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Supplementary Material for Synthesis of Bulky Aryl Group-Substituted Chiral Bis(guanidino)iminophosphoranes as Uncharged Chiral Organosuperbase Catalysts

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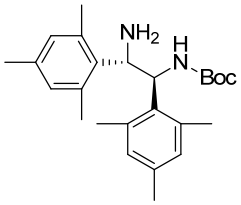
General Information

Unless otherwise noted, the reactions were carried out with dried glassware under an atmosphere of standard grade nitrogen gas. ^{1}H NMR spectra were recorded on a JEOL ECS-400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance or tetramethylsilane (TMS) as the internal standard ($CDCl_3$: 7.26 ppm, DMSO: 2.50 ppm, TMS: 0.00 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad peak), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a JEOL ECS-400 (101 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm, DMSO: 39.5 ppm). ^{31}P NMR spectra were recorded on a JEOL ECS-400 (162 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the $(PhO)_3PO$ (–17.8 ppm) resonance as the external standard. Infrared spectra were recorded on a JASCO FT/IR-6300 type A spectrometer. High resolution mass spectra analysis was performed on a Waters XEVO QTOF MS and JEOL JMS-T100GC. Optical rotations were measured on a Rudolph Research Analytical Autopol V Plus. HPLC was performed on SHIMADZU HPLC systems LC-20A. Silica gel flash column chromatography was performed on BIOTAGE Isolera LS system (SNAP cartridge HP-sil). Reverse phase gel flash column chromatography was performed on BIOTAGE Isolera LS system (SNAP cartridge KP-C18-HS). Silica gel preparative thin layer chromatography was performed on Merck PLC silica gel 60 F_{254}. X-ray crystallographic analysis was performed on a RIGAKU R-AXIS RAPID.

Materials

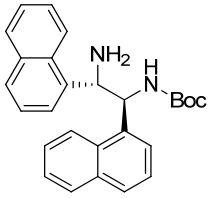
Unless otherwise noted, materials were purchased from Wako Pure Chemical Industries, Ltd., Tokyo Chemical Industry Co., LTD., Kanto Chemical Co., Inc., Aldrich Inc., and other commercial suppliers and were used without purification. Toluene was used a dehydrated grade purchased from Kanto Chemical Co., Inc. for asymmetric amination reactions.

1*tert*-Butyl [(1*S*,2*S*)-2-amino-1,2-bis(2,4,6-trimethylphenyl)ethyl]carbamate (4b)



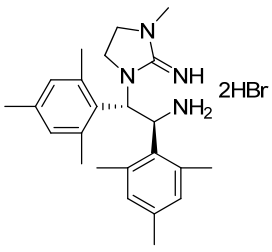
To a solution of (1*S*,2*S*)-1,2-bis(2,4,6-trimethylphenyl)ethane-1,2-diamine (**3b**) (2.0 g, 6.75 mmol) in MeOH (24 mL) was added 47% HBr aq. (0.79 mL, 6.75 mmol) at rt, and then H_2O (2.8 mL) and Boc_2O (1.62 g, 7.42 mmol) was added. After stirring for 12 h, H_2O (21.2 mL) was added to the mixture and then the mixture was basified with 25% NaOH aq. until over pH 14. The mixture was extracted with toluene (20 mL × 3), and the combined organic layer was washed with 20% NaCl aq. and dried over Na_2SO_4. The solvent was removed, and the residue was purified by silica gel column chromatography (SNAP cartridge HP-sil 50 g, CH_2Cl_2/EtOAc = 100/0 to 0/100) to give **4b** (1.82 g, 68% yield) as colorless powder. ^{1}H-NMR (DMSO-d_6, 400 MHz, 100 °C) δ 1.33 (9H, s), 1.98-2.15 (19H, br m), 4.47 (1H, d, J = 9.8 Hz), 5.09-5.13 (1H, m), 6.61-6.65 (4H, br m). ^{13}C-NMR (DMSO-d_6, 101 MHz, 100 °C) δ 19.5-19.7 (br m), 27.8, 51.8, 53.3, 77.4, 129.0 (br), 134.3, 134.5, 135.5-135.6 (br m), 137.3, 154.7. IR (KBr) 3385, 3336, 3006, 2975, 2922, 2868, 2732, 1696, 1611, 1576, 1481, 1458, 1390, 1365, 1301, 1246, 1172, 1114, 1072, 1044, 1032, 1012, 873, 851, 774, 752, 735, 681, 621, 610, 589, 572, 541, 444 cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{37}N_2O_2$: 397.2855. found: 397.2860.

***tert*-Butyl [(1*S*,2*S*)-2-amino-1,2-bis(1-naphthyl)ethyl]carbamate (4c)**



To a solution of (1*S*,2*S*)-1,2-bis(1-naphthyl)ethane-1,2-diamine (**3c**) (3.19 g, 10.2 mmol) in MeOH (57 mL) and THF (57 mL) was added 47% HBr aq. (1.19 mL, 10.2 mmol) at rt, and then H_2O (4.5 mL) and Boc_2O (2.45 g, 11.2 mmol) was added, and the mixture was refluxed for 12 h. Additional Boc_2O (0.60 g, 2.3 mmol) was added, and the mixture was refluxed for 12 h. H_2O (40 mL) was added to the mixture and then the mixture was basified with 25% NaOH aq. until over pH 14. The mixture was extracted with CH_2Cl_2 (40 mL × 3), and the combined organic layer was washed with 20% NaCl aq. and dried over Na_2SO_4. The solvent was removed, and the residue was purified by silica gel column chromatography (SNAP cartridge HP-sil 50 g, CH_2Cl_2/MeOH = 100/0 to 95/5) to give **4c** (2.61 g, 61% yield) as colorless powder. ^{1}H-NMR ($CDCl_3$, 400 MHz, 60 °C) δ 1.31-1.44 (12H, br m), 5.18 (1H, br s), 5.82 (1H, br s), 6.18 (1H, br s), 7.44-7.87 (12H, m), 8.19-8.24 (2H, m). ^{13}C-NMR ($CDCl_3$, 101 MHz, 60 °C) δ 28.2, 28.3, 53.1, 54.3, 54.3, 54.3, 79.3, 122.8, 123.2, 123.6, 124.1, 125.3, 125.5, 125.7, 126.2, 126.2, 127.9, 128.1, 129.0, 129.2, 130.9, 130.9, 131.1, 134.2, 134.3, 138.2, 138.6, 155.6. IR (KBr) 3384, 3328, 3050, 3004, 2975, 2929, 2868, 1716, 1596, 1579, 1512, 1479, 1392, 1366, 1335, 1306, 1240, 1164, 1093, 1072, 1048, 1031, 1024, 1000, 970, 951, 925, 906, 893, 870, 860, 846, 799, 781, 734, 688, 651, 627, 569, 558, 533, 520, 504, 495, 432 cm^{-1}. HRMS (ESI): calcd. for $C_{27}H_{29}N_2O_2$: 413.2229. found: 413.2239.

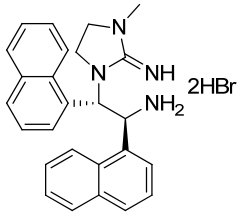
(1*S*,2*S*)-2-(2-imino-3-methylimidazolidin-1-yl)-1,2-bis(2,4,6-trimethylphenyl)ethanamine dihydrobromide (6b)



A solution of monoBoc-diamine **4b** (1.5 g, 3.8 mmol) and cyanamide **5** (0.8 g, 4.9 mmol) in EtOH (4.5 mL) was refluxed for 6 days.

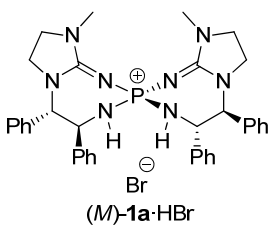
After cooling to 50 °C, 47% HBr aq. (1.1 mL, 9.1 mmol) was added to the mixture. The mixture was stirred for 12 h at the same temperature. EtOH and H_2O in the mixture were removed azeotropically with CH_3CN, and the residue was purified by silica gel column chromatography (SNAP cartridge HP-sil 50 g, CH_2Cl_2/MeOH = 100/0 to 90/10) to give **6b** (1.84 g, 90% yield) as colorless powder. The crude **11d** was suspended in CH_3CN (130 mL) at rt, and the precipitate was collected by filtration and dried in vacuo (8.8 g, 92%) as colorless powder. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.86 (3H, s), 2.16 (3H, s), 2.19 (3H, s), 2.24 (3H, s), 2.47 (3H, s), 2.58 (3H, s), 3.01-3.02 (1H, br m), 3.20 (3H, s), 3.43 (1H, br s), 4.09-4.17 (2H, br m), 5.56 (1H, br s), 6.15-6.17 (1H, br m), 6.56 (2H, s), 6.87 (1H, s), 6.89 (1H, s), 8.50 (2H, br s), 8.87 (3H, br s). ^{13}C-NMR ($CDCl_3$, 101 MHz) δ 20.6, 20.8, 21.3, 21.9, 22, 34.3, 42.4, 47.7, 55.1, 58.7, 126.9, 127.1, 130.4, 130.7, 131.3, 131.9, 136.3, 137, 138.7, 138.8, 139.3, 156.7. IR (KBr) 3327, 3261, 3096, 3008, 2965, 2919, 2582, 1998, 1664, 1609, 1560, 1482, 1461, 1426, 1379, 1309, 1270, 1214, 1164, 1144, 1103, 1055, 1032, 1000, 951, 852, 804, 701, 691, 663, 631, 610, 588, 560, 521, 510, 492, 430, 420 m^{-1}. HRMS (ESI): calcd. for $C_{24}H_{35}N_4$: 379.2862. found: 379.2866.

(1*S*,2*S*)-2-(2-imino-3-methylimidazolidin-1-yl)-1,2-bis(1-naphthyl)ethanamine dihydrobromide (6c)

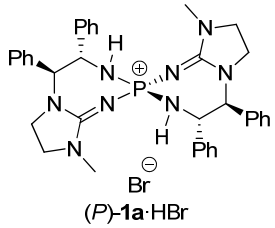


A solution of monoBoc-diamine **4c** (2.4 g, 5.8 mmol) and cyanamide **5** (1.23 g, 7.56 mmol) in EtOH (7.2 mL) was refluxed for 3 days. Additional cyanamide **5** (0.28 g, 1.74 mmol) was added, and the mixture was refluxed for 4 days. Additional cyanamide **5** (0.28 g, 1.74 mmol) was added again, and the mixture was refluxed for 3 days. After cooling to 50 °C, 47% HBr aq. (1.6 mL, 13.9 mmol) was added to the mixture. The mixture was stirred for 12 h at the same temperature. Additional 47% HBr aq. (1.6 mL, 13.9 mmol) was added to the mixture and the mixture was stirred for 12 h at the same temperature. EtOH and H_2O in the mixture were removed azeotropically with CH_3CN, and the residue was purified by crystallization from CH_3CN (10 mL) and dried in vacuo (2.41 g, 75%) as colorless powder. ^{1}H-NMR (DMSO-D_6, 400 MHz) δ 2.69 (1H, q, J = 10.0 Hz), 2.98 (3H, s), 3.42 (3H, s), 3.47 (3H, t, J = 7.9 Hz), 3.60 (1H, q, J = 10.0 Hz), 4.49 (1H, t, J = 8.2 Hz), 6.51 (1H, br s), 6.89 (1H, d, J = 10.4 Hz), 7.12 (1H, t, J = 7.6 Hz), 7.29 (1H, t, J = 7.9 Hz), 7.48-7.92 (9H, m), 8.32-8.39 (2H, m), 8.97-9.07 (6H, m). ^{13}C-NMR (DMSO-D_6, 101 MHz) δ 32.9, 40.1, 41.8, 47.5, 48.7, 55.5, 122.2, 123.9, 124.3, 125.0, 126.3, 127.0, 127.5, 127.9, 128.7, 129.2, 129.5, 129.7, 130.3, 131.0, 133.2, 133.5, 158.0. IR (KBr) 3421, 3337, 3229, 3097, 3013, 2995, 2969, 2927, 2893, 2874, 2627, 2611, 2552, 1952, 1670, 1609, 1593, 1571, 1548, 1514, 1495, 1463, 1444, 1423, 1401, 1374, 1363, 1350, 1309, 1275, 1255, 1245, 1210, 1170, 1144, 1119, 1097, 1058, 1038, 978, 955, 866, 803, 793, 777, 740, 694, 640, 632, 600, 571, 558, 537, 513, 477, 437 m^{-1}. HRMS (ESI): calcd. for $C_{26}H_{27}N_4$: 395.2236. found: 395.2235.

(4*S*,4'*S*,5*S*,5'*S*)-9,9'-dimethyl-4,4',5,5'-tetraphenyl-4,4',5,7',8,8',9,9'-octahydro-3H,5'H,7H-2,2'-spirobi[imidazo[2,1-d][1,3,5,2]triazaphosphepine] hydrobromide ((*M*)-1a**·HBr and (*P*)-**1a**·HBr)**



(*M*)-**1a**·HBr



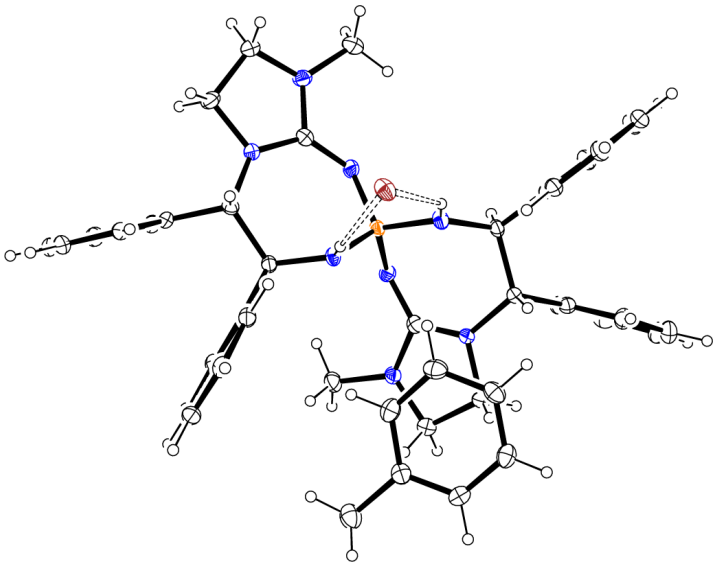
(*P*)-**1a**·HBr

To a suspension of aminoguanidine hydrobromide **6a** (5.0 g, 11.0 mmol) in sulforane (300 mL) was added 1 M solution of $LiN(SiMe_3)_2$ in THF (46.0 mL, 46.0 mmol) at rt, and then a solution of PCl_5 (1.25 g, 6.0 mmol) and DMAP (0.73 g, 6.0 mmol) in sulforane (45 mL) was added to the solution at rt. After stirring for 1 h, the reaction was quenched with 10 % NH_4Br aq. (300 mL),

and the mixture was extracted with CH_2Cl_2 three times. The combined organic layer was washed with NaBr aq. and water several times to remove sulforane, and then dried over Na_2SO_4. After concentration, the residue was purified by silica gel column chromatography (SNAP cartridge HP-sil 100 g, EtOAc/MeOH = 90/10 and then CH_2Cl_2/MeOH = 90/10) to separate (*M*)-**1a**·HBr and (*P*)-**1a**·HBr. Crude (*M*)-**1a**·HBr was further purified by crystallization from toluene (6 mL) at rt to give (*M*)-**1a**·HBr mono-toluene solvate (0.60 g, 14% yield from a half amount of **6a**). Crude (*P*)-**1a**·HBr was further purified by silica gel column chromatography (SNAP cartridge HP-sil 50 g, CH_2Cl_2/MeOH = 90/10) and crystallization from THF (3 mL) to give (*P*)-**1a**·HBr (0.16 g, 4% yield from a half amount of **6a**).

(*M*)-**1a**·HBr: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 2.35 (3H, s), 2.82 (6H, s), 2.97-3.04 (2H, m), 3.26-3.45 (6H, m), 4.65 (2H, d, J = 10.5 Hz), 4.96-5.05 (2H, m), 6.14 (2H, t, J = 8.9 Hz), 6.91-6.94 (4H, m), 7.12-7.28 (21H, m). ^{13}C-NMR ($CDCl_3$, 101 MHz) δ 21.4, 32.2, 45.3, 45.7, 58.4, 58.5, 71.7, 125.2, 127.3, 127.6, 127.6, 127.8, 128.1, 128.4, 128.4, 128.9, 137.7, 138.8, 139.5, 139.6, 158.7, 158.8. ^{31}P-NMR ($CDCl_3$, 202 MHz) δ 19.7.

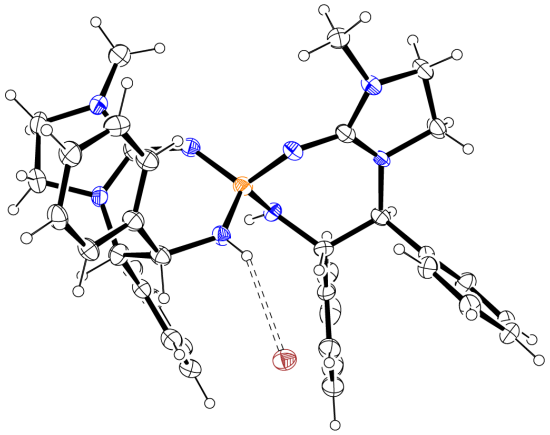
The single crystal of (*M*)-**1a**·HBr for X-ray crystallographic analysis was obtained by recrystallization from toluene as toluene solvate.



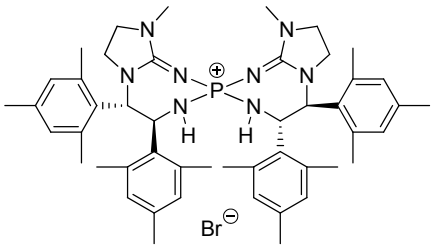
(*P*)-**1a**·HBr: mp 298 °C (decomp.). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.02 (6H, s), 3.11 (2H, q, J = 8.8 Hz), 3.26-3.51 (6H, m), 4.18-4.20 (2H, m), 4.90-4.99 (4H, m), 6.97-7.04 (10H, m), 7.18-7.25 (6H, m), 7.33-7.35 (4H, m). ^{13}C-NMR ($CDCl_3$, 101 MHz) δ 33.0, 46.4, 46.5, 60.2, 67.4, 127.4, 127.5, 127.6, 128.1, 128.3, 128.6, 136.4, 140.6, 140.6, 158.2, 158.3. ^{31}P-NMR ($CDCl_3$, 162 MHz) δ 9.5. IR (KBr) 3369, 3331, 3134, 3088, 3059, 3030, 2932, 2870, 2790, 1727, 1642, 1591, 1579, 1519, 1484, 1455, 1407, 1358, 1336, 1277, 1234, 1210, 1184, 1155, 1081, 1038, 999, 988, 958, 941, 919, 904, 845, 834, 809, 789, 775, 755, 739, 716, 704, 695, 665, 649, 600, 590, 556, 540, 521, 512, 503, 432, 419, 413 cm^{-1}. HRMS (ESI): calcd. for $C_{36}H_{40}N_8P$: 615.3114. found: 615.3123. $[\alpha]_D^{25}$ 7.9 (*c* 1.01, $CHCl_3$).

The precise yield was determined by HPLC assay (absolute calibration method using the isolated (*M*)-**1a**·HBr as reference standard) of the reaction mixture diluted with AcOH/CH_3CN = 3/97, Waters XSELECT HSS C18 2.5μm 2.1 × 50 mm, CH_3CN/0.1% TFA aq. = 25/75 to 95/5 linear gradient over 6 min, 0.5 mL/min, 40 °C, 220 nm, 3.6min [(*M*)-**1a**], 3.9 min [(*P*)-**1a**].

The single crystal of (*P*)-**1a**·HBr for X-ray crystallographic analysis was obtained by recrystallization from 2-PrOH and *n*-hexane.



(4*S*,4'*S*,5*S*,5'*S*)-9,9'-dimethyl-4,4',5,5'-tetrakis(2,4,6-trimethylphenyl)-4,4',5,7',8,8',9,9'-octahydro-3H,5'H,7H-2,2'-spirobi[imidazo[2,1-d][1,3,5,2]triazaphosphepine] hydrobromide (**1b**·HBr)



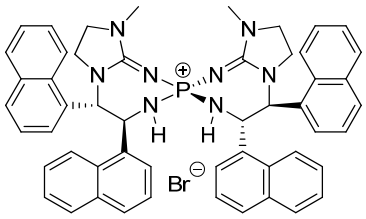
1b·HBr

Bis(guanidine)iminophosphorane hydrobromide **1b**·HBr was synthesized from aminoguanidine hydrobromide **6b** (1.5 g, 2.78 mmol) with the same procedure as **1a**·HBr. Crude **1b**·HBr was purified by reverse phase gel column chromatography (SNAP cartridge KP-C18 60 g, CH_3CN/1% NH_4Br aq. = 50/50 to 95/5) and silica gel column chromatography (SNAP cartridge HP-sil 50 g, CH_2Cl_2/MeOH = 95/5) to separate each diastereomer. Separated each isomer of **1b**·HBr was dissolved in CH_2Cl_2 (5 mL) respectively and the solutions were washed with 10% NH_4Br aq. (5 mL). The respective solutions were dried over Na_2SO_4, and the solvents were removed to give major isomer of **1b**·HBr (77 mg, 6% yield from a half amount of **6b**) and minor isomer of **1b**·HBr (58 mg, 5% yield from a half amount of **6b**) respectively.

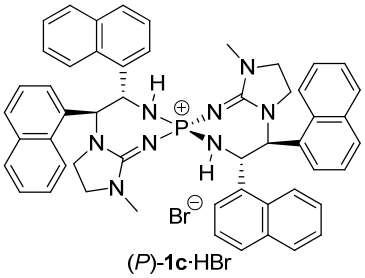
Major isomer of **1b**·HBr: mp 238 °C (decomp.). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.70 (6H, s), 1.76 (6H, s), 2.15-2.17 (12H, m), 2.57 (6H, s), 2.79 (6H, s), 2.87 (6H, s), 2.94-2.98 (2H, m), 3.31-3.52 (6H, m), 4.38 (2H, d, J = 3.7 Hz), 5.30 (2H, d, J = 11.0 Hz), 5.67-5.74 (2H, m), 6.49-6.51 (4H, m), 6.78 (2H, s), 6.85 (2H, s). ^{13}C-NMR ($CDCl_3$, 101 MHz) δ 20.1, 20.3, 20.6, 20.6, 21.5, 22.0, 32.4, 45.1, 45.7, 49.2, 62.5, 129.0, 129.5, 130.0, 131.0, 131.5, 132.3, 132.3, 136.4, 136.7, 137.4, 138.4, 157.7, 157.9. ^{31}P-NMR ($CDCl_3$, 162 MHz) δ 16.4. IR (KBr) 3412, 3160, 3003, 2953, 2920, 2871, 2733, 1724, 1610, 1565, 1513, 1480, 1452, 1397, 1338, 1325, 1273, 1228, 1210, 1169, 1137, 1064, 1021, 956, 910, 851, 797, 743, 732, 707, 659, 638, 618, 608, 599, 586, 568, 556, 446, 406 cm^{-1}. HRMS (ESI): calcd. for $C_{48}H_{64}N_8P$: 783.4992. found: 783.5000. $[\alpha]_D^{25}$ –317.4 (*c* 1.02, $CHCl_3$).

Minor isomer of **1b**·HBr: mp 205 °C (decomp.). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.91 (6H, s), 1.68 (6H, s), 2.10 (6H, s), 2.15 (6H, s), 2.28 (6H, s), 2.75 (6H, s), 2.98-3.07 (8H, m), 3.45-3.84 (8H, m), 5.11 (2H, td, J = 12.4, 8.1 Hz), 5.33 (2H, d, J = 11.6 Hz), 6.35 (2H, s), 6.46 (2H, s), 6.69 (2H, s), 6.82 (2H, s). ^{13}C-NMR ($CDCl_3$, 101 MHz) δ 19.3, 20.0, 20.5, 20.6, 20.6, 21.2, 32.8, 45.5, 45.9, 49.2, 49.3, 63.1, 129.1, 129.5, 129.7, 131.1, 131.2, 131.5, 131.5, 134.9, 135.6, 137.3, 137.5, 137.6, 138.1, 158.1. ^{31}P-NMR ($CDCl_3$, 162 MHz) δ 15.4. IR (KBr) 3439, 2954, 2922, 2870, 2734, 1724, 1611, 1558, 1515, 1482, 1453, 1394, 1345, 1288, 1271, 1230, 1163, 1137, 1076, 1018, 1006, 990, 956, 893, 851, 797, 743, 732, 711, 694, 638, 626, 609, 587, 576, 556, 465, 455, 444, 433, 425, 416 cm^{-1}. HRMS (ESI): calcd. for $C_{48}H_{64}N_8P$: 783.4992. found: 783.5021. $[\alpha]_D^{25}$ –219.7 (*c* 1.01, $CHCl_3$).

(4*S*,4'*S*,5*S*,5'*S*)-9,9'-dimethyl-4,4',5,5'-tetrakis(1-naphthyl)-4,4',5,7',8,8',9,9'-octahydro-3H,5'H,7H-2,2'-spirobi[imidazo[2,1-d][1,3,5,2]triazaphosphepine] hydrobromide ((*M*)-**1c**·HBr and (*P*)-**1c**·HBr)



(*M*)-**1c**·HBr



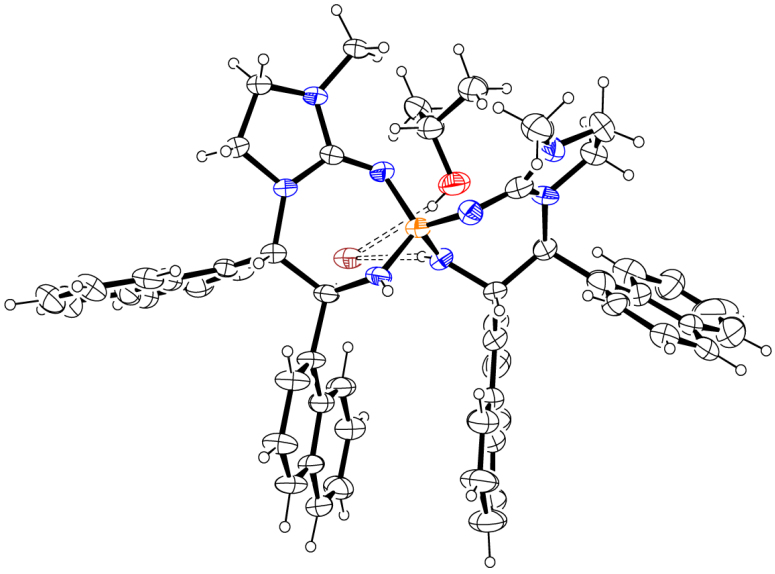
(*P*)-**1c**·HBr

Bis(guanidine)iminophosphorane hydrobromide **1c**·HBr was synthesized from aminoguanidine hydrobromide **6c** (2.0 g, 3.59 mmol) with the same procedure as **1a**·HBr. Crude **1c**·HBr was purified by silica gel column chromatography (SNAP cartridge HP-sil 50 g, CH_2Cl_2/MeOH = 95/5) to separate each diastereomer. Separated each isomer of **1c**·HBr was crystallized from toluene (6 mL for major isomer and 4 mL for minor isomer) respectively to give (*M*)-**1c**·HBr as toluene solvate (205 mg, 12% yield from a half amount of **6c**) and (*P*)-**1c**·HBr (83 mg, 5% yield from a half amount of **6c**) respectively.

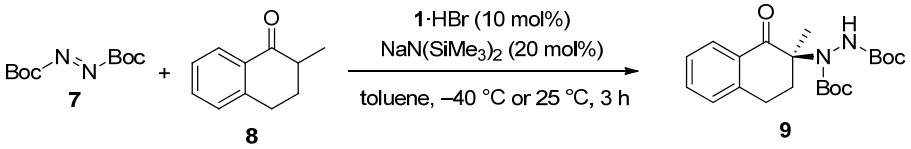
(*M*)-**1c**·HBr: mp 332 °C (decomp.). ^{1}H-NMR (DMSO-d_6, 400 MHz, 100 °C) δ 2.31 (3H, s), 2.88-2.96 (8H, m), 3.29 (6H, br s), 5.37 (2H, br s), 5.77 (2H, d, J = 8.5 Hz), 6.11-6.17 (2H, m), 7.16-8.00 (33H, m). ^{13}C-NMR (DMSO-d_6, 101 MHz, 100 °C) δ 20.3, 31.8, 45.2, 45.3, 52.5, 52.8, 66.0, 66.0, 121.8, 122.3, 122.3, 122.3, 122.4, 122.4, 124.3, 124.5, 124.6, 124.7, 124.8, 124.9, 125.1, 125.5, 126.0, 126.1, 126.1, 126.1, 127.5, 127.9, 128.0, 128.2, 129.5, 130.1, 132.7, 132.8, 133.4, 135.4, 135.5, 135.6, 136.7, 156.9, 157.0. ^{31}P-NMR (DMSO-d_6, 162 MHz, 100 °C) δ 17.1. IR (KBr) 3646, 3410, 3053, 2943, 2874, 1624, 1596, 1555, 1509, 1480, 1453, 1388, 1359, 1295, 1280, 1264, 1234, 1208, 1165, 1144, 1075, 1032, 1019, 1006, 990, 953, 912, 856, 778, 737, 715, 697, 645, 623, 611, 605, 579, 567, 555, 534, 508, 489, 466, 454, 429, 411 cm^{-1}. HRMS (ESI): calcd. for $C_{52}H_{48}N_8P$: 815.3740. found: 815.3746. $[\alpha]_D^{25}$ –337.8 ° (*c* 1.02, $CHCl_3$).

(*P*)-**1c**·HBr: mp 298 °C (decomp.). ^{1}H-NMR (DMSO-d_6, 400 MHz, 100 °C) δ 2.81-2.91 (8H, m), 3.22-3.42 (6H, m), 5.78-5.85 (2H, m), 6.06-6.14 (2H, m), 6.49 (2H, br s), 6.98-7.91 (28H, m). ^{13}C-NMR (DMSO-d_6, 101 MHz, 100 °C) δ 20.4, 31.9, 44.9, 45.4, 52, 64.9, 121.7, 122.2, 124.1, 124.3, 124.4, 124.4, 124.7, 124.9, 125.6, 127.2, 127.6, 127.9, 128.1, 128.3, 129.7, 130.3, 132.4, 132.5, 133.5, 135.3, 135.4, 136.8, 157.9, 157.9. ^{31}P-NMR (DMSO-d_6, 162 MHz, 100 °C) δ 19.2. IR (KBr) 3637, 3396, 3046, 3010, 2936, 2873, 1569, 1507, 1481, 1450, 1396, 1360, 1293, 1263, 1236, 1207, 1169, 1142, 1078, 1050, 1020, 983, 954, 888, 859, 786, 775, 735, 638, 605, 581, 567, 555, 508, 445, 409, 579, 567, 555, 534, 508, 489, 466, 454, 429, 411 cm^{-1}. HRMS (ESI): calcd. for $C_{52}H_{48}N_8P$: 815.3740. found: 815.3745. $[\alpha]_D^{25}$ 15.0 (*c* 1.01, $CHCl_3$).

The single crystal of (*P*)-**1c**·HBr for X-ray crystallographic analysis was obtained by recrystallization from 2-PrOH and *n*-hexane as 2-PrOH solvate.



Typical procedure of enatioselective amination (9)

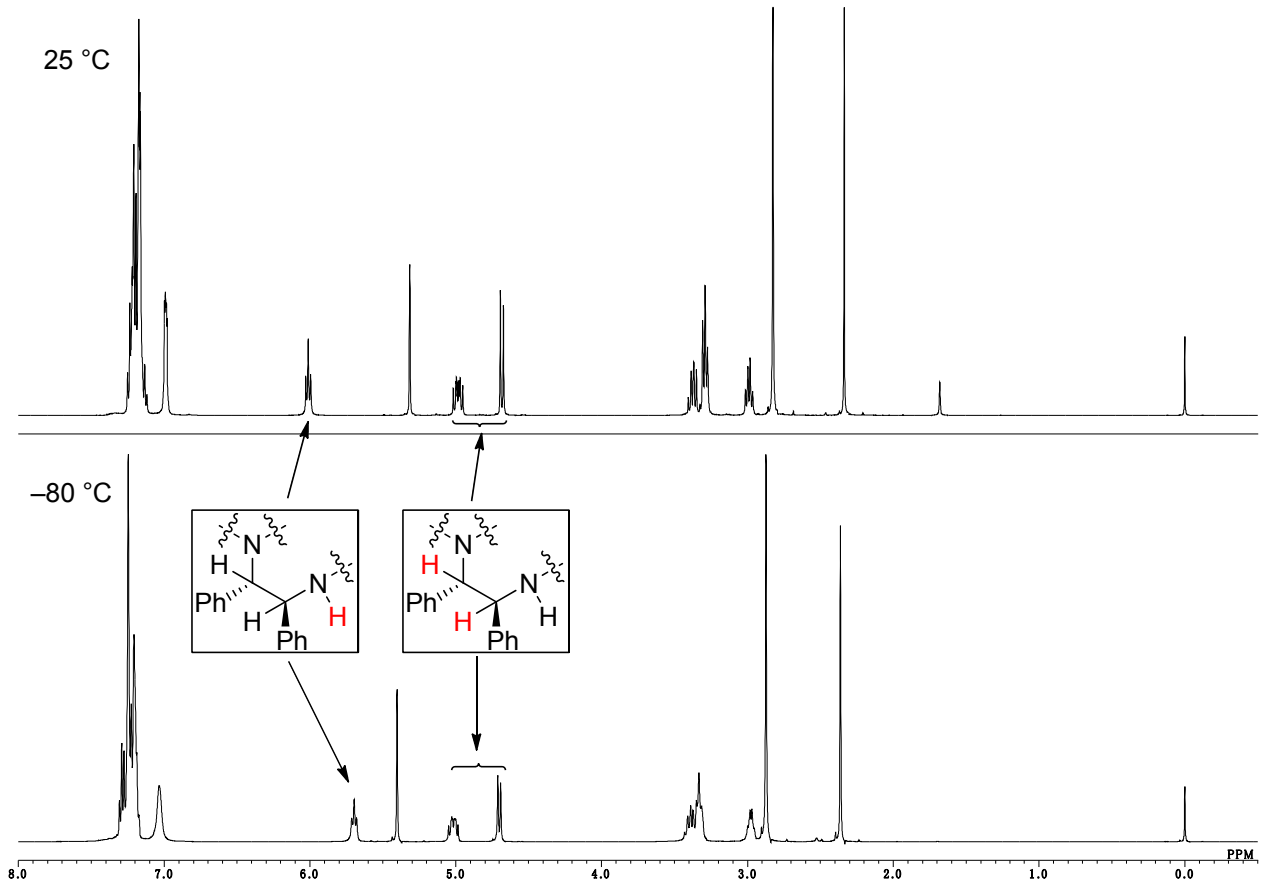


A suspension of ketone **8** (0.5 mmol) and catalyst bis(guanidino)iminophosphorane **1**·HBr (0.01 mmol) in dehydrated toluene (1 mL) was degassed under vacuum and sonication. 0.6 M $NaN(SiMe_3)_2$ in toluene (33.3 μL, 0.02 mmol) was added to the suspension at rt, and the mixture was stirred for ca. 1 min. After temperature control (to –40 °C or 25 °C), di-tert-butyl azodicarboxylate **7** (23.0 mg, 0.1mmol) was added in one potion. After stirring for 3 h at the same temperature, the reaction was quenched by addition of AcOH (5 μL). The mixture was purified with preparative thin layer chromatography (*n*-hexane/acetone = 9/1) to give product **9**. HPLC analysis DAICEL Chiralpak IA-3 2.1×150 mm, n-hexane/2-PrOH = 95/5, 0.4 mL/min, 40 °C, 246 nm, 3.4 min (major) 6.2 min (minor)

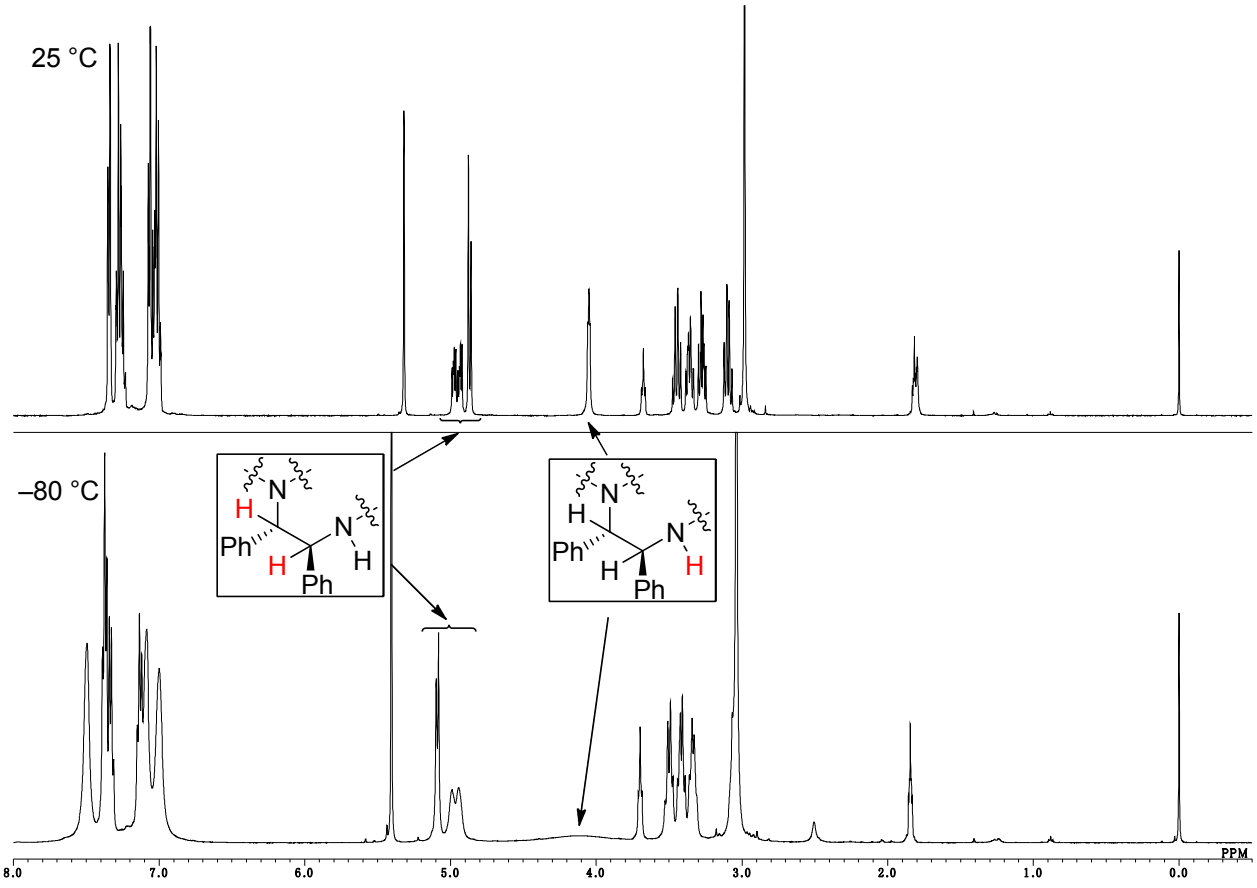
Low temperature NMR analyses of (*M*)-1a·HBr and (*P*)-1a·HBr

(*M*)-**1a**·HBr and (*P*)-**1a**·HBr were analyzed at 25 °C and –80 °C in CD_2Cl_2 respectively. Noticeable broadening was detected in the analysis of (*P*)-**1a**·HBr at –80 °C. These NMR spectra were recorded on a JEOL ECA-500 (500 MHz) spectrometer.

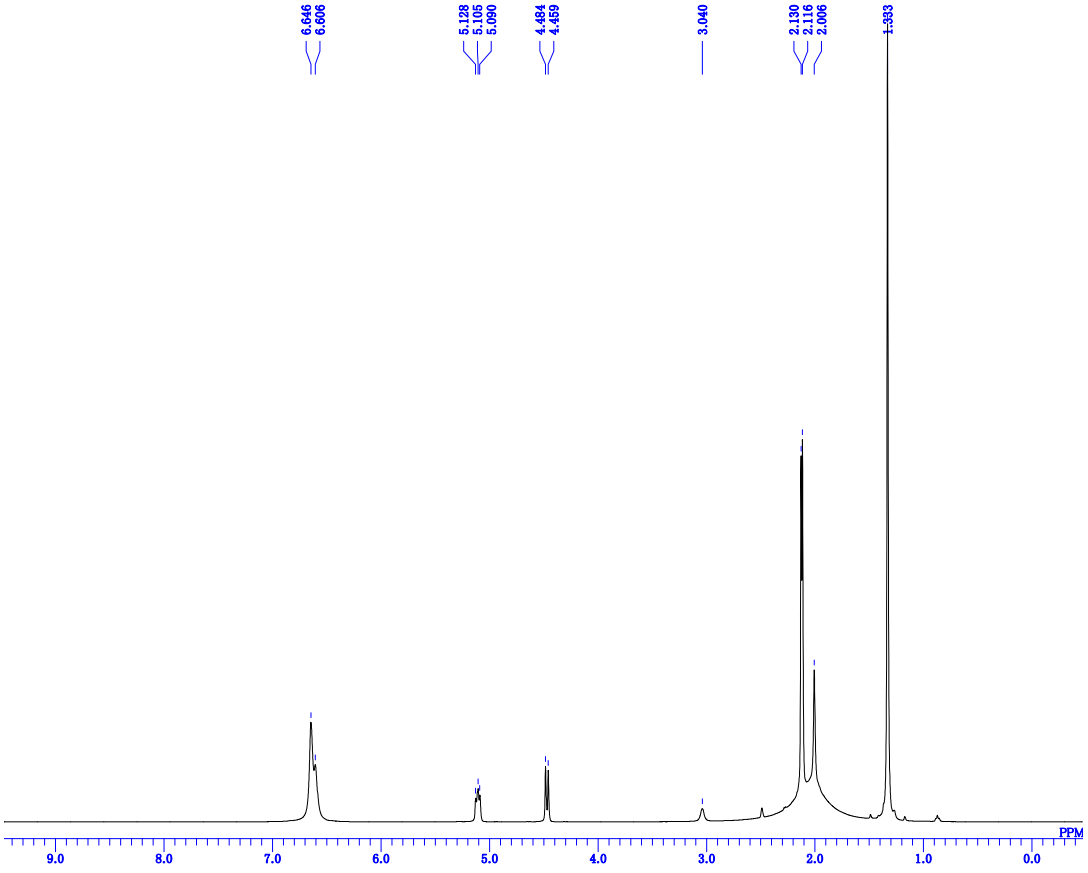
(*M*)-**1a**·HBr



(*P*)-**1a**·HBr



4b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5.105
5.090
4.484
4.459
3.040
2.130
2.116
2.006
1.333
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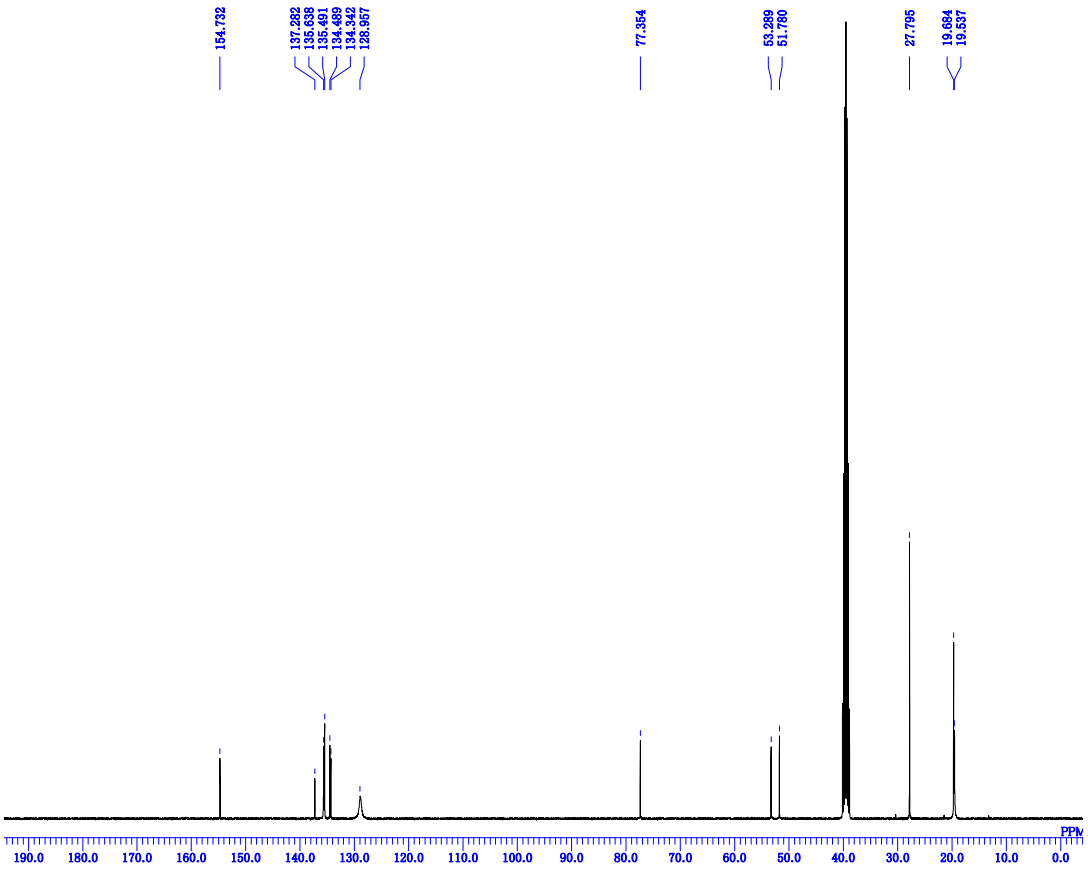
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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137.282
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135.491
134.489
134.342
128.957
77.354
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51.780
27.795
19.684
19.537
PPM
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
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80.0
70.0
60.0
50.0
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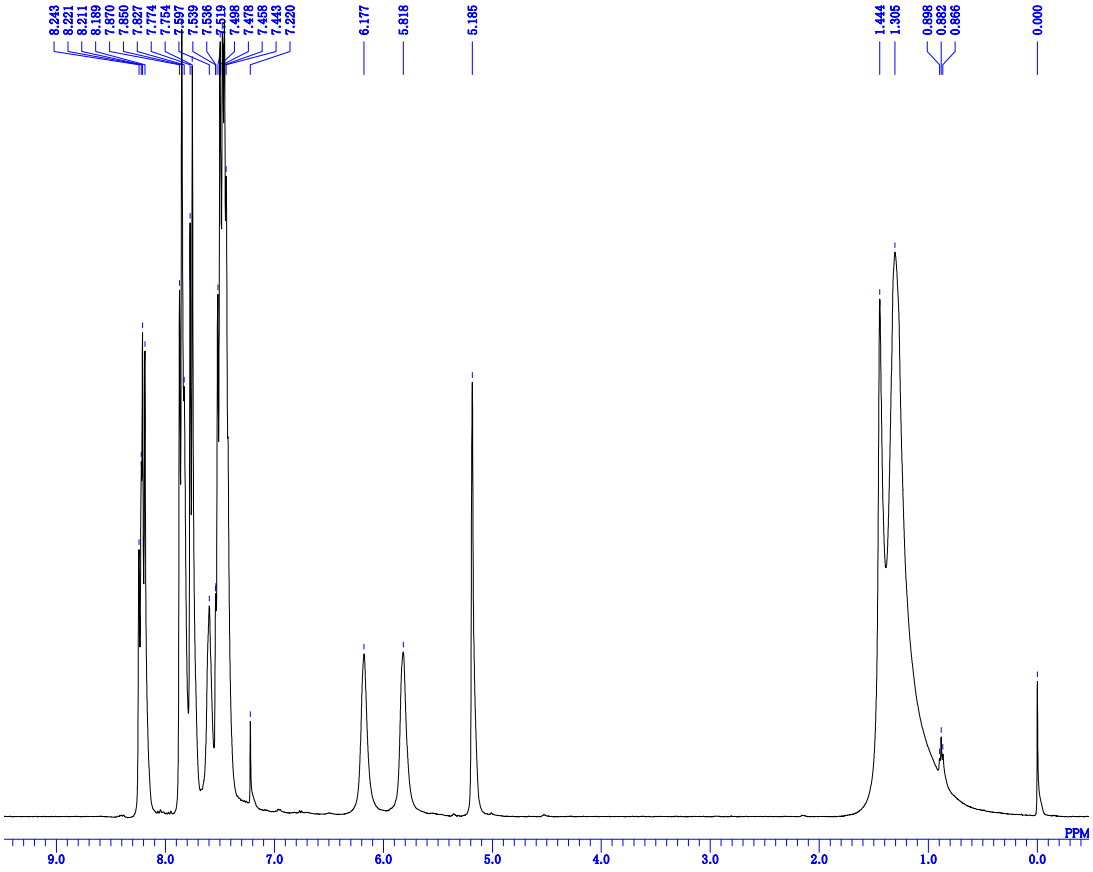
30.0
20.0
10.0
0.0

4c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8.211
8.189
7.870
7.850
7.827
7.774
7.754
7.597
7.539
7.536
7.519
7.498
7.478
7.468
7.443
7.220
6.177
5.818
5.185
1.444
1.305
0.898
0.882
0.866
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8.0
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6.0
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4.0
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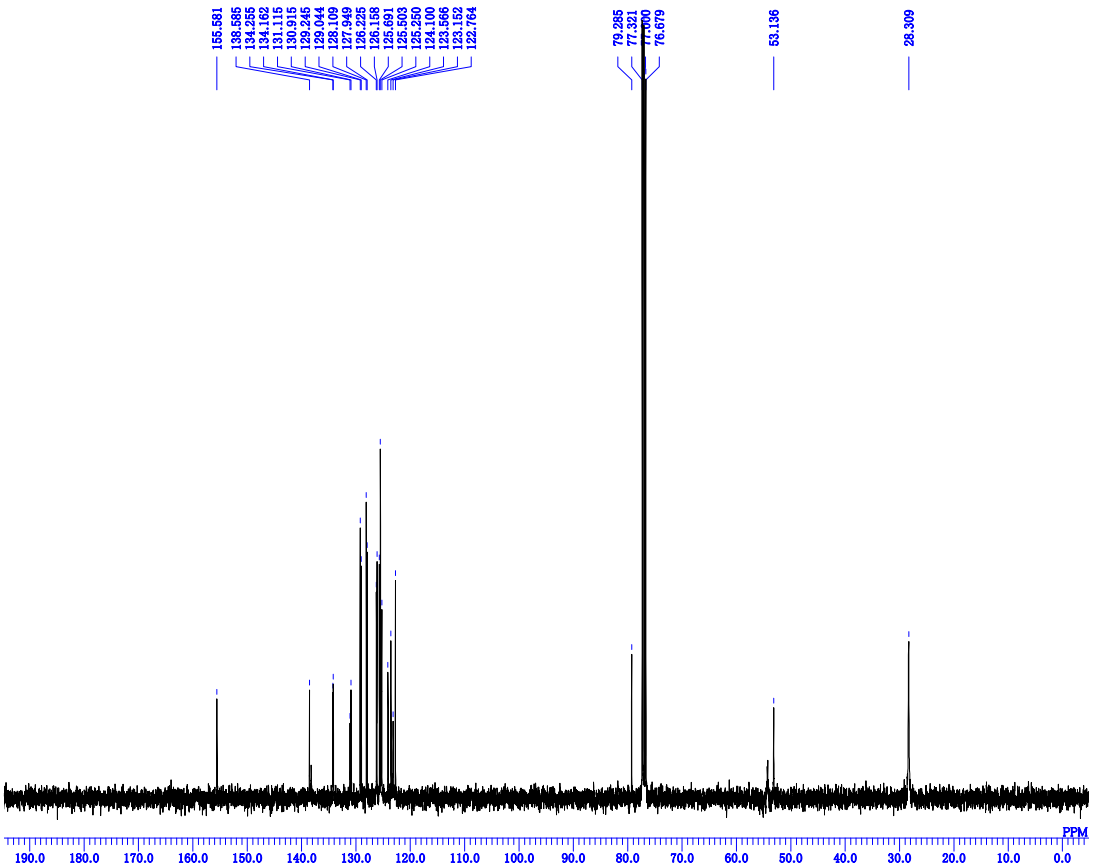
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131.115
130.915
129.245
129.044
128.109
127.949
126.225
126.158
125.691
125.503
125.250
124.100
123.566
123.152
122.764
79.285
77.321
77.000
76.679
53.136
28.309
PPM
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170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
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80.0
70.0
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50.0
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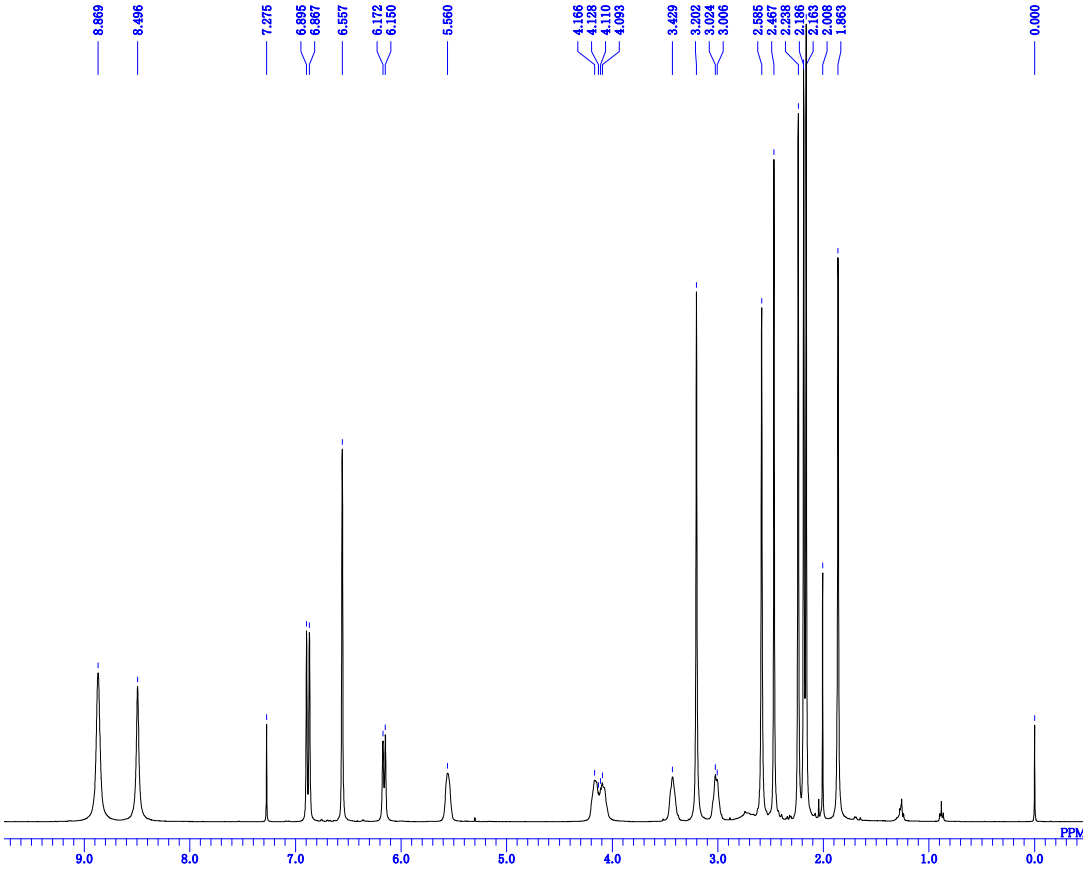
30.0
20.0
10.0
0.0

6b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7.275
6.895
6.867
6.557
6.172
6.150
5.560
4.166
4.128
4.110
4.093
3.429
3.202
3.024
3.006
2.585
2.467
2.238
2.186
2.163
2.008
1.863
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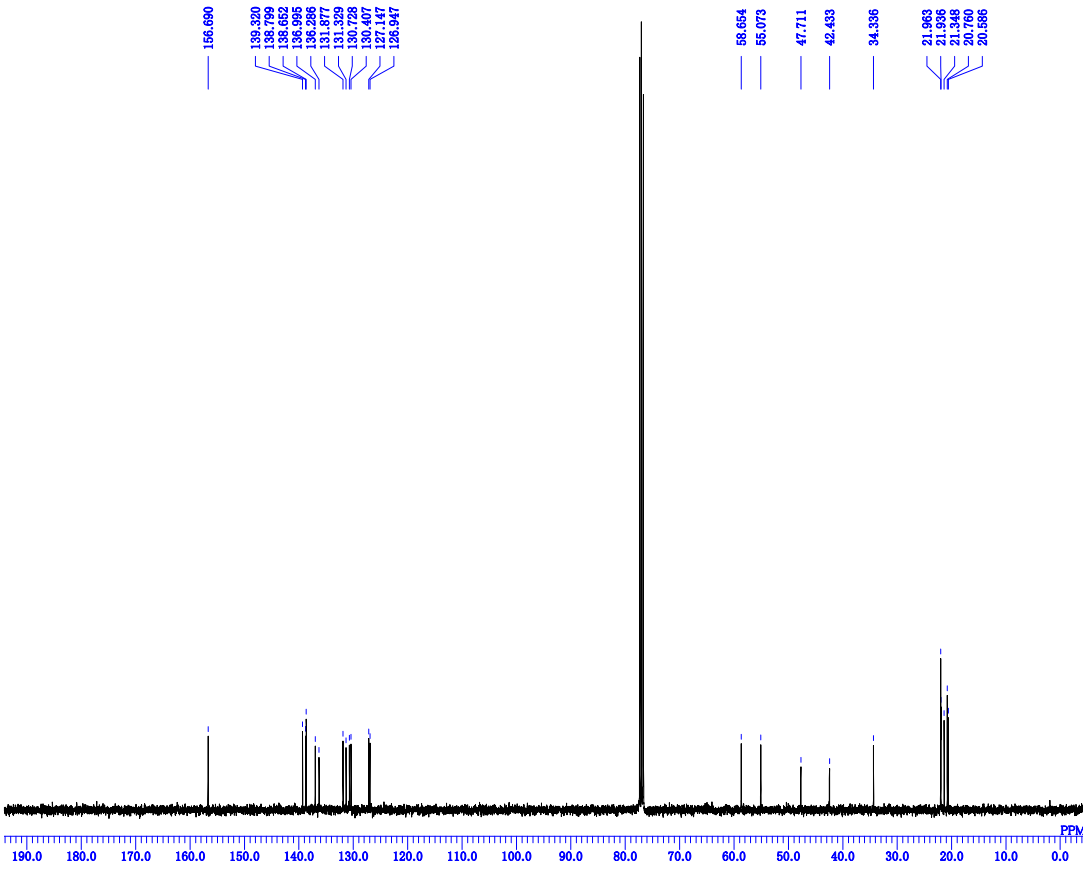
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131.877
131.329
130.728
130.407
127.147
126.947
58.654
55.073
47.711
42.433
34.336
21.963
21.936
21.348
20.760
20.586
PPM
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180.0
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160.0
150.0
140.0
130.0
120.0
110.0
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60.0
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30.0
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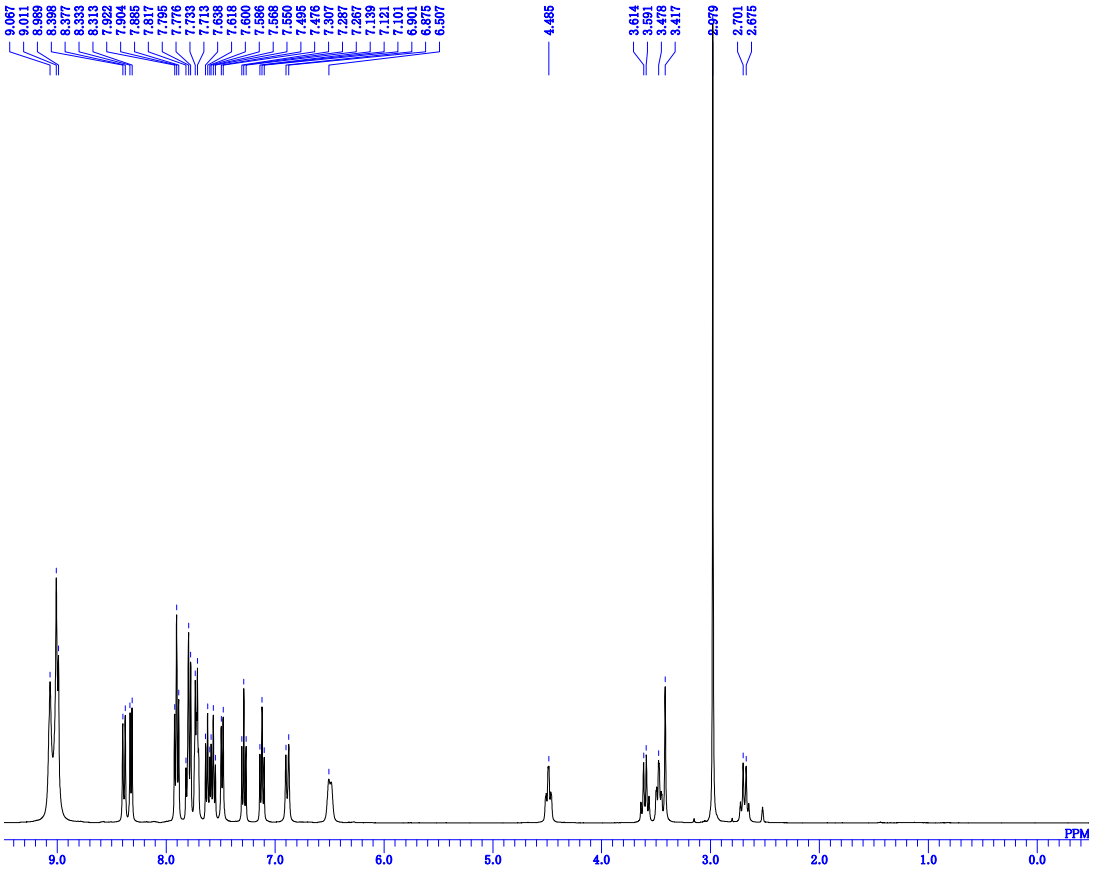
10.0
0.0

6c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8.377
8.333
8.313
7.922
7.904
7.885
7.817
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7.776
7.733
7.713
7.638
7.618
7.600
7.586
7.568
7.550
7.495
7.476
7.397
7.267
7.259
7.121
7.101
6.901
6.875
6.507
4.485
3.614
3.591
3.478
3.417
2.979
2.701
2.675
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4.0
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1.0
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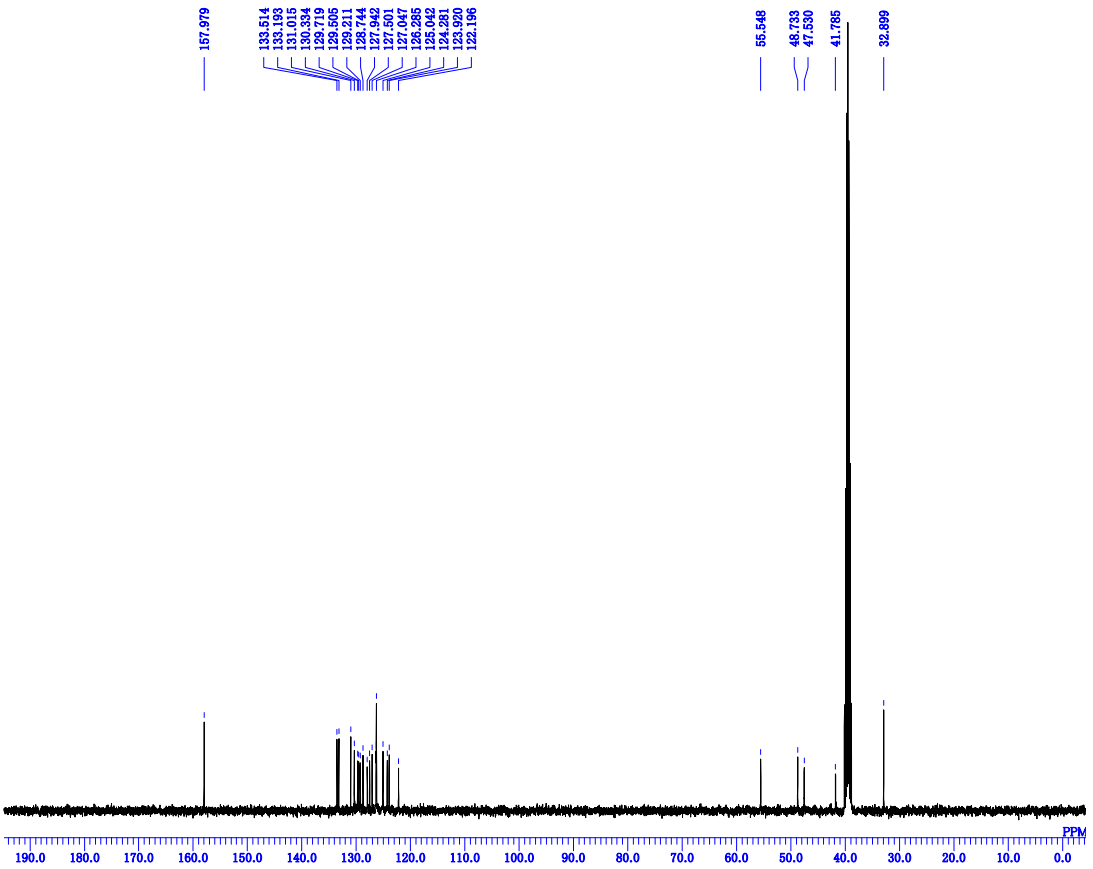
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133.193
131.015
130.334
129.719
129.505
129.211
128.744
127.942
127.501
127.047
126.285
125.042
124.281
123.920
122.196
55.548
48.733
47.530
41.785
32.899
PPM
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160.0
150.0
140.0
130.0
120.0
110.0
100.0
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80.0
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60.0
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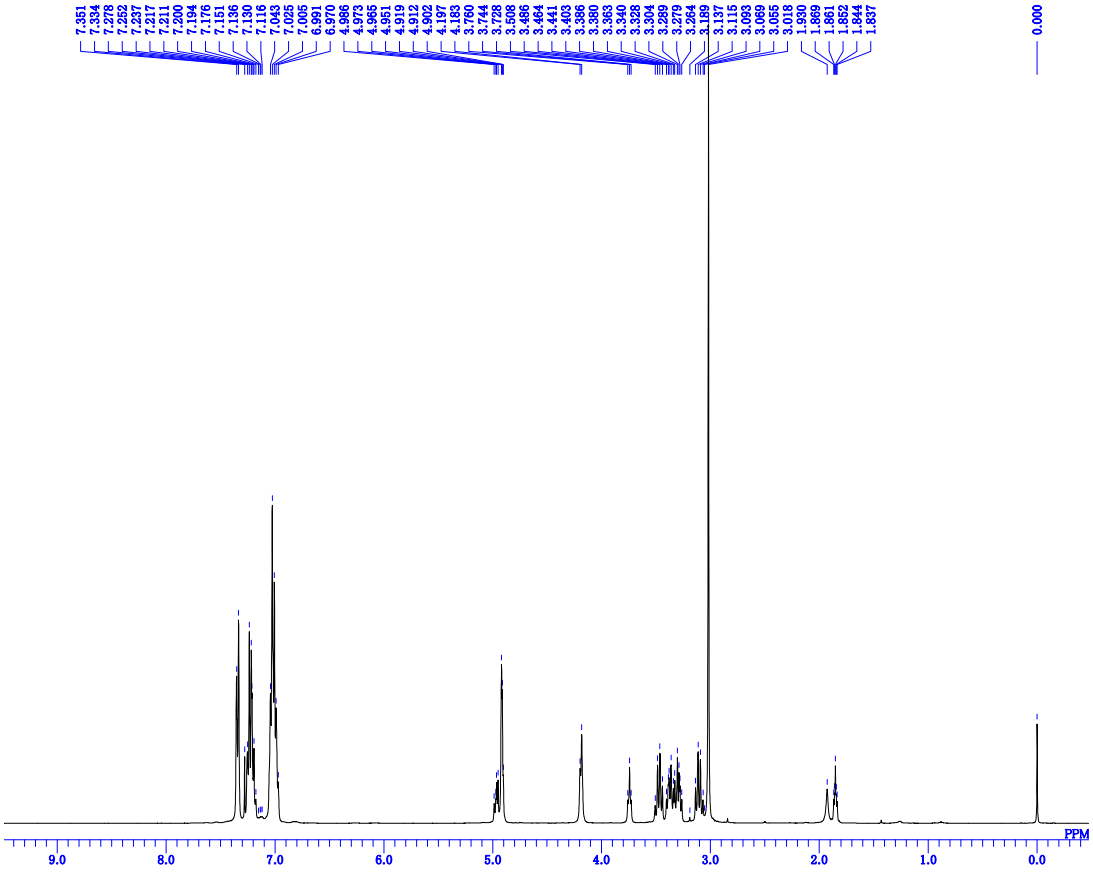
(*P*)-**1a**·HBr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7.200
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7.151
7.136
7.130
7.116
7.043
7.025
7.005
6.991
6.970
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4.973
4.965
4.951
4.919
4.912
4.902
4.197
4.183
3.760
3.744
3.728
3.508
3.466
3.464
3.441
3.403
3.386
3.380
3.363
3.340
3.328
3.304
3.289
3.279
3.264
3.189
3.137
3.115
3.093
3.069
3.055
3.018
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1.869
1.861
1.852
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1.837
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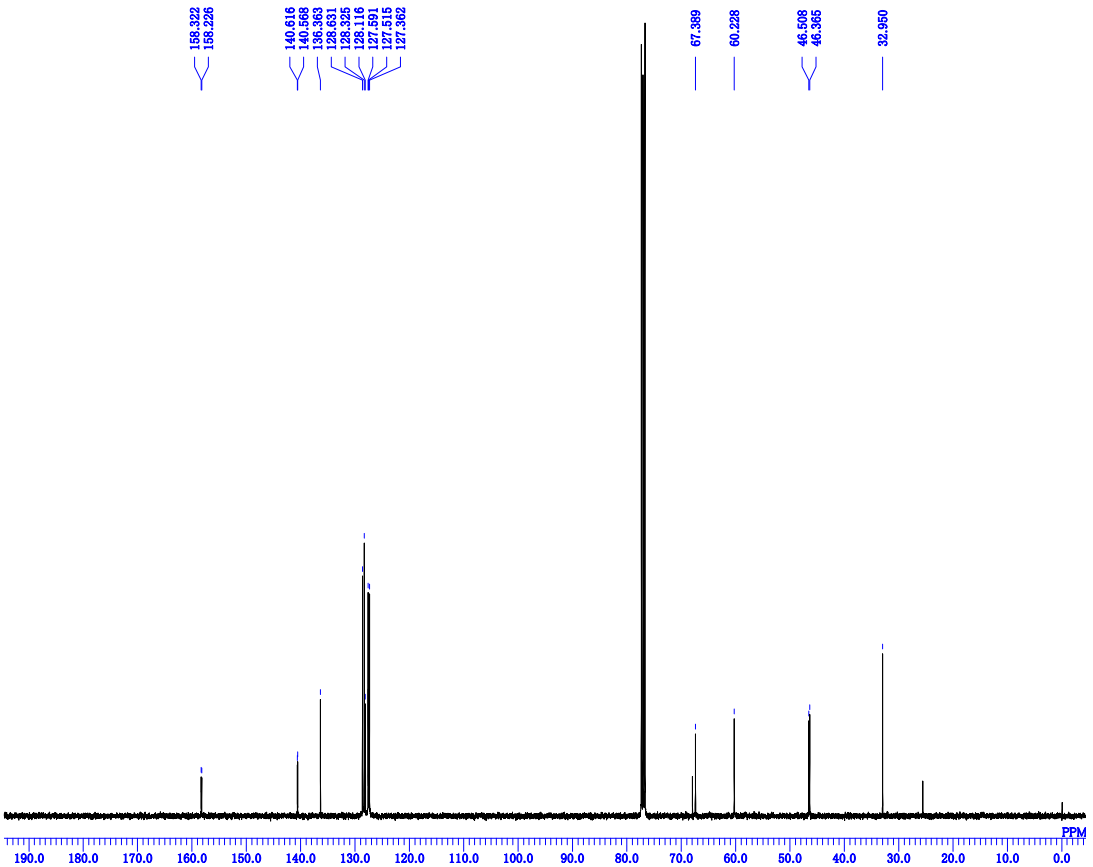
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128.116
127.591
127.515
127.362
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60.228
46.508
46.365
32.950
PPM
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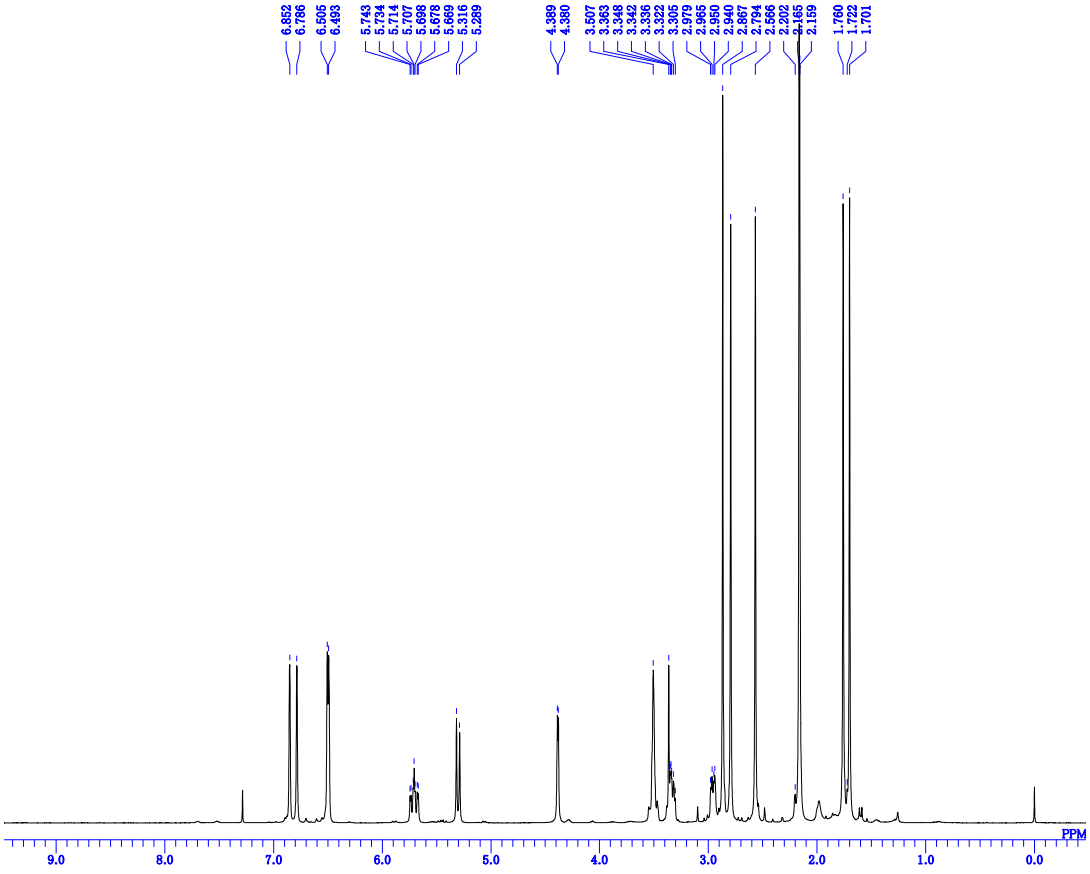
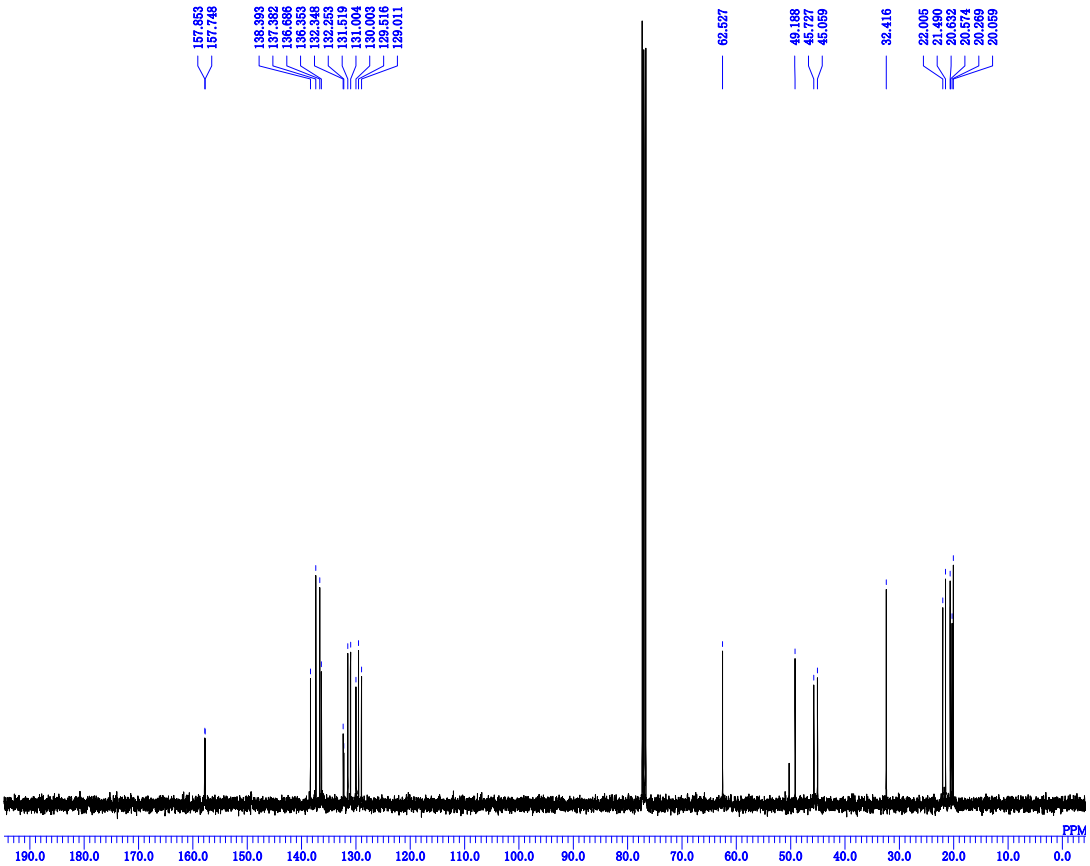
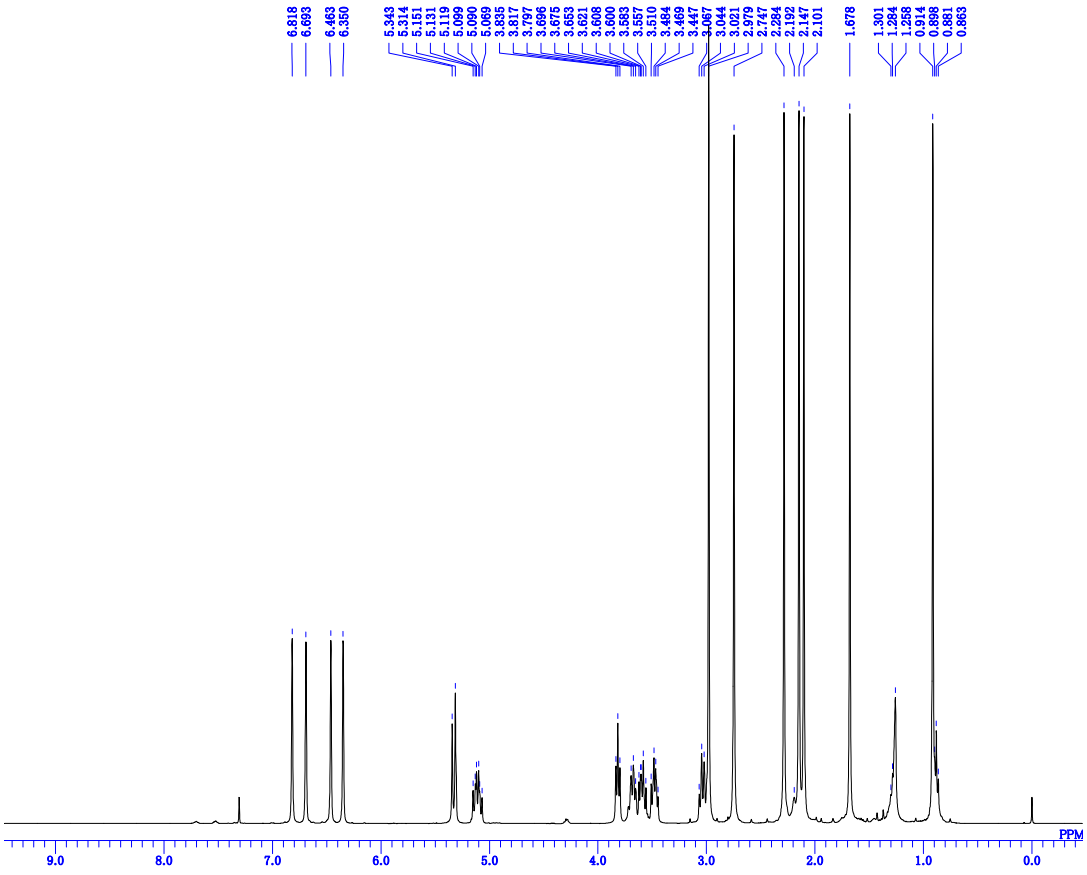
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0

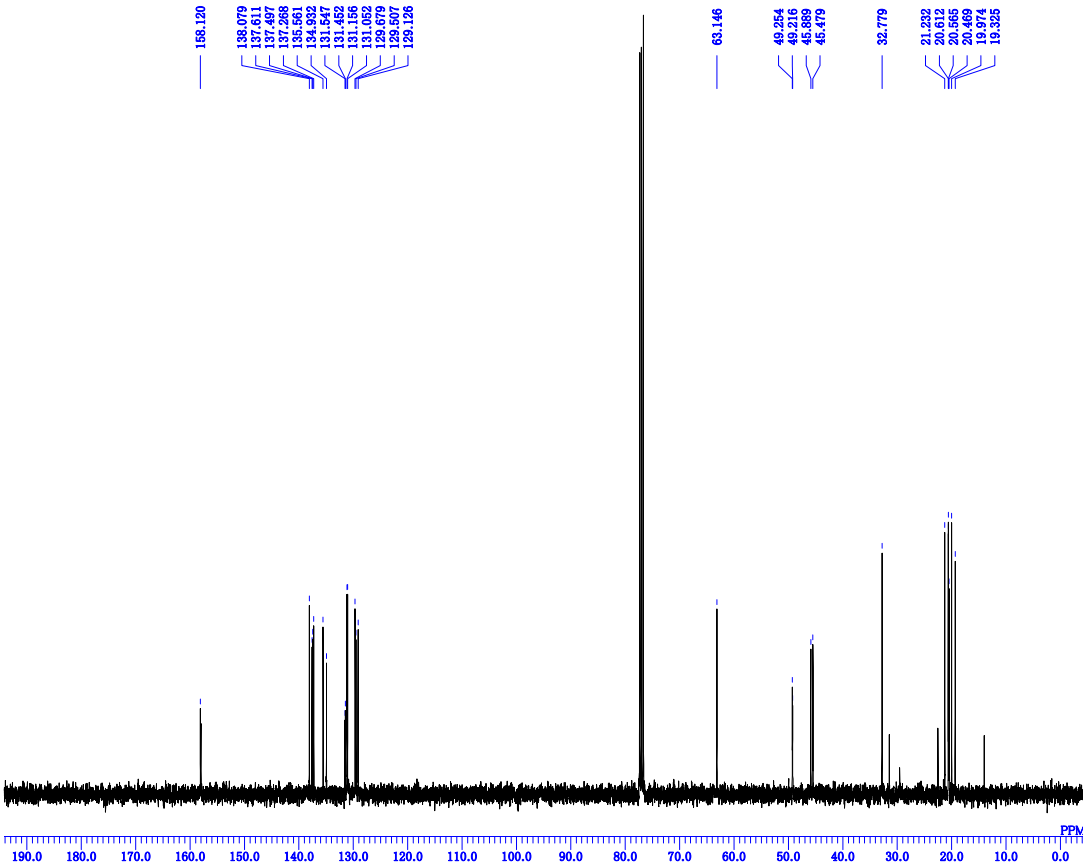
Major isomer of **1b**·HBr



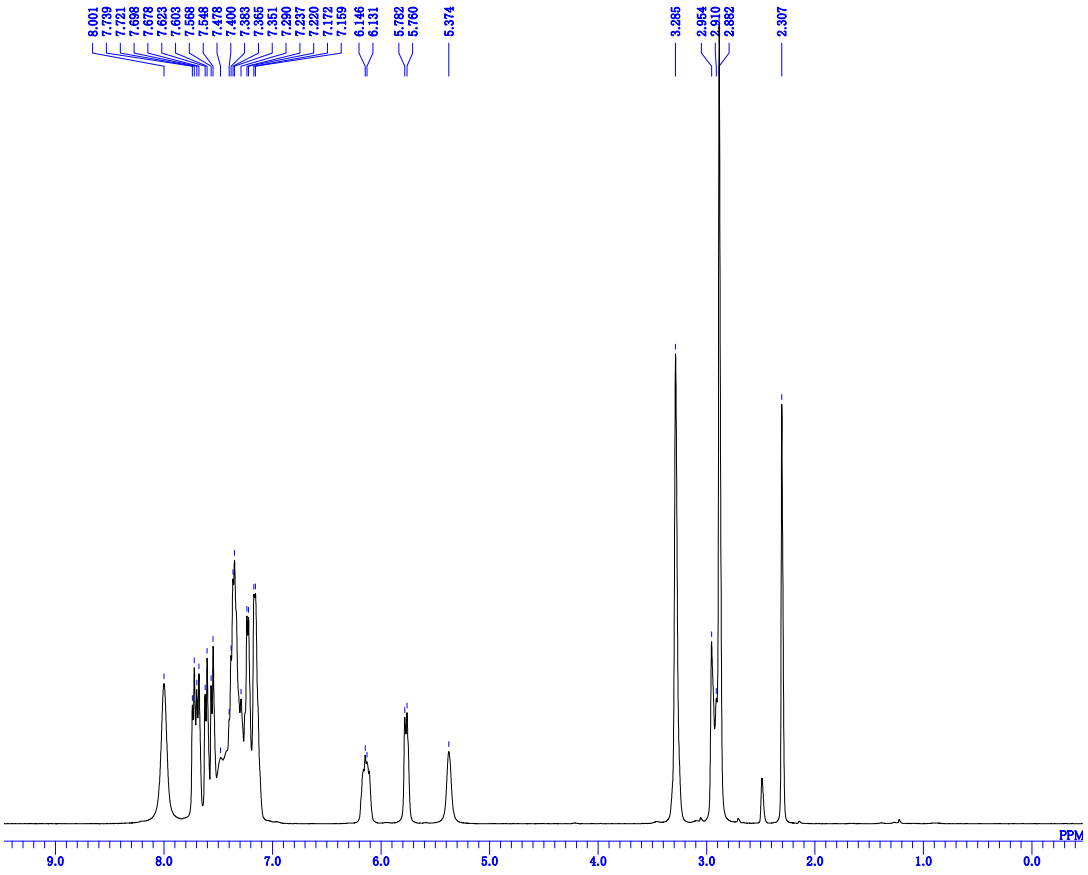


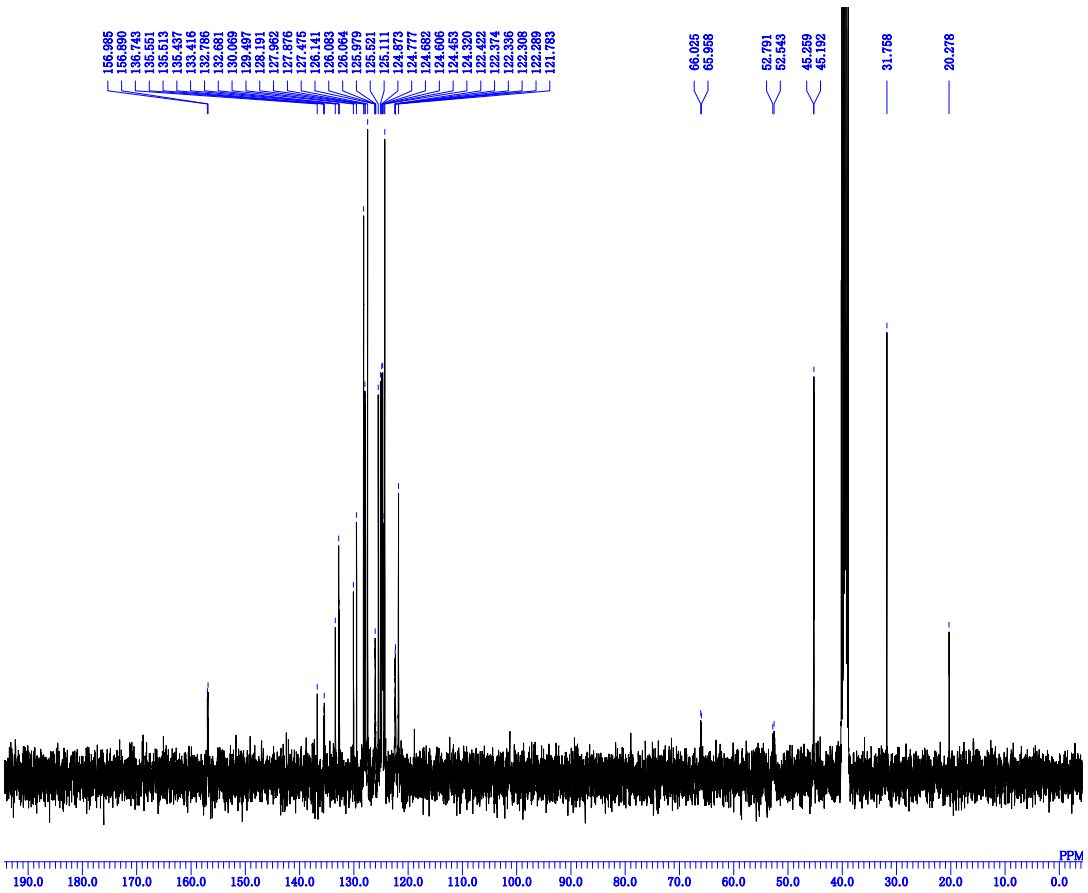
Minor isomer of **1b**·HBr



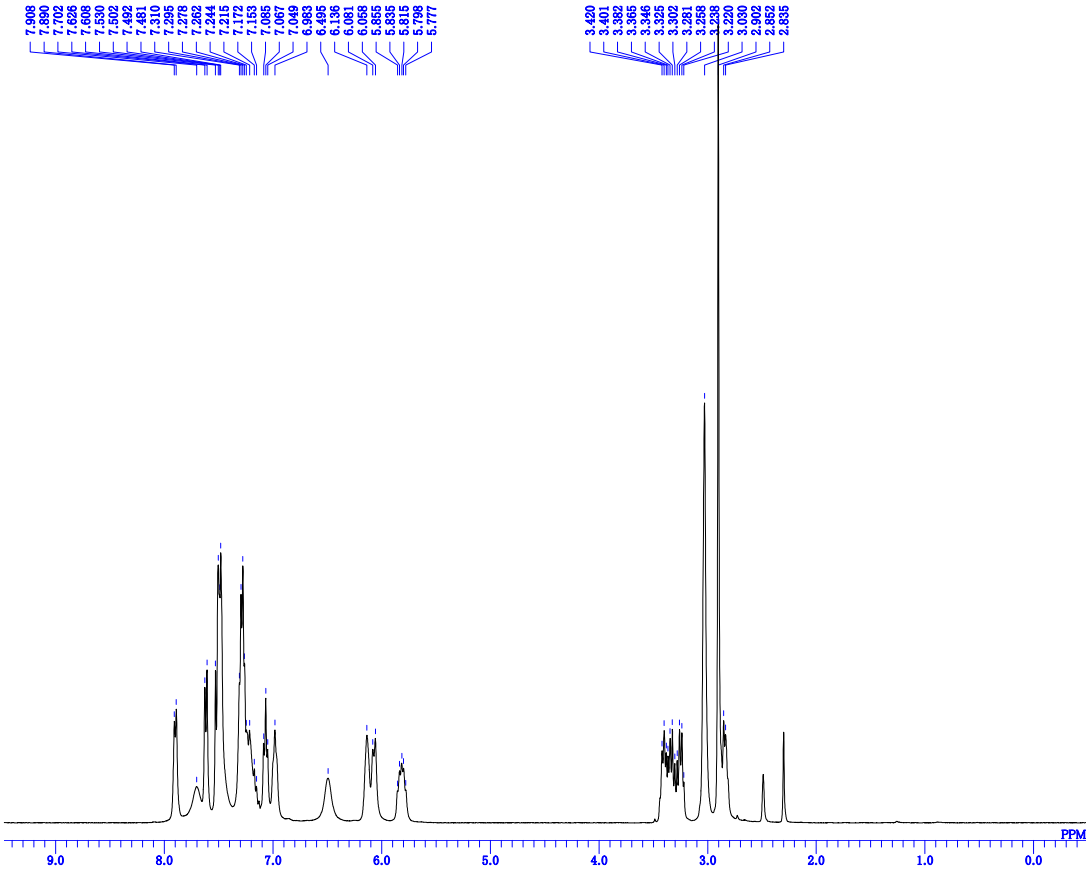


(*M*)-**1c**·HBr (toluene solvate)





(*P*)-**1c**·HBr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6.496
6.136
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6.058
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5.815
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3.382
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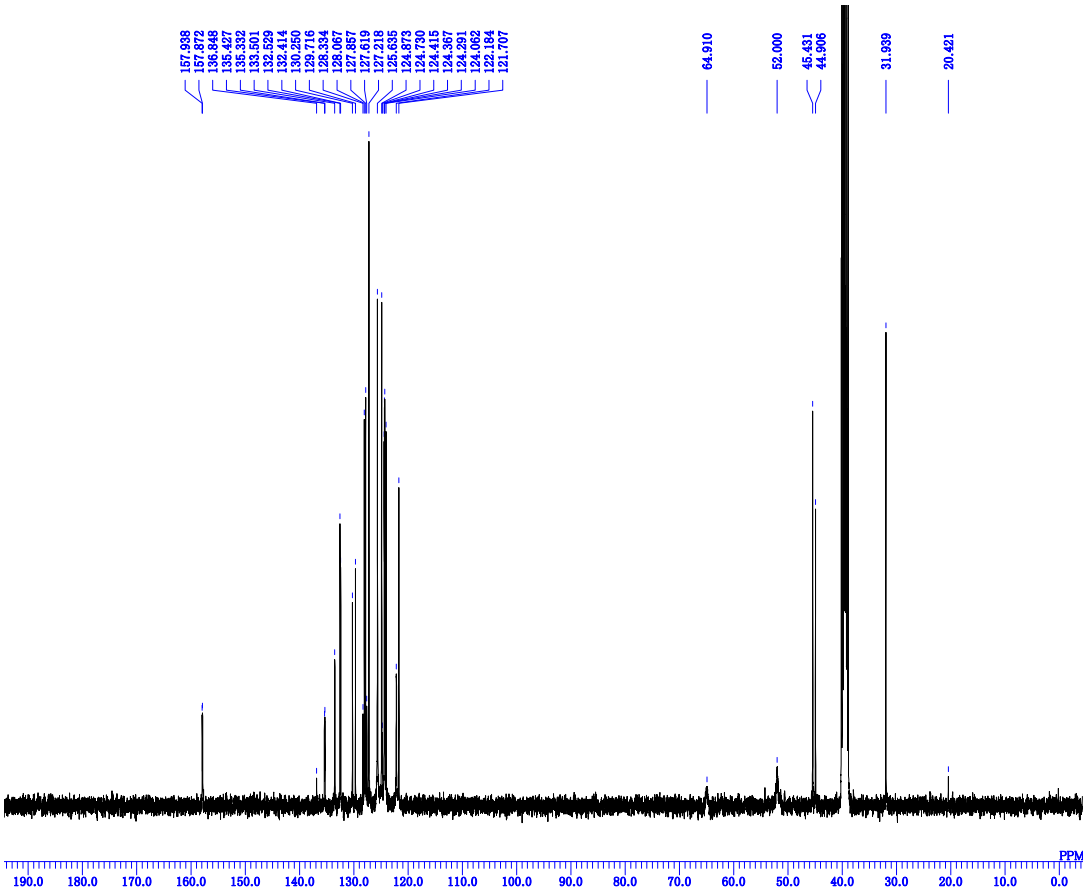
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127.619
127.218
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44.906
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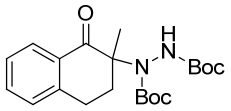
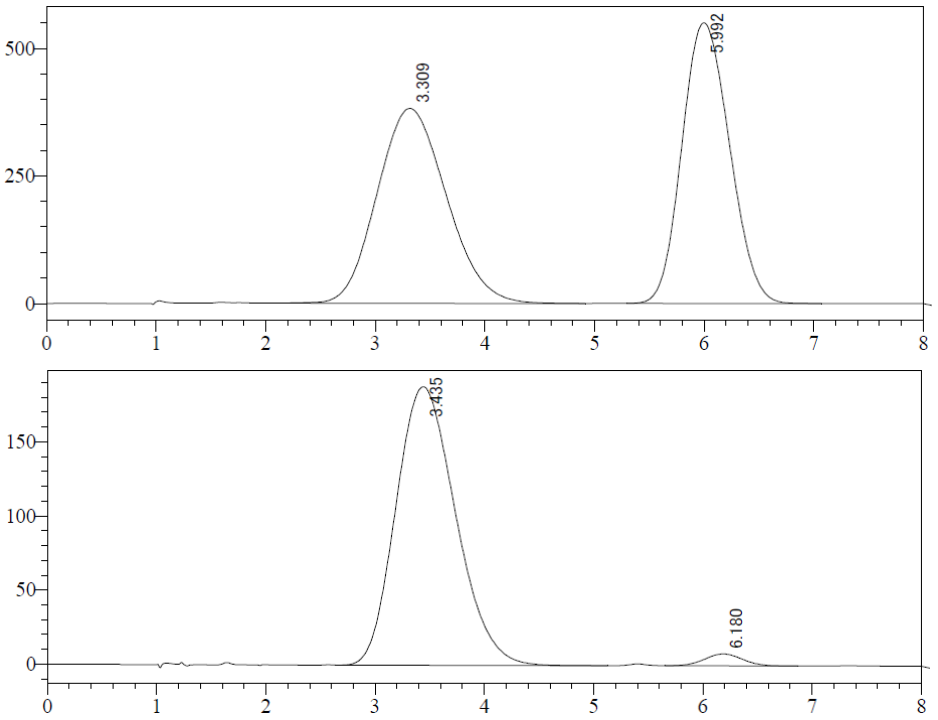

O
H
N
N
Boc
Boc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3
4
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6
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8
150
100
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0
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6.180
0
1
2
3
4
5
6
7
8