# Supporting Information for
# Catalytic Asymmetric Protonation of α-Amino Acid-Derived Ketene Disilyl Acetals Using *P*-Spiro Diaminodioxaphosphonium Barfates as Chiral Proton

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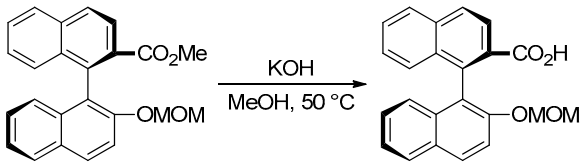
**General Information:** Infrared spectra were recorded on a JASCO FT/IR-300E spectrometer. $^{1}$H NMR spectra were recorded on a JEOL JNM-ECS400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance ($CD_3OD$; 3.31 ppm and $C_6D_6$; 7.16 ppm) or tetramethylsilane (0.0 ppm) resonance as the internal standard ($CDCl_3$). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, septet = sept, m = multiplet, and br = broad) and coupling constants (Hz). $^{13}$C NMR spectra were recorded on a JEOL JNM-ECS400 (101 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$; 77.16 ppm and $C_6D_6$; 128.06 ppm). $^{19}$F NMR spectra were recorded on a JEOL JNM-ECS400 (376 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from $CF_3C_6H_5$ (–64.0 ppm) resonance as the external standard. $^{31}$P NMR spectra were recorded on a JEOL JNM-ECS400 (162 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from $H_3PO_4$ (0.0 ppm) resonance as the external standard. Optical rotations were measured on a JASCO DIP-1000 polarimeter. The high resolution mass spectra were measured on a JEOL JMS-700 (MStation). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm). Flash column chromatography was performed on silica gel 60 (spherical, 40-50 μm; Kanto Chemical Co., Inc.). Enantiomeric excesses were determined by HPLC analysis using chiral columns (ϕ 4.6 mm x 250 mm, DAICEL CHIRALPAK AS-H (ASH), CHIRALCEL OJ-H (OJH), and CHIRALPAK IA (IA)) with hexane (H), isopropyl alcohol (IPA), and ethanol (EtOH) as eluent. All reactions were performed under argon (Ar) atmosphere unless otherwise noted. Tetrahydrofuran (THF), toluene, and $CH_2Cl_2$ were supplied from Kanto Chemical Co., Inc. as "Dehydrated solvent system". Methyl 2'-(methoxymethoxy)-[1,1'-binaphthalene]-2-carboxylate (**S1**) was prepared in enantiomerically pure form according to the literature methods.[1] Other simple chemicals were purchased and used as such.

[1] Uraguchi, D.; Koshimoto, K.; Ooi, T. *Chem. Commun.* **2010**, *46*, 300.

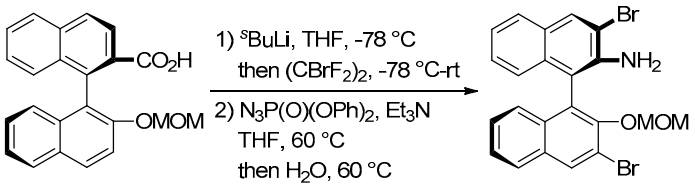
**Experimental Section:**

**Preparation and Characterization of *P*-Spiro Diaminodioxaphosphonium Barfate 1·HBArF**




**S1** **S2**

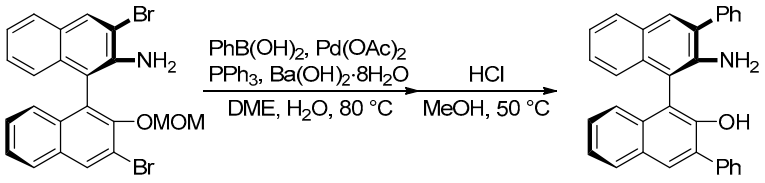
**Representative Procedure for Preparation of S2:** Methyl ester **S1** (1.86 g, 5.0 mmol) was dissolved to a methanolic solution of KOH (2.0 M, 10.0 mL) and the solution was stirred for 18 h at 50 °C. After being cooled to room temperature, water was introduced to the reaction mixture. The aqueous phase was washed with $Et_2O$ and the organic layer was extracted with water twice. The combined aqueous phases were acidified by the addition of an aqueous $KHSO_4$ solution (2.0 M) and extracted with ethyl acetate (EA) twice. The combined organic phases were dried over $Na_2SO_4$, filtered, and evaporated to dryness to give **S2** (1.79 g, 5.0 mmol, quantitative). **S2:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.12 (1H, d, $J$ = 8.4 Hz), 7.98 (1H, d, $J$ = 8.4 Hz), 7.95 (1H, d, $J$ = 8.4 Hz), 7.93 (1H, d, $J$ = 8.4 Hz), 7.87 (1H, d, $J$ = 8.4 Hz), 7.54 (1H, ddd, $J$ = 8.4, 5.6, 2.8 Hz), 7.50 (1H, d, $J$ = 8.4 Hz), 7.33 (1H, ddd, $J$ = 8.4, 7.2, 1.2 Hz), 7.29-7.24 (2H, m), 7.18 (1H, ddd, $J$ = 8.4, 7.2, 1.2 Hz), 6.92 (1H, d, $J$ = 8.4 Hz), 5.00 (1H, d, $J$ = 6.8 Hz), 4.95 (1H, d, $J$ = 6.8 Hz), 3.01 (3H, s), O-H proton was not found due to broadening; $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 172.2, 151.8, 138.0, 135.5, 133.9, 133.0, 129.7, 128.1$_3$, 128.0$_6$, 128.0$_0$, 127.9, 126.8, 126.6, 126.5, 125.1, 124.1, 123.0, 116.5, 94.9, 55.8, three carbons were not found probably due to overlapping; IR (KBr) 2958, 1697, 1464, 1285, 1242, 1149, 1035, 1014, 920, 805, 754 cm$^{-1}$; HRMS (FAB) Calcd for $C_{23}H_{18}O_4$ ([M]$^+$) 358.1205. Found 358.1211.




**S2** **S3**

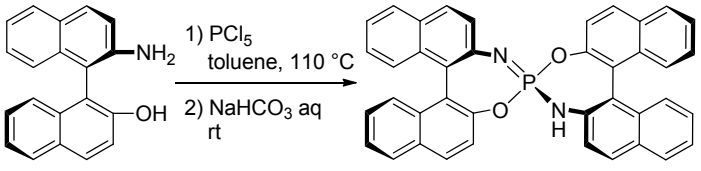
**Representative Procedure for Preparation of S3:** To a solution of **S2** (1.79 g, 5.0 mmol) in THF (50.0 mL) was slowly added $^s$BuLi (1.0 M in cyclohexane/$^n$hexane, 35.0 mL, 35.0 mmol) at –78 °C. After being stirred for 1 h, $(CBrF_2)_2$ (4.2 mL, 35.0 mmol) was added dropwise to the reaction mixture and the resulting solution was allowed to warm to room temperature. The reaction mixture was then poured into a saturated aqueous solution of $NH_4Cl$. The aqueous layer was basified by the addition of NaOH and the organic phase was extracted with an aqueous solution of NaOH (0.50 M). The combined aqueous phases were acidified by addition of an aqueous $KHSO_4$ solution (2.0 M) and extracted with EA twice. After drying over $Na_2SO_4$ and filtration, the organic solvent was removed under vacuum. The residual solid was dissolved in THF (50.0 mL) and the addition of $Et_3N$ (0.70 mL, 5.0 mmol) and $N_3P(O)(OPh)_2$ (1.07 mL, 5.0 mmol) to the solution was followed by stirring for 2 h at 60 °C. Water (20.0 mL) was added to the reaction mixture and the resulting solution was stirred overnight at 60 °C. The reaction mixture was cooled to room temperature and the aqueous phase was extracted with EA twice. The combined organic phases were washed with brine, dried over $Na_2SO_4$, and filtered. All volatiles were removed by

evaporation and the crude material was purified by column chromatography on silica gel (H/EA = 20:1-8:1 as eluent) to give **S3** (0.76 g, 1.56 mmol, 31%) as yellow solid. **S3:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.29 (1H, s), 8.15 (1H, s), 7.83 (1H, d, $J$ = 8.2 Hz), 7.70 (1H, dd, $J$ = 7.2, 2.4 Hz), 7.46 (1H, ddd, $J$ = 8.2, 7.2, 1.4 Hz), 7.32 (1H, ddd, $J$ = 8.2, 7.2, 1.4 Hz), 7.27-7.19 (3H, m), 6.93 (1H, dd, $J$ = 7.2, 2.4 Hz), 4.83 (1H, d, $J$ = 6.0 Hz), 4.78 (1H, d, $J$ = 6.0 Hz), 4.11 (2H, brs), 2.80 (3H, s); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 150.2, 140.3, 133.5, 133.3, 132.3, 132.1, 128.2, 127.5, 127.4, 127.3, 127.2$_0$, 127.1$_6$, 126.6, 125.8, 124.4, 123.3, 118.0, 114.3, 112.5, 99.3, 56.9, one carbon was not found probably due to overlapping; IR (neat) 3435, 1644, 1357, 1155 cm$^{-1}$; HRMS (FAB) Calcd for $C_{22}H_{17}Br_2NO_2$ ([M]$^+$) 486.9609. Found 486.9618.




**S3** **S4**

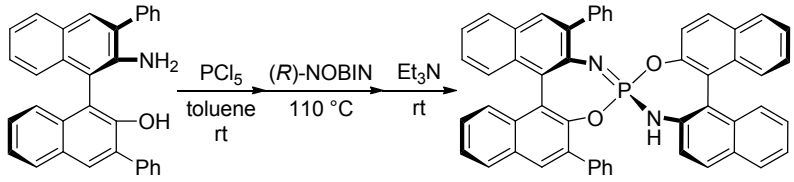
**Representative Procedure for Preparation of S4:** A solid of **S3** (0.76 g, 1.56 mmol), $PhB(OH)_2$ (0.56 g, 4.7 mmol), $Ba(OH)_2 \cdot 8H_2O$ (1.96 g, 6.2 mmol), $Pd(OAc)_2$ (34.8 mg, 0.16 mmol), and $PPh_3$ (0.16 g, 0.62 mmol) were dissolved to DME (16.0 mL) and $H_2O$ (1.6 mL). The reaction mixture was degassed three times and stirred overnight at 80 °C. After being cooled to room temperature, the resulting mixture was diluted with a saturated aqueous solution of $NH_4Cl$ and extracted with EA three times. The organic phases were combined and the solvent was removed under vacuum. The crude residue was dissolved in a methanolic solution of HCl (1.0 M, 16.0 mL) and the solution was stirred for 1 h at 50 °C. A saturated aqueous solution of $NaHCO_3$ was added to the reaction mixture and the aqueous layer was extracted with EA three times. The combined organic phases were dried over $Na_2SO_4$, filtered and concentrated. The crude product was purified by column chromatography on silica gel (H/$CHCl_3$ = 2:1-1:1 as eluent) to afford **S4** (0.54 g, 1.2 mmol, 79%) as pale yellow solid. **S4:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.99 (1H, s), 7.91 (1H, d, $J$ = 8.2 Hz), 7.83-7.79 (1H, m), 7.82 (1H, s), 7.76 (2H, d, $J$ = 7.2 Hz), 7.61 (2H, d, $J$ = 7.2 Hz), 7.51 (2H, t, $J$ = 7.2 Hz), 7.48 (2H, t, $J$ = 7.2 Hz), 7.45-7.35 (3H, m), 7.33-7.21 (4H, m), 7.11 (1H, d, $J$ = 8.2 Hz), 5.47 (1H, s), 3.91 (2H, brs); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 149.6, 142.0, 139.0, 138.1, 133.7, 132.7, 131.0, 130.8, 130.7$_4$, 130.6$_8$, 129.8, 129.7, 129.5, 129.1, 128.5, 128.4, 128.2, 128.0, 127.6, 127.4, 127.1, 124.6, 124.2, 123.8, 123.0, 115.6, 108.9, one carbon was not found probably due to overlapping; IR (KBr) 3464, 3351, 3056, 1622, 1496, 1430, 1239, 1197, 1142, 895, 787, 748 cm$^{-1}$; HRMS (FAB) Calcd for $C_{32}H_{24}NO^+$ ([M+H]$^+$) 438.1858. Found 438.1853.




**1a**

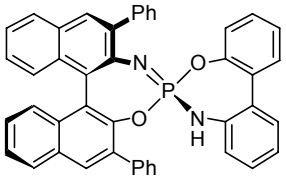
**Representative Procedure for Preparation of 1a:** To a solution of $PCl_5$ (20.8 mg, 0.10 mmol) in toluene (1.0 mL) was added (*R*)-2'-amino-1,1'-binaphthyl-2-ol [(*R*)-NOBIN] (57.1 mg, 0.2 mmol) at room temperature and the

reaction mixture was stirred for 5 h at 110 °C. The resulting mixture was poured into a saturated aqueous solution of $NaHCO_3$ and the aqueous phase was extracted with EA three times. The combined organic phases were dried over $Na_2SO_4$. After filtration and evaporation of the solvent, the crude material was dissolved in a minimum amount of chloroform and nearly colorless solid of pure iminophosphorane **1a** (32.2 mg, 0.054 mmol, 54%) was precipitated by the addition of methanol. **1a:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.07 (2H, d, $J$ = 8.0 Hz), 7.99 (2H, d, $J$ = 8.0 Hz), 7.97 (2H, d, $J$ = 8.0 Hz), 7.92 (2H, d, $J$ = 7.0 Hz), 7.48 (2H, d, $J$ = 8.0 Hz), 7.45 (2H, t, $J$ = 8.0 Hz), 7.43 (2H, d, $J$ = 8.0 Hz), 7.38 (2H, t, $J$ = 8.0 Hz), 7.33-7.18 (8H, m), one proton was not found probably due to broadening; $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 146.8 (d, $J_{P\text{-}C}$ = 6.8 Hz), 139.9 (d, $J_{P\text{-}C}$ = 2.9 Hz), 133.3 (d, $J_{P\text{-}C}$ = 1.9 Hz), 133.0, 131.8, 130.6 (d, $J_{P\text{-}C}$ = 1.9 Hz), 130.5, 130.0, 128.3, 128.2, 127.7, 127.2, 126.4, 126.1, 125.7, 125.6, 125.0, 124.3 (d, $J_{P\text{-}C}$ = 4.8 Hz), 123.3 (d, $J_{P\text{-}C}$ = 4.8 Hz), 120.9 (d, $J_{P\text{-}C}$ = 1.9 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ 29.0; IR (KBr) 3353, 3052, 1592, 1506, 1460, 1367, 1323, 1230, 1210, 1118, 974, 941, 876, 811, 750 cm$^{-1}$; HRMS (FAB) Calcd for $C_{40}H_{26}N_2O_2P^+$ ([M+H]$^+$) 597.1726. Found 597.1735.



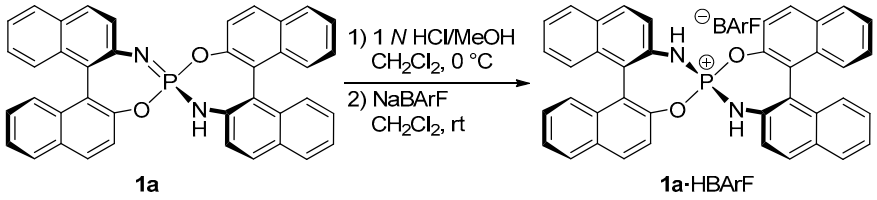

**S4** **1b**

**Representative Procedure for Preparation of 1b:** To a solution of $PCl_5$ (20.8 mg, 0.10 mmol) in toluene (1.0 mL) was added **S4** (43.8 mg, 0.10 mmol) at room temperature and the reaction mixture was stirred for 1 h. Then, (*R*)-NOBIN (34.2 mg, 0.12 mmol) was added and the reaction mixture was stirred overnight at 110 °C. After being cooled to room temperature, the reaction mixture was treated with triethylamine (0.14 mL, 1.0 mmol) in the same pot and all volatiles were evaporated. Purification of the residue by column chromatography on silica gel (H/EA = 20/1-6/1 as eluent) gave iminophosphorane **1b** (59.1 mg, 0.079 mmol, 79%) as white solid. **1b:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.19 (1H, s), 8.07 (1H, d, $J$ = 1.4 Hz), 8.00 (1H, d, $J$ = 8.2 Hz), 7.93 (1H, d, $J$ = 8.2 Hz), 7.80-7.62 (5H, m), 7.50-7.43 (1H, m), 7.40-6.91 (20H, m), 6.64 (1H, d, $J$ = 8.2 Hz), 6.27 (1H, d, $J$ = 8.2 Hz), 5.81 (1H, br); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 146.3 (d, $J_{P\text{-}C}$ = 6.8 Hz), 144.8 (d, $J_{P\text{-}C}$ = 6.8 Hz), 139.6, 137.0, 136.7, 133.5, 133.2, 133.0, 132.5, 132.4, 131.8, 131.2, 130.9, 130.8, 130.0, 129.7, 129.3, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.7, 127.2, 127.1, 126.4, 126.1, 125.9 (d, $J_{P\text{-}C}$ = 3.7 Hz), 125.6, 125.1, 124.3, 120.7, fifteen carbons were not found probably due to broadening or overlapping; $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ 25.0; IR (KBr) 2925, 1722, 1593, 1497, 1408, 1262, 1030, 875, 804, 750 cm$^{-1}$; HRMS (FAB) Calcd for $C_{52}H_{34}N_2O_2P^+$ ([M+H]$^+$) 749.2352. Found 749.2330.



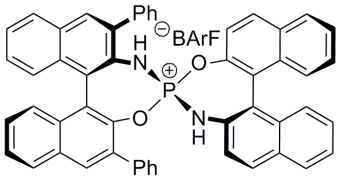

**1c:** Following above procedure with using 2'-amino-1,1'-biphenyl-2-ol (**2**) instead of (*R*)-NOBIN, the title compound was prepared in 38% yield. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.18 (1H, s), 8.05 (1H, d, $J$ = 1.6 Hz), 8.02 (1H, d, $J$ = 7.8 Hz), 7.94 (1H, d, $J$ = 7.8 Hz), 7.75 (2H, d, $J$ = 7.8 Hz), 7.68 (2H, d, $J$ = 8.7 Hz), 7.49 (1H, ddd, $J$ = 7.8, 5.6, 2.0 Hz), 7.40 (1H, t, $J$ = 7.8 Hz), 7.36-7.11 (12H, m), 7.08 (1H, t, $J$ = 7.8 Hz), 6.93 (1H, t, $J$ = 7.8 Hz), 6.88 (1H, t, $J$ = 7.8 Hz), 6.77 (1H, t, $J$ = 7.8 Hz), 6.48 (1H, d, $J$ = 7.8 Hz), 6.06 (1H, d, $J$ = 7.8 Hz), one proton was not found

probably due to broadening; $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 147.1 (d, $J_{P\text{-}C}$ = 6.8 Hz), 144.7 (d, $J_{P\text{-}C}$ = 7.2 Hz), 139.4, 137.1, 136.7, 133.5 (d, $J_{P\text{-}C}$ = 1.9 Hz), 133.4 (d, $J_{P\text{-}C}$ = 2.9 Hz), 132.8, 131.8, 131.2, 130.7$_5$,130.7$_1$, 130.6, 130.5, 130.0, 129.8, 129.1, 128.8, 128.5, 128.4, 128.2, 127.9, 127.8, 127.3, 127.2, 126.7, 126.3, 126.1, 125.9, 125.4$_4$, 125.3$_7$, 125.2$_6$, 124.6, 124.4, 121.6 (d, $J_{P\text{-}C}$ = 3.9 Hz), five carbons were not found probably due to broadening or overlapping; $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ 23.6; IR (KBr) 3340, 3056, 1600, 1496, 1407, 1265, 1181, 1109, 948, 913, 753 cm$^{-1}$; HRMS (FAB) Calcd for $C_{44}H_{30}N_2O_2P^+$ ($[M+H]^+$) 649.2039. Found 649.2025.



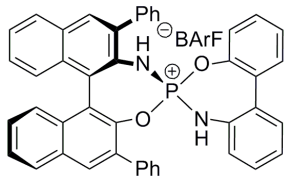

**1a** **1a**·HBArF

**Representative Procedure for Preparation of Chiral Arylaminophosphonium Barfate 1·HBArF:** To a solution of iminophosphorane **1a** (32.2 mg, 0.054 mmol) in $CH_2Cl_2$ (1.0 mL) was added a methanolic solution of HCl (1.0 M, 0.10 mL) at 0 °C. After being stirred for 5 min at 0 °C, all volatiles were evaporated to dryness. Treatment of a solution of the residual solid in $CH_2Cl_2$ (1.0 mL) with NaBArF (43.1 mg, 0.049 mmol) was followed by stirring for 5 min. Water was then introduced to the reaction mixture and the aqueous phase was extracted with $CH_2Cl_2$ three times. The combined organic phases were dried over $Na_2SO_4$ and filtered. Concentration under vacuum furnished phosphonium barfate **1a**·HBArF (75.1 mg, 0.051 mmol, quantitative) as white solid. **1a·HBArF:** $^1$H NMR (400 MHz, $CD_3OD$) $\delta$ 8.32 (2H, d, $J$ = 8.7 Hz), 8.21 (2H, d, $J$ = 8.7 Hz), 8.10 (2H, d, $J$ = 8.7 Hz), 8.02 (2H, d, $J$ = 8.7 Hz), 7.67-7.47 (20H, m), 7.35-7.24 (4H, m), 7.21 (2H, d, $J$ = 8.7 Hz), 7.17 (2H, d, $J$ = 8.7 Hz), two protons were not found probably due to deuterating; $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 161.8 (q, $J_{B\text{-}C}$ = 50.6 Hz), 144.4 (d, $J_{P\text{-}C}$ = 8.7 Hz), 135.0, 132.4, 132.3 (q, $J_{F\text{-}C}$ = 15.5 Hz), 129.4, 129.2, 128.8, 128.5, 128.3, 128.0, 127.6, 127.2, 126.9, 124.7 (q, $J_{F\text{-}C}$ = 275.8 Hz), 124.1, 124.0$_3$, 123.9$_7$, 123.6, 122.2 (d, $J_{P\text{-}C}$ = 3.9 Hz), 118.6, 118.5, 118.3, 117.6, one carbon was not found probably due to broadening or overlapping; $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ 34.7; $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ –63.8; IR (KBr) 3384, 1510, 1356, 1279, 1123, 994, 886, 812, 753, 713 cm$^{-1}$; HRMS (FAB) Calcd for $C_{40}H_{26}N_2O_2P^+$ ($[M\text{-}BArF]^+$) 597.1726. Found 597.1719; $[\alpha]_D^{24}$ –102.1 ($c$ = 0.53, $CHCl_3$).



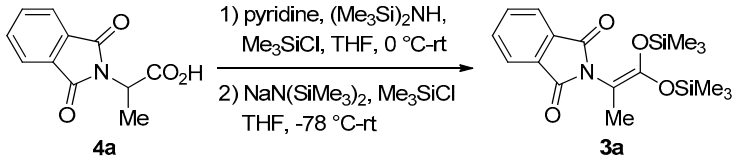

**1b·HBArF:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.45 (1H, s), 8.23 (1H, s), 8.11 (1H, d, $J$ = 8.2 Hz), 8.07 (1H, d, $J$ = 8.2 Hz), 7.86-7.74 (4H, m), 7.72 (8H, br), 7.66-7.58 (3H, m), 7.50-7.14 (19H, m), 7.04 (1H, d, $J$ = 8.2 Hz), 6.92 (1H, d, $J$ = 8.2 Hz), 6.83 (1H, d, $J$ = 8.2 Hz), 6.34 (1H, d, $J$ = 8.2 Hz), two protons were not found probably due to broading; $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 161.8 (q, $J_{B\text{-}C}$ = 50.6 Hz), 143.5 (d, $J_{P\text{-}C}$ = 8.7 Hz), 142.0 (d, $J_{P\text{-}C}$ = 8.7 Hz), 136.9, 134.9, 134.5 (d, $J_{P\text{-}C}$ = 3.3 Hz), 134.3, 133.2, 133.1, 132.7, 132.3, 132.1, 132.0, 131.8 (q, $J_{F\text{-}C}$ = 16.4 Hz), 131.5, 131.1 (d, $J_{P\text{-}C}$ = 2.9 Hz), 130.5, 129.4, 129.1 (d, $J_{P\text{-}C}$ = 2.9 Hz), 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0$_1$, 127.9$_7$, 127.6, 127.4$_8$, 127.4$_5$, 127.2, 127.1$_0$, 127.0$_6$, 126.6$_2$, 126.5$_7$, 125.1 (d, $J_{P\text{-}C}$ = 2.6 Hz), 124.7 (q, $J_{F\text{-}C}$ = 276.7 Hz), 124.9, 123.0, 122.6, 121.2$_6$, 121.2$_1$, 117.8, 117.5$_9$, seven carbons were not found probably due to broadening or overlapping; $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ 32.7; $^{19}$F NMR (376 MHz,

$CDCl_3$) $\delta$ –63.9; IR (KBr) 3347, 1610, 1356, 1280, 1128, 1019, 995, 887, 839, 712 $cm^{-1}$; HRMS (FAB) Calcd for $C_{52}H_{34}N_2O_2P^+$ ([M-BArF]$^+$) 749.2352. Found 749.2330; $[\alpha]_D^{26}$ –382.0 ($c$ = 0.51, $CHCl_3$).

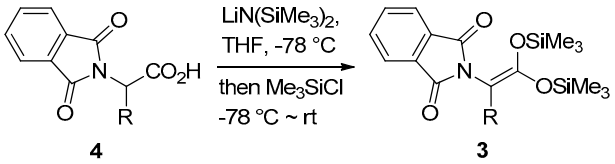



**1c·HBArF:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.41 (1H, s), 8.21 (1H, s), 8.10 (1H, d, $J$ = 8.2 Hz), 8.08 (1H, d, $J$ = 8.2 Hz), 7.75 (2H, d, $J$ = 8.2 Hz), 7.67 (8H, s), 7.64 (1H, d, $J$ = 8.2 Hz), 7.62 (1H, d, $J$ = 8.2 Hz), 7.54-7.11 (17H, m), 7.46 (4H, s), 6.98 (1H, t, $J$ = 8.2 Hz), 6.70 (1H, d, $J$ = 8.2 Hz), 6.17 (1H, d, $J$ = 8.2 Hz), two protons were not found probably due to broadening; $^{13}$C NMR (101MHz, $CDCl_3$) $\delta$ 161.8 (q, $J_{B\text{-}C}$ = 50.6 Hz), 144.6 (d, $J_{P\text{-}C}$ = 7.8 Hz), 142.0 (d, $J_{P\text{-}C}$ = 8.7 Hz), 136.7, 134.9, 134.3, 133.0, 132.8, 132.6 (q, $J_{F\text{-}C}$ = 14.5 Hz), 132.4, 132.0, 131.4 (d, $J_{P\text{-}C}$ = 2.4 Hz), 131.3, 130.7, 130.5, 130.3, 129.5, 129.4, 129.3, $129.1_8$, $129.1_5$, 129.1, $129.0_0$, $128.9_5$, 128.8, 128.7, $128.5_8$, $128.5_5$, $128.5_2$, 128.5, 128.4, 128.3, 128.1, 128.0, 127.5, 127.2, $126.8_1$, $126,7_6$, 125.3, 124.9 (d, $J_{P\text{-}C}$ = 2.2 Hz), 124.7(q, $J_{F\text{-}C}$ = 276.7 Hz), $124.3_1$, $124.2_5$, 120.6 (d, $J_{P\text{-}C}$ = 4.8 Hz), 117.6; $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ 31.0; $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ –63.9; IR (KBr) 3346, 3061, 1356, 1279, 1126, 1016, 992, 757, 712 $cm^{-1}$; HRMS (FAB) Calcd for $C_{44}H_{30}N_2O_2P^+$ ([M-BArF]$^+$) 649.2064. Found 649.2064; $[\alpha]_D^{30}$ –295.04 ($c$ = 0.14, $CHCl_3$).

**Preparation and Charactrization of Ketene Disilyl Acetals 3:**



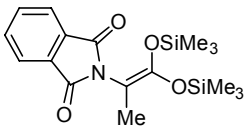

**Method I**[2]**:** To a solution of **4a** (1.1 g, 5.0 mmol) in THF (0.50 mL) was slowly added pyridine (0.25 mL) at 0 °C. After being stirred for 30 min at 0 °C, $(Me_3Si)_2NH$ (1.0 mL, 5.0 mmol) and $Me_3SiCl$ (0.58 mL, 2.5 mmol) were introduced to the reaction mixture. The resulting suspension was stirred for 12 h at room temperature. The reaction mixture was filtered through a pad of Celite with $Et_2O$ and the filtrate was concentrated. Without purification, the crude material was used for subsequent step. The solution of the crude silyl ester in THF (5.0 mL) was added slowly to a solution of $NaN(SiMe_3)_2$ in THF (1.0 M, 7.5 mL, 7.5 mmol) at –78 °C and the reaction mixture was stirred for 1 h before addition of $Me_3SiCl$ (2.1 mL, 9.0 mmol). The reaction mixture was then allowed to warm to room temperature and stirred there overnight. The resulting mixture was concentrated and the residue was filtered through a pad of florisil with $Et_2O$. Concentration of the filtrate under vacuum gave ketene disilyl acetals **3a** in analytically pure form.



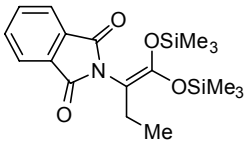

**Method II**[3]**:** To a solution of $(Me_3Si)_2NH$ (0.58 mL, 2.8 mmol) in THF (1.5 mL) was added $^n$BuLi (1.67 M in $^n$hexane, 1.7 mL, 2.8 mmol) dropwise at 0 °C. After being stirred for 30 min at 45 °C, the mixture was cooled to

[2] Rotzoll, S.; Ullah, E.; Görls, H.; Fischer, C.; Langer, P. *Tetrahedron* **2007**, *63*, 2647.
[3] Nakamura, S.; Kaneeda, M.; Ishihara, K.; Yamamoto, H. *J. Am. Chem. Soc.* **2000**, *122*, 8120.

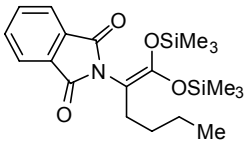
–78 °C and the carboxylic acid **4** (1.0 mmol) in THF (5.0 mL) was slowly introduced. The reaction mixture was stirred for 1 h at –78 °C and, subsequently, $Me_3SiCl$ (0.38 mL, 3.0 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. After removal of all volatiles in vacuo, the residue was filtered by suction through a pad of Celite with $Et_2O$. The filtrate was concentrated and purification of the crude residue by standard column chromatography on silica gel (H/EA = 5:1) afforded ketene disilyl acetals **3**.



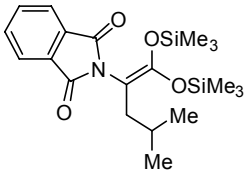
**3a:** The synthesis was performed according to the Method I and title compound was obtained as pale yellow solid in 80% yield.[4] $^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 7.53 (2H, dd, $J$ = 5.5, 3.0 Hz), 6.89 (2H, dd, $J$ = 5.5, 3.0 Hz), 1.99 (3H, s), 0.28 (9H, s), 0.09 (9H, s); $^{13}$C NMR (101 MHz, $C_6D_6$) $\delta$ 167.4, 150.2, 133.5, 133.0, 123.0, 90.8, 15.0, 0.3, 0.2; IR (neat) 2957, 1712, 1693, 1397, 1252, 1159, 851 cm$^{-1}$; HRMS (FAB) Calcd for $C_{17}H_{26}NO_4Si_2^+$ ([M+H]$^+$) 364.1401. Found 364.1404.



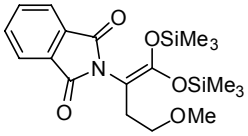
**3b:** The synthesis was performed according to the Method II and title compound was obtained as yellow solid in 74% yield. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.85 (2H, dd, $J$ = 5.2, 3.2 Hz), 7.71 (2H, dd, $J$ = 5.2, 3.2 Hz), 2.33 (2H, q, $J$ = 7.6 Hz), 0.90 (3H, t, $J$ = 7.6 Hz), 0.32 (9H, s), 0.04 (9H, s); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 168.4, 149.4, 133.9, 132.4, 123.2, 95.7, 21.5, 12.0, 0.4, 0.2; IR (neat) 2966, 1716, 1688, 1386, 1253, 1165, 882, 849 cm$^{-1}$; HRMS (FAB) Calcd for $C_{18}H_{27}NO_4Si_2^+$ ([M+H]$^+$) 377.1501. Found 377.1490.



**3c:** The synthesis was performed according to the Method II and title compound was obtained as orange viscous oil in 81% yield. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.84 (2H, dd, $J$ = 5.6, 3.2 Hz), 7.71 (2H, dd, $J$ = 5.6, 3.2 Hz), 2.29 (2H, t, $J$ = 7.8 Hz) 1.36-1.23 (4H, m), 0.85 (3H, t, $J$ = 6.9 Hz), 0.32 (9H, s), 0.05 (9H, s); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 168.3, 149.7, 133.9, 132.4, 123.2, 94.7, 29.7, 28.2, 22.6, 14.1, 0.5, 0.3; IR (neat) 2958, 1716, 1687, 1386, 1268, 1254, 1157, 881, 849 cm$^{-1}$; HRMS (FAB) Calcd for $C_{20}H_{32}NO_4Si_2^+$ ([M+H]$^+$) 406.1870. Found 406.1870.

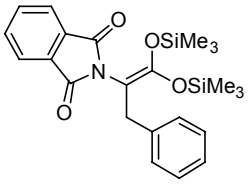


**3d:** The synthesis was performed according to the Method II and title compound was obtained as orange viscous oil in 36% yield. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.83 (2H, dd, $J$ = 5.6, 3.2 Hz), 7.70 (2H, dd, $J$ = 5.6, 3.2 Hz), 2.16 (2H, d, $J$ = 6.9 Hz), 1.52 (1H, nonet, $J$ = 6.9 Hz), 0.91 (6H, d, $J$ = 6.9 Hz), 0.32 (9H, s), 0.07 (9H, s); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 168.3, 150.4, 133.9, 132.4, 123.2, 94.0, 37.7, 27.0, 22.7, 0.7, 0.4; IR (neat) 2955, 1715, 1685, 1385, 1253, 1159, 848, 722 cm$^{-1}$; HRMS (FAB) Calcd for $C_{20}H_{32}NO_4Si_2^+$ ([M+H]$^+$) 406.1870. Found 406.1883.

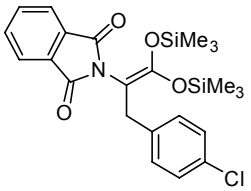


**3e:** The synthesis was performed according to the Method II and title compound was obtained as orange viscous oil in 34% yield. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.82 (2H, dd, $J$ = 5.6, 3.2 Hz), 7.69 (2H, dd, $J$ = 5.6, 3.2 Hz), 3.37 (2H, t, $J$ = 7.3 Hz), 3.18 (3H, s), 2.54 (2H, t, $J$ = 7.3 Hz), 0.31 (9H, s), 0.03 (9H, s); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 168.2, 150.8, 133.9, 132.4, 123.2, 91.3, 71.2, 58.6, 29.0, 0.4, 0.2; IR (neat) 2961, 1716, 1687, 1387, 1254, 1164, 1112, 883, 849 cm$^{-1}$; HRMS (FAB) Calcd for $C_{19}H_{30}NO_5Si_2^+$ ([M+H]$^+$) 408.1663. Found 408.1662.

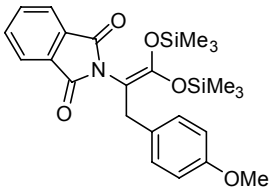
[4] Method II was also applicable to prepare **3a**.



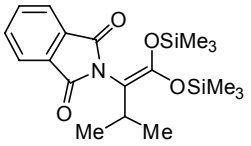
**3f:** The synthesis was performed according to the Method II and title compound was obtained as pale yellow solid in 62% yield. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.73 (2H, dd, $J$ = 5.6, 3.2 Hz), 7.62 (2H, dd, $J$ = 5.6, 3.2 Hz), 7.23 (2H, d, $J$ = 7.6 Hz), 7.17 (2H, t, $J$ = 7.6 Hz), 7.08 (1H, t, $J$ = 7.6 Hz), 3.76 (2H, s), 0.33 (9H, s), 0.09 (9H, s); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 167.7, 150.5, 138.9, 133.8, 132.2, 128.9, 128.2, 126.1, 123.1, 93.4, 34.2, 0.6, 0.3; IR (neat) 2957, 1716, 1684, 1386, 1270, 1091, 880, 846, 725 cm$^{-1}$; HRMS (FAB) Calcd for $C_{23}H_{30}NO_4Si_2^+$ ([M+H]$^+$) 440.1713. Found 440.1693.



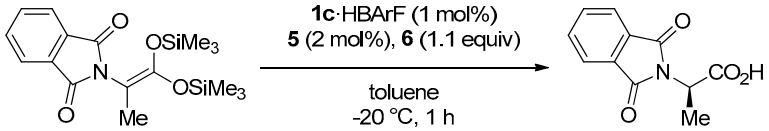
**3g:** The synthesis was performed according to the Method II and title compound was obtained as yellow solid in 49% yield. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.75 (2H, dd, $J$ = 5.2, 3.2 Hz), 7.65 (2H, dd, $J$ = 5.2, 3.2 Hz), 7.17 (2H, d, $J$ = 8.4 Hz), 7.14 (2H, d, $J$ = 8.4 Hz), 3.71 (2H, s), 0.32 (9H, s), 0.08 (9H, s); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 167.8, 150.8, 137.5, 133.9, 132.1, 131.8, 130.2, 128.3, 123.2, 92.8, 33.7, 0.6, 0.3; IR (neat) 2959, 1716, 1683, 1385, 1271, 1254, 1087, 881, 849 cm$^{-1}$; HRMS (FAB) Calcd for $C_{23}H_{29}ClNO_4Si_2^+$ ([M+H]$^+$) 474.1324. Found 474.1321.



**3h:** The synthesis was performed according to the Method II and title compound was obtained as orange viscous oil in 45% yield. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.73 (2H, dd, $J$ = 5.6, 3.2 Hz), 7.63 (2H, dd, $J$ = 5.6, 3.2 Hz), 7.13 (2H, d, $J$ = 8.4 Hz), 6.71 (2H, d, $J$ = 8.4 Hz), 3.70 (3H, s), 3.69 (2H, s), 0.33 (9H, s), 0.08 (9H, s); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 167.8, 158.0, 150.3, 133.8, 132.2, 130.8, 129.8, 123.1, 113.6, 93.7, 55.2, 33.3, 0.6, 0.3; IR (neat) 2958, 1716, 1683, 1511, 1385, 1270, 1252, 1085, 881, 849 cm$^{-1}$; HRMS (FAB) Calcd for $C_{24}H_{32}NO_5Si_2^+$ ([M+H]$^+$) 470.1819. Found 470.1842.

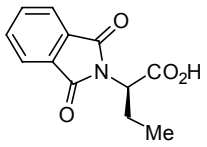


**3i:** The synthesis was performed following the Method II and title compound was obtained as yellow solid in 57% yield. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.84 (2H, dd, $J$ = 5.6, 3.0 Hz), 7.71 (2H, dd, $J$ = 5.6, 3.0 Hz), 2.89 (1H, sept, $J$ = 6.9 Hz), 1.00 (6H, d, $J$ = 6.9 Hz), 0.33 (9H, s), 0.02 (9H, s); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 169.2, 149.1, 133.9, 132.4, 123.2, 99.3, 28.5, 21.2, 0.5, 0.2; IR (neat) 2962, 1721, 1681, 1379, 1254, 1086, 849, 719 cm$^{-1}$; HRMS (FAB) Calcd for $C_{19}H_{30}NO_4Si_2^+$ ([M+H]$^+$) 392.1713. Found 392.1696.

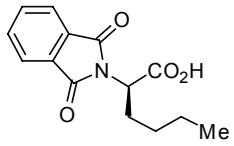



**Representative Procedure for Chiral Arylaminophosphonium Barfate 1·HBArF-Catalyzed Asymmetric Protonation Reaction:** To a solution of 2,6-dimethylphenol (**6**) (13.4 mg, 0.11 mmol), **1c**·HBArF (1.5 mg, 1.0 μmol), and 2,6-di-*tert*-butylpyridine (**5**) (0.050 M in toluene, 40.0 μL, 2.0 μmol) in toluene (0.60 mL) was slowly added a solution of **3a** (36.4 mg, 0.10 mmol) in toluene (0.40 mL) at –20 °C. After being stirred for 1 h, the reaction mixture was directly subjected to the purification by column chromatography on silica gel (H/EA = 4:1-0:100 as eluent) and *N*-phthaloyl alanine (**4a**) was obtained quantitatively. Subsequently, **4a** was treated with

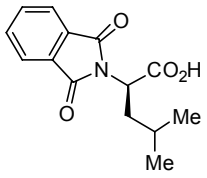
$Ag_2O$ (69.5 mg, 0.30 mmol) in MeI (1.0 mL) to give the corresponding methyl ester. The enantiomeric excess of the methyl ester of **4a** thus obtained was determined by chiral stationary phase HPLC analysis. **4a:** Analytical and spectral data agree with literature.[5] $[\alpha]_D^{27}$ 14.2 (*c* = 0.22, MeOH) for 97% ee. **Methyl ester of 4a:** Analytical and spectral data agree with literature.[5] HPLC OJH, hexane (H)/isopropyl alcohol (IPA) = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 20.8 min (*R*), 23.9 min (*S*).



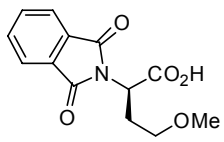
**4b:** Analytical and spectral data agree with literature.[6] $[\alpha]_D^{28}$ 19.4 (*c* = 0.48, MeOH) for 95% ee. **Methyl ester of 4b:** HPLC OJH, H/IPA = 10:1, flow rate = 0.5 mL/min, λ = 260 nm, 27.1 min (*R*), 29.1 min (*S*); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.88 (2H, dd, *J* = 5.2, 2.8 Hz), 7.75 (2H, dd, *J* = 5.2, 2.8 Hz), 4.78 (1H, dd, *J* = 9.6, 6.0 Hz), 3.74 (3H, s), 2.34-2.19 (2H, m), 0.94 (3H, t, *J* = 7.6 Hz). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 170.0, 167.9, 134.3, 131.9, 123.7, 53.7, 52.8, 22.3, 11.0; IR (neat) 2955, 1746, 1719, 1388, 1268, 1221, 898, 719 cm$^{-1}$; HRMS (FAB) Calcd for $C_{13}H_{14}NO_4^+$ ($[M+H]^+$) 248.0923. Found 248.0932.



**4c:** Analytical and spectral data agree with literature.[7] $[\alpha]_D^{28}$ 21.0 (*c* = 0.34, MeOH) for 95% ee. **Methyl ester of 4c:** HPLC OJH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 8.6 min (*S*), 9.2 min (*R*); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.88 (2H, dd, *J* = 6.0, 3.2 Hz), 7.75 (2H, dd, *J* = 6.0, 3.2 Hz), 4.85 (1H, dd, *J* = 10.4, 4.8 Hz), 3.73 (3H, s), 2.32-2.16, (2H, m), 1.44-1.19 (4H, m), 0.87 (3H, t, *J* = 7.1 Hz). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 170.1, 167.9, 134.3, 131.9, 123.7, 52.9, 52.3, 28.6, 28.5, 22.2, 14.0; IR (neat) 2956, 2928, 1748, 1717, 1467, 1388, 1250, 720 cm$^{-1}$; HRMS (FAB) Calcd for $C_{15}H_{18}NO_4^+$ ($[M+H]^+$) 276.1236. Found 276.1242.



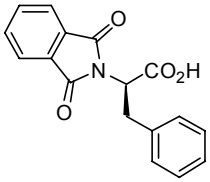
**4d:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.86 (2H, dd, *J* = 5.6, 3.2 Hz), 7.74 (2H, dd, *J* = 5.6, 3.2 Hz), 5.00 (1H, dd, *J* = 11.8, 4.0 Hz), 2.37 (1H, ddd, *J* = 14.8, 11.8, 4.0 Hz), 1.95 (1H, ddd, *J* = 14.8, 10.4, 4.0 Hz), 1.57-1.42 (1H, m), 0.95 (3H, d, *J* = 6.9 Hz), 0.93 (3H, d, *J* = 6.9 Hz), O-H proton was not found due to broadening; $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 176.1, 167.8, 134.3, 131.8, 123.7, 50.5, 37.1, 25.2, 23.2, 21.1; IR (KBr) 2967, 1713, 1387, 1283, 930, 715 cm$^{-1}$; HRMS (FAB) Calcd for $C_{14}H_{16}NO_4^+$ ($[M+H]^+$) 262.1079. Found 262.1087; $[\alpha]_D^{27}$ 14.0 (*c* = 0.38, MeOH) for 90% ee. **Methyl ester of 4d:** HPLC OJH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 7.3 min (*S*), 10.0 min (*R*); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.87 (2H, dd, *J* = 5.6, 3.2 Hz), 7.75 (2H, dd, *J* = 5.6, 3.2 Hz), 4.96 (1H, dd, *J* = 11.9, 4.1 Hz), 3.73 (3H, s), 2.34 (1H, ddd, *J* = 14.4, 11.9, 4.1 Hz), 1.96 (1H, ddd, *J* = 14.4, 10.8, 4.1 Hz), 1.56-1.43 (1H, m), 0.96 (3H, d, *J* = 6.9 Hz), 0.93 (3H, d, *J* = 6.9 Hz). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 170.4, 167.9, 134.3, 132.0, 123.7, 52.9, 50.7, 37.4, 25.2, 23.3, 21.1; IR (neat) 2957, 1746, 1714, 1469, 1387, 1254, 1216, 720 cm$^{-1}$; HRMS (FAB) Calcd for $C_{15}H_{18}NO_4^+$ ($[M+H]^+$) 276.1236. Found 276.1233.



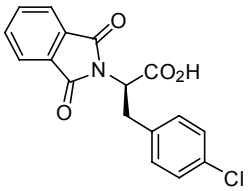
**4e:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.87 (2H, dd, *J* = 5.6, 3.2 Hz), 7.74 (2H, dd, *J* = 5.6, 3.2 Hz), 5.12 (1H, dd, *J* = 10.0, 4.8 Hz), 3.53 (1H, dt, *J* = 10.0, 4.8 Hz), 3.35 (1H, td, *J* = 10.0, 4.0 Hz), 3.26 (3H, s), 2.57 (1H, ddt, *J* = 13.6, 10.0, 4.8 Hz), 2.44 (1H, dddd, *J* = 13.6, 10.0, 4.8, 4.0 Hz), O-H proton was not found due to broadening; $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 174.3, 167.7, 134.4,

[5] Shendage, D. M.; Fröhlich, R.; Haufe, G. *Org. Lett.* **2004**, *6*, 3675.
[6] Castano, A. M.; Echavarren, A. M. *Organometallics* **1994**, *13*, 2262.
[7] Wong, M.-K.; Chung, N.-W.; He, L.; Yang, D. *J. Am. Chem. Soc.* **2003**, *125*, 158.

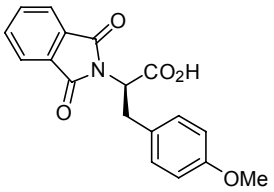
131.9, 123.7, 69.2, 58.9, 49.6, 29.0; IR (KBr) 3163, 1780, 1746, 1705, 1399, 1192, 1119, 721 $cm^{-1}$; HRMS (FAB) Calcd for $C_{13}H_{14}NO_5^+$ ($[M+H]^+$) 264.0871. Found 264.0883; $[\alpha]_D^{26}$ 28.7 (*c* = 0.46, MeOH) for 94% ee. **Methyl ester of 4e:** HPLC ASH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 11.0 min (*R*), 11.9 min (*S*); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.88 (2H, dd, *J* = 5.6, 3.2 Hz), 7.75 (2H, dd, *J* = 5.6, 3.2 Hz), 5.09 (1H, dd, *J* = 10.0, 4.6 Hz), 3.74 (3H, s), 3.50 (1H, dt, *J* = 10.1, 4.6 Hz), 3.32 (1H, ddd, *J* = 10.1, 8.2, 4.0 Hz), 3.23 (3H, s), 2.54 (1H, ddt, *J* = 13.5, 10.0, 4.6 Hz), 2.44 (1H, dddd, *J* = 13.5, 8.4, 4.6, 4.0 Hz). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 170.0, 167.8, 134.3, 132.0, 123.7, 69.1, 58.8, 52.9, 49.6, 29.1; IR (neat) 2925, 1736, 1709, 1385, 1255, 1113, 1008, 896, 769, 717 $cm^{-1}$; HRMS (FAB) Calcd for $C_{14}H_{16}NO_5^+$ ($[M+H]^+$) 278.1029. Found 278.1029.



**4f:** Analytical and spectral data agree with literature.[8a] $[\alpha]_D^{27}$ 193.8 (*c* = 0.58, MeOH) for 94% ee. **Methyl ester of 4f:** Analytical and spectral data agree with literature.[8b] HPLC OJH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 18.5 min (minor), 25.9 min (major).



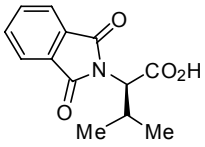
**4g:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.80 (2H, dd, *J* = 5.6, 2.8 Hz), 7.71 (2H, dd, *J* = 5.6, 2.8 Hz), 7.16 (2H, d, *J* = 8.4 Hz), 7.10 (2H, d, *J* = 8.4 Hz), 5.19 (1H, dd, *J* = 10.0, 6.7 Hz), 3.60 (1H, dd, *J* = 14.6, 10.0 Hz), 3.54 (1H, dd, *J* = 14.6, 6.7 Hz), O-H proton was not found due to broadening; $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 174.3, 167.5, 134.9, 134.5, 133.0, 131.5, 130.3, 129.0, 123.8, 52.8, 33.9; IR (KBr) 2923, 1776, 1717, 1388, 1291, 1113, 1099, 722 $cm^{-1}$; HRMS (FAB) Calcd for $C_{17}H_{13}ClNO_4^+$ ($[M+H]^+$) 330.0533. Found 330.0548; $[\alpha]_D^{28}$ 166.8 (*c* = 0.50, MeOH) for 90% ee. **Methyl ester of 4g:** HPLC OJH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 22.6 min (*S*), 29.7 min (*R*); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.80 (2H, dd, *J* = 5.6, 3.2 Hz), 7.71 (2H, dd, *J* = 5.6, 3.2 Hz), 7.16 (2H, d, *J* = 8.7 Hz), 7.10 (2H, d, *J* = 8.7 Hz), 5.12 (1H, dd, *J* = 10.8, 8.0 Hz), 3.78 (3H, s), 3.58 (1H, dd, *J* = 14.6, 8.0 Hz), 3.52 (1H, dd, *J* = 14.6, 10.8 Hz). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 169.3, 168.4, 167.6, 135.3, 134.4, 132.9, 131.6, 130.3, 128.9, 123.7, 53.1, 34.2; IR (neat) 2952, 1747, 1715, 1492, 1388, 1243, 1093, 772, 719 $cm^{-1}$; HRMS (FAB) Calcd for $C_{18}H_{15}NO_4Cl^+$ ($[M+H]^+$) 344.0690. Found 344.0696.



**4h:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.01 (1H, br), 7.78 (2H, dd, *J* = 5.6, 2.8 Hz), 7.68 (2H, dd, *J* = 5.6, 2.8 Hz), 7.07 (2H, d, *J* = 8.7 Hz), 6.72 (2H, d, *J* = 8.7 Hz), 5.18 (1H, dd, *J* = 8.9, 7.5 Hz), 3.70 (3H, s), 3.55 (1H, dd, *J* = 14.8, 8.9 Hz), 3.51 (1H, dd, *J* = 14.8, 7.5 Hz); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 174.8, 167.6, 158.5, 134.3, 131.6, 130.0, 128.4, 123.7, 114.1, 55.2, 53.3, 33.6; IR (KBr) 3214, 1773, 1712, 1612, 1516, 1395, 1250, 1171, 1118, 722 $cm^{-1}$; HRMS (FAB) Calcd for $C_{18}H_{16}NO_5^+$ ($[M+H]^+$) 326.1028. Found 326.1016; $[\alpha]_D^{30}$ 169.43 (*c* = 0.35, MeOH) for 93% ee. **Methyl ester of 4h:** HPLC IA, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 15.2 min (*S*), 18.1 min (*R*); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.78 (2H, dd, *J* = 5.2, 3.2 Hz), 7.69 (2H, dd, *J* = 5.2, 3.2 Hz), 7.07 (2H, d, *J* = 8.5 Hz), 6.71 (2H, d, *J* = 8.5 Hz), 5.11 (1H, dd, *J* = 10.8, 6.0 Hz), 3.78 (3H, s), 3.70 (3H, s), 3.54 (1H, dd, *J* = 14.2, 6.0 Hz), 3.48 (1H, dd, *J* = 14.2, 10.8 Hz). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 169.6, 167.6, 158.5, 134.2, 131.7, 130.0, 128.8,

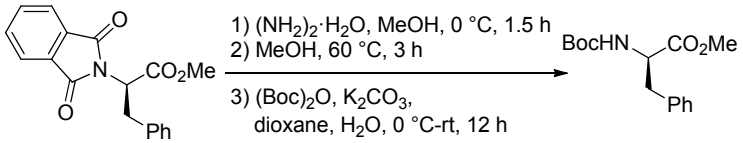
[8] (a) Severino, B.; Fiorino, F.; Esposito, A.; Frecentese, F.; Angelis, F. D.; Perissutti, E.; Caliendo, G.; Santagada, V. *Tetrahedron* **2009**, *65*, 206. (b) Navarre, L.; Martinez, R.; Genet, J.-P.; Laure, D.-S. *J. Am. Chem. Soc.* **2008**, *130*, 6159.

123.6, 114.1, 55.2, 53.5, 53.0, 33.9; IR (neat) 2953, 2837, 1746, 1714, 1514, 1389, 1249, 1179, 720 $cm^{-1}$; HRMS (FAB) Calcd for $C_{19}H_{18}NO_5^+$ ($[M+H]^+$) 340.1185. Found 340.1194.




**4i:** Analytical and spectral data agree with literature.[5,9a] **Methyl ester of 4i:** Analytical and spectral data agree with literature.[5,9b] HPLC OJH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 8.4 min (minor), 10.8 min (major).

**Deprotection-Reprotection of Methyl Ester of 4f:**




To a solution of the methyl ester of **4f** (32.6 mg, 0.11 mmol) in MeOH (2.1 mL) was added $(NH_2)_2 \cdot H_2O$ (10.0 μL, 0.21 mmol) at 0 °C and the solution was stirred for 1.5 h. The resulting mixture was diluted with saturated aqueous solution of $NaHCO_3$ and the aqueous layer was extracted with EA twice. The combined organic phases were washed with brine, dried over $Na_2SO_4$, filtered, and concentrated under vacuum. The residue was dissolved in MeOH (1.0 mL) and stirred for 3 h at 60 °C. After being cooled to room temperature, the white solid was removed by filtration through a pad of Celite with EA. The filtrate was concentrated to give crude phenylalanine methyl ester. To a solution of the crude material in 1,4-dioxane (0.60 mL) and $H_2O$ (0.30 mL) were added $K_2CO_3$ (29.0 mg, 0.21 mmol) and $(Boc)_2O$ (25 μL, 0.12 mmol) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 12 h. The resulting mixture was diluted with water and the aqueous layer was extracted with EA. The organic phase was washed with brine and dried over $Na_2SO_4$. After filtration and concentration under vacuum, the crude residue was purified by column chromatography on silica gel (H/EA = 5:1-3:1 as eluent) to give *N*-Boc phenylalanine methyl ester (17.8 mg, 0.067 mmol, 64%) as white solid, whose enantiomeric excess was determined by chiral HPLC analysis [OJH, H/ethanol (EtOH) = 20:1, flow rate = 0.5 mL/min, λ = 210 nm, 13.3 min (*R*), 15.4 min (*S*)].

[9] (a) Casimir, J. R.; Guichard, G.; Tourwe, D.; Briand, J.-P. *Synthesis* **2001**, 1985. (b) Casimir, J. R.; Guichard, G.; Briand, J.-P. *J. Org. Chem.* **2002,** *67,* 3764.

**Crystallographic Structure Determination:**

**Recrystallization of 1a:** Iminophsphorane **1a** was recrystallized from $CHCl_3$/MeOH solvent system at room temperature.

The single crystal thus obtained was mounted on CryoLoop. Data of X-ray diffraction were collected at 153 K on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An absorption correction was made using SADABS. The structure was solved by direct methods and Fourier syntheses, and refined by full-matrix least squares on $F^2$ by using SHELXTL.[10] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to nitrogen atoms were located from a difference synthesis and their coordinates and isotropic thermal parameters refined. The other hydrogen atoms were placed in calculated positions and isotropic thermal parameters refined. The crystallographic data were summarized in the following table.

**Table S1**. Crystal data and structure refinement for $(\mathbf{1a})_2 \cdot CH_3OH \cdot 3CHCl_3$.

| | | |
|---|---|---|
| Empirical formula | C84 H57 Cl9 N4 O5 P2 | |
| Formula weight | 1583.33 | |
| Temperature | 153(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1) | |
| Unit cell dimensions | a = 15.478(3) Å | α = 90°. |
| | b = 14.753(3) Å | β = 95.025(4)°. |
| | c = 16.184(3) Å | γ = 90°. |
| Volume | 3681.3(11) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.428 $Mg/m^3$ | |
| Absorption coefficient | 0.444 $mm^{-1}$ | |
| F(000) | 1624 | |
| Crystal size | 0.30 x 0.30 x 0.08 $mm^3$ | |
| Theta range for data collection | 1.75 to 28.39°. | |
| Index ranges | -20<=h<=16, -19<=k<=19, -19<=l<=21 | |
| Reflections collected | 28185 | |
| Independent reflections | 18050 [R(int) = 0.0333] | |
| Completeness to theta = 28.39° | 99.5 % | |
| Absorption correction | Empirical | |
| Max. and min. transmission | 0.9654 and 0.8784 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 18050 / 1 / 947 | |
| Goodness-of-fit on $F^2$ | 1.052 | |
| Final R indices [I>2sigma(I)] | $R_1$ = 0.0618, $wR_2$ = 0.1501 | |
| R indices (all data) | $R_1$ = 0.0730, $wR_2$ = 0.1591 | |
| Absolute structure parameter | –0.05(5) | |
| Largest diff. peak and hole | 0.733 and –0.831 e.$Å^{-3}$ | |

[10] Sheldrick, G. M. SHELXTL 5.1, Bruker AXS Inc., Madison, Wisconsin, 1997.

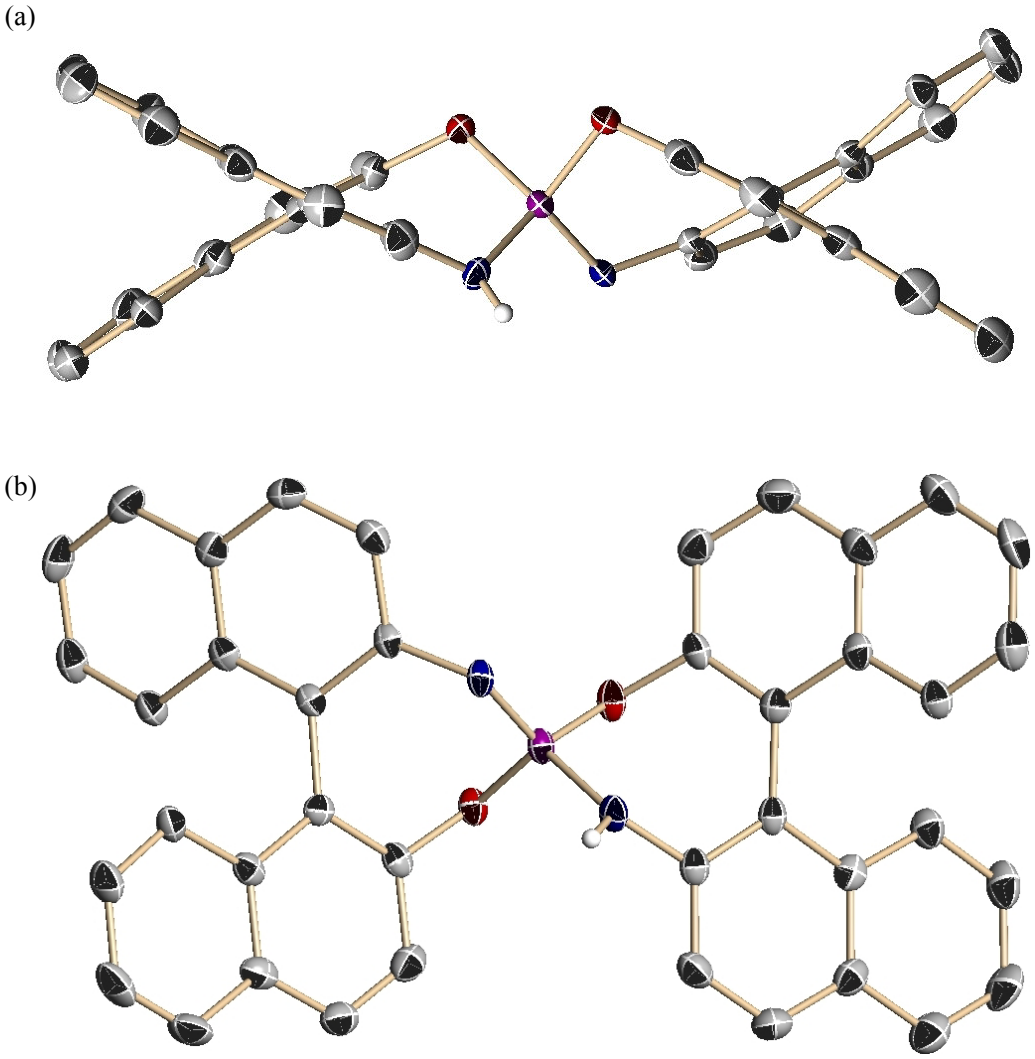



**Figure S1.** ORTEP diagrams of chiral iminophosphorane **1a**. (a) Side view (b) Top view. All calculated hydrogen atoms and solvent molecules are omitted for clarity. Purple = phosphorus, blue = nitrogen, red = oxygen, black = carbon.

**Recrystallization of 1b:** Iminophosphorane **1b** was recrystallized from acetone/hexane solvent system at room temperature.

The single crystal thus obtained was mounted on CryoLoop. Data of X-ray diffraction were collected at 153 K on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An absorption correction was made using SADABS. The structure was solved by direct methods and Fourier syntheses, and refined by full-matrix least squares on $F^2$ by using SHELXTL.[12] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to nitrogen atoms were located from a difference synthesis and their coordinates and isotropic thermal parameters refined. The other hydrogen atoms were placed in calculated positions and isotropic thermal parameters refined. The crystallographic data were summarized in the following table.

**Table S2**. Crystal data and structure refinement for **1b**·$2C_3H_6O$.

| | | |
|---|---|---|
| Empirical formula | C58 H45 N2 O4 P1 | |
| Formula weight | 864.93 | |
| Temperature | 153(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | P2(1)2(1)2 | |
| Unit cell dimensions | a = 27.528(5) Å | α = 90°. |
| | b = 12.447(2) Å | β = 90°. |
| | c = 13.383(2) Å | γ = 90°. |
| Volume | 4585.6(14) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.253 $Mg/m^3$ | |
| Absorption coefficient | 0.111 $mm^{-1}$ | |
| F(000) | 1816 | |
| Crystal size | 0.10 x 0.10 x 0.02 $mm^3$ | |
| Theta range for data collection | 2.21 to 20.96°. | |
| Index ranges | -36<=h<=36, -13<=k<=16, -15<=l<=17 | |
| Reflections collected | 34830 | |
| Independent reflections | 11404 [R(int) = 0.0830] | |
| Completeness to theta = 28.36° | 99.5 % | |
| Absorption correction | Empirical | |
| Max. and min. transmission | 0.989 and 0.998 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 11404 / 0 / 594 | |
| Goodness-of-fit on $F^2$ | 1.113 | |
| Final R indices [I>2sigma(I)] | $R_1$ = 0.0835, $wR_2$ = 0.1446 | |
| R indices (all data) | $R_1$ = 0.1117, $wR_2$ = 0.1557 | |
| Absolute structure parameter | 0.02(13) | |
| Largest diff. peak and hole | 0.418 and –0.431 e.$Å^{-3}$ | |

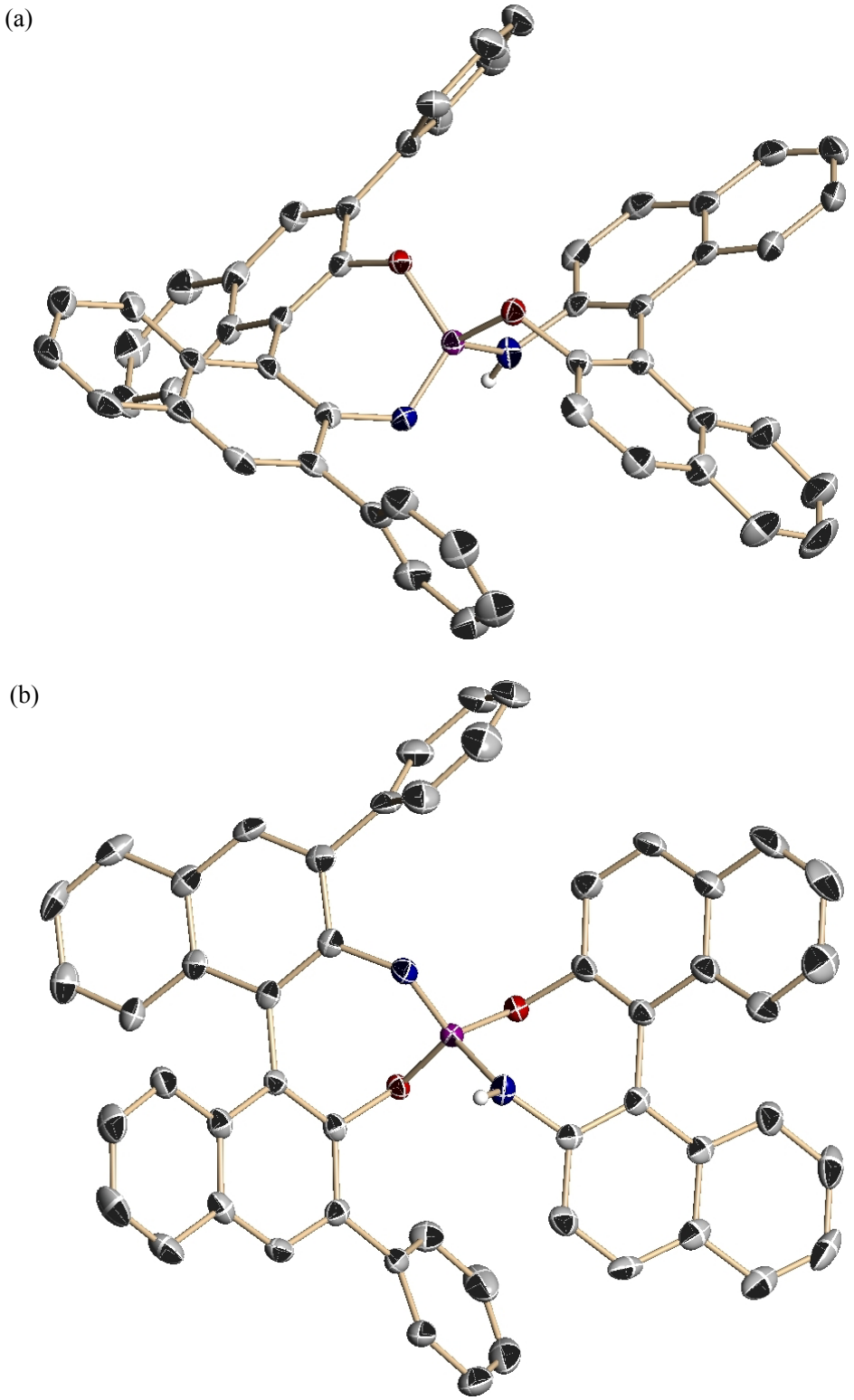
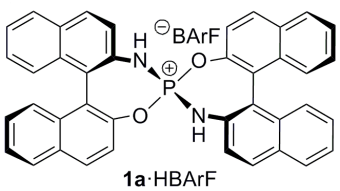



**Figure S2.** ORTEP diagrams of chiral iminophosphorane **1b**. (a) Side view (b) Top view. All calculated hydrogen atoms and solvent molecules are omitted for clarity. Purple = phosphorus, blue = nitrogen, red = oxygen, black = carbon.

**Copies of $^{1}$H and $^{13}$C NMR spectra:**

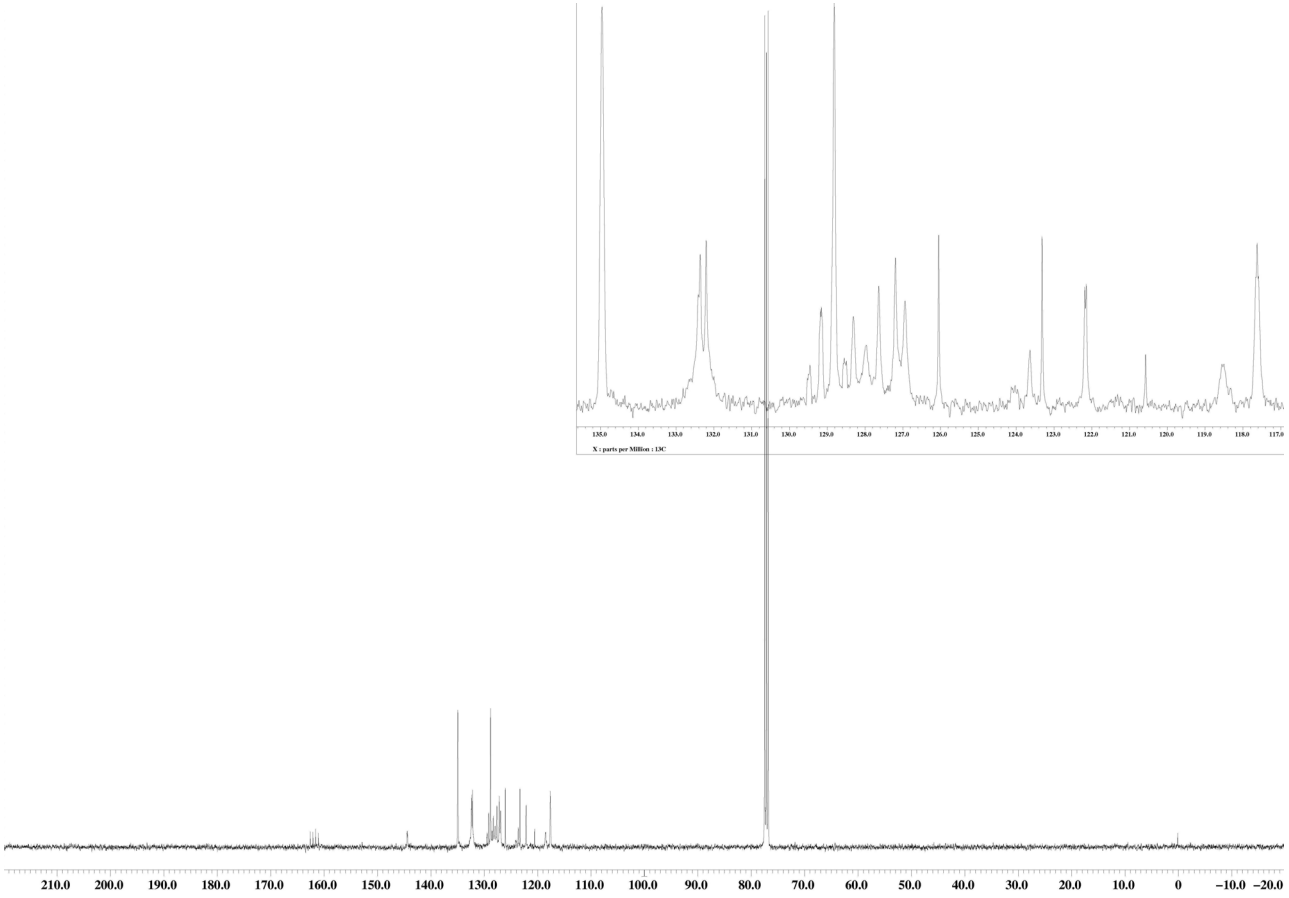


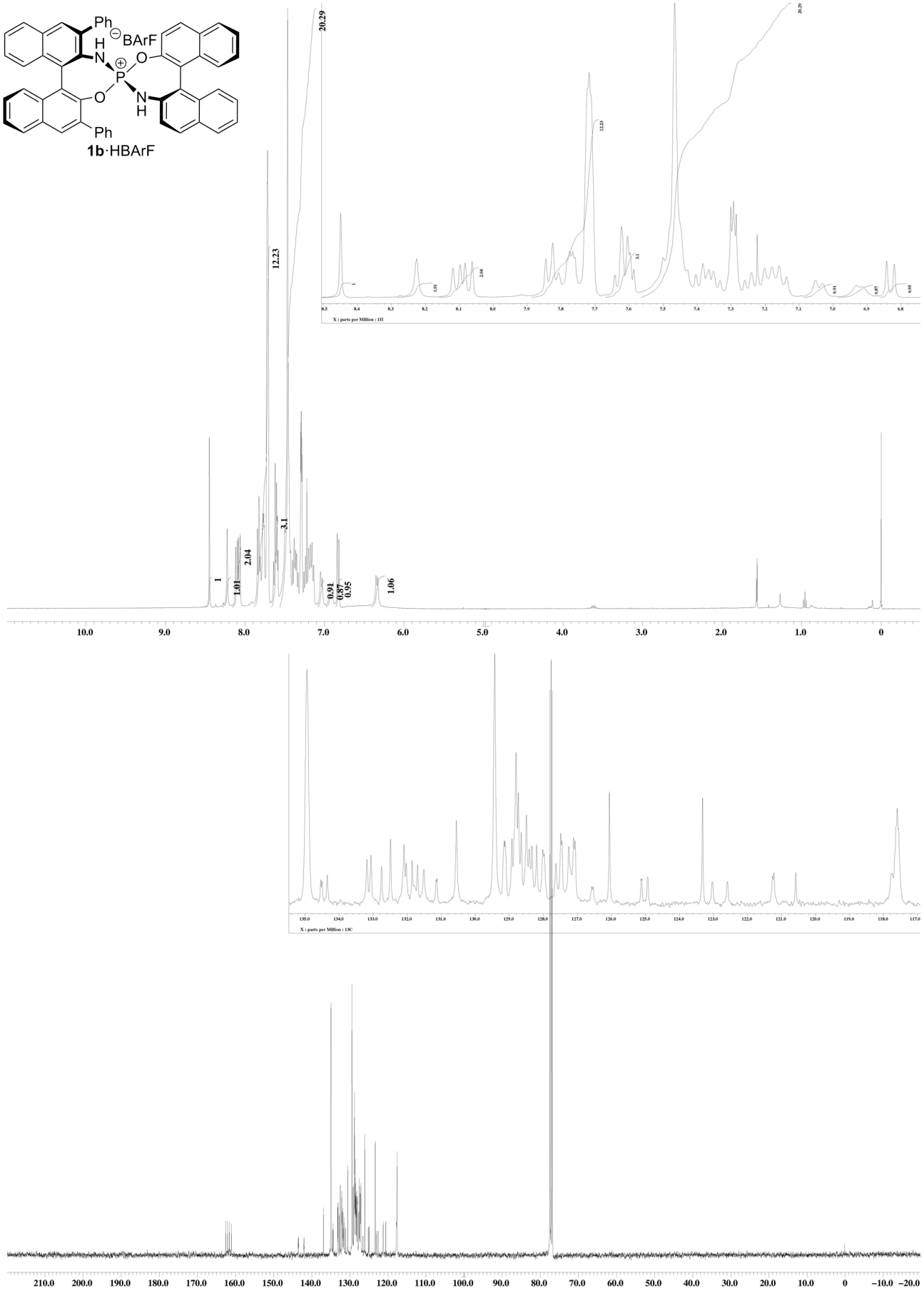

**1a**·HBArF










Ph
BArF
H
N
O
P
O
N
H
Ph
1b·HBArF
20.29
12.23
3.1
2.04
1.01
1
0.91
0.87
0.95
1.06
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H
X : parts per Million : 13C
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
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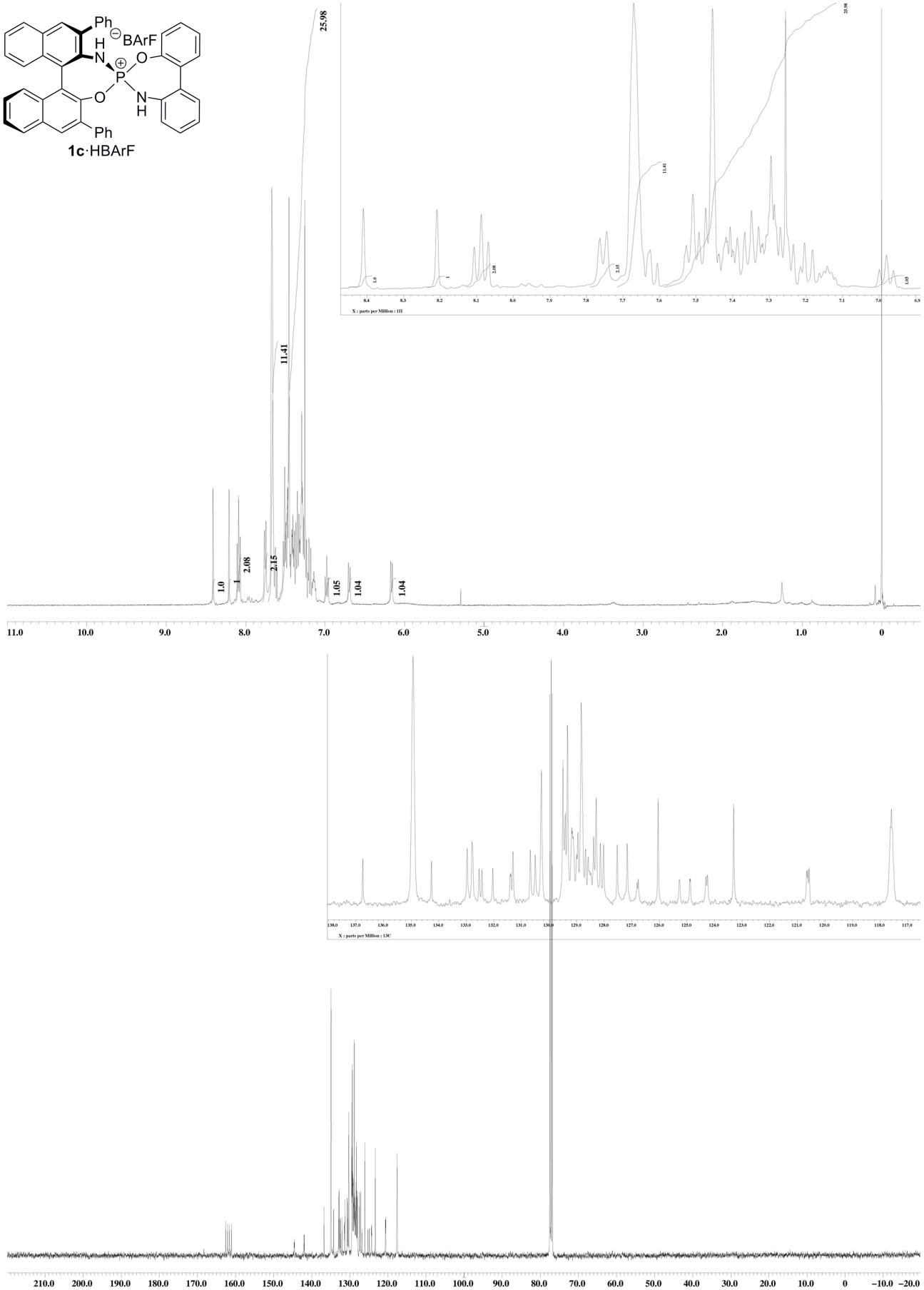
30.0
20.0
10.0
0
−10.0
−20.0


Ph
BArF
H
N
O
P
O
N
H
Ph
1c·HBArF
25.98
11.41
2.08
2.15
1.0
1
1.05
1.04
1.04
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H
X : parts per Million : 13C
210.0
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
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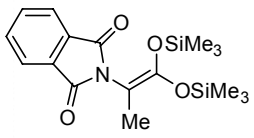
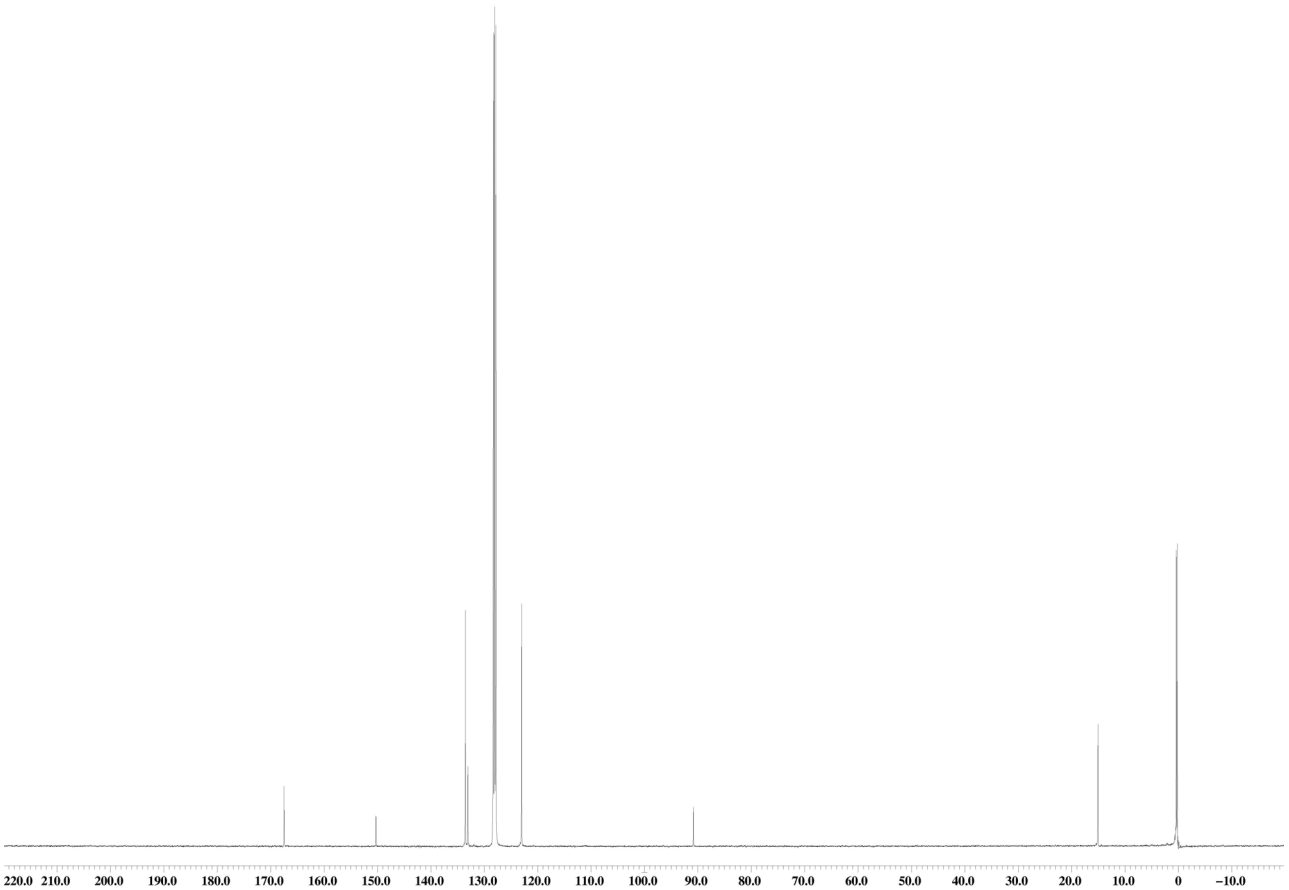
−10.0
−20.0


O
OSiMe3
N
OSiMe3
O
Me

**3a**


8.97
9.0
3.09
1.84
2.01
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0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120.0
110.0
100.0
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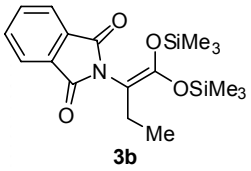
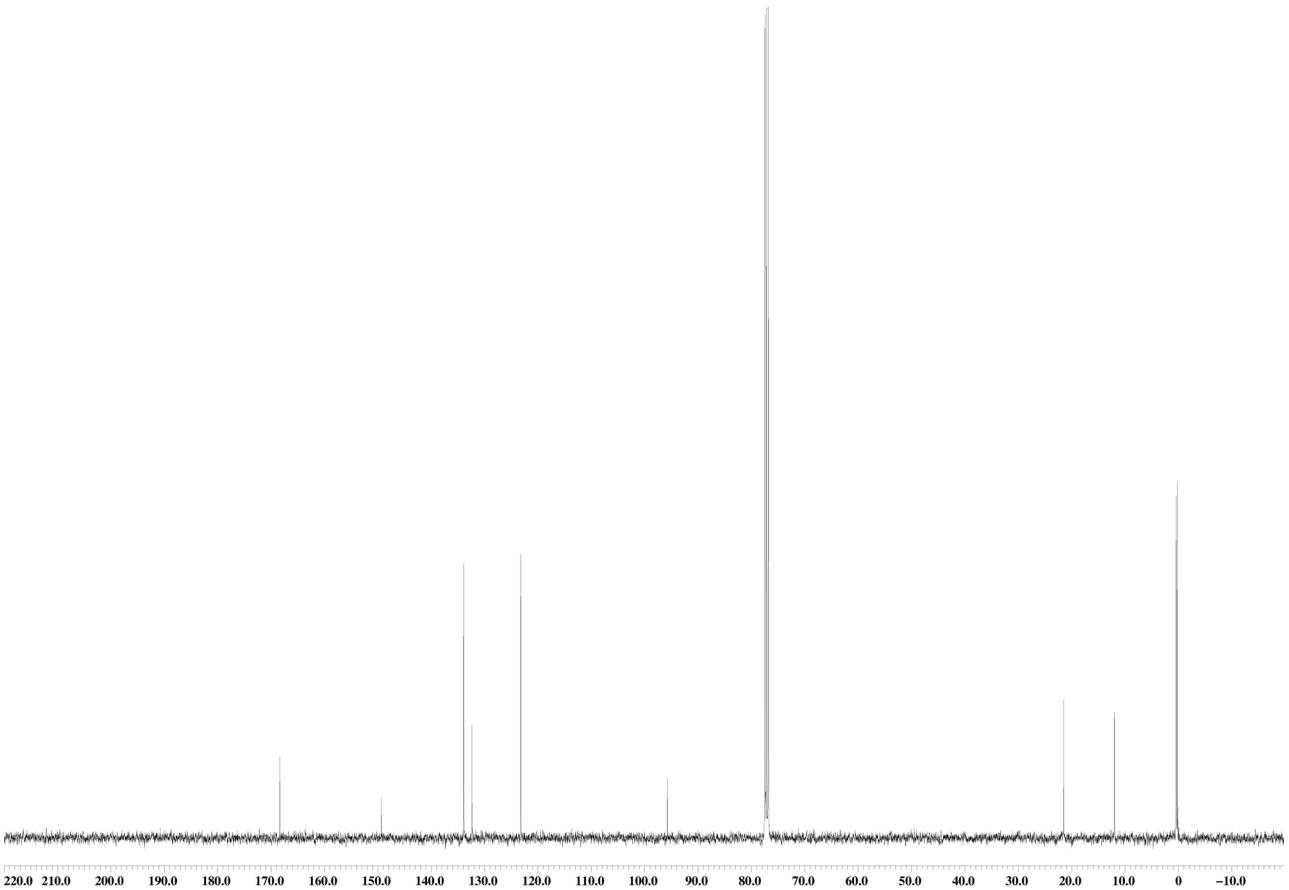
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0


O
OSiMe3
N
OSiMe3
O
Me

**3b**


9
8.79
3.16
2.16
2.03
1.92
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0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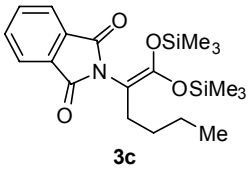
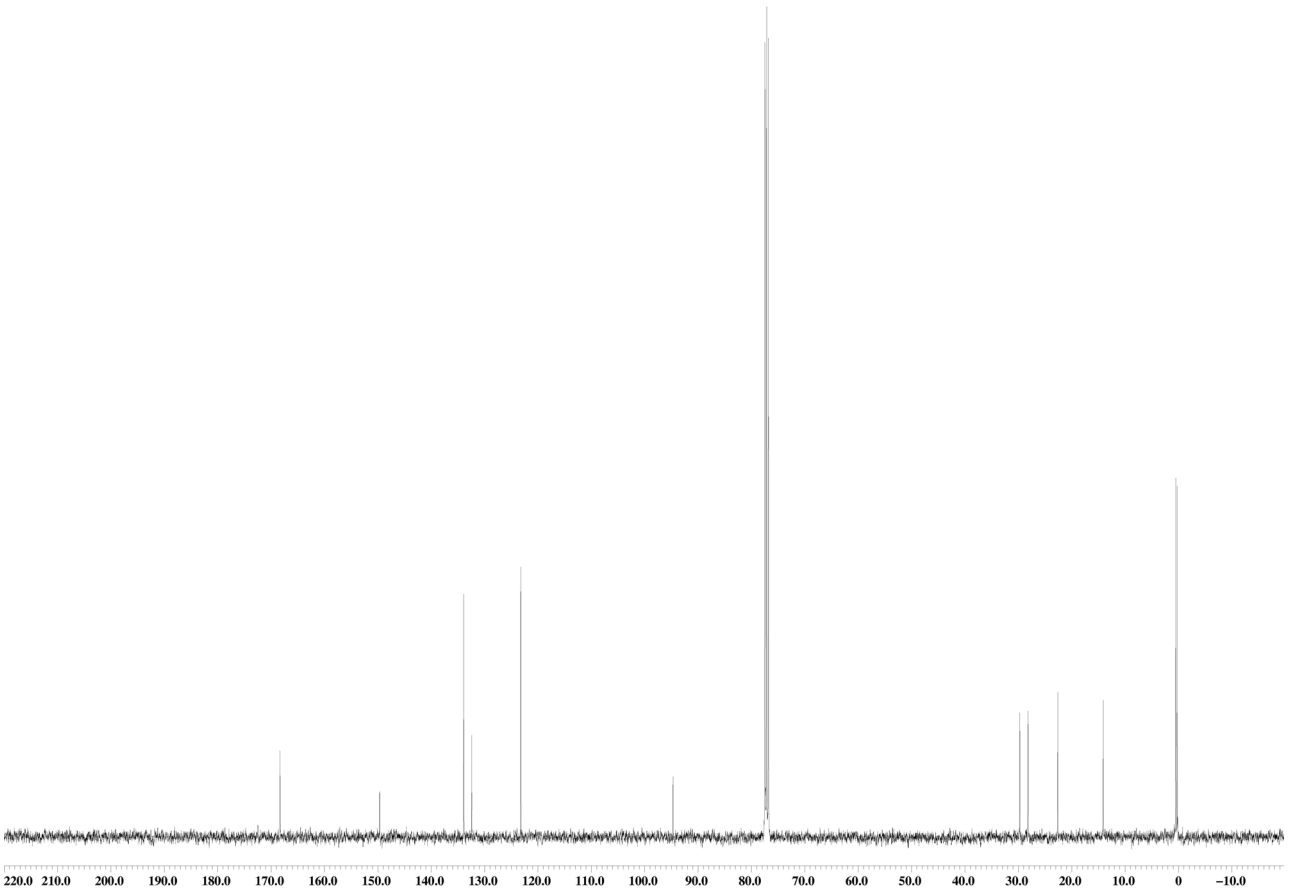
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0


O
OSiMe3
N
OSiMe3
O
Me

**3c**


9.06
9
4.37
3.18
2.11
1.91
2.04
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0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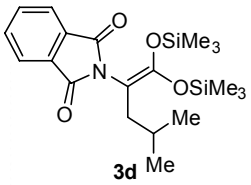
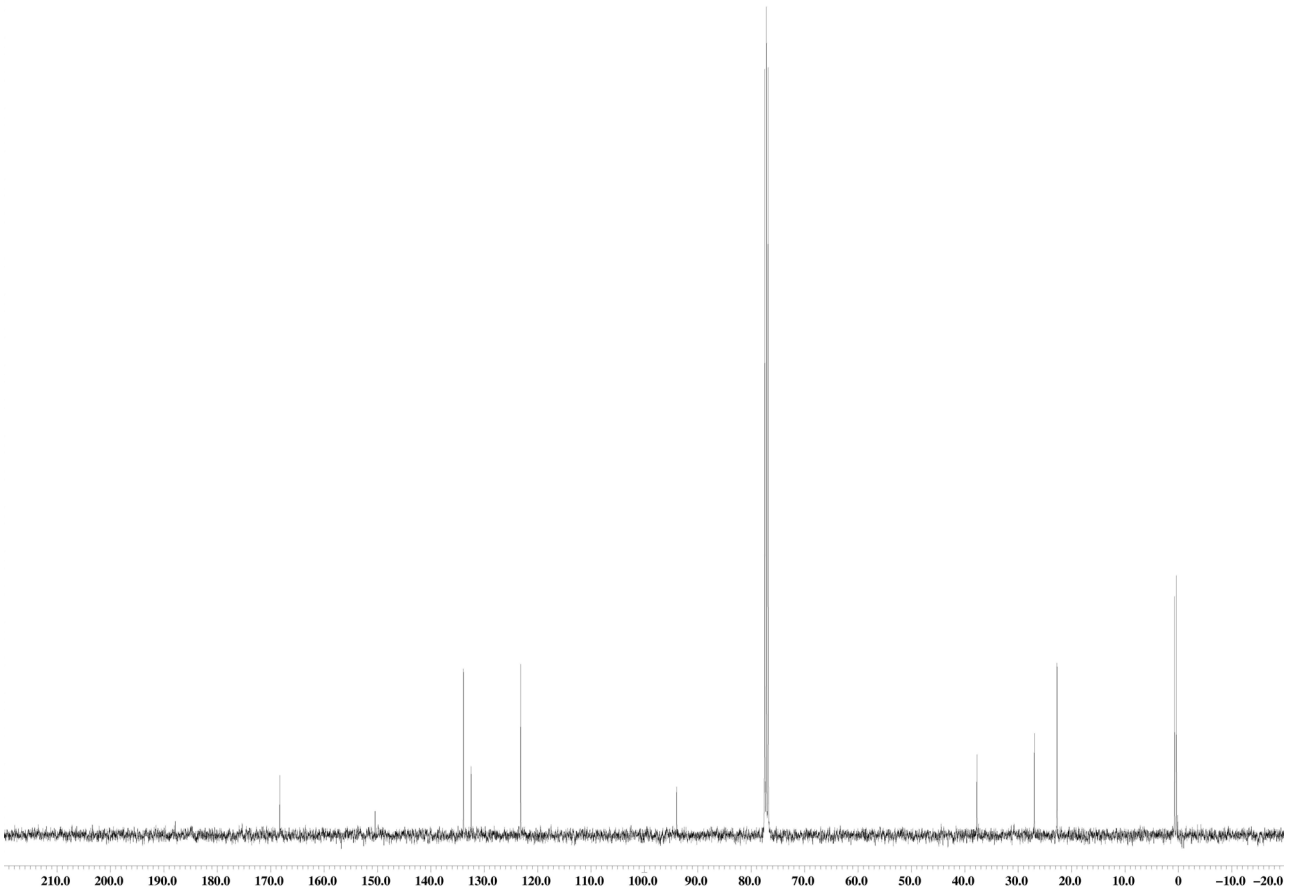
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0


O
OSiMe3
N
OSiMe3
O
Me
Me

**3d**


1.88
2.05
2.12
1.04
6.56
8.83
9
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0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140.0
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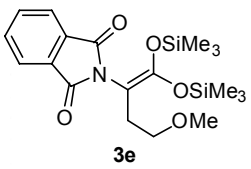
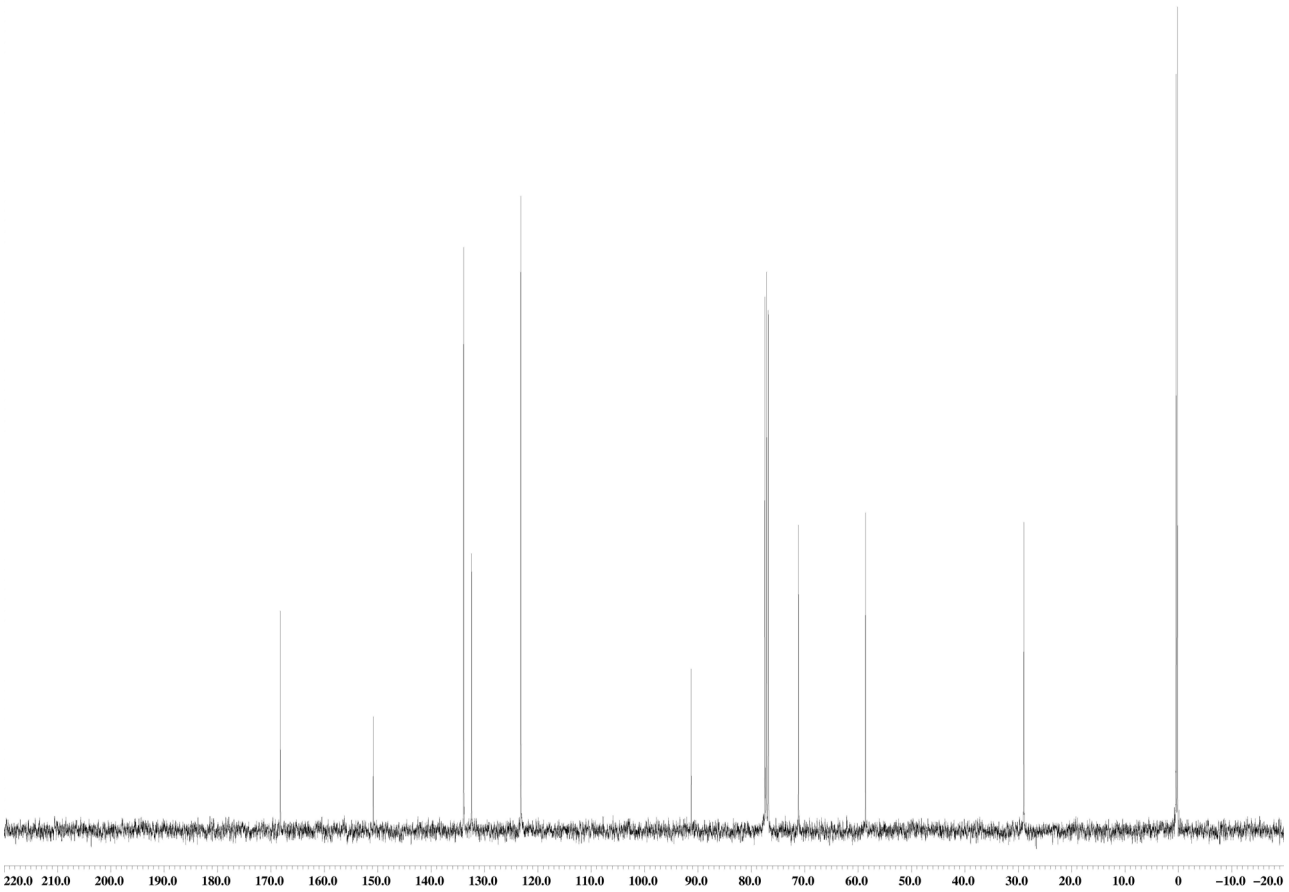
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
−20.0


O
OSiMe3
N
OSiMe3
O
OMe

**3e**


9.06
9
3.03
1.9
2.02
2.0
2.05
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0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180.0
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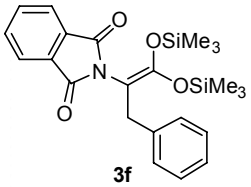
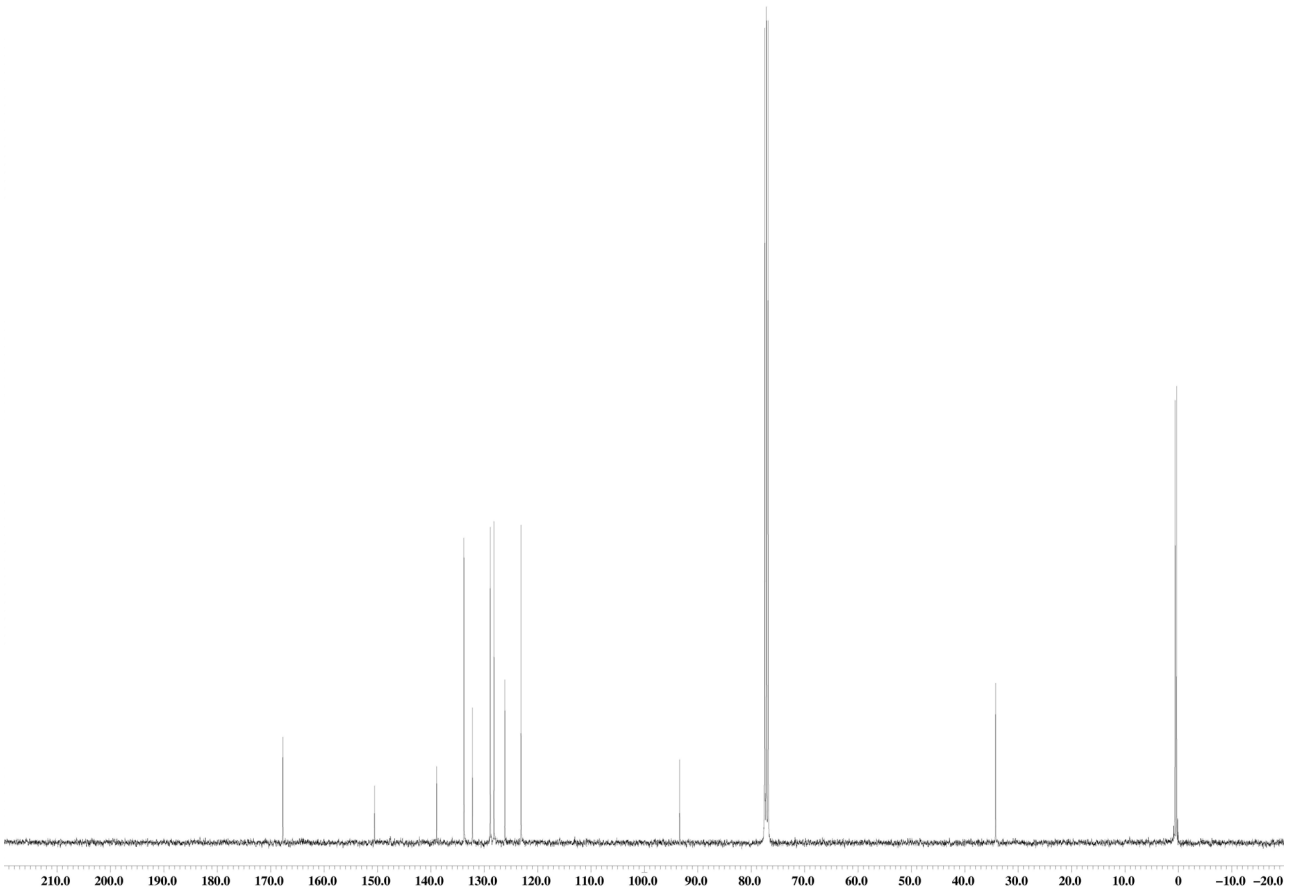
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
−20.0


O
N
O
OSiMe3
OSiMe3

**3f**


8.93
9
1.96
2.07
1.91
2.08
1.01
2.09
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0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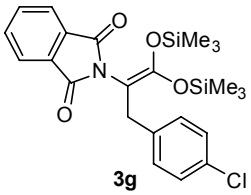
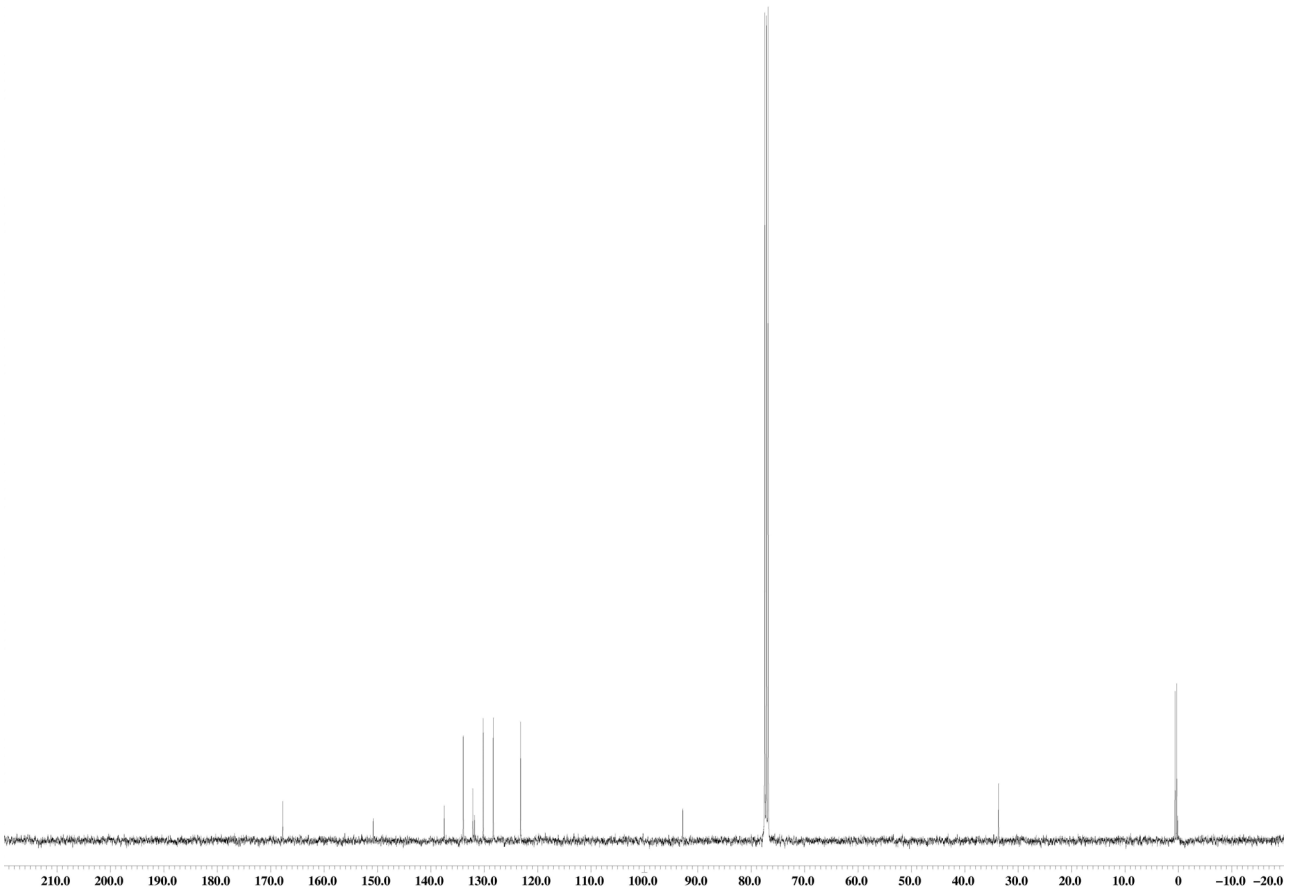
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
−20.0


O
OSiMe3
N
OSiMe3
O
Cl

**3g**


8.89
3.87
1.88
1.99
2.05
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0


210.0
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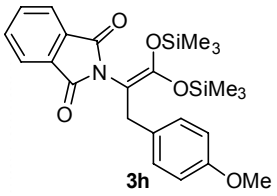
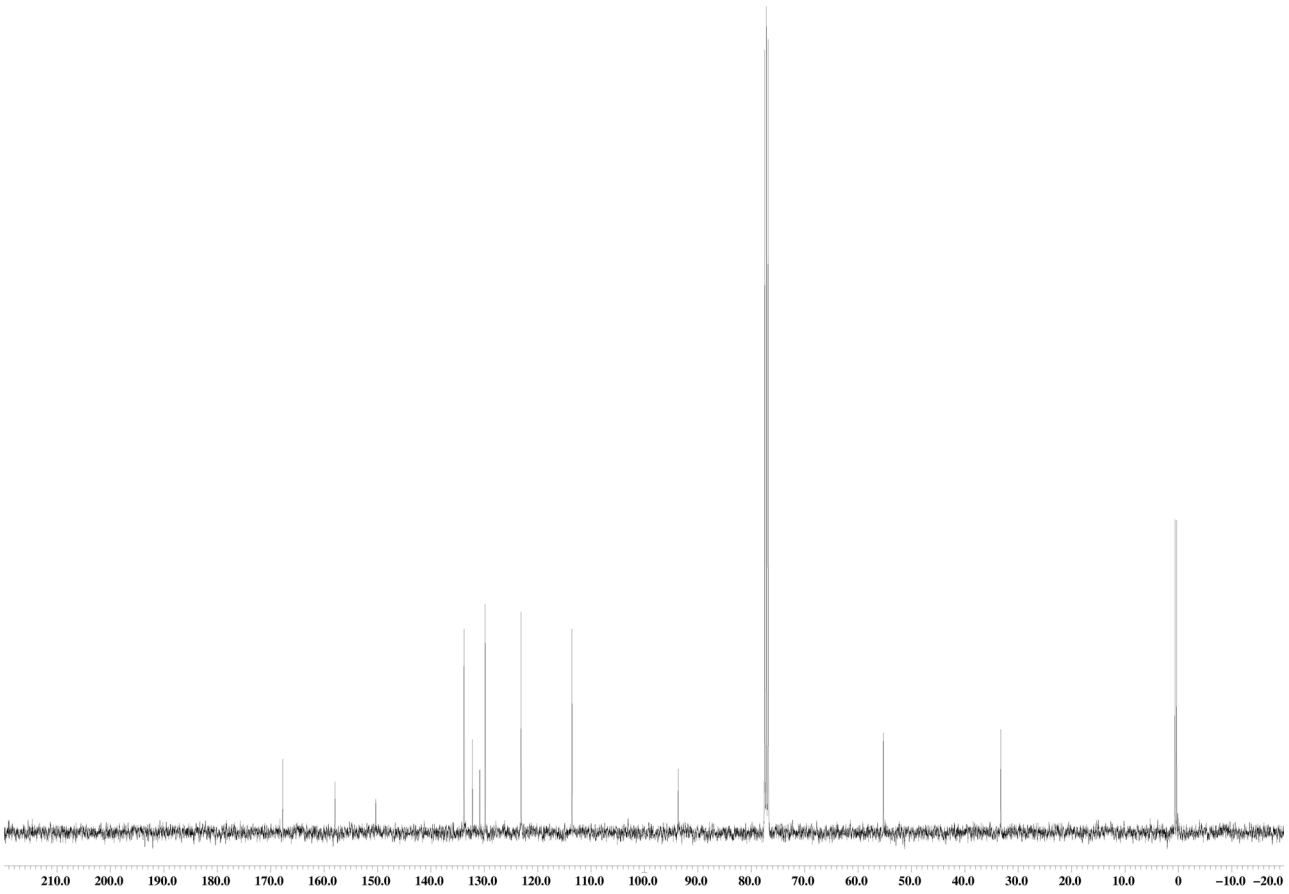
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
−20.0


O
OSiMe3
N
OSiMe3
O
3h
OMe


8.9
9
5.14
1.85
1.98
1.94
1.96
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0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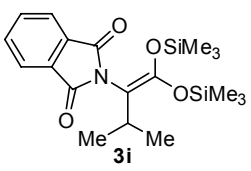
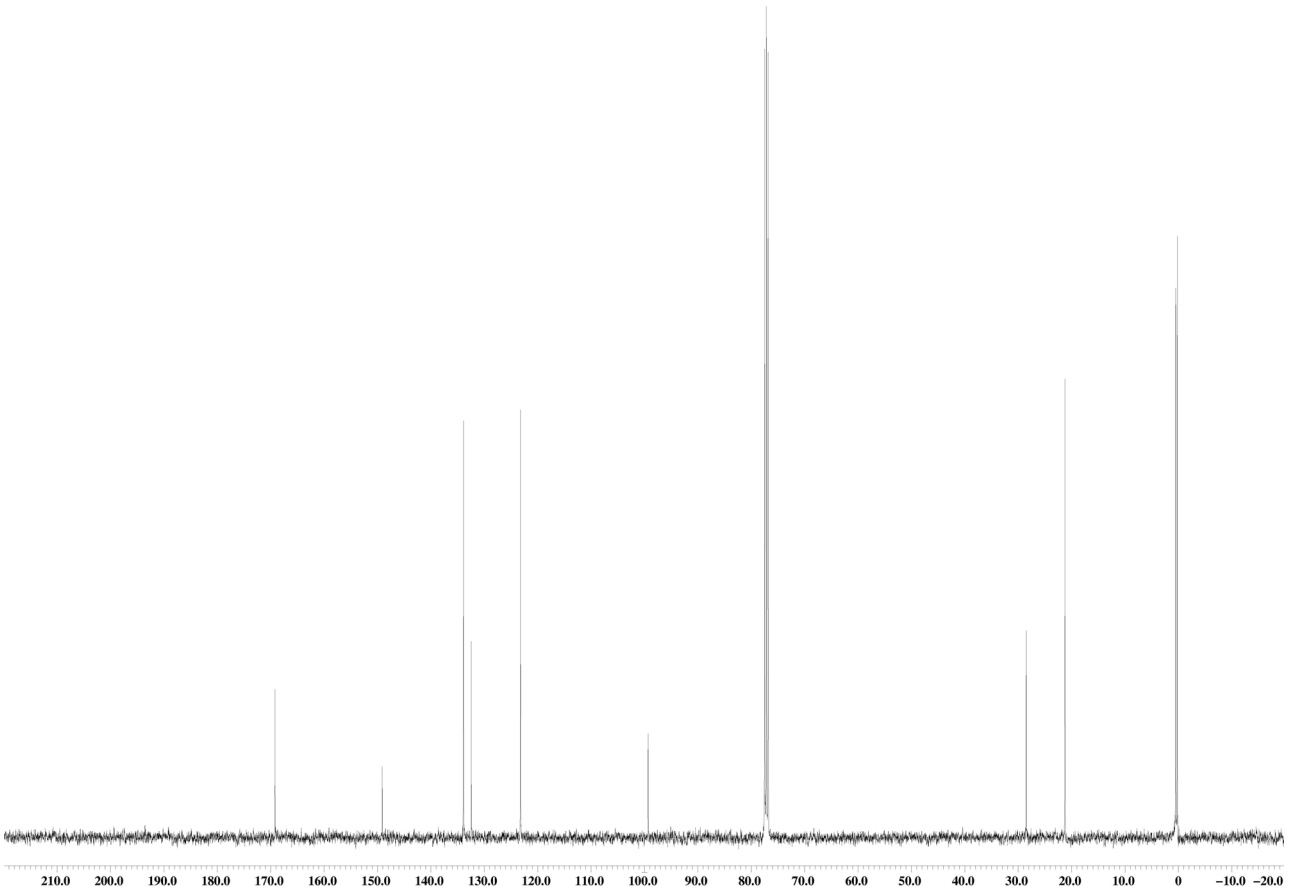
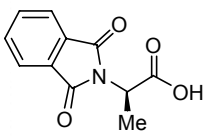
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
−20.0


O
OSiMe3
N
OSiMe3
O
Me
Me

**3i**

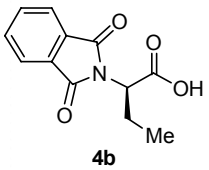

8.9
6.14
1.88
2.0
0.99
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0


210.0
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
−10.0
−20.0


O
O
N
OH
O
Me

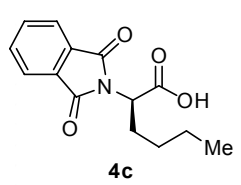
**4a**


3.2
2.07
1.96
1
0.47
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0


O
O
N
OH
O
Me

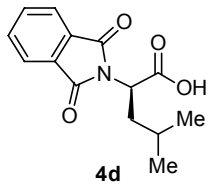
**4b**


3.12
2.09
2.0
1.87
1
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0


O
O
N
OH
O
Me

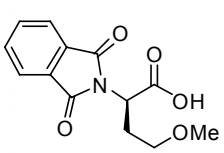
**4c**


0.38
1.93
2.03
1
2.07
4.18
3.07
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0


O
O
N
OH
O
Me
Me

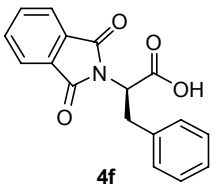
**4d**


1.9
2.04
1
1.07
1.03
1.02
6.28
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0



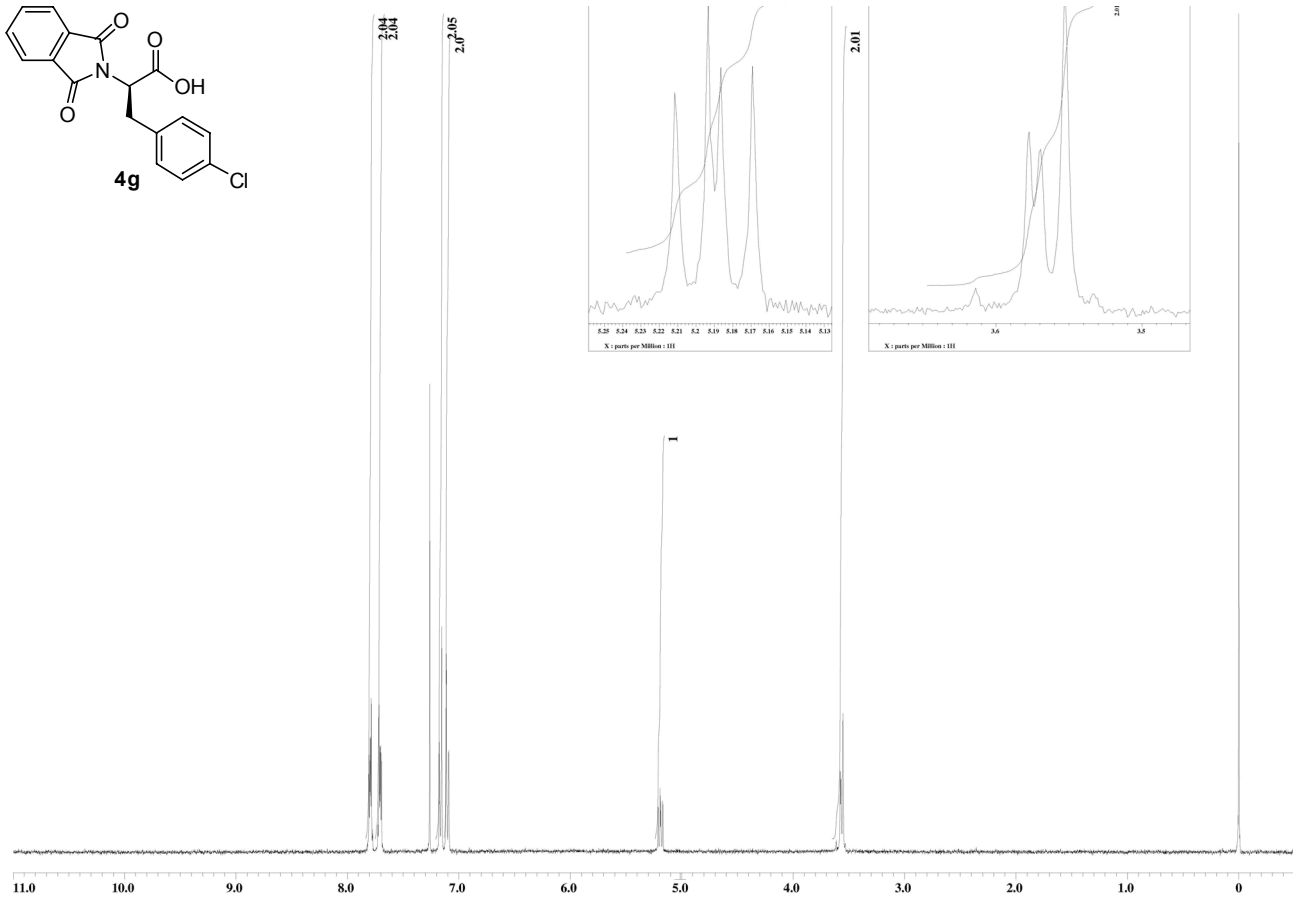
**4e**

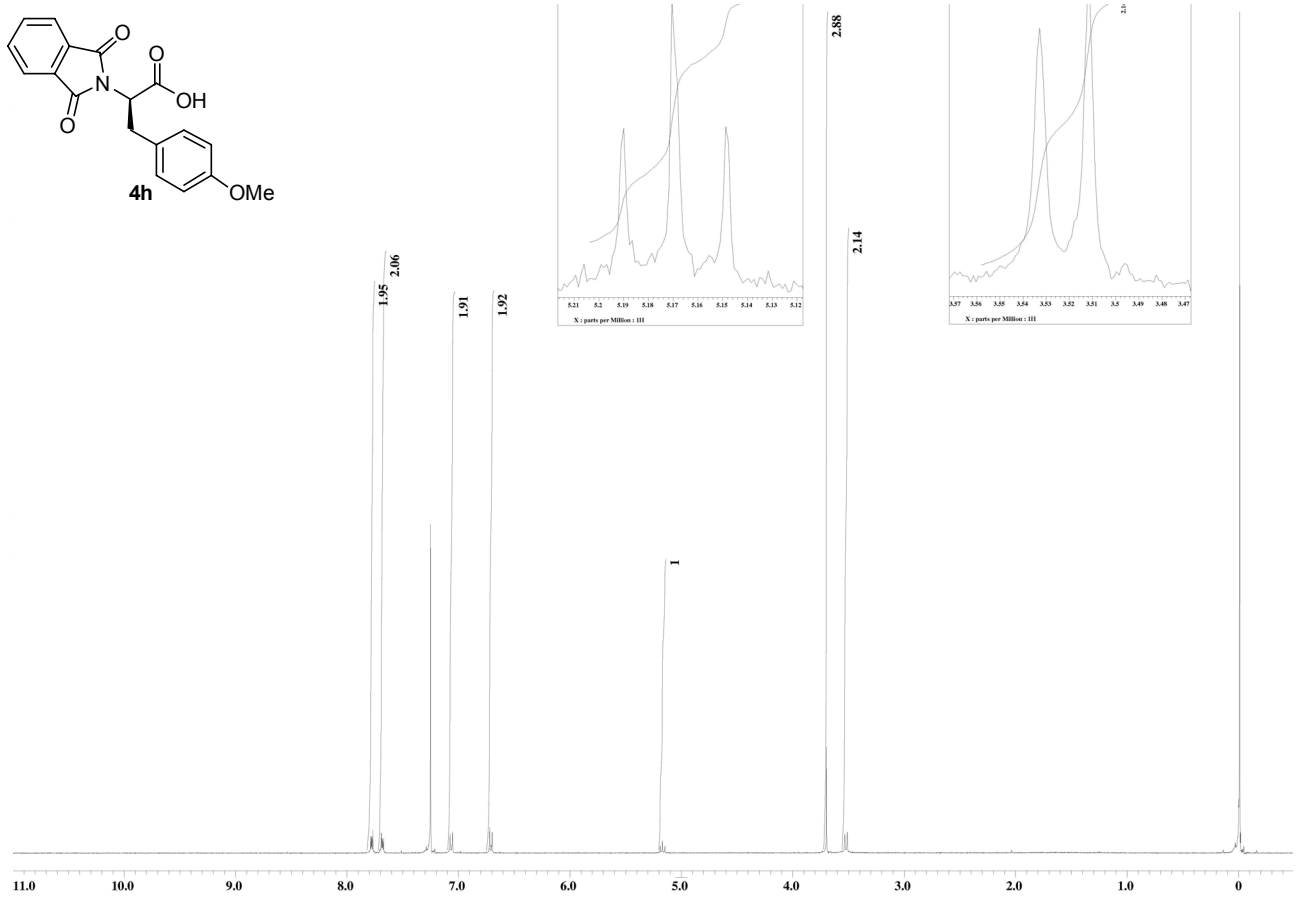

1.92
2.01
1
1.02
1.02
2.94
1.01
1.05
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

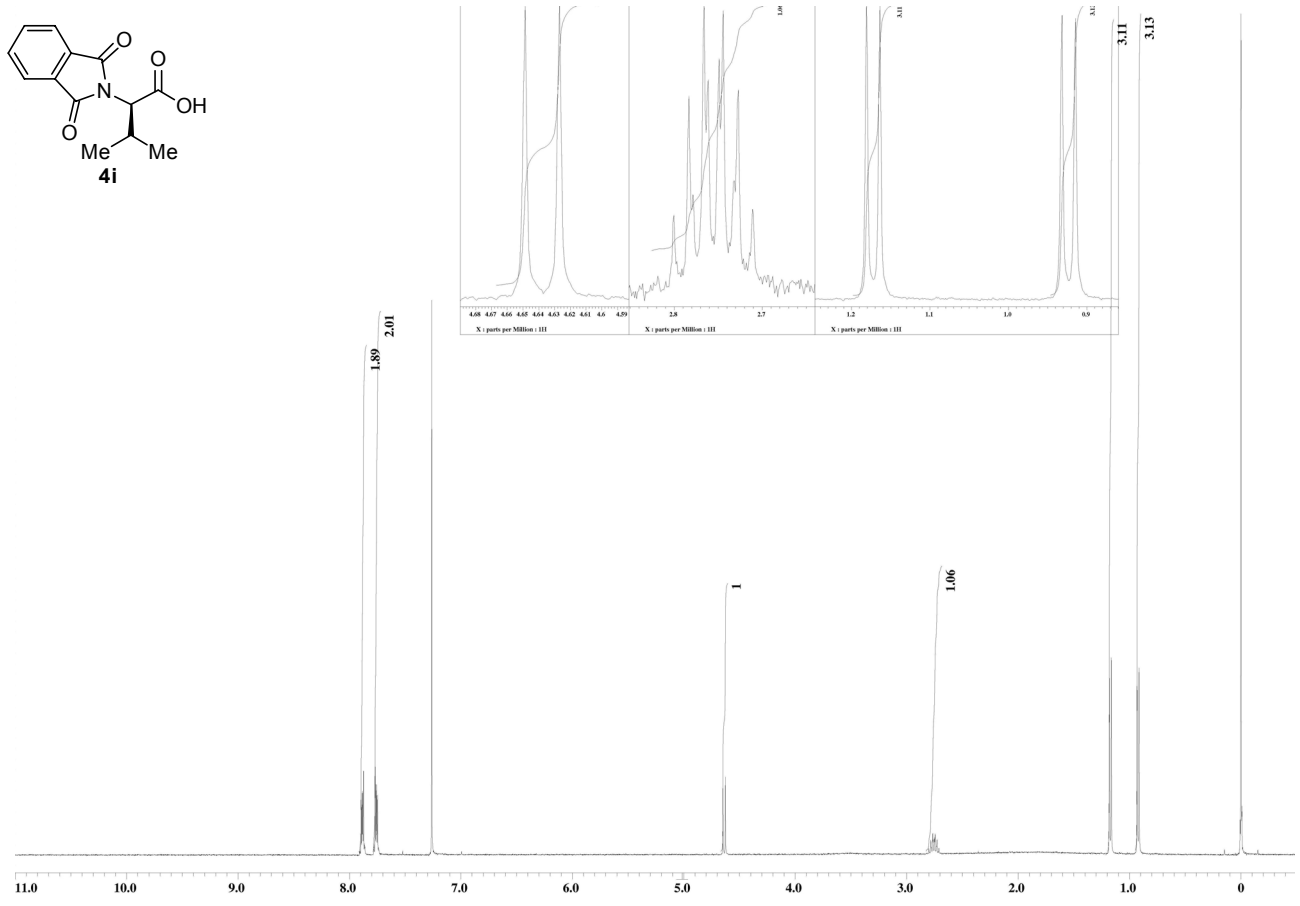


**4f**


5.02
1.94
1.99
1
2.09
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0


4g
Cl
2.04
2.04
2.05
2.01
1
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0


4h
OMe
1.95
2.06
1.91
1.92
2.88
2.14
1
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0


O
O
N
OH
O
Me
Me
4i
1.89
2.01
1
1.06
3.11
3.13
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0