Supporting Information

Sequential Reaction of Arynes *via* Insertion into the π-Bond of Amides and Trapping Reaction with Dialkylzincs

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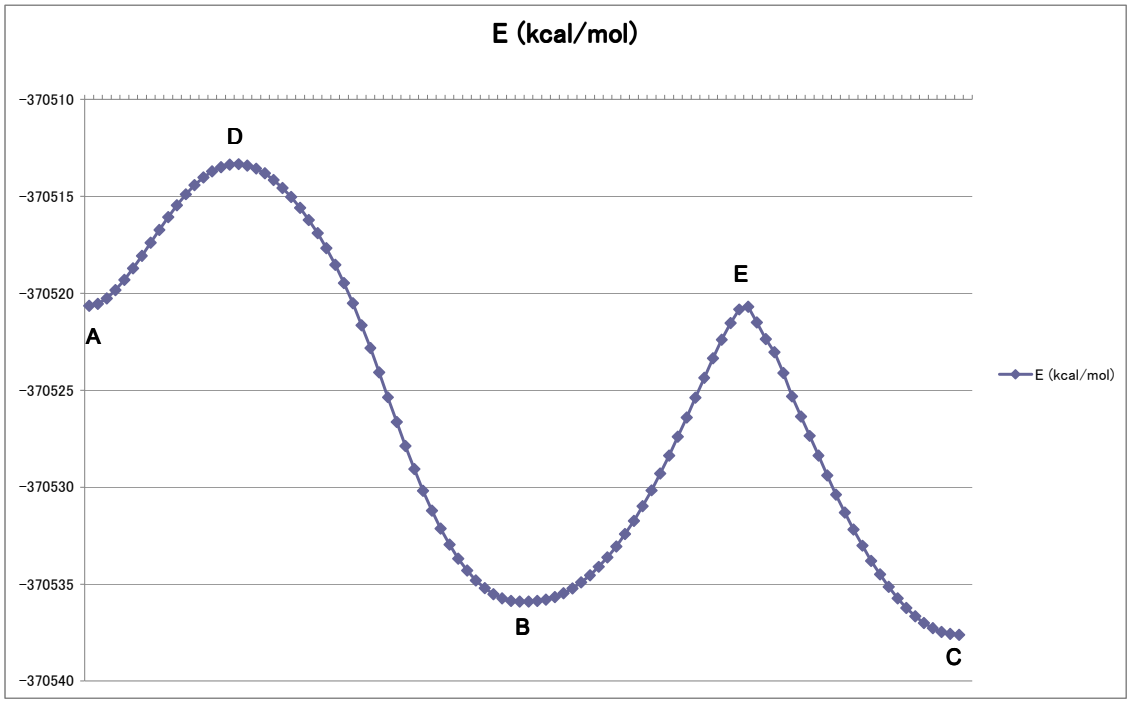
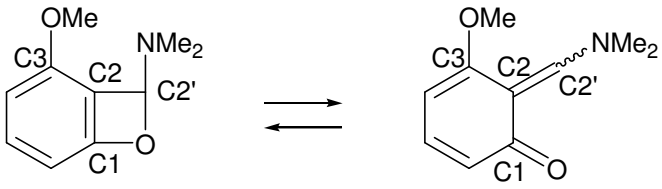
Results of Calculation Studies on Possible Intermediates A-C.

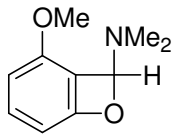
Calculation studies were performed on Hartree-Fock 6-311G* by using Spartan'08 Essential Edition (WAVEFUNCTION, INC).



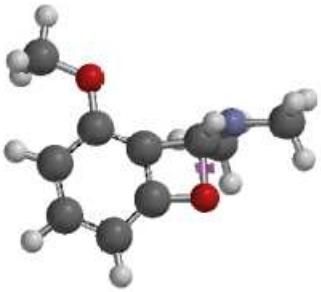


System	Bond Length (C2' and O atom at C1)	Dihedral Angle (C3-C2 and C2'-N)	Energy (au)
A	1.501 Å		−590.461743
B	2.675 Å	−21.41°	−590.486051
C	2.906 Å	−163.29°	−590.488774
D	1.908 Å		−590.450099
E		−93.80°	−590.461818
3-Methoxybenzyne			−343.343682
DMF			−247.045380

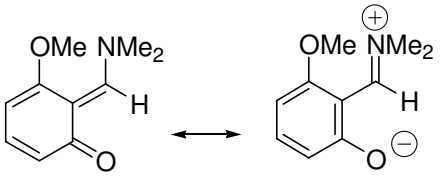
The four-membered intermediate **A**



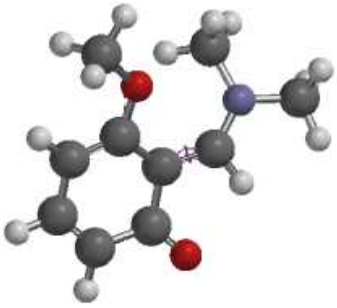
A



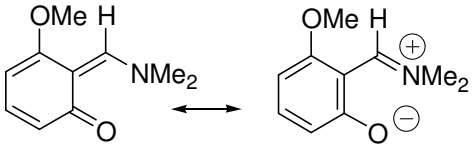
The quinone methide *E*-form **B**



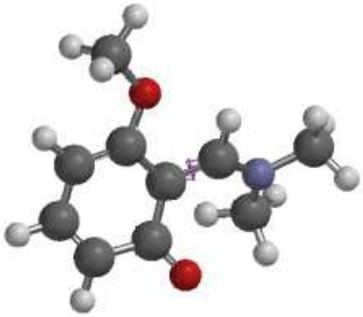
B



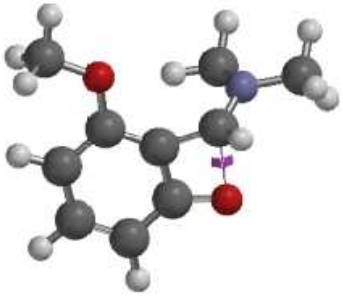
The quinone methide *Z*-form **C**



C



Transition state **D**



Transition state **E**

Experimental Section

General. Melting points were taken on a BUCHI B-540 or Yanaco MP-J3 and are uncorrected. Infrared spectra were measured on a JASCO FT/IR-4100. ^{1}H-NMR spectra were measured on a JEOL ECX-400 PSK (400 MHz) or Varian NMRS 600 (600 MHz). ^{13}C-NMR spectra were measured on a JEOL ECX-400 PSK (101 MHz) or Varian NMRS 600 (126 MHz) with $CDCl_3$ or CD_3OD as an internal standard (77.0 or 49.0 ppm, respectively). ^{19}F-NMR spectra were measured on a JEOL ECX-400 PSK (376 MHz) with C_6F_6 as an internal standard (-162.2 ppm). Low and high resolution mass spectra (EI-MS, CI-MS, ESI-MS and HRMS) were obtained by use of a Hitachi M-4100 GC/MS spectrometer or Thermo Fisher Scientific Exactive LC/MS spectrometer. Elemental analyses were measured on Yanaco CHN CORDER MT-5. For silica gel column chromatography, SiliCycle Inc. SiliaFlash F60 was used. The anhydrous TBAF was prepared from TBAF·3H_2O by heating the hydrate at 40 °C for 6 hours, at 60 °C for 12 hours, at 80 °C for 6 hours, and then at 120 °C for 12 hours under reduced pressure. The prepared anhydrous TBAF was used as a solution by addition of appropriate solvent such as DMF, CH_3CN, and so on. Products **2**,[1] **3**,[2] **10**,[3] **15**,[4] and **16**[5] are known compounds.

1. Experimental Procedure for Reaction of Aryne Precursor 1 with DMF (Table 1).

(1) For the reactions using the 3.0 or 10 equiv. of DMF, see: To a solution of 3-methoxy-2-(trimethylsilyl)phenyl triflate **1** (53 μL, 0.20 mmol) and DMF (0.60 mmol or 2.0 mmol) in CH_3CN, THF, CH_2Cl_2, or CH_3OH (1.4 mL) was added TBAF (1.0 M solution in corresponding solvent, 0.60 mL, 0.60 mmol) under argon atmosphere at room temperature. After stirring at the same temperature for 3 hours, H_2O (0.1 mL) was added to the reaction mixture. The reaction mixture was concentrated under reduced pressure. Purification of the residue by flash silica gel column chromatography (AcOEt:hexane =1:20–1:8 with 2% CH_2Cl_2) afforded the product **2**.

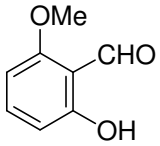
(2) For the reactions using DMF as a solvent, see: To a solution of TBAF, CsF, $TBAHF_2$, or TBAT (0.60 mmol) in DMF (1.2 mL) was added a solution of 3-methoxy-2-(trimethylsilyl)phenyl triflate **1** (53 μL, 0.20 mmol) in DMF (0.8 mL) under argon atmosphere at room temperature. After stirring at the same temperature for 3 hours, H_2O (0.1 mL) was added to the reaction mixture. The reaction mixture was concentrated under reduced pressure. Purification of the residue by flash silica gel column chromatography (AcOEt:hexane =1:20–1:8 with 2% CH_2Cl_2) afforded the product **2**.

2. Reaction of Aryne Precursor 1 with DMA (Scheme 1).

To a solution of TBAF (157 mg, 0.60 mmol) in DMA (1.2 mL) was added a solution of 3-methoxy-2-(trimethylsilyl)phenyl triflate **1** (53 μL, 0.20 mmol) in DMA (0.8 mL) under argon atmosphere at room temperature. After stirring at the same temperature for 3 hours, H_2O (0.1 mL) was added to the reaction mixture. The reaction mixture was concentrated under reduced pressure. Purification of the residue by flash silica gel column chromatography (AcOEt:hexane =1:20–1:8 with 2% CH_2Cl_2) afforded the products **2** (11.3 mg, 34%) and **4** (3.8 mg, 10%).

3. Characterization Data of Obtained Compounds 2-4:

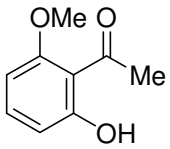
Aldehyde (**2**) [1)]



2

Colorless crystals. mp 73.5-74.5 °C (AcOEt-hexane). IR ($CHCl_3$) 1646 cm^{-1}. ^1H NMR ($CDCl_3$) δ 11.97 (1H, s), 10.34 (1H, s), 7.41 (1H, dd, *J* = 8.0, 8.5 Hz), 6.52 (1H, d, *J* = 8.5 Hz), 6.38 (1H, d, *J* = 8.0 Hz), 3.89 (3H, s); ^{13}C NMR ($CDCl_3$) δ 194.5, 163.6, 162.5, 138.4, 110.8, 109.9, 101.0, 55.8; MS (EI^+) *m/z* 84 (100), 153 ($M+H^+$, 9); HRMS (EI^+) calcd for $C_8H_9O_3$ ($M+H^+$): 153.0552. Found: 153.0553; Elemental analysis (%) calcd for $C_8H_8O_3$: C, 63.15; H, 5.30; O, 31.55, found: C, 63.14, H, 5.32.

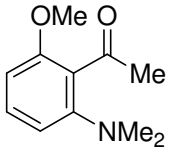
Ketone (**3**) [2)]



3

Colorless crystals. mp 57-57.5 °C (AcOEt-hexane). IR ($CHCl_3$) 1623 cm^{-1}. ^1H NMR ($CDCl_3$) δ 13.23 (1H, s), 7.33 (1H, t, *J* = 8.0 Hz), 6.56 (1H, dd, *J* = 8.0, 1.0 Hz), 6.39 (1H, dd, *J* = 8.0, 1.0 Hz), 3.90 (3H, s), 2.67 (3H, s); ^{13}C NMR ($CDCl_3$) δ 205.1, 164.6, 161.5, 136.0, 111.3, 110.7, 101.1, 55.6, 33.7; MS (EI^+) *m/z* 83 (100), 166 (M^+, 3); HRMS (EI^+) calcd for $C_9H_{10}O_3$ (M^+): 166.0630. Found: 166.0646.

Ketone (**4**)



4

Colorless oil. IR ($CHCl_3$) 1702 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.23 (1H, br t, *J* = 8.0 Hz), 6.67 (1H, br d, *J* = 8.0 Hz), 6.56 (1H, br d, *J* = 8.0 Hz), 3.78 (3H, s), 2.72 (6H, s), 2.50 (3H, s); ^{13}C NMR ($CDCl_3$) δ 205.2, 156.2, 151.8, 130.2, 125.3, 111.0, 104.7, 55.8, 44.8, 31.8; MS (EI^+) *m/z* 83 (100), 193 (M^+, 0.4); HRMS (EI^+) calcd for $C_{11}H_{15}NO_2$ (M^+): 193.1103. Found: 193.1121.

4. General Procedure for Trapping Reaction Using Dialkylzincs.

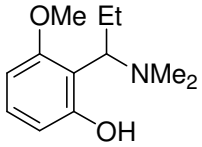
To a suspension of CsF (91 mg, 0.60 mmol) in DMF (1.2 mL) was added a solution of aryne precursor **1**, **9**, **11**, or **13** (0.20 mmol) in DMF (0.8 mL) under argon atmosphere at room temperature. After stirring at the same temperature for 15 minutes, Et_2Zn (1.05 M in hexane, 0.95 mL, 1.0 mmol), Me_2Zn (1.0 M in hexane, 1.0 mL, 1.0 mmol), or Ph_2Zn (220 mg, 1.0 mmol) was added to the reaction mixture at room temperature. After stirring at the same temperature for 12 hours, H_2O (0.1 mL) was added to the reaction mixture. The reaction mixture was concentrated under reduced pressure. Purification of the residue by flash silica gel column chromatography (AcOEt:hexane =1:20–1:0 with 2% CH_2Cl_2) afforded the products **5a-c**, **5a-*d***, **10**, **12a**, **12b**, **14**, and **15**.

5. Experimental Procedure for Trapping Reaction Using 1-Formylpiperidine 7.

To a solution of TBAF (157 mg, 0.60 mmol) and 1-formylpiperidine **7** in CH_3CN (1.2 mL) was added a solution of 3-methoxy-2-(trimethylsilyl)phenyl triflate **1** (53 μL, 0.20 mmol) in CH_3CN (0.8 mL) under argon atmosphere at room temperature. After stirring at the same temperature for 15 minutes, Et_2Zn (1.05 M in hexane, 0.95 mL, 1.0 mmol) was added to the reaction mixture. After stirring at the same temperature for 12 hours, H_2O (0.1 mL) was added to the reaction mixture. The reaction mixture was concentrated under reduced pressure. Purification of the residue by flash silica gel column chromatography (AcOEt:hexane =1:20–1:0 with 2% CH_2Cl_2) afforded the product **8** (20.1 mg, 40%).

6. Characterization Data of Obtained Compounds 5a-c, 5a-*d*, 8, 10, 12a, 12b, 14, and 15.

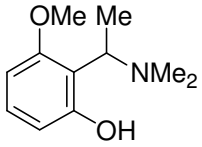
Ethylated Product (**5a**)



5a

Colorless oil. ^{1}H NMR ($CDCl_3$) δ 7.06 (1H, t, *J* = 8.0 Hz), 6.44 (1H, dd, *J* = 8.0, 1.0 Hz), 6.35 (1H, dd, *J* = 8.0, 1.0 Hz), 3.76 (3H, s), 3.74 (1H, m), 2.33 (6H, s), 1.88-1.72 (2H, m), 0.76 (3H, t, *J* = 7.5 Hz); The exchangeable proton peak of OH group was not clearly detected. ^{13}C NMR ($CDCl_3$) δ 158.7, 157.9, 128.1, 113.7, 109.6, 101.1, 64.4, 55.3, 43.3 (br s), 24.9, 9.5; MS (EI^+) *m/z* 153 (100), 209 (M^+, 13); HRMS (EI^+) calcd for $C_{12}H_{19}NO_2$ (M^+): 209.1416. Found: 209.1421.

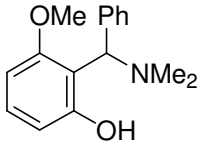
Methylated Product (**5b**)



5b

Colorless oil. ^{1}H NMR ($CDCl_3$) δ 7.04 (1H, t, *J* = 8.0 Hz), 6.44 (1H, dd, *J* = 8.0, 1.0 Hz), 6.34 (1H, dd, *J* = 8.0, 1.0 Hz), 3.84 (1H, t, *J* = 6.5 Hz), 3.78 (3H, s), 2.33 (6H, br s), 1.33 (3H, d, *J* = 6.5 Hz); The exchangeable proton peak of OH group was not clearly detected. ^{13}C NMR ($CDCl_3$) δ 158.3, 157.0, 128.0, 116.1, 109.7, 101.2, 59.4, 55.5, 43.4 (br s), 18.7; MS (EI^+) *m/z* 180 (100), 195 (M^+, 51); HRMS (EI^+) calcd for $C_{11}H_{17}NO_2$ (M^+): 195.1259. Found: 195.1275.

Phenylated Product (**5c**)

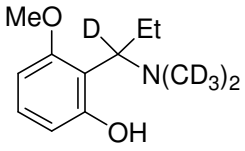


5c

Colorless crystals. mp 150-151 °C (AcOEt-hexane). ^{1}H NMR ($CDCl_3$) δ 7.48 (2H, br d, *J* = 7.0 Hz), 7.27-7.17 (3H, m), 7.03 (1H, t, *J* = 8.0 Hz), 6.49 (1H, dd, *J* = 8.0, 1.0 Hz), 6.26 (1H, dd, *J* = 8.0, 1.0 Hz), 4.69 (1H, s), 3.70 (3H, s), 2.27 (6H, br s); The exchangeable proton peak of OH group was not clearly detected. ^{13}C NMR ($CDCl_3$) δ 157.9, 157.4, 141.2, 128.4 (2C), 127.4, 114.8, 109.9, 101.5, 70.2, 55.5, 44.2 (br s); One carbon peak was missing due to overlapping. MS (EI^+) *m/z* 211 (100), 257 (M^+, 37); HRMS (EI^+) calcd for $C_{16}H_{19}NO_2$ (M^+): 257.1416. Found:

257.1431; Elemental analysis (%) calcd for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44; O, 12.44, found: C, 74.68, H, 7.44, N, 5.44.

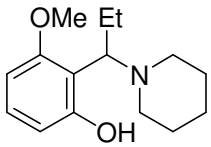
Deuterated Product (**5a-*d***)



5a-*d*

Colorless oil. ^{1}H NMR ($CDCl_3$) δ 7.07 (1H, t, *J* = 8.0 Hz), 6.45 (1H, br d, *J* = 8.0 Hz), 6.35 (1H, br d, *J* = 8.0 Hz), 3.76 (3H, s), 1.88-1.78 (2H, m), 0.76 (3H, t, *J* = 7.5 Hz); The exchangeable proton peak of OH group was not clearly detected. ^{13}C NMR ($CDCl_3$) δ 158.8, 158.0, 128.1, 113.6, 109.6, 101.2, 63.9 (t, *J* = 18 Hz), 55.3, 24.8, 9.5; One carbon peak of $N(CD_3)_2$ group was not clearly detected due to the presence of rotamer and D-C coupling. MS (EI^+) *m/z* 187 (100), 216 (M^+, 16); HRMS (EI^+) calcd for $C_{12}H_{12}D_7NO_2$ (M^+): 216.1848. Found: 216.1856.

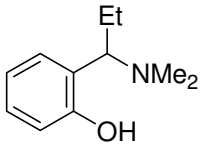
Piperidine derivative (**8**)



8

Colorless oil. ^{1}H NMR (CD_3OD) δ 7.02 (1H, t, *J* = 8.0 Hz), 6.40 (1H, br dd, *J* = 8.0, 1.0 Hz), 6.32 (1H, br dd, *J* = 8.0, 1.0 Hz), 3.92 (1H, dd, *J* = 8.0, 4.0 Hz), 3.74 (3H, s), 2.65-2.45 (4H, br m), 1.89-1.52 (8H, m), 0.74 (3H, t, *J* = 7.5 Hz); The exchangeable proton peak of OH group was not clearly detected. ^{13}C NMR (CD_3OD) δ 160.0, 159.7, 129.4, 114.5, 110.5, 102.4, 64.6, 55.8, 52.8 (br s), 27.1, 25.2, 24.9, 9.8; MS (EI^+) *m/z* 83 (100), 249 (M^+, 0.1); HRMS (EI^+) calcd for $C_{15}H_{23}NO_2$ (M^+): 249.1729. Found: 249.1738.

Adduct (**10**) [3)]

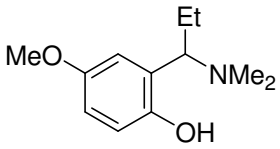


10

Colorless oil. ^{1}H NMR ($CDCl_3$) δ 7.18 (1H, dt, *J* = 8.0, 2.0 Hz), 6.96 (1H, dd, *J* = 7.5, 2.0 Hz), 6.87 (1H, dd, *J* = 8.0, 1.0 Hz), 6.81 (1H, dt, *J* = 7.5, 1.0 Hz), 3.43 (1H, br dd, *J* = 9.5, 4.0 Hz), 2.47 (6H, s), 2.09-1.83 (2H, m), 0.79 (3H, t, *J* = 7.5 Hz); The exchangeable proton peak of OH group was not clearly detected. ^{13}C NMR ($CDCl_3$) δ 156.5, 129.2, 129.1, 123.3, 119.1, 116.7,

71.7, 42.6, 23.5, 10.8; MS (EI^+) *m/z* 84 (100), 179 (M^+, 0.1); HRMS (EI^+) calcd for $C_{11}H_{17}NO$ (M^+): 179.1310. Found: 179.1329.

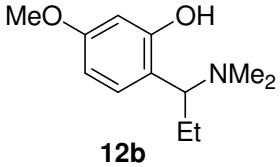
Isomer (**12a**)



12a

Colorless oil. ^1H NMR ($CDCl_3$) δ 6.75-6.68 (2H, m), 6.49 (1H, d, *J* = 3.0 Hz), 3.74 (3H, s), 3.05 (1H, dd, *J* = 9.5, 4.0 Hz), 2.33 (6H, s), 1.94-1.84 (1H, m), 1.81-1.69 (1H, m), 0.78 (3H, t, *J* = 7.5 Hz); The exchangeable proton peak of OH group was not clearly detected. ^{13}C NMR ($CDCl_3$) δ 152.0, 150.8, 126.2, 116.6, 115.3, 112.7, 72.7, 55.7, 43.1, 24.4, 10.9; MS (EI^+) *m/z* 84 (100), 209 (M^+, 8); HRMS (EI^+) calcd for $C_{12}H_{19}NO_2$ (M^+): 209.1416. Found: 209.1431.

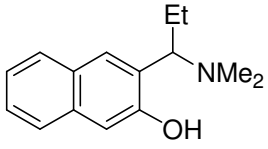
Isomer (**12b**)



12b

Colorless oil. ^1H NMR ($CDCl_3$) δ 6.88 (1H, d, *J* = 9.0 Hz), 6.81 (1H, dd, *J* = 9.0, 3.0 Hz), 6.62 (1H, d, *J* = 3.0 Hz), 3.77 (3H, s), 3.74 (1H, m), 2.62 (6H, s), 2.01 (2H, m), 0.84 (3H, t, *J* = 7.5 Hz); The exchangeable proton peak of OH group was not clearly detected. ^{13}C NMR ($CDCl_3$) δ 153.1, 149.4, 121.8, 117.7, 115.0, 114.7, 70.4, 55.8, 42.1, 22.3, 10.8; MS (ESI^+) *m/z* 210 ($M+H^+$); HRMS (ESI^+) calcd for $C_{12}H_{19}NO_2$ ($M+H^+$): 210.1494. Found: 210.1491.

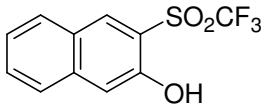
Adduct (**14**)



14

Yellow solid. mp 85-86 °C (CH_2Cl_2-hexane). Sublimation (ca.80 °C). ^1H NMR ($CDCl_3$) δ 7.67 (2H, br d, *J* = 8.5 Hz), 7.34-7.39 (2H, m), 7.26 (1H, m), 7.16 (1H, br s), 3.28 (1H, dd, *J* = 10.0, 4.0 Hz), 2.38 (6H, s), 2.05-1.95 (1H, m), 1.87-1.76 (1H, m), 0.77 (3H, t, *J* = 7.5 Hz); The exchangeable proton peak of OH group was not clearly detected. ^{13}C NMR ($CDCl_3$) δ 155.4, 134.2, 128.2, 128.0, 127.6, 127.3, 126.0, 125.8, 122.9, 110.5, 73.2, 43.2, 24.3, 11.2; MS (EI^+) *m/z* 200 (100), 229 (M^+, 21); HRMS (EI^+) calcd for $C_{15}H_{19}NO$ (M^+): 229.1467. Found: 229.1454.

Rearrangement product (**15**) [4)]

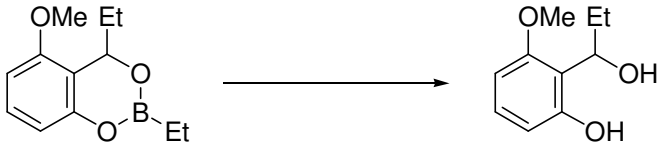


15

Yellow crystals. mp 120-121 °C (benzene-hexane). Sublimation (ca.102 °C). ^{1}H NMR ($CDCl_3$) δ 8.44 (1H, s), 7.96 (1H, s, offset by D2O), 7.89 (1H, d, *J* = 8.0 Hz), 7.76 (1H, d, *J* = 8.0 Hz), 7.64 (1H, ddd, *J* = 1.5, 1.5, 7,5 Hz), 7.46 (2H, m); ^{13}C NMR ($CDCl_3$) δ 151.8, 139.5, 135.7, 131.5, 129.6, 127.3, 126.7, 125.8, 119.8 (q, *J* = 327 Hz),115.1, 114.6; ^{19}F NMR ($CDCl_3$) δ -79.3; MS (EI^+) *m/z* 115 (100), 276 (M^+, 87); HRMS (EI^+) calcd for $C_{11}H_7F_3O_3S$ (M^+): 276.0068. Found: 276.0068.

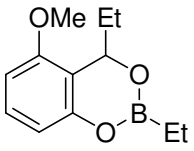
6. Characterization Data of Compound 6 and Corresponding Alcohol 16

The unstable adduct **6** was easily hydrolyzed into the corresponding alcohol **16** during purification by column chromatography. Thus, the structure of unstable adduct **6** was confirmed by ^{1}H NMR and low resolution mass. The characterization of alcohol **16** also supported the formation of **6**.



6 **16**

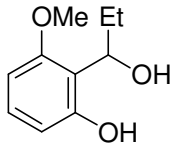
Adduct (**6**)



6

Colorless oil. ^{1}H NMR ($CDCl_3$) δ 7.13 (1H, t, *J* = 8.0 Hz), 6.56 (2H, br t, *J* = 8.0 Hz), 5.19 (1H, dd, *J* = 6.5, 3.5 Hz), 3.80 (3H, s), 1.90-1.67 (2H, m), 1.03-0.86 (8H, m); MS (EI^+) *m/z* 191 (100), 220 (M^+, 14).

Alcohol (**16**) [5]



16

Colorless oil. ^{1}H NMR ($CDCl_3$) δ 8.59 (1H, s), 7.09 (1H, t, *J* = 8.0 Hz), 6.51 (1H, d, *J* = 8.0 Hz), 6.39 (1H, d, *J* = 8.0 Hz), 5.32 (1H, t, *J* = 6.5 Hz), 3.77 (3H, s), 2.49 (1H, br s), 1.92-1.75 (2H, m), 0.99 (3H, t, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 157.1, 156.6, 128.7, 115.4, 110.2, 101.9, 71.8, 55.5, 29.3, 10.0; MS (EI^+) *m/z* 153 (100), 182 (M^+, 54); HRMS (EI^+) calcd for $C_{10}H_{14}O_3$ (M^+): 182.0943. Found: 182.0962.

References

1) Haight, A. R.; Bailey, A. E.; Baker, W. S.; Cain, M. H.; Copp, R. R.; DeMattei, J. A.; Ford, K. L.; Henry, R. F.; Hsu, M. C.; Keyes, R. F.; King, S. A.; McLaughlin, M. A.; Melcher, L. M.; Nadler, W. R.; Oliver, P. A.; Parekh, S. I.; Patel, H. H.; Seif, L. S.; Staeger, M. A.; Wayne, G. S.; Wittenberger, S. J.; Zhang, W. *Org. Proc. Res. Dev.* **2004**, *8*, 897-902.

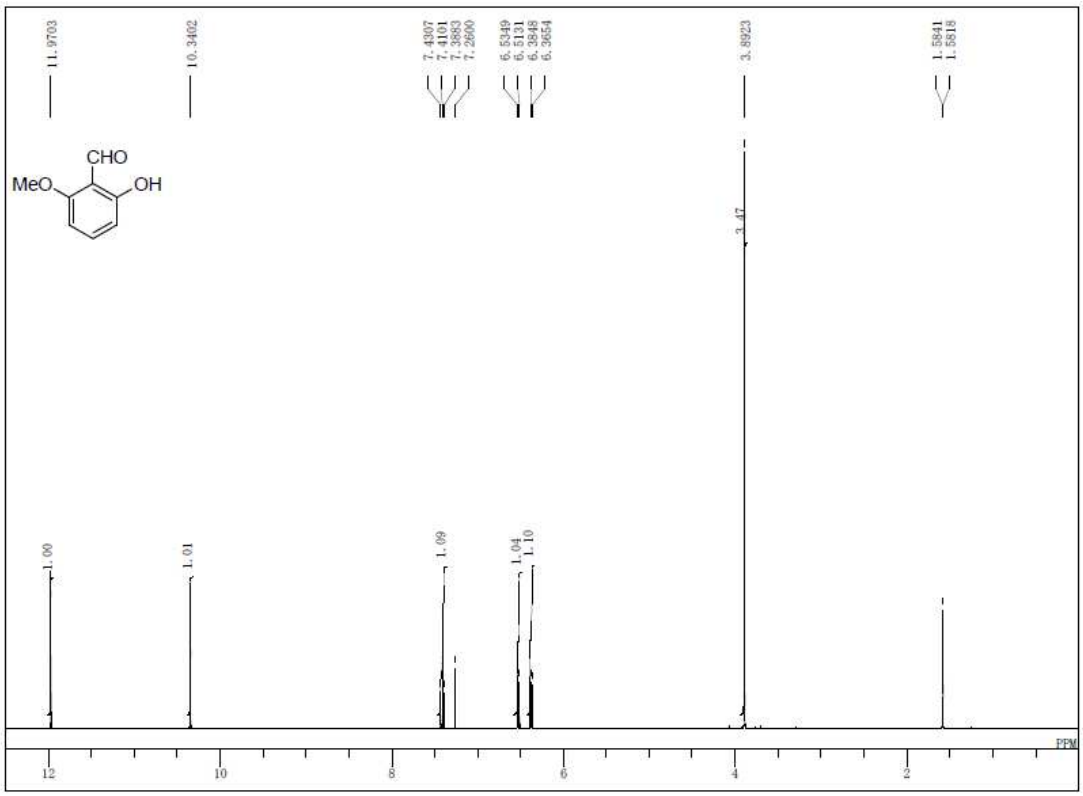
2) Lau, C. K.; Belanger, Patrice C.; Dufresne, C.; Scheigetz, J. *J. Org. Chem.* **1987**, *52*, 1670-1673.

3) Davies, R. E.; Haworth, R. D.; Jones, B.; Lamberton, A.. H. *J. Chem. Soc.* **1947**, 191-196.

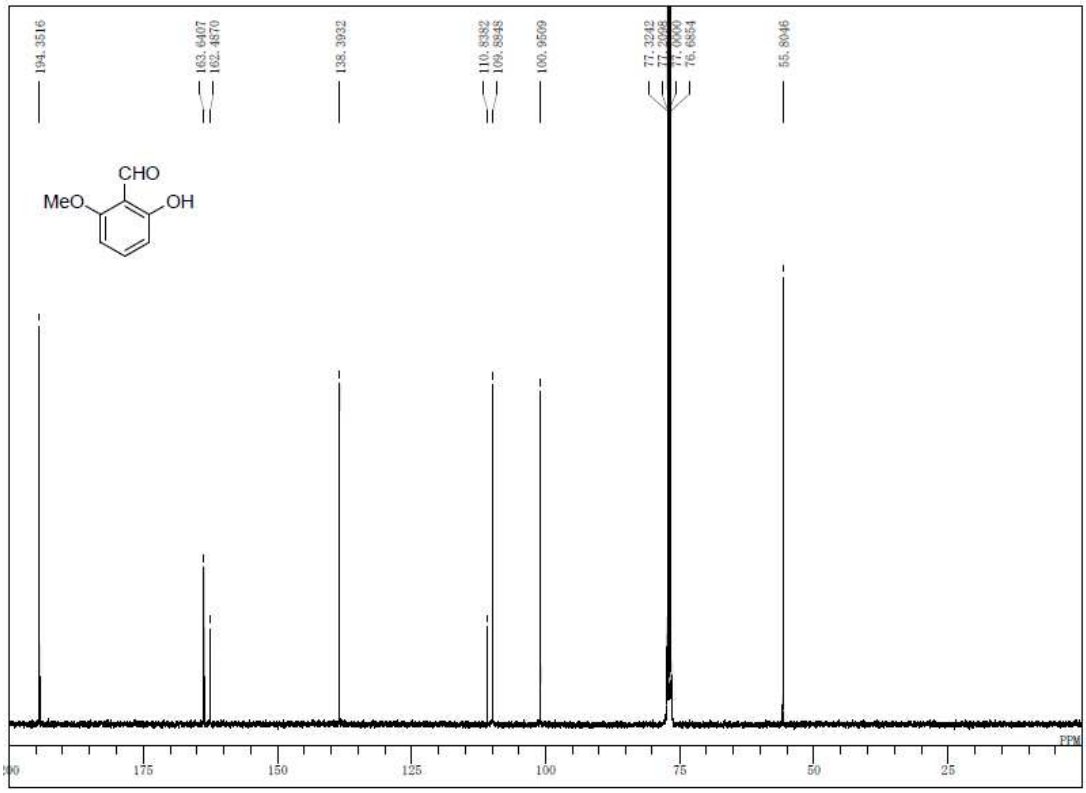
4) Dyke, A. M.; Gill, D. M.; Harvey, J. N.; Hester, A. J.; Lloyd-Jones, G. C.; Muñoz, M. P.; Shepperson, I. R. *Angew. Chem. Int. Ed.* **2008**, *47*, 5067-5070.

5) Revenko, Y. M.; Shamshurin, A. A. *Izv. Akad. Nauk Mold. SSR., Ser. Khim. Biol. Nauk* **1965**, 58-61.

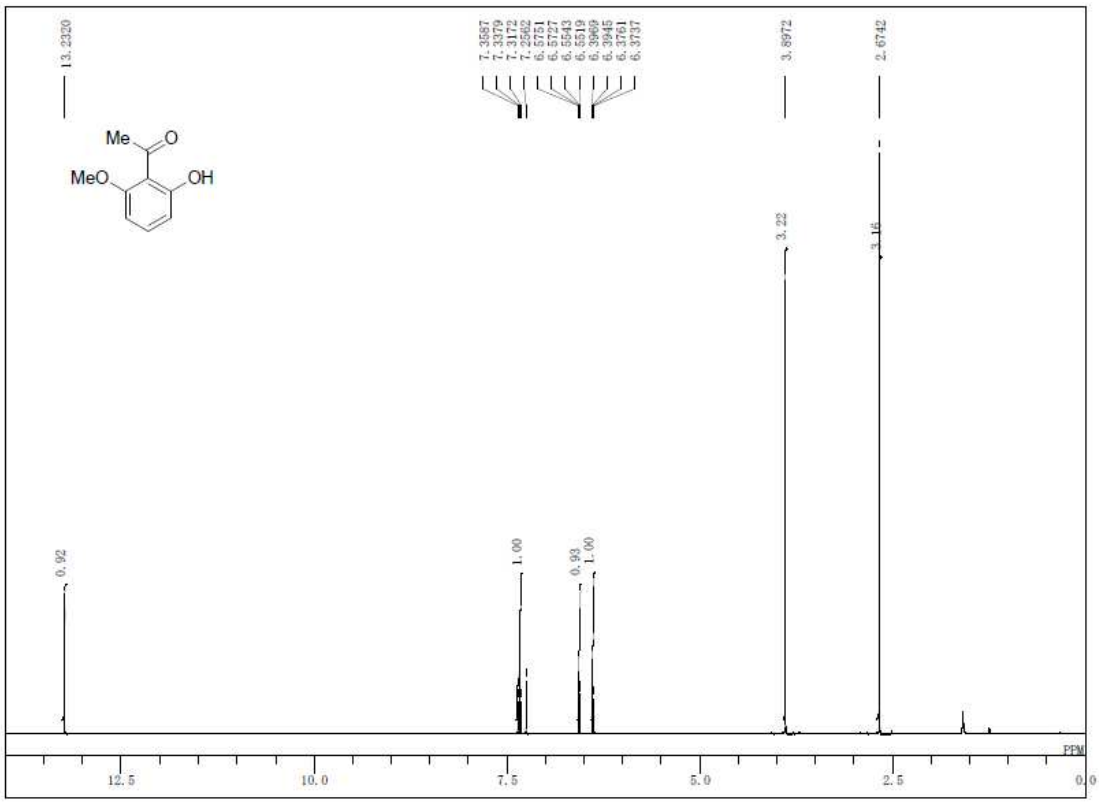
^{1}H NMR ($CDCl_3$) of **2**



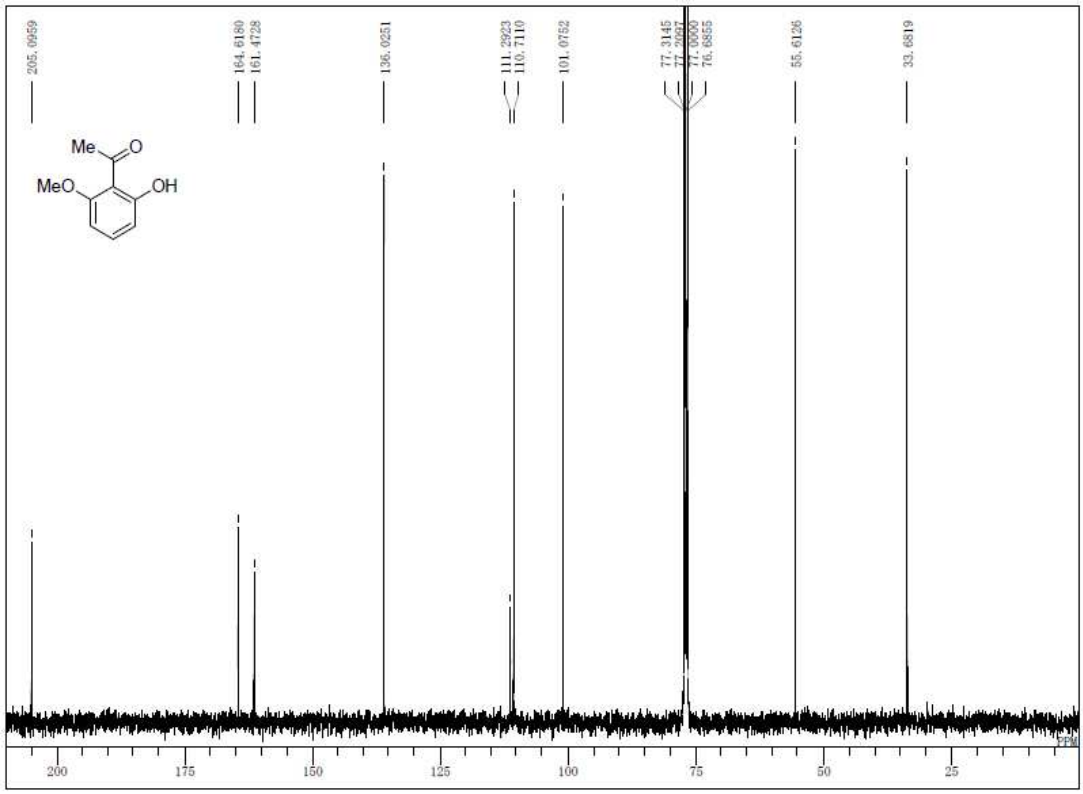
^{13}C NMR ($CDCl_3$) of **2**



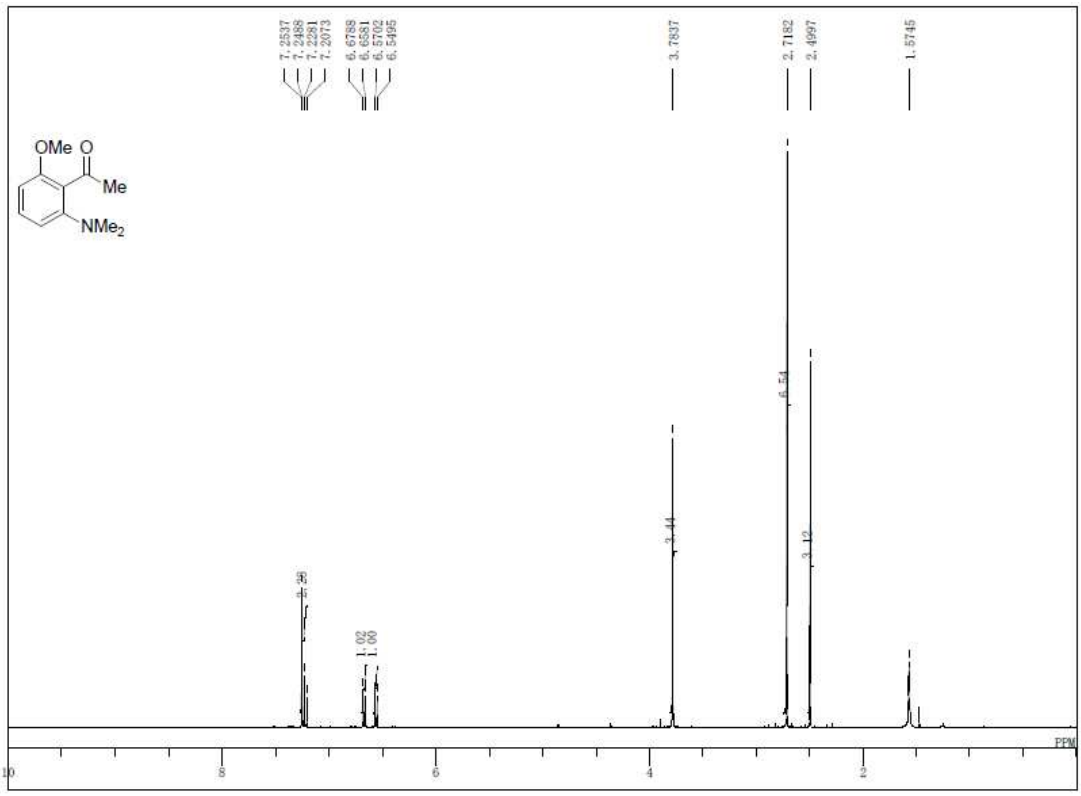
^{1}H NMR ($CDCl_3$) of **3**



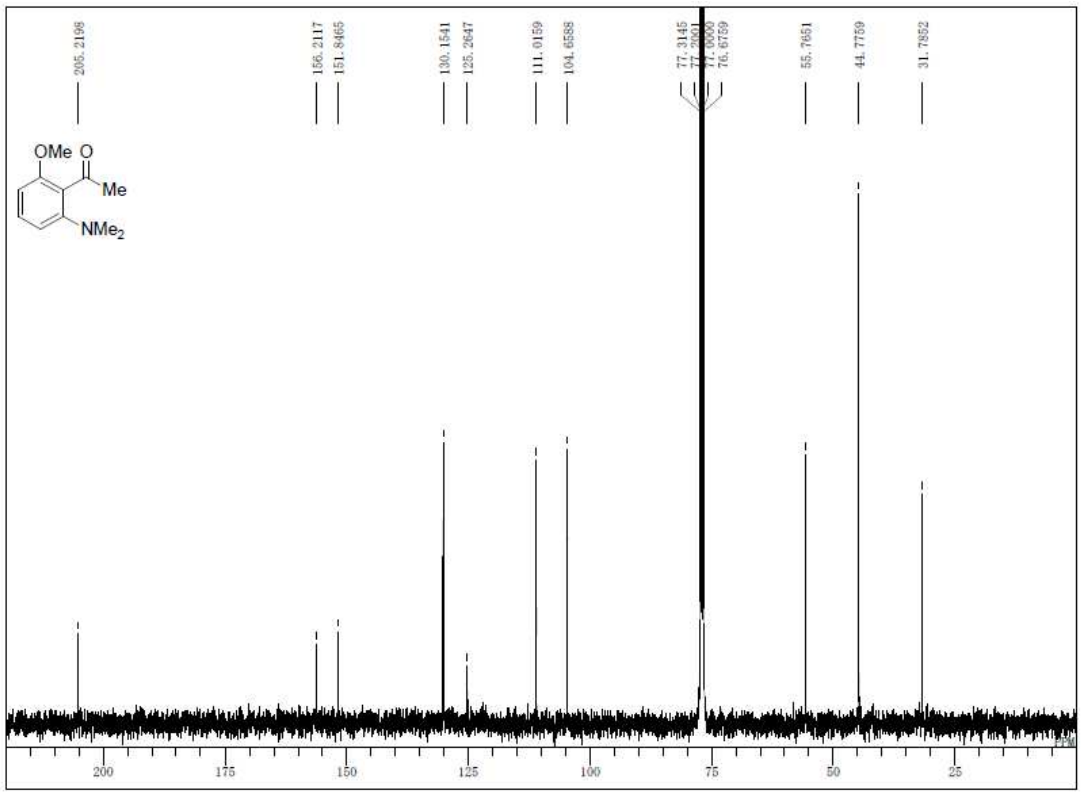
^{13}C NMR ($CDCl_3$) of **3**



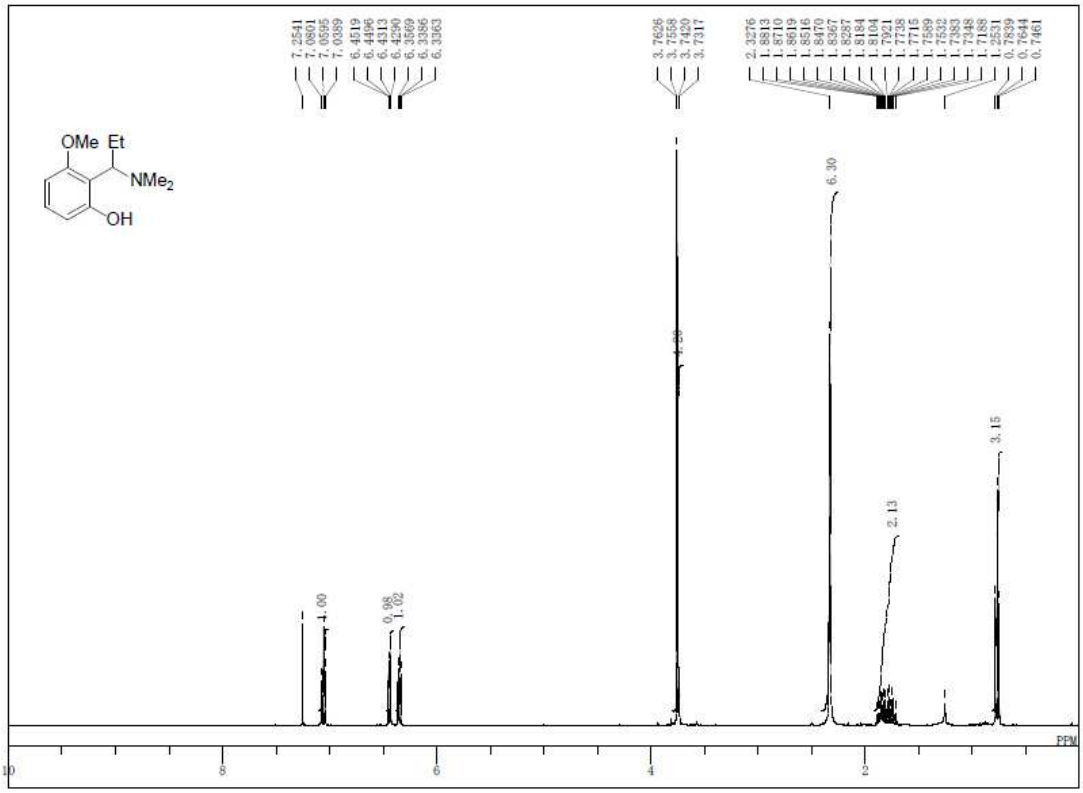
^{1}H NMR ($CDCl_3$) of **4**



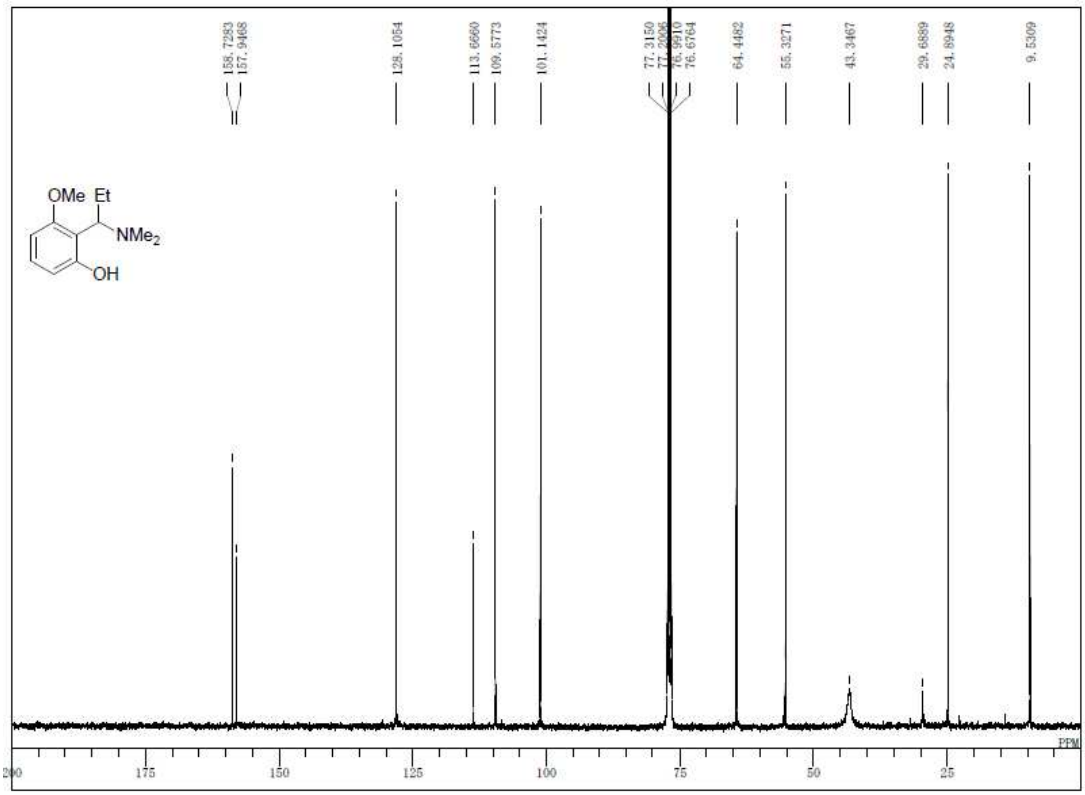
^{13}C NMR ($CDCl_3$) of **4**



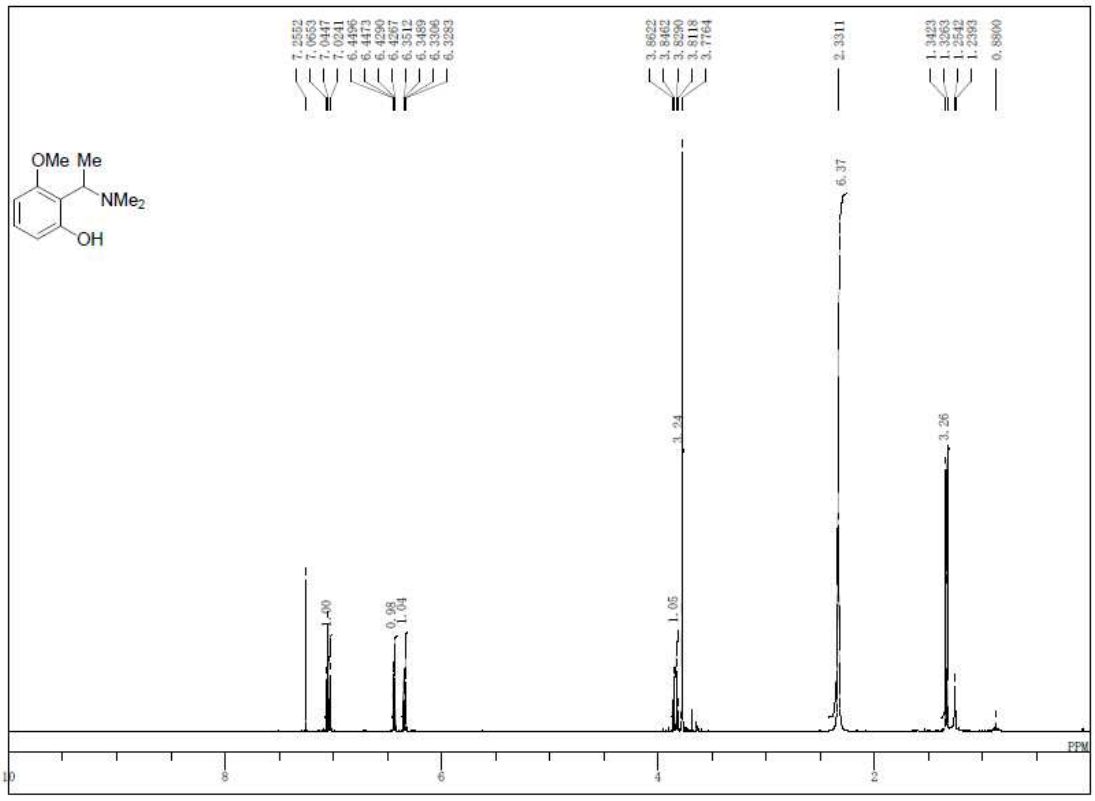
^{1}H NMR ($CDCl_3$) of **5a**



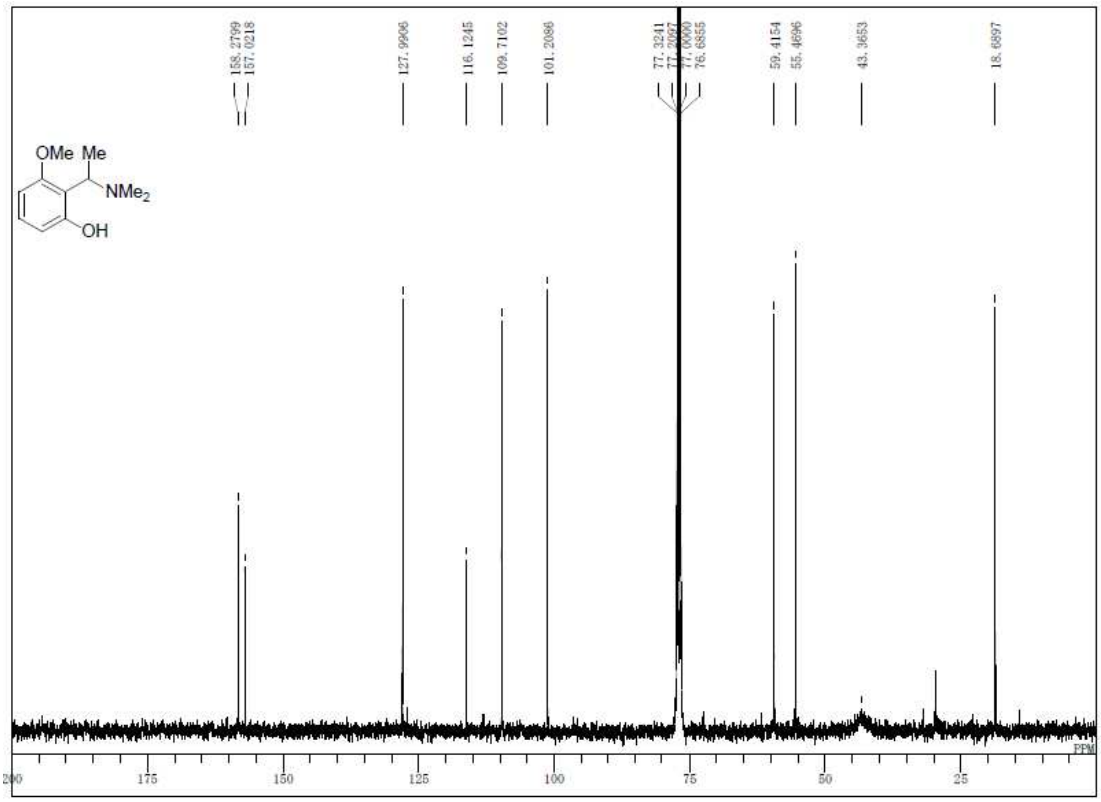
^{13}C NMR ($CDCl_3$) of **5a**



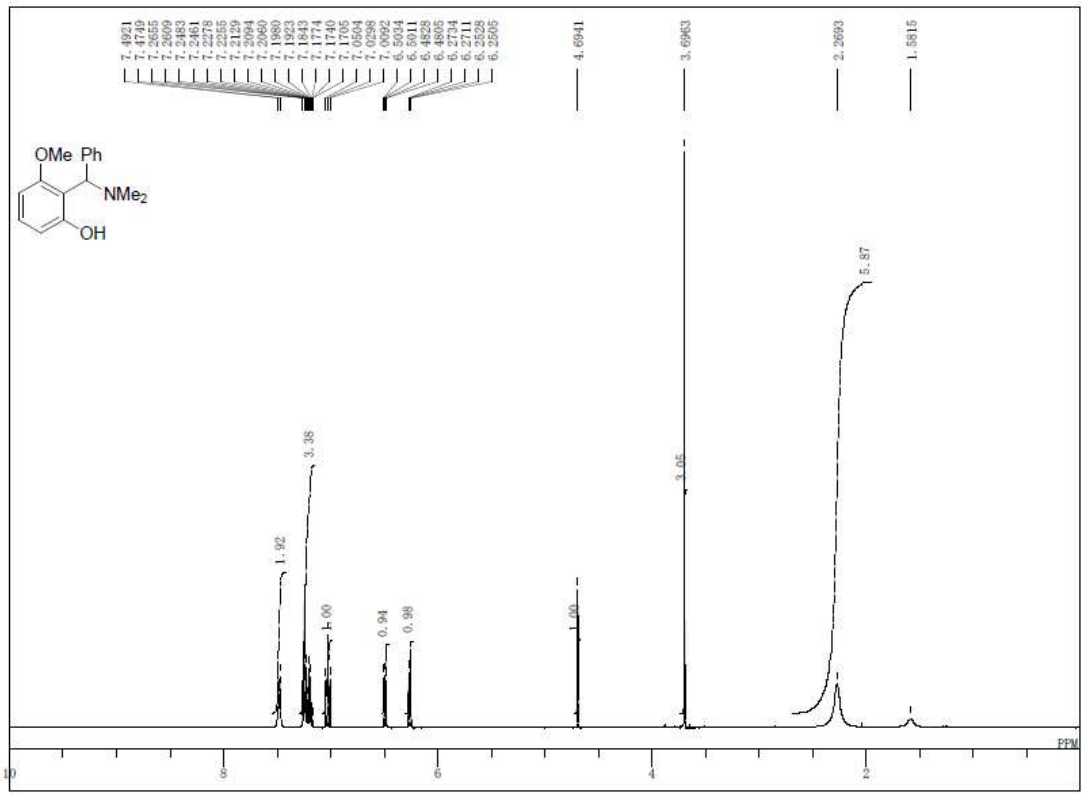
^{1}H NMR ($CDCl_3$) of **5b**



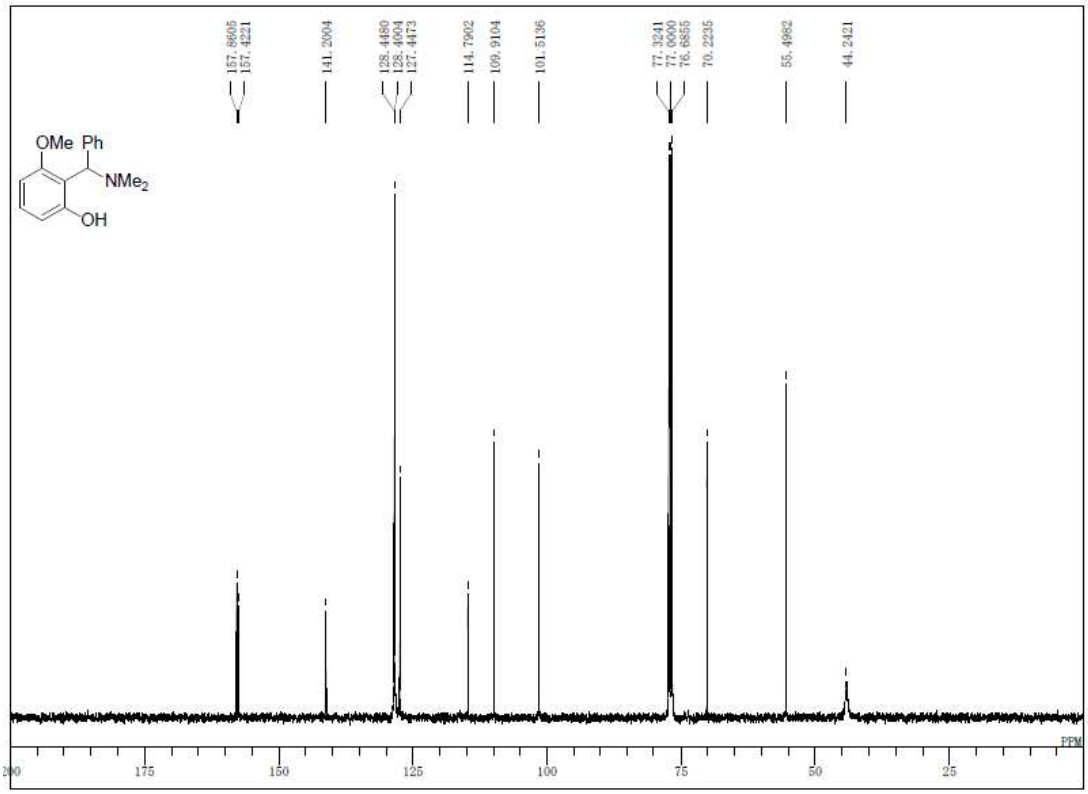
^{13}C NMR ($CDCl_3$) of **5b**



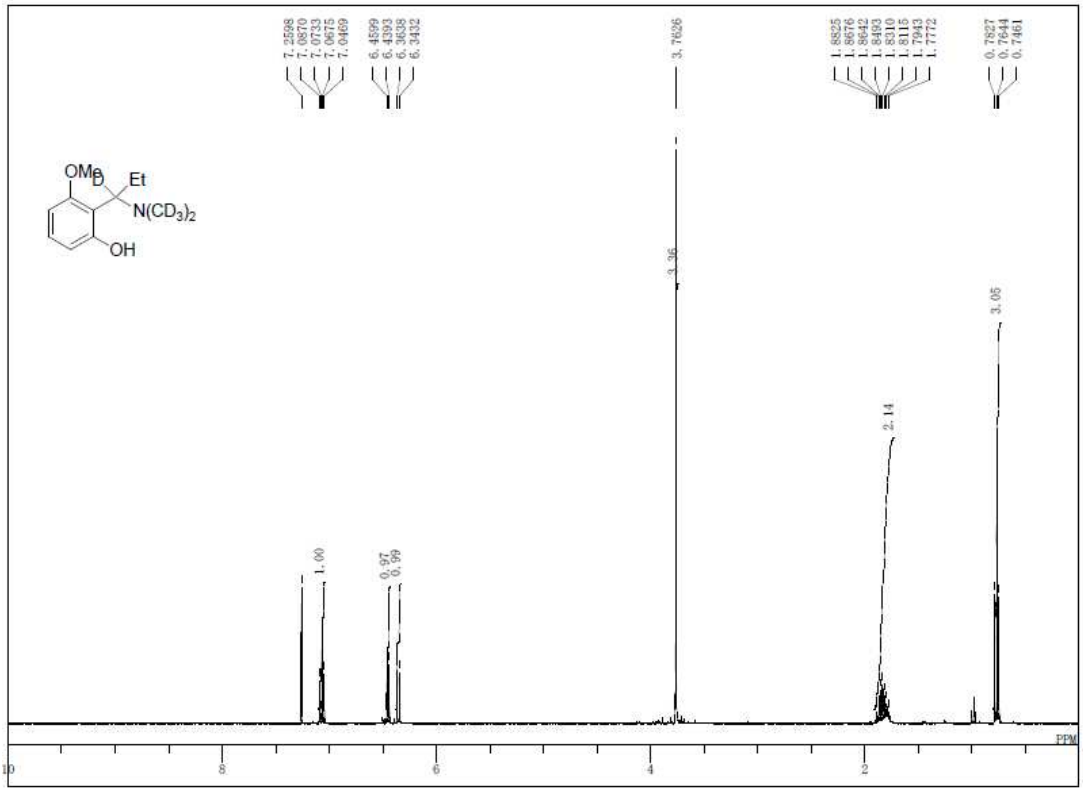
^{1}H NMR ($CDCl_3$) of **5c**



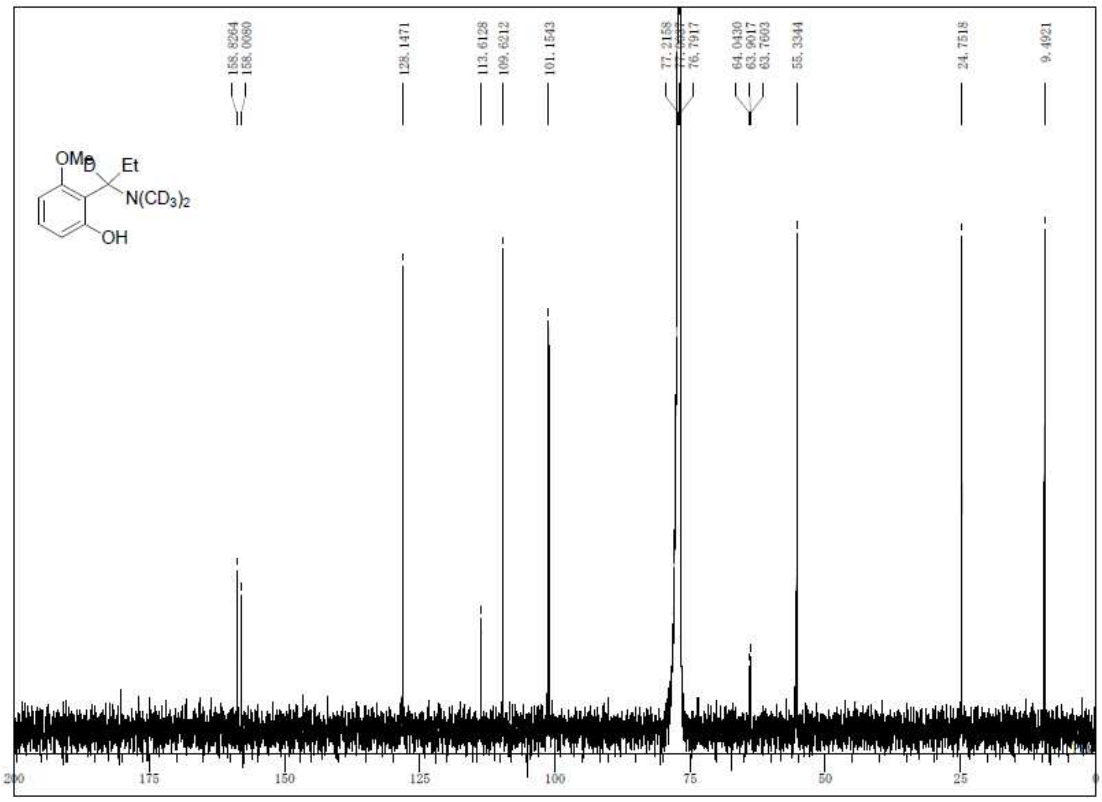
^{13}C NMR ($CDCl_3$) of **5c**



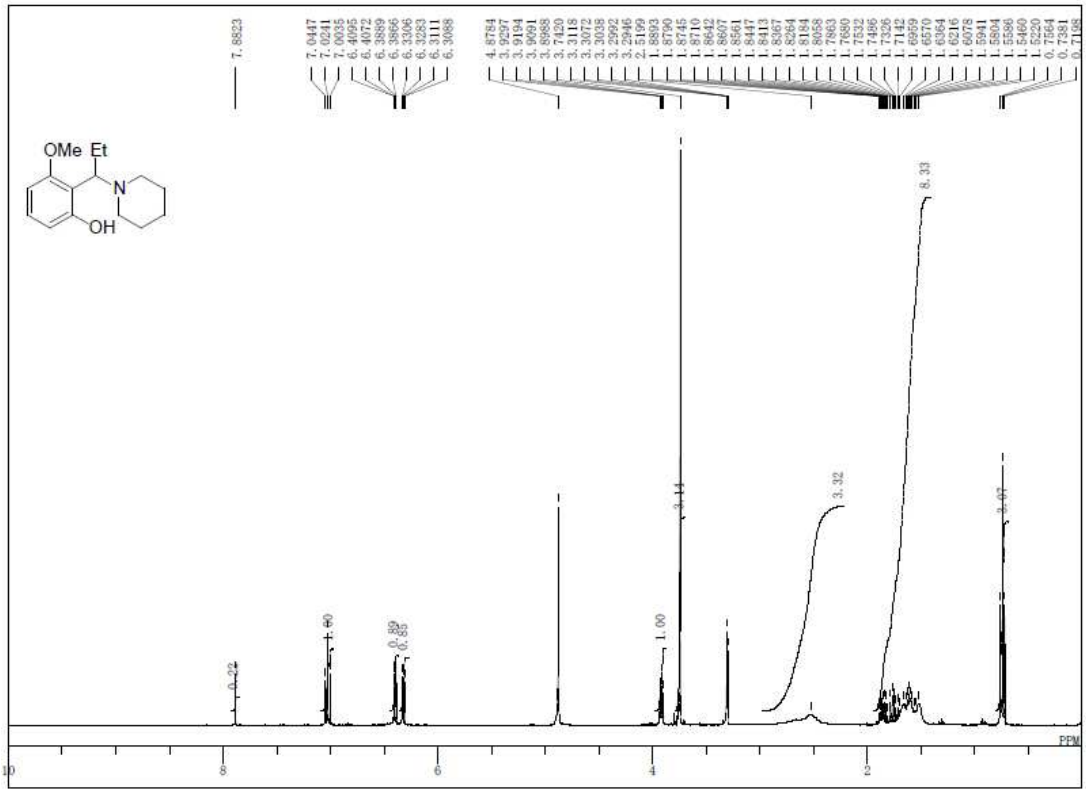
^{1}H NMR ($CDCl_3$) of **5a-*d***



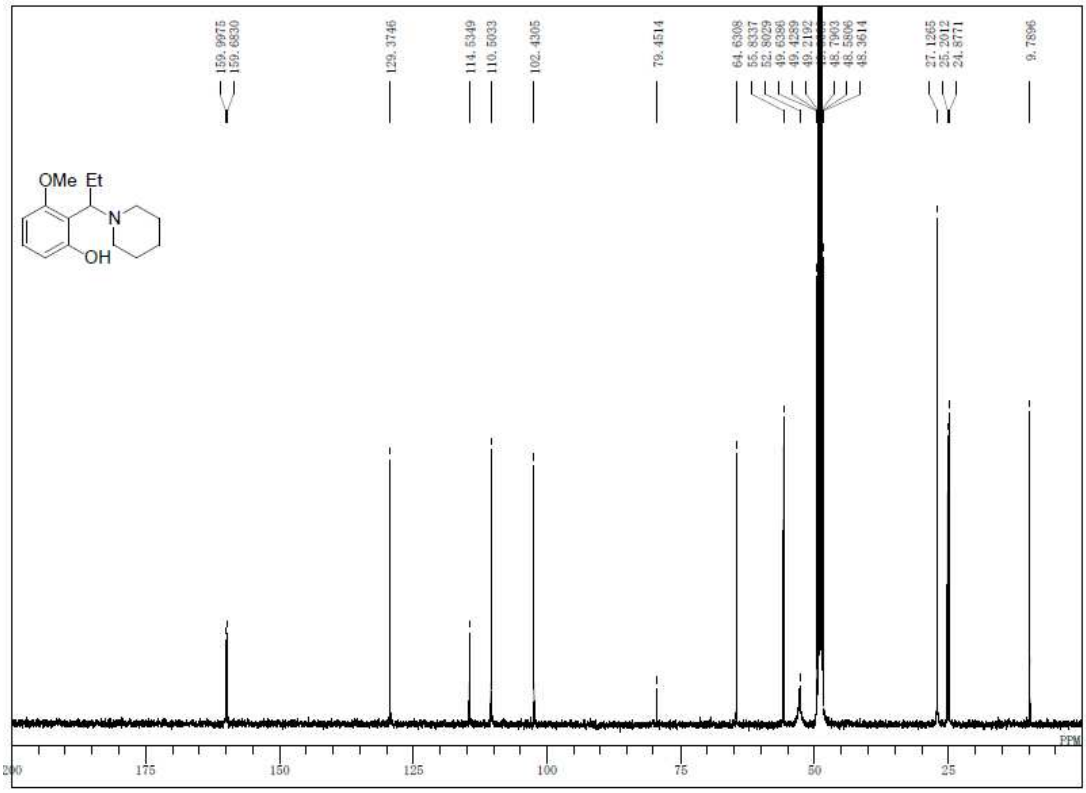
^{13}C NMR ($CDCl_3$) of **5a-*d***



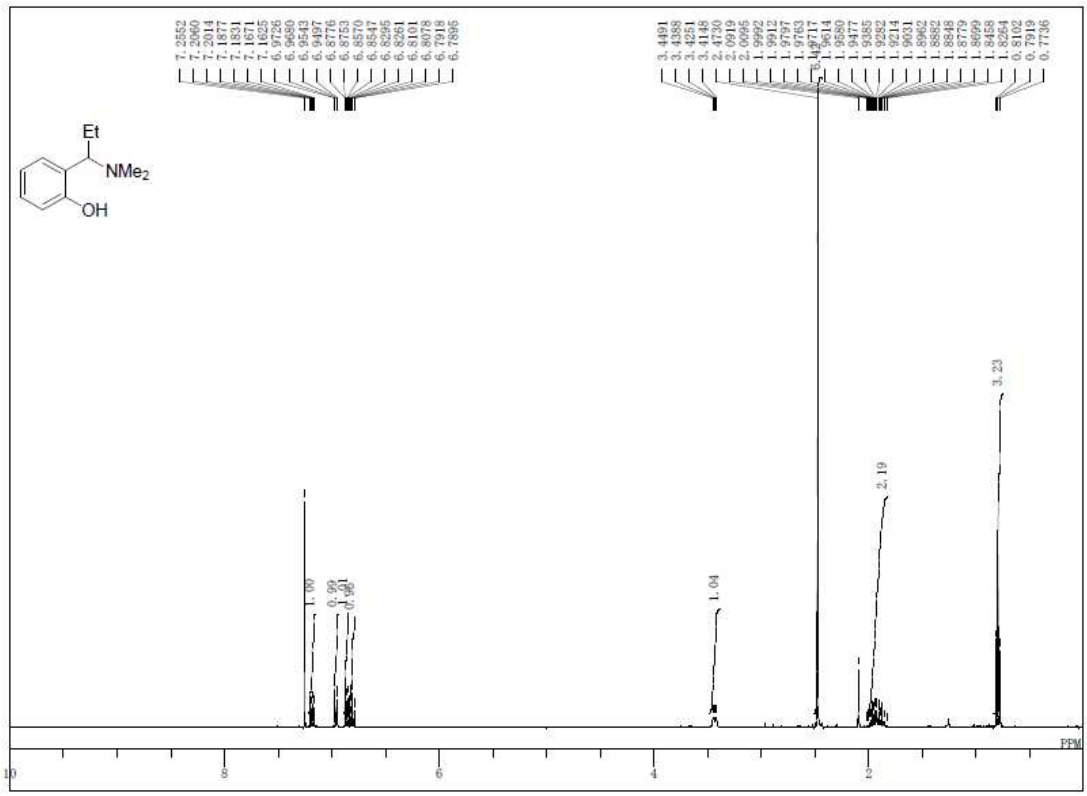
^{1}H NMR (CD_3OD) of **8**



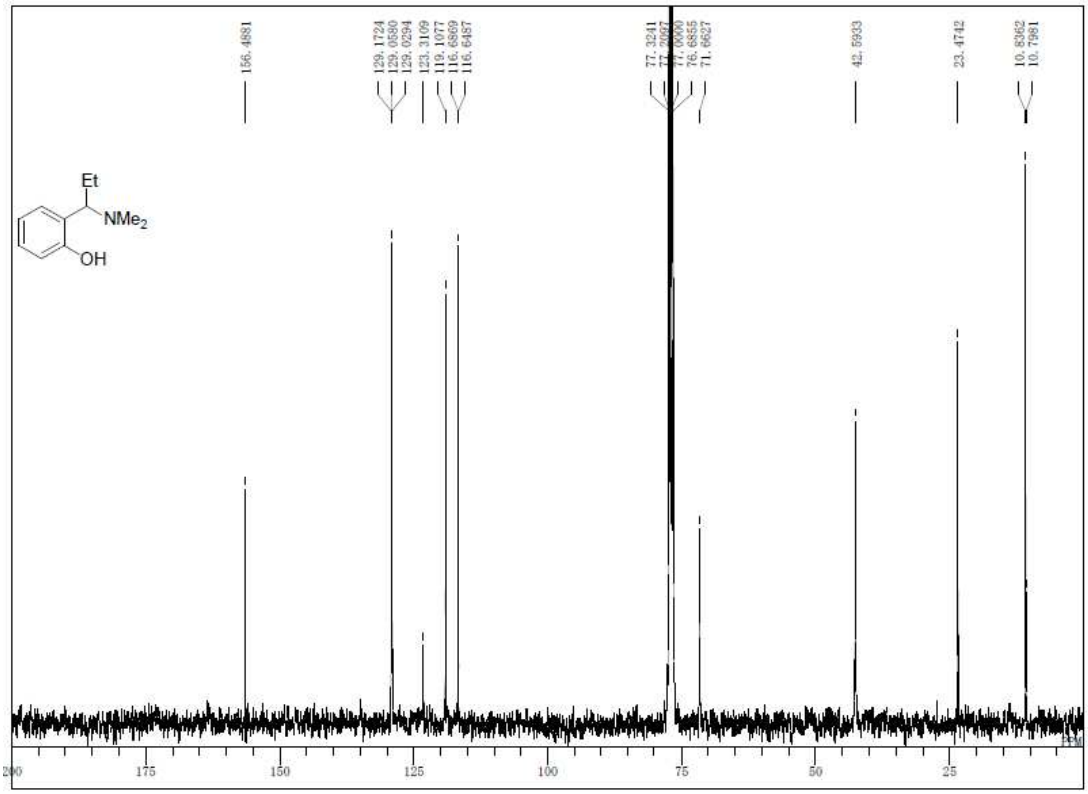
^{13}C NMR (CD_3OD) of **8**



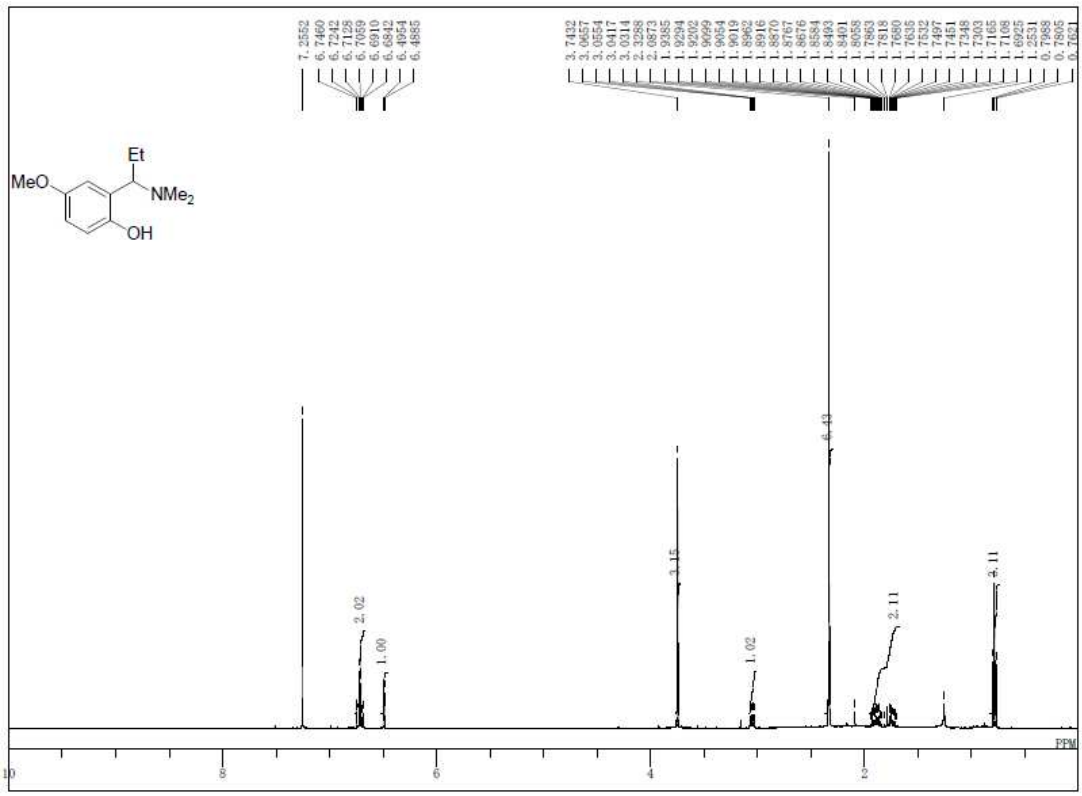
^{1}H NMR ($CDCl_3$) of **10**



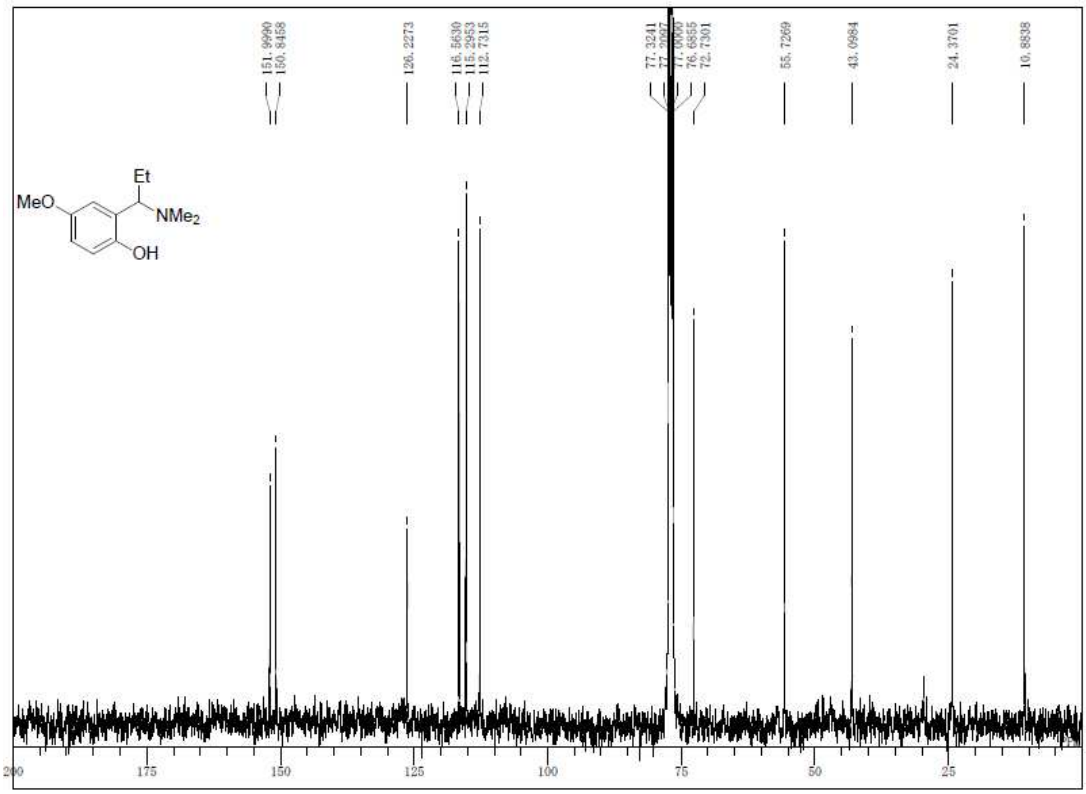
^{13}C NMR ($CDCl_3$) of **10**



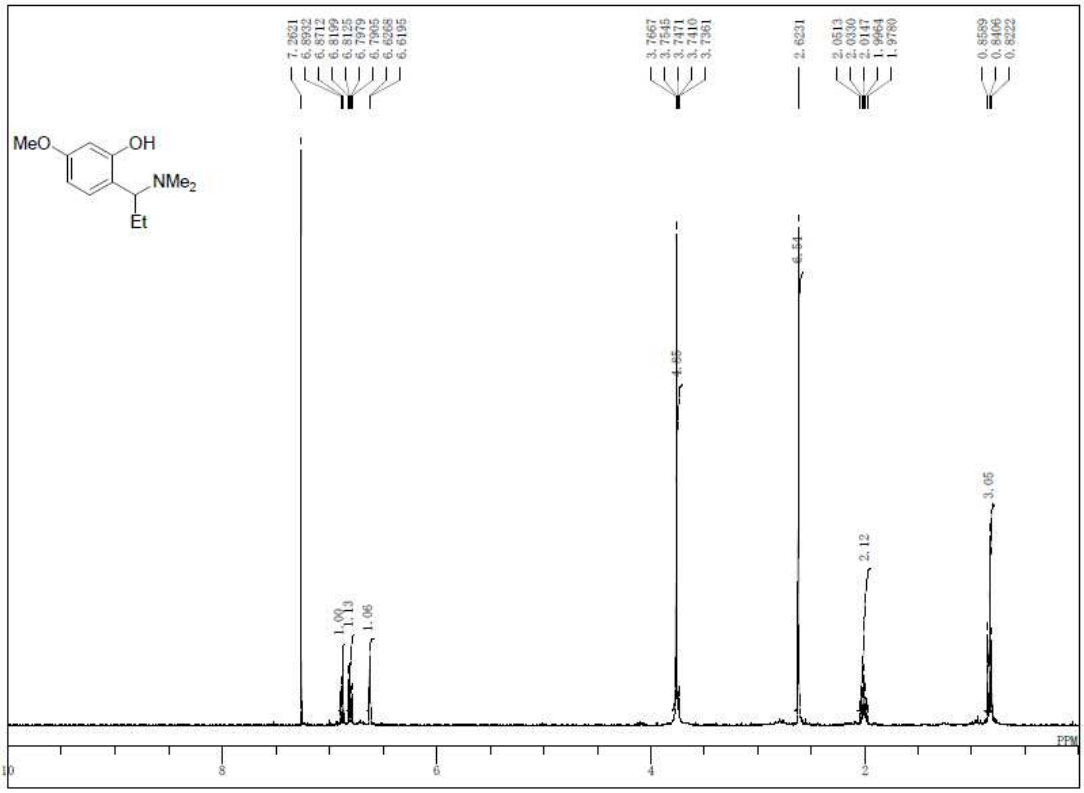
^{1}H NMR ($CDCl_3$) of **12a**



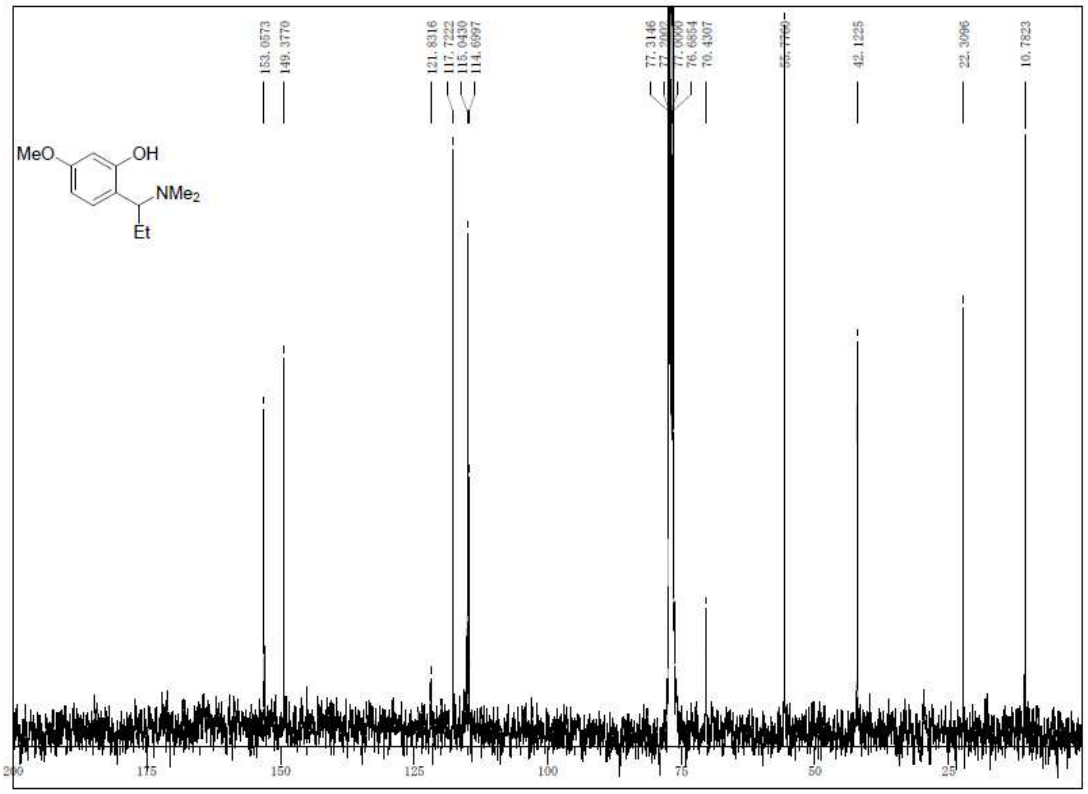
^{13}C NMR ($CDCl_3$) of **12a**



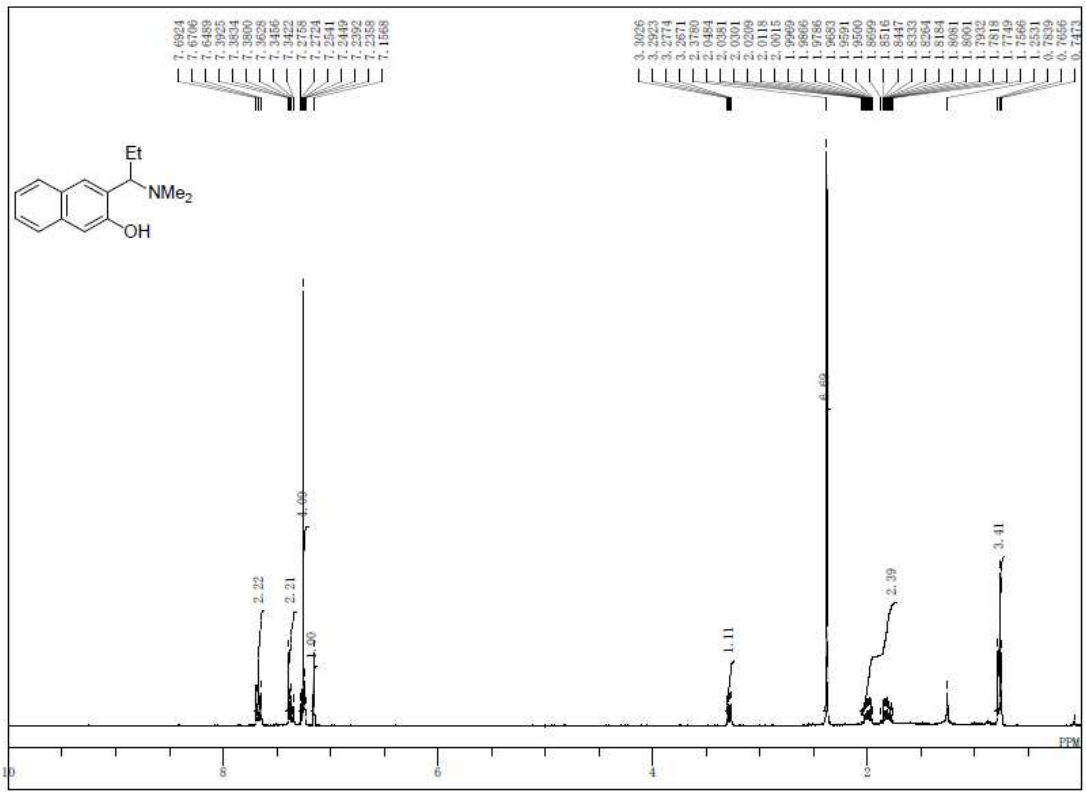
^{1}H NMR ($CDCl_3$) of **12b**



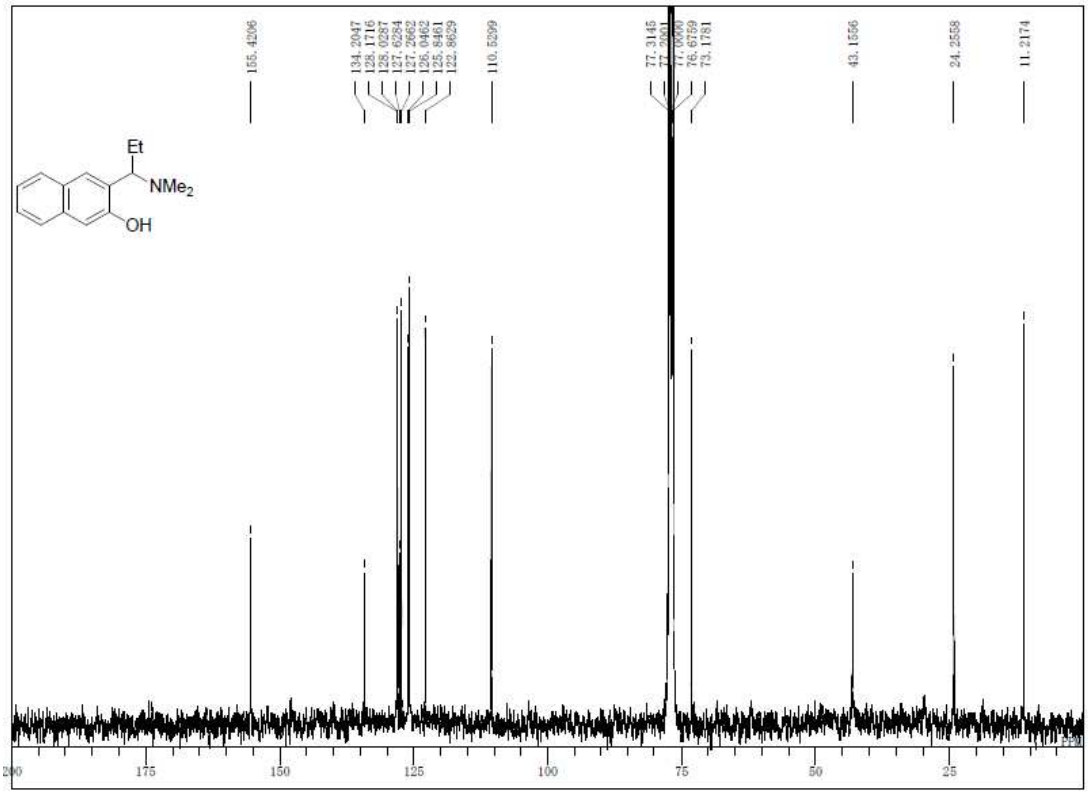
^{13}C NMR ($CDCl_3$) of **12b**



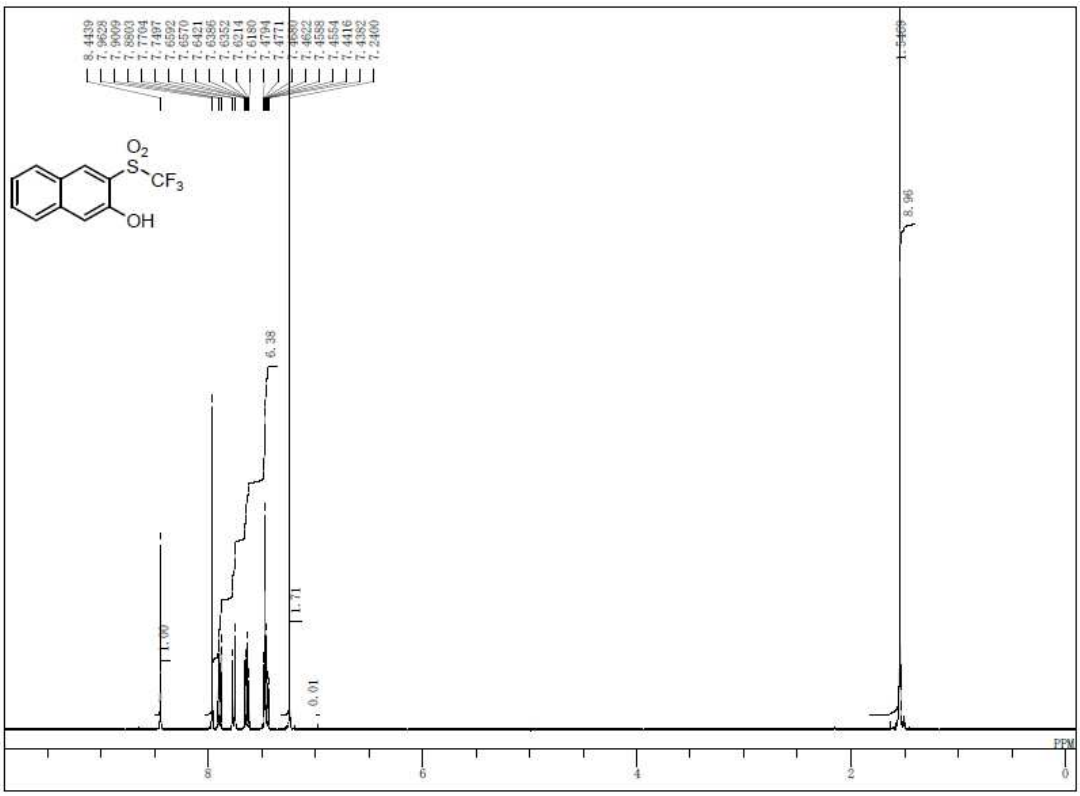
^{1}H NMR ($CDCl_3$) of **14**



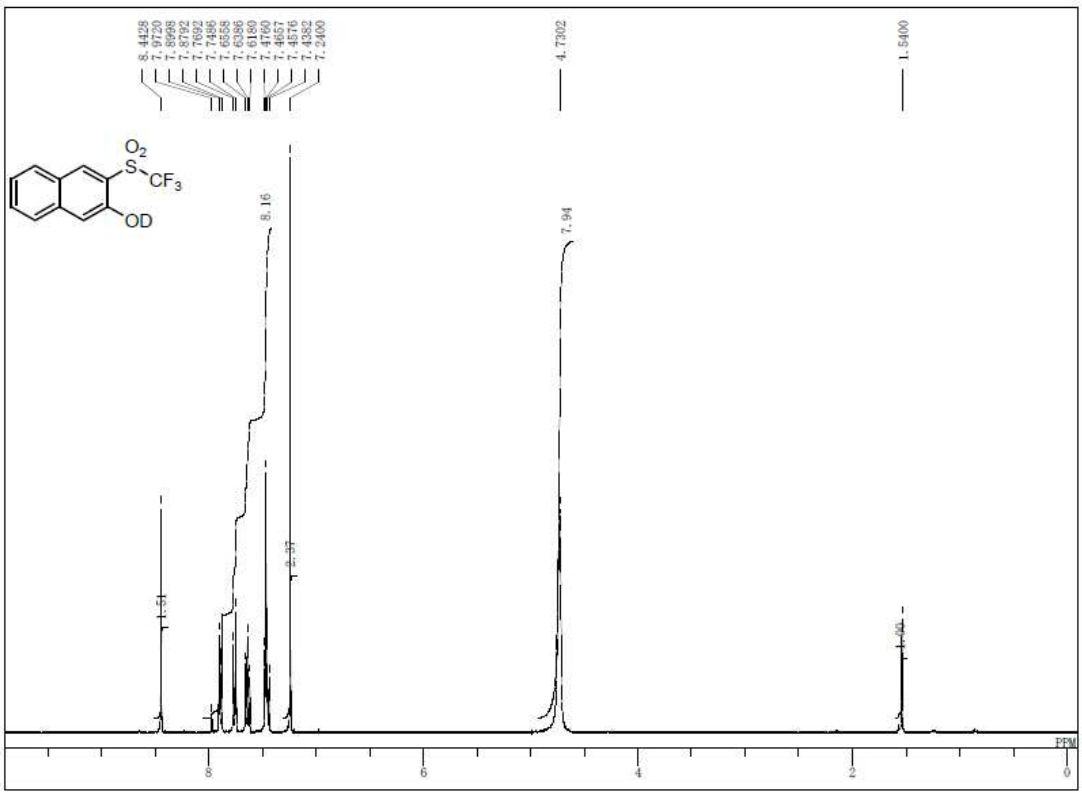
^{13}C NMR ($CDCl_3$) of **14**



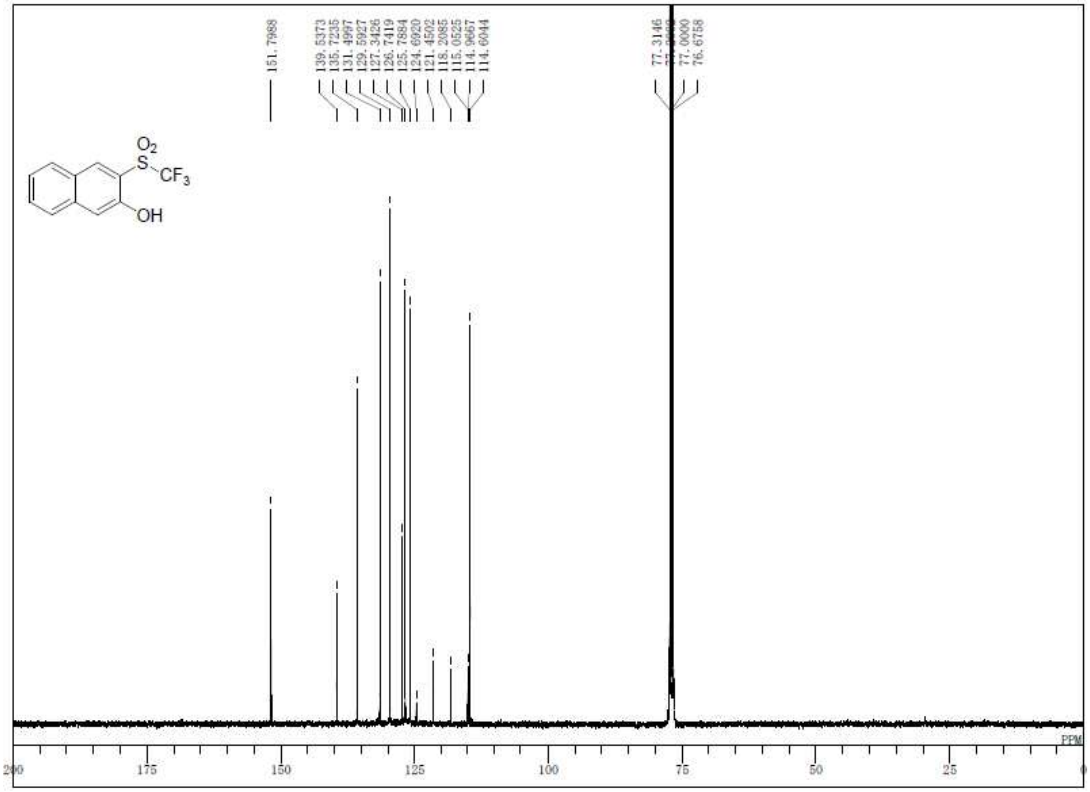
^{1}H NMR ($CDCl_3$) of **15**



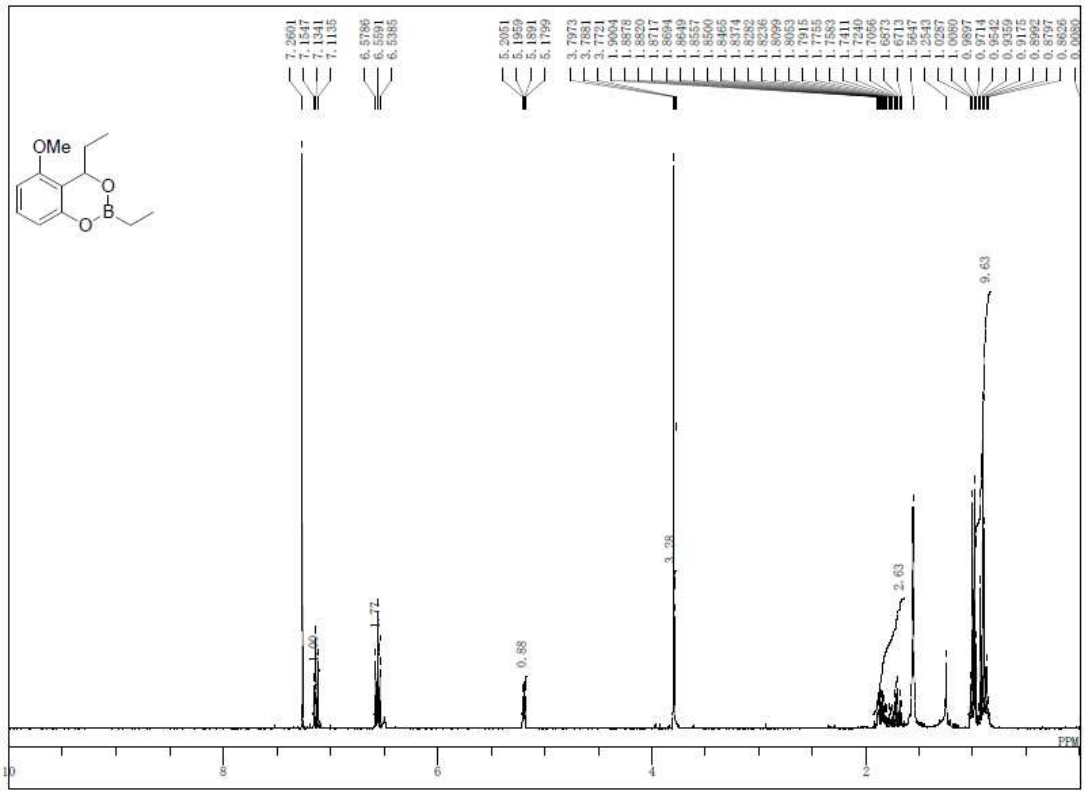
^{1}H NMR ($CDCl_3$) of **15** + D_2O



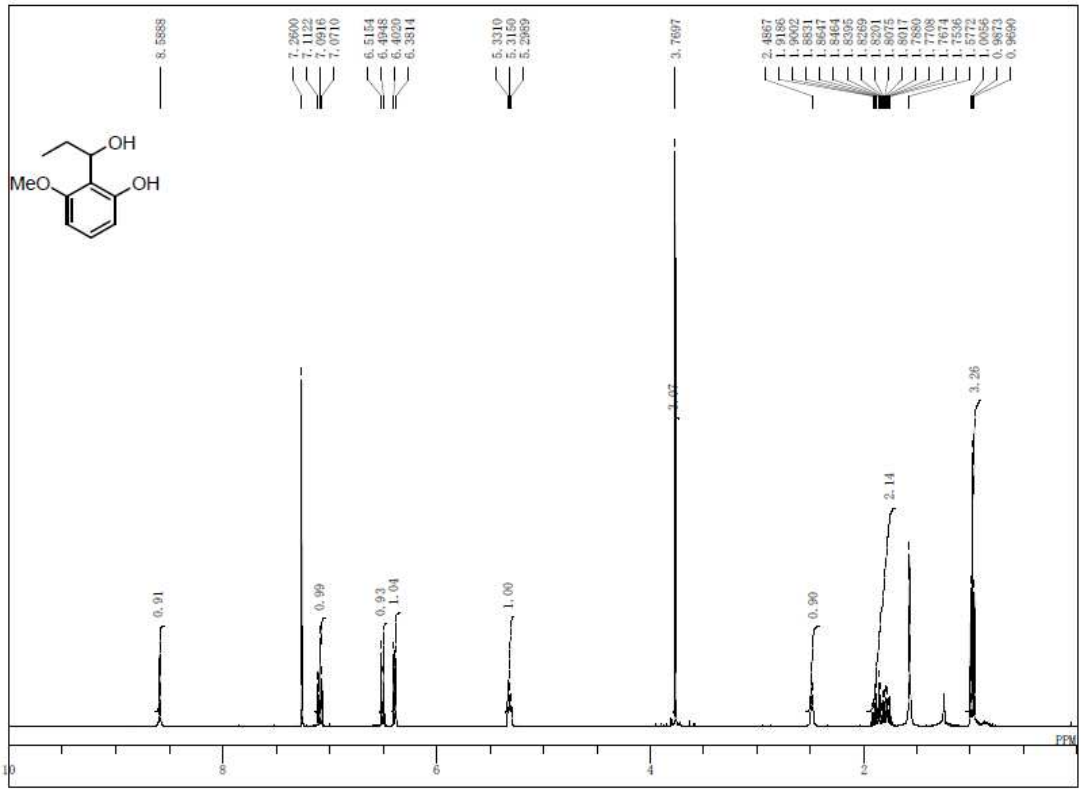
^{13}C NMR ($CDCl_3$) of **15**



^{1}H NMR ($CDCl_3$) of **6**



^{1}H NMR ($CDCl_3$) of **16**



^{13}C NMR ($CDCl_3$) of **16**