

Supporting Information

Electrochemical synthesis of γ -keto sulfones containing β -quaternary carbon center via 1,2-migration

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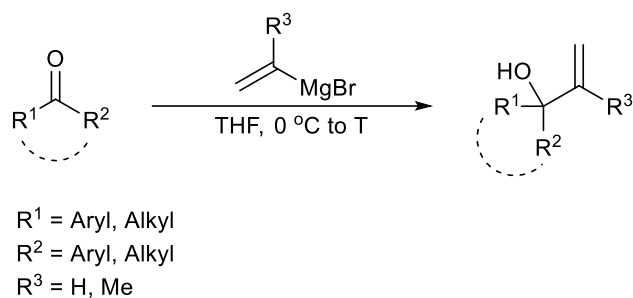
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1. General information

^1H -NMR and ^{13}C -NMR spectra were recorded in CDCl_3 solution on a Bruker Avance 400 spectrometer at 20~25 °C. ^1H NMR spectra were reported in parts per million using tetramethylsilane TMS ($\delta = 0.00$ ppm) as an internal standard. The data of ^1H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd= doublet of doublets, dt = doublet of triplets, m = multiplet), coupling constants (J , Hz), and integration. ^{13}C NMR spectra were reported in parts per million using solvent CDCl_3 ($\delta = 77.2$ ppm) as an internal standard. The data of ^{13}C NMR are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet), and coupling constants (J , Hz). Reactions were monitored by TLC and column chromatography was performed using silica gel. Commercially available reagents were used without further purification unless otherwise specified.

1.1 Preparation of allylic alcohols

The raw materials (**1**) were prepared according to literature procedures.¹⁻⁶ To a two-necked flask under argon atmosphere loaded with a solution of ketone (5 mmol) in anhydrous THF (5 mL), then Grignard reagent (1.0 M in THF, 5.5 mL, 5.5 mmol, 1.1 eq.) was dropwise added via syringe under vigorous stirring in ice-bath. After continuously stirring for 0.5 h, the mixture was warmed to room temperature (or 50 °C) and stirred for 5 h. Then it was detected by TLC and aqueous NH_4Cl (6 mL) was added at 0 °C to quench the reaction. Removed THF solvent. Subsequently, the mixture was extracted with EtOAc (5 mL \times 3) and the combined organic layer was dried with anhydrous magnesium. The solvent was removed in vacuo by a rotary evaporator and the final crude was purified by chromatography on silica gel to yield desired allylic alcohol.

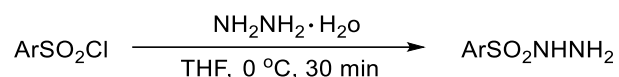


For α , α -diaryl allylic alcohols (1a-m): 0 °C to rt.

For α -alkyl, α -aryl allylic alcohols (1m-r) and α , α -dialkyl allylic alcohols (1s-z):
0 °C to 50 °C.

1.2 Preparation of aryl sulfonylhydrazides

The raw materials (**2**) were prepared according to literature procedures.⁷⁻¹⁰ To a two-necked flask under argon atmosphere charged with arylsulfonyl chloride (5 mmol) in THF solution (25 mL), and subsequently added hydrazine hydrate (15 mmol, 3 eq.) dropwise under ice bath conditions. After stirring at 0 °C for 30 minutes, detected by TLC. Then evaporated THF solution in vacuum, and extracted the aqueous solution of crudes with ethyl acetate (30 mL \times 3). Organic layer was dried over anhydrous magnesium and removed solvents. Then the crude was purified by chromatography on silica gel to obtain desired aryl sulfonylhydrazides.



1.3 Preparation of γ -keto sulfones

An undivided cell was equipped with graphite plate anode (10 \times 10 \times 3 mm) and foamed nickel cathode (10 \times 10 \times 2 mm). Allyl alcohols **1** (0.25 mmol), sulfonyl hydrazines **2** (0.5 mmol, 2 eq.) and Bu₄NBF₄ electrolyte (0.5 mmol) were respectively added into the cell with a 6 mL solution of MeCN/H₂O (5/1). The mixture exposed to air was stirred and electrolyzed under constant current conditions (15 mA) at room temperature for 4 hours. Then it was extracted with ethyl acetate (15 mL \times 3), and

dried over anhydrous MgSO₄. After concentrating in vacuum, the residue was purified by column chromatography on silica gel to get target γ -keto sulfone possessing β -quaternary carbon center.

1.4 Gram-scale reaction

An undivided round-bottomed flask (250 mL) was equipped with graphite plate anode (10 × 10 × 3 mm) and foamed nickel cathode (10 × 10 × 2 mm), which were connected to a power supply. 2-methyl-1,1-diphenylprop-2-en-1-ol **1a** (5 mmol), 4-methylbenzenesulfonhydrazide **2a** (10 mmol, 2 eq.) and Bu₄NBF₄ electrolyte (10 mmol) were respectively added into the cell with a solution of MeCN/H₂O (120 mL, 5/1). The mixture exposed to air was stirred and electrolyzed under constant current conditions (15 mA) at room temperature for 72 hours. Then evaporated MeCN solvent in vacuum and extracted with ethyl acetate (50 mL × 3). After drying over anhydrous MgSO₄ and concentrating in vacuum, the residue was purified by column chromatography on silica gel to obtain target γ -keto sulfone **3aa** (1.27 g, 84%).

1.5 Reductive reaction

A round bottomed flask was filled with γ -keto sulfone (**3aa**, 0.5 mmol, 189.2 mg) in ethanol solution (2 mL). Added sodium borohydride (1.0 mmol, 2 eq.) slowly to it under ice bath conditions. The mixture was continuously stirred for 2 hours at room temperature and detected by TLC. Quenched the reaction by adding dilute hydrochloric acid dropwise under ice bath condition. Washed with saturated salt water and ethyl acetate (15 mL × 3). After drying with anhydrous MgSO₄ and concentrating in vacuum, the mixture was purified by column chromatography on silica gel and obtained γ -hydroxyl sulfone **6** (129.2 mg, 68%).

1.6 Control experiments

Add three equivalents of 2,2,6,6-tetramethylpiperidiny-1-oxide (TEMPO) or butylated hydroxytoluene (BHT) to the standard reaction system, and other operations are the same as **1.3**.

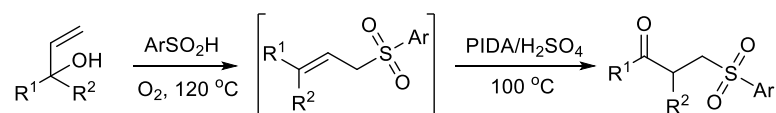
1.7 Cyclic voltammetry (CV) experiments

Cyclic voltammetry experiments were carried out in a three-electrode cell (25 mL) at room temperature. A steady glassy carbon electrode was used as the working electrode, while a platinum wire was used as the counter electrode and an Ag/AgCl electrode was used as reference. A mixed CH₃CN/H₂O (12 mL, 5/1) solution containing 1 mmol nBu₄NBF₄ was added into the cell. 0.5 mmol **1a** was added to determine the oxidation potential of itself. 0.1 mmol **2a** was added to determine the oxidation potential of **2a**. The scan rate was 0.1 V/s, ranging from 0 V to 3 V.

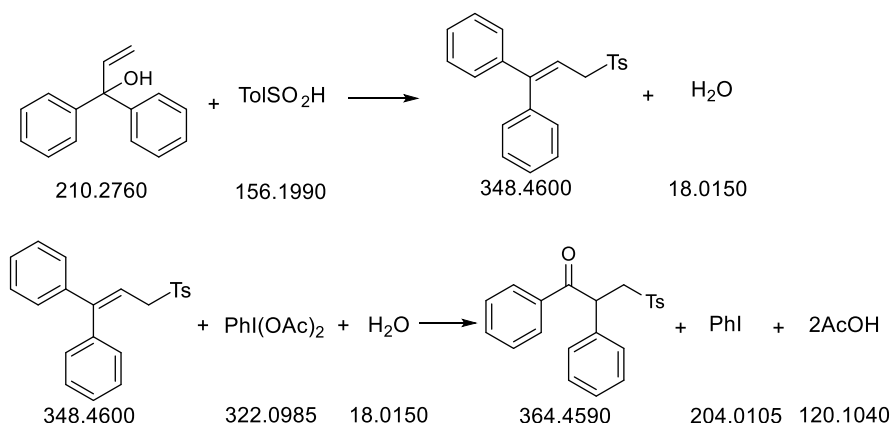
2. Green metrics

Taking standard reactions as examples and calculations are conducted using atom economy (atom efficiency) and theoretical environmental factor (E-factor) as representative green metrics¹¹⁻¹³.

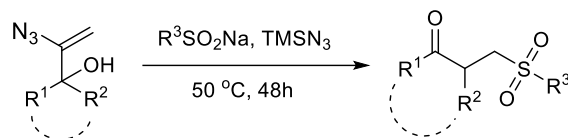
- (a) Ji's work¹⁴: two steps, unstable PIDA, heating and other by-products (PhI, AcOH, etc.).



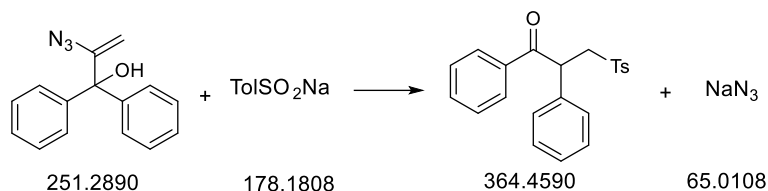
While R¹ = R² = Ph: Atom efficiency = 0.53, E_{theor} = 0.89.



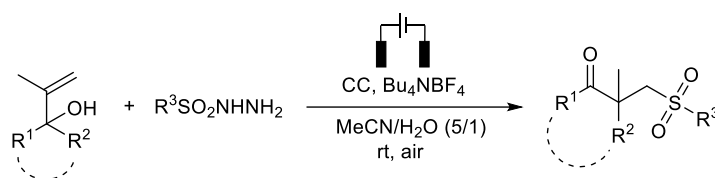
- (b) Wang's work¹⁵: unstable and toxic azides, high temperature, 6 equivalents of sodium p-toluenesulfonate, and many by-products (TsNH₂, TMSOH, NaN₃, etc.)



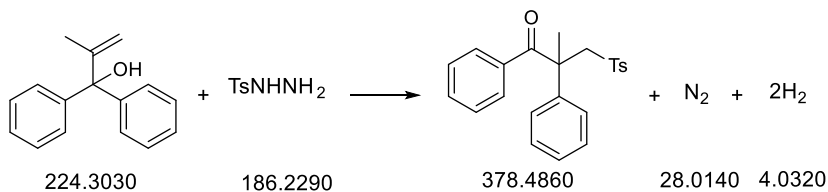
While $R^1 = R^2 = \text{Ph}$: Atom efficiency = 0.85, $E_{\text{theor}} = 0.18$.



(c) Our work: room temperature, one step, without oxidants and catalysts, only H_2 and N_2 by-products.



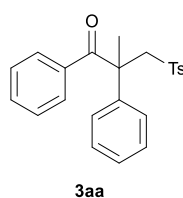
While $R^1 = R^2 = \text{Ph}$: Atom efficiency = 0.92, $E_{\text{theor}} = 0.08$.



Overall, this electrochemical strategy for constructing γ -keto sulfones has higher atom economy and lower theoretical environmental factor, which is in line with the concept of green chemistry.

3. Characterization of the products

2-methyl-1,2-diphenyl-3-tosylpropan-1-one (3aa)



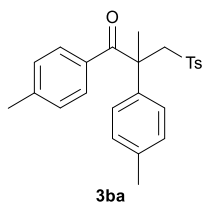
White solid, 84.2 mg, 89% yield, mp 102-104 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.49 (d, $J = 8.0$ Hz, 2H), 7.32-7.26 (m, 2H), 7.25-7.20 (m, 6H), 7.16-7.12 (m, 4H), 4.00 (d, $J = 14.4$ Hz, 1H), 3.72 (d, $J = 14.4$ Hz, 1H), 2.32 (s, 3H), 2.04 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 201.31, 144.14, 139.52, 138.81, 136.35, 131.95, 129.74, 129.37, 129.36, 128.22, 128.08, 127.68, 126.77, 65.70, 53.81, 22.26, 21.71.

HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{22}\text{O}_3\text{SNa}$ 401.1182, found 401.1186.

2-methyl-1,2-di-*p*-tolyl-3-tosylpropan-1-one (3ba)



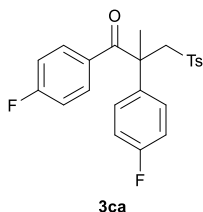
White solid, 87.4 mg, 86% yield, mp 88-90 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.02 (t, *J* = 8.0 Hz, 4H), 3.99 (d, *J* = 14.8 Hz, 1H), 3.84 (d, *J* = 14.8 Hz, 1H), 2.38 (s, 3H), 2.29 (s, 3H), 2.28 (s, 3H), 2.09 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 200.77, 143.86, 142.65, 138.79, 137.73, 136.50, 133.26, 129.90, 129.73, 129.53, 128.84, 127.64, 126.66, 65.81, 53.37, 22.27, 21.66, 21.57, 21.14.

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₅H₂₆O₃SNa 429.1495, found 429.1497.

1,2-bis(4-fluorophenyl)-2-methyl-3-tosylpropan-1-one (3ca)



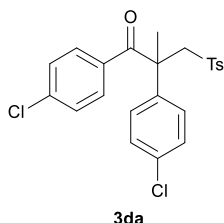
White solid, 82.9 mg, 80% yield, mp 134-136 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.41-7.38 (m, 2H), 7.26-7.21 (m, 4H), 6.98-6.90 (m, 4H), 3.94 (d, *J* = 14.8 Hz, 1H), 3.83 (d, *J* = 14.8 Hz, 1H), 2.34 (s, 3H), 2.02 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 199.42, 164.99 (d, *J* = 242.6 Hz), 162.49 (d, *J* = 236.1 Hz), 144.36, 138.64, 135.03 (d, *J* = 3.4 Hz), 132.23 (d, *J* = 9.1 Hz), 131.89 (d, *J* = 3.3 Hz), 129.79, 128.70 (d, *J* = 8.2 Hz), 127.64, 116.39 (d, *J* = 21.5 Hz), 115.51 (d, *J* = 21.8 Hz), 65.60, 53.26, 22.50, 21.72.

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₃H₂₀F₂O₃SNa 437.0993, found 437.0996.

1,2-bis(4-chlorophenyl)-2-methyl-3-tosylpropan-1-one (3da)



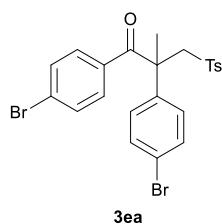
White solid, 88.3 mg, 79% yield mp 100-102 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.16-7.08 (m, 8H), 3.85 (d, *J* = 14.4 Hz, 1H), 3.78 (d, *J* = 14.8 Hz, 1H), 2.41 (s, 3H), 2.11 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 199.59, 144.41, 138.77, 138.38, 137.48, 134.56, 133.86, 130.96, 129.79, 129.57, 128.72, 128.35, 127.60, 65.37, 53.33, 22.18, 21.75.

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₃H₂₀Cl₂O₃SNa 469.0402, found 469.0405.

1,2-bis(4-bromophenyl)-2-methyl-3-tosylpropan-1-one (3ea)



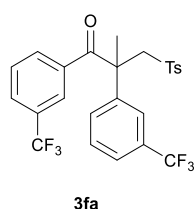
White solid, 88.5 mg, 66% yield, mp 118-119 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.23-7.19 (m, 4H), 7.09 (d, *J* = 8.8 Hz, 2H), 3.89 (dd, *J* = 18.0, 14.8 Hz, 2H), 2.42 (s, 3H), 2.08 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 199.67, 144.39, 138.25, 137.87, 134.23, 132.48, 131.70, 131.04, 129.79, 128.66, 127.55, 127.43, 122.77, 65.22, 53.34, 22.08, 21.77.

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₃H₂₀Br₂O₃SNa 558.9372, found 558.9373.

2-methyl-3-tosyl-1,2-bis(3-(trifluoromethyl)phenyl)propan-1-one (3fa)



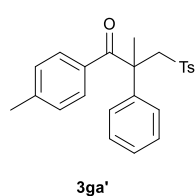
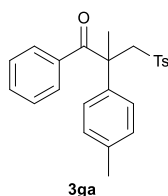
Colourless oil, 115.7 mg, 90% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.51 (s, 1H), 7.46-7.40 (m, 5H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.33-7.26 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 3.95 (d, *J* = 14.8 Hz, 1H), 3.82 (d, *J* = 14.8 Hz, 1H), 2.29 (s, 3H), 2.07 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 199.36, 144.64, 139.86, 138.12, 136.32, 132.19, 131.91 (q, *J* = 32.7 Hz), 131.10 (q, *J* = 24.0 Hz), 130.45, 130.11, 129.86, 129.04, 128.76 (q, *J* = 3.5 Hz), 127.57, 126.21 (q, *J* = 4.0 Hz), 125.30 123.62 (q, *J* = 3.7 Hz), 123.71 (q, *J* = 271.0 Hz), 123.62 (q, *J* = 3.7 Hz), 123.49 (q, *J* = 273.6 Hz), 65.01, 53.66, 22.04, 21.59.

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₅H₂₀F₆O₃SNa 537.0930, found 537.0932.

2-methyl-1-phenyl-2-(p-tolyl)-3-tosylpropan-1-one (3ga) and 2-methyl-2-phenyl-1-(p-tolyl)-3-tosylpropan-1-one (3ga')



Colourless oil, 90.3 mg, 92% yield.

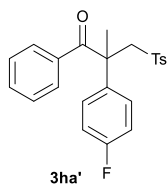
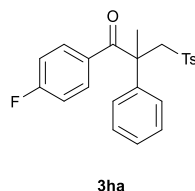
¹H NMR (400 MHz, CDCl₃): First isomer: δ 7.46 (d, *J* = 7.6 Hz, 2H), 7.30-7.25 (overlapped, 2H), 7.19-7.15 (overlapped, 3H), 7.13-7.06 (overlapped, 4H), 6.97 (d, *J* = 7.6 Hz, 2H), 3.95 (d, *J* = 14.4 Hz, 1H), 3.73 (d, *J* = 14.8 Hz, 1H), 2.31 (s, 3H), 2.22 (s, 3H), 2.00 (s, 3H). Second isomer: δ 7.46 (d, *J* = 7.6 Hz, 2H), 7.30-7.25 (overlapped, 2H), 7.19-7.15 (overlapped, 3H), 7.13-7.06 (overlapped, 4H), 6.93 (d, *J* =

7.6 Hz, 2H), 3.95 (d, $J = 14.4$ Hz, 1H), 3.73 (d, $J = 14.8$ Hz, 1H), 2.30 (s, 3H), 2.20 (s, 3H), 2.04 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): First isomer: δ 201.42, 143.97, 142.74, 138.74, 137.87, 136.26, 131.85, 129.98, 129.59, 129.34, 128.16, 127.65, 126.59, 65.69, 53.39, 22.20, 21.67, 21.14. Second isomer: δ 200.59, 144.01, 139.70, 138.80, 136.39, 133.17, 129.70, 129.66, 129.25, 128.87, 127.93, 127.62, 126.78, 65.76, 53.74, 22.30, 21.67, 21.57.

HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{24}\text{H}_{24}\text{O}_3\text{SNa}$ 415.1338, found 415.1337.

1-(4-fluorophenyl)-2-methyl-2-phenyl-3-tosylpropan-1-one (3ha) and 2-(4-fluorophenyl)-2-methyl-1-phenyl-3-tosylpropan-1-one (3ha')



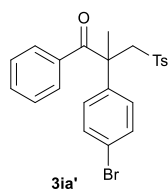
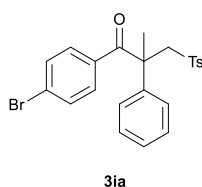
White solid, 86.1 mg, 87% yield, mp 99-107 °C.

^1H NMR (400 MHz, CDCl_3): First isomer: δ 7.55 (t, $J = 8.8$ Hz, 2H), 7.41-7.38 (overlapped, 2H), 7.33 (d, $J = 6.8$ Hz, 2H), 7.28 (overlapped, 2H), 7.22 (t, $J = 8.0$ Hz, 2H), 6.90 (t, $J = 8.4$ Hz, 3H), 4.04 (d, $J = 14.4$ Hz, 1H), 3.78 (d, $J = 14.4$ Hz, 1H), 2.39 (s, 3H), 2.11 (s, 3H). Second isomer: δ 7.55 (t, $J = 8.8$ Hz, 2H), 7.41-7.38 (overlapped, 1H), 7.28 (overlapped, 3H), 7.26 (d, $J = 2.8$ Hz, 2H), 7.23 (t, $J = 8.0$ Hz, 2H), 6.96 (t, $J = 8.4$ Hz, 3H), 3.97 (d, $J = 14.8$ Hz, 1H), 3.85 (d, $J = 14.4$ Hz, 1H), 2.40 (s, 3H), 2.10 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): First isomer: δ 199.61, 164.78 (d, $J = 255.1$ Hz), 144.20, 139.44, 138.62, 132.25(d, $J = 3.5$ Hz), 132.19, 132.13 (d, $J = 6.8$ Hz), 129.76, 129.46, 127.66, 126.72, 115.36 (d, $J = 21.8$ Hz), 65.68, 53.79, 22.32, 21.71. Second isomer: δ 201.07, 162.48 (d, $J = 249.1$ Hz), 144.28, 138.75, 135.92, 135.03 (d, $J = 3.5$ Hz), 129.75, 129.39, 128.71 (d, $J = 8.2$ Hz), 128.31, 128.20, 127.62, 116.25 (d, $J = 21.5$ Hz), 65.56, 53.23, 22.41, 21.69.

HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{21}\text{FO}_3\text{SNa}$ 419.1088, found 419.1089.

1-(4-bromophenyl)-2-methyl-2-phenyl-3-tosylpropan-1-one (3ia) and 2-(4-bromophenyl)-2-methyl-1-phenyl-3-tosylpropan-1-one (3ia')



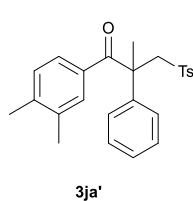
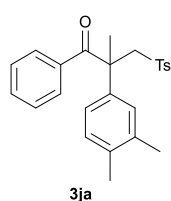
Colourless oil, 94.9 mg, 83% yield.

¹H NMR (400 MHz, CDCl₃): First isomer: δ 7.47 (dt, *J* = 8.4, 2.0 Hz, 2H), 7.32-7.43 (overlapped, 3H), 7.20-7.16 (overlapped, 3H), 7.14-7.09 (overlapped, 5H), 3.97 (d, *J* = 14.8 Hz, 1H), 3.68 (d, *J* = 14.8 Hz, 1H), 2.30 (s, 3H), 2.00 (s, 3H). Second isomer: δ 7.39 (dt, *J* = 8.4, 2.0 Hz, 2H), 7.32-7.43 (overlapped, 3H), 7.20-7.16 (overlapped, 3H), 7.14-7.09 (overlapped, 3H), 7.03 (dt, *J* = 8.8, 2.0 Hz, 2H), 3.84 (s, 2H), 2.32 (s, 3H), 2.00 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): First isomer: δ 200.13, 144.18, 139.22, 138.10, 134.90, 131.46, 130.91, 129.73, 129.44, 128.19, 127.60, 126.90, 126.63, 65.51, 53.73, 22.18, 21.65. Second isomer: δ 200.64, 144.21, 138.66, 138.30, 135.62, 132.27, 132.22, 129.69, 129.38, 128.68, 128.30, 127.49, 122.48, 65.27, 53.29, 22.09, 21.68.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₃H₂₂BrO₃S 457.0468, found 457.0468.

2-(3,4-dimethylphenyl)-2-methyl-1-phenyl-3-tosylpropan-1-one (3ja) and 1-(3,4-dimethylphenyl)-2-methyl-2-phenyl-3-tosylpropan-1-one (3ja')



White solid, 76.2 mg, 75% yield, mp 132-137 °C.

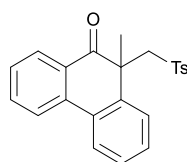
¹H NMR (400 MHz, CDCl₃): First isomer: δ 7.41 (dt, *J* = 8.4, 2.0 Hz, 2H), 7.29-7.25 (m, 3H), 7.21-7.15 (overlapped, 4H), 7.08-7.05 (m, 3H), 3.93 (d, *J* = 14.8 Hz, 1H), 3.78 (d, *J* = 14.4 Hz, 1H), 2.29 (s, 3H), 2.10 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H). Second isomer: δ 7.46 (dt, *J* = 8.4, 2.0 Hz, 2H), 7.21-7.15 (overlapped, 1H), 7.14-7.10 (m, 3H), 6.98-6.90 (m, 3H), 6.88-6.80 (m, 3H), 3.95 (d, *J* = 14.4 Hz, 1H), 3.72 (d, *J* = 14.8 Hz, 1H), 2.29 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): First isomer: δ 201.46, 143.74, 139.77, 138.66, 137.38, 136.48, 136.36, 131.78, 130.50, 129.38, 129.18, 128.11, 127.62, 127.59, 127.08, 65.67, 53.22, 22.12, 21.62, 19.90, 19.45. Second isomer: δ 200.78, 143.95, 141.45, 138.82, 136.65, 136.49, 133.60, 130.86, 127.95, 129.62, 129.33, 127.87, 127.62, 126.78, 123.97, 65.79, 53.74, 22.26, 21.62, 19.87, 19.79.

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₅H₂₆O₃SNa 429.1495, found 429.1496.

10-methyl-10-(tosylmethyl)phenanthren-9(10*H*)-one (3ka)

White solid, 82.8 mg, 88% yield, mp 127-128 °C.

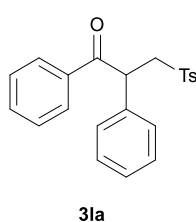


¹H NMR (400 MHz, CDCl₃): δ 8.09 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.38-7.26 (m, 5H), 7.19-7.14 (m, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 4.51 (d, *J* = 14.4 Hz, 1H), 3.91 (d, *J* = 14.4 Hz, 1H), 2.26 (s, 3H), 1.35 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 198.62, 144.26, 138.83, 137.84, 137.03, 134.89, 129.58, 129.31, 128.92, 128.51, 128.34, 128.11, 128.08, 127.93, 127.85, 124.02, 123.22, 64.83, 49.12, 30.78, 21.67.

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₃H₂₀O₃SNa 399.1025, found 399.1024.

1,2-diphenyl-3-tosylpropan-1-one (3la)¹⁵

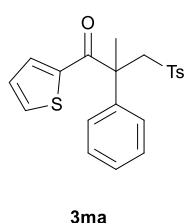


White solid, 56.5 mg, 62% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.82 (d, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.19-7.10 (m, 7H), 5.21 (dd, *J* = 8.8, 3.6 Hz, 1H), 4.34 (dd, *J* = 14.0, 8.8 Hz, 1H), 3.35 (dd, *J* = 14.0, 3.6 Hz, 1H), 2.31 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 196.03, 144.86, 136.66, 136.54, 135.64, 133.58, 129.96, 129.53, 129.03, 128.74, 128.29, 128.26, 128.11, 59.46, 47.68, 21.76.

2-methyl-2-phenyl-1-(thiophen-2-yl)-3-tosylpropan-1-one (3ma)



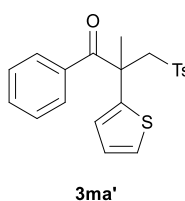
Colourless oil, 39.5 mg, 41% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.39-7.35 (m, 3H), 7.18-7.12 (m, 5H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.90 (dd, *J* = 4.0, 1.2 Hz, 1H), 6.76 (dd, *J* = 4.8, 4.0 Hz, 1H), 3.89 (d, *J* = 15.2 Hz, 1H), 3.83 (d, *J* = 14.8 Hz, 1H), 2.30 (s, 3H), 2.12 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 193.81, 143.97, 140.51, 139.16, 138.53, 133.97, 133.51, 129.66, 129.01, 128.18, 127.78, 127.74, 127.60, 64.96, 53.80, 22.78, 21.69.

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₁H₂₀O₃S₂Na 407.0746, found 407.0746.

2-methyl-1-phenyl-2-(thiophen-2-yl)-3-tosylpropan-1-one (3ma')



Colourless oil, 19.2 mg, 20% yield.

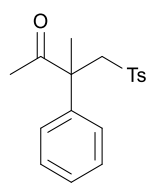
¹H NMR (400 MHz, CDCl₃): δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.37-7.32 (m, 3H), 7.23-7.18 (m, 5H), 6.87 (d, *J* = 4.4 Hz, 1H), 6.83 (dd, *J* =

3.6, 1.2 Hz, 2H), 4.19 (d, $J = 14.4$ Hz, 1H), 3.63 (d, $J = 14.0$ Hz, 1H), 2.35 (s, 3H), 2.08 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 200.73, 144.47, 138.70, 136.83, 131.78, 129.88, 128.78, 128.27, 127.81, 126.27, 126.06, 66.08, 51.74, 24.02, 21.76.

HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{20}\text{O}_3\text{S}_2\text{Na}$ 407.0746, found 407.0746.

3-methyl-3-phenyl-4-tosylbutan-2-one (3na)



3na

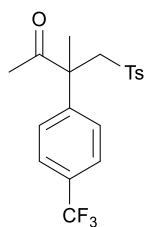
Colourless oil, 64.9 mg, 82% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.54 (dt, $J = 8.0, 1.8$ Hz, 2H), 7.25-7.21 (m, 3H), 7.18 (d, $J = 7.6$ Hz, 2H), 7.16-7.13 (m, 2H), 3.92 (d, $J = 14.8$ Hz, 1H), 3.66 (d, $J = 14.4$ Hz, 1H), 2.38 (s, 3H), 2.03 (s, 3H), 1.96 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 207.44, 144.15, 138.57, 138.44, 129.70, 129.03, 127.85, 127.61, 126.56, 63.88, 54.26, 25.11, 21.63, 20.06.

HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{20}\text{O}_3\text{SNa}$ 339.1025, found 339.1024.

3-methyl-4-tosyl-3-(4-(trifluoromethyl)phenyl)butan-2-one (3oa)



3oa

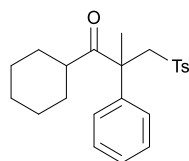
White solid, 63.4 mg, 66% yield, mp 89-91 °C.

^1H NMR (400 MHz, CDCl_3): δ 7.35 (t, $J = 7.2$ Hz, 4H), 7.17 (d, $J = 8.0$ Hz, 2H), 7.08 (d, $J = 7.6$ Hz, 2H), 3.74 (dd, $J = 16.4, 15.2$ Hz, 2H), 2.30 (s, 3H), 1.98 (s, 3H), 1.86 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 206.82, 144.45, 142.09, 137.90, 129.79, 129.32 (q, $J = 160.1$ Hz), 127.56, 127.38, 125.89 (q, $J = 3.7$ Hz), 123.95 (q, $J = 273.2$ Hz) 63.44, 54.31, 25.13, 21.58, 19.99.

HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{19}\text{F}_3\text{O}_3\text{SNa}$ 407.0899, found 407.0897.

1-cyclohexyl-2-methyl-2-phenyl-3-tosylpropan-1-one (3pa)



3pa

White solid, 81.7 mg, 85% yield, mp 92-94 °C.

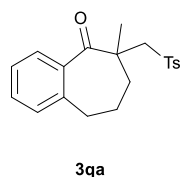
^1H NMR (400 MHz, CDCl_3): δ 7.41 (d, $J = 8.0$ Hz, 2H), 7.13-7.11 (m, 3H), 7.08 (s, 1H), 7.06-7.03 (m, 3H), 3.79 (d, $J = 14.8$ Hz, 1H), 3.63 (d, $J = 14.8$ Hz, 1H), 2.32-2.25 (m, 4H), 1.99 (s, 3H), 1.68-1.62

(m, 2H), 1.49-1.40 (m, 2H), 1.35-1.16 (m, 2H), 1.09-1.03 (m, 2H), 0.90-0.78 (m, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 212.34, 143.96, 138.55, 137.41, 129.63, 128.76, 127.82, 127.61, 127.17, 63.91, 54.45, 45.94, 30.92, 30.84, 25.65, 25.63, 25.56, 21.64, 19.16.

HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₂₃H₂₈O₃SNa 407.1651, found 407.1649.

6-methyl-6-(tosylmethyl)-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one (3qa)



Colourless oil, 55.6 mg, 65% yield.

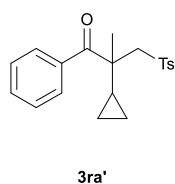
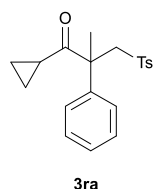
¹H NMR (400 MHz, CDCl₃): δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.35-7.19 (m, 5H), 7.68 (d, *J* = 6.4 Hz, 1H), 3.46 (d, *J* = 14.0 Hz, 1H), 3.37 (d, *J* = 14.0 Hz, 1H), 2.78-2.71 (m, 1H), 2.69-2.62 (m, 1H), 2.36 (s, 3H),

2.21-2.13 (m, 1H), 1.93-1.84 (m, 1H), 1.37 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 210.97, 144.67, 140.20, 138.83, 136.96, 131.19, 130.00, 128.69, 128.67, 127.73, 126.80, 63.97, 49.47, 35.08, 33.29, 22.93, 22.83, 21.74.

HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₂₀H₂₂O₃SNa 365.1182, found 365.1182.

1-cyclopropyl-2-methyl-2-phenyl-3-tosylpropan-1-one (3ra) and 2-cyclopropyl-2-methyl-1-phenyl-3-tosylpropan-1-one (3ra')



Colourless oil, 70.8 mg, 82% yield.

¹H NMR (400 MHz, CDCl₃): First isomer: δ 7.40-7.30 (overlapped, 2H), 7.15-7.12 (m, 3H), 7.07-7.04 (m, 4H), 3.79 (d, *J* = 14.8 Hz, 1H), 3.66 (d, *J* = 14.8

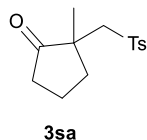
Hz, 1H), 2.28 (s, 3H), 2.00 (s, 3H), 1.55-1.49 (m, 1H), 0.89 (t, *J* = 4.4 Hz, 2H), 0.50-0.44 (m, 2H). Second isomer: δ 7.71-7.68 (m, 2H), 7.64-7.62 (m, 2H), 7.40-7.30 (overlapped, 3H), 7.25 (d, *J* = 8.4 Hz, 2H), 3.87 (d, *J* = 13.6 Hz, 1H), 3.45 (d, *J* = 14.0 Hz, 1H), 2.36 (s, 3H), 1.22 (s, 3H), 1.16-1.12 (m, 1H), 0.78-0.73 (m, 1H), 0.56-0.52 (m, 2H), 0.36-0.31 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) First isomer: δ 209.90, 143.92, 139.38, 138.74, 129.92, 129.59, 128.84, 127.72, 127.68, 63.79, 54.31, 21.61, 20.33, 17.40, 11.46, 2.41.

Second isomer: δ 207.08, 144.49, 138.92, 138.44, 130.70, 128.04, 127.76, 127.56, 127.20, 65.64, 49.53, 21.71, 19.31, 18.70, 12.73, 3.19.

HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{20}H_{22}O_3SNa$ 365.1182, found 365.1181.

2-methyl-2-(tosylmethyl)cyclopentan-1-one (3sa)



3sa

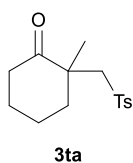
Colourless oil, 48.6 mg, 73% yield.

1H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, $J = 8.4$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 2H), 3.24 (s, 2H), 2.50-2.42 (m, 1H), 2.37 (s, 3H), 2.33-2.23 (m, 2H), 2.06-1.97 (m, 2H), 1.90-1.79 (m, 1H), 1.08 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 219.60, 144.84, 138.46, 130.05, 127.78, 62.51, 47.27, 36.28, 34.36, 22.41, 21.77, 18.90.

HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{14}H_{18}O_3SNa$ 289.0869, found 289.0870.

2-methyl-2-(tosylmethyl)cyclohexan-1-one (3ta)



3ta

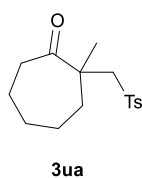
Colourless oil, 51.9 mg, 74% yield.

1H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, $J = 8.4$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 2H), 3.45 (d, $J = 14.4$ Hz, 1H), 3.27 (d, $J = 14.4$ Hz, 1H), 2.49-2.40 (m, 1H), 2.37-2.32 (m, 4H), 2.13-2.10 (m, 2H), 1.94-1.86 (m, 1H), 1.77-1.68 (m, 3H), 1.30 (s, 3H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 212.13, 144.58, 139.02, 129.94, 127.73, 63.47, 48.67, 38.06, 37.73, 26.60, 23.30, 21.72, 21.05.

HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{15}H_{20}O_3SNa$ 303.1025, found 303.1025.

2-methyl-2-(tosylmethyl)cycloheptan-1-one (3ua)



3ua

Colourless oil, 52.2 mg, 71% yield.

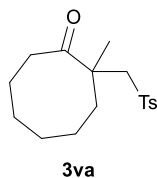
1H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, $J = 8.4$ Hz, 2H), 7.27 (d, $J = 7.6$ Hz, 2H), 3.30 (dd, $J = 18.8, 14.4$ Hz, 2H), 2.66-2.60 (m, 1H), 2.56-2.47 (m, 2H), 2.37 (s, 3H), 1.69 (dd, $J = 14.4, 8.8$ Hz, 1H), 1.63-1.52 (m, 5H), 1.46-1.39 (m, 1H), 1.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 214.88, 144.69, 138.81, 130.01, 127.77, 63.24, 50.74, 40.83, 35.22, 30.47, 25.91, 24.54, 24.21, 21.76.

HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{16}H_{22}O_3SNa$ 317.1182, found 317.1181.

2-methyl-2-(tosylmethyl)cyclooctan-1-one (3va)

Colourless oil, 51.7 mg, 67% yield.



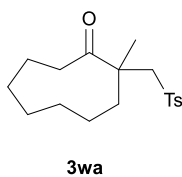
1H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, $J = 8.4$ Hz, 2H), 7.27 (d, $J = 7.6$ Hz, 2H), 3.49 (d, $J = 14.8$ Hz, 1H), 3.08 (d, $J = 14.4$ Hz, 1H), 2.71 (td, $J = 11.6, 3.2$ Hz, 1H), 2.37-2.30 (m, 4H), 2.18-2.05 (m, 2H), 1.84-1.76 (m, 1H), 1.71-1.58 (m, 3H), 1.55-1.42 (m, 2H), 1.37 (s, 3H), 1.31-1.21 (m, 1H), 0.84-0.74 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 217.48, 144.62, 139.07, 129.99, 127.69, 59.12, 50.56, 35.86, 32.45, 30.16, 26.18, 25.03, 24.37, 22.66, 21.72.

HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{17}H_{24}O_3SNa$ 331.1338, found 331.1339.

2-methyl-2-(tosylmethyl)cyclononan-1-one (3wa)

Colourless oil, 52.4 mg, 65% yield.



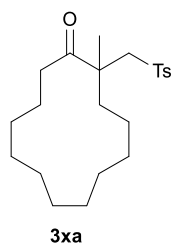
1H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, $J = 8.4$ Hz, 2H), 7.27 (d, $J = 7.6$ Hz, 2H), 3.46 (d, $J = 14.4$ Hz, 1H), 3.14 (d, $J = 14.4$ Hz, 1H), 2.85-2.78 (m, 1H), 2.37 (s, 3H), 2.23-2.17 (m, 1H), 2.06-1.99 (m, 1H), 1.80-1.65 (m, 3H), 1.50-1.43 (m, 4H), 1.37-1.30 (m, 4H), 1.29-1.22 (m, 2H), 1.16-1.08 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 215.23, 144.59, 139.09, 129.98, 127.70, 61.07, 51.99, 34.20, 33.69, 25.31, 24.62, 23.16, 22.38, 21.73, 21.27, 20.29.

HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{18}H_{26}O_3SNa$ 345.1495, found 345.1496.

2-methyl-2-(tosylmethyl)cyclotridecan-1-one (3xa)

White solid, 56.8 mg, 60% yield, mp 112-114 °C.

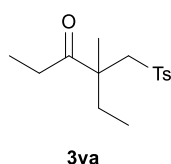


1H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, $J = 8.4$ Hz, 2H), 7.26 (d, $J = 8.4$ Hz, 2H), 3.83 (d, $J = 14.0$ Hz, 1H), 2.94 (d, $J = 13.6$ Hz, 1H), 2.80-2.72 (m, 1H), 2.53-2.46 (m, 1H), 2.36 (s, 3H), 2.01-1.94 (m, 1H), 1.61 (s, 3H), 1.48-1.39 (m, 2H), 1.31-1.05 (m, 17H).

¹³C NMR (101 MHz, CDCl₃): δ 212.95, 144.53, 138.92, 129.96, 127.73, 64.42, 50.21, 40.68, 37.03, 26.81, 26.36, 26.20, 25.22, 24.71, 23.81, 23.23, 21.87, 21.76, 20.95, 20.62.

HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₂₂H₃₄O₃SNa 401.2121, found 401.2123.

4-methyl-4-(tosylmethyl)hexan-3-one (3ya)



Colourless oil, 48.0 mg, 68% yield.

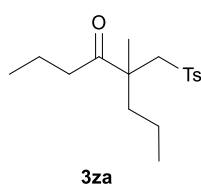
¹H NMR (400 MHz, CDCl₃): δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 3.66 (d, *J* = 14.0 Hz, 1H), 3.10 (d, *J* = 14.0 Hz, 1H), 2.66-2.57 (m, 1H), 2.50-2.42 (m, 1H), 2.37 (s, 3H), 1.67-1.60 (m, 1H),

1.54-1.47 (m, 4H), 1.00 (t, *J* = 7.2 Hz, 3H), 0.74 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 213.37, 144.60, 138.81, 129.98, 127.78, 63.17, 50.34, 32.62, 31.46, 21.75, 20.80, 8.54, 7.90.

HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₁₅H₂₂O₃SNa 305.1182, found 305.1184.

5-methyl-5-(tosylmethyl)octan-4-one (3za)



Colourless oil, 50.4 mg, 65% yield.

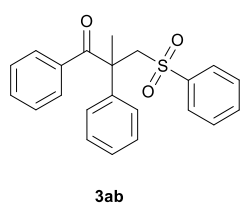
¹H NMR (400 MHz, CDCl₃): δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 3.64 (d, *J* = 14.0 Hz, 1H), 3.11 (d, *J* = 14.0 Hz, 1H), 2.60-2.52 (m, 1H), 2.44-2.39 (m, 1H), 2.37 (s, 3H), 1.61-1.52 (m,

3H), 1.49 (s, 3H), 1.44-1.36 (m, 1H), 1.16-1.06 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3H), 0.79 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 212.69, 144.57, 138.86, 129.97, 127.76, 63.18, 50.25, 41.90, 39.93, 21.76, 21.33, 17.43, 16.99, 14.52, 13.84.

HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₁₇H₂₆O₃SNa 333.1495, found 333.1497.

2-methyl-1,2-diphenyl-3-(phenylsulfonyl)propan-1-one (3ab)



White solid, 78.4 mg, 86% yield, mp 109-111 °C.

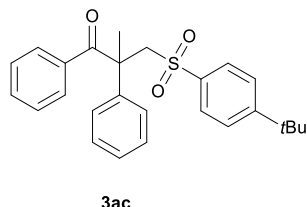
¹H NMR (400 MHz, CDCl₃): δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 6.4 Hz, 2H), 7.29-7.24 (m, 3H), 7.22-7.17 (m, 5H), 7.13 (t, *J* = 8.0 Hz, 2H), 3.99 (d, *J* = 14.4 Hz,

1H), 3.76 (d, *J* = 14.4 Hz, 1H), 2.04 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 201.19, 141.58, 139.25, 136.19, 133.19, 131.98, 129.35, 129.10, 128.21, 128.15, 127.58, 126.76, 65.60, 53.75, 22.20.

HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₂₂H₂₀O₃SNa 387.1025, found 387.1025.

3-((4-(*tert*-butyl)phenyl)sulfonyl)-2-methyl-1,2-diphenylpropan-1-one (3ac)



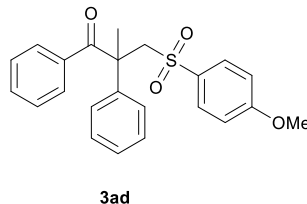
Colourless oil, 96.7 mg, 92% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.49 (dt, *J* = 8.4, 2.0 Hz, 2H), 7.30 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.27-7.09 (m, 10H), 3.97 (d, *J* = 14.8 Hz, 1H), 3.77 (d, *J* = 14.8 Hz, 1H), 2.03 (s, 3H), 1.22 (s, 9H).

¹³C NMR (101 MHz, CDCl₃): δ 201.19, 156.86, 139.21, 138.46, 136.22, 131.90, 129.31, 129.26, 128.15, 128.04, 127.43, 126.77, 126.05, 65.44, 53.66, 35.20, 31.14, 22.14.

HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₂₆H₂₈O₃SNa 443.1651, found 443.1651.

3-((4-methoxyphenyl)sulfonyl)-2-methyl-1,2-diphenylpropan-1-one (3ad)



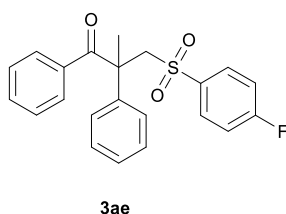
Colourless oil, 51.3 mg, 52% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.52 (dt, *J* = 8.4, 2.0 Hz, 2H), 7.32-7.28 (m, 1H), 7.26 (s, 1H), 7.24-7.19 (m, 6H), 7.17-7.13 (m, 2H), 6.79 (dt, *J* = 10.0, 2.4 Hz, 2H), 3.99 (d, *J* = 14.4 Hz, 1H), 3.77 (s, 3H), 3.72 (d, *J* = 14.4 Hz, 1H), 2.03 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 201.37, 163.40, 139.56, 136.39, 133.46, 131.95, 129.84, 129.40, 129.36, 128.23, 128.11, 126.80, 114.32, 65.86, 55.81, 53.82, 22.28.

HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₂₃H₂₂O₄SNa 417.1131, found 417.1133.

3-((4-fluorophenyl)sulfonyl)-2-methyl-1,2-diphenylpropan-1-one (3ae)



Colourless oil, 92.7 mg, 97% yield.

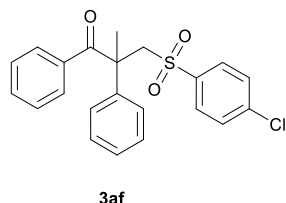
¹H NMR (400 MHz, CDCl₃): δ 7.60-7.57 (m, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.20 (s, 5H), 7.14 (t, *J* = 8.0 Hz, 2H), 6.98 (t, *J* = 8.4 Hz, 2H), 3.97 (d, *J* = 14.4 Hz,

1H), .3.79 (d, $J = 14.8$ Hz, 1H), 2.04 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 201.14, 164.47 (d, $J = 256.5$ Hz), 139.08, 137.66 (d, $J = 3.1$ Hz), 136.04, 132.12, 130.51 (d, $J = 9.7$ Hz), 129.43, 129.41, 128.28, 128.26, 126.87, 116.32 (d, $J = 22.6$ Hz), 65.90, 53.80, 22.13.

HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{19}\text{FO}_3\text{SNa}$ 405.0931, found 405.0932.

3-((4-chlorophenyl)sulfonyl)-2-methyl-1,2-diphenylpropan-1-one (3af)



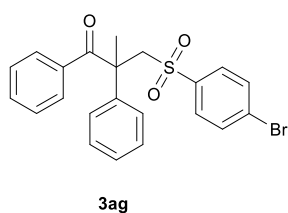
White solid, 85.8 mg, 86% yield, mp 89-91 °C.

^1H NMR (400 MHz, CDCl_3): δ 7.49 (dt, $J = 8.4, 2.4$ Hz, 2H), 7.31-7.23 (m, 5H), 7.19 (s, 5H), 7.14 (t, $J = 8.0$ Hz, 2H), 3.96 (d, $J = 14.8$ Hz, 1H), .3.79 (d, $J = 14.4$ Hz, 1H), 2.03 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 201.03, 139.93, 139.81, 138.98, 135.94, 132.10, 129.40, 129.38, 129.33, 129.12, 128.24, 128.22, 126.83, 65.80, 53.75, 22.10.

HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{19}\text{ClO}_3\text{SNa}$ 421.0636, found 421.0635.

3-((4-bromophenyl)sulfonyl)-2-methyl-1,2-diphenylpropan-1-one (3ag)



White solid, 92.0 mg, 83% yield, mp 109-111 °C.

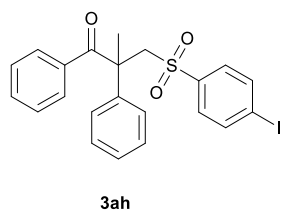
^1H NMR (400 MHz, CDCl_3): δ 7.47-7.41 (m, 4H), 7.31 (t, $J = 7.6$ Hz, 1H), 7.25 (d, $J = 8.0$ Hz, 2H), 7.20 (s, 5H), 7.15 (t, $J = 7.6$ Hz, 2H), 3.96 (d, $J = 14.8$ Hz, 1H), .3.80 (d, $J = 14.4$ Hz,

1H), 2.04 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 201.10, 140.51, 139.02, 135.99, 132.38, 132.17, 129.47, 129.44, 129.25, 128.48, 128.30, 128.28, 126.90, 65.86, 53.81, 22.13.

HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{19}\text{BrO}_3\text{SNa}$ 465.0130, found 465.0130.

3-((4-iodophenyl)sulfonyl)-2-methyl-1,2-diphenylpropan-1-one (3ah)



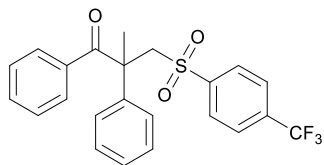
White solid, 90.7 mg, 74% yield, mp 96-97 °C.

^1H NMR (400 MHz, CDCl_3): δ 7.66 (dt, $J = 8.4, 2.0$ Hz, 2H), 7.33-7.23 (m, 5H), 7.21-7.18 (m, 5H), 7.15 (t, $J = 8.0$ Hz, 2H), 3.95 (d, $J = 14.8$ Hz, 1H), .3.79 (d, $J = 14.8$ Hz, 1H), 2.03 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 201.06, 141.14, 139.01, 138.34, 136.00, 132.13, 129.46, 129.42, 129.06, 128.28, 128.24, 126.88, 101.05, 65.79, 53.78, 22.12.

HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₂₂H₁₉IO₃SNa 512.9992, found 512.9990.

2-methyl-1,2-diphenyl-3-((4-(trifluoromethyl)phenyl)sulfonyl)propan-1-one (3ai)



3ai

White solid, 103.7 mg, 96% yield, mp 87-89 °C.

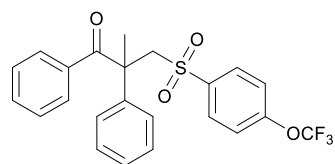
¹H NMR (400 MHz, CDCl₃): δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.33-7.29 (m, 1H), 7.27-7.23 (m, 2H), 7.16-7.13 (m, 7H), 3.96 (d, *J* = 14.8 Hz, 1H), 3.89 (d,

J = 14.8 Hz, 1H), 2.06 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 200.94, 144.76, 138.66, 135.78, 134.71 (q, *J* = 22.6 Hz), 132.26, 129.48, 129.43, 128.40, 128.32, 128.28, 126.97, 126.18 (q, *J* = 3.7 Hz), 123.31 (q, *J* = 274.2 Hz), 65.75, 53.78, 22.05.

HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₂₃H₁₉F₃O₃SNa 455.0899, found 455.0899.

2-methyl-1,2-diphenyl-3-((4-(trifluoromethoxy)phenyl)sulfonyl)propan-1-one (3aj)



3aj

White solid, 95.3 mg, 85% yield, mp 99-101 °C.

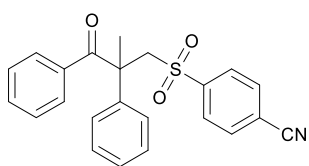
¹H NMR (400 MHz, CDCl₃): δ 7.58 (dt, *J* = 8.8, 2.8 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.25-7.23 (m, 2H), 7.19-7.15 (m, 6H), 7.12 (t, *J* = 8.4 Hz, 3H), 3.94 (d, *J* = 14.8

Hz, 1H), 3.87 (d, *J* = 15.2 Hz, 1H), 2.05 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 201.04, 152.46, 139.74, 138.75, 135.88, 132.19, 129.91, 129.46, 129.40, 128.31, 128.30, 126.99, 120.98, 120.36 (q, *J* = 260.4 Hz), 65.81, 53.75, 22.06.

HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₂₃H₁₉F₃O₄SNa 471.0848, found 471.0848.

4-((2-methyl-3-oxo-2,3-diphenylpropyl)sulfonyl)benzonitrile (3ak)



3ak

White solid, 79.8 mg, 82% yield, mp 139-140 °C.

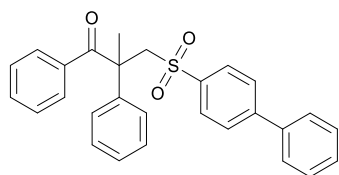
¹H NMR (400 MHz, CDCl₃): δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J*

= 8.0 Hz, 2H), 7.17-7.12 (m, 7H), 3.95 (d, $J = 14.8$ Hz, 1H), 3.88 (d, $J = 13.2$ Hz, 1H), 2.05 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 200.81, 145.37, 138.64, 135.60, 132.76, 132.30, 129.44, 128.42, 128.33, 128.31, 126.95, 117.35, 116.73, 65.86, 53.80, 22.01.

HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{19}\text{NO}_3\text{SNa}$ 412.0978, found 412.0984.

3-([1,1'-biphenyl]-4-ylsulfonyl)-2-methyl-1,2-diphenylpropan-1-one (3al)



3al

White solid, 41.8 mg, 38% yield, mp 58-60 °C.

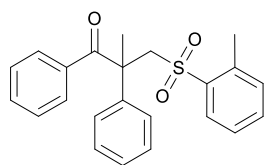
^1H NMR (400 MHz, CDCl_3): δ 7.63 (dt, $J = 8.4, 2.0$ Hz, 2H), 7.52-7.47 (m, 4H), 7.42-7.37 (m, 2H), 7.36-7.33 (m, 1H), 7.32-7.17 (m, 8H), 7.16-7.12 (m, 2H), 4.02 (d, $J =$

14.8 Hz, 1H), 3.83 (d, $J = 14.4$ Hz, 1H), 2.06 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 201.24, 146.11, 140.05, 139.48, 139.26, 136.20, 132.03, 129.41, 129.39, 129.22, 128.70, 128.25, 128.18, 128.13, 127.76, 127.50, 126.88, 65.72, 53.80, 22.23.

HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{28}\text{H}_{24}\text{O}_3\text{SNa}$ 463.1338, found 463.1339.

2-methyl-1,2-diphenyl-3-(*o*-tolylsulfonyl)propan-1-one (3am)



3am

Colourless oil, 73.8 mg, 78% yield.

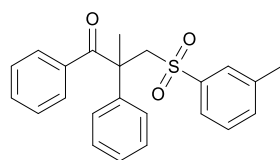
^1H NMR (400 MHz, CDCl_3): δ 7.63 (dd, $J = 8.4, 0.8$ Hz, 1H), 7.33-7.26 (m, 2H), 7.25-7.17 (m, 7H), 7.14-7.10 (m, 4H), 3.99 (d, $J = 14.4$ Hz, 1H), 3.74 (d, $J = 14.4$ Hz, 1H), 2.53 (s, 3H),

2.03 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 201.26, 139.53, 139.49, 137.66, 136.24, 133.35, 132.60, 131.96, 129.75, 129.35, 129.33, 128.21, 128.16, 126.66, 126.56, 64.49, 53.73, 22.28, 20.42.

HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{22}\text{O}_3\text{SNa}$ 401.1182, found 401.1182.

2-methyl-1,2-diphenyl-3-(*m*-tolylsulfonyl)propan-1-one (3an)



3an

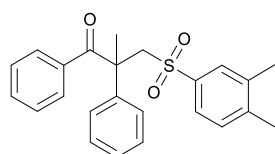
White solid, 81.4 mg, 86% yield, mp 99-101 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.42 (dt, *J* = 6.8, 2.0 Hz, 1H), 7.32-7.12 (m, 13H), 3.96 (d, *J* = 14.8 Hz, 1H), 3.79 (d, *J* = 14.4 Hz, 1H), 2.26 (s, 3H), 2.04 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 201.27, 141.45, 139.29, 136.27, 134.04, 132.00, 129.42, 129.28, 129.02, 128.25, 128.13, 127.98, 126.87, 124.72, 65.58, 53.76, 22.31, 21.41.

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₃H₂₂O₃SNa 401.1182, found 401.1180.

3-((3,4-dimethylphenyl)sulfonyl)-2-methyl-1,2-diphenylpropan-1-one (3ao)



3ao

White solid, 85.4 mg, 87% yield, mp 135-136 °C.

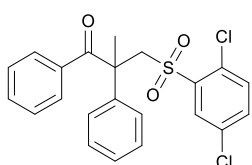
¹H NMR (400 MHz, CDCl₃): δ 7.35 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.26-7.24 (m, 3H), 7.22-7.19 (m, 5H), 7.15 (t, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 1H), 3.97 (d, *J* =

14.8 Hz, 1H), 3.75 (d, *J* = 14.4 Hz, 1H), 2.21 (s, 3H), 2.16 (s, 3H), 2.03 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 201.31, 142.86, 139.52, 138.88, 137.78, 136.38, 131.92, 130.24, 129.39, 129.25, 128.46, 128.21, 128.00, 126.82, 125.14, 65.64, 53.77, 22.36, 20.08, 19.88.

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₄H₂₄O₃SNa 415.1338, found 415.1335.

3-((2,5-dichlorophenyl)sulfonyl)-2-methyl-1,2-diphenylpropan-1-one (3ap)



3ap

White solid, 81.3 mg, 75% yield, mp 143-145 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.39-7.38 (m, 1H), 7.36-7.33 (m, 3H), 7.30-7.26 (m, 2H), 7.25-7.21 (m, 3H), 7.19 (s, 1H), 7.17-7.14 (m, 3H), 4.70 (d, *J* = 15.6 Hz, 1H), 3.89 (d, *J* = 15.6 Hz,

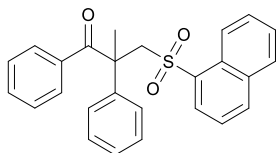
1H), 2.10 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 200.60, 139.43, 137.71, 135.28, 133.91, 133.49, 132.46, 132.37, 131.09, 130.31, 129.74, 129.06, 128.67, 128.31, 127.10, 63.36, 53.59, 22.44.

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₂H₁₈Cl₂O₃SNa 455.0246, found 455.0248.

2-methyl-3-(naphthalen-1-ylsulfonyl)-1,2-diphenylpropan-1-one (3aq)

White solid, 63.2mg, 61% yield, mp 83-85 °C.



3aq

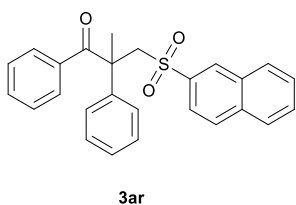
¹H NMR (400 MHz, CDCl₃): δ 8.51 (d, *J* = 8.4 Hz, 1H), 7.90 (t, *J* = 7.6 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.58-7.54 (m, 1H), 7.51-7.47 (m, 1H), 7.34-7.24 (m, 4H), 7.14-7.08 (m, 7H), 4.14 (d, *J* = 14.8 Hz, 1H), 3.98 (d, *J* = 14.8 Hz, 1H), 2.09 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 201.17, 139.21, 136.22, 136.13, 134.88, 134.15, 132.01, 130.17, 129.45, 129.23, 129.14, 128.79, 128.52, 128.23, 128.09, 126.95, 126.72, 124.49, 124.25, 64.68, 53.87, 22.45.

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₆H₂₂O₃SNa 437.1182, found 437.1181.

2-methyl-3-(naphthalen-2-ylsulfonyl)-1,2-diphenylpropan-1-one (3ar)

Colourless oil, 56.0 mg, 54% yield.



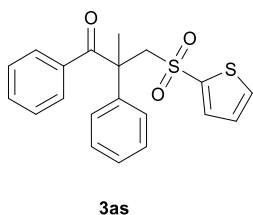
¹H NMR (400 MHz, CDCl₃): δ 8.12 (d, *J* = 1.6 Hz, 1H), 7.87-7.84 (m, 3H), 7.69 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.65-7.55 (m, 2H), 7.39-7.32 (m, 3H), 7.30-7.26 (m, 2H), 7.22-7.15 (m, 4H), 7.10-7.06 (m, 1H), 4.12 (d, *J* = 14.4 Hz, 1H), 3.96 (d, *J* = 14.8 Hz, 1H), 2.15 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 201.21, 139.08, 138.32, 136.19, 135.09, 132.13, 132.01, 129.61, 129.45, 129.42, 129.41, 129.24, 129.17, 128.24, 128.19, 127.99, 127.56, 126.82, 122.45, 65.45, 53.81, 22.32.

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₆H₂₂O₃SNa 437.1182, found 437.1180.

2-methyl-1,2-diphenyl-3-(thiophen-2-ylsulfonyl)propan-1-one (3as)

Colourless oil, 52.8 mg, 57% yield.



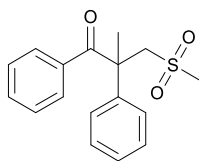
¹H NMR (400 MHz, CDCl₃): δ 7.50 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.32-7.27 (m, 3H), 7.26-7.24 (m, 5H), 7.23-7.20 (m, 1H), 7.16-7.13 (m, 2H), 6.89 (dd, *J* = 5.2, 4.0 Hz, 1H), 4.10 (d, *J* = 14.8 Hz, 1H), 3.89 (d, *J* = 14.8 Hz, 1H), 2.04 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 201.05, 142.99, 139.22, 136.04, 133.70, 133.61, 132.10, 129.46, 129.44, 128.26, 128.24, 127.72, 126.85, 67.17, 53.97, 22.13.

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₀H₁₈O₃S₂Na 393.0590, found 393.0588.

2-methyl-3-(methylsulfonyl)-1,2-diphenylpropan-1-one (3at)

White solid, 64.3 mg, 85% yield, mp 118-120 °C.



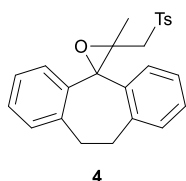
3at

¹H NMR (400 MHz, CDCl₃): δ 7.46-7.36 (m, 8H), 7.26-7.23 (m, 2H), 3.75 (dd, *J* = 17.2, 15.2 Hz, 2H), 2.37 (s, 3H), 2.08 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 201.16, 139.44, 135.42, 132.43, 129.82, 129.74, 128.64, 128.35, 127.07, 65.03, 53.71, 43.47, 21.71.

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₁₇H₁₈O₃SNa 325.0869, found 325.0869.

3'-methyl-3'-(tosylmethyl)-10,11-dihydrospiro[dibenzo[*a,d*][7]annulene-5,2'-oxirane] (4)



4

White solid, 73.8 mg, 73% yield, mp 167-169 °C.

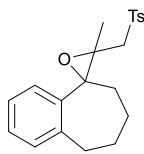
¹H NMR (400 MHz, CDCl₃): δ 7.60 (dt, *J* = 8.4, 2.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.24-7.22 (m, 1H), 7.13-7.00 (m, 5H), 6.85 (t, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 3.34-3.27 (m, 1H), 3.23-3.15

(m, 2H), 2.94 (d, *J* = 14.4 Hz, 1H), 2.90-2.78 (m, 2H), 2.41 (s, 3H), 1.32 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 144.77, 137.90, 137.86, 137.69, 137.41, 135.94, 129.95, 129.76, 128.89, 128.58, 128.25, 128.17, 126.21, 126.07, 125.89, 125.71, 68.76, 64.07, 59.87, 32.64, 31.77, 21.87, 18.14.

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₁₇H₁₈O₃SNa 427.1338, found 427.1332.

(5S)-3'-methyl-3'-(tosylmethyl)-6,7,8,9-tetrahydrospiro[benzo[7]annulene-5,2'-oxirane] (5)



5

White solid, 54.3 mg, 61% yield, mp 95-97 °C.

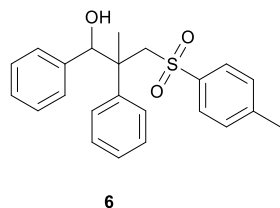
¹H NMR (400 MHz, CDCl₃): δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 6.0 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.43 (d, *J* = 7.6 Hz, 1H), 3.07 (d, *J* = 15.6 Hz, 1H),

2.70-2.54 (m, 3H), 2.40 (s, 3H), 1.93-1.63 (m, 8H), 1.31-1.25 (m, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 144.64, 139.93, 139.27, 137.63, 129.60, 129.22, 128.62, 128.03, 126.26, 125.91, 68.69, 61.54, 60.04, 36.08, 33.36, 27.32, 27.28, 21.85, 18.67.

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₁₇H₁₈O₃SNa 379.1338, found 379.1333.

2-methyl-1,2-diphenyl-3-tosylpropan-1-ol (**6**)



6

White solid, 129.4 mg, 68% yield, mp 115-117 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.54 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.15-7.04 (m, 10H), 6.79 (d, *J* = 7.6 Hz, 2H), 4.99 (s, 1H), 3.74 (d, *J* = 14.4 Hz, 1H), 3.60 (d, *J* = 14.4 Hz, 1H), 2.54 (s, 1H), 2.33 (s, 3H), 1.61 (s, 3H).

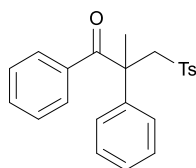
¹³C NMR (101 MHz, CDCl₃): δ 144.42, 140.49, 139.54, 138.54, 129.86, 128.25, 127.98, 127.84, 127.63, 127.10, 80.63, 64.33, 47.03, 21.74, 20.71.

HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₁₇H₁₈O₃SNa 403.1338, found 403.1337.

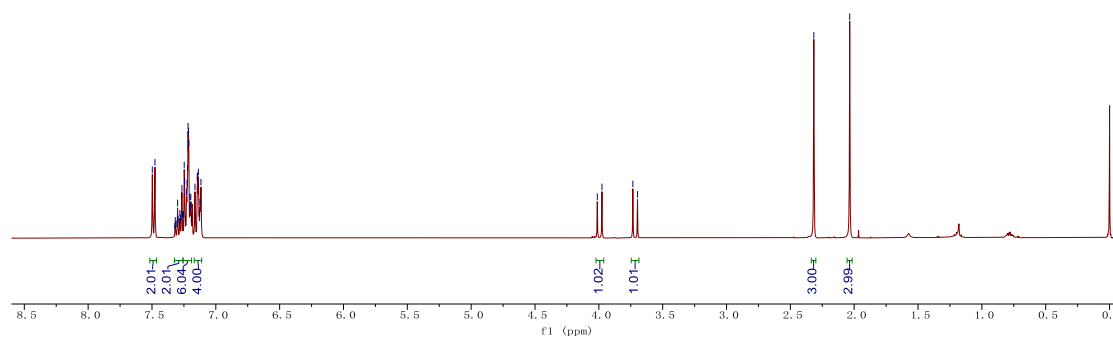
4. References

1. X. Mo and D. G. Hall, *J. Am. Chem. Soc.*, 2016, **138**, 10762-10765.
2. P. Xu, K. Hu, Z. Gu, Y. Cheng and C. Zhu, *Chem. Commun.*, 2015, **51**, 7222-7225.
3. L. Zheng, H. Huang, C. Yang and W. Xia, *Org. Lett.*, 2015, **17**, 1034-1037.
4. Z. Deng, J. Wei, L. Liao, H. Huang and X. Zhao, *Org. Lett.*, 2015, **17**, 1834-1837.
5. G. Barker, D. G. Johnson, P. C. Young, S. A. Macgregor and A.-L. Lee, *Chem. Eur. J.*, 2015, **21**, 13748-13757.
6. K. Zhang, T. Liang, Y. Wang, C. He, M. Hu, X.-H. Duan and L. Liu, *Org. Chem. Front.*, 2022, **9**, 966-972.
7. J. Yang, G. Li, K. Yu, B. Xu, and Q. Chen, *J. Org. Chem.* 2022, **87**, 1208-1217.
8. H. -D. Zuo, W.-J. Hao, C. -F. Zhu, C. Guo, S. -J. Tu, and B. Jiang, *Org. Lett.*, 2020, **22**, 4471-4477.
9. J. R. Thondur, D. S. Sharada, and G. Satyanarayana, *Org. Lett.*, 2023, **25**, 2793-2797.
10. Y. Yuan, Y. Cao, Y. Lin, Y. Li, Z. Huang, and A. Lei, *ACS Catal.*, 2018, **8**, 10871-10875.
11. R. A. Sheldon, *Green Chem.*, 2007, **9**, 1273-1283.
12. K. V. Aken, L. Streckowski, and L. Patiny, *Beilstein J. Org. Chem.*, **2**, 3-9.
13. B. M. Trost, *Angew. Chem. Int. Ed.*, 1995, **34**, 259-281.
14. X. -Q. Chu, H. Meng, X. -P. Xu, and S. -J. Ji, *Chem. Eur. J.*, 2015, **21**, 11359-11368.
15. X. Zhang, Z. Zhang, J. -N. Song, and Z. Wang, *Chem. Sci.*, 2020, **11**, 7921-7926.

5. ^1H NMR and ^{13}C NMR of products



3aa ^1H NMR (400 MHz, CDCl_3)



201.310

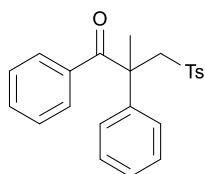
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131.948
129.743
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128.221
128.081
127.683
126.768

77.519 CDCl_3
77.201 CDCl_3
76.883 CDCl_3

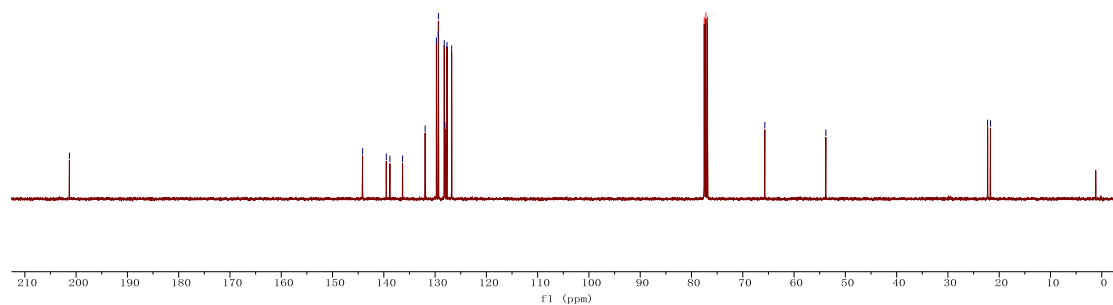
65.705

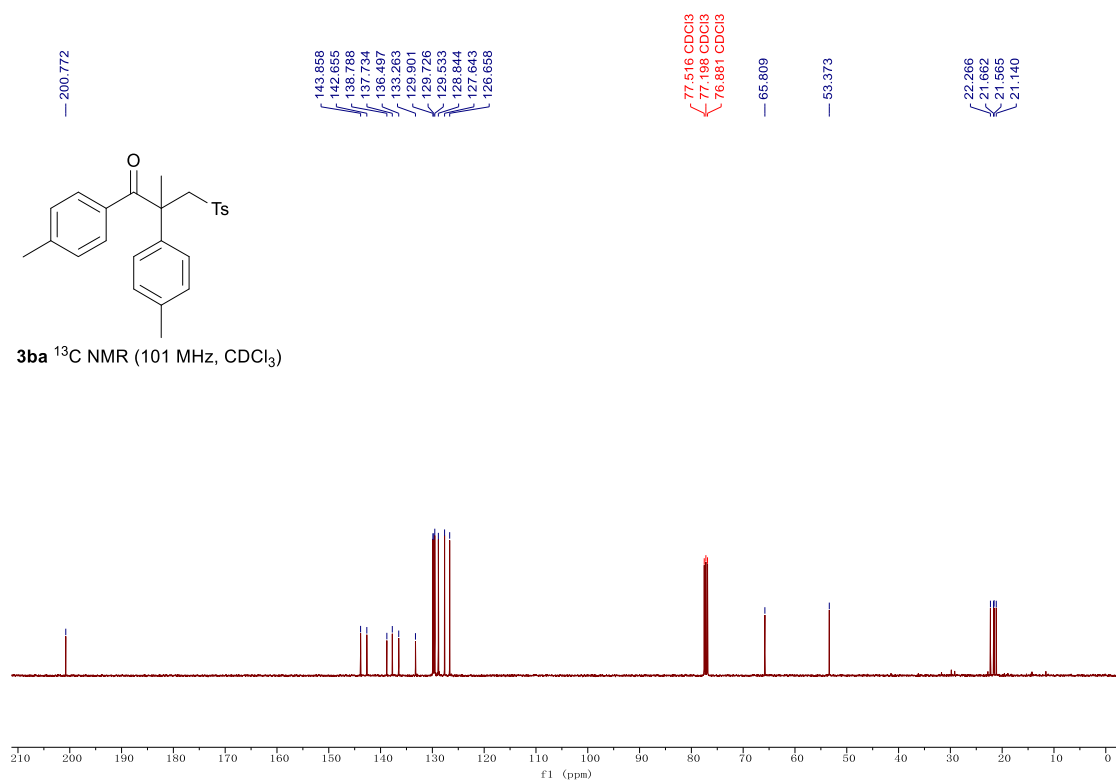
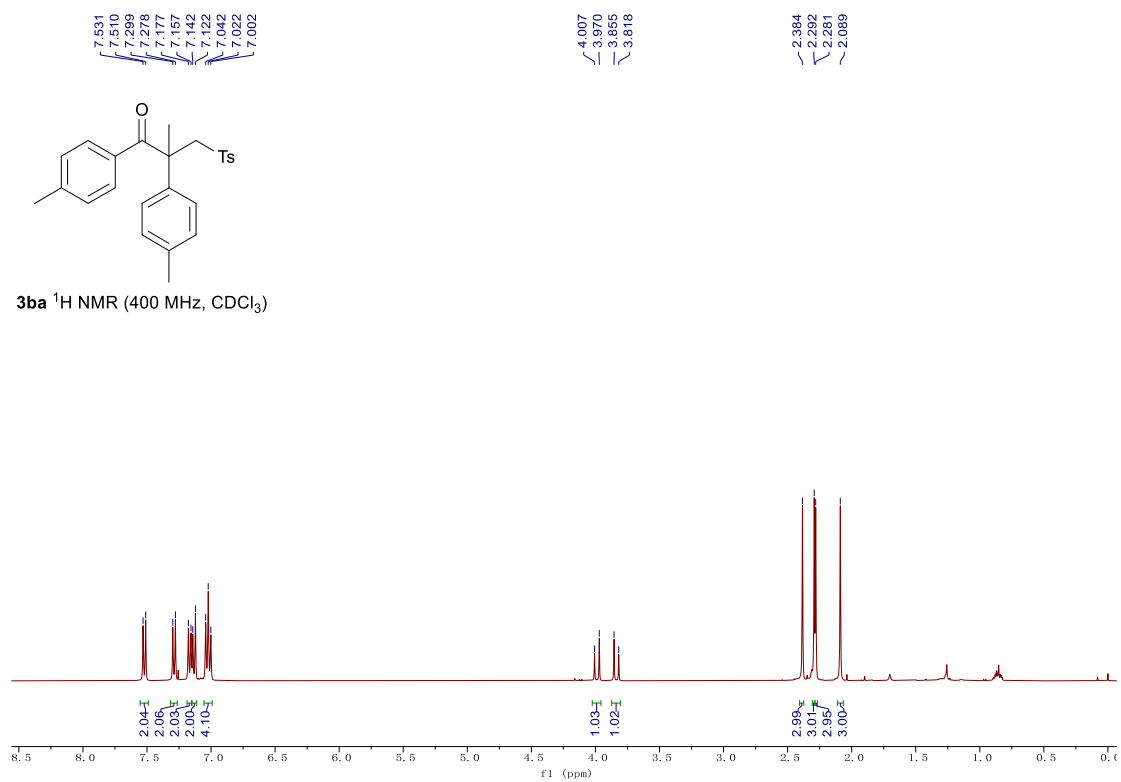
53.805

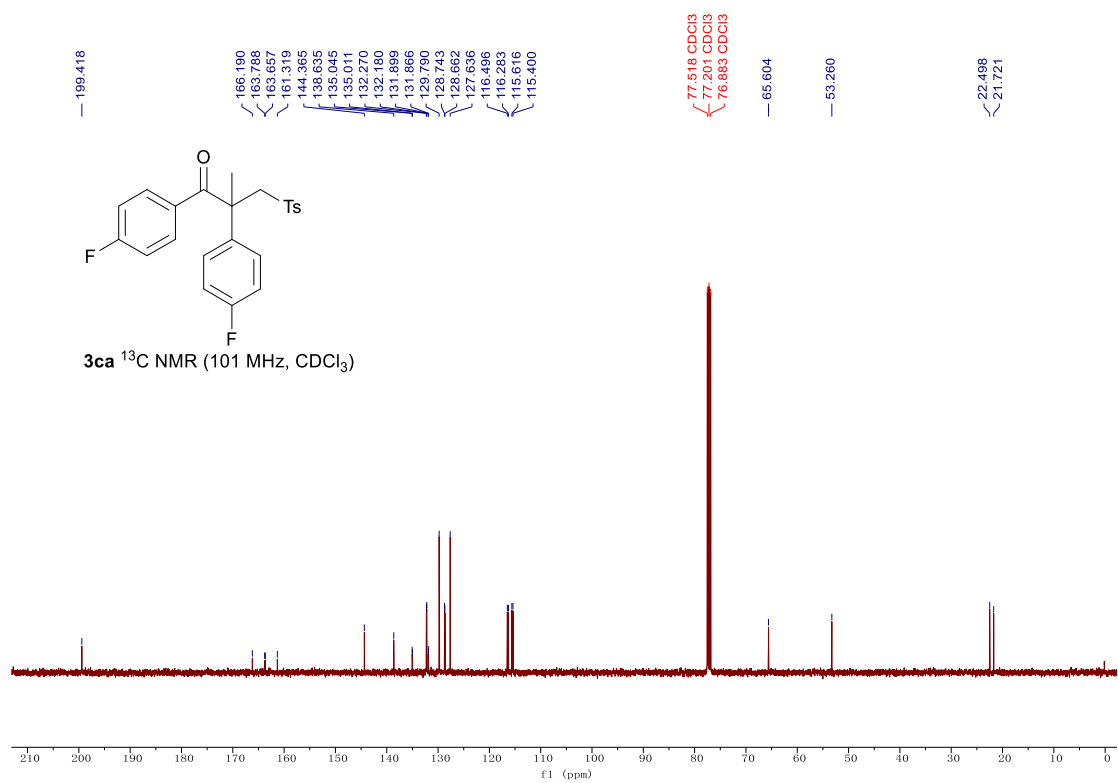
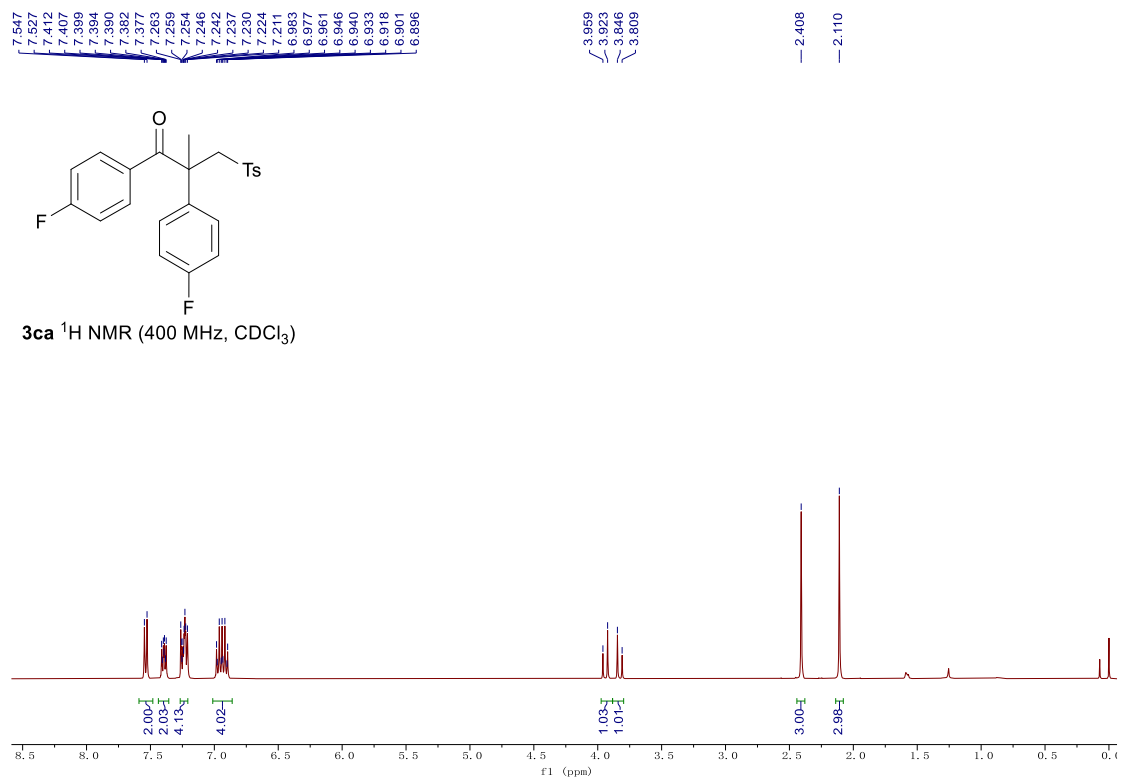
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21.707

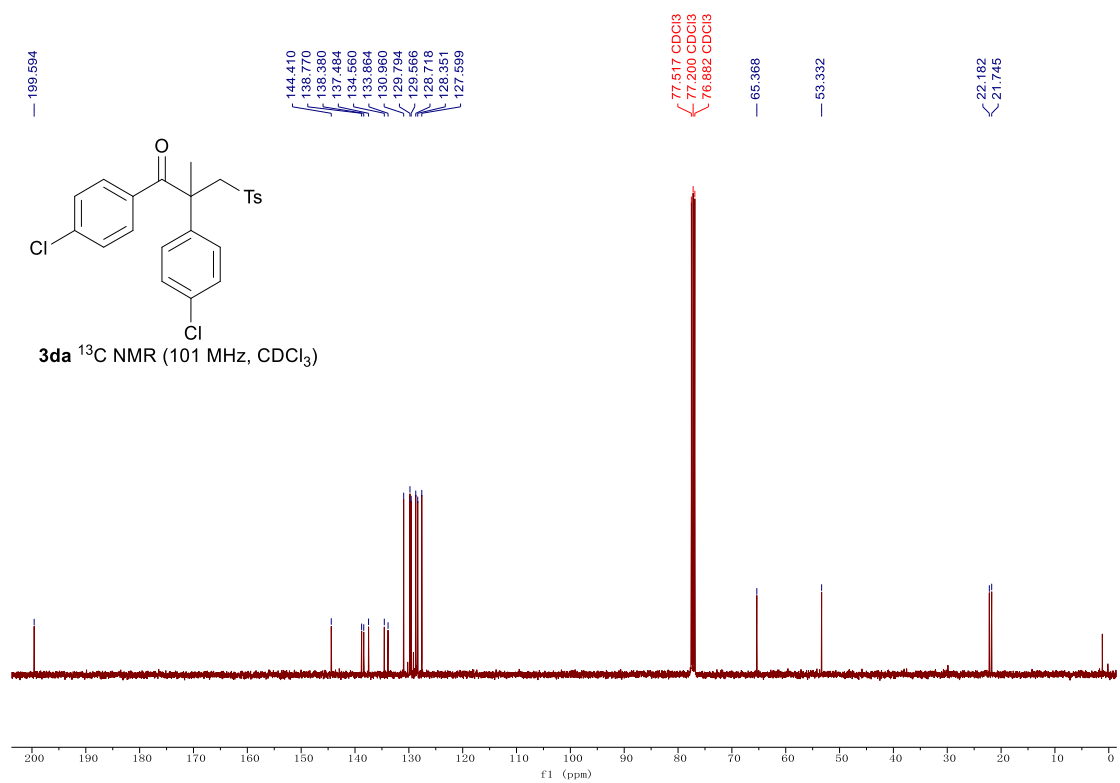
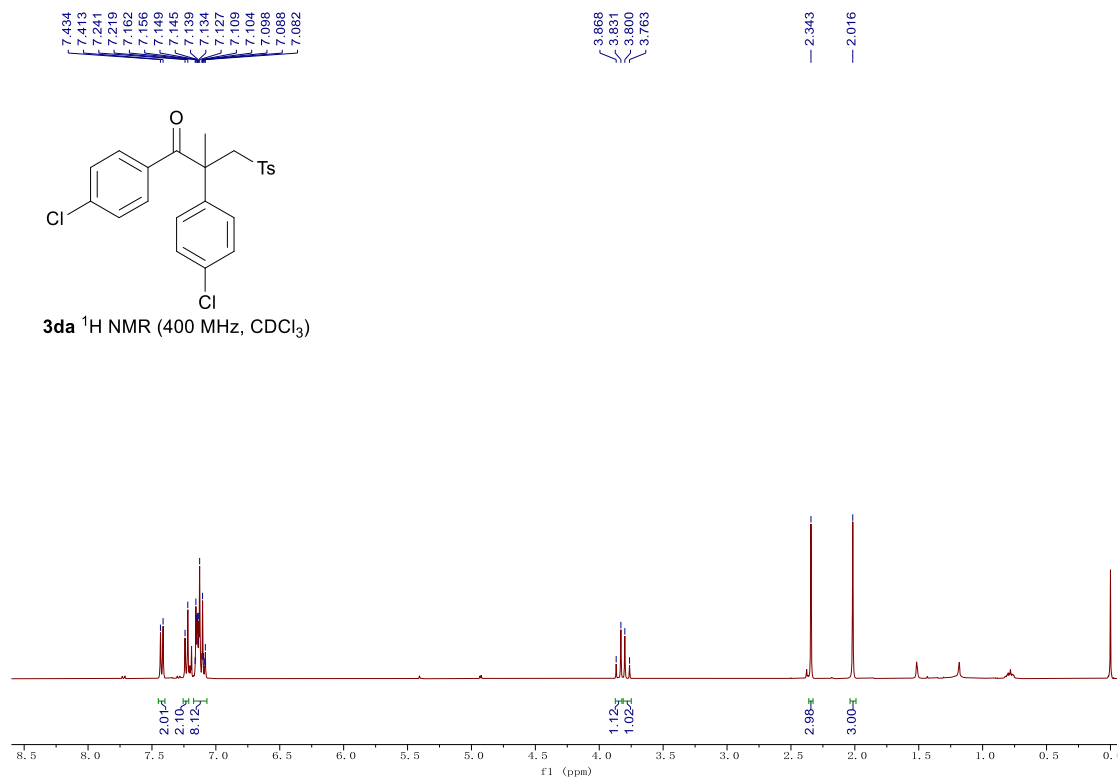


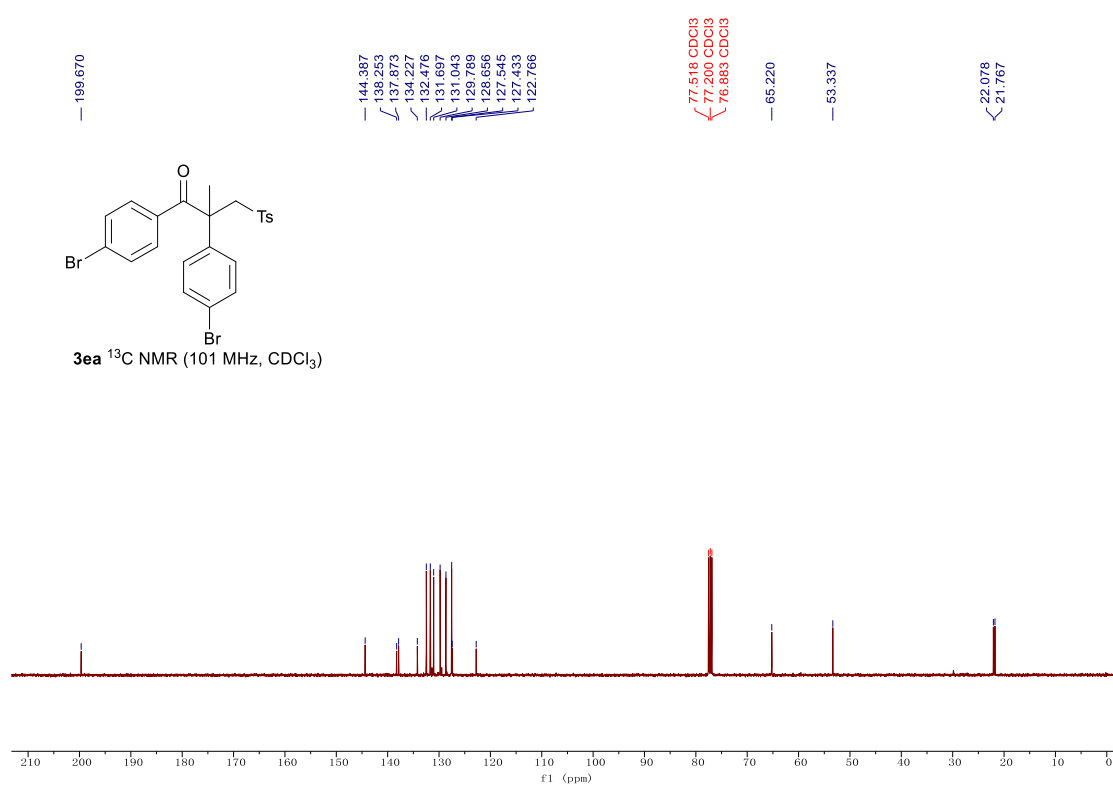
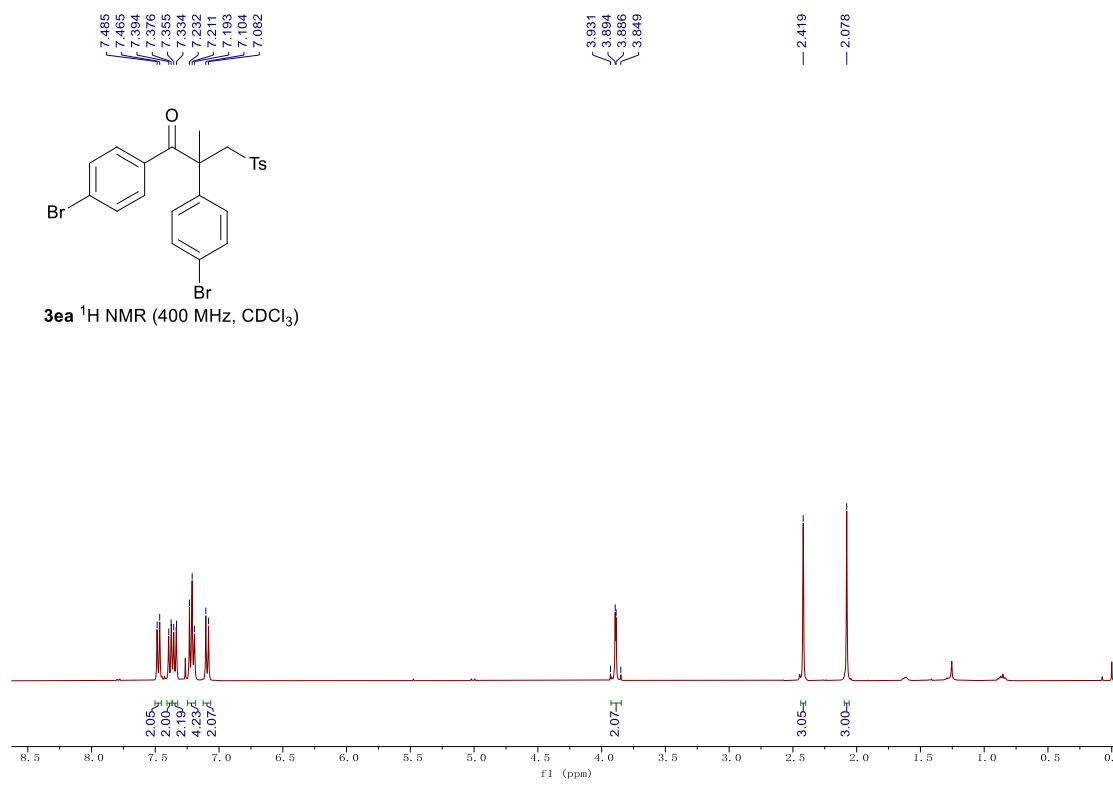
3aa ^{13}C NMR (101 MHz, CDCl_3)







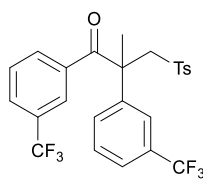




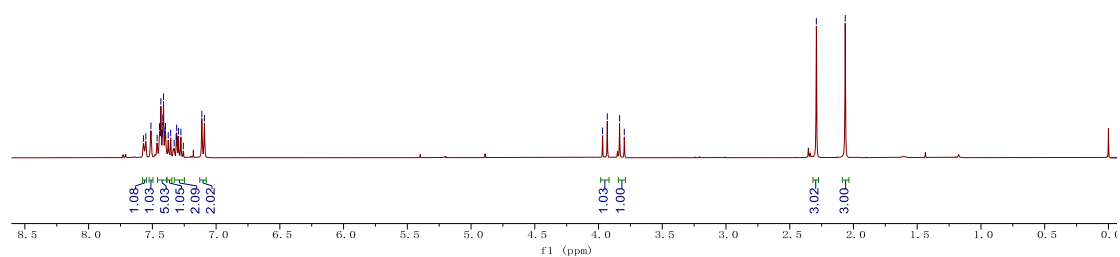
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7.439
7.433
7.429
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7.417
7.412
7.402
7.397
7.396
7.356
7.326
7.314
7.309
7.305
7.295
7.276
7.257
7.112
7.092

3.968
3.931
3.835
3.798

2.291
2.065



3fa ^1H NMR (400 MHz, CDCl_3)



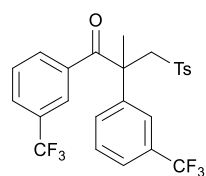
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144.637
139.861
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136.318
132.399
132.186
132.076
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131.585
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130.831
130.824
130.494
130.108
129.882
129.038
128.816
128.781
128.746
128.711
127.566
126.274
126.234
126.195
126.156
125.351
125.314
125.277
125.241
125.068
124.847
123.676
123.639
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122.138
119.646
119.429

77.507 CDCl_3
77.189 CDCl_3
76.871 CDCl_3

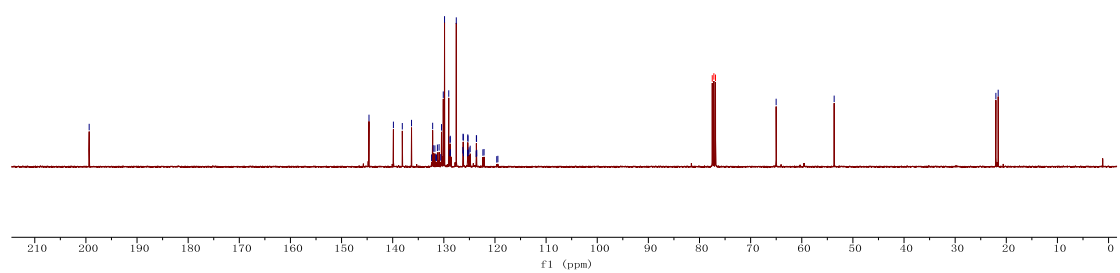
65.012

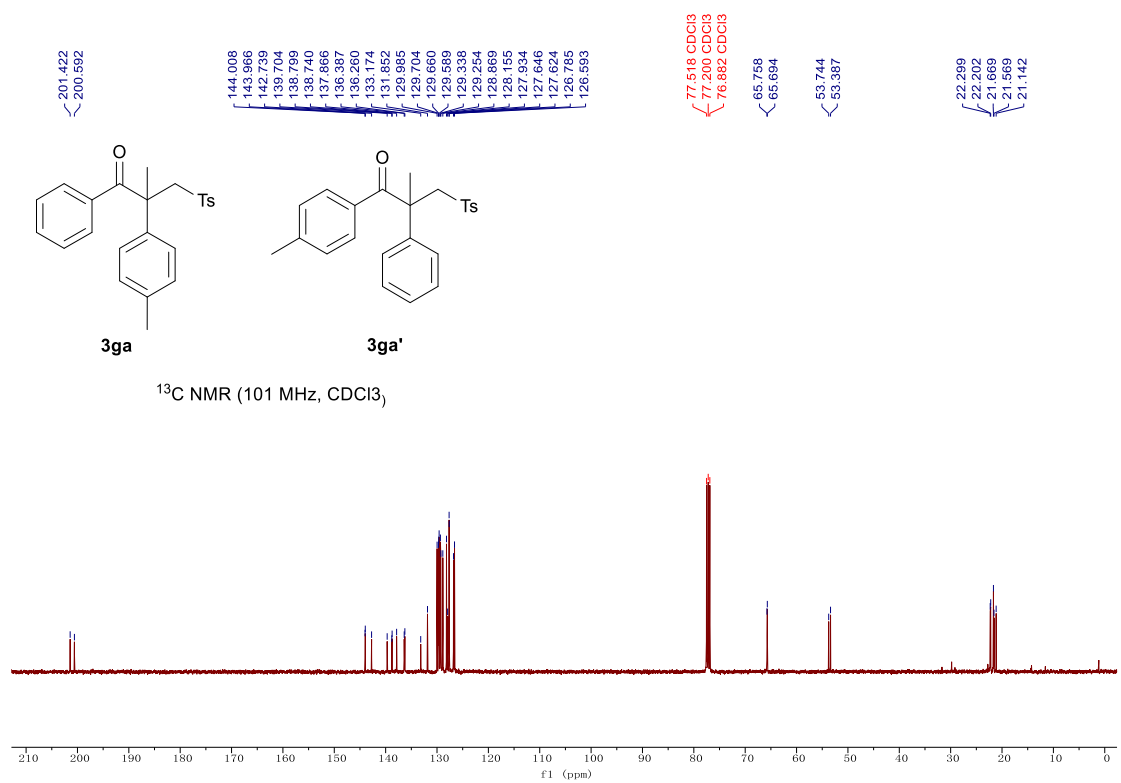
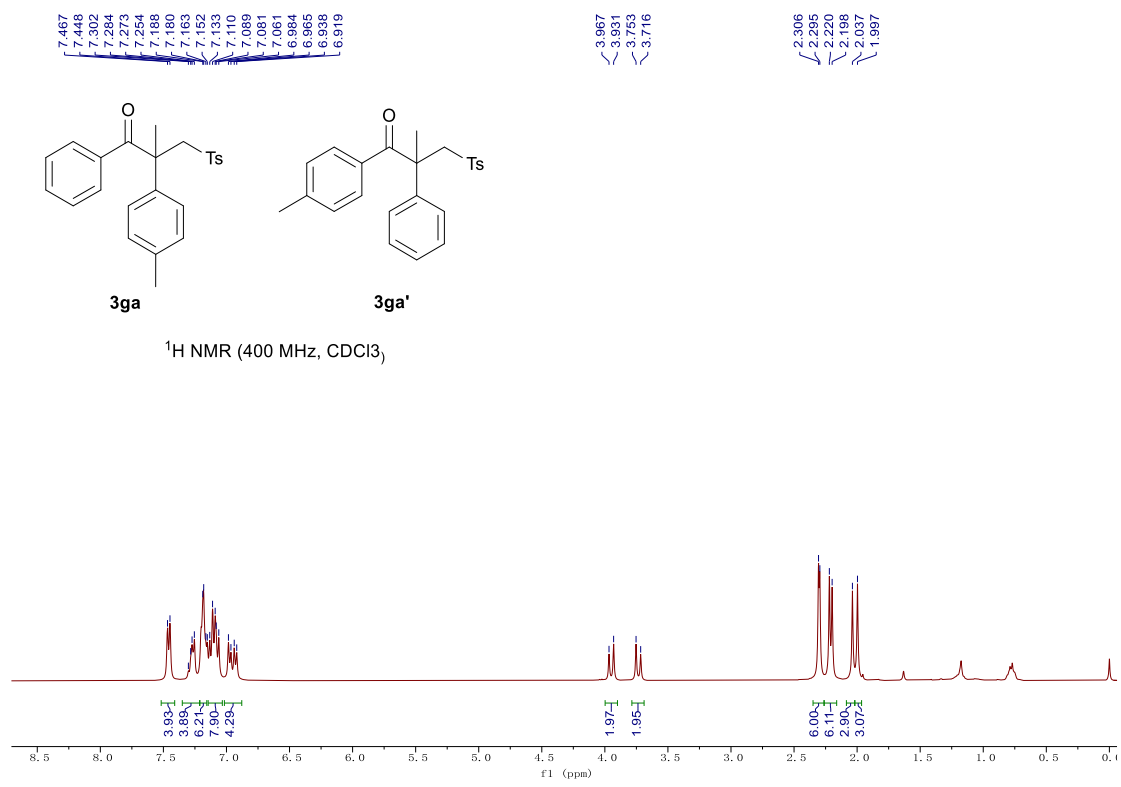
53.665

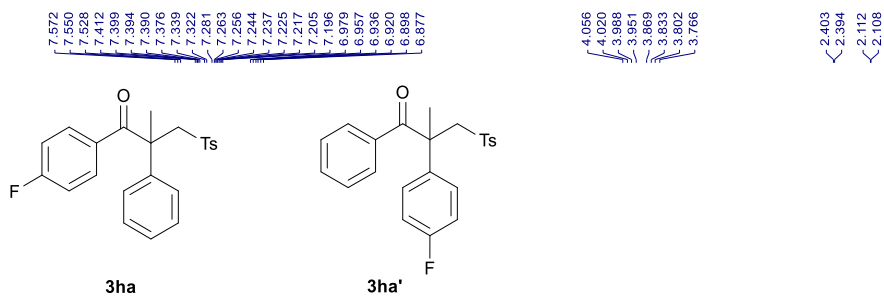
22.037
21.587



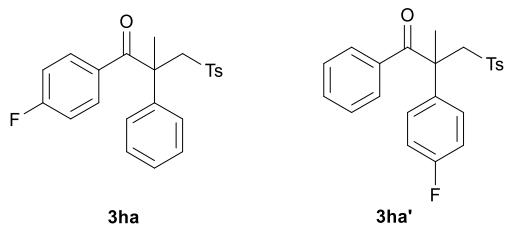
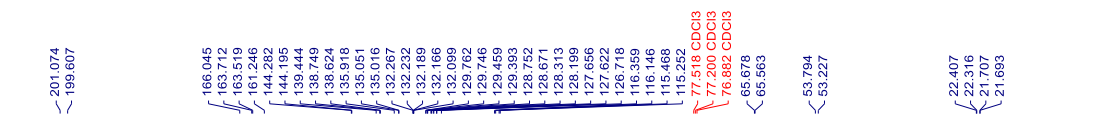
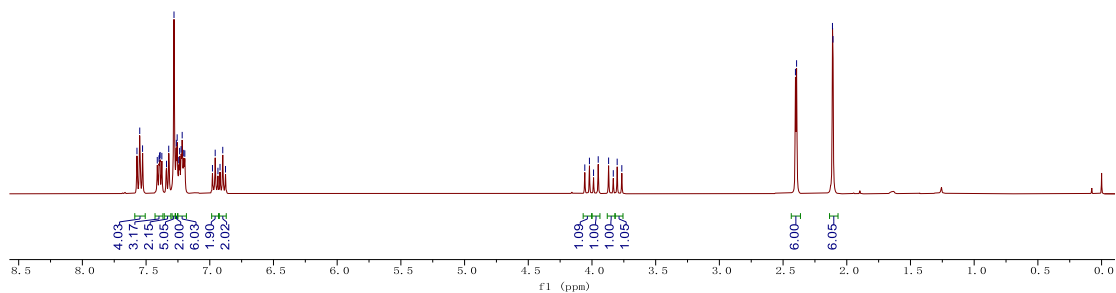
3fa ^{13}C NMR (101 MHz, CDCl_3)



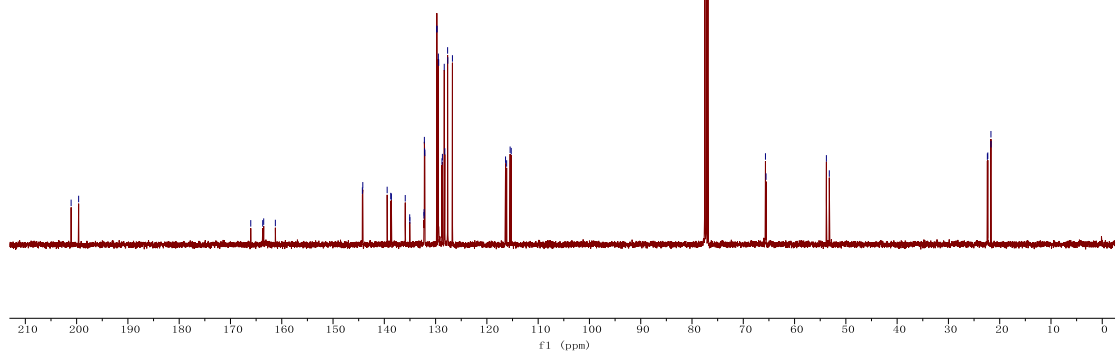


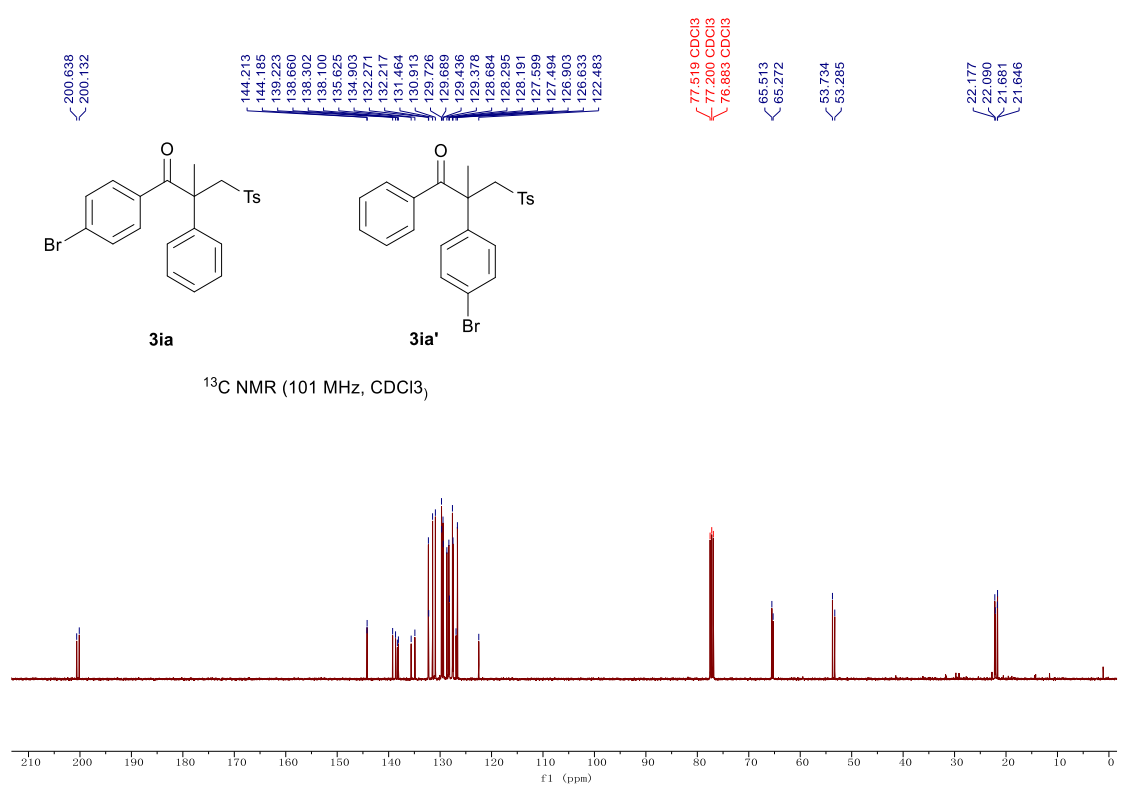
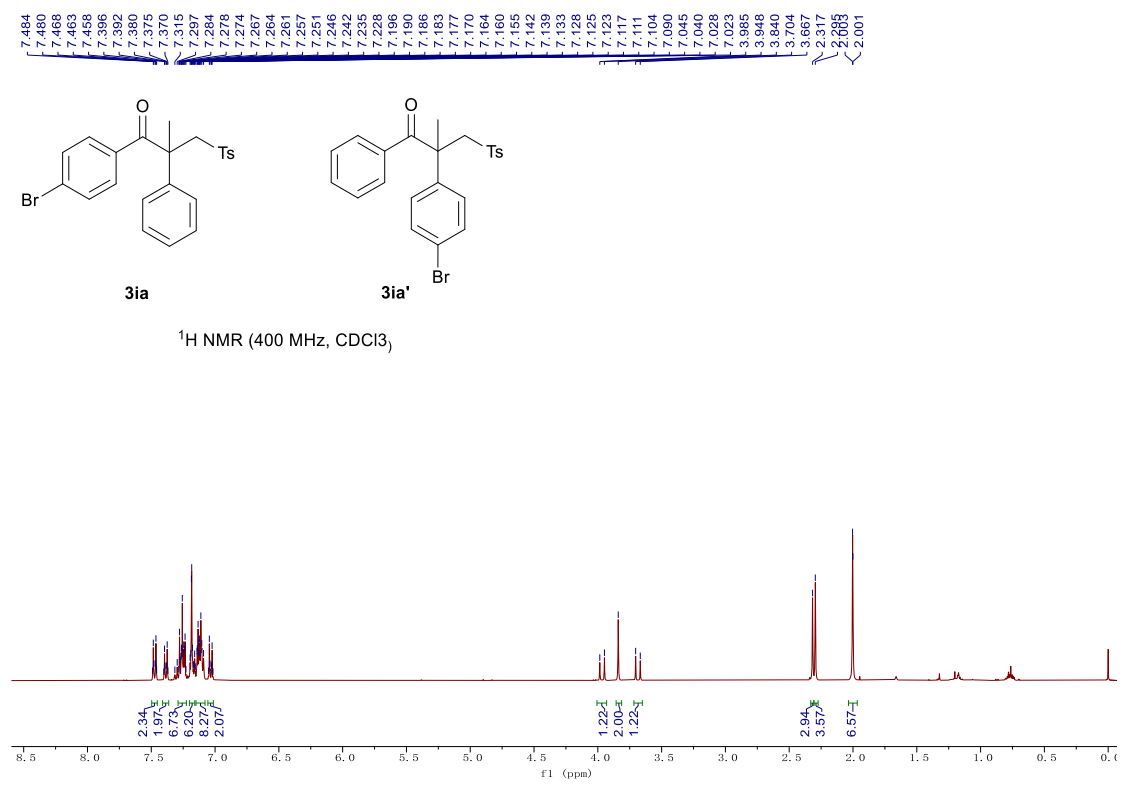


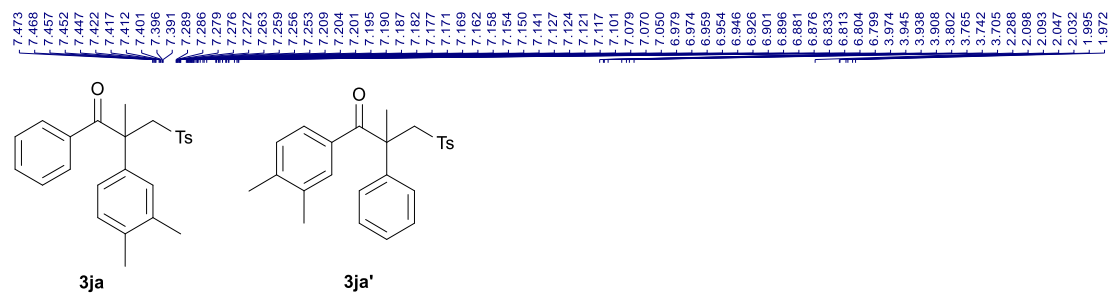
¹H NMR (400 MHz, CDCl₃)



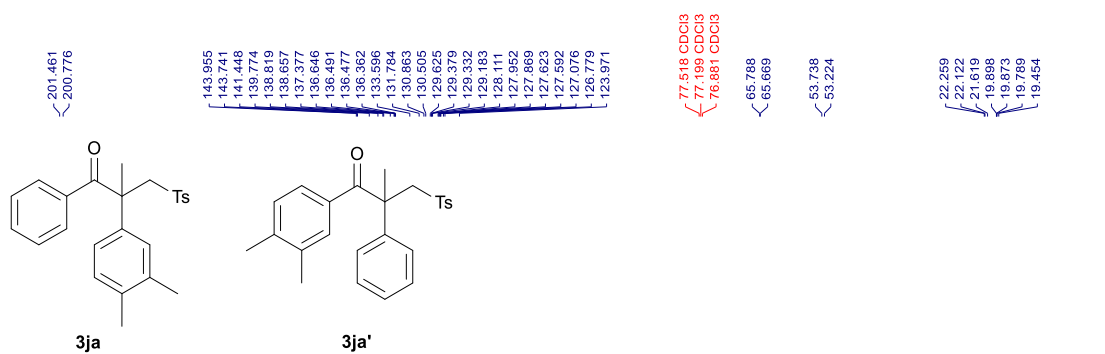
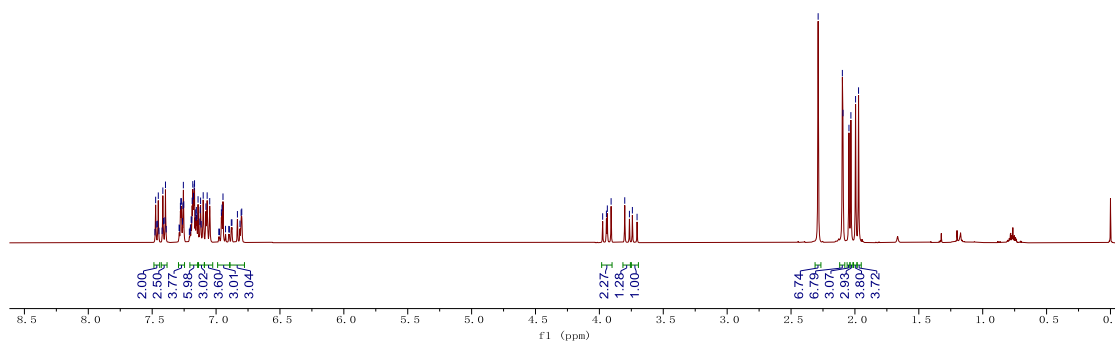
¹³C NMR (101 MHz, CDCl₃)



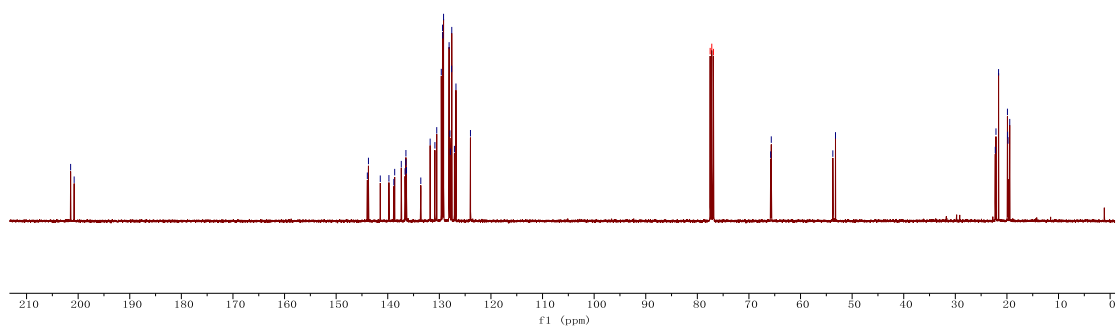


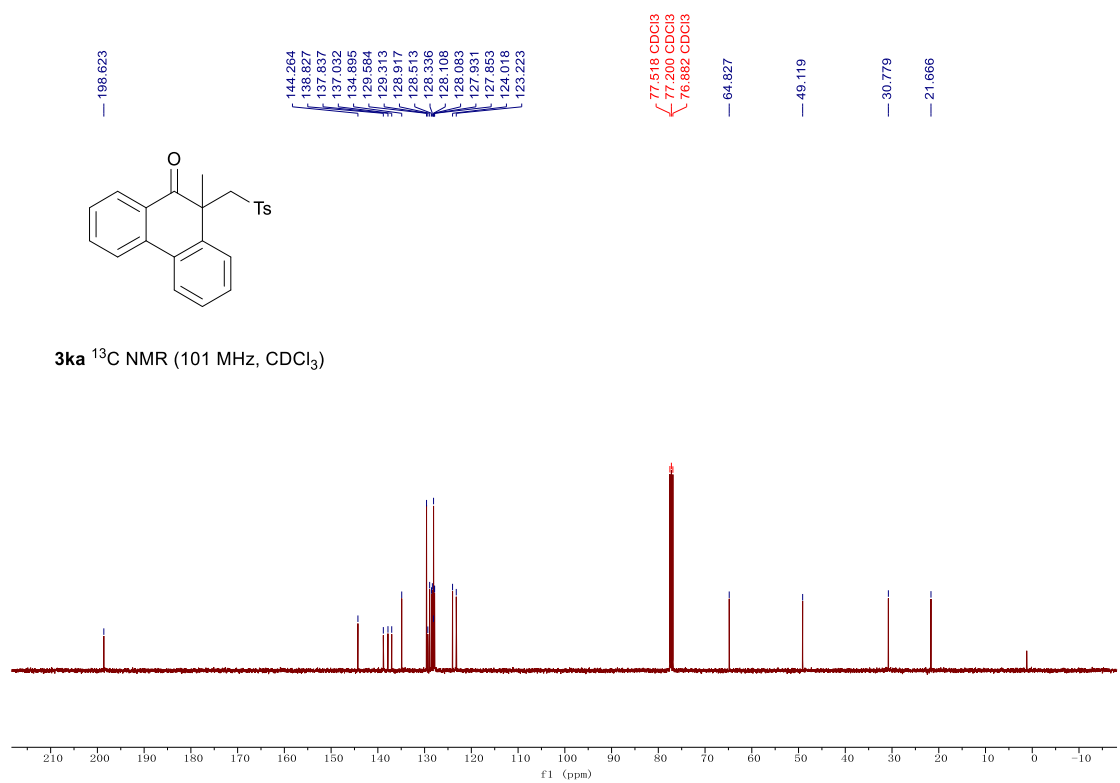
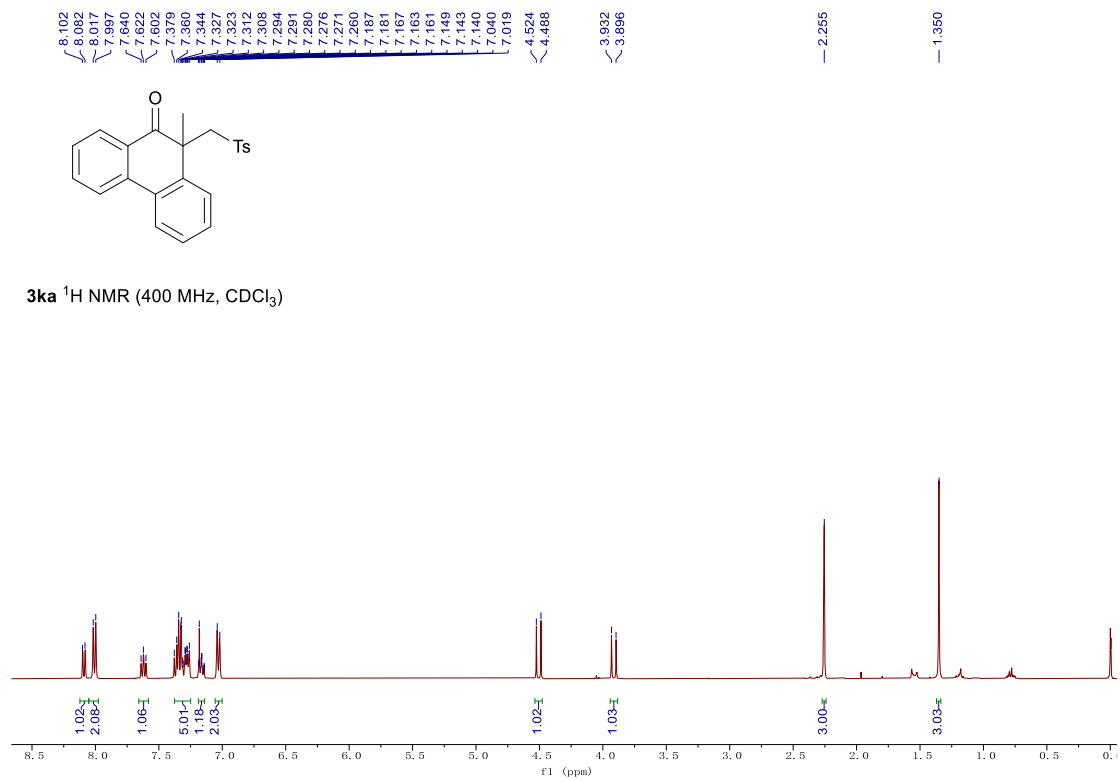


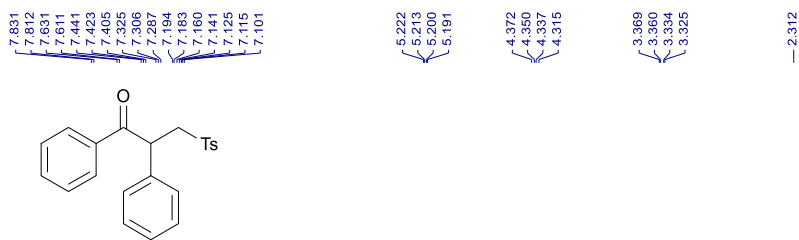
¹H NMR (400 MHz, CDCl₃)



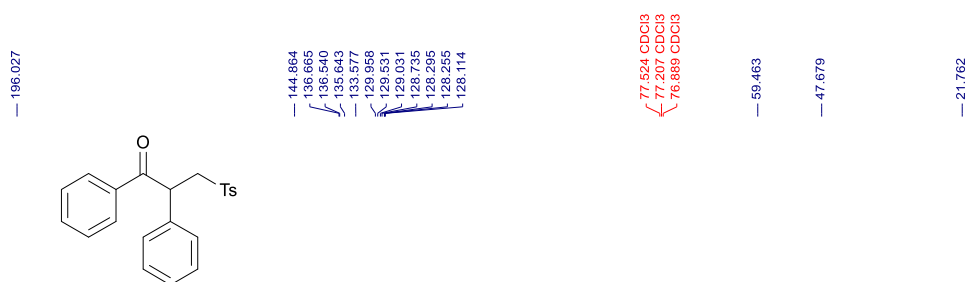
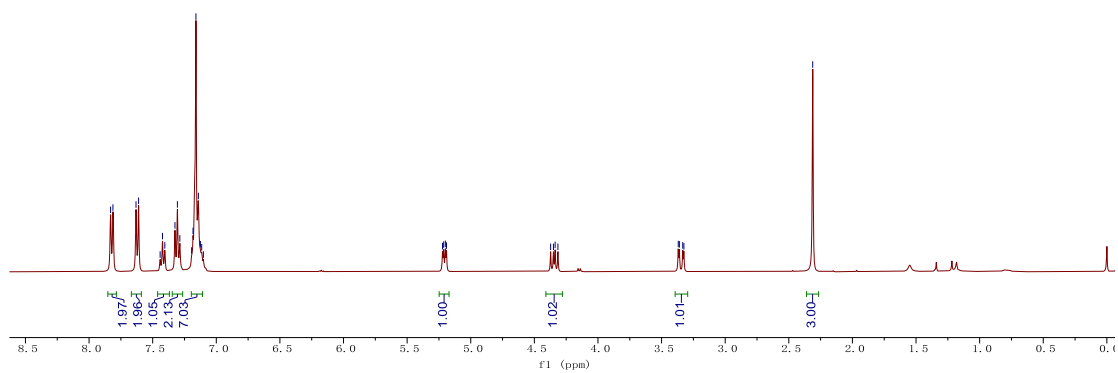
¹³C NMR (101 MHz, CDCl₃)



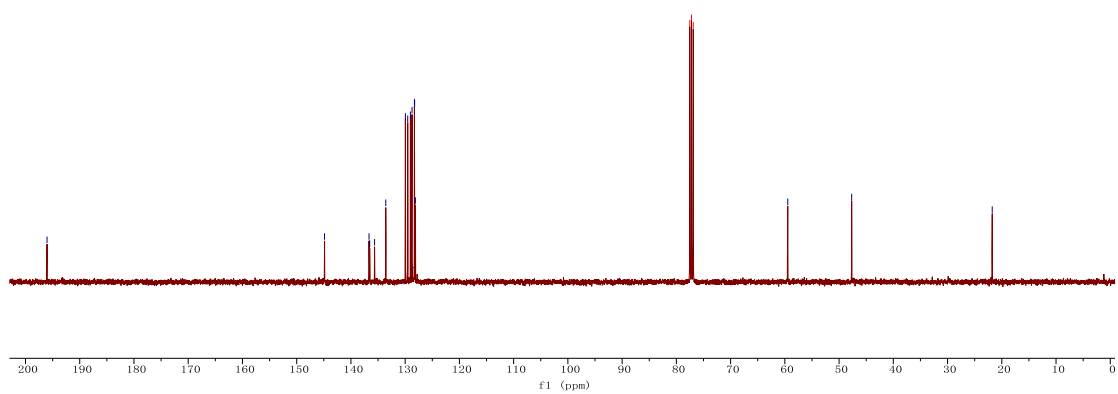


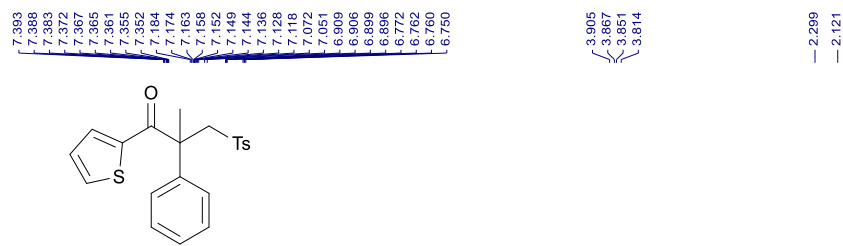


3la ^1H NMR (400 MHz, CDCl_3)

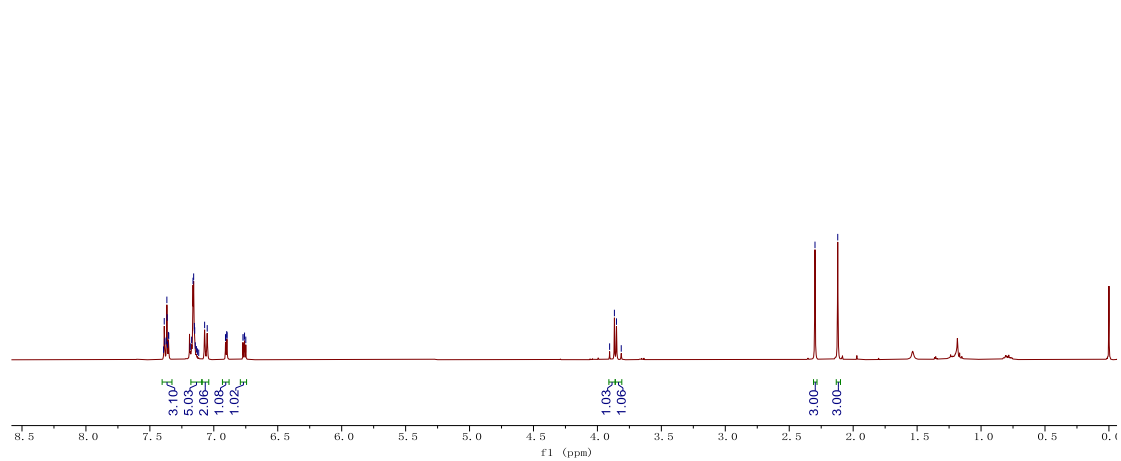


3la ^{13}C NMR (101 MHz, CDCl_3)

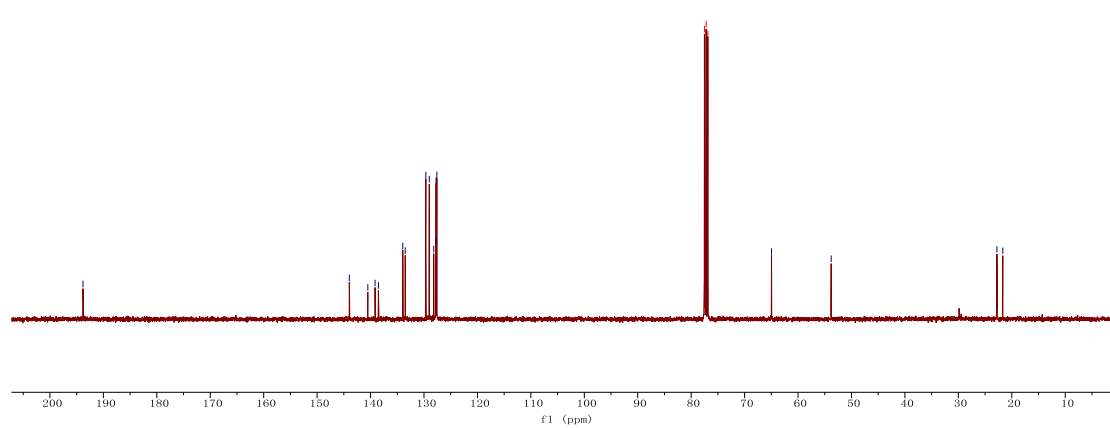




3ma ^1H NMR (400 MHz, CDCl_3)



3ma ^{13}C NMR (101 MHz, CDCl_3)

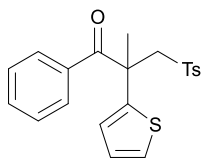


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6.827

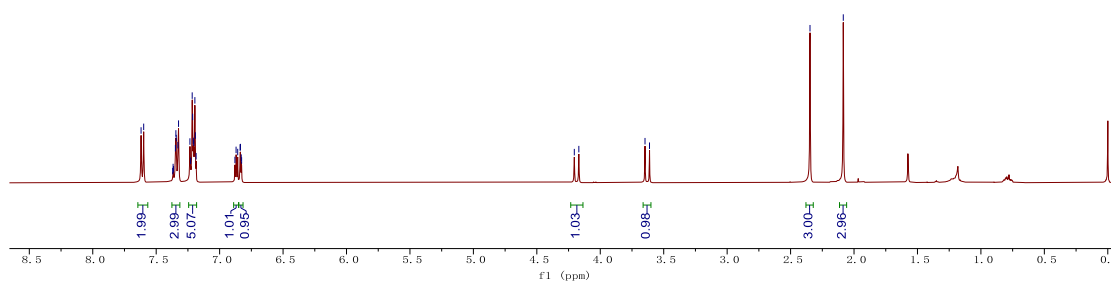
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4.169

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2.347
2.085



3ma ^1H NMR (400 MHz, CDCl_3)



200.732

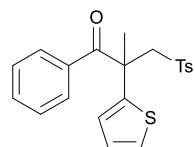
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77.514 CDCl_3
77.196 CDCl_3
76.879 CDCl_3

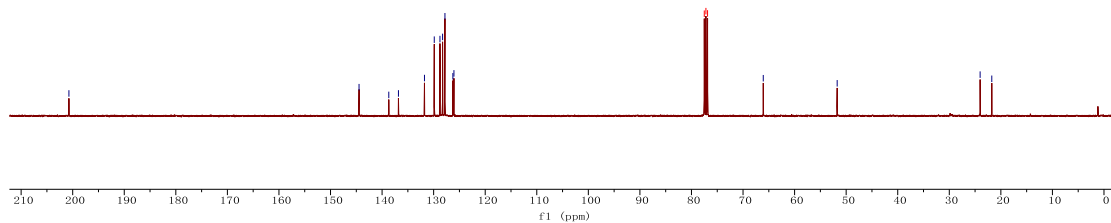
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51.744

24.921
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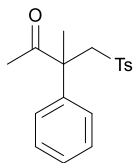
3ma ^{13}C NMR (101 MHz, CDCl_3)



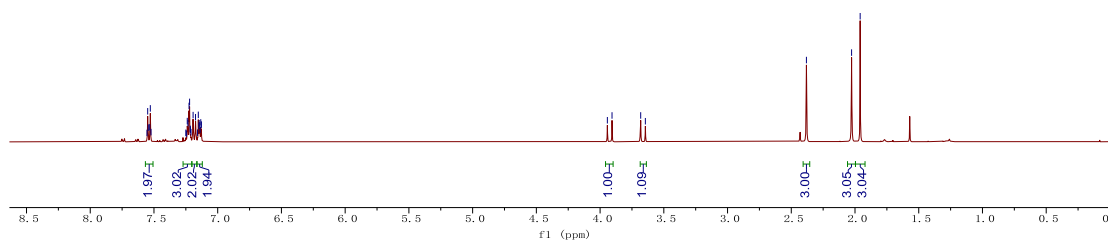
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7.147
7.145
7.141
7.138
7.133
7.128

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3.681
3.645

2.381
2.027
1.960



3na ^1H NMR (400 MHz, CDCl_3)



207.437

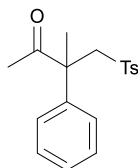
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126.562

77.518 CDCl_3
77.200 CDCl_3
76.862 CDCl_3

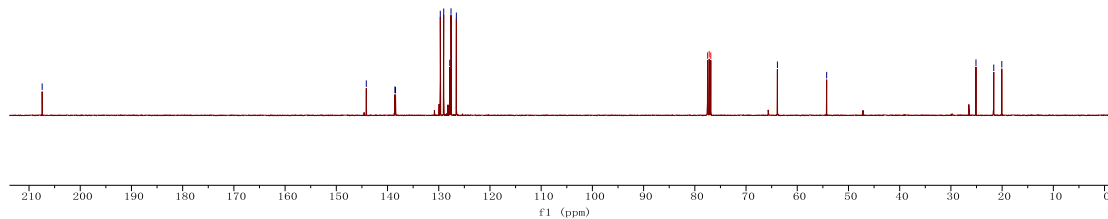
63.877

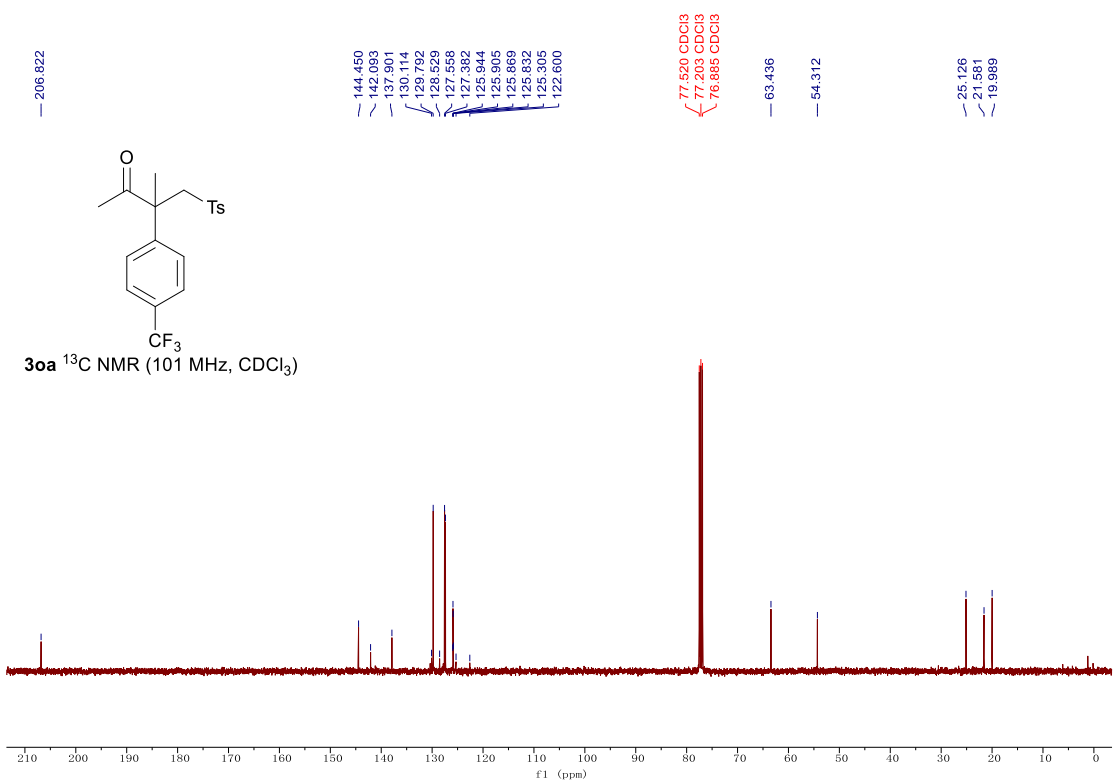
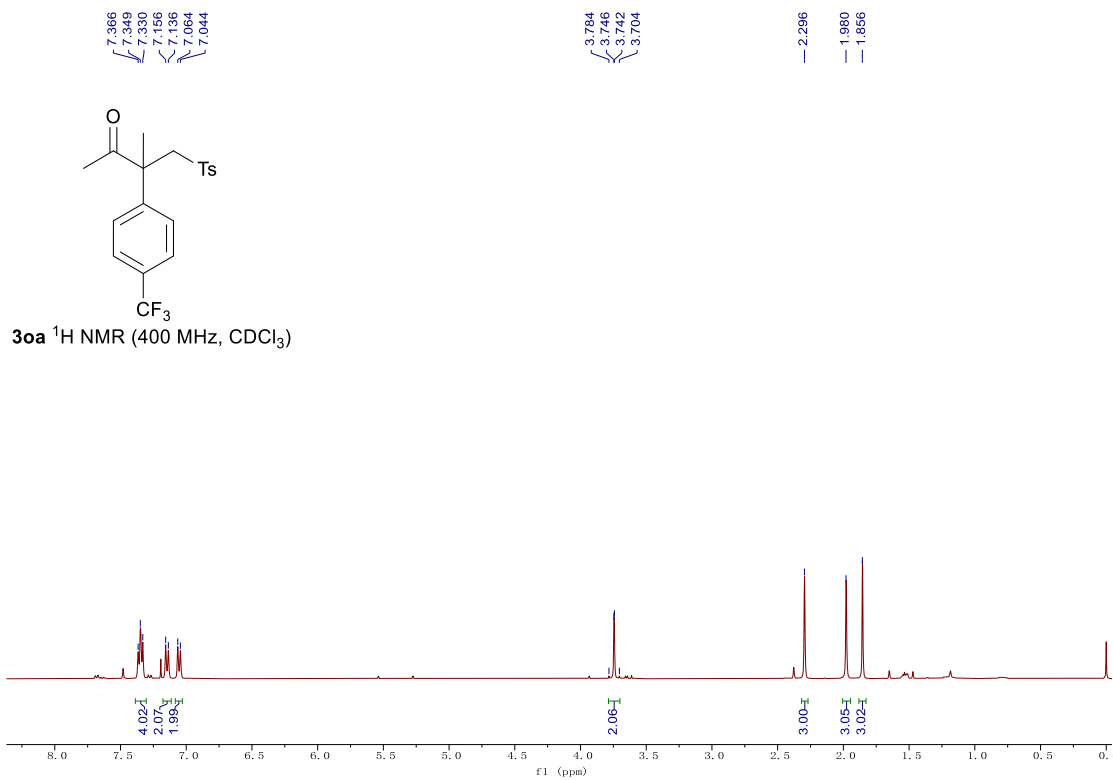
54.256

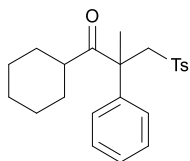
25.106
21.631
20.061



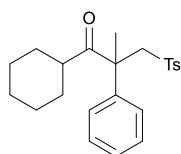
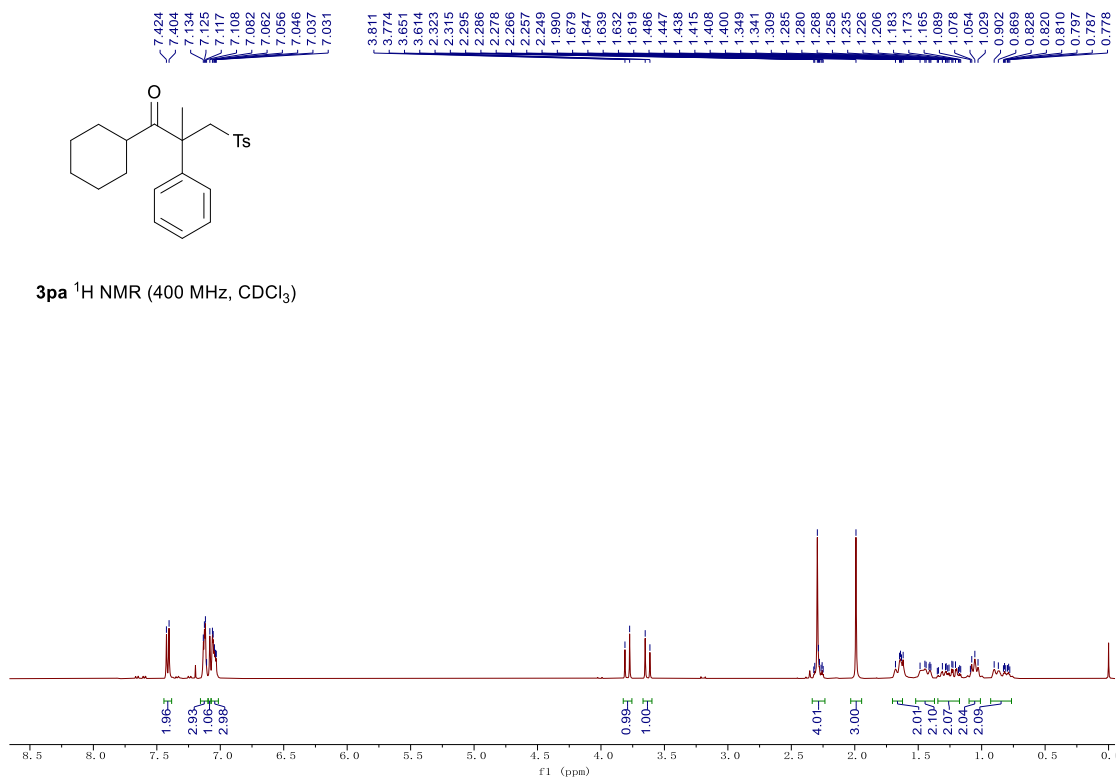
3na ^{13}C NMR (101 MHz, CDCl_3)



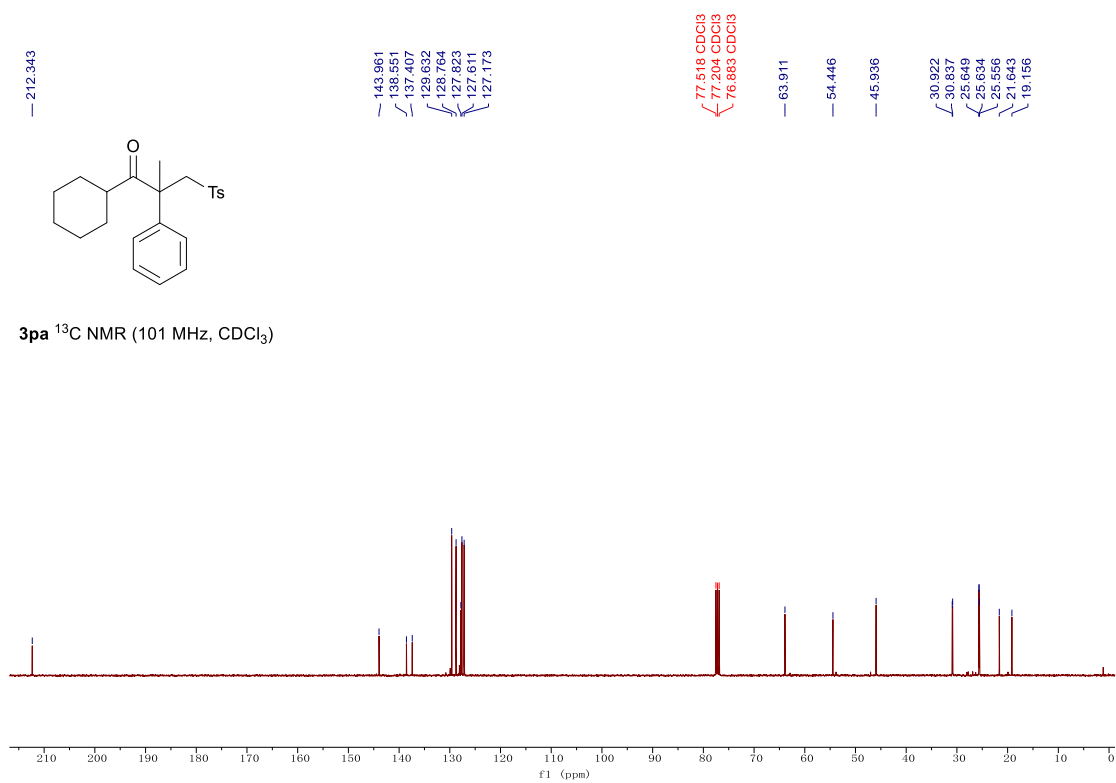


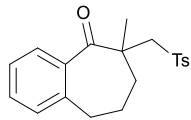


3pa ^1H NMR (400 MHz, CDCl_3)

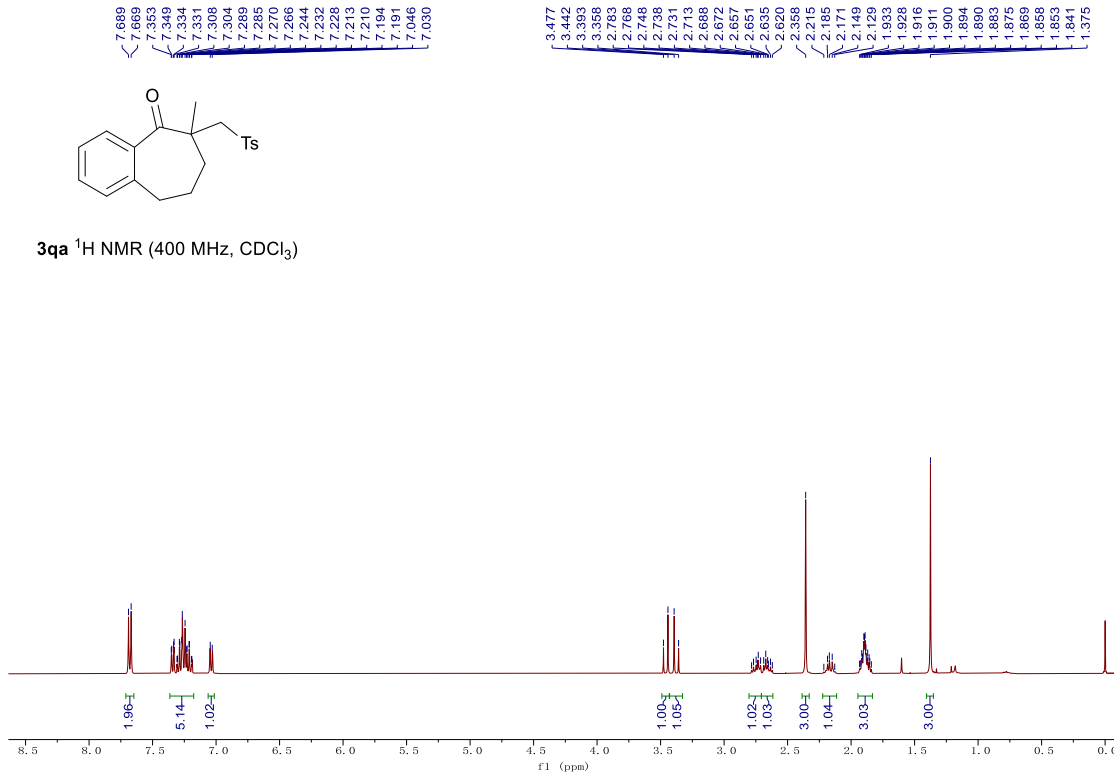


3pa ^{13}C NMR (101 MHz, CDCl_3)

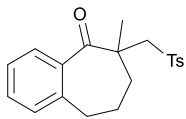




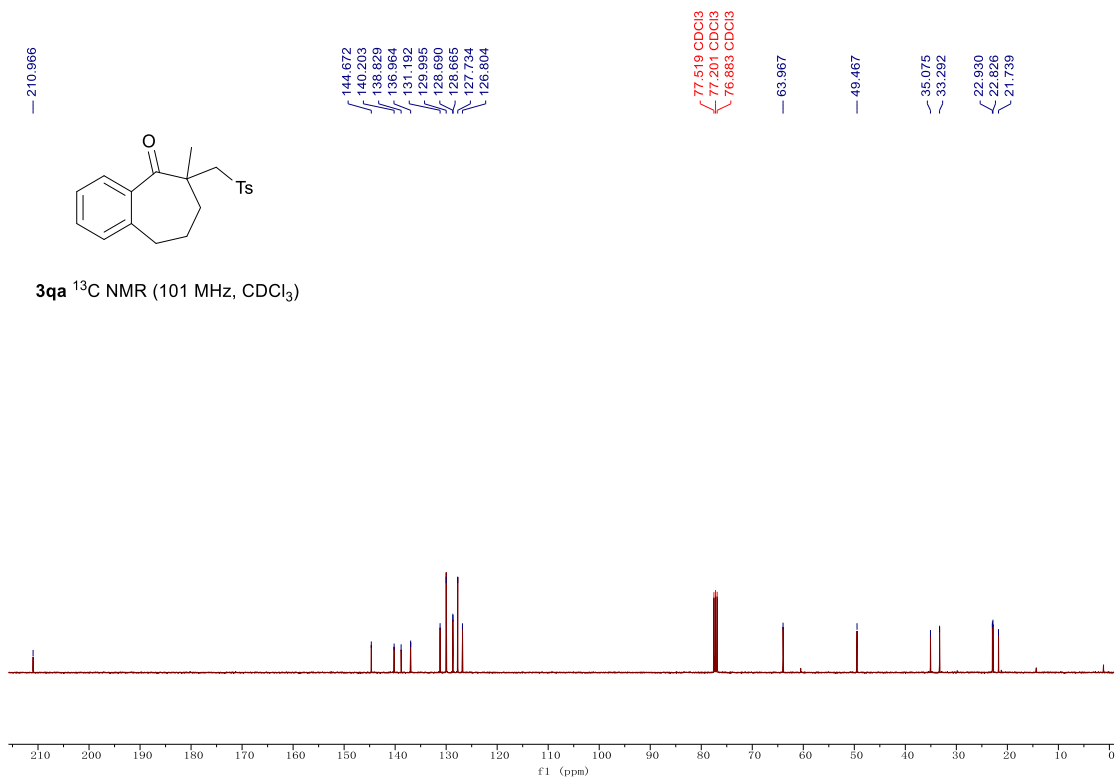
3qa ^1H NMR (400 MHz, CDCl_3)



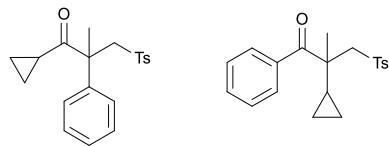
210.966



3qa ^{13}C NMR (101 MHz, CDCl_3)



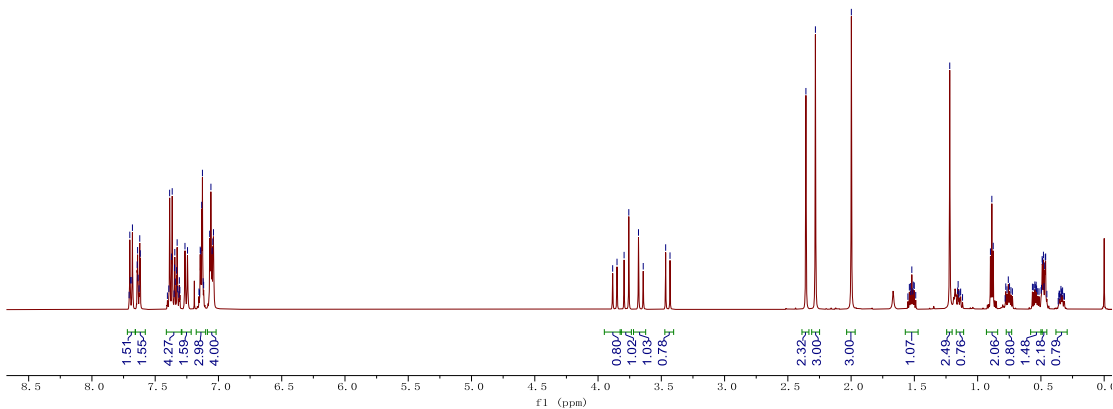
7.701
7.696
7.685
7.680
7.642
7.639
7.635
7.627
7.622
7.618
7.392
7.386
7.370
7.365
7.347
7.345
7.341
7.331
7.326
7.322
7.309
7.265
7.244
7.146
7.140
7.132
7.127
7.121
7.117
7.069
7.060
7.050
7.045
7.039
3.884
3.850
3.794
3.757
3.680
3.643
3.466
3.431
3.431
2.357
2.282
1.998
1.540
1.532
1.520
1.509
1.501
1.221
1.154
0.899
0.888
0.877
0.778
0.758
0.748
0.567
0.557
0.548
0.544
0.538
0.534
0.495
0.490
0.487
0.480
0.476
0.466
0.462



3ra

3ra'

¹H NMR (400 MHz, CDCl₃)



209.902
207.079

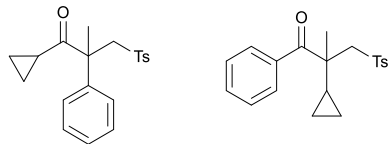
144.486
143.917
139.379
138.925
136.737
136.440
130.700
129.917
129.592
128.837
128.040
127.757
127.719
127.679
127.562
127.203

77.518 CDCl₃
77.200 CDCl₃
76.862 CDCl₃

65.640
63.791

54.307
49.534

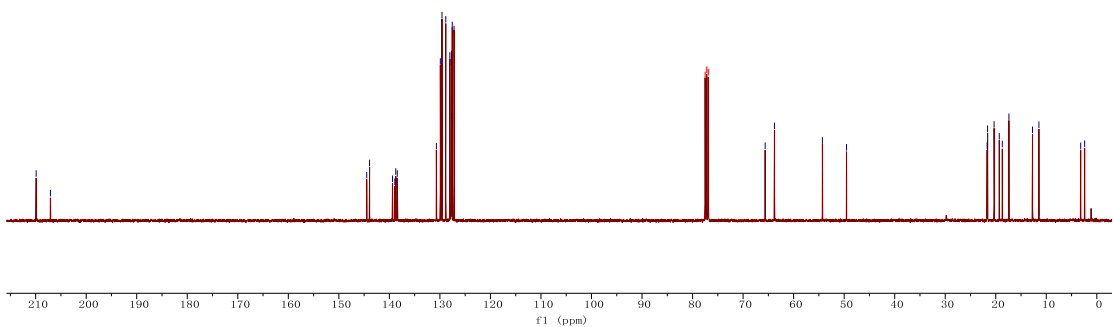
21.714
21.613
20.332
19.306
18.705
17.395
12.728
11.465
3.191
2.410

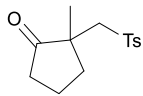


3ra

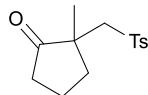
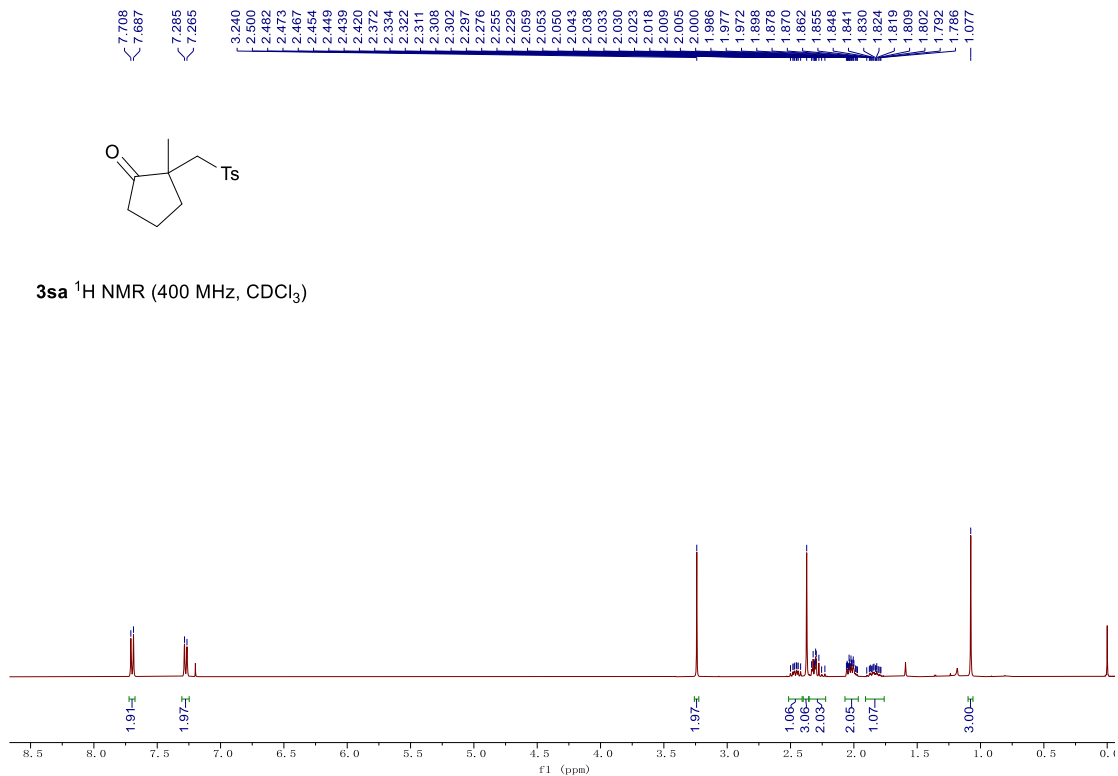
3ra'

¹³C NMR (101 MHz, CDCl₃)

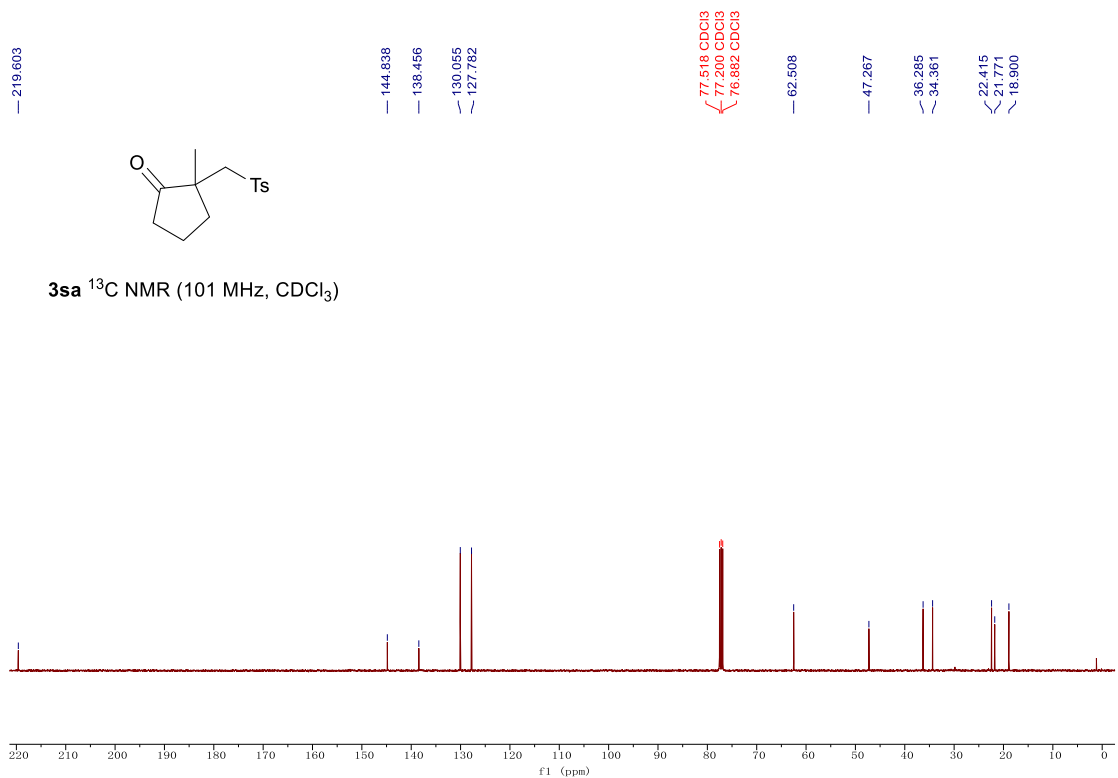




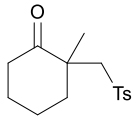
3sa ¹H NMR (400 MHz, CDCl₃)



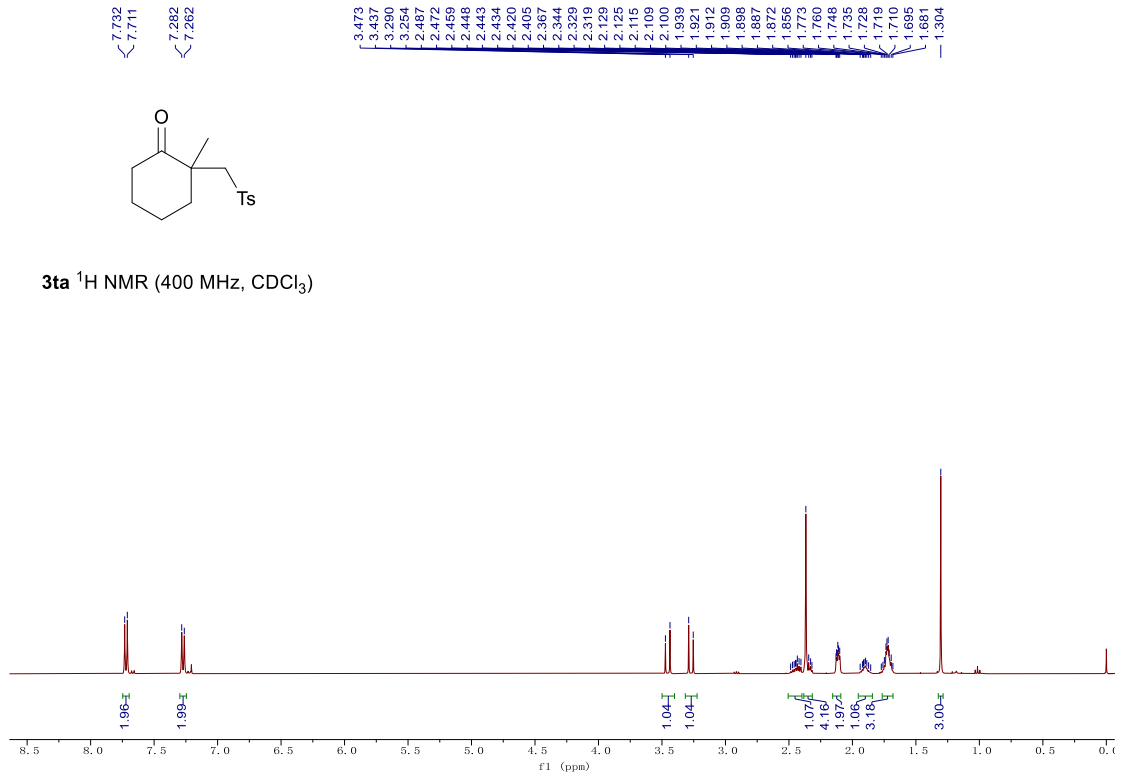
3sa ¹³C NMR (101 MHz, CDCl₃)



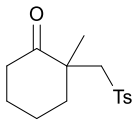
7.732
7.711
7.282
7.262



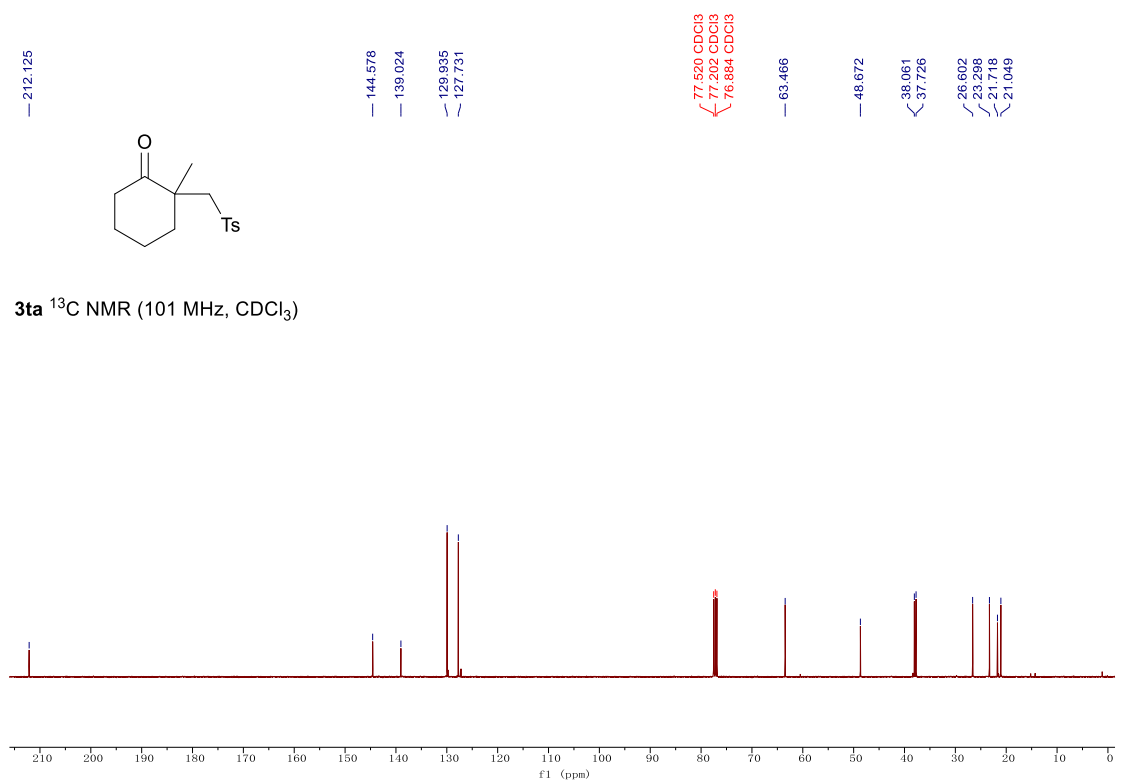
3ta ¹H NMR (400 MHz, CDCl₃)



212.125

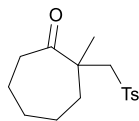


3ta ¹³C NMR (101 MHz, CDCl₃)

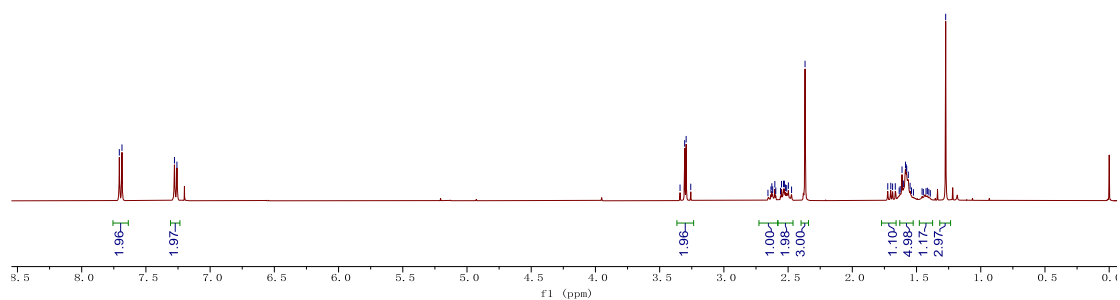


7.707
7.686
7.278
7.259

3.341
3.305
3.294
3.258
2.657
2.634
2.626
2.620
2.603
2.596
2.559
2.551
2.536
2.529
2.521
2.511
2.498
2.473
2.368
1.724
1.700
1.686
1.665
1.655
1.626
1.613
1.602
1.580
1.564
1.550
1.539
1.426
1.416
1.373



3ua ^1H NMR (400 MHz, CDCl_3)



214.876

144.688

138.809

130.009

127.772

77.521 CDCl_3

77.204 CDCl_3

76.886 CDCl_3

63.245

50.744

40.827

35.220

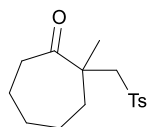
30.468

25.914

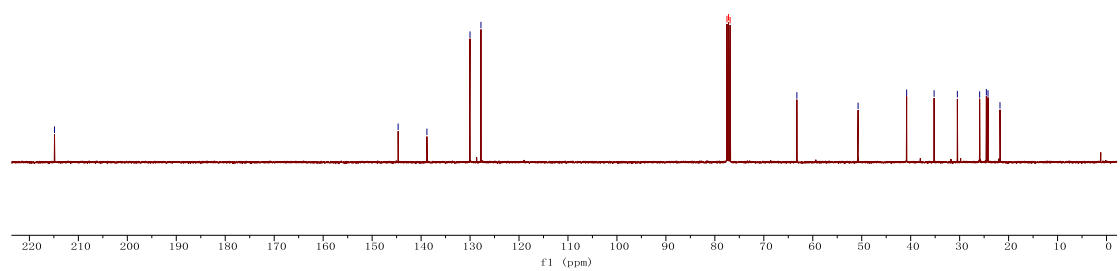
24.544

24.206

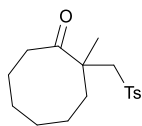
21.760



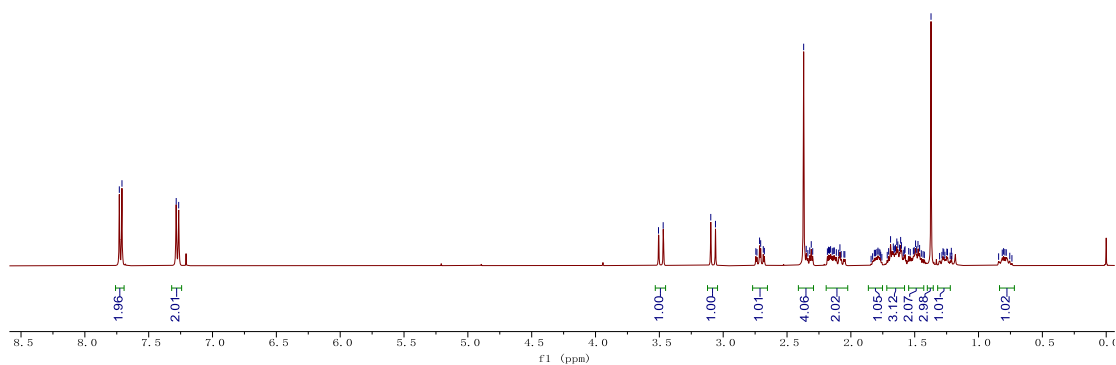
3ua ^{13}C NMR (101 MHz, CDCl_3)



7.730
7.709
7.284
7.265
3.507
3.470
3.097
3.061
2.744
2.736
2.715
2.706
2.686
2.678
2.370
2.350
2.337
2.322
2.310
2.299
2.164
2.165
2.157
2.156
2.146
2.138
2.129
2.114
2.095
2.086
2.076
2.054
1.816
1.808
1.788
1.779
1.772
1.704
1.689
1.668
1.662
1.656
1.650
1.640
1.632
1.618
1.610
1.604
1.591
1.581
1.576
1.547
1.535
1.510
1.504
1.493
1.485
1.474
1.462
1.448
1.434
1.372
1.278
1.272
1.248
1.243
1.213
1.0814
0.804
0.794
0.783



3va ^1H NMR (400 MHz, CDCl_3)



— 217.476

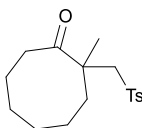
— 144.625
— 139.070

— 129.985
— 127.685

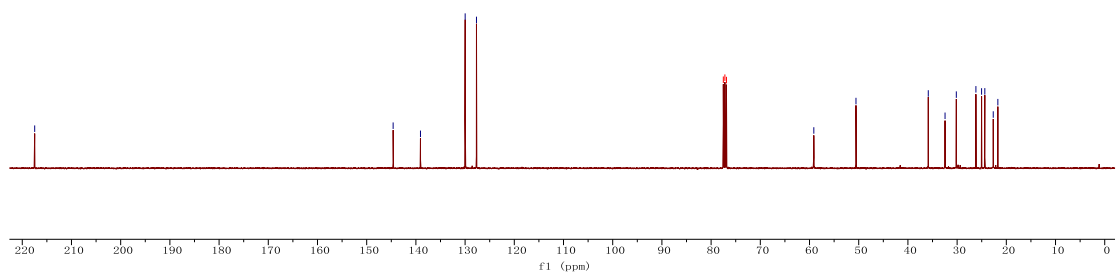
77.517 CDCl_3
77.199 CDCl_3
76.881 CDCl_3

— 59.124
— 50.557

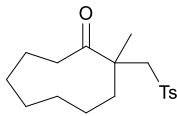
35.861
32.453
30.162
26.180
25.028
24.368
22.656
21.719



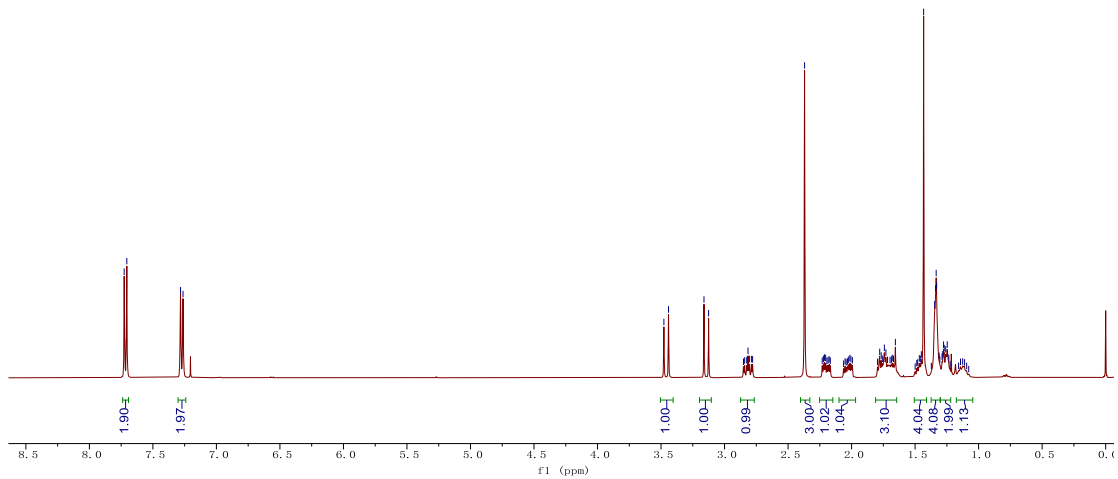
3va ^{13}C NMR (101 MHz, CDCl_3)



7.726
7.705
7.282
7.265
3.447
3.441
3.162
3.126
2.851
2.842
2.825
2.815
2.805
2.789
2.779
2.370
2.231
2.222
2.214
2.204
2.194
2.185
2.177
2.167
2.051
2.043
2.031
2.026
2.014
2.004
1.994
1.984
1.796
1.779
1.767
1.758
1.742
1.730
1.717
1.697
1.687
1.680
1.670
1.655
1.487
1.480
1.467
1.459
1.451
1.433
1.346
1.339
1.334
1.330
1.310
1.285
1.285
1.285
1.276
1.271
1.259
1.247
1.235
1.143
1.126
1.110



3wa ^1H NMR (400 MHz, CDCl_3)



215.231

144.588

139.087

129.982

127.704

77.518 CDCl_3

77.199 CDCl_3

76.881 CDCl_3

61.075

51.990

34.199

33.685

25.311

24.623

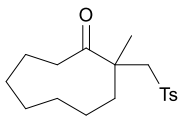
23.160

22.382

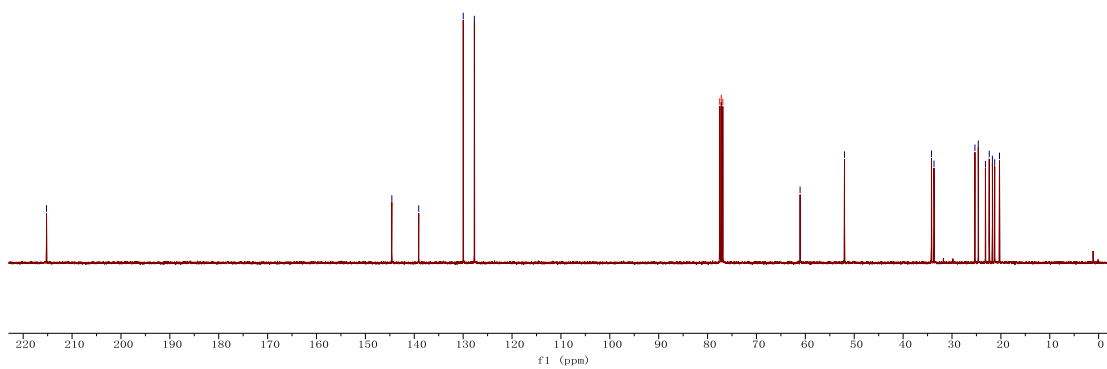
21.735

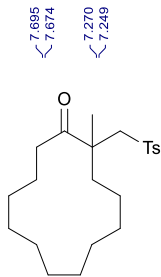
21.266

20.285

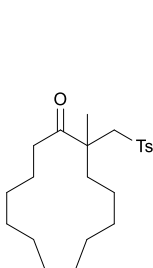
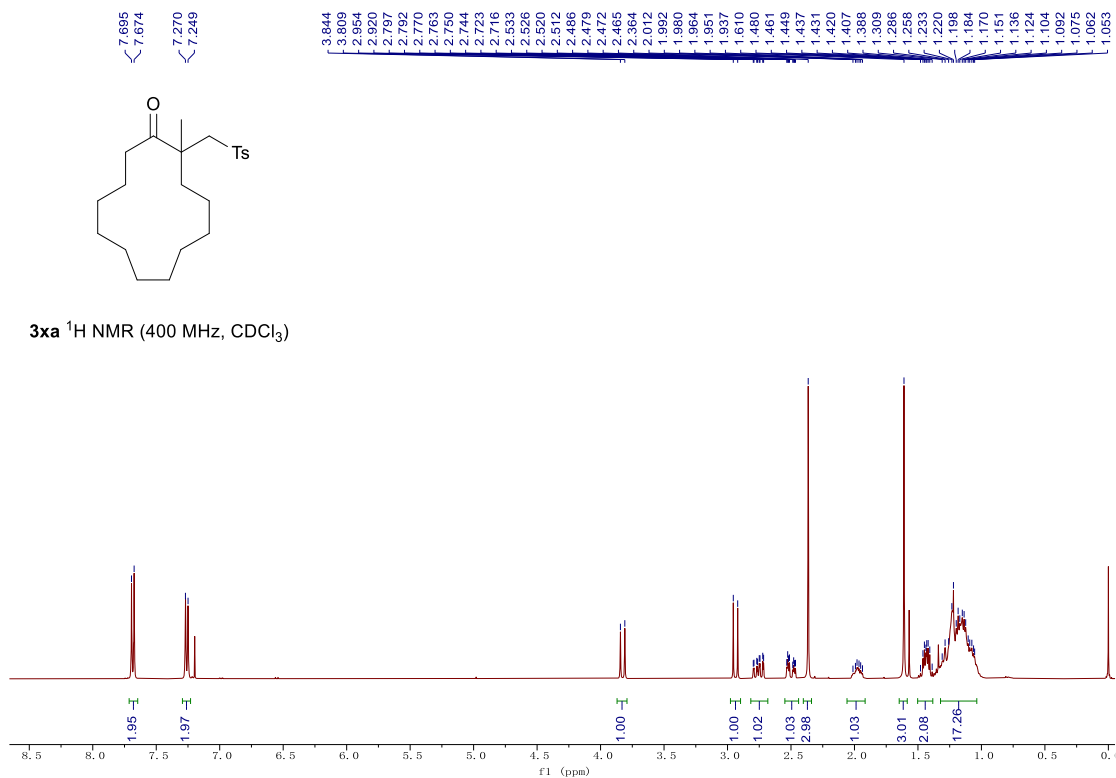


3wa ^{13}C NMR (101 MHz, CDCl_3)

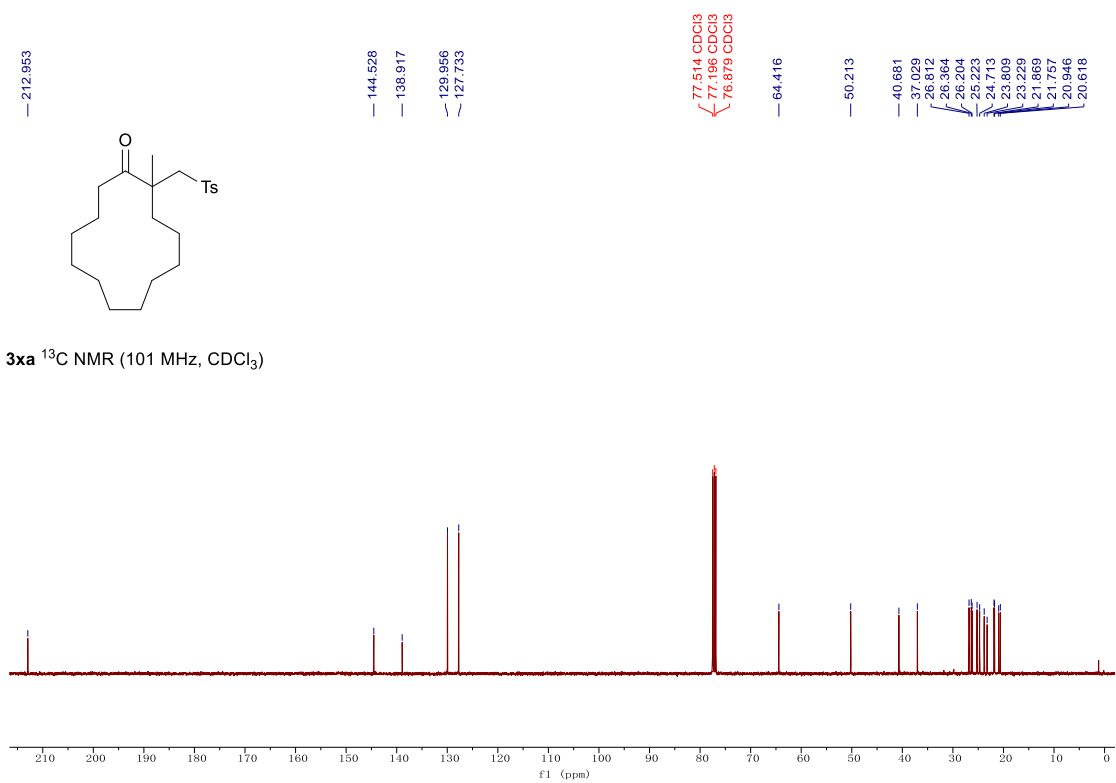


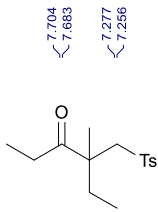


3xa ¹H NMR (400 MHz, CDCl₃)

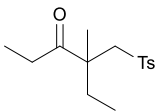
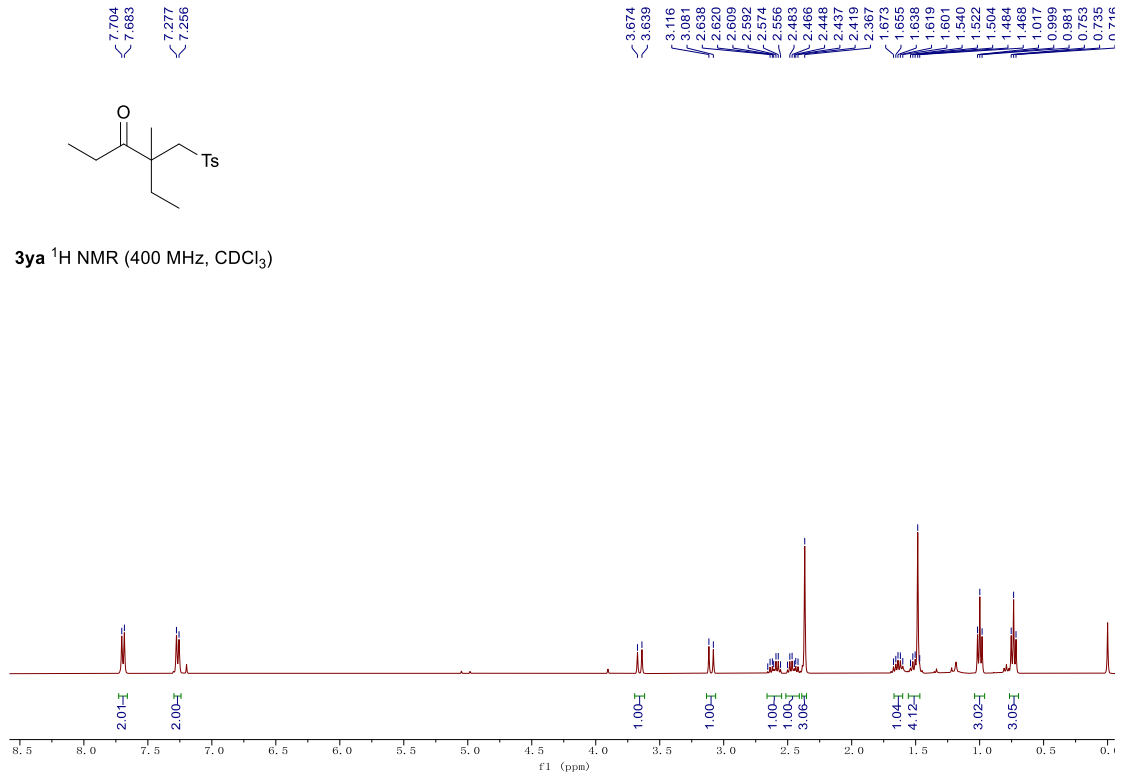


3xa ¹³C NMR (101 MHz, CDCl₃)

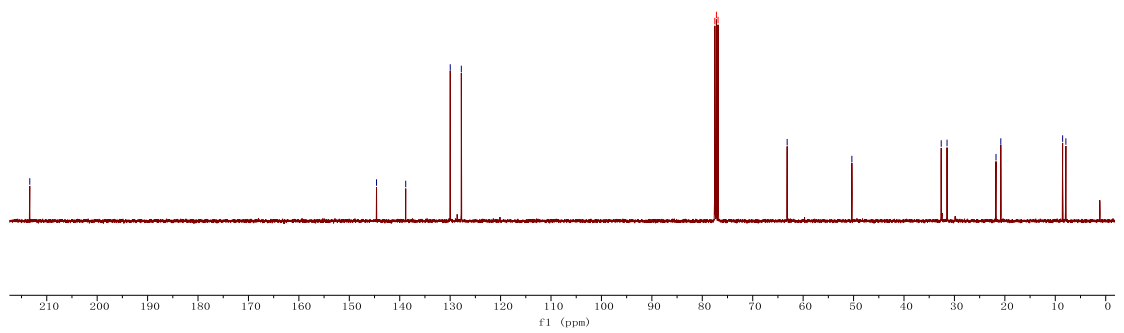


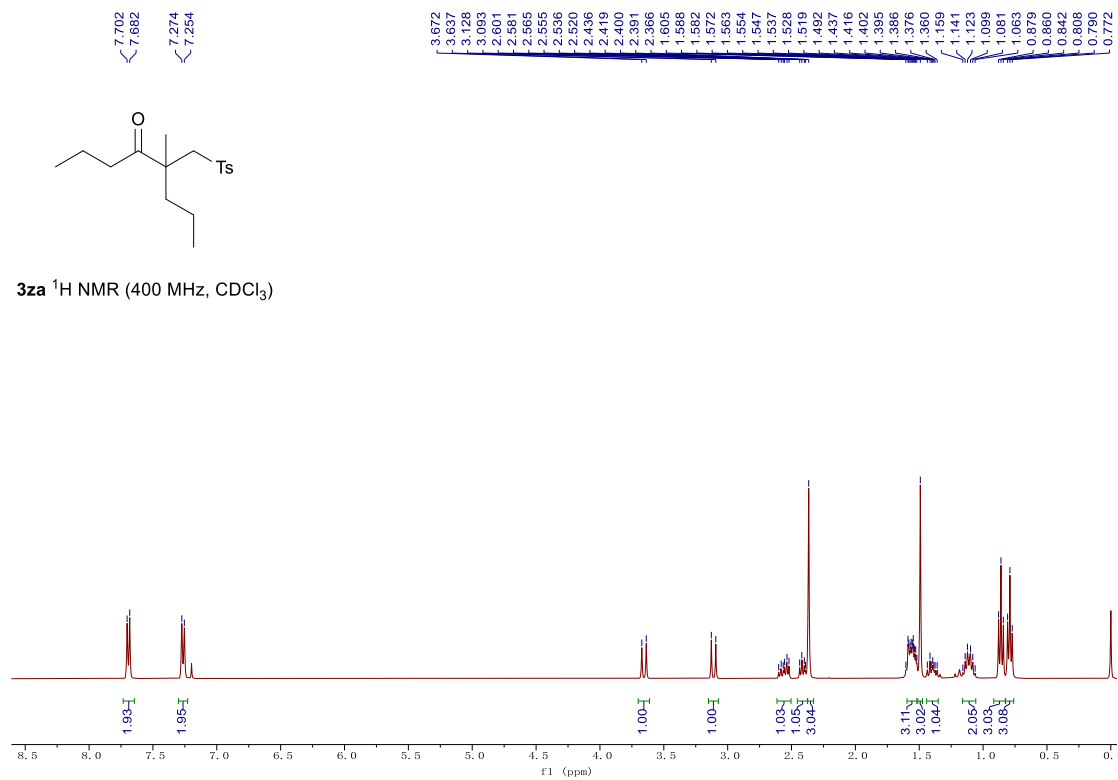


3ya ^1H NMR (400 MHz, CDCl_3)

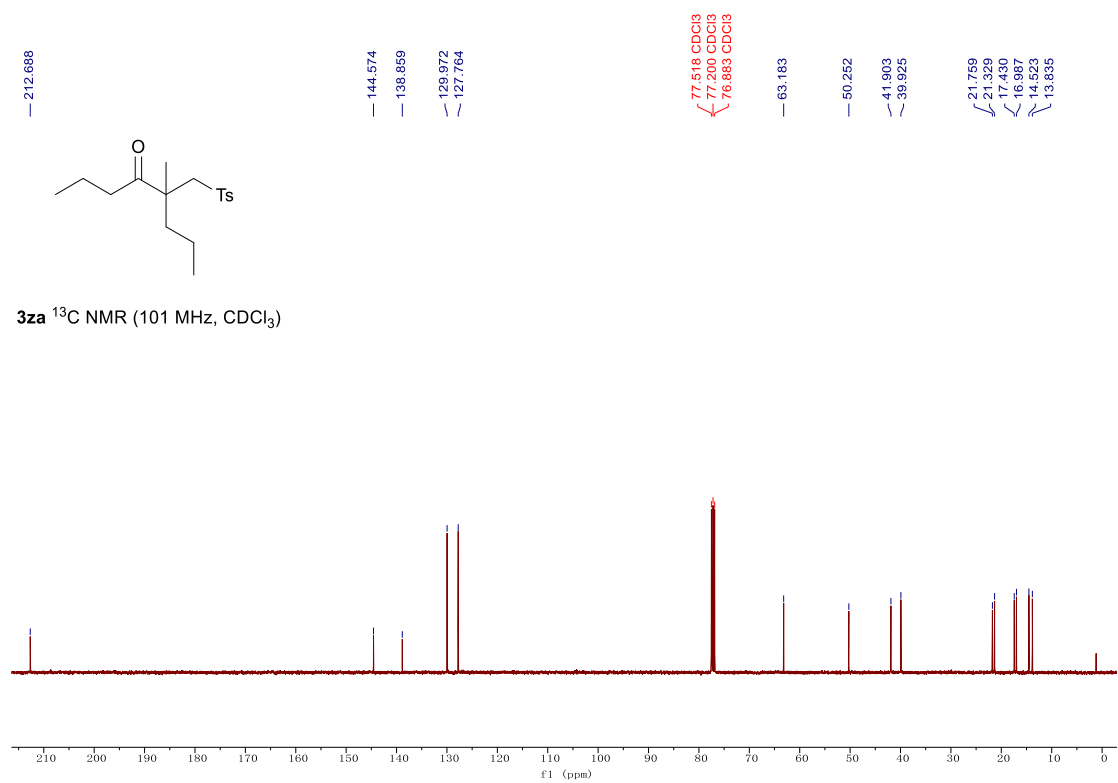


3ya ^{13}C NMR (101 MHz, CDCl_3)





3za ^1H NMR (400 MHz, CDCl_3)

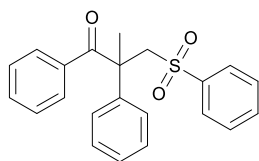


3za ^{13}C NMR (101 MHz, CDCl_3)

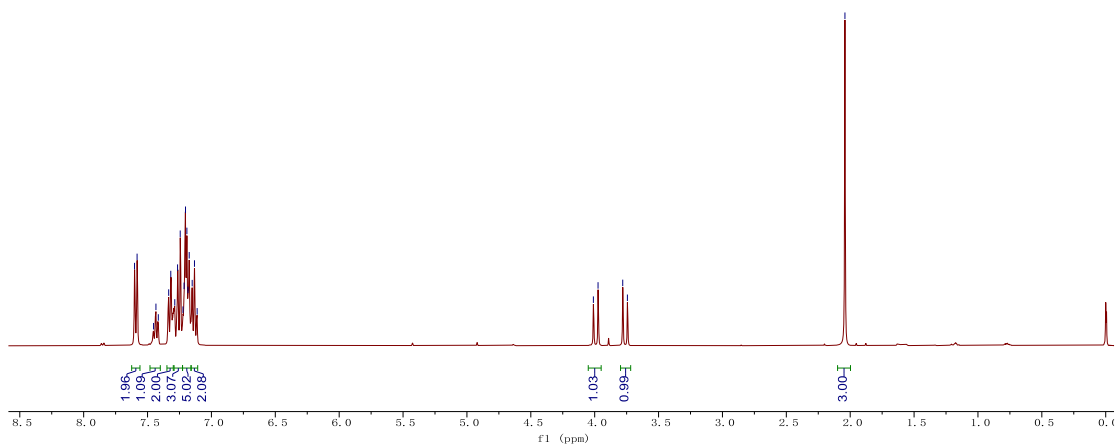
7.602
7.582
7.453
7.434
7.416
7.334
7.316
7.285
7.265
7.244
7.223
7.214
7.203
7.192
7.184
7.174
7.151
7.133
7.112

4.010
3.974
3.780
3.744

2.041



3ab ^1H NMR (400 MHz, CDCl_3)



201.185

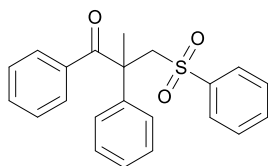
141.585
139.247
136.186
133.186
131.976
129.349
129.100
128.207
128.151
127.577
126.758

77.516 CDCl_3
77.203 CDCl_3
76.883 CDCl_3

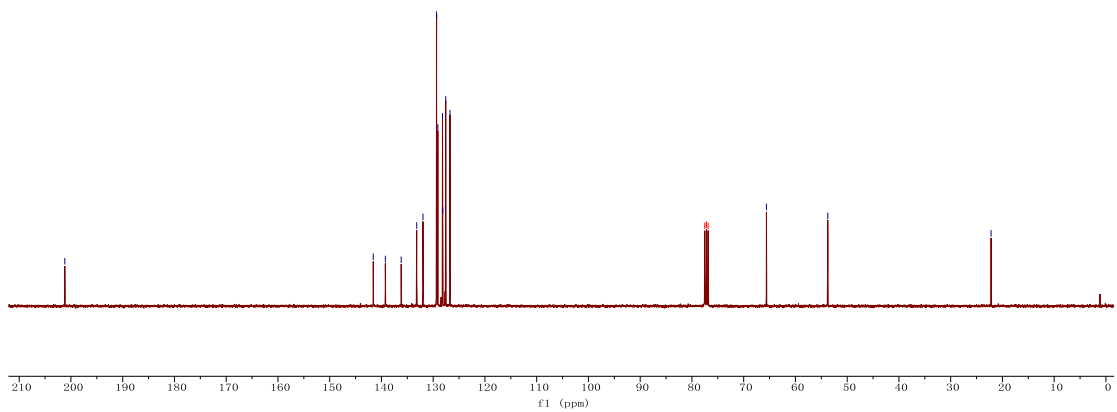
65.603

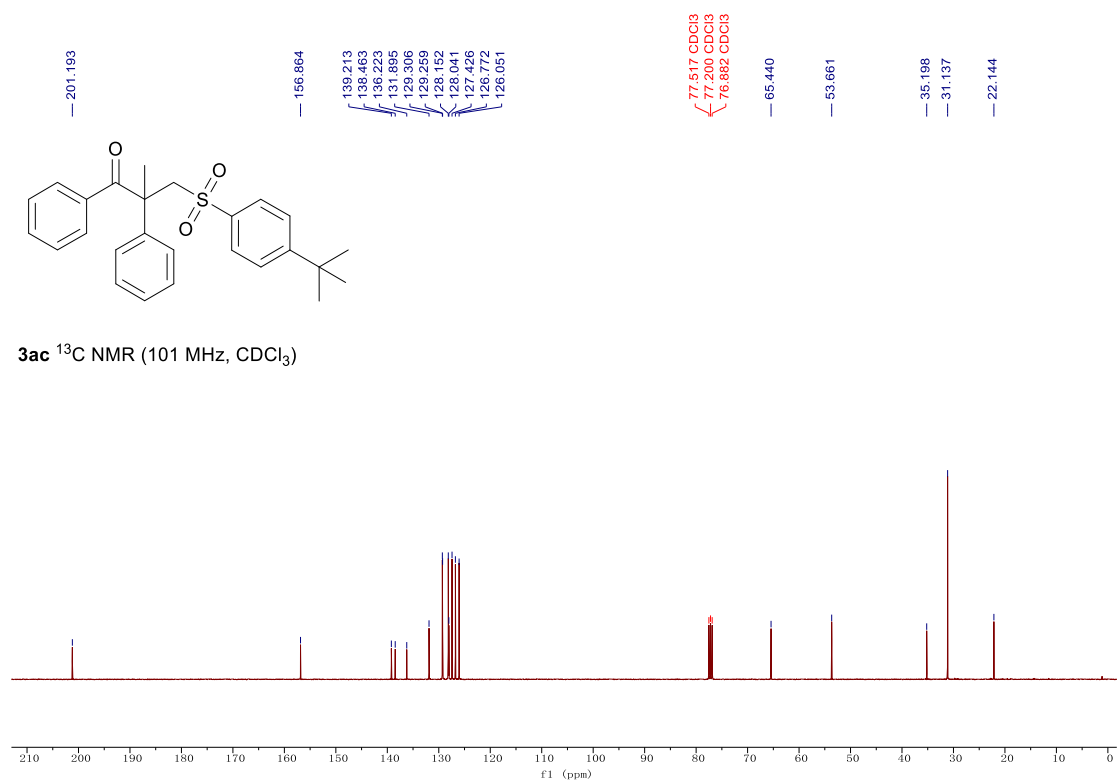
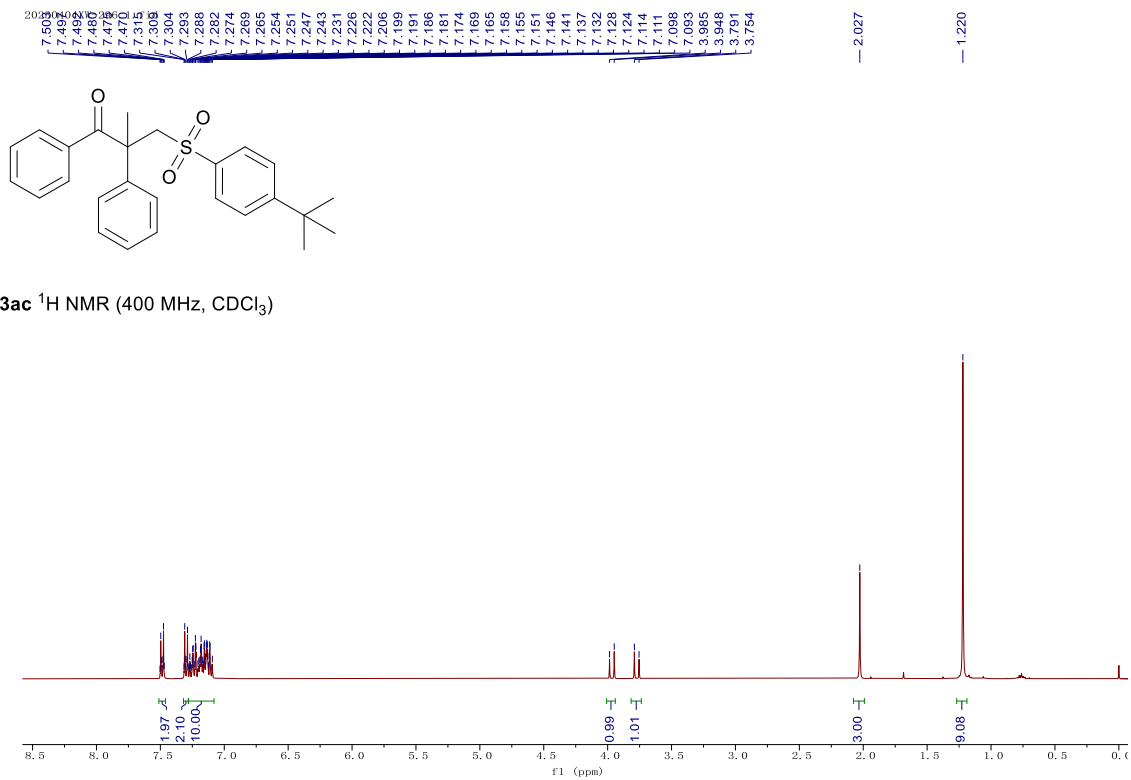
53.754

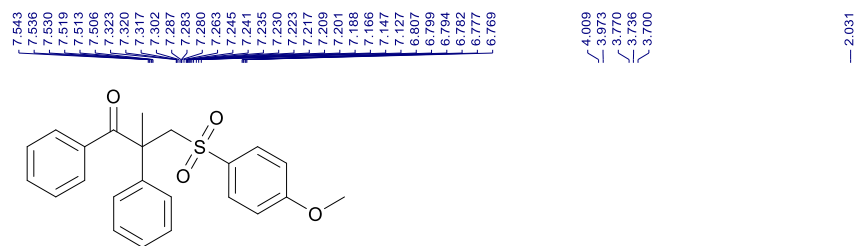
22.196



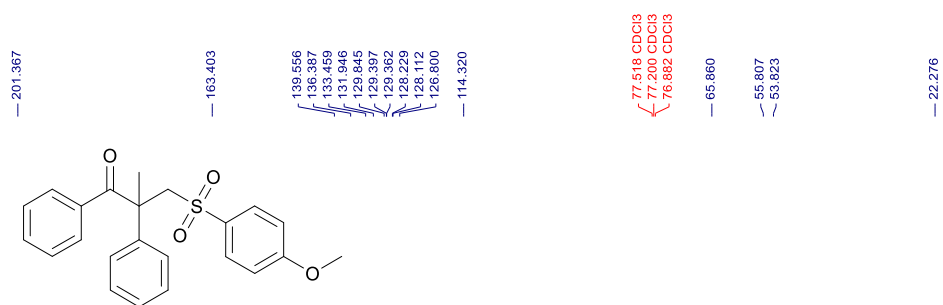
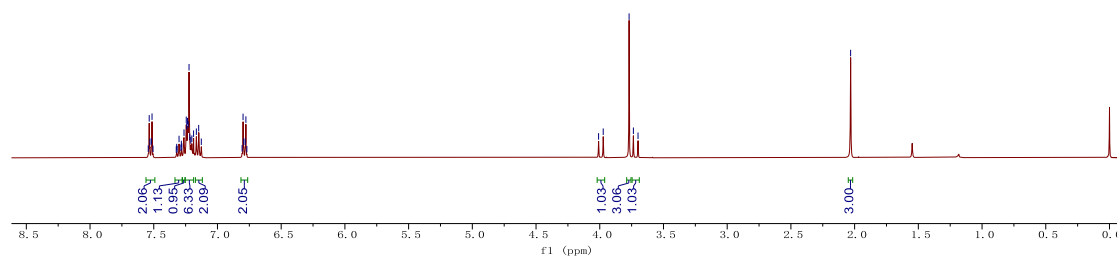
3ab ^{13}C NMR (101 MHz, CDCl_3)



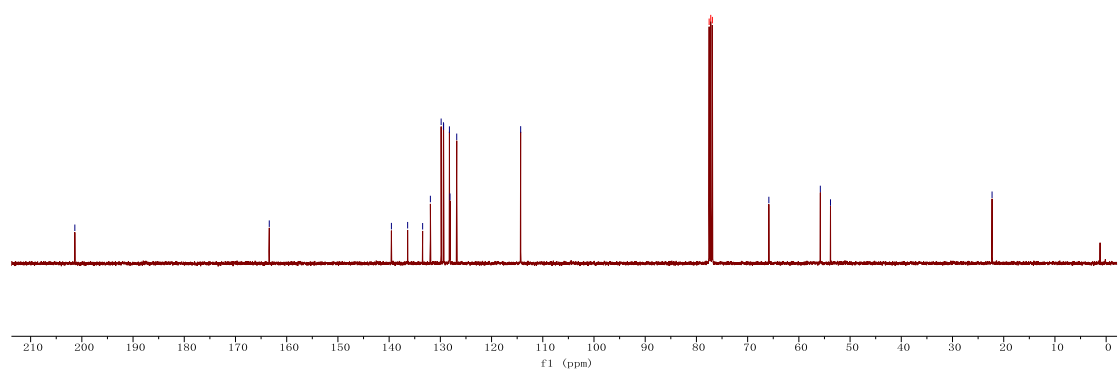


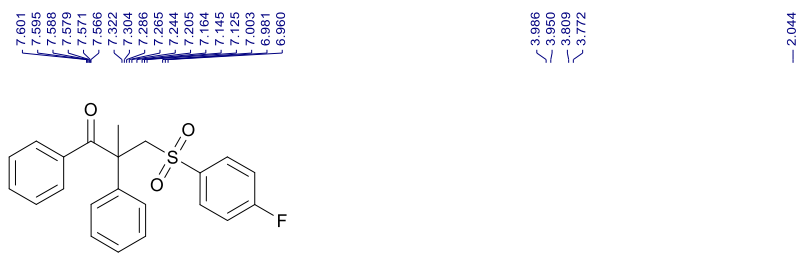


3ad ^1H NMR (400 MHz, CDCl_3)

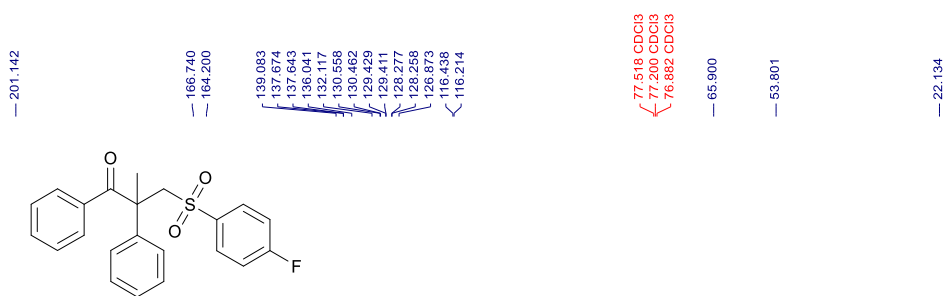
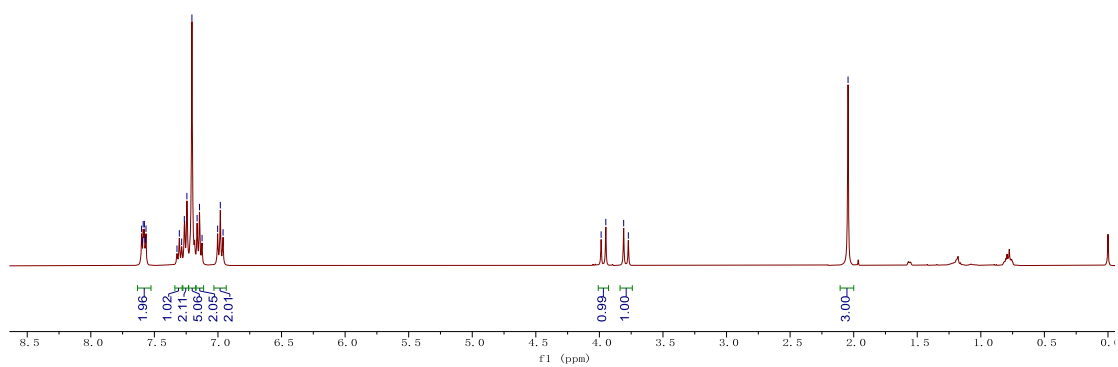


3ad ^{13}C NMR (101 MHz, CDCl_3)

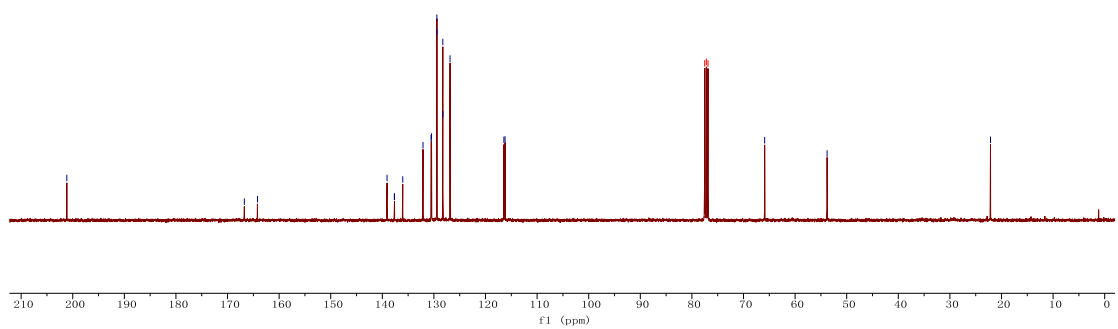




3ae ^1H NMR (400 MHz, CDCl_3)



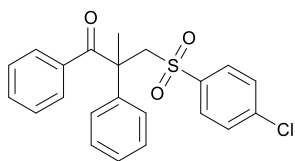
3ae ^{13}C NMR (101 MHz, CDCl_3)



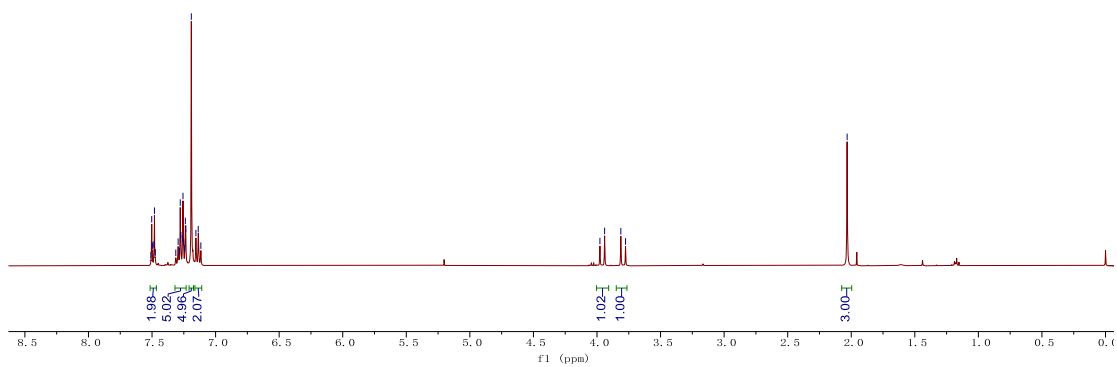
7.509
7.502
7.498
7.486
7.481
7.475
7.313
7.295
7.285
7.278
7.273
7.261
7.257
7.251
7.243
7.238
7.234
7.191
7.155
7.137
7.116

3.977
3.940
3.812
3.776

2.032



3af ^1H NMR (400 MHz, CDCl_3)



201.028

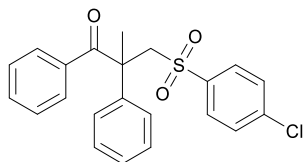
138.935
138.808
138.962
135.942
132.102
128.401
128.379
128.323
128.116
128.215
128.220
126.831

77.515 CDCl_3
77.197 CDCl_3
76.878 CDCl_3

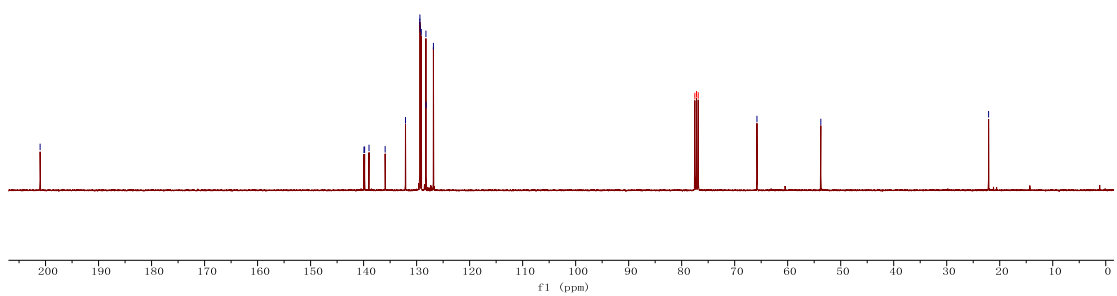
65.798

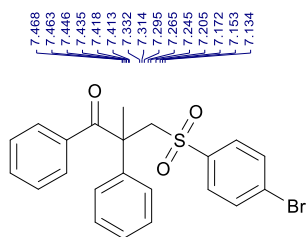
53.749

22.097

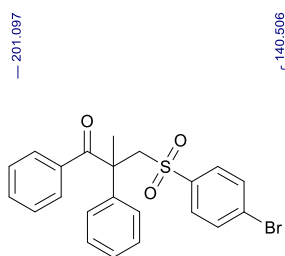
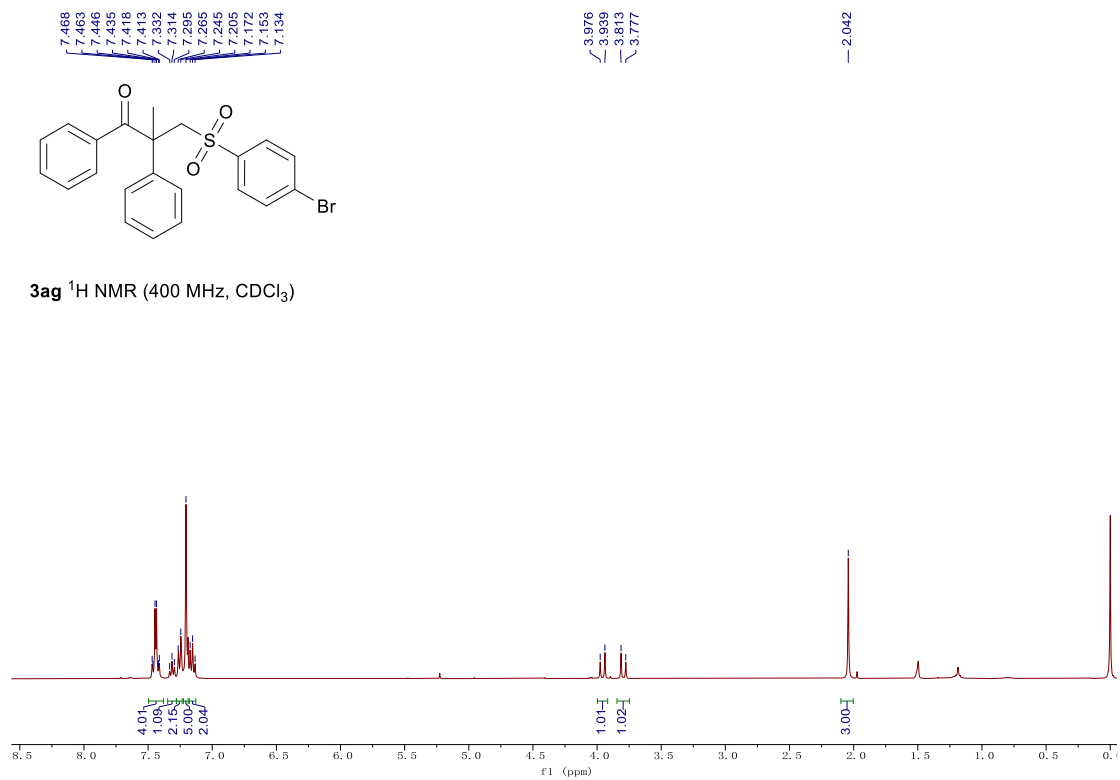


3af ^{13}C NMR (101 MHz, CDCl_3)

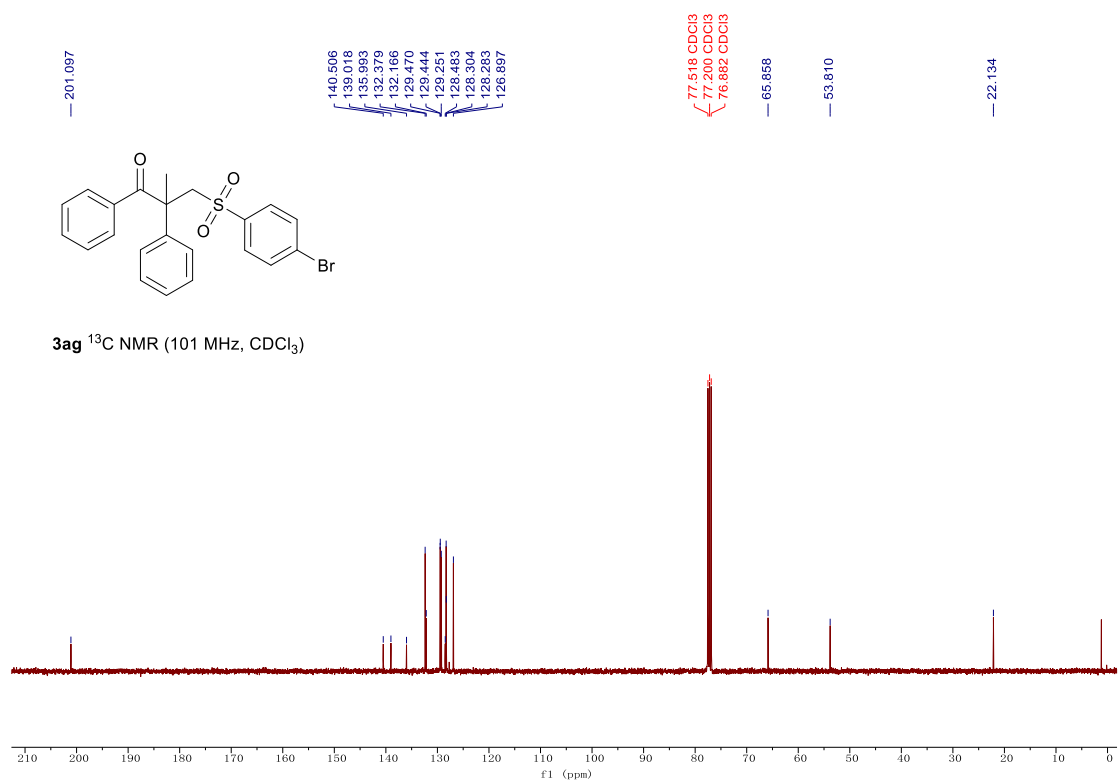




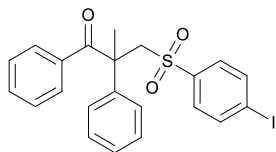
3ag ^1H NMR (400 MHz, CDCl_3)



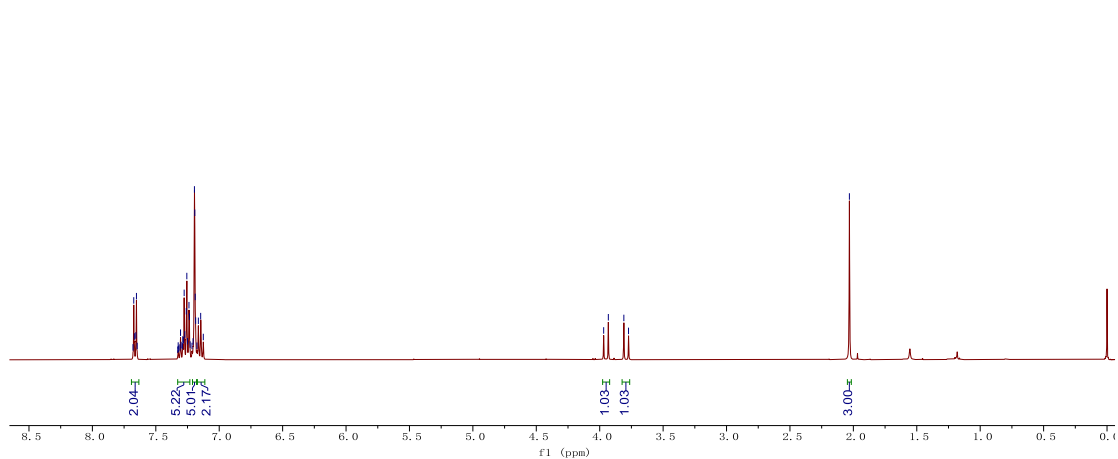
3ag ^{13}C NMR (101 MHz, CDCl_3)



7.680
7.664
7.657
7.653
7.647
7.327
7.323
7.320
7.310
7.305
7.301
7.290
7.287
7.283
7.276
7.272
7.260
7.255
7.250
7.238
7.235
7.230
7.215
7.206
7.195
7.189
7.186
7.176
7.164
7.146
7.125
3.969
3.932
3.810
3.773



3ah ^1H NMR (400 MHz, CDCl_3)



201.062

141.140
139.006
138.339
135.995
132.134
129.458
129.422
129.057
128.284
128.242
126.877

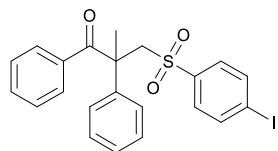
101.052

77.517 CDCl_3
77.200 CDCl_3
76.882 CDCl_3

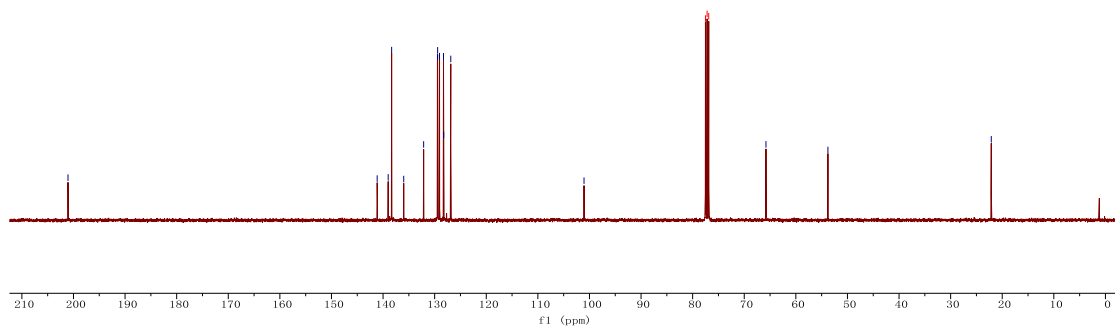
65.792

53.783

22.123



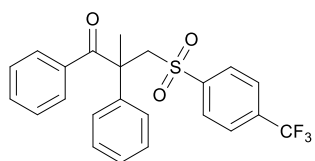
3ah ^{13}C NMR (101 MHz, CDCl_3)



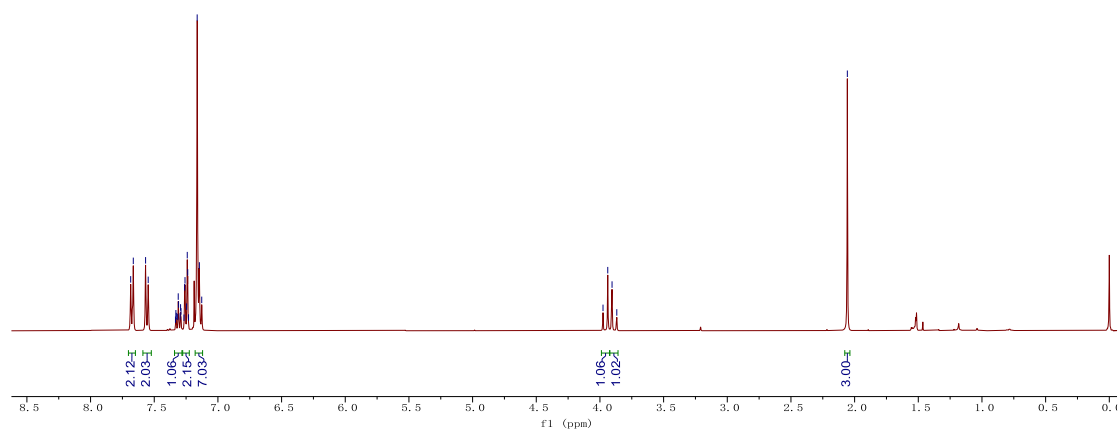
7.685
7.664
7.568
7.547
7.533
7.330
7.327
7.316
7.312
7.309
7.297
7.285
7.280
7.265
7.256
7.246
7.241
7.237
7.231
7.163
7.145
7.127

3.876
3.839
3.905
3.868

2.057



3ai ^1H NMR (400 MHz, CDCl_3)



200.939

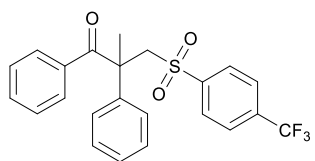
144.757
138.682
137.151
134.646
132.257
129.482
129.435
128.397
128.323
128.281
127.329
126.970
126.231
126.195
126.157
126.120
124.672
121.957
119.235

77.519 CDCl_3
77.202 CDCl_3
76.864 CDCl_3

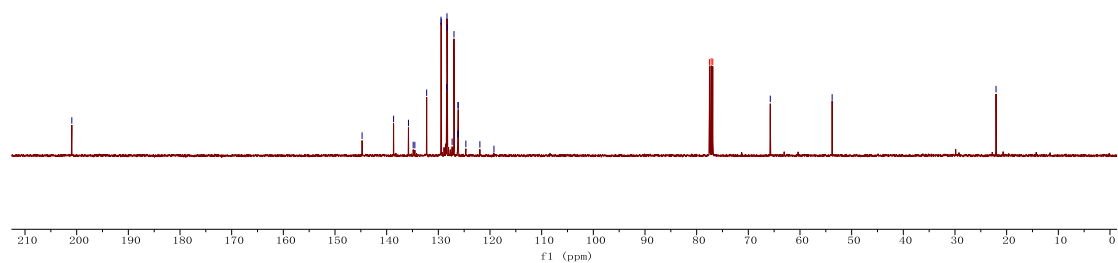
65.748

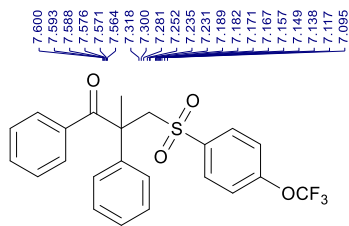
53.777

22.054

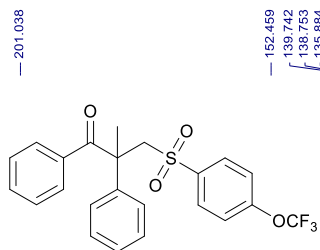
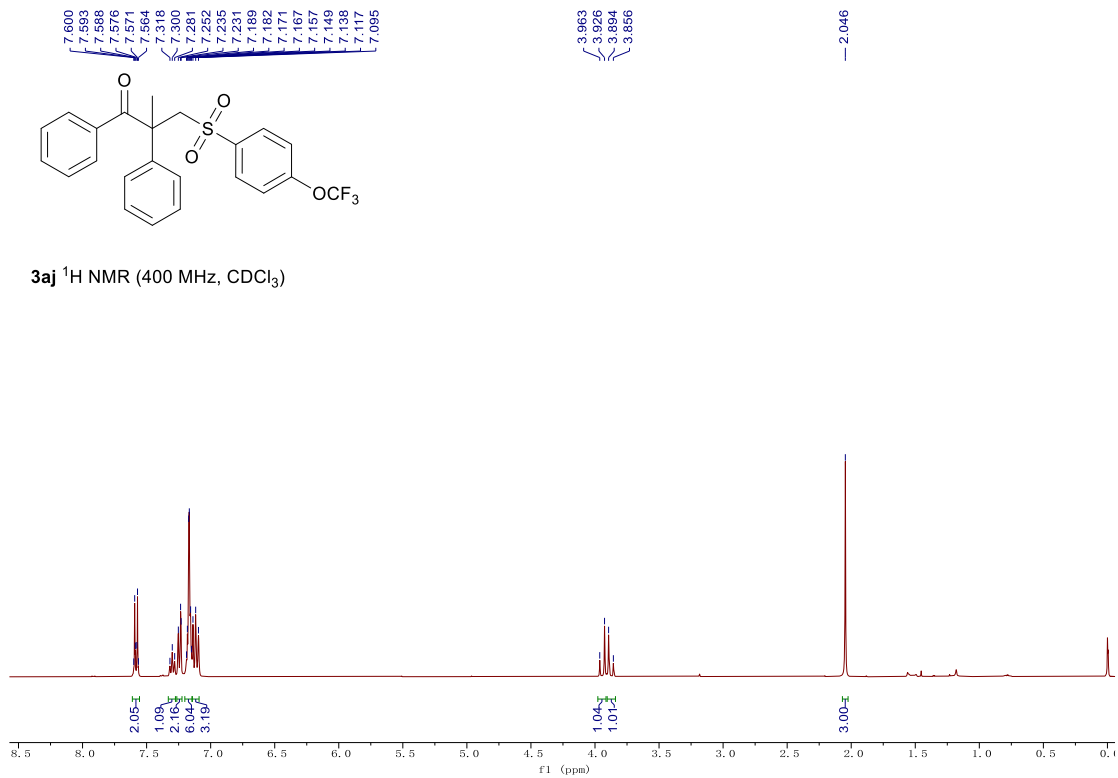


3ai ^{13}C NMR (101 MHz, CDCl_3)

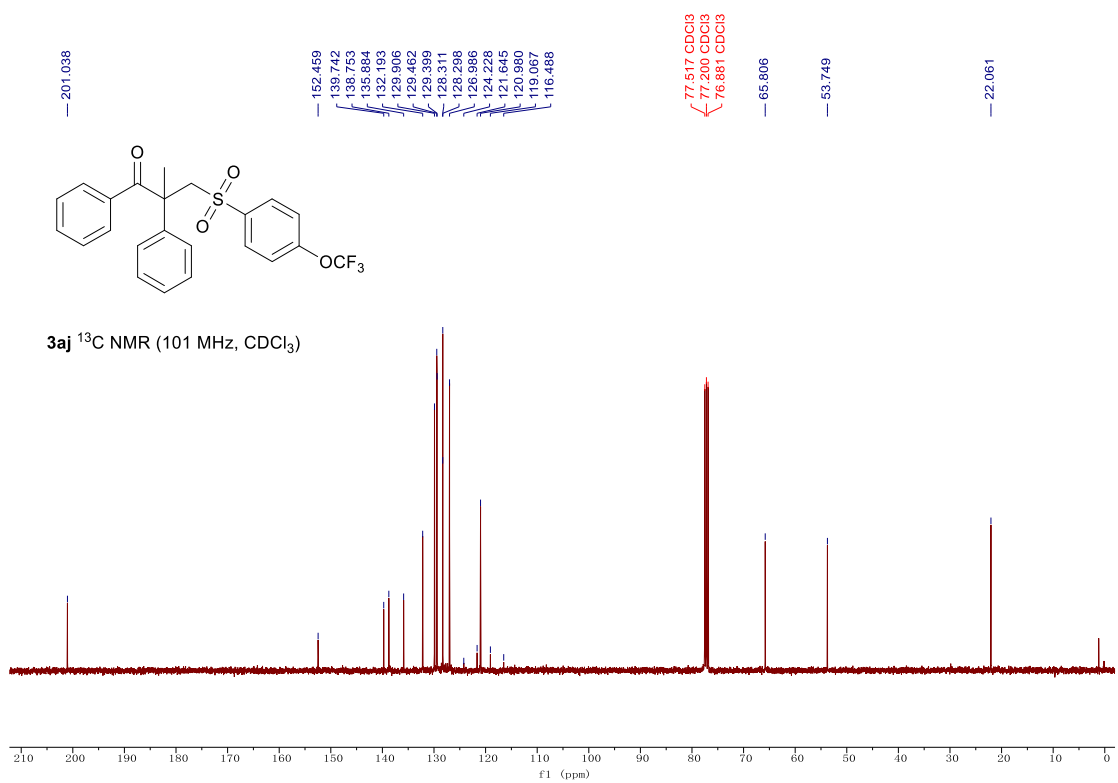


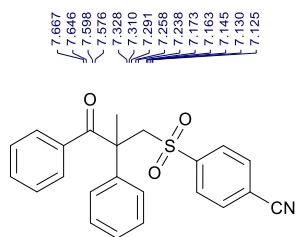


3aj ^1H NMR (400 MHz, CDCl_3)

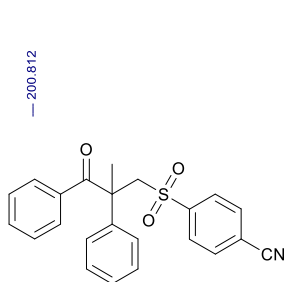
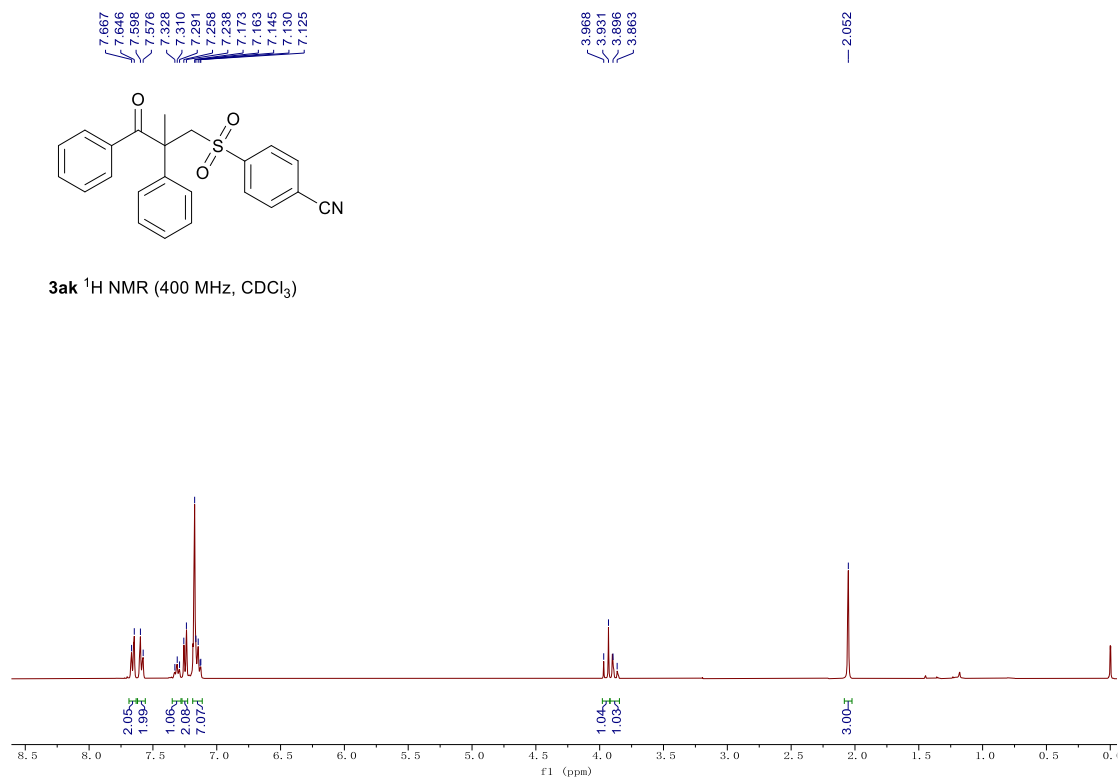


3aj ^{13}C NMR (101 MHz, CDCl_3)

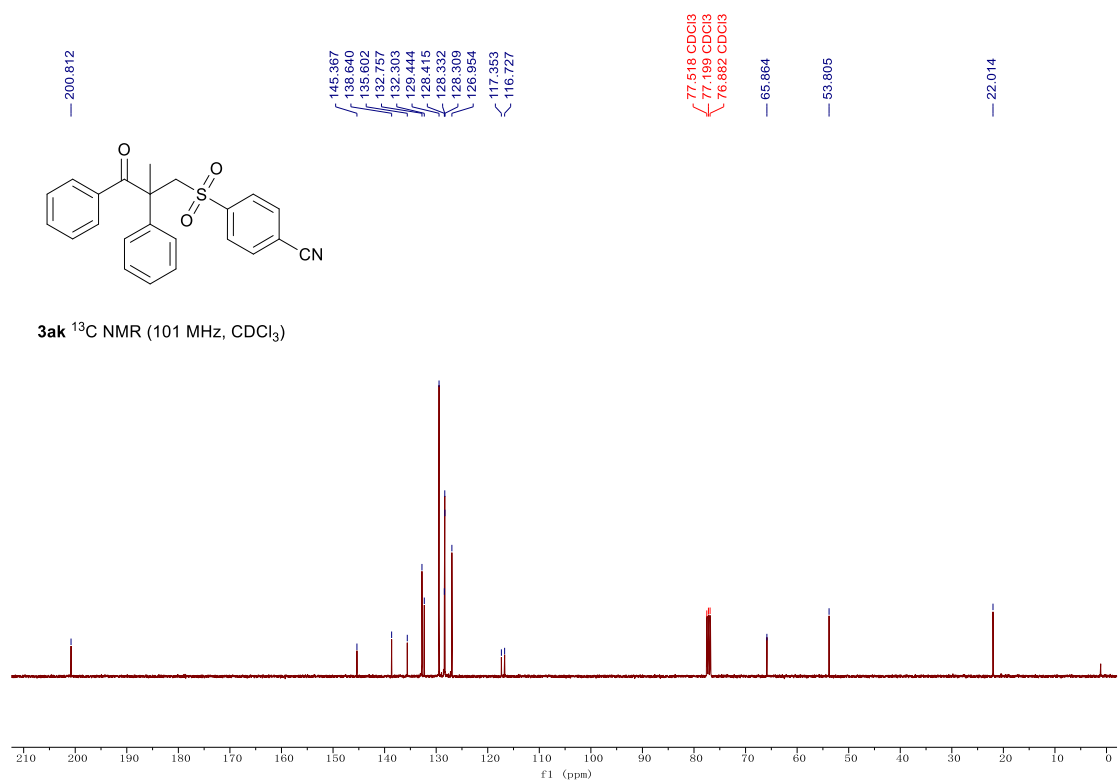




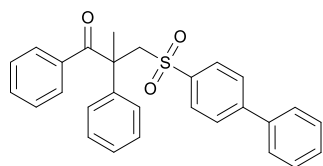
3ak ^1H NMR (400 MHz, CDCl_3)



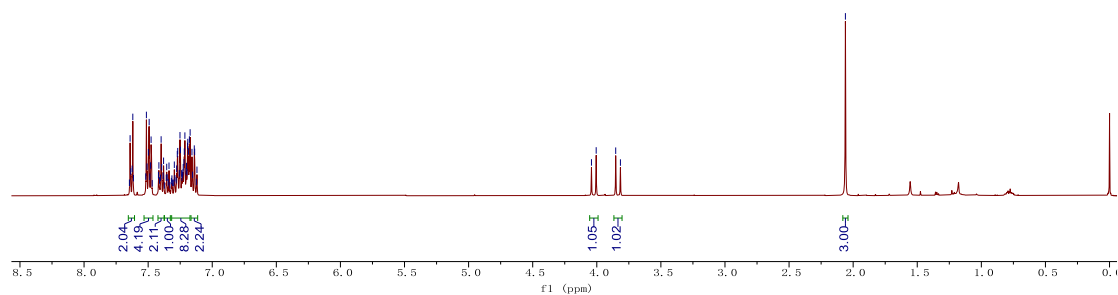
3ak ^{13}C NMR (101 MHz, CDCl_3)



7.646
7.641
7.636
7.625
7.620
7.615
7.519
7.514
7.509
7.498
7.487
7.481
7.468
7.420
7.416
7.411
7.404
7.399
7.394
7.383
7.380
7.374
7.359
7.355
7.352
7.343
7.337
7.330
7.319
7.314
7.311
7.300
7.296
7.291
7.281
7.277
7.273
7.269
7.262
7.252
7.246
7.239
7.236
7.233
7.229
7.226
7.220
7.218
7.213
7.203
7.201
7.197
7.193
7.191
7.186
7.178
7.172
7.158
7.153
7.140
7.137
7.124
7.119
4.042
3.985
3.977
3.916
2.060



3a1 ¹H NMR (400 MHz, CDCl₃)



— 201.236

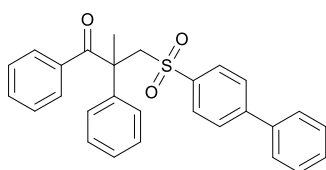
— 146.109
— 140.051
— 139.476
— 139.264
— 136.196
— 132.033
— 129.411
— 129.393
— 129.216
— 128.697
— 128.253
— 128.178
— 128.133
— 127.789
— 127.495
— 126.883

— 77.519 CDCl₃
— 77.201 CDCl₃
— 76.884 CDCl₃

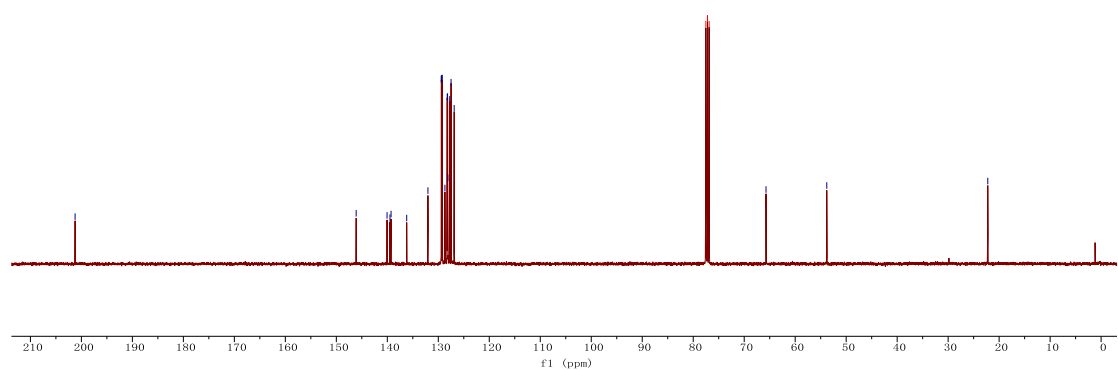
— 65.723

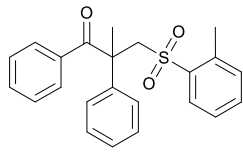
— 53.805

— 22.227

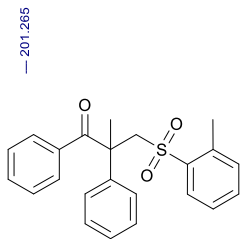
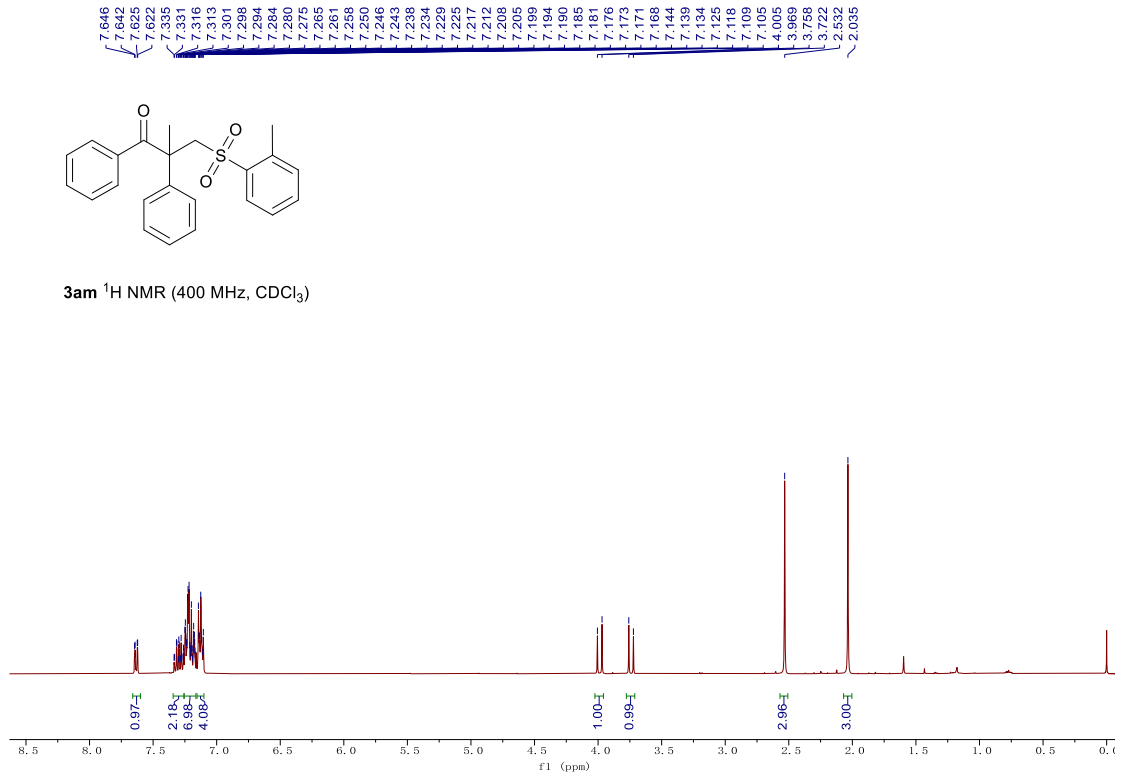


3a1 ¹³C NMR (101 MHz, CDCl₃)

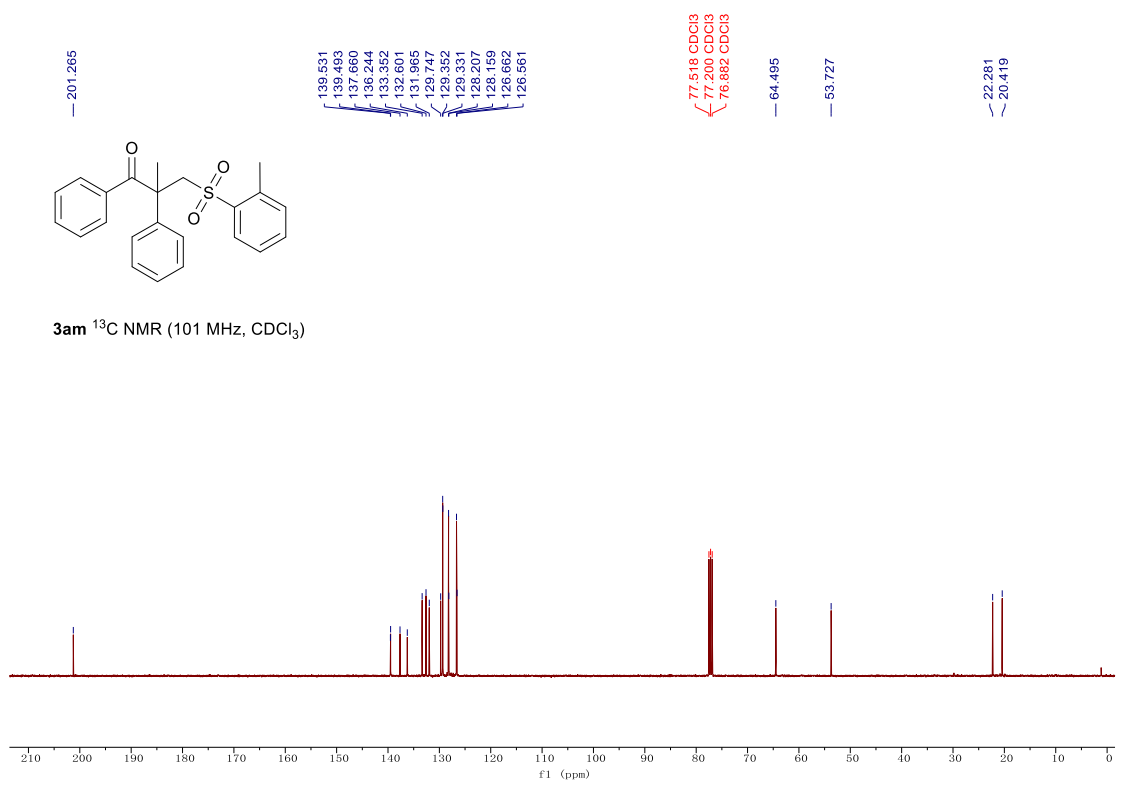


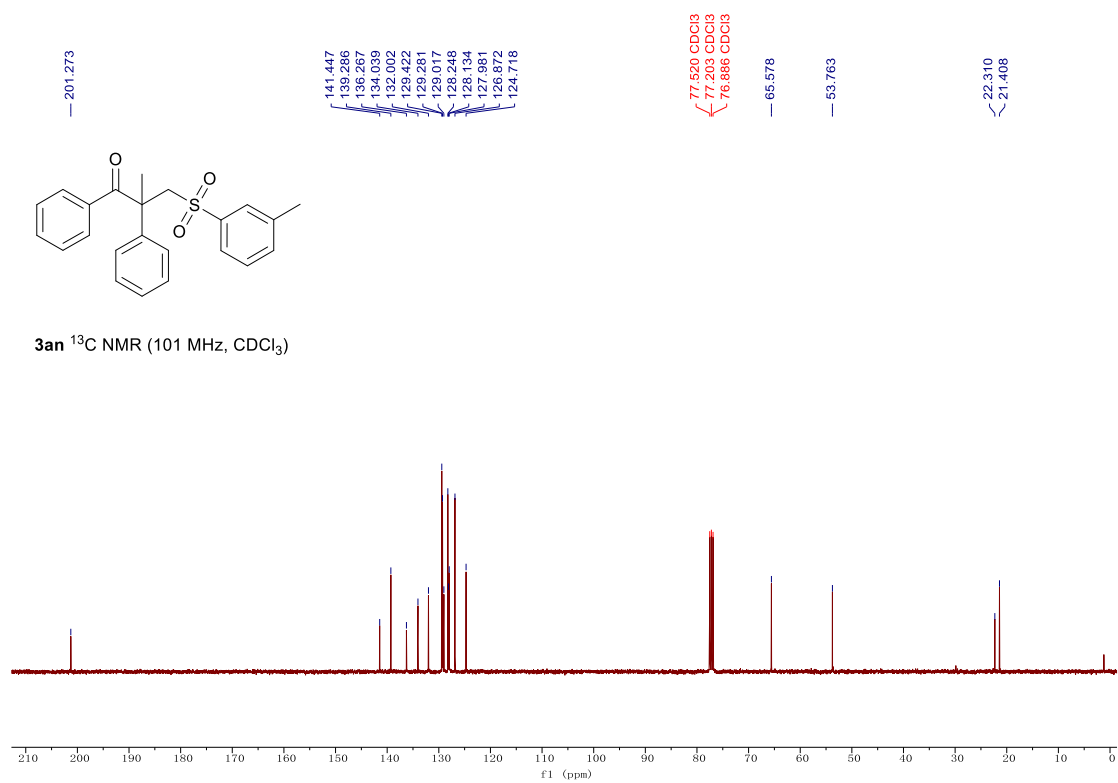
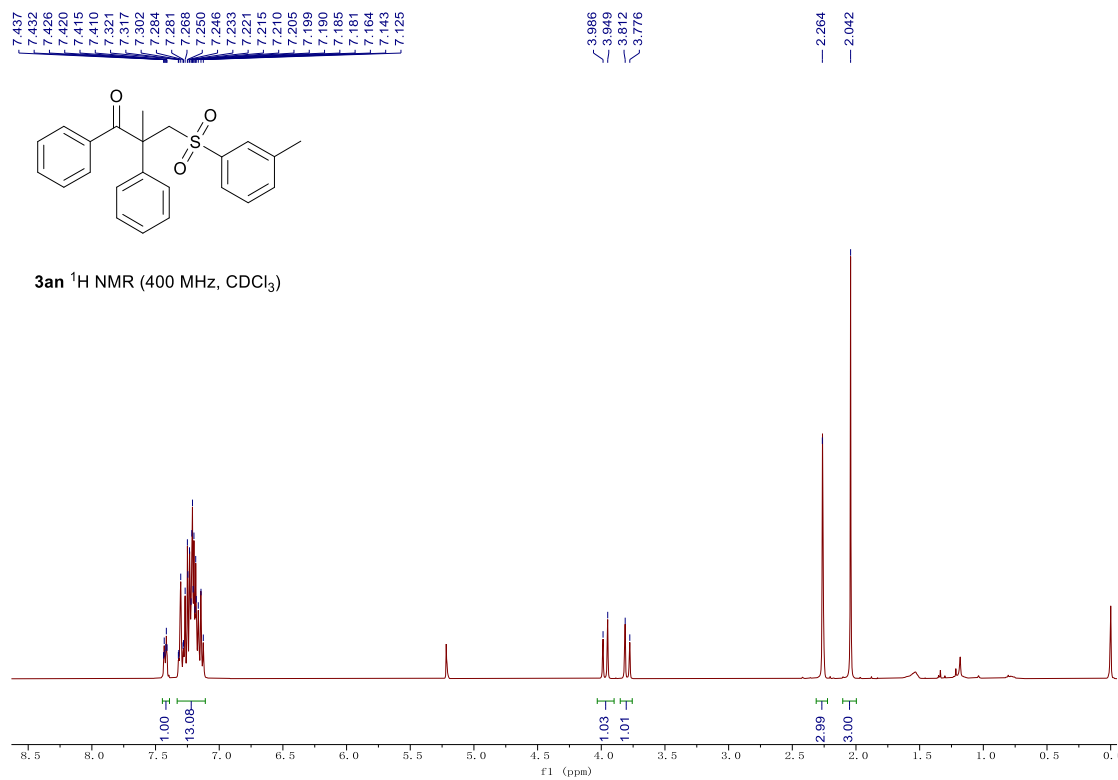


3am ^1H NMR (400 MHz, CDCl_3)



3am ^{13}C NMR (101 MHz, CDCl_3)

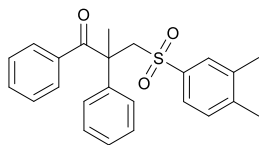




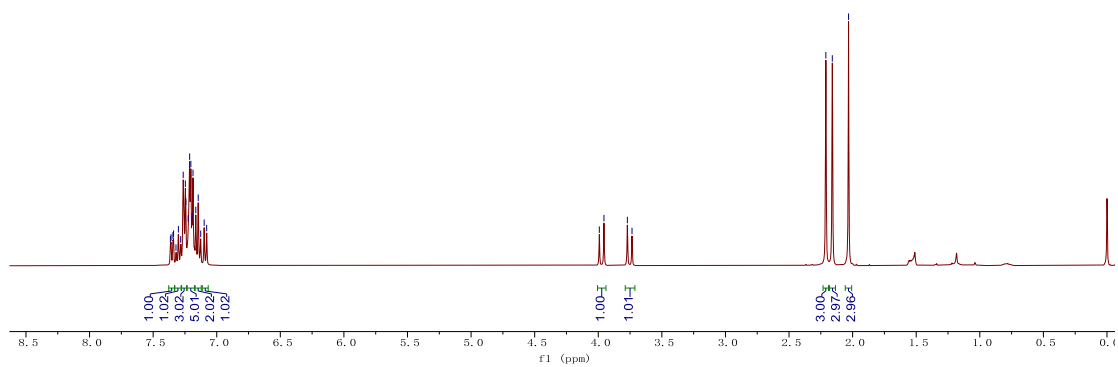
7.364
7.359
7.345
7.339
7.326
7.320
7.285
7.284
7.247
7.243
7.225
7.213
7.204
7.194
7.187
7.165
7.146
7.126
7.099
7.079

3.992
3.955
3.771
3.735

2.211
2.160
2.052



3ao ^1H NMR (400 MHz, CDCl_3)



201.313

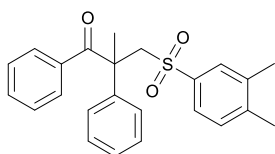
142.863
138.819
137.819
137.760
136.376
131.924
130.238
129.386
129.253
128.458
128.213
127.999
126.823
125.138

77.520 CDCl_3
77.203 CDCl_3
76.885 CDCl_3

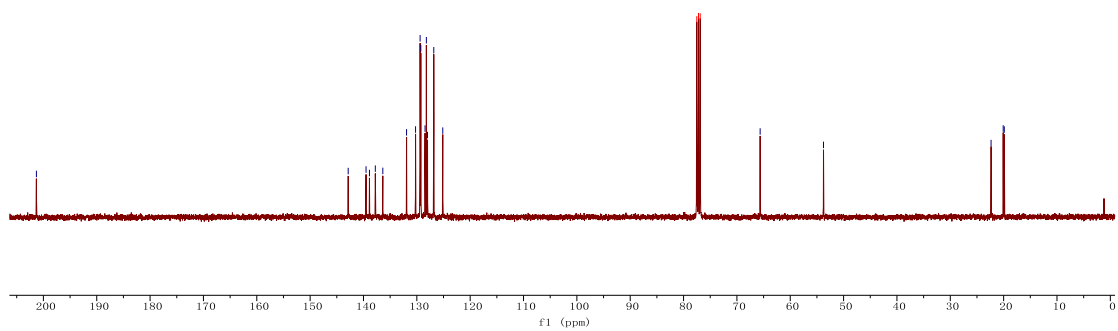
65.643

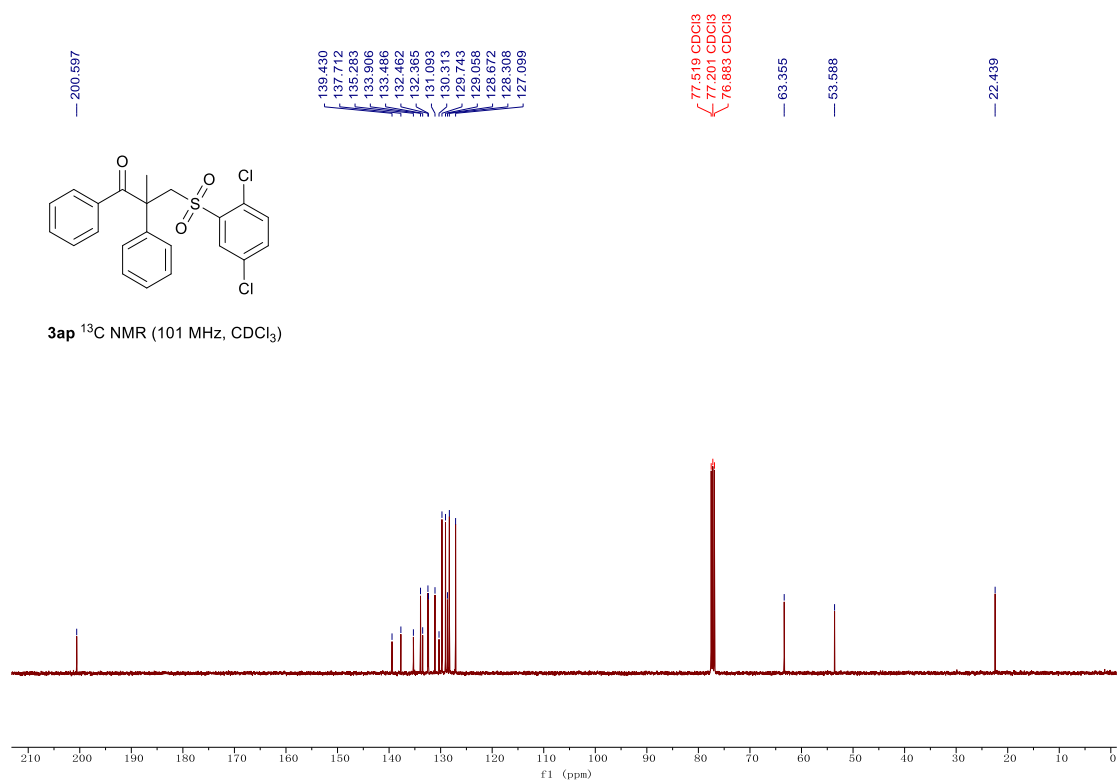
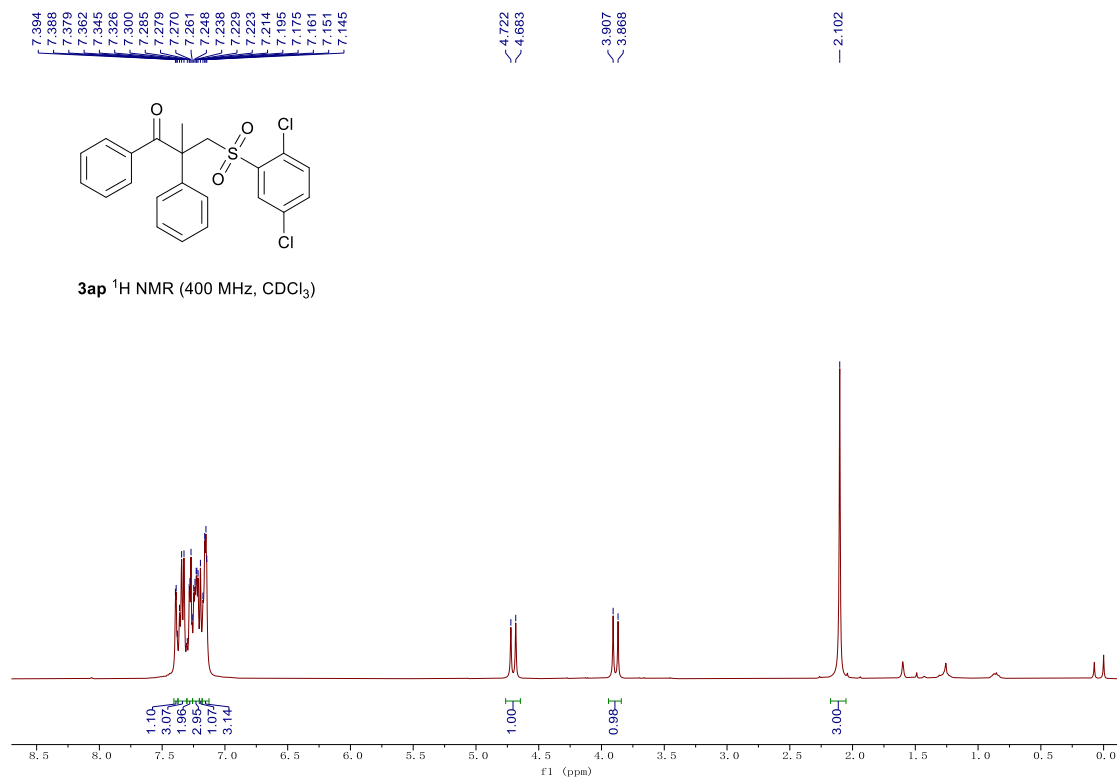
53.766

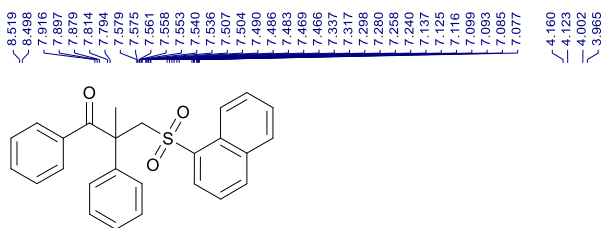
22.357
20.084
19.880



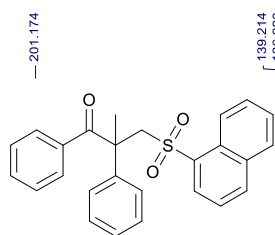
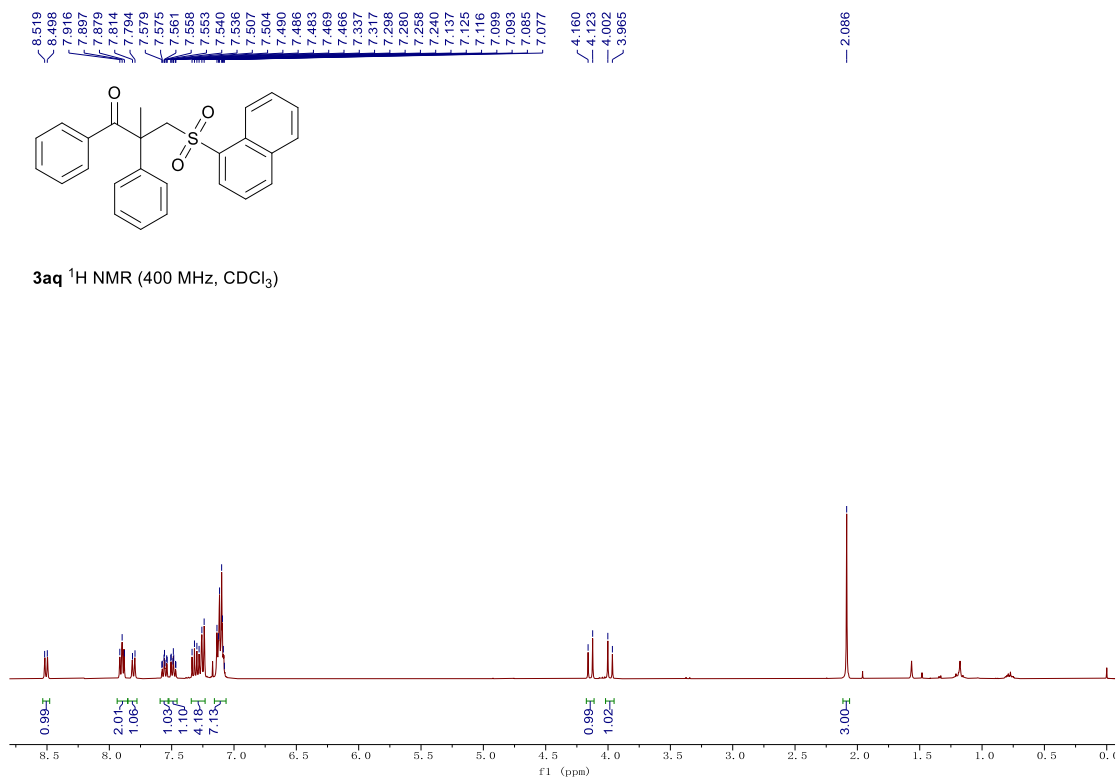
3ao ^{13}C NMR (101 MHz, CDCl_3)



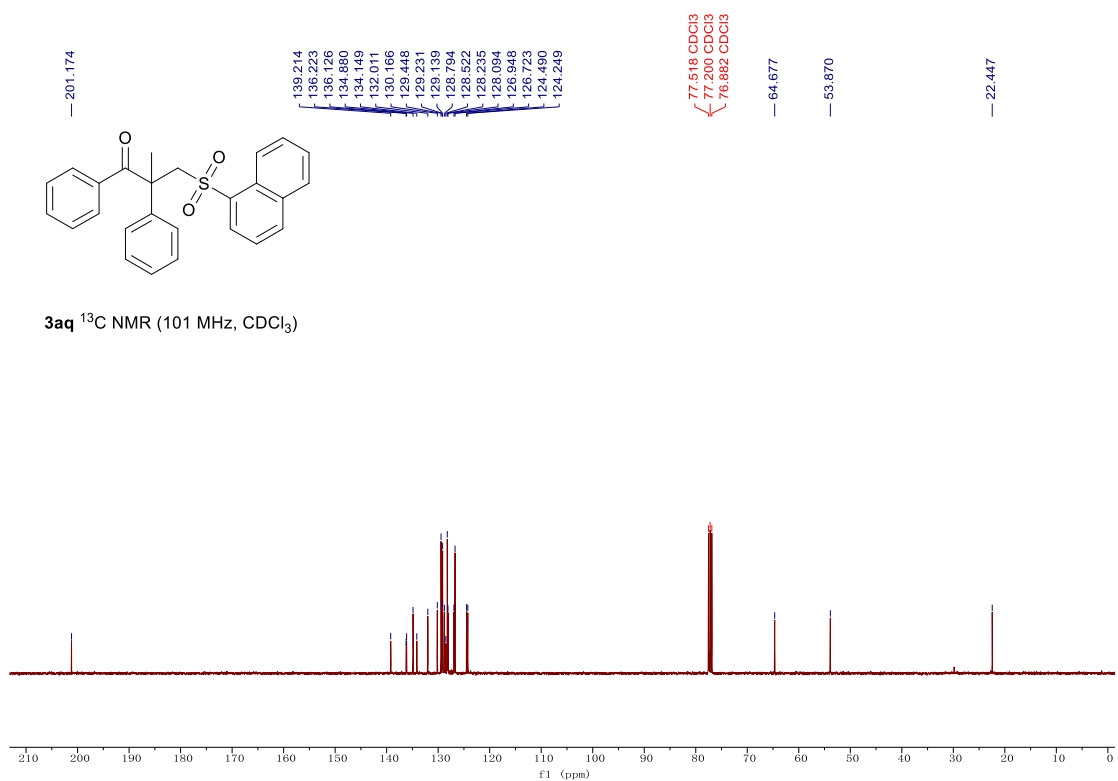


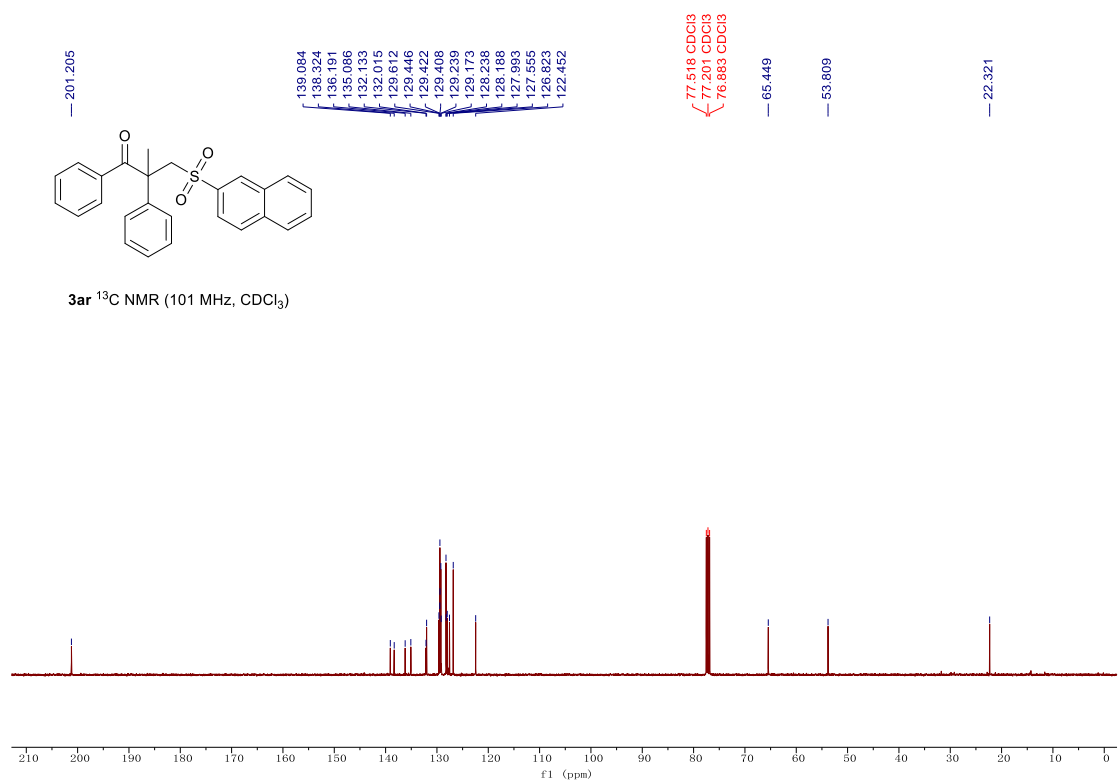
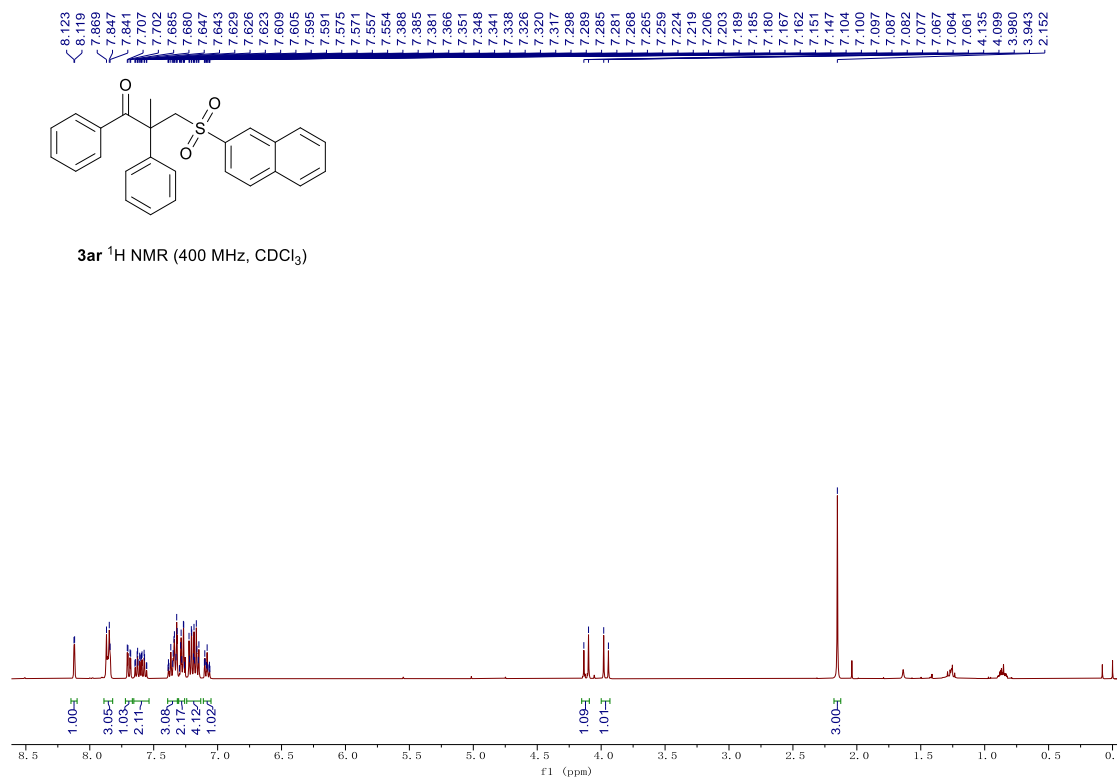


3aq ¹H NMR (400 MHz, CDCl₃)

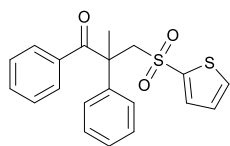


3aq ¹³C NMR (101 MHz, CDCl₃)

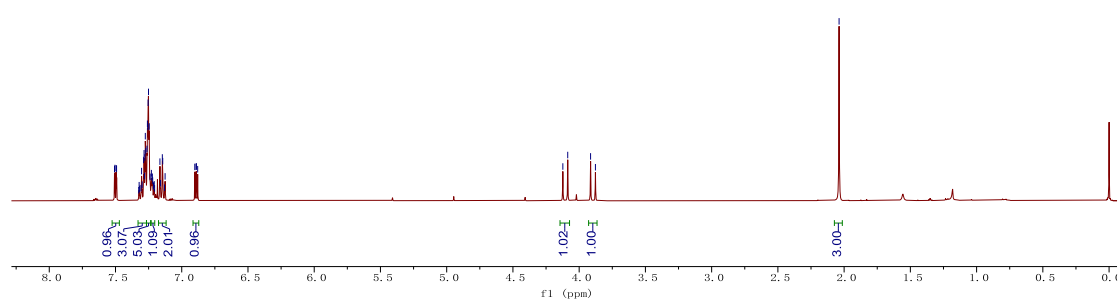




7.508
7.504
7.495
7.492
7.325
7.322
7.318
7.308
7.303
7.299
7.288
7.284
7.281
7.276
7.272
7.262
7.259
7.257
7.254
7.251
7.246
7.238
7.229
7.225
7.222
7.219
7.213
7.211
7.208
7.205
7.165
7.160
7.146
7.144
7.130
7.126
6.902
6.892
6.889
4.140
4.120
4.086
3.914
3.877



3as ¹H NMR (400 MHz, CDCl₃)



201.046

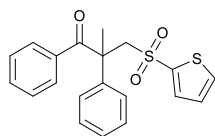
142.990
136.717
136.040
133.696
133.611
132.098
129.482
129.440
128.263
128.236
127.721
126.848

77.516 CDCl₃
77.201 CDCl₃
76.865 CDCl₃

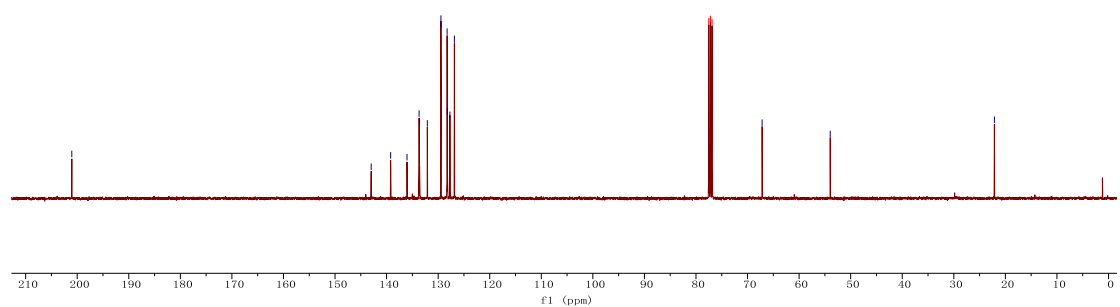
67.174

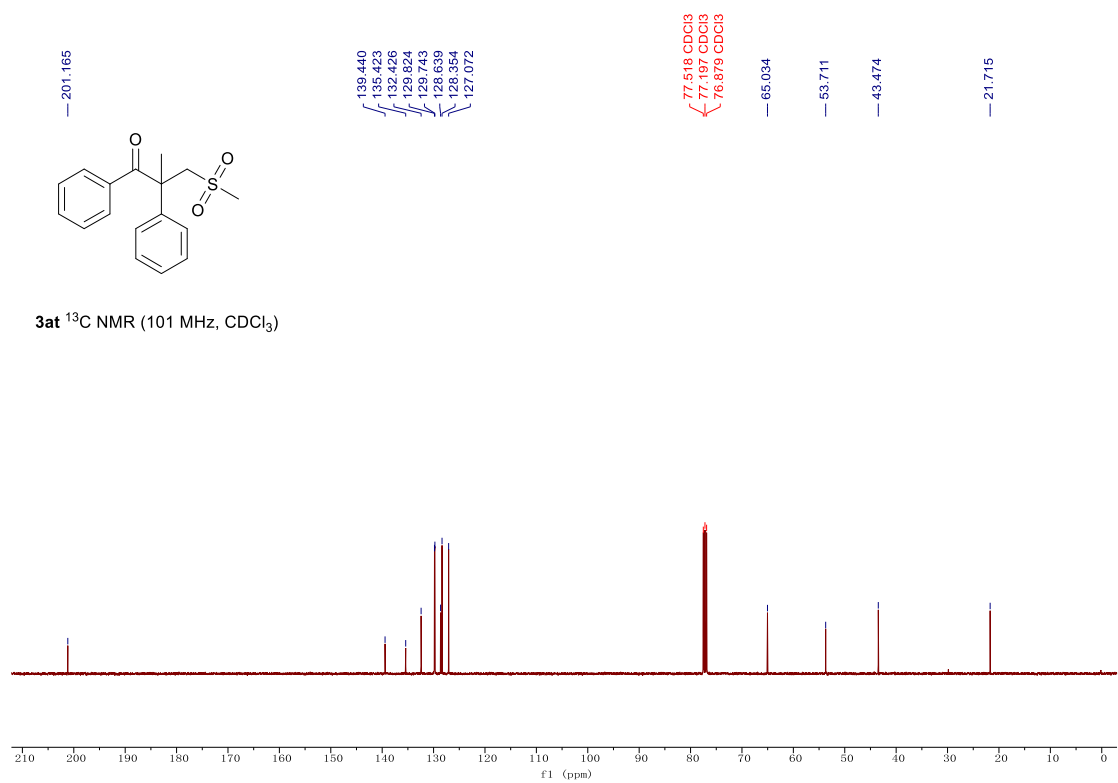
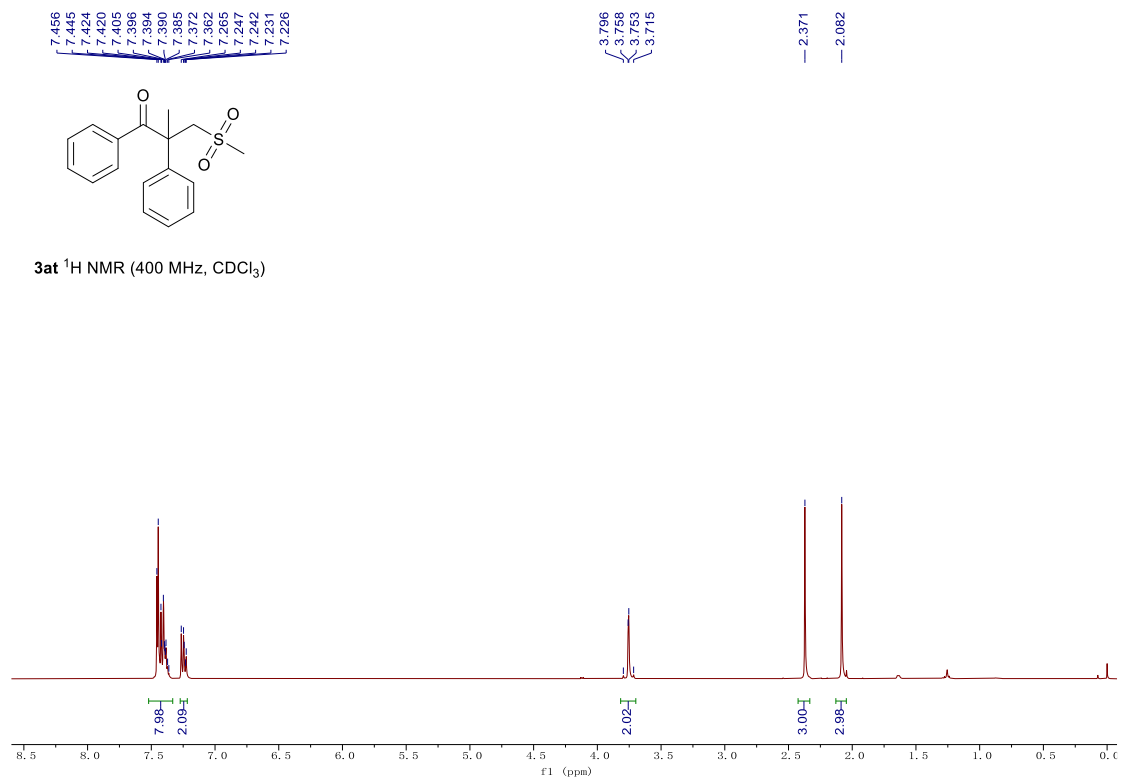
53.966

22.126

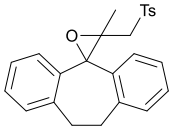


3as ¹³C NMR (101 MHz, CDCl₃)

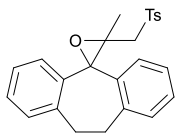
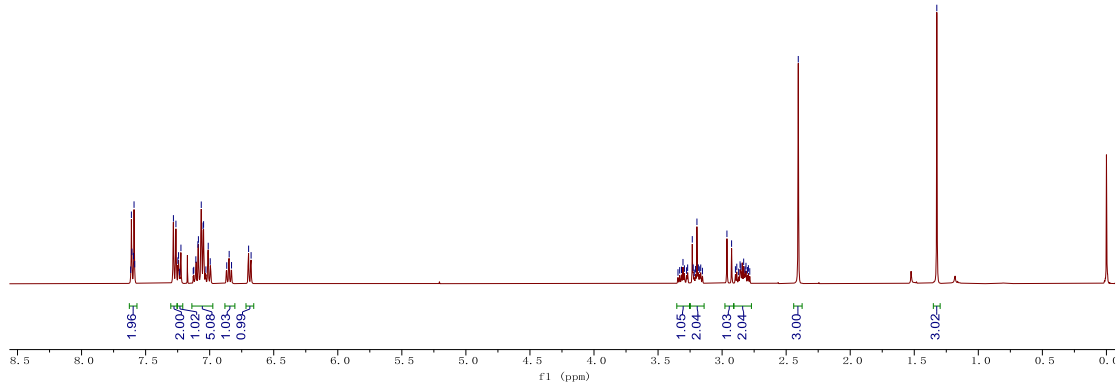




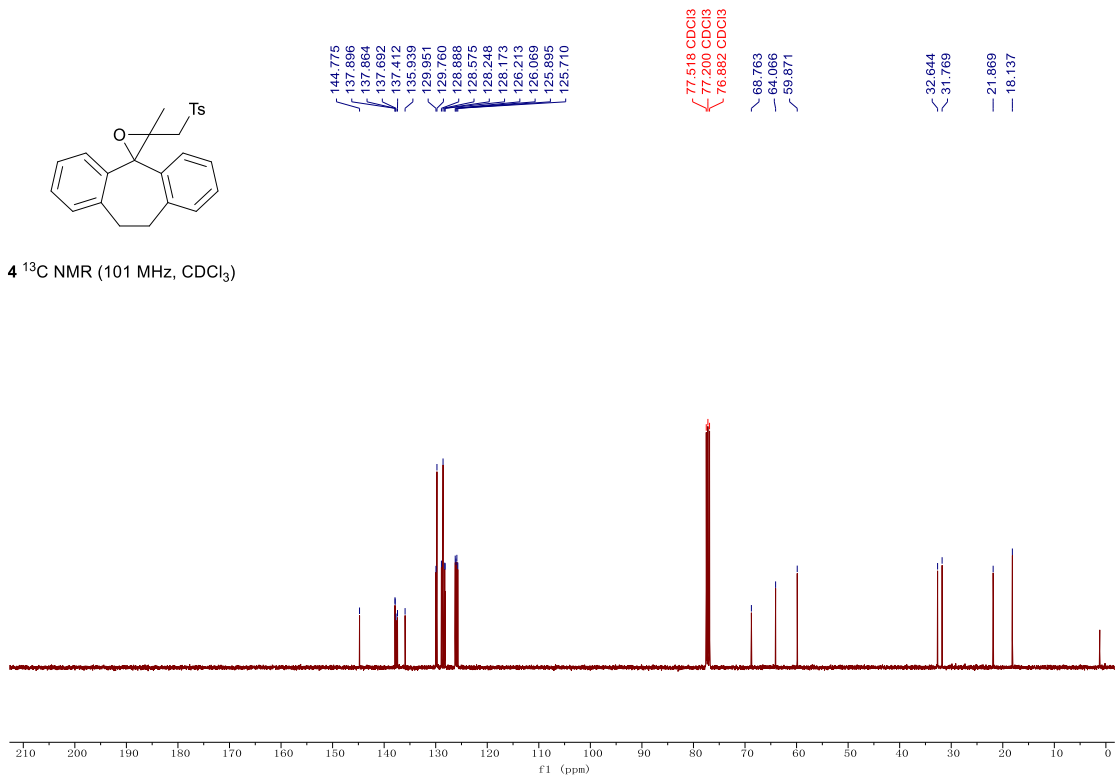
7.616
7.611
7.607
7.595
7.590
7.585
7.283
7.263
7.248
7.243
7.234
7.224
7.128
7.124
7.108
7.092
7.088
7.066
7.051
7.047
7.030
7.011
6.989
6.982
6.948
6.929
6.896
6.877
3.344
3.331
3.317
3.305
3.294
3.277
3.269
3.233
3.226
3.217
3.207
3.196
3.185
3.175
3.167
3.154
2.962
2.926
2.896
2.865
2.871
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1.852
1.832
2.821
2.814
2.802
2.795
2.784
2.405
1.324

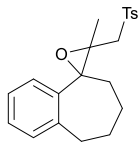


4 ¹H NMR (400 MHz, CDCl₃)

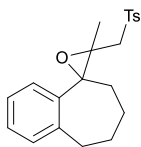
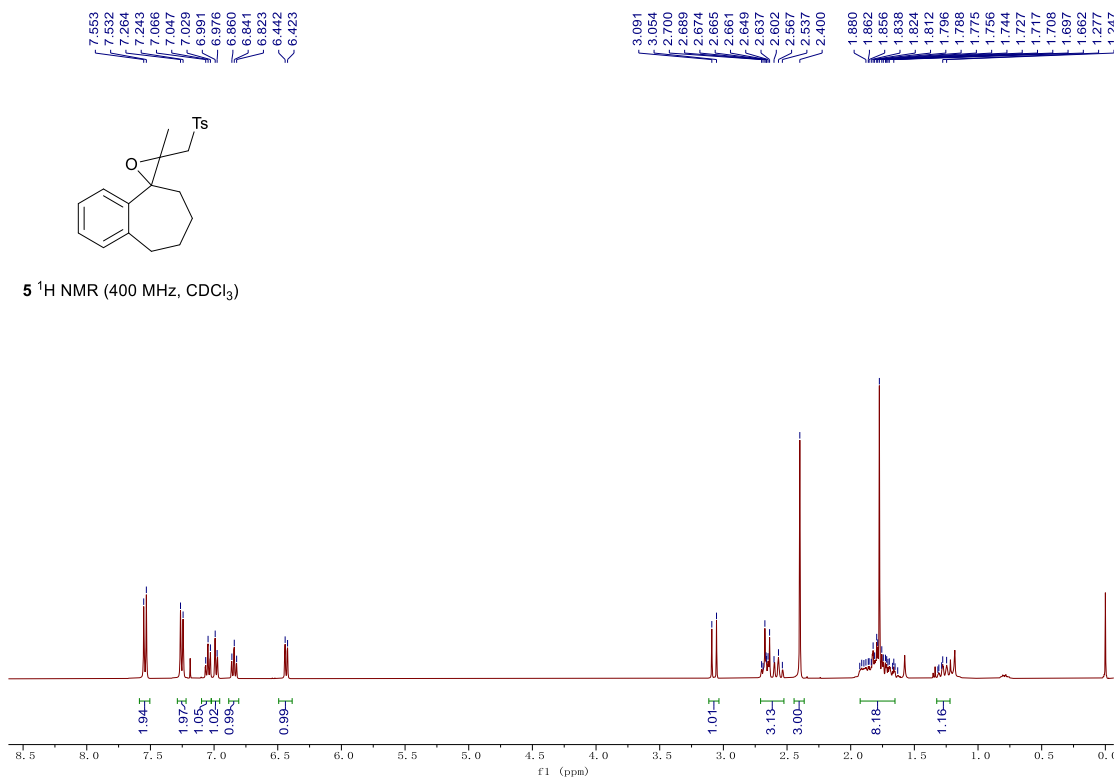


4 ¹³C NMR (101 MHz, CDCl₃)





5 ^1H NMR (400 MHz, CDCl_3)



5 ^{13}C NMR (101 MHz, CDCl_3)

