

Supporting Information *for*

A Quick, Mild and Efficient Bromination Using CFBSA/KBr System

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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. 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 ¹⁹F NMR spectra were recorded on a Bruker spectrometer at 376 MHz. The ¹³C 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 mass spectrometer with electron impact.

2. Typical procedures

Standard procedure for the bromination of 1,3-diketones and β -keto esters: To a mixture of CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) in acetonitrile (8 mL) with stirring for 10 min at room temperature. Then carbonyl compounds (1.0 mmol, 1.0 eq.) were added to it with stirring at room temperature. The reaction was monitored by thin layer chromatography until completion. After the complete conversion of starting material, the mixture was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel.

Standard procedure for the bromination of heterocycles: To a mixture of CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) in acetonitrile (8 mL) with stirring 10 min at room temperature. Then heterocycles (1.0 mmol, 1.0 eq.) were added to it with stirring at room temperature. The reaction was monitored by thin layer chromatography until completion. After the complete conversion of starting material, the mixture was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel.

Standard procedure for the bromination of aromatic amines: To a mixture of CFBSA (2.2 mmol, 2.2 eq.) and KBr (2.5 mmol, 2.5 eq.) in acetonitrile (8 mL) with stirring for 10 min at room temperature. Then aromatic amines (1.0 mmol, 1.0 eq.) were added to it with stirring at room temperature. The reaction was monitored by thin layer chromatography until completion. After the complete conversion of starting material, the mixture was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel.

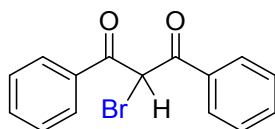
NOTES: Some substrates including p-methylaniline, N-phenylacetamide and indolin-2-one would convert completely and mono-brominated products were formed with 1.2 eq. CFBSA and 1.5 eq. KBr. For substrates that N-methyl-3-methylanilines and N-ethyl-3-methylanilines, addition of 3.2 eq. CFBSA and 3.5 eq. KBr would promote the starting materials to transform into tribromide products.

Standard procedure for the bromination of phenols: To a mixture of CFBSA (2.2 mmol, 2.2 eq.) and KBr (2.5 mmol, 2.5 eq.) in acetonitrile (8 mL) with stirring for 10 min at room temperature. Then phenols (1.0 mmol, 1.0 eq.) were added to it with stirring at room temperature. The reaction was monitored by thin layer chromatography until completion. After the complete conversion of starting material, the mixture was evaporated under reduced pressure. The residue

was purified by column chromatography on silica gel.

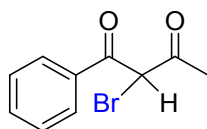
NOTES: For substrates that phenol and β -naphthol, addition of 3.2 eq. CFBSA/3.5 eq. KBr and 1.2 eq. CFBSA/1.5 eq. KBr would promote the starting materials to transform into tri-brominated and mono-brominated compounds respectively.

3. Analytical Data for the Products



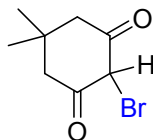
2-Bromo-1,3-diphenylpropane-1,3-dione.¹ (**1a**)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **1a** in 94% yield. White solid; $R_f = 0.61$ (10% ethyl acetate/petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.00-7.98 (m, 4H), 7.62-7.59 (m, 2H), 7.49-7.46 (m, 4H), 6.55 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 185.10, 134.20, 131.25, 130.69, 128.78, 70.02.



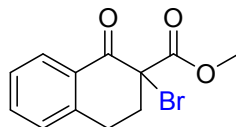
2-Bromo-1-phenylbutane-1,3-dione.¹ (**2a**)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **2a** in 89% yield. Yellow oil; $R_f = 0.54$ (10% ethyl acetate/petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.00-7.97 (m, 2H), 7.66-7.62 (m, 1H), 7.53-7.49 (m, 2H), 5.62 (s, 1H), 2.46 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 198.34, 190.04, 134.62, 133.86, 129.39, 129.14, 53.03, 27.24.



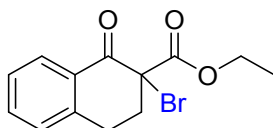
2-Bromo-5,5-dimethylcyclohexane-1,3-dione.¹ (**3a**)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **3a** in 88% yield. White solid; $R_f = 0.50$ (50% ethyl acetate/petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.01 (s, 4H), 1.01 (s, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 192.95, 66.55, 48.34, 30.71, 27.89.



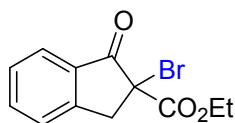
Methyl 2-bromo-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate.² (**4a**)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **4a** in 97% yield. Yellow oil; $R_f = 0.35$ (10% ethyl acetate/petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.10 (d, $J = 8.0$ Hz, 1H), 7.54 (t, $J = 7.2$ Hz, 1H), 7.36 (t, $J = 7.2$ Hz, 1H), 7.28-7.26 (m, 1H), 3.86 (s, 3H), 3.27-3.19 (m, 1H), 3.06-2.94 (m, 2H), 2.61-2.54 (m, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 187.64, 168.07, 142.51, 134.54, 129.50, 129.22, 128.90, 127.44, 64.90, 54.16, 35.81, 26.88.



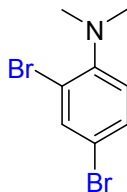
Ethyl 2-bromo-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate.² (5a)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **5a** in 94% yield. Pale yellow oil; $R_f = 0.35$ (10% ethyl acetate/petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.10 (dd, $J = 1.2$ Hz, 8.0 Hz, 1H), 7.56-7.52 (m, 1H), 7.38-7.35 (m, 1H), 7.28-7.26 (m, 1H), 4.31 (q, $J = 7.2$, 14.0 Hz, 2H), 3.27-3.19 (m, 1H), 3.06-2.95 (m, 2H), 2.60-2.54 (m, 1H), 1.30 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 187.70, 167.47, 142.49, 134.44, 129.66, 129.19, 128.88, 127.41, 65.25, 63.39, 35.80, 26.94, 14.07.



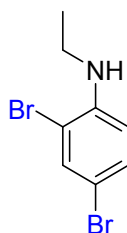
Ethyl 2-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate.³ (6a)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **6a** in 93% yield. Yellow oil; $R_f = 0.35$ (10% ethyl acetate/petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.88-7.86 (m, 1H), 7.72-7.68 (m, 1H), 7.48-7.45 (m, 2H), 4.32-4.24 (m, 2H), 4.20 (d, $J = 18.0$ Hz, 1H), 3.68 (d, $J = 18.0$ Hz, 1H), 1.29 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 195.31, 167.16, 150.31, 136.42, 132.39, 128.70, 126.43, 126.10, 63.70, 58.61, 44.00, 14.08.



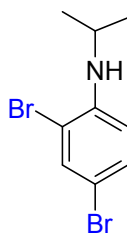
2,4-Dibromo-N,N-dimethylaniline.⁴ (7a)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **7a** in 88% yield. Yellow oil; $R_f = 0.45$ (petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.68 (d, $J = 2.4$ Hz, 1H), 7.35 (dd, $J = 8.8$, 2.4 Hz, 1H), 6.93 (d, $J = 8.8$ Hz, 1H), 2.77 (s, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 151.20, 136.13, 131.10, 121.74, 119.75, 115.47, 44.19.



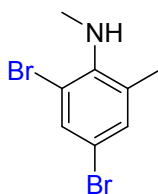
2,4-Dibromo-N-ethylaniline. (8a)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **8a** in 92% yield. White solid; $R_f = 0.35$ (petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.53 (d, $J = 2.0$ Hz, 1H), 7.26 (dd, $J = 8.8$, 2.0 Hz, 1H), 6.50 (d, $J = 8.8$ Hz, 1H), 4.32 (s, br, 1H), 3.17 (q, $J = 7.2$, 14.4 Hz, 2H), 1.30 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 144.24, 134.35, 131.33, 112.40, 109.88, 107.94, 38.64, 14.63.



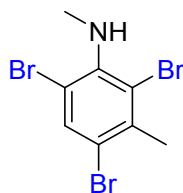
2,4-Dibromo-N-isopropylaniline. (9a)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **9a** in 86% yield. White oil; $R_f = 0.35$ (petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.52 (d, $J = 2.4$ Hz, 1H), 7.25 (dd, $J = 8.8, 2.4$ Hz, 1H), 6.50 (d, $J = 8.8$ Hz, 1H), 4.18 (s, br, 1H), 3.65-3.56 (m, 1H), 1.24 (d, $J = 6.0$ Hz, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 143.46, 134.50, 131.26, 112.85, 110.06, 107.48, 44.57, 22.84.



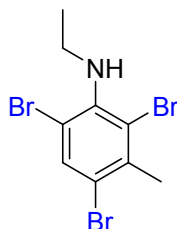
2,4-Dibromo-N,6-dimethylaniline. (10a)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **10a** in 80% yield. Yellow oil; $R_f = 0.50$ (petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.47 (d, $J = 2.4$ Hz, 1H), 7.19 (d, $J = 2.4$ Hz, 1H), 3.66 (s, br, 1H), 2.79 (s, 3H), 2.33 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 146.16, 133.54, 132.73, 132.29, 117.47, 113.74, 35.17, 19.53.



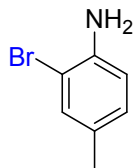
2,4,6-Tribromo-N,3-dimethylaniline. (11a)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **11a** in 75% yield. Yellow oil; $R_f = 0.45$ (petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.70 (s, 1H), 3.61 (s, br, 1H), 2.92 (s, 3H), 2.54 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 146.12, 137.86, 135.13, 120.65, 117.00, 113.91, 35.26, 24.87.



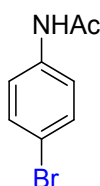
2,4,6-Tribromo-N-ethyl-3-methylaniline. (12a)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **12a** in 88% yield. Pale Yellow oil; $R_f = 0.50$ (petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.69 (s, 1H), 3.27 (q, $J = 7.2, 14.4$ Hz, 2H), 2.54 (s, 3H), 1.22 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 145.04, 137.83, 135.07, 121.08, 116.96, 114.39, 43.24, 24.94, 16.01.



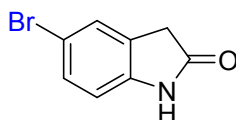
2-Bromo-4-methylaniline.⁵ (13a)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **13a** in 72% yield. Pale brown oil; $R_f = 0.50$ (petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.24 (d, $J = 1.2$ Hz, 1H), 6.93-6.90 (m, 1H), 6.69-6.67 (m, 1H), 3.71 (s, br, 2H), 2.23 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 141.65, 132.85, 129.12, 115.91, 109.44, 20.22.



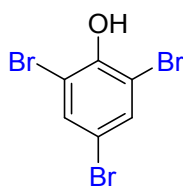
N-(4-bromophenyl)acetamide.⁵ (14a)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **14a** in 92% yield. Drab yellow solid; $R_f = 0.25$ (25% ethyl acetate/petroleum ether); $^1\text{H NMR}$ (400 MHz, $\text{CH}_3\text{CN}-d_3$) δ 8.40 (s, br, 1H), 7.50-7.48 (m, 2H), 7.45-7.42 (m, 2H), 2.04 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, $\text{DMSO}-d_6$) δ 168.47, 138.68, 131.48, 120.85, 114.47, 24.02.



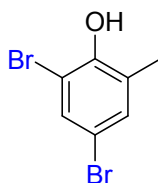
5-Bromoindolin-2-one.⁶ (15a)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **15a** in 90% yield. Light yellow solid; $R_f = 0.45$ (25% ethyl acetate/petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.97 (s, br, 1H), 7.36-7.34 (m, 2H), 6.75 (d, $J = 8.8$ Hz, 1H), 3.54 (s, 2H). $^{13}\text{C NMR}$ (100 MHz, $\text{DMSO}-d_6$) δ 175.90, 143.00, 130.07, 128.52, 127.22, 112.79, 110.88, 35.76.



2,4,6-Tribromophenol.⁷ (16a)

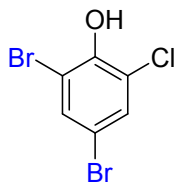
Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **16a** in 72% yield. Yellow solid; $R_f = 0.35$ (10% ethyl acetate/petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.59 (s, 2H), 5.86 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 149.09, 134.38, 112.84, 110.55.



2,4-Dibromo-6-methylphenol.⁷ (17a)

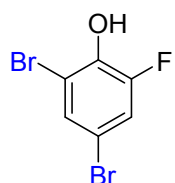
Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **17a** in 70%

yield. Yellow solid; $R_f = 0.25$ (10% ethyl acetate/petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.43 (d, $J = 2.0$ Hz, 1H), 7.20 (d, $J = 2.0$ Hz, 1H), 5.52 (s, 1H), 2.27 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 149.90, 133.22, 131.40, 127.82, 112.16, 110.57, 16.69.



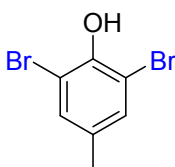
2,4-Dibromo-6-chlorophenol.⁷ (18a)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **18a** in 93% yield. White solid; $R_f = 0.25$ (10% ethyl acetate/petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.55 (d, $J = 2.4$ Hz, 1H), 7.45 (d, $J = 2.4$ Hz, 1H), 5.86 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 148.33, 133.75, 131.57, 121.67, 112.38, 110.96.



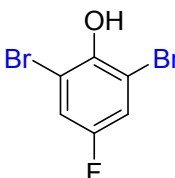
2,4-Dibromo-6-fluorophenol.⁸ (19a)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **19a** in 95% yield. Yellow solid; $R_f = 0.25$ (10% ethyl acetate/petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.43 (t, $J = 2.0$ Hz, 1H), 7.23 (dd, $J = 9.6, 2.0$ Hz, 1H), 5.61 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 150.82 (d, $J = 248.1$ Hz), 141.22 (d, $J = 14.3$ Hz), 130.24 (d, $J = 3.8$ Hz), 119.22 (d, $J = 21.4$ Hz), 111.75 (d, $J = 9.2$ Hz), 111.53 (d, $J = 2.6$ Hz). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -131.03.



2,6-Dibromo-4-methylphenol.⁷ (20a)

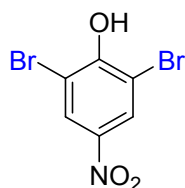
Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **20a** in 66% yield. White solid; $R_f = 0.25$ (10% ethyl acetate/petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.26 (s, 2H), 5.71 (s, 1H), 2.26 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 147.26, 132.54, 109.55, 100.12, 20.12.



2,6-Dibromo-4-fluorophenol. (21a)

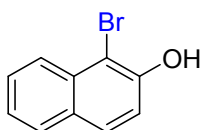
Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **21a** in 89% yield. White solid; $R_f = 0.25$ (10% ethyl acetate/petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.26 (s, 1H), 7.24 (s, 1H), 5.70 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 155.85 (d, $J = 245.1$ Hz), 146.57 (d, $J = 3.3$ Hz), 119.31 (d, $J = 25.4$ Hz), 109.43 (d, $J = 10.4$ Hz). $^{19}\text{F NMR}$ (376 MHz,

CDCl₃) δ -120.50.



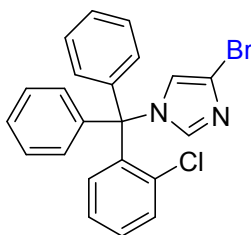
2,6-Dibromo-4-nitrophenol.⁷ (22a)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **22a** in 97% yield. Yellow solid; $R_f = 0.25$ (10% ethyl acetate/petroleum ether); ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.38 (s, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 157.53, 140.01, 127.95, 111.12.



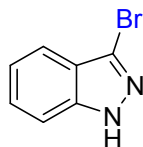
1-Bromonaphthalen-2-ol.⁷ (23a)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **23a** in 93% yield. Pale yellow solid; $R_f = 0.35$ (10% ethyl acetate/petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, $J = 8.4$ Hz, 1H), 7.79 (d, $J = 8.0$ Hz, 1H), 7.75 (d, $J = 8.4$ Hz, 1H), 7.60-7.55 (m, 1H), 7.42-7.38 (m, 1H), 7.27 (d, $J = 8.0$ Hz, 1H), 5.92 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 150.72, 132.43, 129.83, 129.48, 128.36, 127.99, 125.47, 124.30, 117.30, 106.28.



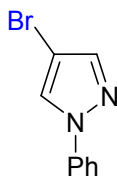
4-Bromo-1-((2-chlorophenyl)diphenylmethyl)-1H-imidazole. (24a)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **24a** in 77% yield. White solid; $R_f = 0.50$ (50% ethyl acetate/petroleum ether); mp 198-199°C. ¹H NMR (400 MHz, CDCl₃) δ 7.44-7.28 (m, 10H), 7.18-7.16 (m, 4H), 6.92 (dd, $J = 8.0, 2.4$ Hz, 1H), 6.73 (d, $J = 1.6$ Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 140.20, 139.77, 138.82, 135.64, 132.50, 130.48, 130.26, 130.24, 128.59, 128.33, 127.30, 120.81, 114.87, 76.00. IR (KBr) $\nu = 3066, 1585, 1488, 1464, 1444, 1433, 1217, 767, 751, 707, 667$. HRMS-EI (m/z) *calcd.* for (C₂₂H₁₆BrClN₂) 422.0185; found 422.0191.



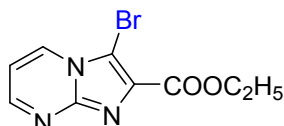
3-Bromo-1H-indazole.⁹ (25a)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **25a** in 93% yield. White solid; $R_f = 0.25$ (10% ethyl acetate/petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 10.33 (s, br, 1H), 7.66 (d, $J = 8.0$ Hz, 1H), 7.52-7.45 (m, 2H), 7.27-7.24 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 141.31, 128.28, 123.24, 123.14, 122.01, 120.31, 110.38.



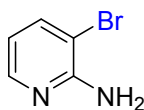
4-Bromo-1-phenyl-1H-pyrazole.¹⁰ (26a)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **26a** in 93% yield. White solid; $R_f = 0.75$ (10% ethyl acetate/petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.94 (s, 1H), 7.68 (s, 1H), 7.65-7.63 (m, 2H), 7.48-7.44 (m, 2H), 7.34-7.30 (m, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 141.64, 139.74, 129.68, 127.19, 127.15, 119.15, 95.76.



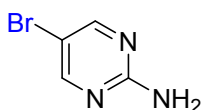
Ethyl 3-bromoimidazo[1,2-a]pyrimidine-2-carboxylate.¹¹ (27a)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **27a** in 93% yield. Bright yellow solid; $R_f = 0.50$ (50% ethyl acetate/petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.71 (dd, $J = 4.0, 2.0$ Hz, 1H), 8.52 (dd, $J = 7.2, 2.0$ Hz, 1H), 7.09 (dd, $J = 7.2, 4.0$ Hz, 1H), 4.50 (q, $J = 7.2, 14.0$ Hz, 2H), 1.46 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 162.04, 152.85, 147.68, 135.00, 132.56, 110.90, 99.07, 61.85, 14.43.



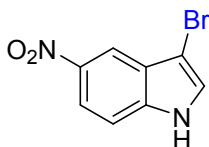
3-Bromopyridin-2-amine.¹² (28a)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **28a** in 83% yield. Yellowish-brown solid; $R_f = 0.45$ (50% ethyl acetate/petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.09 (d, $J = 2.4$ Hz, 1H), 7.51 (dd, $J = 8.8, 2.4$ Hz, 1H), 6.44 (d, $J = 8.8$ Hz, 1H), 4.49 (s, 2H). $^{13}\text{C NMR}$ (400 MHz, CDCl_3) δ 156.96, 148.32, 140.55, 110.38, 108.40.



5-Bromopyrimidin-2-amine.⁵ (29a)

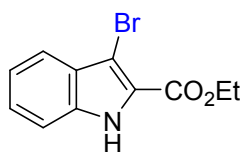
Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **29a** in 93% yield. White solid; Precipitated in acetonitrile. $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 8.30 (s, 1H), 6.90 (s, br, 1H). $^{13}\text{C NMR}$ (100 MHz, $\text{DMSO-}d_6$) δ 162.03, 158.07, 105.11.



3-Bromo-5-nitro-1H-indole. (30a)

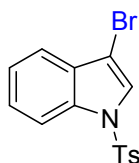
Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **30a** in 93% yield. Yellow solid; $R_f = 0.45$ (50% ethyl acetate/petroleum ether); $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 12.21 (s, br, 1H), 8.31 (d, $J = 2.4$ Hz, 1H), 8.07 (dd, $J = 9.2, 2.4$ Hz, 1H), 7.88 (d, $J = 2.8$ Hz, 1H), 7.63 (d, $J = 9.2$ Hz, 1H). $^{13}\text{C NMR}$ (100 MHz, $\text{DMSO-}d_6$) δ 141.36, 138.57, 129.08, 125.64,

117.51, 114.94, 113.00, 91.03.



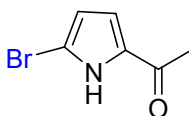
Ethyl 3-bromo-1H-indole-2-carboxylate.¹³ (31a)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **31a** in 93% yield. White solid; $R_f = 0.35$ (10% ethyl acetate/petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.11 (s, br, 1H), 7.68 (d, $J = 8.0$ Hz, 1H), 7.42-7.36 (m, 2H), 7.26-7.21 (m, 1H), 4.47 (q, $J = 7.2, 14.4$ Hz 2H), 1.46 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 161.12, 135.44, 128.14, 126.72, 124.25, 121.61, 121.47, 112.12, 98.46, 61.62, 14.50.



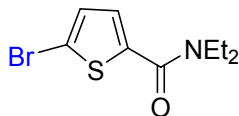
3-Bromo-1-tosyl-1H-indole.¹⁴ (32a)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **32a** in 69% yield. Off-white solid; $R_f = 0.45$ (10% ethyl acetate/petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.99 (d, $J = 8.4$ Hz, 1H), 7.77 (d, $J = 8.4$ Hz, 2H), 7.62 (s, 1H), 7.49 (m, 1H), 7.40-7.36 (m, 1H), 7.33-7.29 (m, 1H), 7.24 (d, $J = 8.0$ Hz, 2H), 2.35 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 145.51, 134.99, 134.40, 130.17, 129.90, 127.07, 125.88, 124.92, 124.02, 120.19, 113.73, 99.73, 21.75.



1-(5-bromo-1H-pyrrol-2-yl)ethan-1-one.¹⁵ (33a)

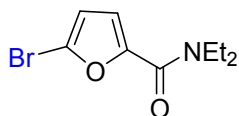
Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **33a** in 69% yield. White solid; $R_f = 0.45$ (50% ethyl acetate/petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.62 (s, br, 1H), 7.02 (dd, $J = 2.8, 1.2$ Hz, 1H), 6.89 (dd, $J = 2.8, 1.2$ Hz, 1H), 2.42 (s, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 186.32, 131.10, 109.30, 106.56, 105.77, 27.96.



5-Bromo-N,N-diethylthiophene-2-carboxamide.¹⁶ (34a)

Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **34a** in 94% yield. Yellow oil; $R_f = 0.35$ (25% ethyl acetate/petroleum ether); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.08 (d, $J = 4.0$ Hz, 1H), 6.99 (d, $J = 4.0$ Hz, 1H), 3.52 (q, $J = 7.2, 14.0$ Hz, 4H), 1.24 (t, $J = 7.2$ Hz, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 159.70, 148.72, 143.63, 115.90, 111.31, 42.84, 41.41, 14.81, 13.00.

Notes: The ethyl peaks from the amide group are broad peaks in $^{13}\text{C NMR}$ due to restricted rotation.

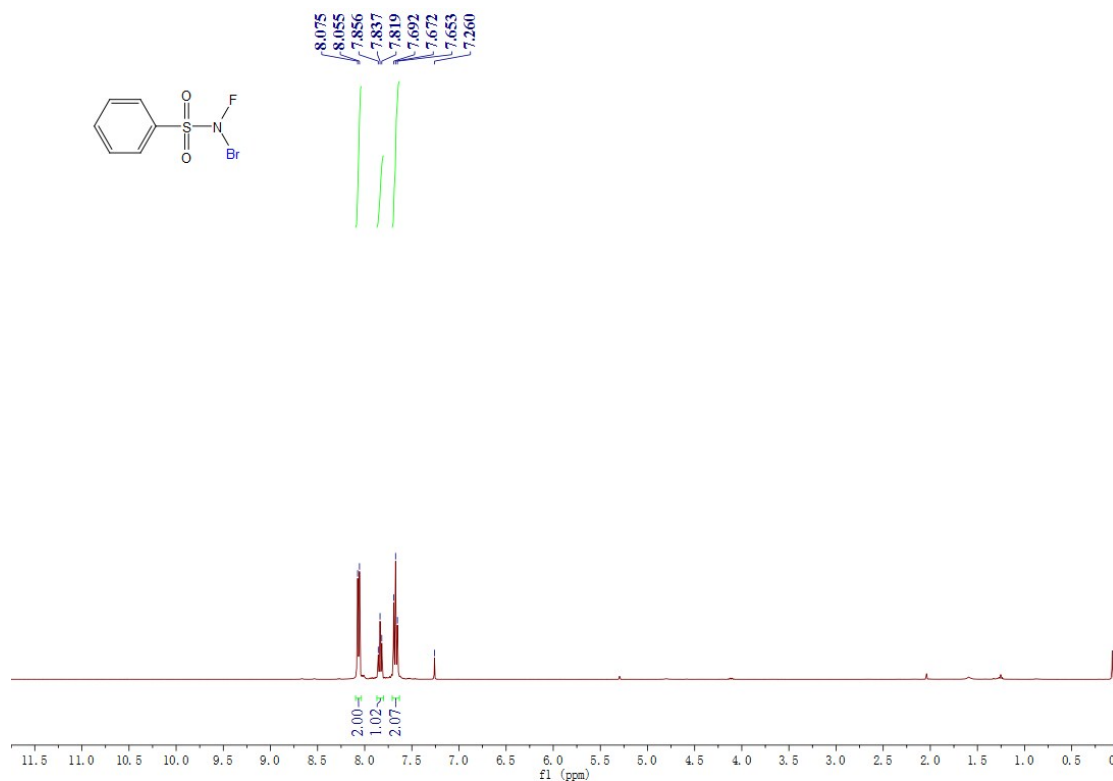


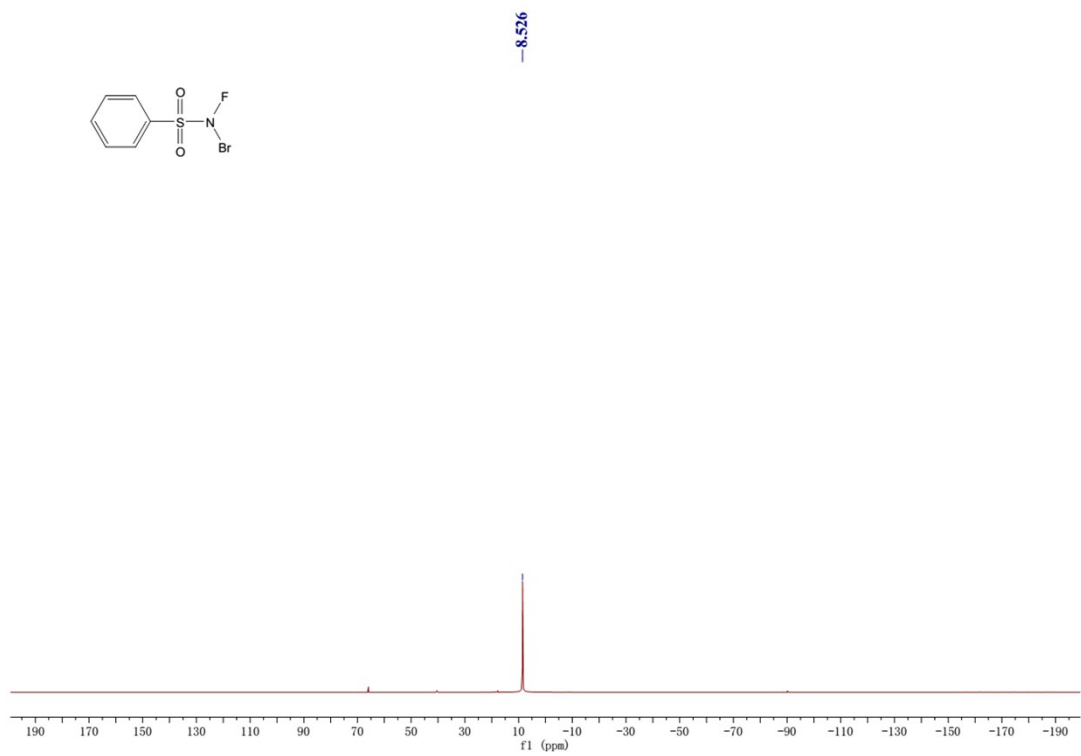
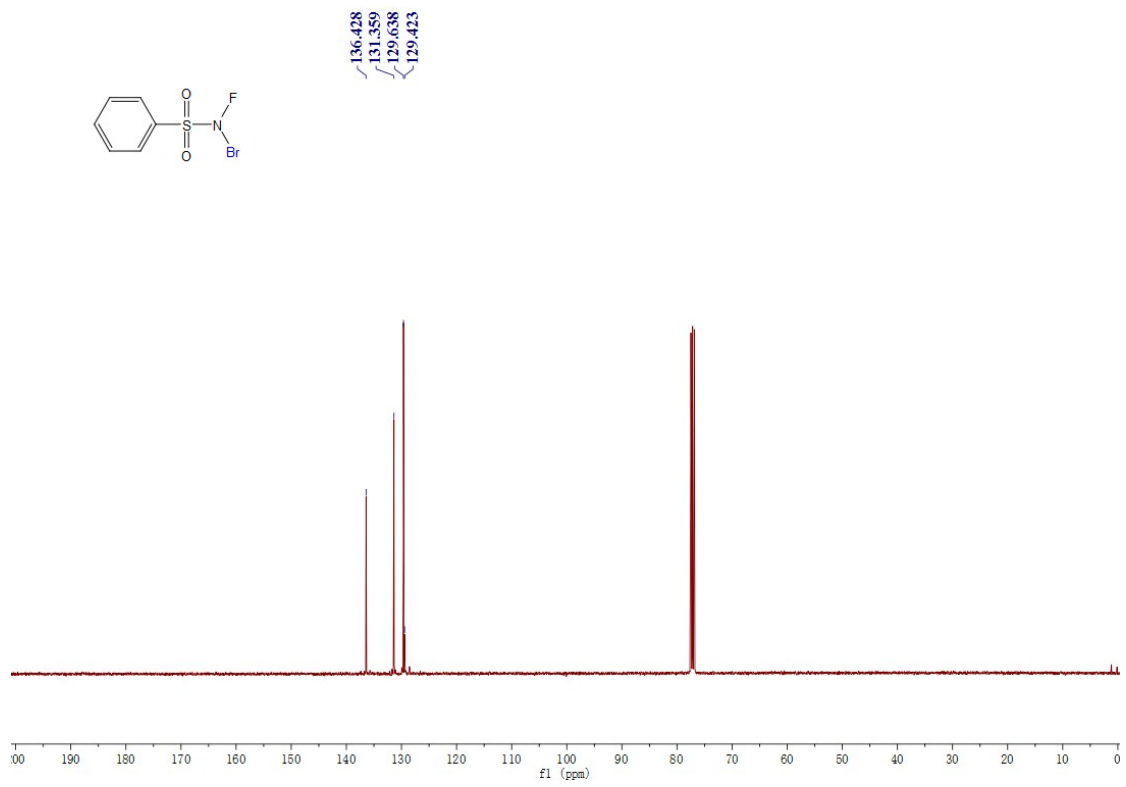
5-Bromo-N,N-diethylfuran-2-carboxamide.¹⁶ (35a)

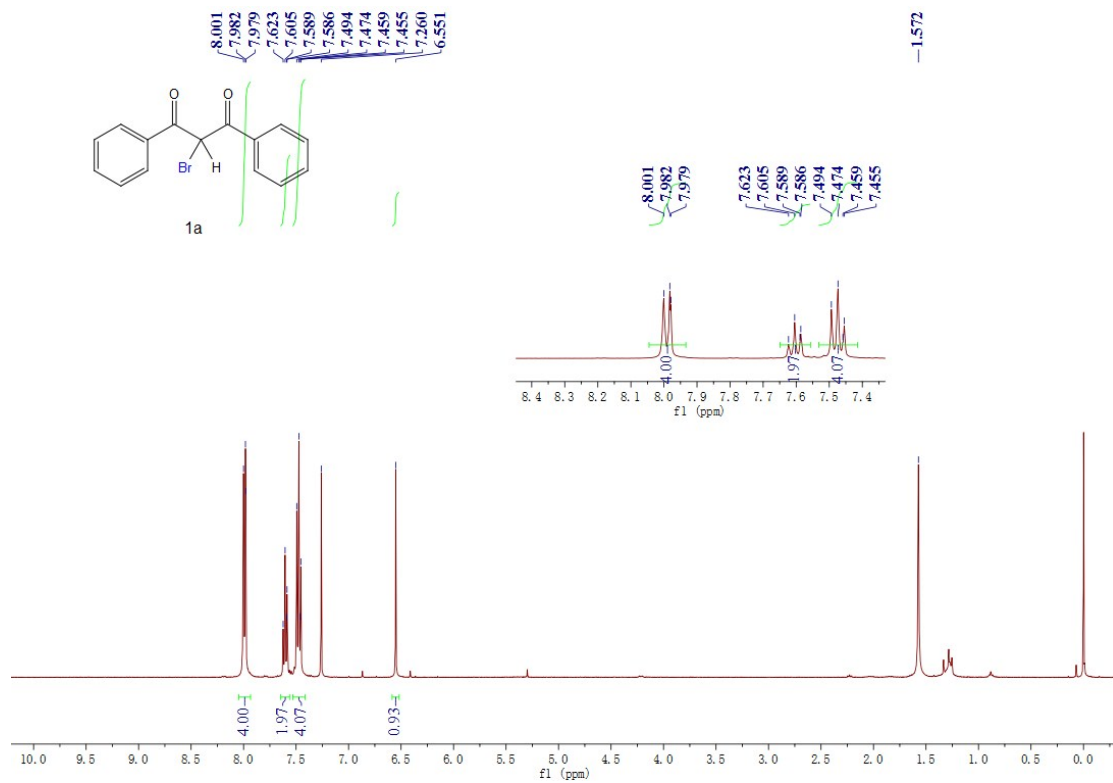
Procedure: Using CFBSA (1.2 mmol, 1.2 eq.) and KBr (1.5 mmol, 1.5 eq.) provided **35a** in 61% yield. Yellow oil; $R_f = 0.25$ (25% ethyl acetate/petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 7.07 (d, $J = 4.0$ Hz, 1H), 6.98 (d, $J = 4.0$ Hz, 1H), 3.51 (q, $J = 7.2, 14.4$ Hz, 4H), 1.23 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.35, 150.30, 123.83, 118.33, 113.26, 42.83, 41.48, 14.74, 12.72.

Notes: The ethyl peaks from the amide group are broad peaks in ^{13}C NMR due to restricted rotation.

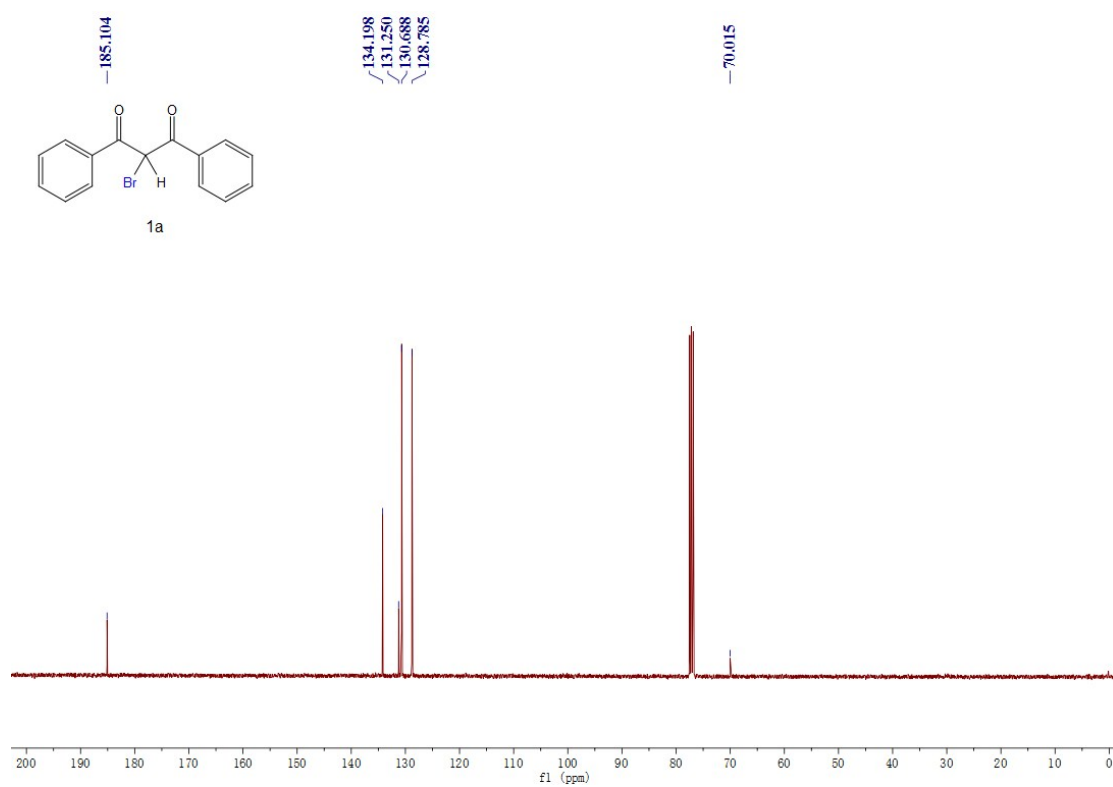
4. ^1H , ^{19}F and ^{13}C NMR spectra

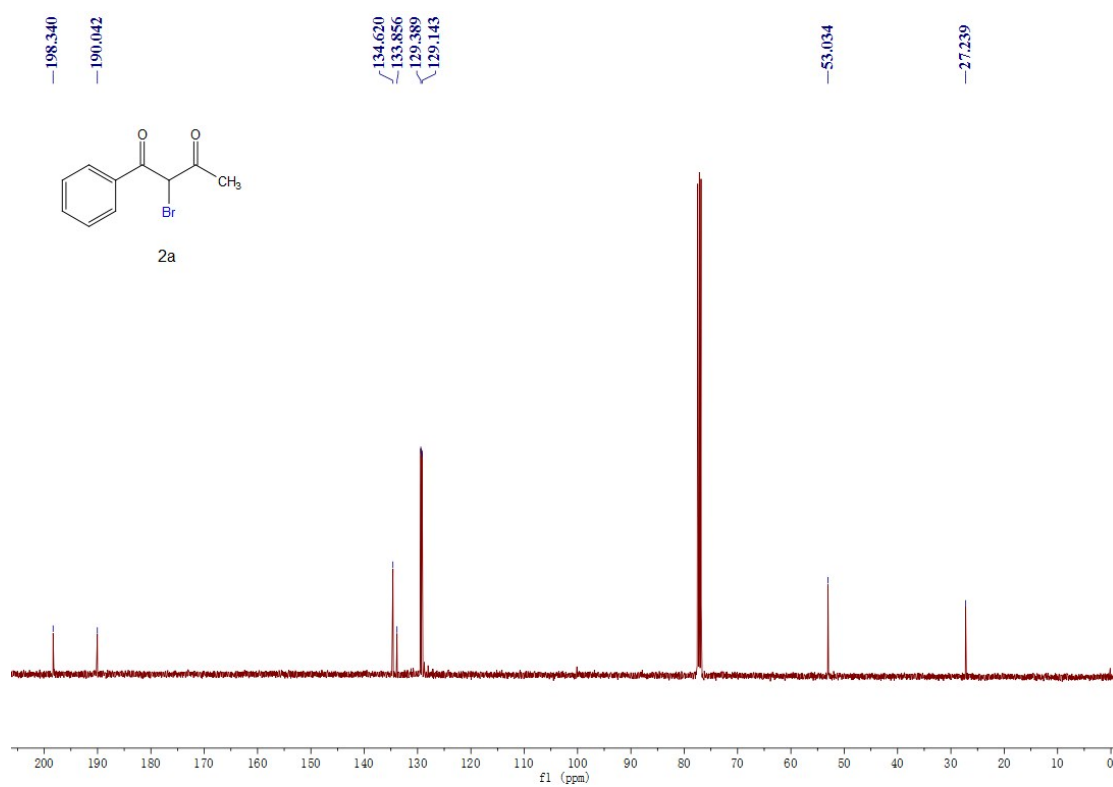
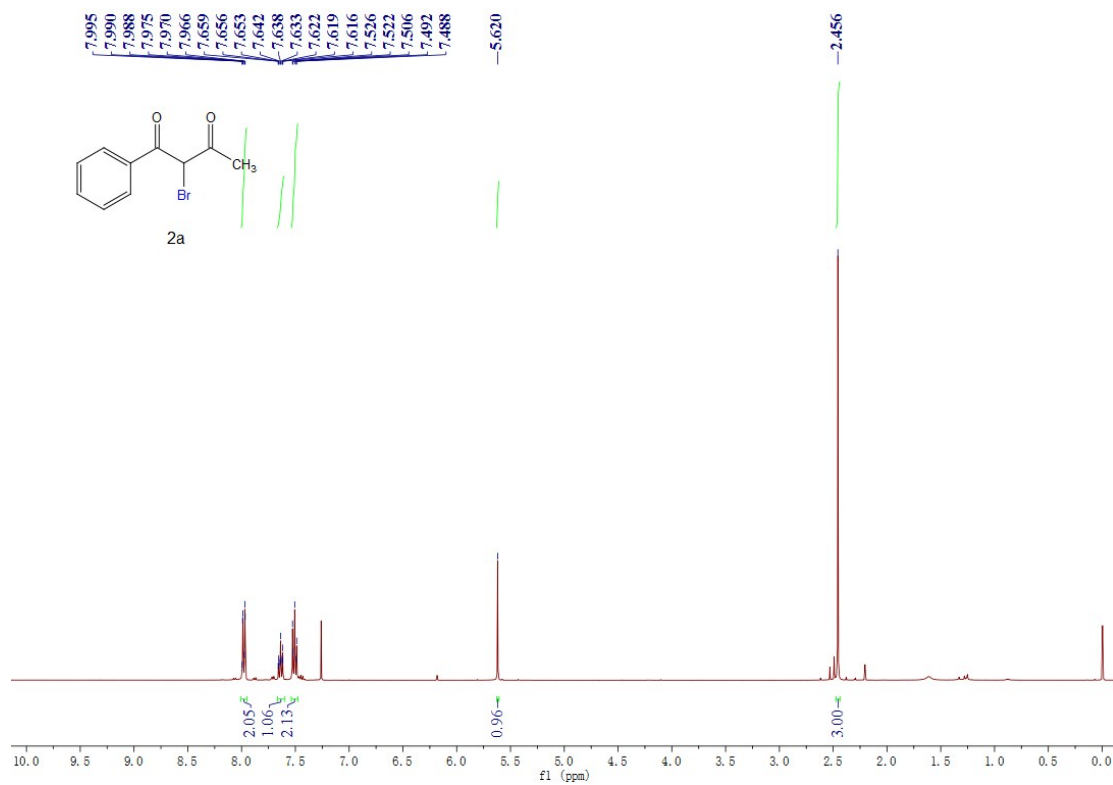


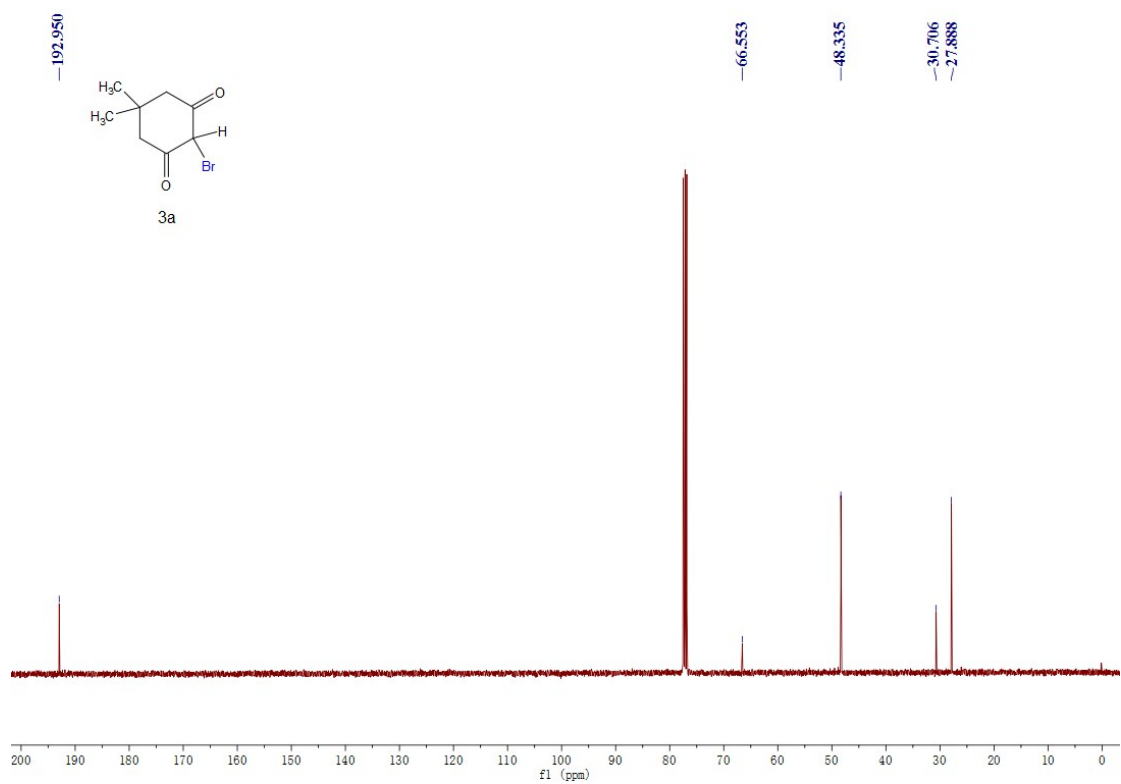
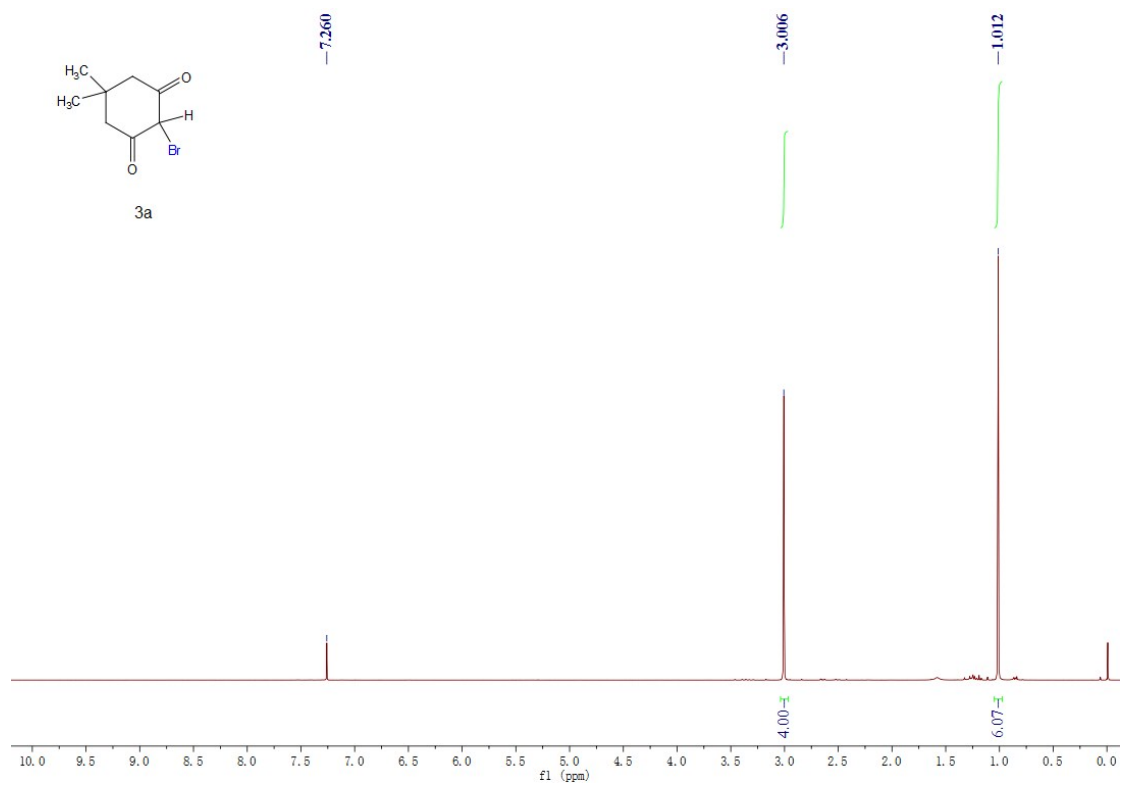


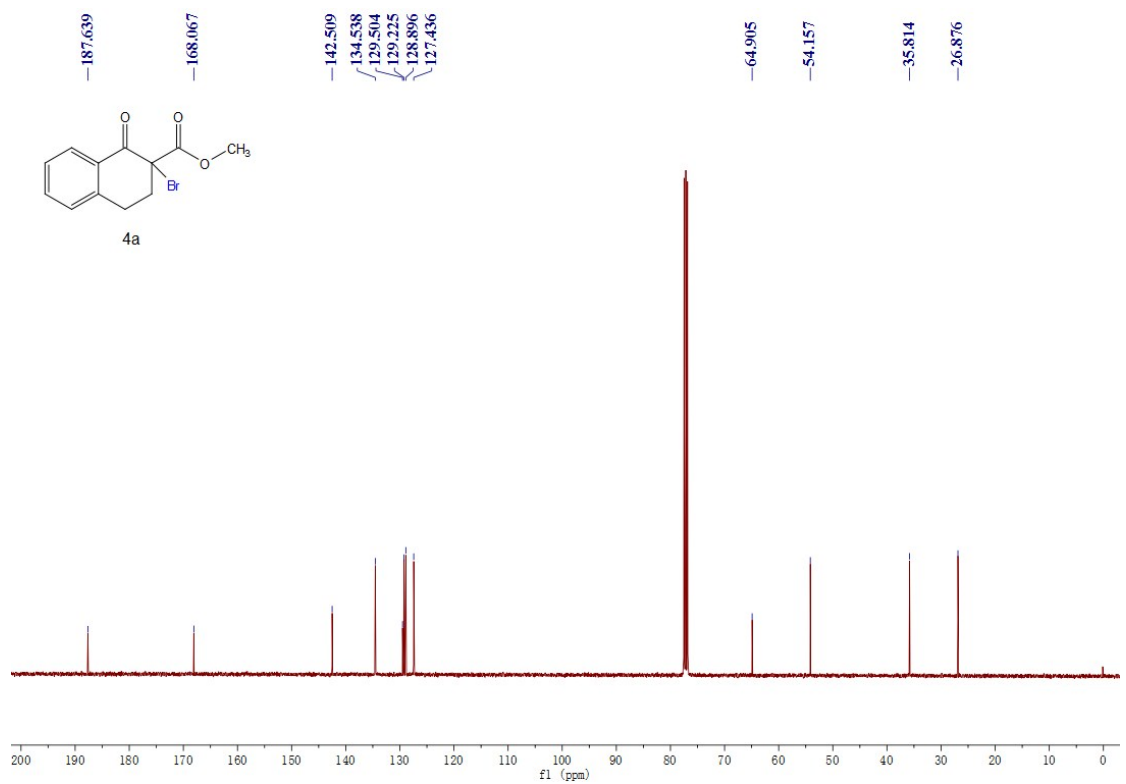
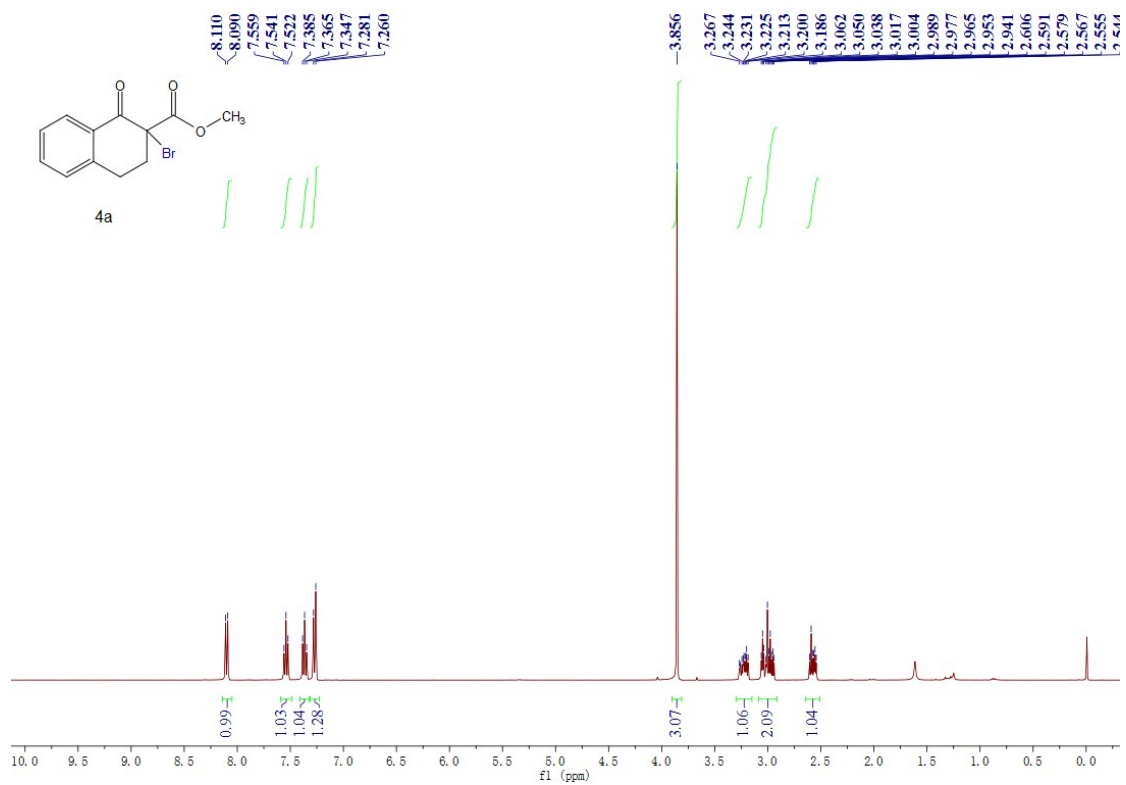


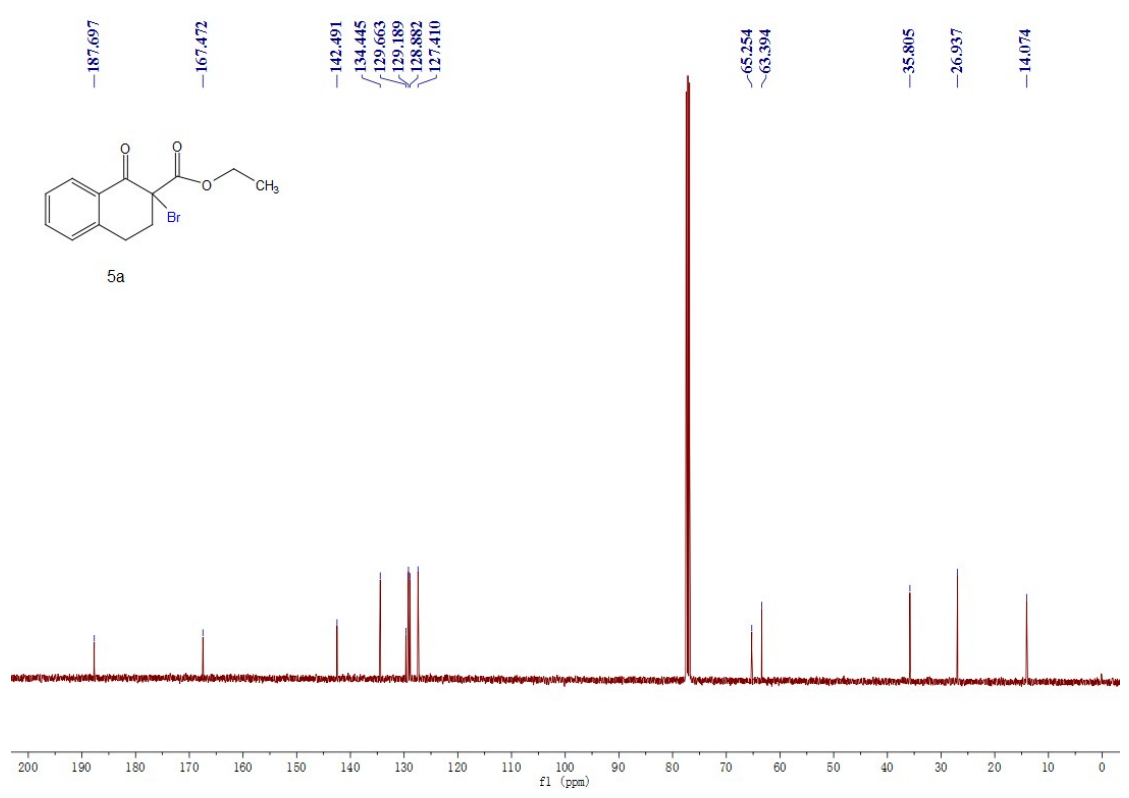
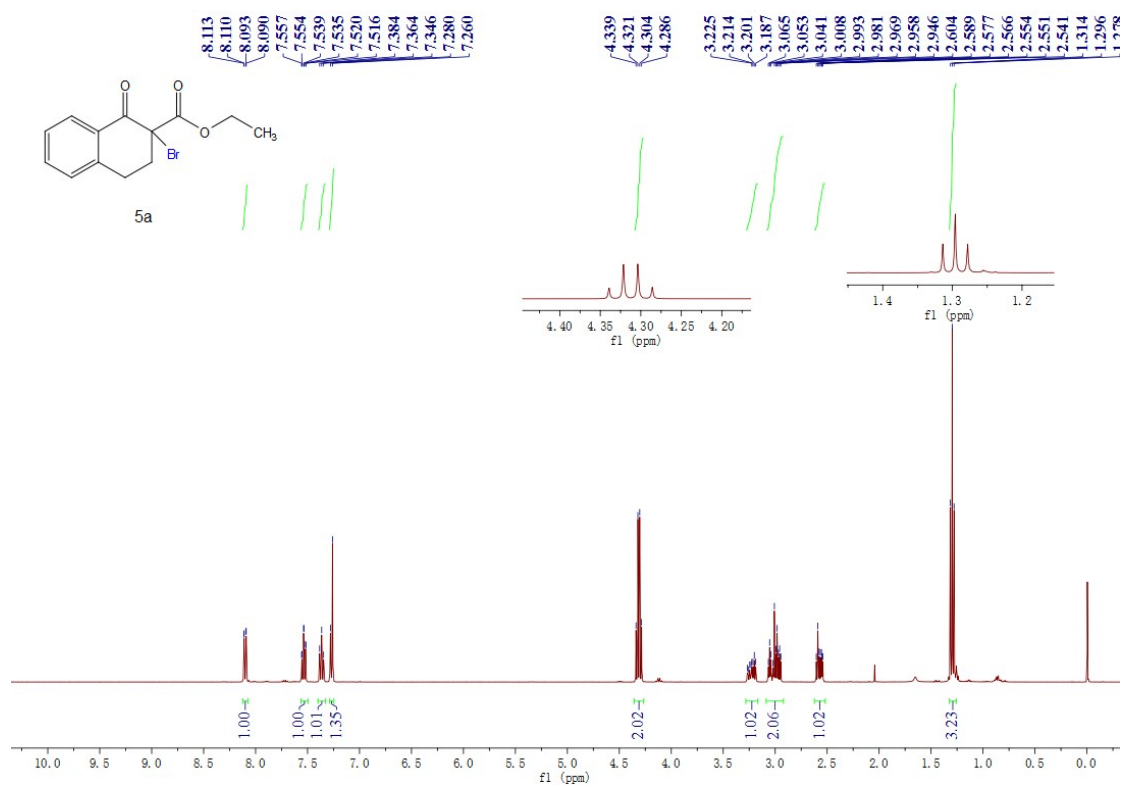
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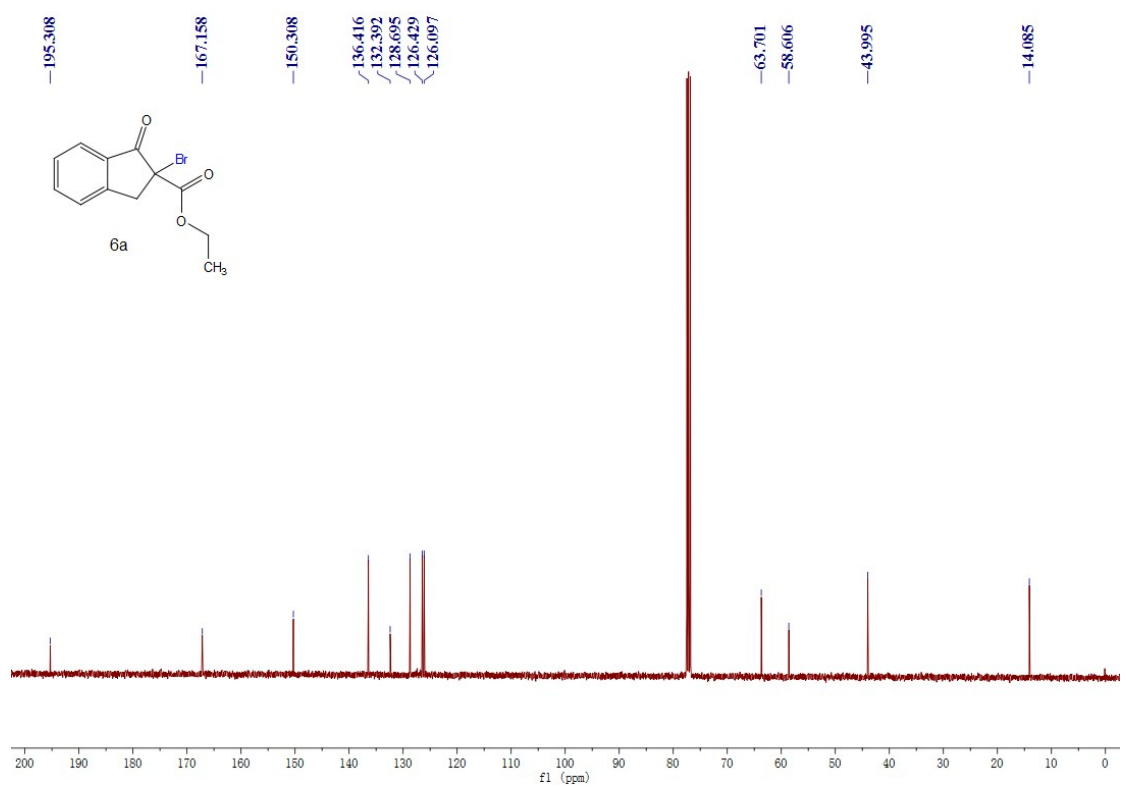
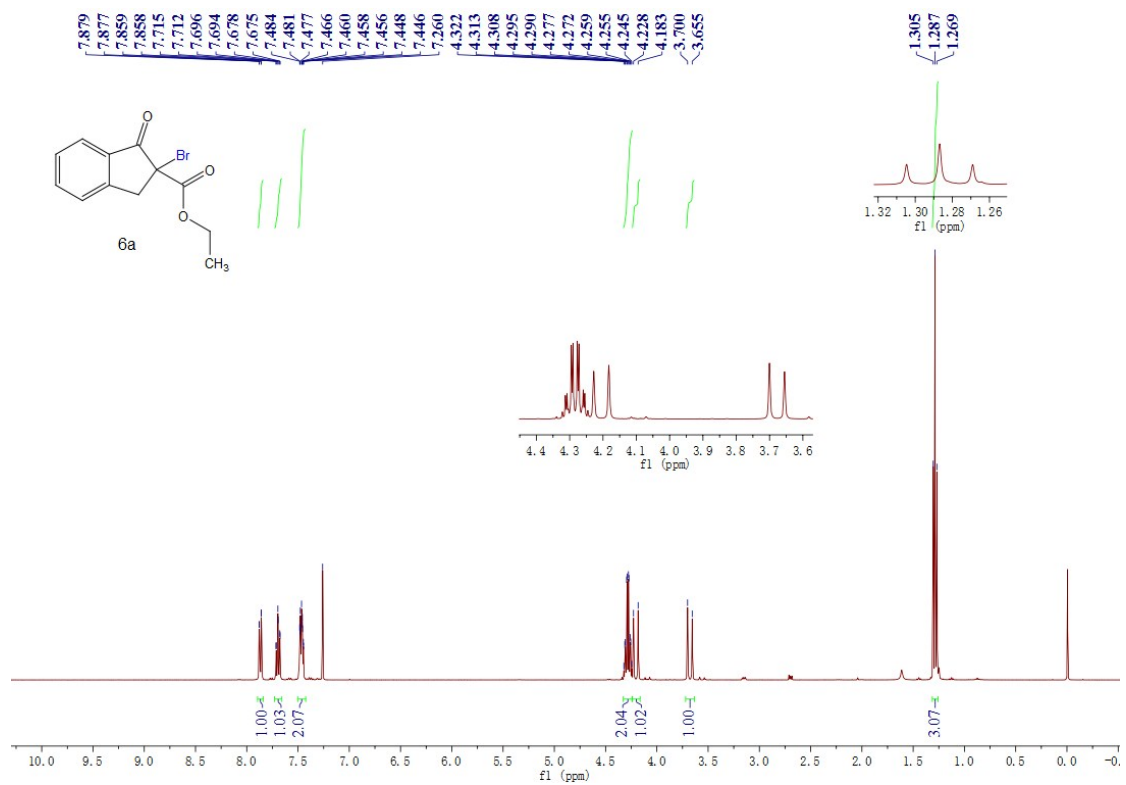


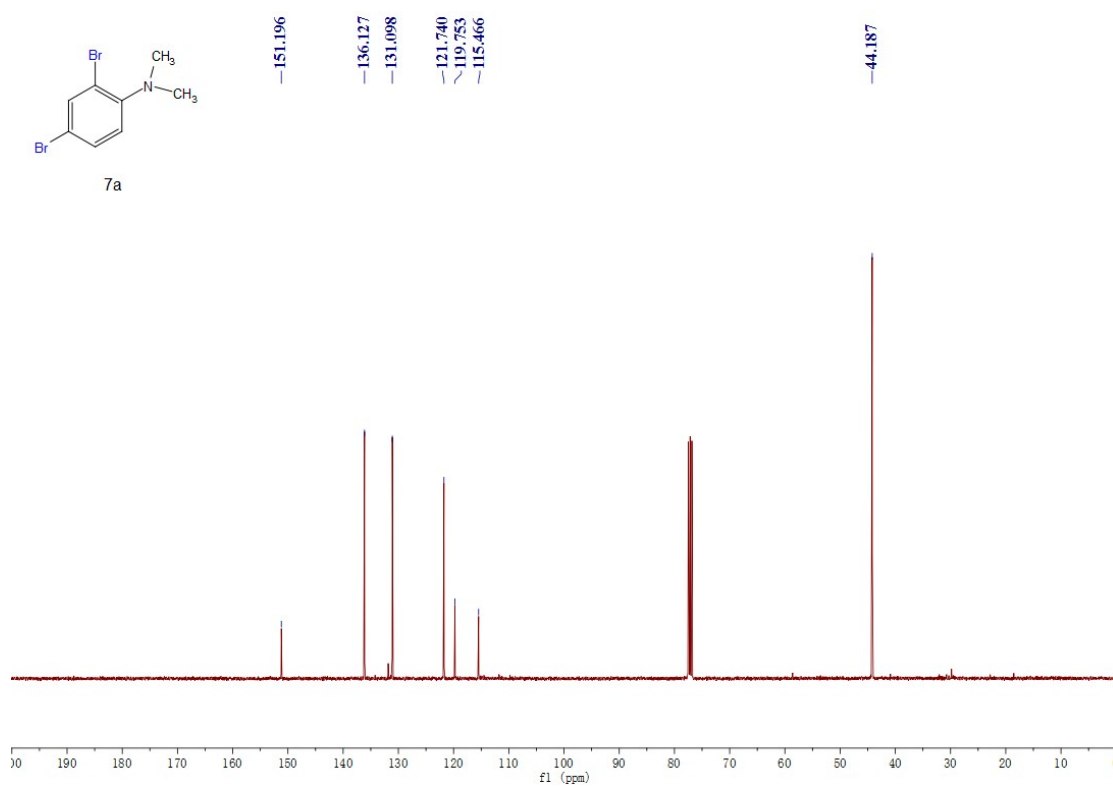
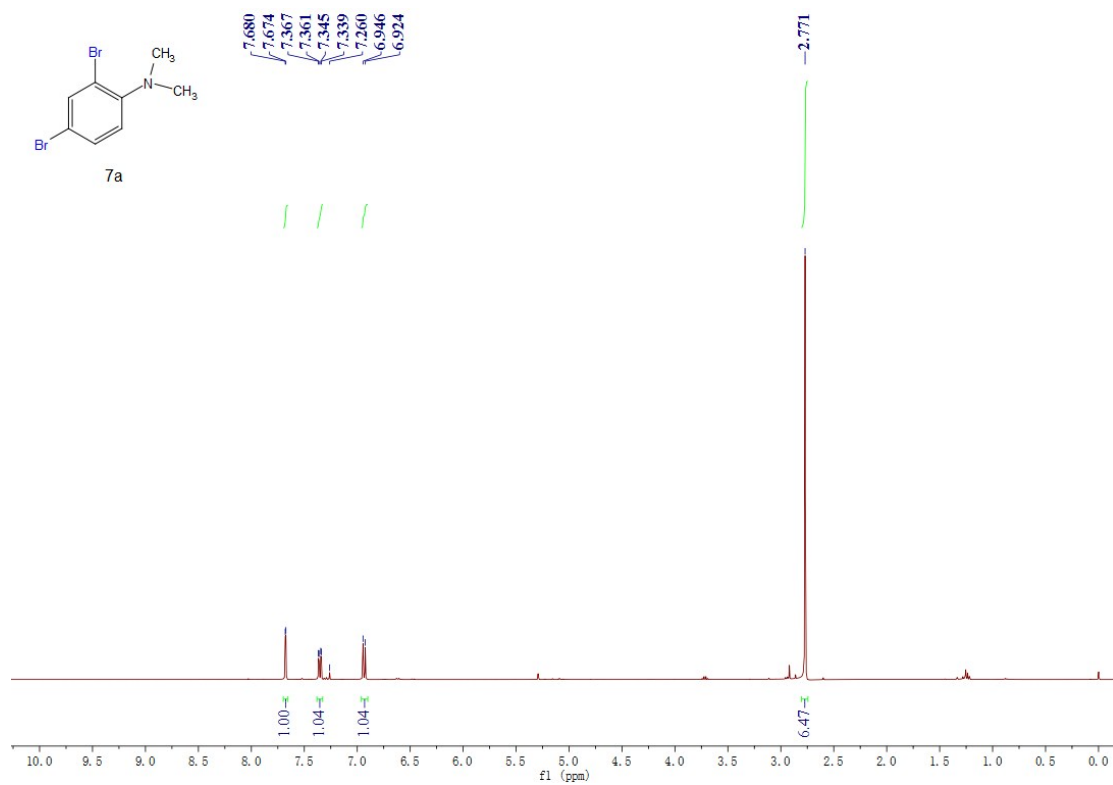


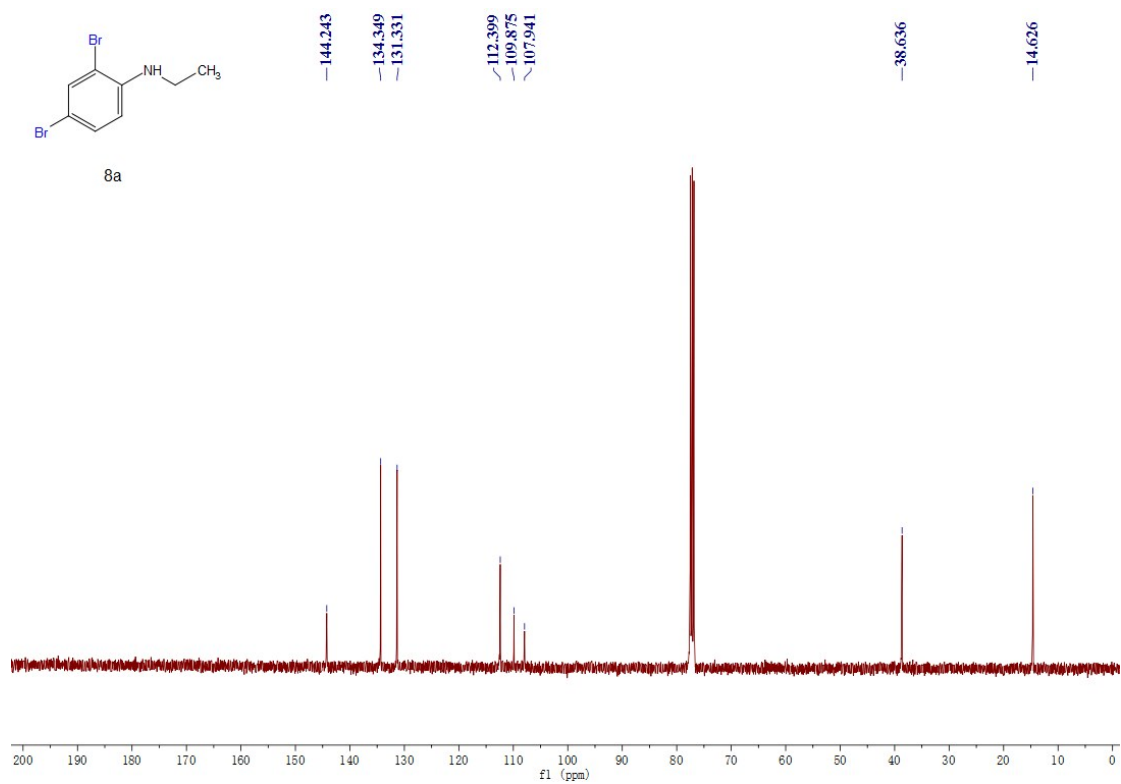
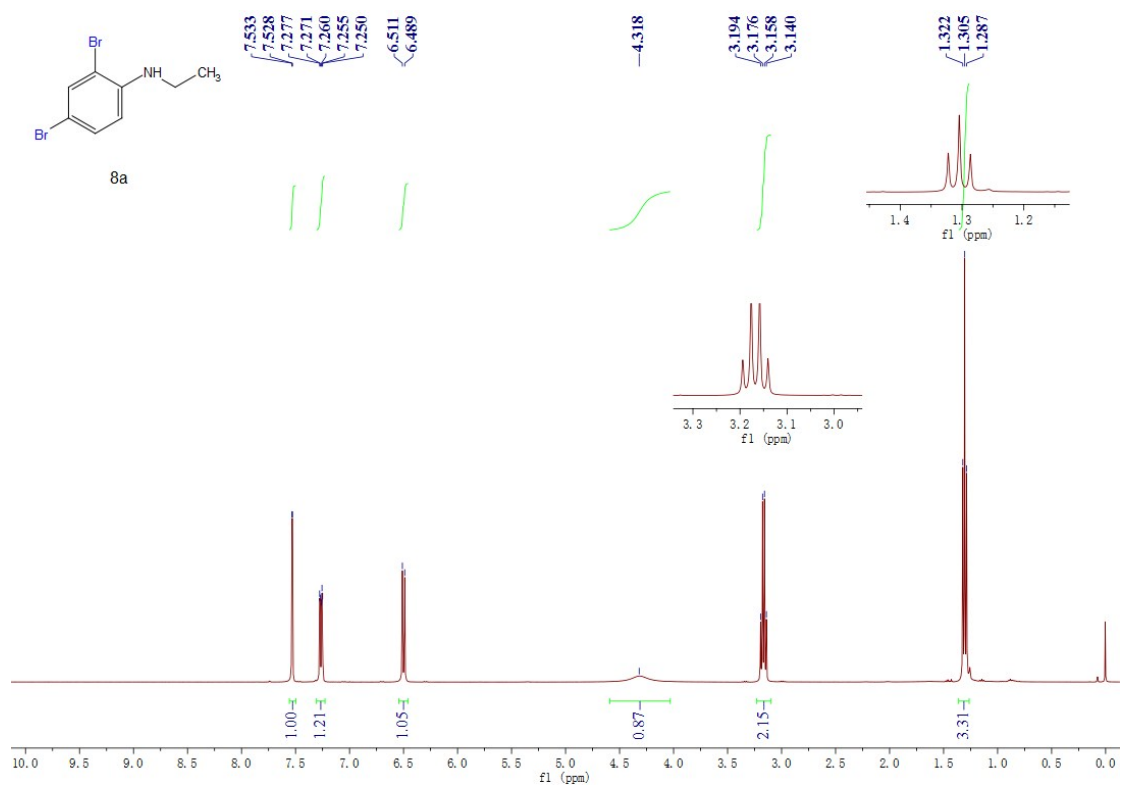


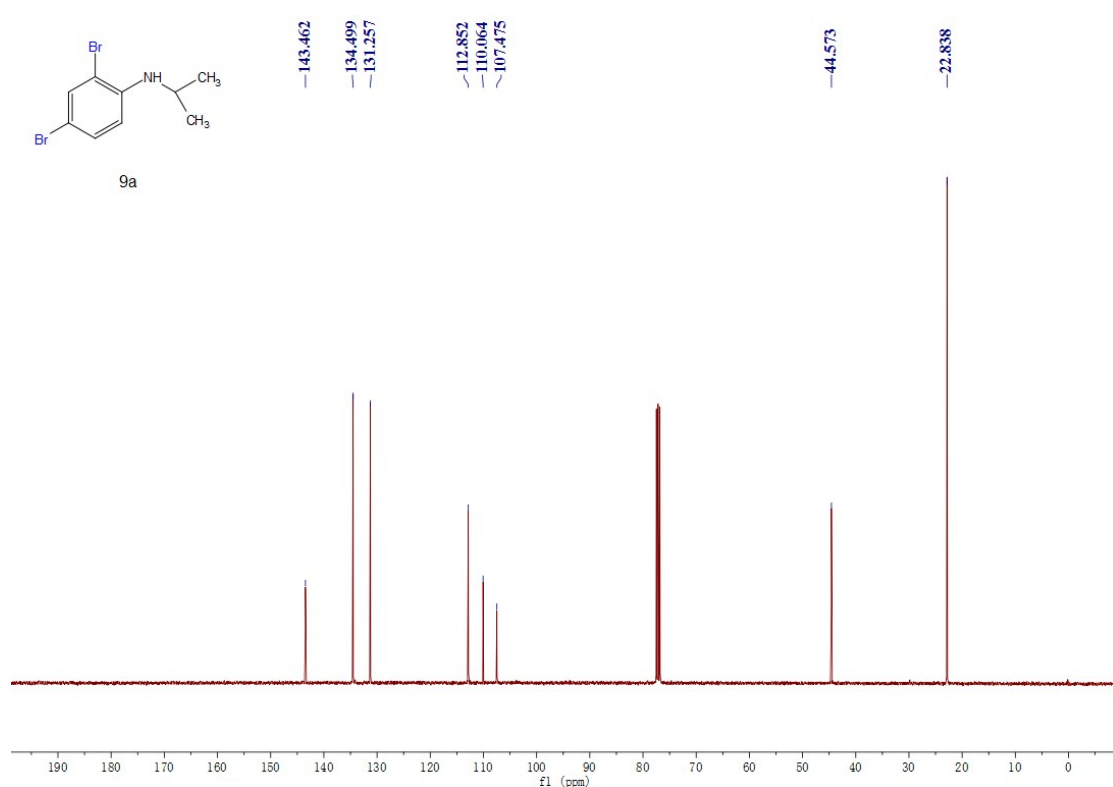
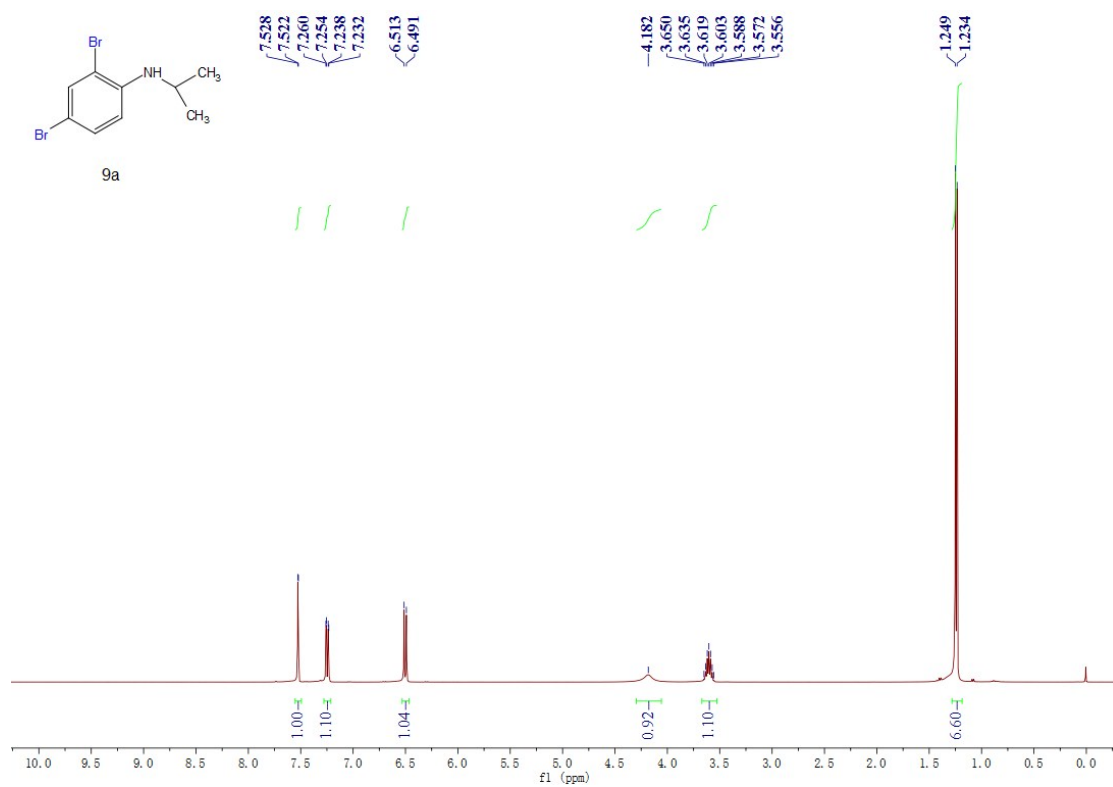


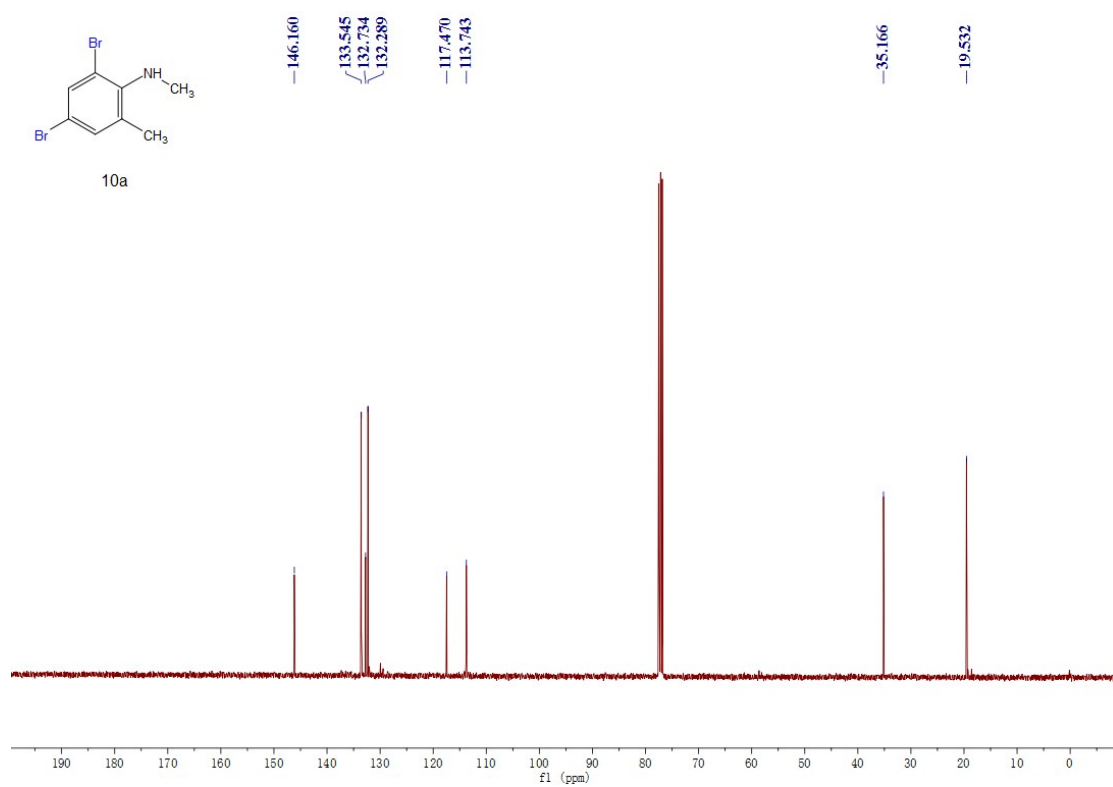
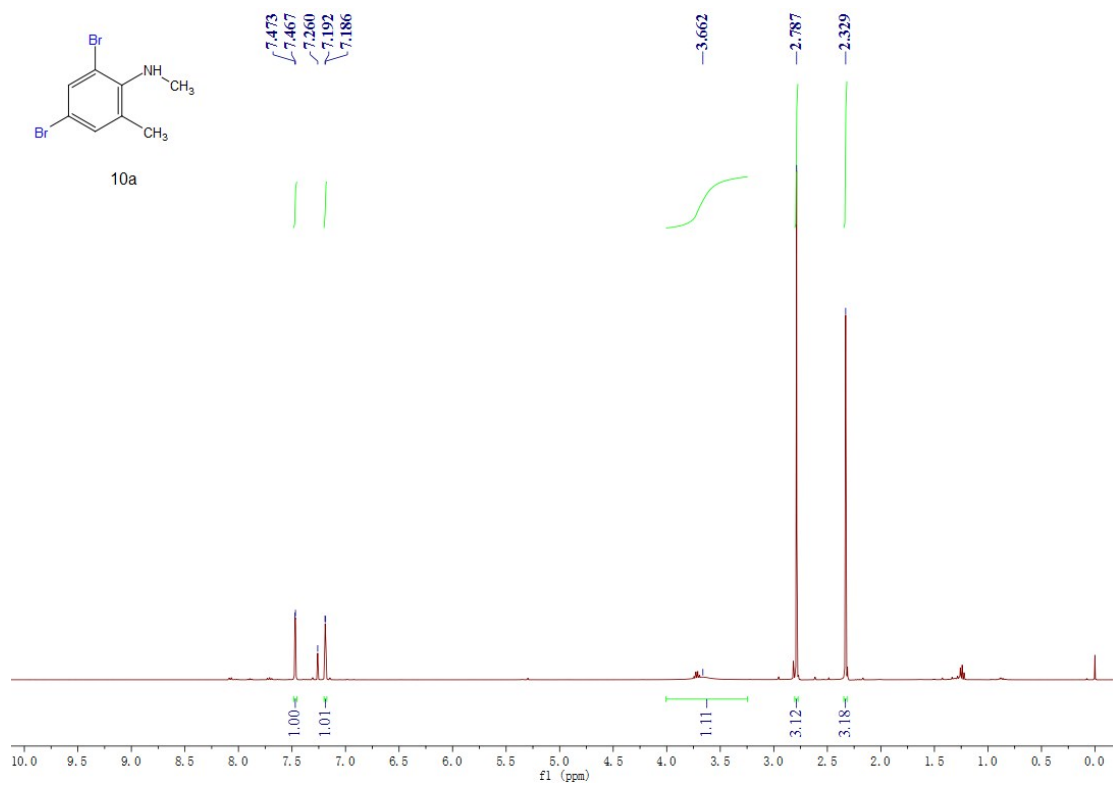


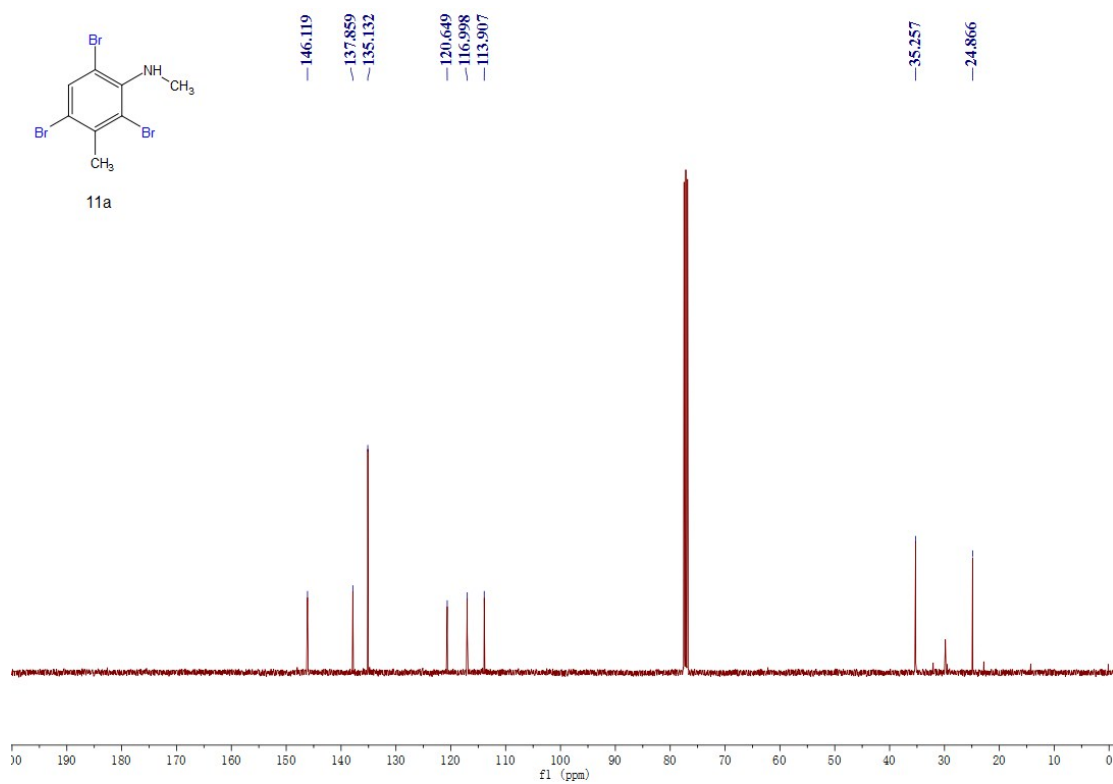
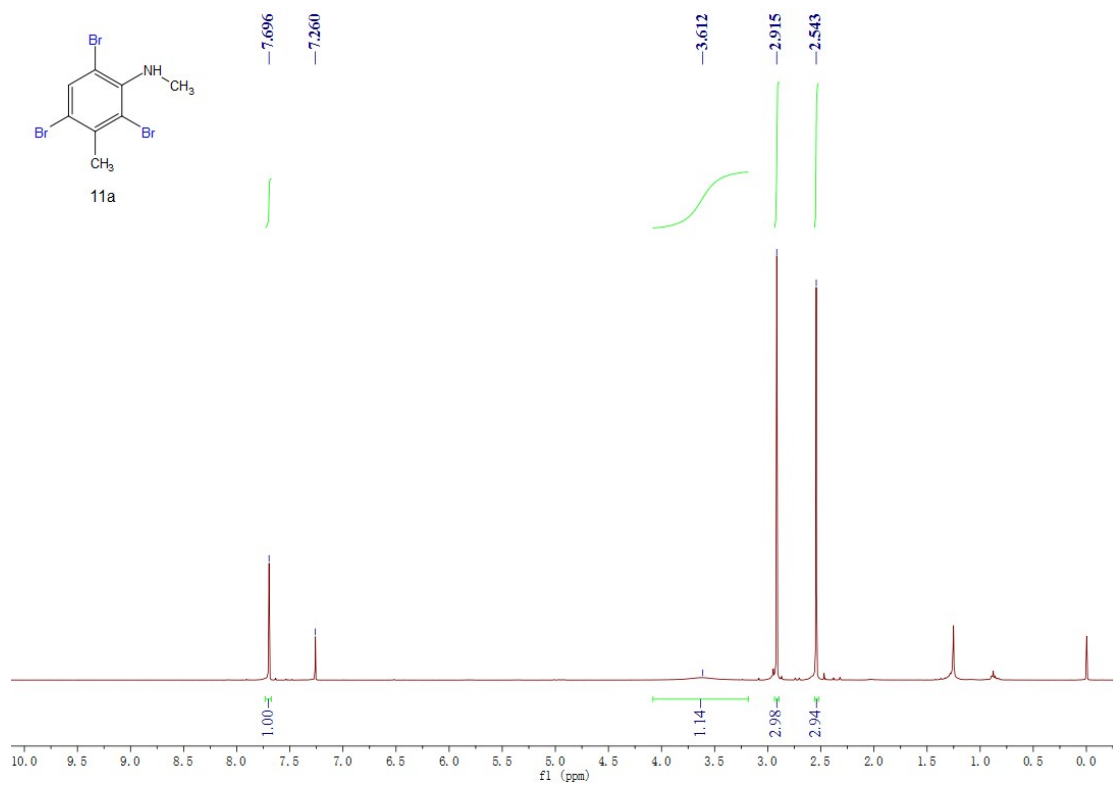


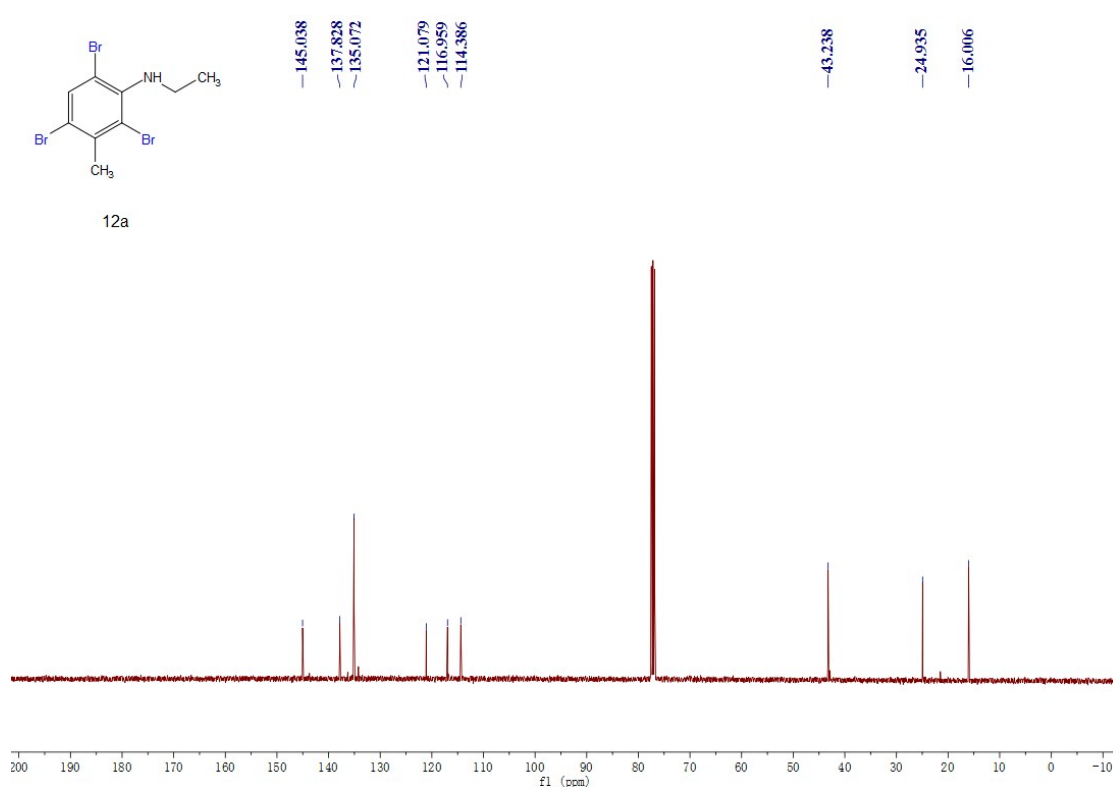
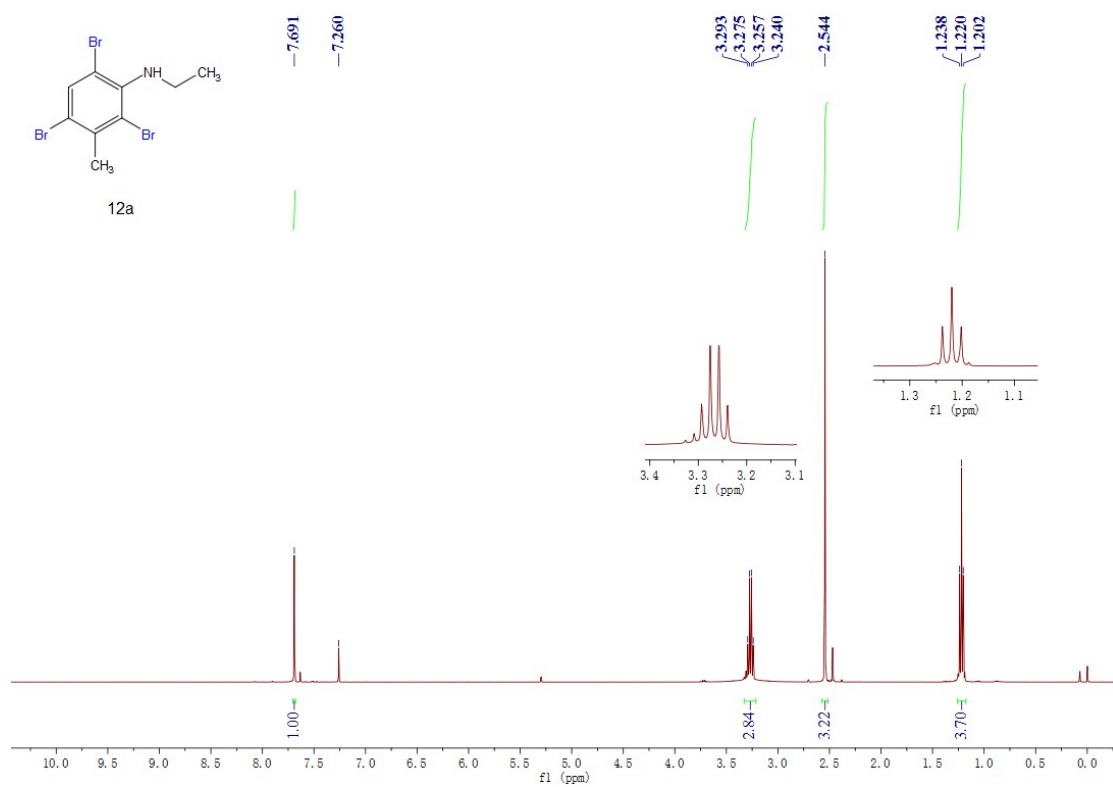


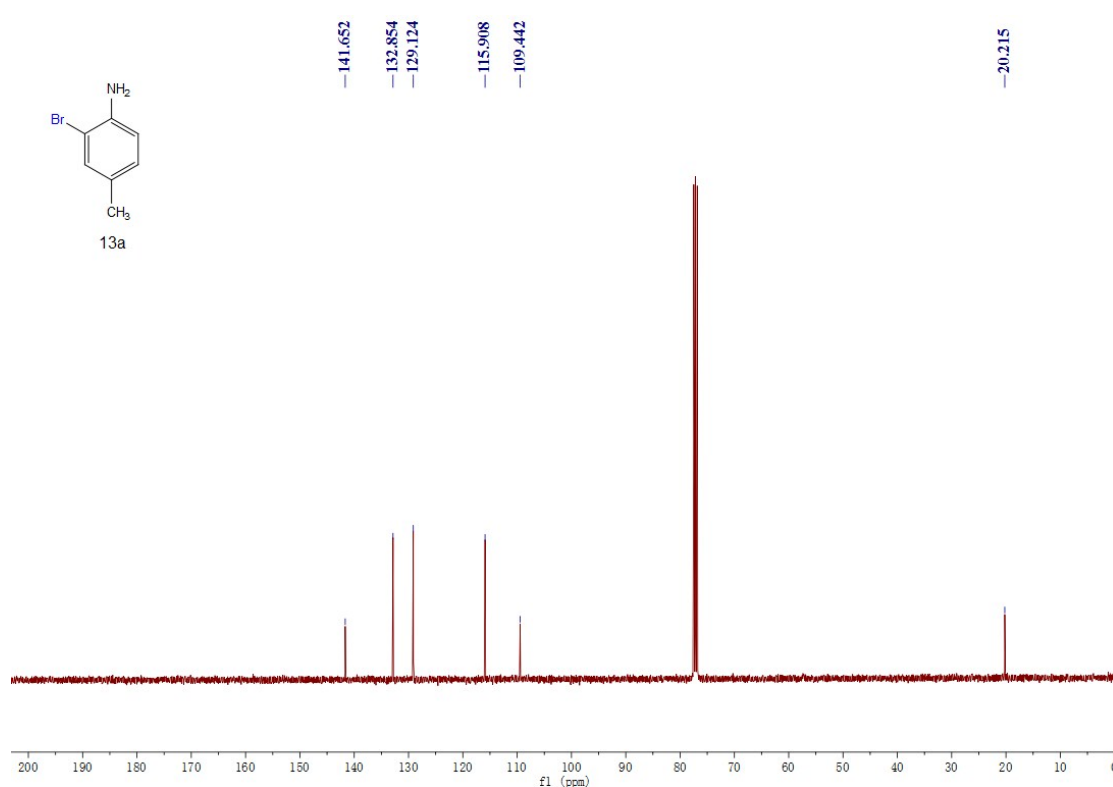
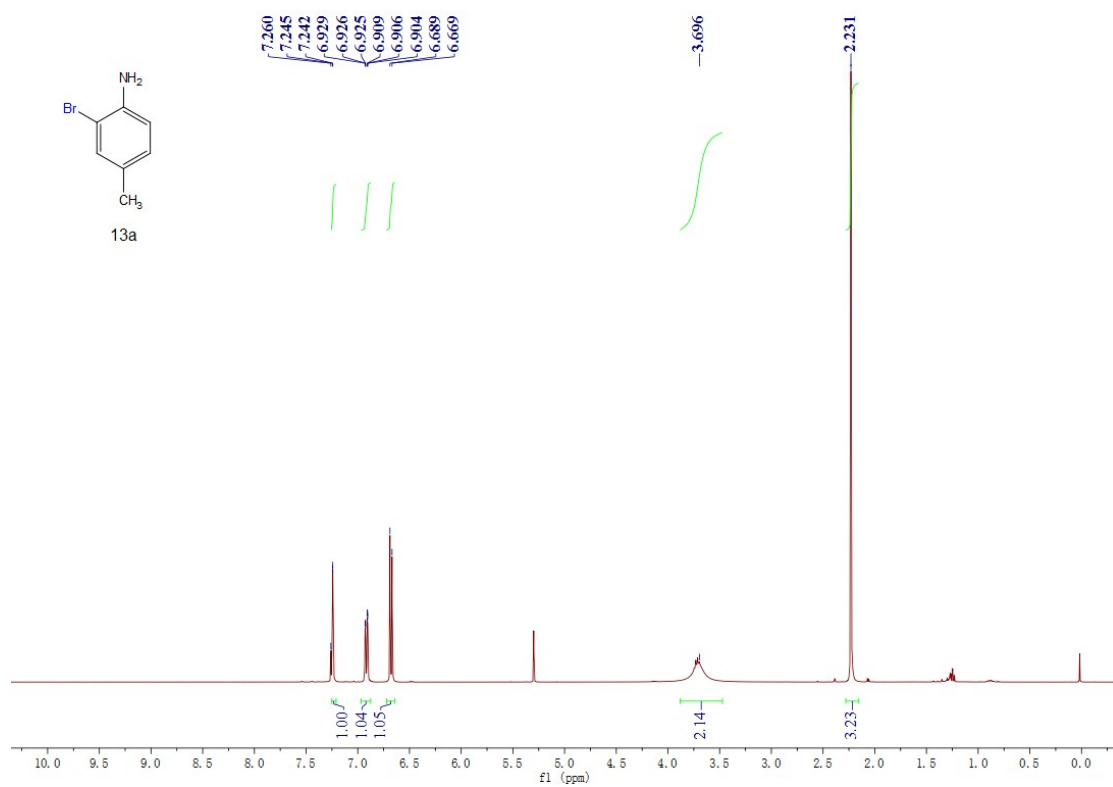


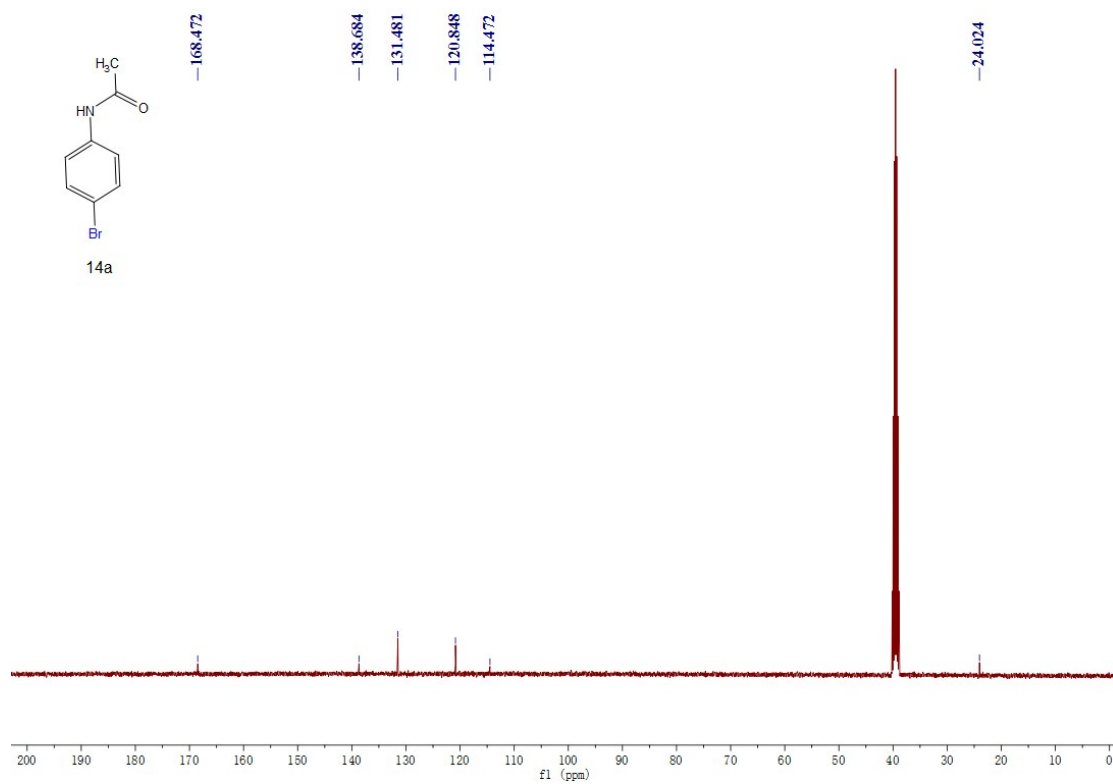
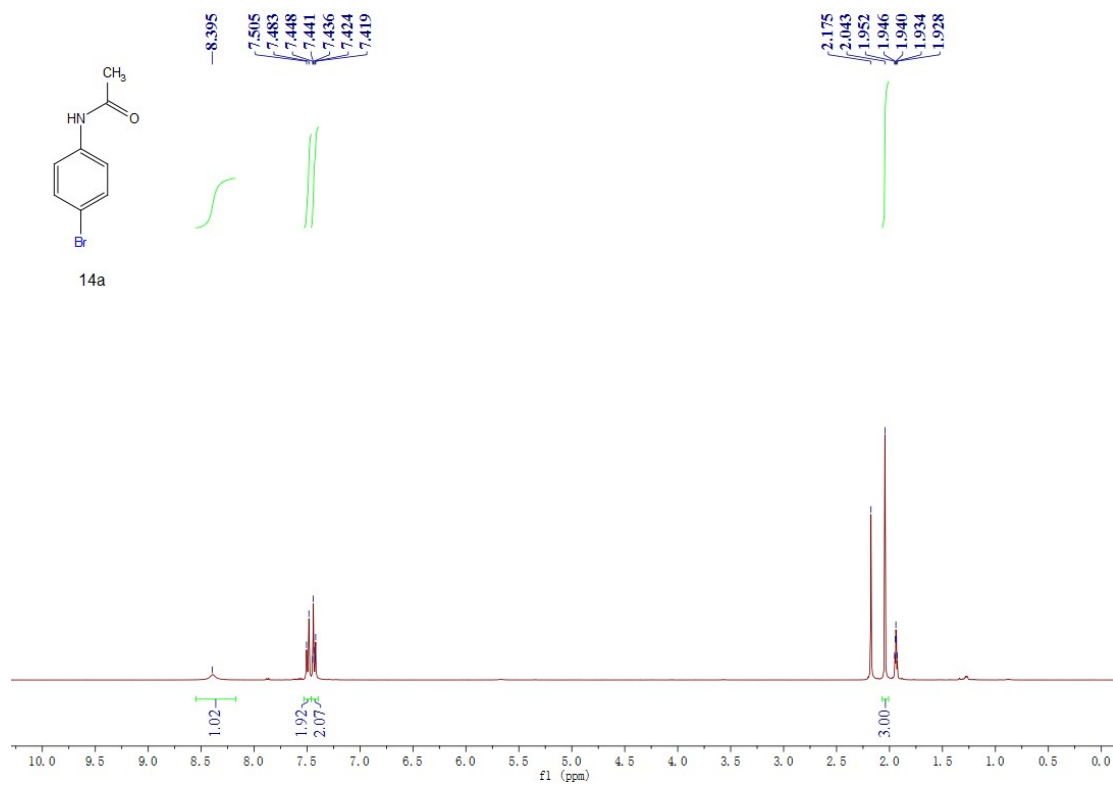


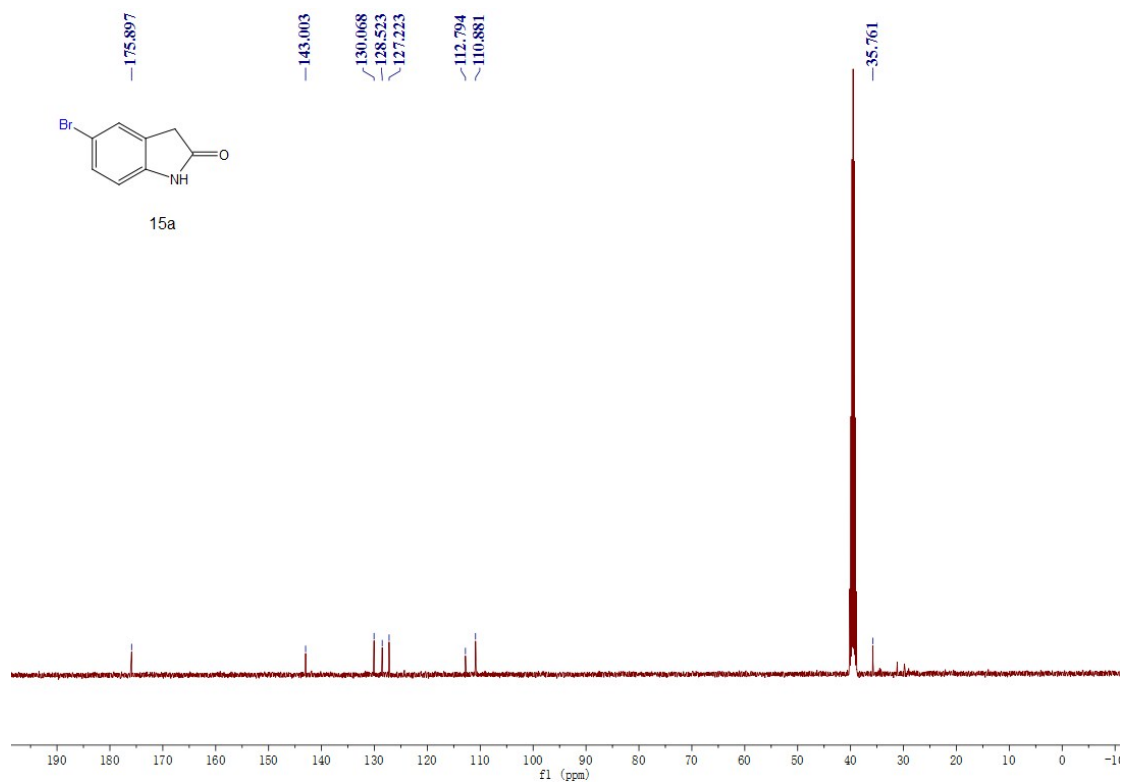
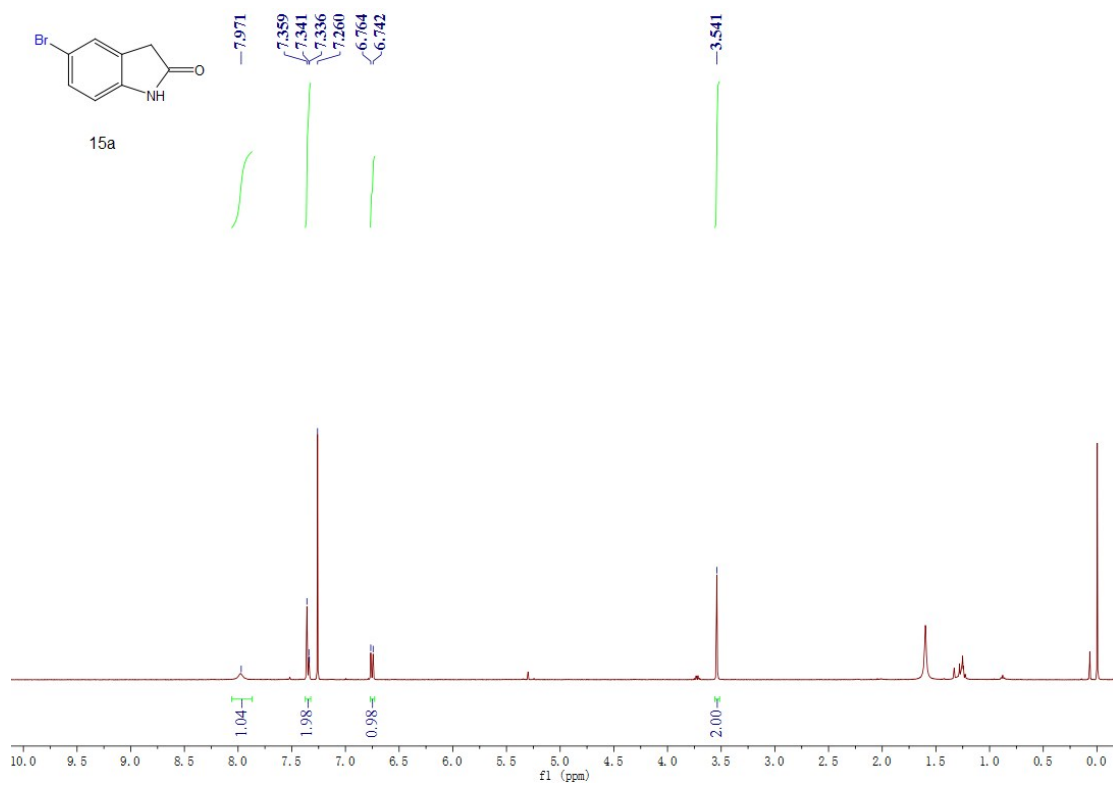


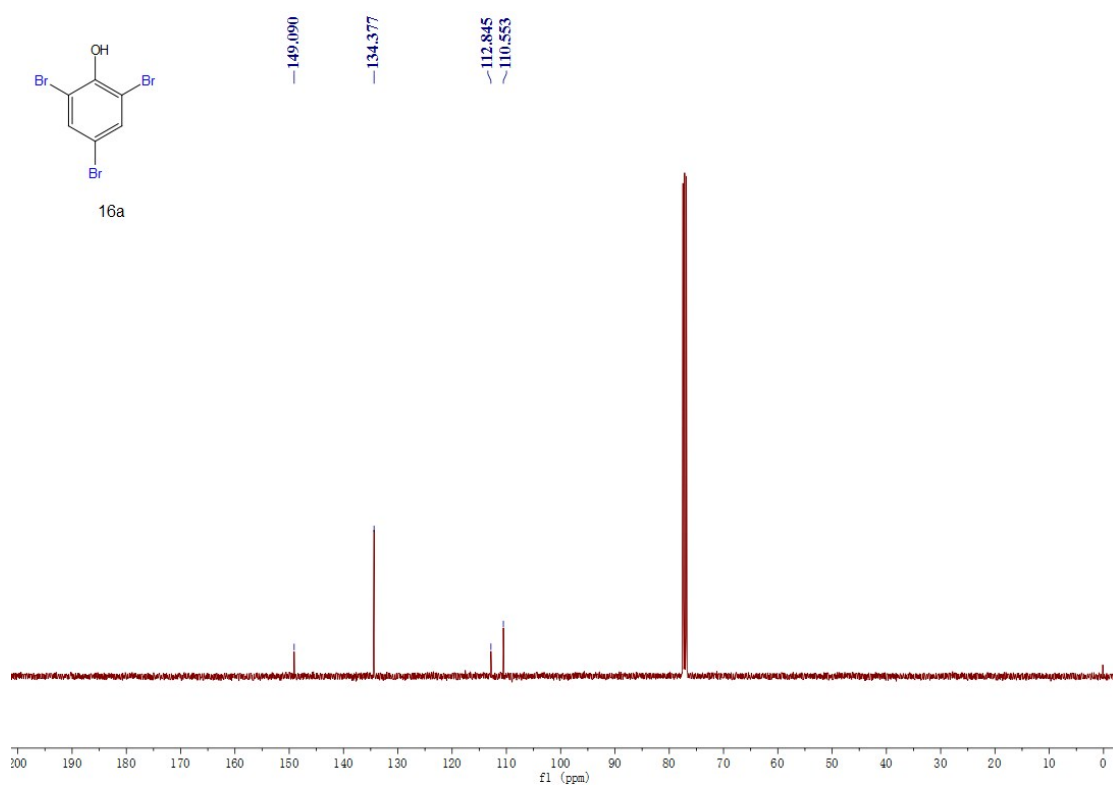
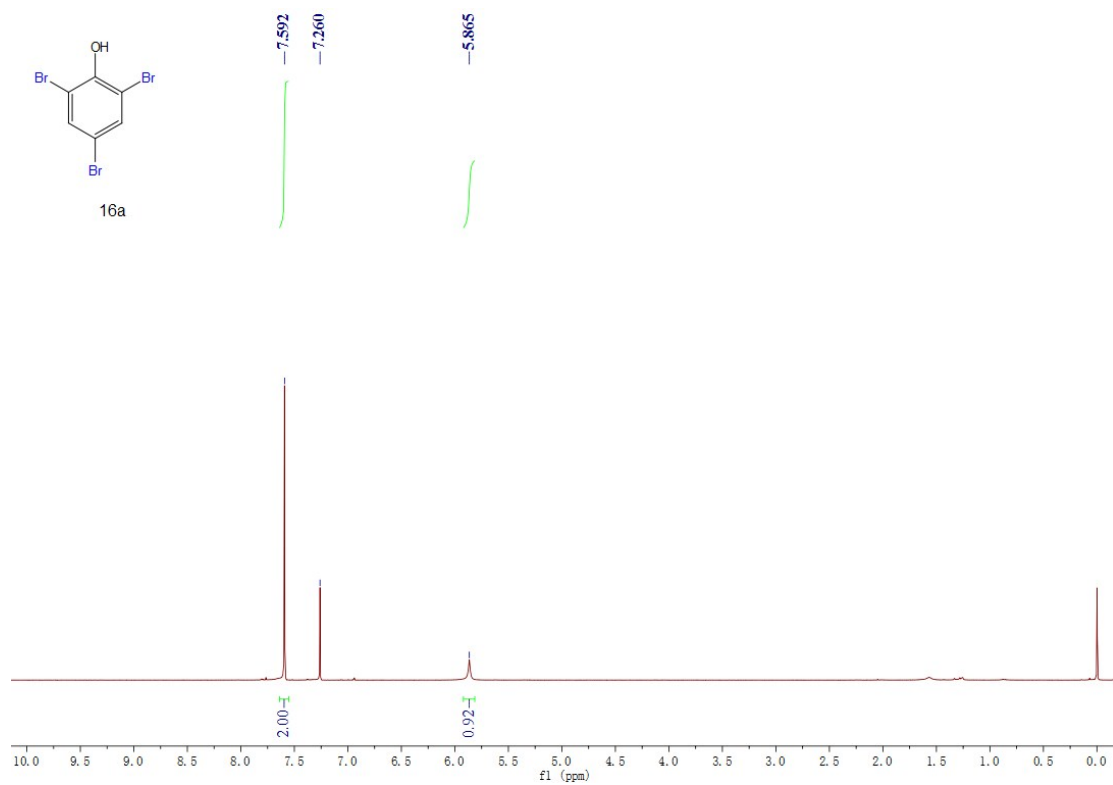


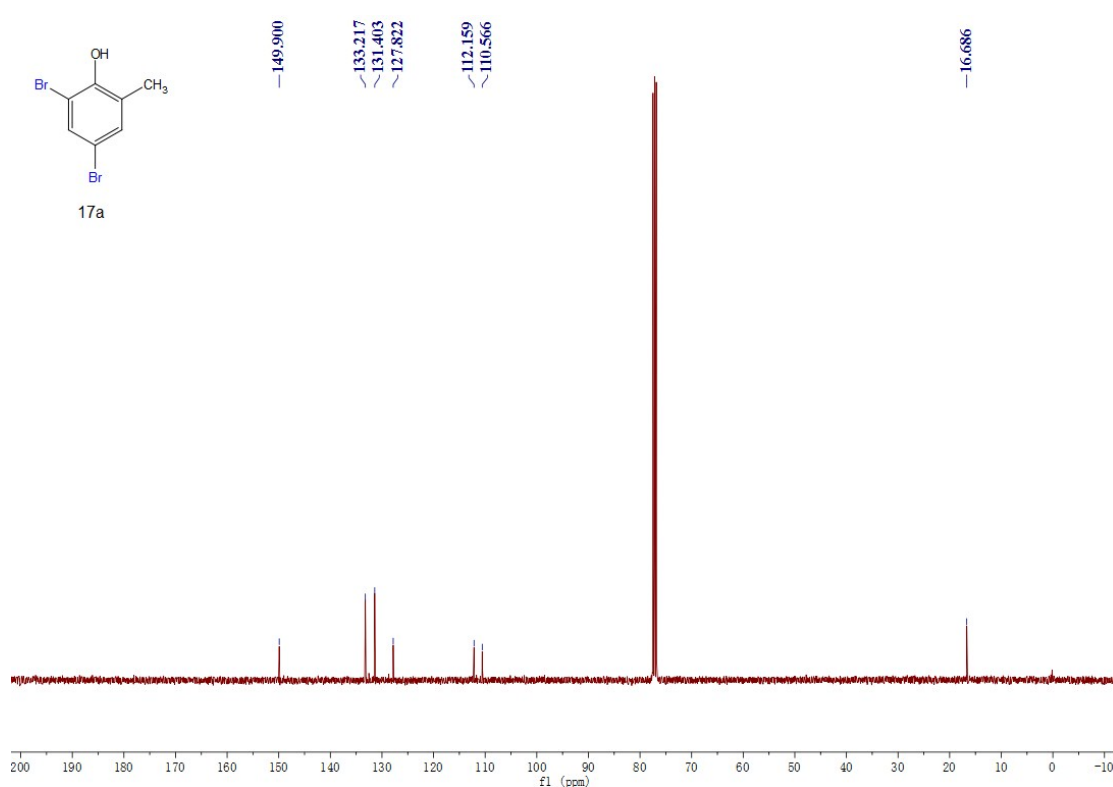
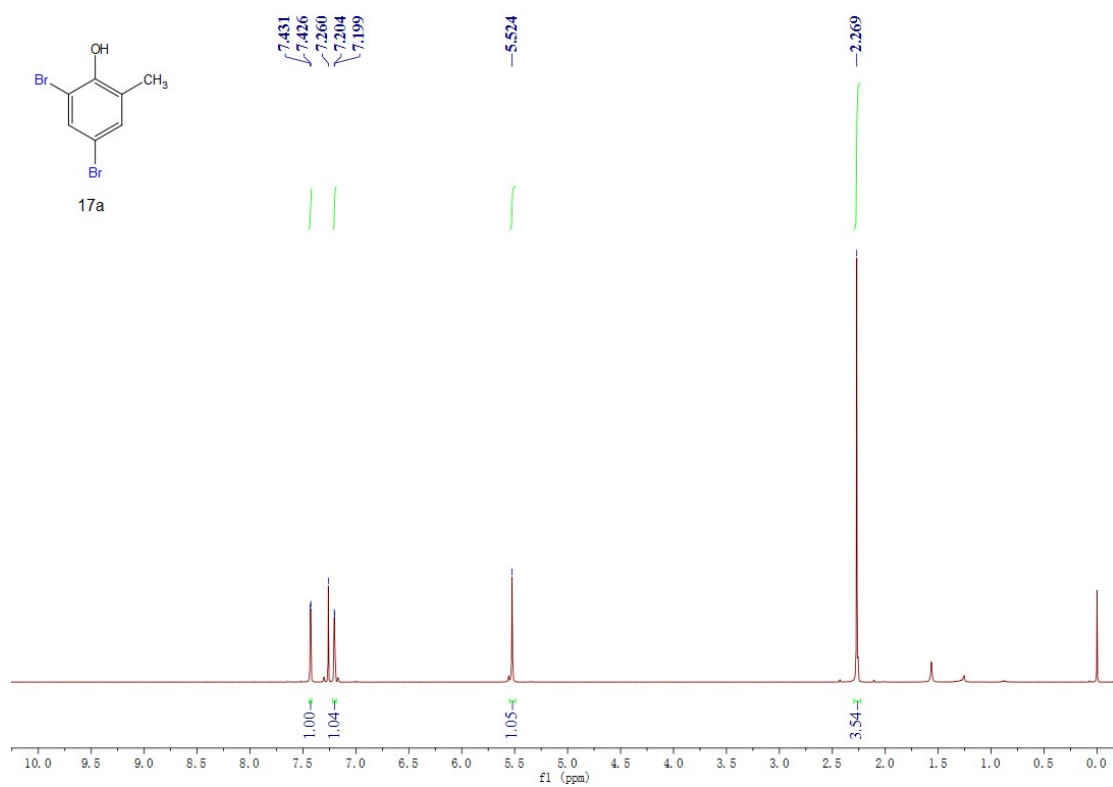


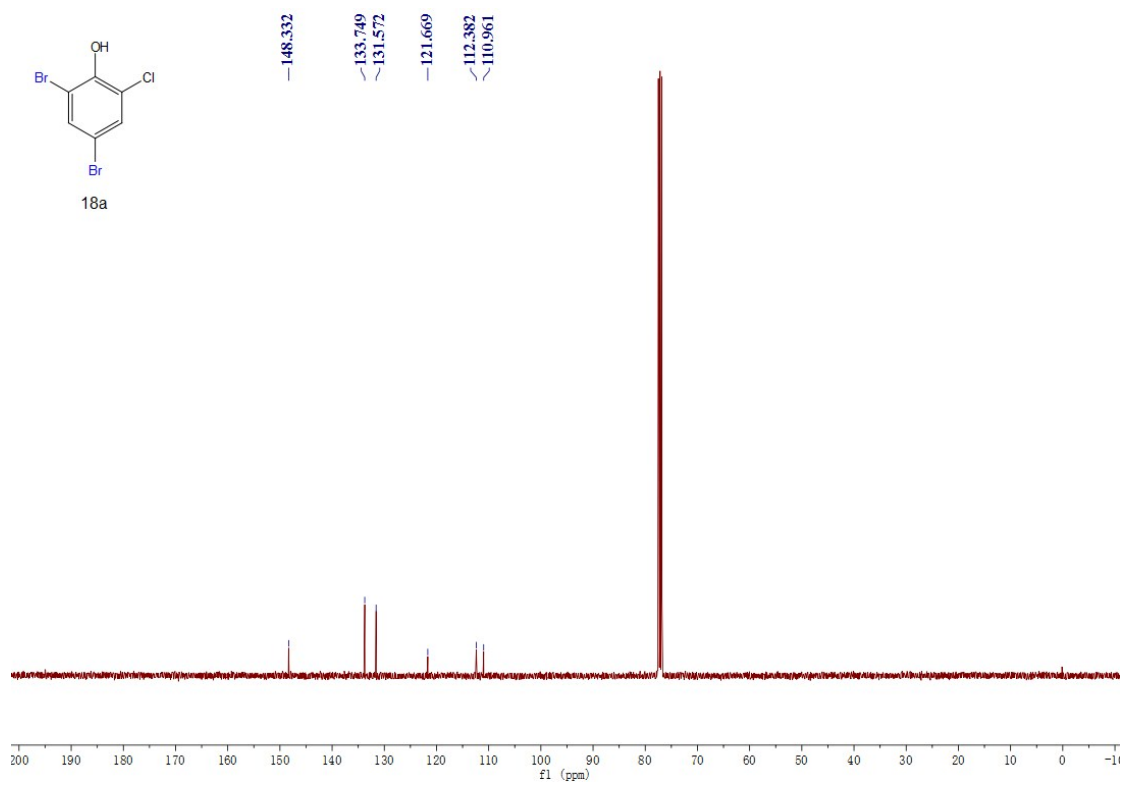
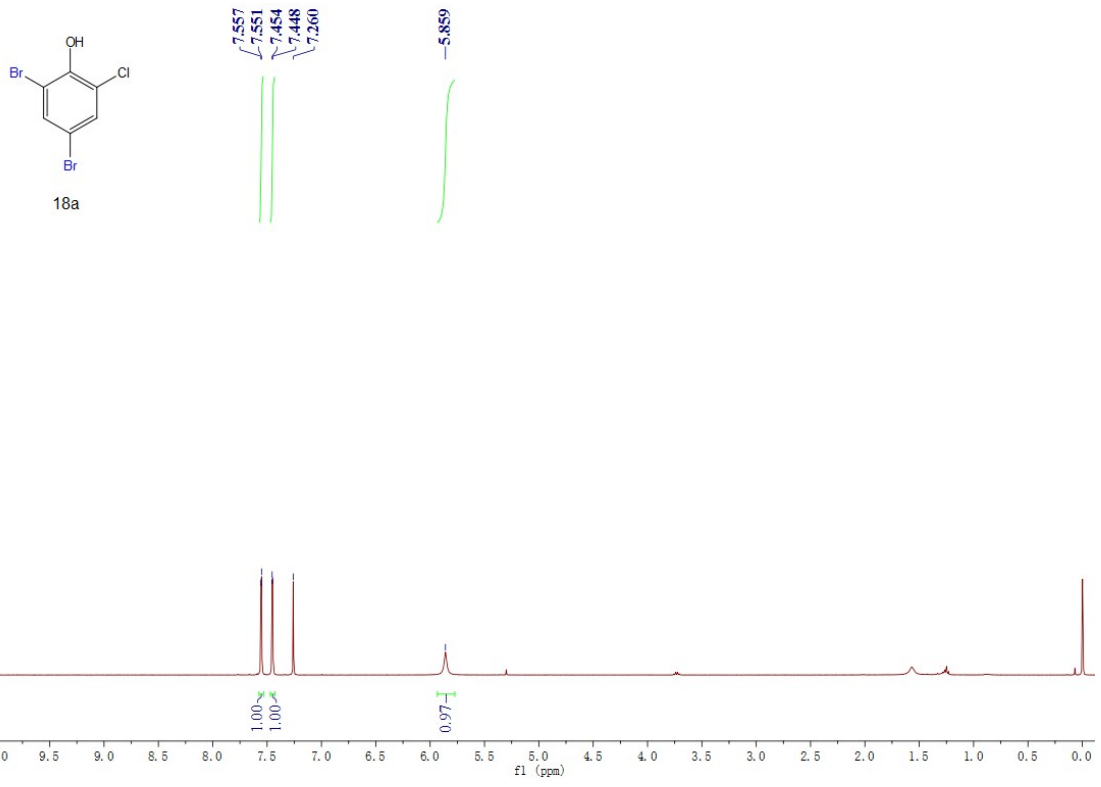


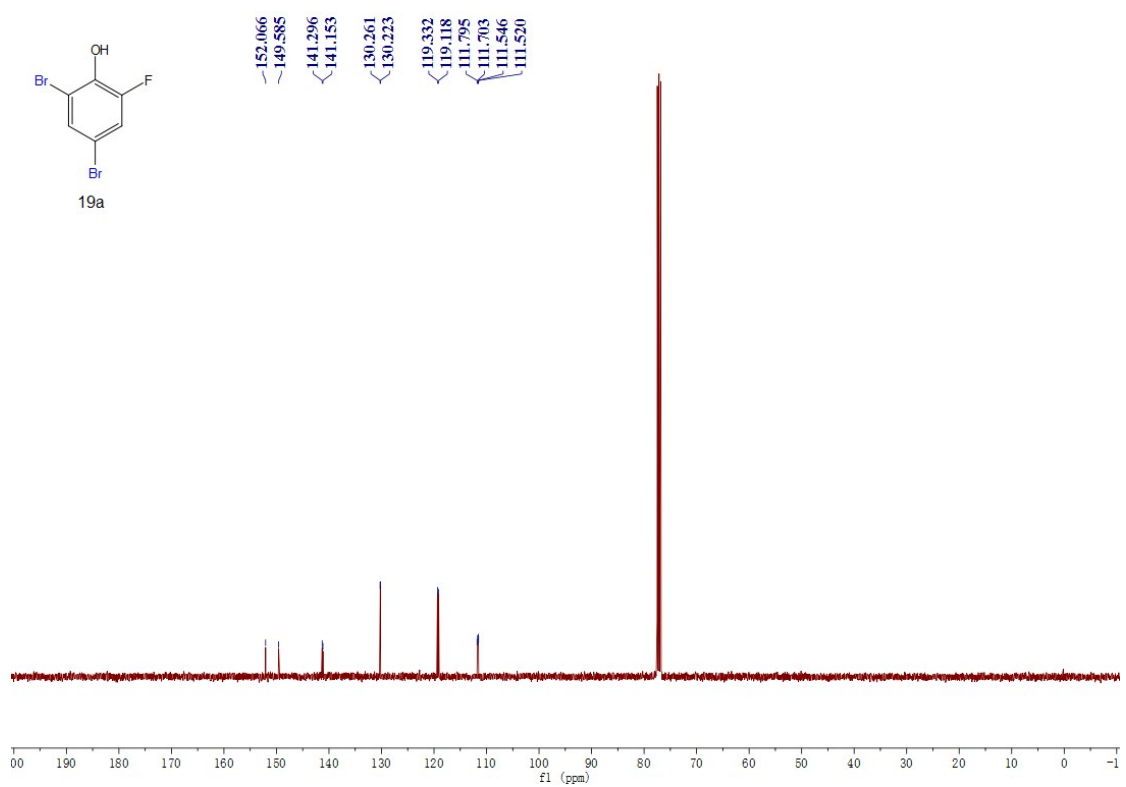
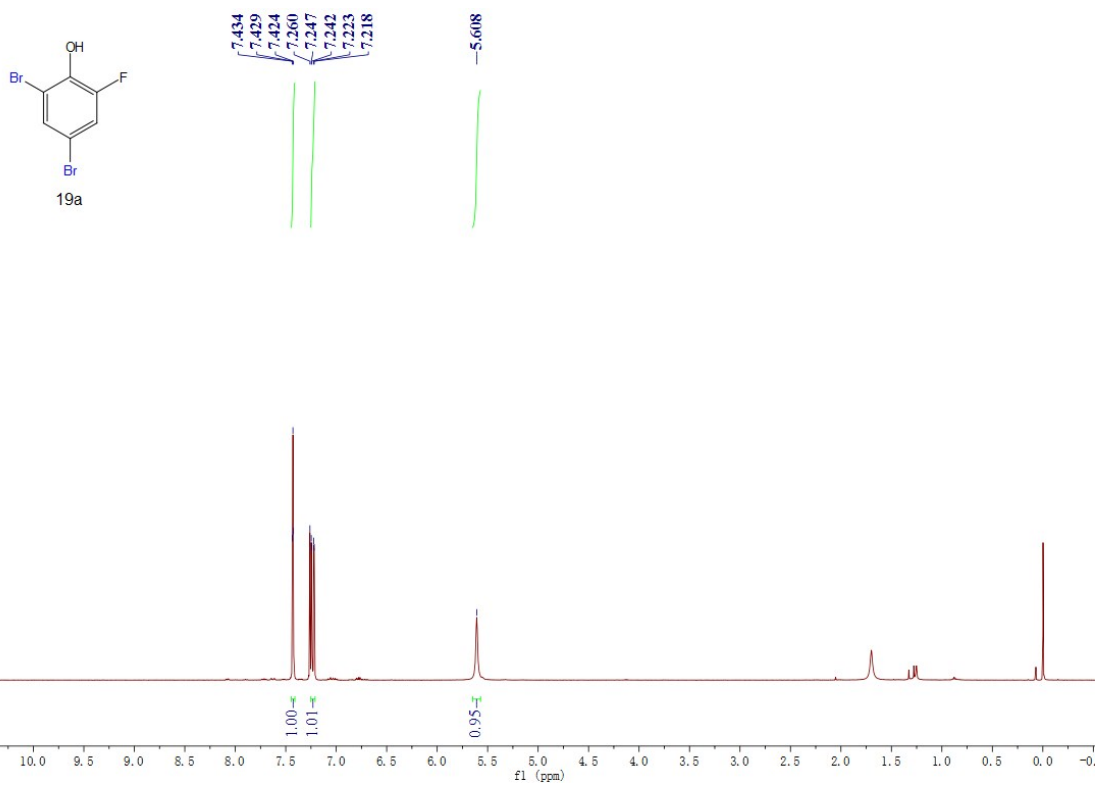


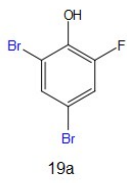




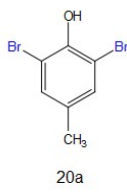
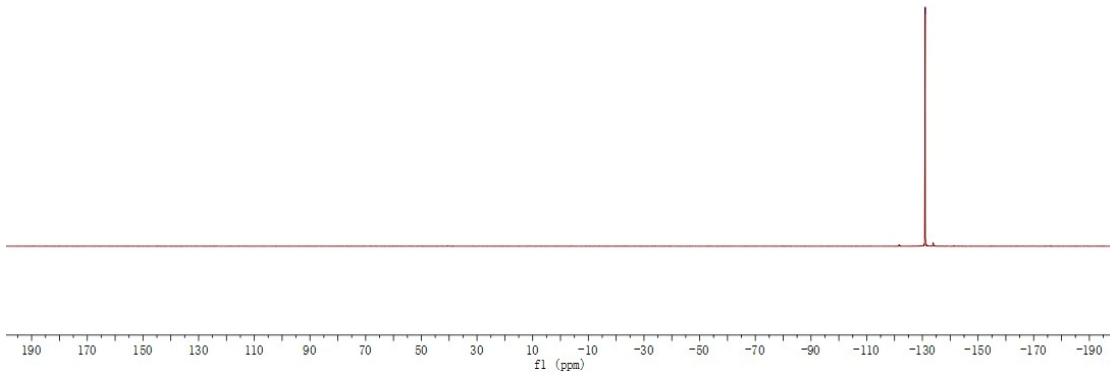








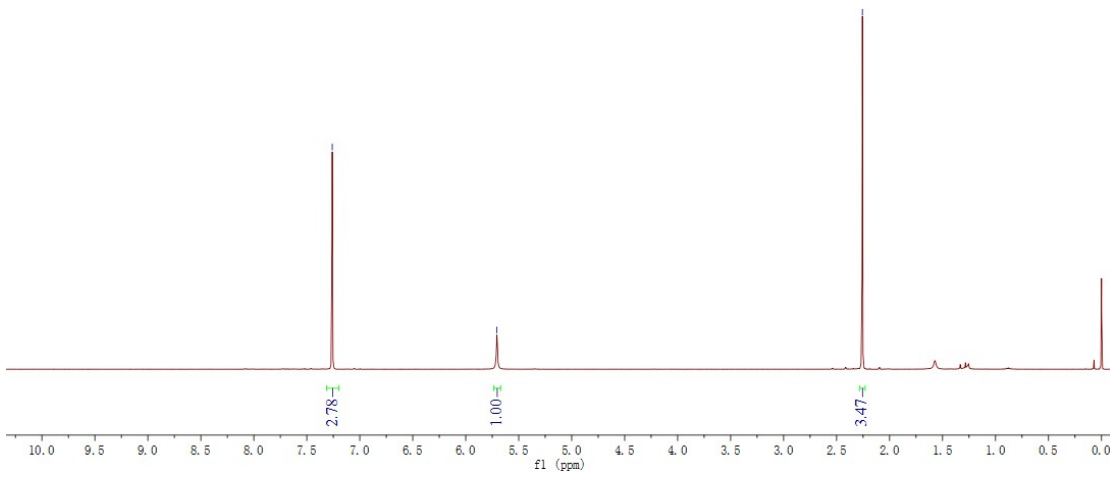
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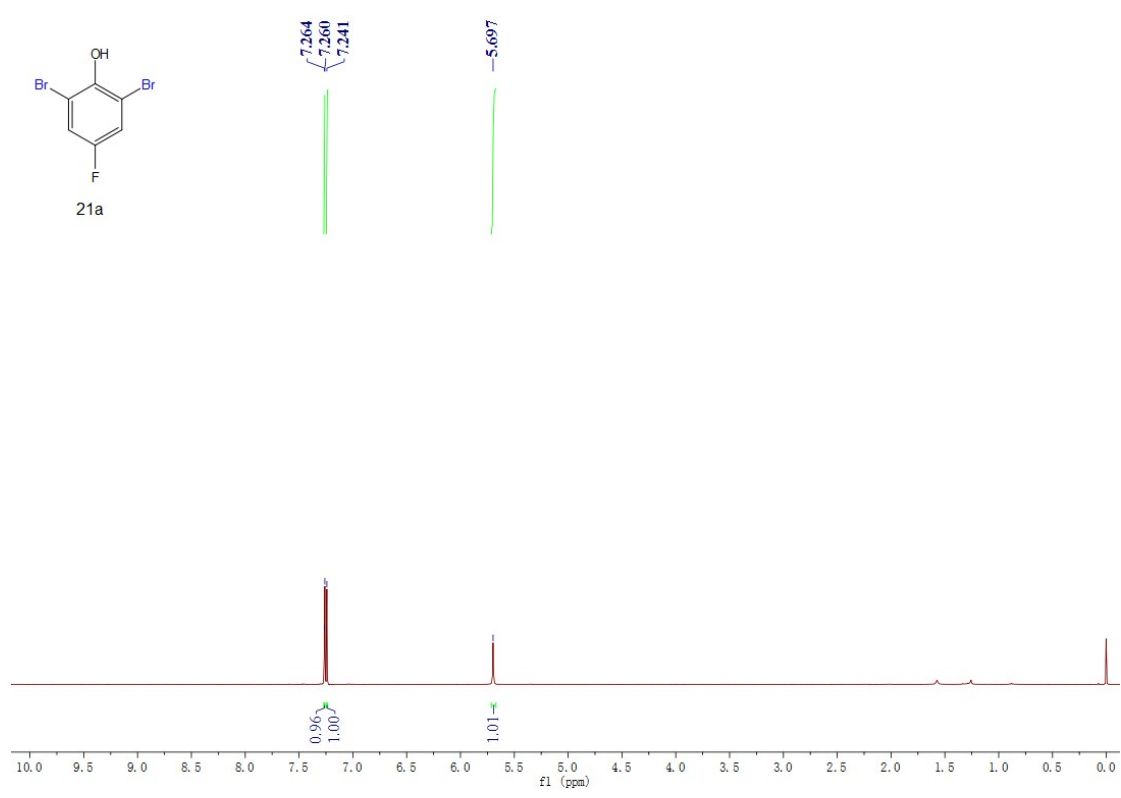
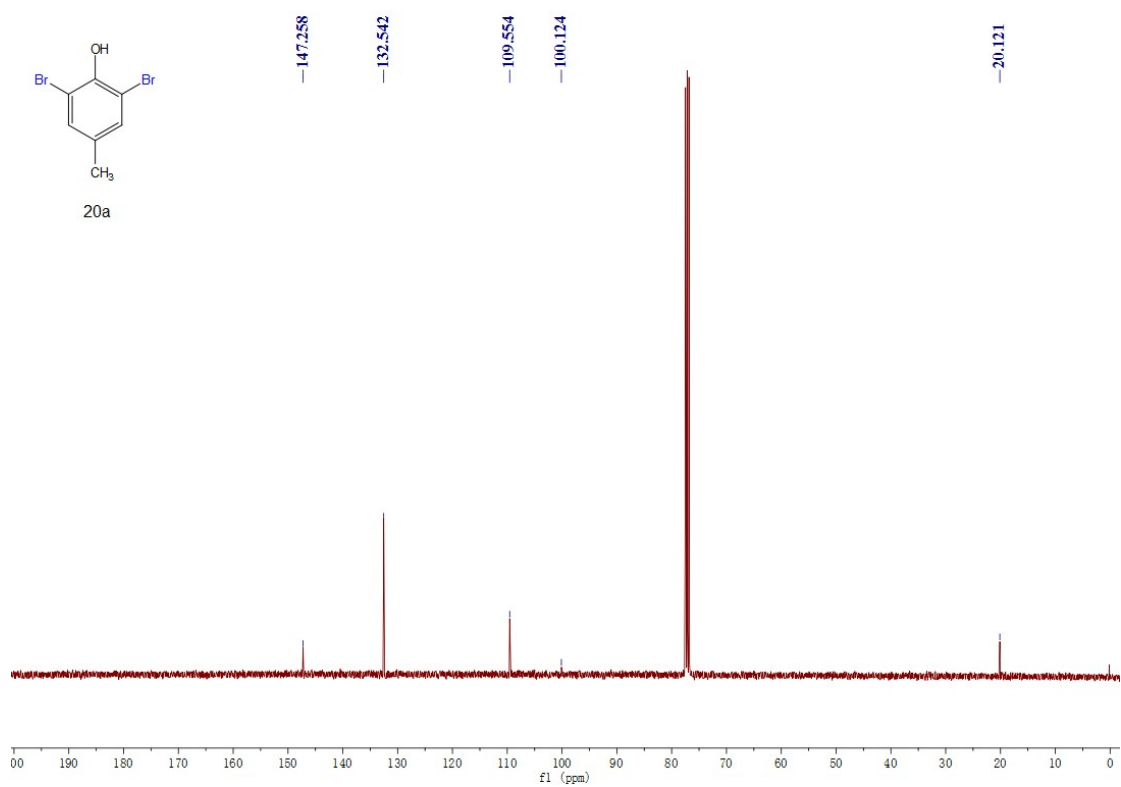


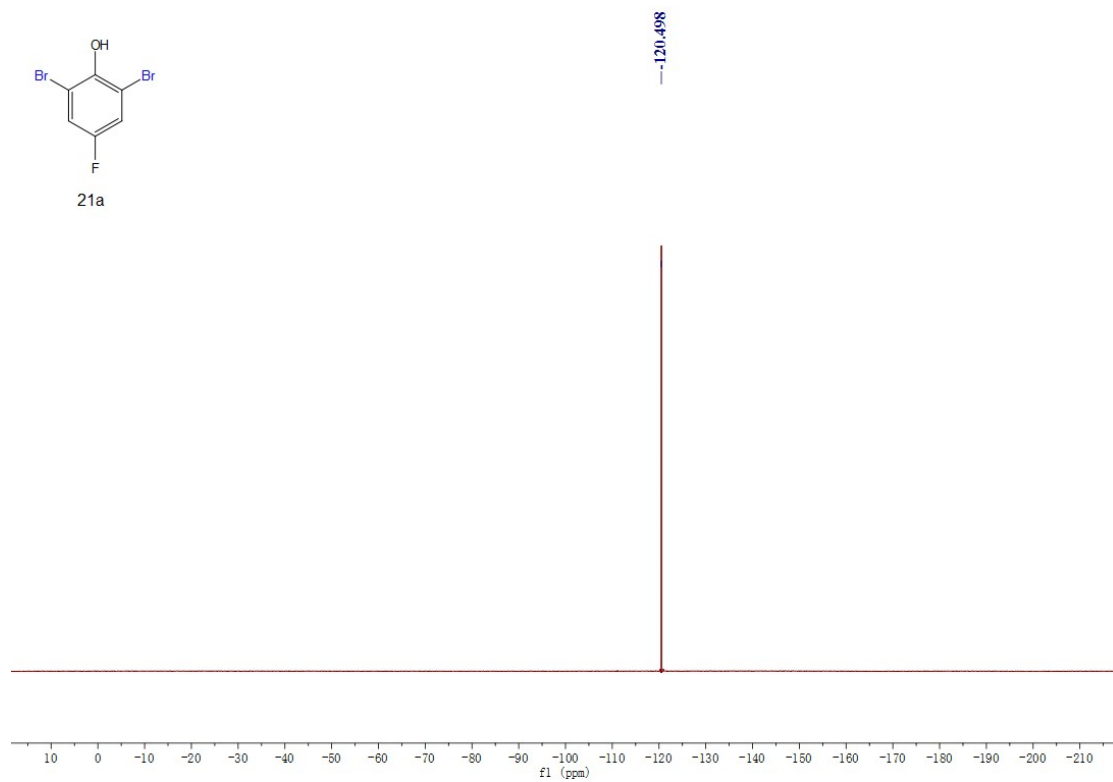
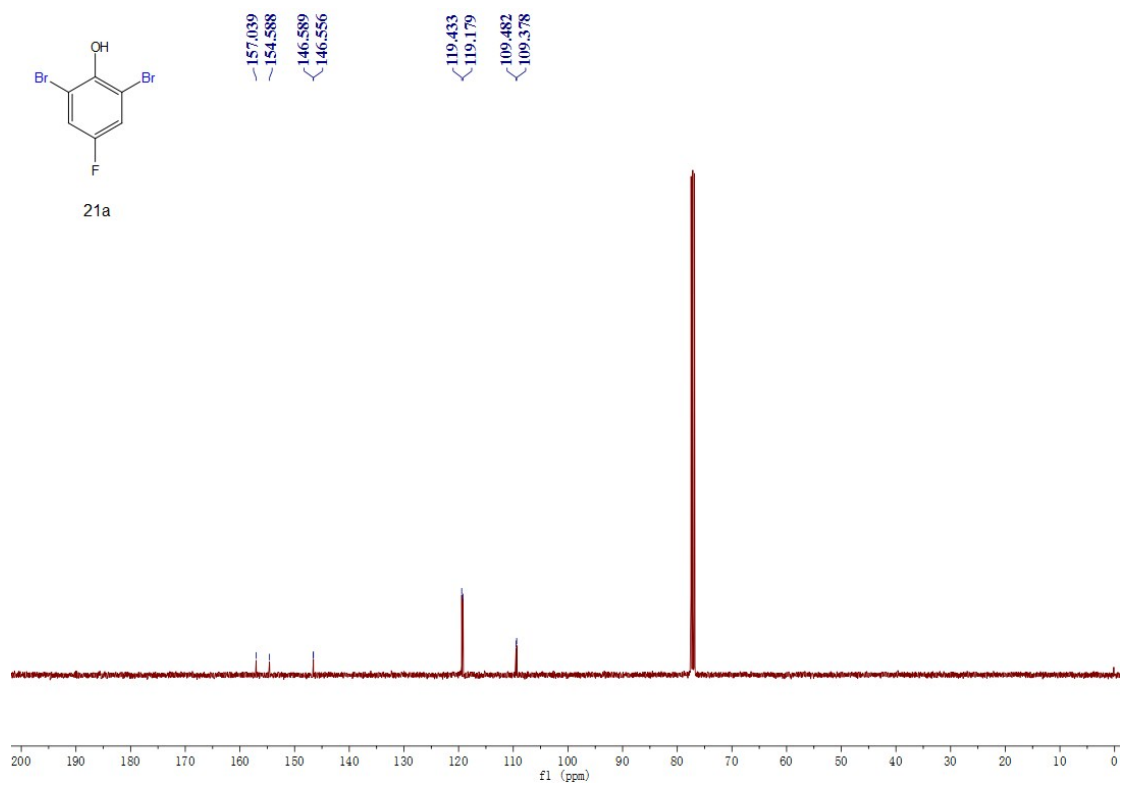
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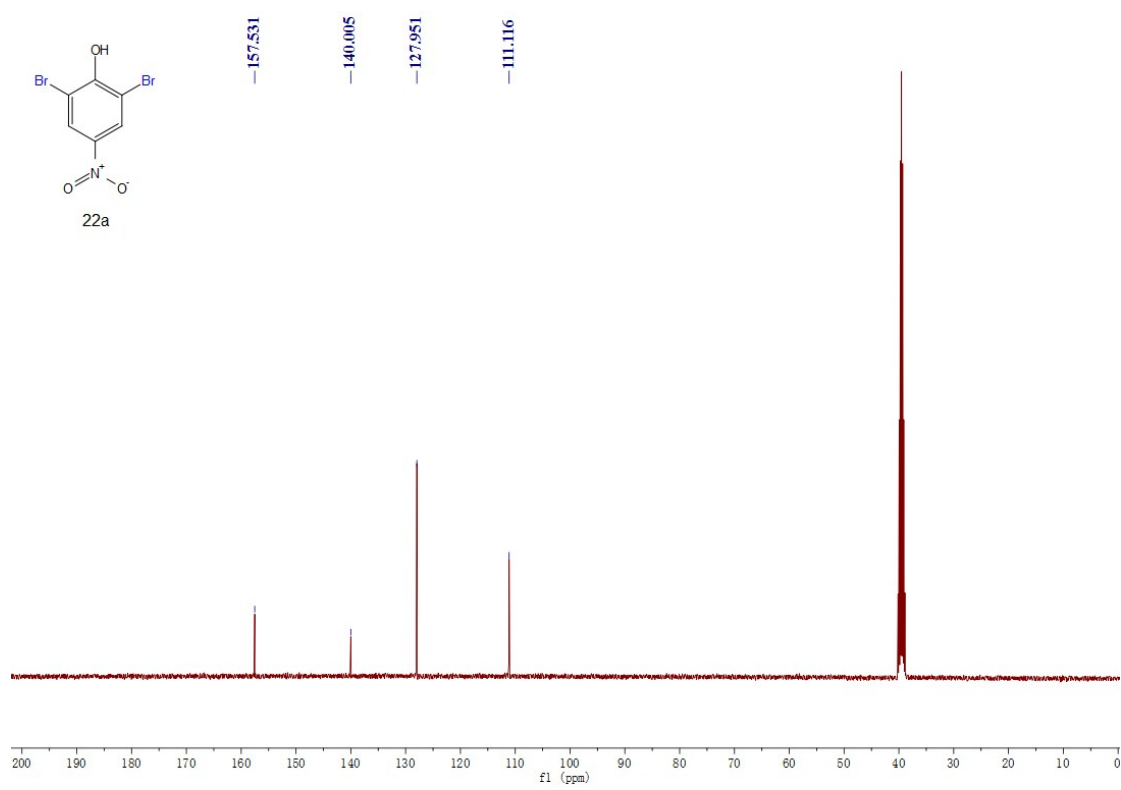
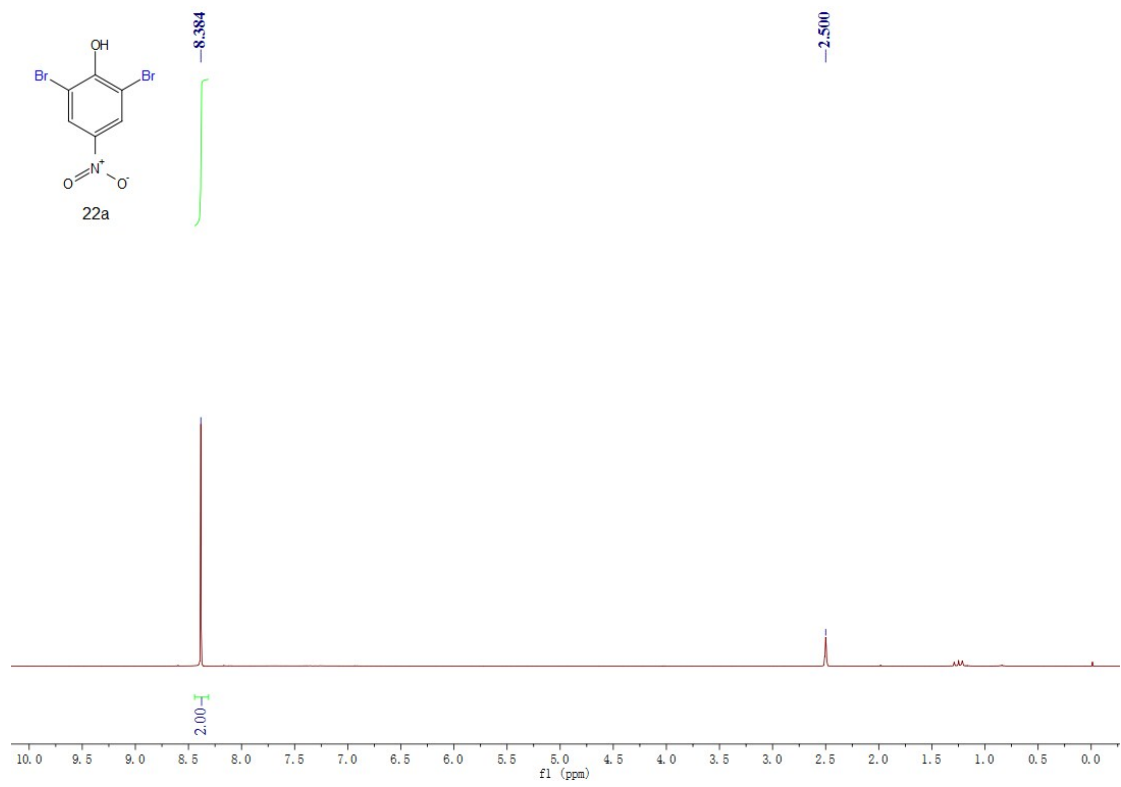
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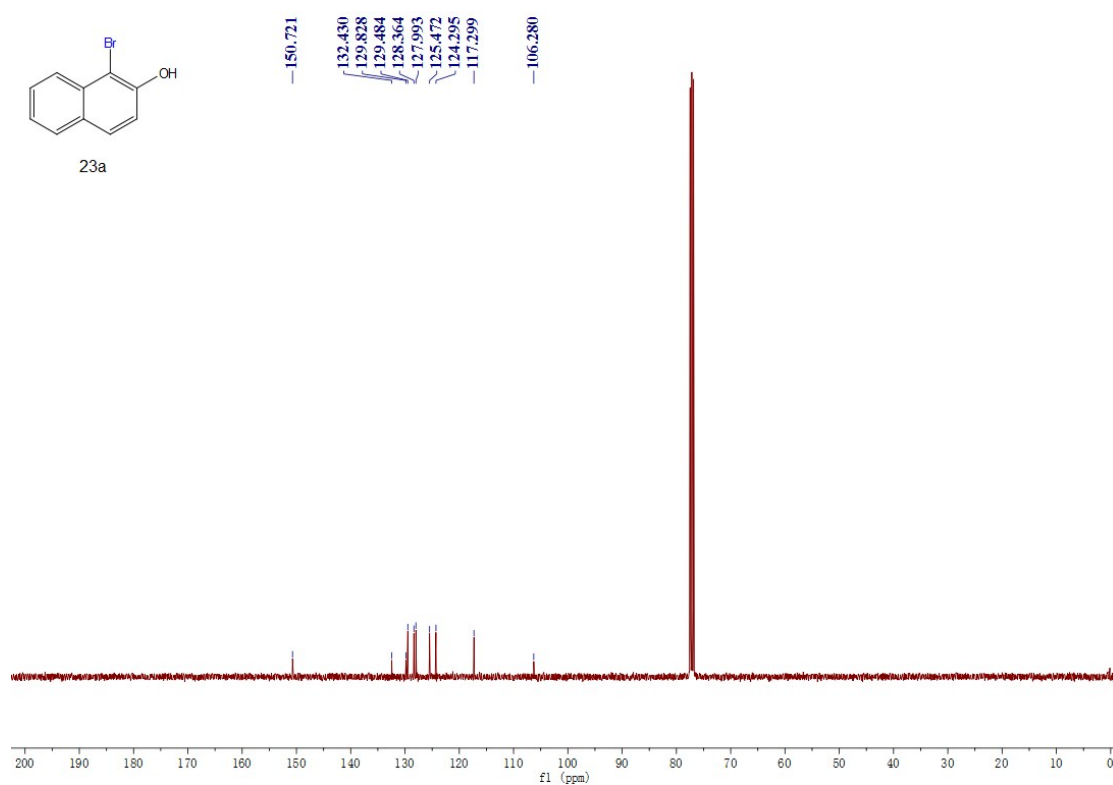
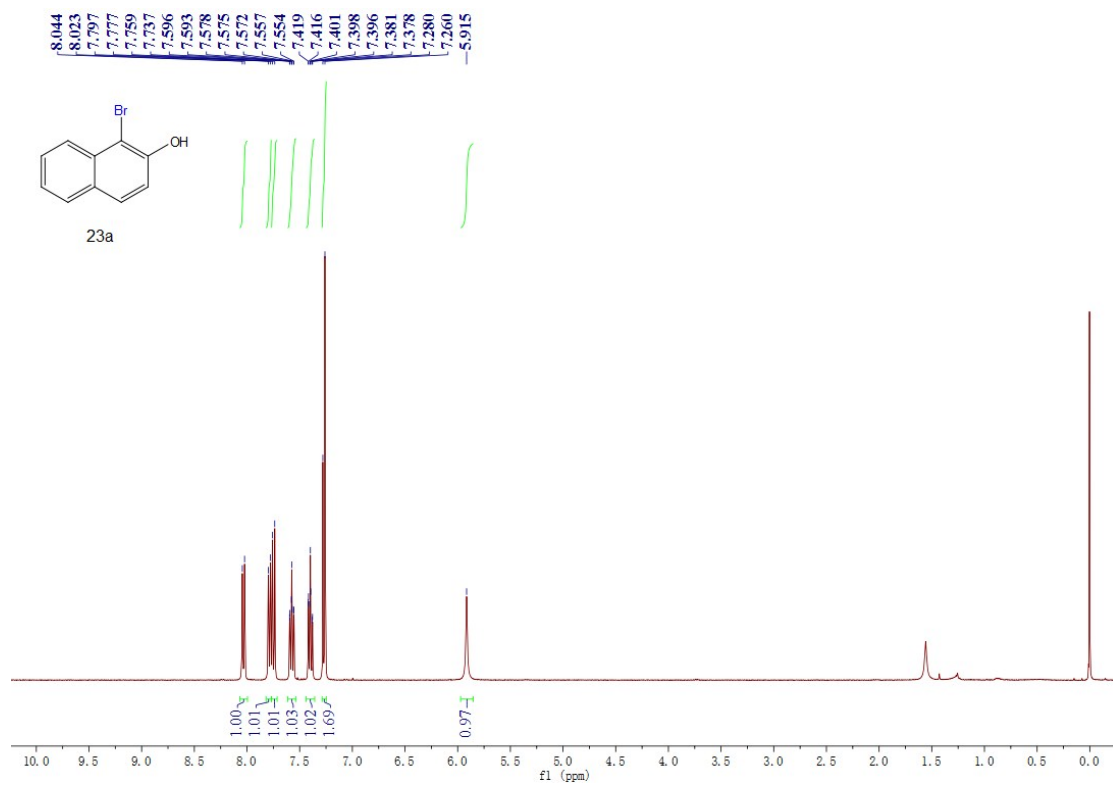
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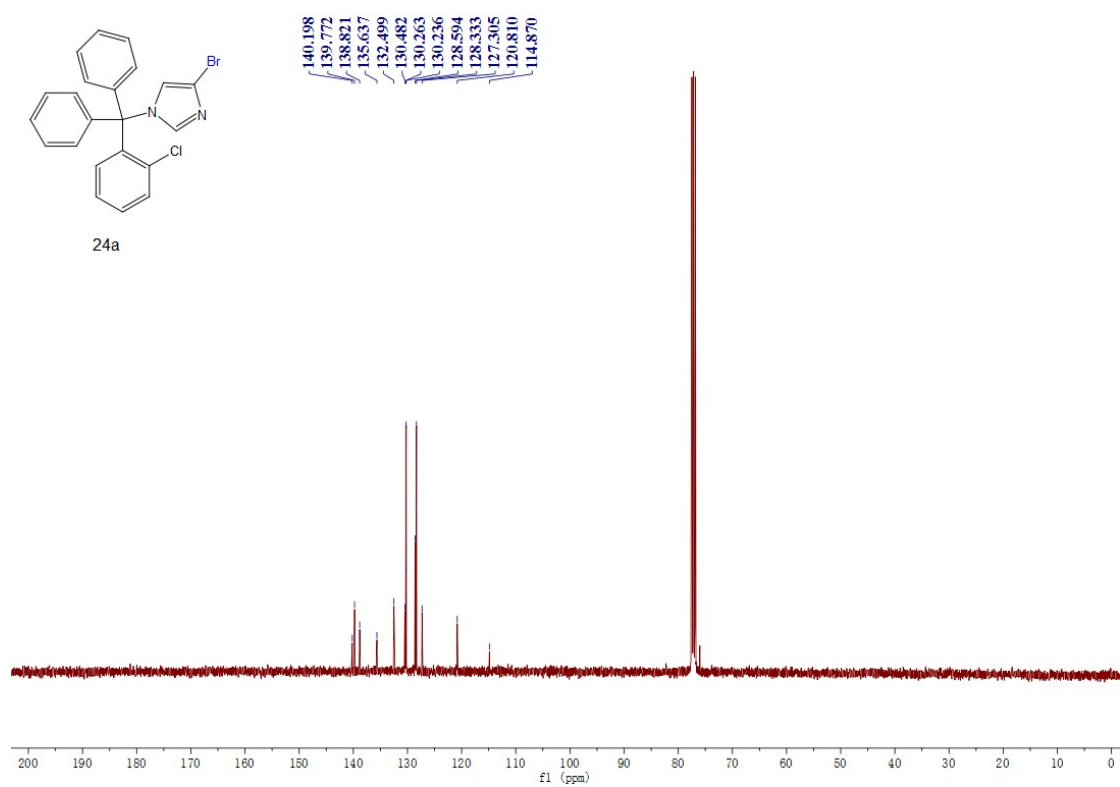
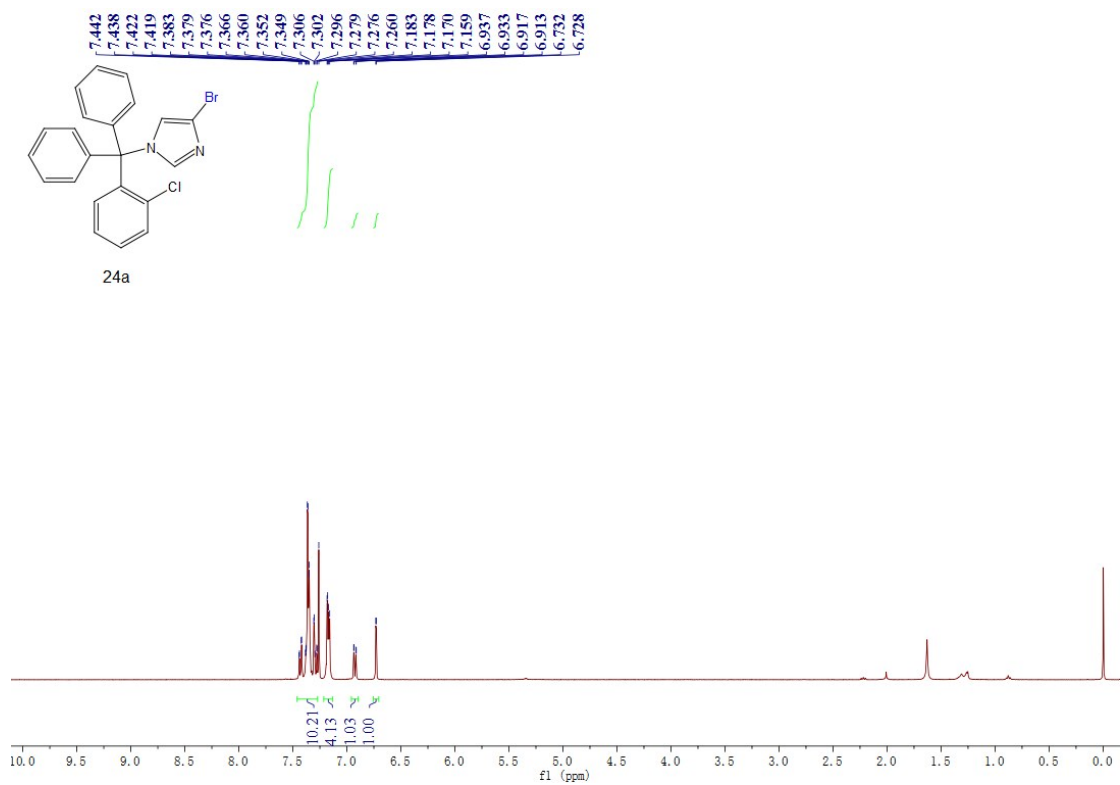


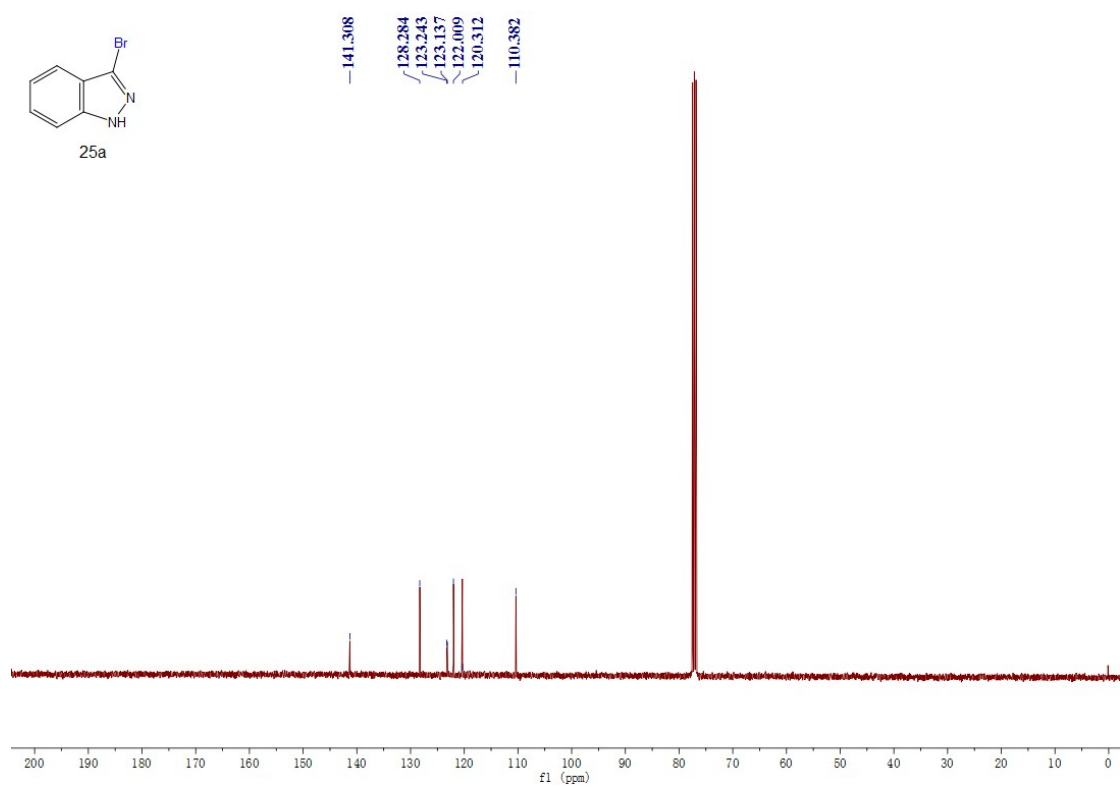
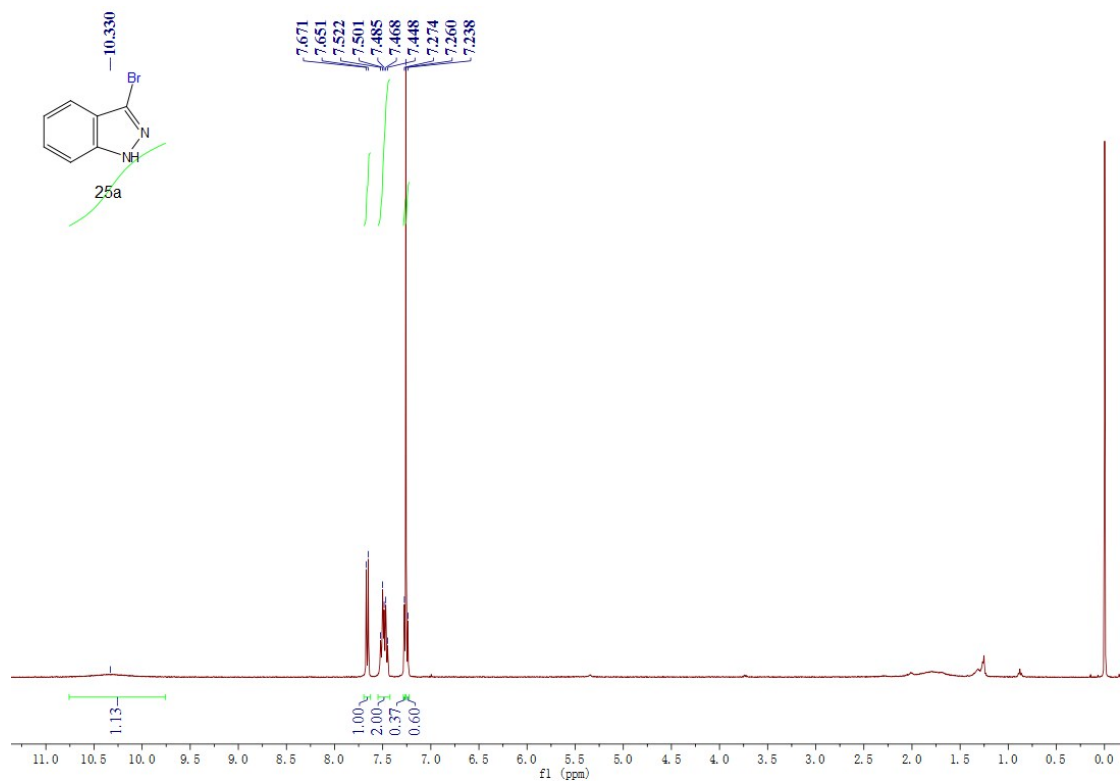


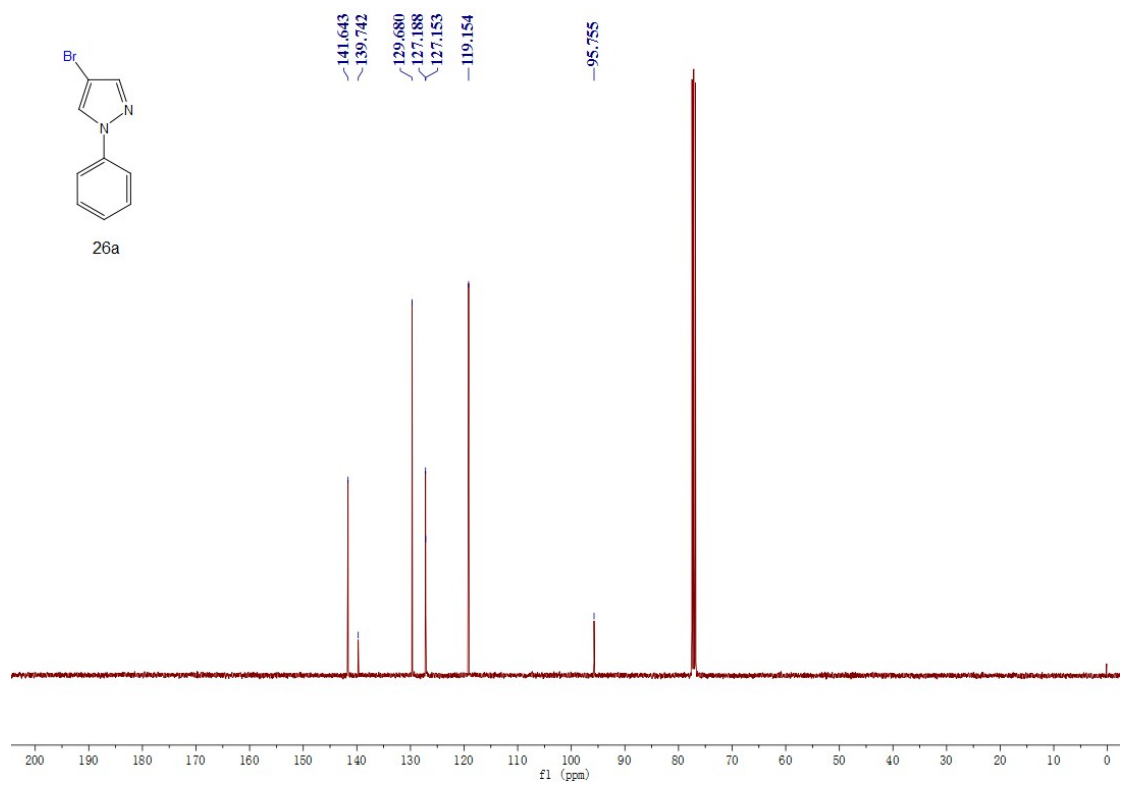
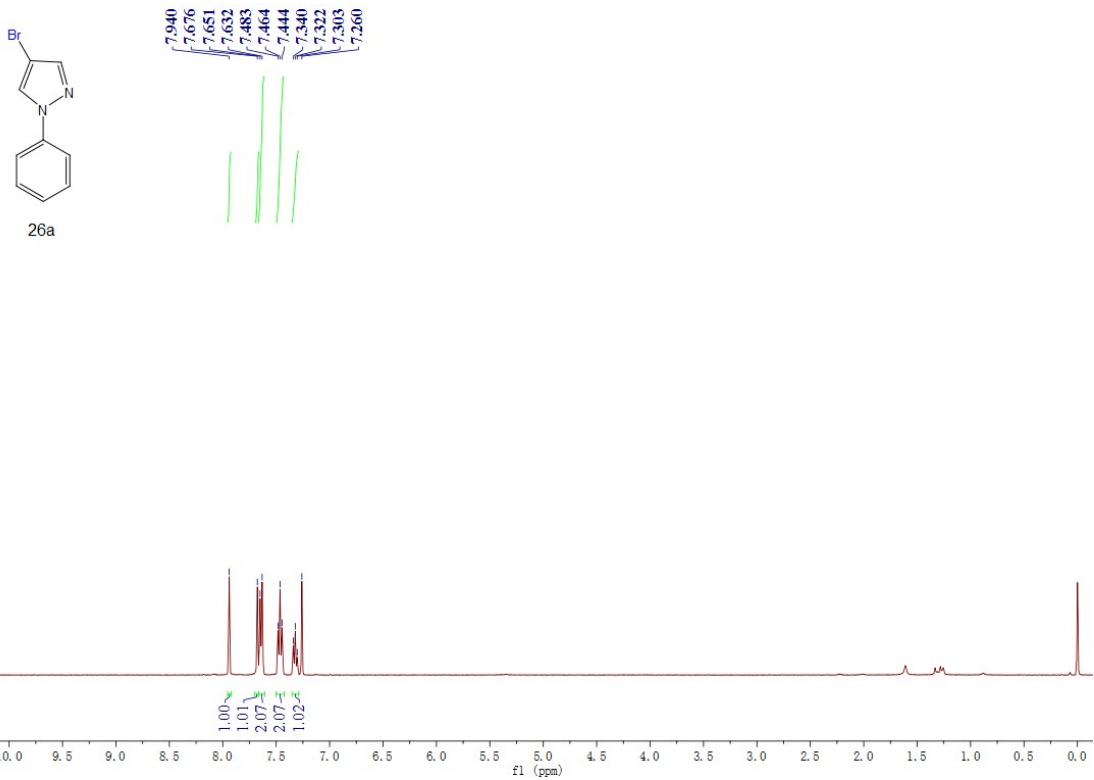


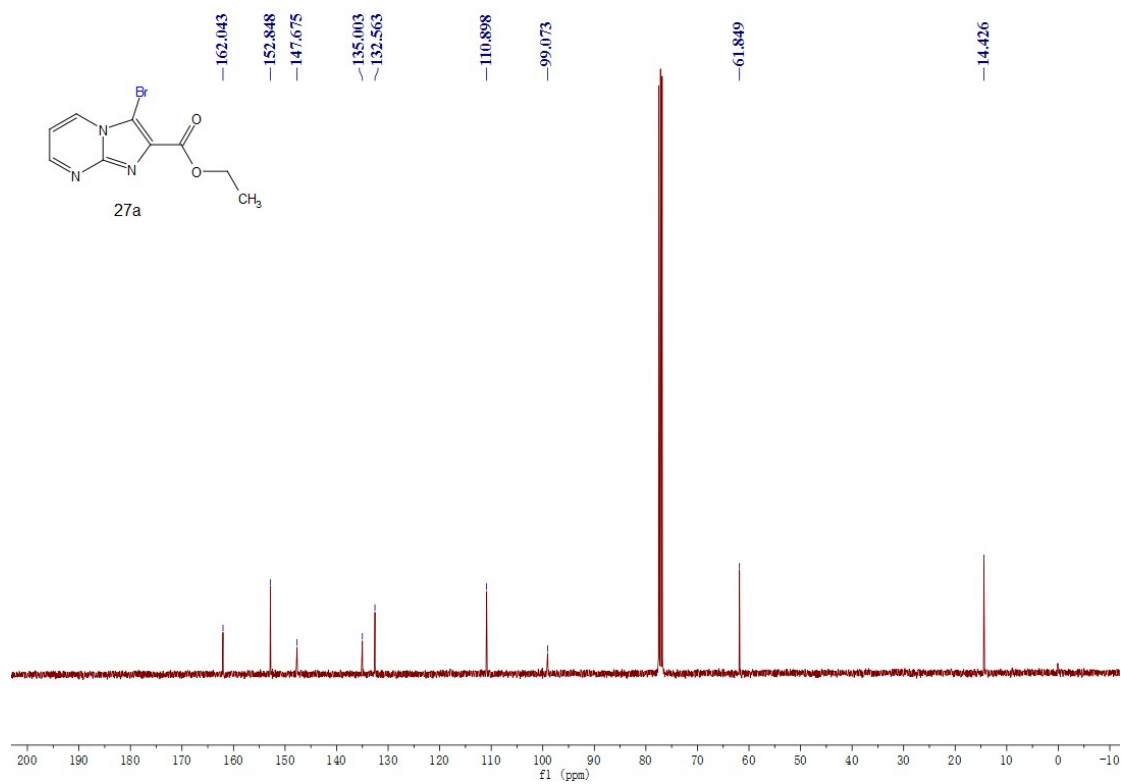
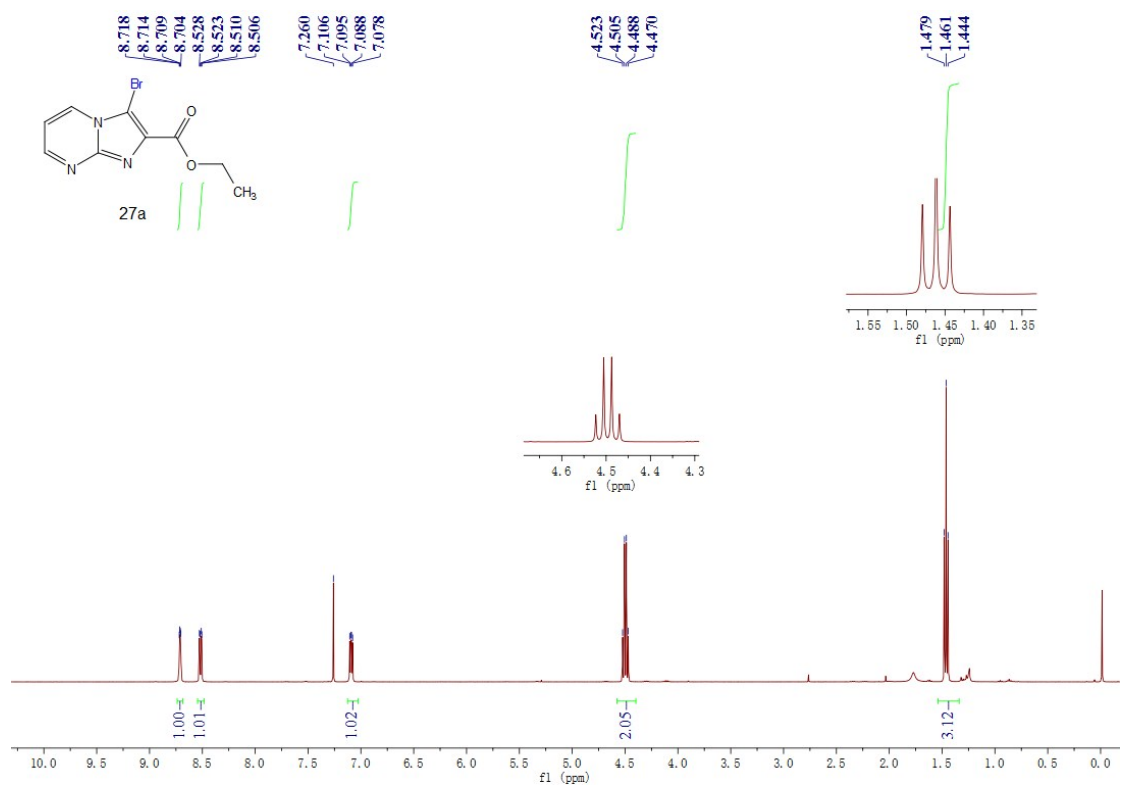


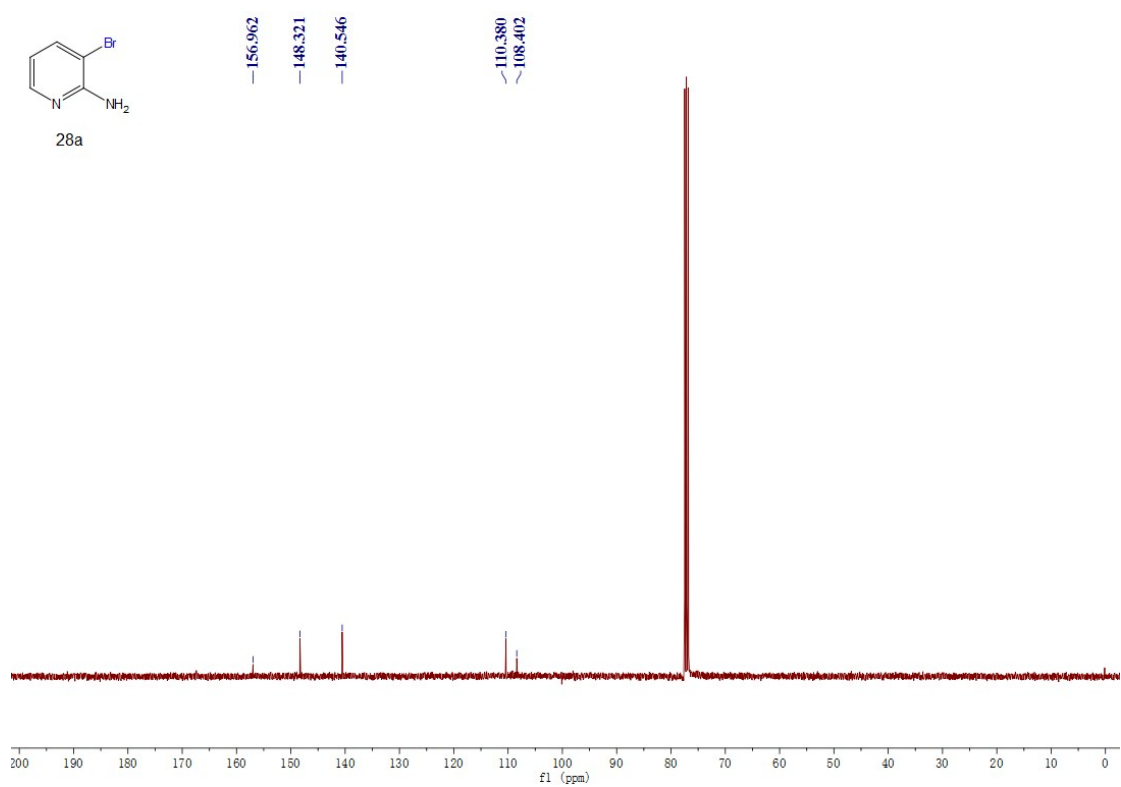
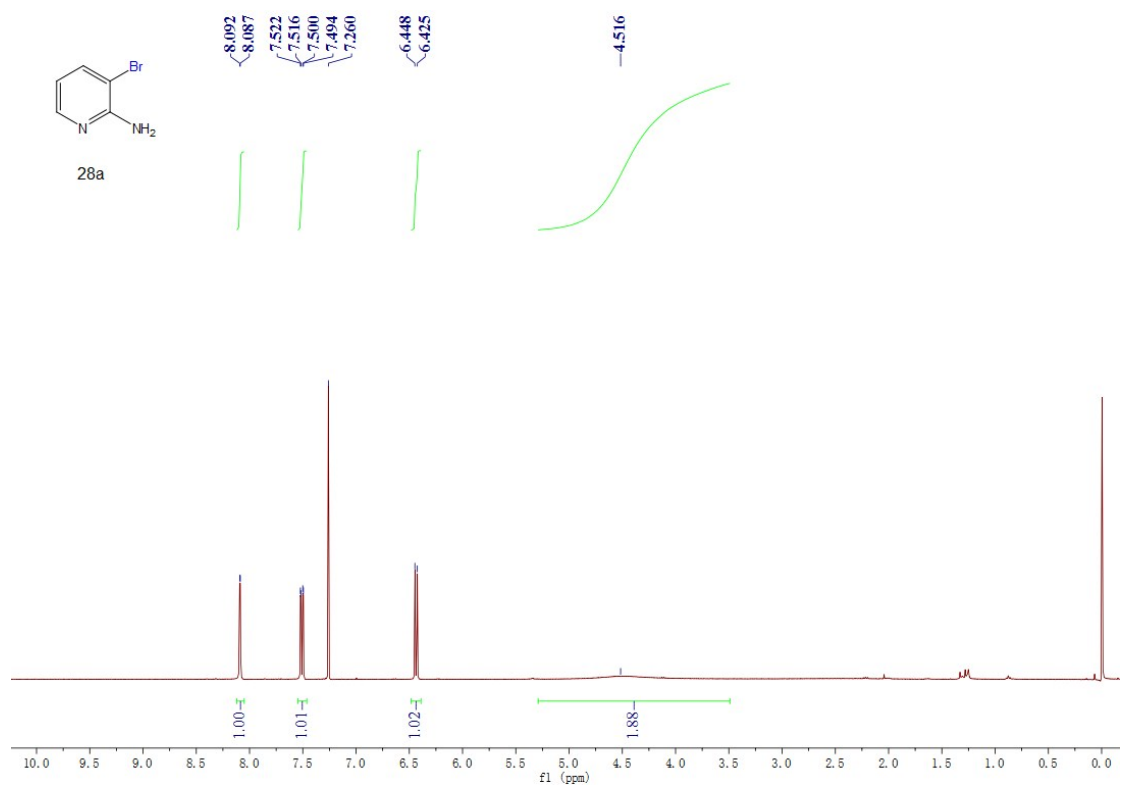


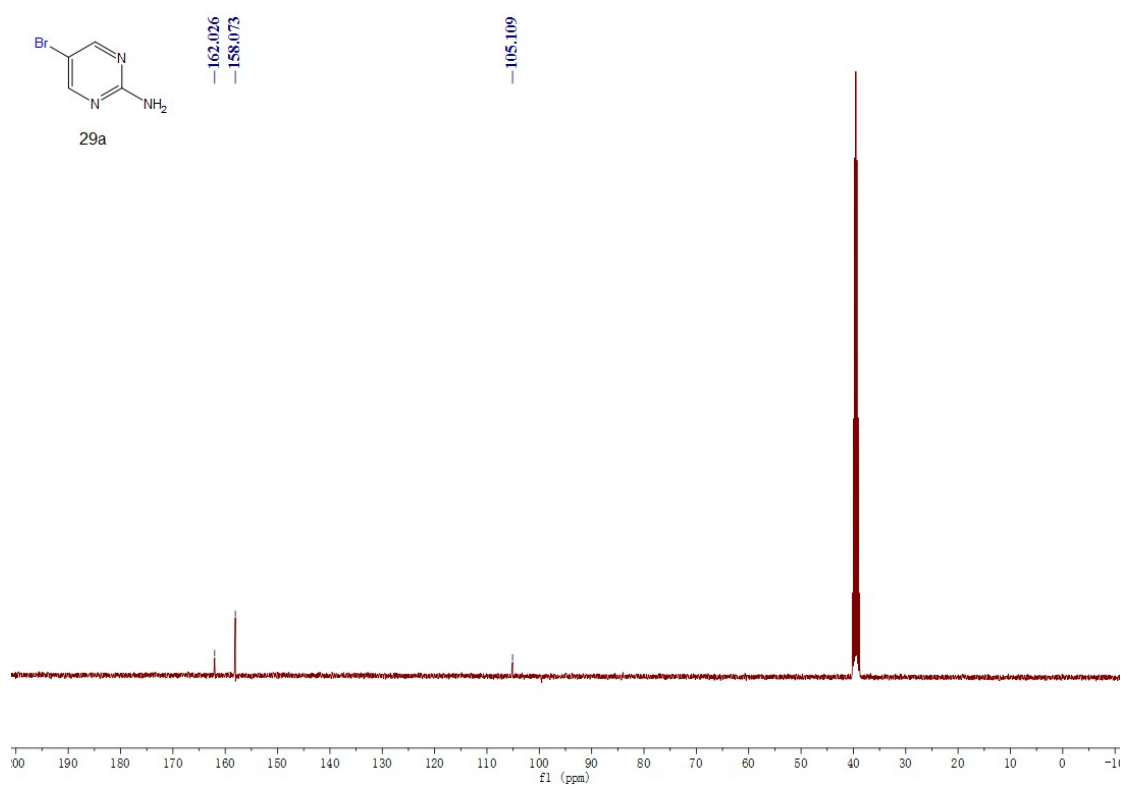
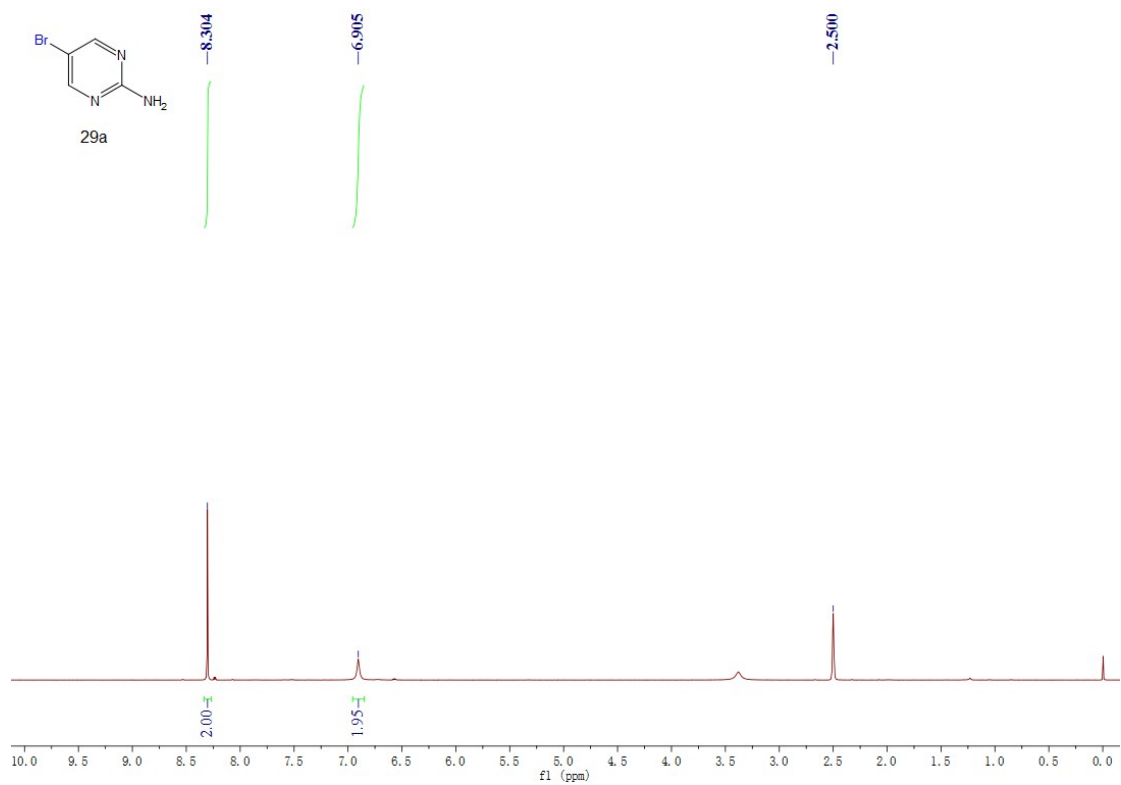


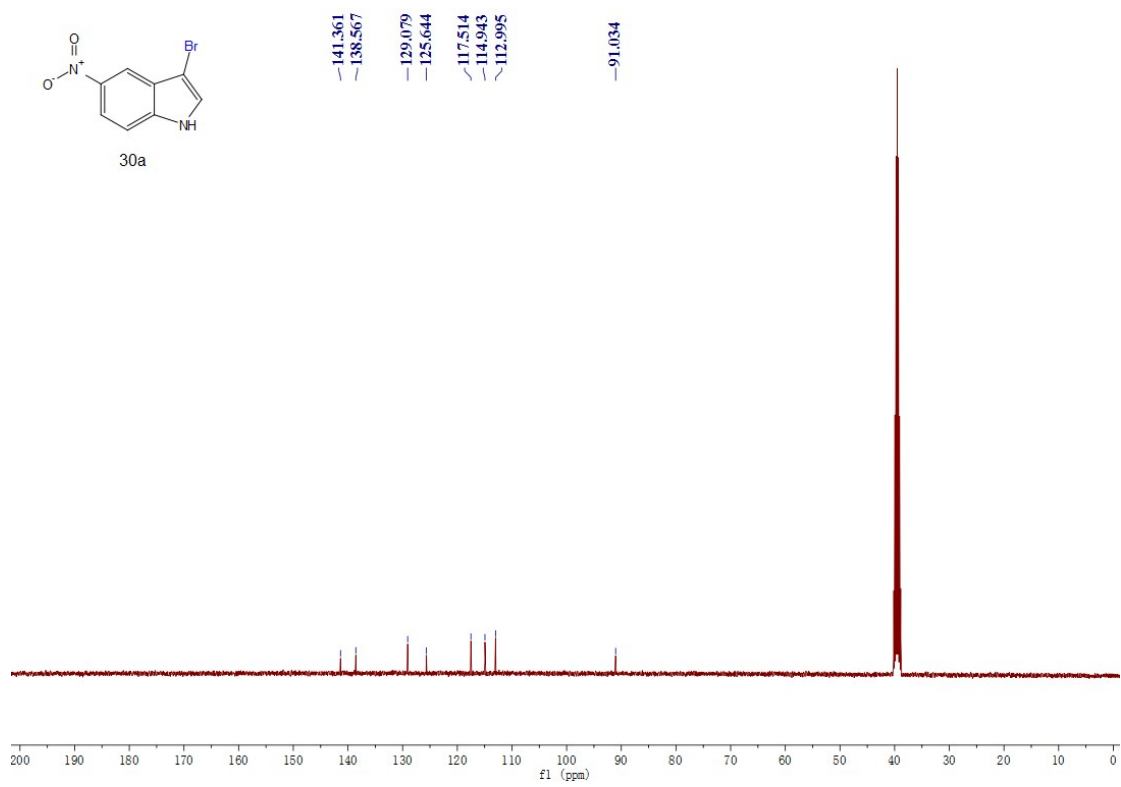
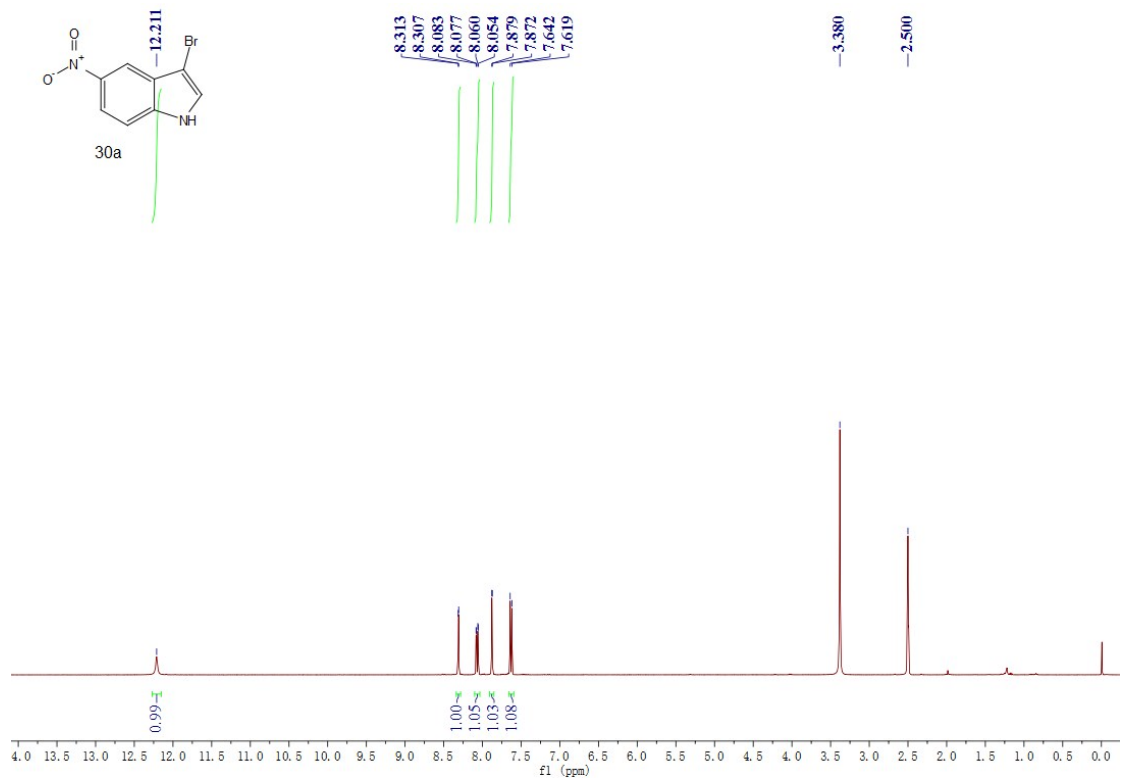


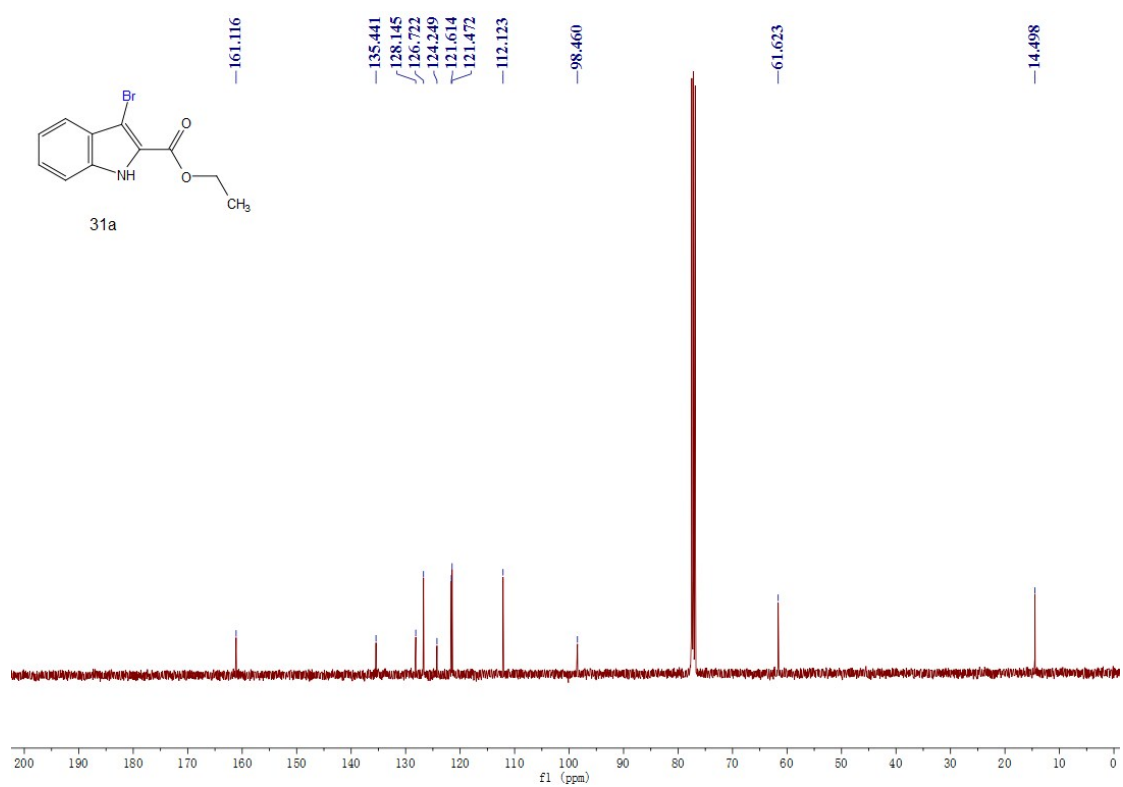
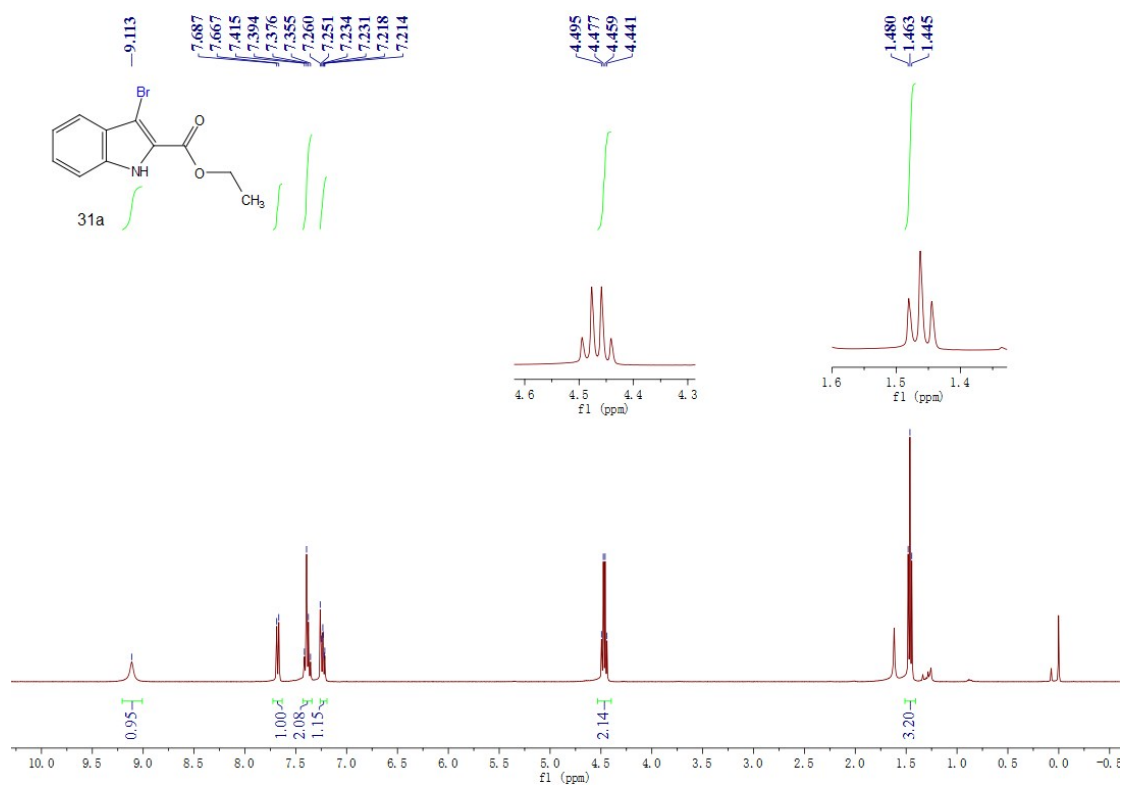


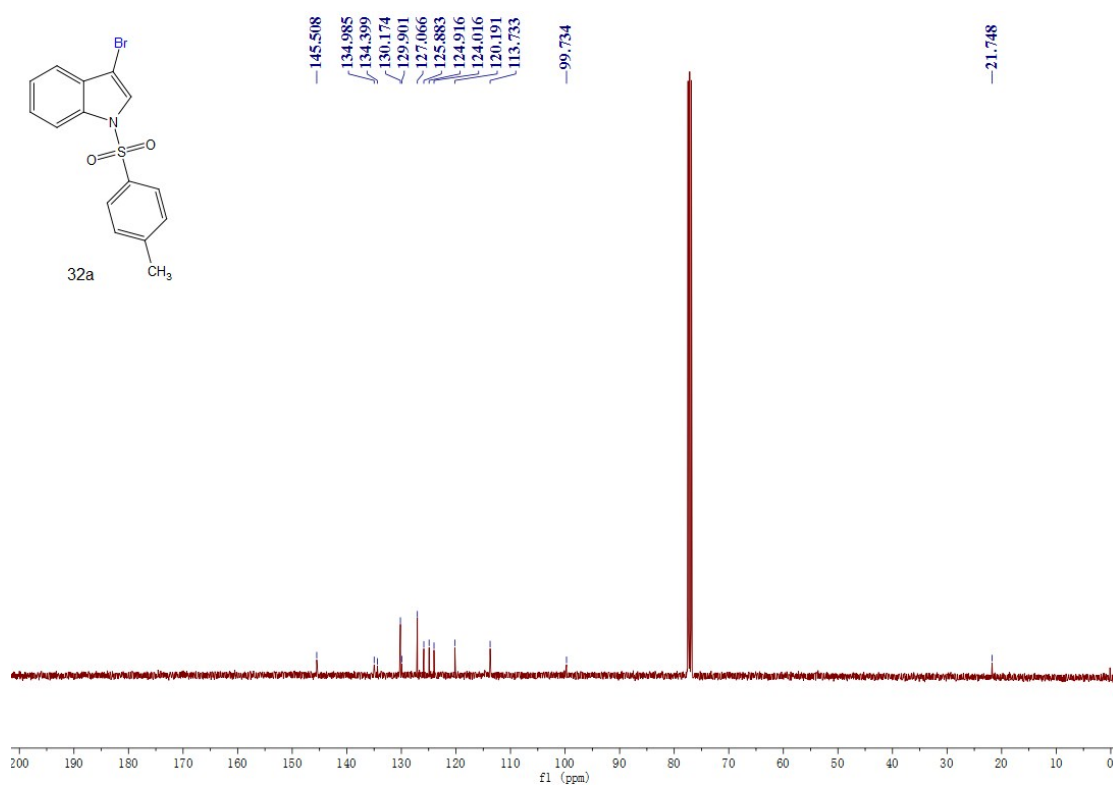
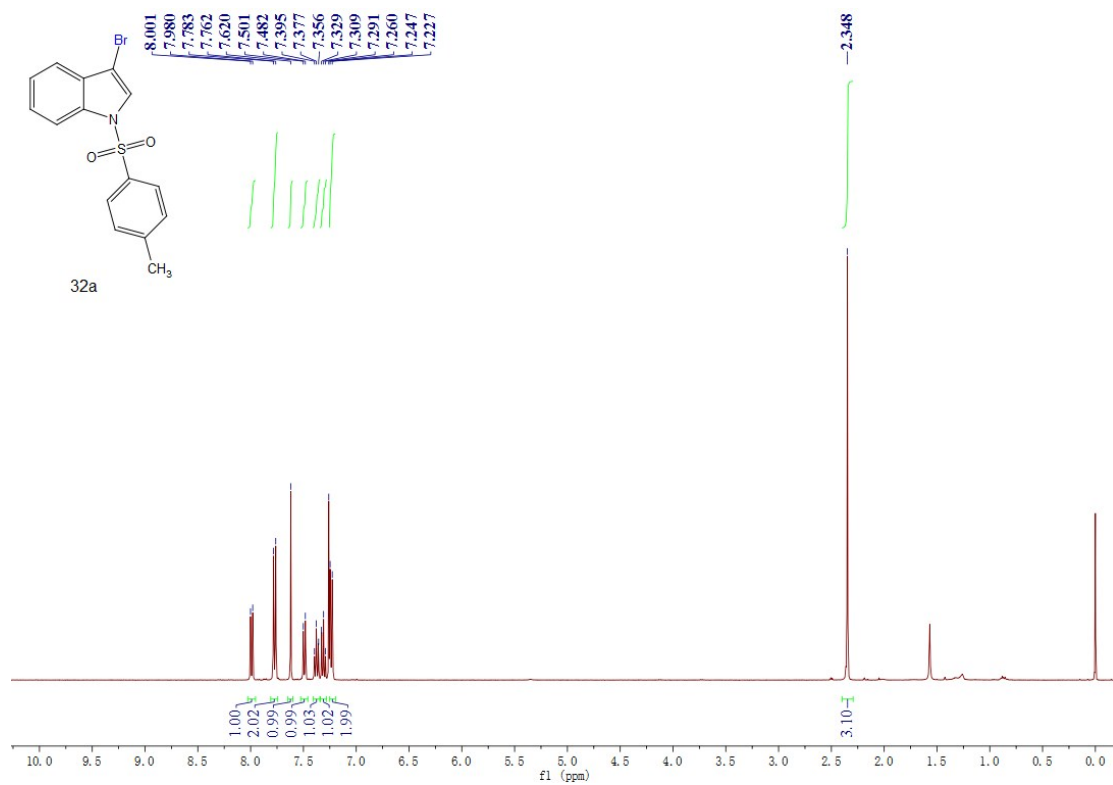


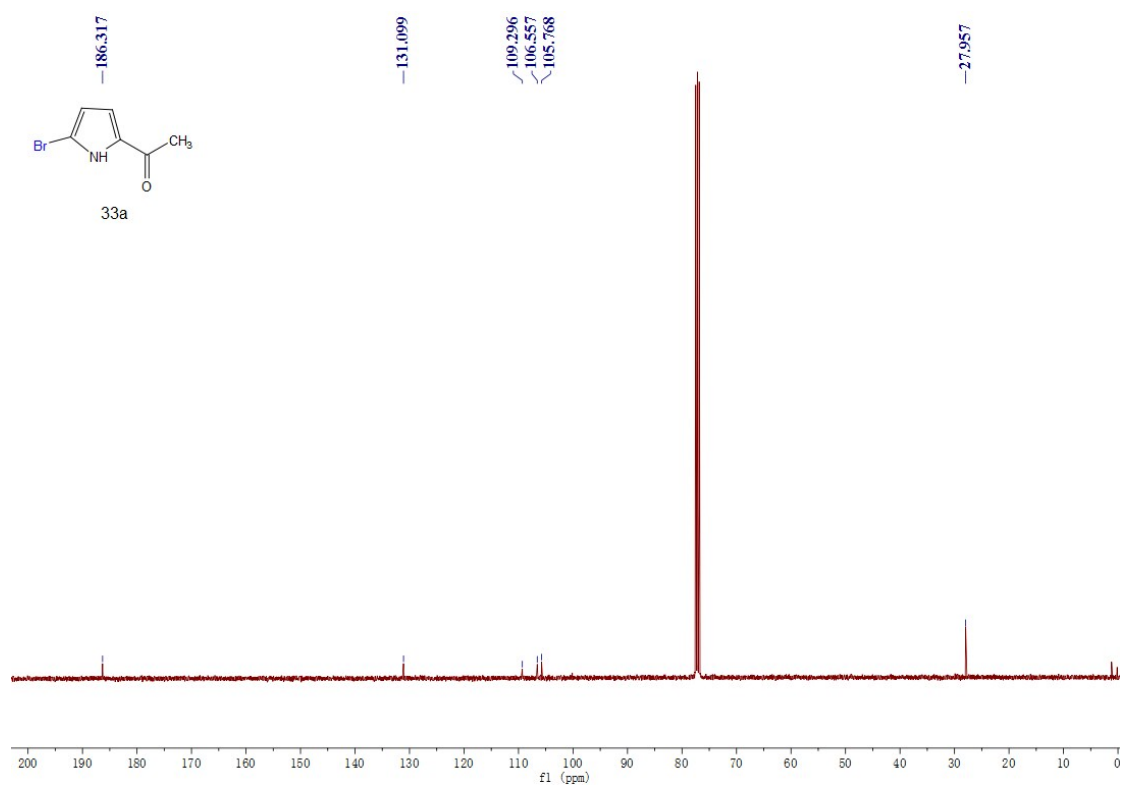
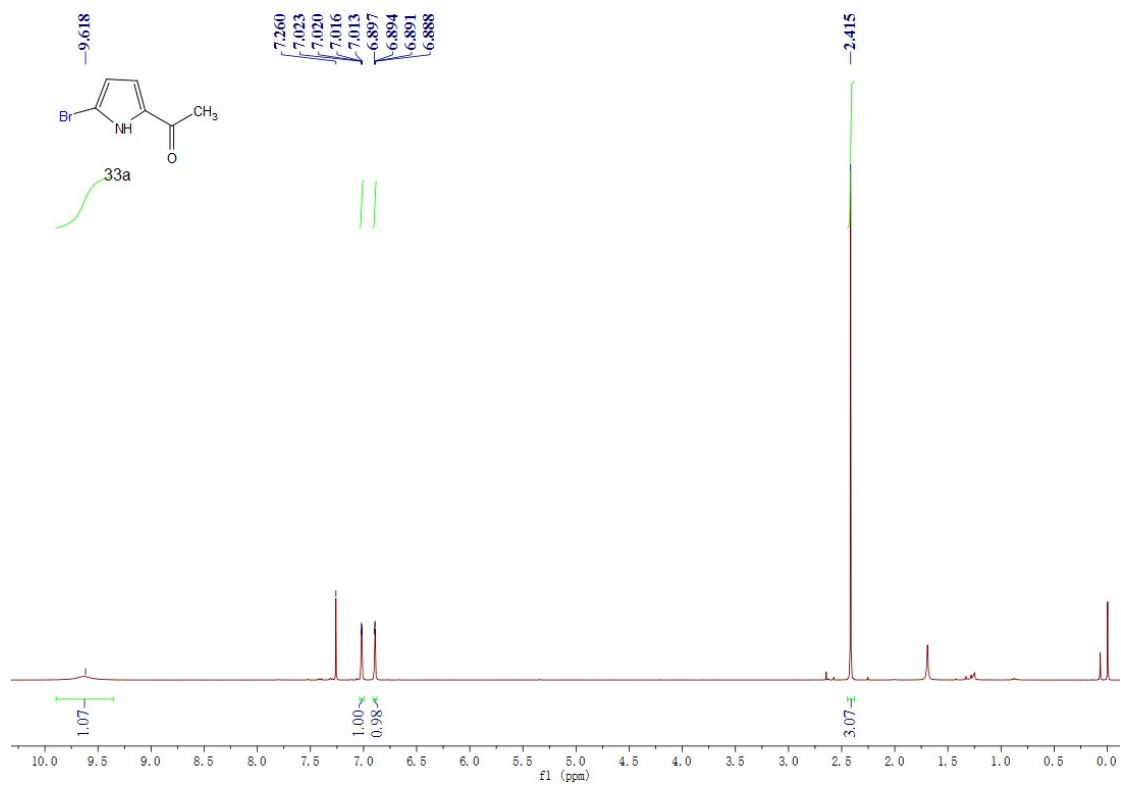


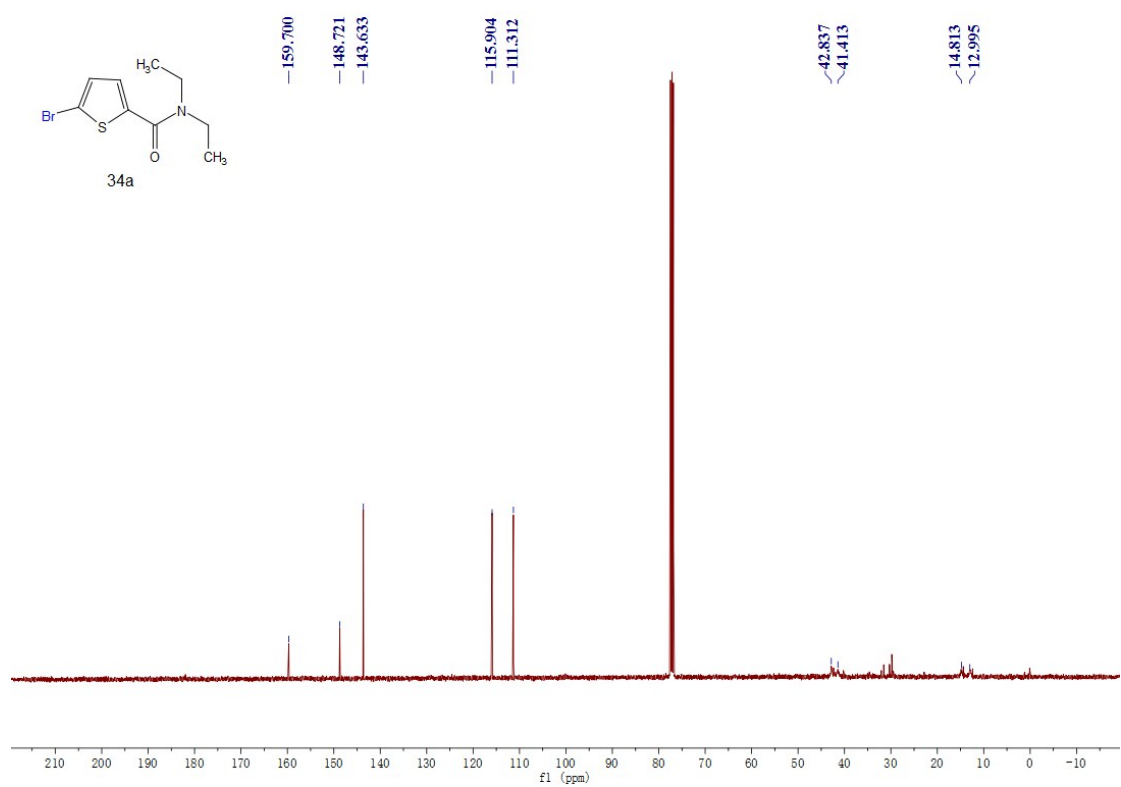
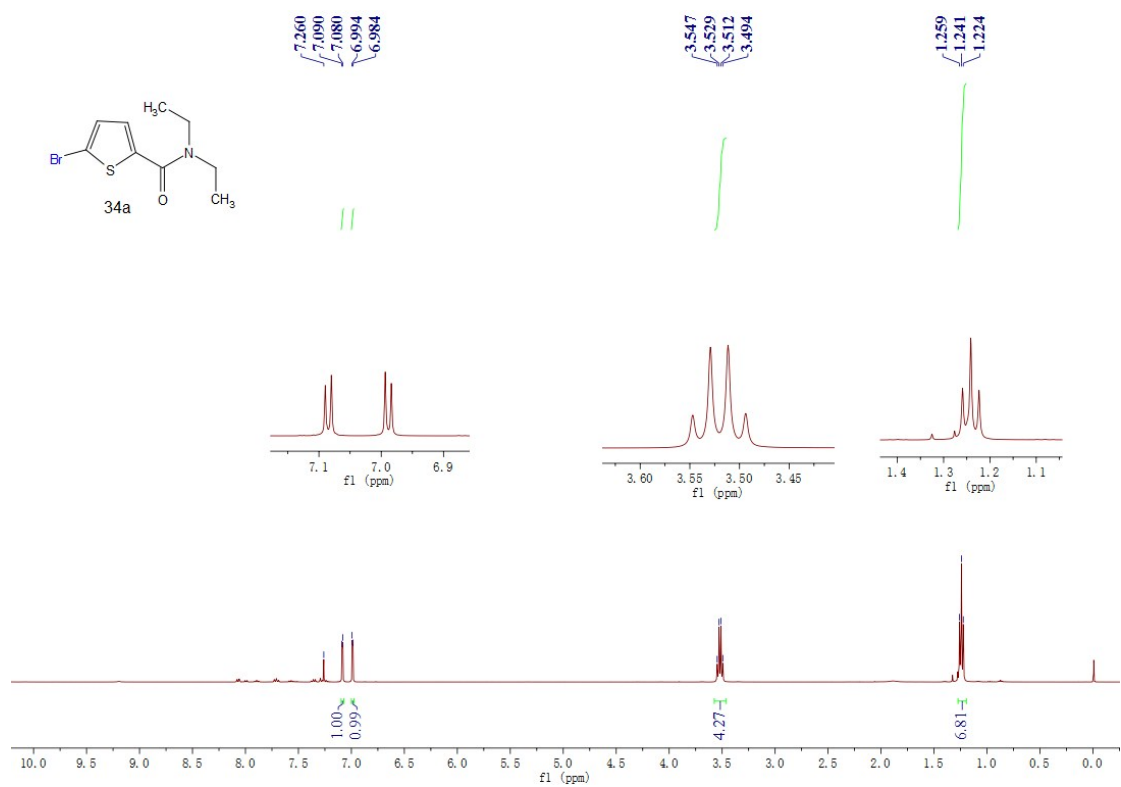


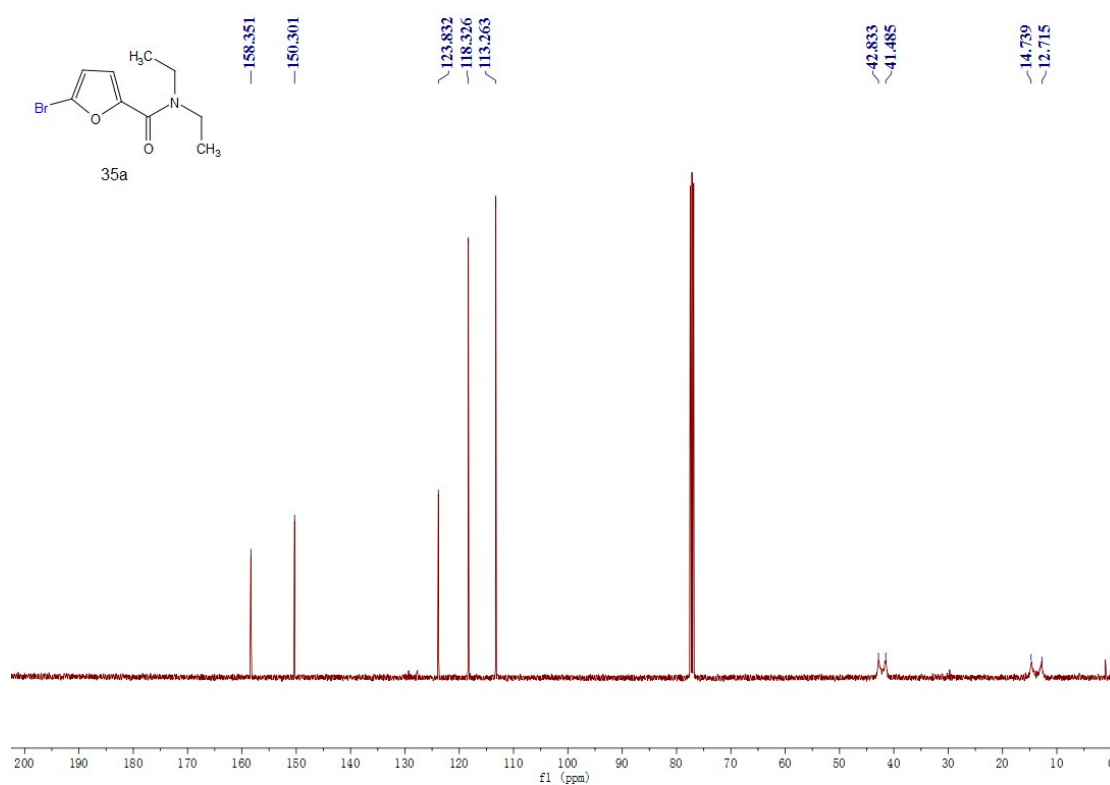
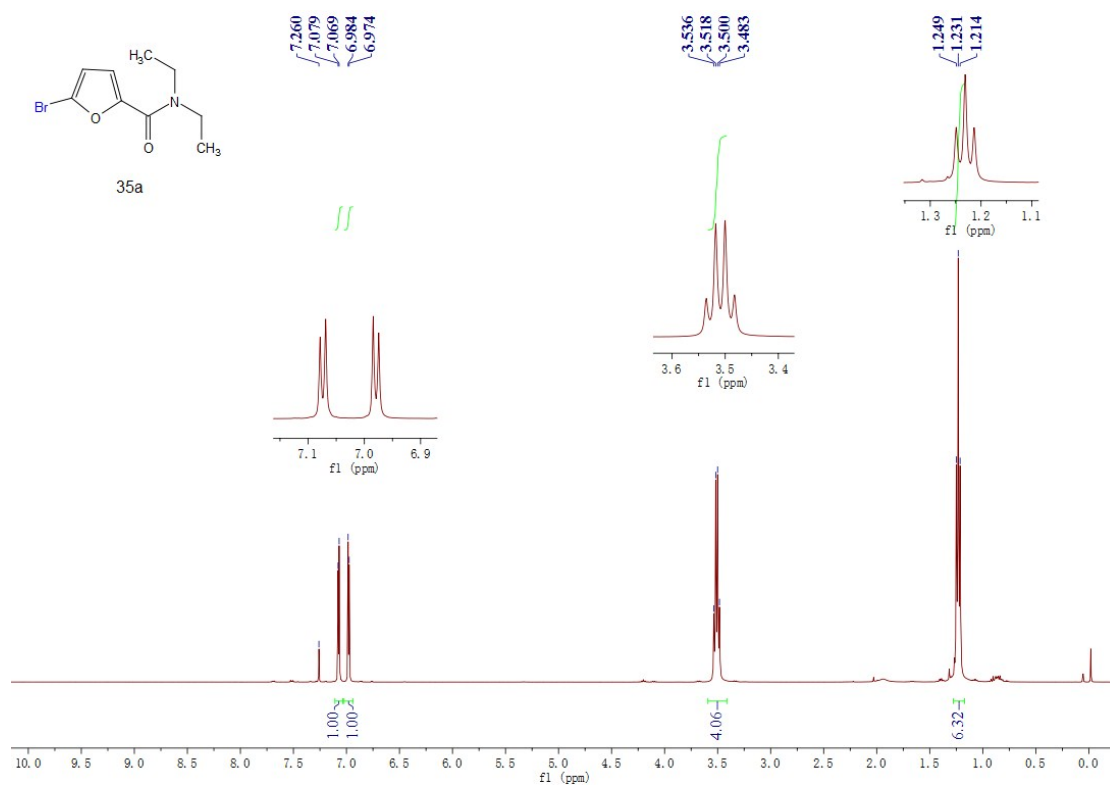












5. Notes and References

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