Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Synthesis of α-Aminoketone from *N*-Sulfonyl-1,2,3-Triazole via *N*-Sulfinyl Imine Generated by Intramolecular Oxygen Transfer

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1. General comments

Analytical thin layer chromatography (TLC) was performed using Silica Gel HSGF254 pre-coated plates. Flash column chromatography was performed using 200-300 Mesh silica gel. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded using Brucker Avance IIDMX 400MHz spectrometers. Chemical shift (δ) is reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS, 0.00 ppm) or solvent residual signal in $CDCl_3$ (7.26 ppm). Coupling constants (*J*) are reported in Hz. Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; Carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra were recorded using a Brucker Avance II DMX 400 spectrometer at 100 MHz. Chemical shift is reported in ppm relative to the carbon resonance of $CDCl_3$ (77.00 ppm). High resolution mass spectra (HRMS) were obtained by Center for Instrumental Analysis of Zhejiang Sci-Tech University using a Waters TOFMS GCT Premier instrument. The results are reported as m/e (relative ratio). Accurate masses are reported for the molecular ion (M^+) or a suitable fragment ion. The solvents 1,2-DCE, $CHCl_3$, DCM were distilled from CaH_2 and kept under nitrogen atmosphere; THF and toluene were distilled over sodium and kept under nitrogen atmosphere before used.

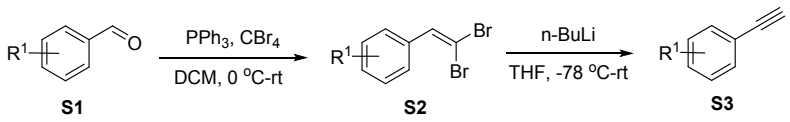
2. Results and discussion on the failure of PIDA and selectfluor

It's confirmed from ^{1}H NMR that PIDA could react with $Rh_2(piv)_4$ but the newly formed rhodium species could not react with triazole **1a** and most of **1a** could be recovered. It's assumed that OAc group might coordinate with rhodium, which would deactivate the catalyst.

When selectfluor replacing NFSI, ^{1}H NMR monitor illustrated that selectfluor could accelerate the decomposition of **1a**, but neither **11aa** nor **9a** was detected. If $Rh_2(piv)_4$ (5 mol%) was treated with NFSI (5 mol%) in refluxing DCE for 15 min first, then triazole **1a** (1 equiv) and selectfluor (1 equiv) were added together. The reaction was kept in refluxing DCE until **1a** was disappeared, then **10a** was added and the reaction mixture was stirred for one hour. Only 2.5% yield of the desired product **11aa** was observed from ^{1}H NMR of the crude mixture with 1,3,5-trimethoxybenzene as internal standard. This indicated that selectfluor was not involved in the desired reaction at all.

3. Synthetic procedures of *N*-sulfonyl-1,2,3–triazoles

3.1 General procedures for preparation of alkynes



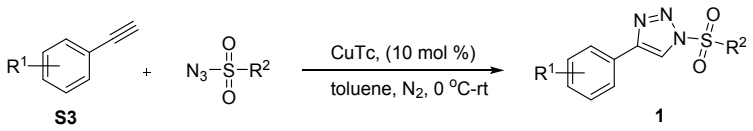
3.1.1 Synthesis of polysubstituted (2,2-dibromovinyl)benzenes (S2)[1]

General Procedure: To a solution of **S1** (10 mmol) and CBr_4 (6.63 g, 20 mmol) in CH_2Cl_2 (10 mL) was added the solution of PPh_3 (10.48 g, 40 mmol) in CH_2Cl_2 (10 mL) via syringe at 0 °C. After stirring for 30 min, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE) to afford **S2**.

3.1.2 Synthesis of polysubstituted-ethynylbenzene (S3)[1]

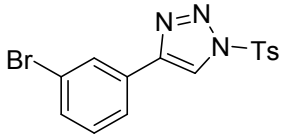
General Procedure: To a solution of **S2** (10 mmol) in THF (10 mL) *n*-BuLi (20 mmol, 8.3 mL, 2.4 M in hexane) was added drop wise at –78 °C. After stirring for 4.0 h, MeOH (8 mL) was added and the mixture was stirred for an additional 1.0 h, then the reaction was quenched with saturated aqueous NH_4Cl solution at 0 °C, and the aqueous phase was extracted with Et_2O. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE) to afford **S3.**

3.2 General procedure for synthesis of *N*-sulfonyl-1,2,3-triazoles



Under a nitrogen atmosphere, dry toluene was added to a flask charged with copper (I) thiophene-2-carboxylate (CuTC, 0.1 equiv in regards to alkyne) and the alkyne **S3** (1 equiv, 0.33 M). The reaction mixture was cooled in an ice-water bath. Subsequently, the sulfonyl azide (1.2 equiv) was added slowly as the limiting reagent to avoid a run-away exotherm, and the reaction mixture was allowed to warm to room temperature and stirred until TLC analysis showed that alkyne was completely consumed. The reaction mixture filtered through a short plug of silica gel. The filtrate was concentrated and then purified by flash chromatography with PE/EtOAc (3:1) as eluent to give the corresponding product **1**.

1a-c, **1e-i** and **1k-p** were reported in ref 2, **1d** was reported in ref 3, **1j** was reported in ref 4, **1q** was reported in ref 5.



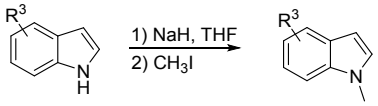
4-(3-bromophenyl)-1-tosyl-1*H*-1,2,3-triazole (1n): white solid, yield: 68%;

^{1}H NMR(400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.02 (d, *J* = 8.3 Hz, 2H), 7.98 (t, *J* = 1.6 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 8.9 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 1H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.53, 145.93, 132.97, 132.03, 130.93, 130.53, 129.06, 128.76, 124.62, 123.09, 119.37, 21.84.

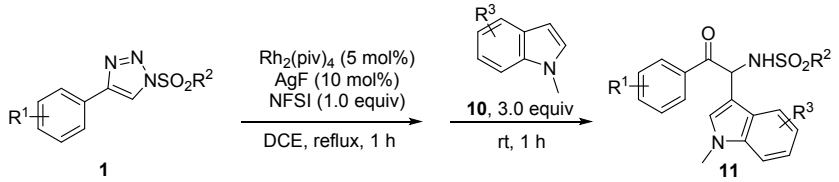
HRMS (ESI) calcd for $C_{18}H_{19}N_2O_3S^+$ 377.9906, found 377.9910.

4. Synthetic procedures of *N*-methylindoles[6]

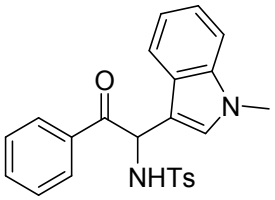


General procedure: Under a nitrogen atmosphere, a solution of indole (5.0 mmol) in dry THF (10 mL) was added to a flask charged with NaH (6.0 mmol) at 0 °C. After the mixture was stirred for15 min, a solution of CH_3I (5.0 mmol) in 5 mL THF was added dropwise at 0 °C. The reaction mixture was stirred overnight. Then 10 mL saturated NH_4Cl solution was added. The mixture was extracted with EtOAc (3×20 mL). The organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography with PE/EtOAc (20:1) as eluent to afford *N*-methylindole.

5. Reaction scope



General procedure: Under a nitrogen atmosphere, DCE (10 mL) was added to a reaction flask charged with *N*-sulfonyl-1,2,3-triazole **1** (0.5 mmol), NFSI (0.5 mmol), $Rh_2(piv)_4$ (0.025 mmol) and AgF (0.05 mmol). The reaction was stirred at reflux until TLC indicated the total consumption of the triazole. The reaction mixture was then cooled to rt, and *N*-methylindole **10** (1.5 mmol) was added. After the reaction was completed (monitored by TLC), the reaction mixture was filtered through a short plug of silica gel. The filtrate was concentrated and then purified by flash column chromatography with PE/EtOAc (2:1) as eluent to afford **11**.

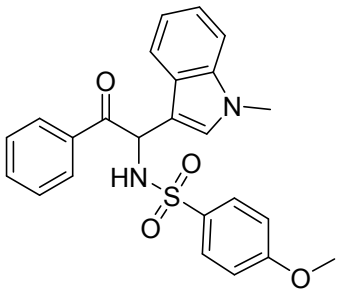


4-methyl-*N*-(1-(1-methyl-1*H*-indol-3-yl)-2-oxo-2-phenylethyl)benzenesulfonamide (11aa): 180.0 mg, white solid, m.p.: 116-118 °C, yield: 86%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.3 Hz, 2H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.49 – 7.41 (m, 3H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.23 – 7.15 (m, 1H), 7.15 – 7.06 (m, 2H), 6.90 (d, *J* = 8.1 Hz, 2H), 6.76 (s, 1H), 6.31 (d, *J* = 8.0 Hz, 1H), 6.13 (d, *J* = 8.0 Hz, 1H), 3.55 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.64, 142.71, 137.39, 137.14, 134.23, 133.61, 128.84, 128.75, 128.68, 128.54, 126.97, 125.95, 122.37, 120.16, 119.13, 109.34, 108.76, 54.62, 32.70, 21.33.

HRMS (ESI) calcd for $C_{24}H_{23}N_2O_3S^+$ 419.1424, found 419.1436.



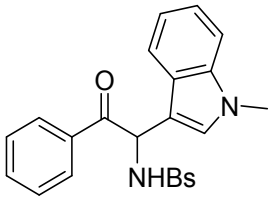
4-methoxy-*N*-(1-(1-methyl-1*H*-indol-3-yl)-2-oxo-2-phenylethyl)benzenesulfonamide (11ba): 156.4 mg, light yellow solid, m.p.: 157-159 °C, yield: 72%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.5 Hz, 2H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.23 – 7.06 (m, 3H), 6.76 (s, 1H), 6.57 (d, *J* = 8.8 Hz, 2H), 6.30 (d, *J* = 8.1 Hz, 1H), 6.10 (br, 1H), 3.71 (s, 3H), 3.56 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.70, 162.39, 137.17, 134.24, 133.62, 132.04, 129.09, 128.70, 128.56, 126.01, 122.39,

120.17, 119.16, 113.36, 109.35, 108.80, 55.44, 54.58, 32.71.

HRMS (ESI) calcd for $C_{24}H_{23}N_2O_4S^+$ 435.1373, found 435.1367.

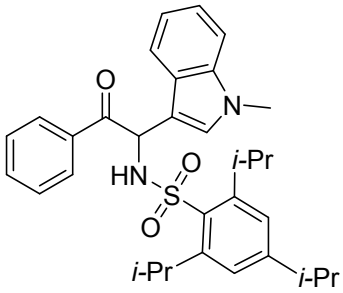


4-bromo-*N*-(1-(1-methyl-1*H*-indol-3-yl)-2-oxo-2-phenylethyl)benzenesulfonamide (11ca): 158.7 mg, white solid, m.p.: 165-166 °C, yield: 66%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.7 Hz, 2H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.35 – 7.29 (m, 4H), 7.24 – 7.18 (m, 1H), 7.17 – 7.06 (m, 4H), 6.77 (s, 1H), 6.34 (d, *J* = 7.4 Hz, 1H), 6.29 (d, *J* = 7.4 Hz, 1H), 3.56 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.95, 139.44, 137.02, 133.94, 133.82, 131.04, 128.84, 128.77, 128.67, 128.30, 126.59, 125.80, 122.57, 120.35, 118.98, 109.56, 108.33, 54.83, 32.74.

HRMS (ESI) calcd for $C_{23}H_{20}BrN_2O_3S^+$ 483.0373, found 483.0382.

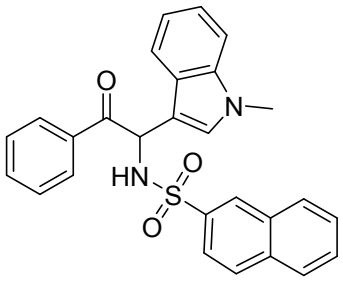


2,4,6-triisopropyl-*N*-(1-(1-methyl-1*H*-indol-3-yl)-2-oxo-2-phenylethyl)benzenesulfonamide (11da): 147.0 mg, white solid, m.p.: 244-246 °C, yield: 55%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.2 Hz, 2H), 7.49 – 7.39 (m, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.25 – 7.15 (m, 2H), 7.10-7.03 (m, 3H), 6.72 (s, 1H), 6.33 (d, *J* = 8.4 Hz, 1H), 5.98 (d, *J* = 8.4 Hz, 1H), 4.13 (hept, *J* = 6.8 Hz, 2H), 3.61 (s, 3H), 2.86 (hept, *J* = 6.8 Hz, 1H), 1.22 (d, *J* = 6.8 Hz, 12H), 1.05 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.39, 152.72, 150.26, 137.22, 134.46, 133.52, 133.11, 128.67, 128.56, 128.34, 126.07, 123.54, 122.44, 120.09, 118.96, 109.49, 109.37, 53.53, 34.15, 32.84, 29.89, 24.83, 24.69, 23.68, 23.58.

HRMS (ESI) calcd for $C_{32}H_{39}N_2O_3S^+$ 531.2676, found 531.2683.



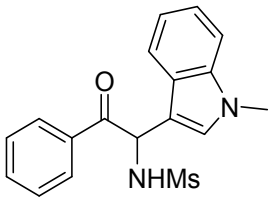
***N*-(1-(1-methyl-1*H*-indol-3-yl)-2-oxo-2-phenylethyl)naphthalene-2-sulfonamide (11ea):** 126.8 mg, white solid, yield: 56%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.68 – 7.63 (m, 1H), 7.62

– 7.36 (m, 7H), 7.29 – 7.19 (m, 1H), 7.09 (dd, *J* = 5.8, 2.8 Hz, 2H), 6.86 (dd, *J* = 5.8, 2.8 Hz, 1H), 6.62 (s, 1H), 6.41 (d, *J* = 7.4 Hz, 1H), 6.28 (d, *J* = 7.4 Hz, 1H), 3.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.16, 137.33, 136.78, 134.24, 134.01, 133.63, 131.51, 129.34, 129.04, 128.65, 128.53, 128.38, 128.29, 128.09, 127.52, 126.88, 125.96, 122.35, 122.28, 120.21, 118.94, 109.26, 108.43, 54.71, 32.30.

HRMS (ESI) calcd for $C_{27}H_{23}N_2O_3S^+$ 455.1424, found 455.1423.

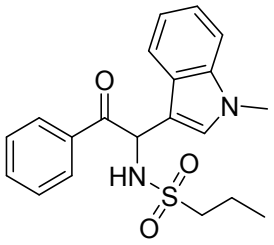


***N*-(1-(1-methyl-1*H*-indol-3-yl)-2-oxo-2-phenylethyl)methanesulfonamide (11fa):** 108.3 mg, white solid, m.p.: 189-190 °C, yield: 63%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.23 (m, 2H), 7.20 (t, *J* = 6.8 Hz, 1H), 7.02 (s, 1H), 6.46 (d, *J* = 6.8 Hz, 1H), 5.87 (d, *J* = 6.8 Hz, 1H), 3.71 (s, 3H), 2.64 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.56, 137.25, 134.06, 133.80, 128.94, 128.76, 128.71, 125.77, 122.73, 120.59, 119.09, 109.74, 109.21, 54.95, 42.17, 33.01.

HRMS (ESI) calcd for $C_{18}H_{19}N_2O_3S^+$ 343.1111, found 343.1110.

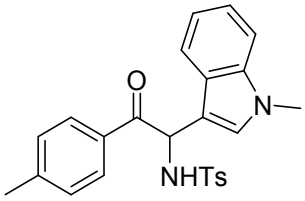


***N*-(1-(1-methyl-1*H*-indol-3-yl)-2-oxo-2-phenylethyl)propane-1-sulfonamide (11ga):** 136.5 mg, light yellow solid, m.p.: 138-140 °C, yield: 74%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 2H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.30 – 7.21(m, 2H), 7.18 (t, *J* = 6.8 Hz, 1H), 7.03 (s, 1H), 6.44 (d, *J* = 6.7 Hz, 1H), 5.84 (d, *J* = 6.7 Hz, 1H), 3.70 (s, 3H), 2.79 – 2.64(m, 1H), 2.57 – 2.42 (m, 1H), 1.82 – 1.48 (m, 2H), 0.69 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.78, 137.26, 134.15, 133.72, 128.92, 128.81, 128.68, 125.75, 122.67, 120.48, 119.10, 109.69, 109.41, 55.89, 54.85, 32.98, 17.32, 12.63.

HRMS (ESI) calcd for $C_{20}H_{23}N_2O_3S^+$ 371.1424, found 371.1428.

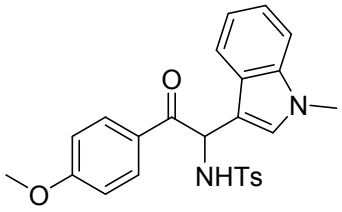


4-methyl-*N*-(1-(1-methyl-1*H*-indol-3-yl)-2-oxo-2-(*p*-tolyl)ethyl)benzenesulfonamide (11ha): 107.5 mg, white solid, m.p.: 95-97 °C, yield: 50%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.22 – 7.04 (m, 5H), 6.91 (d, *J* = 8.1 Hz, 2H), 6.74 (s, 1H), 6.28 (d, *J* = 8.0 Hz, 1H), 6.10 (d, *J* = 8.0 Hz, 1H), 3.56 (s, 3H), 2.30 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.16, 144.67, 142.63, 137.45, 137.11, 131.66, 129.26, 128.82, 128.69, 126.94, 125.97, 122.30, 120.10, 119.19, 109.29, 109.07, 54.51, 21.66, 21.34.

HRMS (ESI) calcd for $C_{25}H_{25}N_2O_3S^+$ 433.1580, found 433.1594.

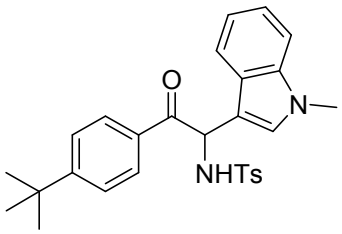


***N*-(2-(4-methoxyphenyl)-1-(1-methyl-1*H*-indol-3-yl)-2-oxoethyl)-4-methylbenzenesulfonamide (11ia):** 95.2 mg, light yellow solid, m.p.: 149-151 °C, yield: 42%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.22 – 7.06 (m, 3H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.81 – 6.72 (m, 3H), 6.25 (d, *J* = 8.0 Hz, 1H), 6.18 – 6.07 (m, 1H), 3.77 (s, 3H), 3.56 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.99, 163.90, 142.58, 137.50, 137.09, 131.07, 128.77, 128.59, 127.06, 126.94, 125.98, 122.28, 120.08, 119.21, 113.79, 109.35, 109.26, 55.45, 54.28, 32.67, 21.32.

HRMS (ESI) calcd for $C_{25}H_{24}N_2NaO_4S^+$ 471.1349, found 471.1349.

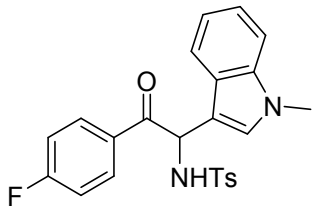


***N*-(2-(4-(tert-butyl)phenyl)-1-(1-methyl-1*H*-indol-3-yl)-2-oxoethyl)-4-methylbenzenesulfonamide (11ja):** 169.2 mg, yellow solid, m.p.: 91-93 °C, yield: 71%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.22 – 7.05 (m, 3H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.77 (s, 1H), 6.29 (d, *J* = 7.8 Hz, 1H), 6.12 (d, *J* = 7.8 Hz, 1H), 3.56 (s, 3H), 2.23 (s, 3H), 1.25 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.11, 157.55, 142.57, 137.48, 137.11, 131.54, 128.77, 128.70, 126.96, 126.01, 125.52, 122.30, 120.11, 119.18, 109.27, 109.07, 54.46, 35.13, 32.70, 30.95, 21.33.

HRMS (ESI) calcd for $C_{28}H_{31}N_2O_3S^+$ 475.2050, found 475.2052.

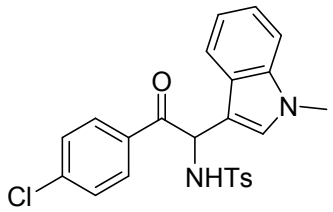


***N*-(2-(4-fluorophenyl)-1-(1-methyl-1*H*-indol-3-yl)-2-oxoethyl)-4-methylbenzenesulfonamide (11ka):** 136.5 mg, white solid, m.p.: 90-92 °C, yield: 62%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.80 (m, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 2H), 7.25 – 7.06 (m, 3H), 6.97 (t, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 7.9 Hz, 2H), 6.76 (s, 1H), 6.25 (d, *J* = 8.0 Hz, 1H), 6.07 (d, *J* = 8.0 Hz, 1H), 3.58 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.09, 165.89 (d, *J* = 256.5 Hz), 142.75, 137.28 (d, *J* = 25.8 Hz), 131.40 (d, *J* = 9.5 Hz), 130.60, 128.84, 128.66, 126.96, 125.84, 122.48, 120.25, 119.03, 115.89, 115.67, 109.38, 108.64, 54.59, 32.74, 21.33.

HRMS (ESI) calcd for $C_{24}H_{22}FN_2O_3S^+$ 437.1330, found 437.1331.

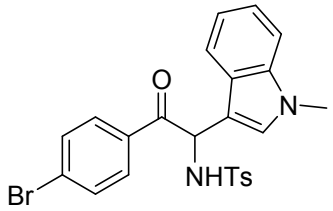


***N*-(2-(4-chlorophenyl)-1-(1-methyl-1*H*-indol-3-yl)-2-oxoethyl)-4-methylbenzenesulfonamide (11la):** 164.9 mg, brown solid, m.p.: 69-71 °C, yield: 75%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.22 – 7.06 (m, 3H), 6.92 (d, *J* = 8.1 Hz, 2H), 6.77 (s, 1H), 6.25 (d, *J* = 8.0 Hz, 1H), 6.10 (d, *J* = 8.0 Hz, 1H), 3.56 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.47, 142.78, 140.10, 137.37, 137.15, 132.52, 130.06, 128.92, 128.86, 128.78, 126.95, 125.79, 122.48, 120.27, 118.98, 109.42, 108.42, 54.69, 32.74, 21.35.

HRMS (ESI) calcd for $C_{24}H_{21}ClN_2NaO_3S^+$ 475.0854, found 475.0851.

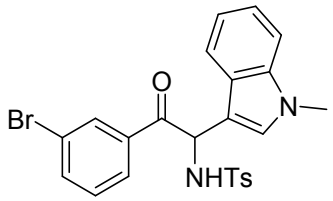


***N*-(2-(4-bromophenyl)-1-(1-methyl-1*H*-indol-3-yl)-2-oxoethyl)-4-methylbenzenesulfonamide (11ma):** 201.5 mg, white solid, m.p.: 153-155 °C, yield: 81%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.22 – 7.05 (m, 3H), 6.92 (d, *J* = 8.1 Hz, 2H), 6.76 (s, 1H), 6.24 (d, *J* = 8.0 Hz, 1H), 6.08 (d, *J* = 8.0 Hz, 1H), 3.57 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.68, 142.80, 137.37, 137.15, 132.94, 131.92, 130.12, 128.87, 128.75, 128.73, 126.94, 125.79, 122.50, 120.29, 118.97, 109.42, 108.40, 54.65, 32.75, 21.35.

HRMS (ESI) calcd for $C_{24}H_{21}BrN_2NaO_3S^+$ 519.0348, found 519.0351.

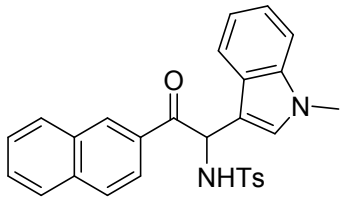


***N*-(2-(3-bromophenyl)-1-(1-methyl-1*H*-indol-3-yl)-2-oxoethyl)-4-methylbenzenesulfonamide (11na):** 185.1 mg, brown solid, m.p.: 135-137 °C, yield: 74%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (t, *J* = 1.6 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.24 – 7.07 (m, 4H), 6.94 (d, *J* = 8.2 Hz, 2H), 6.76 (s, 1H), 6.23 (d, *J* = 8.1 Hz, 1H), 6.02 (d, *J* = 8.1 Hz, 1H), 3.59 (s, 3H), 2.27 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.51, 142.93, 137.25, 137.20, 136.42, 136.01, 131.53, 130.11, 128.92, 128.75, 127.15, 127.00, 125.79, 122.91, 122.55, 120.34, 119.00, 109.43, 108.10, 54.74, 32.78, 21.37.

HRMS (ESI) calcd for $C_{24}H_{21}BrN_2NaO_3S^+$ 519.0348, found 519.0353.

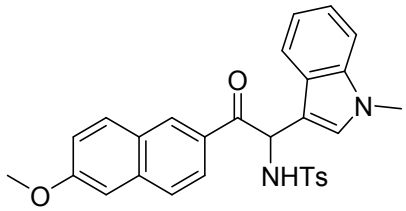


4-methyl-*N*-(1-(1-methyl-1*H*-indol-3-yl)-2-(naphthalen-2-yl)-2-oxoethyl)benzenesulfonamide (11oa): 153.9 mg, brown solid, m.p.: 81-93 °C, yield: 66%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.89 – 7.65 (m, 5H), 7.59 – 7.43 (m, 4H), 7.24 – 7.08 (m, 3H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.79 (s, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 6.15 (d, *J* = 8.0 Hz, 1H), 3.55 (s, 3H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.64, 142.74, 137.43, 137.16, 135.72, 132.23, 131.54, 130.63, 129.71, 128.88, 128.70, 128.67, 128.42, 127.68, 127.00, 126.88, 126.01, 123.99, 122.41, 120.22, 119.19, 109.35, 108.99, 54.72, 32.71, 21.30.

HRMS (ESI) calcd for $C_{28}H_{24}N_2NaO_3S^+$ 491.1400, found 491.1405.

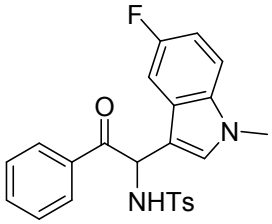


***N*-(2-(6-methoxynaphthalen-2-yl)-1-(1-methyl-1*H*-indol-3-yl)-2-oxoethyl)-4-methylbenzenesulfonamide (11pa):** 124.2 mg, white solid, yield: 50%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.80 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.75 – 7.65 (m, 2H), 7.61 (d, *J* = 8.7 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.23 – 7.09 (m, 4H), 7.05 (d, *J* = 2.3 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 2H), 6.78 (s, 1H), 6.43 (d, *J* = 8.2 Hz, 1H), 6.14 (d, *J* = 8.2 Hz, 1H), 3.90 (s, 3H), 3.56 (s, 3H), 2.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.28, 160.12, 142.68, 137.53, 137.45, 137.14, 131.30, 130.48, 129.50, 128.85, 128.61,

127.57, 127.04, 126.99, 126.05, 124.77, 122.36, 120.16, 119.83, 119.25, 109.30, 105.71, 55.43, 54.53, 32.69, 21.29.
HRMS (ESI) calcd for $C_{29}H_{26}N_2NaO_4S^+$ 521.1505, found 521.1508.

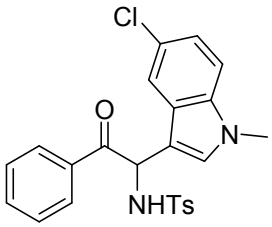


***N*-(1-(5-fluoro-1-methyl-1*H*-indol-3-yl)-2-oxo-2-phenylethyl)-4-methylbenzenesulfonamide (11ab):** 148.3 mg, brown solid, m.p.: 152-153 °C, yield: 68%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.3 Hz, 2H), 7.50 – 7.43 (m, 3H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.16 (dd, *J* = 9.5, 2.3 Hz, 1H), 7.02 (dd, *J* = 8.9, 4.3 Hz, 1H), 6.95 – 6.87 (m, 3H), 6.85 (s, 1H), 6.23 (d, *J* = 7.8 Hz, 1H), 6.16 (d, *J* = 7.8 Hz, 1H), 3.56 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.38, 158.13 (d, *J* = 236.1 Hz), 142.86, 137.31, 134.07, 133.75, 130.37, 128.86, 128.69, 128.61, 126.97, 126.16 (d, *J* = 10.3 Hz), 110.78 (d, *J* = 26.5 Hz), 110.13 (d, *J* = 9.7 Hz), 108.69 (d, *J* = 4.0 Hz), 104.15 (d, *J* = 24.3 Hz), 54.50, 32.99, 21.31.

HRMS (ESI) calcd for $C_{24}H_{21}FN_2NaO_3S^+$ 459.1149, found 459.1149.

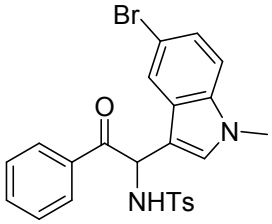


***N*-(1-(5-chloro-1-methyl-1*H*-indol-3-yl)-2-oxo-2-phenylethyl)-4-methylbenzenesulfonamide (11ac):** 140.7 mg, brown solid, m.p.: 165-166 °C, yield: 62%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.3 Hz, 2H), 7.50 – 7.44 (m, 3H), 7.38 (d, *J* = 1.8 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.10 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.02 (d, *J* = 8.7 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 2H), 6.84 (s, 1H), 6.21 (d, *J* = 7.9 Hz, 1H), 6.13 (d, *J* = 7.9 Hz, 1H), 3.56 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.38, 142.97, 137.21, 135.52, 134.03, 133.79, 130.13, 128.93, 128.72, 128.65, 127.00, 126.80, 126.11, 122.71, 118.52, 110.43, 108.48, 54.33, 32.96, 21.38.

HRMS (ESI) calcd for $C_{24}H_{21}ClN_2NaO_3S^+$ 475.0854, found 475.0861.



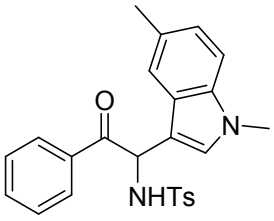
***N*-(1-(5-bromo-1-methyl-1*H*-indol-3-yl)-2-oxo-2-phenylethyl)-4-methylbenzenesulfonamide (11ad):** 166.7 mg, brown solid, m.p.:169-171 °C, yield: 67%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.3 Hz, 2H), 7.52 (d, *J* = 1.7 Hz, 1H), 7.50 – 7.45 (m, 3H), 7.33 (t, *J* = 7.8

Hz, 2H), 7.23 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.00 – 6.92 (m, 3H), 6.82 (s, 1H), 6.21 (d, *J* = 7.8 Hz, 1H), 6.12 (d, *J* = 7.8 Hz, 1H), 3.56 (s, 3H), 2.26 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.37, 142.95, 137.20, 135.78, 134.03, 133.78, 129.96, 128.93, 128.71, 128.64, 127.42, 126.98, 125.28, 121.58, 113.67, 110.83, 108.42, 54.28, 32.92, 21.39.

HRMS (ESI) calcd for $C_{24}H_{21}BrN_2NaO_3S^+$ 519.0348, found 519.0356.

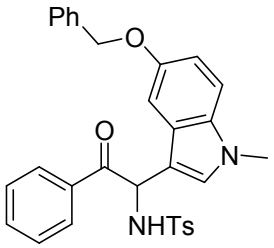


***N*-(1-(1,5-dimethyl-1*H*-indol-3-yl)-2-oxo-2-phenylethyl)-4-methylbenzenesulfonamide (11ae):** 157.4 mg, light yellow solid, m.p.: 166-168 °C, yield: 73%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.4 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.35 – 7.26 (m, 3H), 7.07 – 6.98 (m, 2H), 6.95 (d, *J* = 8.1 Hz, 2H), 6.70 (s, 1H), 6.25 (d, *J* = 8.2 Hz, 1H), 6.03 (d, *J* = 8.2 Hz, 1H), 3.54 (s, 3H), 2.42 (s, 3H), 2.26 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.73, 142.76, 137.40, 135.63, 134.31, 133.55, 129.48, 128.90, 128.68, 128.53, 127.08, 126.19, 124.03, 118.61, 109.06, 108.09, 54.59, 32.75, 21.46, 21.35.

HRMS (ESI) calcd for $C_{25}H_{24}N_2NaO_3S^+$ 455.1400, found 455.1417.

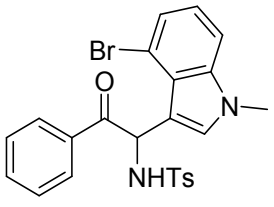


***N*-(1-(5-(benzyloxy)-1-methyl-1*H*-indol-3-yl)-2-oxo-2-phenylethyl)-4-methylbenzenesulfonamide (11af):** 163.5 mg, white solid, m.p.: 174-176 °C, yield: 62%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.4 Hz, 2H), 7.54 (d, *J* = 7.3 Hz, 2H), 7.49 – 7.26 (m, 8H), 7.12 (d, *J* = 2.2 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 1H), 6.95 – 6.83 (m, 3H), 6.72 (s, 1H), 6.24 (d, *J* = 7.9 Hz, 1H), 6.05 (d, *J* = 7.9 Hz, 1H), 5.16 – 5.05 (m, 2H), 3.53 (s, 3H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.51, 153.58, 142.62, 137.56, 137.38, 134.23, 133.59, 132.55, 129.15, 128.72, 128.67, 128.55, 127.90, 127.82, 126.90, 126.26, 113.51, 110.14, 108.10, 102.23, 70.72, 54.75, 32.85, 21.31.

HRMS (ESI) calcd for $C_{31}H_{28}N_2NaO_4S^+$ 547.1662, found 547.1667.

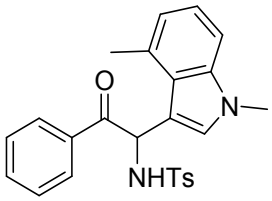


***N*-(1-(4-bromo-1-methyl-1*H*-indol-3-yl)-2-oxo-2-phenylethyl)-4-methylbenzenesulfonamide (11ag):** 143.1 mg, white solid, m.p.: 191-192 °C, yield: 67%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.38 – 7.29 (m, 3H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.07 – 6.98 (m, 3H), 6.83 (s, 1H), 5.92 (d, *J* = 8.5 Hz, 1H), 3.56 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.24, 142.82, 138.24, 137.75, 134.33, 133.40, 130.79, 129.22, 128.94, 128.57, 127.37, 124.97, 123.88, 123.05, 113.81, 109.59, 108.95, 53.19, 33.10, 21.36.

HRMS (ESI) calcd for $C_{24}H_{21}BrN_2NaO_3S^+$ 519.0348, found 519.0349.

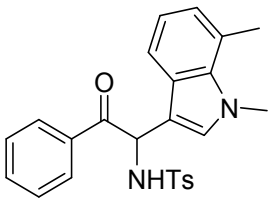


***N*-(1-(1,4-dimethyl-1*H*-indol-3-yl)-2-oxo-2-phenylethyl)-4-methylbenzenesulfonamide (11ah):** 148.9 mg, light yellow solid, m.p.: 165-167 °C, yield: 69%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.7 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.20 – 7.11 (m, 1H), 7.09 – 7.01 (m, 3H), 6.95 (d, *J* = 7.0 Hz, 1H), 6.62 (s, 1H), 6.57 (d, *J* = 9.0 Hz, 1H), 5.71 (br, 1H), 3.55 (s, 3H), 2.88 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.34, 143.04, 137.76, 137.55, 134.81, 133.34, 131.02, 129.33, 129.19, 128.72, 128.57, 127.25, 124.75, 122.59, 122.21, 108.91, 107.48, 55.31, 32.94, 21.42, 20.46.

HRMS (ESI) calcd for $C_{25}H_{25}N_2O_3S^+$ 433.1580, found 433.1585.

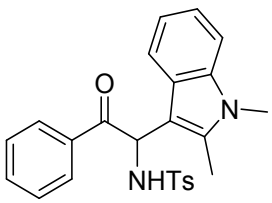


***N*-(1-(1,7-dimethyl-1*H*-indol-3-yl)-2-oxo-2-phenylethyl)-4-methylbenzenesulfonamide (11ai):** 151.1 mg, light yellow solid, m.p.: 134-136 °C, yield: 70%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.7 Hz, 2H), 7.52 – 7.40 (m, 4H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.00 – 6.90 (m, 3H), 6.87 (d, *J* = 7.0 Hz, 1H), 6.63 (s, 1H), 6.25 (d, *J* = 8.1 Hz, 1H), 6.04 (br, 1H), 3.82 (s, 3H), 2.63 (s, 3H), 2.26 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.69, 142.65, 137.40, 135.86, 134.27, 133.58, 130.28, 128.80, 128.64, 128.53, 127.06, 127.02, 125.06, 121.30, 120.47, 117.12, 108.44, 54.51, 36.76, 21.31, 19.51.

HRMS (ESI) calcd for $C_{25}H_{24}N_2NaO_3S^+$ 455.1400, found 455.1407.



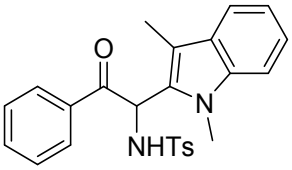
***N*-(1-(1,2-dimethyl-1*H*-indol-3-yl)-2-oxo-2-phenylethyl)-4-methylbenzenesulfonamide (11aj):** 144.7 mg, yellow

solid, m.p.: 203-204 °C, yield: 67%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.6 Hz, 2H), 7.45-7.34 (m, 2H), 7.33 – 7.19 (m, 4H), 7.13 – 6.93 (m, 3H), 6.74 (d, *J* = 8.0 Hz, 2H), 6.36 (d, *J* = 6.0 Hz, 1H), 6.27 (d, *J* = 6.0 Hz, 1H), 3.40 (s, 3H), 2.35 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.11, 142.12, 137.54, 136.58, 135.50, 134.30, 133.47, 128.50, 128.48, 128.17, 126.33, 125.53, 121.13, 120.00, 118.17, 108.54, 104.94, 55.27, 29.22, 21.27, 10.44.

HRMS (ESI) calcd for $C_{25}H_{24}N_2NaO_3S^+$ 455.1400, found 455.1399.

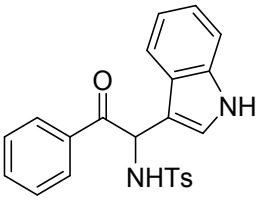


***N*-(1-(1,3-dimethyl-1*H*-indol-2-yl)-2-oxo-2-phenylethyl)-4-methylbenzenesulfonamide (11ak):** 108.7 mg, light yellow solid, m.p.: 174-176 °C, yield: 50%;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.79 (d, *J* = 7.4 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.34 – 7.26 (m, 4H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.70 (d, *J* = 8.2 Hz, 2H), 6.37 (d, *J* = 4.0 Hz, 1H), 6.29 (d, *J* = 4.0 Hz, 1H), 3.36 (s, 3H), 2.36 (s, 3H), 2.05 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.57, 142.95, 137.17, 136.89, 134.08, 133.93, 128.77, 128.56, 127.65, 127.55, 126.32, 122.57, 119.07, 119.01, 111.72, 108.71, 55.25, 29.86, 21.16, 9.04.

HRMS (ESI) calcd for $C_{25}H_{25}N_2O_3S^+$ 433.1580, found 433.1585.

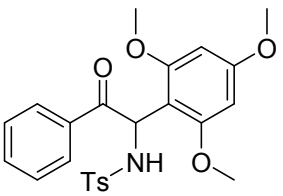


***N*-(1-(1*H*-indol-3-yl)-2-oxo-2-phenylethyl)-4-methylbenzenesulfonamide (11al):** 147.1 mg, brown solid, m.p.: 77-79 °C, yield: 72%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.29 – 7.21 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 2.2 Hz, 1H), 6.30 (d, *J* = 8.0 Hz, 1H), 6.18 (d, *J* = 8.0 Hz, 1H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.81, 142.98, 137.11, 136.33, 134.15, 133.66, 129.09, 128.65, 128.54, 126.90, 125.31, 124.50, 122.69, 120.42, 118.89, 111.45, 110.20, 54.85, 21.33.

HRMS (ESI) calcd for $C_{23}H_{21}N_2O_3S^+$ 405.1267, found 405.1267.



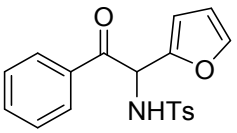
4-methyl-*N*-(2-oxo-2-phenyl-1-(2,4,6-trimethoxyphenyl)ethyl)benzenesulfonamide (11am): white solid, yield: 75%;

^{1}H NMR(400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.4 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.27 (t, *J* = 7.4

Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.30 (d, *J* = 7.7 Hz, 1H), 6.23 (d, *J* = 7.7 Hz, 1H), 5.85 (s, 2H), 3.71 (s, 6H), 3.69 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.94, 161.71, 158.26, 142.53, 137.81, 134.77, 132.83, 128.97, 128.18, 128.16, 127.01, 106.68, 90.82, 55.72, 55.24, 53.93, 21.42.

HRMS (ESI) calcd for $C_{24}H_{26}NO_6S^+$ 456.1475, found 456.1471.

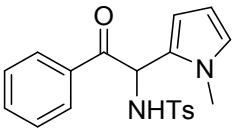


***N*-(1-(furan-2-yl)-2-oxo-2-phenylethyl)-4-methylbenzenesulfonamide (11an):** white solid, yield: 62%

^{1}H NMR(400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.4 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.18 (s, 1H), 7.14 (d, *J* = 8.2 Hz, 2H), 6.19 (d, *J* = 3.2 Hz, 1H), 6.16 (m, 2H), 6.11 (d, *J* = 7.6 Hz, 1H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.61, 148.16, 143.30, 143.25, 137.27, 134.19, 133.54, 129.46, 128.85, 128.75, 127.00, 110.86, 109.95, 55.47, 21.46.

HRMS (ESI) calcd for $C_{19}H_{18}NO_4S^+$ 356.0951, found 356.0946.

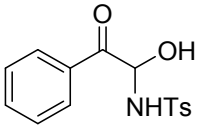


4-methyl-*N*-(1-(1-methyl-*1H*-pyrrol-2-yl)-2-oxo-2-phenylethyl)benzenesulfonamide (11ao): white solid, yield: 67%

^{1}H NMR(400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.7 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.59 (s, 1H), 6.02 (d, *J* = 8.9 Hz, 1H), 5.91 (t, *J* = 3.1 Hz, 1H), 5.80 (d, *J* = 8.7 Hz, 1H), 5.76 – 5.70 (m, 1H), 3.72 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.63, 143.44, 136.83, 134.38, 133.72, 129.52, 128.60, 128.42, 127.14, 124.76, 124.71, 110.73, 107.54, 54.74, 34.18, 21.45.

HRMS (ESI) calcd for $C_{20}H_{21}N_2O_3S^+$ 369.1267, found 369.1272.



***N*-(1-hydroxy-2-oxo-2-phenylethyl)-4-methylbenzenesulfonamide (9a):** white solid, m.p.: 144-146 °C

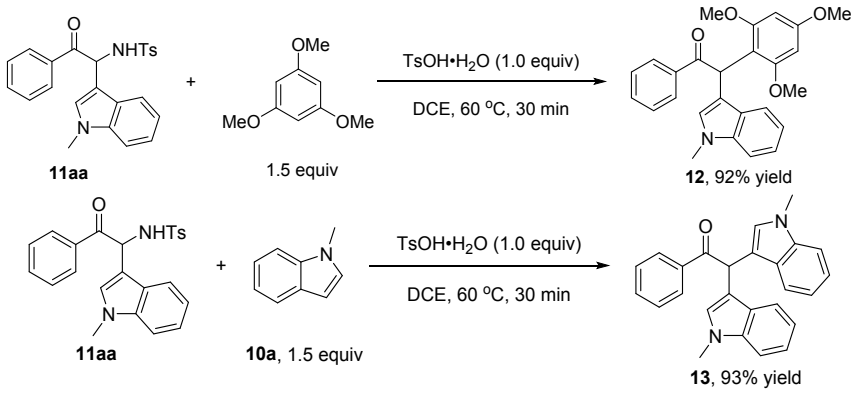
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.4 Hz, 2H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 6.23 (dd, *J* = 10.0, 7.4 Hz, 1H), 5.43 (d, *J* = 10.0 Hz, 1H), 4.27 (d, *J* = 7.4 Hz, 1H), 2.49 (s, 3H)..

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.15, 144.05, 138.03, 134.95, 131.89, 129.96, 129.77, 128.98, 127.25, 75.96, 21.59.

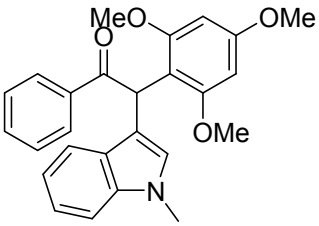
HRMS (ESI) calcd for $C_{15}H_{15}NNaO_4S^+$ 328.0614, found 328.0620.

6. Procedure for derivation of products

6.1 Synthesis of 12 & 13[7]



General procedure: In a dry flask, **11aa** (0.10 mmol) and TsOH (0.10 mmol) were dissolved in DCE (2 mL) under air atmosphere operation. 1,3,5-Trimethoxybenzene (0.15 mmol) or *N*-methyl indole (0.15 mmol) was added and the solution was stirred for 30 minutes at 60 °C. After the completion of the reaction (monitored by TLC), the mixture was filtered through a short plug of silica gel. The filtrate was concentrated and then purified by flash column chromatography with PE/EtOAc (10:1~5:1) as eluent to afford the corresponding product **12** or **13**.

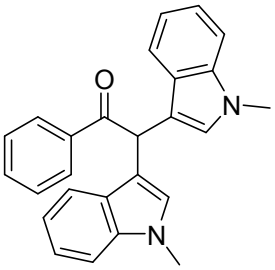


2-(1-methyl-1*H*-indol-3-yl)-1-phenyl-2-(2,4,6-trimethoxyphenyl)ethan-1-one (12): 38.1 mg, yield: 92%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.9 Hz, 2H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.32 – 7.23 (m, 3H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.83 (s, 1H), 6.26 (s, 1H), 6.06 (s, 2H), 3.74 (s, 3H), 3.72 (s, 6H), 3.70 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.27, 160.36, 158.00, 137.74, 136.82, 131.59, 128.49, 128.28, 128.00, 127.87, 121.02, 119.53, 118.67, 112.05, 111.38, 109.07, 91.13, 55.68, 55.23, 41.64, 32.74.

HRMS (ESI) calcd for $C_{26}H_{25}NNaO_4^+$ 438.1676, found 438.1672.



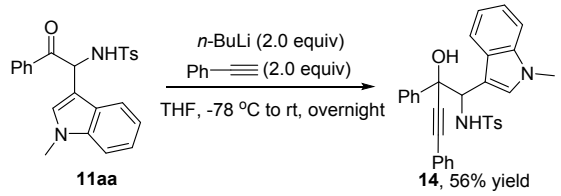
2,2-bis(1-methyl-1*H*-indol-3-yl)-1-phenylethan-1-one (13): 35.3 mg, yield: 93%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.7 Hz, 2H), 7.56 (d, *J* = 7.9 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.24 – 7.17 (m, 2H), 7.07 (t, *J* = 7.4 Hz, 2H), 6.88 (s, 2H), 6.52 (s, 1H), 3.68 (s, 6H).

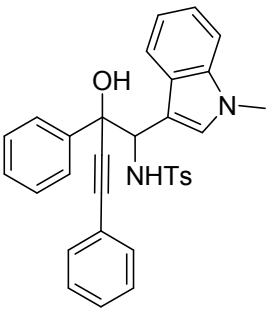
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.67, 137.34, 137.10, 132.81, 128.81, 128.61, 128.57, 127.13, 121.76, 119.20, 119.04, 112.90, 109.40, 41.78, 32.79.

HRMS (ESI) calcd for $C_{26}H_{22}N_2NaO^+$ 401.1624, found 401.1628.

6.2 Synthesis of 14[8]



Procedure: To a solution of Phenylacetylene (0.80 mmol) in THF (2 mL), *n*-BuLi (0.80 mmol, 0.33 mL, 2.4 M in hexane) was added dropwise at –78 °C under a nitrogen atmosphere. After stirring for 0.5 h, the reaction mixture was warmed to rt. A solution of **11aa** (0.40 mmol) in THF (2 mL) was added to the reaction mixture and the solution was stirred overnight. Then the reaction was quenched with saturated NH_4Cl aqueous at 0 °C, and the aqueous phase was extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel with PE/EtOAc (3:1) as eluent to afford **14**.

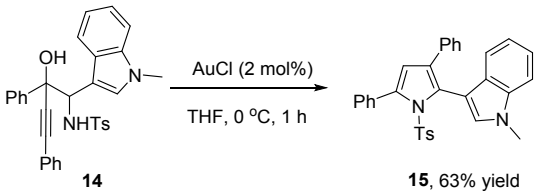


***N*-((2S)-2-hydroxy-1-(1-methyl-1*H*-indol-3-yl)-2,4-diphenylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (14):** 174.3 mg, yield: 56%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (m, *2*H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.43 (m, 2H), 7.32 (m, *3*H), 7.26 (m, 2H), 7.22 (m, 2H), 7.15 (m, 2H), 7.05 – 6.97 (m, 1H), 6.77 (d, *J* = 8.2 Hz, 2H), 6.75 (s, 1H), 5.38 (t, *J* = 8.9 Hz, 1H), 4.98 (d, *J* = 8.4 Hz, 1H), 3.59 (s, 3H), 2.98 (d, *J* = 2.2 Hz, 1H), 2.21 (s, 3H).

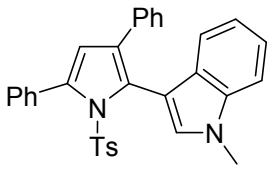
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.38, 140.65, 136.91, 136.50, 131.91, 128.89, 128.84, 128.63, 128.36, 128.24, 128.00, 127.40, 126.87, 126.66, 121.96, 121.74, 119.76, 119.61, 109.74, 109.03, 89.24, 88.23, 76.40, 61.31, 32.68, 21.30.
HRMS (ESI) calcd for $C_{32}H_{28}N_2NaO_3S^+$ 543.1713, found 543.1709.

6.3 Synthesis of 15[9]



14 **15**, 63% yield

Procedure: Under air atmosphere, THF (0.5 mL) was added to an open tube containing substrate **14** (0.10 mmol) and AuCl (2 mol%) at 0°C. After TLC analysis showed the reaction to be complete, it was filtered through a short plug of silica with EtOAc and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE:EtOAc = 5:1) to afford the product **15**.



3-(3,5-diphenyl-1-tosyl-1*H*-pyrrol-2-yl)-1-methyl-1*H*-indole (15): 31.9 mg, yield: 63%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (br, 1H), 7.45 (m, 7H), 7.15 (m, 4H), 7.05 – 6.90 (m, 5H), 6.81 (s, 1H), 6.76 (d, *J* = 7.0 Hz, 2H), 4.40 (s, 3H), 2.39 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 143.21, 140.54, 138.78, 138.58, 137.82, 137.15, 135.61, 129.43, 129.22, 128.58, 128.48, 127.78, 127.27, 126.81, 126.17, 122.91, 122.75, 122.07, 121.89, 119.06, 114.68, 109.17, 32.87, 21.52.
HRMS (ESI) calcd for $C_{32}H_{26}N_2NaO_2S^+$ 525.1607, found 525.1613.

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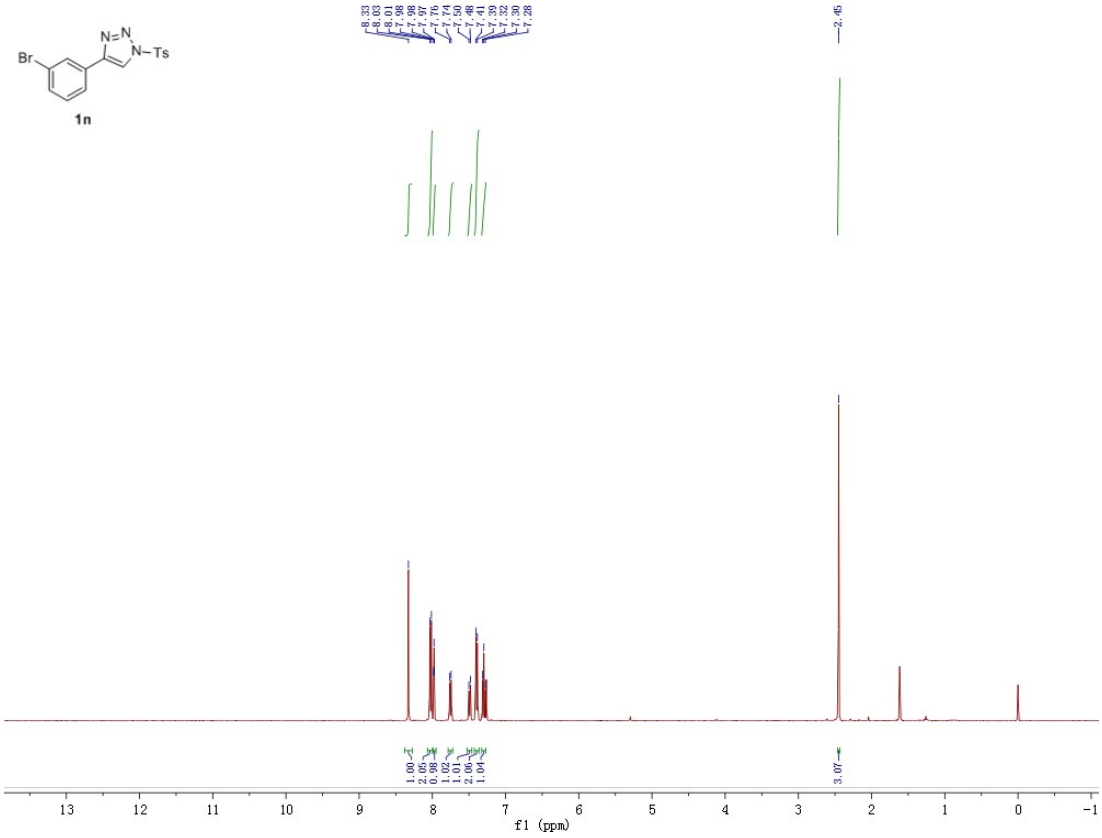
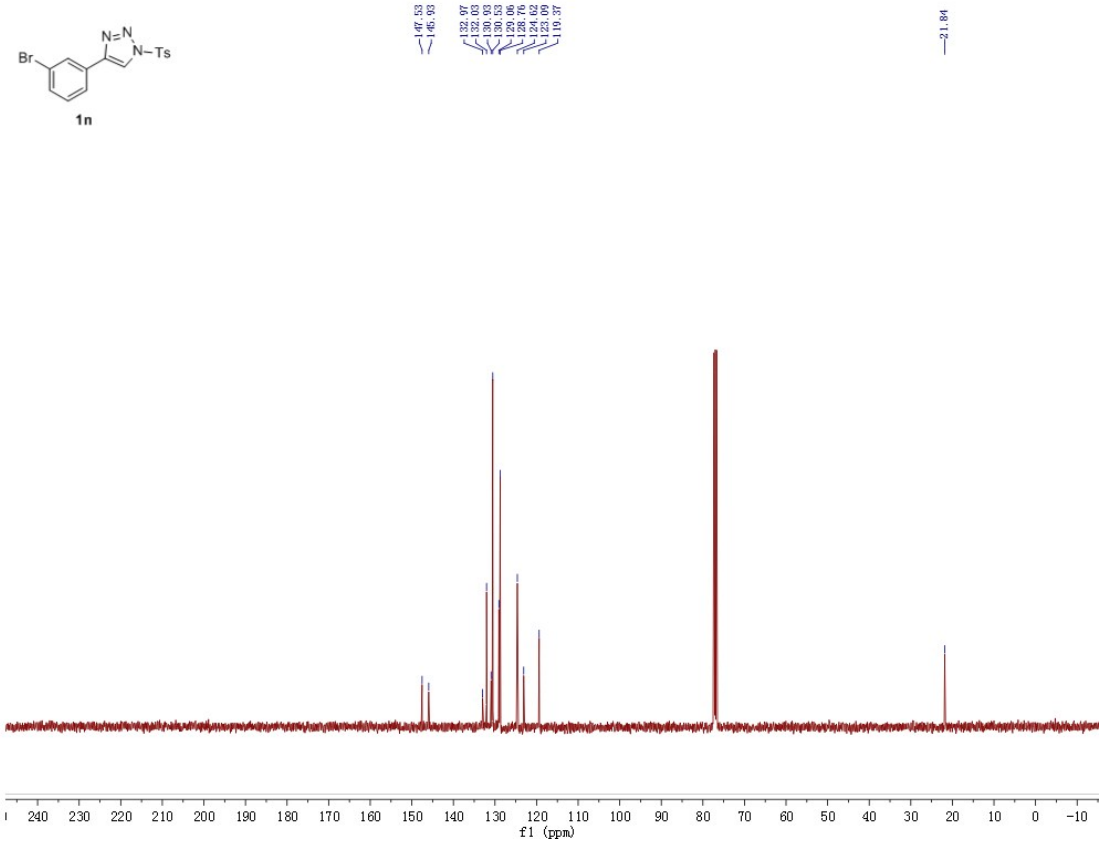
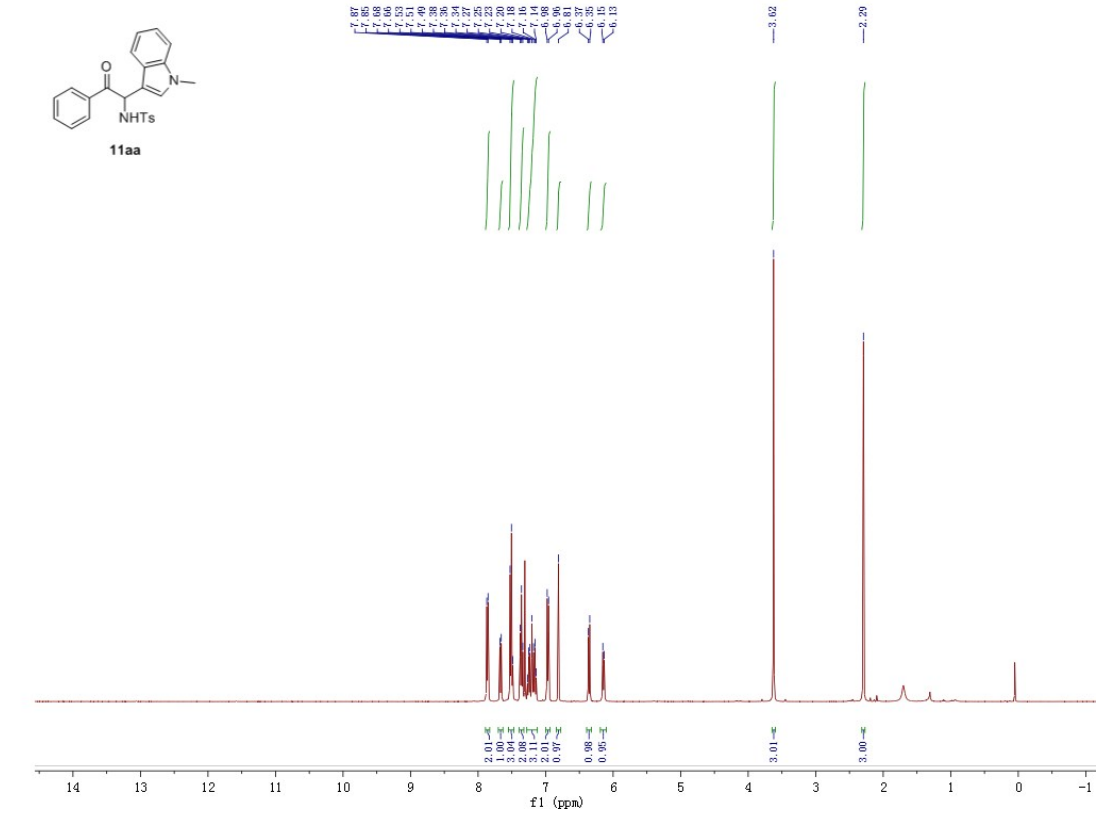
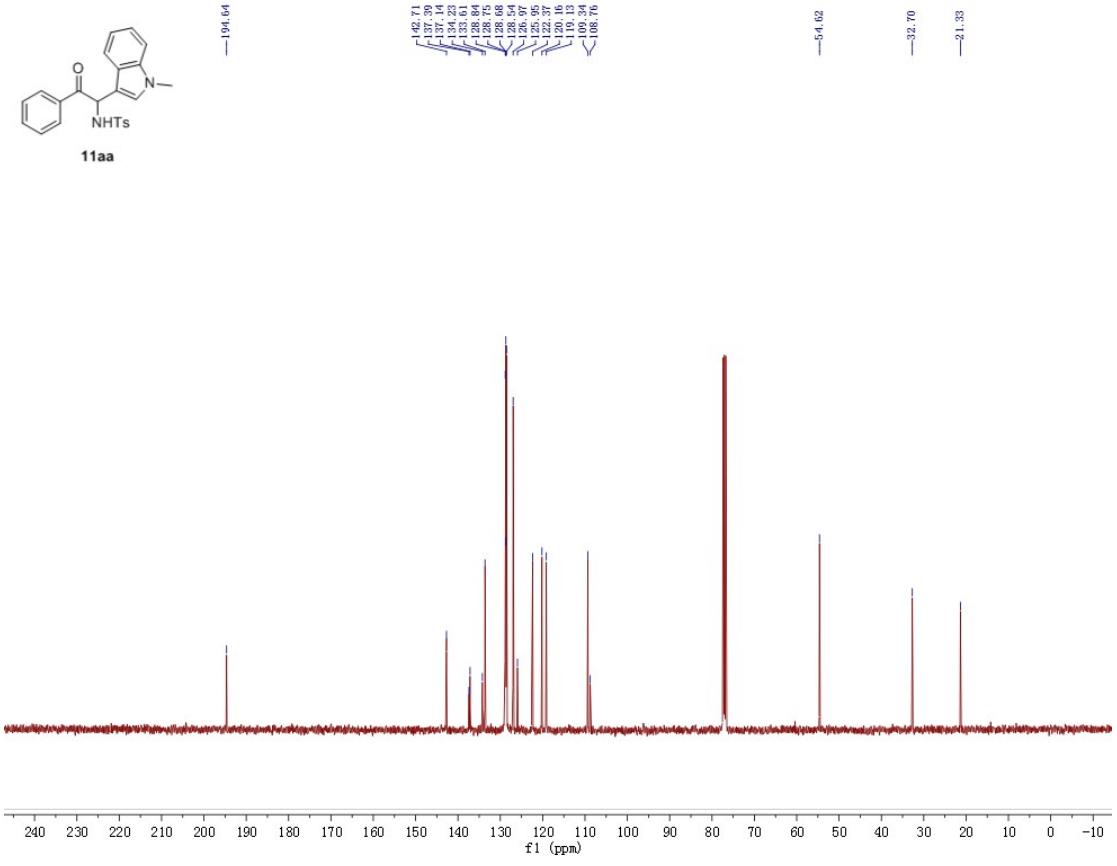
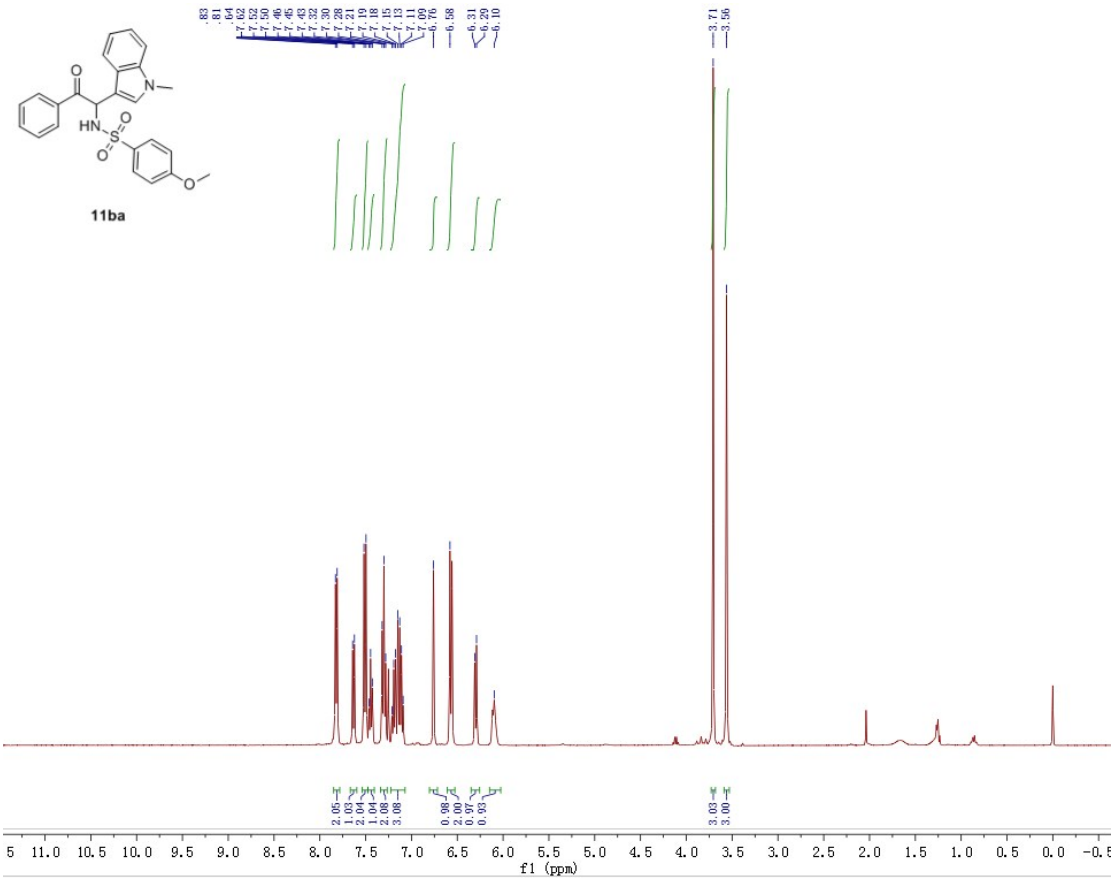
8. ^{1}H and ^{13}C NMR spectra for new compounds






11aa
f1 (ppm)


11aa
f1 (ppm)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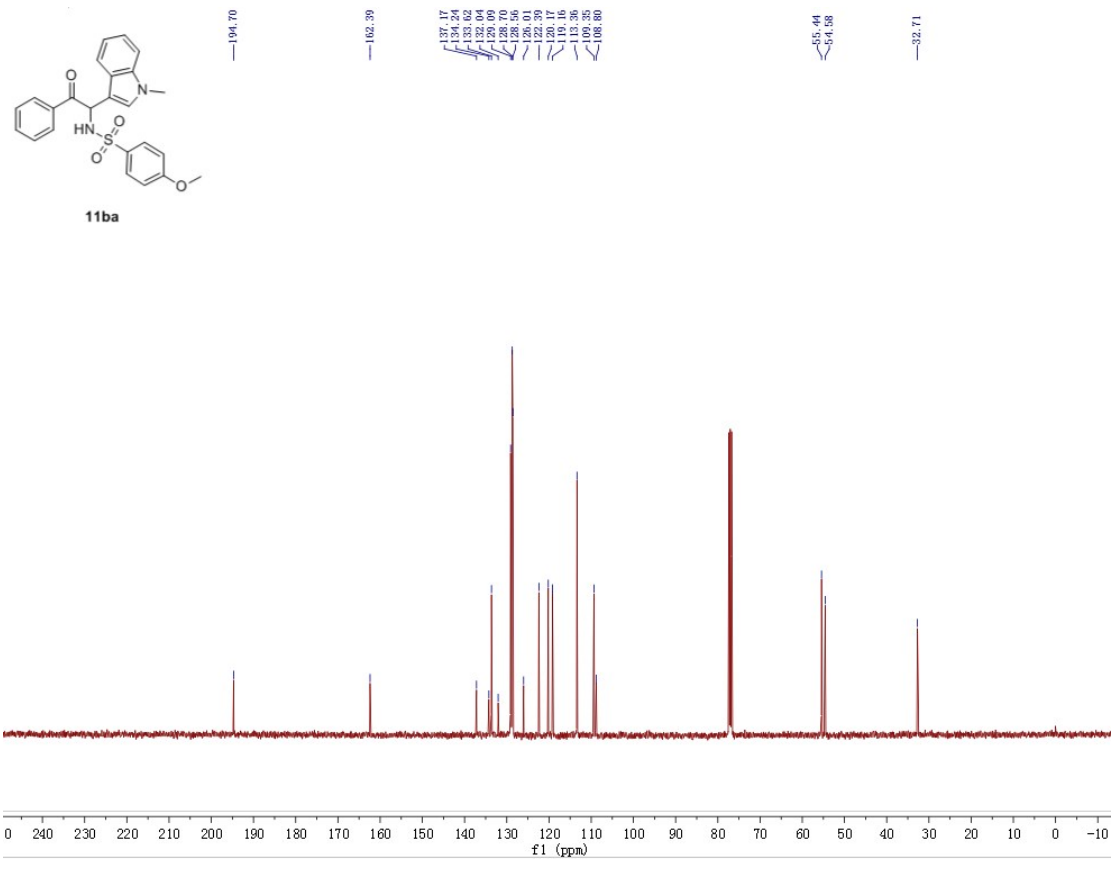
f1 (ppm)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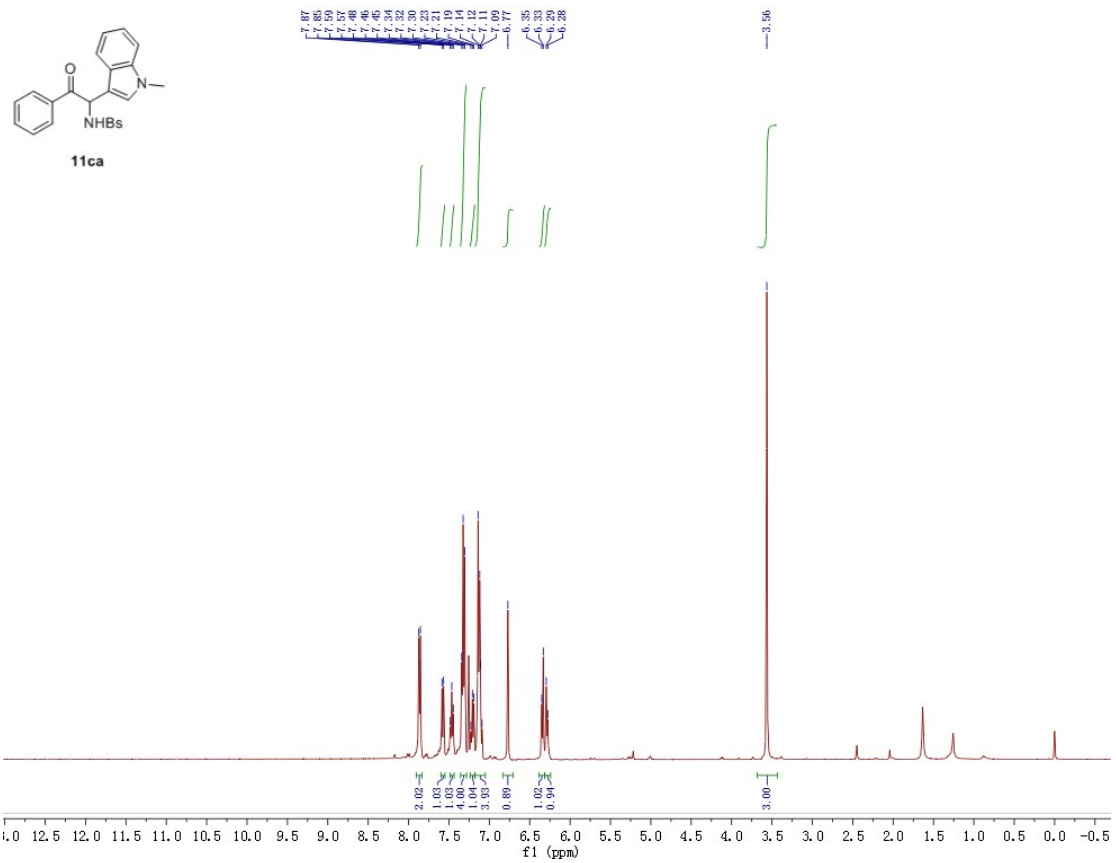
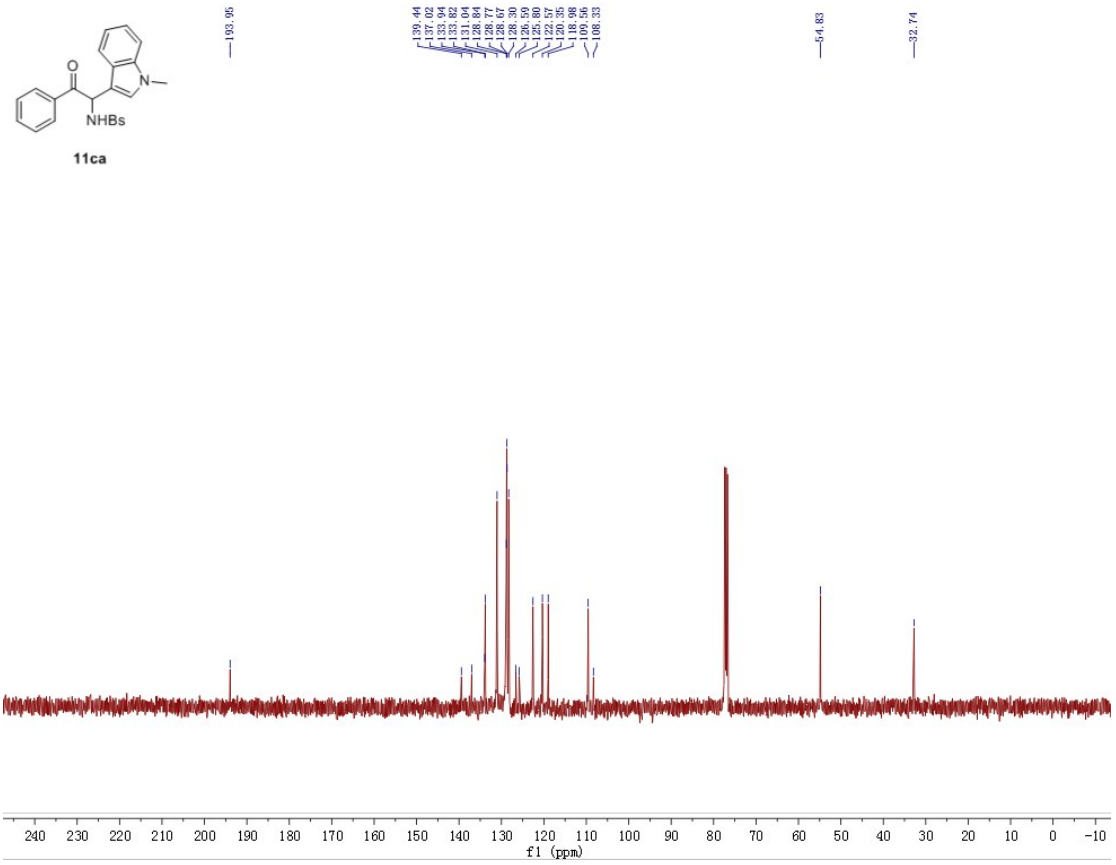
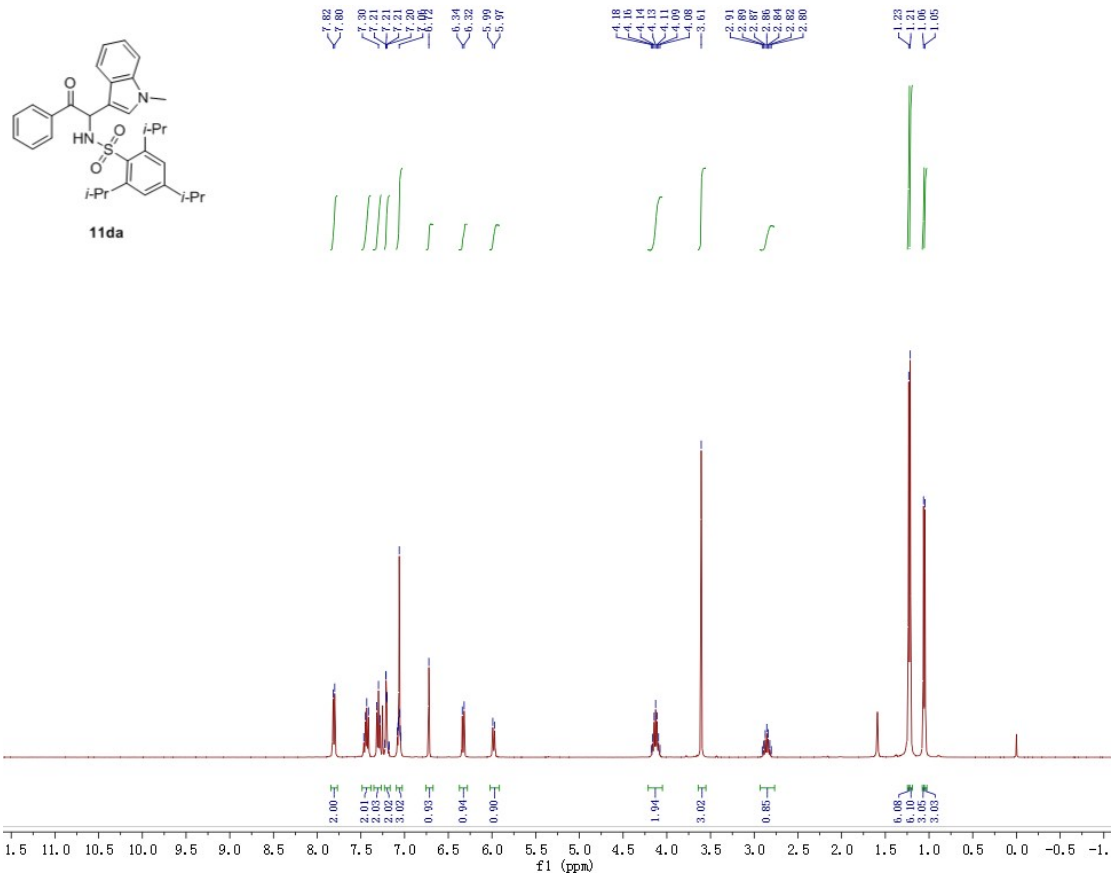
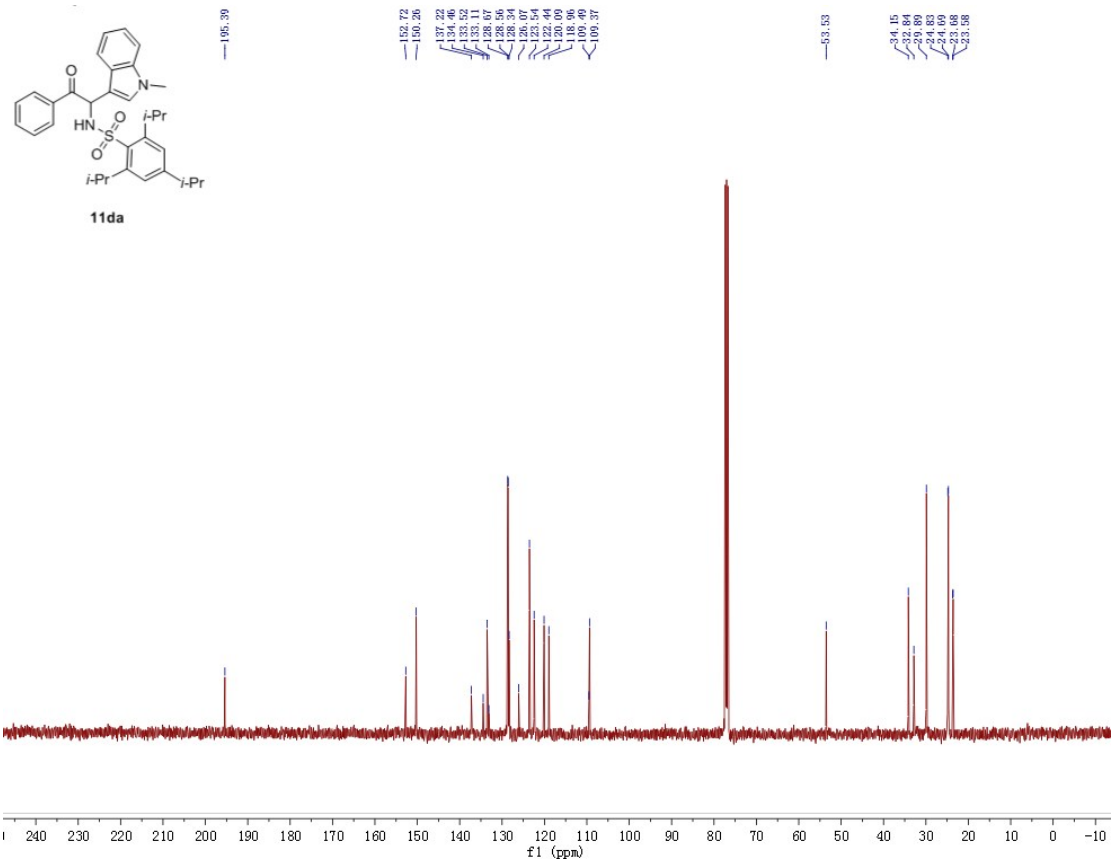
f1 (ppm)


NHBs
11ca
f1 (ppm)


NHBs
11ca
f1 (ppm)


11da
f1 (ppm)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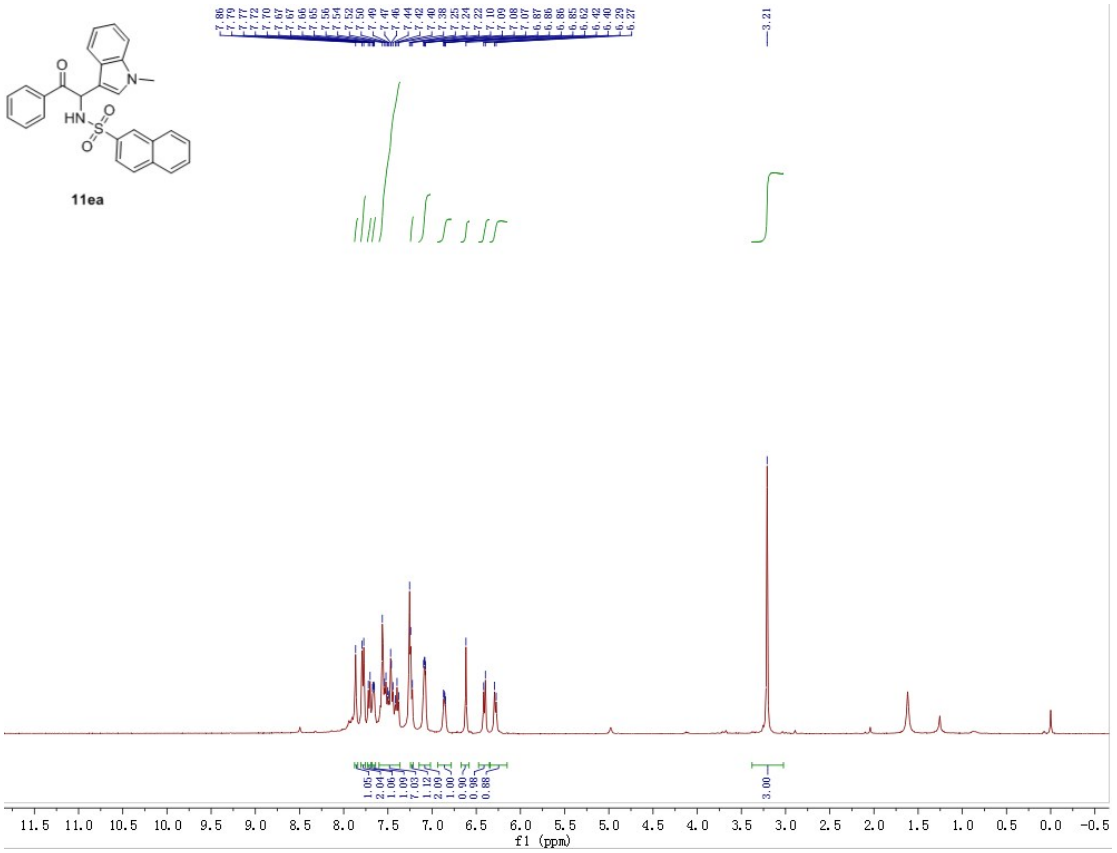
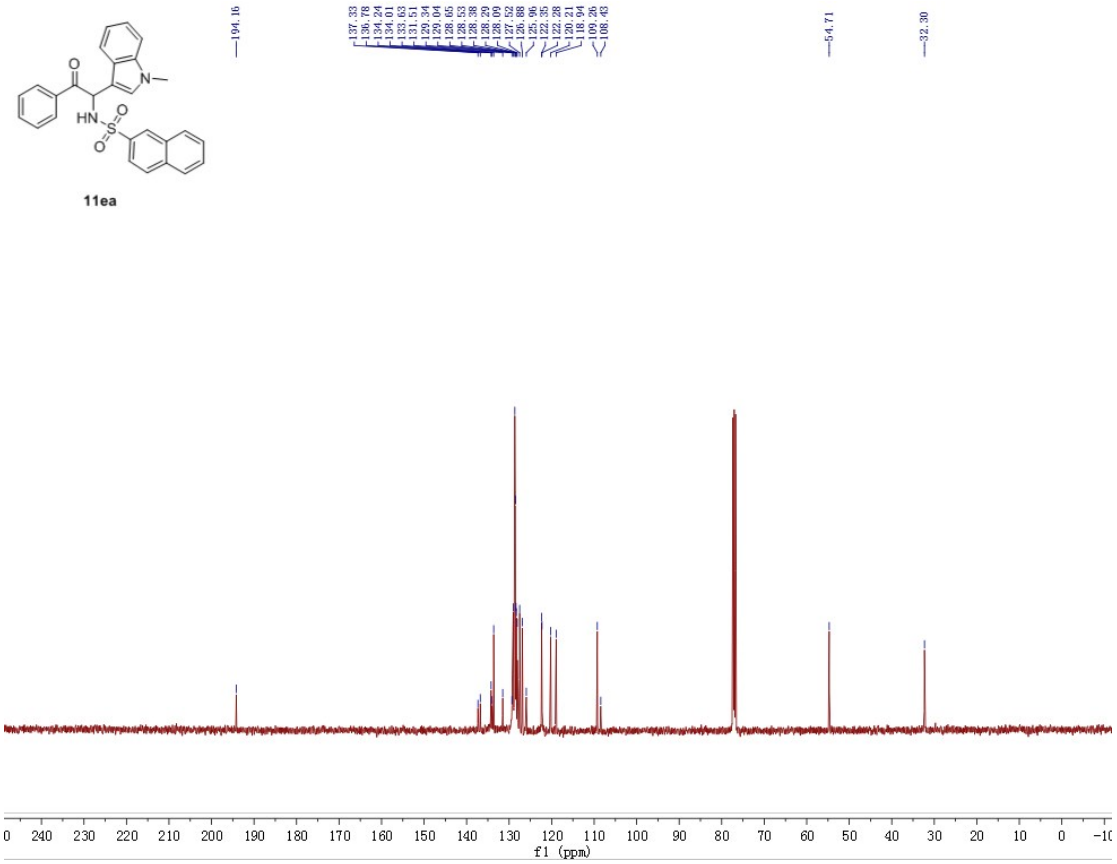
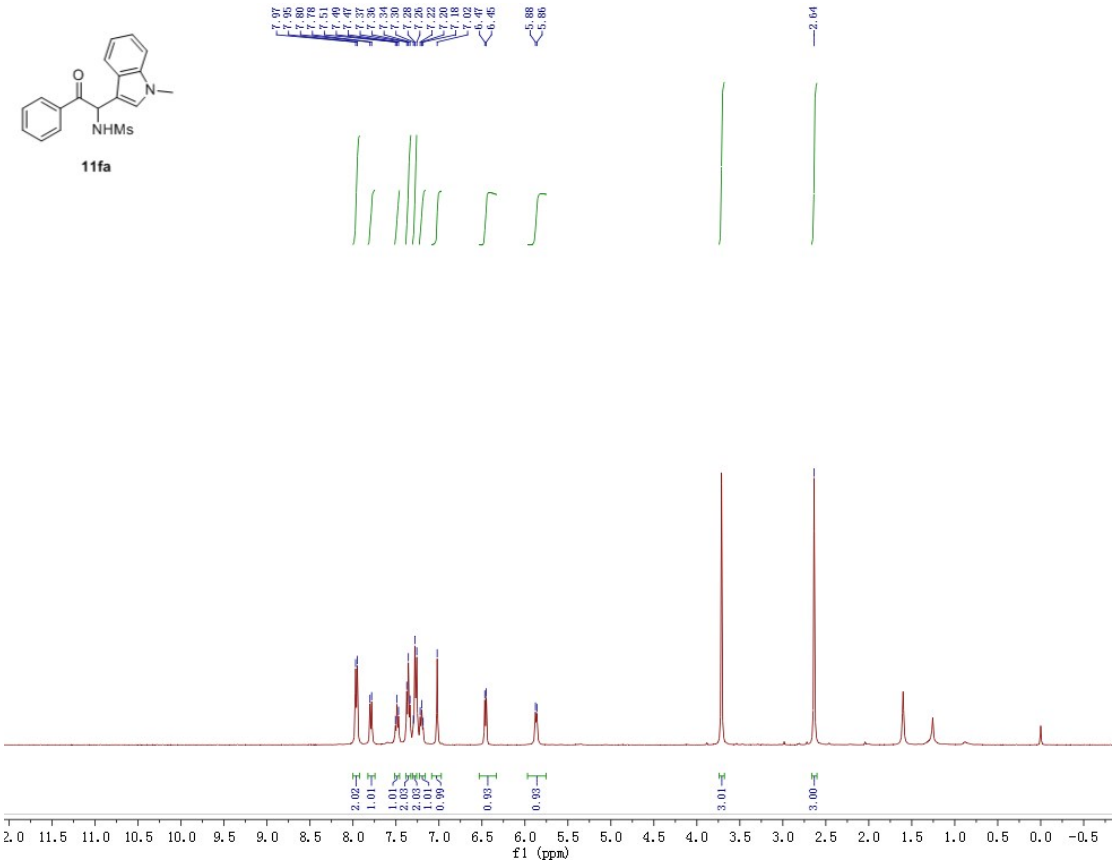
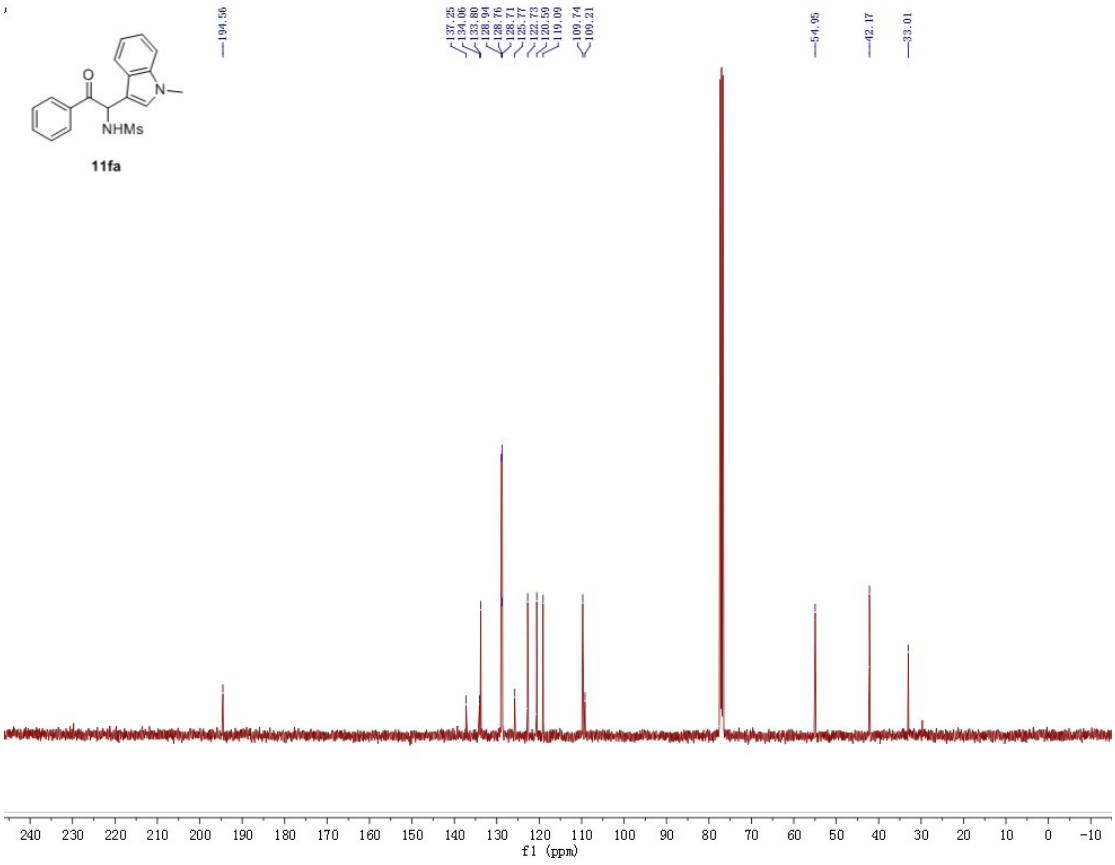
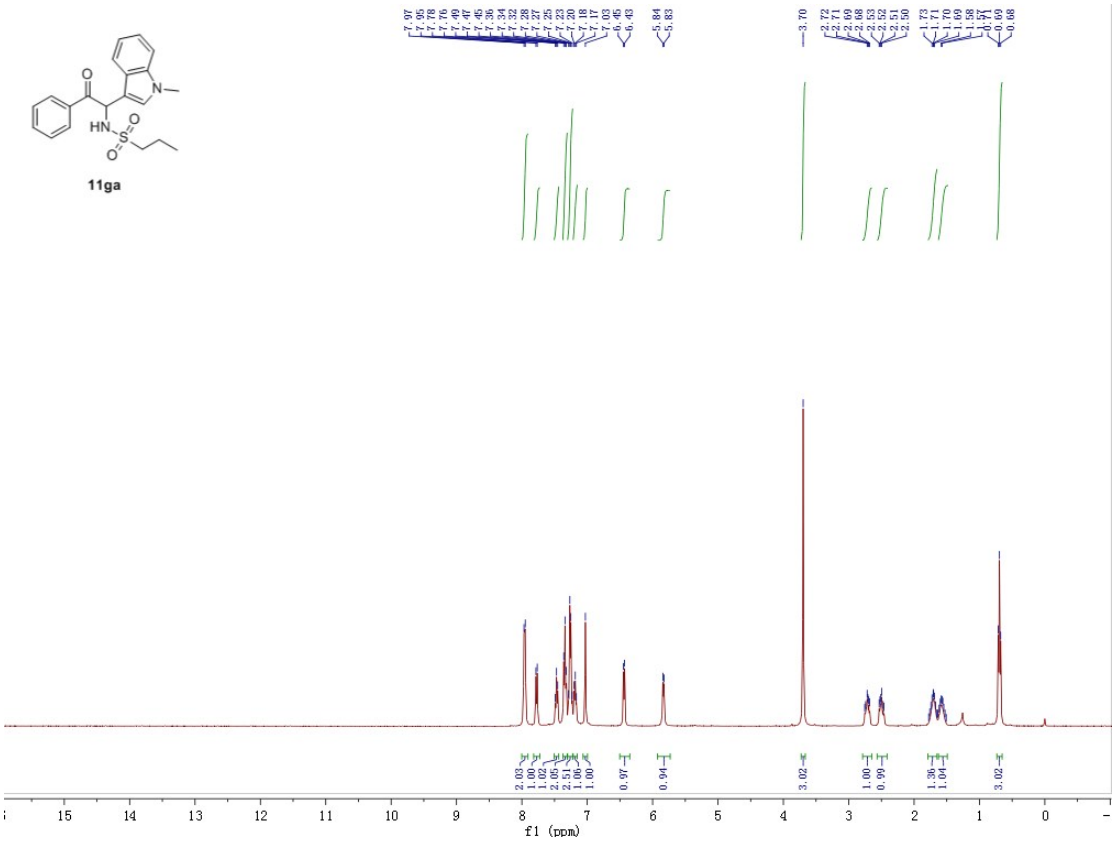
f1 (ppm)

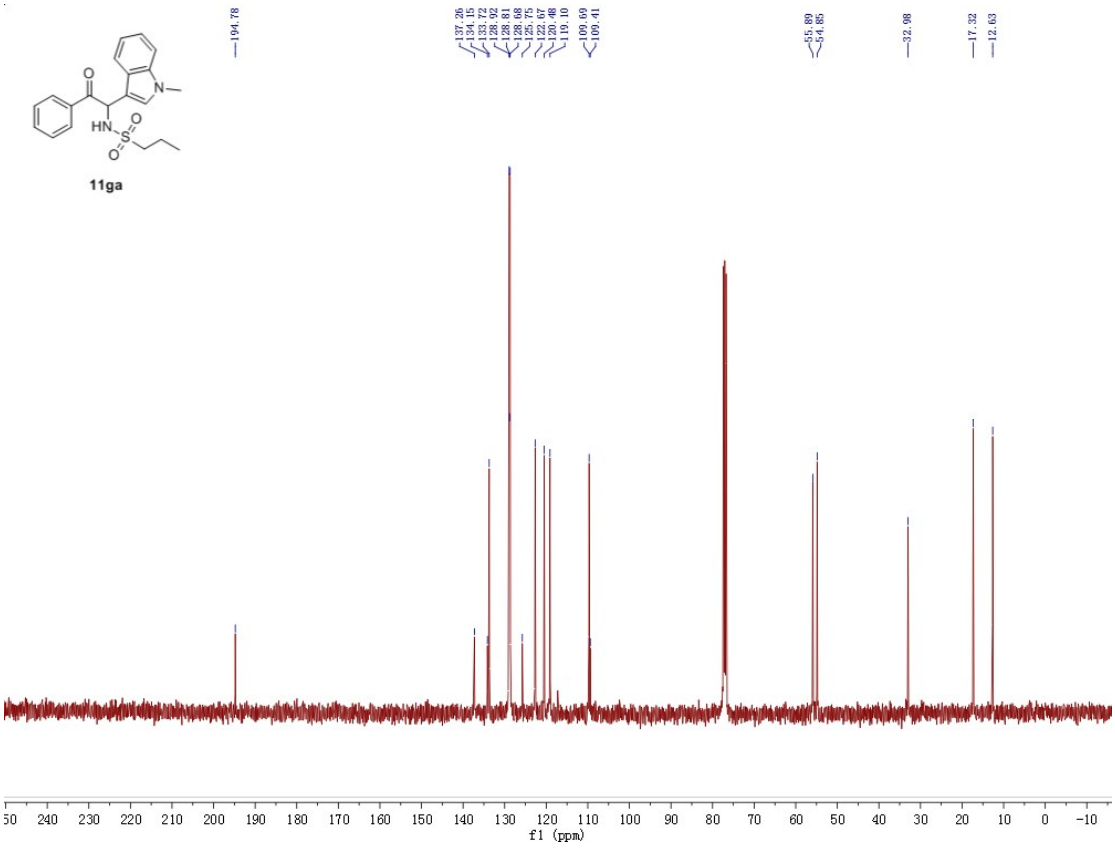

11ea
f1 (ppm)

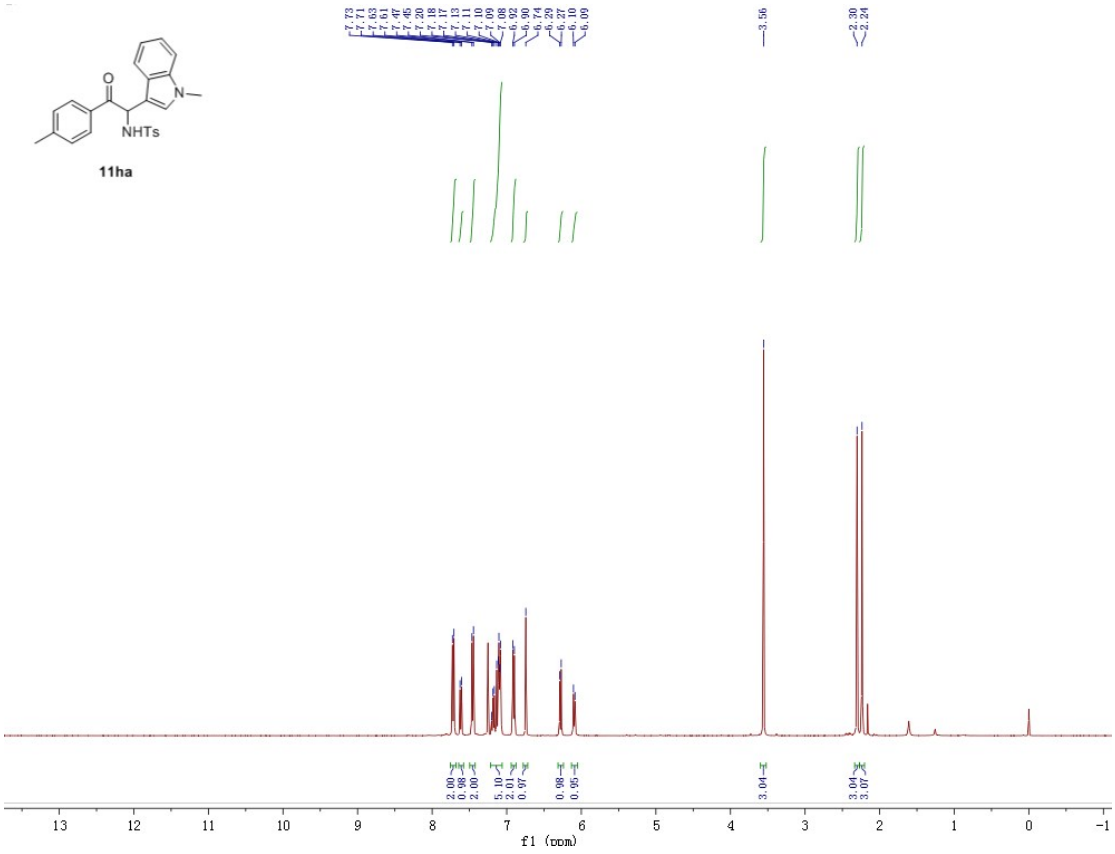

11ea
f1 (ppm)

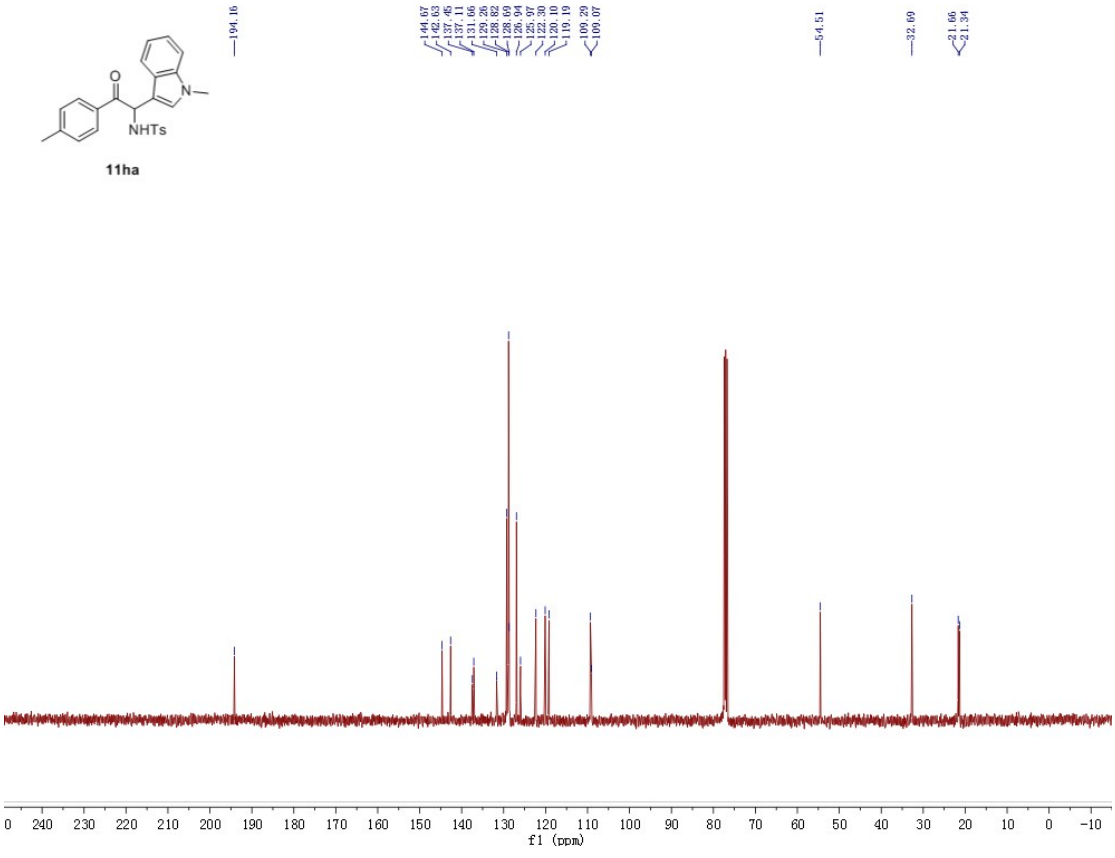

11fa
NHMs
7.97
7.95
7.80
7.78
7.51
7.49
7.47
7.37
7.36
7.34
7.30
7.28
7.26
7.22
7.20
7.18
7.02
6.47
6.45
5.88
5.86
2.64
2.02
1.01
1.01
2.03
2.03
1.01
0.99
0.93
0.93
3.01
3.00
f1 (ppm)

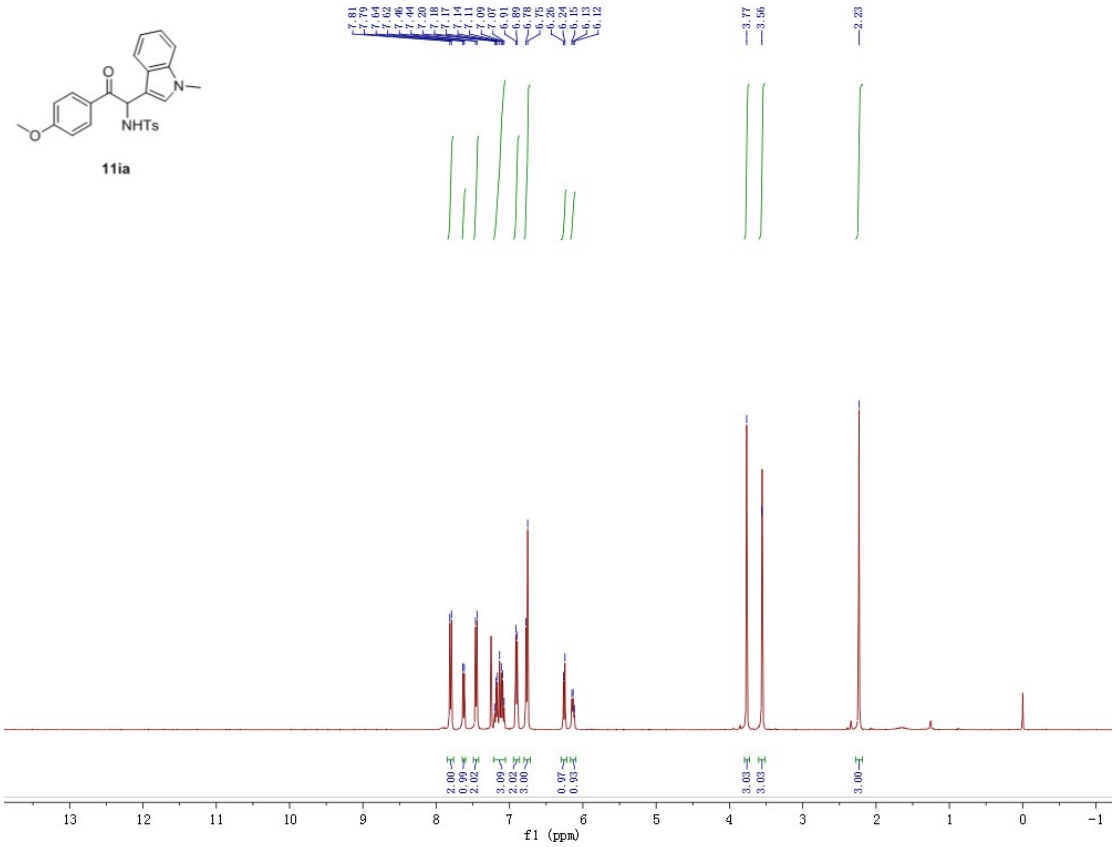

11fa
NHMs
194.56
137.25
134.06
133.80
128.94
128.76
128.71
125.77
122.73
120.59
119.09
109.74
109.21
54.95
42.17
33.01
f1 (ppm)

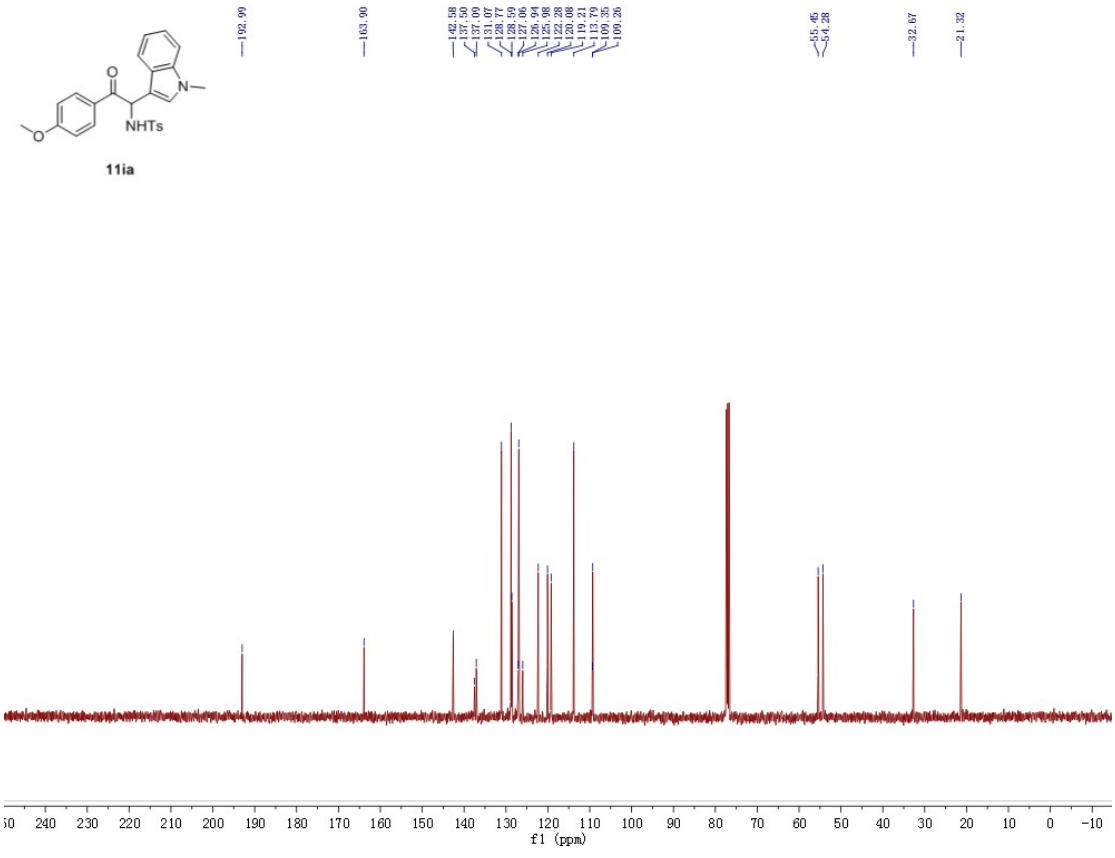

11ga
f1 (ppm)


11ga
f1 (ppm)


11ha
f1 (ppm)


11ha
f1 (ppm)


11ia
7.81
7.79
7.64
7.62
7.46
7.44
7.20
7.18
7.17
7.14
7.11
7.09
7.07
6.91
6.89
6.78
6.75
6.26
6.24
6.15
6.13
6.12
3.77
3.56
2.23
2.00
2.99
2.02
3.09
2.02
3.00
0.97
0.93
3.03
3.03
3.00
f1 (ppm)


11ia
192.99
163.90
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137.50
137.09
131.07
128.77
128.59
127.06
126.94
125.98
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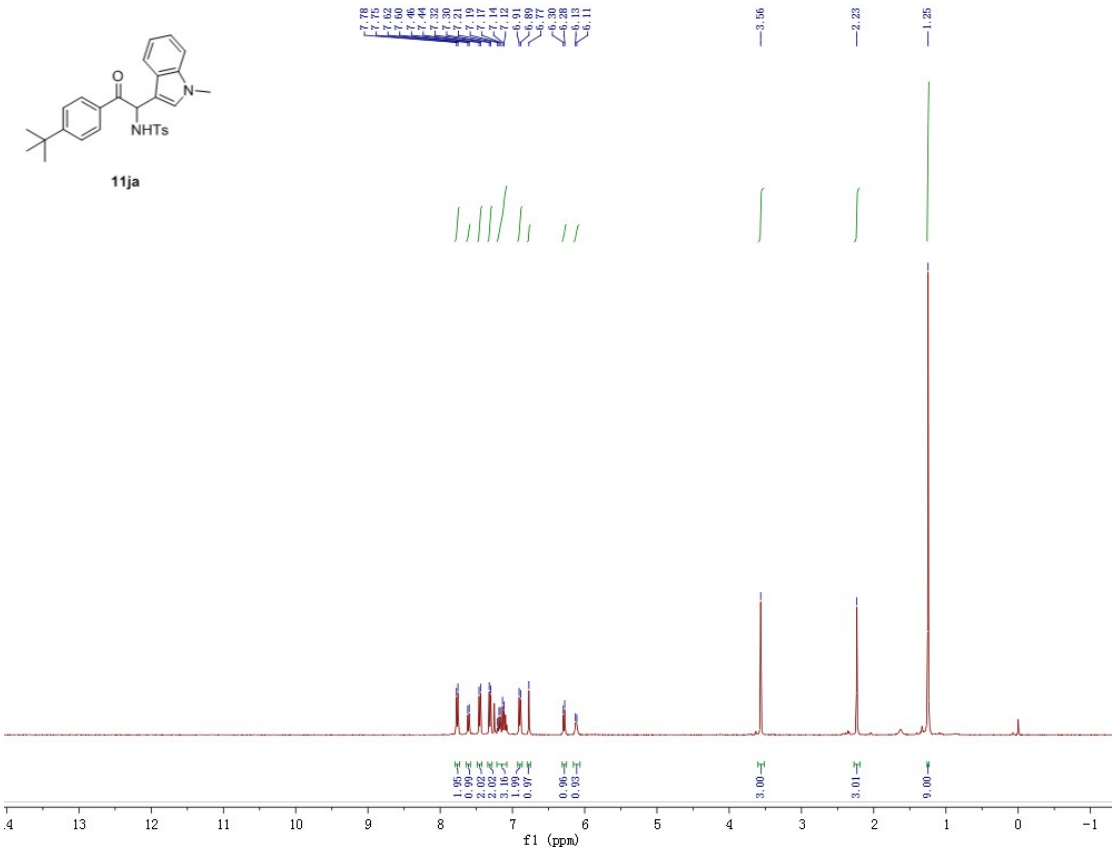
109.26
55.45
54.28
32.67
21.32
f1 (ppm)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7.78
7.75
7.62
7.60
7.46
7.44
7.32
7.30
7.21
7.19
7.17
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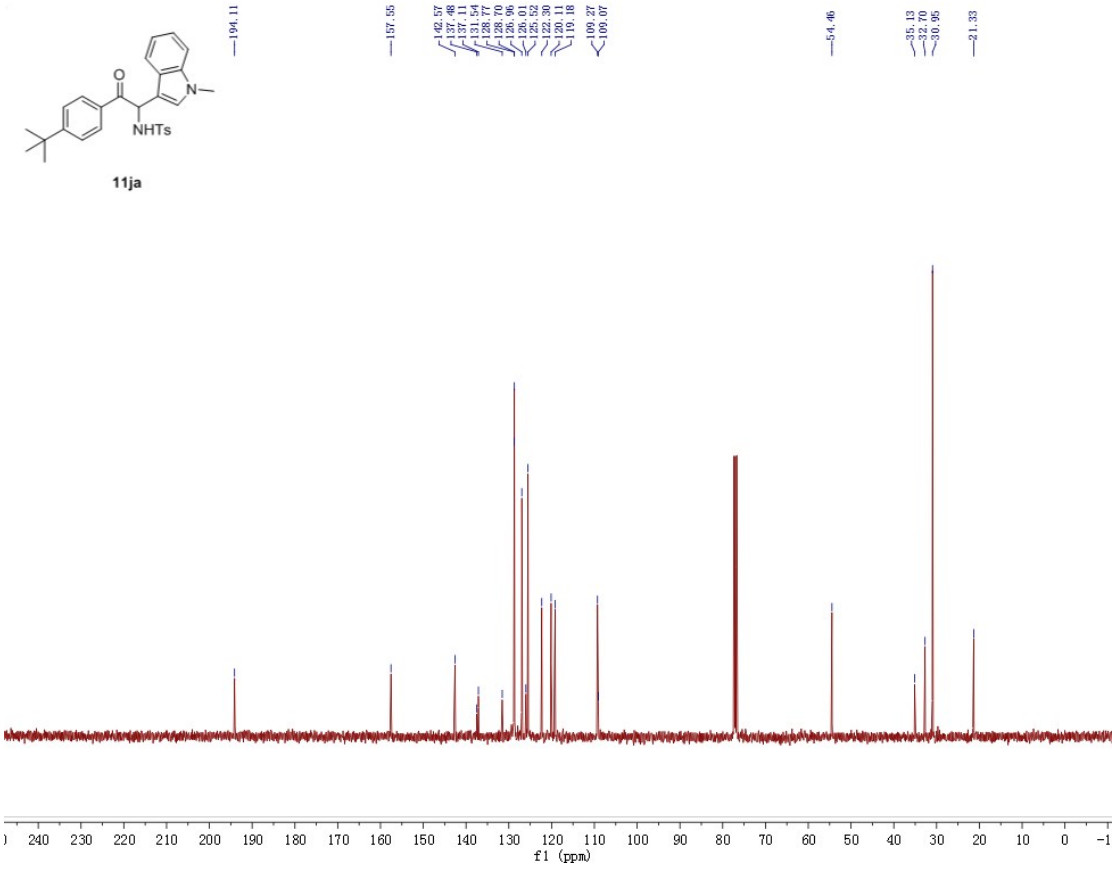
7.12
6.91
6.89
6.77
6.30
6.28
6.13
6.11
3.56
2.23
1.25
1.95
0.99
2.02
3.05
1.99
0.97
0.96
0.93
3.00
3.01
9.00
f1 (ppm)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157.55
142.57
137.48
137.11
131.54
128.77
128.70
126.96
126.01
125.52
122.30
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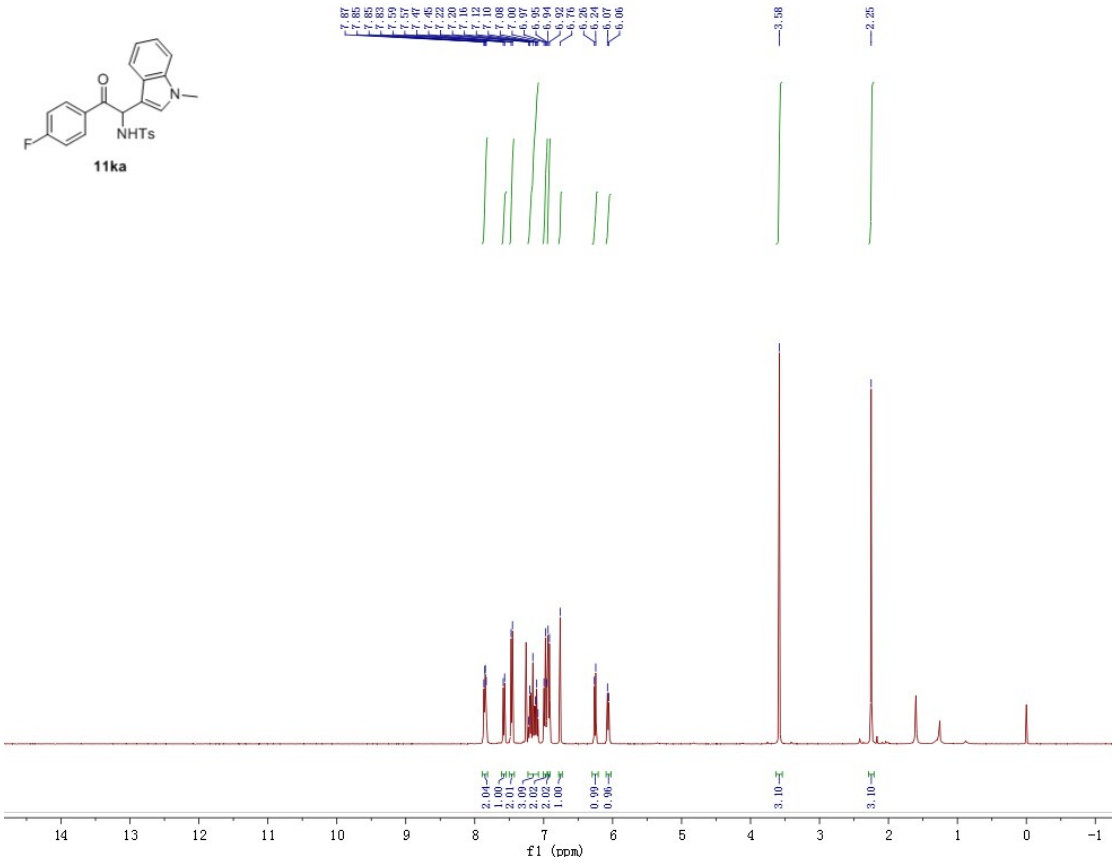
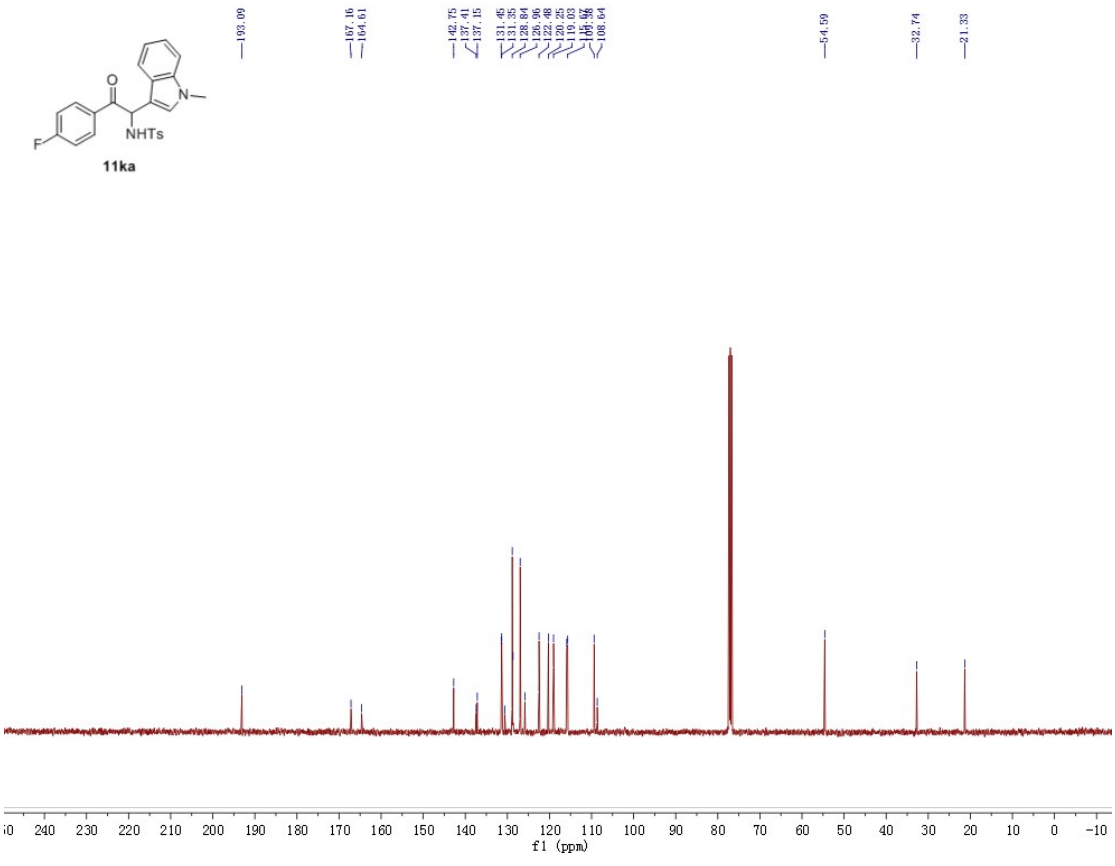
119.18
109.27
109.07
54.46
35.13
32.70
30.95
21.33
f1 (ppm)


11ka
f1 (ppm)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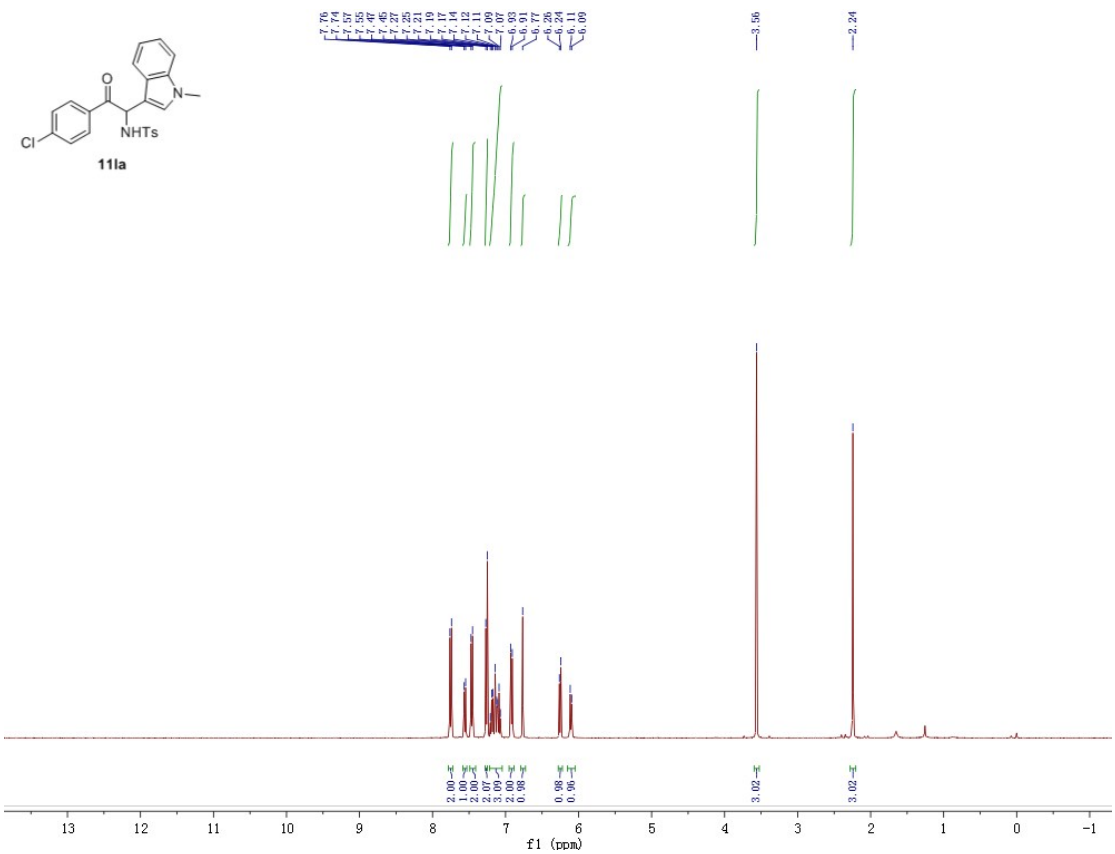
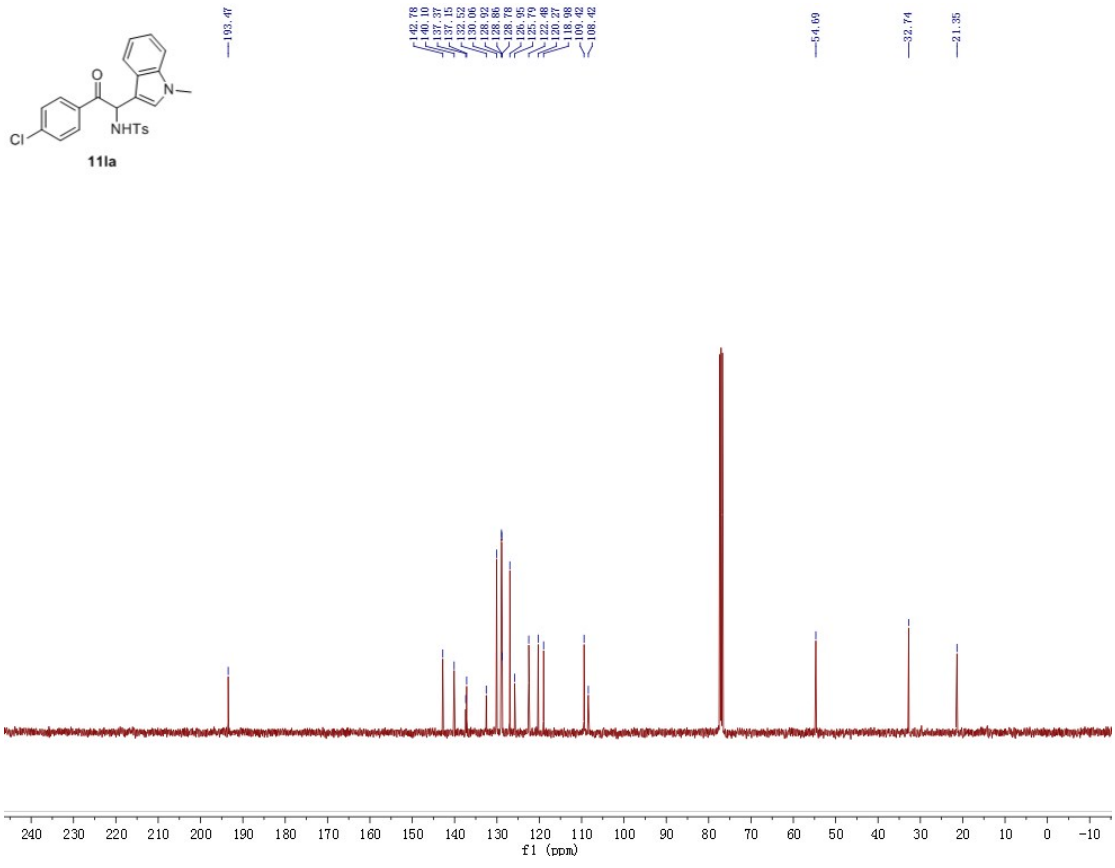
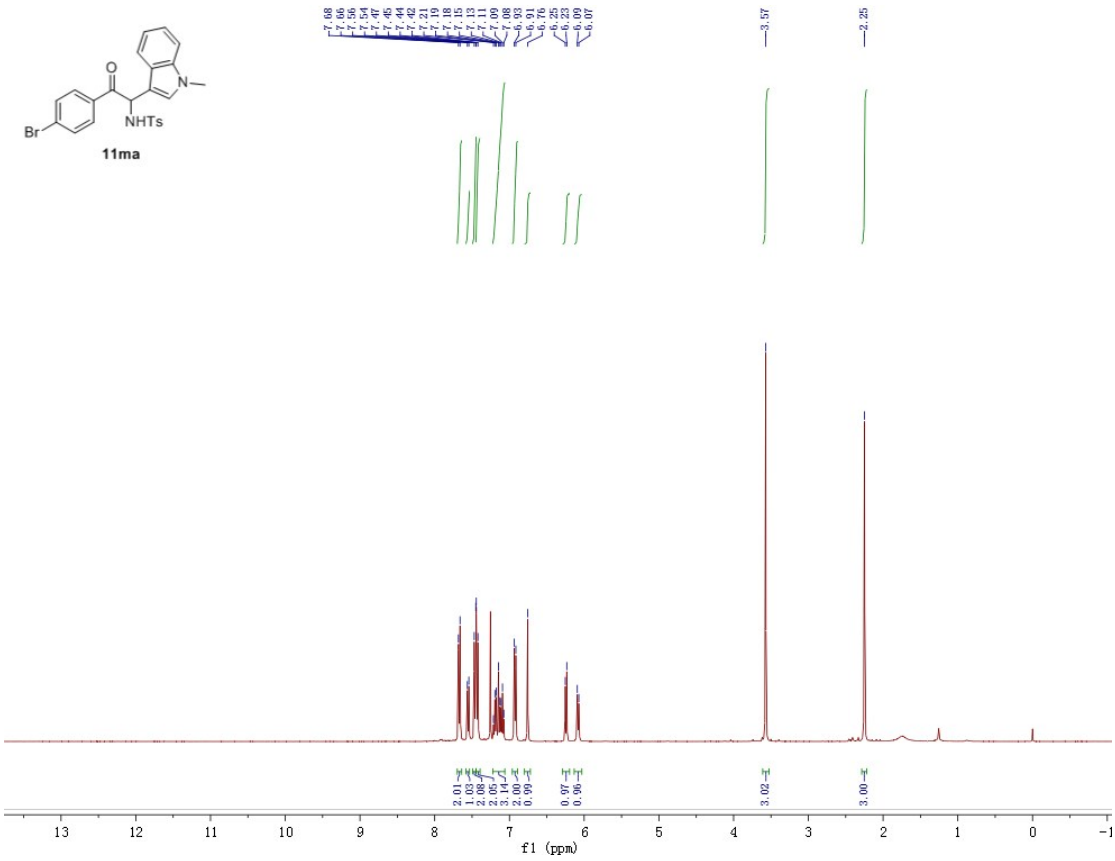
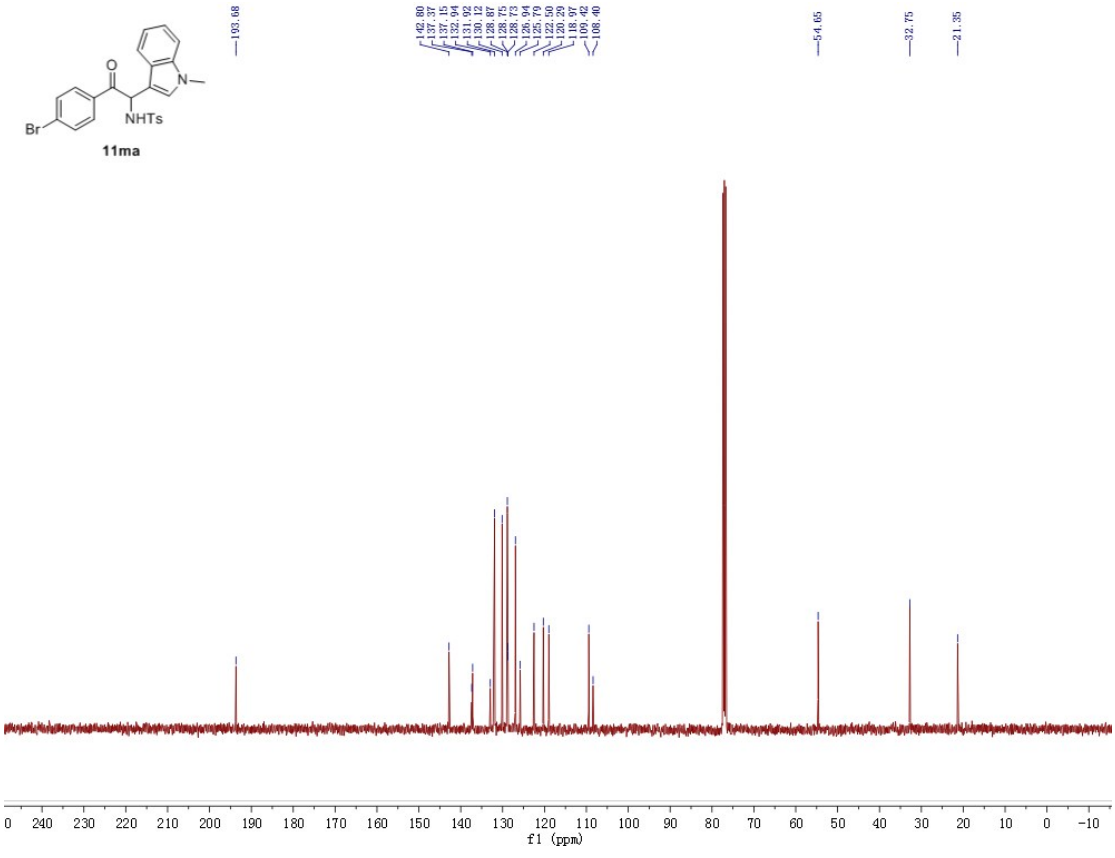
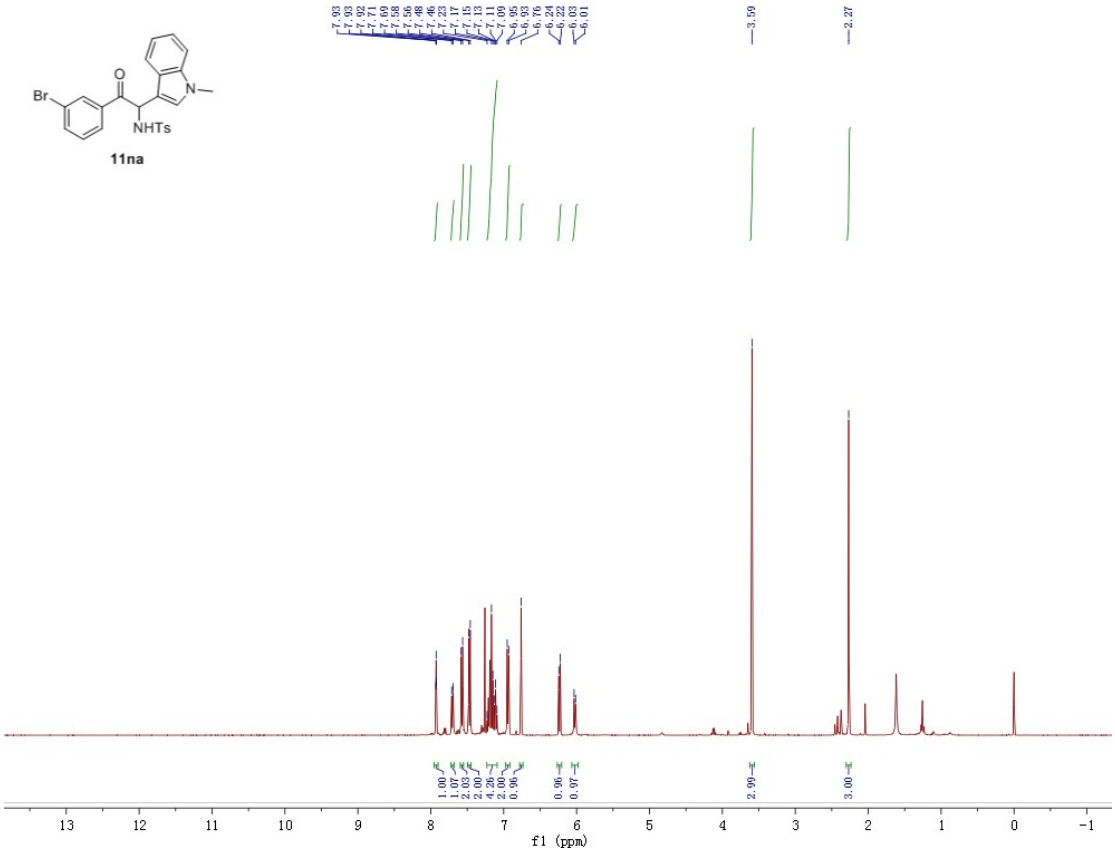
f1 (ppm)

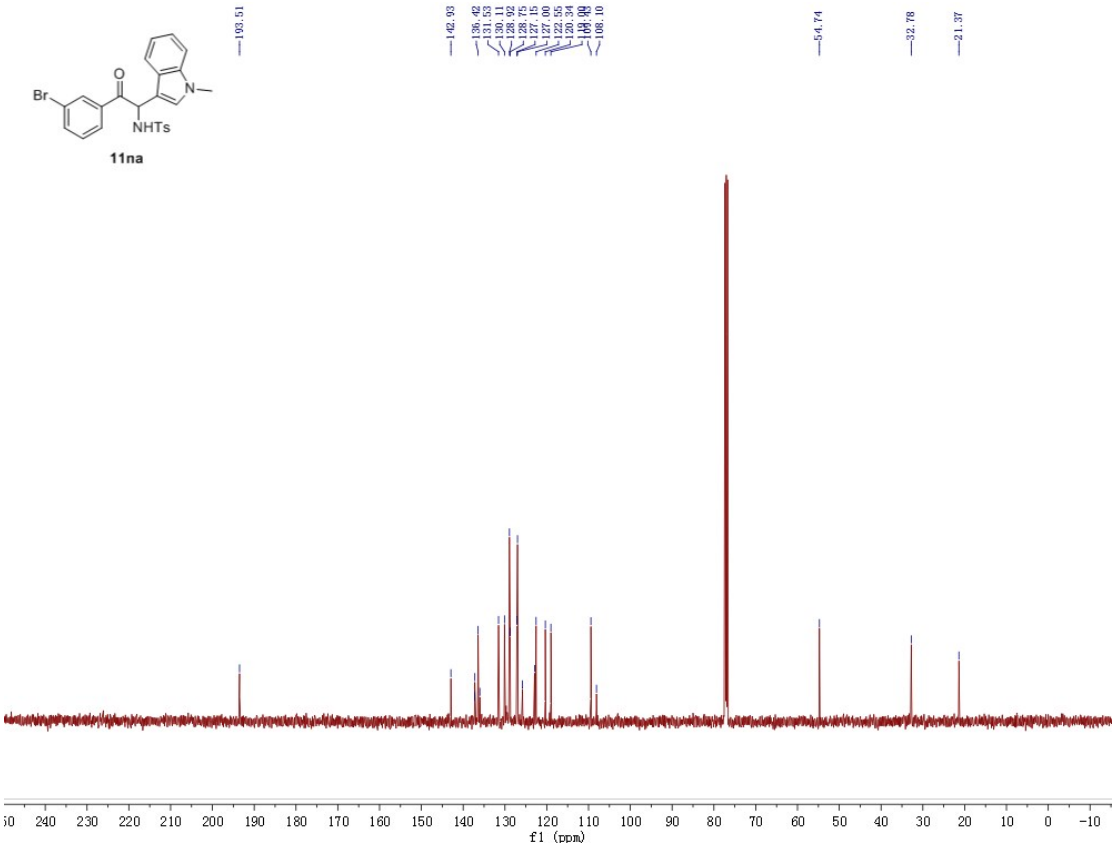

11la
f1 (ppm)


11la
f1 (ppm)


11ma
f1 (ppm)


11ma
f1 (ppm)


Br
O
N
NHTs
11na
7.93
7.93
7.92
7.71
7.69
7.56
7.56
7.48
7.46
7.23
7.17
7.15
7.13
7.11
7.09
6.95
6.93
6.76
6.24
6.22
6.03
6.01
3.59
2.27
1.00
1.07
2.03
2.00
2.26
2.00
0.96
0.96
0.97
2.99
3.00
f1 (ppm)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N
NHTs
11na
193.51
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136.42
131.53
130.11
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127.15
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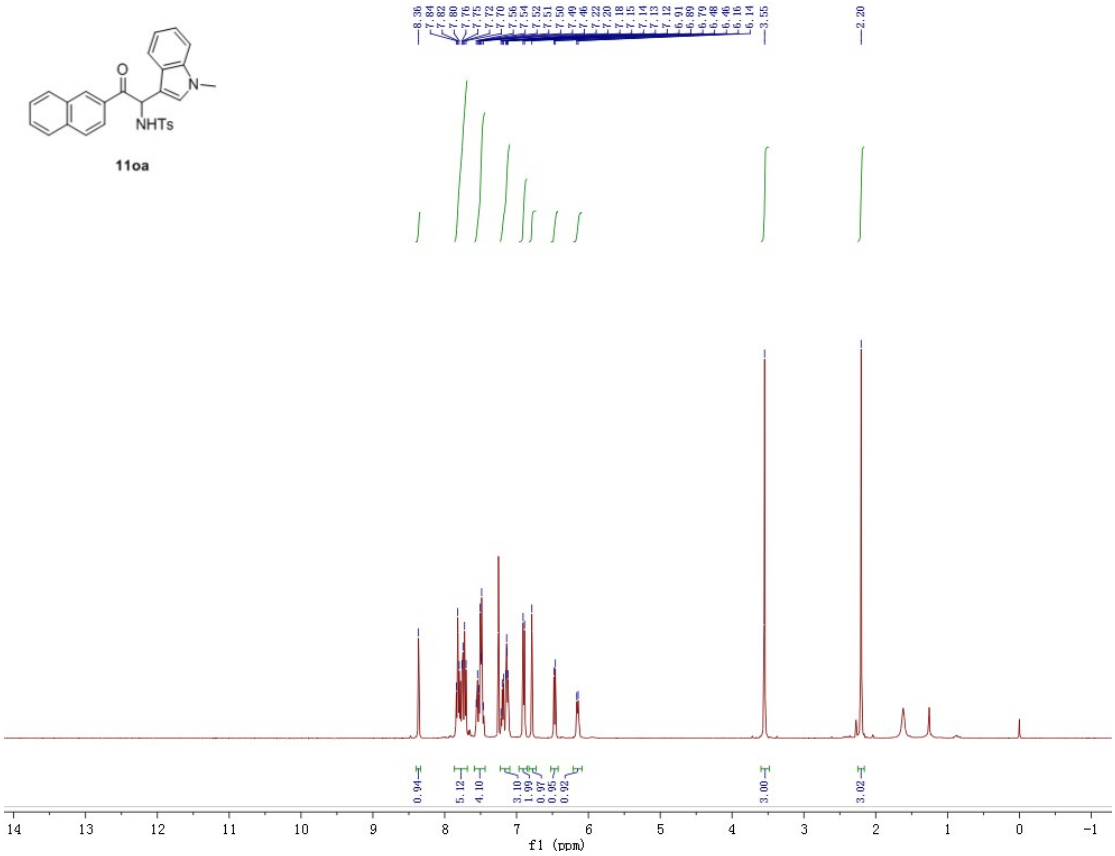
108.10
64.74
32.78
21.37
f1 (ppm)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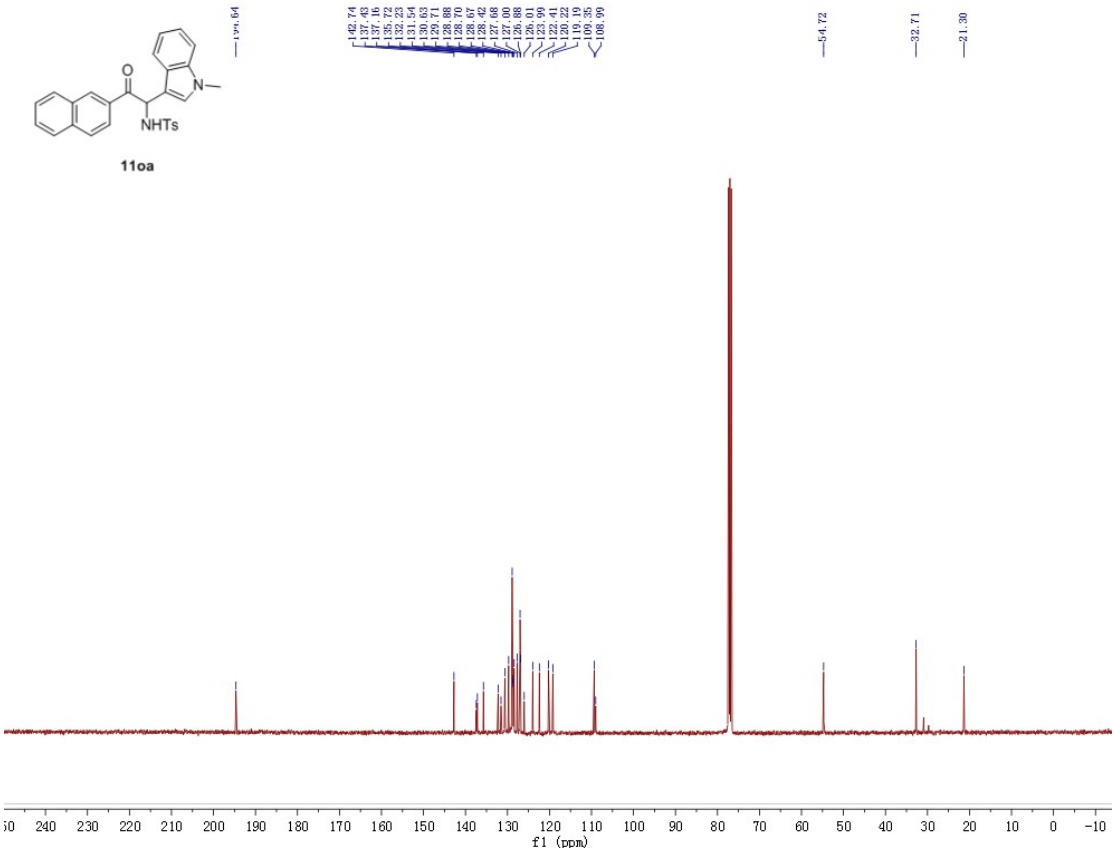
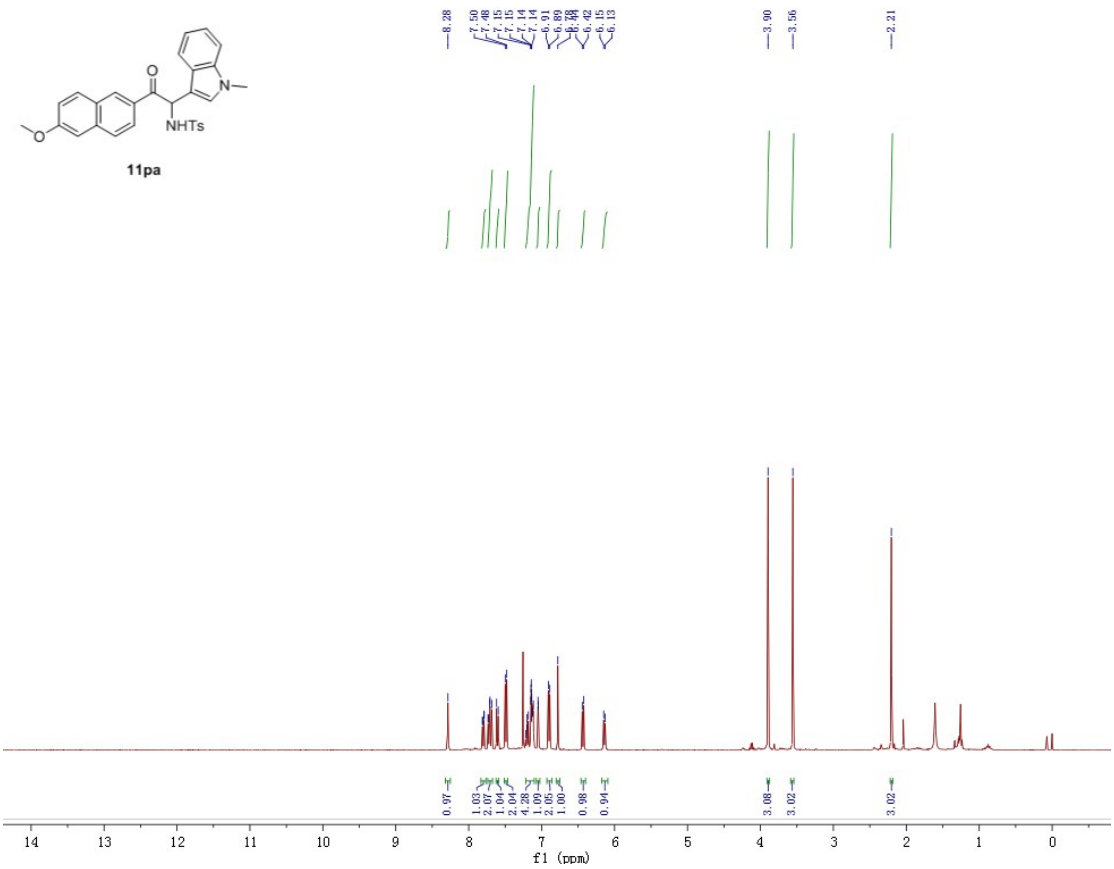
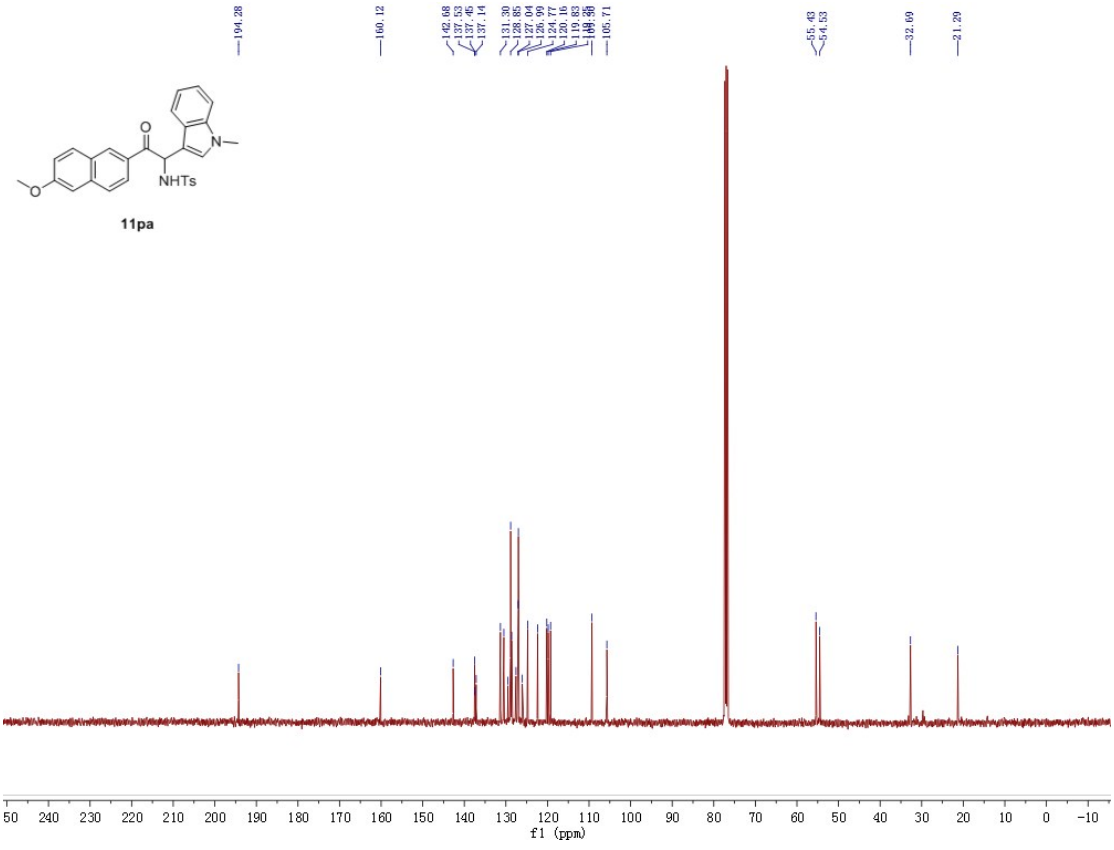
f1 (ppm)


11oa
f1 (ppm)


11pa
8.28
7.50
7.48
7.15
7.15
7.14
7.14
6.91
6.89
6.88
6.42
6.15
6.13
3.90
3.56
2.21
0.97
1.03
2.07
1.04
2.04
4.28
1.09
2.05
1.00
0.98
0.94
3.08
3.02
3.02
f1 (ppm)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160.12
142.68
137.53
137.45
137.14
131.30
128.85
127.04
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124.77
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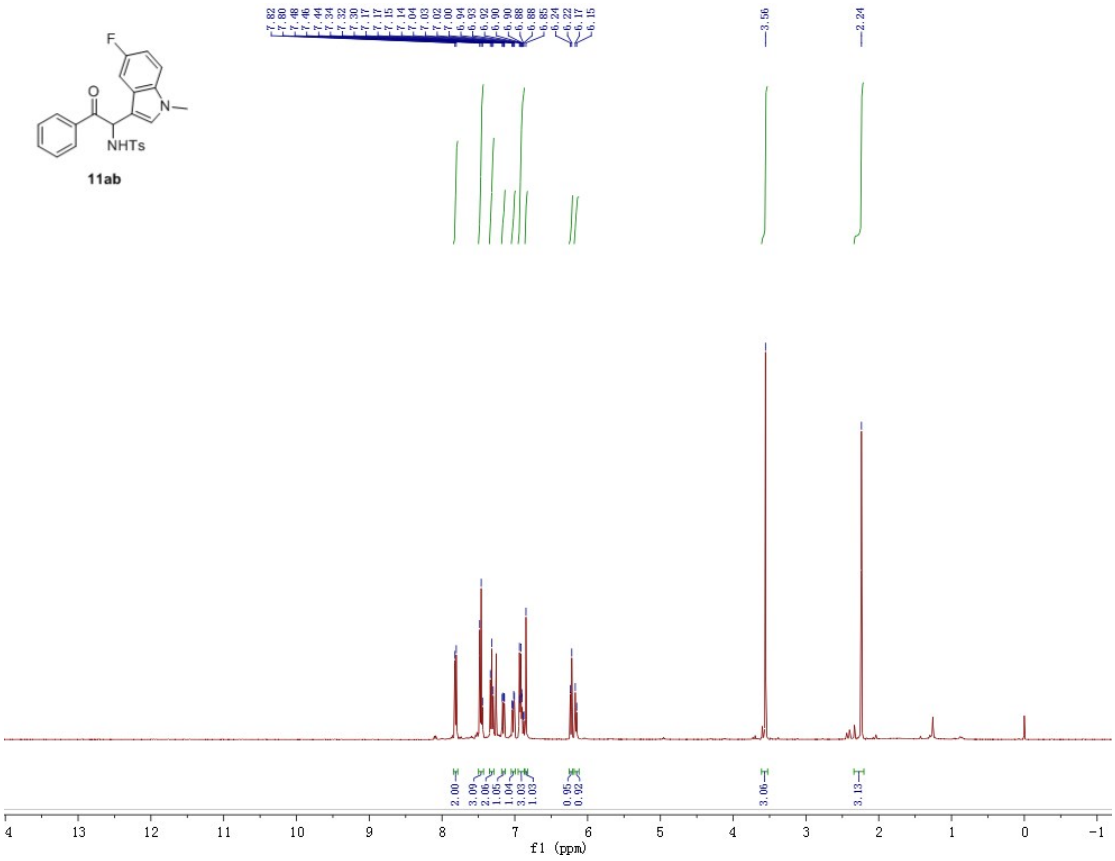
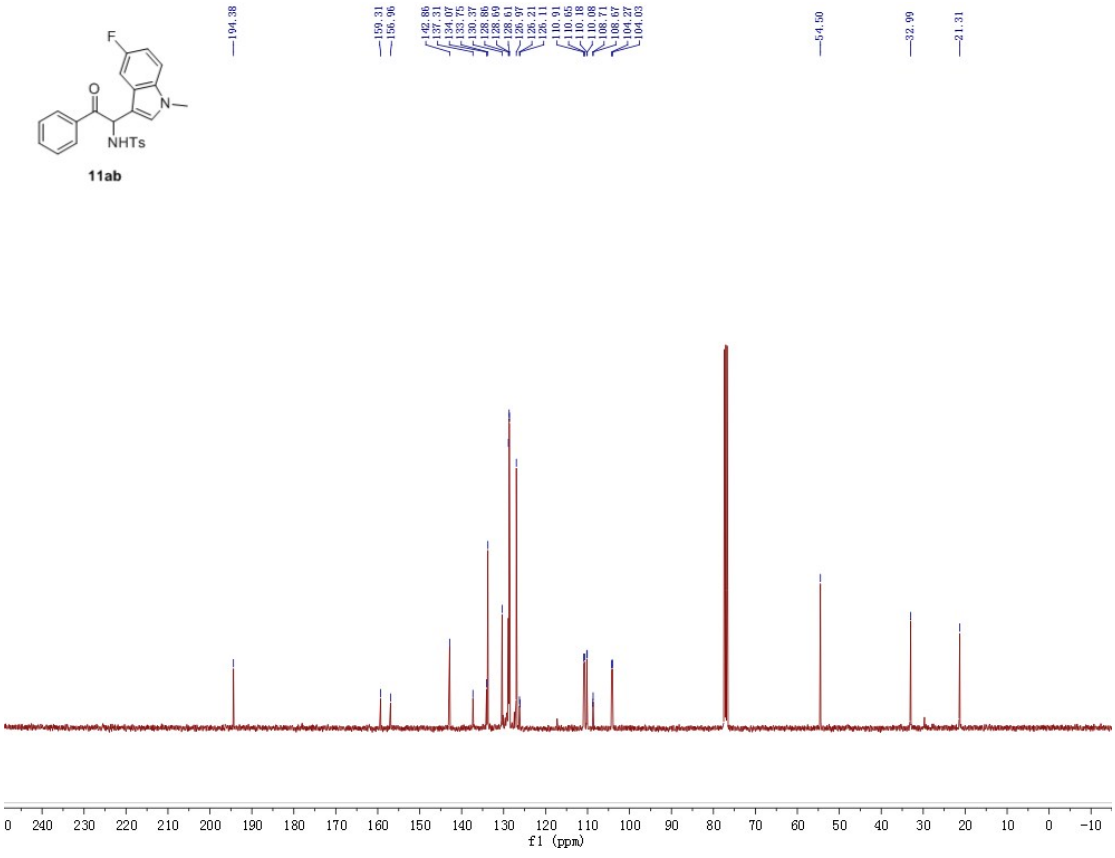
55.43
54.53
32.69
21.29
f1 (ppm)


F
O
N
NHTs
11ab
7.82
7.80
7.48
7.46
7.44
7.34
7.32
7.30
7.17
7.17
7.15
7.14
7.04
7.03
7.02
7.00
6.94
6.93
6.92
6.90
6.90
6.88
6.85
6.24
6.22
6.17
6.15
3.56
2.24
2.00
3.09
2.06
1.05
1.04
3.03
1.03
0.95
0.92
3.06
3.13
f1 (ppm)


F
O
N
NHTs
11ab
194.38
159.31
156.96
142.86
137.31
134.97
133.75
130.37
128.86
128.69
128.61
126.27
126.21
126.11
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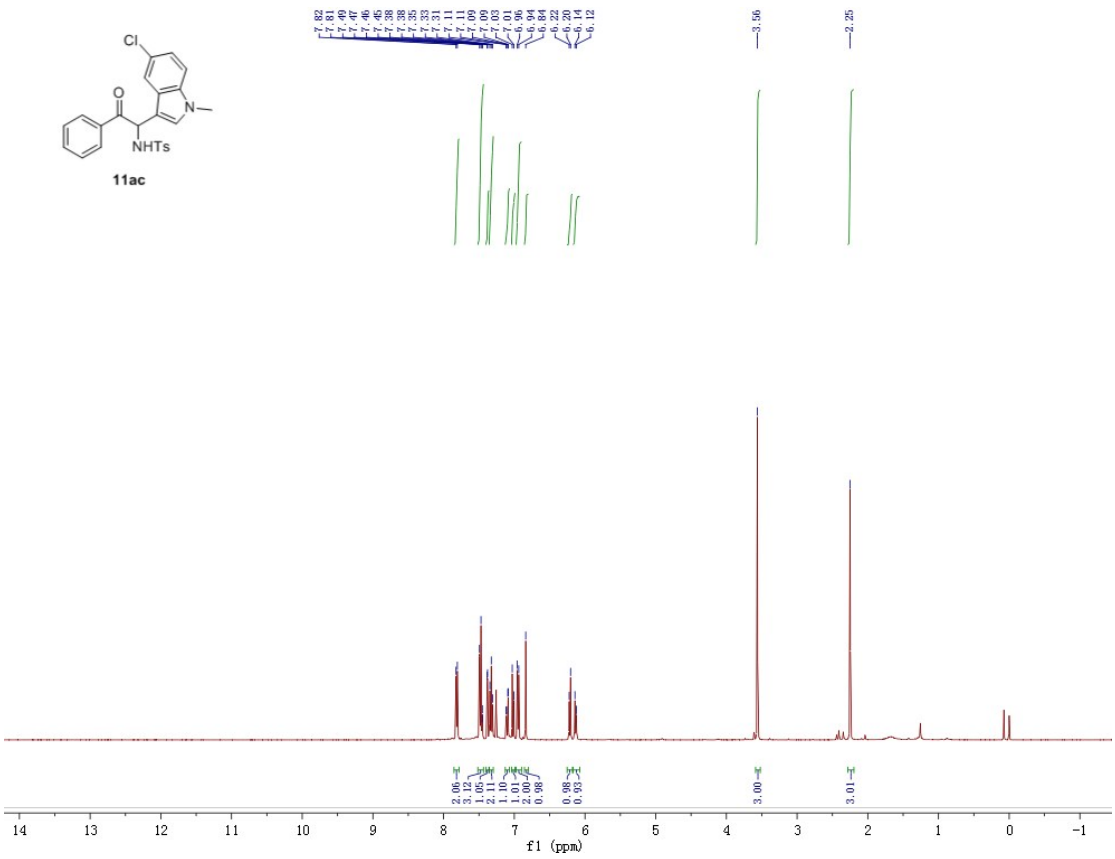
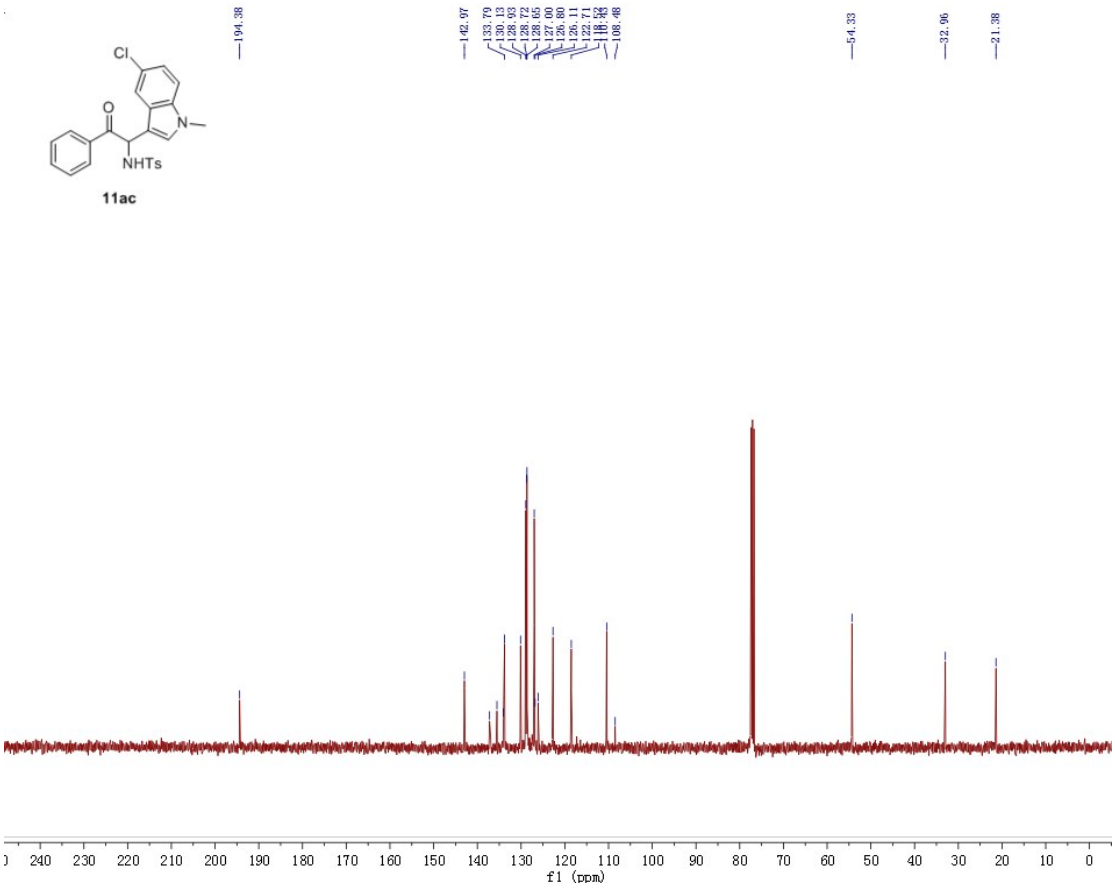
110.65
110.18
110.08
109.71
108.67
104.27
104.03
54.50
32.99
21.31
f1 (ppm)


Cl
O
N
NHTs
11ac
7.82
7.81
7.49
7.47
7.46
7.45
7.38
7.35
7.33
7.31
7.11
7.09
7.03
7.01
6.98
6.94
6.84
6.22
6.20
6.14
6.12
3.56
2.25
2.06
3.12
1.05
2.11
1.10
1.01
2.00
0.98
0.98
0.93
3.00
3.01
f1 (ppm)


Cl
O
N
NHTs
11ac
194.38
142.97
133.79
130.13
128.93
128.72
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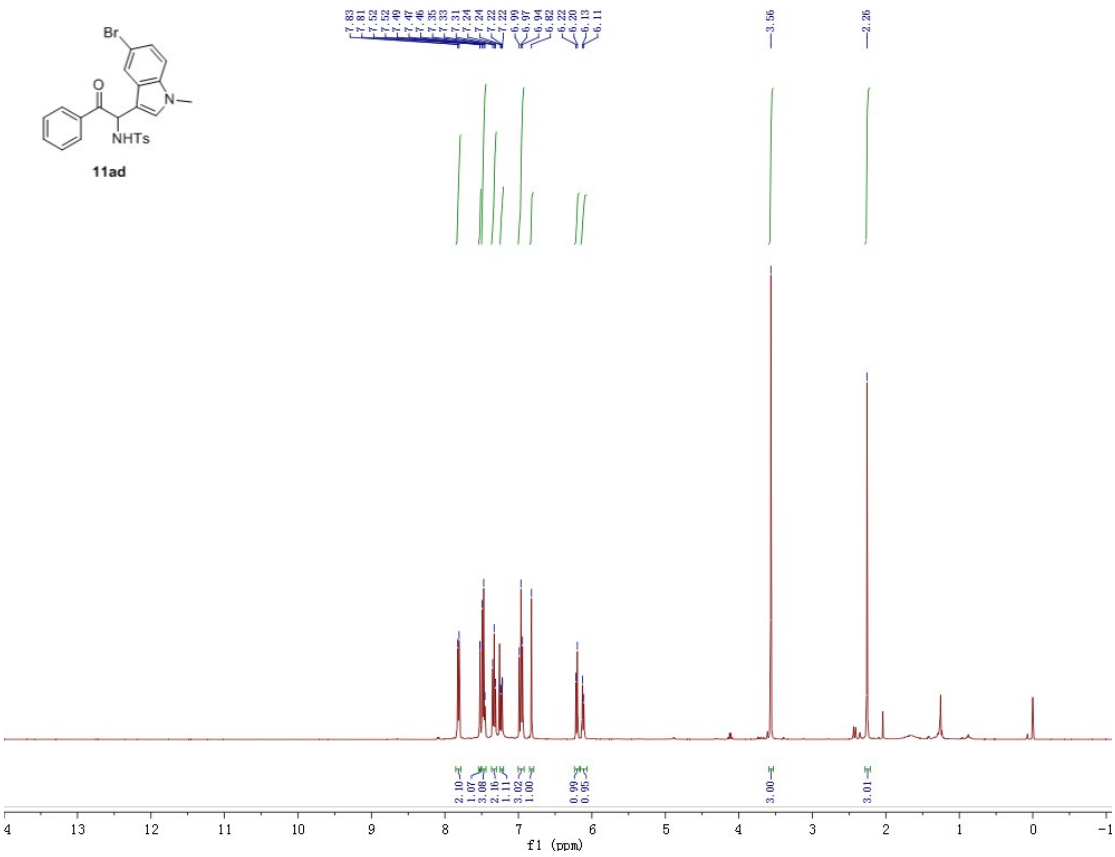
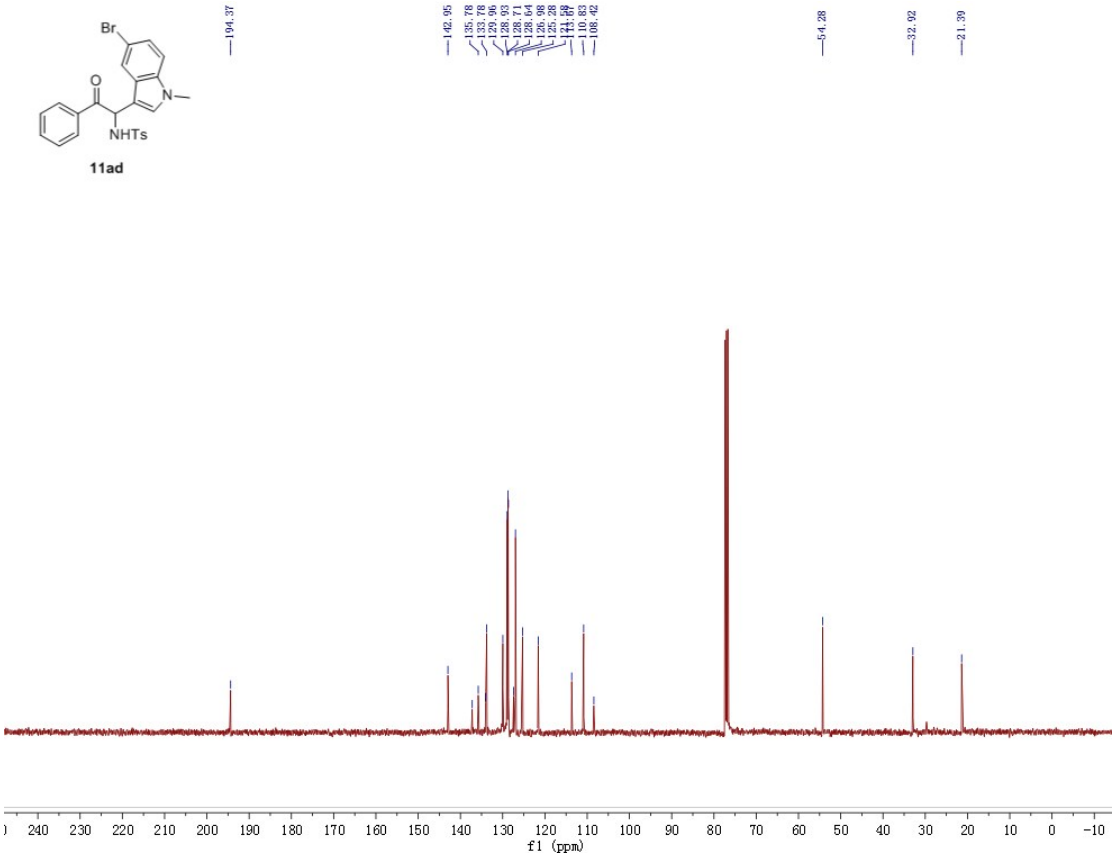
127.00
126.89
126.11
122.71
108.48
54.33
32.96
21.38
f1 (ppm)


Br
O
N
NHTs
11ad
7.83
7.81
7.52
7.49
7.46
7.35
7.33
7.31
7.24
7.22
6.99
6.97
6.94
6.82
6.22
6.20
6.13
6.11
3.56
2.26
2.10
1.07
3.08
2.16
1.11
3.02
1.00
0.99
0.95
3.00
3.01
f1 (ppm)


Br
O
N
NHTs
11ad
194.37
142.95
135.78
133.78
129.96
128.93
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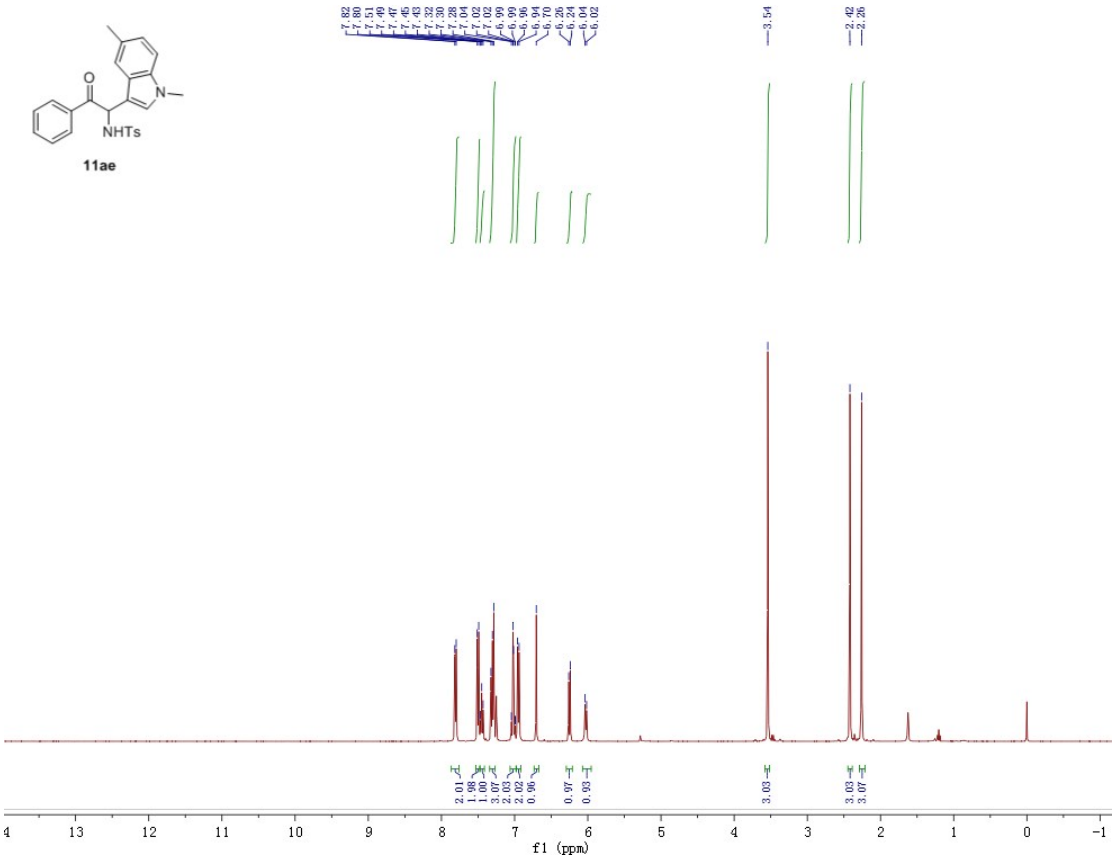
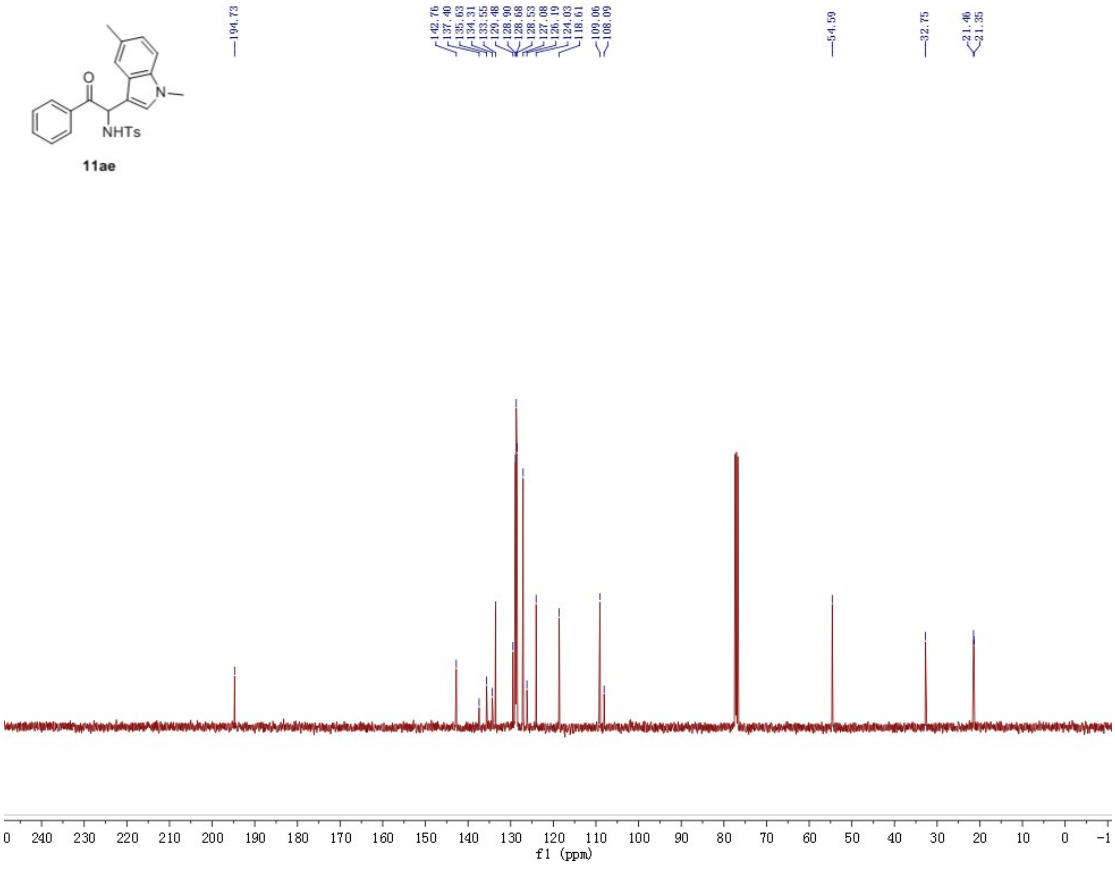
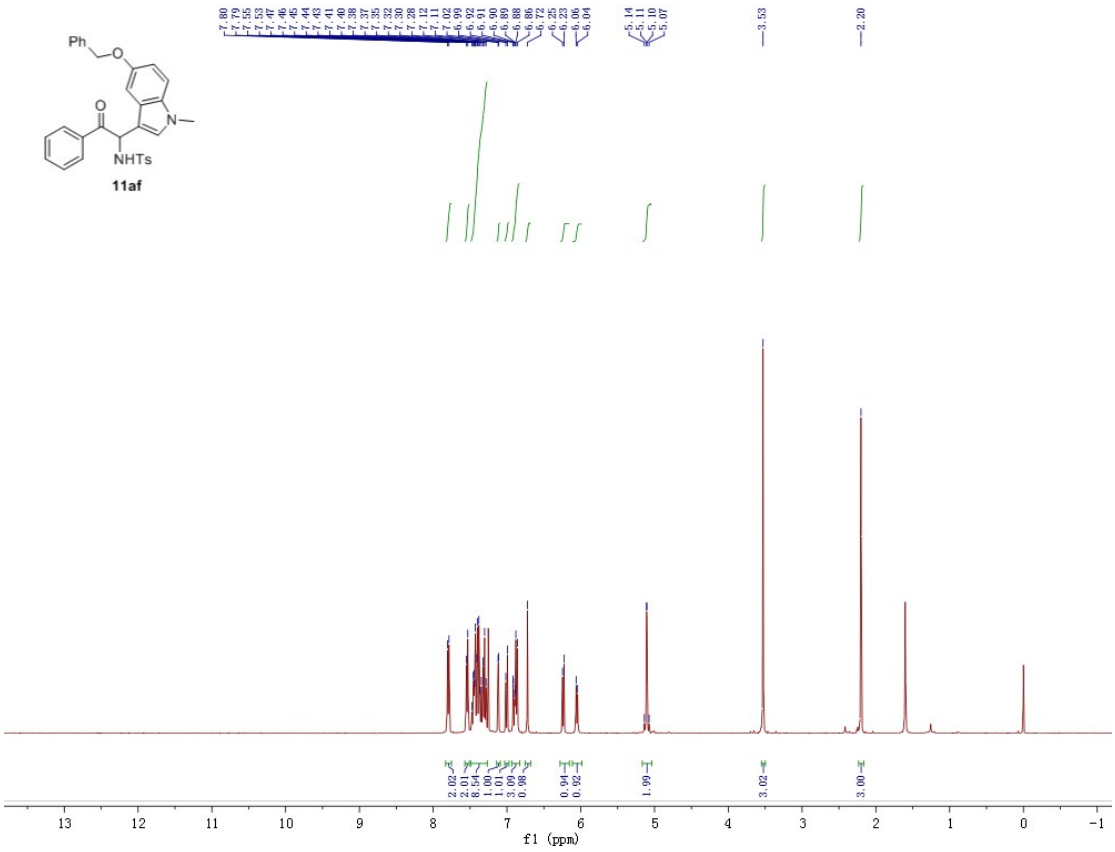
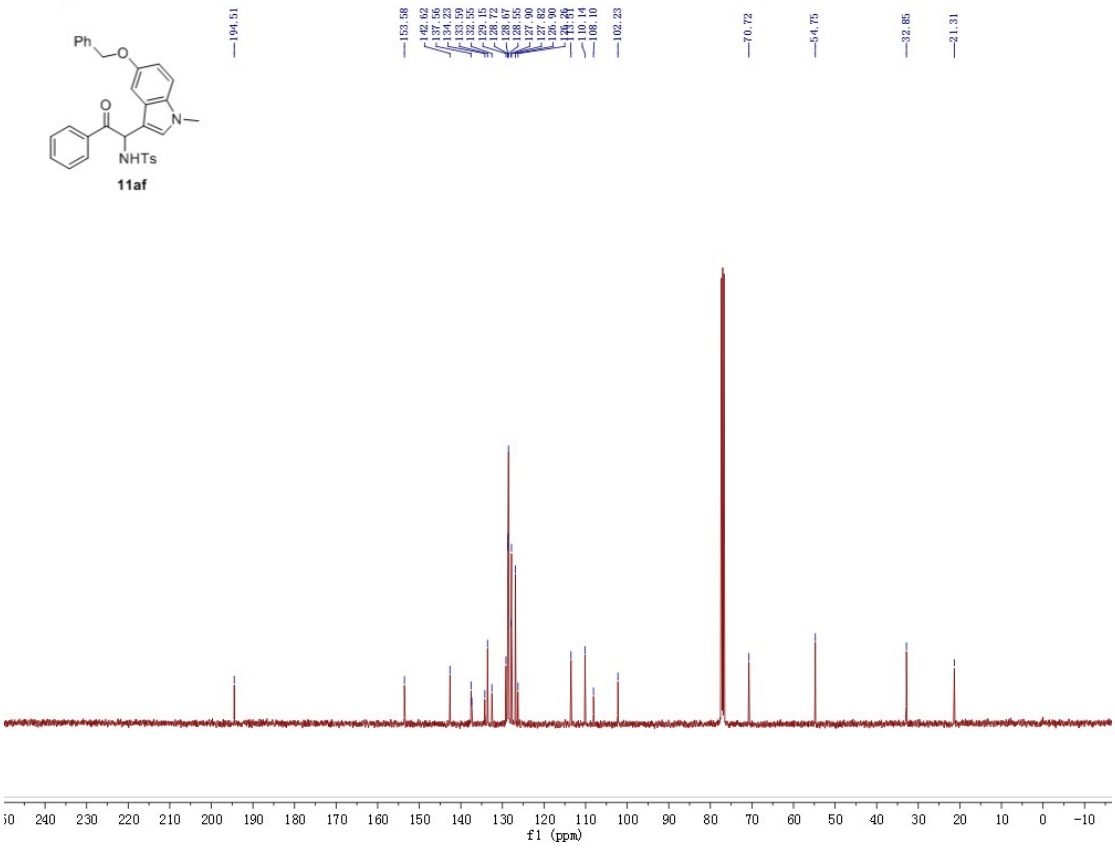
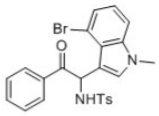
128.64
126.98
125.28
110.83
108.42
54.28
32.92
21.39
f1 (ppm)


11ae
f1 (ppm)


11ae
f1 (ppm)

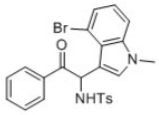

Ph
O
N
NHTs
11af
f1 (ppm)


Ph
O
N
NHTs
11af
f1 (ppm)


Br
O
N
NHTs

11ag

7.98
7.96
7.61
7.59
7.34
7.33
7.31
7.14
7.12
7.01
6.99
5.91
3.56
2.28
2.00
1.98
1.07
3.18
2.00
3.10
1.01
0.94
3.04
3.04
f1 (ppm)


Br
O
N
NHTs

11ag

195.24
142.82
138.24
137.75
134.33
133.40
130.79
129.22
128.94
128.57
124.37
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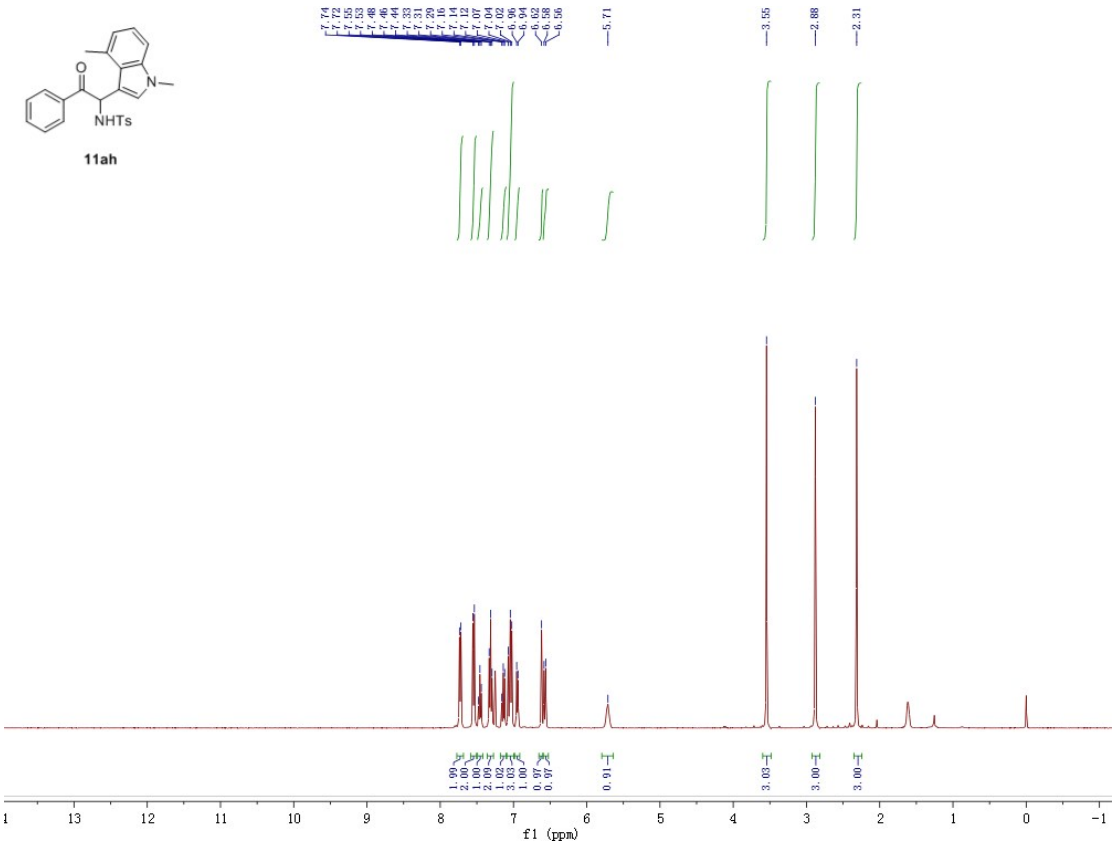
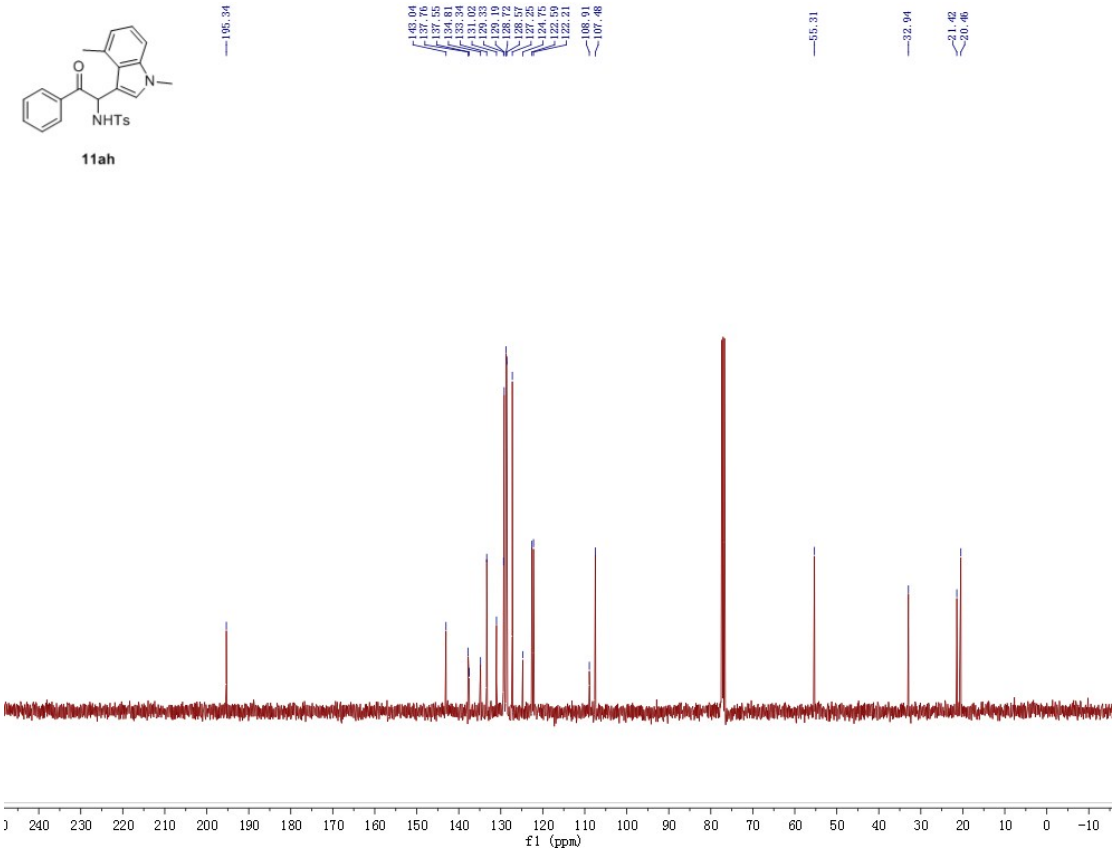
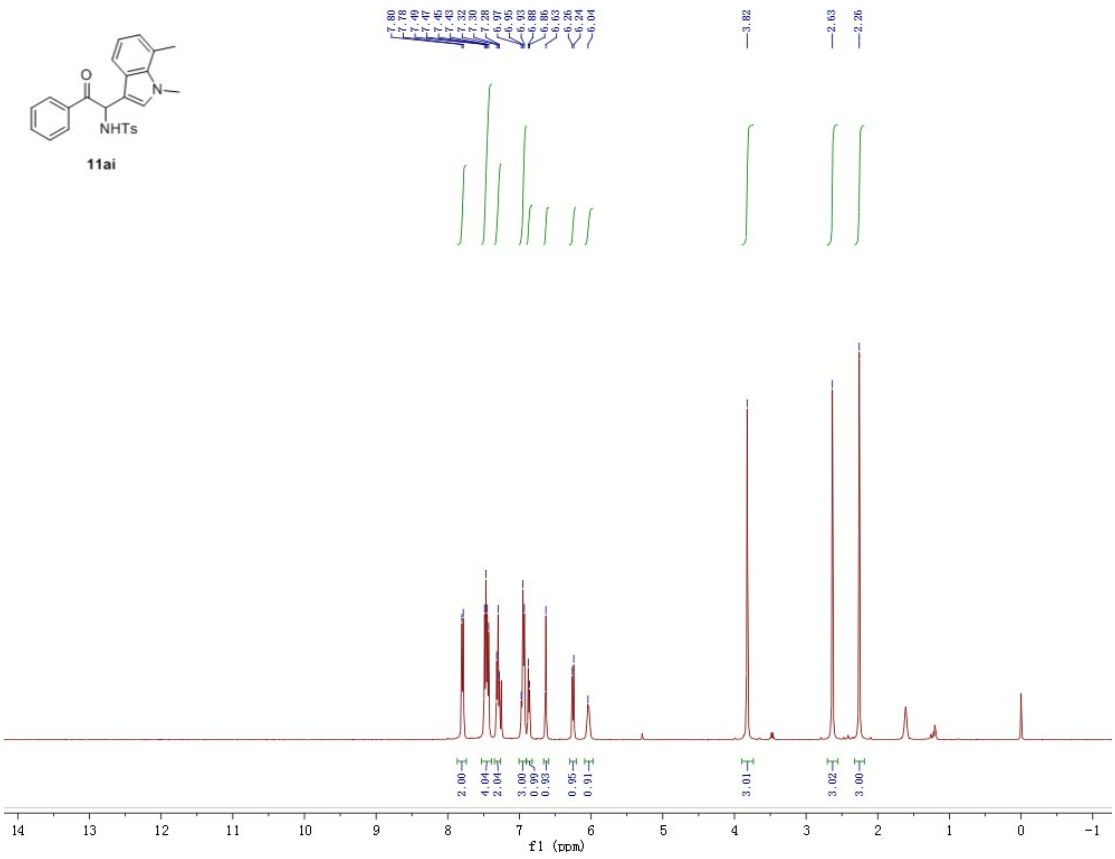
123.88
123.05
113.81
109.59
108.95
53.19
33.10
21.36
f1 (ppm)


11ah
f1 (ppm)


11ah
f1 (ppm)


11ai
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7.32
7.30
7.28
6.97
6.95
6.93
6.88
6.86
6.63
6.26
6.24
6.04
3.82
2.63
2.26
2.00
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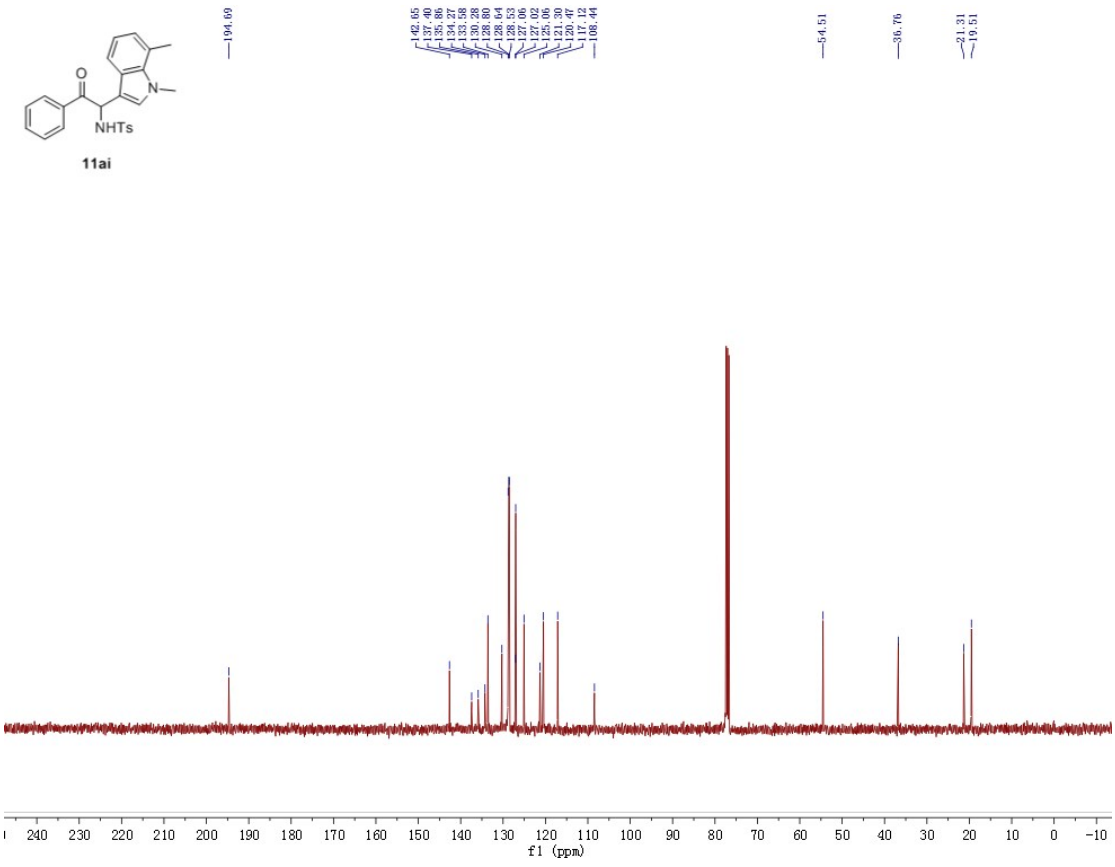
2.04
3.00
0.93
0.95
0.91
3.01
3.02
3.00
f1 (ppm)


11ai
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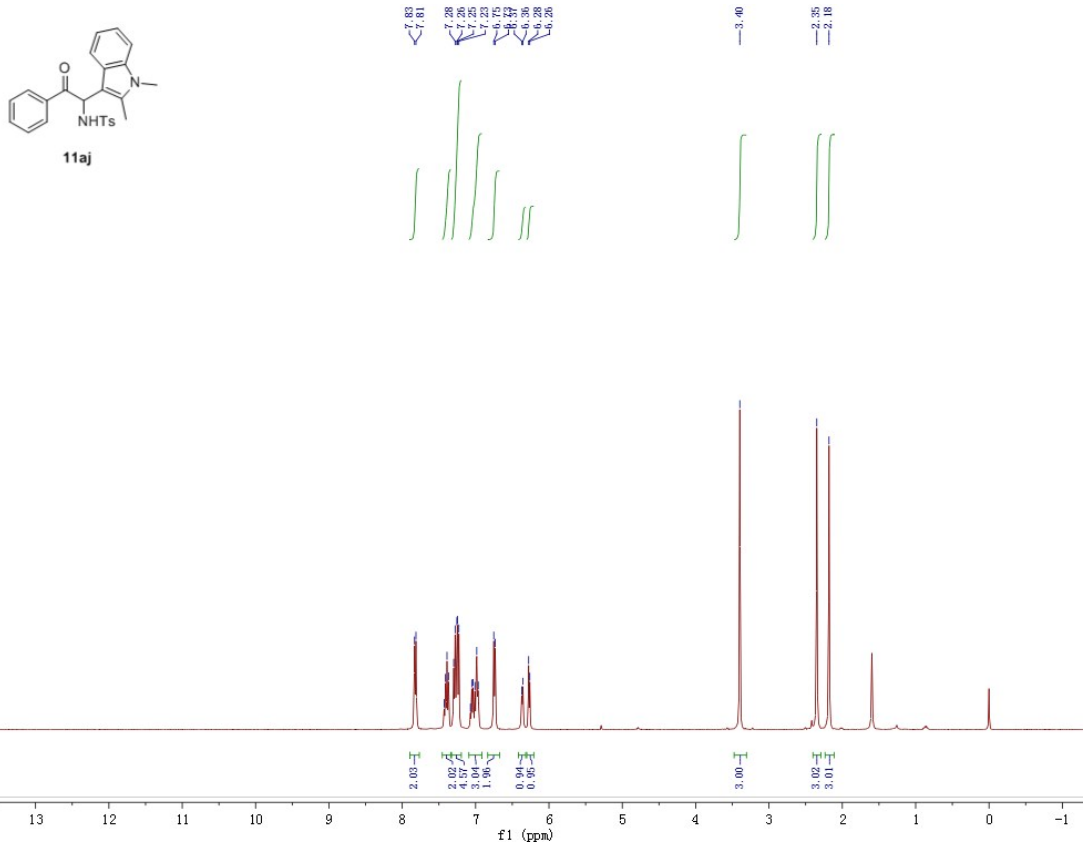
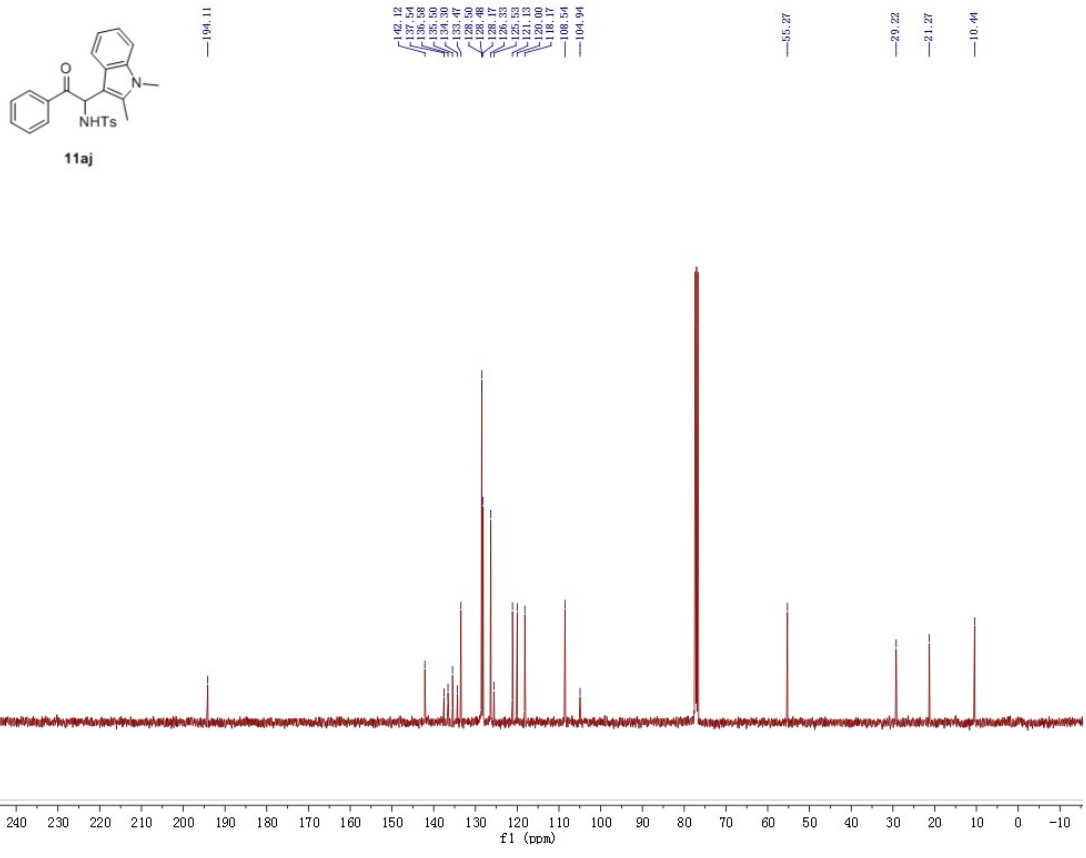
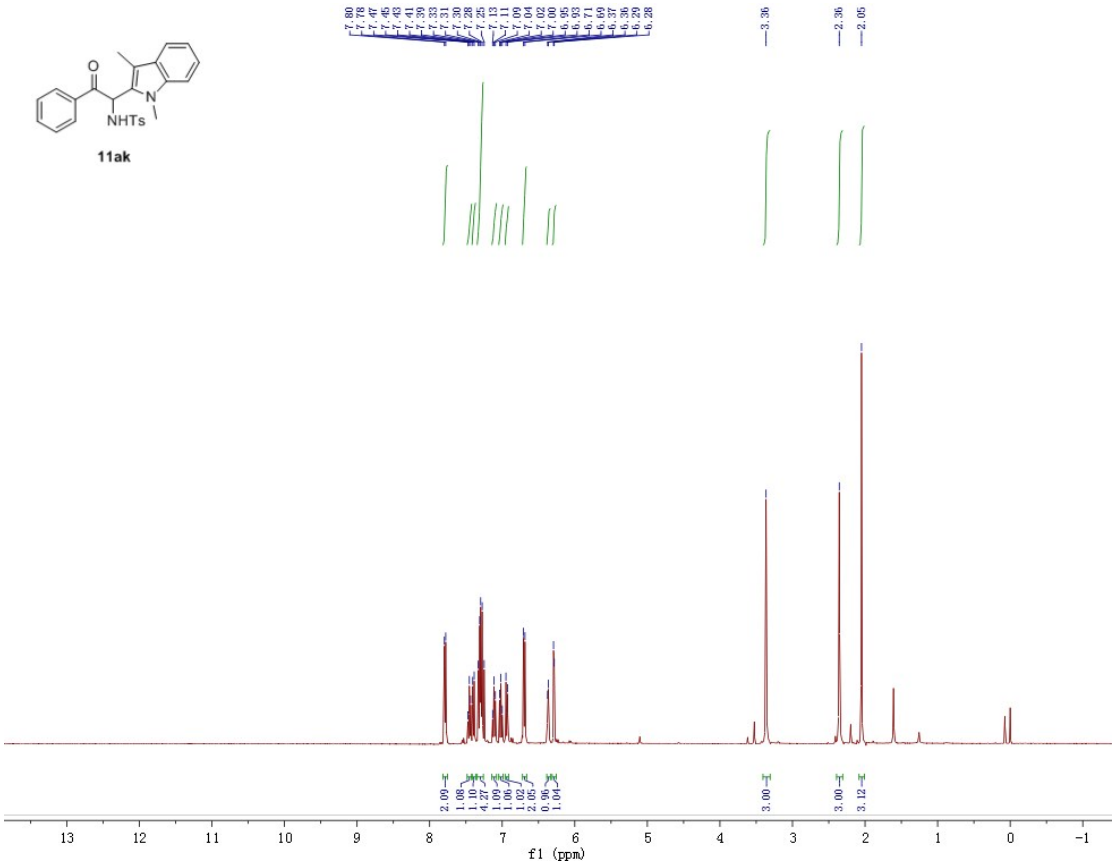
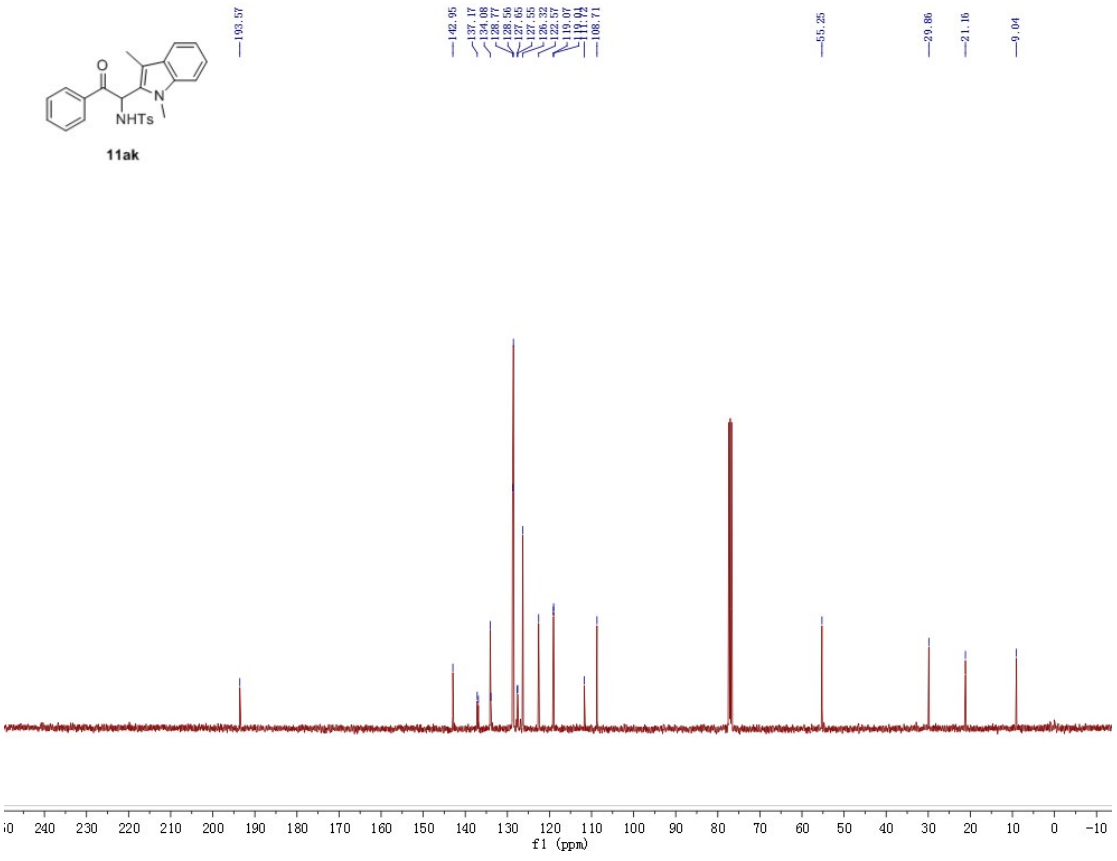
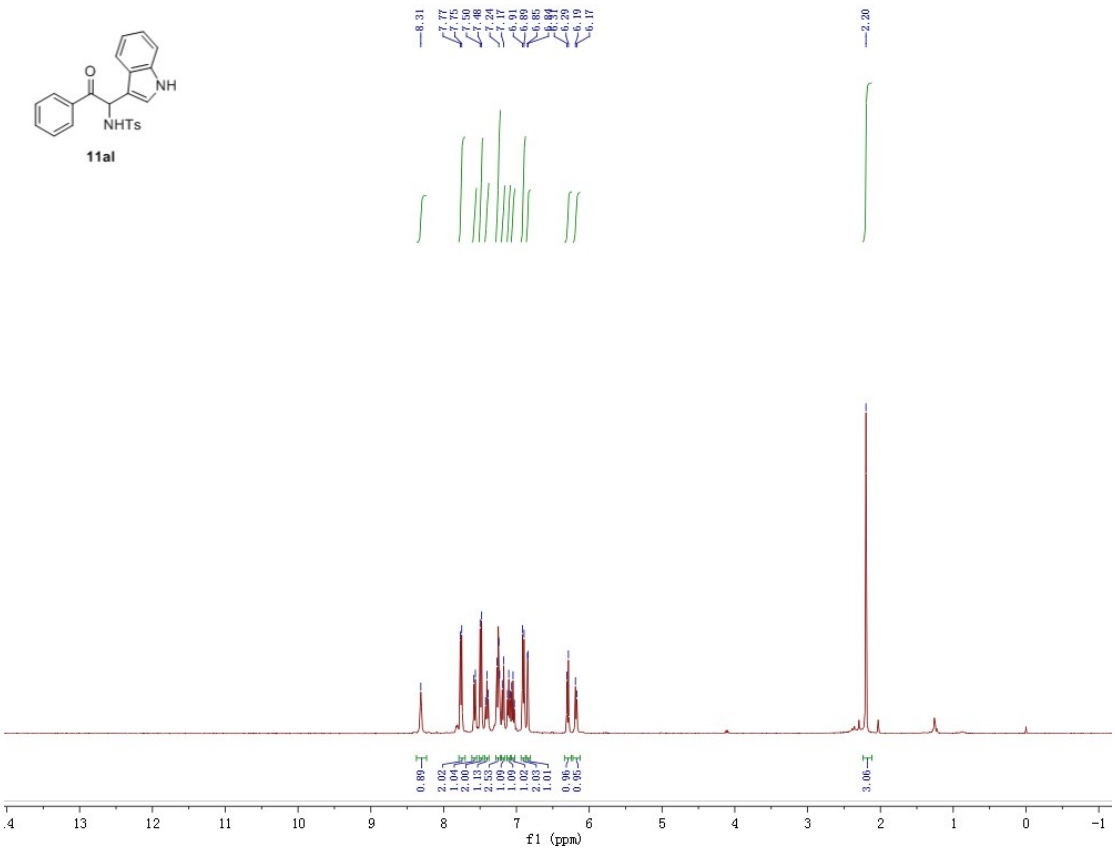
137.40
135.86
134.27
133.98
130.28
128.80
128.64
128.53
127.06
127.02
125.06
121.30
120.47
117.12
108.44
54.51
36.76
21.31
19.51
f1 (ppm)

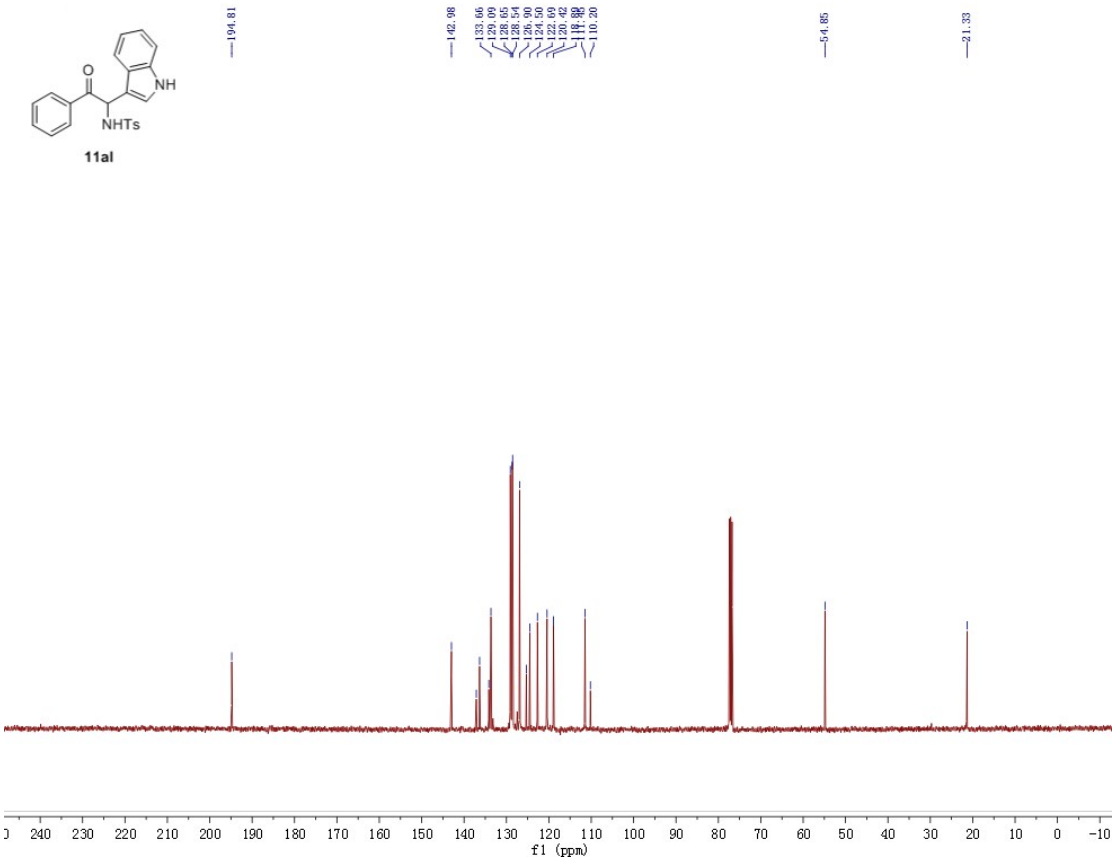

11aj
7.83
7.81
7.28
7.26
7.25
7.23
6.75
6.37
6.36
6.28
6.26
3.40
2.35
2.18
2.03
2.02
4.57
3.04
1.96
0.94
0.95
3.00
3.02
3.01
f1 (ppm)

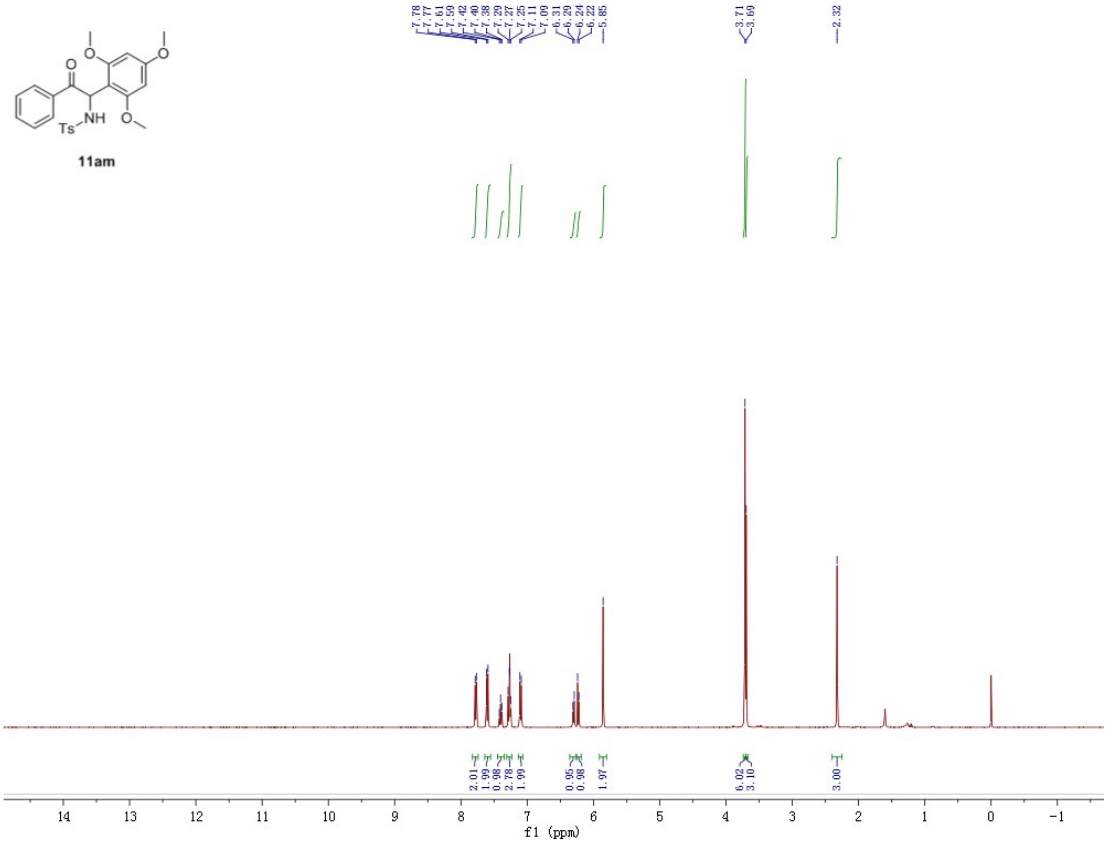

11aj
194.11
142.12
137.54
136.58
135.50
134.30
133.47
128.50
128.48
128.17
126.33
125.53
121.13
120.00
118.17
108.54
104.94
55.27
29.22
21.27
10.44
f1 (ppm)

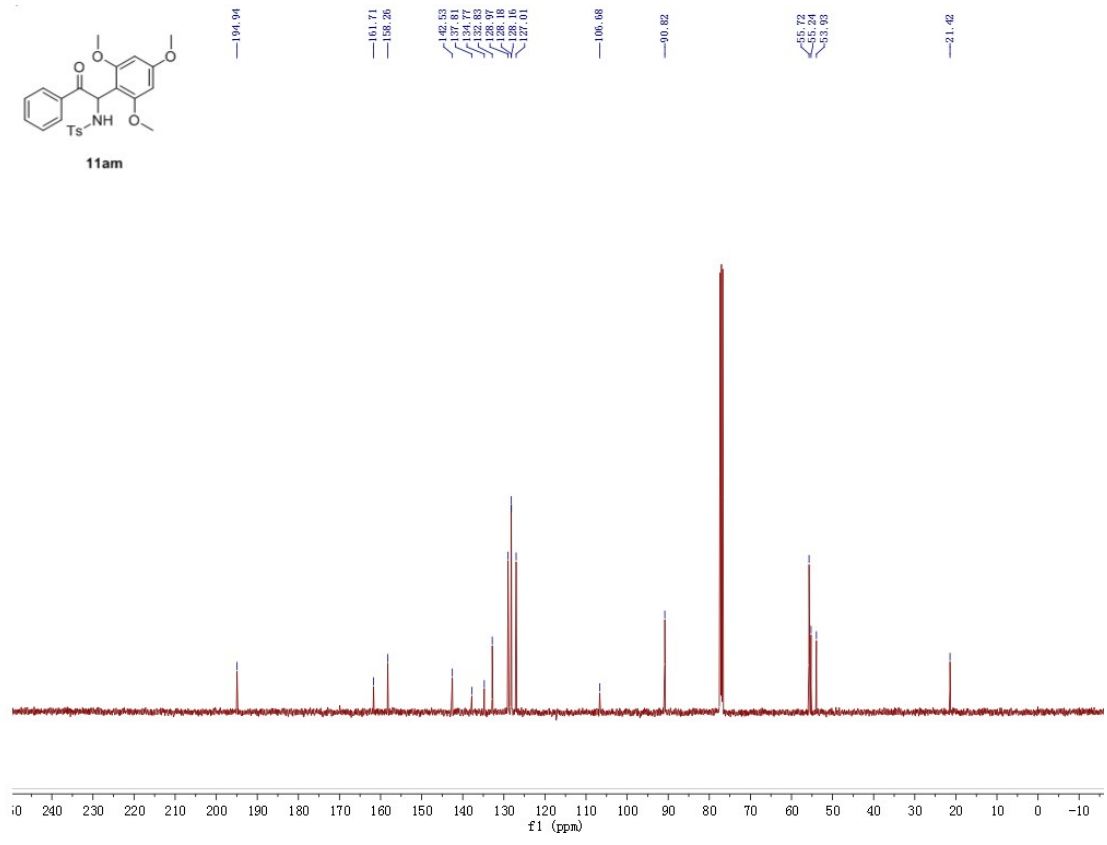

11ak
7.80
7.78
7.47
7.45
7.43
7.41
7.39
7.33
7.31
7.30
7.28
7.25
7.13
7.11
7.09
7.04
7.02
7.00
6.95
6.93
6.71
6.69
6.37
6.36
6.29
6.28
3.36
2.36
2.05
2.09
1.08
1.10
4.27
1.09
1.06
1.02
2.05
0.96
1.04
3.00
3.00
3.12
f1 (ppm)

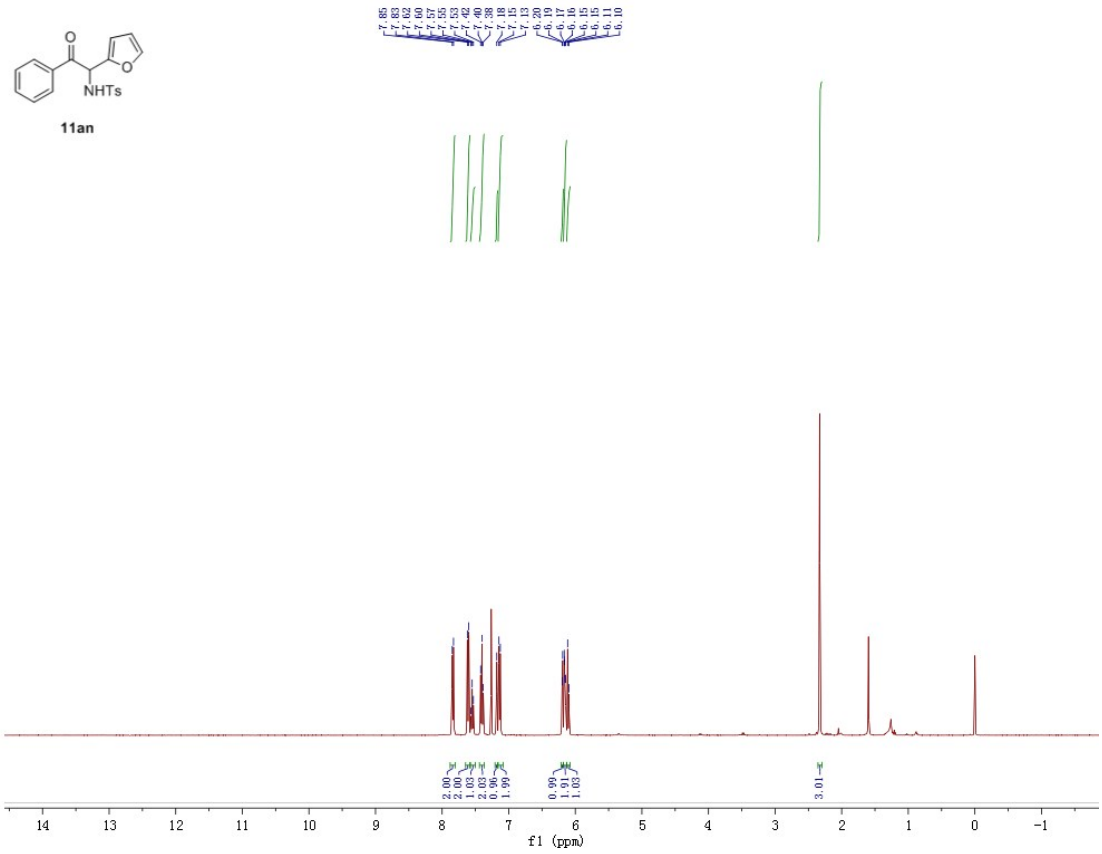

11ak
193.57
142.95
137.17
134.08
128.77
128.56
128.05
127.55
126.32
122.57
119.07
117.92
117.24
108.71
55.25
29.86
21.16
9.04
f1 (ppm)

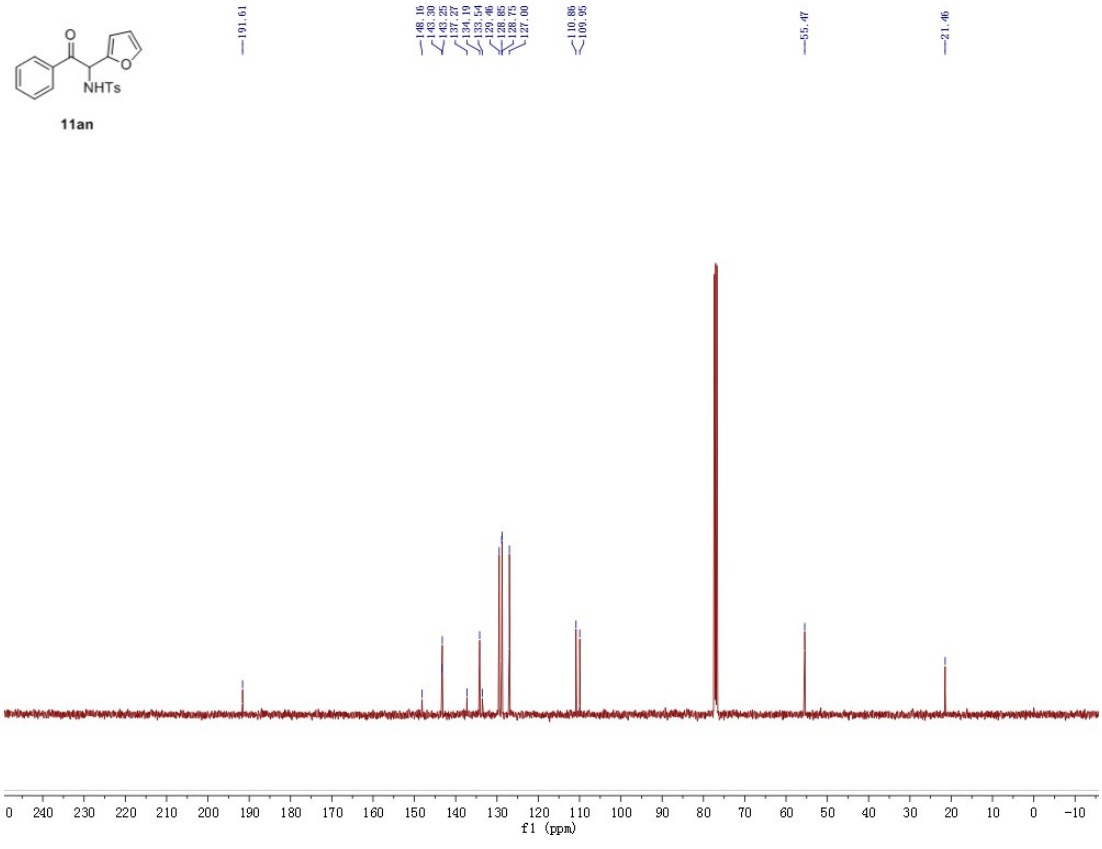

11al
f1 (ppm)

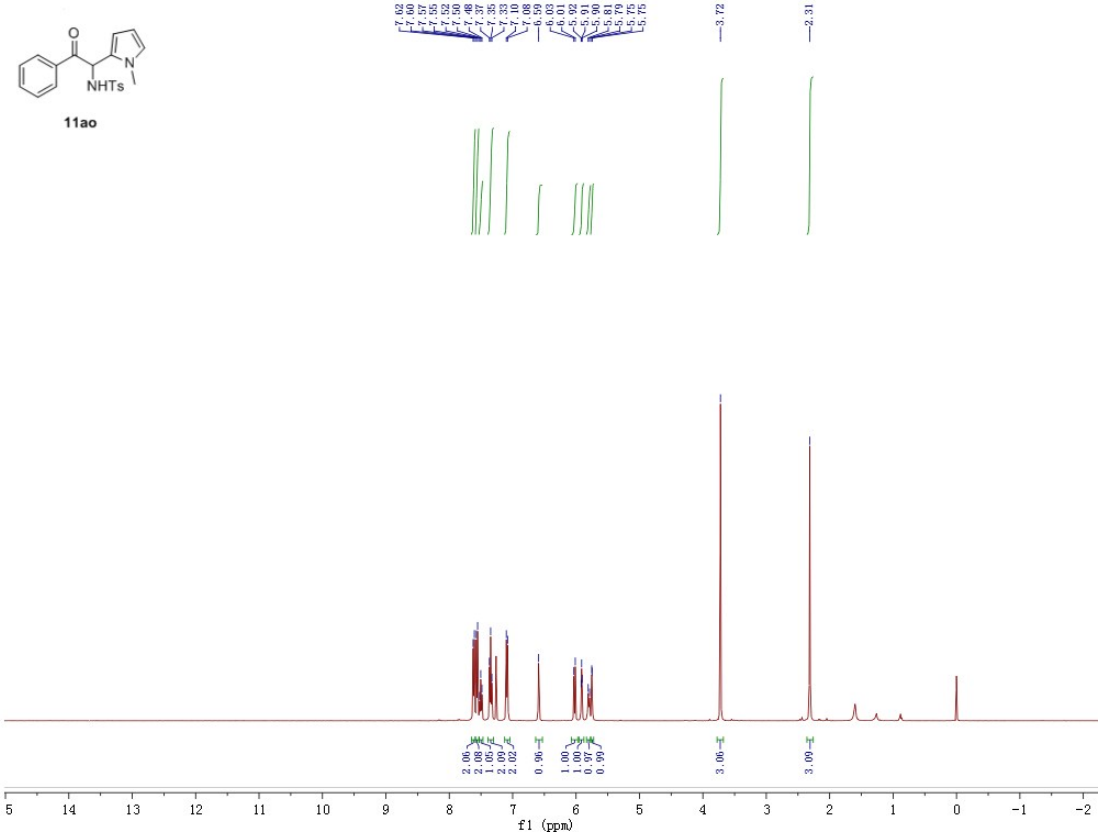

11al
f1 (ppm)

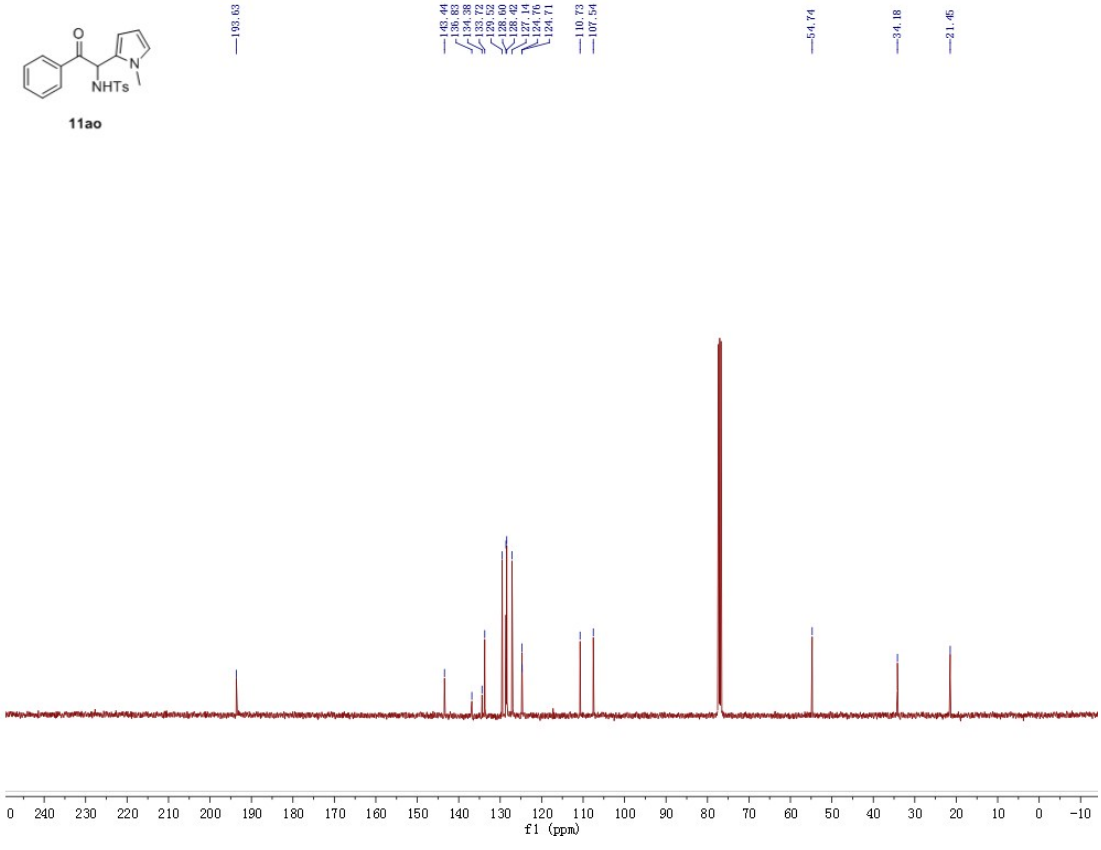

11am
f1 (ppm)

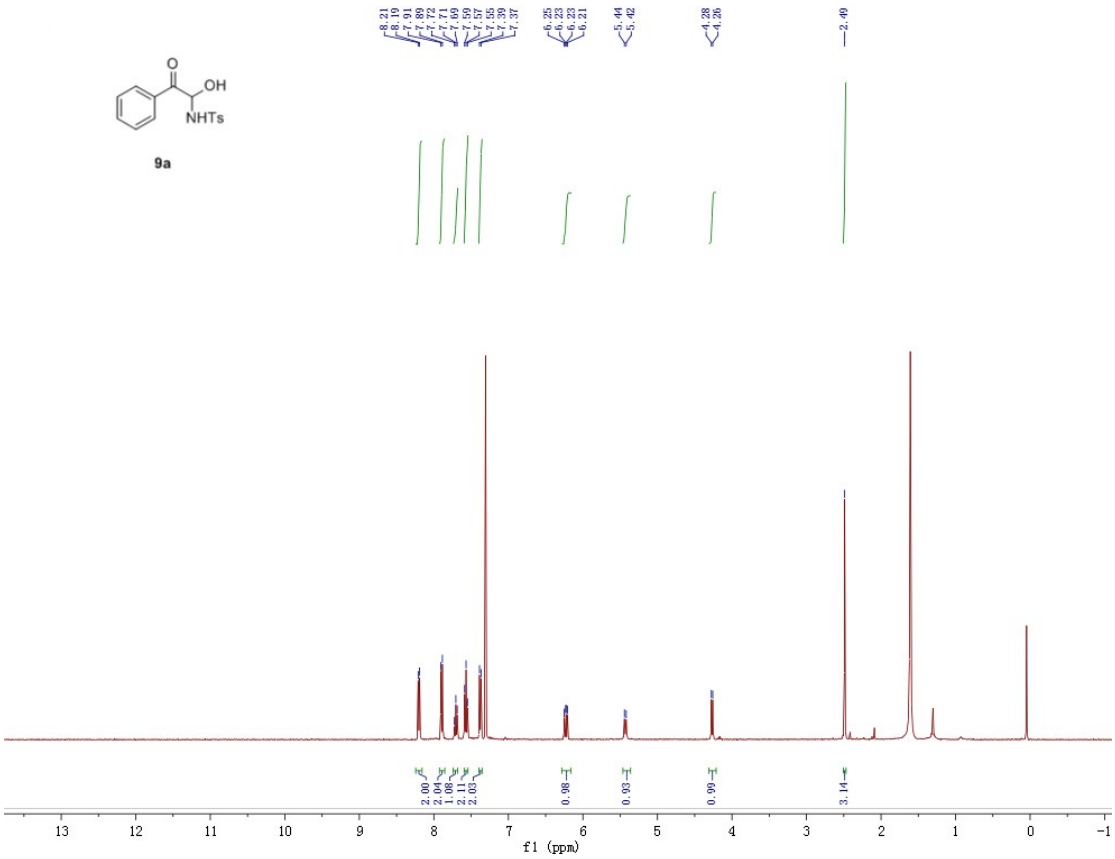

11am
f1 (ppm)

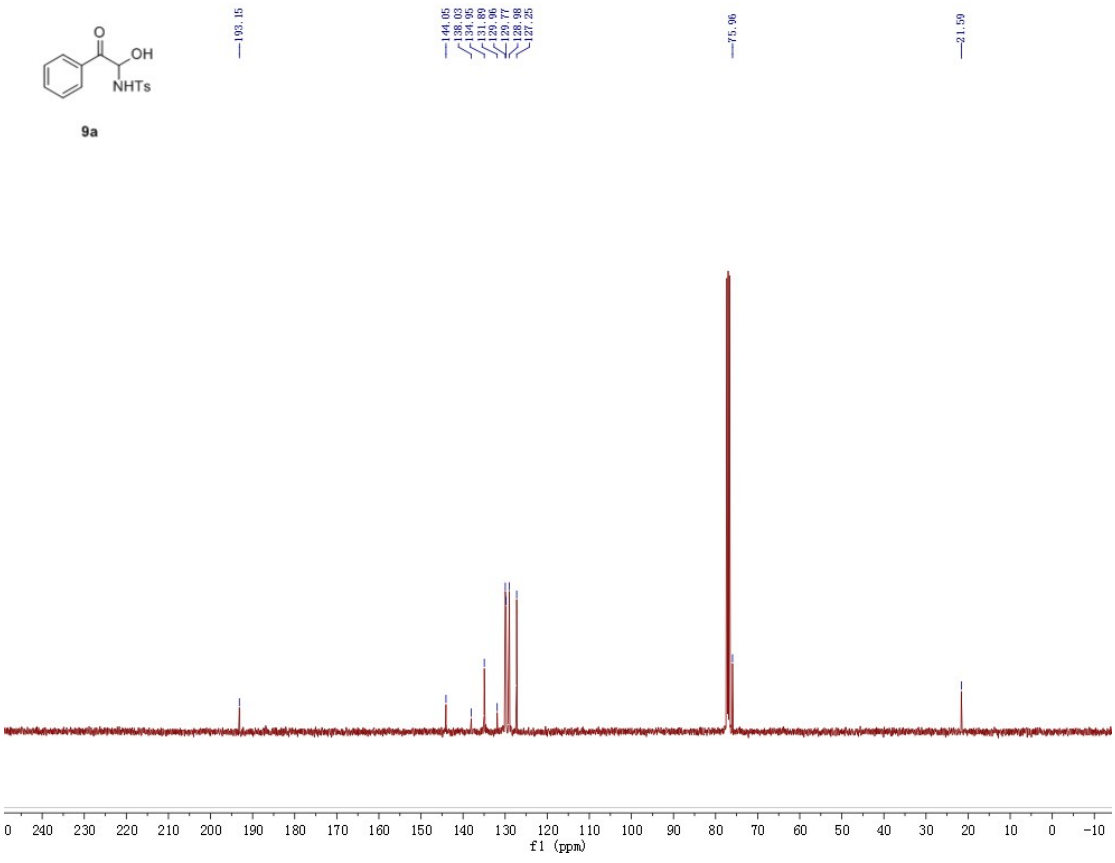

11an
f1 (ppm)

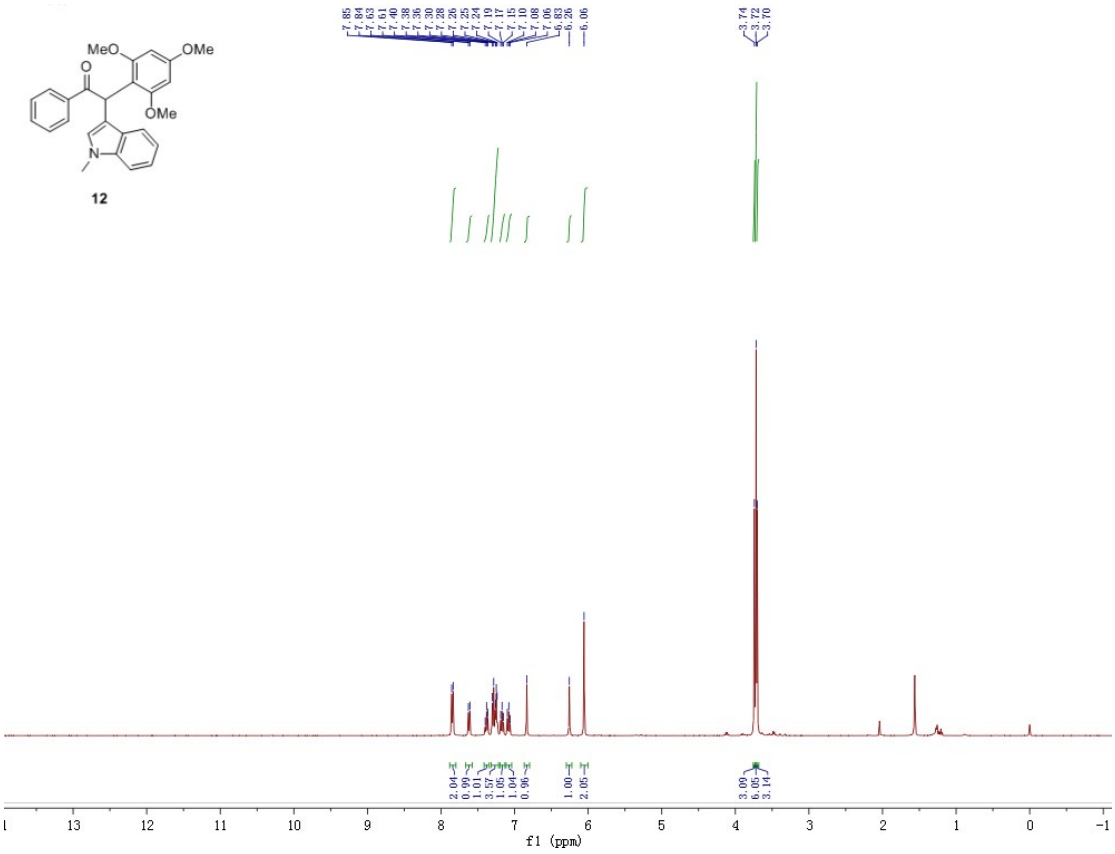

11an
f1 (ppm)

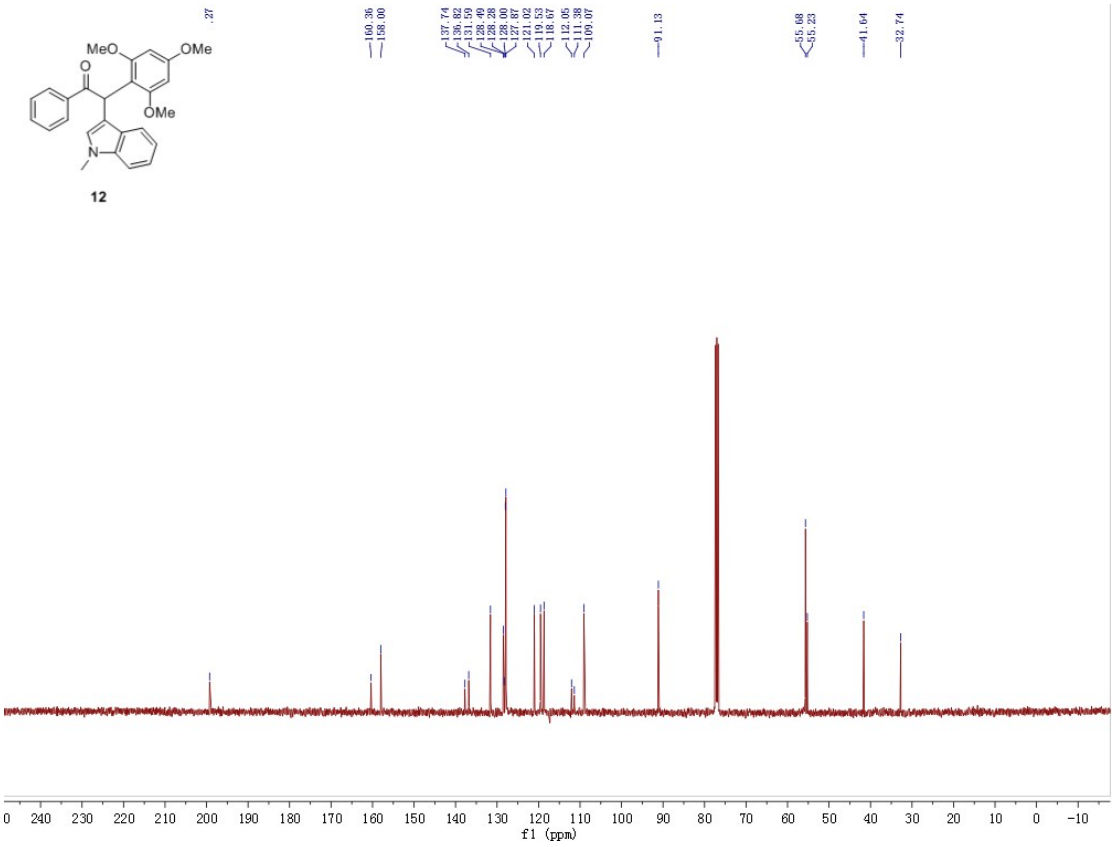

11ao
7.62
7.60
7.57
7.55
7.52
7.50
7.48
7.37
7.35
7.33
7.10
7.08
6.59
6.03
6.01
5.92
5.91
5.90
5.81
5.79
5.75
5.75
3.72
2.31
2.06
2.08
1.05
2.09
2.02
0.96
1.00
1.00
0.97
0.99
3.06
3.09
f1 (ppm)

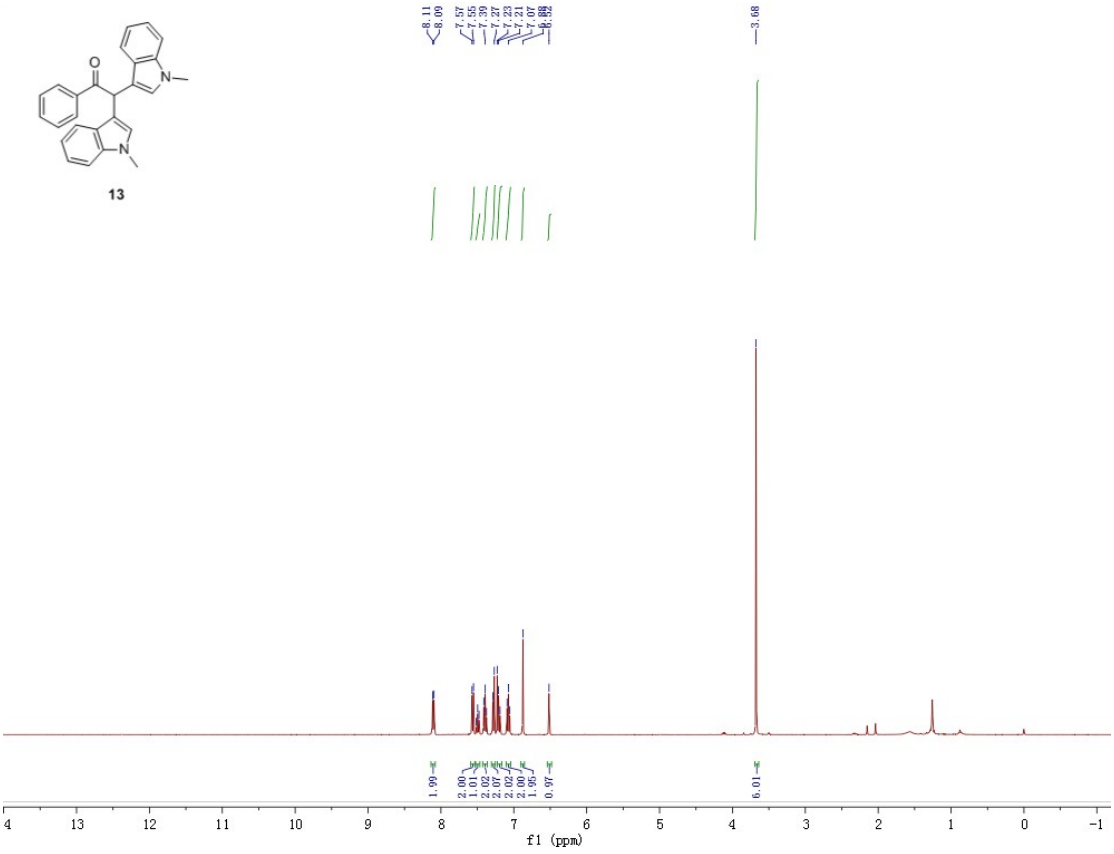

11ao
193.63
143.44
136.83
134.38
133.72
129.52
128.60
128.42
127.14
124.76
124.71
110.73
107.54
54.74
34.18
21.45
f1 (ppm)

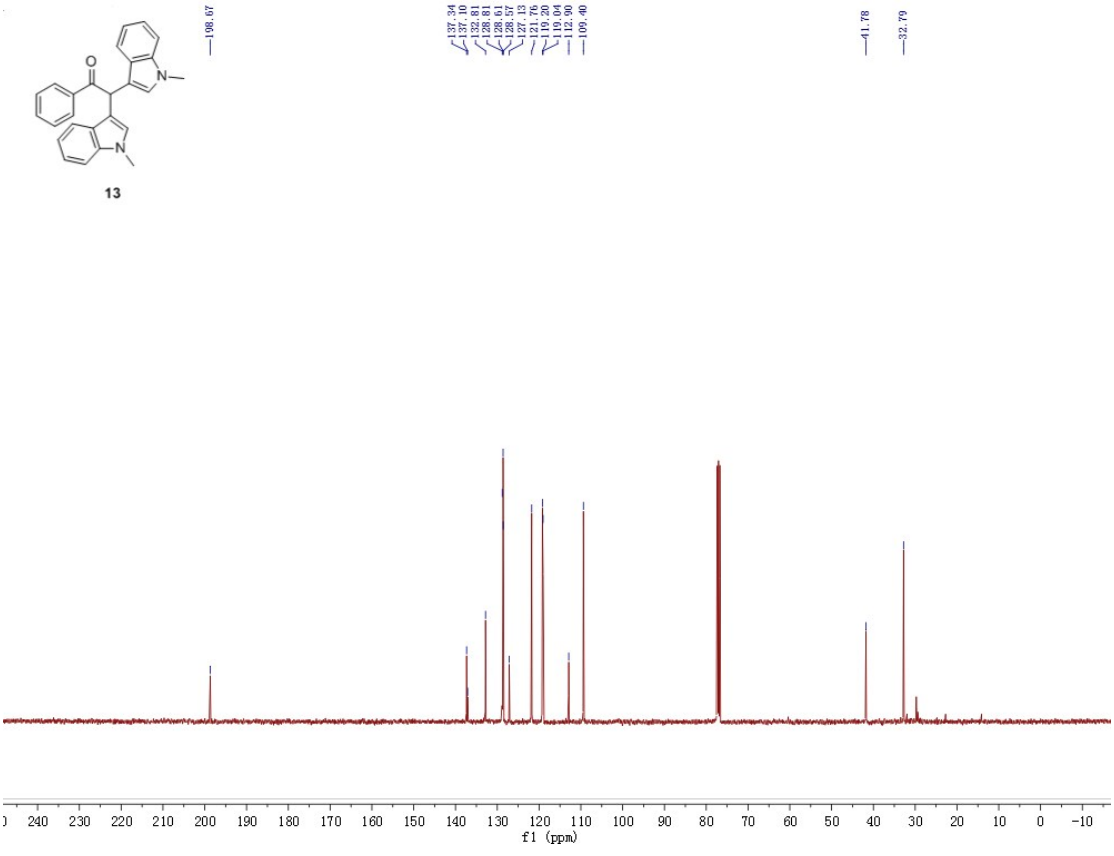

8.21
8.19
7.91
7.89
7.72
7.71
7.69
7.59
7.57
7.55
7.39
7.37
6.25
6.23
6.23
6.21
5.44
5.42
4.28
4.26
2.49
O
OH
NHTs
9a
2.00
2.04
1.08
2.11
2.03
0.98
0.93
0.99
3.14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

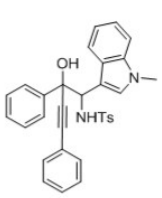

193.15
144.05
138.03
134.95
131.89
129.96
129.77
128.98
127.25
75.96
21.59
O
OH
NHTs
9a
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


MeO
OMe
O
OMe
N
12
f1 (ppm)

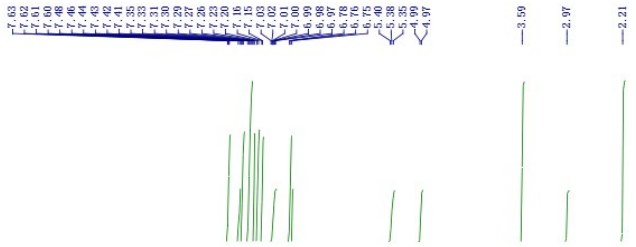

MeO
OMe
O
OMe
N
12
f1 (ppm)

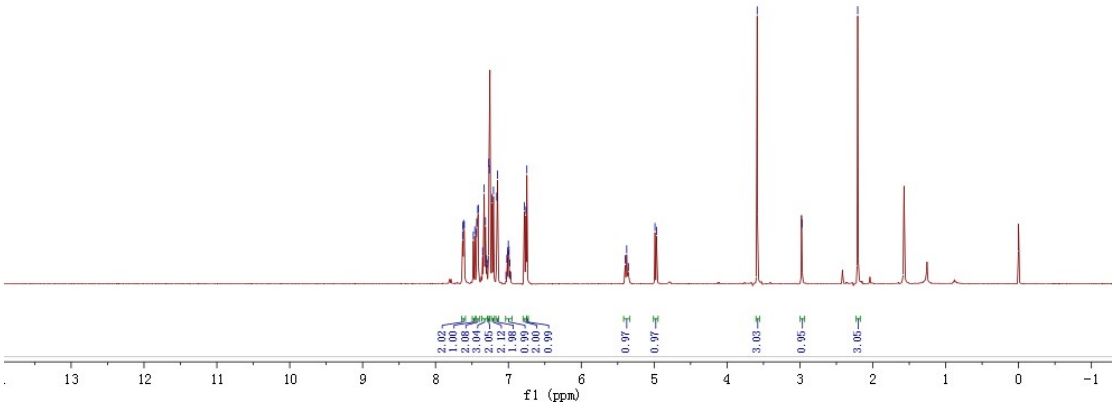

13
8.11
8.09
7.57
7.55
7.39
7.27
7.23
7.21
7.07
6.92
3.68
1.99
2.00
1.01
2.02
2.07
2.02
2.00
1.95
0.97
6.01
f1 (ppm)

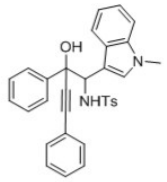

13
198.67
137.34
137.10
132.81
128.81
128.61
128.57
127.13
123.76
121.20
119.04
112.90
109.40
41.78
32.79
f1 (ppm)


OH
N
NHTs

14

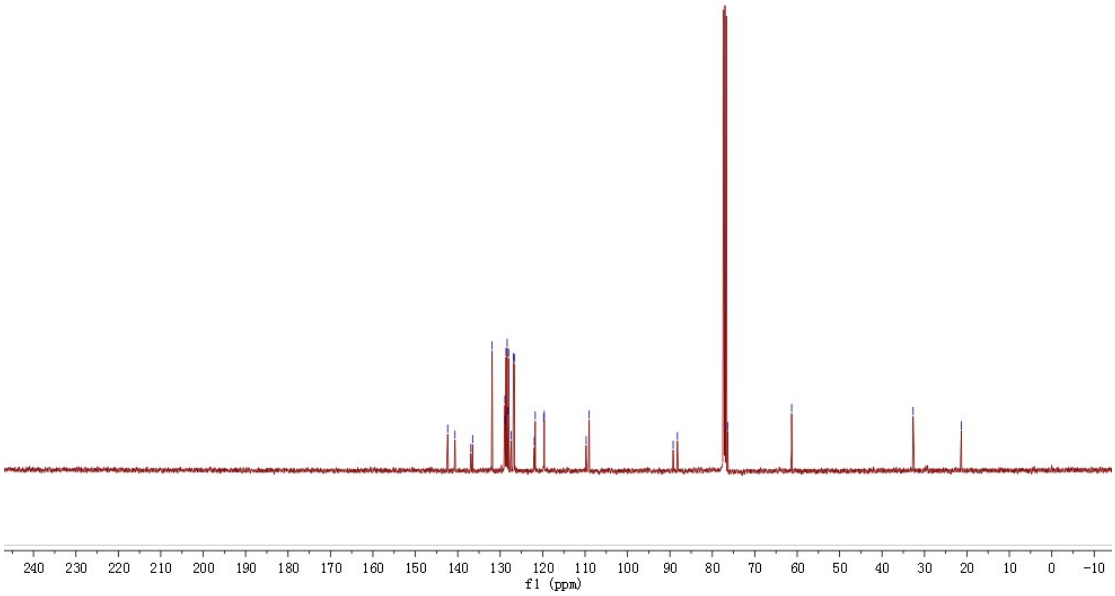

7.63
7.62
7.61
7.60
7.48
7.46
7.44
7.43
7.42
7.41
7.35
7.33
7.31
7.30
7.29
7.27
7.26
7.23
7.20
7.16
7.15
7.03
7.02
7.01
7.00
6.99
6.98
6.97
6.78
6.76
6.75
5.40
5.38
5.35
4.99
4.97
3.59
2.97
2.21

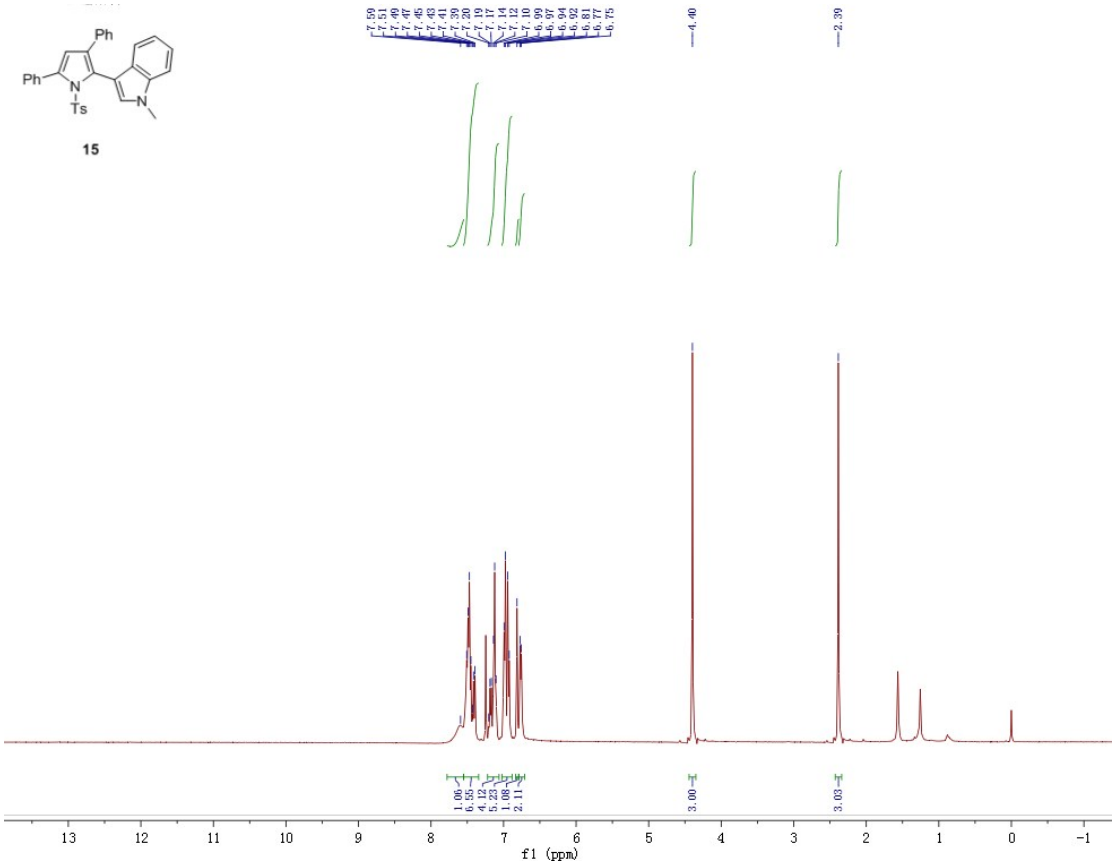

2.02
1.00
2.08
3.04
2.05
2.12
1.98
0.99
2.00
0.99
0.97
0.97
3.03
0.95
3.05
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

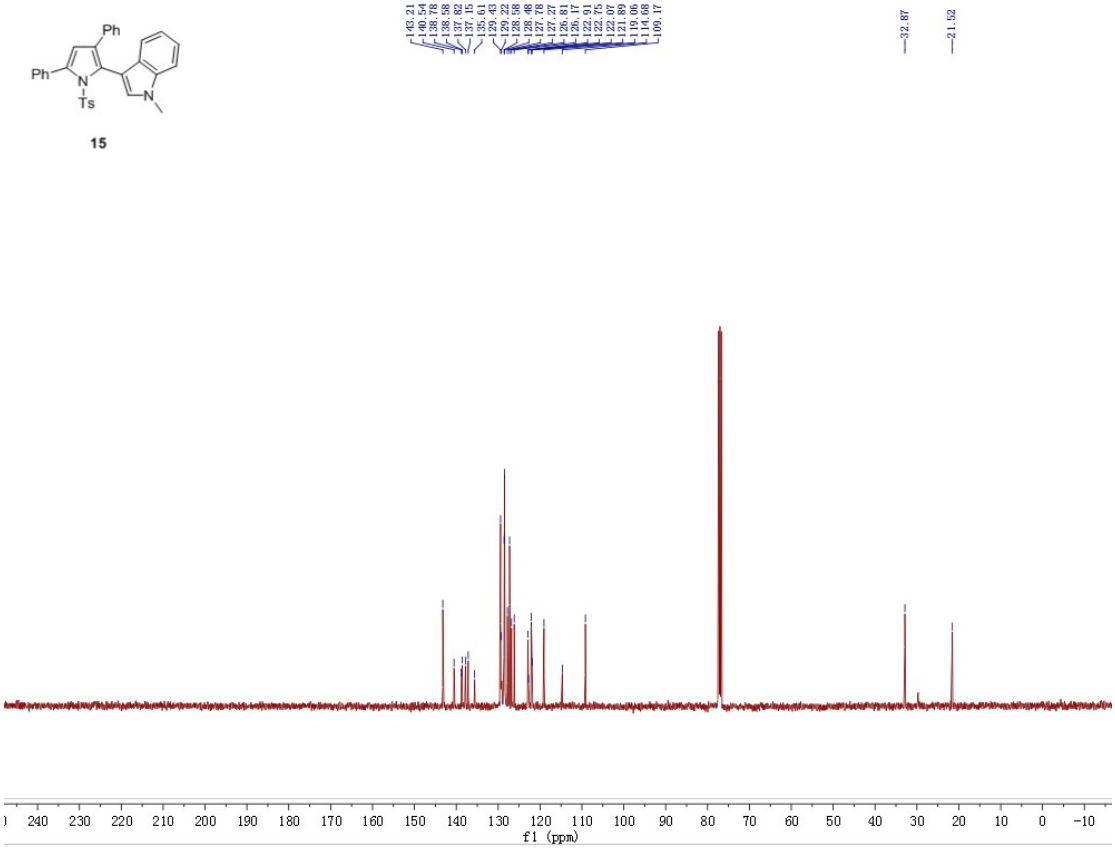

OH
N
NHTs

14


142.38
140.65
136.91
136.50
131.91
128.89
128.84
128.63
128.36
128.24
128.00
127.40
126.87
126.66
121.96
121.74
119.76
119.61
109.74
109.03
89.24
88.23
76.40
61.31
32.68
21.30


240
230
220
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)


Ph
Ph
N
Ts
N
15
7.59
7.51
7.49
7.47
7.45
7.43
7.41
7.39
7.20
7.19
7.17
7.14
7.12
7.10
6.99
6.97
6.94
6.92
6.81
6.77
6.75
4.40
2.39
1.06
6.55
4.12
5.23
1.08
2.11
3.00
3.03
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


Ph
Ph
N
Ts
N
15
146.21
140.54
138.78
138.58
137.82
137.15
135.61
129.43
129.22
128.58
128.48
127.78
127.27
126.61
126.17
122.91
122.75
122.07
121.89
119.06
114.68
109.17
32.87
21.52
240
230
220
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)