Supporting Information

1,2,3-Triazole as Special "X-Factor" in Promoting Hashmi Phenol Synthesis

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I. General Methods and materials:

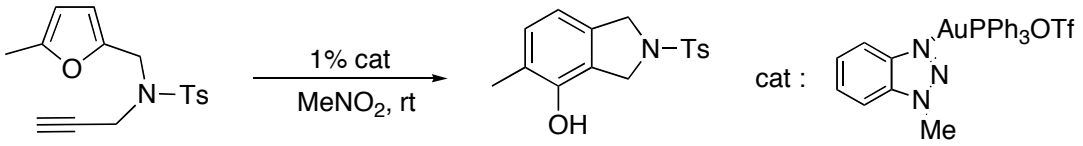
All of the reactions dealing with air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 600 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or $CDCl_3$ (δ 7.26 ppm) for ^{1}H and $CDCl_3$ (δ 77.0 ppm) for ^{13}C. Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain. Melting points were measured on a Mel-Temp 1001D apparatus and uncorrected. HRMS were recorded on LTQ-FTUHRA spectrometer.

Substrates **1a-1f** were synthesized according to the literature as below:

1. Carrettin, S.; Blanco, M. C.; Corma, A.; Hashmi, A. S. K. *Adv. Synth. Catal.* **2006,** *348*, 1283-1288.

2. Hashmi, A. S. K, Wölfle, M.; Ata, F.; Hamzic, M.; Salath, R.; Frey, W. *Adv. Synth. Catal*. **2006**, *348*, 2501-2508.

Representative procedure for Hashmi phenol synthesis



To a solution of (60 mg, 0.2 mmol) in nitromethane (2.6 mL, 0.075 M), was added Au(I) catalyst (Me-Bt-$AuPPh_3OTf$) (1.5 mg, 0.002 mol). The reaction mixture was stirred at room temperature, and monitored by TLC. After the reaction was completed, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (ethyl acetate/hexane, V/V, 3 : 1) to give (yield: 57 mg, 95%) as colorless crystals.

Procedure for NMR study for $Ph_3PAuOTf$ + substrate

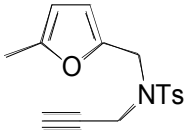
In a NMR tube, a solution Ph_3PAuCl (20 mg, 0.04 mmol) in $CDCl_3$ (1 mL) was prepared. At the same time, the internal standard (85% H_3PO_4 in sealed capillary) for ^{31}P NMR was added, the solution was used for ^{31}P NMR study firstly. Then AgOTf (10 mg, 0.04 mmol) was added in situ, and the NMR tube was shacked for some times. Then run the ^{31}P NMR experiment. After the substrate (60 mg, 0.2 mmol) was added to the NMR tube directly, the solution was turned brown very quickly. The Au species and reaction were monitored by ^{31}P NMR and ^{1}H NMR spectroscopy.

Procedure for NMR study for Me-Bt-$AuPPh_3OTf$ + substrate

In a NMR tube, a solution Me-Bt-$AuPPh_3OTf$ (30 mg, 0.04 mmol) in $CDCl_3$ (1 mL) was prepared.

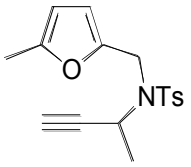
At the same time, the internal standard (85% H_3PO_4 in sealed capillary) for ^{31}P NMR was added, the solution was used for ^{31}P NMR study first. After the substrate (60 mg, 0.2 mmol) was added to the NMR tube directly, the solution was turned yellow very quickly. The Au species and reaction were monitored by ^{31}P NMR and ^{1}H NMR spectroscopy.

II. Compounds Characterization



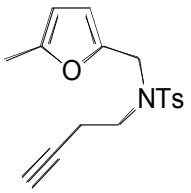
1a

4-methyl-N-((5-methylfuran-2-yl)methyl)-N-(prop-2-ynyl)benzenesulfonamide 1a: white solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 6.15 (d, *J* = 3.0 Hz, 1H), 5.86 (d, *J* = 3.0 Hz, 1H), 4.38 (s, 2H), 4.02 (d, *J* = 3.0 Hz, 2H), 2.42 (s, 3H), 2.20 (s, 3H), 2.06 (t, *J* = 3.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 152.8, 146.5, 143.5, 136.1, 129.4, 127.8, 111.0, 106.2, 76.6, 73.7, 42.8, 36.0, 21.5, 13.5; HRMS Calculated for $[C_{16}H_{17}NO_3S+H]^+$: 304.09291, Found: 304. 10019.



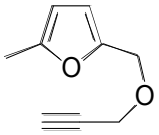
1b

N-(but-3-yn-2-yl)-4-methyl-N-((5-methylfuran-2-yl)methyl)benzenesulfonamide 1b: white solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.15 (d, *J* = 3.0 Hz, 1H), 5.85 (d, *J* = 3.0 Hz, 1H), 4.90 (q, *J* = 7.2 Hz, 1H), 4.51 (d, *J* = 16.2 Hz, 1H), 4.26 (d, *J* = 16.2 Hz, 1H), 2.41(s, 3H), 2.20 (s, 3H), 2.17 (d, *J* = 2.4 Hz, 1H), 1.31 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 151.7, 148.7, 143.3, 136.6, 129.4, 127.5, 110.1, 106.3, 81.0, 73.3, 45.7, 41.1, 22.0, 21.5, 13.4; HRMS Calculated for $[C_{17}H_{19}NO_3S+Na]^+$: 340.09779, Found: 340.09792.



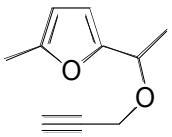
1c

N-(but-3-ynyl)-4-methyl-N-((5-methylfuran-2-yl)methyl)benzenesulfonamide 1c: white solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.66 (d, *J* = 9.0 Hz, 2H), 7.24 (d, *J* = 9.0 Hz, 2H), 6.04 (d, *J* = 3.0 Hz, 1H), 5.81 (d, *J* = 3.0 Hz, 1H), 4.38(s, 2H), 3.27 (t, *J* = 7.8 Hz, 2H), 2.40 (s, 3H), 2.36 (t, *J* = 7.8 Hz, 2H), 2.12 (s, 3H), 1.94 (t, *J* = 3.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 152.4, 147.3, 143.1, 136.9, 129.5, 127.3, 110.6, 106.2, 81.0, 70.0, 46.0, 44.6, 21.4, 19.1, 13.4; HRMS Calculated for $[C_{17}H_{19}NO_3S+H]^+$: 318.10856, Found: 318.11584.



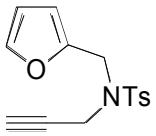
1d

2-methyl-5-((prop-2-ynyloxy)methyl)furan 1d: colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.21 (d, *J* = 3.0 Hz, 1H), 5.89 (d, *J* = 3.0 Hz, 1H), 4.46 (s, 2H), 4.12 (t, *J* = 2.4 Hz, 2H), 2.44 (t, *J* = 2.4 Hz, 1H), 2.26(s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 152.7, 148.7, 111.0, 106.0, 79.3, 74.5, 62.9, 56.2, 13.3; HRMS Calculated for $[C_9H_{10}O_2+H]^+$: 151.06808, Found: 151.07536.



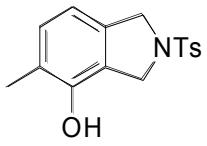
1e

2-methyl-5-(1-(prop-2-ynyloxy)ethyl)furan 1e: colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.16 (d, *J* = 3.0 Hz, 1H), 5.89 (d, *J* = 3.0 Hz, 1H), 4.62 (q, *J* = 6.6 Hz, 1H), 4.11 (d, *J* = 15.6 Hz, 1H), 3.97 (d, *J* = 15.6 Hz, 1H), 2.39 (t, *J* = 2.4 Hz, 1H), 2.26(s, 3H)), 1.51 (dd, *J* = 6.6 Hz, 1.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 152.2, 152.1, 108.8, 105.8, 79.9, 74.0, 69.1, 55.1, 19.4, 13.4; HRMS Calculated for $[C_{10}H_{12}O_2+H]^+$: 165.08373, Found: 165.09101.



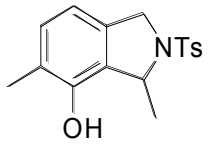
1f

N-(furan-2-ylmethyl)-4-methyl-N-(prop-2-ynyl)benzenesulfonamide 1f: white solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.35 (s, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.28-6.31 (m, 2H), 4.43 (s, 2H), 4.02 (d, *J* = 2.4 Hz, 2H), 2.43(s, 3H), 2.07 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 148.6, 143.6, 142.9, 136.0, 129.5, 127.7, 110.4, 110.0, 76.5, 73.9, 42.7, 36.1, 21.5; HRMS Calculated for $[C_{15}H_{15}NO_3S+H]^+$: 290.07726, Found: 290.08459.



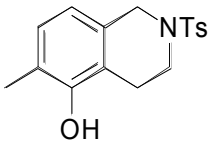
3a

5-methyl-2-tosylisoindolin-4-ol 3a: white solid, yield 95%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 (dd, *J* = 6.6 Hz, 1.8 Hz, 2H), 7.30 (dd, *J* = 6.6 Hz, 1.8 Hz, 2H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 4.60 (d, *J* = 13.8 Hz, 2H), 4.599 (d, *J* = 13.2 Hz, 2H), 2.40 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 149.0, 143.6, 135.8, 133.8, 130.7, 129.8, 127.6, 122.6, 122.1, 114.4, 54.0, 51.5, 21.5, 15.1; HRMS Calculated for $[C_{15}H_{16}NO_3S+H]^+$: 291.08509, Found: 291.09237.



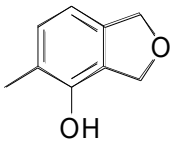
3b

3,5-dimethyl-2-tosylisoindolin-4-ol 3b: white solid, yield 93%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.73 (dt, *J* = 8.4 Hz, 1.8 Hz, 2H), 7.24 (dt, *J* = 8.4 Hz, 1.8 Hz, 2H), 6.96 (d, *J* = 7.2 Hz, 1H), 6.61 (d, *J* = 7.2 Hz, 1H), 5.11 (qd, *J* = 6.6 Hz, 3.6 Hz, 1H), 4.68 (d, *J* = 13.8 Hz, 1H), 4.53 (d, *J* = 13.8 Hz, 1H), 2.36 (s, 3H), 2.19 (s, 3H), 1.67 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 148.9, 143.3, 135.2, 135.1, 130.6, 129.7, 127.8, 127.3, 122.0, 114.3, 60.8, 53.4, 22.2, 21.4, 15.1; HRMS Calculated for $[C_{17}H_{19}NO_3S+H]^+$: 318.10856, Found: 318.09584.



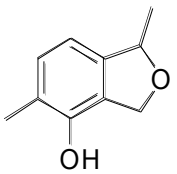
3c

6-methyl-2-tosyl-1,2,3,4-tetrahydroisoquinolin-5-ol 3c: white solid, yield 88%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.55 (d, *J* = 7.8 Hz, 1H), 4.18 (s, 2H), 3.35 (t, *J* = 6.0 Hz, 2H), 2.82 (t, *J* = 6.0 Hz, 2H), 2.42 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 151.4, 143.6, 133.3, 130.9, 129.7, 128.4, 127.8, 120.5, 119.6, 118.2, 47.4, 43.5, 23.2, 21.5, 15.4; HRMS Calculated for $[C_{17}H_{19}NO_3S+H]^+$: 318.10856, Found: 318.11584.



3d

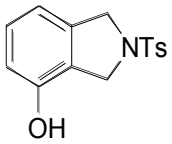
5-methyl-1,3-dihydroisobenzofuran-4-ol 3d: white solid, yield 94%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.04 (d, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 7.2 Hz, 1H), 5.12 (s, 2H), 5.09 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 148.2, 139.2, 130.5, 125.2, 121.6, 112.9, 74.0, 71.6, 15.0; HRMS Calculated for $[C_9H_{10}O_2+H]^+$: 151.06808, Found: 151.07536.



3e

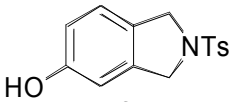
1,5-dimethyl-1,3-dihydroisobenzofuran-4-ol 3e: white sold, yield 90%. ^{1}H NMR (600 MHz,

$CDCl_3$): δ 7.05 (d, *J* =7.2 Hz, 1H), 6.64 (d, *J* = 7.2 Hz, 1H), 5.32 (q, *J* = 6.0 Hz, 1H), 5.16 (d, *J* = 12.0 Hz, 1H), 5.05 (d, *J* = 12.0 Hz, 1H), 2.26 (s, 3H), 1.48 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 148.1, 143.5, 130.6, 125.0, 122.1, 112.8, 80.6, 70.2, 21.8, 15.1; HRMS Calculated for $[C_{10}H_{12}O_2+H]^+$: 165.08373, Found: 165.09101.



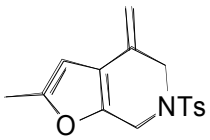
3f

2-tosylisoindolin-4-ol 3f: white solid, yield 82% for two isomers. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.10 (dd, *J* = 7.2 Hz, 6.6 Hz, 1H), 6.73 (d, *J* = 7.2 Hz, 1H), 6.61 (d, *J* = 6.6 Hz, 1H), 4.61 (dd, *J* = 7.2 Hz, 1.8 Hz, 4H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 150.8, 143.8, 138.4, 133.8, 129.8, 129.4, 127.6, 122.8, 114.8, 114.0, 54.1, 51.5, 21.5; HRMS Calculated for $[C_{15}H_{15}NO_3S+H]^+$: 290.07726, Found: 290.08454.



3f'

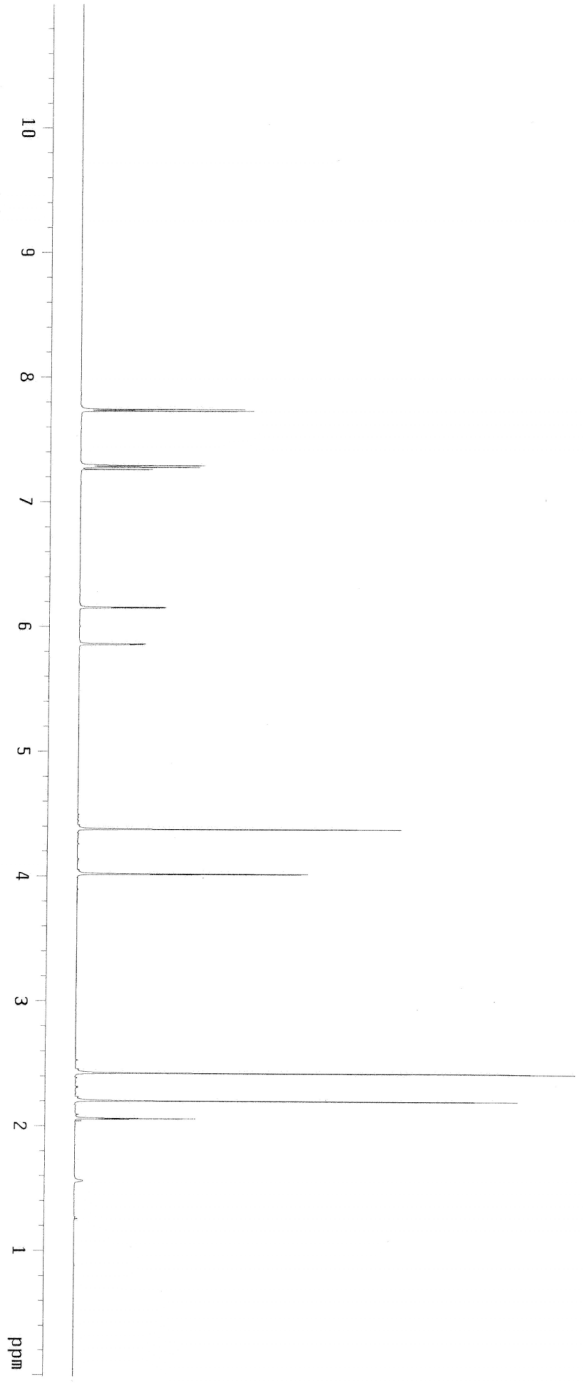
2-tosylisoindolin-5-ol 3f': white solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.63 (s, 1H), 4.53 (d, *J* = 7.8 Hz, 4H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 155.5, 143.7, 137.7, 133.8, 129.8, 128.0, 127.6, 123.5, 115.1, 109.4, 53.7, 53.2, 21.5; HRMS Calculated for $[C_{15}H_{15}NO_3S+H]^+$: 290.07726, Found: 290.08454.



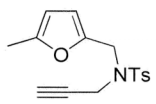
4a

2-methyl-4-methylene-6-tosyl-4,5,6,7-tetrahydrofuro[2,3-c]pyridine 4a: colorless oil, yield 29%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 5.92 (s, 1H), 4.94 (s, 1H), 4.86 (s, 1H), 4.30 (s, 2H), 3.95 (s, 2H), 2.38 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 152.4, 145.4, 143.6, 134.2, 132.8, 129.4, 127.6, 118.9, 106.6, 101.8, 49.4, 43.6, 21.5, 13.4; HRMS Calculated for $[C_{15}H_{16}NO_3S+H]^+$: 291.08509, Found: 291.09237.

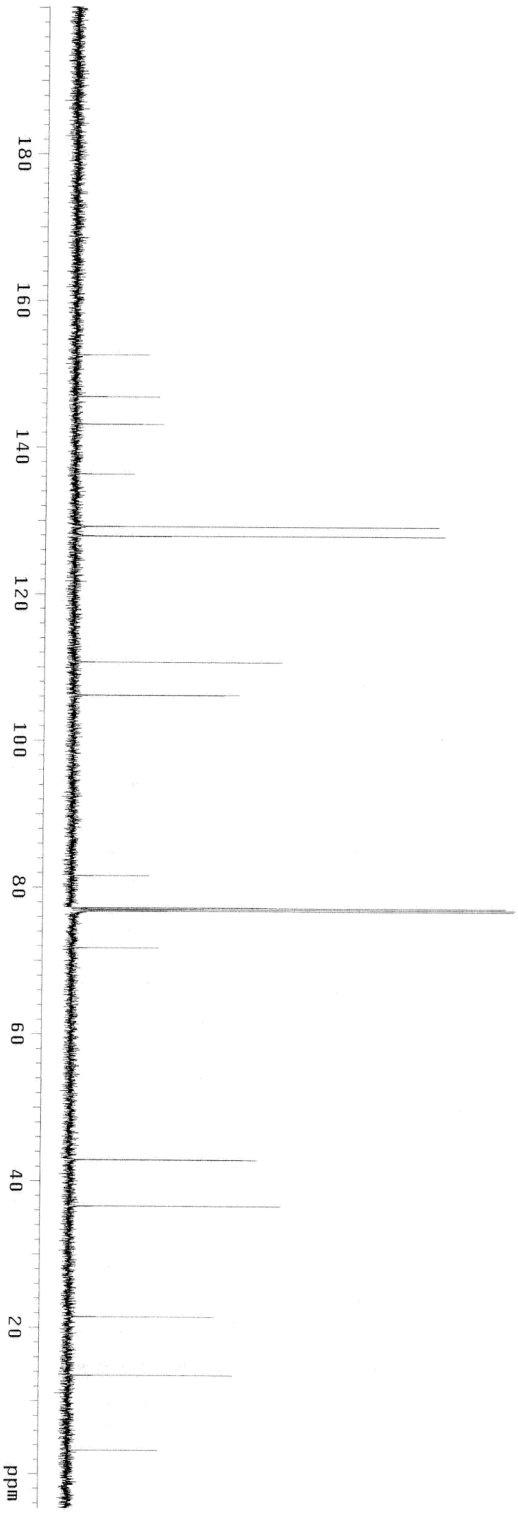
III. NMR spectra data



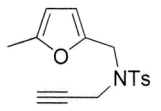
1a



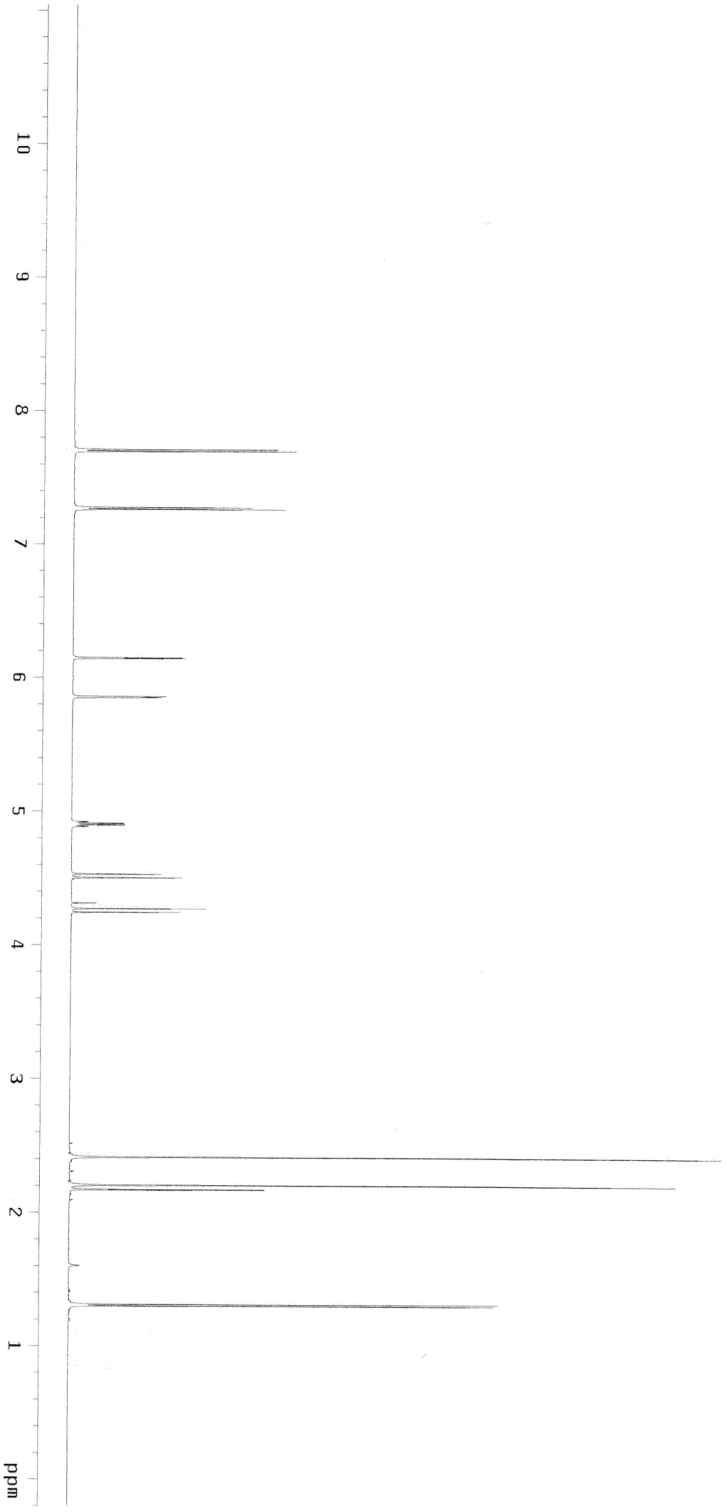
600MHz ^{1}H NMR



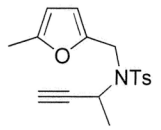
1a



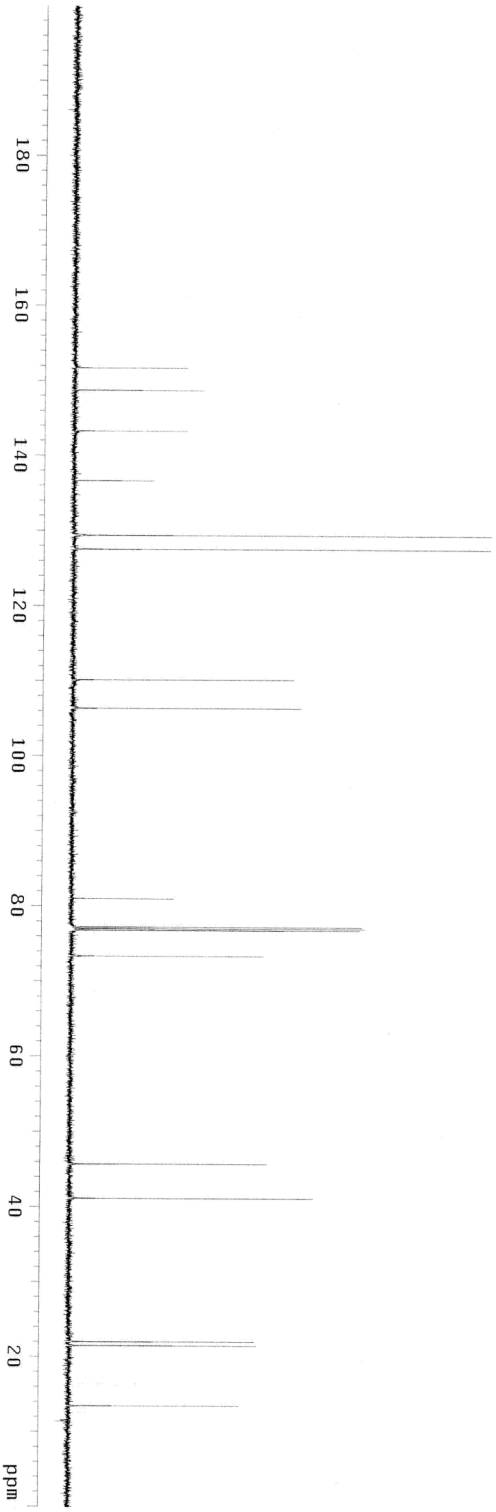
150MHz ^{13}C NMR



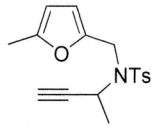
1b



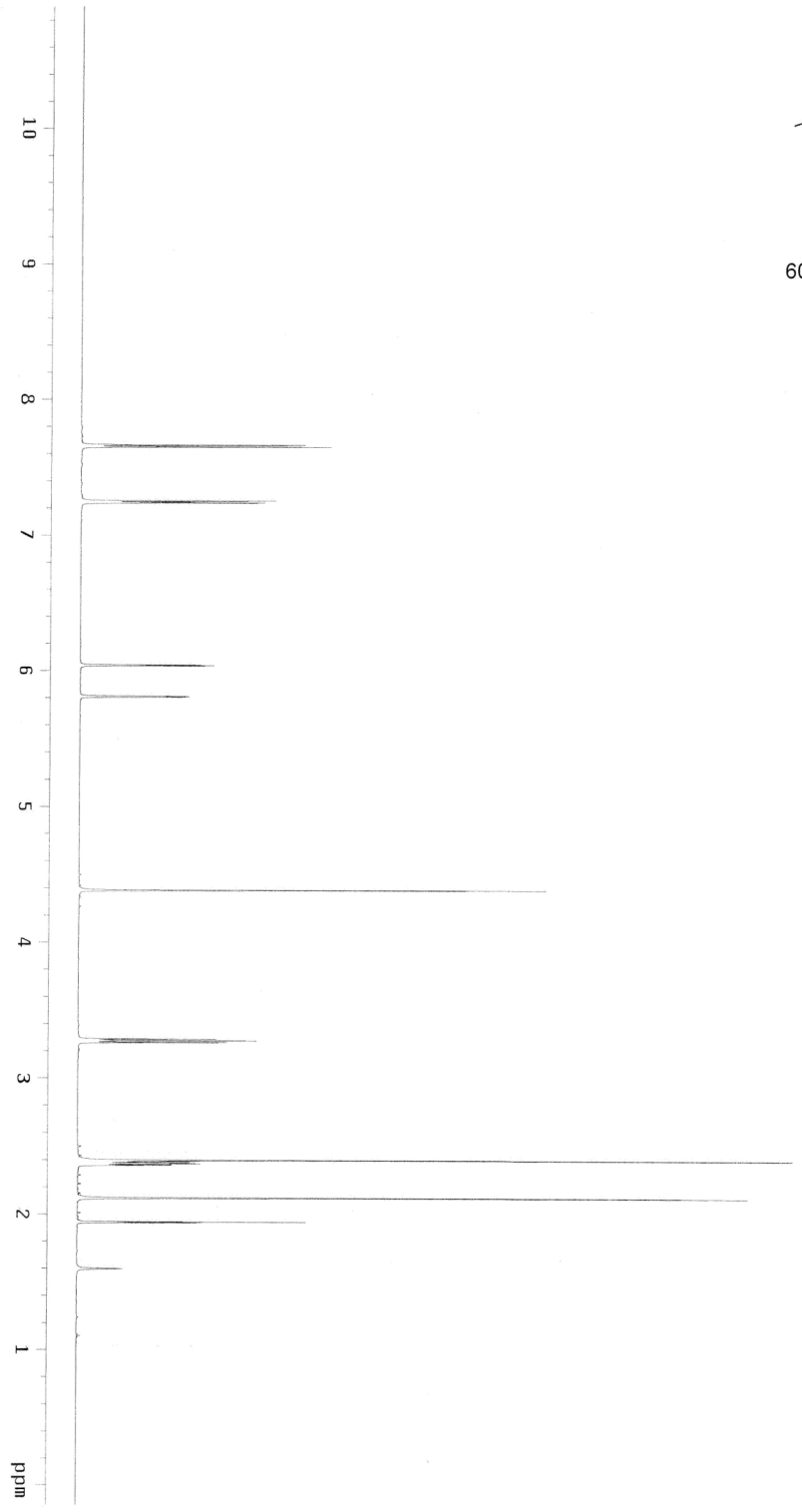
600MHz ^{1}H NMR



1b



150MHz ^{13}C NMR



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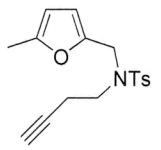
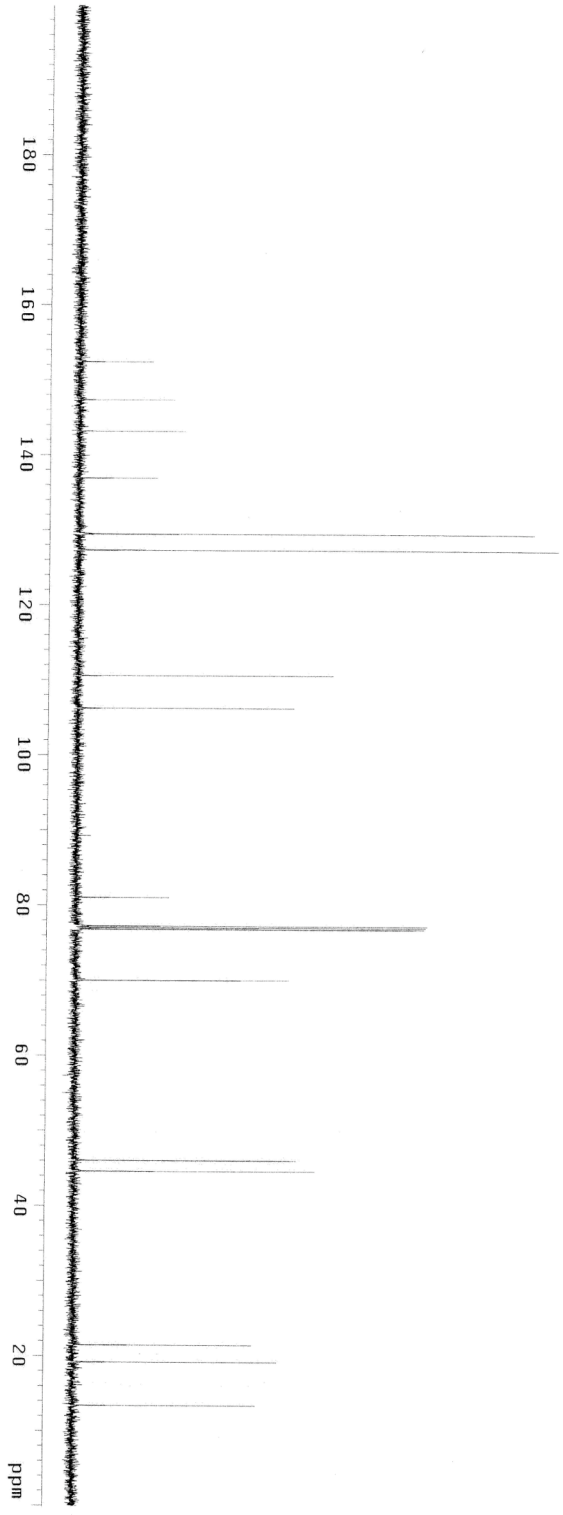


600MHz ^{1}H NMR



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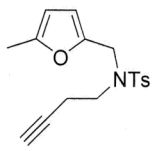
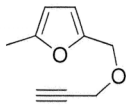
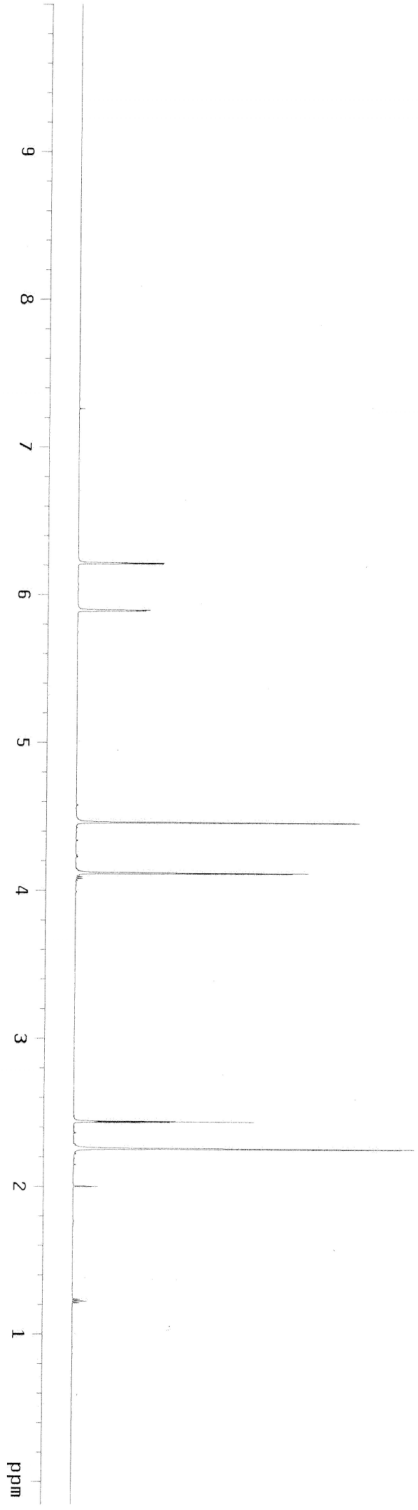


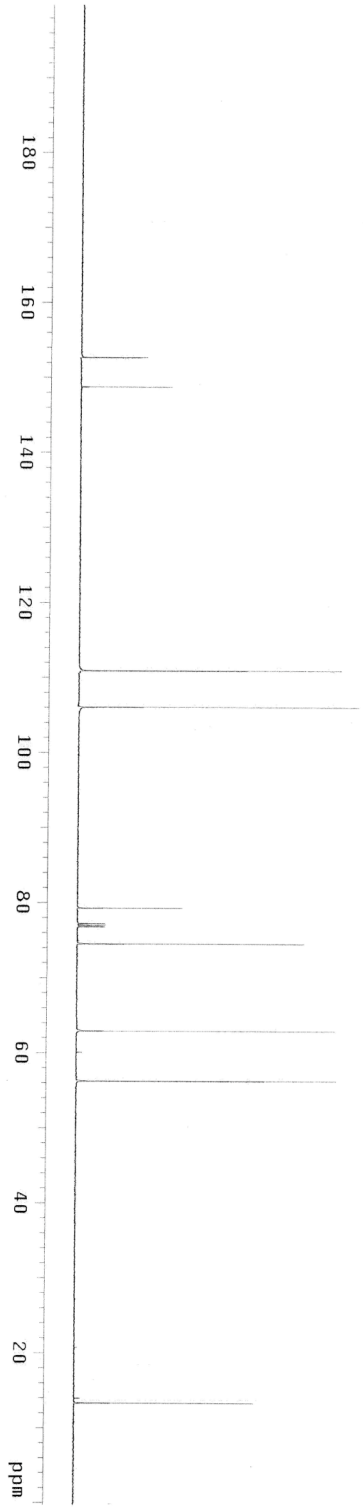
150MHz ^{13}C NMR

1d



600MHz ^{1}H NMR





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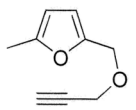
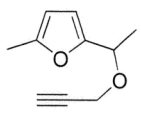
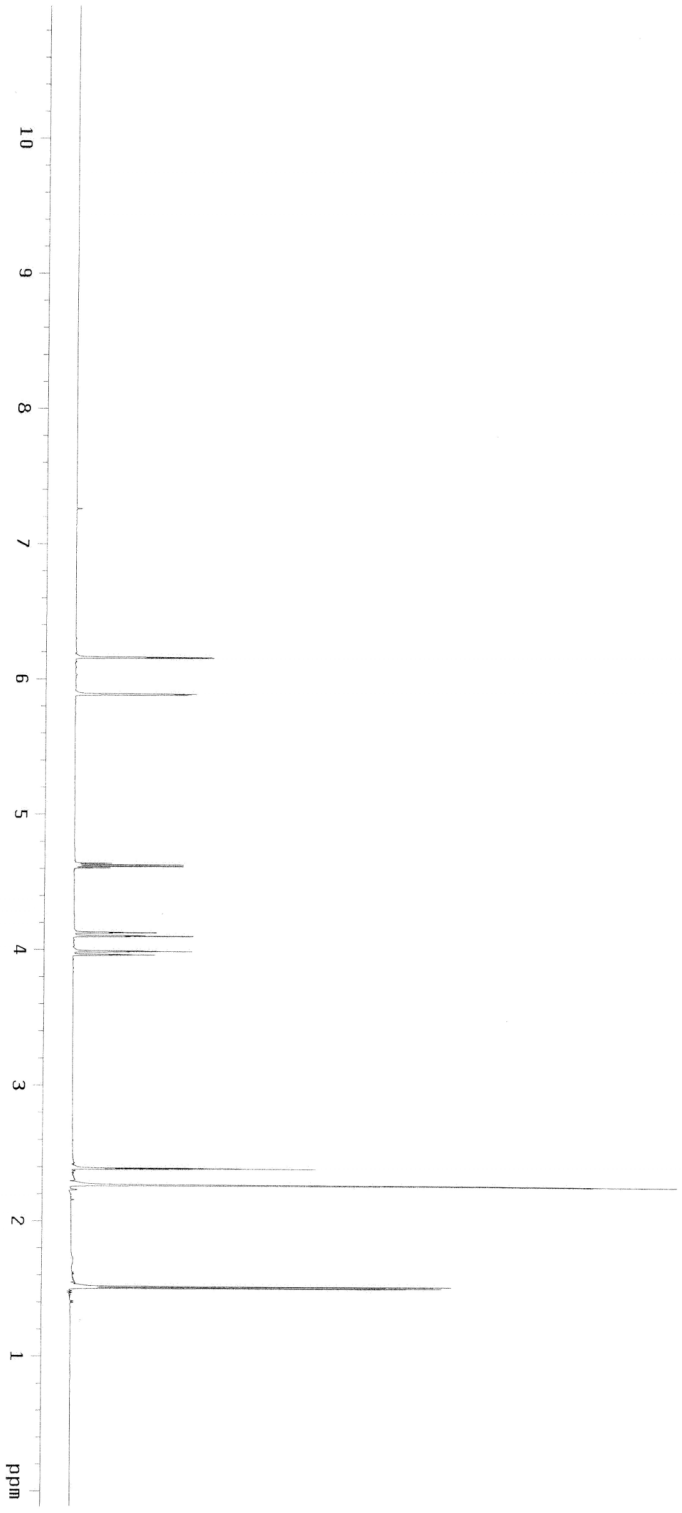


150 MHz ^{13}C NMR

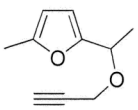
1e



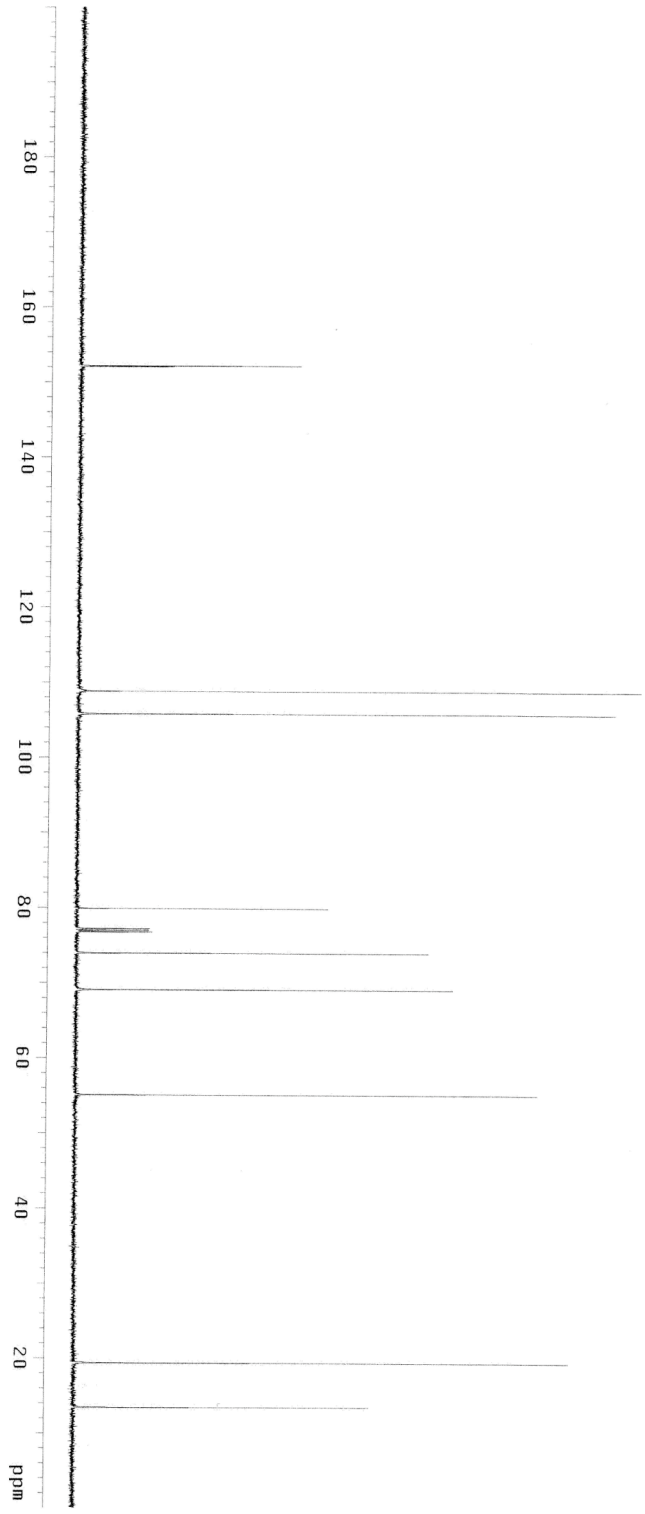
600MHz ^{1}H NMR

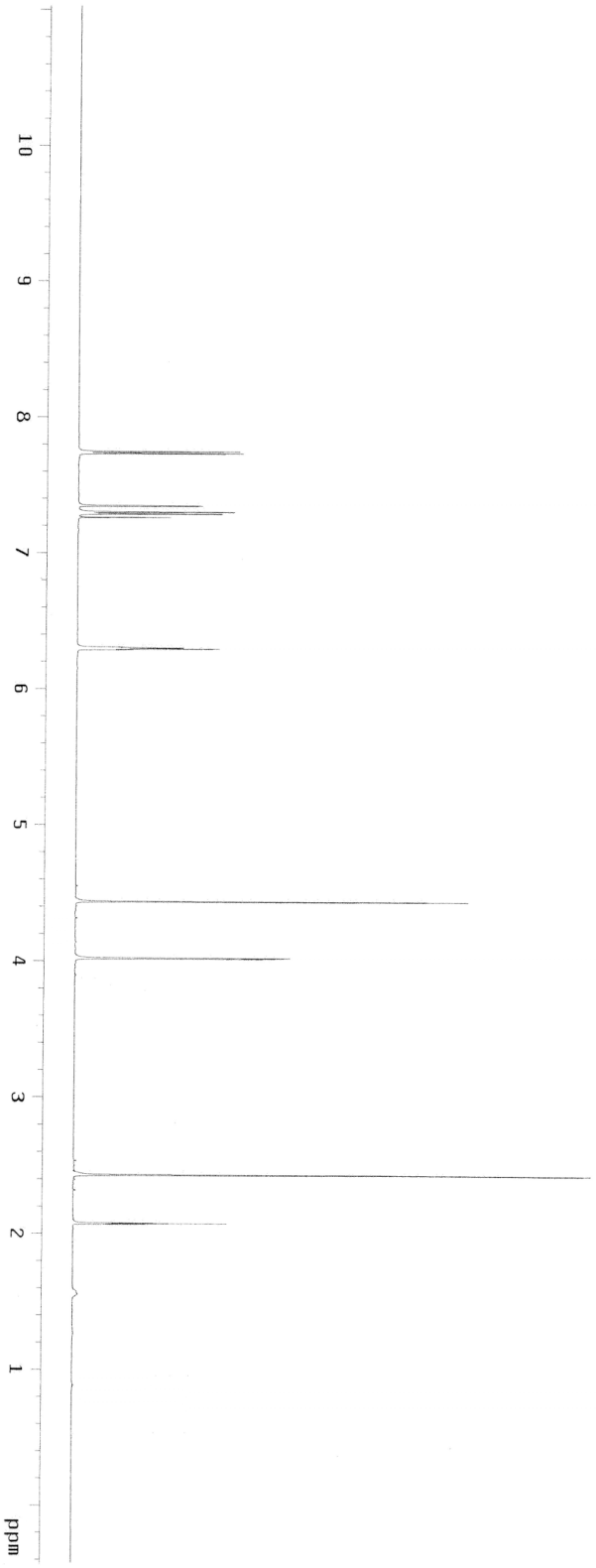


1e



150MHz ^{13}C NMR





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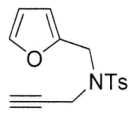
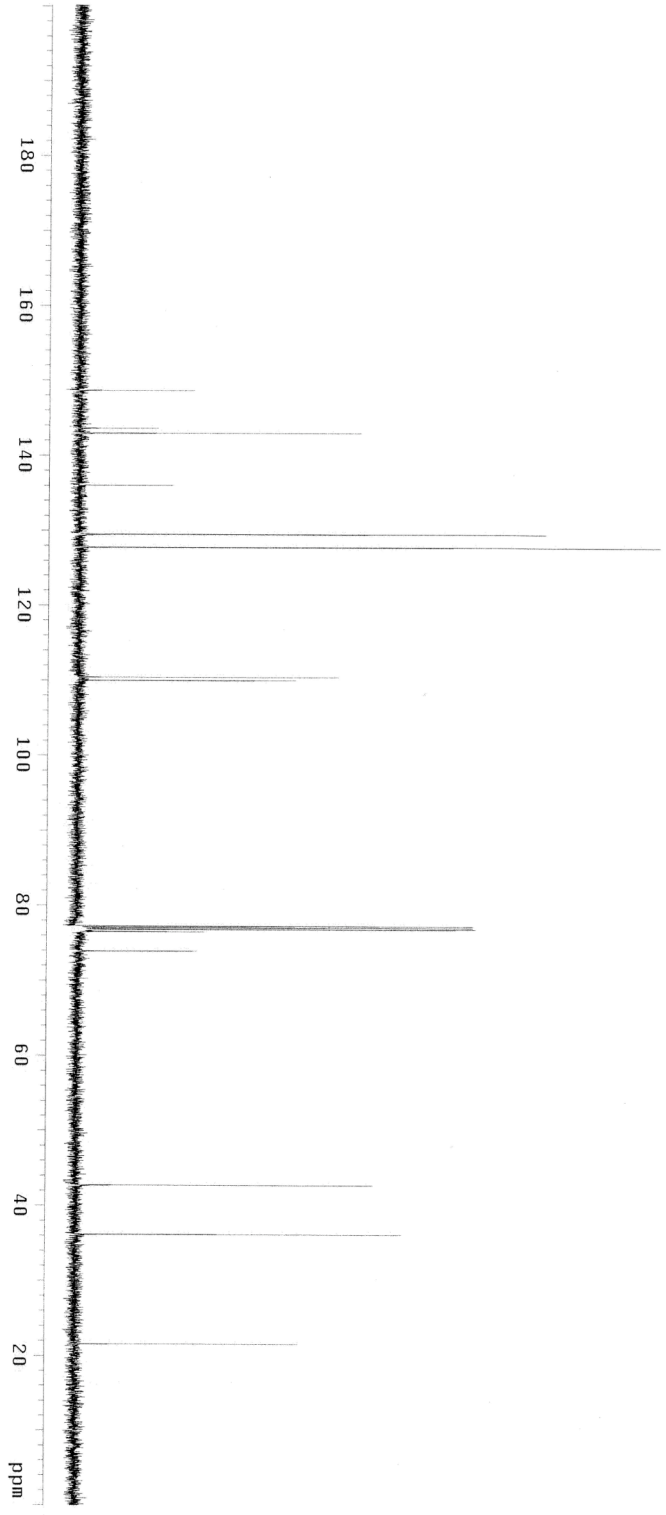


600MHz ^{1}H NMR



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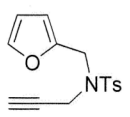
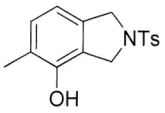
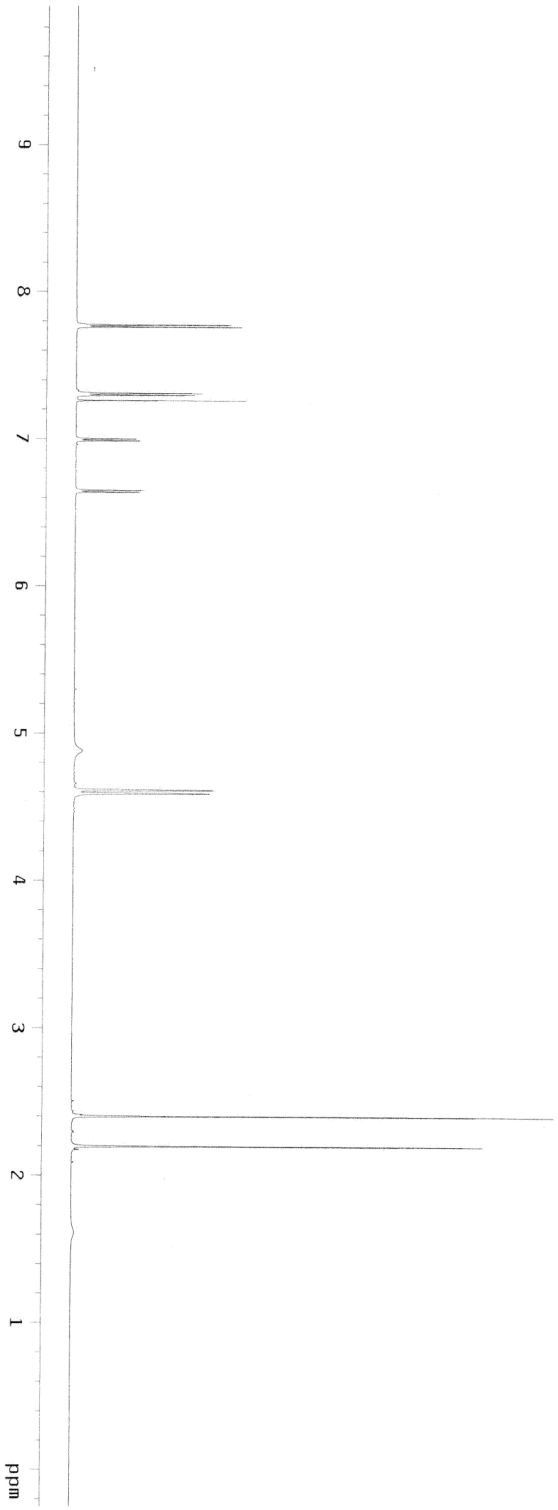


150 MHz ^{13}C NMR

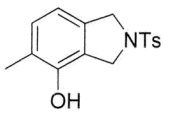
3a



600MHz ^{1}H NMR

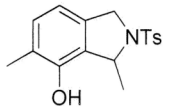


3a

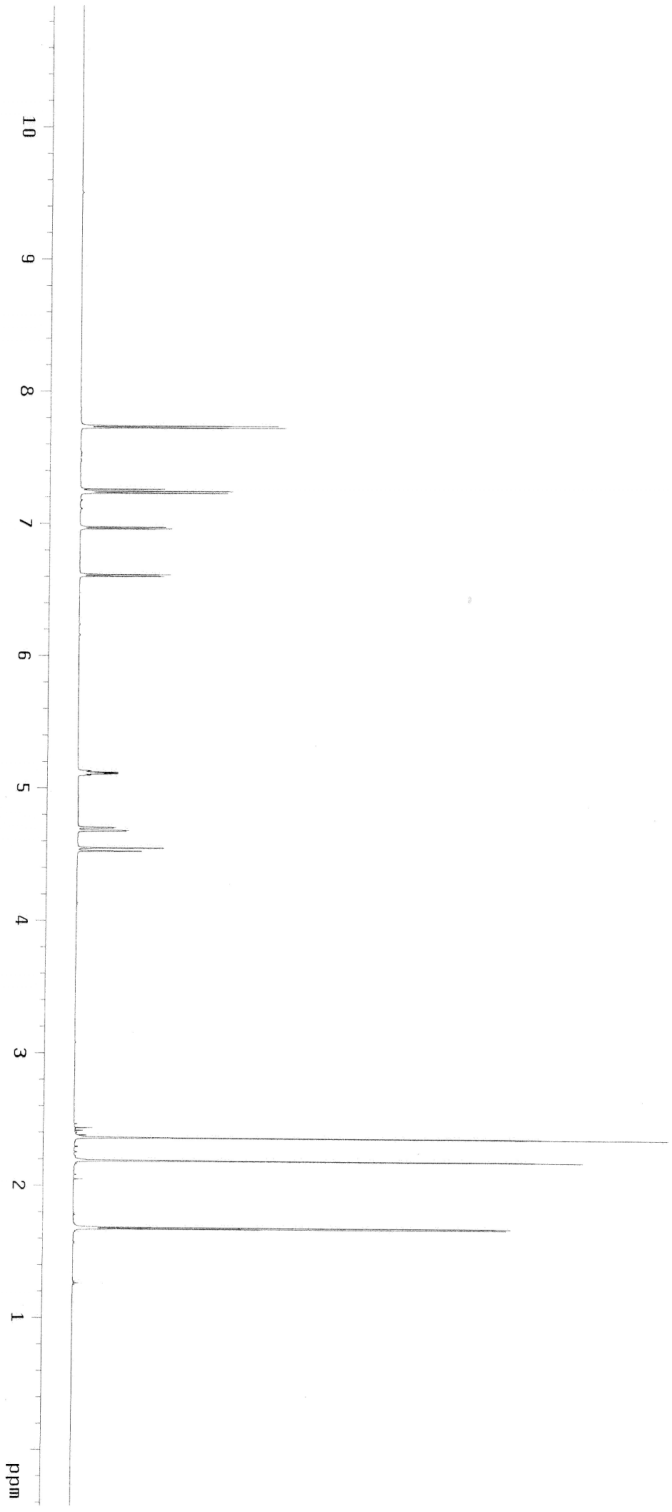


150MHz ^{13}C NMR

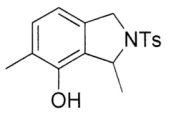
3b



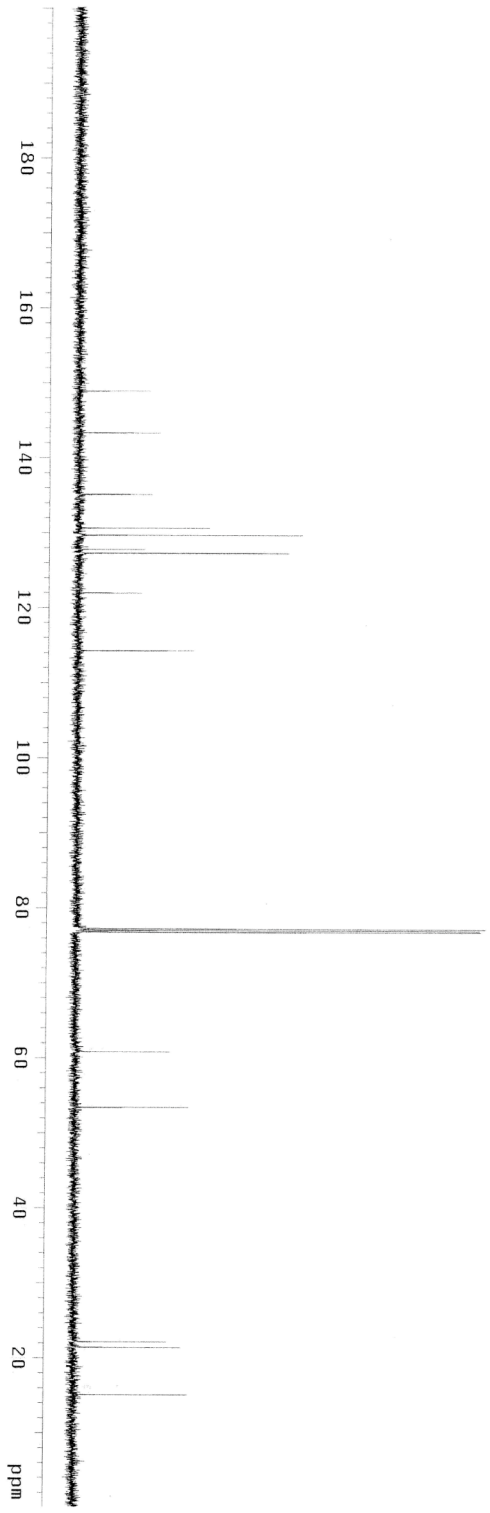
600MHz ^{1}H NMR



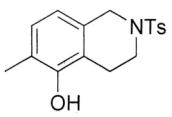
3b



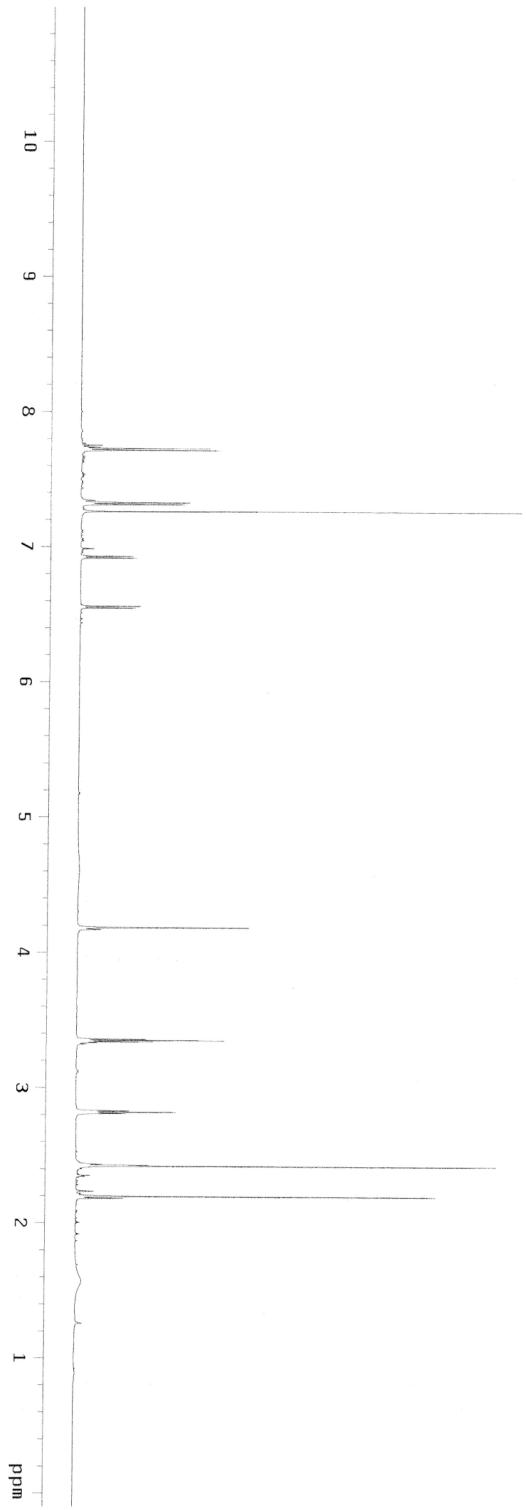
150MHz ^{13}C NMR



3c



600MHz ^{1}H NMR



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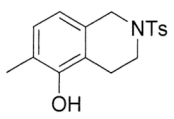
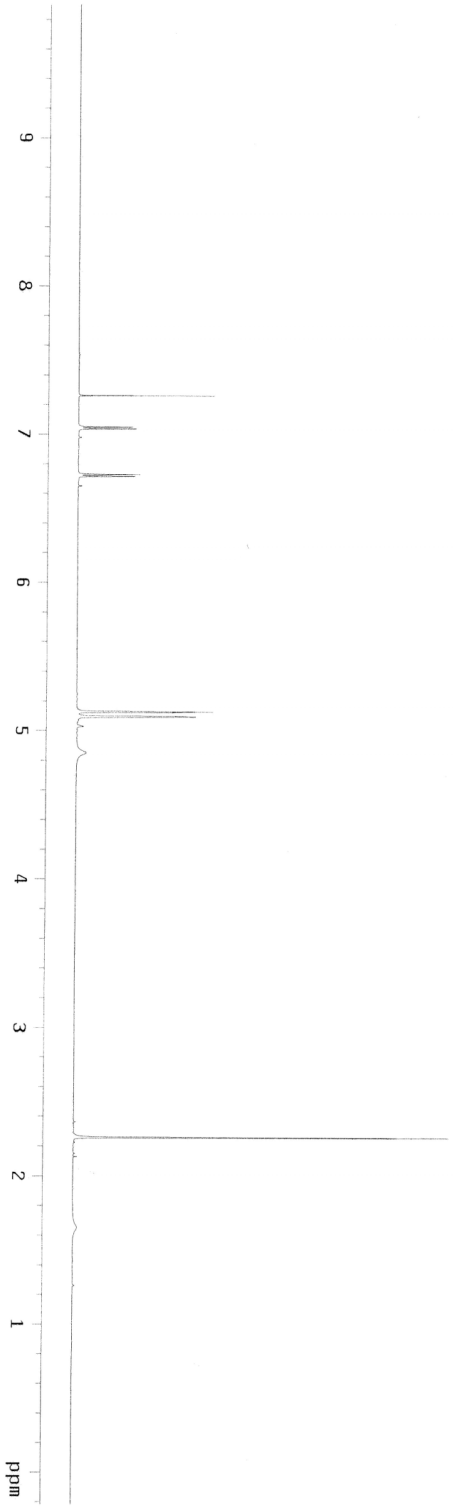
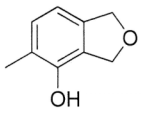


150MHz ^{13}C NMR

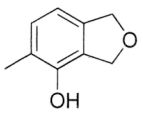


3d



600MHz ^{1}H NMR

3d



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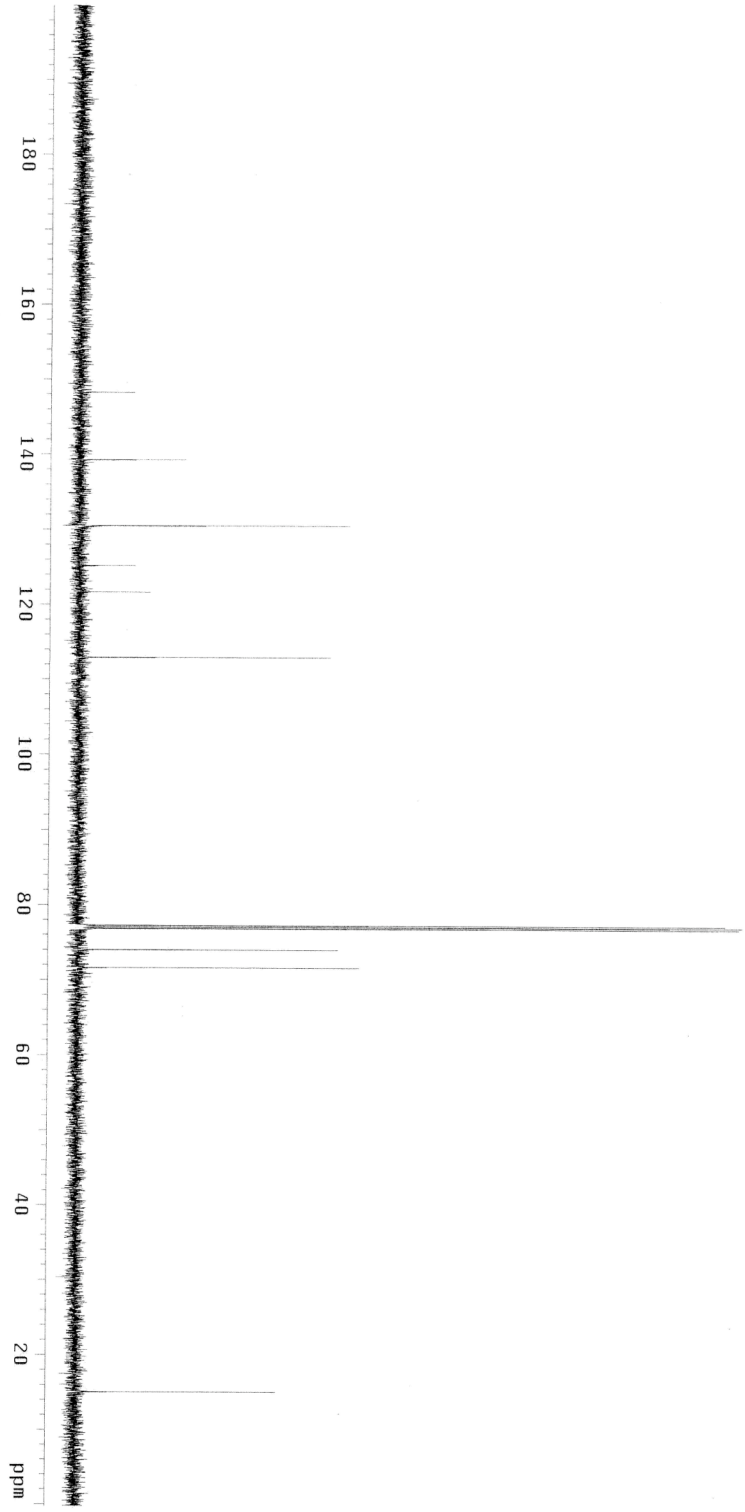
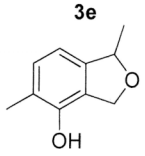
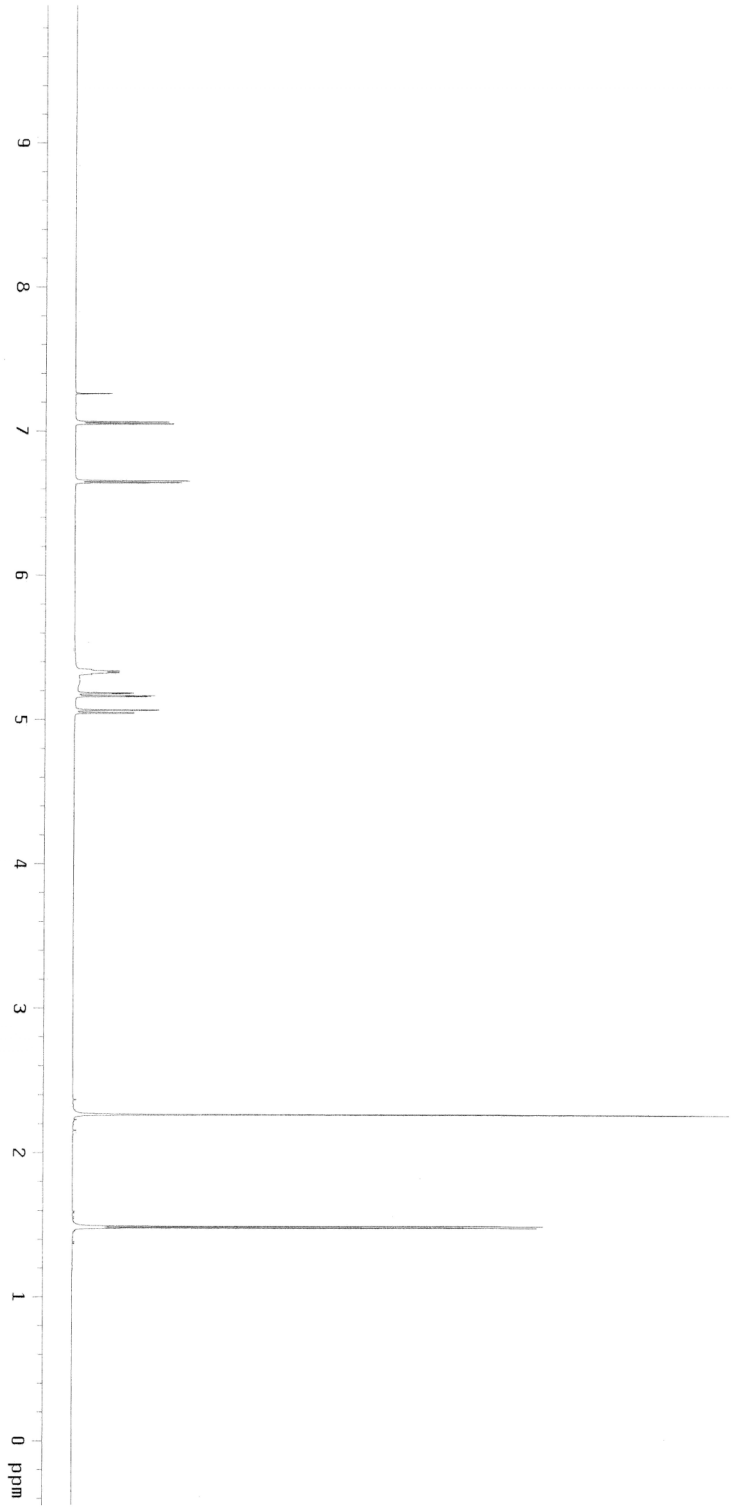
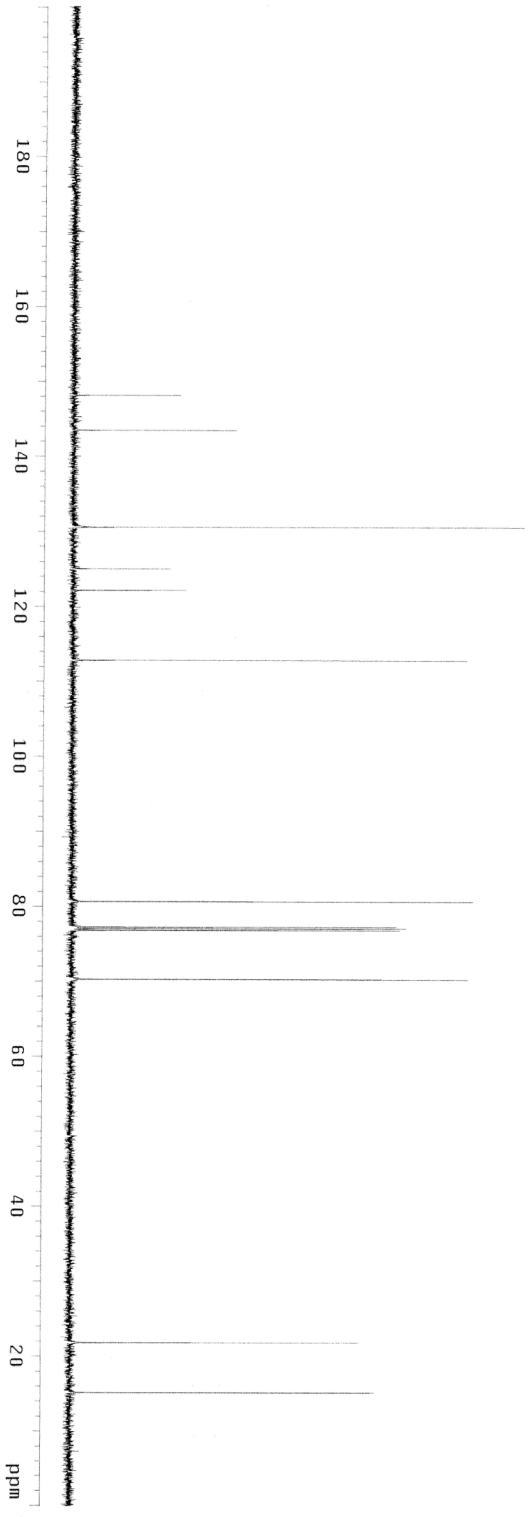


3e



600MHz ^{1}H NMR





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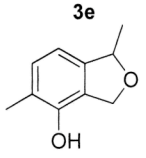
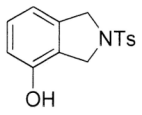
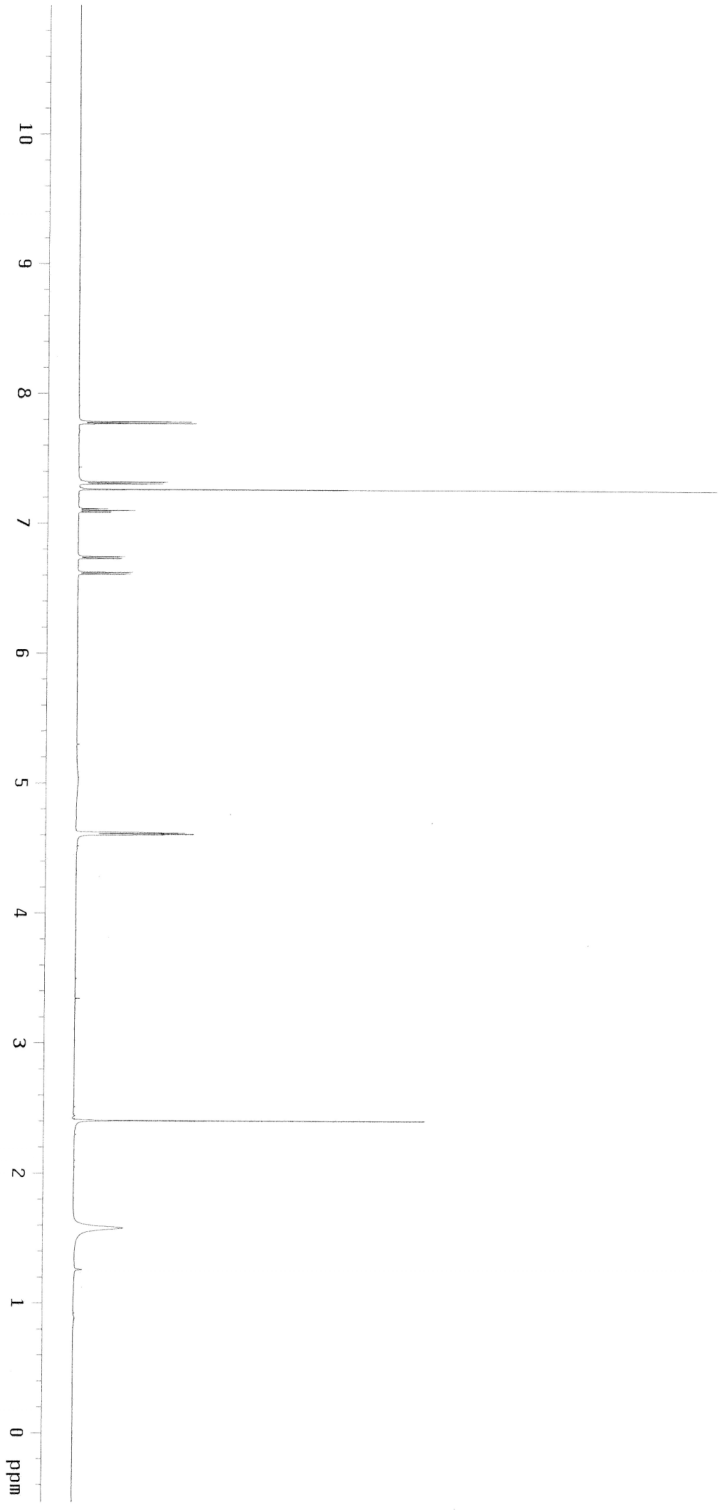


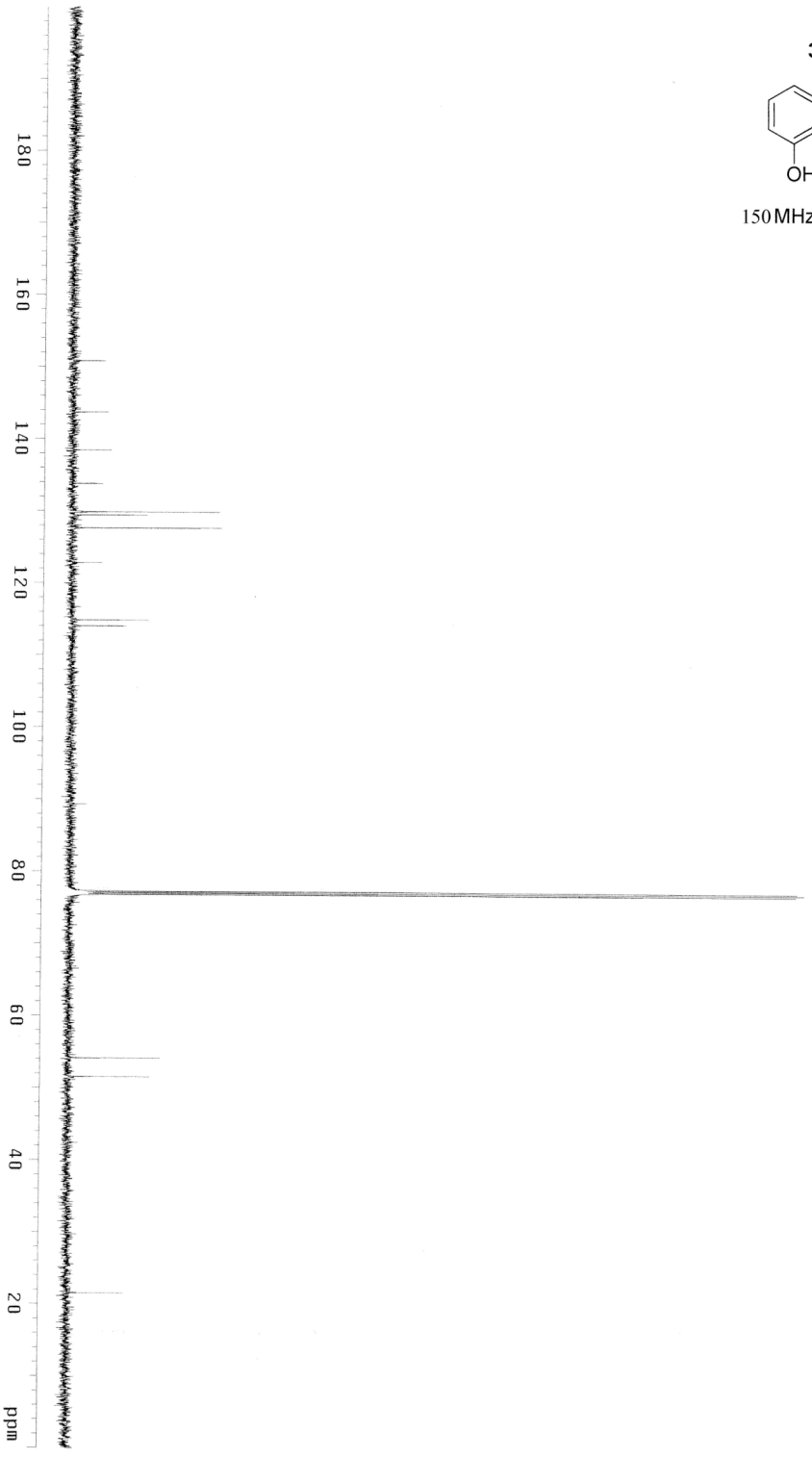
150MHz ^{13}C NMR

3f



600MHz ^{1}H NMR





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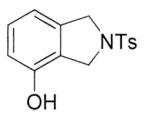
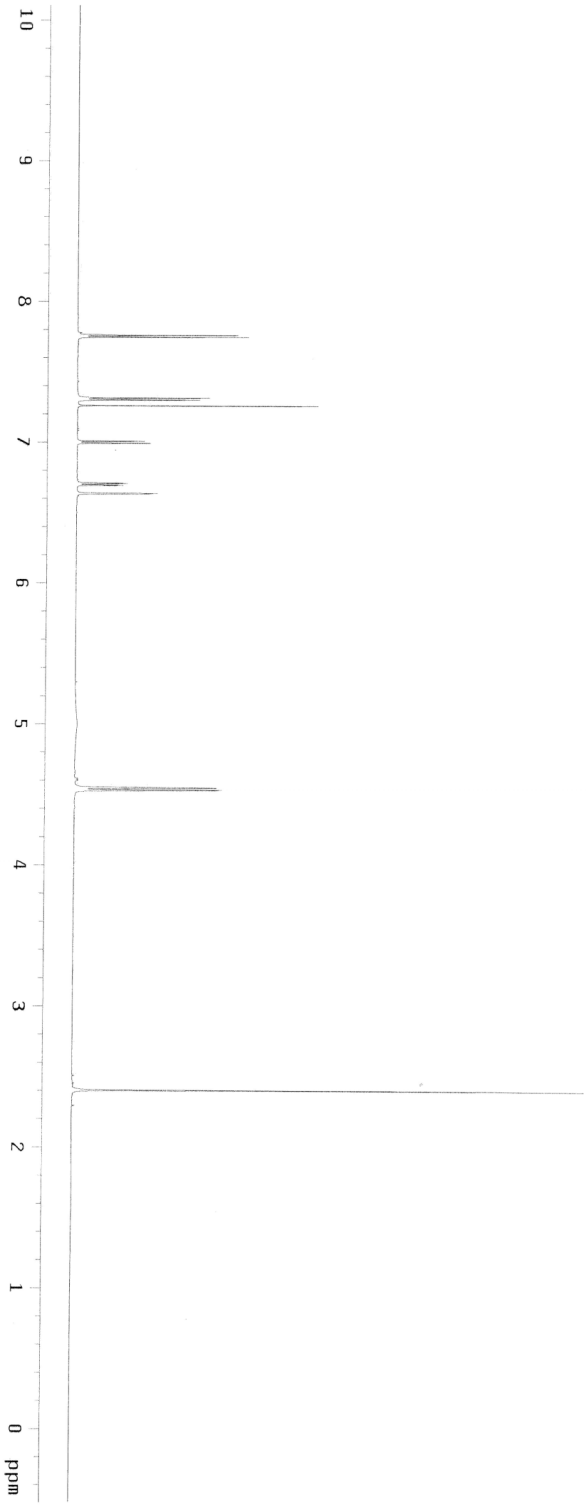


150 MHz ^{13}C NMR



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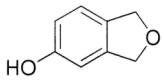
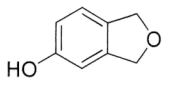
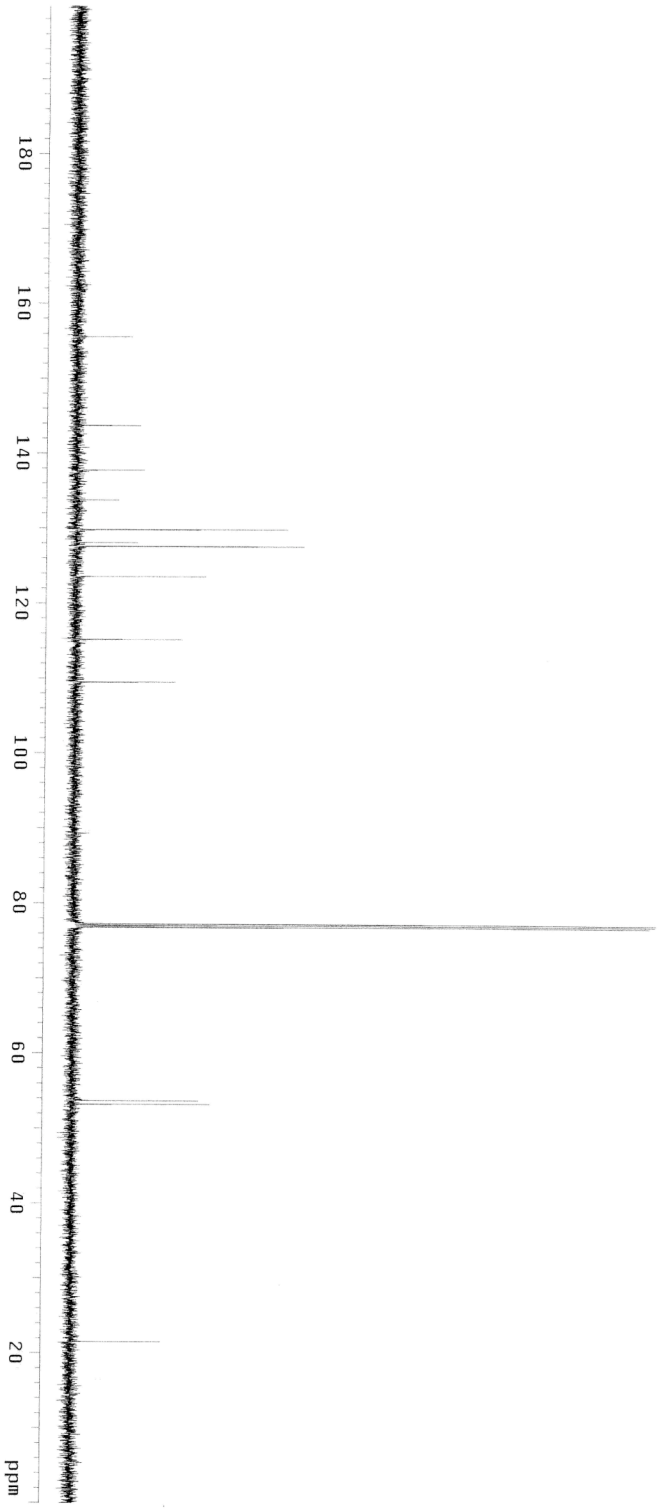


600MHz ^{1}H NMR

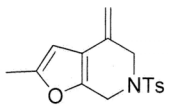
3f'



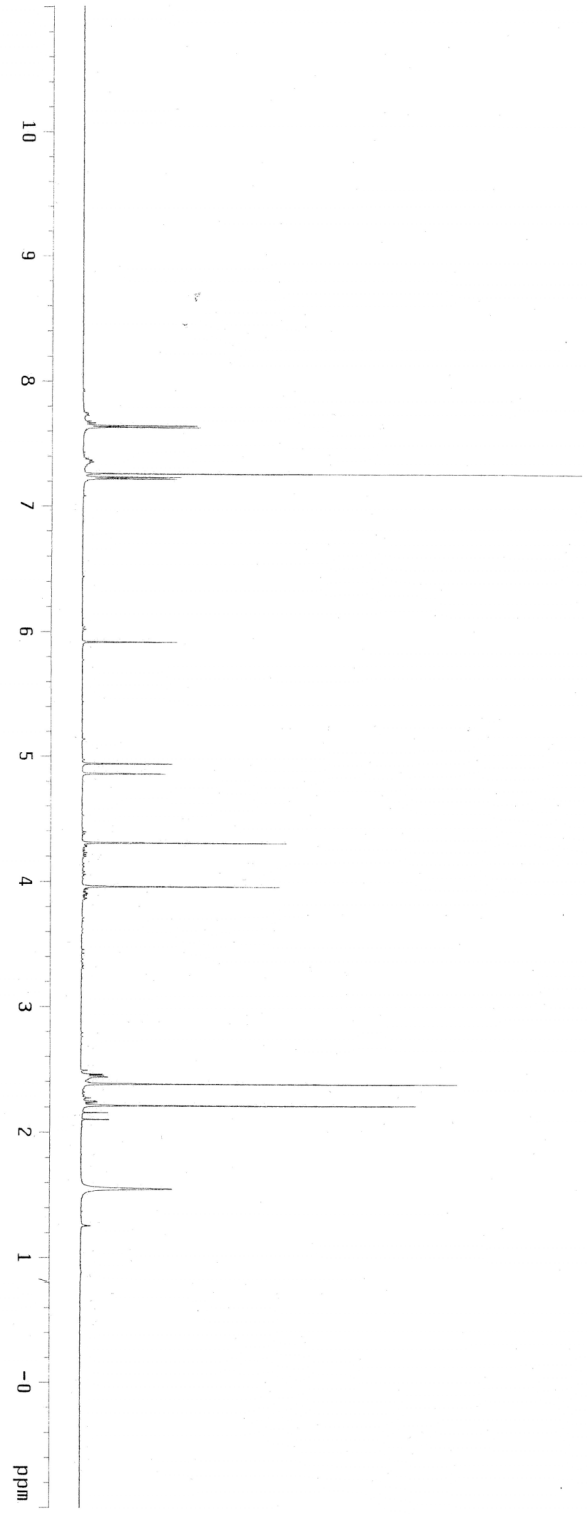
150MHz ^{13}C NMR



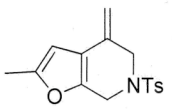
4a



600MHz ^{1}H NMR



4a



150MHz ^{13}C NMR