Supporting Information

Catalytic Enantioselective Approach to Tetrol Bearing Vicinal All-Carbon Quaternary Stereogenic Centers

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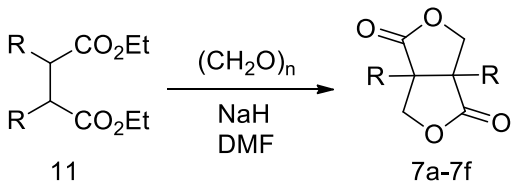
General Information

Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use. Melting points were measured on a SGW X-4. Melting points are uncorrected. NMR spectras were recorded on Bruker ARX 300 spectrometer and Bruker ARX 400 spectrometer, which were recorded in ppm (δ) downfield of TMS (δ = 0) in deuterated solvent. Signal splitting patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), or multiplet (m), with coupling constants (J) in hertz. Mass spectra were conducted at Micromass Q-Tof instrument (ESI) and Agilent Technologies 5973N (EI). HPLC analyses were performed on Shimadzu SPD-20A using Daicel Chiralpak AD-H, IB Column. Values of optical rotation were measured on Rudolph Automatic Polarimeter A21101 at the wavelength of the sodium D-line (589 nm).

Diesters **11**[1] and tetraester **12**[2] were prepared following procedures in the literature.

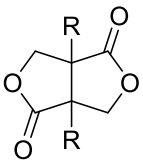
General Procedure for Preparation of 7a-7f



11 7a-7f

To a solution of diester 11[1] (10 mmol) and paraformaldehyde (0.9 g, 30 mmol) in DMF (10 mL) was added NaH (0.12 g, 3 mmol). The reaction was allowed to stir at 50 ºC until the starting material disappeared. The reaction mixture was diluted with ethyl acetate and quenched by saturated NH_4Cl. Then the organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel column chromatography (ethyl acetate / petroleum ether) to give the product **7a-7f** (62-95% yield) as white solid.

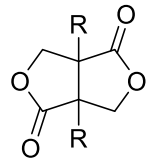
3a,6a-diphenyltetrahydro-1H,4H-furo[3,4-c]furan-1,4-dione (7a)



R=Ph

White solid. Analytical data for **7a**: mp: 148-149 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.22 (m, 6H), 6.92-6.80 (m, 4H), 5.13 (d, *J* = 9.6 Hz, 2H), 4.87 (d, *J* = 9.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.58, 130.86, 129.13, 128.99, 127.38, 72.16, 60.95. IR (neat, cm^{-1}): ν = 1766, 1486, 1446, 1258, 1164, 1024, 948, 752, 731. HRMS (EI) m/z M^+: Calcd for $C_{18}H_{14}O_4$: 294.0892. Found: 294.0896.

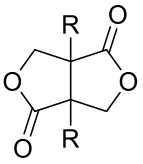
3a,6a-bis(4-methoxyphenyl)tetrahydro-1H,4H-furo[3,4-c]furan-1,4-dione (7b)



R=*p*-OMe-Ph

White solid. Analytical data for **7b**: mp: 174 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (s, 8H), 5.03 (d, *J* = 9.6 Hz, 2H), 4.72 (d, *J* = 9.6 Hz, 2H), 3.76 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.86, 159.75, 128.73, 122.60, 114.46, 72.29, 60.33, 55.32. IR (neat, cm^{-1}): ν = 1773, 1609, 1516, 1485, 1300, 1252, 1185, 1058, 1024, 802. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{20}H_{18}O_6Na$: 377.1001. Found: 377.0985.

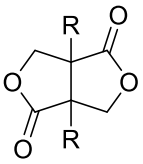
3a,6a-bis(4-chlorophenyl)tetrahydro-1H,4H-furo[3,4-c]furan-1,4-dione (7c)



R=*p*-Cl-Ph

White solid. Analytical data for **7c**: mp: 176 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.23 (m, 4H), 6.88-6.75 (m, 4H), 5.11 (d, *J* = 9.7 Hz, 2H), 4.78 (d, *J* = 9.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.70, 135.48, 129.53, 129.18, 128.74, 72.13, 60.30. IR (neat, cm^{-1}): ν = 1775, 1497, 1279, 1157, 1097, 1036, 856, 807, 737. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{18}H_{12}Cl_2O_4Na$: 385.0010. Found: 384.9995.

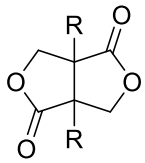
3a,6a-di-p-tolyltetrahydro-1H,4H-furo[3,4-c]furan-1,4-dione (7d)



R=*p*-Me-Ph

White solid. Analytical data for **7d**: mp: 200-202 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.2 Hz, 4H), 6.73 (d, *J* = 8.3 Hz, 4H), 5.05 (d, *J* = 9.5 Hz, 2H), 4.79 (d, *J* = 9.5 Hz, 2H), 2.28 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.78, 138.90, 129.76, 127.86, 127.24, 72.23, 60.44, 21.02. IR (neat, cm^{-1}): ν = 1772, 1517, 1250, 1150, 1061, 1015, 957, 793, 724. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{20}H_{18}O_4Na$: 345.1103. Found: 345.1085.

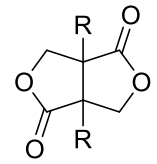
3a,6a-bis(3-(trifluoromethyl)phenyl)tetrahydro-1H,4H-furo[3,4-c]furan-1,4-dione (7e)



R=*m*-CF_3-Ph

White solid. Analytical data for **7e**: mp: 168-170 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.8 Hz, 2H), 7.46 (t, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 6.84 (s, 2H), 5.13 (d, *J* = 9.9 Hz, 2H), 4.81 (d, *J* = 9.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.16, 131.66, 131.61, 130.83, 130.06, 126.15 (q, J_{C-F} = 16.0 Hz), 124.44, 124.35 (q, J_{C-F} = 16.0 Hz), 72.18, 61.26. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.20. IR (neat, cm^{-1}): ν = 1775, 1462, 1326, 1159, 1119, 1016, 891, 790. HRMS (EI) m/z M^+: Calcd for $C_{20}H_{12}F_6O_4$: 430.0640. Found: 430.0638.

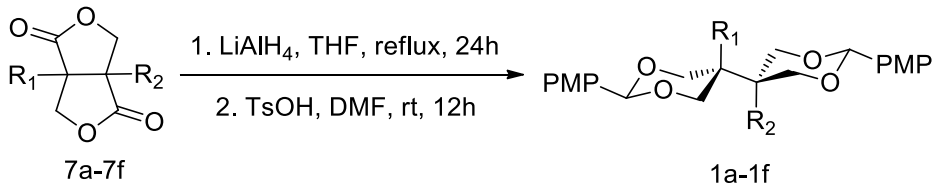
3a,6a-di(naphthalen-2-yl)tetrahydro-1H,4H-furo[3,4-c]furan-1,4-dione (7f)



R=2-Naphthyl

White solid. Analytical data for **7f**: mp: 228-230 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.63 (m, 4H), 7.60-7.43 (m, 8H), 6.77 (dd, *J* = 8.7, 2.1 Hz, 2H), 5.23 (d, *J* = 9.6 Hz, 2H), 5.04 (d, *J* = 9.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.52, 132.94, 132.82, 128.90, 128.18, 128.10, 127.57, 127.40, 127.22, 126.96, 124.14, 72.55, 61.11. IR (neat, cm^{-1}): ν = 1771, 1450, 1275, 1157, 1028, 1009, 993, 861, 745. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{26}H_{18}O_4Na$: 417.1103. Found: 417.1084.

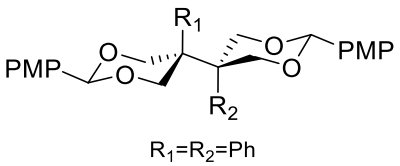
General Procedure for Preparation of 1a-1f[3]



7a-7f 1a-1f

A solution of **7** (10 mmol) in 30 mL of dry THF was added slowly to a suspension of 1.9 g (50 mmol) $LiAlH_4$ in 20 mL of dry THF. The reaction mixture was refluxed for 24 hours. It was then cooled to 0 ºC and 20 mL of water in 20 ml of ethanol was added slowly with vigorous stirring and then filtered. The precipitate was refluxed in CH_3OH (three 50-mL portions) and filtered. The combined filtrate was concentrated. Then 10 mL of MeOH was added. It was neutralized (to pH 1-2) with concentrated hydrochloric acid and concentrated. Then, TsOH (5%), *p*-Anisaldehyde dimethyl acetal (30 mmol), and DMF (15 mL) was added. The reaction mixture was allowed to stir at room temperature for 6-12 hours. The reaction mixture was diluted with ethyl acetate and H_2O. Then the organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel column chromatography (ethyl acetate / petroleum ether) to give the product **1a-1f** as white solid in 16-28% yields for two steps.

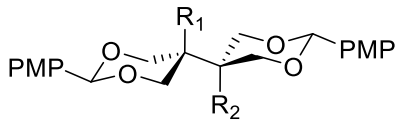
(2,5-*cis*,2',5'-*cis*)-2,2'-bis(4-methoxyphenyl)-5,5'-diphenyl-5,5'-bi(1,3-dioxane) (1a)



R_1=R_2=Ph

White solid. Analytical data for **1a**: mp: 293-295 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.20 (m, 10H), 6.92 (d, *J* = 8.4 Hz, 4H), 6.69 (d, *J* = 8.4 Hz, 4H), 5.33 (s, 2H), 4.74 (d, *J* = 11.1 Hz, 4H), 4.13 (d, *J* = 11.2 Hz, 4H), 3.68 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.09, 137.59, 130.47, 129.35, 127.96, 127.62, 126.75, 113.65, 102.28, 70.61, 55.27, 44.91. IR (neat, cm^{-1}): ν = 1613, 1518, 1390, 1304, 1249, 1104, 1029, 979, 829, 702. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{34}H_{34}O_6Na$: 561.2253. Found: 561.2254.

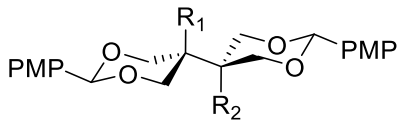
(2,5-*cis*,2',5'-*cis*)-2,2',5,5'-tetrakis(4-methoxyphenyl)-5,5'-bi(1,3-dioxane) (1b)



R_1=R_2=*p*-MeO-Ph

White solid. Analytical data for **1b**: mp: 236-237 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.15 (m, 4H), 6.99-6.94 (m, 4H), 6.94-6.88 (m, 4H), 6.74-6.69 (m, 4H), 5.34 (s, 2H), 4.67 (d, *J* = 11.2 Hz, 4H), 4.12 (d, *J* = 11.3 Hz, 4H), 3.86 (s, 6H), 3.71 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.99, 156.95, 129.42, 129.30, 128.48, 126.53, 112.56, 112.15, 101.16, 69.62, 54.18, 43.40. IR (neat, cm^{-1}): ν = 1612, 1517, 1375, 1245, 1124, 1082, 1026, 845, 807. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{36}H_{38}O_8Na$: 621.2464. Found: 621.2466.

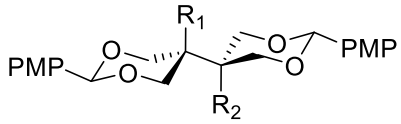
(2,5-*cis*,2',5'-*cis*)-5,5'-bis(4-chlorophenyl)-2,2'-bis(4-methoxyphenyl)-5,5'-bi(1,3-dioxane) (1c)



R_1=R_2=*p*-Cl-Ph

White solid. Analytical data for **1c**: mp: 234-235 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.32 (m, 4H), 7.17-7.11 (m, 4H), 7.00-6.94 (m, 4H), 6.77-6.72 (m, 4H), 5.38 (s, 2H), 4.65 (d, *J* = 11.2 Hz, 4H), 4.14 (d, *J* = 11.3 Hz, 4H), 3.72 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.18, 135.85, 132.84, 130.68, 129.96, 128.13, 127.50, 113.69, 102.40, 70.41, 55.25, 44.80. IR (neat, cm^{-1}): ν = 1614, 1515, 1386, 1244, 1123, 1079, 1024, 971, 839, 804, 750. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{34}H_{32}Cl_2O_6Na$: 629.1474. Found: 629.1473.

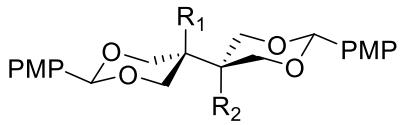
(2,5-*cis*,2',5'-*cis*)-2,2'-bis(4-methoxyphenyl)-5,5'-di-p-tolyl-5,5'-bi(1,3-dioxane) (1d)



R_1=R_2=*p*-Me-Ph

White solid. Analytical data for **1d**: mp: 200 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (s, 8H), 7.02-6.96 (m, 4H), 6.76-6.71 (m, 4H), 5.34 (s, 2H), 4.72 (d, *J* = 11.2 Hz, 4H), 4.11 (d, *J* = 11.3 Hz, 4H), 3.71 (s, 6H), 2.42 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.02, 136.09, 134.60, 130.59, 129.17, 128.65, 127.58, 113.60, 102.17, 70.66, 55.23, 44.51, 21.05. IR (neat, cm^{-1}): ν = 1612, 1516, 1385, 1248, 1173, 1121, 1020, 922, 830, 773. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{34}H_{38}O_6Na$: 589.2566. Found: 589.2575.

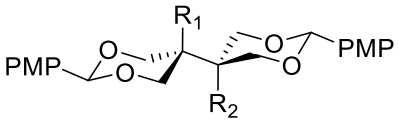
(2,5-*cis*,2',5'-*cis*)-2,2'-bis(4-methoxyphenyl)-5,5'-bis(3-(trifluoromethyl)phenyl)-5,5'-bi(1,3-dioxane) (1e)



R_1=R_2=*m*-CF_3-Ph

White solid. Analytical data for **1e**: mp: 285 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.58 (m, 2H), 7.54-7.46 (m, 2H), 7.42-7.34 (m, 2H), 7.33-7.26 (m, 2H), 7.01-6.94 (m, 4H), 6.80-6.72 (m, 4H), 5.50 (s, 2H), 4.76 (d, *J* = 11.2 Hz, 4H), 4.33 (d, *J* = 11.4 Hz, 4H), 3.75 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.20, 138.20, 132.36, 130.36 (d, J_{C-F} = 132 Hz), 129.68, 128.42, 127.45, 125.85 (q, J_{C-F} = 16.0 Hz), 125.42, 123.94 (q, J_{C-F} = 16.0 Hz), 113.67, 102.40, 70.17, 55.22, 45.47. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.76. IR (neat, cm^{-1}): ν = 1614, 1517, 1394, 1331, 1244, 1125, 1032, 928, 831, 770. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{34}H_{32}F_6O_6Na$: 697.2001. Found: 697.2004.

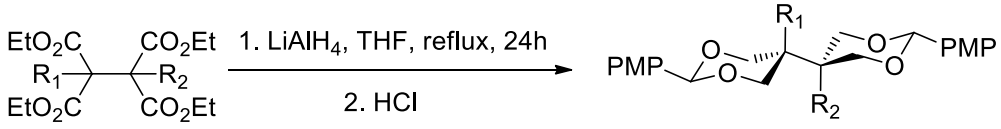
(2,5-*cis*,2',5'-*cis*)-2,2'-bis(4-methoxyphenyl)-5,5'-di(naphthalen-2-yl)-5,5'-bi(1,3-dioxane) (1f)



R_1=R_2=2-Naphthyl

White solid. Analytical data for **1f**: mp: 243 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.86 (m, 4H), 7.86-7.79 (m, 4H), 7.58-7.47 (m, 6H), 6.99-6.88 (m, 4H), 6.69-6.60 (m, 4H), 5.35 (s, 2H), 4.97 (d, *J* = 11.2 Hz, 4H), 4.27 (d, *J* = 11.5 Hz, 4H), 3.65 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.02, 135.23, 133.00, 132.19, 130.22, 128.92, 128.44, 127.53, 127.40, 127.33, 127.06, 126.15, 125.99, 113.57, 102.41, 70.79, 55.18, 45.41. IR (neat, cm^{-1}): ν = 1612, 1514, 1377, 1242, 1170, 1134, 1074, 1026, 806, 777. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{42}H_{38}O_6Na$: 661.2566. Found: 661.2563.

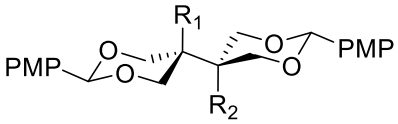
General Procedure for Preparation of 1g, 1l[3]



12 1g,1l

A solution of tetraester **12**[2] (10 mmol) in 30 mL of dry THF was added slowly with cooling and vigorous stirring to a suspension of 1.9g (50 mmol) lithium aluminum hydride in 20 mL of dry THF. The reaction mixture was refluxed for 24h. It was then cooled to 0 ºC and 20 mL of water in 20 mL of ethanol was added slowly with vigorous and filtered. The precipitate was refluxed in CH_3OH (three 50-mL portions) and then filtered. The combined filtrate was concentrated. 10 mL of MeOH was added. It was neutralized (to pH 1-2) with concentrated hydrochloric acid and concentrated. Then, *p*-Anisaldehyde dimethyl acetal (30 mmol) and 3 drops of concentrated hydrochloric acid was added. The reaction mixture was allowed to stir at 55ºC for 30 min. After completion of the reaction, Et_2O (30 mL) was added and filtered. The obtained white solid was washed with H_2O and Et_2O to give the product in 52% (**1g**) and 45% (**1l**) yields for two steps.

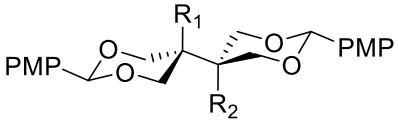
(2,5-*cis*,2',5'-*cis*)-2,2'-bis(4-methoxyphenyl)-5,5'-dimethyl-5,5'-bi(1,3-dioxane) (1g)



R_1=R_2=Me

White solid. Analytical data for **1g**: mp: 196-197 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.38 (m, 4H), 6.94-6.86 (m, 4H), 5.35 (s, 2H), 4.05 (d, *J* = 10.8 Hz, 4H), 3.87 (d, *J* = 11.1 Hz, 4H), 3.81 (s, 6H), 1.37 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.12, 130.71, 127.40, 113.74, 101.84, 71.77, 55.34, 35.99, 16.10. IR (neat, cm^{-1}): ν = 1616, 1520, 1427, 1394, 1256, 1158, 1057, 975, 928, 829. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{24}H_{30}O_6Na$: 437.1940. Found: 437.1946.

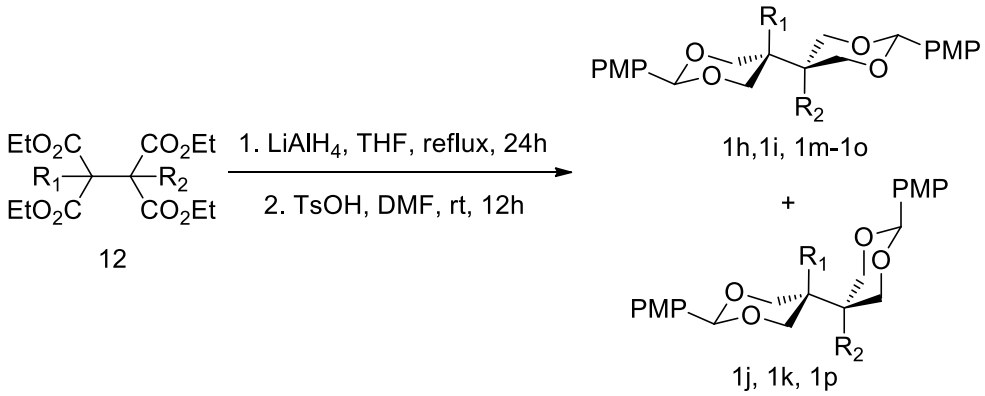
(2,5-*cis*,2',5'-*cis*)-2,2'-bis(4-methoxyphenyl)-5-methyl-5,5'-bi(1,3-dioxane) (1l)



R_1=Me, R_2=H

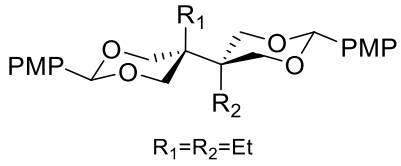
White solid. Analytical data for **1l**: mp: 187-189 ºC. ^{1}H NMR (400 MHz, d^6-acetone) δ 7.48-7.32 (m, 4H), 7.01-6.84 (m, 4H), 5.54 (s, 1H), 5.52 (s, 1H), 4.44-4.32 (m, 2H), 4.16-4.06 (m, 2H), 4.06-3.95 (m, 2H), 3.80 (s, 3H), 3.79 (s, 3H),, 3.64-3.55 (m, 2H), 2.70-2.59 (m, 1H), 0.78 (s, 3H). ^{13}C NMR (101 MHz, d^6-acetone) δ 160.91, 160.73, 132.79, 132.23, 128.43, 128.37, 114.15, 113.98, 102.29, 102.02, 75.00, 69.59, 55.53, 55.50, 38.16, 33.48, 16.94. IR (neat, cm^{-1}): ν = 1613, 1515, 1385, 1249, 1170, 1099, 1023, 976, 820. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{23}H_{28}O_6Na$: 423.1784. Found: 423.1783.

General Procedure for Preparation of 1h-1k, 1m-1p[3]



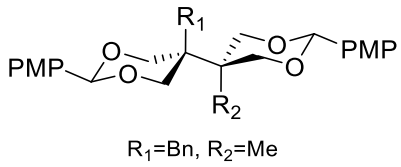
A solution of tetraester **12**[2] (10 mmol) in 30 ml of dry THF was added slowly dropwise with cooling and vigorous stirring to a suspension of 1.9g (50 mmol) $LiAlH_4$ in 20 mL of dry THF. The reaction mixture was refluxed for 24h. It was then cooled to 0 ºC and 20 mL of water in 20 mL of ethanol was added slowly with vigorous and filtered. The precipitate was refluxed in CH_3OH (three 50-mL portions) and then filtered. The combined filtrate was concentrated. 10 mL of MeOH was added. It was neutralized (to pH 1-2) with concentrated hydrochloric acid and concentrated. Then, TsOH (5%), *p*-Anisaldehyde dimethyl acetal (30 mmol), DMF (15 mL) was added. The reaction mixture was allowed to stir at rt for 6-12 hours. The reaction mixture was diluted with ethyl acetate and H_2O. Then the organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel column chromatography (ethyl acetate / petroleum ether) and recrystallized from Et_2O to give the product as white solid in 12%-32% yields for two steps.

(2,5-*cis*,2',5'-*cis*)-5,5'-diethyl-2,2'-bis(4-methoxyphenyl)-5,5'-bi(1,3-dioxane) (1h)



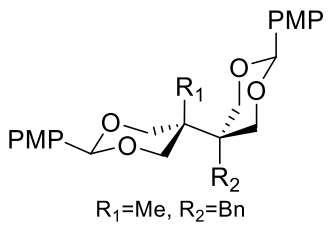
White solid. Analytical data for **1h**: mp: 150 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.35 (m, 4H), 7.95-7.85 (m, 4H), 5.37 (s, 2H), 4.06-3.92 (m, 8H), 3.80 (s, 6H), 2.02 (q, *J* = 7.6 Hz, 4H), 1.13 (t, *J* = 7.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.11, 130.83, 127.43, 113.73, 101.35, 70.29, 55.33, 39.42, 22.91, 10.93. IR (neat, cm^{-1}): ν = 1614, 1514, 1378, 1249, 1171, 1085, 1024, 948, 814, 782. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{26}H_{34}O_6Na$: 465.2253. Found: 465.2254.

(2,5-*cis*,2',5'-*cis*)-5-benzyl-2,2'-bis(4-methoxyphenyl)-5'-methyl-5,5'-bi(1,3-dioxane) (1i)



White solid. Analytical data for **1i**: mp: 108-110 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.34 (m, 4H), 7.30-7.12 (m, 5H), 6.87-6.75 (m, 4H), 5.39 (s, 1H), 5.16 (s, 1H), 4.06 (dd, *J* = 39.2, 11.3 Hz, 4H), 3.81 (d, *J* = 10.9 Hz, 2H), 3.75-3.64 (m, 8H), 3.28 (s, 2H), 1.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.25, 160.09, 139.44, 131.08, 130.67, 130.65, 128.50, 127.61, 127.31, 126.44, 113.83, 113.71, 102.24, 101.55, 71.76, 69.72, 55.36, 55.33, 40.65, 37.47, 34.99, 16.74. IR (neat, cm^{-1}): ν = 1614, 1518, 1389, 1298, 1247, 1172, 1099, 1024, 960, 922, 817. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{30}H_{34}O_6Na$: 513.2253. Found: 513.2254.

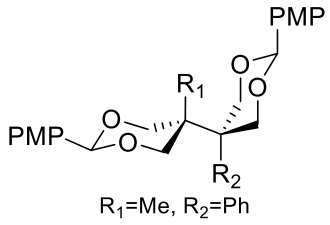
(2,5-*trans*,2',5'-*cis*)-5-benzyl-2,2'-bis(4-methoxyphenyl)-5'-methyl-5,5'-bi(1,3-dioxane) (1j)



R1=Me, R2=Bn

White solid. Analytical data for **1j**: mp: 175-176 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.38-7.27 (m, 5H), 7.09 (d, *J* = 6.9 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.45 (s, 1H), 5.07 (s, 1H), 4.46 (d, *J* = 11.5 Hz, 4H), 4.20 (d, *J* = 11.3 Hz, 2H), 3.85-3.70 (m, 4H), 2.49 (s, 2H), 1.60 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.05, 160.04, 136.51, 131.19, 130.82, 130.27, 128.48, 127.51, 127.49, 126.88, 113.74, 113.72, 101.75, 101.49, 74.48, 70.59, 55.34, 55.30, 38.68, 38.20, 36.34, 17.01. IR (neat, cm^{-1}): ν = 1614, 1518, 1391, 1299, 1249, 1172, 1100, 1025, 987, 818, 750. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{30}H_{34}O_6Na$: 513.2253. Found: 513.2257.

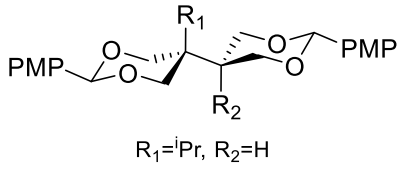
(2,5-*cis*,2',5'-*trans*)-2,2'-bis(4-methoxyphenyl)-5-methyl-5'-phenyl-5,5'-bi(1,3-dioxane) (1k)



R1=Me, R2=Ph

White solid. Analytical data for **1k**: mp: 172-174 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.6 Hz, 2H), 7.51-7.40 (m, 4H), 7.35-7.25 (m, 1H), 7.05-6.98 (m, 2H), 6.96-6.90 (m, 2H), 6.76-6.70 (m, 2H),, 5.57 (s, 1H), 5.44 (s, 1H), 5.14 (d, *J* = 11.7 Hz, 2H), 4.59 (d, *J* = 11.7 Hz, 2H), 4.38 (d, *J* = 12.4 Hz, 2H), 3.82 (s, 3H), 3.72 (s, 3H), 3.50 (d, *J* = 12.5 Hz, 2H), 0.61 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.22, 160.02, 139.05, 131.00, 130.38, 129.68, 127.97, 127.65, 127.61, 126.22, 113.86, 113.59, 102.57, 102.19, 74.99, 72.45, 55.36, 55.24, 46.43, 36.09, 16.80. IR (neat, cm^{-1}): ν = 1613, 1516, 1383, 1300, 1246, 1172, 1117, 1084, 1011, 821, 723. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{29}H_{32}O_6Na$: 499.2097. Found: 499.2104.

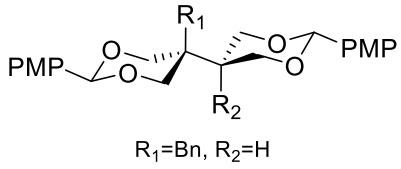
(2,5-*cis*,2',5'-*cis*)-5-isopropyl-2,2'-bis(4-methoxyphenyl)-5,5'-bi(1,3-dioxane) (1m)



R1=^{i}Pr, R2=H

White solid. Analytical data for **1m**: mp: 125-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 8.6, 1.8 Hz, 4H), 6.89 (t, *J* = 9.3 Hz, 4H), 5.45 (s, 1H), 5.33 (s, 1H), 4.47 (dd, *J* = 11.5, 3.7 Hz, 2H), 4.27 (t, *J* = 11.2 Hz, 2H), 4.16 (d, *J* = 12.1 Hz, 2H), 3.79 (d, *J* = 4.9 Hz, 6H), 3.74 (d, *J* = 12.1 Hz, 2H), 2.60 – 2.49 (m, 1H), 1.64-1.53 (m, 1H), 0.96 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.11, 159.93, 131.17, 130.55, 127.55, 127.35, 113.78, 113.63, 101.52, 101.47, 72.80, 71.21, 55.33, 55.30, 37.83, 37.03, 32.20, 17.50. IR (neat, cm^{-1}): ν = 1612, 1513, 1378, 1244, 1173, 1094, 1028, 984, 813, 781. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{25}H_{32}O_6Na$: 451.2097. Found: 451.2110.

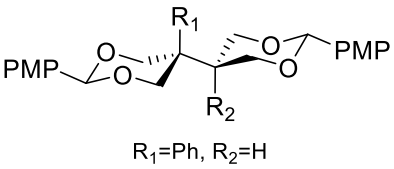
(2,5-*cis*,2',5'-*cis*)-5-benzyl-2,2'-bis(4-methoxyphenyl)-5,5'-bi(1,3-dioxane) (1n)



R1=Bn, R2=H

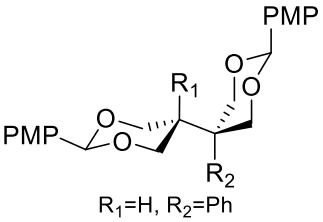
White solid. Analytical data for **1n**: mp: 164-165 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.6 Hz, 2H), 7.43-7.28 (m, 7H), 6.95 (dd, *J* = 18.3, 8.6 Hz, 4H), 5.51 (s, 1H), 5.38 (s, 1H), 4.25 (dd, *J* = 11.3, 3.7 Hz, 2H), 4.06-3.88 (m, 6H), 3.85 (d, *J* = 8.9 Hz, 6H), 3.26 (s, 2H), 2.28-2.14 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.26, 160.09, 137.40, 131.04, 130.67, 130.58, 128.52, 127.58, 127.33, 126.68, 113.84, 113.70, 102.38, 101.56, 71.52, 67.35, 55.37, 55.33, 37.43, 36.34, 35.88. IR (neat, cm^{-1}): ν = 1615, 1518, 1385, 1249, 1174, 1106, 1078, 1027, 964, 831, 874, 747. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{29}H_{32}O_6Na$: 499.2097. Found: 499.2104.

(2,5-*trans*,2',5'-*cis*)-2,2'-bis(4-methoxyphenyl)-5-phenyl-5,5'-bi(1,3-dioxane) (1o)



White solid. Analytical data for **1o**: mp: 211-213 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.38 (m, 3H), 7.35-7.28 (m, 2H), 7.19-7.10 (m, 2H), 6.90-6.70 (m, 4H), 5.56 (s, 1H), 5.20 (s, 1H), 4.75 (d, *J* = 11.4 Hz, 2H), 4.24-4.04 (m, 4H), 3.79 (d, *J* = 5.6 Hz, 3H), 3.74 (s, 3H), 3.66 (t, *J* = 11.4 Hz, 2H), 2.40-2.30 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.12, 160.04, 139.04, 130.58, 130.33, 128.62, 127.75, 127.62, 127.26, 126.76, 113.65, 102.36, 101.51, 72.35, 68.04, 55.30, 55.27, 41.19, 39.89. IR (neat, cm^{-1}): ν = 1613, 1515, 1381, 1248, 1169, 1104, 1083, 1024, 823, 782. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{28}H_{30}O_6Na$: 485.1940. Found: 485.1941.

(2,5-*cis*,2',5'-*cis*)-2,2'-bis(4-methoxyphenyl)-5-phenyl-5,5'-bi(1,3-dioxane) (1p)

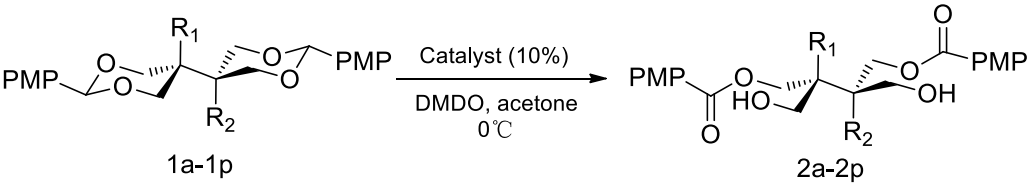


White solid. Analytical data for **1p**: mp: 165 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.40-7.25 (m, 5H), 7.04 (d, *J* = 7.6 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.38 (s, 1H), 5.25 (s, 1H), 4.70 (d, *J* = 11.6 Hz, 2H), 4.38 (dd, *J* = 11.1, 3.5 Hz, 2H), 3.95 (d, *J* = 11.6 Hz, 2H), 3.88-3.70 (m, 8H), 3.04-2.93 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.26, 159.95, 139.72, 131.03, 130.30, 128.86, 127.69, 127.48, 127.38, 125.15, 113.81, 113.62, 101.86, 101.33, 72.86, 69.69, 55.37, 55.30, 39.29, 38.40. IR (neat, cm^{-1}): ν = 1614, 1517, 1382, 1245, 1130, 1087, 1033, 974, 807, 734. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{28}H_{30}O_6Na$: 485.1940. Found: 485.1942.

Procedure for Preparation of Dimethyldioxirane (DMDO)[4]

To a vigorously stirring solution of 40 mL H_2O, 40 mL acetone, and 32g $NaHCO_3$ at room temperature was added 60 g Oxone in a portion. Simultaneously, reduced pressure (ca. 30 mm, water aspirator) was connected to the receiving flask cooled by liquid nitrogen. After about 1 hour, the receiving flask was taken out, and the fresh DMDO was transferred to a 100 mL round flask. The DMDO was used directly without any further treatment. The concentration of DMDO is determined through titration (~0.1 mmol/mL).

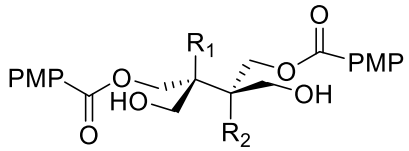
General Procedure for Oxidative Desymmetrization of 1a-1p[5]



To a flame-dried Schlenk tube were added substrate **1** (0.025 mmol) and catalyst 10 mol%. The tube was put into ice-water bath. To the mixture was added 2 mL fresh-made DMDO* (~0.1 mmol/mL). The mixture was stirred at 0 ℃ until the starting material disappeared (monitored by TLC). The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (DCM: CH_3OH = 20:1) to afford a mixture of diastereomers **2** and **2'**.

(*DMDO was used immediately after preparation, and the concentration of DMDO was determined to be ~0.1 mmol/mL. The concentration dropped from ~0.1 mmol/mL to ~0.07 mmol/mL after storage for one week at -20 ℃.)

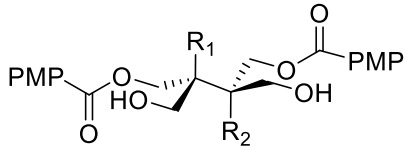
(2*R*, 3*R*)-2,3-bis(hydroxymethyl)-2,3-diphenylbutane-1,4-diyl bis(4-methoxybenzoate) (2a)



R_1=R_2=Ph

White solid, 94%, 15.8:1 d.r., >99% *ee*. Analytical data for **2a**: $[\alpha]_D^{20}$ = +26.8° (c = 0.38, CH_3OH). mp: 89-90 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.8 Hz, 4H), 7.25-7.14 (m, 6H), 6.95-6.84 (m, 4H), 6.79 (d, *J* = 8.9 Hz, 4H), 5.36 (d, *J* = 11.5 Hz, 2H), 5.00 (d, *J* = 11.5 Hz, 2H), 4.46 (d, *J* = 12.4 Hz, 2H), 3.92 (d, *J* = 12.4 Hz, 2H), 3.79 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.14, 163.56, 138.06, 131.72, 128.57, 127.45, 127.02, 121.90, 113.64, 63.09, 62.81, 55.41, 52.12. IR (neat, cm^{-1}): ν = 2920, 1705, 1604, 1511, 1253, 1166, 1101, 1026, 845, 767. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{34}H_{34}O_8Na$: 593.2151. Found: 593.2161. The enantiomeric ratio was determined by Daicel Chiralpak AD-H, Hexanes/IPA = 80:20, 1.5 mL/min, λ = 254nm, t_R(major) = 22.16 min, t_R(minor) = 32.99 min. Analytical data for the isomer of **2a**: white solid, mp: 83°C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.87-7.78 (m, 4H), 7.26-7.20 (m, 6H), 7.00-6.93 (m, 4H), 6.89-6.82 (m, 4H), 5.14 (d, *J* = 11.8 Hz, 2H), 4.98 (d, *J* = 11.7 Hz, 2H), 4.40 (d, *J* = 12.1 Hz, 2H), 4.15 (d, *J* = 12.1 Hz, 2H), 3.81 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.82, 163.64, 137.82, 131.76, 128.54, 127.71, 127.18, 121.92, 113.77, 64.07, 62.73, 55.46, 52.81. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{34}H_{34}O_8Na$: 593.2151. Found: 593.2158.

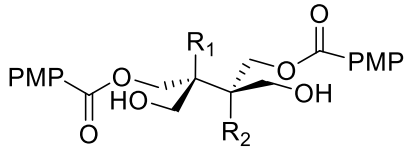
(2*R*, 3*R*)-2,3-bis(hydroxymethyl)-2,3-bis(4-methoxyphenyl)butane -1,4-diyl bis(4-methoxybenzoate) (2b)



R_1=R_2=*p*-OMe-Ph

White solid, 93%, 18:1 d.r., >99% *ee*. Analytical data for **2b**: $[\alpha]_D^{20}$ = +4.8° (c = 0.63, CH_3OH). mp: 116 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.76-7.70 (m, 4H), 6.87-6.72 (m, 12H), 5.29 (d, *J* = 11.5 Hz, 2H), 4.94 (d, *J* = 11.5 Hz, 2H), 4.39 (d, *J* = 11.9 Hz, 2H), 3.89 (d, *J* = 12.5 Hz, 2H), 3.80 (d, *J* = 2.8 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.17, 163.57, 158.21, 131.74, 130.01, 129.69, 121.95, 113.66, 112.74, 63.39, 62.98, 55.42, 55.16, 51.77. IR (neat, cm^{-1}): ν = 2818, 1707, 1605, 1513, 1255, 1167, 1103, 1025, 768. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{34}H_{38}O_{10}Na$: 653.2363. Found: 653.2370. The enantiomeric ratio was determined by Daicel Chiralpak AD-H, Hexanes/IPA = 70:30, 2.0 mL/min, λ = 254nm, t_R(major) = 8.91 min, t_R(minor) = 18.83 min.

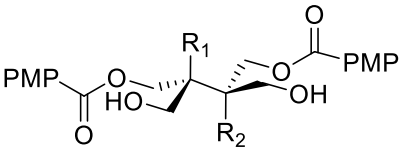
(2*R*, 3*R*)-2,3-bis(4-chlorophenyl)-2,3-bis(hydroxymethyl)butane-1,4-diyl bis(4-methoxybenzoate) (2c)



R_1=R_2=*p*-Cl-Ph

White solid, 93%, 13:1 d.r., >99% *ee*. Analytical data for **2c**: $[\alpha]_D^{20}$ = +10.4° (c = 0.50, CH_3OH). mp: 109 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.72-7.65 (m, 4H), 7.22 (d, *J* = 8.9 Hz, 4H), 6.95-6.83 (br, 4H), 6.83-6.77 (m, 4H), 5.36 (d, *J* = 11.7 Hz, 2H), 5.06 (d, *J* = 11.6 Hz, 2H), 4.29 (d, *J* = 12.2 Hz, 2H), 3.84-3.73 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.13, 163.74, 136.45, 133.17, 131.73, 130.01, 127.71, 121.55, 113.74, 62.96, 62.50, 55.43, 52.12. IR (neat, cm^{-1}): ν = 2919, 1712, 1604, 1508, 1253, 1169, 1096, 1028, 846, 793, 765. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{34}H_{32}Cl_2O_8Na$: 661.1372. Found: 661.1376. The enantiomeric ratio was determined by Daicel Chiralpak IB, Hexanes/IPA = 80:20, 1.5 mL/min, λ = 254nm, t_R(major) = 10.05 min, t_R(minor) = 11.20 min.

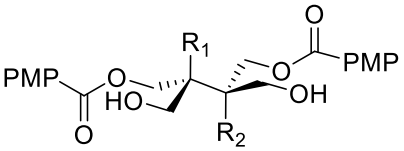
(2*R*, 3*R*)-2,3-bis(hydroxymethyl)-2,3-di-p-tolylbutane-1,4-diyl bis(4-methoxybenzoate) (2d)



R_1=R_2=*p*-Me-Ph

White solid, 88%, 11:1 d.r., >99% *ee*. Analytical data for **2d**: $[\alpha]_D^{20}$ = +9.4° (c = 0.53, CH_3OH). mp: 105-107 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.82-7.68 (m, 4H), 7.02 (d, *J* = 8.0 Hz, 4H), 6.90-6.73 (m, 8H), 5.26 (d, *J* = 11.5 Hz, 2H), 4.91 (d, *J* = 11.5 Hz, 2H), 4.43 (d, *J* = 12.3 Hz, 2H), 3.95 (d, *J* = 12.3 Hz, 2H), 3.80 (s, 6H), 2.31 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.13, 163.55, 136.54, 134.85, 131.75, 128.44, 128.19, 122.01, 113.64, 63.62, 62.86, 55.42, 51.81, 20.96. IR (neat, cm^{-1}): ν = 2919, 1692, 1604, 1512, 1255, 1166, 1102, 1027, 846, 767. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{36}H_{38}O_8Na$: 621.2464. Found: 621.2465. The enantiomeric ratio was determined by Daicel Chiralpak IB, Hexanes/IPA = 80:20, 1.5 mL/min, λ = 254nm, t_R(major) = 9.13 min, t_R(minor) = 10.08 min.

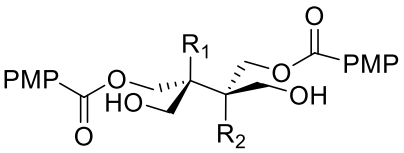
(2*R*, 3*R*)-2,3-bis(hydroxymethyl)-2,3-bis(3-(trifluoromethyl)phenyl) butane-1,4-diyl bis(4-methoxybenzoate) (2e)



R_1=R_2=*m*-CF_3-Ph

White solid, 89%, 6:1 d.r., >99% *ee*. Analytical data for **2e**: $[\alpha]_D^{20}$ = +14.9° (c = 0.51, CH_3OH). mp: 202-204 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.8 Hz, 4H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.35-7.15 (br, 2H), 7.10-6.90 (br, 2H), 6.79 (d, *J* = 8.8 Hz, 4H), 5.47 (d, *J* = 11.6 Hz, 2H), 5.26-5.05 (br, 2H), 4.40-4.20 (br, 2H), 3.86-3.70 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.14, 163.81, 138.94, 131.75, 130.14, 129.82, 128.18, 125.27, 124.15 (q, J_{C-F} = 16.0 Hz), 122.56, 121.34, 113.74, 62.70, 62.13, 55.43, 52.72. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.57. IR (neat, cm^{-1}): ν = 2918, 1695, 1609, 1524, 1328, 1260, 1169, 1117, 1015, 763, 710. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{36}H_{32}F_6O_8Na$: 729.1899. Found: 729.1901. The enantiomeric ratio was determined by Daicel Chiralpak IB, Hexanes/IPA = 80:20, 1.5 mL/min, λ = 254nm, t_R(major) = 7.71 min, t_R(minor) = 8.55 min.

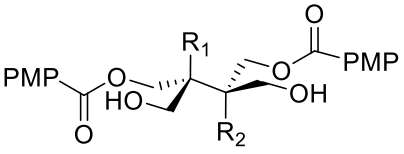
(2*R*, 3*R*)-2,3-bis(hydroxymethyl)-2,3-di(naphthalen-2-yl)butane-1,4-diyl bis(4-methoxybenzoate) (2f)



R_1=R_2=2-Naphthyl

White solid, 96%, 12:1 d.r., >99% *ee*. Analytical data for **2f**: $[\alpha]_D^{20}$ = -29.3° (c = 0.92, CH_3OH). mp: 92-94 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.70-7.56 (m, 8H), 7.51-7.41 (m, 4H), 7.34-7.28 (br, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.71 (d, *J* = 8.9 Hz, 4H), 5.52 (d, *J* = 10.1 Hz, 2H), 5.30-5.06 (br, 2H), 4.58 (d, *J* = 12.1 Hz, 2H), 4.12-3.96 (br, 2H), 3.74 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.18, 163.55, 135.72, 132.56, 132.23, 131.70, 128.28, 127.98, 127.92, 127.24, 126.62, 126.18, 125.94, 121.79, 113.63, 63.30, 63.22, 55.36, 52.56. IR (neat, cm^{-1}): ν = 2920, 1690, 1604, 1510, 1255, 1166, 1100, 1024, 845, 766. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{42}H_{38}O_8Na$: 693.2464. Found: 693.2464. The enantiomeric ratio was determined by Daicel Chiralpak IB, Hexanes/IPA = 80:20, 1.5 mL/min, λ = 254nm, t_R(major) = 12.69 min, t_R(minor) = 15.65 min.

(2*R*, 3*R*)-2,3-bis(hydroxymethyl)-2,3-dimethylbutane-1,4-diyl bis(4-methoxybenzoate) (2g)

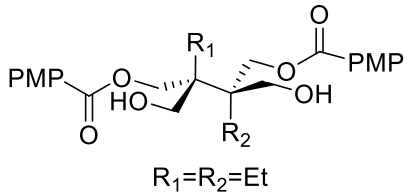


R_1=R_2=Me

White solid, 84%, 8:1 d.r., >99% *ee*. Analytical data for **2g**: $[\alpha]_D^{20}$ = -4.0° (c = 0.50, CH_3OH). mp: 141-142 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.05-7.95 (m, 4H), 6.98-6.87 (m, 4H),

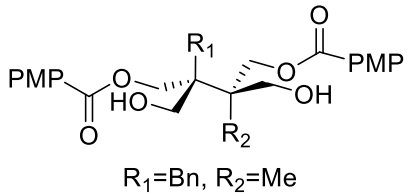
4.66 (d, *J* = 11.3 Hz, 2H), 4.36 (d, *J* = 11.2 Hz, 2H), 3.86 (s, 6H), 3.75 (d, *J* = 12.3 Hz, 2H), 3.57 (d, *J* = 12.3 Hz, 2H), 1.06 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.94, 163.64, 131.74, 122.18, 113.78, 66.20, 64.61, 55.48, 43.30, 16.81. IR (neat, cm^{-1}): ν = 2921, 1703, 1675, 1605, 1511, 1460, 1259, 1167, 1101, 1030, 843, 765. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{24}H_{30}O_8Na$: 469.1838. Found: 469.1839. The enantiomeric ratio was determined by Daicel Chiralpak AD-H, Hexanes/IPA = 80:20, 1.5 mL/min, λ = 254nm, t_R(major) = 12.87 min, t_R(minor) = 13.92 min.

(2*R*, 3*R*)-2,3-diethyl-2,3-bis(hydroxymethyl)butane-1,4-diyl bis(4-methoxybenzoate) (2h)



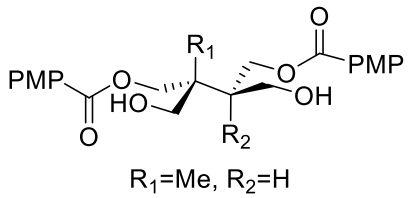
Colorless oil, 61%, 18:1 d.r., >99% *ee*. Analytical data for **2h**: $[\alpha]_D^{20}$ = -3.2° (c = 0.44, CH_3OH). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.90 (m, 4H), 6.98-6.86 (m, 4H), 4.47 (q, *J* = 12.0 Hz, 4H), 3.89-3.77 (m, 10H), 1.79 (ddd, *J* = 14.6, 7.2, 3.0 Hz, 4H), 1.02 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.43, 163.54, 131.60, 122.34, 113.79, 65.82, 62.95, 55.48, 46.12, 22.95, 9.14. IR (neat, cm^{-1}): ν = 2920, 1706, 1604, 1511, 1462, 1251, 1166, 1100, 1024, 846, 768. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{26}H_{34}O_8Na$: 497.2151. Found: 497.2151. The enantiomeric ratio was determined by Daicel Chiralpak AD-H, Hexanes/IPA = 90:10, 1.5 mL/min, λ = 254nm, tR(major) = 20.49 min, tR(minor) = 22.66 min.

(2*R*, 3*R*)-2-benzyl-2,3-bis(hydroxymethyl)-3-methylbutane-1,4-diyl bis(4-methoxybenzoate) (2i)



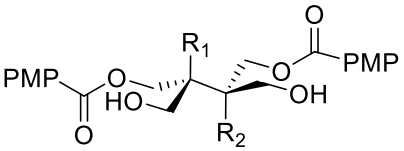
Colorless oil, 94%, 5:1 d.r., 92% *ee*. Analytical data for **2i**: $[\alpha]_D^{20}$ = +39.6° (c = 0.46, CH_3OH). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.98 (m, 2H), 7.90-7.83 (m, 2H), 7.25-7.12 (m, 5H), 6.95-6.87 (m, 4H), 4.79 (d, *J* = 11.3 Hz, 1H), 4.53 (d, *J* = 11.3 Hz, 1H), 4.32 (dd, *J* = 29.0, 12.2 Hz, 2H), 3.88-3.75 (m, 9H), 3.69 (d, *J* = 12.1 Hz, 1H), 3.06 (s, 2H), 1.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.77, 166.08, 163.65, 163.56, 137.25, 131.71, 131.62, 130.77, 128.35, 126.55, 122.21, 122.19, 113.82, 113.77, 67.17, 66.19, 65.49, 63.11, 55.48, 55.48, 46.14, 44.35, 36.08, 17.46. IR (neat, cm^{-1}): ν = 2919, 1709, 1604, 1551, 1255, 1165, 1099, 1026, 845, 767. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{30}H_{34}O_8Na$: 545.2151. Found: 545.2155. The enantiomeric ratio was determined by Daicel Chiralpak AD-H, Hexanes/IPA = 90:10, 1.5 mL/min, λ = 254nm, t_R(major) = 48.88 min, t_R(minor) = 44.34 min.

(2*R*, 3*R*)-2,3-bis(hydroxymethyl)-2-methylbutane-1,4-diyl bis(4-methoxybenzoate) (2l)



Colorless oil, 85%, 5:1 d.r., 98% *ee*. Analytical data for **2l**: $[\alpha]_D^{20}$ = +7.0° (c = 0.77, CH_3OH). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.84 (m, 4H), 6.83 (t, *J* = 8.5 Hz, 4H), 4.60-4.45 (m, 2H), 4.27 (dd, *J* = 30.0, 11.3 Hz, 2H), 3.90-3.72 (m, 8H), 3.54 (dd, *J* = 36.6, 11.8 Hz, 2H), 2.07-1.96 (m, 1H), 1.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.92, 166.62, 163.62, 131.73, 131.71, 122.11, 113.78, 113.74, 67.84, 65.67, 62.30, 59.58, 55.47, 55.46, 44.85, 41.23, 41.10, 18.82. IR (neat, cm^{-1}): ν = 2919, 1678, 1604, 1510, 1419, 1257, 1167, 1101, 1028, 843, 769. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{23}H_{28}O_8Na$: 455.1682. Found: 455.1685. The *ee* of **2l** was determined by transforming **2l** to **8**. And analytical data for **8** was given below.

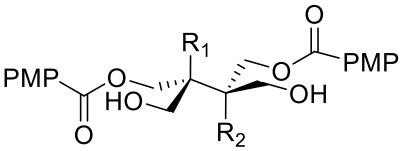
(2*R*, 3*R*)-2,3-bis(hydroxymethyl)-2-isopropylbutane-1,4-diyl bis(4-methoxybenzoate) (2m)



R_1=^{i}Pr, R_2=H

Colorless oil, 76%, 8:1 d.r., >99% *ee*. Analytical data for **2m**: $[\alpha]_D^{20}$ = +8.1° (c = 0.67, CH_3OH). ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (t, *J* = 8.9 Hz, 4H), 6.90 (dd, *J* = 12.3, 8.9 Hz, 4H), 4.90-4.77 (m, 1H), 4.49 (dd, *J* = 11.2, 3.9 Hz, 1H), 4.29 (dd, *J* = 57.0, 12.1 Hz, 2H), 3.96-3.80 (m, 8H), 3.60 (dd, *J* = 43.7, 12.3 Hz, 2H), 2.46-2.38 (m, 1H), 2.35 (dt, *J* = 13.8, 7.0 Hz, 1H), 1.09 (d, *J* = 6.8 Hz, 3H), 1.00 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.15, 166.17, 163.59, 163.52, 131.76, 131.61, 122.28, 122.06, 113.78, 113.66, 64.48, 62.42, 61.41, 58.42, 55.46, 44.90, 42.39, 28.49, 17.49, 17.39. IR (neat, cm^{-1}): ν = 2919, 1706, 1604, 1511, 1251, 1165, 1099, 1024, 845, 768. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{25}H_{32}O_8Na$: 483.1995. Found: 483.2019. The enantiomeric ratio was determined by Daicel Chiralpak AD-H, Hexanes/IPA = 90:10, 1.0 mL/min, λ = 254nm, t_R(major) = 34.28 min, t_R(minor) = 32.37 min.

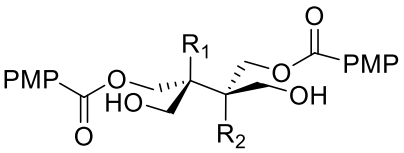
(2*R*, 3*R*)-2-benzyl-2,3-bis(hydroxymethyl)butane-1,4-diyl bis(4-methoxybenzoate) (2n)



R_1=Bn, R_2=H

Colorless oil, 75%, 5:1 d.r., >99% *ee*. Analytical data for **2n**: $[\alpha]_D^{20}$ = +17.3° (c = 0.45, CH_3OH). ^1H NMR (400 MHz, $CDCl_3$) δ 8.05-7.97 (m, 4H), 7.32-7.19 (m, 5H), 7.00-6.88 (m, 4H), 4.74 (d, *J* = 6.7 Hz, 2H), 4.54 (d, *J* = 11.6 Hz, 1H), 4.18 (d, *J* = 11.7 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.84-3.72 (m, 2H), 3.57 (dd, *J* = 27.7, 12.3 Hz, 2H), 2.88 (dd, *J* = 48.3, 13.7 Hz, 2H), 2.18-2.10 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.86, 166.62, 163.77, 163.63, 136.25, 131.79, 130.67, 128.49, 126.81, 122.18, 121.99, 113.90, 113.74, 64.36, 62.76, 61.29, 58.26, 55.52, 55.48, 44.82, 42.77, 37.58. IR (neat, cm^{-1}): ν = 2919, 1706, 1604, 1511, 1252, 1165, 1099, 1024, 845, 767. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{29}H_{32}O_8Na$: 531.1995. Found: 531.2006. The enantiomeric ratio was determined by Daicel Chiralpak AD-H, Hexanes/IPA = 80:20, 1.5 mL/min, λ = 254nm, t_R(major) = 15.32 min, t_R(minor) = 20.97 min.

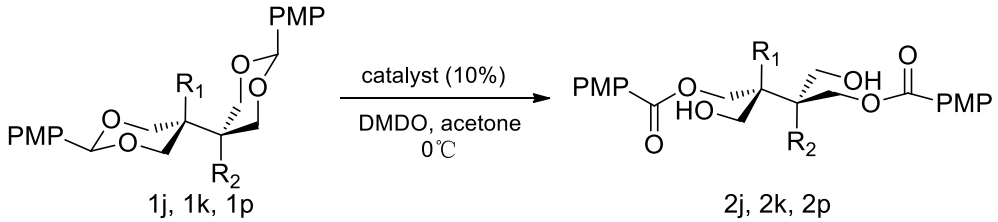
(2*S*, 3*R*)-2,3-bis(hydroxymethyl)-2-phenylbutane-1,4-diyl bis(4-methoxybenzoate) (2o)



R_1=Ph, R_2=H

Colorless oil, 88%, 8:1 d.r., >99% *ee*. Analytical data for **2o**: $[\alpha]_D^{20}$ = -22.3° (c = 0.53, CH_3OH). ^1H NMR (400 MHz, $CDCl_3$) δ 7.93-7.86 (m, 2H), 7.79-7.72 (m, 2H), 7.45-7.33 (m, 4H), 7.26-7.22 (m, 1H), 6.92-6.77 (m, 4H), 5.03 (d, *J* = 11.4 Hz, 1H), 4.79 (d, *J* = 11.4 Hz, 1H), 4.57 (dd, *J* = 11.3, 8.6 Hz, 1H), 4.29-4.22 (m, 2H), 4.11 (d, *J* = 12.1 Hz, 1H), 3.86-3.78 (m, 8H), 2.52-2.42 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.95, 166.61, 163.63, 163.55, 141.14, 131.77, 131.65, 128.78, 127.00, 126.49, 122.02, 121.99, 113.67, 65.89, 62.98, 62.03, 59.07, 55.45, 55.41, 48.20, 46.86. IR (neat, cm^{-1}): ν = 2918, 1706, 1604, 1511, 1254, 1165, 1098, 1021, 845, 765, 695. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{28}H_{30}O_8Na$: 517.1838. Found: 517.1839. The enantiomeric ratio was determined by Daicel Chiralpak IB, Hexanes/IPA = 80:20, 0.2 mL/min, λ = 254nm, t_R(major) = 84.59 min, t_R(minor) = 88.63 min.

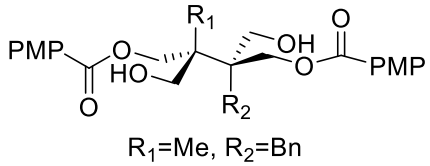
General Procedure for Oxidative Desymmetrization of 1j, 1k, 1p[5]



To a flame-dried Schlenk tube were added substrate **1j**, **1k** or **1p** (0.025 mmol) and catalyst 10 mol%. The tube was put into ice-water bath. To the mixture was added 2 mL fresh-made DMDO* (~0.1 mmol/mL). The mixture was stirred at 0 ºC until the starting material disappeared (monitored by TLC). The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (DCM: CH_3OH = 20:1) to afford product **2j**, **2k**, **2p**.

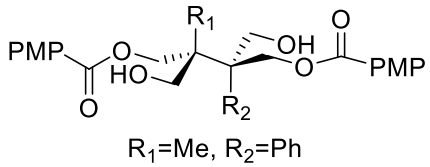
(*DMDO was used immediately after preparation, and the concentration of DMDO was determined to be ~0.1 mmol/mL. The concentration dropped from ~0.1 mmol/mL to ~0.07 mmol/mL after storage for one week at -20 ºC.)

(2*S*, 3*R*)-2-benzyl-2,3-bis(hydroxymethyl)-3-methylbutane-1,4-diyl bis(4-methoxybenzoate) (2j)



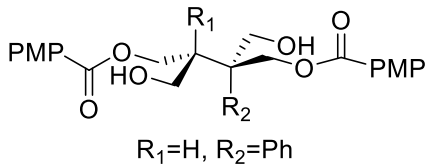
Colorless oil, 89%, 5:1 d.r., 98% *ee*. Analytical data for **2j**: $[\alpha]_D^{20}$ = -32.9° (c = 0.79, CH_3OH). ^1H NMR (400 MHz, $CDCl_3$) δ 8.01-7.97 (m, 2H), 7.88-7.82 (m, 2H), 7.35-7.30 (m, 2H), 7.29-7.23 (m, 4H), 7.21-7.15 (m, 1H), 6.94-6.87 (m, 4H), 4.95 (d, *J* = 11.2 Hz, 1H), 4.53 (d, *J* = 11.3 Hz, 1H), 4.37 (d, *J* = 12.2 Hz, 1H), 4.14 (d, *J* = 12.2 Hz, 1H), 3.90-3.80 (m, 8H), 3.59 (dd, *J* = 12.4, 9.3 Hz, 2H), 3.21 (d, *J* = 13.2 Hz, 1H), 2.80 (d, *J* = 13.2 Hz, 1H), 1.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.28, 166.00, 163.74, 163.55, 136.81, 131.84, 131.60, 130.89, 128.33, 126.56, 122.11, 121.98, 113.80, 67.12, 66.59, 64.25, 61.69, 55.50, 55.47, 46.11, 44.73, 35.06, 17.13. IR (neat, cm^{-1}): ν = 2356, 1710, 1605, 1258, 1102, 1056, 766. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{30}H_{34}O_8Na$: 545.2151. Found: 545.2158. The enantiomeric ratio was determined by Daicel Chiralpak AD-H, Hexanes/IPA = 90:10, 1.5 mL/min, λ = 254nm, t_R(major) = 38.60 min, t_R(minor) = 56.35 min.

(2*R*, 3*S*)-2,3-bis(hydroxymethyl)-2-methyl-3-phenylbutane-1,4-diyl bis(4-methoxybenzoate) (2k)



Colorless oil, 87%, 4:1 d.r., >99% *ee*. Analytical data for **2k**: $[\alpha]_D^{20}$ = -26.5° (c = 0.76, CH_3OH). ^1H NMR (400 MHz, $CDCl_3$) δ 8.04-7.92 (m, 2H), 7.87-7.72 (m, 2H), 7.42-7.31 (m, 4H), 7.29-7.23 (m, 1H), 7.00-6.90 (m, 2H), 6.87-6.80 (m, 2H), 5.32 (d, *J* = 11.8 Hz, 1H), 5.16 (d, *J* = 11.8 Hz, 1H), 4.53 (d, *J* = 12.2 Hz, 1H), 4.29 (d, *J* = 11.6 Hz, 1H), 4.14 (d, *J* = 11.6 Hz, 1H), 4.02 (d, *J* = 12.2 Hz, 1H), 3.87 (s, 3H), 3.85-3.78 (m, 4H), 3.63 (d, *J* = 12.2 Hz, 1H), 1.06 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.11, 166.42, 163.66, 163.63, 138.70, 131.75, 131.71, 128.14, 127.95, 127.04, 122.07, 121.88, 113.86, 113.70, 67.99, 65.05, 63.30, 62.73, 55.50, 55.44, 51.62, 44.67, 17.12. IR (neat, cm^{-1}): ν = 2919, 1704, 1604, 1511, 1253, 1165, 1099, 1023, 845, 767. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{29}H_{32}O_8Na$: 531.1995. Found: 531.2102. The enantiomeric ratio was determined by Daicel Chiralpak IB, Hexanes/IPA = 80:20, 0.3 mL/min, λ = 254nm, t_R(major) = 42.39 min, t_R(minor) = 44.72 min.

(2*R*, 3*R*)-2,3-bis(hydroxymethyl)-2-phenylbutane-1,4-diyl bis(4-methoxybenzoate) (2p)



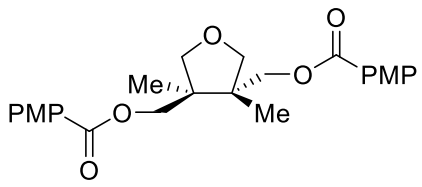
R_1=H, R_2=Ph

Colorless oil, 91%, 8:1 d.r., >99% *ee*. Analytical data for **2p**: $[\alpha]_D^{20}$ = -1.0° (c = 0.58, CH_3OH). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.91 (m, 2H), 7.88-7.82 (m, 2H), 7.50-7.44 (m, 2H), 7.41-7.34 (m, 2H), 7.29-7.22 (m, 1H), 6.92-6.83 (m, 4H), 4.92 (d, *J* = 11.7 Hz, 1H), 4.82 (d, *J* = 11.7 Hz, 1H), 4.42 (qd, *J* = 11.5, 5.8 Hz, 2H), 4.22 (d, *J* = 12.0 Hz, 1H), 4.01 (d, *J* = 12.1 Hz, 1H), 3.92 (dd, *J* = 11.9, 5.8 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 3.77 (dd, *J* = 12.0, 4.0 Hz, 1H), 2.68-2.61 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.71, 166.57, 163.62, 140.95, 131.74, 131.72, 128.83, 127.07, 126.88, 122.00, 121.94, 113.75, 113.72, 65.49, 64.92, 62.90, 60.09, 55.47, 55.46, 49.08, 47.33. IR (neat, cm^{-1}): ν = 2919, 1705, 1604, 1511, 1468, 1256, 1165, 1098, 1019, 845, 798. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{28}H_{30}O_8Na$: 517.1838. Found: 517.1839. The enantiomeric ratio was determined by Daicel Chiralpak IB, Hexanes/IPA = 80:20, 0.2 mL/min, λ = 254nm, t_R(major) = 73.80 min, t_R(minor) = 79.59 min.

General Procedure for the synthesis of 3, 8, 9[6]

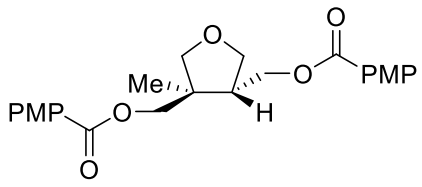
To a dry 25 mL round-bottom flask were added 1.12 g TsCl (5.8 mmol, 2.2 equiv), 32 mg DMAP (0.27 mmol, 0.10 equiv), 0.74 mL Et_3N (5.4 mmol, 2.0 equiv), and 6 mL DCM. The resulting mixture was cooled to 0 ºC, and a solution of **2** in 6 mL DCM was added dropwise. The mixture was allowed to warm to room temperature and stirred overnight. The solution was then washed with sat. aq. $NaHCO_3$ (1×12 mL) and H_2O (1×12 mL). The combined aqueous layers were extracted with DCM (12 mL) and the combined organic layers were dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate / petroleum ether) to afford product **3**, **8**, **9** in 90%-95% yield.

((3*R*, 4*R*)-3,4-dimethyltetrahydrofuran-3,4-diyl)bis(methylene) bis(4-methoxybenzoate) (3)



White solid, Analytical data for **3**: $[\alpha]_D^{20}$ = -7.1° (c = 0.79, $CHCl_3$). mp: 107-108 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.4, 5.9 Hz, 4H), 7.06-6.85 (m, 4H), 4.46-4.27 (m, 4H), 4.09 (t, *J* = 9.0 Hz, 2H), 3.90 (s, 3H), 3.89 (s, 3H), 3.81 (dd, *J* = 8.6, 6.0 Hz, 2H), 1.28 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.25, 163.55, 131.60, 122.29, 113.79, 77.12, 68.01, 55.47, 46.57, 17.24. IR (neat, cm^{-1}): ν = 2357, 1726, 1604, 1455, 1276, 1164, 1052, 750, 714. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{24}H_{28}O_7Na$: 451.1733. Found: 451.1735.

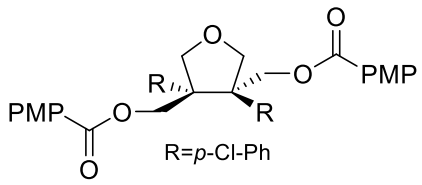
((3*R*, 4*R*)-3-methyltetrahydrofuran-3,4-diyl)bis(methylene) bis(4-methoxybenzoate) (8)



Colorless oil, Analytical data for **8**: $[\alpha]_D^{20}$ = -8.4° (c = 0.38, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-7.91 (m, 4H), 7.04-6.88 (m, 4H), 4.56 (dd, *J* = 11.3, 6.7 Hz, 1H), 4.48-4.30 (m, 3H), 4.29-4.20 (m, 1H), 4.01 (d, *J* = 8.7 Hz, 1H), 3.89 (s, 6H), 3.66 (d, *J* = 8.8 Hz, 1H), 2.62 (dq, *J* = 15.7, 7.8 Hz, 1H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.19, 163.52, 131.63, 122.27, 113.74, 77.23, 71.04, 66.70, 62.82, 55.46, 47.66, 44.60, 21.80. IR (neat, cm^{-1}): ν = 2917, 1698, 1605, 1511, 1464, 1258,

1167, 1094, 1024, 847, 799, 769. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{23}H_{26}O_7Na$: 437.1576 Found: 437.1574. The enantiomeric ratio was determined by Daicel Chiralpak AD-H, Hexanes/IPA = 90:10, 0.6 mL/min, λ = 254nm, t_R(major) = 58.34 min, t_R(minor) = 52.72 min.

((3*R*, 4*R*)-3,4-bis(4-chlorophenyl)tetrahydrofuran-3,4-diyl)bis(methylene) bis(4-methoxybenzoate) (9)

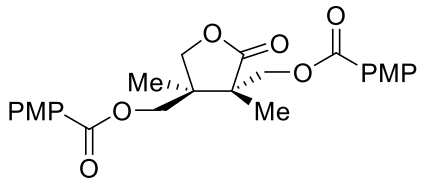


White solid, Analytical data for **9**: $[\alpha]_D^{20}$ = -44.5° (c = 0.40, $CHCl_3$). mp: 191-192 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.8 Hz, 4H), 7.40 (dd, *J* = 25.5, 8.6 Hz, 8H), 6.80 (d, *J* = 8.8 Hz, 4H), 4.60 (dd, *J* = 10.4, 6.5 Hz, 4H), 4.32 (d, *J* = 9.5 Hz, 2H), 3.87 (d, *J* = 11.6 Hz, 2H), 3.80 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.69, 163.54, 136.90, 133.60, 131.42, 129.02, 128.79, 121.68, 113.69, 77.16, 67.11, 55.43, 54.66. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{34}H_{30}Cl_2O_7Na$: 643.1266. Found: 643.1236.

Procedure for the synthesis of 4[7]

To a 10 mL round-bottom flask were added **2g** (0.1 mmol, 1.0 equiv) and 1 mL acetone. The resulting mixture was cooled to 0 °C, and 2 mL Jones reagent was added dropwise. The mixture was allowed to stir at 0 °C for 30 min. The reaction mixture was then diluted with EtOAc (3 × 10 mL) and washed with brine, the combined organic layers were dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate / petroleum ether) to afford product **4** in 81% yield.

((3*S*, 4*S*)-3,4-dimethyl-2-oxotetrahydrofuran-3,4-diyl)bis(methylene) bis(4-methoxybenzoate) (4)

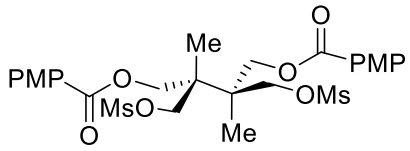


Colorless oil, Analytical data for **4**: $[\alpha]_D^{20}$ = 5.5° (c = 0.58, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.90 (m, 4H), 6.98-6.87 (m, 4H), 4.49 (d, *J* = 11.4 Hz, 1H), 4.37 (d, *J* = 9.1 Hz, 1H), 4.32 (dd, *J* = 11.4, 5.0 Hz, 2H), 4.24 (dd, *J* = 12.9, 10.5 Hz, 2H), 3.86 (d, *J* = 1.9 Hz, 6H), 1.32 (s, 3H), 1.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.70, 165.94, 165.51, 163.82, 131.82, 131.75, 121.57, 121.48, 113.94, 74.68, 68.82, 66.80, 55.50, 55.48, 47.01, 43.81, 15.79, 14.21. IR (neat, cm^{-1}): ν = 2919, 1709, 1604, 1511, 1468, 1255, 1165, 1085, 1019, 845, 766. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{24}H_{26}O_8Na$: 465.1525. Found: 465.1525.

Procedure for the synthesis of 10[8]

To a dry 10 mL round-bottom flask were added MsCl (0.3 mmol), DMAP (0.01 mmol), Et_3N (0.3 mmol), and 1 mL dry DCM. The resulting mixture was cooled to 0 °C, and a solution of **2g** (0.1 mmol) in 1 mL dry DCM was added dropwise. The mixture was allowed to warm to room temperature and was allowed to stir overnight. The solution was then washed with sat. aq. $NaHCO_3$ and H_2O. The combined aqueous layers were extracted with DCM and the combined organic layers were dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate / petroleum ether) to afford product **10** in 99% yield.

(2*S*, 3*S*)-2,3-dimethyl-2,3-bis(((methylsulfonyl)oxy)methyl)butane-1,4-diyl bis(4-methoxybenzoate) (10)

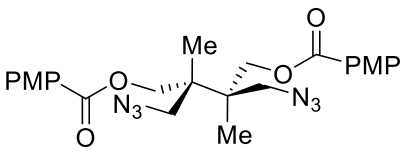


Colorless oil, Analytical data for **10**: $[\alpha]_D^{20}$ = +2.4° (c = 0.50, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 8.07-7.92 (m, 4H), 6.99-6.87 (m, 4H), 4.53-4.32 (m, 8H), 3.86 (s, 6H), 3.00 (s, 6H), 1.20 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.80, 163.76, 131.70, 121.71, 113.95, 70.19, 65.35, 55.50, 42.21, 37.40, 16.51. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{26}H_{34}O_{12}S_2Na$: 625.1389. Found: 625.1421.

Procedure for the synthesis of 5[8]

To a 10 mL round-bottom flask were added **10** (0.1 mmol), NaN_3 (0.3 mmol), Bu_4NI (0.02 mmol), and 1 mL of DMF. The mixture was allowed to stir at 120 ºC for 2d. The reaction mixture was diluted with ethyl acetate and H_2O. Then the organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel column chromatography (ethyl acetate / petroleum ether) to give the product **5** in 62% yield.

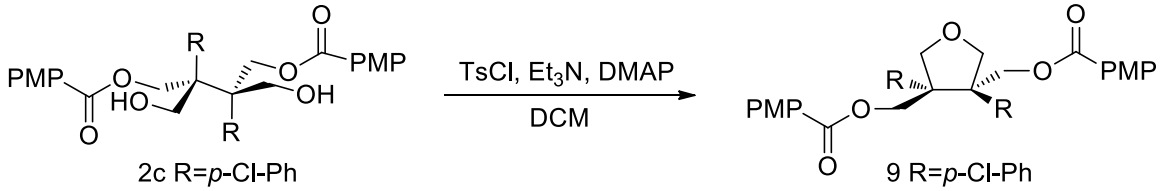
(2*R*, 3*R*)-2,3-bis(azidomethyl)-2,3-dimethylbutane-1,4-diyl bis(4-methoxybenzoate) (5)



Colorless oil. Analytical data for **5**: $[\alpha]_D^{20}$ = 18.7° (c = 0.50, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.03-7.91 (m, 4H), 6.98-6.87 (m, 4H), 4.42-4.32 (m, 4H), 3.87 (s, 6H), 3.65 (dd, *J* = 48.3, 12.4 Hz, 4H), 1.13 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.90, 163.62, 131.59, 122.10, 113.86, 66.52, 55.49, 42.55, 29.71, 17.65. IR (neat, cm^{-1}): ν = 2923, 2099, 1710, 1605, 1511, 1462, 1253, 1165, 1095, 1027, 846,768. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{24}H_{28}N_6O_6Na$: 519.1968. Found: 519.1968.

Determination of the Absolute Stereochemistry

The absolute configurations of products were determined by transforming **2c** to **9** and the absolute configuration of **9** was determined by X-Ray Crystallographic Analysis. The stereochemistry of the other products was assigned by analogy.



2c R=*p*-Cl-Ph　　9 R=*p*-Cl-Ph

X-Ray Crystallographic Analysis of **9** (CCDC number: 1052043)

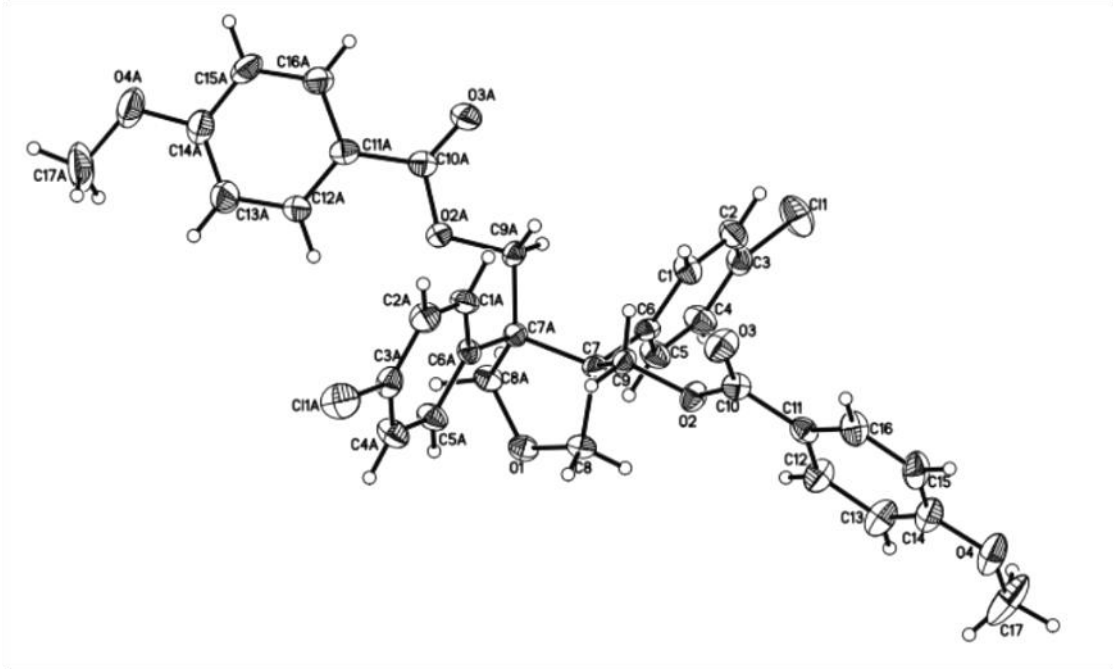


Figure 1. X-ray structure of 9

Determination of the relative configuration of acetals[9]

The relative configurations of acetals were determined by X-Ray Crystallographic Analysis of **1a**, **1h**, **1j**. The relative configurations of other acetals were assigned by analogy.

X-Ray Crystallographic Analysis of **1a** (CCDC number: 1052042)

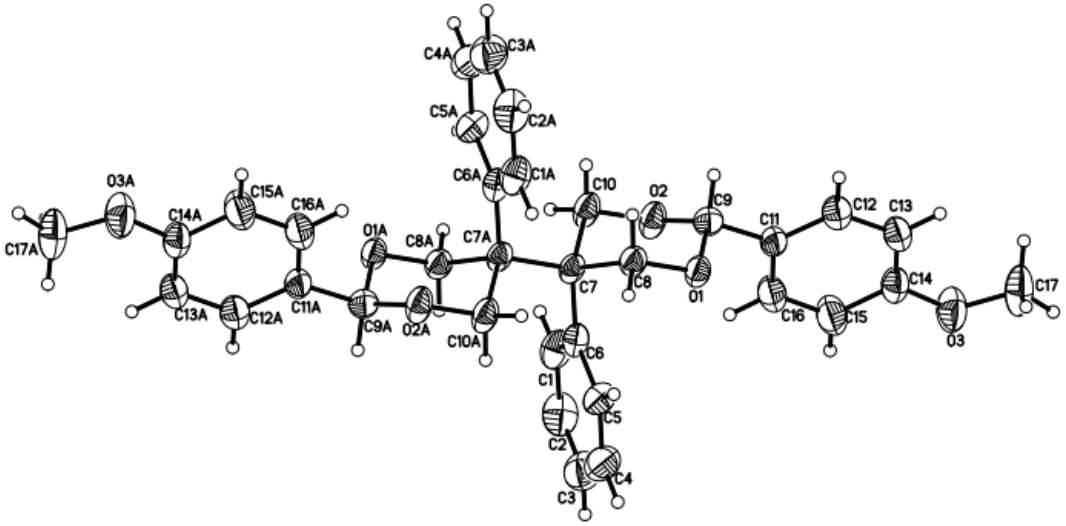


Figure 2. X-ray structure of **1a**

X-Ray Crystallographic Analysis of **1h** (CCDC number: 1052039)

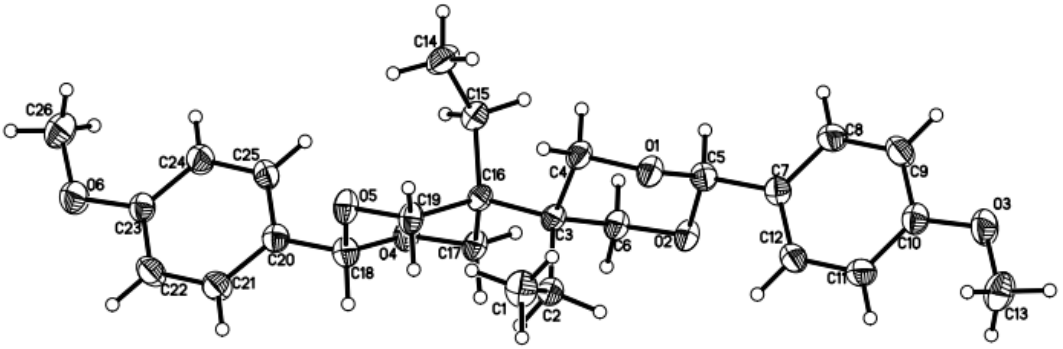


Figure 3. X-ray structure of **1h**

X-Ray Crystallographic Analysis of **1j** (CCDC number: 1052038)

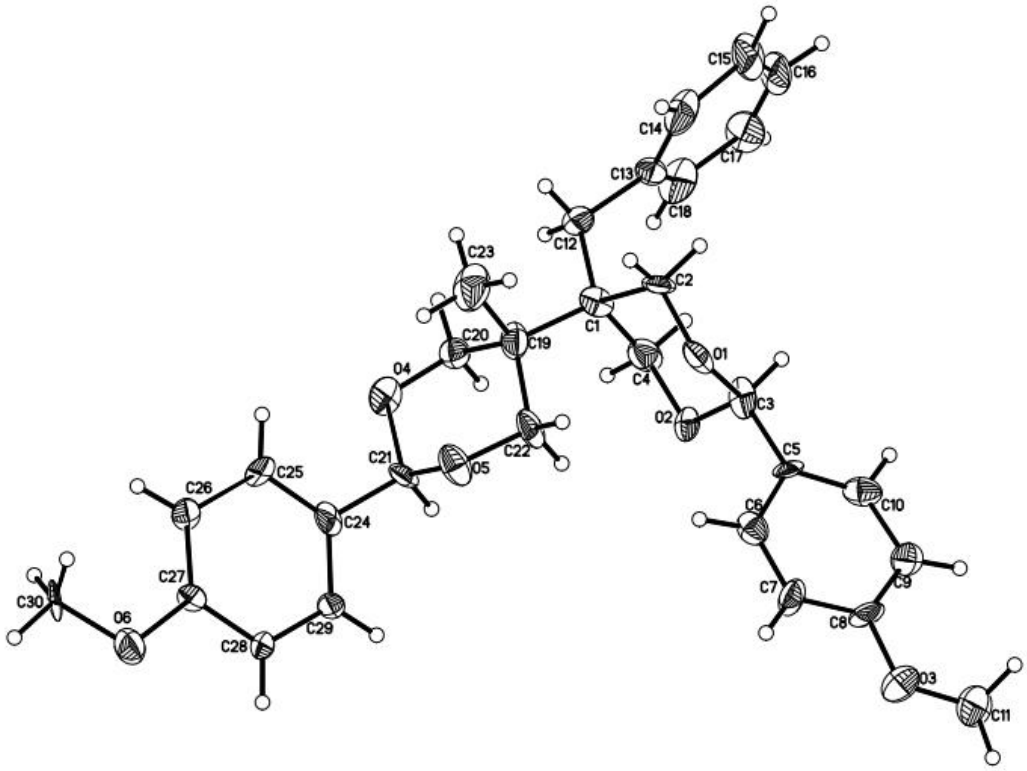
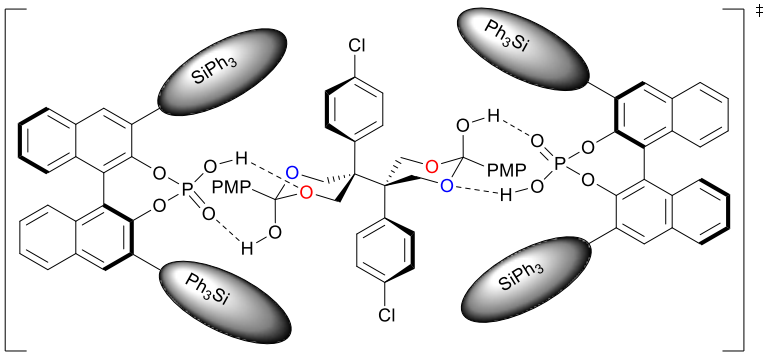


Figure 4. X-ray structure of **1j**

Suggested transition state



On the basis of the experimental results and our previous DFT calculations about desymmetrization of 1,3-diols via oxidative cleavage of benzylidene acetals. We proposed a reaction pathway, diacetal **1c** was oxidized to form an "ortho ester" intermediate, which underwent an intramolecular [1,3]-proton shift process which can be facilitated in the presence of triphenylsilyl substituted BINOL phosphoric acid **A8**, stereoselectivity was controlled through two hydrogen bonds formed by each phosphoric acid and the "ortho ester" intermediate. Thus given the product **2c** as (R, R) configuration.

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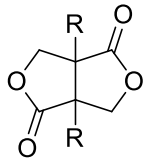
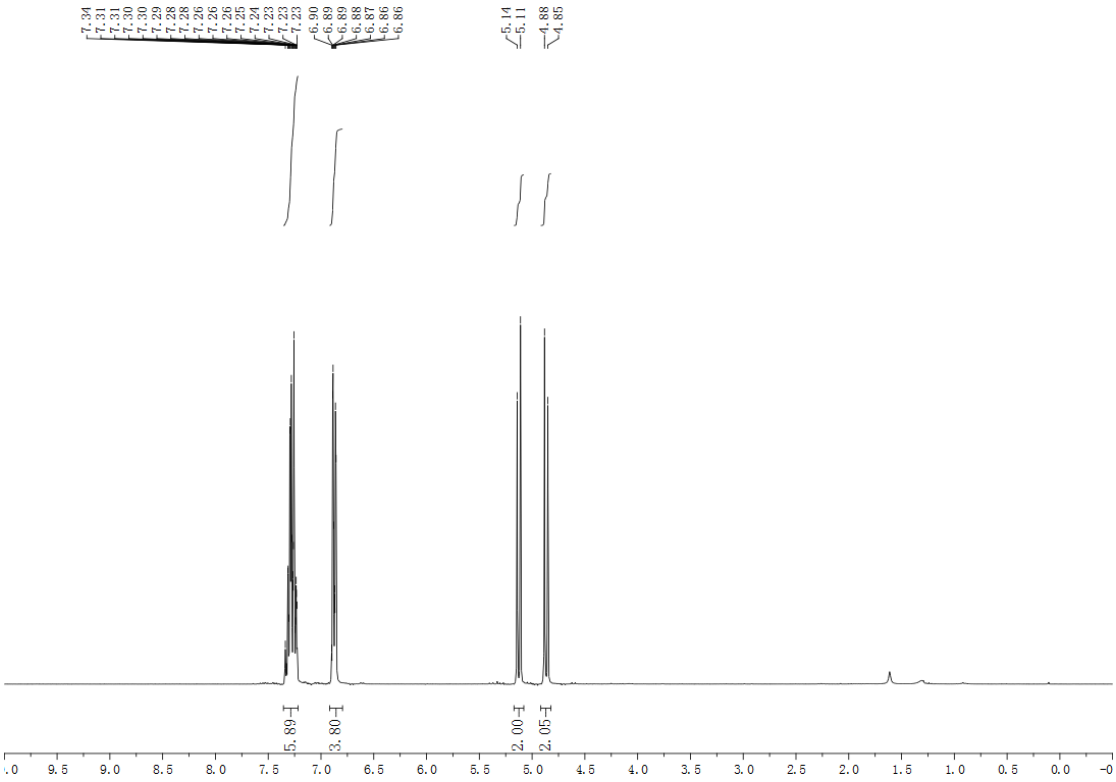
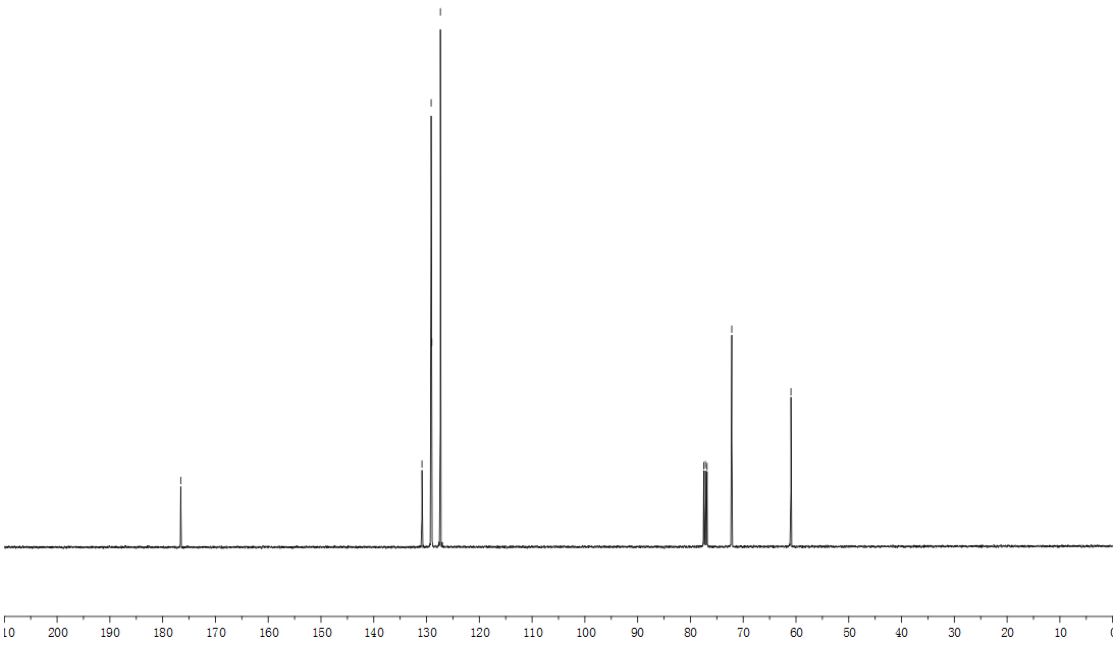
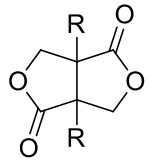


7a R=Ph

^{1}H NMR and ^{13}C NMR of **7a**

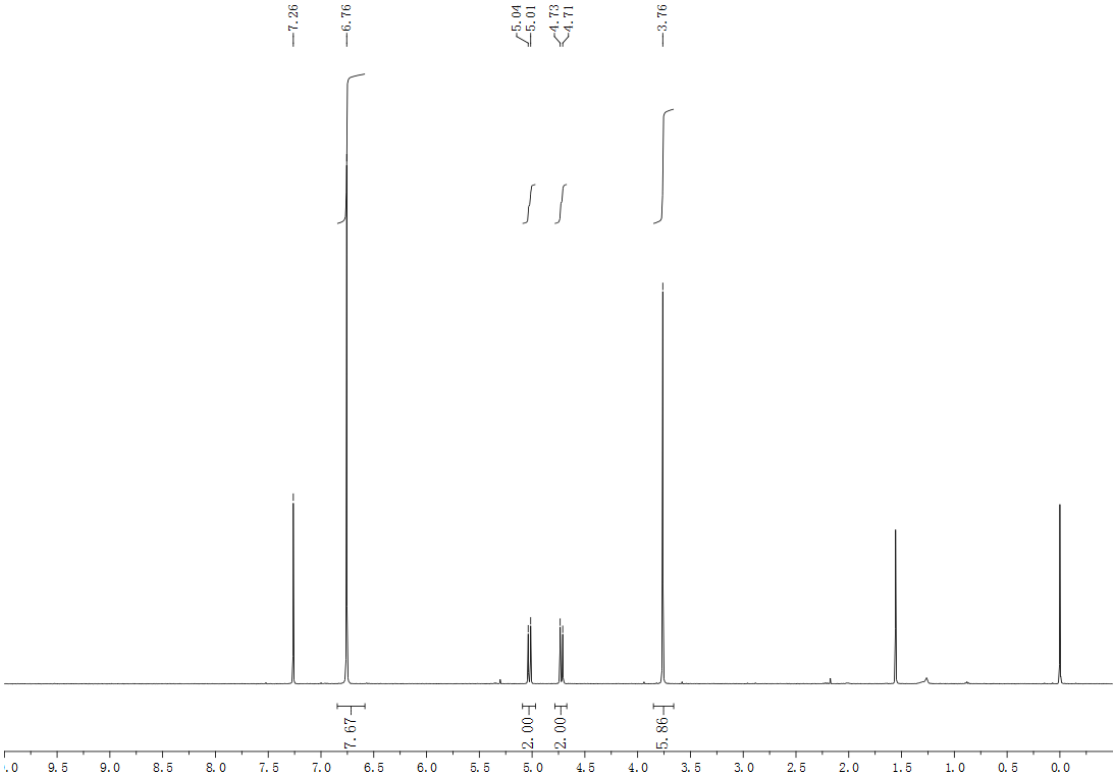


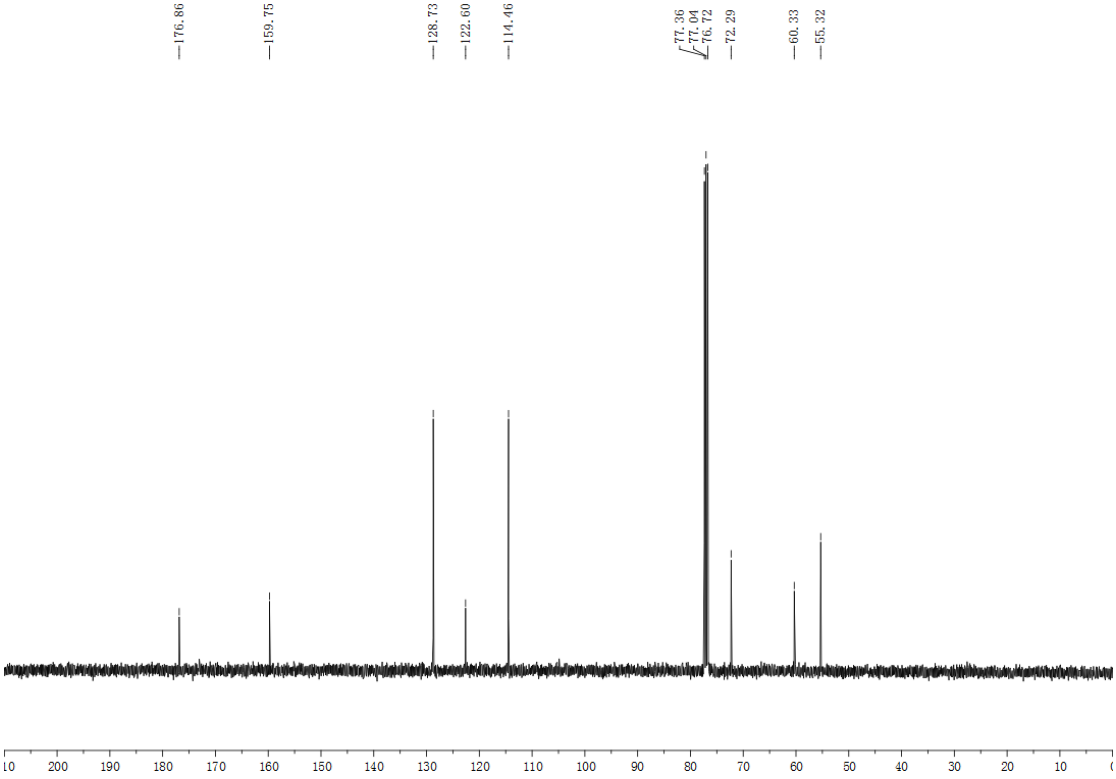


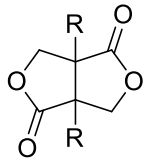


7b R=*p*-OMePh

^{1}H NMR and ^{13}C NMR of **7b**

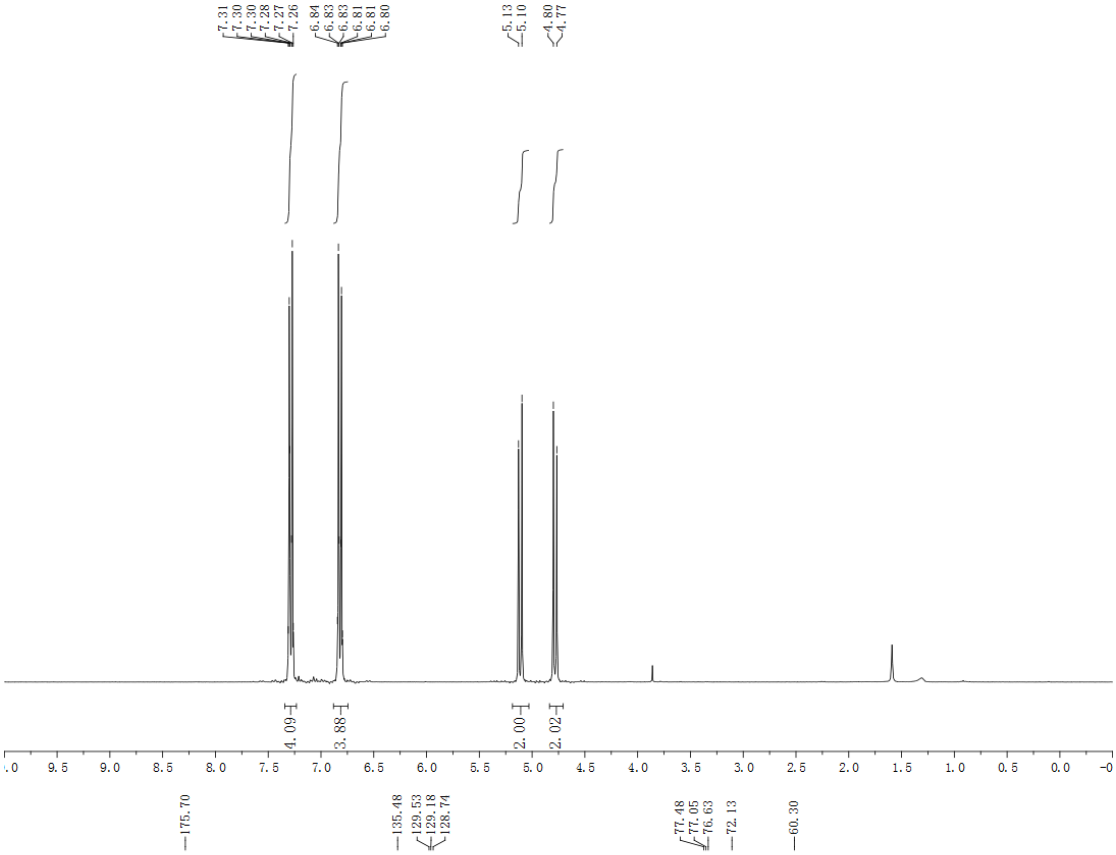


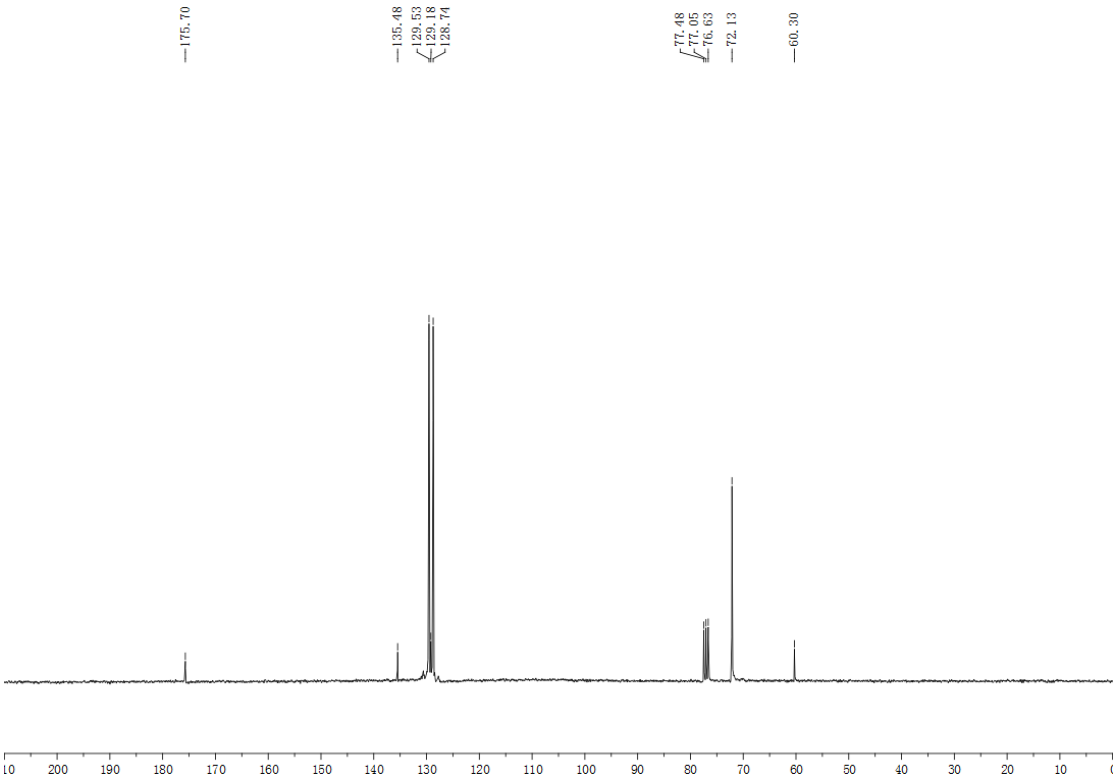


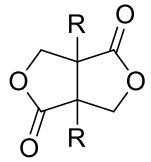


7c R=*p*-Cl-Ph

^{1}H NMR and ^{13}C NMR of **7c**

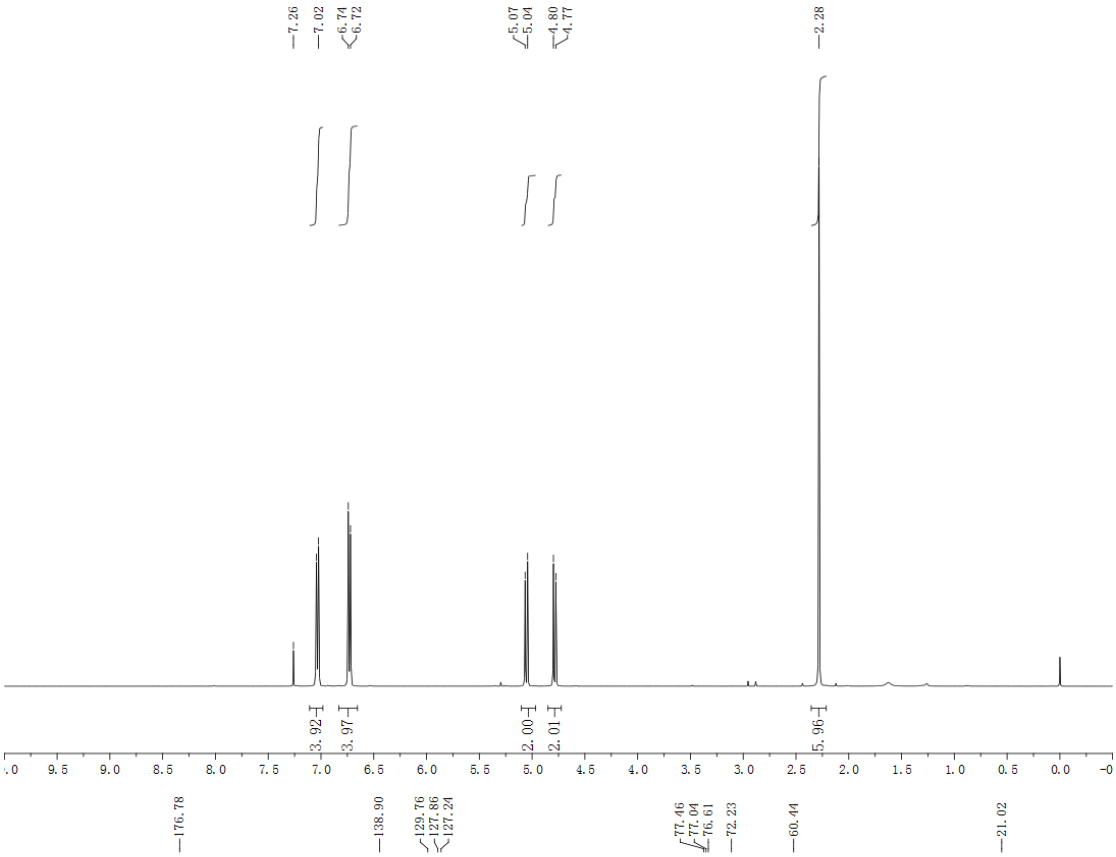


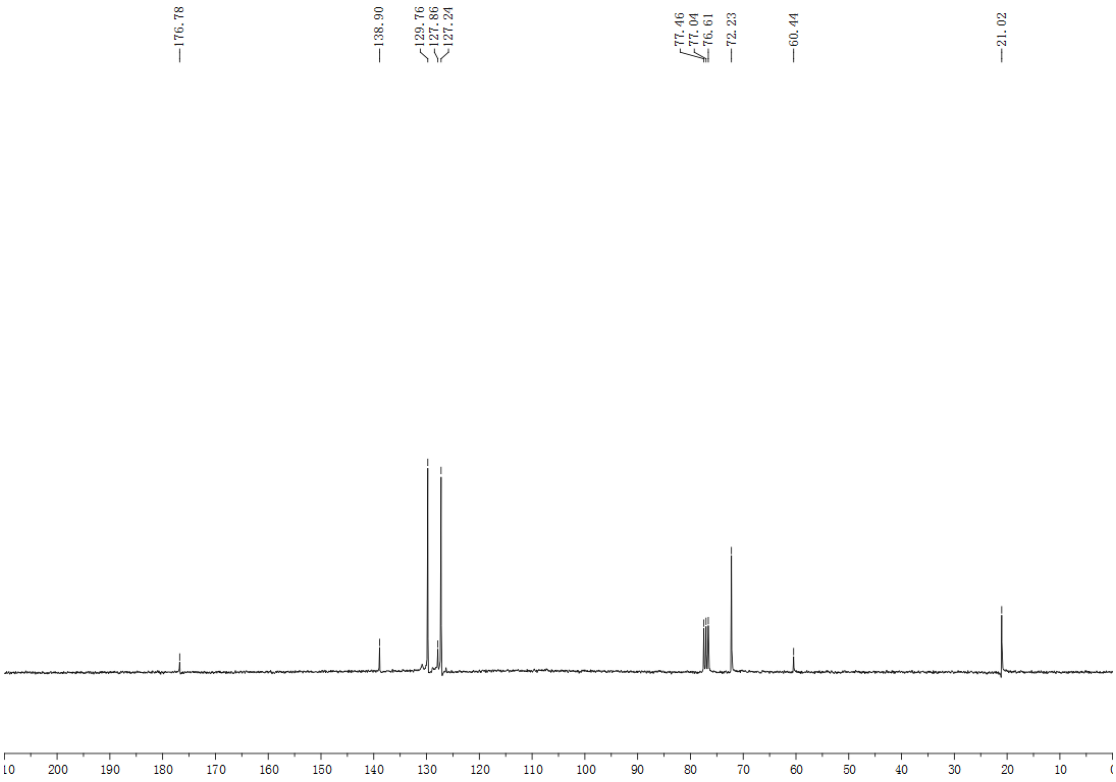


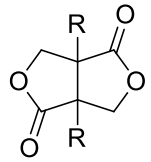


7d R=*p*-Me-Ph

^{1}H NMR and ^{13}C NMR of **7d**

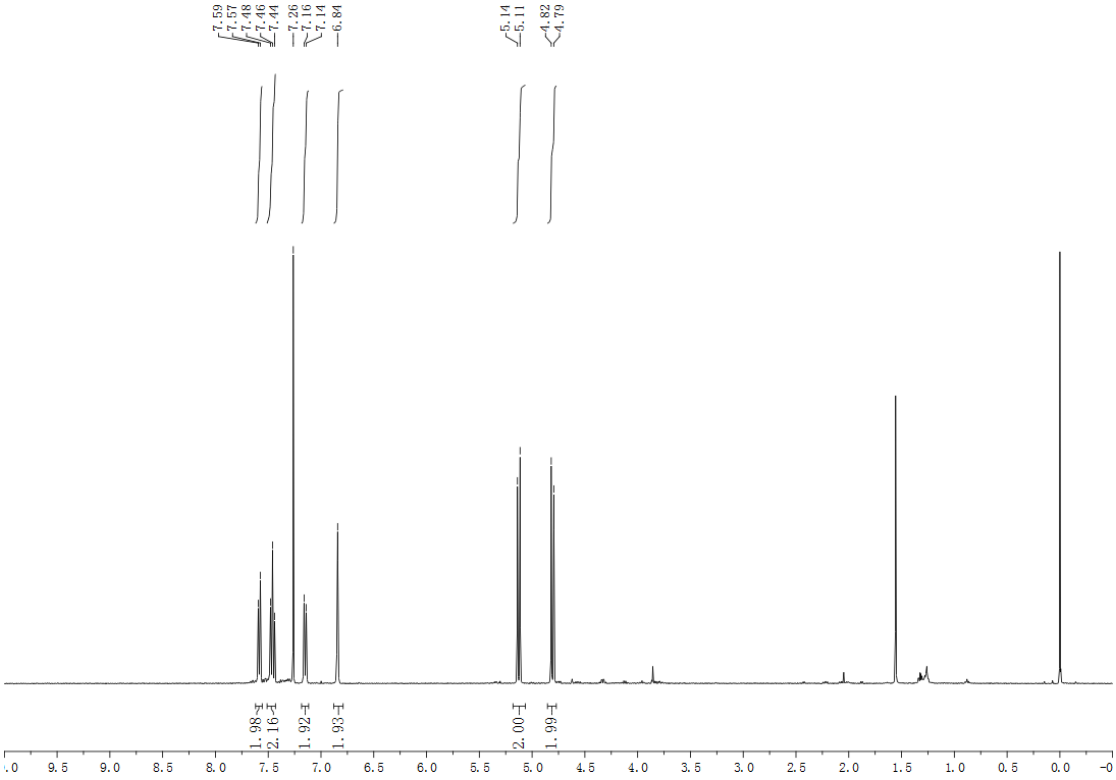


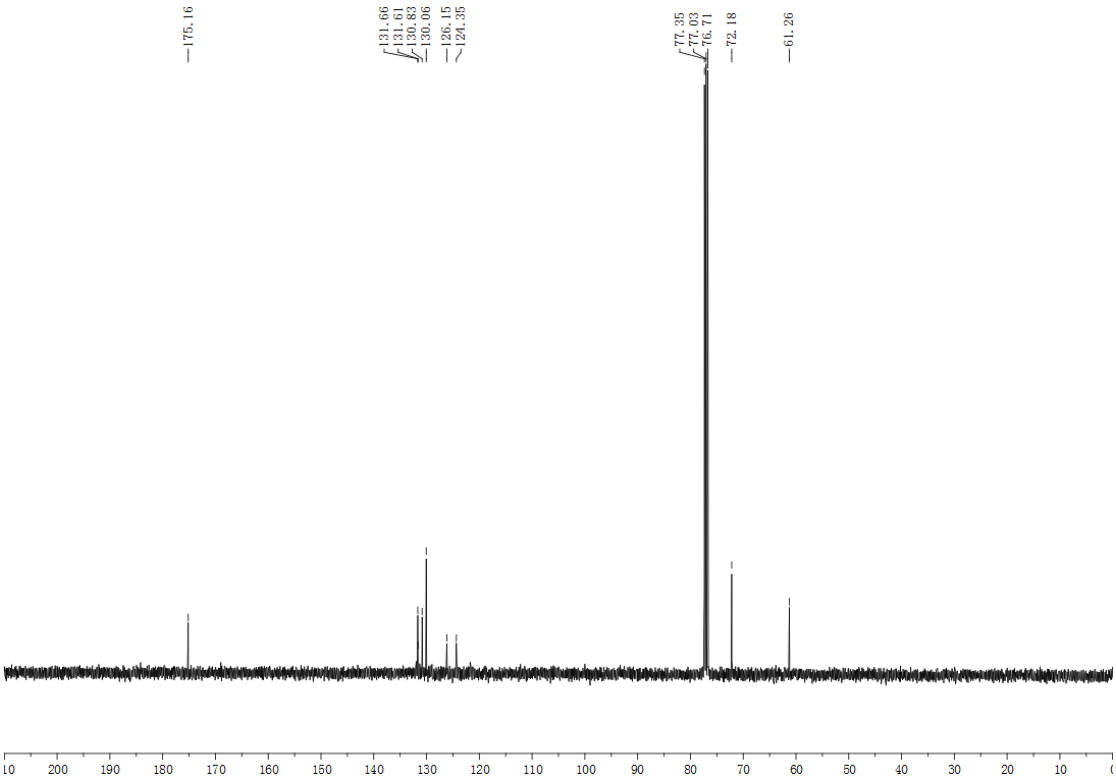




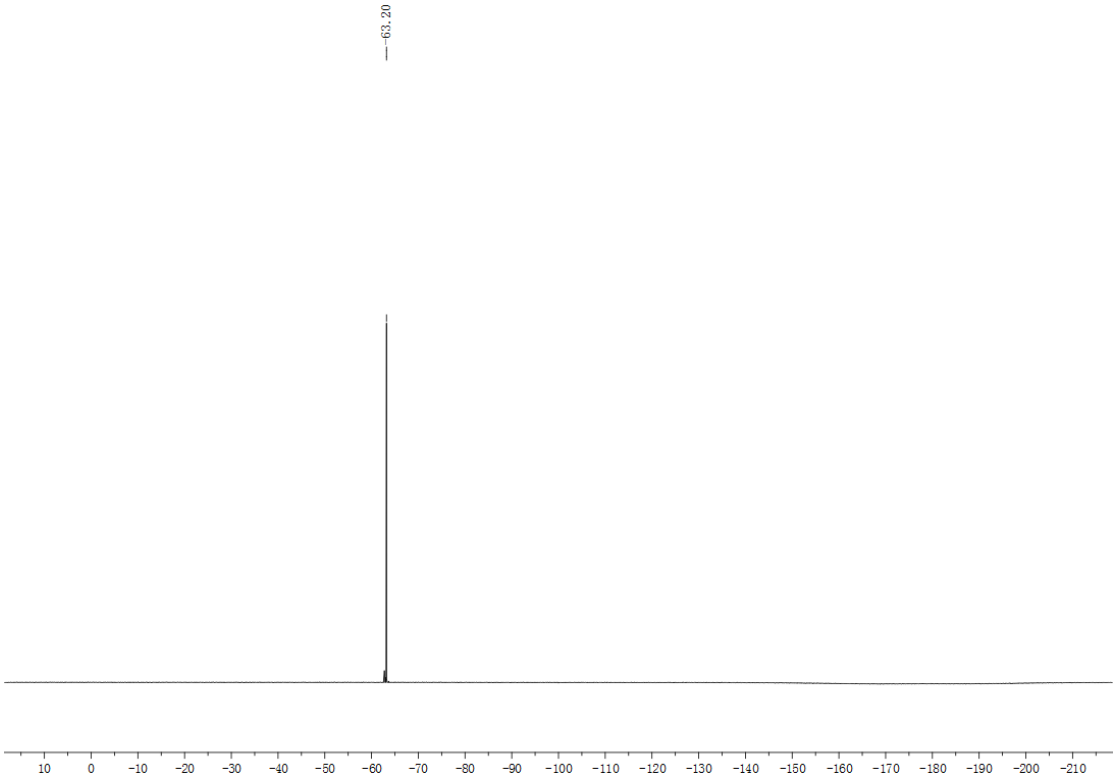
7e R=*m*-CF_3-Ph

^{1}H NMR and ^{13}C NMR of **7e**





^{19}F NMR of **7e**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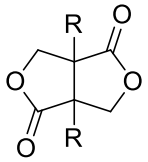
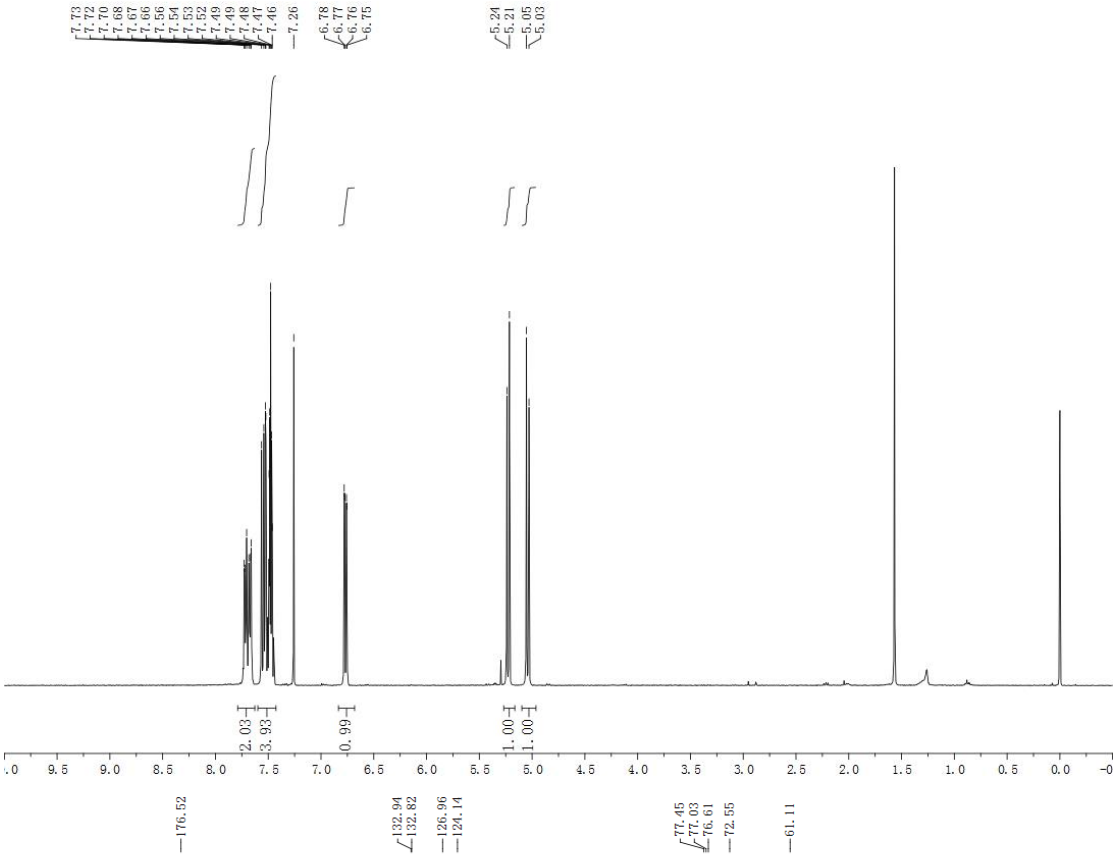
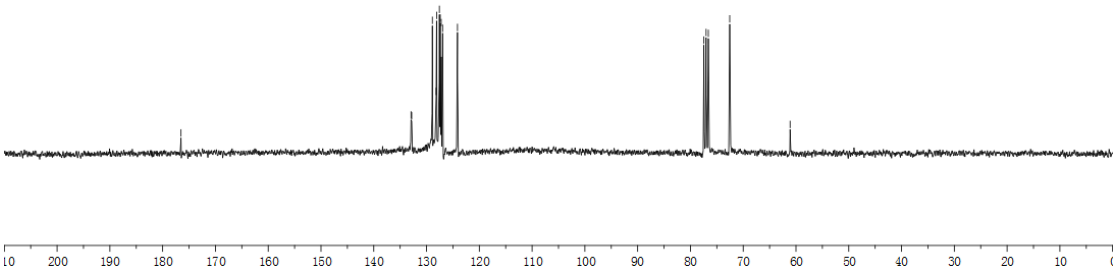
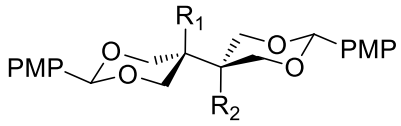


7f R=*2*-Naphthyl

^{1}H NMR and ^{13}C NMR of **7f**

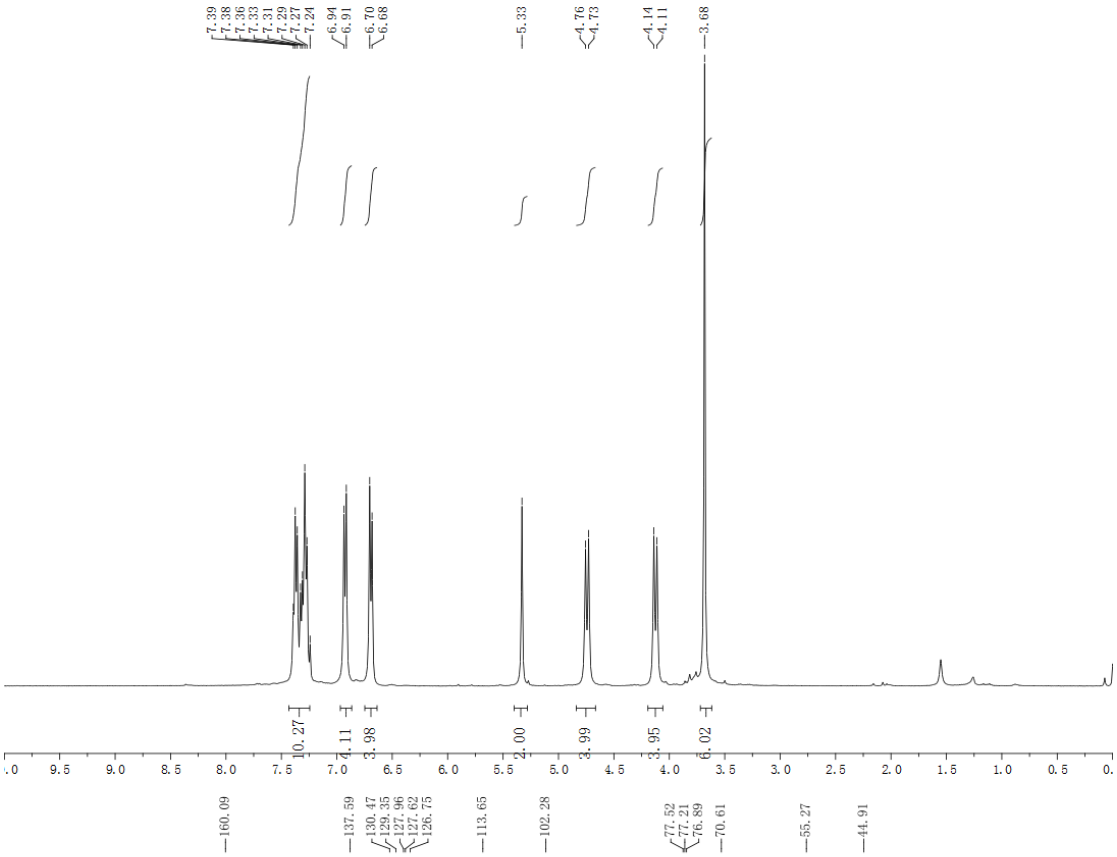


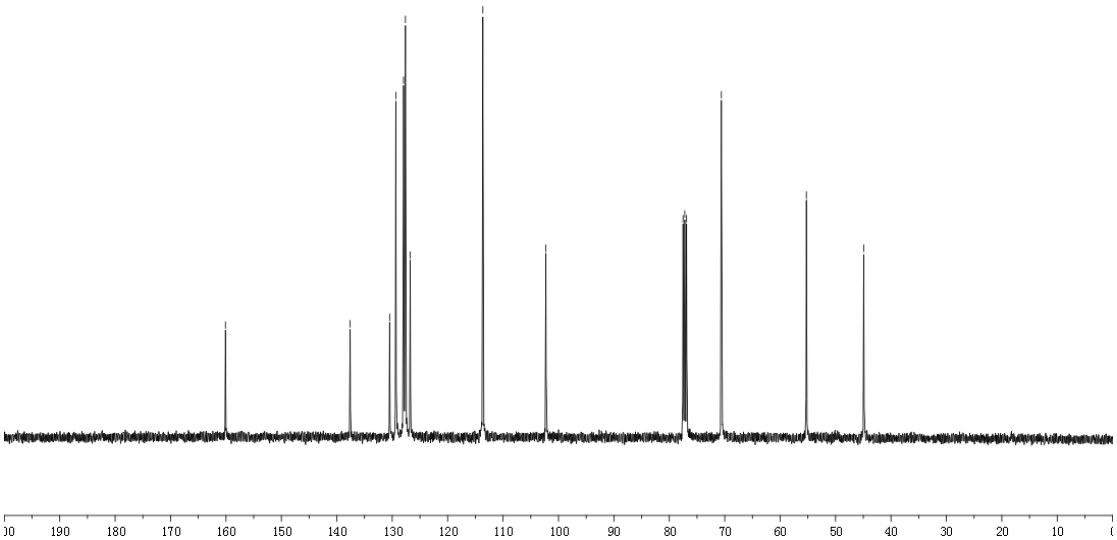


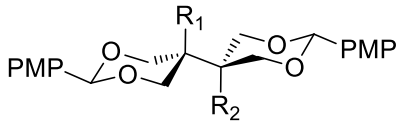


1a R_1=R_2=Ph

^{1}H NMR and ^{13}C NMR of **1a**

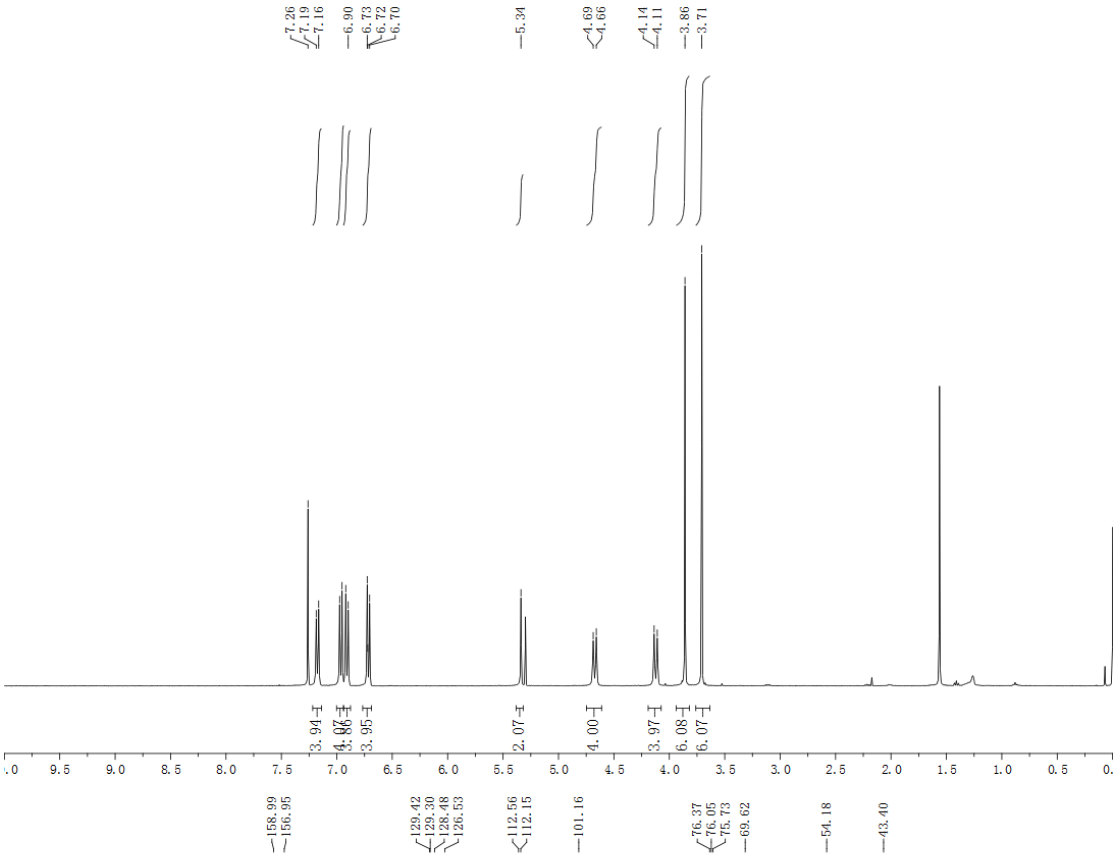


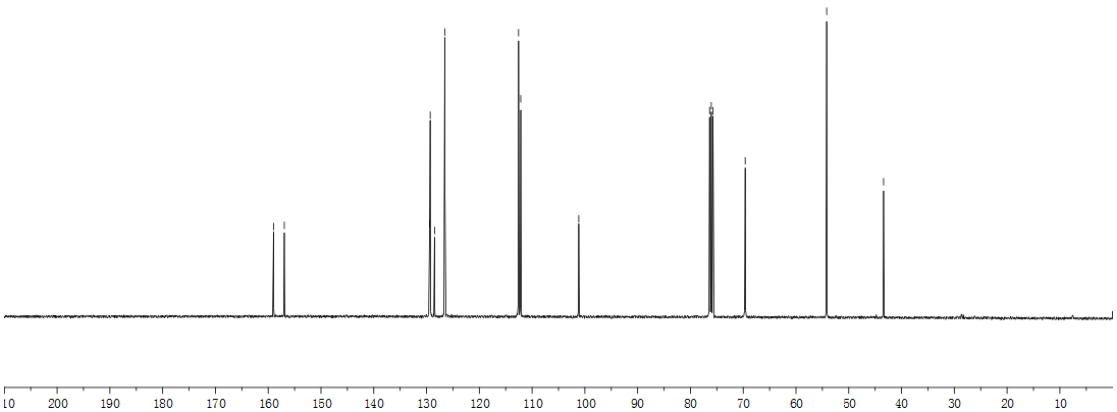


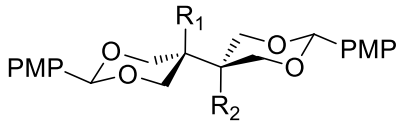


1b R_1=R_2=*p*-MeO-Ph

^{1}H NMR and ^{13}C NMR of **1b**

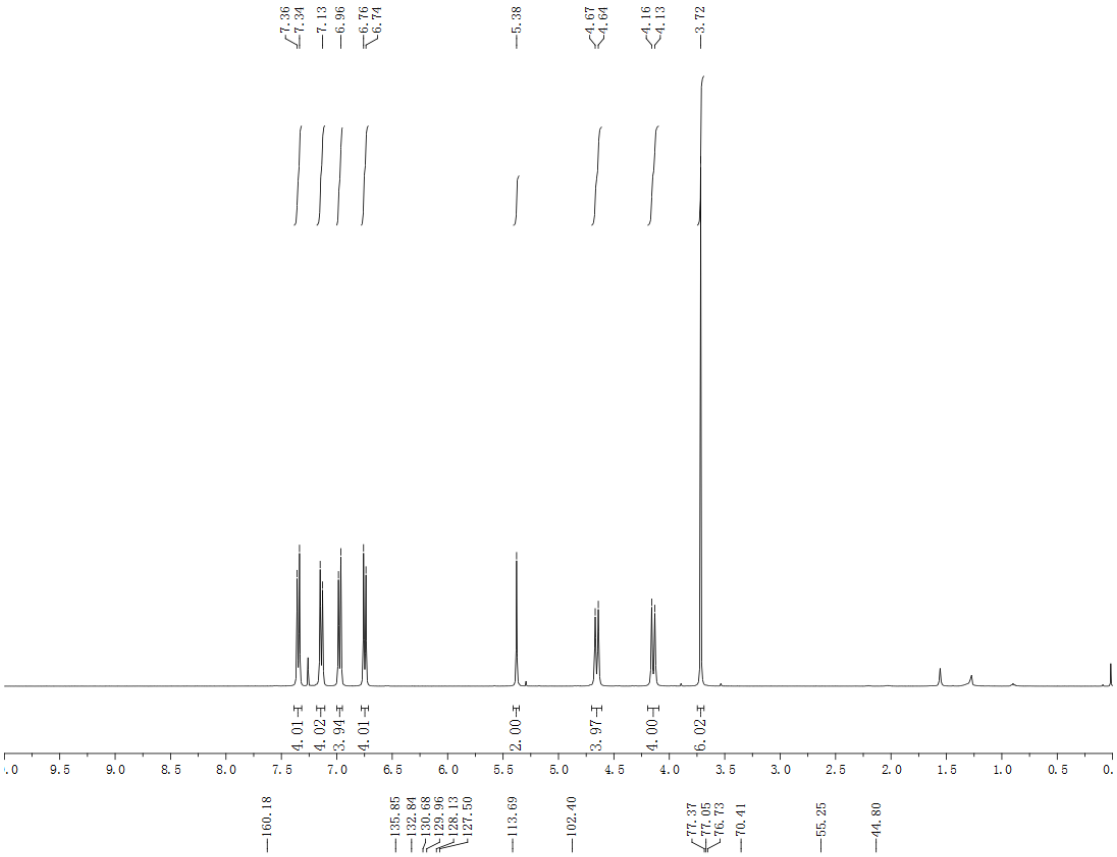


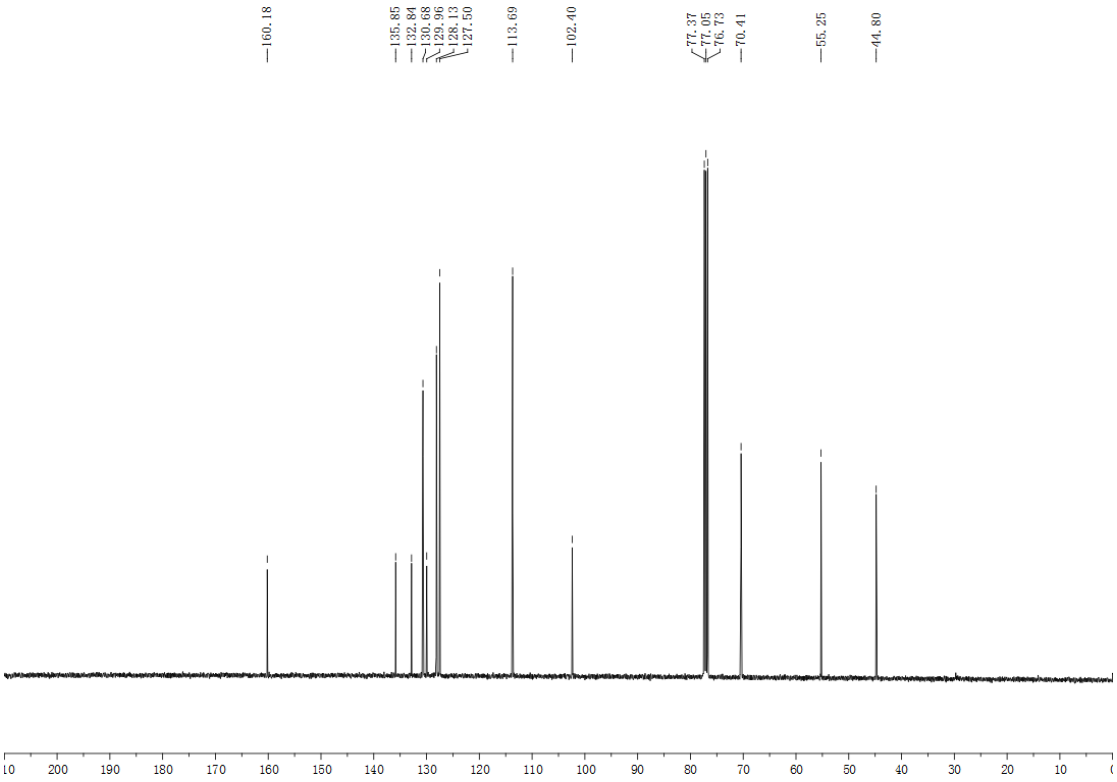


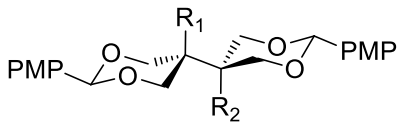


1c R_1=R_2=*p*-Cl-Ph

^{1}H NMR and ^{13}C NMR of **1c**

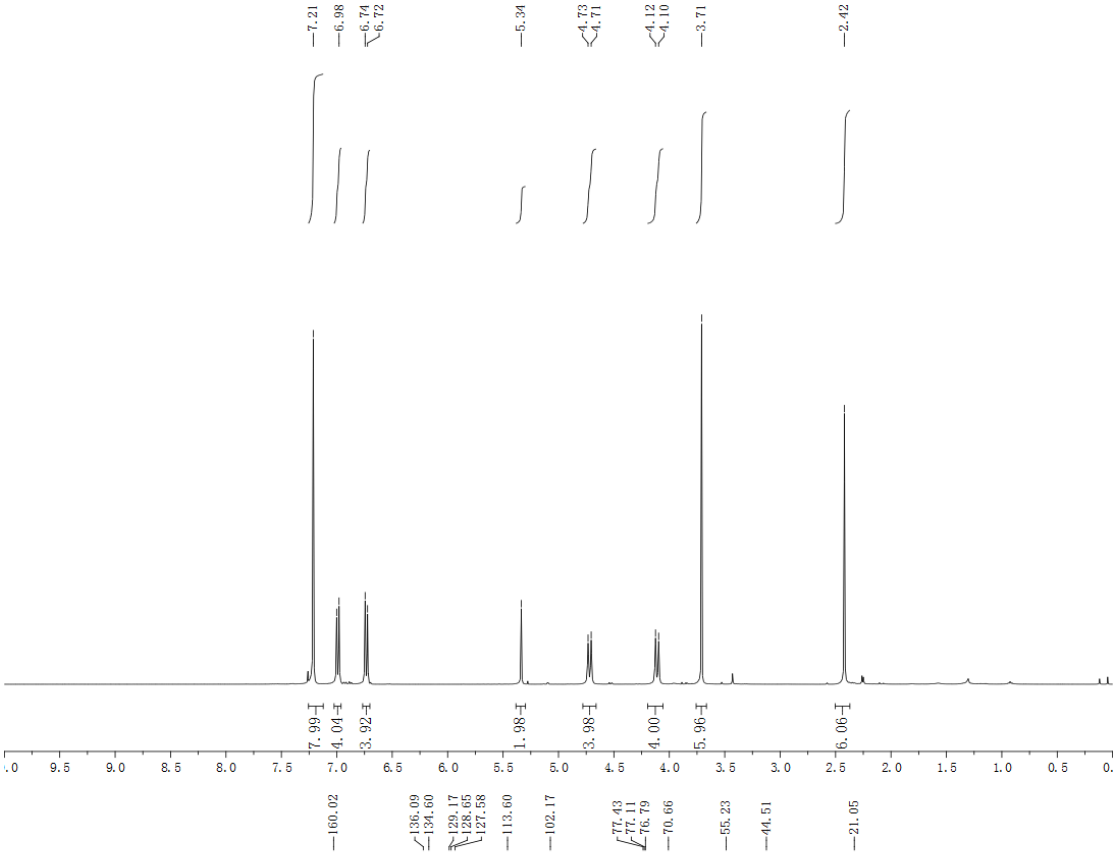


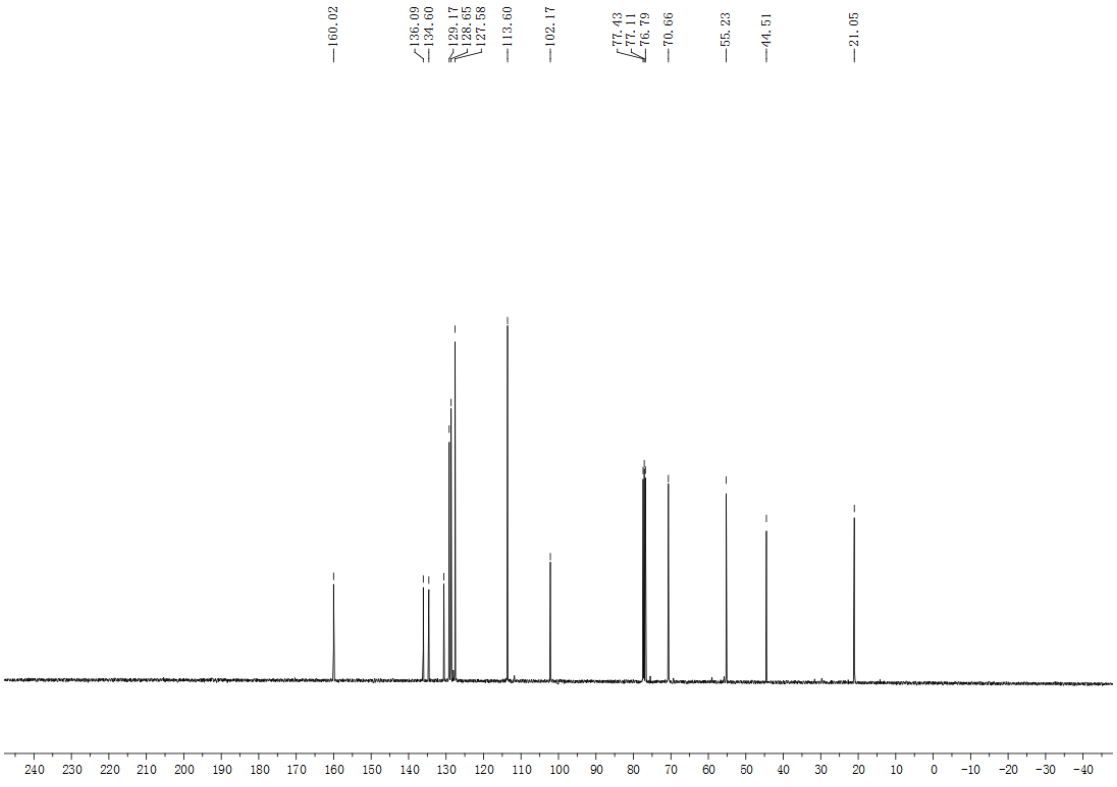


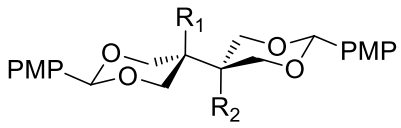


1d R_1=R_2=*p*-Me-Ph

^{1}H NMR and ^{13}C NMR of **1d**

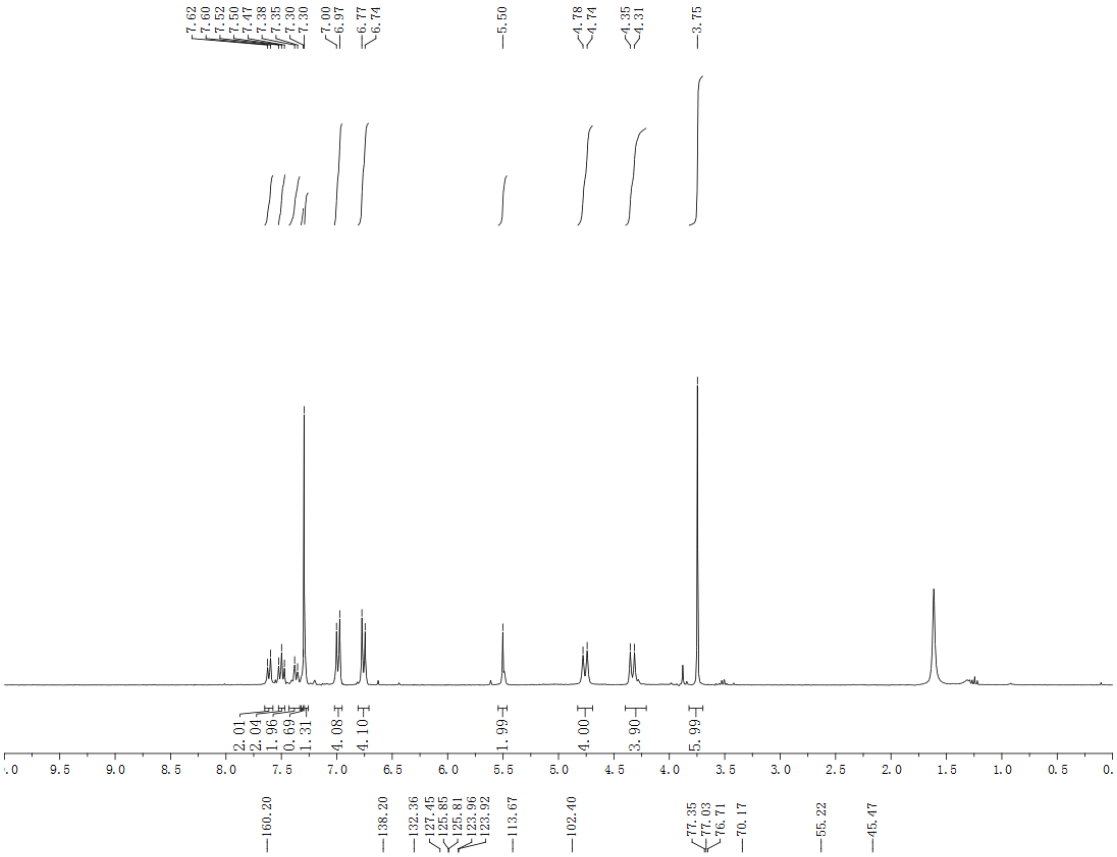


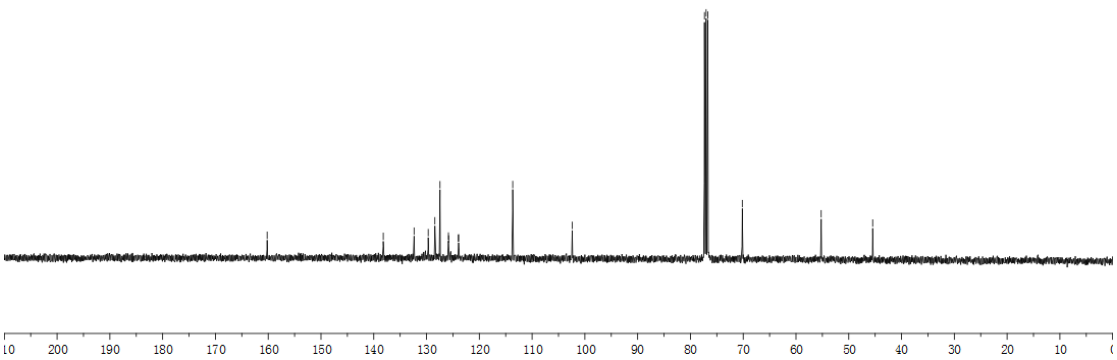




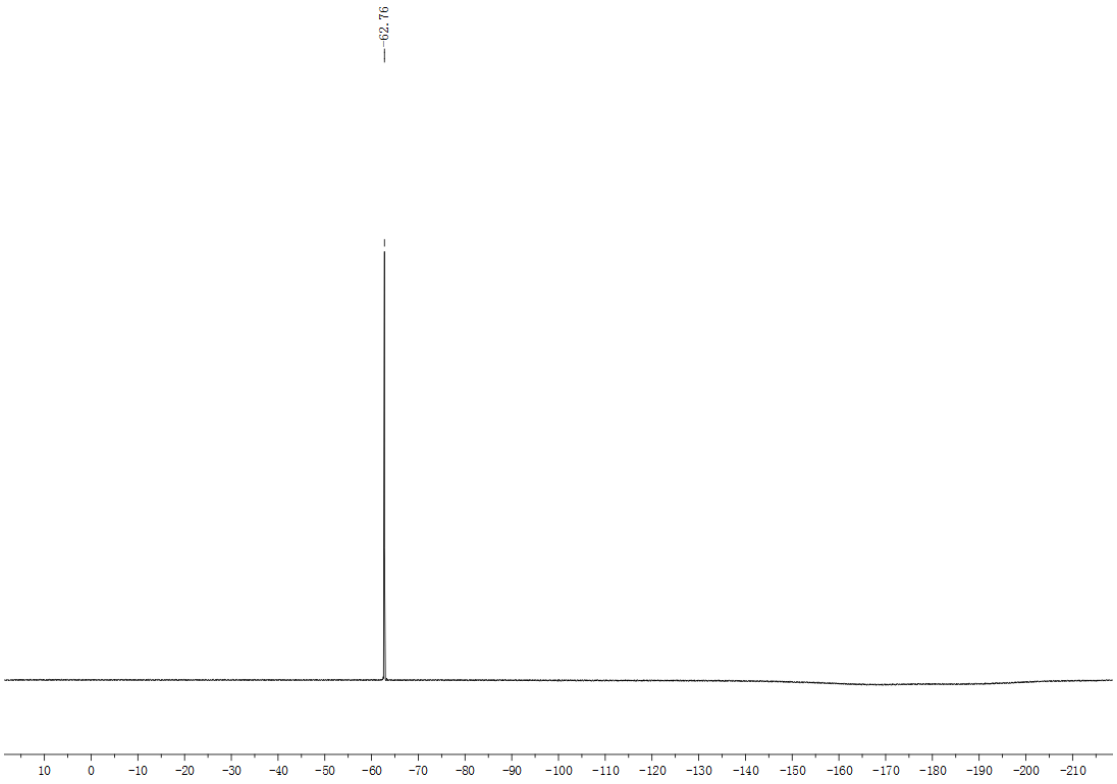
1e R_1=R_2=*m*-CF_3-Ph

^{1}H NMR and ^{13}C NMR of **1e**





^{19}F NMR of **1e**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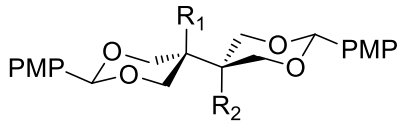
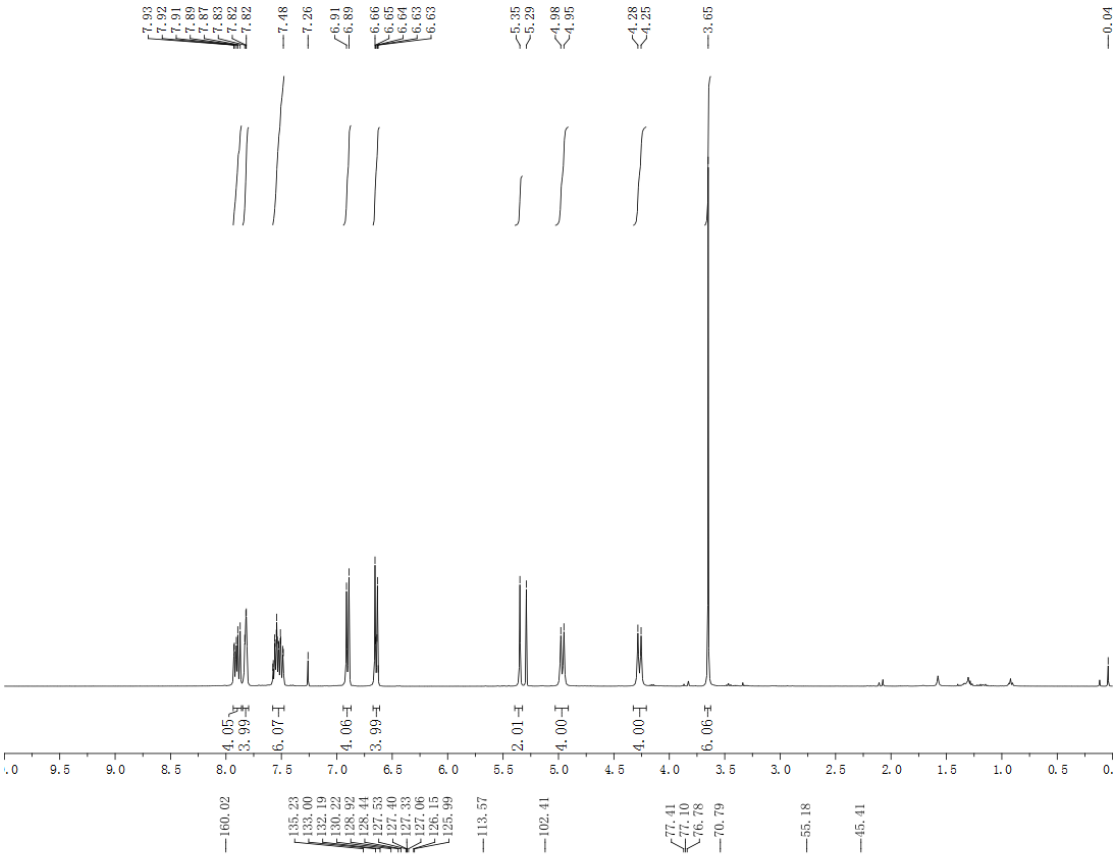
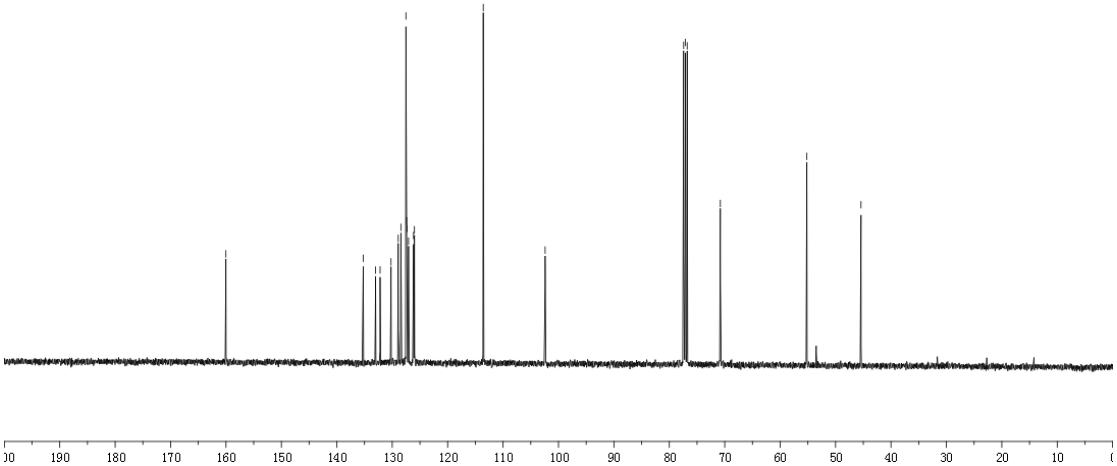
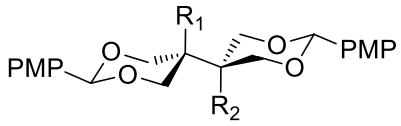


1f R_1=R_2=2-Naphthyl

^{1}H NMR and ^{13}C NMR of **1f**

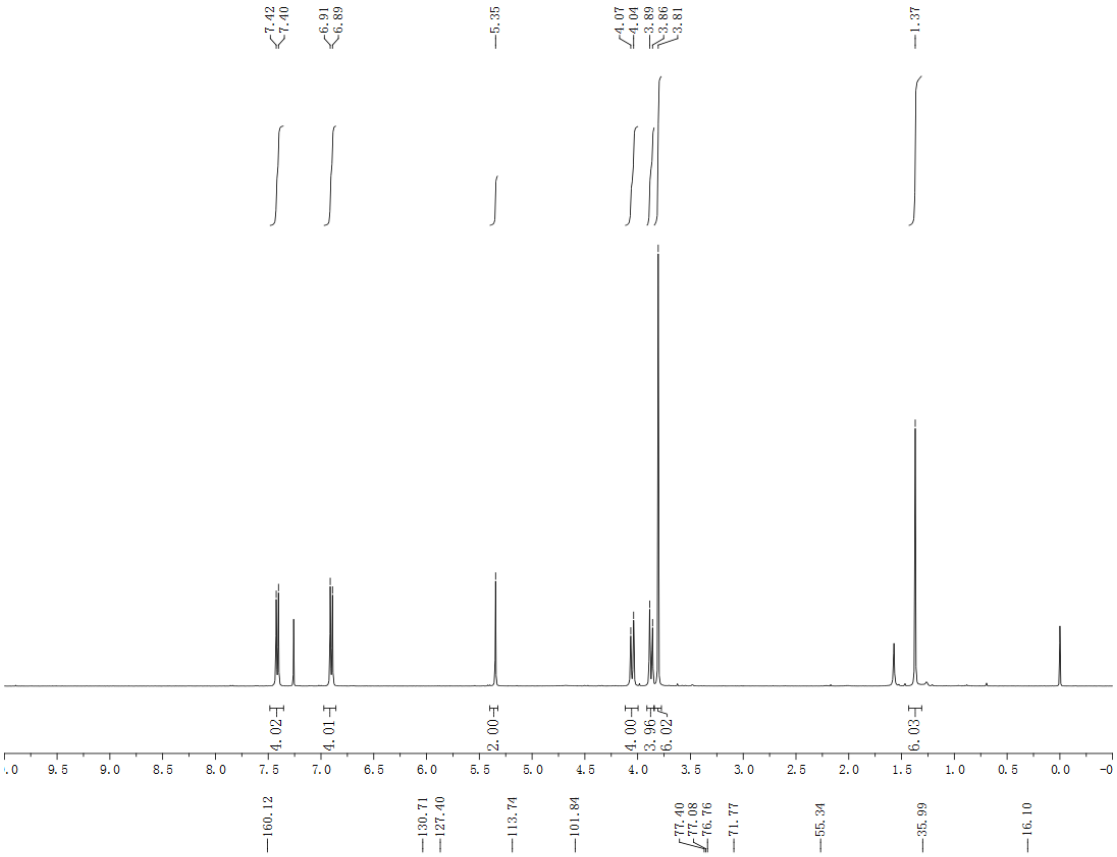


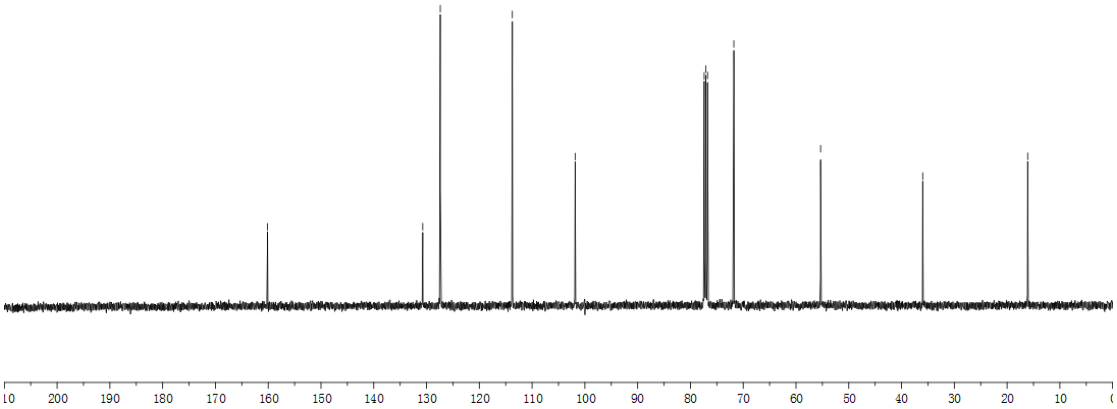


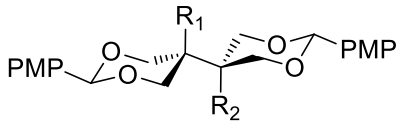


1g R_1=R_2=Me

^{1}H NMR and ^{13}C NMR of **1g**

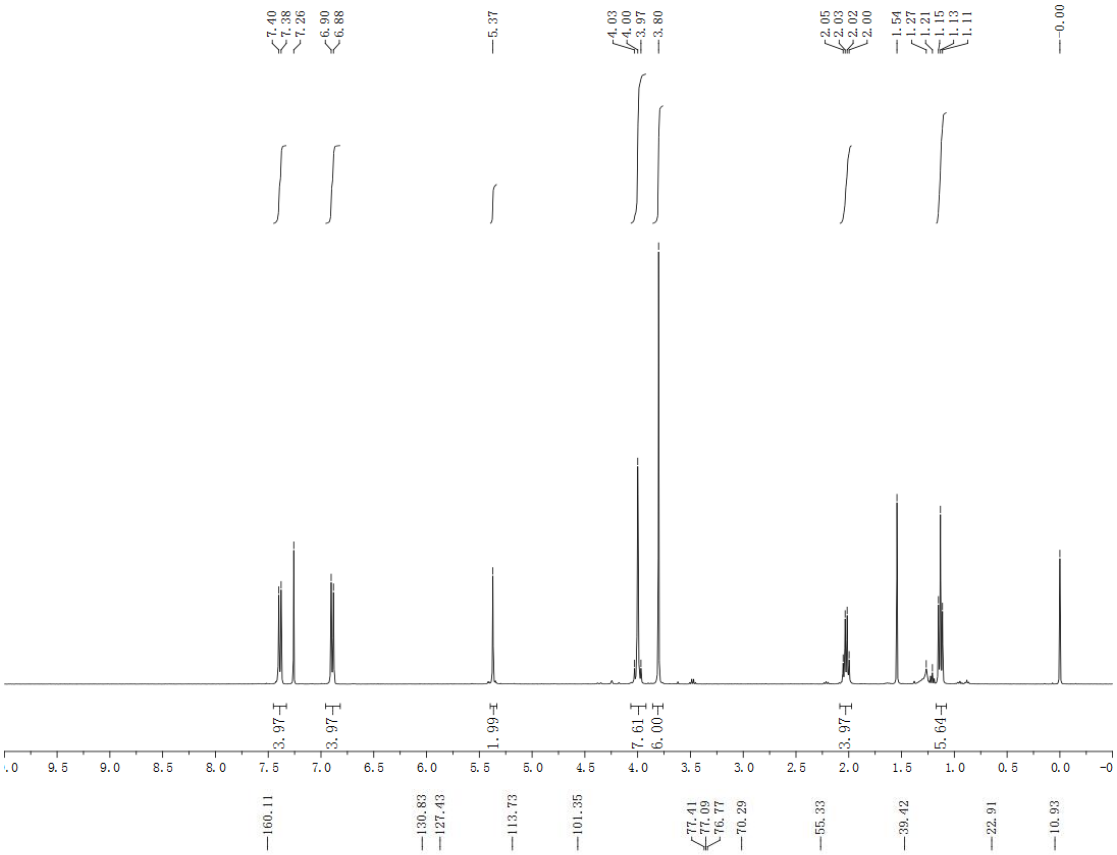


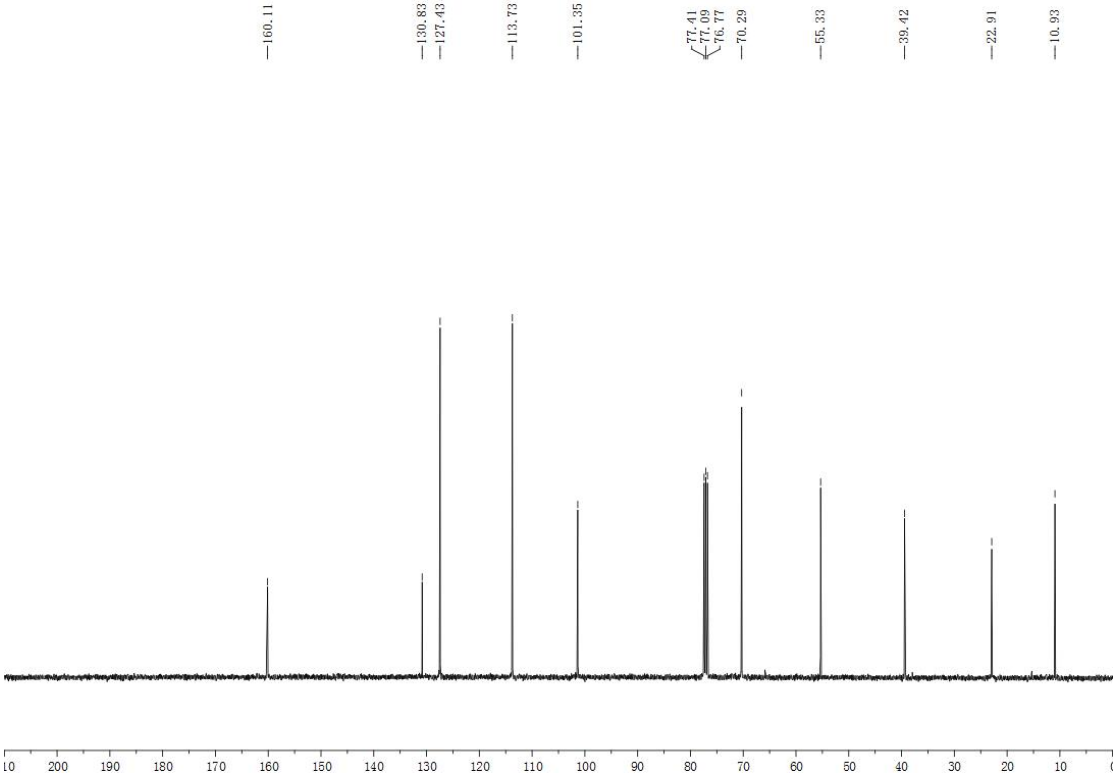


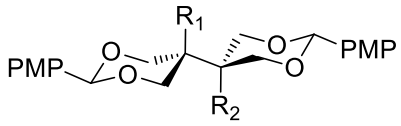


1h R_1=R_2=Et

^{1}H NMR and ^{13}C NMR of **1h**

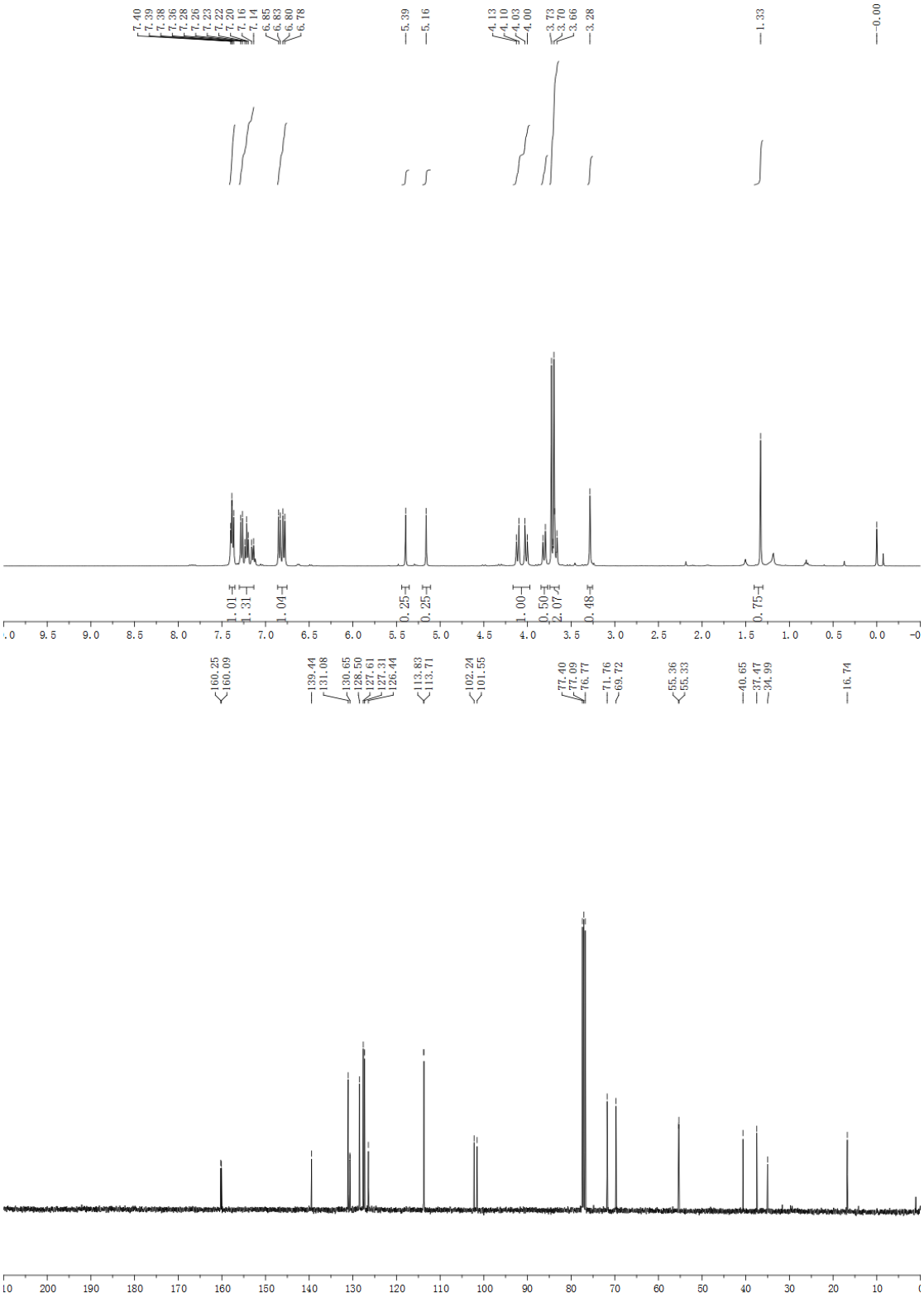


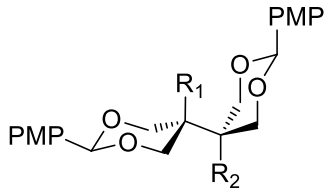




1i R_1=Bn, R_2=Me

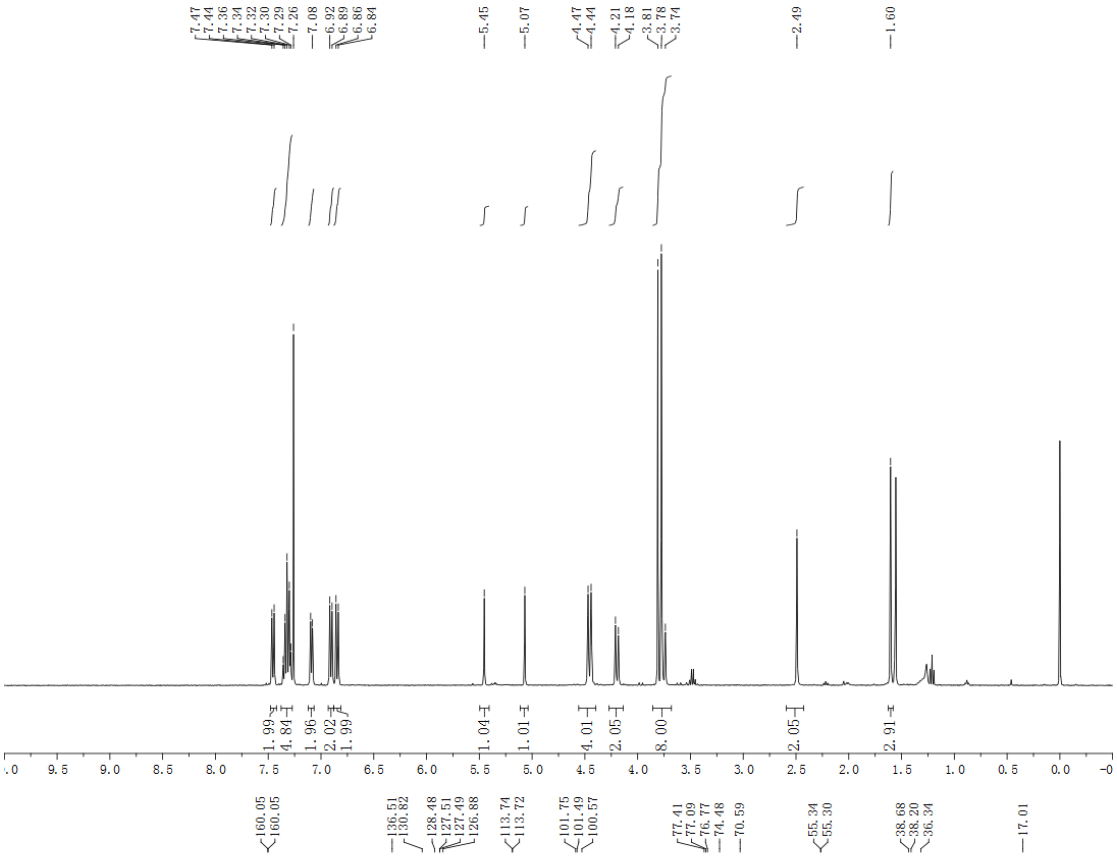
^{1}H NMR and ^{13}C NMR of **1i**

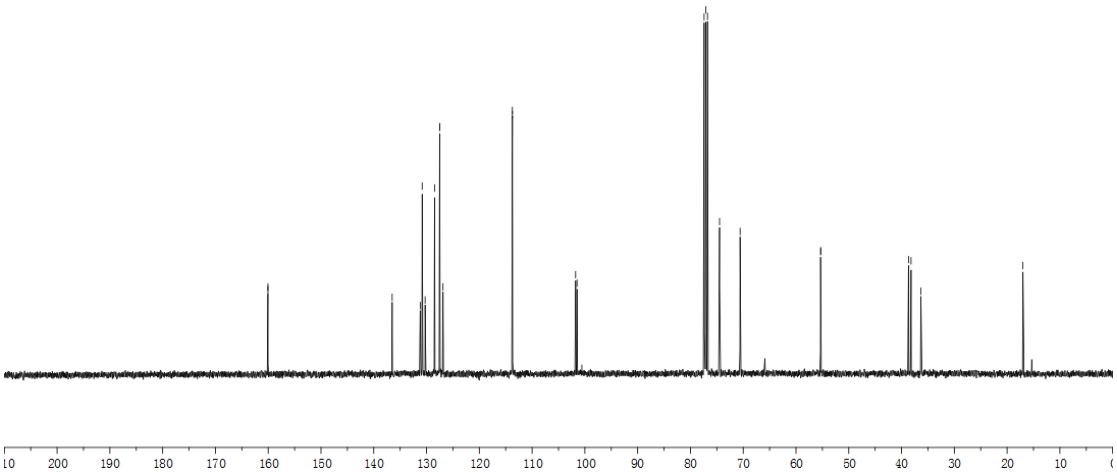


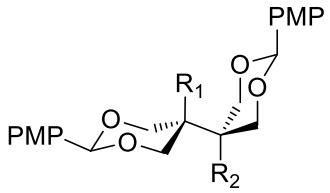


1j R_1=Me, R_2=Bn

^{1}H NMR and ^{13}C NMR of **1j**

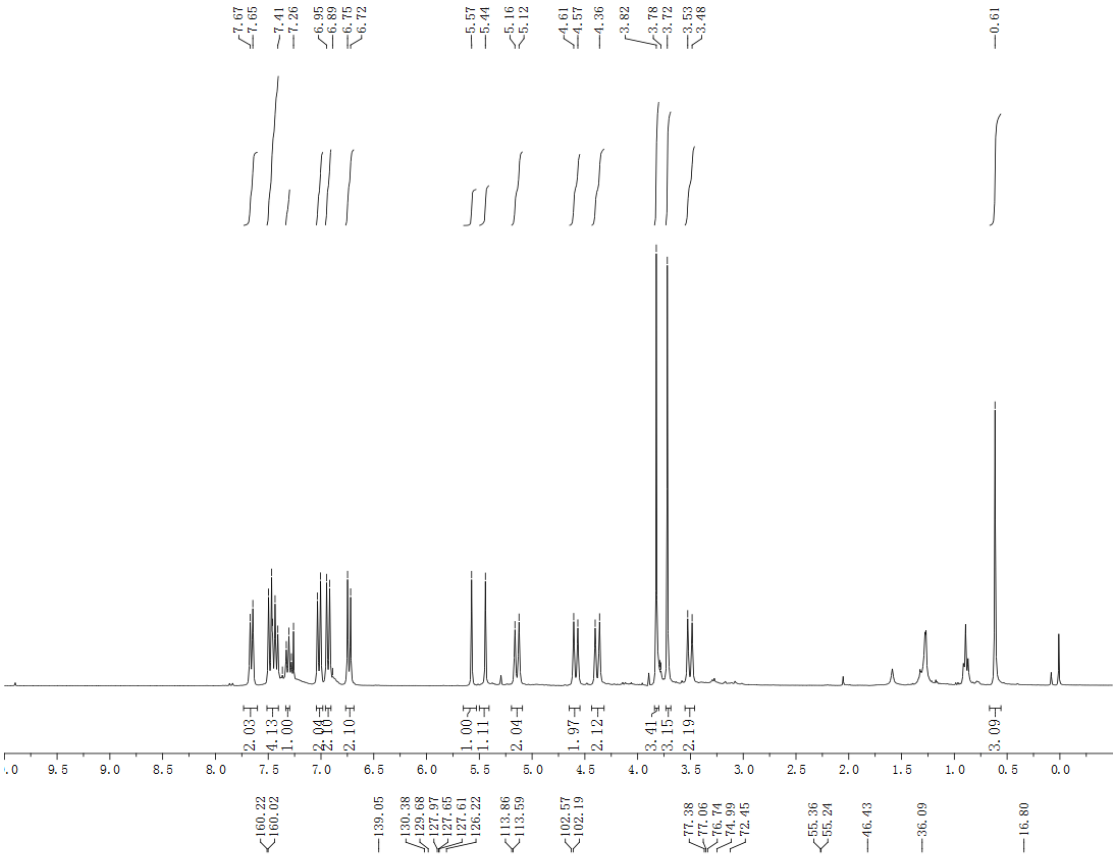


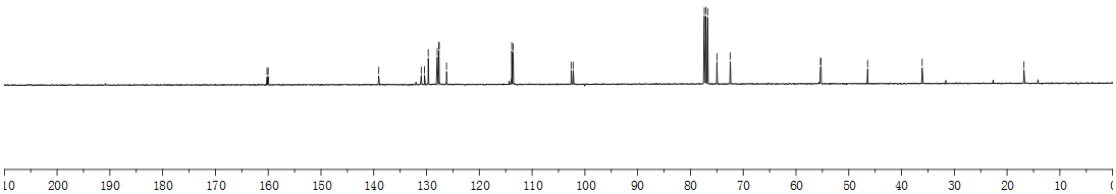


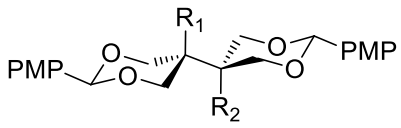


1k R_1=Me, R_2=Ph

^{1}H NMR and ^{13}C NMR of **1k**

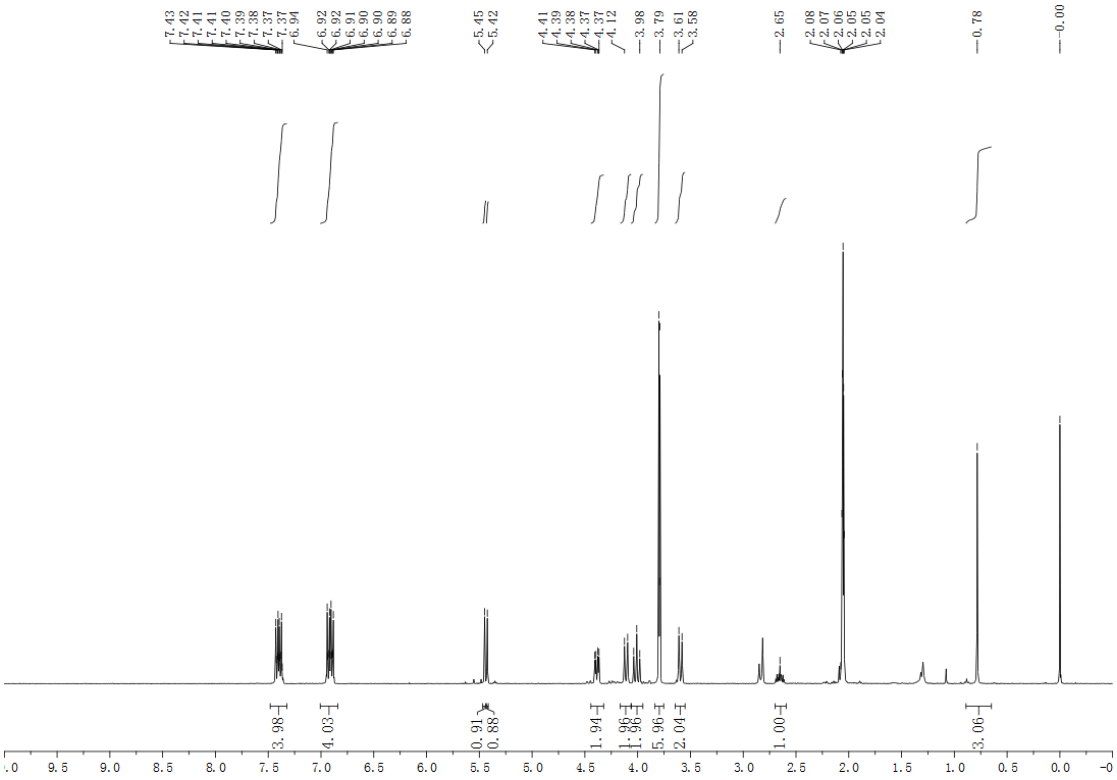


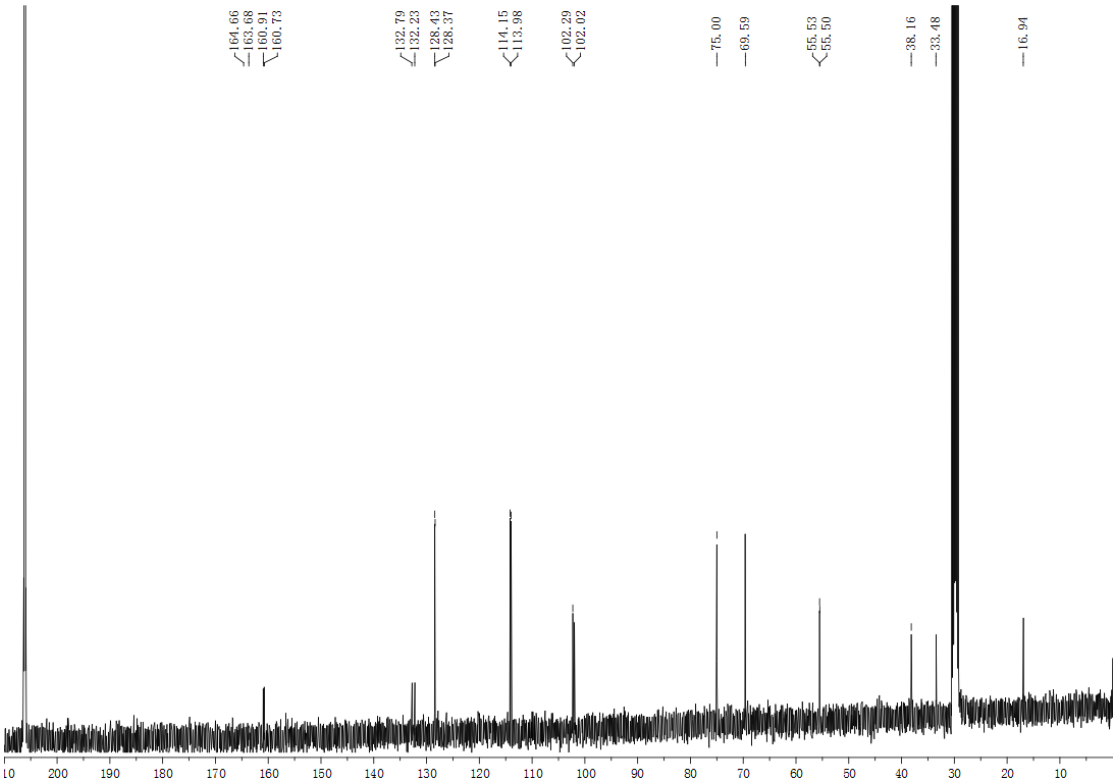


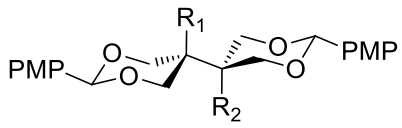


1l R_1=Me, R_2=H

^{1}H NMR and ^{13}C NMR of **1l**

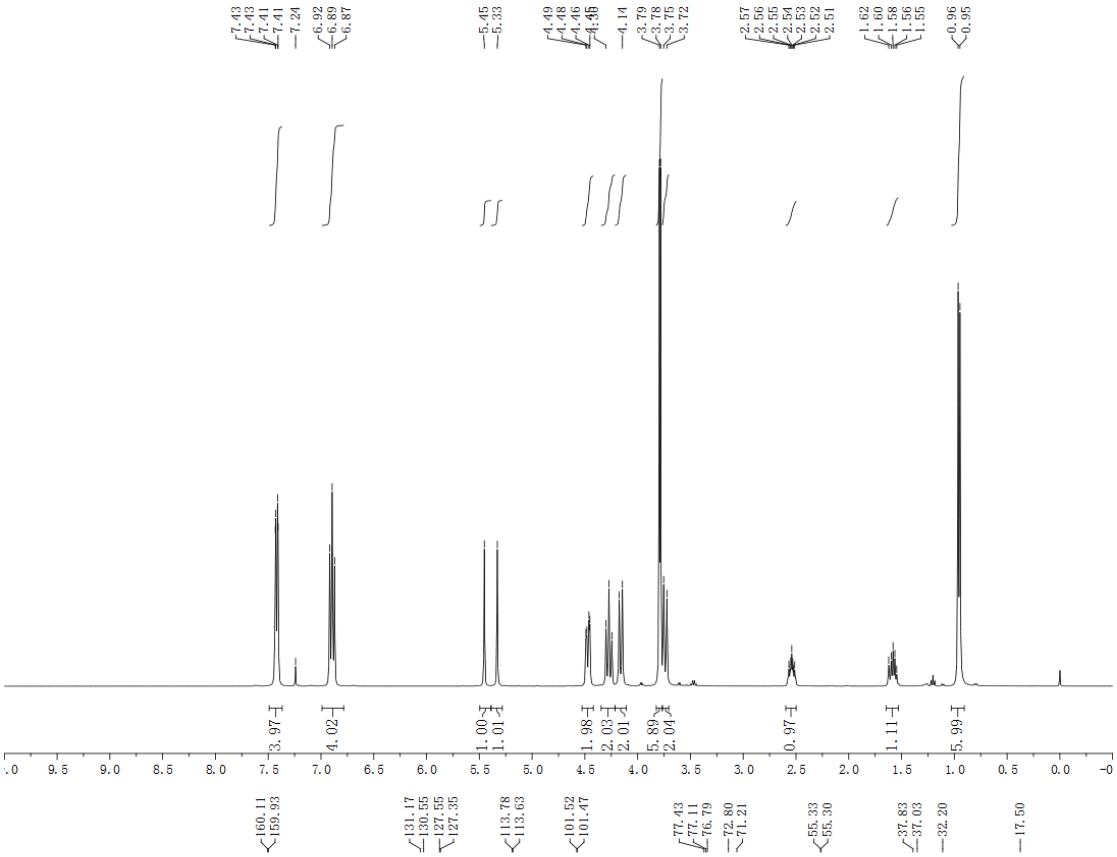


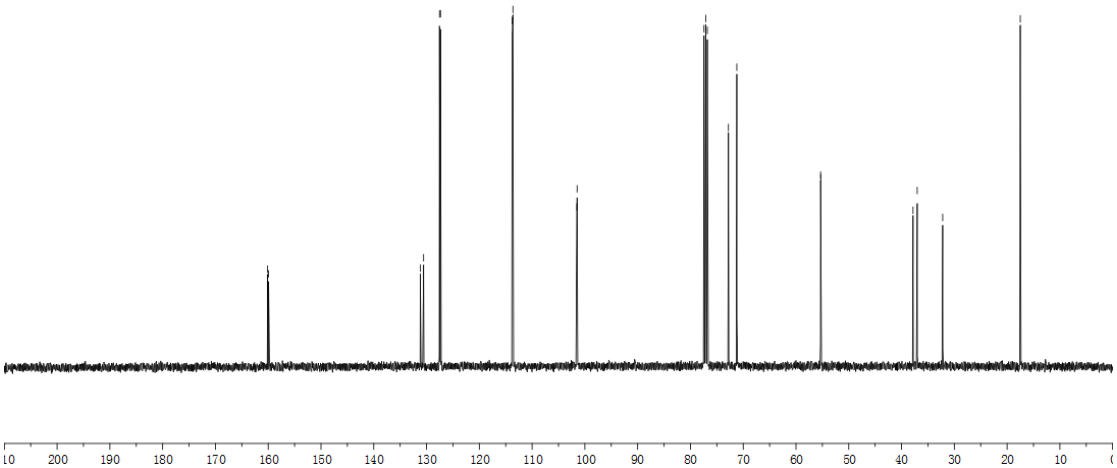


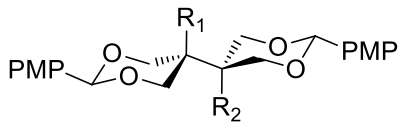


1m R_1=^{i}Pr, R_2=H

^{1}H NMR and ^{13}C NMR of **1m**

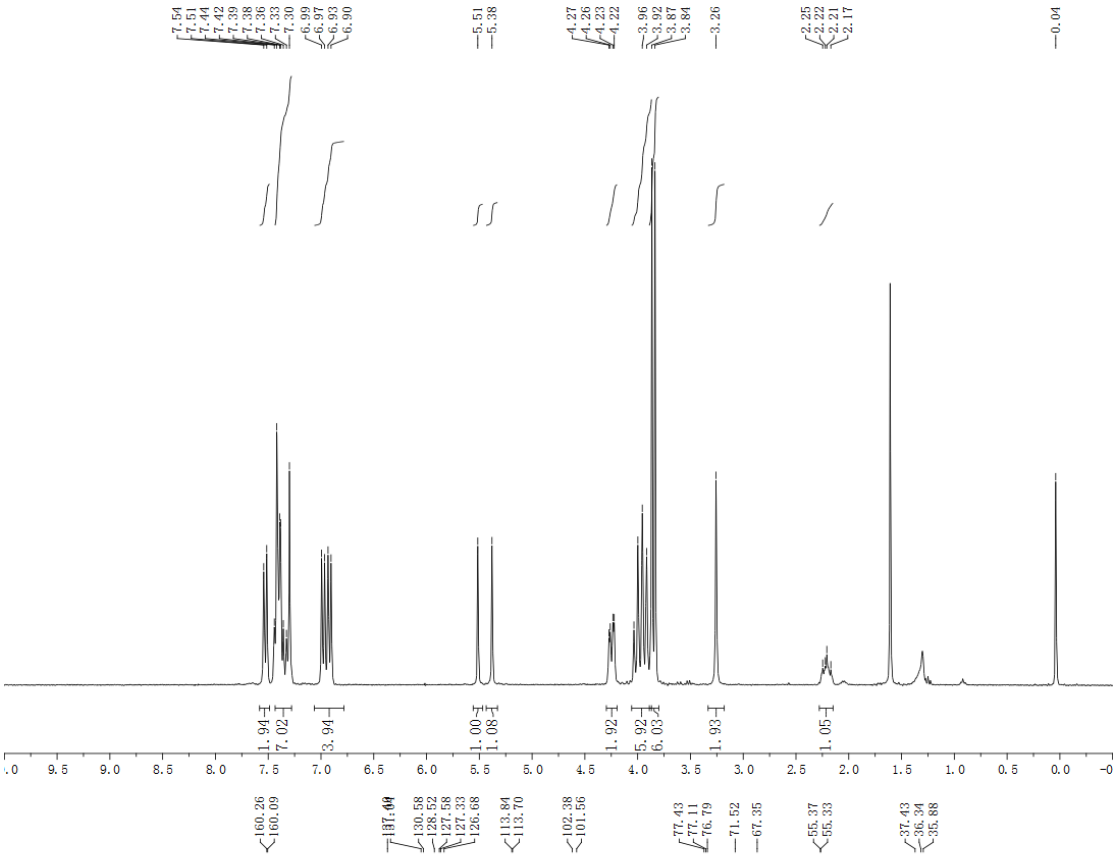


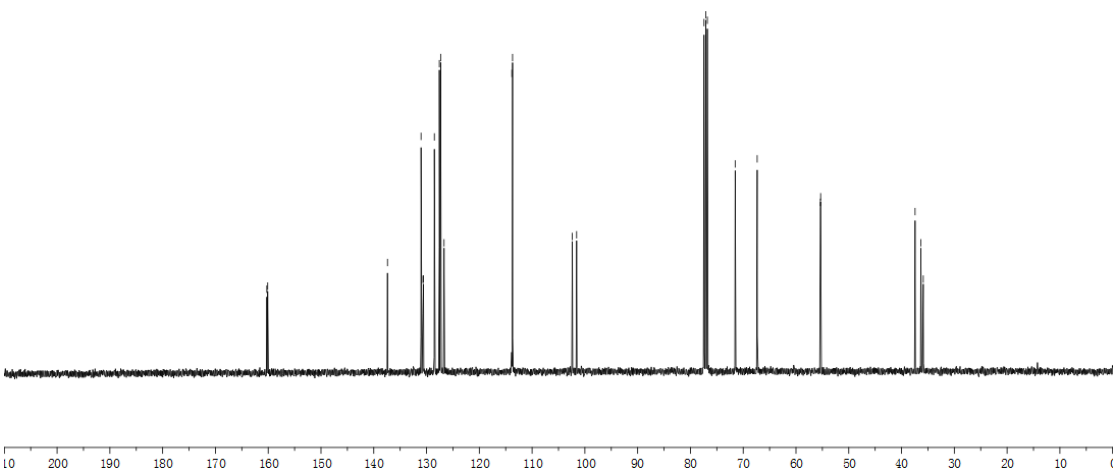


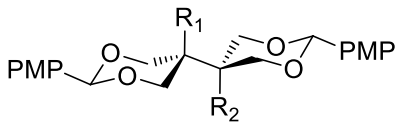


1n R_1=Bn, R_2=H

^{1}H NMR and ^{13}C NMR of **1n**

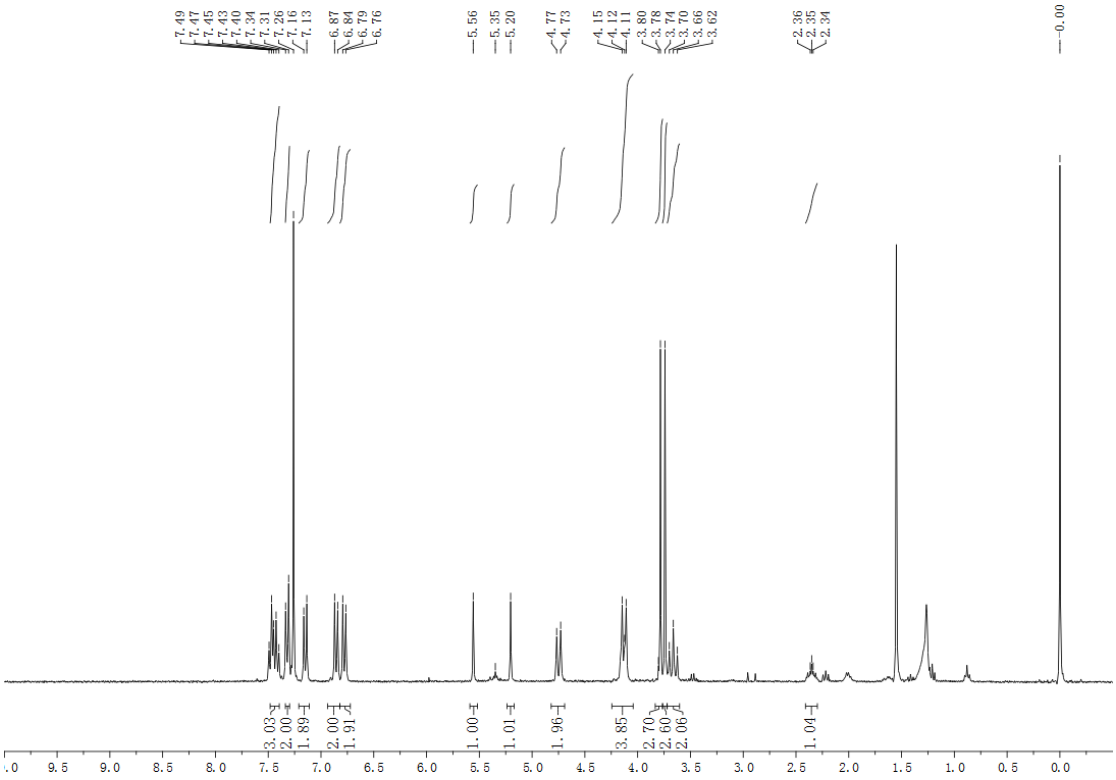


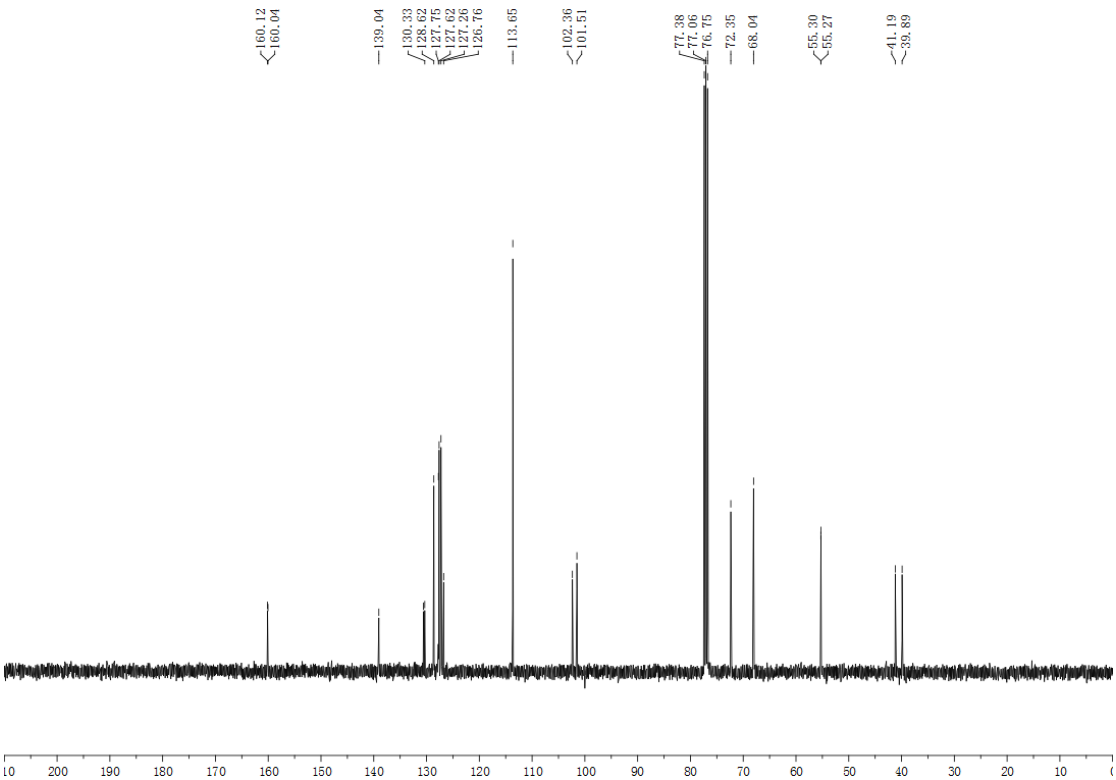


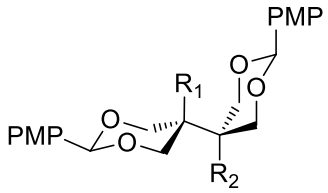


1o R_1=ph, R_2=H

^{1}H NMR and ^{13}C NMR of **1o**

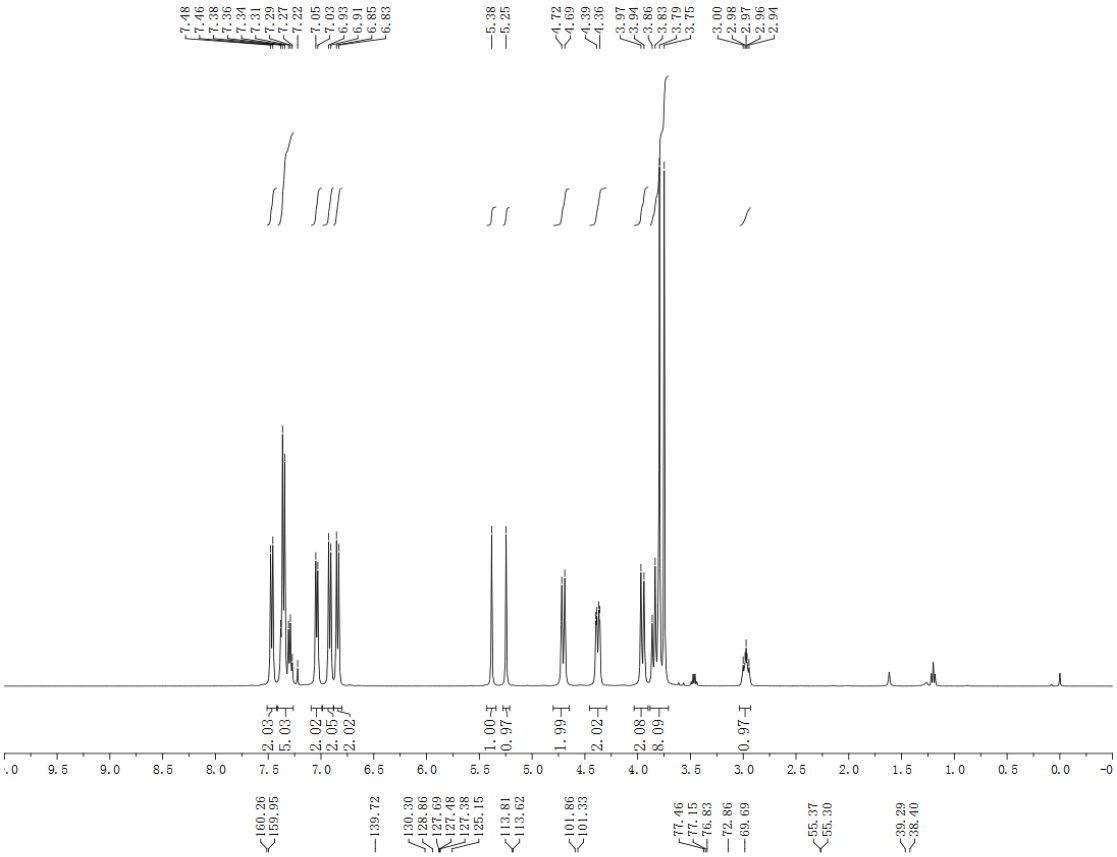


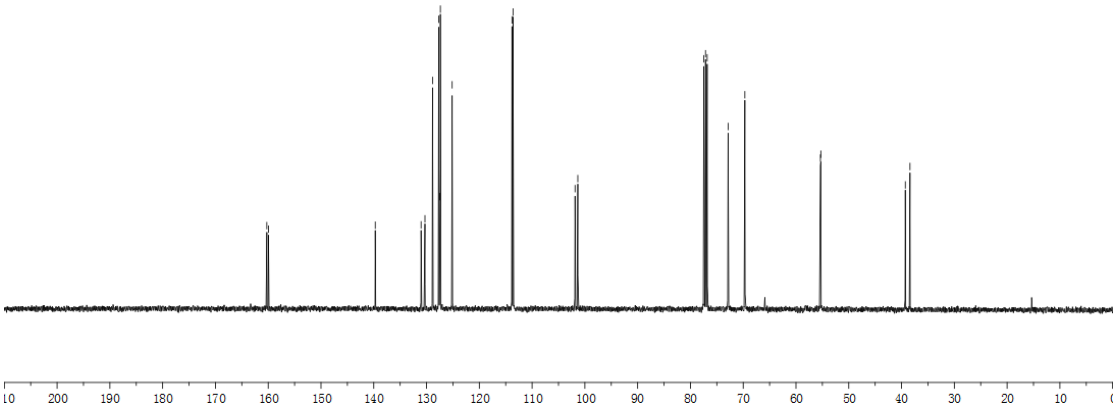


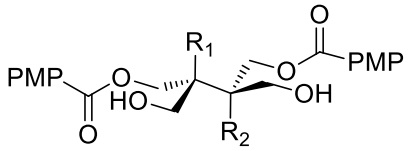


1p R_1=H, R_2=Ph

^{1}H NMR and ^{13}C NMR of **1p**

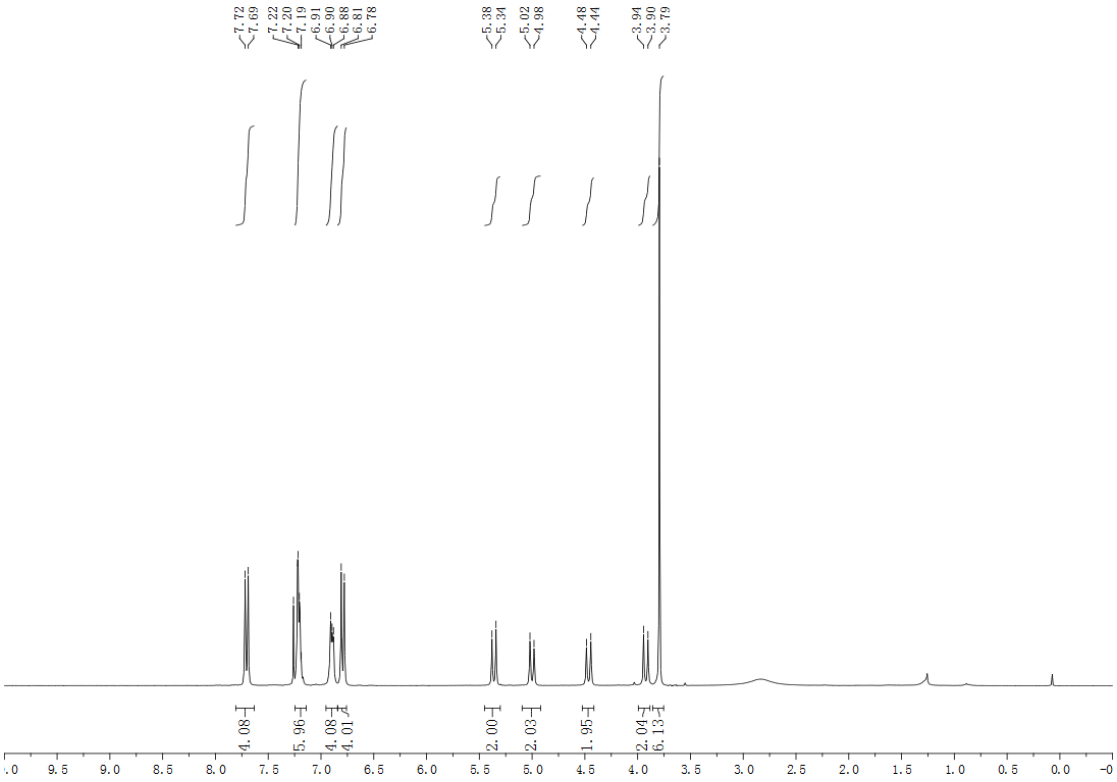


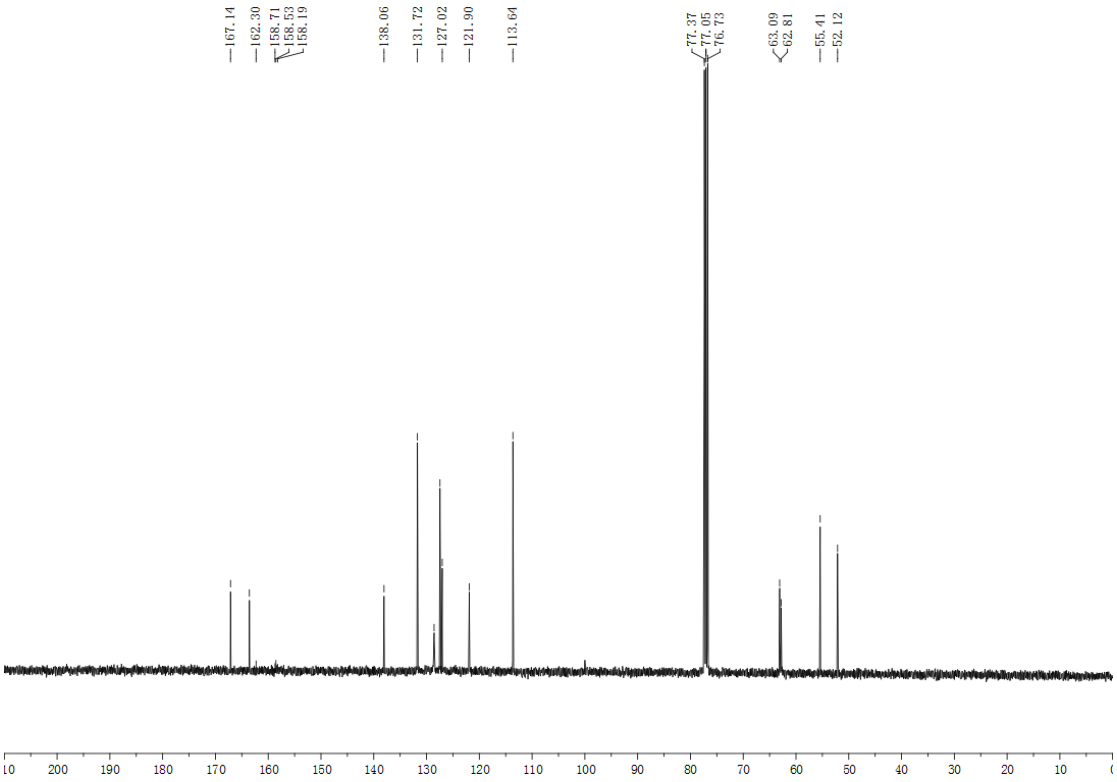




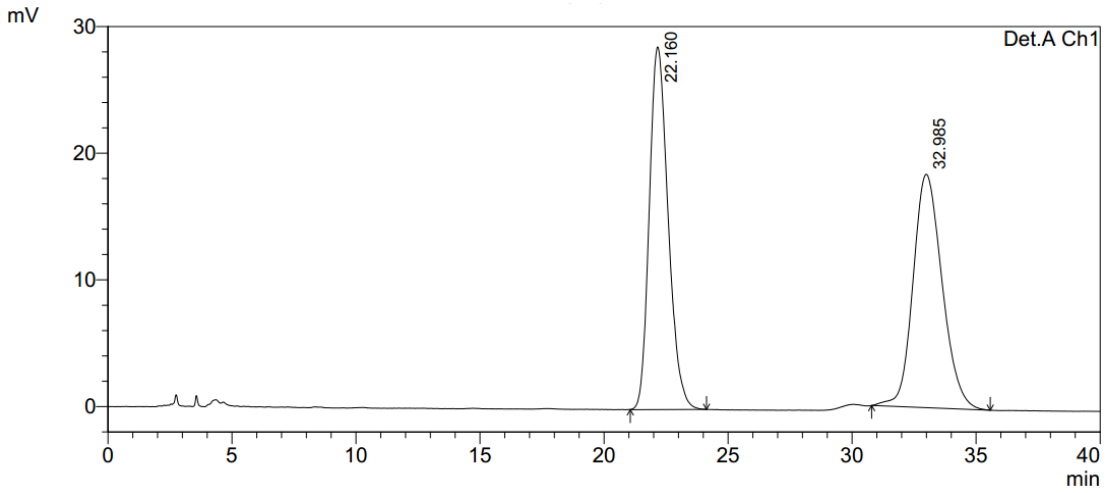
2a R_1=R_2=Ph

^{1}H NMR and ^{13}C NMR of **2a**



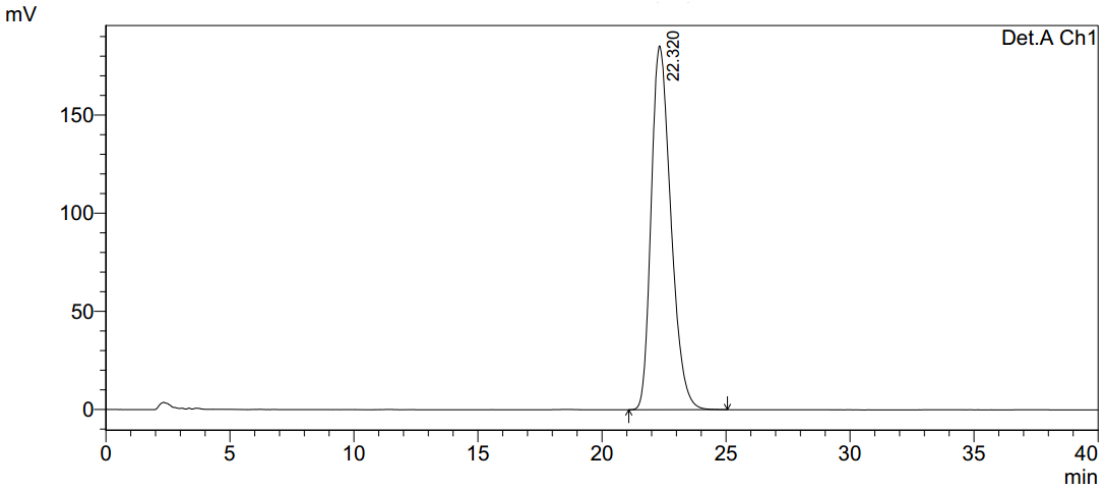


HPLC of 2a



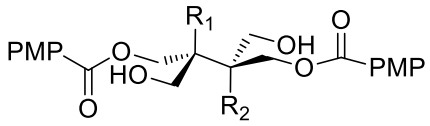
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.160	1508939	28629	50.087	60.848
2	32.985	1503690	18421	49.913	39.152
Total		3012630	47050	100.000	100.000



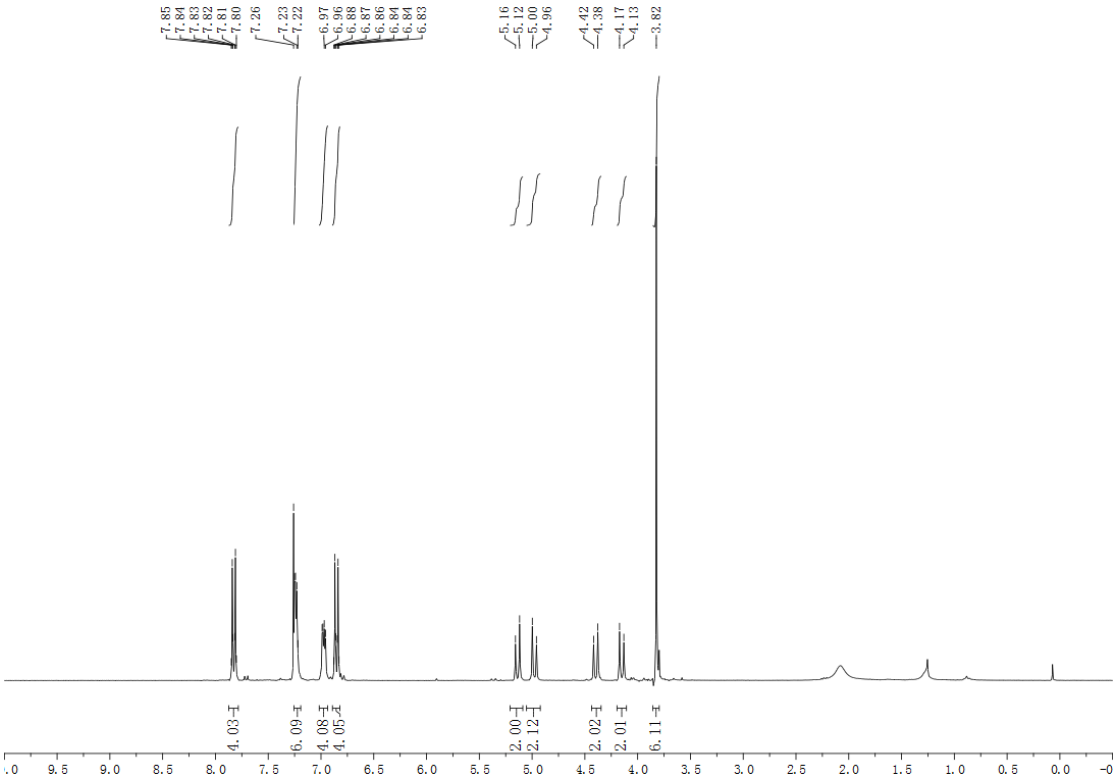
Detector A Ch1 254nm

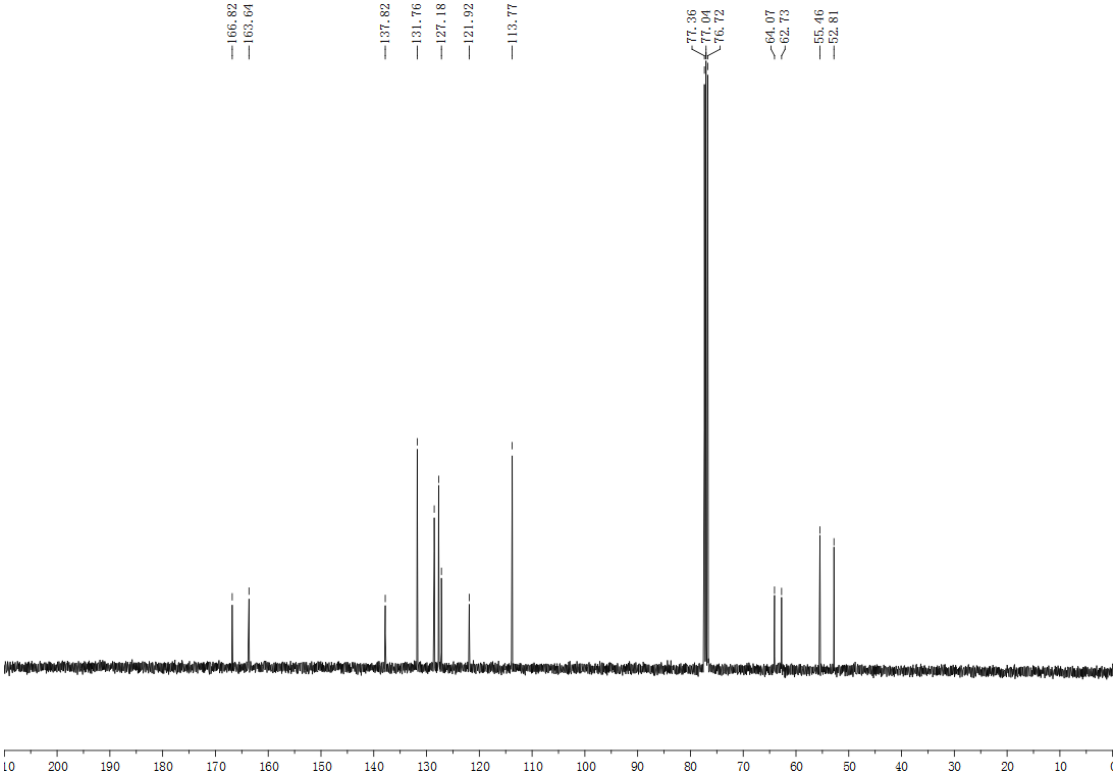
Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.320	10242487	185419	100.000	100.000
Total		10242487	185419	100.000	100.000

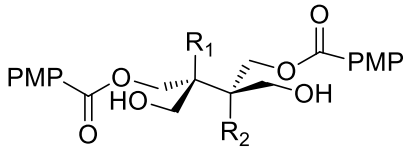


R_1=R_2=Ph
the isomer of 2a

^{1}H NMR and ^{13}C NMR of the isomer of **2a**

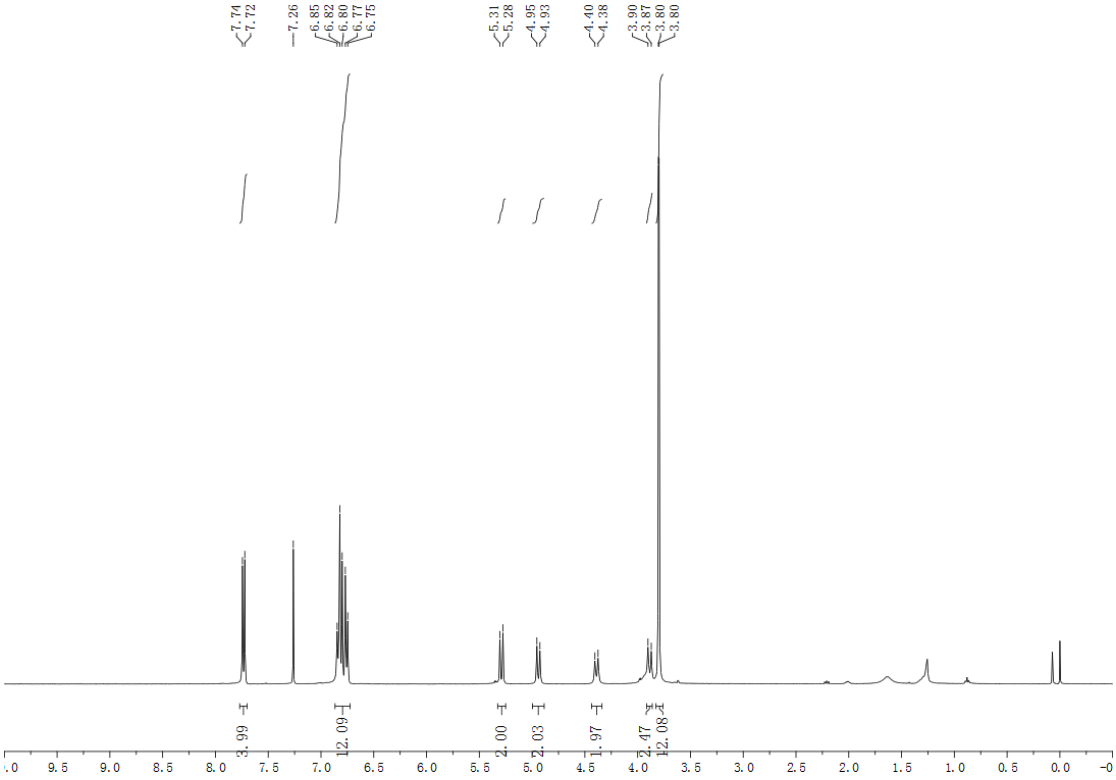


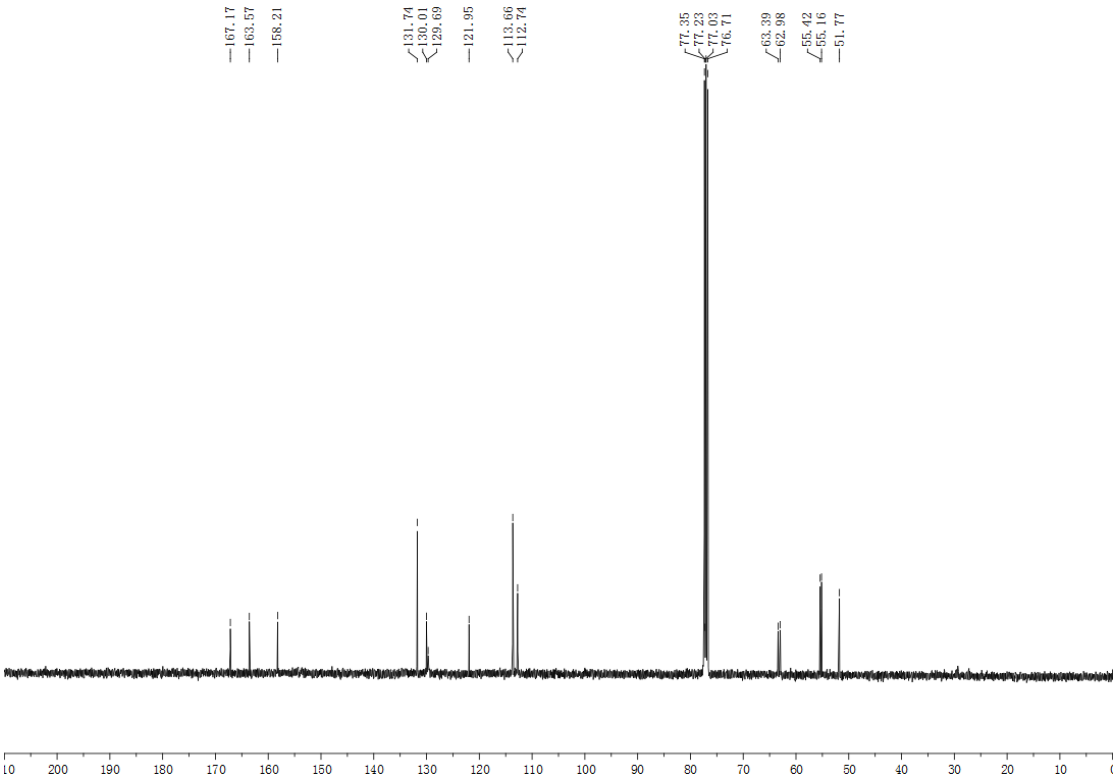




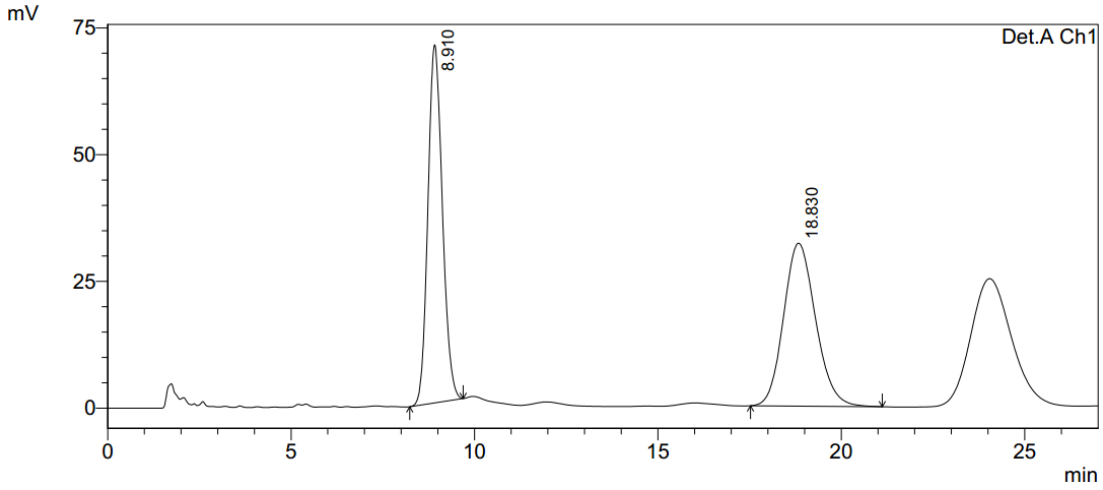
2b R_1=R_2=*p*-OMe-Ph

^{1}H NMR and ^{13}C NMR of **2b**

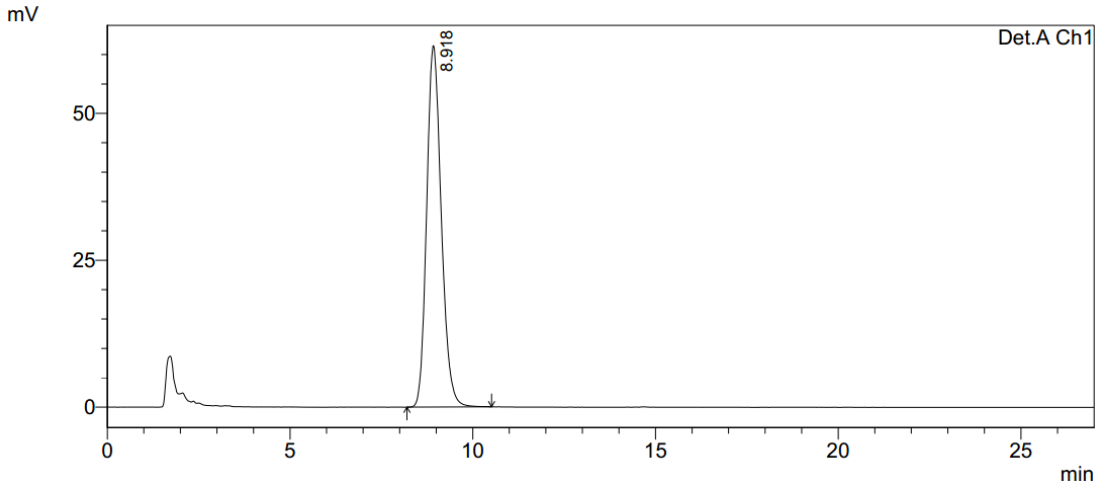




HPLC of 2b

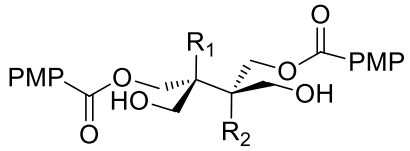


Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.910	1937837	70649	49.856	68.724
2	18.830	1949016	32151	50.144	31.276
Total		3886854	102800	100.000	100.000



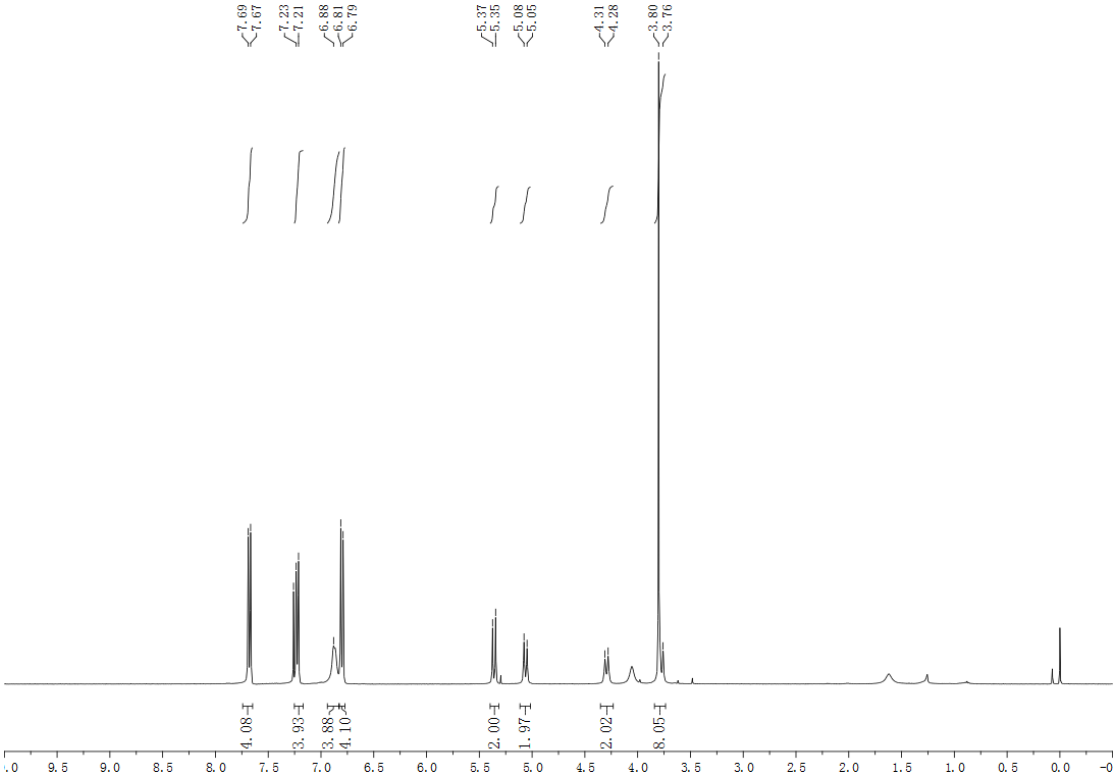
Detector A Ch1 254nm

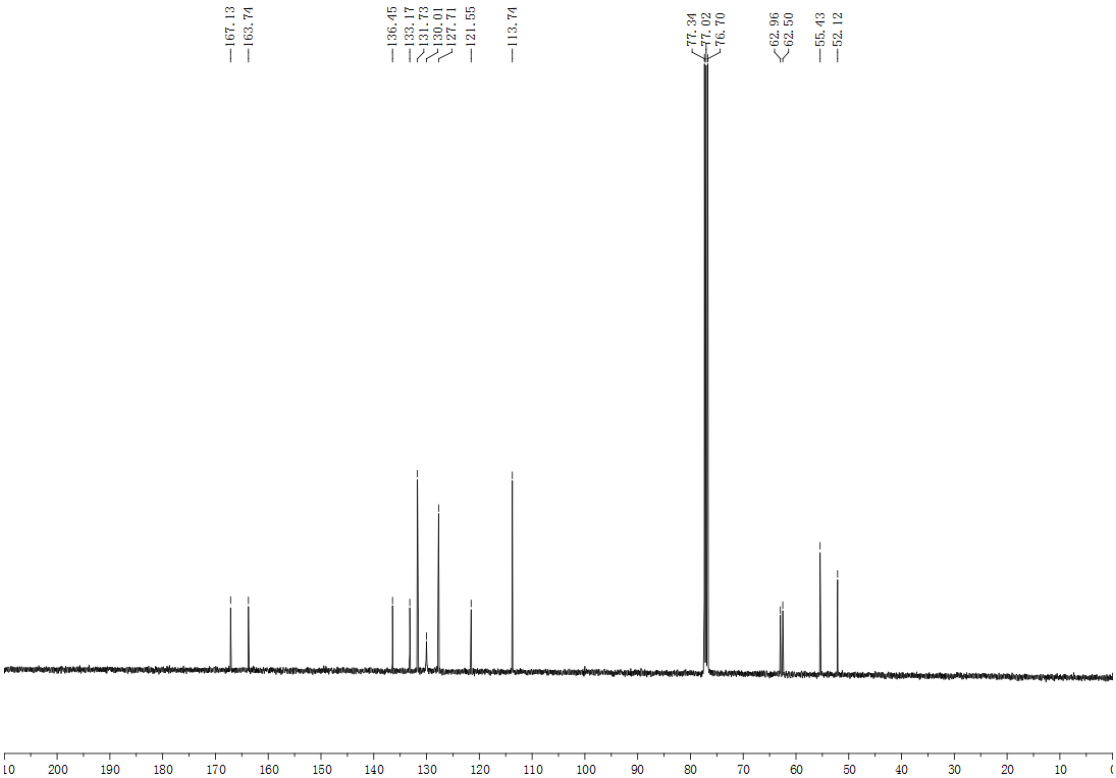
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.918	1710769	61522	100.000	100.000
Total		1710769	61522	100.000	100.000



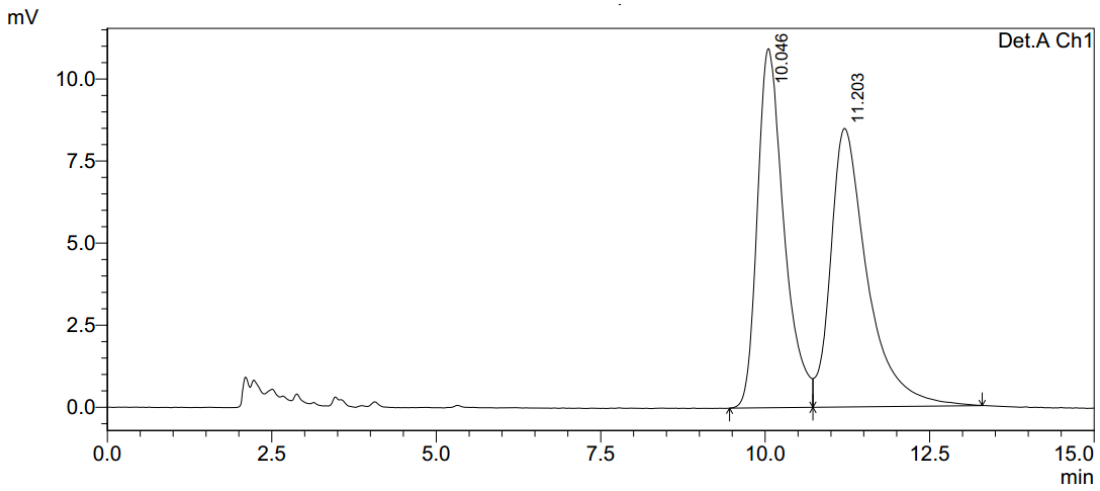
2c R_1=R_2=*p*-Cl-Ph

^{1}H NMR and ^{13}C NMR of **2c**



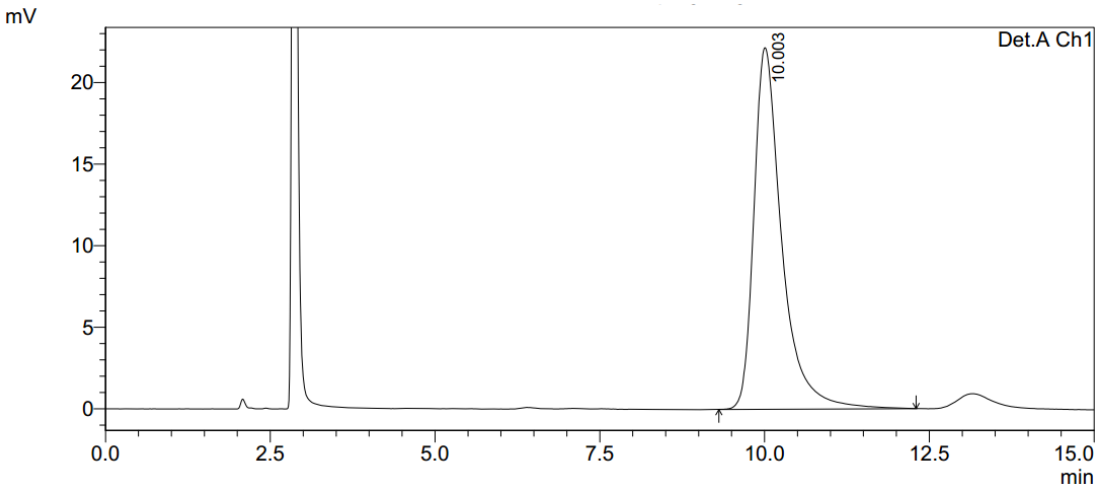


HPLC of **2c**



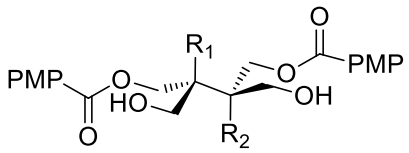
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.046	308718	10943	48.342	56.311
2	11.203	329892	8490	51.658	43.689
Total		638610	19434	100.000	100.000



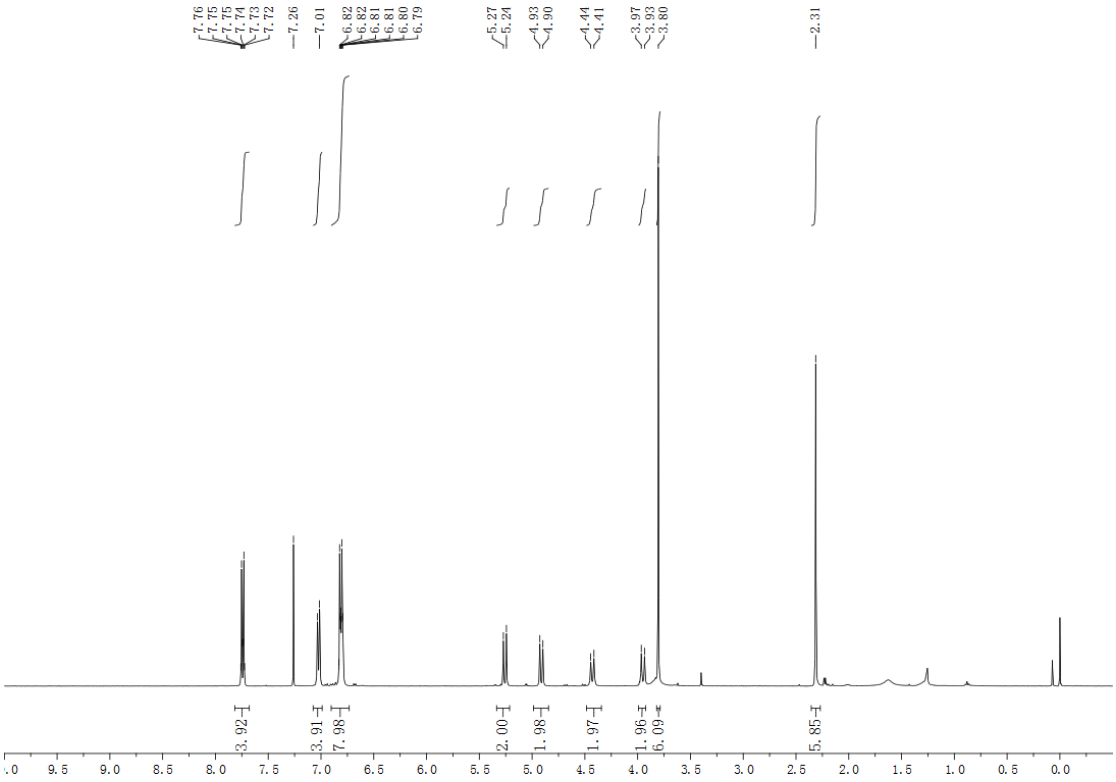
Detector A Ch1 254nm

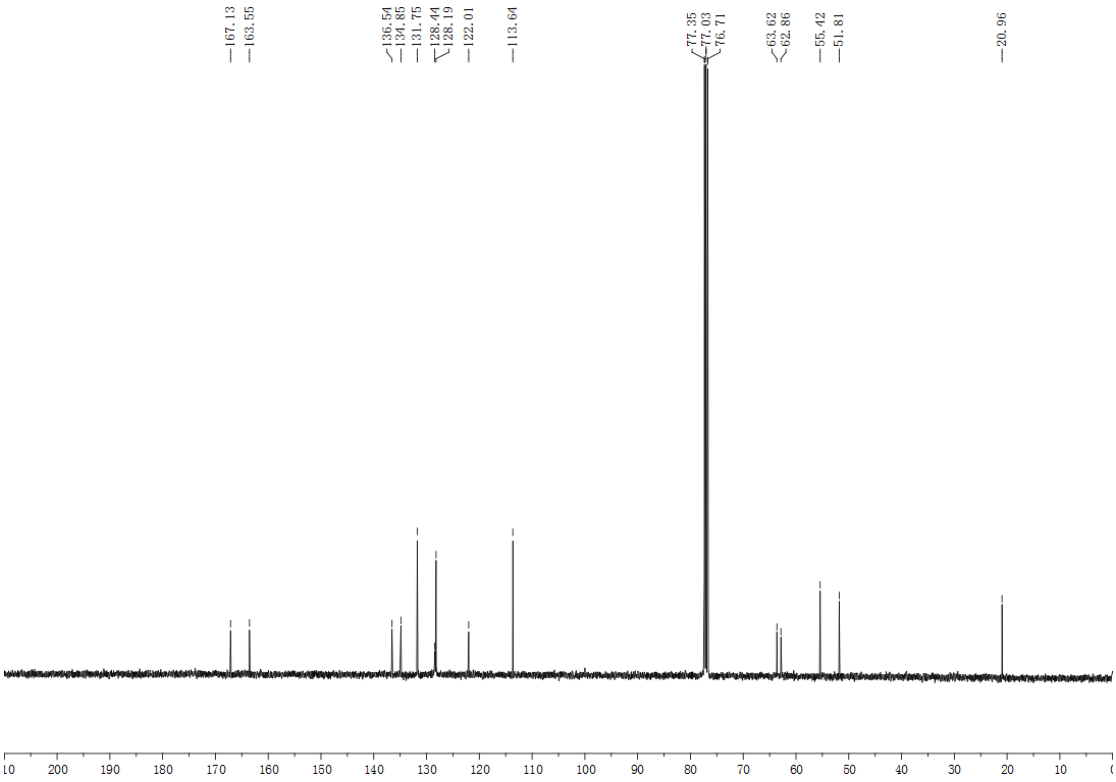
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.003	653293	22172	100.000	100.000
Total		653293	22172	100.000	100.000



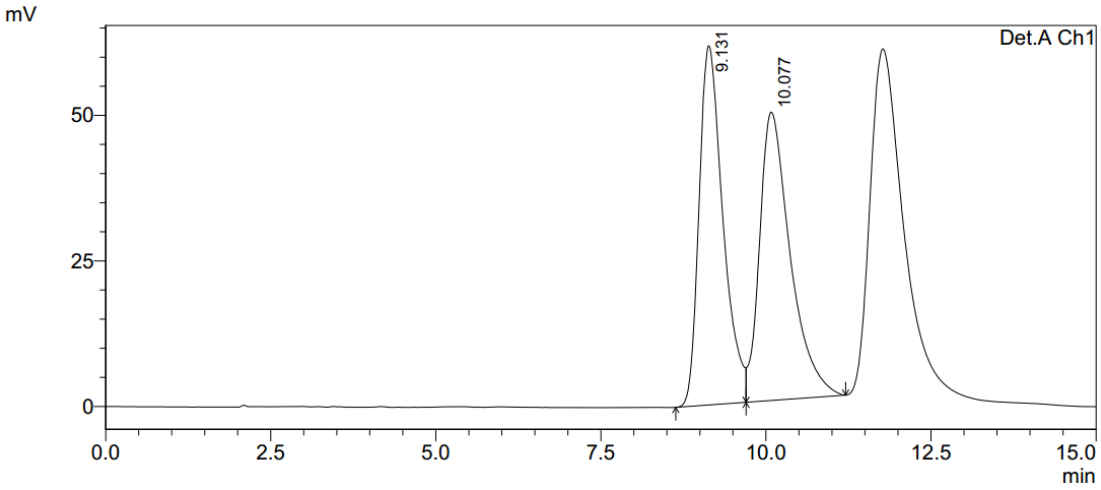
2d R_1=R_2=*p*-Me-Ph

^{1}H NMR and ^{13}C NMR of **2d**



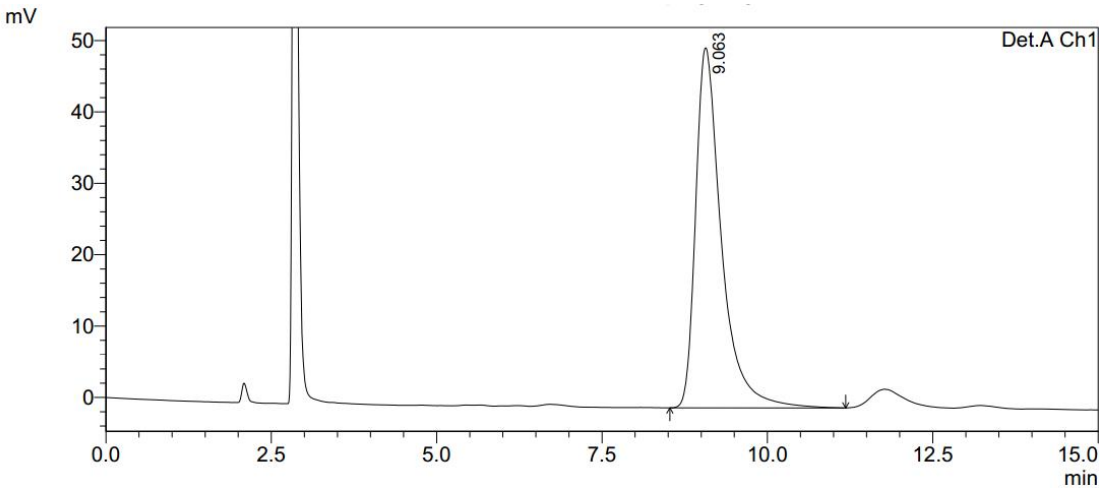


HPLC of **2d**



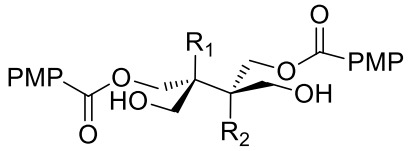
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.131	1555772	61698	49.234	55.475
2	10.077	1604208	49520	50.766	44.525
Total		3159980	111218	100.000	100.000



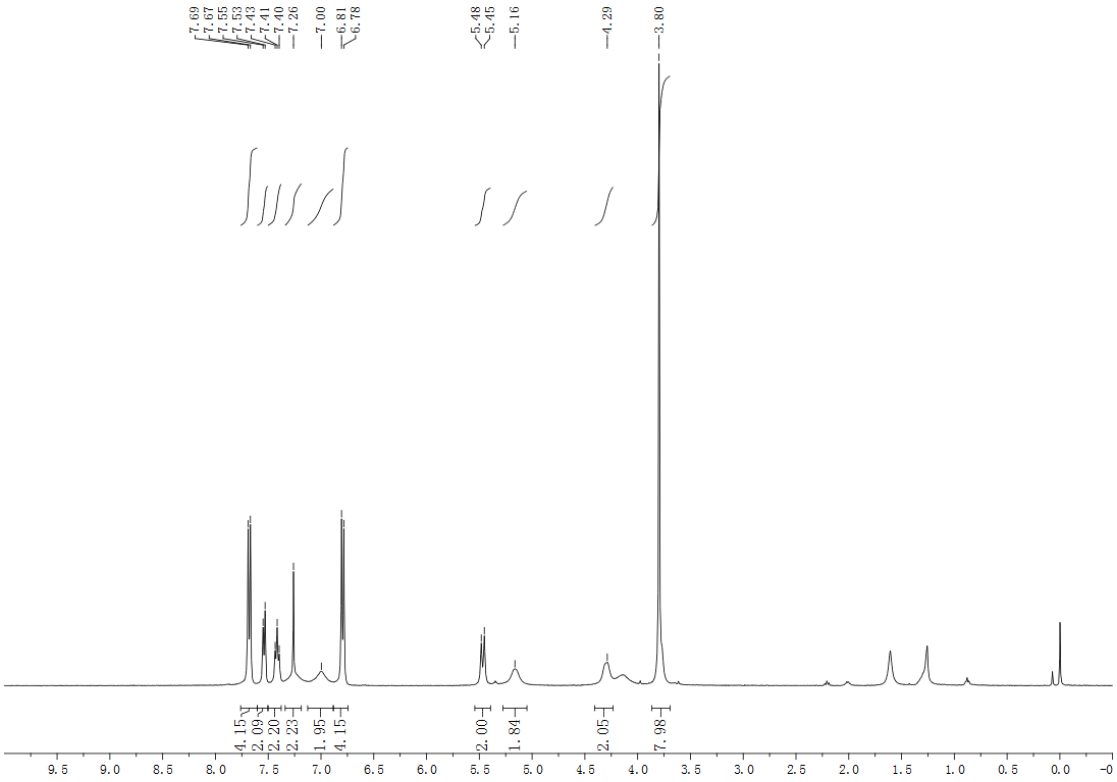
Detector A Ch1 254nm

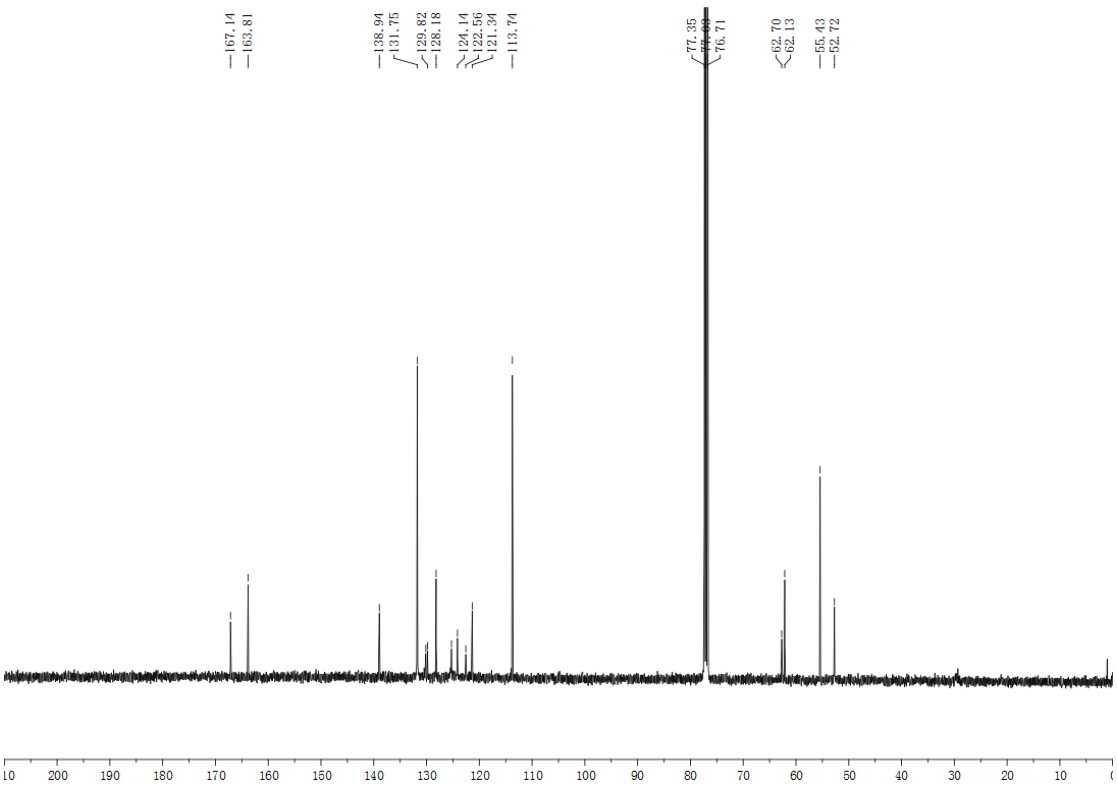
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.063	1367793	50444	100.000	100.000
Total		1367793	50444	100.000	100.000



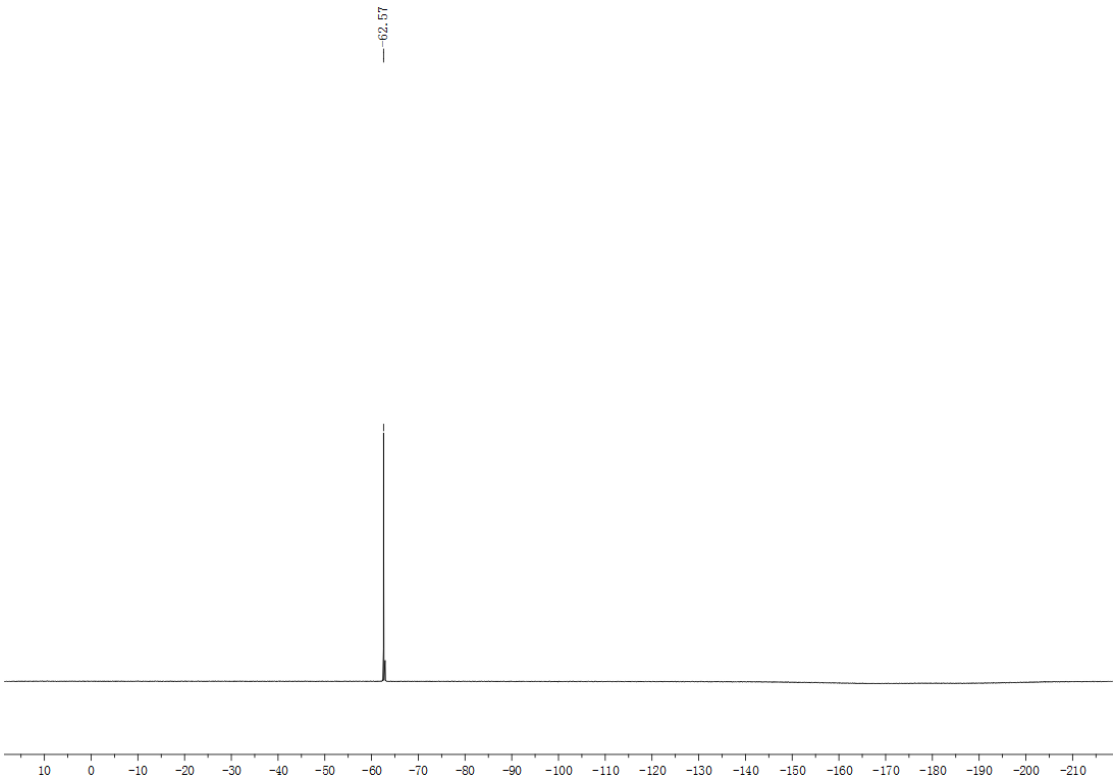
2e R_1=R_2=*m*-CF_3-Ph

^{1}H NMR and ^{13}C NMR of **2e**

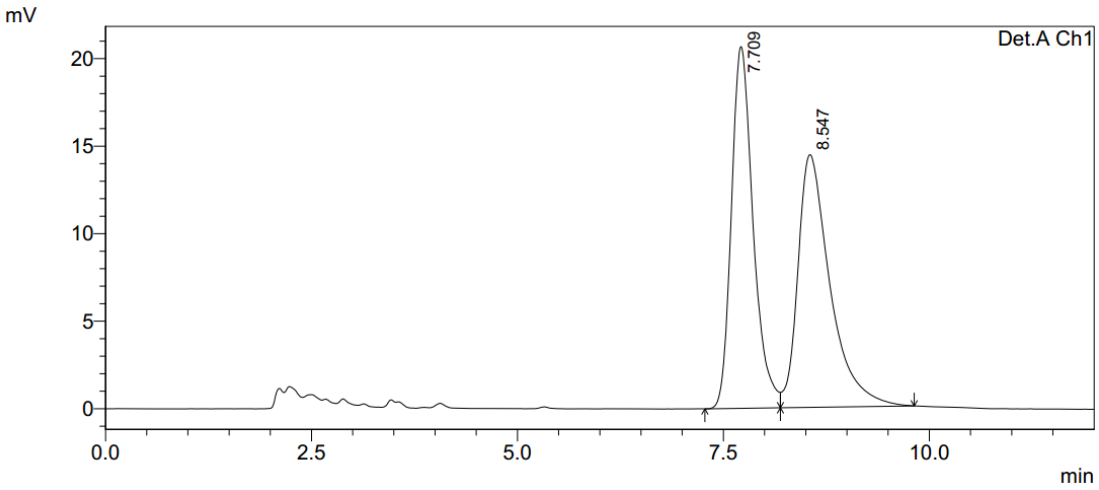




^{19}F NMR of **2e**

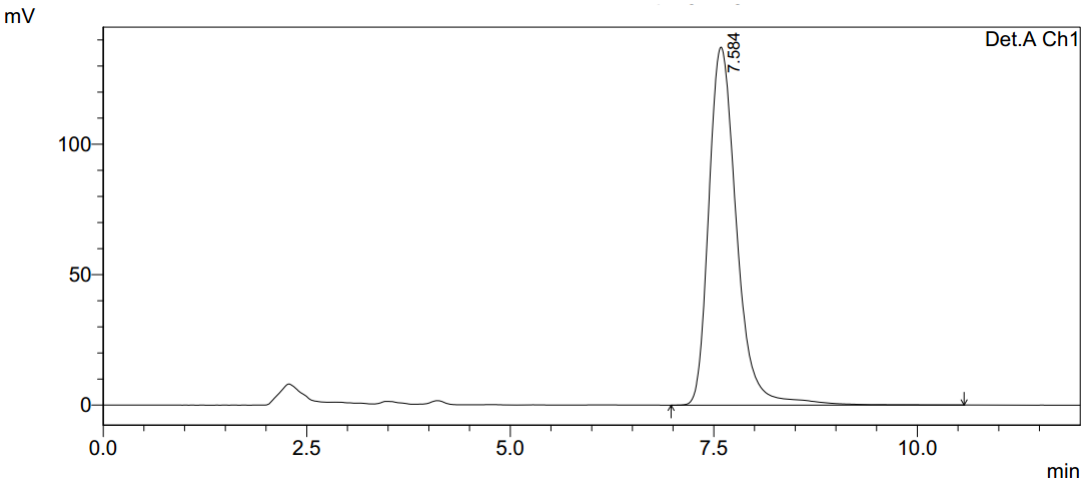

−62.57
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210

HPLC of **2e**



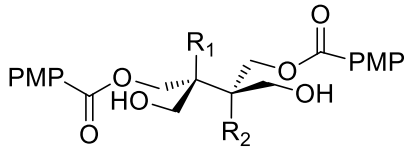
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.709	379685	20662	49.216	58.867
2	8.547	391787	14438	50.784	41.133
Total		771472	35100	100.000	100.000



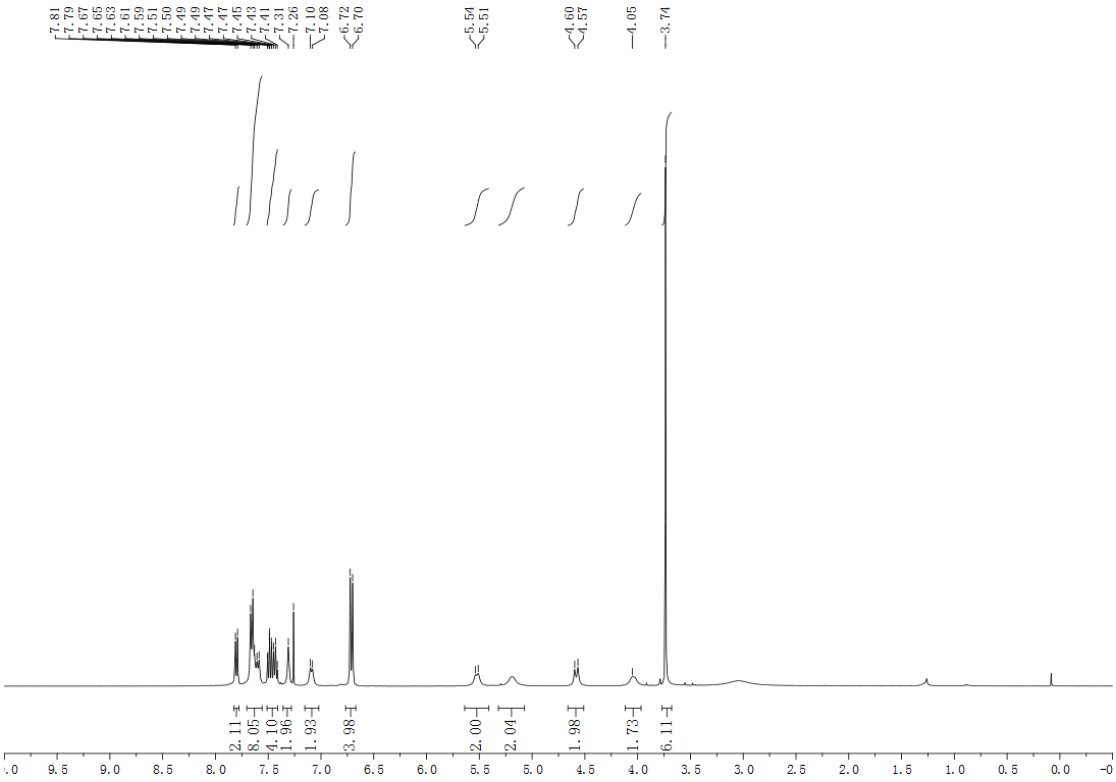
Detector A Ch1 254nm

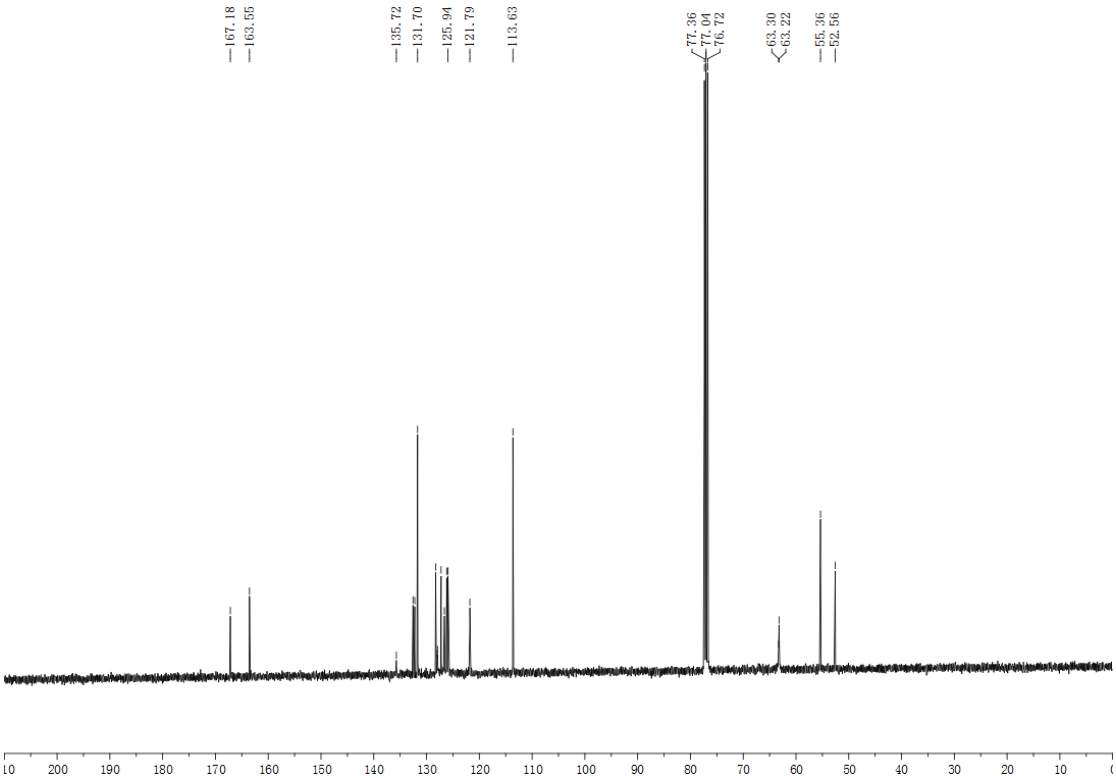
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.584	3261476	137252	100.000	100.000
Total		3261476	137252	100.000	100.000



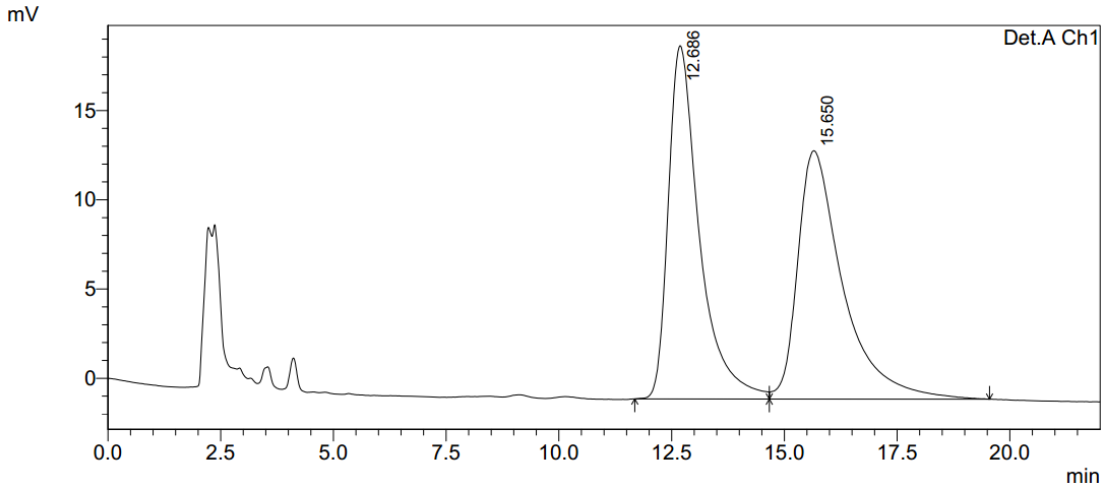
2f R_1=R_2=2-Naphthyl

^{1}H NMR and ^{13}C NMR of **2f**



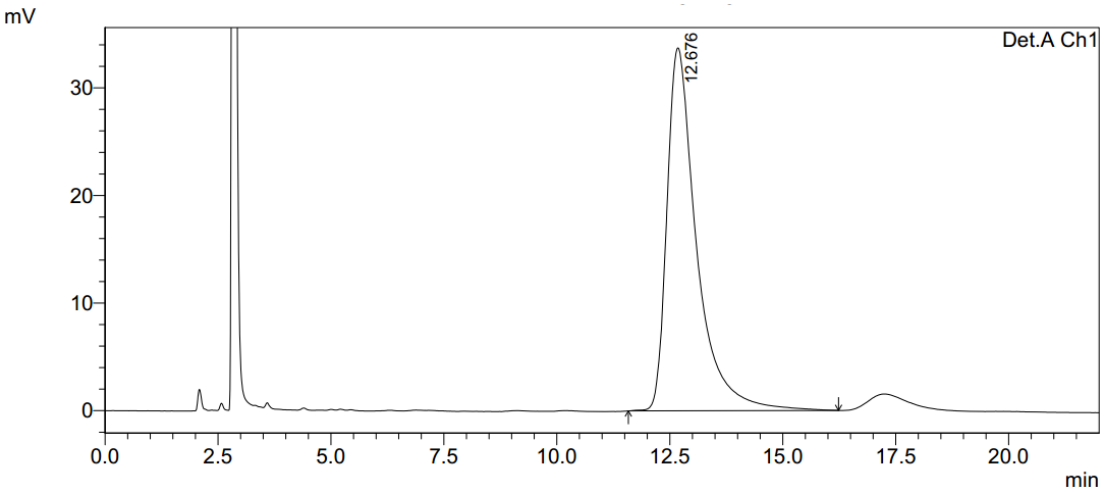


HPLC of **2f**



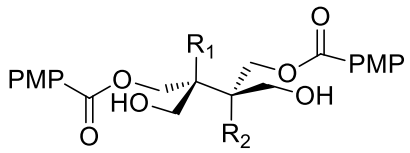
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.686	950209	19792	49.495	58.727
2	15.650	969611	13910	50.505	41.273
Total		1919820	33703	100.000	100.000



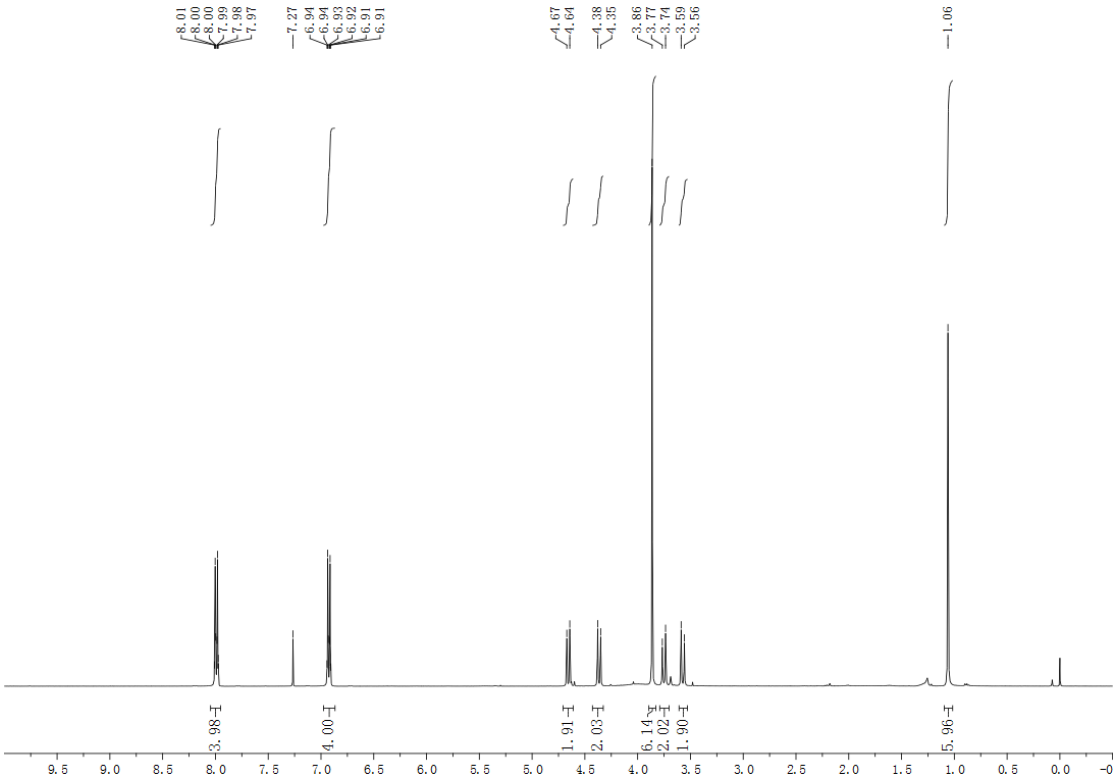
Detector A Ch1 254nm

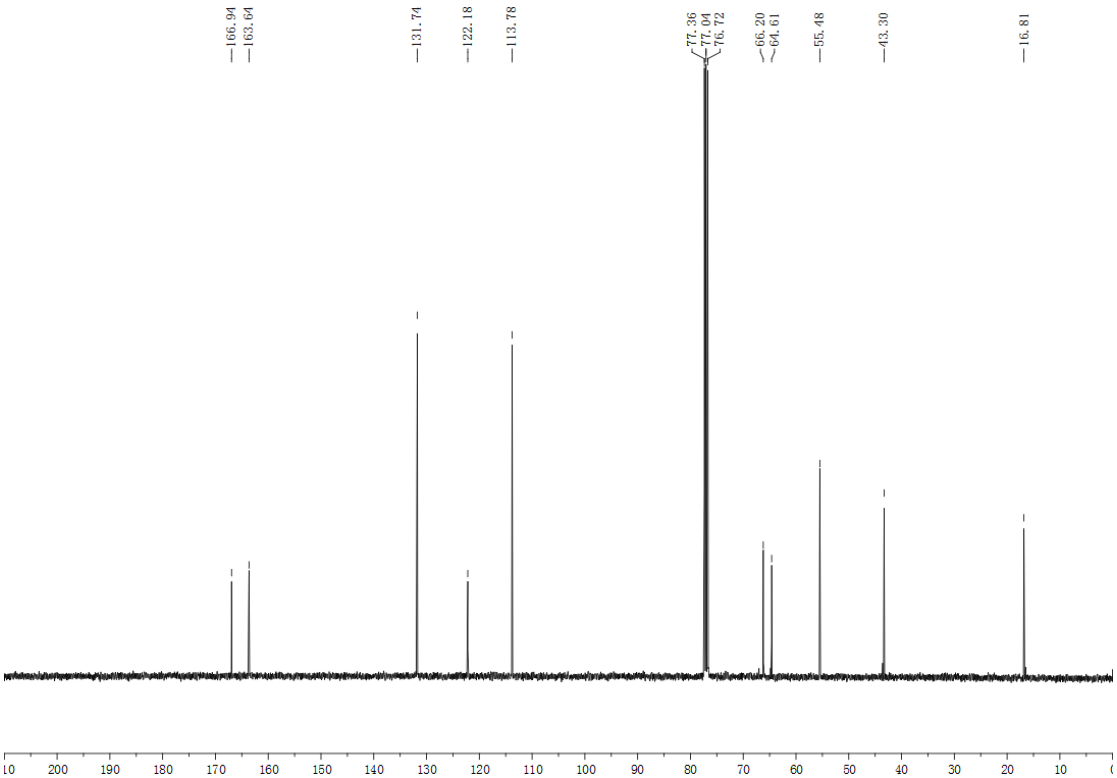
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.676	1542237	33727	100.000	100.000
Total		1542237	33727	100.000	100.000



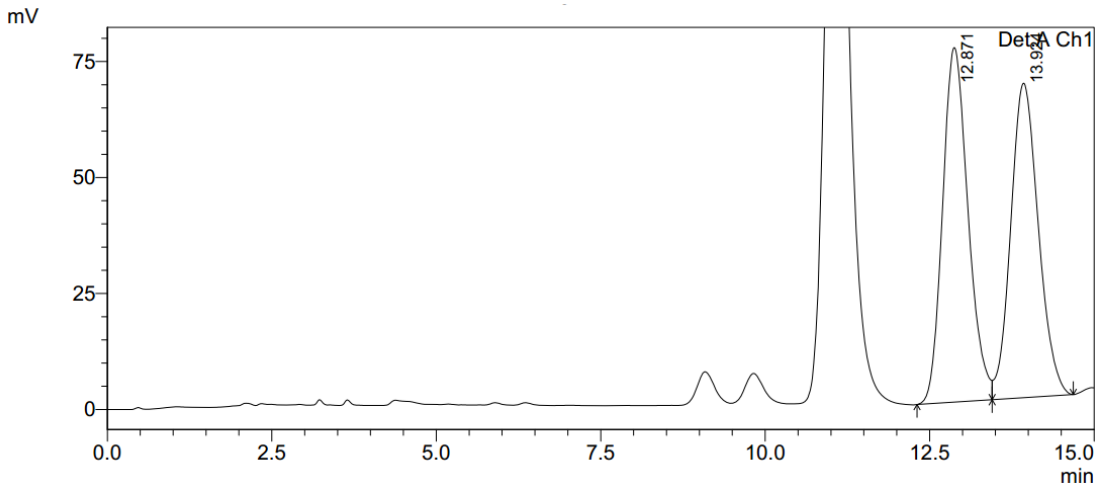
2g R_1=R_2=Me

^{1}H NMR and ^{13}C NMR of **2g**



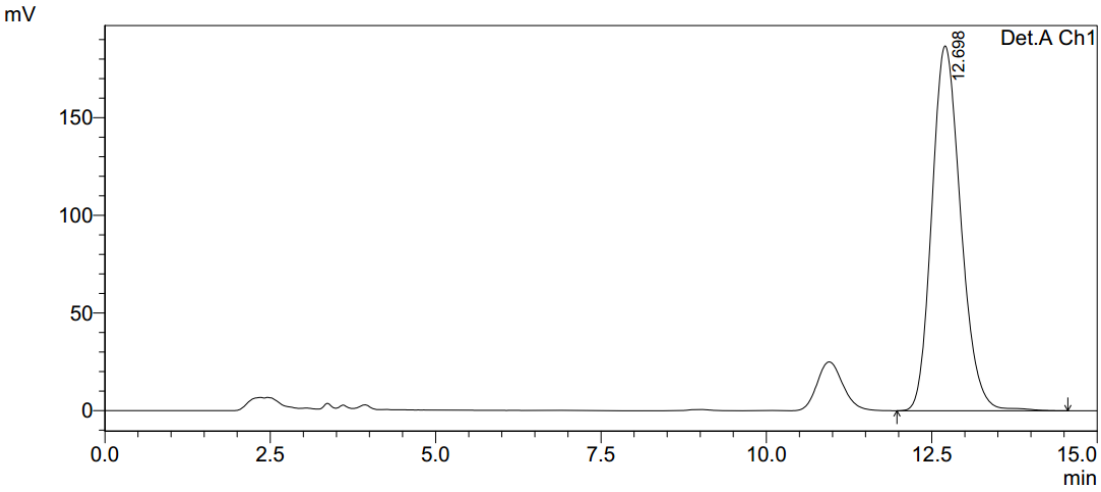


HPLC of **2g**



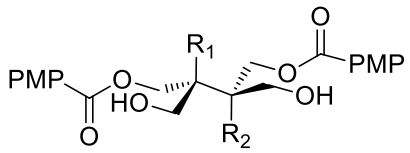
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.871	2056614	76423	50.931	52.994
2	13.924	1981446	67788	49.069	47.006
Total		4038060	144211	100.000	100.000



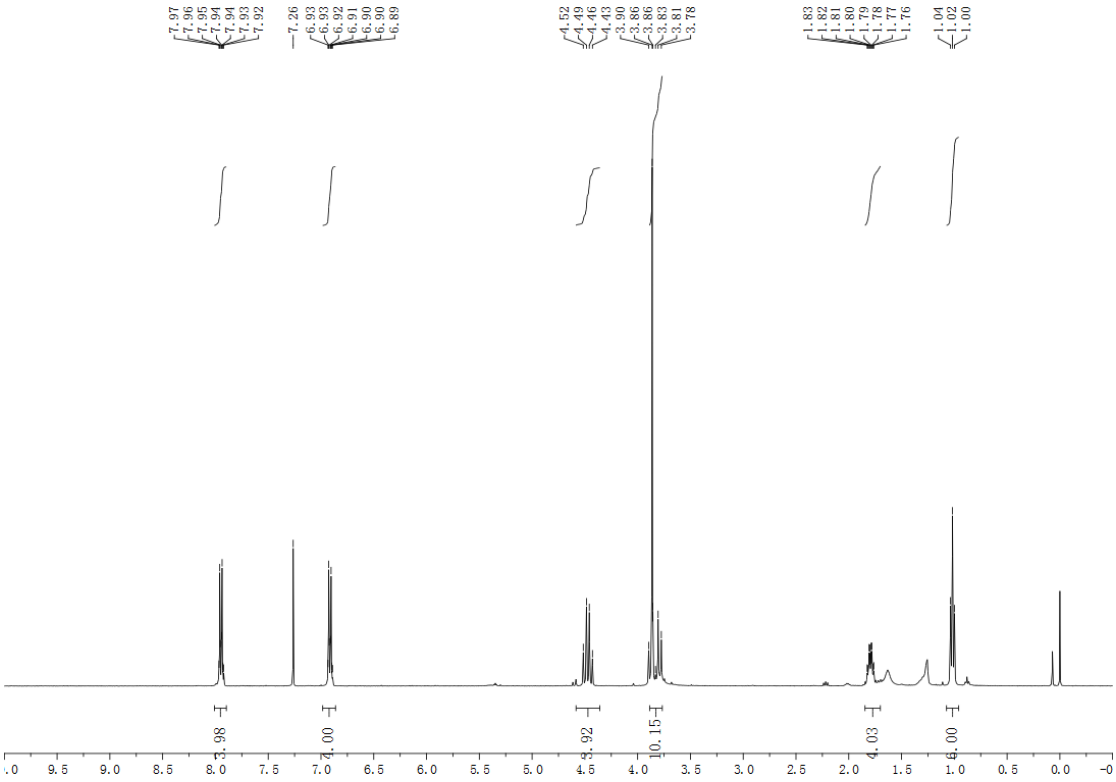
Detector A Ch1 254nm

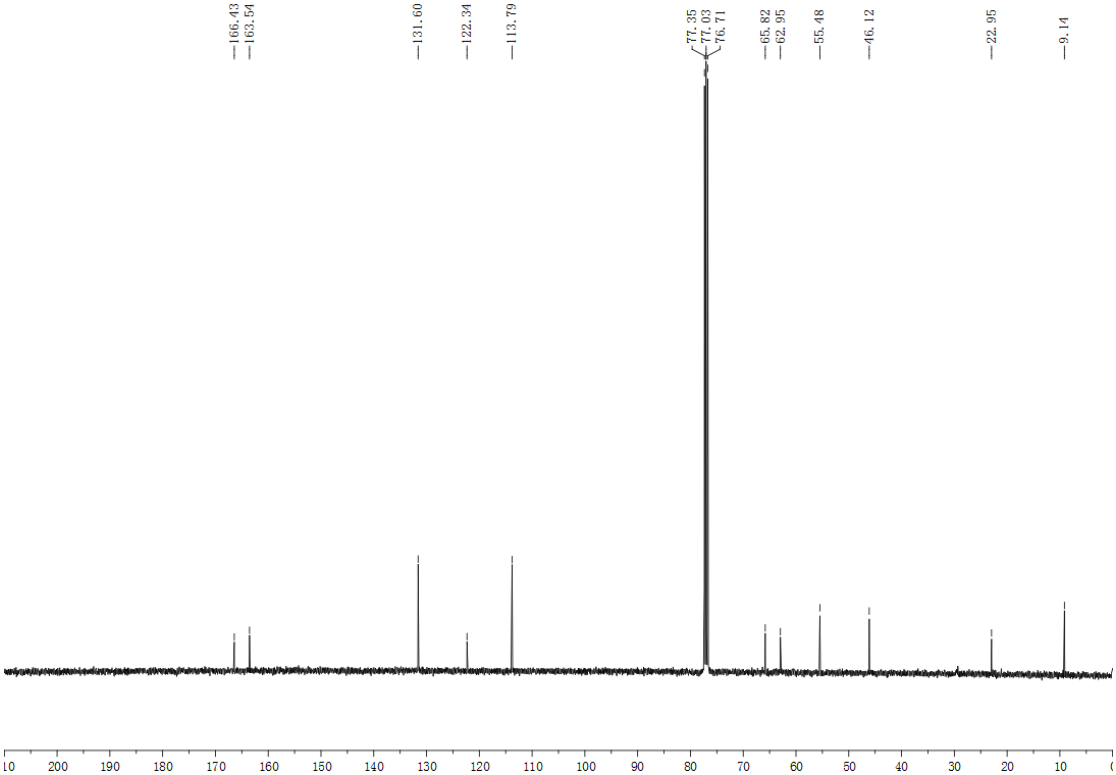
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.698	5682976	186841	100.000	100.000
Total		5682976	186841	100.000	100.000



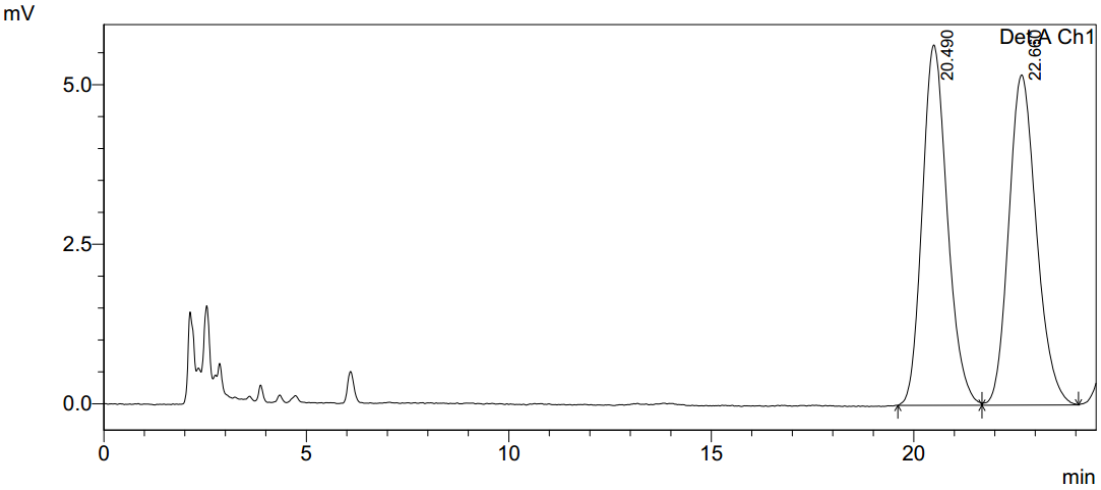
2h R_1=R_2=Et

^{1}H NMR and ^{13}C NMR of **2h**



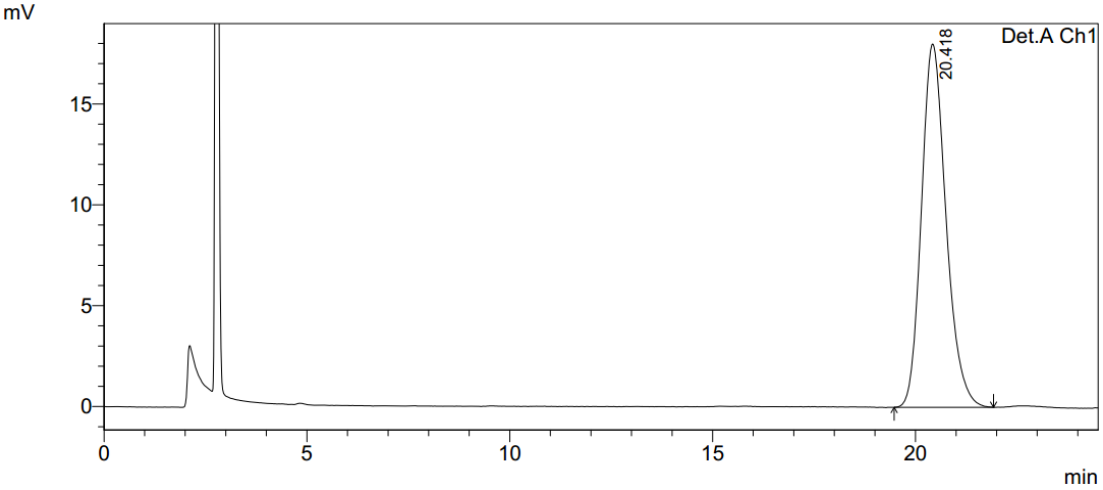


HPLC of **2h**



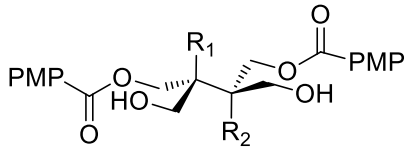
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.490	243499	5646	49.691	52.185
2	22.660	246524	5174	50.309	47.815
Total		490022	10820	100.000	100.000



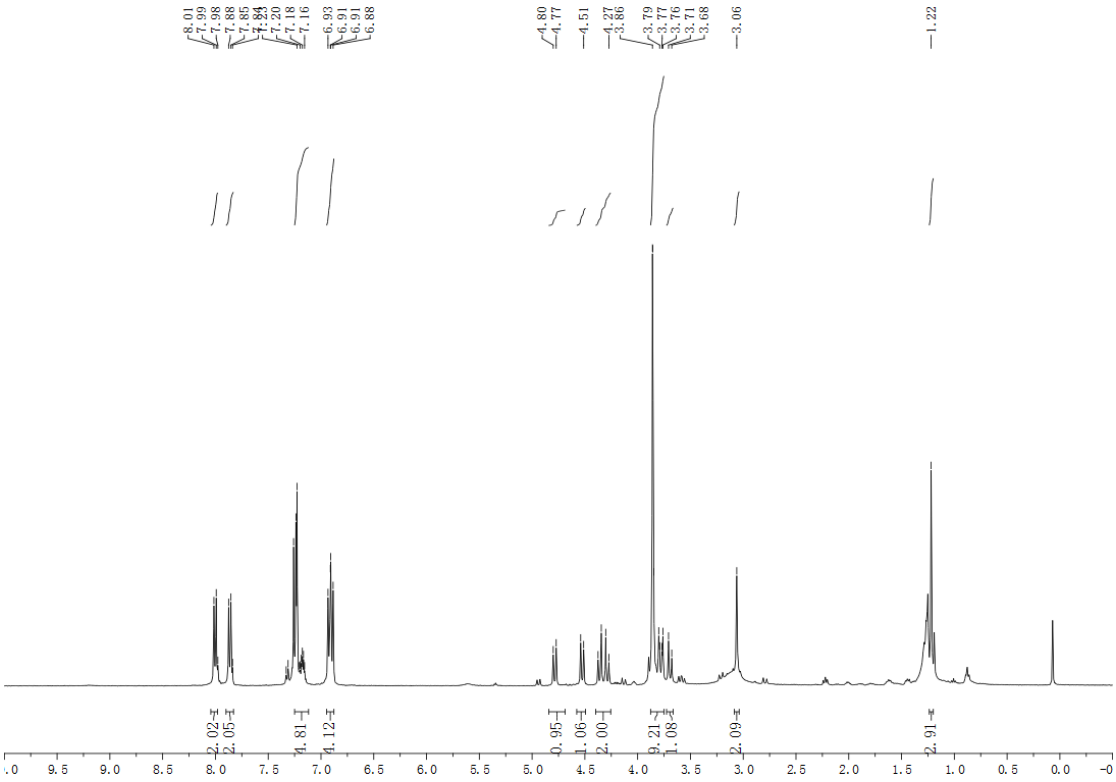
Detector A Ch1 254nm

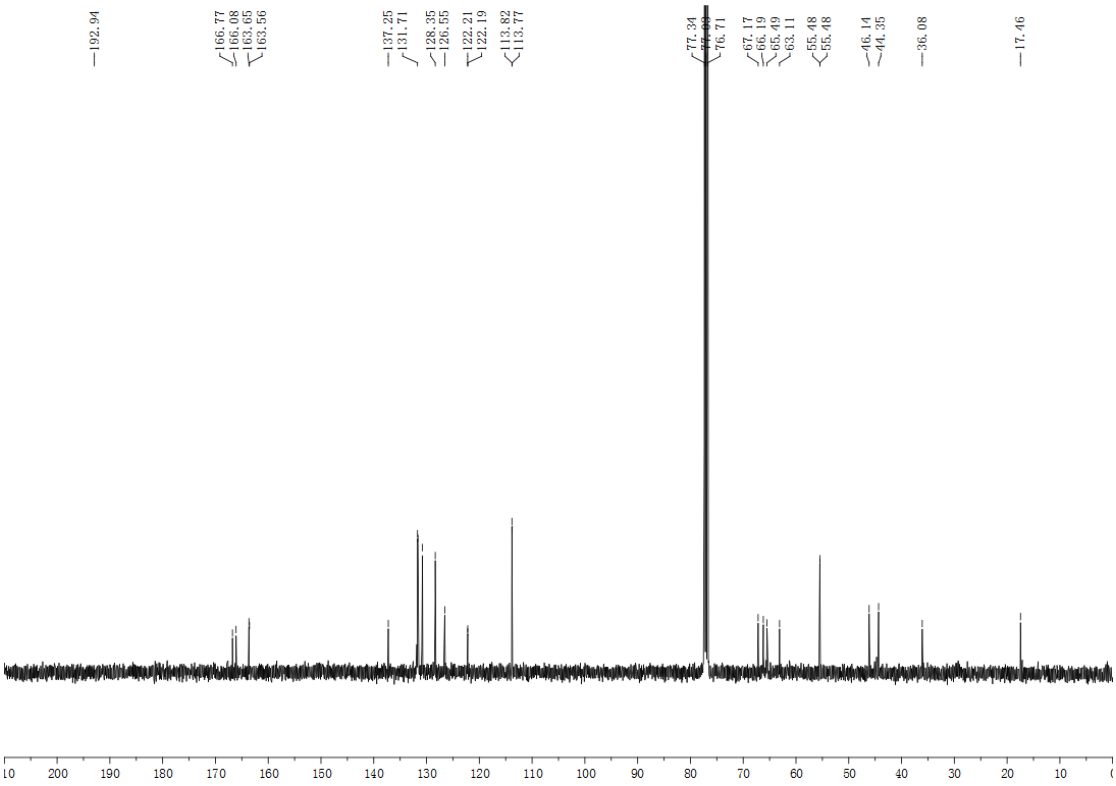
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.418	758817	18011	100.000	100.000
Total		758817	18011	100.000	100.000



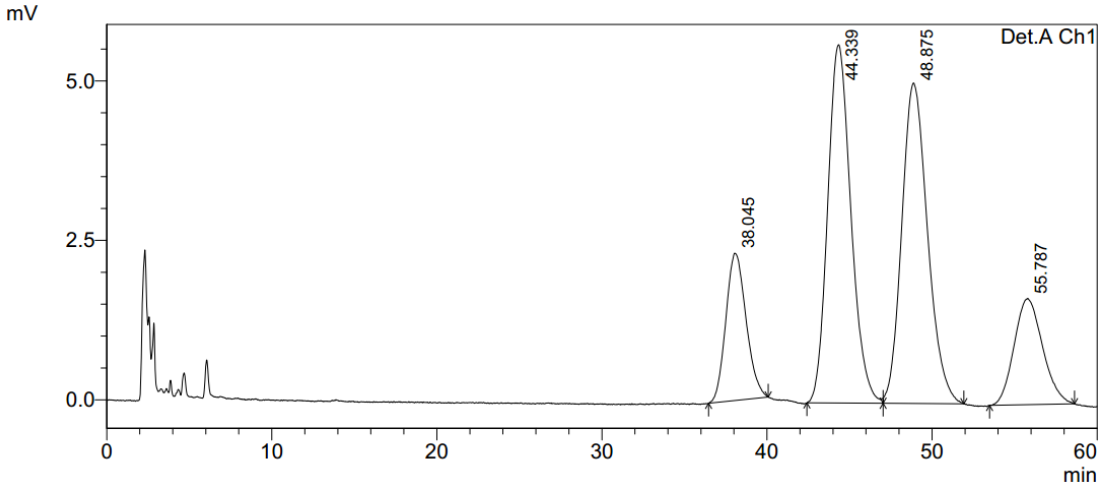
2i R_1=Bn, R_2=Me

^{1}H NMR and ^{13}C NMR of **2i**



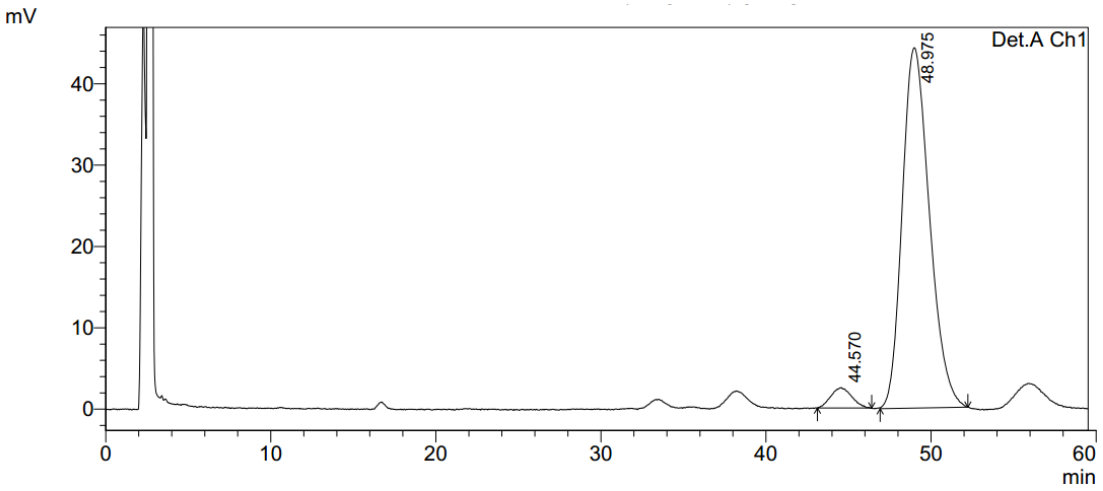


HPLC of **2i**



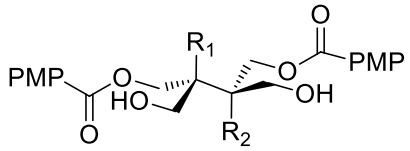
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	38.045	196757	2310	13.190	15.803
2	44.339	549111	5617	36.810	38.425
3	48.875	545979	5025	36.600	34.377
4	55.787	199894	1666	13.400	11.396
Total		1491740	14619	100.000	100.000



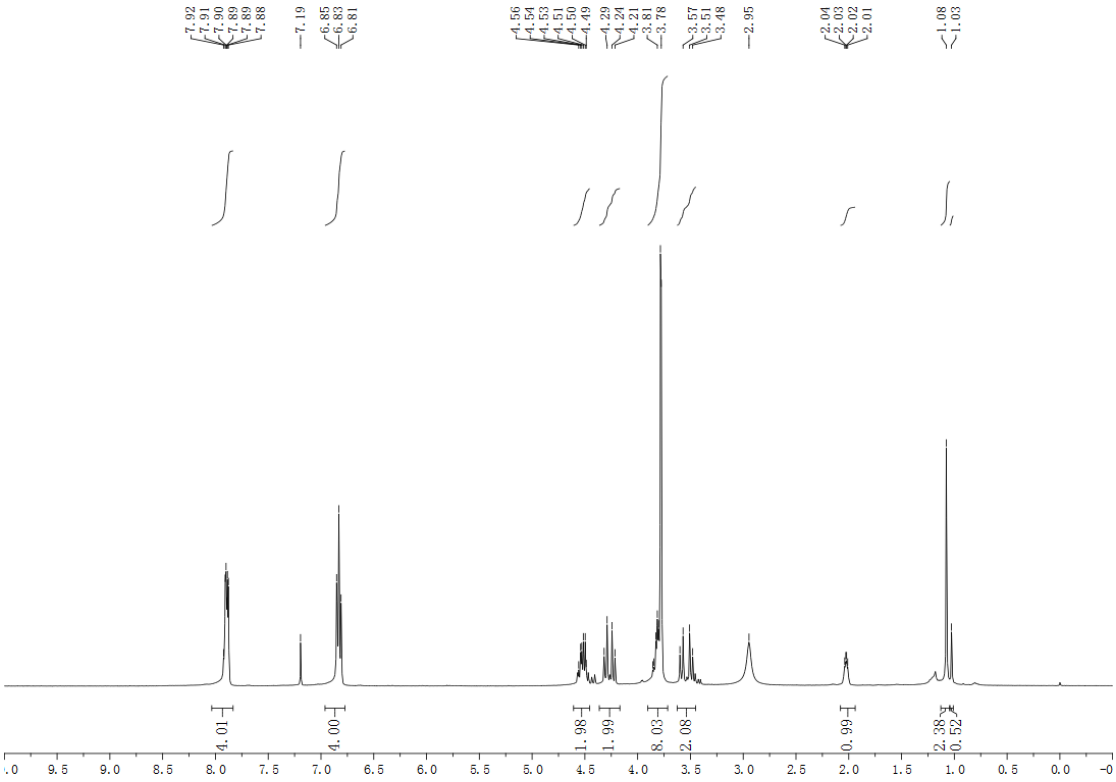
Detector A Ch1 254nm

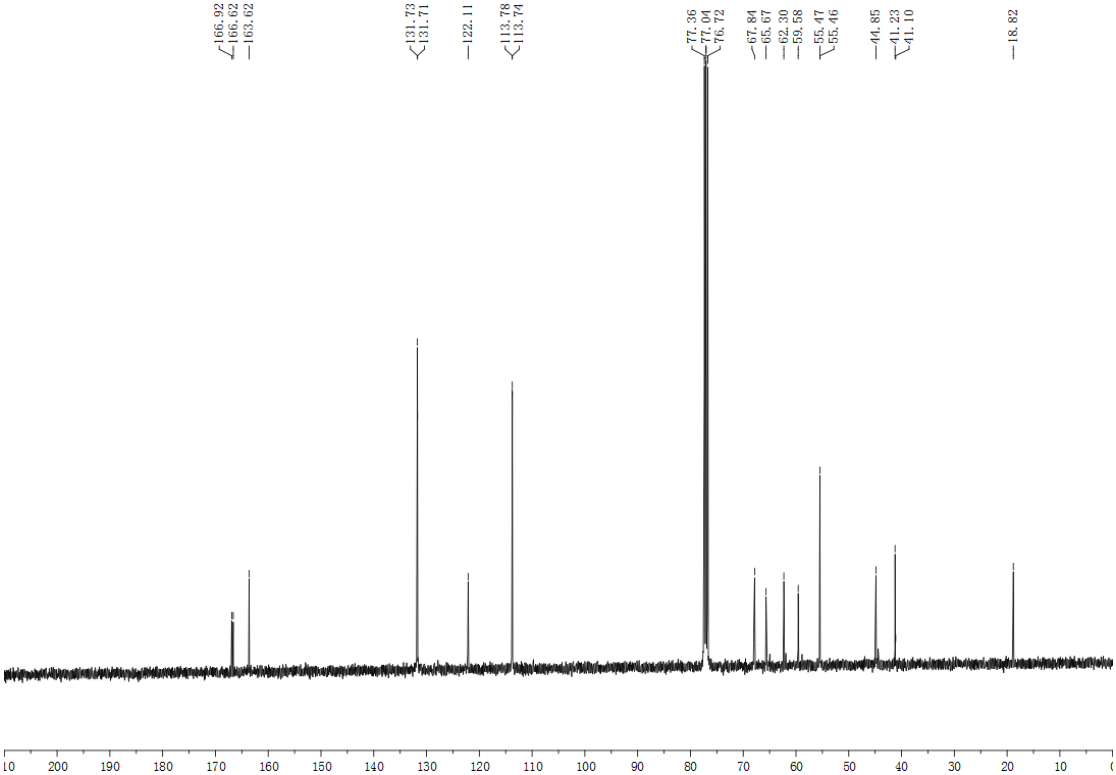
Peak#	Ret. Time	Area	Height	Area %	Height %
1	44.570	218229	2499	4.113	5.338
2	48.975	5087705	44314	95.887	94.662
Total		5305934	46813	100.000	100.000

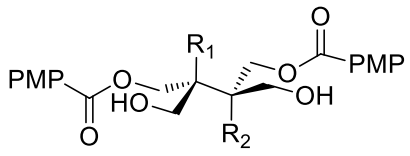


2l R_1=Me, R_2=H

^{1}H NMR and ^{13}C NMR of **2l**

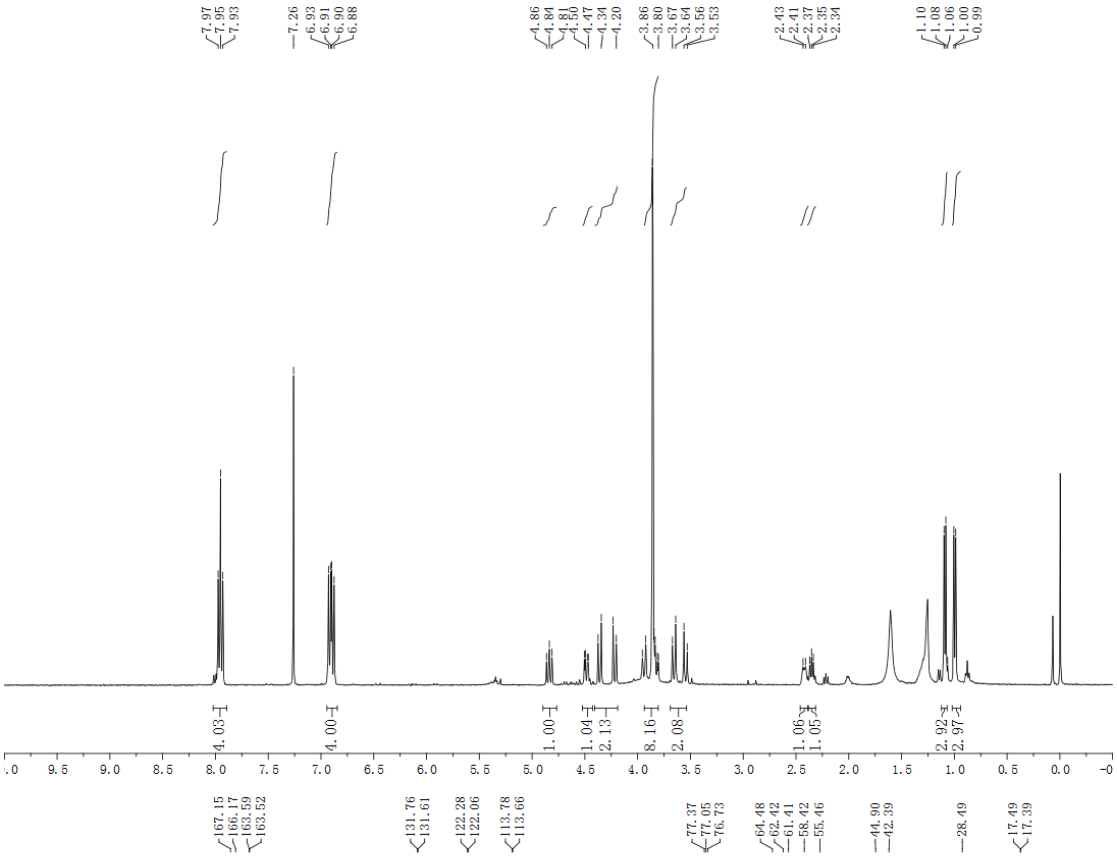


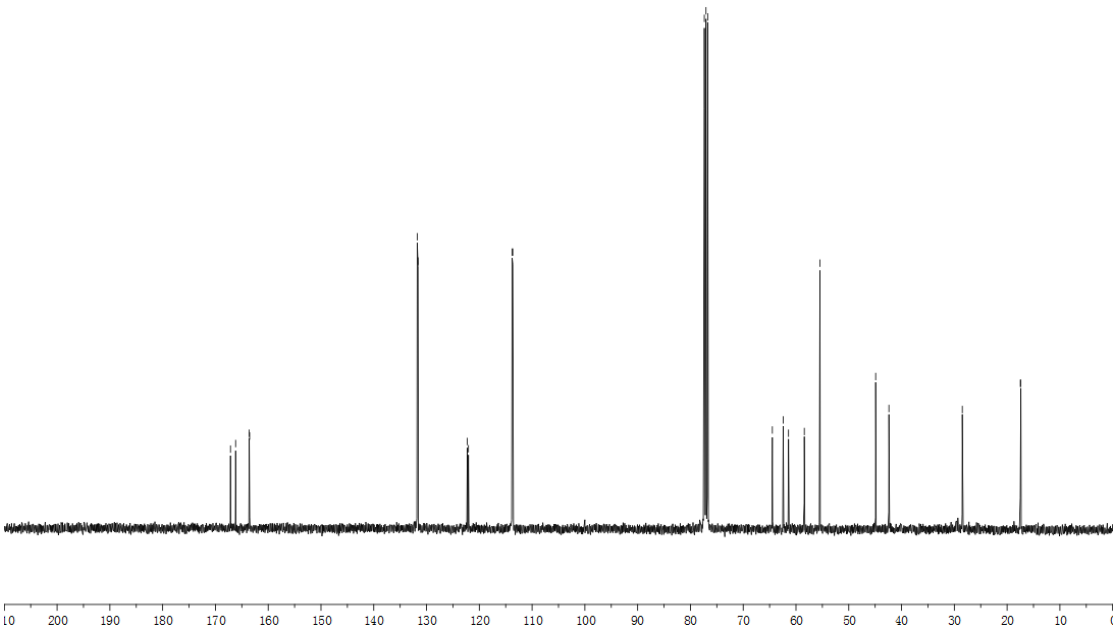




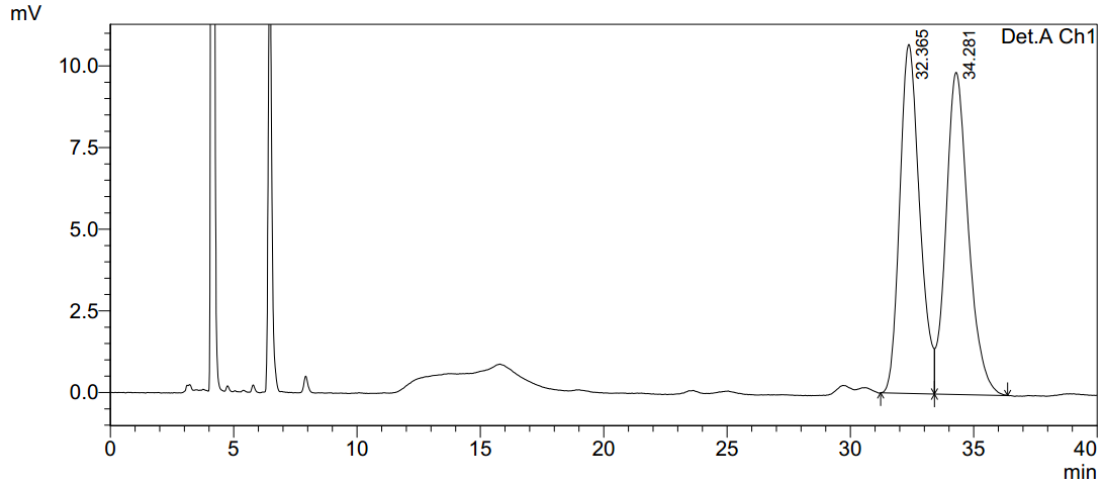
2m R_1=^{i}Pr, R_2=H

^{1}H NMR and ^{13}C NMR of **2m**



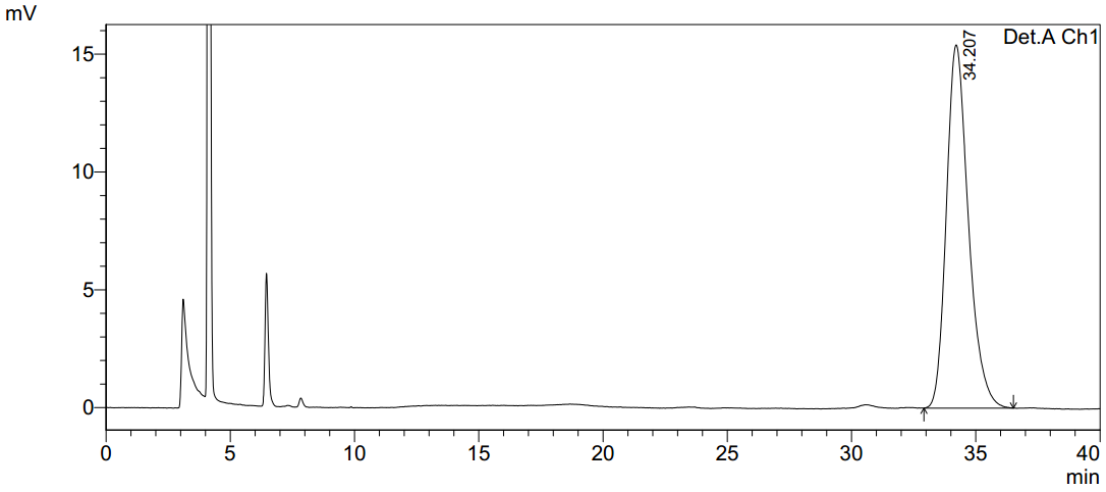


HPLC of **2m**



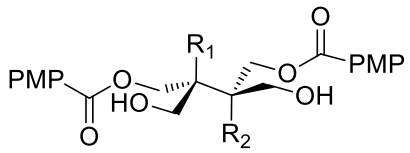
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.365	598535	10686	48.973	52.000
2	34.281	623631	9864	51.027	48.000
Total		1222167	20550	100.000	100.000



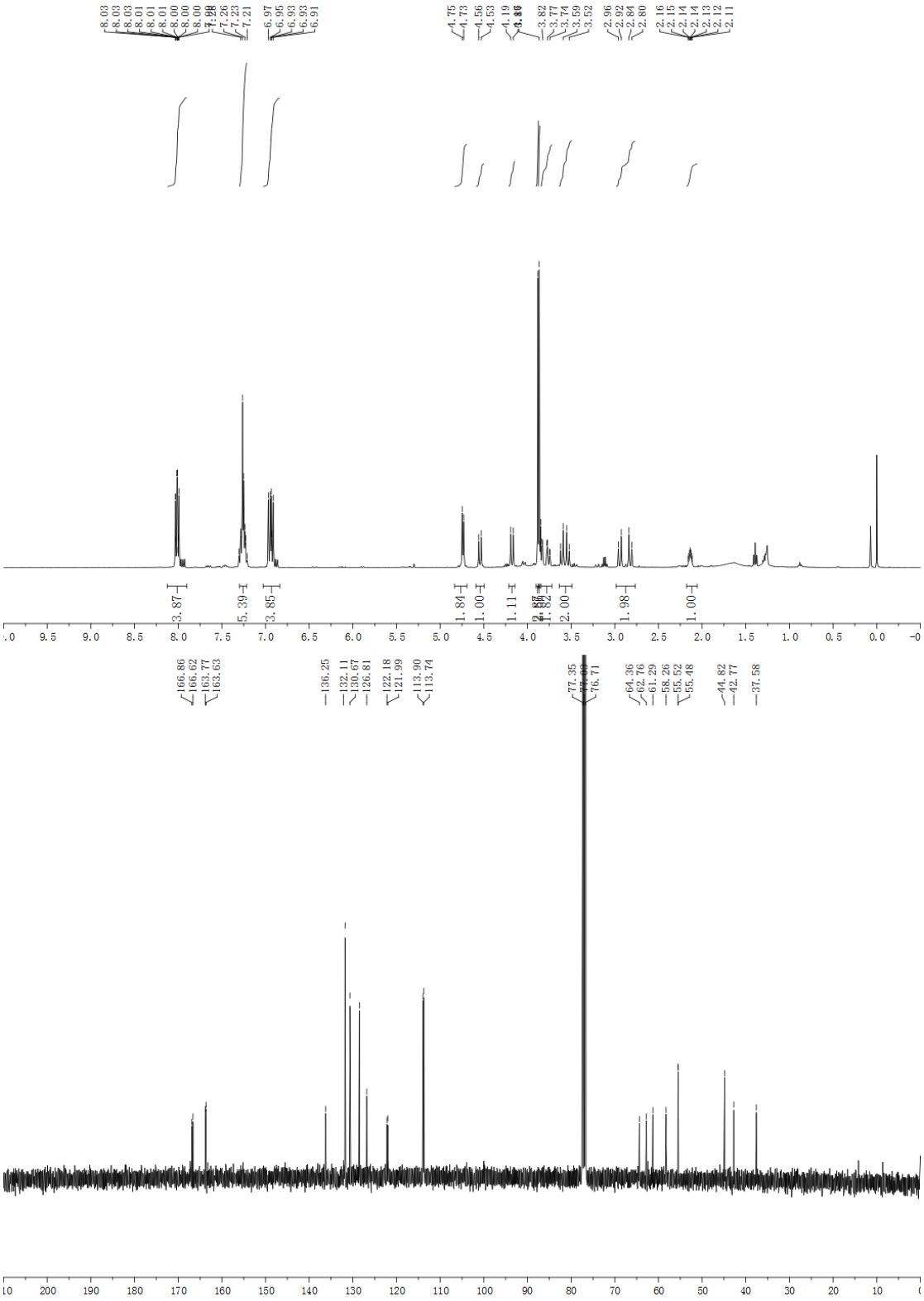
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.207	951128	15414	100.000	100.000
Total		951128	15414	100.000	100.000

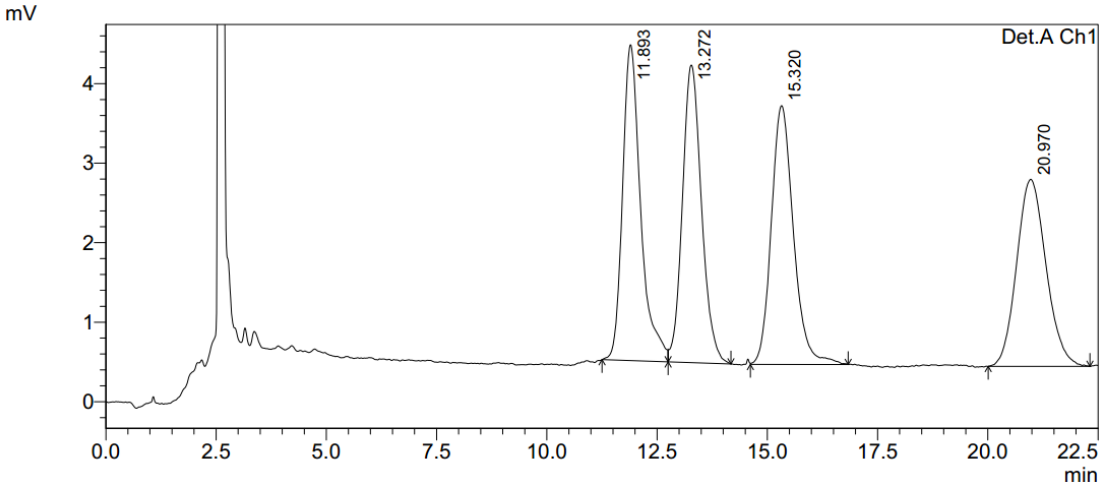


2n R_1=Bn, R_2=H

^{1}H NMR and ^{13}C NMR of **2n**

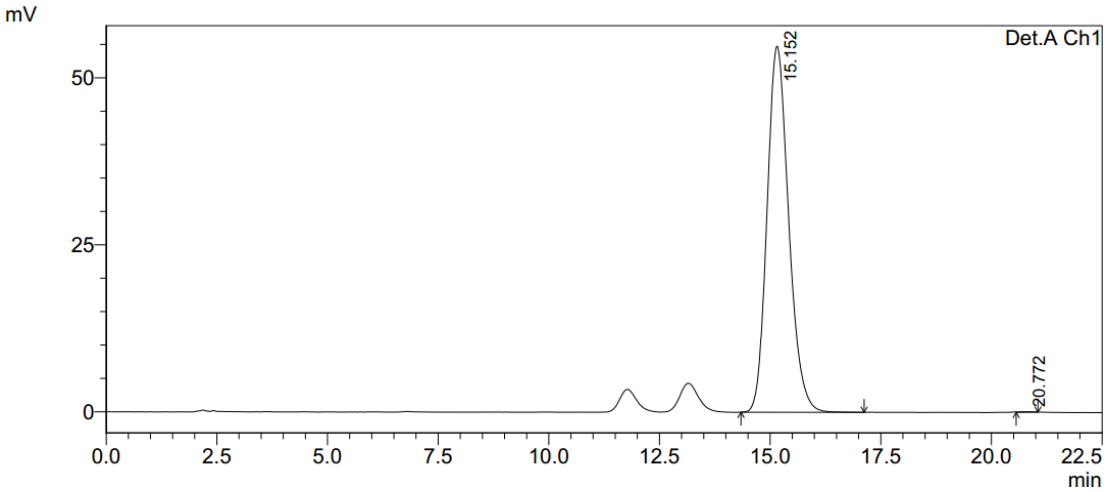


HPLC of **2n**



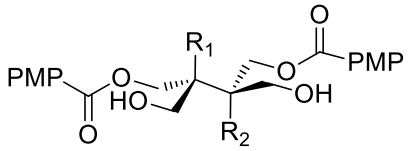
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.893	113228	3972	25.253	29.815
2	13.272	112738	3743	25.144	28.098
3	15.320	113406	3255	25.293	24.432
4	20.970	109003	2352	24.311	17.656
Total		448375	13321	100.000	100.000



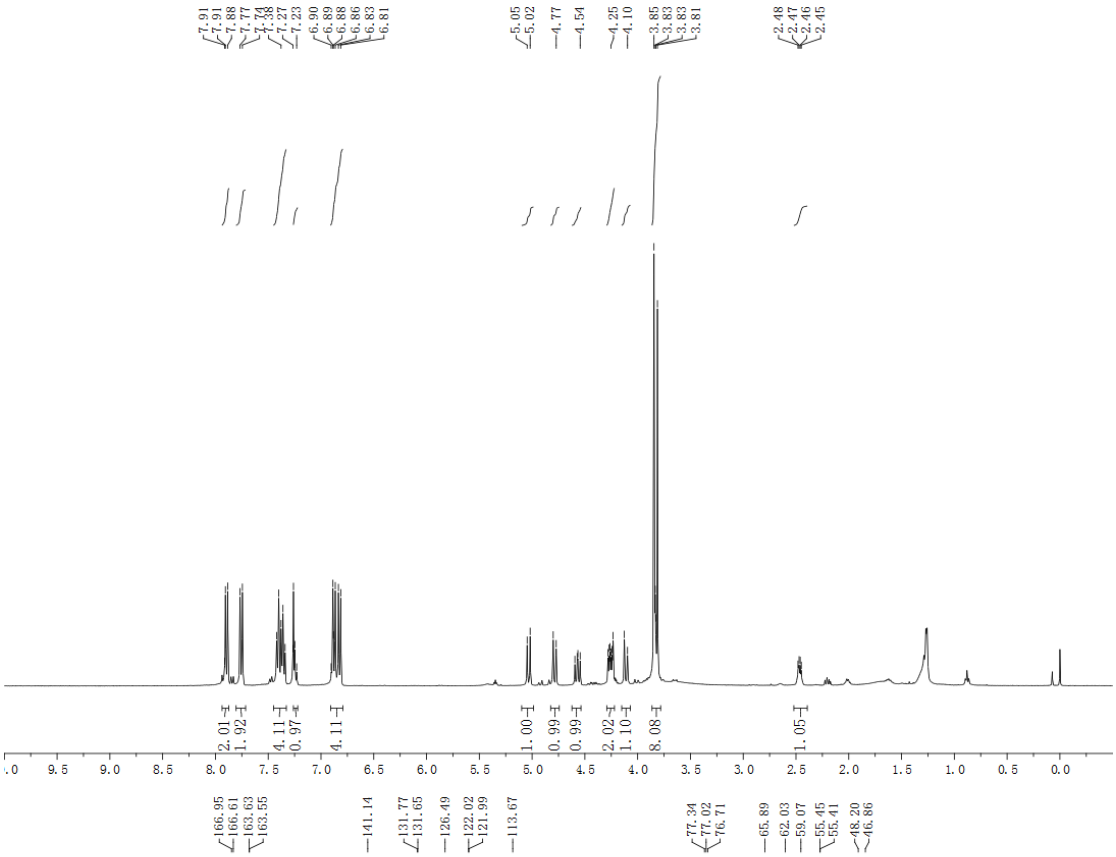
Detector A Ch1 254nm

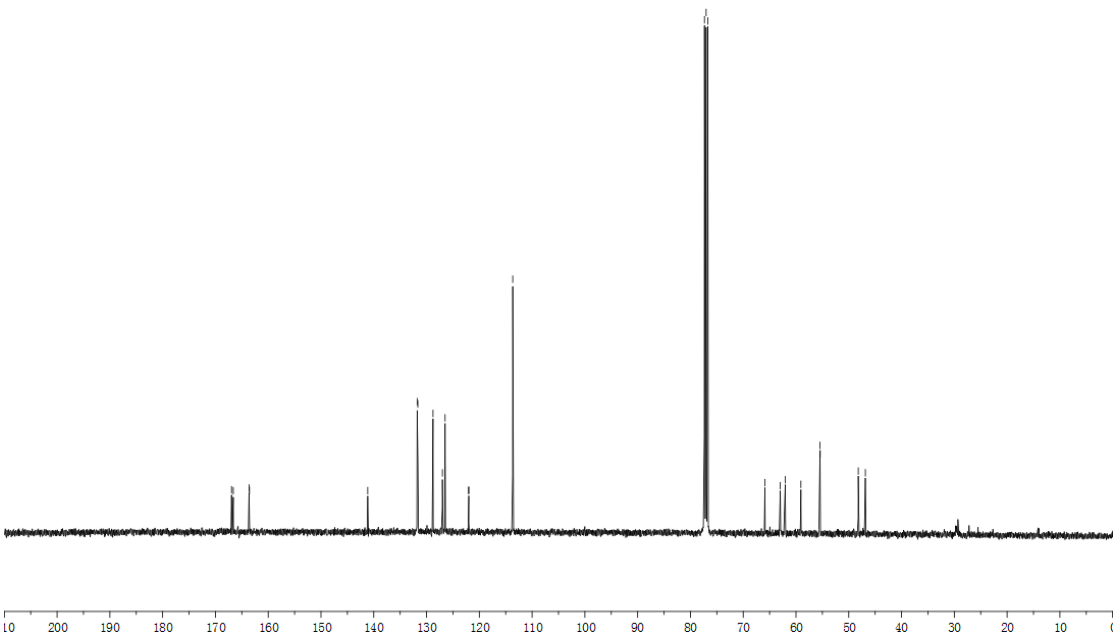
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.152	1861567	54828	99.900	99.852
2	20.772	1862	81	0.100	0.148
Total		1863429	54909	100.000	100.000



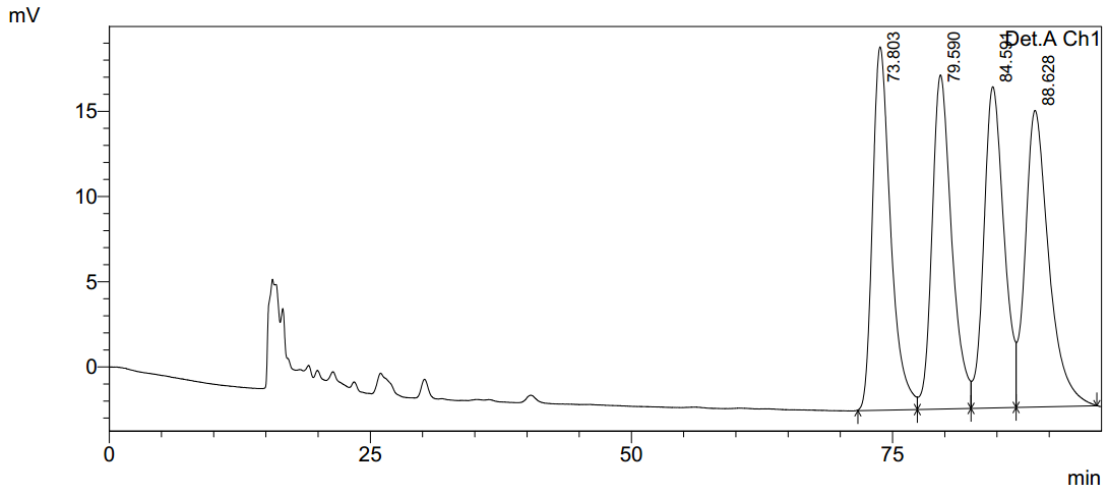
2o R_1=Ph, R_2=H

^{1}H NMR and ^{13}C NMR of **2o**



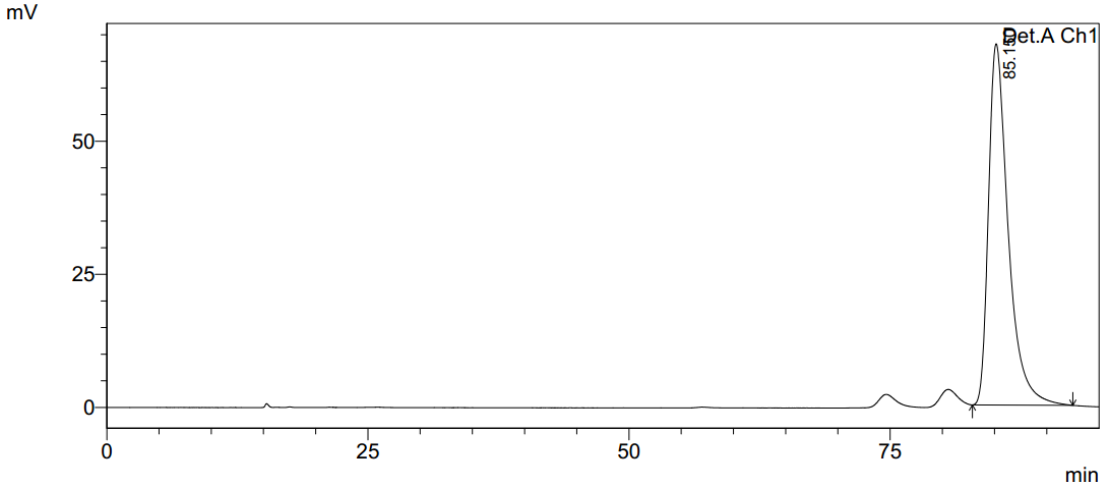


HPLC of **2o**



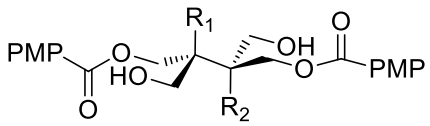
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	73.803	2576184	21325	24.748	27.634
2	79.590	2564243	19597	24.633	25.394
3	84.591	2528115	18847	24.286	24.423
4	88.628	2741120	17401	26.332	22.549
Total		10409662	77170	100.000	100.000



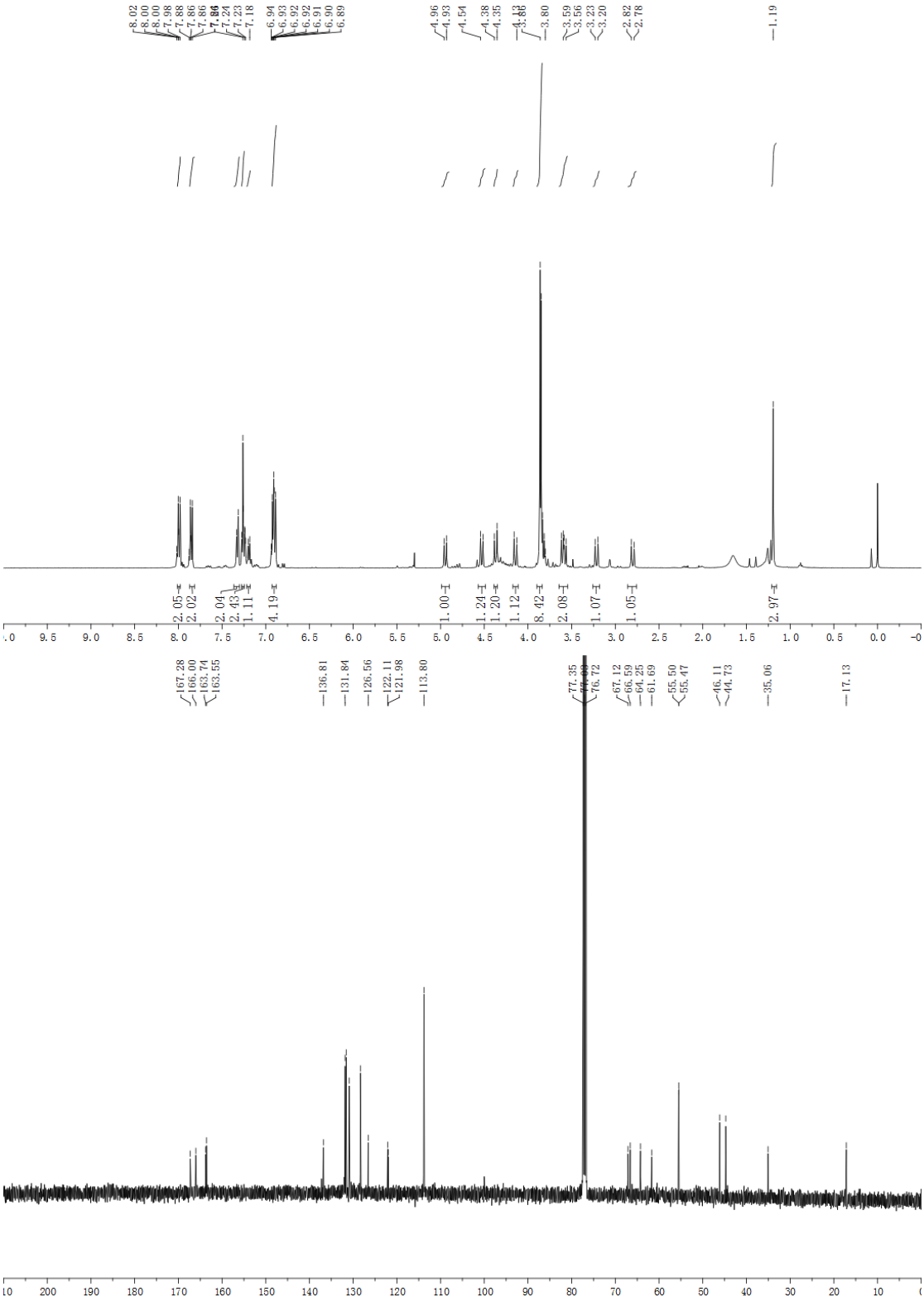
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	85.150	8894760	67852	100.000	100.000
Total		8894760	67852	100.000	100.000

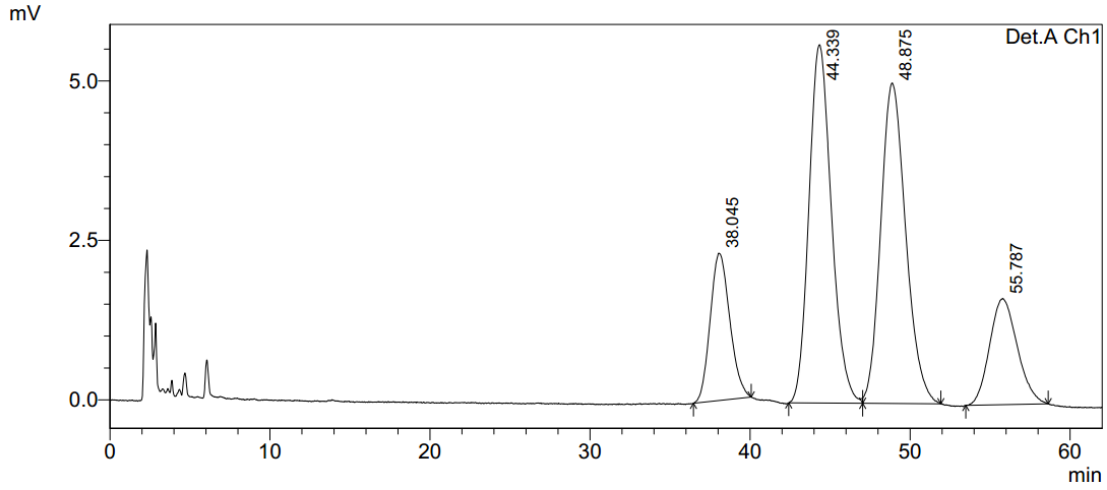


2j R_1=Me, R_2=Bn

^{1}H NMR and ^{13}C NMR of **2j**

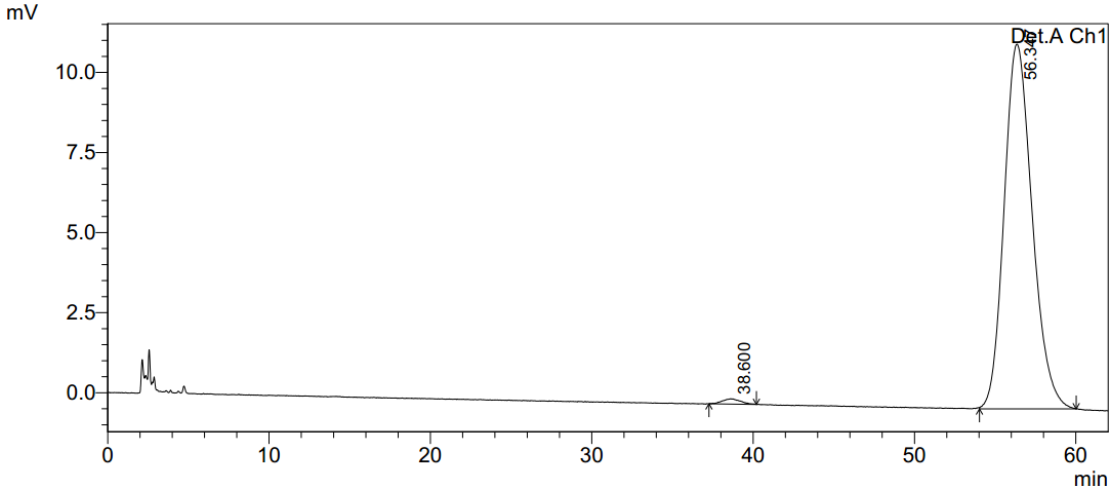


HPLC of **2j**



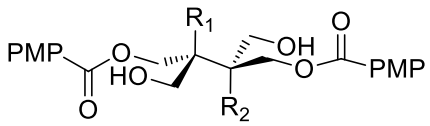
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	38.045	196757	2310	13.190	15.803
2	44.339	549111	5617	36.810	38.425
3	48.875	545979	5025	36.600	34.377
4	55.787	199894	1666	13.400	11.396
Total		1491740	14619	100.000	100.000



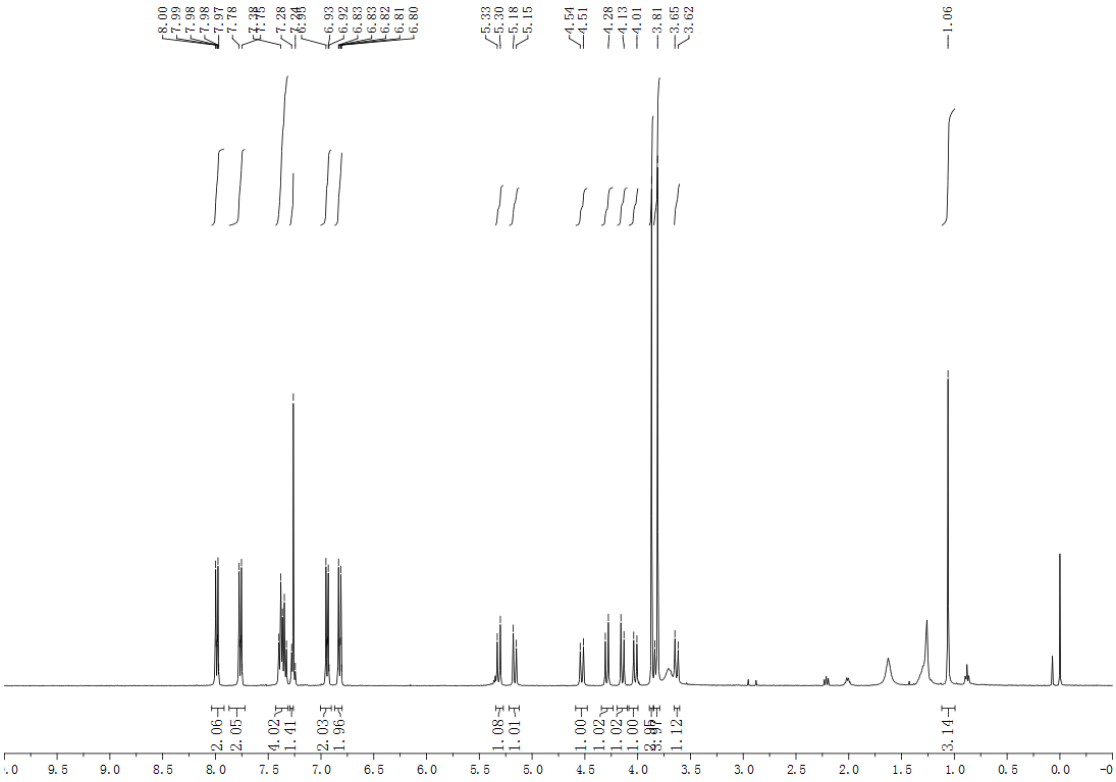
Detector A Ch1 254nm

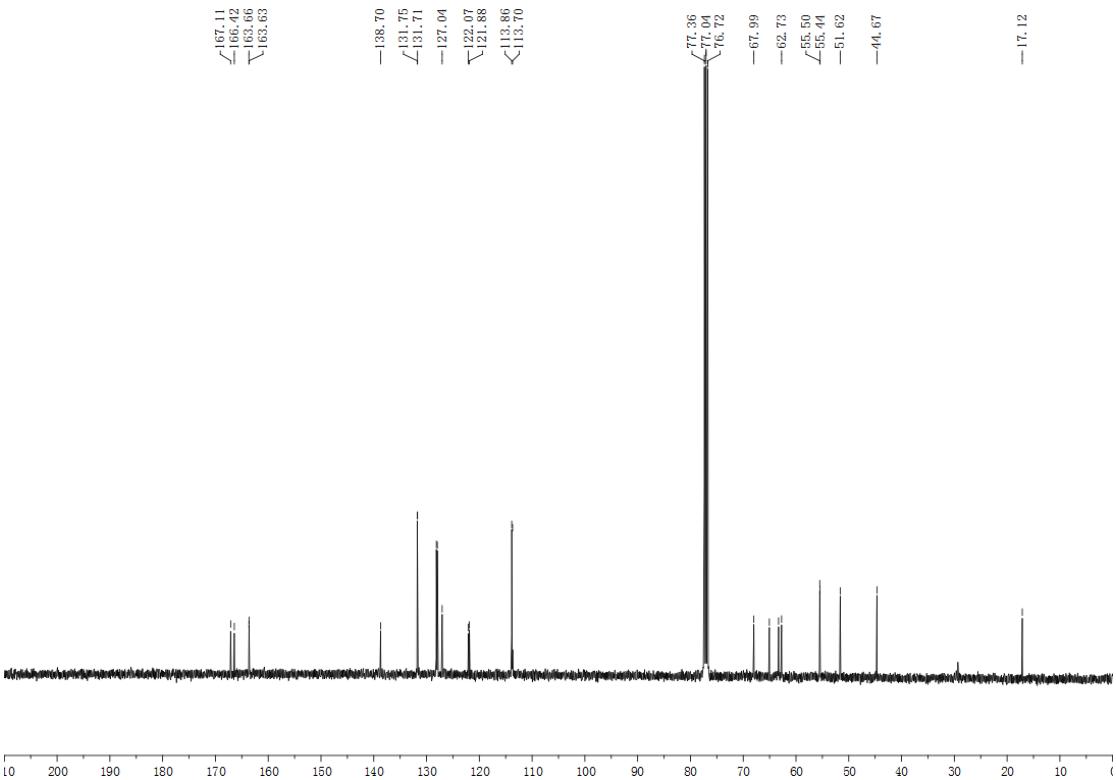
Peak#	Ret. Time	Area	Height	Area %	Height %
1	38.600	12937	166	0.931	1.441
2	56.347	1376357	11385	99.069	98.559
Total		1389294	11552	100.000	100.000



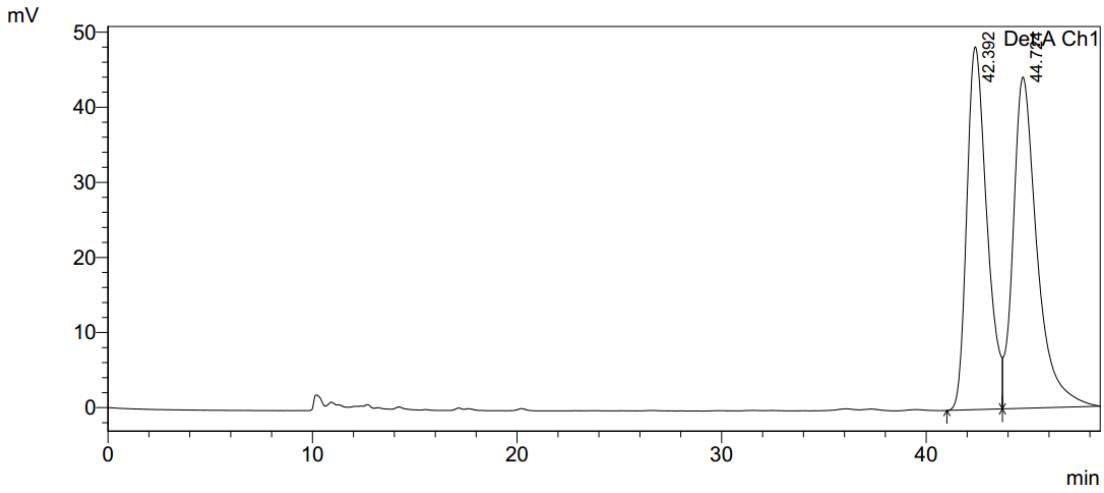
2k R_1=Me, R_2=Ph

^{1}H NMR and ^{13}C NMR of **2k**



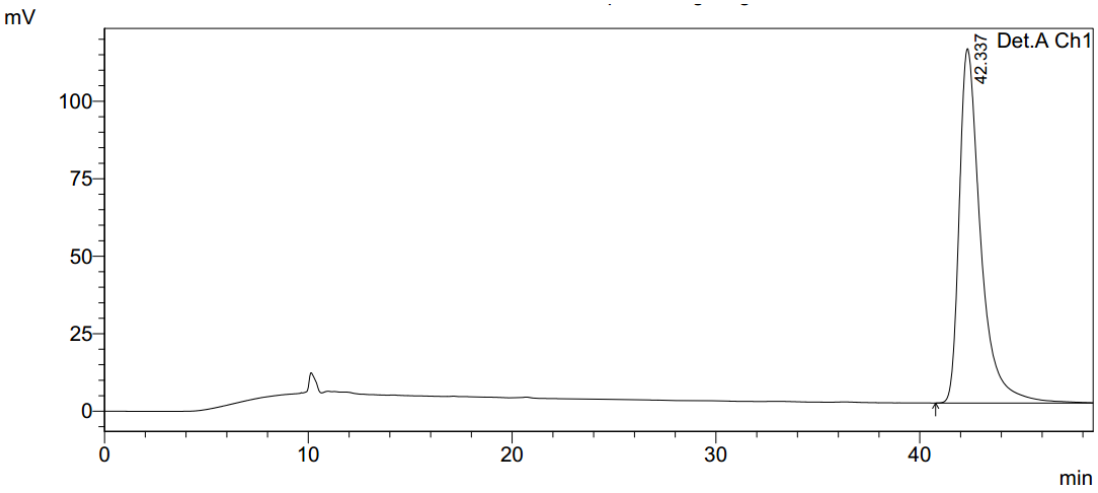


HPLC of **2k**



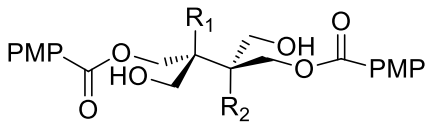
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	42.392	3291141	48311	47.824	52.270
2	44.724	3590635	44114	52.176	47.730
Total		6881776	92425	100.000	100.000



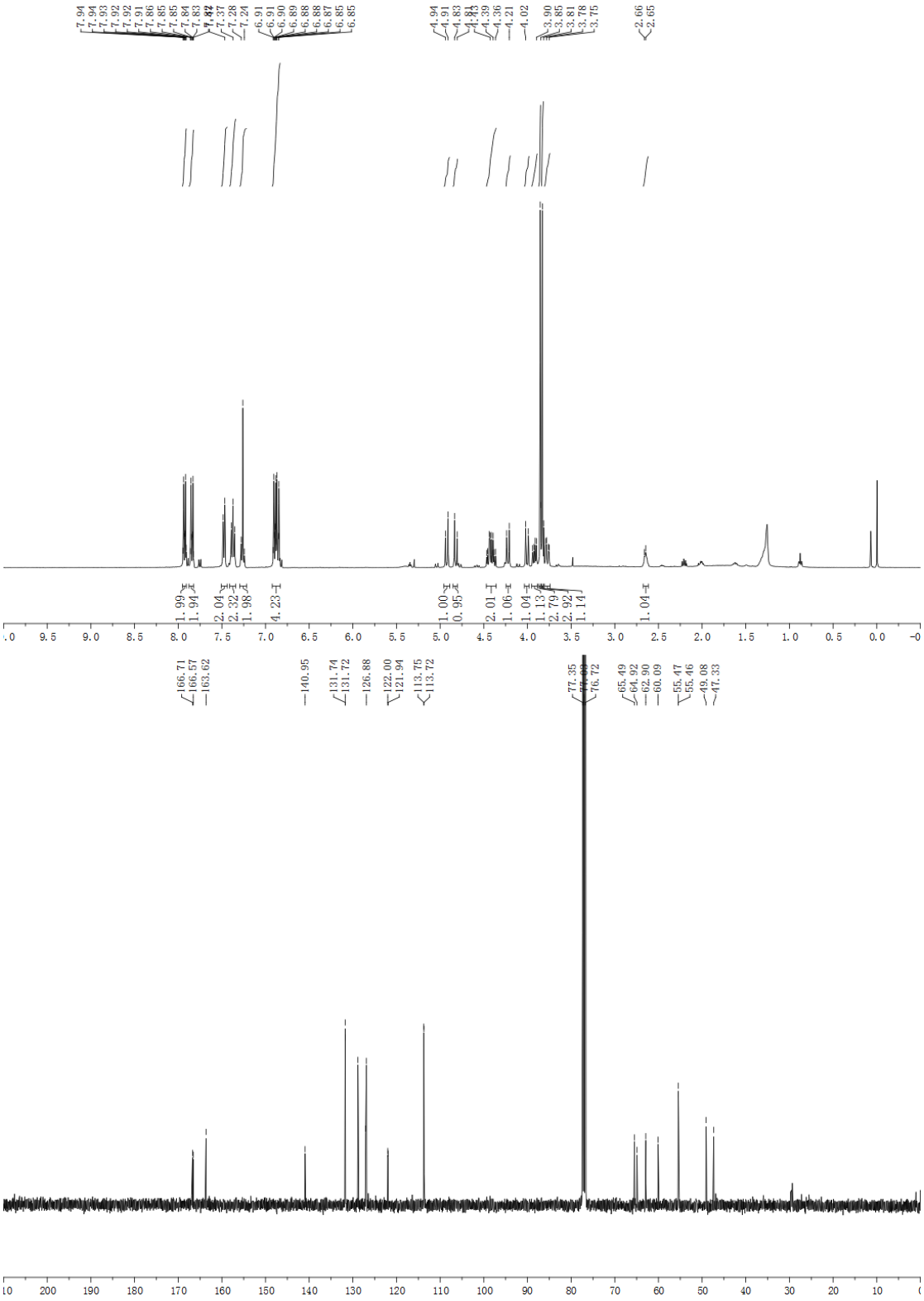
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	42.337	8319933	114302	100.000	100.000
Total		8319933	114302	100.000	100.000

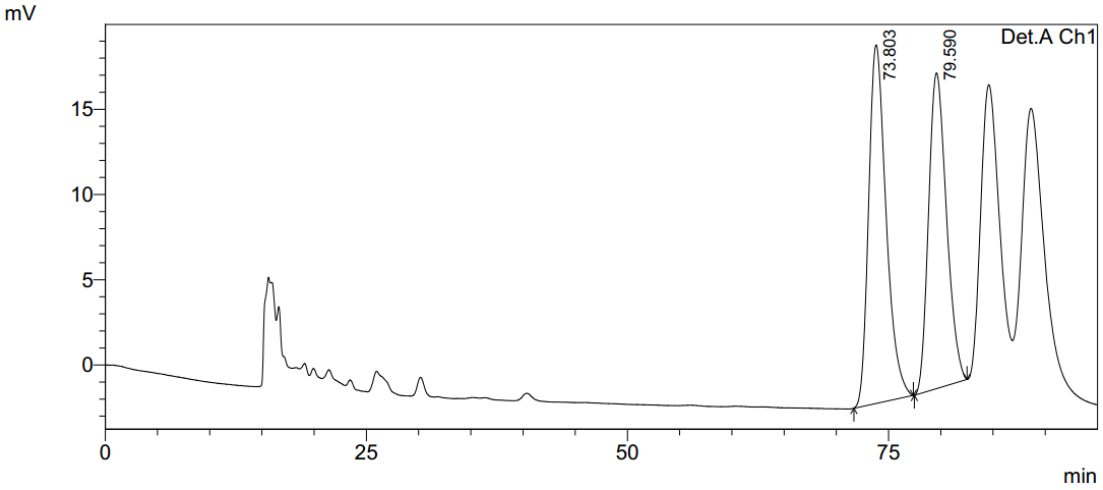


2p R_1=H, R_2=Ph

^{1}H NMR and ^{13}C NMR of **2p**

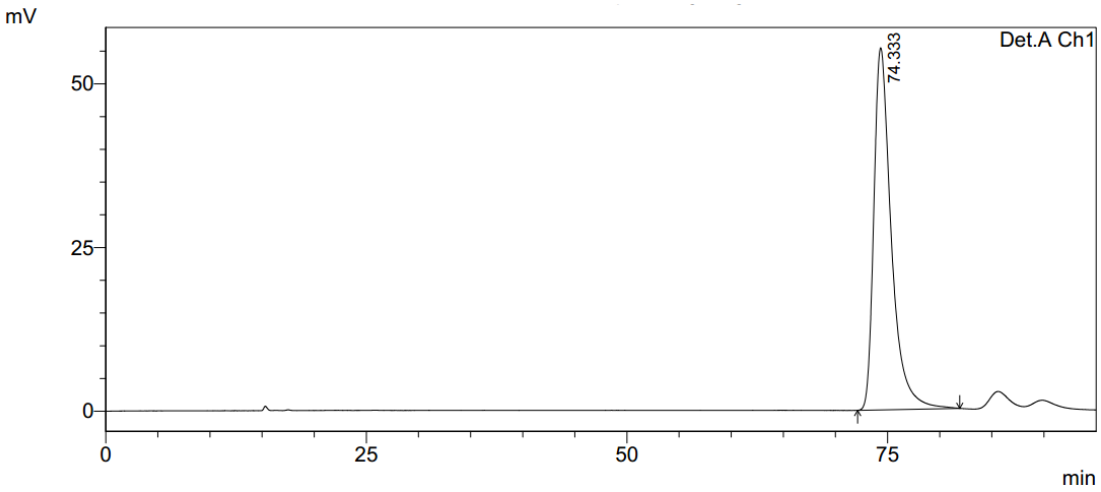


HPLC of **2p**



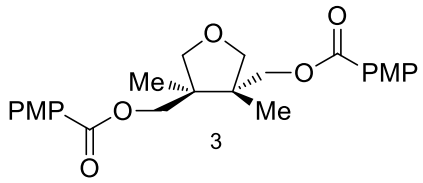
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	73.803	2449192	21041	52.554	53.194
2	79.590	2211167	18514	47.446	46.806
Total		4660358	39555	100.000	100.000



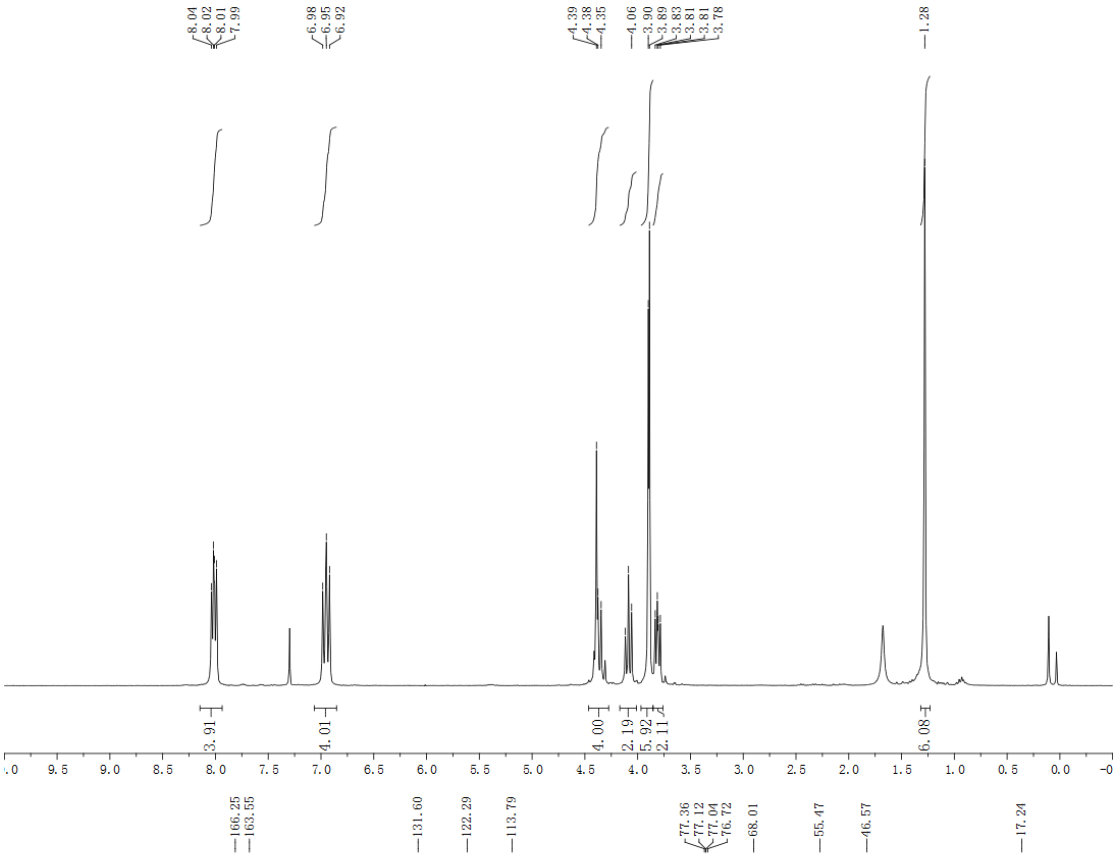
Detector A Ch1 254nm

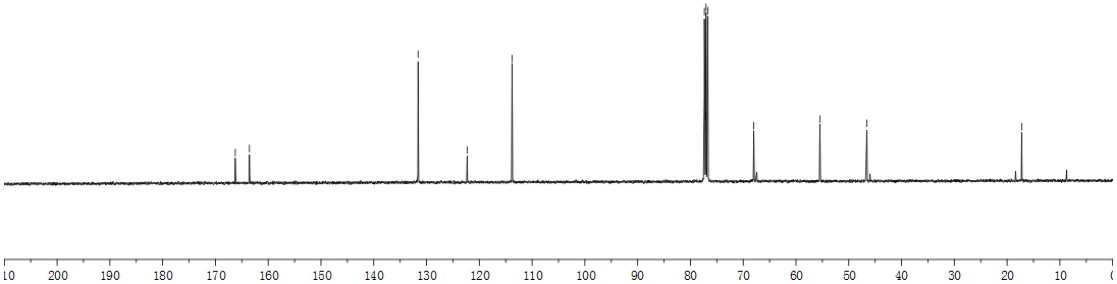
Peak#	Ret. Time	Area	Height	Area %	Height %
1	74.333	6447149	55326	100.000	100.000
Total		6447149	55326	100.000	100.000

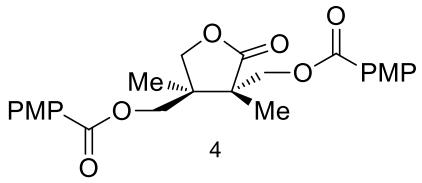


3

^{1}H NMR and ^{13}C NMR of **3**

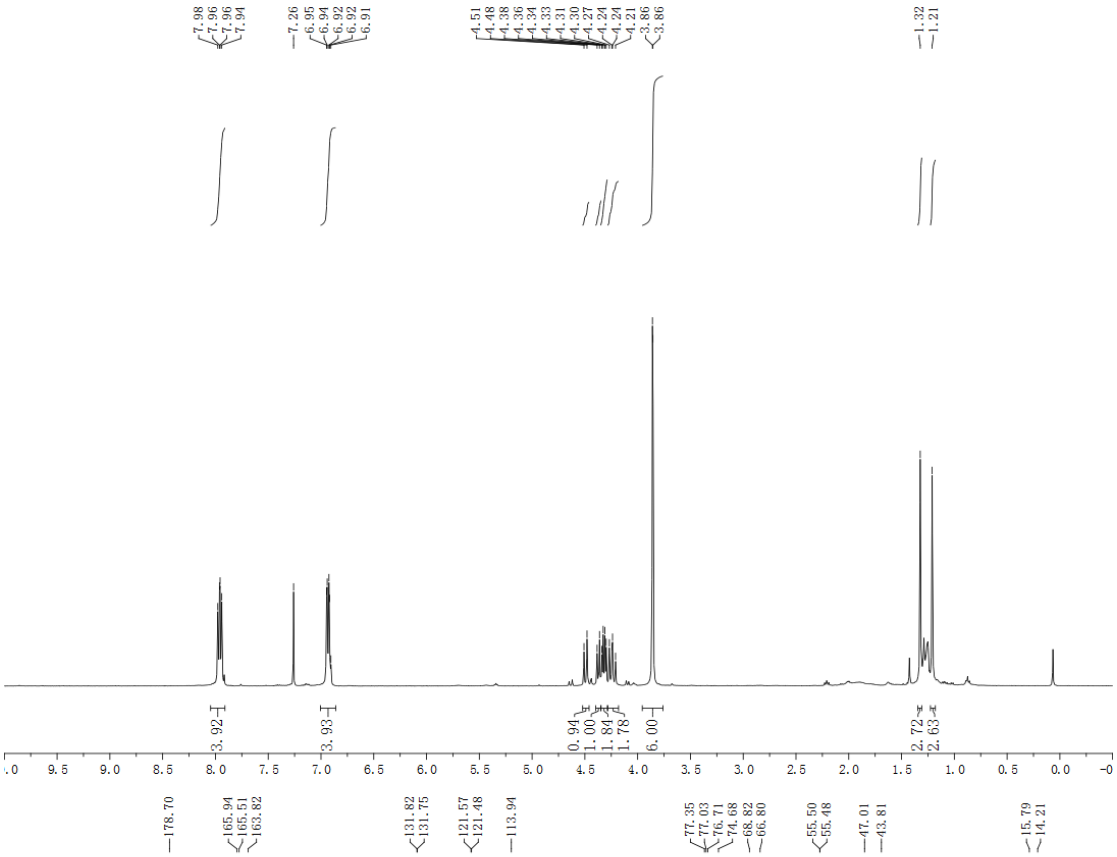


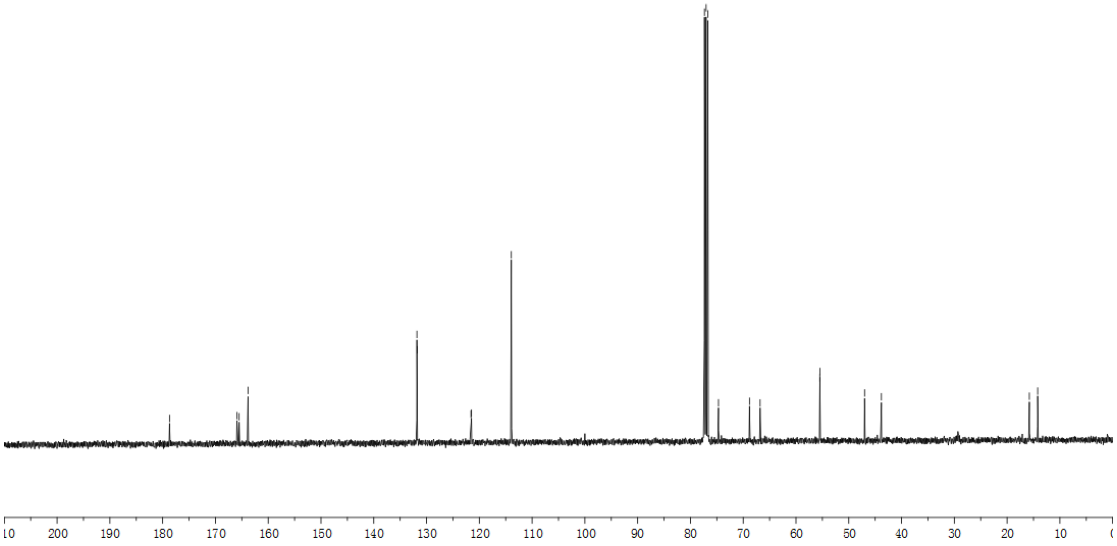


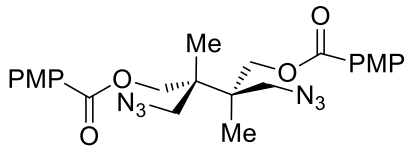


4

^{1}H NMR and ^{13}C NMR of **4**

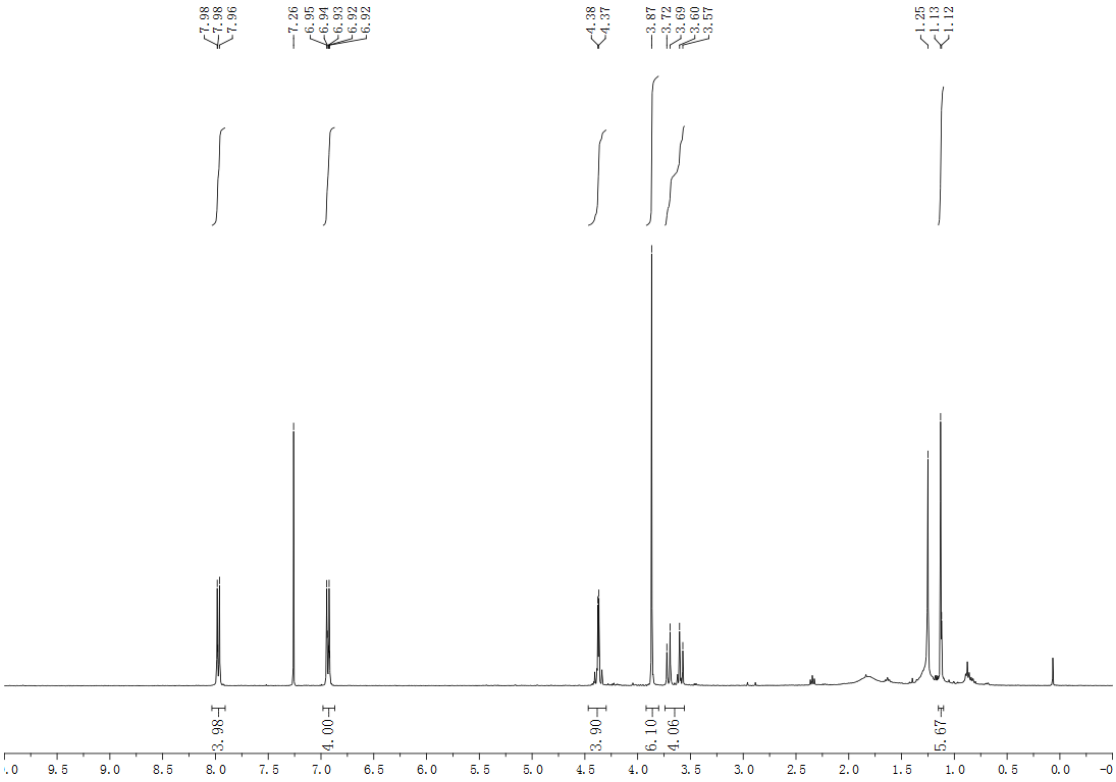


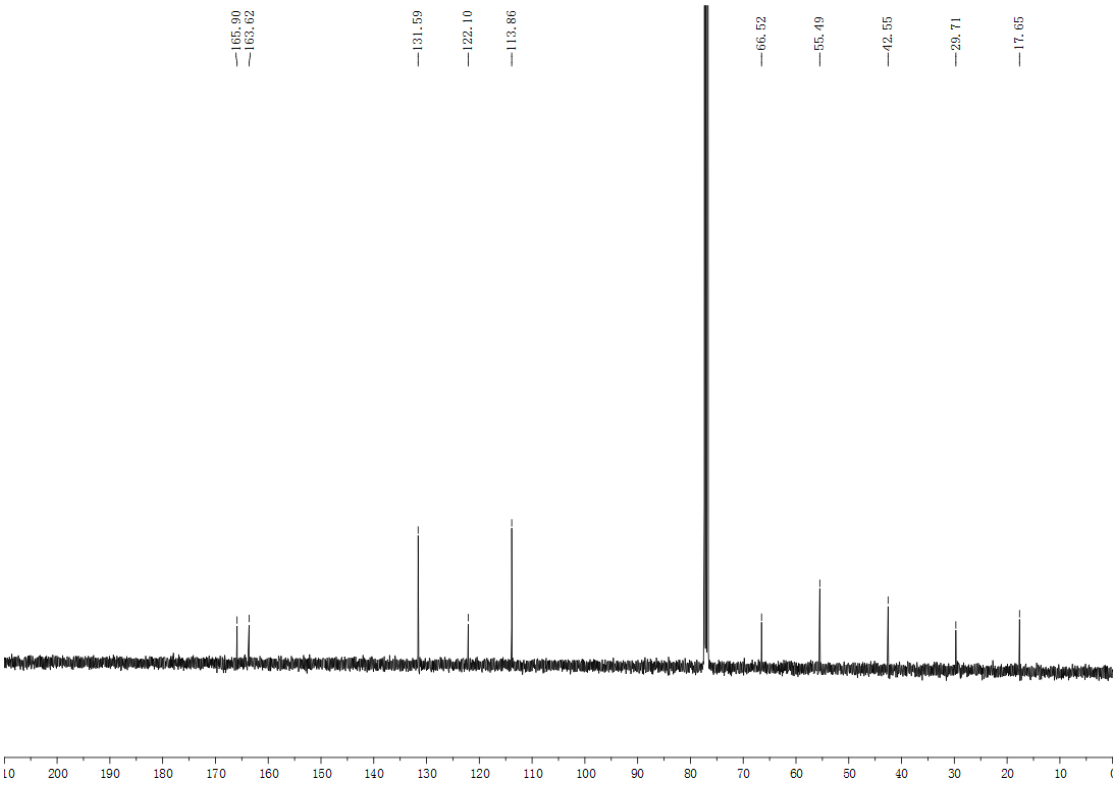


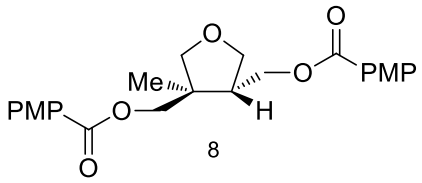


5

^{1}H NMR and ^{13}C NMR of **5**

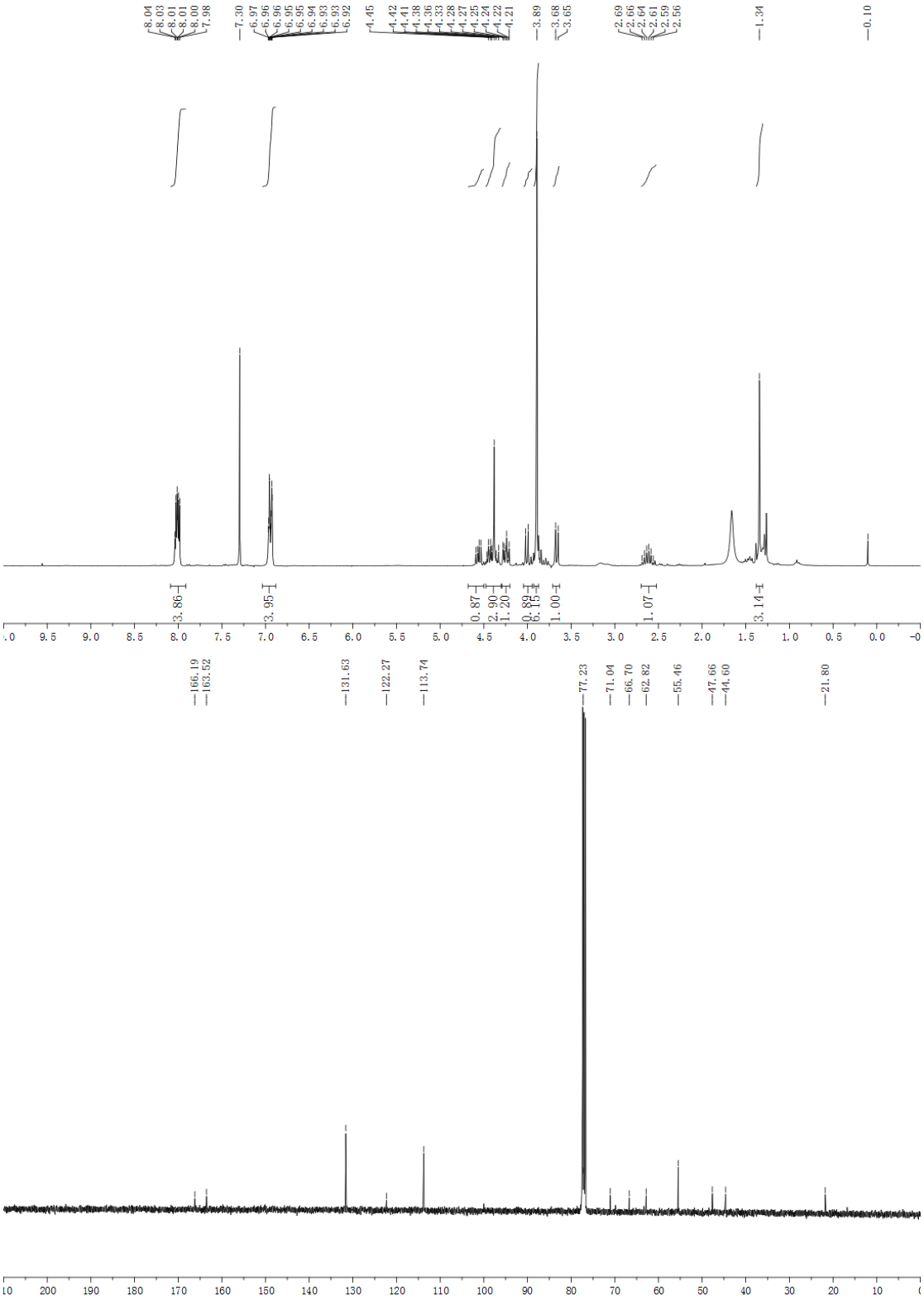




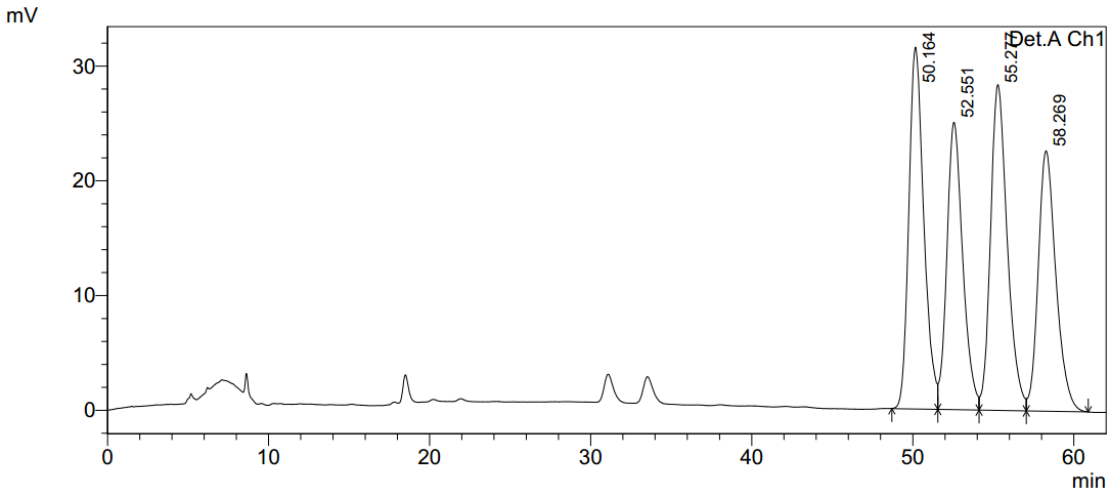


8

^{1}H NMR and ^{13}C NMR of **8**

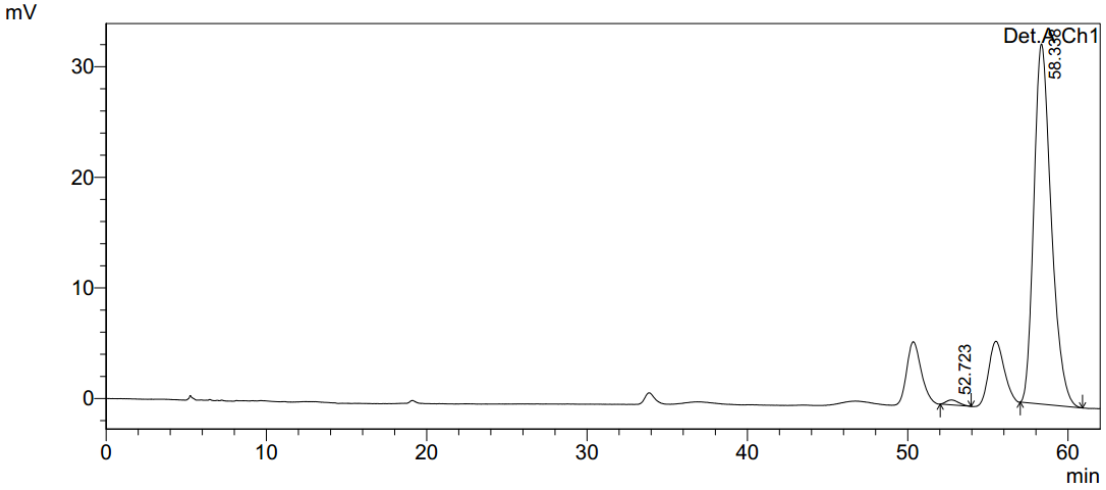


HPLC of **8**



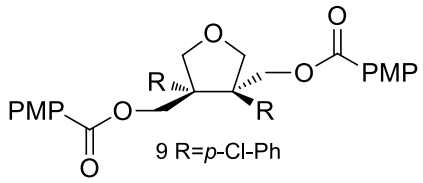
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	50.164	2034234	31542	26.961	29.295
2	52.551	1719091	25043	22.784	23.258
3	55.277	2057640	28388	27.271	26.365
4	58.269	1734157	22700	22.984	21.082
Total		7545123	107673	100.000	100.000

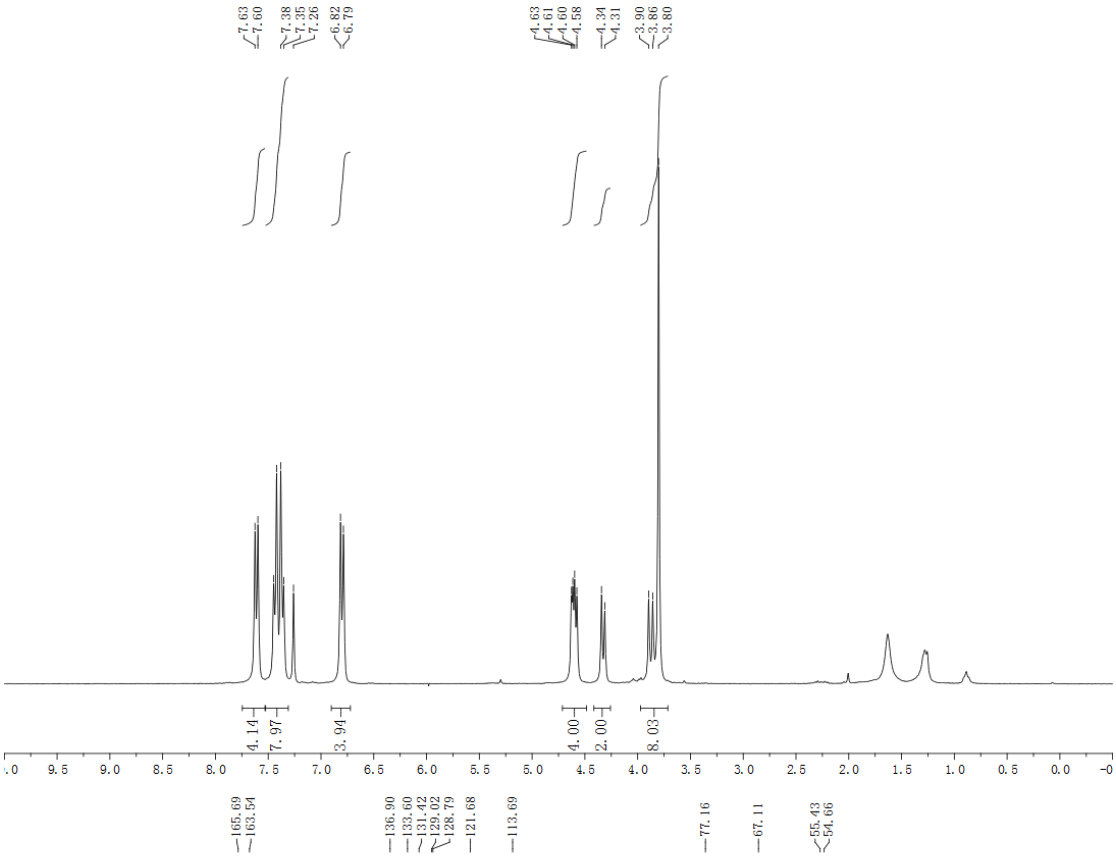


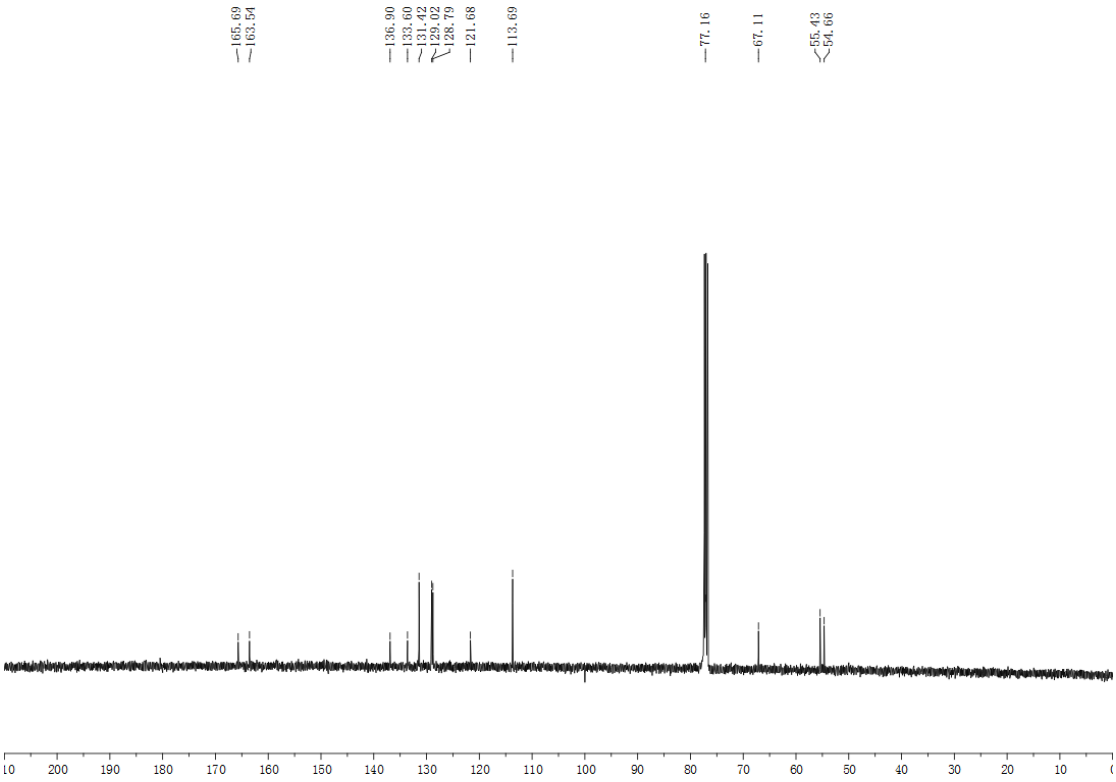
Detector A Ch1 254nm

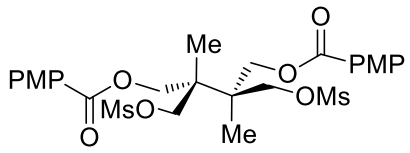
Peak#	Ret. Time	Area	Height	Area %	Height %
1	52.723	24141	451	0.975	1.365
2	58.338	2450693	32556	99.025	98.635
Total		2474834	33006	100.000	100.000



^{1}H NMR and ^{13}C NMR of **9**







10

^{1}H NMR and ^{13}C NMR of **10**