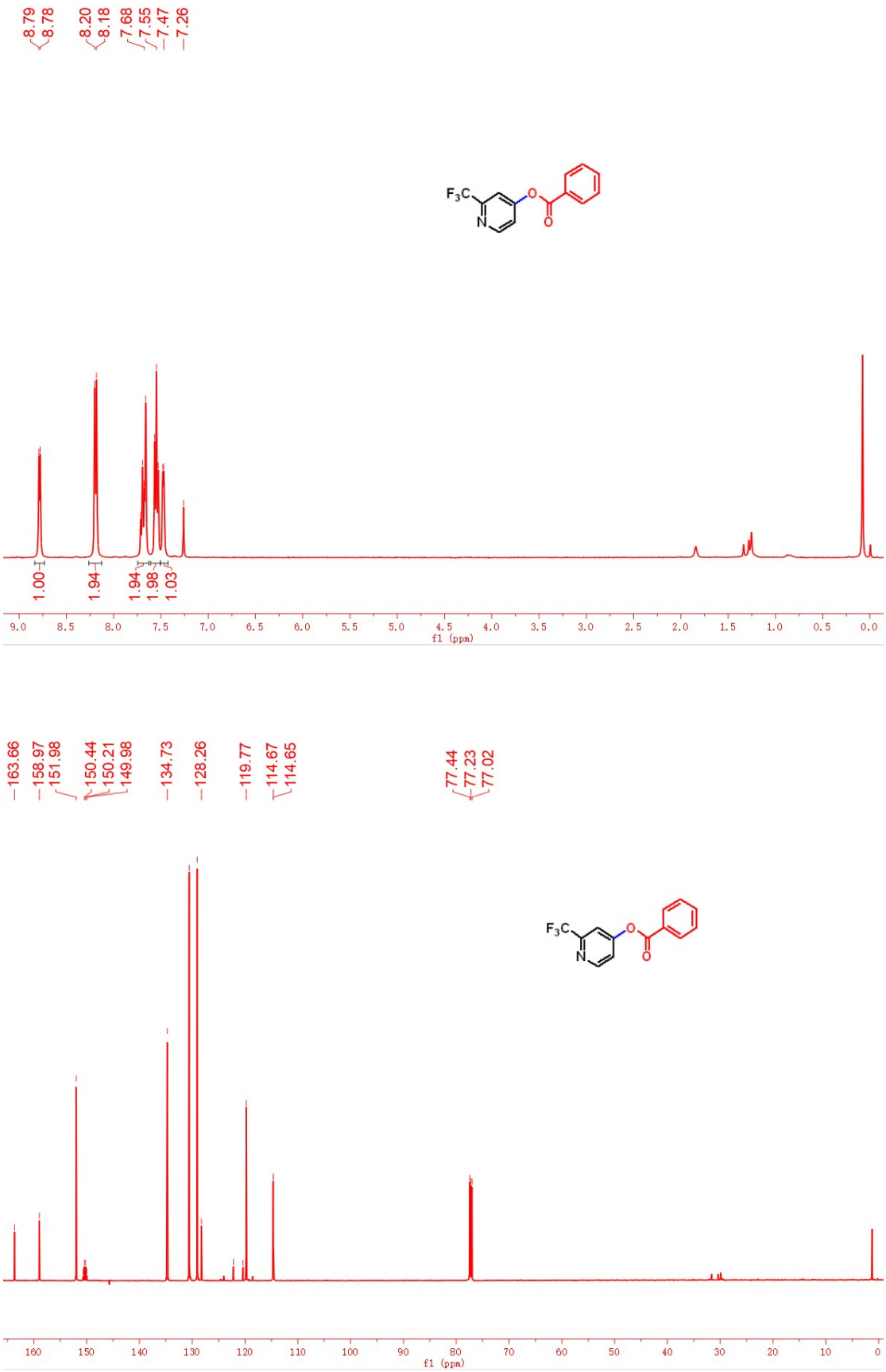


Fig. S46 The ^{1}H and ^{13}C NMR spectra for 3-methyl-4-(trifluoromethyl)phenyl benzoate (**3pa**)

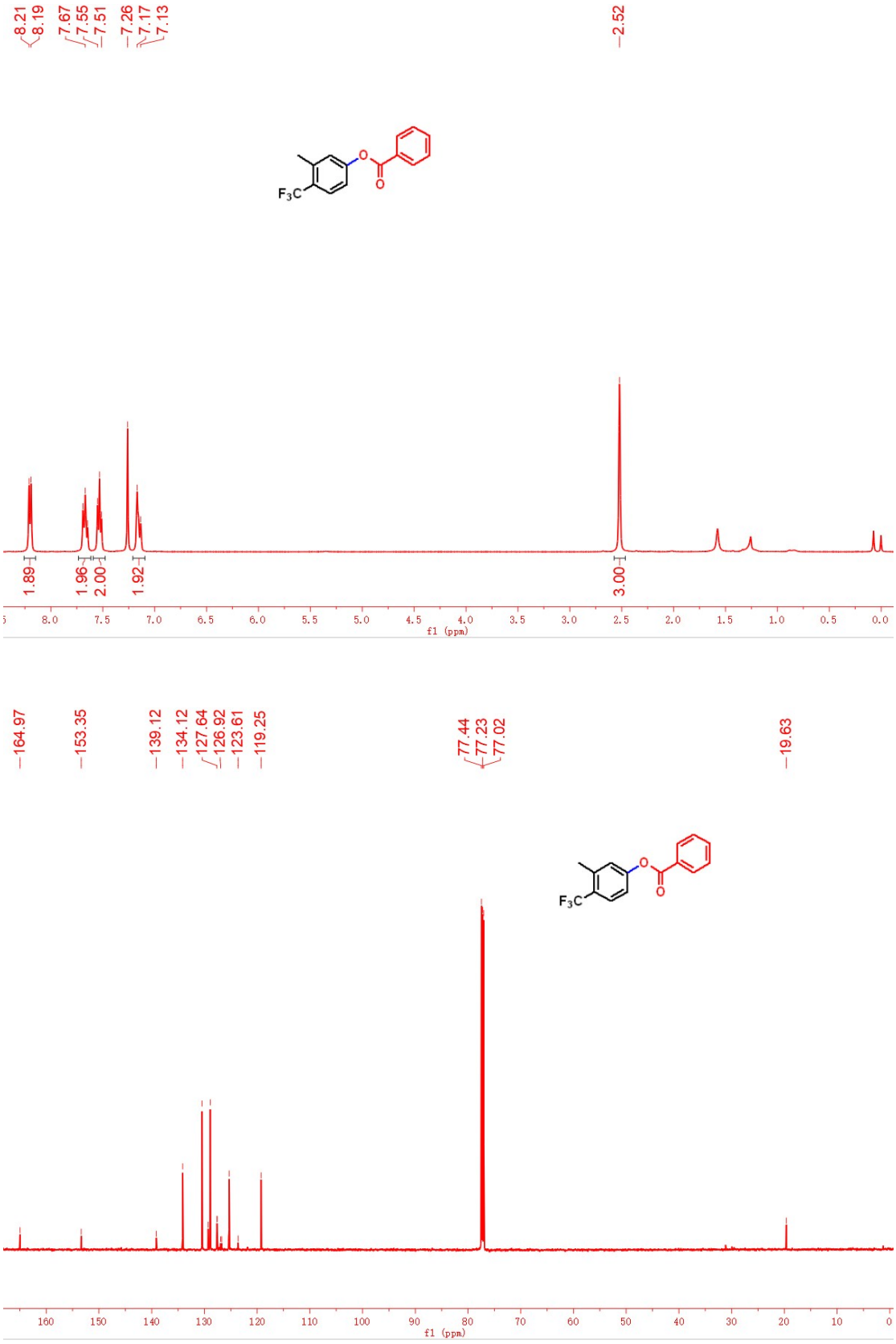


Fig. S47 The ^{1}H and ^{13}C NMR spectra for Phenyl benzoate (**3qa**)

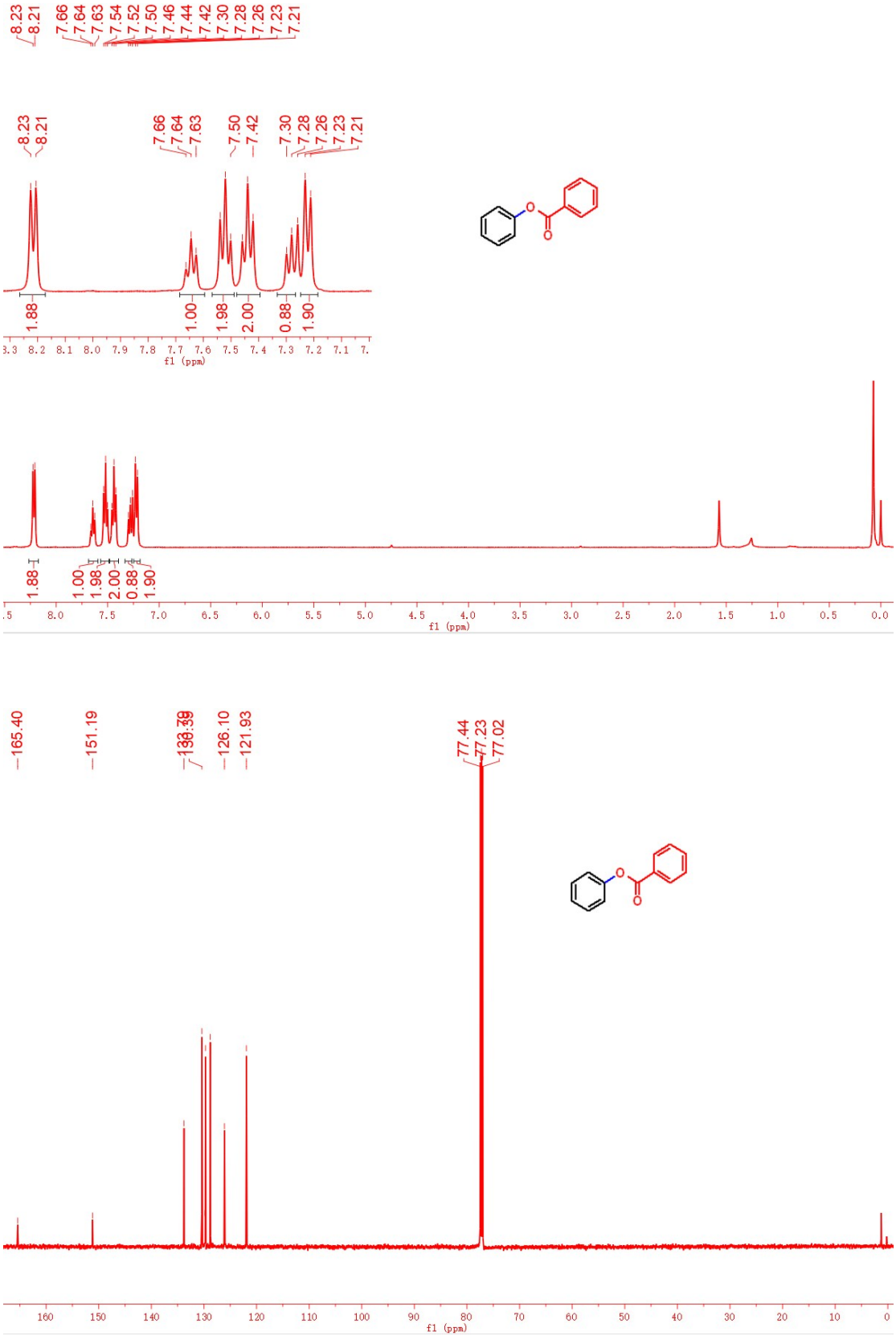


Fig. S48 The ^{1}H and ^{13}C NMR spectra for *p*-tolyl benzoate (**3ra**)