Supporting Information for

A $Hg(OTf)_2$-Catalyzed Enolate Umpolung Reaction Enables the Synthesis of Coumaran-3-ones and Indolin-3-ones

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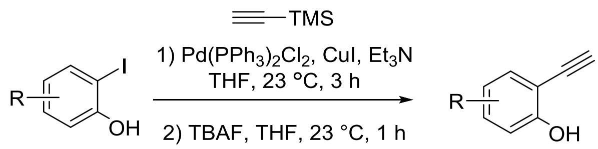
1. General Methods.

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 ℃ on Bruker Avance 400 Ultrashield apparatus (400 MHz, $CDCl_3$ as solvent). Mass spectra were recorded on a Waters LCT Premier Spectrometer (ESI). Infrared spectra of **2d** and **6i** were recorded on a Nicolet AVATER FTIR330 spectrometer as thin film and are reported in reciprocal centimeter (cm^{-1}). IR data of other products have been reported in previous publications.[1]

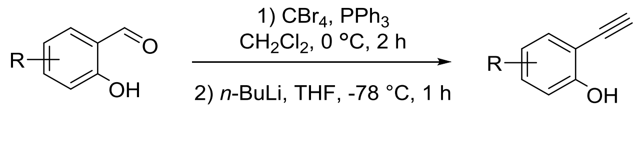
Note 1: The NMR spectra of compounds **2a, 8a'-c'** were calibrated to 7.26 ppm ($CHCl_3$ in $CDCl_3$). All other compounds were calibrated to 0 ppm (TMS in $CDCl_3$).

Note 2: Warning! $Hg(OTf)_2$ and the organomercury intermediates generated during the reactions might be toxic. Please take special care when operating reactions and disposing mercury containing waste.

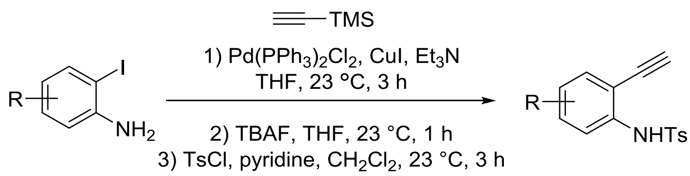
2. Procedures for the preparation of substrates.



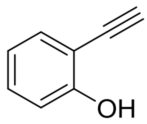
General procedure A: $Pd(PPh_3)_2Cl_2$ (0.06 mmol), CuI (0.12 mmol) and Et_3N (9 mmol) were added sequentially to a solution of 2-iodophenol (3 mmol) and trimethylsilylacetylene (4.5 mmol) in THF (10 mL) at 23 °C and the mixture was stirred at this temperature for 3 h before it was quenched with saturated aqueous NH_4Cl (10 mL). The aqueous layer was extracted with Et_2O (10 mL) and the combined organic layer was washed sequentially with 0.1 N HCl (10 mL), water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was dissolved in THF (15 mL) and tetrabutylammonium fluoride (4.5 mL, 1.0 M in THF, 4.5 mmol) was added dropwise. The reaction mixture was then stirred at 23 ℃ for 1 h before it was quenched with saturated aqueous NH_4Cl (15 mL). The aqueous layer was extracted with Et_2O 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=10/1) to give 2-ethynylphenol. Substrates **1b**, **1g** and **1h** were synthesized using general procedure A.



General procedure B: To a stirred solution of salicylaldehyde (10 mmol) and carbon tetrabromide (20 mmol) in dichloromethane (10 mL) was added triphenylphosphine (40 mmol) in portions over a period of 20 minutes at 0 ℃ temperature. The reaction mixture was allowed to stir at 0 ℃ temperature for 2 h before it was quenched with water (15 mL). The reaction mixture was extracted with dichloromethane (2 x 20 mL) and the organic layers were washed with brine (10 mL). The organic layers were dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (hexane/EtOAc=10/1) to give product. The product was then dissolved in THF (40 mL) and *n*-BuLi (15 mL, 2.0 M in hexanes, 30 mmol) was added dropwise at -78 °C and the mixture was stirred at -78 °C for 1 h before it was quenched with saturated aqueous NH_4Cl (50 mL). The aqueous layer was extracted with Et_2O (50 mL) and the combined organic layer was washed sequentially with water (50 mL) and brine (50 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (hexane/EtOAc=10/1) to give 2-ethynylphenol. Substrates **1c**, **1d**, **1e**, **1f**, **1i**, **1j**, **1k** and **1l** were synthesized using general procedure B.



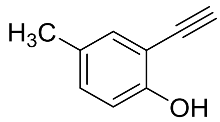
General procedure C: $Pd(PPh_3)_2Cl_2$ (0.06 mmol), CuI (0.12 mmol) and Et_3N (9 mmol) were added sequentially to a solution of 2-iodoaniline (3 mmol) and trimethylsilylacetylene (4.5 mmol) in THF (10 mL) at 23 °C and the mixture was stirred at this temperature for 3 h before it was quenched with saturated aqueous NH_4Cl (10 mL). The aqueous layer was extracted with Et_2O (10 mL) and the combined organic layer was washed sequentially with 0.1 N HCl (10 mL), water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was dissolved in THF (15 mL) and tetrabutylammonium fluoride (4.5 mL, 1.0 M in THF, 4.5 mmol) was added dropwise. The reaction mixture was then stirred at 23 ℃ for 1 h before it was quenched with saturated aqueous NH_4Cl (15 mL). The aqueous layer was extracted with Et_2O 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=5/1) to give 2-ethynylaniline which was dissolved in dichloromethane (3 mL). Tosyl chloride (3.6 mmol) and pyridine (12 mmol) was added and the mixture was stirred at 23 °C for 3 h before it was quenched with saturated aqueous NH_4Cl (5 mL). The aqueous layer was extracted with dichloromethane (5 mL) and the combined organic layer was washed sequentially with 0.1 N HCl (5 mL), water (5 mL) and brine (5 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (hexane/EtOAc=3/1) to give *N*-tosyl-2-ethynylaniline. Substrates **5a-i** were synthesized using general procedure C.



1a

Substrate **1a** was purchased from commercial sources and used without purification.

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.37 (dd, J = 7.5, 1.5 Hz, 1H), 7.27 (td, J = 7.5, 1.5 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 6.86 (t, J = 8.0 Hz, 1H), 5.89 (s, 1H), 3.45 (s, 1H). The data is in accordance with the literature.[2]

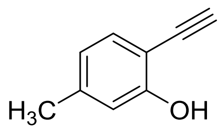


1b 333 mg, overall yield: 84%, colorless oil.

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.21 (d, J = 2.2 Hz, 1H), 7.14 – 7.06 (m, 1H), 6.87 (d, J = 8.3 Hz, 1H), 5.73 (s, 1H), 3.46 (s, 1H), 2.28 (s, 3H).

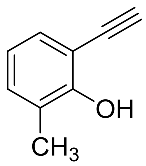
^{13}**C NMR** (101 MHz, $CDCl_3$) δ 155.3, 132.1, 131.7, 129.6, 114.7, 107.9, 83.9, 78.6, 20.3.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for C_9H_9O 133.0653; Found 133.0655.



1c 581 mg, overall yield: 44%, colorless oil.

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.25 (d, J = 8.0 Hz, 1H), 6.76 (s, 1H), 6.67 (d, J = 7.5 Hz, 1H), 5.75 (s, 1H), 3.41 (s, 1H), 2.31 (s, 3H). The data is in accordance with the literature.[2]

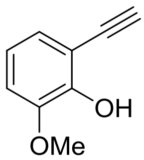


1d 554 mg, overall yield: 42%, colorless oil.

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.25 (dd, J = 7.7, 1.6 Hz, 1H), 7.15 (ddt, J = 7.5, 1.7, 0.9 Hz, 1H), 6.80 (t, J = 7.6 Hz, 1H), 5.89 (s, 1H), 3.48 (s, 1H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 132.2, 129.4, 124.1, 119.9, 107.6, 84.0, 78.7, 15.9.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for C_9H_9O 133.0653; Found 133.0651.

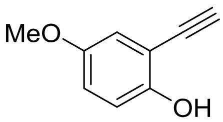


1e 725 mg, overall yield: 49%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (dd, J = 7.7, 1.6 Hz, 1H), 6.89 (dd, J = 8.1, 1.5 Hz, 1H), 6.85 – 6.80 (m, 1H), 6.01 (s, 1H), 3.92 (s, 3H), 3.38 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 146.6, 125.0, 119.8, 111.7, 108.5, 82.0, 78.9, 56.1.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_9H_9O_2$ 149.0603; Found 149.0606.

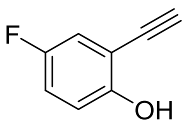


1f 770 mg, overall yield: 52%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 – 6.90 (m, 1H), 6.89 (d, J = 1.2 Hz, 2H), 5.54 (s, 1H), 3.77 (s, 3H), 3.47 (s, 1H).

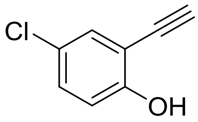
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 151.7, 118.0, 115.8, 115.7, 108.3, 84.0, 78.5, 55.8.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_9H_9O_2$ 149.0603; Found 149.0608.



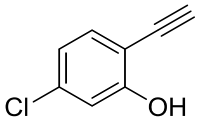
1g 326 mg, overall yield: 80%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (dd, J = 8.4 Hz, 2.8 Hz, 1H), 7.04 – 6.96 (m, 1H), 6.90 (dd, J = 9.0 Hz, 4.8 Hz, 1H), 5.66 (s, 1H), 3.50 (s, 1H). The data is in accordance with the literature.[3]



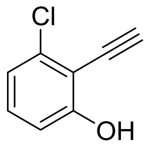
1h 403 mg, overall yield: 88%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 2.4 Hz, 1H), 7.21 (dd, J = 8.8, 2.4 Hz, 1H), 6.88 (d, J = 8.8 Hz, 1H), 5.79 (s, 1H), 3.48 (s, 1H). The data is in accordance with the literature.[2]



1i 687 mg, overall yield: 45%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 2.0 Hz, 1H), 7.29 (d, J = 8.3 Hz, 1H), 6.92 (dd, J = 8.3, 2.0 Hz, 1H), 5.76 (s, 1H), 3.45 (s, 1H). The data is in accordance with the literature.[4]

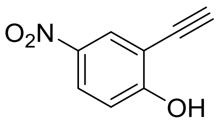


1j 595 mg, overall yield: 39%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, J = 8.2 Hz, 1H), 7.00 (dd, J = 8.0, 1.0 Hz, 1H), 6.90 (dd, J = 8.3, 1.0 Hz, 1H), 5.96 (s, 1H), 3.78 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 135.8, 130.7, 121.1, 113.1, 109.2, 89.0, 75.4.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for C_6H_6ClO 153.0107; Found 153.0104.

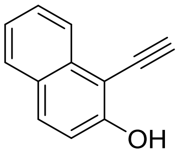


1k 505 mg, overall yield: 31%, light yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 2.8 Hz, 1H), 8.20 (dd, J = 9.1, 2.8 Hz, 1H), 7.08 (d, J = 9.1 Hz, 1H), 3.61 (s, 1H).

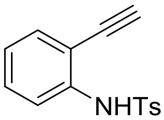
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 141.1, 128.3, 126.7, 115.5, 109.2, 86.4, 76.1.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_8H_6NO_3$ 164.0348; Found 164.0344.



1l 722 mg, overall yield: 43%, white solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (dq, J = 8.3, 0.9 Hz, 1H), 8.04 (d, J = 9.0 Hz, 1H), 7.89 (dt, J = 8.2, 0.9 Hz, 1H), 7.75 (ddd, J = 8.3, 7.0, 1.3 Hz, 1H), 7.54 (ddd, J = 8.3, 7.0, 1.3 Hz, 1H), 7.32 – 7.29 (m, 1H), 5.73 (s, 1H), 3.43 (s, 1H). The data is in accordance with the literature.[5]

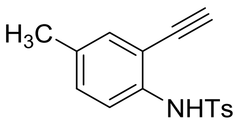


5a 520 mg, overall yield: 64%, light yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.69 (m, 2H), 7.61 (dd, J = 8.4, 1.1 Hz, 1H), 7.36 (dd, J = 7.7, 1.5 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.26 (s, 1H), 7.24 (d, J = 8.1 Hz, 2H), 7.03 (td, J = 7.6, 1.1 Hz, 1H), 3.39 (s, 1H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 138.5, 135.9, 132.5, 130.2, 129.7, 127.4, 124.2, 119.3, 112.7, 84.4, 78.6, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{13}NNaO_2S$ 294.0565; Found 294.0569.

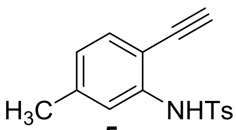


5b 599 mg, overall yield: 70%, light yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.65 (m, 2H), 7.51 (d, J = 8.3 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.18 – 7.08 (m, 3H), 3.32 (s, 1H), 2.38 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 136.0, 135.9, 134.2, 132.8, 131.0, 129.6, 127.4, 119.96, 113.0, 83.8, 78.8, 21.6, 20.5.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{15}NNaO_2S$ 308.0723; Found 308.0728.

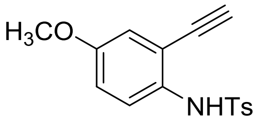


5c 616 mg, overall yield: 72%, light yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 7.46 – 7.42 (m, 1H), 7.26 – 7.18 (m, 4H), 6.83 (ddd, J = 7.9, 1.7, 0.8 Hz, 1H), 3.34 (s, 1H), 2.36 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 140.8, 138.3, 136.0, 132.2, 129.6, 127.3, 125.2, 120.1, 109.9, 83.8, 78.8, 21.8, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{15}NNaO_2S$ 308.0723; Found 308.0729.

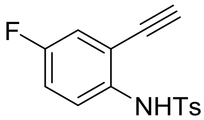


5d 686 mg, overall yield: 76%, brown solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.60 (m, 2H), 7.56 (d, J = 9.0 Hz, 1H), 7.24 – 7.19 (m, 2H), 6.90 (dd, J = 9.0, 3.0 Hz, 1H), 6.84 (d, J = 3.0 Hz, 1H), 3.76 (s, 3H), 3.25 (s, 1H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 143.9, 135.8, 131.5, 129.5, 127.4, 123.2, 116.7, 116.6, 115.2, 83.6, 78.7, 55.5, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{15}NNaO_3S$ 324.0672; Found 324.0678.

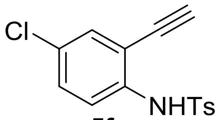


5e 512 mg, overall yield: 59%, yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.64 (m, 2H), 7.61 (ddt, J = 9.1, 5.1, 1.2 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.10 (s, 1H), 7.04 (td, J = 8.4, 2.3 Hz, 2H), 3.37 (s, 1H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0 (d, J = 246.4 Hz), 144.3, 135.6, 134.7 (d, J = 3.0 Hz), 129.7, 127.4, 122.5 (d, J = 9.1 Hz), 118.9 (d, J = 24.2 Hz), 117.5 (d, J = 22.2 Hz), 115.1 (d, J = 10.1 Hz), 85.0, 77.6 (d, J = 3.0 Hz), 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{12}FNNaO_2S$ 312.0472; Found 312.0477.

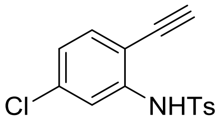


5f 569 mg, overall yield: 62%, brown solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.67 (m, 2H), 7.57 (d, J = 8.9 Hz, 1H), 7.33 (d, J = 2.4 Hz, 1H), 7.30 – 7.23 (m, 4H), 3.42 (s, 1H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 137.1, 135.6, 132.0, 130.4, 129.8, 129.5, 127.0, 120.7, 114.3, 85.4, 77.4, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{12}ClNNaO_2S$ 328.0174; Found 328.0178.

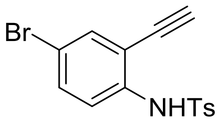


5g 597 mg, overall yield: 65%, brown solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 2H), 7.64 (d, J = 2.0 Hz, 1H), 7.31 – 7.26 (m, 4H), 7.01 (dd, J = 8.3, 2.0 Hz, 1H), 3.45 (s, 1H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 139.5, 136.2, 135.6, 133.3, 129.8, 127.3, 124.3, 119.3, 110.7, 85.3, 77.7, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{12}ClNNaO_2S$ 328.0174; Found 328.0179.

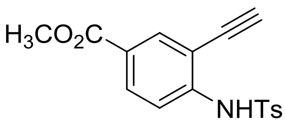


5h 567 mg, overall yield: 54%, brown solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.67 (m, 2H), 7.51 (d, J = 8.8 Hz, 1H), 7.47 (d, J = 2.3 Hz, 1H), 7.41 (dd, J = 8.8, 2.3 Hz, 1H), 7.26 (d, J = 8.1 Hz, 2H), 7.21 (s, 1H), 3.44 (s, 1H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 137.6, 135.6, 134.9, 133.2, 129.8, 127.3, 120.8, 116.8, 114.5, 85.6, 77.2, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{12}BrNNaO_2S$ 371.9671; Found 371.9676.



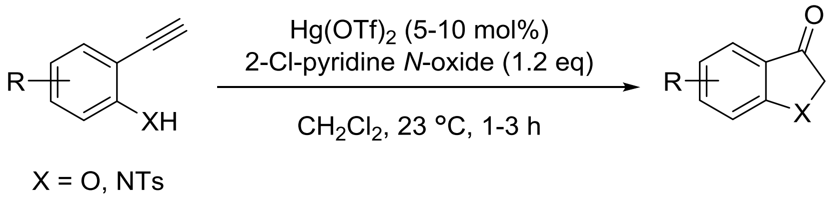
5i 543 mg, overall yield: 55%, yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 2.0 Hz, 1H), 7.94 (dd, J = 8.7, 2.0 Hz, 1H), 7.78 – 7.74 (m, 2H), 7.63 (d, J = 8.7 Hz, 1H), 7.28 – 7.24 (m, 2H), 3.88 (s, 3H), 3.51 (s, 1H), 2.38 (s, 3H).

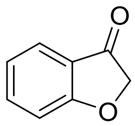
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 144.6, 142.2, 135.6, 134.1, 131.4, 129.9, 127.3, 125.5, 117.2, 111.7, 85.5, 77.6, 52.2, 21.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}NO_4S$ 330.0803; Found 330.0807.

3. Procedure for the synthesis of coumaran-3-ones and indolin-3-ones



General procedure: 2-Cl-pyridine *N*-oxide (77.7 mg, 0.6 mmol) and $Hg(OTf)_2$ (12.5 mg, 0.025 mmol) were added sequentially to a solution of 2-ethynyl phenol (or 2-ethynyl tosylaniline, 0.5 mmol) in CH_2Cl_2 (2 mL) and the mixture was stirred at 23 °C for 1 h. Then CH_2Cl_2 (10 ml) was added and the resulting mixture was washed sequentially with 0.1 N HCl (10 mL), 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 the corresponding coumaran-3-one (or indolin-3-one). Note: 0.05 mmol of $Hg(OTf)_2$ and 3 h of reaction time were needed for 2-ethynyl tosylanilines.

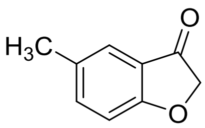


2a 61.6 mg, 92%, white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (dd, J = 7.7, 1.4 Hz, 1H), 7.62 (ddd, J = 8.5, 7.2, 1.5 Hz, 1H), 7.15 (d, J = 8.4 Hz, 1H), 7.12 – 7.07 (m, 1H), 4.63 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.9, 174.0, 137.9, 124.1, 122.0, 121.2, 113.7, 74.7.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_8H_7O_2$ 135.0448; Found 135.0444.

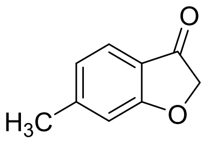


2b 65.9 mg, 89%, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 2H), 7.04 (dd, J = 8.4, 2.0 Hz, 1H), 4.66 – 4.58 (m, 2H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.0, 172.5, 139.2, 131.6, 123.4, 121.0, 113.2, 74.96, 20.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_9H_9O_2$ 149.0604; Found 149.0609.

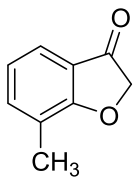


2c 63.6 mg, 86%, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.9 Hz, 1H), 6.95 (dt, J = 1.5, 0.8 Hz, 1H), 6.92 (dd, J = 7.9, 1.2 Hz, 1H), 4.62 (s, 2H), 2.45 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2, 174.6, 150.0, 123.6, 123.6, 118.8, 113.6, 74.95, 22.5.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_9H_9O_2$ 149.0604; Found 149.0610.



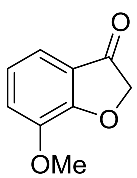
2d 62.9 mg, 85%, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 1H), 7.44 (dt, J = 7.3, 1.1 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 4.66 (s, 2H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.4, 172.8, 138.2, 123.8, 121.9, 121.3, 120.6, 74.70, 14.2.

IR (neat): 2930, 1710, 1618, 1492, 1422, 1288, 1130, 815, 726.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_9H_9O_2$ 149.0604; Found 149.0606.

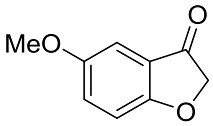


2e 69.7 mg, 85%, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, J = 7.7, 1.2 Hz, 1H), 7.10 (dd, J = 7.9, 1.2 Hz, 1H), 7.01 (t, J = 7.8 Hz, 1H), 4.66 (s, 2H), 3.95 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.7, 164.0, 146.8, 122.5, 122.4, 118.3, 115.1, 75.1, 56.2.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_9H_8NaO_3$ 187.0373; Found 187.0377.

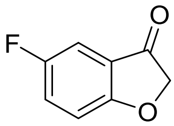


2f 72.2 mg, 88%, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (dd, J = 9.0, 2.8 Hz, 1H), 7.10 – 7.06 (m, 2H), 4.65 (s, 2H), 3.82 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 169.4, 155.0, 127.9, 121.1, 114.5, 103.8, 75.46, 55.9.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_9H_8NaO_3$ 187.0373; Found 187.0379.

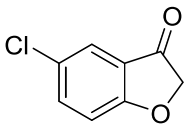


2g 68.4 mg, 90%, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 2H), 7.14 – 7.09 (m, 1H), 4.68 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.3, 170.2, 157.8 (d, J = 244.4 Hz), 125.6 (d, J = 26.3 Hz), 121.6 (d, J = 8.1 Hz), 114.8 (d, J = 8.1 Hz), 109.1 (d, J = 24.2 Hz), 75.7.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_8H_5FNaO_2$ 175.0173; Found 175.0179.

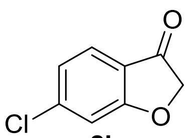


2h 80.9 mg, 96%, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.60 (m, 1H), 7.55 (dd, J = 8.8, 2.4 Hz, 1H), 7.10 (d, J = 8.8 Hz, 1H), 4.67 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 172.2, 137.7, 127.6, 123.5, 122.3, 115.0, 75.4.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_8H_5ClNaO_2$ 190.9875; Found 190.9871.

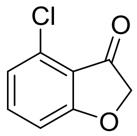


2i 78.4 mg, 93%, white solid.

¹H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.2 Hz, 1H), 7.19 (d, J = 1.6 Hz, 1H), 7.10 (dd, J = 8.2, 1.6 Hz, 1H), 4.68 (s, 2H).

¹³C NMR (101 MHz, $CDCl_3$) δ 198.2, 174.1, 144.2, 124.8, 123.1, 119.8, 114.1, 75.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_8H_5ClNaO_2$ 190.9875; Found 190.9878.

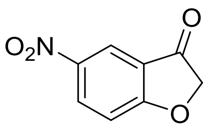


2j 76.7 mg, 91%, white solid.

¹H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, J = 8.4, 7.8 Hz, 1H), 7.03 (m, 2H), 4.66 (s, 2H).

¹³C NMR (101 MHz, $CDCl_3$) δ 196.7, 174.6, 138.0, 131.7, 123.1, 118.3, 112.1, 75.0.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_8H_5ClNaO_2$ 190.9875; Found 190.9876.

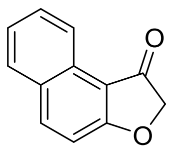


2k 85.0 mg, 95%, light yellow solid.

¹H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 2.5 Hz, 1H), 8.55 (dd, J = 9.1, 2.5 Hz, 1H), 7.33 – 7.26 (m, 1H), 4.85 (s, 2H).

¹³C NMR (101 MHz, $CDCl_3$) δ 197.2, 176.5, 143.0, 132.8, 121.5, 121.0, 114.4, 76.4.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_8H_6NO_4$ 180.0296; Found 180.0292.

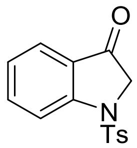


2l 84.6 mg, 92%, white solid.

¹H NMR (400 MHz, $CDCl_3$) δ 8.79 (dq, J = 8.3, 0.9 Hz, 1H), 8.09 (d, J = 9.0 Hz, 1H), 7.86 (dt, J = 8.2, 0.9 Hz, 1H), 7.69 (ddd, J = 8.3, 7.0, 1.3 Hz, 1H), 7.50 (ddd, J = 8.3, 7.0, 1.3 Hz, 1H), 7.32 – 7.26 (m, 1H), 4.78 (s, 2H).

¹³C NMR (101 MHz, $CDCl_3$) δ 199.3, 176.7, 139.8, 129.9, 129.2, 129.1, 128.5, 125.5, 123.2, 114.0, 113.3, 75.5.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_9O_2$ 185.0605; Found 180.0601.

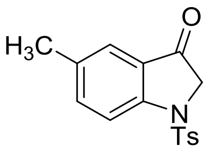


6a 122.0 mg, 85%, light yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 8.4, 0.8 Hz, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.70 – 7.65 (m, 2H), 7.32 – 7.26 (m, 2H), 7.23 – 7.17 (m, 1H), 4.15 (s, 2H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.8, 153.6, 145.2, 137.3, 133.5, 130.1, 127.1, 125.0, 124.4, 124.0, 115.9, 56.1, 21.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{14}NO_3S$ 288.0699; Found 288.0695.

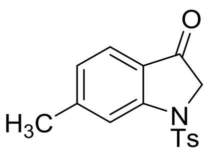


6b 134.0 mg, 89%, light yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.5 Hz, 1H), 7.73 – 7.68 (m, 2H), 7.50 (dd, J = 8.5, 1.9 Hz, 1H), 7.44 (dt, J = 1.9, 0.9 Hz, 1H), 7.27 (d, J = 8.3 Hz, 2H), 4.12 (s, 2H), 2.39 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.9, 151.8, 145.0, 138.5, 134.2, 133.3, 130.0, 127.2, 125.2, 124.0, 115.9, 56.4, 21.6, 20.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}NO_3S$ 302.0852; Found 302.0857.

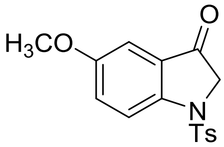


6c 132.4 mg, 88%, light yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dt, J = 1.5, 0.7 Hz, 1H), 7.75 – 7.70 (m, 2H), 7.54 (d, J = 7.9 Hz, 1H), 7.29 (d, J = 7.7 Hz, 2H), 7.01 (ddd, J = 7.9, 1.4, 0.7 Hz, 1H), 4.12 (s, 2H), 2.52 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 154.0, 149.3, 145.1, 133.6, 130.1, 127.1, 125.6, 124.1, 122.9, 116.0, 56.4, 22.8, 21.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}NO_3S$ 302.0852; Found 302.0855.

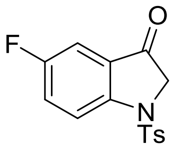


6d 145.8 mg, 92%, yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, J = 9.1, 0.5 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.34 – 7.24 (m, 3H), 7.05 (d, J = 2.7 Hz, 1H), 4.13 (s, 2H), 3.81 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.9, 156.8, 148.3, 145.1, 133.0, 130.1, 127.2, 126.6, 126.1, 117.7, 104.8, 56.7, 55.8, 21.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}NO_4S$ 318.0802; Found 318.0806.

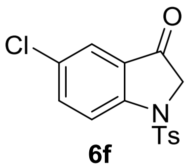


6e 122.0 mg, 80%, yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, J = 9.1, 3.9 Hz, 1H), 7.68 (d, J = 8.1 Hz, 2H), 7.40 (td, J = 8.7, 2.8 Hz, 1H), 7.30 – 7.25 (m, 3H), 4.16 (s, 2H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9 (d, J = 3.0 Hz), 160.6, 158.1, 149.9, 145.4, 133.1, 130.2, 127.2, 124.8 (d, J = 25.3 Hz), 117.7 (d, J = 8.1 Hz), 109.9 (d, J = 24.2 Hz), 56.8, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{12}FNNaO_3S$ 328.0423; Found 328.0426.

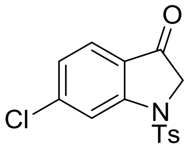


6f 135.2 mg, 84%, yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.8 Hz, 1H), 7.74 – 7.70 (m, 2H), 7.65 – 7.59 (m, 2H), 7.31 (d, J = 8.1 Hz, 2H), 4.17 (s, 2H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4, 151.9, 145.5, 137.1, 133.1, 130.2, 130.1, 127.1, 126.3, 123.9, 117.2, 56.5, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{12}ClNNaO_3S$ 344.0125; Found 344.0123.

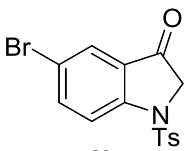


6g 127.2 mg, 79%, yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 1.6 Hz, 1H), 7.73 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.3 Hz, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.14 (dd, J = 8.2, 1.6 Hz, 1H), 4.14 (s, 2H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.3, 154.1, 145.6, 144.0, 133.3, 130.3, 127.1, 125.3, 124.8, 123.4, 116.0, 56.3, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{12}ClNNaO_3S$ 344.0125; Found 344.0127.

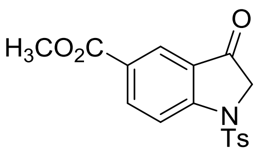


6h 137.2 mg, 75%, brown solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 9.4 Hz, 1H), 7.74 (dq, J = 4.3, 2.1 Hz, 2H), 7.72 – 7.67 (m, 2H), 7.29 (d, J = 8.2 Hz, 2H), 4.14 (s, 2H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 152.4, 145.5, 139.8, 133.2, 130.3, 127.1, 127.1, 126.7, 117.6, 117.3, 56.4, 21.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{13}BrNO_3S$ 365.9802; Found 365.9807.



6i 126.0 mg, 73%, yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 – 8.33 (m, 2H), 8.09 (dd, J = 8.6, 0.8 Hz, 1H), 7.78 – 7.74 (m, 2H), 7.34 – 7.30 (m, 2H), 4.23 (s, 2H), 3.94 (s, 3H), 2.42 (s, 3H).

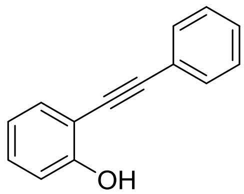
^{13}C NMR (101 MHz, $CDCl_3$) δ 193.7, 165.5, 156.2, 145.7, 138.3, 133.4, 130.3, 127.1, 126.5, 126.0, 124.9, 115.4, 56.6, 52.5, 21.6.

IR (neat): 2930, 1716, 1602, 1488, 1445, 1363, 1280, 1165, 1090, 1028, 913, 745, 662, 589, 545.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}NO_5S$ 346.0747; Found 346.0743.

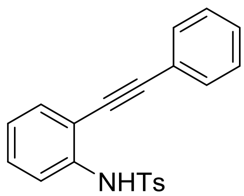
4. Procedure for the preparation of compounds 7a-c and 8a'-c'

Compound **7a**,[6] **7b**[7] and **7c**[8] were prepared by reported procedures. **8a'-c'** were prepared by the same procedure as the preparation of coumaran-3-ones.



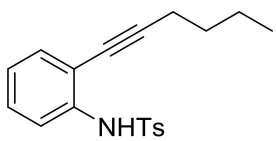
7a 305 mg, 91%, colorless oil.

^{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.[6]



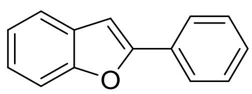
7b 425 mg, 82%, yellow solid.

^{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]



7c 363 mg, 84%, yellow solid.

^{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]

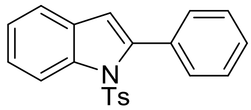


8a', 92.2 mg, 95%, white solid.

^{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 156.0, 155.0, 130.6, 129.3, 128.8, 128.6, 125.0, 124.3, 123.0, 121.0, 111.2, 101.4.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{11}O$ 195.0810; Found 195.0814.

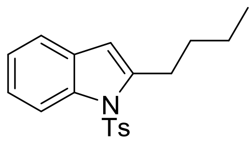


8b', 159.6 mg, 92%, yellow solid.

^{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 144.5, 142.1, 138.3, 134.7, 132.4, 130.6, 130.3, 129.2, 128.6, 127.5, 126.8, 124.8, 124.3, 120.7, 116.7, 113.6, 21.5.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{18}NO_2S$ 348.1058; Found 348.1051.



8c', 142.2 mg, 87%, yellow solid.

^{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 144.6, 142.5, 137.2, 136.3, 129.8, 129.7, 126.2, 123.7, 123.4, 120.0, 114.8, 108.6, 31.0, 28.7, 22.5, 21.5, 13.9.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{22}NO_2S$ 328.1371; Found 328.1376.

5. References

(1) For compounds **2a-b**, **2g-i** and **2k**, see: (a) Shu, C.; Liu, R.; Liu, S.; Li, J.-Q.; Yu, Y.-F.; He, Q.; Lu, X.; Ye, L.-W. *Chem. Asian J.* **2015**, *10*, 91. For compound **2c**, see: (b) González, A. G.; Barrera, J. B.; Hernández, C. Y. *Heterocycles* **1992**, *34*, 1311. For compound **2e**, see: (c) Jung, M. E.; Abrecht, S. *J. Org. Chem.* **1988**, *53*, 423. For compound **2f**, see: (d) Tomaszewski, Z.; Johnson, M. P.; Huang, X.; Nichols, D. E. *J. Med. Chem.* **1992**, *35*, 2061. For compound **2j**, see: (e) Mulholland, T. P. C.; Honeywood, R. I. W.; Preston, H. D.; Rosevear, D. T. *J. Chem. Soc.* **1965**, 4939. For compound **2i**, see: (f) Anderson, N. G.; Parvez, M.; Keay, B. A. *Org. Lett.* **2000**, *2*, 2817. For compounds **6a-h**, see: (g) Shu, C.; Li, L.; Xiao, X.-Y.; Yu, Y.-F.; Ping, Y.-F.; Zhou, J.-M.; Ye, L.-W. *Chem. Commun.* **2014**, *50*, 8689. For compound **8a'**, see: (h) Duan, X.-F.; Zeng, J.; Zhang, Z.-B.; Zi, G.-F. *J. Org. Chem.* **2007**, *72*, 10283. For compounds **8b'** and **8c'**, see: (i) Yin, Y.; Ma, W.; Chai, Z.; Zhao, G. *J. Org. Chem.* **2007**, *72*, 5731.

(2) Sahani, R. L.; Patil, M. D.; Wagh, S. B.; Liu, R.-S. *Angew. Chem., Int. Ed.*, **2018**, *57*, 14878.

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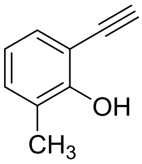
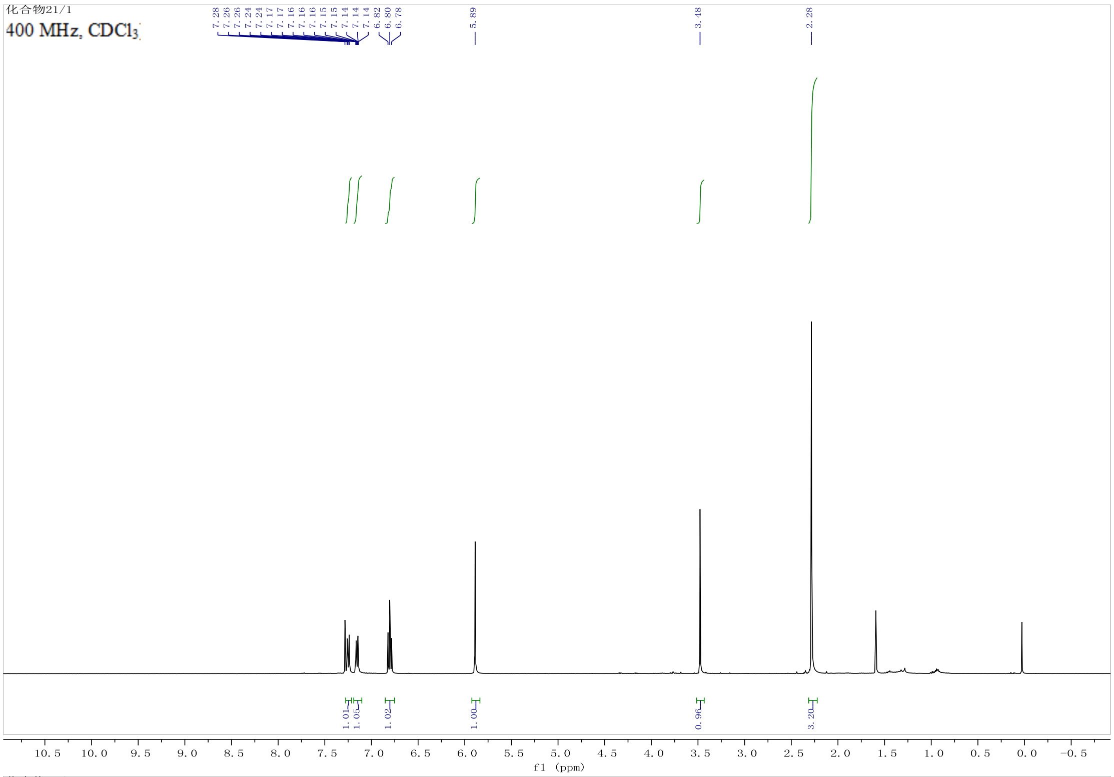
(7) Chong, E.; Blum, S. A. *J. Am. Chem. Soc*. **2015**, *137*, 10144.

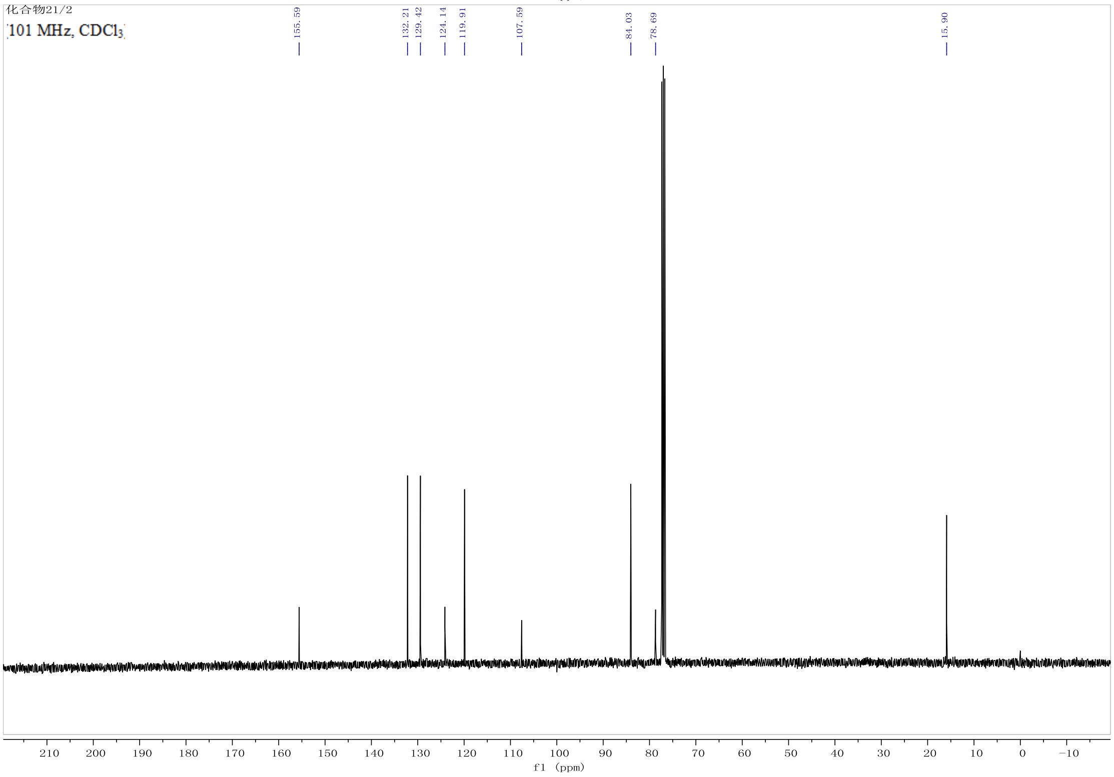
(8) Liu, J.; Xie, X.; Liu, Y. *Chem. Commun*. **2013**, *49*, 11794.

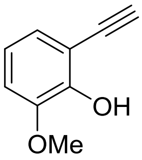
6. ^{1}H NMR and ^{13}C NMR Spectra



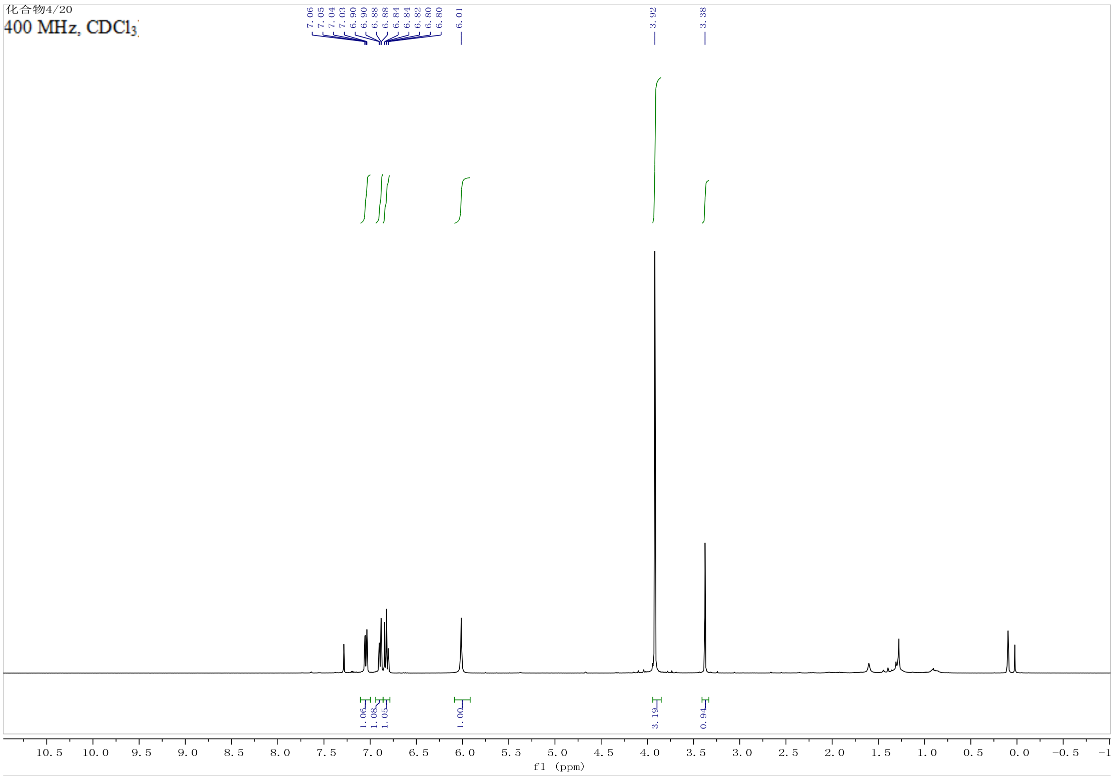
1d



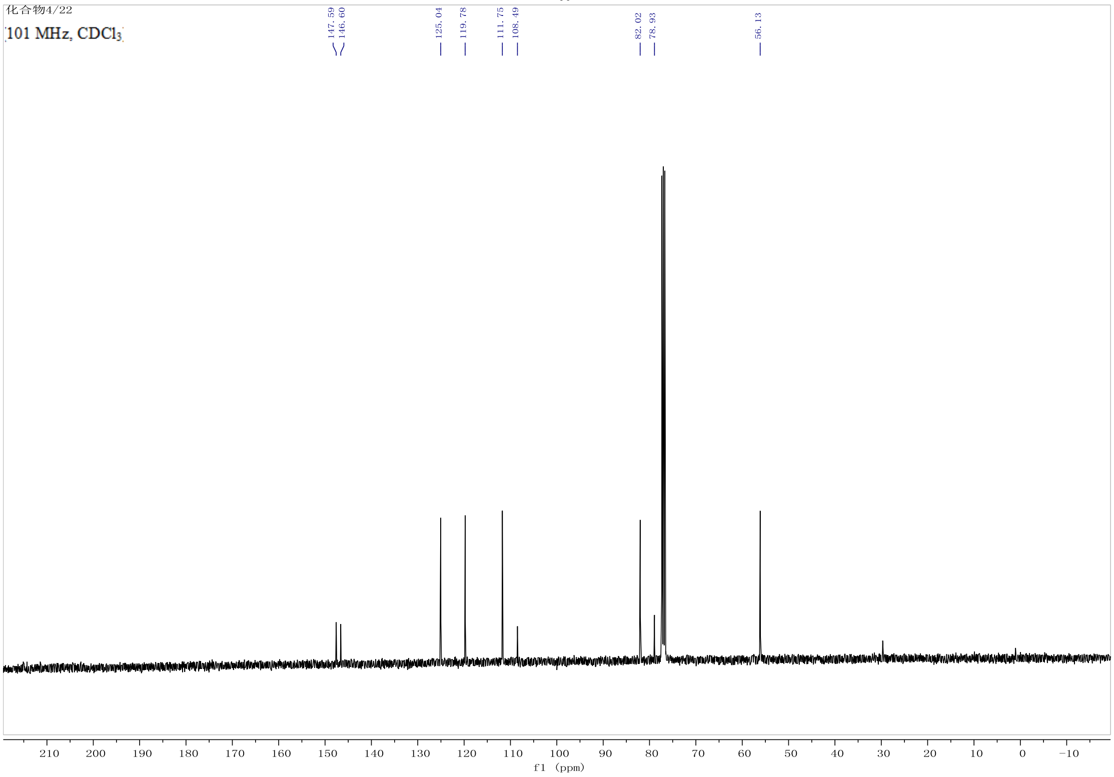




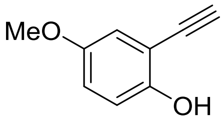
1e



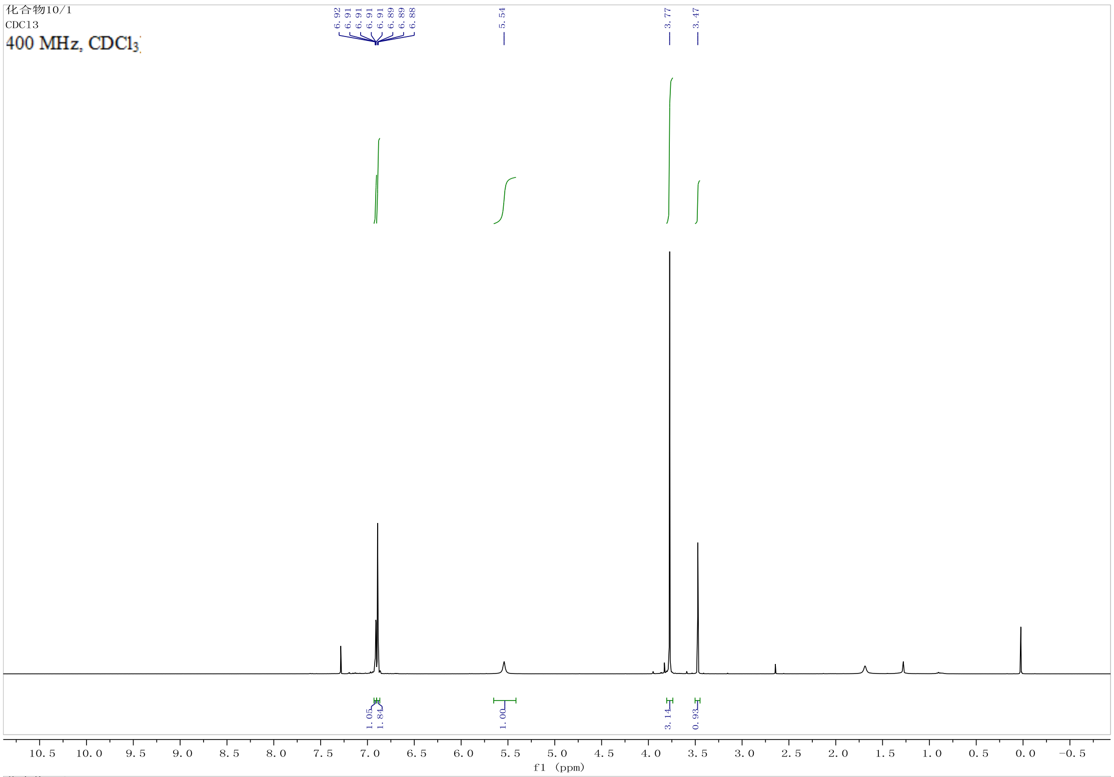
化合物4/20
400 MHz, CDCl3
7.06 7.05 7.04 7.03 6.90 6.90 6.88 6.88 6.84 6.84 6.82 6.82 6.80 6.80
6.01
3.92
3.38
1.06 1.08 1.05
1.00
3.19
0.94
f1 (ppm)

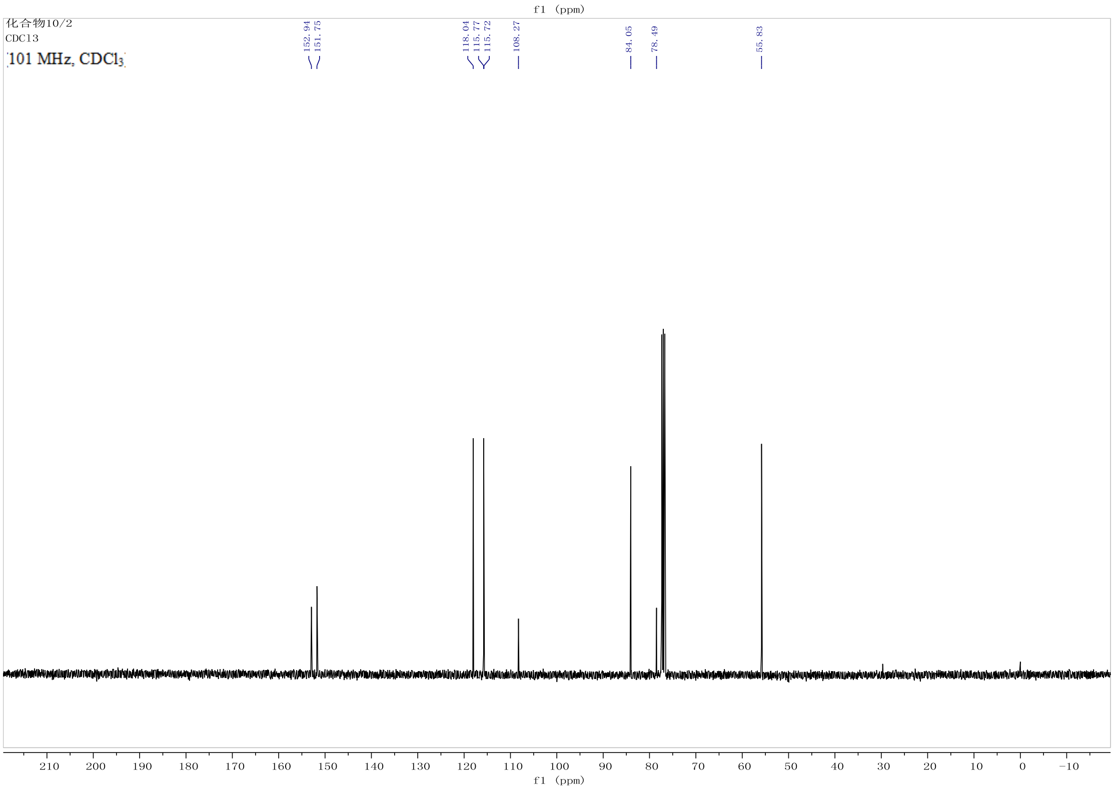


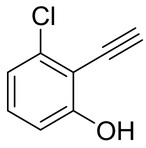
化合物4/22
101 MHz, CDCl3
147.59 146.60
125.04
119.78
111.75
108.49
82.02
78.93
56.13
f1 (ppm)


MeO
OH

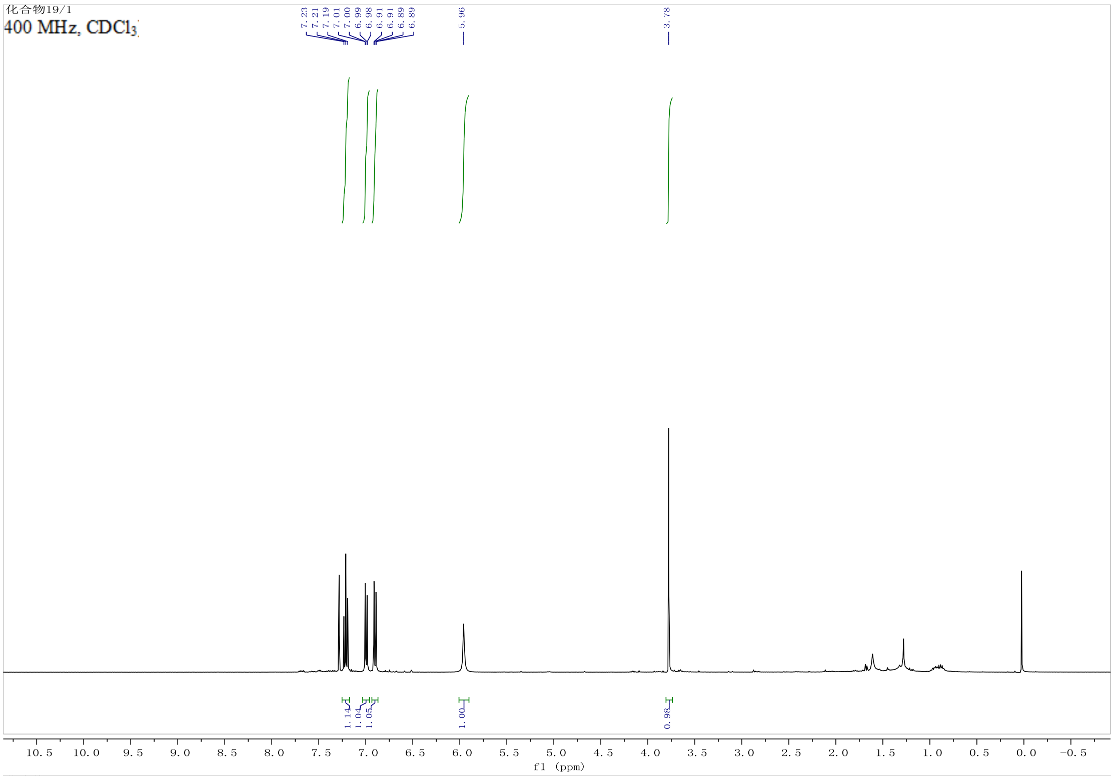
1f

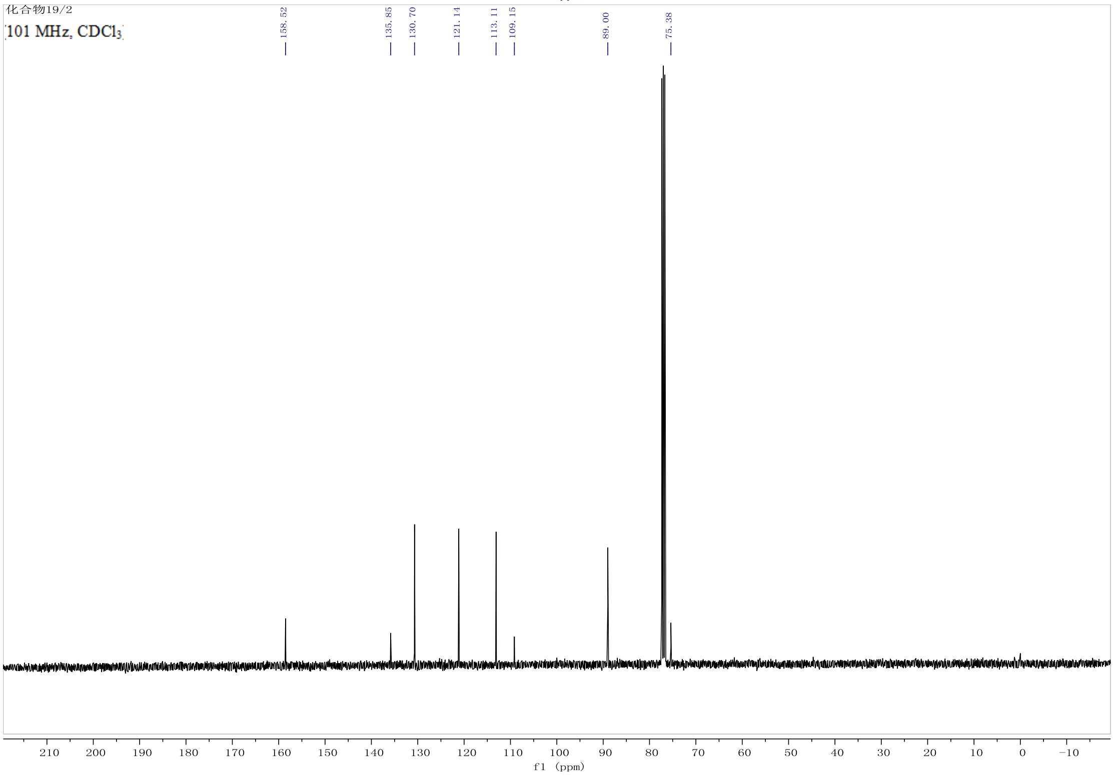

化合物10/1
CDCl3
400 MHz, CDCl3
6.92
6.91
6.91
6.91
6.91
6.89
6.89
6.88
5.54
3.77
3.47
1.05
1.84
1.00
3.14
0.93
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

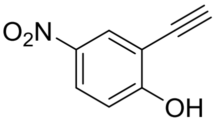

化合物10/2
CDCl3
101 MHz, CDCl3
152.94
151.75
118.04
115.77
115.72
108.27
84.05
78.49
55.83
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Cl
OH

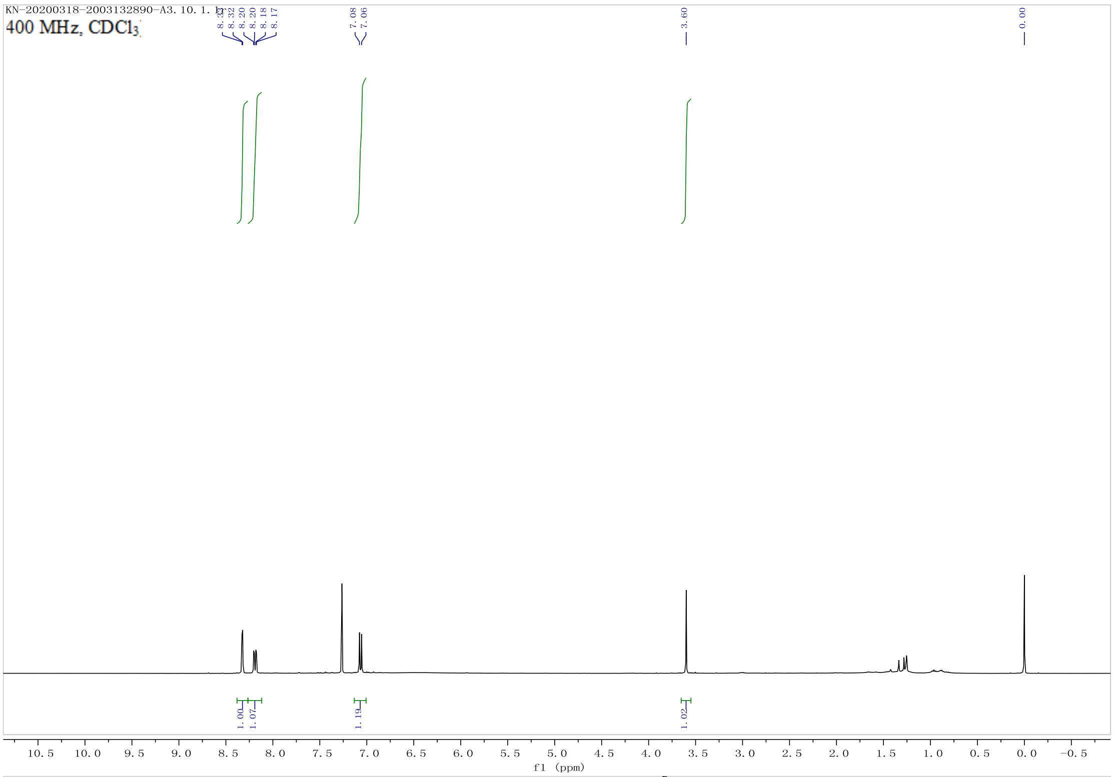
1j


化合物19/1
400 MHz, CDCl3
7.23
7.21
7.19
7.01
7.00
6.99
6.98
6.91
6.91
6.89
6.89
5.96
3.78
1.14
1.04
1.05
1.00
0.98
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)

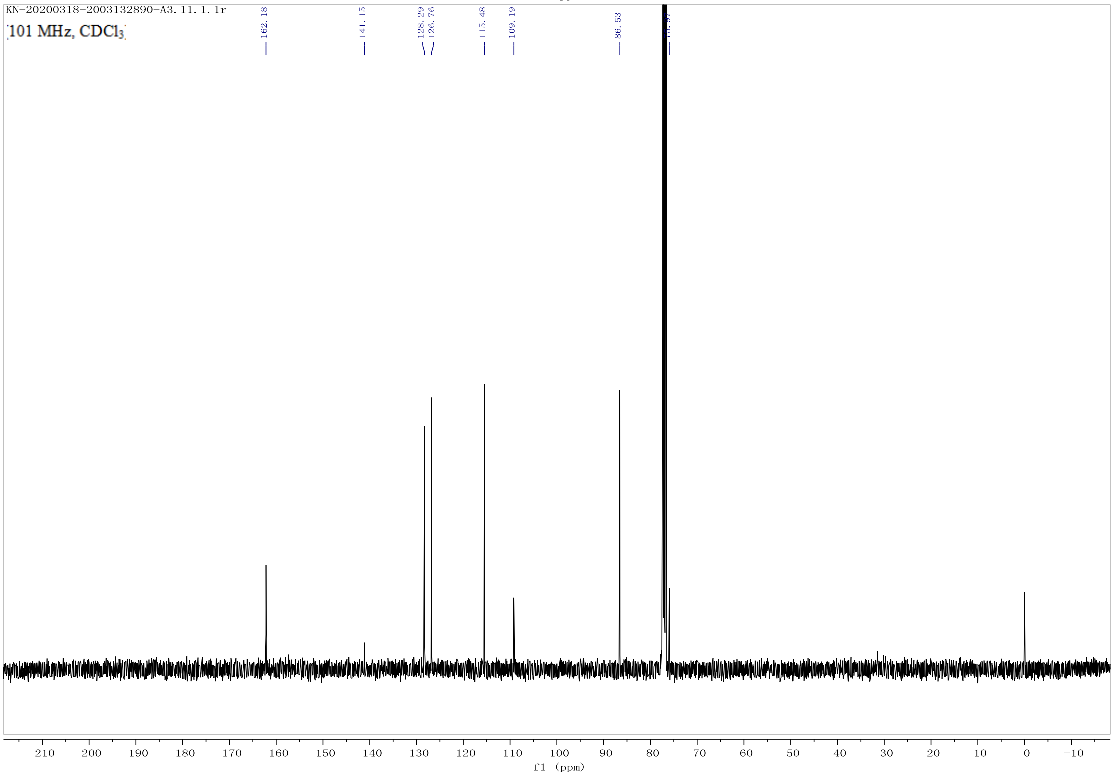

化合物19/2
101 MHz, CDCl3
158.52
135.85
130.70
121.14
113.11
109.15
89.00
75.38
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



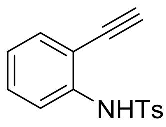
1k



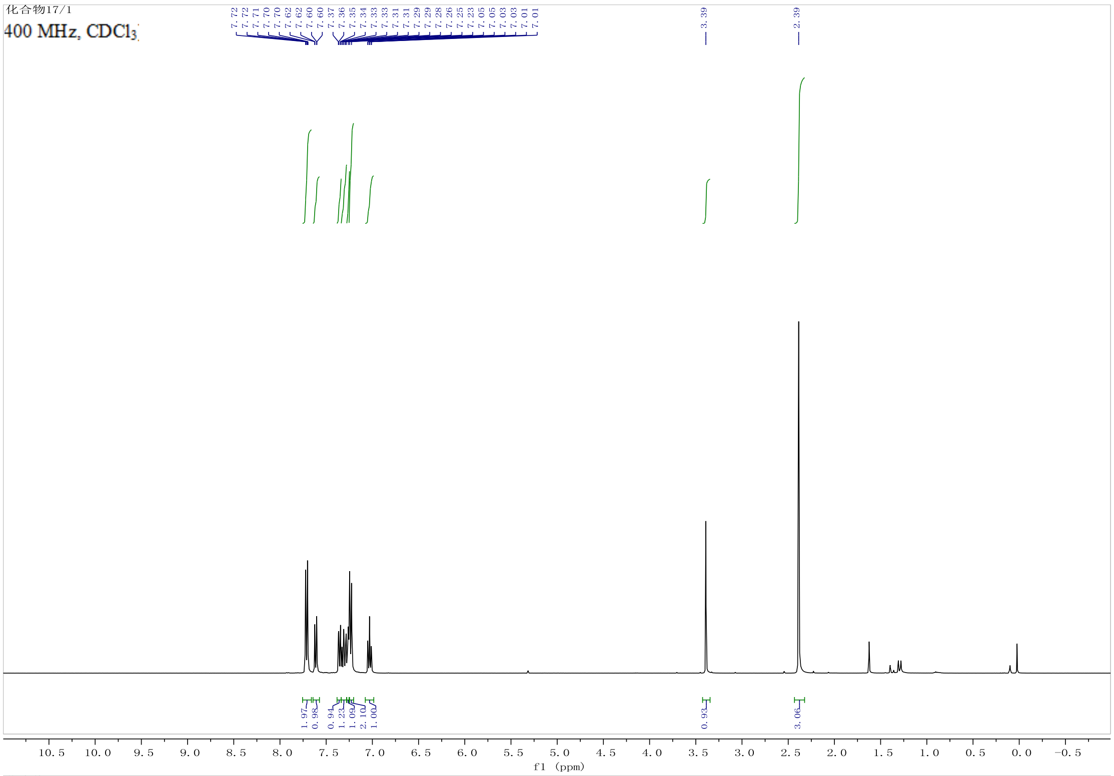
KN-20200318-2003132890-A3.10.1.1r
400 MHz, CDCl3
7.08
7.06
3.60
0.00
1.00
1.07
1.19
1.02
f1 (ppm)



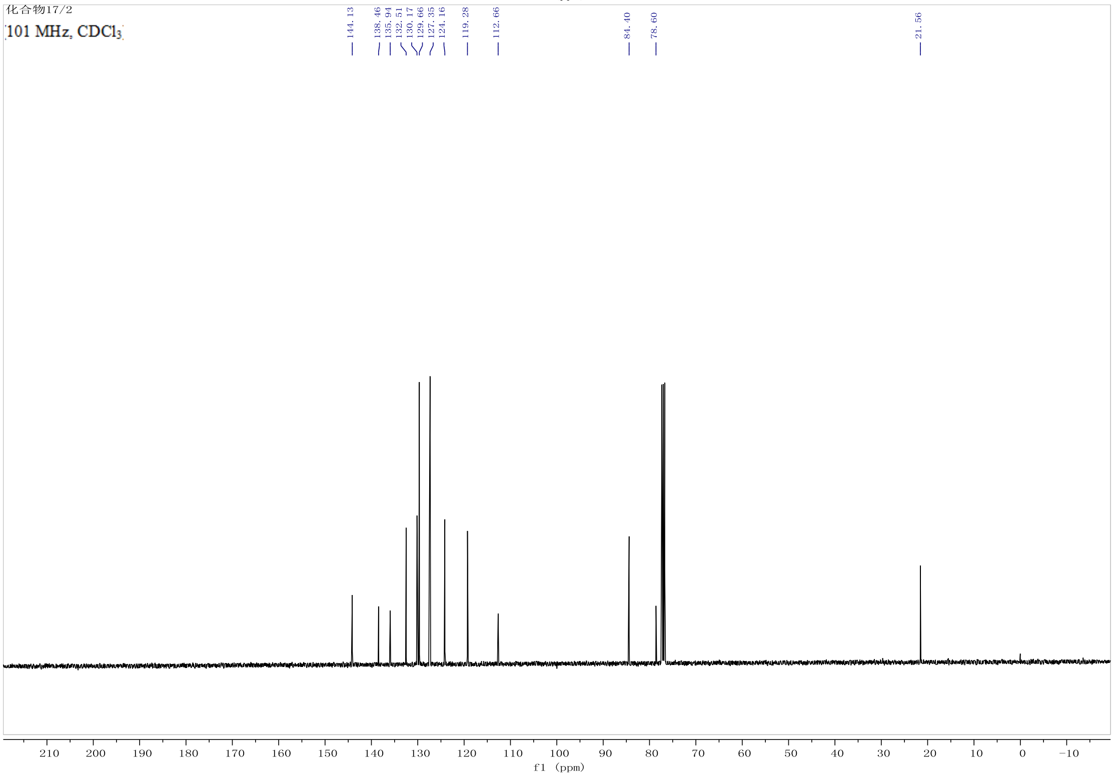
KN-20200318-2003132890-A3.11.1.1r
101 MHz, CDCl3
162.18
141.15
128.29
126.76
115.48
109.19
86.53
f1 (ppm)



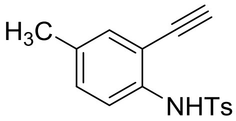
5a



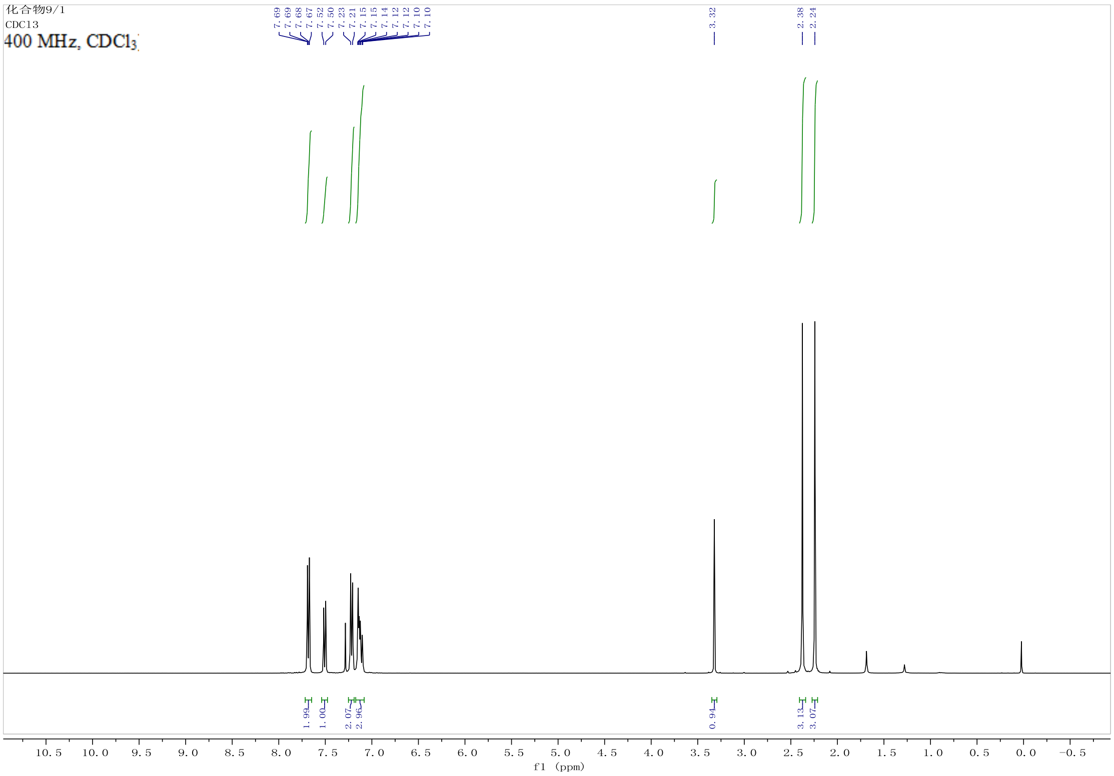
化合物17/1
400 MHz, CDCl3
f1 (ppm)

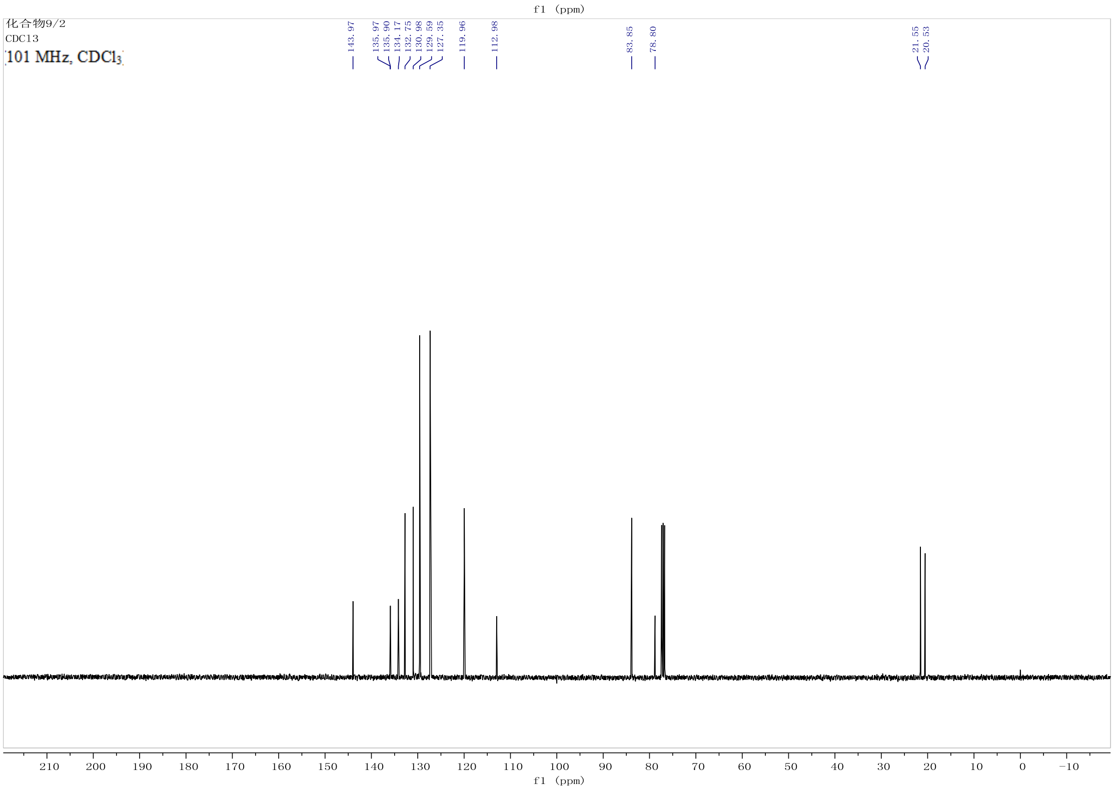


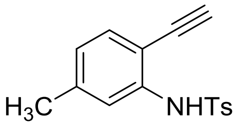
化合物17/2
101 MHz, CDCl3
144.13
138.46
135.94
132.51
130.17
129.66
127.35
124.16
119.28
112.66
84.40
78.60
21.56
f1 (ppm)


H3C
NHTs

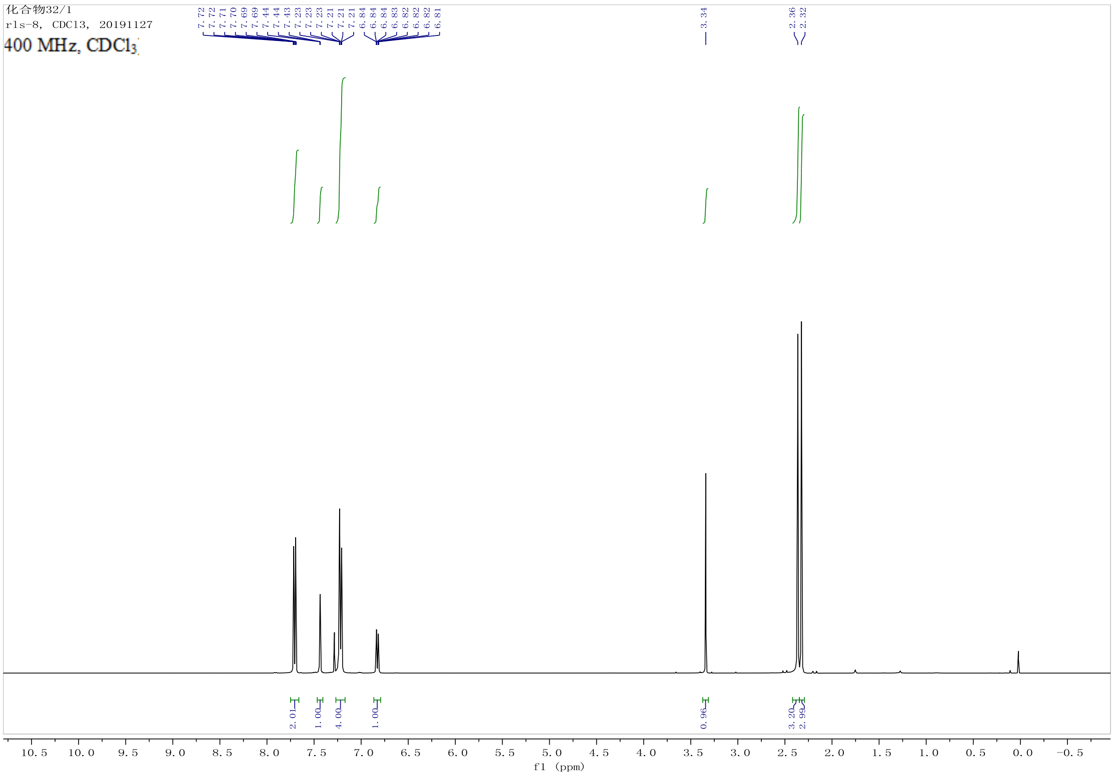
5b

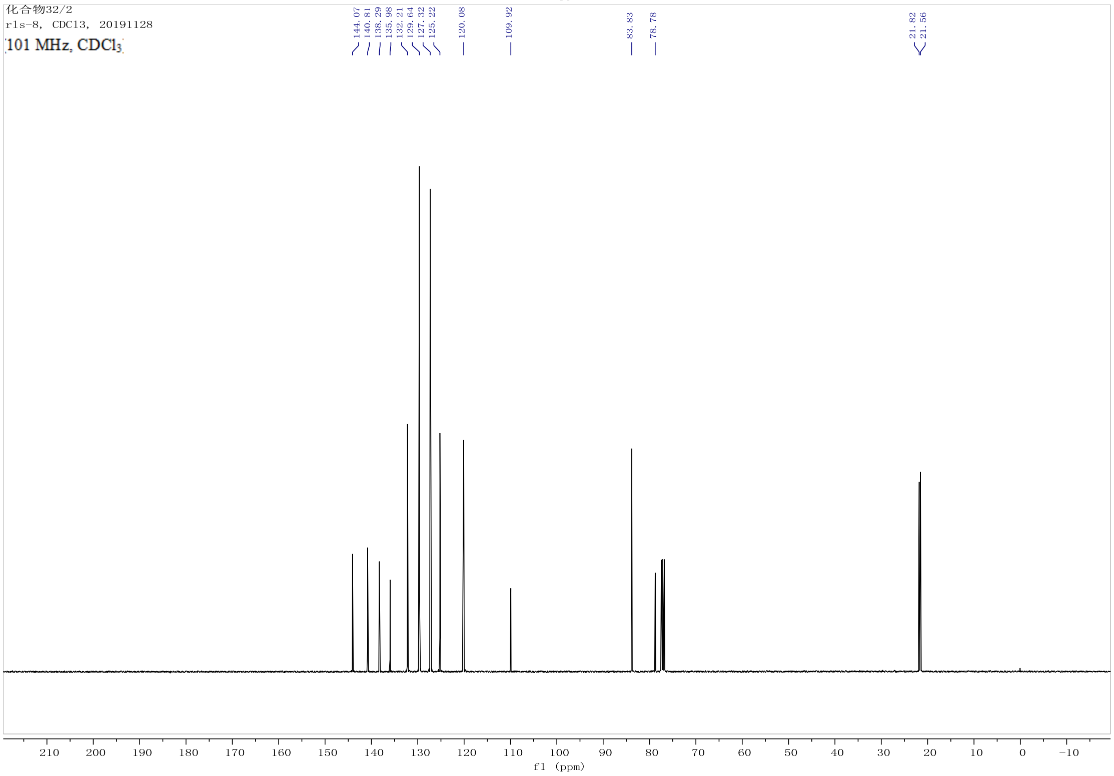

化合物9/1
CDC13
400 MHz, CDCl3
f1 (ppm)

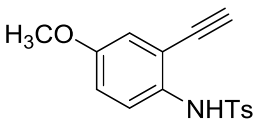

化合物9/2
CDC13
101 MHz, CDCl3
f1 (ppm)



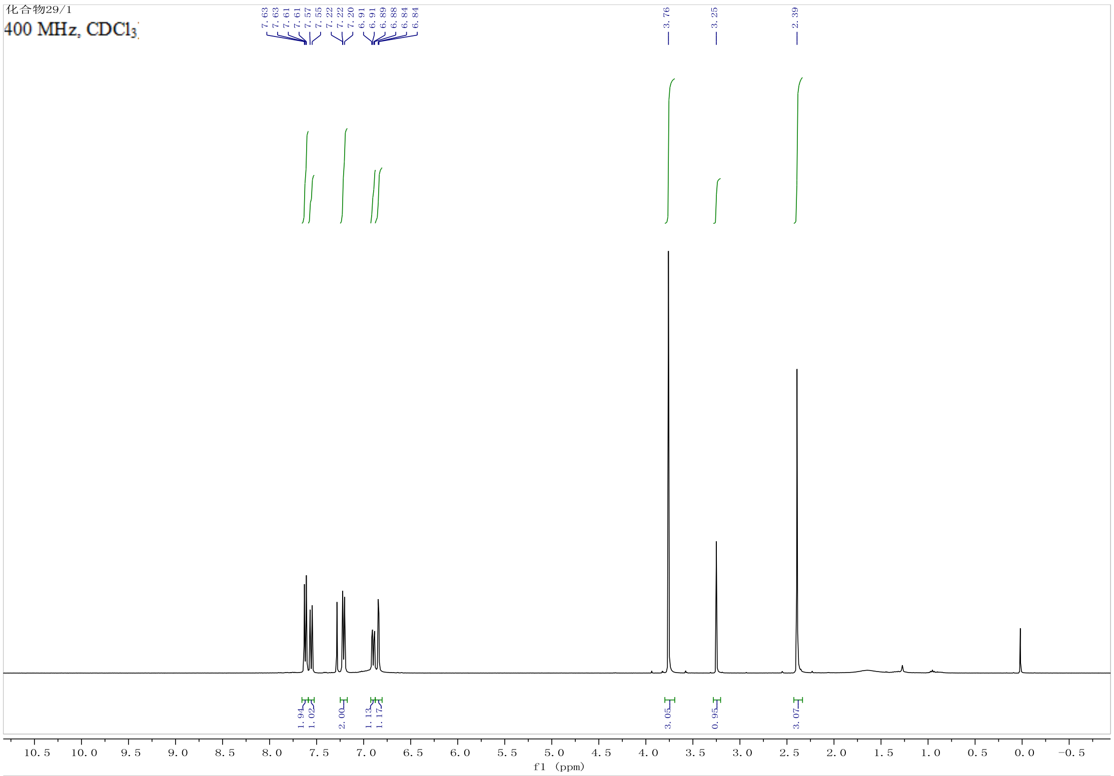
5c

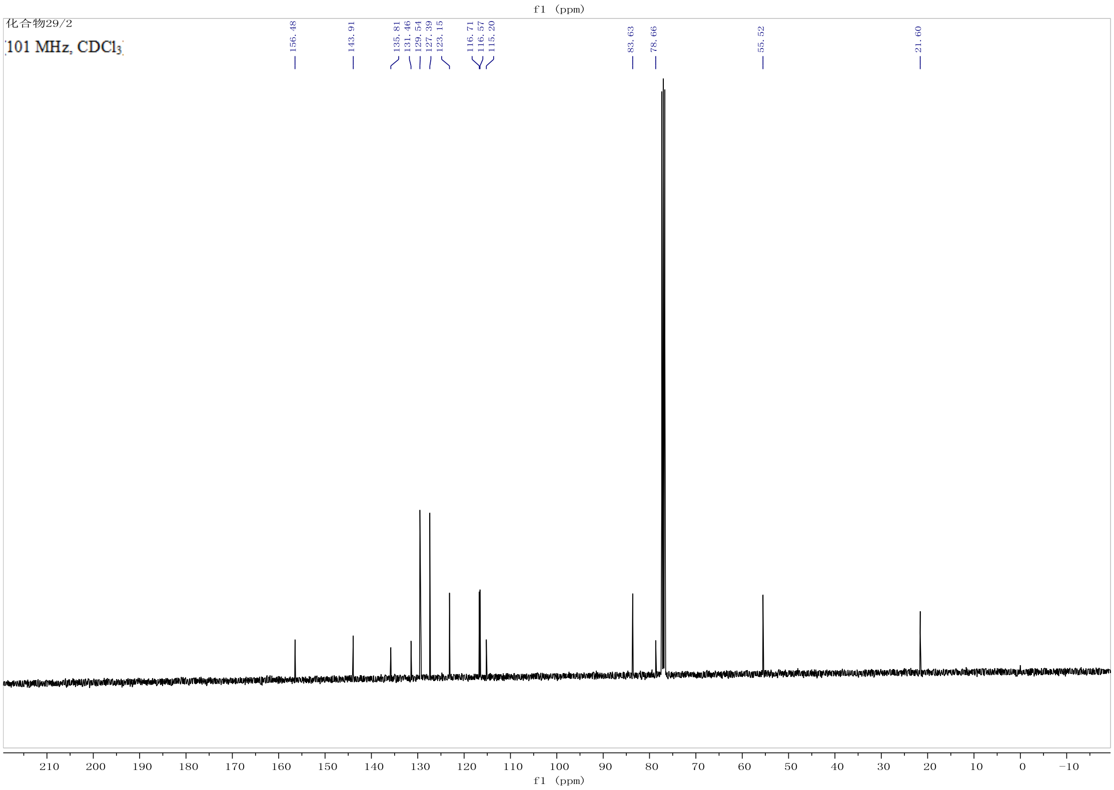

化合物32/1
rls-8, CDCl3, 20191127
400 MHz, CDCl3
7.72 7.72 7.71 7.70 7.69 7.69 7.44 7.44 7.43 7.23 7.23 7.23 7.21 7.21 7.21 6.84 6.84 6.84 6.83 6.82 6.82 6.82 6.81
3.34
2.36 2.32
2.01 1.00 4.00 1.00 0.96 3.20 2.99
f1 (ppm)

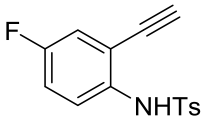

化合物32/2
rls-8, CDCl3, 20191128
101 MHz, CDCl3
144.07 140.81 138.29 135.98 132.21 129.64 127.32 125.22 120.08 109.92 83.83 78.78 21.82 21.56
f1 (ppm)


H3CO
NHTs

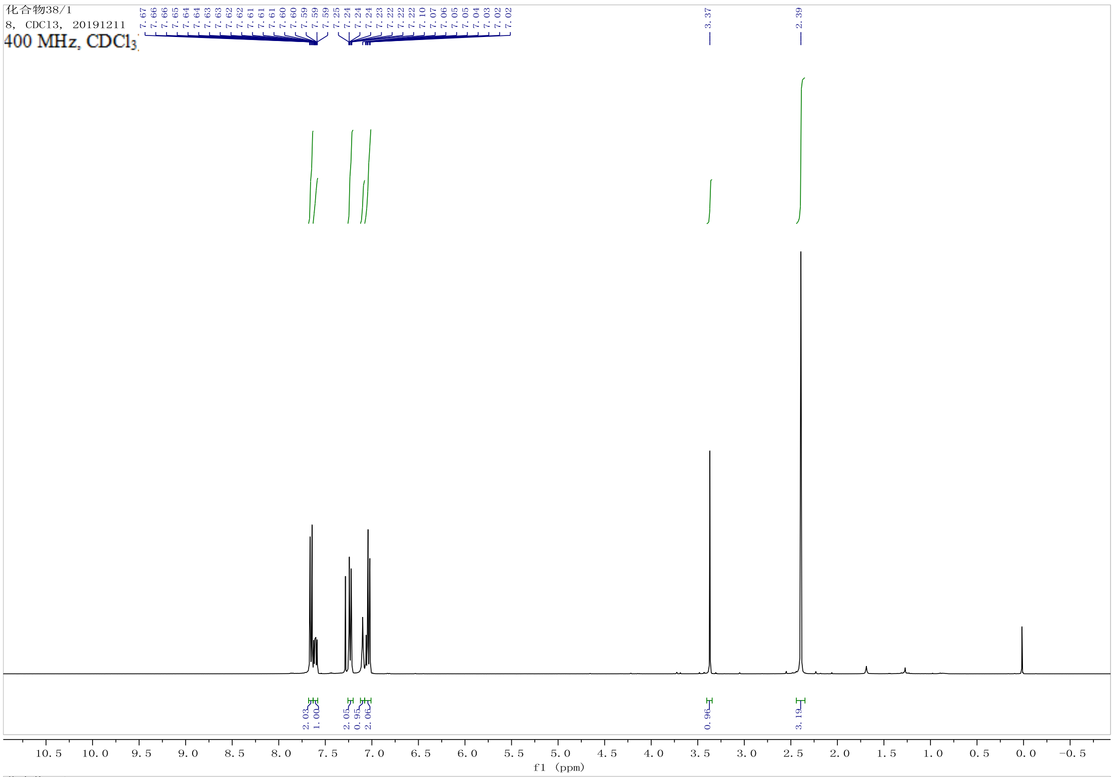
5d

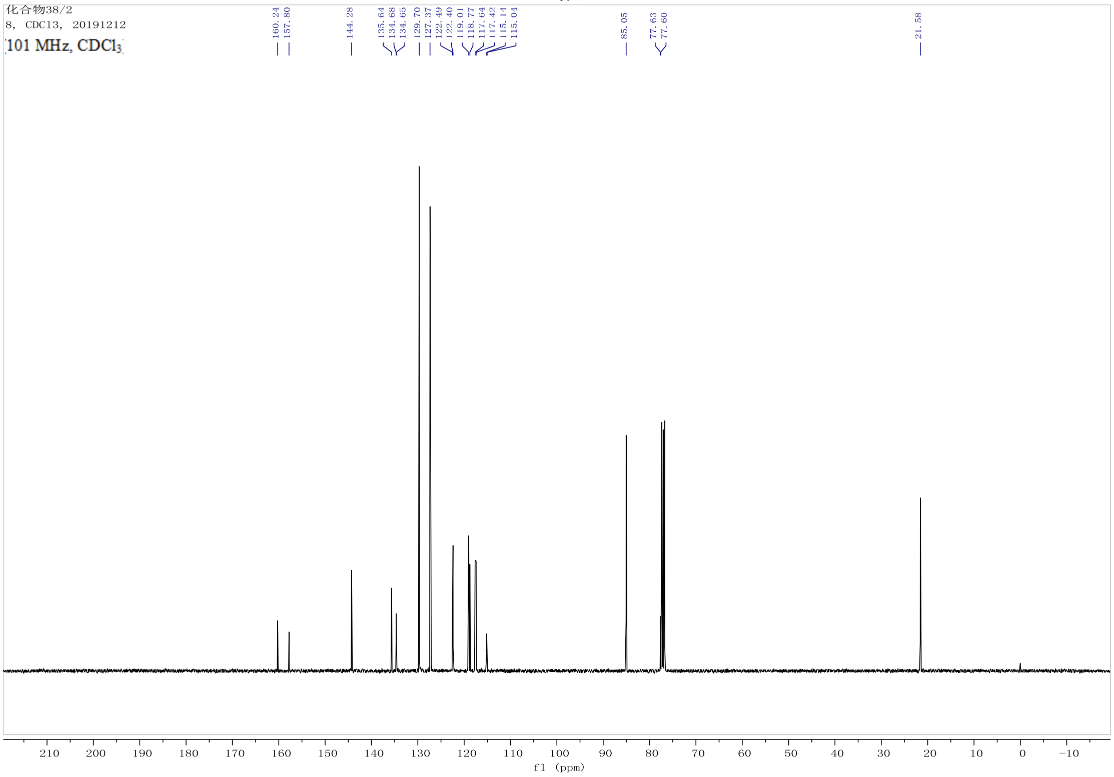

化合物29/1
400 MHz, CDCl3
7.63 7.63 7.61 7.61 7.57 7.55 7.22 7.22 7.20 6.91 6.91 6.89 6.88 6.84 6.84
3.76
3.25
2.39
1.94 1.02 2.00 1.13 1.17 3.05 0.95 3.07
f1 (ppm)

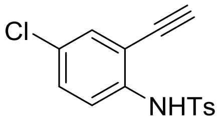

化合物29/2
101 MHz, CDCl3
156.48
143.91
135.81 131.46 129.54 127.39 123.15
116.71 116.57 115.20
83.63
78.66
55.52
21.60
f1 (ppm)


F
NHTs

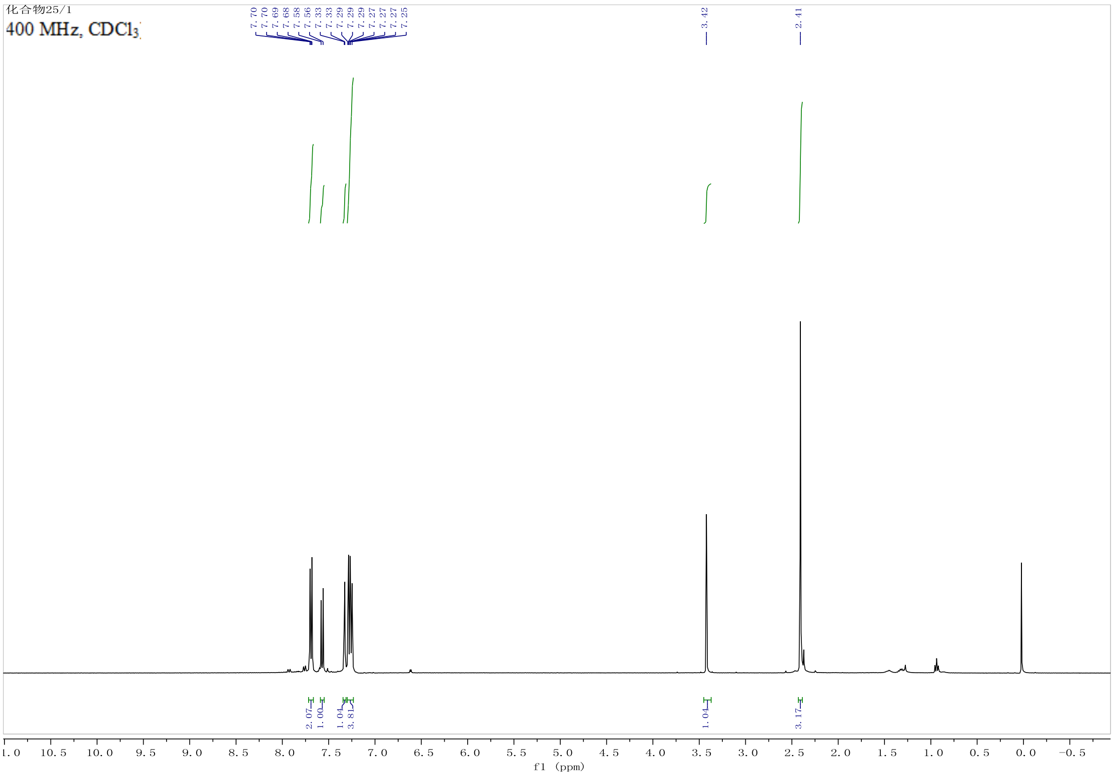
5e

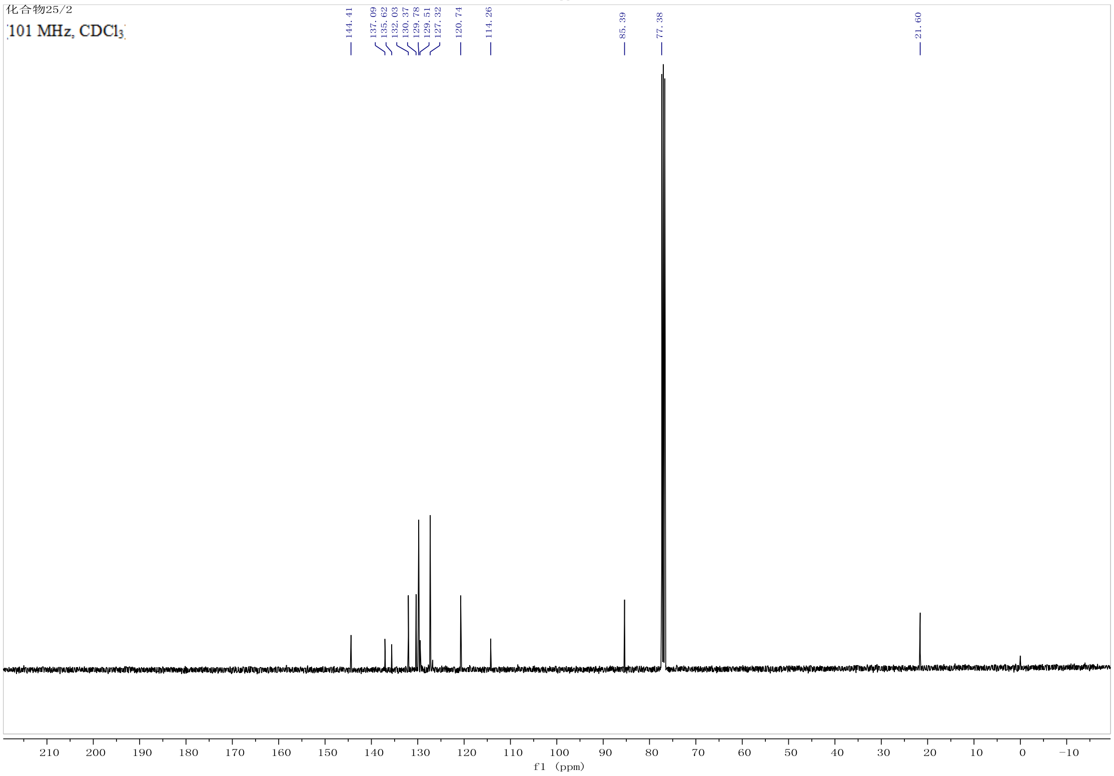

化合物38/1
8, CDCl3, 20191211
400 MHz, CDCl3
f1 (ppm)

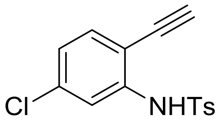

化合物38/2
8, CDCl3, 20191212
101 MHz, CDCl3
f1 (ppm)


Cl
NHTs

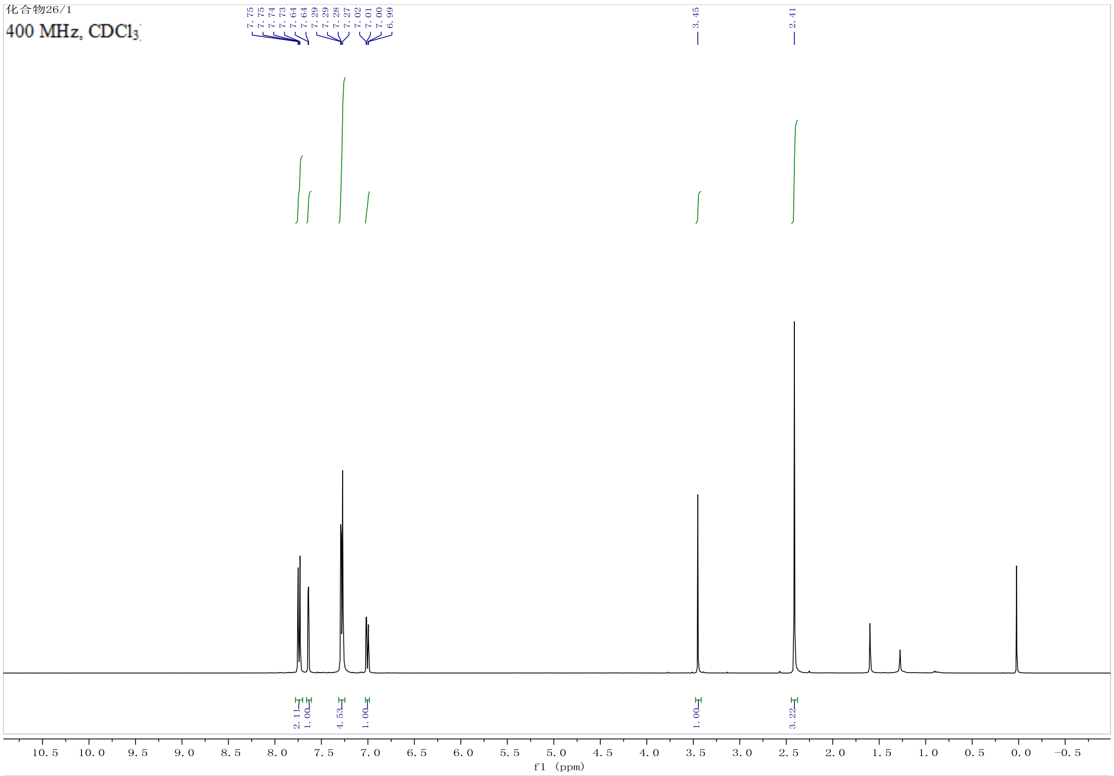
5f


化合物25/1
400 MHz, CDCl3
7.70 7.70 7.69 7.68 7.58 7.56 7.33 7.33 7.29 7.29 7.29 7.27 7.27 7.27 7.25
3.42
2.41
2.07 1.00 1.04 3.81
1.04
3.17
f1 (ppm)

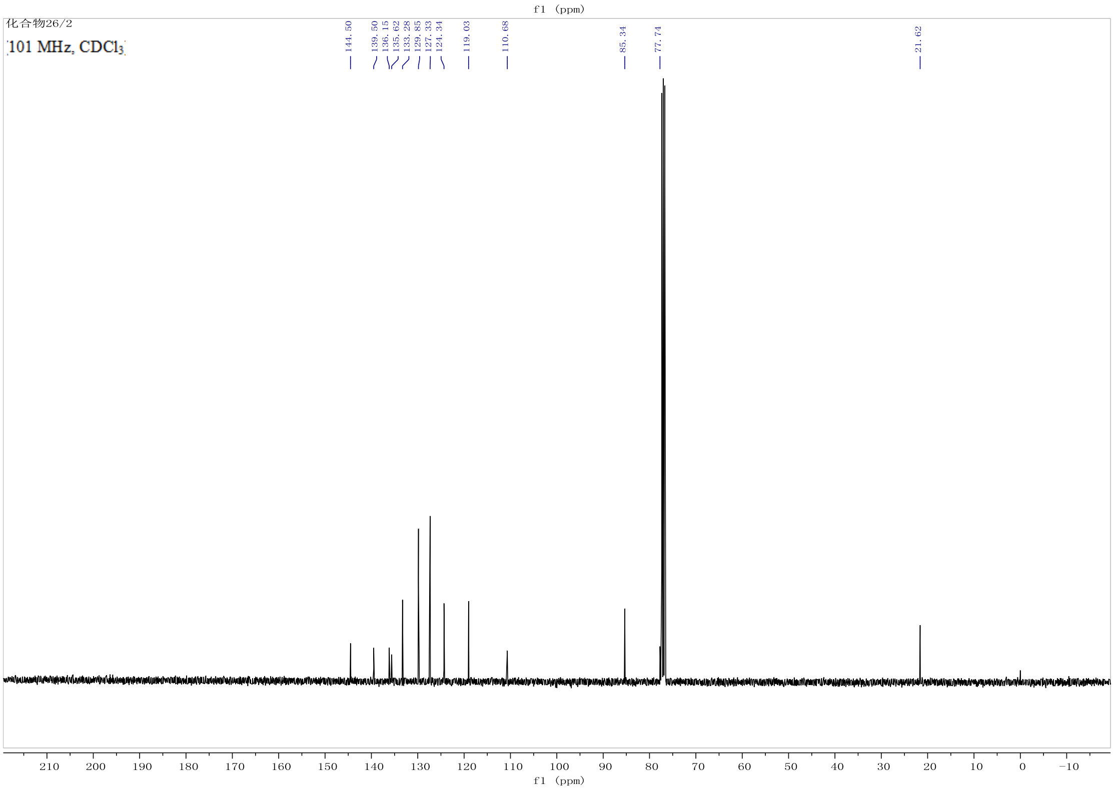

化合物25/2
101 MHz, CDCl3
144.41 137.09 135.62 132.03 130.37 129.78 129.51 127.32 120.74 114.26
85.39
77.38
21.60
f1 (ppm)



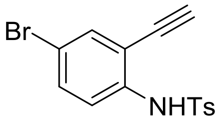
5g



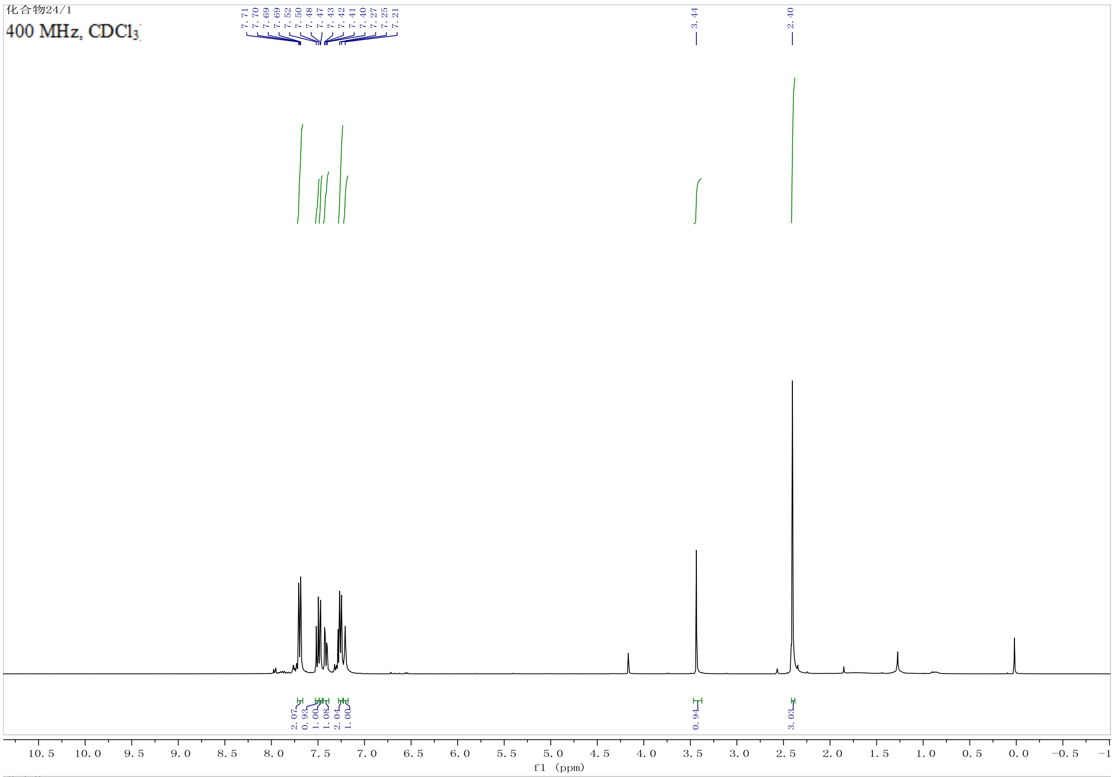
化合物26/1
400 MHz, CDCl3
7.75
7.75
7.74
7.73
7.64
7.64
7.29
7.29
7.28
7.27
7.02
7.01
7.00
6.99
3.45
2.41
2.11
1.00
4.53
1.00
1.00
3.22
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

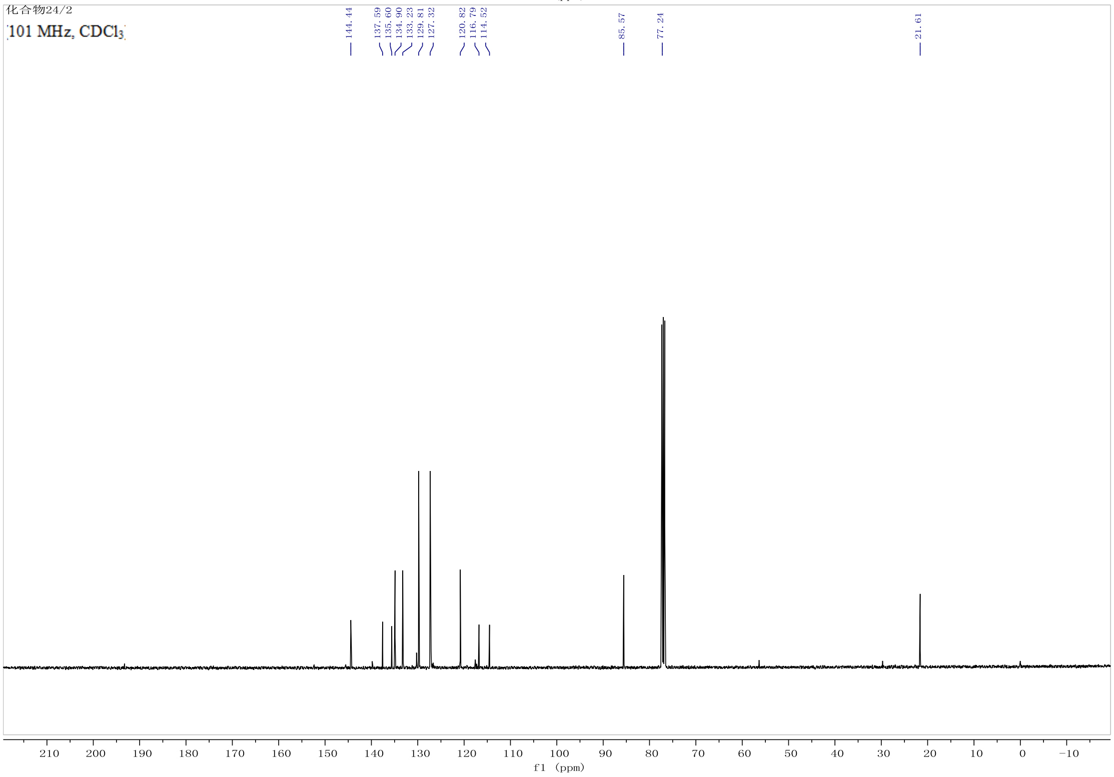


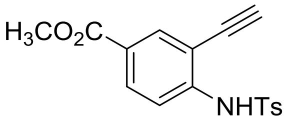
化合物26/2
101 MHz, CDCl3
144.50
139.50
136.15
135.62
133.28
129.85
127.33
124.34
119.03
110.68
85.34
77.74
21.62
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



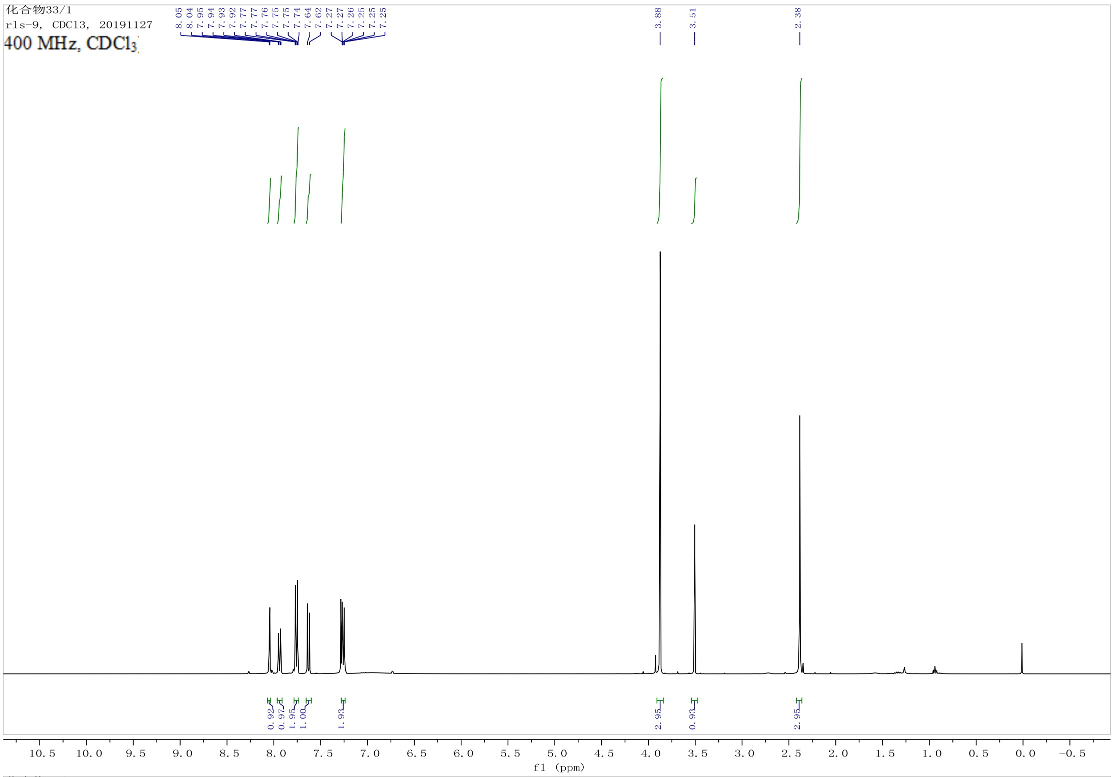
5h

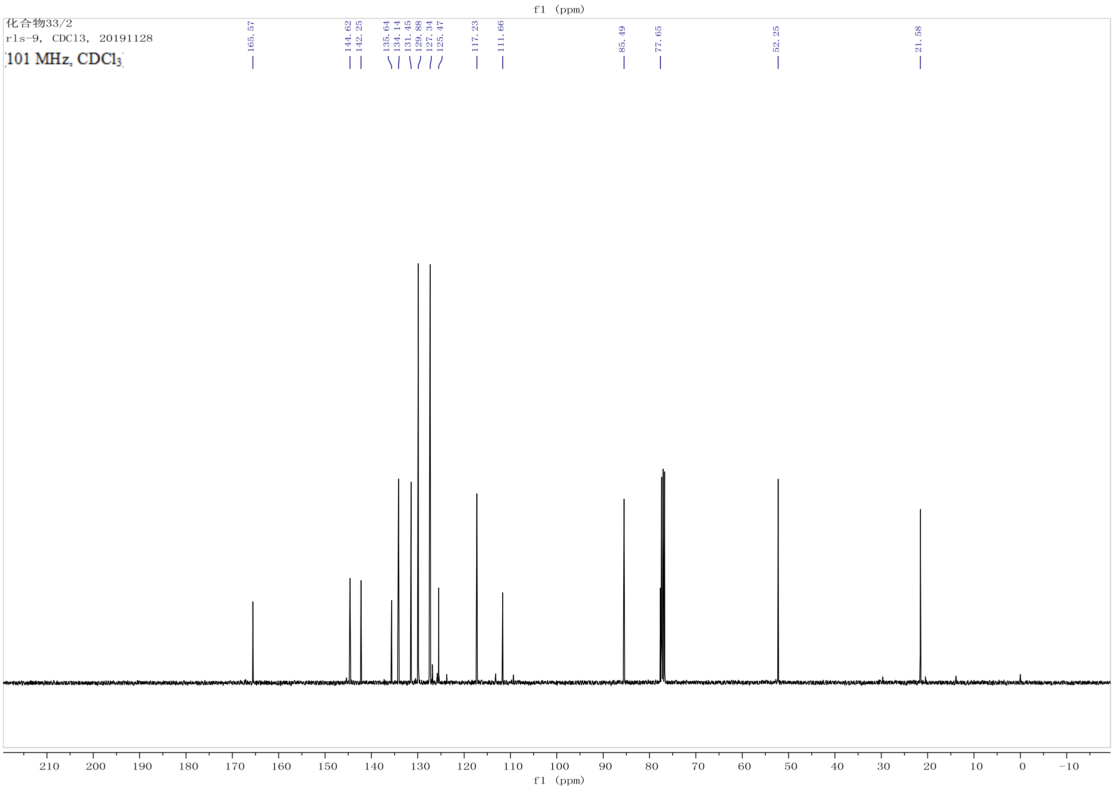

化合物24/1
400 MHz, CDCl3
f1 (ppm)

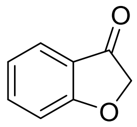

化合物24/2
101 MHz, CDCl3
144.44
137.59
135.60
134.90
133.23
129.81
127.32
120.82
116.79
114.52
85.57
77.24
21.61
f1 (ppm)



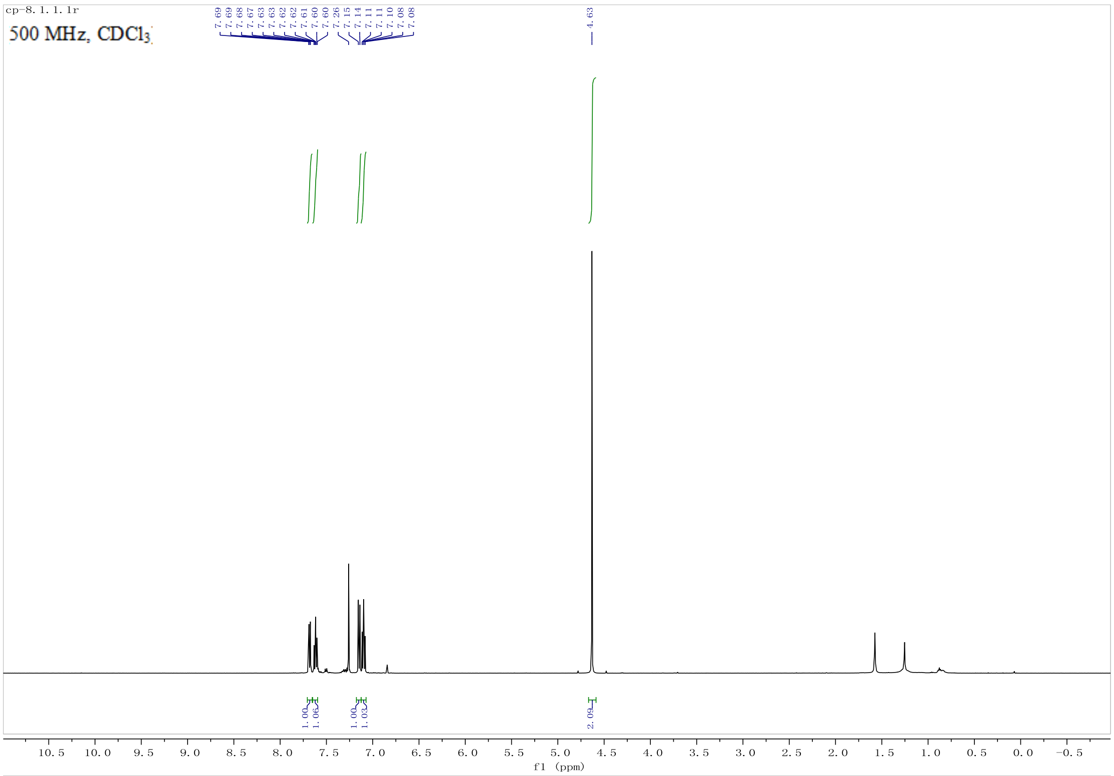
5i

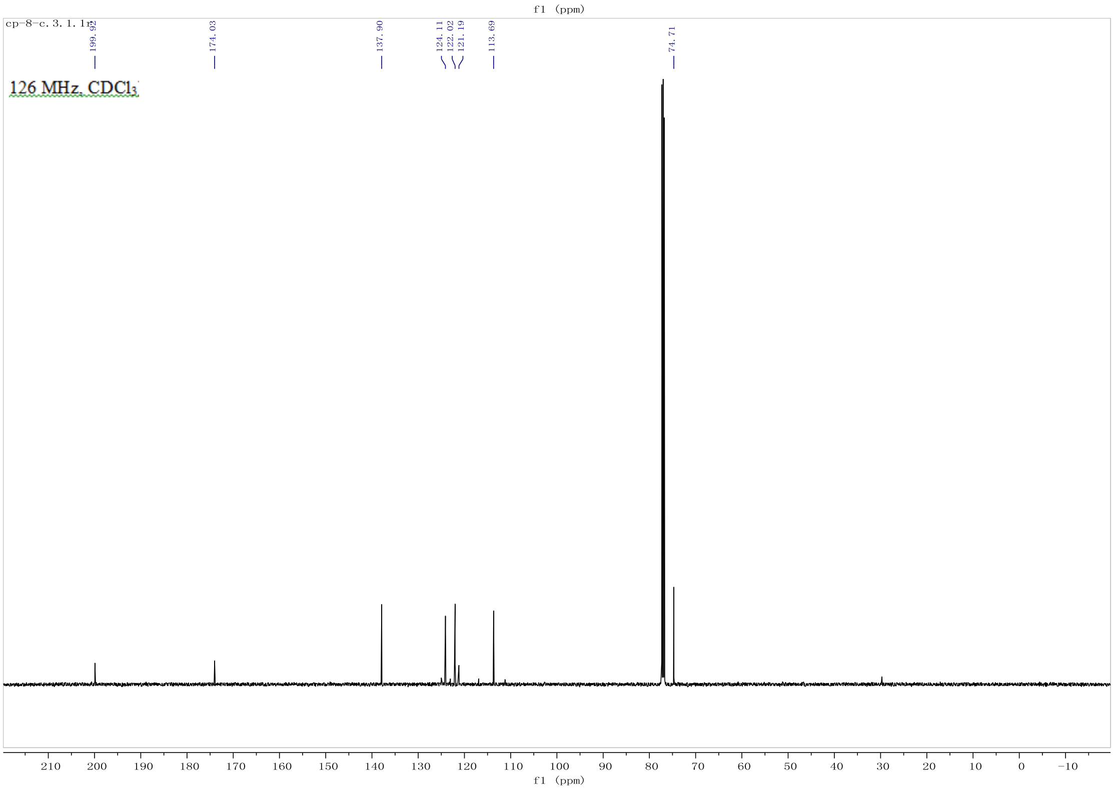

化合物33/1
rls-9, CDCl3, 20191127
400 MHz, CDCl3
8.05 8.04 7.95 7.94 7.93 7.92 7.77 7.77 7.76 7.75 7.75 7.74 7.64 7.62 7.27 7.27 7.26 7.25 7.25 7.25
3.88
3.51
2.38
0.92 0.97 1.95 1.00 1.93
2.95 0.93 2.95
f1 (ppm)

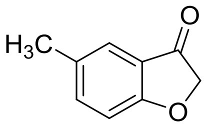

化合物33/2
rls-9, CDCl3, 20191128
101 MHz, CDCl3
165.57
144.62 142.25
135.64 134.14 131.45 129.88 127.34 125.47
117.23 111.66
85.49
77.65
52.25
21.58
f1 (ppm)



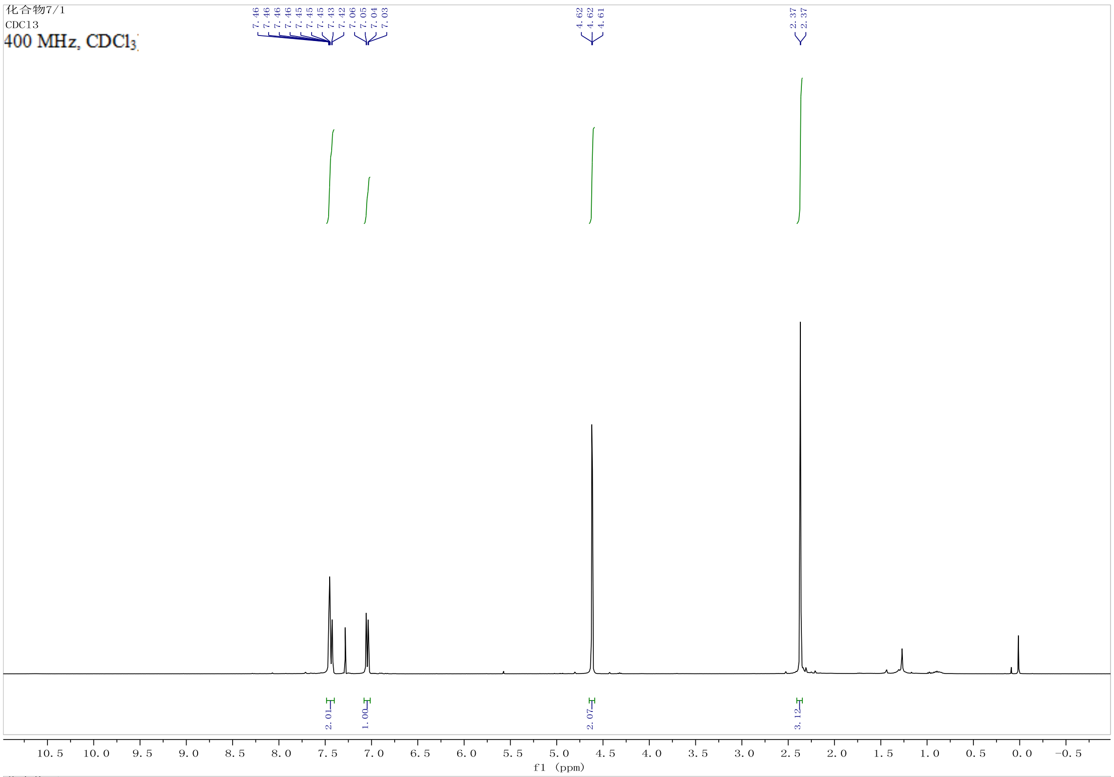
2a

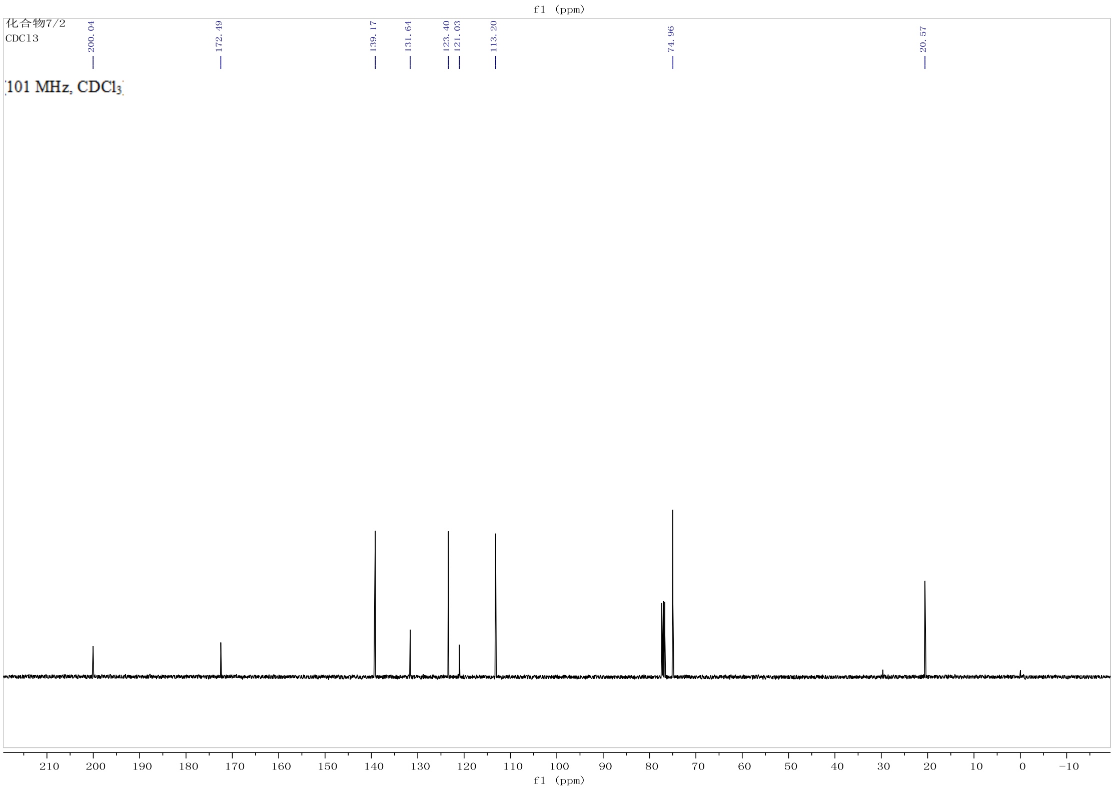

cp-8.1.1.1r
500 MHz, CDCl3
7.69
7.69
7.68
7.67
7.63
7.63
7.62
7.61
7.60
7.60
7.26
7.15
7.14
7.11
7.11
7.10
7.08
7.08
4.63
1.00
1.06
1.00
1.03
2.09
f1 (ppm)

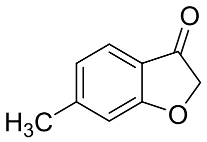

cp-8-c.3.1.1r
126 MHz, CDCl3
199.92
174.03
137.90
124.11
122.02
121.19
113.69
74.71
f1 (ppm)


H3C
O
O

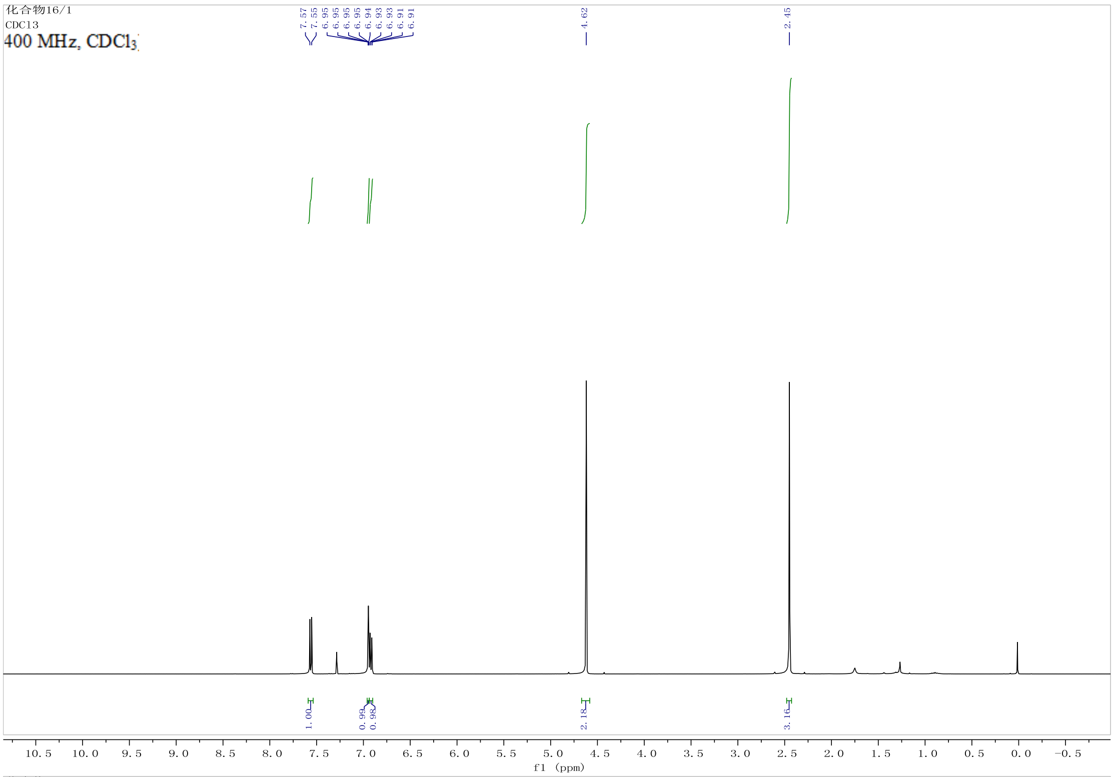
2b

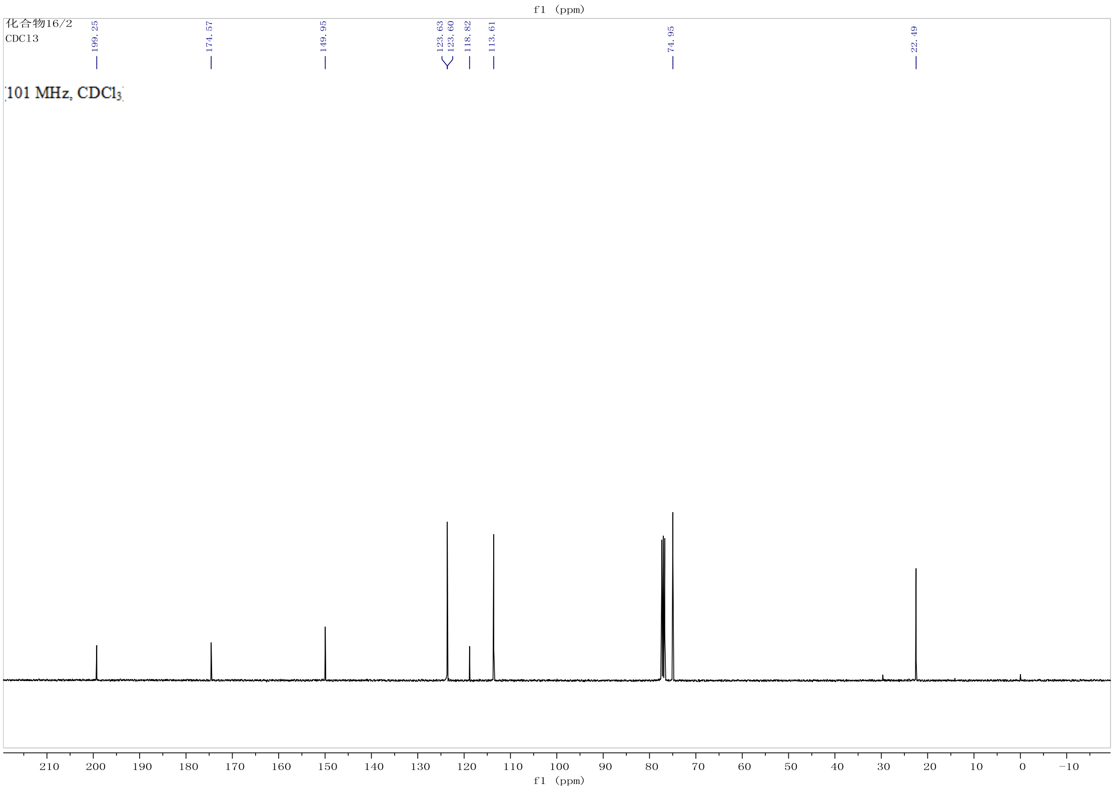

化合物7/1
CDC13
400 MHz, CDCl3
7.46
7.46
7.46
7.46
7.45
7.45
7.45
7.43
7.42
7.06
7.05
7.04
7.03
4.62
4.62
4.61
2.37
2.37
2.01
1.00
2.07
3.12
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

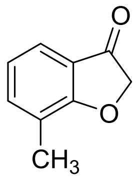

化合物7/2
CDC13
200.04
172.49
139.17
131.64
123.40
121.03
113.20
74.96
20.57
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



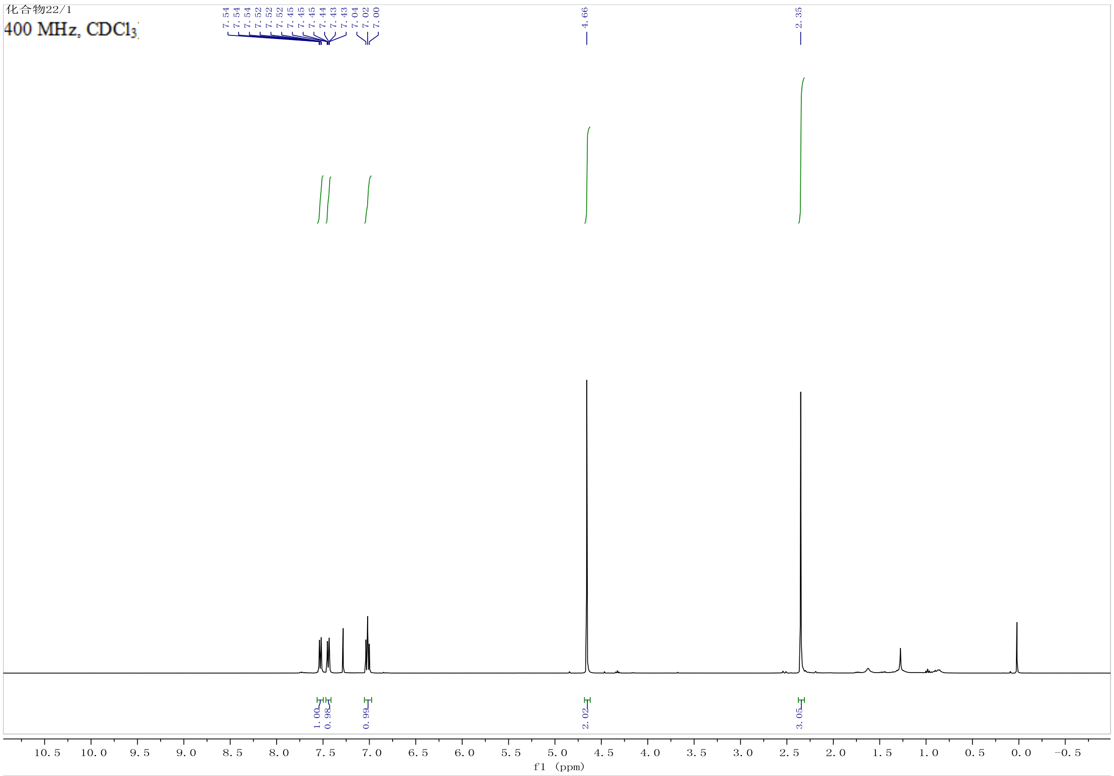
2c

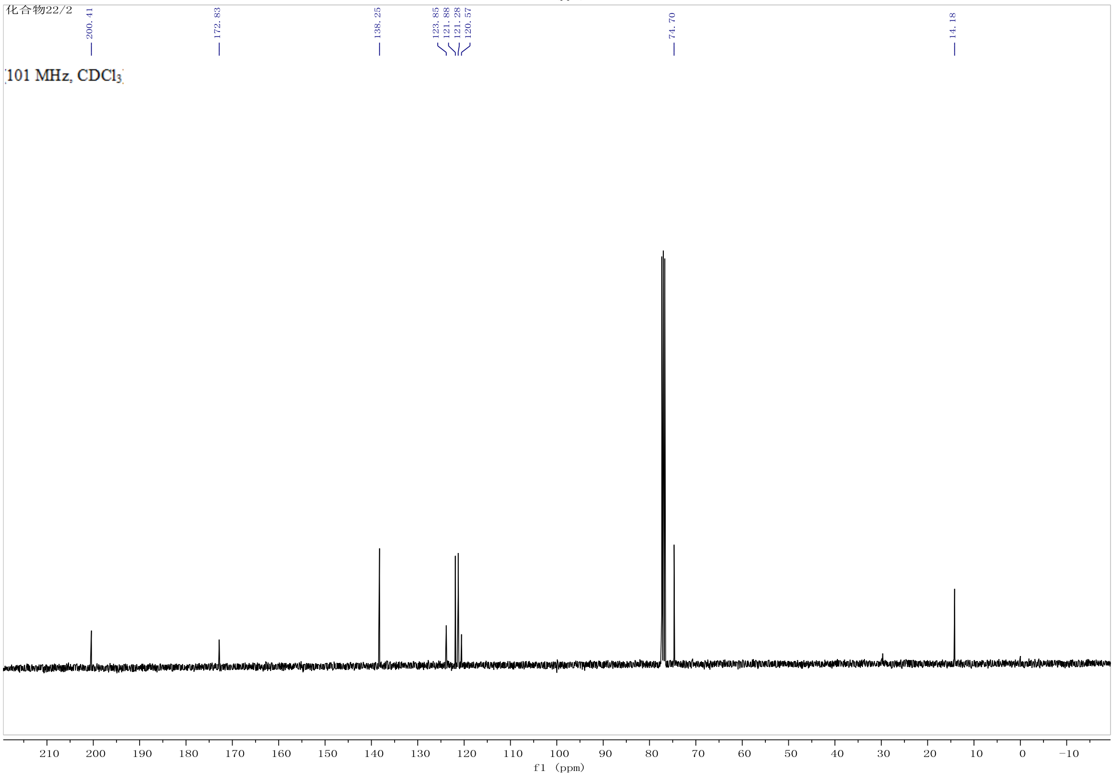

化合物16/1
CDC13
400 MHz, CDCl3
7.57
7.55
6.95
6.95
6.95
6.95
6.94
6.93
6.93
6.91
6.91
4.62
2.45
1.00
0.99
0.98
2.18
3.16
f1 (ppm)

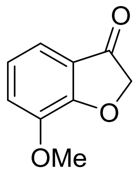

化合物16/2
CDC13
101 MHz, CDCl3
199.25
174.57
149.95
123.63
123.60
118.82
113.61
74.95
22.49
f1 (ppm)



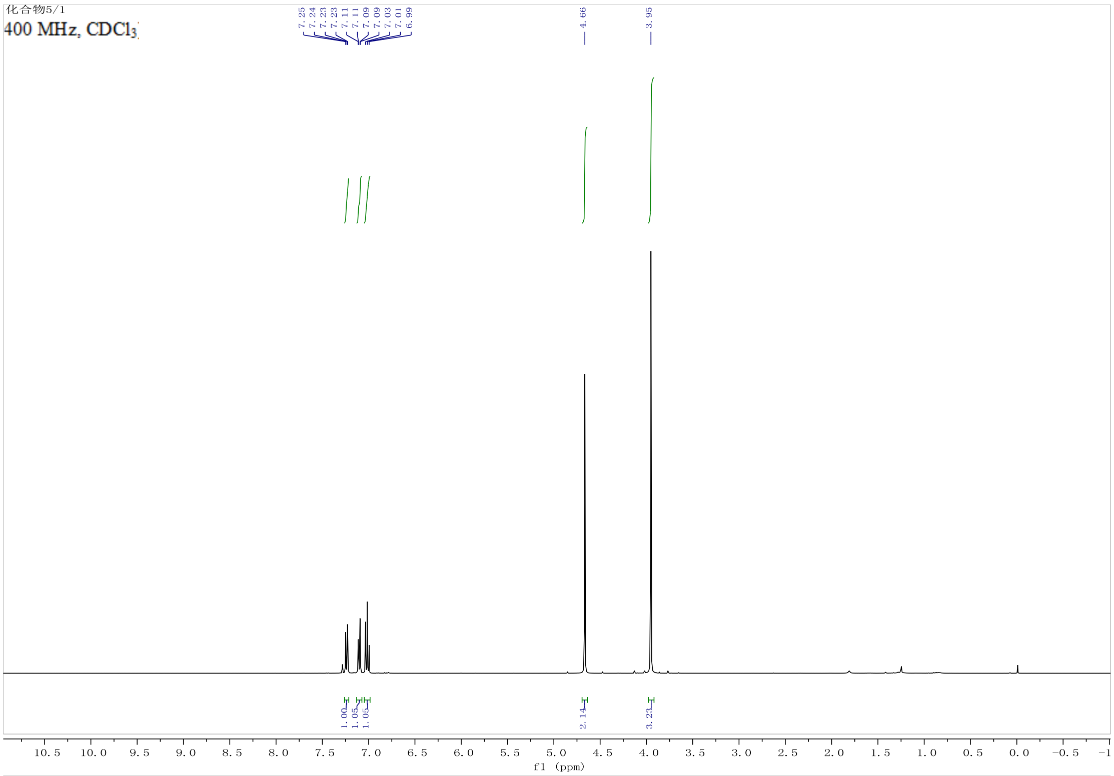
2d


化合物22/1
400 MHz, CDCl3
7.54
7.54
7.54
7.52
7.52
7.52
7.45
7.45
7.45
7.44
7.43
7.43
7.04
7.02
7.00
4.66
2.35
1.00
0.98
0.99
2.02
3.05
f1 (ppm)

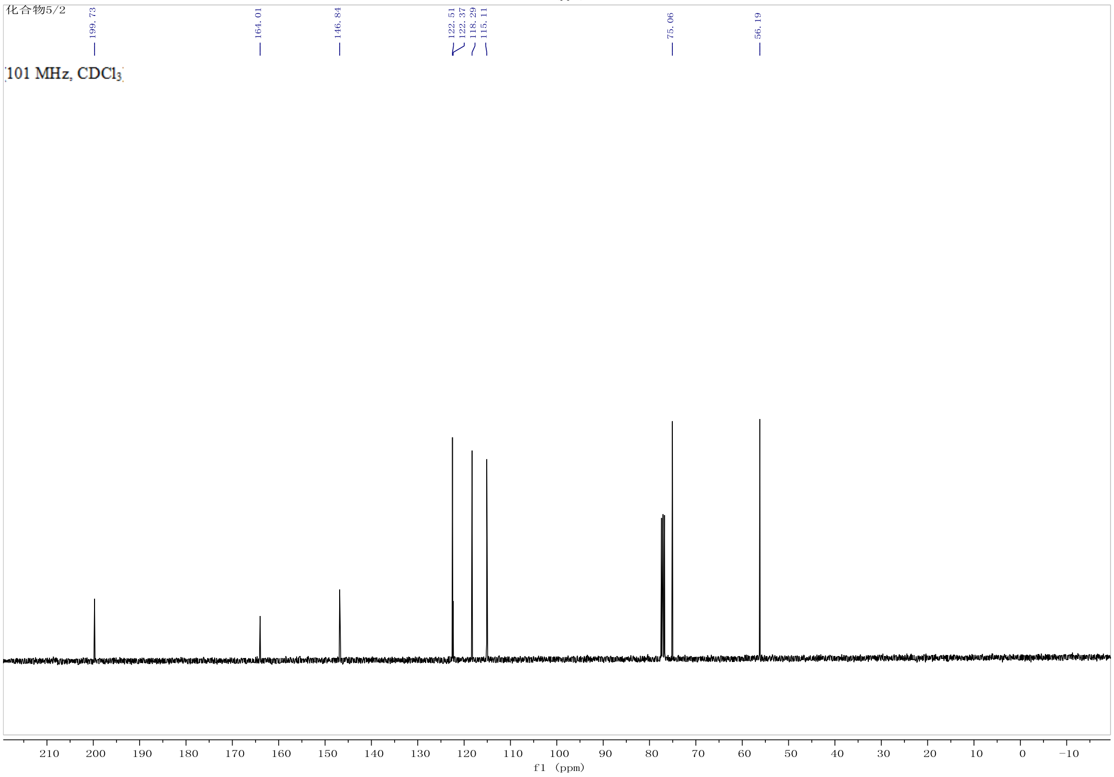

化合物22/2
101 MHz, CDCl3
200.41
172.83
138.25
123.85
121.88
121.28
120.57
74.70
14.18
f1 (ppm)



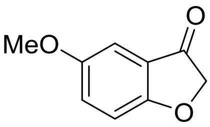
2e



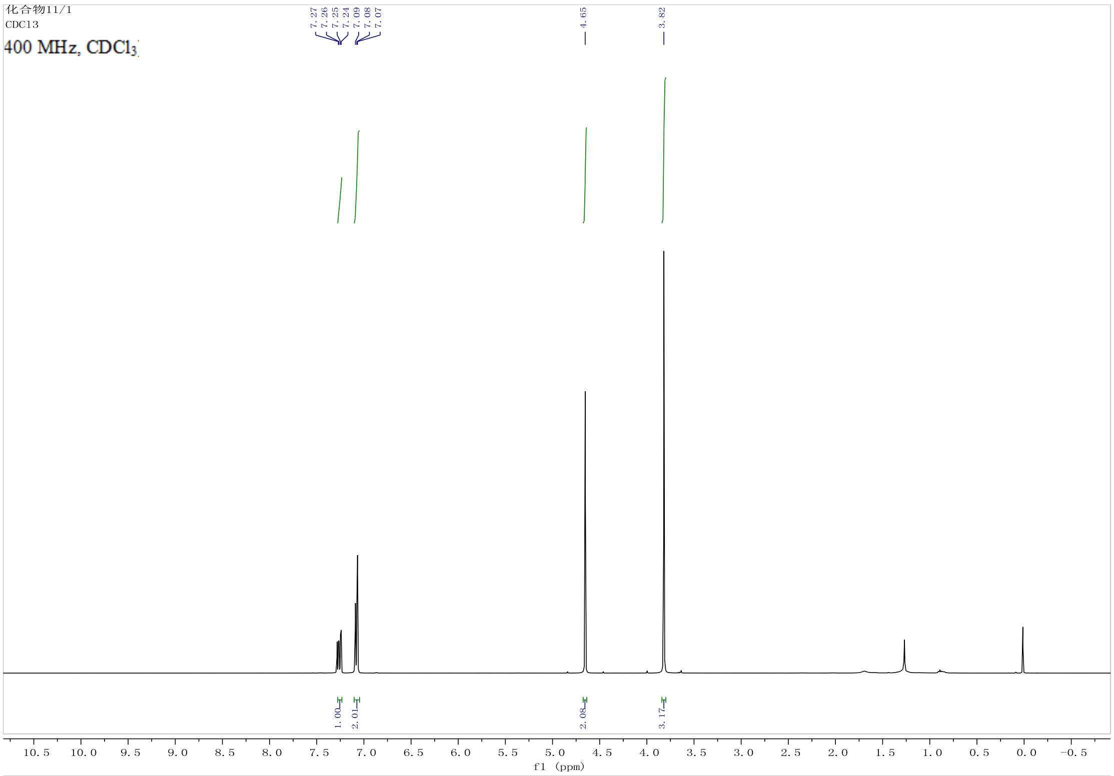
化合物5/1
400 MHz, CDCl3
7.25
7.24
7.23
7.23
7.11
7.11
7.09
7.09
7.03
7.01
6.99
4.66
3.95
1.00
1.05
1.03
2.14
3.23
f1 (ppm)



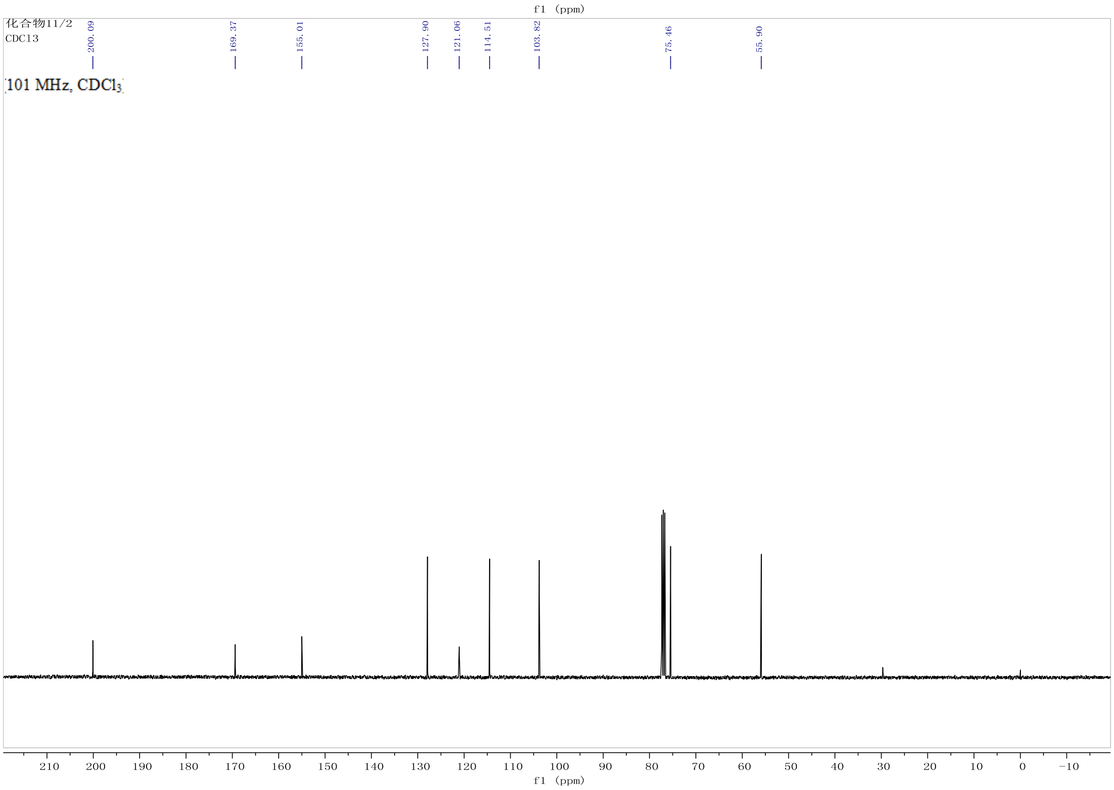
化合物5/2
101 MHz, CDCl3
199.73
164.01
146.84
122.51
122.37
118.29
115.11
75.06
56.19
f1 (ppm)



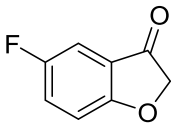
2f



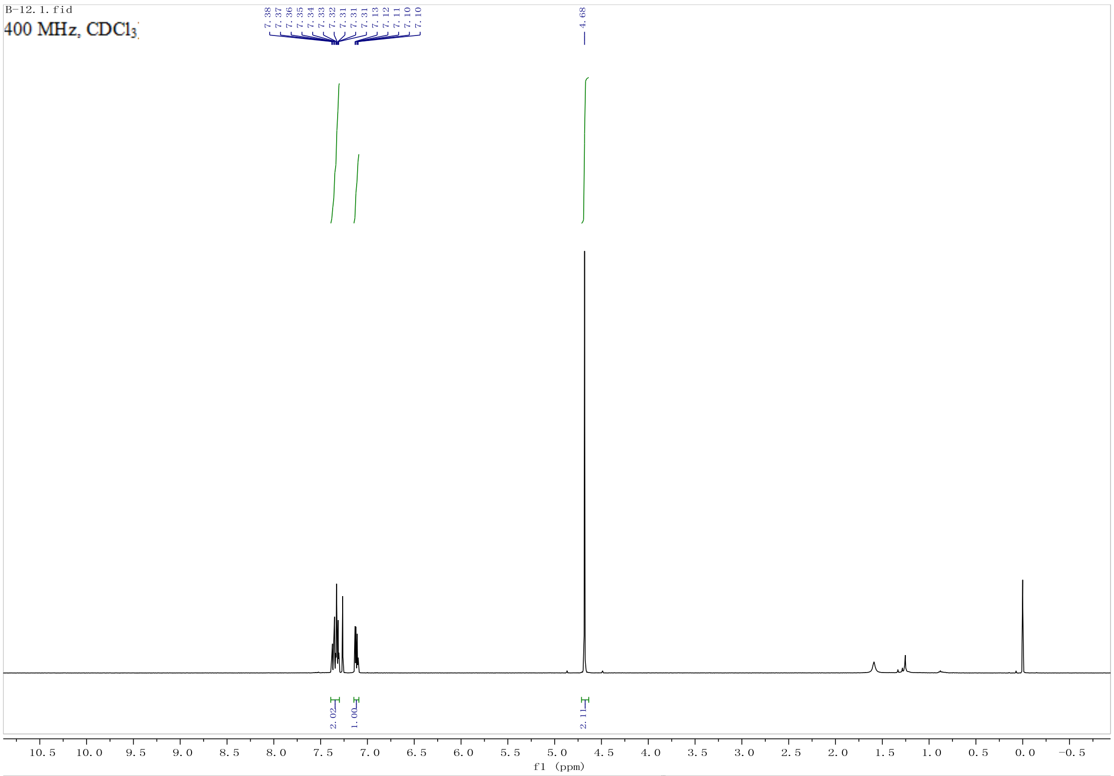
化合物11/1
CDC13
400 MHz, CDCl3
7.27 7.26 7.25 7.24 7.09 7.08 7.07
4.65
3.82
1.00 2.01 2.08 3.17
f1 (ppm)

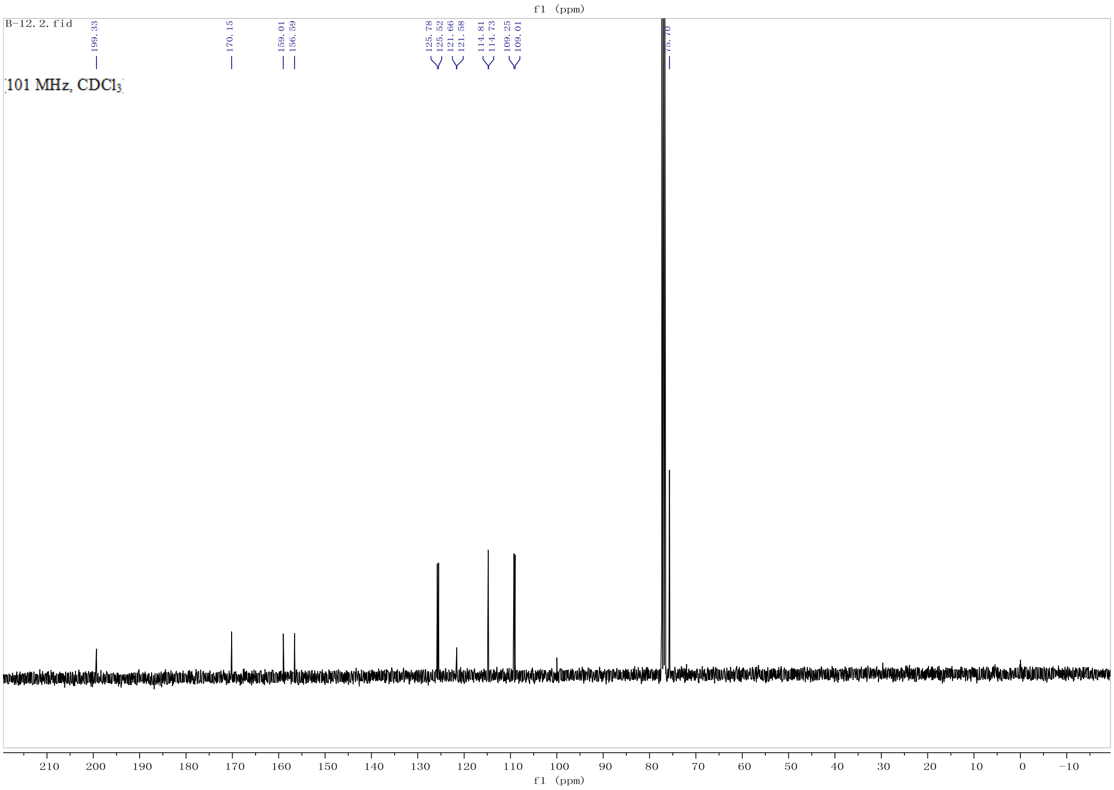


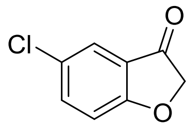
化合物11/2
CDC13
101 MHz, CDCl3
200.09 169.37 155.01 127.90 121.06 114.51 103.82 75.46 55.90
f1 (ppm)



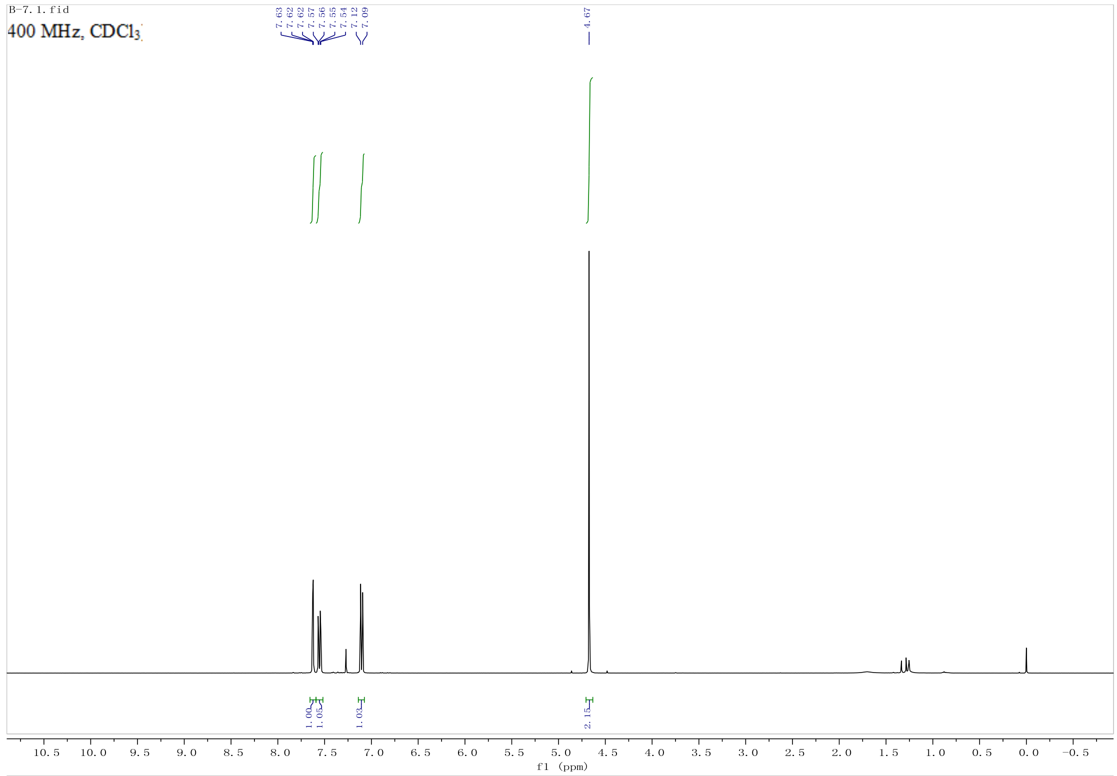
2g


B-12.1.fid
400 MHz, CDCl3
7.38 7.37 7.36 7.35 7.34 7.33 7.32 7.31 7.31 7.31 7.13 7.12 7.11 7.10 7.10
4.68
2.02 1.00 2.11
f1 (ppm)

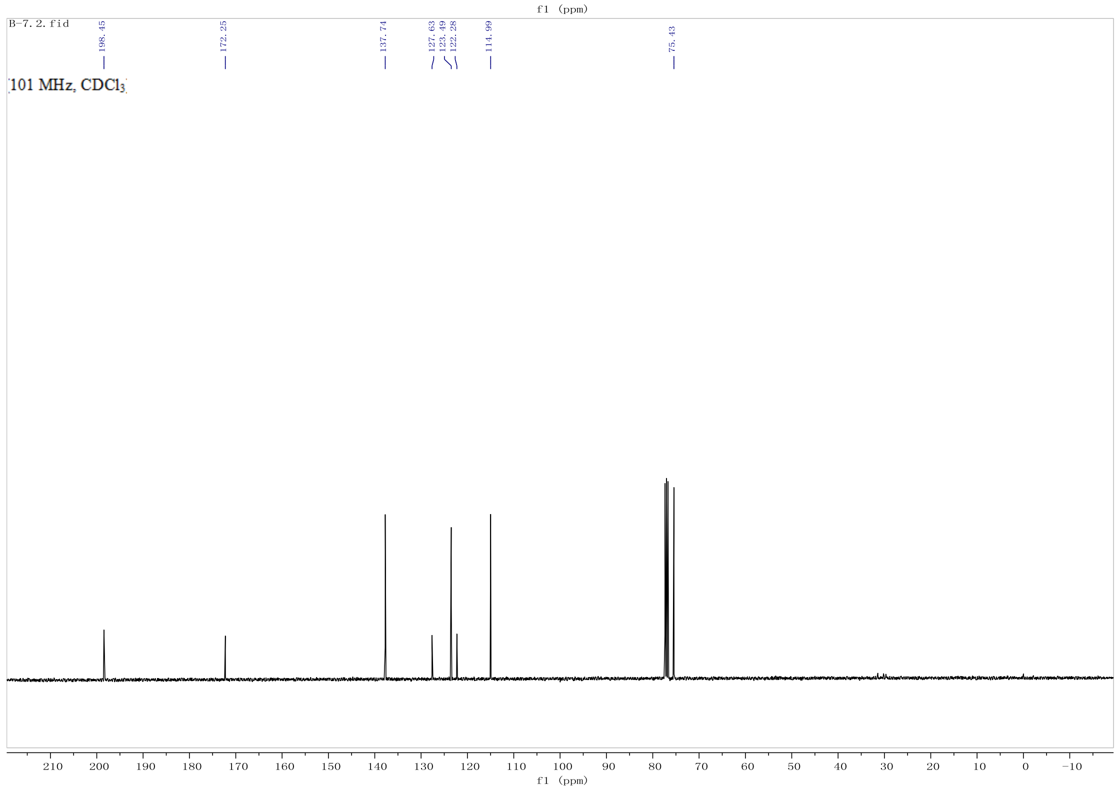

B-12.2.fid
101 MHz, CDCl3
199.33
170.15
159.01 156.59
125.78 125.52 121.66 121.58 114.81 114.73 109.25 109.01
f1 (ppm)



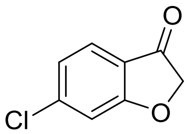
2h



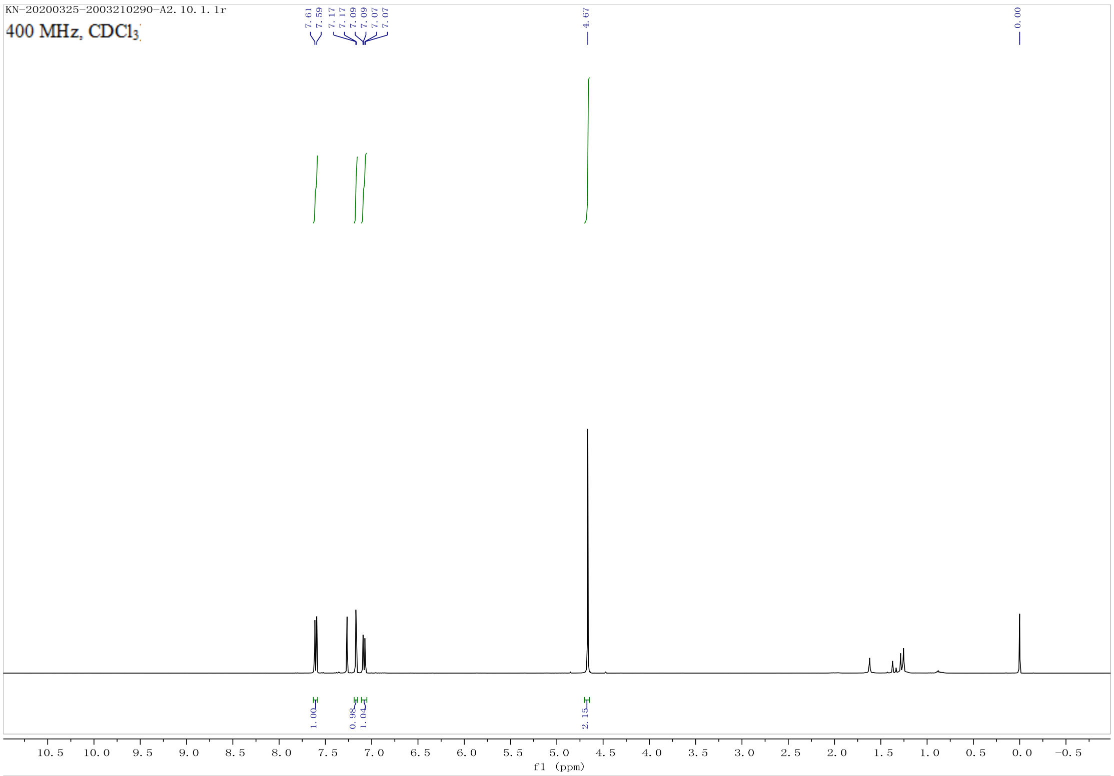
B-7.1.fid
400 MHz, CDCl3
7.63 7.62 7.62 7.57 7.56 7.55 7.54 7.12 7.09
4.67
1.00 1.05 1.03 2.15
f1 (ppm)

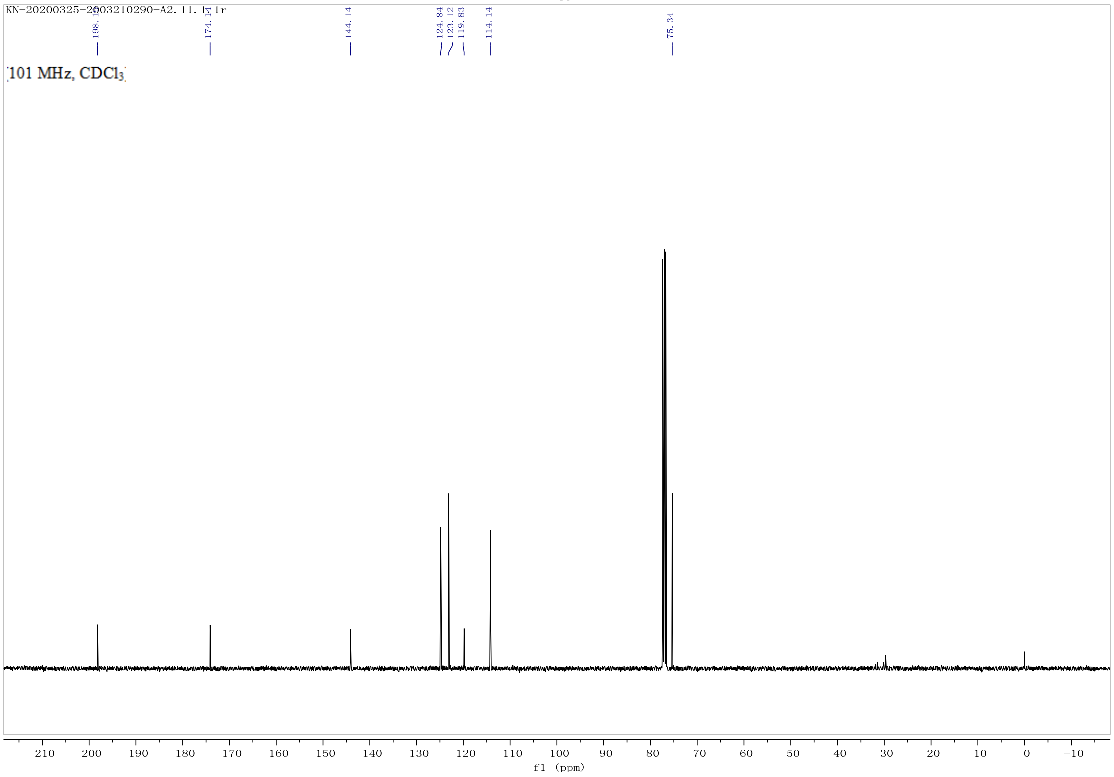


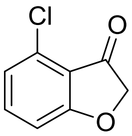
B-7.2.fid
101 MHz, CDCl3
198.45
172.25
137.74
127.63 123.49 122.28
114.99
75.43
f1 (ppm)



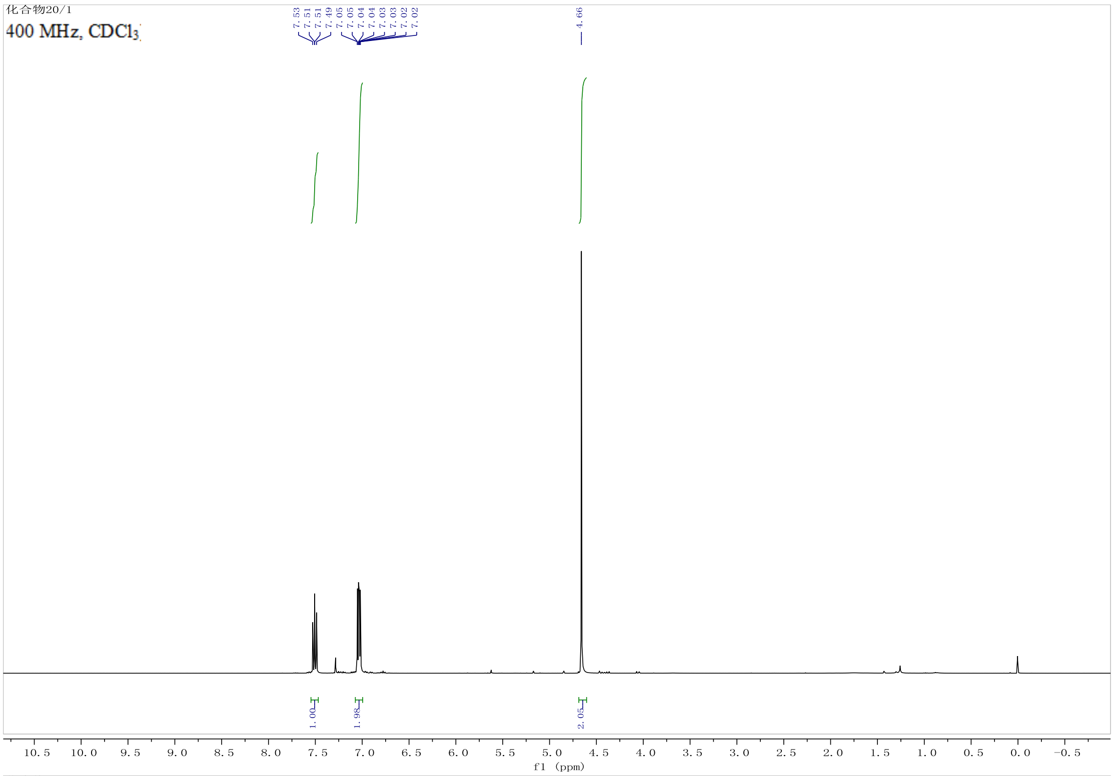
2i


KN-20200325-2003210290-A2.10.1.1r
400 MHz, CDCl3
7.61
7.59
7.17
7.17
7.09
7.09
7.07
7.07
4.67
0.00
1.00
0.98
1.04
2.15
f1 (ppm)

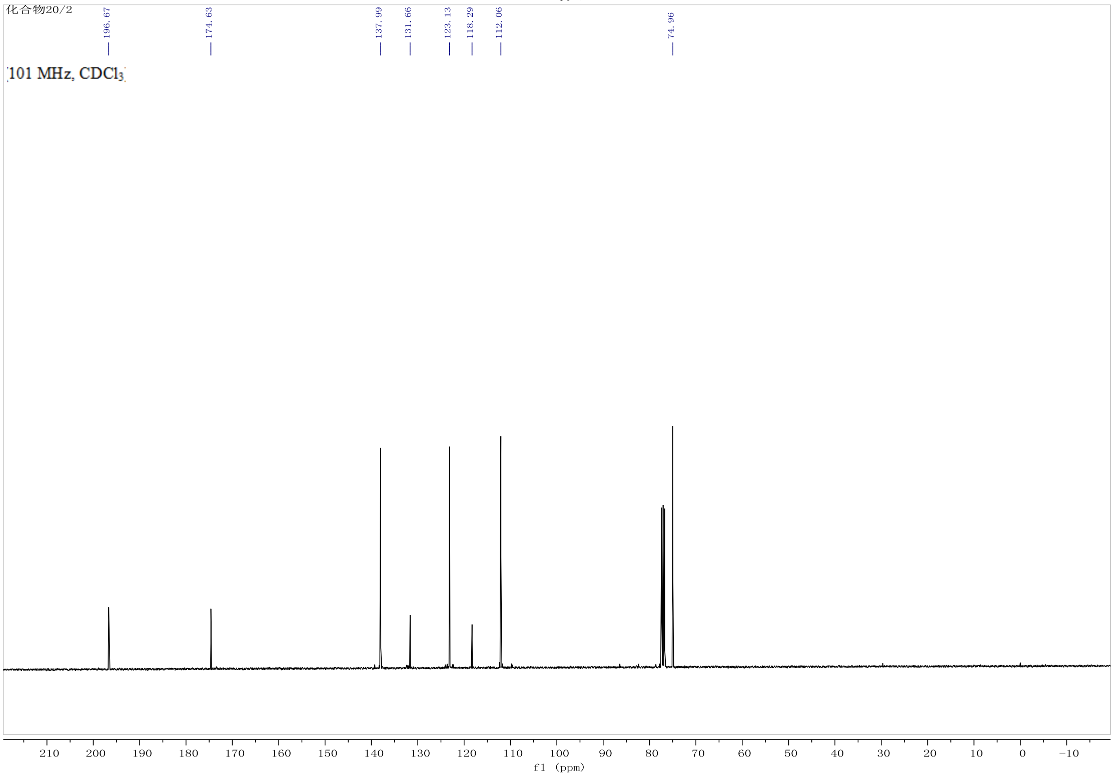

101 MHz, CDCl3
144.14
124.84
123.12
119.83
114.14
75.34
f1 (ppm)



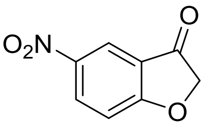
2j



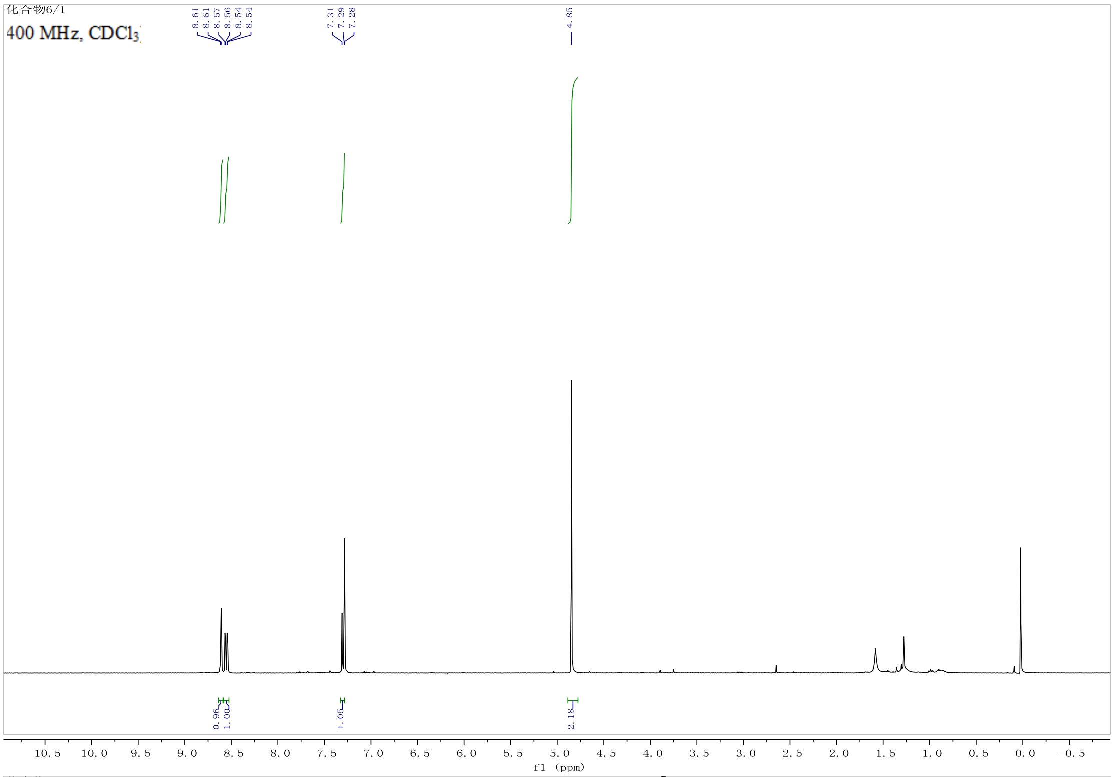
化合物20/1
400 MHz, CDCl3
7.53
7.51
7.51
7.49
7.05
7.05
7.04
7.04
7.03
7.03
7.02
7.02
4.66
1.00
1.98
2.05
f1 (ppm)

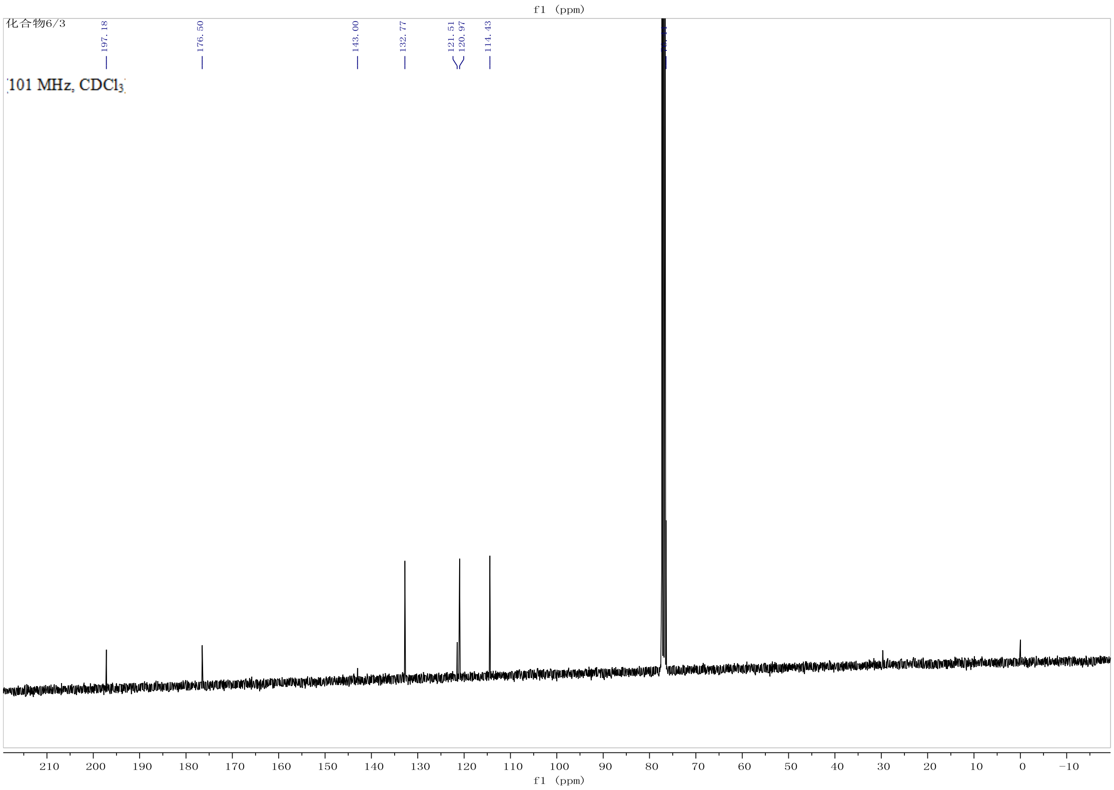


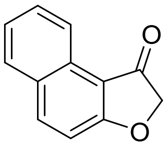
化合物20/2
101 MHz, CDCl3
196.67
174.63
137.99
131.66
123.13
118.29
112.06
74.96
f1 (ppm)



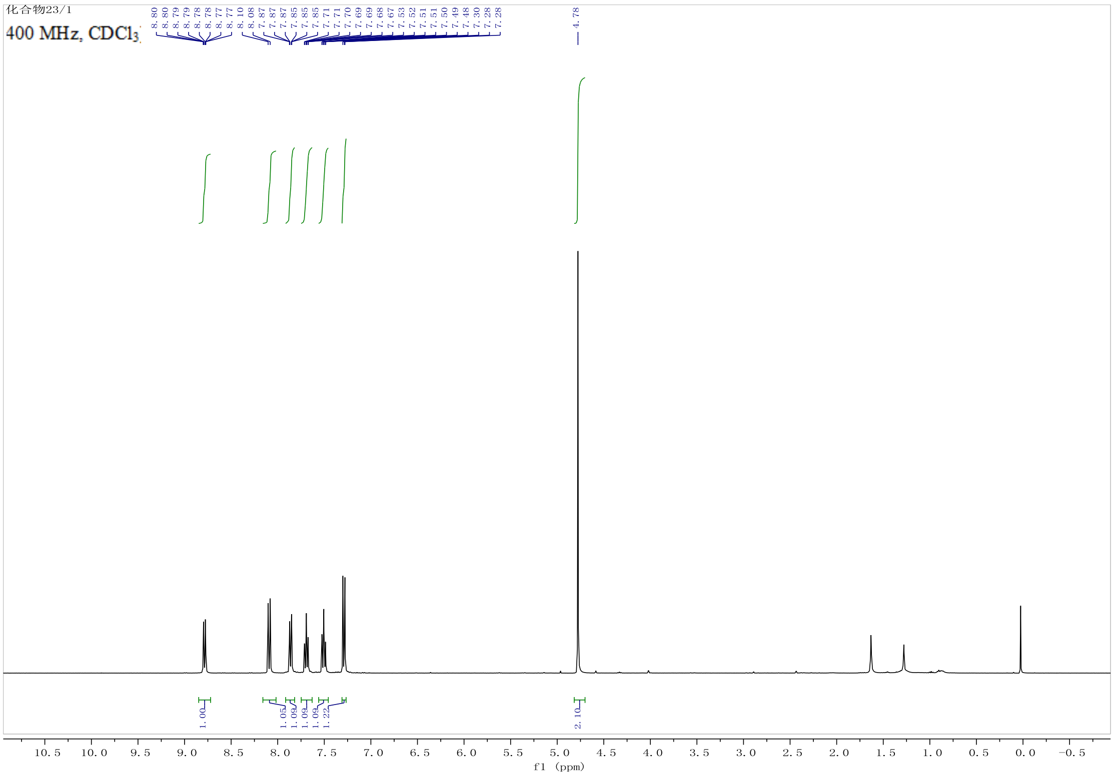
2k


化合物6/1
400 MHz, CDCl3
8.61
8.61
8.57
8.56
8.54
8.54
7.31
7.29
7.28
4.85
0.96
1.00
1.05
2.18
f1 (ppm)

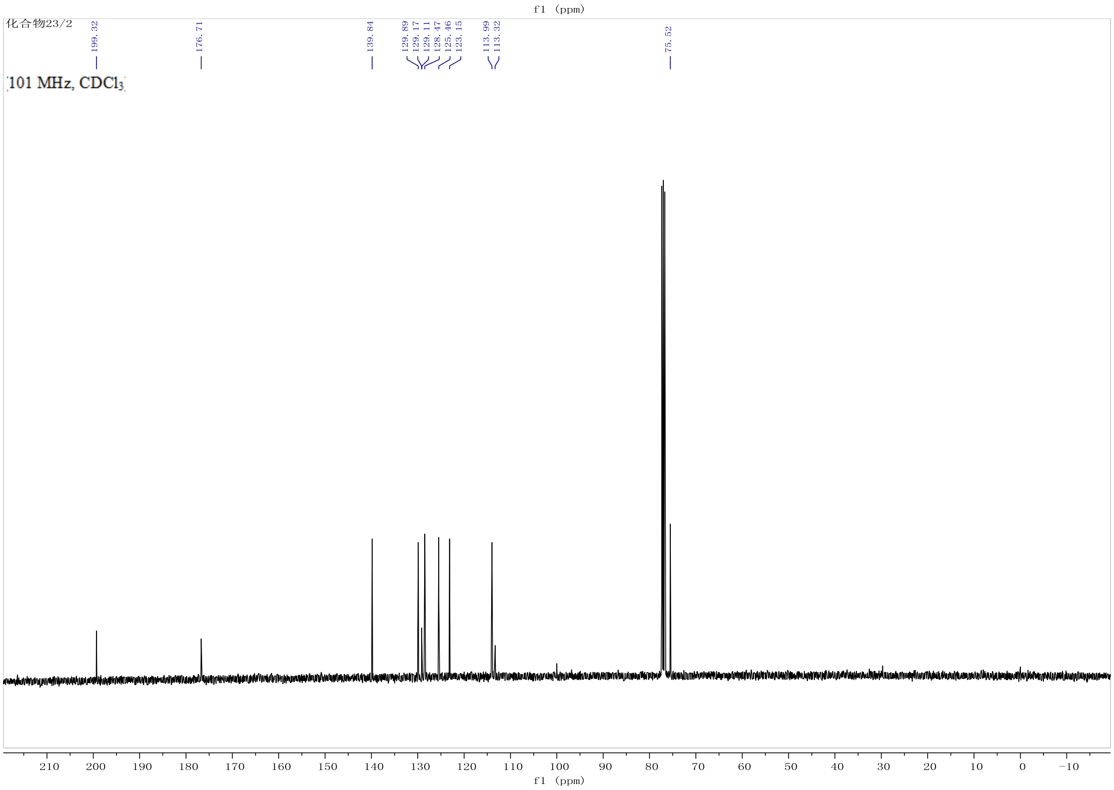

化合物6/3
101 MHz, CDCl3
197.18
176.50
143.00
132.77
121.51
120.97
114.43
f1 (ppm)



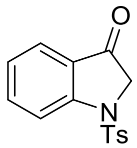
2l



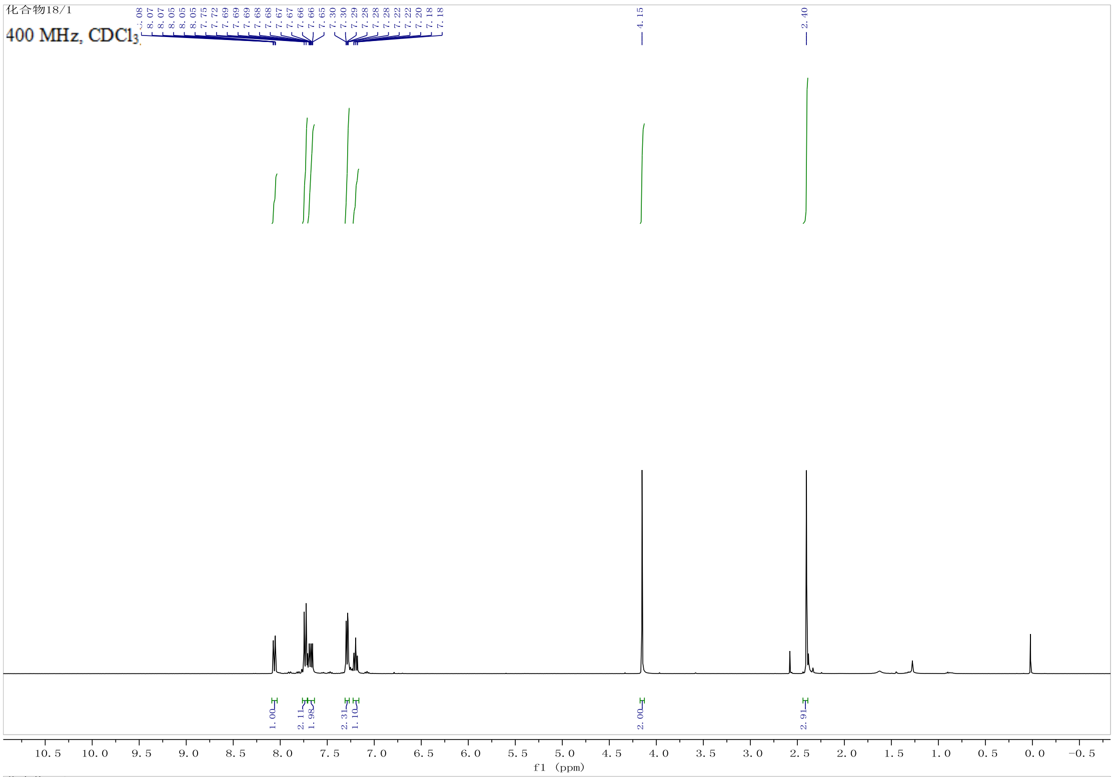
化合物23/1
400 MHz, CDCl3
8.80 8.80 8.79 8.79 8.78 8.78 8.77 8.77 8.10 8.08 7.87 7.87 7.87 7.85 7.85 7.85 7.85 7.71 7.71 7.70 7.69 7.69 7.68 7.67 7.53 7.52 7.51 7.51 7.50 7.49 7.48 7.30 7.28 7.28
4.78
1.00 1.05 1.09 1.09 1.09 1.22 2.10
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



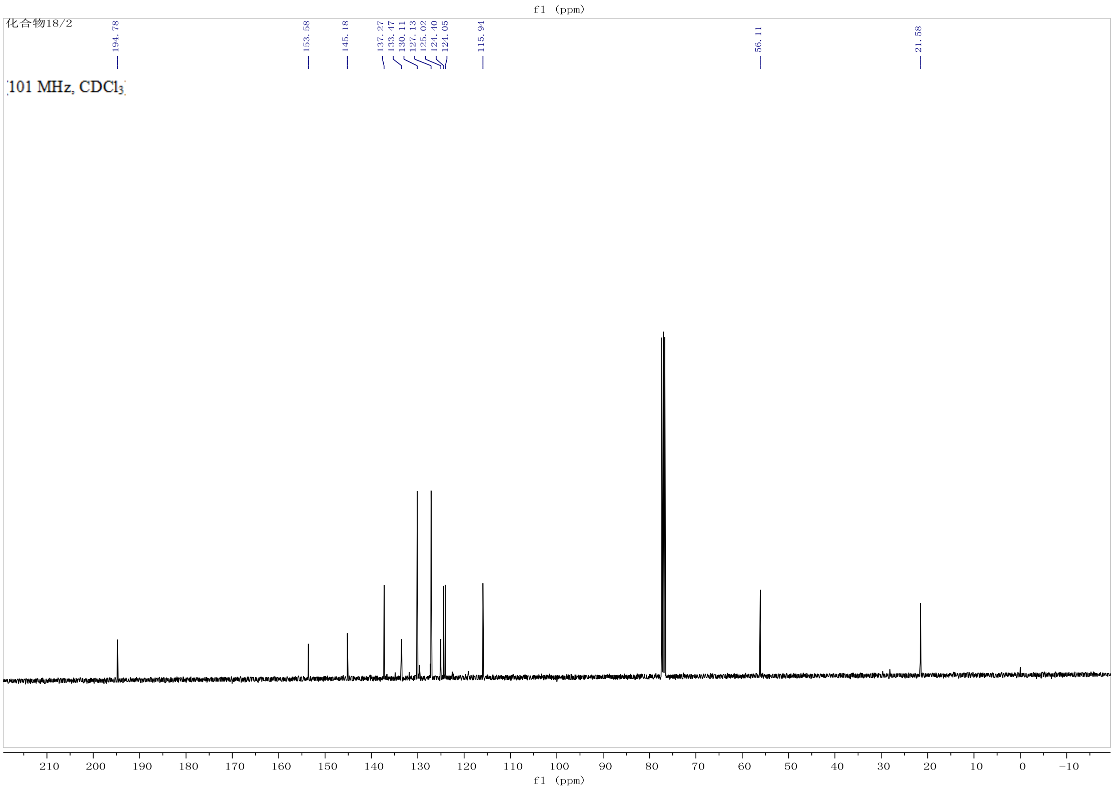
化合物23/2
101 MHz, CDCl3
199.32
176.71
139.84
129.89 129.17 129.11 128.47 125.46 123.15
113.99 113.32
75.52
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



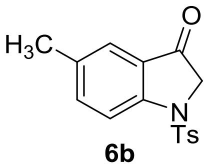
6a



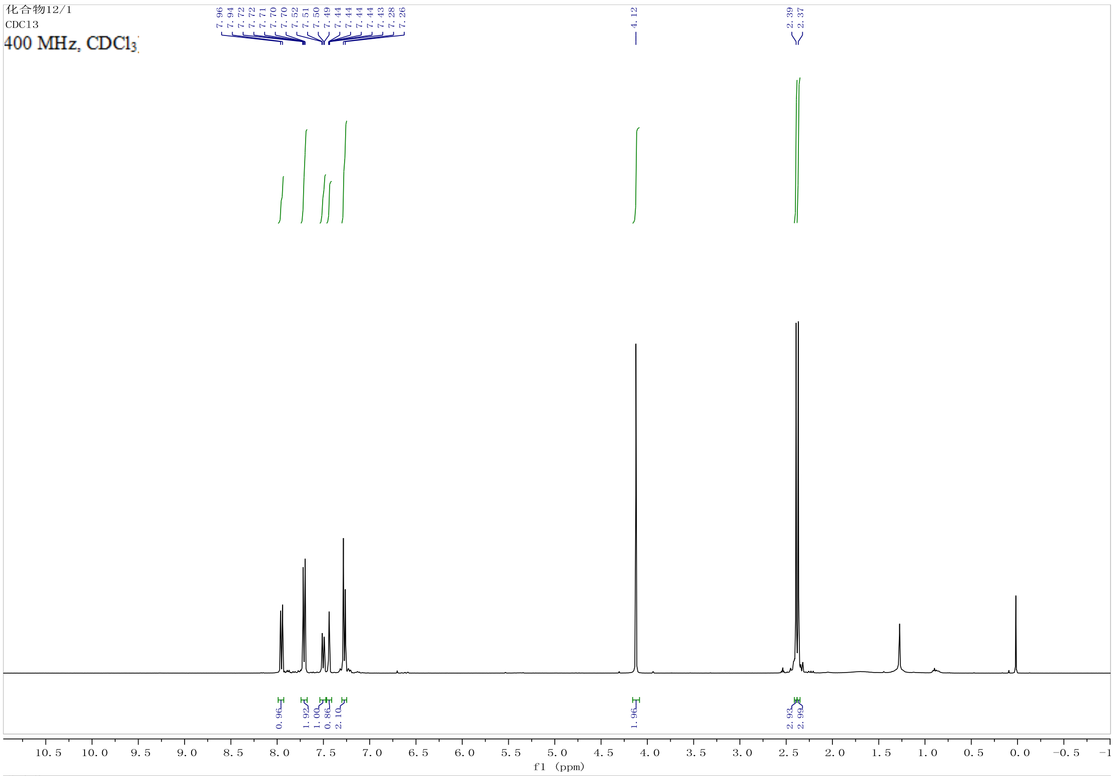
化合物18/1
400 MHz, CDCl3
4.15
2.40
f1 (ppm)

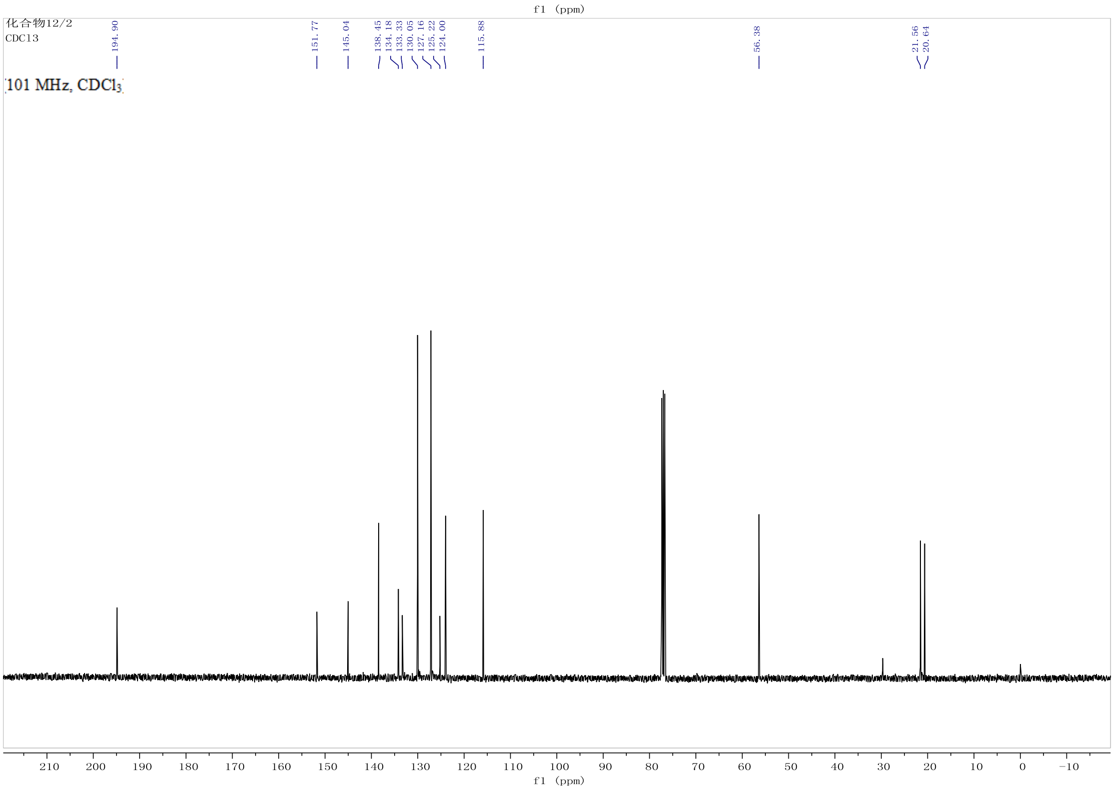


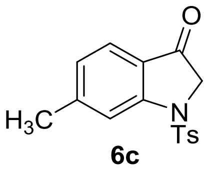
化合物18/2
101 MHz, CDCl3
194.78
153.58
145.18
137.27
133.47
130.11
127.13
125.02
124.40
124.05
115.94
56.11
21.58
f1 (ppm)



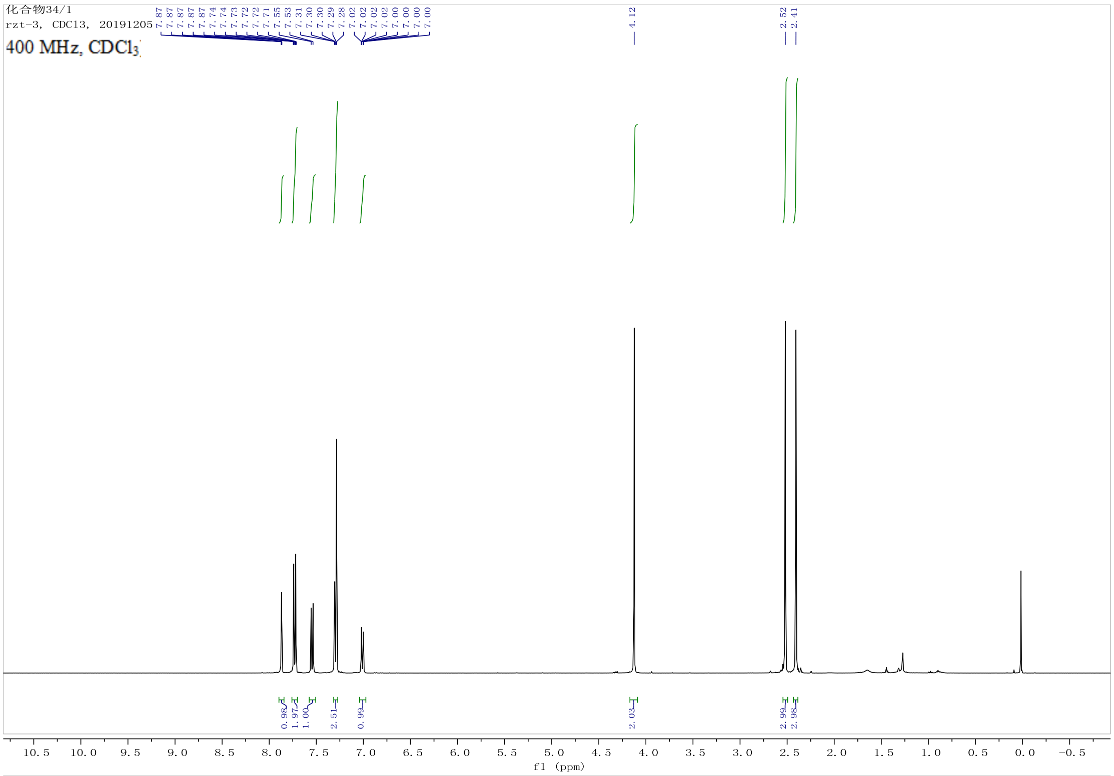
6b

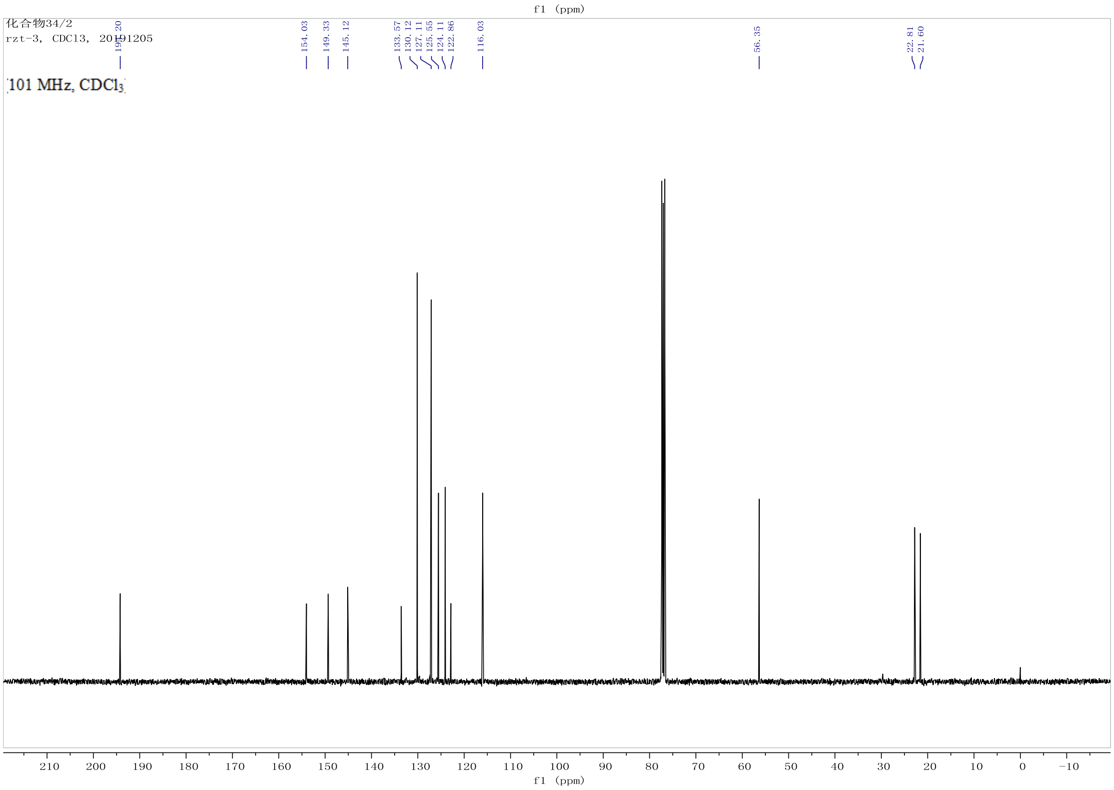

化合物12/1
CDC13
400 MHz, CDCl3
7.96
7.94
7.72
7.72
7.71
7.70
7.70
7.52
7.51
7.50
7.49
7.44
7.44
7.44
7.43
7.28
7.26
4.12
2.39
2.37
0.96
1.92
1.00
0.86
2.10
1.96
2.93
2.99
f1 (ppm)

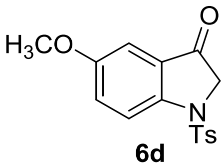

化合物12/2
CDC13
101 MHz, CDCl3
194.90
151.77
145.04
138.45
134.18
133.33
130.05
127.16
125.22
124.00
115.88
56.38
21.56
20.64
f1 (ppm)



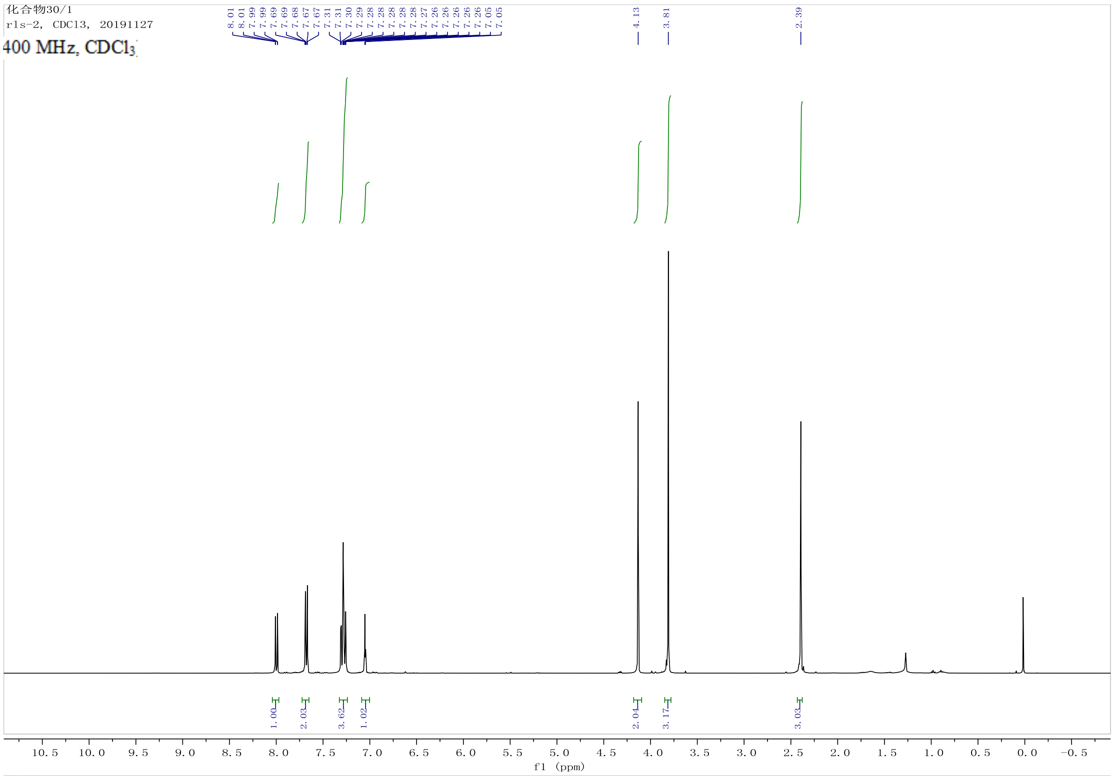
6c

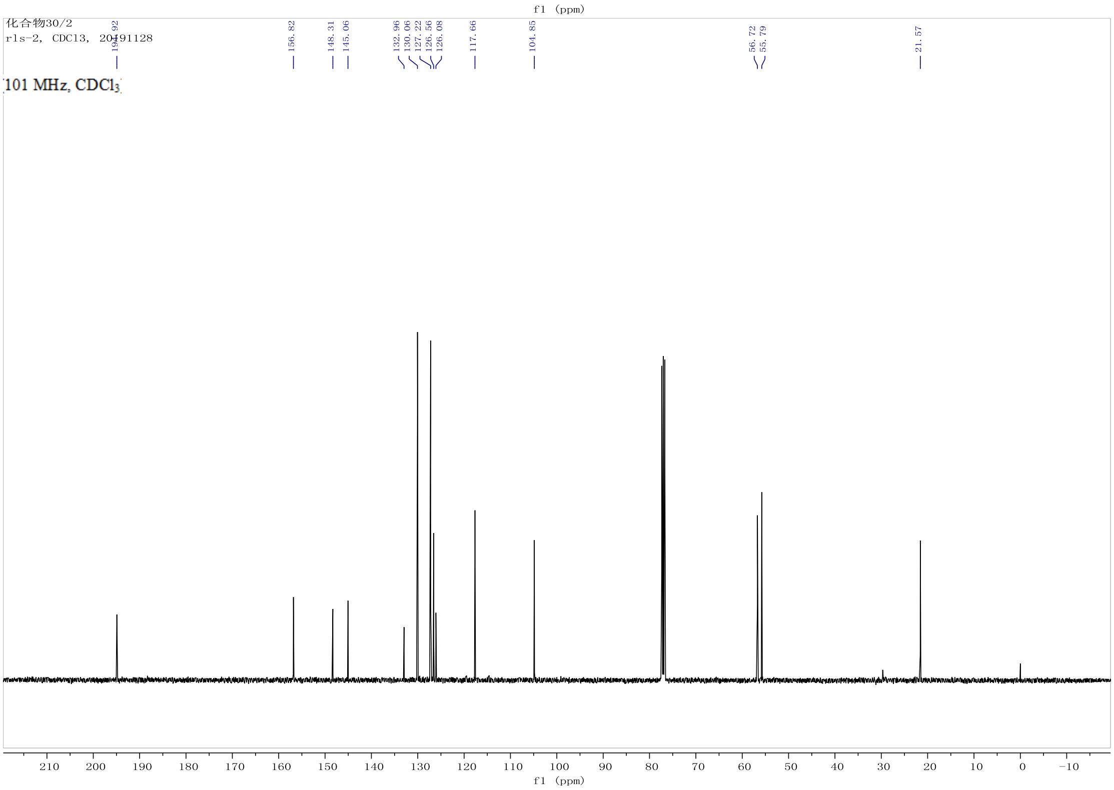

化合物34/1
rzt-3, CDCl3, 20191205
400 MHz, CDCl3
4.12
2.52
2.41
f1 (ppm)

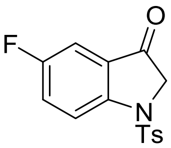

化合物34/2
rzt-3, CDCl3, 20191205
101 MHz, CDCl3
154.03
149.33
145.12
133.57
130.12
127.11
125.55
124.11
122.86
116.03
56.35
22.81
21.60
f1 (ppm)


H3CO
O
N
Ts

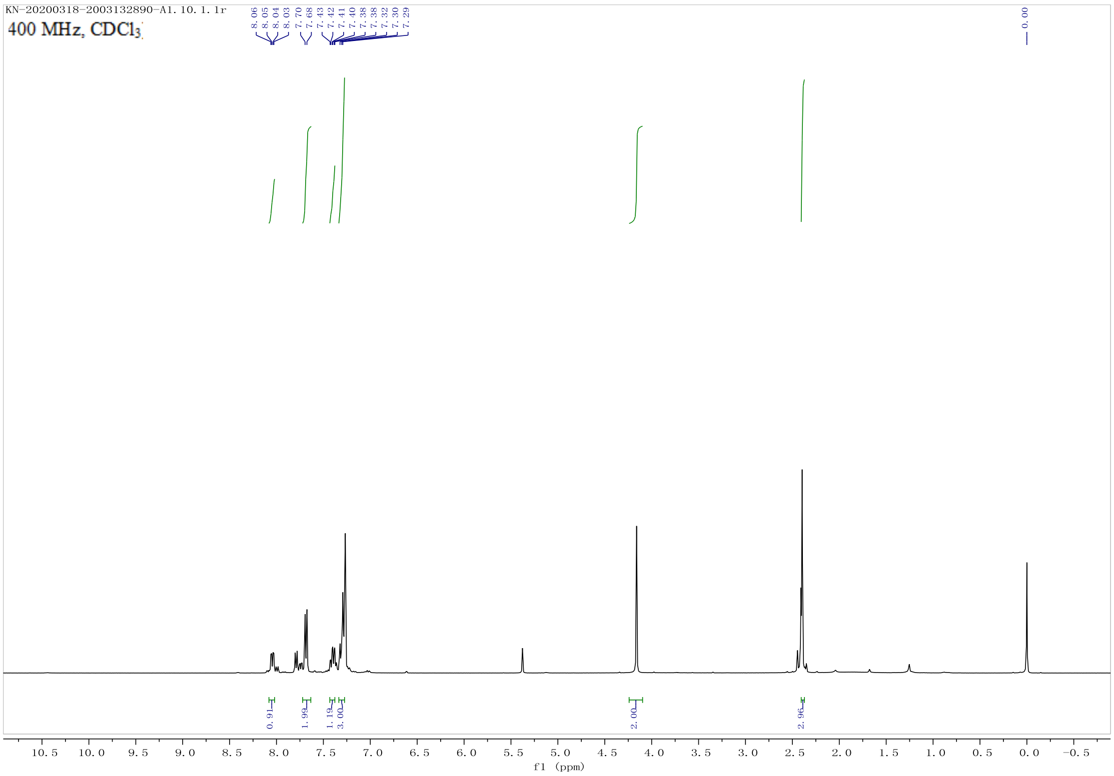
6d


化合物30/1
rls-2, CDCl3, 20191127
400 MHz, CDCl3
4.13
3.81
2.39
1.00
2.03
3.62
1.02
2.04
3.17
3.03
f1 (ppm)

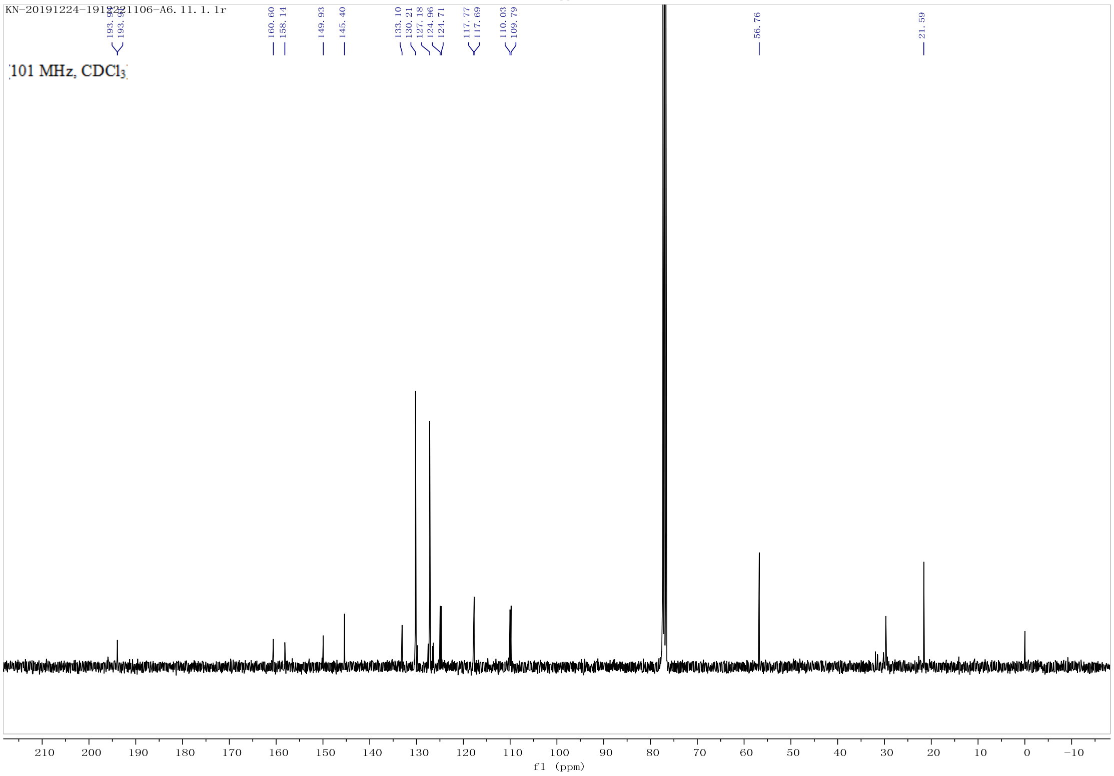

化合物30/2
rls-2, CDCl3, 20191128
101 MHz, CDCl3
156.82
148.31
145.06
132.96
130.06
127.22
126.56
126.08
117.66
104.85
56.72
55.79
21.57
f1 (ppm)



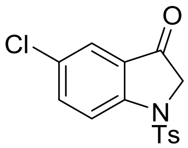
6e



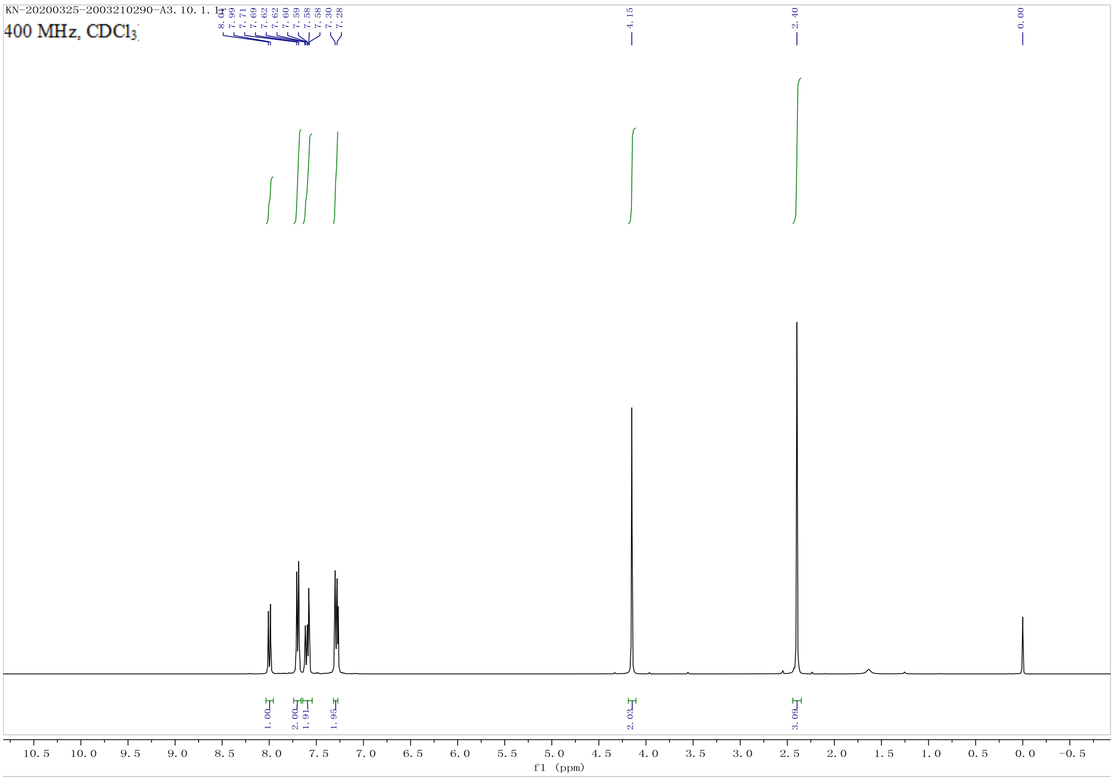
KN-20200318-2003132890-A1.10.1.1r
400 MHz, CDCl3
f1 (ppm)

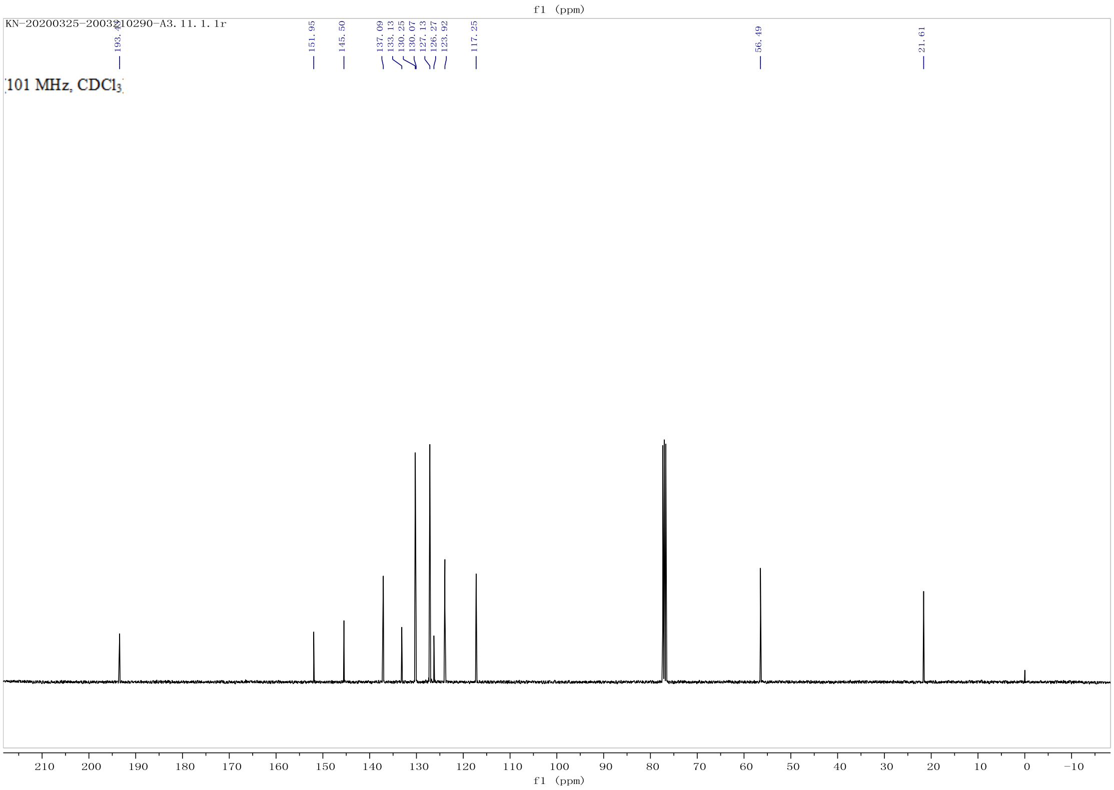


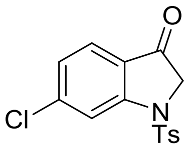
101 MHz, CDCl3
f1 (ppm)


O
Cl
N
Ts

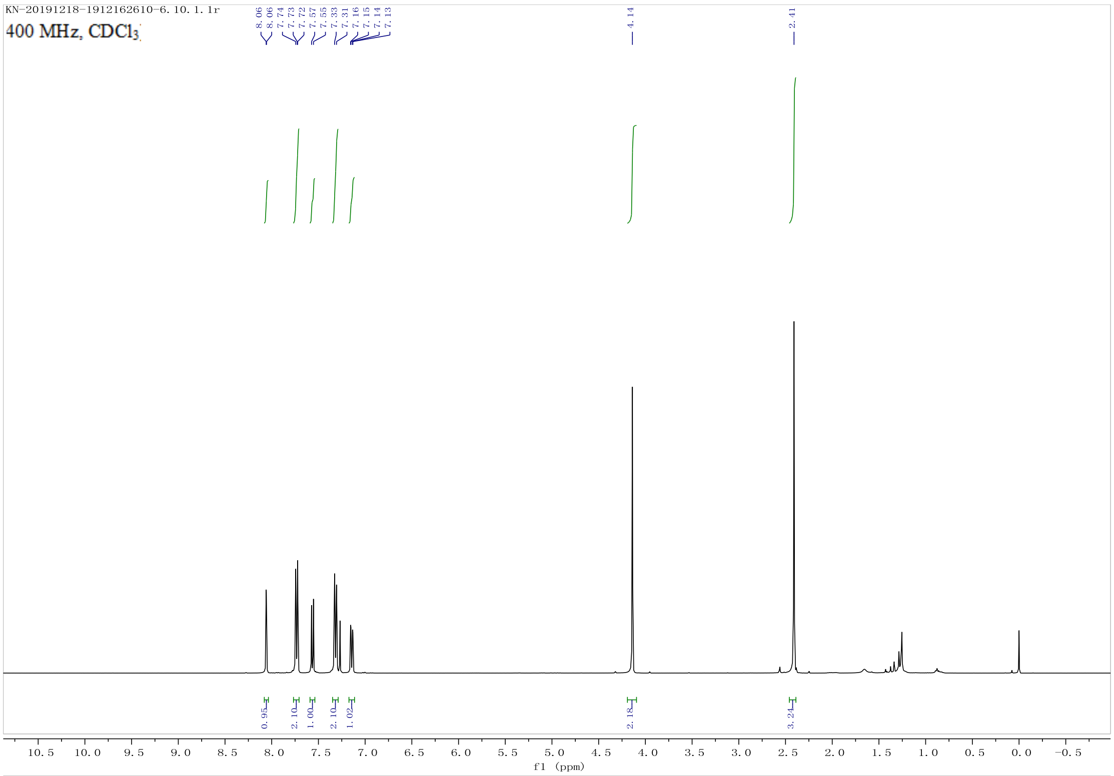
6f

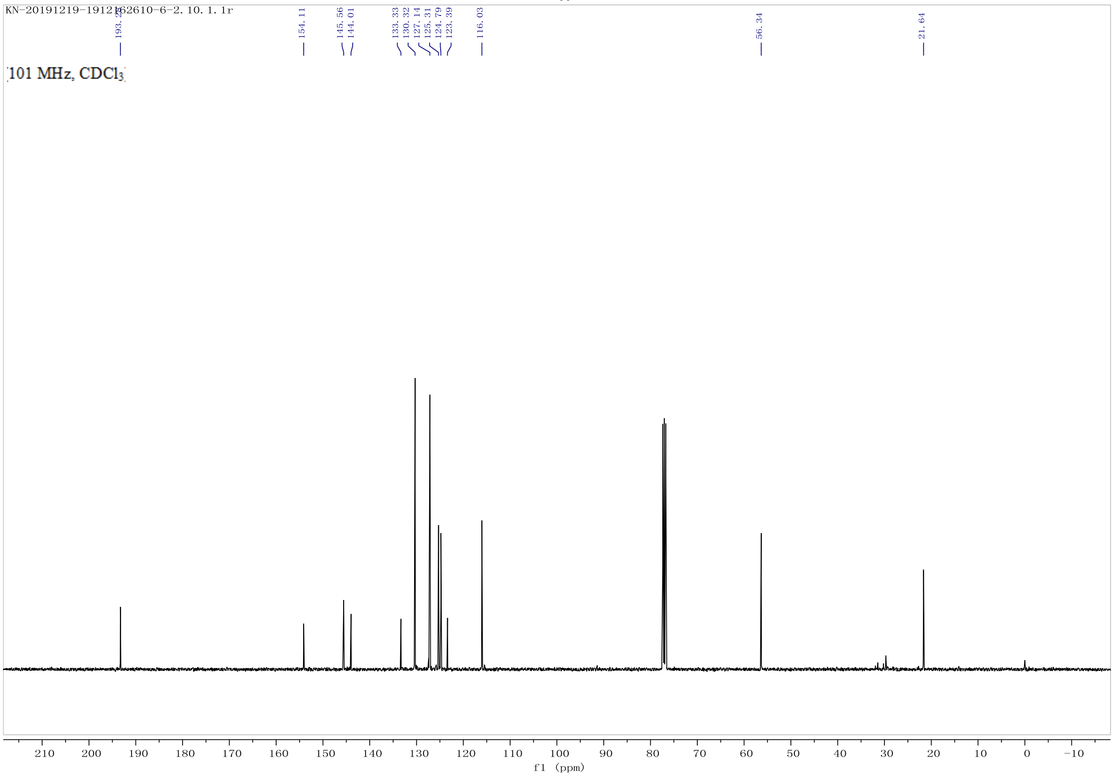

KN-20200325-2003210290-A3.10.1.1r
400 MHz, CDCl3
4.15
2.40
0.00
f1 (ppm)

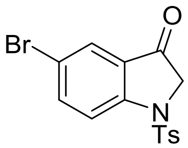

KN-20200325-2003210290-A3.11.1.1r
101 MHz, CDCl3
151.95
145.50
137.09
133.13
130.25
130.07
127.13
126.27
123.92
117.25
56.49
21.61
f1 (ppm)


O
Cl
N
Ts

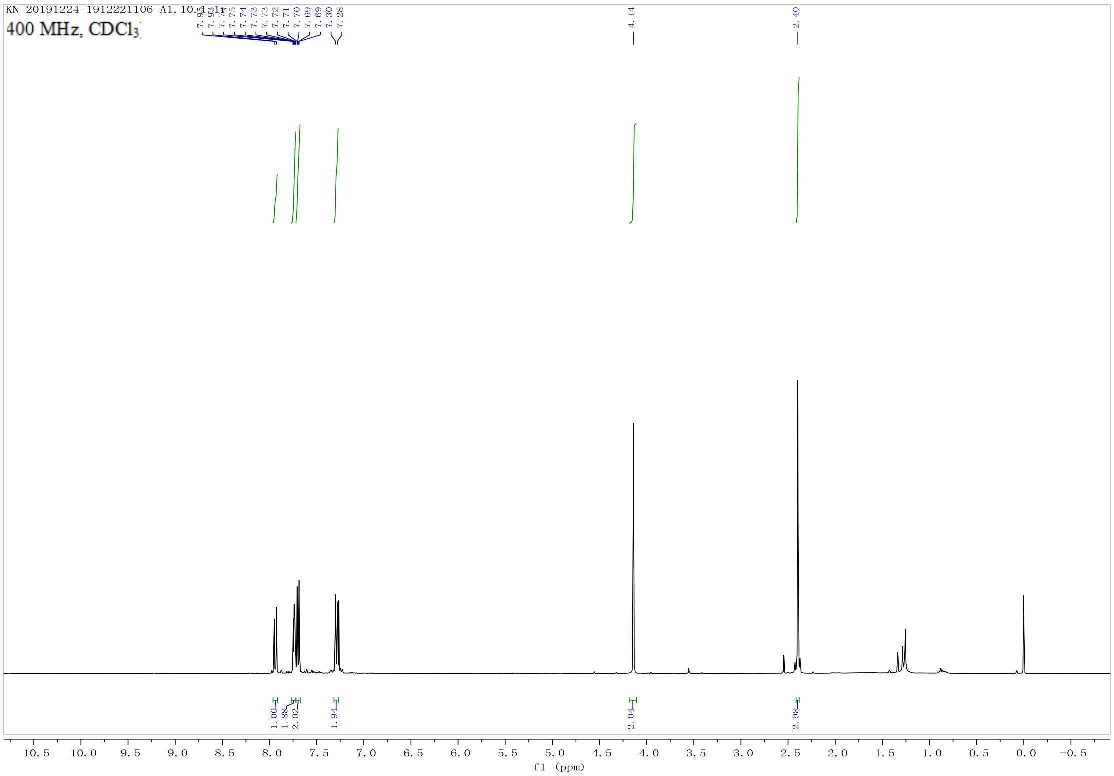
6g

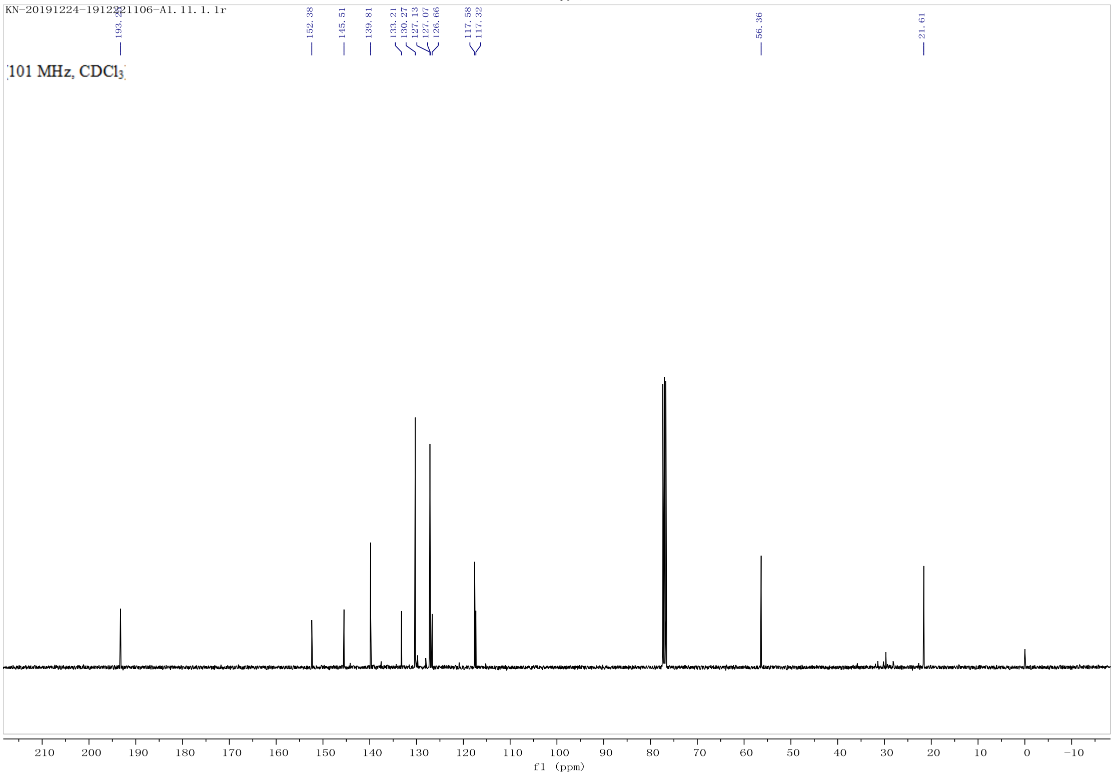

KN-20191218-1912162610-6.10.1.1r
400 MHz, CDCl3
8.06
8.06
7.74
7.73
7.72
7.57
7.55
7.33
7.31
7.16
7.15
7.14
7.13
4.14
2.41
0.95
2.10
1.00
2.10
1.02
2.18
3.24
f1 (ppm)

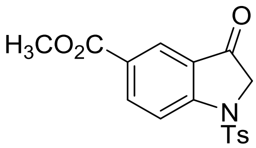

KN-20191219-1912162610-6-2.10.1.1r
101 MHz, CDCl3
154.11
145.56
144.01
133.33
130.32
127.14
125.31
124.79
123.39
116.03
56.34
21.64
f1 (ppm)



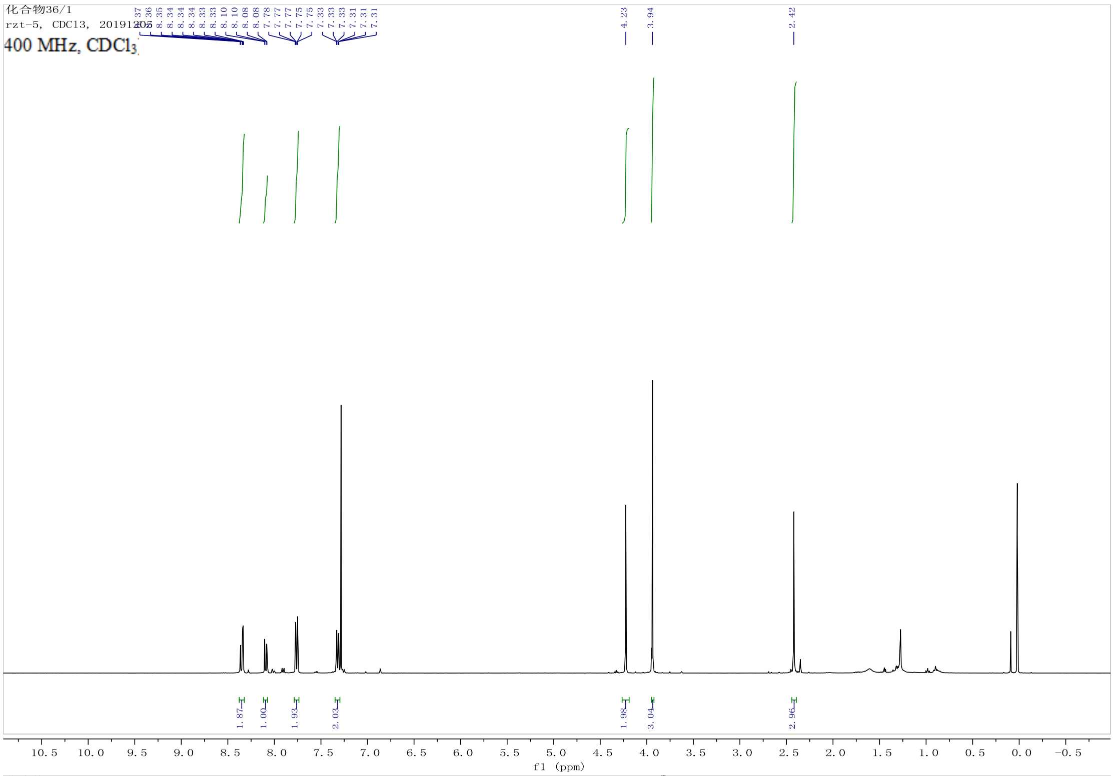
6h

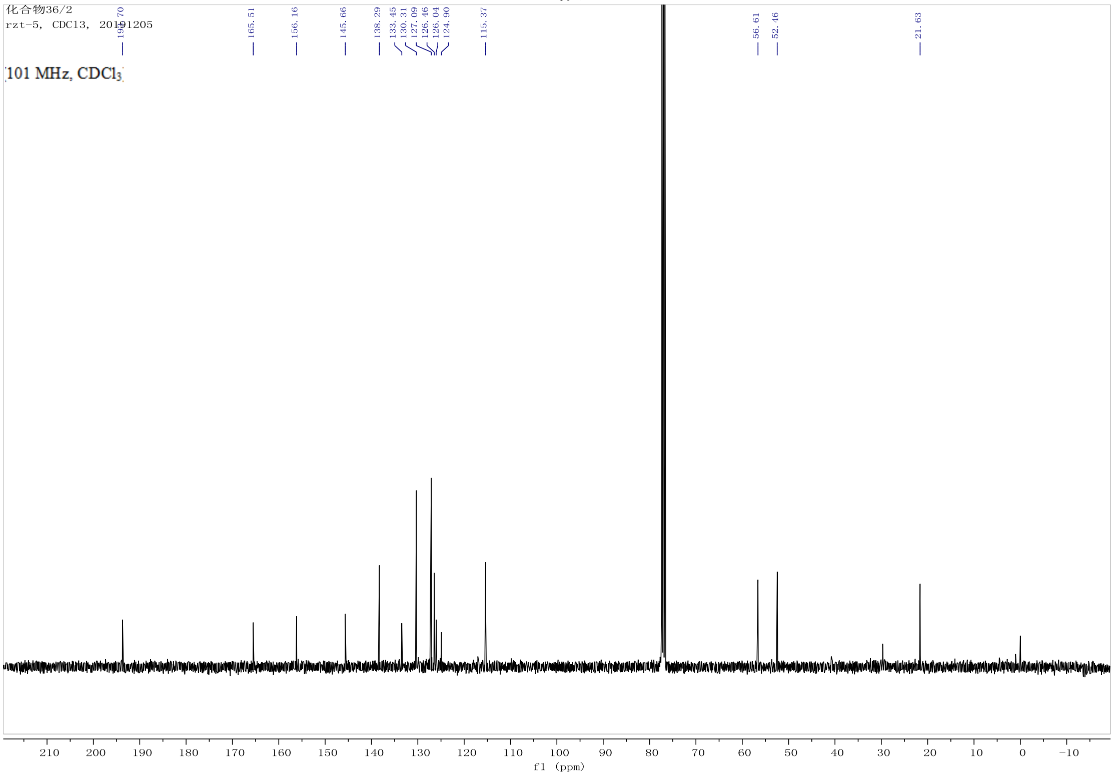

KN-20191224-1912221106-A1.10.1.1r
400 MHz, CDCl3
4.14
2.40
f1 (ppm)

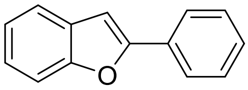

KN-20191224-1912221106-A1.11.1.1r
101 MHz, CDCl3
152.38
145.51
139.81
133.21
130.27
127.13
127.07
126.66
117.58
117.32
56.36
21.61
f1 (ppm)


H3CO2C
O
N
Ts

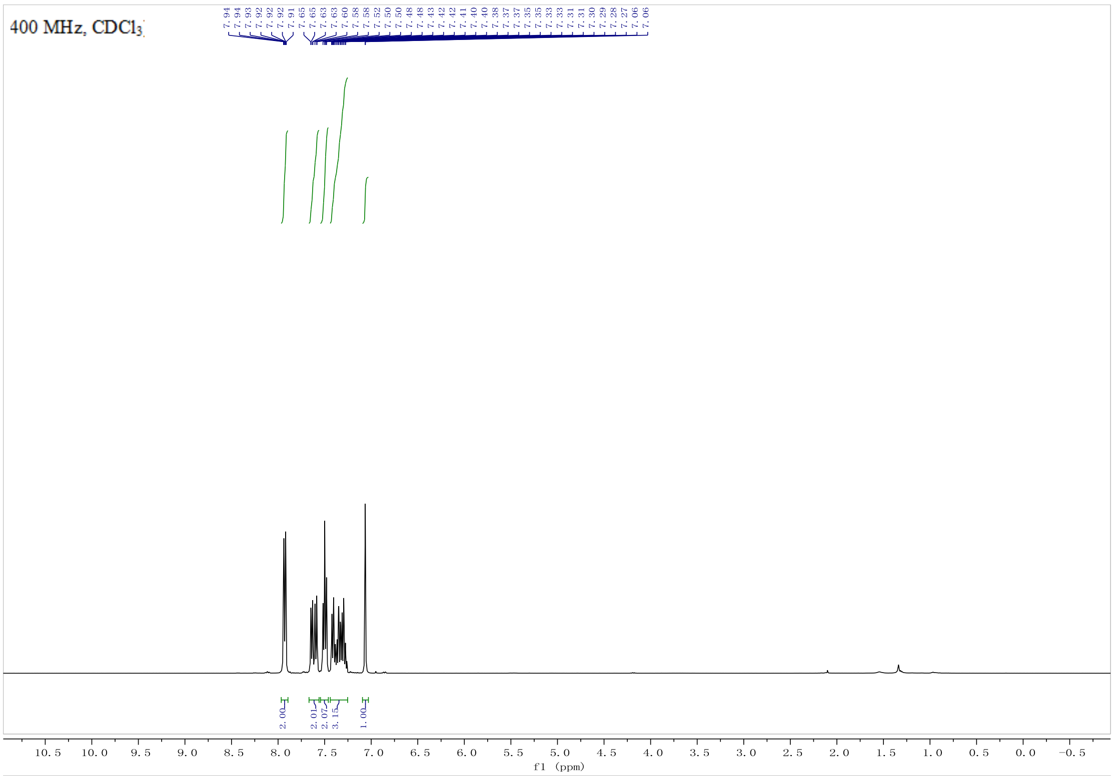
6i

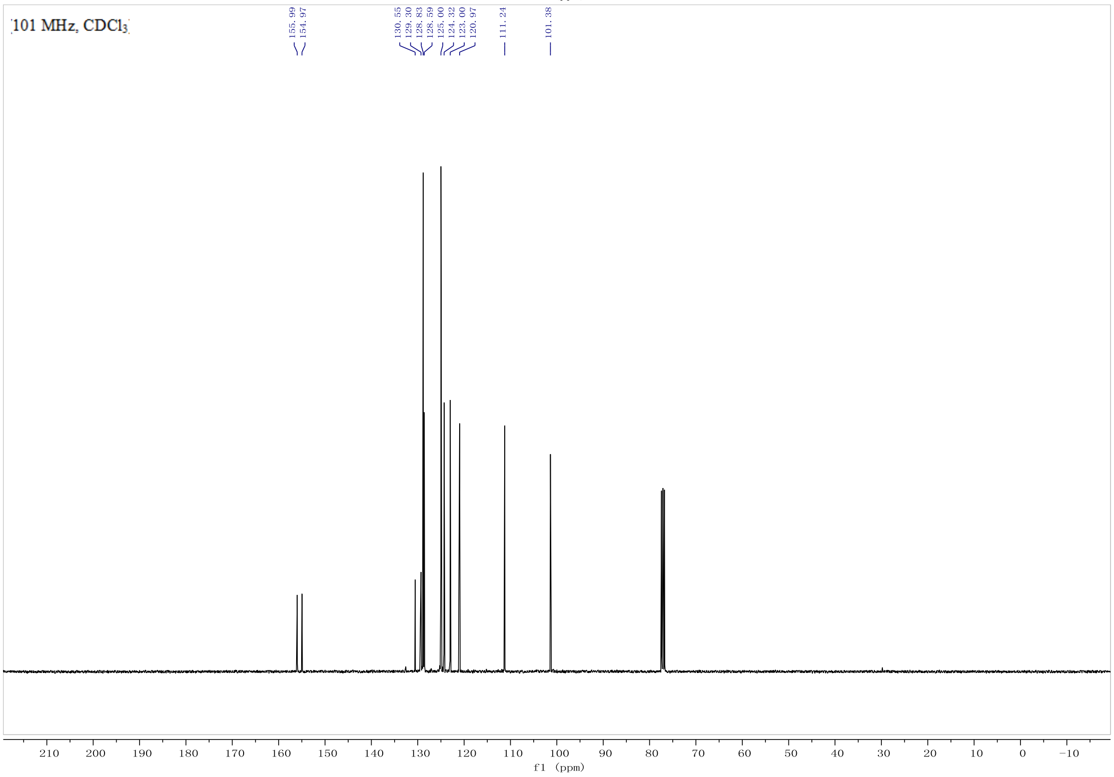

化合物36/1
rzt-5, CDCl3, 20191205
400 MHz, CDCl3
f1 (ppm)

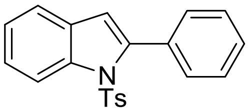

化合物36/2
rzt-5, CDCl3, 20191205
101 MHz, CDCl3
f1 (ppm)



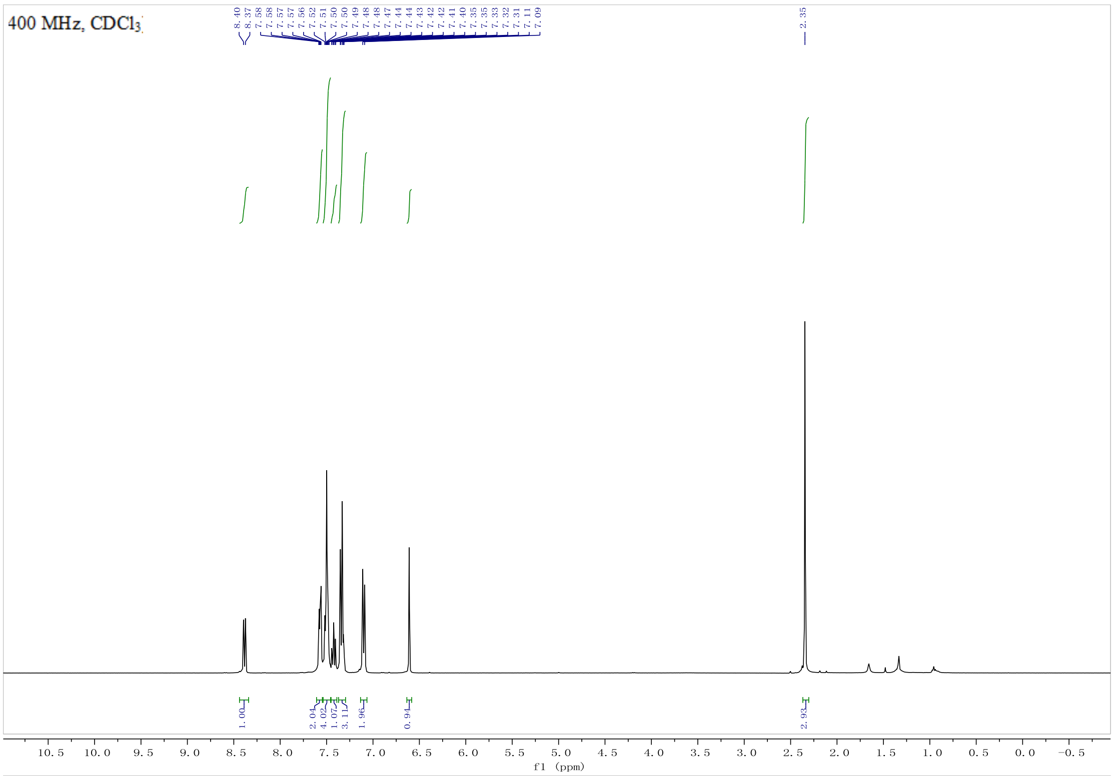
8a'

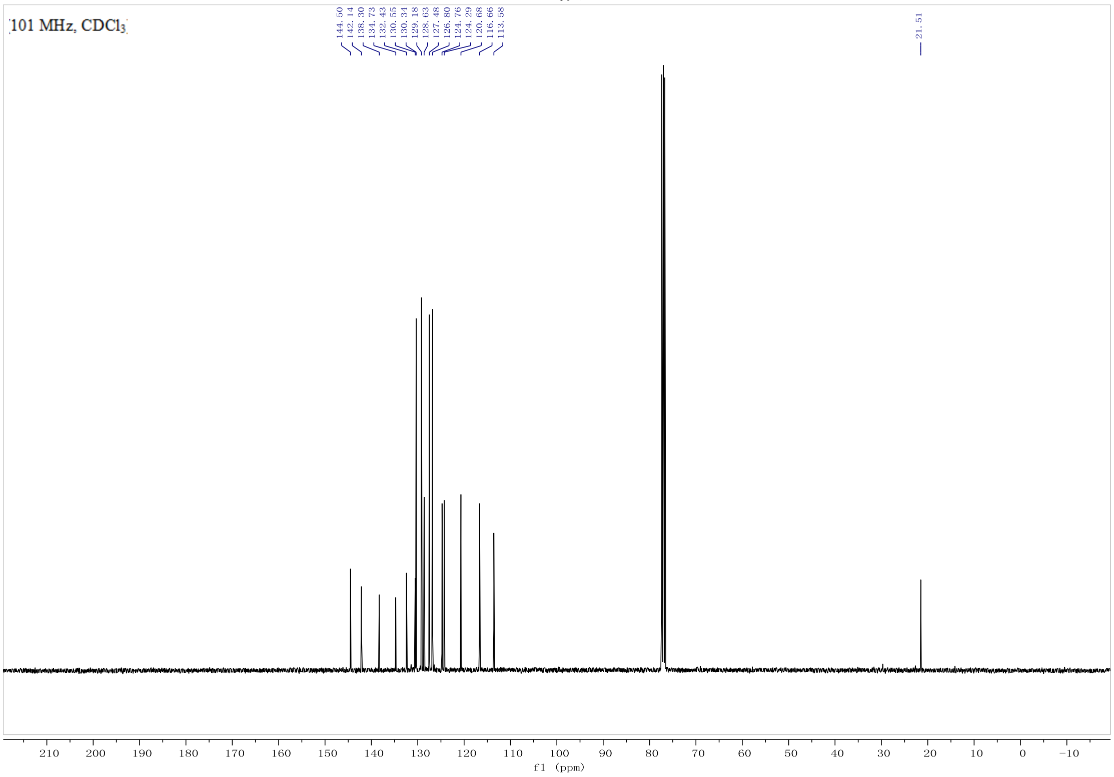

400 MHz, CDCl3
7.94 7.94 7.93 7.92 7.92 7.92 7.91 7.65 7.65 7.63 7.63 7.60 7.58 7.58 7.52 7.50 7.50 7.48 7.48 7.43 7.42 7.42 7.41 7.40 7.40 7.38 7.37 7.37 7.35 7.35 7.33 7.33 7.31 7.31 7.30 7.29 7.28 7.27 7.06 7.06
2.00 2.01 2.07 3.15 1.00
f1 (ppm)

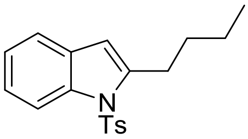

101 MHz, CDCl3
155.99 154.97 130.55 129.30 128.83 128.59 125.00 124.32 123.00 120.97 111.24 101.38
f1 (ppm)



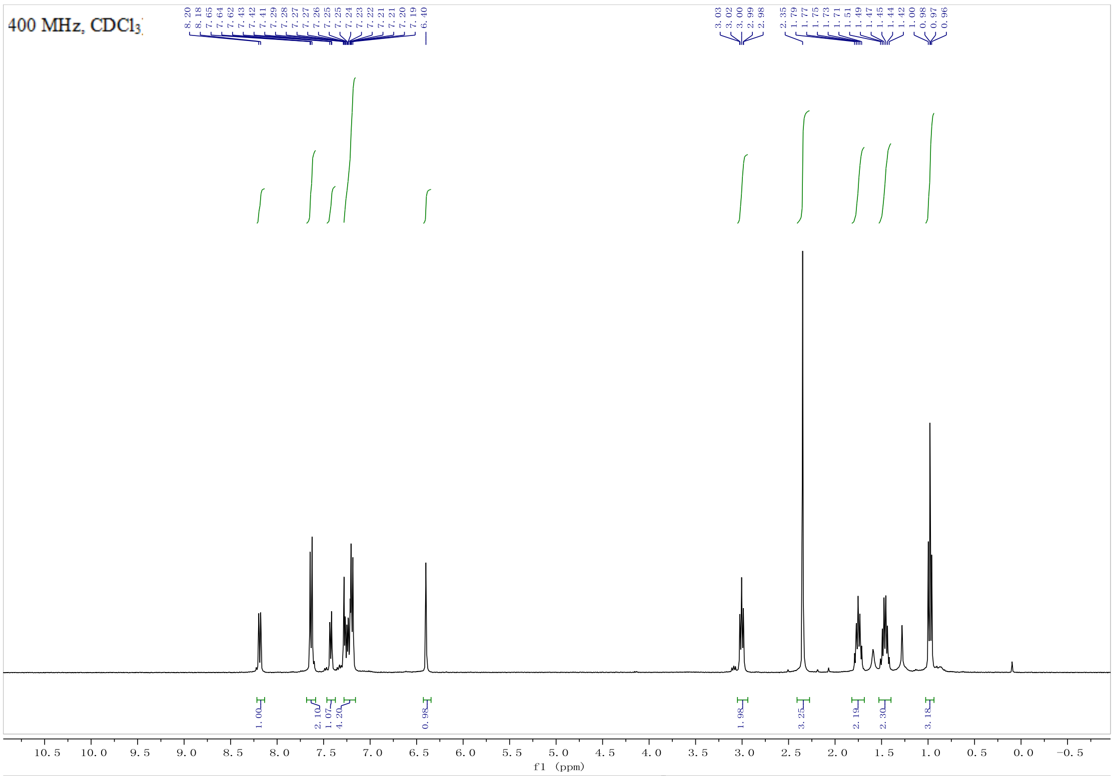
8b'

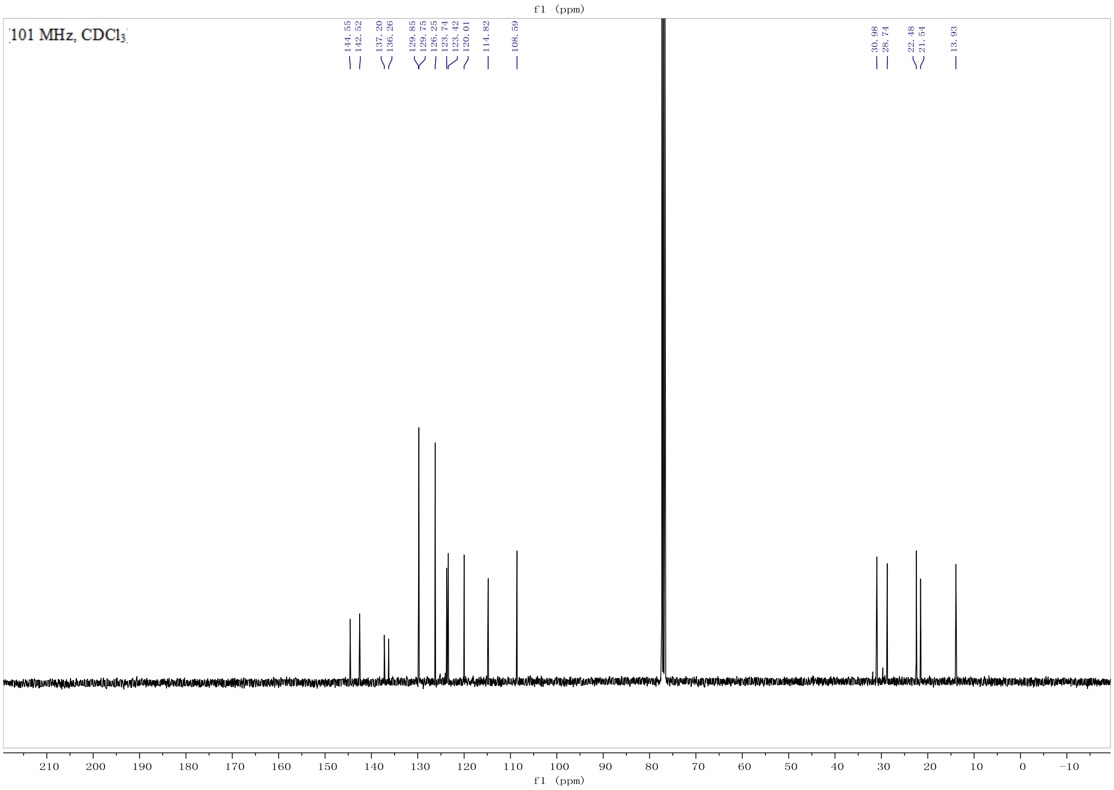





N
Ts

8c'


400 MHz, CDCl3
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
1.00 2.10 1.07 4.20 0.98 1.98 3.25 2.19 2.30 3.18
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)


101 MHz, CDCl3
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)