Supporting Information

Addition and *in situ* halo-cyclization of ω-alkenyl Grignard reagents with aldehydes, ketone, carbon dioxide and azodicarboxylate

Yasutomo Yamamoto*, Misa Shimizu, Ai Ohara, Akari Miyawaki, and Kiyoshi Tomioka*

Faculty of Pharmaceutical Sciences, Doshisha Women's College of Liberal Arts

Kodo, Kyotanabe 610-0395, Japan

yayamamo@dwc.doshisha.ac.jp; tomioka@pharm.kyoto-u.ac.jp

General

All melting points are uncorrected. Silica gel was used for column chromatography. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) were measured in $CDCl_3$ and chemical shift values and coupling constants are presented in ppm δ relative to tetramethylsilane and Hz, respectively. Abbreviations are as follows: s, singlet; d, doublet; m, multiplet. ^{13}C peak multiplicity assignments were made based on DEPT data. IR spectroscopy of oil and solid samples were measured as neat liquid films and KBr pellets, respectively. The wave numbers of maximum absorption peaks of IR spectroscopy are presented in cm^{-1}. Grignard reagents **1b-f** were prepared as THF solution from the corresponding alkyl halide and magnesium. Aldehydes **2a-d** and acetophenone (**8**) were distillated prior to use. Dehydrated solvents were purchased and used without further desiccation. Other reagents were purchased and used as received.

General procedure for the oxidative cyclization

Table 1, Entry 1. 2-(Bromomethyl)-5-phenyltetrahydrofuran (3a)[1]

Under argon atmosphere to the solution of 3-butenylmagnesium bromide (**1a**) (0.5 M solution in THF, 2.4 mL, 1.2 mmol) in THF (1.6 mL) was added benzaldehyde (**2a**) (102 μL, 1.0 mmol) at 0 °C over 5 min. After stirring for 0.5 h at the same temperature, a solution of $PhI(OAc)_2$ (1.29 g, 4.0 mmol) in 1,2-dichloroethane (11 mL) was added at 0 °C over 5 min. The reaction mixture was stirred for 1 h at room temperature. To the mixture was added satd $Na_2S_2O_3$ (10 mL) and extracted with AcOEt three times. The combined organic layers were dried over Na_2SO_4 and concentrated. The resulting crude mixture was purified by silica gel column chromatography (hexane/AcOEt 10/1) to give **3a** (142 mg, 60%, *cis*/*trans* 1/2.3) as a pale yellow oil. ^{1}H NMR: 1.90-1.95 (2H, m), 2.27

[1] Hartung, J.; Kneuer, R.; Laug, S.; Schmidt, P.; Špehar, K.; Svoboda, I.; Fuess, H. *Eur. J. Org. Chem.* **2003**, 4033–4052.

(1H, m), 2.41 (1H, m), 3.46 (1H, dd, *J* = 6.9, 10.3), 3.55 (1H, dd, *J* = 4.6, 10.3), 4.30 (0.3H, m, *cis* H-2), 4.49 (0.7H, m, *trans* H-2), 4.95 (0.3H, dd, *J* = 6.3, 8.6, *cis* H-5), 5.09 (0.7H, dd, *J* = 6.9, 7.4, *trans* H-5), 7.26-7.34 (5H, m).

Table 1, Entry 2. 2-(Bromomethyl)-5-(4-chlorophenyl)tetrahydrofuran (3b)

Column chromatography (toluene/AcOEt 1/0 to 3/1) gave **3b** (246 mg, 91% from 1 mmol of **2b**, *cis*/*trans* 1/2.8) as a pale yellow oil. Diastereomers were partially separated by column chromatography (hexane/acetone 20/1) to give pure *trans*-**3b** and a mixture of *cis*/*trans*-**3b** (*cis*/*trans* 1/0.16).

trans-**3b**: colorless oil. ^{1}H NMR: 1.87-2.03 (2H, m), 2.23-2.36 (2H, m), 3.43 (1H, dd, *J* = 6.9, 10.3), 3.52 (1H, dd, *J* = 4.6, 10.3), 3.78 (3H, s), 4.45 (1H, m), 5.02 (1H, dd, *J* = 6.3, 7.5), 6.86 (2H, d, *J* = 8.6), 7.24 (2H, d, *J* = 8.6). ^{13}C NMR: 31.2 (CH_2), 35.1 (CH_2), 36.1 (CH_2), 55.3 (CH_3), 78.5 (CH), 81.3 (CH), 113.7 (CH), 127.0 (CH), 134.5 (C), 159.0 (C). IR: 2935, 1612, 1513. MS (EI) *m/z*: 271 (M^+). HRMS-DART *m/z*: $[M+H]^+$ calcd for $C_{12}H_{16}BrO_2$, 271.0334; found, 271.0333.

cis-**3b**: ^{1}H NMR: 1.85-1.98 (2H, m), 2.17-2.26 (2H, m), 3.48 (1H, dd, *J* = 6.3, 10.3), 3.54 (1H, dd, *J* = 5.2, 10.3), 3.80 (3H, s), 4.31 (1H, m), 4.89 (1H, dd, *J* = 6.3, 8.6), 6.88 (2H, m), 7.30 (2H, m). ^{13}C NMR: 30.4 (CH_2), 34.2 (CH_2), 36.2 (CH_2), 55.3 (CH_3), 78.5 (CH), 81.9 (CH), 113.8 (CH), 127.2 (CH), 134.1 (C), 159.1 (C). IR: 2958, 1613, 1513. MS (EI) *m/z*: 271 (M^+). HRMS-DART *m/z*: $[M+H]^+$ calcd for $C_{12}H_{16}BrO_2$, 271.0334; found, 271.0328. IR, MS and HRMS data described above were those of a mixture of diastereomers (*cis*/*trans* 1/0.16). ^{1}H and ^{13}C NMR data of *cis*-**3b** was determined by comparing the NMR data of pure *trans*-**3b** and those of a mixture of *cis*/*trans*-**3b**.

Table 1, Entry 3. 2-(Bromomethyl)-5-(4-chlorophenyl)tetrahydrofuran (3c)

Column chromatography (hexane/AcOEt 20/1) gave **3c** (121 mg, 44% from 1 mmol of **2c**, *cis*/*trans* 1/4.1) as a pale yellow oil. Diastereomers were separated by column chromatography (hexane/toluene 2/1).

trans-**3c**: colorless oil. ^{1}H NMR: 1.83-1.93 (2H, m), 2.25 (1H, m), 2.41 (1H, m), 3.45 (1H, dd, *J* = 6.3, 10.3), 3.53 (1H, dd, *J* = 4.5, 10.3), 4.52 (1H, m), 5.06 (1H, dd, *J* = 6.3, 8.0), 7.25-7.27 (2H, m), 7.29-7.31 (2H, m). ^{13}C NMR: 31.1 (CH_2), 35.3 (CH_2), 35.9 (CH_2), 78.7 (CH), 80.8 (CH), 126.9 (CH), 129.0 (CH), 133.0 (C), 141.2 (C), IR: 2925, 1730, 1492. MS (EI) *m/z*: 276 (M^+). HRMS-DART *m/z*: $[M+H]^+$ calcd for $C_{11}H_{13}BrClO$, 274.9838; found, 274.9846.

cis-**3c**: colorless oil. ^{1}H NMR: 1.84 (1H, m), 1.95 (1H, m), 2.20 (1H, m), 2.30 (1H, m), 3.50 (1H, dd, *J* = 6.3, 10.3), 3.55 (1H, dd, *J* = 5.2, 10.3), 4.33 (1H, m), 4.91 (1H, dd, *J* = 6.9, 8.0), 7.29-7.31 (4H, m). ^{13}C NMR: 30.3 (CH_2), 34.4 (CH_2), 35.8 (CH_2) 78.5 (CH), 81.3 (CH), 128.5 (CH), 133.6 (C), 140.2 (C). IR: 2930, 1740, 1500. MS (EI) *m/z*: 276 (M^+). HRMS-DART *m/z*: $[M+H]^+$ calcd for $C_{11}H_{13}BrClO$, 274.9838; found, 274.9834.

Table 1, Entry 4. 2-(Bromomethyl)-5-phenethyltetrahydrofuran (3d)

Column chromatography (hexane/AcOEt 40/1) gave **3d** (207 mg, 77% from 1 mmol of **2d**, *cis/trans* 1/1.5) as a colorless oil. Diastereomers were partially separated by column chromatography (hexane/AcOEt 40/1) to give pure *trans*-**3d** and a mixture of *cis*/*trans*-**3d** (*cis*/*trans* 1/0.6).

trans-**3d**: colorless oil. ^{1}H NMR: 1.59 (1H, m), 1.73-1.79 (2H, m), 1.91 (1H, m), 2.07 (1H, m), 2.16 (1H, m), 2.67 (1H, ddd, *J* = 6.3, 9.8, 13.8), 2.62 (1H, ddd, *J* = 6.0, 10.3, 13.8), 3.35 (1H, dd, *J* = 6.9, 10.0), 3.46 (1H, dd, *J* = 5.2, 10.0), 4.04 (1H, dddd, *J* = 5.8, 5.8, 7.2, 7.2), 4.26 (1H, dddd, *J* = 5.2, 6.9, 6.9, 6.9), 7.16-7.20 (3H, m), 7.25-7.29 (2H, m). ^{13}C NMR: 30.9 (CH_2), 31.9 (CH_2), 32.4 (CH_2), 36.1 (CH_2), 37.3 (CH_2), 77.7 (CH), 79.3 (CH), 125.8 (CH), 128.31 (CH), 128.37 (CH), 141.9 (C). IR: 2931, 1602, 1454. MS (EI) *m/z*: 268 (M^+). HRMS-DART *m/z*: $[M+H]^+$ calcd for $C_{13}H_{18}BrO$, 269.0541; found, 269.0534.

cis-**3d**: ^{1}H NMR: 1.59 (1H, m), 1.75-1.83 (2H, m), 1.93 (1H, m), 1.97-2.11 (2H, m), 2.67 (1H, m), 2.74 (1H, m), 3.35 (1H, dd, *J* = 6.9, 9.8), 3.45 (1H, dd, *J* = 5.2, 9.8), 3.94 (1H, dddd, *J* = 6.3, 6.9, 6.9, 6.9), 4.15 (1H, dddd, *J* = 5.2, 6.3, 6.3, 6.9), 7.17-7.21 (3H, m), 7.26-7.29 (2H, m). ^{13}C NMR: 30.0 (CH_2), 30.8 (CH_2), 32.3 (CH_2), 35.9 (CH_2), 37.6 (CH_2), 78.1 (CH), 79.8 (CH), 125.7 (CH), 128.29 (CH), 128.34 (CH), 141.9 (C). IR: 2929, 1602, 1495, 1454. MS (EI) *m/z*: 268 (M^+). HRMS-DART *m/z*: $[M+H]^+$ calcd for $C_{13}H_{18}BrO$, 269.0541; found, 269.0533. IR, MS and HRMS data described above were those of a mixture of diastereomers (*cis*/*trans* 1/0.6). ^{1}H and ^{13}C NMR data of *cis*-**3d** was determined by comparing the NMR data of pure *trans*-**3d** and those of a mixture of *cis*/*trans*-**3d**.

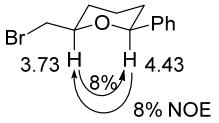
Scheme 3. 2-(Bromomethyl)-6-phenyltetrahydro-2*H*-pyran (3e)

Column chromatography (hexane/AcOEt 20/1) gave **3e** (108 mg, 42% from 1 mmol of **2a**, *cis/trans* 7/1) as a colorless oil. Diastereomers were separated by column chromatography (hexane/toluene 2/1 to 1/2).

trans-**3e**: colorless oil. ^{1}H NMR: 1.50-1.76 (4H, m), 1.92-2.08 (2H, m), 3.48 (1H, dd, *J* = 5.7, 10.3), 3.54 (1H, dd, *J* = 6.9, 10.3), 3.92 (1H, m), 4.91 (1H, dd, *J* = 5.2, 5.2), 7.25-7.47 (5H, m). ^{13}C NMR: 18.6 (CH_2), 28.3 (CH_2), 28.9 (CH_2), 34.5 (CH_2), 71.1 (CH), 73.1 (CH), 126.6 (CH), 127.2 (CH), 128.5 (CH), 141.0 (C). IR: 3028, 2927, 2853, 1494. HRMS-DART *m/z*: $[M+H]^+$ calcd for $C_{12}H_{16}BrO$, 255.0385; found, 255.0375.

cis-**3e**: ^{1}H NMR: 1.39 (1H, m), 1.49 (1H, m), 1.71 (1H, m), 1.83-1.89 (2H, m), 2.00 (1H, m), 3.41 (1H, dd, *J* = 5.7, 10.3), 3.48 (1H, dd, *J* = 5.7, 10.3), 3.73 (1H, dddd, *J* = 2.0, 5.7, 5.7, 11.2), 4.43 (1H, dd, *J* = 2.0, 17.2), 7.22-7.38 (5H, m). ^{13}C NMR: 23.6 (CH_2), 29.5 (CH_2), 33.2 (CH_2), 35.9 (CH_2), 77.3 (CH), 79.9 (CH), 125.8 (CH), 127.4 (CH), 128.3 (CH), 142.8 (C). IR: 3030, 2937, 2855, 1491. HRMS-DART *m/z*: $[M+H]^+$ calcd for $C_{12}H_{16}BrO$, 255.0385; found, 255.0393.

The relative configuration was determined by NOE correlation as shown right.

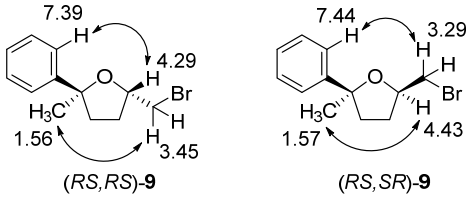


Scheme 3. 3-Bromo-2,2-dimethyl-6-phenyltetrahydro-2*H*-pyran[1] (3f) and 2-(2-bromopropan-2-yl)-5-phenyltetrahydrofuran[1] (3g)

Column chromatography (hexane/AcOEt 20/1) gave **3f** (117 mg, 43% from 1 mmol of **2a**, only *trans* isomer was observed) as a colorless oil and **3g** (32 mg, 12% from 1 mmol of **2a**, *cis*/*trans* 1/1.7) as a colorless oil. The structure and relative configuration of **3f** and **3g** were determined based on the reported NMR data.[1]

Scheme 4. 2-(Bromomethyl)-5-(phenyl)-5-(methyl)tetrahydrofuran (9)

Under argon atmosphere to the solution of $ZnCl_2$ (13.6 mg 0.1 mmol) and 3-butenylmagnesium bromide (**1a**) (0.5 M solution in THF, 2.4 mL, 1.2 mmol) in THF (1.6 mL) was added acetophenone (**8**) (117 μL, 1.0 mmol) at 0 °C over 5 min. After stirring for 0.5 h at the same temperature, a solution of $PhI(OAc)_2$ (1.29 g, 4.0 mmol) in 1,2-dichloroethane (11 mL) was added at 0 °C over 5 min. The reaction mixture was stirred for 1 h at room temperature. To the reaction mixture was added satd $Na_2S_2O_3$ (10 mL) and extracted with AcOEt three times. The combined organic layers were dried over Na_2SO_4, and concentrated. The resulting crude mixture was purified by silica gel column chromatography (hexane/Et_2O 50/1) to give **9** (139 mg, 55%, dr 1/1) as a colorless oil. Diastereomers were separated by column chromatography (hexane/toluene 2/1). The relative configuration was determined by ^{1}H-NOESY correlation as shown below.



(*RS*,*RS*)-**9**: colorless oil. ^{1}H NMR: 1.56 (3H, s), 1.86-1.99 (2H, m), 2.11 (1H, ddd, *J* = 8.3, 8.3, 12.3), 2.27 (1H, ddd, J = 5.4, 7.7, 12.3), 3.45 (1H, dd, *J* = 6.6, 10.3), 3.54 (1H, dd, *J* = 4.6, 10.3), 4.29 (1H, m), 7.22 (1H, m), 7.33 (2H, m), 7.39 (2H, m). ^{13}C NMR: 30.1 (CH_2), 30.4 (CH_3), 36.2 (CH_2), 38.9 (CH_2), 77.8 (CH), 86.0 (C), 124.5 (CH), 126.5 (CH), 128.2 (CH), 147.5 (C). IR: 2970, 2926, 2854, 1445. MS (EI) *m/z*: 254 (M^+). HRMS-DART *m/z*: $[M+H]^+$ calcd for $C_{12}H_{16}BrO$, 255.0385; found, 255.0379.

(*RS*,*SR*)-**9**: colorless oil. ^{1}H NMR: 1.57 (3H, s), 1.75 (1H, m), 2.13 (1H, m), 2.21-2.31 (2H, m), 3.29 (1H, dd, *J* = 7.5, 10.0), 3.50 (1H, dd, *J* = 5.5, 10.0), 4.43 (1H, m), 7.23 (1H, m), 7.32 (2H, m), 7.44 (2H, m). ^{13}C NMR: 29.8 (CH_3), 30.7 (CH_2), 35.7 (CH_2), 39.2 (CH_2), 78.7 (CH), 85.8 (C), 124.6 (CH), 126.6 (CH), 128.1 (CH), 148.1 (C). IR (neat): 2969, 2925, 2854, 1445. MS (EI) *m/z*: 254 (M^+). HRMS-DART *m/z*: $[M+H]^+$ calcd for $C_{12}H_{16}BrO$, 255.0385; found, 255.0386.

Scheme 5. 2-(Iodomethyl)-5-(4-methoxyphenyl)-2-methyltetrahydrofuran (10)

Column chromatography (hexane/AcOEt 10/1) gave **10** (289 mg, 87% from 1 mmol of **2b**, dr 1/1) as a colorless oil. Diastereomers were separated by column chromatography (hexane/AcOEt 20/1).

The less polar isomer: colorless oil. ^{1}H NMR: 1.55 (s, 3H), 1.87-2.04 (m, 2H), 2.18 (m, 1H), 2.29 (m, 1H), 3.36 (d, 1H, *J* = 10.0), 3.41 (d, 1H, *J* = 10.0), 3.80 (s, 3H), 5.00 (dd, 1H, *J* = 6.0, 9.4), 6.86 (m, 2H), 7.25 (m, 2H). ^{13}C NMR: 18.0 (CH_2), 26.6 (CH_3), 35.7 (CH_2), 37.6 (CH_2), 55.2 (CH_3), 81.5 (CH), 81.7 (C), 113.7 (CH), 127.1 (CH), 134.3 (C), 159.0 (C). IR: 2968, 1613, 1513. HRMS-DART *m/z*: $[M+H]^+$ calcd for $C_{13}H_{18}IO_2$, 322.0352; found, 333.0359.

The more polar isomer: colorless oil. ^{1}H NMR: 1.52 (s, 3H), 1.90-1.99 (m, 2H), 2.17-2.32 (m, 2H), 3.36 (d, 1H, *J* = 10.0), 3.41 (d, 1H, *J* = 10.0), 3.80 (s, 3H), 4.95 (dd, 1H, *J* = 6.0, 9.2), 6.87 (d, 2H, *J* = 8.3), 7.34 (d, 2H, *J* = 8.3). ^{13}C NMR: 17.8 (CH_2), 26.4 (CH_3), 35.6 (CH_2), 37.4 (CH_2), 55.3 (CH_3), 81.1 (CH), 81.4 (C), 113.7 (CH), 127.2 (CH), 134.2 (C), 159.0 (C). IR: 2968, 1613, 1514. HRMS-DART *m/z*: $[M+H]^+$ calcd for $C_{13}H_{18}IO_2$, 322.0352; found, 333.0342.

Scheme 5. 2-(Chloromethyl)-5-(4-chlorophenyl)tetrahydrofuran (11)

Column chromatography (hexane/AcOEt 10/1) gave **11** (44 mg, 19% from 1 mmol of **2c**, *cis/trans* 1/1.3) as a colorless oil. Diastereomers were partially separated by column chromatography (hexane/AcOEt 20/1) to give pure *trans*-**11** and a mixture of *cis*/*trans*-**11** (*cis*/*trans* 1/0.1).

trans-**11**: colorless oil. ^{1}H NMR: 1.86 (m, 1H), 1.95 (m, 1H), 2.21 (m, 1H), 2.40 (m, 1H), 3.61 (dd, 1H, *J* = 6.0, 11.2), 3.66 (dd, 1H, *J* = 4.9, 11.2), 4.47 (m, 1H), 5.05 (dd, 1H, *J* = 6.3, 8.0), 7.24-7.31 (m, 4H). ^{13}C NMR: 29.9 (CH_2), 35.1 (CH_2), 47.1 (CH_2), 79.0 (CH), 80.8 (CH), 126.9 (CH), 128.5 (CH), 132.9 (C), 141.4 (C). IR: 2951, 2871, 1492. HRMS-DART *m/z*: $[M+H]^+$ calcd for $C_{11}H_{13}Cl_2O$, 231.0344; found, 231.0341.

cis-**11**: ^{1}H NMR: 1.82 (m, 1H), 1.97 (m, 1H), 2.17 (m, 1H), 2.30 (m, 1H), 3.63 (dd, 1H, *J* = 5.8, 11.2), 3.67 (dd, 1H, *J* = 4.9, 11.2), 4.33 (m, 1H), 4.90 (dd, 1H, *J* = 6.8, 8.6), 7.28-7.32 (m, 4H). ^{13}C NMR: 29.4 (CH_2), 34.5 (CH_2), 47.1 (CH_2), 78.9 (CH), 81.3 (CH), 127.3 (CH), 128.6 (CH), 133.2 (C), 140.9 (C). IR: 2953, 2873, 1492. HRMS-DART *m/z*: $[M+H]^+$ calcd for $C_{11}H_{13}Cl_2O$, 231.0344; found, 231.0346. IR, MS and HRMS data described above were those of a mixture of diastereomers (*cis*/*trans* 1/0.1). ^{1}H and ^{13}C NMR data of *cis*-**11** was determined by comparing the NMR data of pure *trans*-**3d** and those of a mixture of *cis*/*trans*-**11**.

Scheme 6. 3-(Bromomethyl)isobenzofuran-1(3*H*)-one (13)

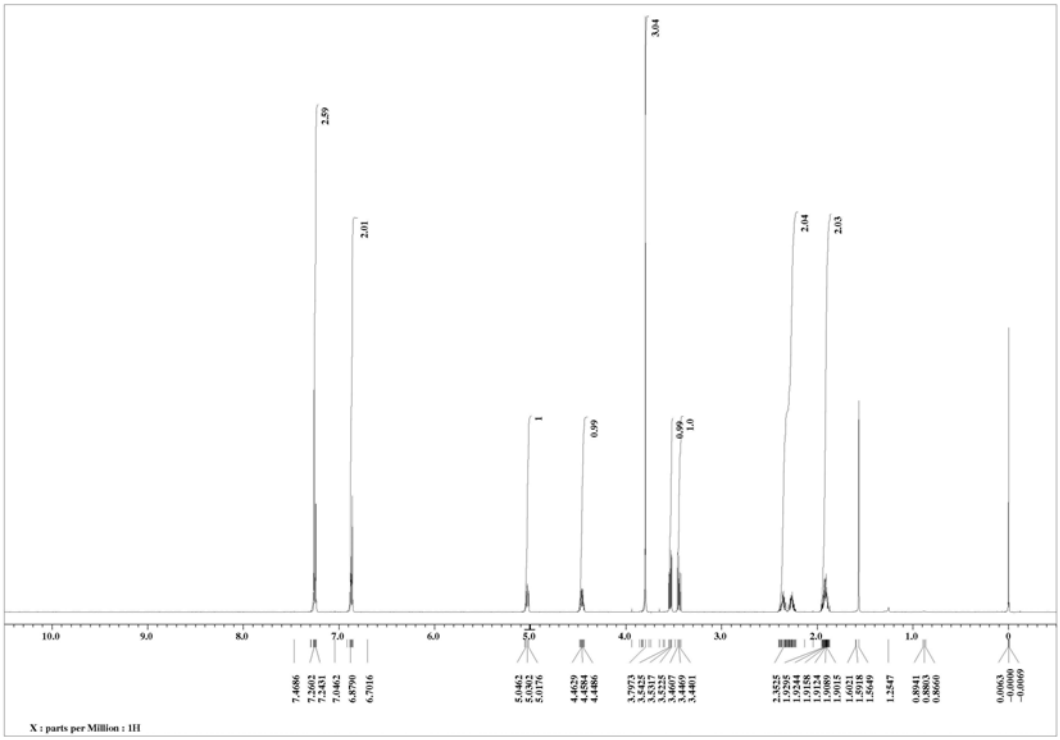
Under argon atmosphere to the solution of (2-vinylphenyl)magnesium bromide (**1d**) (0.4 M solution in THF, 2.5 mL, 1.0 mmol) in THF (15 mL) was bubbled carbon dioxide gas, generated from dry ice and passed through $CaCl_2$ drying tube, for 0.5 h at 0 °C. After stirring for 0.5 h at the same

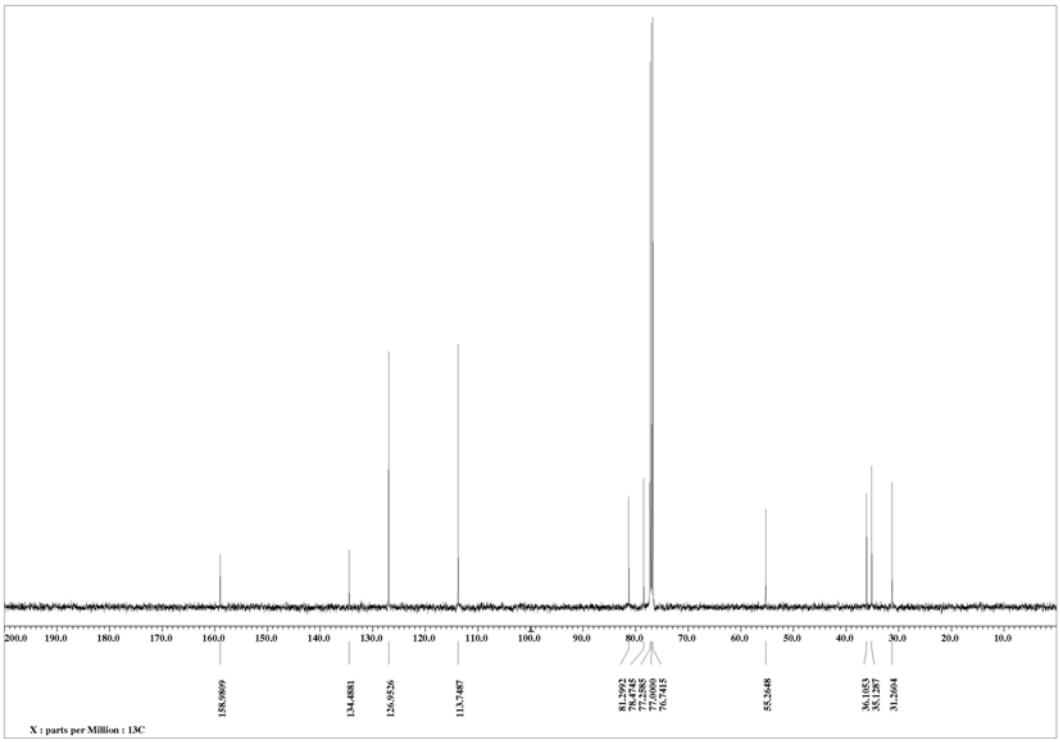
temperature, a solution of $PhI(OAc)_2$ (1.29 g, 4.0 mmol) in 1,2-dichloroethane (11 mL) was added at 0 °C over 5 min. The reaction mixture was stirred for 1 h at room temperature. To the reaction mixture was added satd $Na_2S_2O_3$ (10 mL). The separated aqueous layer was acidified with 10% sulfuric acid (2 mL) to pH 2 and extracted with AcOEt (5 mL) three times. The combined organic layers were dried over sodium sulfate, and concentrated. The resulting crude mixture was purified by silica gel column chromatography (hexane/acetone 20/1) to give **13** (98 mg, 43%) as colorless solids of mp 68-70 °C. ^{1}H NMR: 3.75 (1H, dd, *J* = 5.2, 10.9), 3.78 (1H, dd, *J* = 5.2, 10.9), 7.59-7.65 (2H, m), 7.73 (1H, t, *J* = 7.5), 7.94 (1H, d, *J* = 7.5). ^{13}C NMR: 32.1 (CH_2), 78.6 (CH), 122.4 (CH), 125.8 (CH), 126.4 (C), 130.0 (CH), 134.3 (CH), 147.1 (C), 169.4 (C). IR: 1764. FABMS *m*/*z*: 227 $[M+H]^+$. HRMS–FAB *m*/*z*: $[M+H]^+$ calcd for $C_9H_8BrO_2$, 226.9702; found, 226.9717.

Scheme 6. 3-(Bromomethyl)-1,2-(di-*tert*-butyldicarboxyl)pyrazolidine (15)

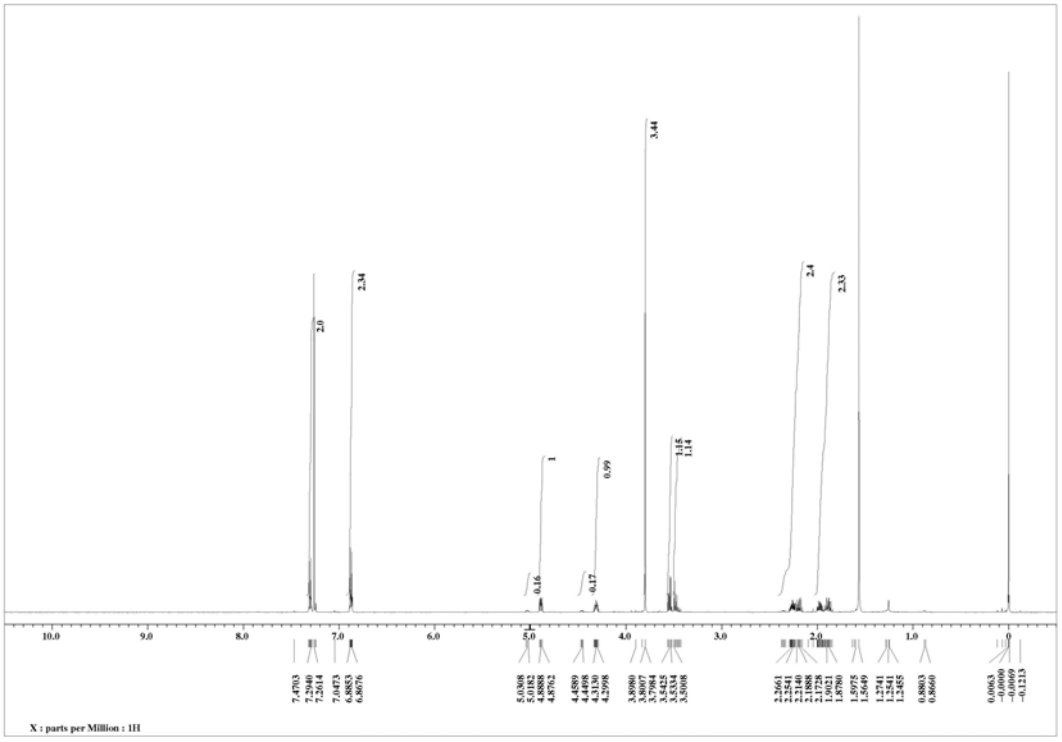
Column chromatography ($CHCl_3$/AcOEt 100/1) gave **15** (248 mg, 68% from 1 mmol of **14**) as a colorless oil. ^{1}H NMR: 1.47 (9H, s), 1.48 (9H, s), 1.99 (1H, m), 2.33 (1H, m), 3.15 (1H, m), 3.24 (1H, dd, *J* =8.6, 9.7), 3.62 (1H, d, *J* = 9.8), 4.09 (1H, dd, *J* = 8.6, 11.5), 4.39 (1H, m) ^{13}C NMR: 28.17 (CH_3), 28.21 (CH_3), 31.6 (CH_2), 34.8 (CH_2), 46.7 (CH_2), 59.2 (CH), 81.4 (C), 81.5 (C), 156.3 (C). IR: 2979, 1698. MS (EI) *m/z*: 364 (M^+). HRMS-ESI *m/z*: $[M+Na]^+$ calcd for $C_{14}H_{25}BrN_2O_4Na$, 387.0895; found, 387.0887.

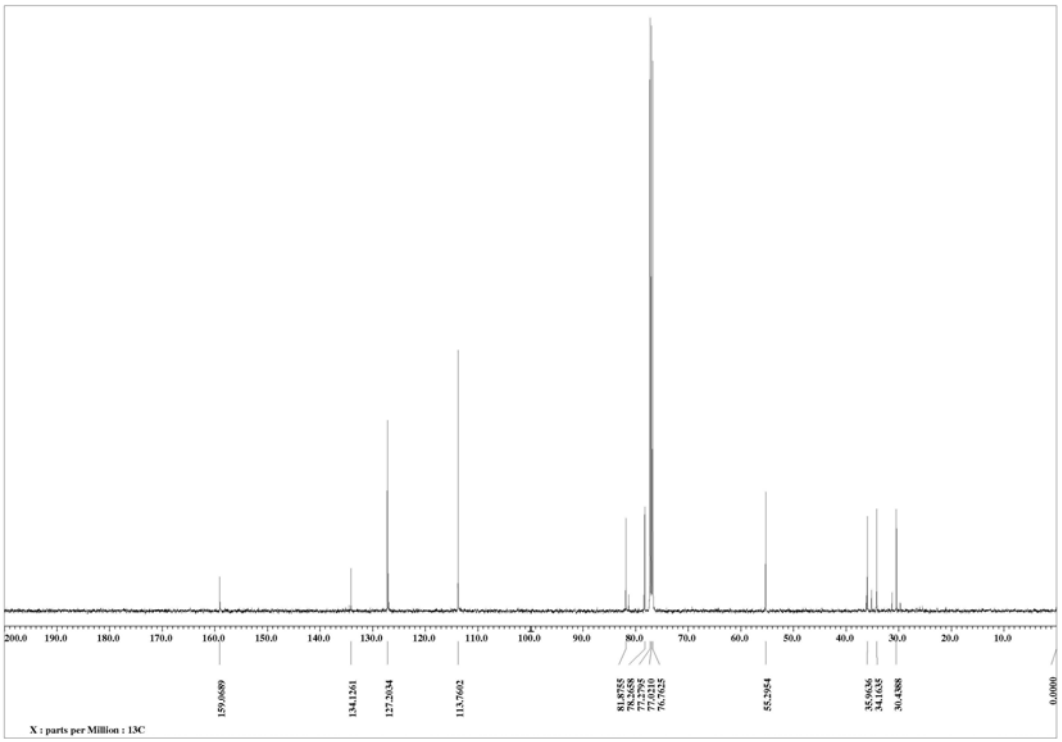
^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) of *trans*-**3b**



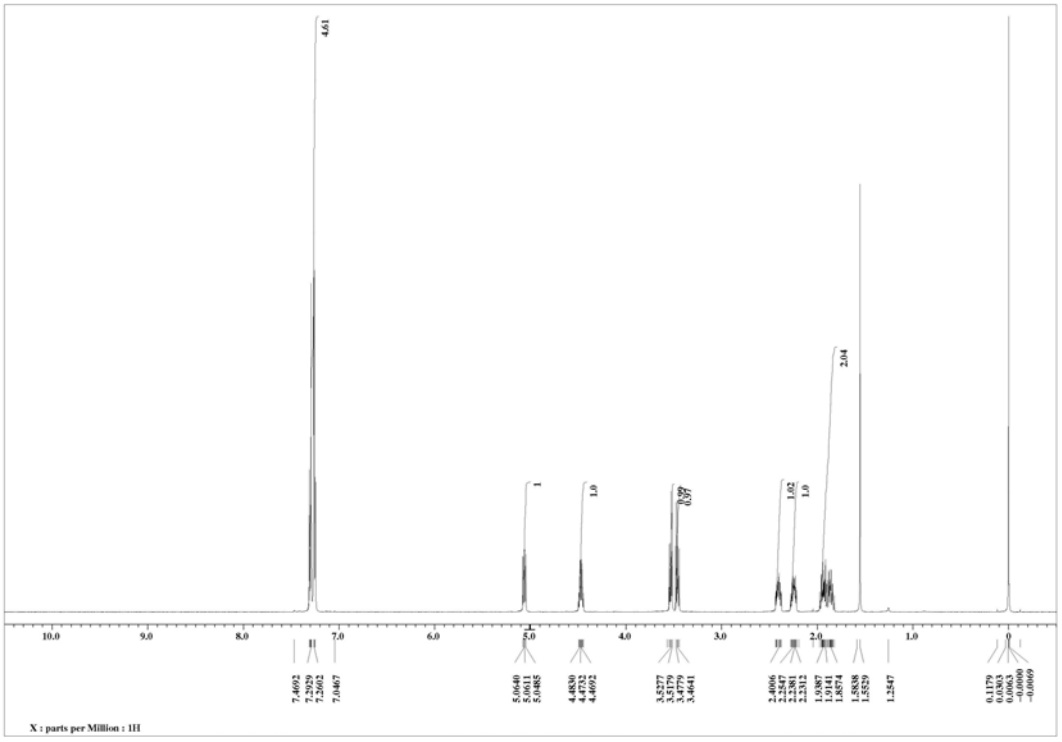


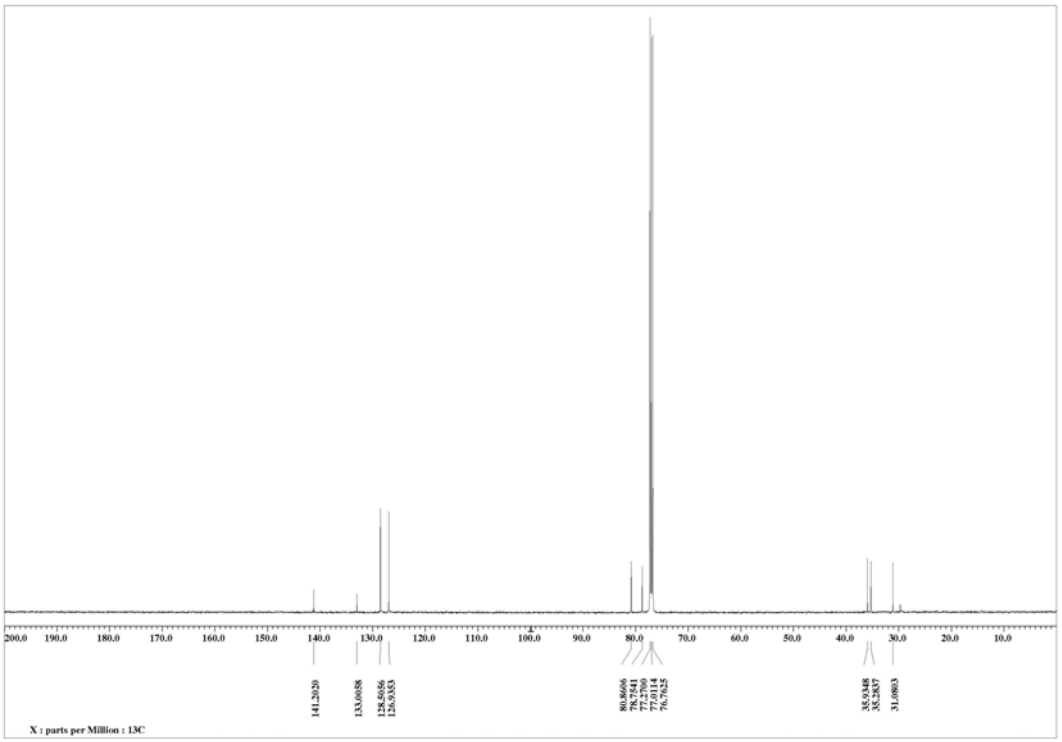
^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) of *cis*-major **3b** (*cis*/*trans* 1/0.16)



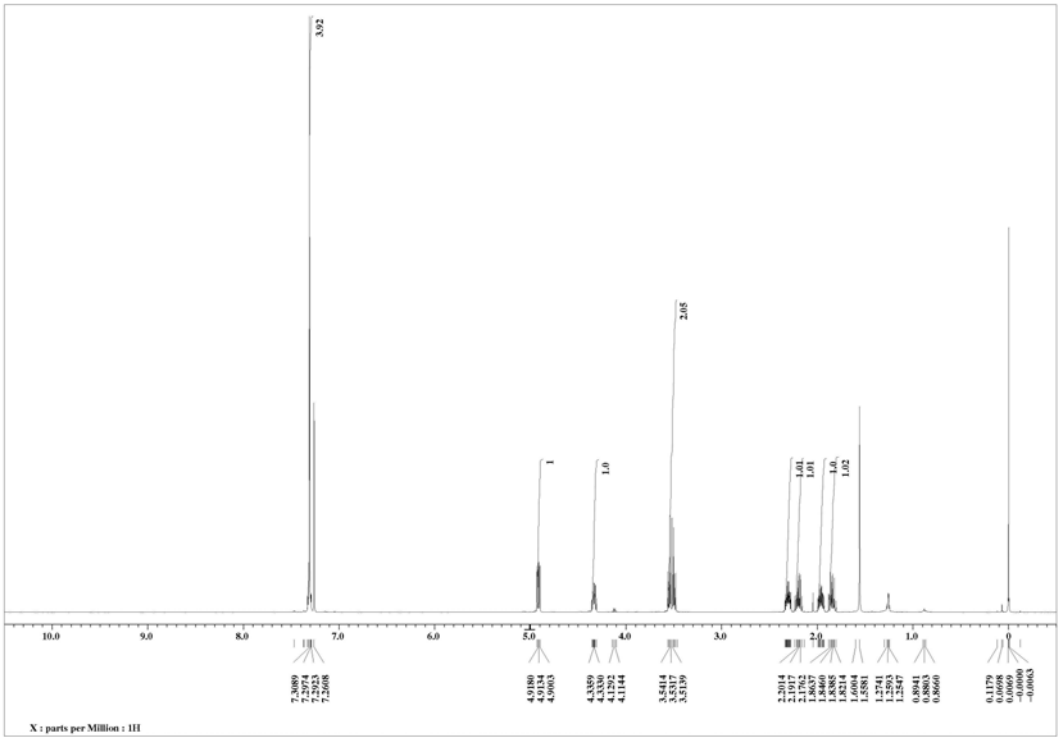


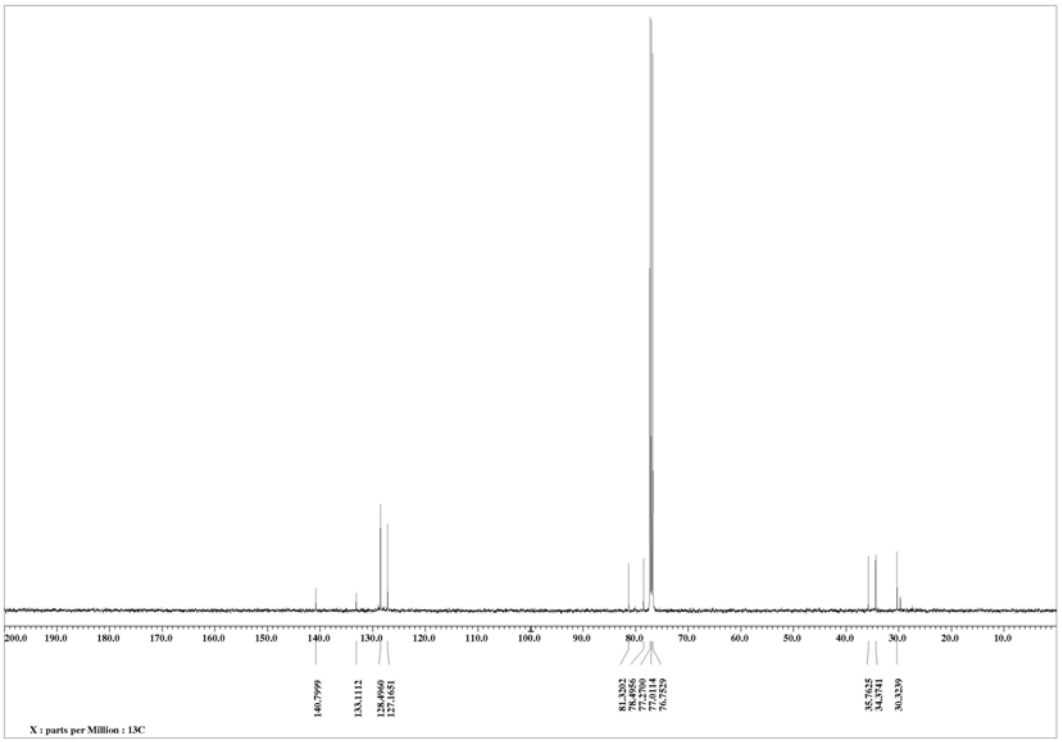
^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) of *trans*-**3c**



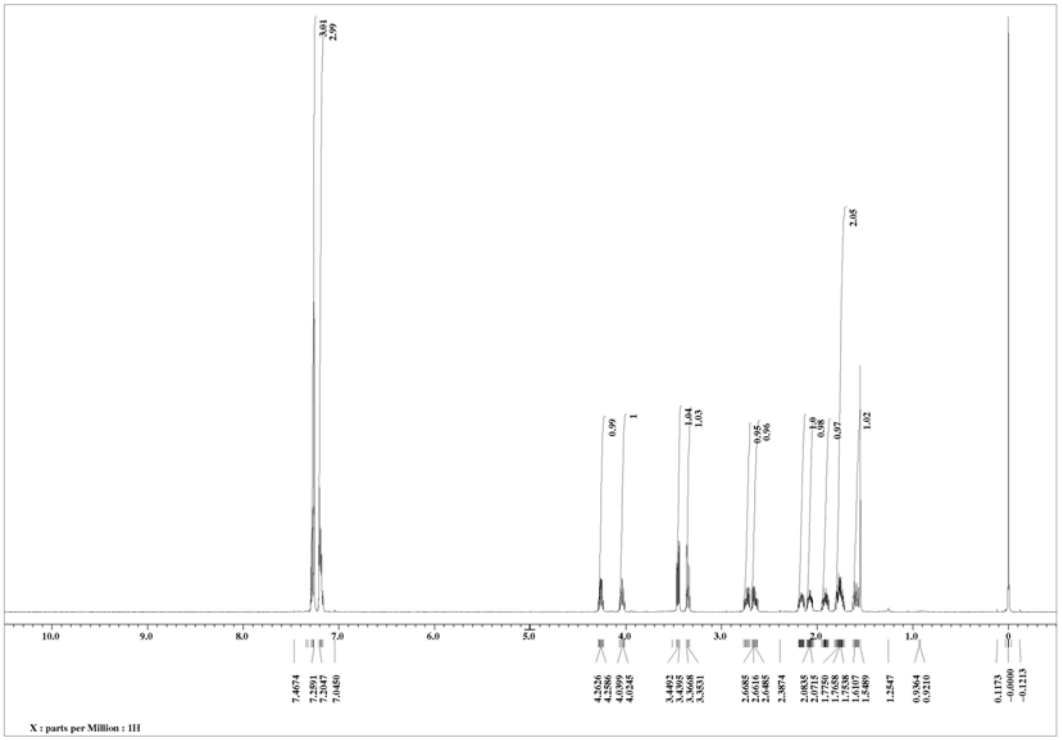


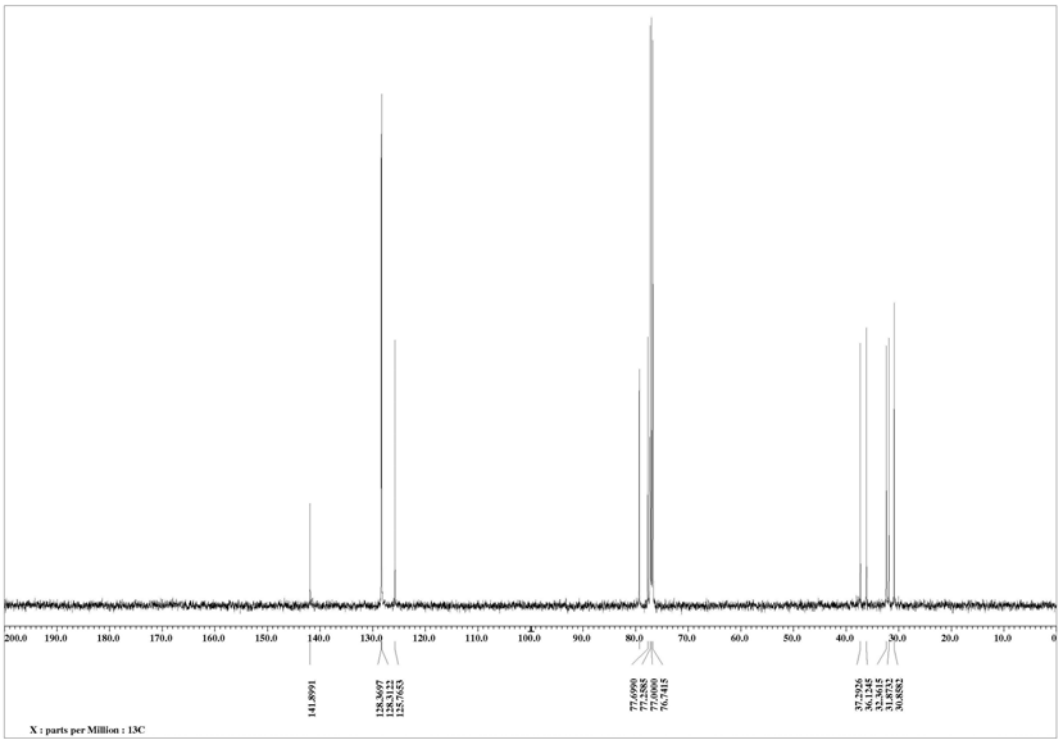
^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) of *cis*-**3c**



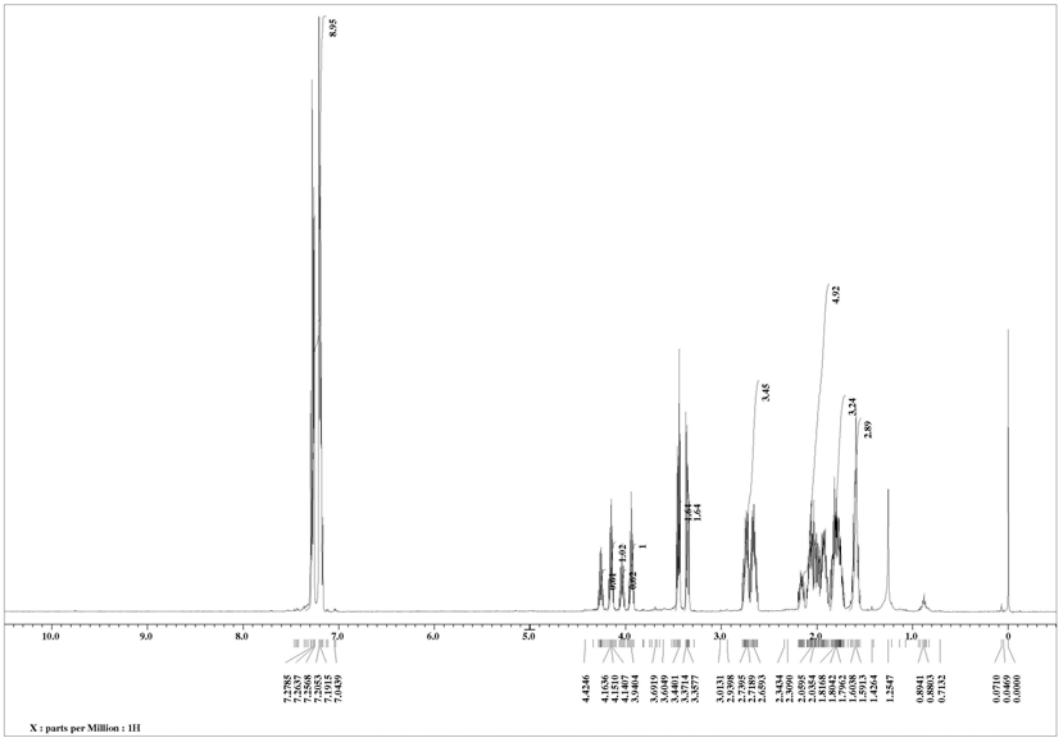


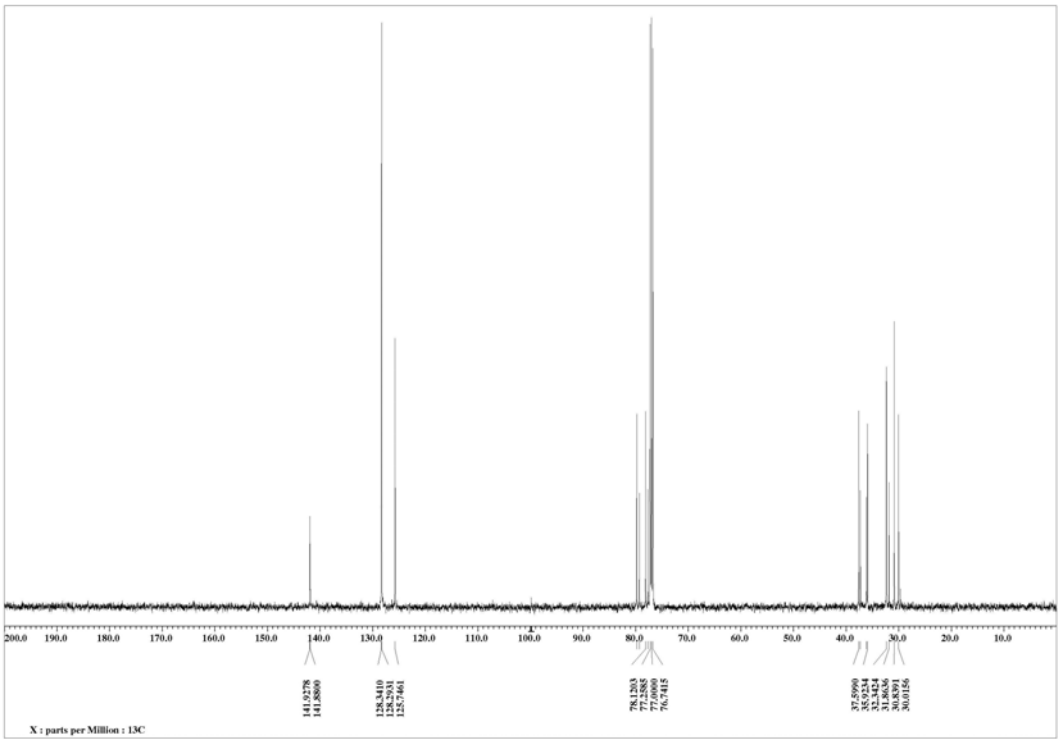
^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) of *trans*-**3d**



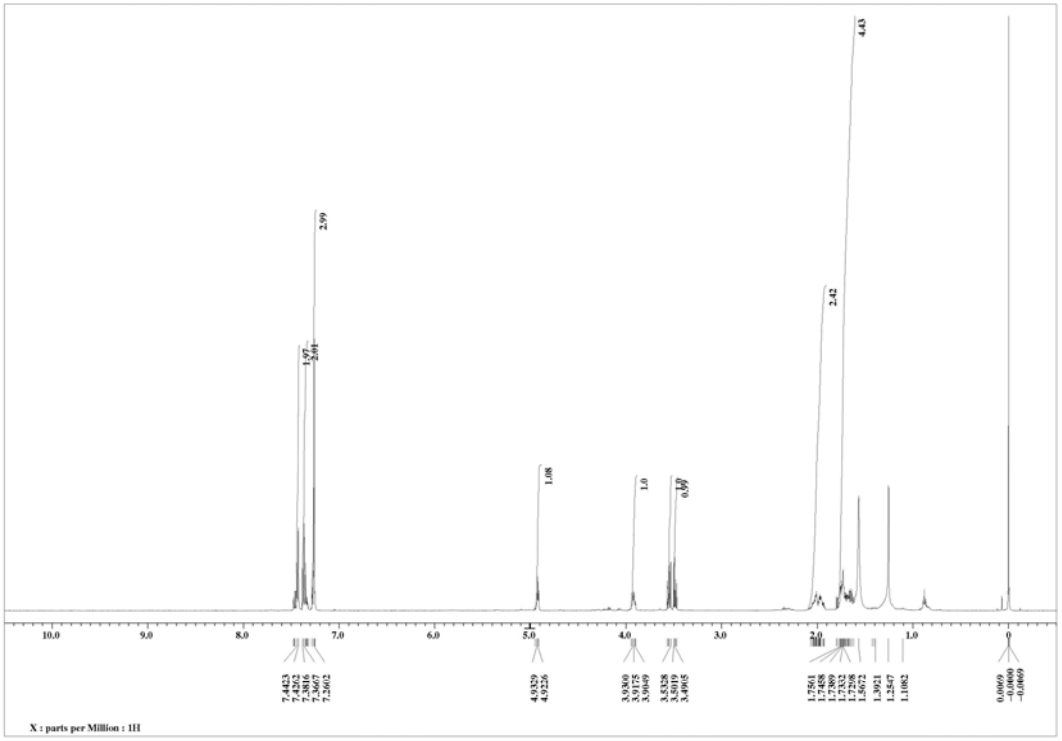


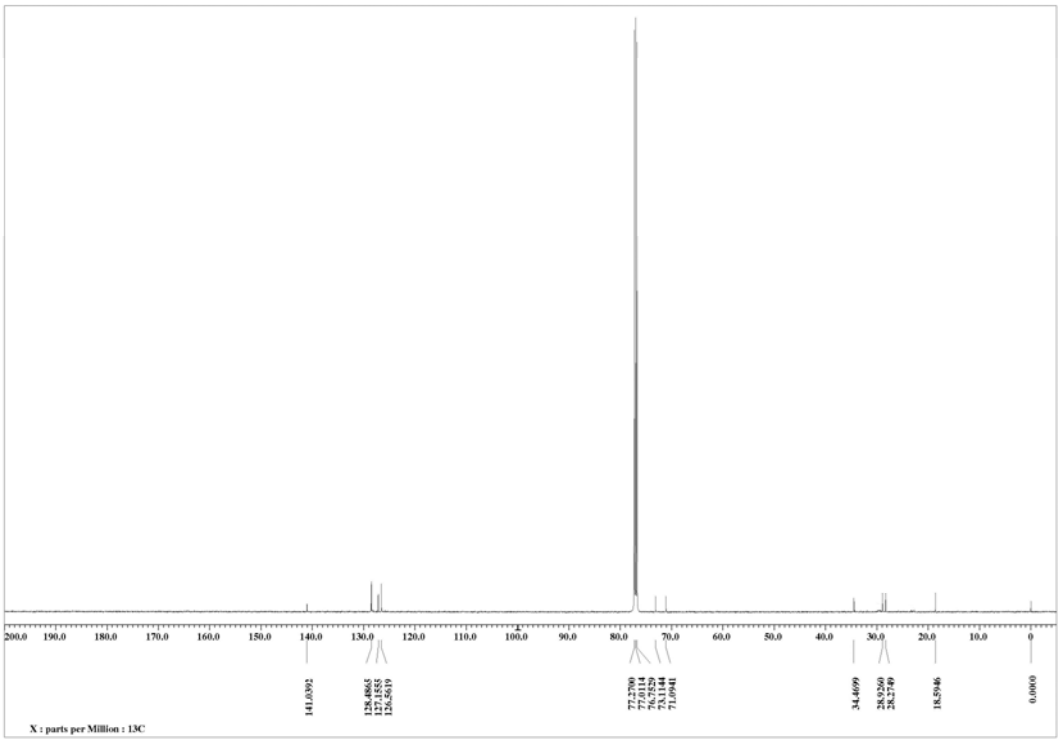
^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) of *cis*-major **3d** (*cis*/*trans* 1/0.6)



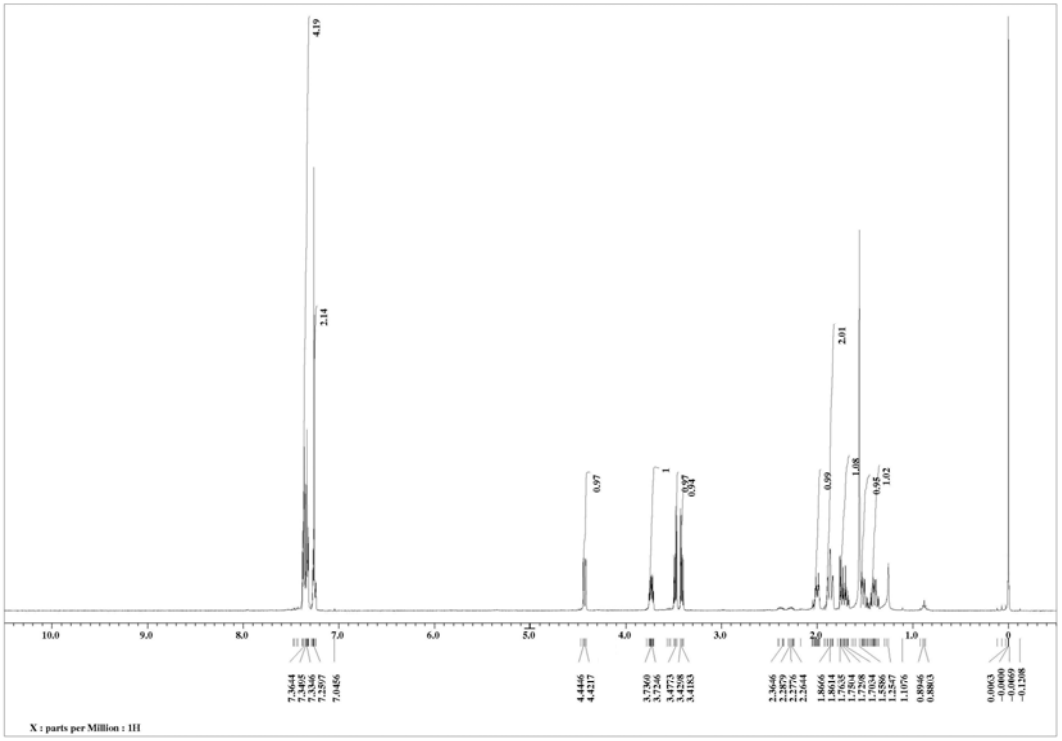


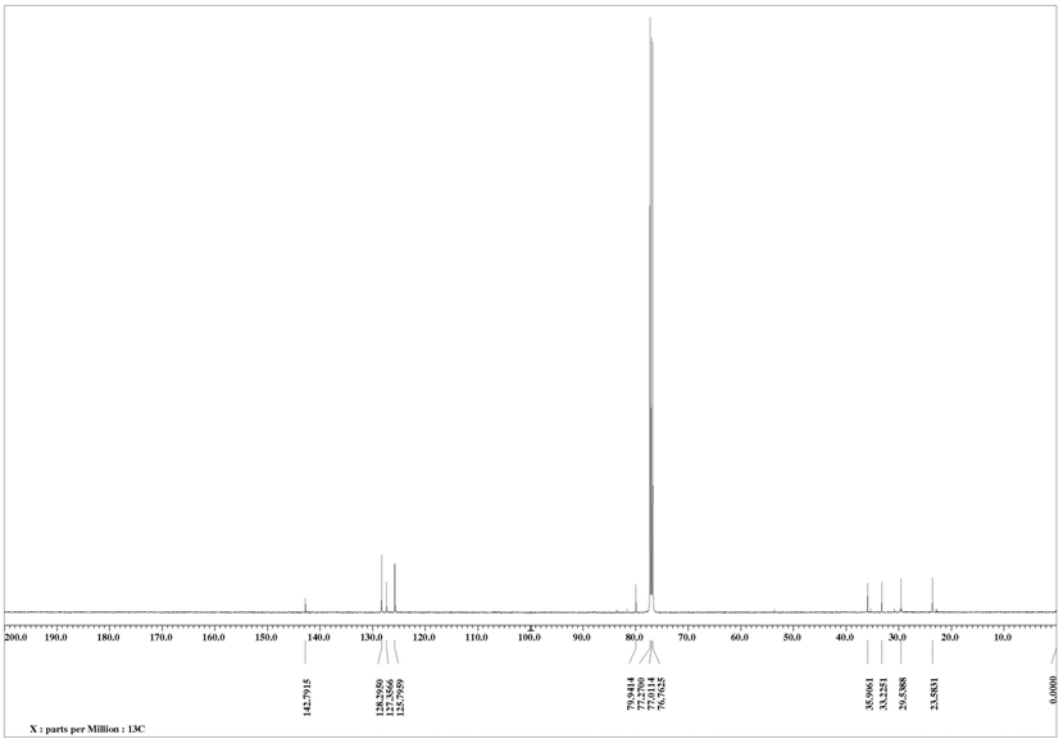
^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) of *trans*-**3e**



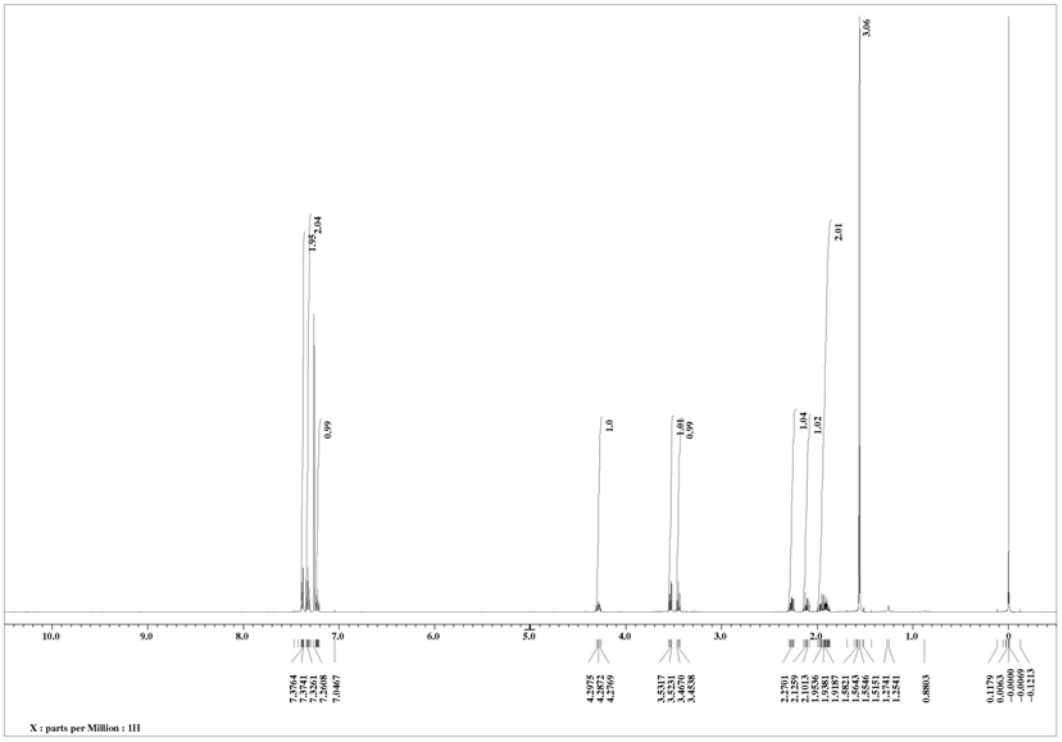


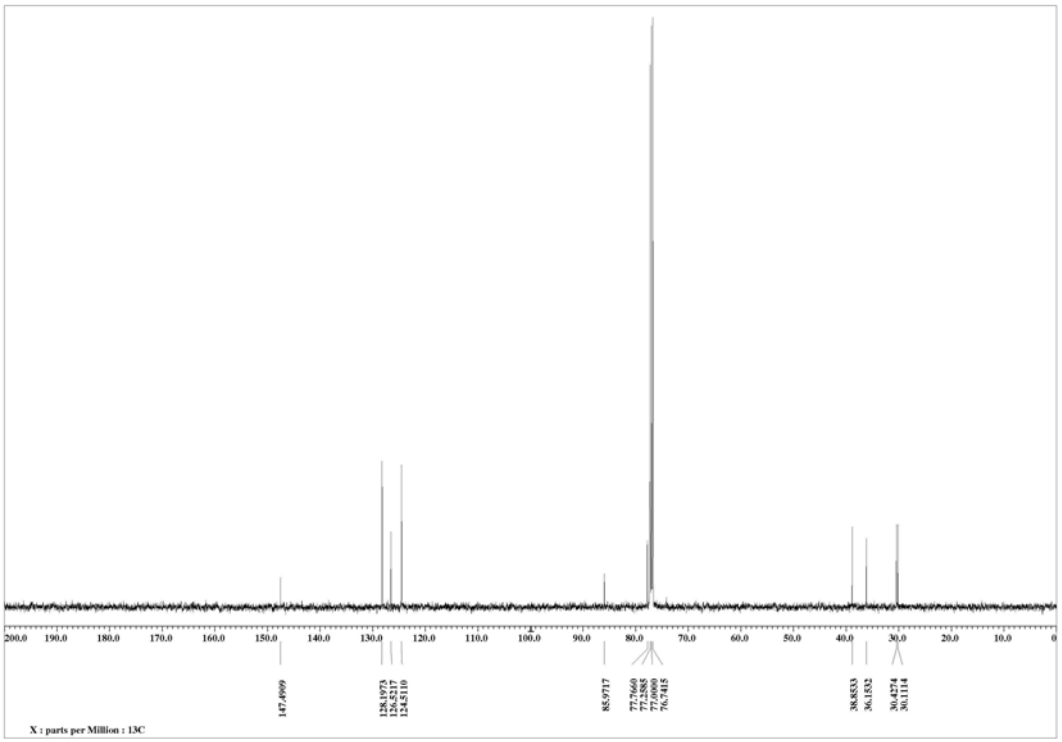
^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) of *cis*-**3e**



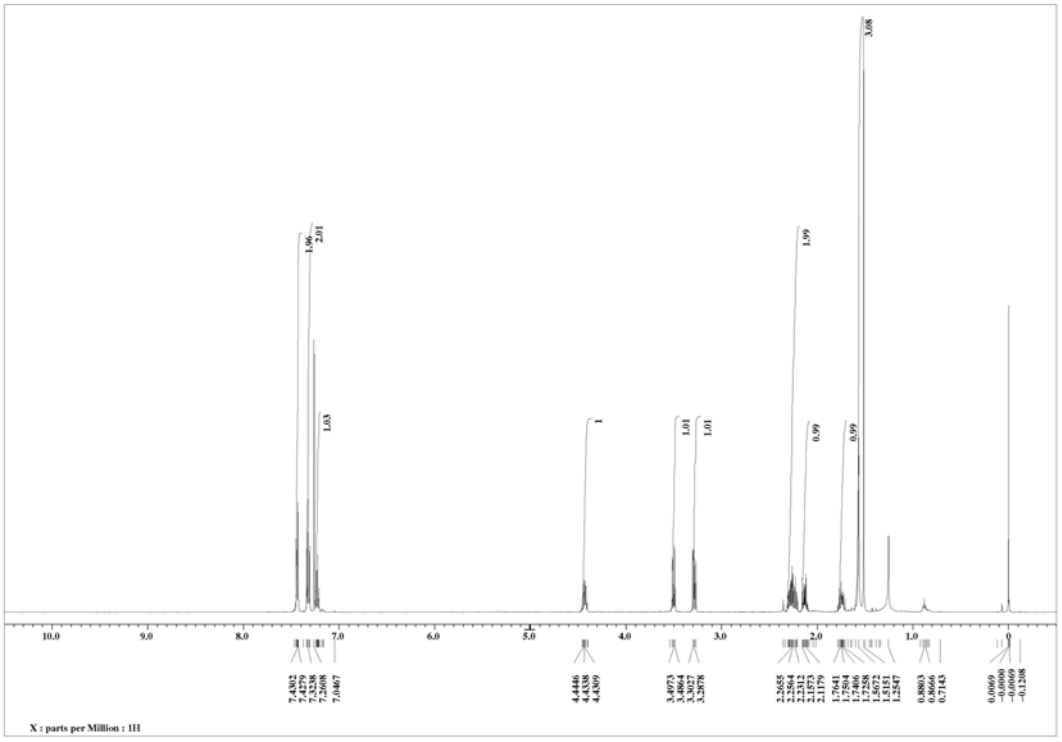


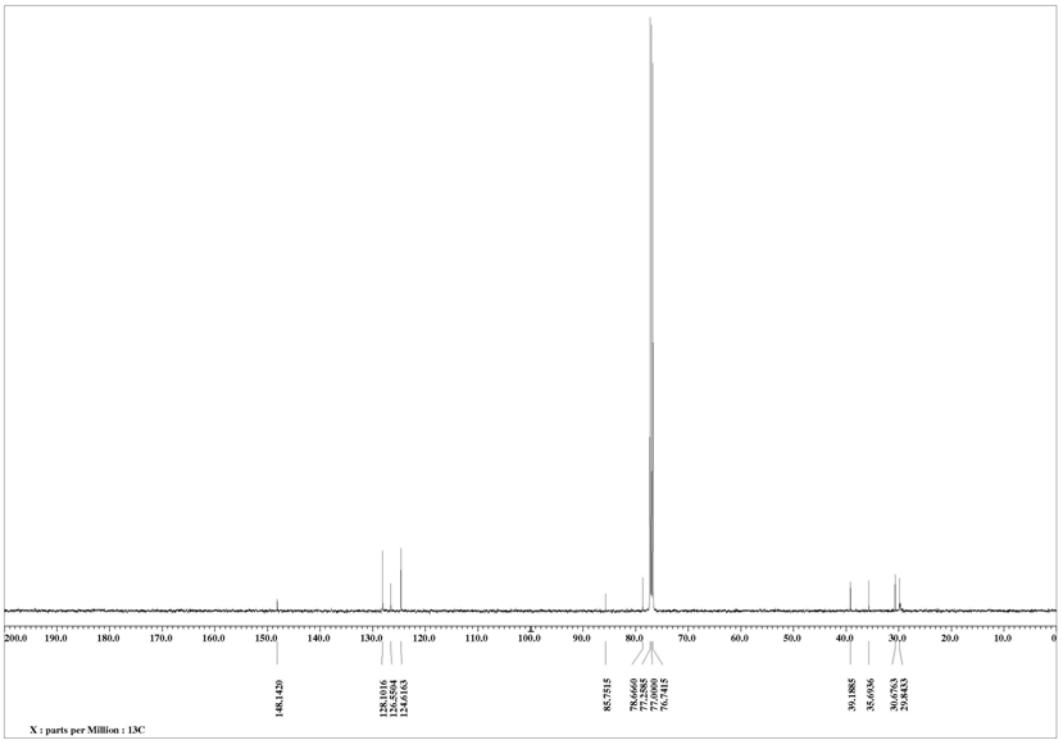
^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) of (*RS*,*RS*)-**9**



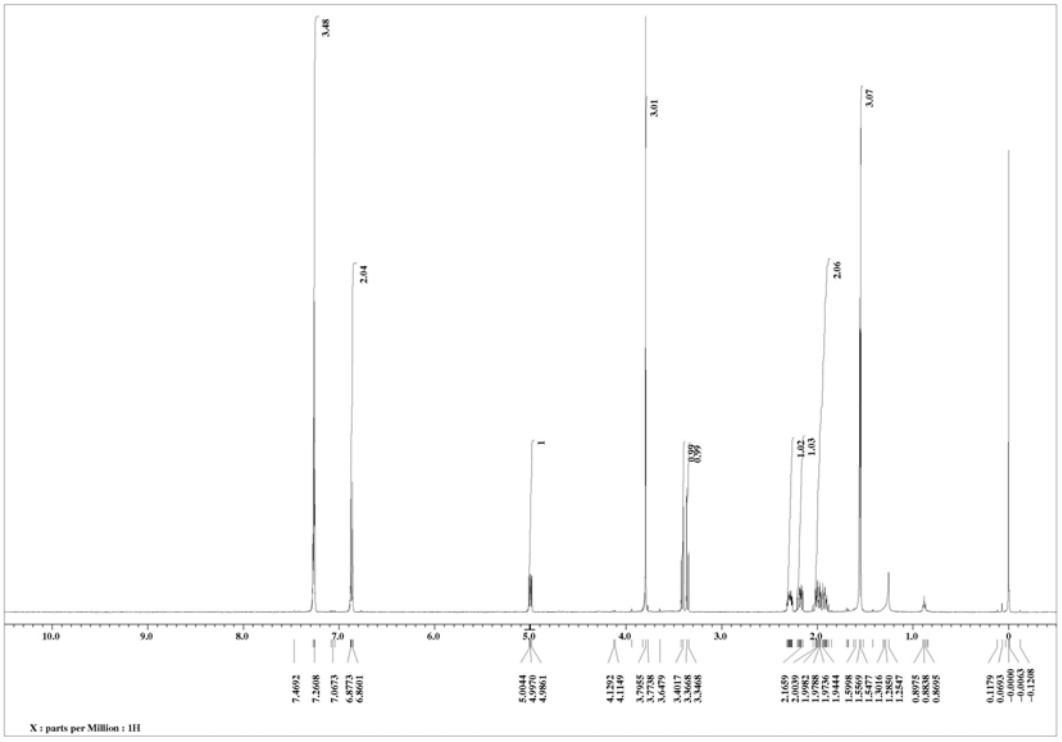


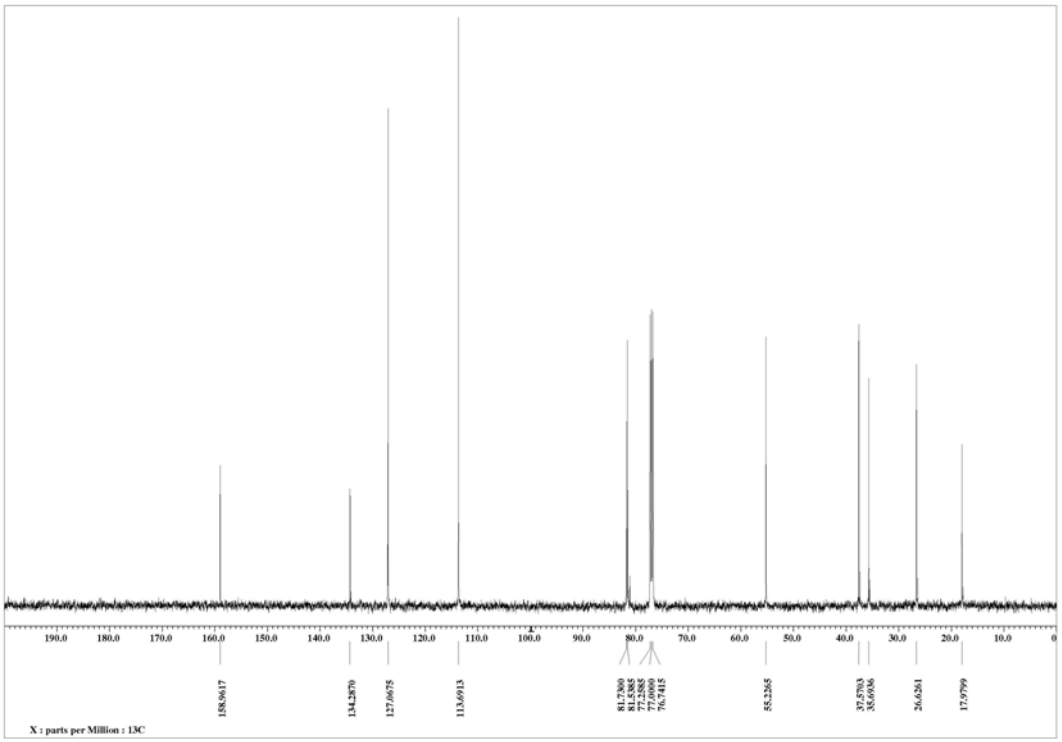
^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) of (*RS*,*SR*)-**9**



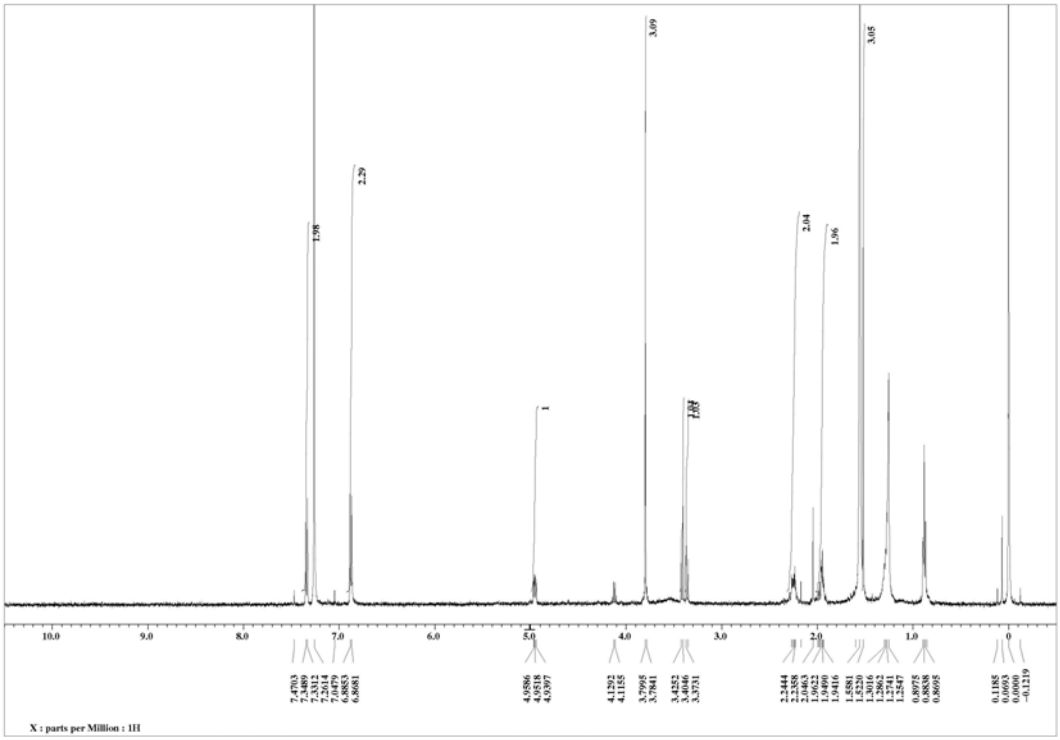


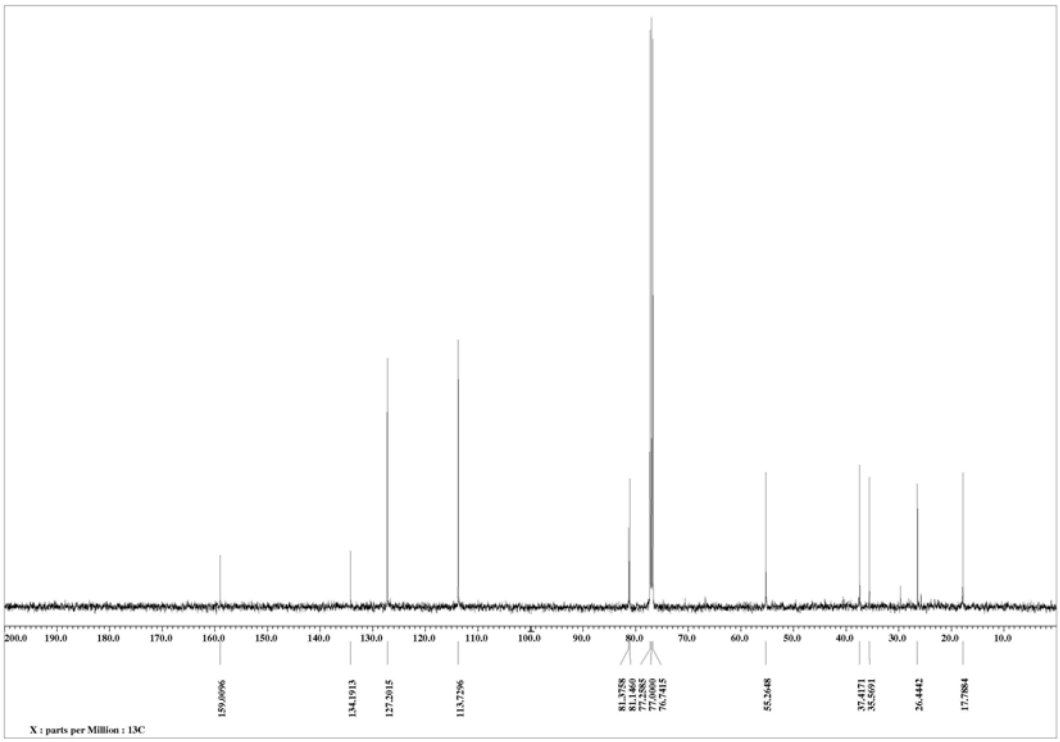
^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) of **10**, the less polar isomer



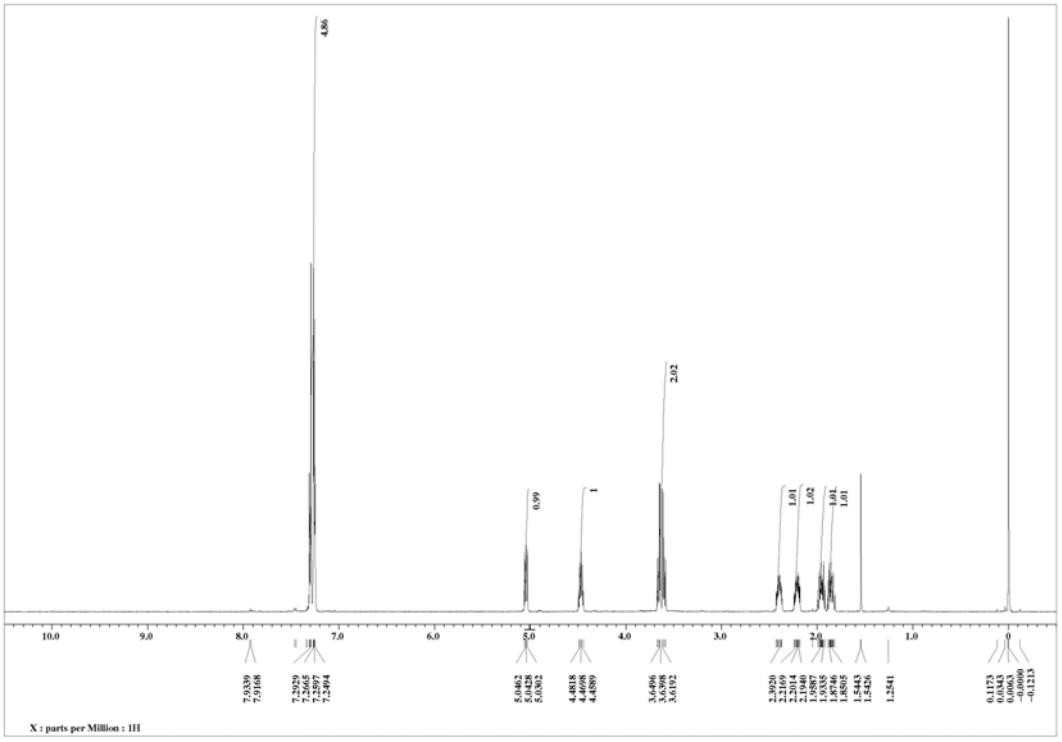


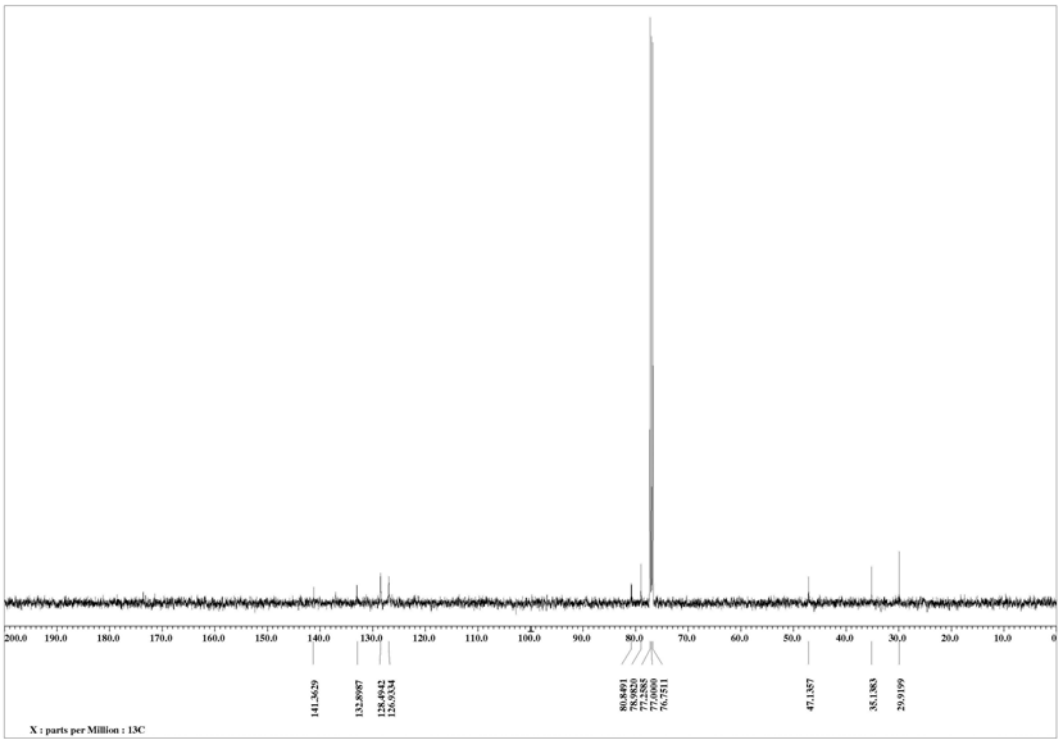
^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) of **10**, the more polar isomer



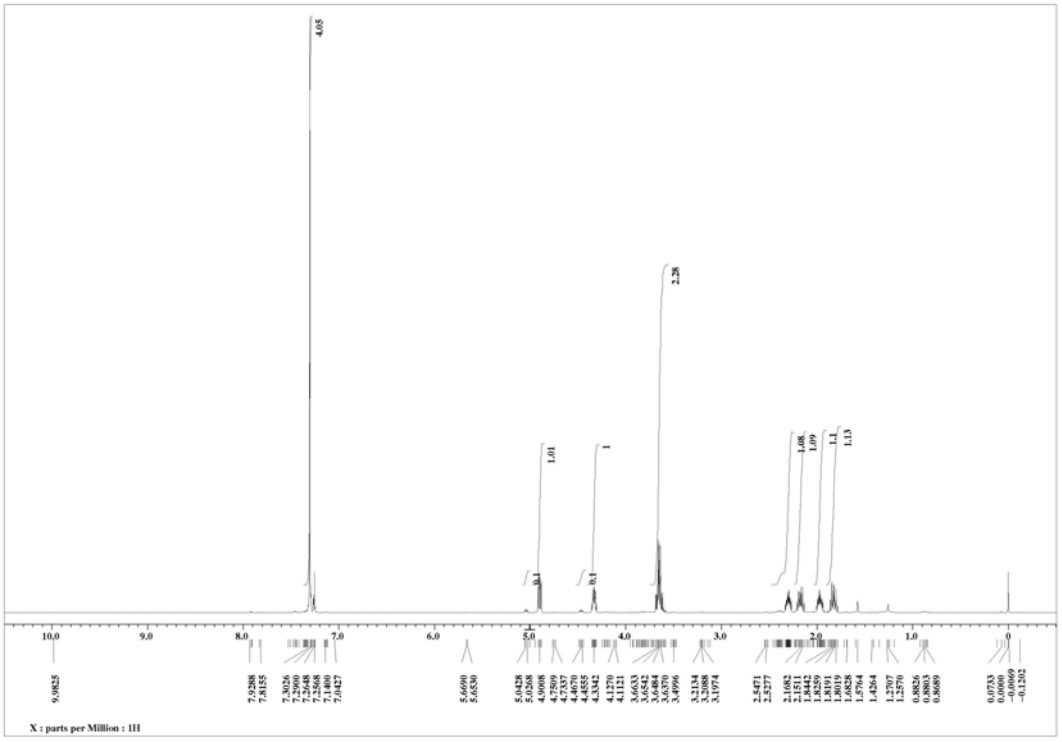


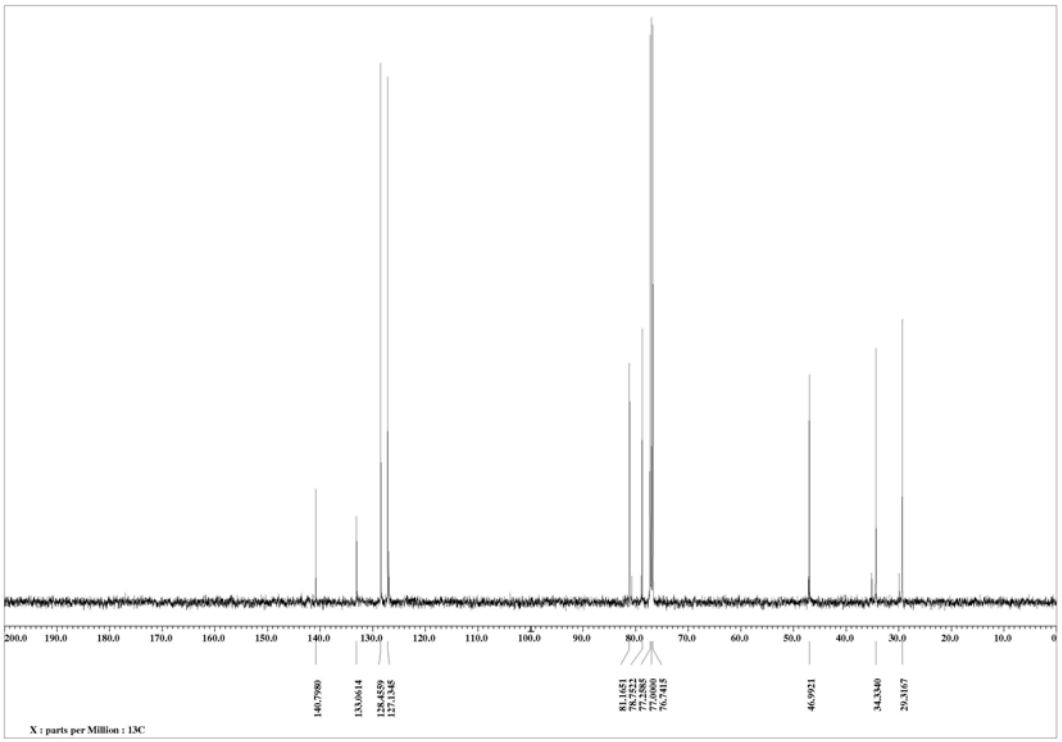
^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) of *trans*-**11**



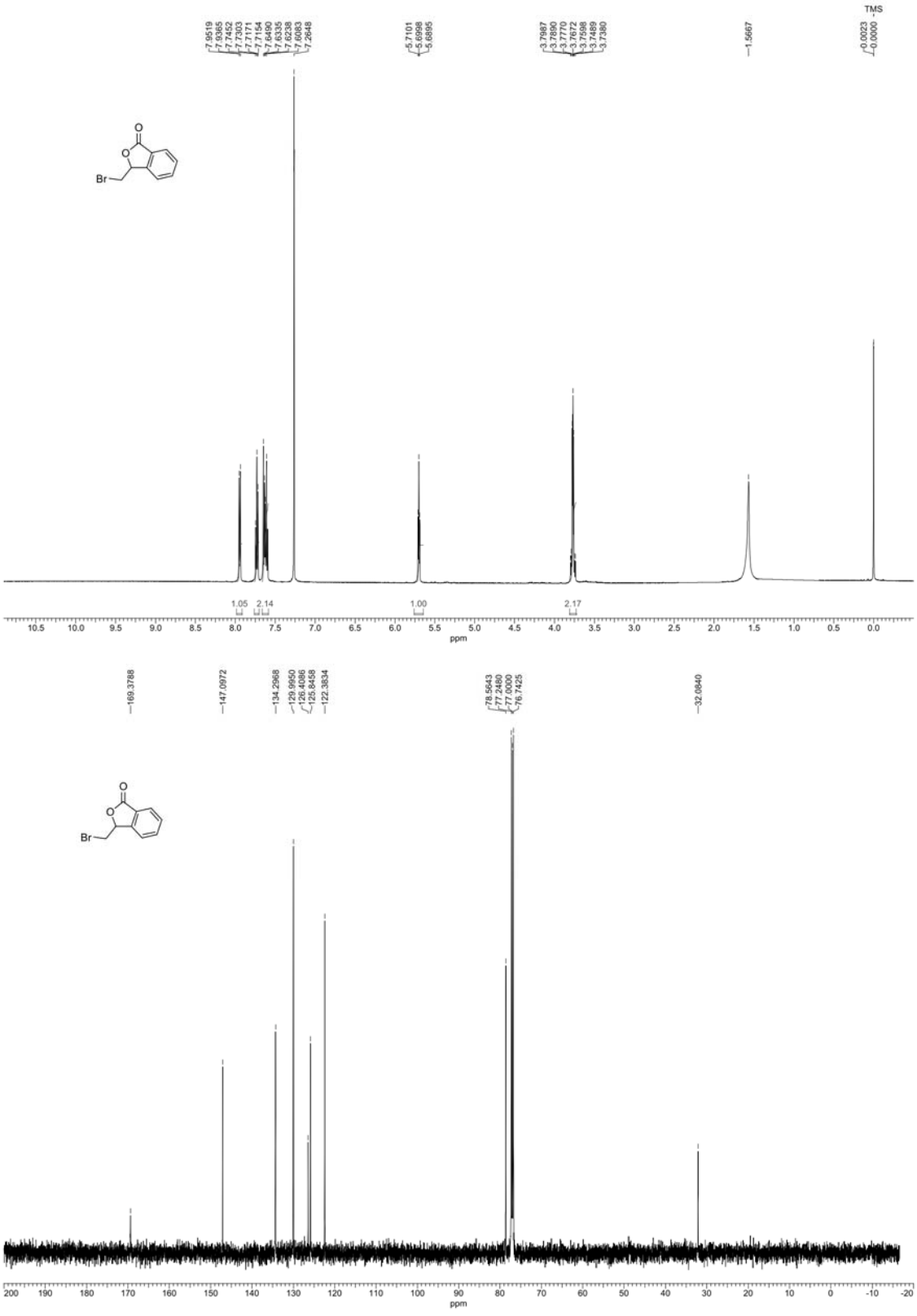


^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) of *cis*-major **11** (*cis*/*trans* 1/0.1)





^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) of **13**



^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) of **15**