Supporting Information

One-pot $FeCl_3$-catalyzed sustainable synthesis of pyrimidines using ammonium iodide, aldehydes and alkyl lactate as raw materials

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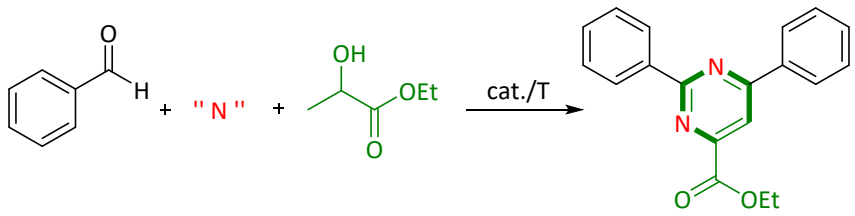
Table of Contents

1. General information

All reagents were obtained from commercial suppliers and used without further purification. All compounds were characterized by full spectroscopic data. The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III 400MHz (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz, ^{19}F NMR: 376 MHz) using $CDCl_3$ and DMSO-d_6 as solvent with TMS as internal standard. Chemical shifts are given in ppm (δ) referenced to $CDCl_3$ with 7.26 for ^{1}H and 76.01 for ^{13}C, DMSO-d_6 with 2.50 for ^{1}H and 39.46 for ^{13}C. Signals are abbreviated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and coupling constants are expressed in hertz; HRMS were performed on an Agilent LC/MSD TOF instrument. The reactions were monitored by thin-layer chromatography (TLC) using silica gel GF254. Column chromatography was performed with 200-300 mesh silica gel. The structure of product **4a** (CCDC file Number 2307938) was further confirmed by X-ray diffraction collected on a diffractometer with graphite mono-chromate Mo Kα radiation. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2. Optimization of reaction conditions

Table S1 Optimization of reaction conditions for synthesis of **4a**[a]



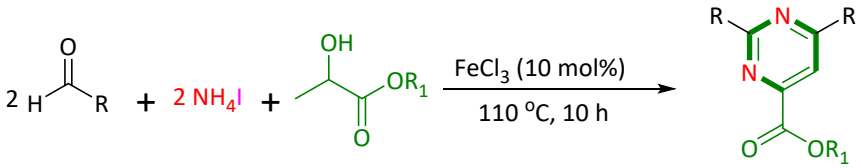
1a **2a** **3a** **4a**

Entry	Acid	'' N ''	Temp (°C)	1a:2a	Time (h)	Yield [b] (%)
1	TfOH	NH_4I	100	1:1	7	25
2	no	NH_4I	100	1:1	7	nr
3	$AlCl_3$	NH_4I	100	1:1	7	18
4	*p*-TSA	NH_4I	100	1:1	7	trace
5	$CuCl_2$	NH_4I	100	1:1	7	36
6	AcOH	NH_4I	100	1:1	7	10
7	$FeCl_2$	NH_4I	100	1:1	7	60
8	$FeCl_3$	NH_4I	100	1:1	7	75
9	LA	NH_4I	100	1:1	7	trace

10	$FeCl_3$	NH_4Br	100	1:1	7	10
11	$FeCl_3$	NH_4Cl	100	1:1	7	15
12	$FeCl_3$	$NH_3{\cdot}H_2O$	100	1:1	7	trace
13	$FeCl_3$	NH_4HCO_3	100	1:1	7	trace
14	$FeCl_3$	NH_4SCN	100	1:1	7	trace
15	$FeCl_3$	$C_5H_{14}N_2$	100	1:1	7	no
16	$FeCl_3$	NH_4OAc	100	1:1	7	5
17	$FeCl_3$	NH_4I	60	1:1	7	trace
18	$FeCl_3$	NH_4I	90	1:1	7	60
19	$FeCl_3$	NH_4I	110	1:1	7	75
20	$FeCl_3$	NH_4I	120	1:1	7	70
21	$FeCl_3$	NH_4I	110	1:1	2	no
22	$FeCl_3$	NH_4I	110	1:1	3	20
23	$FeCl_3$	NH_4I	110	1:1	4	60
24	$FeCl_3$	NH_4I	110	1:1	5	65
25	$FeCl_3$	NH_4I	110	1:1	6	70
26	$FeCl_3$	NH_4I	110	1:1	9	80
27	$FeCl_3$	NH_4I	110	1:1	10	88
28	$FeCl_3$	NH_4I	110	1:1	11	87
29[c]	$FeCl_3$	NH_4I	110	1:1	10	82
30[d]	$FeCl_3$	NH_4I	110	1:1	10	85
31[e]	**$FeCl_3$**	**NH_4I**	**110**	**1:1**	**10**	**91**
32[f]	$FeCl_3$	NH_4I	110	1:1	10	60
33[d,g]	$FeCl_3$	NH_4I	110	1:1	10	trace

[a] Reaction conditions: **1a** (0.50 mmol), **2a** (0.50 mmol), and acid (0.05 mmol) in 0.3 mL **3a**, stirred for 10 h. [b] Isolated yield relative to **1a**. [c] With 0.50 mmol $FeCl_3$. [d] With 0.10 mmol $FeCl_3$. [e] With 0.05 mmol $FeCl_3$. [f] With 0.01 mmol $FeCl_3$. [g] EL (0.50 mmol) was used in Dimethyl sulfoxide (2.0mL).

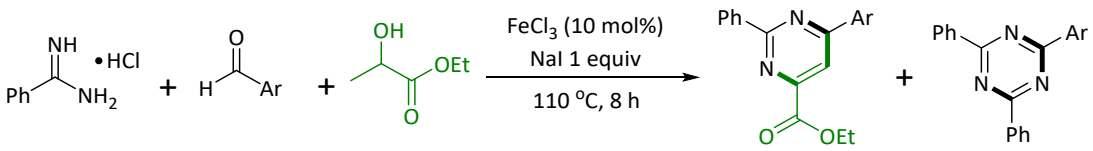
3. Experimental methods for synthesis of two pyrimidines



1 **2** **3** **4**

Aldehyde **1** (0.50 mmol), ammonium **2** (0.50 mmol), alkyl lactate **3** (0.3 mL), and $FeCl_3$ (0.05 mmol) were added to the 25.0 mL round bottom flask. The mixture was stirred at 110 °C for 10 hours. The reaction mixture was then mixed with water (10.0 mL), and the suspension was extracted with ethyl acetate (3 × 10.0 mL); The organic phase was dried and filtered on anhydrous Na_2SO_4. The solution evaporates under reduced pressure to remove organic solvents. The residue was purified by flash silica gel column chromatography with petroleum ether (PE) and ethyl acetate (EA) as eluents.

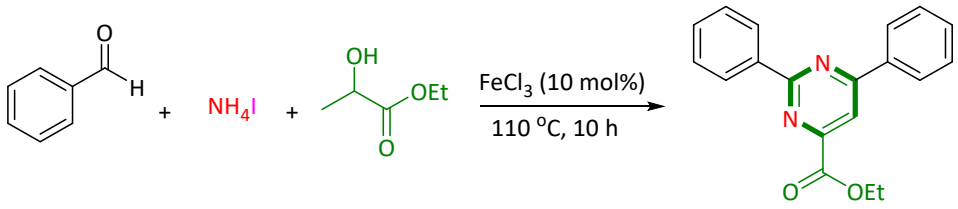
4. Synthesis of asymmetric pyrimidines



1 **2** **3** **4** **5**

Benzimidamide hydrochloride **1** (0.50 mmol), aldehyde **2** (0.50 mmol), alkyl lactate **3** (0.3 mL), NaI (0.50 mmol), and $FeCl_3$ (0.05 mmol) were added to the 25.0 mL round bottom flask. The mixture was stirred at 110 °C for 8 hours. The reaction mixture was then mixed with water (10.0 mL), and the suspension was extracted with ethyl acetate (3 × 10.0 mL); The organic phase was dried and filtered on anhydrous Na_2SO_4. The solution evaporates under reduced pressure to remove organic solvents. The residue was purified by flash silica gel column chromatography with petroleum ether (PE) and ethyl acetate (EA) as eluents.

5. Scale-up synthesis of 4a



21.25 mmol
2.26 g

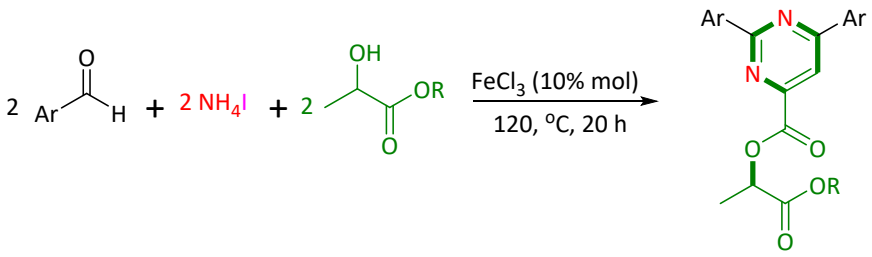
21.25 mmol
3.08 g

85.00 mmol
10.00g

4a, 75%, 2.42 g

Benzaldehyde (21.25 mmol), ammonium iodide (21.25 mmol), EL (85.00 mmol), and $FeCl_3$ (2.13 mmol) were added to the 250.0 mL round bottom flask. The mixture was stirred at 110 °C for 10 h in an air atmosphere. When finished, cool to room temperature and add 100.0 mL water. The suspension was extracted with ethyl acetate (3 × 100.0 mL). The combined organic solution was dried with anhydrous Na_2SO_4. After filtration, the solution was decompressed to remove the solvent, and the residue was purified by flash silica gel column chromatography with petroleum ether and ethyl acetate as eluent.

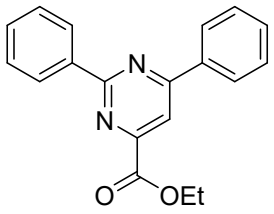
6. Reuse of alkyl lactate



1 **2** **3** **6**

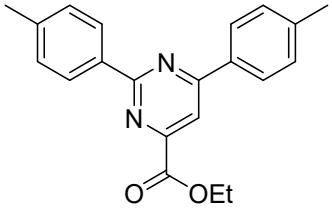
Benzaldehyde **1** (0.50 mmol), ammonium iodide **2** (0.50 mmol), alkyl lactate **3** (0.3 mL), and $FeCl_3$ (0.05 mmol) were added to the 25.0 mL round bottom flask. The mixture was stirred at 120 °C for 20 h in an air atmosphere. When finished, cool to room temperature and add 10.0 mL water. The suspension was extracted with ethyl acetate (3 × 10.0 mL) The combined organic solution was dried with anhydrous Na_2SO_4. After filtration, the solution was decompressed to remove the solvent, and the residue was purified by flash silica gel column chromatography with petroleum ether and ethyl acetate as eluent.

7. Characterization data of all products



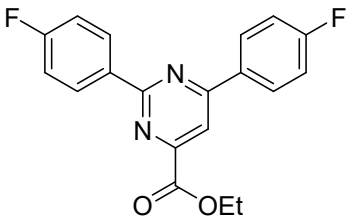
Ethyl 2,6-diphenylpyrimidine-4-carboxylate (4a)

Yield: 69.2 mg; 91%; White solid; mp: 126–127 °C; (petroleum ether/ethyl acetate =100:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69–8.62 (m, 2H), 8.34–8.26 (m, 3H), 7.57 (m, 3H), 7.55–7.51 (m, 3H), 4.55 (q, J = 7.1 Hz, 2H), 1.51 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.4, 165.1, 156.7, 137.4, 136.6, 131.7, 131.3, 129.2, 128.9, 128.8, 127.6, 114.2, 62.7, 14.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{17}N_2O_2^+$ 305.1285; Found 305.1286.



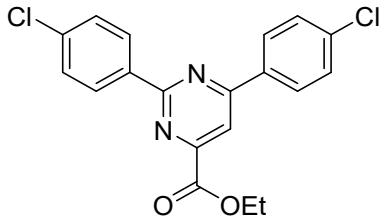
Ethyl 2,6-di-*p*-tolylpyrimidine-4-carboxylate (4b)

Yield: 73.1 mg; 88%; White solid; mp: 152–153 °C; (petroleum ether/ethyl acetate =90:1, V/V); ^{1}H NMR (400 MHz, DMSO) δ 8.43–8.38 (m, 2H), 8.25 (m, 3H), 7.37 (t, J = 8.1 Hz, 4H), 4.44 (q, J = 7.1 Hz, 2H), 2.39 (s, 6H), 1.40 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO) δ 165.1, 164.2, 163.8, 156.3, 141.9, 141.2, 134.0, 132.8, 129.7, 129.4, 128.0, 127.3, 113.3, 62.0, 21.1, 21.0, 14.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{21}N_2O_2^+$ 333.1598; Found 333.1597.



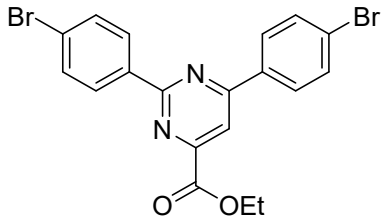
Ethyl 2,6-bis(4-fluorophenyl)pyrimidine-4-carboxylate (4c)

Yield: 72.3 mg; 85%; White solid; mp: 124–125 °C; (petroleum ether/ethyl acetate =95:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67–8.61 (m, 2H), 8.31–8.26 (m, 2H), 8.21 (s, 1H), 7.25 (s, 1H), 7.25–7.23 (m, 1H), 7.21 (t, J = 1.9 Hz, 1H), 7.20–7.18 (m, 1H), 4.54 (q, J = 7.1 Hz, 2H), 1.50 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 165.2, 164.0, 163.7, 163.3, 162.8, 155.5, 132.3, 132.2, 131.5, 131.4, 129.9, 129.8, 128.6, 128.5, 115.3, 115.1, 114.7, 114.5, 112.5, 61.6, 13.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.27 (s, 1F), -109.42 (s,1F); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{15}F_2N_2O_2^+$ 341.1096; Found 341.1095.



Ethyl 2,6-bis(4-chlorophenyl)pyrimidine-4-carboxylate (4d)

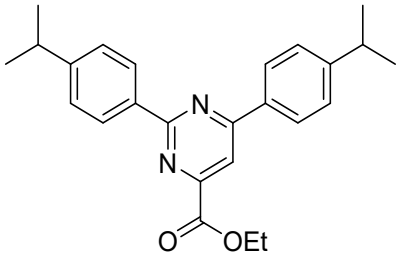
Yield: 78.1 mg; 84%; White solid; mp: 113–114 °C; (petroleum ether/ethyl acetate =100:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60–8.55 (m, 2H), 8.24 (m, 2H), 8.22 (m, 1H), 7.56–7.52 (m, 2H), 7.51–7.47 (m, 2H), 4.55 (q, J = 7.2 Hz, 2H), 1.50 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 164.6, 164.4, 156.7, 138.0, 137.6, 135.5, 134.6, 130.0, 129.4, 128.9, 128.7, 113.9, 62.6, 14.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{15}Cl_2N_2O_2^+$ 373.0505; Found 373.0509.



Ethyl 2,6-bis(4-bromophenyl)pyrimidine-4-carboxylate (4e)

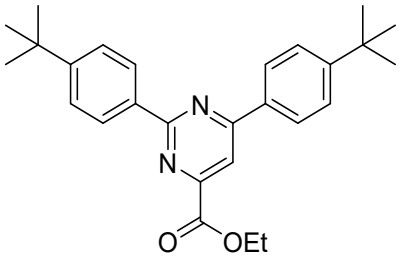
Yield: 95.4 mg; 83%; White solid; mp: 147–148 °C; (petroleum ether/ethyl acetate =80:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52–8.47 (m, 2H), 8.24 (s, 1H), 8.17–8.12 (m, 2H), 7.72–7.68 (m, 2H), 7.67–7.63 (m, 2H), 4.54 (q, J = 7.1 Hz, 2H), 1.50 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 164.8, 164.7, 156.9, 136.1, 135.3, 132.6, 132.0,

130.4, 129.1, 126.7, 126.4, 114.1, 62.9, 14.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{15}Br_2N_2O_2^+$ 460.9495; Found 460.9492.



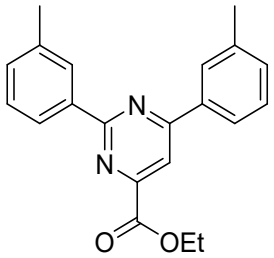
Ethyl 2,6-bis(4-isopropylphenyl)pyrimidine-4-carboxylate (4f)

Yield: 77.6 mg; 80%; Yellowish oily; (petroleum ether/ethyl acetate =70:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59–8.54 (m, 2H), 8.23 (m, 3H), 7.44–7.36 (m, 4H), 4.54 (q, *J* = 7.1 Hz, 2H), 3.01 (m, 2H), 1.50 (t, *J* = 7.1 Hz, 3H), 1.32 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.5, 165.3, 156.4, 153.0, 152.4, 135.3, 134.4, 129.0, 127.7, 127.3, 126.8, 113.7, 62.6, 62.5, 34.4, 34.3, 24.0, 14.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{29}N_2O_2^+$ 389.2224; Found 389.2221.



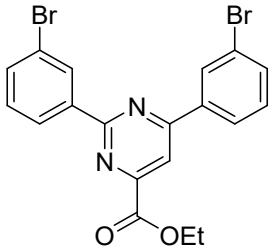
Ethyl 2,6-bis(4-(*tert*-butyl)phenyl)pyrimidine-4-carboxylate (4g)

Yield: 84.3 mg; 81%; Yellowish oily; (petroleum ether/ethyl acetate =90:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60–8.52 (m, 2H), 8.28–8.18 (m, 3H), 7.62–7.51 (m, 4H), 4.54 (q, *J* = 7.1 Hz, 2H), 1.50 (t, *J* = 7.2 Hz, 3H), 1.44 (s, 1H), 1.39 (d, *J* = 2.5, 16H), 1.34 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.5, 165.3, 156.5, 155.2, 154.6, 134.9, 134.0, 128.7, 127.4, 126.2, 125.7, 113.7, 62.6, 35.2, 35.1, 31.5, 31.4, 14.5, 14.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{33}N_2O_2^+$ 417.2537; Found 417.2539.



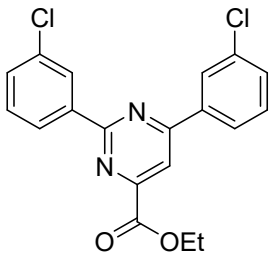
Ethyl 2,6-di-*m*-tolylpyrimidine-4-carboxylate (4h)

Yield: 66.5 mg; 80%; White solid; mp: 93–94 °C; (petroleum ether/ethyl acetate =70:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 6.5 Hz, 2H), 7.42 (s, 1H), 7.29–7.22 (m, 2H), 6.64–6.57 (m, 2H), 6.55–6.49 (m, 2H), 3.72 (q, J = 7.1 Hz, 2H), 1.66 (d, J = 3.0 Hz, 6H), 0.68 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 165.6, 165.2, 156.5, 139.0, 138.4, 137.4, 136.6, 132.5, 132.1, 129.4, 129.2, 128.7, 128.2, 126.1, 124.8, 114.3, 62.7, 21.8, 14.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{21}N_2O_2^+$ 333.1598; Found 333.1599.



Ethyl 2,6-bis(3-bromophenyl)pyrimidine-4-carboxylate (4i)

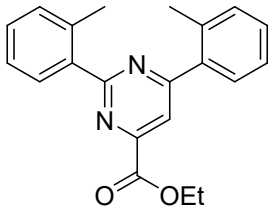
Yield: 90.8 mg; 79%; White solid; mp: 107–108 °C; (petroleum ether/ethyl acetate =100:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (t, J = 1.8 Hz, 1H), 8.57 (m, 1H), 8.41 (t, J = 1.9 Hz, 1H), 8.25 (s, 1H), 8.19 (m, 1H), 7.68 (m, 2H), 7.43 (m, 2H), 4.56 (q, J = 7.2 Hz, 2H), 1.51 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 164.7, 164.2, 157.1, 139.2, 138.4, 134.8, 134.5, 131.8, 130.9, 130.7, 130.4, 127.6, 126.2, 123.6, 123.2, 114.8, 62.9, 14.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{15}Br_2N_2O_2^+$ 460.9495; Found 460.9496.



Ethyl 2,6-bis(3-chlorophenyl)pyrimidine-4-carboxylate (4j)

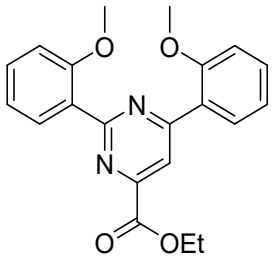
Yield: 72.5 mg; 78%; White solid; mp: 99–100 °C; (petroleum ether/ethyl acetate =80:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (t, J = 1.8 Hz, 1H), 8.51 (m, 1H), 8.27–8.22 (m, 2H), 8.12 (m, 1H), 7.55–7.43 (m, 4H), 4.55 (q, J = 7.1 Hz, 2H), 1.51 (t, J = 7.1 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 164.6, 164.3, 157.0, 138.9, 138.1, 135.5, 135.0, 131.8, 131.5, 130.6, 130.1, 128.8, 127.7, 127.0, 125.7, 114.7, 62.9, 14.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{15}Cl_2N_2O_2^+$ 372.0432; Found 372.0433.



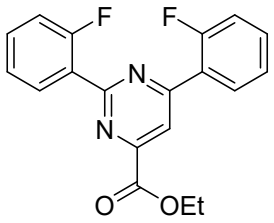
Ethyl 2,6-di-*o*-tolylpyrimidine-4-carboxylate (4k)

Yield: 58.1 mg; 70%; Yellowish oily; (petroleum ether/ethyl acetate =90:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.97 (dd, J = 7.5, 1.8 Hz, 1H), 7.58 (dd, J = 7.8, 1.7 Hz, 1H), 7.42–7.29 (m, 6H), 4.52 (q, J = 7.1 Hz, 2H), 2.65 (s, 3H), 2.52 (s, 3H), 1.47 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 167.9, 165.1, 155.6, 138.1, 137.8, 137.8, 136.6, 131.6, 131.6, 131.2, 130.2, 130.0, 126.5, 126.2, 117.8, 62.7, 21.7, 20.9, 14.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{21}N_2O_2^+$ 333.1598; Found 333.1597.



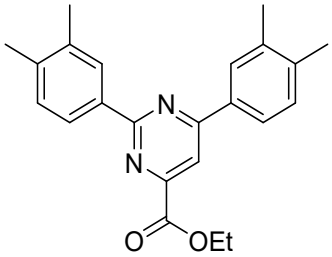
Ethyl 2,6-bis(2-methoxyphenyl)pyrimidine-4-carboxylate (4l)

Yield: 65.5 mg; 72%; White solid; mp: 76–77 °C; (petroleum ether/ethyl acetate =80:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28–8.22 (m, 2H), 8.20 (t, J = 2.0 Hz, 1H), 7.89–7.80 (m, 2H), 7.45 (q, J = 8.3 Hz, 2H), 7.09 (m, 2H), 4.54 (q, J = 7.1 Hz, 2H), 3.93 (d, J = 2.8 Hz, 6H), 1.50 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.2, 165.1, 160.4, 160.1, 156.6, 138.8, 138.0, 130.3, 129.8, 121.5, 120.0, 117.4, 117.3, 114.4, 113.8, 112.9, 62.7, 55.6, 55.59, 14.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{21}N_2O_4^+$ 365.1496; Found 365.1493.



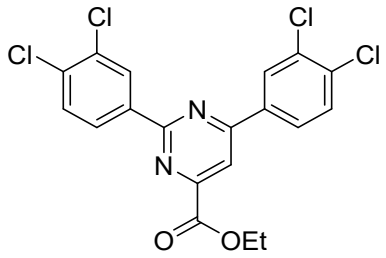
Fthyl 2,6-bis(2-fluorophenyl)pyrimidine-4-carboxylate (4m)

Yield: 66.3 mg; 78%; White solid; mp: 124–125 °C; (petroleum ether/ethyl acetate =90:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 1.6 Hz, 1H), 8.36 (m, 1H), 8.23 (m, 1H), 7.49 (m, 2H), 7.37–7.28 (m, 2H), 7.25–7.17 (m, 2H), 4.54 (q, J = 7.1 Hz, 2H), 1.48 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 164.1, 163.2, 162.8, 160.7, 160.5, 156.6, 133.3, 133.2, 132.6, 132.5, 132.4, 132.3, 131.4, 131.3, 125.2, 125.1, 124.4, 124.3, 118.5, 118.4, 117.3, 117.0, 116.9, 116.7, 62.8, 14.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.87, (s, 1F), -114.26 (s, 1F); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{15}F_2N_2O_2^+$ 341.1096; Found 341.1094.



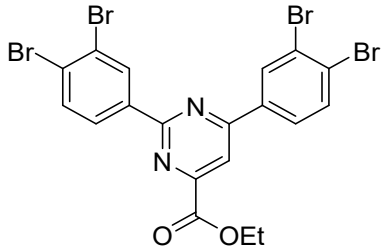
Ethyl 2,6-bis(3,4-dimethylphenyl)pyrimidine-4-carboxylate (4n)

Yield: 77.4 mg; 86%; White solid; mp: 99–100 °C; (petroleum ether/ethyl acetate =50:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42-8.35 (m, 2H), 8.20 (s, 1H), 8.07–8.00 (m, 2H), 7.30 (m, 2H), 4.55 (q, J = 7.1 Hz, 2H), 2.40 (d, J = 2.1 Hz, 6H), 2.36 (d, J = 3.4 Hz, 6H), 1.51 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 165.6, 165.4, 156.3, 140.8, 140.2, 137.5, 136.9, 135.2, 134.3, 130.5, 130.1, 129.8, 128.7, 126.5, 125.1, 113.6, 62.6, 20.2, 20.1, 14.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{25}N_2O_2^+$ 361.1911; Found 361.1913.



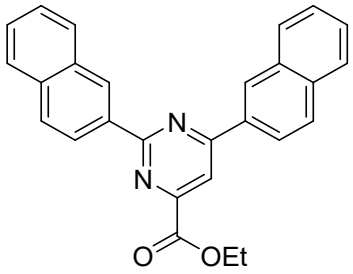
Ethyl 2,6-bis(3,4-dichlorophenyl)pyrimidine-4-carboxylate (4o)

Yield: 93.5 mg; 85%; White solid; mp: 123–124 °C; (petroleum ether/ethyl acetate =60:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 2.0 Hz, 1H), 8.46 (m, 1H), 8.36 (d, J = 2.1 Hz, 1H), 8.24 (s, 1H), 8.09 (m, 1H), 7.62 (m, 2H), 4.56 (q, J = 7.1 Hz, 2H), 1.51 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 164.2, 163.7, 157.2, 136.92, 136.4, 136.1, 136.0, 134.0, 133.3, 131.4, 130.9, 130.7, 129.5, 128.0, 126.7, 114.6, 63.1, 14.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{13}Cl_4N_2O_2^+$ 440.9726; Found 440.9725.



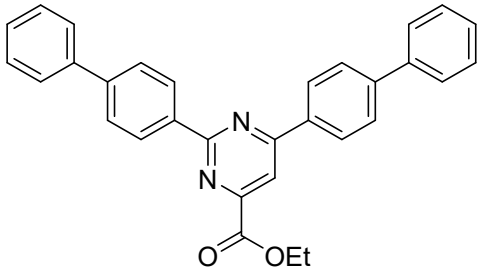
Ethyl 2,6-bis(3,4-dibromophenyl)pyrimidine-4-carboxylate (4p)

Yield: 123.2 mg; 80%; White solid; mp: 168–169 °C; (petroleum ether/ethyl acetate =70:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, J = 2.0 Hz, 1H), 8.48 (d, J = 2.1 Hz, 1H), 8.39 (m, 1H), 8.22 (s, 1H), 8.03 (m, 1H), 7.78 (m, 2H), 4.56 (q, J = 7.1 Hz, 2H), 1.51 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 164.2, 163.6, 157.2, 137.5, 136.7, 134.6, 134.1, 133.8, 132.5, 129.0, 128.7, 128.7, 127.3, 126.2, 125.6, 114.6, 63.1, 14.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{13}Br_4N_2O_2^+$ 616.7705; Found 616.7709.



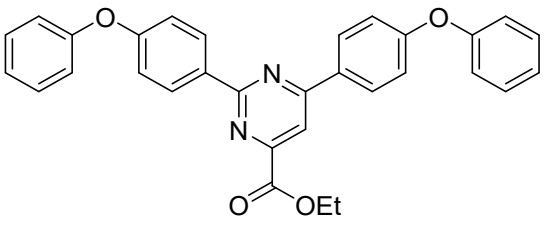
Ethyl 2,6-di(naphthalen-2-yl)pyrimidine-4-carboxylate (4q)

Yield: 87.9 mg; 87%; White solid; mp: 133–134 °C; (petroleum ether/ethyl acetate =60:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25–9.21 (m, 1H), 8.84–8.77 (m, 2H), 8.48–8.41 (m, 2H), 8.12–7.98 (m, 4H), 7.96–7.89 (m, 2H), 7.63-7.52 (m, 4H), 4.61 (q, J = 7.1 Hz, 2H), 1.56 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 165.5, 165.2, 156.7, 135.2, 135.1, 134.8, 133.9, 133.6, 133.5, 129.6, 129.5, 129.4, 129.1, 128.5, 128.3, 128.2, 128.1, 128.0, 127.5, 127.0, 126.5, 125.7, 124.2, 114.5, 62.8, 14.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{21}N_2O_2^+$ 405.1598; Found 405.1596.



Ethyl 2,6-di([1,1'-biphenyl]-4-yl)pyrimidine-4-carboxylate (4r)

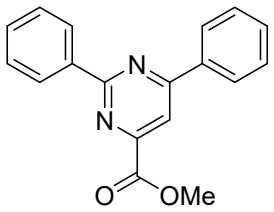
Yield: 96.9 mg; 85%; White solid; mp: 170–171 °C; (petroleum ether/ethyl acetate =100:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78–8.72 (m, 2H), 8.43–8.37 (m, 2H), 8.32 (s, 1H), 7.83–7.76 (m, 4H), 7.70 (m, 4H), 7.53–7.47 (m, 4H), 7.45–7.38 (m, 2H), 4.57 (q, J = 7.1 Hz, 2H), 1.53 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.2, 165.1, 156.6, 144.5, 144.0, 140.8, 140.3, 136.4, 135.4, 129.4, 129.3, 129.2, 129.1, 128.2, 128.1, 128.0, 127.9, 127.5, 127.4, 127.3, 114.0, 62.7, 14.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{25}N_2O_2^+$ 457.1911; Found 457.1910.



Ethyl 2,6-bis(4-phenoxyphenyl)pyrimidine-4-carboxylate (4s)

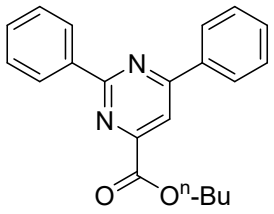
Yield: 102.5 mg; 84%; Yellowish oily; (petroleum ether/ethyl acetate =90:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (m, 1H), 8.30 (t, J = 2.1 Hz, 1H), 8.24 (s, 1H), 8.01–7.95 (m, 2H), 7.49 (m, 2H), 7.37 (m, 4H), 7.20–7.11 (m, 4H), 7.10–7.05 (m, 4H), 4.52 (q, J = 7.1 Hz, 2H), 1.48 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 164.9, 164.8, 158.3, 157.7, 157.6, 157.1, 156.8, 139.3, 138.3, 130.6, 130.2, 130.1, 130.0, 124.0,

123.9, 123.4, 122.4, 121.9, 121.8, 119.6, 119.2, 119.0, 118.0, 114.5, 62.7, 14.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{25}N_2O_4^+$ 489.1809; Found 489.1808.



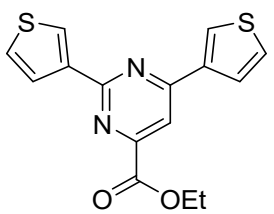
Methyl 2,6-diphenylpyrimidine-4-carboxylate (4t)

Yield: 53.4 mg; 75%; White solid; mp: 122–123 °C; (petroleum ether/ethyl acetate =80:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68–8.62 (m, 2H), 8.33–8.29 (m, 3H), 7.59–7.56 (m, 3H), 7.55–7.51 (m, 3H), 4.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 165.7, 165.5, 156.3, 137.4, 136.6, 131.8, 131.4, 129.3, 128.9, 128.8, 127.7, 114.3, 53.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{15}N_2O_2^+$ 291.1128; Found 291.1124.



Butyl 2,6-diphenylpyrimidine-4-carboxylate (4u)

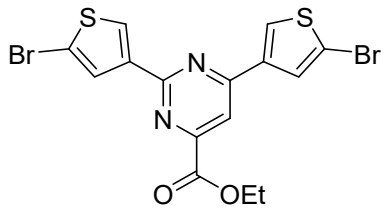
Yield: 75.6 mg; 91%; White solid; mp: 65–66 °C; (petroleum ether/ethyl acetate =90:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (m, 2H), 8.33–8.25 (m, 3H), 7.54 (m, 6H), 4.49 (t, J = 6.8 Hz, 2H), 1.92–1.83 (m, 2H), 1.55 (m, 2H), 1.04 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.4, 165.1, 156.6, 137.4, 136.6, 131.8, 131.6, 131.3, 129.2, 128.8, 128.7, 127.6, 114.1, 66.5, 30.8, 30.6, 19.4, 19.2, 14.0, 13.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{21}N_2O_2^+$ 333.1598; Found 333.1599.



Ethyl 2,6-di(thiophen-3-yl)pyrimidine-4-carboxylate (4v)

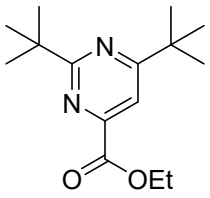
Yield: 69.5 mg; 88%; White solid; mp: 97–98 °C; (petroleum ether/ethyl acetate =80:1,

V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (m, 1H), 8.29 (m, 1H), 8.02 (d, J = 4.2 Hz, 2H), 7.84 (m, 1H), 7.47 (m, 1H), 7.39 (m, 1H), 4.52 (q, J = 7.1 Hz, 2H), 1.49 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 162.7, 162.0, 156.5, 141.4, 140.0, 129.2, 128.1, 128.0, 127.3, 126.4, 126.2, 113.8, 62.7, 14.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{13}N_2O_2S_2^+$ 317.0413; Found 317.0416.



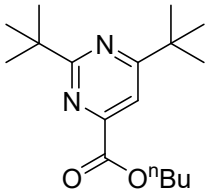
Ethyl 2,6-bis(5-bromothiophen-3-yl)pyrimidine-4-carboxylate (4w)

Yield: 97.9 mg; 83%; White solid; mp: 108–109 ^{o}C; (petroleum ether/ethyl acetate =90:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 1.6 Hz, 1H), 8.14 (d, J = 1.6 Hz, 1H), 7.99–7.93 (m, 2H), 7.78 (d, J = 1.6 Hz, 1H), 4.51 (q, J = 7.1 Hz, 2H), 1.48 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 161.5, 160.9, 156.8, 141.3, 140.0, 130.5, 130.4, 129.1, 129.0, 114.4, 113.7, 113.1, 62.8, 14.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{11}Br_2N_2O_2S_2^+$ 472.8623; Found 472.8625.



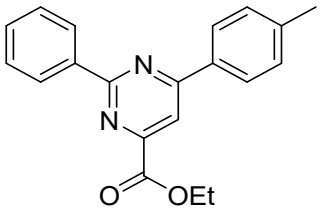
Ethyl 2,6-di-*tert*-butylpyrimidine-4-carboxylate (4x)

Yield: 52.2 mg; 79%; Yellowish oily; (petroleum ether/ethyl acetate =120:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 1.7 Hz, 1H), 4.45 (m, 2H), 1.43 (d, J = 1.8 Hz, 12H), 1.36 (d, J = 1.7 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.4, 177.3, 165.8, 155.3, 112.9, 62.3, 40.0, 38.2, 29.8, 29.6, 14.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{25}N_2O_2^+$ 265.1912; Found 265.1911.



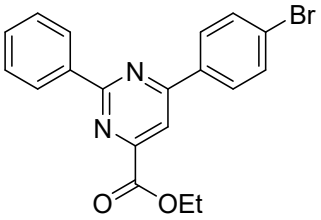
Butyl 2,6-di-*tert*-butylpyrimidine-4-carboxylate (4y)

Yield: 54.8 mg; 75%; Yellowish oily; (petroleum ether/ethyl acetate =150:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 4.39 (t, J = 6.7 Hz, 2H), 1.79 (m, 2H), 1.49 (m, 2H), 1.43 (d, J = 1.7 Hz, 9H), 1.36 (d, J = 1.5 Hz, 9H), 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.3, 177.3, 165.9, 155.4, 112.9, 66.1, 40.0, 38.2, 30.8, 29.8, 29.6, 19.4, 14.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{29}N_2O_2^+$ 293.2224; Found 293.2223.



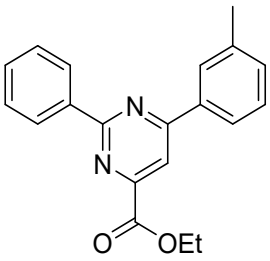
Ethyl 2-phenyl-6-(*p*-tolyl)pyrimidine-4-carboxylate (4aa)

Yield: 108.2 mg; 68%; White solid; mp: 79–80 °C; (petroleum ether/ethyl acetate =90:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69–8.63 (m, 2H), 8.26 (s, 1H), 8.23–8.18 (m, 2H), 7.53 (m, 3H), 7.38–7.35 (m, 2H), 4.55 (q, J = 7.2 Hz, 2H), 2.46 (d, J = 2.3 Hz, 3H), 1.51 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.4, 165.2, 156.5, 142.3, 137.5, 133.8, 131.3, 130.0, 128.9, 128.8, 127.6, 113.9, 62.7, 21.8, 14.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{19}N_2O_2^+$ 319.1441; Found 319.1440.



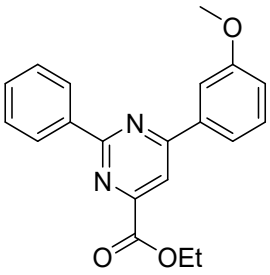
Ethyl 6-(4-bromophenyl)-2-phenylpyrimidine-4-carboxylate (4ab)

Yield: 114.6 mg; 60%; White solid; mp: 111–112 °C; (petroleum ether/ethyl acetate =80:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67–8.59 (m, 2H), 8.25 (s, 1H), 8.21–8.15 (m, 2H), 7.73–7.67 (m, 2H), 7.56–7.50 (m, 3H), 4.55 (q, J = 7.1 Hz, 2H), 1.51 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 165.1, 165.0, 156.9, 137.2, 135.5, 132.5, 131.5, 129.1, 128.9, 128.8, 126.5, 113.9, 62.8, 14.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{16}BrN_2O_2^+$ 383.0390; Found 383.0392.



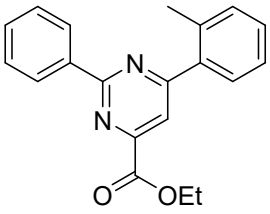
Ethyl 2-phenyl-6-(*m*-tolyl)pyrimidine-4-carboxylate (4ac)

Yield: 103.4 mg; 65%; White solid; mp: 88–89 °C; (petroleum ether/ethyl acetate =70:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70–8.62 (m, 2H), 8.27 (s, 1H), 8.09 (d, *J* = 12.6 Hz, 2H), 7.58–7.49 (m, 3H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 4.55 (q, *J* = 7.2 Hz, 2H), 2.50 (s, 3H), 1.51 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 165.4, 165.2, 156.6, 139.0, 137.5, 136.6, 132.5, 131.3, 129.2, 128.9, 128.8, 128.2, 124.9, 114.3, 62.7, 21.8, 14.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{19}N_2O_2^+$ 319.1441; Found 319.1443.



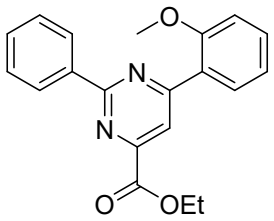
Ethyl 6-(3-methoxyphenyl)-2-phenylpyrimidine-4-carboxylate (4ad)

Yield: 105.2 mg; 63%; White solid; mp: 82–83 °C; (petroleum ether/ethyl acetate =70:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70-8.62 (m, 2H), 8.27 (s, 1H), 7.92–7.82 (m, 2H), 7.57–7.45 (m, 4H), 7.11 (m, 1H), 4.55 (q, *J* = 7.1 Hz, 2H), 3.95 (s, 3H), 1.51 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.4, 165.1, 160.5, 156.6, 138.0, 137.3, 131.4, 130.3, 128.9, 128.8, 120.1, 117.4, 114.4, 113.0, 62.8, 55.7, 14.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{19}N_2O_3^+$ 335.1390; Found 335.1392.



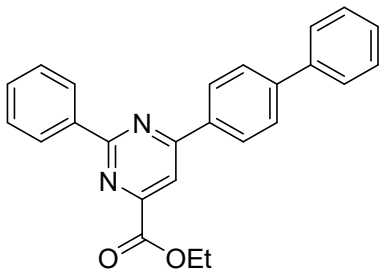
Ethyl 2-phenyl-6-(*o*-tolyl)pyrimidine-4-carboxylate (4ae)

Yield: 103.4 mg; 65%; White solid; mp: 94–95 °C; (petroleum ether/ethyl acetate =80:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63–8.56 (m, 2H), 8.01 (s, 1H), 7.60 (s, 1H), 7.54–7.49 (m, 3H), 7.43–7.34 (m, 3H), 4.54 (q, J = 7.1 Hz, 2H), 2.56 (s, 3H), 1.49 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 165.1, 165.0, 156.1, 137.7, 137.4, 136.9, 131.7, 131.4, 130.2, 130.1, 128.9, 128.8, 126.5, 118. 4, 62.7, 21.0, 14.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{19}N_2O_2^+$ 319.1441; Found 319.1440.



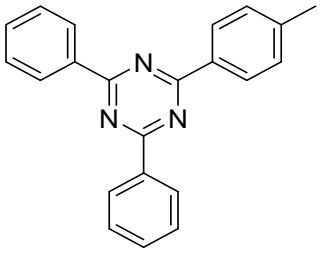
Ethyl 6-(2-methoxyphenyl)-2-phenylpyrimidine-4-carboxylate (4af)

Yield: 103.6 mg; 62%; White solid; mp: 90–91 °C; (petroleum ether/ethyl acetate =90:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70–8.58 (m, 2H), 8.54 (s, 1H), 8.26 (m, 1H), 7.54–7.46 (m, 4H), 7.16 (m, 1H), 7.06 (d, J = 8.3 Hz, 1H), 4.53 (d, J = 7.2 Hz, 2H), 3.96 (s, 3H), 1.50 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 165.1, 165.0, 158.6, 155.5, 137.7, 132.5, 131.5, 131.1, 128.8, 128.7, 126.0, 121.4, 119.3, 111.8, 62.5, 55.9, 14.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{19}N_2O_3^+$ 335.1390; Found 335.1391.



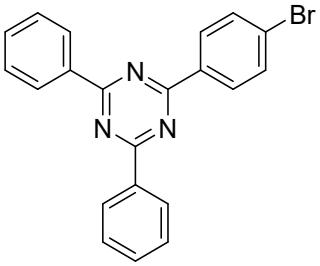
Ethyl 6-([1,1'-biphenyl]-4-yl)-2-phenylpyrimidine-4-carboxylate (4ag)

Yield: 125.5 mg; 66%; White solid; mp: 109–110 °C; (petroleum ether/ethyl acetate =100:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71–8.65 (m, 2H), 8.41–8.37 (m, 2H), 8.32 (s, 1H), 7.81–7.78 (m, 2H), 7.70–7.67 (m, 2H), 7.55 (m, 3H), 7.52–7.47 (m, 2H), 7.44–7.39 (m, 1H), 4.56 (q, J = 7.1 Hz, 2H), 1.52 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.5, 165.2, 156.6, 144.5, 140.3, 137.4, 135.4, 131.4, 129.2, 128.9, 128.8, 128.2, 128.1, 127.9, 127.4, 114.1, 62.7, 14.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{21}N_2O_2^+$ 381.1598; Found 381.1599.



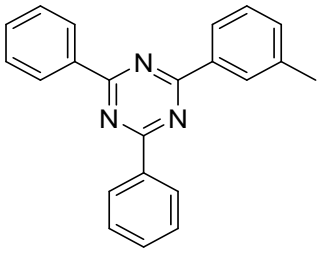
2,4-diphenyl-6-(*p*-tolyl)-1,3,5-triazine (5aa)

Yield: 51.7 mg; 32%; White solid; mp: 195–197 °C; (petroleum ether/ethyl acetate =200:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80–8.75 (m, 4H), 8.69–8.65 (m, 2H), 7.63–7.54 (m, 6H), 7.37 (d, J = 8.0 Hz, 2H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 171.7, 143.3, 136.6, 133.8, 132.6, 129.6, 129.2, 129.1, 128.8, 22.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{21}N_2O_2^+$ 381.1598; Found 381.1599.



2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine (5ab)

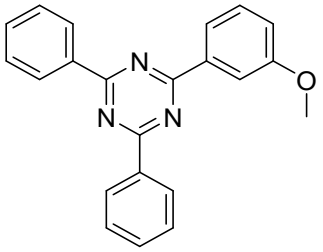
Yield: 77.4 mg; 40%; White solid; mp: 206–207 °C; (petroleum ether/ethyl acetate =100:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78–8.71 (m, 4H), 8.64–8.59 (m, 2H), 7.72–7.67 (m, 2H), 7.63–7.54 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 171.0, 136.2, 135.4, 132.8, 132.1, 130.7, 129.2, 128.9, 127.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{15}BrN_3^+$ 388.0444; Found 388.0446.



2,4-diphenyl-6-(*m*-tolyl)-1,3,5-triazine (5ac)

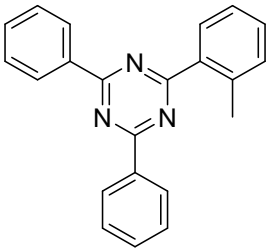
Yield: 56.5 mg; 35%; White solid; mp: 200–201 °C; (petroleum ether/ethyl acetate =150:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83–8.75 (m, 4H), 8.59 (m, 2H), 7.64–7.56

(m, 6H), 7.50–7.40 (m, 2H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 171.7, 138.5, 136.5, 136.4, 133.5, 132.6, 129.6, 129.2, 128.8, 128.7, 126.4, 21.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{18}N_3^+$ 324.1495; Found 324.1496.



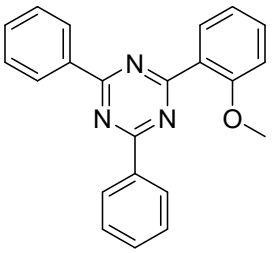
2-(3-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine (5ad)

Yield: 62.7 mg; 37%; White solid; mp: 160–163 °C; (petroleum ether/ethyl acetate =170:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82–8.72 (m, 4H), 8.38 (d, *J* = 7.7 Hz, 1H), 8.31 (s, 1H), 7.64–7.55 (m, 6H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 3.96 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 171.6, 160.1, 137.9, 136.4, 132.7, 129.8, 129.2, 128.8, 121.7, 118.6, 114.0, 55.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{18}N_3O^+$ 340.1444; Found 340.1445.



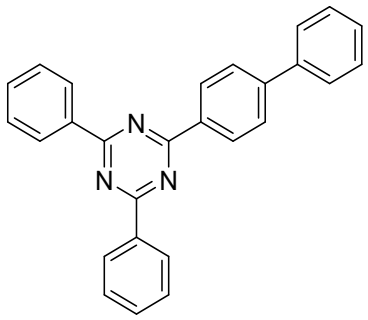
2,4-diphenyl-6-(*o*-tolyl)-1,3,5-triazine (5ae)

Yield: 56.5 mg; 35%; White solid; mp: 198–199 °C; (petroleum ether/ethyl acetate =180:1, V/V); 1H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 7.4 Hz, 4H), 8.36 (d, *J* = 7.6 Hz, 1H), 7.61 (m, 6H), 7.44 (m, 3H), 2.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 171.5, 139.3, 136.5, 136.3, 132.7, 132.1, 131.5, 131.2, 129.2, 128.9, 126.3, 22.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{18}N_3^+$ 324.1495; Found 324.1494.



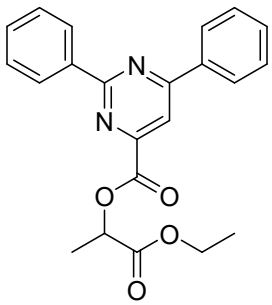
2-(2-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine (5af)

Yield: 64.4 mg; 38%; White solid; mp: 158–160 °C; (petroleum ether/ethyl acetate =160:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, J = 7.3 Hz, 4H), 8.18 (d, J = 7.7 Hz, 1H), 7.63–7.52 (m, 7H), 7.19–7.10 (m, 2H), 4.01 (d, J = 1.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 171.6, 159.4, 136.6, 132.7, 132.6, 132.5, 129.2, 128.8, 127.0, 121.0, 113.0, 56.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{18}N_3O^+$ 340.1444; Found 340.1443.



2-([1,1'-biphenyl]-4-yl)-4,6-diphenyl-1,3,5-triazine (5ag)

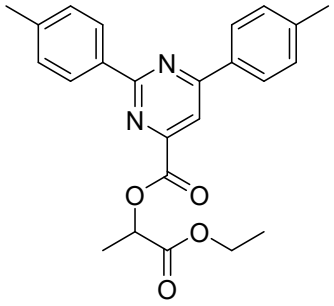
Yield: 65.5 mg; 34%; White solid; mp: 145–146 °C; (petroleum ether/ethyl acetate =120:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91–8.75 (m, 6H), 7.83–7.79 (m, 2H), 7.74–7.70 (m, 2H), 7.66–7.56 (m, 6H), 7.54–7.48 (m, 2H), 7.43 (d, J = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 171.6, 145.4, 140.6, 136.5, 135.4, 132.7, 129.77, 129.2, 129.1, 128.9, 128.2, 127.5, 127.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{20}N_3^+$ 386.1652; Found 386.1651.



1-ethoxy-1-oxopropan-2-yl 2,6-diphenylpyrimidine-4-carboxylate (6a)

Yield: 131.7 mg; 77%; White solid; mp: 130–132 °C; (petroleum ether/ethyl acetate =150:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71–8.64 (m, 2H), 8.30 (q, J = 3.1 Hz, 3H), 7.60–7.51 (m, 6H), 5.44 (q, J = 7.0 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 1.75 (d, J = 7.1 Hz, 3H), 1.32 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 166.3, 165.4, 164.4,

155.8, 137.2, 136.4, 131.8, 131.4, 129.2, 128.9, 128.7, 127.6, 114.5, 70.6, 61.9, 17.2, 14.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{21}N_2O_4^+$ 377.1497; Found 377.1496.



1-ethoxy-1-oxopropan-2-yl 2,6-di-p-tolylpyrimidine-4-carboxylate (6b)

Yield: 145.5 mg; 72%; White solid; mp: 142–144 °C; (petroleum ether/ethyl acetate =180:1, V/V); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59–8.51 (m, 2H), 8.26–8.16 (m, 3H), 7.34 (m, 4H), 5.47–5.37 (m, 1H), 4.27 (m, 2H), 2.45 (d, J = 5.7 Hz, 6H), 1.74 (m, 3H), 1.32 (t, J = 7.2, 1.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 166.2, 165.5, 164.6, 155.7, 142.2, 141.6, 134.8, 133.9, 130.0, 129.5, 128.9, 127.6, 113.9, 70.6, 61.9, 21.8, 21.7, 17.2, 14.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{25}N_2O_4^+$ 405.1809; Found 405.1808.

8. ^{1}H NMR and ^{13}C NMR spectra for products

^{1}H NMR and ^{13}C NMR of **4a**

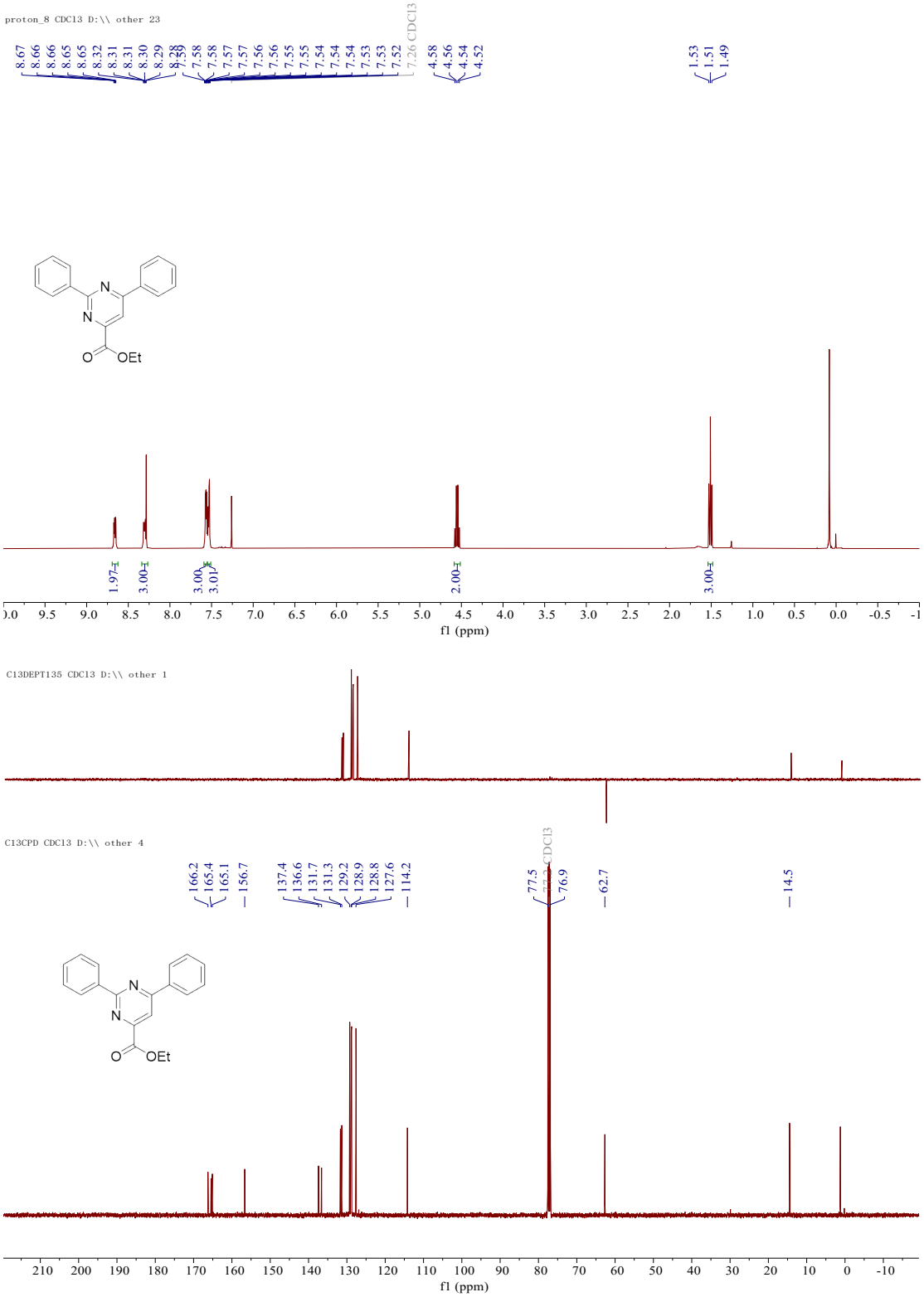


Figure S1 ^{1}H NMR and ^{13}C NMR spectrum of (**4a**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4b**

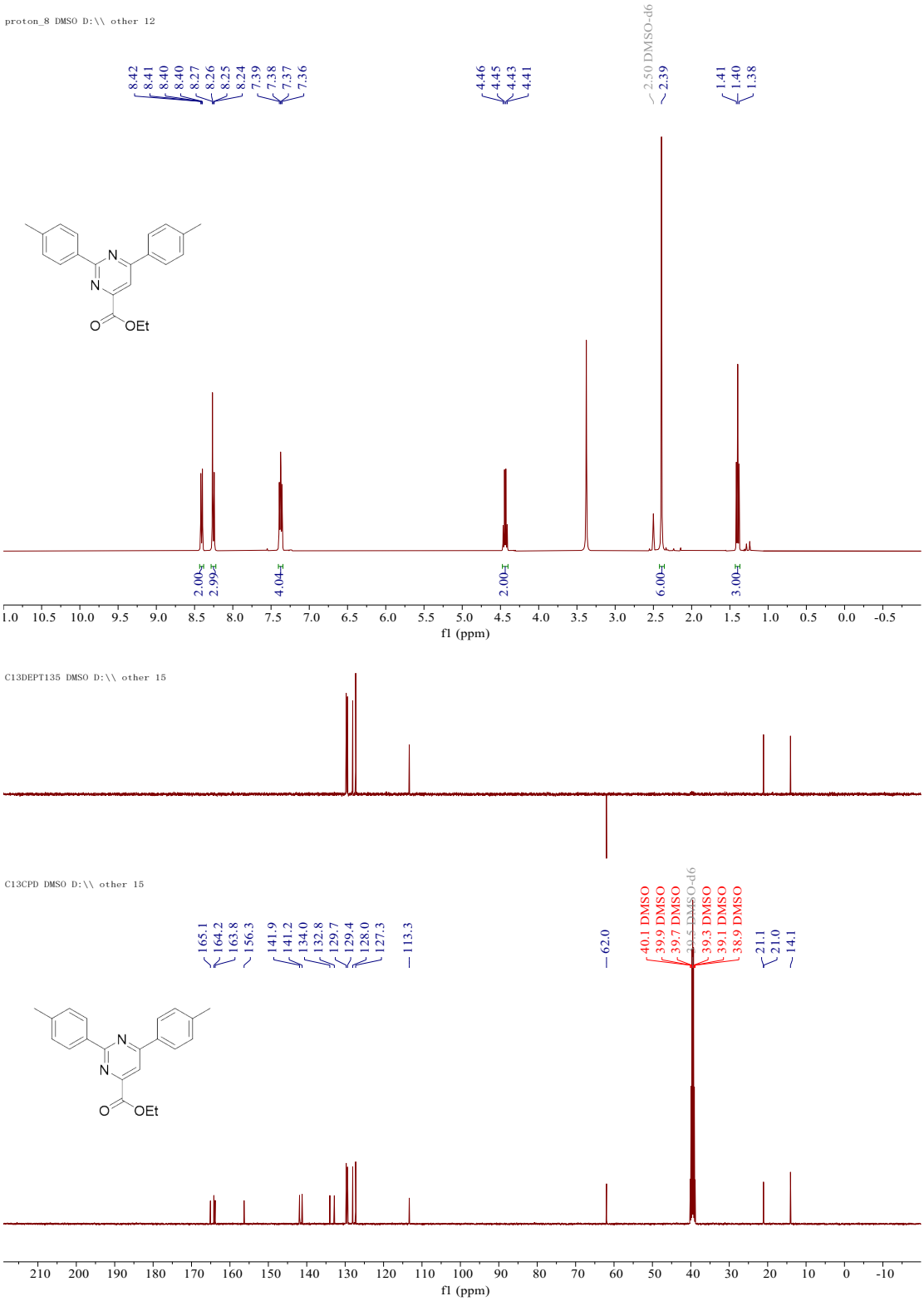


Figure S2 ^{1}H NMR and ^{13}C NMR spectrum of (**4b**) in DMSO.

^{1}H NMR and ^{13}C NMR of **4c**

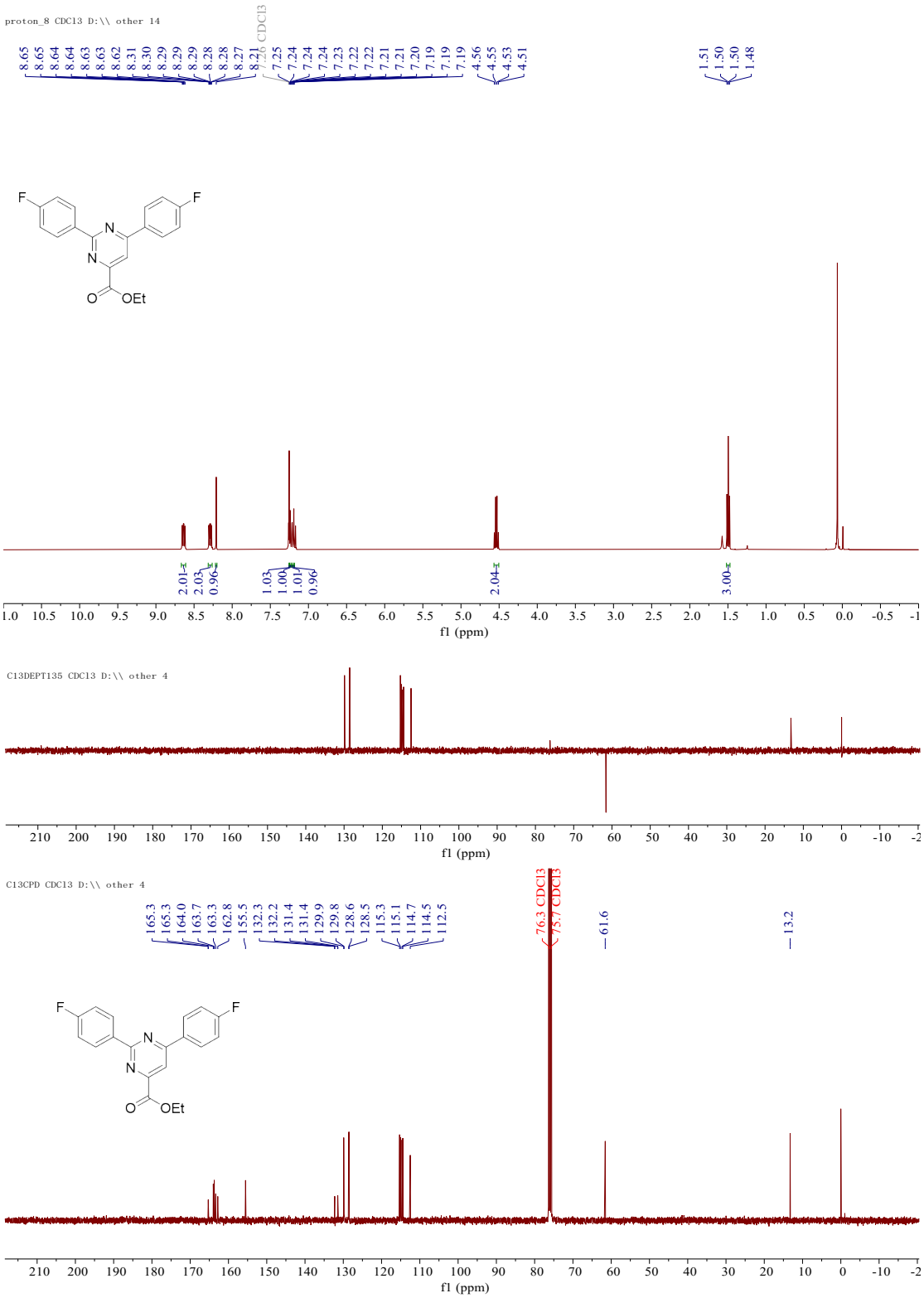


Figure S3 ^{1}H NMR and ^{13}C NMR spectrum of (**4c**) in DMSO.

^{19}F NMR **4c**

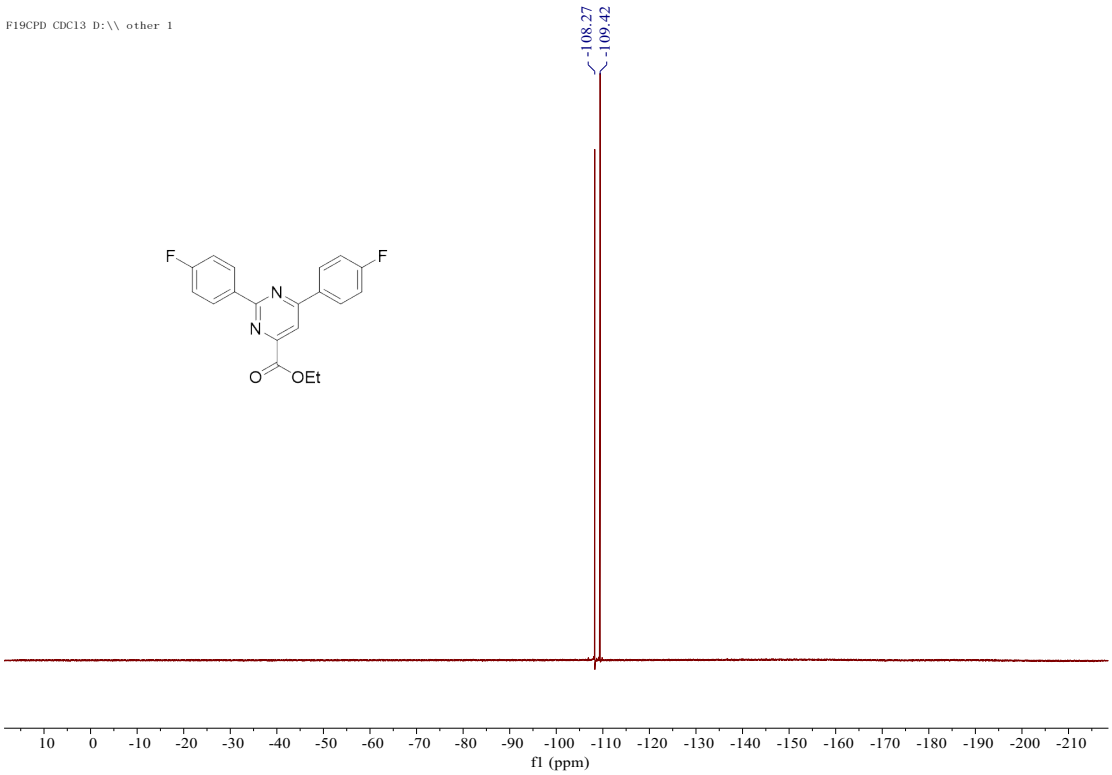


Figure S4 ^{19}F NMR spectrum of (**4c**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4d**

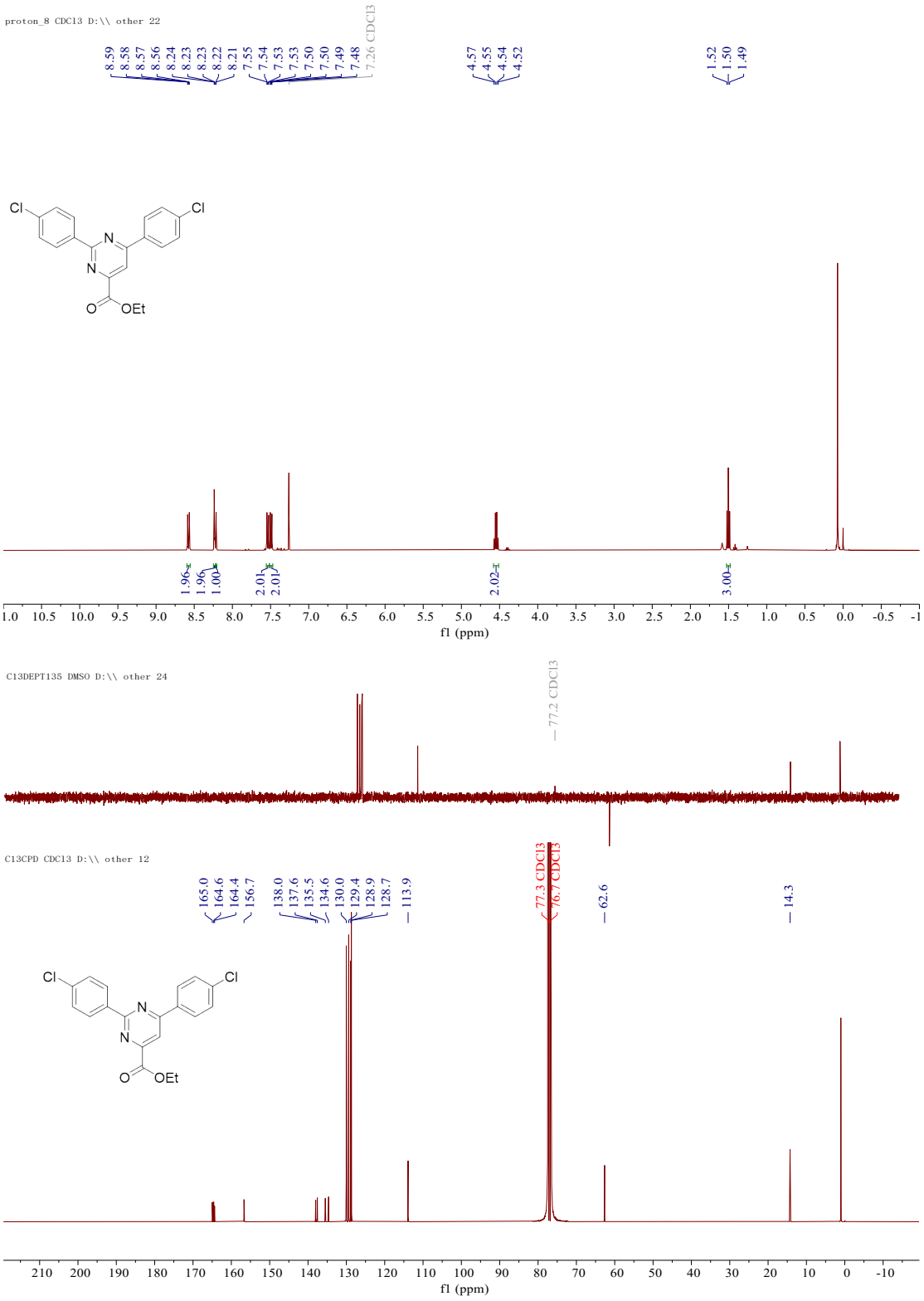


Figure S5 ^{1}H NMR and ^{13}C NMR spectrum of (**4d**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4e**

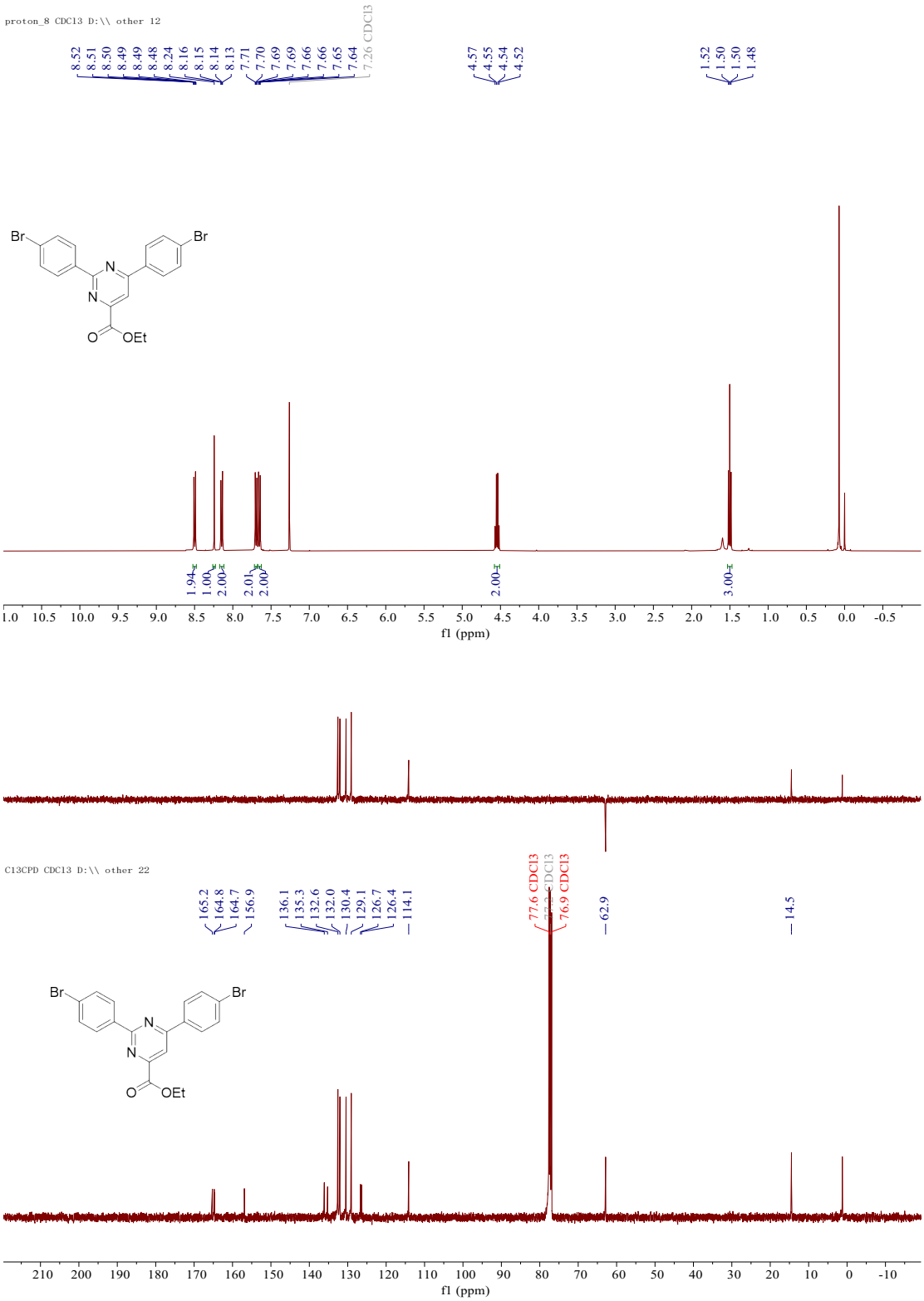


Figure S6 ^{1}H NMR and ^{13}C NMR spectrum of (**4e**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4f**

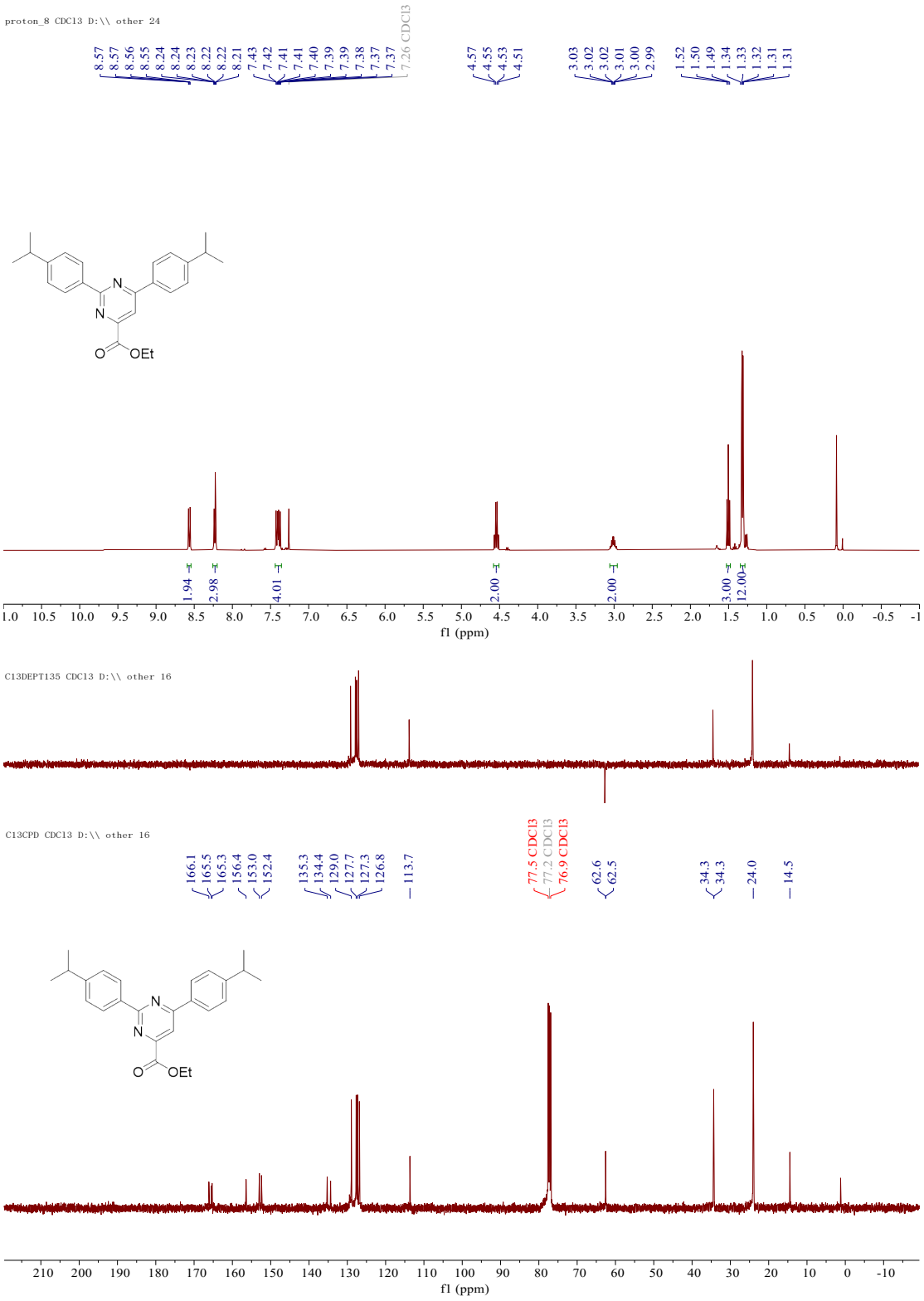


Figure S7 ^{1}H NMR and ^{13}C NMR spectrum of (**4f**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4g**

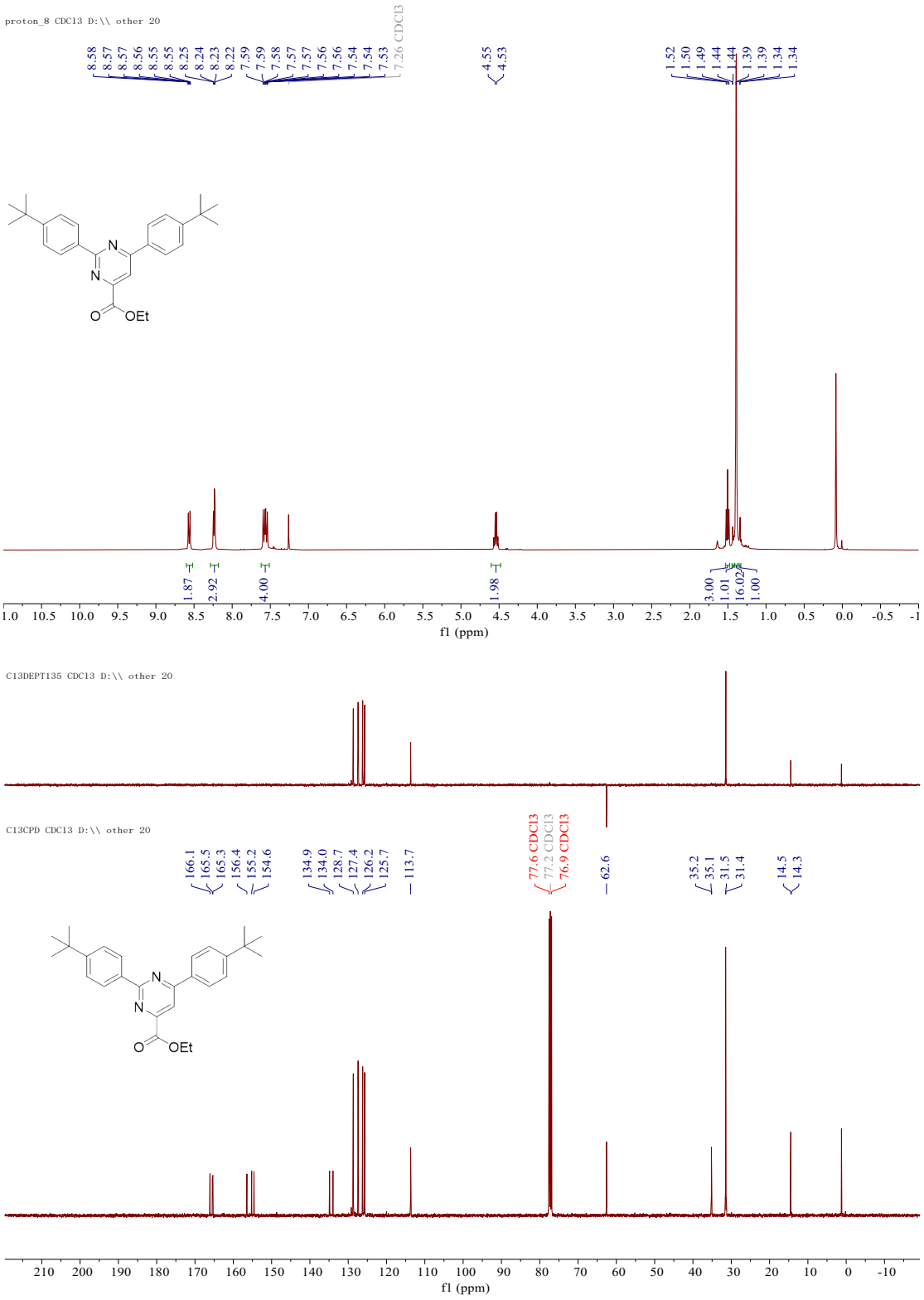


Figure S8 ^{1}H NMR and ^{13}C NMR spectrum of (**4g**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4h**

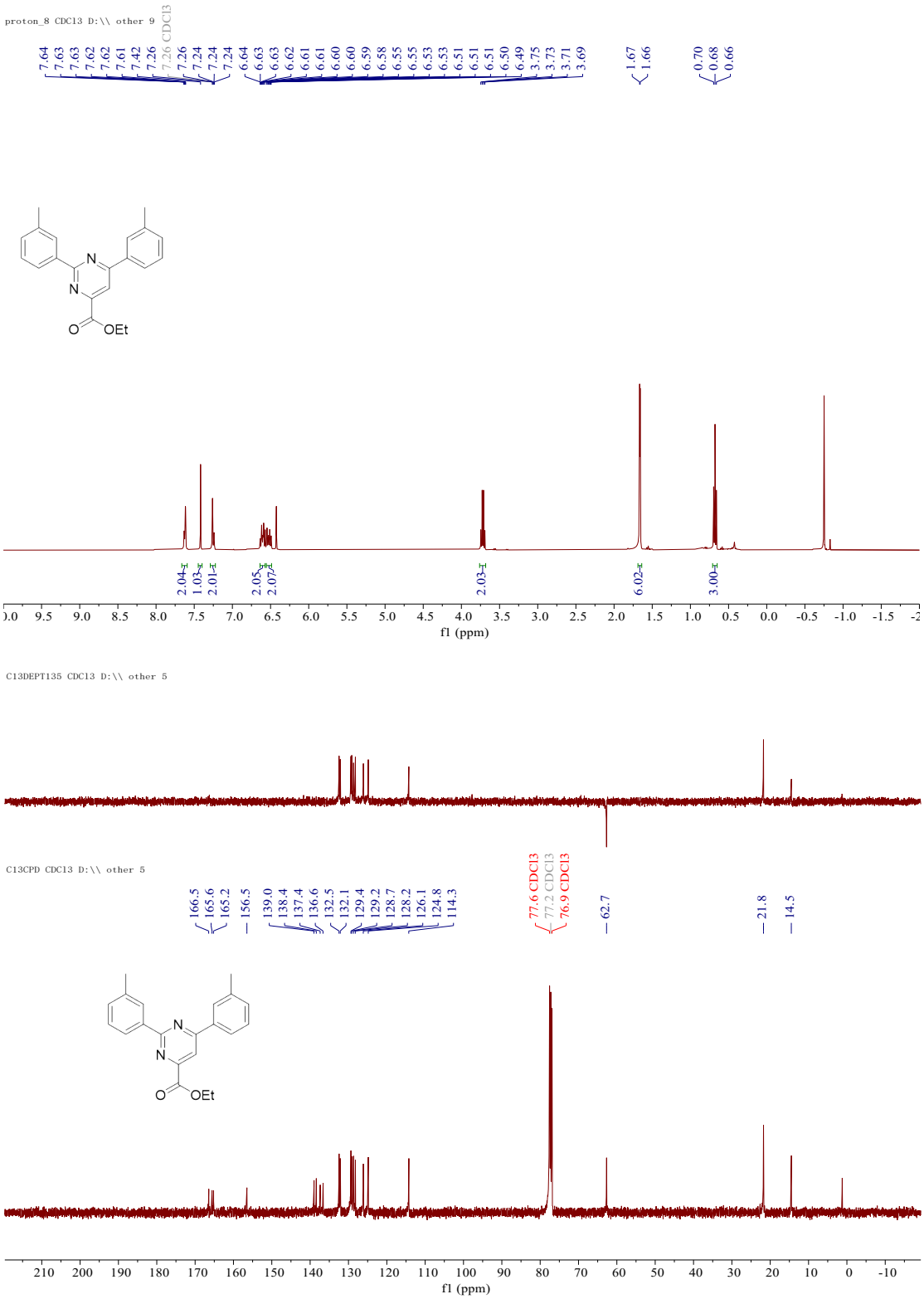


Figure S9 ^{1}H NMR and ^{13}C NMR spectrum of (**4h**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4i**

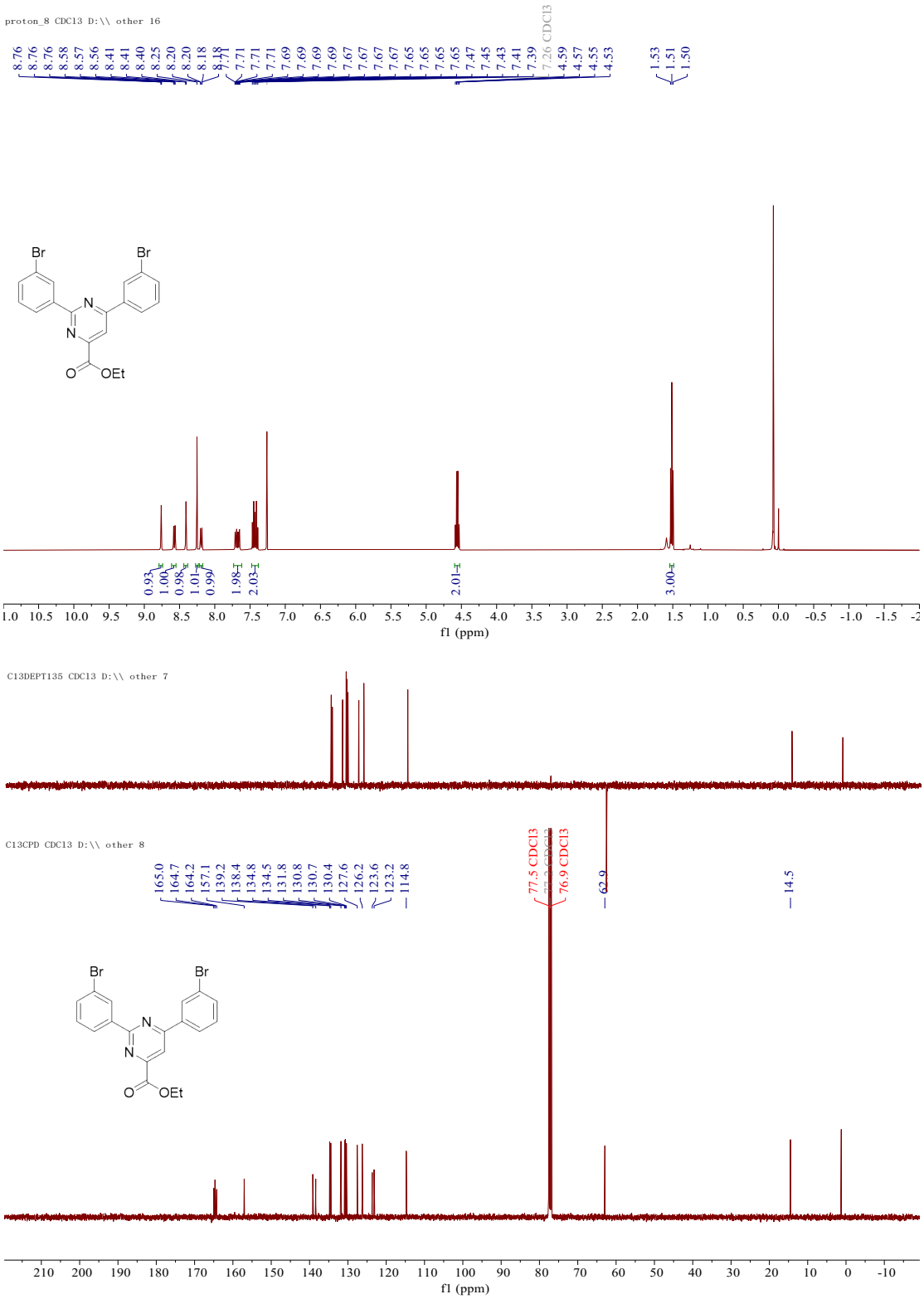


Figure S10 ^{1}H NMR and ^{13}C NMR spectrum of (**4i**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4j**

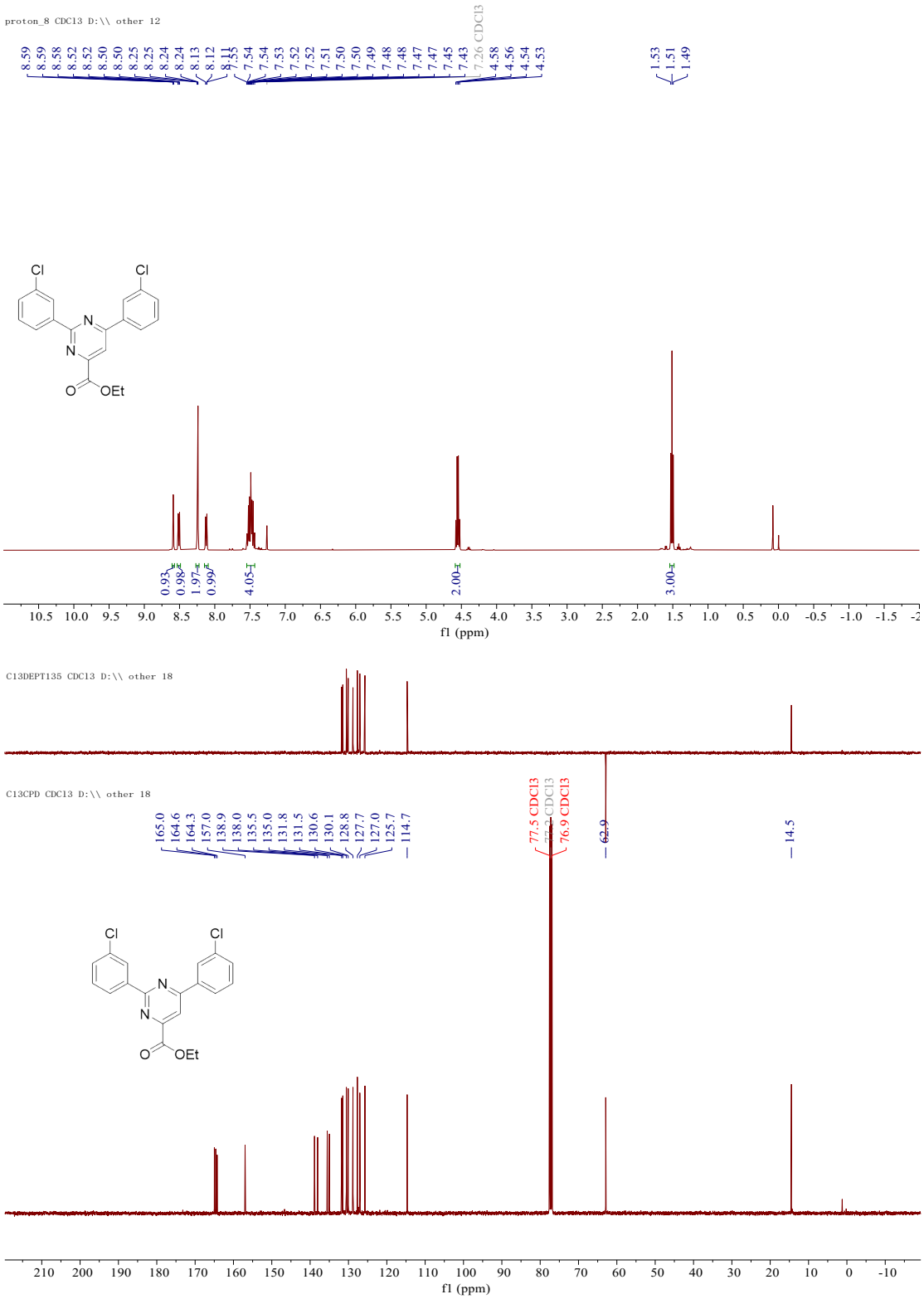


Figure S11 ^{1}H NMR and ^{13}C NMR spectrum of (**4j**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4k**

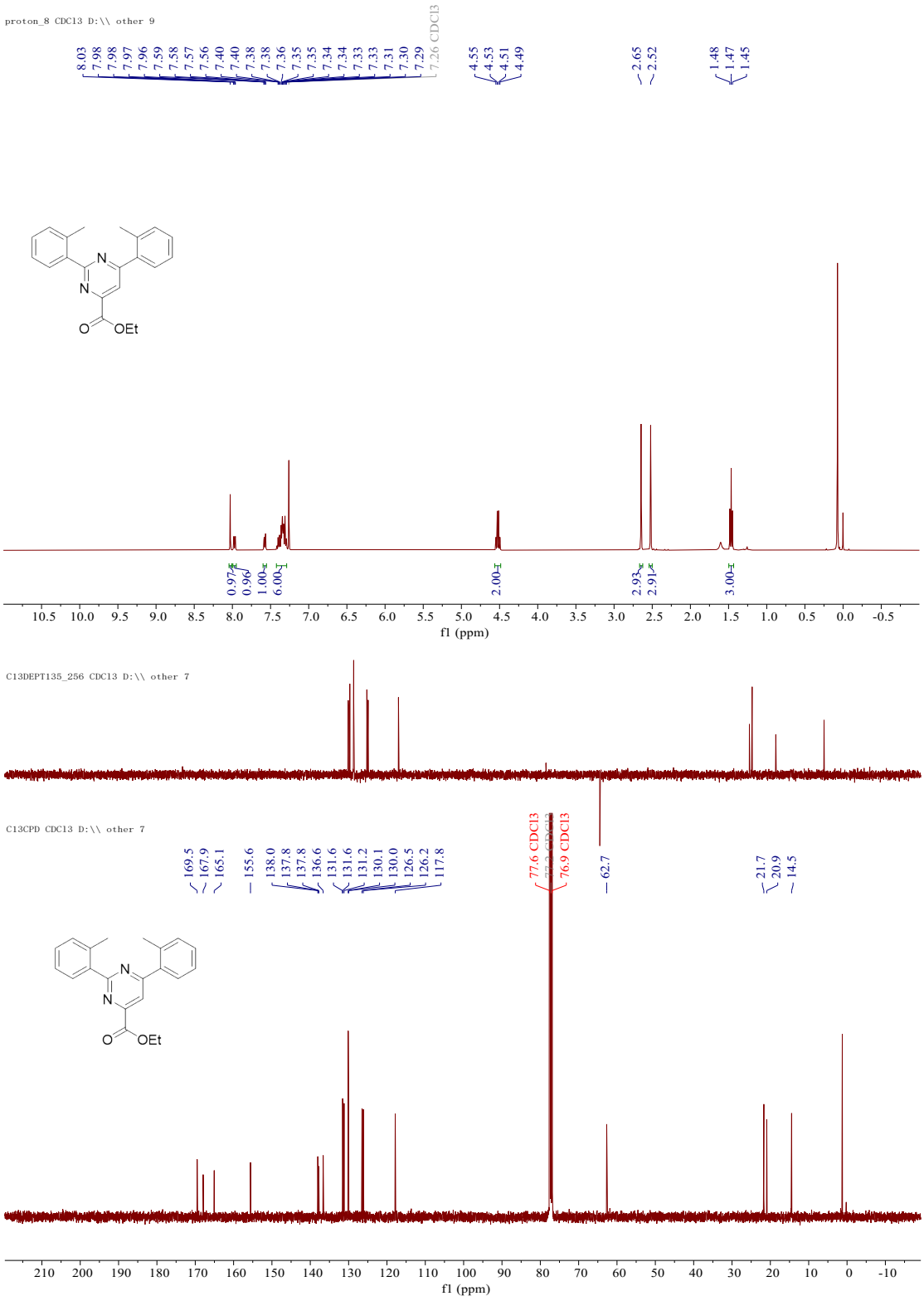


Figure S12 ^{1}H NMR and ^{13}C NMR spectrum of (**4k**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4l**

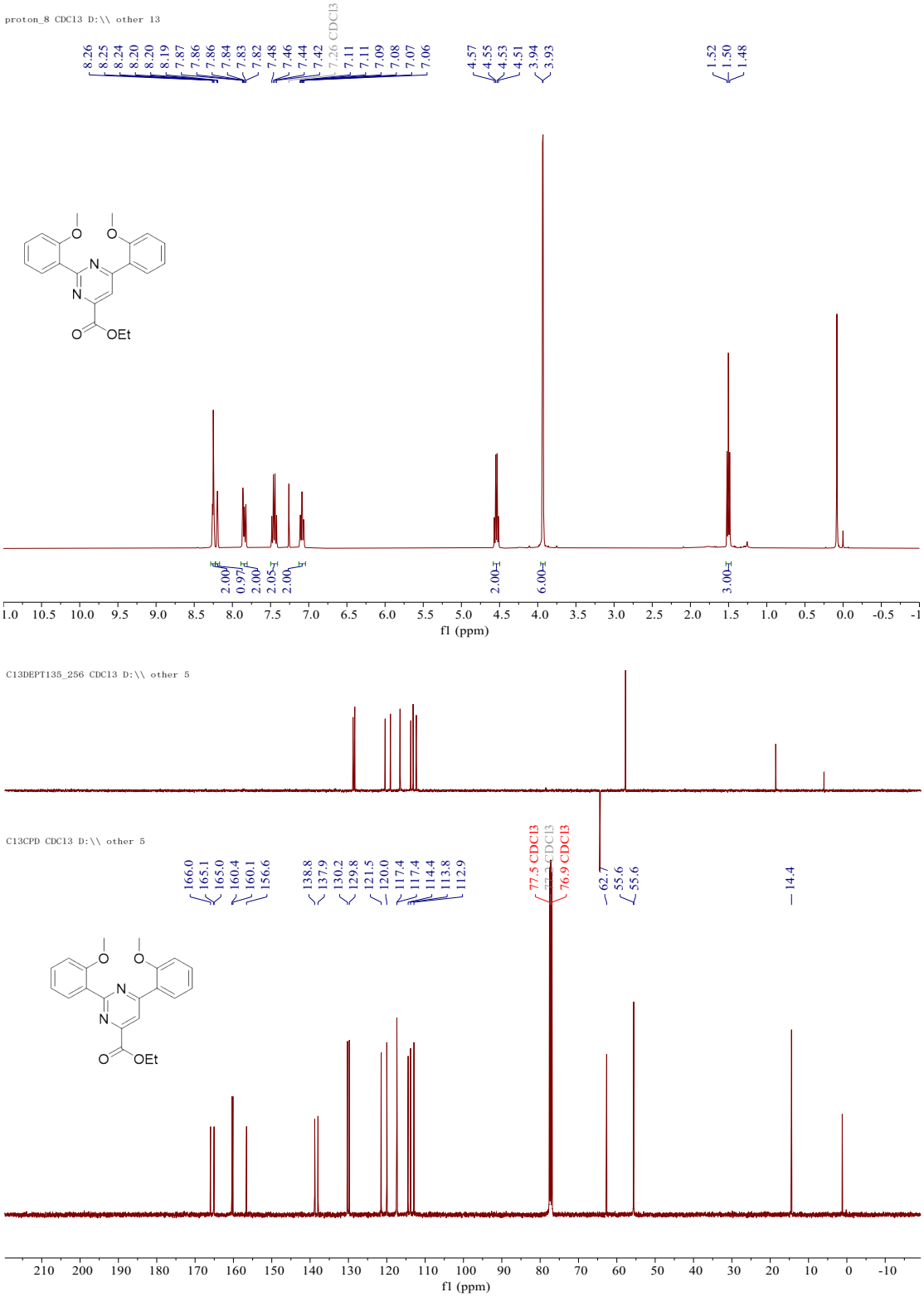


Figure S13 ^{1}H NMR and ^{13}C NMR spectrum of (**4l**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4m**

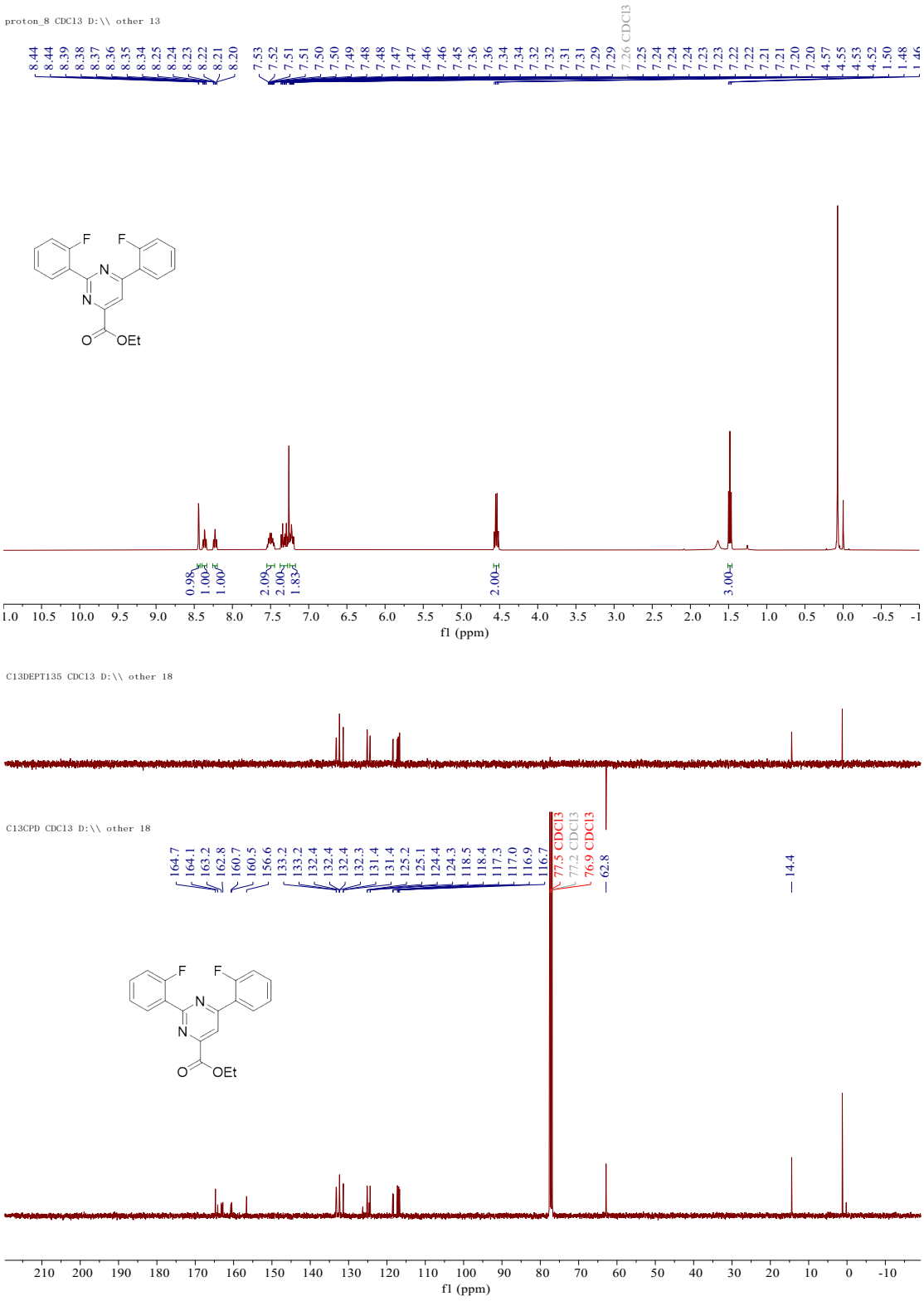


Figure S14 ^{1}H NMR and ^{13}C NMR spectrum of (**4m**) in $CDCl_3$.

^{19}F NMR **4m**

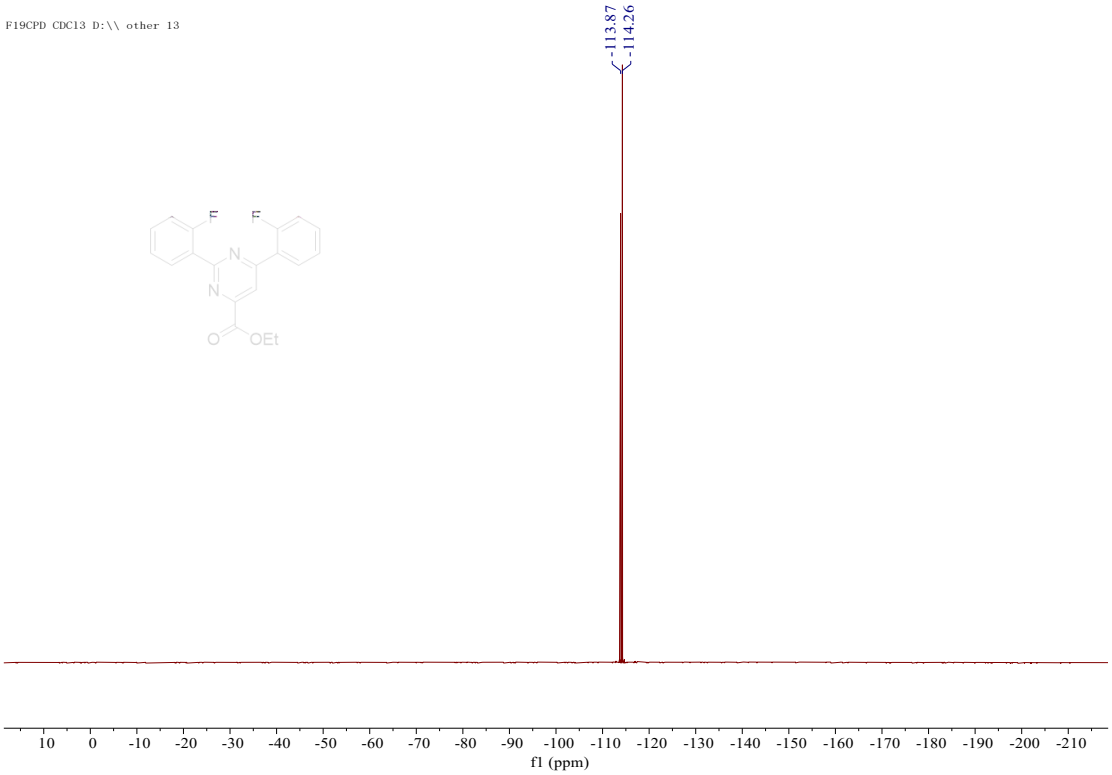


Figure S15 ^{19}F NMR spectrum of (**4m**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4n**

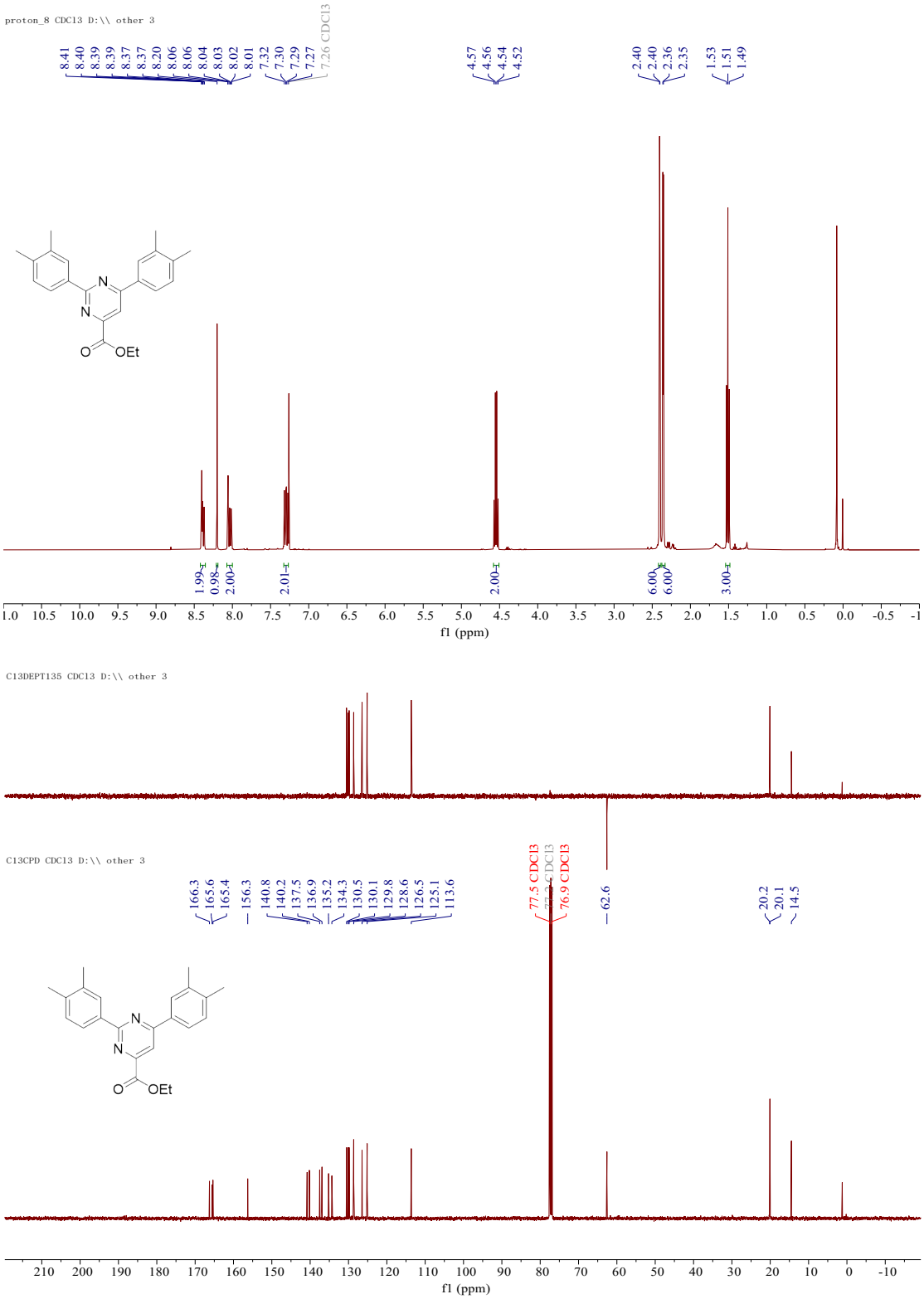


Figure S16 ^{1}H NMR and ^{13}C NMR spectrum of (**4n**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4o**

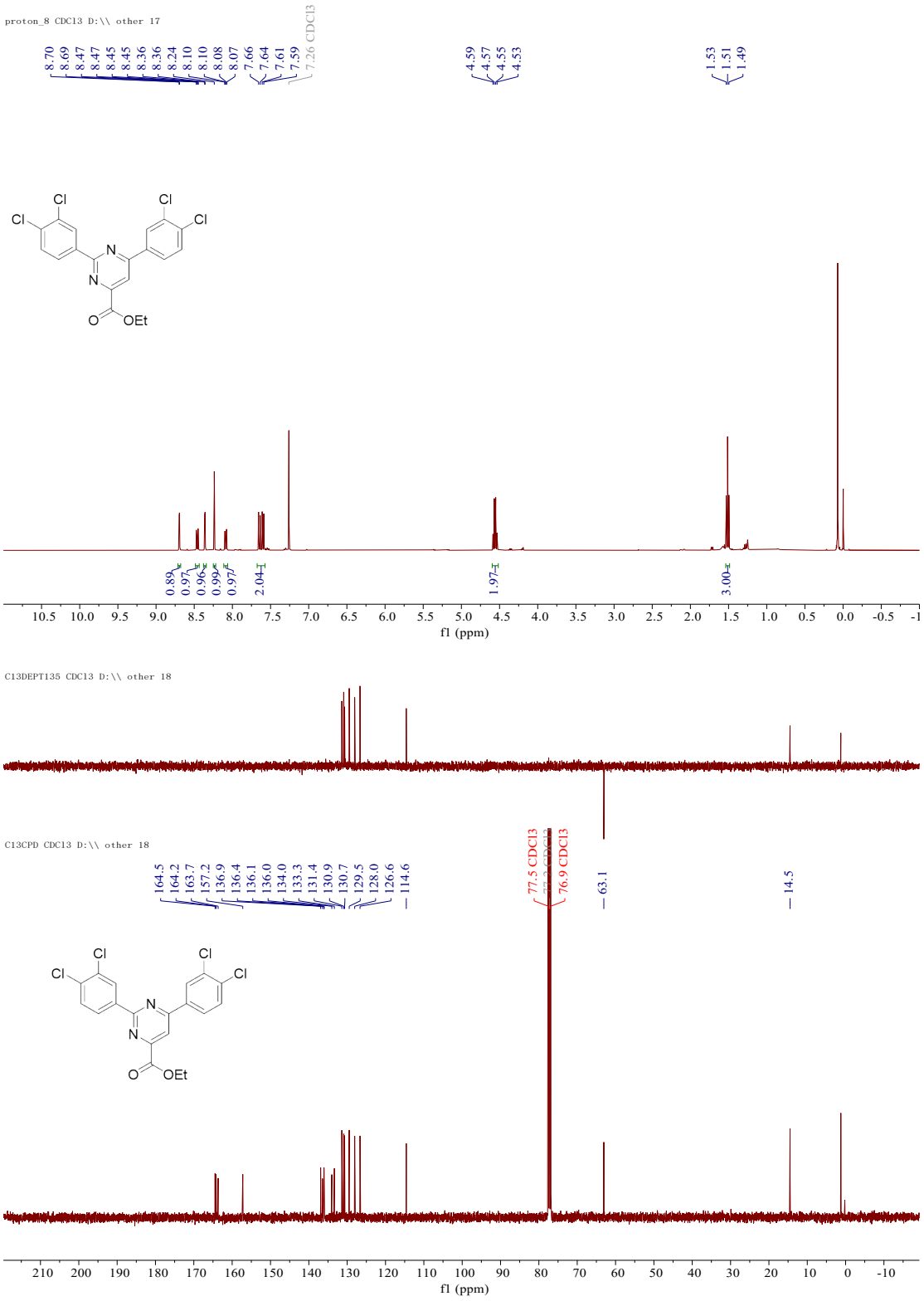


Figure S17 ^{1}H NMR and ^{13}C NMR spectrum of (**4o**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4p**

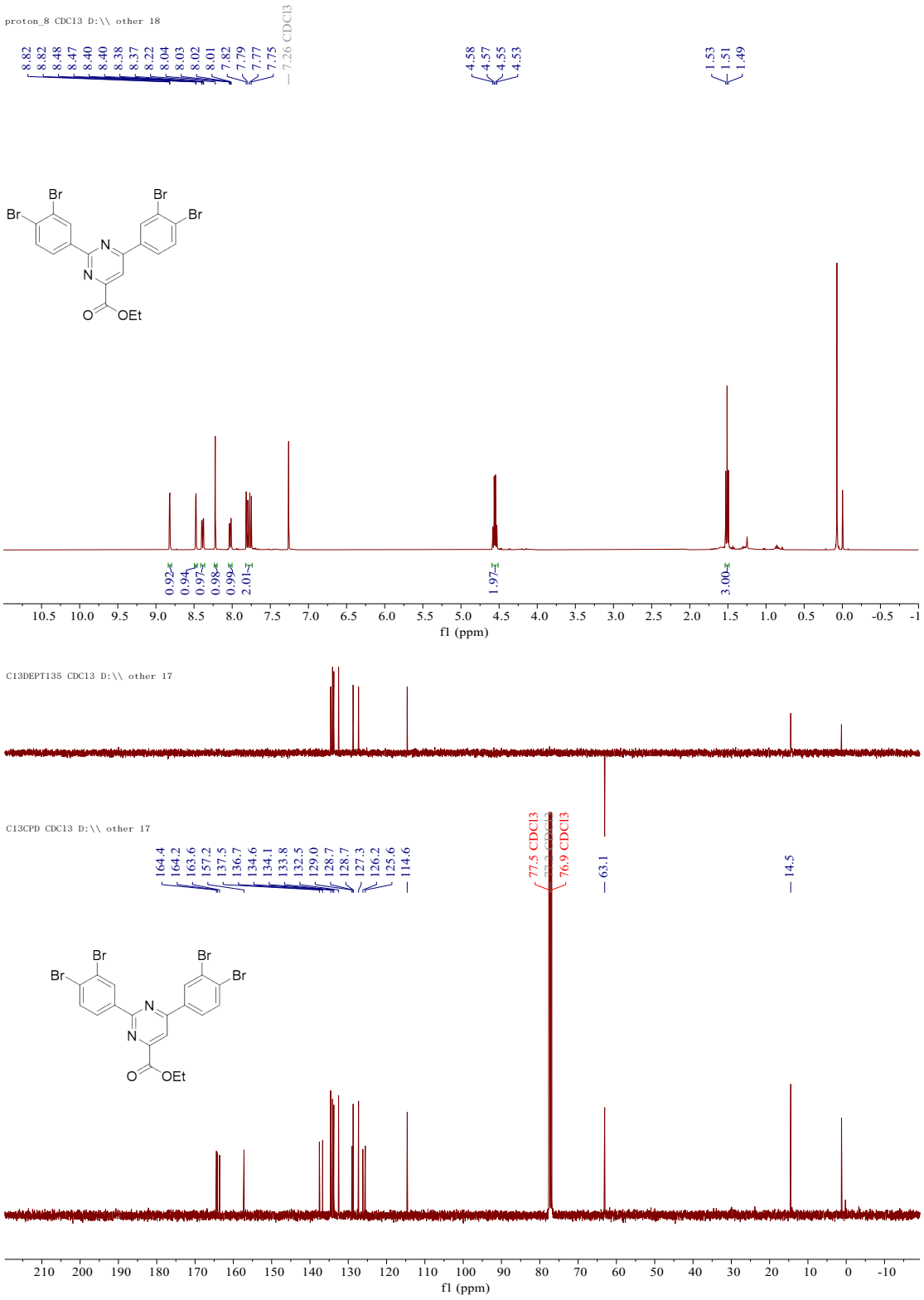


Figure S18 ^{1}H NMR and ^{13}C NMR spectrum of (**4p**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4q**

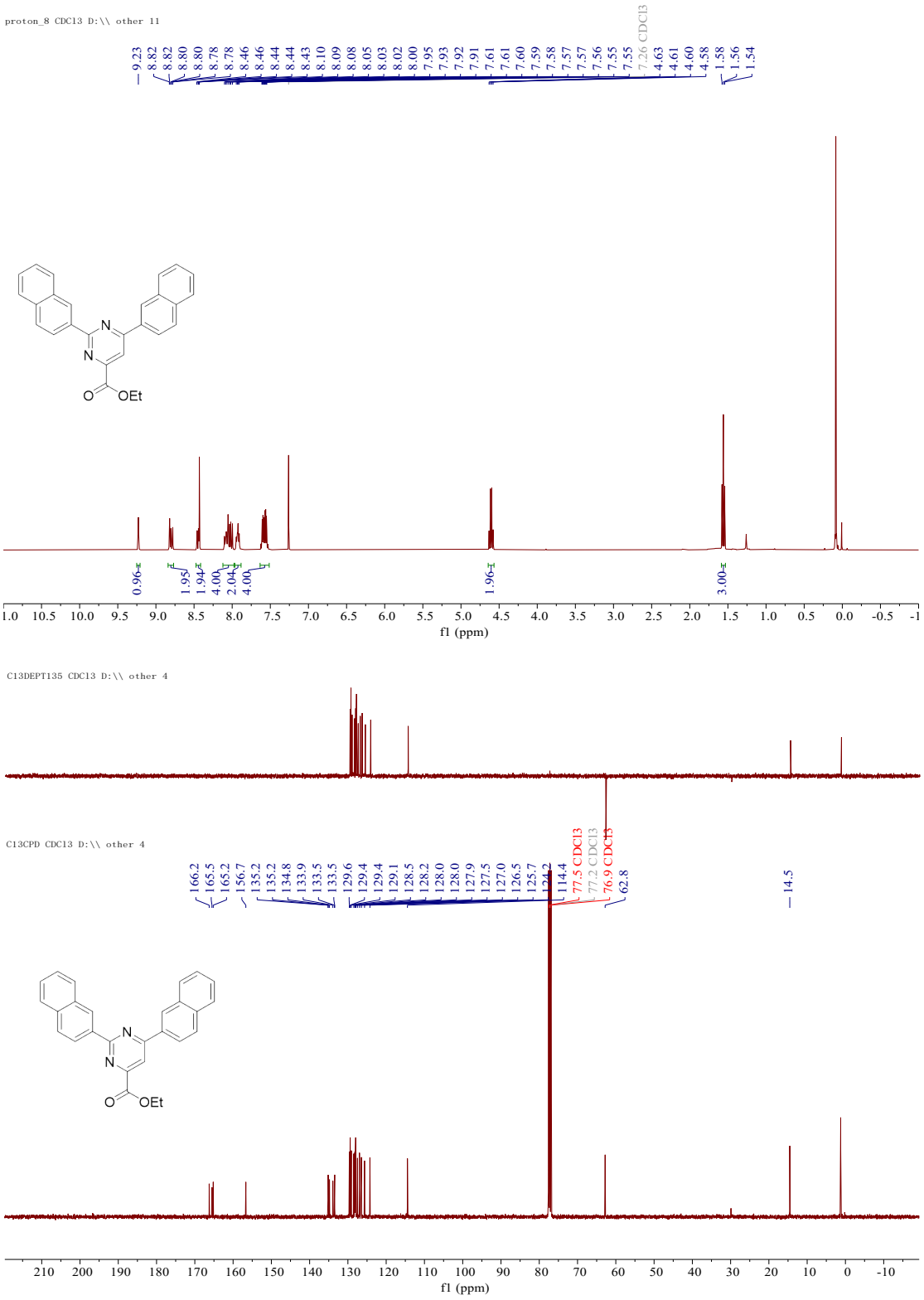


Figure S19 ^{1}H NMR and ^{13}C NMR spectrum of (**4q**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4r**

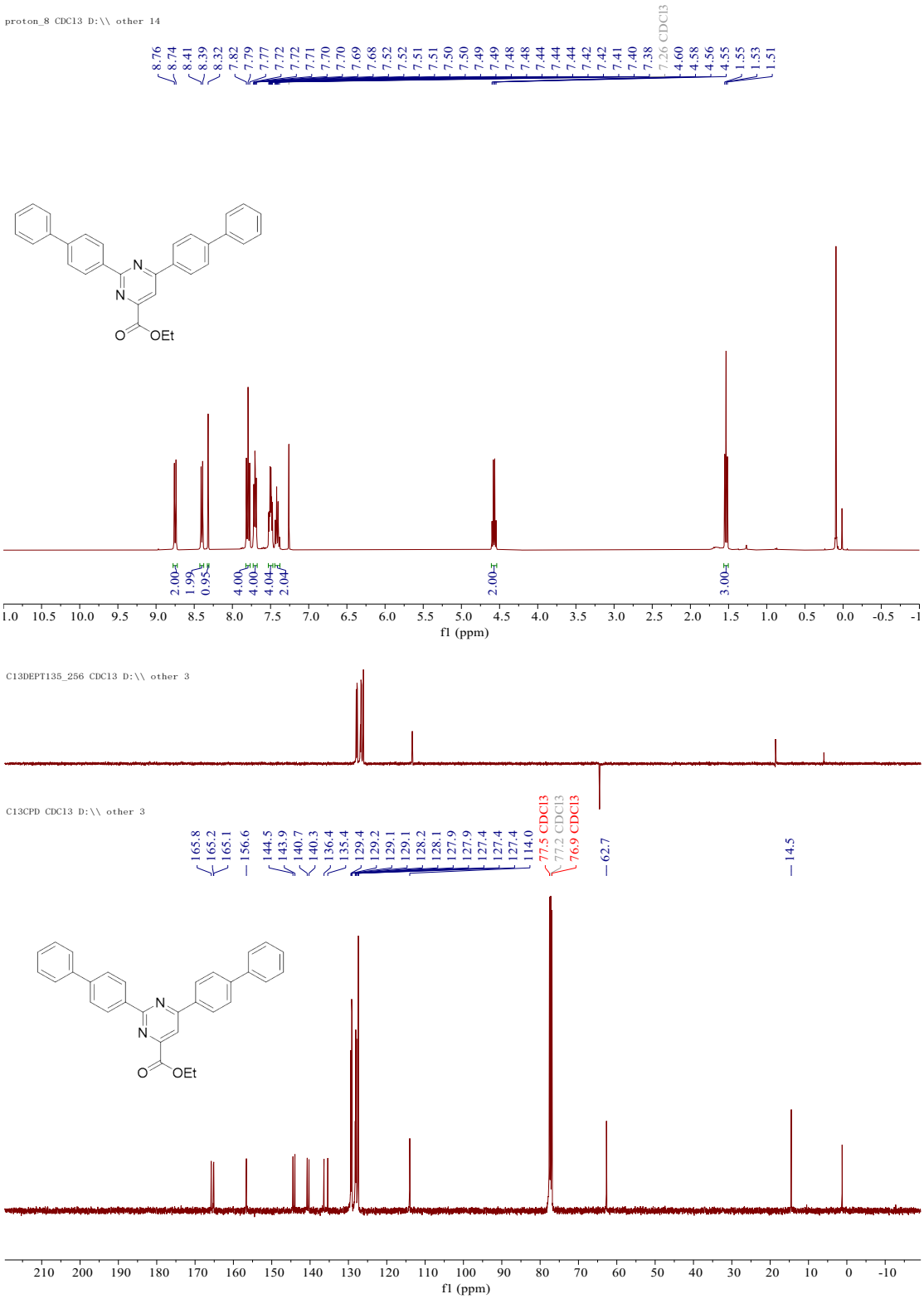


Figure S20 ^{1}H NMR and ^{13}C NMR spectrum of (**4r**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4s**

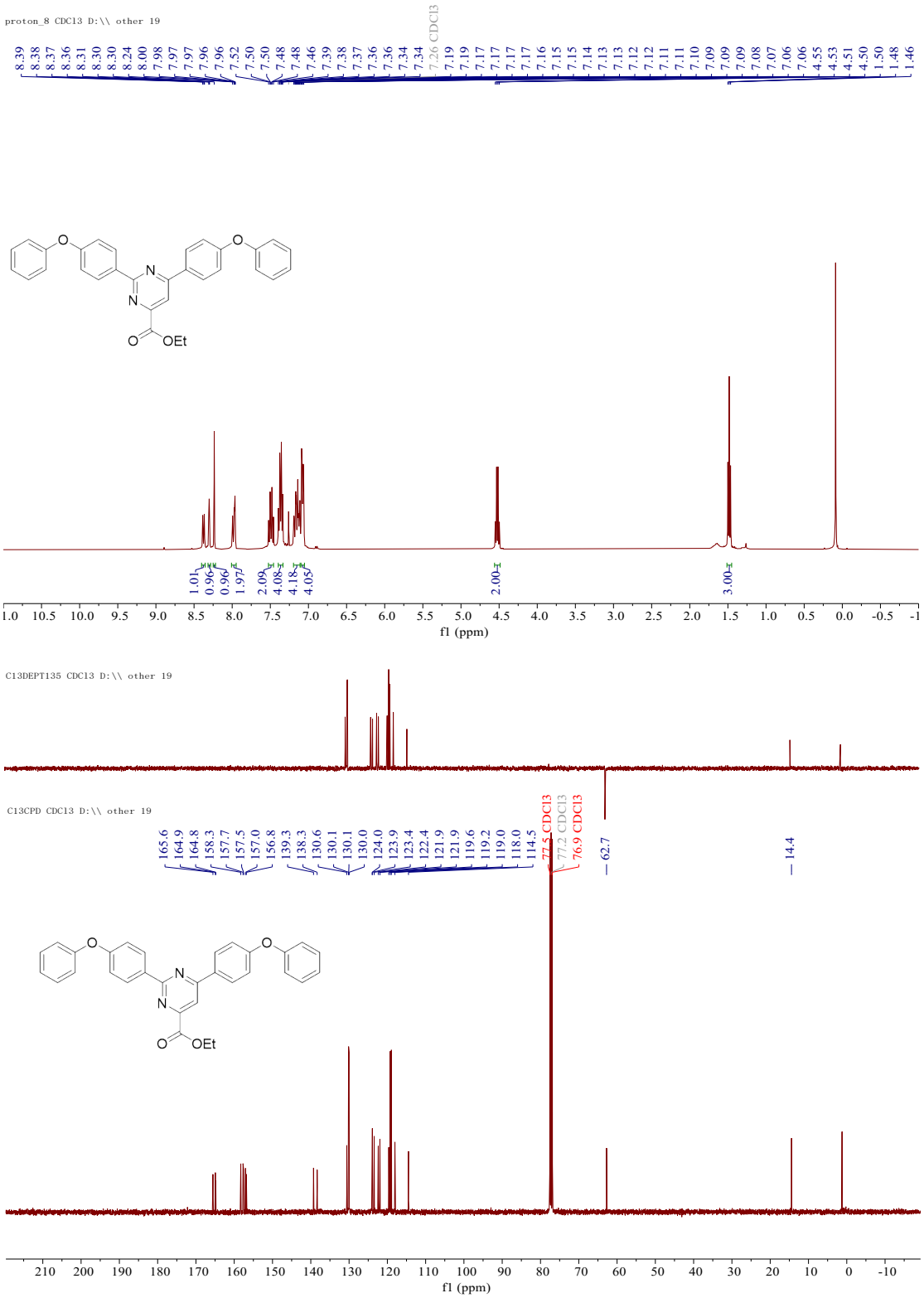


Figure S21 ^{1}H NMR and ^{13}C NMR spectrum of (**4r**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4t**

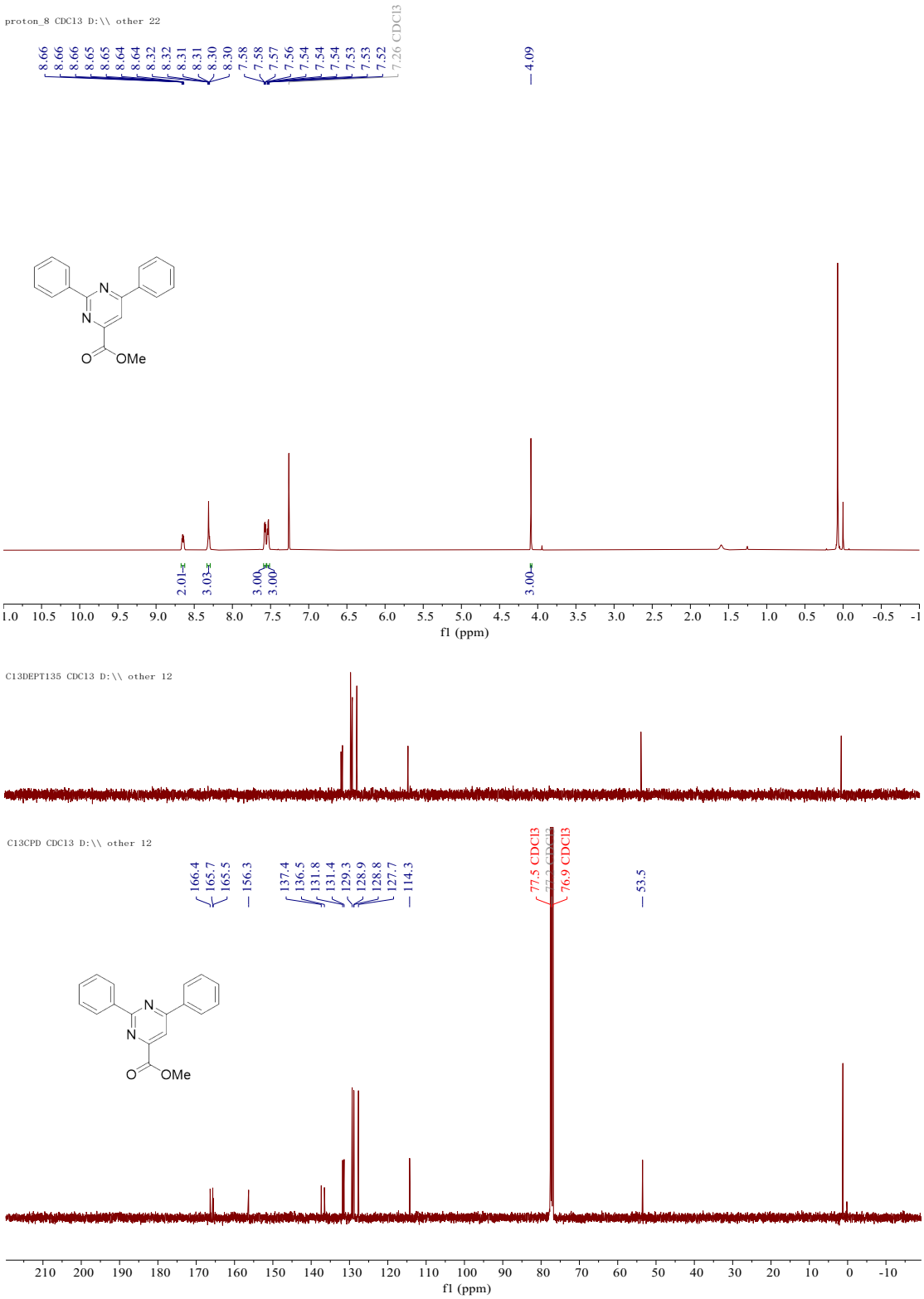


Figure S22 ^{1}H NMR and ^{13}C NMR spectrum of (**4t**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4u**

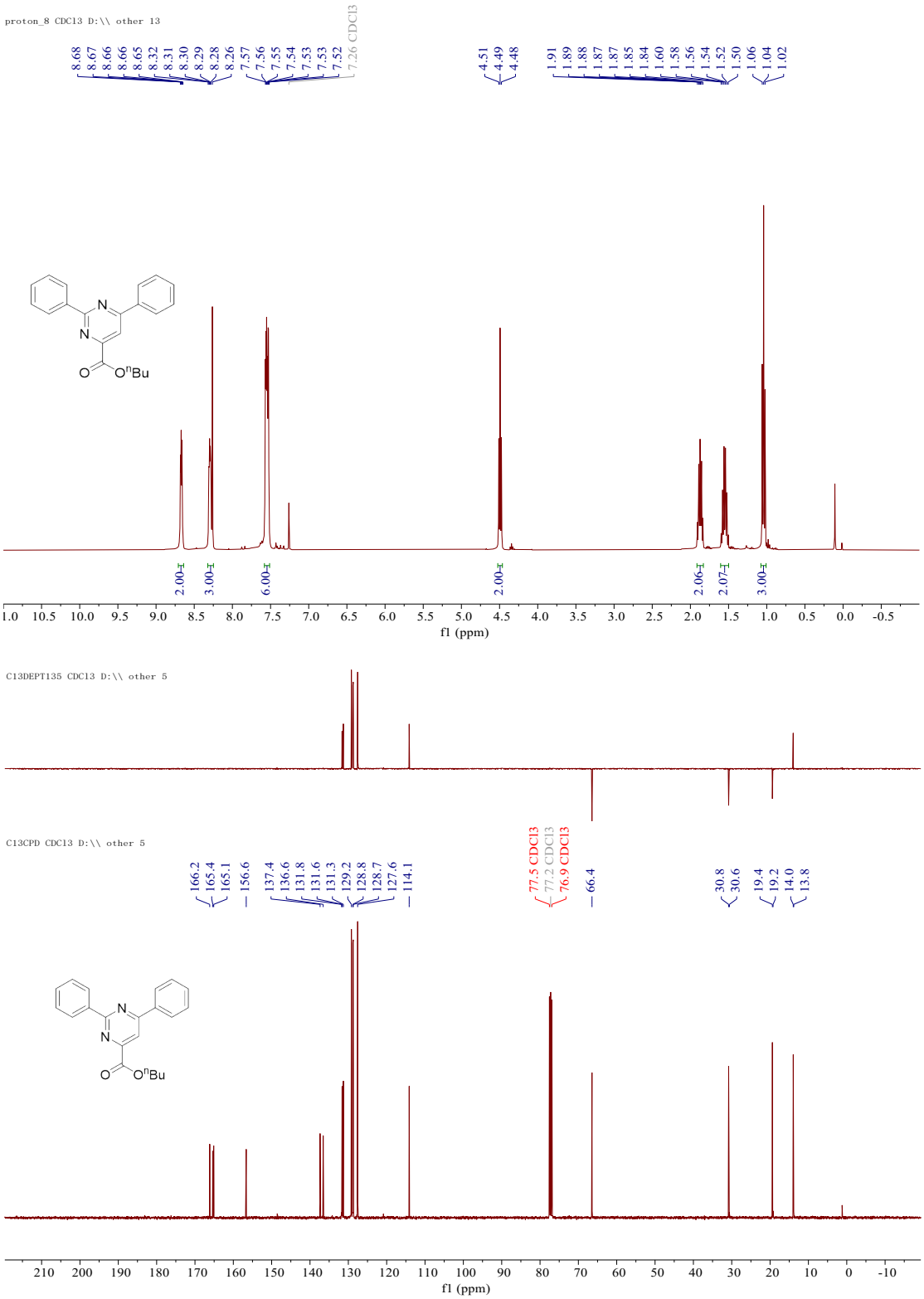


Figure S23 ^{1}H NMR and ^{13}C NMR spectrum of (**4u**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4v**

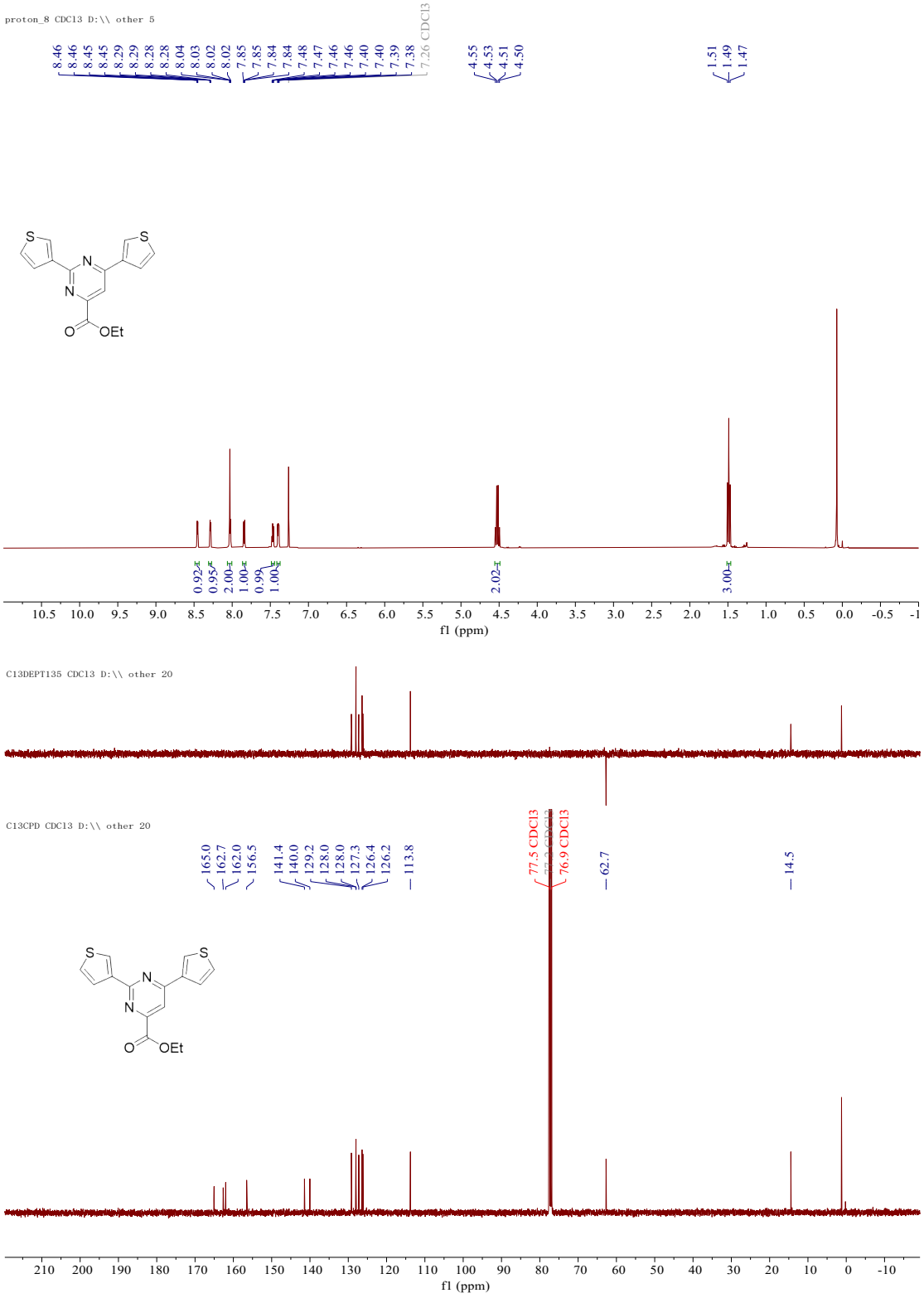


Figure S24 ^{1}H NMR and ^{13}C NMR spectrum of (**4v**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4w**

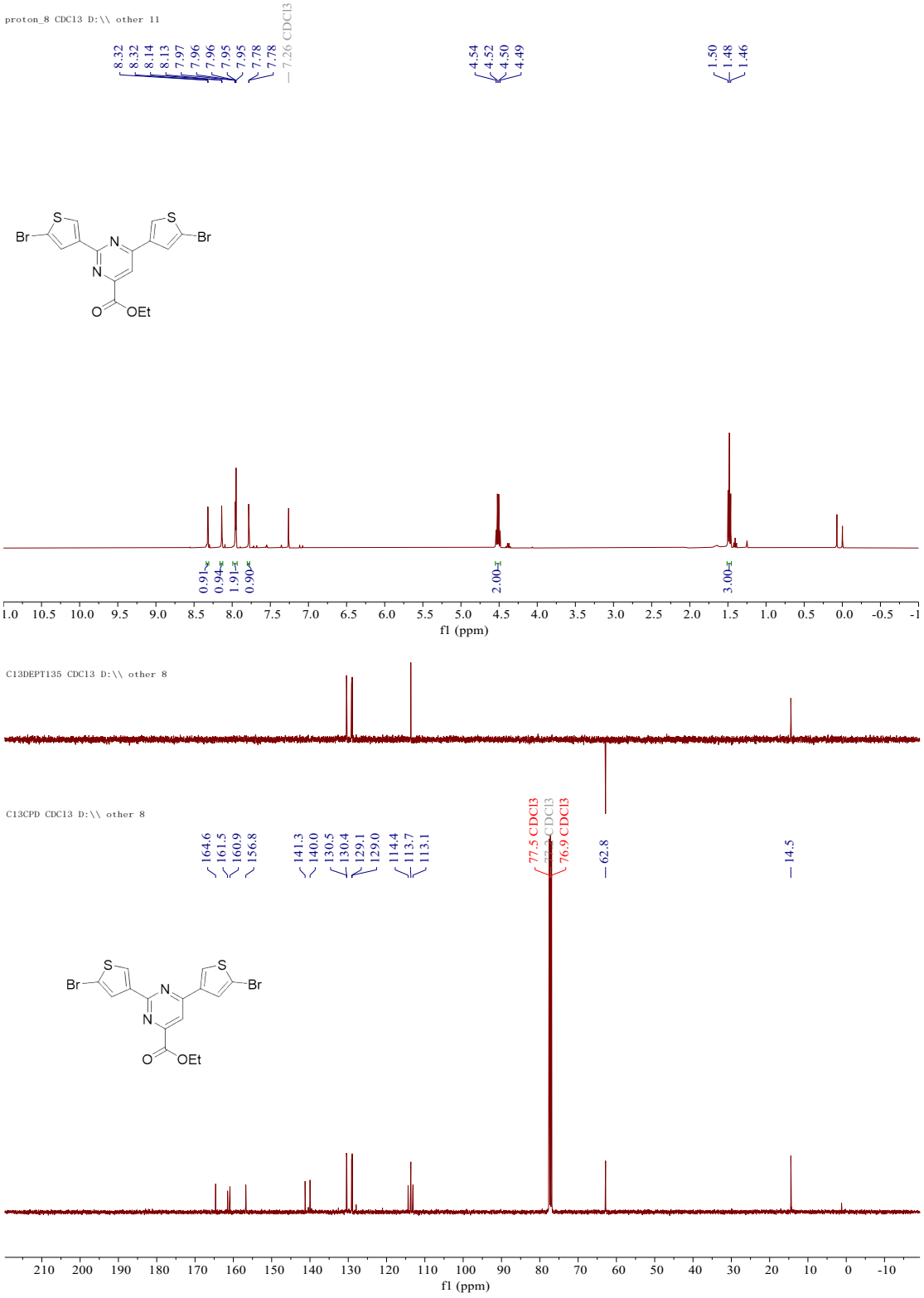


Figure S25 ^{1}H NMR and ^{13}C NMR spectrum of (**4w**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4x**

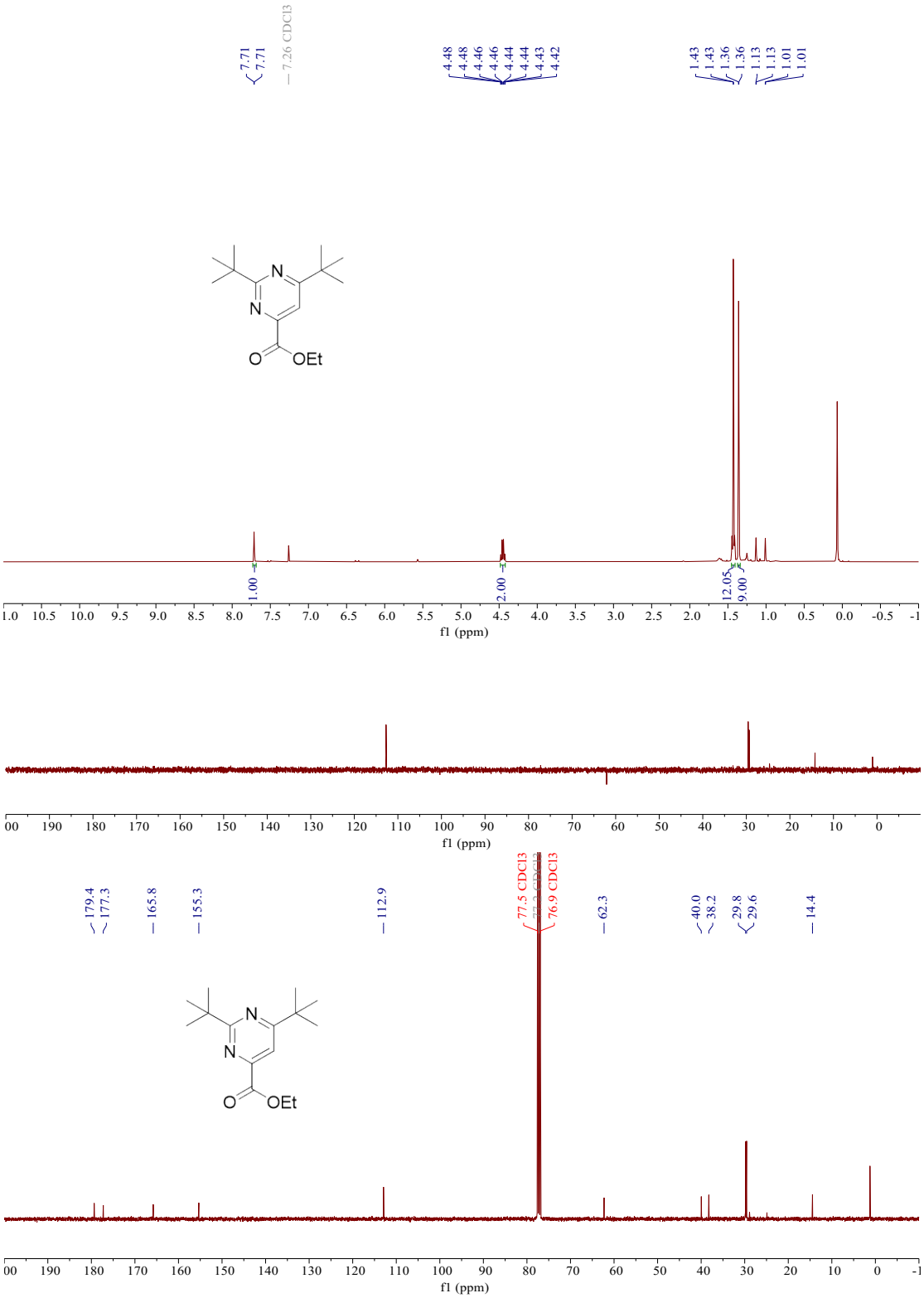


Figure S26 ^{1}H NMR and ^{13}C NMR spectrum of (**4x**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4y**

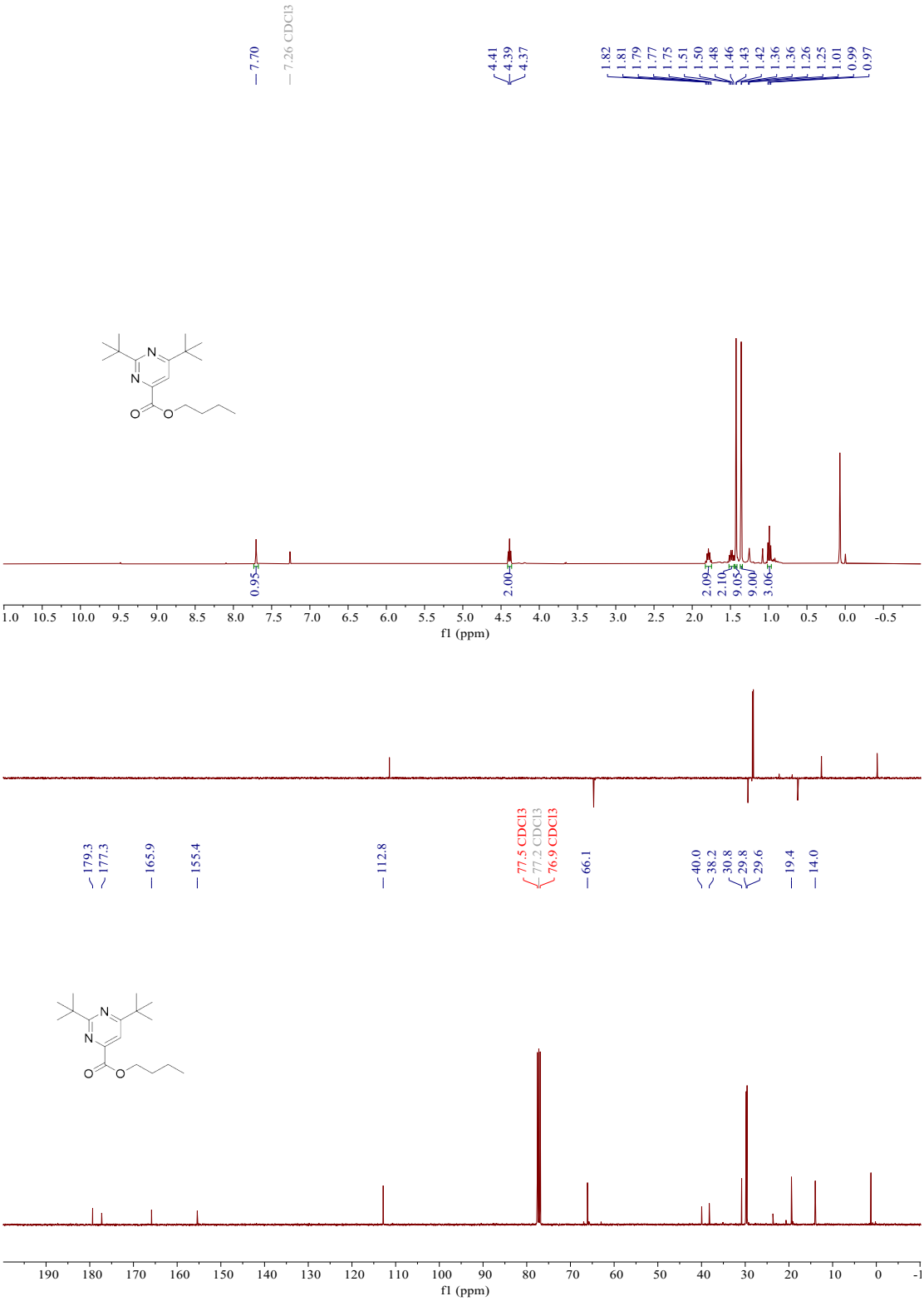


Figure S27 ^{1}H NMR and ^{13}C NMR spectrum of (**4y**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4aa**

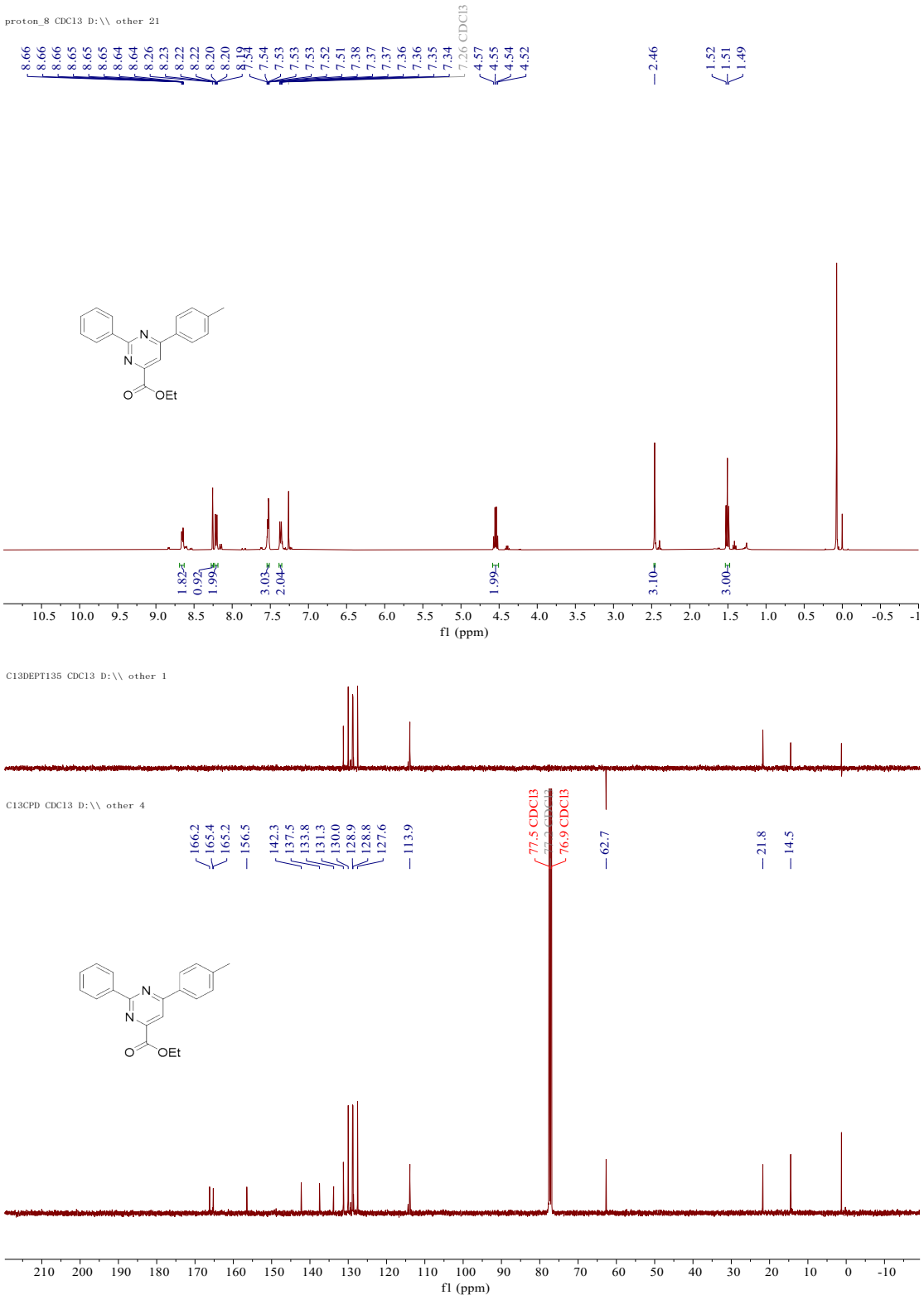


Figure S28 ^{1}H NMR and ^{13}C NMR spectrum of (**4aa**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4ab**

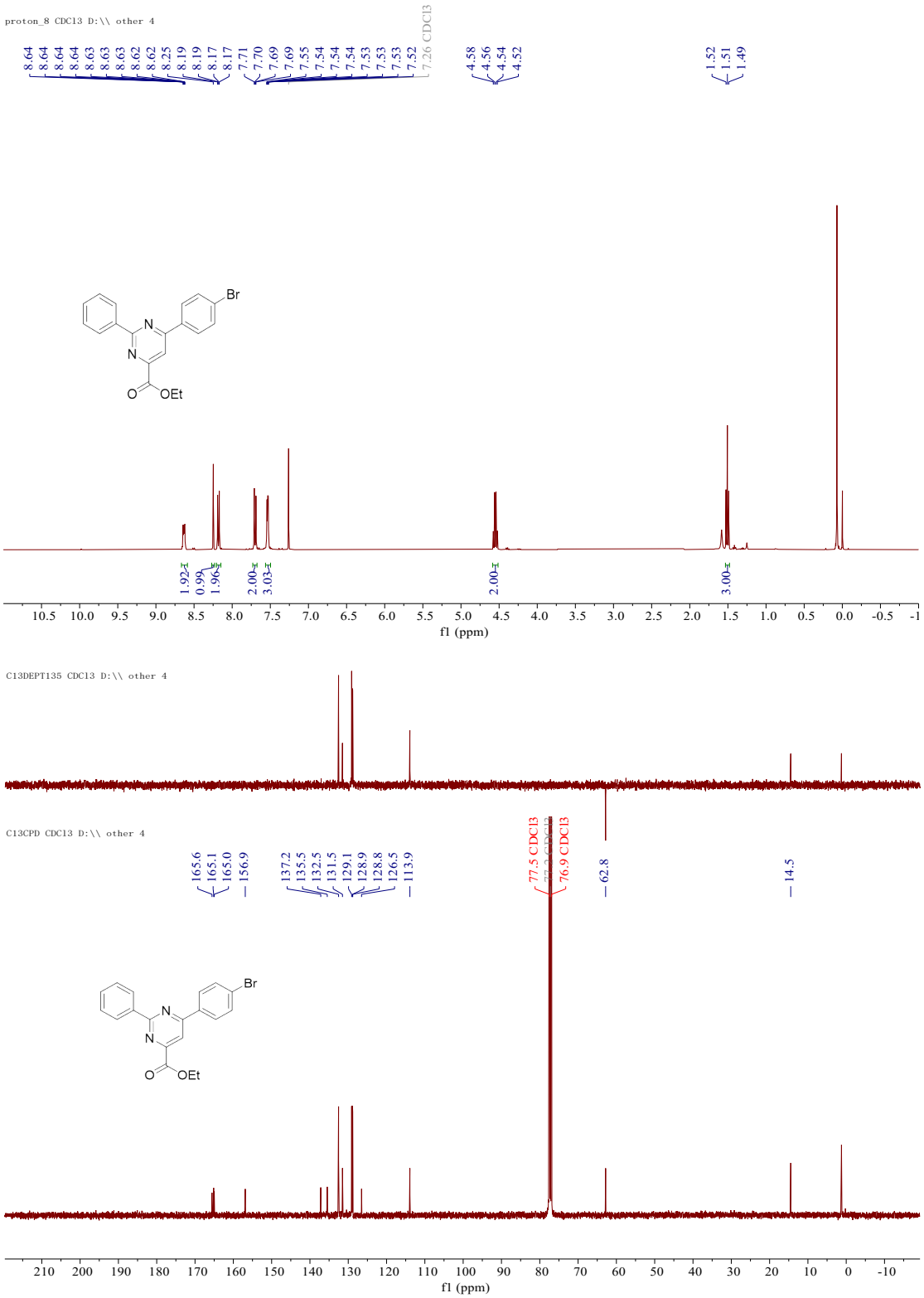


Figure S29 ^{1}H NMR and ^{13}C NMR spectrum of (**4ab**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4ac**

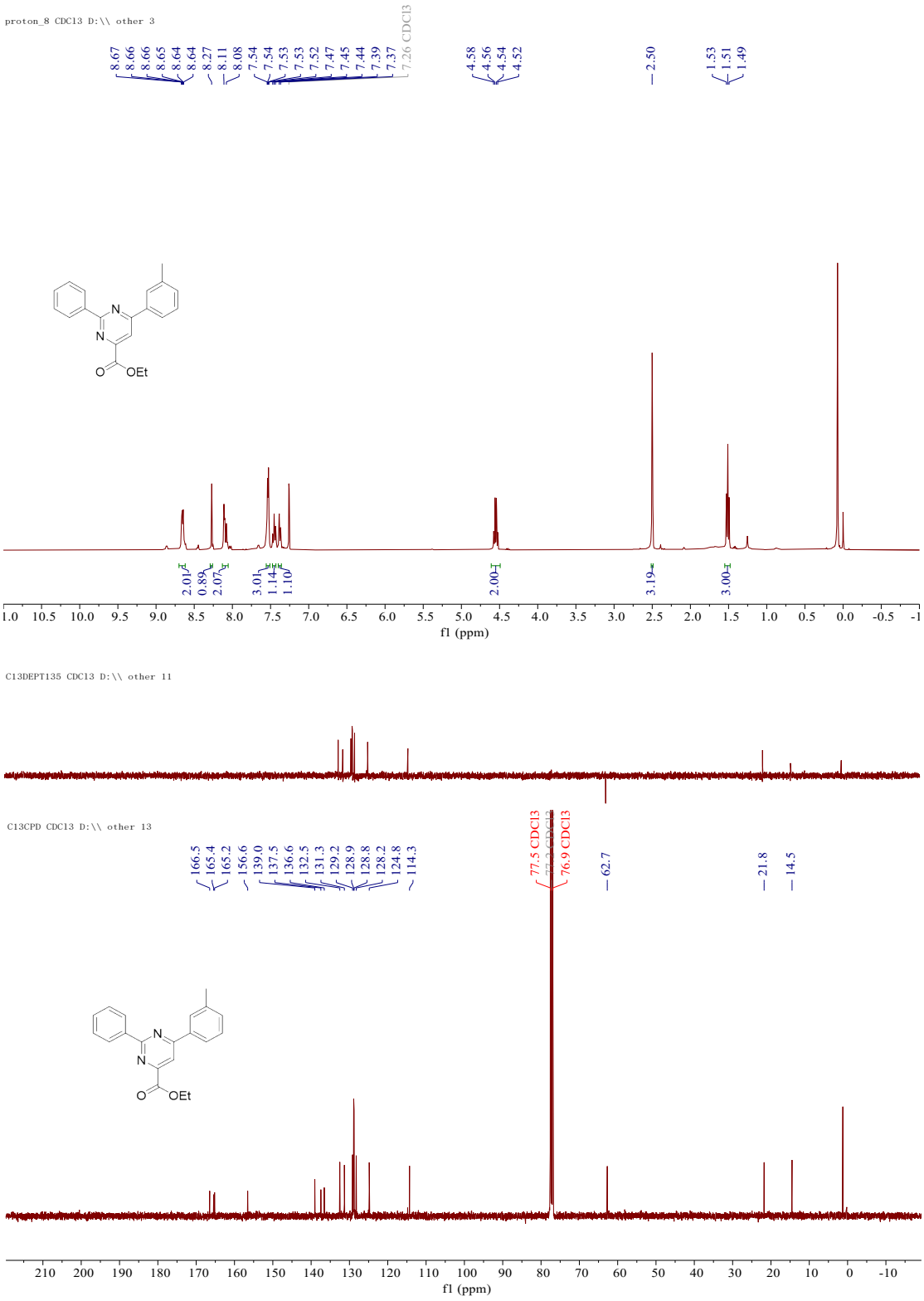


Figure S30 ^{1}H NMR and ^{13}C NMR spectrum of (**4ac**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4ad**

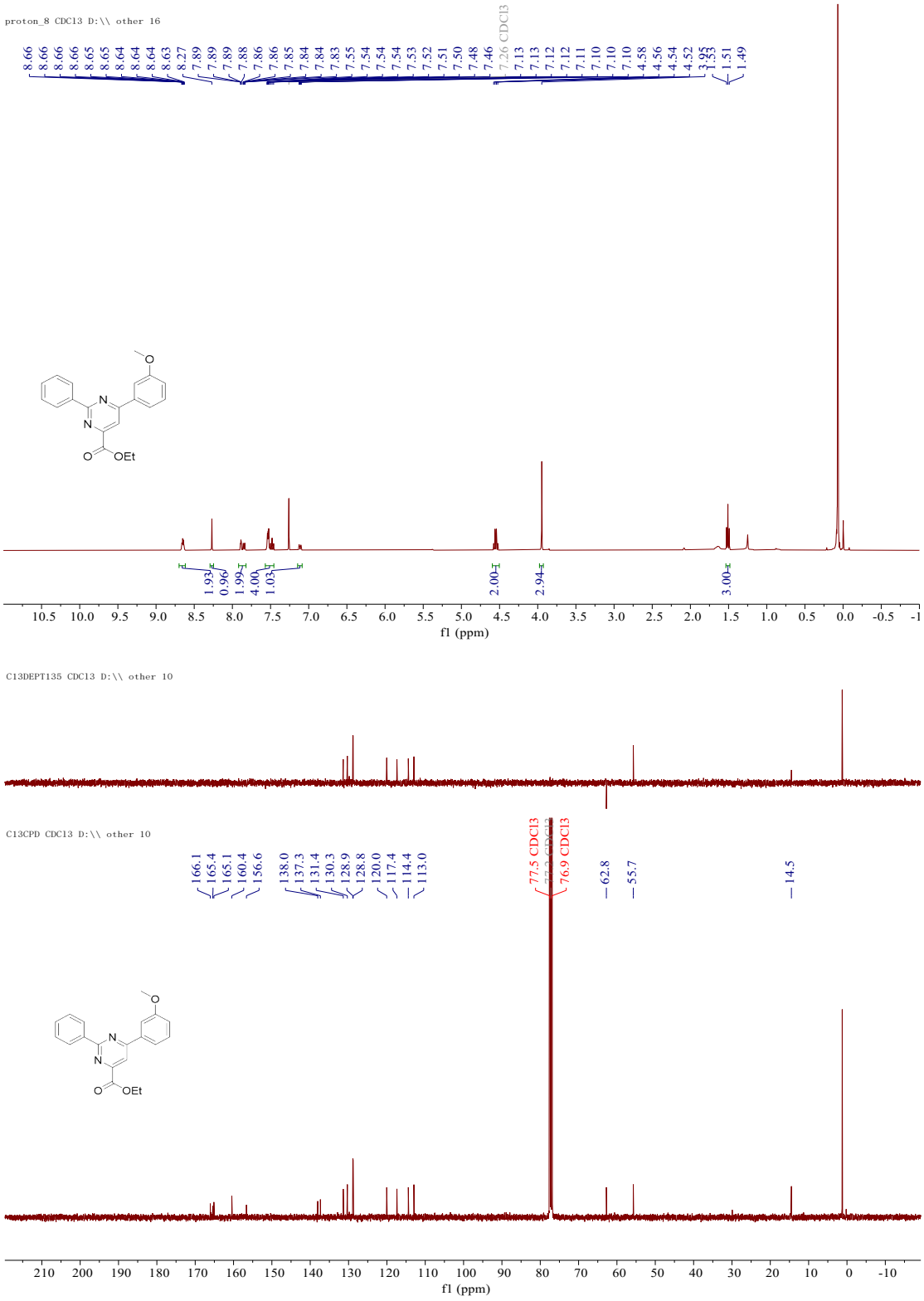


Figure S31 ^{1}H NMR and ^{13}C NMR spectrum of (**4ad**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4ae**

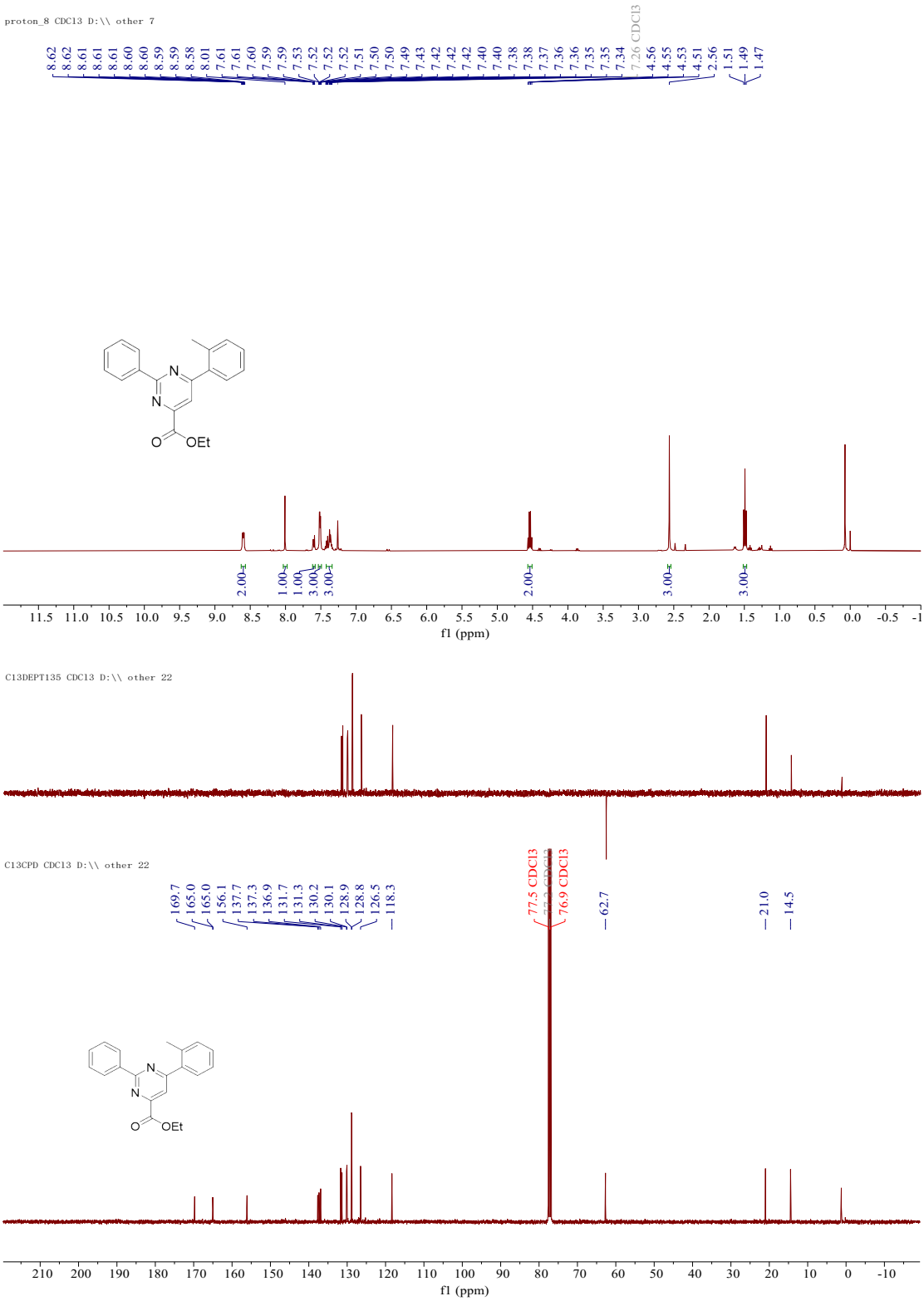


Figure S32 ^{1}H NMR and ^{13}C NMR spectrum of (**4ae**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4af**

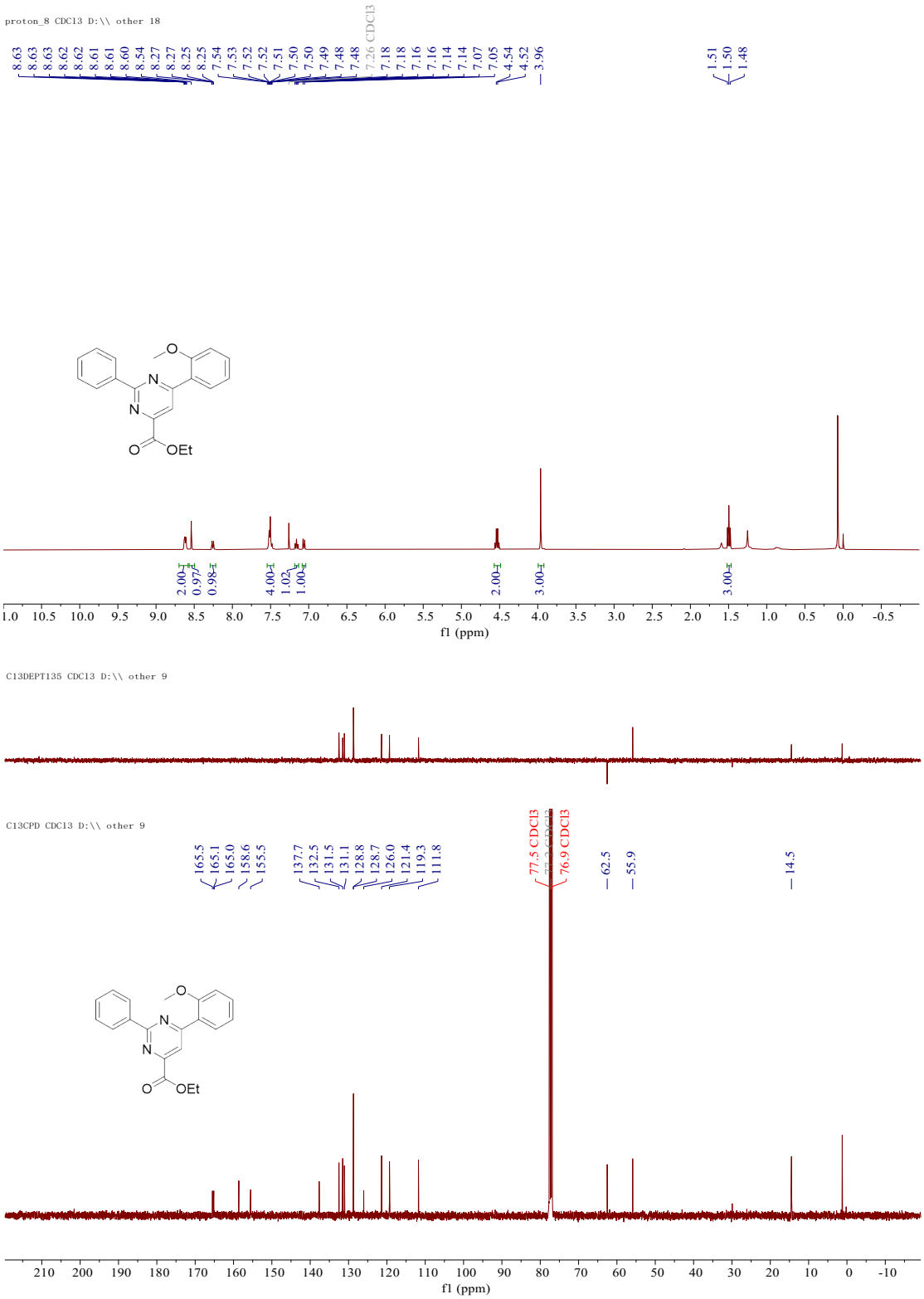


Figure S33 ^{1}H NMR and ^{13}C NMR spectrum of (**4af**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **4ag**

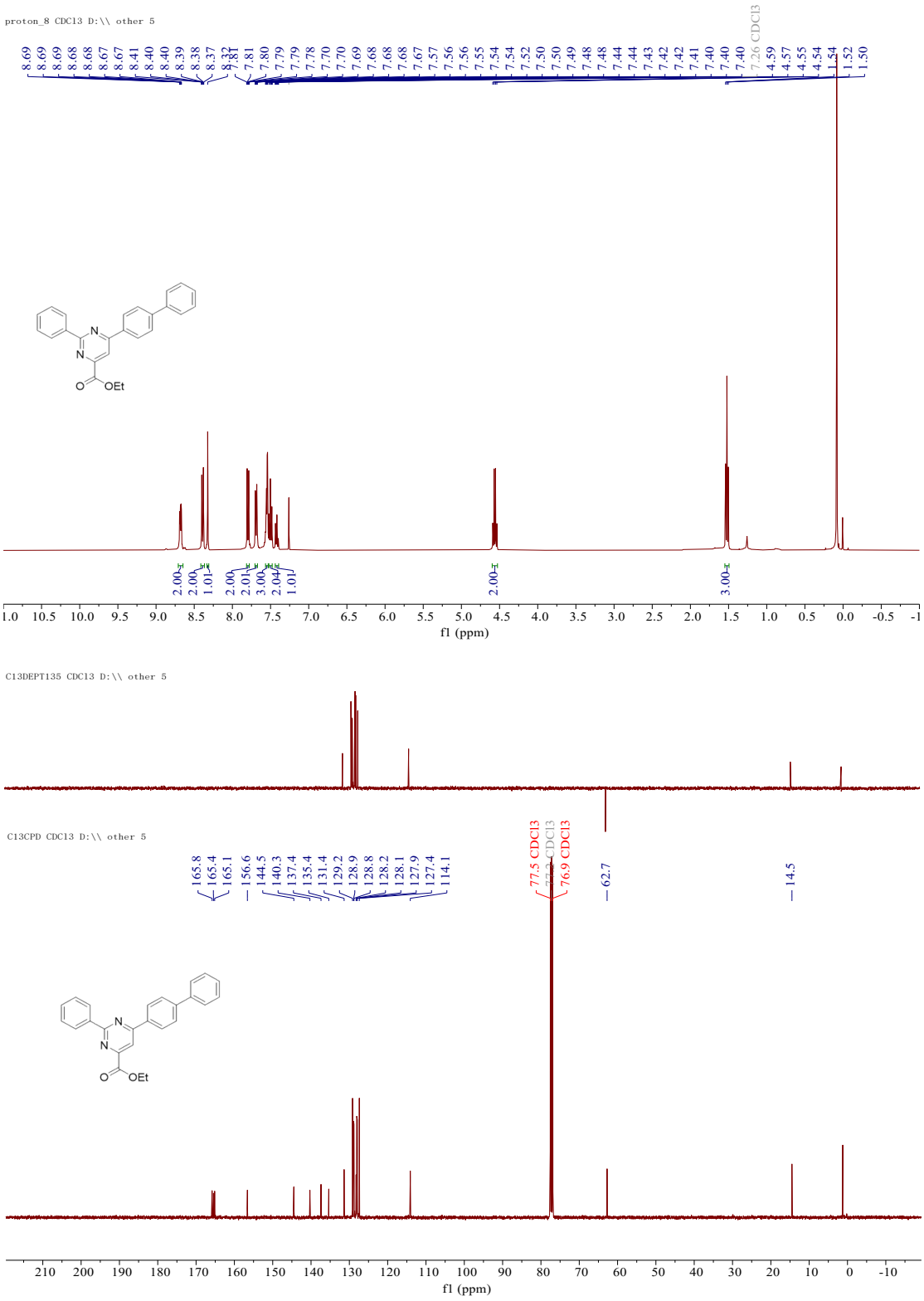


Figure S34 ^{1}H NMR and ^{13}C NMR spectrum of (**4ag**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **5aa**

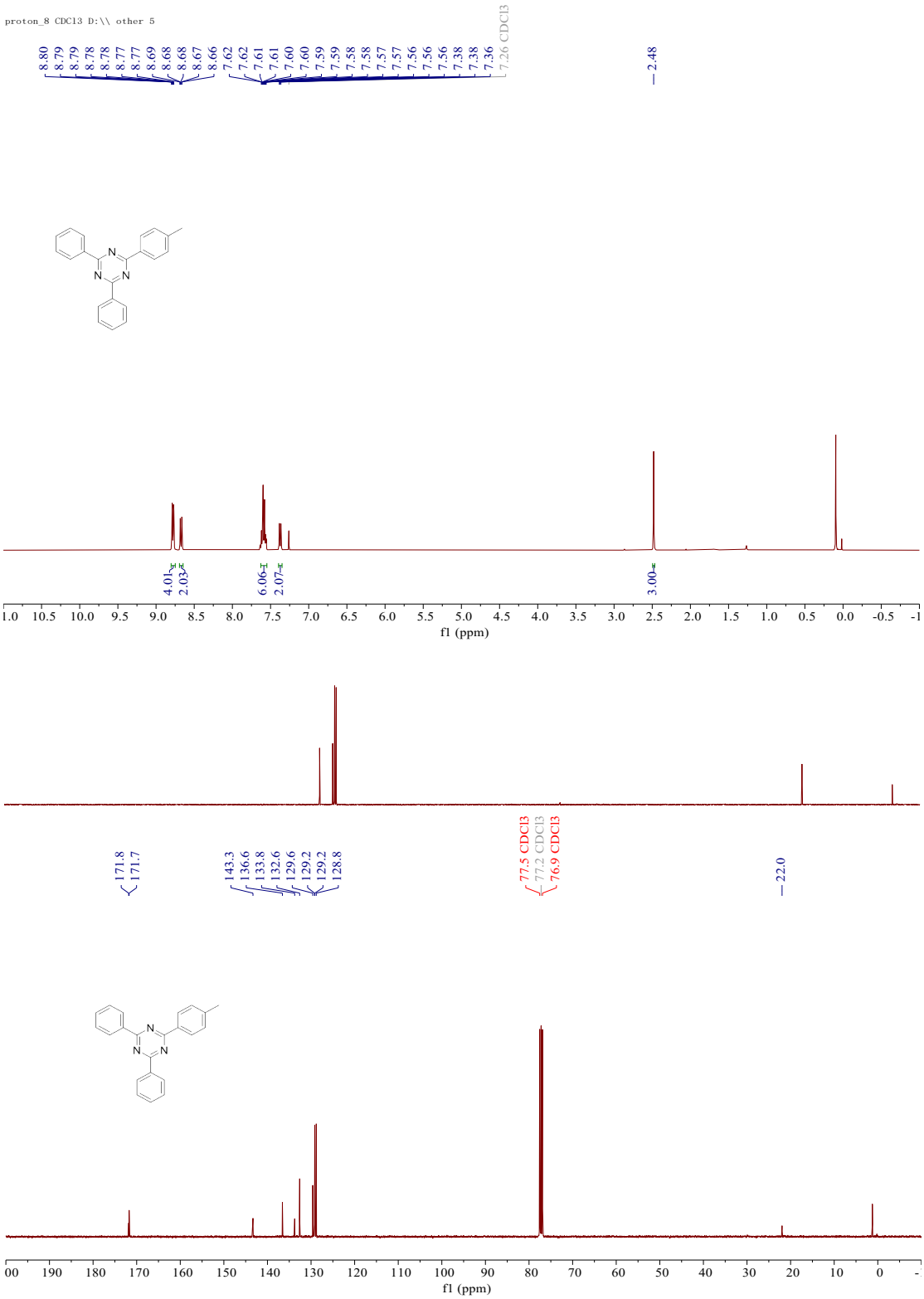


Figure S35 ^{1}H NMR and ^{13}C NMR spectrum of (**5aa**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **5ab**

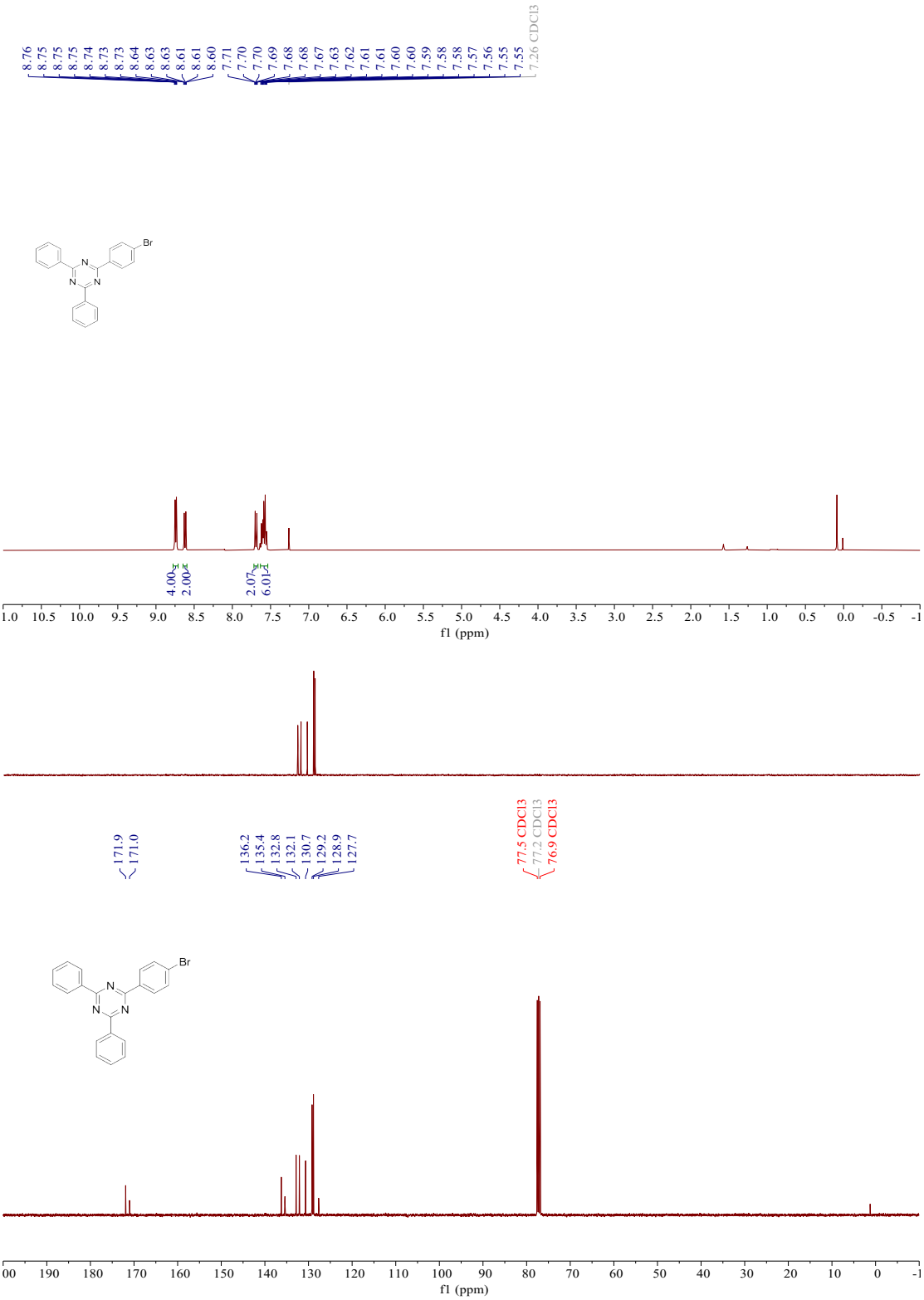


Figure S36 ^{1}H NMR and ^{13}C NMR spectrum of (**5ab**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **5ac**

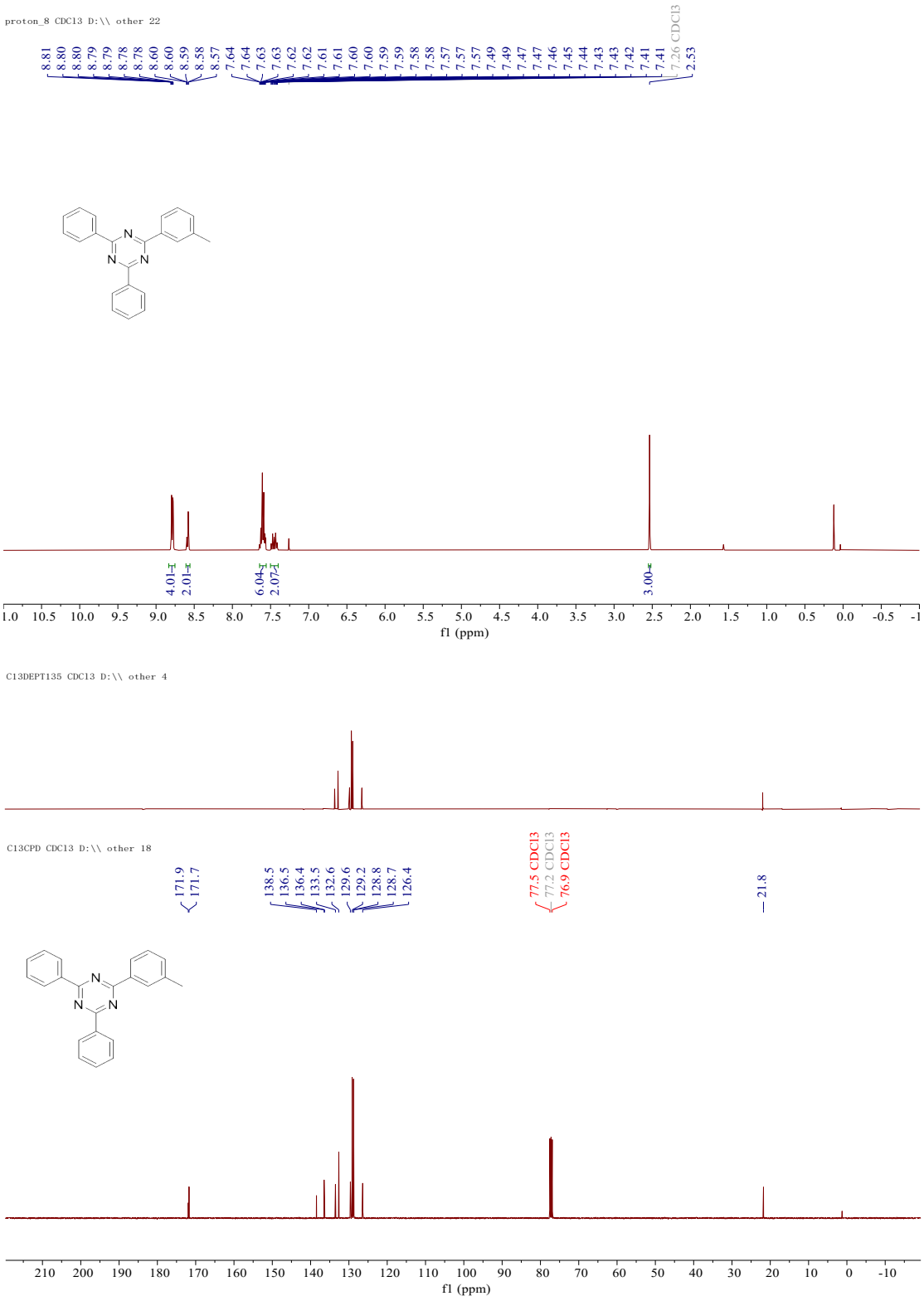


Figure S37 ^{1}H NMR and ^{13}C NMR spectrum of (**5ac**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **5ad**

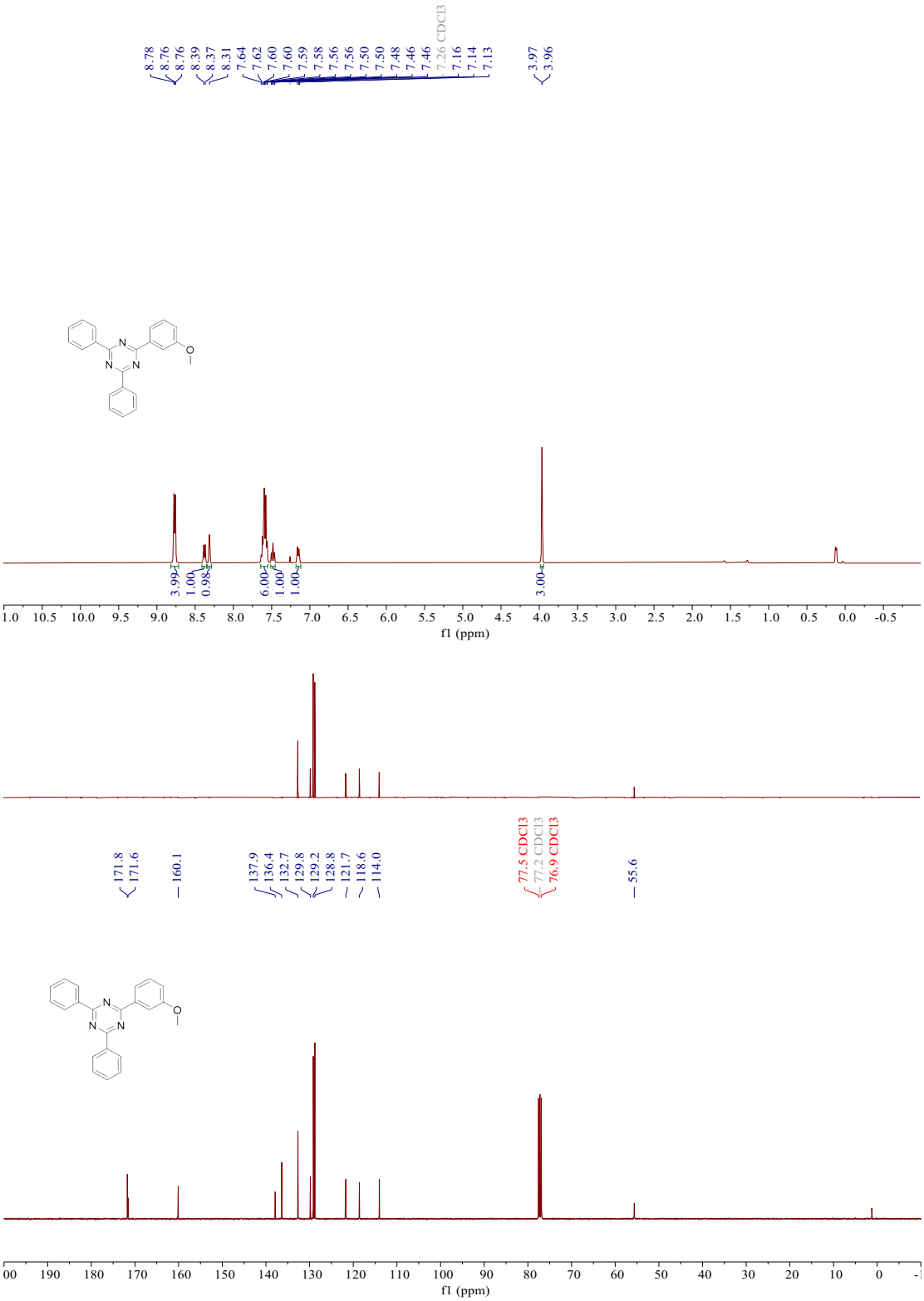


Figure S38 ^{1}H NMR and ^{13}C NMR spectrum of (**5ad**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **5ae**

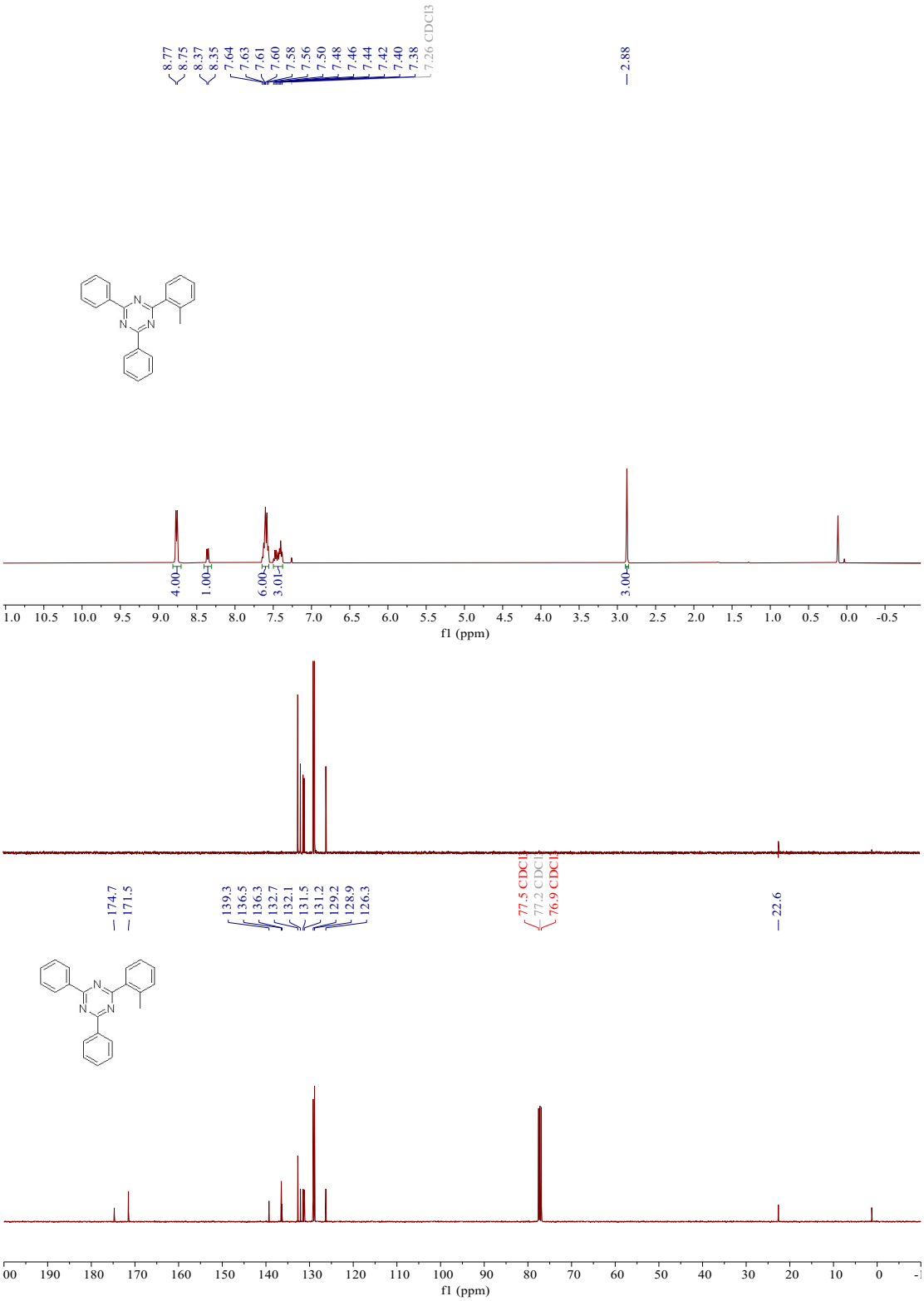


Figure S39 ^{1}H NMR and ^{13}C NMR spectrum of (**5ae**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **5af**

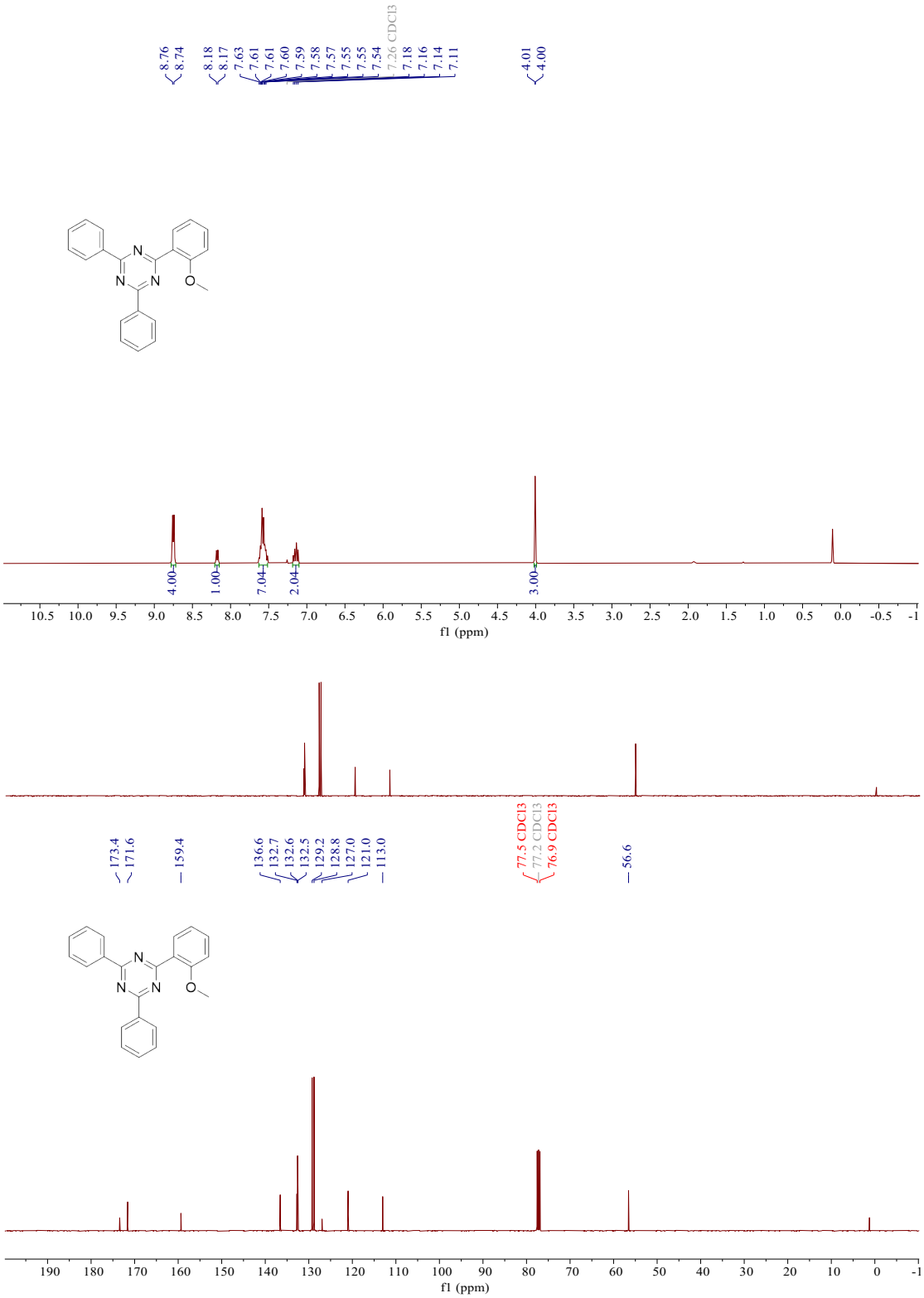


Figure S40 ^{1}H NMR and ^{13}C NMR spectrum of (**5af**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **5ag**

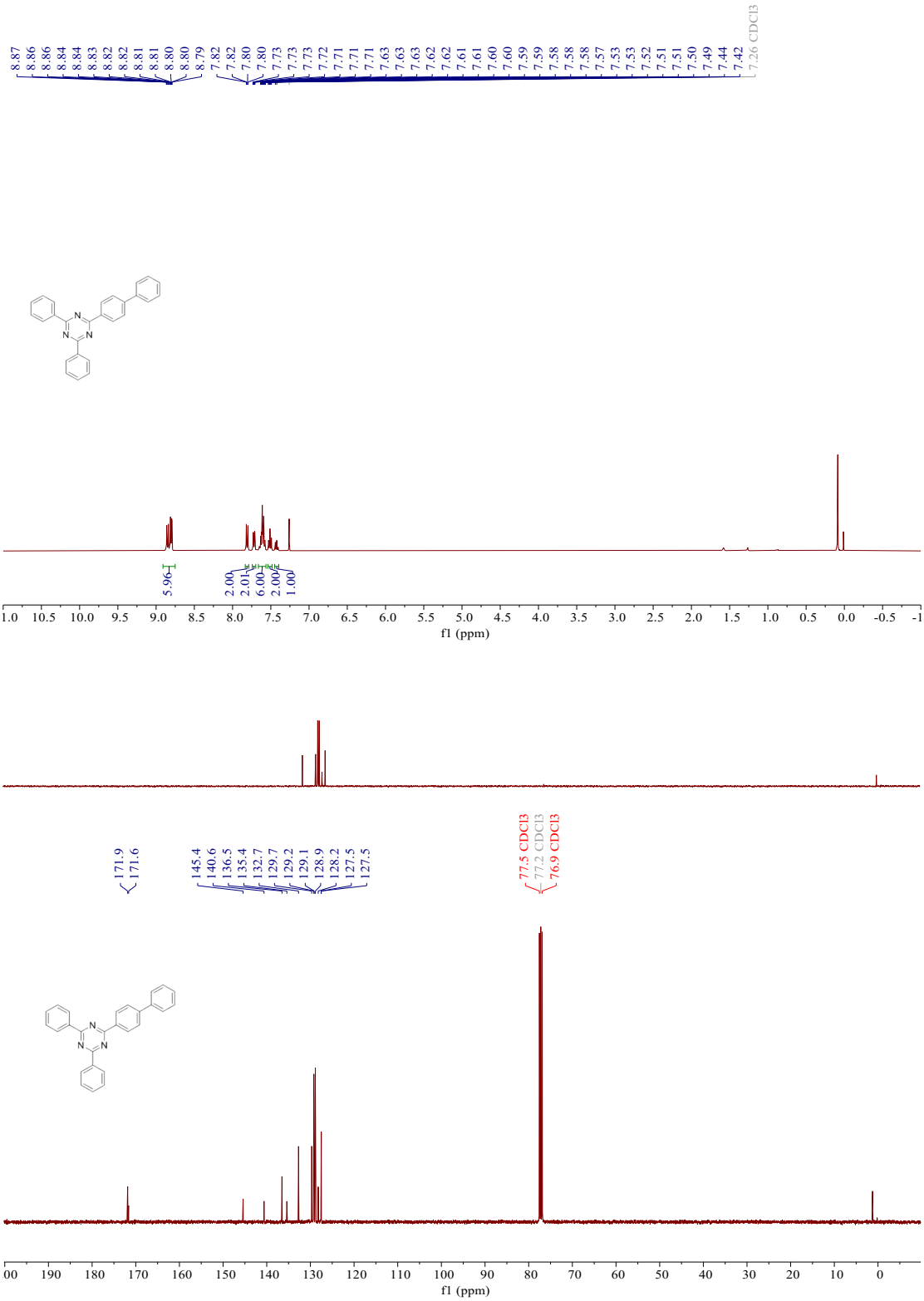


Figure S41 ^{1}H NMR and ^{13}C NMR spectrum of (**5ag**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **6a**

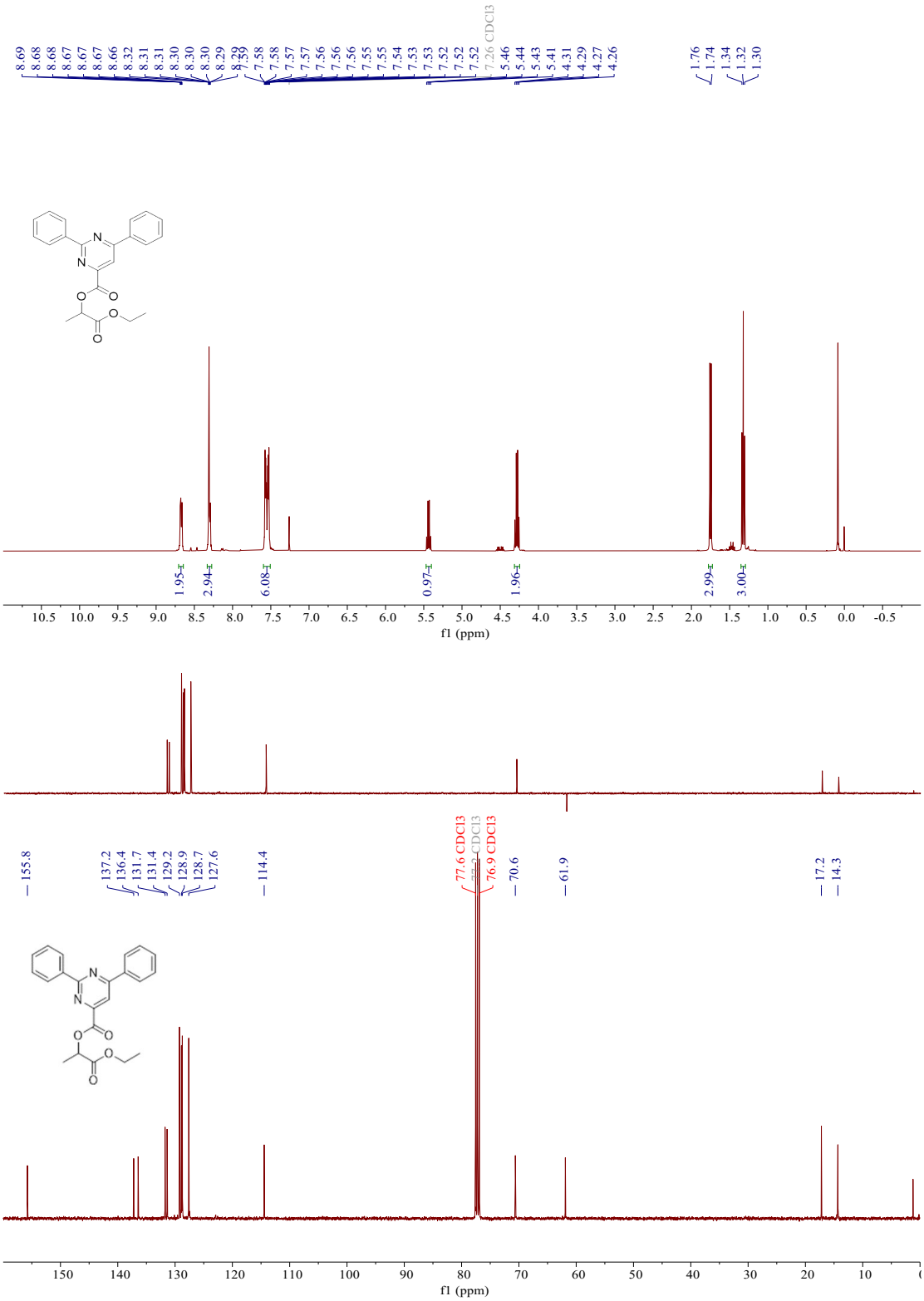


Figure S42 ^{1}H NMR and ^{13}C NMR spectrum of (**6a**) in $CDCl_3$.

^{1}H NMR and ^{13}C NMR of **6b**

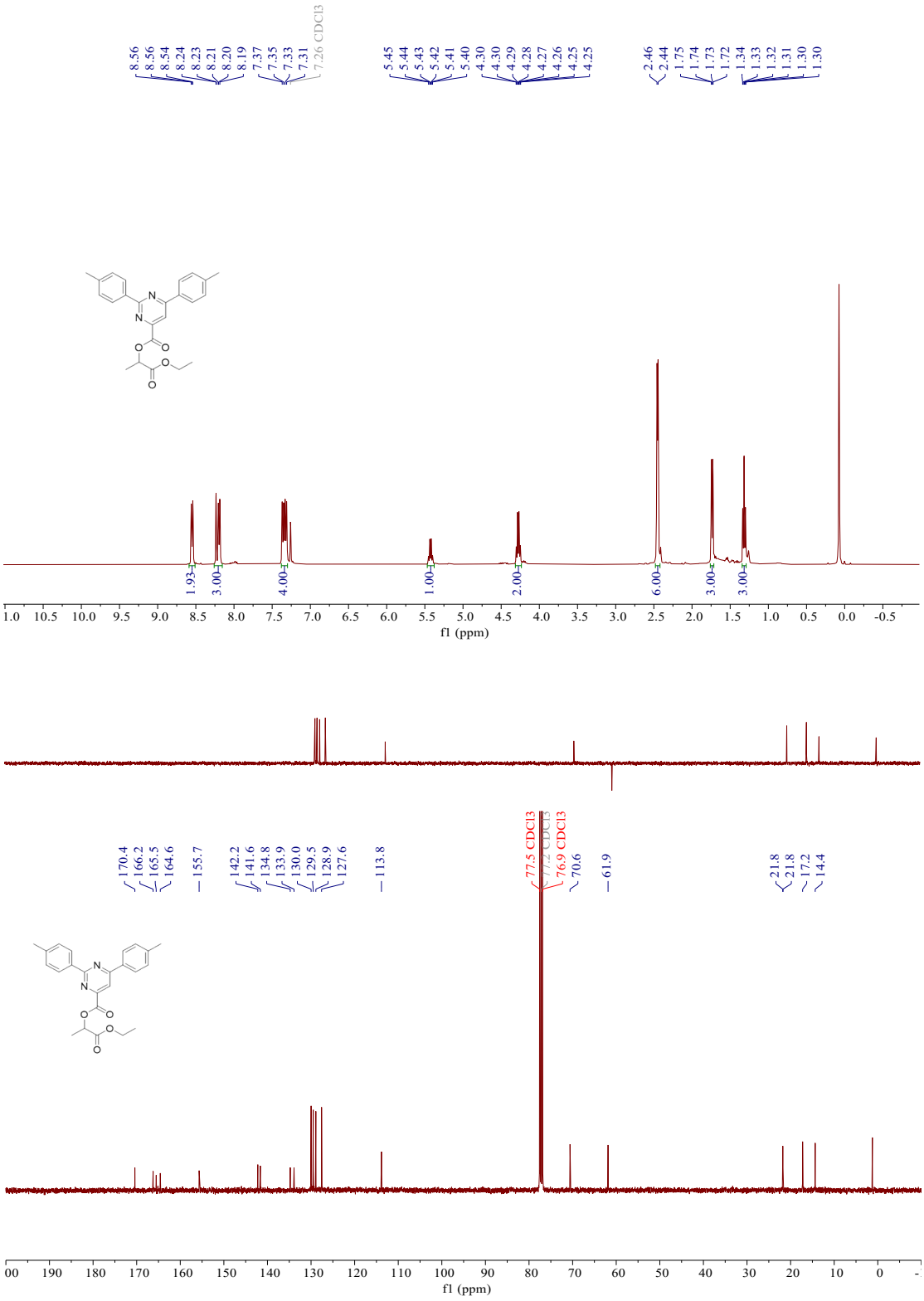
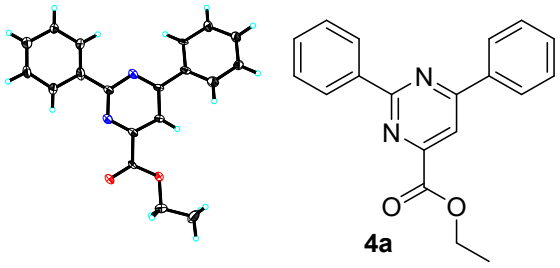


Figure S43 ^{1}H NMR and ^{13}C NMR spectrum of (**6b**) in $CDCl_3$.

9. X-ray Structure and Data of 4a

Sample preparation: In a 10.0 mL glass bottle, 15.0 mg of pure **4a** was completely dissolved in the mixed solvent of 3.0 mL EA, and then 2.0 mL of PE was added slowly. Several days later, the crystal was grown at room temperature.

A suitable crystal was selected on a BRUKER D8 QUEST diffractometer. The crystal was kept at 150(2) K during data collection.



4a

CCDC **2307938**

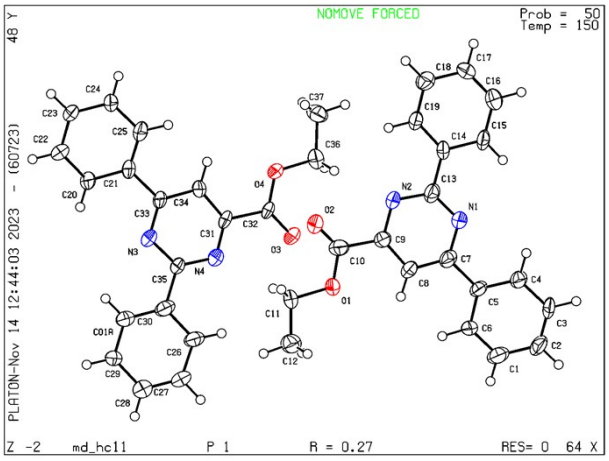


Figure S44 Displacement ellipsoids are drawn at the 30% probability level.

Crystal data and structure refinement for **4a** (CCDC: **2307938**)

Table S2 Crystal data and structure refinement for **4a**.

Identification code	global
Empirical formula	$C_{19}H_{16}N_2O_2$
Formula weight	304.34
Temperature	150(2) K
Wavelength	1.54178 Å

Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 7.3522(7) Å	□= 103.317(3)°.
	b = 10.6585(10) Å	□= 104.368(4)°.
	c = 10.8591(10) Å	□ = 104.813(3)°.
Volume	756.72(12) $Å^3$	
Z	2	
Density (calculated)	1.336 Mg/m^3	
Absorption coefficient	0.706 mm^{-1}	
F(000)	320	
Crystal size	0.680 x 0.440 x 0.200 mm^3	
Theta range for data collection	4.52 to 73.92°.	
Index ranges	-8<=h<=9, -13<=k<=13, -13<=l<=13	
Reflections collected	14697	
Independent reflections	4658 [R(int) = 0.0770]	
Completeness to theta = 73.92°	91.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.87 and 0.26	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4658 / 3 / 418	
Goodness-of-fit on F^2	2.665	
Final R indices [I>2sigma(I)]	R1 = 0.2662, wR2 = 0.5610	
R indices (all data)	R1 = 0.2791, wR2 = 0.5743	
Absolute structure parameter	0.2(6)	
Largest diff. peak and hole	0.854 and -0.869 e.$Å^{-3}$	

10. HRMS of intermediate 5, 7, 8, 9, 12, 13, and 14

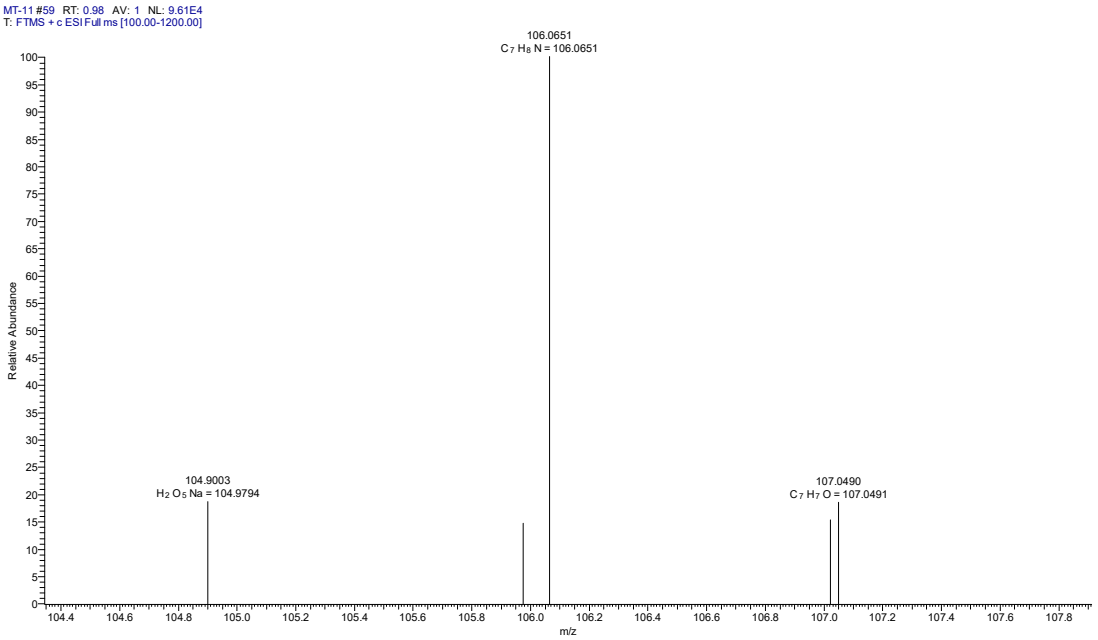


Figure S45 HRMS of intermediate **5**

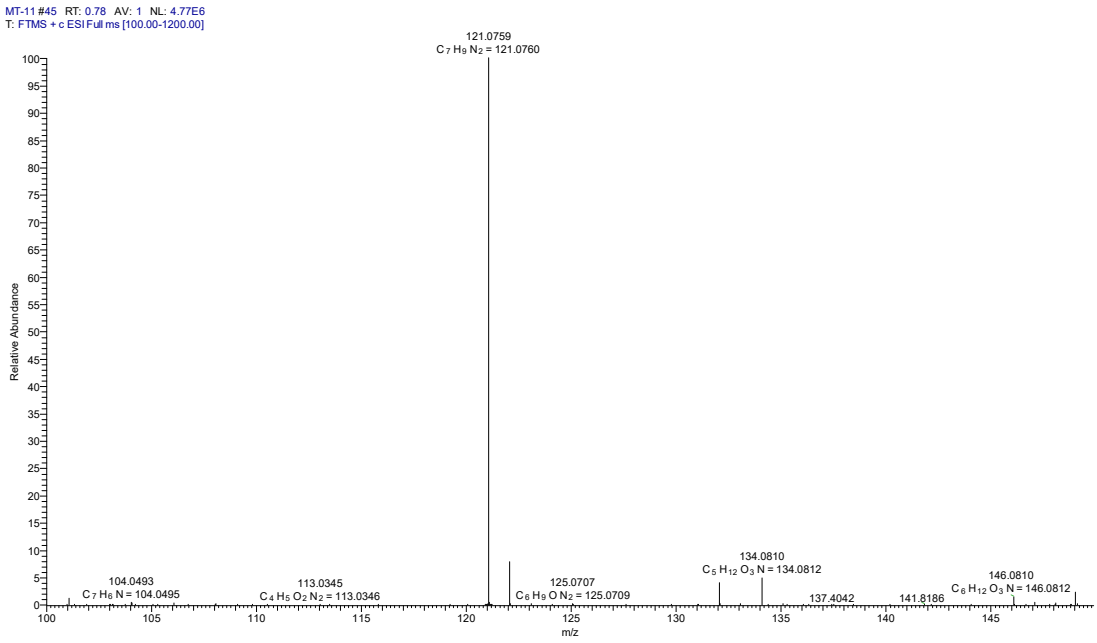


Figure S46 HRMS of intermediate **7**

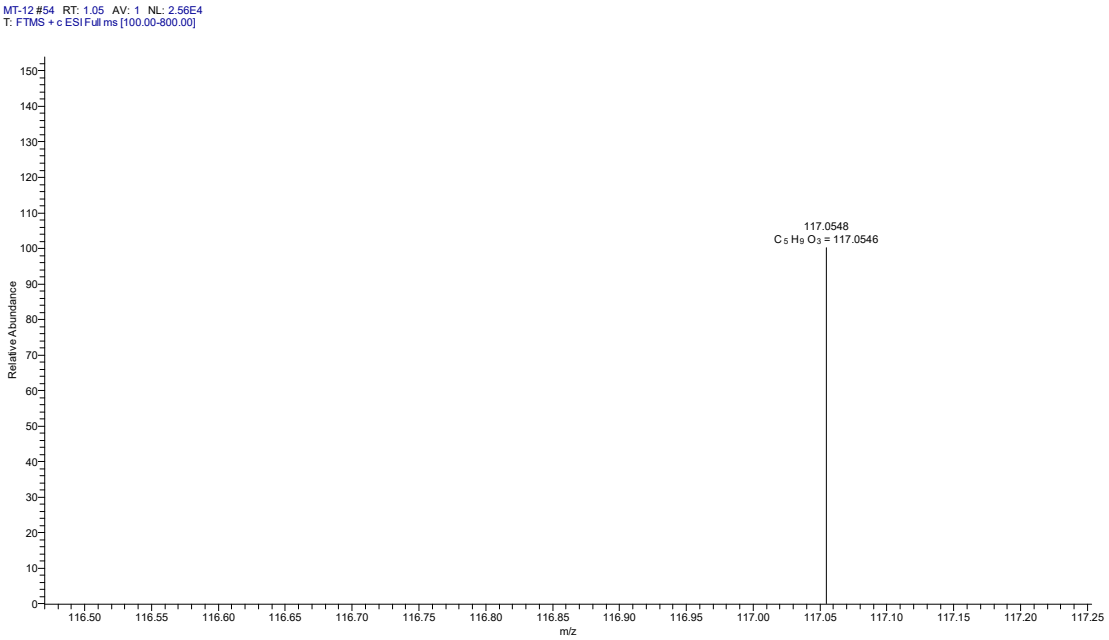


Figure S47 HRMS of intermediate **8**

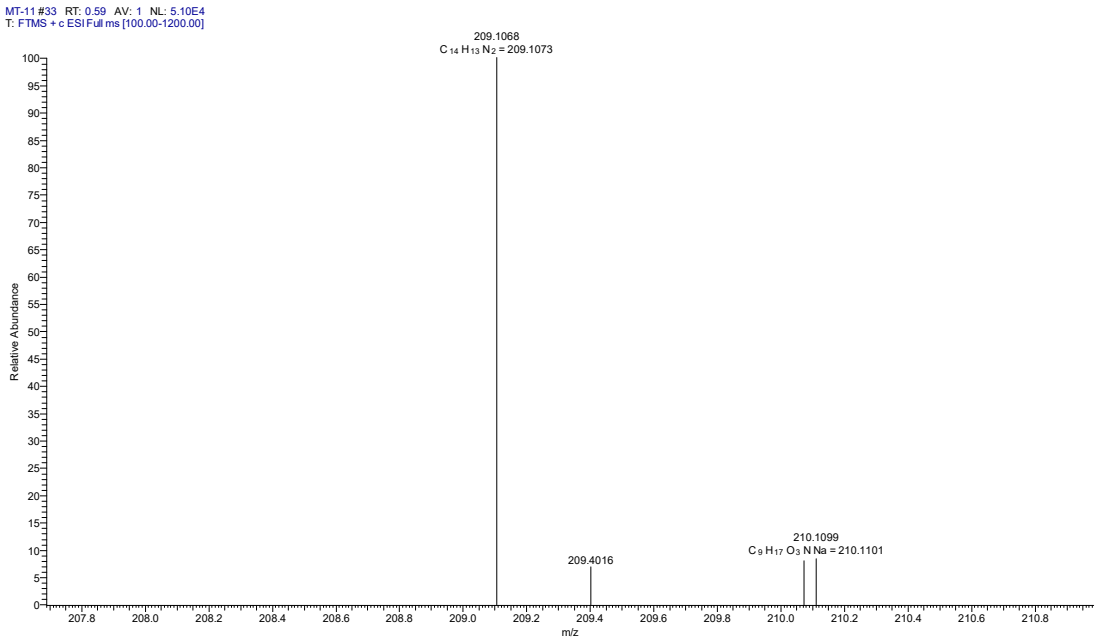


Figure S48 HRMS of intermediate **9**

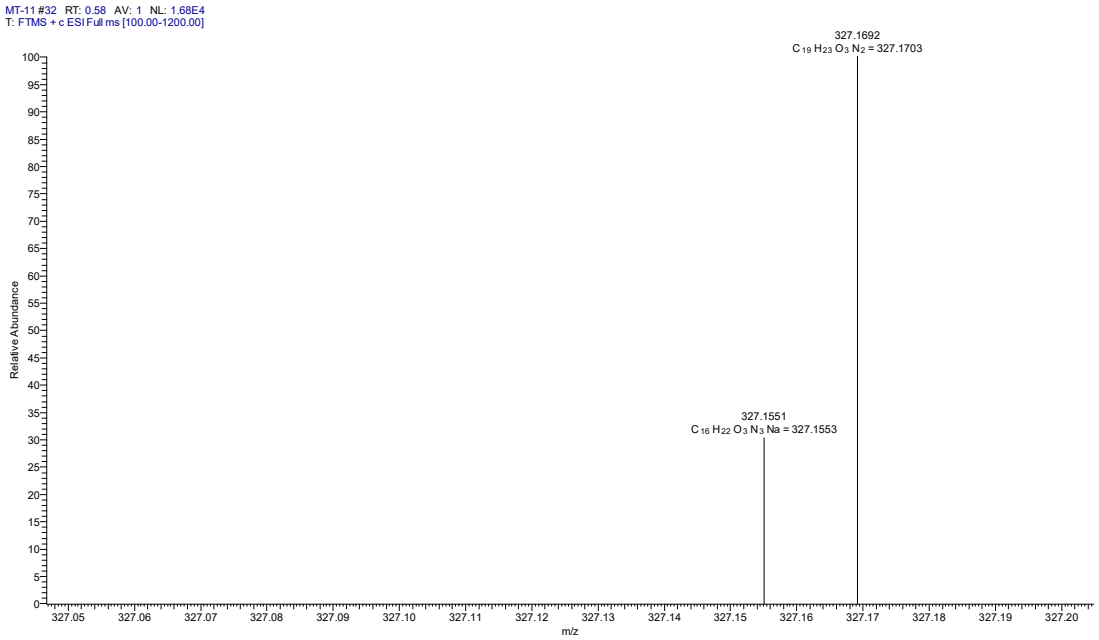


Figure S49 HRMS of intermediate **12**

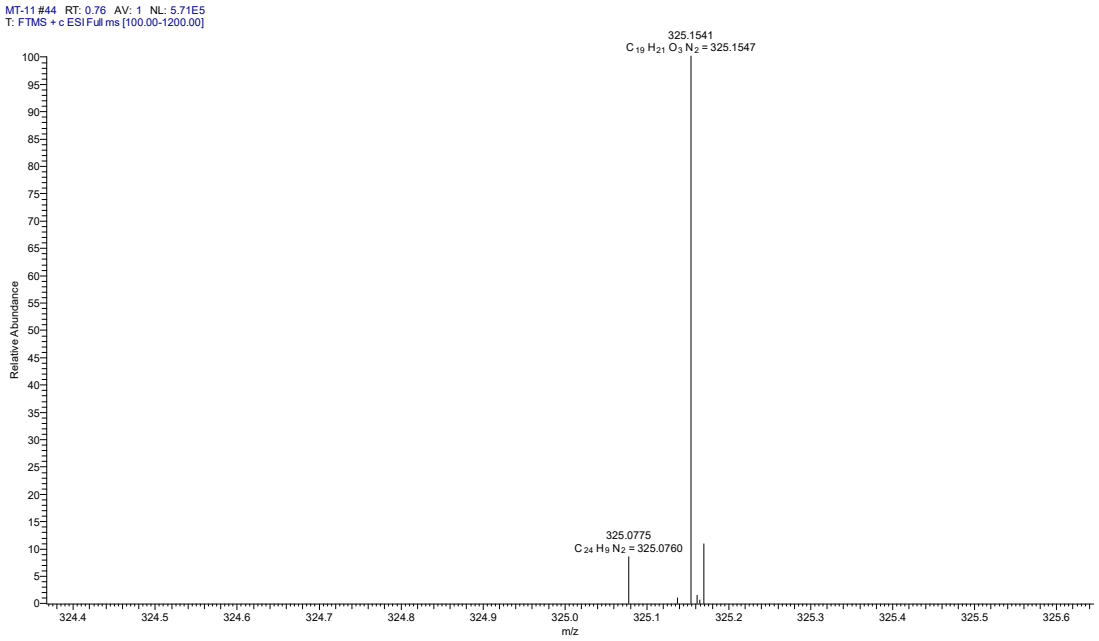


Figure S50 HRMS of intermediate **13**

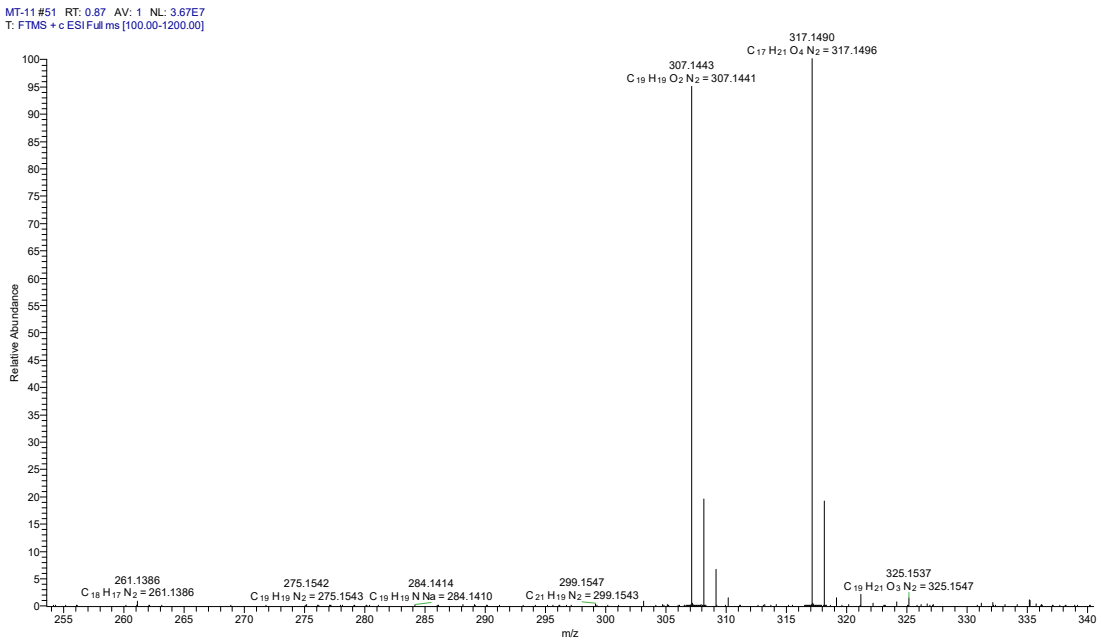


Figure S51 HRMS of intermediate **14**

11. Green chemistry metrics analysis

1). Comparing chemistries by a single factor

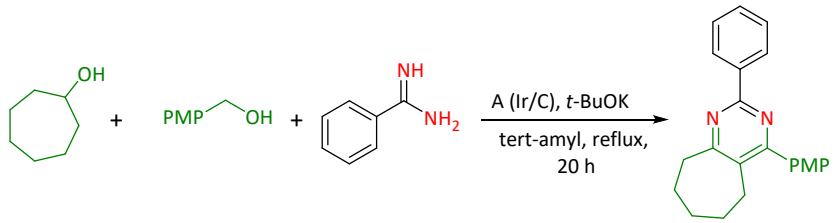
The following formulae were used for calculating Process Mass Intensity (PMI), and E-factor.

$$\textbf{PMI} = \frac{\textbf{Total mass of input material in the whole process}}{\textbf{Mass of product}}$$

E-Factor = PMI–1

In previous reports, Processes I and III involved the preparation of more complex catalysts, hence the values of mass intensity (PMI) and E-factor were greater than those of IV and V. The values of PMI and E-factor for Processes I and III are shown in the table S3 below.

Previous report, Process I (biomass alcohol as raw material)[1]



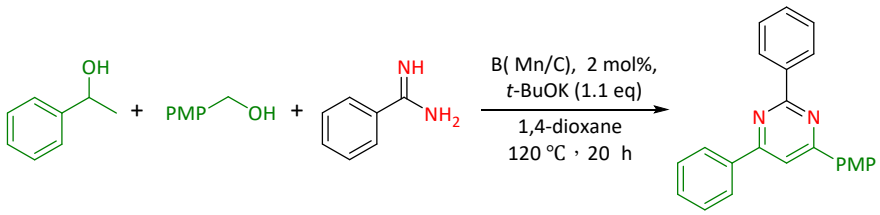
1 2 3 5a

Synthesis **A**: Step I, 6-(4-(Trifluoromethyl)phenyl)-1,3,5-triazine-2,4-diamine (30.0 mmol, 7.65 g) was dissolved in 200 mL THF and triethylamine (80.0 mmol, 11.0 mL) was added and the solution was cooled to 0 °C. Then chlorodiisopropylphosphine (60.0 mmol, 9.6 mL) was added drop wise with a syringe. The solution was allowed to warm to room temperature and stirred over night at 50 °C. The suspension was filtered over a glass filter frit with a pad of celite (4 cm) and washed with 50 mL of THF. The solvent was concentrated in vacuo, recrystallized in toluene yielding (4-(4CF_3)-Ph)Tr(NHP(iPr)$_2$)$_2$ as colorless crystals (13.6 g = 27.9 mmol = 93 %). Step II, [IrOMe(cod)]$_2$ (2.0 mmol, 1.32 g) was dissolved in 40 mL THF and subsequently a solution of (4-(4-CF_3)Ph)Tr(NHP(iPr)$_2$)$_2$ (4.0 mmol, 1.95 g) dissolved in THF was added drop wise. A red solution was obtained. The solution was stirred over night at 50 °C. The solvent was removed in vacuo, yielding a deep red solid in quantitative yield.

Under dry N_2 atmosphere (glove box) an ovendried 50 mL Schlenk tube was charged with a magnetic stirring bar, cycloheptanol (20 mmol, 2.40 mL), 4methoxybenzyl alcohol (11 mmol 1.36 mL), benzamidine (10 mmol, 1.20 g), catalyst **A** (55 mg, 0.7 mmol, 0.7 mol%) and *tert*-amyl alcohol (20 mL). The tube was sealed, taken out of the glove box and a reflux condenser was attached under argon stream. A pressure equalizer (bubble counter) was connected to the top outlet of the condenser and the reaction mixture was heated to reflux for 24 h. Within few minutes of heating the color of the reaction mixture turned from red to yellow. After cooling, the reaction was quenched with water (20 mL) and extracted with ethyl acetate (3x 100 mL). The combined organic phase was dried over Na_2SO_4, concentrated by rotary evaporation, and subjected to column chromatography (column dimensions: height 23 cm, diameter 4 cm, packed with pentane). Gradient elution (pentane/diethyl ether, 25:1 → 20:1) gave the title compound **5a** (2.55 g, 7.72 mmol, 77%).

PMI (I) > PMI (V), E-Factor (I) > E-Factor (V)

Previous report, Process III (biomass alcohol as raw material)[2]



1a 2a 3a 4b

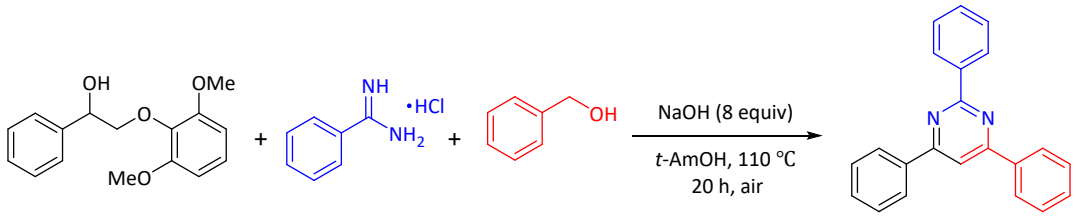
Synthesis **B**: Using a nitrogen-filled glove box, a schlenk tube was charged with a magnetic stirring bar and a suspension of PNP-Ligand (1 eq.) and bromopentacarbonylmanganese(I) (1 eq) in toluene. The tube was sealed, removed from the glove box and a reflux condenser was attached under argon stream. The top of the condenser was connected to a bubble counter. The reaction was heated to 100 °C (oil bath) which led to a orange solution and then to precipitation of the complex. After heating overnight, the reaction was cooled and the toluene phase was removed by filtration. After drying under heating (100 °C oil bath) and high vacuum the corresponding complex was obtained typically as orange to bright yellow powder.

Using a nitrogen-filled glove box, a 25 mL Schlenk tube was charged with a magnetic

stirring bar, *t*-BuOK (1.1 mmol, 123 mg), precatalyst **B** (0.02, 2 mol %, 1 mL from a 0.02 M stock solution), **1a** (1.5 mmol), **2a** (1.5 mmol), **3a** (1.0 mmol) and 1,4-dioxane (2 mL). The tube was closed with a glass stopper and removed from the glove box. A reflux condenser was evacuated and refilled with argon and then attached to the Schlenk tube maintaining an argon stream. A bubble counter was attached to the top of the condenser and the whole system was purged with argon for 15 seconds. After 20 h the reation was cooled, quenched with half-saturated brine and extracted with MTBE (4 x 15 mL). The combined organic phase was dried over Na_2SO_4 and concentrated. Purification by column chromatography on silica gel gave the product **4b** (266 mg, 0.787 mmol, 79 %).

PMI (III) > PMI (V), E-Factor (III) > E-Factor (V)

Previous report, Process IV (biomass alcohol as raw material)[3]



1a **2a** **3a** **4**

Reported procedures for process IV do not always contain all the required information; therefore, some realistic assumptions were used where appropriate and are italicized in the calculations given below. Drying agents, when used, were not included in the calculations.

Lignin model compound **1a** (0.4 mmol), benzamidine hydrochloride **2a** (0.2 mmol), the primary alcohol **3a** (0.4 mmol), NaOH (1.6 mmol), and *t*-AmOH (4 mL) were placed in the pressure tube (35 mL). The mixture was sealed and heated to 110 °C for 20 h. After the reaction, Water (10 mL) was added, and the resulting mixture was extracted with ethyl acetate (3 x 10 mL). The organic phases were combined and dried over anhydrous Na_2SO_4. The solid was filtered out and the solution was subjected to vacuum evaporation to remove solvent. Finally, the residue was subjected to silica column chromatography (PE /EtOAc = 9:1, *total* 85 mL) to give compound **4** (0.046g, 74%).

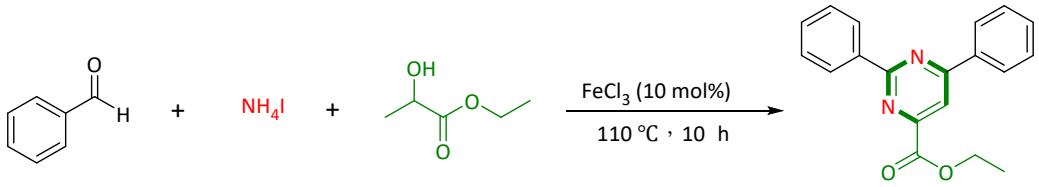
Materials used for metrics calculations: Lignin model compound **1a** (0.4 mmol, 0.110

g), benzamidine hydrochloride **2a** (0.2 mmol, 0.031 g), the primary alcohol **3a** (0.4 mmol, 0.043 g), NaOH (1.6 mmol, 0.064 g), and *t*-AmOH (4 mL, 3.2 g), EtOAc (30 mL, 27 g), H_2O (10 mL, 10 g), PE: EtOAc (85 mL, 68 g), compound **4** (0.046g, 0.15 mmol).

$$\textbf{PMI} = \frac{\textbf{0.110+0.031+0.043+0.064+3.2+27+10+68}}{\textbf{0.046}} = \textbf{2357.57}$$

E-Factor = 2357.57–1 = 2356.57

Current work, process biomass alcohol and inorganic ammonium as raw materials (this work)



1a **2a** **3a** **4a**

Aldehyde **1** (0.50 mmol), ammonium **2** (0.50 mmol), alkyl lactate **3** (0.3 mL), and $FeCl_3$ (0.05 mmol) were added to the 25.0 mL round bottom flask. The mixture was stirred at 110 °C for 10 hours. The reaction mixture was then mixed with water (10.0 mL), and the suspension was extracted with ethyl acetate (3 × 10.0 mL); The organic phase was dried and filtered on anhydrous Na_2SO_4. The solution evaporates under reduced pressure to remove organic solvents. The residue was purified by flash silica gel column chromatography with petroleum ether and ethyl acetate (PE /EtOAc =100:1, *total* 85 mL) as eluents to obtain the target product **4a** (0.069g, 91 %).

Materials used for metrics calculations: Aldehyde **1** (0.50 mmol, 0.053 g), ammonium **2** (0.50 mmol, 0.072 g), alkyl lactate **3** (0.3 mL, 0.3 g), $FeCl_3$ (0.05 mmol, 0.008 g), EtOAc (30 mL, 27 g), H_2O (10 mL, 10 g), PE: EtOAc (85 mL, 67 g) compound **4** (0.069g, 0.23 mmol).

$$\textbf{PMI} = \frac{\textbf{0.053+0.072+0.3+0.008+27+10+67}}{\textbf{0.069}} = \textbf{1513.52}$$

E-Factor = 1513.52–1 = 1512.52

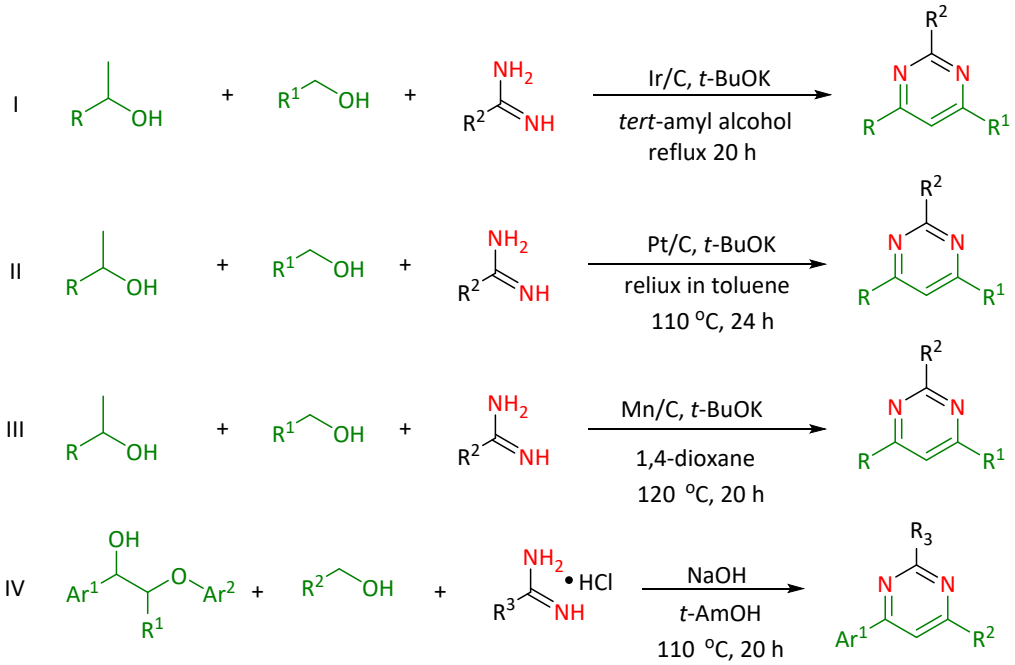
Table S3 Green metrics (PMI, E-factor) for processes I, III, IVV

Process	Yield (%)	PMI(g/g)	E-factor (g/g)
I	77%	>V	>V
III	79 %	>V	>V
IV	74%	2357.57	2356.57
V	91 %	1513.52	1512.52

2). Qualitative comparison by several factors

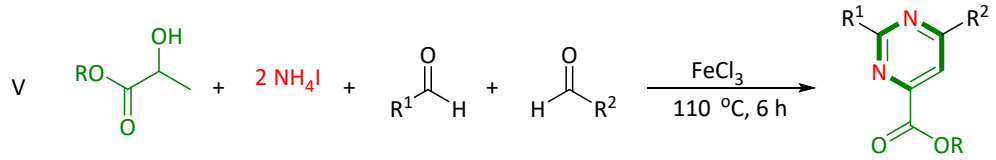
Previous report, Process a[2-4], and Current work, Process b (this work)

(a) Previous synthesis of pyrimidines from alcohols and amidines



(b) Synthesis of pyrimidines from alcohols and inorganic ammonium salts

This work:



a). Energy usage/global warming

Consumption of energy: In the previous work (Processes a I-IV), although the reaction temperature is similar to our work (Process b V), the reaction duration is longer, and the consumption of energy is greater.

b). Human carcinogenicity

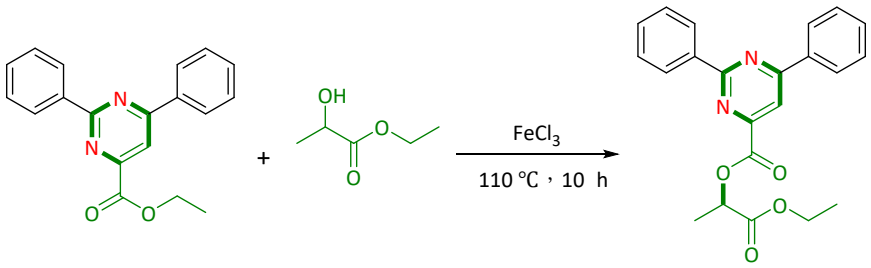
Toluene in Processes a II was established as a Group 3 carcinogen on October 27, 2017, 2017, by the International Agency for Research on Cancer of the World Health Organization. 1-4 dioxane in process a III was established as a Group 2B carcinogen on October 27, 2017, by the International Agency for Research on Cancer of the World Health Organization. Solvents were added in all Processes a I-IV, while no additional solvents were added in our work, which reduces the risk of carcinogenicity.

c). Mass of waste

In a complete reaction, several solvents, catalysts, additives, etc. are added in addition to the reactants. In Processes a I-IV solvents, catalysts, and bases (additives) are all added, in our work only the catalyst ($FeCl_3$) is added. Therefore, our work produces less waste volume during the reaction process.

NH_4I as a reactant does not only provide a source of ''N'', but the remaining iodide ions also catalyze the synthesis of azetidines (the importance of iodide ions for the reaction has been explored). We utilize the atoms added to the reaction as much as possible to avoid generating more Mass of waste.

In the derivatization experiment, we achieved the reuse of the remaining ethyl lactate and catalyst to avoid the waste of ethyl lactate and the reuse of the catalyst.



d). Resource depletion

Many studies on the conversion of biomass alcohols to chemicals have used metals for receptor-free dehydrogenation of alcohols into carbon-based reactive intermediates. Most of the previous technologies used precious metals (Processes a I-II) or complex metal complexes (Processes a I-III), where precious metals are limited in nature and their use in large quantities can lead to resource depletion, and the synthesis of metal complexes requires several more extensive steps and raw materials. Our present technique (Process b V) uses only the simple ionic form of the earth's abundant metal ($FeCl_3$). $FeCl_3$ not only serves as a carrier for alcohol

dehydrogenation but also catalyzes the formation of nitrogen-containing heterocycles as a Lewis acid. Thus, our present technology has an advantage over previous technologies in terms of catalysts.

3). Life cycle thinking.

Toluene, ammonia, oxygen, ethanol, hydrogen, and chlorine are raw materials for the synthesis of benzamidine hydrochloride acid salt Figure 51 (previous report)[5], The process for the synthesis of benzamidine hydrochloride acid salt requires more raw materials and operational steps, so it requires more energy and energy consumption, and generates more waste. Alcohol dehydrogenation produces aldehyde; ammonia, hydrogen, and iodine produce inorganic ammonium salts Figure 51 (current work), Our process synthesizes the intermediate benzamidine with simple inorganic ammonium salts and aldehydes and enables the synthesis of pyrimidine compounds.

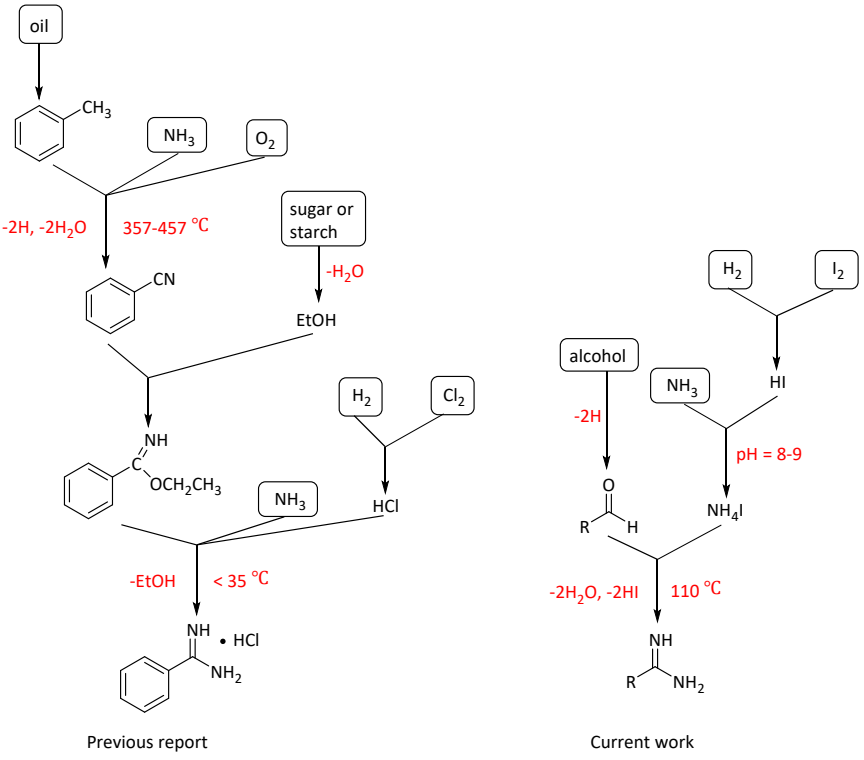


Figure S52 Two routes to the synthesis of benzamidine

12. Notes and references

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