Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Rhodium-catalyzed reaction of diazoquinones with allylboronates to synthesize allylphenols

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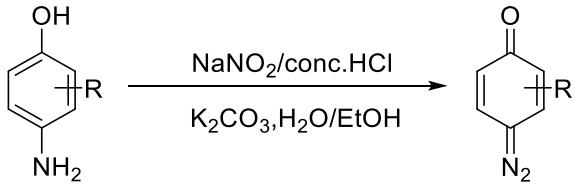
Contents

1. Experimental Section

1.1 General Information

All commercial reagents were used as provided without further purification. The diazoquinones were prepared according to the literature.[1] Allylboronic acid pinacol ester **2a** and other allylboronates were prepared according to the literature. [2,3] The reactions were monitored by thin layer chromatography (TLC) on silica gel GF254 coated 0.2 mm plates (Branch of Qingdao Haiyang Chemical plant). The product spots were visualized with UV and iodine (I_2). Flash column chromatography were performed using silica gel (200-300 mesh, Branch of Qingdao Haiyang Chemical plant) and a gradient solvent system (EtOAc/*n*-hexane as eluent). ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker Avance 300 or Ascend 600 spectrometer. Chemical shifts (δ) were measured with tetramethylsilane (TMS) as internal reference. High Resolution Mass Spectrometry (HR-MS) data were obtained on AB SCIEX TripleTOF 5600+ mass spectrometer.

1.2 General Procedure for the Preparation of Diazoquinones

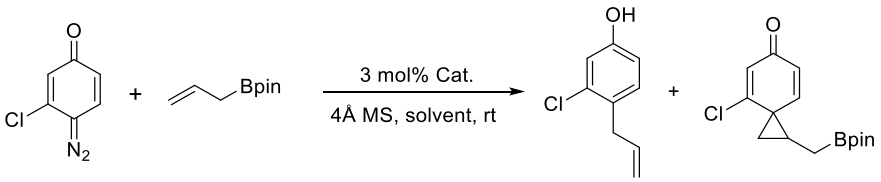


1

Aminophenols (10 mmol, 1.0 equiv.) were dissolved in EtOH (40 mL) and cooled to 0 °C, and then HCl (8.4 mL, 12 N, 10 equiv.) was added slowly to the solution. This mixture was stirred at this temperature for 10 min, then an ice-cold solution of $NaNO_2$ (2.1 g, 3.0 equiv. in 4 mL H_2O) was added dropwise over 10 minutes. The resulting mixture was stirred for 2 h at 0 °C, and diluted with cold CH_2Cl_2 (150 mL) followed by addition of 10 g of ice. Then the mixture was stirred vigorously while a cold solution of K_2CO_3 (9.2 g, 6.7 equiv. in 9 mL H_2O) was added slowly. The organic layers were then separated and the aqueous layer was then extracted with CH_2Cl_2 (50 mL). The combined organic layer was then washed with brine (50 mL), and dried over Na_2SO_4. Evaporation in vacuo resulted in a solid. All of the diazo quinones were kept at -20 °C under dark conditions and used without further purification unless otherwise stated.

1.3 General Procedure for the Reaction of Diazoquinones with Allylboronates to Synthesize Allylphenols

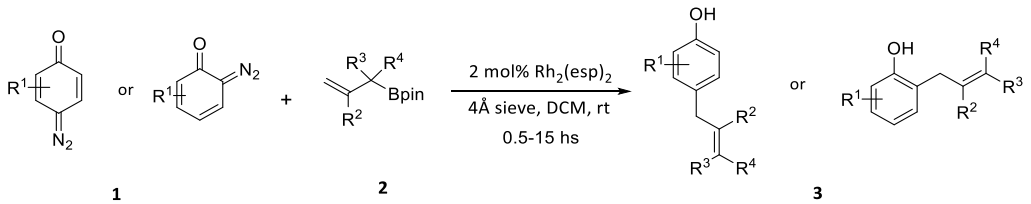
(1) General Procedure for Reaction Condition Screening



1a **2a** **3aa** **not observed**

Diazoquinone (46.4 mg, 0.3 mmol, 1.0 equiv.) and 4Å molecular sieves (60-75 mg) were added to a flame-dried 10 mL Schlenk tube with a magnetic stir bar. The tube was sealed, evacuated and flushed with argon three times. Then commercial anhydrous solvent (1.0 mL, noted in Table 1) was added. The mixture was stirred for 1 minute followed by adding allylboronate **2a** (151.2 mg, 0.9 mmol, 3.0 equiv.), catalyst and 1.0 mL solvent. The reaction mixture was then stirred for the indicated temperature and time in Table 1. Upon completion, the reaction was cooled to ambient temperature and was filtered and washed with CH_2Cl_2 (20 mL). The filtrate was concentrated by vacuum and the residue was purified by flash column chromatography on silica gel to give the corresponding product.

(2) General Procedure for the $Rh_2(esp)_2$-Catalyzed Reaction of Diazoquinones with Allylboronates to Synthesize Allylphenols

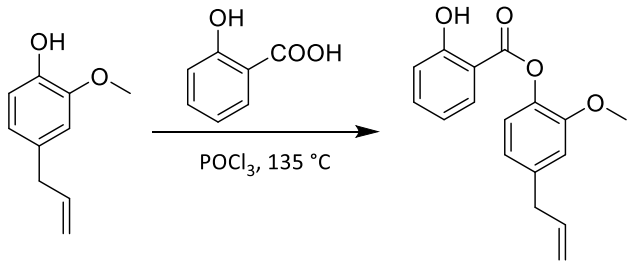


1 **2** **3**

Diazoquinone (0.3 mmol, 1.0 equiv.) and 4Å molecular sieves (60~75 mg) were added to a flame-dried 10 mL Schlenk tube with a magnetic stir bar. The tube was sealed, evacuated and flushed with argon three times. Then commercial anhydrous CH_2Cl_2 (1.0 mL) was added. The mixture was stirred for 1 minute followed by adding allylboronate (0.9 mmol, 3.0 equiv. see in Table 2), $Rh_2(esp)_2$ (2 mol%, 4.55 mg) and 1.0 mL CH_2Cl_2. The reaction mixture was then stirred at room temperature until the complete consumption of diazoquinone as monitored by TLC analysis. Upon completion, the reaction was filtered and washed with CH_2Cl_2 (20 mL). The filtrate was

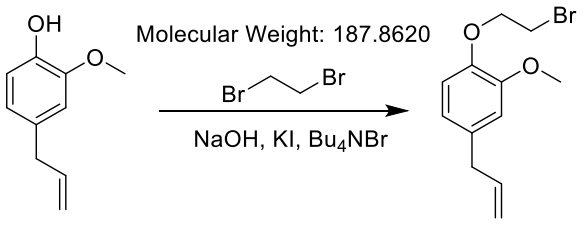
concentrated by vacuum and the residue was purified by flash column chromatography on silica gel to give the corresponding product.

1.4 Procedure for the Synthesis of Compounds 4 and 6



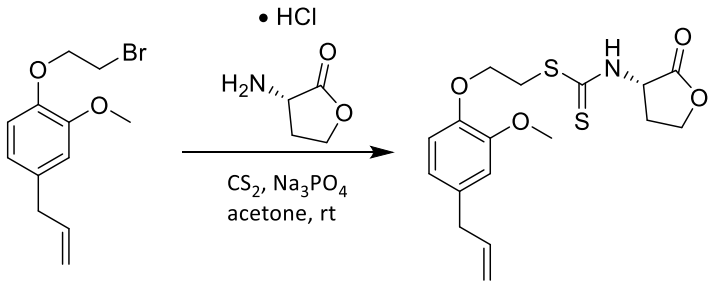
3qa **4**

Salicylic acid (16.6 mg, 0.12 mmol) was melted with the allylphenol **3qa** (16.4 mg, 0.1 mmol) at 135 °C. Phosphoryl chloride (12.2 mg, 0.08 mol) was then added gradually and the temperature was moderated until the evolution of hydrogen chloride had ceased. The reaction mixture was cooled in ice, water (25 mL) was added and the product was obtained by trituration of the organic precipitate. The reaction mixture was then washed with aqueous sodium carbonate (4 M, 50 mL) to remove any unreacted acid. Non-crystalline products were extracted with dichloromethane (3 × 50 mL), the extracts washed with water (2 × 50 mL), dried ($MgSO_4$), the solvent was removed and the residue was purified by flash column chromatography on silica gel to give the corresponding product **4**.



3qa **5**

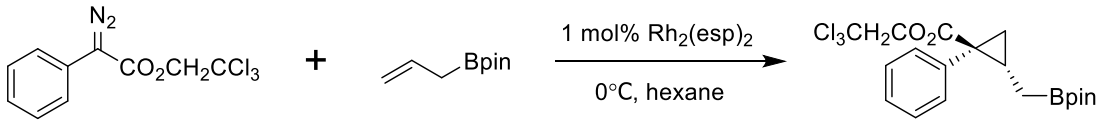
Allylphenols **3qa** (147.8 mg, 0.9 mmol), NaOH (43.2 mg, 1.08 mmol), Bu_4NBr (45 mg, 0.14 mmol) and KI (45 mg, 0.27 mmol) were dissolved in distilled water (15 mL), and heated 90 °C, 1,2-dibromoethane (253.6 mg, 1.35 mmol) was added dropwise. The reaction mixture was then stirred at 100 °C. Organic phase was separated; aqueous phase was extracted with CH_2Cl_2 (2 × 30 mL). The combined organic phase was washed with 10% NaOH and water, and then solvent was evaporated. The residue was purified by flash column chromatography on silica gel to give the corresponding product **5**.



5 **6**

To a solution of (*L*)-Homoserine lactone hydrochloride (82 mg, 0.6 mmol) and $Na_3PO_4 \cdot 12H_2O$ (342 mg, 1.5 mmol) in acetone (10 mL) was added CS_2 (76 µL, 1.26 mmol). After 0.5 h stirring, the compounds **5** were added. About 2 h later, the solvent was removed under vacuum, the resulting residue was dissolved with CH_2Cl_2 and then washed with brine. The organic layer was dried over $MgSO_4$, the solvent was removed and the residue was purified by flash column chromatography on silica gel to give the corresponding product **6**.

1.5 Procedure for Control experiments



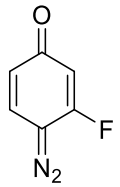
7 **2a** **8**

An oven dried Schlenk flask equipped with a magnetic stir bar was charged with the $Rh_2(esp)_2$ catalyst (1 mol%) under argon. The allylboronate **2a** (84 mg, 0.5 mmol, 5.0 equiv.) and n-hexane (1 mL) were added and the resulting solution cooled to 0°C. A solution of the diazo compound **7** (29.2 mg, 0.1 mmol) in n-hexane (3 mL) was added dropwise over 10 min. The resulting mixture was stirred at 0°C until TLC analysis indicated the complete consumption of the diazo compound. The reaction solution was concentrated by vacuum and the residue was purified by flash column chromatography on silica gel to give the corresponding product **8**.

2. Characterization Data of Compounds

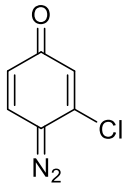
2.1 Characterization Data of Diazoquinones

4-diazo-3-fluorocyclohexa-2,5-dien-1-one (1b)



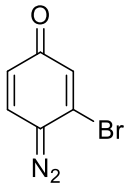
yellow solid, 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (t, *J* = 9.3 Hz, 1H), 6.29 (d, *J* = 9.8 Hz, 1H), 6.19 (d, *J* = 14.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.2, 183.0, 163.0, 159.5, 126.5, 125.5, 109.9, 109.8. HR-MS (ESI): Calcd for $C_6H_3FN_2ONa^+$ $[M+Na]^+$: 161.0121; found: 161.0132.

3-chloro-4-diazocyclohexa-2,5-dien-1-one (1a)[1]



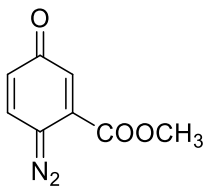
yellow solid, 90% yield. ^{1}H NMR(300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 9.8 Hz, 1H), 6.61 (d, *J* = 1.9 Hz, 1H), 6.43 (dd, *J* = 9.8, 1.9 Hz, 1H). ^{13}C NMR(75 MHz, $CDCl_3$) δ 181.1, 135.0, 129.6, 126.6, 125.9, 85.3.

3-bromo-4-diazocyclohexa-2,5-dien-1-one (1c) [1]



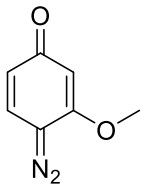
yellow solid, 85% yield. ^{1}H NMR(300 MHz, $CDCl_3$) δ 7.41 (d, *J* = 9.7 Hz, 1H), 6.77 (s, 1H), 6.42 (d, *J* = 9.8 Hz, 1H). ^{13}C NMR(75 MHz, $CDCl_3$) δ 180.9, 130.2, 130.1, 126.0, 123.1, 80.7.

Methyl 6-diazo-3-oxocyclohexa-1,4-diene-1-carboxylate (1d) [1]



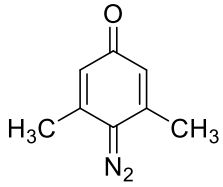
yellow solid, 84% yield. ^{1}H NMR (300 MHz, DMSO) δ 7.91 (d, *J* = 9.7 Hz, 1H), 6.70 (s, 1H), 6.34 (d, *J* = 9.7 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (75 MHz, DMSO) δ 180.5, 164.0, 134.9, 131.8, 127.9, 126.6, 75.7, 53.6.

4-diazo-3-methoxycyclohexa-2,5-dien-1-one (1e)



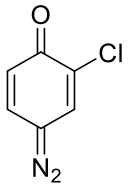
brown solid, 80% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, *J* = 9.7 Hz, 1H), 6.19 (d, *J* = 10.6 Hz, 1H), 5.92 (s, 1H), 3.88 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.2, 161.4, 126.9, 123.4, 103.9, 56.4. HR-MS (ESI): Calcd for $C_7H_6N_2O_2Na^+$ $[M+Na]^+$: 173.0321; found: 173.0327.

4-diazo-3,5-dimethylcyclohexa-2,5-dien-1-one (1f)



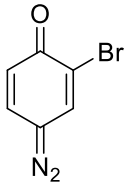
yellow solid, 75% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.22 (s, 2H), 2.24 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 139.6, 125.9, 100.3, 18.3. HR-MS (ESI): Calcd for $C_8H_8N_2ONa^+$ $[M+Na]^+$: 171.0529; found: 171.0538.

2-chloro-4-diazocyclohexa-2,5-dien-1-one (1g) [1]



black solid, 68% yield. ^{1}H NMR(300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 2.7 Hz, 1H), 7.48 (d, *J* = 9.7 Hz, 1H), 6.51 (d, *J* = 9.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.1, 129.7, 129.3, 127.3, 125.8, 74.9.

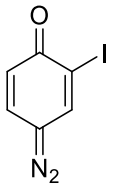
2-bromo-4-diazocyclohexa-2,5-dien-1-one (1h)



black solid, 66% yield.^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J* = 2.7 Hz, 1H), 7.44 (dd, *J* = 9.7, 2.7 Hz, 1H), 6.51 (d, *J* = 9.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.2, 130.5, 129.5,

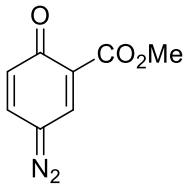
125.3, 120.5, 75.2. HR-MS (ESI): Calcd for $C_6H_3BrN_2ONa^+$ $[M+Na]^+$: 220.9321; found: 220.9330.

4-diazo-2-iodocyclohexa-2,5-dien-1-one (1i)



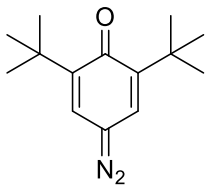
black solid, 70% yield. ^1H NMR (300 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.46 (d, *J* = 12.4 Hz, 1H), 6.46 (d, *J* = 9.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.3, 136. 8, 129.8, 123.1, 108.3, 99.3. HR-MS (ESI): Calcd for $C_6H_3IN_2ONa^+$ $[M+Na]^+$: 268.9182; found: 268.9186.

methyl 3-diazo-6-oxocyclohexa-1,4-diene-1-carboxylate (1j)[4]



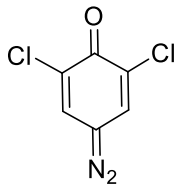
yellow solid, 80% yield. ^1H NMR (300 MHz, DMSO) δ 8.48 (d, *J* = 3.0 Hz, 1H), 7.74 (dd, *J* = 9.8, 3.0 Hz, 1H), 6.25 (d, *J* = 9.8 Hz, 1H), 3.70 (s, 3H). ^{13}C NMR (75 MHz, DMSO) δ 177.3, 165.5, 138.5, 131.3, 127.7, 124.8, 78.1, 52.0.

2,6-di-tert-butyl-4-diazocyclohexa-2,5-dien-1-one (1k)[4]



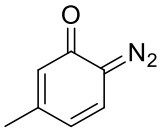
red solid, 50% yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.18 (s, 2H), 1.33 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.1, 146.8, 130.1, 122.4, 71.0, 36.0, 29.1.

2,6-dichloro-4-diazocyclohexa-2,5-dien-1-one (1l)[1]



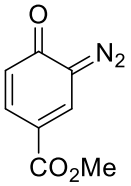
brown solid, 60% yield. ^1H NMR (300 MHz, DMSO) δ 8.27 (s, 2H). ^{13}C NMR (75 MHz, DMSO) δ 169.1, 130.0, 125.0, 78.5.

6-diazo-3-methylcyclohexa-2,4-dien-1-one (1m)[4]



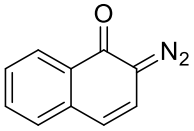
brown solid, 80% yield.^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.9 Hz, 1H), 6.50 (t, *J* = 1.2 Hz, 1H), 6.13 (dd, *J* = 9.0, 1.5 Hz, 1H), 2.21 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.3, 151.2, 123.4, 123.0, 118.5, 83.5, 22.8.

methyl 3-diazo-4-oxocyclohexa-1,5-diene-1-carboxylate (1n)[5]



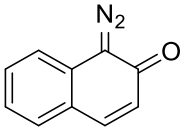
brown solid, 85% yield.^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, *J* = 2.4 Hz, 1H), 7.86 (dd, *J* = 9.8, 2.4 Hz, 1H), 6.66 (d, *J* = 9.8 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.6, 164.2, 138.2, 129.9, 124.9, 117.2, 86.8, 52.3.

2-diazonaphthalen-1(2H)-one (1o)[6]



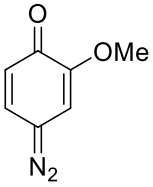
brown solid, 85% yield.^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 6.9 Hz, 1H), 7.42 – 7.28 (m, 2H), 6.77 (d, *J* = 9.4 Hz, 1H), 6.44 (d, *J* = 9.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.0, 137.5, 132.6, 129.4, 128.2, 127.0, 125.2, 117.2, 116.3.

1-diazonaphthalen-2(1H)-one (1p)[7]



brown solid, 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 – 7.32 (m, 3H), 7.22 – 7.01 (m, 2H), 6.50 (d, *J* = 9.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.2, 140.3, 130.1, 129.8, 127.2, 126.0, 125.6, 124.7, 119.7, 77.2.

4-diazo-2-methoxycyclohexa-2,5-dien-1-one (1q)

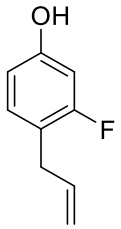


black solid, 60% yield.^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.41 (dd, *J* = 9.5, 2.7 Hz, 1H), 6.54 (d, *J* = 2.6 Hz, 1H), 6.45 (d, *J* = 9.5 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (75 MHz,

$CDCl_3$) δ 176.2, 152.1, 129.3, 125. 2, 101.5, 55.7. HR-MS (ESI): Calcd for $C_7H_6N_2O_2Na^+$ $[M+Na]^+$: 173.0321; found: 173.0328.

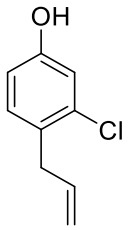
2.2 Characterization Data of Allylphenols

4-allyl-3-fluorophenol (3ba)



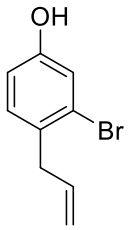
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow oil, 42.9 mg, 94% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.02 (t, *J* = 8.5 Hz, 1H), 6.56 (d, *J* = 9.9 Hz, 2H), 5.93 (ddt, *J* = 17.8, 9.1, 6.4 Hz, 1H), 5.57 (s, 1H), 5.11 – 4.98 (m, 2H), 3.32 (d, *J* = 6.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.2, 136.3, 131.1, 118.9, 115.7, 111.1, 103.3, 102.9, 32.4. HR-MS (ESI): Calcd for $C_9H_8FO^-$ $[M-H]^-$: 151.0565; found: 151.0571.

4-allyl-3-chlorophenol (3aa)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow oil, 47.0 mg, 93% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.3 Hz, 1H), 6.89 (s, 1H), 6.71 (d, *J* = 8.3 Hz, 1H), 6.03 – 5.85 (m, 1H), 5.70 (s, 1H), 5.15 – 4.97 (m, 2H), 3.43 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5, 136.0, 134.4, 131.1, 129.9, 116.5, 116.1, 114.22, 36.76. HR-MS (ESI): Calcd for $C_9H_8ClO^-$ $[M-H]^-$: 167.0269; found: 167.0270.

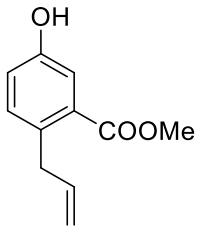
4-allyl-3-bromophenol (3ca)[1]



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow oil, 54.3 mg, 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (dd, *J* = 5.4, 2.7 Hz, 2H), 6.75 (dd, *J* = 8.4, 2.5 Hz, 1H), 5.94 (ddt, *J* = 16.6, 10.2, 6.4 Hz, 1H), 5.17 (s, 1H), 5.13 –

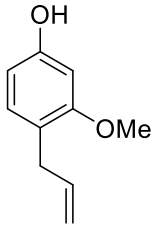
4.99 (m, 2H), 3.43 (d, *J* = 6.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5, 136.1, 131.0, 124.5, 119.6, 116.2, 114.8, 39.3.

methyl 2-allyl-5-hydroxybenzoate (3da)[1]



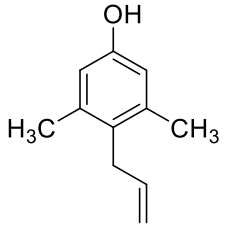
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 49.0 mg, 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, *J* = 2.7 Hz, 1H), 7.13 (d, *J* = 8.3 Hz, 1H), 6.95 (dd, *J* = 8.3, 2.7 Hz, 1H), 6.05 – 5.88 (m, 1H), 5.82 (s, 1H), 5.07 – 4.90 (m, 2H), 3.87 (s, 3H), 3.65 (d, *J* = 6.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.5, 154.1, 137.8, 133.3, 132.4, 130.4, 119.6, 117.3, 115.3, 52.2, 37.7.

4-allyl-3-methoxyphenol (3ea)[8]



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow oil, 41.9 mg, 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.95 (d, *J* = 8.0 Hz, 1H), 6.44 – 6.31 (m, 2H), 6.04 – 5.87 (m, 1H), 5.50 (s, 1H), 5.07 – 4.95 (m, 2H), 3.78 (s, 3H), 3.28 (d, *J* = 6.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.2, 155.6, 137.5, 130.1, 120.4, 114.9, 106.7, 99.0, 55.4, 33.6.

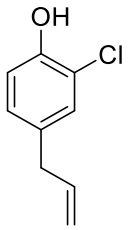
4-allyl-3,5-dimethylphenol (3fa)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow oil, 41.4 mg, 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.53 (s, 2H), 5.97 – 5.79 (m, 1H), 5.04 – 4.78 (m, 3H), 3.32 (d, *J* = 5.4 Hz, 2H), 2.24 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$)

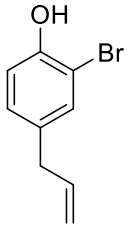
δ 153.3, 138.2, 135.7, 114.7, 32.9, 19.9. HR-MS (ESI): Calcd for $C_{11}H_{13}O^-$ $[M-H]^-$: 161.0972; found: 161.0959.

4-allyl-2-chlorophenol (3ga)[2]



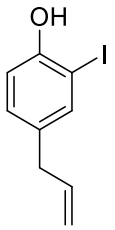
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow oil, 45.5 mg, 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 (s, 1H), 7.04 – 6.89 (m, 2H), 5.90 (ddd, *J* = 13.4, 10.3, 7.9 Hz, 1H), 5.46 (s, 1H), 5.13 – 5.01 (m, 2H), 3.30 (d, *J* = 6.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.6, 137.0, 133.3, 128.8, 128.6, 119.7, 116.1, 116.1, 39.1.

4-allyl-2-bromophenol (3ha)[9]



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow oil, 47.9 mg, 75% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (s, 1H), 7.07 – 6.99 (m, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 5.99 – 5.82 (m, 1H), 5.41 (s, 1H), 5.13 – 5.00 (m, 2H), 3.30 (d, *J* = 6.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.5, 137.0, 133.7, 131.8, 129.4, 116.2, 115.9, 110.1, 39.0.

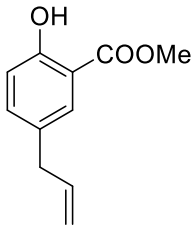
4-allyl-2-iodophenol (3ia)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow oil, 49.9 mg, 64% yield.^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.06 (d, *J* = 8.3 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 5.91 (ddt, *J* = 18.0, 9.2, 6.7 Hz, 1H), 5.19 (s, 1H), 5.11 – 5.02 (m, 2H), 3.28 (d, *J* = 6.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 137.9, 137.1,

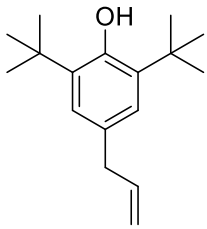
134.2, 130.5, 116.1, 114.9, 85.6, 38.7. HR-MS (ESI): Calcd for $C_9H_8IO^-$ $[M-H]^-$: 258.9626; found: 258.9635.

methyl 5-allyl-2-hydroxybenzoate (3ja)



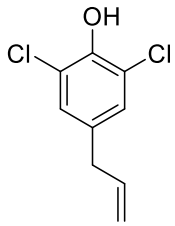
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 31.7 mg, 55% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.62 (s, 1H), 7.64 (s, 1H), 7.28 (d, *J* = 10.3 Hz, 1H), 6.92 (d, *J* = 8.6 Hz, 1H), 6.05 – 5.78 (m, 1H), 5.19 – 4.90 (m, 2H), 3.94 (s, 3H), 3.32 (d, *J* = 6.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 160.0, 137.2, 136.3, 130.7, 129.4, 117.6, 116.0, 112.1, 52.2, 39.1. HR-MS (ESI): Calcd for $C_{11}H_{11}O_3^-$ $[M-H]^-$:191.0714; found: 191.0714.

4-allyl-2,6-di-tert-butylphenol (3ka)[10]



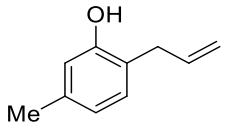
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50/1. colorless oil, 50.3 mg, 68% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00 (s, 2H), 5.99 (ddt, *J* = 16.8, 10.0, 6.8 Hz, 1H), 5.17 – 4.99 (m, 3H), 3.33 (d, *J* = 6.8 Hz, 2H), 1.45 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.1, 138.2, 135.8, 130.6, 125.0, 115.2, 40.2, 34.3, 30.3.

4-allyl-2,6-dichlorophenol (3la)



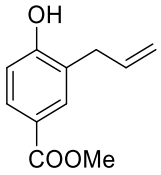
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow oil, 57.3 mg, 94% yield.^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (s, 2H), 5.86 (tdd, *J* = 20.4, 13.5, 4.1 Hz, 2H), 5.16 – 5.01 (m, 2H), 3.27 (d, *J* = 6.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.1, 136.2, 133.4, 128.3, 120.9, 116.8, 38.8. HR-MS (ESI): Calcd for $C_9H_7Cl_2O^-$ $[M-H]^-$: 200.9879; found: 200.9883.

2-allyl-5-methylphenol (3ma)[11]



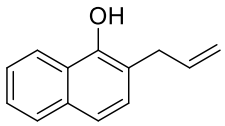
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow oil, 20.0 mg, 45% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.98 (d, *J* = 7.6 Hz, 0H), 6.77 – 6.59 (m, -1H), 6.11 – 5.91 (m, 0H), 5.21 – 5.07 (m, -1H), 4.93 (s, -1H), 3.37 (d, *J* = 6.2 Hz, -2H), 2.28 (s, -3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.0, 137.9, 136.7, 130.2, 122.1, 121.7, 116.5, 34.8, 21.0.

methyl 3-allyl-4-hydroxybenzoate (3na)[12]



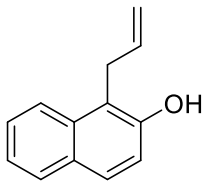
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. orange oil, 25.9 mg, 45% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.76 (m, 2H), 6.84 (d, *J* = 8.9 Hz, 1H), 6.10 – 5.91 (m, 1H), 5.82 (s, 1H), 5.23 – 5.10 (m, 2H), 3.88 (s, 3H), 3.44 (d, *J* = 6.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 158.4, 135.7, 132.4, 130.1, 125.3, 122.8, 122.3, 117.0, 115.6, 51.9, 34.9.

2-allylnaphthalen-1-ol (3oa)[13]



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow oil, 45.9 mg, 83% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 – 8.13 (m, 1H), 7.84 – 7.73 (m, 1H), 7.54 – 7.34 (m, 3H), 7.23 (d, *J* = 8.3 Hz, 1H), 6.09 (ddt, *J* = 16.5, 10.1, 6.2 Hz, 1H), 5.55 (s, 1H), 5.34 – 5.20 (m, 2H), 3.59 (dt, *J* = 6.2, 1.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.6, 136.1, 133.8, 128.5, 127.5, 125.8, 125.3, 121.3, 120.4, 117.8, 117.0, 35.8.

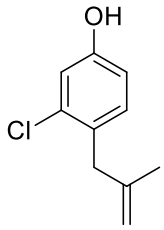
1-allylnaphthalen-2-ol (3pa)[14]



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow oil, 45.9 mg, 83% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.6 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 8.8 Hz, 1H), 6.09 (ddt, *J* = 16.1, 10.8, 5.8 Hz, 1H), 5.22 – 5.02 (m, 3H), 3.84

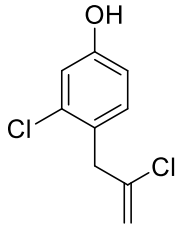
(d, *J* = 5.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.7, 133.2, 128.6, 128.3, 126.5, 123.2, 123.0, 118.0, 116.0, 29.3.

3-chloro-4-(2-methylallyl)phenol (3ab)



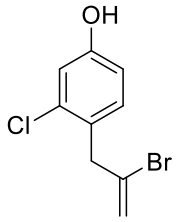
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow oil, 44.9 mg, 82% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.3 Hz, 1H), 6.89 (d, *J* = 2.4 Hz, 1H), 6.70 (dd, *J* = 8.3, 2.4 Hz, 1H), 5.54 (s, 1H), 4.82 (s, 1H), 4.60 (s, 1H), 3.36 (s, 2H), 1.73 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5, 144.0, 134.8, 131.6, 129.6, 116.4, 114.1, 111.9, 40.5, 22.4. HR-MS (ESI): Calcd for $C_{10}H_{10}ClO^-$ [M-H]$^-$: 181.0426; found: 181.0432.

3-chloro-4-(2-chloroallyl)phenol (3ac)



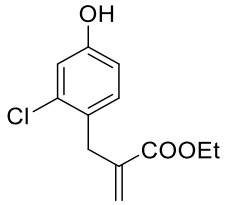
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow oil, 49.3 mg, 81% yield.^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.4 Hz, 1H), 6.90 (d, *J* = 2.5 Hz, 1H), 6.73 (dd, *J* = 8.4, 2.5 Hz, 1H), 5.27 (s, 1H), 5.16 (s, 1H), 5.05 (s, 1H), 3.68 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.3, 140.0, 135.0, 131. 9, 126.8, 116.6, 114.2, 113.8, 42.0. HR-MS (ESI): Calcd for $C_9H_7Cl_2O^-$ [M-H]$^-$: 200.9879; found: 200.9881.

4-(2-bromoallyl)-3-chlorophenol (3ad)



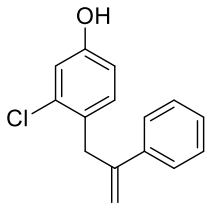
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow oil, 55.0 mg, 74% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.3 Hz, 1H), 6.90 (d, *J* = 2.5 Hz, 1H), 6.73 (dd, *J* = 8.3, 2.5 Hz, 1H), 5.51 (s, 1H), 5.48 (s, 1H), 5.05 (s, 1H), 3.79 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.3, 134.9, 131.9, 131.0, 127.2, 118.2, 116.6, 114.2, 44.2. HR-MS (ESI): Calcd for $C_9H_7BrClO^-$ [M-H]$^-$: 244.9374; found: 244.9378.

ethyl 2-(2-chloro-4-hydroxybenzyl)acrylate (3ae)



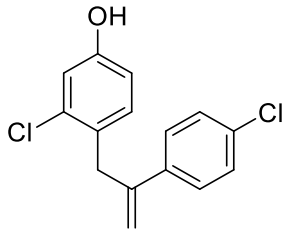
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 41.2 mg, 57% yield.^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.3 Hz, 1H), 6.89 (d, *J* = 2.6 Hz, 1H), 6.69 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.24 (s, 1H), 5.35 – 5.31 (m, 1H), 5.29 (s, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.67 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 154.9, 138.7, 134.8, 131.8, 128.4, 126.2, 116.5, 114.2, 60.9, 34.6, 14.2. HR-MS (ESI): Calcd for $C_{12}H_{12}ClO_3^-$ [M-H]$^-$: 239.0480; found: 239.0492.

3-chloro-4-(2-phenylallyl)phenol (3af)



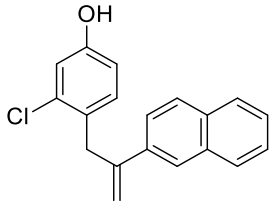
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow oil, 55.1 mg, 75% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.0 Hz, 2H), 7.31 (t, *J* = 6.7 Hz, 3H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.89 (d, *J* = 2.5 Hz, 1H), 6.65 (dd, *J* = 8.3, 2.5 Hz, 1H), 5.48 (s, 1H), 5.07 (s, 1H), 4.87 (s, 1H), 3.84 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ154.8, 145.8, 140.8, 134.7, 134.2, 128.3, 127.6, 126.0, 116.4, 114.3, 114.1, 37.9. HR-MS (ESI): Calcd for $C_{15}H_{12}ClO^-$ [M-H]$^-$: 243.0582; found: 243.0589.

3-chloro-4-(2-(4-chlorophenyl)allyl)phenol (3ag)



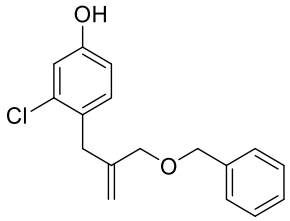
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow oil, 67.8 mg, 81% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 6.6 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.89 (d, *J* = 2.5 Hz, 1H), 6.65 (dd, *J* = 8.4, 2.5 Hz, 1H), 5.46 (s, 1H), 4.95 (s, 1H), 4.91 (s, 1H), 3.81 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7, 144.8, 139.1, 134.7, 133.3, 131.4, 128.8, 128.4, 127.4, 116.4, 114.9, 114.2, 37.8. HR-MS (ESI): Calcd for $C_{15}H_{11}Cl_2O^-$ [M-H]$^-$: 277.0192; found: 277.0208.

3-chloro-4-(2-(naphthalen-2-yl)allyl)phenol (3ah)



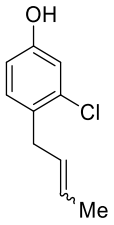
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow solid, 72.5 mg, 82% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 – 7.78 (m, 4H), 7.67 – 7.61 (m, 1H), 7.47 – 7.42 (m, 2H), 7.10 (d, *J* = 8.4 Hz, 1H), 6.90 (d, *J* = 2.5 Hz, 1H), 6.63 (dd, *J* = 8.4, 2.5 Hz, 1H), 5.64 (s, 1H), 5.00 (s, 1H), 3.97 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7, 145.7, 137.9, 134.7, 133.4, 132.9, 131.5, 129.2, 128.3, 127.9, 127.5, 126.2, 125.9, 124.8, 124.5, 116.4, 114.9, 114.2, 37.9. HR-MS (ESI): Calcd for $C_{19}H_{14}ClO^-$ [M-H]$^-$: 293.0739; found: 293.0748.

4-(2-((benzyloxy)methyl)allyl)-3-chlorophenol (3ai)



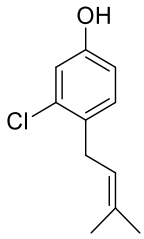
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow oil, 58.0 mg, 67% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H), 7.05 (d, *J* = 8.3 Hz, 1H), 6.85 (d, *J* = 2.1 Hz, 1H), 6.64 (dd, *J* = 8.3, 2.2 Hz, 1H), 5.81 (s, 1H), 5.15 (s, 1H), 4.81 (s, 1H), 4.53 (s, 2H), 4.00 (s, 2H), 3.46 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9, 153.9, 143.9, 138.0, 134.8, 131.8, 128.5, 128.5, 128.0, 127.8, 116.5, 114.2, 72.8, 72.0, 36.3. HR-MS (ESI): Calcd for $C_{17}H_{16}ClO_2^-$ [M-H]$^-$:287.0844; found: 287.0853.

(E)-4-(but-2-en-1-yl)-3-chlorophenol and (Z)-4-(but-2-en-1-yl)-3-chlorophenol (3aj)



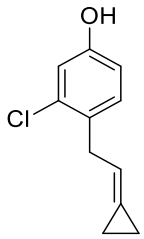
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow oil, 35.1 mg, 64% yield. The ratio between E and Z was determined to be 2/3.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (dd, *J* = 8.3, 4.0 Hz, 1H), 6.87 (d, *J* = 2.5 Hz, 1H), 6.68 (dd, *J* = 8.4, 2.0 Hz, 1H), 5.57 (m, 2H), 5.26 (s, 1H), 3.42-3.32 (m, 2H), 1.73 – 1.67 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4, 154.4, 134.2, 130.9, 130.8, 130.6, 128.5, 127.7, 126.8, 125.4, 116.4, 116.3, 114.1, 35.6, 30.1, 17.9, 12.9. HR-MS (ESI): Calcd for $C_{10}H_{10}ClO^-$ [M-H]$^-$: 181.0426; found: 181.0432.

3-chloro-4-(3-methylbut-2-en-1-yl)phenol (3ak)



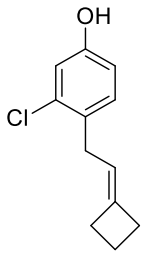
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow oil, 43.1 mg, 73% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.3 Hz, 1H), 6.86 (d, *J* = 2.4 Hz, 1H), 6.67 (dd, *J* = 8.3, 2.4 Hz, 1H), 5.26 (q, *J* = 7.4 Hz, 1H), 5.10 (s, 1H), 3.34 (d, *J* = 7.3 Hz, 2H), 1.73 (d, *J* = 11.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.4, 130.4, 121.7, 120.9, 116.3, 115.9, 114.0, 113.8, 31.2, 29.7, 25.8, 17.9, 14.1. HR-MS (ESI): Calcd for $C_{11}H_{12}ClO^-$ [M-H]$^-$: 195.0582; found: 195.0583.

3-chloro-4-(2-cyclopropylideneethyl)phenol (3al)



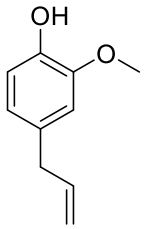
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow oil, 39.1 mg, 67% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.3 Hz, 1H), 6.87 (d, *J* = 2.4 Hz, 1H), 6.67 (dd, *J* = 8.3, 2.4 Hz, 1H), 5.89 (tt, *J* = 4.7, 2.4 Hz, 1H), 5.02 (s, 1H), 3.53 (d, *J* = 6.5 Hz, 2H), 1.11 – 0.94 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4, 134.3, 131.0, 130.9, 123.4, 116.3, 115.5, 114.0, 35.1, 2.4, 2.0. HR-MS (ESI): Calcd for $C_{11}H_{10}ClO^-$ [M-H]$^-$: 193.0426; found: 193.0433.

3-chloro-4-(2-cyclobutylideneethyl)phenol (3am)



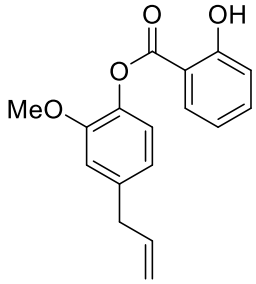
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow oil, 37.6 mg, 60% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.3 Hz, 1H), 6.86 (d, *J* = 2.6 Hz, 1H), 6.67 (dd, *J* = 8.3, 2.6 Hz, 1H), 5.19 (tp, *J* = 7.1, 2.2 Hz, 1H), 4.72 (s, 1H), 3.23 (d, *J* = 7.2 Hz, 2H), 2.77 – 2.59 (m, 4H), 1.96 (p, *J* = 8.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.2, 144.9, 144.1, 141.8, 130.7, 117.4, 116.3, 114.0, 31.2, 30.9, 29.4, 17.0. HR-MS (ESI): Calcd for $C_{11}H_{12}ClO^-$ [M-H]$^-$: 207.0582; found: 207.0589.

4-allyl-2-methoxyphenol (3qa)[15]



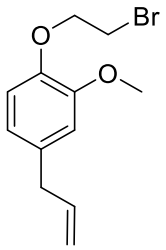
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. colorless oil, 37.4 mg, 76% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.86 (d, *J* = 8.5 Hz, 1H), 6.70 (dd, *J* = 4.0, 2.3 Hz, 2H), 5.96 (ddt, *J* = 16.8, 10.1, 6.7 Hz, 1H), 5.53 (s, 1H), 5.13 – 5.02 (m, 2H), 3.88 (s, 3H), 3.33 (d, *J* = 6.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.5, 143.9, 137.9, 132.0, 121.2, 115.5, 114.3, 111.2, 55.9, 39.9.

4-allyl-2-methoxyphenyl 2-hydroxybenzoate (4)



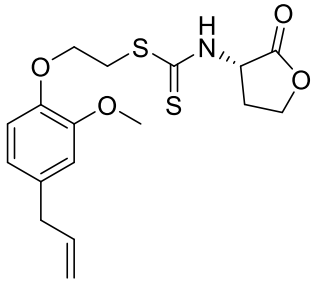
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow oil, 21.3 mg, 75% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.53 (s, 1H), 8.12 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.54 (ddd, *J* = 8.7, 7.5, 1.7 Hz, 1H), 7.13 – 7.01 (m, 2H), 7.01 – 6.94 (m, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.00 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.24 – 5.04 (m, 2H), 3.83 (s, 3H), 3.43 (d, *J* = 6.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6, 162.1, 151.0, 139.7, 137.3, 137.0, 136.3, 130.7, 122.5, 120.8, 119.4, 117.7, 116.3, 112.9, 111.9, 55.9, 40.1. HR-MS (ESI): Calcd for $C_{17}H_{15}O_4^-$ $[M-H]^-$: 283.0976; found: 283.0971.

4-allyl-1-(2-bromoethoxy)-2-methoxybenzene (5)



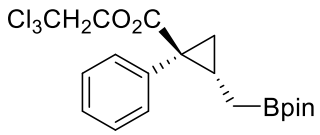
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow oil, 185.5 mg, 80% yield. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.85 (dd, *J* = 7.9, 4.4 Hz, 1H), 6.72 (d, *J* = 8.5 Hz, 2H), 5.95 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.14 – 5.02 (m, 2H), 4.35 – 4.25 (m, 2H), 3.86 (s, 3H), 3.70 – 3.56 (m, 2H), 3.34 (d, *J* = 6.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.8, 145.8, 137.5, 134.4, 120.6, 115.8, 115.2, 112.8, 69.5, 56.0, 39.8, 29.0. HR-MS (ESI): Calcd for $C_{12}H_{16}BrO_2^+$ $[M+H]^+$:271.0328; found:271.0327.

2-(3-allyl-5-methoxyphenoxy)ethyl(S)-(2-oxotetrahydrofuran-3-yl)carbamodithioate (6)



Eluent for flash column chromatography: petroleum ether/ethyl acetate =1/1. yellow oil, 163.2 mg, 74% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, *J* = 6.0 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.71 (d, *J* = 7.3 Hz, 2H), 5.94 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.33 – 5.17 (m, 1H), 5.12 – 5.01 (m, 2H), 4.47 (t, *J* = 8.8 Hz, 1H), 4.37 – 4.22 (m, 3H), 3.84 (s, 3H), 3.68 (dt, *J* = 12.8, 6.4 Hz, 1H), 3.62 – 3.51 (m, 1H), 3.32 (d, *J* = 6.7 Hz, 2H), 3.01 (td, *J* = 8.6, 7.9, 3.9 Hz, 1H), 2.18 (qd, *J* = 11.7, 9.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.4, 174.3, 149.4, 145.9, 137.5, 134.0, 120.7, 115.8, 114.4, 112.7, 68.3, 66.2, 60.0, 55.0, 39.8, 34.9, 29.5, 29.3. HR-MS (ESI): Calcd for $C_{17}H_{21}NNaO_4S_2^+$ $[M+Na]^+$:390.0810; found: 390.0815.

2,2,2-trichloroethyl 1-phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cyclopropane-1-carboxylate (8)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20/1. yellow oil, 33.8 mg, 78% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.23 (m, 5H), 4.86 (d, *J* = 11.9 Hz, 1H), 4.51 (d, *J* = 11.9 Hz, 1H), 2.06 (q, *J* = 7.0 Hz, 1H), 1.90 (dd, *J* = 9.0, 4.2 Hz, 1H), 1.22 (d, *J* = 3.2 Hz, 13H), 0.69 (dd, *J* = 16.5, 6.4 Hz, 1H), 0.37 (dd, *J* = 16.4, 8.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.1, 135.1, 131.8, 127.9, 127.3, 95.2, 83.3, 74.1, 33.7, 25.7, 24.9, 24.8, 22.8. HR-MS (ESI): Calcd for$C_{19}H_{24}BCl_3O_4Na^+$ $[M+Na]^+$: 455.0725; found: 455.0727.

3. References

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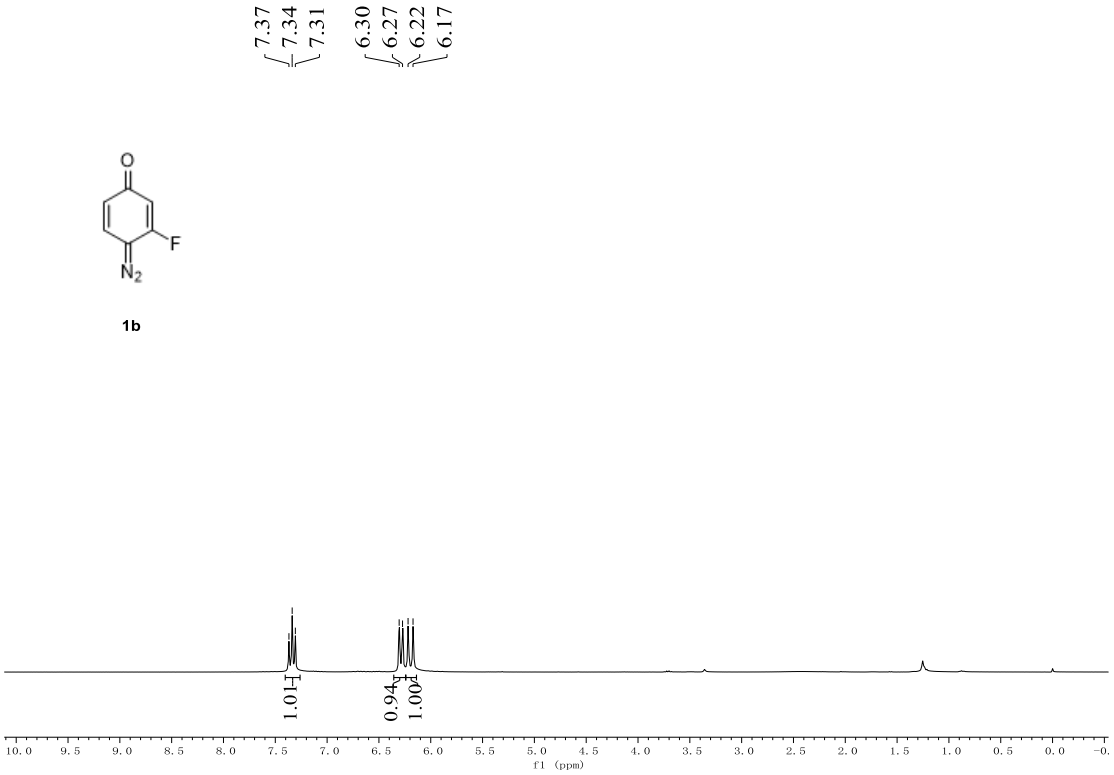
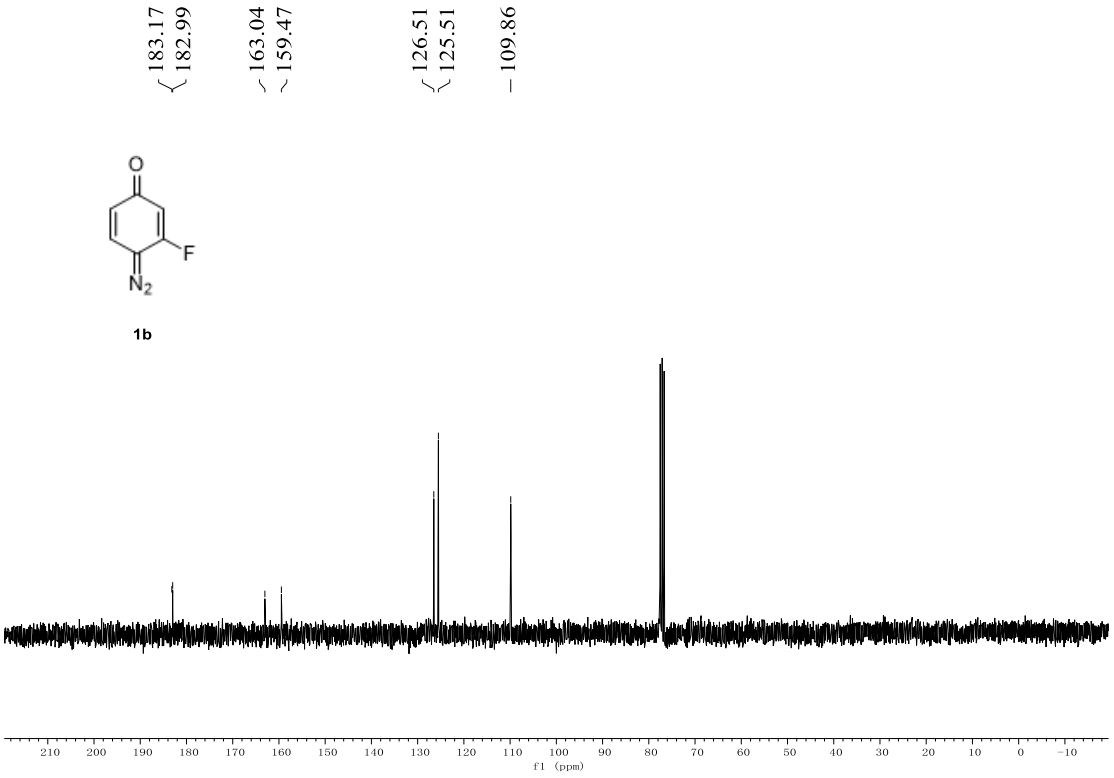
4. NMR Spectra of Compounds

NMR Spectrum for Diazoquinones

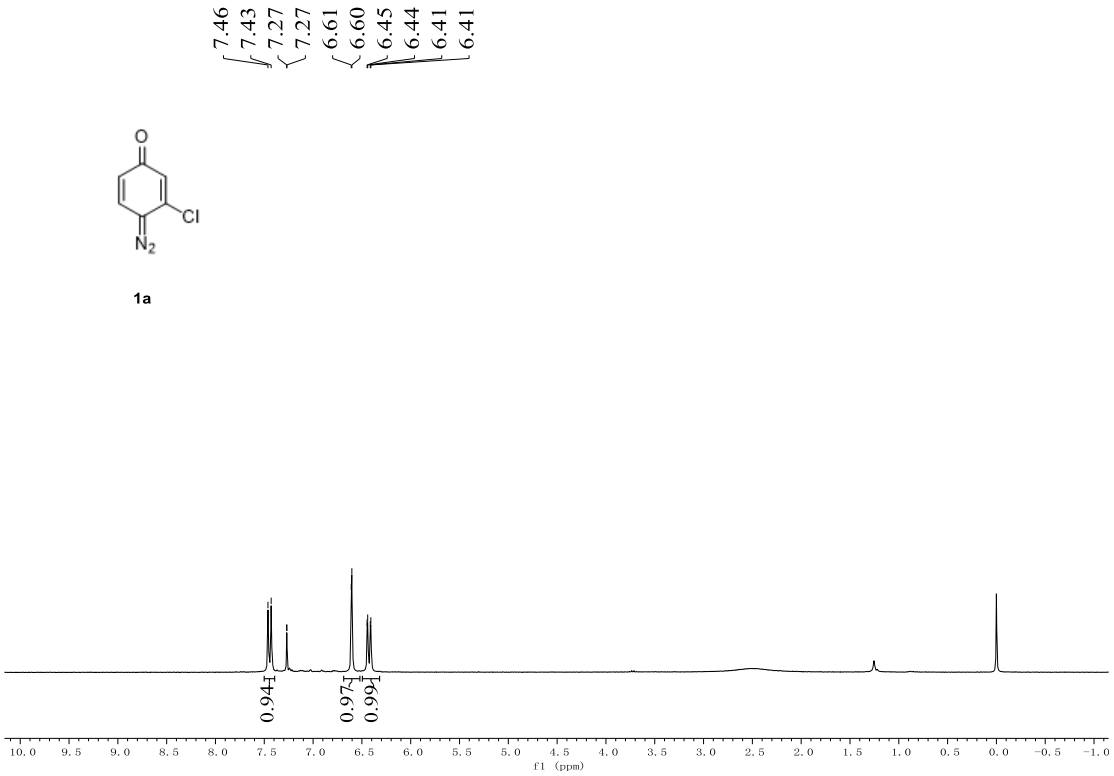
^{1}H NMR (300 MHz, $CDCl_3$)



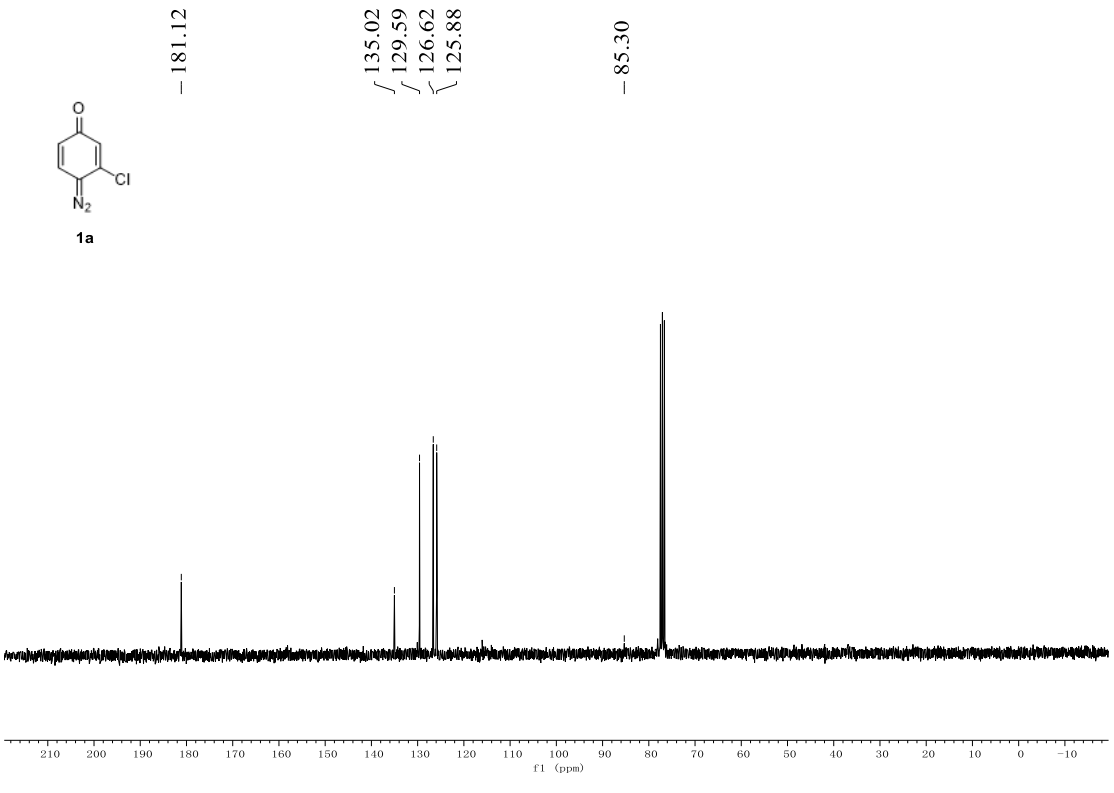
^{13}C NMR (75 MHz, $CDCl_3$)



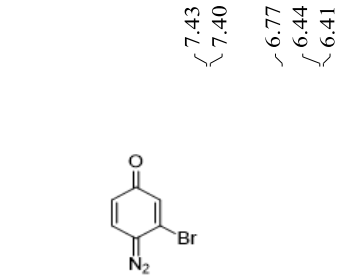
^{1}H NMR (300 MHz, $CDCl_3$)



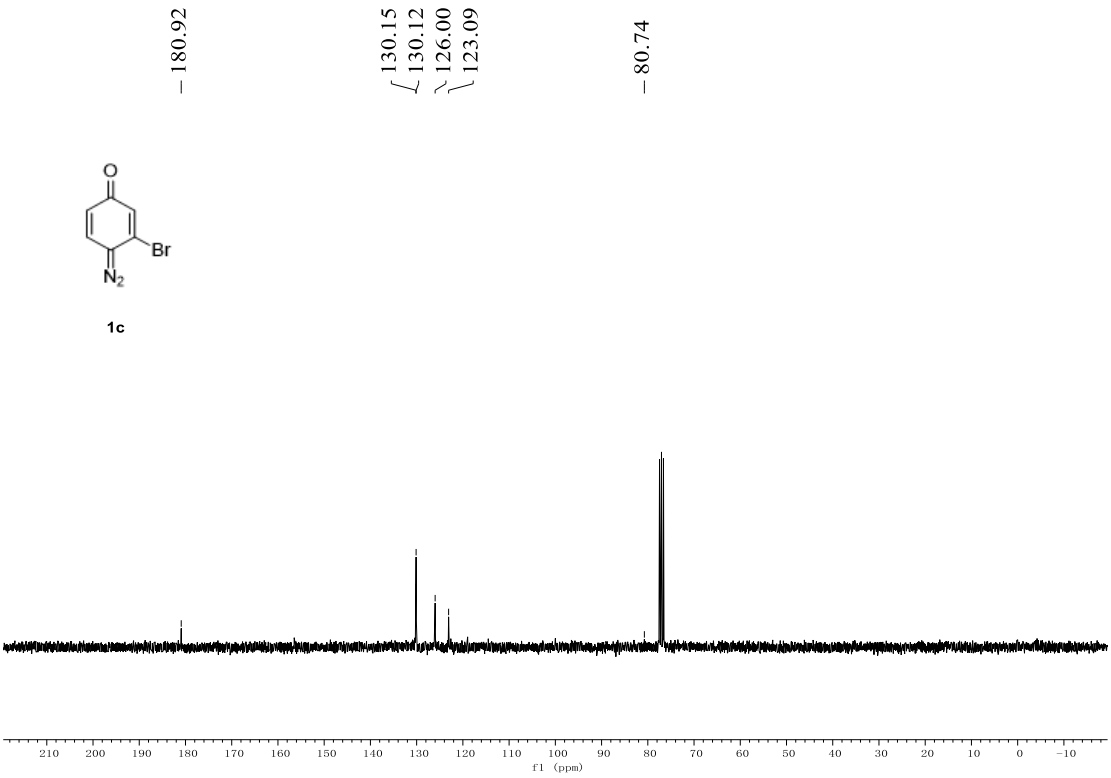
^{13}C NMR (75 MHz, $CDCl_3$)



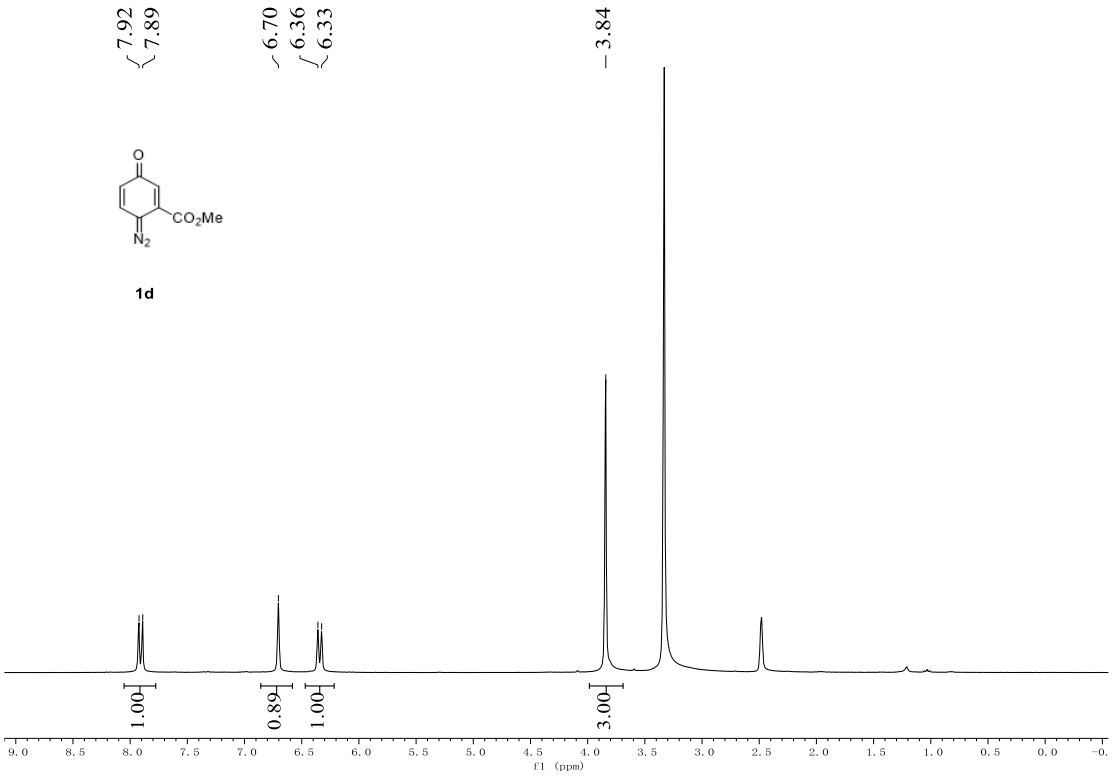
^{1}H NMR (300 MHz, $CDCl_3$)



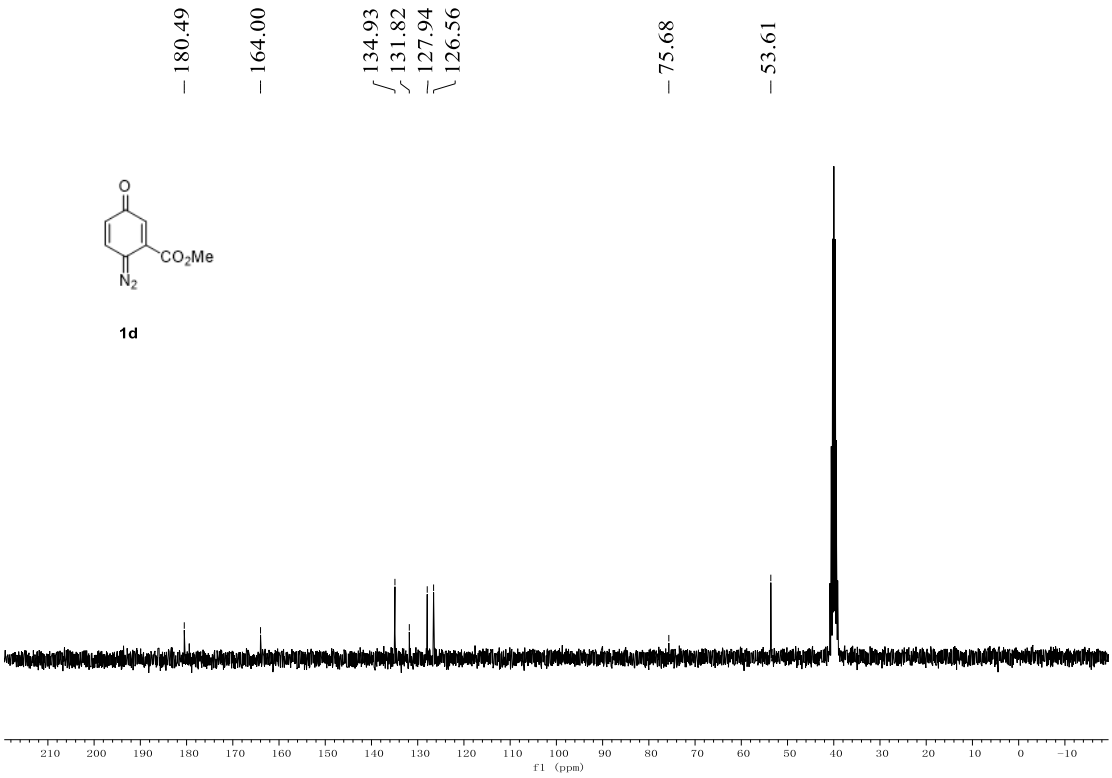
^{13}C NMR (75 MHz, $CDCl_3$)



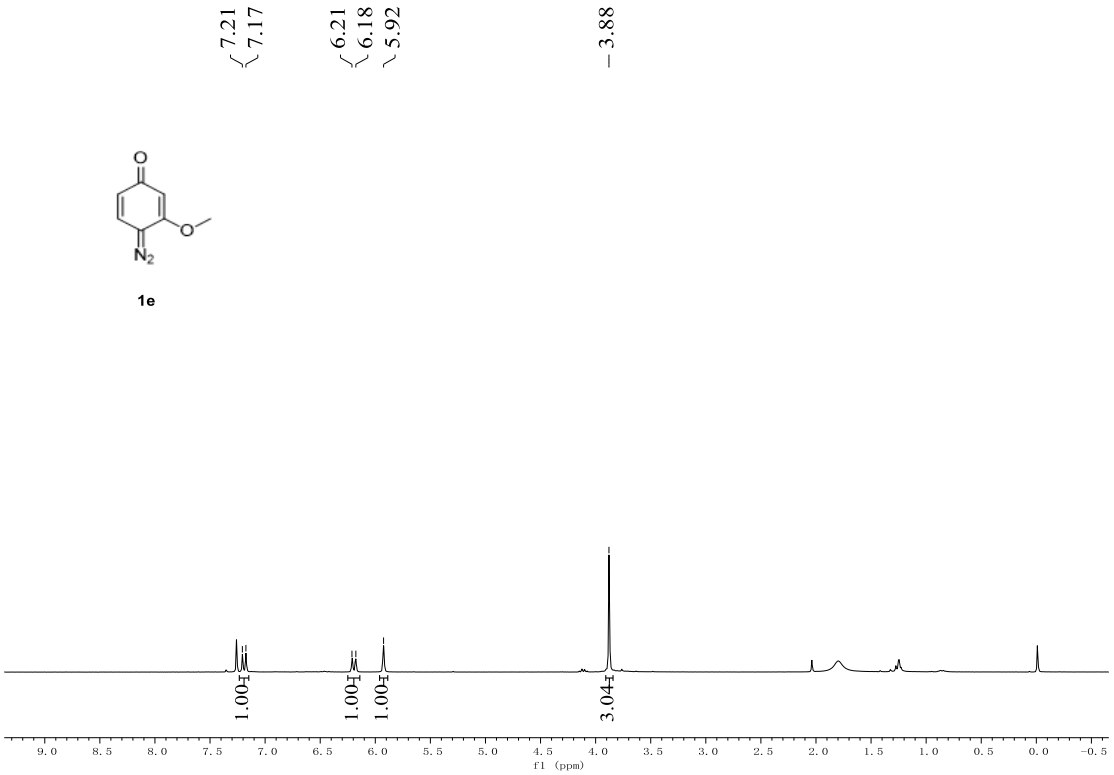
^{1}H NMR (300 MHz, DMSO)



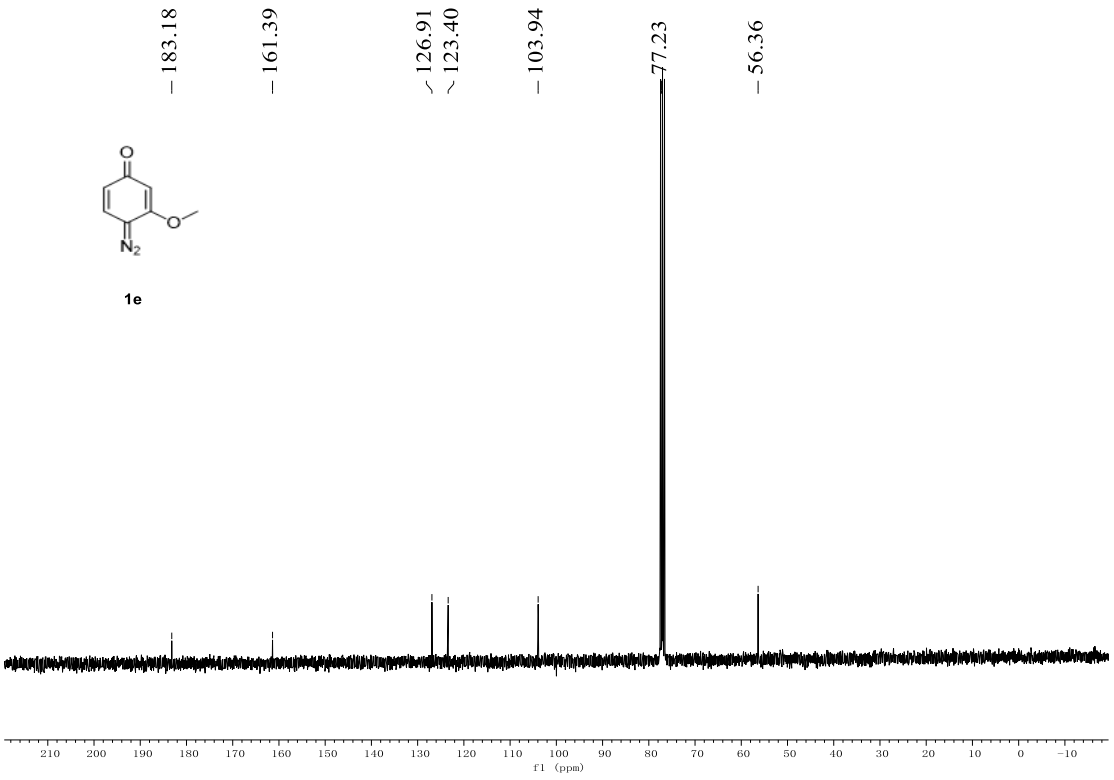
^{13}C NMR (75 MHz, DMSO)



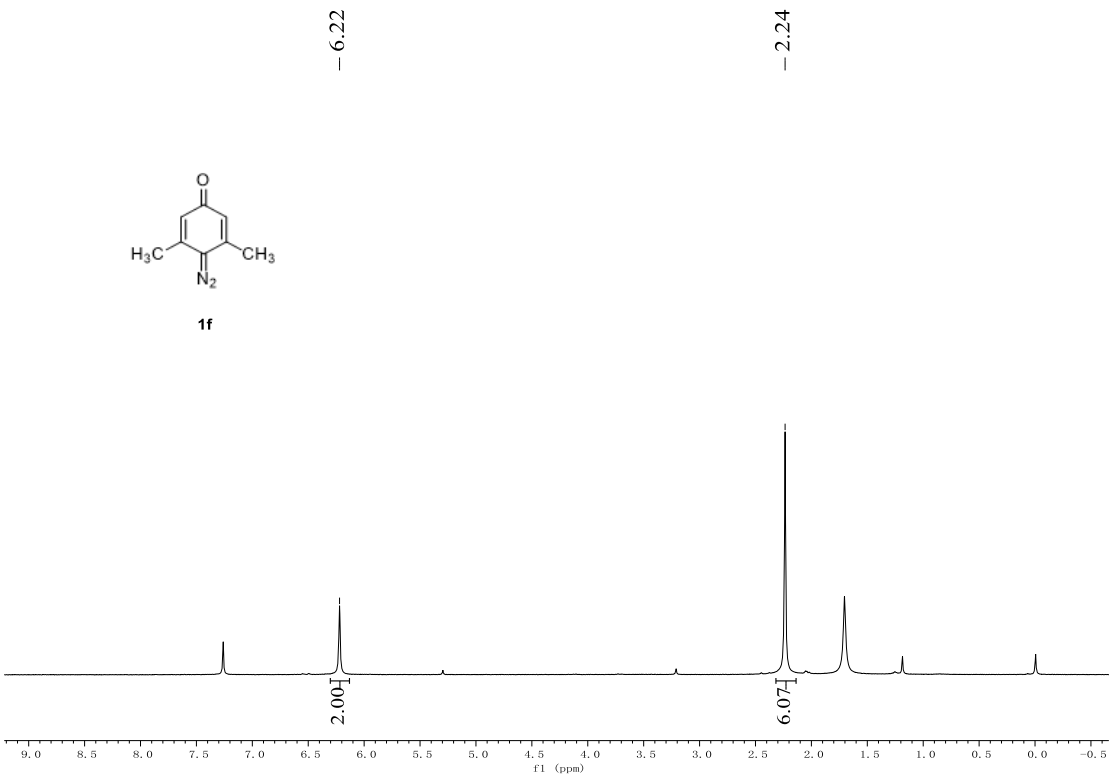
^{1}H NMR (300 MHz, $CDCl_3$)



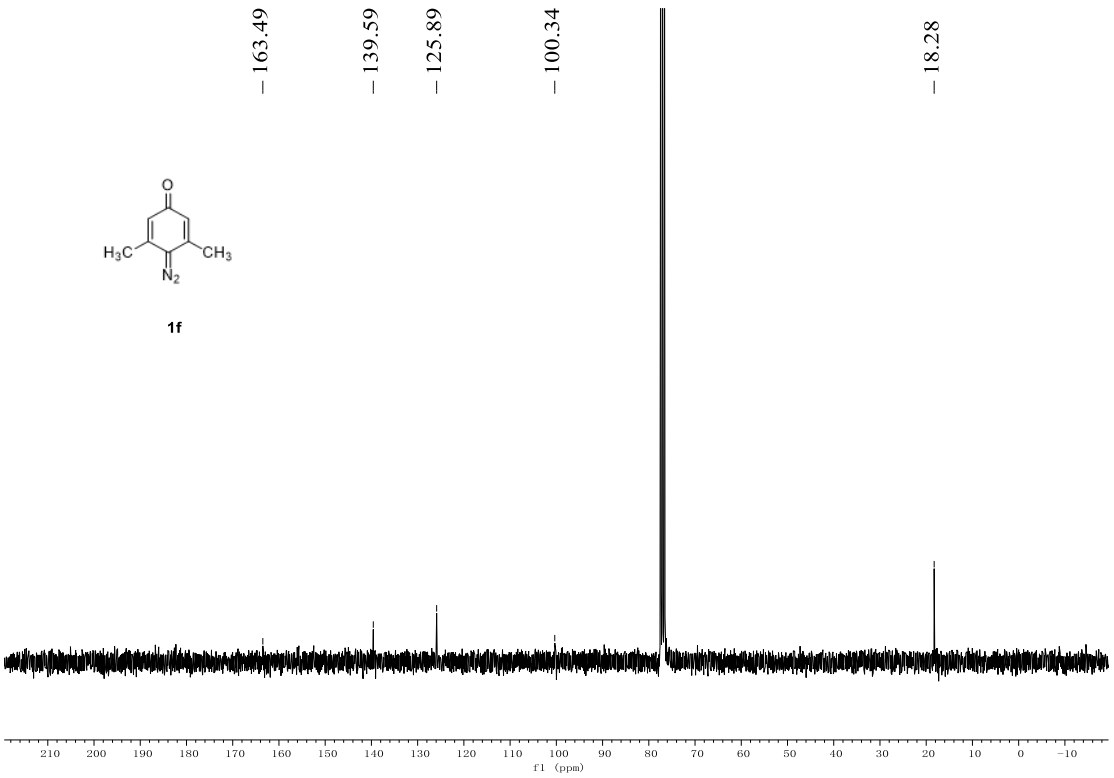
^{13}C NMR (75 MHz, $CDCl_3$)



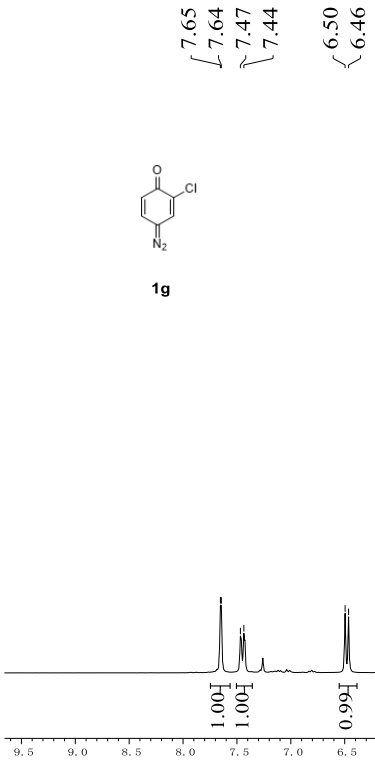
^{1}H NMR (300 MHz, $CDCl_3$)



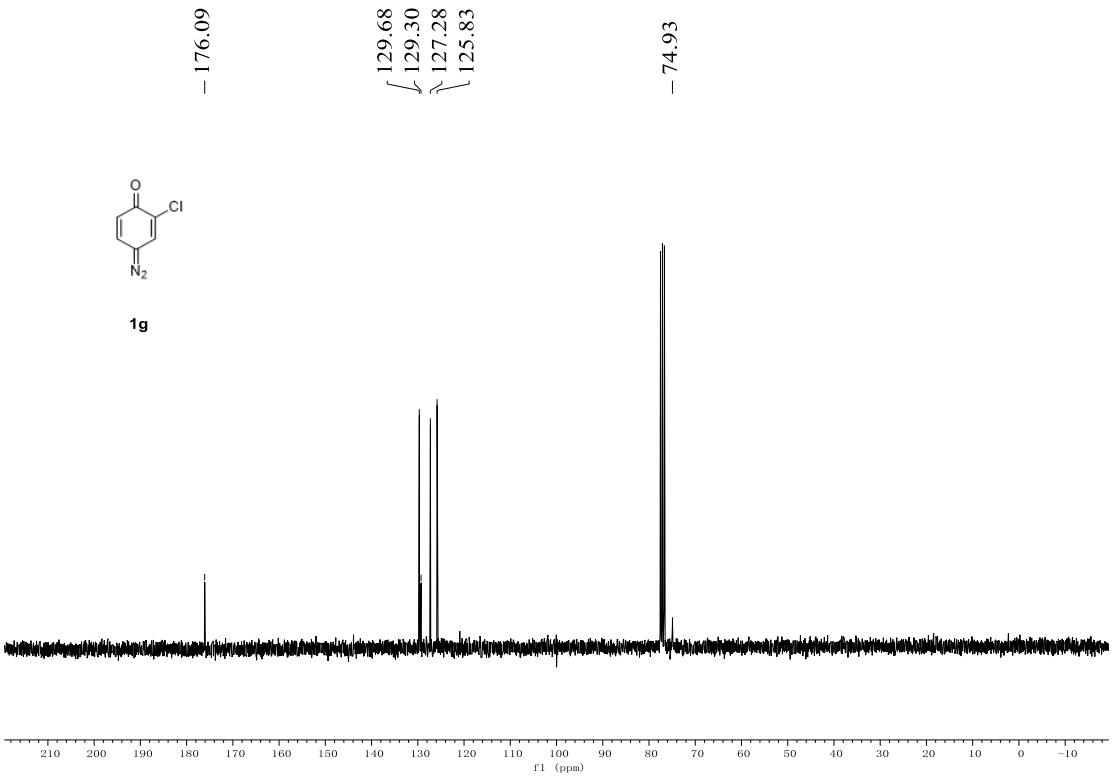
^{13}C NMR (75 MHz, $CDCl_3$)



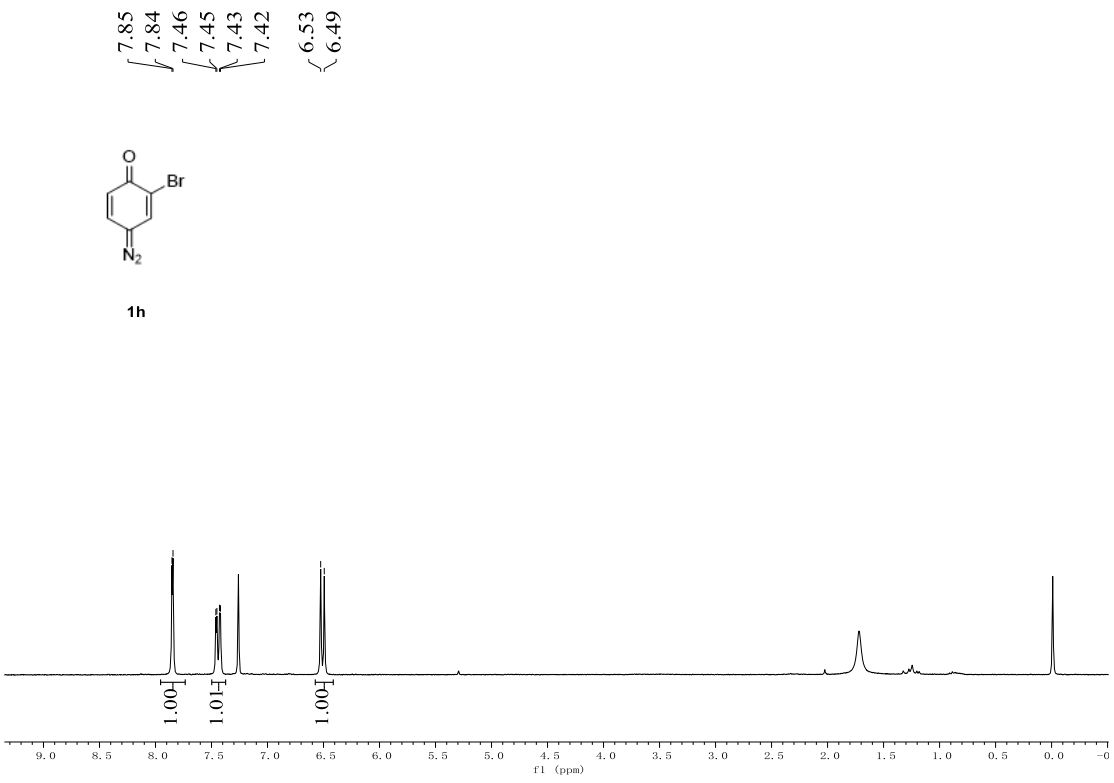
^{1}H NMR (300 MHz, $CDCl_3$)



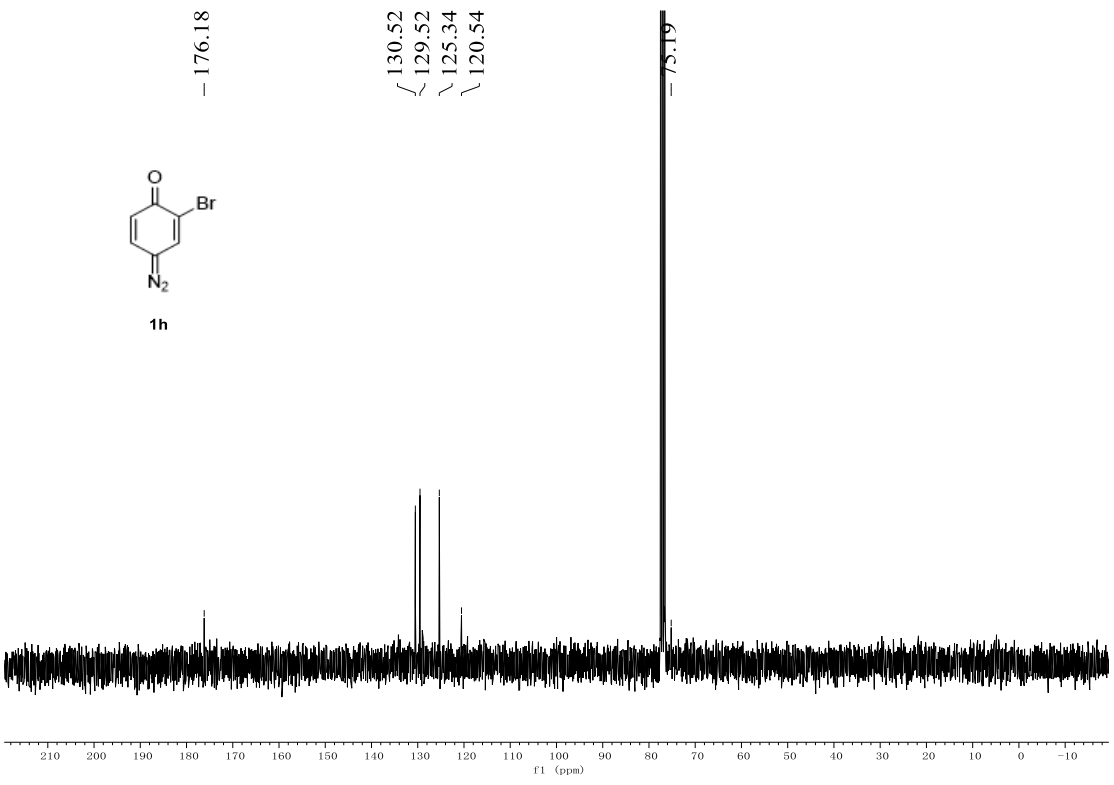
^{13}C NMR (75 MHz, $CDCl_3$)



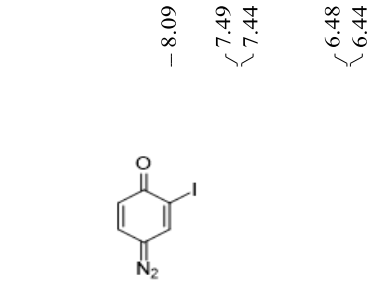
^{1}H NMR (300 MHz, $CDCl_3$)



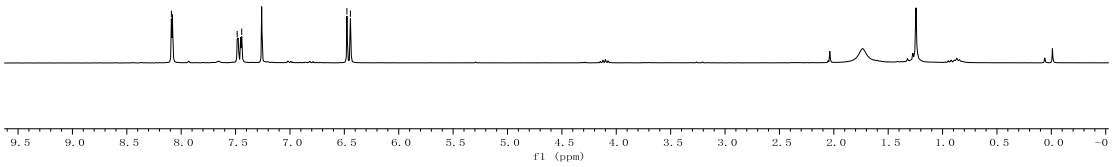
^{13}C NMR (75 MHz, $CDCl_3$)



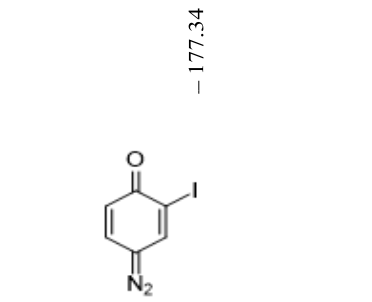
^{1}H NMR (300 MHz, $CDCl_3$)



1i



^{13}C NMR (75 MHz, $CDCl_3$)



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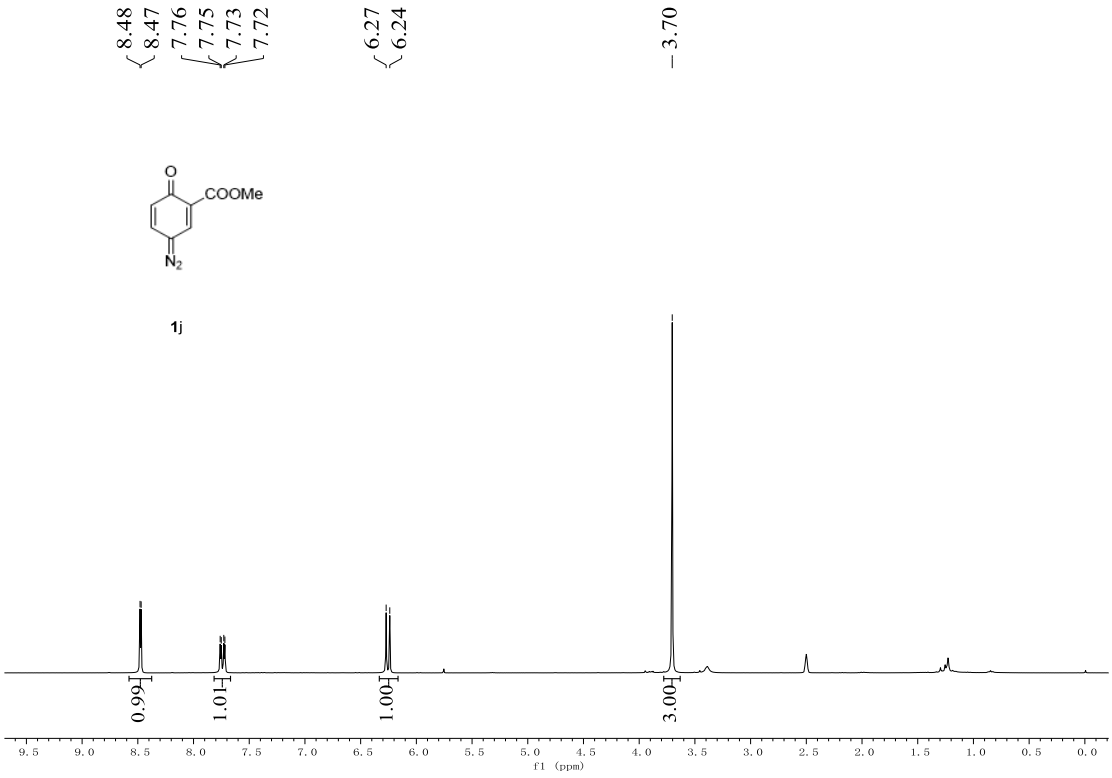
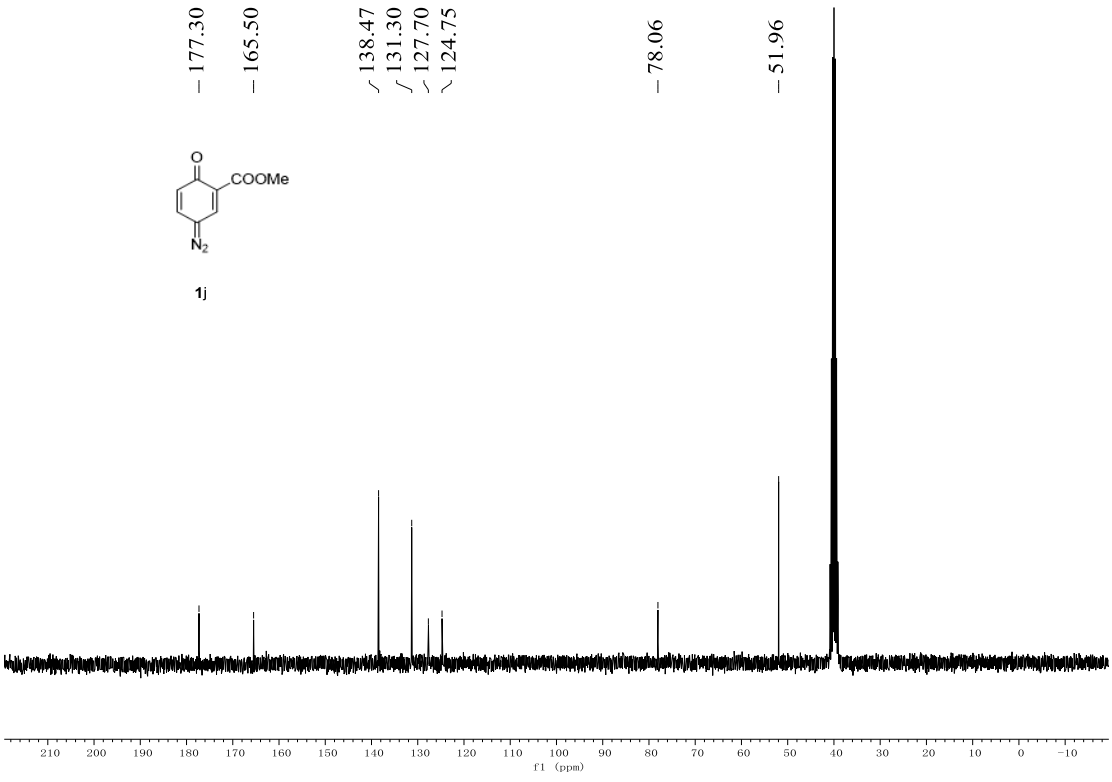
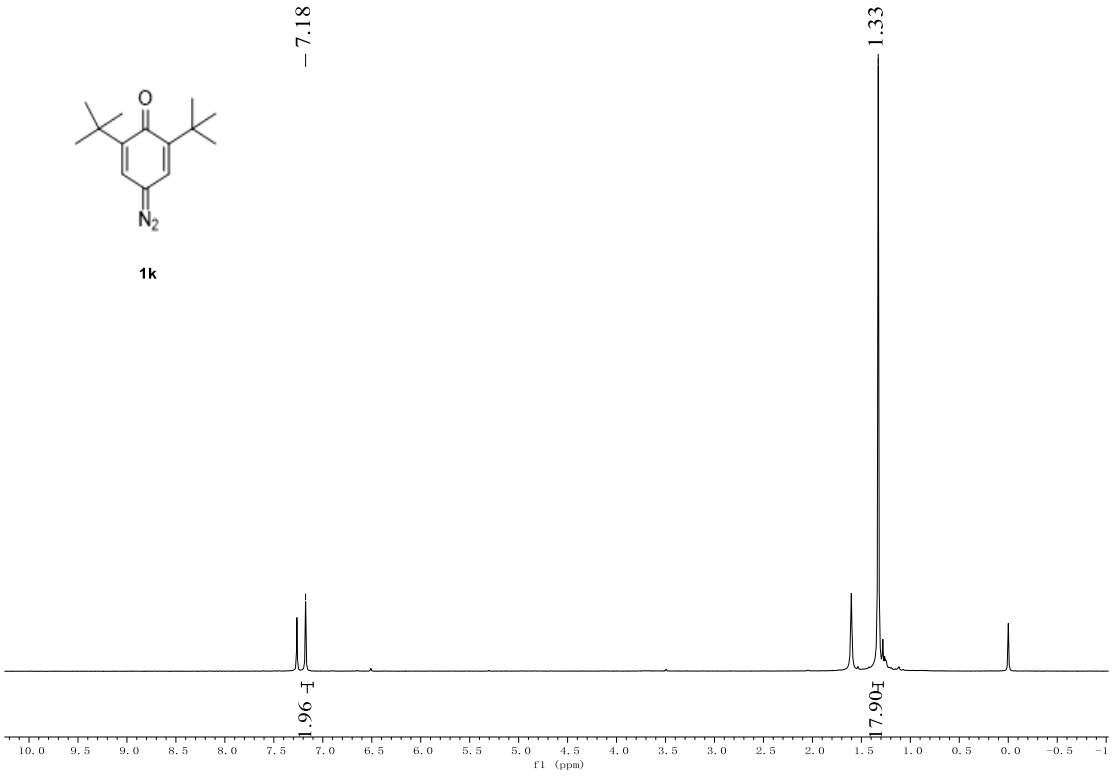
^{1}H NMR (300 MHz, DMSO)



^{13}C NMR (75 MHz, DMSO)



^{1}H NMR (300 MHz, $CDCl_3$)



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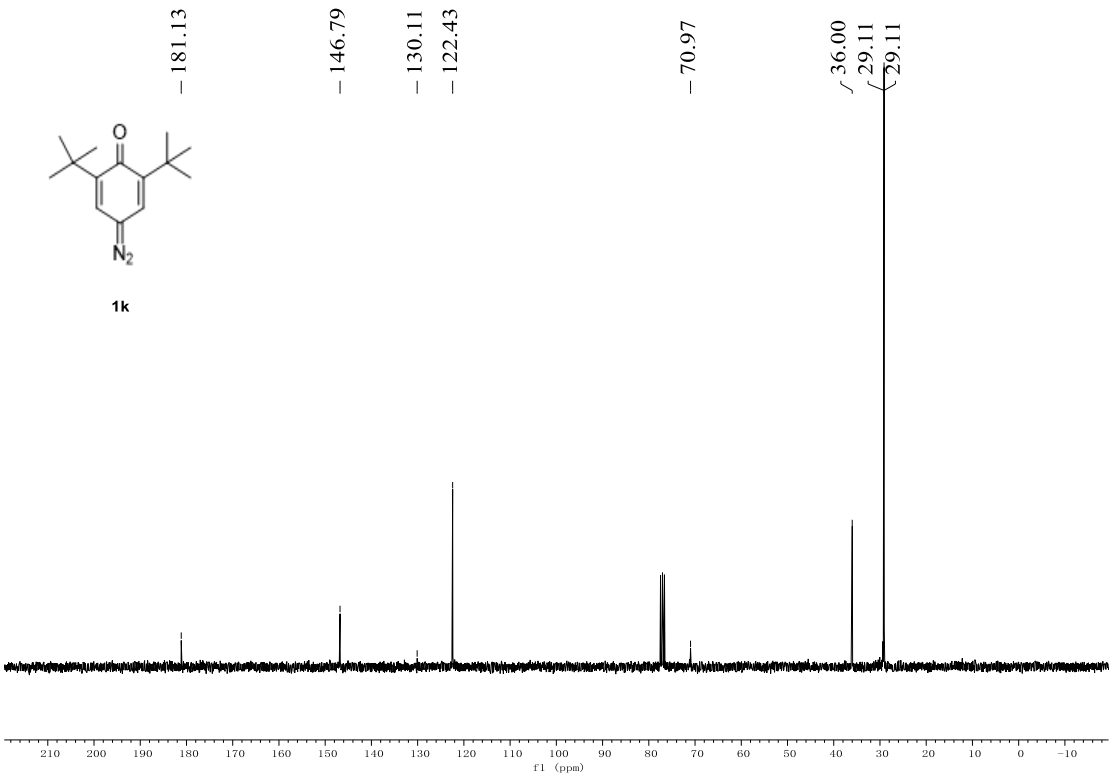
^{13}C NMR (75 MHz, $CDCl_3$)



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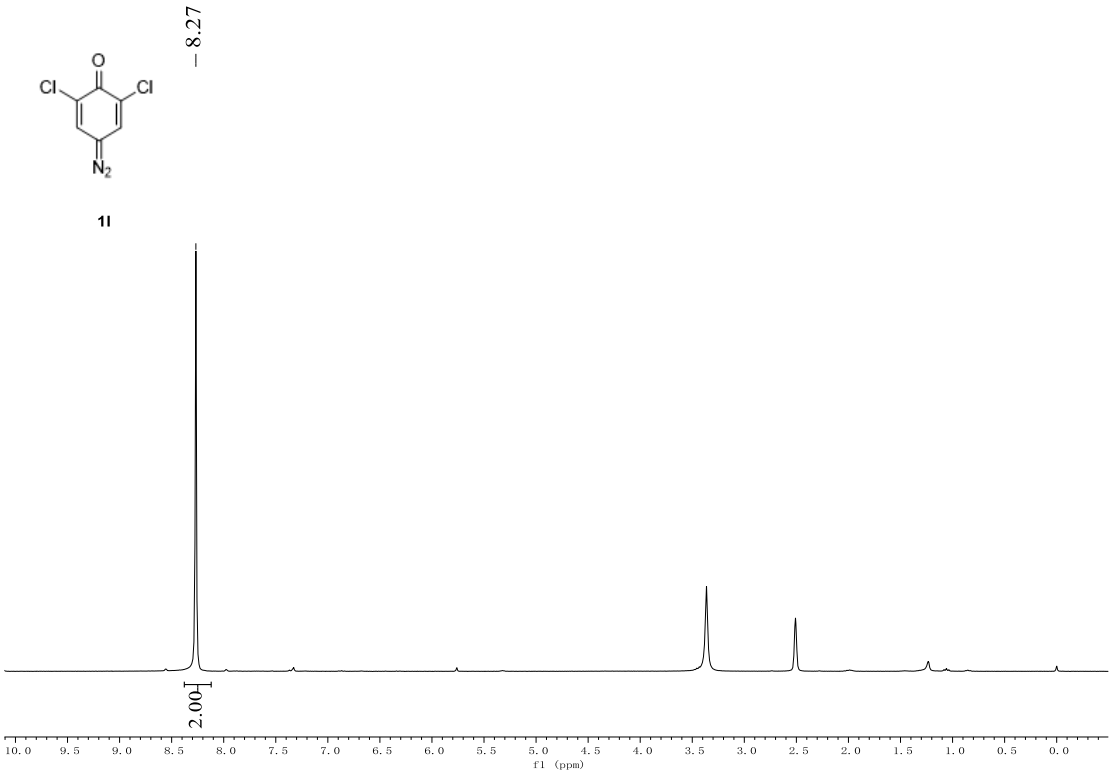
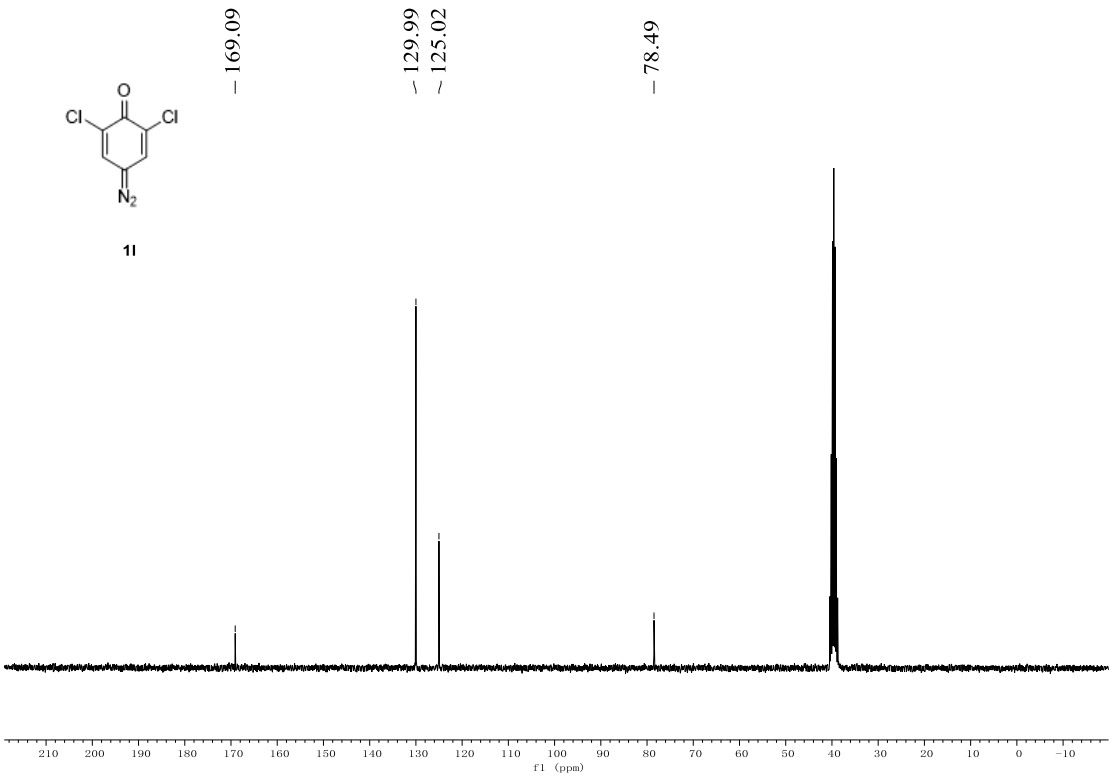
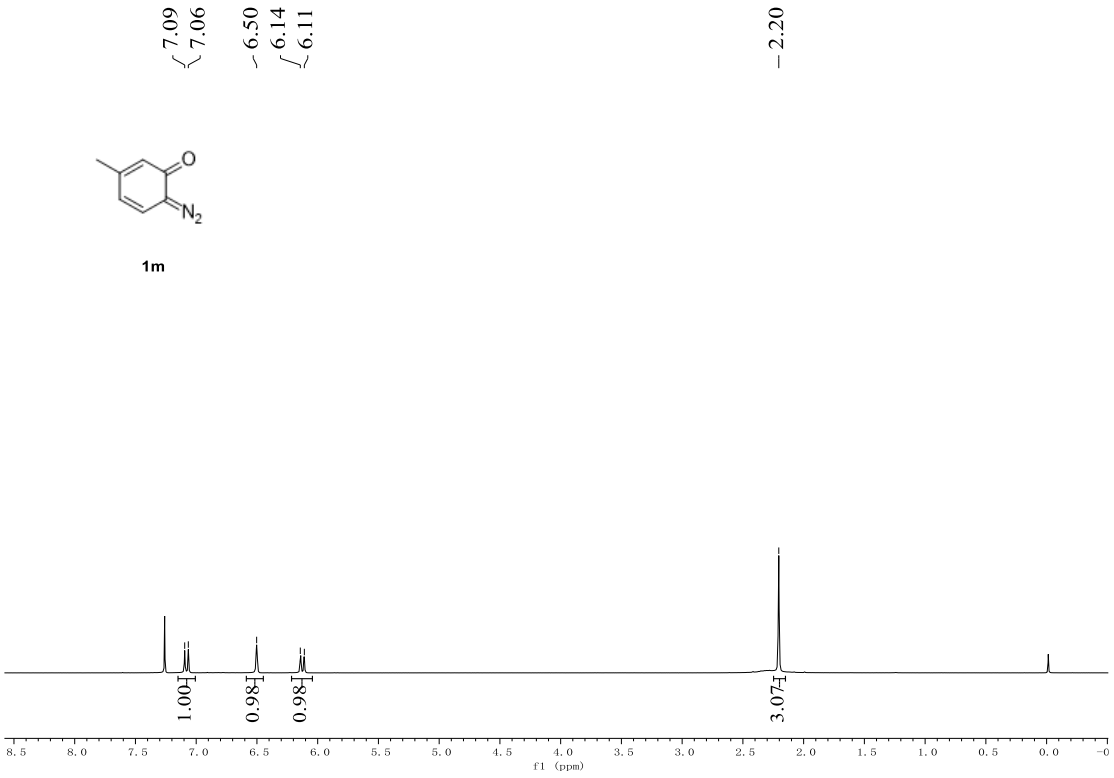
^{1}H NMR (300 MHz, DMSO)



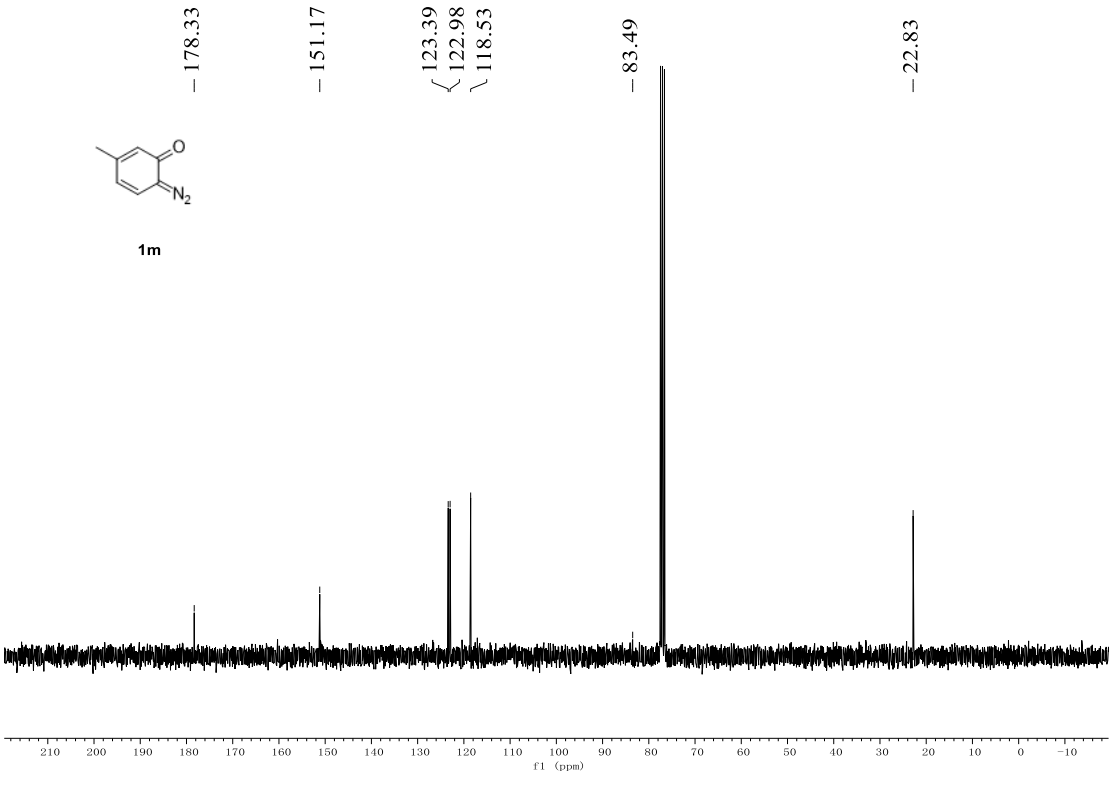
^{13}C NMR (75 MHz, DMSO)



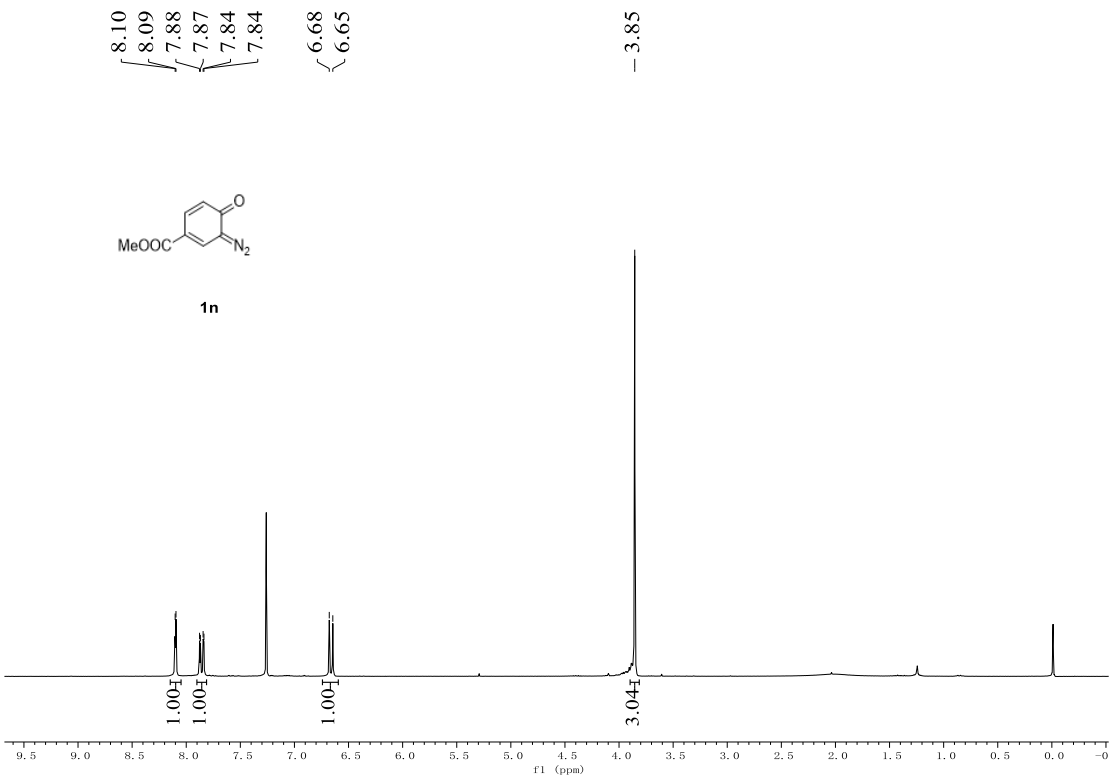
^{1}H NMR (300 MHz, $CDCl_3$)



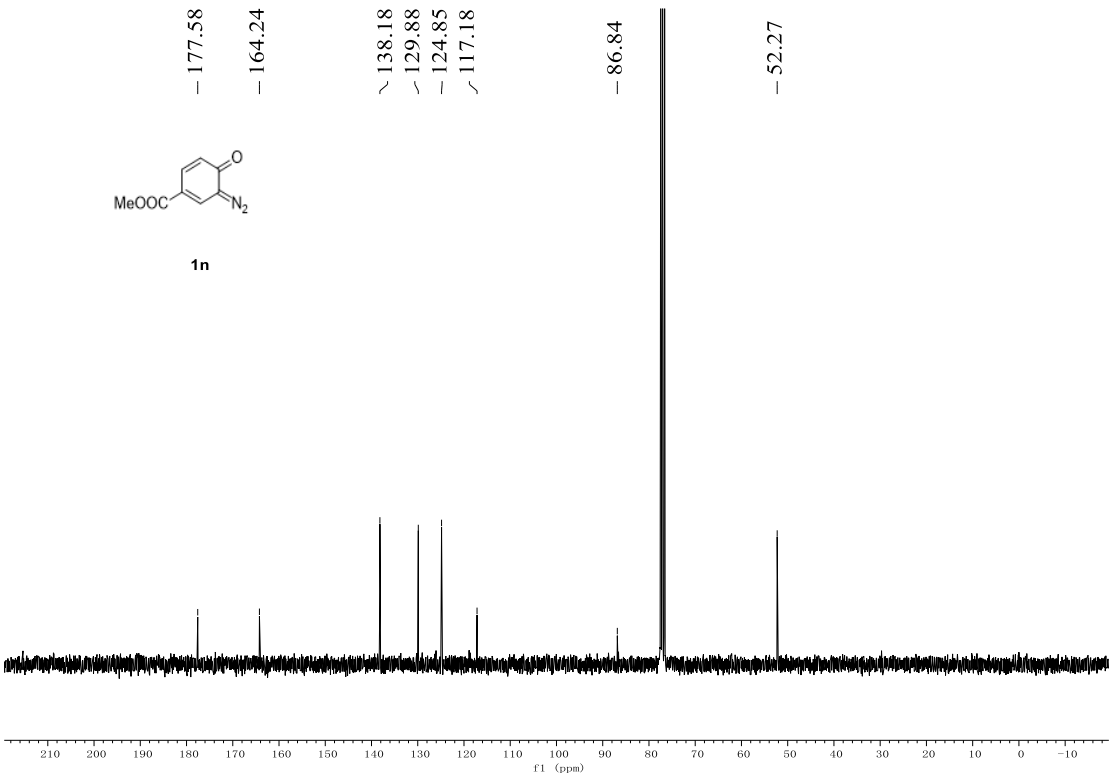
^{13}C NMR (75 MHz, $CDCl_3$)



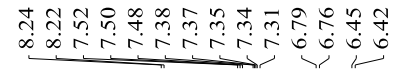
^{1}H NMR (300 MHz, $CDCl_3$)

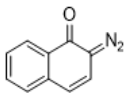


^{13}C NMR (75 MHz, $CDCl_3$)



^{1}H NMR (300 MHz, $CDCl_3$)





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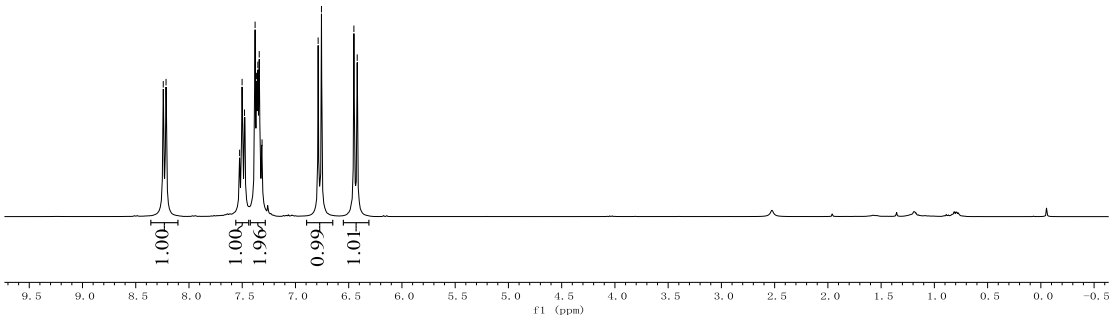
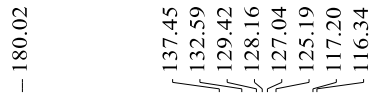
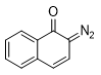


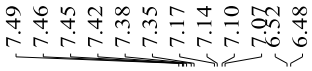
^{13}C NMR (75 MHz, $CDCl_3$)

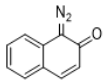




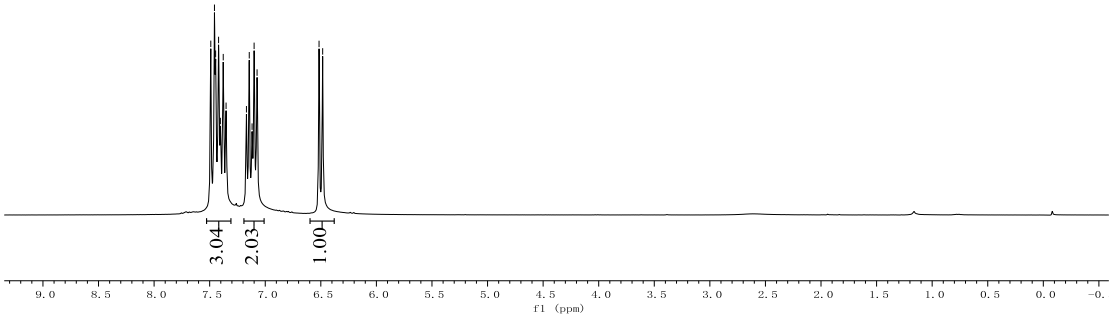
1o

^{1}H NMR (300MHz, $CDCl_3$)

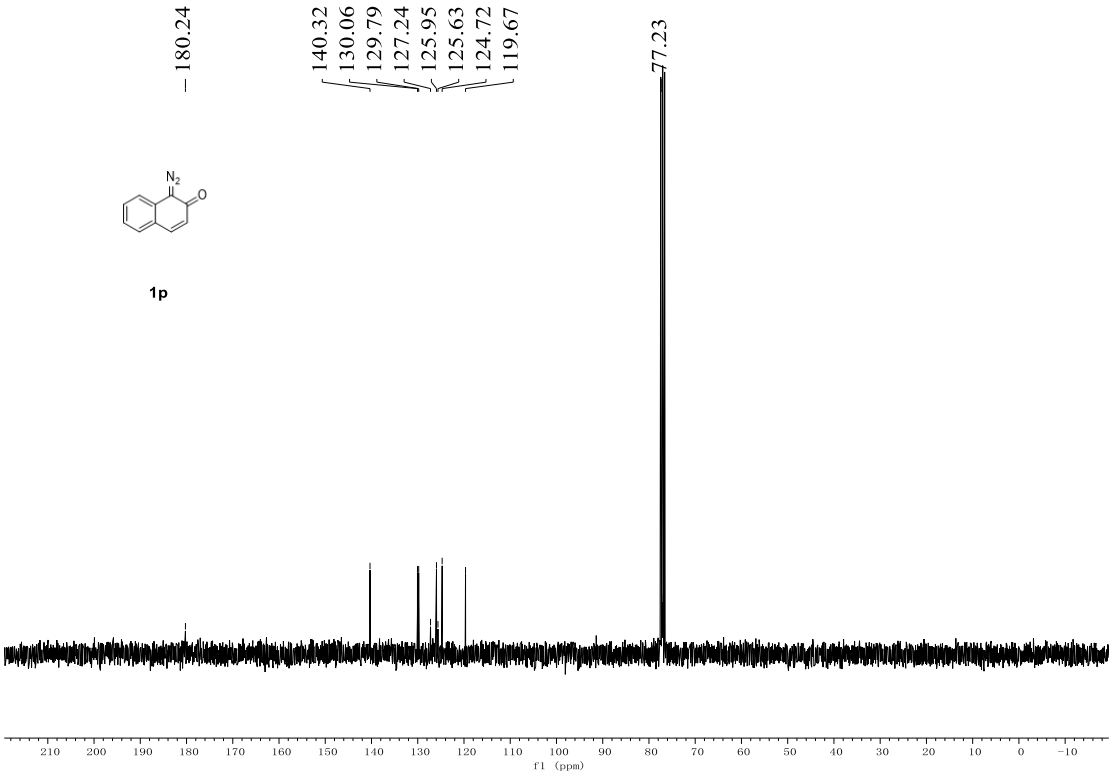




1p

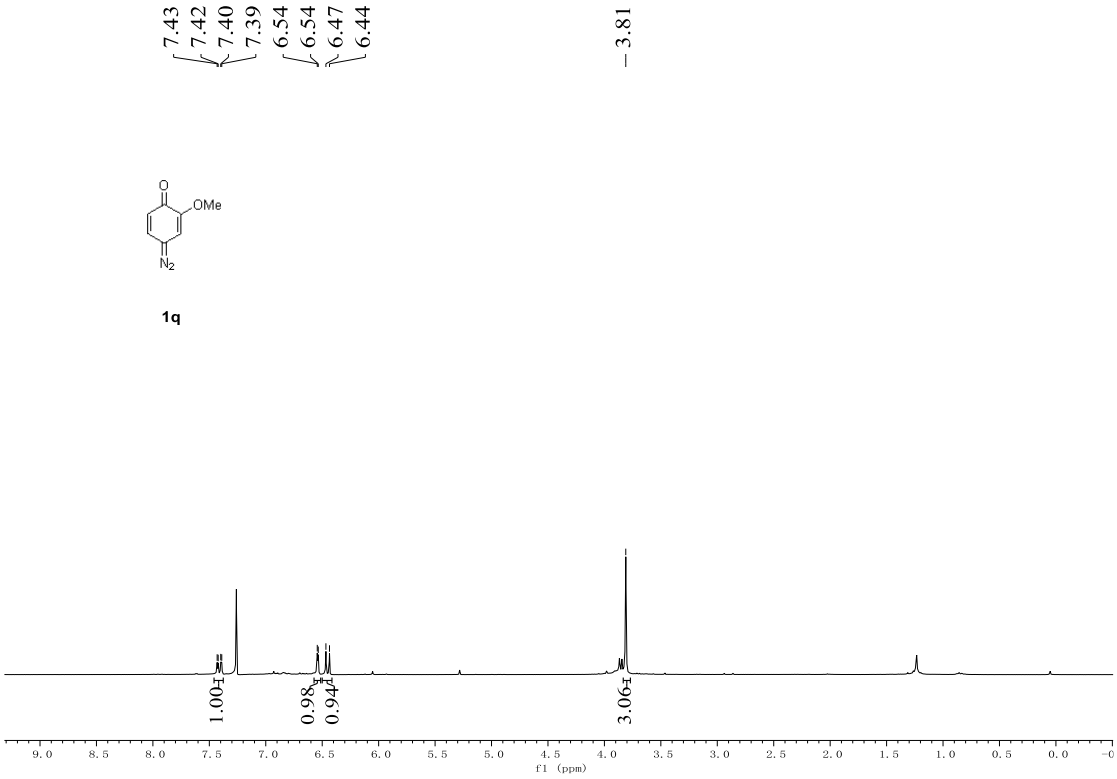


^{13}C NMR (75 MHz, $CDCl_3$)

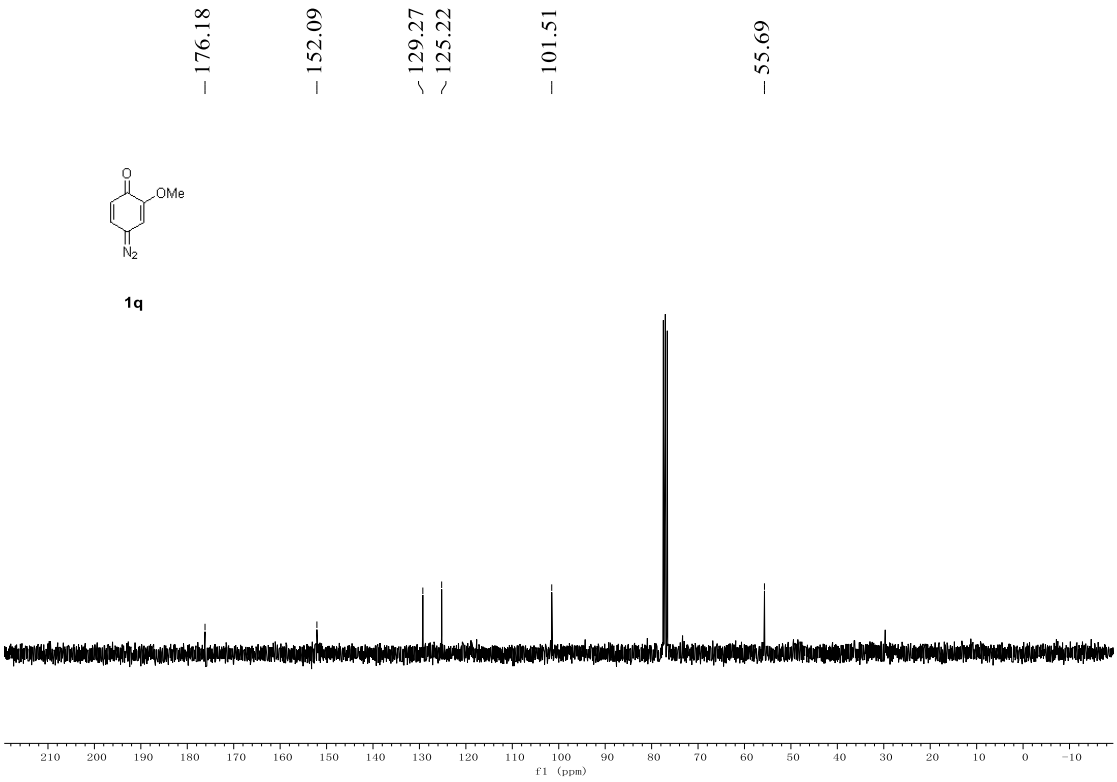


1p

^{1}H NMR (300 MHz, $CDCl_3$)

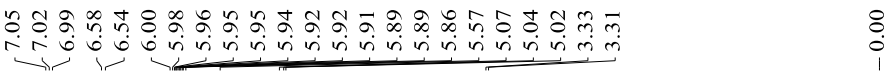


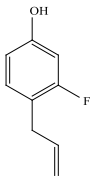
^{13}C NMR (75 MHz, $CDCl_3$)



NMR Spectrum for Products

^{1}H NMR (300 MHz, $CDCl_3$)





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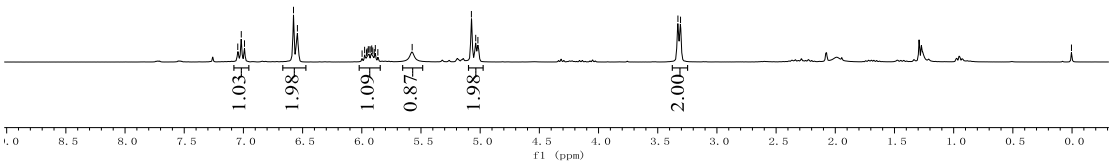
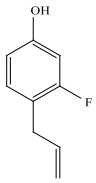


^{13}C NMR (75 MHz, $CDCl_3$)



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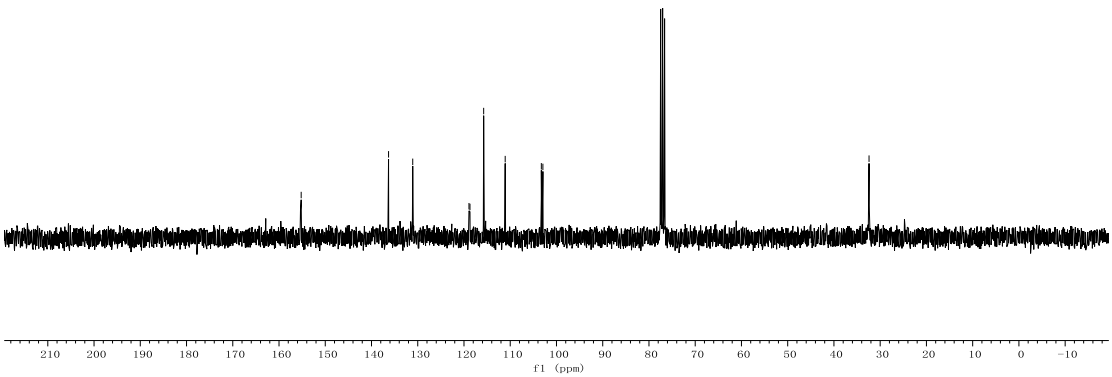
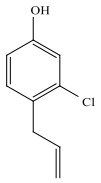


^{1}H NMR (300 MHz, $CDCl_3$)



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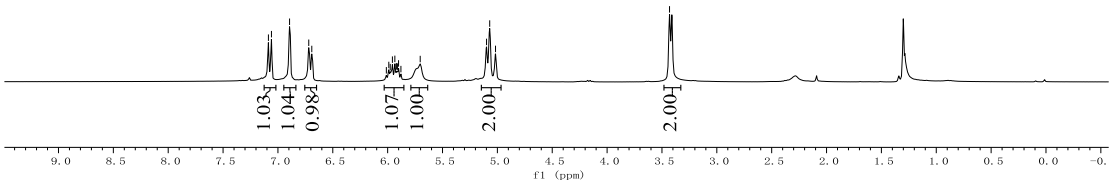
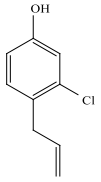


^{13}C NMR (75 MHz, $CDCl_3$)



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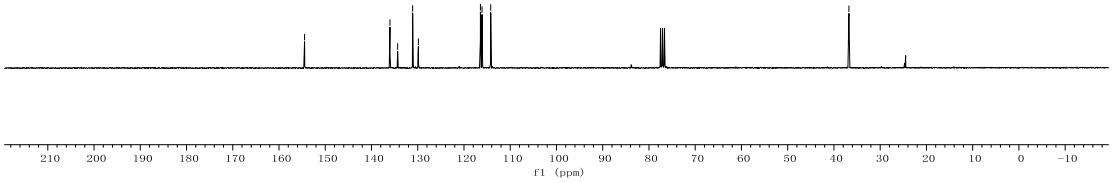
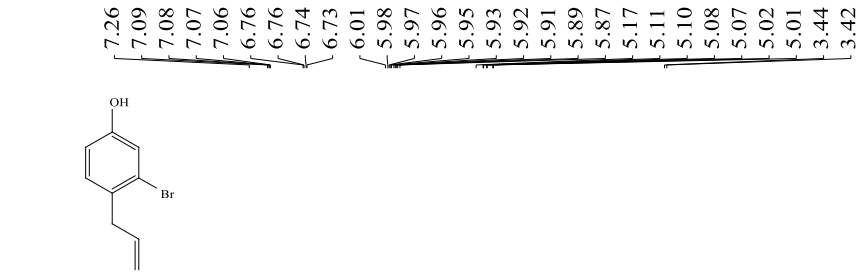
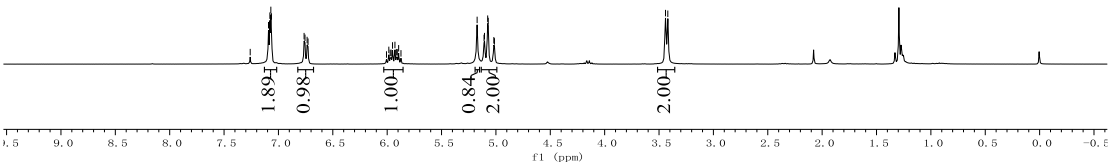


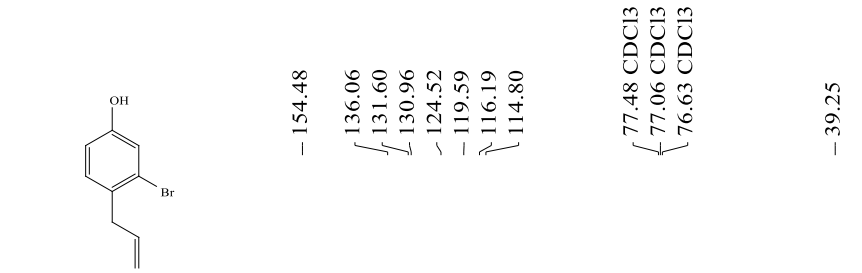
^{1}H NMR (300 MHz, $CDCl_3$)



3ca



^{13}C NMR (75 MHz, $CDCl_3$)



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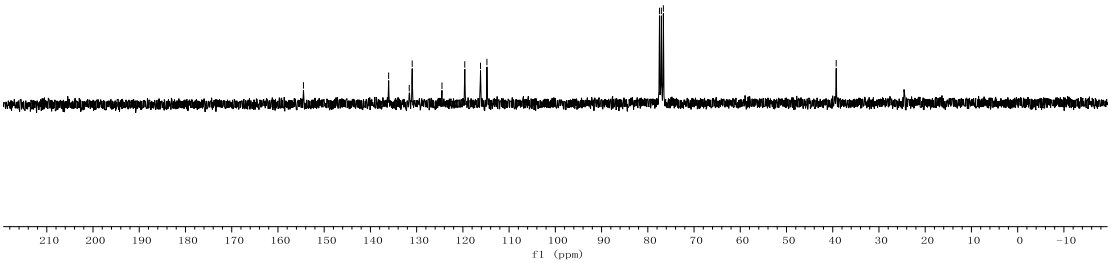
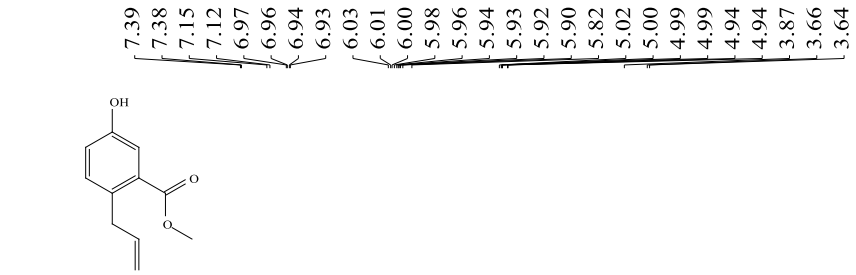


^{1}H NMR (300 MHz, $CDCl_3$)



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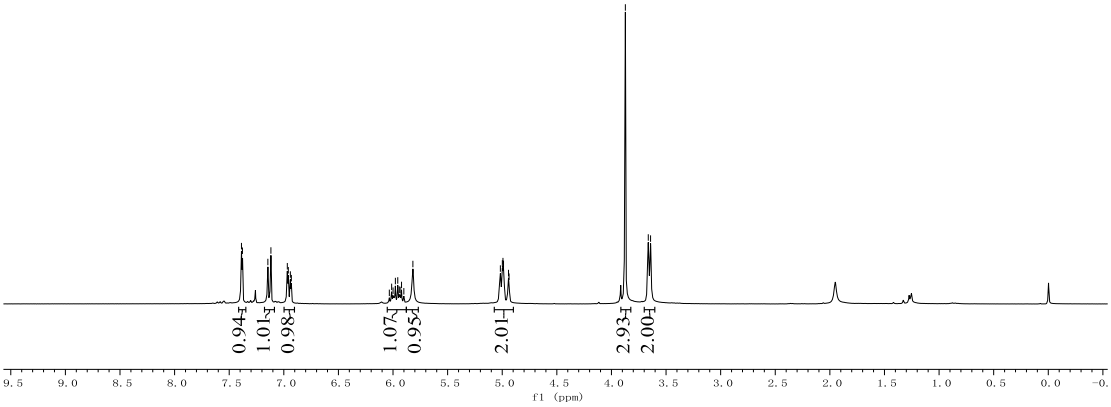
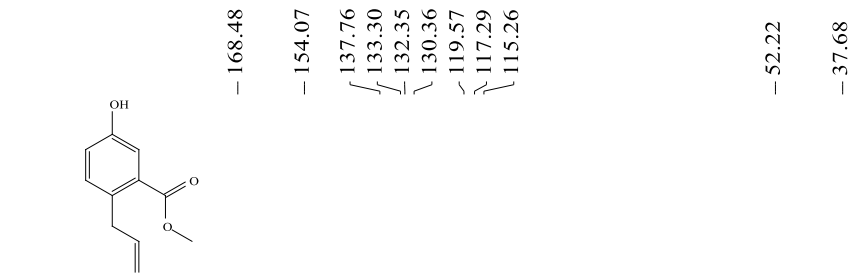


^{13}C NMR (75 MHz, $CDCl_3$)



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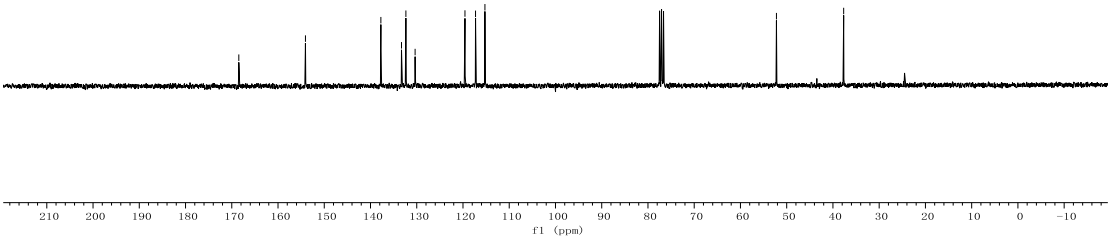
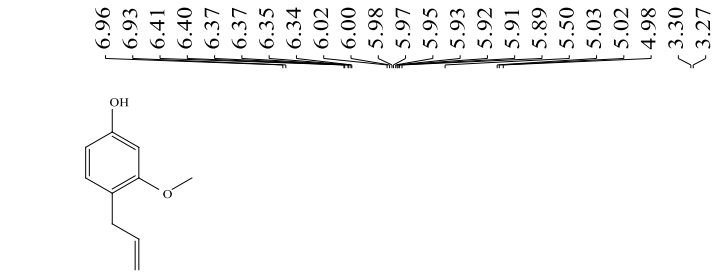


^{1}H NMR (300 MHz, $CDCl_3$)



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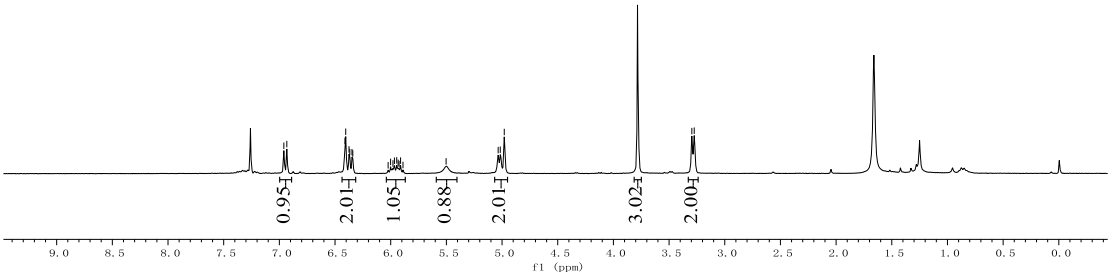
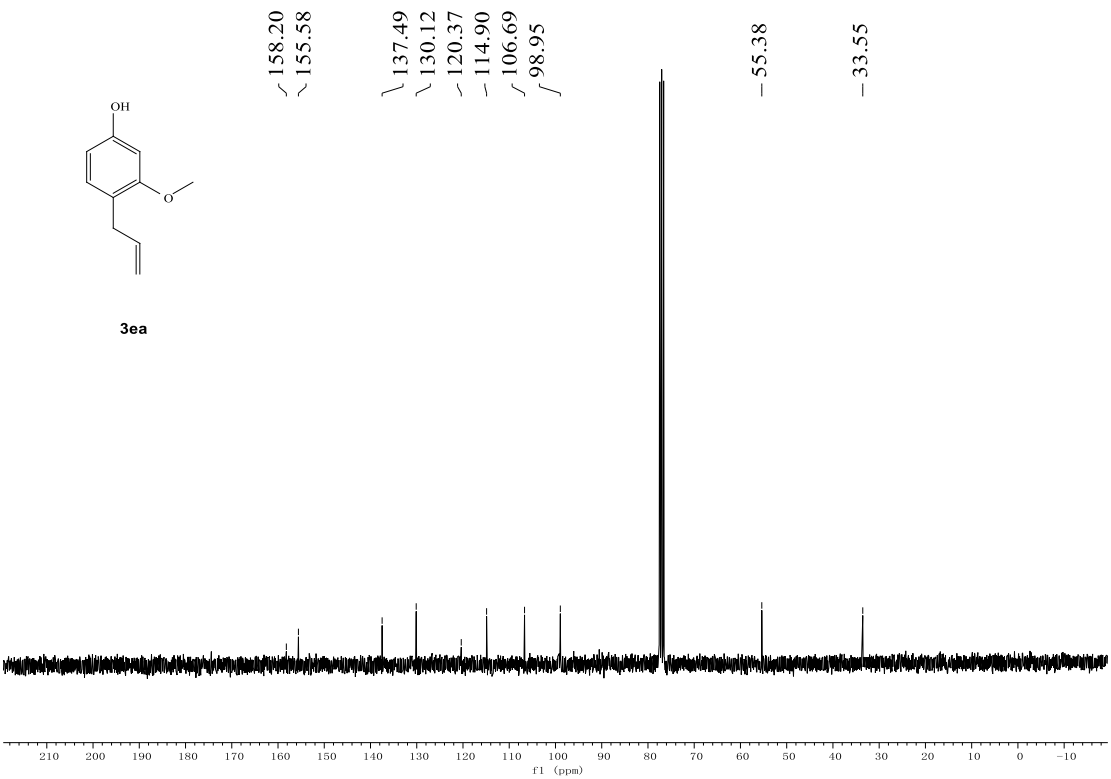
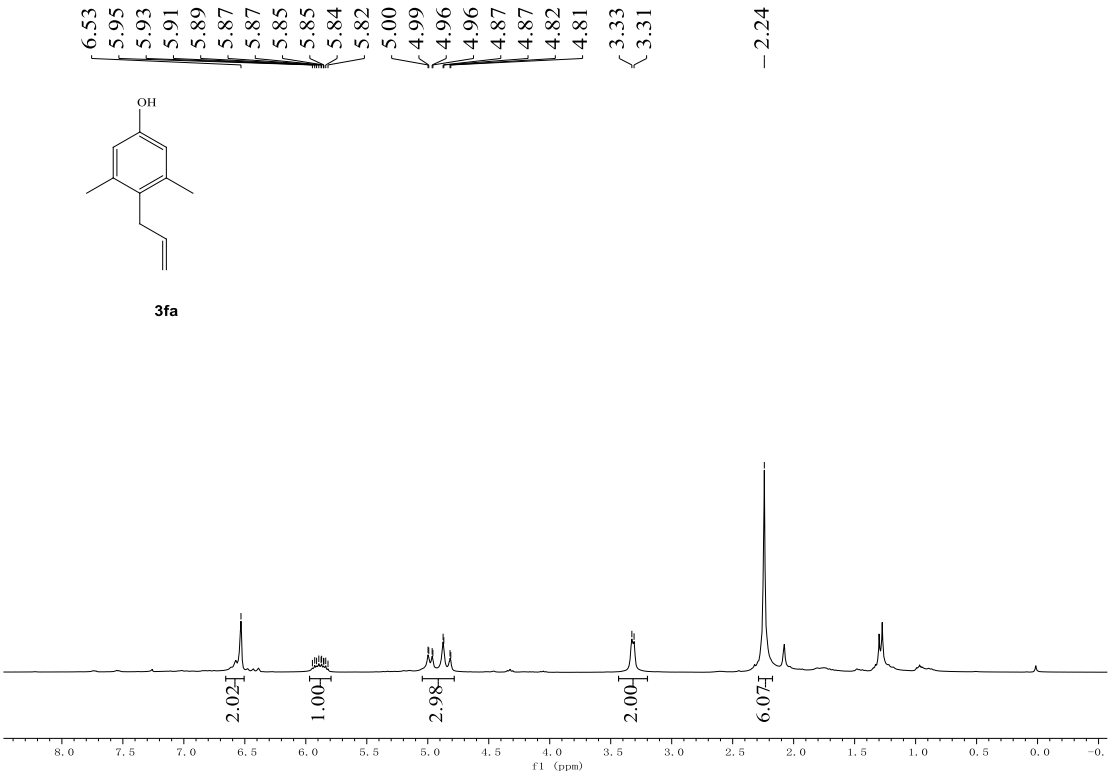


^{13}C NMR (75 MHz, $CDCl_3$)



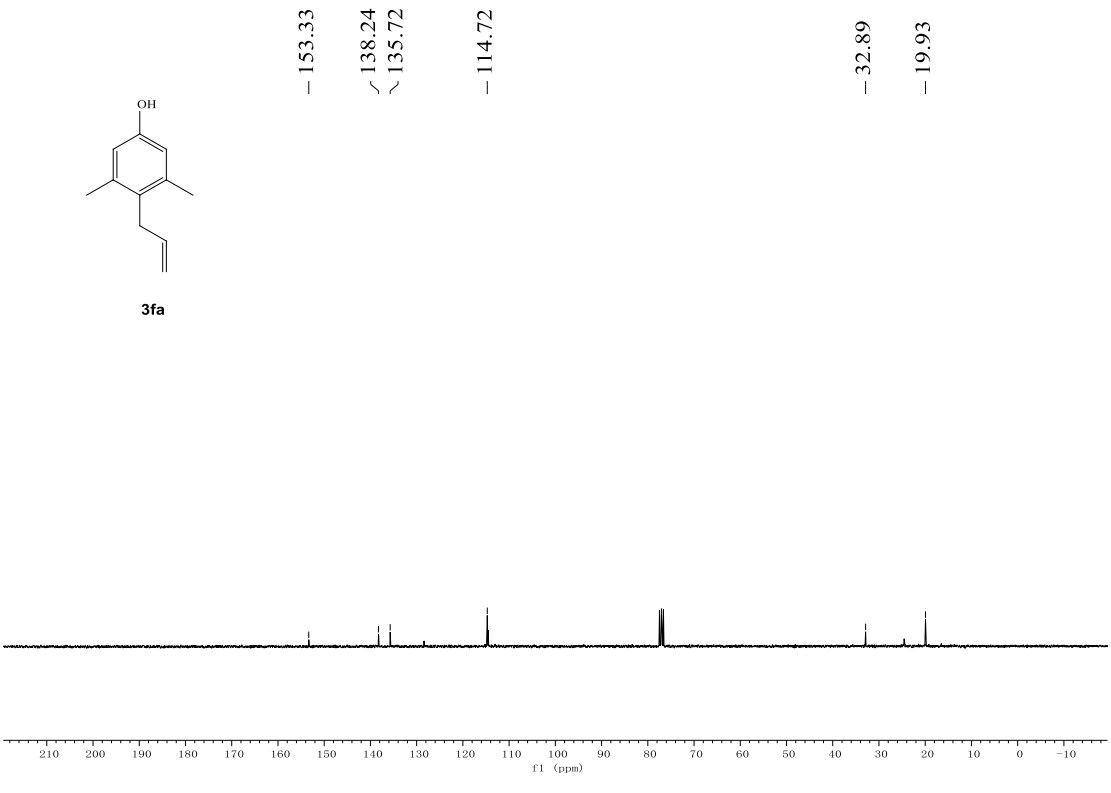
3ea

^{1}H NMR (300 MHz, $CDCl_3$)



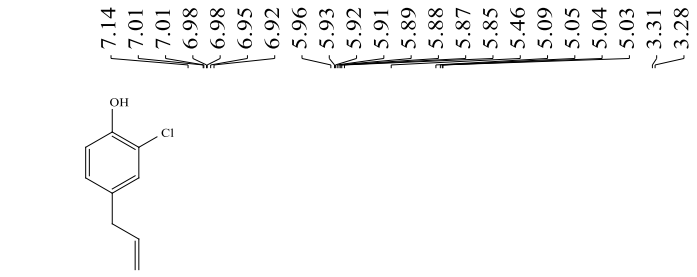
3fa

^{13}C NMR (75 MHz, $CDCl_3$)

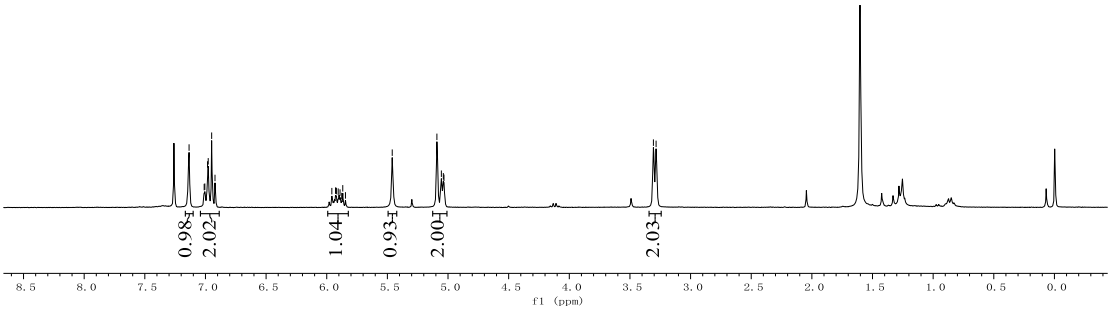


3fa

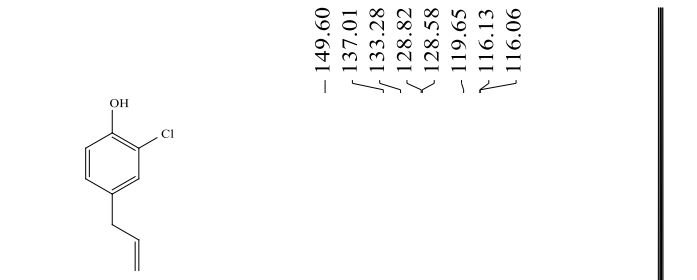
^{1}H NMR (300 MHz, $CDCl_3$)



3ga

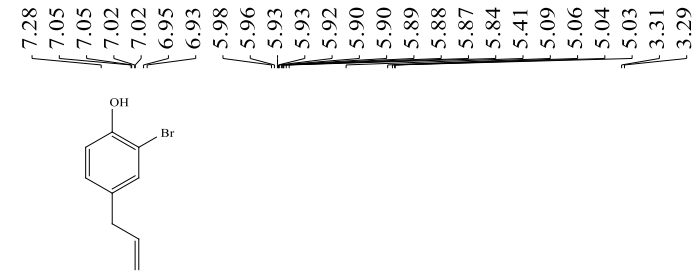


^{13}C NMR (75 MHz, $CDCl_3$)

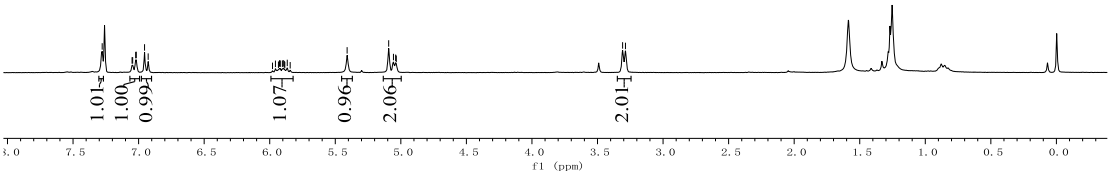


3ga

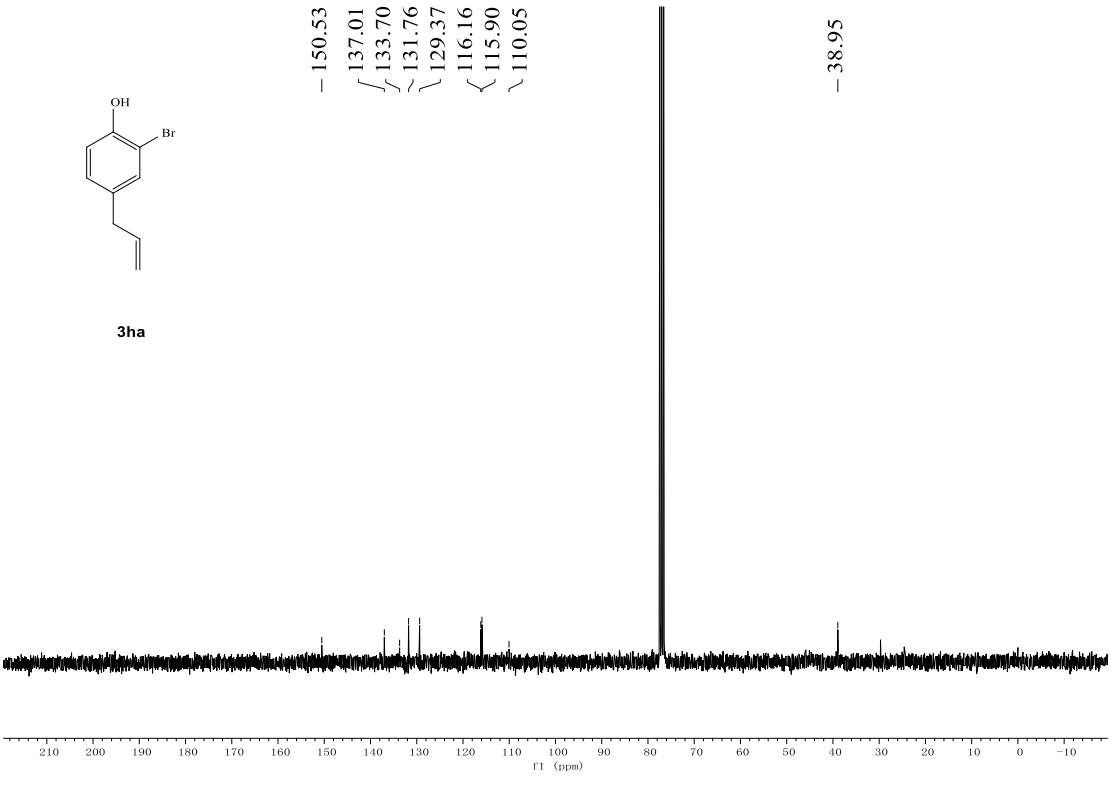
^{1}H NMR (300 MHz, $CDCl_3$)



3ha



^{13}C NMR (75 MHz, $CDCl_3$)



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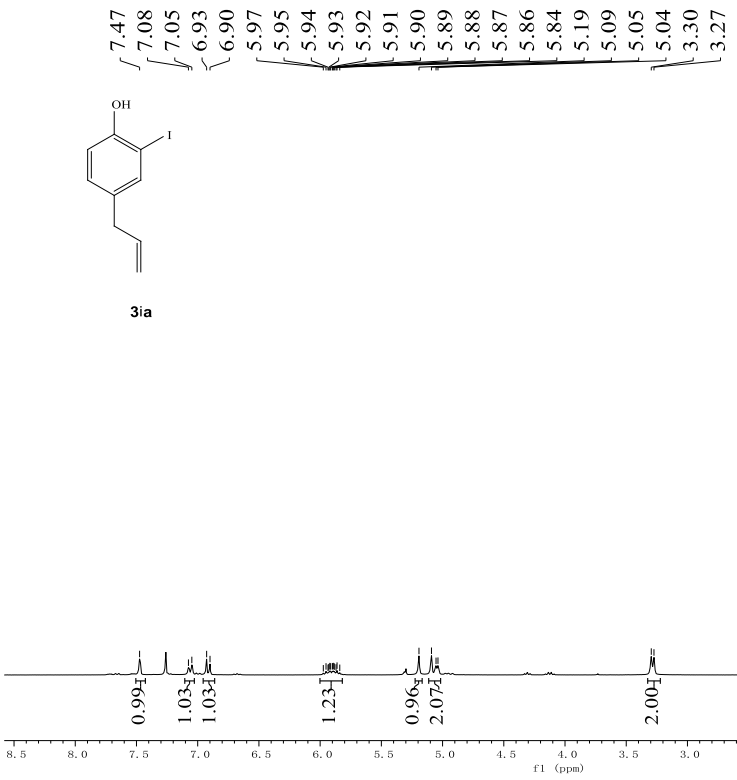
^{1}H NMR (300 MHz, $CDCl_3$)



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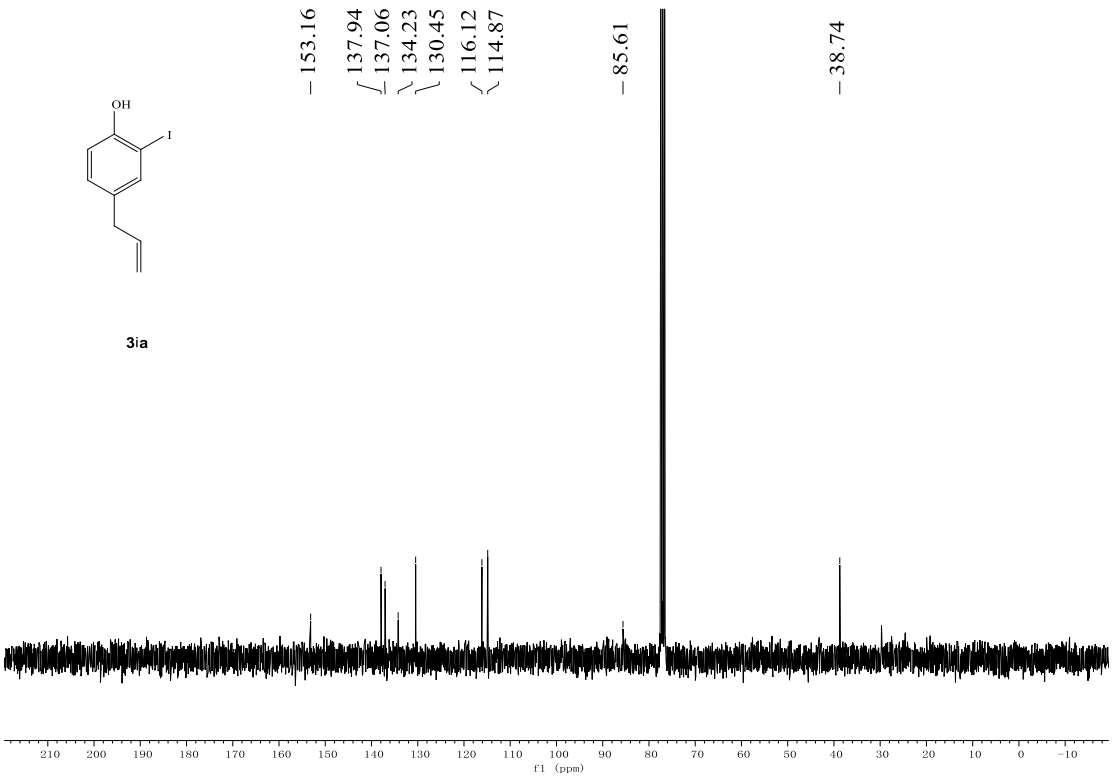
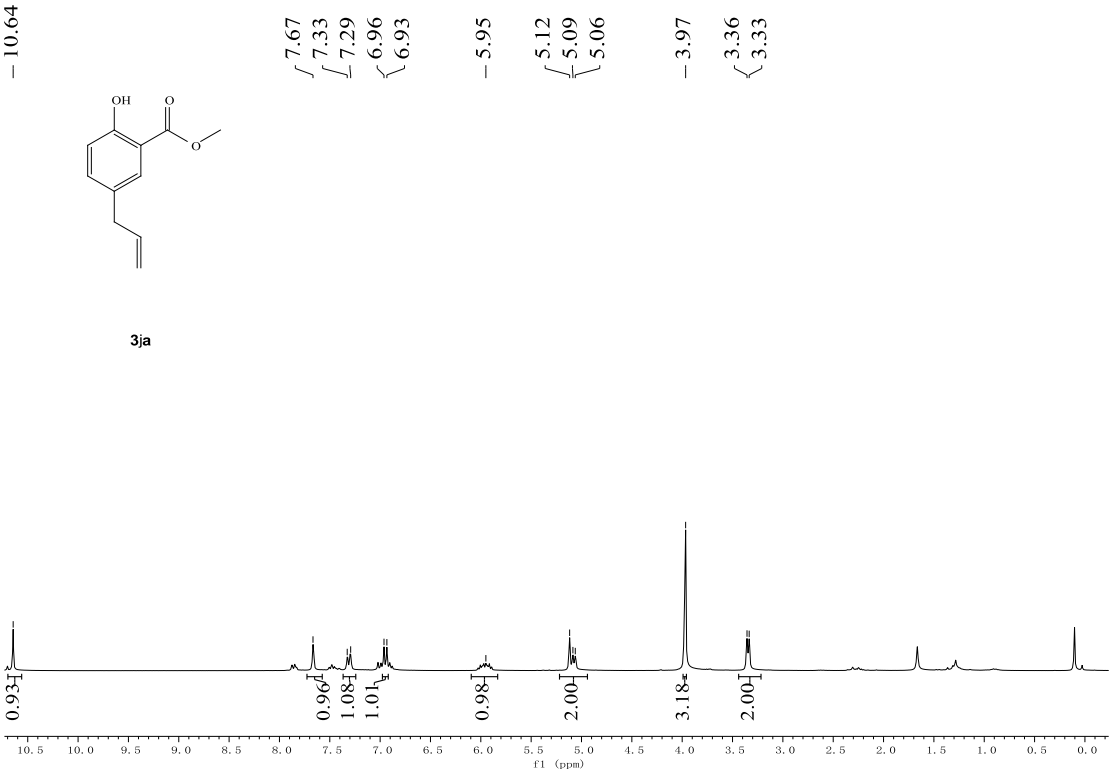
^{13}C NMR (75 MHz, $CDCl_3$)



3ia

^{1}H NMR (300 MHz, $CDCl_3$)



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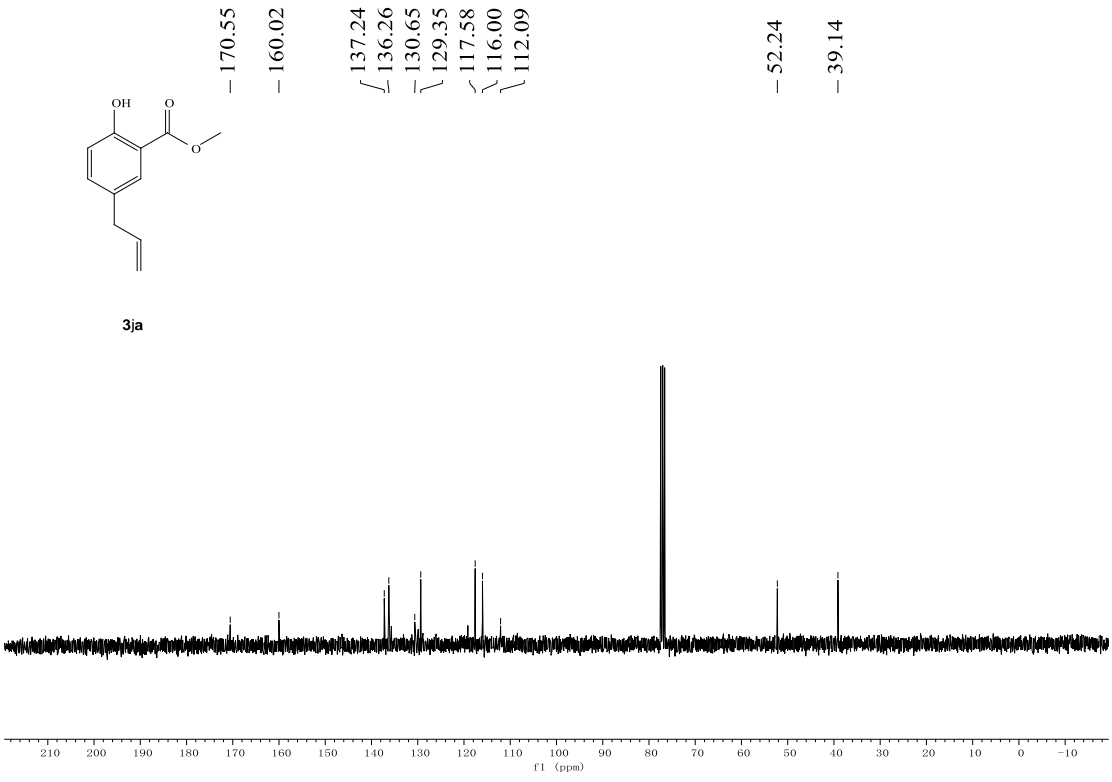
^{13}C NMR (75 MHz, $CDCl_3$)



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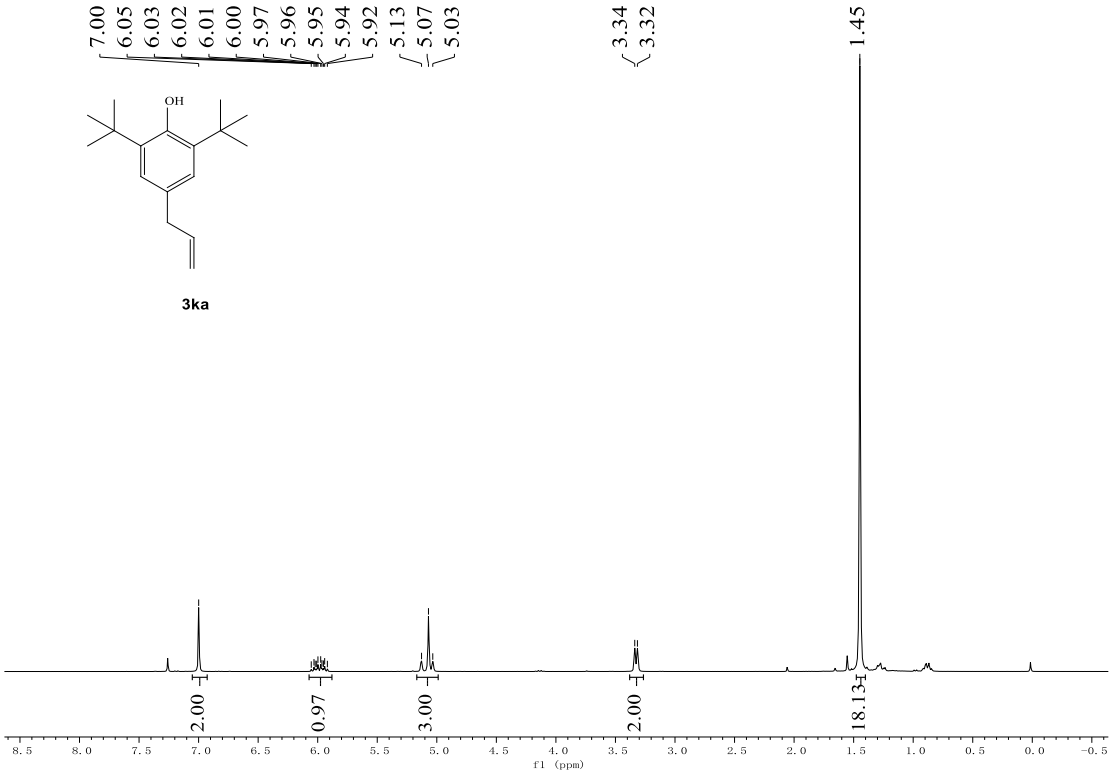

3ka

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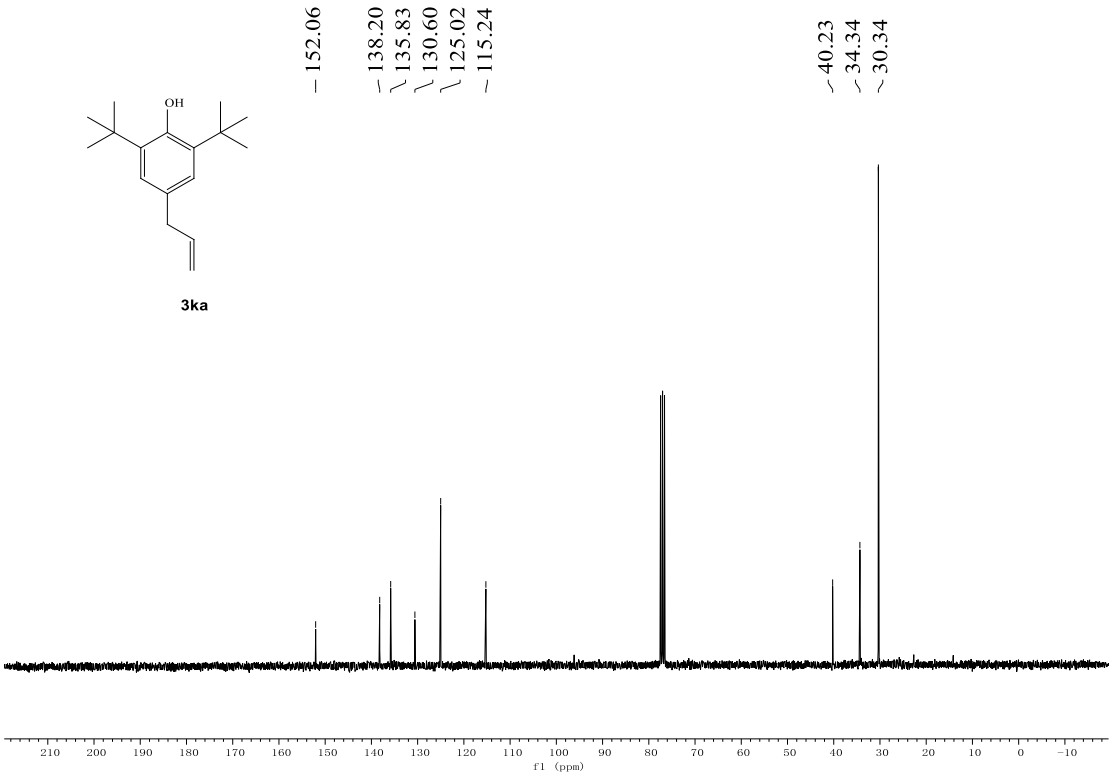

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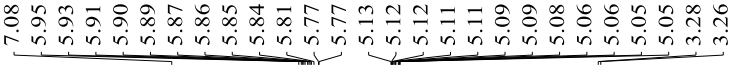

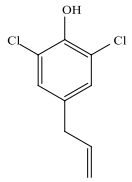

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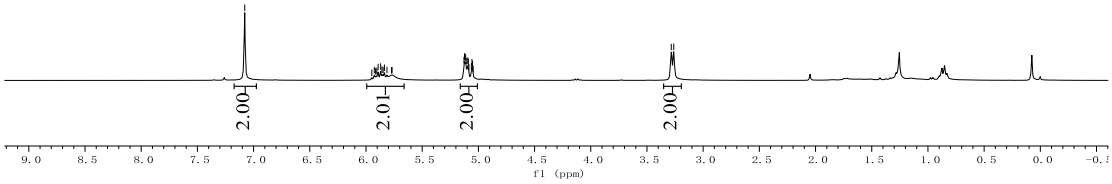
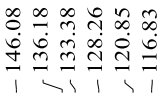
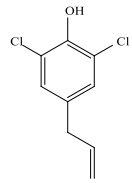


^{13}C NMR (75 MHz, $CDCl_3$)





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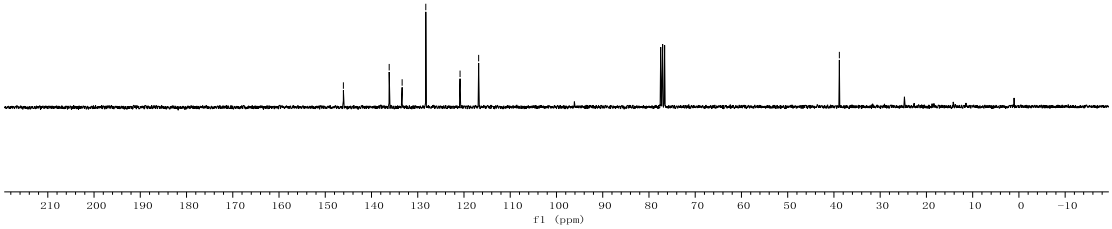
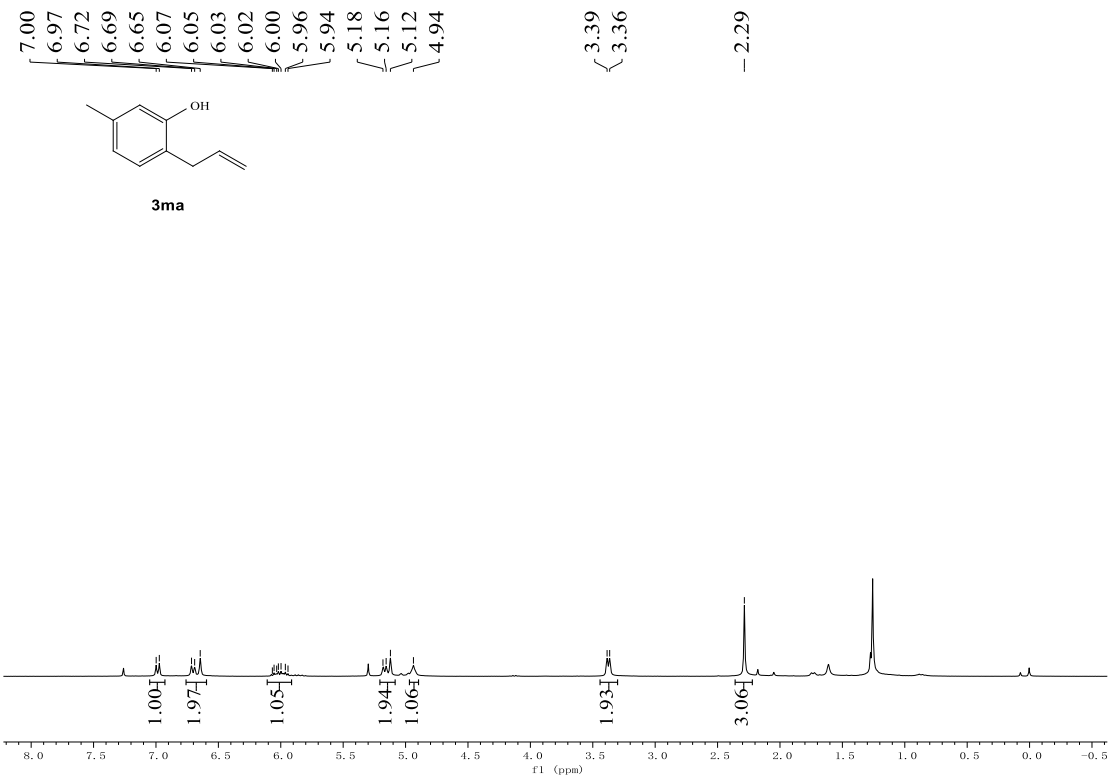


^{1}H NMR (300 MHz, $CDCl_3$)



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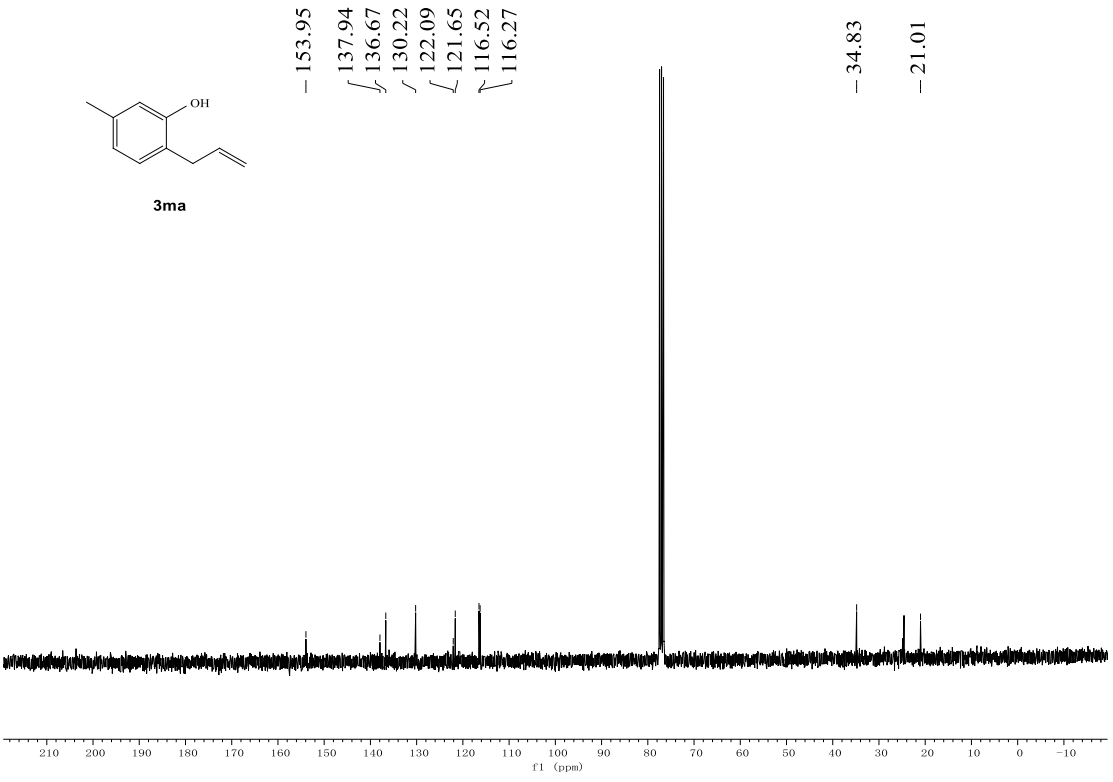
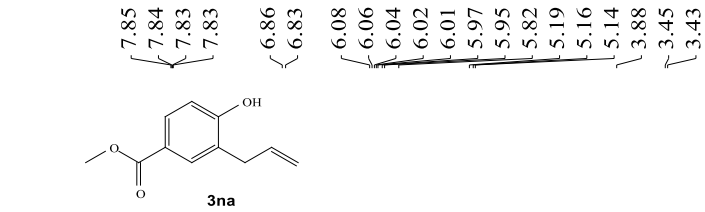
^{13}C NMR (75 MHz, $CDCl_3$)



3ma

^{1}H NMR (300 MHz, $CDCl_3$)



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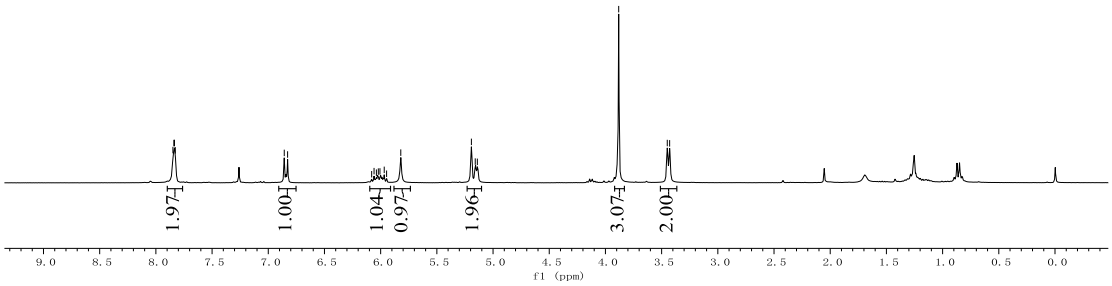
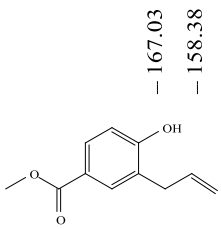


^{13}C NMR (75 MHz, $CDCl_3$)



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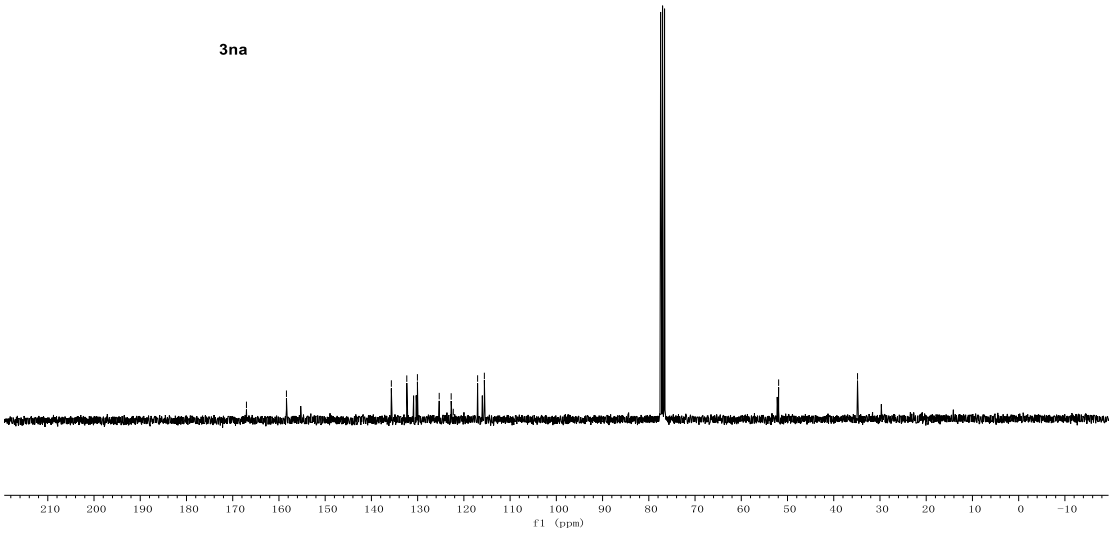

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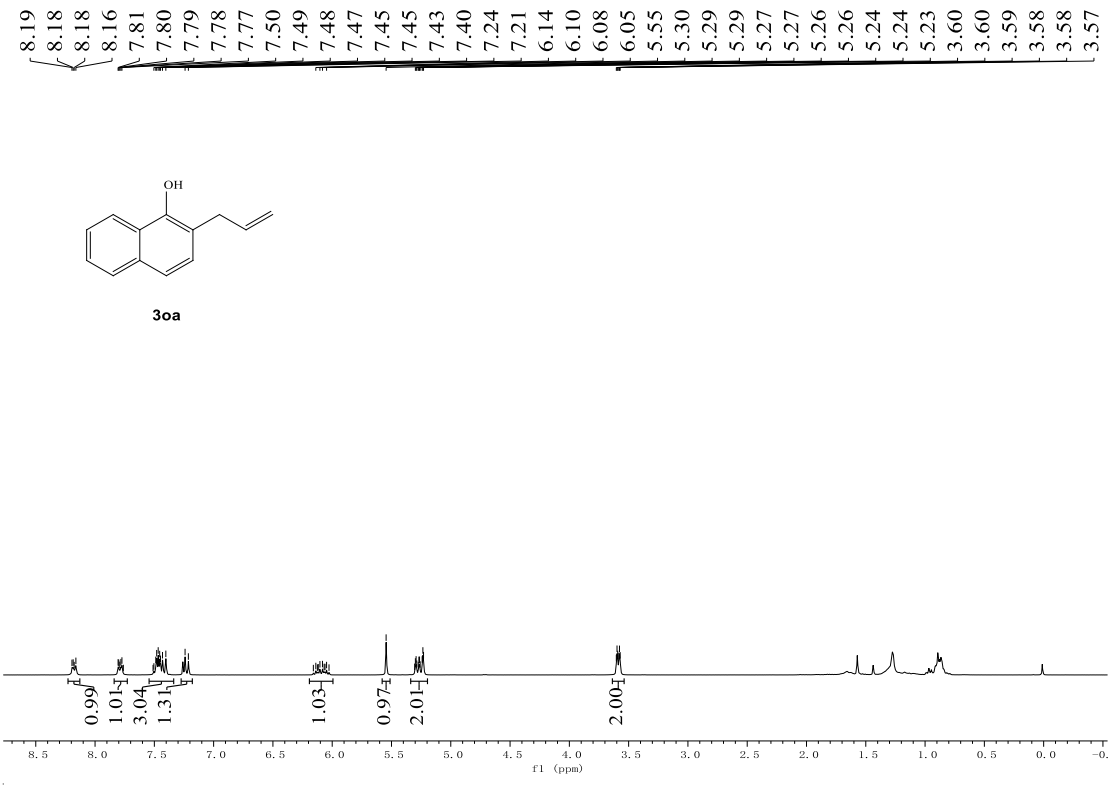
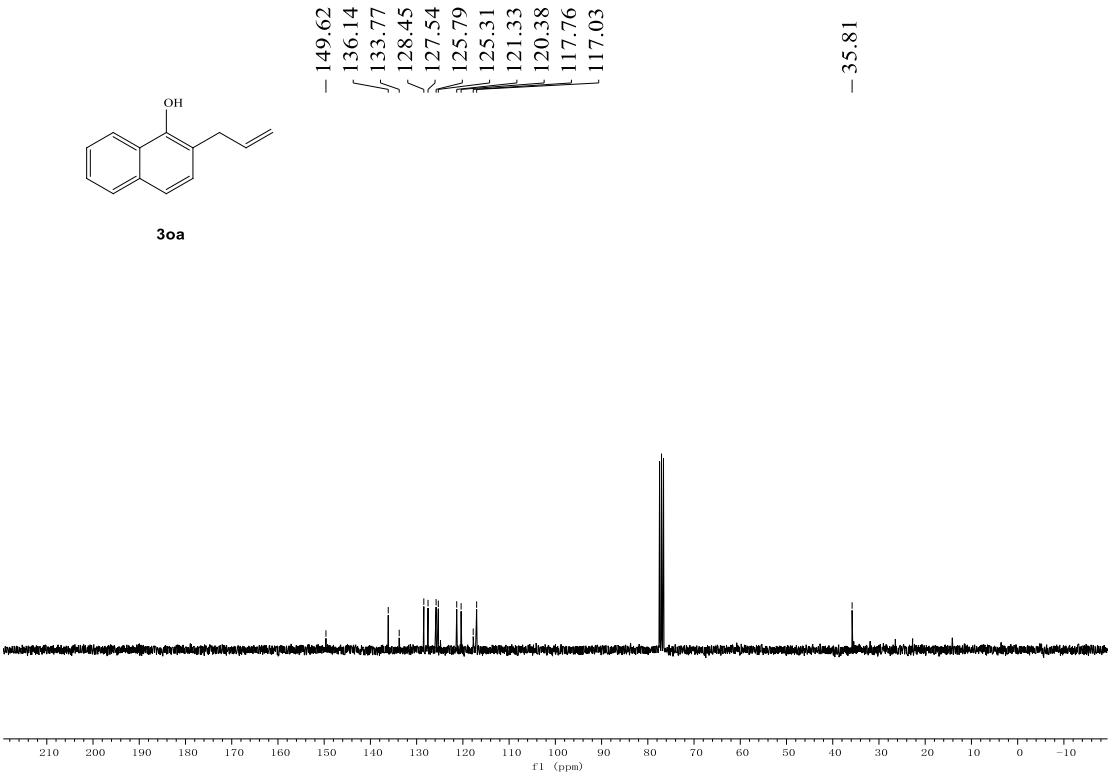
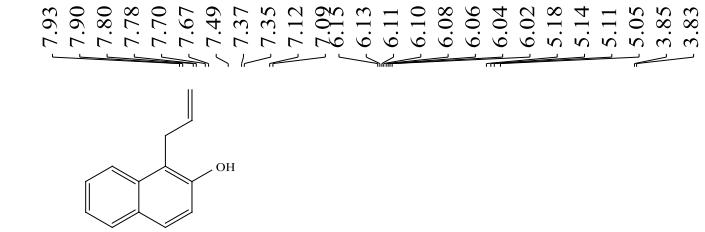


^{13}C NMR (75 MHz, $CDCl_3$)



^{1}H NMR (300 MHz, $CDCl_3$)



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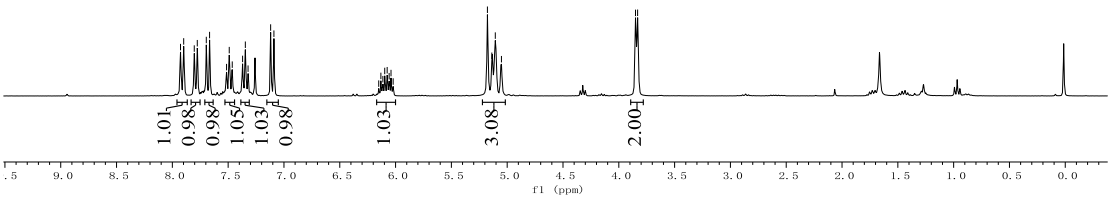
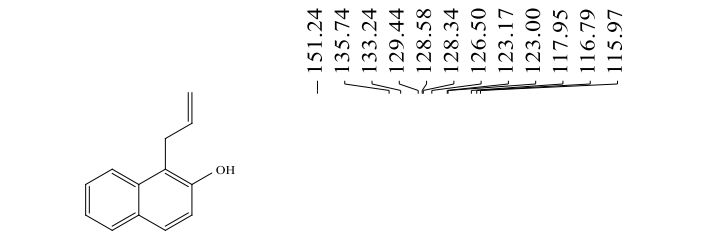


^{13}C NMR (75 MHz, $CDCl_3$)



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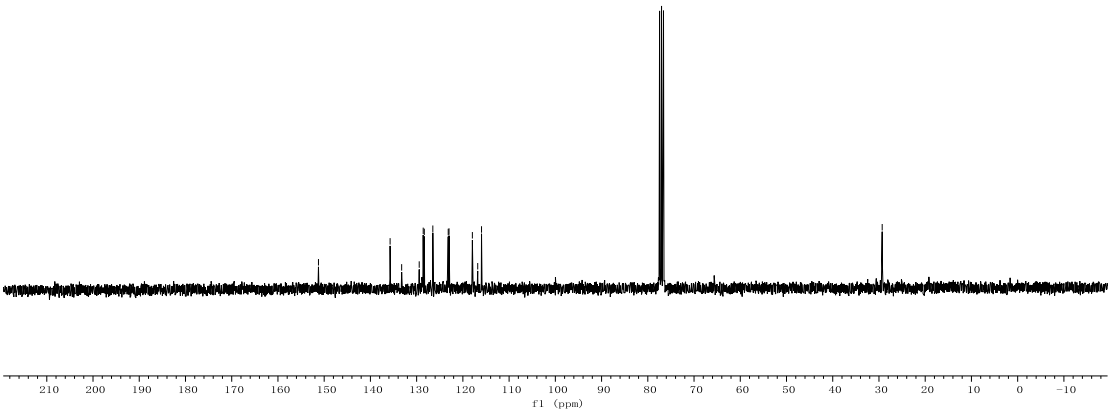

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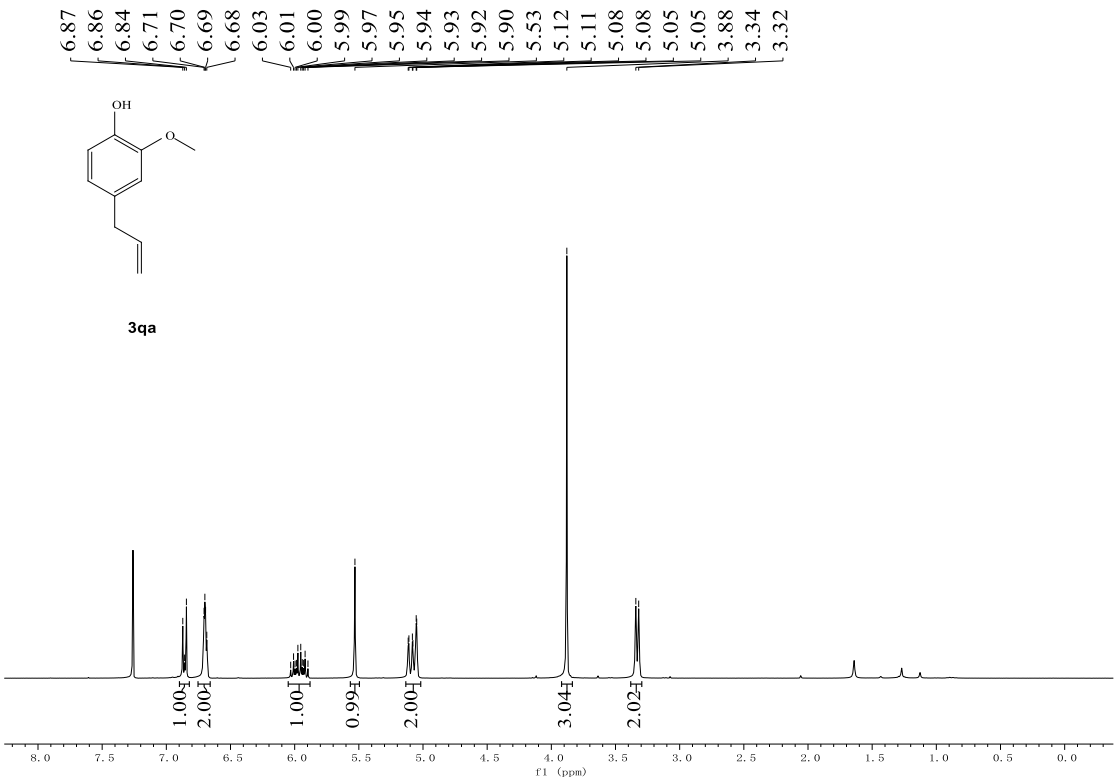
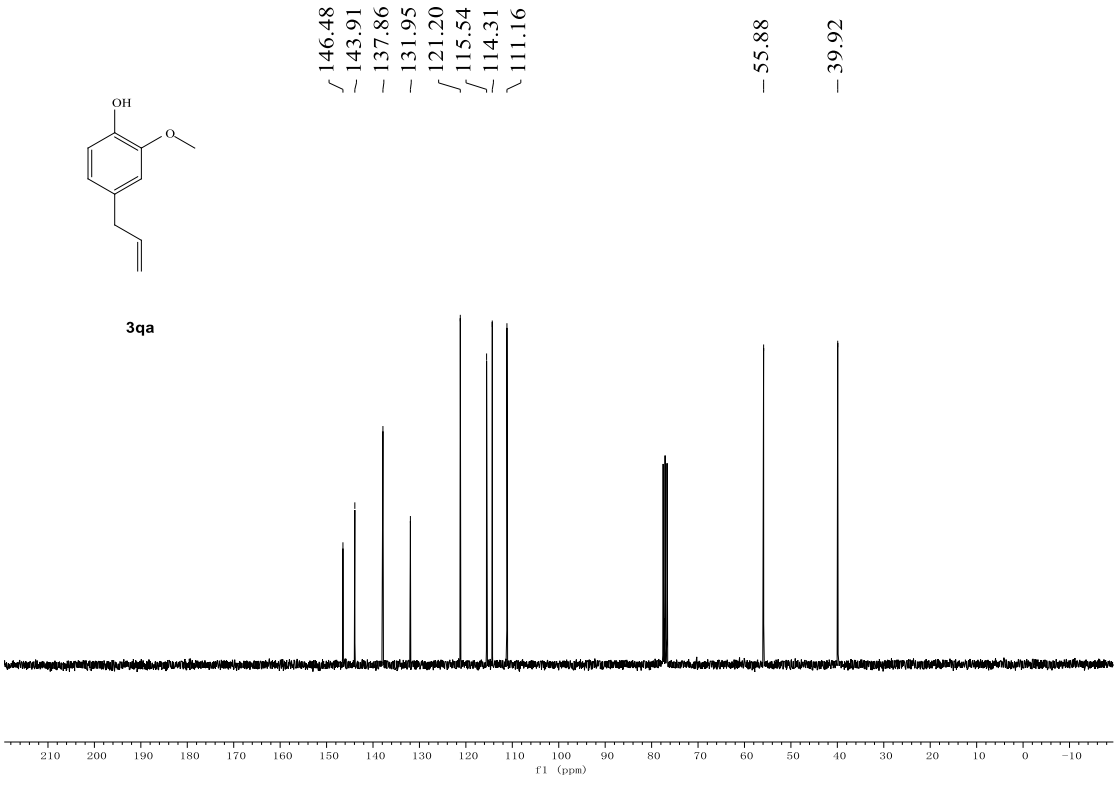
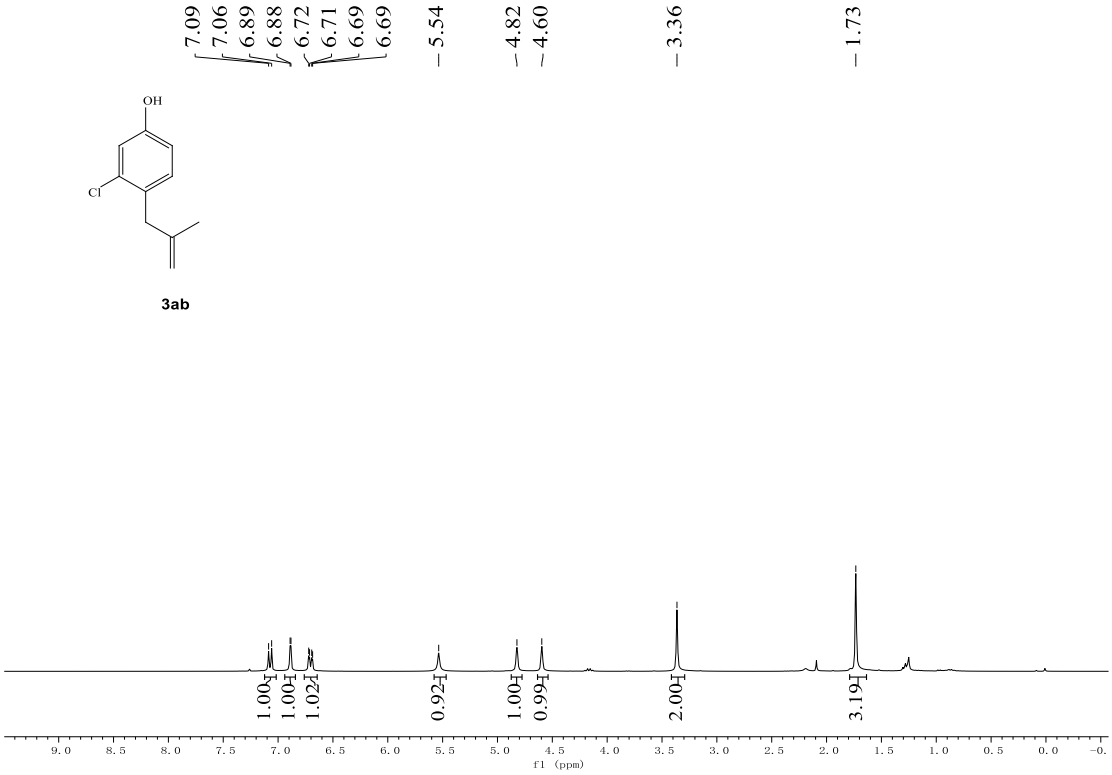


^{13}C NMR (75 MHz, $CDCl_3$)

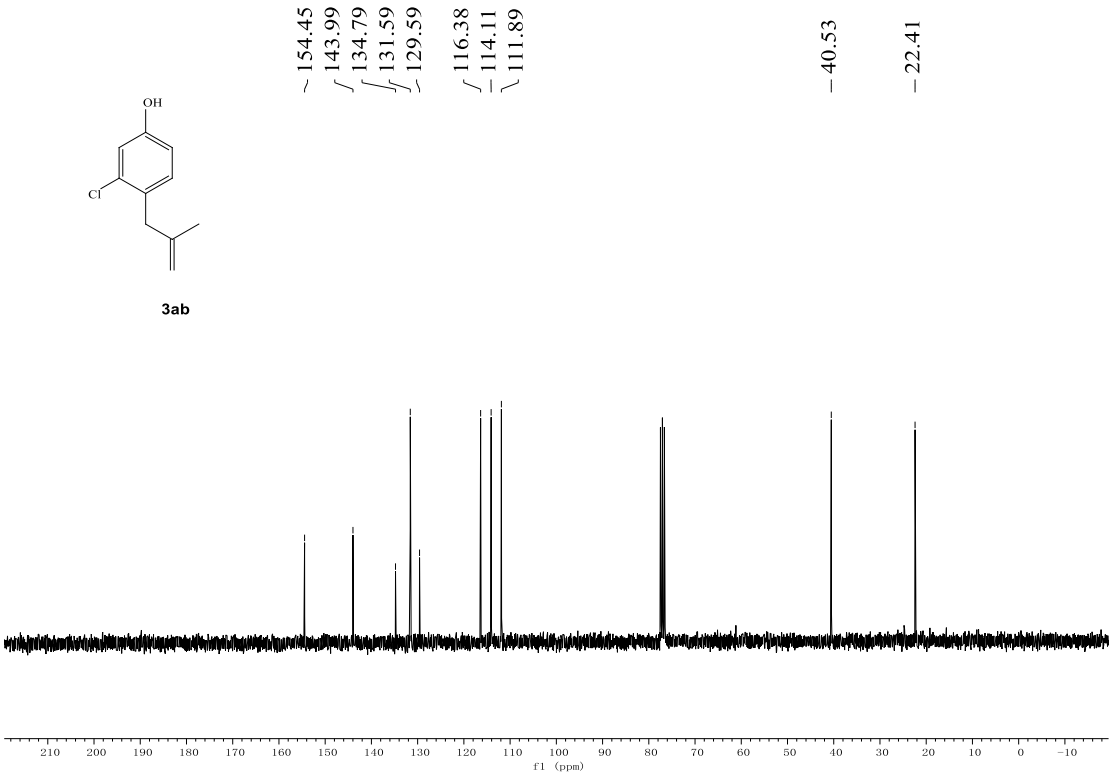


^{1}H NMR (300 MHz, $CDCl_3$)



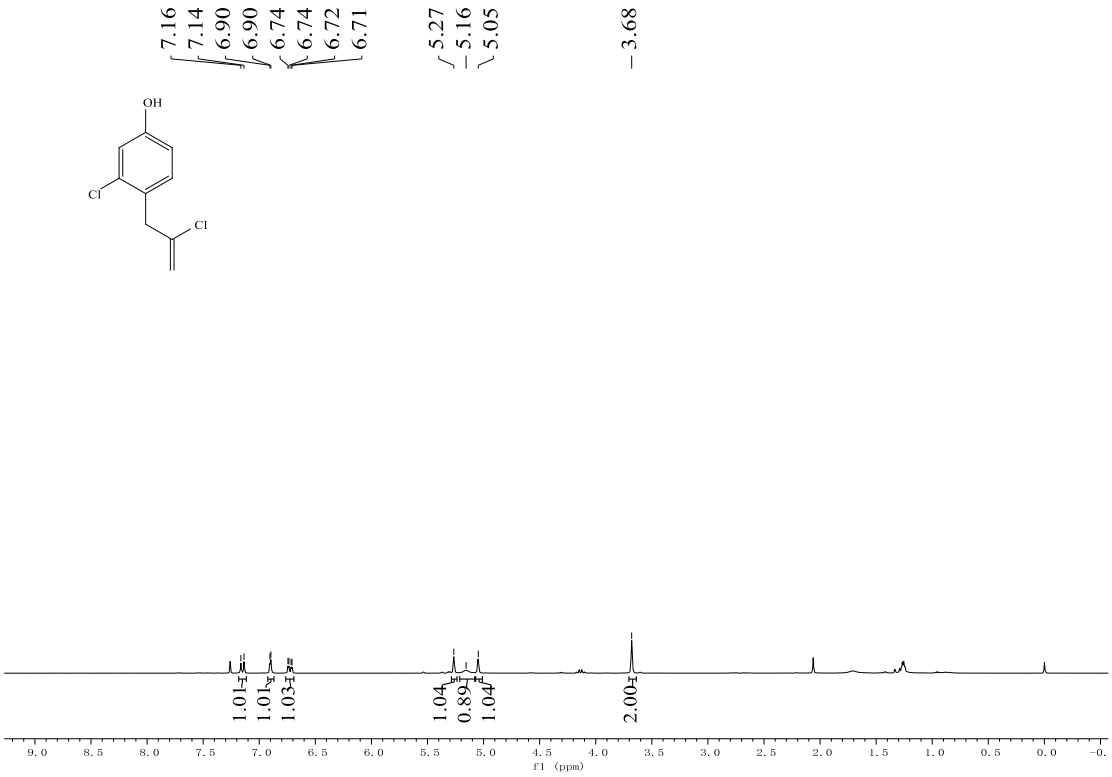
3ab

^{13}C NMR (75 MHz, $CDCl_3$)

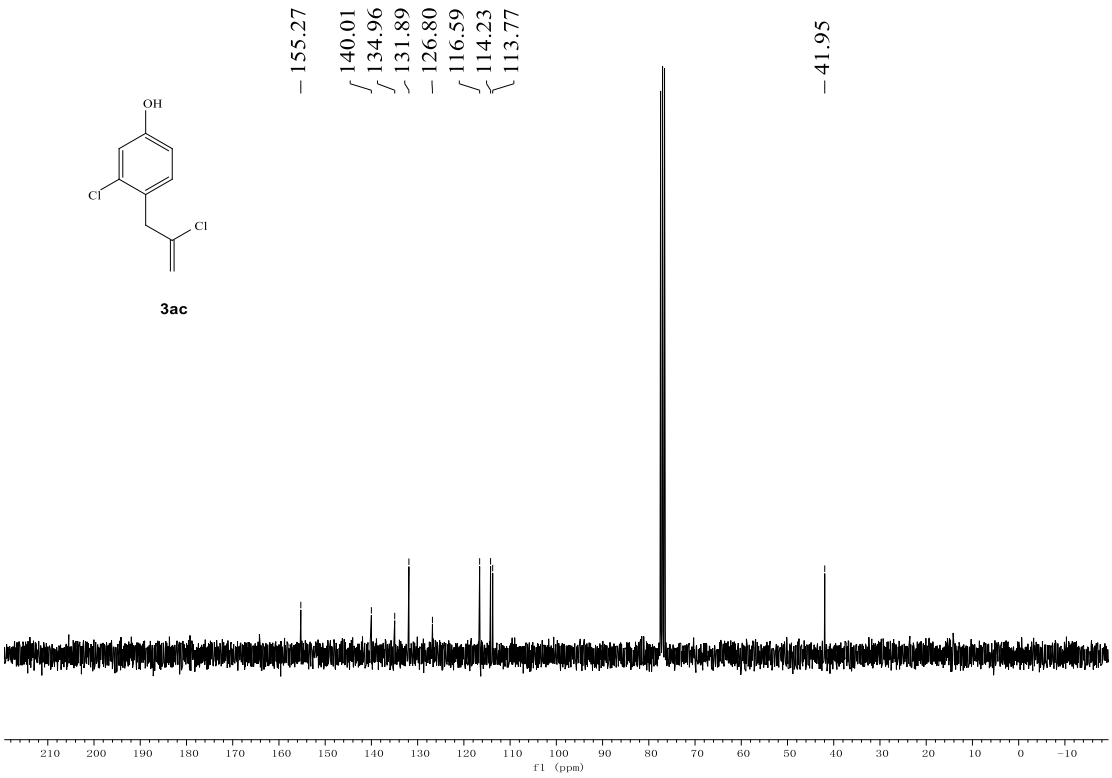


3ab

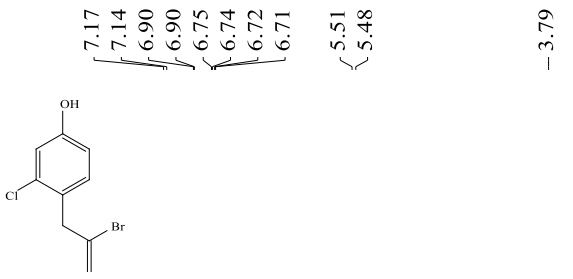
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)



^{1}H NMR (300 MHz, $CDCl_3$)



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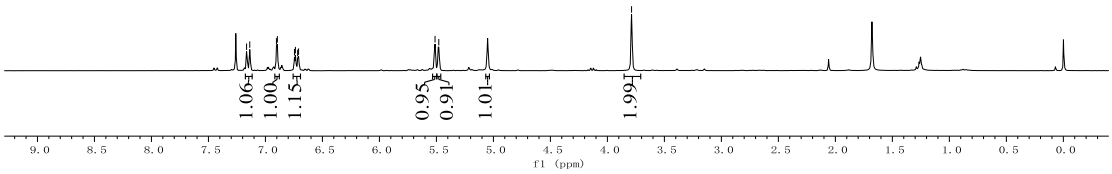
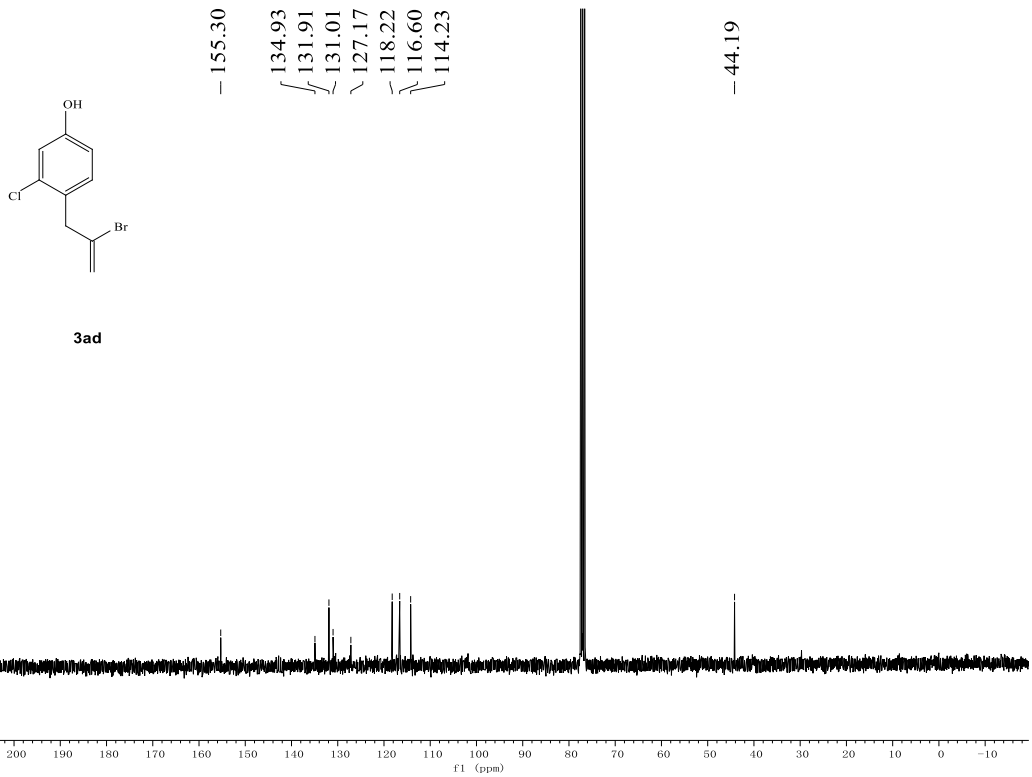


^{13}C NMR (75 MHz, $CDCl_3$)



3ad

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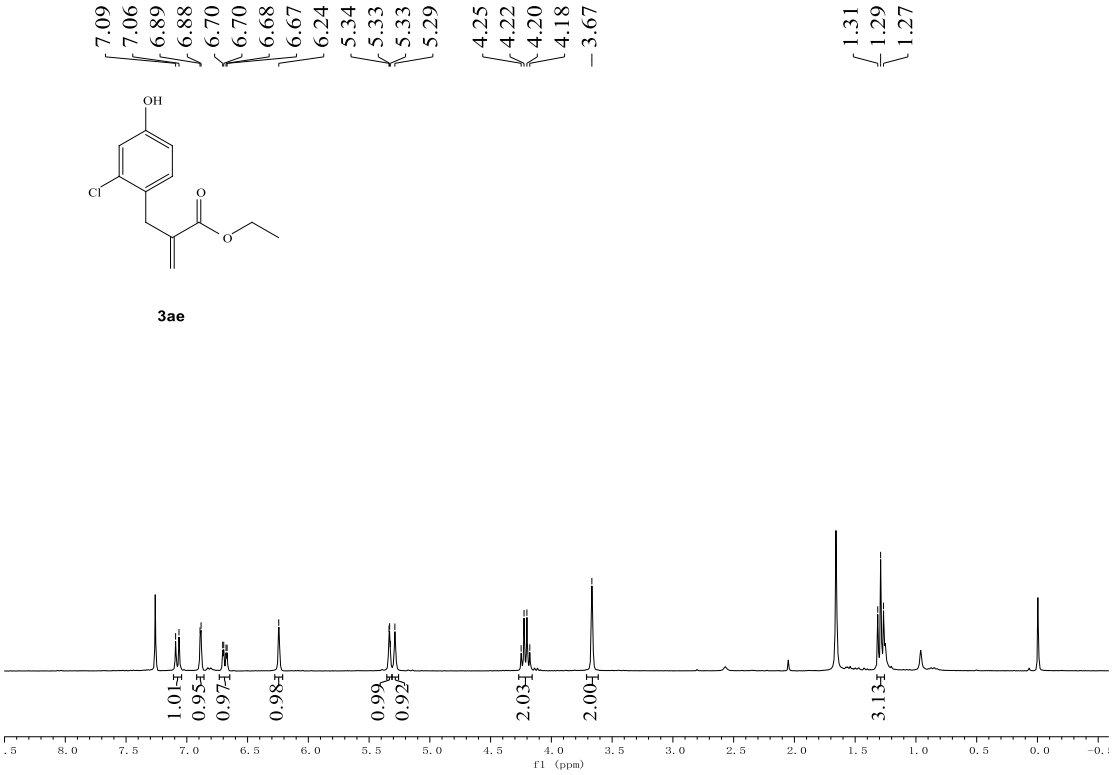
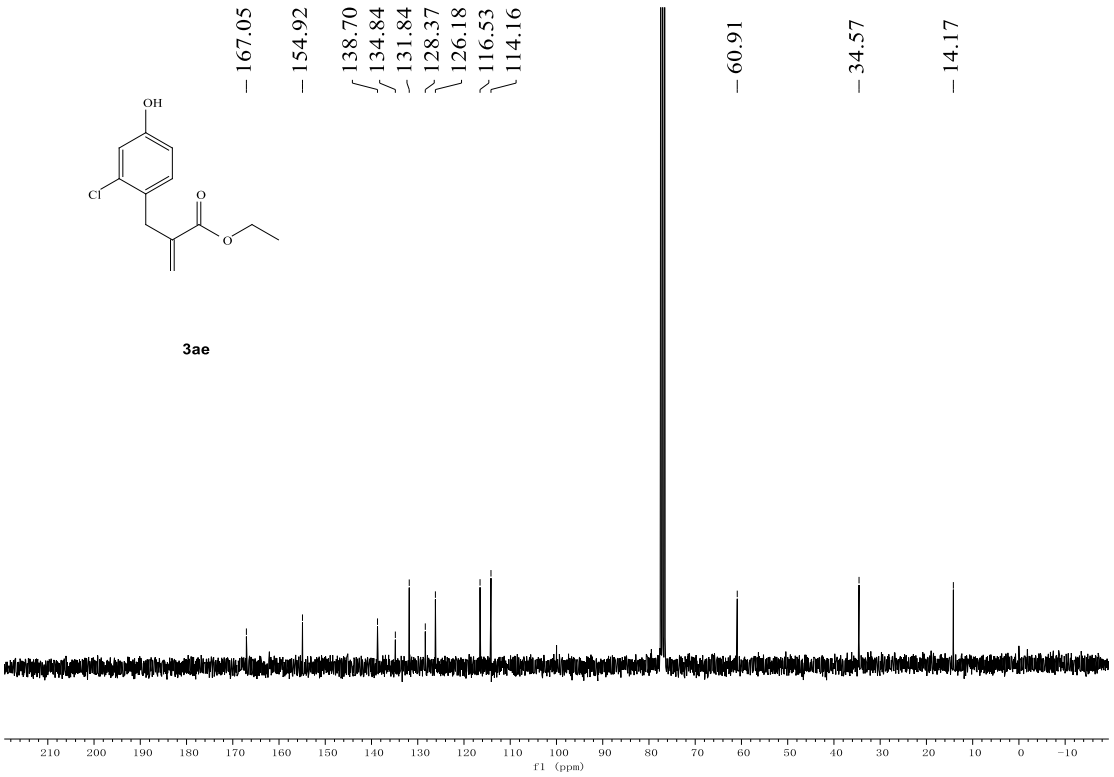


^{13}C NMR (75 MHz, $CDCl_3$)



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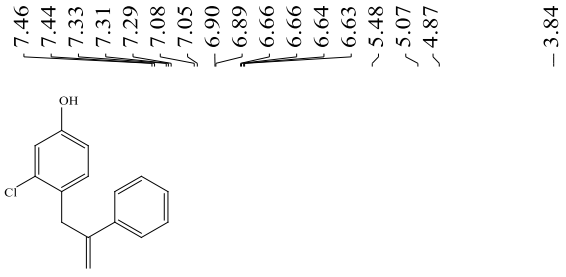

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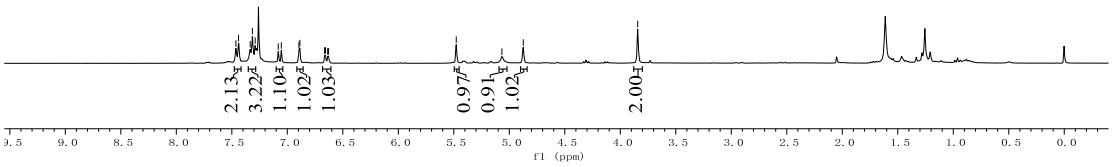
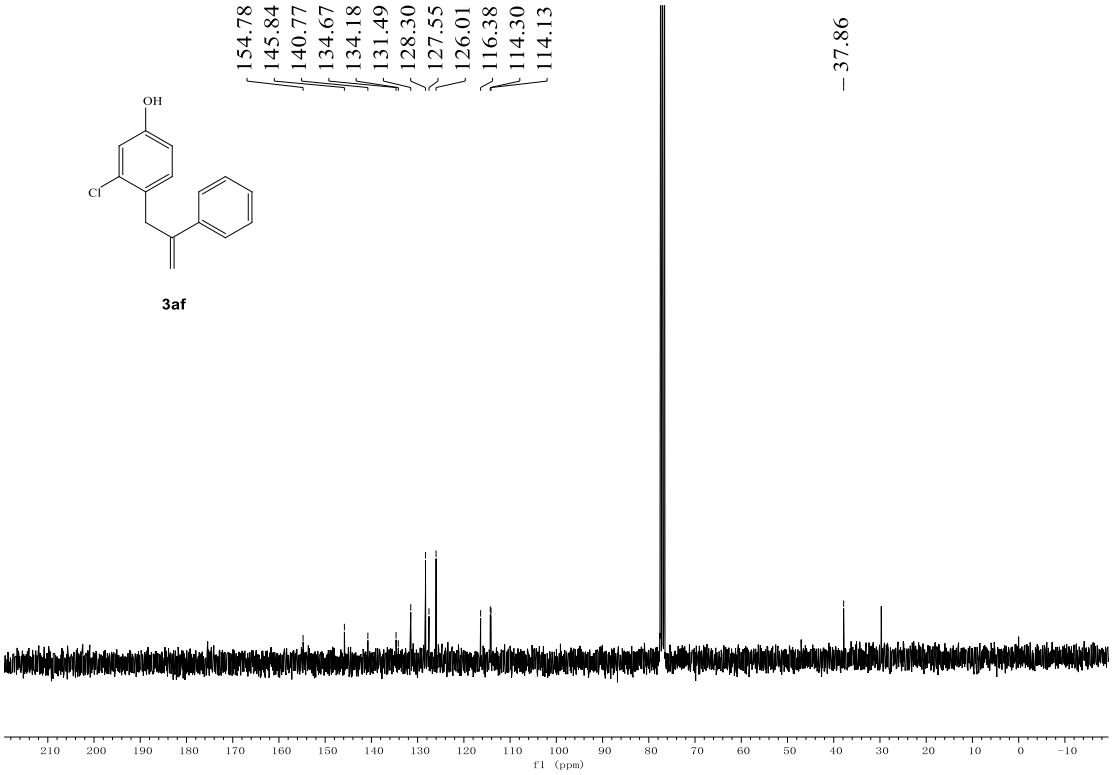


^{13}C NMR (75 MHz, $CDCl_3$)



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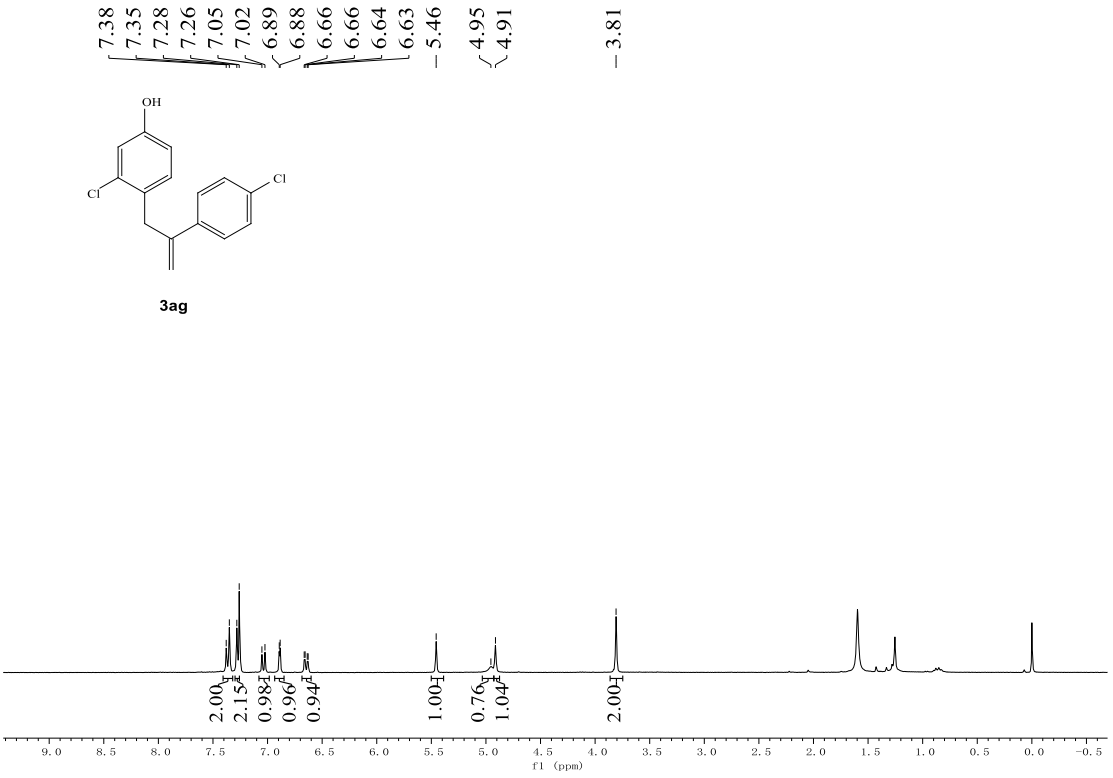
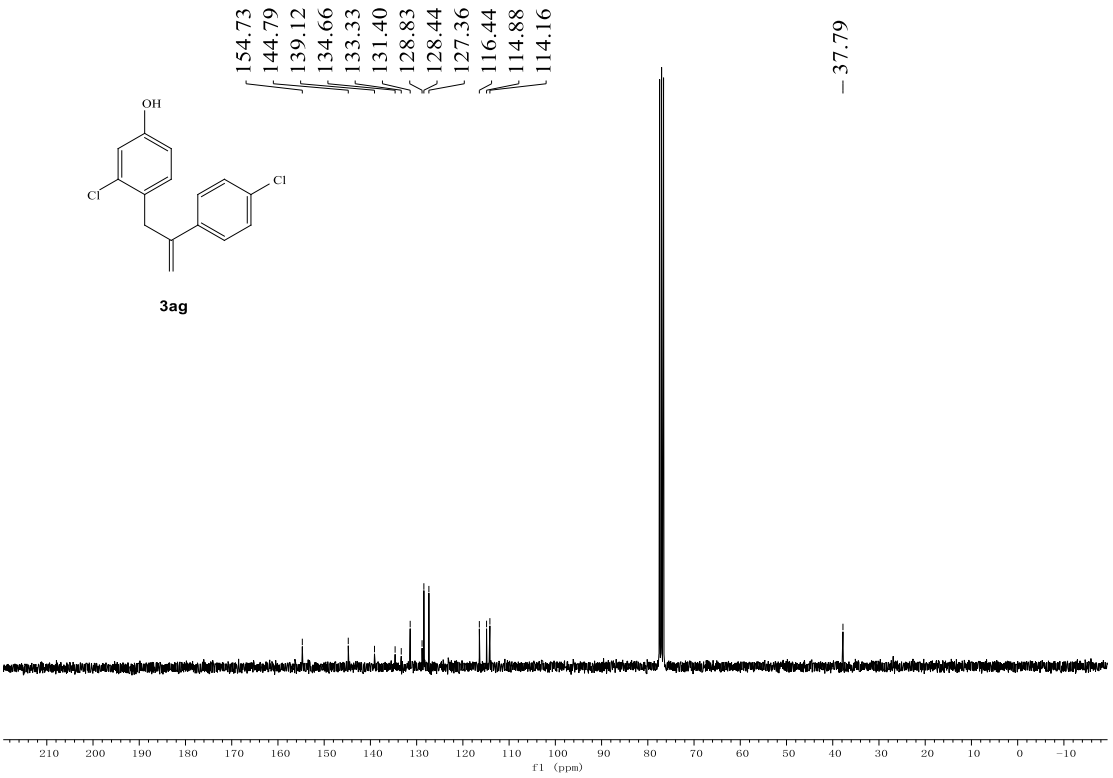
^{1}H NMR (300 MHz, $CDCl_3$)



3ag

^{13}C NMR (75 MHz, $CDCl_3$)



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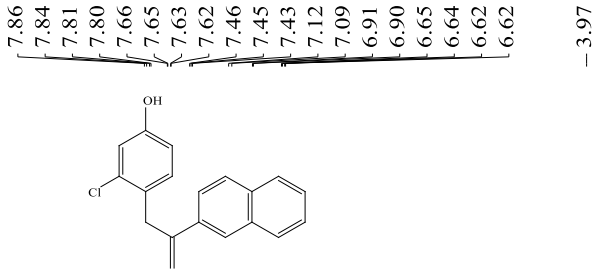
^{1}H NMR (300 MHz, $CDCl_3$)



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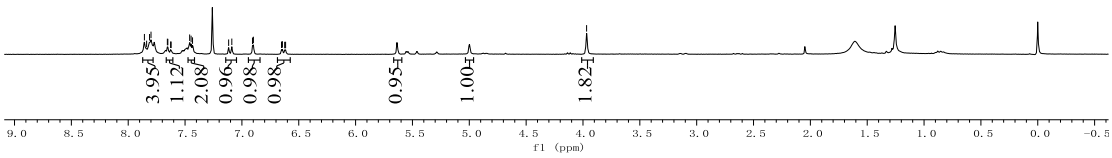
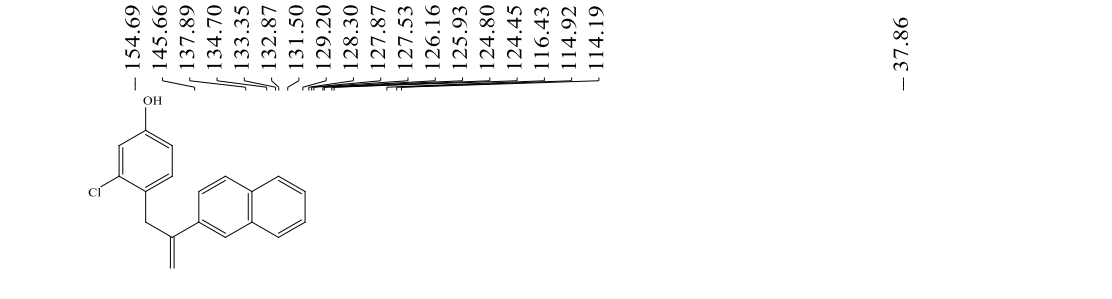


^{13}C NMR (75 MHz, $CDCl_3$)



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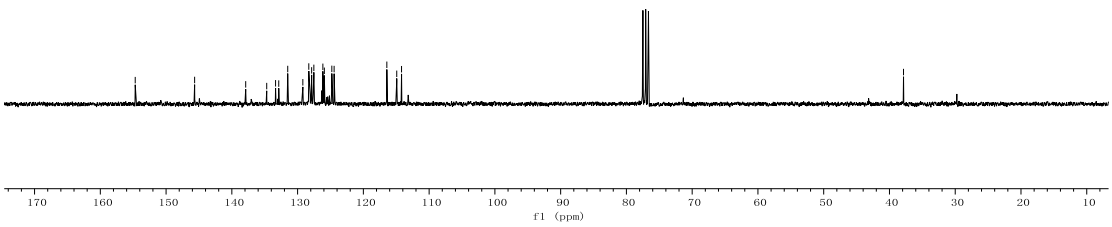
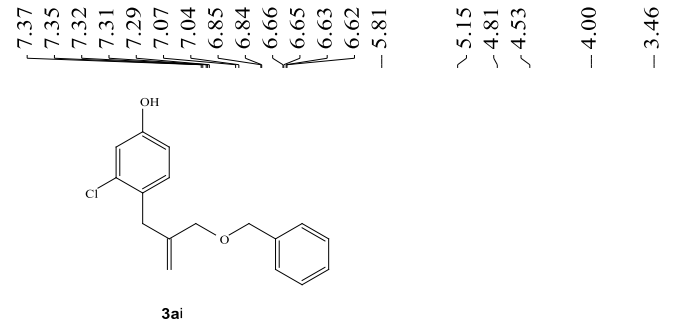


^{1}H NMR (300 MHz, $CDCl_3$)



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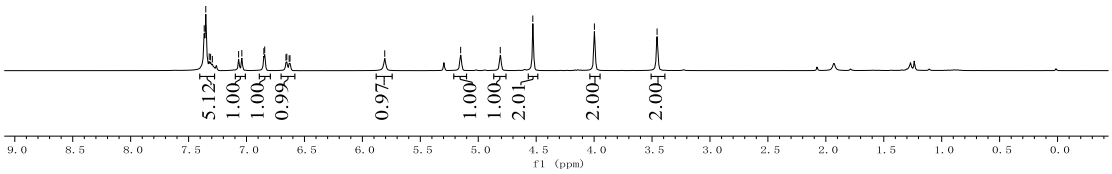
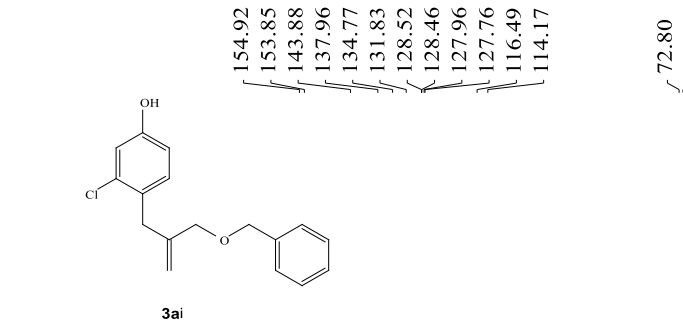


^{13}C NMR (75 MHz, $CDCl_3$)



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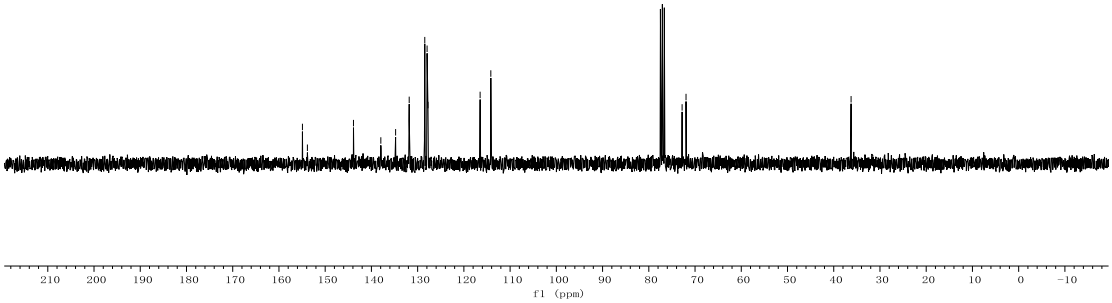
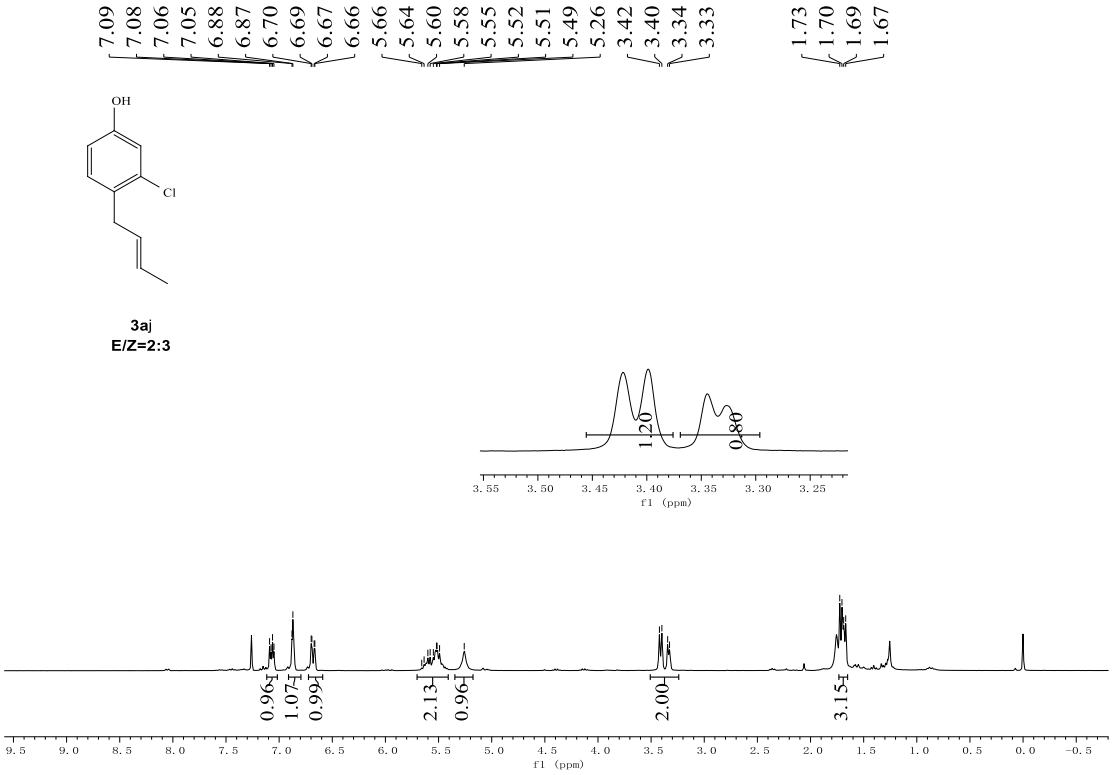
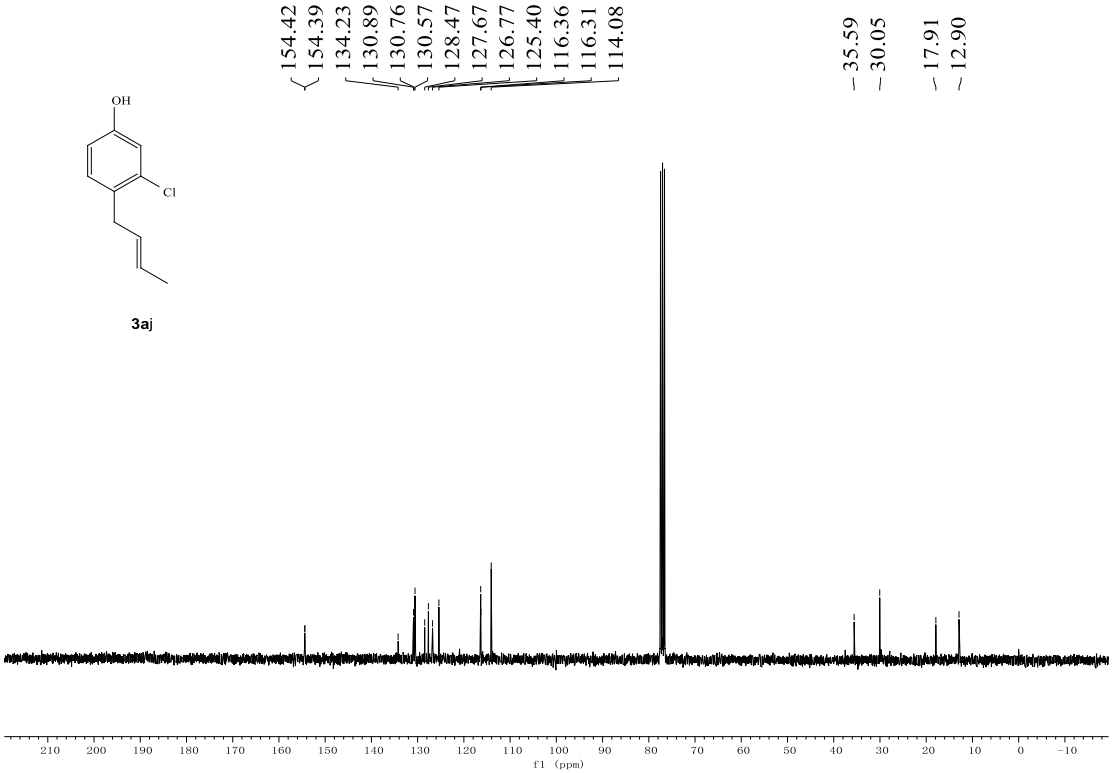


^{1}H NMR (300 MHz, $CDCl_3$)



3aj
E/Z=2:3

^{13}C NMR (75 MHz, $CDCl_3$)



3aj

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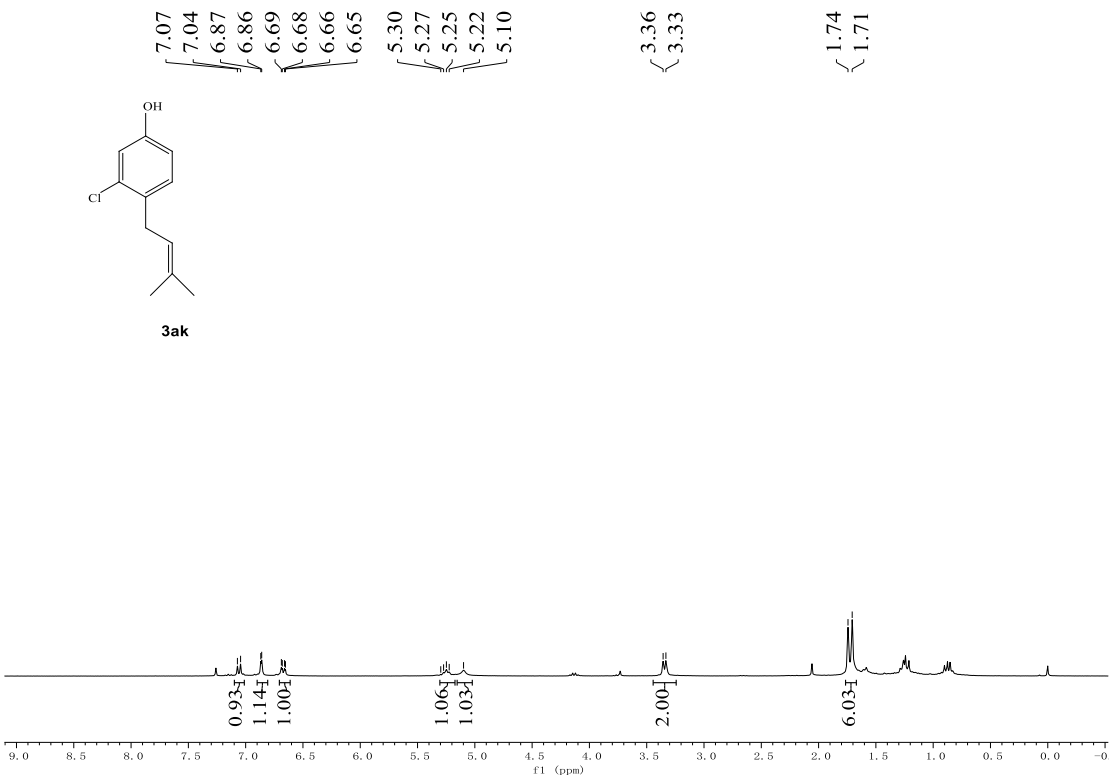

3ak

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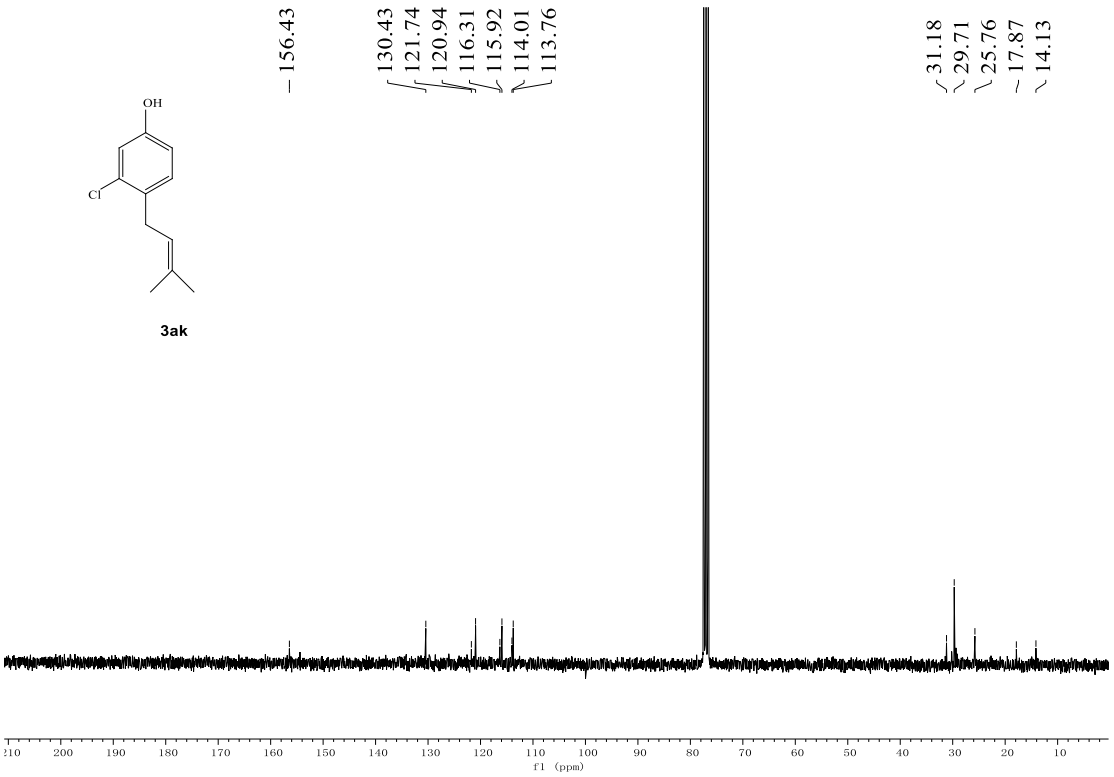

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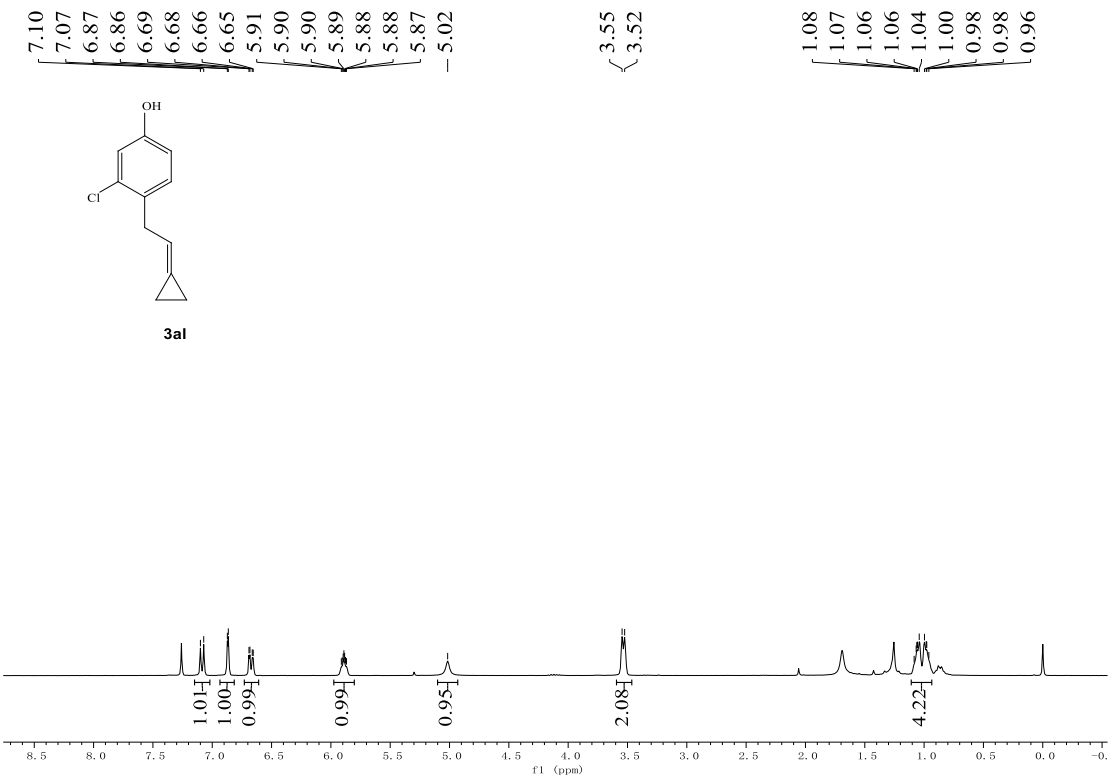
^{1}H NMR (300 MHz, $CDCl_3$)



3al

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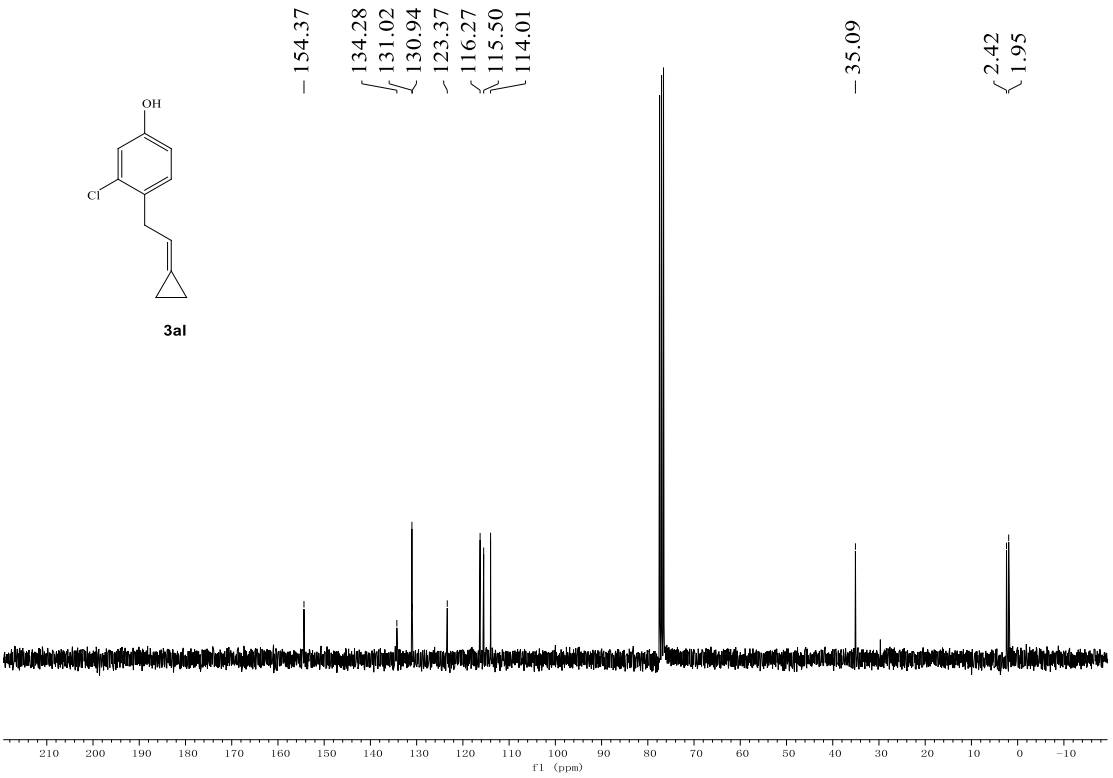
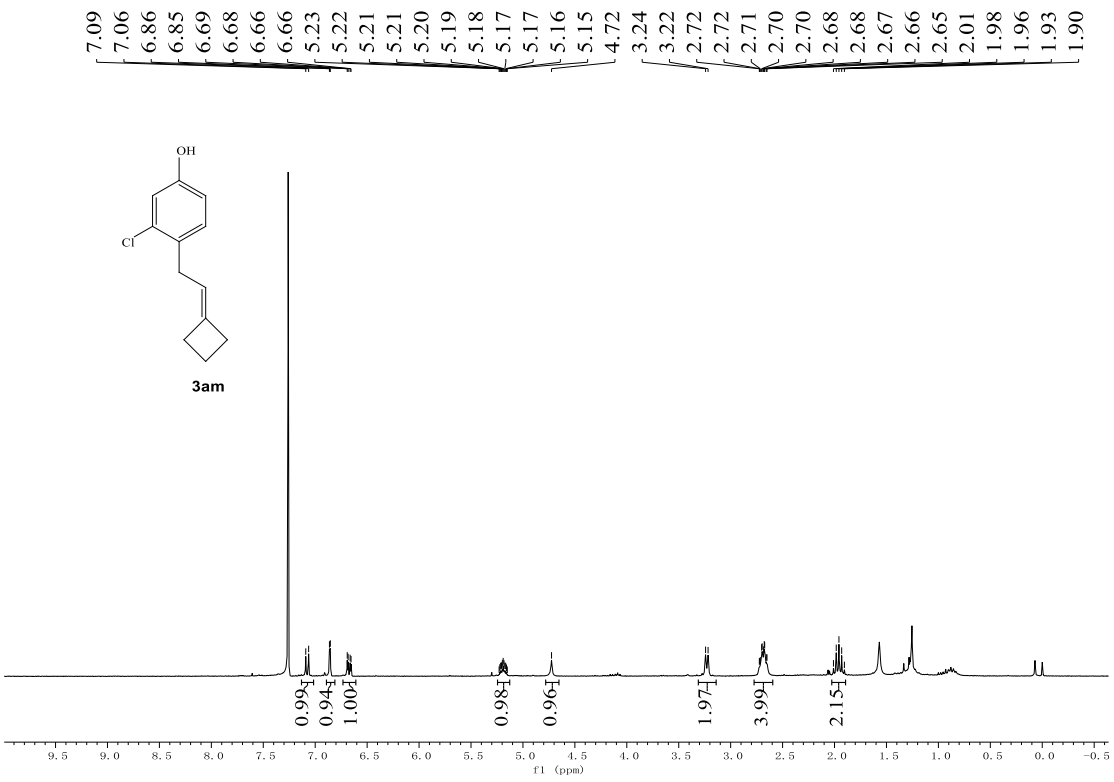
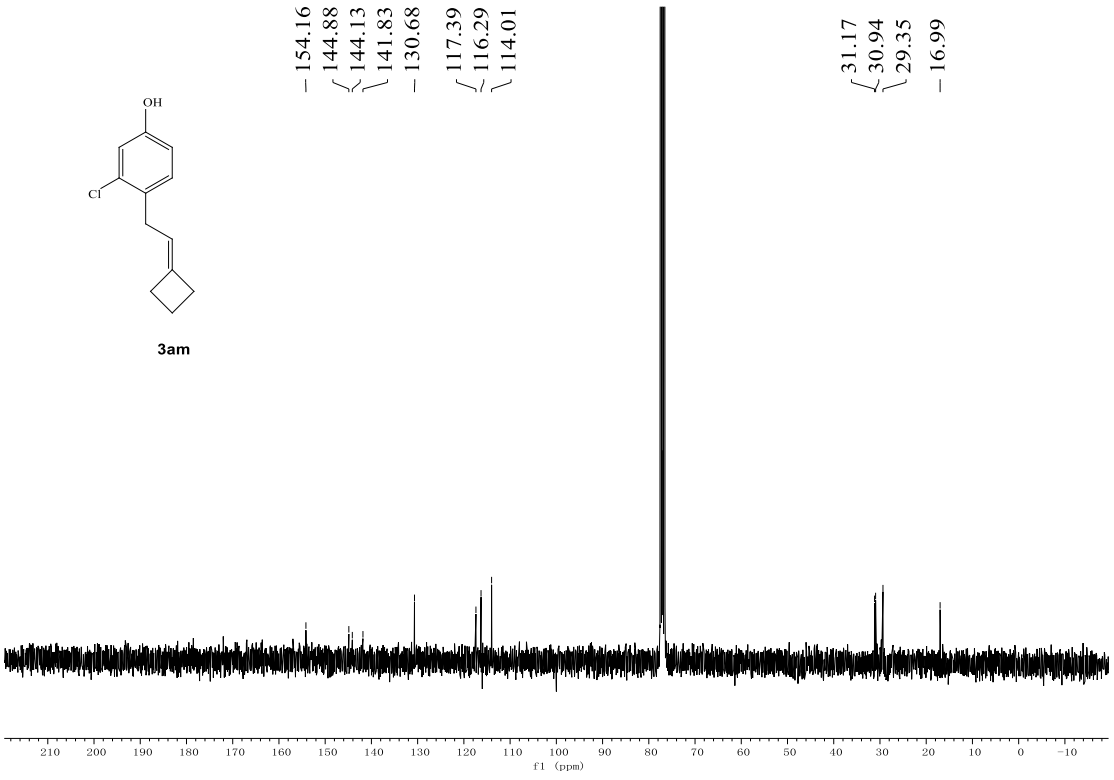


3al

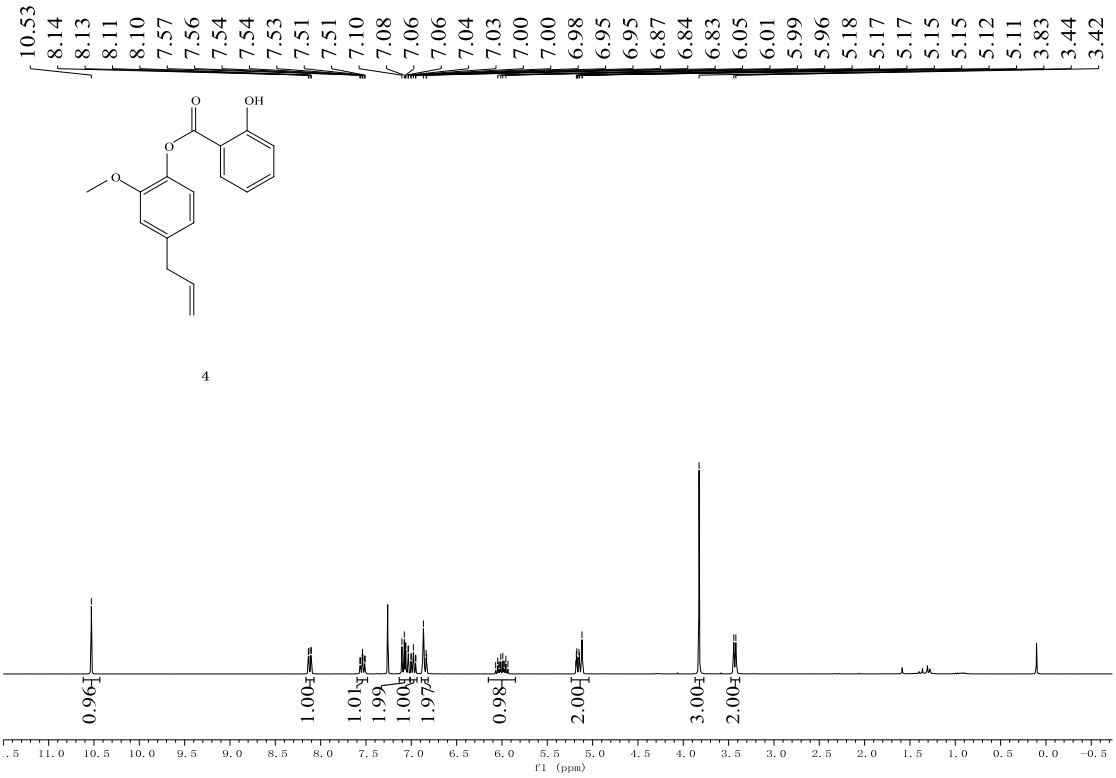
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

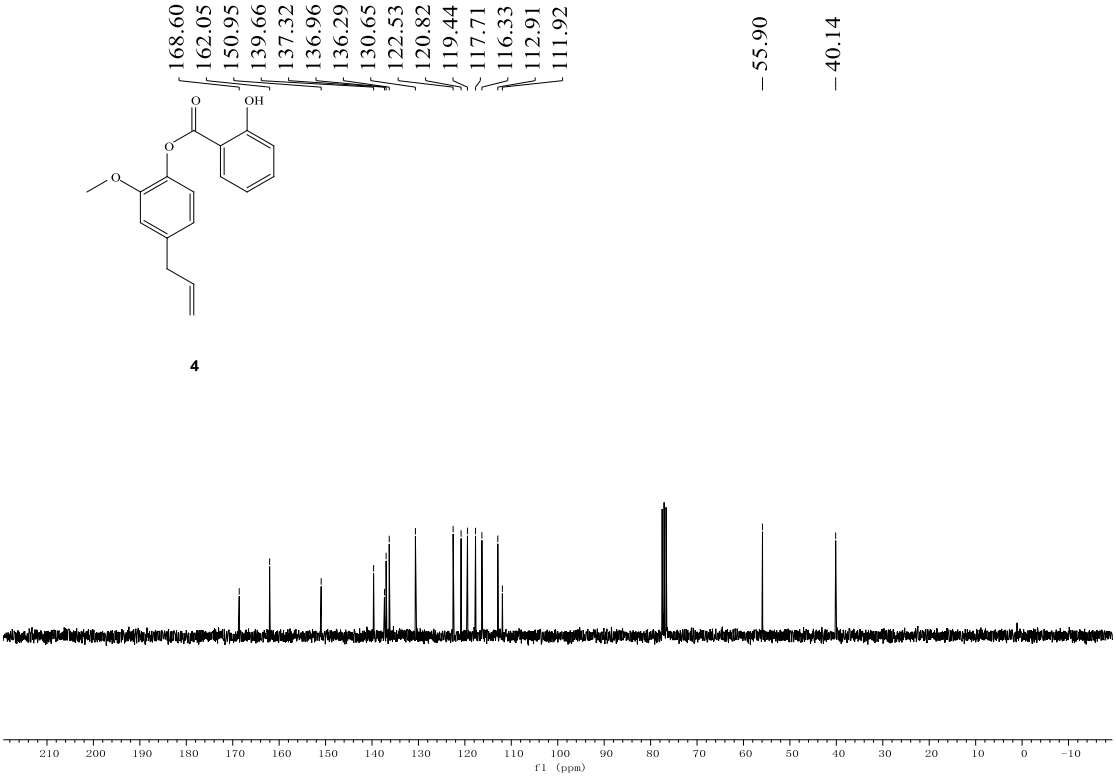


^{1}H NMR (300 MHz, $CDCl_3$)



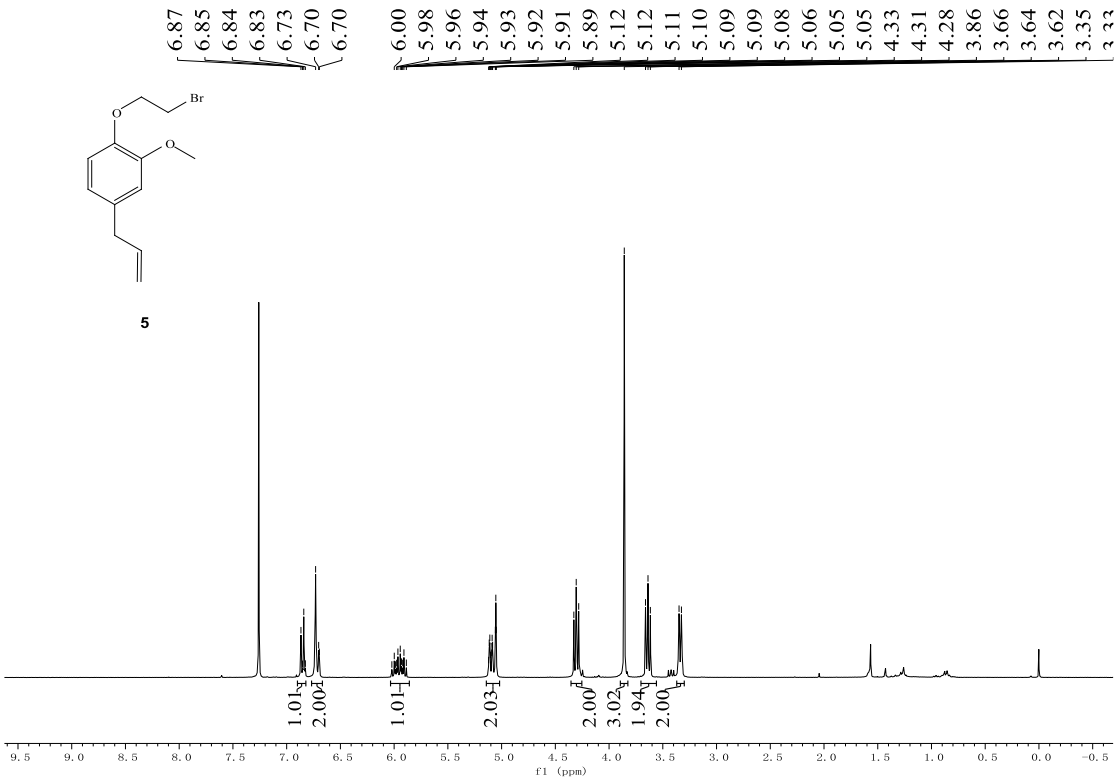
4

^{13}C NMR (75 MHz, $CDCl_3$)

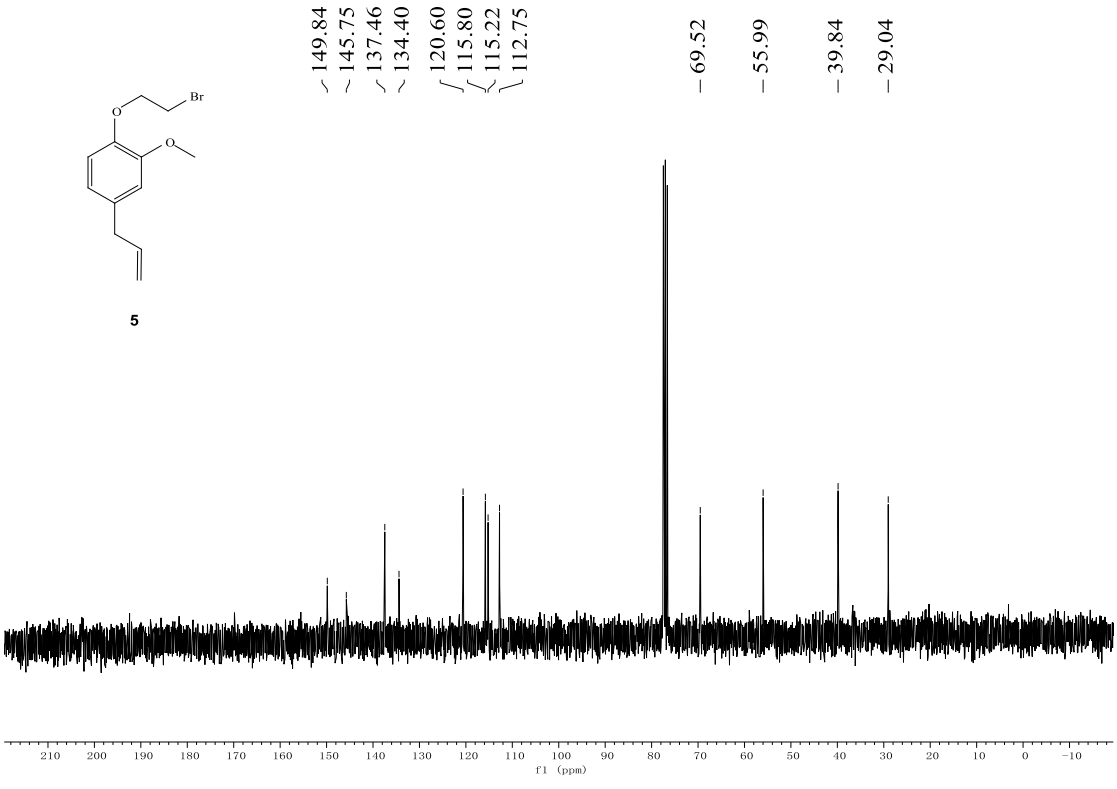


4

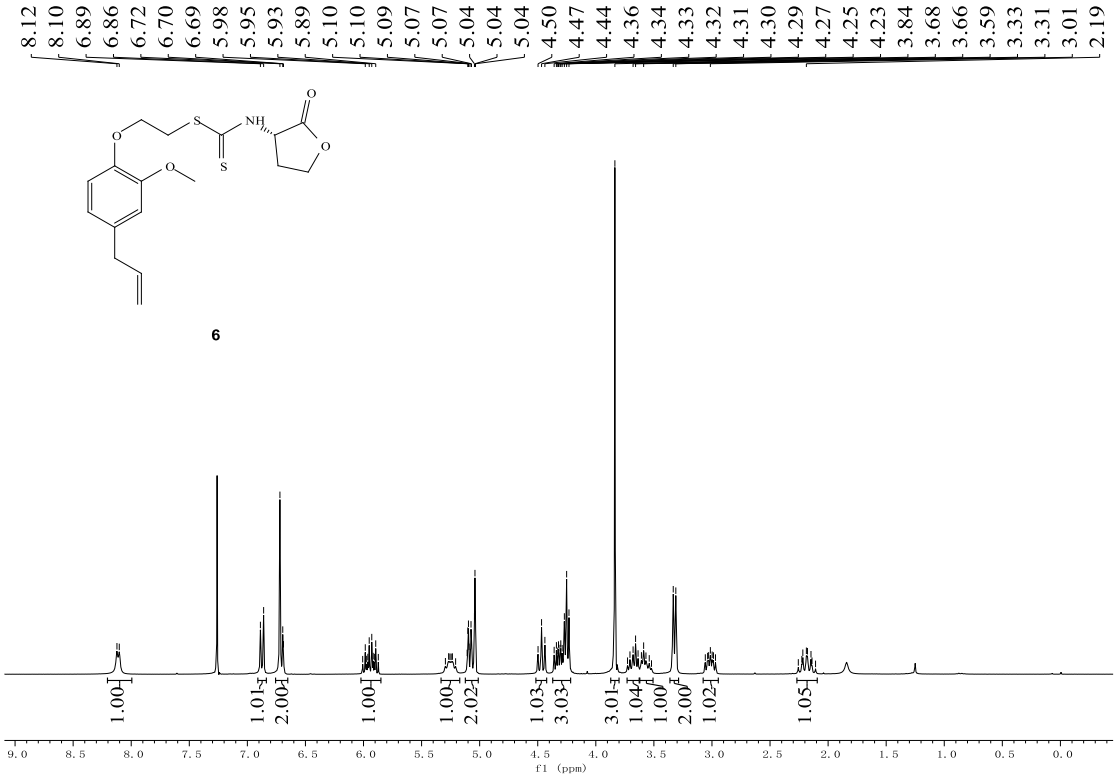
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

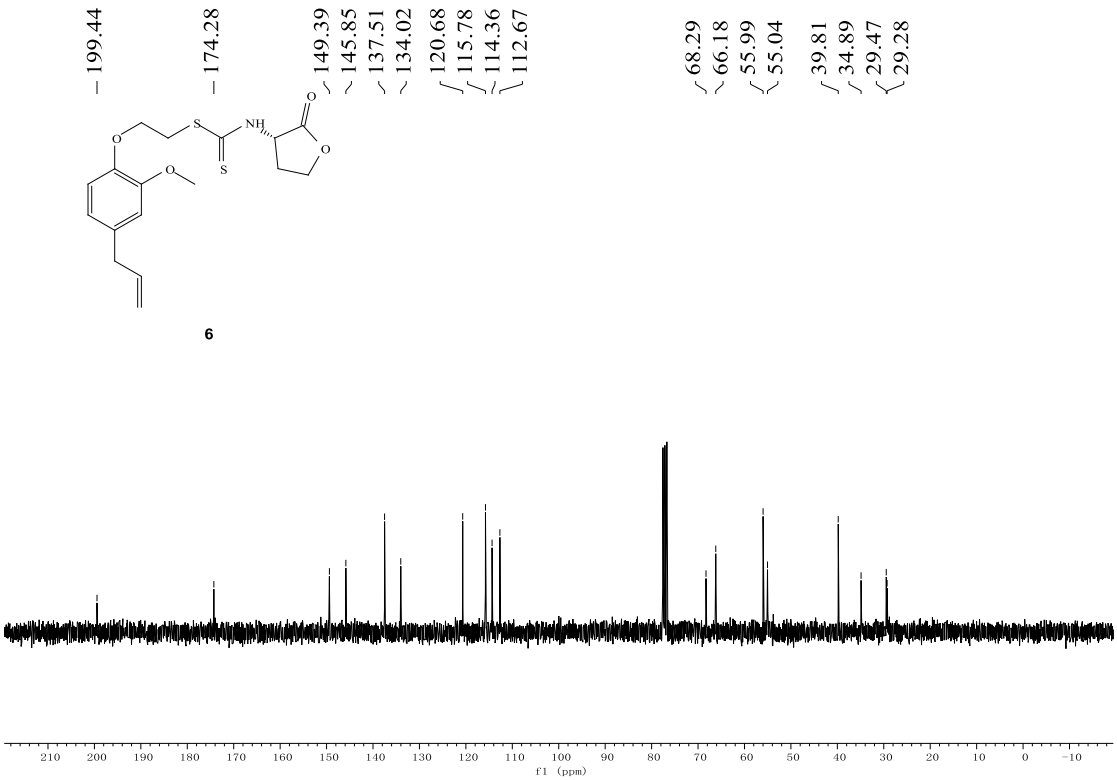


^{1}H NMR (300 MHz, $CDCl_3$)



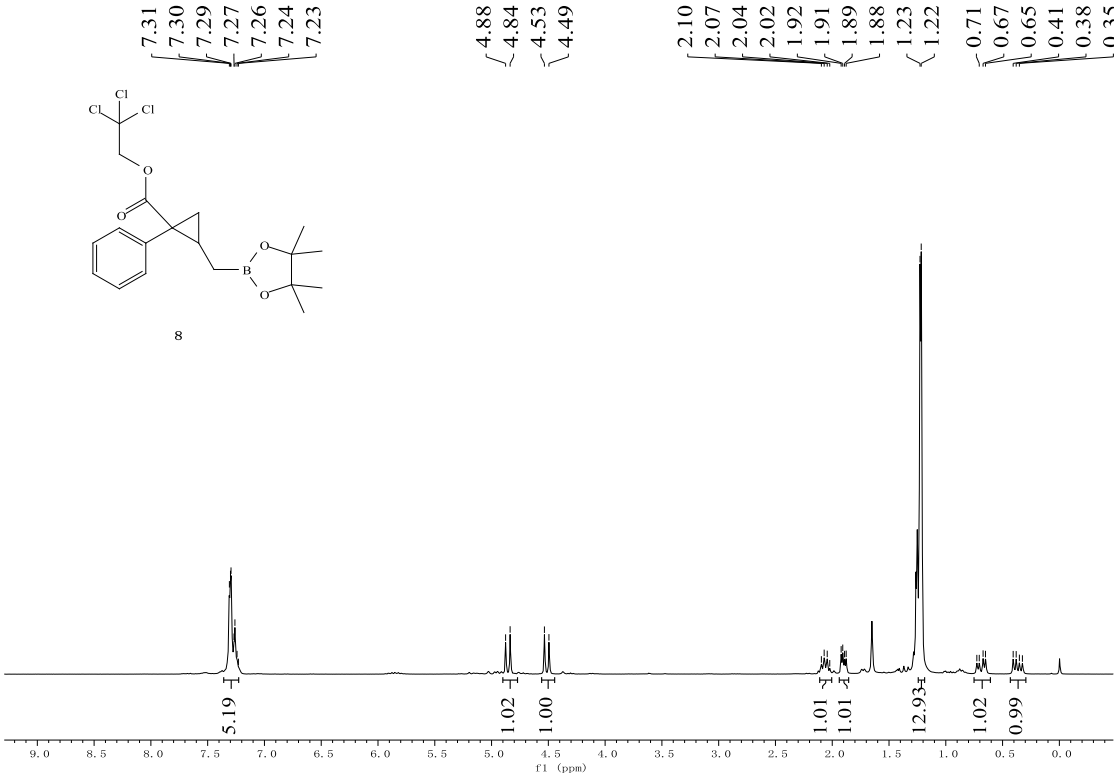
6

^{13}C NMR (75 MHz, $CDCl_3$)



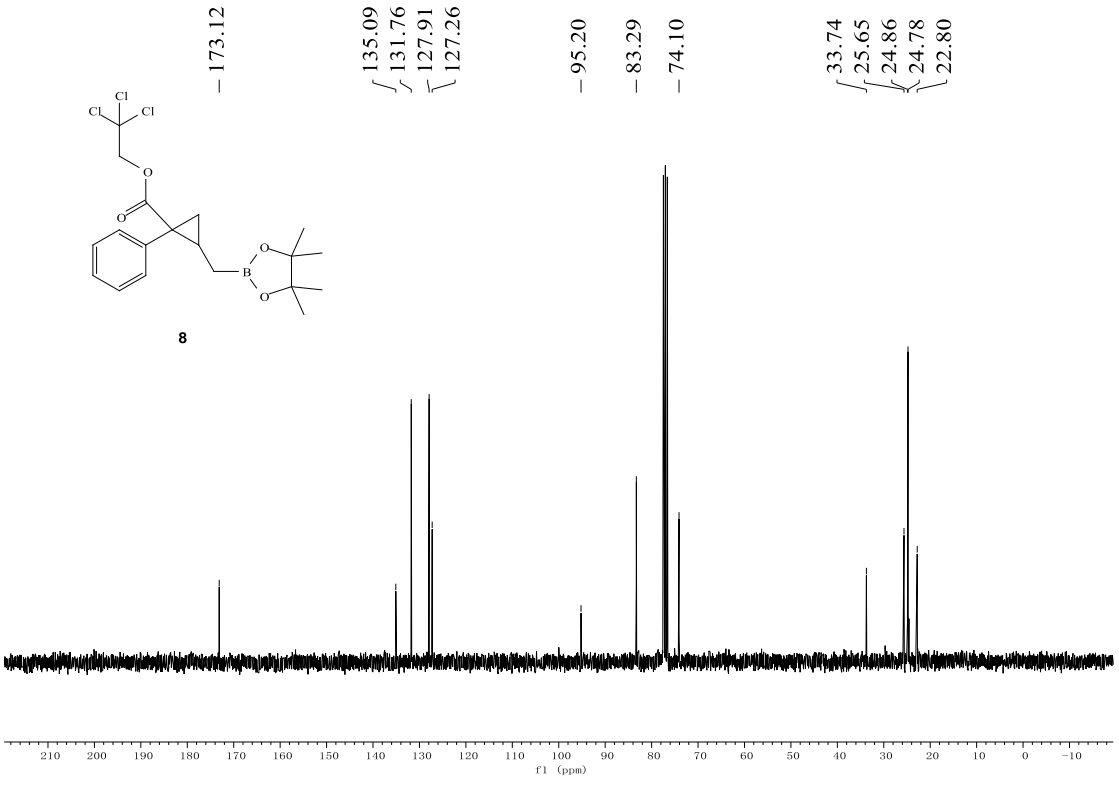
6

^{1}H NMR (300 MHz, $CDCl_3$)



8

^{13}C NMR (75 MHz, $CDCl_3$)



8