

Supplementary Information

Metal-free polychloromethyl radical-initiated cyclization of unactivated *N*-allylindoles towards pyrrolo[1,2-*a*]indoles

Yujia Shan, Zixian Yang, Jin-Tao Yu,* Changduo Pan*

Email: yujintao@cczu.edu.cn; panchangduo@jsut.edu.cn

Table of Contents

1. General Considerations	S2
2. General Synthetic Procedures	S2
3. Mechanism Studies	S4
4. Characterization Data for the Products	S6
5. References	S19
6. Copies of the ¹ H NMR and ¹³ C NMR Spectra	S20

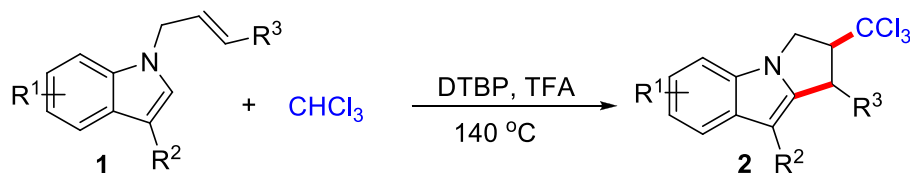
1. General Considerations

General Information: Unless otherwise noted, all chemicals were purchased and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature on 400 MHz NMR spectrometer (100 MHz for ^{13}C). NMR experiments are reported in δ units, parts per million (ppm), and were referenced to CDCl_3 (d 7.26 or 77.0) as the internal standard. The coupling constants J are given in Hz. Column chromatography was performed using EM Silica gel 60 (300-400 mesh).

2. General Synthetic Procedures

All indole derivatives **1** were prepared according to the previous reports.^[1]

General procedure for the synthesis of trichloromethylated 2,3-dihydro-1H-pyrrolo[1,2-a]indoles (2):

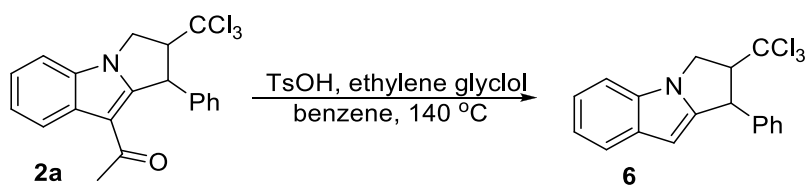


Under air, the mixture of **1** (0.2 mmol), DTBP (3 eq), TFA (2 eq) and chloroform (or CCl_4) (2 mL) was added to a Schlenk tube and sealed. The mixture was stirred at 140 °C for 12 hours. Then, the solvent was evaporated under reduced pressure, and the residue was purified by silica gel flash column chromatography to obtain product **2**.

General procedure for the synthesis of dichloromethylated and dibromomethylated 2,3-dihydro-1H-pyrrolo[1,2-a]indoles (3 or 5):

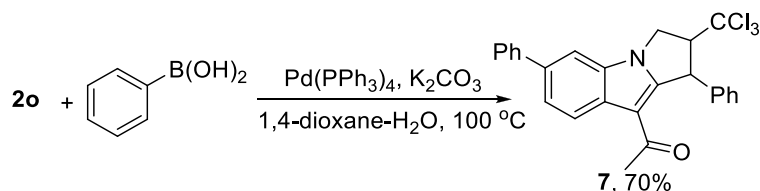
Under air, the mixture of **1** (0.2 mmol), DTBP (3 eq), TFA (1 eq), NaOAc (1 eq) and dichloromethane (or dibromomethane) (2 mL) were added to a Schlenk tube and sealed. The mixture was stirred at 140 °C for 12 hours. Then, the solvent was evaporated under reduced pressure, and the residue was purified by silica gel flash column chromatography to obtain product **3** (or **5**).

Derivatization reactions

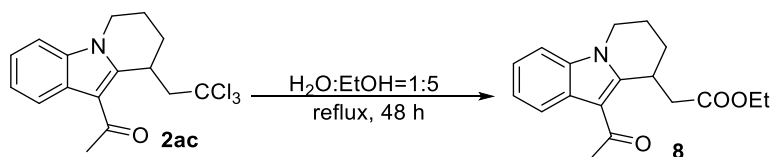


A mixture of **2a** (39.2 mg, 0.1 mmol), TsOH (95 mg, 5 equiv.) and ethylene glycol (50 mg, 8 equiv.) in 2.0 mL of benzene was stirred under 120 °C for 36 hours and cooled.^[2] Saturated sodium bicarbonate solution (1 mL) was added and the

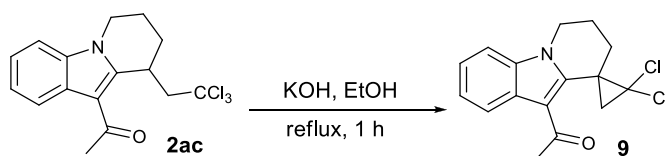
organic layer was separated. Combined organic phase were dried over anhydrous Na_2SO_4 , evaporated under vacuum and purified by silica gel flash column chromatography to give **6** (23 mg, 66% yield) .



Under N_2 , a 20 mL Schlenk tube was equipped with a stir bar and charged with **2o** (47.2 mg, 0.1 mmol), PhB(OH)_2 (14.6 mg, 1.2 mmol), K_2CO_3 (45.5 mg, 3.3 mmol), $\text{Pd(PPh}_3)_4$ (5.8 mg, 5 mol %), 0.5 mL of dioxane and 0.5 mL of H_2O , sealed with a Teflon lined cap.^[3] The mixture was stirred at 100 °C for 12 h. Upon the completion of the reaction, the mixture was poured into ethyl acetate (5 mL $\times$ 3). The organic layer was separated and dried over Na_2SO_4 and then filtered. The resulting residue was purified by silica gel flash column chromatography to afford **7** (32.7 mg, 70%).



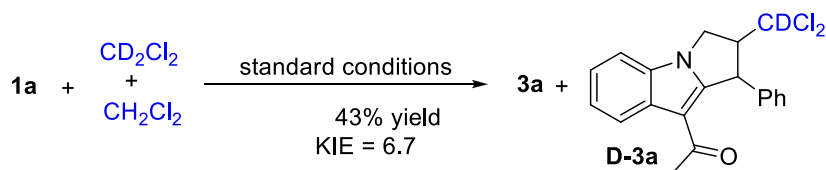
Under air, the mixture of **2ac** (34.5 mg, 0.1 mmol), H_2O (0.5 mL) and EtOH (2.5 mL) heated to reflux and stirred for 48 h.^[4] Upon the completion of the reaction, the mixture was extracted with acetate (5 mL $\times$ 3). The organic layers were collected and dried over Na_2SO_4 and then filtered. The resulting residue was purified by silica gel flash column chromatography to afford **8** (15.1 mg, 50%).



A mixture of **2ac** (34.5 mg, 0.1 mmol) and KOH (56 mg, 10 eq) in EtOH (6 mL) was added into a flask and reflux for 1 h. After the completion of the reaction, the mixture was cooled to room temperature. Afterwards, ice was added and neutralized by 1N HCl. The mixture was extracted by acetate (5 mL $\times$ 3) and washed with brine (5 mL $\times$ 3).^[5] The combined organic layers were dried and concentrated under reduced pressure. The residue was purified using silica gel flash column chromatography to afford the compound **9** (19.2 mg, 62%).

3. Mechanism Studies

3.1 The KIE experiment:



The mixture of **1a** (0.1 mmol), DTBP (3 eq), TFA (1 eq), NaOAc (1 equiv), CH₂Cl₂ (0.5 mL) and CD₂Cl₂ (0.5 mL) was added to a sealed tube. The mixture was stirred at 140 °C for 12 hours. Then, the solvent was evaporated under reduced pressure, and the residue was purified by silica gel flash column chromatography to obtain product **3a** and **D-3a** in 43% yield. A KIE value of 6.69 was observed.

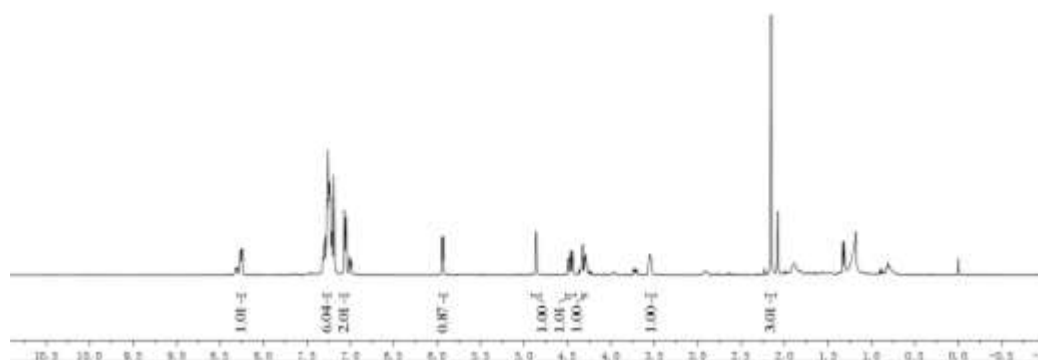
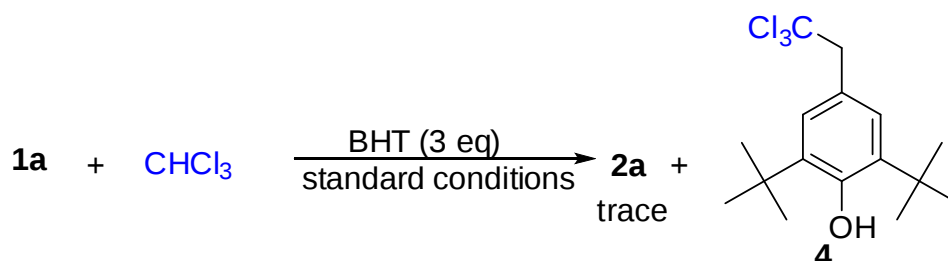


Figure S1 ¹H NMR spectrum of the KIE experiment

3.2 Radical inhibiting and trapping experiment



Under air, the mixture of **1** (0.1 mmol), DTBP (3 eq), TFA (2 eq), chloroform (2 mL) and BHT (3 eq) was added to a Schlenk tube and sealed. The mixture was stirred at 140 °C for 12 hours. Only trace amount of product **2a** was formed. The adduct **4** formed from BHT and trichloromethyl radical was detected by GCMS.

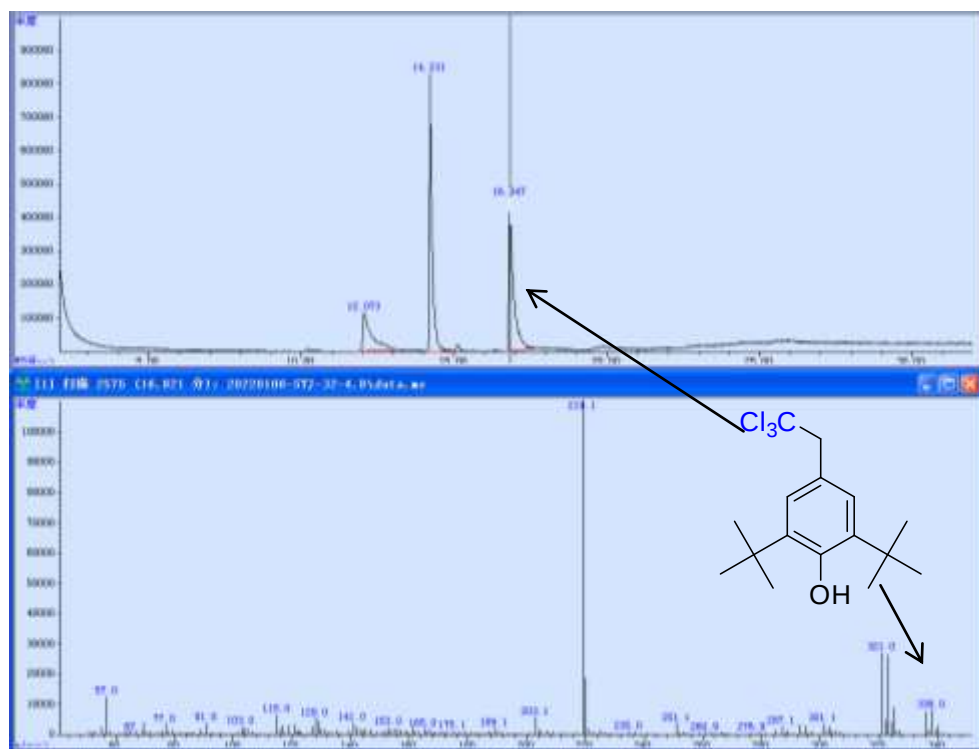
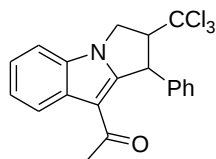
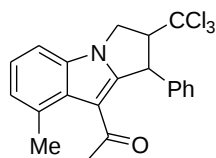


Figure S2 GC spectrum of the reaction mixture and MS spectrum of adduct **4**

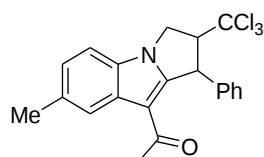
4. Characterization Data for the Products



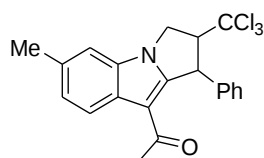
1-(1-phenyl-2-(trichloromethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (2a), 63.3 mg, 81% yield), yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.33-8.30 (m, 1H), 7.41-7.39 (m, 1H), 7.35-7.28 (m, 5H), 7.19-7.17 (m, 2H), 5.16 (d, J = 1.9 Hz, 1H), 4.65 (dd, J = 12.4, 8.1 Hz, 1H), 4.55 (dd, J = 12.4, 2.7 Hz, 1H), 4.04 (dt, J = 8.2, 2.4 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.5, 151.0, 140.3, 132.2, 130.8, 129.3, 127.9, 127.4, 123.0, 123.0, 122.7, 110.6, 110.1, 101.1, 71.7, 50.0, 47.0, 29.9. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{17}\text{Cl}_3\text{NO}$ [$\text{M}+\text{H}^+$]: 392.0370, found 392.0375.



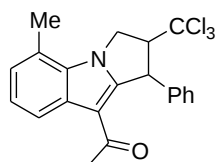
1-(8-methyl-1-phenyl-2-(trichloromethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (2b), 56.7 mg, 70% yield), yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.28 (m, 3H), 7.24-7.20 (m, 2H), 7.17-7.13 (m, 2H), 7.08 (d, J = 6.8 Hz, 1H), 5.13 (d, J = 2.0 Hz, 1H), 4.59 (dd, J = 12.4, 7.9 Hz, 1H), 4.51 (dd, J = 12.4, 2.7 Hz, 1H), 3.98 (dt, J = 7.9, 2.3 Hz, 1H), 2.75 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.8, 149.6, 140.4, 133.9, 133.0, 129.5, 129.4, 128.1, 127.3, 125.2, 123.4, 113.1, 107.5, 101.1, 71.6, 50.5, 46.8, 30.6, 23.2. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{19}\text{Cl}_3\text{NO}$ [$\text{M}+\text{H}^+$]: 406.0527, found 406.0533.



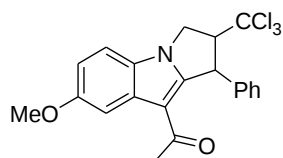
1-(7-methyl-1-phenyl-2-(trichloromethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (2c), 55.1 mg, 68% yield), yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.15 (s, 1H), 7.35-7.28 (m, 4H), 7.19-7.15 (m, 3H), 5.15 (d, J = 1.8 Hz, 1H), 4.62 (dd, J = 12.4, 8.0 Hz, 1H), 4.52 (dd, J = 12.4, 2.6 Hz, 1H), 4.02 (dt, J = 8.1, 2.3 Hz, 1H), 2.52 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.5, 151.0, 140.4, 132.7, 131.1, 130.5, 129.3, 127.9, 127.4, 124.5, 122.5, 110.2, 109.7, 101.1, 71.7, 50.1, 47.0, 29.8, 21.8. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{19}\text{Cl}_3\text{NO}$ [$\text{M}+\text{H}^+$]: 406.0527, found 406.0533.



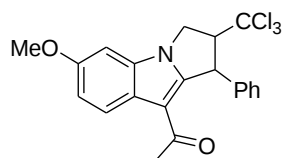
1-(6-methyl-1-phenyl-2-(trichloromethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (2d, 58.3 mg, 72% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.17 (d, $J = 8.2$ Hz, 1H), 7.34-7.28 (m, 3H), 7.22 (s, 1H), 7.19-7.17 (m, 3H), 5.14 (d, $J = 2.4$ Hz, 1H), 4.61 (dd, $J = 12.4, 8.0$ Hz, 1H), 4.52 (dd, $J = 12.4, 2.7$ Hz, 1H), 4.03 (dt, $J = 8.1, 2.4$ Hz, 1H), 2.53 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.5, 150.7, 140.4, 133.1, 132.6, 129.3, 128.5, 127.9, 127.4, 124.7, 122.3, 110.4, 110.1, 101.1, 71.7, 50.0, 46.9, 29.7, 21.7. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{19}\text{Cl}_3\text{NO}$ [$\text{M}+\text{H}^+$]: 406.0527, found 406.0533.



1-(5-methyl-1-phenyl-2-(trichloromethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (2e, 48.6 mg, 60% yield), yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, $J = 8.1$ Hz, 1H), 7.35-7.30 (m, 3H), 7.20-7.18 (m, 3H), 7.06 (d, $J = 7.2$ Hz, 1H), 5.14 (d, $J = 1.9$ Hz, 1H), 4.94 (dd, $J = 12.3, 8.0$ Hz, 1H), 4.85 (dd, $J = 12.4, 2.7$ Hz, 1H), 4.00-3.98 (m, 1H), 2.79 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.5, 151.4, 140.5, 131.9, 131.1, 129.3, 127.8, 127.4, 124.7, 123.1, 121.0, 120.4, 110.5, 101.2, 71.7, 49.8, 49.3, 30.0, 18.2. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{19}\text{Cl}_3\text{NO}$ [$\text{M}+\text{H}^+$]: 406.0527, found 406.0533.

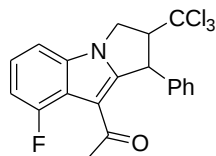


1-(7-methoxy-1-phenyl-2-(trichloromethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (2f, 64.0 mg, 76% yield), yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, $J = 2.4$ Hz, 1H), 7.35-7.26 (m, 4H), 7.17-7.15 (m, 2H), 6.96 (dd, $J = 8.8, 2.4$ Hz, 1H), 5.12 (d, $J = 1.8$ Hz, 1H), 4.61 (dd, $J = 12.4, 8.1$ Hz, 1H), 4.51 (dd, $J = 12.4, 2.7$ Hz, 1H), 4.01 (dt, $J = 8.1, 2.3$ Hz, 1H), 3.90 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.5, 156.8, 150.8, 140.3, 131.8, 129.4, 128.0, 127.4, 127.2, 113.2, 110.7, 110.4, 104.6, 101.1, 71.8, 55.9, 50.3, 47.1, 29.6. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{19}\text{Cl}_3\text{NO}_2$ [$\text{M}+\text{H}^+$]: 422.0476, found 422.0465.

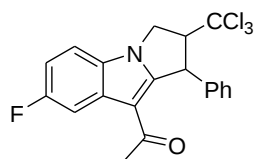


1-(6-methoxy-1-phenyl-2-(trichloromethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (2g, 58.9 mg, 70% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.20 (d, $J = 8.7$ Hz, 1H), 7.34-7.28 (m, 3H), 7.18 (d, $J = 7.8$ Hz, 2H), 6.99-6.96 (m, 1H), 6.87 (t, $J = 1.7$ Hz, 1H), 5.12 (d, $J = 1.9$ Hz, 1H), 4.60 (dd, $J = 12.3, 8.1$ Hz, 1H),

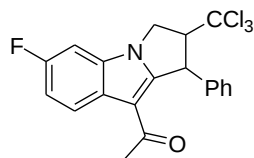
4.50 (dd, $J = 12.3, 2.6$ Hz, 1H), 4.02 (dt, $J = 8.3, 2.2$ Hz, 1H), 3.90 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.5, 156.9, 149.9, 140.5, 133.0, 129.3, 127.9, 127.4, 124.7, 123.5, 112.2, 110.5, 101.1, 93.7, 71.8, 55.8, 49.9, 46.8, 29.7. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{19}\text{Cl}_3\text{NO}_2$ [$\text{M}+\text{H}^+$]: 422.0476, found 422.0465.



1-(8-fluoro-1-phenyl-2-(trichloromethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (2h), 61.4 mg, 75% yield), yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 7.32-7.28 (m, 2H), 7.26-7.16 (m, 5H), 6.99 (dd, $J = 12.2, 7.5$ Hz, 1H), 5.21 (d, $J = 2.0$ Hz, 1H), 4.64 (dd, $J = 12.4, 8.1$ Hz, 1H), 4.51 (dd, $J = 12.4, 2.7$ Hz, 1H), 4.03 (dt, $J = 8.1, 2.4$ Hz, 1H), 2.53 (d, $J = 3.9$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.8, 157.3, 154.8, 152.6, 140.5, 134.7 (d, $J_{\text{C-F}} = 11.11$ Hz), 128.2 (d, $J_{\text{C-F}} = 172.2$ Hz), 127.6, 123.4 (d, $J_{\text{C-F}} = 8.5$ Hz), 117.7 (d, $J_{\text{C-F}} = 19.4$ Hz), 109.5 (d, $J_{\text{C-F}} = 3.0$ Hz), 108.7 (d, $J_{\text{C-F}} = 22.9$ Hz), 106.5 (d, $J_{\text{C-F}} = 3.7$ Hz), 101.1, 71.5, 50.2, 47.4, 30.5 (d, $J_{\text{C-F}} = 14.1$ Hz). HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{16}\text{Cl}_3\text{FNO}$ [$\text{M}+\text{H}^+$]: 410.0276, found 410.0282.

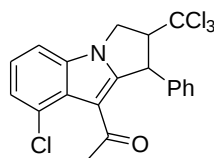


1-(7-fluoro-1-phenyl-2-(trichloromethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (2i), 60.5 mg, 74% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.03 (dt, $J = 10.1, 1.9$ Hz, 1H), 7.35-7.29 (m, 4H), 7.17-7.15 (m, 2H), 7.07-7.02 (m, 1H), 5.14 (d, $J = 1.9$ Hz, 1H), 4.65 (dd, $J = 12.4, 8.0$ Hz, 1H), 4.53 (dd, $J = 12.4, 2.6$ Hz, 1H), 4.03 (dt, $J = 8.1, 2.2$ Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.2, 160.0 (d, $J_{\text{C-F}} = 238.9$ Hz), 152.0, 140.0, 131.6 (d, $J_{\text{C-F}} = 10.9$ Hz), 128.8, 128.4 (d, $J_{\text{C-F}} = 211.3$ Hz), 128.1, 111.3 (d, $J_{\text{C-F}} = 26.6$ Hz), 110.8, 110.7, 110.7, 108.4 (d, $J_{\text{C-F}} = 25.5$ Hz), 101.0, 71.7, 50.2, 47.2, 29.7. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{16}\text{Cl}_3\text{FNO}$ [$\text{M}+\text{H}^+$]: 410.0276, found 410.0282.

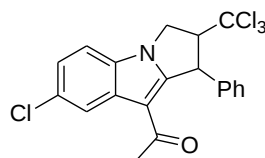


1-(6-fluoro-1-phenyl-2-(trichloromethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (2j), 67.9 mg, 83% yield), yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.30-8.26 (m, 1H), 7.36-7.29 (m, 3H), 7.16 (d, $J = 7.3$ Hz, 2H), 7.10-7.06 (m, 2H), 5.22-5.04 (m, 1H), 4.60 (dd, $J = 12.3, 8.1$ Hz, 1H), 4.50 (dd, $J = 12.4, 2.7$ Hz, 1H), 4.04-4.01 (m, 1H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.4, 160.0 (d, $J_{\text{C-F}} = 241.8$ Hz), 151.1, 140.1, 132.2 (d, $J_{\text{C-F}} = 11.8$ Hz), 129.4, 128.0, 127.3, 127.2, 123.9

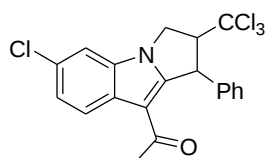
(d, $J_{\text{C-F}} = 9.6$ Hz), 111.4 (d, $J_{\text{C-F}} = 23.7$ Hz), 110.6, 100.9, 96.7 (d, $J_{\text{C-F}} = 26.5$ Hz), 71.7, 49.9, 46.9, 29.7. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{16}\text{Cl}_3\text{FNO}$ $[\text{M}+\text{H}^+]$: 410.0276, found 410.0282.



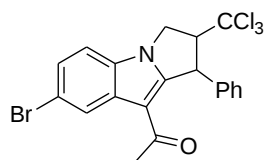
1-(8-chloro-1-phenyl-2-(trichloromethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (2k), 59.5 mg, 70% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.35-7.28 (m, 5H), 7.24-7.20 (m, 1H), 7.16 (d, $J = 8.2$ Hz, 2H), 5.12 (d, $J = 2.4$ Hz, 1H), 4.66 (dd, $J = 12.2, 8.2$ Hz, 1H), 4.53 (dd, $J = 12.2, 3.1$ Hz, 1H), 4.05 (dt, $J = 8.2, 2.8$ Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 194.0, 150.5, 140.3, 133.7, 129.2, 127.9, 127.4, 127.3, 126.7, 124.1, 123.4, 112.2, 108.9, 100.9, 71.4, 49.7, 47.3, 31.9. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{16}\text{Cl}_4\text{NO}$ $[\text{M}+\text{H}^+]$: 425.9981, found 425.9990.



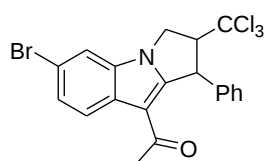
1-(7-chloro-1-phenyl-2-(trichloromethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (2l), 64.6 mg, 76% yield), yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.34 (d, $J = 1.7$ Hz, 1H), 7.36-7.28 (m, 5H), 7.16 (d, $J = 8.2$ Hz, 1H), 5.14 (d, $J = 1.8$ Hz, 1H), 4.64 (dd, $J = 12.4, 8.1$ Hz, 1H), 4.53 (dd, $J = 12.4, 2.7$ Hz, 1H), 4.04 (dt, $J = 8.1, 2.4$ Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.2, 151.8, 139.9, 131.8, 130.6, 129.5, 129.1, 128.1, 127.3, 123.4, 122.4, 111.0, 110.2, 100.9, 71.7, 50.1, 47.1, 29.8. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{16}\text{Cl}_4\text{NO}$ $[\text{M}+\text{H}^+]$: 425.9981, found 425.9990.



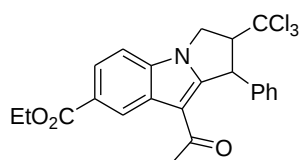
(6-chloro-1-phenyl-2-(trichloromethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (2m), 68.9 mg, 81% yield), yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.25 (d, $J = 8.6$ Hz, 1H), 7.40 (d, $J = 1.8$ Hz, 1H), 7.35-7.27 (m, 4H), 7.17-7.14 (m, 2H), 5.14 (d, $J = 1.8$ Hz, 1H), 4.61 (dd, $J = 12.4, 8.0$ Hz, 1H), 4.52 (dd, $J = 12.4, 2.6$ Hz, 1H), 4.04-4.01 (m, 1H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.3, 151.3, 139.9, 132.6, 129.4, 129.3, 128.9, 128.1, 127.3, 123.8, 123.5, 110.6, 110.1, 100.9, 71.7, 49.9, 46.9, 29.8. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{16}\text{Cl}_4\text{NO}$ $[\text{M}+\text{H}^+]$: 425.9981, found 425.9990.



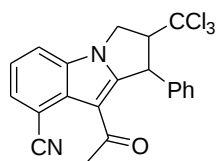
1-(7-bromo-1-phenyl-2-(trichloromethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (2n), 75.0 mg, 80% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.42 (s, 1H), 7.31 (d, $J = 11.9$ Hz, 1H), 7.24-7.16 (m, 4H), 7.06 (d, $J = 7.8$ Hz, 2H), 5.05 (d, $J = 1.9$ Hz, 1H), 4.54 (dd, $J = 12.4, 8.1$ Hz, 1H), 4.44 (dd, $J = 12.5, 2.6$ Hz, 1H), 3.96-3.93 (m, 1H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.2, 151.6, 139.9, 132.3, 130.6, 129.5, 128.1, 127.3, 126.0, 125.4, 116.8, 111.2, 110.2, 100.9, 71.7, 50.0, 47.1, 29.8. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{16}\text{BrCl}_3\text{NO}$ [$\text{M}+\text{H}^+$]: 469.9475, found 469.9463.



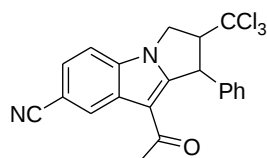
1-(6-bromo-1-phenyl-2-(trichloromethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (2o), 74.1 mg, 79% yield), yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.20 (d, $J = 8.6$ Hz, 1H), 7.56 (s, 1H), 7.41 (d, $J = 8.6$ Hz, 1H), 7.31 (t, $J = 8.4$ Hz, 3H), 7.15 (d, $J = 7.2$ Hz, 2H), 5.13 (s, 1H), 4.61 (dd, $J = 12.4, 8.0$ Hz, 1H), 4.51 (dd, $J = 12.5, 2.6$ Hz, 1H), 4.02 (d, $J = 7.8$ Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.4, 151.2, 139.9, 133.0, 129.7, 129.5, 128.1, 127.1, 126.2, 124.1, 116.4, 113.1, 110.6, 100.9, 71.7, 49.9, 47.0, 29.8. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{16}\text{BrCl}_3\text{NO}$ [$\text{M}+\text{H}^+$]: 469.9475, found 469.9463.



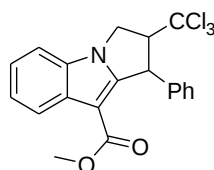
Methyl-9-acetyl-1-phenyl-2-(trichloromethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indole-7-carboxylate (2p), 66.7 mg, 72% yield), yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.99 (s, 1H), 8.03 (dd, $J = 8.5, 1.6$ Hz, 1H), 7.41 (d, $J = 8.5$ Hz, 1H), 7.34-7.28 (m, 3H), 7.17-7.15 (m, 2H), 5.16 (d, $J = 2.0$ Hz, 1H), 4.67 (dd, $J = 12.5, 8.1$ Hz, 1H), 4.57 (dd, $J = 12.5, 2.7$ Hz, 1H), 4.05 (dt, $J = 8.1, 2.3$ Hz, 1H), 3.94 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.3, 167.8, 152.3, 139.9, 134.6, 130.3, 129.4, 128.0, 127.3, 125.0, 124.9, 124.5, 111.3, 109.8, 100.9, 71.7, 52.1, 49.9, 47.0, 30.0. HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{21}\text{Cl}_3\text{NO}_3$ [$\text{M}+\text{H}^+$]: 464.0582, found 464.0573.



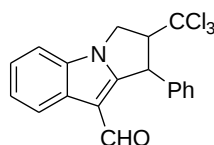
9-acetyl-1-phenyl-2-(trichloromethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indole-8-carbonitrile (2q), 52.4 mg, 63% yield), yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 7.65 (dd, $J = 14.7, 7.8$ Hz, 2H), 7.36-7.29 (m, 4H), 7.12-7.10 (m, 2H), 5.15 (d, $J = 1.8$ Hz, 1H), 4.71 (dd, $J = 12.4, 8.1$ Hz, 1H), 4.59 (dd, $J = 12.5, 2.5$ Hz, 1H), 4.03 (dt, $J = 8.0, 2.2$ Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 191.7, 151.8, 139.4, 132.8, 131.0, 129.6, 129.1, 128.3, 127.2, 122.8, 119.3, 114.9, 111.4, 105.9, 100.7, 71.4, 50.2, 47.2, 30.0. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{16}\text{Cl}_3\text{N}_2\text{O}$ $[\text{M}+\text{H}^+]$: 417.0323, found 417.0328.



9-acetyl-1-phenyl-2-(trichloromethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indole-7-carbonitrile (2r), 53.2 mg, 64% yield), yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.70 (d, $J = 1.4$ Hz, 1H), 7.51 (d, $J = 1.5$ Hz, 1H), 7.46 (d, $J = 8.4$ Hz, 1H), 7.36-7.31 (m, 3H), 7.15 (d, $J = 8.3$ Hz, 2H), 5.16 (d, $J = 1.8$ Hz, 1H), 4.69 (dd, $J = 12.5, 8.0$ Hz, 1H), 4.59 (dd, $J = 12.5, 2.6$ Hz, 1H), 4.06 (dt, $J = 7.9, 2.3$ Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.2, 152.6, 139.4, 133.7, 130.6, 129.6, 128.3, 128.2, 127.3, 126.2, 120.1, 111.0, 110.8, 106.2, 100.7, 71.6, 49.9, 47.1, 29.8. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{16}\text{Cl}_3\text{N}_2\text{O}$ $[\text{M}+\text{H}^+]$: 417.0323, found 417.0328.

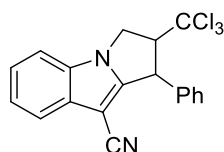


Methyl 1-phenyl-2-(trichloromethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indole-9-carboxylate (2s), 60.3 mg, 74% yield), light yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.22-8.20 (m, 1H), 7.43-7.40 (m, 1H), 7.35-7.27 (m, 5H), 7.22-7.20 (d, $J = 7.4$ Hz, 2H), 5.16 (d, $J = 2.4$ Hz, 1H), 4.73-4.67 (m, 1H), 4.57-4.53 (m, 1H), 4.12-4.08 (m, 1H), 3.70 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 164.7, 151.8, 141.3, 132.2, 131.0, 128.9, 127.5, 127.4, 122.6, 122.4, 122.0, 110.1, 101.2, 100.0, 71.7, 50.7, 49.6, 47.5. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{17}\text{Cl}_3\text{NO}_2$ $[\text{M}+\text{H}^+]$: 408.0319, found 408.0323.

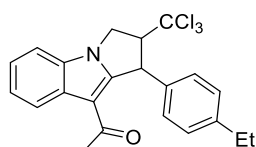


1-phenyl-2-(trichloromethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indole-9-carbaldehyde (2t), 32.4 mg, 43% yield), brown solid; ^1H NMR (400 MHz, CDCl_3) δ 9.55 (s, 1H), 8.17-8.15 (m, 1H), 7.32-7.19 (m, 1H), 7.27-7.21 (m, 4H), 7.16-7.15 (m, 2H), 5.04 (d, $J = 3.9$ Hz, 1H), 4.65 (dd, $J = 12.1, 8.5$ Hz, 1H), 4.45 (dd, $J = 12.1, 4.3$ Hz, 1H),

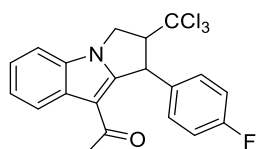
4.14-4.10 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 183.7, 140.6, 132.5, 129.8, 129.4, 128.2, 127.8, 123.7, 123.6, 122.4, 110.2, 110.1, 100.6, 71.5, 48.8, 48.0. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{15}\text{Cl}_3\text{NO}$ [$\text{M}+\text{H}^+$]: 378.0214, found 378.0216.



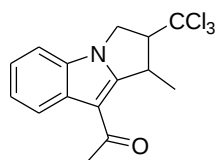
1-phenyl-2-(trichloromethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indole-9-carbonitrile (2u), 49.5 mg, 66% yield, yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.68-7.66 (m, 1H), 7.41-7.28 (m, 6H), 7.24-7.22 (m, 2H), 4.98 (d, J = 3.9 Hz, 1H), 4.70 (dd, J = 11.9, 8.4 Hz, 1H), 4.52 (dd, J = 11.9, 4.3 Hz, 1H), 4.19 (dt, J = 8.4, 4.2 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 152.4, 139.2, 132.2, 131.4, 129.4, 128.3, 127.8, 123.6, 122.6, 120.1, 114.9, 110.8, 100.5, 79.1, 71.2, 48.6, 48.2. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{14}\text{Cl}_3\text{N}_2$ [$\text{M}+\text{H}^+$]: 375.0217, found 375.0220.



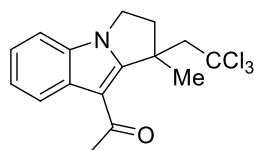
1-(1-(4-ethylphenyl)-2-(trichloromethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethan-1-one (2x), 57.2 mg, 68% yield, white solid; ^1H NMR (400 MHz, CDCl_3) δ 8.34-8.31 (m, 1H), 7.40-7.32 (m, 3H), 7.14 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 5.13 (d, J = 1.9 Hz, 1H), 4.63 (dd, J = 12.4, 8.1 Hz, 1H), 4.53 (dd, J = 12.4, 2.7 Hz, 1H), 4.02 (dt, J = 8.1, 2.4 Hz, 1H), 2.62 (q, J = 7.6 Hz, 2H), 2.31 (s, 3H), 1.22 (t, J = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.6, 151.2, 144.0, 137.5, 132.2, 130.8, 128.8, 127.3, 123.0, 122.9, 122.7, 110.5, 110.0, 101.1, 71.8, 49.7, 46.9, 29.8, 28.5, 15.5. HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{21}\text{Cl}_3\text{NO}$ [$\text{M}+\text{H}^+$]: 420.0683, found 420.0688.



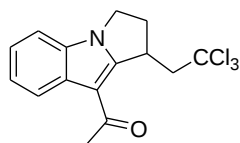
1-(1-(4-fluorophenyl)-2-(trichloromethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethan-1-one (2y), 59.1 mg, 72% yield, yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.26-8.23 (m, 1H), 7.42-7.32 (m, 3H), 7.18-7.14 (m, 2H), 7.03-6.99 (m, 2H), 5.16 (d, J = 2.1 Hz, 1H), 4.65 (dd, J = 12.4, 8.2 Hz, 1H), 4.54 (dd, J = 12.4, 2.9 Hz, 1H), 4.02 (dt, J = 8.1, 2.5 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.4, 162.1 (d, $J_{\text{C-F}}$ = 248.1 Hz), 150.9, 136.3, 136.3, 132.2, 130.6, 129.1 (d, $J_{\text{C-F}}$ = 8.3 Hz), 123.0, 122.4, 116.2 (d, $J_{\text{C-F}}$ = 8.3 Hz), 110.5, 110.2, 101.0, 71.7, 49.3, 47.0, 30.0. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{16}\text{Cl}_3\text{FNO}$ [$\text{M}+\text{H}^+$]: 410.0276, found 410.0280.



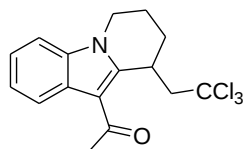
1-(1-methyl-2-(trichloromethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (2z), 20.4 mg, 31% yield), yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.02 (dd, J = 7.1, 1.5 Hz, 1H), 7.34-7.27 (m, 3H), 4.55 (dd, J = 12.3, 8.5 Hz, 1H), 4.40 (dd, J = 12.3, 3.3 Hz, 1H), 4.09-4.03 (m, 1H), 3.76 (dt, J = 8.4, 2.9 Hz, 1H), 2.67 (s, 3H), 1.65 (d, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.9, 154.6, 132.1, 130.3, 122.6, 122.4, 121.4, 110.3, 109.9, 101.3, 69.9, 47.0, 39.9, 30.3, 20.1. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{15}\text{Cl}_3\text{NO}$ [$\text{M}+\text{H}^+$]: 330.0214, found 330.0209.



1-(1-methyl-1-(2,2,2-trichloroethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (2aa), 33.0 mg, 48% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.92-7.90 (m, 1H), 7.35-7.28 (m, 3H), 4.31-4.20 (m, 2H), 3.97 (d, J = 15.5 Hz, 1H), 3.67 (d, J = 15.5 Hz, 1H), 3.46-3.40 (m, 1H), 2.74 (s, 3H), 2.65-2.58 (m, 1H), 1.72 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 193.6, 156.6, 132.1, 130.5, 122.3, 122.1, 121.0, 110.7, 110.5, 98.1, 59.0, 45.7, 43.9, 39.6, 31.5, 25.6. HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{17}\text{Cl}_3\text{NO}$ [$\text{M}+\text{H}^+$]: 344.0370, found 344.0368.

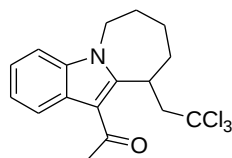


1-(1-(2,2,2-trichloroethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (2ab), 40.8 mg, 62% yield), yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 7.98-7.96 (m, 1H), 7.34-7.27 (m, 3H), 4.26-4.12 (m, 3H), 3.78 (d, J = 14.7 Hz, 1H), 3.10-2.97 (m, 2H), 2.80 (dd, J = 14.8, 10.2 Hz, 1H), 2.70 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 193.4, 153.4, 132.6, 130.1, 122.5, 122.4, 121.2, 110.6, 110.3, 98.7, 55.7, 43.5, 38.0, 33.0, 30.6. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{15}\text{Cl}_3\text{NO}$ [$\text{M}+\text{H}^+$]: 330.0214, found 330.0209.

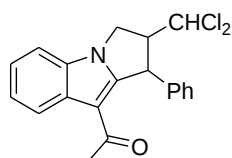


1-(9-(2,2,2-trichloroethyl)-6,7,8,9-tetrahydropyrido[1,2-a]indol-10-yl)ethanone (2ac), 43.9 mg, 64% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.93-7.91 (m, 1H), 7.38-7.28 (m, 3H), 4.59-4.54 (m, 1H), 4.39-4.33 (m, 1H), 3.98-3.90 (m, 1H), 3.48 (dd, J = 14.9, 3.4 Hz, 1H), 2.99 (dd, J = 15.0, 11.1 Hz, 1H), 2.82-2.76 (m, 1H), 2.73 (s, 3H), 2.38-2.29 (m, 1H), 2.16 (d, J = 20.6 Hz, 1H), 1.86-1.77 (m, 1H); ^{13}C

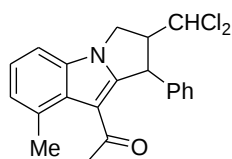
NMR (101 MHz, CDCl₃) δ 193.9, 147.4, 136.3, 126.1, 122.7, 122.3, 120.6, 112.3, 109.9, 98.4, 53.3, 42.7, 33.2, 31.7, 21.1, 17.1. HRMS (ESI) m/z calcd for C₁₆H₁₇Cl₃NO [M+H⁺]: 344.0370, found 344.0377.



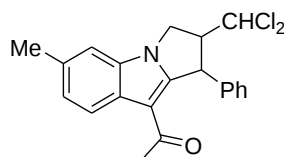
1-(10-(2,2,2-trichloroethyl)-7,8,9,10-tetrahydro-6H-azepino[1,2-a]indol-11-yl)ethanone (2ad, 34.3 mg, 48% yield), yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.93-7.91 (m, 1H), 7.40-7.38 (m, 1H), 7.30-7.27 (m, 2H), 5.49-5.45 (m, 1H), 4.69-4.64 (m, 1H), 4.00-3.94 (m, 1H), 3.25-3.23 (m, 2H), 2.74 (s, 3H), 2.36-2.31 (m, 1H), 2.20-2.14 (m, 1H), 2.05-1.99 (m, 2H), 1.85-1.71 (m, 1H), 1.53-1.46 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 195.7, 149.0, 136.3, 126.0, 122.3, 121.8, 121.0, 115.0, 109.6, 98.9, 55.2, 44.9, 32.2, 32.1, 30.4, 28.4, 24.8. HRMS (ESI) m/z calcd for C₁₇H₁₉Cl₃NO [M+H⁺]: 358.0527, found 358.0531.



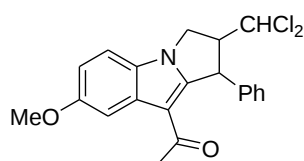
1-(2-(dichloromethyl)-1-phenyl-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (3a, 45.7 mg, 64% yield), yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 8.36-8.33 (m, 1H), 7.39-7.30 (m, 6H), 7.13 (d, J = 7.2 Hz, 2H), 6.02 (d, J = 4.8 Hz, 1H), 4.94 (d, J = 2.9 Hz, 1H), 4.54 (dd, J = 11.7, 7.9 Hz, 1H), 4.38 (dd, J = 11.6, 3.5 Hz, 1H), 3.63-3.60 (m, 1H), 2.23 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 192.8, 151.0, 140.4, 132.4, 130.8, 129.4, 127.9, 127.2, 123.0, 123.0, 122.8, 110.7, 110.1, 74.0, 62.1, 49.2, 45.7, 29.7. HRMS (ESI) m/z calcd for C₂₀H₁₈Cl₂NO [M+H⁺]: 358.0760, found 358.0762.



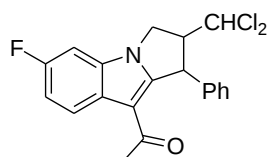
1-(2-(dichloromethyl)-8-methyl-1-phenyl-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (3b, 38.6 mg, 52% yield), yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.29 (m, 3H), 7.24-7.16 (m, 2H), 7.12-7.07 (m, 3H), 5.99 (d, J = 4.9 Hz, 1H), 4.93 (d, J = 3.2 Hz, 1H), 4.49 (dd, J = 11.6, 7.9 Hz, 1H), 4.35 (dd, J = 11.5, 3.6 Hz, 1H), 3.59-3.54 (m, 1H), 2.73 (s, 3H), 2.19 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 193.3, 149.3, 140.4, 133.8, 133.1, 129.5, 129.2, 128.0, 127.2, 125.0, 123.3, 113.2, 107.4, 73.9, 62.1, 49.6, 45.6, 30.6, 23.1. HRMS (ESI) m/z calcd for C₂₁H₂₀Cl₂NO [M+H⁺]: 372.0916, found 372.0909.



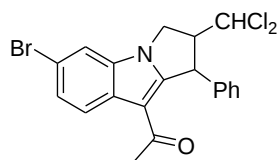
1-(2-(dichloromethyl)-6-methyl-1-phenyl-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (3c), 37.9 mg, 51% yield), yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.19 (d, J = 8.1 Hz, 1H), 7.34-7.28 (m, 3H), 7.18-7.11 (m, 4H), 6.00 (d, J = 4.9 Hz, 1H), 4.91 (d, J = 3.0 Hz, 1H), 4.49 (dd, J = 11.6, 7.9 Hz, 1H), 4.35 (dd, J = 11.6, 3.5 Hz, 1H), 3.62-3.57 (m, 1H), 2.52 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.7, 150.3, 140.6, 133.0, 132.7, 129.3, 128.5, 127.8, 127.2, 124.6, 122.4, 110.7, 110.0, 74.1, 62.2, 49.1, 45.5, 29.7, 21.7. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{20}\text{Cl}_2\text{NO}$ [$\text{M}+\text{H}^+$]: 372.0916, found 372.0909.



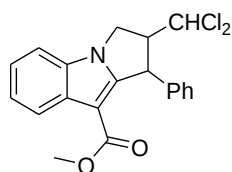
1-(2-(dichloromethyl)-7-methoxy-1-phenyl-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (3d), 39.5 mg, 51% yield), yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, J = 2.4 Hz, 1H), 7.37-7.28 (m, 5H), 7.16-7.14 (m, 2H), 6.98 (dd, J = 8.8, 2.5 Hz, 1H), 6.04 (d, J = 4.7 Hz, 1H), 4.94 (d, J = 3.0 Hz, 1H), 4.53 (dd, J = 11.6, 7.9 Hz, 1H), 4.38-4.35 (m, 1H), 3.93 (s, 3H), 3.64-3.59 (m, 1H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.7, 156.7, 150.6, 140.5, 131.8, 129.4, 127.9, 127.3, 127.2, 113.2, 110.7, 104.6, 74.0, 62.2, 55.9, 49.4, 45.8, 29.7. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{20}\text{Cl}_2\text{NO}_2$ [$\text{M}+\text{H}^+$]: 388.0866, found 388.0862.



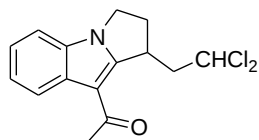
1-(2-(dichloromethyl)-6-fluoro-1-phenyl-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (3e), 48.8 mg, 65% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.32-8.28 (m, 1H), 7.34-7.29 (m, 3H), 7.13-7.11 (m, 2H), 7.06-7.02 (m, 2H), 6.03 (d, J = 4.6 Hz, 1H), 4.91 (d, J = 3.0 Hz, 1H), 4.49 (dd, J = 11.5, 7.9 Hz, 1H), 4.32 (dd, J = 11.5, 3.6 Hz, 1H), 3.64-3.59 (m, 1H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.6, 161.2, 158.8, 151.0, 140.3, 132.4 (d, $J_{\text{C-F}}$ = 12.0 Hz), 128.3 (d, $J_{\text{C-F}}$ = 229.6 Hz), 128.0, 123.9 (d, $J_{\text{C-F}}$ = 9.6 Hz), 111.1, 111.1 (d, $J_{\text{C-F}}$ = 55.1 Hz), 96.7 (d, $J_{\text{C-F}}$ = 26.4 Hz), 73.9, 62.1, 49.1, 45.6, 29.7. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{17}\text{Cl}_2\text{FNO}$ [$\text{M}+\text{H}^+$]: 376.0666, found 376.0672.



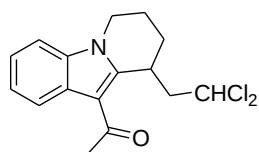
1-(6-bromo-2-(dichloromethyl)-1-phenyl-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (3f), 53.9 mg, 62% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.21 (d, $J = 8.6$ Hz, 1H), 7.52 (s, 1H), 7.41-7.38 (m, 1H), 7.35-7.29 (m, 3H), 7.12-7.10 (m, 2H), 6.02 (d, $J = 4.6$ Hz, 1H), 4.91 (d, $J = 2.9$ Hz, 1H), 4.50 (dd, $J = 11.6, 7.9$ Hz, 1H), 4.35-4.31 (m, 1H), 3.63-3.59 (m, 1H), 2.17 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.6, 151.1, 140.1, 133.1, 129.7, 129.5, 128.0, 127.2, 126.1, 124.1, 116.4, 113.1, 110.8, 73.9, 62.1, 49.0, 45.7, 29.8. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{17}\text{BrCl}_2\text{NO}$ [$\text{M}+\text{H}^+$]: 435.9865, found 435.9877.



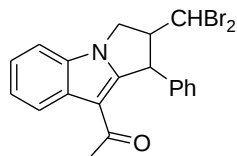
Methyl-2-(dichloromethyl)-1-phenyl-2,3-dihydro-1H-pyrrolo[1,2-a]indole-9-carboxylate (3g), 41.1 mg, 55% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.20-8.18 (m, 1H), 7.38-7.27 (m, 6H), 7.16-7.14 (m, 2H), 6.00 (d, $J = 4.4$ Hz, 1H), 4.88 (d, $J = 4.0$ Hz, 1H), 4.58 (dd, $J = 11.4, 8.1$ Hz, 1H), 4.39 (dd, $J = 11.4, 4.4$ Hz, 1H), 3.68-3.62 (m, 1H), 3.59 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 164.7, 151.4, 141.1, 132.3, 131.0, 128.9, 127.4, 127.3, 122.6, 122.3, 121.9, 110.1, 100.3, 73.9, 62.0, 50.5, 48.9, 45.8. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{18}\text{Cl}_2\text{NO}_2$ [$\text{M}+\text{H}^+$]: 374.0709, found 374.0715.



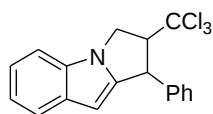
1-(1-(2,2-dichloroethyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethanone (3h), 31.3 mg, 53% yield), yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 8.01-7.99 (m, 1H), 7.34-7.27 (m, 3H), 6.02-5.99 (m, 1H), 4.20-4.17 (m, 2H), 3.96-3.90 (m, 1H), 3.06-2.99 (m, 1H), 2.95-2.87 (m, 1H), 2.69 (s, 3H), 2.62-2.56 (m, 1H), 2.46-2.38 (t, $J = 14.7$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 193.3, 153.8, 132.6, 130.1, 122.4, 122.4, 121.3, 110.5, 110.2, 72.1, 46.4, 43.3, 37.2, 32.9, 30.4. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{16}\text{Cl}_2\text{NO}$ [$\text{M}+\text{H}^+$]: 296.0603, found 296.0604.



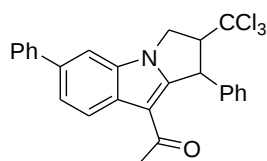
1-(9-(2,2-dichloroethyl)-6,7,8,9-tetrahydropyrido[1,2-*a*]indol-10-yl)ethanone (**3i**, 31.5 mg, 51% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, $J = 8.2$ Hz, 1H), 7.36-7.28 (m, 3H), 6.33 (t, $J = 6.7$ Hz, 1H), 4.34-4.29 (m, 1H), 4.04-3.99 (m, 1H), 3.93-3.85 (m, 1H), 2.74-2.68 (m, 4H), 2.48-2.41 (m, 1H), 2.28-2.11 (m, 3H), 1.93-1.85 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 194.0, 148.4, 136.1, 126.1, 122.6, 122.2, 120.5, 112.2, 109.8, 73.1, 46.9, 42.5, 31.8, 31.7, 23.8, 17.6. HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{18}\text{Cl}_2\text{NO}$ [$\text{M}+\text{H}^+$]: 310.0760, found 310.0756.



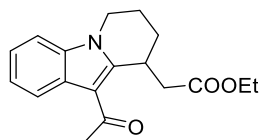
1-(2-(dibromomethyl)-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-9-yl)ethanone (**5**, 40.1 mg, 45% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.34-8.32 (m, 1H), 7.40-7.37 (m, 1H), 7.34-7.30 (m, 5H), 7.16-7.14 (m, 2H), 5.96 (d, $J = 4.3$ Hz, 1H), 4.85 (d, $J = 3.2$ Hz, 1H), 4.54 (dd, $J = 11.5, 7.9$ Hz, 1H), 4.34 (dd, $J = 11.6, 3.8$ Hz, 1H), 3.72-3.68 (m, 1H), 2.23 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.7, 150.8, 140.4, 132.4, 130.8, 129.4, 127.9, 127.3, 123.0, 122.9, 122.7, 110.8, 110.0, 62.7, 51.0, 47.4, 47.2, 29.9. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{18}\text{Br}_2\text{NO}$ [$\text{M}+\text{H}^+$]: 445.9750, found 445.9742.



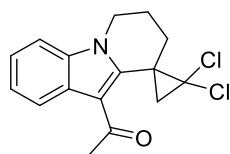
1-phenyl-2-(trichloromethyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (**6**, 23.0 mg, 66% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, $J = 7.9$ Hz, 1H), 7.37-7.26 (m, 6H), 7.22 (t, $J = 7.6$ Hz, 1H), 7.13 (t, $J = 7.5$ Hz, 1H), 6.08 (s, 1H), 4.86 (d, $J = 4.3$ Hz, 1H), 4.67 (dd, $J = 11.3, 8.5$ Hz, 1H), 4.48 (dd, $J = 11.4, 4.7$ Hz, 1H), 4.16 (dt, $J = 8.8, 4.6$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 145.7, 142.3, 133.1, 132.2, 128.9, 128.1, 127.5, 121.0, 119.9, 109.6, 101.3, 94.0, 71.9, 48.2, 47.1. HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{15}\text{Cl}_3\text{N}$ [$\text{M}+\text{H}^+$]: 350.0265, found 350.0269.



1-(1,6-diphenyl-2-(trichloromethyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-9-yl)ethanone (**7**, 32.7 mg, 70% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.34 (d, $J = 8.8$ Hz, 1H), 7.70 (d, $J = 7.8$ Hz, 2H), 7.60 (d, $J = 7.3$ Hz, 2H), 7.48 (t, $J = 7.5$ Hz, 2H), 7.37-7.31 (m, 4H), 7.20 (d, $J = 7.5$ Hz, 2H), 5.17 (d, $J = 1.8$ Hz, 1H), 4.68 (dd, $J = 12.4, 8.0$ Hz, 1H), 4.60 (dd, $J = 12.4, 2.8$ Hz, 1H), 4.07-4.04 (m, 1H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.4, 151.4, 141.5, 140.3, 136.6, 132.8, 131.0, 130.0, 129.4, 128.9, 127.9, 127.4, 127.2, 122.9, 122.7, 108.5, 101.1, 71.7, 50.0, 47.0, 29.9. HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{21}\text{Cl}_3\text{NO}$ [$\text{M}+\text{H}^+$]: 468.0683, found 468.0692.



ethyl 2-(10-acetyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indol-9-yl)acetate (8, 15.1 mg, 50% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.93-7.91 (m, 1H), 7.36-7.27 (m, 3H), 4.32-4.28 (m, 2H), 4.24-4.16 (m, 2H), 3.93-3.86 (m, 1H), 3.02 (dd, J = 16.1, 3.0 Hz, 1H), 2.70 (s, 3H), 2.55 (dd, J = 16.0, 10.8 Hz, 1H), 2.12-2.03 (m, 2H), 1.94-1.86 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 193.7, 172.0, 148.4, 136.1, 126.2, 122.5, 122.0, 120.5, 112.3, 109.7, 60.6, 42.6, 37.6, 31.6, 30.3, 23.8, 17.8, 14.3. HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{22}\text{NO}_3$ [$\text{M}+\text{H}^+$]: 300.1594, found 300.1591.

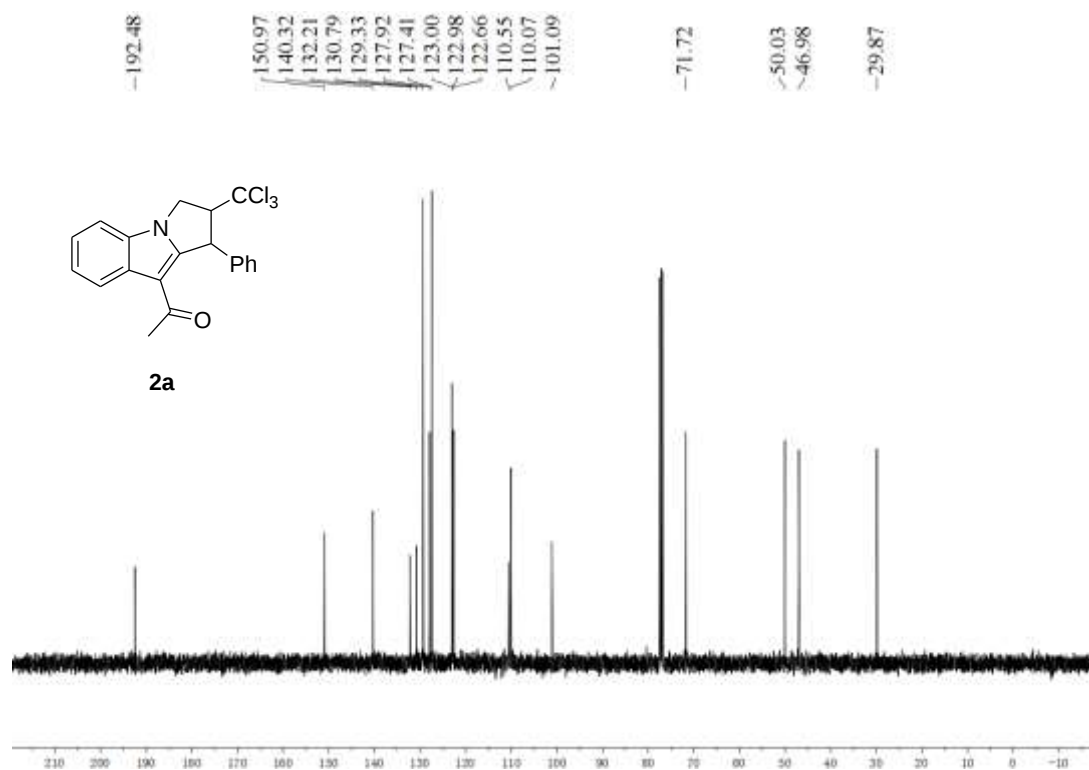
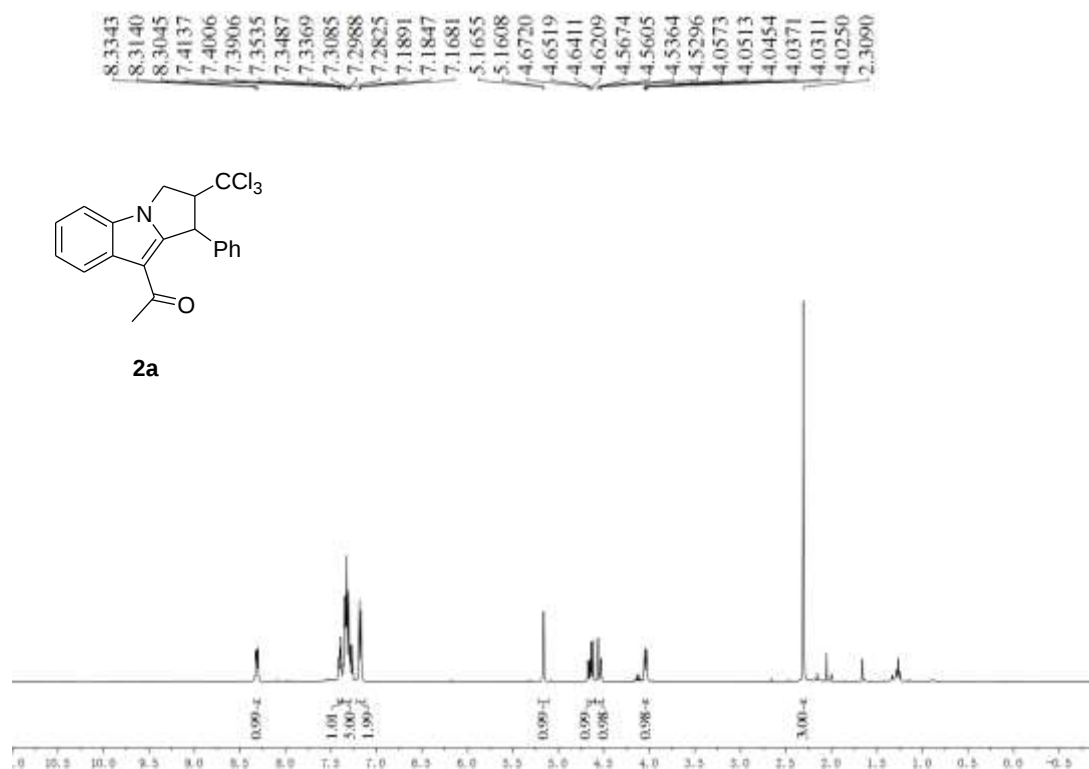


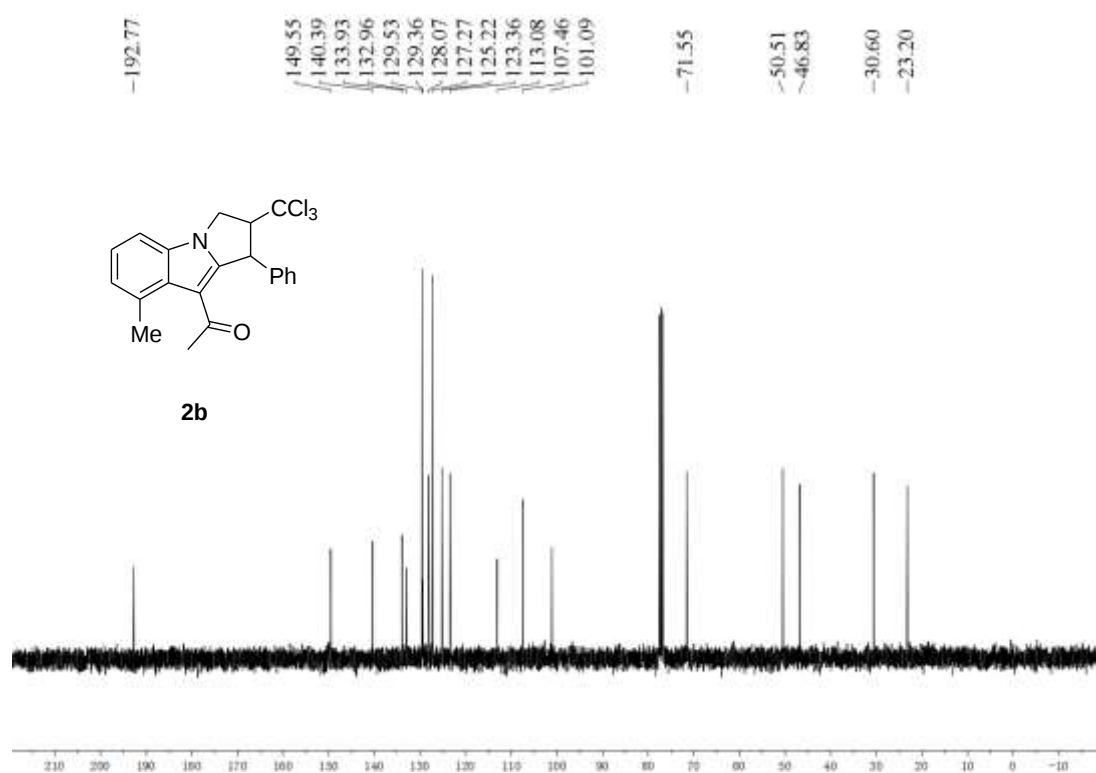
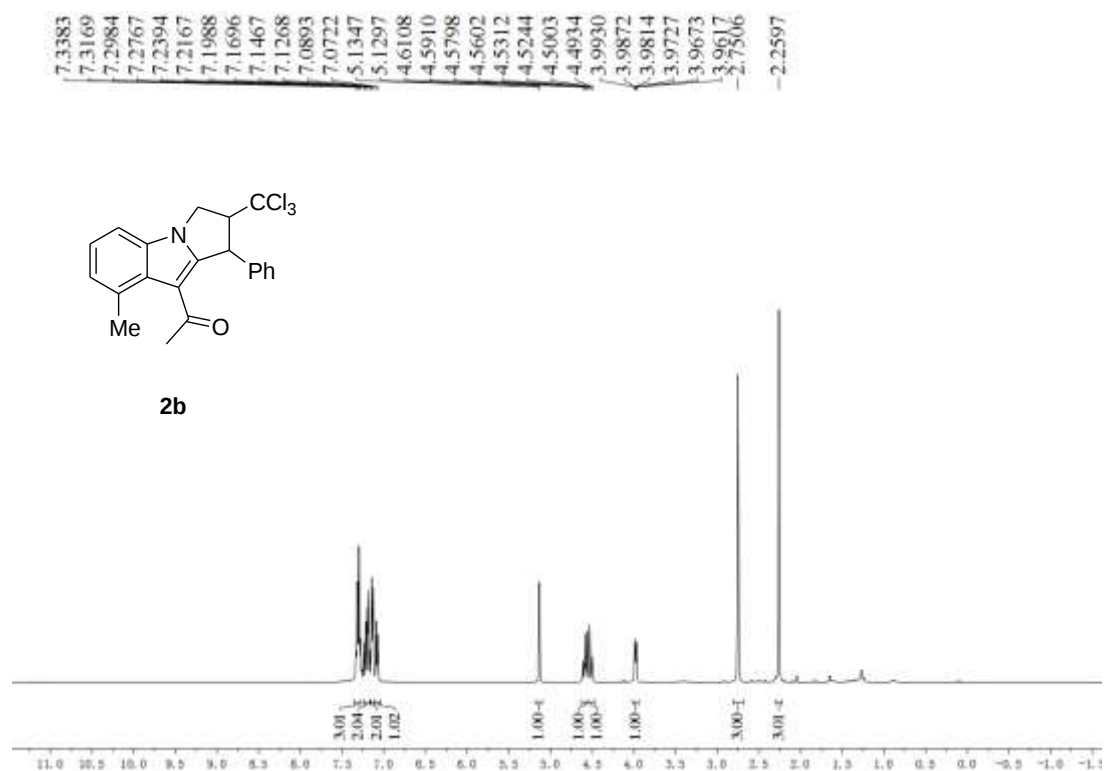
1-(2,2-dichloro-7',8'-dihydro-6'*H*-spiro[cyclopropane-1,9'-pyrido[1,2-*a*]indol]-10'-yl)ethan-1-one (9, 19.2 mg, 62% yield), yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.76-7.74 (m, 1H), 7.33-7.30 (m, 1H), 7.24-7.18 (m, 2H), 4.21-4.14 (m, 1H), 2.98 (d, J = 8.7 Hz, 1H), 2.59 (s, 3H), 2.38-2.28 (m, 2H), 2.07-1.98 (m, 2H), 1.80 (d, J = 8.7 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 196.6, 140.0, 135.4, 125.9, 122.6, 121.8, 120.8, 116.9, 109.4, 67.3, 41.6, 33.7, 33.4, 32.0, 30.2, 21.5. HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{16}\text{Cl}_2\text{NO}$ [$\text{M}+\text{H}^+$]: 308.0603, found 308.0601.

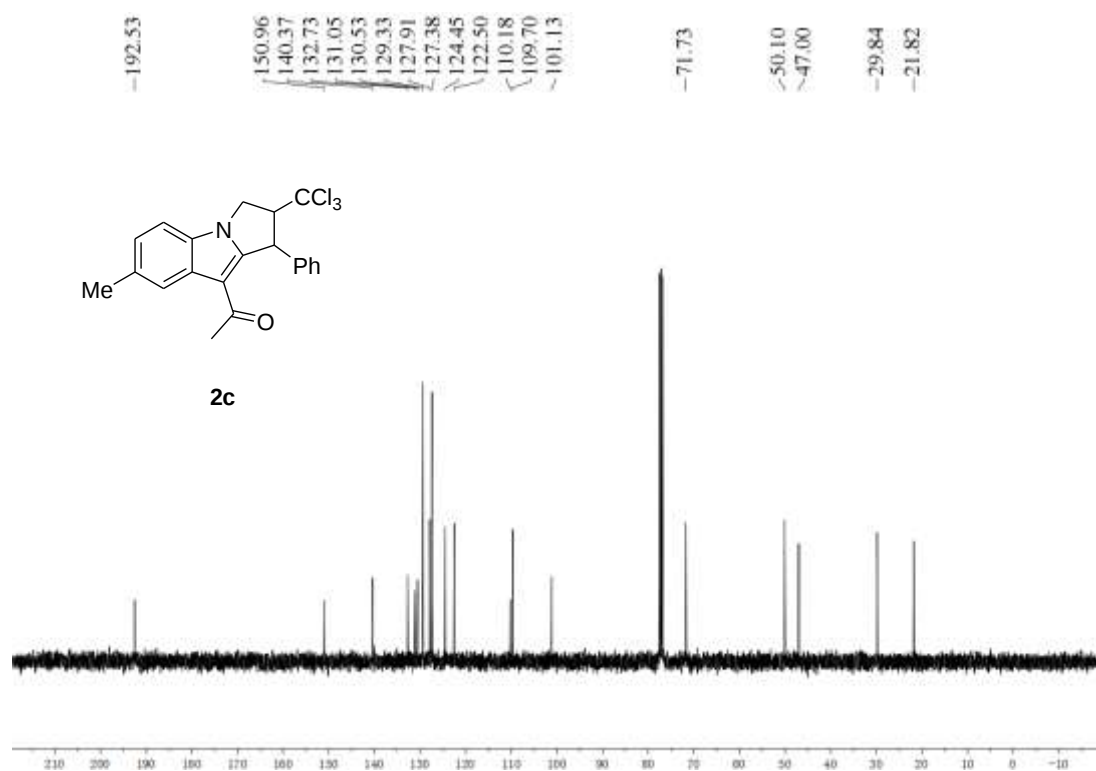
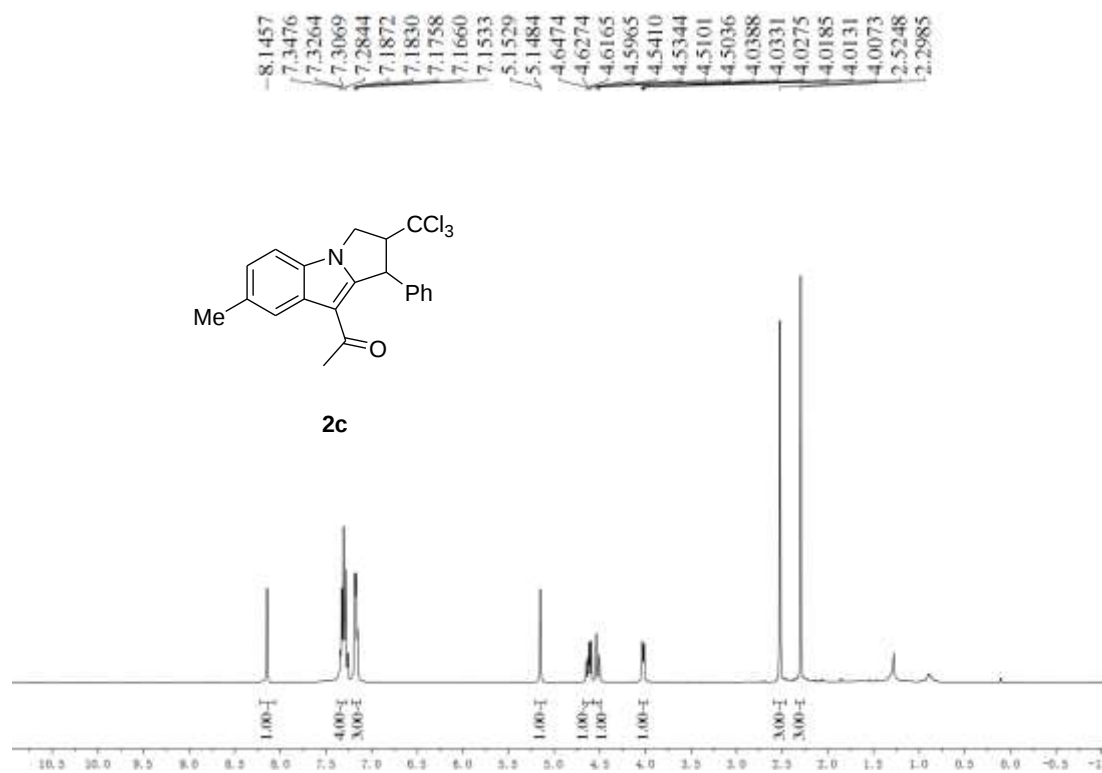
5. References

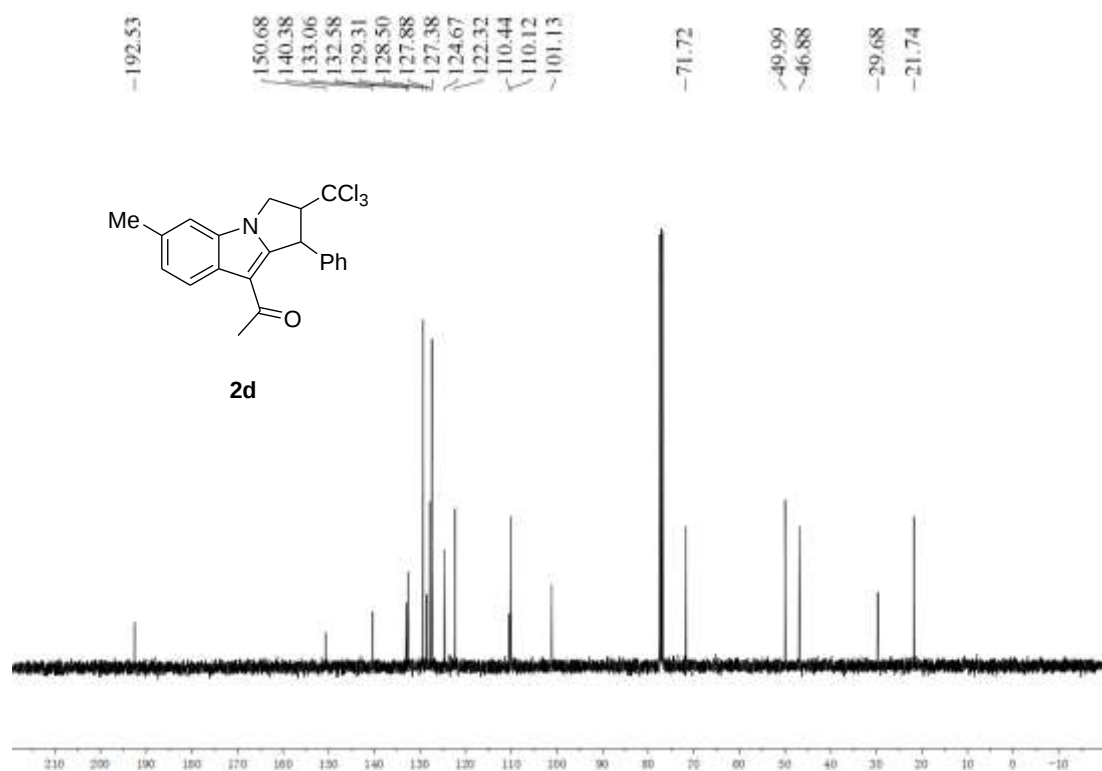
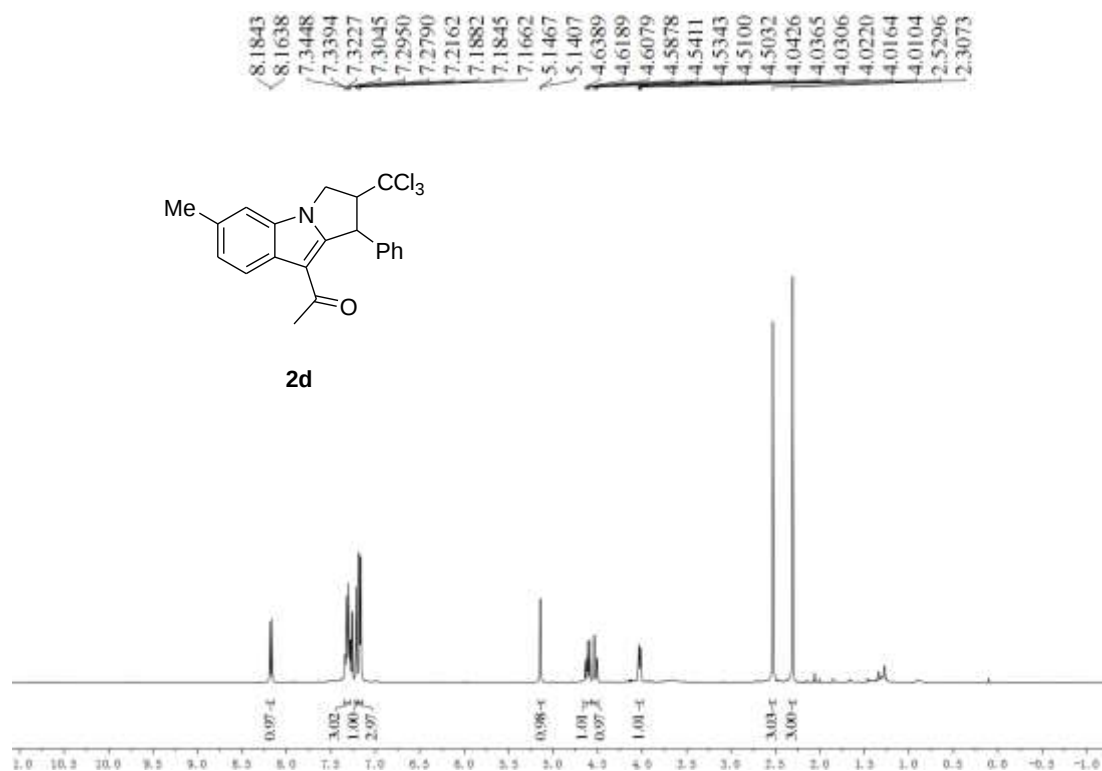
- [1] J-T. Zhang, M-Y. Wu, H. Ju, H-T. Yang, B-Y. Qian, K. Ding, J-P, Wu, M-H. Xie, *Org. Chem. Front.*, 2022, **9**, 32.
- [2] Y-Q. Yang, P. Gao, Y. Zhao and Z-Z. Shi, *Angew. Chem. Int. Ed.*, 2017, **56**, 3966.
- [3] G. Huang, Y. Shan, J.-T. Yu and C. Pan, *Org. Biomol. Chem.*, 2021, **19**, 10085.
- [4] C. Xu, Z. Zhu, Y. Wang, Z. Jing, B. Gao, L. Zhao, and W-K. Dong, *J. Org. Chem.*, 2019, **84**, 2234.
- [5] H. Liu, Z. Yang, J.-T. Yu and C. Pan, *Adv. Synth. Catal.*, 2022, **364**, 1085.

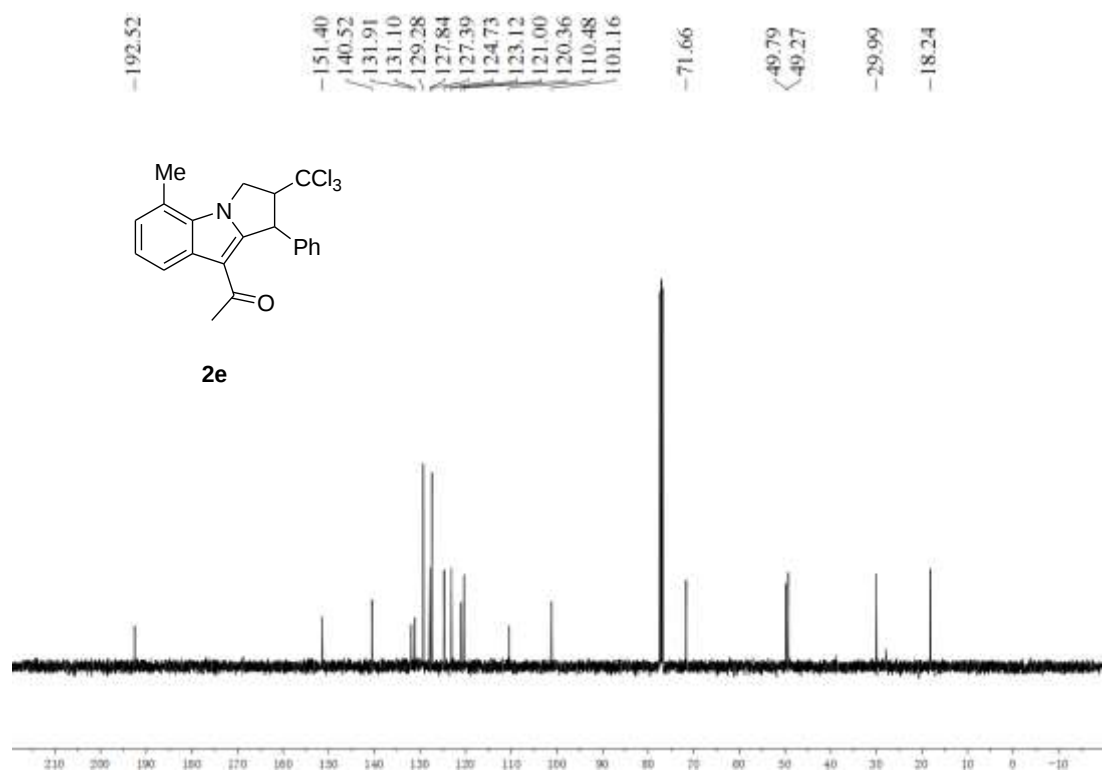
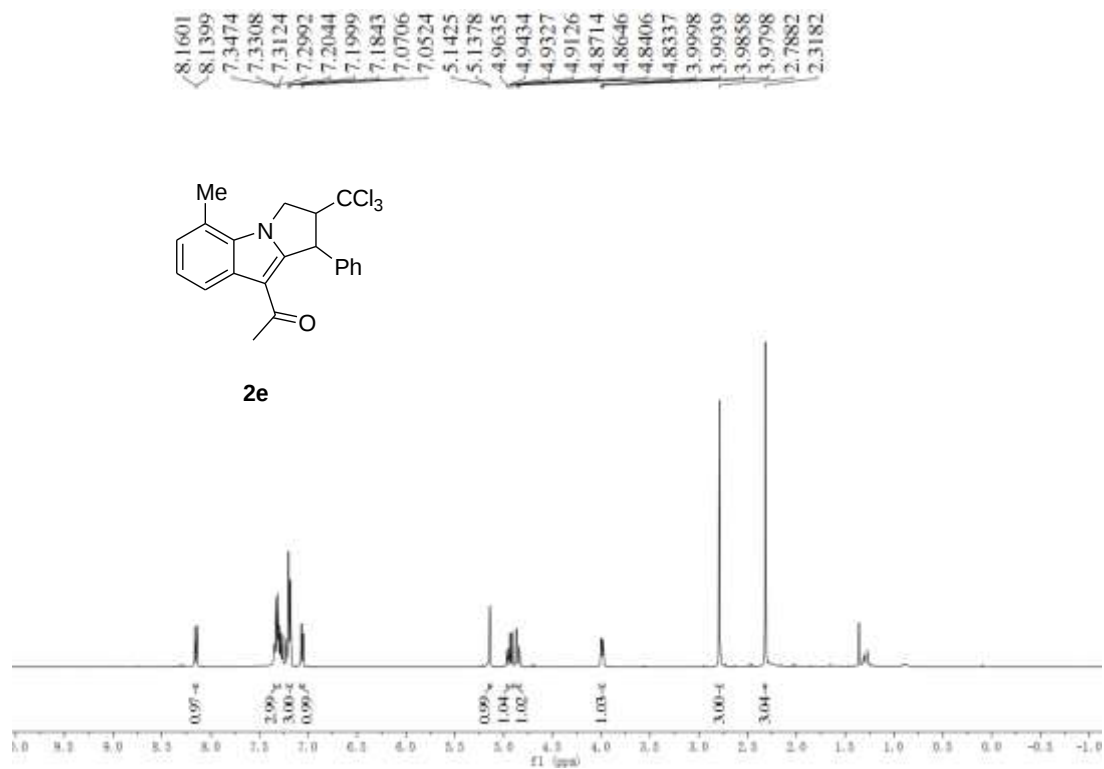
6. Copies of the ^1H NMR and ^{13}C NMR Spectra

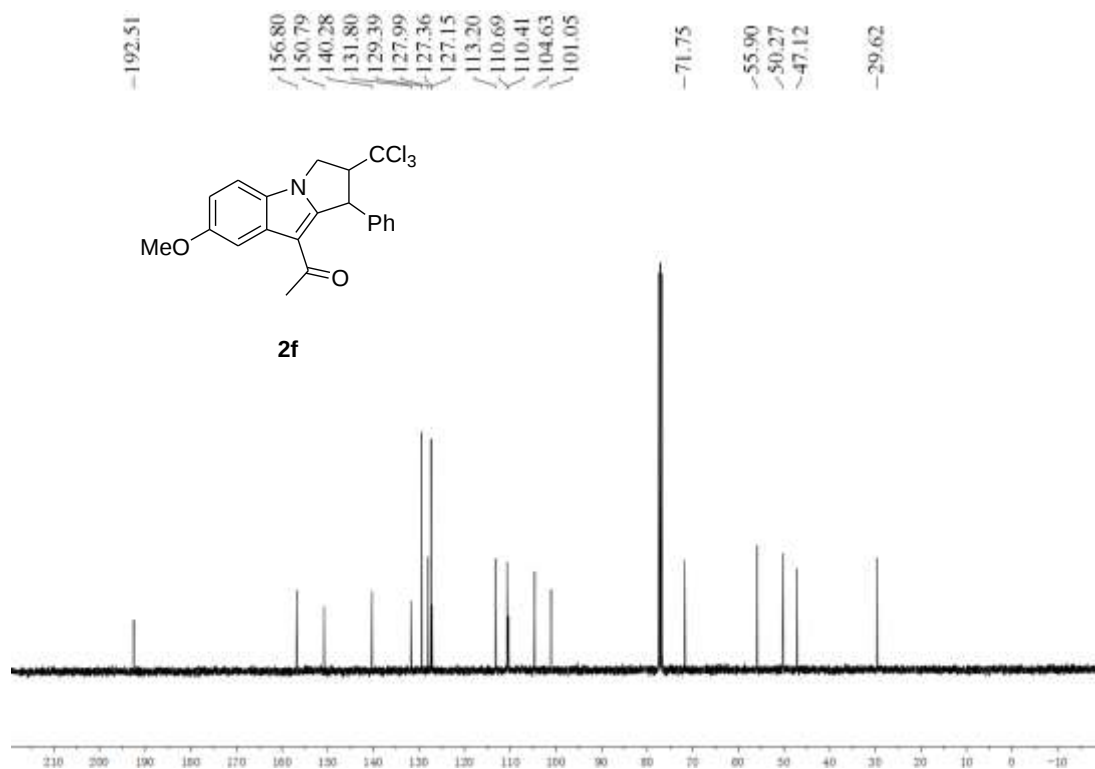
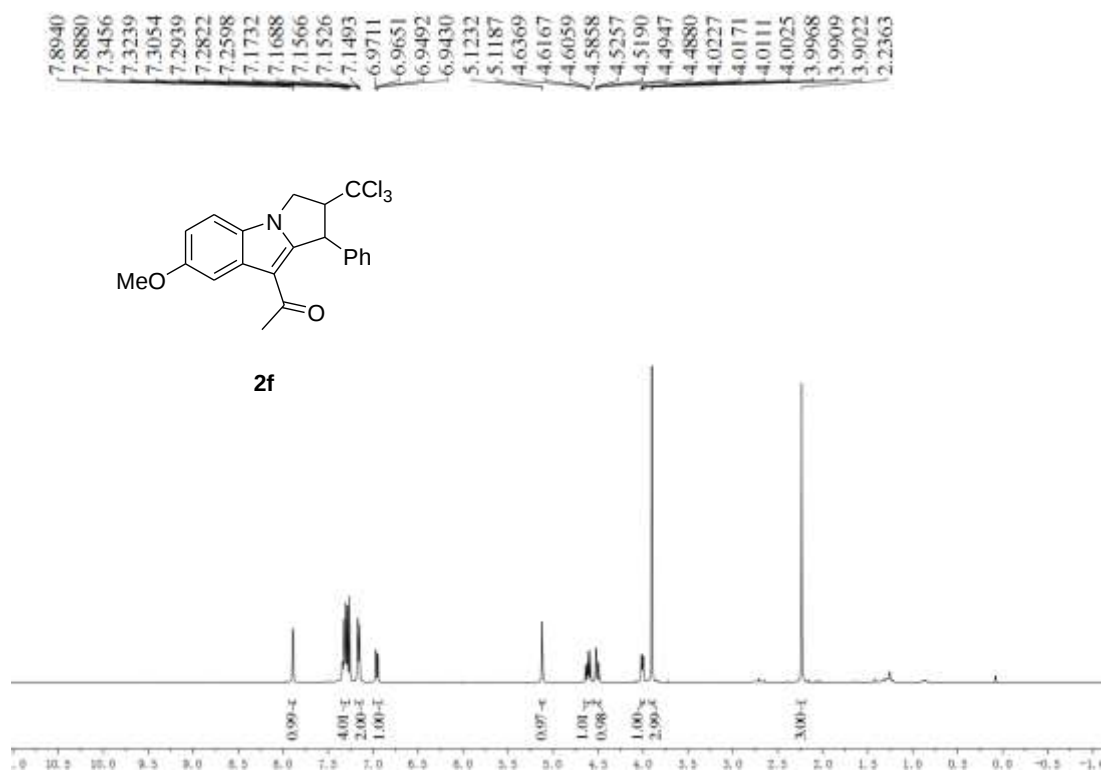


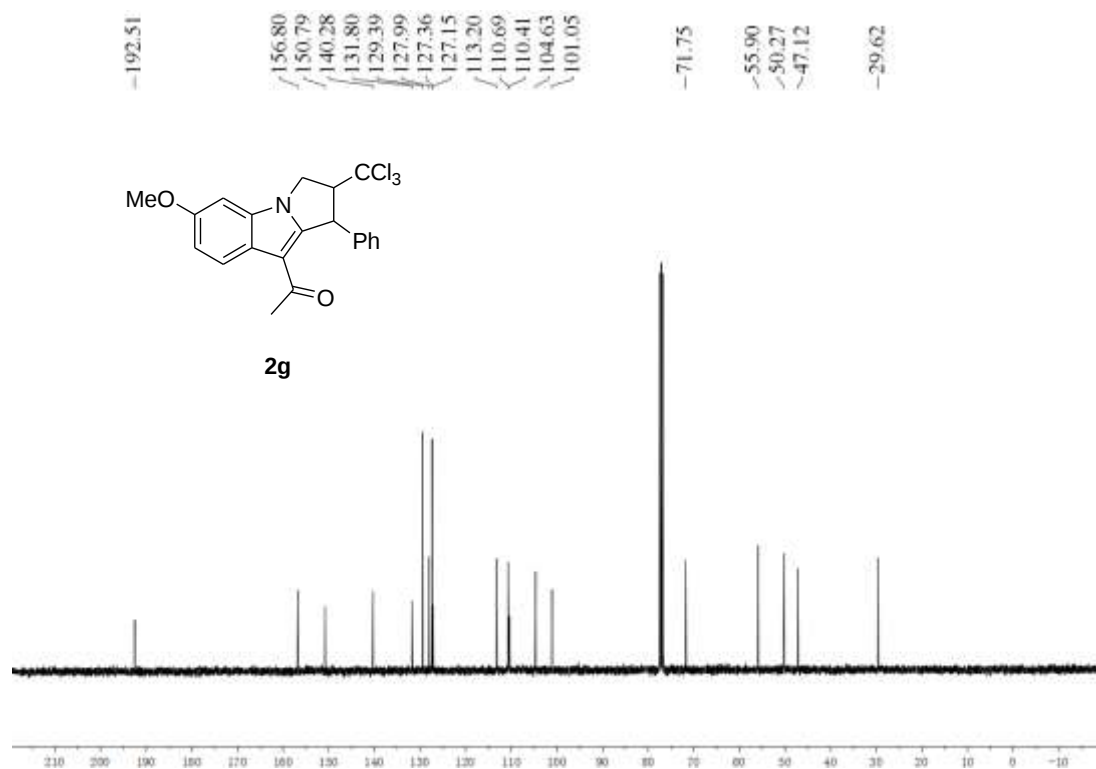
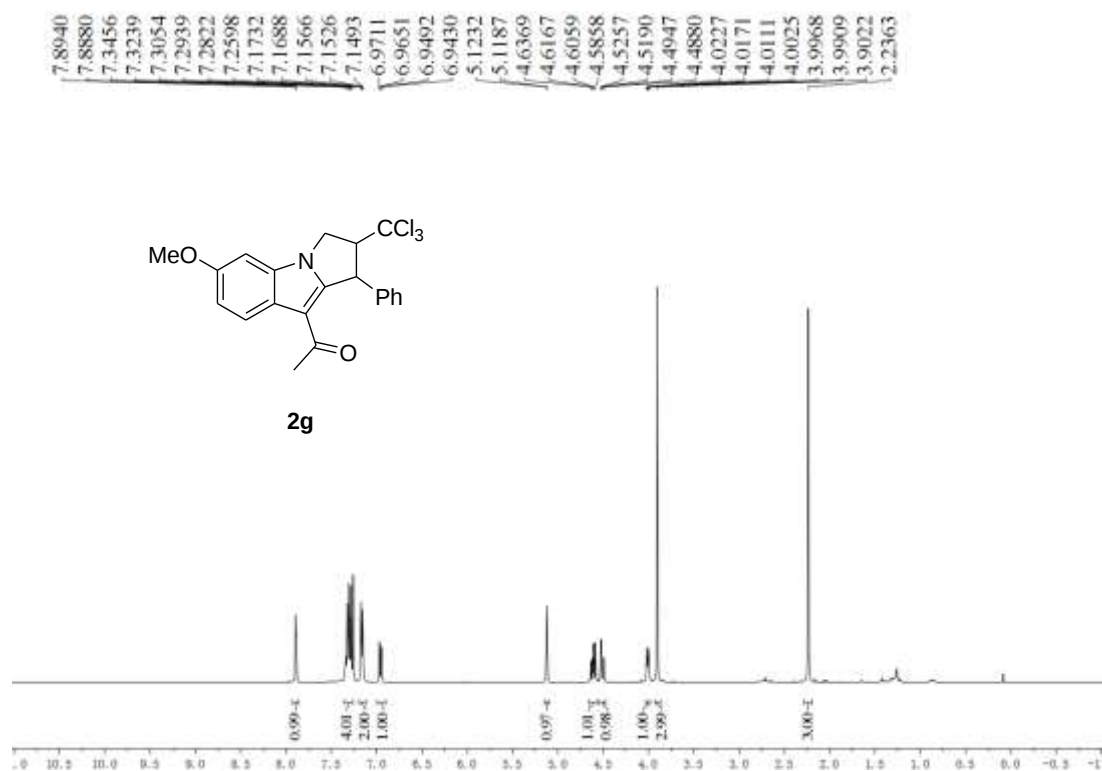




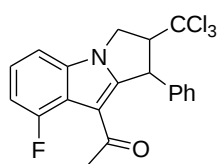




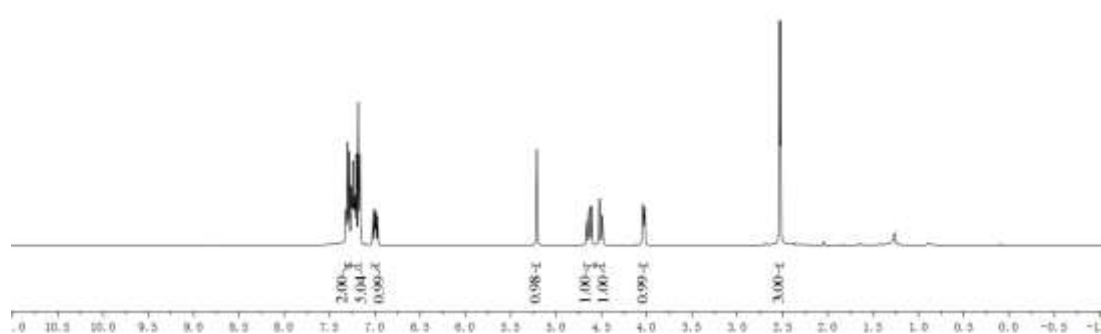




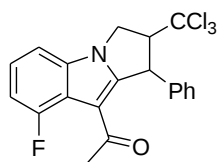
7.3215
7.3181
7.3015
7.2832
7.2630
7.2592
7.2438
7.2334
7.2251
7.2146
7.2044
7.1829
7.1637
7.0195
7.0004
6.9888
6.9702
5.2125
5.2076
4.6609
4.6404
4.6298
4.6097
4.5242
4.5175
4.4931
4.4865
4.0475
4.0414
4.0351
4.0261
4.0207
4.0149
2.5338
2.5241



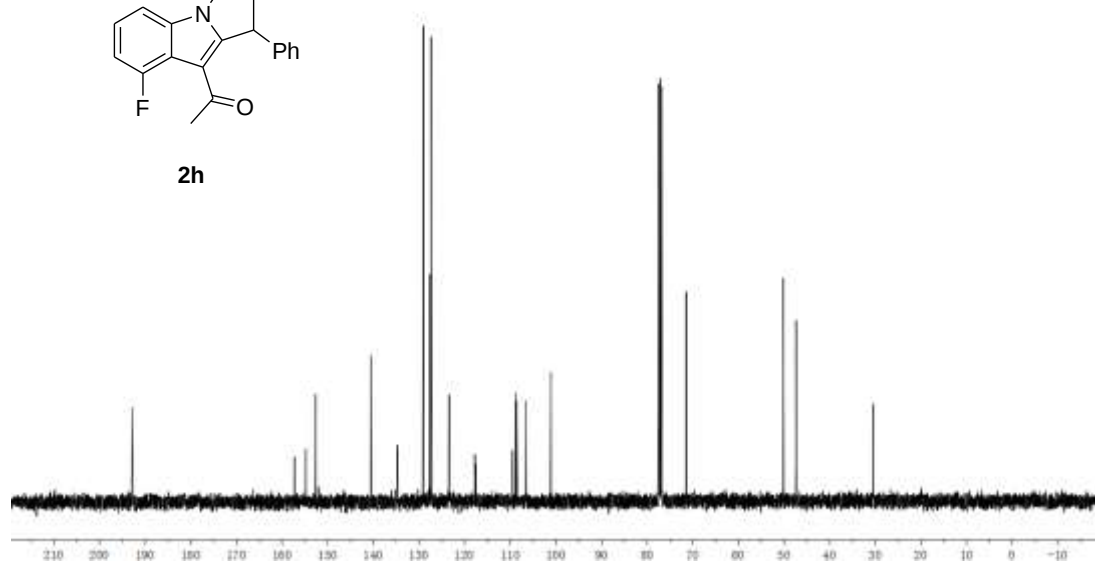
2h

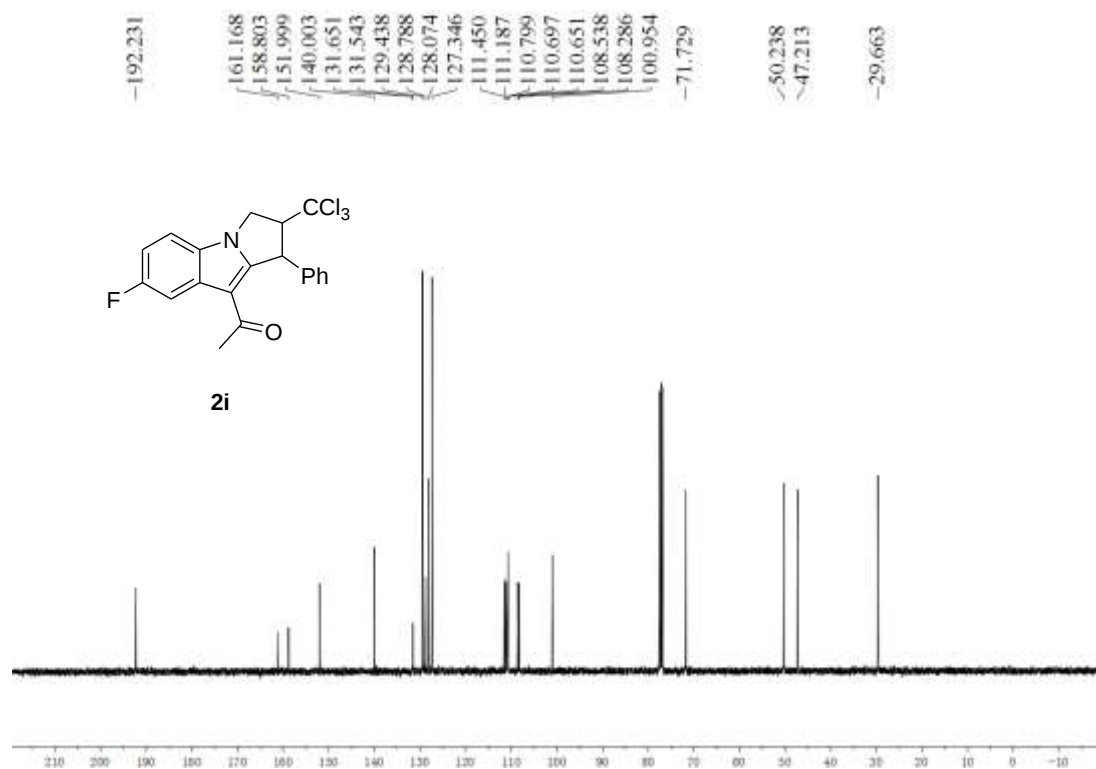
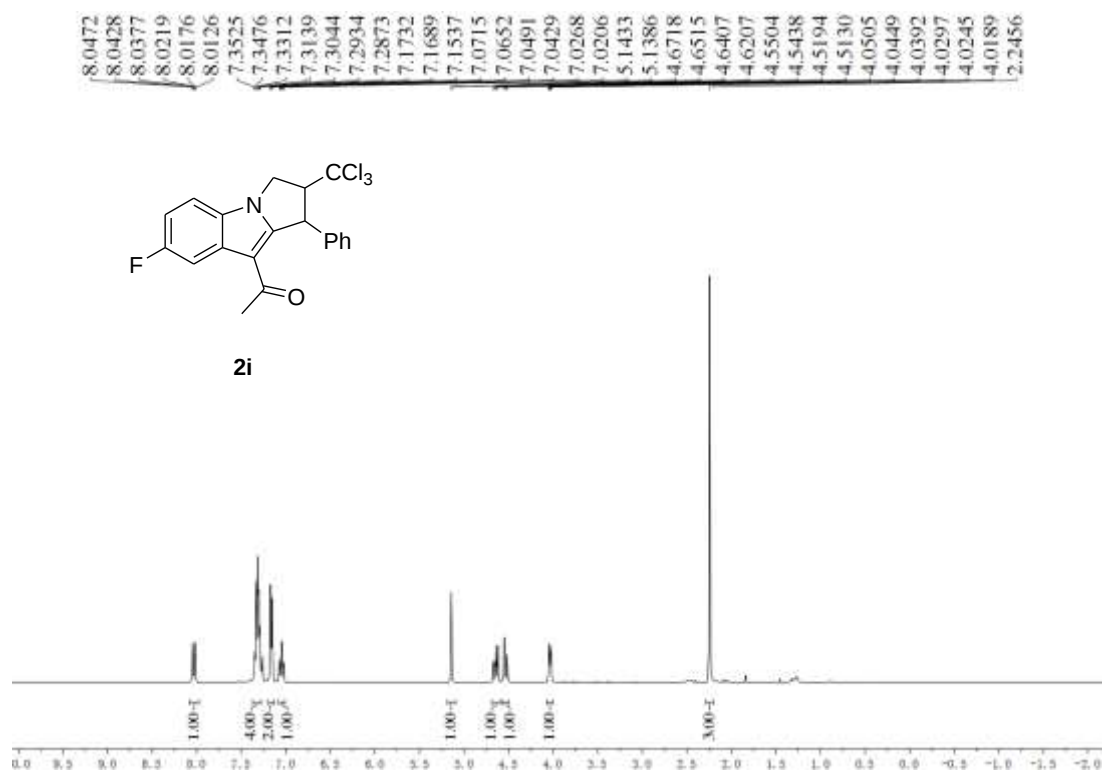


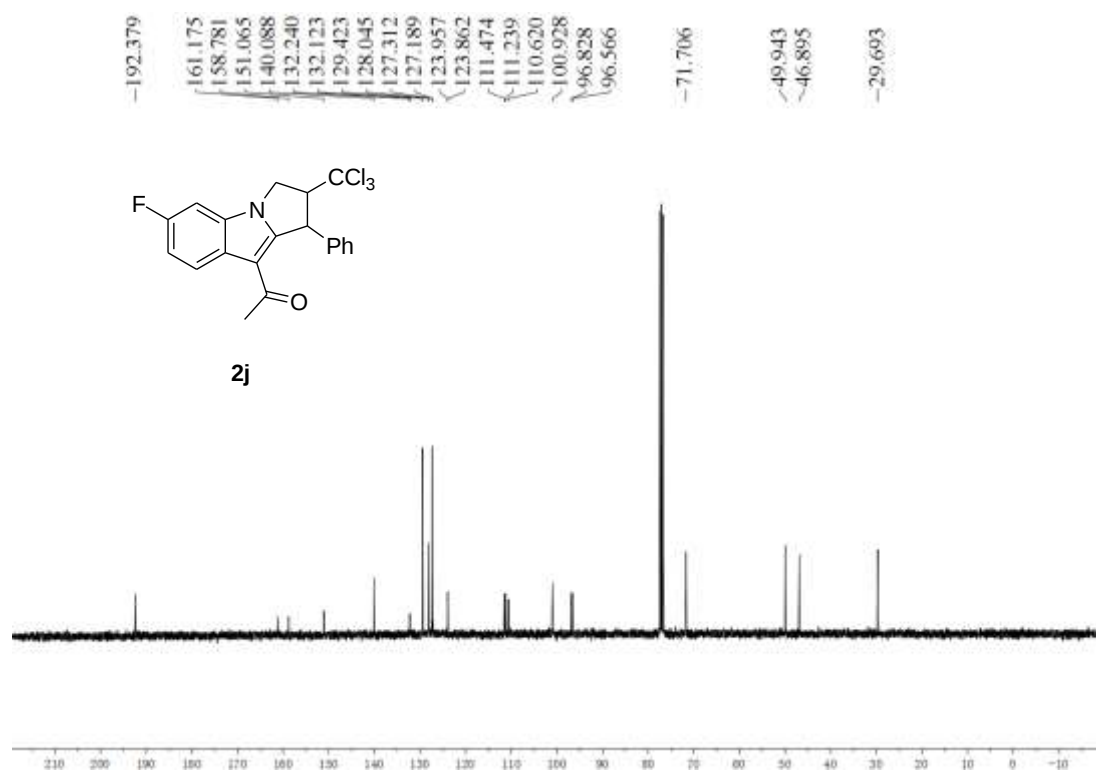
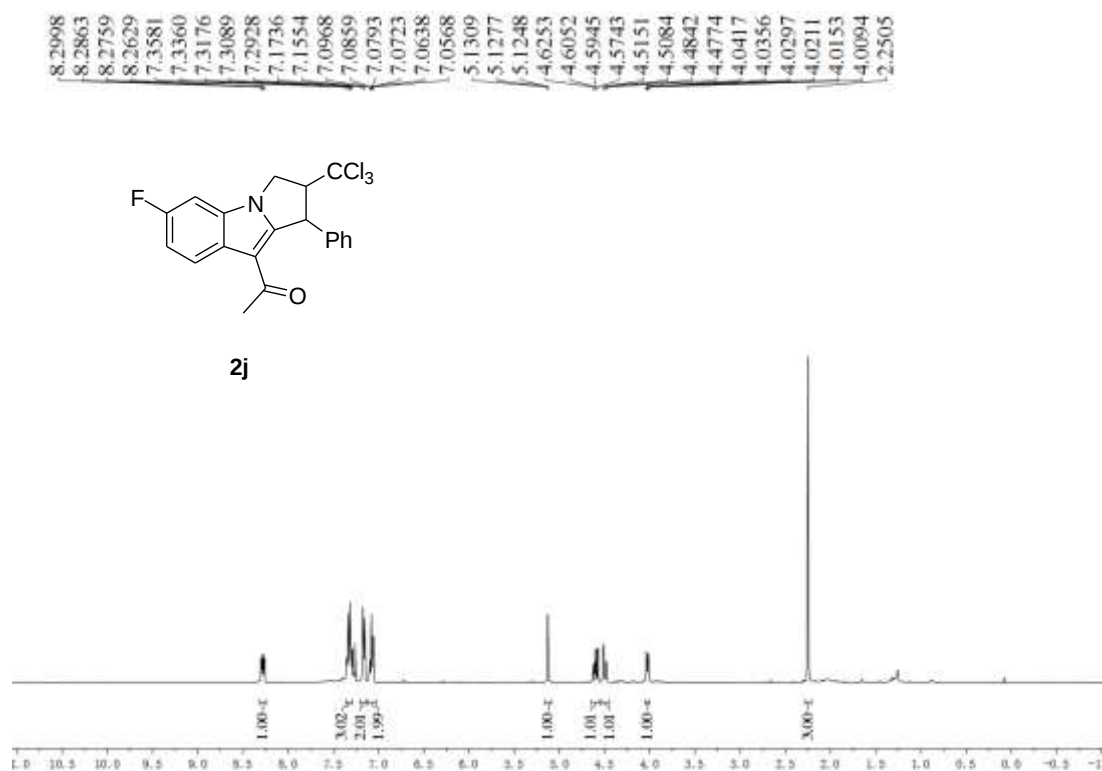
192.768
157.265
154.790
152.636
140.484
134.751
134.641
129.062
127.579
127.357
123.449
123.365
117.763
117.571
109.541
109.513
108.842
108.615
106.593
106.556
101.089
71.469
50.165
47.354
30.596
30.464

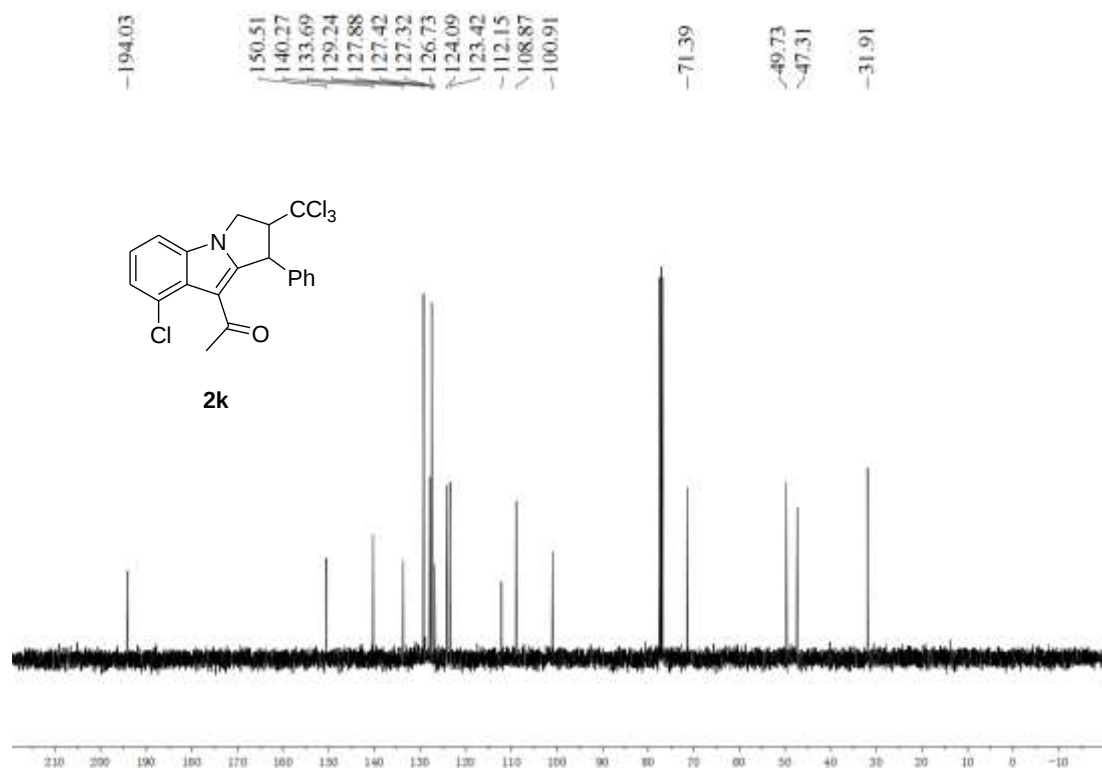
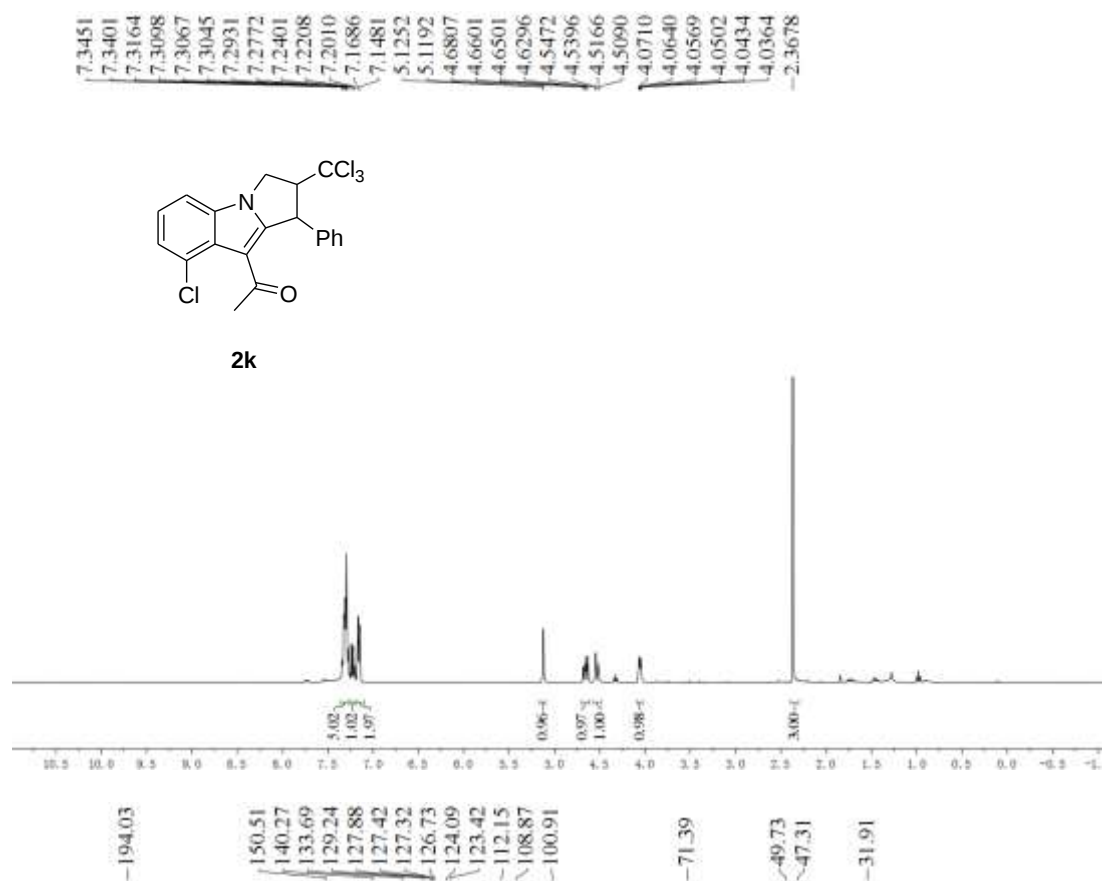


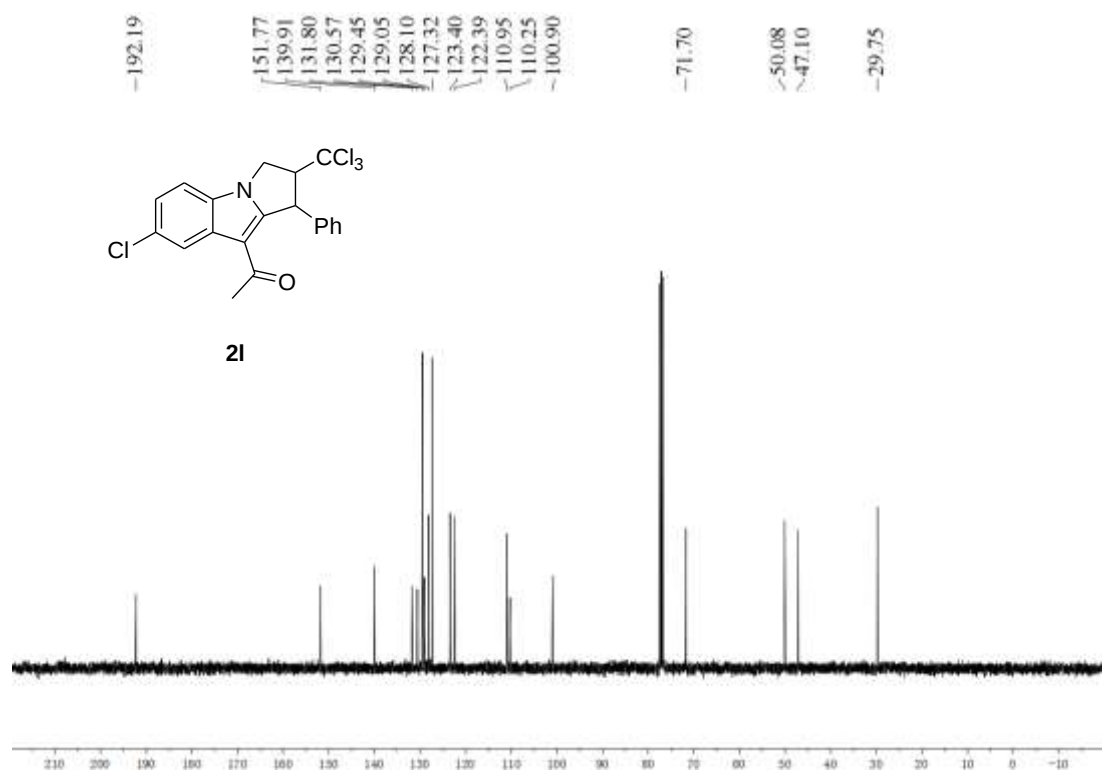
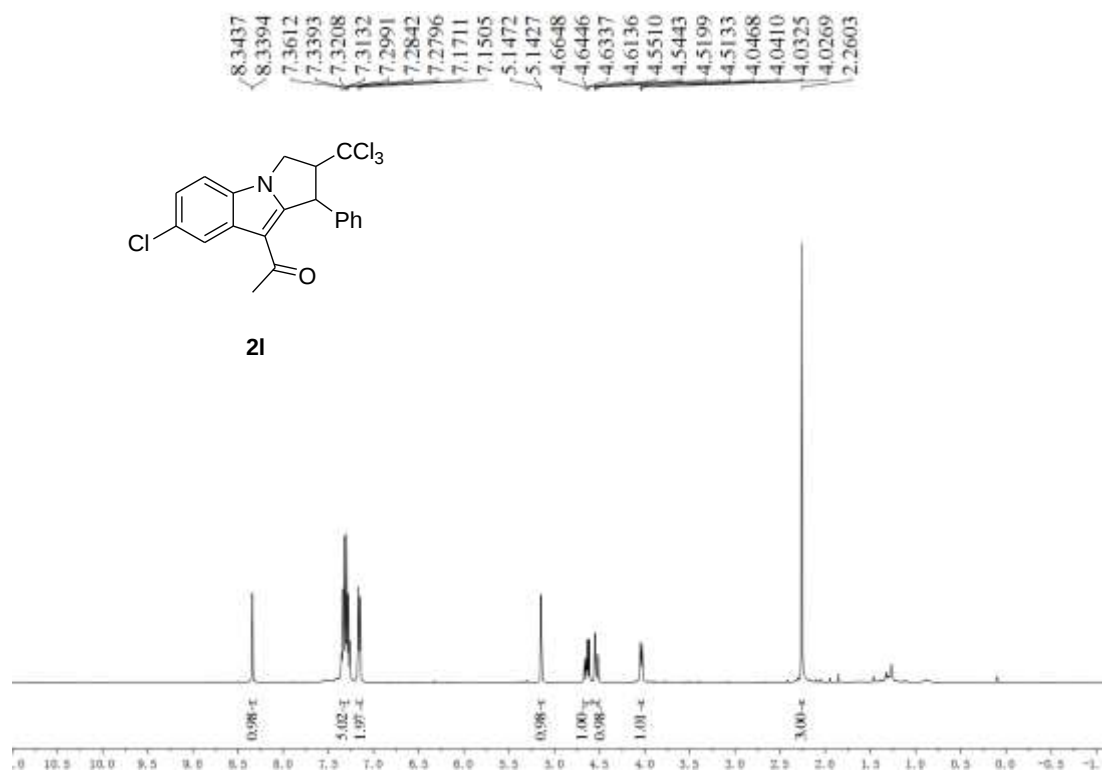
2h

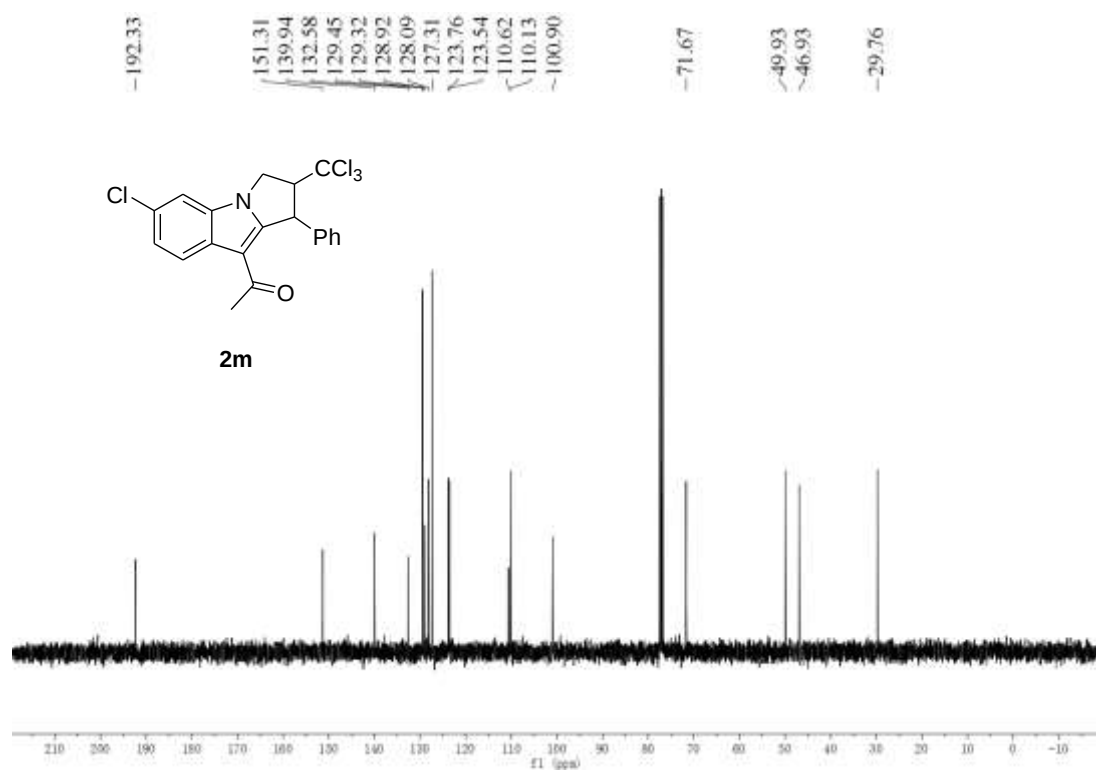
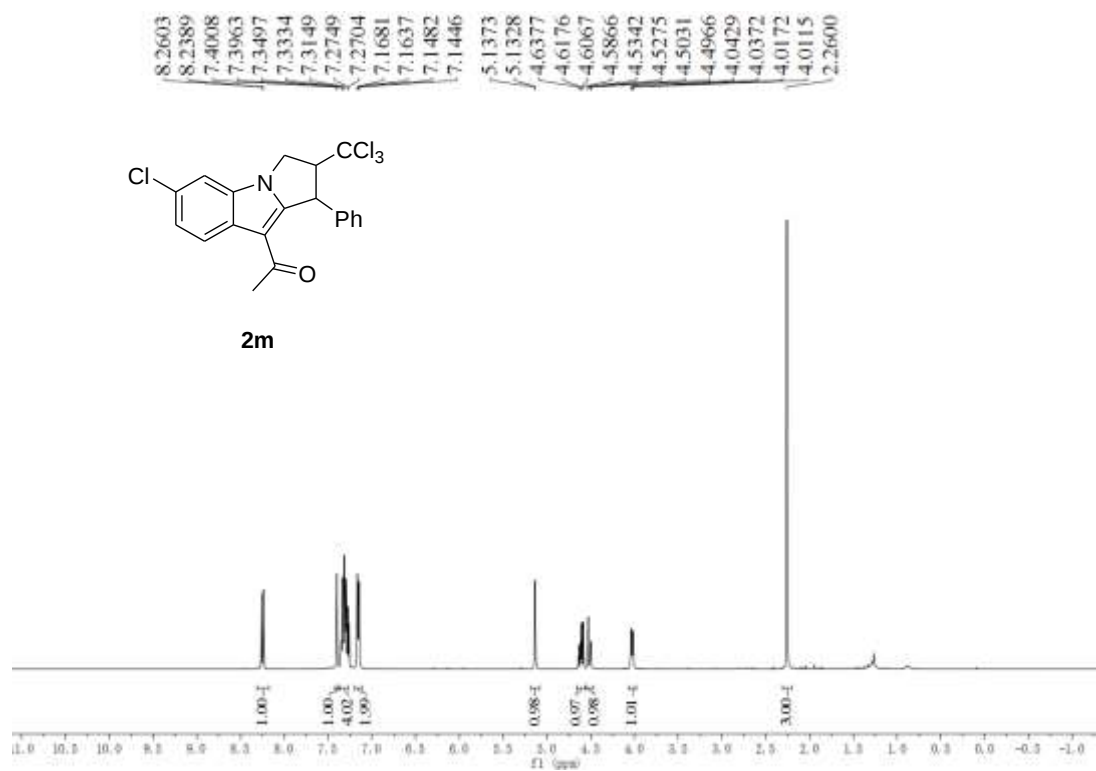


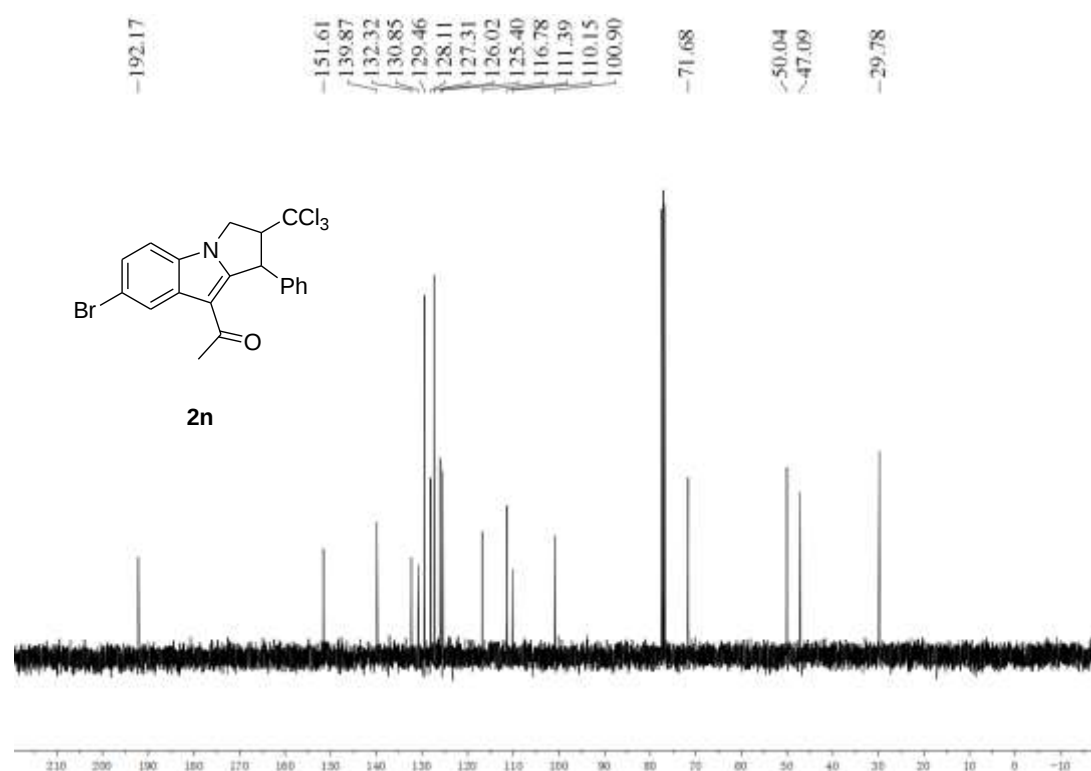
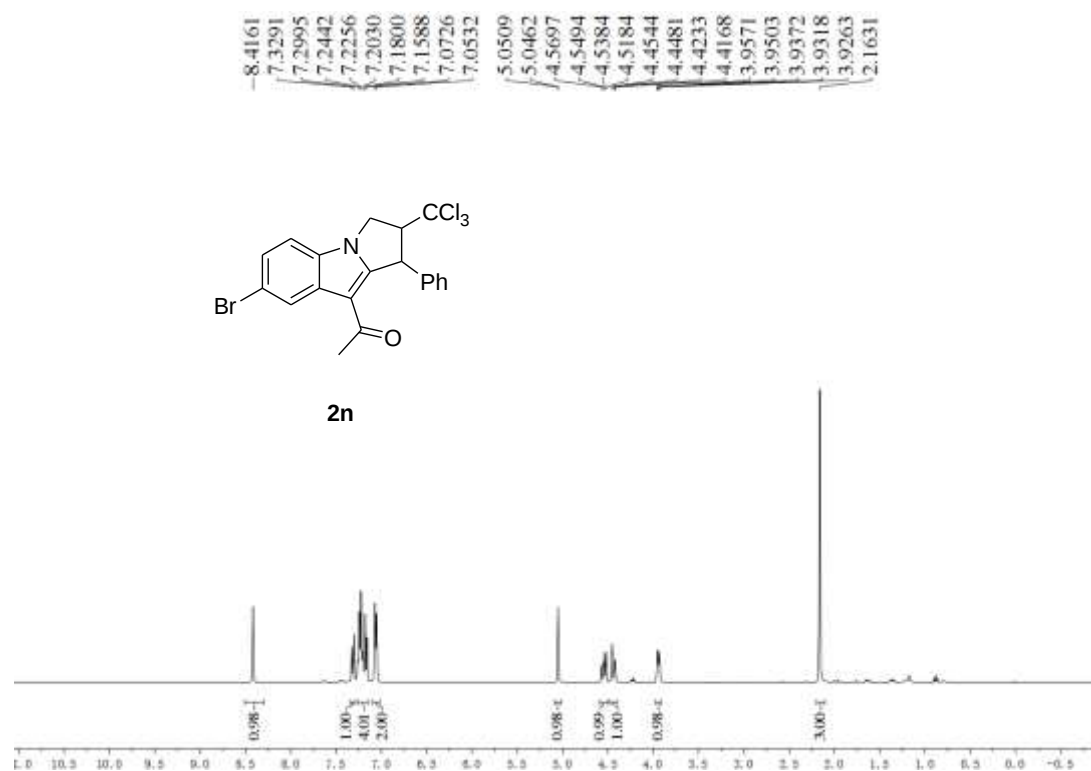


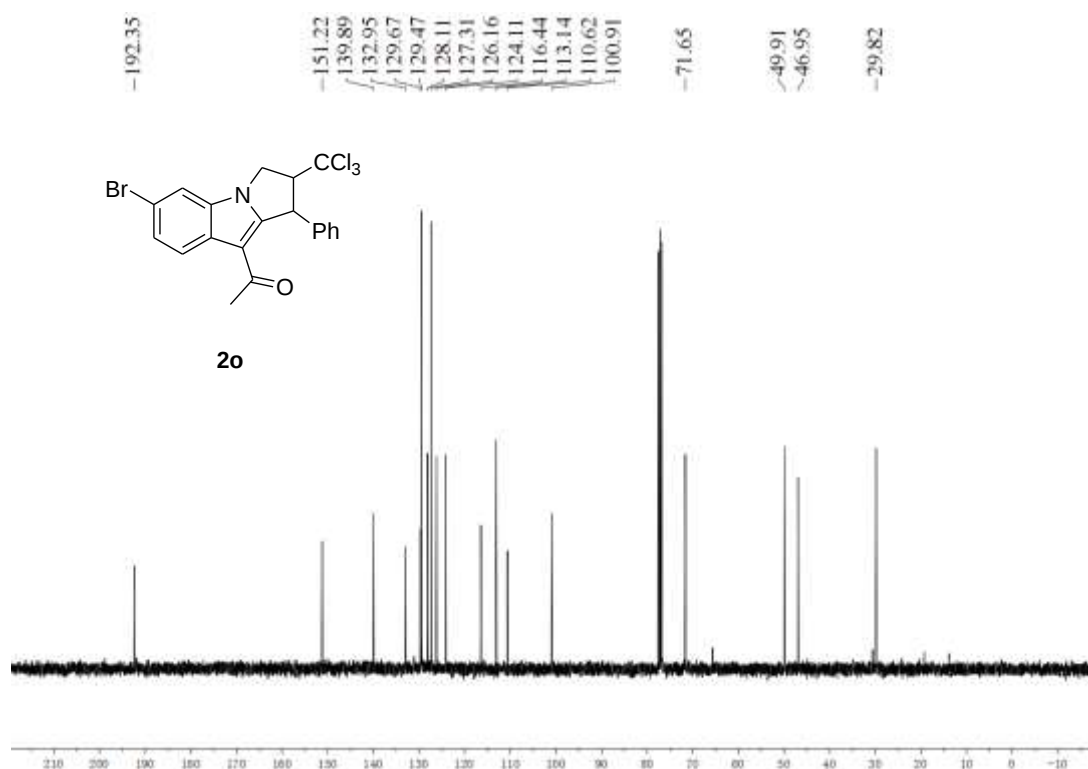
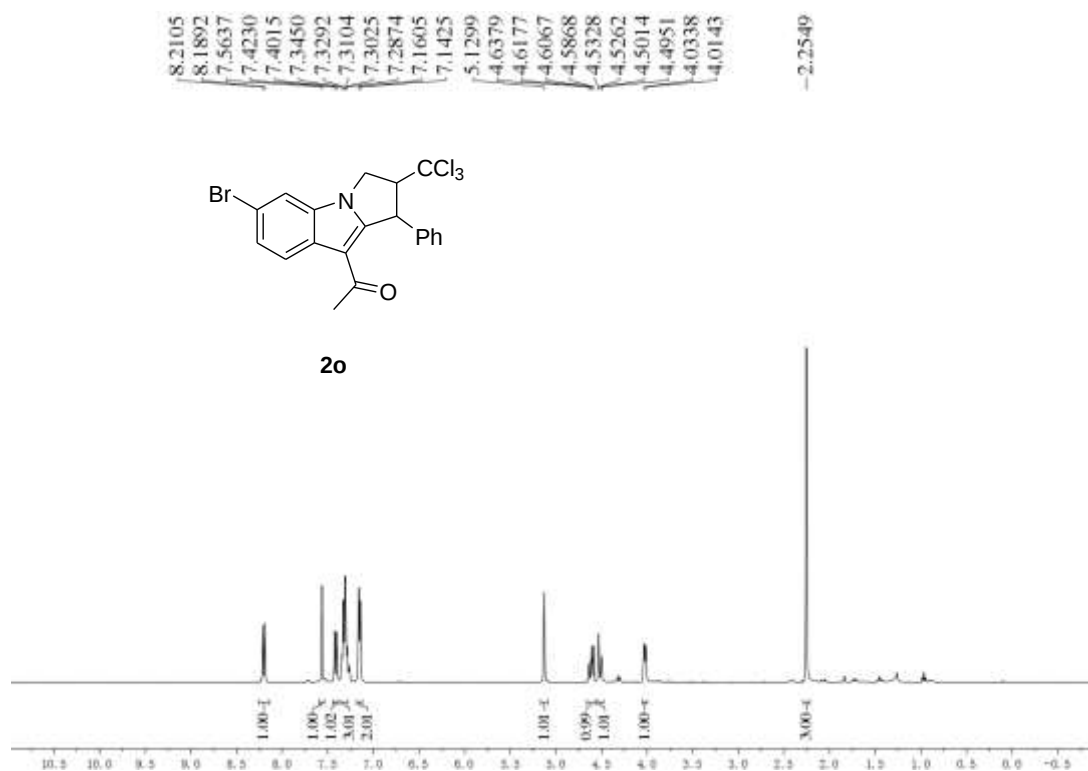


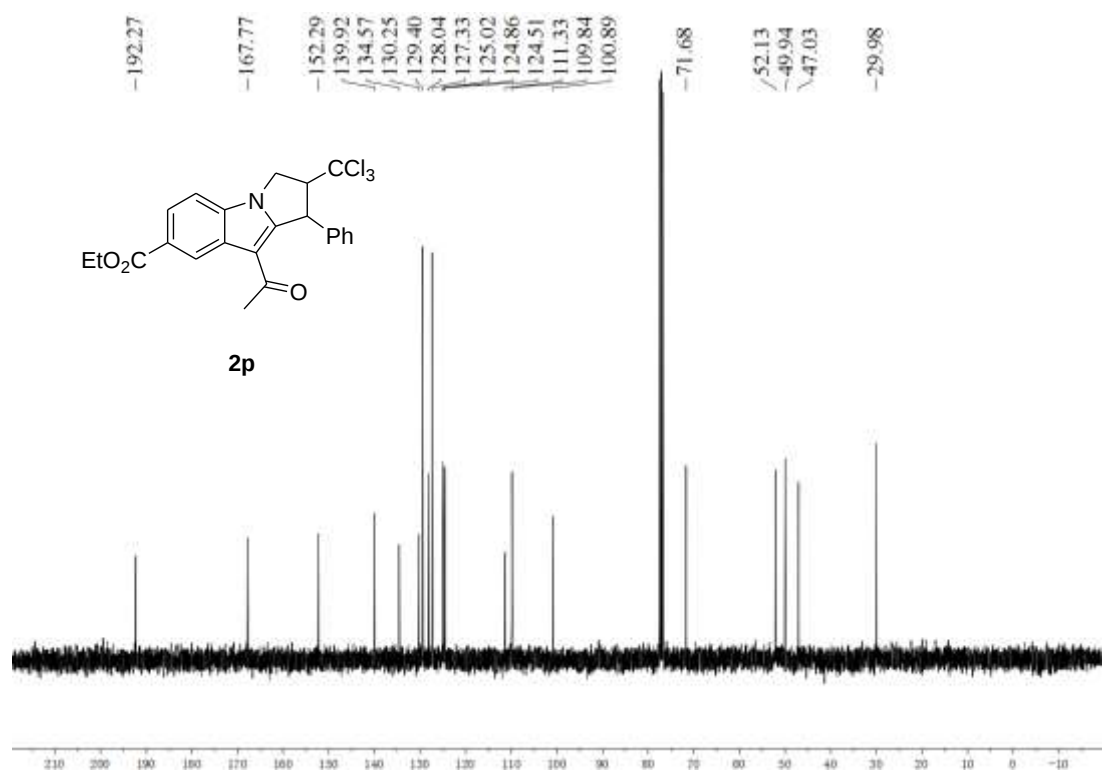
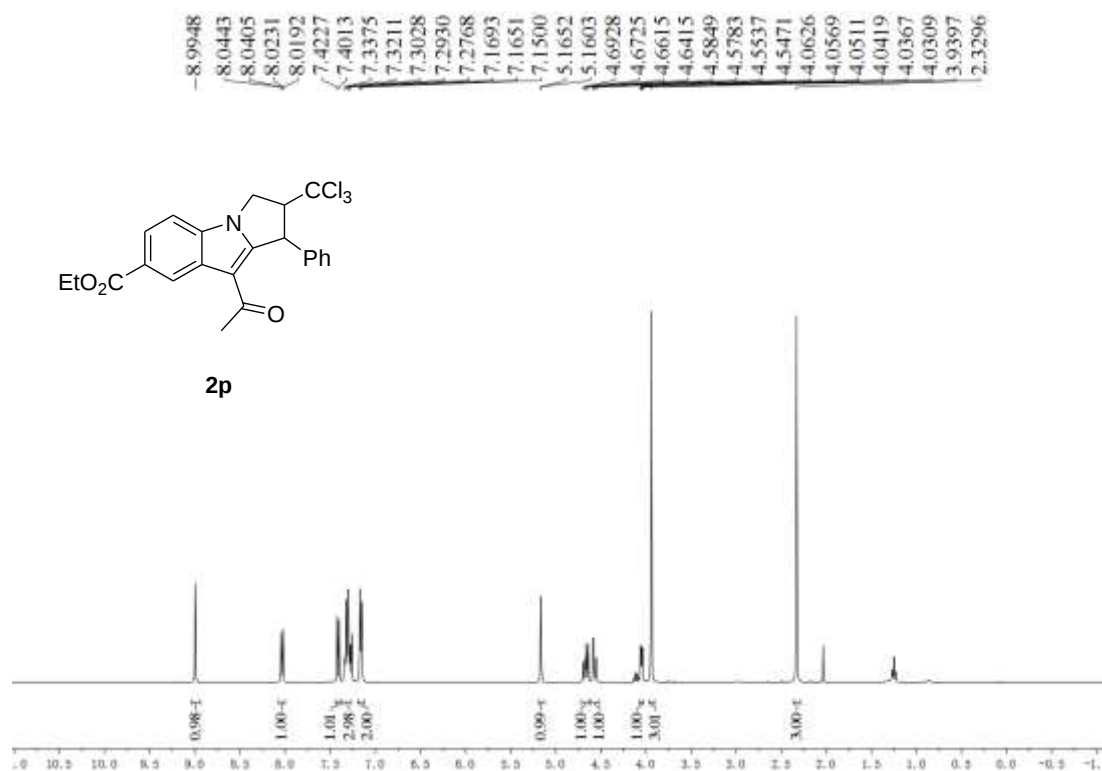


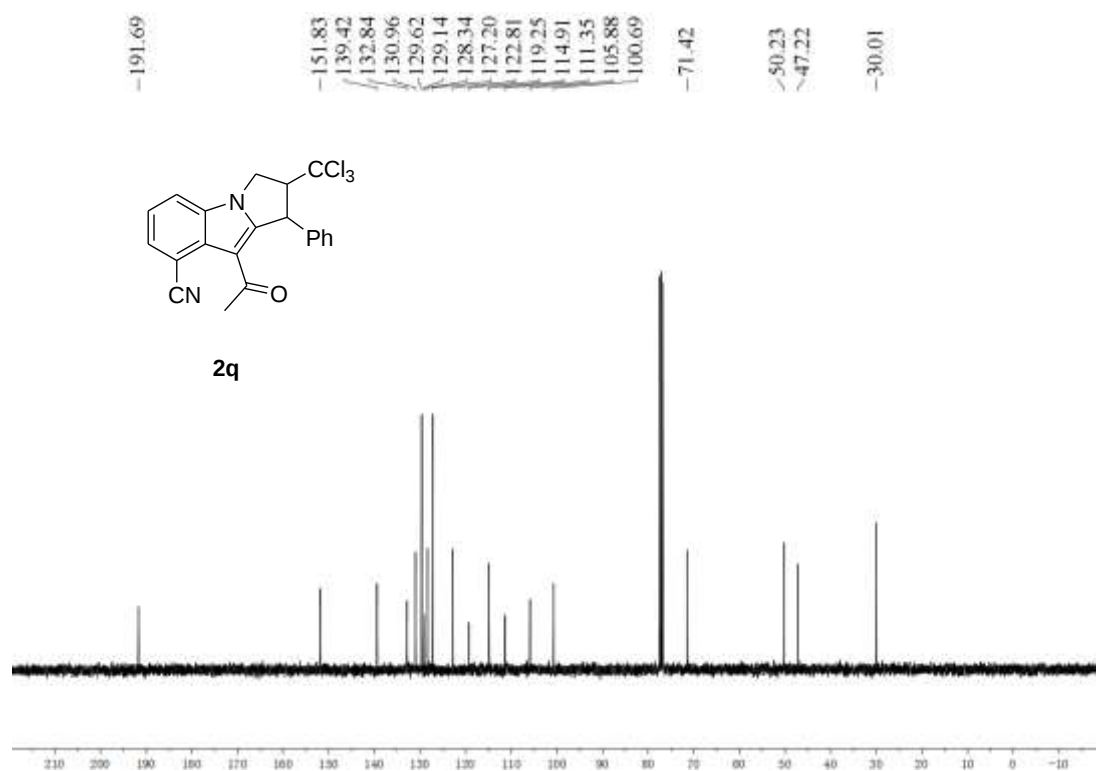
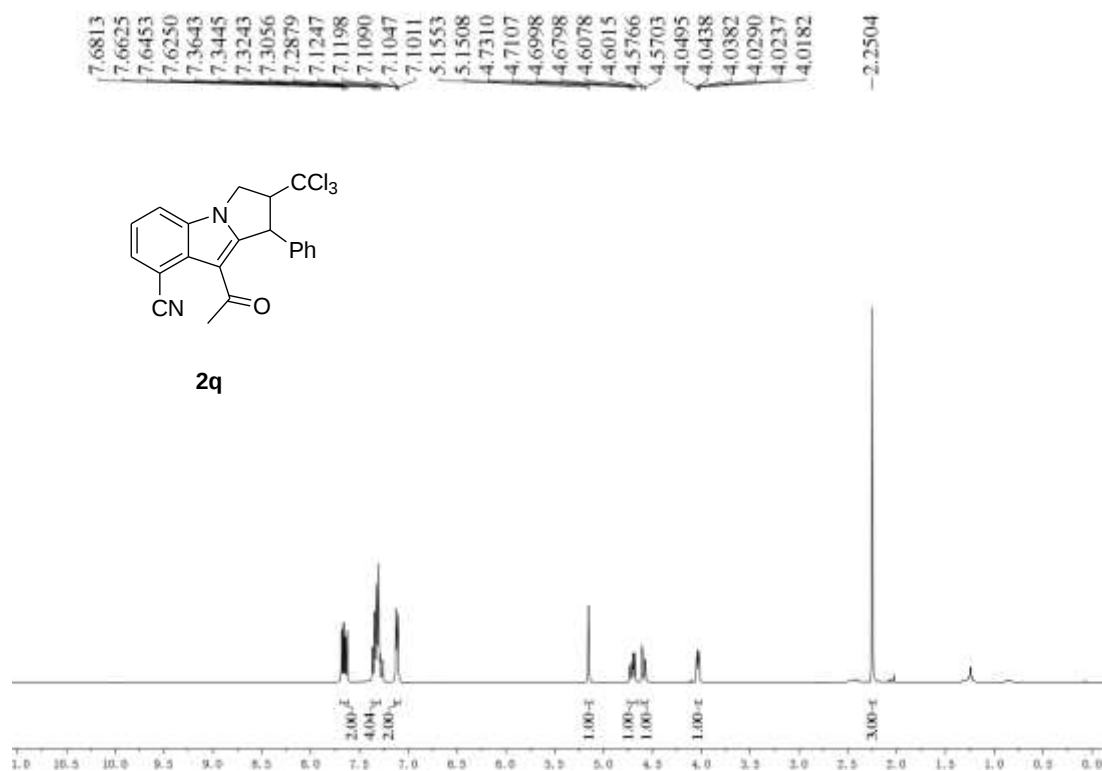


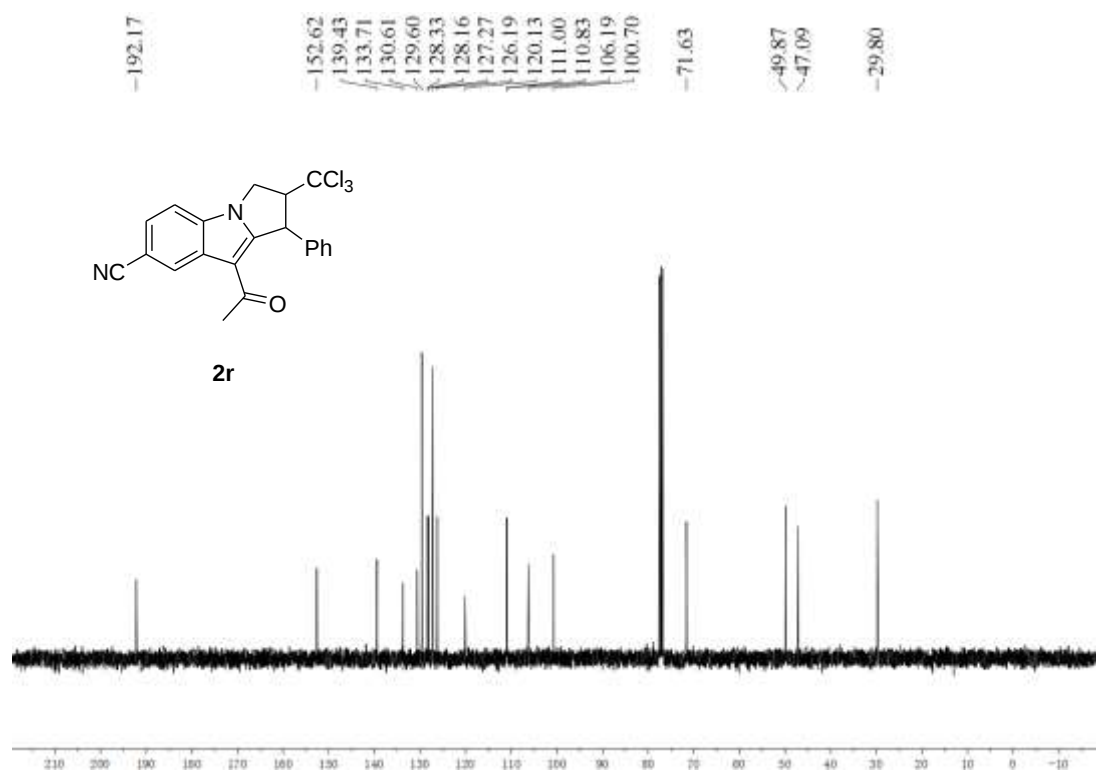
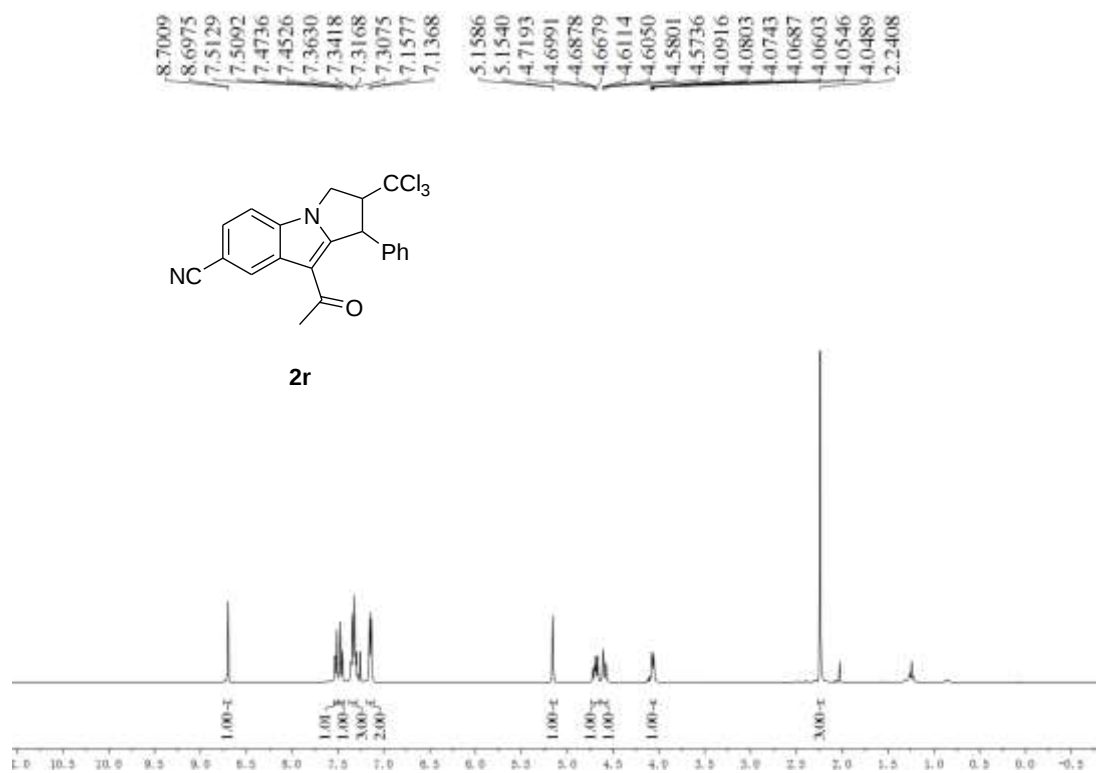


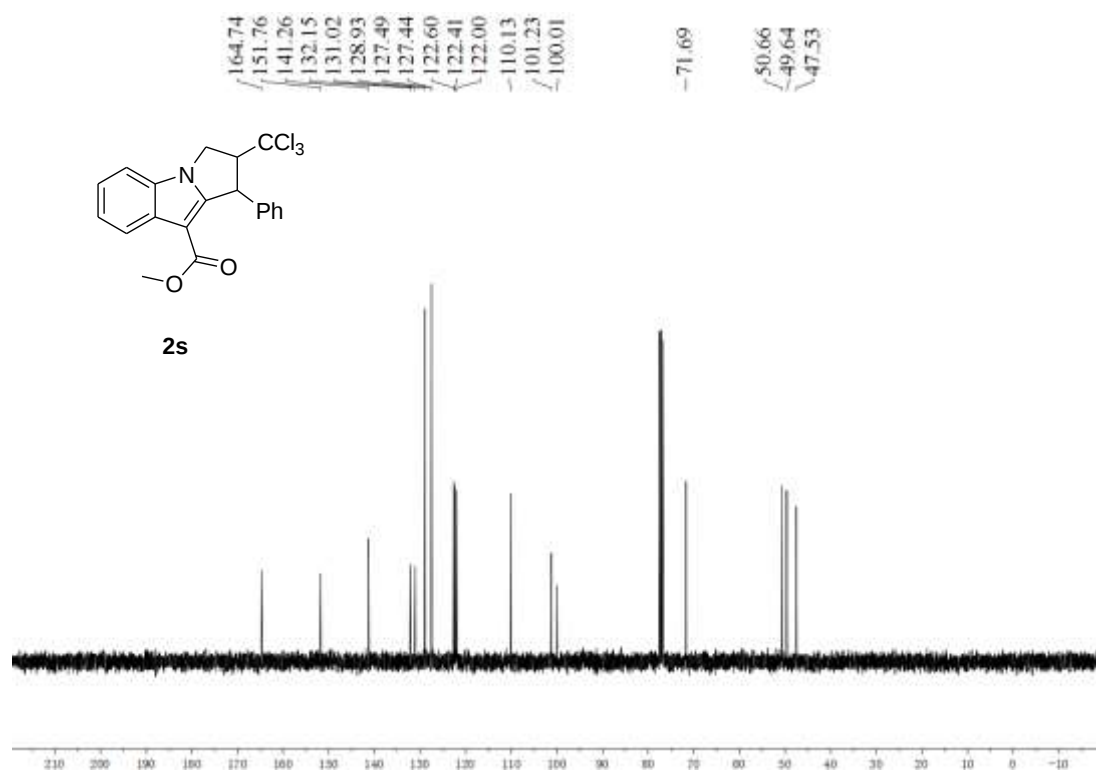
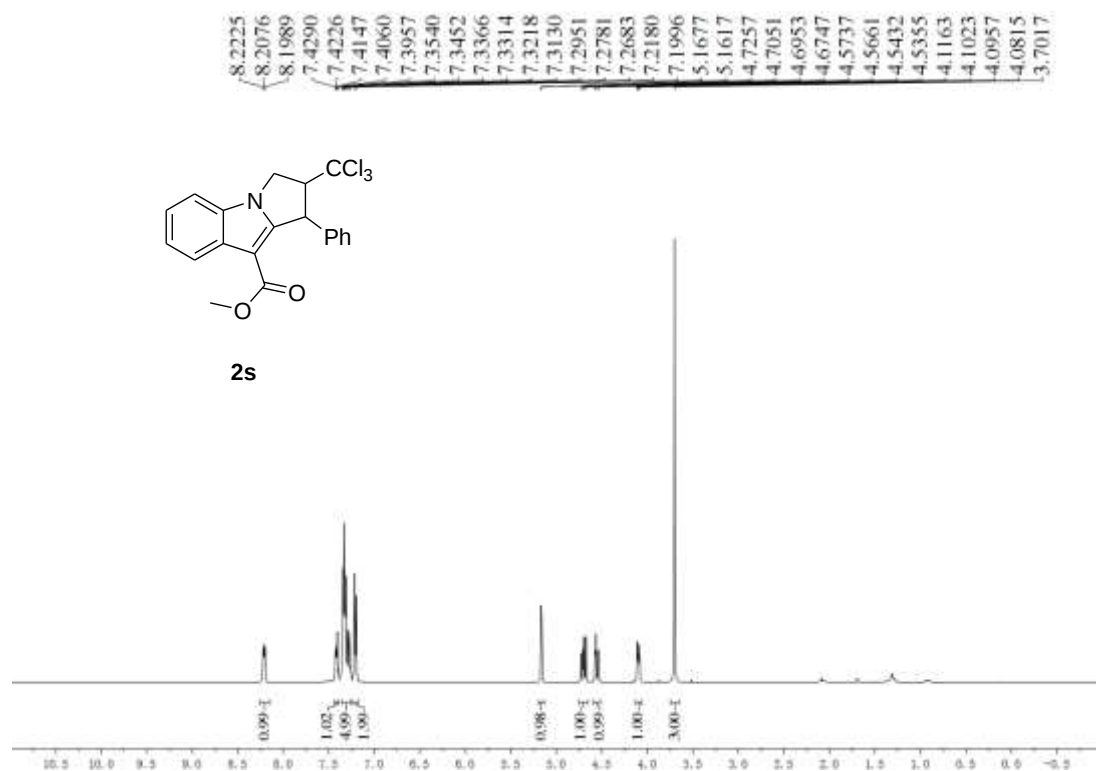


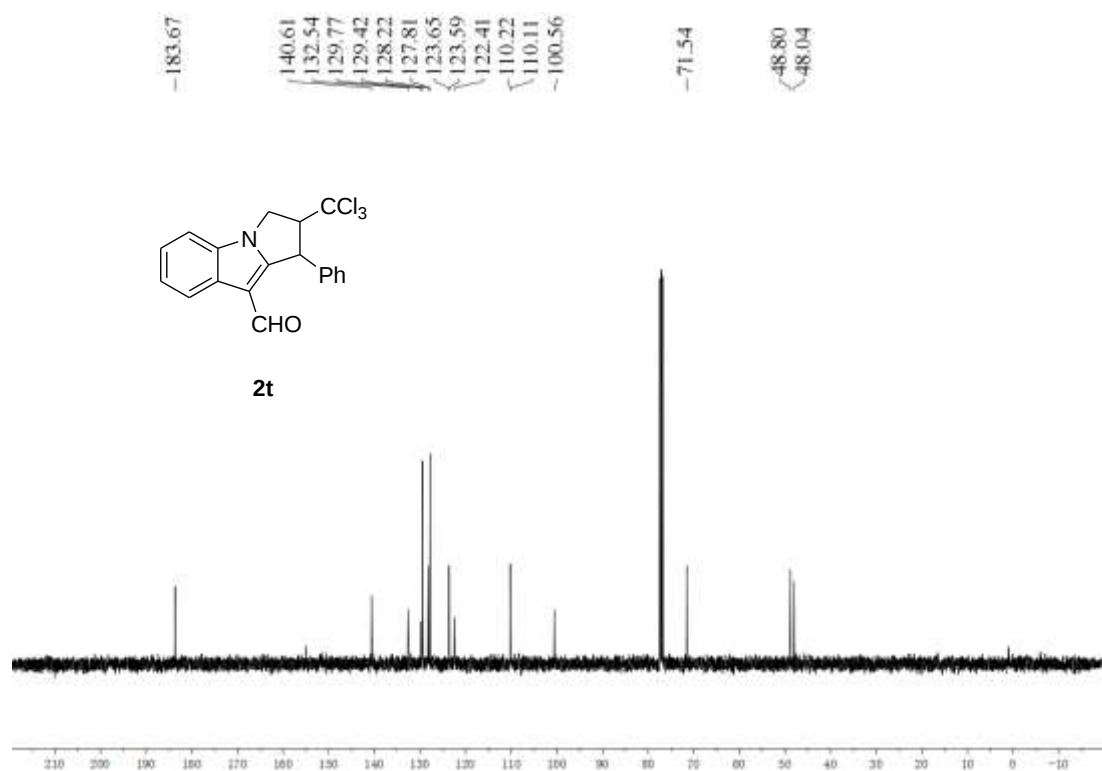
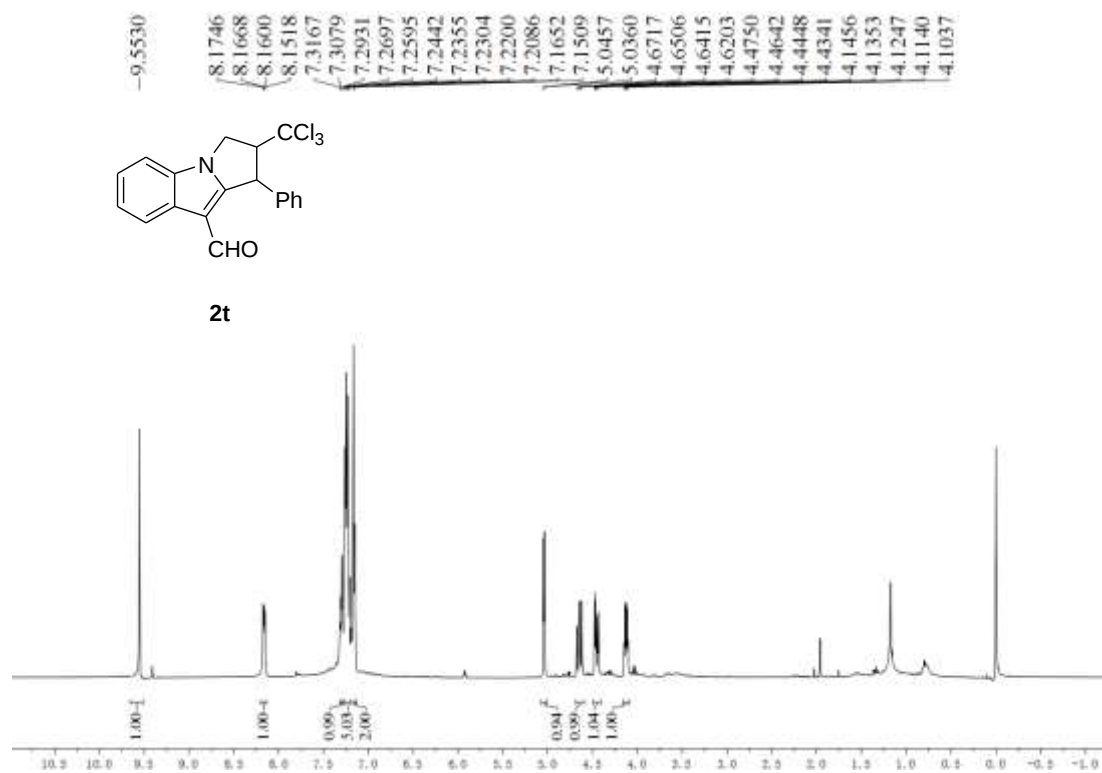


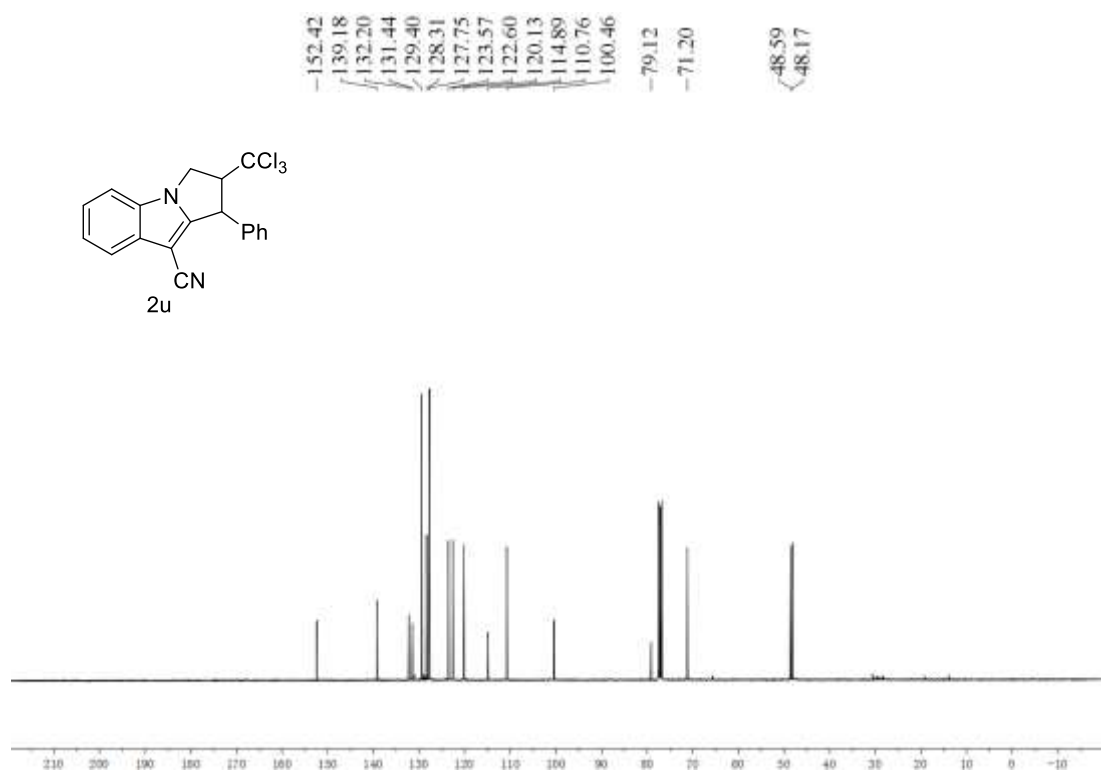
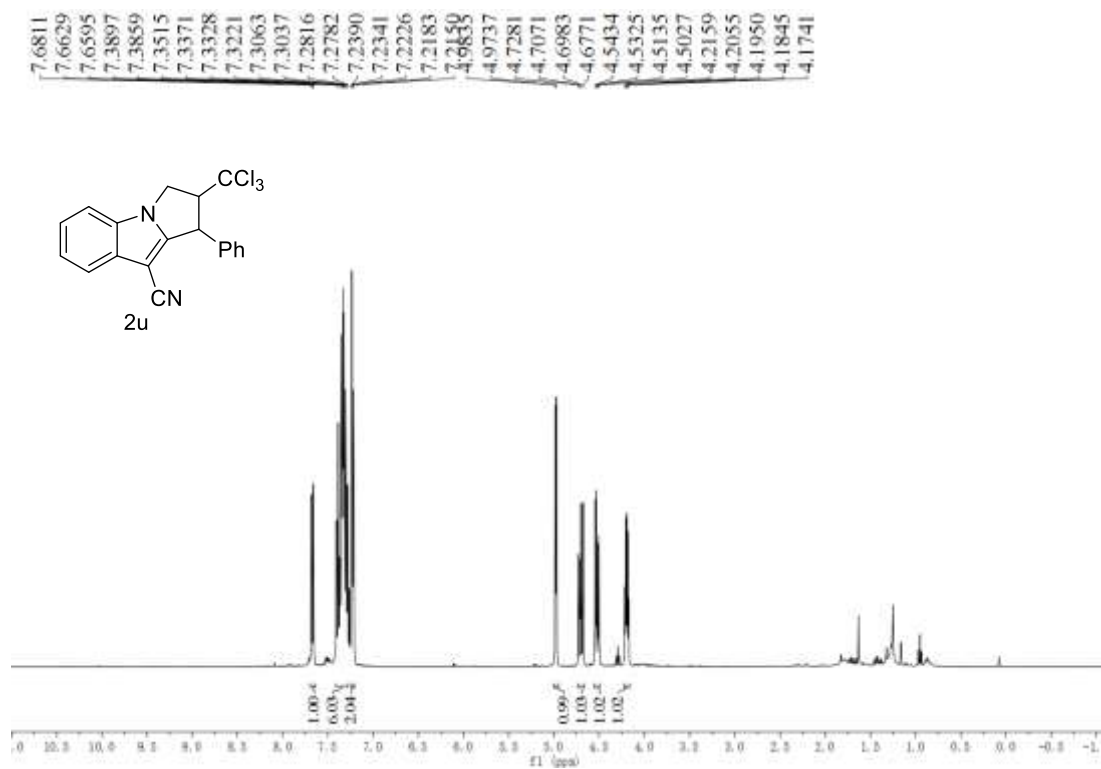


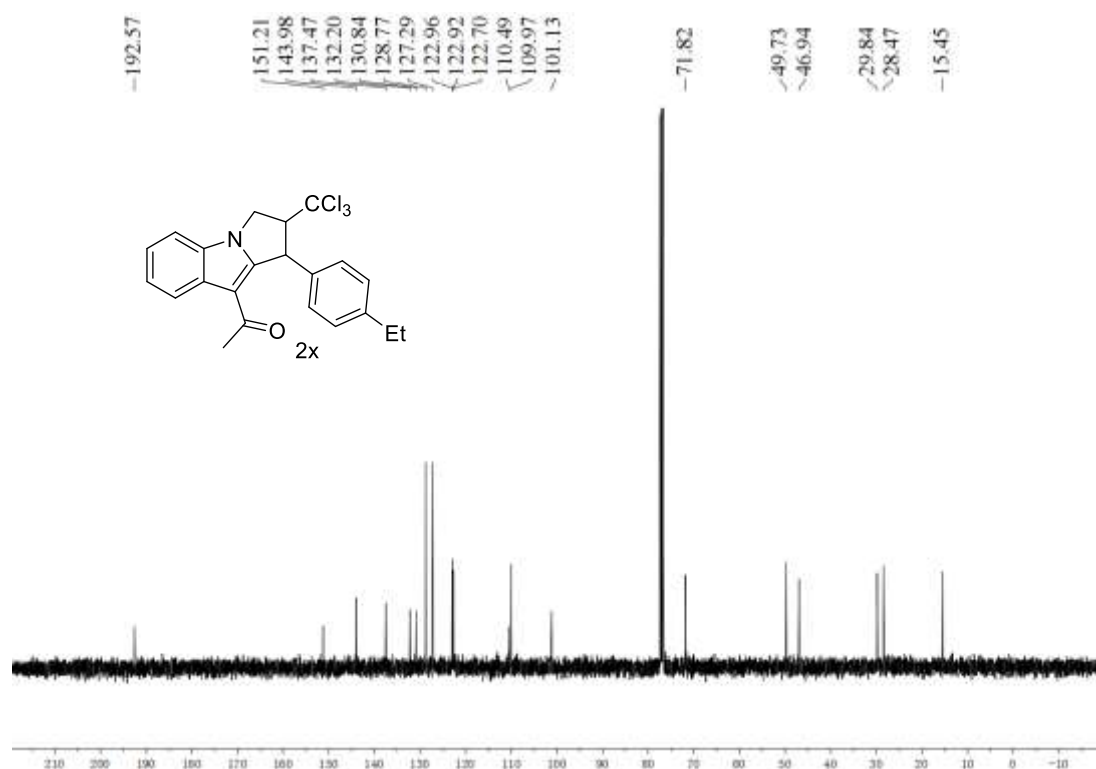
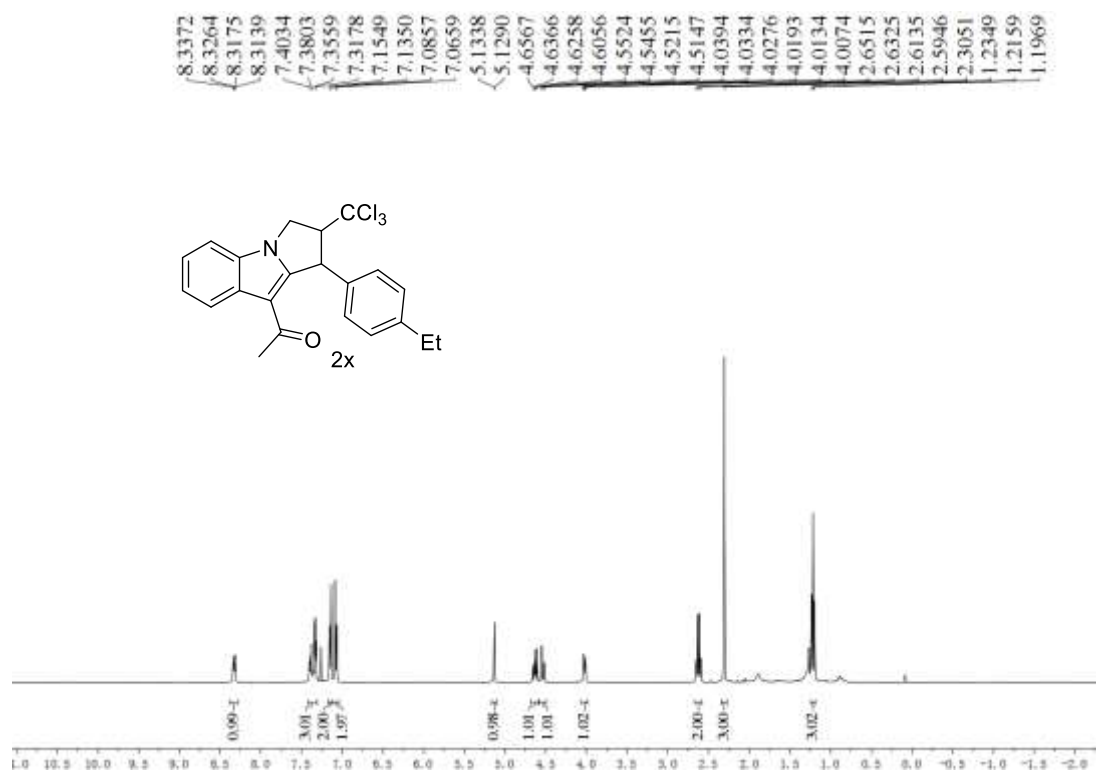


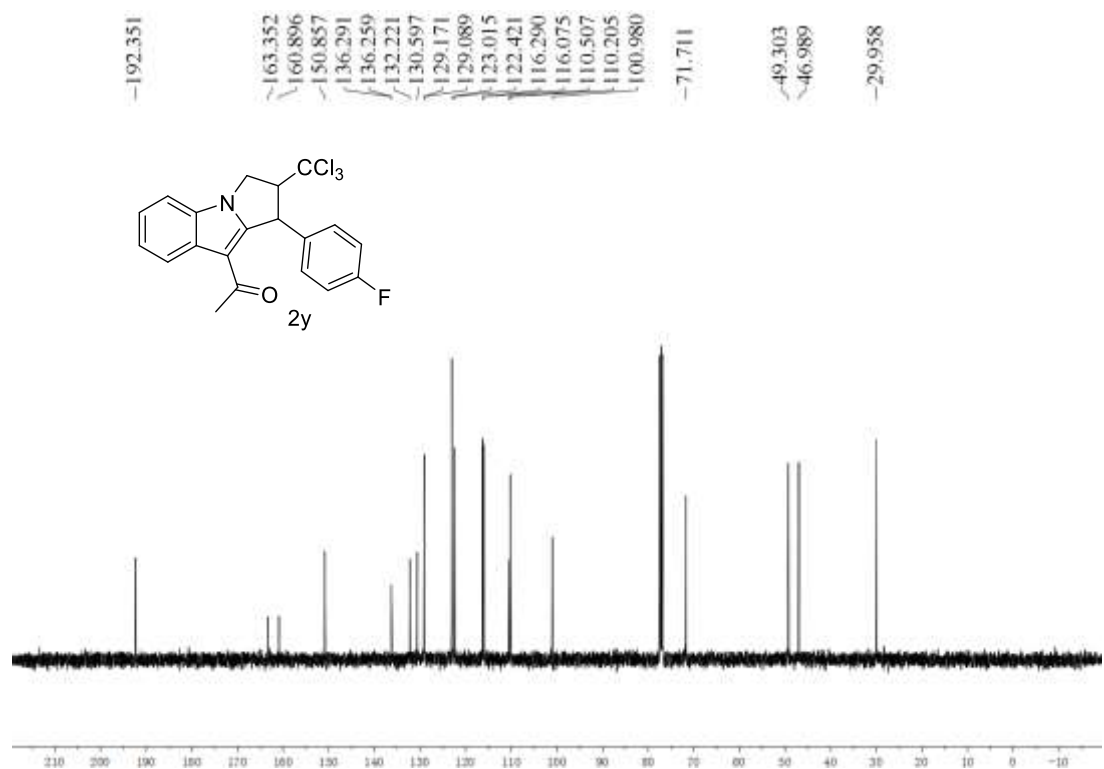
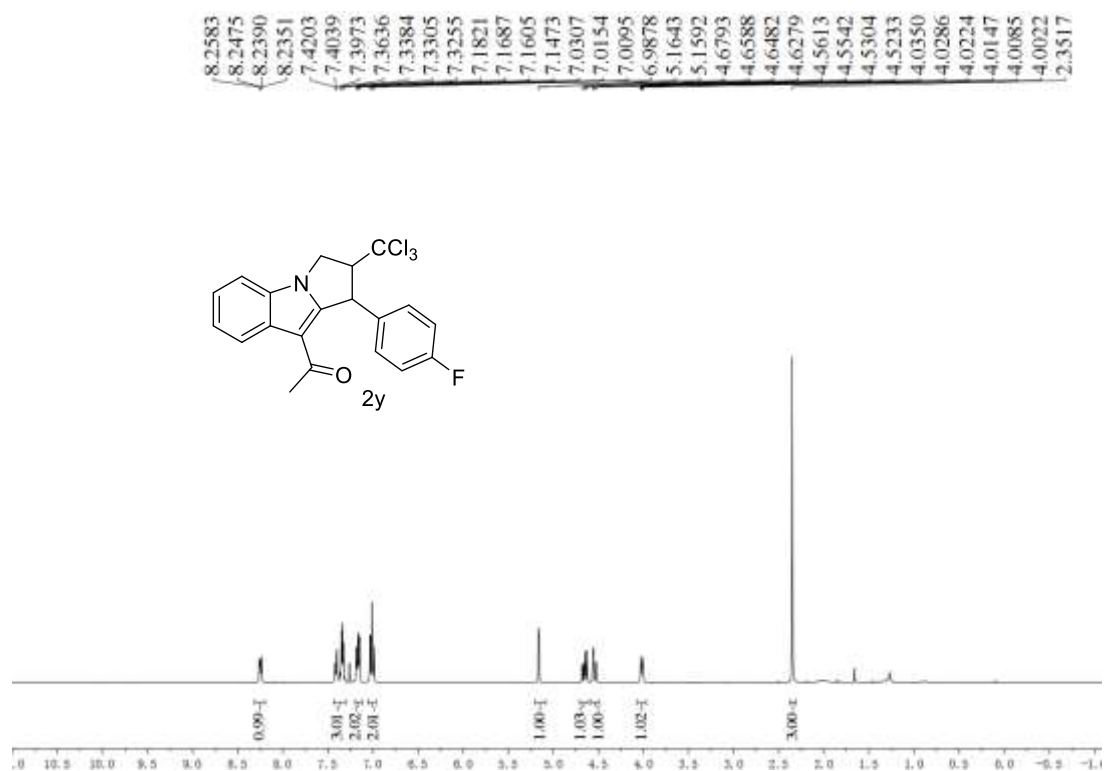


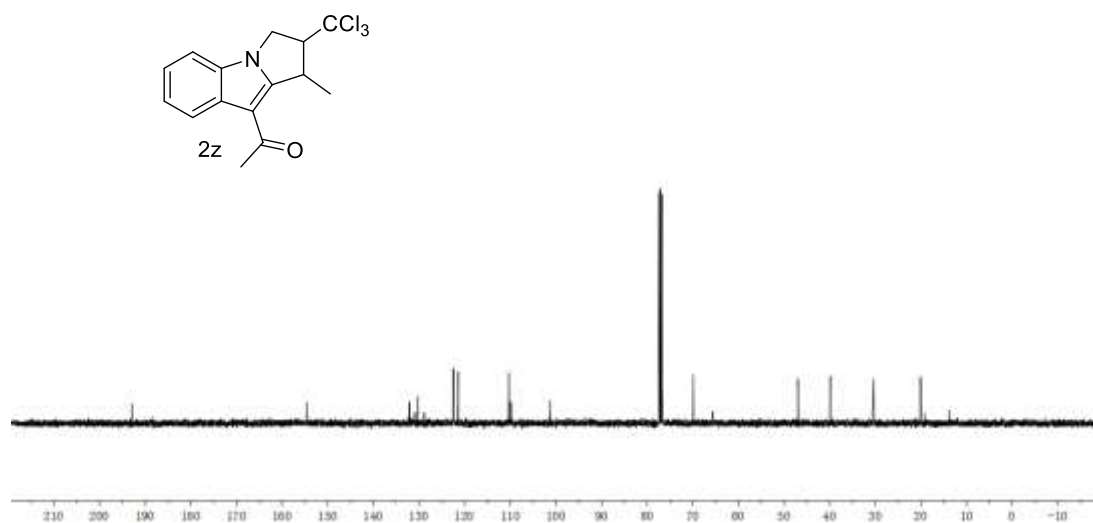
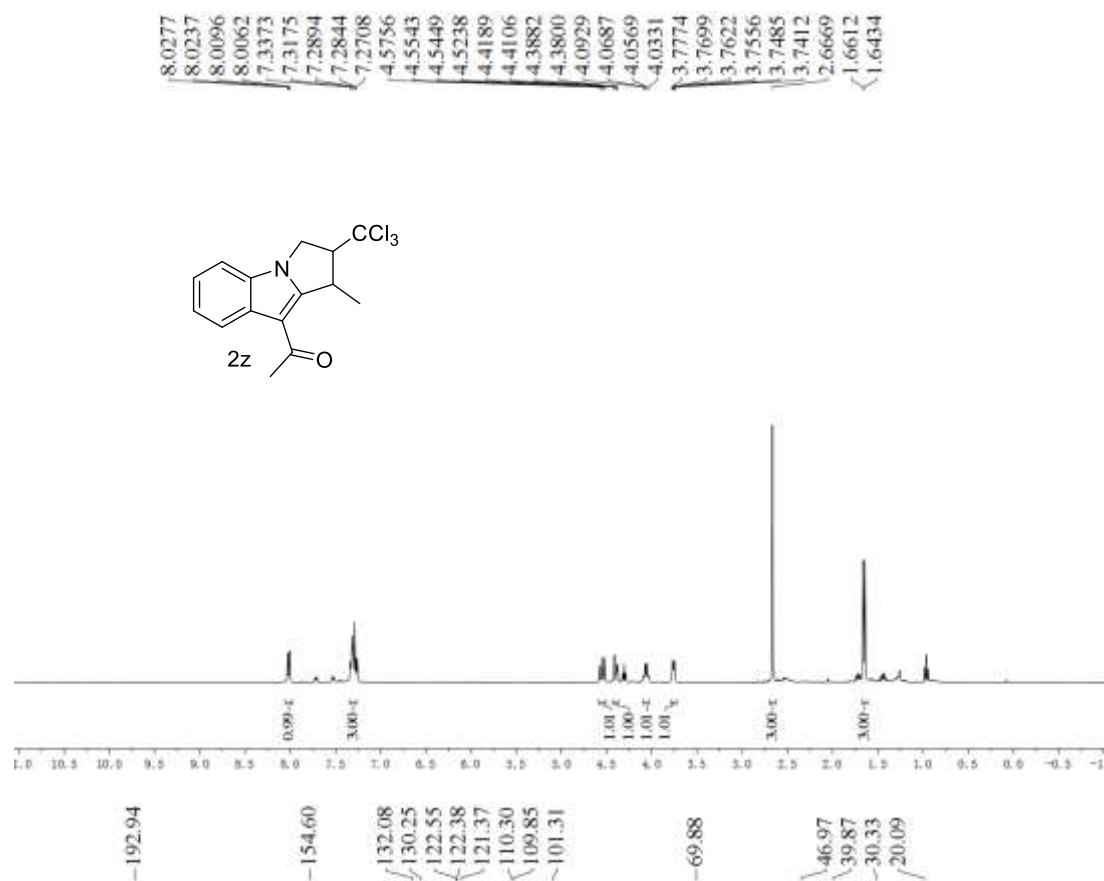


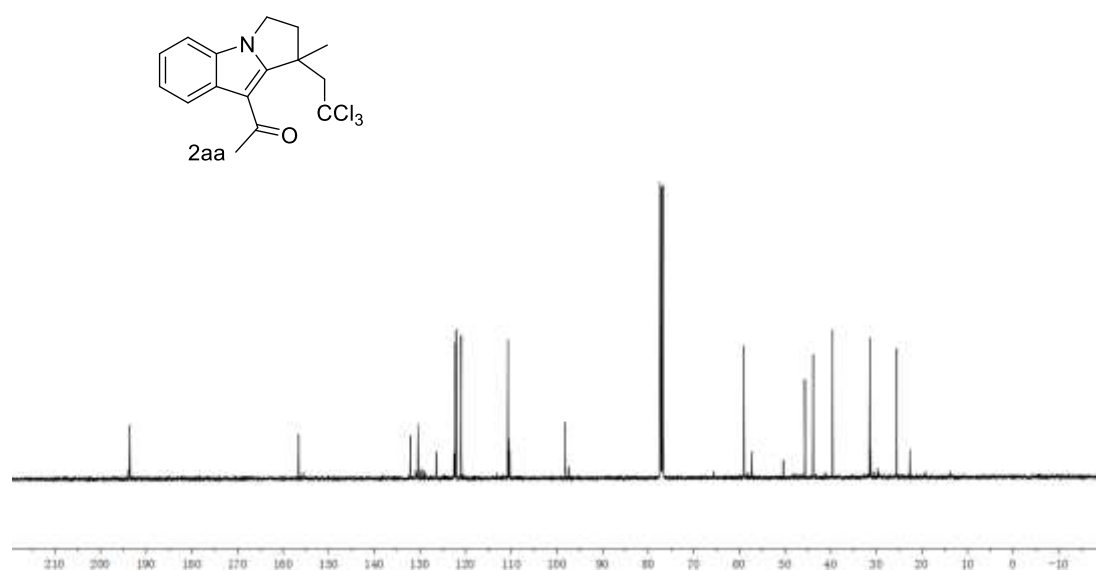
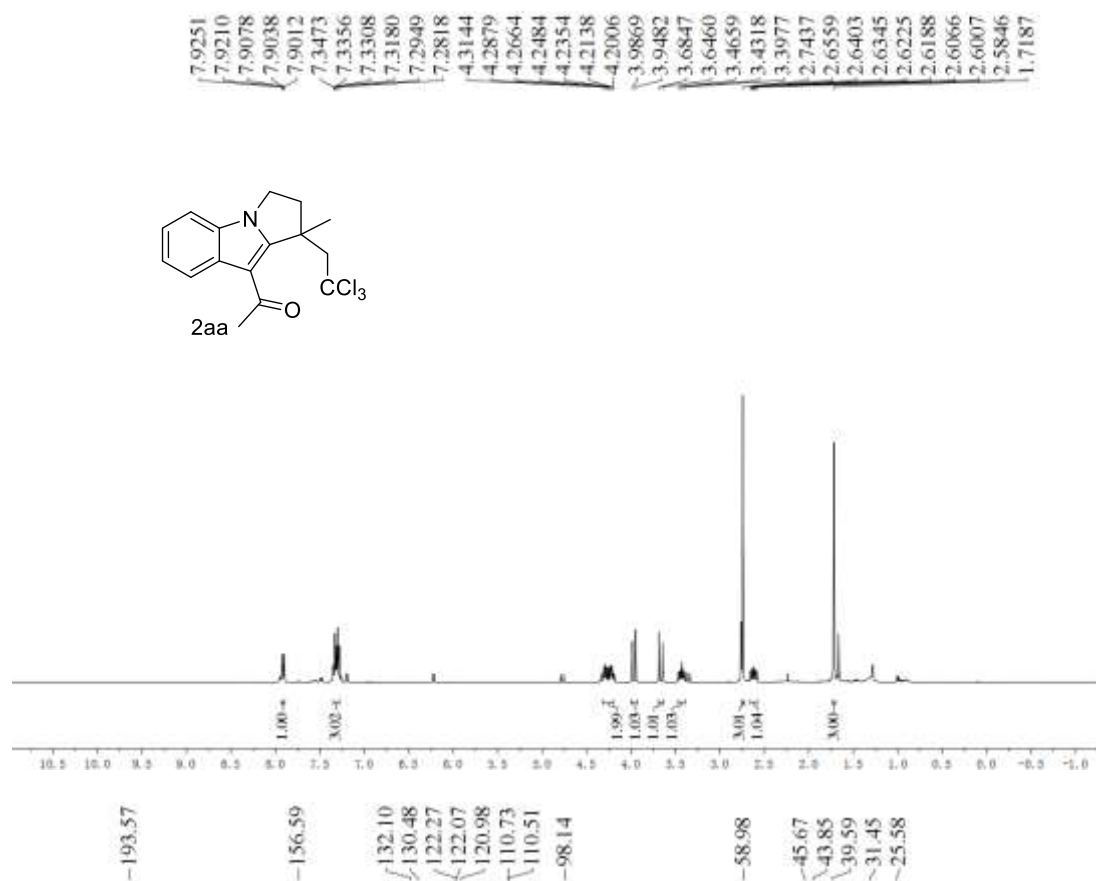


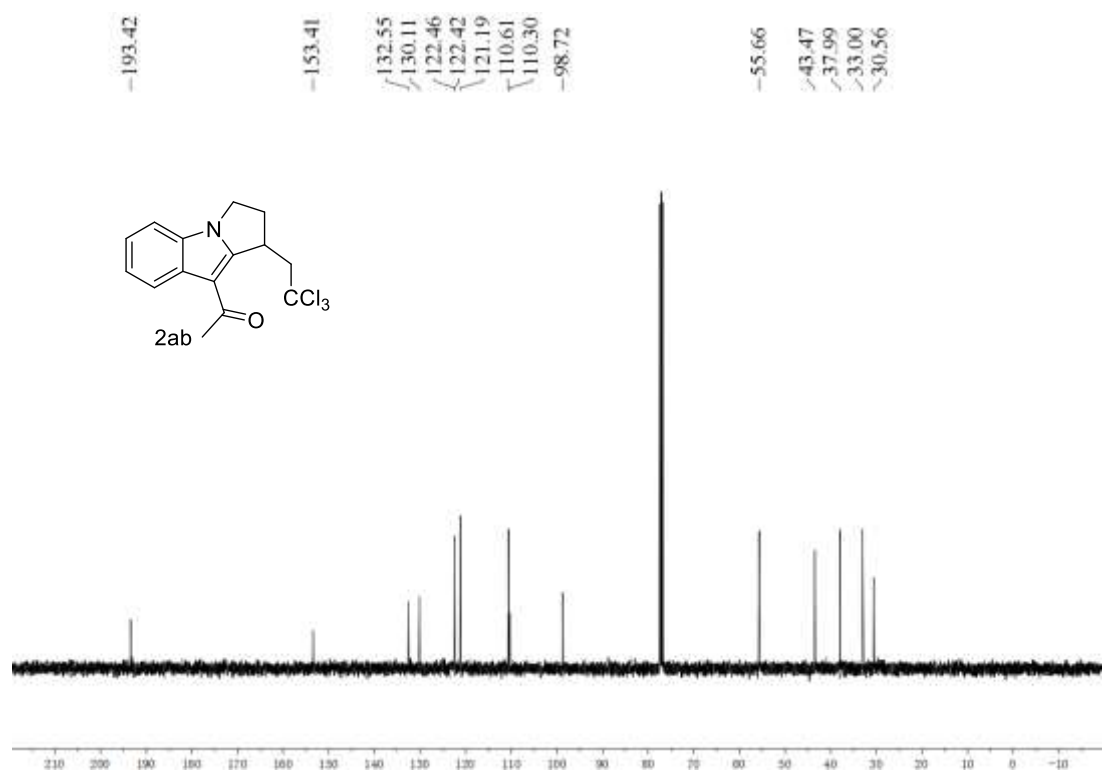
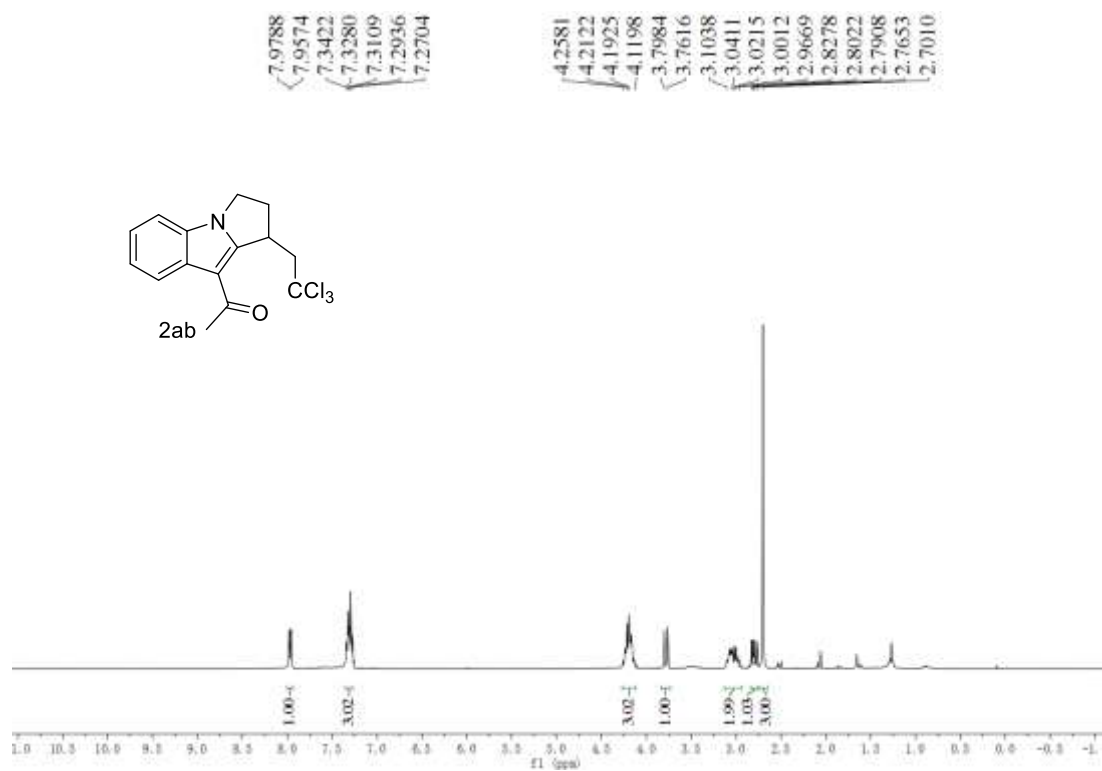


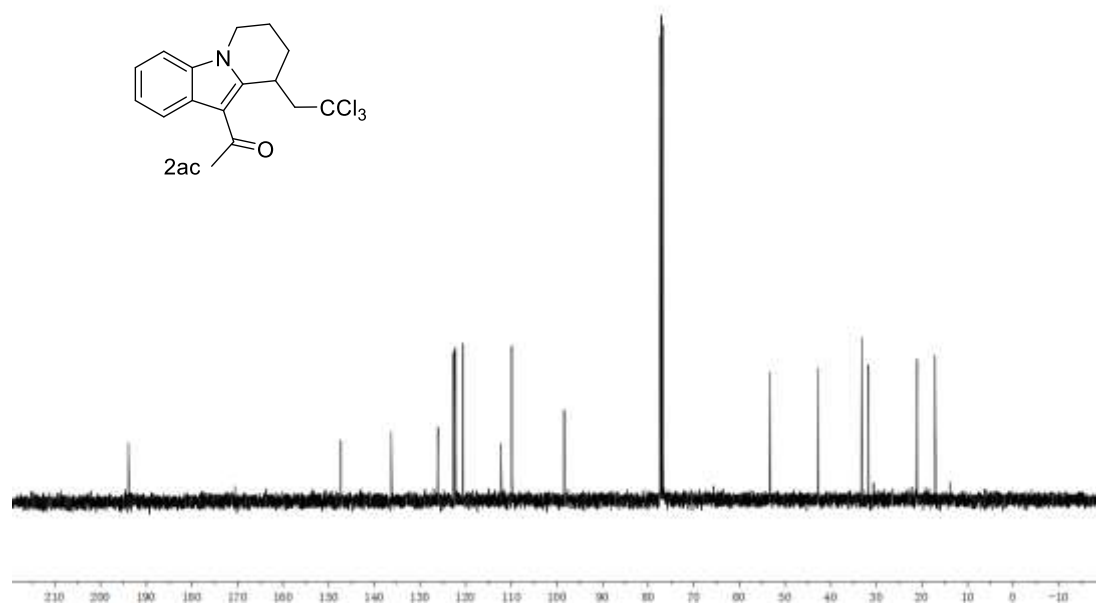
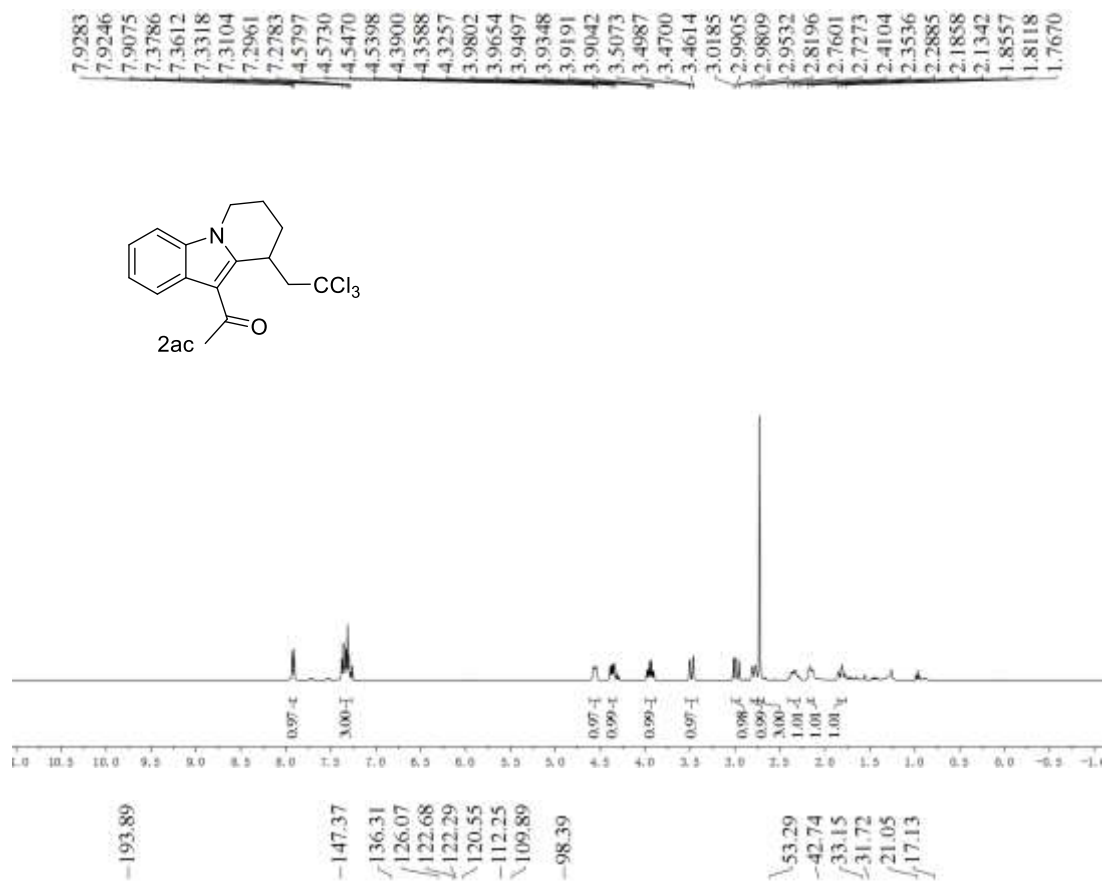


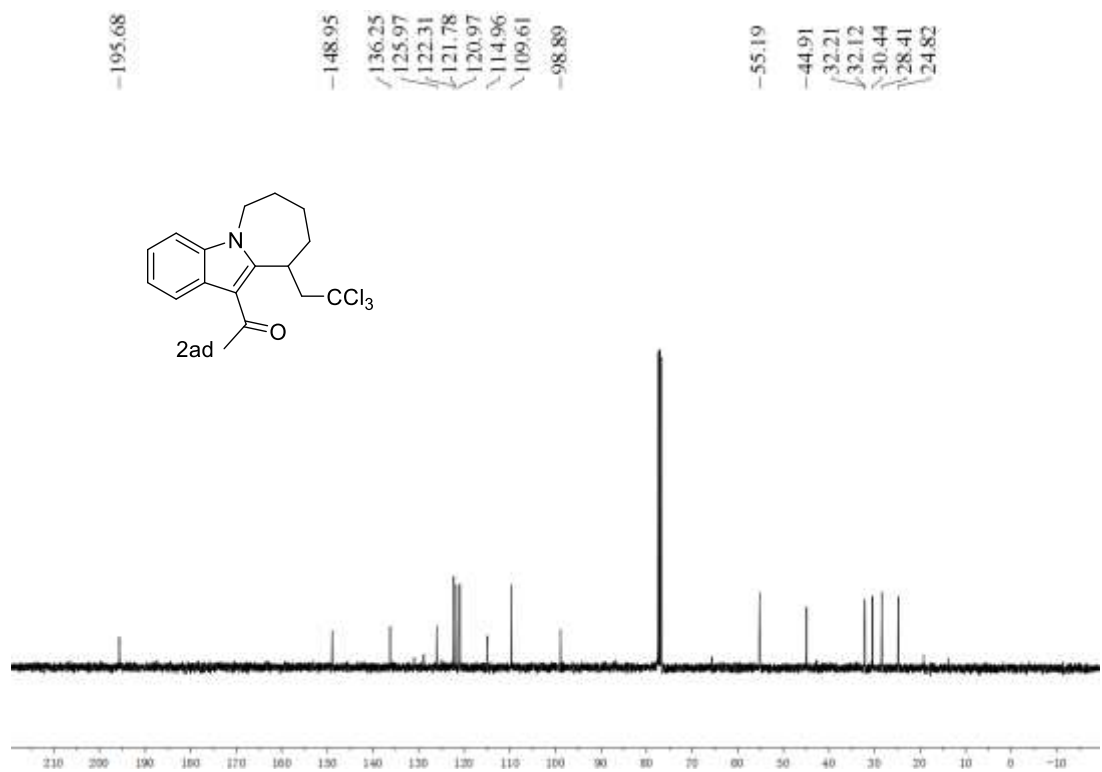
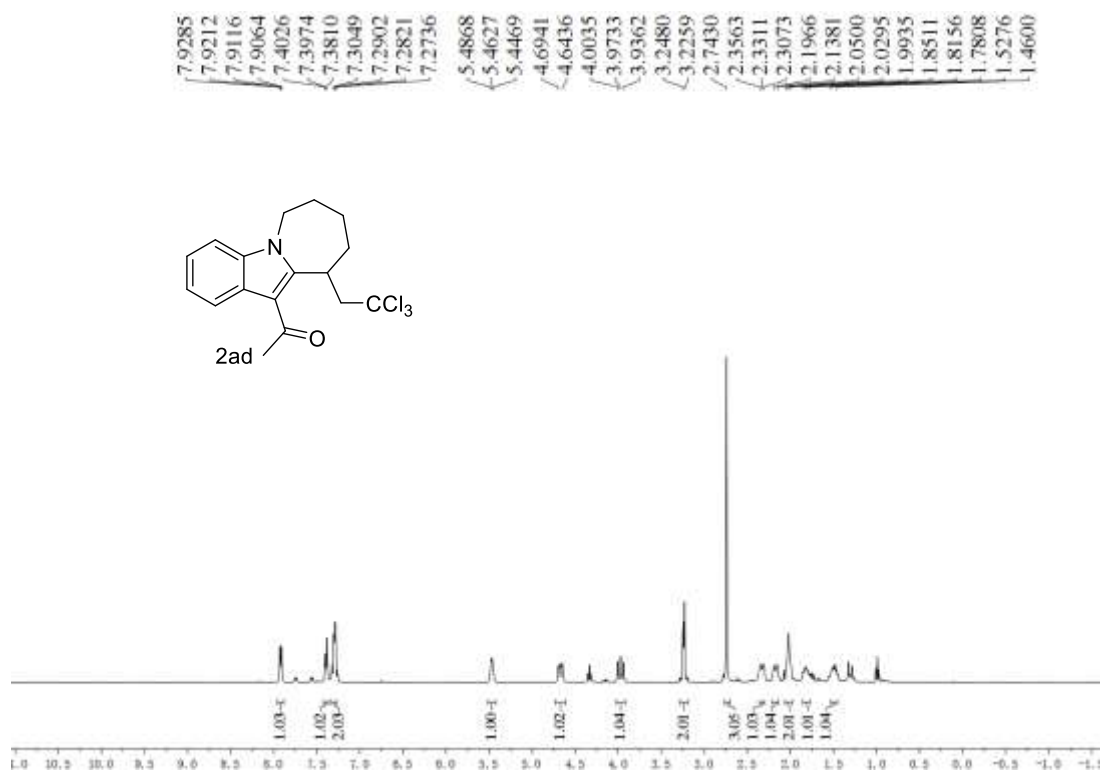


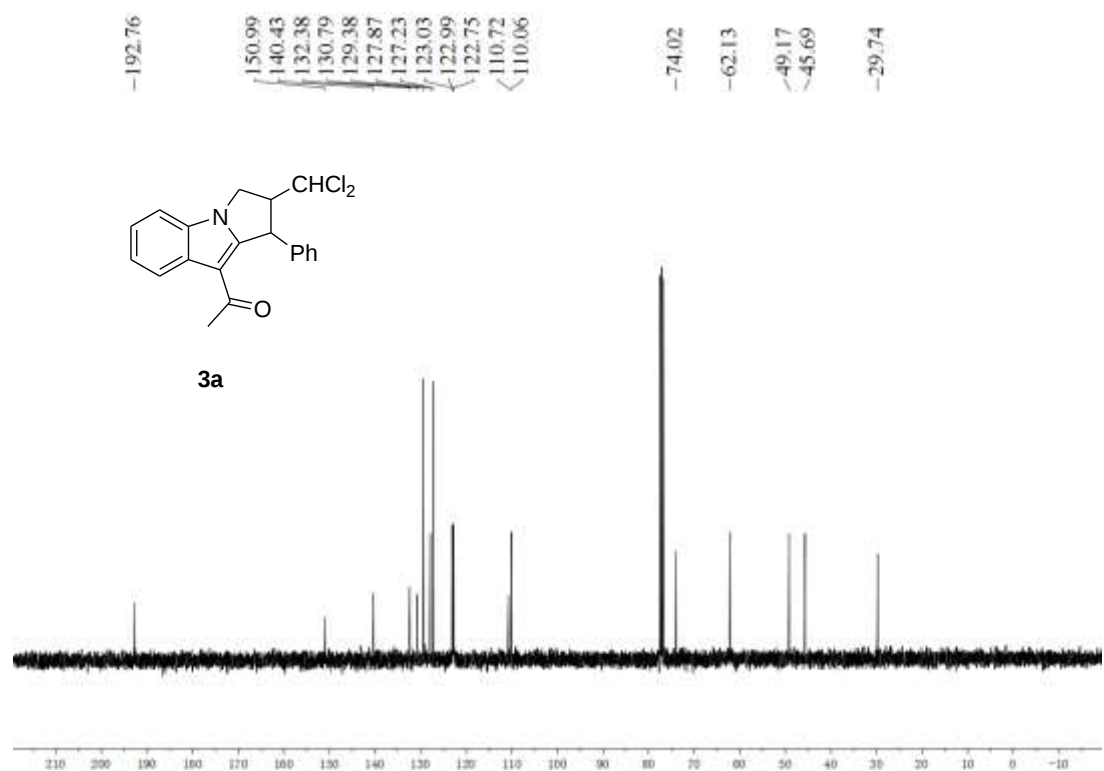
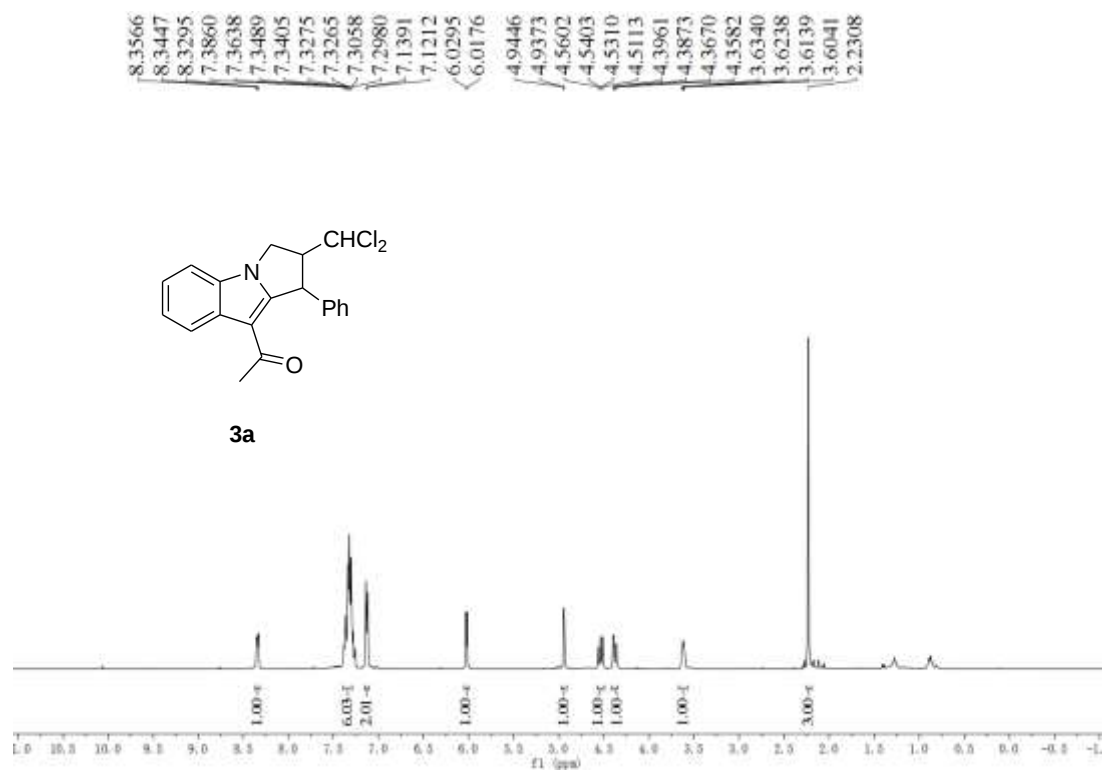


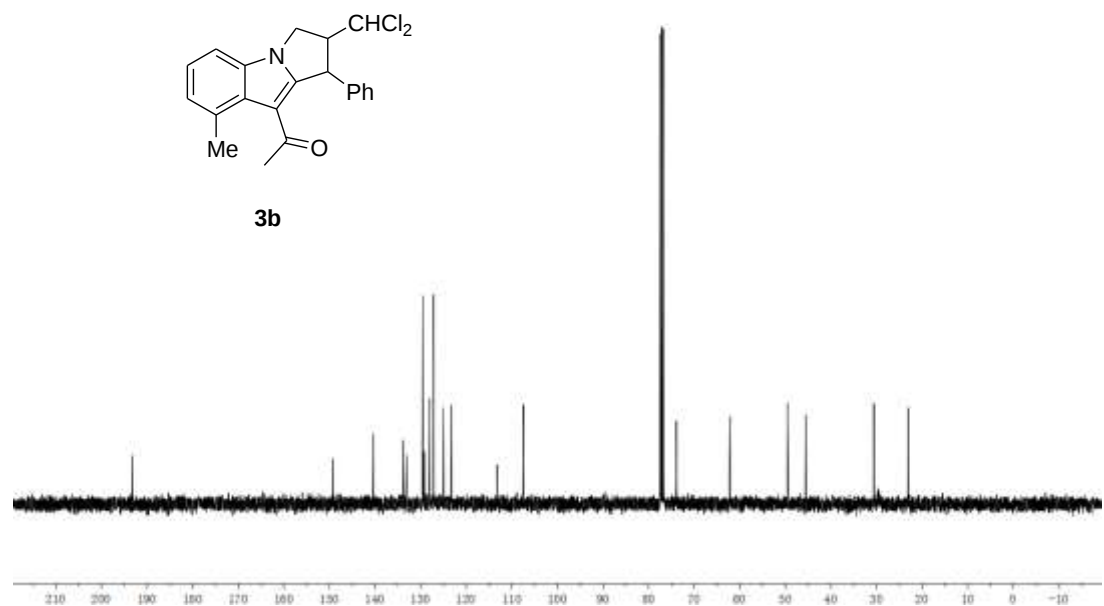
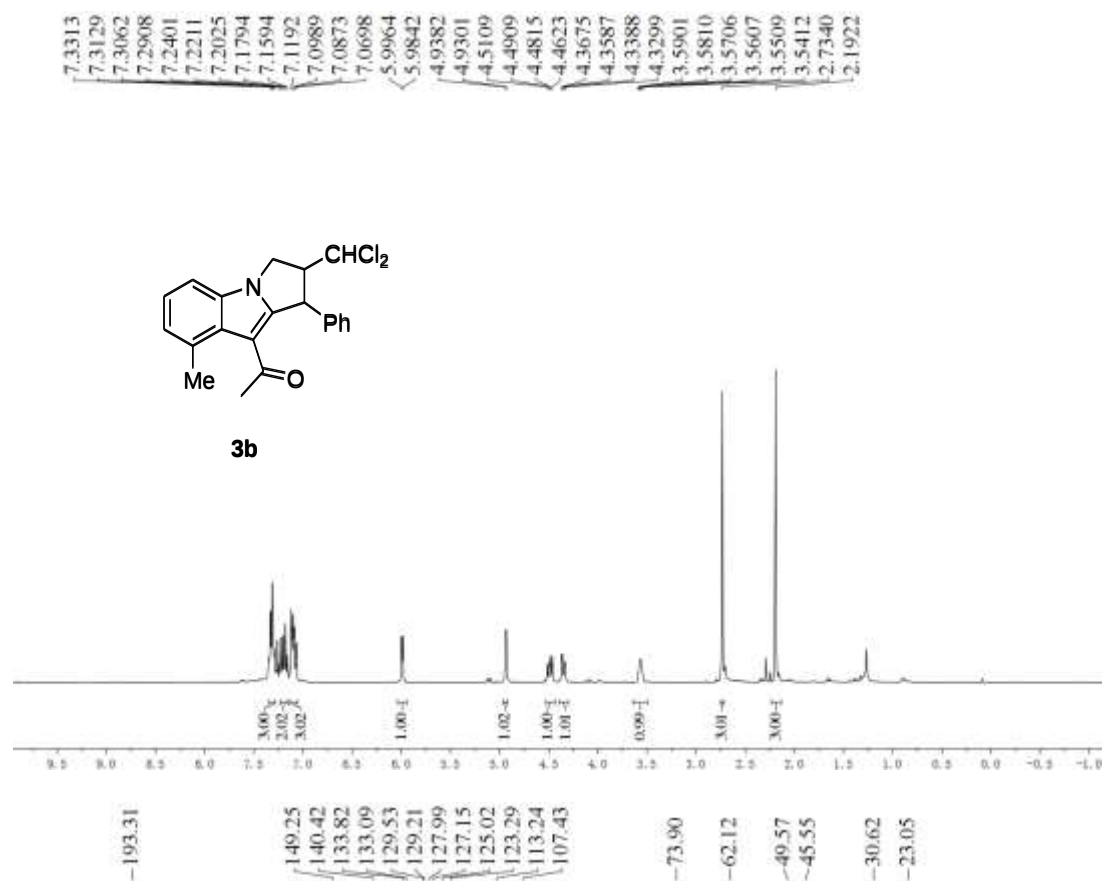


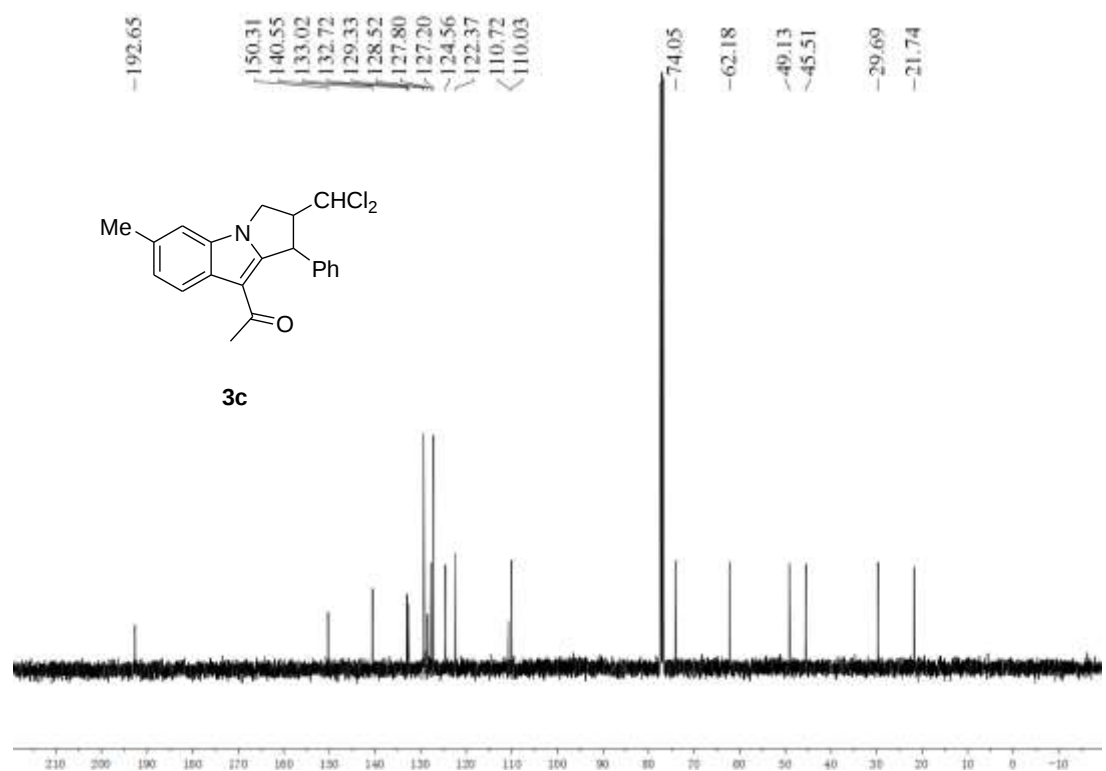
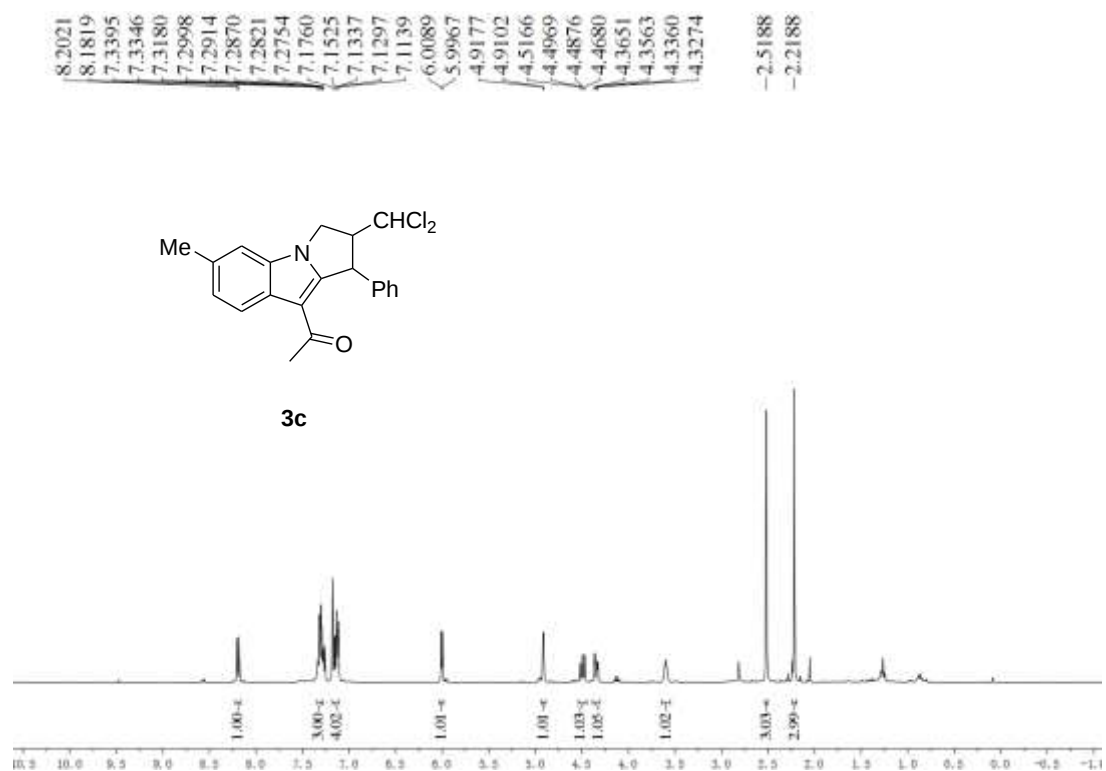


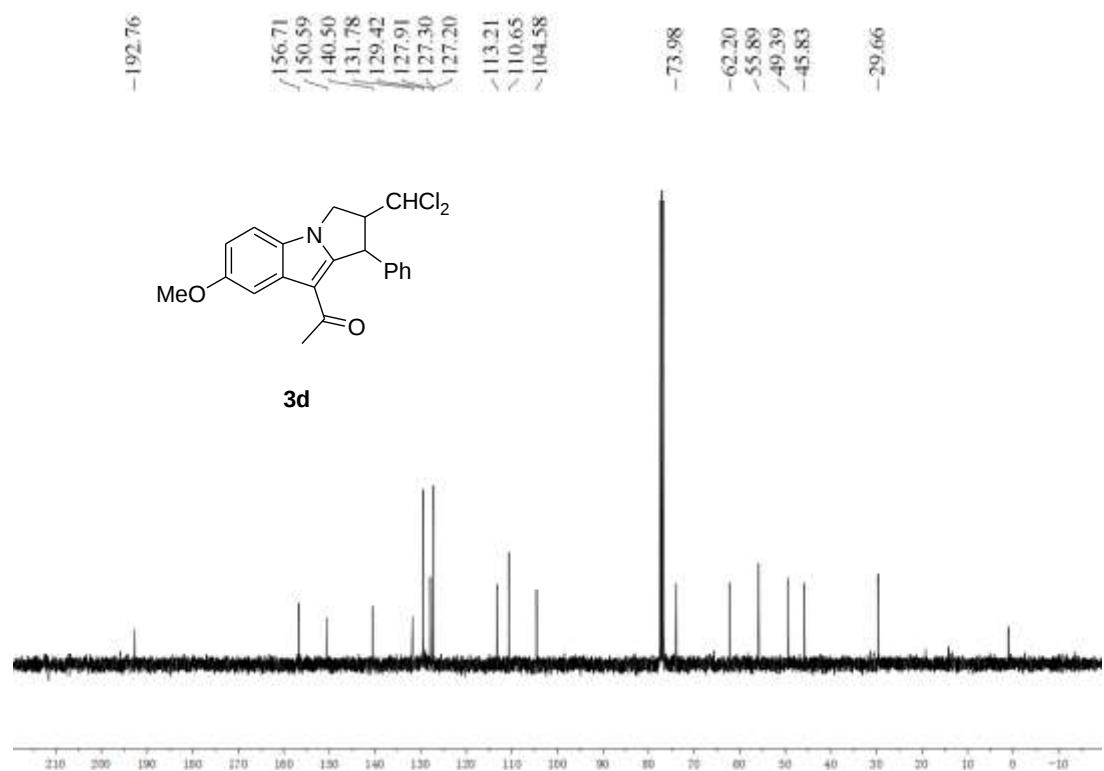
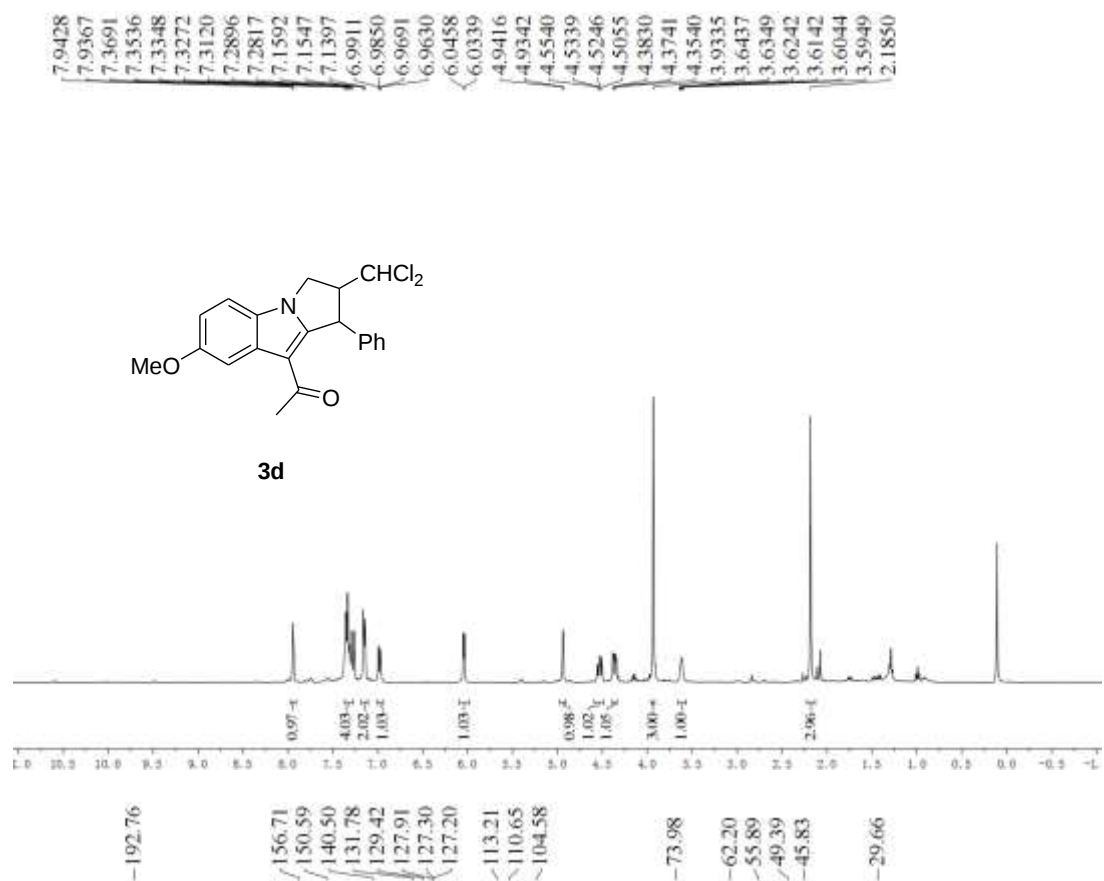


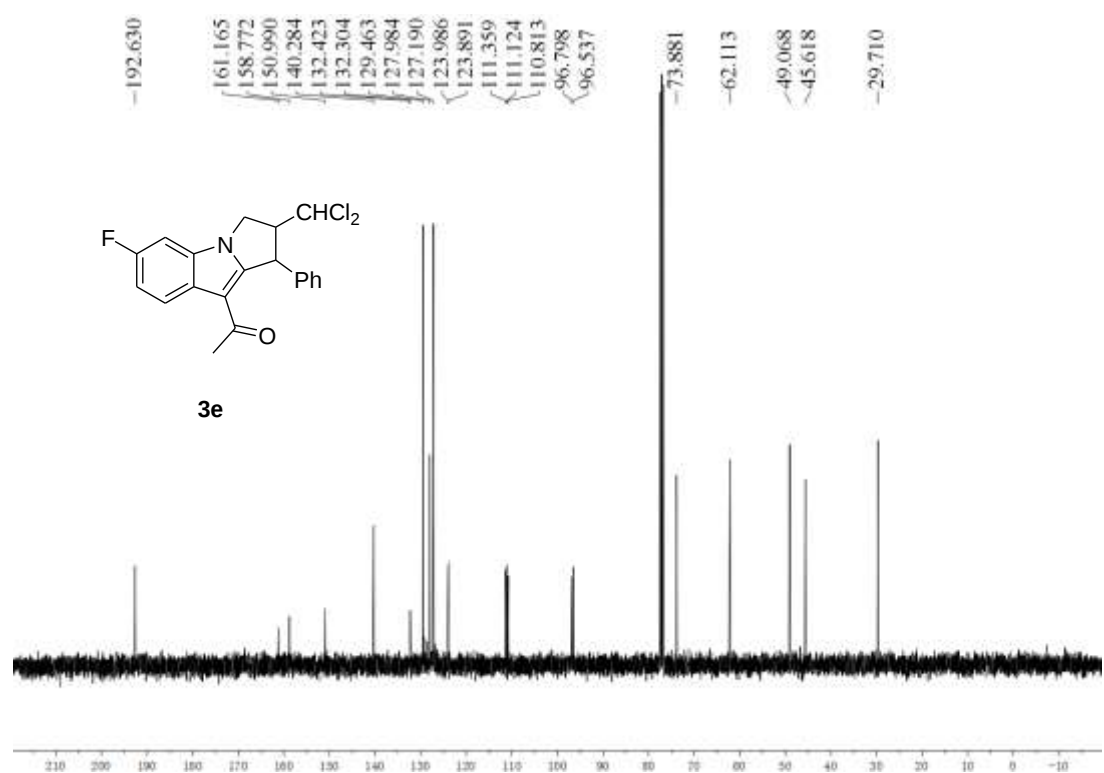
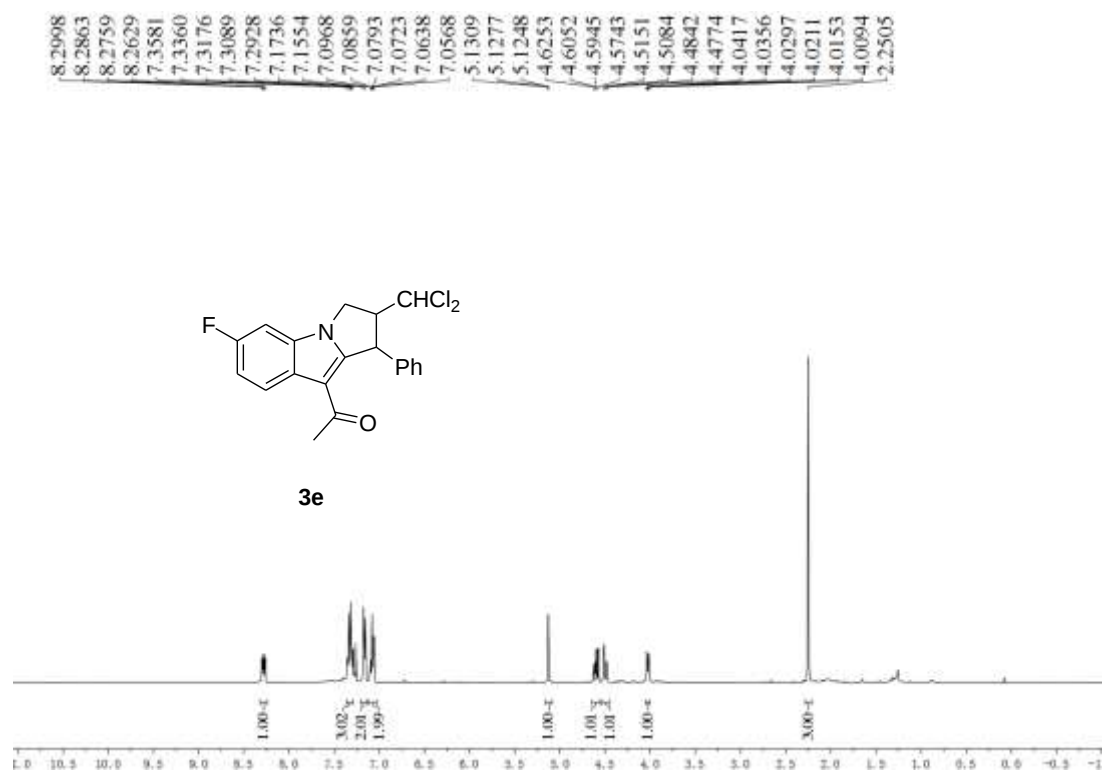


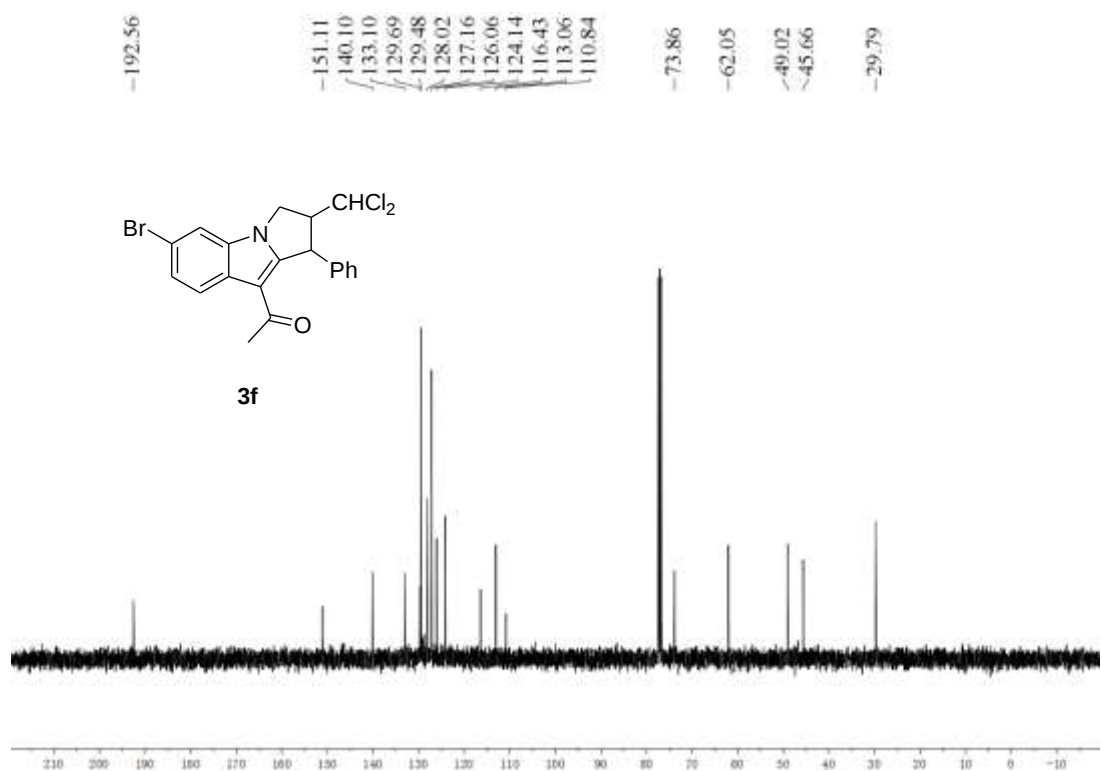
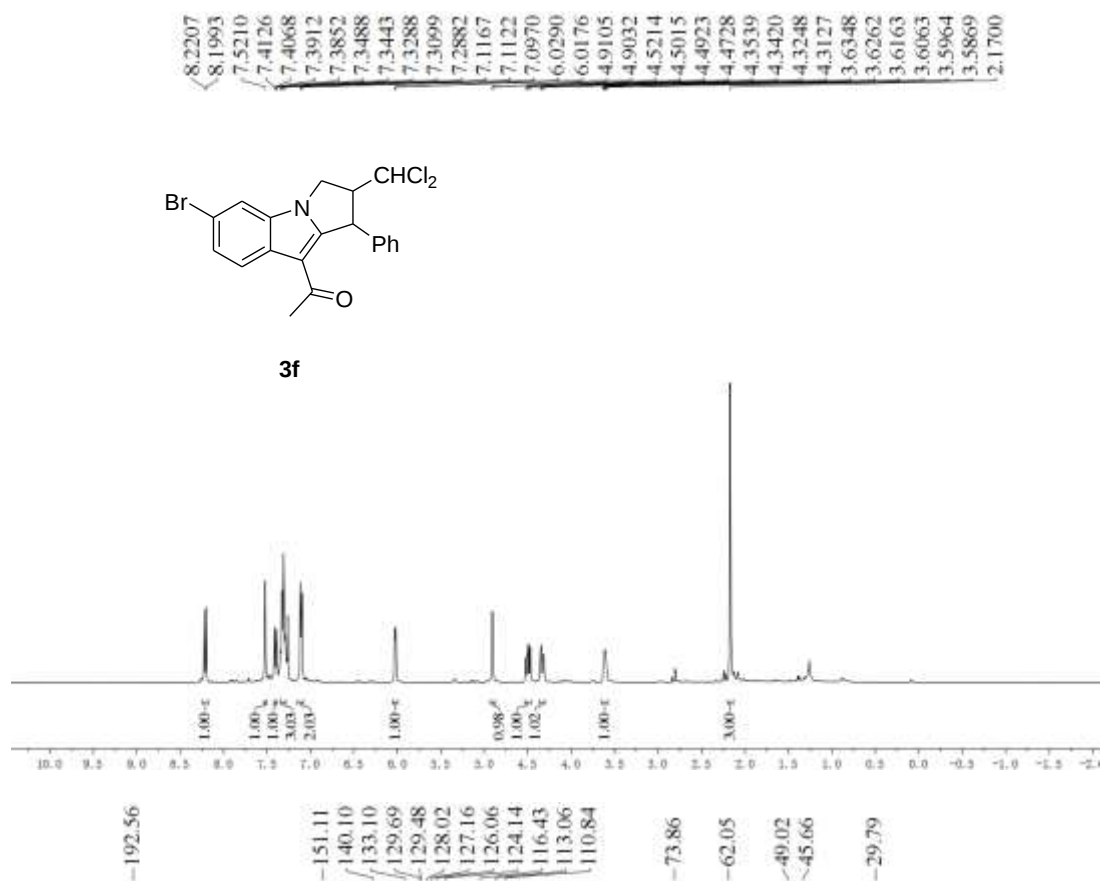


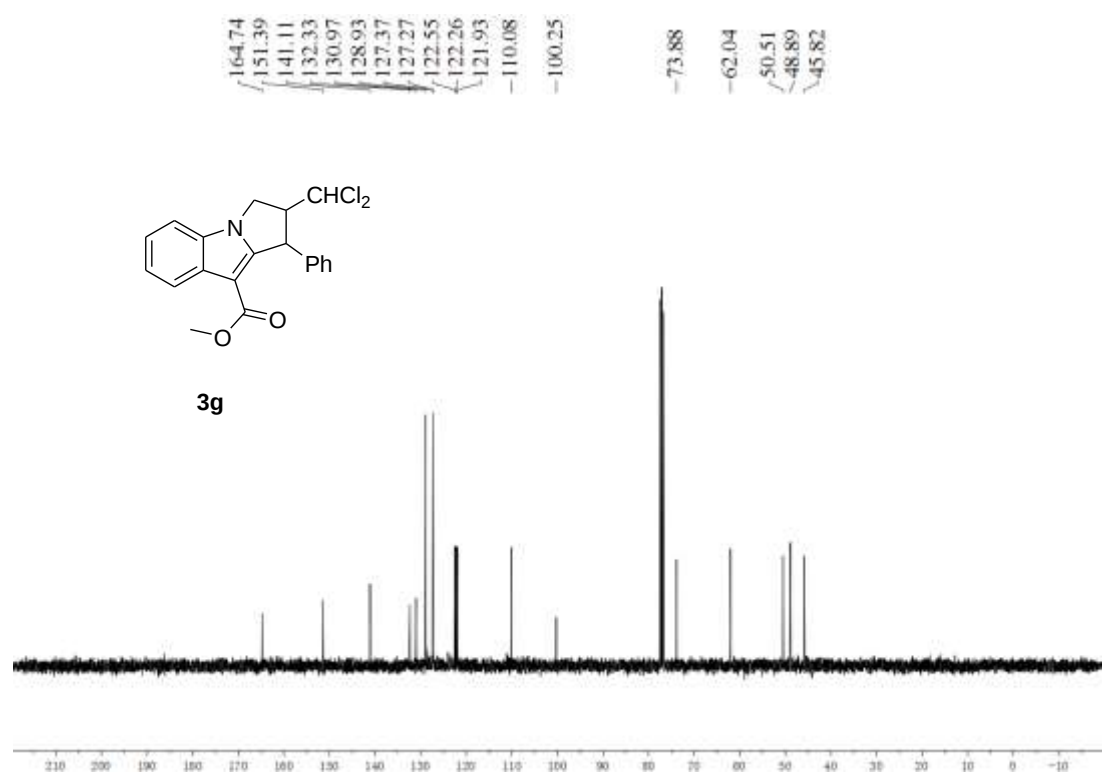
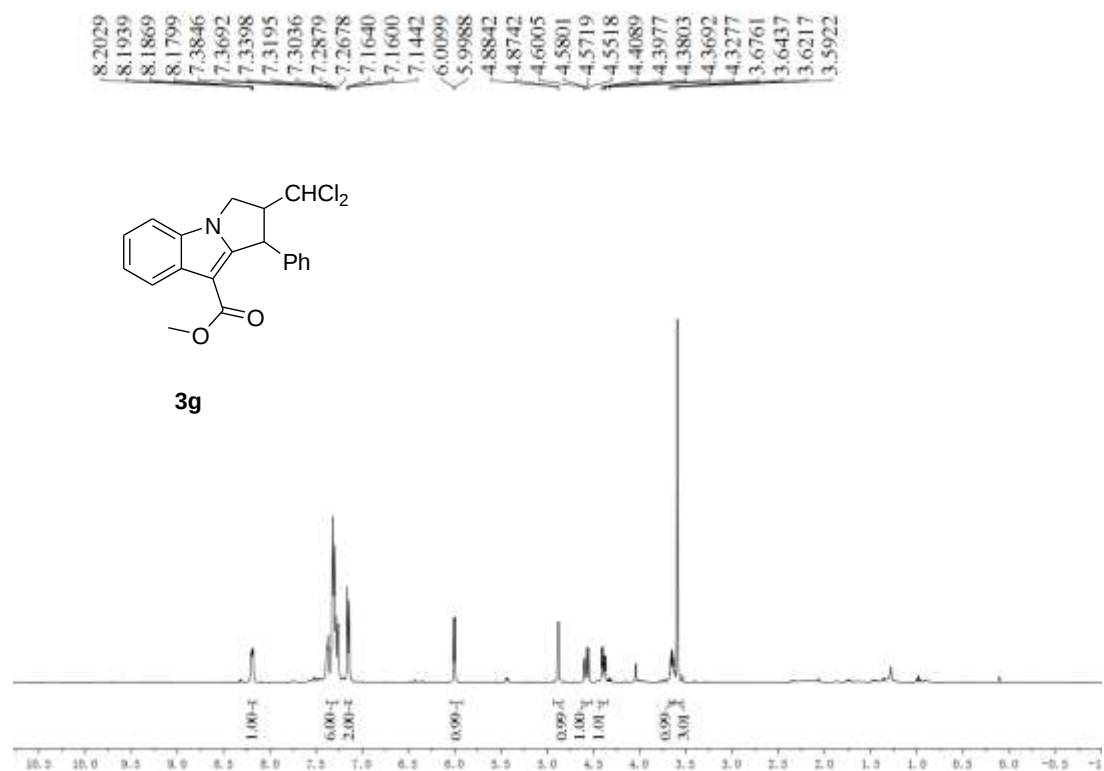


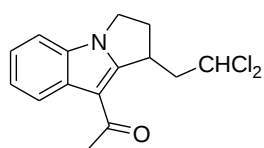




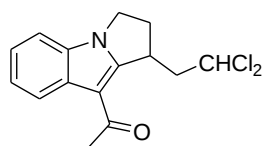
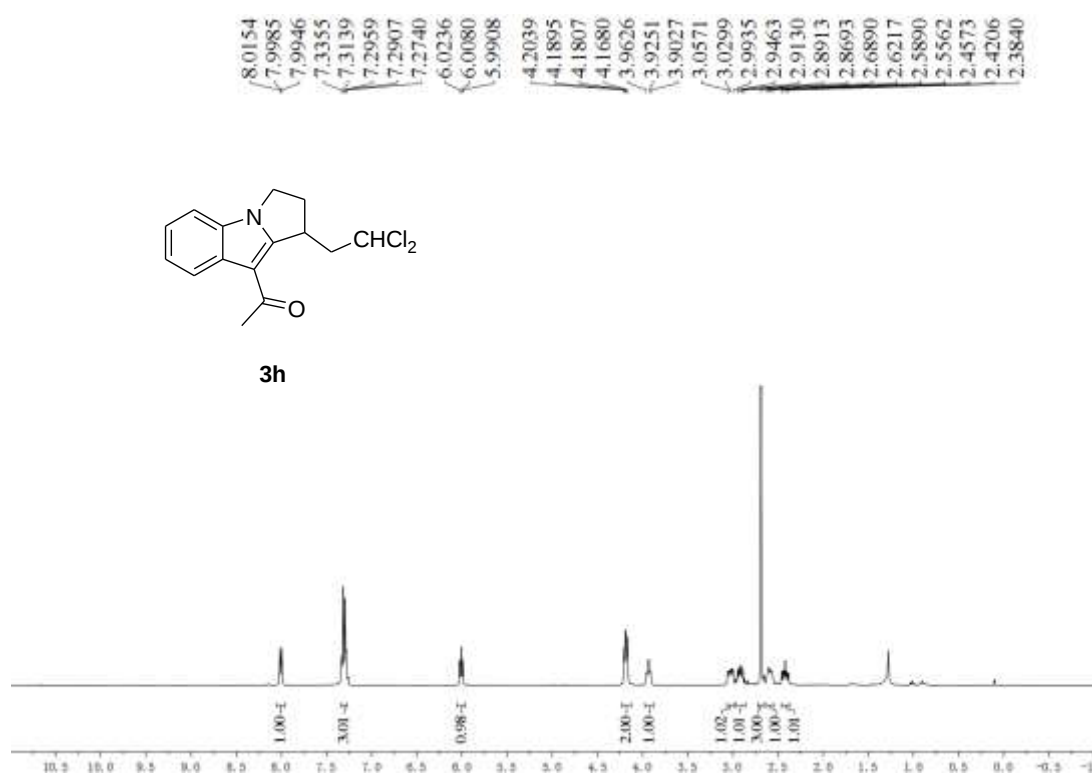








3h



3h

