Supporting Information

CFBSA: A Novel and Practical Chlorinating Reagent

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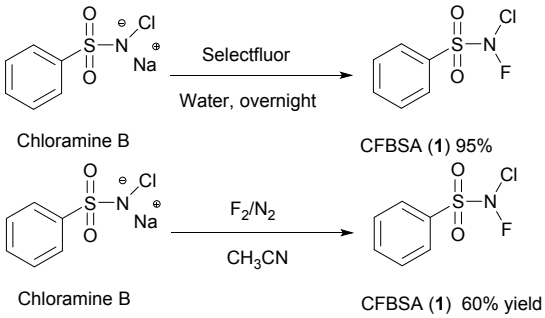
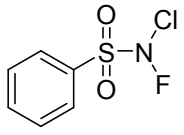
1. General Information

All the starting chemicals were commercially available and used without further purification. Substrates were purchased from Energy chemical Co. Ltd. and Damas-beta Co. Ltd. Fluorinating reagents (Selectfluor) were purchased from Shanghai Science Bio-pharmaceutical Co. Ltd. Dry acetonitrile was obtained by refluxing with CaH_2. Flash column chromatography was performed using silica gel (300-400 mesh). All ^1H NMR spectra were recorded on a Bruker spectrometer at 400 MHz. The ^{19}F NMR spectra were recorded on a Bruker spectrometer at 376 MHz. The ^{13}C NMR spectra were recorded on a Bruker spectrometer at 100 MHz. Chemical shifts (δ value) were reported in ppm down field from internal tetramethylsilane (TMS). *J* values are reported in Hz. IR spectrum (Film) were recorded on a Nicolet 6700 spectrophotometer in the range of 400~4000 cm^{-1}. HRMS (EI) Ms Spectra were recorded on a Waters GCT Premier ms spectrometer with electron impact.



Preparation of *N*-chloro-*N*-fluoro-benzenesulfonamide (CFBSA): (1) To a 250 mL round bottom flask equipped with a large magnetic stir bar, Chloroamine B (5.35 g, 0.025 mol, 1.0 equiv), Selectfluor (13.50 g, 0.038 mol, 1.5 equiv) were all dissolved in water (100 mL) at room temperature. The reaction was allowed to stir at room temperature overnight (~12 h). The mixture was extracted with dichloromethane (3×30 mL), the organic layer was dried with sodium sulfate. Solvent was removed under reduced pressure and the crude product (yellow liquid) was further purified through flash column chromatography. (2) To a 250 mL round bottom flask equipped with a large magnetic stir bar, Chloroamine B (5.35 g, 0.025 mol, 1.0 equiv), 100 mL CH_3CN were added. 20% F_2 was bubbled. The reaction was monitored by TLC. After the disappearance of starting material, the solvent was removed by reduced pressure and the crude product was further purified through flash column chromatography.



***N*-chloro-*N*-fluorobenzenesulfonamide (CFBSA)**. Yellow liquid; R_f = 0.55 (10% ethyl acetate/ petroleumeum ether); ^1H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 7.8 Hz, 2H), 7.86 (t, *J* = 7.5 Hz, 1H), 7.69 (t, *J* = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.78, 131.66, 129.70, 128.74. ^{19}F NMR (376 MHz, $CDCl_3$): δ 17.72 (s, 1F). IR (neat) **ν** = 3071, 1582, 1450，1390, 1190, 1085, 753, 682, 683, 615, 559 cm^{-1}; HRMS-EI (m/z) *calcd.* for ($C_6H_5O_2ClFNS$): 208.9714, *found* 208.9716.

2. Typical procedures

Standard procedure for the chlorination of carbonyl compounds: To a mixture of carbonyl compound (0.25 mmol, 1.0 equiv) and potassium carbonate (0.38 mmol, 1.5 equiv) in acetonitrile (3.0 mL) were added chlorinating reagent (CFBSA, 0.30 mmol, 1.2 equiv) with stirring at room temperature. The reaction was monitored by thin layer chromatography until completion. After the complete conversion of starting material, the reaction mixture was concentrated and directly purified by column chromatography on silica gel.

NOTES: For substrates that showed a mixture of mono and dichlorinated products with 1.2 equiv CFBSA, addition of another 1.2 equiv CFBSA would promote the complete conversion of monochlorinated products into dichlorinated ones.

Standard procedure for the chlorination of heterocycles: To a solution of heterocycle (0.25 mmol, 1.0 equiv) in acetonitrile (3.0 mL) were added chlorinating reagent (CFBSA, 0.30 mmol, 1.2 equiv) with stirring at room temperature. The reaction was monitored by thin layer chromatography until completion. After the complete conversion of starting material, the reaction mixture was concentrated and directly purified by column chromatography on silica gel.

NOTES: For substrates that showed a mixture of mono and dichlorinated products with 1.2 equiv CFBSA, addition of another 1.2 equiv CFBSA would promote the complete conversion of monochlorinated products into dichlorinated ones.

Standard procedure for the chlorination of *N*-alkylaniline analogues: To a solution of N-alkylaniline (0.25 mmol, 1.0 equiv) in acetonitrile (3.0 mL) was added chlorinating reagent CFBSA (0.30 mmol, 1.2 equiv) with stirring at room temperature. The reaction was monitored by thin layer chromatography until completion. After the complete conversion of starting material, the reation mixture were concentrated and directly purified by column chromatography on silica gel.

NOTES: For substrates that showed a mixture of mono and dichlorinated or trichlorinated products with 1.2 equiv CFBSA, addition of another 1.2 equivor 2.4 equiv CFBSA would promote the complete conversion of monochlorinated products into dichlorinated or trichlorinated ones.

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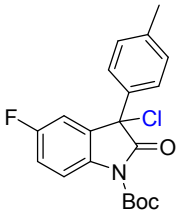
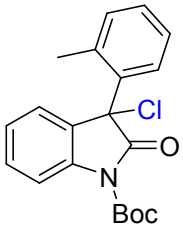
3. Analytical Data for the Products



(2a)

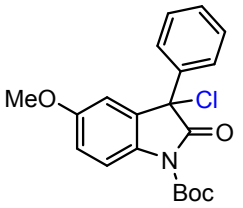
***N-tert*-butoxycarbonyl-3-chloro-3-(4-methylphenyl)-5-fluoro-2-oxindole**.[3] Procedure: Using 1.2 equiv CFBSA provided **2a** in 87% yield. White solid; R_f = 0.61 (10% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 7.98 (dd, *J* = 4.4, 8.4 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.20-7.12 (m, 4H), 2.35 (s, 3H), 1.61 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) **δ** −115.95 (s, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 170.77, 160.26 (d, *J* = 243.9 Hz), 149.08, 139.67, 135.14 (d, *J* = 2.5 Hz), 132.92, 130.79 (d, *J* = 8.4 Hz), 129.52, 127.71, 117.63 (d, *J* = 22.8 Hz), 117.31 (d, *J* = 7.7 Hz), 113.39 (d, *J* =24.7 Hz), 85.41, 66.24 (d, *J* =1.6 Hz), 28.10, 21.23.

On this TLC plate, S: Starting material; R: Reaction mixture: the upper point is the product, the lower point is N-fluorobensulfonamide; C: CFBSA



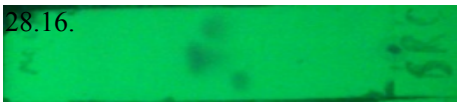
(3a)

***N-tert*-butoxycarbonyl-3-chloro-3-(2-methylphenyl)-2-oxindole**.[3] Procedure: Using 1.2 equiv CFBSA provided **3a** in 86% yield. White solid; R_f = 0.40 (10% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 8.16 (d, *J* = 8.0Hz, 1H), 7.94 (d, 8.0 Hz, 1H), 7.42-7.33 (m, 2H), 7.32-7.27 (m, 1H), 7.16-7.11 (m, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 7.04 (dd, *J* = 1.2, 7.6 Hz, 1H), 1.78 (s, 3H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 171.11, 149.22, 135.17, 131.87, 130.66, 129.37, 129.36, 126.36, 125.58, 124.70, 115.61, 85.28, 69.16, 28.19, 20.17.

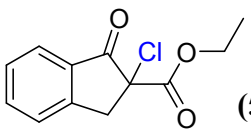


(4a)

***N-tert*-butoxycarbonyl-3-chloro-3-phenyl-5-methoxy-2-oxindole**.[4] Procedure: Using 1.2 equiv CFBSA provided **3a** in 79% yield. White solid; R_f = 0.55 (10% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 7.91 (d, *J* = 8.8 Hz, 1H), 7.53-7.50 (m, 2H), 7.39-7.36 (m, 3H), 7.00-6.94 (m, 2H), 3.81 (s, 3H), 1.61 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 171.14, 157.55, 149.18, 136.46, 132.52, 130.09, 129.30, 128.72, 127.98, 116.89, 116.51, 111.37, 85.08, 67.00, 55.89, 28.16.



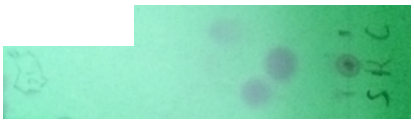
On this TLC plate, S: Starting material; R: Reaction mixture; C: CFBSA



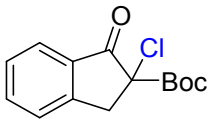
(5a)

Ethyl 2-chloro-1-oxo-indan-2-carboxylate.[5] Procedure: Using 1.2 equiv CFBSA provided **5a** in 89% yield. White solid; R_f = 0.30 (10% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 7.86 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.49-7.44 (m, 2H), 4.27 (q, *J* = 7.2,

14.4 Hz, 2H), 4.09 (d, *J* = 17.6 Hz, 1H), 3.56 (d, *J* = 17.6Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 195.24, 167.23, 150.71, 136.54, 132.63, 128.71, 126.43, 126.08, 68.11, 63.54, 43.53, 14.08.

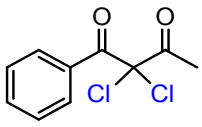


On this TLC plate, S: Starting material; R: Reaction mixture; C: CFBSA



(6a)

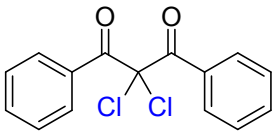
***Tert*-butyl-2-chloro-1-oxo-indan-2-carboxylate**.[6] Procedure: Using 1.2 equiv CFBSA provided **6a** in 83% yield. White solid; R_f = 0.70 (10% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 7.84 (d, *J* = 7.6 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.48-7.43 (m, 2H), 4.00 (d, *J* = 17.6 Hz, 1H), 3.53 (d, *J* = 17.6 Hz, 1H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 195.69, 165.98, 150.76, 136.30, 132.89, 128.56, 126.34, 125.89, 84.52, 68.88, 43.63, 27.80.



(7a)

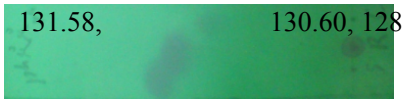
2,2-Dichloro-1-phenyl-1,3-butanedione.[7] Procedure: Using 2.4 equiv CFBSA provided **7a** in 88% yield. White solid; R_f = 0.76 (10% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 8.10-8.05 (m, 2H), 7.66-7.61 (m, 1H), 7.54-7.46 (m, 2H), 2.46 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) **δ** 192.31, 186.02, 134.60, 130.97, 130.68, 128.78, 86.57, 25.04.

On this TLC plate, S: Starting material; R: Reaction mixture; C: CFBSA

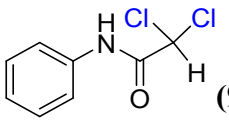


(8a)

1,3-Diphenyl-2,2-dichloro-1,3-propanedione.[8] Procedure: Using 2.4 equiv CFBSA provided **8a** in 86% yield. Yellow solid; R_f = 0.54 (10 % ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.95 (m, 4H), 7.56-7.51 (m, 2H), 7.42-7.37 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.48, 134.39, 131.58, 130.60, 128.82, 87.68.



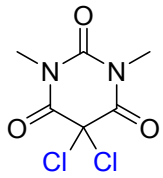
On this TLC plate, S: Starting material; R: Reaction mixture; C: CFBSA



(9a)

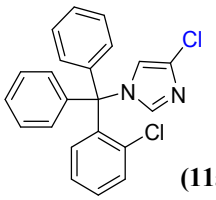
2,2-Dichloro-*N*-phenyl-acetamide.[9] Procedure: Using 2.4 equiv CFBSA provided **9a** in 84% yield. White solid; R_f = 0.31 (10% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 8.18 (s, br, 1H), 7.58-7.54 (m, 2H), 7.41-7.36 (m, 2H), 7.23-7.18 (m, 1H), 6.05 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 161.89, 136.34, 129.37, 125.84, 120.36, 66.99.

On this TLC plate, S: Starting material; R: Reaction mixture; C: CFBSA



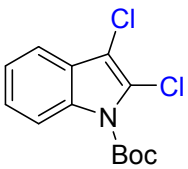
(10a)

5,5-Dichloro-1,3-dimethyl-2,4,6(1*H*,3*H*,5*H*)-pyrimidinetrione.[10] Procedure: Using 2.4 equiv CFBSA provided **10a** in 79% yield. White solid; Rf = 0.35 (10% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 3.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 161.42, 148.86, 71.85, 30.57.



(11a)

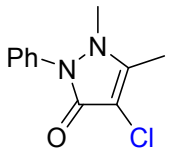
4-Chloro-1-((2-chlorophenyl)diphenylmethyl)-1*H*-imidazole.[1] Procedure: Using 1.2 equiv CFBSA provided **11a** in 77% yield. White solid; R_f = 0.43 (50% ethyl acetate/petroleum ether);^{1}H NMR (400 MHz, $CDCl_3$) **δ** 7.44 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.39-7.36 (m, 7H), 7.32 (s, 1H), 7.29 (dd, *J* = 1.2, *J* = 7.6 Hz, 1H), 7.19-7.16 (m, 4H), 6.94 (dd, J = 1.6, 8.0 Hz, 1H), 6.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 140.16, 139.74, 137.57, 135.61, 132.44, 130.45, 130.20, 129.20, 128.53, 128.28, 127.25, 117.50, 76.00.



(12a)

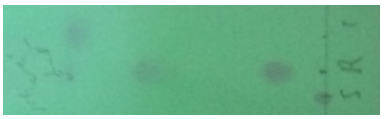
***Tert*-butyl-2,3-chloro-1*H*-indole-1-carboxylate.** Procedure: Using 2.4 equiv CFBSA provided **12a** in 75% yield. Colorless liquid; R_f = 0.55 (5% ethyl acetate/petroleum ether);^{1}H NMR (400

MHz, $CDCl_3$) δ 8.11(d, *J* = 8.0 Hz, 1H), 7.53-7.50 (m, 1H), 7.51 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.38-7.27(m, 2H), 1.69(s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.63, 134.35, 126.00, 125.68, 123.79, 121.76, 117.92, 115.46, 112.18, 85.64, 28.29.IR (neat) **ν** = 3317, 3165, 1743, 1477, 1174, 797, 751, 685, 556 cm^{-1}; HRMS-EI (m/z) *calcd.* for ($C_{13}H_{13}Cl_2NO_2$) 289.0323; *found* 289.0324.

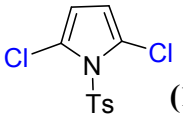


(13a)

4-Chloro-1,2-dihydro-1,5-dimethyl-2-phenyl-3*H*-pyrazol-3-one.[11] Procedure: Using 1.2 equiv CFBSA provided **13a** in 88% yield. White solid; R_f = 0.42 (50% ethyl acetate/petroleum ether); ^{1}HNMR (400 MHz, $CDCl_3$) **δ** 7.46 (t, *J* = 7,6 Hz, 2H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 3.07 (s, 3H), 2.30(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 161.57, 152.01, 134.78, 129.41, 127.22, 124.27, 103.51, 36.59, 11.35.

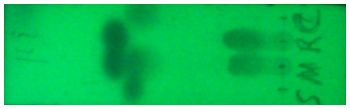


On this product, TLC plate, S: Starting material; R: Reaction mixture:the upper point is the the lower point is N-F bensulfonamide; C: CFBSA

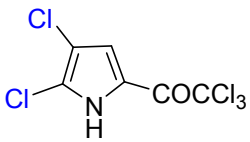


(14a)

2,5-Dichloro-1-tosyl-1*H*-pyrrole.[1] Procedure: Using 2.4 equiv CFBSA provided **14a** in 86% yield. White solid; R_f = 0.66 (10% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 7.89 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.10 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 146.04, 135.46, 130.16, 127.69, 117.67, 112.76, 21.86.

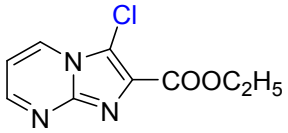


On this TLC plate, S: Starting material; R: Reaction mixture; C: CFBSA; M: Mixture of "S" and "R"



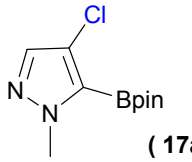
(15a)

2,2,2-Trichloro-1-(4,5-dichloro-1*H*-pyrrol-2-yl)ethanone.[12] Procedure: Using 2.4equiv CFBSA provided **15a** in 78% yield. Yellow solid; R_f = 0.64 (10% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 9.87 (s, 1H), 7.31 (d, *J* = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 172.29, 123.58, 120.49, 120.40, 113.30, 94.05.



(16a)

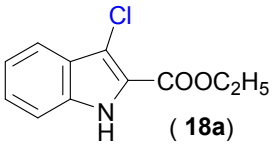
Ethyl 3-chloroimidazo[1,2-a]pyrimidine-2-carboxylate.[1] Procedure: Using 1.2 equiv CFBSA provided **16a** in 89% yield. Yellow solid; R_f = 0.57 (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 8.70 (dd, *J* = 2.0 Hz, 4.0Hz, 1H), 8.47 (dd, *J* = 2.0, 6.8 Hz, 1H), 7.10 (dd, *J* = 4.0, 6.8 Hz, 1H), 4.47 (q, *J* = 6.8, 12 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 161.84, 152.62, 145.77, 132.34, 131.29, 113.14, 110.61, 61.75, 14.40.



(17a)

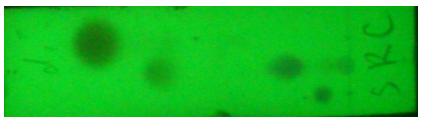
4-Chloro-1-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazole.[1] Procedure: Using 1.2 equiv CFBSA provided **17a** in 89% yield. Yellow solid; R_f = 0.49 (10% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 7.42 (s, 1H), 4.04 (s, 3H), 1.36 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 137.34, 120.01, 100.10, 84.39, 40.59, 24.91.

On this TLC plate, S: Starting material; R: Reaction mixture; C: CFBSA

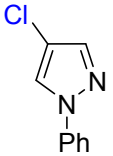


(18a)

Ethyl 3-chloro-1*H*-indole-2-carboxylate.[1] Procedure: Using 1.2 equiv CFBSA provided **18a** in 92% yield. White solid; R_f = 0.67(16% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 9.20 (s, br, 1H), 7.74-7.71 (m, 1H), 7.42-7.35 (m, 2H), 7.25-7.20 (m, 1H), 4.48 (q, *J* = 7.2, 14.4 Hz, 2H), 1.46 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 161.16, 134.86, 126.70, 126.36, 122.52, 121.41, 120.36, 112.59, 112.19, 61.58, 14.50.



On this TLC plate, S: Starting material; R: Reaction mixture; C: CFBSA

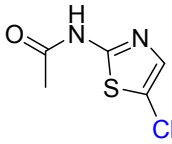


(19a)

4-Chloro-1-phenyl-1*H*-pyrazole.[1] Procedure: Using 1.2 equiv CFBSA provided **19a** in 83% yield. White solid; R_f = 0.40 (16% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) **δ**

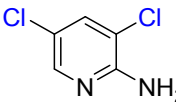
7.9 (s, 1H), 7.65 (s, 1H), 7.64 (d, J = 8.0 Hz, 3H), 7.46 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 139.85, 139.60, 129.68, 127.13, 124.95, 119.09, 112.51.

On this TLC plate, S: Starting material; R: Reaction mixture; C: CFBSA



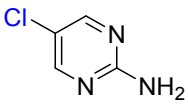
(**20a**)

***N*-(5-chlorothiazol-2-yl)acetamide**.[13] Procedure: Using 1.2 equiv CFBSA provided **20a** in 83% yield. White solid; R_f =0.38 (50% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 7.49 (s, 1H), 3.39 (br,s, 1H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 168.94, 155.96, 135.52, 117.81, 22.23.



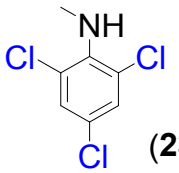
(**21a**)

3,6-dichloropyridin-2-amine.[14] Procedure: Using 2.4 equiv CFBSA provided **21a** in 84% yield. White solid; R_f =0.70 (10% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 7.93 (d, J = 2.0 Hz, 1H), 7.51 (d, J = 2.0 Hz, 1 H), 5.01 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 153.35, 144.37, 136.75, 120.43, 115.30.



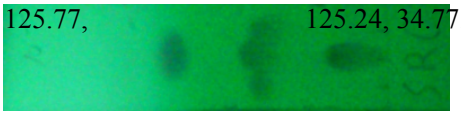
(**22a**)

5-chloropyrimidin-2-amine.[15] Procedure: Using 1.2 equiv CFBSA provided **22a** in 78% yield. White solid; R_f =0.70 (50% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 8.26 (s, 2 H), 6.90 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 162.03, 156.09, 117.23.

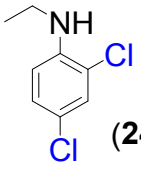


(**23a**)

2,4,6-Trichloro-*N*-methyl benzenamine.[16] Procedure: Using 3.6 equiv CFBSA provided **23a** in 78% yield. Yellow oil; R_f = 0.58 (5% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 7.22 (s, 2H), 3.89 (br s, 1H), 3.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 142.95, 128.68, 125.77, 125.24, 34.77.



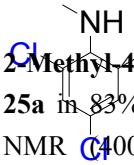
On this TLC plate, S: Starting material; R: Reaction mixture; C: CFBSA



(**24a**)

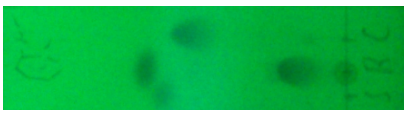
2,4-Dichloro-*N*-ethyl-benzenamine.[17] Procedure: Using 2.4 equiv CFBSA provided **24a** in 81% yield. Yellow oil; R_f = 0.58 (5% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 7.25 (d, *J* = 2.4 Hz, 1H), 7.10 (dd, *J* = 2.4, 8.8 Hz, 1H), 6.58 (d, *J* = 8.8 Hz, 1H), 4.35 (br s, 1H), 3.18 (q, *J* = 7.2,14.4 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 142.95, 128.73, 127.83, 120.93, 119.24, 111.73, 38.43, 14.68.

On this TLC plate, S: Starting material R: Reaction mixture C: CFBSA

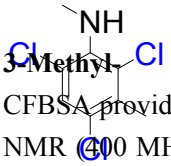


(**25a**)

2-Methyl-4,6-dichloro-*N*-methyl-benzenamine.[18] Procedure: Using 2.4 equiv CFBSA provided **25a** in 83% yield. Yellow oil; R_f = 0.58 (10% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 7.18 (d, *J* = 2.4 Hz, 1H), 7.01 (d, *J* = 2.0 Hz, 1H), 3.73 (s, br, 1H), 2.82 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 144.33, 132.21, 129.97, 126.70, 126.32, 126.17, 35.22, 19.29.

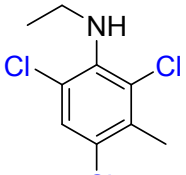


On this TLC plate, S: Starting material; R: Reaction mixture; C: CFBSA



(**26a**)

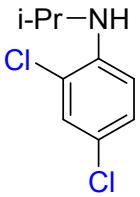
3-Methyl-2,4,6-trichloro-*N*-methyl-benzenamine. Procedure: Using 3.6 equiv CFBSA provided **26a** in 88% yield. Yellow oil. R_f = 0.67 (10% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 7.27 (s, 1H), 3.90 (s, br, 1H), 2.97 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 143.15, 133.94, 128.52, 127.36, 126.58, 123.26, 34.89, 18.23. IR (neat) **ν** = 3396, 2957, 1779, 1453, 1416, 1246, 1125, 818, 727, 647 cm^{-1}.HRMS-EI (m/z) *calcd.* for ($C_8H_8Cl_3N$) 222.9722; *found* 222.9724.



(**27a**)

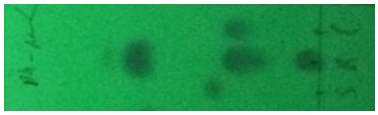
3-Methyl-2,4,6-trichloro-*N*-ethyl-benzenamine. Procedure: Using 3.6 equiv CFBSA provided **27a** in 81% yield. Yellow oil; R_f = 0.71 (10 % ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz,

$CDCl_3$) **δ** 7.28 (s, 1H), 3.74 (s, br, 1H), 3.32 (q, *J* = 7.2, 2H), 2.42 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 141.89, 133.93, 128.45, 127.96, 126.83, 123.87, 42.64, 18.30, 16.11. IR (neat) **ν** = 3379, 2968, 1754, 1445, 1380, 1136, 798, 729, 574 cm^{-1}. HRMS-EI (m/z) *calcd.* for ($C_9H_{10}Cl_3N$) 236.9879; *found* 236.9875.

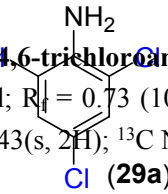


(**28a**)

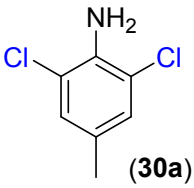
2,4,6-Trichloro-*N*-(1-methylethyl)-benzenamine.[18] Procedure: Using 3.6 equiv CFBSA provided **28a** in 83% yield. Yellow liquid; R_f = 0.64 (10% ethyl acetate/petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 1H), 7.08 (d, *J* = 8.8 Hz, 1H), 6.57 (d, *J* = 8.8 Hz, 1H), 4.21 (s, br, 1H), 3.65-3.57 (m, 1H), 1.24 (d, *J* = 6.4, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.02, 128.93, 127.81, 120.74, 119.46, 112.44, 44.52, 22.85.



On this TLC plate, S: Starting material; R: Reaction mixture; C: CFBSA

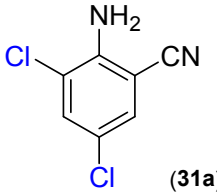


2,4,6-trichloroaniline.[19] Procedure: Using 3.6 equiv CFBSA provided **29a** in 70% yield. Yellow oil; R_f = 0.73 (10% ethyl acetate/petroleum ether); ^1H NMR (400 MHz, CDCl3) **δ** 7.17(s, 2 H), 4.43(s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 139.06, 127.62, 121.86, 119.72.
(**29a**)



(**30a**)

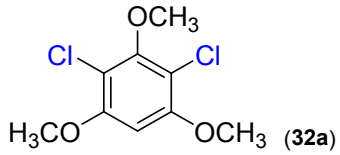
2,6-dichloro-4-methylaniline.[20] Procedure: Using 2.4 equiv CFBSA provided **30a** in 62% yield. Yellow solid; R_f = 0.79 (10% ethyl acetate/petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) **δ** 7.00(s, 2H), 2.21(s, 2H), 1.25(s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 137.69, 128.38, 119.59, 29.84, 20.18.



(**31a**)

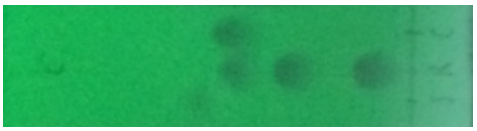
2-amino-3,5-dichlorobenzonitrile.[21] Procedure: Using 2.4 equiv CFBSA provided **31a** in 60% yield. white solid; R_f = 0.30 (10% ethyl acetate/petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) **δ** 7.44 (d, J = 2.4 Hz, 1H), 7.31 (d, J = 2.0 Hz, 1H), 4.85 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ**

145.06, 133.17, 121.97, 120.29, 115.78, 97.64.

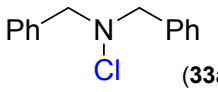


(32a)

1,3,5-Trimethoxy-2,6-dichlorobenzene.[22] Procedure: Using 3.6 equiv CFBSA provided **32a** in 90% yield. White solid; R_f = 0.36 (10% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 6.37 (s, 1H), 3.91 (s, 6H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 154.93, 153.99, 109.84, 93.31, 60.75, 56.66.

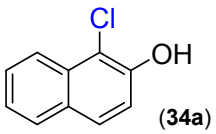


On this TLC plate, S: Starting material; R: Reaction mixture; C: CFBSA



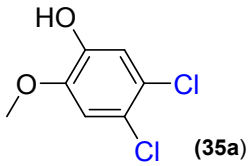
(33a)

***N*-chloro-*N*-(phenylmethyl)-benzenemethanamine**.[23] Procedure: Using 1.2 equiv CFBSA provided **33a** in 75% yield. White liquid; R_f = 0.54 (10% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 7.45-7.33 (m, 10H), 4.19 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 137.19, 129.21, 128.51, 128.00, 67.27**.**



(34a)

3,5-Dichloro-2-methoxyphenol.[24] Procedure: Using 2.4 equiv CFBSA provided **34a** in 64% yield. Yellow liquid; R_f = 0.2 (10% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 7.00 (s, 1H), 6.90 (s, 1H), 5.60 (br, s, 1H), 3.88(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 145.89, 145.03,124.30, 122.78, 116.15, 112.44, 56.50.



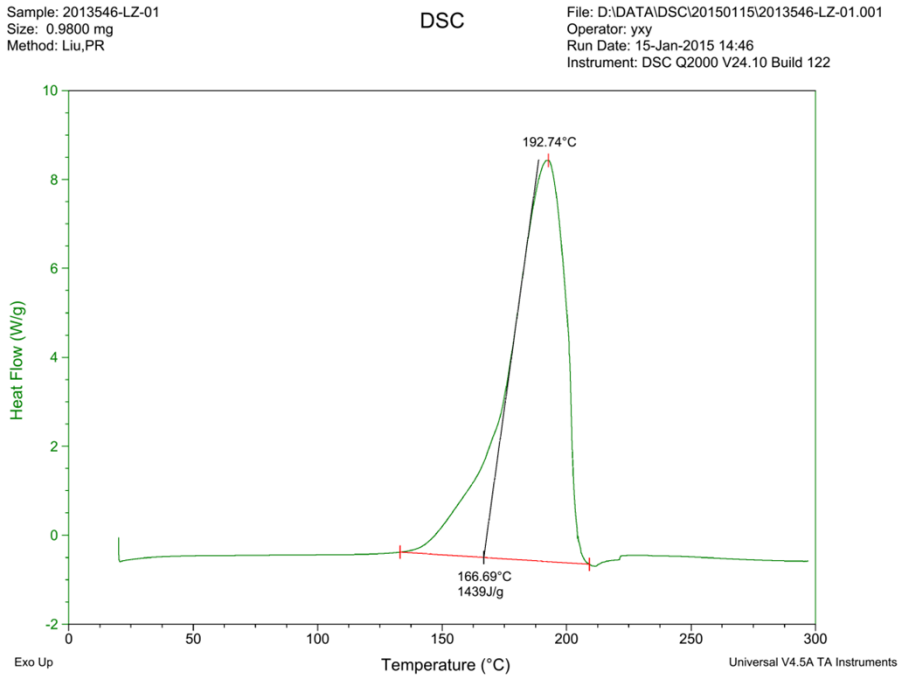
(35a)

1-chloronaphthalen-2-ol.[25] Procedure: Using 1.2 equiv CFBSA provided **35a** in 77% yield. White solid; R_f =0.70 (10% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 8.08 (d, *J* = 8.0 Hz, 1H), 7.45 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.43 (d, *J* = 10.0 Hz, 1H), 7.33 (d, *J* = 7.6Hz, 1H), 6.34 (d, *J* = 10.0Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) **δ** 186.00, 144.99, 140.77, 131.37,130.77, 129.66, 129.365, 127.04, 122.72, 80.59.

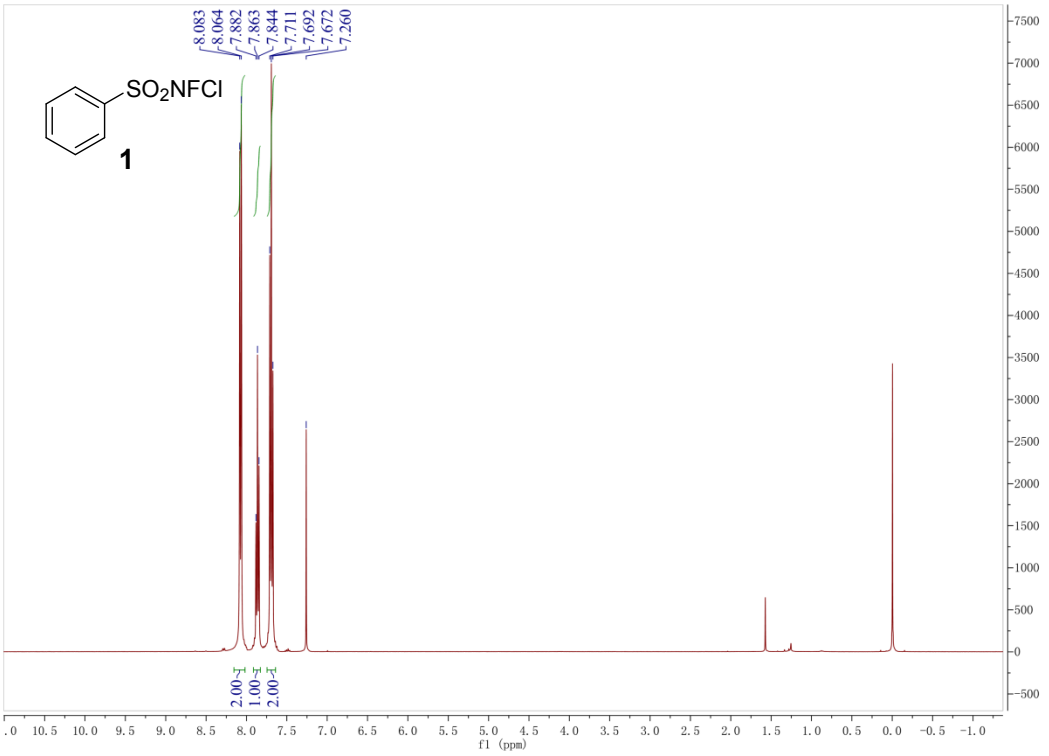
Differential scanning calorimetry (DSC) trace

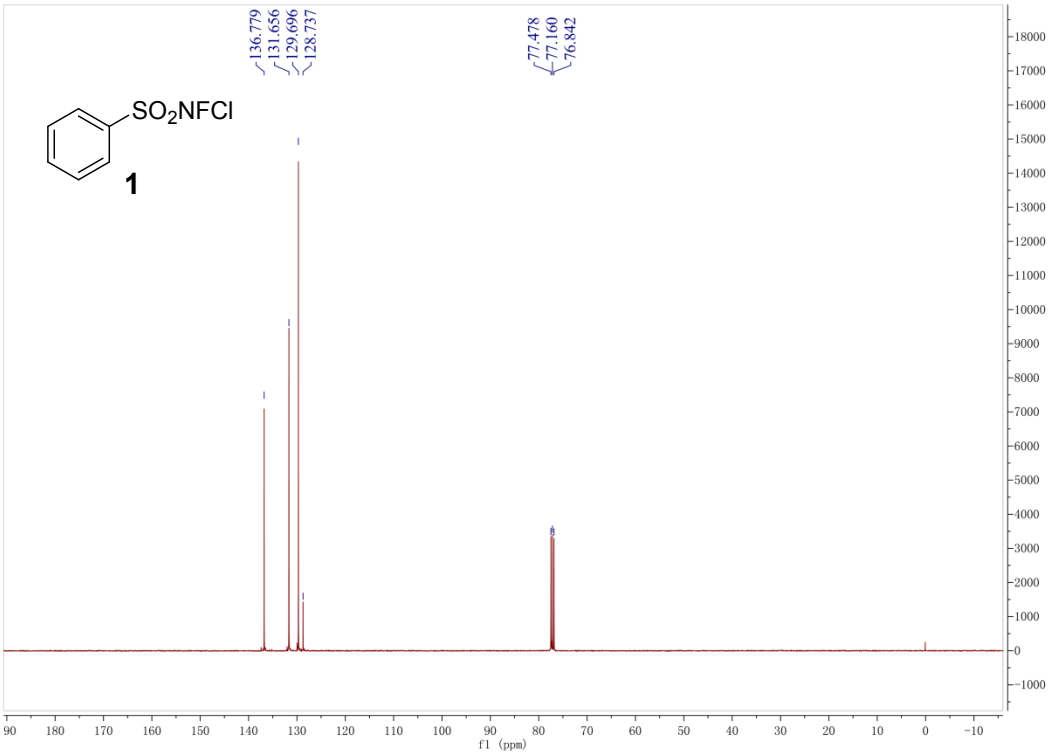
Table 1. DSC analysis of CFBSA

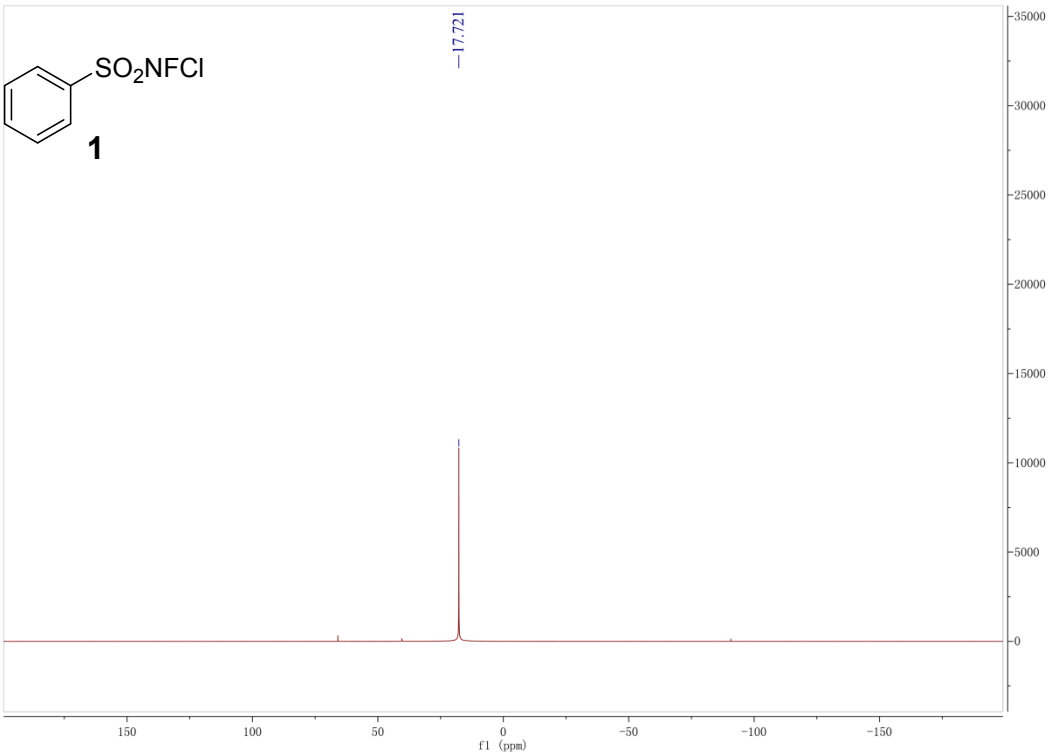
Thermal profile for CFBSA	
Onset Temperature:	130 ℃
Exothermmaximum:	192 ℃
ΔH: Enthalpy	1439J/g

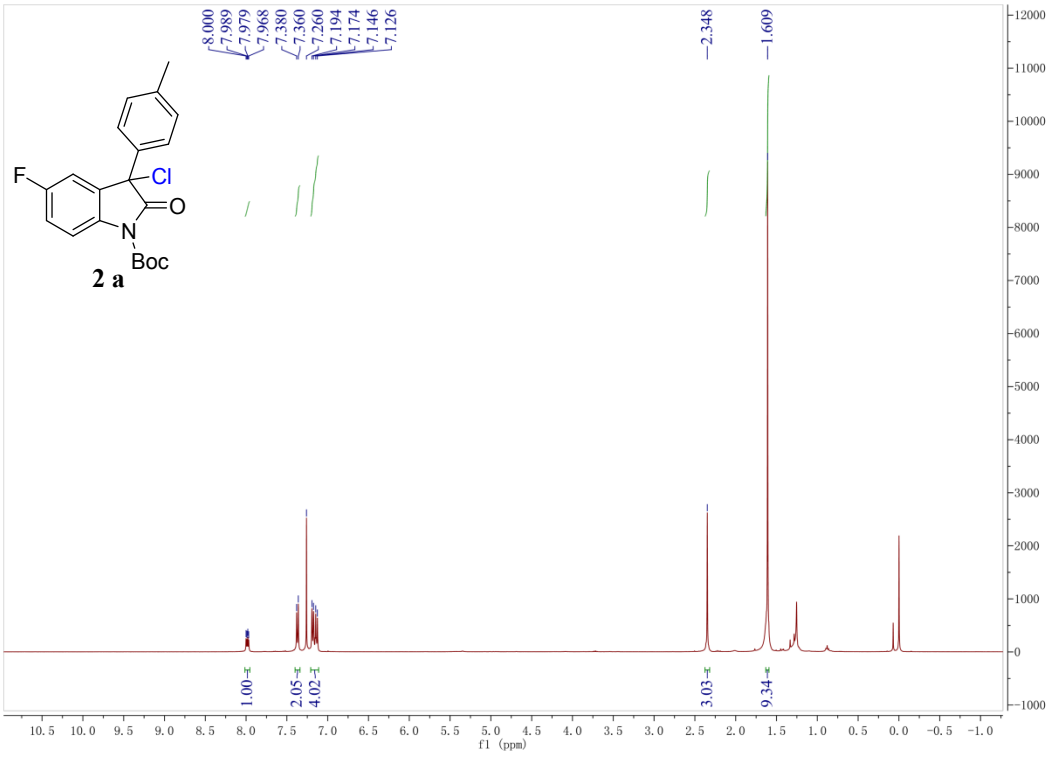


^{1}H, ^{13}C NMR and ^{19}F NMR spectra






SO2NFCl
1
17.721
f1 (ppm)


F
Cl
O
N
Boc
2 a
8.000
7.989
7.979
7.968
7.380
7.360
7.260
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7.126
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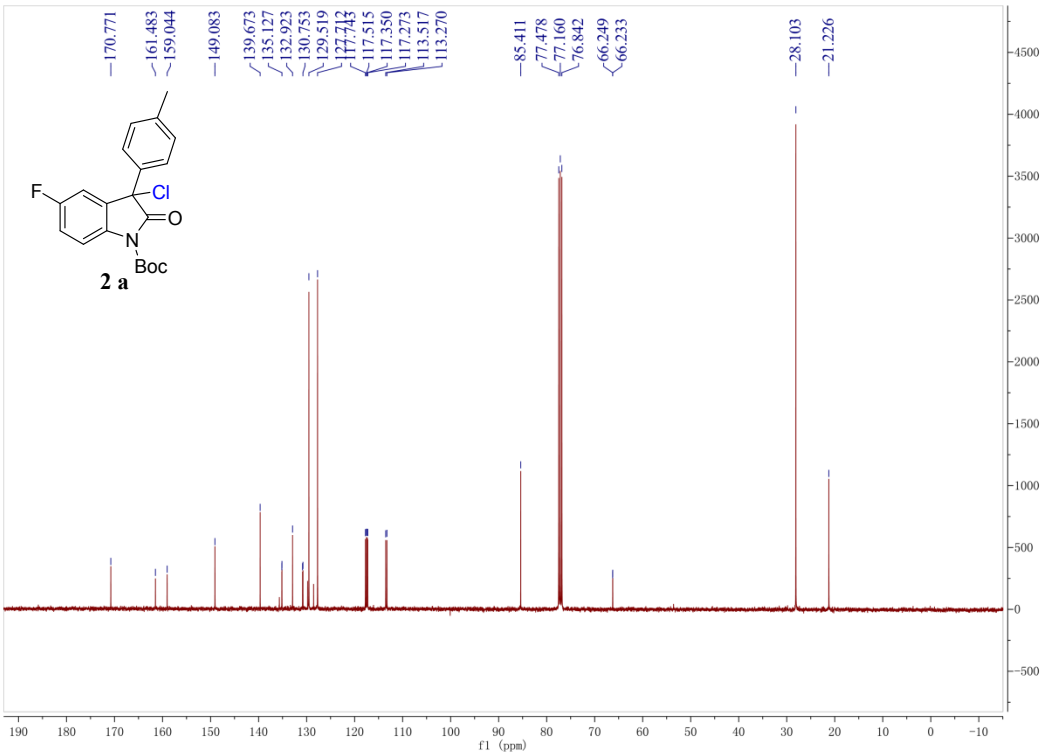
2.05
4.02
3.03
9.34
f1 (ppm)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159.044
149.083
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135.127
132.923
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127.743
117.515
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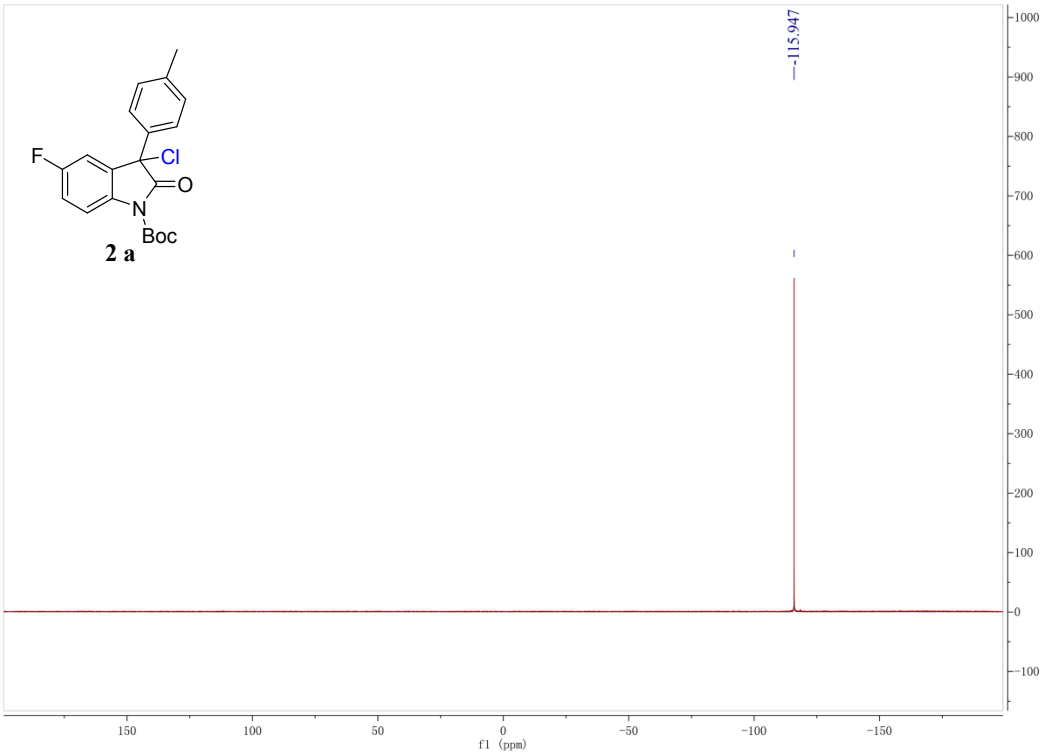
113.517
113.270
85.411
77.478
77.160
76.842
66.249
66.233
28.103
21.226
F
Cl
O
N
Boc
2 a
f1 (ppm)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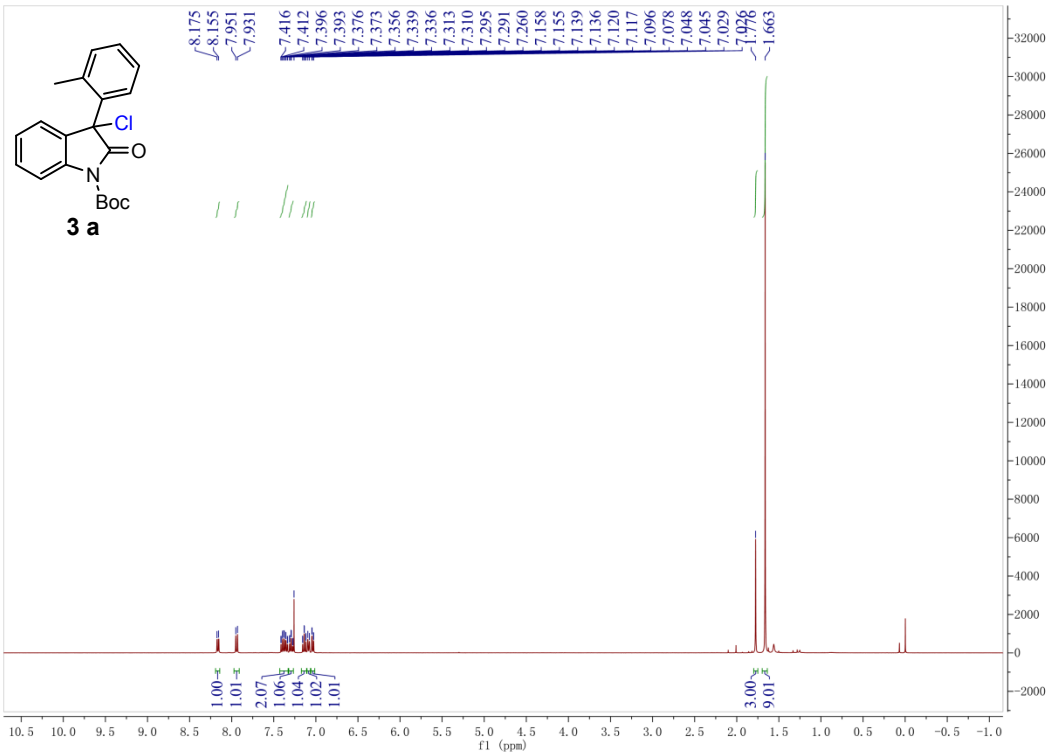
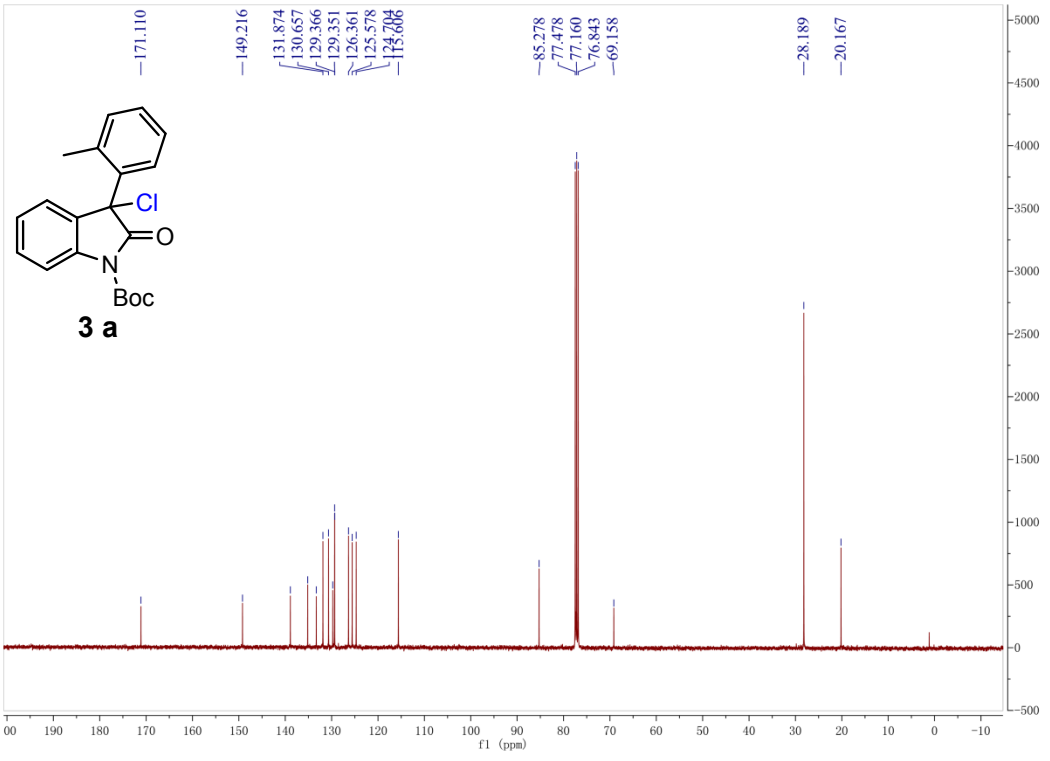
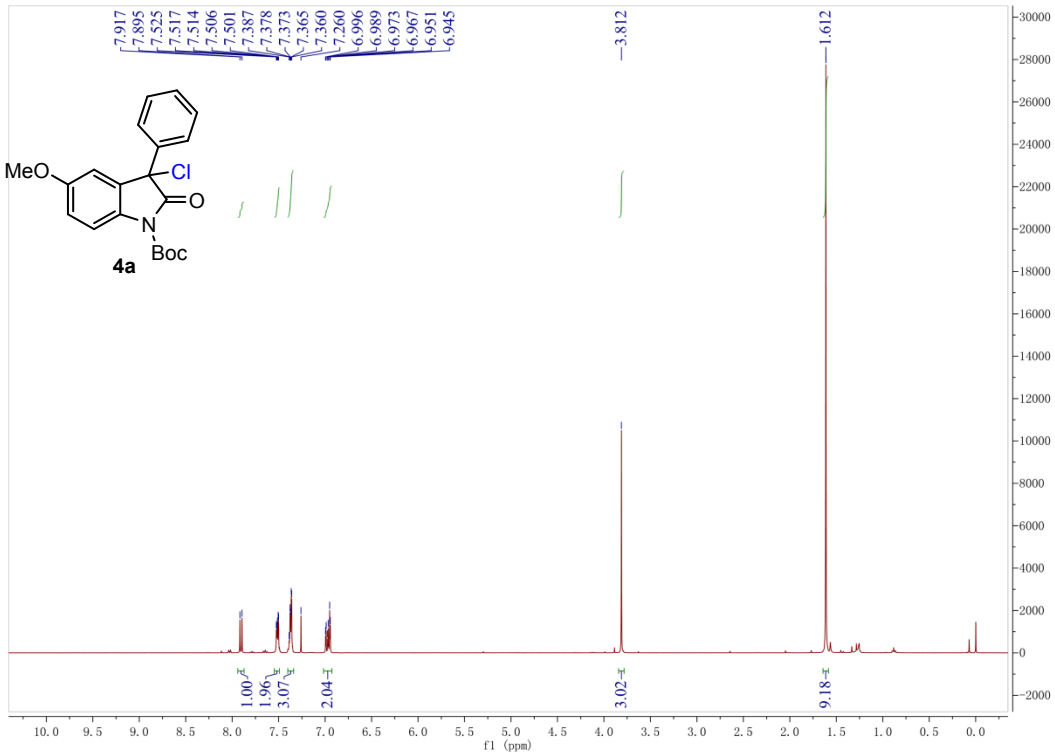
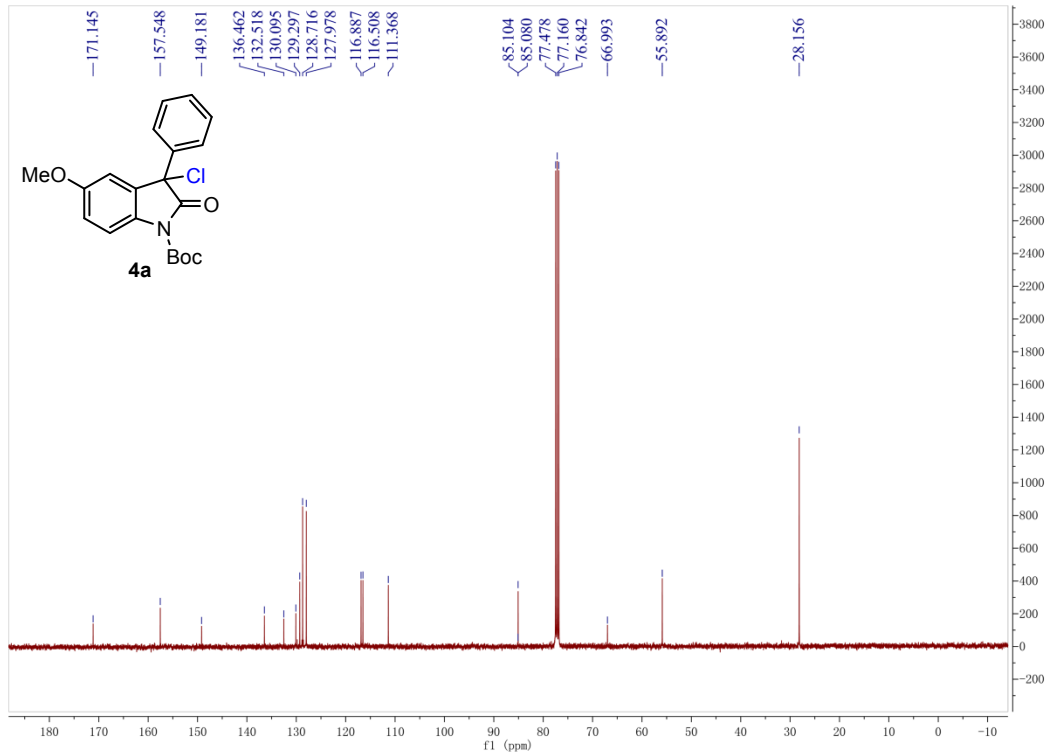
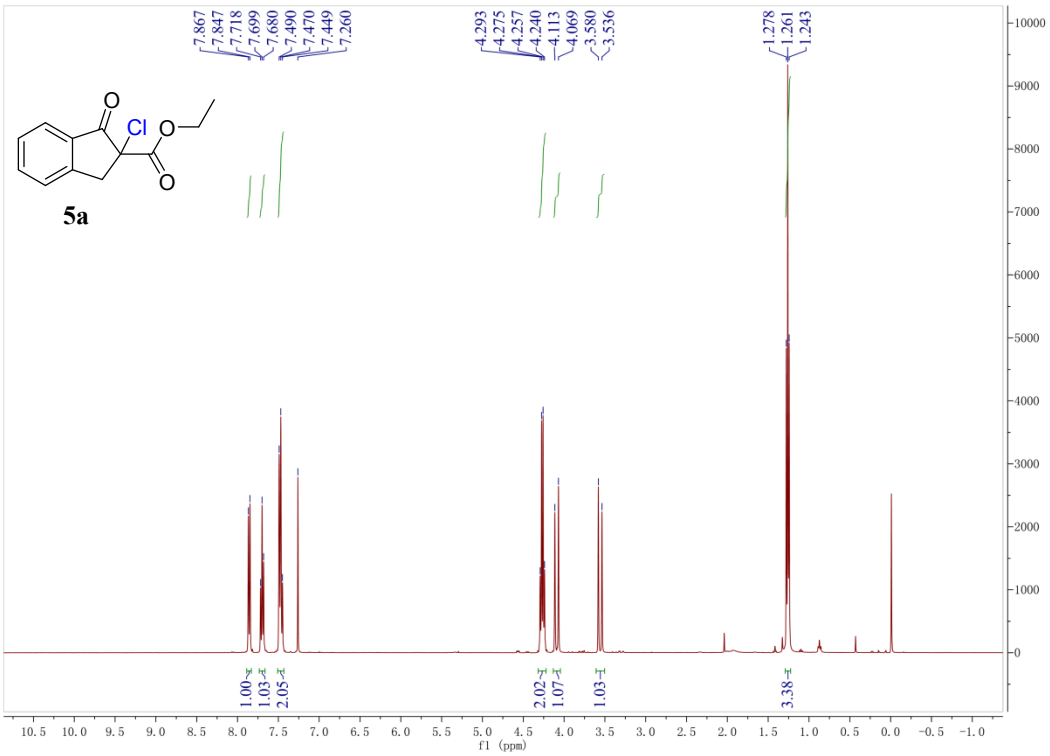
F
Cl
O
N
Boc
2 a
f1 (ppm)

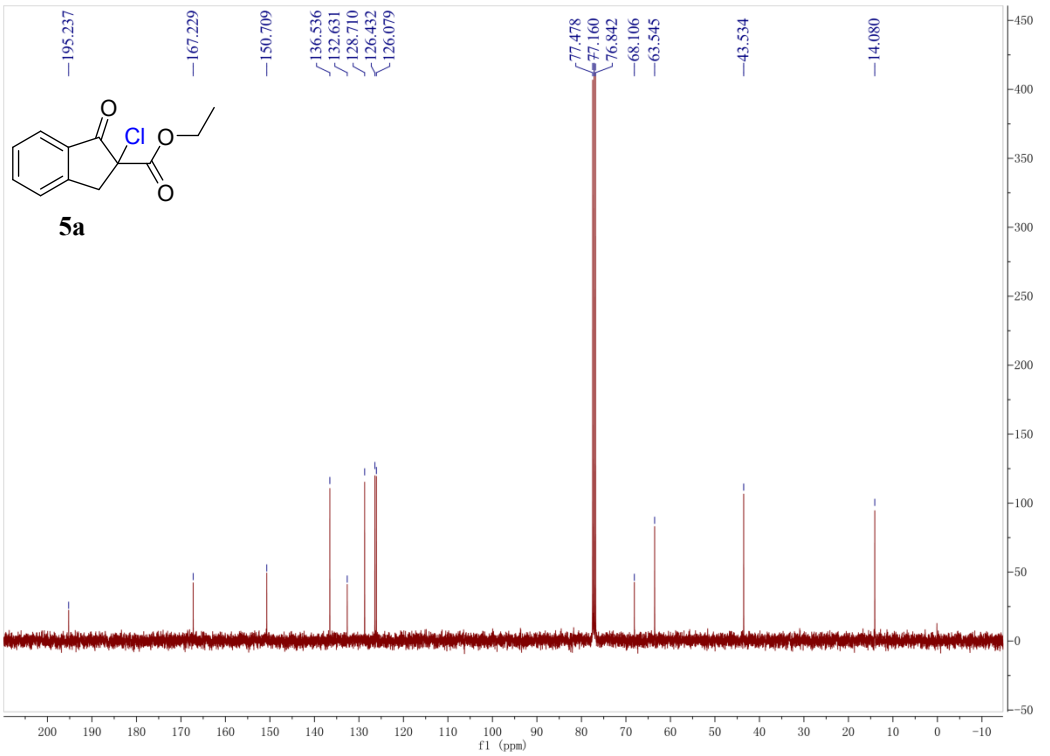

Cl
O
N
Boc
3 a
8.175
8.155
7.951
7.931
7.416
7.412
7.396
7.393
7.376
7.373
7.356
7.339
7.336
7.313
7.310
7.295
7.291
7.260
7.158
7.155
7.139
7.136
7.120
7.117
7.096
7.078
7.048
7.045
7.029
1.776
1.663
1.00
1.01
2.07
1.06
1.04
1.02
1.01
3.00
9.01
f1 (ppm)

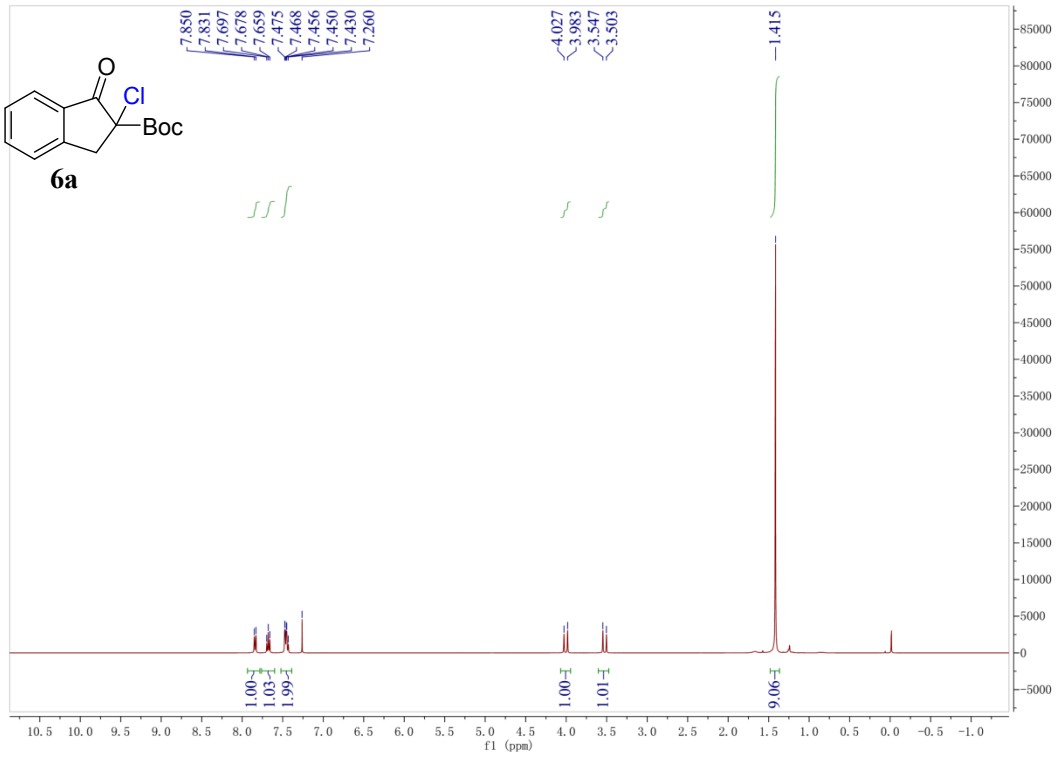

Cl
O
N
Boc
3 a
171.110
149.216
131.874
130.657
129.366
129.351
126.361
125.578
85.278
77.478
77.160
76.843
69.158
28.189
20.167
f1 (ppm)

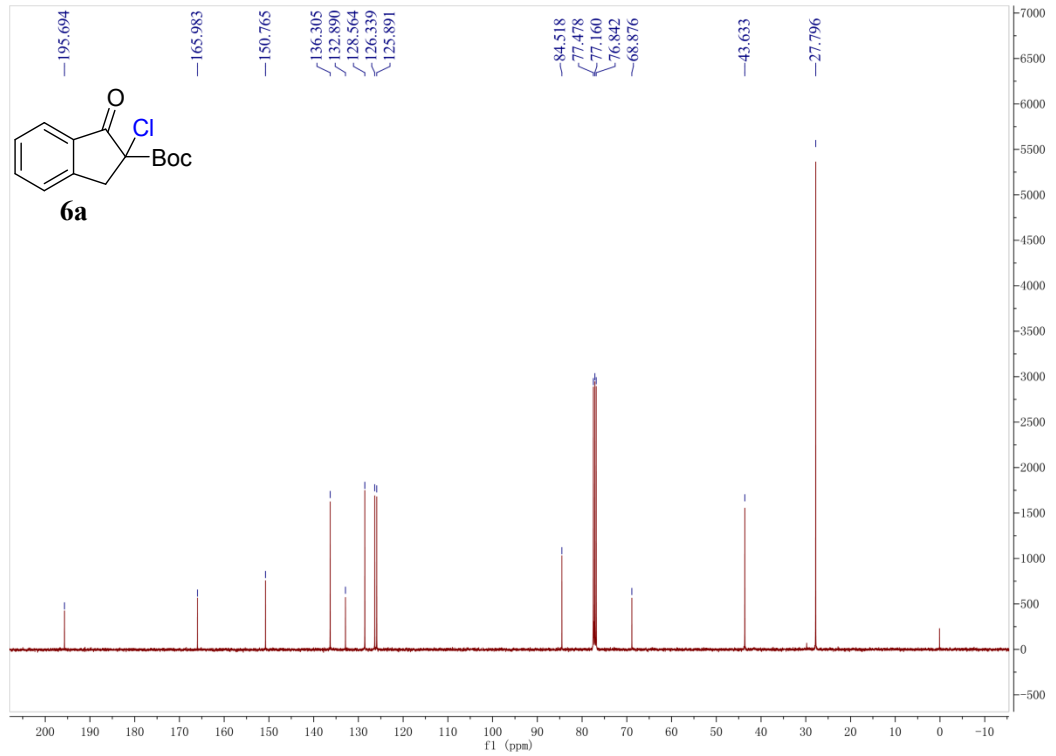

7.917
7.895
7.525
7.517
7.514
7.506
7.501
7.387
7.378
7.373
7.365
7.360
7.260
6.996
6.989
6.973
6.967
6.951
6.945
3.812
1.612
MeO
Cl
O
N
Boc
4a
1.00
1.96
3.07
2.04
3.02
9.18
f1 (ppm)

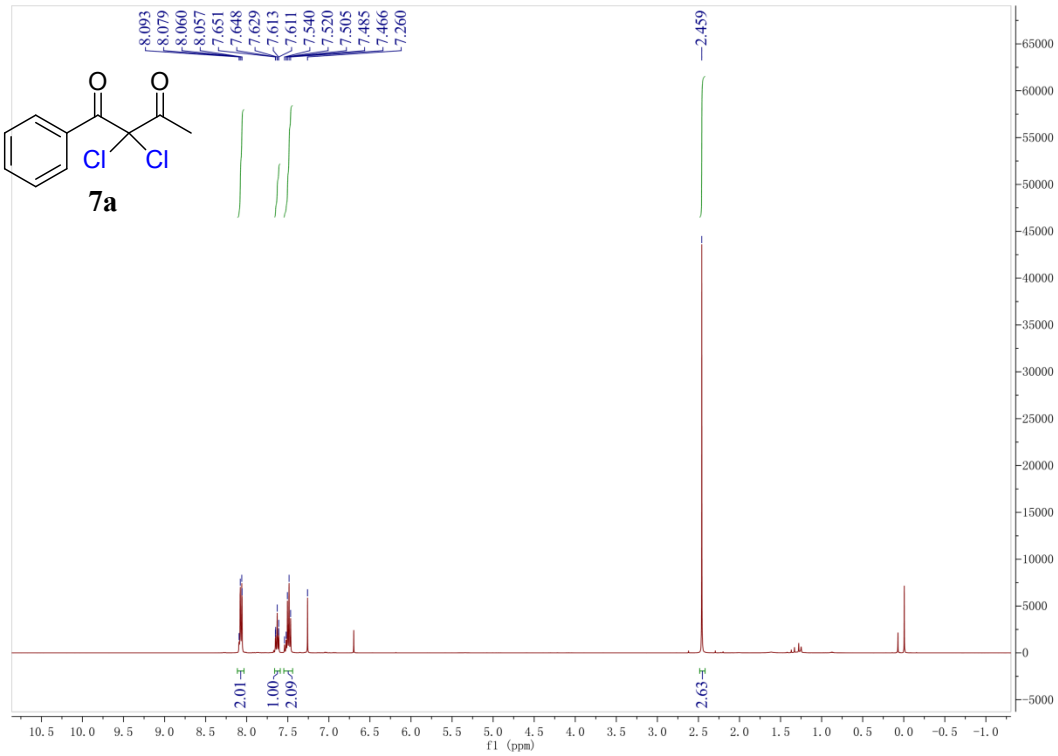

171.145
157.548
149.181
136.462
132.518
130.095
129.297
128.716
127.978
116.887
116.508
111.368
85.104
85.080
77.478
77.160
76.842
66.993
55.892
28.156
MeO
Cl
O
N
Boc
4a
f1 (ppm)

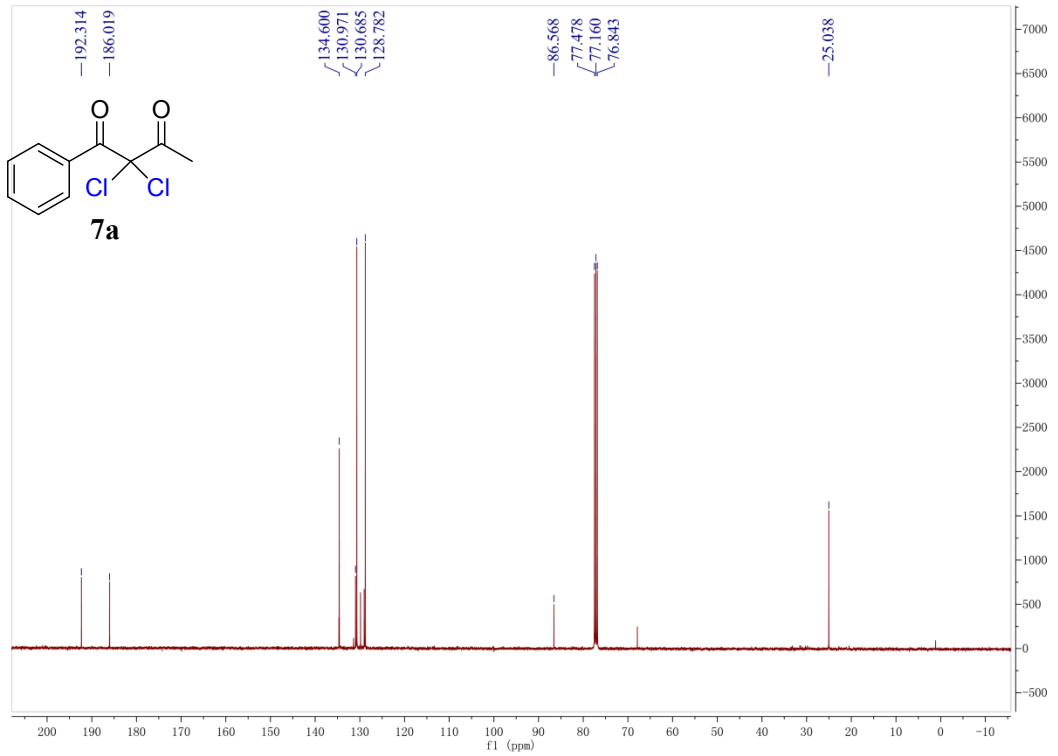

7.867
7.847
7.718
7.699
7.680
7.490
7.470
7.449
7.260
4.293
4.275
4.257
4.240
4.113
4.069
3.580
3.536
1.278
1.261
1.243
Cl
O
O
O
5a
1.00
1.03
2.05
2.02
1.07
1.03
3.38
f1 (ppm)

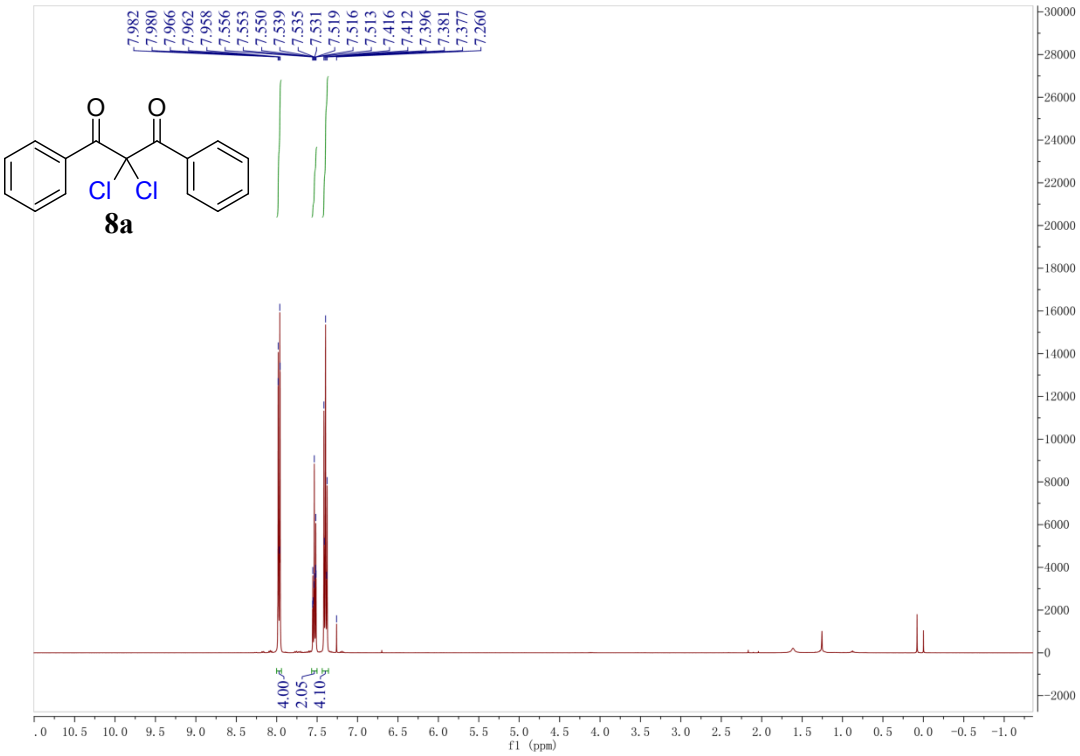

195.237
167.229
150.709
136.536
132.631
128.710
126.432
126.079
77.478
77.160
76.842
68.106
63.545
43.534
14.080
Cl
O
O
O
5a
f1 (ppm)

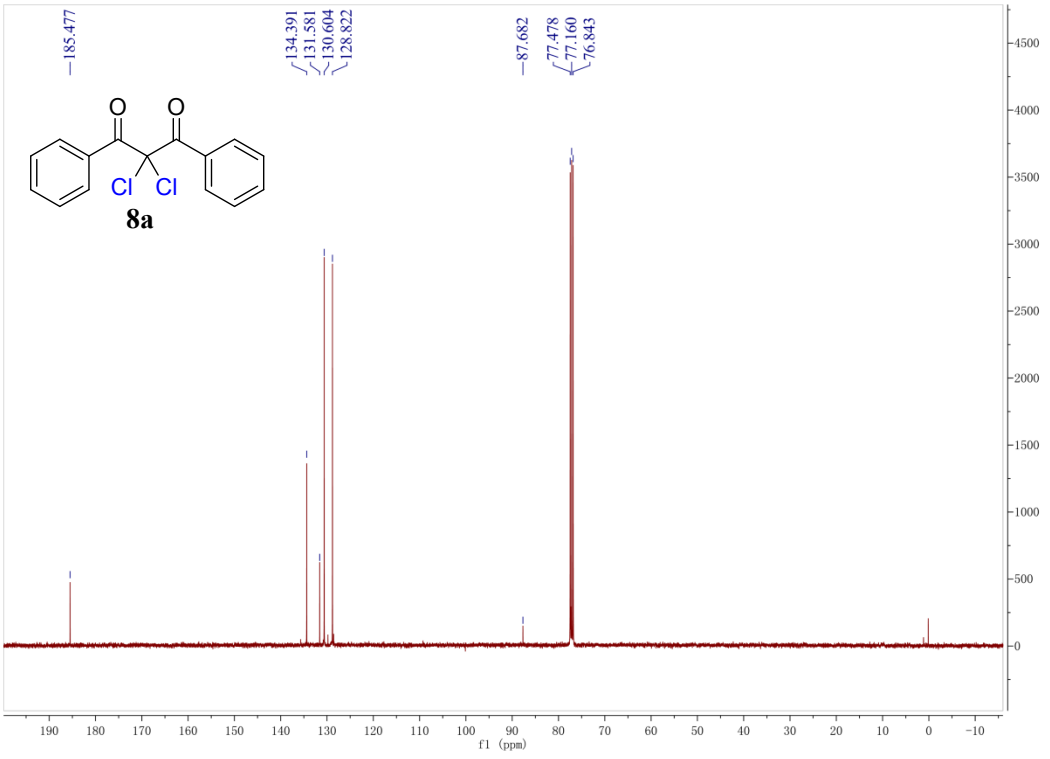

7.850
7.831
7.697
7.678
7.659
7.475
7.468
7.456
7.450
7.430
7.260
4.027
3.983
3.547
3.503
1.415
O
Cl
Boc
6a
1.00
1.03
1.99
1.00
1.01
9.06
f1 (ppm)

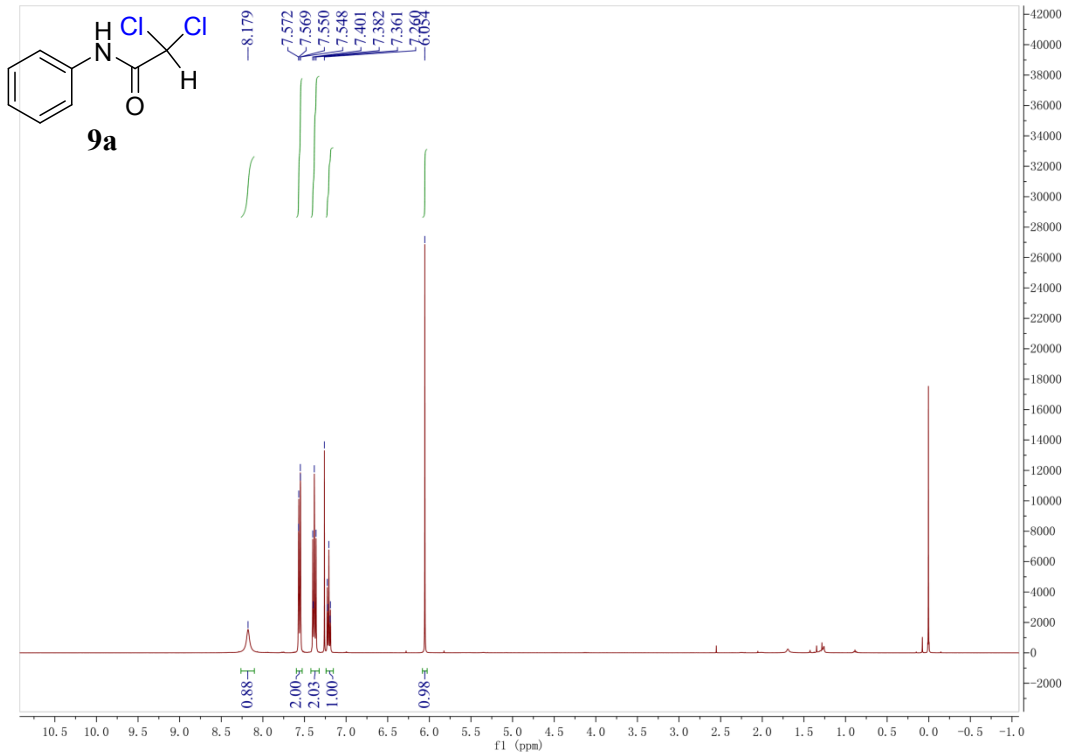

195.694
165.983
150.765
136.305
132.890
128.564
126.339
125.891
84.518
77.478
77.160
76.842
68.876
43.633
27.796
O
Cl
Boc
6a
f1 (ppm)

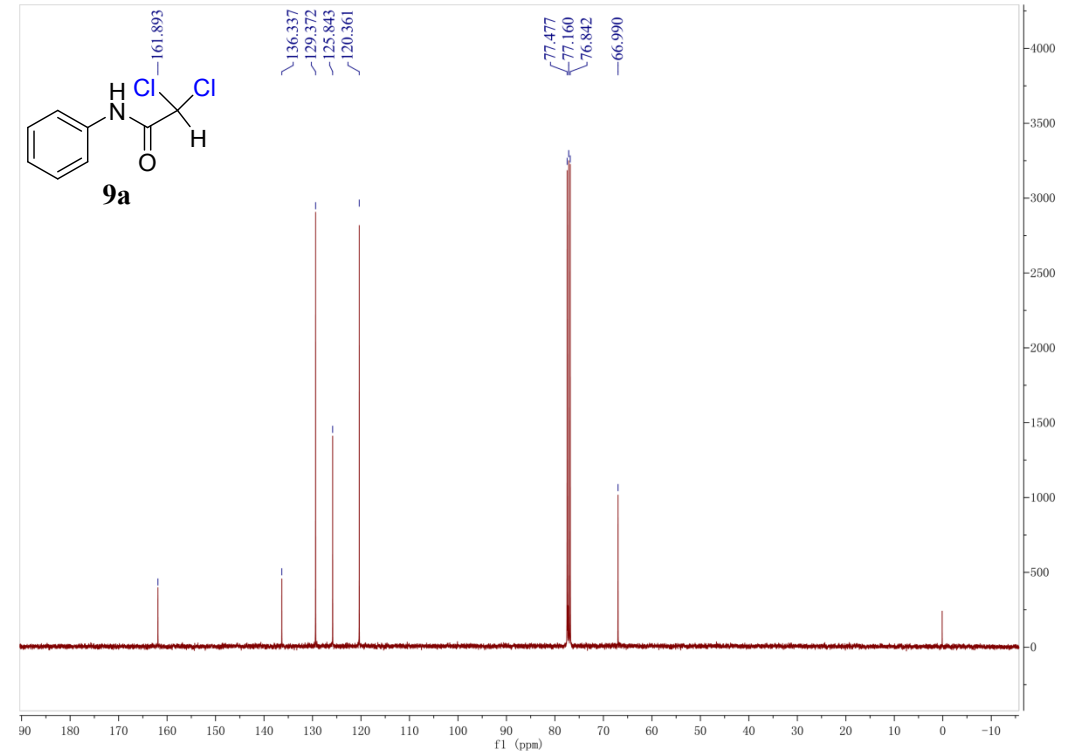

8.093
8.079
8.060
8.057
7.651
7.648
7.629
7.613
7.611
7.540
7.520
7.505
7.485
7.466
7.260
2.459
O
O
Cl
Cl
7a
2.01
1.00
2.09
2.63
f1 (ppm)

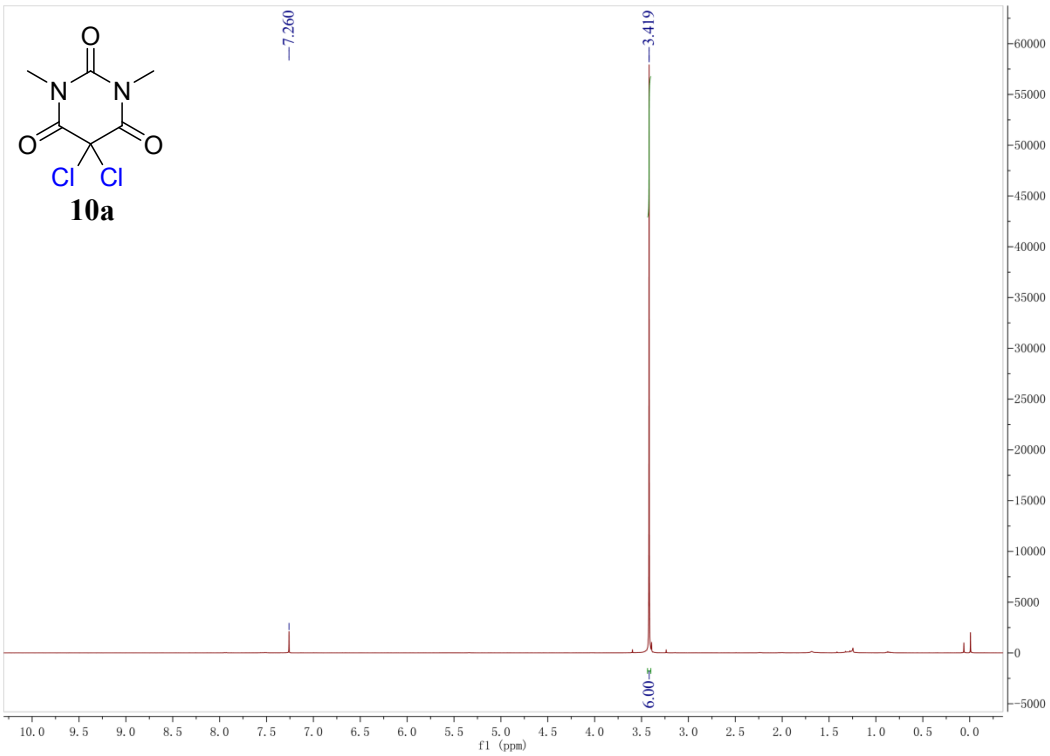

192.314
186.019
134.600
130.971
130.685
128.782
86.568
77.478
77.160
76.843
25.038
O
O
Cl
Cl
7a
f1 (ppm)


7.982
7.980
7.966
7.962
7.958
7.556
7.553
7.550
7.539
7.535
7.531
7.519
7.516
7.513
7.416
7.412
7.396
7.381
7.377
7.260
O
O
Cl
Cl
8a
4.00
2.05
4.10
f1 (ppm)

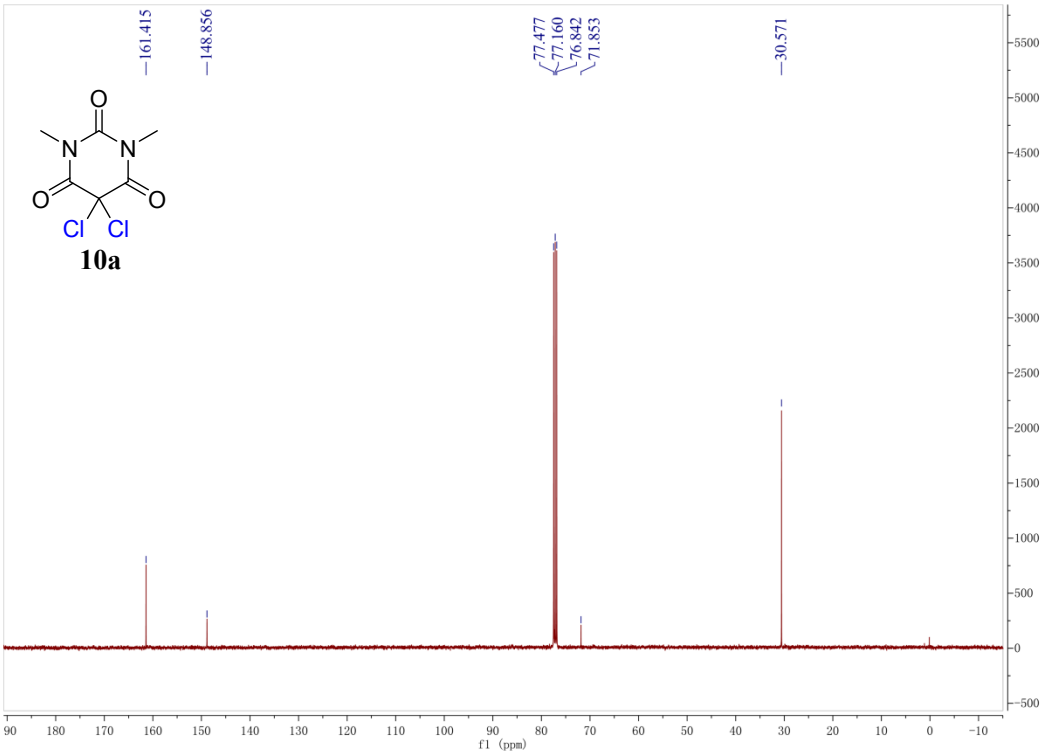

185.477
134.391
131.581
130.604
128.822
87.682
77.478
77.160
76.843
O
O
Cl
Cl
8a
f1 (ppm)


9a
8.179
7.572
7.569
7.550
7.548
7.401
7.382
7.361
7.260
6.054
0.88
2.00
2.03
1.00
0.98
f1 (ppm)

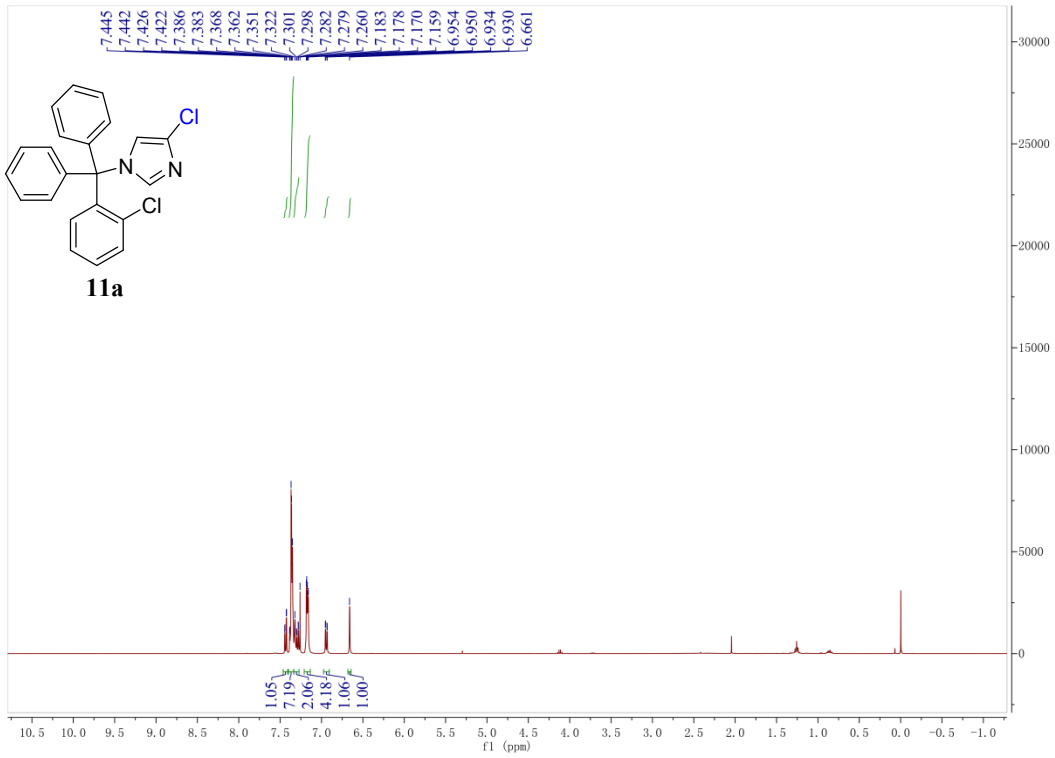

9a
161.893
136.337
129.372
125.843
120.361
77.477
77.160
76.842
66.990
f1 (ppm)

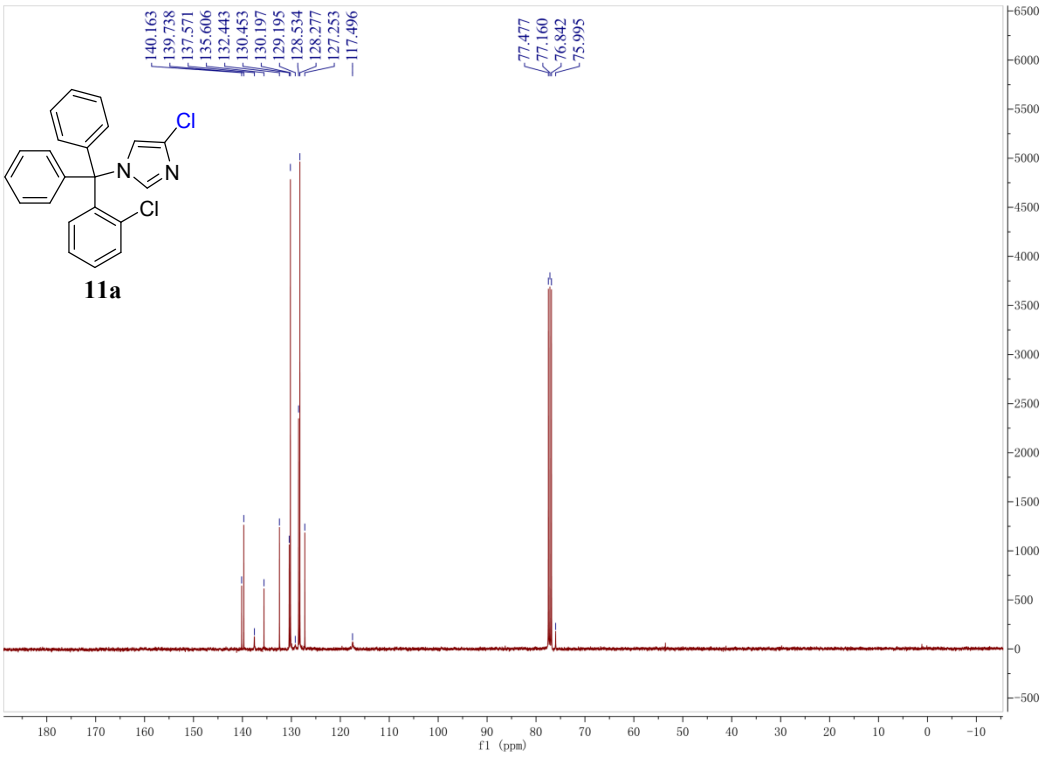

7.260
3.419
6.00
f1 (ppm)

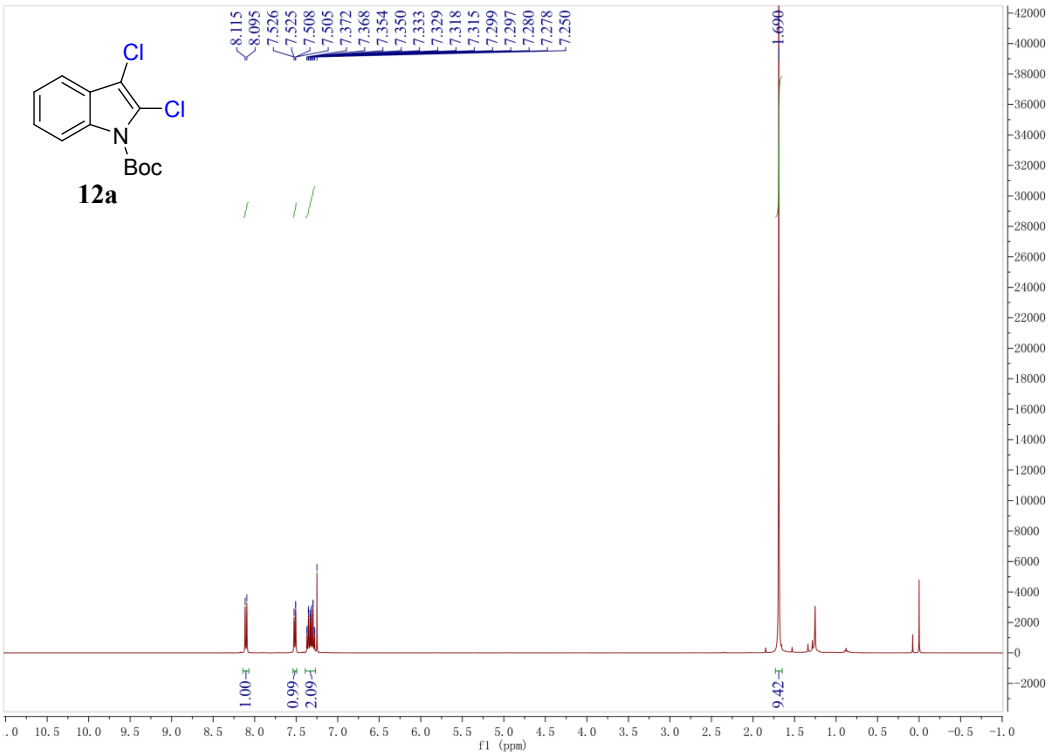
10a

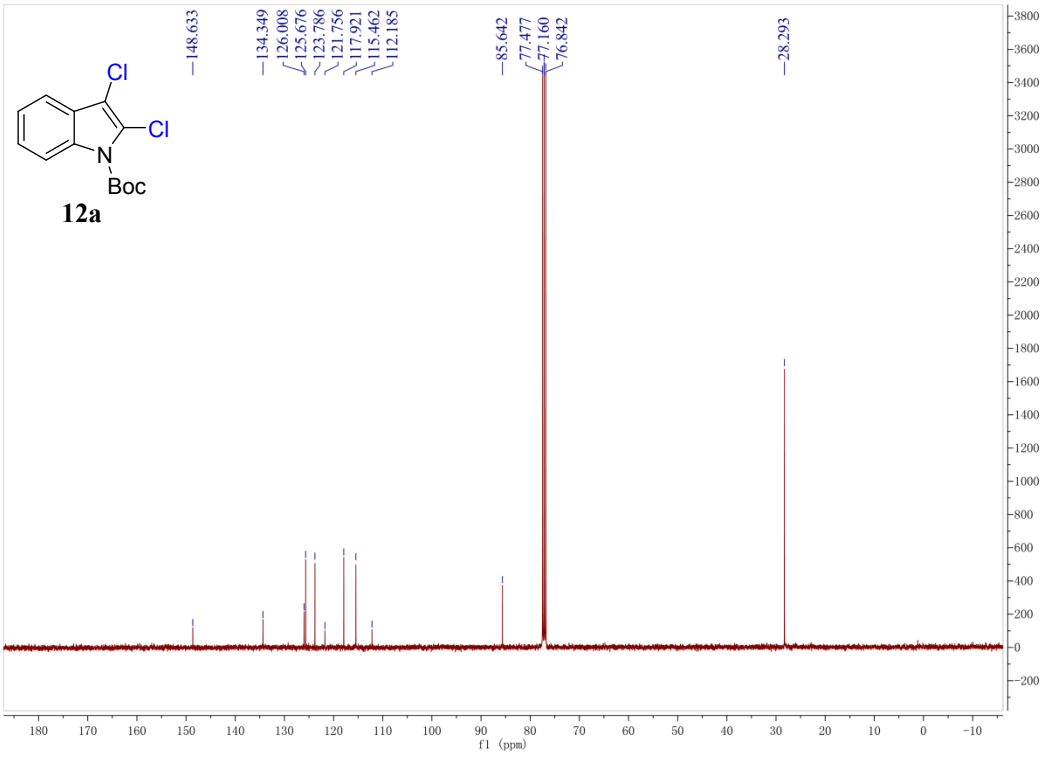

161.415
148.856
77.477
77.160
76.842
71.853
30.571
f1 (ppm)

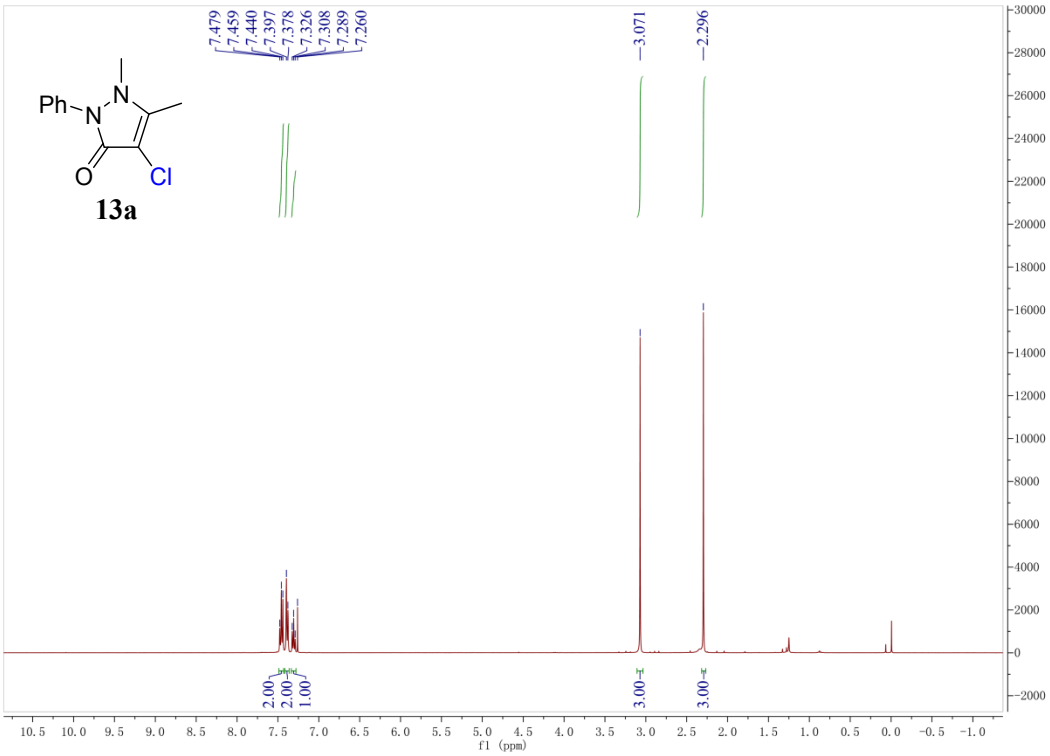
10a

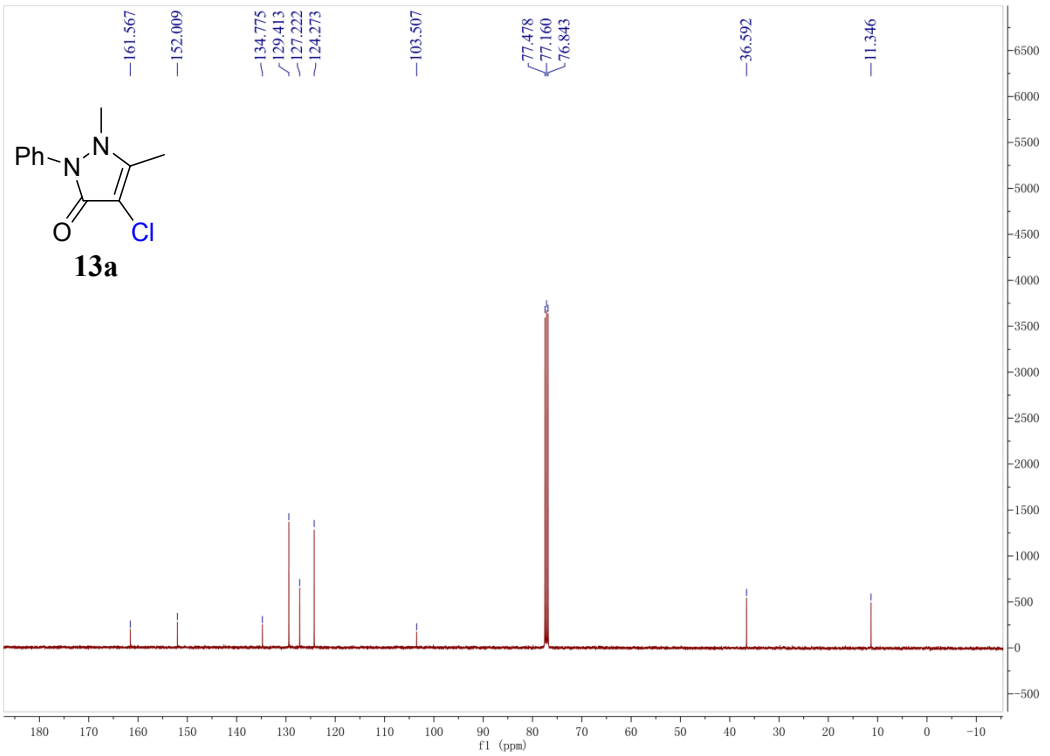

7.445
7.442
7.426
7.422
7.386
7.383
7.368
7.362
7.351
7.322
7.301
7.298
7.282
7.279
7.260
7.183
7.178
7.170
7.159
6.954
6.950
6.934
6.930
6.661
Cl
N
N
Cl
11a
1.05
7.19
2.06
4.18
1.06
1.00
f1 (ppm)

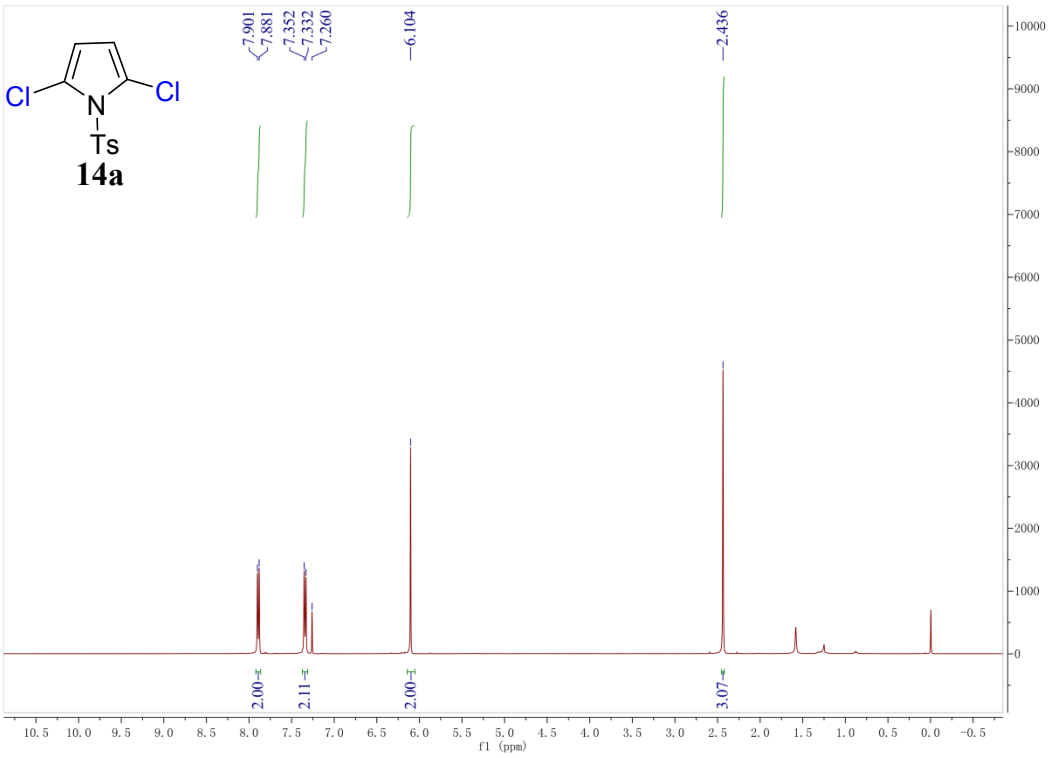

140.163
139.738
137.571
135.606
132.443
130.453
130.197
129.195
128.534
128.277
127.253
117.496
77.477
77.160
76.842
75.995
Cl
N
N
Cl
11a
f1 (ppm)

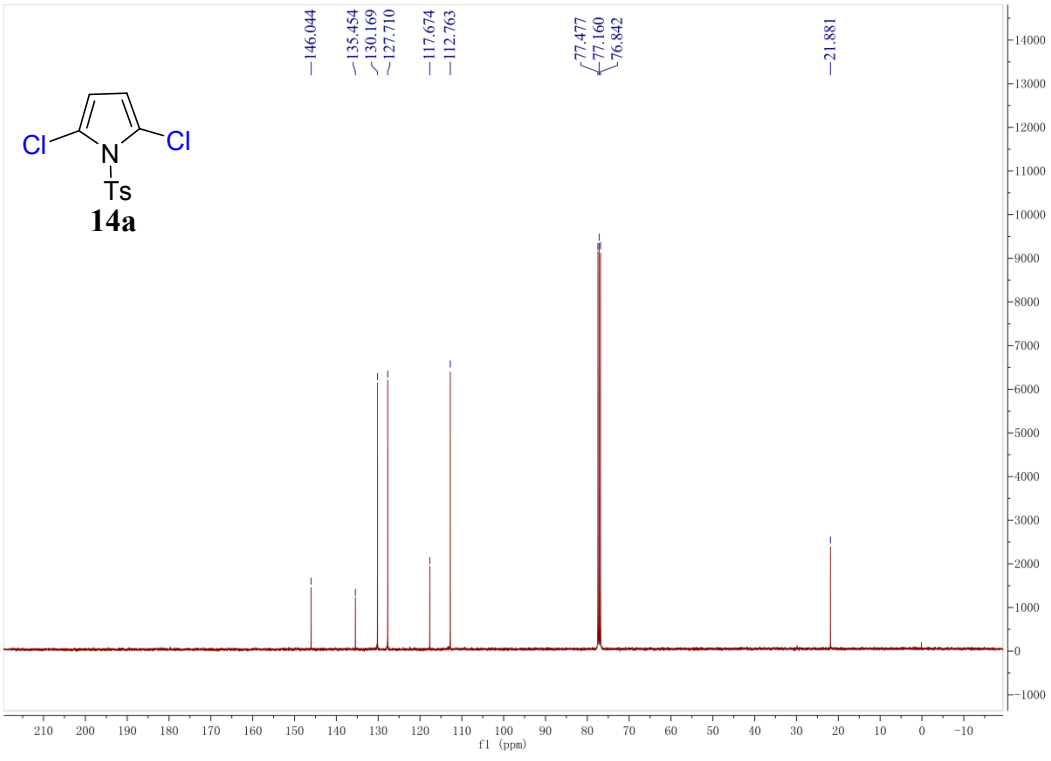

Cl
Cl
N
Boc
12a
8.115
8.095
7.526
7.525
7.508
7.505
7.372
7.368
7.354
7.350
7.333
7.329
7.318
7.315
7.299
7.297
7.280
7.278
7.250
1.690
1.00
0.99
2.09
9.42
f1 (ppm)

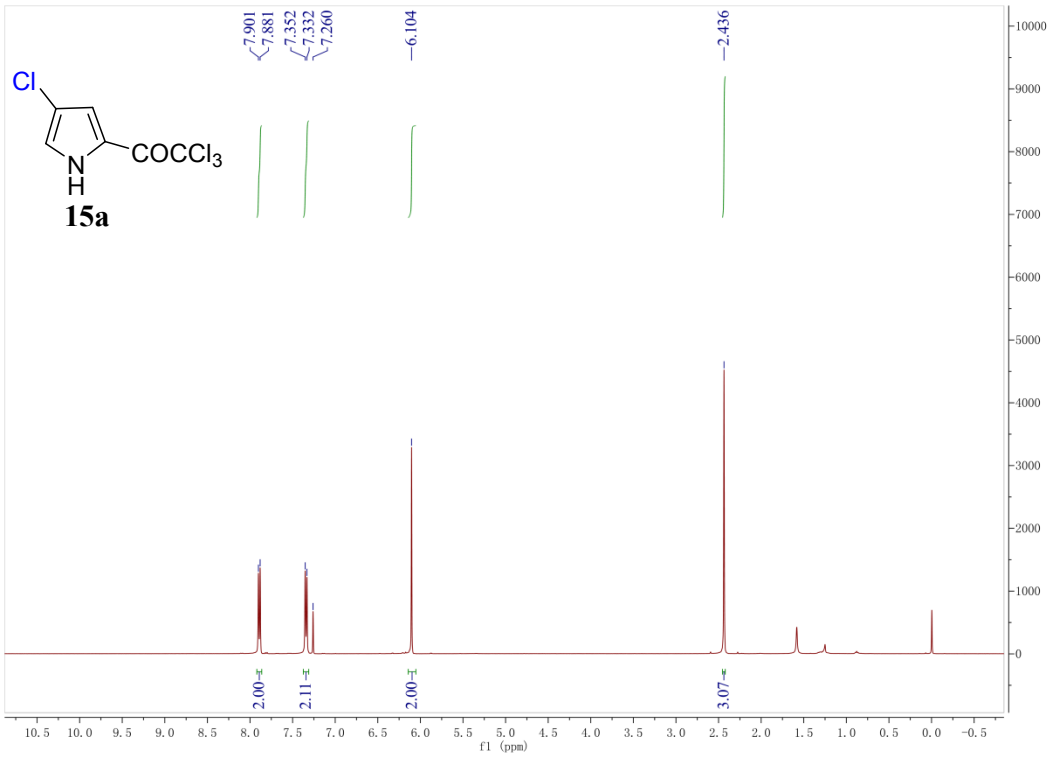

Cl
Cl
N
Boc
12a
148.633
134.349
126.008
125.676
123.786
121.756
117.921
115.462
112.185
85.642
77.477
77.160
76.842
28.293
f1 (ppm)

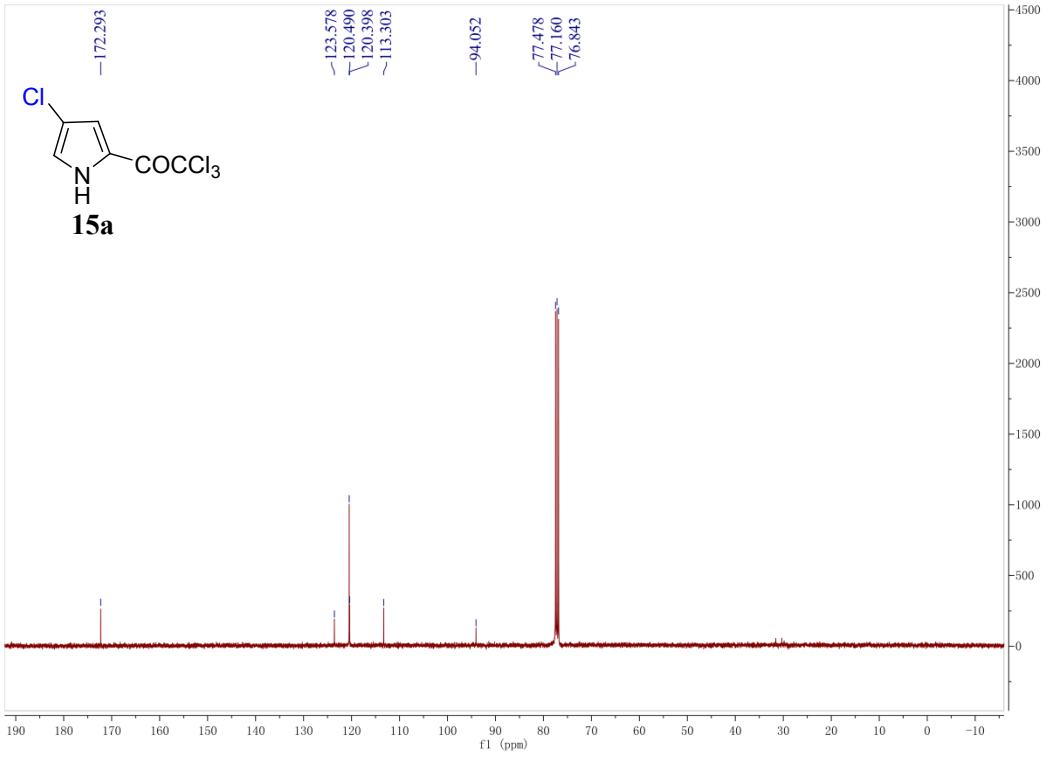

7.479
7.459
7.440
7.397
7.378
7.326
7.308
7.289
7.260
3.071
2.296
Ph
N
N
O
Cl
13a
2.00
2.00
1.00
3.00
3.00
f1 (ppm)

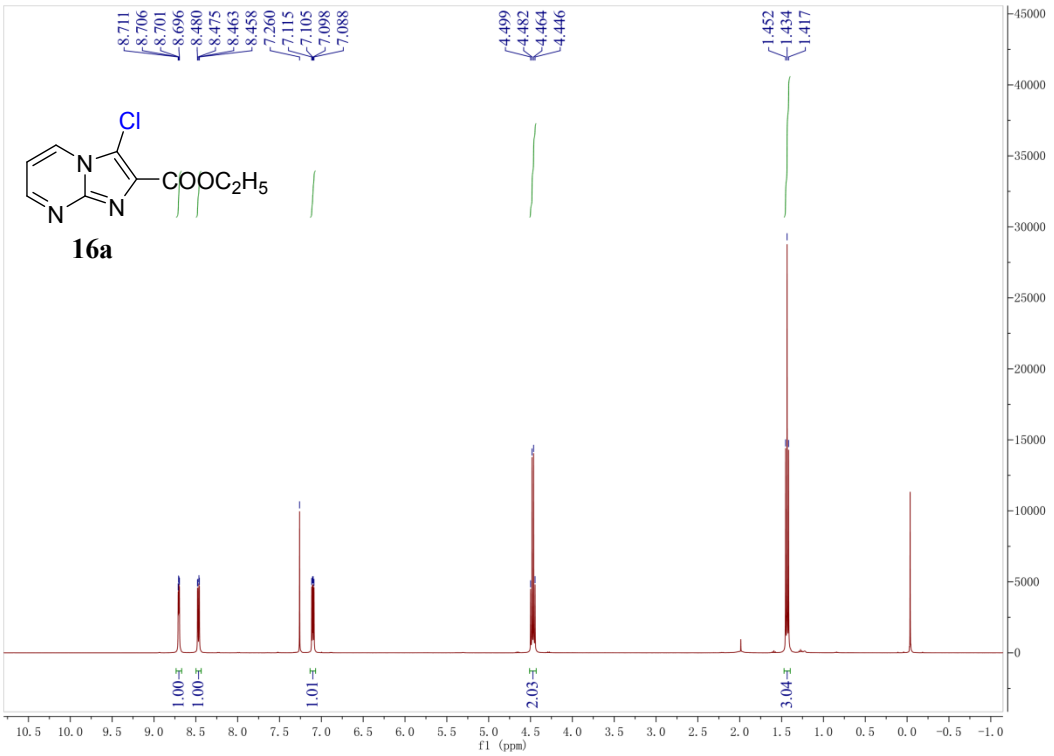

161.567
152.009
134.775
129.413
127.222
124.273
103.507
77.478
77.160
76.843
36.592
11.346
Ph
N
N
O
Cl
13a
f1 (ppm)

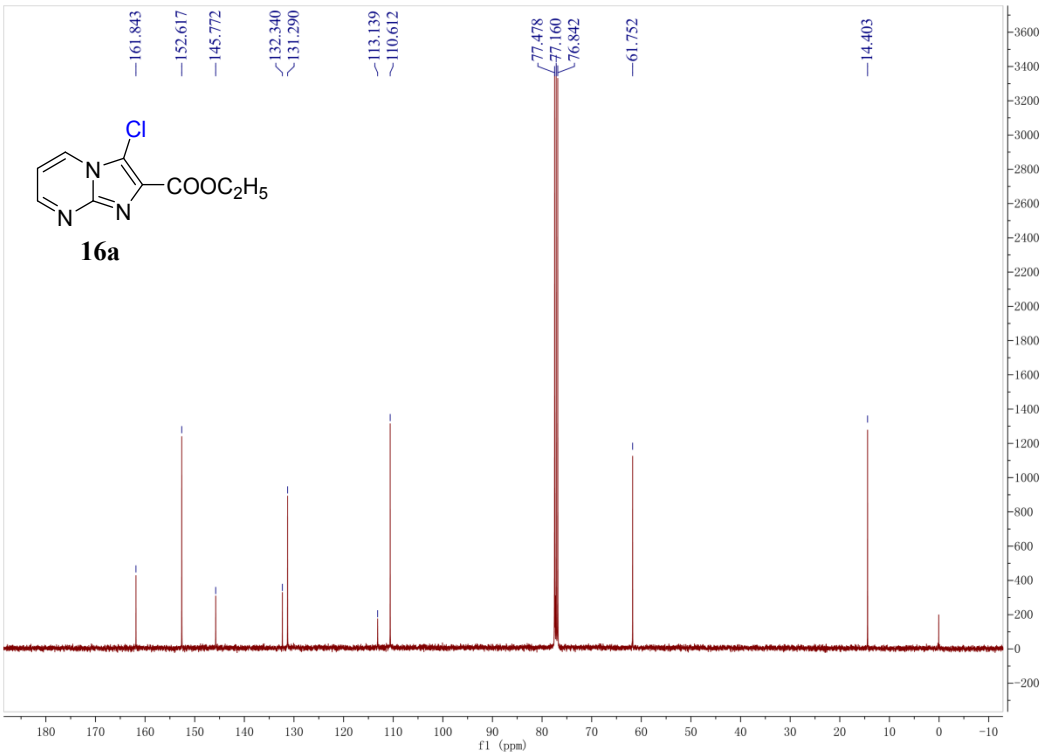

Cl
N
Cl
Ts
14a
7.901
7.881
7.352
7.332
7.260
6.104
2.436
2.00
2.11
2.00
3.07
f1 (ppm)

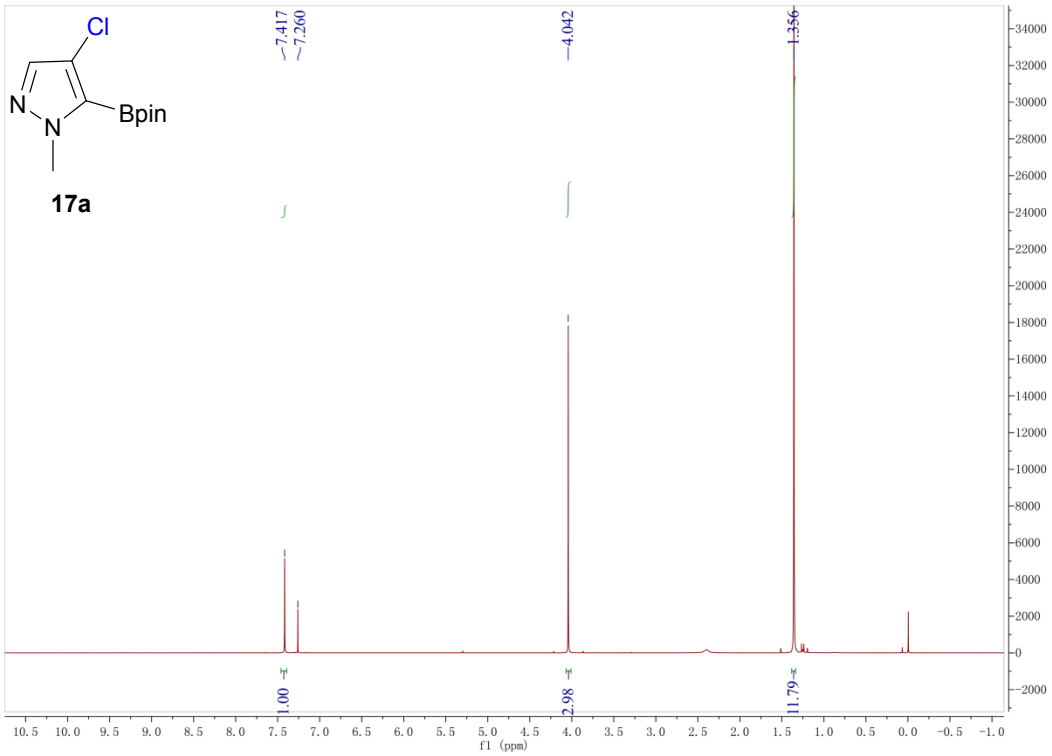

Cl
N
Cl
Ts
14a
146.044
135.454
130.169
127.710
117.674
112.763
77.477
77.160
76.842
21.881
f1 (ppm)

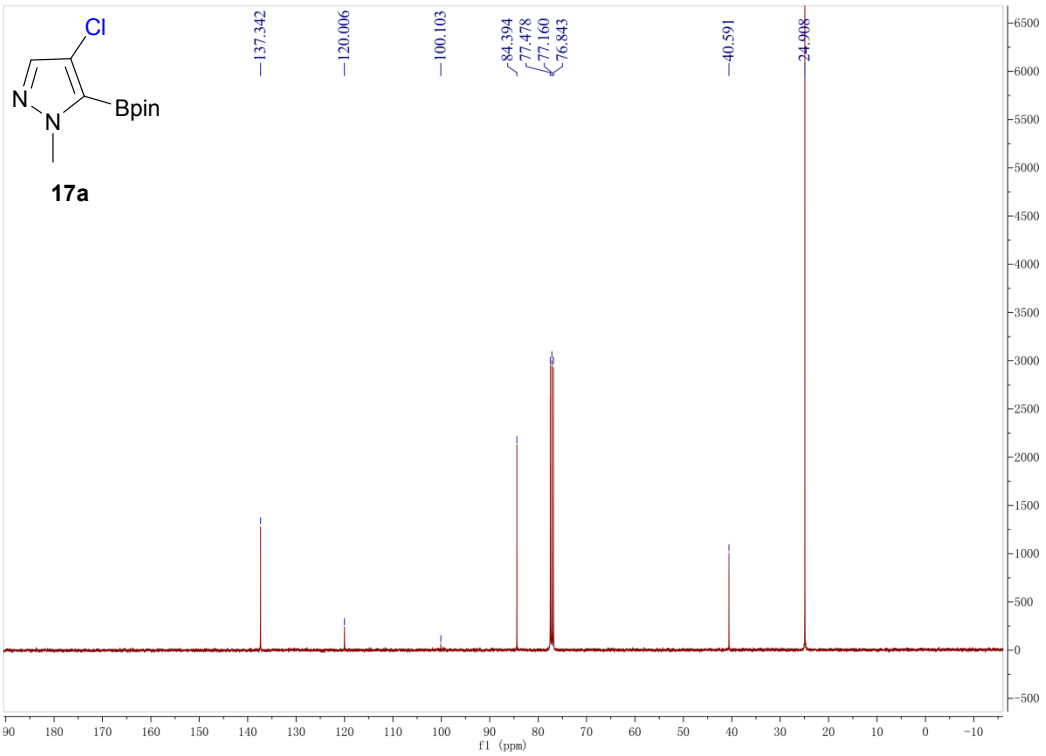

Cl
COCCl3
N
H
15a
7.901
7.881
7.352
7.332
7.260
6.104
2.436
2.00
2.11
2.00
3.07
f1 (ppm)

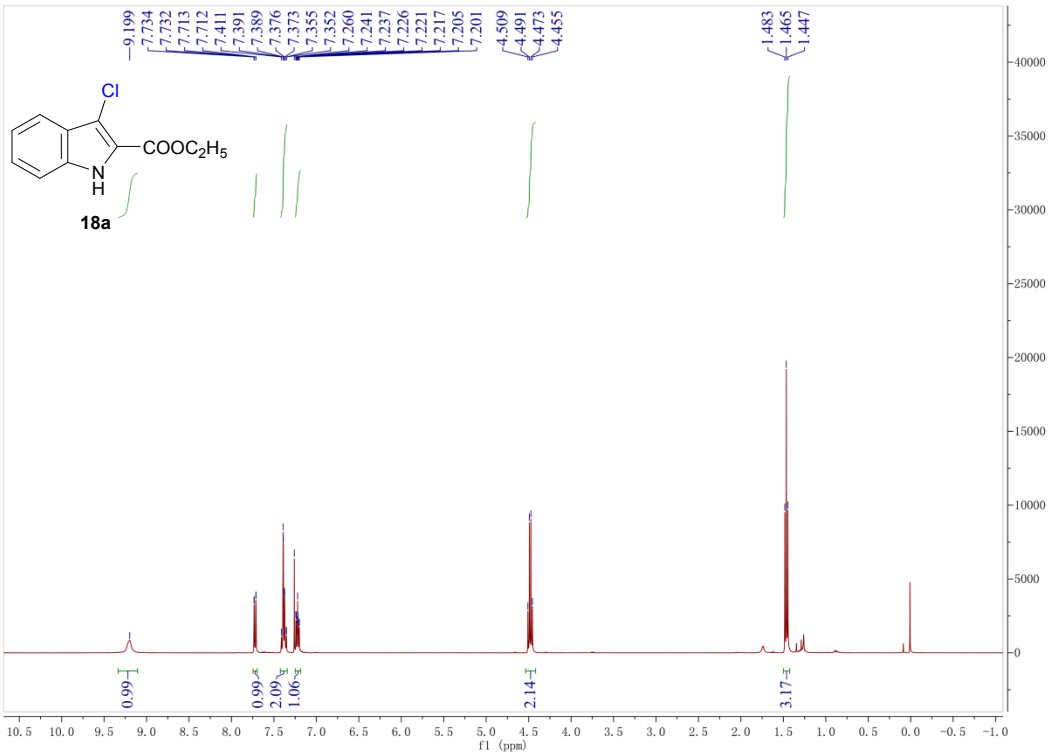

Cl
COCCl3
N
H
15a
172.293
123.578
120.490
120.398
113.303
94.052
77.478
77.160
76.843
f1 (ppm)

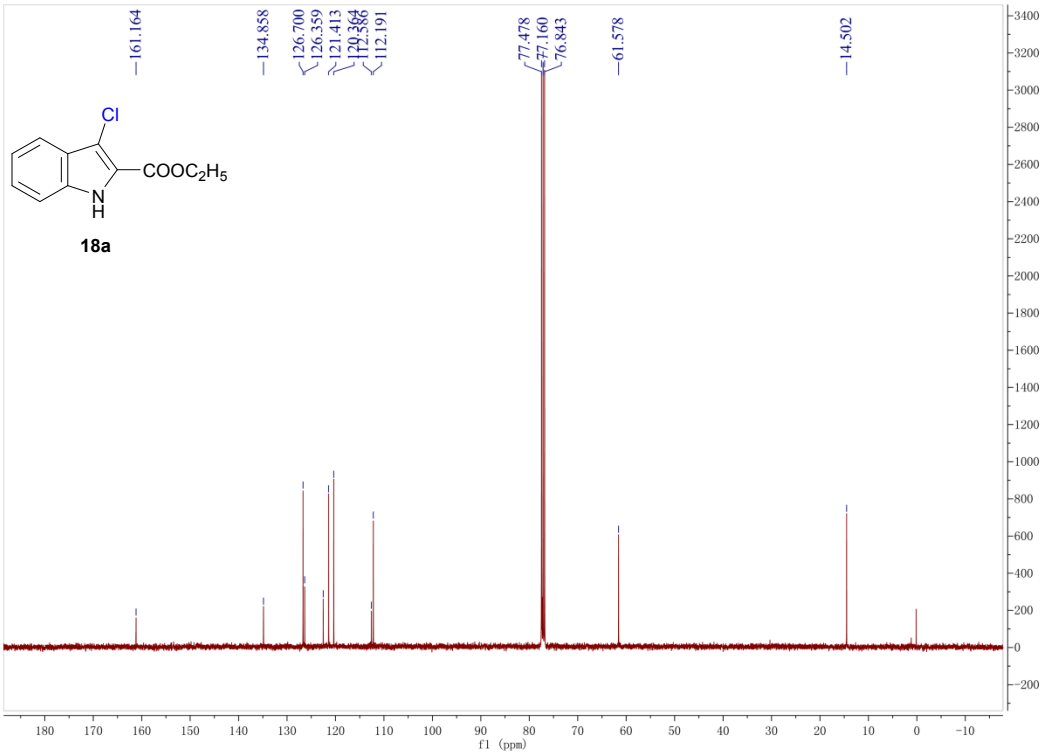

8.711
8.706
8.701
8.696
8.480
8.475
8.463
8.458
7.260
7.115
7.105
7.098
7.088
4.499
4.482
4.464
4.446
1.452
1.434
1.417
Cl
N
N
N
COOC2H5
16a
1.00
1.00
1.01
2.03
3.04
f1 (ppm)

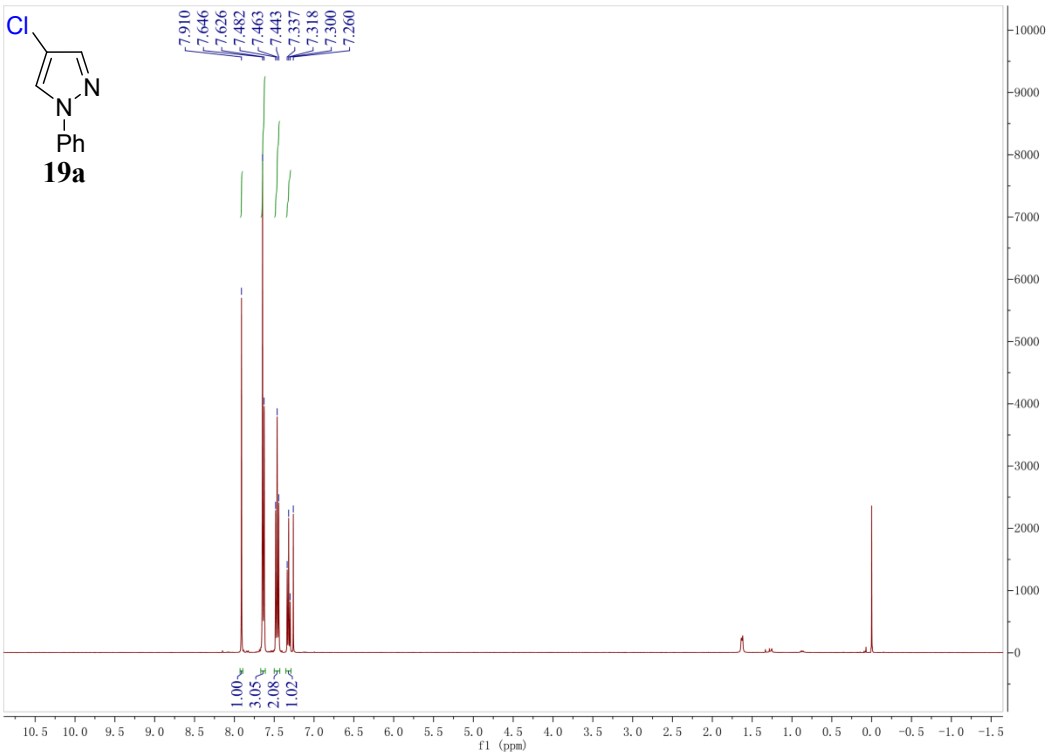

161.843
152.617
145.772
132.340
131.290
113.139
110.612
77.478
77.160
76.842
61.752
14.403
Cl
N
N
N
COOC2H5
16a
f1 (ppm)

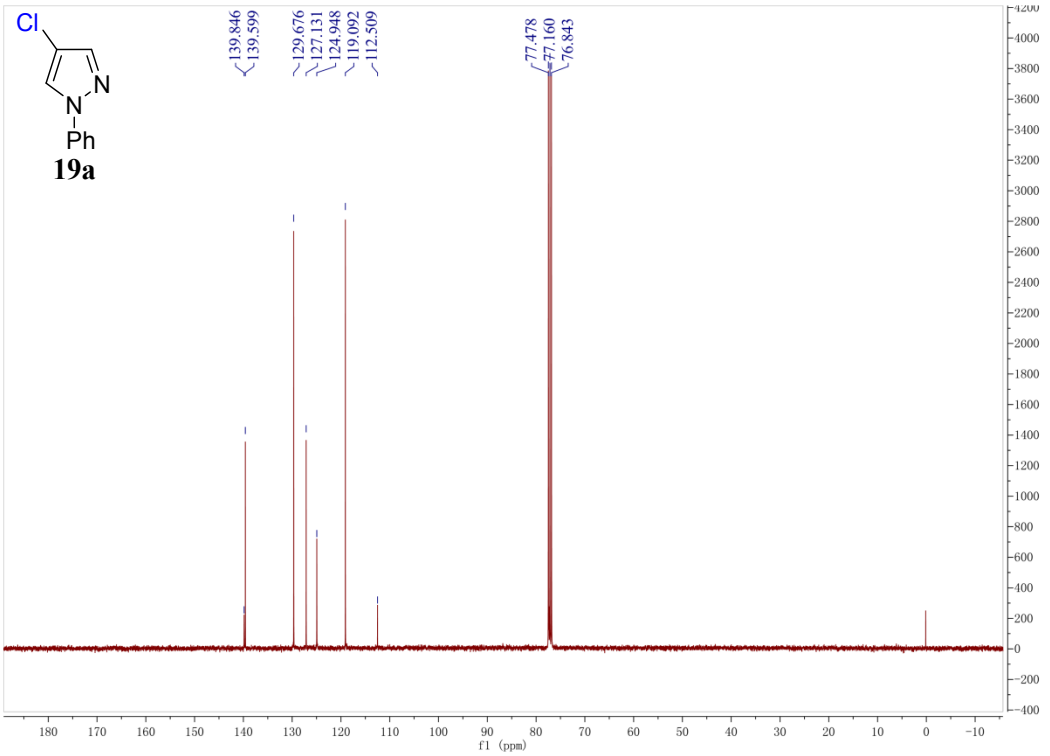

Cl
N
N
Bpin
17a
7.417
7.260
4.042
1.356
1.00
2.98
11.79
f1 (ppm)

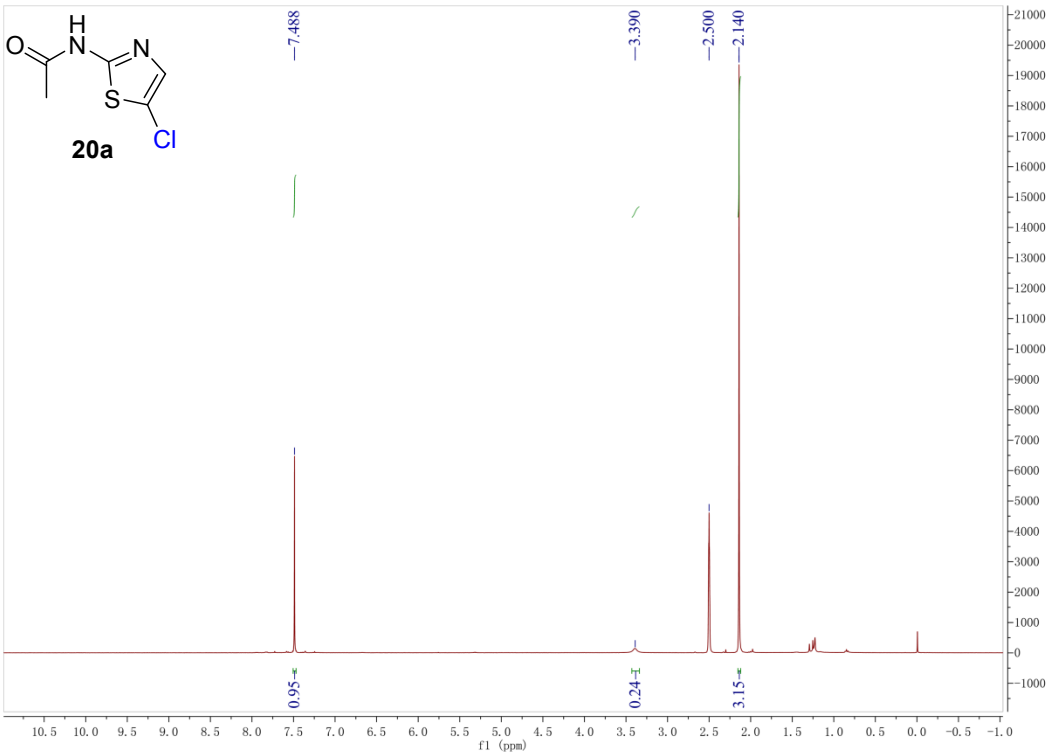

Cl
N
N
Bpin
17a
137.342
120.006
100.103
84.394
77.478
77.160
76.843
40.591
24.908
f1 (ppm)

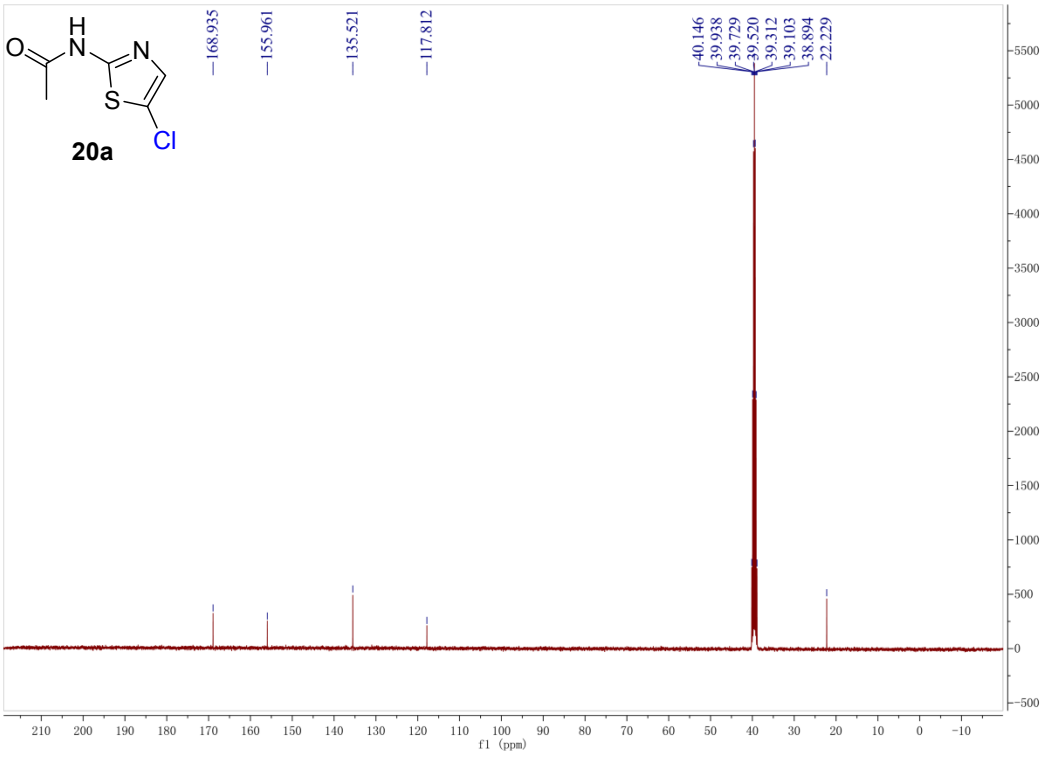

9.199
7.734
7.732
7.713
7.712
7.411
7.391
7.389
7.376
7.373
7.355
7.352
7.260
7.241
7.237
7.226
7.221
7.217
7.205
7.201
4.509
4.491
4.473
4.455
1.483
1.465
1.447
Cl
COOC2H5
N
H
18a
0.99
0.99
2.09
1.06
2.14
3.17
f1 (ppm)

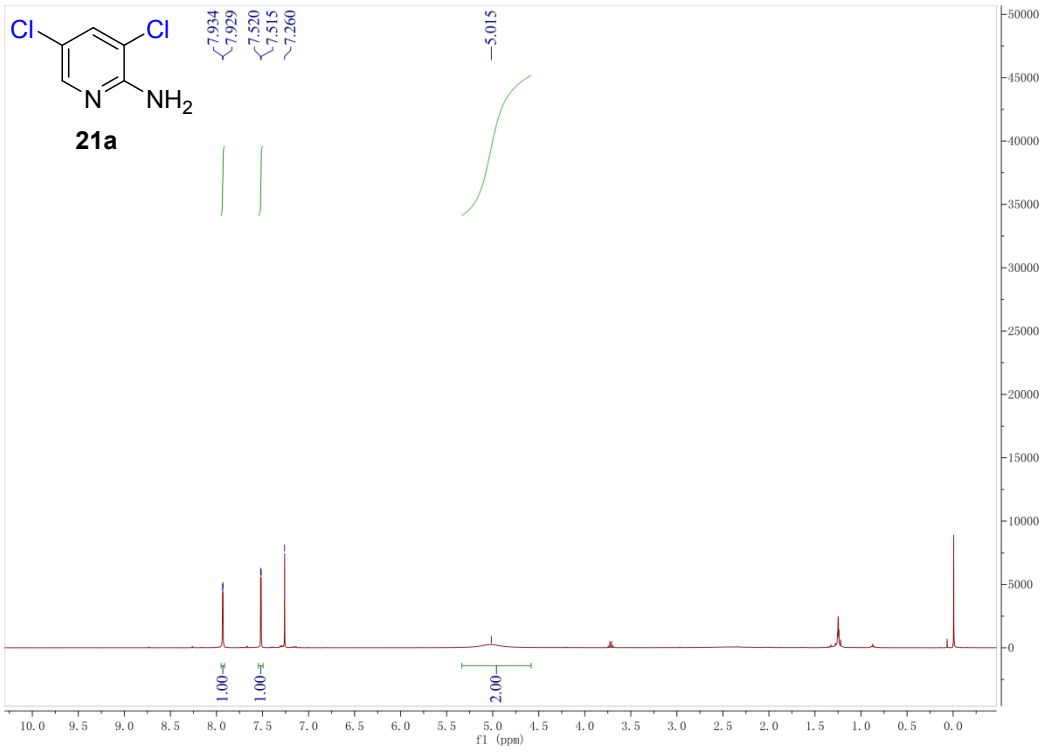

161.164
134.858
126.700
126.359
121.413
120.364
112.586
112.191
77.478
77.160
76.843
61.578
14.502
Cl
COOC2H5
N
H
18a
f1 (ppm)

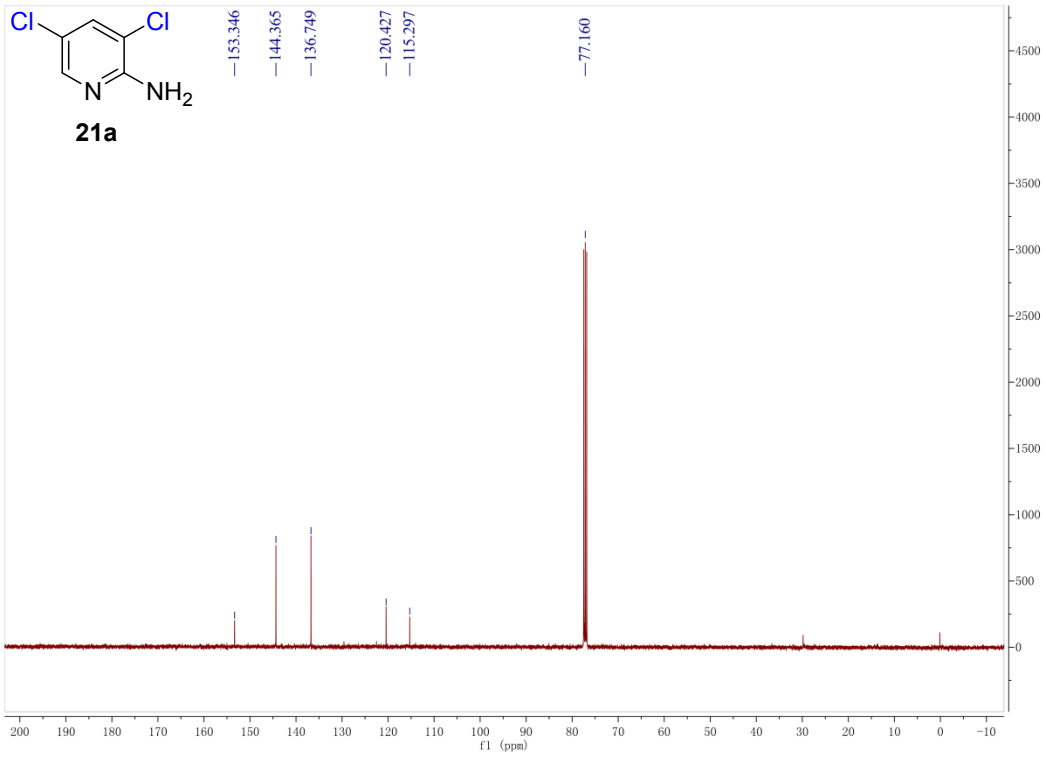

Cl
N
N
Ph
19a
7.910
7.646
7.626
7.482
7.463
7.443
7.337
7.318
7.300
7.260
1.00
3.05
2.08
1.02
f1 (ppm)

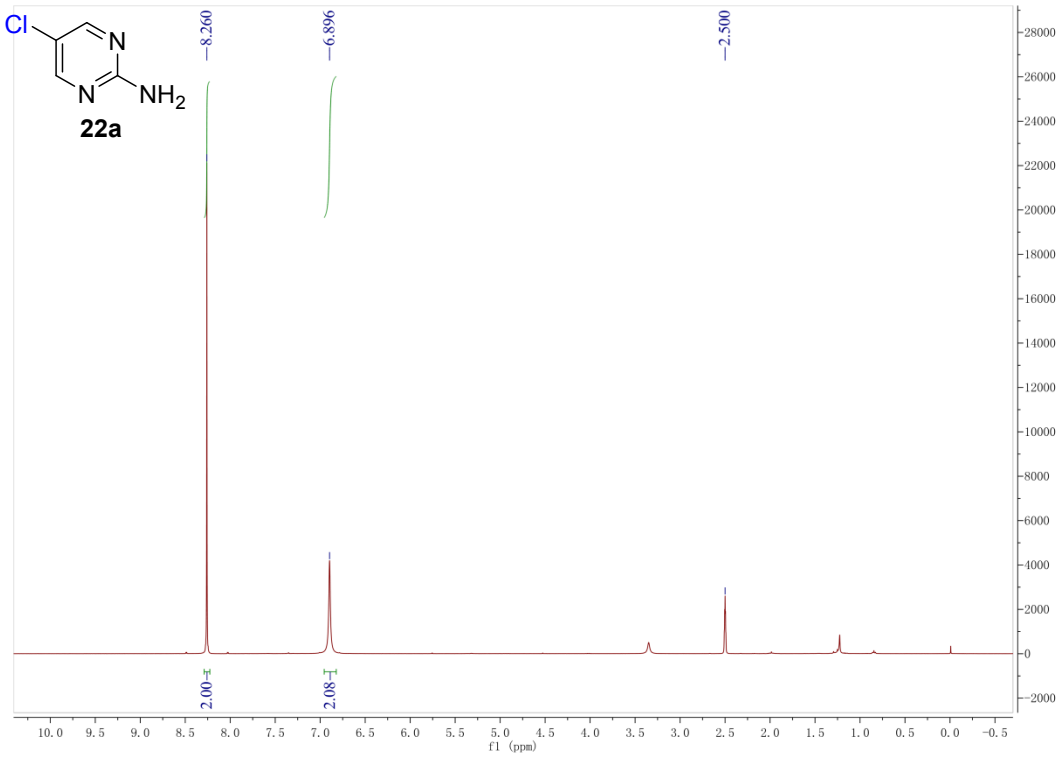

Cl
N
N
Ph
19a
139.846
139.599
129.676
127.131
124.948
119.092
112.509
77.478
77.160
76.843
f1 (ppm)

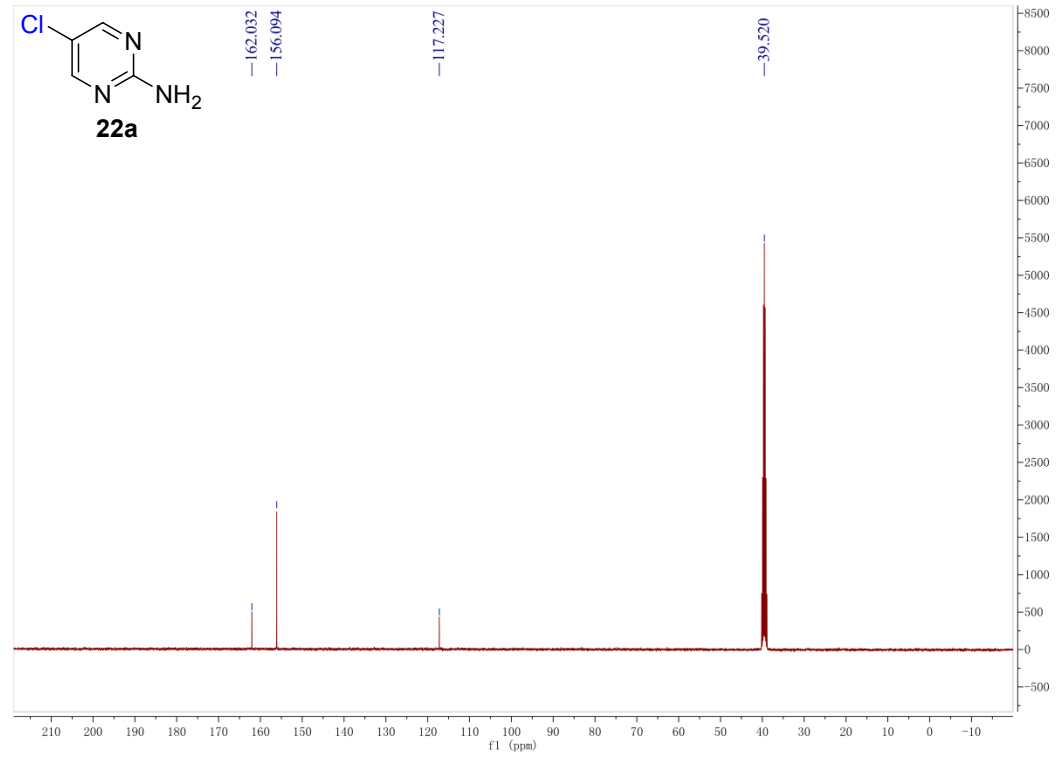

20a
7.488
3.390
2.500
2.140
0.95
0.24
3.15
f1 (ppm)

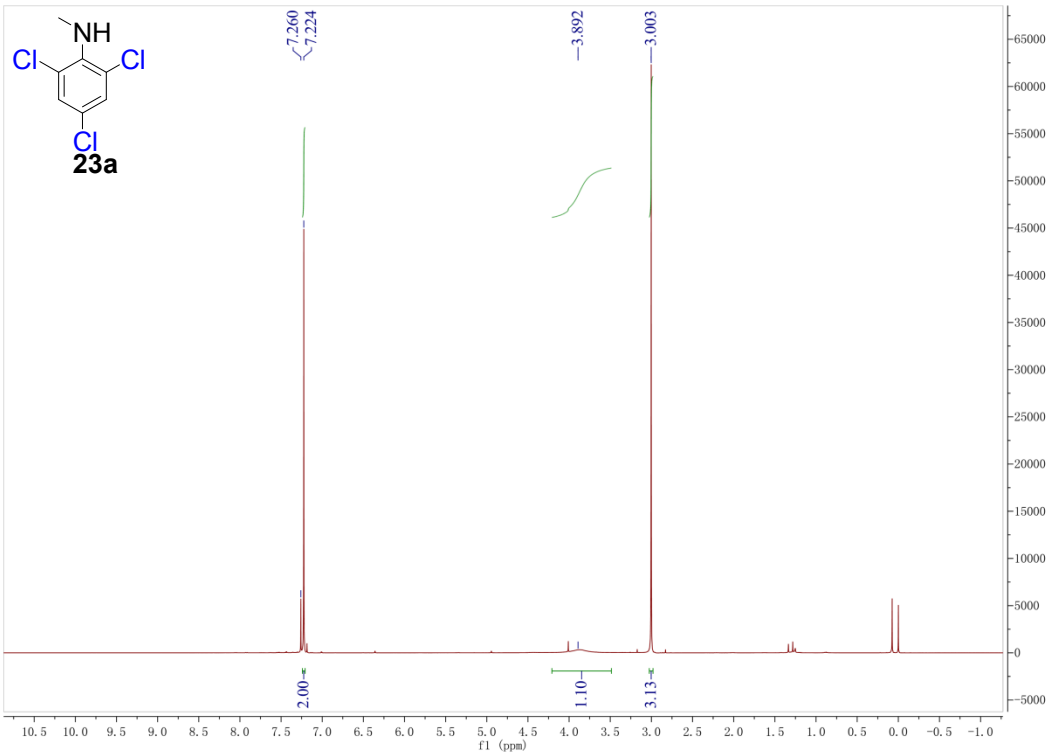

20a
168.935
155.961
135.521
117.812
40.146
39.938
39.729
39.520
39.312
39.103
38.894
22.229
f1 (ppm)

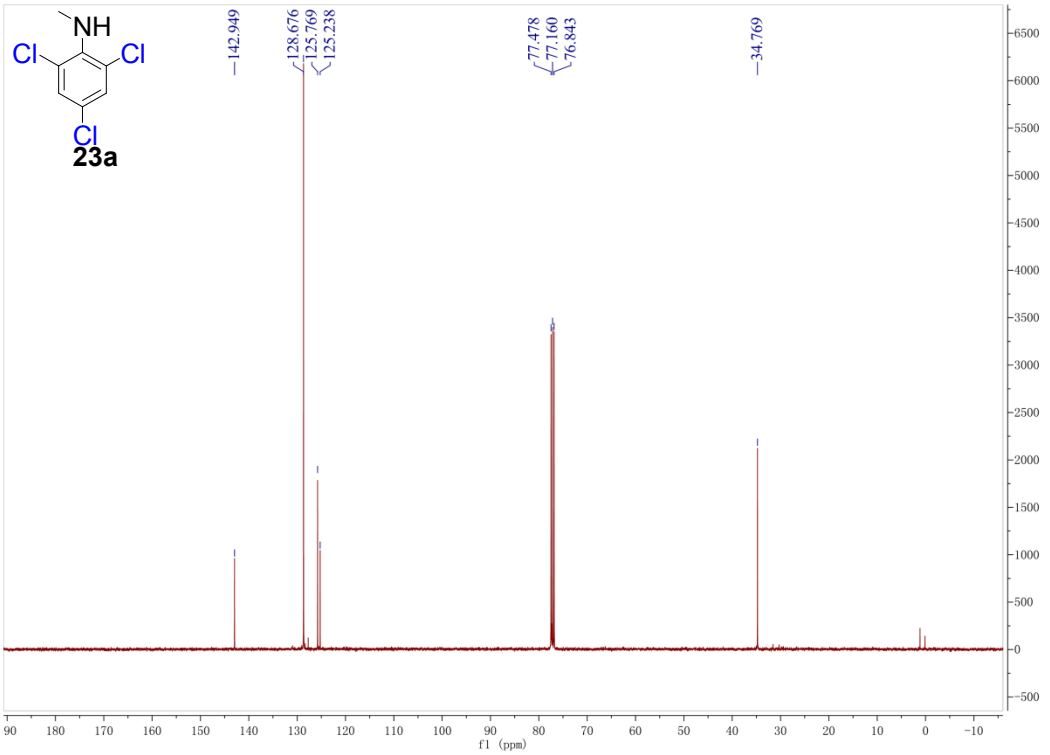

Cl
Cl
N
NH2
21a
7.934
7.929
7.520
7.515
7.260
5.015
1.00
1.00
2.00
f1 (ppm)

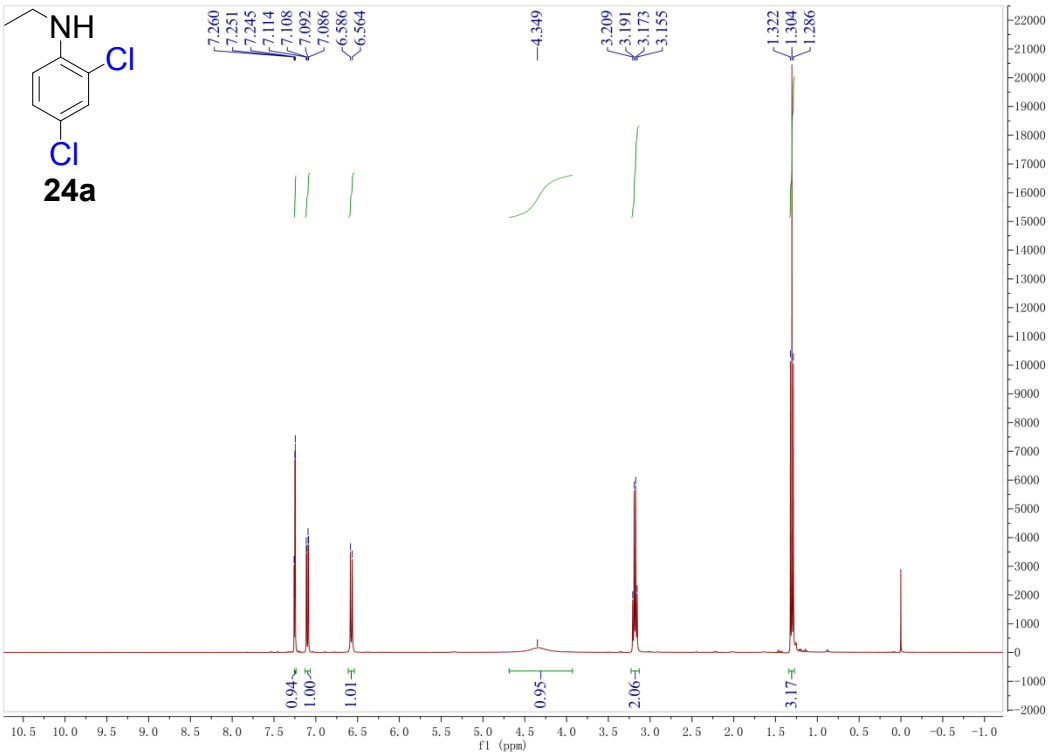

Cl
Cl
N
NH2
21a
153.346
144.365
136.749
120.427
115.297
77.160
f1 (ppm)

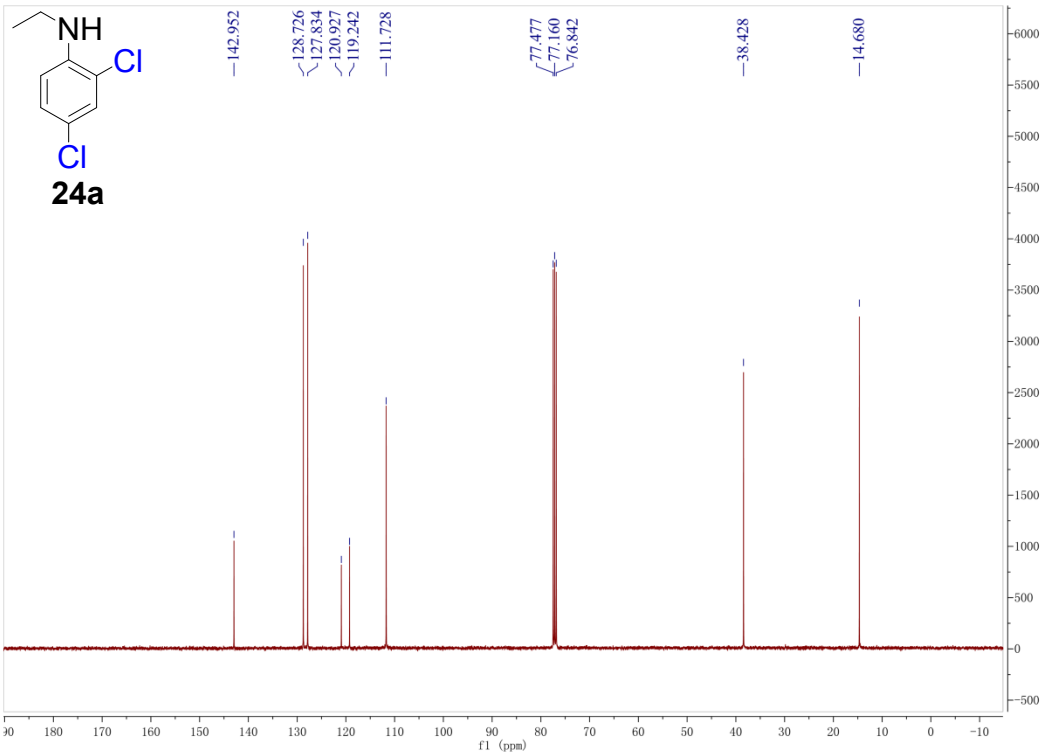

Cl
N
N
NH2
22a
8.260
6.896
2.500
2.00
2.08
f1 (ppm)

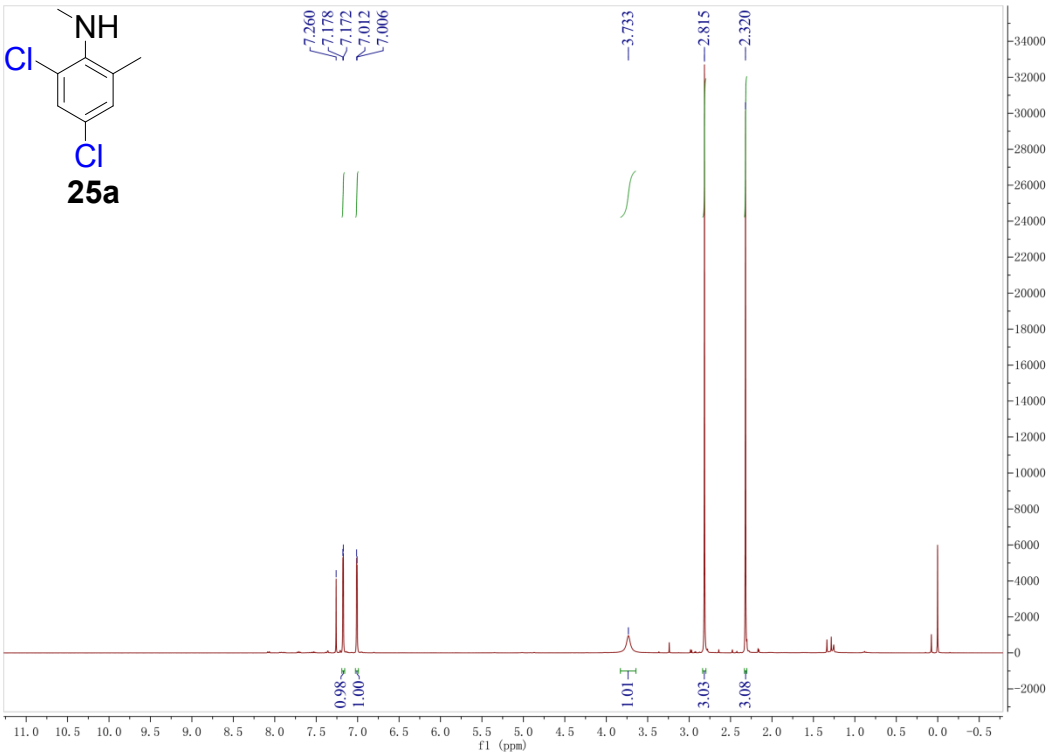

Cl
N
N
NH2
22a
162.032
156.094
117.227
39.520
f1 (ppm)

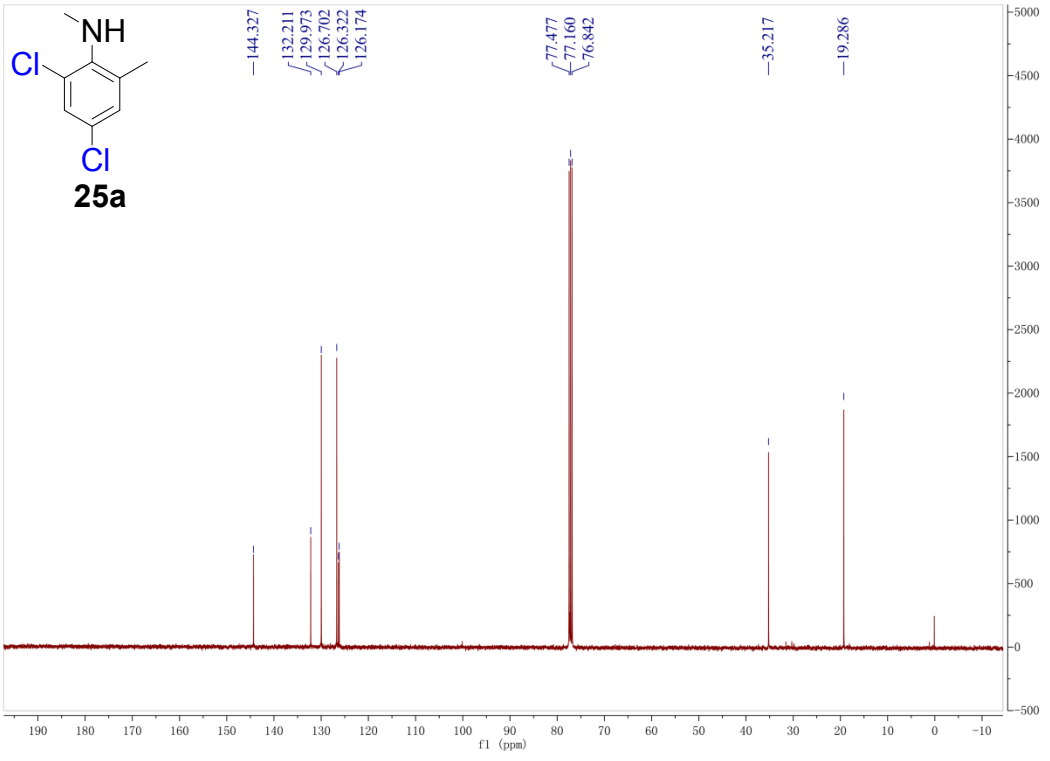

NH
Cl
Cl
Cl
23a
7.260
7.224
3.892
3.003
2.00
1.10
3.13
f1 (ppm)

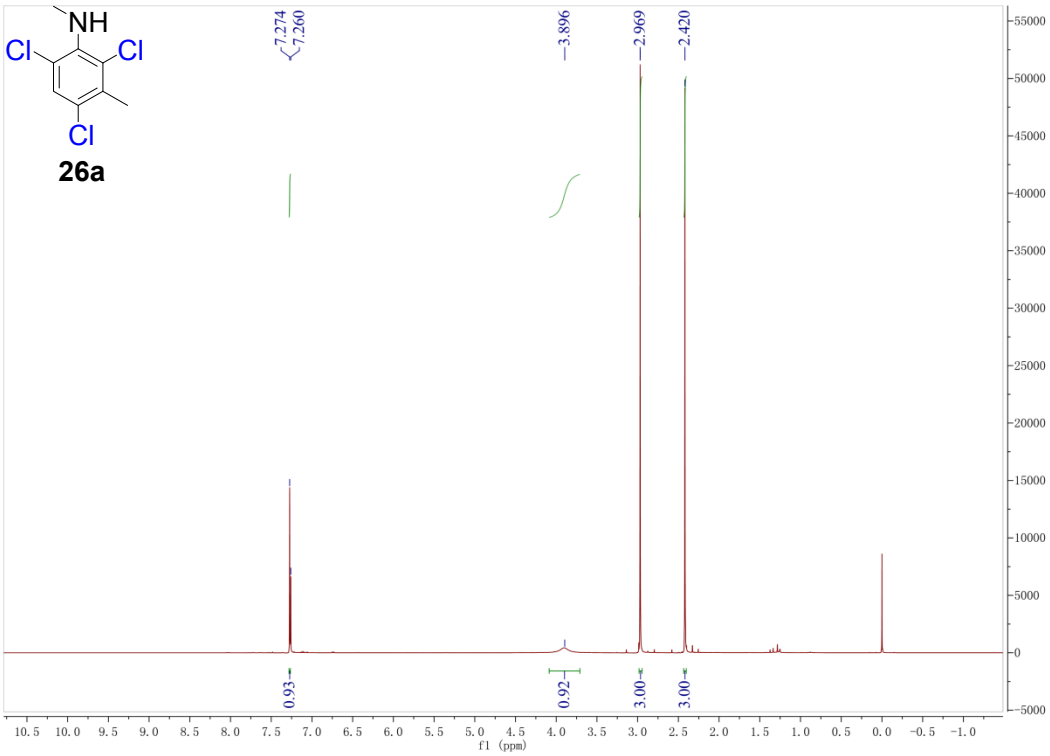

NH
Cl
Cl
Cl
23a
142.949
128.676
125.769
125.238
77.478
77.160
76.843
34.769
f1 (ppm)

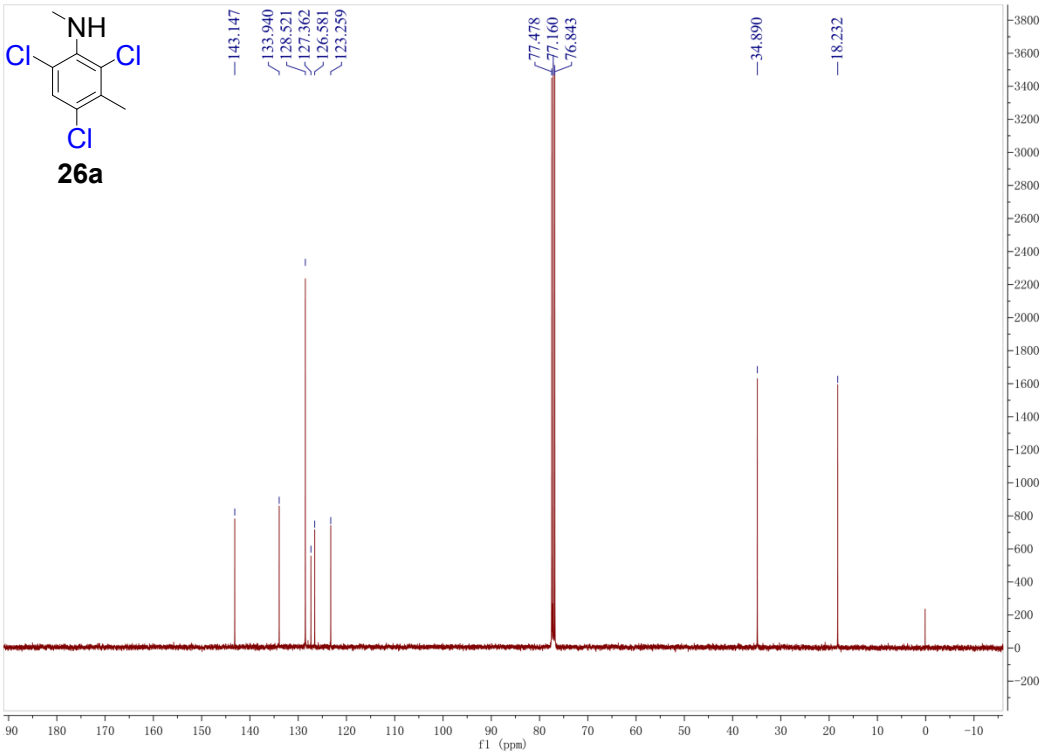

NH
Cl
Cl
24a
7.260
7.251
7.245
7.114
7.108
7.092
7.086
6.586
6.564
4.349
3.209
3.191
3.173
3.155
1.322
1.304
1.286
0.94
1.00
1.01
0.95
2.06
3.17
f1 (ppm)

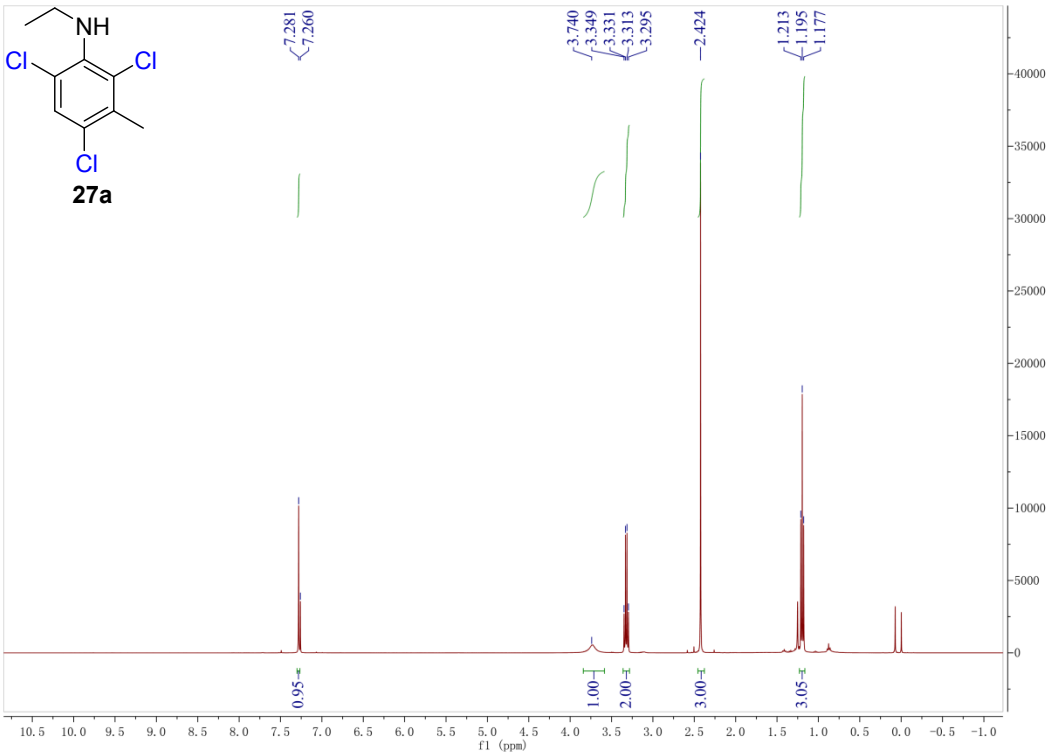

NH
Cl
Cl
24a
142.952
128.726
127.834
120.927
119.242
111.728
77.477
77.160
76.842
38.428
14.680
f1 (ppm)

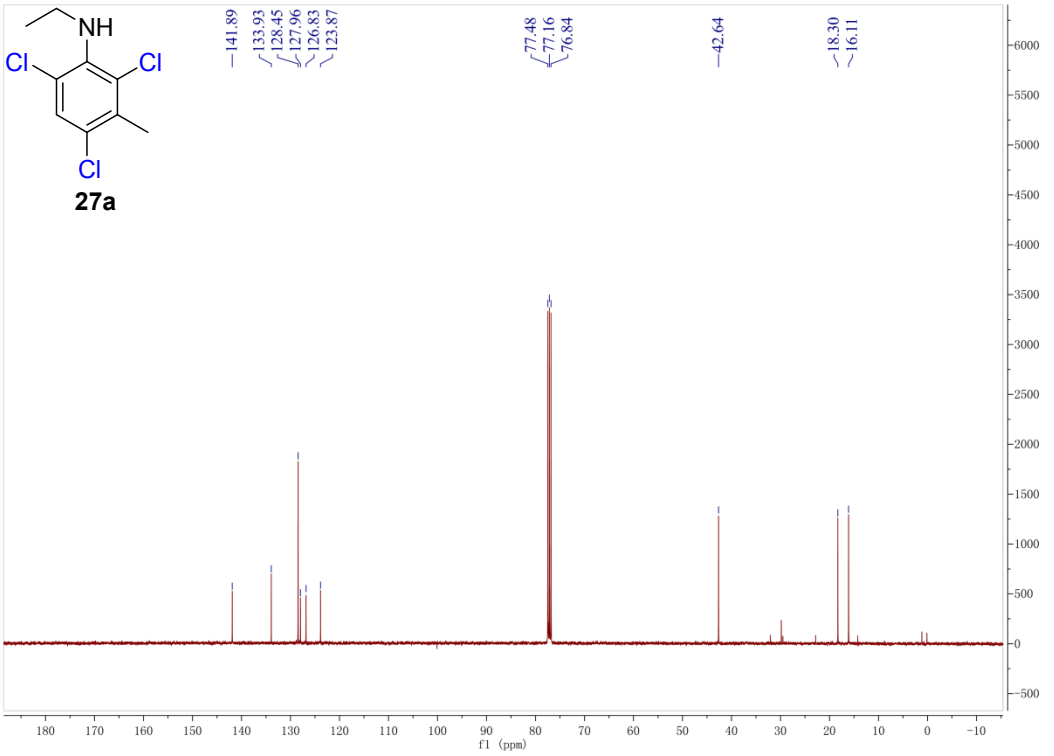

NH
Cl
Cl
25a
7.260
7.178
7.172
7.012
7.006
3.733
2.815
2.320
0.98
1.00
1.01
3.03
3.08
f1 (ppm)

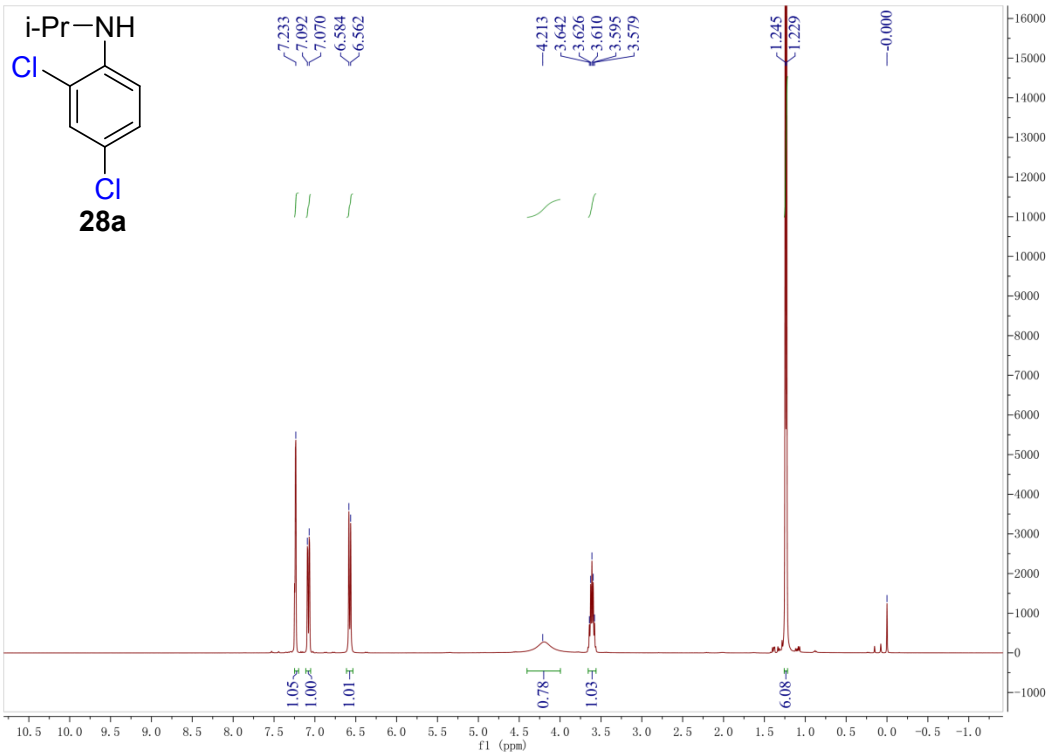

NH
Cl
Cl
25a
144.327
132.211
129.973
126.702
126.322
126.174
77.477
77.160
76.842
35.217
19.286
f1 (ppm)

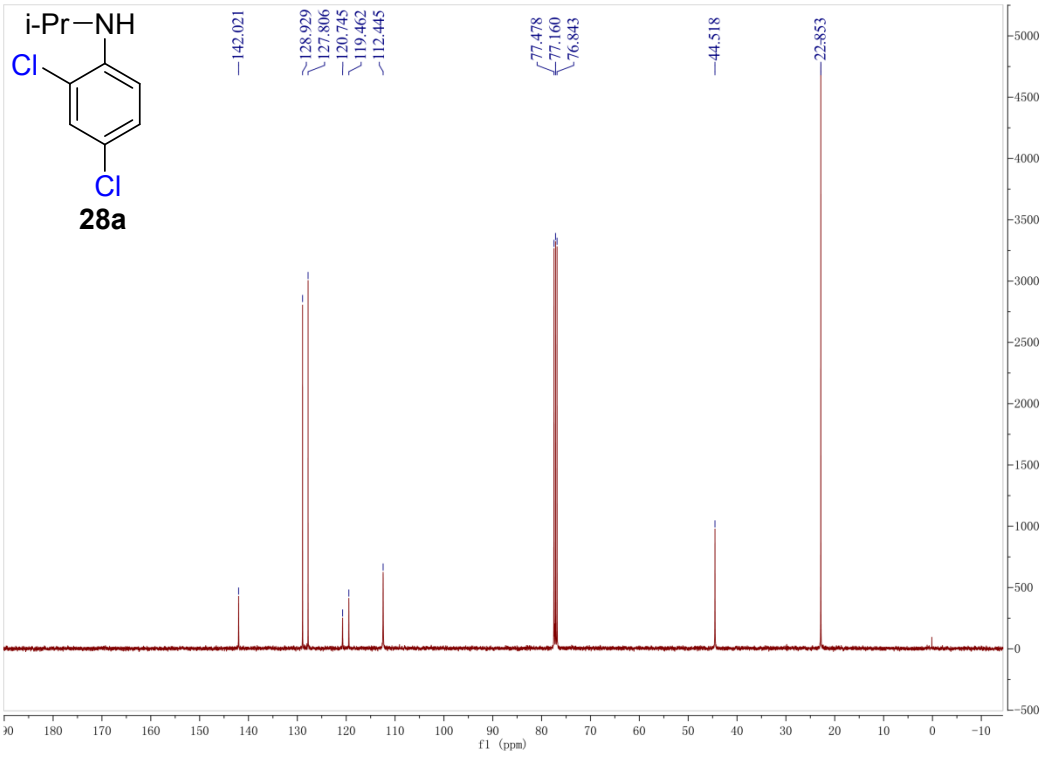

NH
Cl
Cl
Cl
26a
7.274
7.260
3.896
2.969
2.420
0.93
0.92
3.00
3.00
f1 (ppm)

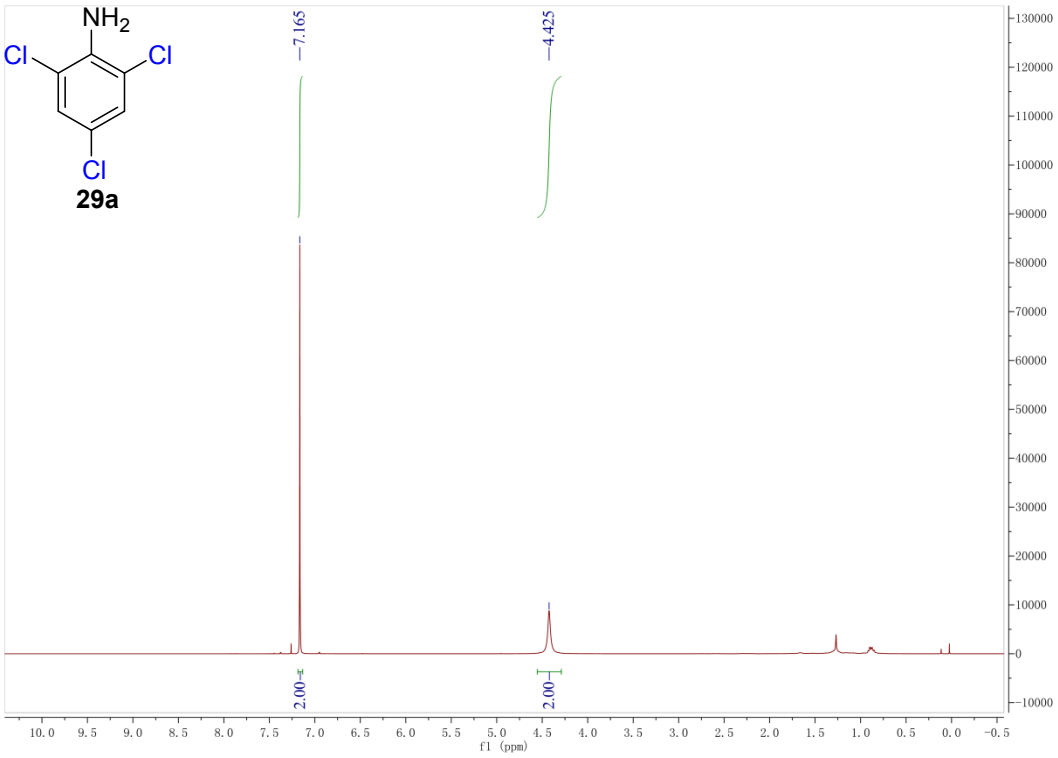

NH
Cl
Cl
Cl
26a
143.147
133.940
128.521
127.362
126.581
123.259
77.478
77.160
76.843
34.890
18.232
f1 (ppm)

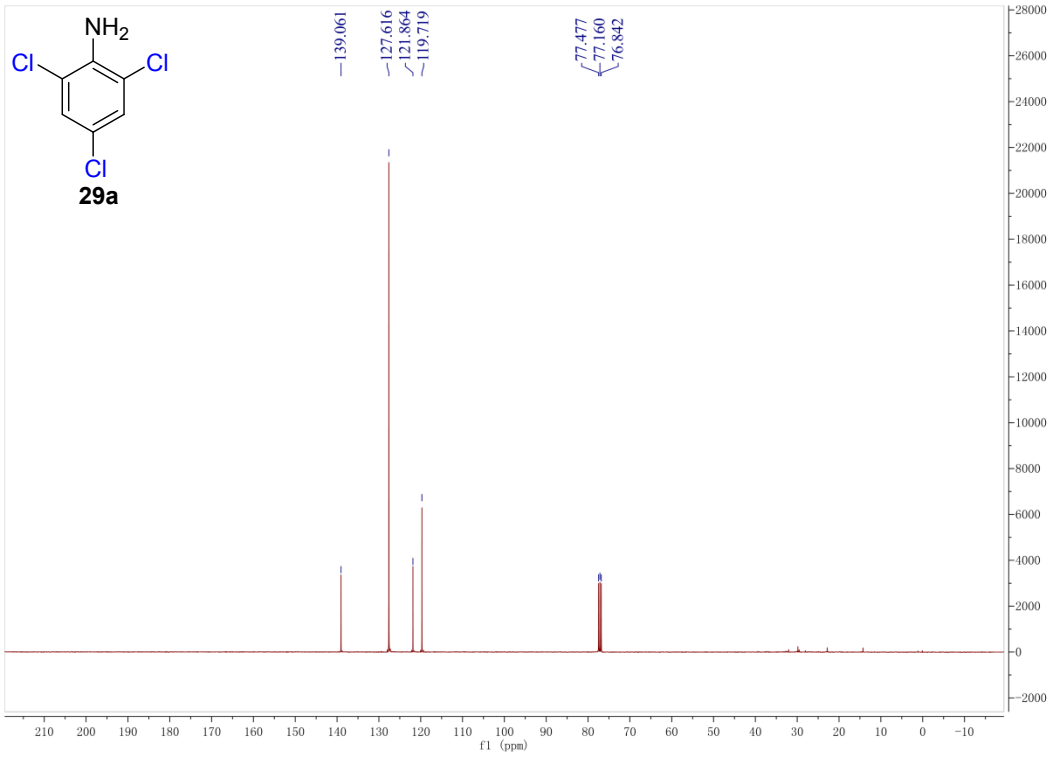

NH
Cl
Cl
Cl
27a
7.281
7.260
3.740
3.349
3.331
3.313
3.295
2.424
1.213
1.195
1.177
0.95
1.00
2.00
3.00
3.05
f1 (ppm)

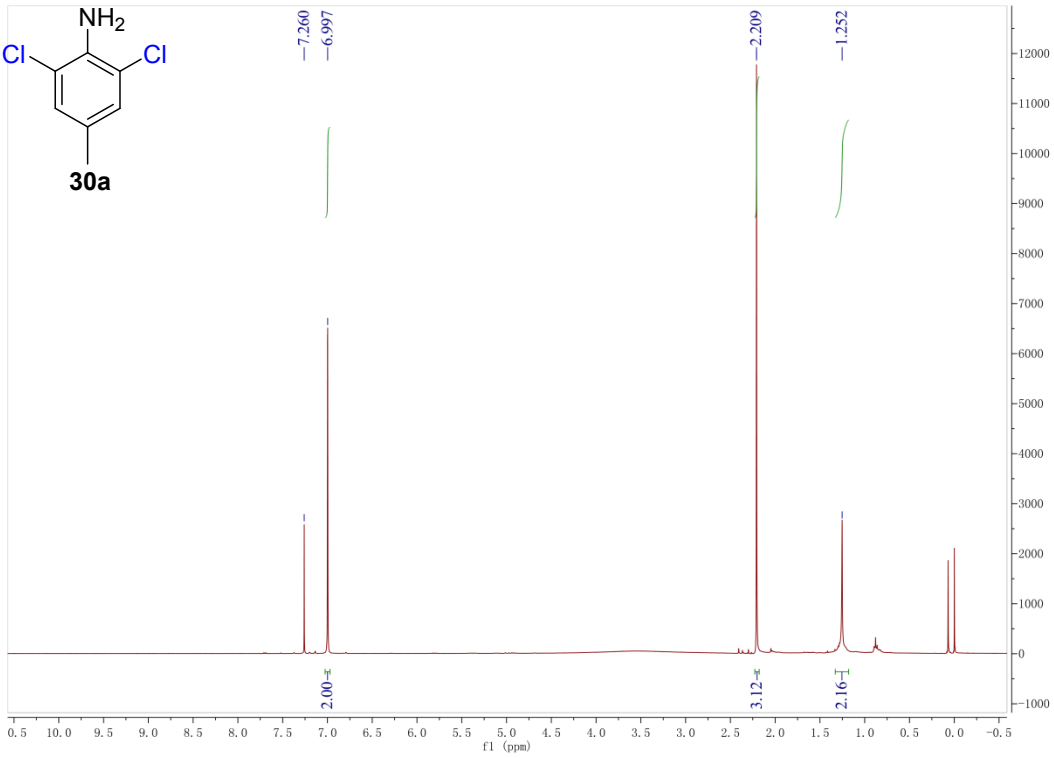

NH
Cl
Cl
Cl
27a
141.89
133.93
128.45
127.96
126.83
123.87
77.48
77.16
76.84
42.64
18.30
16.11
f1 (ppm)

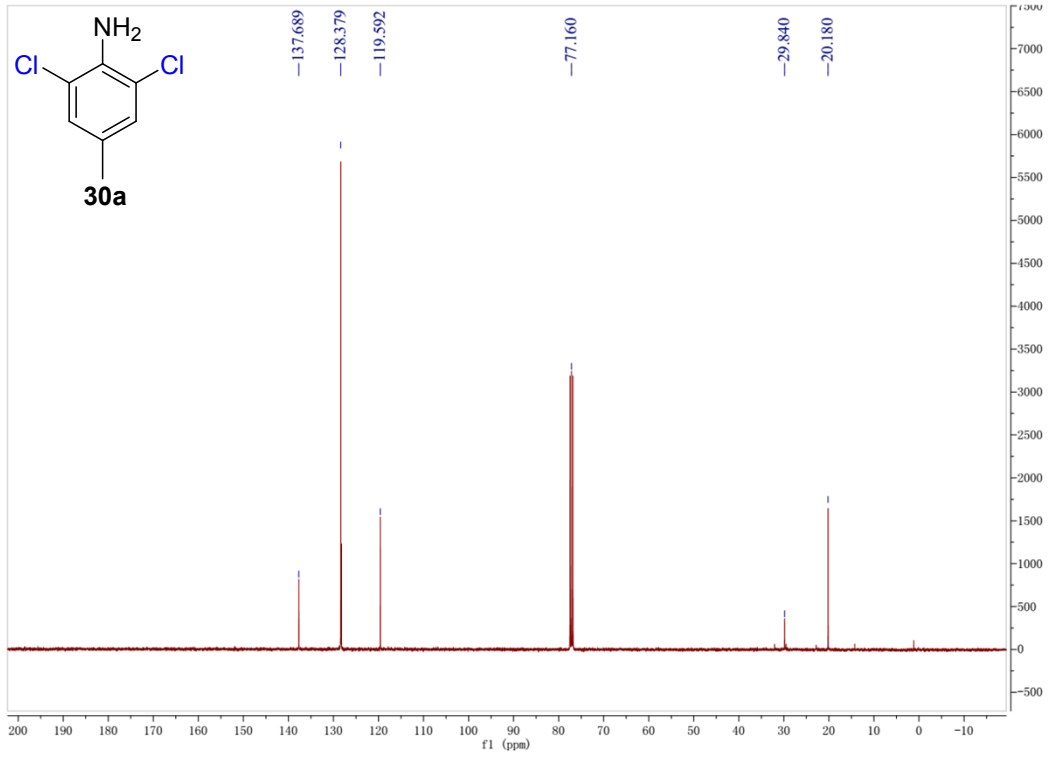

i-Pr—NH
Cl
Cl
28a
7.233
7.092
7.070
6.584
6.562
4.213
3.642
3.626
3.610
3.595
3.579
1.245
1.229
0.000
1.05
1.00
1.01
0.78
1.03
6.08
f1 (ppm)

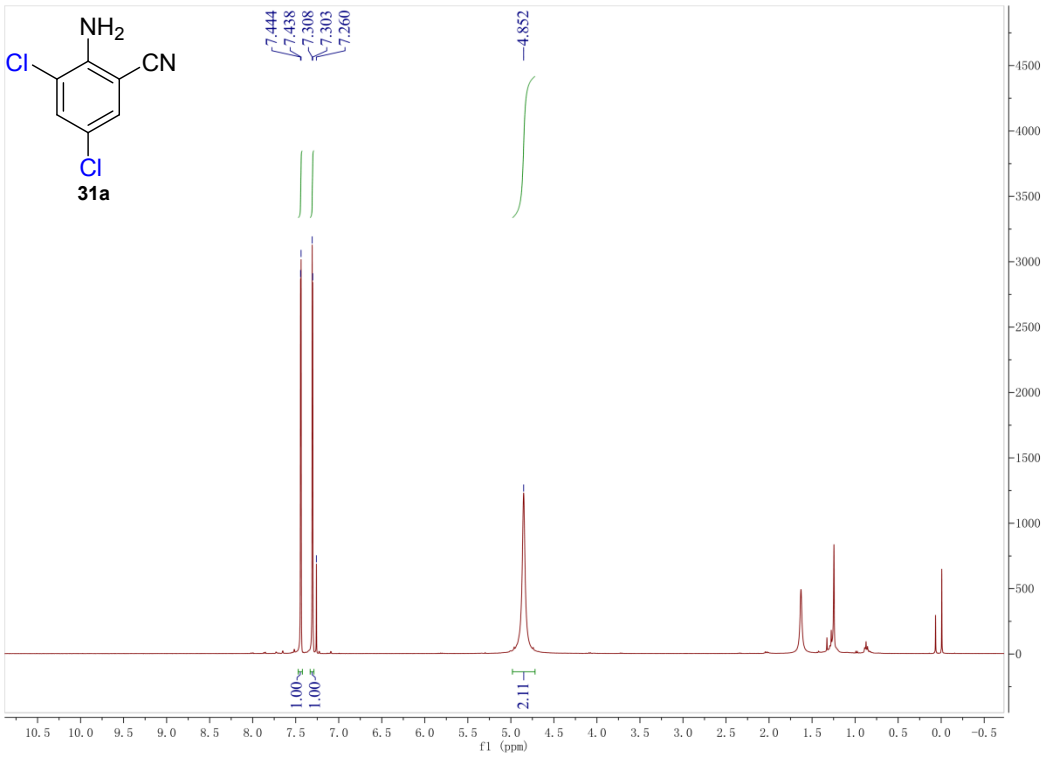

i-Pr—NH
Cl
Cl
28a
142.021
128.929
127.806
120.745
119.462
112.445
77.478
77.160
76.843
44.518
22.853
f1 (ppm)

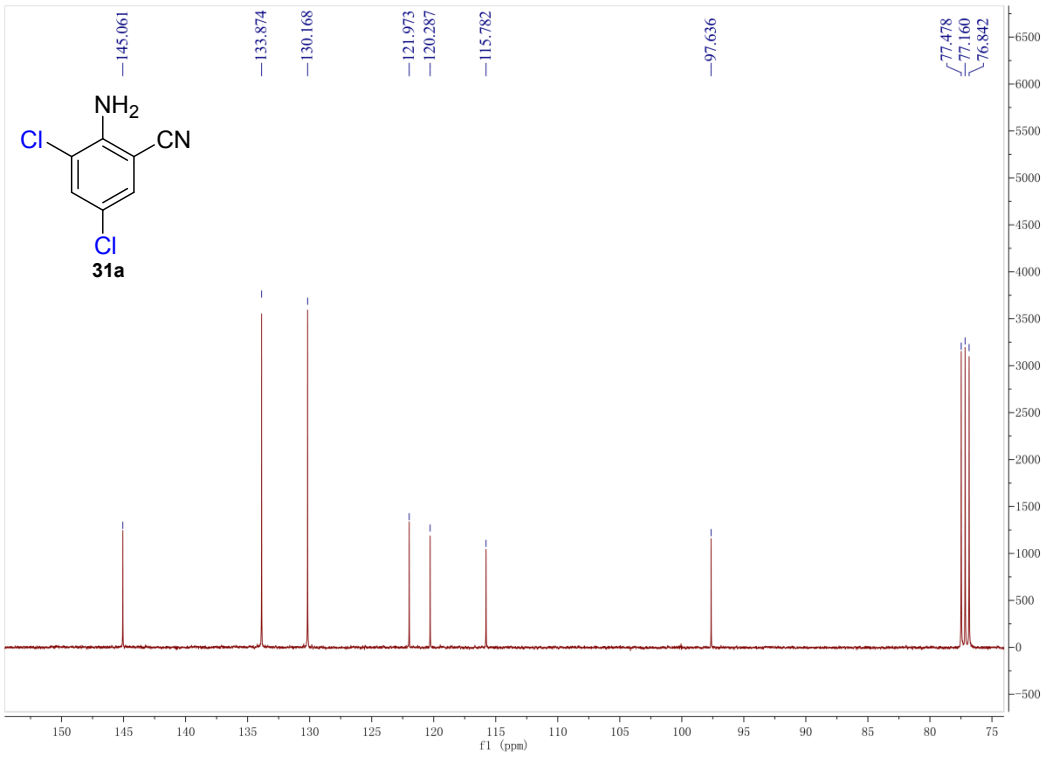

NH2
Cl
Cl
Cl
29a
7.165
4.425
2.00
2.00
f1 (ppm)

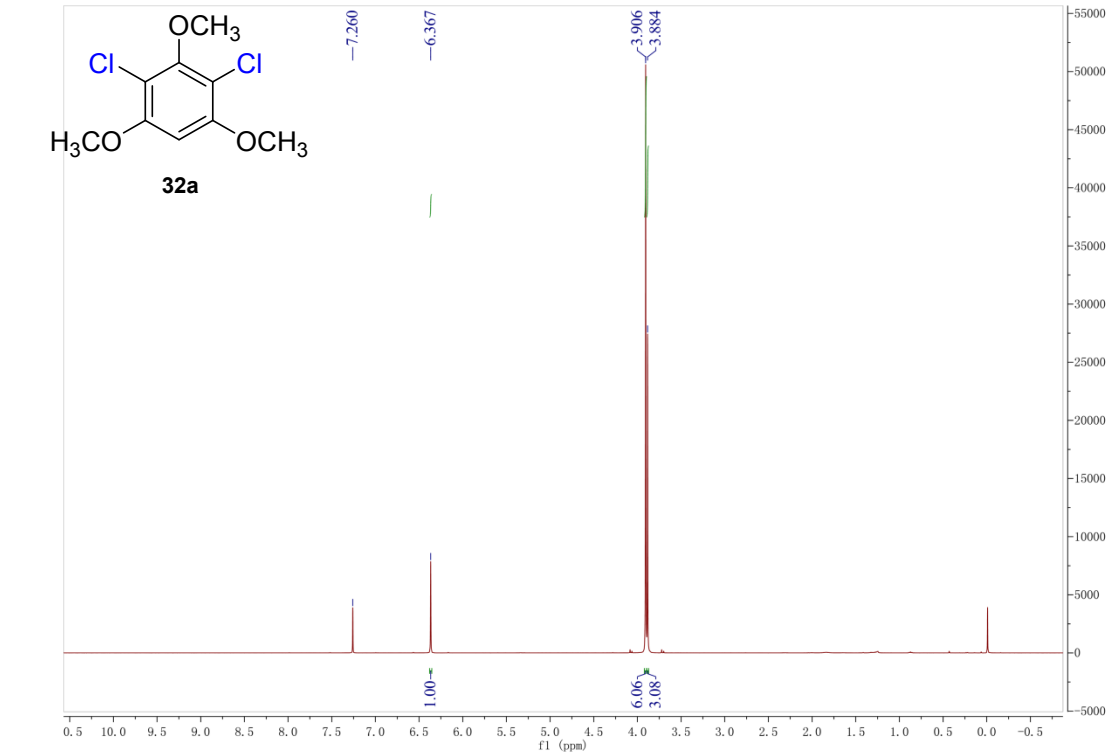

NH2
Cl
Cl
Cl
29a
139.061
127.616
121.864
119.719
77.477
77.160
76.842
f1 (ppm)

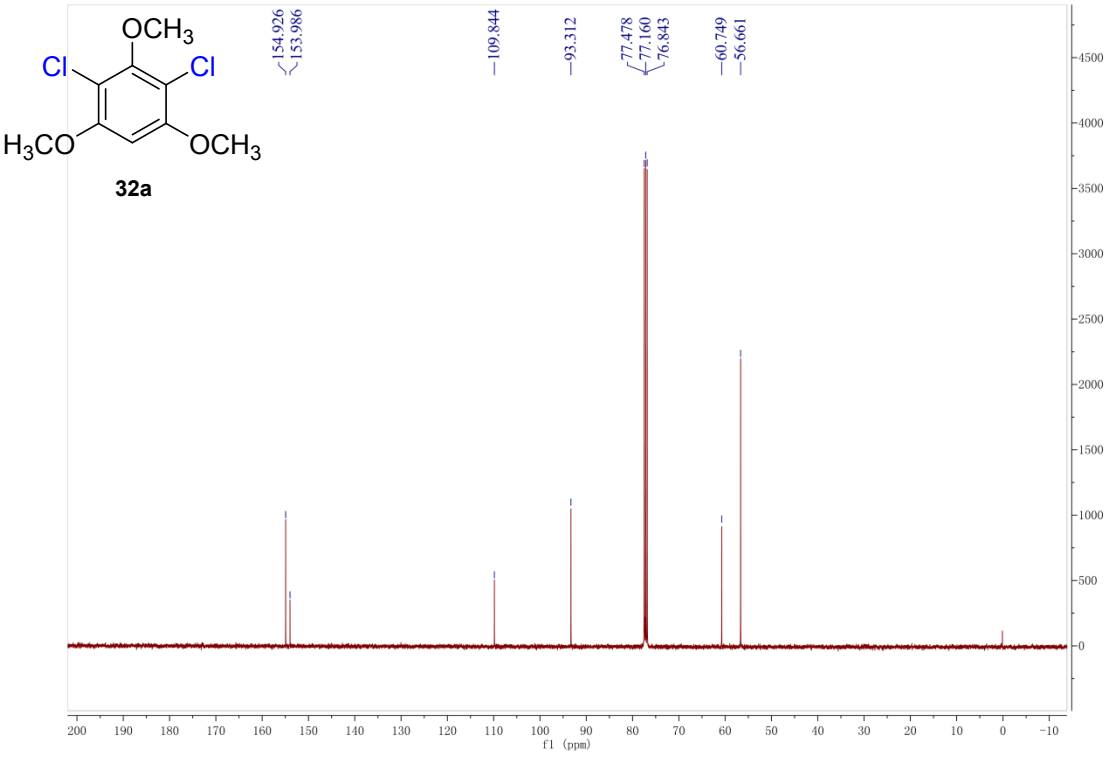

NH2
Cl
Cl
30a
7.260
6.997
2.209
1.252
2.00
3.12
2.16
f1 (ppm)

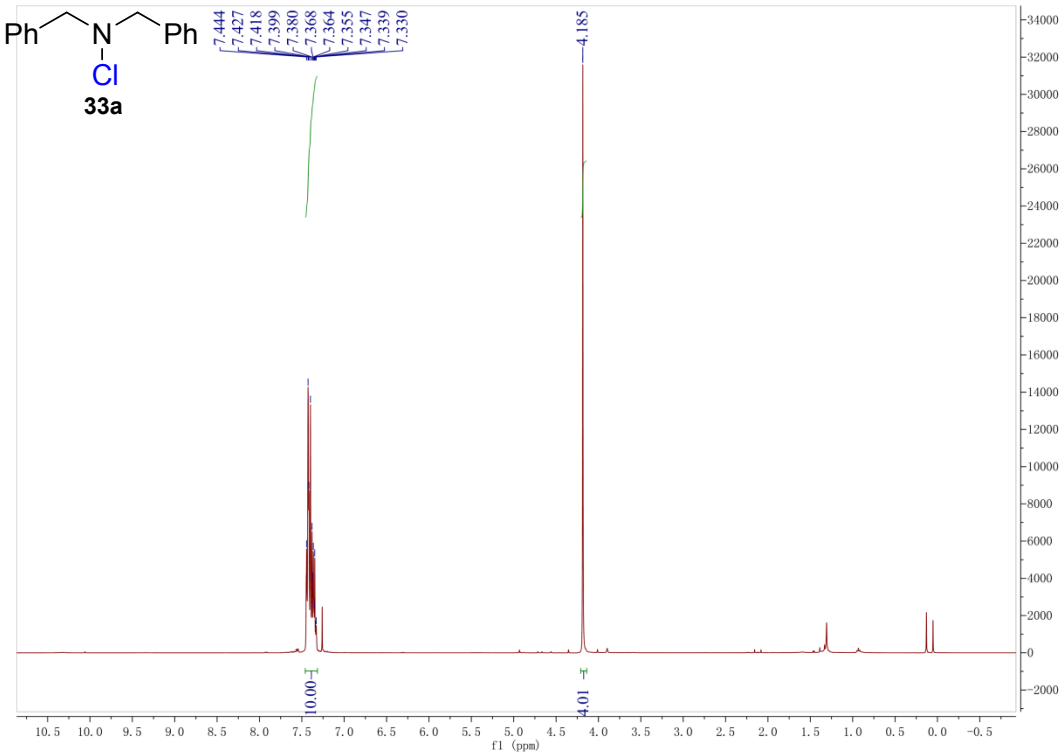

NH2
Cl
Cl
30a
137.689
128.379
119.592
77.160
29.840
20.180
f1 (ppm)


NH2
Cl
CN
Cl
31a
7.444
7.438
7.308
7.303
7.260
4.852
1.00
1.00
2.11
f1 (ppm)


NH2
Cl
CN
Cl
31a
145.061
133.874
130.168
121.973
120.287
115.782
97.636
77.478
77.160
76.842
f1 (ppm)


OCH3
Cl
Cl
H3CO
OCH3
32a
7.260
6.367
3.906
3.884
1.00
6.06
3.08
f1 (ppm)


OCH3
Cl
Cl
H3CO
OCH3
32a
154.926
153.986
109.844
93.312
77.478
77.160
76.843
60.749
56.661
f1 (ppm)


Ph
N
Ph
Cl
33a
7.444
7.427
7.418
7.399
7.380
7.368
7.364
7.355
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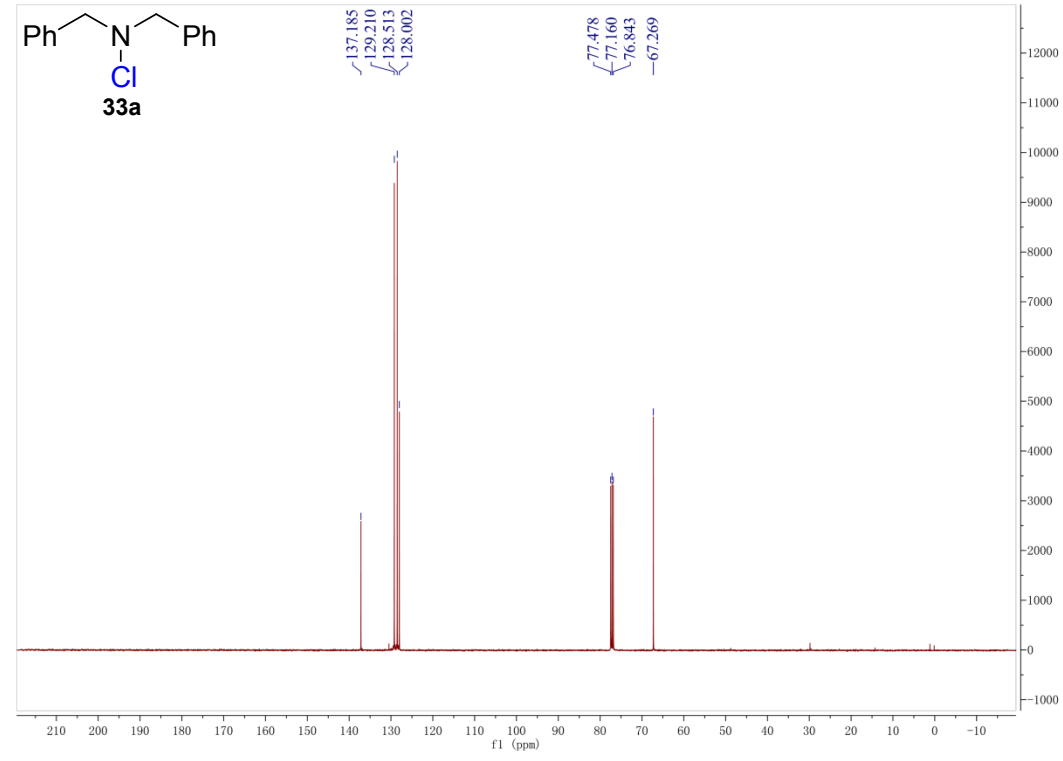
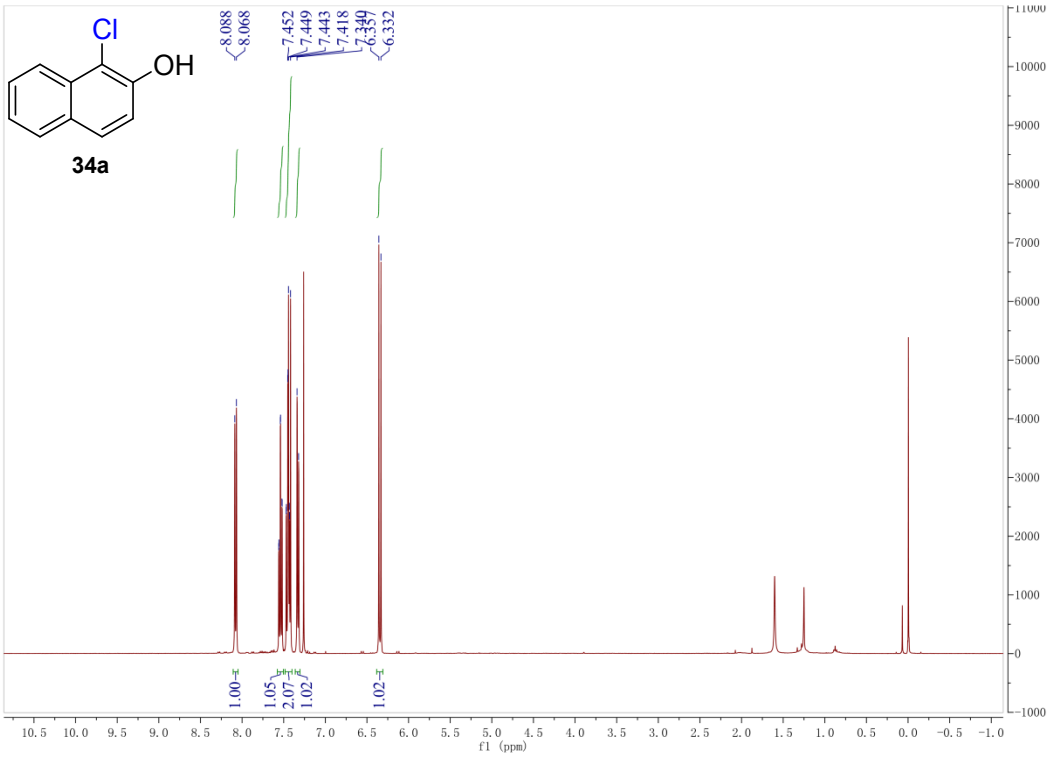
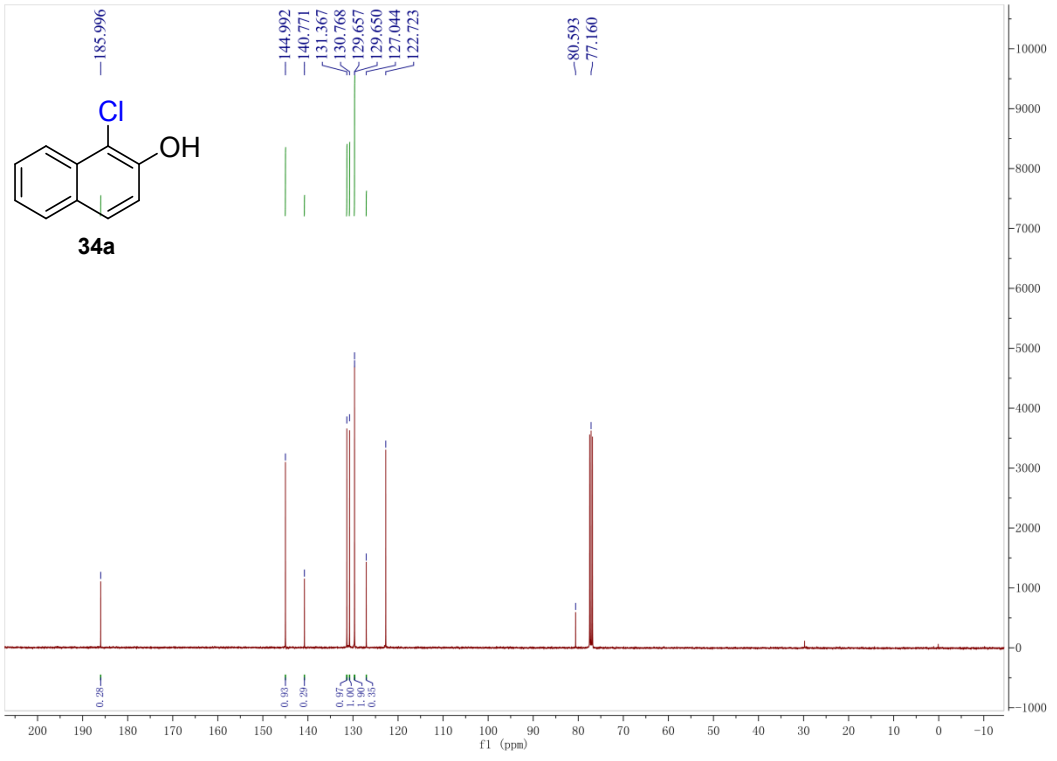
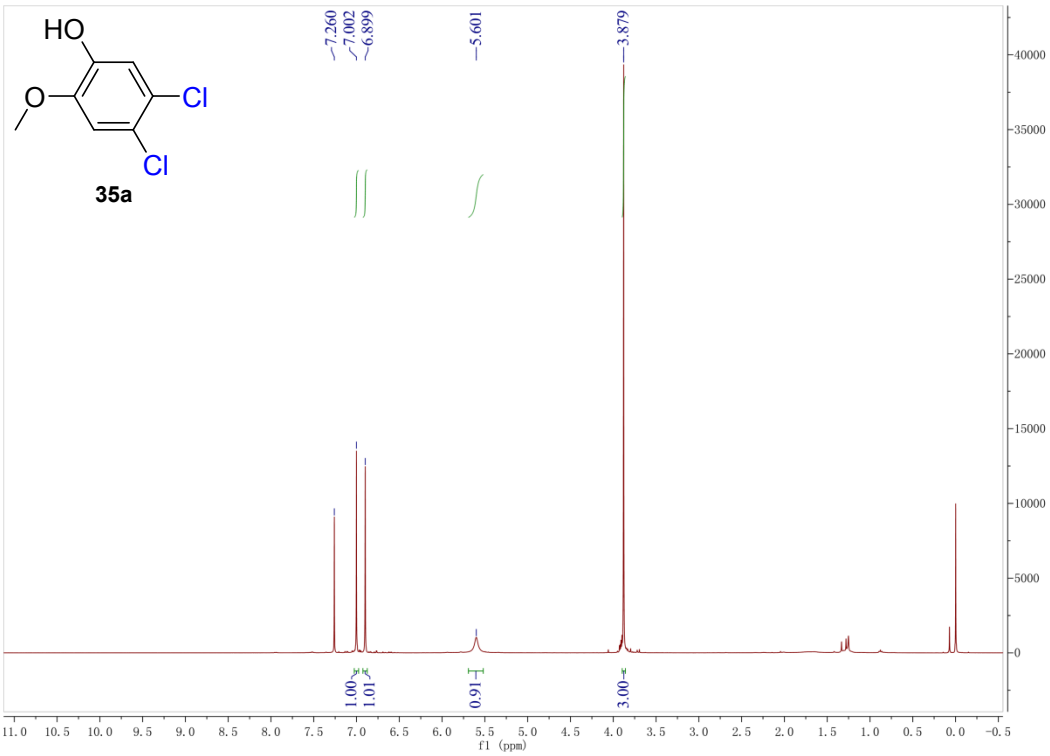
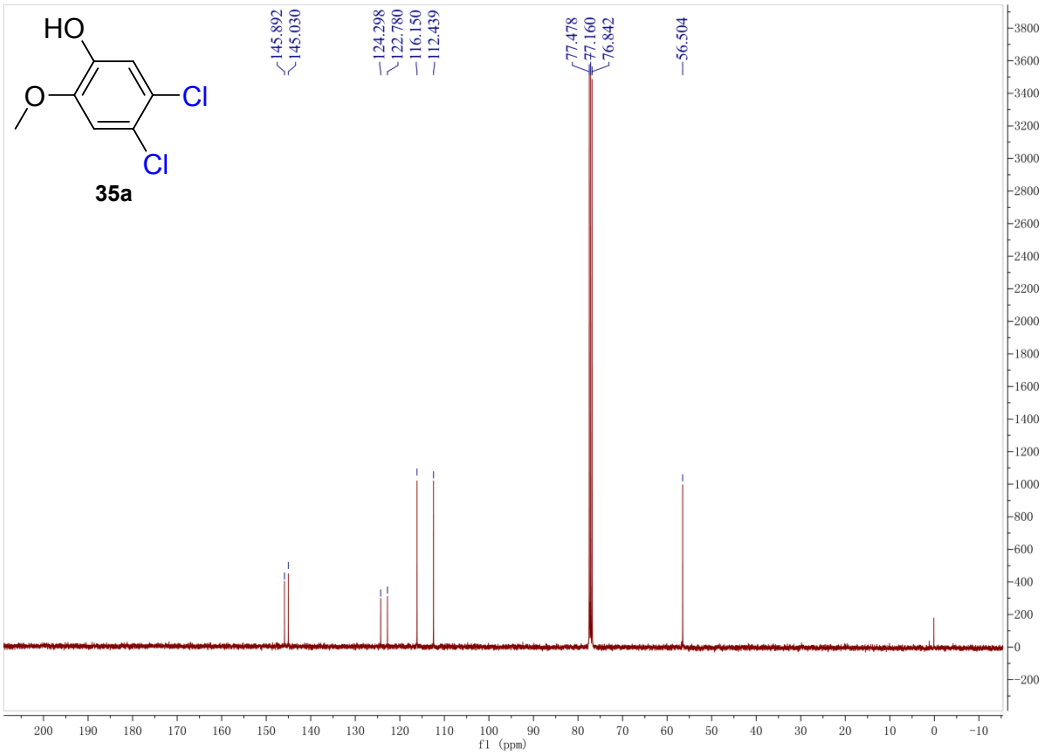
7.339
7.330
4.185
10.00
4.01
f1 (ppm)


Ph
N
Ph
Cl
33a
137.185
129.210
128.513
128.002
77.478
77.160
76.843
67.269
f1 (ppm)


Cl
OH
34a
8.088
8.068
7.452
7.449
7.443
7.418
7.340
6.357
6.332
1.00
1.05
2.07
1.02
1.02
f1 (ppm)

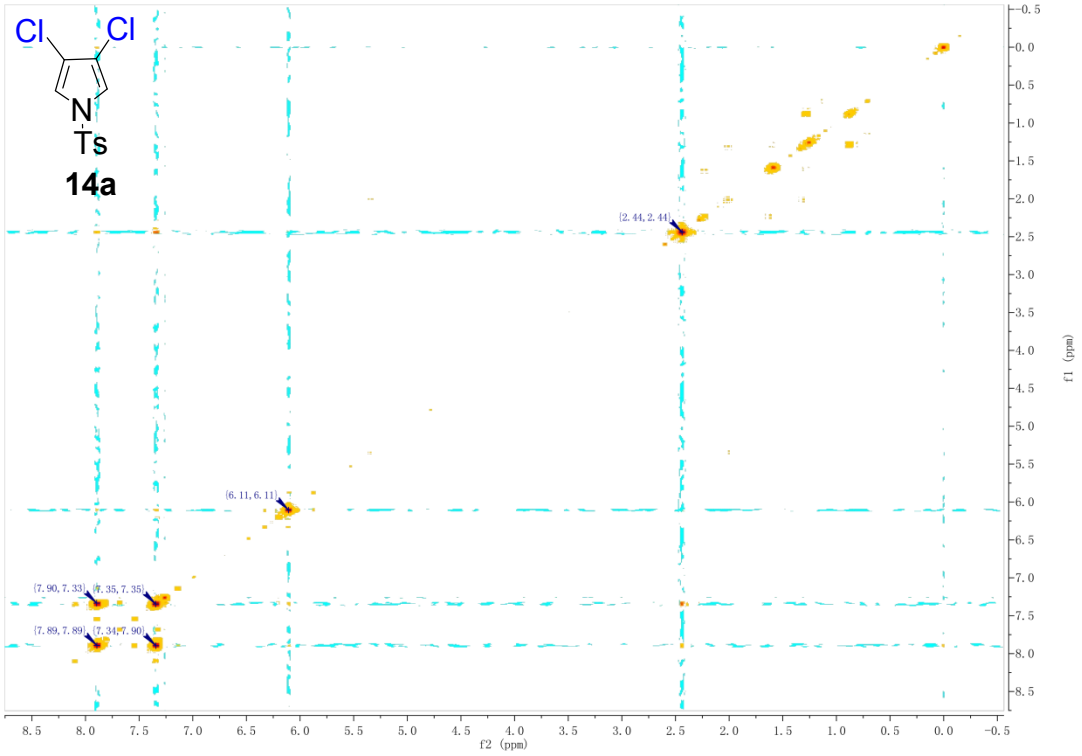

Cl
OH
34a
185.996
144.992
140.771
131.367
130.768
129.657
129.650
127.044
122.723
80.593
77.160
0.28
0.93
0.29
0.97
1.00
1.98
0.95
f1 (ppm)


HO
O
Cl
Cl
35a
7.260
7.002
6.899
5.601
3.879
1.00
1.01
0.91
3.00
f1 (ppm)


HO
O
Cl
Cl
35a
145.892
145.030
124.298
122.780
116.150
112.439
77.478
77.160
76.842
56.504
f1 (ppm)

(Homonuclear chemical shift) Correlation Spectroscopy

1H-1H COSY of 14a



Notes and References

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