Supporting Information for

Facile synthesis of 2-substituted benzo[*b*]furans and indoles by copper-catalyzed intramolecular cyclization of 2-alkynyl phenols and tosylanilines

Zhouting Rong*, Kexin Gao, Lei Zhou, Jianyuan Lin* and Guoying Qian*

College of Biological and Environmental Sciences, Zhejiang Wanli University, Ningbo 315100, People's Republic of China.

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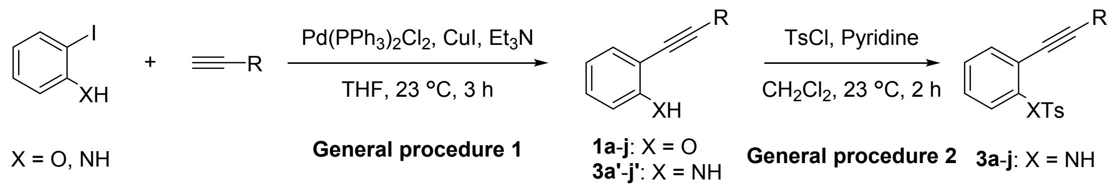
1. General Methods.

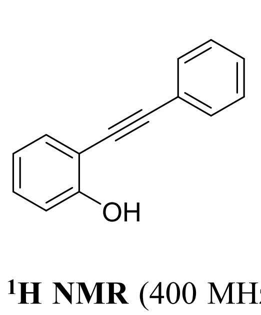
All reactions were carried out in solvents dried using a Solvent Purification System (SPS). Thin layer chromatography was carried out using TLC aluminum sheets coated with 0.2 mm of silica gel (Merck Gf234). Chromatographic purifications were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 40-60 μm). NMR spectra were recorded at 23 ºC on Bruker Avance 400 Ultrashield apparatus. Mass spectra were recorded on a Waters LCT Premier Spectrometer (ESI).

2. Procedure for the preparation of 2-alkynyl phenols and tosylanilines.

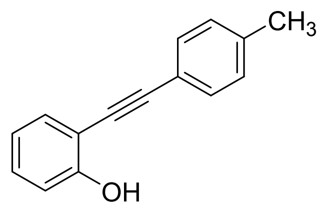


General procedure 1: $Pd(PPh_3)_2Cl_2$ (0.06 mmol), CuI (0.12 mmol) and Et_3N (4.5 mmol) were added sequentially to a solution of 2-iodoaniline (or 2-iodophenol, 3 mmol) and corresponding alkyne (4.5 mmol) in THF (10 mL) at 23 °C and the mixture was stirred at this temperature for 3 h before the solvent was evaporated. The residue was purified by flash column chromatography (hexane/EtOAc) to give 2-alkynyl aniline (or 2-alkynyl phenol).

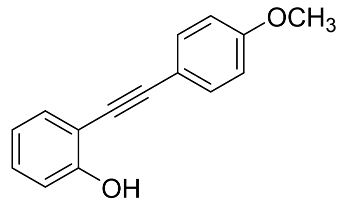
General procedure 2: To a solution of 2-alkynyl aniline (2 mmol) in CH_2Cl_2 (4 mL) was added *p*-toluenesulfonyl chloride (2.4 mmol) and pyridine (8 mmol) at 23 °C and the mixture was stirred at 23 °C for 2 h before it was quenched with saturated aqueous NH_4Cl (10 mL). The aqueous layer was extracted with CH_2Cl_2 (5 mL) and the combined organic layer was washed sequentially with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (hexane/EtOAc) to give 2-alkynyl tosylaniline.



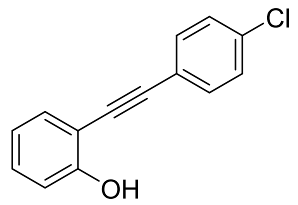
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 - 7.50 (m, 2H), 7.46 - 7.42 (m, 1H), 7.39 - 7.35 (m, 3H), 7.32 - 7.28 (m, 1H), 7.02 - 6.98 (m, 1H), 6.92 (t, J = 7.6 Hz, 1H), 5.84 (br s, 1H). The data is in accordance with the literature.[1]



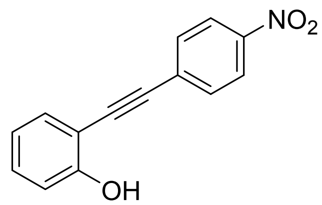
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (m, 3H), 7.25 (m, 1H), 7.14 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.2 Hz, 1H), 6.91 (m, 1H), 6.11 (br s, 1H), 2.35 (s, 3H). The data is in accordance with the literature.[1]



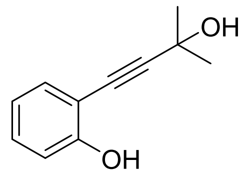
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (m, 2H), 7.41 (dd, J = 7.7, 1.4 Hz, 1H), 7.28 - 7.23 (m, 1H), 6.99 (d, J = 8.2 Hz, 1H), 6.95 - 6.87 (m, 3H), 5.85 (br s, 1H), 3.85 (s, 3H). The data is in accordance with the literature.[2]



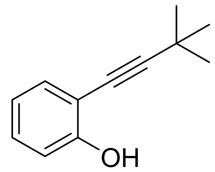
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 - 7.43 (m, 2H), 7.40 (dd, J = 7.6, 1.6 Hz, 1H), 7.33 - 7.31 (m, 2H), 7.27 (ddd, J = 8.4, 7.6, 1.6 Hz, 1H), 6.98 (dd, J = 8.4, 1.2 Hz, 1H), 6.91 (td, J = 8.0, 1.2 Hz, 1H), 5.82 (br s, 1H). The data is in accordance with the literature.[3]



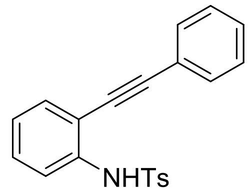
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 7.7 Hz, 1H), 7.33 (t, J = 7.8 Hz, 1H), 7.04 - 6.89 (m, 2H), 5.72 (br s, 1H). The data is in accordance with the literature.[4]



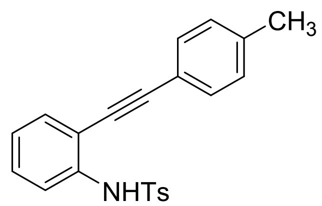
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, J = 7.6, 1.6 Hz, 1H), 7.26 - 7.22 (m, 1H), 6.95 - 6.93 (m, 1H), 6.85 (dt, J = 7.6, 1.2 Hz, 1H), 6.11 (br s, 1H), 2.48 (br s, 1H), 1.66 (s, 6H). The data is in accordance with the literature.[5]



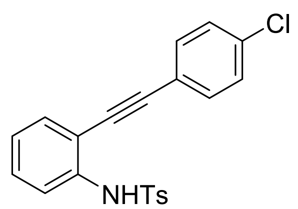
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 7.6 Hz, 1H), 7.17 (m, 1H), 6.91 (d, J = 8.4 Hz, 1H), 6.82 (m, 1H), 5.78 (br s, 1H), 1.34 (s, 9H). The data is in accordance with the literature.[6]



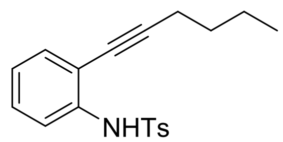
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.3 Hz, 2H), 7.63 (d, J = 8.3 Hz, 1H), 7.49 - 7.45 (m, 2H), 7.42 - 7.36 (m, 4H), 7.32 - 7.27 (m, 1H), 7.20 (br s, 1H), 7.17 (d, J = 8.2 Hz, 2H), 7.07 (t, J = 7.6 Hz, 1H), 2.34 (s, 3H). The data is in accordance with the literature.[7]



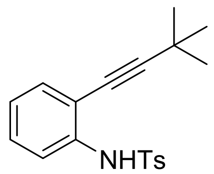
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 1H), 7.37 - 7.33 (m, 3H), 7.28 - 7.25 (m, 2H), 7.18 - 7.13 (m, 4H), 7.04 (td, J = 7.6, 0.8 Hz, 1H), 2.38 (s, 3H), 2.31 (s, 3H). The data is in accordance with the literature.[8]



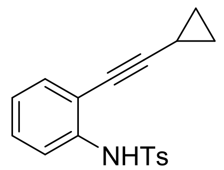
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 - 7.65 (m, 2H), 7.61 (d, J = 8.2 Hz, 1H), 7.39 - 7.33 (m, 5H), 7.29 (td, J = 7.8, 1.6 Hz, 1H), 7.20 (bs, 1H), 7.16 (d, J = 8.0 Hz, 2H), 7.06 (td, J = 1.2, 7.6 Hz, 1H), 2.33 (s, 3H). The data is in accordance with the literature.[8]



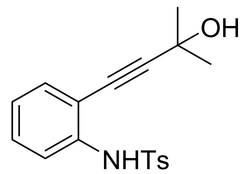
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.6 Hz, 2H), 7.57 (d, J = 8.4 Hz, 1H), 7.28 (bs, 1H), 7.22 - 7.17 (m, 4H), 6.96 (t, J = 8.0 Hz, 1H), 2.40 (t, J = 7.2 Hz, 2H), 2.33 (s, 3H), 1.60 - 1.54 (m, 2H), 1.50 - 1.40 (m, 2H), 0.96 (t, J = 7.6 Hz, 3H). The data is in accordance with the literature.[8]



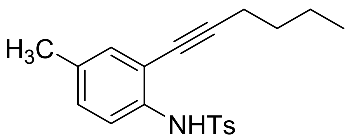
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.3 Hz, 1H), 7.26 - 7.19 (m, 4H), 7.11 (br, 1H), 6.98 (t, J = 8.3 Hz, 1H), 2.36 (s, 3H), 1.32 (s, 9H). The data is in accordance with the literature.[9]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 7.6 Hz, 1H), 7.26 - 7.19 (m, 5H), 6.97 (t, J = 7.6 Hz, 1H), 2.37 (s, 3H), 1.46 - 1.43 (m, 1H), 0.95 - 0.91 (m, 2H), 0.77 - 0.74 (m, 2H). The data is in accordance with the literature.[8]

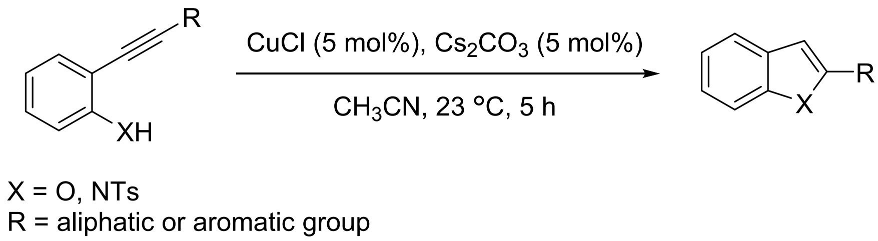


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 7.7 Hz, 1H), 7.24 (t, J = 7.8 Hz, 1H), 7.16 (t, J = 7.4 Hz, 1H), 7.09 (d, J = 8.3 Hz, 2H), 6.73 (s, 1H), 4.98 (br s, 1H), 2.22 (s, 3H), 1.88 (s, 6H). The data is in accordance with the literature.[10]

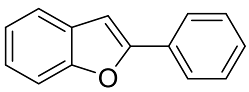


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 1H), 7.18 (d, J = 7.6 Hz, 2H), 7.08 - 7.00 (m, 3H), 2.40 - 2.36 (m, 5H), 2.21 (s, 3H), 1.59 - 1.53 (m, 2H), 1.49 - 1.41 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H). The data is in accordance with the literature.[11]

3. Procedure for the synthesis of 2-substituted benzo[*b*]furans and indoles



CuCl (2.5 mg, 0.025 mmol) and Cs_2CO_3 (8.1 mg, 0.025 mmol) were added to a solution of 2-alkynyl phenol (or 2-alkynyl tosylaniline, 0.5 mmol) in CH_3CN (2 mL) and the mixture was stirred at 23 °C for 5 h. Then Et_2O (10 ml) was added and the resulting mixture was washed sequentially with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (hexane/EtOAc) to give 2-substituted benzo[*b*]furans (or 2-substituted indoles).

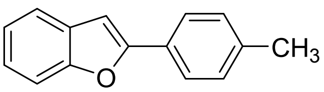


Yield: 95%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 - 7.90 (m, 2H), 7.66 - 7.57 (m, 2H), 7.50 (t, J = 7.6 Hz, 2H), 7.44 - 7.25 (m, 3H), 7.08 - 7.05 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.99, 154.97, 130.55, 129.30, 128.83, 128.59, 125.00, 124.32, 123.00, 120.97, 111.24, 101.38.

HRMS-ESI calculated for $C_{14}H_{11}O$ $[M+H]^+$: 195.0810; found: 195.0814.

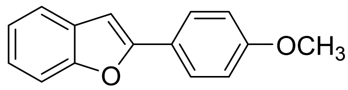


Yield: 90%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.1 Hz, 2H), 7.70 - 7.62 (m, 2H), 7.43 - 7.31 (m, 4H), 7.06 (s, 1H), 2.51 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.27, 154.86, 138.62, 129.54, 129.44, 127.83, 124.96, 124.06, 122.92, 120.81, 111.16, 100.63, 21.43.

HRMS-ESI calculated for $C_{15}H_{13}O$ $[M+H]^+$: 209.0966; found: 209.0962.

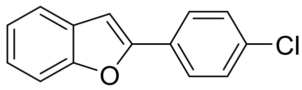


Yield: 89%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 - 7.77 (m, 2H), 7.59 - 7.48 (m, 2H), 7.24 (dtd, J = 16.1, 7.3, 1.4 Hz, 2H), 7.02 - 6.95 (m, 2H), 6.90 (d, J = 1.0 Hz, 1H), 3.87 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.00, 156.07, 154.71, 129.50, 126.43, 123.74, 123.37, 122.83, 120.57, 114.27, 110.99, 99.68, 55.37.

HRMS-ESI calculated for $C_{15}H_{13}O_2$ $[M+H]^+$: 225.0916; found: 225.0920.

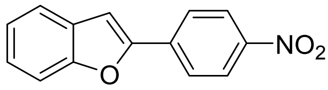


Yield: 93%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 - 7.71 (m, 2H), 7.56 - 7.51 (m, 1H), 7.47 (d, J = 8.1 Hz, 1H), 7.39 - 7.34 (m, 2H), 7.26 (ddd, J = 8.2, 7.2, 1.5 Hz, 1H), 7.23 - 7.17 (m, 1H), 6.95 (d, J = 1.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.91, 154.77, 134.32, 129.07, 129.04, 128.98, 126.13, 124.57, 123.11, 121.02, 111.21, 101.76.

HRMS-ESI calculated for $C_{14}H_{10}ClO$ $[M+H]^+$: 229.0420; found: 229.0426.

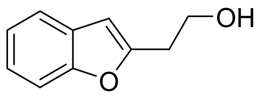


Yield: 77%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 - 8.27 (m, 2H), 8.01 - 7.97 (m, 2H), 7.65 - 7.61 (m, 1H), 7.57 - 7.52 (m, 1H), 7.36 (ddd, J = 8.4, 7.2, 1.4 Hz, 1H), 7.30 - 7.21 (m, 2H).

^{13}**C NMR** (101 MHz, $CDCl_3$) δ 155.44, 153.24, 147.25, 136.27, 128.64, 125.82, 125.21, 124.30, 123.54, 121.63, 111.49, 105.10.

HRMS-ESI calculated for $C_{14}H_{10}NO_3$ $[M+H]^+$: 240.0661; found: 240.0666.

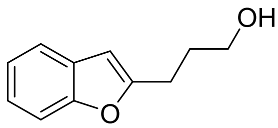


Yield: 83%.

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.50 - 7.43 (m, 1H), 7.42 - 7.36 (m, 1H), 7.23 - 7.12 (m, 2H), 6.44 (d, J = 1.2 Hz, 1H), 3.89 (t, J = 6.3 Hz, 2H), 3.00 - 2.91 (m, 2H), 2.31 (s, 1H).

^{13}**C NMR** (101 MHz, $CDCl_3$) δ 156.04, 154.82, 128.76, 123.54, 122.66, 120.46, 110.88, 103.62, 60.61, 32.03.

HRMS-ESI calculated for $C_{10}H_{10}NaO_2$ $[M+Na]^+$: 185.0578; found: 185.0572.

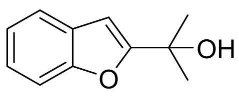


Yield: 86%.

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.50 - 7.44 (m, 1H), 7.42 - 7.37 (m, 1H), 7.22 - 7.14 (m, 2H), 6.39 (q, J = 1.1 Hz, 1H), 3.71 (t, J = 6.3 Hz, 2H), 2.86 (td, J = 7.5, 0.9 Hz, 2H), 1.99 (tt, J = 7.5, 6.3 Hz, 2H), 1.87 (br s, 1H).

^{13}**C NMR** (101 MHz, $CDCl_3$) δ 158.75, 154.69, 128.90, 123.26, 122.51, 120.29, 110.77, 102.24, 61.90, 30.62, 24.81.

HRMS-ESI calculated for $C_{11}H_{12}NaO_2$ $[M+Na]^+$: 199.0735; found: 199.0739.

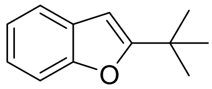


Yield: 81%.

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.47 (dd, J = 7.5, 1.5 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.24 - 7.12 (m, 2H), 6.52 (s, 1H), 2.18 (br s, 1H), 1.62 (s, 6H).

^{13}**C NMR** (101 MHz, $CDCl_3$) δ 163.03, 154.68, 128.32, 123.99, 122.72, 120.99, 111.18, 100.34, 69.33, 28.76.

HRMS-ESI calculated for $C_{11}H_{12}NaO_2$ $[M+Na]^+$: 199.0735; found: 199.0739.

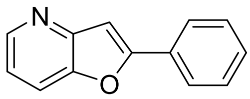


Yield: 91%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 - 7.41 (m, 1H), 7.38 (d, J = 7.8 Hz, 1H), 7.21 - 7.08 (m, 2H), 6.31 (s, 1H), 1.34 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.40, 154.61, 128.92, 123.06, 122.28, 120.33, 110.79, 98.90, 32.97, 28.87.

HRMS-ESI calculated for $C_{12}H_{15}O$ $[M+H]^+$: 175.1123; found: 175.1129.

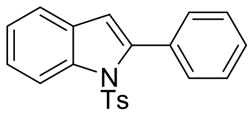


Yield: 88%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 4.8 Hz, 1H), 7.81 (d, J = 7.4 Hz, 2H), 7.67 - 7.63 (m, 1H), 7.38 (t, J = 7.5 Hz, 2H), 7.34 - 7.29 (m, 1H), 7.13 (s, 1H), 7.09 (dd, J = 8.3, 4.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.58, 149.04, 147.97, 146.03, 129.69, 129.52, 128.89, 125.29, 118.75, 117.72, 102.41.

HRMS-ESI calculated for $C_{13}H_{10}NO$ $[M+H]^+$: 196.0762; found: 196.0766.

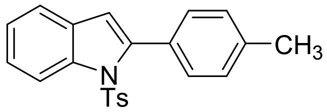


Yield: 95%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 8.4 Hz, 1H), 7.57 (dd, J = 7.2, 2.5 Hz, 2H), 7.53 - 7.48 (m, 4H), 7.42 (ddd, J = 8.5, 7.2, 1.4 Hz, 1H), 7.36 - 7.30 (m, 3H), 7.10 (d, J = 8.1 Hz, 2H), 6.61 (s, 1H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.50, 142.14, 138.30, 134.73, 132.43, 130.55, 130.34, 129.18, 128.63, 127.48, 126.80, 124.76, 124.29, 120.68, 116.66, 113.58, 21.51.

HRMS-ESI calculated for $C_{21}H_{18}NO_2S$ $[M+H]^+$: 348.1058; found: 348.1051.

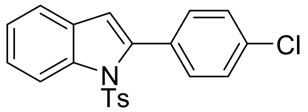


Yield: 91%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 8.4 Hz, 1H), 7.42 (t, J = 7.7 Hz, 3H), 7.34 (ddd, J = 8.5, 7.2, 1.4 Hz, 1H), 7.30 - 7.22 (m, 5H), 7.04 (d, J = 8.1 Hz, 2H), 6.51 (s, 1H), 2.45 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.46, 142.31, 138.61, 138.22, 134.65, 130.67, 130.20, 129.56, 129.17, 128.26, 126.80, 124.62, 124.28, 120.59, 116.68, 113.30, 21.53, 21.46.

HRMS-ESI calculated for $C_{22}H_{20}NO_2S$ $[M+H]^+$: 362.1215; found: 362.1219.

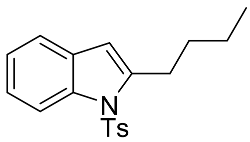


Yield: 94%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 8.4 Hz, 1H), 7.47 - 7.43 (m, 3H), 7.42 - 7.35 (m, 3H), 7.30 - 7.25 (m, 3H), 7.04 (d, J = 8.1 Hz, 2H), 6.55 (s, 1H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.76, 140.83, 138.37, 134.76, 134.49, 131.50, 130.92, 130.47, 129.30, 127.83, 126.72, 125.08, 124.51, 120.85, 116.70, 114.08, 21.54.

HRMS-ESI calculated for $C_{21}H_{17}ClNO_2S$ $[M+H]^+$: 382.0669; found: 382.0665.

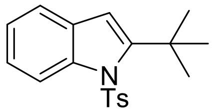


Yield: 88%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.2 Hz, 1H), 7.64 (d, J = 8.3 Hz, 2H), 7.45 - 7.40 (m, 1H), 7.29 - 7.17 (m, 4H), 6.40 (s, 1H), 3.05 - 2.95 (m, 2H), 2.35 (s, 3H), 1.75 (p, J = 7.6 Hz, 2H), 1.46 (h, J = 7.4 Hz, 2H), 0.98 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.55, 142.52, 137.20, 136.26, 129.85, 129.75, 126.25, 123.74, 123.42, 120.01, 114.82, 108.59, 30.98, 28.74, 22.48, 21.54, 13.93.

HRMS-ESI calculated for $C_{19}H_{22}NO_2S$ $[M+H]^+$: 328.1371; found: 328.1376.

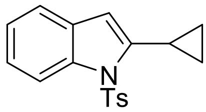


Yield: 88%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 - 8.01 (m, 1H), 7.47 - 7.37 (m, 3H), 7.21 - 7.13 (m, 2H), 7.10 (d, J = 8.2 Hz, 2H), 6.61 (s, 1H), 2.28 (s, 3H), 1.60 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.75, 144.03, 138.95, 136.84, 129.47, 129.24, 126.00, 124.14, 123.62, 120.30, 116.10, 110.76, 35.02, 31.37, 21.48.

HRMS-ESI calculated for $C_{19}H_{22}NO_2S$ $[M+H]^+$: 328.1371; found: 328.1377.

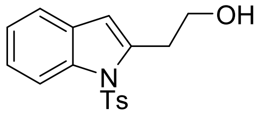


Yield: 85%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.4 Hz, 1H), 7.75 - 7.70 (m, 2H), 7.41 - 7.37 (m, 1H), 7.28 (ddd, J = 8.4, 7.2, 1.4 Hz, 1H), 7.23 - 7.17 (m, 3H), 6.19 (s, 1H), 2.46 (dddd, J = 11.5, 8.4, 5.3, 1.2 Hz, 1H), 2.34 (s, 3H), 1.01 - 0.94 (m, 2H), 0.63 - 0.57 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.62, 144.12, 137.40, 136.58, 129.67, 129.33, 126.60, 123.88, 123.39, 120.21, 114.50, 106.06, 21.56, 9.47, 8.44.

HRMS-ESI calculated for $C_{18}H_{18}NO_2S$ $[M+H]^+$: 312.1058; found: 312.1055.

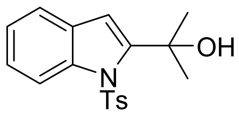


Yield: 90%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 - 8.12 (m, 1H), 7.64 - 7.55 (m, 2H), 7.44 - 7.35 (m, 1H), 7.25 (ddd, J = 8.5, 7.2, 1.4 Hz, 1H), 7.19 (td, J = 7.4, 1.1 Hz, 1H), 7.13 (d, J = 8.1 Hz, 2H), 6.51 - 6.43 (m, 1H), 3.98 (t, J = 6.4 Hz, 2H), 3.31 - 3.22 (m, 2H), 2.66 (br s, 1H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.88, 138.21, 137.24, 135.85, 129.88, 129.73, 126.23, 124.19, 123.69, 120.35, 114.88, 110.57, 61.69, 32.55, 21.53.

HRMS-ESI calculated for $C_{17}H_{17}NNaO_3S$ $[M+Na]^+$: 338.0827; found: 338.0824.

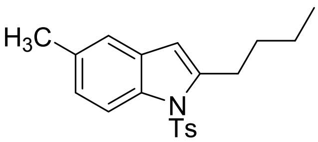


Yield: 90%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.3 Hz, 1H), 7.65 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 7.5 Hz, 1H), 7.14 (dq, J = 23.6, 7.3 Hz, 2H), 7.06 (d, J = 8.1 Hz, 2H), 6.64 (s, 1H), 4.98 (br s, 1H), 2.20 (s, 3H), 1.78 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.39, 144.81, 138.06, 134.99, 129.63, 129.06, 126.59, 125.01, 124.04, 121.08, 115.56, 111.24, 69.34, 31.08, 21.51.

HRMS-ESI calculated for $C_{18}H_{19}NNaO_3S$ $[M+Na]^+$: 352.0983; found: 352.0988.

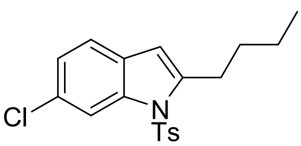


Yield: 86%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.5 Hz, 1H), 7.60 (dd, J = 8.5, 2.0 Hz, 2H), 7.21 - 7.12 (m, 3H), 7.06 (dd, J = 8.5, 1.8 Hz, 1H), 6.33 - 6.27 (m, 1H), 3.01 - 2.92 (m, 2H), 2.39 (s, 3H), 2.32 (s, 3H), 1.78 - 1.66 (m, 2H), 1.44 (h, J = 7.4 Hz, 2H), 0.96 (t, J = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.44, 142.57, 136.27, 135.44, 132.99, 130.11, 129.72, 126.22, 125.07, 120.02, 114.53, 108.53, 31.02, 28.78, 22.48, 21.53, 21.21, 13.94.

HRMS-ESI calculated for $C_{20}H_{24}NO_2S$ $[M+H]^+$: 342.1528; found: 342.1521.



Yield: 82%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 1.7 Hz, 1H), 7.55 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.3 Hz, 1H), 7.13 (dd, J = 13.7, 8.2 Hz, 3H), 6.27 (s, 1H), 2.88 (t, J = 7.7 Hz, 2H), 2.29 (s, 3H), 1.64 (p, J = 7.6 Hz, 2H), 1.37 (h, J = 7.4 Hz, 2H), 0.89 (t, J = 7.3 Hz, 3H).

^{13}**C NMR** (101 MHz, $CDCl_3$) δ 144.93, 143.24, 137.52, 136.05, 129.92, 129.64, 128.28, 126.29, 124.00, 120.66, 114.98, 108.02, 30.82, 28.61, 22.44, 21.56, 13.88.

HRMS-ESI calculated for $C_{19}H_{21}ClNO_2S$ $[M+H]^+$: 362.0982; found: 362.0988.

4. References

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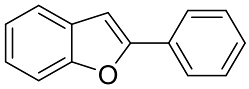
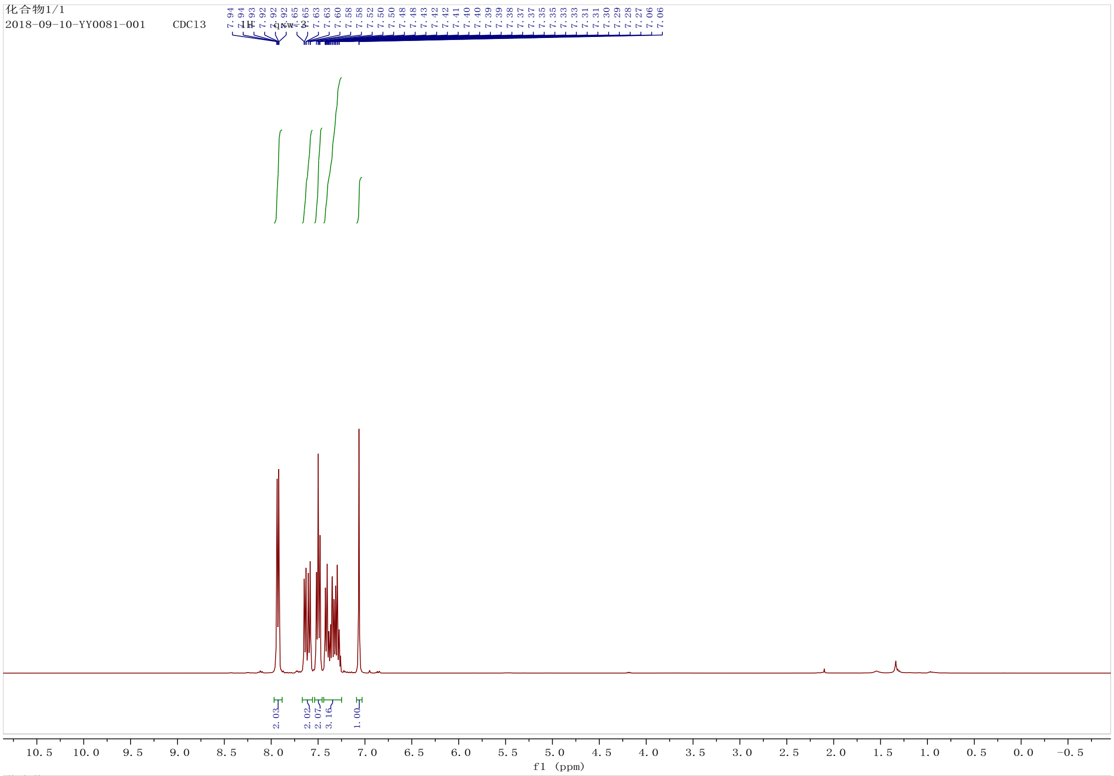
5. ^{1}H NMR and ^{13}C NMR Spectra




化合物1/1
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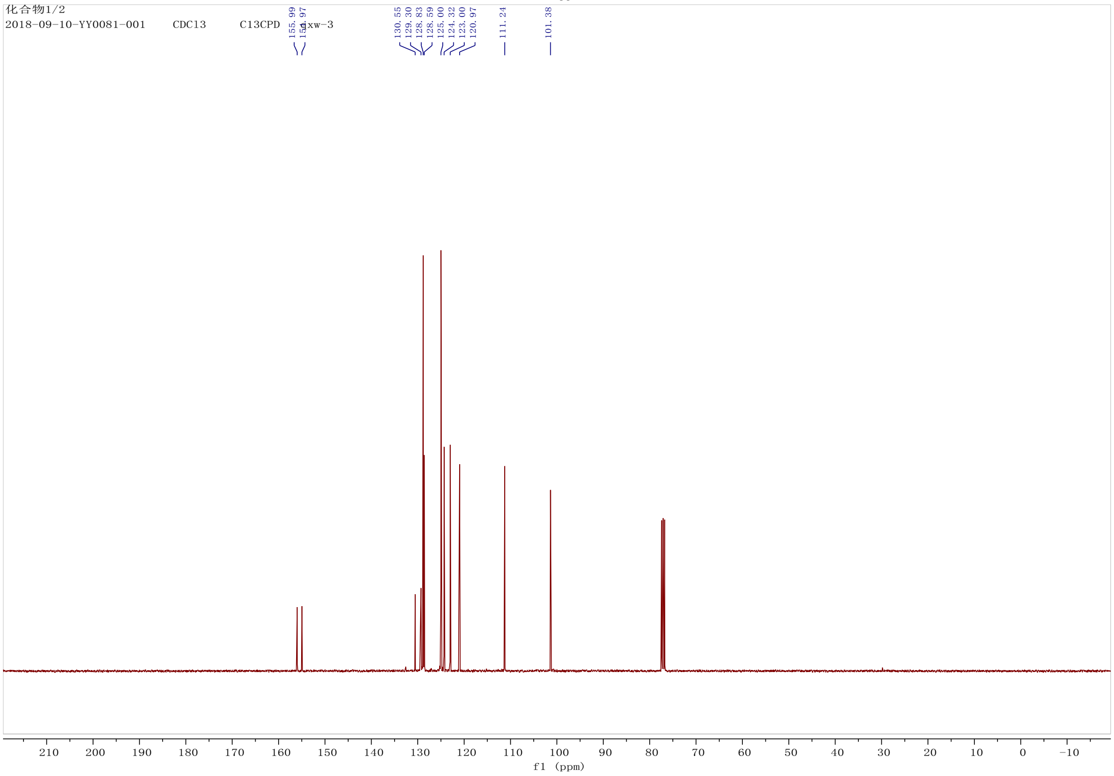
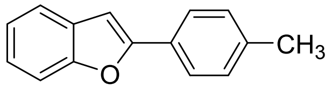
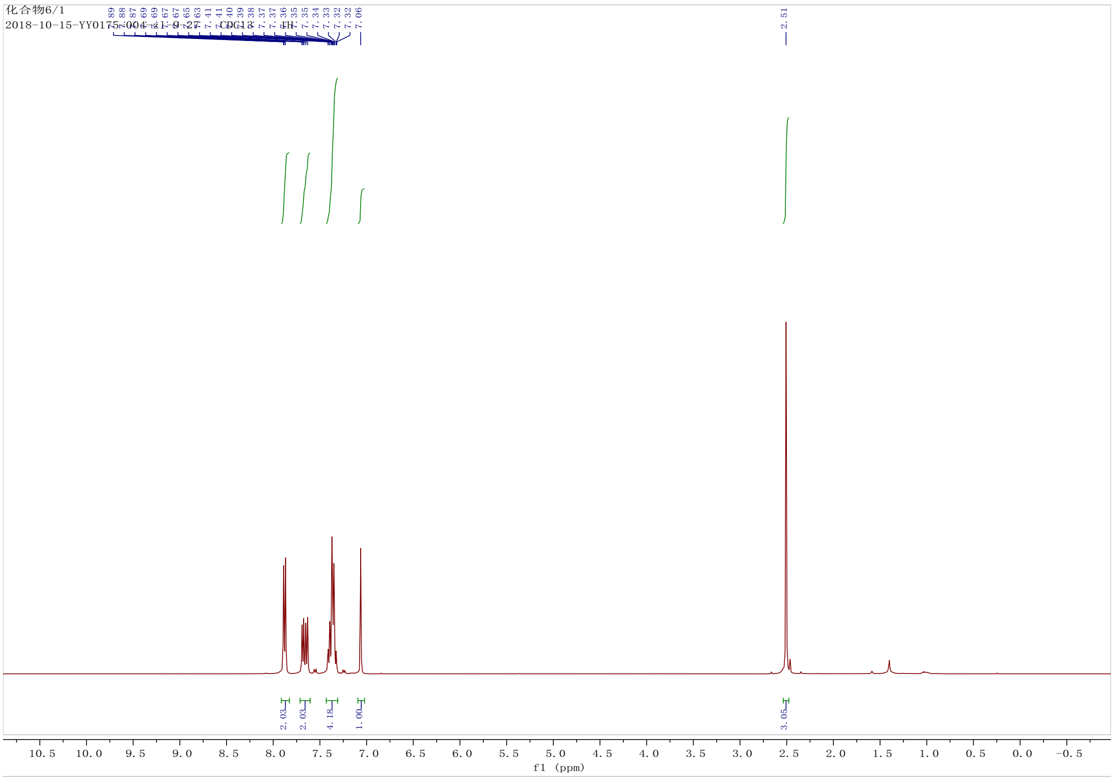
7.94 7.94 7.93 7.92 7.92 7.92 7.65 7.65 7.63 7.63 7.60 7.58 7.58 7.52 7.50 7.50 7.48 7.48 7.43 7.42 7.42 7.41 7.40 7.40 7.39 7.39 7.38 7.37 7.37 7.35 7.35 7.33 7.33 7.31 7.31 7.30 7.29 7.28 7.27 7.06 7.06
2.03
2.02
2.07
3.16
1.00
f1 (ppm)


化合物1/2
2018-09-10-YY0081-001 CDCl3 C13CPD qxw-3
155.99
154.97
130.55
129.30
128.83
128.59
125.00
124.32
123.00
120.97
111.24
101.38
f1 (ppm)




化合物6/1
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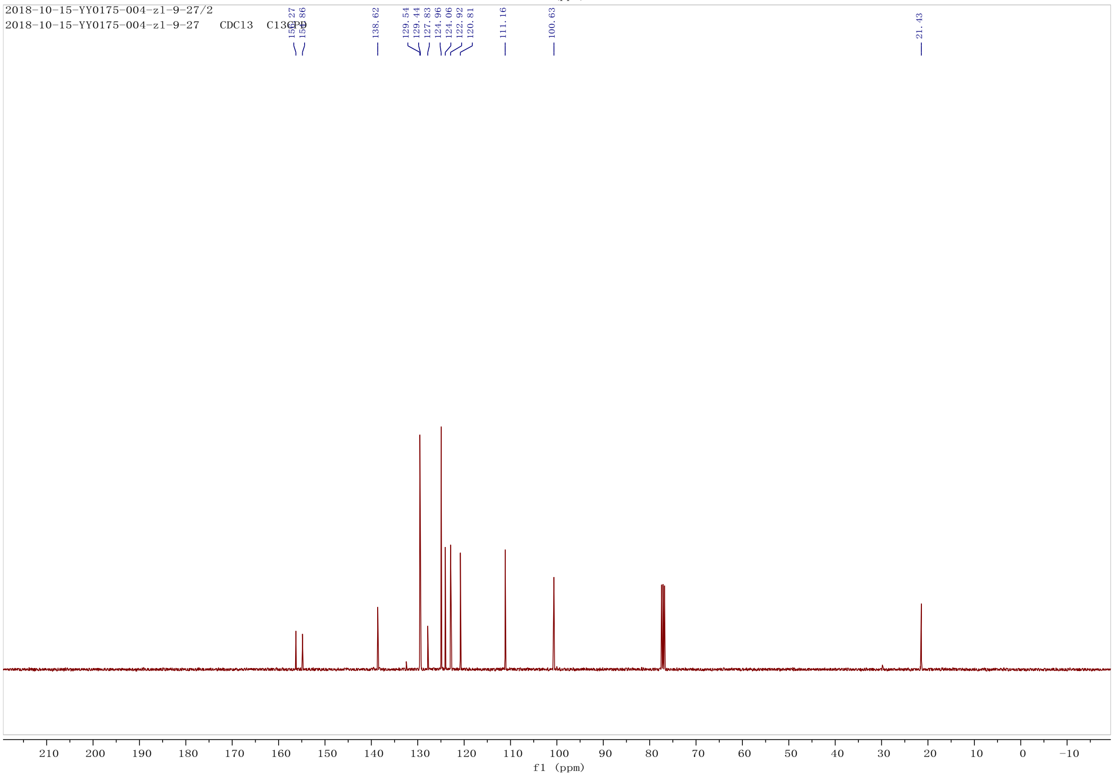
2.03
2.03
4.18
1.00
3.05
f1 (ppm)


2018-10-15-YY0175-004-z1-9-27/2
2018-10-15-YY0175-004-z1-9-27 CDCl3 C13CPD
138.62
129.54
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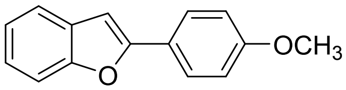
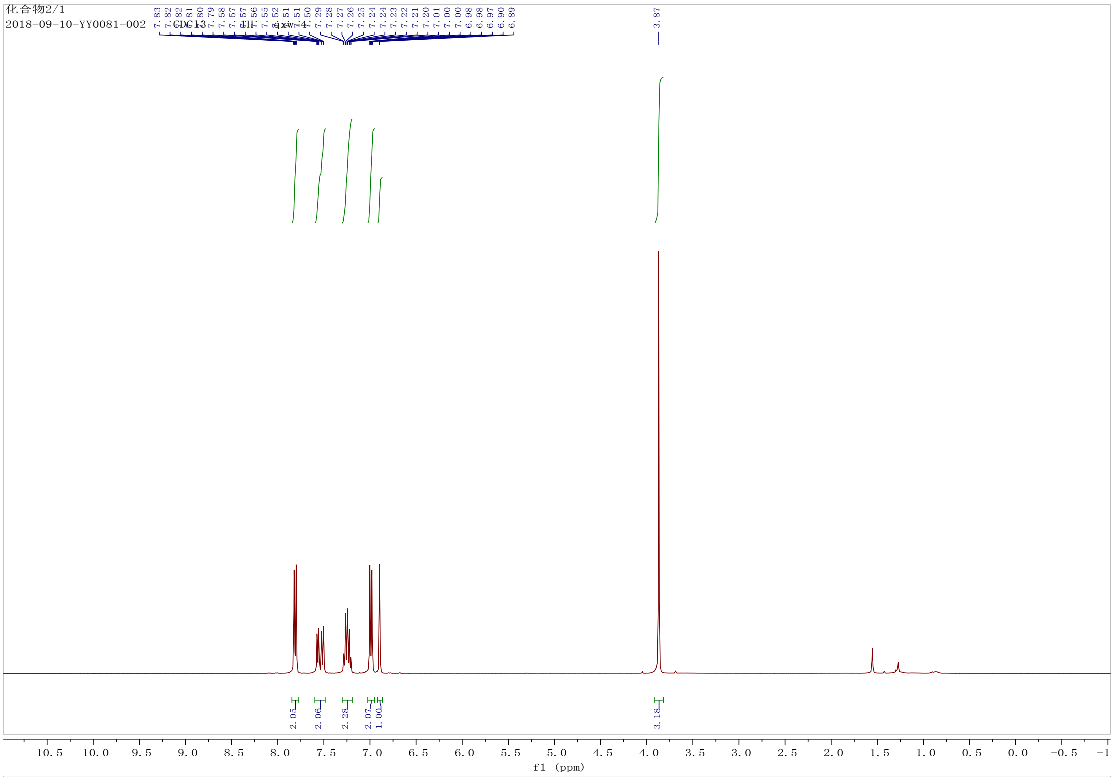
100.63
21.43
f1 (ppm)


OCH3
O


化合物2/1
2018-09-10-YY0081-002 CDCl3 1H qxw-4
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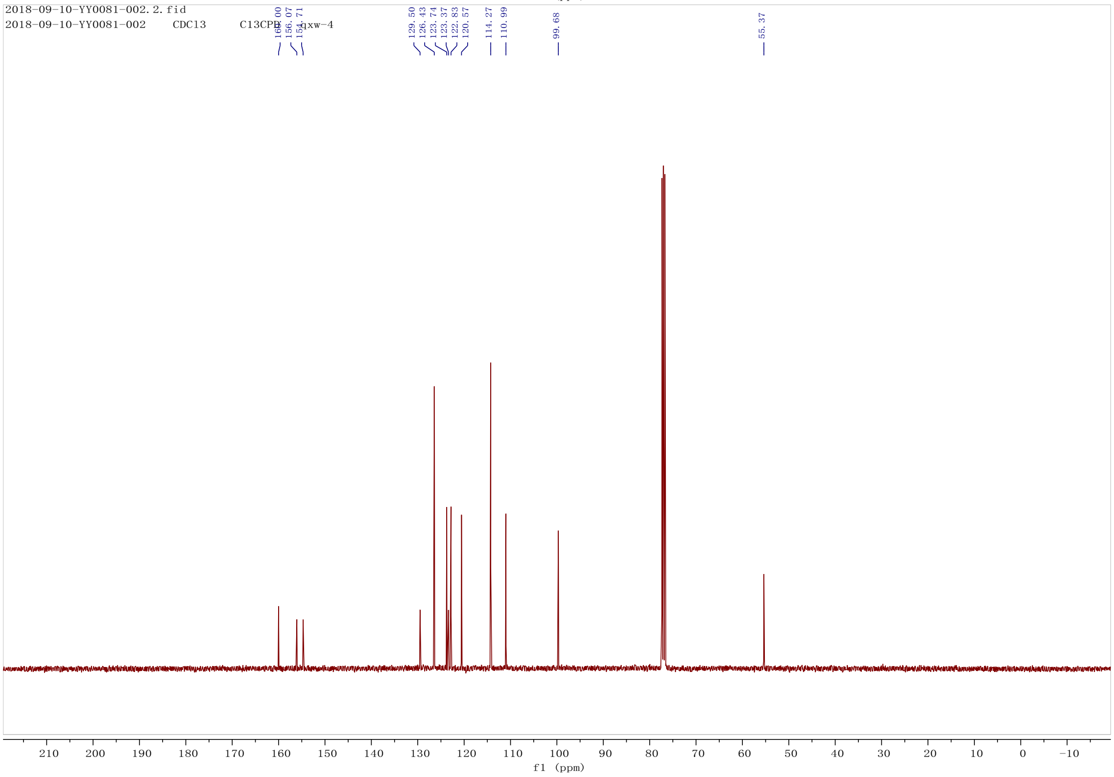
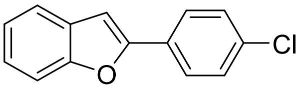
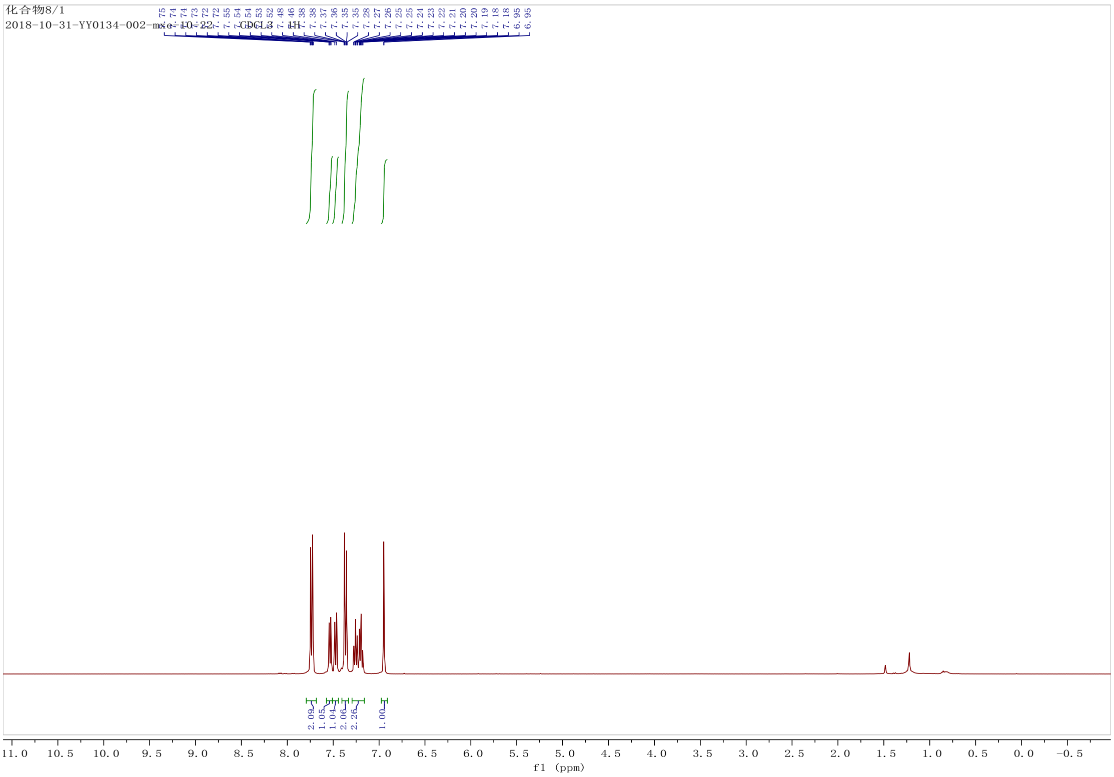
3.87
2.05 2.06 2.28 2.07 1.00 3.18
f1 (ppm)


2018-09-10-YY0081-002.2.fid
2018-09-10-YY0081-002 CDCl3 C13CPD qxw-4
160.00 156.07 154.71
129.50 126.43 123.74 123.37 122.83 120.57
114.27 110.99 99.68 55.37
f1 (ppm)


Cl
O


化合物8/1
2018-10-31-YY0134-002-mxe-10-22 CDCL3 1H
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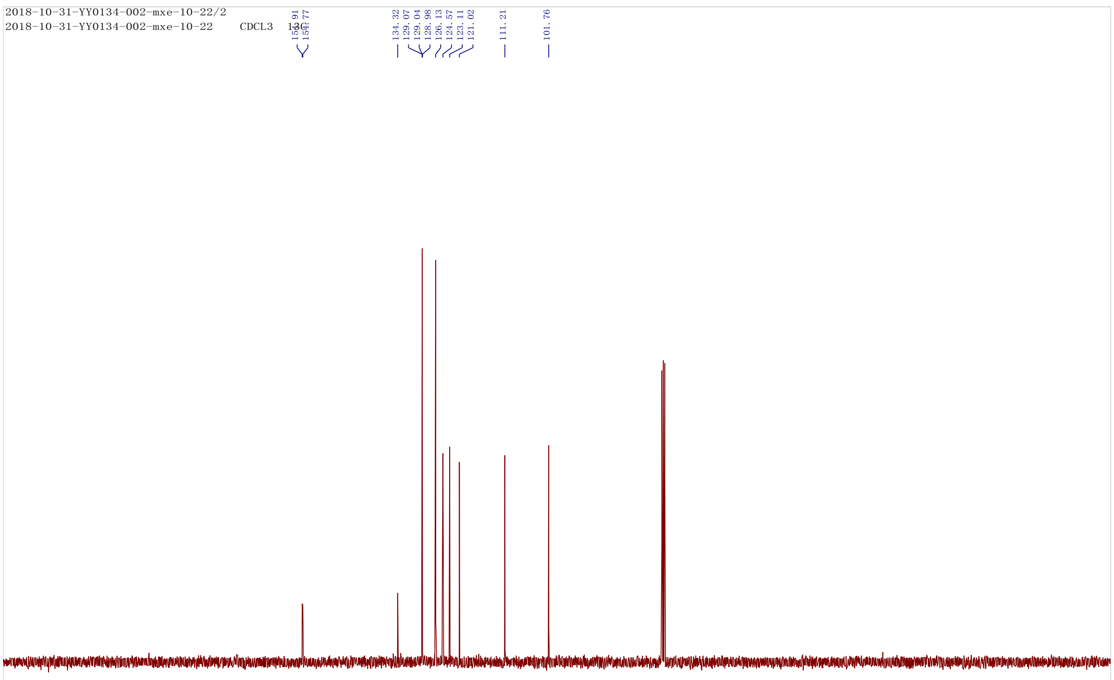
2.09 1.05 1.04 2.06 2.26 1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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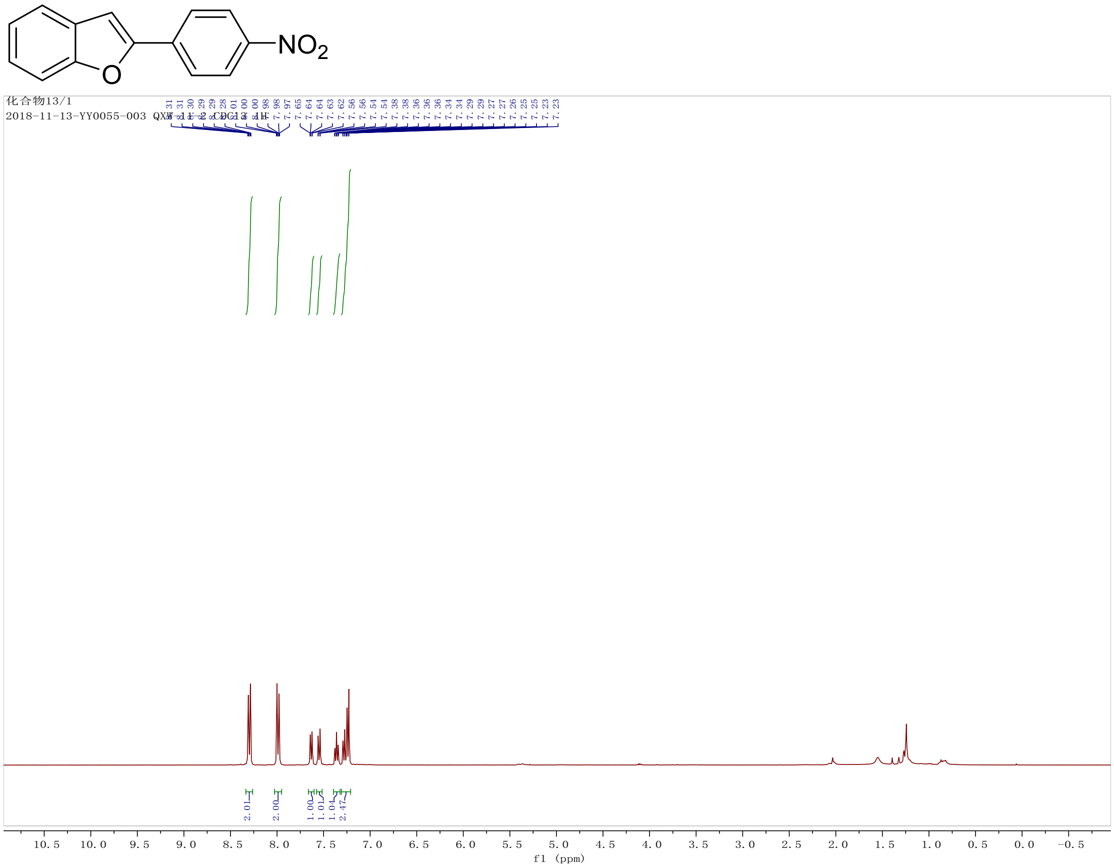
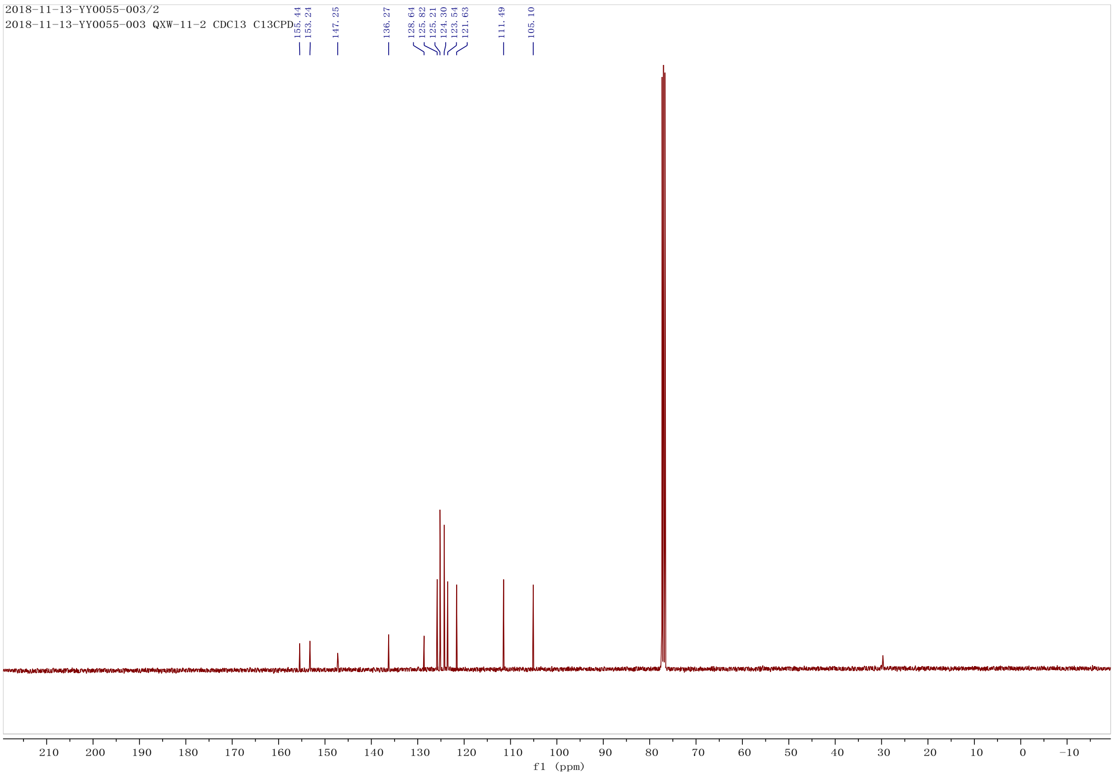
2018-10-31-YY0134-002-mxe-10-22 CDCL3 13C
154.91 154.77 134.32 129.07 129.04 128.98 126.13 124.57 123.11 121.02 111.21 101.76
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NO2
O
化合物13/1
2018-11-13-YY0055-003 QXW-11-2 CDCl3 1H
f1 (ppm)


2018-11-13-YY0055-003/2
2018-11-13-YY0055-003 QXW-11-2 CDCl3 C13CPD
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147.25
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125.21
124.30
123.54
121.63
111.49
105.10
210
200
190
180
170
160
150
140
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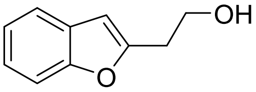
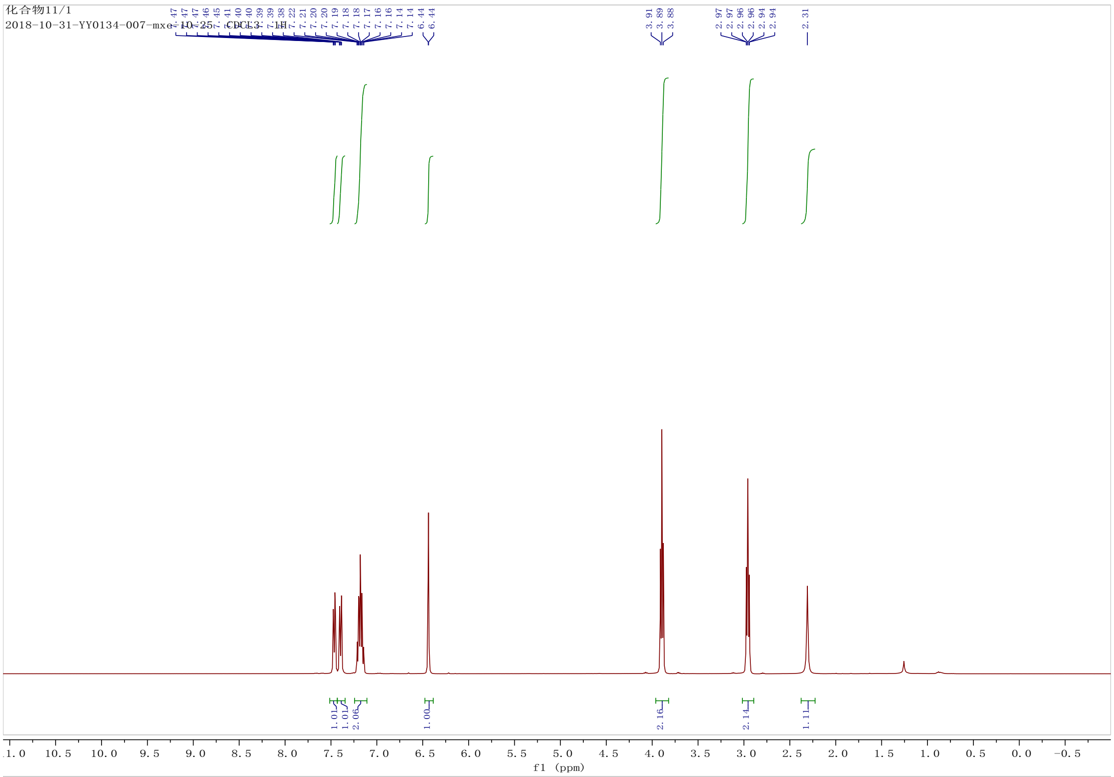
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OH
O


化合物11/1
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3.91
3.89
3.88
2.97
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2.96
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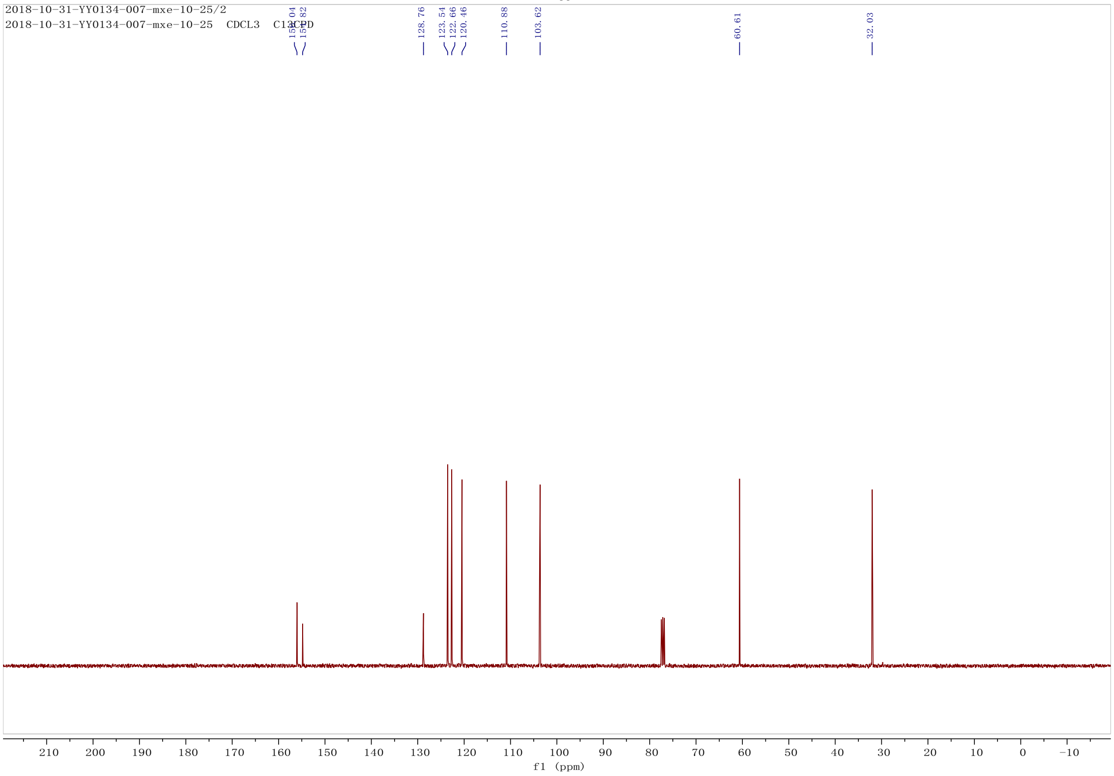
2.14
1.11
f1 (ppm)


2018-10-31-YY0134-007-mxe-10-25/2
2018-10-31-YY0134-007-mxe-10-25 CDCL3 C13CPD
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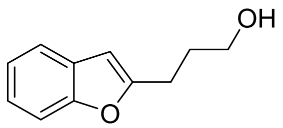
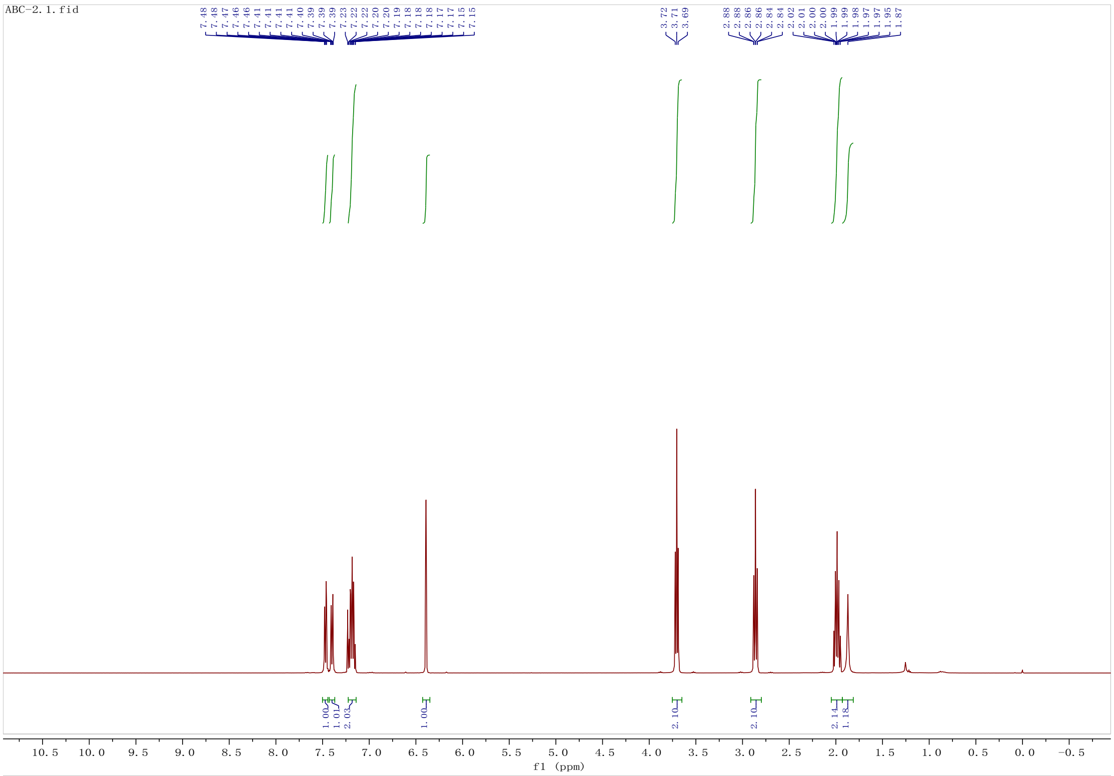
60.61
32.03
f1 (ppm)


OH
O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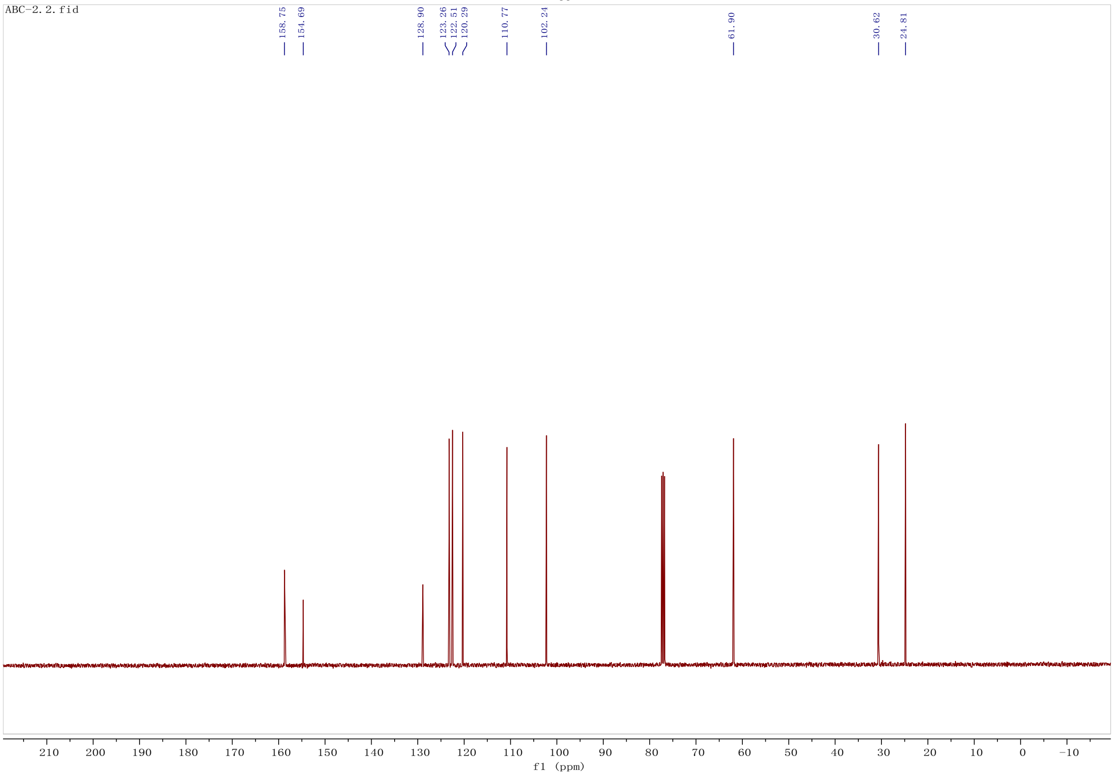
3.72 3.71 3.69
2.88 2.88 2.86 2.86 2.84 2.84 2.02 2.01 2.00 2.00 1.99 1.99 1.98 1.97 1.97 1.95 1.87
1.00 1.01 2.03 1.00 2.10 2.10 2.14 1.18
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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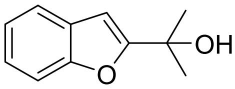
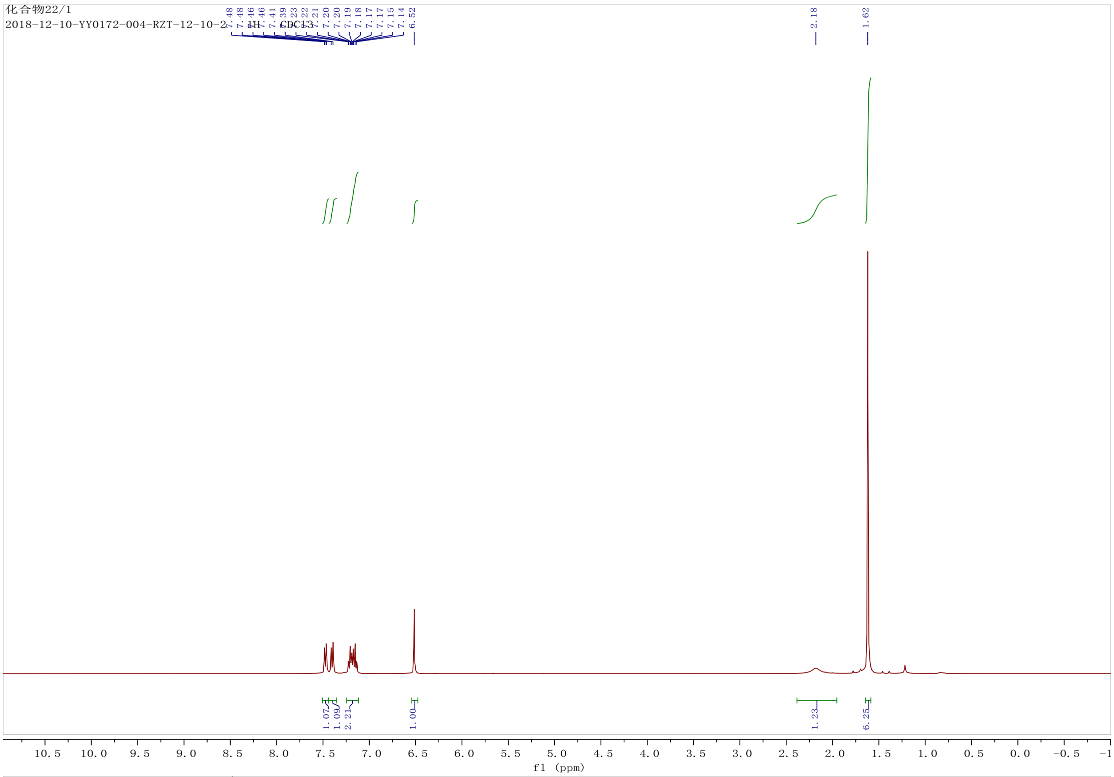
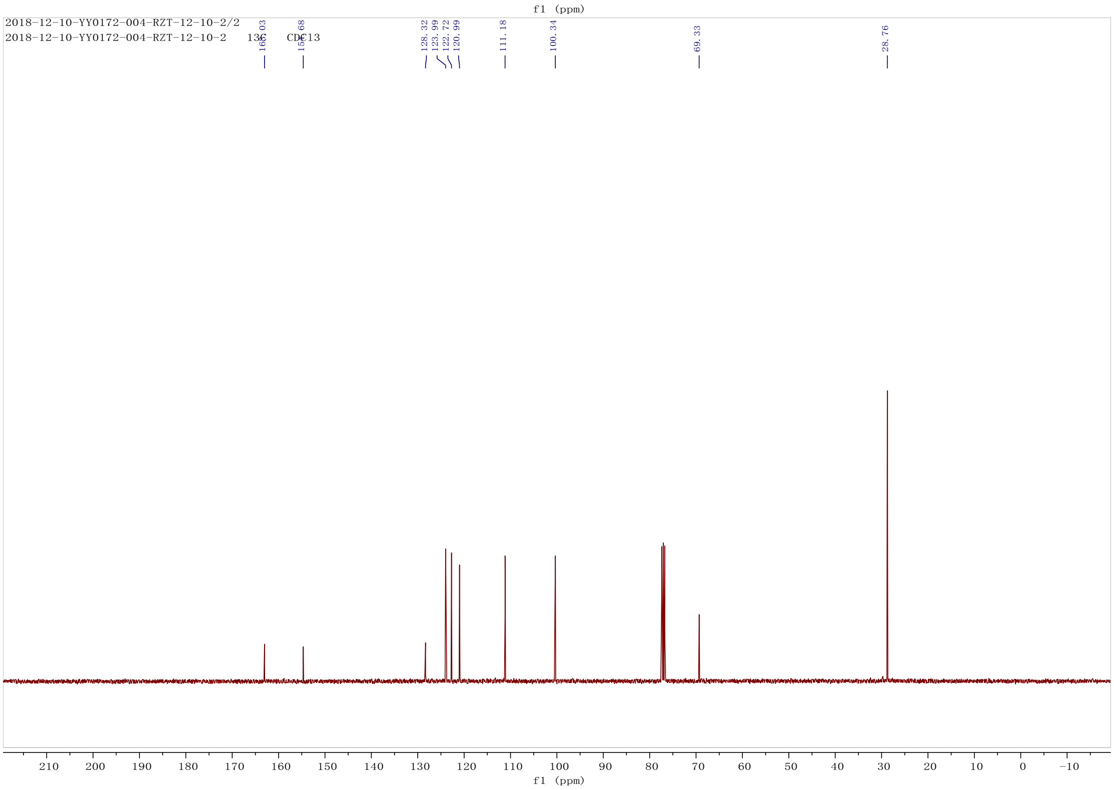
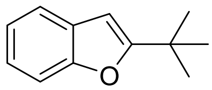
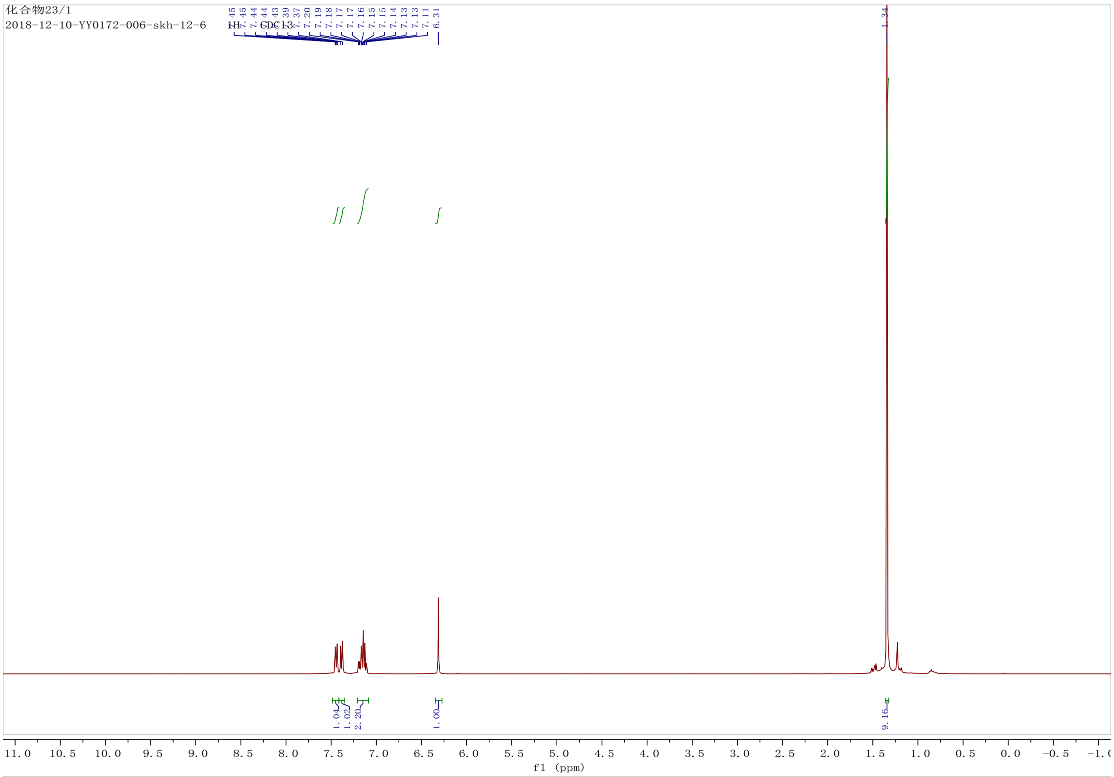
128.90 123.26 122.51 120.29
110.77
102.24
61.90
30.62 24.81
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

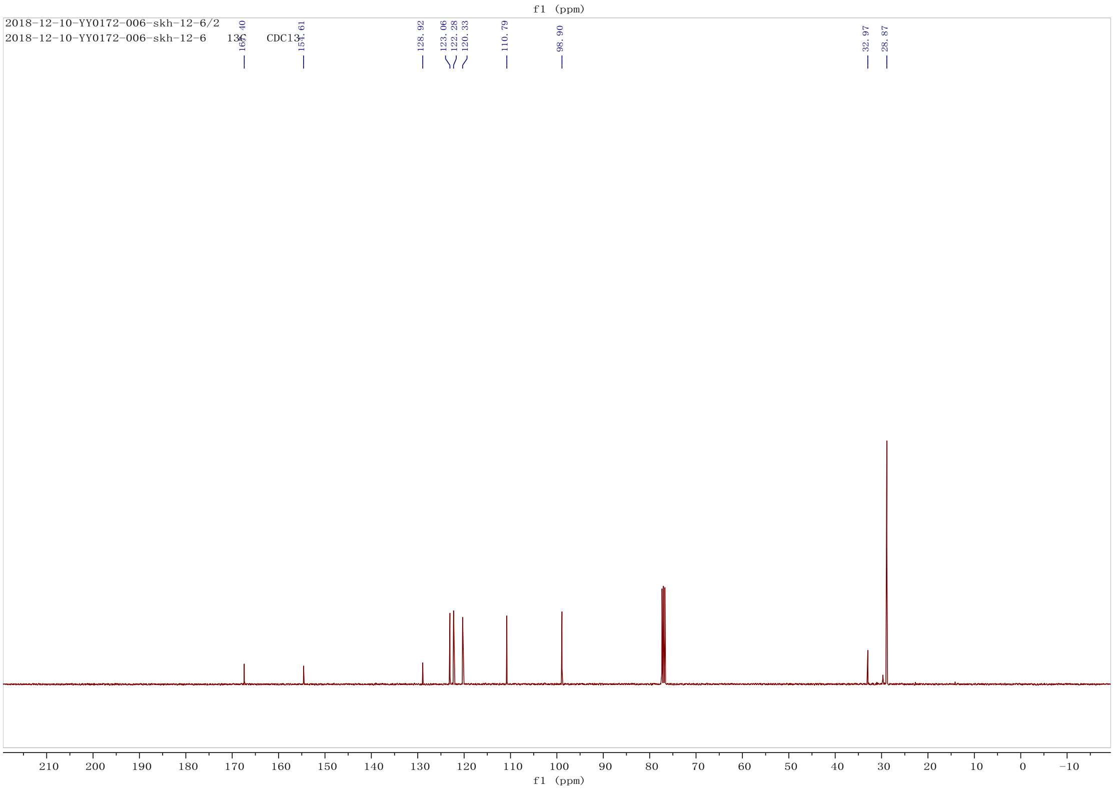

OH
O

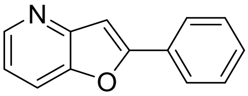

化合物22/1
2018-12-10-YY0172-004-RZT-12-10-2 1H CDCl3
7.48 7.48 7.46 7.46 7.41 7.39 7.23 7.22 7.22 7.21 7.20 7.20 7.19 7.18 7.17 7.17 7.15 7.14 6.52
2.18
1.62
1.07 1.09 2.21 1.00 1.23 6.25
f1 (ppm)

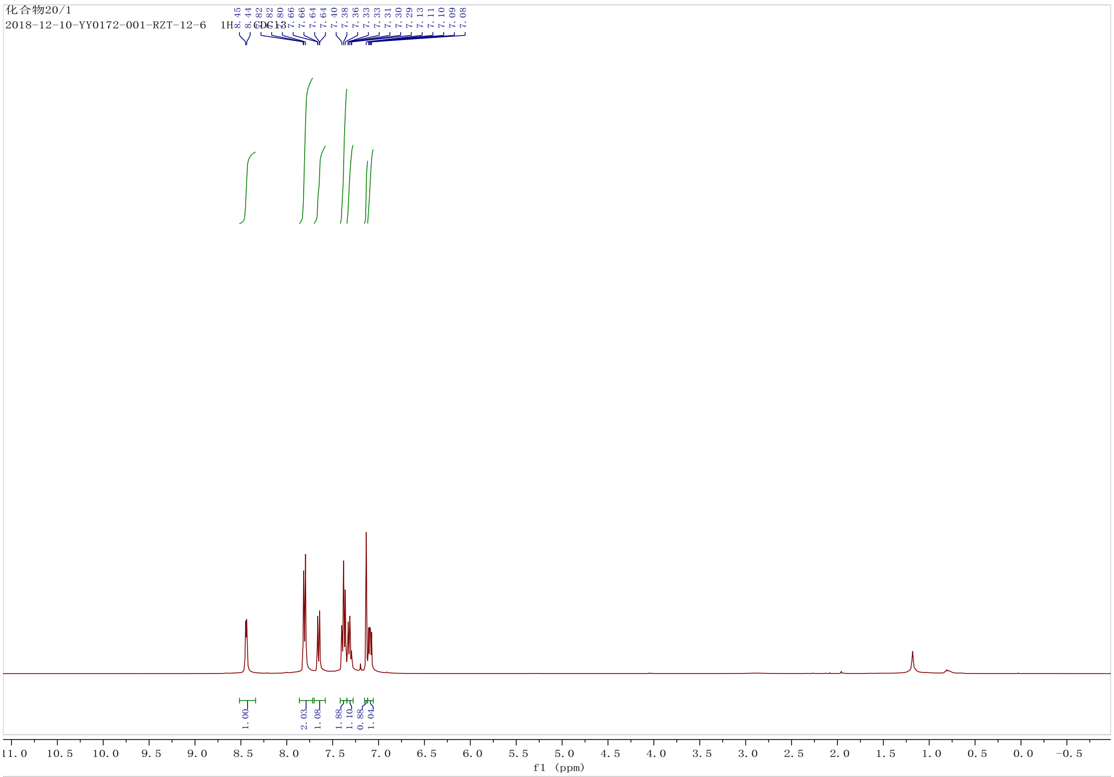

2018-12-10-YY0172-004-RZT-12-10-2/2
2018-12-10-YY0172-004-RZT-12-10-2 13C CDCl3
163.03
154.68
128.32 123.99 122.72 120.99
111.18
100.34
69.33
28.76
f1 (ppm)

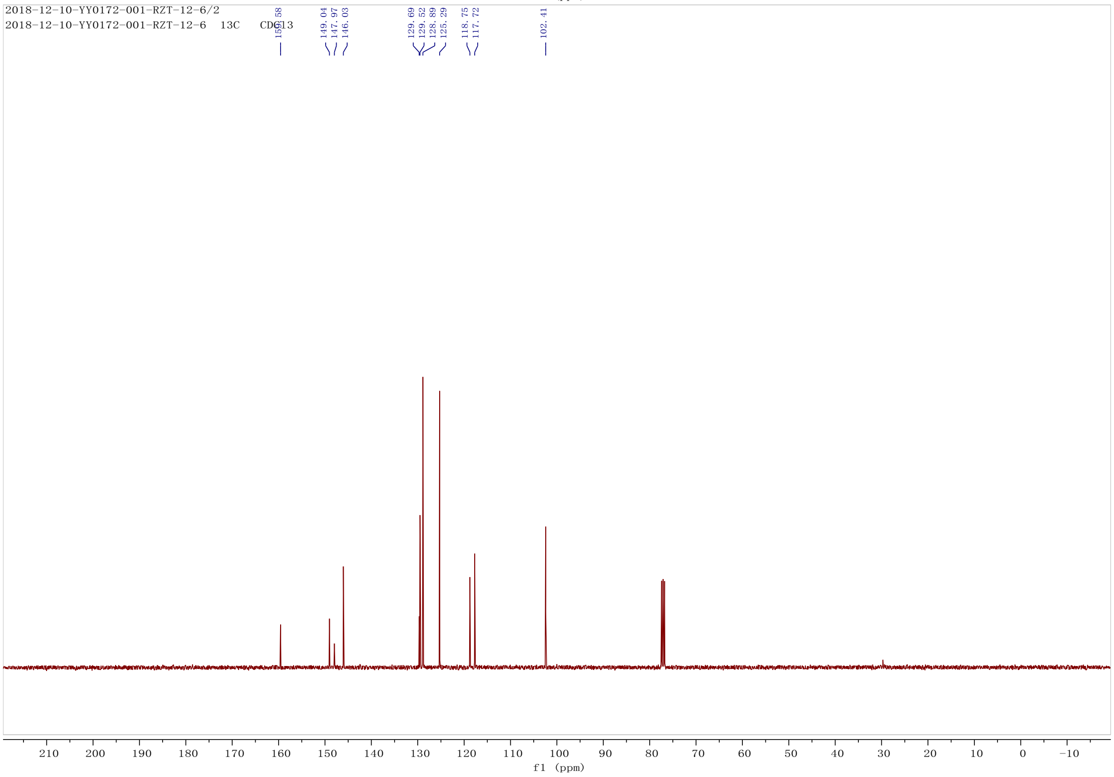


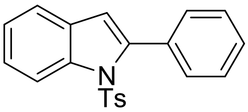

化合物23/1
2018-12-10-YY0172-006-skh-12-6
1H CDCl3
7.45 7.45 7.44 7.43 7.43 7.39 7.37 7.20 7.19 7.18 7.17 7.17 7.16 7.15 7.15 7.14 7.13 7.13 7.11 6.31
1.34
1.04 1.02 2.20 1.00 9.16
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

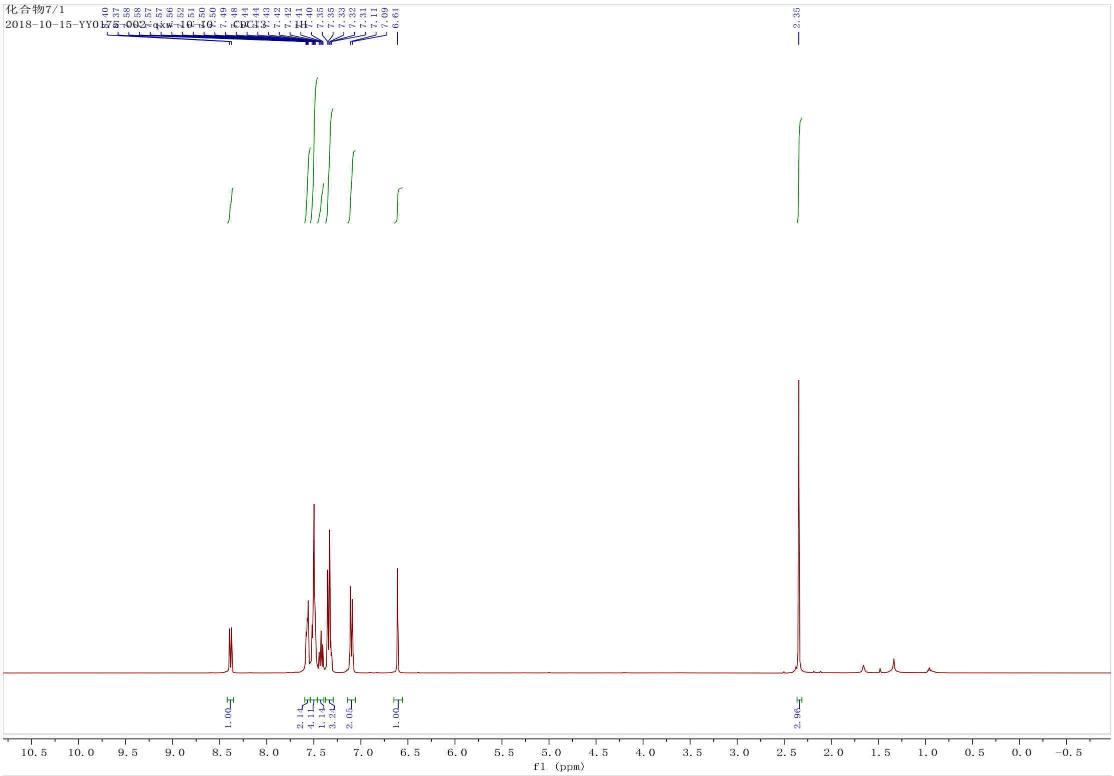

2018-12-10-YY0172-006-skh-12-6/2
2018-12-10-YY0172-006-skh-12-6
13C CDCl3
167.40 154.61 128.92 123.06 122.28 120.33 110.79 98.90 32.97 28.87
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

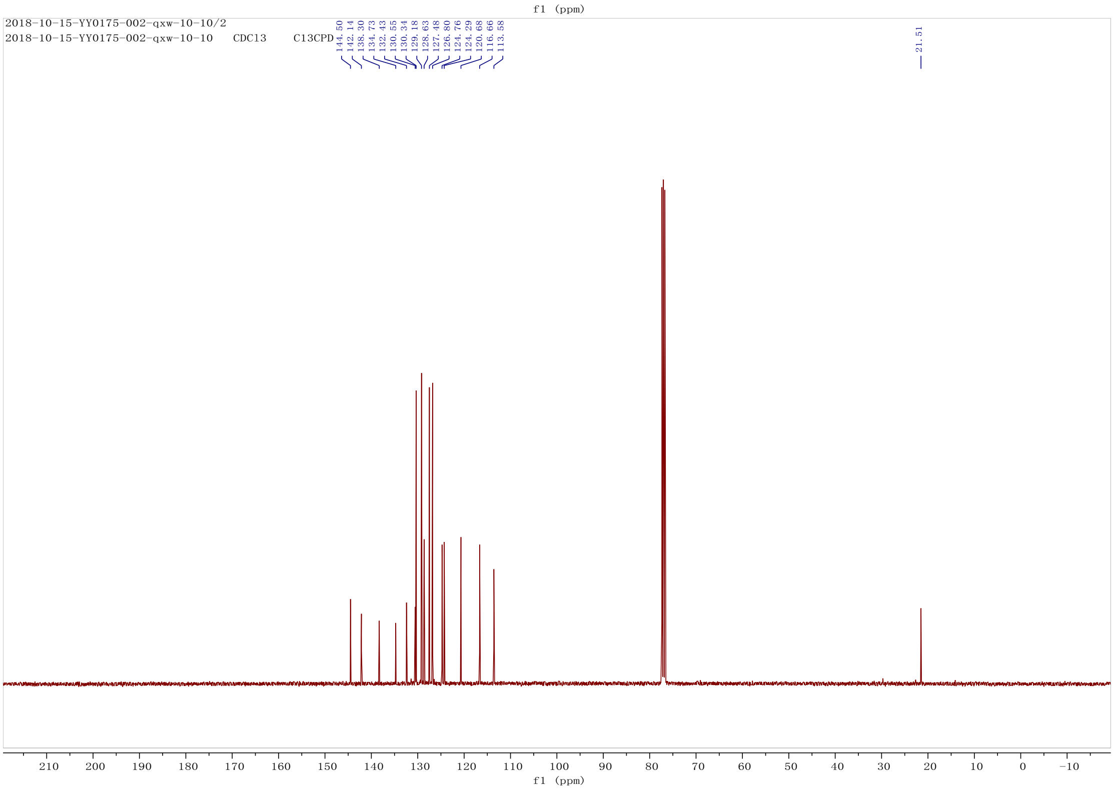

N
O

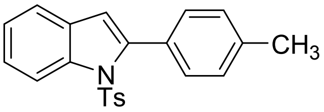

化合物20/1
2018-12-10-YY0172-001-RZT-12-6 1H CDCl3
8.45 8.44 7.82 7.82 7.80 7.66 7.66 7.64 7.64 7.40 7.38 7.36 7.33 7.33 7.31 7.30 7.29 7.13 7.11 7.10 7.09 7.08
1.00 2.03 1.08 1.88 1.10 0.88 1.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

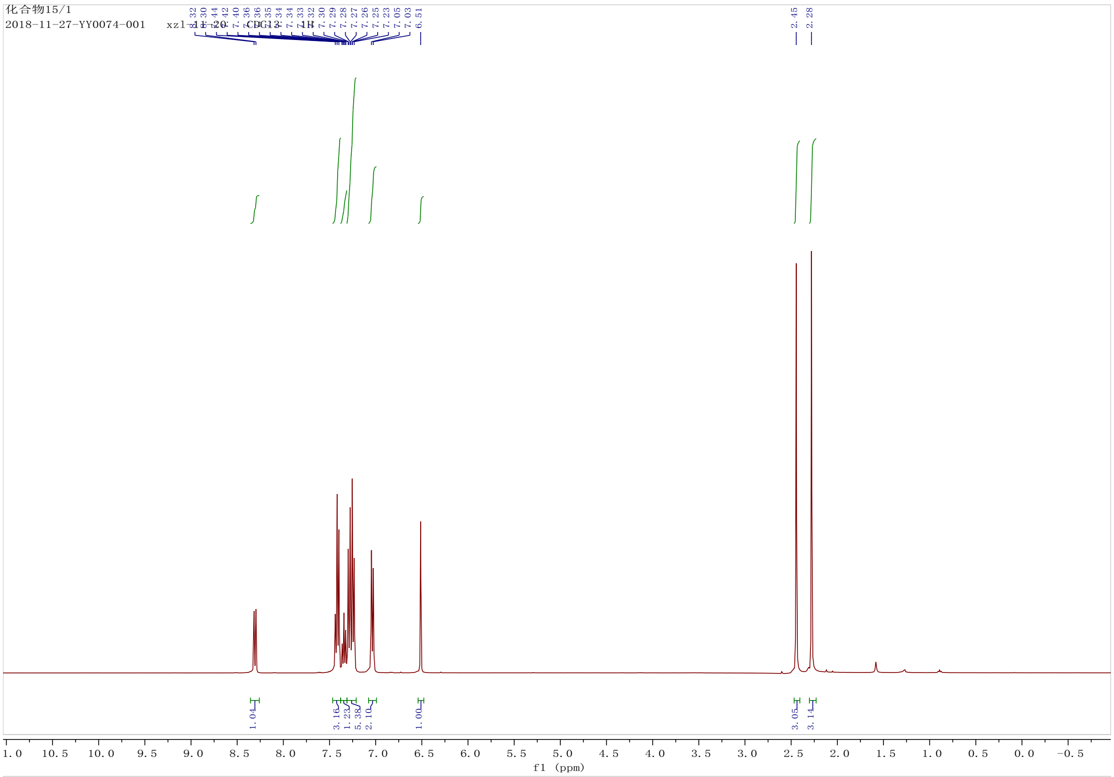

2018-12-10-YY0172-001-RZT-12-6/2
2018-12-10-YY0172-001-RZT-12-6 13C CDCl3
159.58
149.04 147.97 146.03
129.69 129.52 128.89 125.29
118.75 117.72
102.41
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

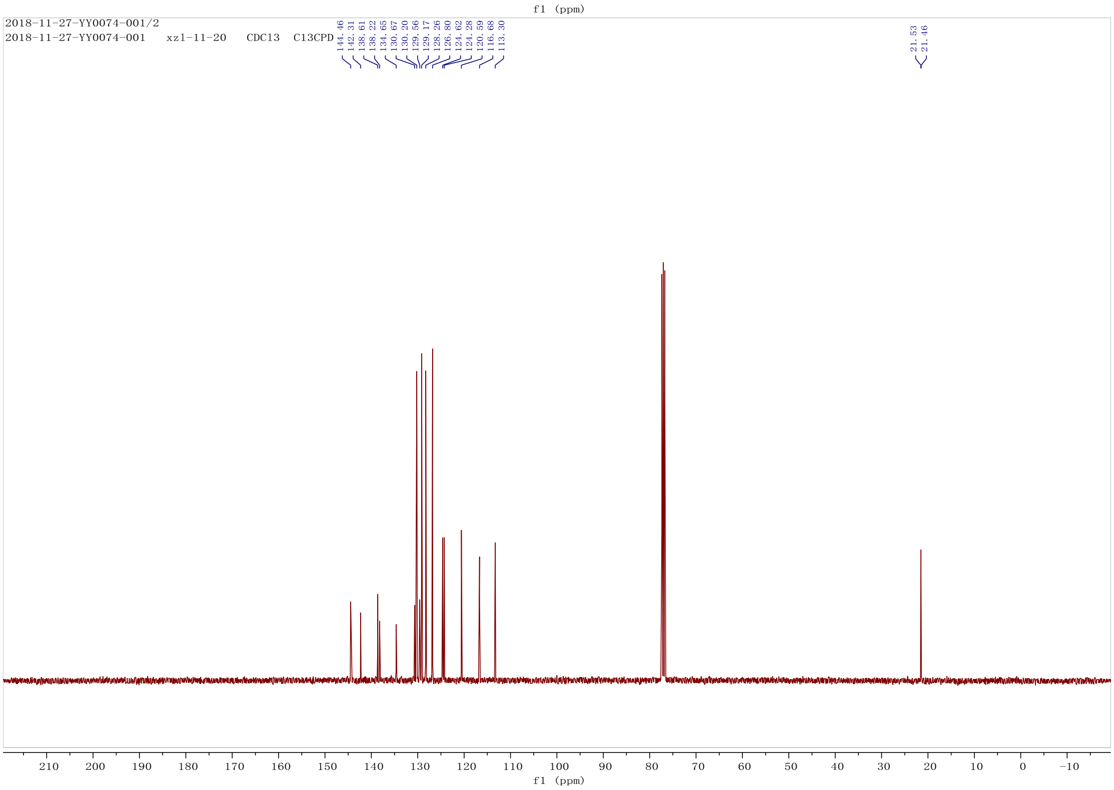

N
Ts

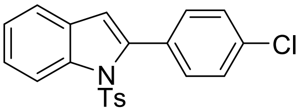

化合物7/1
CDCl3
2.35
f1 (ppm)

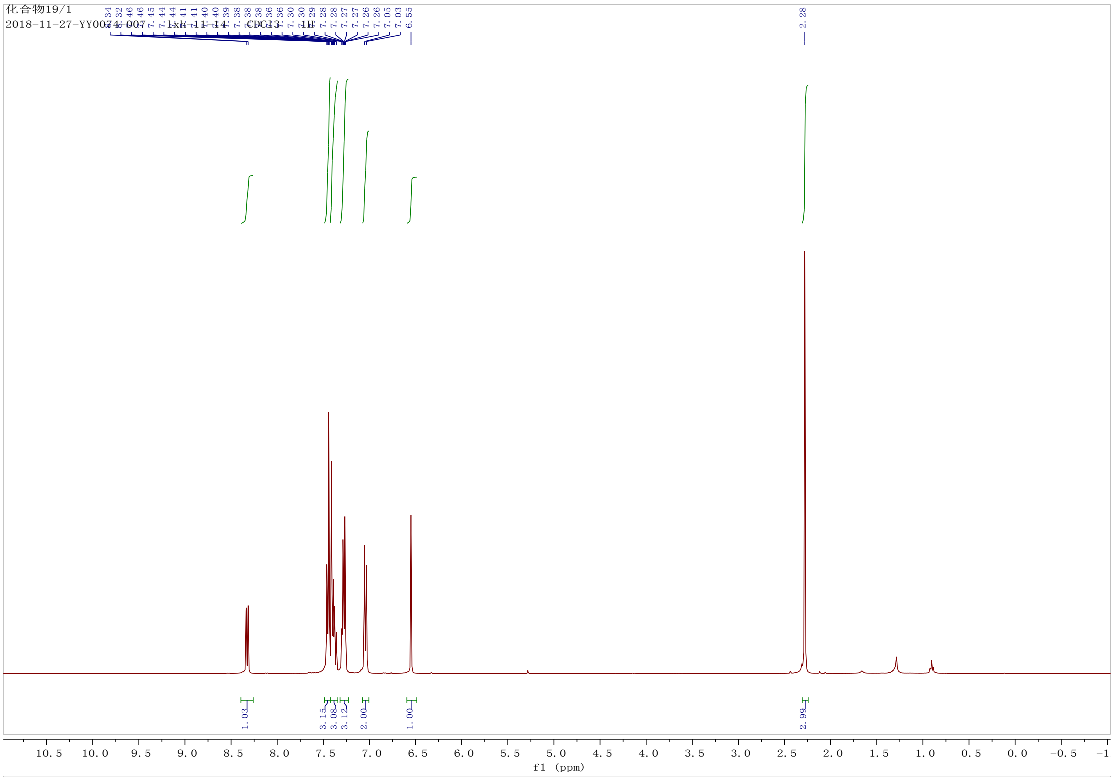

2018-10-15-YY0175-002-qxw-10-10/2
2018-10-15-YY0175-002-qxw-10-10 CDCl3 C13CPD
144.50
142.14
138.30
134.73
132.43
130.55
130.34
129.18
128.63
127.48
126.80
124.76
124.29
120.68
116.66
113.58
21.51
f1 (ppm)

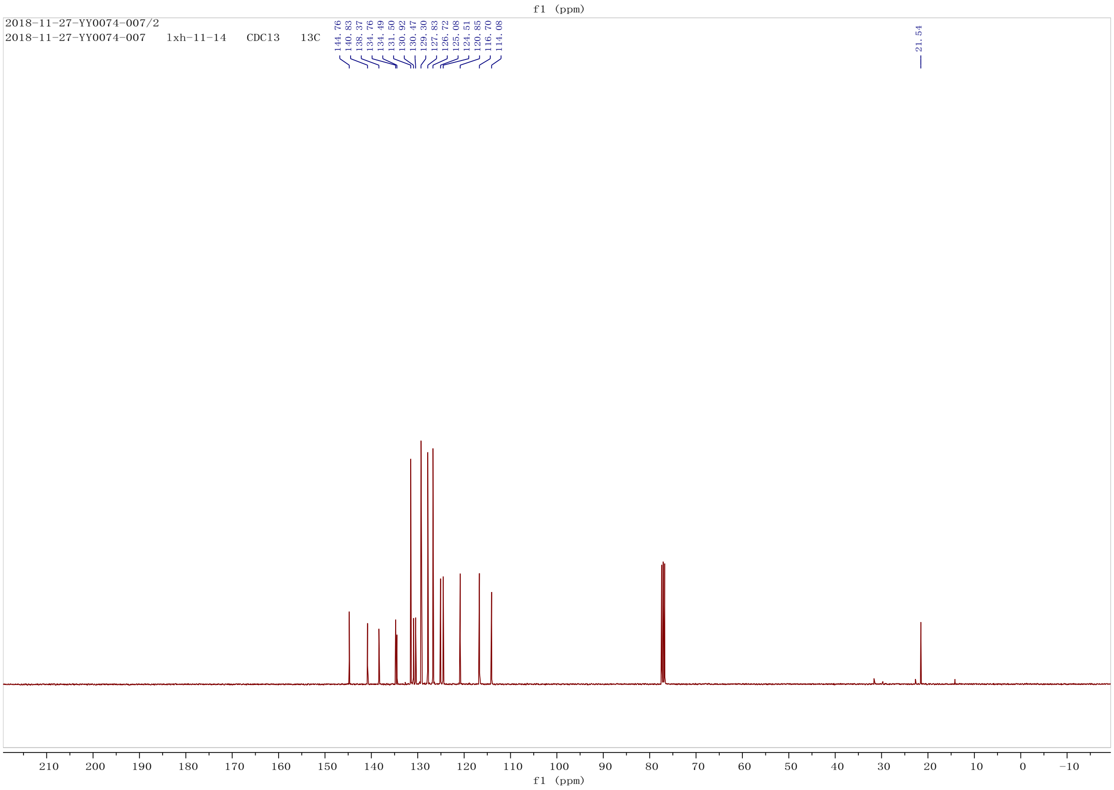

CH3
N
Ts

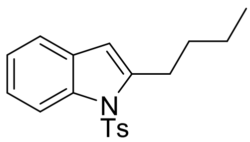

化合物15/1
2018-11-27-YY0074-001 xzl-11-20 CDCl3 1H
8.32
8.30
7.44
7.42
7.40
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.30
7.29
7.28
7.27
7.26
7.25
7.23
7.05
7.03
6.51
2.45
2.28
1.04
3.16
1.23
5.38
2.10
1.00
3.05
3.14
f1 (ppm)

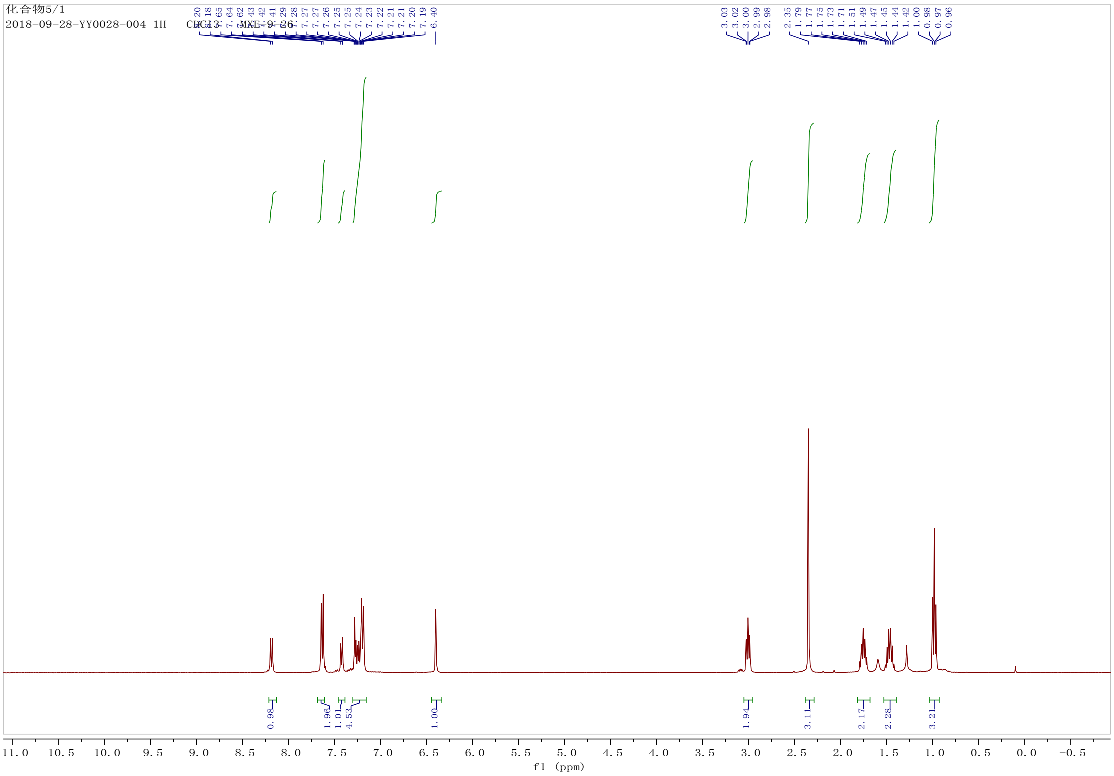

2018-11-27-YY0074-001/2
2018-11-27-YY0074-001 xzl-11-20 CDCl3 C13CPD
144.46
142.31
138.61
138.22
134.65
130.67
130.20
129.56
129.17
128.26
126.80
124.62
124.28
120.59
116.68
113.30
21.53
21.46
f1 (ppm)

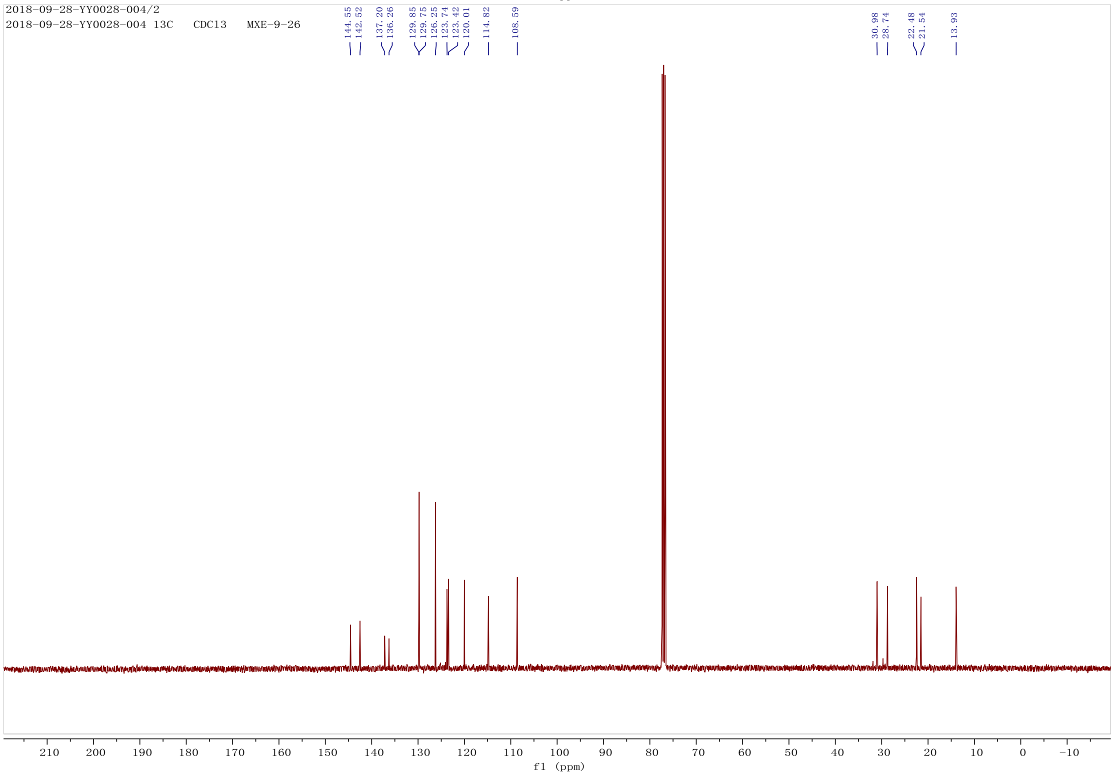

N
Ts
Cl

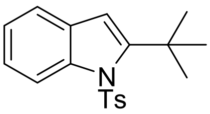

化合物19/1
2018-11-27-YY0074-007 lxh-11-14 CDCl3 1H
2.28
6.55
f1 (ppm)

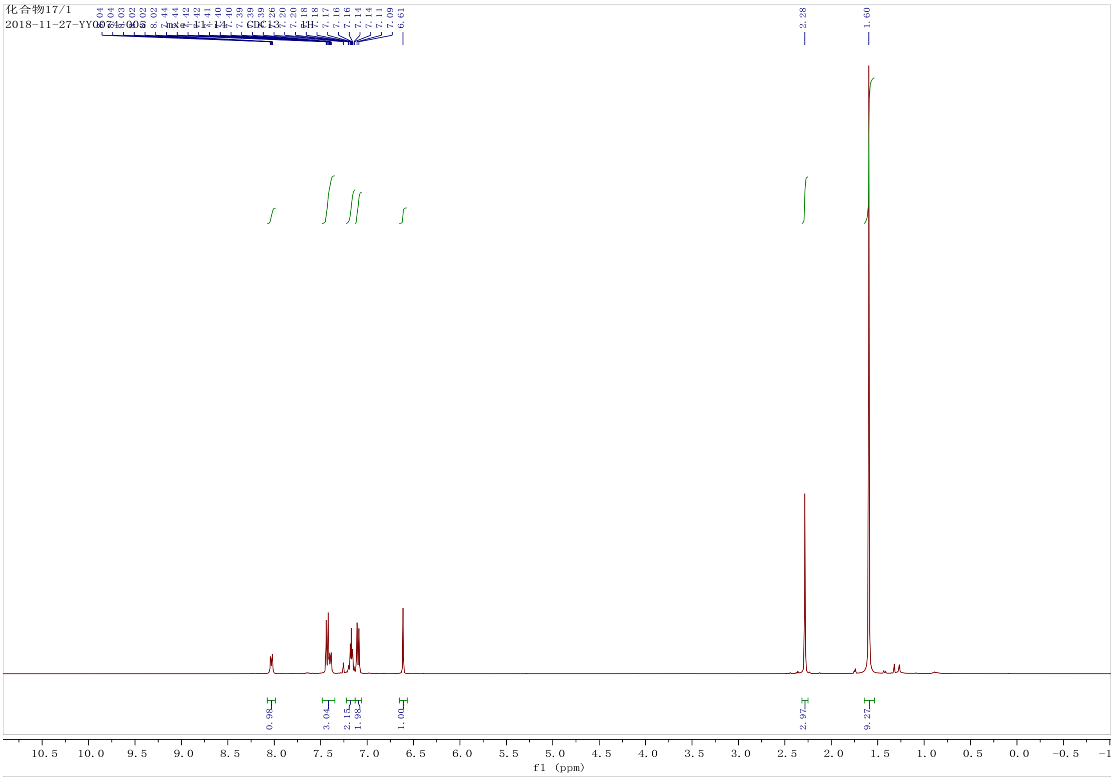

2018-11-27-YY0074-007/2
2018-11-27-YY0074-007 lxh-11-14 CDCl3 13C
144.76
140.83
138.37
134.76
134.49
131.50
130.92
130.47
129.30
127.83
126.72
125.08
124.51
120.85
116.70
114.08
21.54
f1 (ppm)

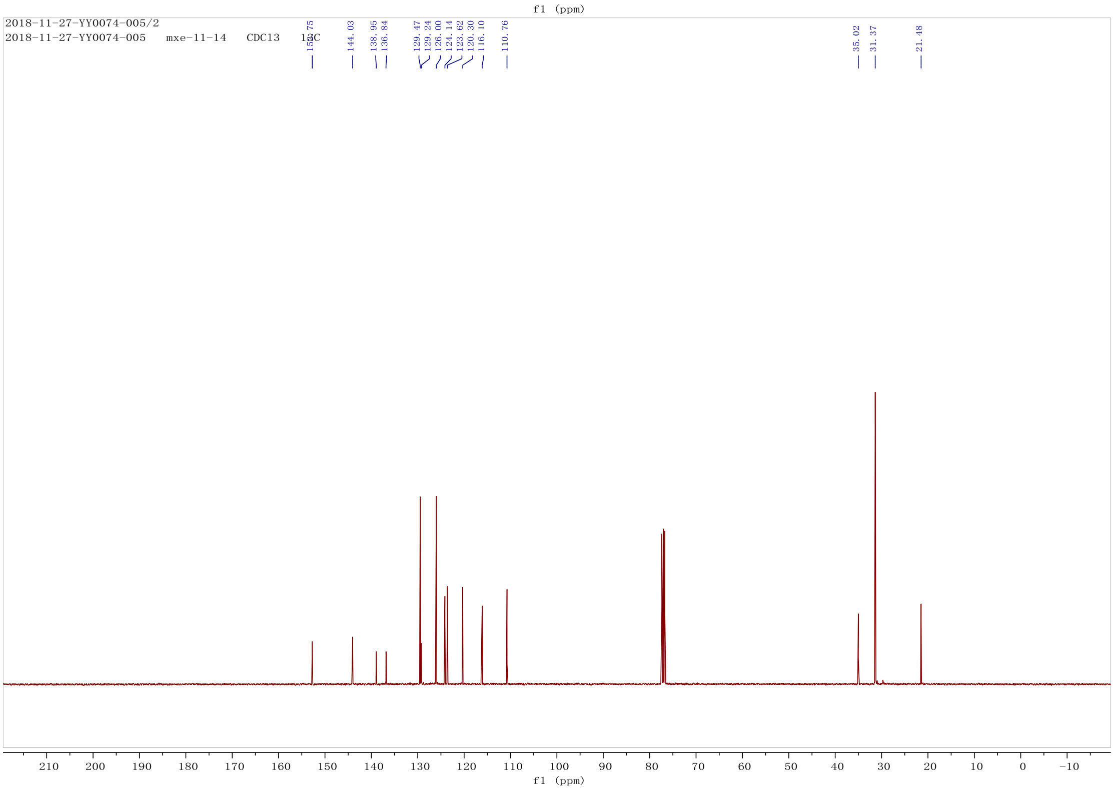

N
Ts

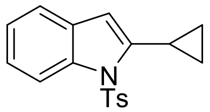

化合物5/1
2018-09-28-YY0028-004 1H CDCl3 MXE-9-26
8.20 8.18 7.65 7.64 7.62 7.43 7.42 7.41 7.29 7.28 7.27 7.27 7.26 7.25 7.25 7.24 7.23 7.22 7.21 7.21 7.20 7.19 6.40
3.03 3.02 3.00 2.99 2.98 2.35 1.79 1.77 1.75 1.73 1.71 1.51 1.49 1.47 1.45 1.44 1.42 1.00 0.98 0.97 0.96
0.98 1.96 1.01 4.53 1.00 1.94 3.11 2.17 2.28 3.21
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

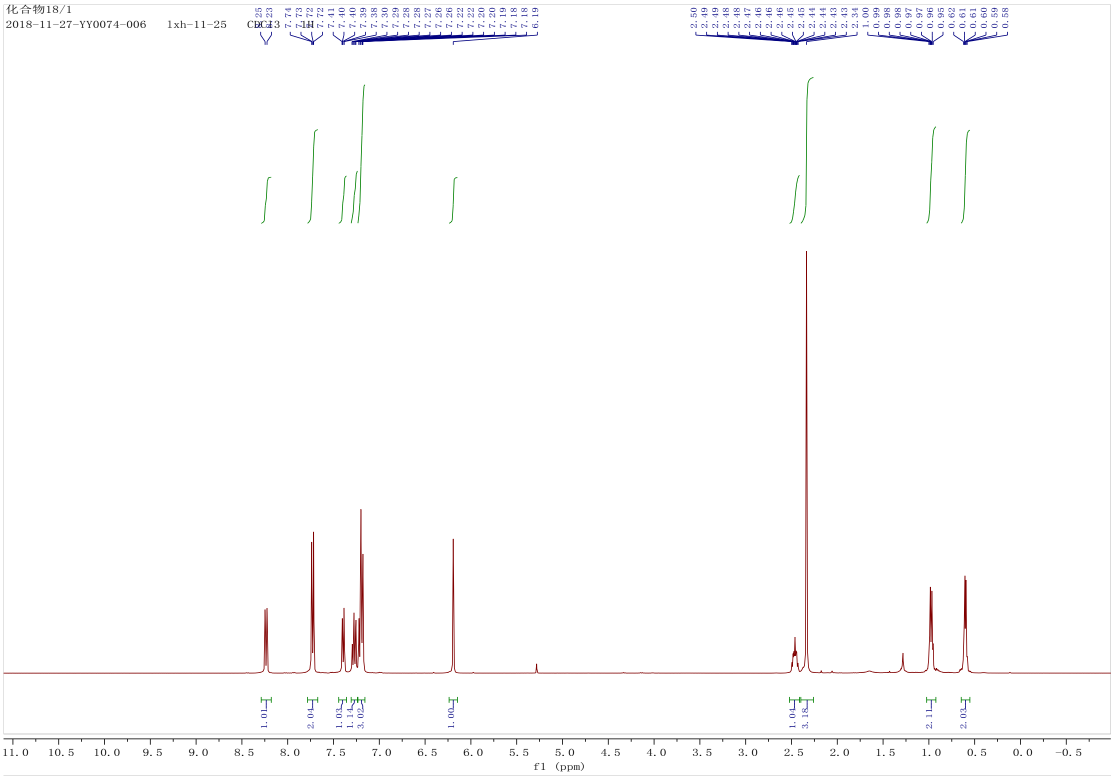

2018-09-28-YY0028-004/2
2018-09-28-YY0028-004 13C CDCl3 MXE-9-26
144.55 142.52 137.20 136.26 129.85 129.75 126.25 123.74 123.42 120.01 114.82 108.59
30.98 28.74 22.48 21.54 13.93
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

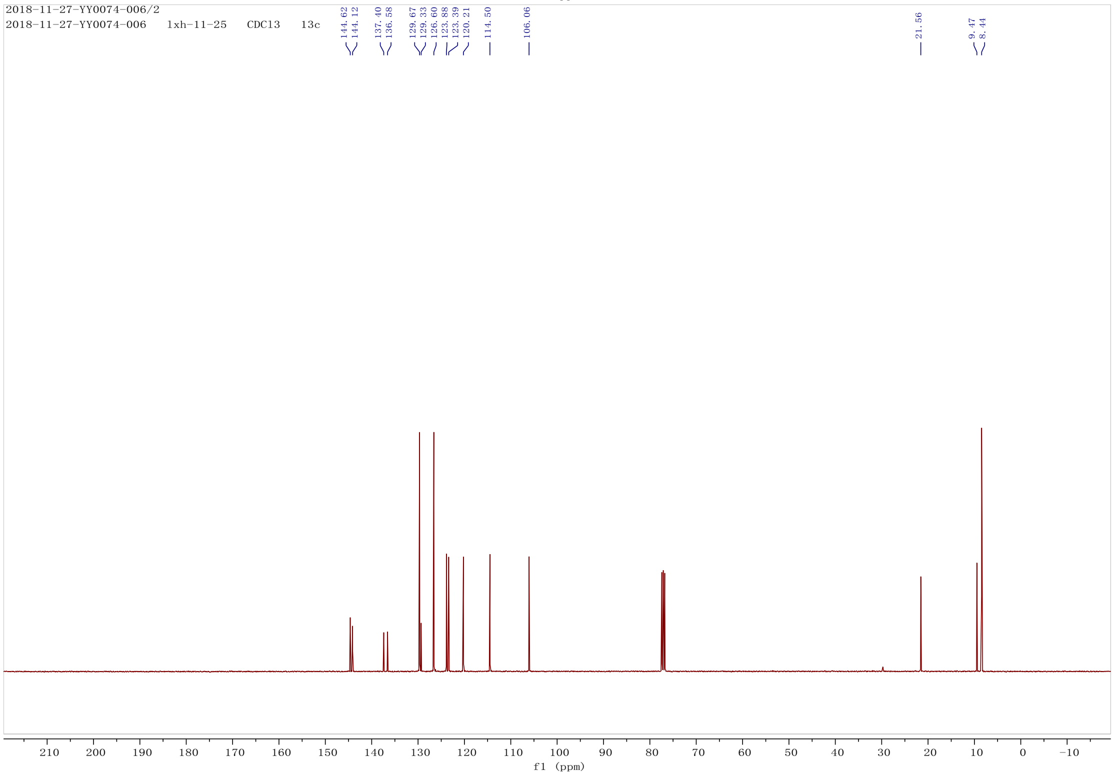

N
Ts

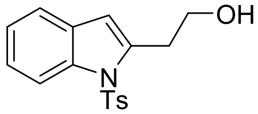

化合物17/1
2018-11-27-YY0074-005
CDCl3
1H
2.28
1.60
0.98
3.04
2.15
1.98
1.00
2.97
9.27
f1 (ppm)

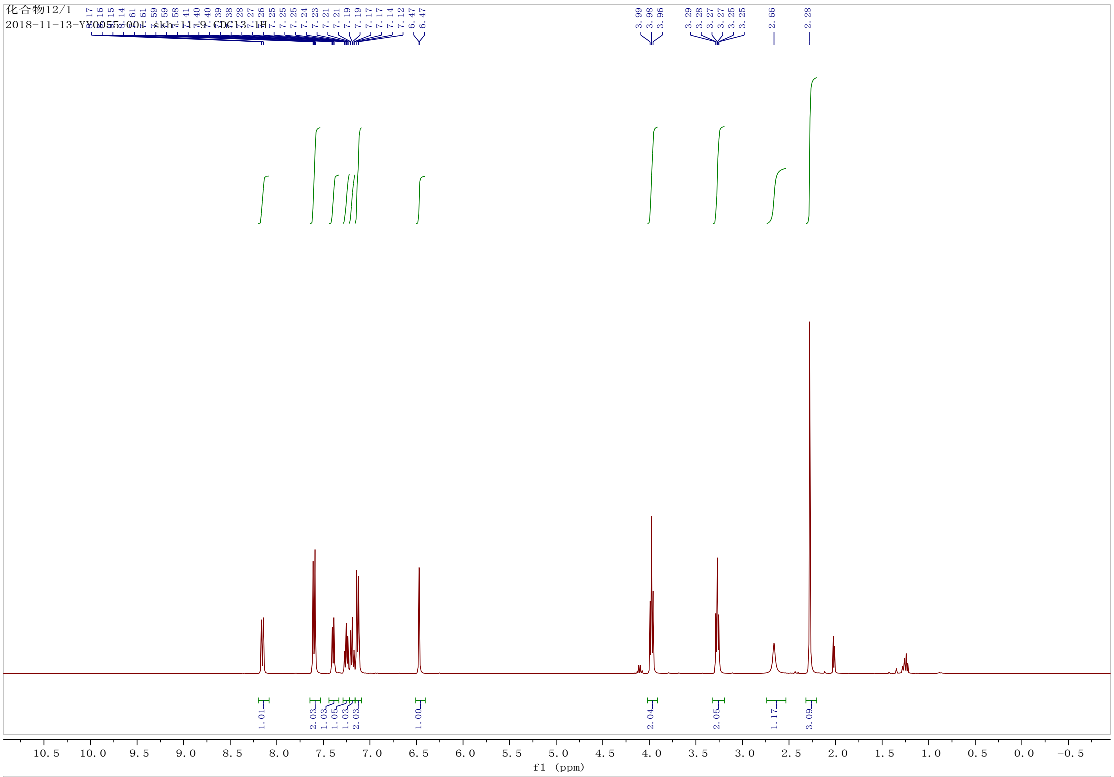

2018-11-27-YY0074-005/2
2018-11-27-YY0074-005 mxe-11-14 CDCl3 13C
144.03
138.95
136.84
129.47
129.24
126.00
124.14
123.62
120.30
116.10
110.76
35.02
31.37
21.48
f1 (ppm)

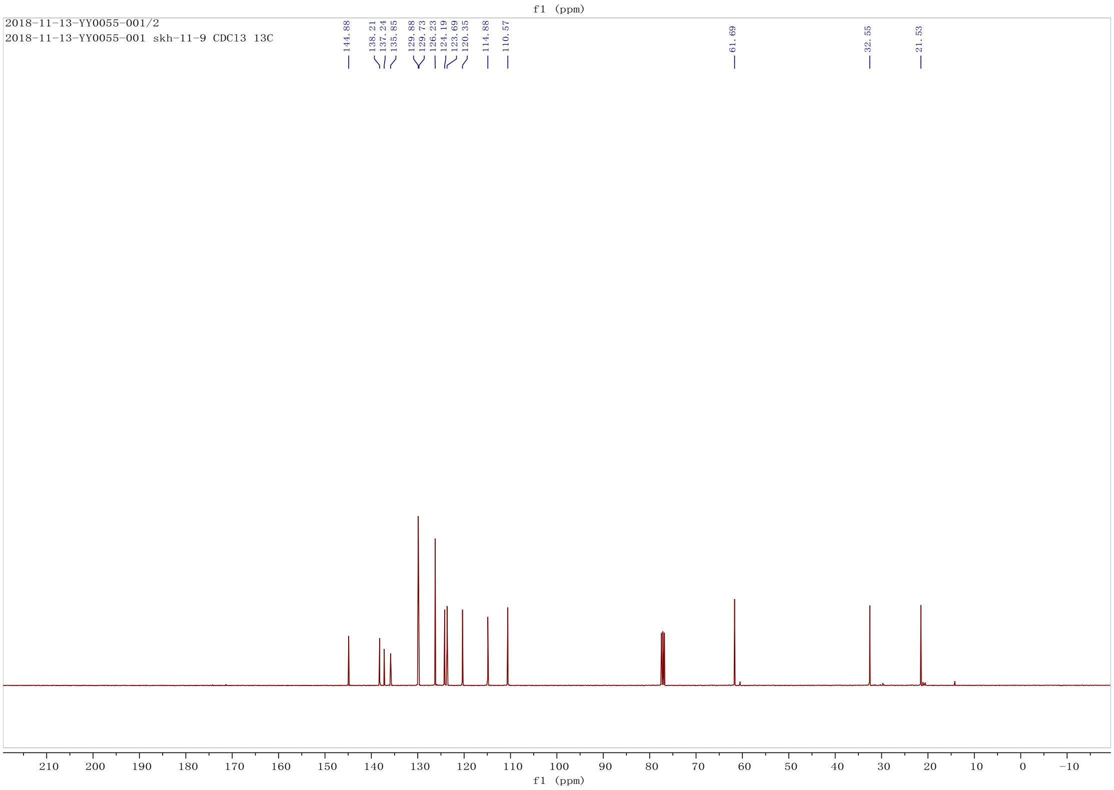


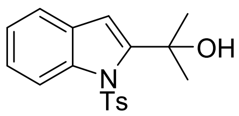

化合物18/1
2018-11-27-YY0074-006 1xh-11-25 CDCl3 1H
f1 (ppm)

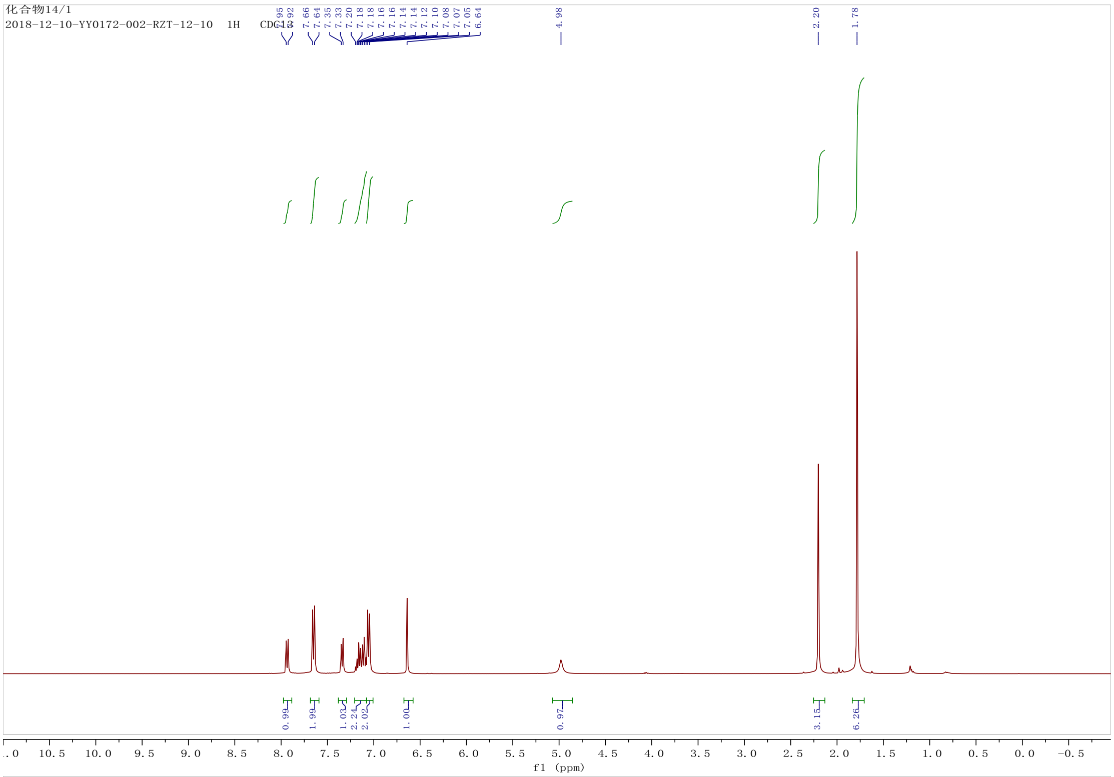

2018-11-27-YY0074-006/2
2018-11-27-YY0074-006 1xh-11-25 CDCl3 13c
144.62
144.12
137.40
136.58
129.67
129.33
126.60
123.88
123.39
120.21
114.50
106.06
21.56
9.47
8.44
f1 (ppm)

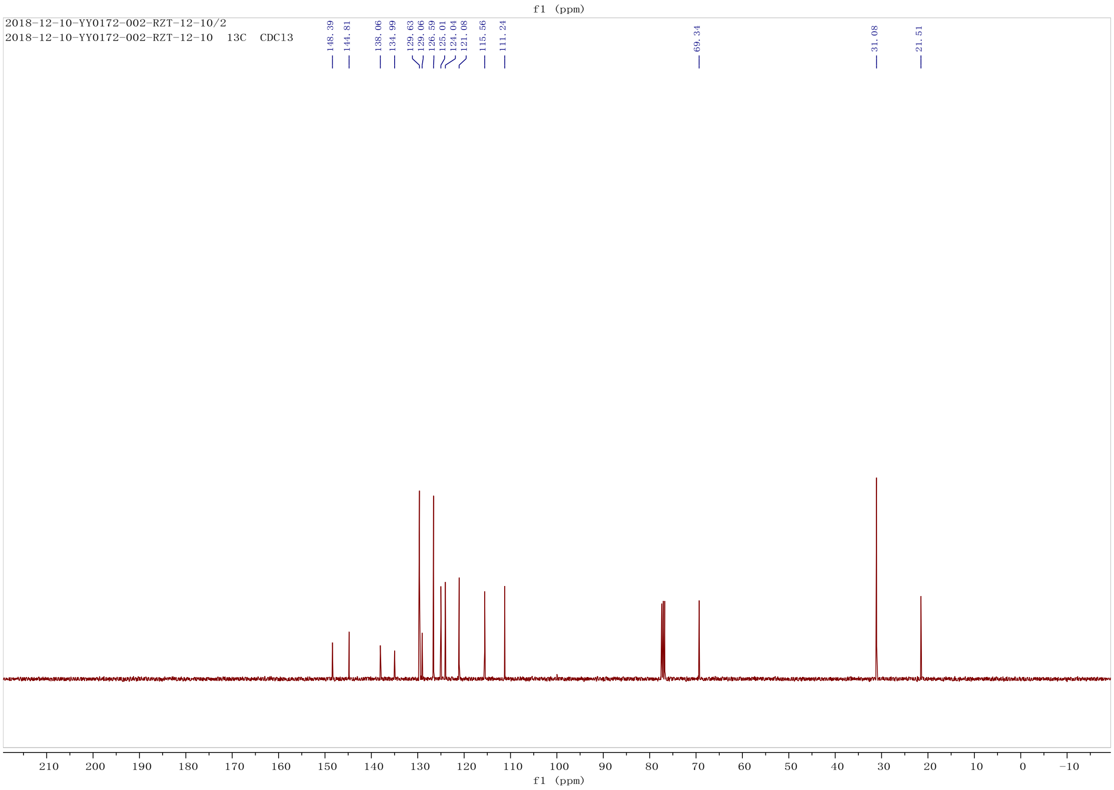

OH
N
Ts

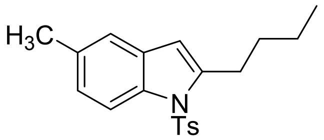

化合物12/1
2018-11-13-YY0055-001 skh-11-9 CDCl3 1H
f1 (ppm)

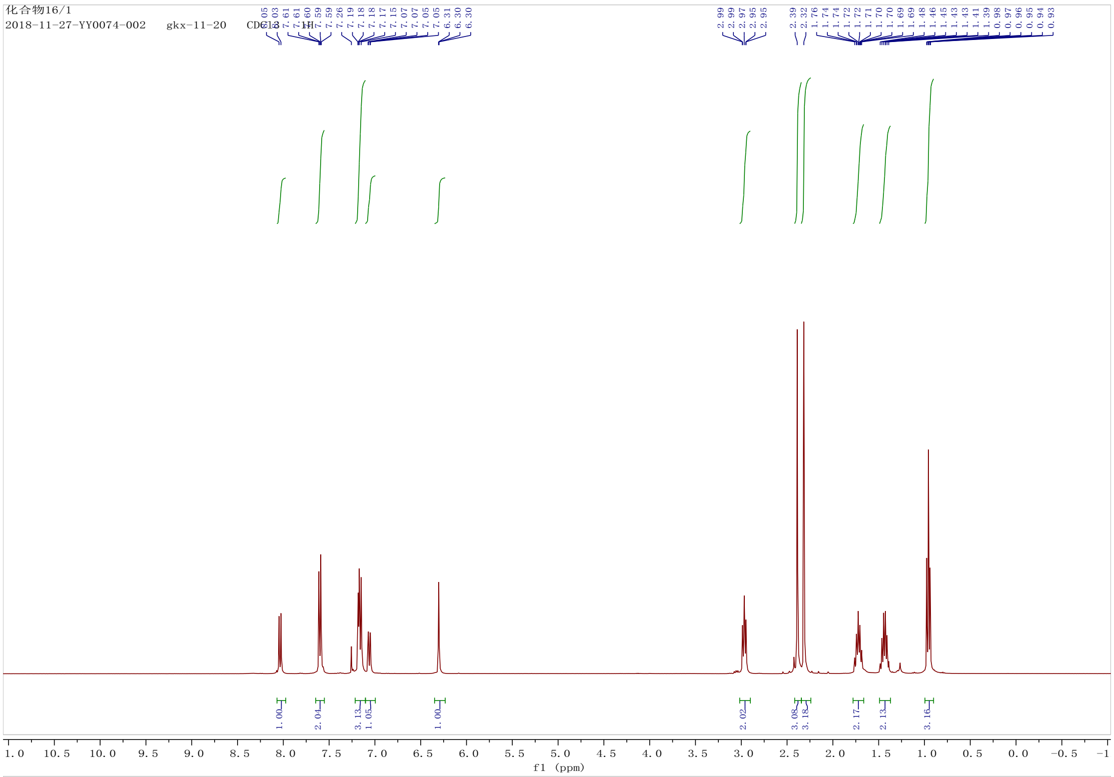

2018-11-13-YY0055-001/2
2018-11-13-YY0055-001 skh-11-9 CDCl3 13C
144.88
138.21
137.24
135.85
129.88
129.73
126.23
124.19
123.69
120.35
114.88
110.57
61.69
32.55
21.53
f1 (ppm)

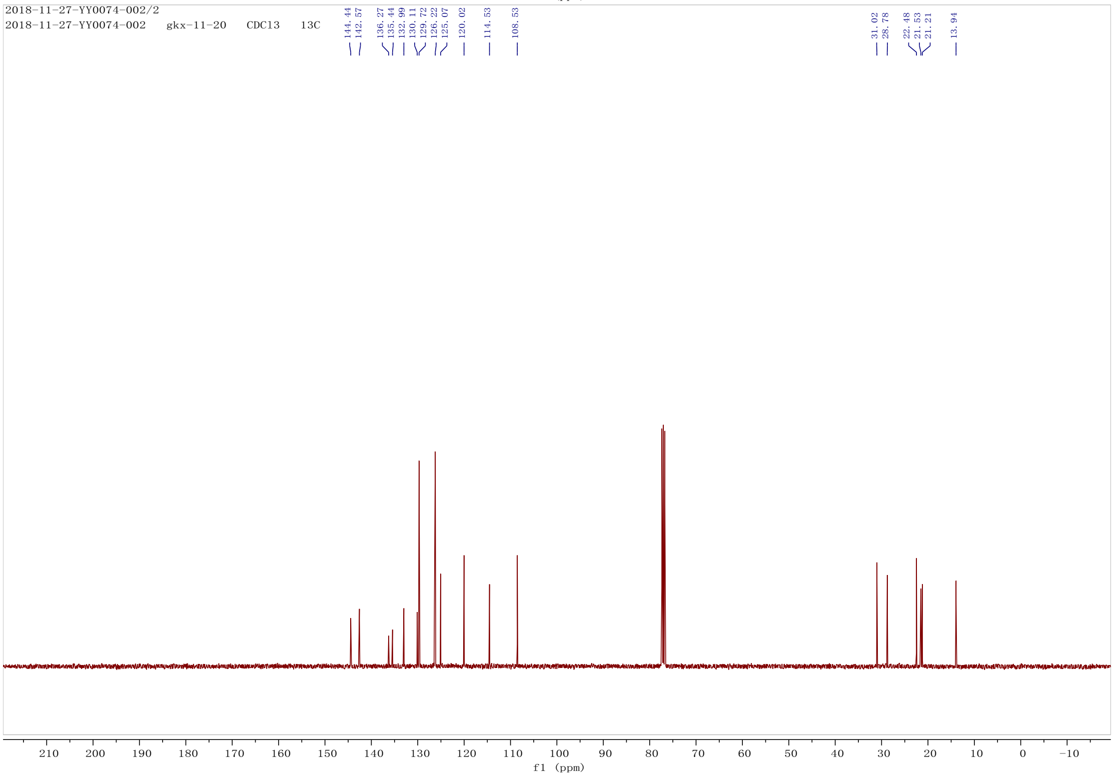

OH
N
Ts

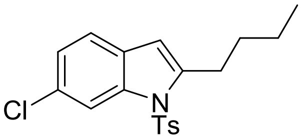

化合物14/1
2018-12-10-YY0172-002-RZT-12-10 1H CDCl3
7.95 7.92 7.66 7.64 7.35 7.33 7.20 7.18 7.18 7.16 7.16 7.14 7.14 7.12 7.10 7.08 7.07 7.05 6.64
4.98
2.20
1.78
0.99 1.98 1.03 2.14 2.02 1.00 0.97 3.15 6.26
f1 (ppm)

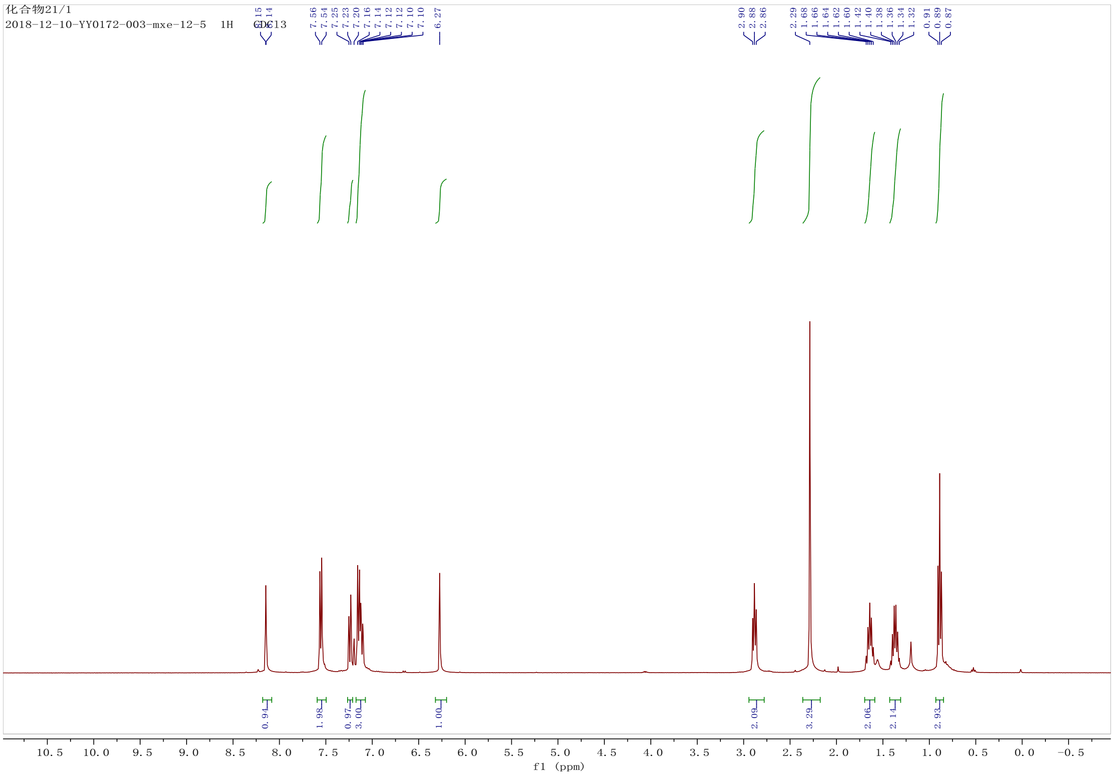

2018-12-10-YY0172-002-RZT-12-10/2
2018-12-10-YY0172-002-RZT-12-10 13C CDCl3
148.39 144.81 138.06 134.99 129.63 129.06 126.59 125.01 124.04 121.08 115.56 111.24
69.34
31.08
21.51
f1 (ppm)


H3C
N
Ts

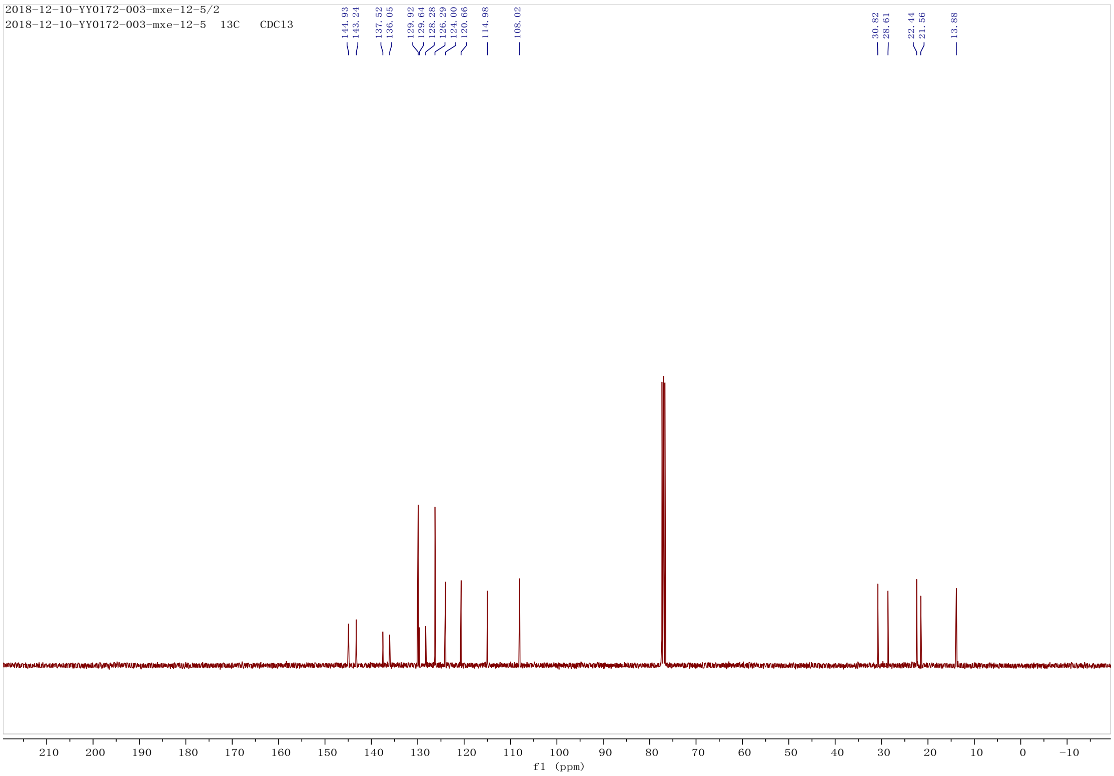

化合物16/1
2018-11-27-YY0074-002 gkx-11-20 CDCl3 1H
8.05 8.03 7.61 7.60 7.59 7.59 7.26 7.19 7.18 7.18 7.17 7.15 7.07 7.07 7.05 7.05 6.31 6.30 6.30
2.99 2.99 2.97 2.95 2.95 2.39 2.32 1.76 1.74 1.74 1.72 1.72 1.71 1.70 1.70 1.69 1.69 1.48 1.46 1.45 1.43 1.43 1.41 1.39 0.98 0.97 0.96 0.95 0.94 0.93
1.00 2.04 3.13 1.05 1.00 2.02 3.08 3.18 2.17 2.13 3.16
f1 (ppm)


2018-11-27-YY0074-002/2
2018-11-27-YY0074-002 gkx-11-20 CDCl3 13C
144.44 142.57 136.27 135.44 132.99 130.11 129.72 126.22 125.07 120.02 114.53 108.53
31.02 28.78 22.48 21.53 21.21 13.94
f1 (ppm)





化合物21/1
2018-12-10-YY0172-003-mxe-12-5 1H CDCl3
8.15
8.14
7.56
7.54
7.25
7.23
7.20
7.16
7.14
7.12
7.12
7.10
7.10
6.27
2.90
2.88
2.86
2.29
1.68
1.66
1.64
1.62
1.60
1.42
1.40
1.38
1.36
1.34
1.32
0.91
0.89
0.87
0.94
1.98
0.97
3.00
1.00
2.09
3.29
2.06
2.14
2.93
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


2018-12-10-YY0172-003-mxe-12-5/2
2018-12-10-YY0172-003-mxe-12-5 13C CDCl3
144.93
143.24
137.52
136.05
129.92
129.64
128.28
126.29
124.00
120.66
114.98
108.02
30.82
28.61
22.44
21.56
13.88
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)