Supplementary Information

Design of bifunctional quaternary phosphonium salt catalysts for CO_2 fixation reaction with epoxides under mild conditions

Shiyao Liu,[a] Naoki Suematsu,[a] Keiji Maruoka[b] and Seiji Shirakawa*[a]

[a]*Department of Environmental Science, Graduate School of Fisheries and Environmental Sciences, Nagasaki University, 1-14, Bunkyo-machi, Nagasaki 852-8521, Japan*

[b]*Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo, Kyoto 606-8502, Japan*

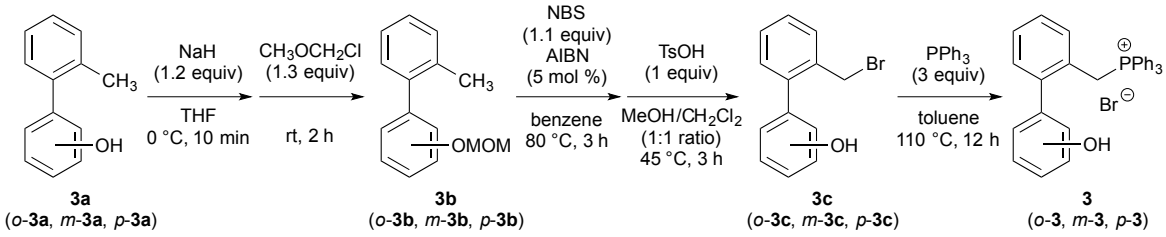
General Information

^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on a JEOL JNM-AL 400 NMR instrument (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, and 162 MHz for ^{31}P NMR). Tetramethylsilane (TMS) served as the internal standard (0 ppm) for ^{1}H NMR, and $CDCl_3$ served as the internal standard (77.0 ppm) for ^{13}C NMR. The following abbreviations were used to express the multiplicities: s = singlet; d = doublet; t = triplet; m = multiplet; br = broad. High-resolution mass spectra (HRMS) were measured on JEOL JMS-700N and JMS-700. Infrared spectra (IR) were measured on a JASCO FT/IR-4200 spectrometer. Optical rotations were measured on a JASCO P-2100 polarimeter. High performance liquid chromatography (HPLC) was performed on Shimadzu LC-20AT and SPD-20A instruments using Daicel Chiralpak AS-3 or ID-3 (4.6 mm × 250 mm) columns. All reactions were monitored by thin-layer chromatography using Merck precoated TLC plates (silica gel 60GF-254, 0.25 mm), with visualization by the use of UV lamp (254 nm), or dyes such as $KMnO_4$. The products were purified by flash column chromatography on silica gel. Dehydrated tetrahydrofuran was purchased from Kanto Chemical.

Experimental Section

1. Synthesis of Catalysts.

1-1. General Procedure for the Synthesis of Catalysts 3 (*o*-3, *m*-3, *p*-3).

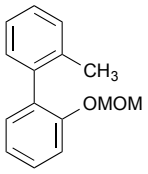


3a (*o*-**3a**, *m*-**3a**, *p*-**3a**) **3b** (*o*-**3b**, *m*-**3b**, *p*-**3b**) **3c** (*o*-**3c**, *m*-**3c**, *p*-**3c**) **3** (*o*-**3**, *m*-**3**, *p*-**3**)

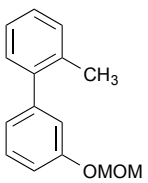
Compounds **3a** (*o*-**3a**, *m*-**3a**, *p*-**3a**) were prepared according to the literature.[1]

1-1-1. Synthesis of compounds 3b (*o*-3b, *m*-3b, *p*-3b).

To a solution of **3a** (8.0 mmol) in THF (15 mL) was added sodium hydride (9.6 mmol, 60% oil suspension) at 0 °C, and stirred for 10 min. To this reaction mixture was added chloromethyl methyl ether (10.4 mmol) at 0 °C, and then the solution was warmed to room temperature. After stirred for 2 h at room temperature, the mixture was quenched with saturated aqueous NH_4Cl. After evaporation to remove THF, organic compounds were extracted with ethyl acetate (15 mL x 3). The combined organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 100:1–30:1 as eluent) to afford **3b** (89–93% yields).

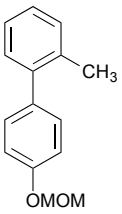


***o*-3b:** 91% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (dt, J = 2.0, 7.8 Hz, 1H), 7.14–7.28 (m, 6H), 7.07 (dt, J = 0.8, 7.2 Hz, 1H), 5.06 (s, 2H), 3.32 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4, 138.6, 136.7, 132.0, 131.1, 130.0, 129.5, 128.5, 127.2, 125.3, 121.9, 115.3, 94.9, 55.9, 20.0; IR (neat): 2953, 2927, 2901, 1479, 1223, 1195, 1151, 1077, 1011, 992, 921, 754, 743, 726 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{16}O_2$: 228.1150 ([M]$^+$), found 228.1151.



***m*-3b:** 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (t, J = 7.6 Hz, 1H), 7.22–7.26 (m, 4H), 6.96–7.04 (m, 3H), 5.20 (s, 2H), 3.50 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.0, 143.4, 141.6, 135.2, 130.3, 129.6,

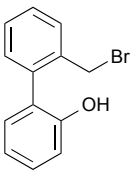
129.0, 127.3, 125.7, 122.8, 117.3, 114.5, 94.5, 55.9, 20.4; IR (neat): 2953, 2930, 2899, 1599, 1581, 1476, 1182, 1150, 1078, 1037, 1006, 989, 922, 756, 727, 703 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{17}O_2$: 229.1229 ($[M+H]^+$), found 229.1227.



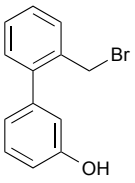
***p*-3b:** 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20–7.27 (m, 6H), 7.08 (d, J = 8.8 Hz, 2H), 5.22 (s, 2H), 3.52 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.2, 141.4, 135.5, 135.4, 130.24, 130.22, 129.8, 127.0, 125.7, 115.8, 94.5, 56.0, 20.5; IR (neat): 2952, 2929, 2898, 1611, 1514, 1482, 1230, 1150, 1077, 1010, 994, 836, 761, 731 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{17}O_2$: 229.1229 ($[M+H]^+$), found 229.1230.

1-1-2. Synthesis of compounds 3c (*o*-3c, *m*-3c, *p*-3c).

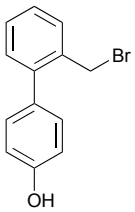
A mixture of **3b** (5.0 mmol), *N*-bromosuccinimide (NBS) (5.5 mmol), and 2,2'-azobis(isobutyronitrile) (AIBN) (0.25 mmol) in benzene (20 mL) was heated at 80 °C for 3 h. After cooled to room temperature, water was added to this reaction mixture. Organic compounds were extracted with ethyl acetate (10 mL x 3). The combined organic layer was dried over Na_2SO_4 and concentrated. The residue was then dissolved in a combined solvent of dichloromethane (5 mL) and methanol (5 mL). To this solution was added *p*-toluenesulfonic acid monohydrate (5.0 mmol), and the mixture was heated at 45 °C for 3 h. After cooled to room temperature, water was added to this reaction mixture and the mixture was evaporated to remove methanol. Organic compounds were extracted with dichloromethane (10 mL x 3). The combined organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 30:1–10:1 as eluent) to afford **3c** (73–76% yields).



***o*-3c:** 76% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (dd, J = 2.0, 7.6 Hz, 1H), 7.38–7.46 (m, 2H), 7.26–7.35 (m, 2H), 7.22 (dd, J = 1.6, 8.0 Hz, 1H), 7.00–7.04 (m, 2H), 4.70 (s, 1H), 4.44 (d, J = 10.0 Hz, 1H), 4.32 (d, J = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.5, 137.2, 136.0, 131.2, 131.1, 130.3, 129.7, 129.1, 125.9, 120.6, 115.8, 31.4; IR (neat): 3512, 3428, 3060, 1475, 1443, 1220, 1198, 1177, 752 cm^{-1}; HRMS (FAB) calcd for $C_{13}H_{12}BrO$: 263.0072 ($[M+H]^+$), found 263.0065.



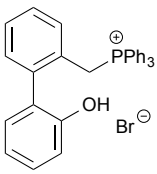
***m*-3c:** 74% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.54 (m, 1H), 7.29–7.39 (m, 3H), 7.23–7.26 (m, 1H), 6.99–7.02 (m, 1H), 6.92–6.94 (m, 1H), 6.86–6.89 (m, 1H), 4.48 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.2, 141.7, 141.5, 135.0, 130.9, 130.2, 129.6, 128.5, 128.0, 121.6, 116.0, 114.5, 32.3; IR (neat): 3367, 3062, 1584, 1475, 1442, 1305, 1219, 1189, 907, 755, 729, 700 cm^{-1}; HRMS (FAB) calcd for $C_{13}H_{11}BrO$: 261.9993 ([M]$^+$), found 261.9992.



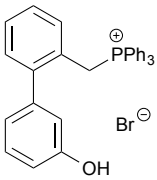
***p*-3c:** 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.53 (m, 1H), 7.31–7.36 (m, 4H), 7.22–7.25 (m, 1H), 6.92 (d, J = 8.8 Hz, 2H), 4.96 (br, 1H), 4.47 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.9, 141.6, 135.2, 132.7, 130.9, 130.5, 130.3, 128.5, 127.7, 115.2, 32.5; IR (neat): 3352, 3062, 3030, 1612, 1516, 1482, 1218, 1173, 835, 759 cm^{-1}; HRMS (FAB) calcd for $C_{13}H_{11}BrO$: 261.9993 ([M]$^+$), found 261.9994.

1-1-3. Synthesis of catalysts 3 (*o*-3, *m*-3, *p*-3).

A mixture of **3c** (3.0 mmol) and triphenylphosphine (9.0 mmol) in toluene (10 mL) was heated at 110 °C for 12 h. After cooled to room temperature, the resulting white precipitate was collected by filtration. Although the collected compound **3** as a white solid was almost pure, the white solid **3** was further purified by flash column chromatography on silica gel (dichloromethane/methanol = 30:1–10:1 as eluent) to afford **3** (86–89% yields).

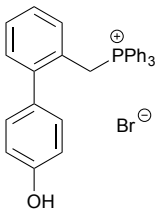


***o*-3:** 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.18 (s, 1H), 7.73–7.77 (m, 3H), 7.64 (d, J = 8.0 Hz, 1H), 7.53–7.59 (m, 6H), 7.33 (t, J = 7.6 Hz, 1H), 7.18–7.23 (m, 6H), 7.09–7.15 (m, 3H), 6.91 (d, J = 8.0 Hz, 1H), 6.48 (t, J = 7.6 Hz, 1H), 5.96 (d, J = 8.0 Hz, 1H), 5.04–5.12 (m, 1H), 4.51–4.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.1, 140.9 (m), 134.9 (d, J = 2.5 Hz), 133.6 (d, J = 9.9 Hz), 131.9, 130.3, 130.17 (d, J = 12.3 Hz), 130.15, 129.1, 129.0 (d, J = 3.3 Hz), 127.7 (d, J = 3.3 Hz), 126.2, 126.1, 119.7, 117.6 (m), 116.8, 116.7, 29.2 (d, J = 48.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ = 21.1; IR (neat): 3057, 2991, 2964, 2196, 1437, 1109, 919, 720, 687 cm^{-1}; HRMS (FAB) calcd for $C_{31}H_{26}OP$: 445.1721 ([M]$^+$), found 445.1722.



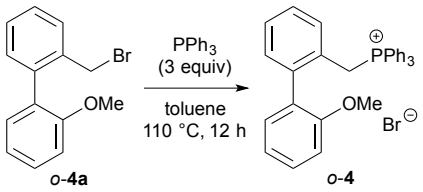
***m*-3:** 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.83 (s, 1H), 7.72–7.77 (m, 3H), 7.52–7.58 (m, 6H), 7.16–7.40 (m, 9H), 7.09 (t, J = 7.6 Hz, 1H), 6.88–6.99

(m, 3H), 5.88 (dd, J = 1.0, 7.6 Hz, 1H), 5.20 (br, 2H); ^{13}C NMR (100 MHz, CD_3OD): δ = 159.0, 145.4, 142.2, 136.5, 135.2 (d, J = 9.9 Hz), 132.1 (m), 131.4 (d, J = 12.3 Hz), 131.0, 130.2, 129.2, 126.4 (m), 121.0, 119.2, 118.3, 117.1, 115.8, 29.2 (d, J = 47.8 Hz); ^{31}P NMR (162 MHz, CD_3OD): δ = 21.3; IR (neat): 3173, 3060, 2889, 2201, 1583, 1473, 1438, 1198, 1110, 917, 753, 725, 687 cm^{-1}; HRMS (FAB) calcd for $C_{31}H_{26}OP$: 445.1721 ($[M]^+$), found 445.1722.



***p*-3:** 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.98 (s, 1H), 7.72–7.77 (m, 3H), 7.53–7.58 (m, 6H), 7.10–7.31 (m, 9H), 7.03 (d, J = 8.8 Hz, 1H), 7.00 (d, J = 8.4 Hz, 2H), 6.31 (d, J = 8.4 Hz, 2H), 5.02 (d, J = 14.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 144.0 (d, J = 5.8 Hz), 135.0 (d, J = 2.5 Hz), 133.8 (d, J = 9.9 Hz), 131.9 (m), 131.0 (m), 130.1 (d, J = 12.4 Hz), 129.6, 129.4, 128.8 (d, J = 3.3 Hz), 128.4 (d, J = 12.4 Hz), 127.5 (d, J = 3.3 Hz), 124.9 (d, J = 8.2 Hz), 117.4, 116.6, 116.4, 28.6 (d, J = 47.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ = 21.5; IR (neat): 3145, 3059, 2197, 1610, 1517, 1482, 1437, 1265, 1111, 917, 720, 687 cm^{-1}; HRMS (FAB) calcd for $C_{31}H_{26}OP$: 445.1721 ($[M]^+$), found 445.1722.

1-2. Synthesis of catalyst *o*-4.

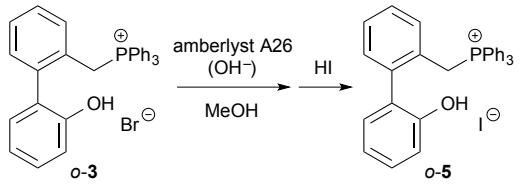


Catalyst *o*-**4** was synthesized from a known compound *o*-**4a**[2] in a similar manner for the synthesis of catalysts **3**.

***o*-4:** 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76–7.80 (m, 3H), 7.55–7.60 (m, 6H), 7.17–7.36 (m, 10H), 7.10 (d, J = 8.0 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 6.71 (t, J = 7.6 Hz, 1H), 6.04 (d, J = 7.2 Hz, 1H), 5.30–5.40 (m, 1H), 4.52 (dd, J = 14.4, 14.4 Hz, 1H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.7, 140.0 (d, J = 5.8 Hz), 135.0, 134.0 (d, J = 9.9 Hz), 131.4 (d, J = 3.3 Hz), 130.9 (m), 130.7, 130.2 (d, J = 13.1 Hz), 129.6, 128.8 (d, J = 3.2 Hz), 128.2 (d, J = 3.3 Hz), 126.5 (d, J = 9.0 Hz), 120.9, 117.8 (d, J = 5.8 Hz), 117.0 (d, J = 4.9 Hz), 111.0, 55.8, 29.5 (d, J = 46.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ = 21.6; IR (neat):

3055, 3006, 2963, 2836, 2173, 1481, 1436, 1263, 1231, 1110, 996, 923, 752, 722, 689 cm^{-1}; HRMS (FAB) calcd for $C_{32}H_{28}OP$: 459.1878 ($[M]^+$), found 459.1879.

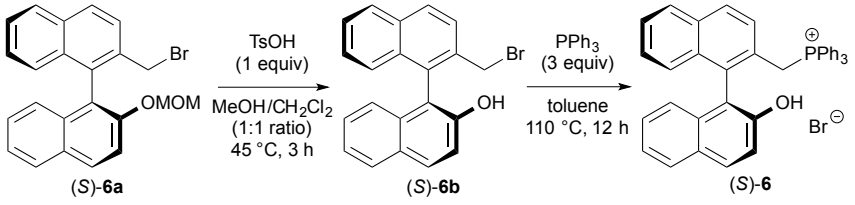
1-3. Synthesis of catalyst *o*-5.



Catalyst *o*-**3** was transformed into the corresponding phosphonium hydroxide by passing through an ion-exchange resin (amberlyst A26, OH^- form) in methanol. The resulting phosphonium hydroxid was then treated with HI (1.3 equiv, 55%) in methanol at room temperature. Solvent was removed and the residue was purified by flash column chromatography on silica gel (dichloromethane/methanol = 30:1–10:1 as eluent) to afford *o*-**5** (81% yield).

***o*-5:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (br, 1H), 7.74–7.78 (m, 3H), 7.54–7.60 (m, 7H), 7.35 (t, J = 7.6 Hz, 1H), 7.11–7.25 (m, 9H), 6.93 (d, J = 7.2 Hz, 1H), 6.52 (t, J = 7.6 Hz, 1H), 5.97 (d, J = 7.2 Hz, 1H), 4.94–5.03 (m, 1H), 4.60–4.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.6, 140.6 (d, J = 5.8 Hz), 135.1 (d, J = 2.4 Hz), 133.8 (d, J = 9.9 Hz), 131.9 (d, J = 3.3 Hz), 130.3 (d, J = 12.4 Hz), 129.3, 129.2 (d, J = 4.1 Hz), 127.9 (d, J = 3.3 Hz), 126.3, 126.2, 126.1, 120.2, 117.6 (d, J = 3.3 Hz), 116.8, 29.3 (d, J = 48.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ = 21.1; IR (neat): 3171, 3057, 2924, 2194, 1484, 1438, 1109, 916, 750, 722, 687 cm^{-1}; HRMS (FAB) calcd for $C_{31}H_{26}OP$: 445.1721 ($[M]^+$), found 445.1722.

1-4. Synthesis of catalyst (*S*)-6.

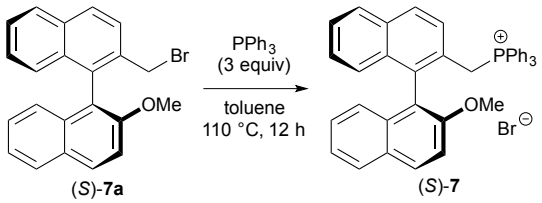


Catalyst (*S*)-**6** was synthesized from a known compound (*S*)-**6a**[3] in a similar manner for the synthesis of catalysts **3**.

(*S*)-6b: 96% yield; $[\alpha]^{25}_{D} = -150.5$ (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 8.4 Hz, 1H), 7.95 (t, J = 7.6 Hz, 2H), 7.89 (d, J = 7.6 Hz, 1H), 7.77 (d, J = 8.8 Hz, 1H), 7.52 (dt, J = 0.8, 7.6 Hz, 1H), 7.30–7.39 (m, 3H), 7.22–7.25 (m, 2H), 6.94 (d, J = 8.8 Hz, 1H), 4.76 (s, 1H), 4.38 (d, J = 10.0 Hz, 1H), 4.29 (d, J = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.3, 136.5, 133.7, 133.5, 132.9, 130.5, 130.3, 130.0, 129.1, 128.24, 128.16, 127.9, 127.4, 127.1, 126.9, 126.1, 124.4, 123.7, 117.8, 115.7, 31.9; IR (neat): 3511, 3419, 3056, 1619, 1596, 1380, 1202, 1172, 1145, 1128, 907, 817, 748, 728 cm^{-1}; HRMS (FAB) calcd for $C_{21}H_{15}BrO$: 362.0306 ($[M]^+$), found 362.0299.

(*S*)-6: 85% yield; $[\alpha]^{26}_{D} = -13.5$ (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.89 (br, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.74–7.80 (m, 3H), 7.61–7.68 (m, 4H), 7.40–7.48 (m, 7H), 7.13–7.28 (m, 9H), 6.88–6.95 (m, 2H), 6.59 (d, J = 8.4 Hz, 1H), 4.57–4.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.4, 136.2 (d, J = 7.4 Hz), 134.9 (d, J = 3.3 Hz), 133.6 (d, J = 9.9 Hz), 133.3, 133.2 (d, J = 2.5 Hz), 133.0 (d, J = 2.5 Hz), 130.1 (d, J = 12.3 Hz), 129.9, 128.3, 128.1 (m), 127.8, 127.3, 126.7, 126.53, 126.47, 124.8 (d, J = 8.3 Hz), 123.6, 122.6, 120.1, 117.6, 116.8, 115.4, 30.5 (d, J = 48.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ = 19.6; IR (neat): 3056, 2193, 1436, 1274, 1108, 920, 822, 727, 687 cm^{-1}; HRMS (FAB) calcd for $C_{39}H_{30}OP$: 545.2034 ($[M]^+$), found 545.2033.

1-5. Synthesis of catalyst (*S*)-7.



Catalyst (*S*)-**7** was synthesized from a known compound (*S*)-**7a**[4] in a similar manner for the synthesis of catalysts **3**.

(*S*)-7: 80% yield; $[\alpha]^{25}_{D} = -120.5$ (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, J = 9.6 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.68–7.75 (m, 4H), 7.43–7.53 (m, 7H), 7.19–7.33 (m, 9H), 7.15 (d, J = 9.2 Hz, 1H), 7.10 (t, J = 7.2 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H), 6.79 (d, J = 8.4 Hz, 1H), 4.80 (dd, J = 14.8, 15.2 Hz, 1H), 4.67 (dd, J = 14.8, 15.2 Hz, 1H), 3.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.5, 135.2 (d, J = 8.2 Hz), 135.0 (d, J = 3.3 Hz), 133.8 (d, J = 9.1 Hz), 133.0 (d, J = 2.4 Hz), 132.8 (m), 130.7, 130.1 (d,

J = 12.4 Hz), 128.7, 128.6 (d, J = 3.3 Hz), 128.4 (d, J = 2.5 Hz), 128.2, 128.0, 127.6, 126.6, 126.5, 126.3, 125.0 (d, J = 8.2 Hz), 123.9 (d, J = 6.8 Hz), 118.5, 117.8, 116.9, 113.2, 55.8, 30.0 (d, J = 48.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ = 20.4; IR (neat): 3056, 2841, 2178, 1436, 1264, 1254, 1108, 1083, 921, 908, 816, 724 cm^{-1}; HRMS (FAB) calcd for $C_{40}H_{32}OP$: 559.2191 ($[M]^+$), found 559.2193.

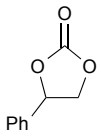
2. General Reaction Procedure.

2-1. General procedure for the reaction of styrene oxide 1a with CO_2 (Table 1).

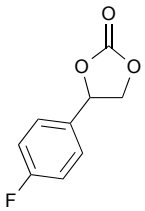
To a mixture of styrene oxide **1a** (2.0 mmol) and catalyst (0.020 mmol, 1 mol %) was added 1,3,5-trimethoxybenzene (0.10 mmol) as an internal standard. The reaction mixture was heated at 60 °C for 24 h under CO_2 atmosphere (1atm, using a balloon). After cooled to room temperature, the reaction solution (50 μL) was added to an NMR tube, and diluted by $CDCl_3$ (0.50 mL). The yield of a cyclic carbonate **2a** was determined by ^{1}H NMR analysis based on 1,3,5-trimethoxybenzene as an internal standard.

2-2. General procedure for the reaction of epoxides 1 with CO_2 catalyzed by *o*-5 (Table 2 and Scheme 4).

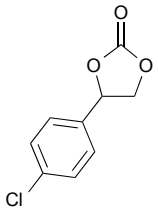
A mixture of epoxide **1** (2.0 mmol) and *o*-**5** (0.020 mmol, 1 mol %) was heated at 60 °C for 24 h under CO_2 atmosphere (1atm, using a balloon). After cooled to room temperature, the reaction mixture was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1–3:1 as eluent) to afford cyclic carbonate **2**.



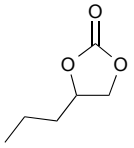
2a:[5] Spectral data completely matched with reported data.[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.48 (m, 5H), 5.68 (dd, J = 7.6, 8.4 Hz, 1H), 4.81 (dd, J = 8.0, 8.8 Hz, 1H), 4.35 (dd, J = 8.0, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 135.7, 129.6, 129.1, 125.8, 77.9, 71.1.



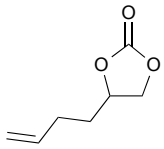
2b:[5] Spectral data completely matched with reported data.[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.39 (m, 2H), 7.12–7.17 (m, 2H), 5.67 (dd, J = 8.0, 8.4 Hz, 1H), 4.81 (dd, J = 8.4, 8.4 Hz, 1H), 4.33 (dd, J = 7.6, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.2 (d, J = 248 Hz), 154.6, 131.5 (d, J = 3.3 Hz), 128.0 (d, J = 8.3 Hz), 116.1 (d, J = 22.3 Hz), 77.3, 71.0.



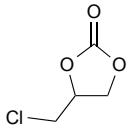
2c:[5] Spectral data completely matched with reported data.[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.66 (dd, *J* = 7.6, 8.0 Hz, 1H), 4.81 (dd, *J* = 8.0, 8.8 Hz, 1H), 4.31 (dd, *J* = 7.6, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.5, 135.5, 134.2, 129.3, 127.2, 77.2, 70.9.



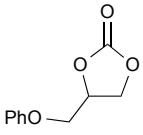
2d:[5] Spectral data completely matched with reported data.[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.68–4.75 (m, 1H), 4.53 (dd, *J* = 8.0, 8.4 Hz, 1H), 4.07 (dd, *J* = 7.2, 8.4 Hz, 1H), 1.77–1.86 (m, 1H), 1.62–1.71 (m, 1H), 1.36–1.57 (m, 2H), 0.99 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.0, 76.8, 69.3, 35.7, 17.6, 13.4.



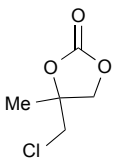
2e:[5] Spectral data completely matched with reported data.[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.74–5.84 (m, 1H), 5.04–5.13 (m, 2H), 4.69–4.77 (m, 1H), 4.53 (dd, *J* = 8.0, 8.8 Hz, 1H), 4.07 (dd, *J* = 7.6, 8.4 Hz, 1H), 2.14–2.32 (m, 2H), 1.90–1.99 (m, 1H), 1.73–1.83 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 136.0, 115.9, 76.2, 69.1, 32.7, 28.4.



2f:[5] Spectral data completely matched with reported data.[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.93–4.99 (m, 1H), 4.60 (dd, *J* = 8.4, 8.8 Hz, 1H), 4.42 (dd, *J* = 6.0, 8.8 Hz, 1H), 3.72–3.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.3, 74.3, 66.8, 43.9.



2g:[5] Spectral data completely matched with reported data.[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (t, *J* = 7.6 Hz, 2H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 5.00–5.06 (m, 1H), 4.62 (dd, *J* = 8.4, 8.8 Hz, 1H), 4.54 (dd, *J* = 6.0, 8.8 Hz, 1H), 4.24 (dd, *J* = 4.0, 10.4 Hz, 1H), 4.15 (dd, *J* = 4.0, 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.7, 154.7, 129.6, 121.9, 114.6, 74.1, 66.8, 66.2.

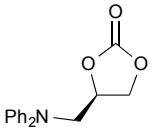


2i:[5] Spectral data completely matched with reported data.[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.52 (d, *J* = 8.8 Hz, 1H), 4.16 (d, *J* = 8.4 Hz, 1H), 3.73 (d, *J* = 11.6 Hz, 1H), 3.59 (d, *J* = 12.4 Hz, 1H), 1.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.8, 81.7, 72.0, 48.2, 23.0.

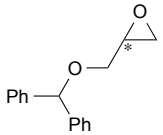
2-3. General procedure for the kinetic resolution of epoxides 1 with CO_2 catalyzed by (*S*)-6 or (*S*)-7 (Scheme 5).

A mixture of epoxide **1** (2.0 mmol) and (*S*)-**6** or (*S*)-**7** (0.020 mmol, 1 mol %) was heated at 50 °C for 12 h (or 20 h) under CO_2 atmosphere (1atm, using a balloon). After cooled to room temperature, the reaction mixture was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1–3:1 as eluent) to afford cyclic carbonate **2h** with recovery of **1h**.

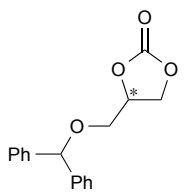
1h:[6] $[\alpha]^{29}_{D}$ = +16.3 (*c* = 1.6, EtOH; 31% ee) [lit.[6a] $[\alpha]^{25}_{D}$ = +41.4 (*c* = 1.1, EtOH; 95% ee (*S*))], HPLC analysis: Daicel Chiralpak ID-3, haxane/2-propanol = 20:1, flow rate = 0.5 mL/min, 254 nm; retention time: 10.5 min (minor) and 11.3 min (major). Spectral data completely matched with reported data.[6] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (t, *J* = 8.4 Hz, 4H), 7.05 (d, *J* = 7.2 Hz, 4H), 6.98 (t, *J* = 7.2 Hz, 2H), 3.97 (dd, *J* = 4.0, 16.0 Hz, 1H), 3.87 (dd, *J* = 4.4, 16.0 Hz, 1H), 3.22–3.26 (m, 1H), 2.79 (dd, *J* = 3.6, 5.2 Hz, 1H), 2.57 (dd, *J* = 3.2, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.9, 129.3, 121.7, 121.0, 53.8, 50.3, 45.9.



2h:[6] HPLC analysis: Daicel Chiralpak AS-3, haxane/2-propanol = 3:1, flow rate = 0.5 mL/min, 254 nm; retention time: 39.1 min (minor) and 43.2 min (major). Spectral data completely matched with reported data.[6] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (t, *J* = 8.8 Hz, 4H), 7.03 (t, *J* = 7.2 Hz, 2H), 6.97 (d, *J* = 7.2 Hz, 4H), 4.92–4.99 (m, 1H), 4.45 (dd, *J* = 8.4, 8.8 Hz, 1H), 4.17 (dd, *J* = 6.8, 8.8 Hz, 1H), 4.11 (dd, *J* = 6.0, 15.6 Hz, 1H), 4.01 (dd, *J* = 6.0, 15.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4, 147.4, 129.5, 122.4, 121.0, 74.5, 67.3, 54.1.



1j:[5] HPLC analysis: Daicel Chiralpak IC-3, haxane/2-propanol = 10:1, flow rate = 0.5 mL/min, 254 nm; retention time: 12.7 min (minor) and 14.0 min (major). Spectral data completely matched with reported data.[6] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23–7.38 (m, 10H), 5.46 (s, 1H), 3.74 (dd, *J* = 2.8, 11.2 Hz, 1H), 3.46 (dd, *J* = 5.6, 11.6 Hz, 1H), 3.20–3.24 (m, 1H), 2.79 (dd, *J* = 4.4, 4.8 Hz, 1H), 2.61 (dd, *J* = 2.8, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.84, 141.76, 128.4, 127.6, 127.5, 127.0, 126.9, 83.9, 69.5, 50.9, 44.4.



2j: HPLC analysis: Daicel Chiralpak IB-3, haxane/2-propanol = 3:1, flow rate = 0.5 mL/min, 254 nm; retention time: 24.7 min (minor) and 29.3 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.37 (m, 10H), 5.42 (s, 1H), 4.82–4.87 (m, 1H), 4.51 (dd, *J* = 8.4, 8.4 Hz, 1H), 4.44 (dd, *J* = 5.8, 8.2 Hz, 1H), 3.74 (dd, *J* = 4.0, 10.8 Hz, 1H), 3.61 (dd, *J* = 3.4, 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.0, 141.1, 141.0, 128.5, 128.4, 127.73, 127.66, 126.7, 126.6, 84.1, 74.9, 67.7, 66.2; IR (neat): 3062, 3029, 2919, 2868, 1791, 1493, 1453, 1389, 1165, 1125, 1103, 1087, 1040, 1027, 742, 697 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{16}O_4$: 284.1049 ($[M]^+$), found 284.1048.

3. Determination of Absolute Configurations of 1h and 2h.

The absolute configuration of major stereoisomer of **1h** was confirmed by comparison of the optical rotation with the literature value.[6a] **1h**: $[\alpha]^{29}_D$ = +16.3 (*c* = 1.6, EtOH; 31% ee) [lit.[6a] $[\alpha]^{25}_D$ = +41.4 (*c* = 1.1, EtOH; 95% ee (*S*))]. Based on the configuration of **1h**, absolute configuration of major stereoisomer of **2h** was determined as *R*.

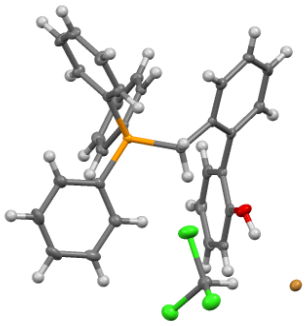
4. X-ray diffraction analysis of catalyst *o*-3.

Catalyst *o*-**3** was recrystallized from chloroform/hexane. Data of X-ray diffraction were collected by a Rigaku Varimax Saturn724+ diffractometer using multi-layer mirror monochromated MoKα (λ = 0.71075 Å) radiation. The structure was solved by direct methods and expanded using Fourier techniques. Some hydrogen atoms were refined isotropically and the rest were refined using the riding model.

The crystallographic data of *o*-**3**·**CHCl$_3$** were summarized in the following table.

empirical formula	$C_{32}H_{27}BrCl_3OP_4$
formula weight	644.80
crystal system	monoclinic
space group	$P2_1/c$ (#14)
a, Å	12.9435(17)
b, Å	13.1900(16)
c, Å	17.350(2)
V , Å^3	2945.4(6)
Z	4
*D*calc, g/cm^3	1.454
T, °C	–180
μ (MoKα), cm^{-1}	17.502
no. of reflns obsd	5175
no. of reflns variable	347
R_1 (I >2σ(I))	0.0253
Rw (All reflections)	0.0567
Goodness of Fit	1.039

The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 1480807). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/data_request/cif.



References

1 (*a*) K. Inamoto, J. Kadokawa and Y. Kondo, *Org. Lett.,* 2013, **15**, 3962; see also: (*b*) B. Tao and D. W. Boykin, *J. Org. Chem.,* 2004, **69**, 4330; (*c*) Y. Izawa, C. Zheng and S. S. Stahl, *Angew. Chem., Int. Ed.,* 2013, **52**, 3672.

2 Y. Kwon, H. Cho and S. Kim, *Org. Lett.,* 2013, **15**, 920.

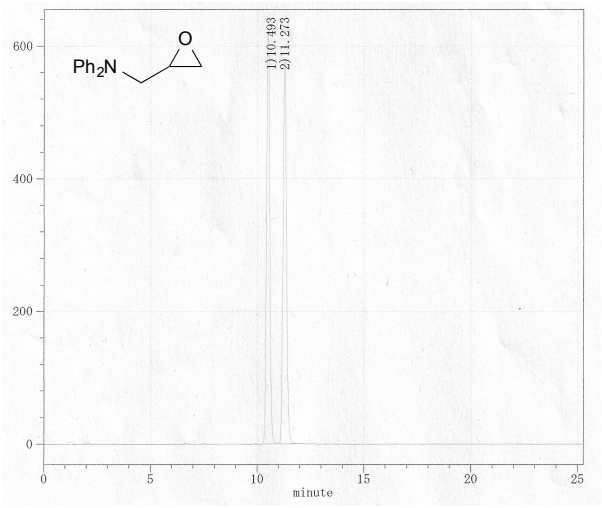
3 A. Hasegawa, Y. Naganawa, M. Fushimi, K. Ishihara and Y. Yamamoto, *Org. Lett.,* 2006, **8**, 3175.

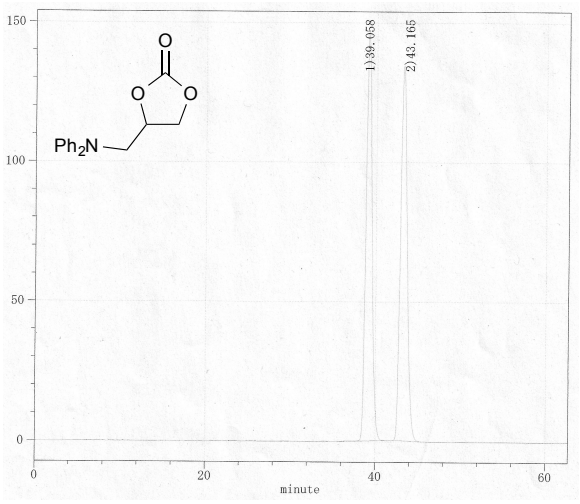
4 (*a*) S. Miyano, S.-i. Okada, T. Suzuki, S. Handa and H. Hashimoto, *Bull. Chem. Soc. Jpn.,* 1986, **59**, 2044; (*b*) J. Liu, H.-X. Zheng, C.-Z. Yao, B.-F. Sun and Y.-B. Kang, *J. Am. Chem. Soc.,* 2016, **138**, 3294.

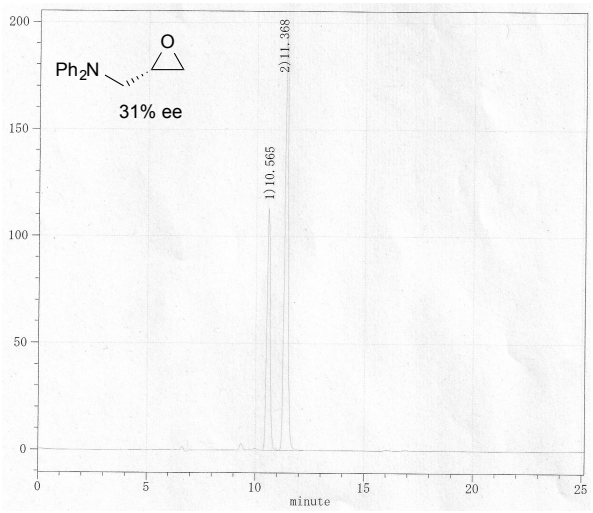
5 (*a*) G. Rokicki, W. Kuran and B. Pogorzelska-Marciniak, *Monatsh. Chem.*, 1984, **115**, 205; (*b*) S. Corsano, G. Strappaghetti, R. Ferrini and R. Sala, *Arch. Pharm.*, 1988, **321**, 731; (*c*) W. Clegg, R. W. Harrington, M. North and R. Pasquale, *Chem.–Eur. J.*, 2010, **16**, 6828; (*d*) L. Wu, H. Yang, H. Wang and J. Lu, *RSC Adv.*, 2015, **5**, 23189; (*e*) H. Büttner, J. Steinbauer and T. Werner, *ChemSusChem*, 2015, **8**, 2655.

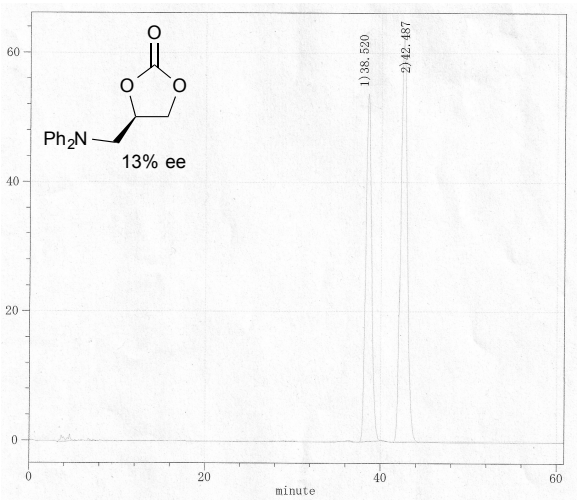
6 (*a*) W. Yamada, Y. Kitaichi, H. Tanaka, T. Kojima, M. Sato, T. Ikeno and T. Yamada, *Bull. Chem. Soc. Jpn.*, 2007, **80**, 1391; (*b*) M. North, S. C. Z. Quek, N. E. Pridmore, A. C. Whitwood and X. Wu, *ACS Catal.*, 2015, **5**, 3398.

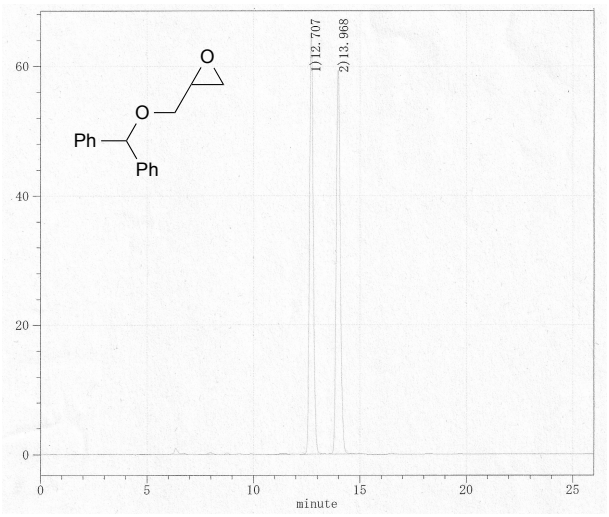
HPLC charts

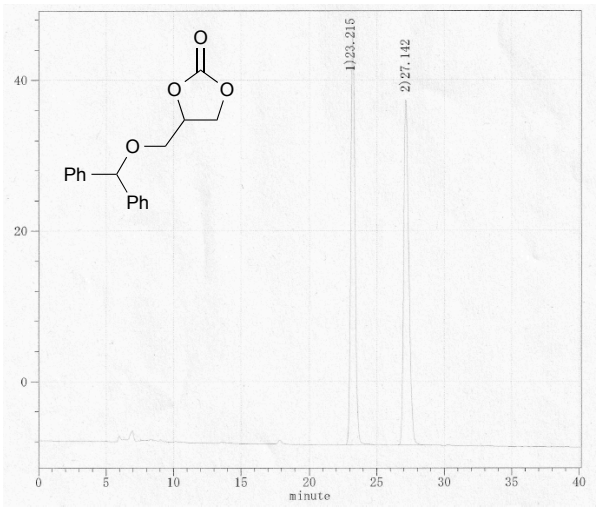

Ph2N
1)10.493
2)11.273
minute

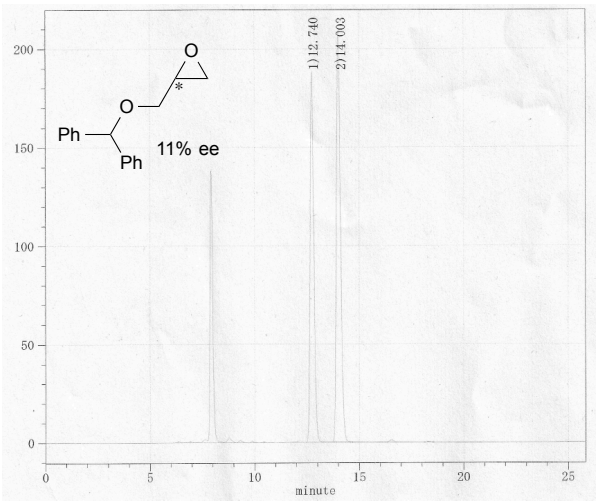

Ph2N
1)39.058
2)43.165
minute

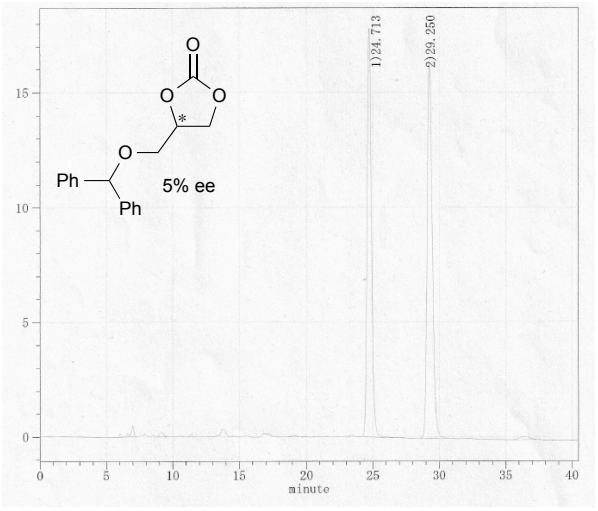

Ph2N
31% ee
1)10.565
2)11.368
minute

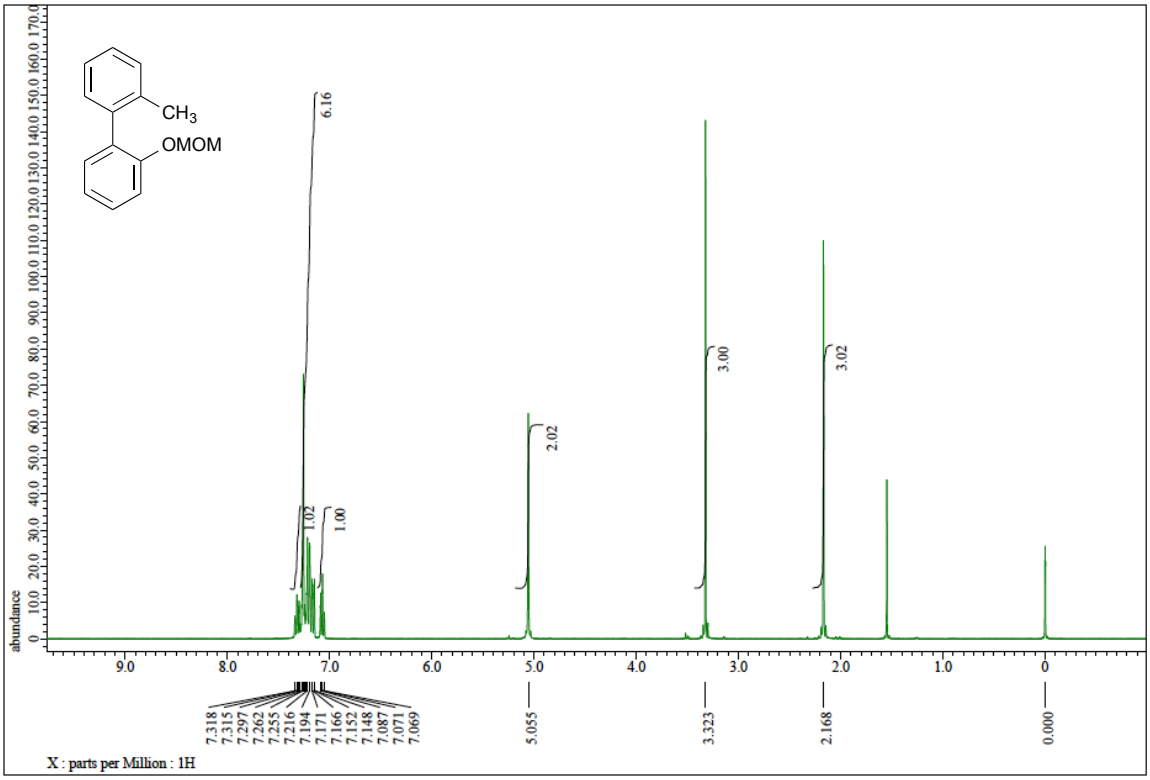

Ph2N
13% ee
1)38.520
2)42.487
minute

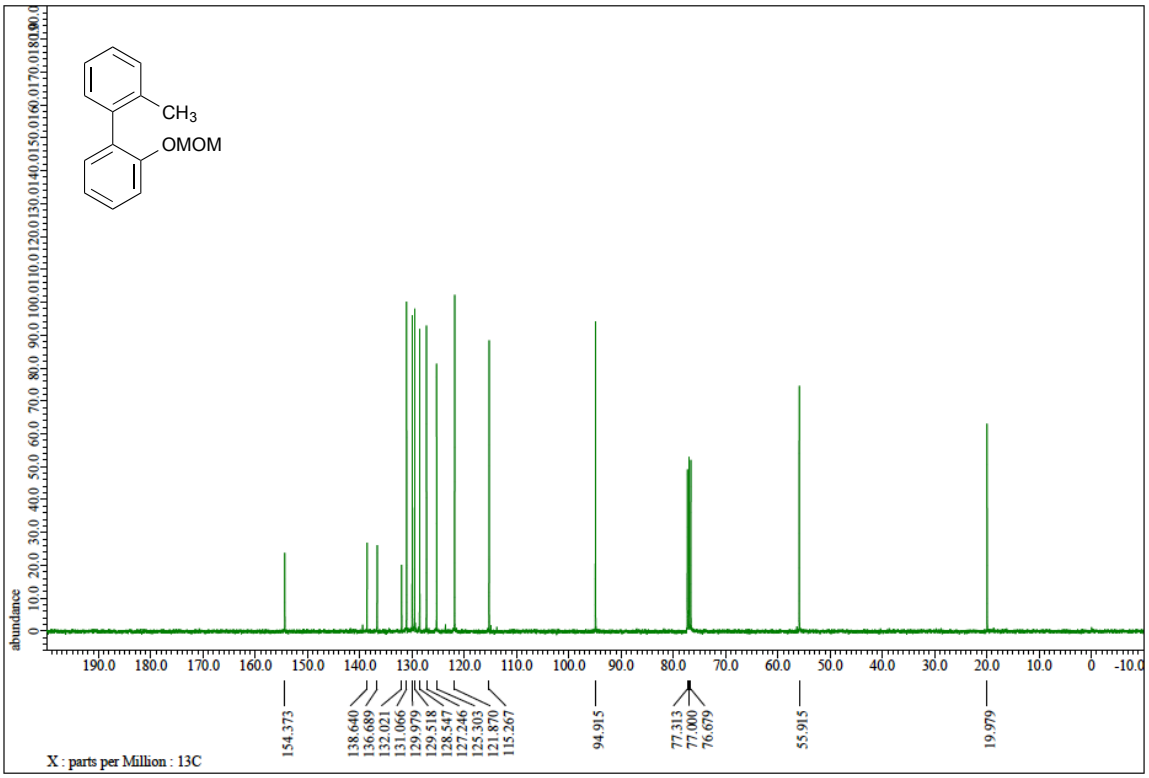

1)12.707
2)13.968
O
O
Ph
Ph
minute

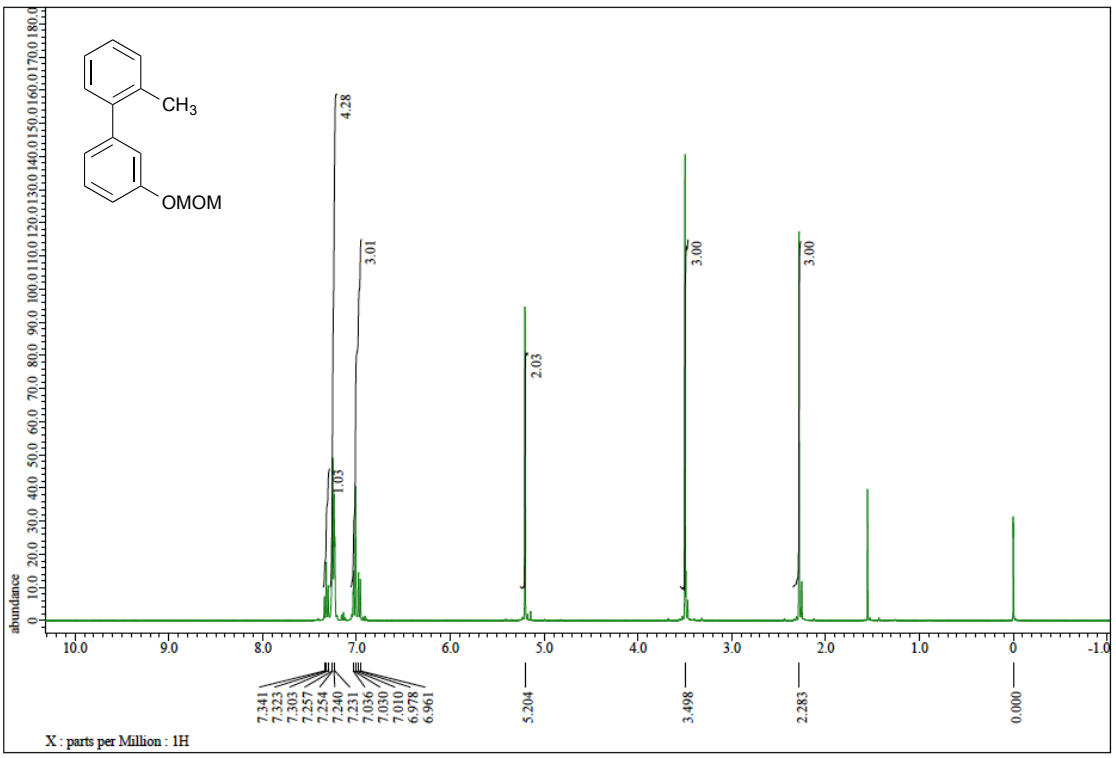

1)23.215
2)27.142
O
O
O
O
Ph
Ph
minute

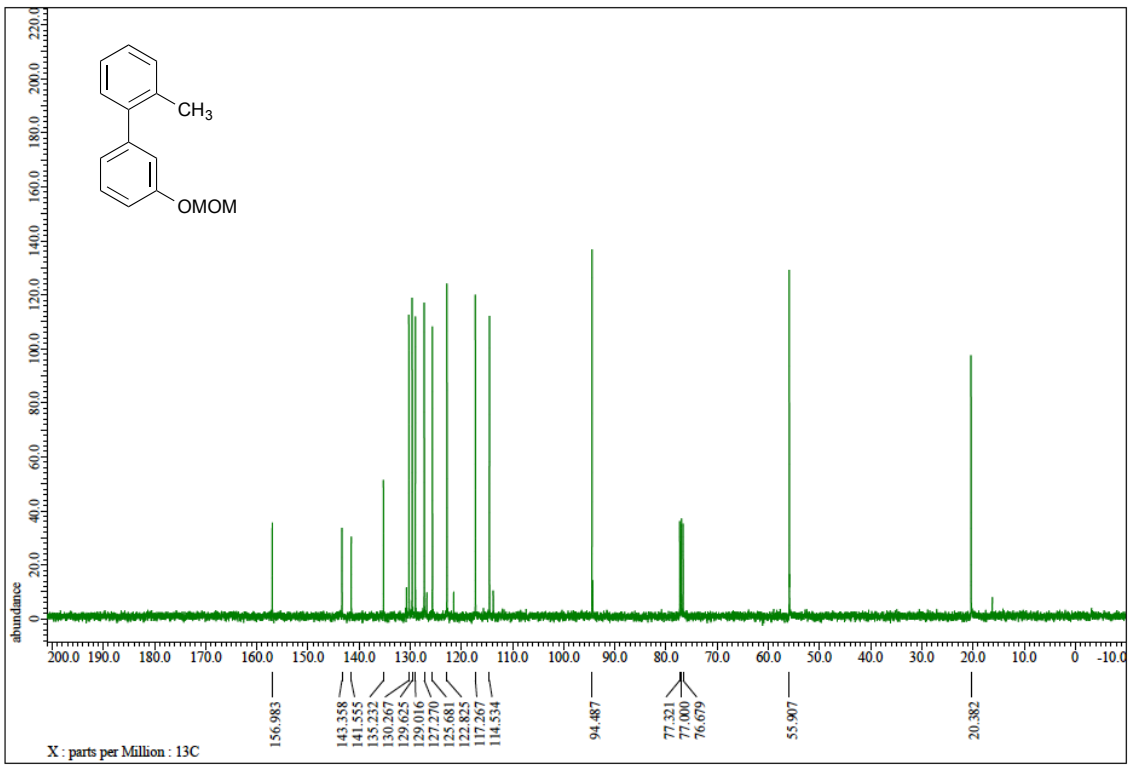

1)12.740
2)14.003
O
*
O
Ph
Ph
11% ee
minute

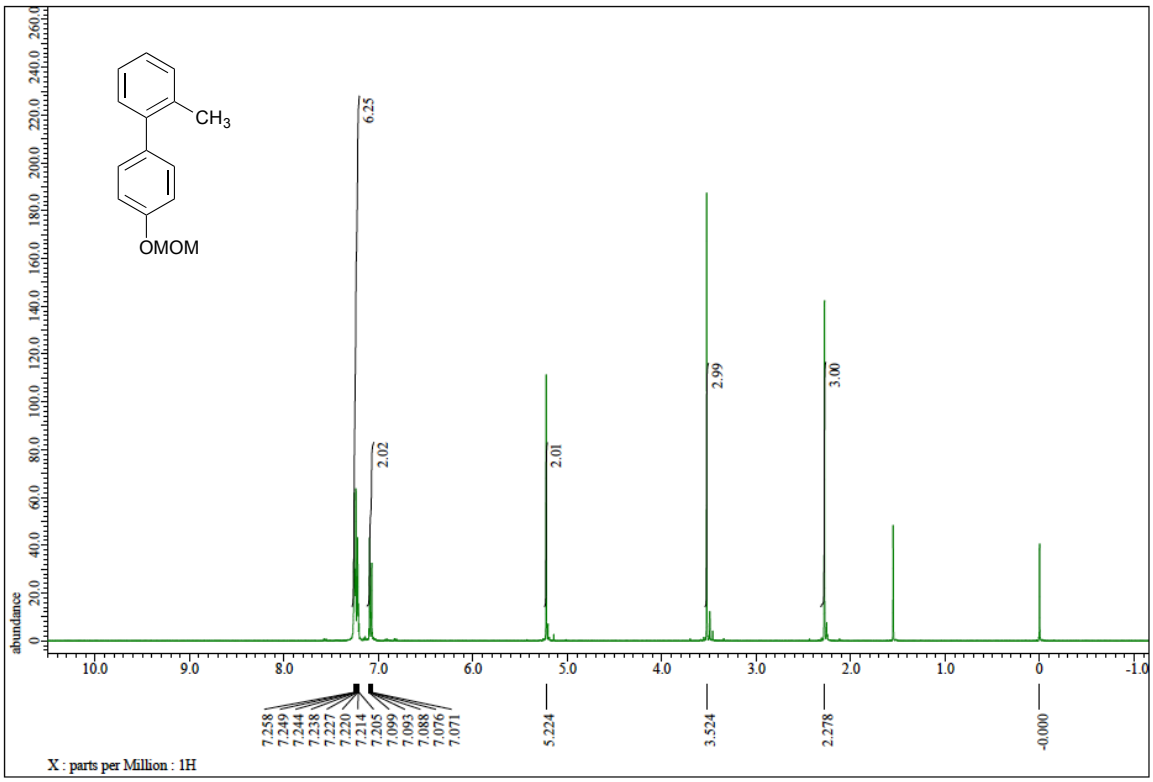

1)24.713
2)29.250
O
O
O
*
O
Ph
Ph
5% ee
minute

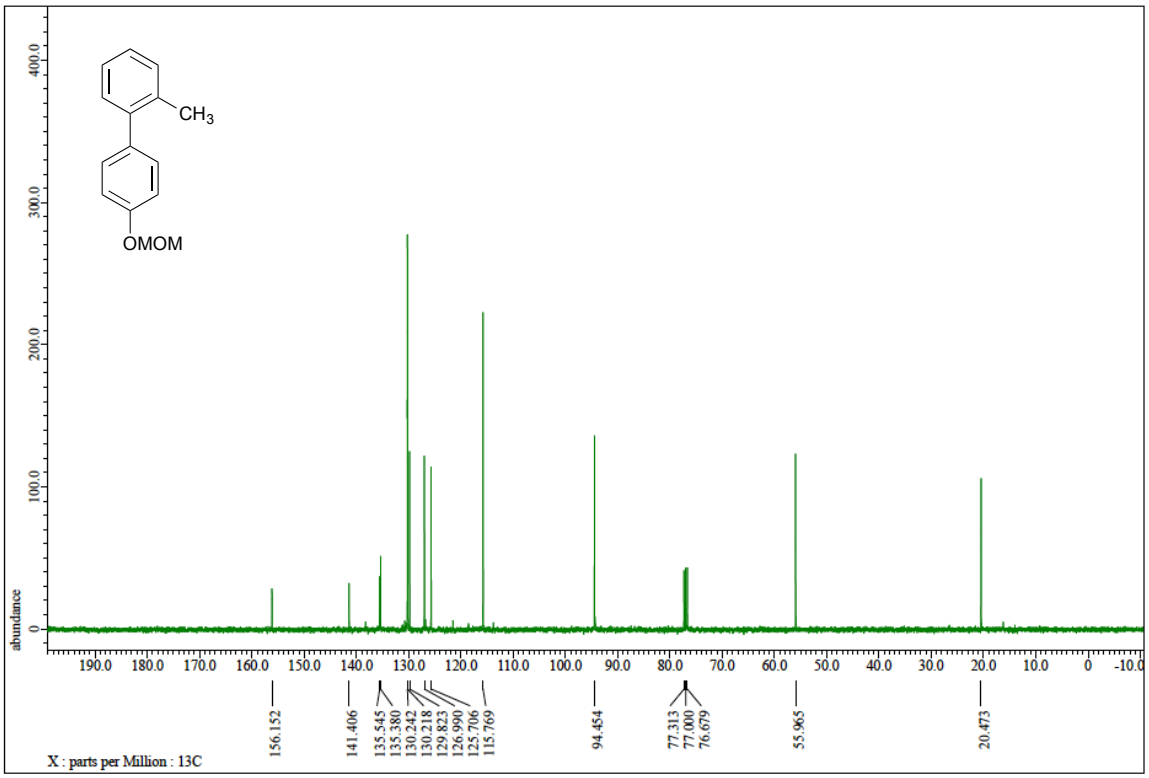

CH3
OMOM
6.16
1.02
1.00
2.02
3.00
3.02
abundance
X : parts per Million : 1H
7.318
7.315
7.297
7.262
7.255
7.216
7.194
7.171
7.166
7.152
7.148
7.087
7.071
7.069
5.055
3.323
2.168
0.000

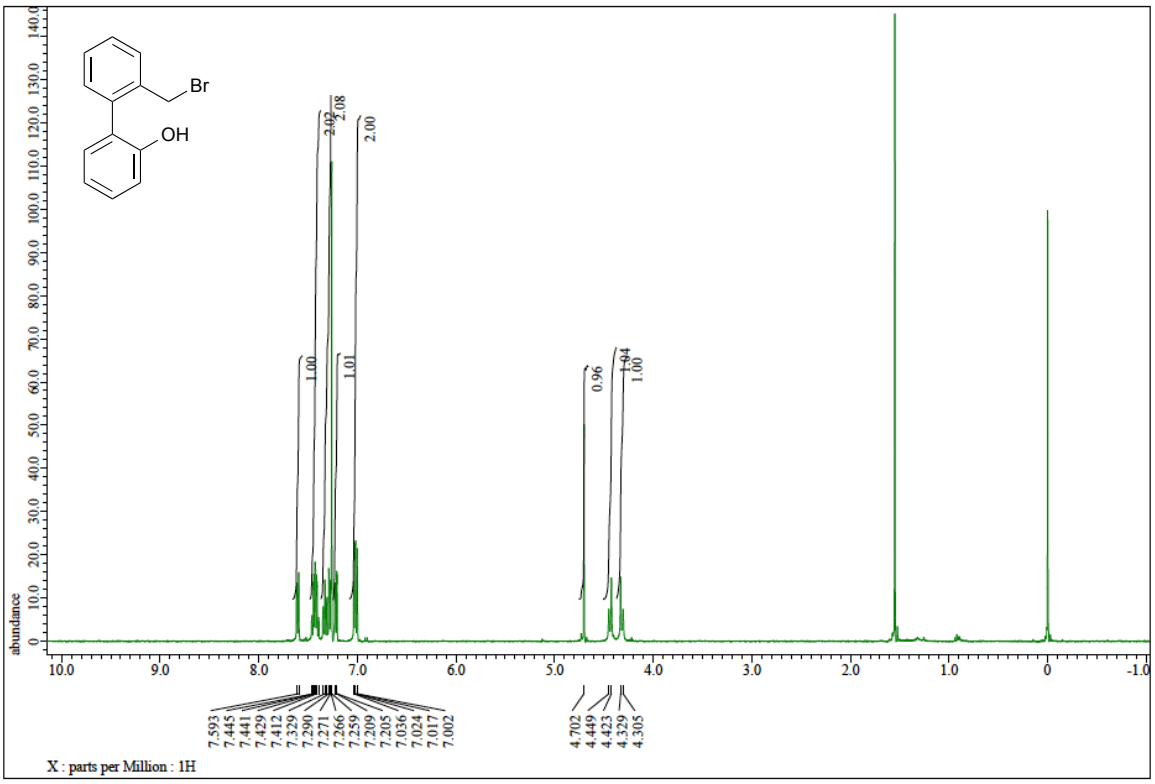

CH3
OMOM
abundance
X : parts per Million : 13C
154.373
138.640
136.689
132.021
131.066
129.979
129.518
128.547
127.246
125.303
121.870
115.267
94.915
77.313
77.000
76.679
55.915
19.979

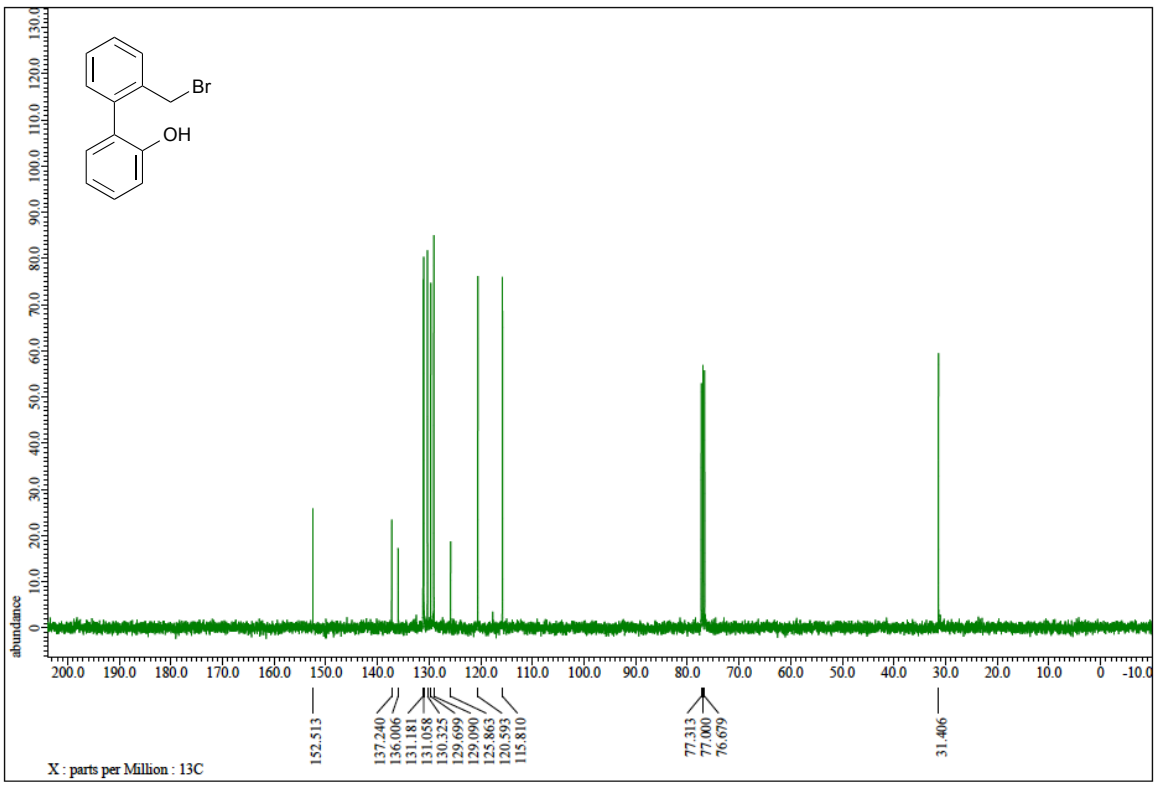

CH3
OMOM
4.28
3.01
1.03
2.03
3.00
3.00
abundance
X : parts per Million : 1H
7.341
7.323
7.303
7.257
7.254
7.240
7.231
7.036
7.030
7.010
6.978
6.961
5.204
3.498
2.283
0.000

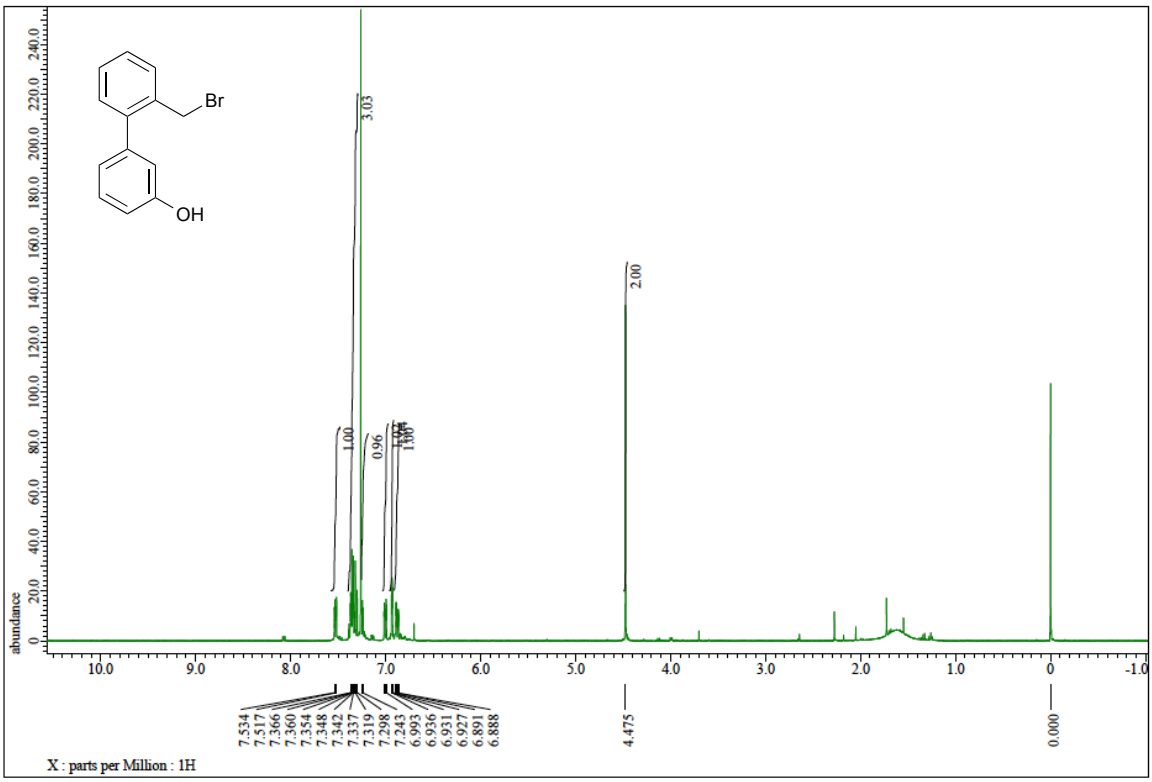

CH3
OMOM
abundance
X : parts per Million : 13C
156.983
143.358
141.555
135.232
130.267
129.625
129.016
127.270
125.681
122.825
117.267
114.534
94.487
77.321
77.000
76.679
55.907
20.382

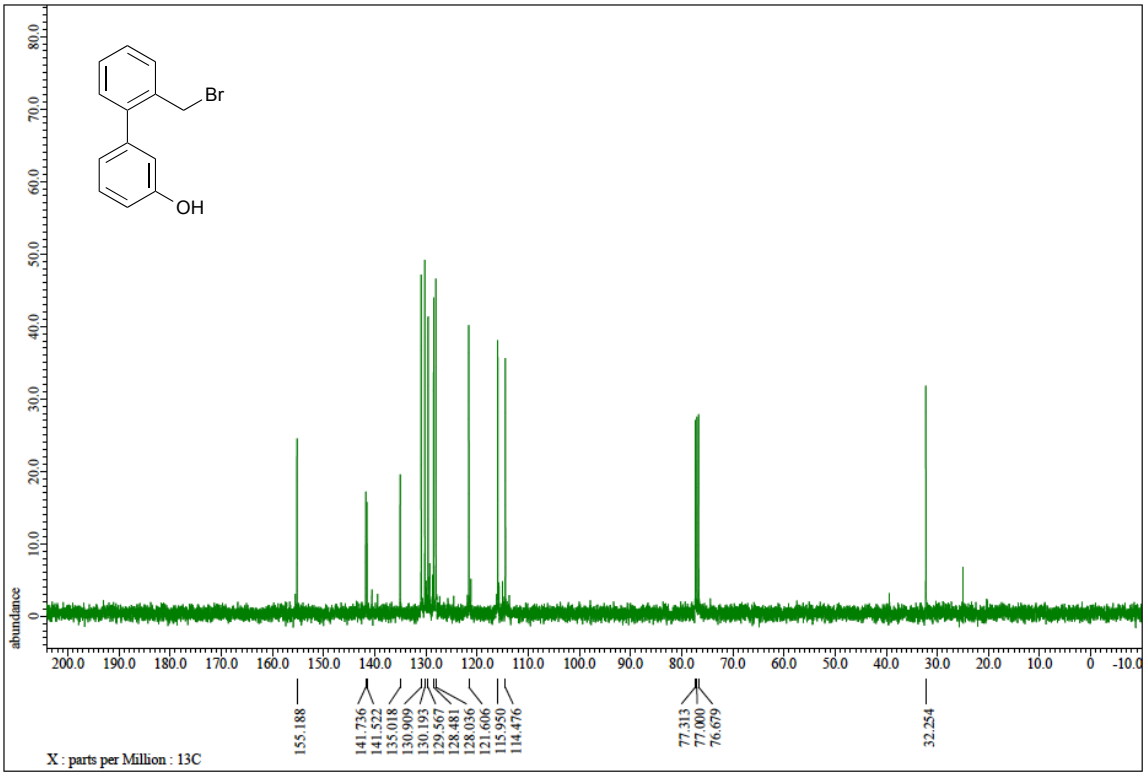

CH3
OMOM
6.25
2.02
2.01
2.99
3.00
abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.258
7.249
7.244
7.238
7.227
7.220
7.214
7.205
7.099
7.093
7.088
7.076
7.071
5.224
3.524
2.278
-0.000
X : parts per Million : 1H

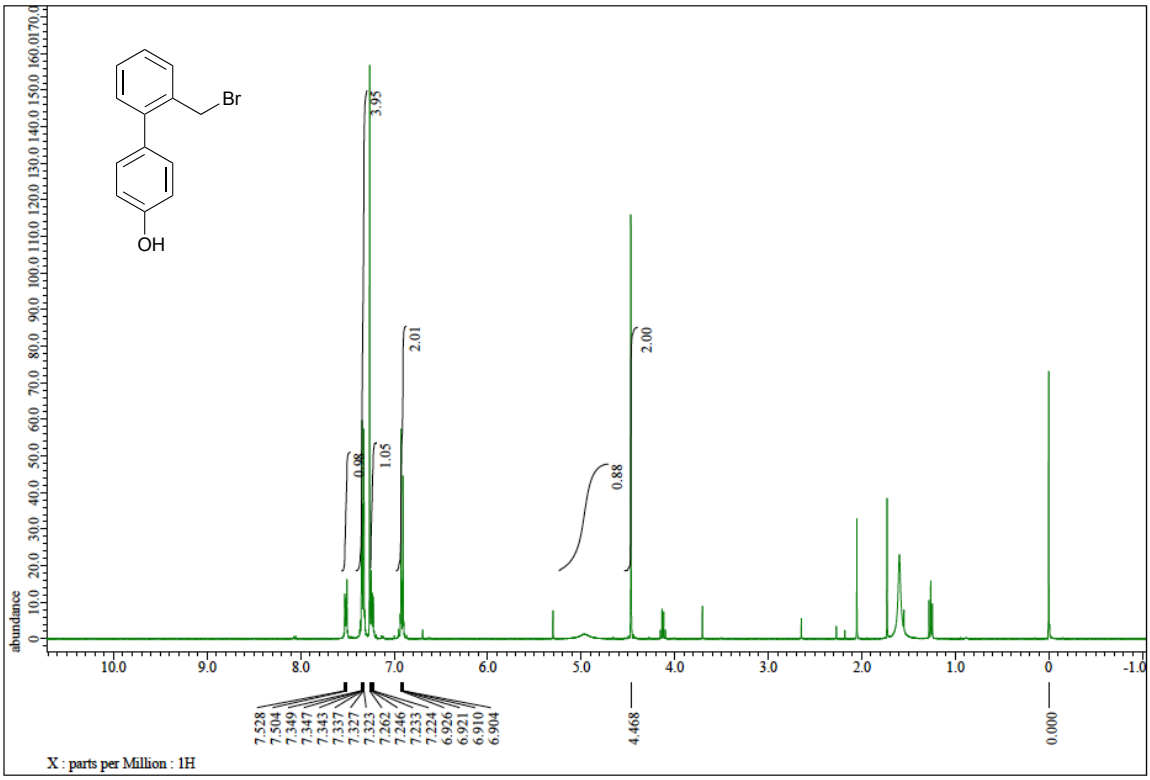

CH3
OMOM
abundance
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
156.152
141.406
135.545
135.380
130.242
130.218
129.823
126.990
125.706
115.769
94.454
77.313
77.000
76.679
55.965
20.473
X : parts per Million : 13C

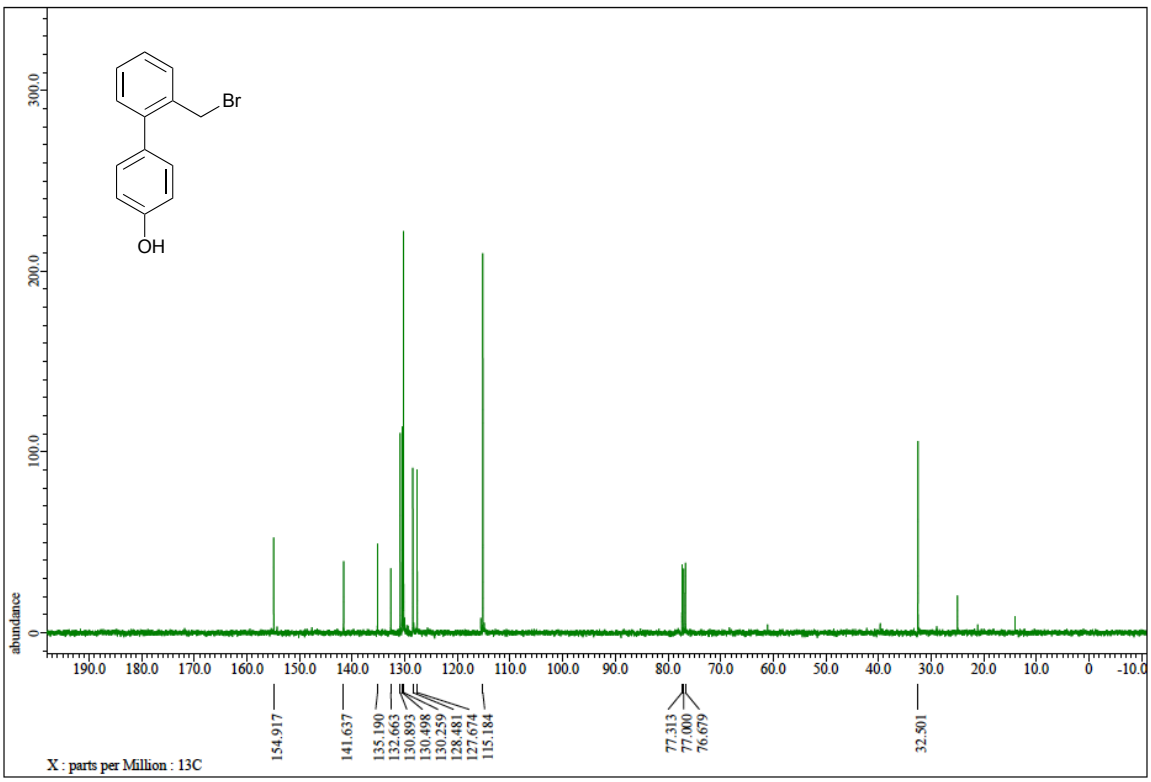

Br
OH
abundance
X : parts per Million : 1H

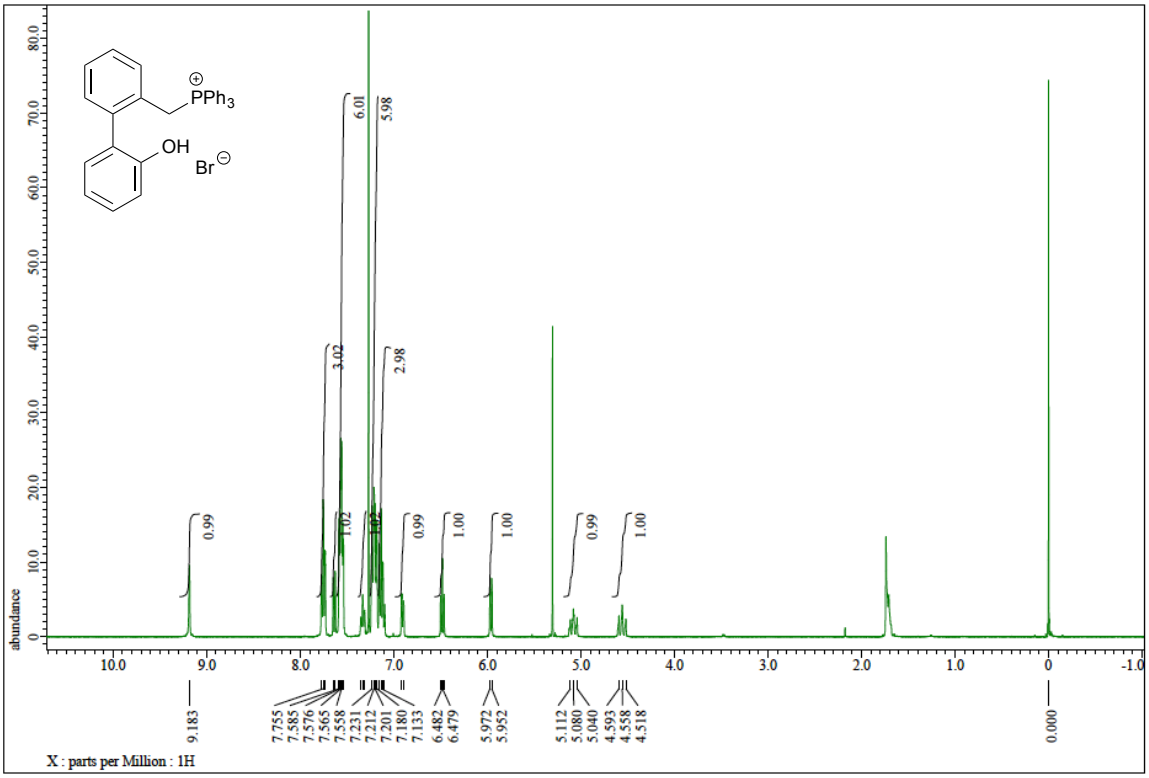

Br
OH
abundance
X : parts per Million : 13C

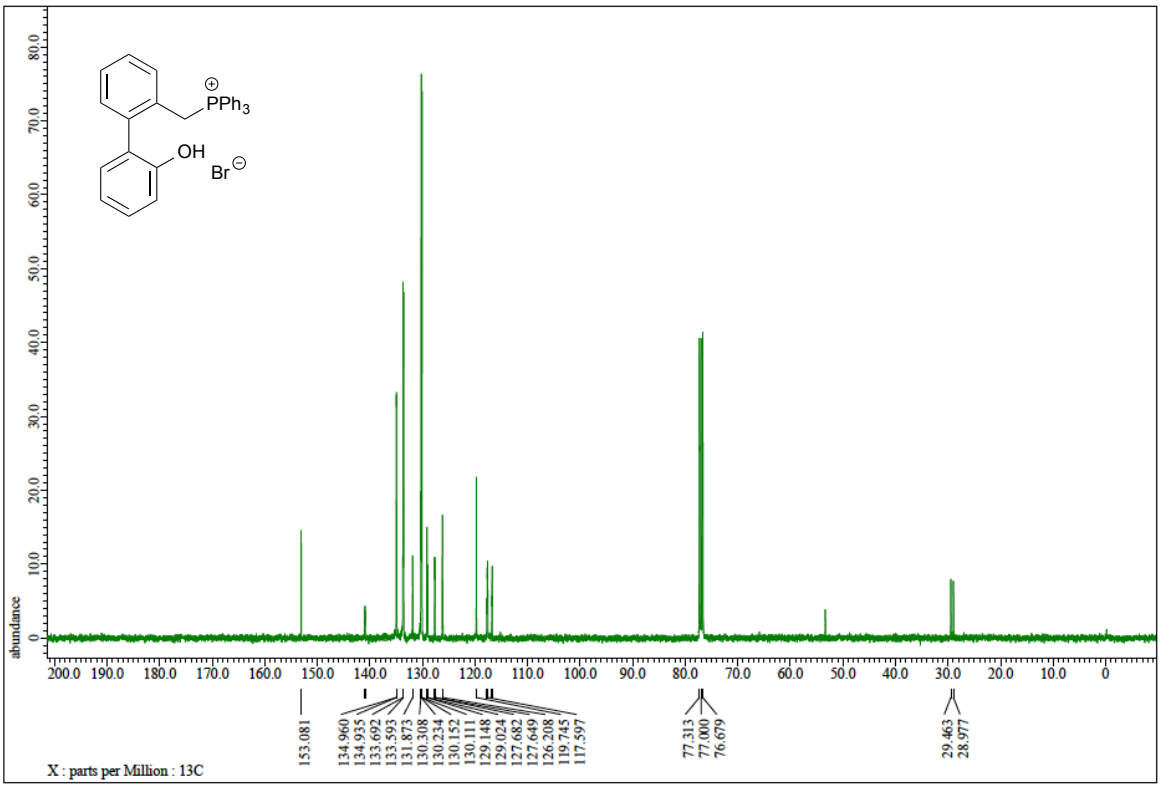

Br
OH
3.03
2.00
1.00
0.96
abundance
7.534
7.517
7.366
7.360
7.354
7.348
7.342
7.337
7.319
7.298
7.243
6.993
6.936
6.931
6.927
6.891
6.888
4.475
0.000
X : parts per Million : 1H

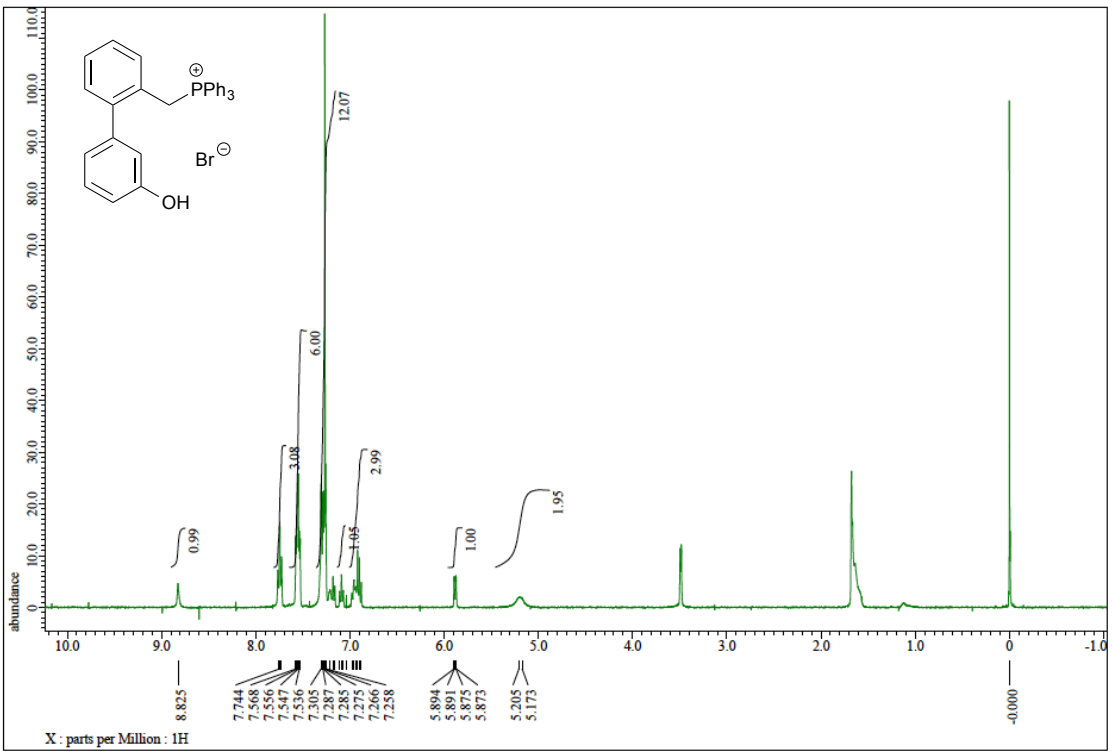

Br
OH
abundance
155.188
141.736
141.522
135.018
130.909
130.193
129.567
128.481
128.036
121.606
115.950
114.476
77.313
77.000
76.679
32.254
X : parts per Million : 13C

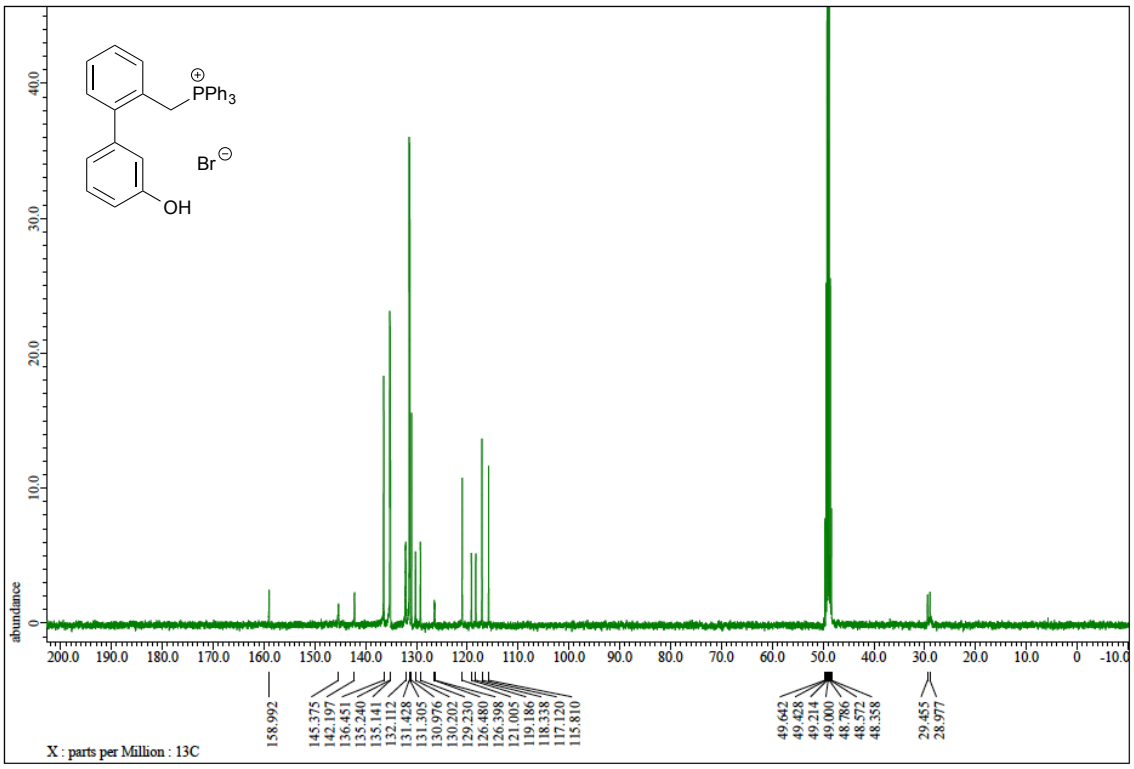

Br
OH
abundance
3.95
2.01
2.00
1.05
0.98
0.88
7.528
7.504
7.349
7.347
7.343
7.337
7.327
7.323
7.262
7.246
7.233
7.224
6.926
6.921
6.910
6.904
4.468
0.000
X : parts per Million : 1H

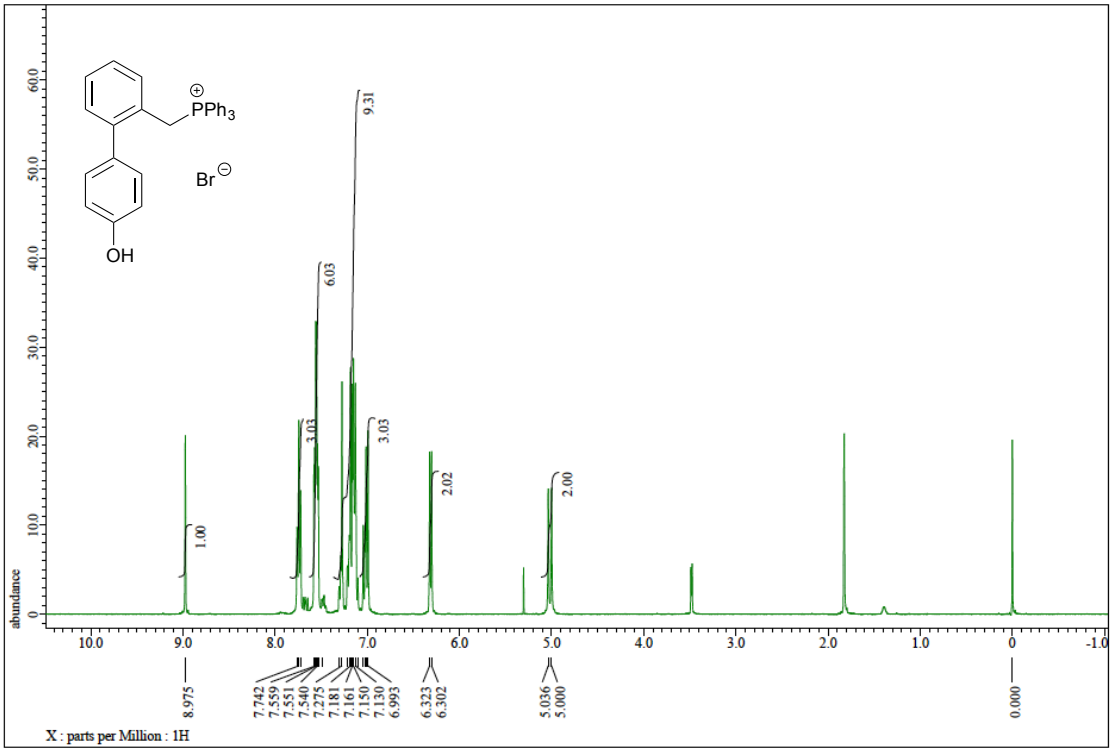

Br
OH
abundance
154.917
141.637
135.190
132.663
130.893
130.498
130.259
128.481
127.674
115.184
77.313
77.000
76.679
32.501
X : parts per Million : 13C

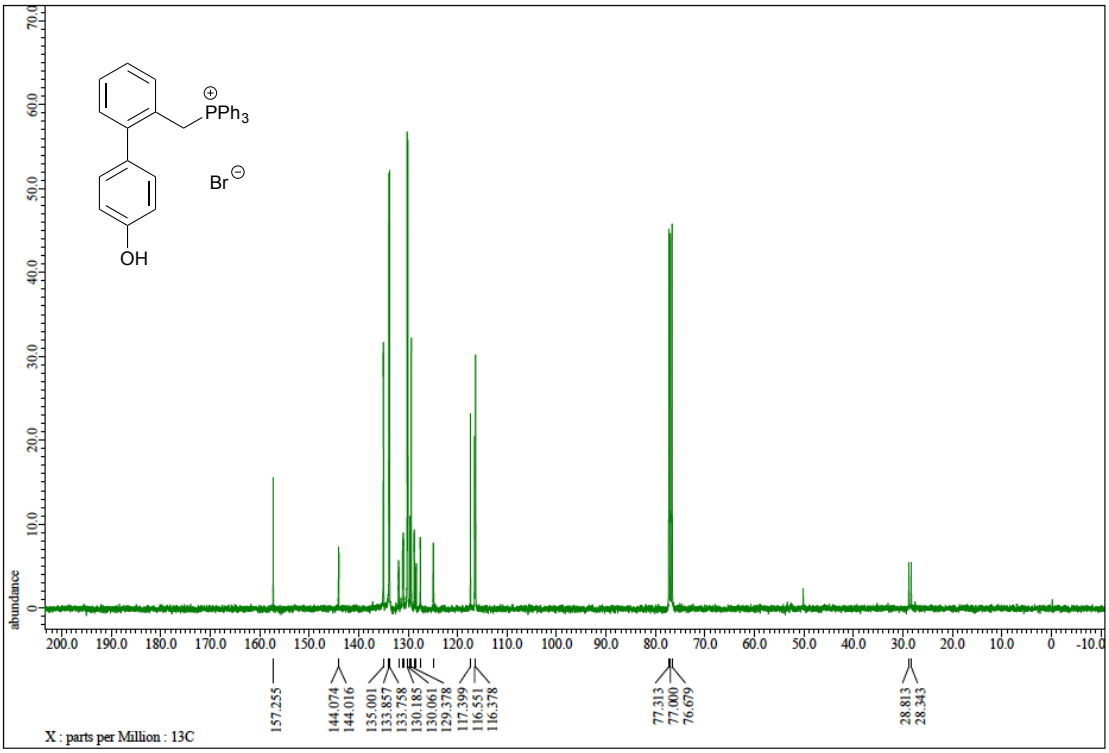

PPh3
OH
Br
abundance
X : parts per Million : 1H

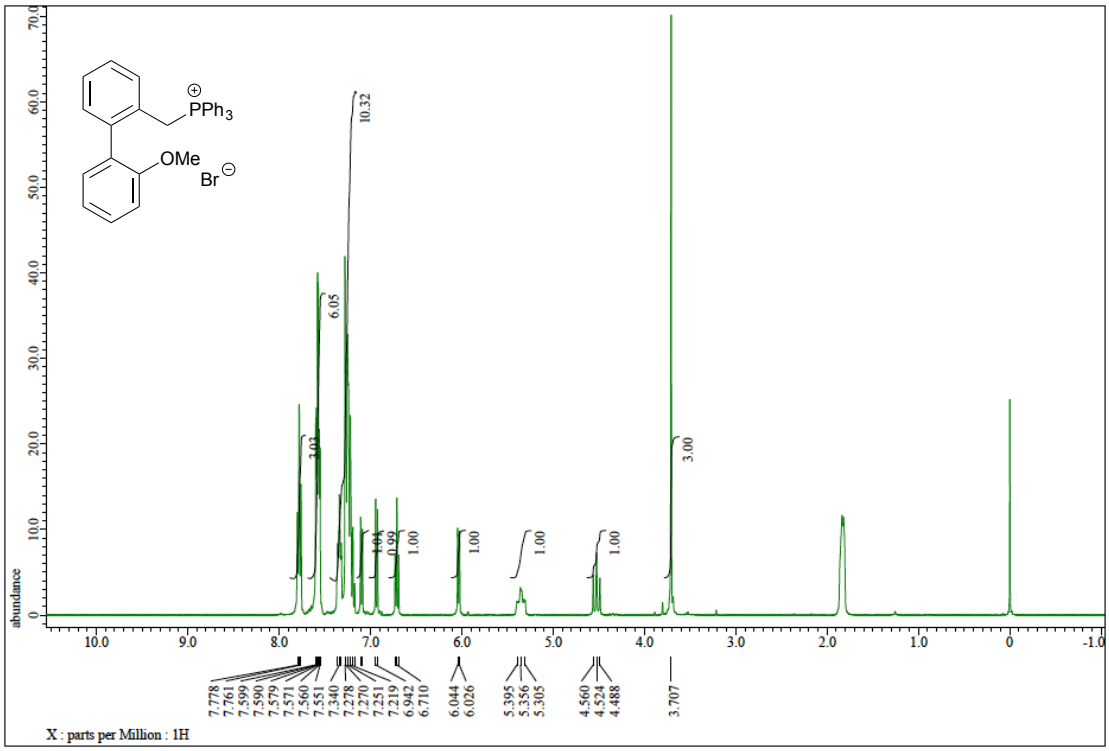

PPh3
OH
Br
abundance
X : parts per Million : 13C

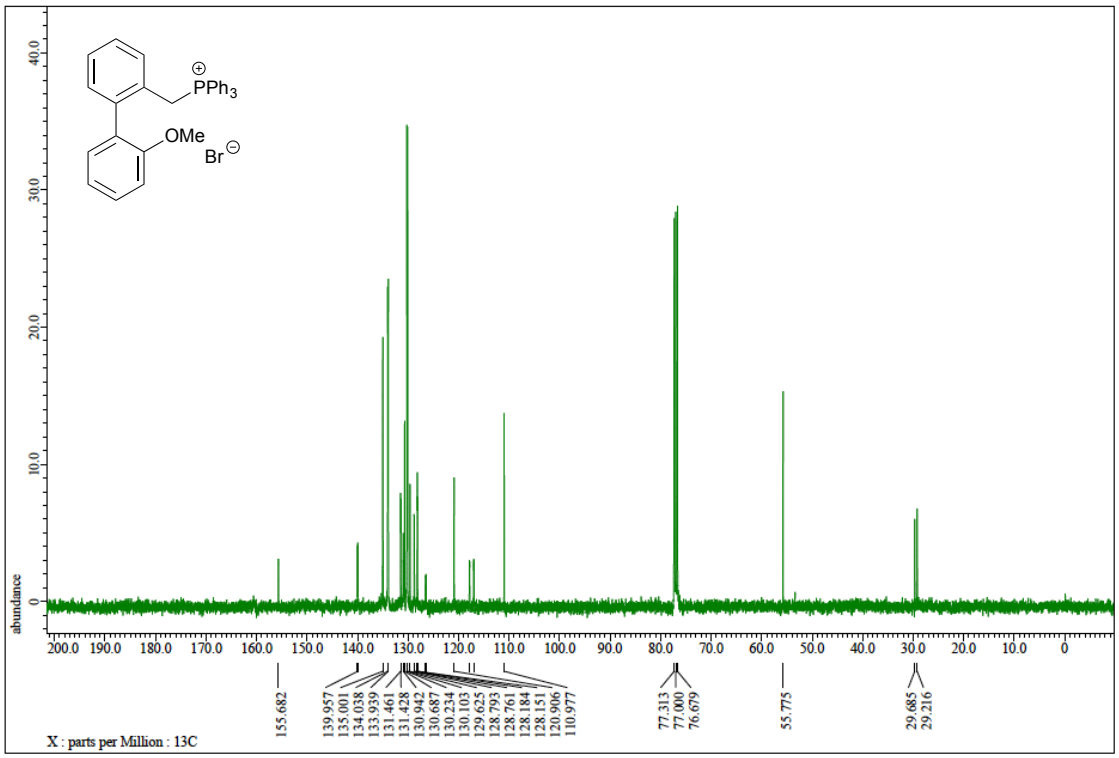

PPh3
Br
OH
12.07
6.00
3.08
2.99
1.95
1.00
1.05
0.99
abundance
X : parts per Million : 1H

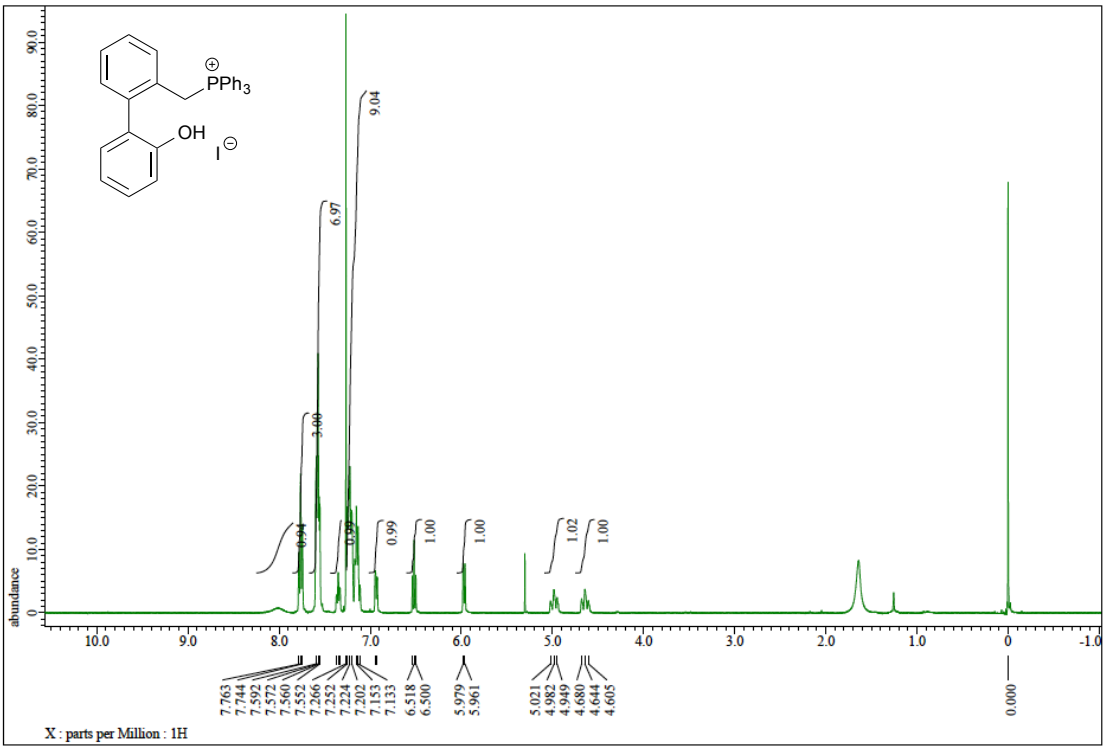

PPh3
Br
OH
abundance
X : parts per Million : 13C

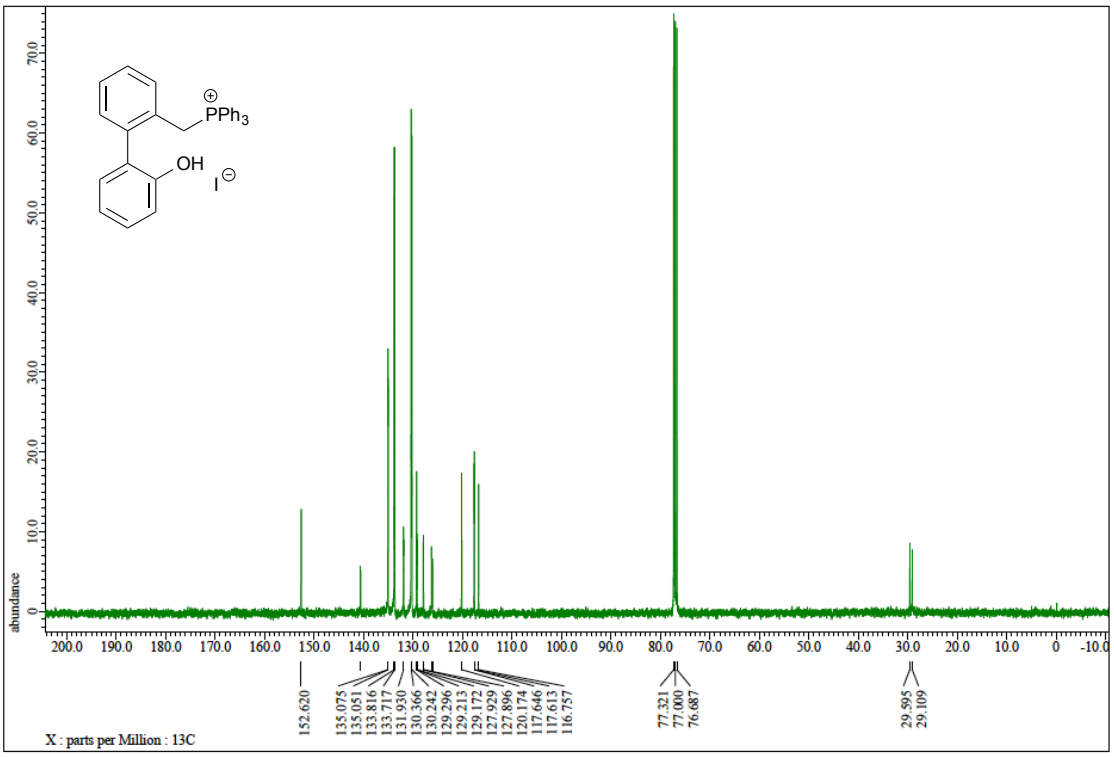

PPh3
Br
OH
9.31
6.03
3.03
3.03
2.02
2.00
1.00
abundance
X : parts per Million : 1H

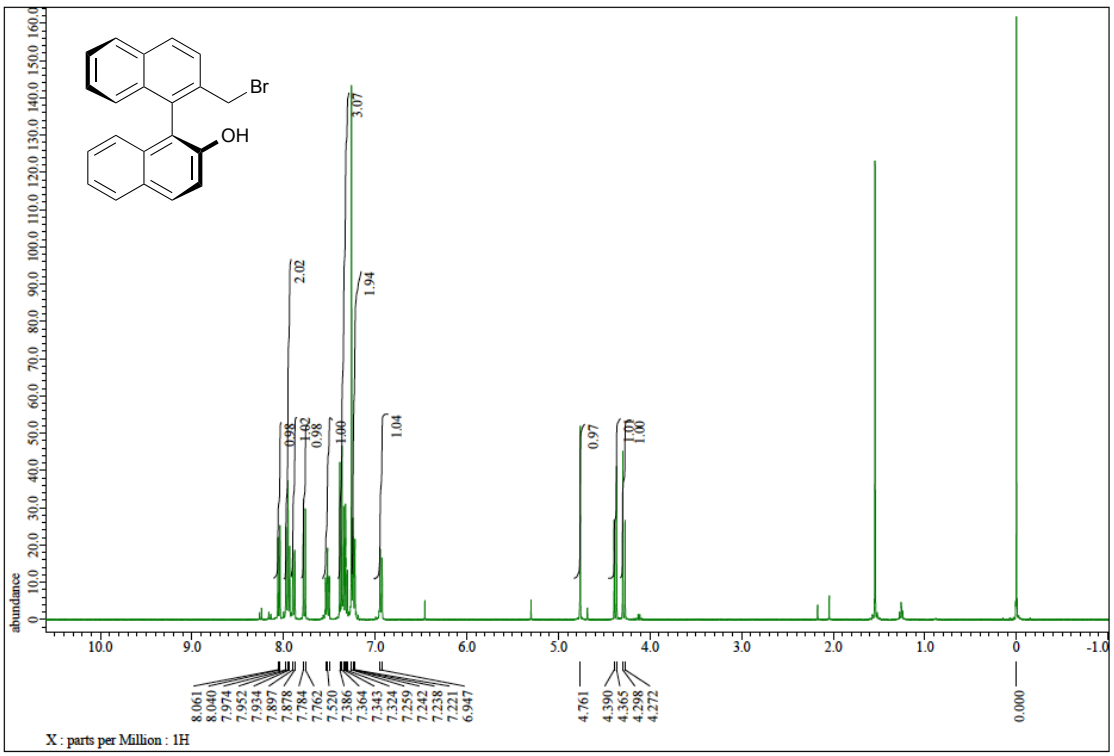

PPh3
Br
OH
abundance
X : parts per Million : 13C

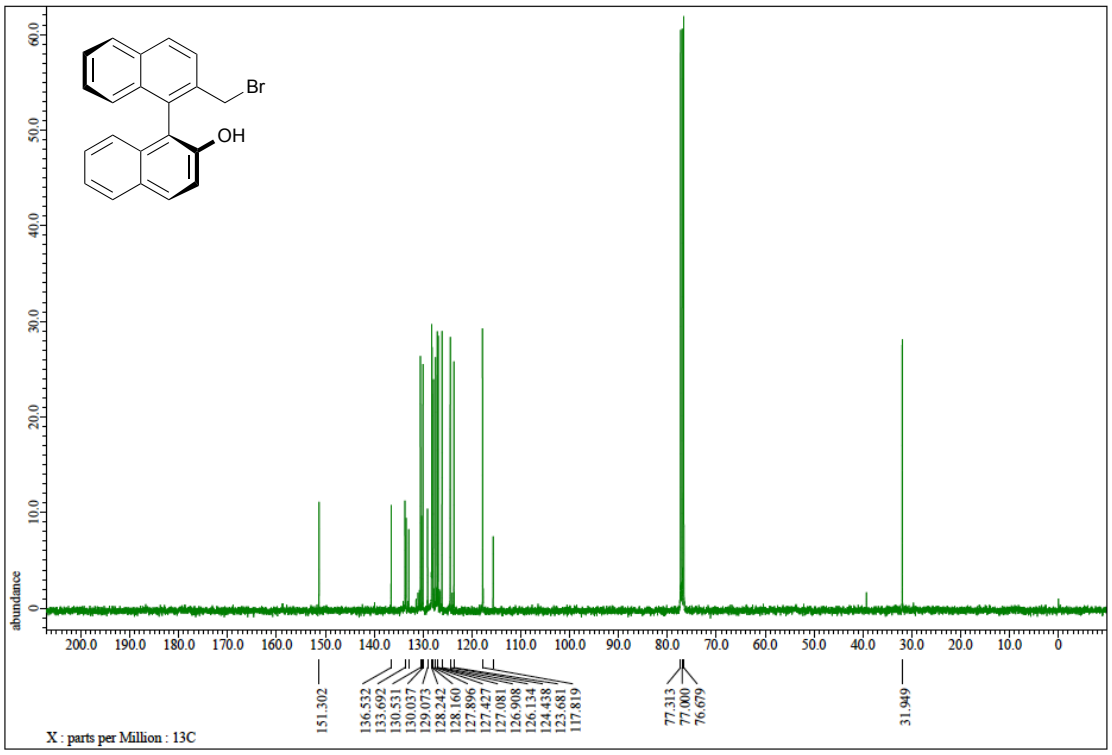

PPh3
OMe
Br
10.32
6.05
3.03
1.01
0.99
1.00
1.00
1.00
1.00
3.00
abundance
X : parts per Million : 1H

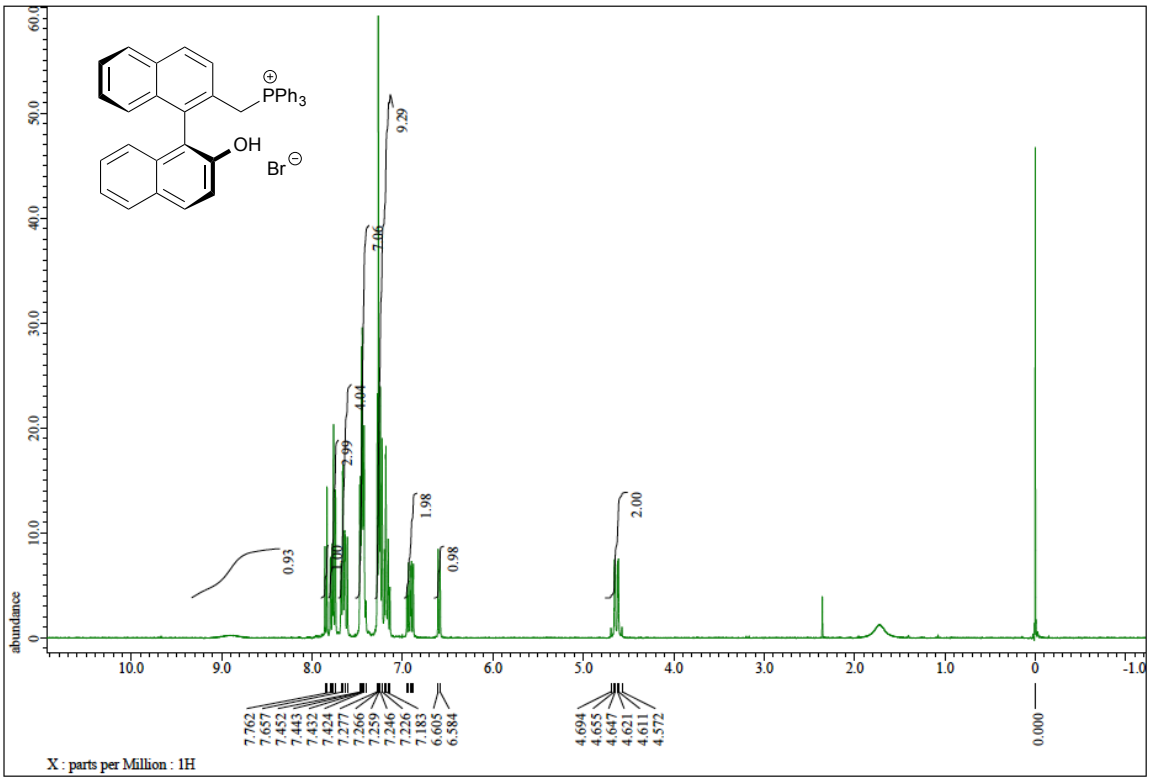

PPh3
OMe
Br
abundance
X : parts per Million : 13C

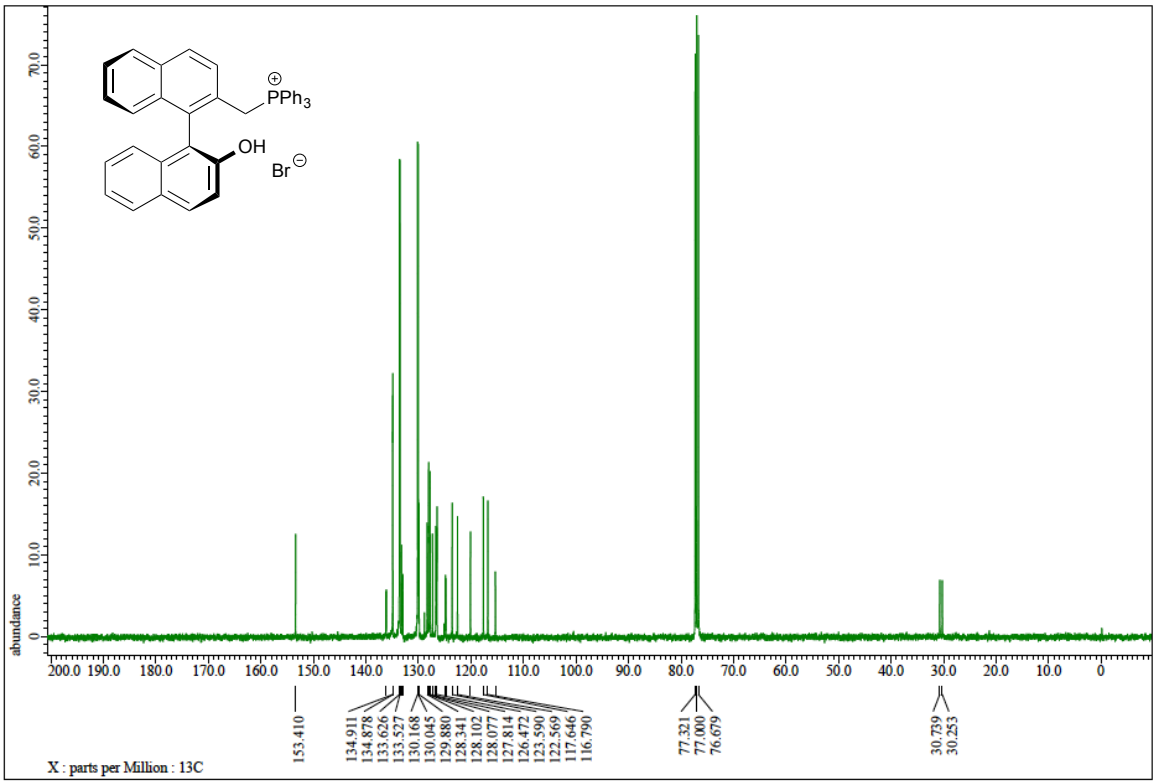

PPh3
OH
I
abundance
X : parts per Million : 1H

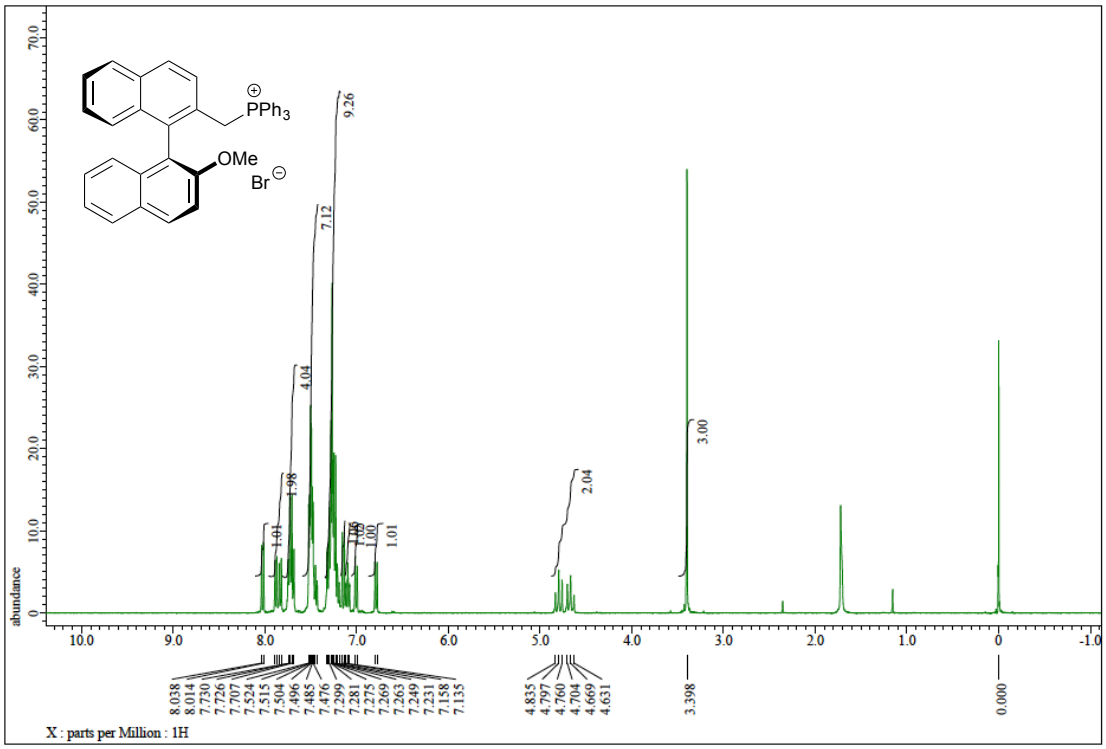

PPh3
OH
I
abundance
X : parts per Million : 13C

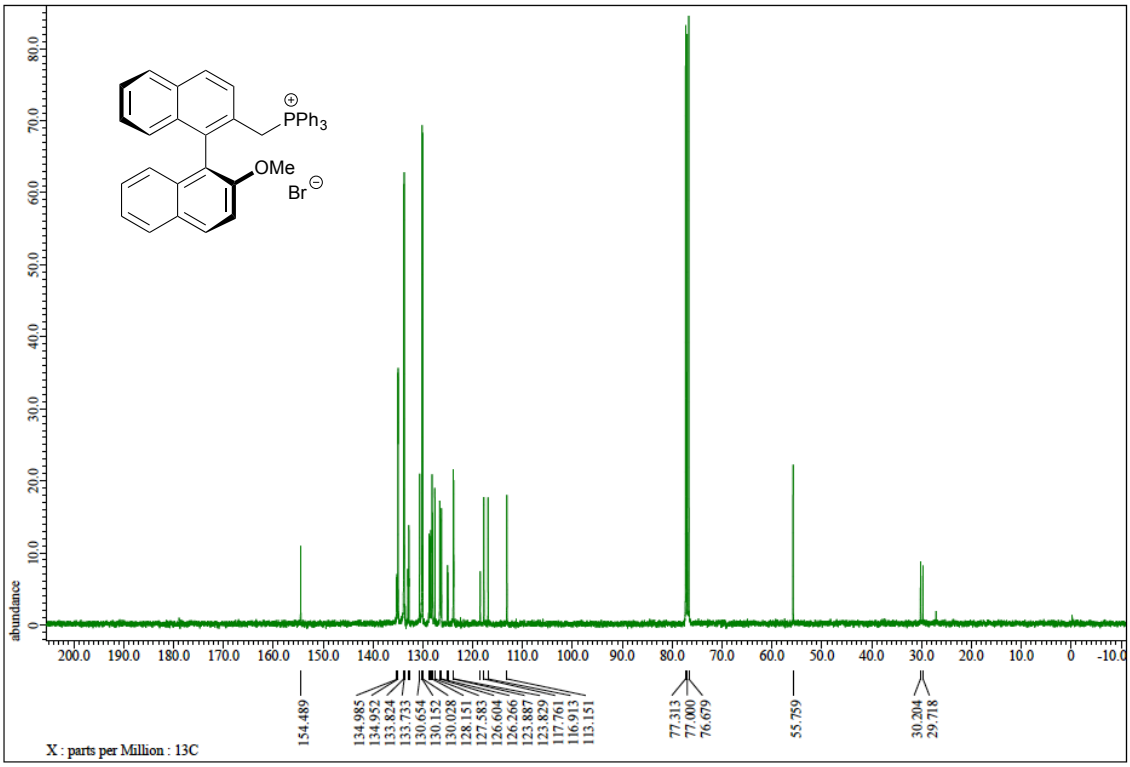

Br
OH
abundance
X : parts per Million : 1H

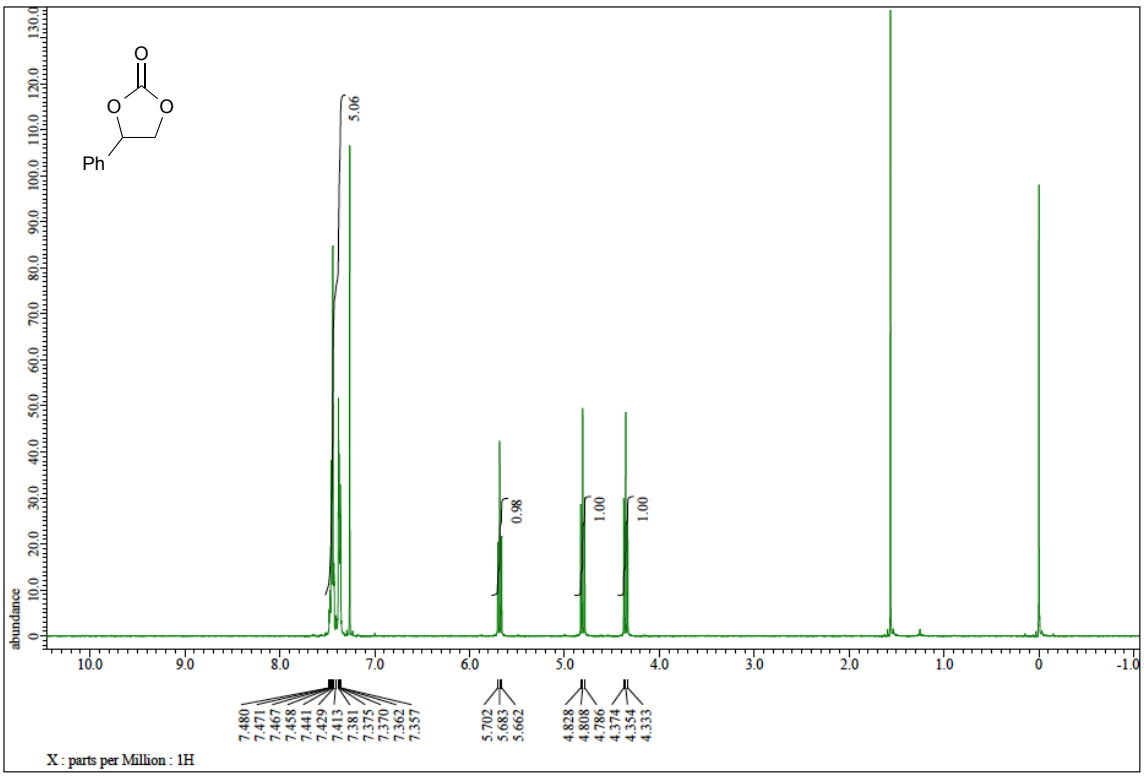

Br
OH
abundance
X : parts per Million : 13C

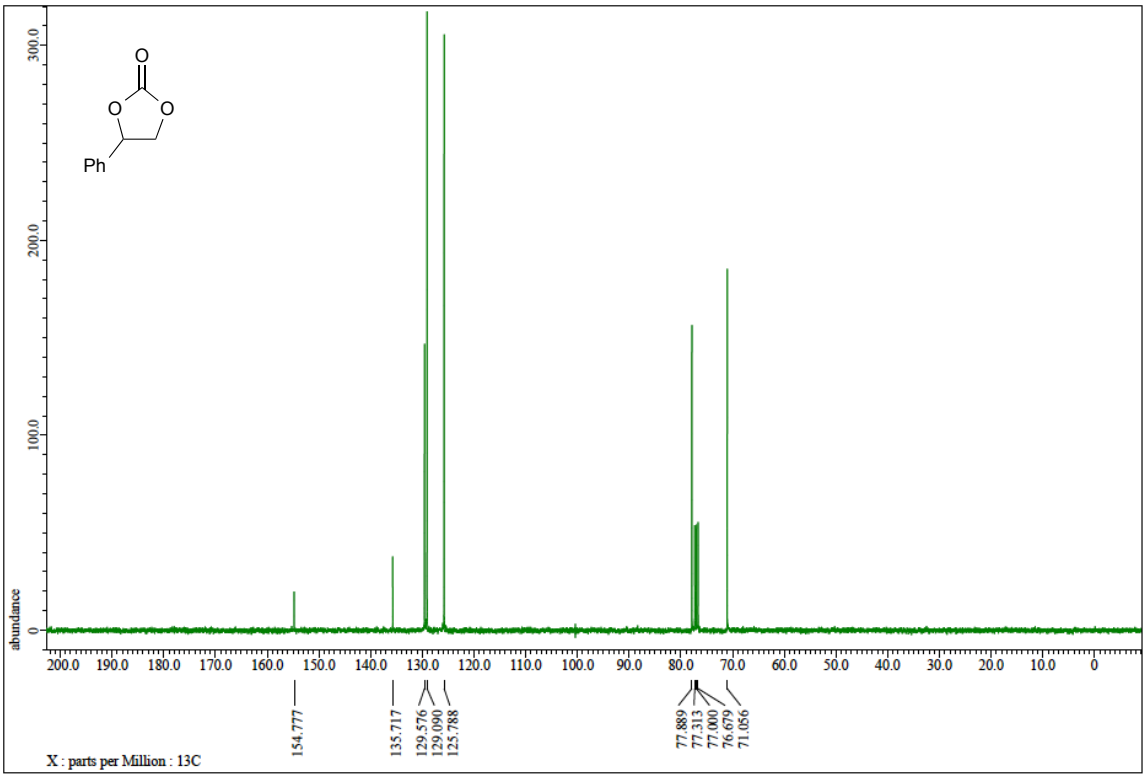

PPh3
OH
Br
9.29
7.96
4.04
2.99
2.00
1.98
1.00
0.98
0.93
abundance
X : parts per Million : 1H

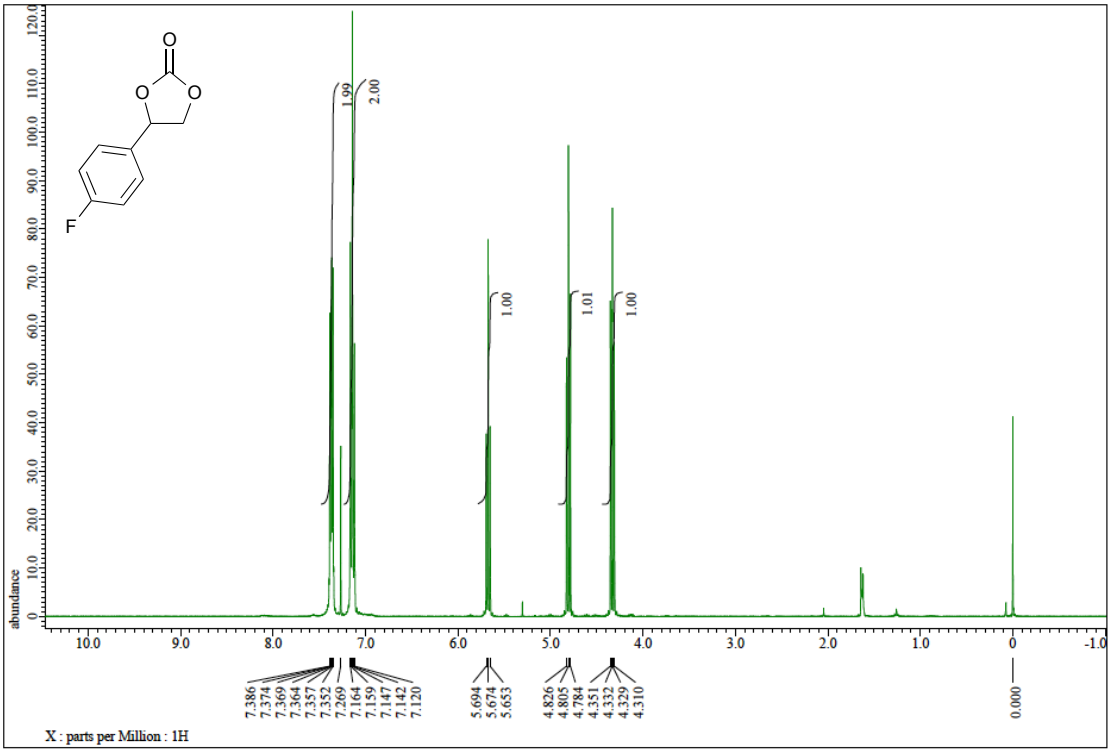

PPh3
OH
Br
abundance
X : parts per Million : 13C

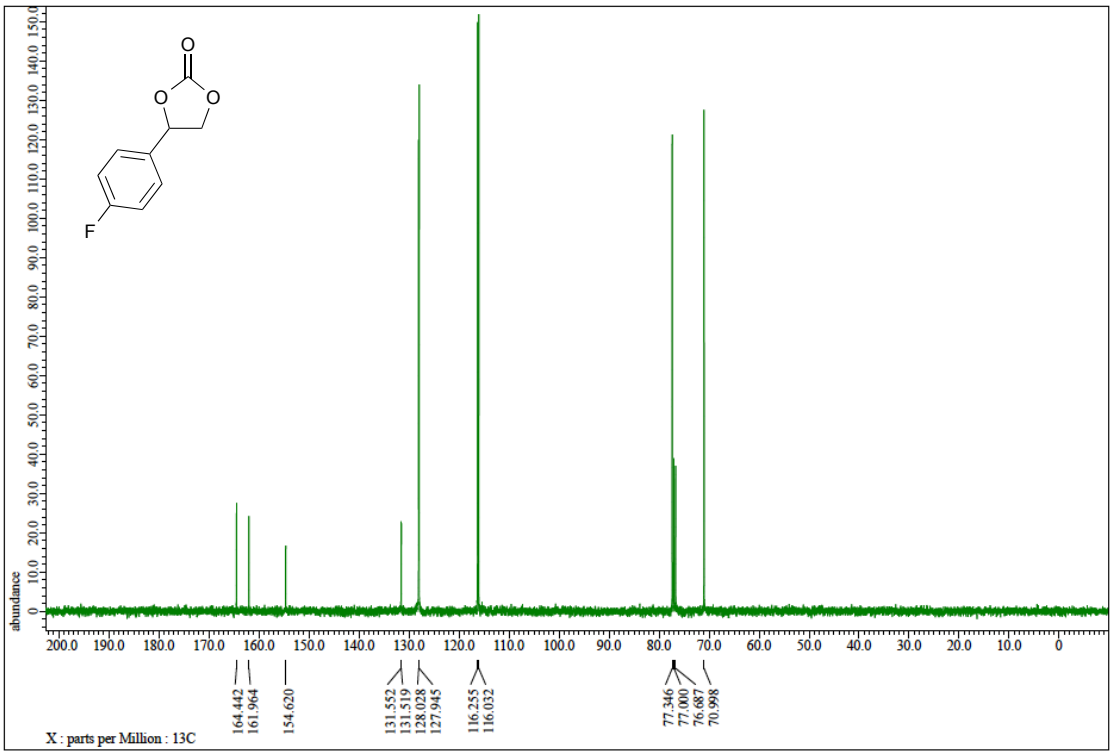

PPh3
OMe
Br
abundance
X : parts per Million : 1H

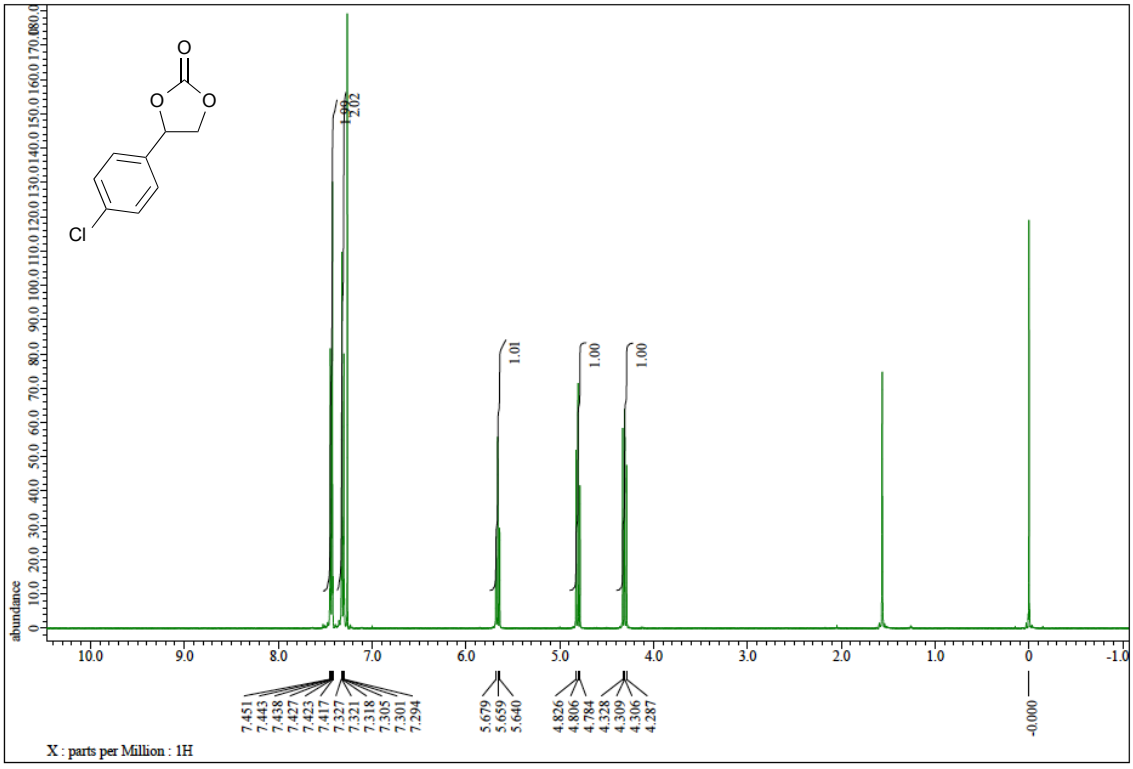

PPh3
OMe
Br
abundance
X : parts per Million : 13C

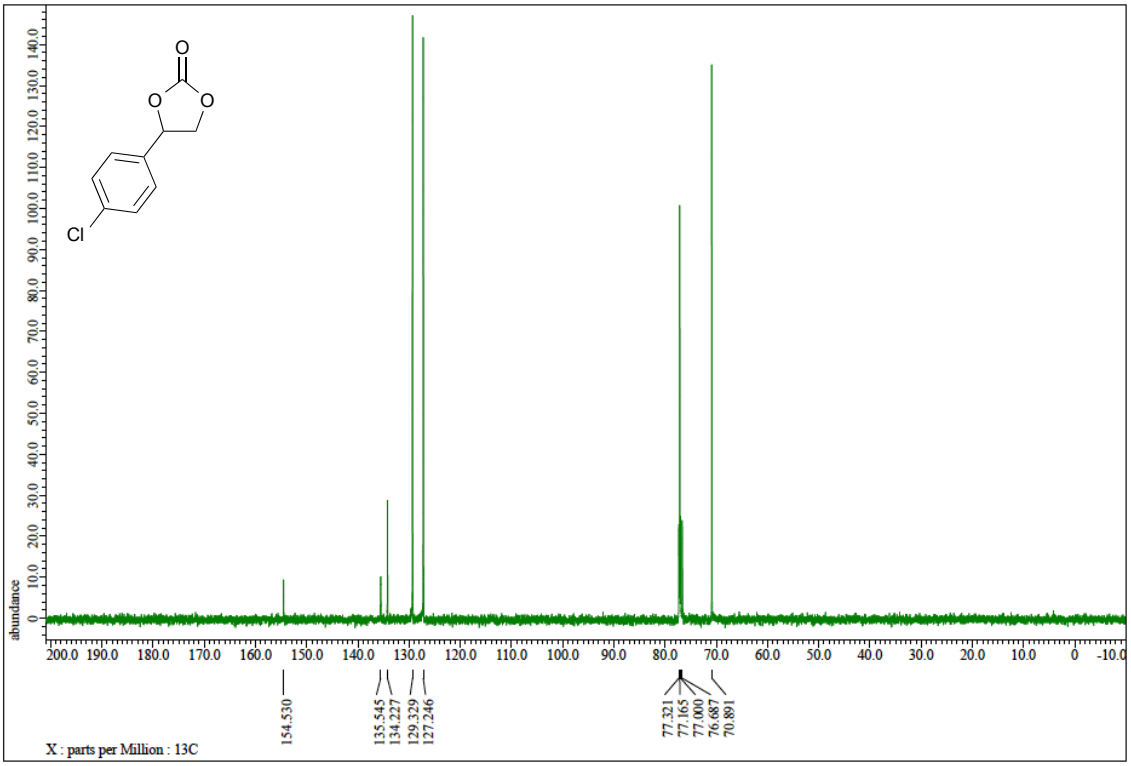

O
O
O
Ph
5.06
0.98
1.00
1.00
abundance
X : parts per Million : 1H
7.480
7.471
7.467
7.458
7.441
7.429
7.413
7.381
7.375
7.370
7.362
7.357
5.702
5.683
5.662
4.828
4.808
4.786
4.374
4.354
4.333

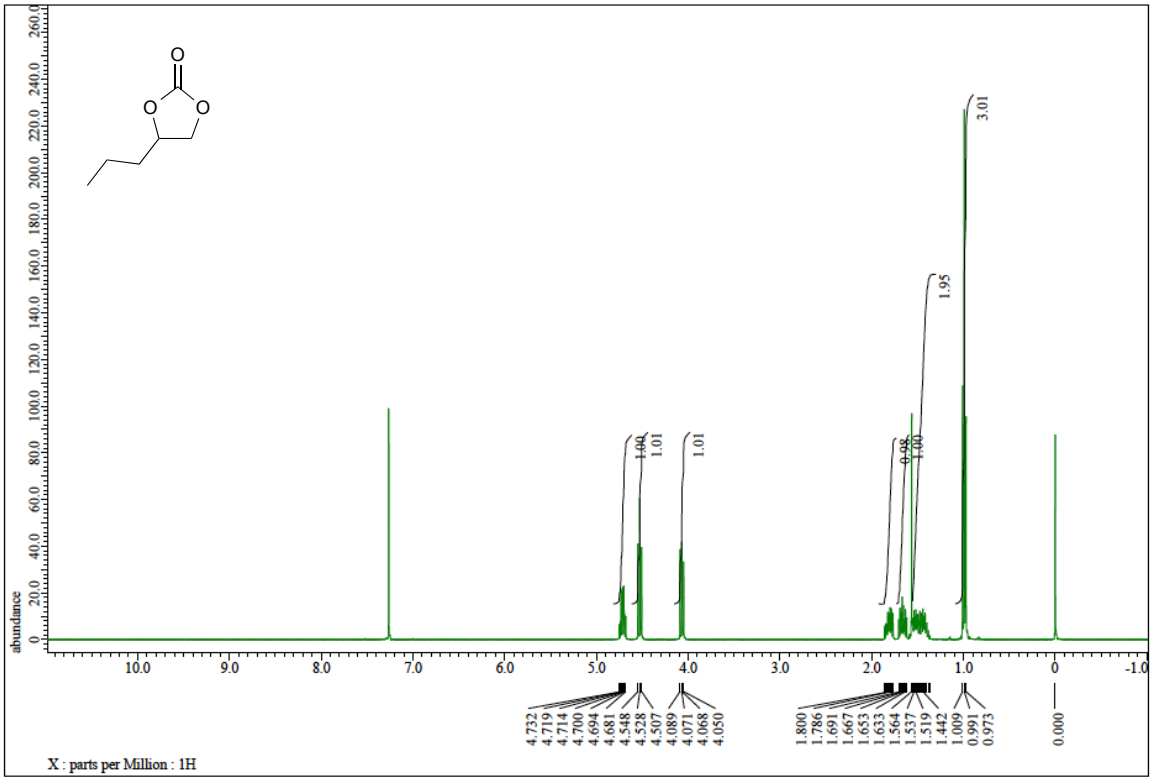

O
O
O
Ph
abundance
X : parts per Million : 13C
154.777
135.717
129.576
129.090
125.788
77.889
77.313
77.000
76.679
71.056

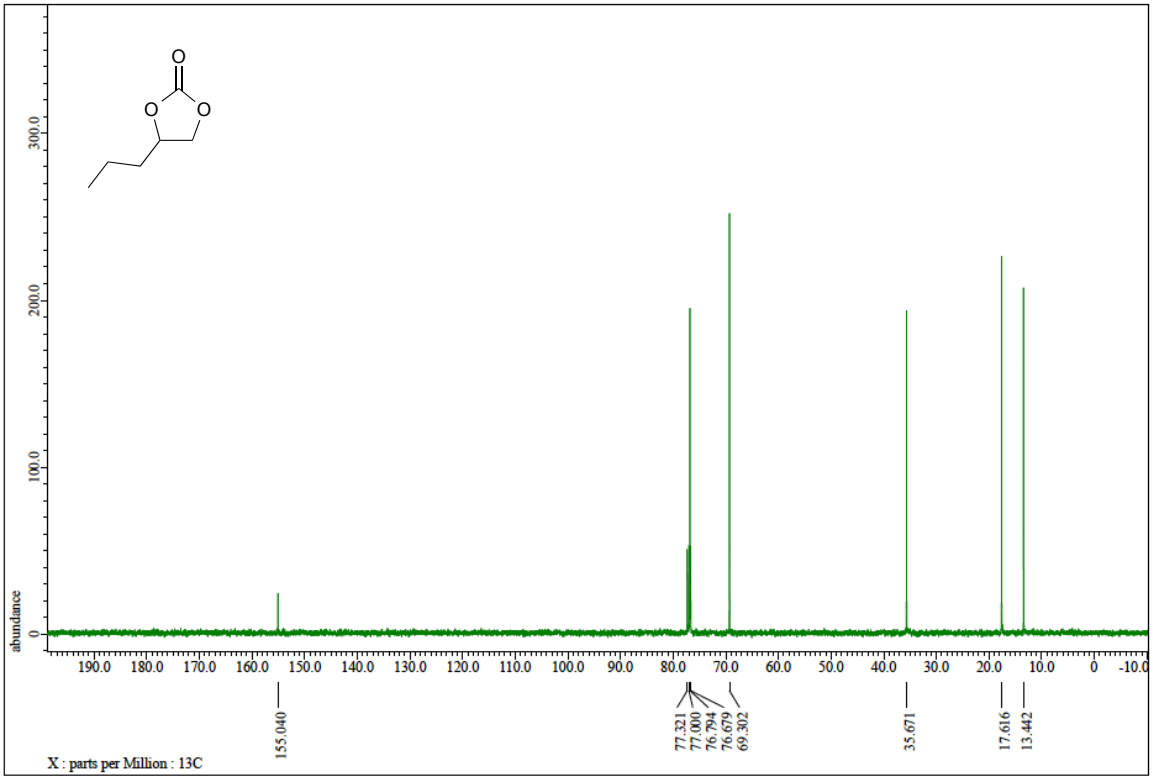

O
O
O
F
1.99
2.00
1.00
1.01
1.00
abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.386
7.374
7.369
7.364
7.357
7.352
7.269
7.164
7.159
7.147
7.142
7.120
5.694
5.674
5.653
4.826
4.805
4.784
4.351
4.332
4.329
4.310
0.000
X : parts per Million : 1H

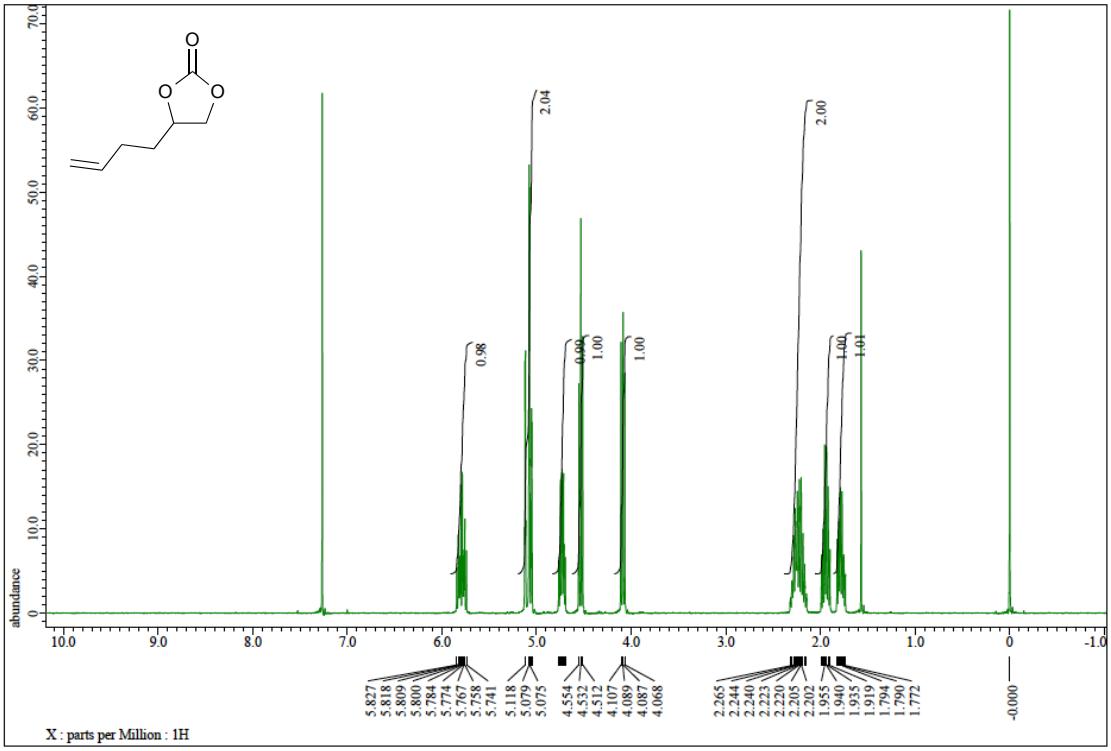

O
O
O
F
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
164.442
161.964
154.620
131.552
131.519
128.028
127.945
116.255
116.032
77.346
77.000
76.687
70.998
X : parts per Million : 13C

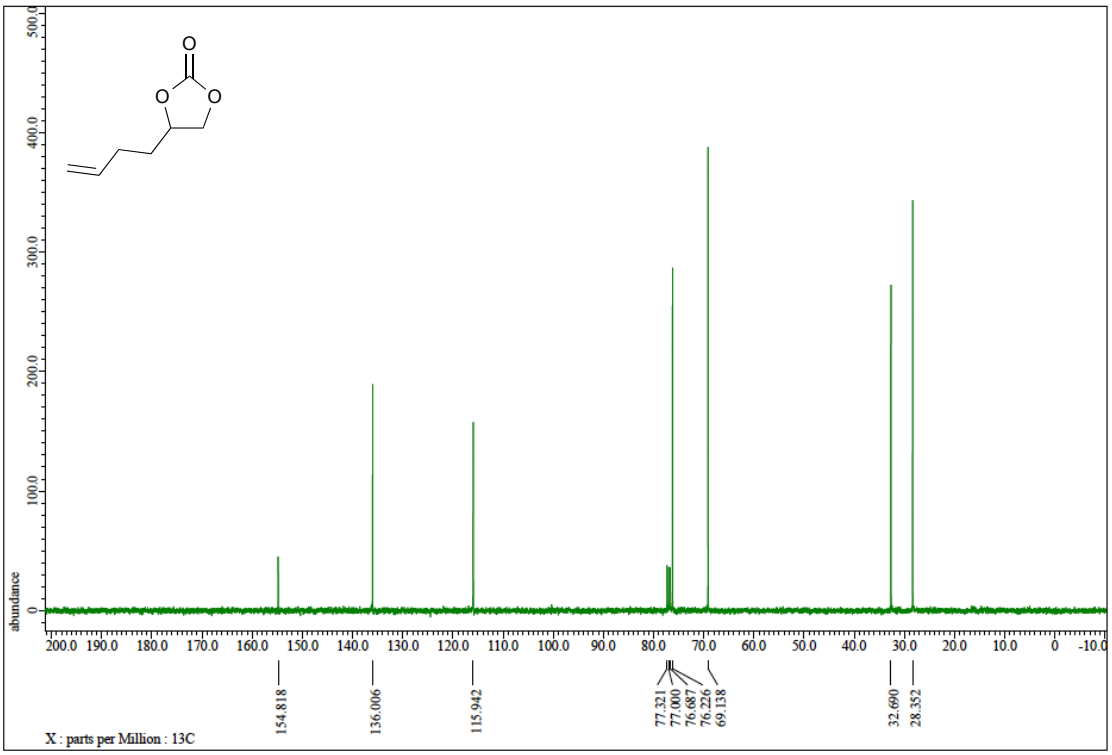

O
O
O
Cl
1.01
1.00
1.00
2.02
abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.451
7.443
7.438
7.427
7.423
7.417
7.327
7.321
7.318
7.305
7.301
7.294
5.679
5.659
5.640
4.826
4.806
4.784
4.328
4.309
4.306
4.287
-0.000
X : parts per Million : 1H

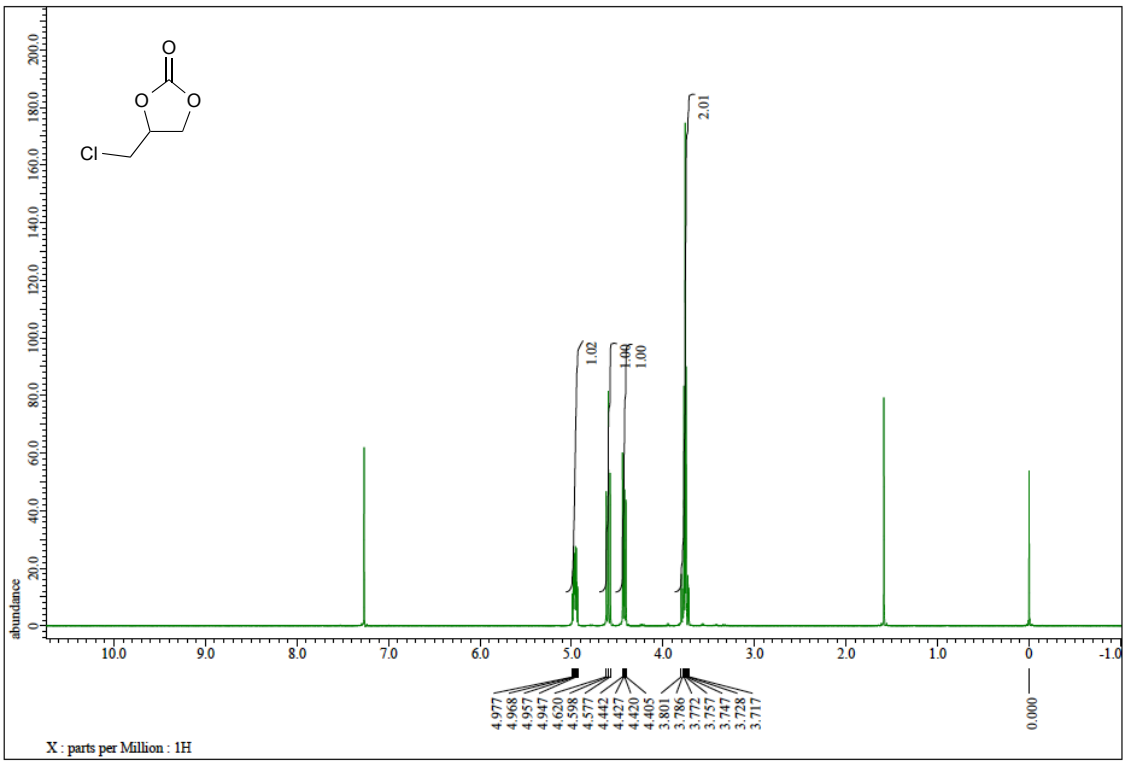

O
O
O
Cl
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
154.530
135.545
134.227
129.329
127.246
77.321
77.165
77.000
76.687
70.891
X : parts per Million : 13C

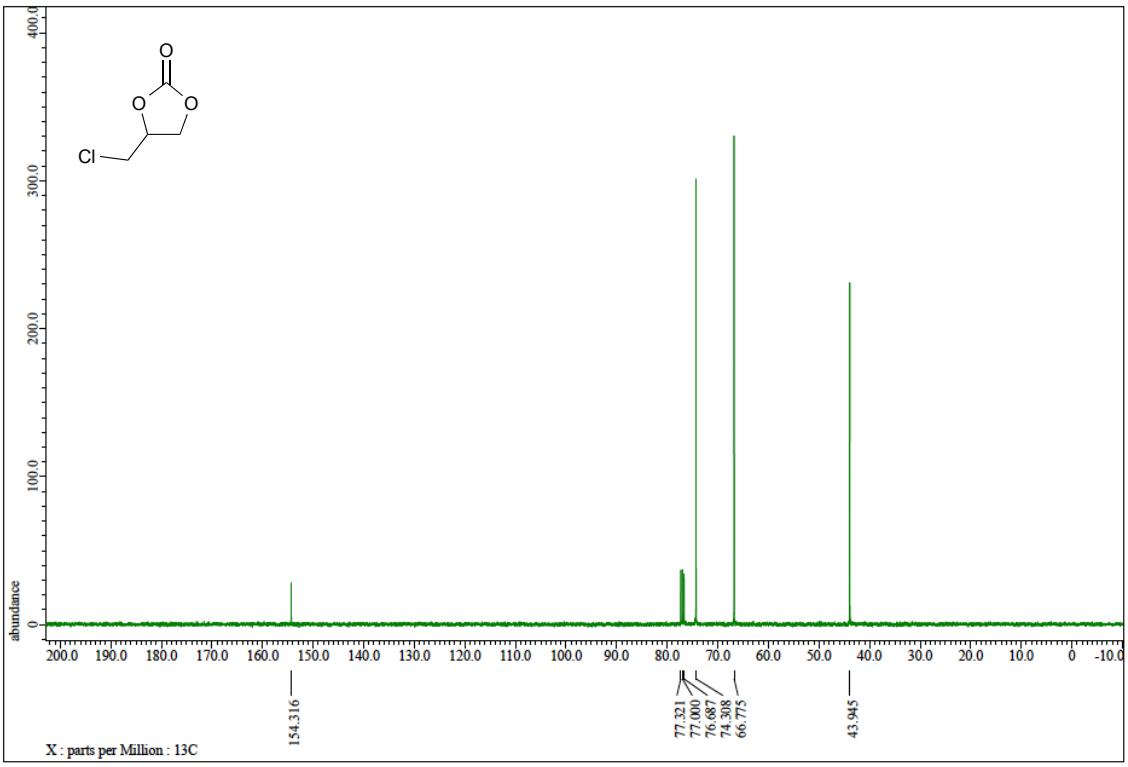

abundance
X : parts per Million : 1H
3.01
1.95
1.01
1.01
1.00
0.98
1.00
4.732
4.719
4.714
4.700
4.694
4.681
4.548
4.528
4.507
4.089
4.071
4.068
4.050
1.800
1.786
1.691
1.667
1.653
1.633
1.564
1.537
1.519
1.442
1.009
0.991
0.973
0.000

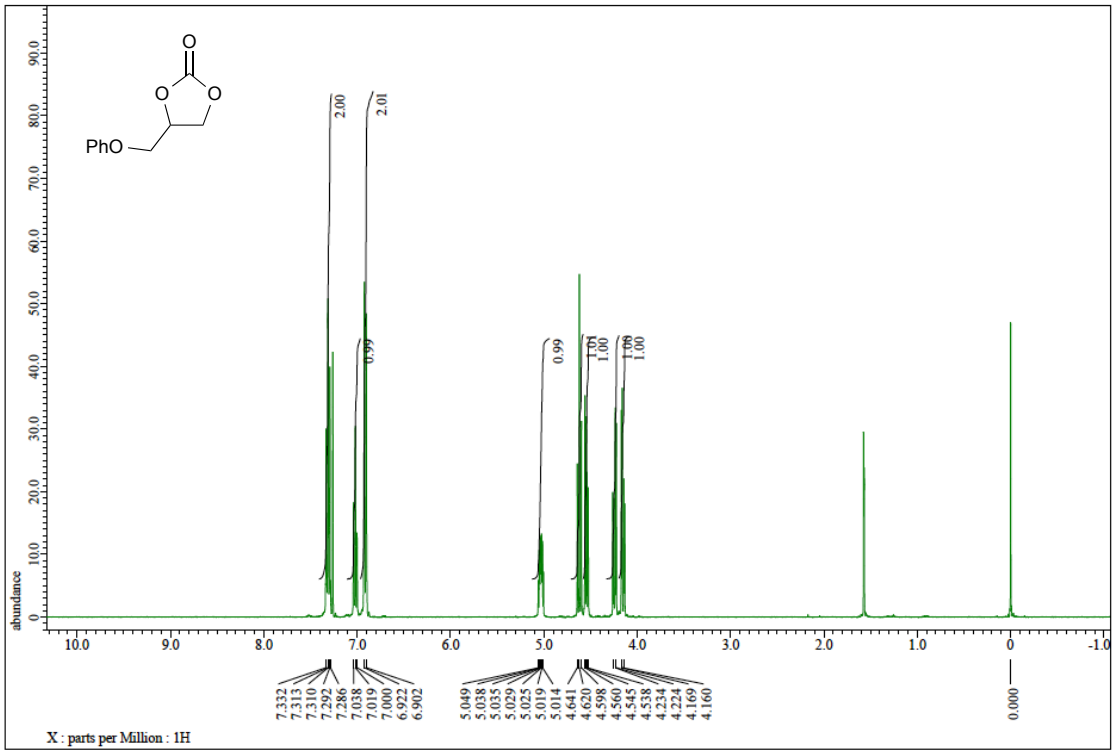

abundance
X : parts per Million : 13C
155.040
77.321
77.000
76.794
76.679
69.302
35.671
17.616
13.442

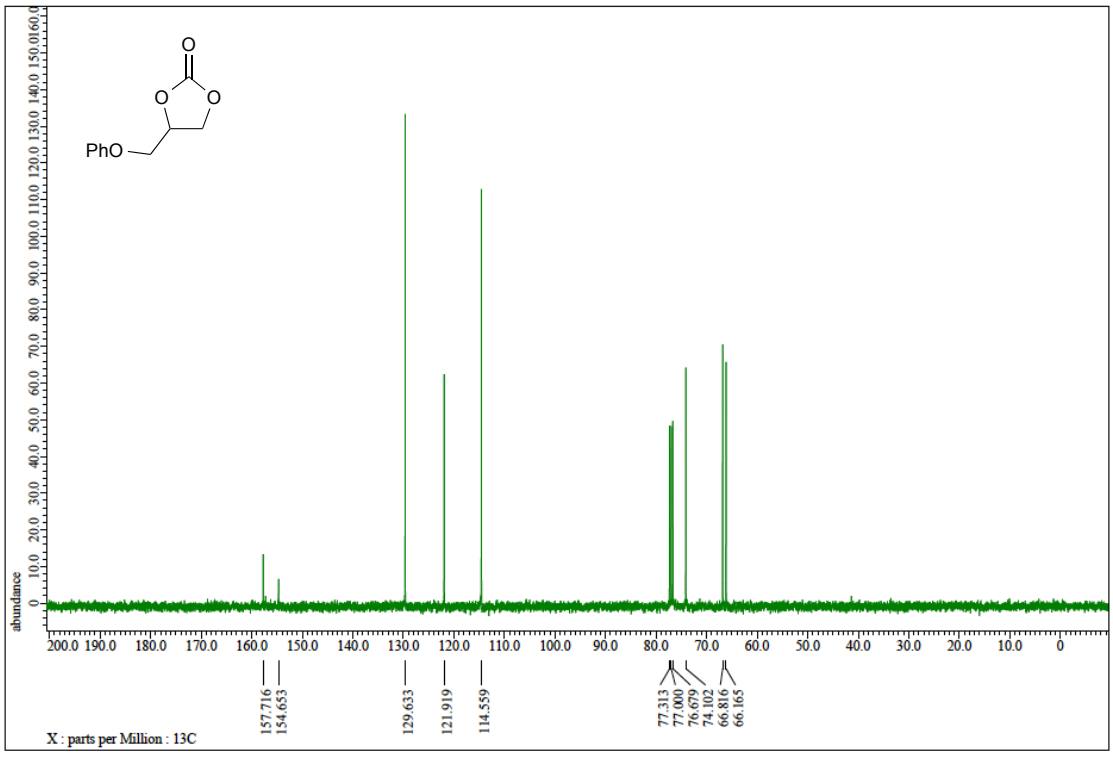

abundance
X : parts per Million : 1H
0.98
2.04
1.00
0.99
1.00
2.00
1.00
1.01
5.827
5.818
5.809
5.800
5.784
5.774
5.767
5.758
5.741
5.118
5.079
5.075
4.554
4.532
4.512
4.107
4.089
4.087
4.068
2.265
2.244
2.240
2.223
2.220
2.205
2.202
1.955
1.940
1.935
1.919
1.794
1.790
1.772
-0.000

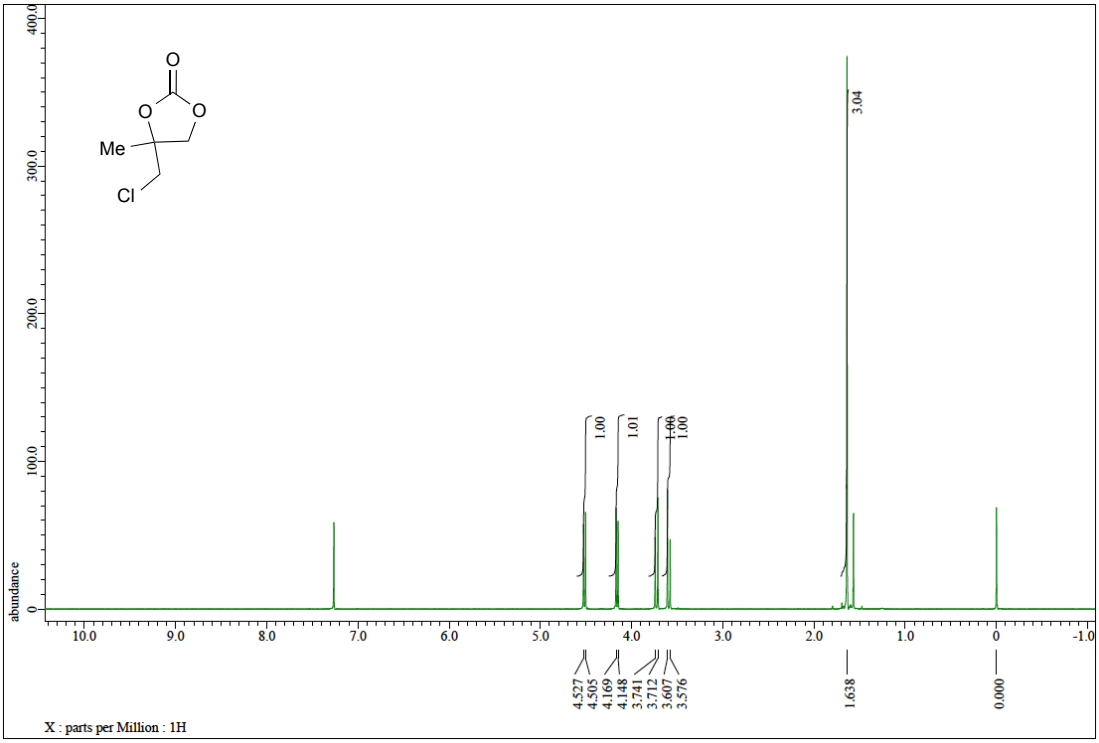

abundance
X : parts per Million : 13C
154.818
136.006
115.942
77.321
77.000
76.687
76.226
69.138
32.690
28.352

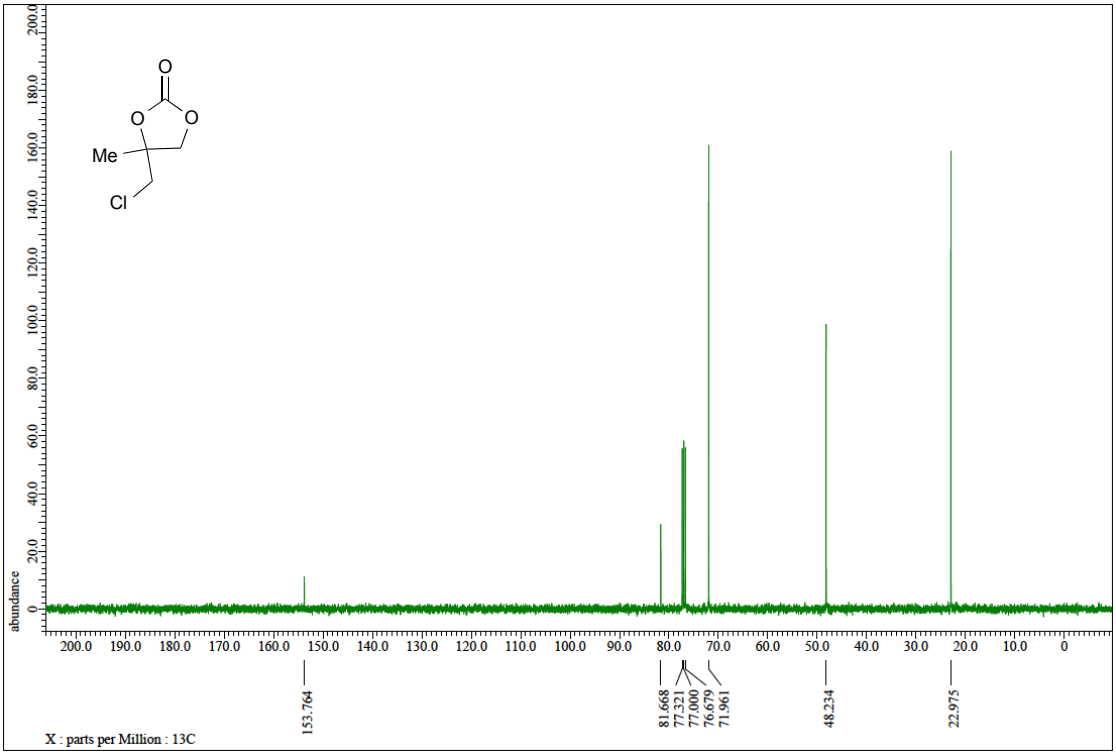

O
O
O
Cl
2.01
1.02
1.00
abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
4.977
4.968
4.957
4.947
4.620
4.598
4.577
4.442
4.427
4.420
4.405
3.801
3.786
3.772
3.757
3.747
3.728
3.717
0.000
X : parts per Million : 1H

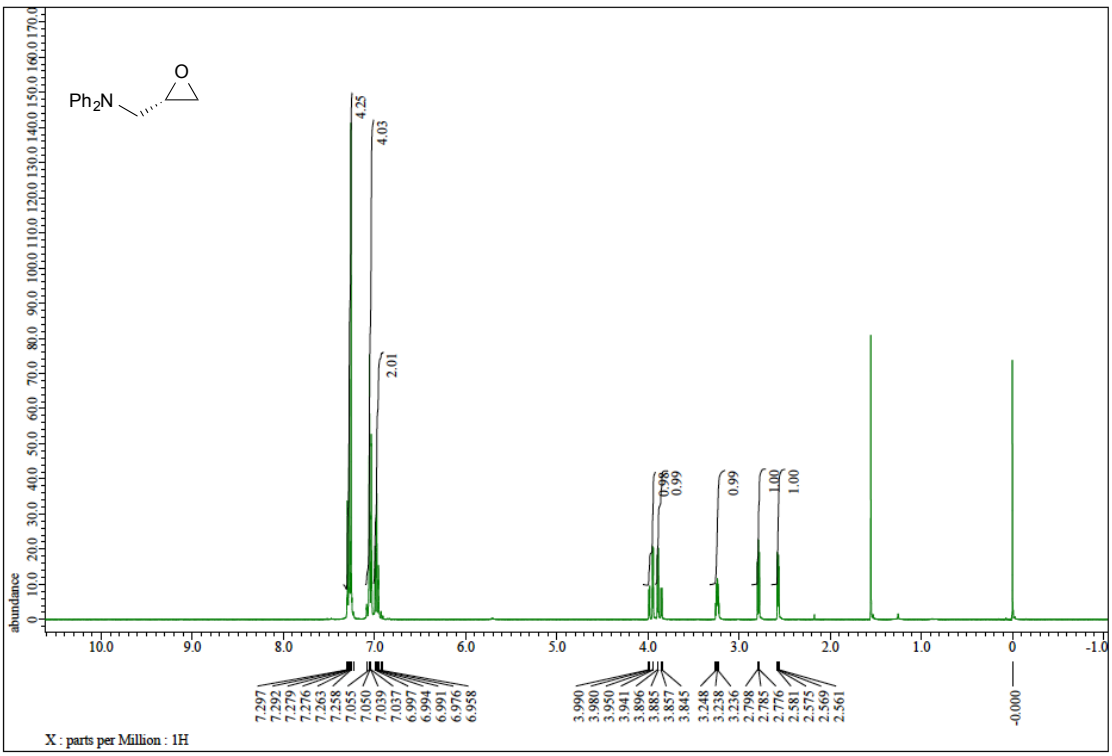

O
O
O
Cl
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
154.316
77.321
77.000
76.687
74.308
66.775
43.945
X : parts per Million : 13C

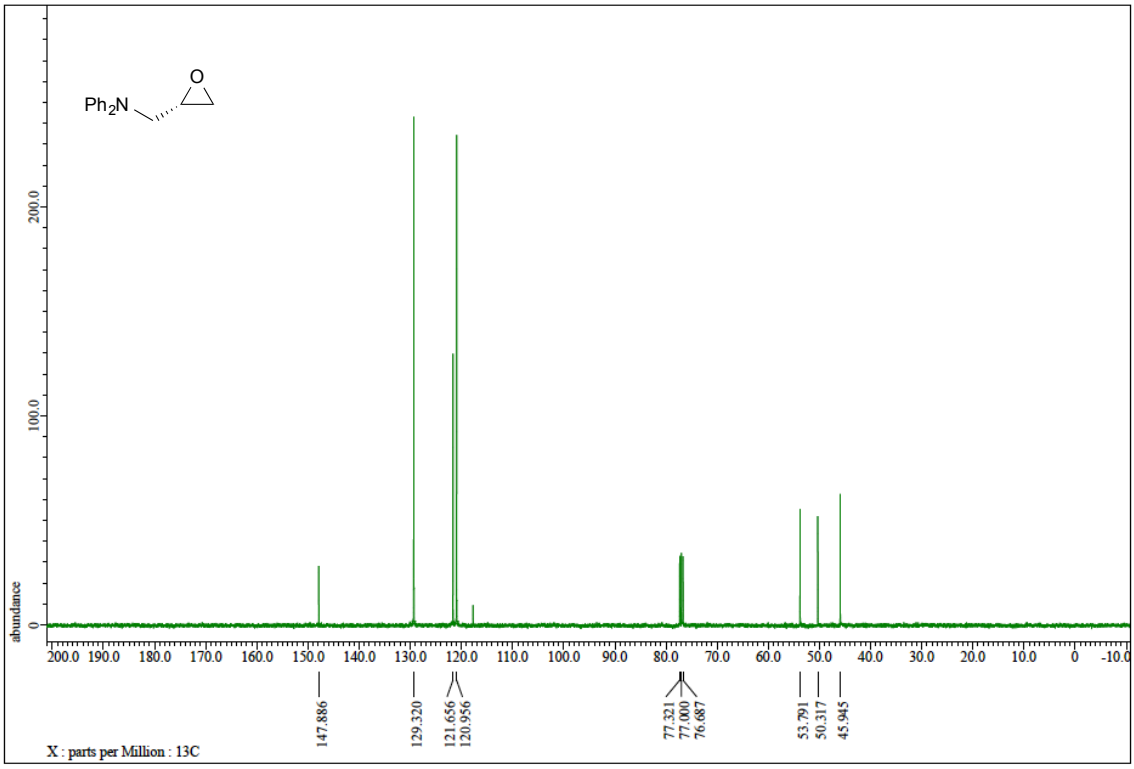

PhO
abundance
X : parts per Million : 1H

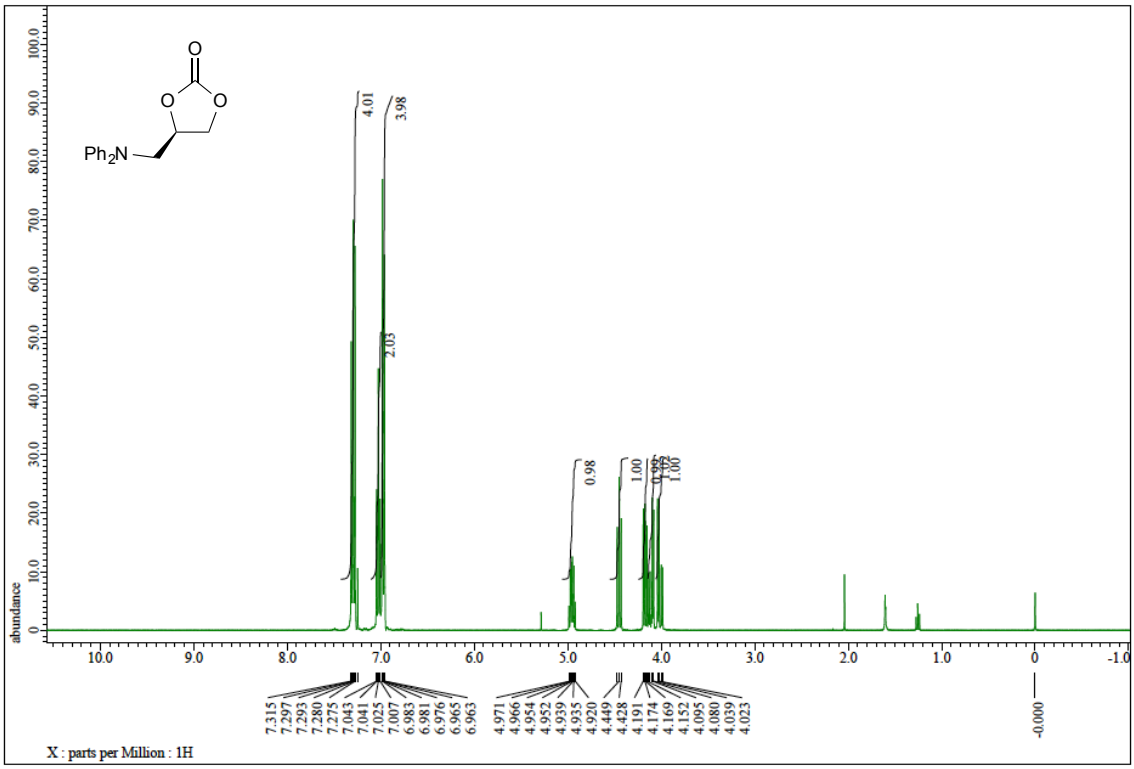

PhO
abundance
X : parts per Million : 13C

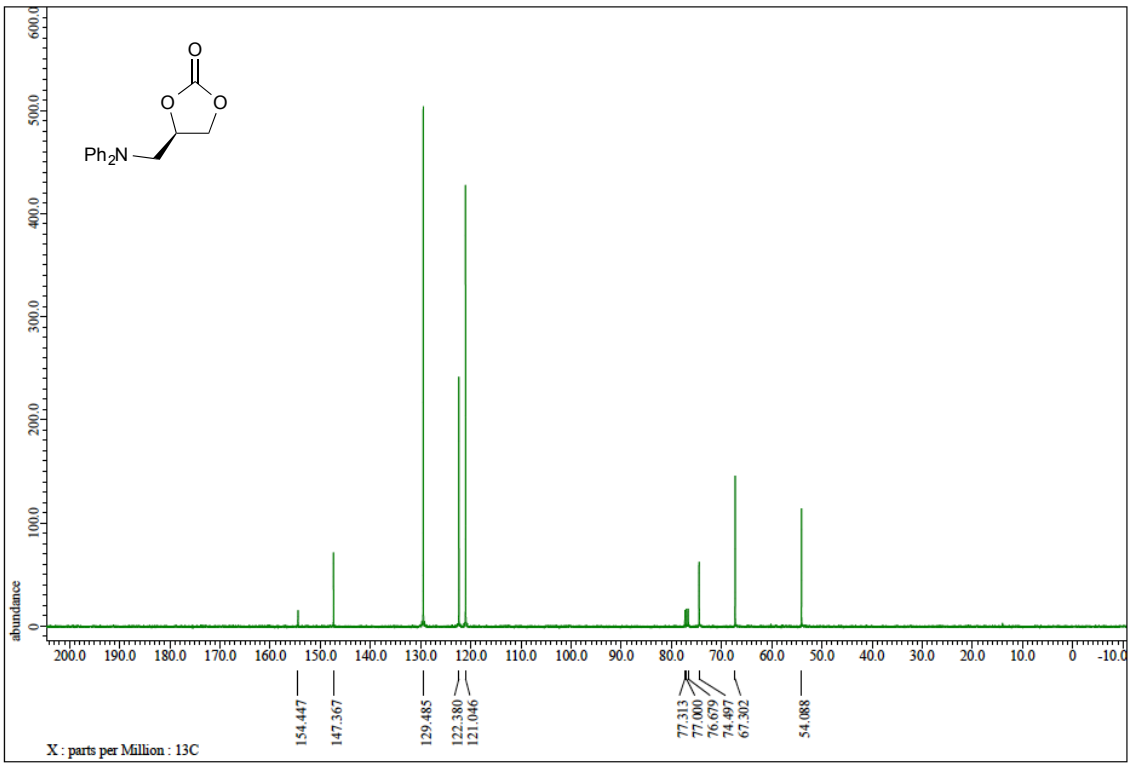

O
O
O
Me
Cl
abundance
400.0
300.0
200.0
100.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
1.00
1.01
1.00
1.00
3.04
4.527
4.505
4.169
4.148
3.741
3.712
3.607
3.576
1.638
0.000
X : parts per Million : 1H

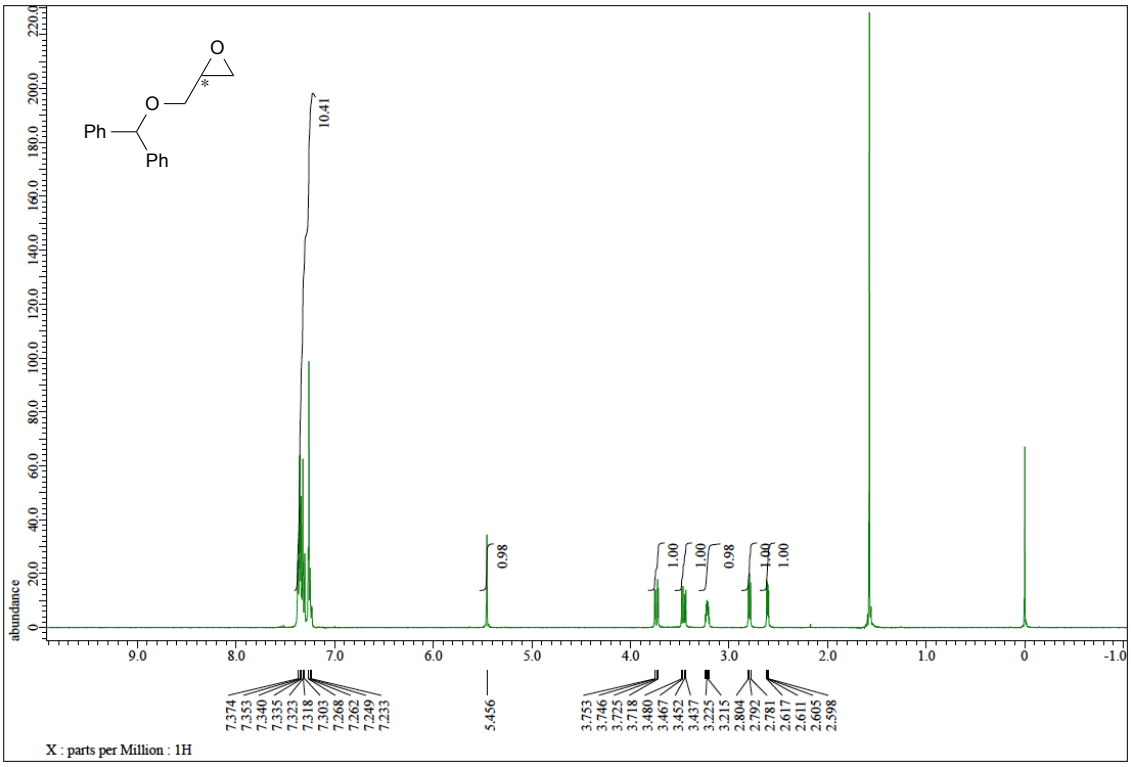

O
O
O
Me
Cl
abundance
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
153.764
81.668
77.321
77.000
76.679
71.961
48.234
22.975
X : parts per Million : 13C

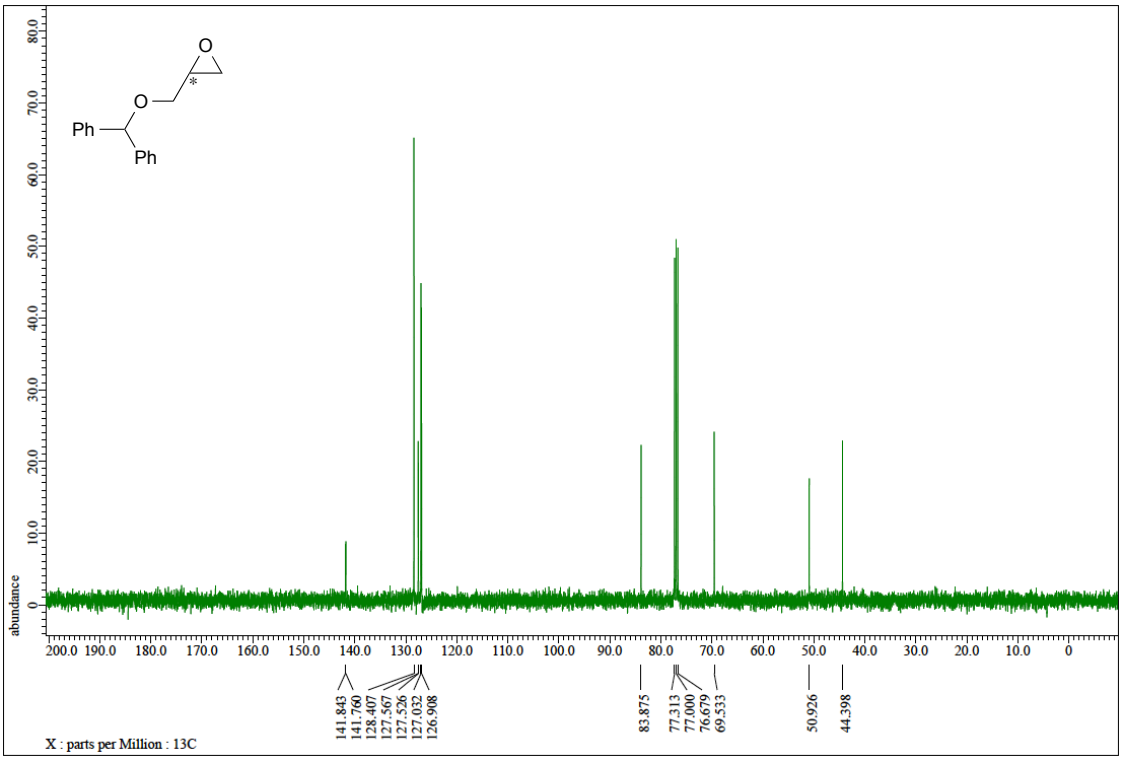

Ph2N
O
4.25
4.03
2.01
0.98
0.99
0.99
1.00
1.00
abundance
X : parts per Million : 1H

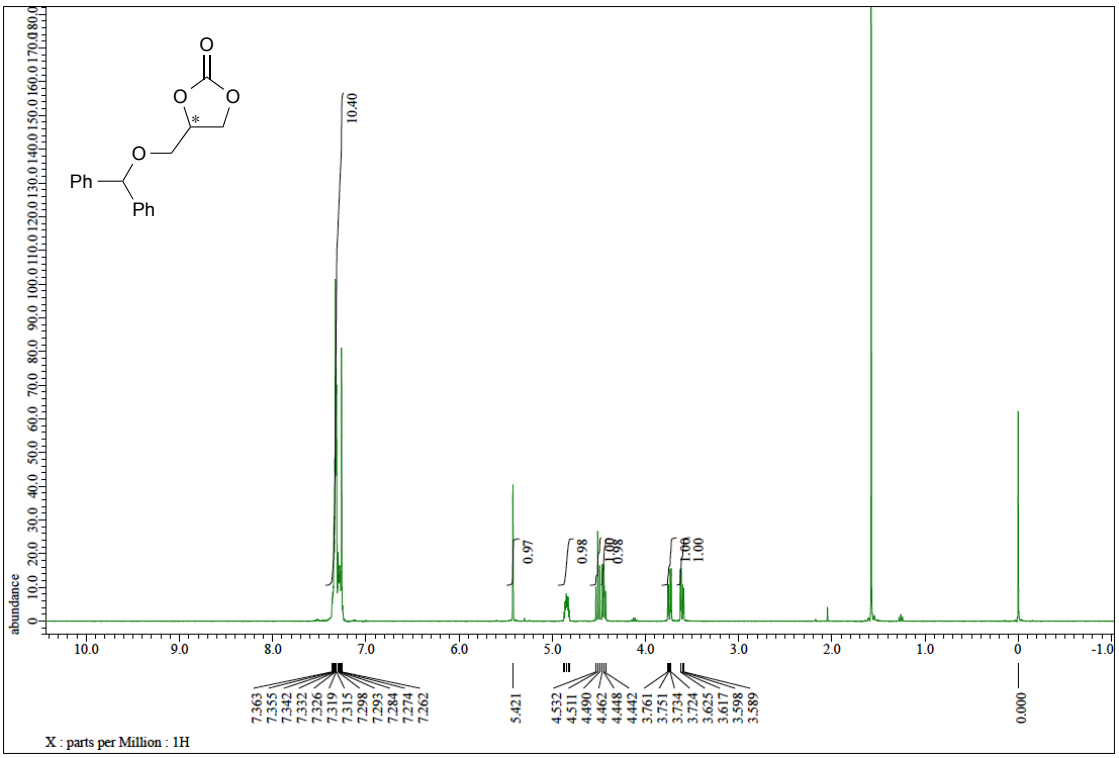

Ph2N
O
abundance
147.886
129.320
121.656
120.956
77.321
77.000
76.687
53.791
50.317
45.945
X : parts per Million : 13C

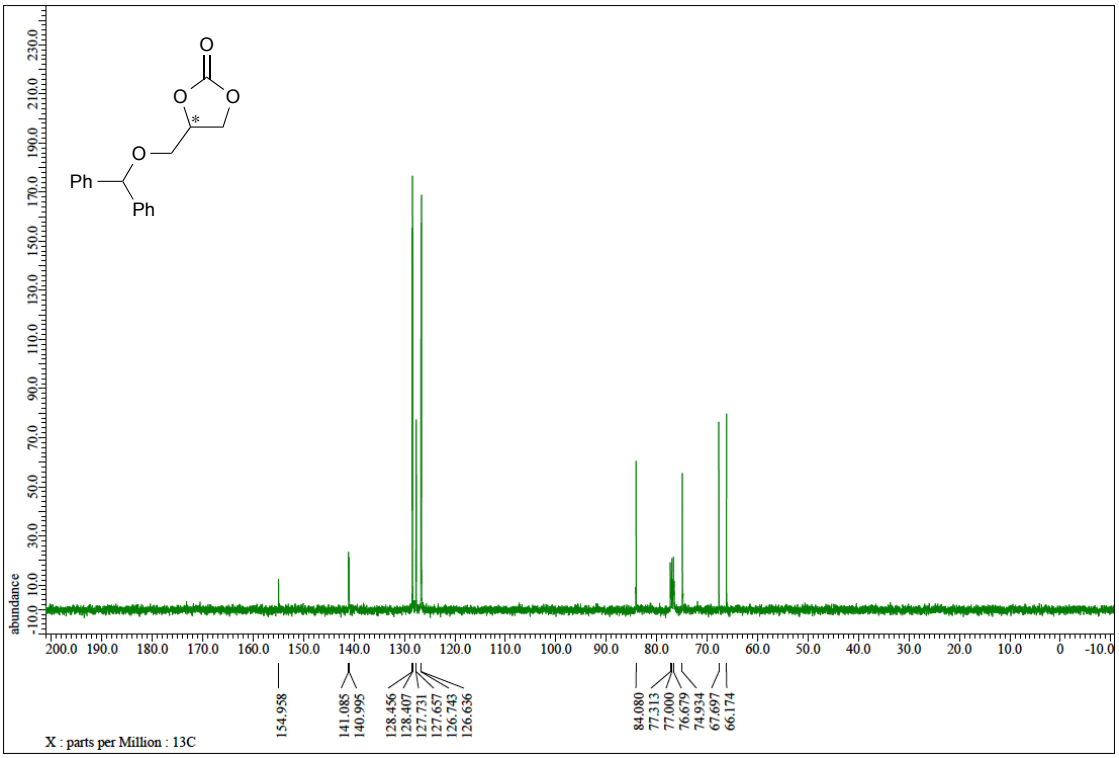

Ph2N
4.01
3.98
2.03
0.98
1.00
1.00
abundance
X : parts per Million : 1H


Ph2N
154.447
147.367
129.485
122.380
121.046
77.313
77.000
76.679
74.497
67.302
54.088
abundance
X : parts per Million : 13C


O
O
Ph
Ph
10.41
0.98
1.00
1.00
0.98
1.00
1.00
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.374
7.353
7.340
7.335
7.323
7.318
7.303
7.268
7.262
7.249
7.233
5.456
3.753
3.746
3.725
3.718
3.480
3.467
3.452
3.437
3.225
3.215
2.804
2.792
2.781
2.617
2.611
2.605
2.598
X : parts per Million : 1H


O
O
Ph
Ph
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
141.843
141.760
128.407
127.567
127.526
127.032
126.908
83.875
77.313
77.000
76.679
69.533
50.926
44.398
X : parts per Million : 13C


O
O
O
*
O
Ph
Ph
10.40
0.97
0.98
1.06
1.00
abundance
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0
7.363 7.355 7.342 7.332 7.326 7.319 7.315 7.298 7.293 7.284 7.274 7.262
5.421
4.532 4.511 4.490 4.462 4.448 4.442
3.761 3.751 3.734 3.724 3.625 3.617 3.598 3.589
0.000
X : parts per Million : 1H


O
O
O
*
O
Ph
Ph
abundance
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
154.958
141.085 140.995
128.456 128.407 127.731 127.657 126.743 126.636
84.080 77.313 77.000 76.679 74.934 67.697 66.174
X : parts per Million : 13C