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Studies on Asymmetric Hydroesterification of Enimides. A Possible Approach to Optically Active β−Amino Acid Derivatives

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Supporting Information

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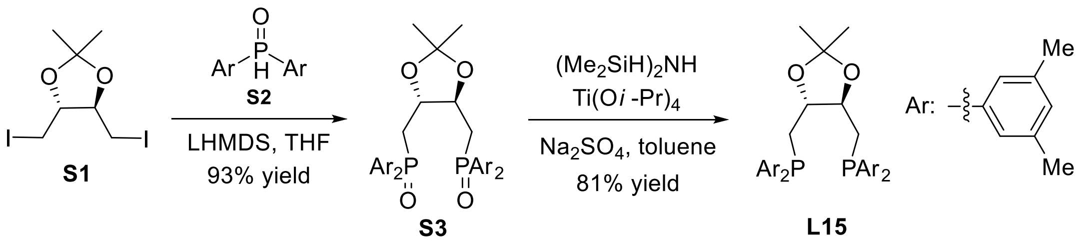
General Methods. All commercially available reagents were used without further purification unless otherwise noted. All dry solvents were purified with solvent purification system before use. Column chromatography was performed on silica gel (300-400 mesh). ^{1}H NMR spectra were recorded on a 400 MHz NMR spectrometer, ^{13}C NMR spectra were recorded on a 100 MHz NMR spectrometer, and ^{31}P NMR spectra were recorded on a 162 MHz NMR spectrometer. IR spectra were recorded on a FT-IR spectrometer. Melting points were uncorrected. Phenyl formate was prepared according to the reported procedures.[1] Enimide **1a-1j** were synthesized according to the literature procedures.[2] Ligand **L15** was prepared as described in Scheme S1.

1) (a) Y. Katafuchi, T. Fujihara, T. Iwai, J. Terao, and Y. Tsuji, *Adv. Synth. Catal.*, **2011**, *353*, 475–482; (b) T. Ueda, H. Konishi, and K. Manabe, *Org. Lett.*, **2012**, *14*, 3100–3103.
2) (a) V. I. Timokhin, N. R. Anastasi, and S. S. Stahl, *J. Am. Chem. Soc.*, **2003**, *125*, 12996-12997; (b) J. L. Brice, J. E. Harang, V. I. Timokhin, N. R. Anastasi, and S. S. Stahl, *J. Am. Chem. Soc.*, **2005**, *127*, 2868-2869.



Scheme S1. Synthesis of L15

Procedure for phosphine oxide S2. To a solution of diethyl phosphite (1.38 g, 10.0 mmol) in THF (10 mL) at 0 °C under Ar atmosphere, was added dropwise 3.5-dimethylphenylmagnesium bromide (0.5 M in THF) (50.0 mL, 25.0 mmol). Upon stirring at 0 °C for 10 min and at rt for 16 h, the reaction mixture was quenched by slow addition of sat. aqueous NH_4Cl solution at 0 °C, extracted with ether, washed with brine, dried over Na_2SO_4, filtered, concentrated under reduced pressure, and purified by column chromatography (silica gel, eluent: petroleum ether:ethyl acetate = 1:1) to give phosphine oxide **S2** as a white solid (2.09 g, 81% yield).[1] IR (film) 1600, 1275, 1192, 1128, 954, 691, 589 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 477.6 Hz, 1H), 7.29 (dd, *J* = 14.0 Hz, 4H), 7.17 (s, 2H), 2.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8 (d, *J* = 13.4 Hz,), 134.4 (d, *J* = 3.0 Hz), 131.4 (d, *J* = 100 Hz), 128.3 (d, *J* = 11.5 Hz), 21.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.8.

1) M. Jin and M. Nakamura, *Chem. Lett.*, 2013, **42**, 1035-1037.

Procedure for phosphine oxide S3: To a solution of phosphine oxide **S2** (2.84 g, 11.0 mmol) and 4,5-bis(iodomethyl)-2,2-dimethyl-1,3-dioxolane **S1**[1] (1.91 g, 5.0 mmol) in THF (20 mL) at 0 °C under Ar atmosphere, was added dropwise LHMDS (1.0 M THF solution) (11.0 mL, 11.0 mmol). Upon stirring at 0 °C for 18 h, the reaction mixture was quenched with sat. aqueous NH_4Cl, extracted with ethyl acetate (3 × 40 mL), washed with brine, dried over anhydrous Na_2SO_4, filtered, concentrated under reduced pressure, and purified by column chromatography (silica gel, eluent: CH_2Cl_2:MeOH = 30:1) to give phosphine oxide **S3** as a white solid (2.99 g, 93% yield).[2] $[\alpha]_D^{25}$ = +22.8 (*c* 1.0, $CHCl_3$); IR (film) 1599, 1377, 1181, 1127, 852, 695 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 12.0 Hz, 8H), 7.08 (d, *J* = 2.0 Hz, 4H), 4.13-4.09 (m, 2H), 2.62-2.52 (m, 4H), 2.30 (s, 24H), 1.21 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4 (d, *J* = 12.5 Hz), 138.1 (d, *J* = 12.4 Hz), 133.559 (d, *J* = 46.1 Hz), 133.558 (d, *J* = 2.9 Hz), 133.4 (d, *J* = 2.9 Hz), 132.6 (d, *J* = 46.2 Hz), 128.8 (d, *J* = 9.5 Hz), 128.4 (d, *J* = 9.4 Hz), 109.4, 76.7 (dd, *J* = 11.2, 3.2 Hz), 33.4 (d, *J* = 70.4 Hz), 27.0, 21.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.8;

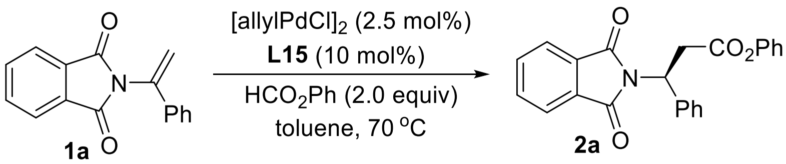
1) For preparation of **S1**, see: S. P. Khanapure, N. Najafi, S. Manna, J.-J. Yang, and J. Rokach, *J. Org. Chem.*, **1995**, *60*, 7548-7551.
2) Y. Ohmaru, N. Sato, M. Mizutani, S. Kotani, M. Sugiura, and M. Nakajima, *Org. Biomol. Chem.*, 2012, **10**, 4562–4570.

Procedure for ligand L15: To a mixture of phosphine oxide **S3** (2.99 g, 4.65 mmol) and anhydrous Na_2SO_4 (0.299 g) in dry toluene (15 mL) at rt under Ar atmosphere, were added dropwise $(Me_2SiH)_2NH$ (1.55 g, 11.6 mmol) and Ti(O*i*-Pr)$_4$ (1.322 g, 4.65 mmol) successively.[1] Upon stirring at 60 ℃ for 24 h, the reaction mixture was cooled to rt, filtered, washed with cold pentane, concentrated under reduced pressure, and purified by column chromatography (silica gel, eluent: petroleum ether:ethyl acetate = 20:1) to give ligand **L15** as a viscous liquid (2.30 g, 81% yield).[2] $[\alpha]_D^{25}$ = -4.5 (*c* 1.0, $CHCl_3$); IR (film) 1598, 1259, 1091, 1038, 843, 801, 691 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 7.6 Hz, 4H), 7.04 (d, *J* = 7.6 Hz, 4H), 6.95 (s, 2H), 6.93 (s, 2H), 3.87-3.80 (m, 2H), 2.43-2.20 (m, 4H), 2.27 (s, 24H), 1.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5 (d, *J* = 12.2 Hz), 138.1 (d, *J* = 12.3 Hz), 138.0 (d, *J* = 7.4 Hz), 137.9 (d, *J* = 7.1 Hz), 131.0, 130.84, 130.75, 130.52, 130.47, 130.34, 108.9, 80.0 (dd, *J* = 14.3, 7.2 Hz), 32.4 (dd, *J* = 15.2, 3.3 Hz), 27.5, 21.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ -23.8; HRMS (ESI) m/z $(M+H)^+$ Calcd for $C_{39}H_{49}O_2P_2$ 611.3202; found 611.3207.

1) C. Petit, A. Favre-Reguillon, B. Albela, L. Bonneviot, G. Mignani, and M. Lemaire, *Organometallics*, **2009**, *28*, 6379–6382.

2) P. Koschker, M. Kähny, and B. Breit, *J. Am. Chem. Soc.*, **2015**, *137*, 3131-3137.

Representative procedure for asymmetric hydroesterification (Table 3, 2a).



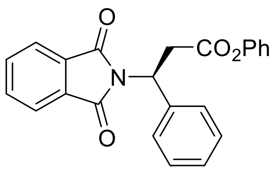
To a mixture of $(\eta^3\text{-}C_3H_5)_2Pd_2Cl_2$ (0.0018 g, 0.0050 mmol), **L15** (0.0122 g, 0.020 mmol), and enimide **1a** (0.0499 g, 0.20 mmol) in toluene (0.1 mL), was added HCO_2Ph (0.0488 g, 0.40 mmol) via syringe. The vial was purged with Ar to remove the air and tightly sealed with a septum cap. Upon stirring at 70 °C for 60 h, the reaction mixture was cooled to rt, and purified by flash chromatography (silica gel, eluent: petroleum ether:ethyl acetate = 8:1) to give amino ester **2a** as a white solid (0.0728 g, 98% yield, 83:17 er) (***Racemate synthesis:*** Enimide **1** and amino ester **2** were found to be inseparable by chromatography. To have complete conversions, racemates of amino esters **2** were prepared with 10 mol% racemic DIOP [by combining 50% (+)-DIOP and 50% (-)-DIOP] at 90 °C for 72 h).

Procedure for gram scale asymmetric hydroesterification reaction (Scheme 3).

To a mixture of $(\eta^3\text{-}C_3H_5)_2Pd_2Cl_2$ (0.0274 g, 0.075 mmol), **L15** (0.1832 g, 0.30 mmol), and enimide **1a** (0.7478 g, 3.0 mmol) in toluene (1.5 mL), was added HCO_2Ph (0.7327 g, 6.0 mmol) via syringe. The vial was purged with Ar to remove the air and tightly sealed with a septum cap. Upon stirring at 70 °C for 60 h, the reaction mixture was cooled to rt, and purified by flash chromatography (silica gel, eluent: petroleum ether:ethyl acetate = 8:1) to give amino ester **2a** as a white solid (1.066 g, 96% yield, 83:17 er).

Recrystallization: A portion of the amino ester (0.8722 g) was completely dissolved in a mixture of ethyl acetate (25 mL) and petroleum ether (30 mL) at 65 °C. The resulting solution was cooled to room temperature and the solvent was allowed to evaporate slowly for 4 days. The mixture was filtered to give a white solid (0.3679 g, 42% yield, 63:37 er). The mother liquid was concentrated under reduced pressure to give a white solid (0.4983 g, 57% yield, 97.5:2.5 er), which was dissolved again in a mixture of ethyl acetate (10 mL) and petroleum ether (20 mL) at 65 °C. The resulting solution was placed at room temperature for 3 days, allowing slow evaporation of the solvent. The mixture was filtered to give a white solid (0.136 g, 16% yield, 92:8 er). The mother liquid was concentrated under reduced pressure to give a white solid (0.3598 g, 41% yield, 99:1 er).

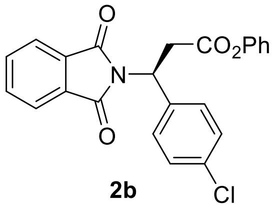
Table 3, 2a



2a

White solid; mp. 120.5-122.4 ^{o}C; $[\alpha]_D^{25}$ = -11.6 (*c* 1.0, $CHCl_3$) (83:17 er); IR (film) 1757, 1711, 1387, 1195, 720 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.79 (m, 2H), 7.70-7.66 (m, 2H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.40-7.30 (m, 5H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 2H), 5.96 (dd, *J* = 10.0, 5.6 Hz, 1H), 4.06 (dd, *J* = 16.8, 10.4 Hz, 1H), 3.54 (dd, *J* = 16.8, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 168.3, 150.5, 138.4, 134.3, 131.9, 129.6, 129.0, 128.6, 128.1, 126.1, 123.6, 121.6, 51.1, 36.3; HRMS (ESI) m/z $(M+Na)^+$ Calcd for $C_{23}H_{17}NO_4Na$ 394.1050; found 394.1050.

Table 3, 2b

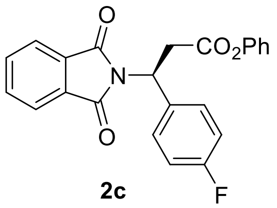


2b

(X-ray structure)

White solid; mp. 138.3-140.0 ºC; $[\alpha]_D^{25}$ = -11.0 (*c* 1.0, $CHCl_3$) (82:18 er); IR (film) 1758, 1711, 1492, 1386, 1195, 717 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86-7.75 (m, 2H), 7.75-7.66 (m, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.37-7.28 (m, 4H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 2H), 5.92 (dd, *J* = 10.0, 6.4 Hz, 1H), 3.98 (dd, *J* = 16.4, 9.6 Hz, 1H), 3.54 (dd, *J* = 16.4, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 168.1, 150.4, 136.9, 134.5, 134.4, 131.8, 129.61, 129.56, 129.2, 126.2, 123.7, 121.5, 50.35, 36.2; HRMS (ESI) m/z: $(M+Na)^+$ Calcd for $C_{23}H_{16}ClNO_4Na$ 428.0660; found 428.0660.

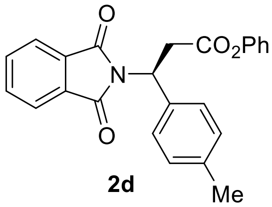
Table 3, 2c



2c

White solid; mp. 111.4-113.4 ºC; $[\alpha]_D^{25}$ = -15.8 (*c* 1.0, $CHCl_3$) (83:17 er); IR (film) 1757, 1710, 1387, 1162, 717 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85-7.75 (m, 2H), 7.72-7.66 (m, 2H), 7.64-7.57 (m, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.05 (t, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 7.6 Hz, 2H), 5.93 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.99 (dd, *J* = 16.8, 10.0 Hz, 1H), 3.54 (dd, *J* = 16.4, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 168.2, 162.7 (d, *J* = 245.9 Hz), 150.4, 134.34, 134.31 (d, *J* = 5.2 Hz), 131.8, 130.0 (d, *J* = 8.2 Hz), 129.6, 126.2, 123.6, 121.5, 115.9 (d, *J* = 21.3 Hz), 50.4, 36.4; HRMS (ESI) m/z: $(M+Na)^+$ Calcd for $C_{23}H_{16}FNO_4Na$ 412.0956; found 412.0955.

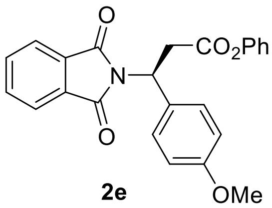
Table 3, 2d



2d

White solid; mp. 87.9-89.6 °C; $[\alpha]_D^{25}$ = -11.8 (*c* 1.0, $CHCl_3$) (83:17 er); IR (film) 1758, 1712, 1369, 1195, 717 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84-7.78 (m, 2H), 7.70-7.65 (m, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.21-7.15 (m, 3H), 6.98 (d, *J* = 8.0 Hz, 2H), 5.94 (dd, *J* = 10.0, 6.0 Hz, 1H), 4.04 (dd, *J* = 16.4, 10.0 Hz, 1H), 3.53 (dd, *J* = 16.4, 5.6 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 168.2, 150.5, 138.3, 135.5, 134.2, 131.9, 129.6, 129.5, 128.0, 126.1, 123.5, 121.6, 50.8, 36.3, 21.3; HRMS (ESI) m/z: $(M+Na)^+$ calcd for $C_{24}H_{19}NO_4Na$ 408.1206; found 408.1208.

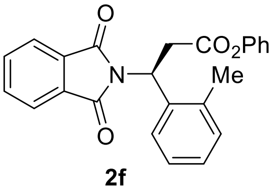
Table 3, 2e



2e

White solid; mp. 112.4-114.5 °C; $[\alpha]_D^{25}$ = -16.8 (*c* 1.0, $CHCl_3$) (82:18 er); IR (film) 1757, 1710, 1387, 1194, 717 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83-7.78 (m, 2H), 7.70-7.65 (m, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.91 (dd, t, *J* = 10.0, 6.0 Hz, 1H), 4.01 (dd, *J* = 16.4, 10.0 Hz, 1H), 3.79 (s, 3H), 3.52 (dd, *J* = 16.4, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 168.3, 159.6, 150.5, 134.2, 132.0, 130.6, 129.6, 129.5, 126.1, 123.5, 121.6, 114.3, 55.5, 50.5, 36.5; HRMS (ESI) m/z: $(M+Na)^+$ Calcd for $C_{24}H_{19}NO_5Na$ 424.1155; found 424.1154.

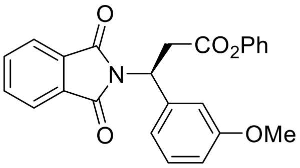
Table 3, 2f



2f

White solid; mp. 80.0-81.6 °C; $[\alpha]_D^{25}$ = -2.8 (*c* 1.0, $CHCl_3$) (82:18 er); IR (film) 1755, 1711, 1353, 1193, 717 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.84-7.76 (m, 2H), 7.72-7.65 (m, 2H), 7.35-7.15 (m, 6H), 6.96 (d, *J* = 7.6 Hz, 2H), 6.16 (dd, *J* = 10.0, 6.4 Hz, 1H), 3.98 (dd, *J* = 16.4, 9.6 Hz, 1H), 3.49 (dd, *J* = 16.4, 6.0 Hz, 1H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 168.5, 150.5, 136.7, 136.5, 134.3, 131.9, 131.0, 129.6, 128.5, 128.3, 126.6, 126.1, 123.5, 121.6, 47.8, 36.9, 19.9; HRMS (ESI) m/z: $(M+Na)^+$ Calcd for $C_{24}H_{19}NO_4Na$ 408.1206; found 408.1206.

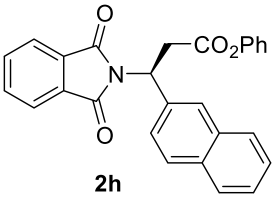
Table 3, 2g



2g

White solid; mp. 85.5-87.3 °C; $[\alpha]_D^{25}$ = -8.3 (*c* 1.0, $CHCl_3$) (82:18 er); IR (film) 1756, 1708, 1363, 1193, 722 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83-7.78 (m, 2H), 7.70-7.64 (m, 2H), 7.35-7.26 (m, 3H), 7.21-7.15 (m, 3H), 7.01-6.96 (m, 2H), 6.86 (dd, *J* = 8.0, 1.6 Hz, 1H), 5.93 (dd, *J* = 10.0, 5.6 Hz, 1H), 4.06 (dd, *J* = 16.4, 10.4 Hz, 1H), 3.81 (s, 3H), 3.53 (dd, *J* = 16.8, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 168.2, 160.0, 150.5, 139.9, 134.2, 131.9, 130.0, 129.5, 126.1, 123.5, 121.5, 120.2, 113.9, 113.7, 55.4, 51.0, 36.2; HRMS (ESI) m/z: $(M+Na)^+$ Calcd for $C_{24}H_{19}NO_5Na$ 424.1155; found 424.1154.

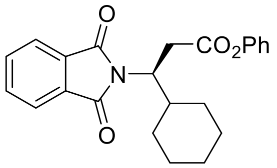
Table 3, 2h



2h

White solid; mp. 92.5-94.5 °C; $[\alpha]_D^{25}$ = -8.7 (*c* 1.0, $CHCl_3$) (81:19 er); IR (film) 1756, 1710, 1382, 1193, 721 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.90-7.80 (m, 5H), 7.73 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.71-7.65 (m, 2H), 7.52-7.45 (m, 2H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.13 (dd, *J* = 10.0, 5.6 Hz, 1H), 4.16 (dd, *J* = 16.4, 10.0 Hz, 1H), 3.66 (dd, *J* = 16.8, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 168.3, 150.5, 135.8, 134.3, 133.4, 133.2, 131.9, 129.6, 128.9, 128.4, 127.8, 127.2, 126.63, 126.60, 126.1, 125.7, 123.6, 121.6, 51.2, 36.3; HRMS (ESI) m/z: $(M+Na)^+$ Calcd for $C_{27}H_{19}NO_4Na$ 444.1206; found 444.1207.

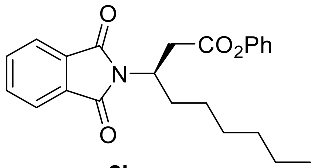
Table 3, 2i



2i

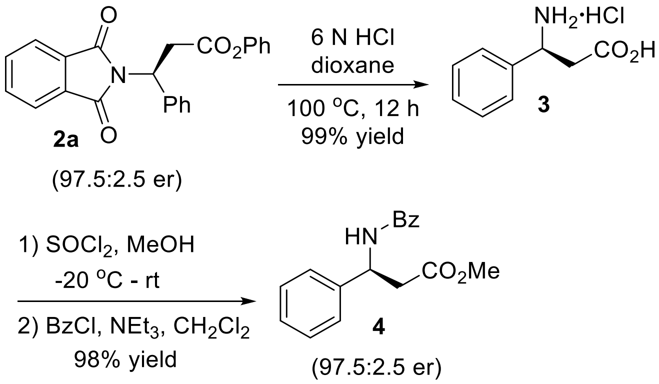
White solid; mp. 126.9-128.2 ºC; $[\alpha]_D^{25}$ = -19.9 (*c* 1.0, $CHCl_3$) (76:24 er); IR (film) 1758, 1710, 1371, 1192, 721 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.79 (m, 2H), 7.71-7.65 (m, 2H), 7.28 (t, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 2H), 4.49 (td, *J* = 10.8, 4.0 Hz, 1H), 3.47 (dd, *J* = 15.6, 11.2 Hz, 1H), 3.10 (dd, *J* = 16.0, 4.0 Hz, 1H), 2.20-2.05 (m, 1H), 1.94 (d, *J* = 12.4 Hz, 1H), 1.81 (d, *J* = 13.2 Hz, 1H), 1.75-1.55 (m, 3H), 1.37-0.90 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 168.6, 150.5, 134.1, 131.8, 129.5, 126.0, 123.4, 121.5, 53.3, 39.5, 34.7, 30.7, 29.9, 26.1, 25.9, 25.8; HRMS (ESI) m/z: $(M+Na)^+$ Calcd for $C_{23}H_{23}NO_4Na$ 400.1519; found 400.1519.

Table 3, 2j



2j

Colorless oil; $[\alpha]_D^{25}$ = -11.0 (*c* 1.0, $CHCl_3$) (72:28 er); IR (film) 1758, 1710, 1371, 1193, 720 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.80 (m, 2H), 7.73-7.67 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 4.84-4.73 (m, 1H), 3.44 (dd, *J* = 16.0, 10.0 Hz, 1H), 3.03 (dd, *J* = 16.0, 5.2 Hz, 1H), 2.25-2.10 (m, 1H), 1.87-1.77 (m, 1H), 1.40-1.20 (m, 8H), 0.85 (t, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 168.5, 150.5, 134.2, 131.9, 129.5, 126.0, 123.5, 121.6, 48.3, 37.3, 32.6, 31.8, 28.9, 26.5, 22.7, 14.2; HRMS (ESI) m/z: $(M+Na)^+$ Calcd for $C_{23}H_{25}NO_4Na$ 402.1676; found 402.1674.



Scheme 4 The synthesis and derivatization of β-amino acid.

Procedure for amino acid 3. A solution of amino ester **2a** (0.1857 g, 0.50 mmol) in 6 N HCl (15 mL) and dioxane (1.0 mL) was stirred at 100 °C for 12 h.[1] The reaction mixture was cooled to rt and washed with ether (3x5.0 mL). The aqueous phase was concentrated to give amino acid hydrochloride **3** as a white solid (0.1008 g, 99% yield). mp. 178.3-180.2 °C; $[\alpha]^{25}_D$ = +2.0 (c 1.0, H_2O) [litt.[2] $[\alpha]^{25}_D$ = +2.8 (c 0.28, H_2O) for 97.5:2.5 er, for *S*-configuration]; ^1H NMR (400 MHz, D_2O) δ 7.49-7.41 (m, 5H), 4.75 (t, J = 7.2 Hz, 1H), 3.16 (dd, J = 17.2, 8.0 Hz, 1H), 3.06 (dd, J = 17.2, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, D_2O) δ 173.5, 135.1, 129.6, 129.3, 126.9, 51.4, 37.7.

Procedure for amino ester 4. [1a]To a solution of amino acid hydrochloride **3** (0.0403 g, 0.20 mmol) in MeOH (1.0 mL) at -20 °C, was added $SOCl_2$ (0.436 g, 3.6 mmol) dropwise. The reaction mixture was warmed to rt, stirred overnight, and concentrated. The resulting residue was dissolved in CH_2Cl_2 (2.0 mL), followed by the successive addition of NEt_3 (0.060 g, 0.60 mmol) and BzCl (0.042 g, 0.30 mmol). Upon stirring at rt for 30 min, the reaction mixture was concentrated and purified by flash chromatography (silica gel, petroleum ether:EtOAc = 5:1 to 3:1) to afford *N*-benzoyl amino ester **4** (0.0555 g, 98% yield, 97.5:2.5 er). mp. 114.8-116.7 °C; $[\alpha]^{25}_D$ = +16.9 (c 1.0, $CHCl_3$) (97.5:2.5

er), [litt.[3] $[\alpha]^{20}_{D}$ = -20.6 (*c* 0.85, $CHCl_3$) for *R*-configuration]; IR (film) 3348, 1732, 1635 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.2 Hz, 2H), 7.66-7.56 (m, 1H), 7.53-7.46 (m, 1H), 7.44-7.36 (m, 2H), 7.36-7.27 (m, 4H), 7.27-7.21 (m, 1H), 5.65-5.30 (m, 1H), 3.61 (s, 3H), 3.02 (dd, *J* = 15.6, 5.6 Hz, 1H), 2.92 (dd, *J* = 15.6, 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 166.8, 140.7, 134.3, 131.8, 128.9, 128.7, 127.8, 127.2, 126.4, 52.1, 50.0, 39.8;

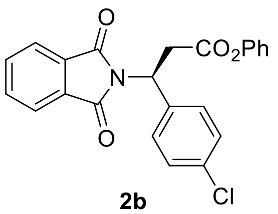
1) (a) X. Xiao, M. Liu, C. Rong, F. Xue, S. Li, Y. Xie and Y. Shi, *Org. Lett.*, 2012, **20**, 5270-5273; (b) C.-H. Lee, J.-S. Lee, H.-K. Na, D.-W. Yoon, H. Miyaji, W.-S. Cho and J. L. Sessler, *J. Org. Chem.*, 2005, **70**, 2067-2074.

2) (a) E. Forró, T. Paál, G. Tasnádi and F. Fülöp, *Adv. Synth. Catal.*, 2006, **348**, 917-923; (b) J. Lai, S. Sayalero, A. Ferrali, L. Osorio-Planes, F. Bravo, C. Rodriguez-Escrich and M. A. Pericàs, *Adv. Synth. Catal.*, 2018, **360**, 2914-2924.

3) P. Gizecki, R. Dhal, L. Toupet and G. Dujardin, *Org. Lett.*, 2000, **2**, 585-588.

The X-ray structure of compound **2b**

Compound **2b** (0.10 g, >99:1 er) was dissolved in ethyl acetate (2 mL) and petroleum ether (6 mL). The solvent was allowed to slowly evaporate at rt to get a colorless crystal suitable for X-ray diffraction analysis. The intensity data were collected on a D8 VENTURE instrument. The data were outlined below.



2b

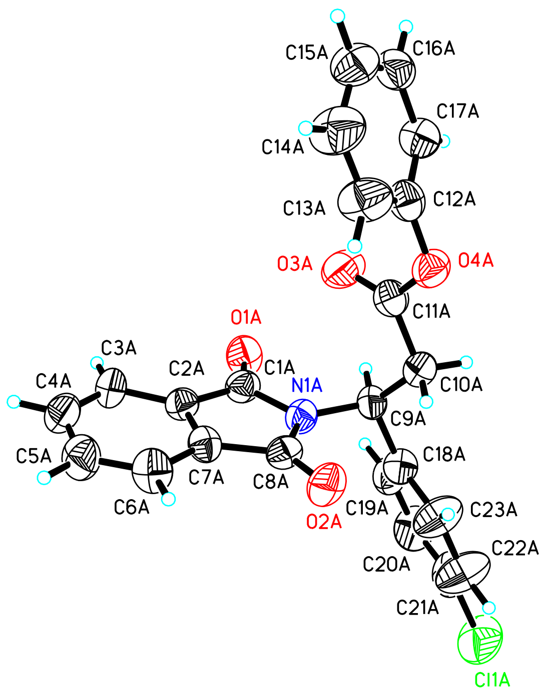


Figure S-1. Ortep diagram of compound **2b** (the thermal ellipsoids are drawn at the 30% probability level).

Table S1. Crystal data and structure refinement for **2b**.

Identification code	**2b**	
Empirical formula	C23 H16 Cl N O4	
Formula weight	405.82	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P 1	
Unit cell dimensions	a = 10.606(3) Å	α= 65.747(7)°.
	b = 14.275(4) Å	β= 88.159(7)°.
	c = 15.503(5) Å	γ = 71.091(7)°.
Volume	2010.6(10) $Å^3$	
Z	4	
Density (calculated)	1.341 Mg/m^3	
Absorption coefficient	0.219 mm^{-1}	
F(000)	840	
Crystal size	0.170 x 0.140 x 0.110 mm^3	
Theta range for data collection	2.044 to 25.499°.	
Index ranges	-12<=h<=12, -17<=k<=16, -16<=l<=18	
Reflections collected	23840	
Independent reflections	11905 [R(int) = 0.0480]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6010	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11905 / 118 / 1103	
Goodness-of-fit on F^2	1.008	
Final R indices [I>2sigma(I)]	R1 = 0.0722, wR2 = 0.1841	
R indices (all data)	R1 = 0.1436, wR2 = 0.2434	
Absolute structure parameter	0.06(5)	
Extinction coefficient	0.016(3)	
Largest diff. peak and hole	0.285 and -0.230 e.$Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	6160(4)	5861(3)	11844(3)	134(1)
Cl(1A)	7259(5)	6712(4)	7241(3)	162(2)
Cl(1B)	5702(3)	7134(3)	3614(2)	116(1)
Cl(1C)	4157(7)	6168(4)	-1873(3)	190(2)
N(1)	8673(9)	9479(7)	8783(6)	85(2)
N(1A)	9693(7)	8808(6)	3123(5)	70(2)
N(1B)	3096(6)	3766(6)	6932(5)	65(2)
N(1C)	2481(9)	4331(8)	2600(7)	96(3)
O(1)	8103(9)	10822(8)	9298(8)	132(3)
O(2)	9900(8)	8148(9)	8302(7)	121(3)
O(3)	7536(9)	11258(8)	6966(6)	110(2)
O(4)	7356(9)	10476(8)	6028(7)	113(3)
O(1A)	11900(7)	8542(6)	3522(6)	96(2)
O(2A)	7812(7)	8818(6)	2428(5)	93(2)
O(3A)	9891(8)	10998(6)	2249(6)	125(3)
O(4A)	7799(7)	12121(6)	1664(5)	88(2)
O(1B)	4044(10)	2601(8)	6246(7)	122(3)
O(2B)	1545(7)	4832(8)	7529(7)	108(3)
O(3B)	4636(7)	1486(7)	8617(5)	94(2)
O(4B)	4705(7)	2537(5)	9335(5)	86(2)
O(1C)	394(10)	4457(10)	2075(8)	142(4)
O(2C)	4151(8)	4454(9)	3419(7)	140(4)
C(1)	8961(12)	10178(11)	9103(10)	97(3)
C(2)	10399(11)	9978(11)	9080(9)	99(4)
C(3)	11180(13)	10422(12)	9331(11)	123(5)
C(4)	12483(18)	10061(15)	9286(13)	139(5)
C(5)	13068(15)	9194(18)	9065(12)	141(6)
C(6)	12252(12)	8745(13)	8763(9)	113(4)
C(7)	10937(11)	9151(11)	8777(8)	91(3)
C(8)	9819(10)	8824(11)	8599(8)	87(3)
C(9)	7324(10)	9501(9)	8606(8)	90(3)
C(10)	7013(11)	9624(11)	7625(8)	102(4)
C(11)	7335(12)	10545(12)	6812(11)	98(4)

C(12)	7717(14)	11257(11)	5290(10)	98(4)
C(13)	6821(12)	12209(10)	4696(9)	94(3)
C(14)	7240(16)	12922(12)	3927(11)	113(4)
C(15)	8510(20)	12709(19)	3782(13)	138(6)
C(16)	9429(17)	11707(19)	4399(17)	139(6)
C(17)	9041(15)	10978(13)	5153(13)	119(4)
C(18)	7014(9)	8557(9)	9415(8)	80(3)
C(19)	6372(12)	8735(11)	10136(10)	97(3)
C(20)	6142(12)	7890(13)	10875(9)	102(4)
C(21)	6526(11)	6874(10)	10905(9)	93(3)
C(22)	7090(19)	6718(12)	10185(13)	147(6)
C(23)	7398(17)	7524(12)	9461(12)	136(6)
C(1A)	11070(10)	8473(8)	3060(8)	75(3)
C(2A)	11241(9)	8014(8)	2355(7)	71(2)
C(3A)	12412(10)	7544(9)	2033(8)	84(3)
C(4A)	12246(13)	7178(10)	1374(9)	99(3)
C(5A)	10988(15)	7218(11)	1046(8)	103(4)
C(6A)	9915(12)	7685(10)	1357(8)	94(3)
C(7A)	10017(10)	8081(8)	2043(7)	70(2)
C(8A)	8987(10)	8610(8)	2514(6)	69(2)
C(9A)	9120(9)	9430(7)	3687(7)	71(2)
C(10A)	8106(10)	10514(8)	3068(8)	84(3)
C(11A)	8716(12)	11207(9)	2270(9)	90(3)
C(12A)	8234(10)	12802(9)	867(8)	82(3)
C(13A)	8115(14)	12721(12)	42(10)	120(4)
C(14A)	8556(17)	13362(14)	-748(10)	133(5)
C(15A)	9095(13)	14090(11)	-690(9)	106(4)
C(16A)	9234(10)	14150(9)	142(10)	98(3)
C(17A)	8834(11)	13473(9)	960(8)	89(3)
C(18A)	8610(10)	8742(9)	4561(7)	78(3)
C(19A)	9443(11)	8138(10)	5417(9)	97(3)
C(20A)	9036(16)	7507(12)	6258(10)	118(4)
C(21A)	7800(17)	7489(11)	6219(9)	115(4)
C(22A)	6967(15)	8035(15)	5416(11)	139(6)
C(23A)	7373(13)	8673(12)	4579(9)	118(4)
C(1B)	3090(12)	3074(11)	6514(8)	87(3)
C(2B)	1656(13)	3107(12)	6482(9)	103(4)
C(3B)	1110(20)	2560(20)	6115(13)	190(9)

C(4B)	-370(30)	2830(30)	6208(18)	248(16)
C(5B)	-990(20)	3460(30)	6613(14)	227(16)
C(6B)	-410(15)	3972(18)	6906(10)	153(7)
C(7B)	965(12)	3756(13)	6859(9)	103(4)
C(8B)	1813(10)	4221(10)	7152(8)	84(3)
C(9B)	4244(9)	4030(8)	7140(7)	73(3)
C(10B)	5379(9)	2998(8)	7786(8)	84(3)
C(11B)	4893(9)	2266(10)	8586(8)	76(3)
C(12B)	4221(10)	1890(9)	10117(8)	80(3)
C(13B)	5076(11)	1005(9)	10854(8)	83(3)
C(14B)	4558(14)	380(10)	11585(9)	97(3)
C(15B)	3215(14)	615(11)	11614(9)	96(3)
C(16B)	2372(12)	1530(12)	10868(10)	102(4)
C(17B)	2845(11)	2169(9)	10132(9)	88(3)
C(18B)	4636(8)	4772(8)	6265(7)	63(2)
C(19B)	4069(12)	5874(10)	5938(8)	94(3)
C(20B)	4381(11)	6613(9)	5108(9)	95(3)
C(21B)	5292(10)	6195(10)	4618(7)	79(3)
C(22B)	5833(11)	5101(11)	4886(9)	95(3)
C(23B)	5478(11)	4397(10)	5705(9)	89(3)
C(1C)	1081(13)	4575(11)	2591(10)	103(4)
C(2C)	671(10)	5058(9)	3288(8)	81(3)
C(3C)	-525(13)	5460(12)	3543(11)	114(4)
C(4C)	-566(16)	5886(11)	4200(10)	108(4)
C(5C)	551(16)	5897(9)	4597(9)	102(4)
C(6C)	1778(13)	5486(9)	4315(8)	94(3)
C(7C)	1838(10)	5056(9)	3683(7)	77(3)
C(8C)	2991(13)	4588(11)	3271(9)	97(3)
C(9C)	3470(13)	3714(11)	2173(9)	108(4)
C(10C)	3200(20)	2683(11)	2320(10)	153(6)
O(3C)	2850(30)	1390(30)	3706(18)	184(6)
O(4C)	4970(30)	1270(20)	3720(20)	227(9)
C(11C)	3720(30)	1800(30)	3340(20)	193(7)
C(12C)	3730(30)	382(19)	4603(14)	168(6)
C(13C)	2890(30)	-180(20)	4569(13)	159(6)
C(14C)	2720(30)	-990(20)	5400(18)	154(6)
C(15C)	3390(30)	-1244(18)	6265(13)	148(6)
C(16C)	4230(20)	-690(20)	6300(14)	158(6)

C(17C)	4400(20)	130(20)	5469(19)	164(6)
O(3')	2040(20)	2400(14)	3735(14)	144(6)
O(4')	3801(18)	1060(13)	3712(13)	97(3)
C(11')	2960(20)	2040(18)	3339(16)	103(4)
C(12')	3385(19)	541(13)	4632(10)	98(3)
C(13')	3040(20)	-379(15)	4825(11)	97(4)
C(14')	3000(20)	-1073(13)	5761(13)	103(4)
C(15')	3301(18)	-847(13)	6504(10)	108(4)
C(16')	3648(17)	73(15)	6311(11)	103(4)
C(17')	3689(17)	767(12)	5375(12)	99(4)
C(18C)	3523(13)	4351(9)	1140(8)	89(3)
C(19C)	2471(16)	4906(15)	468(12)	140(5)
C(20C)	2740(20)	5482(13)	-535(9)	136(5)
C(21C)	3950(20)	5440(15)	-687(13)	127(5)
C(22C)	5020(20)	4921(16)	-13(16)	160(7)
C(23C)	4738(14)	4331(13)	909(11)	136(6)

Table S3. Bond lengths [Å] and angles [°] for **2b**.

Cl(1)-C(21)	1.720(13)
Cl(1A)-C(21A)	1.725(13)
Cl(1B)-C(21B)	1.740(11)
Cl(1C)-C(21C)	1.749(17)
N(1)-C(8)	1.376(14)
N(1)-C(1)	1.395(14)
N(1)-C(9)	1.453(12)
N(1A)-C(8A)	1.390(12)
N(1A)-C(1A)	1.396(12)
N(1A)-C(9A)	1.475(11)
N(1B)-C(1B)	1.386(14)
N(1B)-C(8B)	1.403(13)
N(1B)-C(9B)	1.467(12)
N(1C)-C(8C)	1.409(14)
N(1C)-C(1C)	1.410(14)
N(1C)-C(9C)	1.466(14)
O(1)-C(1)	1.197(13)
O(2)-C(8)	1.208(13)
O(3)-C(11)	1.217(15)
O(4)-C(11)	1.259(15)
O(4)-C(12)	1.378(15)
O(1A)-C(1A)	1.205(11)
O(2A)-C(8A)	1.182(10)
O(3A)-C(11A)	1.187(12)
O(4A)-C(11A)	1.327(12)
O(4A)-C(12A)	1.397(12)
O(1B)-C(1B)	1.189(12)
O(2B)-C(8B)	1.197(13)
O(3B)-C(11B)	1.212(13)
O(4B)-C(11B)	1.357(13)
O(4B)-C(12B)	1.390(12)
O(1C)-C(1C)	1.195(14)
O(2C)-C(8C)	1.197(13)
C(1)-C(2)	1.460(16)
C(2)-C(3)	1.344(17)
C(2)-C(7)	1.394(17)

C(3)-C(4)	1.32(2)
C(3)-H(3)	0.9300
C(4)-C(5)	1.37(2)
C(4)-H(4)	0.9300
C(5)-C(6)	1.42(2)
C(5)-H(5)	0.9300
C(6)-C(7)	1.329(16)
C(6)-H(6)	0.9300
C(7)-C(8)	1.478(16)
C(9)-C(10)	1.493(15)
C(9)-C(18)	1.540(14)
C(9)-H(9)	0.9800
C(10)-C(11)	1.529(17)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(12)-C(13)	1.338(16)
C(12)-C(17)	1.366(18)
C(13)-C(14)	1.384(18)
C(13)-H(13)	0.9300
C(14)-C(15)	1.31(2)
C(14)-H(14)	0.9300
C(15)-C(16)	1.40(2)
C(15)-H(15)	0.9300
C(16)-C(17)	1.37(2)
C(16)-H(16)	0.9300
C(17)-H(17)	0.9300
C(18)-C(19)	1.359(15)
C(18)-C(23)	1.368(17)
C(19)-C(20)	1.365(17)
C(19)-H(19)	0.9300
C(20)-C(21)	1.355(17)
C(20)-H(20)	0.9300
C(21)-C(22)	1.315(17)
C(22)-C(23)	1.359(18)
C(22)-H(22)	0.9300
C(23)-H(23)	0.9300
C(1A)-C(2A)	1.467(14)
C(2A)-C(7A)	1.360(13)

C(2A)-C(3A)	1.392(13)
C(3A)-C(4A)	1.364(17)
C(3A)-H(3A)	0.9300
C(4A)-C(5A)	1.419(17)
C(4A)-H(4A)	0.9300
C(5A)-C(6A)	1.308(16)
C(5A)-H(5A)	0.9300
C(6A)-C(7A)	1.416(15)
C(6A)-H(6A)	0.9300
C(7A)-C(8A)	1.471(13)
C(9A)-C(10A)	1.495(13)
C(9A)-C(18A)	1.516(14)
C(9A)-H(9A)	0.9800
C(10A)-C(11A)	1.511(14)
C(10A)-H(10C)	0.9700
C(10A)-H(10D)	0.9700
C(12A)-C(13A)	1.345(15)
C(12A)-C(17A)	1.363(14)
C(13A)-C(14A)	1.369(18)
C(13A)-H(13A)	0.9300
C(14A)-C(15A)	1.370(19)
C(14A)-H(14A)	0.9300
C(15A)-C(16A)	1.344(17)
C(15A)-H(15A)	0.9300
C(16A)-C(17A)	1.396(15)
C(16A)-H(16A)	0.9300
C(17A)-H(17A)	0.9300
C(18A)-C(23A)	1.346(16)
C(18A)-C(19A)	1.388(16)
C(19A)-C(20A)	1.395(17)
C(19A)-H(19A)	0.9300
C(20A)-C(21A)	1.324(18)
C(20A)-H(20A)	0.9300
C(21A)-C(22A)	1.328(19)
C(22A)-C(23A)	1.395(18)
C(22A)-H(22A)	0.9300
C(23A)-H(23A)	0.9300
C(1B)-C(2B)	1.508(16)

C(2B)-C(7B)	1.309(17)
C(2B)-C(3B)	1.400(19)
C(3B)-C(4B)	1.51(3)
C(3B)-H(3B)	0.9300
C(4B)-C(5B)	1.30(4)
C(4B)-H(4B)	0.9300
C(5B)-C(6B)	1.31(3)
C(5B)-H(5B)	0.9300
C(6B)-C(7B)	1.395(18)
C(6B)-H(6B)	0.9300
C(7B)-C(8B)	1.456(17)
C(9B)-C(18B)	1.484(13)
C(9B)-C(10B)	1.529(13)
C(9B)-H(9B)	0.9800
C(10B)-C(11B)	1.463(15)
C(10B)-H(10E)	0.9700
C(10B)-H(10F)	0.9700
C(12B)-C(13B)	1.365(15)
C(12B)-C(17B)	1.385(14)
C(13B)-C(14B)	1.352(15)
C(13B)-H(13B)	0.9300
C(14B)-C(15B)	1.357(17)
C(14B)-H(14B)	0.9300
C(15B)-C(16B)	1.382(17)
C(15B)-H(15B)	0.9300
C(16B)-C(17B)	1.339(16)
C(16B)-H(16B)	0.9300
C(17B)-H(17B)	0.9300
C(18B)-C(19B)	1.358(14)
C(18B)-C(23B)	1.364(13)
C(19B)-C(20B)	1.401(16)
C(19B)-H(19B)	0.9300
C(20B)-C(21B)	1.348(15)
C(20B)-H(20B)	0.9300
C(21B)-C(22B)	1.357(15)
C(22B)-C(23B)	1.388(15)
C(22B)-H(22B)	0.9300
C(23B)-H(23B)	0.9300

C(1C)-C(2C)	1.489(16)
C(2C)-C(3C)	1.333(15)
C(2C)-C(7C)	1.397(14)
C(3C)-C(4C)	1.377(18)
C(3C)-H(3C)	0.9300
C(4C)-C(5C)	1.360(18)
C(4C)-H(4C)	0.9300
C(5C)-C(6C)	1.381(17)
C(5C)-H(5C)	0.9300
C(6C)-C(7C)	1.344(15)
C(6C)-H(6C)	0.9300
C(7C)-C(8C)	1.457(15)
C(9C)-C(18C)	1.492(16)
C(9C)-C(10C)	1.512(18)
C(9C)-H(9C)	0.9800
C(10C)-C(11')	1.53(2)
C(10C)-C(11C)	1.54(2)
C(10C)-H(10G)	0.9567
C(10C)-H(10H)	0.9564
C(10C)-H(10X)	0.9607
C(10C)-H(10Y)	0.9611
O(3C)-C(11C)	1.25(2)
O(3C)-C(12C)	1.57(3)
O(4C)-C(11C)	1.31(2)
C(12C)-C(13C)	1.3900
C(12C)-C(17C)	1.3900
C(13C)-C(14C)	1.3900
C(13C)-H(13C)	0.9300
C(14C)-C(15C)	1.3900
C(14C)-H(14C)	0.9300
C(15C)-C(16C)	1.3900
C(15C)-H(15C)	0.9300
C(16C)-C(17C)	1.3900
C(16C)-H(16C)	0.9300
C(17C)-H(17C)	0.9300
O(3')-C(11')	1.225(19)
O(4')-C(11')	1.28(2)
O(4')-C(12')	1.44(2)

C(12')-C(13')	1.3900
C(12')-C(17')	1.3900
C(13')-C(14')	1.3900
C(13')-H(13')	0.9300
C(14')-C(15')	1.3900
C(14')-H(14')	0.9300
C(15')-C(16')	1.3900
C(15')-H(15')	0.9300
C(16')-C(17')	1.3900
C(16')-H(16')	0.9300
C(17')-H(17')	0.9300
C(18C)-C(23C)	1.321(17)
C(18C)-C(19C)	1.335(18)
C(19C)-C(20C)	1.50(2)
C(19C)-H(19C)	0.9300
C(20C)-C(21C)	1.28(2)
C(20C)-H(20C)	0.9300
C(21C)-C(22C)	1.35(2)
C(22C)-C(23C)	1.41(2)
C(22C)-H(22C)	0.9300
C(23C)-H(23C)	0.9300

C(8)-N(1)-C(1)	111.1(10)
C(8)-N(1)-C(9)	124.7(10)
C(1)-N(1)-C(9)	124.0(9)
C(8A)-N(1A)-C(1A)	112.1(8)
C(8A)-N(1A)-C(9A)	126.8(8)
C(1A)-N(1A)-C(9A)	120.6(8)
C(1B)-N(1B)-C(8B)	111.2(8)
C(1B)-N(1B)-C(9B)	127.4(8)
C(8B)-N(1B)-C(9B)	121.4(8)
C(8C)-N(1C)-C(1C)	110.9(9)
C(8C)-N(1C)-C(9C)	116.6(9)
C(1C)-N(1C)-C(9C)	131.5(10)
C(11)-O(4)-C(12)	115.8(11)
C(11A)-O(4A)-C(12A)	117.5(8)
C(11B)-O(4B)-C(12B)	117.5(8)
O(1)-C(1)-N(1)	122.0(10)

O(1)-C(1)-C(2)	131.4(12)
N(1)-C(1)-C(2)	106.5(11)
C(3)-C(2)-C(7)	121.4(12)
C(3)-C(2)-C(1)	130.3(14)
C(7)-C(2)-C(1)	108.2(10)
C(4)-C(3)-C(2)	118.7(15)
C(4)-C(3)-H(3)	120.6
C(2)-C(3)-H(3)	120.7
C(3)-C(4)-C(5)	121.8(15)
C(3)-C(4)-H(4)	119.1
C(5)-C(4)-H(4)	119.1
C(4)-C(5)-C(6)	119.7(14)
C(4)-C(5)-H(5)	120.1
C(6)-C(5)-H(5)	120.1
C(7)-C(6)-C(5)	117.1(15)
C(7)-C(6)-H(6)	121.4
C(5)-C(6)-H(6)	121.4
C(6)-C(7)-C(2)	120.8(12)
C(6)-C(7)-C(8)	131.8(13)
C(2)-C(7)-C(8)	107.1(10)
O(2)-C(8)-N(1)	127.1(10)
O(2)-C(8)-C(7)	125.9(11)
N(1)-C(8)-C(7)	106.9(11)
N(1)-C(9)-C(10)	112.9(9)
N(1)-C(9)-C(18)	111.4(8)
C(10)-C(9)-C(18)	115.1(9)
N(1)-C(9)-H(9)	105.5
C(10)-C(9)-H(9)	105.5
C(18)-C(9)-H(9)	105.5
C(9)-C(10)-C(11)	115.9(10)
C(9)-C(10)-H(10A)	108.3
C(11)-C(10)-H(10A)	108.3
C(9)-C(10)-H(10B)	108.3
C(11)-C(10)-H(10B)	108.3
H(10A)-C(10)-H(10B)	107.4
O(3)-C(11)-O(4)	126.6(13)
O(3)-C(11)-C(10)	119.3(13)
O(4)-C(11)-C(10)	114.1(13)

C(13)-C(12)-C(17)	121.0(14)
C(13)-C(12)-O(4)	122.6(13)
C(17)-C(12)-O(4)	116.2(13)
C(12)-C(13)-C(14)	119.6(12)
C(12)-C(13)-H(13)	120.2
C(14)-C(13)-H(13)	120.2
C(15)-C(14)-C(13)	121.7(15)
C(15)-C(14)-H(14)	119.1
C(13)-C(14)-H(14)	119.1
C(14)-C(15)-C(16)	118.2(17)
C(14)-C(15)-H(15)	120.9
C(16)-C(15)-H(15)	120.9
C(17)-C(16)-C(15)	121.3(16)
C(17)-C(16)-H(16)	119.3
C(15)-C(16)-H(16)	119.3
C(16)-C(17)-C(12)	118.1(15)
C(16)-C(17)-H(17)	120.9
C(12)-C(17)-H(17)	120.9
C(19)-C(18)-C(23)	117.9(12)
C(19)-C(18)-C(9)	119.4(11)
C(23)-C(18)-C(9)	122.7(11)
C(18)-C(19)-C(20)	119.7(12)
C(18)-C(19)-H(19)	120.2
C(20)-C(19)-H(19)	120.2
C(21)-C(20)-C(19)	121.6(12)
C(21)-C(20)-H(20)	119.2
C(19)-C(20)-H(20)	119.2
C(22)-C(21)-C(20)	118.5(12)
C(22)-C(21)-Cl(1)	122.5(11)
C(20)-C(21)-Cl(1)	118.8(11)
C(21)-C(22)-C(23)	121.4(13)
C(21)-C(22)-H(22)	119.3
C(23)-C(22)-H(22)	119.3
C(22)-C(23)-C(18)	120.7(13)
C(22)-C(23)-H(23)	119.7
C(18)-C(23)-H(23)	119.7
O(1A)-C(1A)-N(1A)	125.0(10)
O(1A)-C(1A)-C(2A)	129.8(9)

N(1A)-C(1A)-C(2A)	105.2(9)
C(7A)-C(2A)-C(3A)	121.9(10)
C(7A)-C(2A)-C(1A)	108.8(8)
C(3A)-C(2A)-C(1A)	129.4(10)
C(4A)-C(3A)-C(2A)	115.6(11)
C(4A)-C(3A)-H(3A)	122.2
C(2A)-C(3A)-H(3A)	122.2
C(3A)-C(4A)-C(5A)	123.9(11)
C(3A)-C(4A)-H(4A)	118.0
C(5A)-C(4A)-H(4A)	118.0
C(6A)-C(5A)-C(4A)	118.0(11)
C(6A)-C(5A)-H(5A)	121.0
C(4A)-C(5A)-H(5A)	121.0
C(5A)-C(6A)-C(7A)	120.8(11)
C(5A)-C(6A)-H(6A)	119.6
C(7A)-C(6A)-H(6A)	119.6
C(2A)-C(7A)-C(6A)	119.6(9)
C(2A)-C(7A)-C(8A)	109.0(8)
C(6A)-C(7A)-C(8A)	131.3(9)
O(2A)-C(8A)-N(1A)	125.7(9)
O(2A)-C(8A)-C(7A)	129.3(9)
N(1A)-C(8A)-C(7A)	105.0(8)
N(1A)-C(9A)-C(10A)	110.4(8)
N(1A)-C(9A)-C(18A)	110.4(8)
C(10A)-C(9A)-C(18A)	114.7(8)
N(1A)-C(9A)-H(9A)	107.0
C(10A)-C(9A)-H(9A)	107.0
C(18A)-C(9A)-H(9A)	107.0
C(9A)-C(10A)-C(11A)	112.0(8)
C(9A)-C(10A)-H(10C)	109.2
C(11A)-C(10A)-H(10C)	109.2
C(9A)-C(10A)-H(10D)	109.2
C(11A)-C(10A)-H(10D)	109.2
H(10C)-C(10A)-H(10D)	107.9
O(3A)-C(11A)-O(4A)	124.3(10)
O(3A)-C(11A)-C(10A)	123.0(10)
O(4A)-C(11A)-C(10A)	112.3(9)
C(13A)-C(12A)-C(17A)	122.2(11)

C(13A)-C(12A)-O(4A)	118.2(11)
C(17A)-C(12A)-O(4A)	119.5(10)
C(12A)-C(13A)-C(14A)	119.5(13)
C(12A)-C(13A)-H(13A)	120.2
C(14A)-C(13A)-H(13A)	120.2
C(15A)-C(14A)-C(13A)	119.6(13)
C(15A)-C(14A)-H(14A)	120.2
C(13A)-C(14A)-H(14A)	120.2
C(16A)-C(15A)-C(14A)	120.5(12)
C(16A)-C(15A)-H(15A)	119.8
C(14A)-C(15A)-H(15A)	119.8
C(15A)-C(16A)-C(17A)	120.5(12)
C(15A)-C(16A)-H(16A)	119.7
C(17A)-C(16A)-H(16A)	119.7
C(12A)-C(17A)-C(16A)	117.5(11)
C(12A)-C(17A)-H(17A)	121.3
C(16A)-C(17A)-H(17A)	121.2
C(23A)-C(18A)-C(19A)	115.9(11)
C(23A)-C(18A)-C(9A)	124.5(10)
C(19A)-C(18A)-C(9A)	119.5(10)
C(18A)-C(19A)-C(20A)	123.0(12)
C(18A)-C(19A)-H(19A)	118.5
C(20A)-C(19A)-H(19A)	118.5
C(21A)-C(20A)-C(19A)	117.4(12)
C(21A)-C(20A)-H(20A)	121.3
C(19A)-C(20A)-H(20A)	121.3
C(20A)-C(21A)-C(22A)	122.2(13)
C(20A)-C(21A)-Cl(1A)	119.0(12)
C(22A)-C(21A)-Cl(1A)	118.8(14)
C(21A)-C(22A)-C(23A)	120.2(14)
C(21A)-C(22A)-H(22A)	119.9
C(23A)-C(22A)-H(22A)	119.9
C(18A)-C(23A)-C(22A)	121.2(12)
C(18A)-C(23A)-H(23A)	119.4
C(22A)-C(23A)-H(23A)	119.4
O(1B)-C(1B)-N(1B)	124.5(10)
O(1B)-C(1B)-C(2B)	131.0(12)
N(1B)-C(1B)-C(2B)	104.5(10)

C(7B)-C(2B)-C(3B)	123.8(15)
C(7B)-C(2B)-C(1B)	108.5(10)
C(3B)-C(2B)-C(1B)	127.7(16)
C(2B)-C(3B)-C(4B)	110.8(19)
C(2B)-C(3B)-H(3B)	124.6
C(4B)-C(3B)-H(3B)	124.6
C(5B)-C(4B)-C(3B)	122.4(19)
C(5B)-C(4B)-H(4B)	118.8
C(3B)-C(4B)-H(4B)	118.8
C(4B)-C(5B)-C(6B)	123(2)
C(4B)-C(5B)-H(5B)	118.6
C(6B)-C(5B)-H(5B)	118.6
C(5B)-C(6B)-C(7B)	118(2)
C(5B)-C(6B)-H(6B)	120.8
C(7B)-C(6B)-H(6B)	120.8
C(2B)-C(7B)-C(6B)	121.7(14)
C(2B)-C(7B)-C(8B)	110.6(11)
C(6B)-C(7B)-C(8B)	127.6(16)
O(2B)-C(8B)-N(1B)	124.8(10)
O(2B)-C(8B)-C(7B)	129.9(12)
N(1B)-C(8B)-C(7B)	105.2(11)
N(1B)-C(9B)-C(18B)	112.1(7)
N(1B)-C(9B)-C(10B)	111.2(8)
C(18B)-C(9B)-C(10B)	115.7(8)
N(1B)-C(9B)-H(9B)	105.6
C(18B)-C(9B)-H(9B)	105.6
C(10B)-C(9B)-H(9B)	105.6
C(11B)-C(10B)-C(9B)	112.4(8)
C(11B)-C(10B)-H(10E)	109.1
C(9B)-C(10B)-H(10E)	109.1
C(11B)-C(10B)-H(10F)	109.1
C(9B)-C(10B)-H(10F)	109.1
H(10E)-C(10B)-H(10F)	107.9
O(3B)-C(11B)-O(4B)	119.8(9)
O(3B)-C(11B)-C(10B)	126.0(12)
O(4B)-C(11B)-C(10B)	114.2(11)
C(13B)-C(12B)-C(17B)	120.6(11)
C(13B)-C(12B)-O(4B)	121.1(9)

C(17B)-C(12B)-O(4B)	118.3(10)
C(14B)-C(13B)-C(12B)	119.0(11)
C(14B)-C(13B)-H(13B)	120.5
C(12B)-C(13B)-H(13B)	120.5
C(13B)-C(14B)-C(15B)	122.0(12)
C(13B)-C(14B)-H(14B)	119.0
C(15B)-C(14B)-H(14B)	119.0
C(14B)-C(15B)-C(16B)	117.9(12)
C(14B)-C(15B)-H(15B)	121.0
C(16B)-C(15B)-H(15B)	121.0
C(17B)-C(16B)-C(15B)	121.9(11)
C(17B)-C(16B)-H(16B)	119.0
C(15B)-C(16B)-H(16B)	119.0
C(16B)-C(17B)-C(12B)	118.6(11)
C(16B)-C(17B)-H(17B)	120.7
C(12B)-C(17B)-H(17B)	120.7
C(19B)-C(18B)-C(23B)	116.5(10)
C(19B)-C(18B)-C(9B)	120.8(9)
C(23B)-C(18B)-C(9B)	122.5(9)
C(18B)-C(19B)-C(20B)	123.3(10)
C(18B)-C(19B)-H(19B)	118.4
C(20B)-C(19B)-H(19B)	118.4
C(21B)-C(20B)-C(19B)	117.5(10)
C(21B)-C(20B)-H(20B)	121.2
C(19B)-C(20B)-H(20B)	121.2
C(20B)-C(21B)-C(22B)	121.4(11)
C(20B)-C(21B)-Cl(1B)	116.4(10)
C(22B)-C(21B)-Cl(1B)	122.2(9)
C(21B)-C(22B)-C(23B)	119.2(11)
C(21B)-C(22B)-H(22B)	120.4
C(23B)-C(22B)-H(22B)	120.4
C(18B)-C(23B)-C(22B)	121.9(11)
C(18B)-C(23B)-H(23B)	119.1
C(22B)-C(23B)-H(23B)	119.1
O(1C)-C(1C)-N(1C)	124.7(12)
O(1C)-C(1C)-C(2C)	128.9(12)
N(1C)-C(1C)-C(2C)	106.3(10)
C(3C)-C(2C)-C(7C)	121.1(11)

C(3C)-C(2C)-C(1C)	132.0(11)
C(7C)-C(2C)-C(1C)	106.9(9)
C(2C)-C(3C)-C(4C)	117.5(13)
C(2C)-C(3C)-H(3C)	121.3
C(4C)-C(3C)-H(3C)	121.3
C(5C)-C(4C)-C(3C)	122.8(13)
C(5C)-C(4C)-H(4C)	118.6
C(3C)-C(4C)-H(4C)	118.6
C(4C)-C(5C)-C(6C)	118.7(12)
C(4C)-C(5C)-H(5C)	120.6
C(6C)-C(5C)-H(5C)	120.6
C(7C)-C(6C)-C(5C)	119.1(12)
C(7C)-C(6C)-H(6C)	120.4
C(5C)-C(6C)-H(6C)	120.4
C(6C)-C(7C)-C(2C)	120.7(10)
C(6C)-C(7C)-C(8C)	129.6(11)
C(2C)-C(7C)-C(8C)	109.7(10)
O(2C)-C(8C)-N(1C)	124.1(11)
O(2C)-C(8C)-C(7C)	129.7(12)
N(1C)-C(8C)-C(7C)	106.1(10)
N(1C)-C(9C)-C(18C)	114.0(10)
N(1C)-C(9C)-C(10C)	110.1(11)
C(18C)-C(9C)-C(10C)	109.6(11)
N(1C)-C(9C)-H(9C)	107.6
C(18C)-C(9C)-H(9C)	107.6
C(10C)-C(9C)-H(9C)	107.6
C(9C)-C(10C)-C(11')	113.7(16)
C(9C)-C(10C)-C(11C)	111(2)
C(9C)-C(10C)-H(10G)	107.5
C(11C)-C(10C)-H(10G)	107.4
C(9C)-C(10C)-H(10H)	109.1
C(11C)-C(10C)-H(10H)	111.1
H(10G)-C(10C)-H(10H)	110.6
C(9C)-C(10C)-H(10X)	109.2
C(11')-C(10C)-H(10X)	109.6
C(9C)-C(10C)-H(10Y)	108.3
C(11')-C(10C)-H(10Y)	106.8
H(10X)-C(10C)-H(10Y)	109.1

C(11C)-O(3C)-C(12C)	100(2)
O(3C)-C(11C)-O(4C)	119(3)
O(3C)-C(11C)-C(10C)	111(2)
O(4C)-C(11C)-C(10C)	127(3)
C(13C)-C(12C)-C(17C)	120.0
C(13C)-C(12C)-O(3C)	89(2)
C(17C)-C(12C)-O(3C)	141(2)
C(12C)-C(13C)-C(14C)	120.0
C(12C)-C(13C)-H(13C)	120.0
C(14C)-C(13C)-H(13C)	120.0
C(15C)-C(14C)-C(13C)	120.0
C(15C)-C(14C)-H(14C)	120.0
C(13C)-C(14C)-H(14C)	120.0
C(14C)-C(15C)-C(16C)	120.0
C(14C)-C(15C)-H(15C)	120.0
C(16C)-C(15C)-H(15C)	120.0
C(15C)-C(16C)-C(17C)	120.0
C(15C)-C(16C)-H(16C)	120.0
C(17C)-C(16C)-H(16C)	120.0
C(16C)-C(17C)-C(12C)	120.0
C(16C)-C(17C)-H(17C)	120.0
C(12C)-C(17C)-H(17C)	120.0
C(11')-O(4')-C(12')	105.5(16)
O(3')-C(11')-O(4')	124(2)
O(3')-C(11')-C(10C)	124.0(19)
O(4')-C(11')-C(10C)	112.1(17)
C(13')-C(12')-C(17')	120.0
C(13')-C(12')-O(4')	118.5(13)
C(17')-C(12')-O(4')	119.1(14)
C(12')-C(13')-C(14')	120.0
C(12')-C(13')-H(13')	120.0
C(14')-C(13')-H(13')	120.0
C(15')-C(14')-C(13')	120.0
C(15')-C(14')-H(14')	120.0
C(13')-C(14')-H(14')	120.0
C(14')-C(15')-C(16')	120.0
C(14')-C(15')-H(15')	120.0
C(16')-C(15')-H(15')	120.0

C(17')-C(16')-C(15')	120.0
C(17')-C(16')-H(16')	120.0
C(15')-C(16')-H(16')	120.0
C(16')-C(17')-C(12')	120.0
C(16')-C(17')-H(17')	120.0
C(12')-C(17')-H(17')	120.0
C(23C)-C(18C)-C(19C)	120.0(13)
C(23C)-C(18C)-C(9C)	114.5(12)
C(19C)-C(18C)-C(9C)	125.5(12)
C(18C)-C(19C)-C(20C)	117.3(13)
C(18C)-C(19C)-H(19C)	121.4
C(20C)-C(19C)-H(19C)	121.4
C(21C)-C(20C)-C(19C)	118.2(15)
C(21C)-C(20C)-H(20C)	120.9
C(19C)-C(20C)-H(20C)	120.9
C(20C)-C(21C)-C(22C)	125.6(17)
C(20C)-C(21C)-Cl(1C)	115.0(17)
C(22C)-C(21C)-Cl(1C)	119.4(15)
C(21C)-C(22C)-C(23C)	114.1(17)
C(21C)-C(22C)-H(22C)	123.0
C(23C)-C(22C)-H(22C)	123.0
C(18C)-C(23C)-C(22C)	124.5(15)
C(18C)-C(23C)-H(23C)	117.7
C(22C)-C(23C)-H(23C)	117.7

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x 10^3$) for **2b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	156(3)	112(3)	123(3)	-31(2)	33(2)	-59(2)
Cl(1A)	182(4)	144(3)	113(3)	-20(2)	61(3)	-46(3)
Cl(1B)	120(2)	126(3)	91(2)	-26(2)	23(2)	-56(2)
Cl(1C)	325(7)	168(4)	104(3)	-57(3)	81(4)	-123(5)
N(1)	87(6)	83(6)	91(6)	-42(5)	4(5)	-28(5)
N(1A)	58(5)	74(5)	74(5)	-31(4)	9(4)	-18(4)
N(1B)	42(4)	73(5)	80(5)	-32(4)	1(3)	-20(3)
N(1C)	79(6)	115(7)	100(7)	-63(6)	9(5)	-20(5)
O(1)	92(6)	141(7)	216(11)	-122(8)	19(6)	-43(5)
O(2)	90(5)	156(8)	158(8)	-104(7)	25(5)	-44(5)
O(3)	121(6)	109(6)	100(6)	-41(5)	29(5)	-44(5)
O(4)	141(7)	114(7)	93(6)	-41(6)	0(5)	-58(6)
O(1A)	64(4)	113(6)	124(6)	-68(5)	-2(4)	-23(4)
O(2A)	52(4)	116(6)	107(5)	-49(4)	0(3)	-21(4)
O(3A)	82(5)	83(5)	142(7)	3(5)	24(5)	-13(4)
O(4A)	77(4)	83(5)	83(5)	-20(4)	15(4)	-20(4)
O(1B)	129(7)	135(7)	154(8)	-102(7)	39(6)	-59(6)
O(2B)	75(5)	131(7)	124(7)	-70(6)	16(4)	-21(4)
O(3B)	94(5)	103(6)	95(5)	-47(5)	18(4)	-41(5)
O(4B)	83(4)	78(5)	90(5)	-26(4)	7(4)	-31(4)
O(1C)	125(7)	223(11)	155(8)	-129(8)	17(6)	-90(7)
O(2C)	65(5)	208(11)	152(8)	-96(8)	-8(5)	-26(6)
C(1)	85(8)	94(8)	126(10)	-64(8)	5(7)	-27(7)
C(2)	73(7)	105(9)	123(10)	-41(8)	-14(7)	-41(7)
C(3)	81(9)	130(11)	171(14)	-68(10)	5(8)	-43(8)
C(4)	106(12)	154(14)	169(15)	-56(12)	13(10)	-75(11)
C(5)	78(9)	190(17)	153(14)	-65(13)	40(9)	-54(11)
C(6)	76(8)	168(12)	121(10)	-73(9)	17(7)	-57(8)
C(7)	73(8)	120(9)	89(8)	-44(7)	11(6)	-44(7)
C(8)	73(7)	113(9)	91(8)	-54(7)	17(5)	-37(7)
C(9)	64(6)	91(7)	113(9)	-32(7)	-11(5)	-37(6)
C(10)	95(8)	120(9)	95(8)	-30(7)	-14(6)	-59(7)
C(11)	95(8)	111(10)	102(10)	-46(9)	12(7)	-51(7)

C(12)	110(10)	82(8)	101(9)	-32(8)	-4(8)	-38(8)
C(13)	84(7)	86(8)	96(9)	-33(8)	0(7)	-15(7)
C(14)	115(11)	95(9)	117(11)	-44(9)	10(9)	-24(8)
C(15)	168(17)	185(18)	148(14)	-124(15)	84(13)	-105(15)
C(16)	97(11)	160(16)	200(20)	-120(16)	29(12)	-40(12)
C(17)	93(10)	119(11)	165(15)	-85(11)	16(9)	-27(9)
C(18)	61(6)	87(8)	92(8)	-41(7)	9(5)	-20(5)
C(19)	90(8)	87(8)	116(10)	-49(8)	-1(7)	-25(6)
C(20)	101(8)	115(11)	98(9)	-51(8)	22(7)	-40(8)
C(21)	85(7)	93(9)	102(9)	-43(7)	10(6)	-30(6)
C(22)	235(19)	82(9)	143(13)	-61(10)	83(13)	-66(11)
C(23)	185(15)	104(11)	142(13)	-72(10)	76(11)	-59(10)
C(1A)	63(6)	76(6)	83(7)	-30(6)	7(5)	-25(5)
C(2A)	72(7)	67(6)	70(6)	-25(5)	14(5)	-24(5)
C(3A)	70(7)	95(8)	87(7)	-48(7)	21(5)	-19(6)
C(4A)	96(9)	100(8)	98(9)	-40(7)	40(7)	-33(7)
C(5A)	130(11)	115(9)	74(7)	-51(7)	27(7)	-40(8)
C(6A)	89(8)	108(9)	86(8)	-48(7)	-3(6)	-25(7)
C(7A)	73(6)	66(6)	64(6)	-27(5)	4(5)	-15(5)
C(8A)	62(6)	73(6)	66(6)	-22(5)	3(5)	-24(5)
C(9A)	63(5)	68(6)	84(7)	-38(6)	13(5)	-16(5)
C(10A)	76(6)	80(7)	93(8)	-35(6)	26(6)	-27(6)
C(11A)	73(7)	66(7)	110(9)	-27(6)	14(7)	-11(6)
C(12A)	72(6)	81(7)	88(8)	-40(6)	0(5)	-15(6)
C(13A)	143(11)	154(12)	106(10)	-66(10)	16(8)	-90(10)
C(14A)	181(15)	164(14)	79(9)	-53(10)	31(9)	-89(13)
C(15A)	118(10)	111(10)	73(8)	-20(7)	11(6)	-42(8)
C(16A)	83(7)	83(8)	120(11)	-41(8)	10(7)	-23(6)
C(17A)	97(7)	92(8)	75(7)	-33(6)	5(6)	-32(6)
C(18A)	78(7)	79(7)	70(7)	-29(6)	6(5)	-22(6)
C(19A)	77(7)	93(8)	106(10)	-38(8)	12(7)	-14(6)
C(20A)	111(11)	117(11)	85(9)	-20(8)	-8(8)	-14(9)
C(21A)	134(12)	102(9)	73(8)	-25(7)	32(8)	-14(9)
C(22A)	130(12)	185(15)	95(10)	-26(11)	16(9)	-90(11)
C(23A)	104(9)	162(13)	83(8)	-30(8)	10(7)	-67(9)
C(1B)	88(8)	110(9)	91(8)	-59(7)	25(6)	-50(7)
C(2B)	109(9)	150(11)	86(8)	-50(8)	16(7)	-90(9)
C(3B)	250(20)	320(30)	150(14)	-142(17)	70(14)	-220(20)

C(4B)	260(30)	480(50)	160(20)	-150(20)	59(17)	-310(30)
C(5B)	162(19)	460(50)	103(14)	-90(20)	24(12)	-190(30)
C(6B)	103(10)	290(20)	97(10)	-79(12)	23(7)	-117(12)
C(7B)	79(8)	164(12)	82(8)	-50(8)	9(6)	-64(8)
C(8B)	70(7)	102(8)	77(7)	-29(6)	5(5)	-39(6)
C(9B)	70(6)	75(6)	78(6)	-38(5)	5(5)	-23(5)
C(10B)	58(5)	88(7)	98(8)	-32(6)	1(5)	-24(5)
C(11B)	58(6)	87(8)	70(7)	-24(6)	6(5)	-22(5)
C(12B)	77(7)	76(7)	100(8)	-47(7)	18(6)	-30(6)
C(13B)	74(6)	73(7)	86(8)	-28(6)	3(6)	-14(6)
C(14B)	110(10)	99(9)	88(8)	-47(7)	21(7)	-36(8)
C(15B)	111(10)	102(9)	91(8)	-43(8)	26(7)	-54(8)
C(16B)	77(7)	122(10)	110(10)	-56(9)	25(7)	-30(8)
C(17B)	70(7)	83(7)	99(8)	-34(6)	6(6)	-17(6)
C(18B)	53(5)	68(6)	78(6)	-40(5)	7(5)	-23(5)
C(19B)	98(8)	96(9)	80(8)	-37(7)	23(6)	-25(7)
C(20B)	90(8)	75(7)	104(9)	-40(7)	1(7)	-6(6)
C(21B)	73(6)	92(8)	70(6)	-30(6)	13(5)	-32(6)
C(22B)	85(7)	97(9)	119(10)	-63(8)	30(7)	-32(7)
C(23B)	92(7)	84(7)	104(9)	-48(7)	24(6)	-40(6)
C(1C)	98(9)	122(10)	120(10)	-71(8)	19(8)	-51(8)
C(2C)	57(6)	92(7)	102(8)	-49(6)	14(5)	-26(5)
C(3C)	94(9)	132(11)	129(11)	-60(10)	29(8)	-50(8)
C(4C)	127(12)	101(9)	86(9)	-37(8)	33(8)	-31(8)
C(5C)	146(12)	75(7)	81(8)	-37(6)	14(8)	-28(8)
C(6C)	115(10)	89(8)	70(7)	-25(6)	-3(6)	-32(7)
C(7C)	79(7)	87(7)	65(6)	-32(6)	12(5)	-28(6)
C(8C)	85(8)	120(9)	90(8)	-54(7)	2(6)	-25(7)
C(9C)	112(9)	113(10)	105(10)	-51(8)	40(7)	-42(8)
C(10C)	240(20)	80(9)	130(12)	-39(9)	32(12)	-57(11)
O(3C)	219(14)	160(11)	124(9)	-29(8)	5(9)	-45(10)
O(4C)	239(17)	184(14)	163(13)	-9(12)	-1(13)	-36(13)
C(11C)	222(15)	165(12)	134(10)	-24(9)	1(10)	-46(11)
C(12C)	214(14)	150(10)	115(9)	-40(8)	3(9)	-50(9)
C(13C)	211(14)	143(11)	109(9)	-46(8)	2(9)	-52(9)
C(14C)	210(14)	141(11)	104(9)	-49(8)	2(9)	-54(10)
C(15C)	210(14)	138(11)	97(9)	-52(8)	1(9)	-57(10)
C(16C)	213(14)	146(11)	104(9)	-47(8)	0(9)	-54(10)

C(17C)	214(14)	148(11)	111(9)	-44(8)	1(9)	-53(9)
O(3')	147(10)	93(9)	147(11)	-19(8)	71(9)	-32(8)
O(4')	98(7)	96(6)	105(7)	-47(6)	29(6)	-38(5)
C(11')	108(8)	92(7)	113(8)	-44(7)	40(7)	-39(6)
C(12')	98(6)	100(6)	105(7)	-48(6)	18(6)	-40(5)
C(13')	99(7)	97(7)	106(7)	-51(6)	20(6)	-38(6)
C(14')	104(7)	101(7)	106(8)	-47(7)	23(7)	-35(6)
C(15')	106(7)	109(7)	104(8)	-42(7)	19(7)	-33(6)
C(16')	103(7)	107(7)	102(7)	-50(7)	13(6)	-33(6)
C(17')	99(7)	103(7)	102(7)	-51(6)	13(6)	-36(6)
C(18C)	90(8)	91(8)	81(8)	-37(7)	22(7)	-23(6)
C(19C)	107(10)	166(14)	136(13)	-55(12)	11(10)	-45(10)
C(20C)	166(15)	139(13)	66(8)	-22(8)	-6(8)	-32(11)
C(21C)	146(14)	144(13)	139(14)	-87(12)	79(13)	-80(12)
C(22C)	148(16)	142(14)	154(17)	-38(13)	13(14)	-36(12)
C(23C)	86(9)	149(13)	102(10)	-15(10)	19(7)	-4(8)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{3}) for **2b**.

	x	y	z	U(eq)
H(3)	10810	10973	9533	148
H(4)	13019	10405	9409	167
H(5)	13998	8900	9112	170
H(6)	12621	8191	8565	136
H(9)	6721	10170	8634	108
H(10A)	6065	9744	7525	123
H(10B)	7507	8940	7589	123
H(13)	5922	12391	4798	113
H(14)	6606	13570	3503	135
H(15)	8780	13211	3282	166
H(16)	10327	11532	4294	167
H(17)	9661	10312	5561	143
H(19)	6092	9428	10125	116
H(20)	5711	8016	11369	122
H(22)	7282	6041	10170	177
H(23)	7875	7371	8993	163
H(3A)	13253	7484	2253	100
H(4A)	13003	6885	1124	119
H(5A)	10928	6920	622	124
H(6A)	9075	7759	1124	112
H(9A)	9855	9578	3914	85
H(10C)	7721	10901	3455	100
H(10D)	7388	10398	2799	100
H(13A)	7736	12232	7	144
H(14A)	8490	13305	-1320	160
H(15A)	9366	14544	-1230	128
H(16A)	9600	14648	173	117
H(17A)	8972	13479	1547	107
H(19A)	10311	8154	5430	117
H(20A)	9612	7115	6824	142
H(22A)	6111	7993	5412	167
H(23A)	6777	9058	4023	142

H(3B)	1589	2091	5850	227
H(4B)	-858	2531	5968	297
H(5B)	-1891	3545	6698	272
H(6B)	-900	4469	7140	184
H(9B)	3925	4449	7518	87
H(10E)	5834	2611	7413	101
H(10F)	6026	3204	8029	101
H(13B)	5999	834	10854	99
H(14B)	5140	-229	12084	116
H(15B)	2873	175	12119	116
H(16B)	1448	1706	10878	122
H(17B)	2262	2787	9641	106
H(19B)	3443	6152	6283	112
H(20B)	3974	7364	4902	114
H(22B)	6433	4827	4527	114
H(23B)	5824	3650	5875	106
H(3C)	-1302	5454	3287	137
H(4C)	-1394	6179	4379	130
H(5C)	490	6175	5050	122
H(6C)	2552	5508	4559	113
H(9C)	4356	3496	2510	130
H(10G)	2253	2861	2238	183
H(10H)	3615	2434	1859	183
H(10X)	3946	2225	2142	183
H(10Y)	2405	2885	1915	183
H(13C)	2444	-7	3989	190
H(14C)	2159	-1364	5376	185
H(15C)	3277	-1788	6822	177
H(16C)	4680	-856	6880	190
H(17C)	4964	501	5492	196
H(13')	2834	-530	4327	116
H(14')	2765	-1688	5890	123
H(15')	3274	-1312	7130	130
H(16')	3852	224	6808	124
H(17')	3921	1383	5246	119
H(19C)	1606	4934	616	168
H(20C)	2047	5860	-1034	163
H(22C)	5875	4950	-146	192

H(23C)	5455	3898	1388	163

Table S6. Torsion angles [°] for **2b**.

C(8)-N(1)-C(1)-O(1)	179.5(13)
C(9)-N(1)-C(1)-O(1)	3.6(19)
C(8)-N(1)-C(1)-C(2)	2.5(13)
C(9)-N(1)-C(1)-C(2)	-173.4(10)
O(1)-C(1)-C(2)-C(3)	5(3)
N(1)-C(1)-C(2)-C(3)	-178.7(15)
O(1)-C(1)-C(2)-C(7)	-178.3(15)
N(1)-C(1)-C(2)-C(7)	-1.7(14)
C(7)-C(2)-C(3)-C(4)	0(2)
C(1)-C(2)-C(3)-C(4)	176.7(14)
C(2)-C(3)-C(4)-C(5)	-5(3)
C(3)-C(4)-C(5)-C(6)	8(3)
C(4)-C(5)-C(6)-C(7)	-5(2)
C(5)-C(6)-C(7)-C(2)	0(2)
C(5)-C(6)-C(7)-C(8)	-173.8(13)
C(3)-C(2)-C(7)-C(6)	3(2)
C(1)-C(2)-C(7)-C(6)	-174.6(11)
C(3)-C(2)-C(7)-C(8)	177.6(13)
C(1)-C(2)-C(7)-C(8)	0.3(13)
C(1)-N(1)-C(8)-O(2)	-178.9(13)
C(9)-N(1)-C(8)-O(2)	-3.0(19)
C(1)-N(1)-C(8)-C(7)	-2.3(12)
C(9)-N(1)-C(8)-C(7)	173.6(9)
C(6)-C(7)-C(8)-O(2)	-8(2)
C(2)-C(7)-C(8)-O(2)	177.8(13)
C(6)-C(7)-C(8)-N(1)	175.4(13)
C(2)-C(7)-C(8)-N(1)	1.2(13)
C(8)-N(1)-C(9)-C(10)	-49.9(14)
C(1)-N(1)-C(9)-C(10)	125.5(12)
C(8)-N(1)-C(9)-C(18)	81.5(13)
C(1)-N(1)-C(9)-C(18)	-103.1(12)
N(1)-C(9)-C(10)-C(11)	-49.5(14)
C(18)-C(9)-C(10)-C(11)	-179.0(10)
C(12)-O(4)-C(11)-O(3)	3.9(19)
C(12)-O(4)-C(11)-C(10)	-176.5(10)
C(9)-C(10)-C(11)-O(3)	-15.8(16)

C(9)-C(10)-C(11)-O(4)	164.6(11)
C(11)-O(4)-C(12)-C(13)	-90.2(14)
C(11)-O(4)-C(12)-C(17)	94.2(14)
C(17)-C(12)-C(13)-C(14)	0.2(19)
O(4)-C(12)-C(13)-C(14)	-175.1(11)
C(12)-C(13)-C(14)-C(15)	-2(2)
C(13)-C(14)-C(15)-C(16)	3(2)
C(14)-C(15)-C(16)-C(17)	-2(2)
C(15)-C(16)-C(17)-C(12)	0(2)
C(13)-C(12)-C(17)-C(16)	1(2)
O(4)-C(12)-C(17)-C(16)	176.6(12)
N(1)-C(9)-C(18)-C(19)	94.9(12)
C(10)-C(9)-C(18)-C(19)	-134.9(11)
N(1)-C(9)-C(18)-C(23)	-82.9(15)
C(10)-C(9)-C(18)-C(23)	47.4(15)
C(23)-C(18)-C(19)-C(20)	0.4(17)
C(9)-C(18)-C(19)-C(20)	-177.4(10)
C(18)-C(19)-C(20)-C(21)	-0.7(18)
C(19)-C(20)-C(21)-C(22)	-2(2)
C(19)-C(20)-C(21)-Cl(1)	-178.3(9)
C(20)-C(21)-C(22)-C(23)	6(3)
Cl(1)-C(21)-C(22)-C(23)	-178.5(14)
C(21)-C(22)-C(23)-C(18)	-6(3)
C(19)-C(18)-C(23)-C(22)	3(2)
C(9)-C(18)-C(23)-C(22)	-179.3(15)
C(8A)-N(1A)-C(1A)-O(1A)	-179.0(10)
C(9A)-N(1A)-C(1A)-O(1A)	8.7(14)
C(8A)-N(1A)-C(1A)-C(2A)	-0.6(10)
C(9A)-N(1A)-C(1A)-C(2A)	-172.9(8)
O(1A)-C(1A)-C(2A)-C(7A)	177.9(11)
N(1A)-C(1A)-C(2A)-C(7A)	-0.5(10)
O(1A)-C(1A)-C(2A)-C(3A)	-0.4(18)
N(1A)-C(1A)-C(2A)-C(3A)	-178.7(9)
C(7A)-C(2A)-C(3A)-C(4A)	1.3(15)
C(1A)-C(2A)-C(3A)-C(4A)	179.3(10)
C(2A)-C(3A)-C(4A)-C(5A)	-2.4(17)
C(3A)-C(4A)-C(5A)-C(6A)	3.8(19)
C(4A)-C(5A)-C(6A)-C(7A)	-3.7(18)

C(3A)-C(2A)-C(7A)-C(6A)	-1.4(14)
C(1A)-C(2A)-C(7A)-C(6A)	-179.8(9)
C(3A)-C(2A)-C(7A)-C(8A)	179.7(9)
C(1A)-C(2A)-C(7A)-C(8A)	1.3(11)
C(5A)-C(6A)-C(7A)-C(2A)	2.7(16)
C(5A)-C(6A)-C(7A)-C(8A)	-178.7(11)
C(1A)-N(1A)-C(8A)-O(2A)	-179.9(9)
C(9A)-N(1A)-C(8A)-O(2A)	-8.2(15)
C(1A)-N(1A)-C(8A)-C(7A)	1.3(10)
C(9A)-N(1A)-C(8A)-C(7A)	173.0(8)
C(2A)-C(7A)-C(8A)-O(2A)	179.6(10)
C(6A)-C(7A)-C(8A)-O(2A)	0.9(18)
C(2A)-C(7A)-C(8A)-N(1A)	-1.6(10)
C(6A)-C(7A)-C(8A)-N(1A)	179.6(10)
C(8A)-N(1A)-C(9A)-C(10A)	-50.2(12)
C(1A)-N(1A)-C(9A)-C(10A)	120.8(9)
C(8A)-N(1A)-C(9A)-C(18A)	77.6(11)
C(1A)-N(1A)-C(9A)-C(18A)	-111.3(9)
N(1A)-C(9A)-C(10A)-C(11A)	-60.6(11)
C(18A)-C(9A)-C(10A)-C(11A)	173.9(9)
C(12A)-O(4A)-C(11A)-O(3A)	10.2(17)
C(12A)-O(4A)-C(11A)-C(10A)	-176.7(9)
C(9A)-C(10A)-C(11A)-O(3A)	-13.1(16)
C(9A)-C(10A)-C(11A)-O(4A)	173.6(9)
C(11A)-O(4A)-C(12A)-C(13A)	97.0(13)
C(11A)-O(4A)-C(12A)-C(17A)	-79.0(12)
C(17A)-C(12A)-C(13A)-C(14A)	-3(2)
O(4A)-C(12A)-C(13A)-C(14A)	-178.8(12)
C(12A)-C(13A)-C(14A)-C(15A)	-1(2)
C(13A)-C(14A)-C(15A)-C(16A)	2(2)
C(14A)-C(15A)-C(16A)-C(17A)	0.1(19)
C(13A)-C(12A)-C(17A)-C(16A)	5.1(16)
O(4A)-C(12A)-C(17A)-C(16A)	-179.1(8)
C(15A)-C(16A)-C(17A)-C(12A)	-3.7(16)
N(1A)-C(9A)-C(18A)-C(23A)	-87.1(13)
C(10A)-C(9A)-C(18A)-C(23A)	38.4(16)
N(1A)-C(9A)-C(18A)-C(19A)	93.5(11)
C(10A)-C(9A)-C(18A)-C(19A)	-141.0(10)

C(23A)-C(18A)-C(19A)-C(20A)	-1.2(18)
C(9A)-C(18A)-C(19A)-C(20A)	178.3(11)
C(18A)-C(19A)-C(20A)-C(21A)	1(2)
C(19A)-C(20A)-C(21A)-C(22A)	1(2)
C(19A)-C(20A)-C(21A)-Cl(1A)	179.6(10)
C(20A)-C(21A)-C(22A)-C(23A)	-1(3)
Cl(1A)-C(21A)-C(22A)-C(23A)	179.8(12)
C(19A)-C(18A)-C(23A)-C(22A)	1(2)
C(9A)-C(18A)-C(23A)-C(22A)	-178.9(13)
C(21A)-C(22A)-C(23A)-C(18A)	1(3)
C(8B)-N(1B)-C(1B)-O(1B)	178.6(12)
C(9B)-N(1B)-C(1B)-O(1B)	-1.4(18)
C(8B)-N(1B)-C(1B)-C(2B)	-0.3(11)
C(9B)-N(1B)-C(1B)-C(2B)	179.7(9)
O(1B)-C(1B)-C(2B)-C(7B)	-179.4(14)
N(1B)-C(1B)-C(2B)-C(7B)	-0.5(14)
O(1B)-C(1B)-C(2B)-C(3B)	0(2)
N(1B)-C(1B)-C(2B)-C(3B)	179.2(14)
C(7B)-C(2B)-C(3B)-C(4B)	1(3)
C(1B)-C(2B)-C(3B)-C(4B)	-179.2(17)
C(2B)-C(3B)-C(4B)-C(5B)	-2(4)
C(3B)-C(4B)-C(5B)-C(6B)	5(5)
C(4B)-C(5B)-C(6B)-C(7B)	-6(4)
C(3B)-C(2B)-C(7B)-C(6B)	-1(2)
C(1B)-C(2B)-C(7B)-C(6B)	178.3(12)
C(3B)-C(2B)-C(7B)-C(8B)	-178.6(14)
C(1B)-C(2B)-C(7B)-C(8B)	1.1(15)
C(5B)-C(6B)-C(7B)-C(2B)	4(2)
C(5B)-C(6B)-C(7B)-C(8B)	-179.3(17)
C(1B)-N(1B)-C(8B)-O(2B)	178.8(11)
C(9B)-N(1B)-C(8B)-O(2B)	-1.2(15)
C(1B)-N(1B)-C(8B)-C(7B)	1.0(11)
C(9B)-N(1B)-C(8B)-C(7B)	-179.0(9)
C(2B)-C(7B)-C(8B)-O(2B)	-179.0(13)
C(6B)-C(7B)-C(8B)-O(2B)	4(2)
C(2B)-C(7B)-C(8B)-N(1B)	-1.3(14)
C(6B)-C(7B)-C(8B)-N(1B)	-178.3(13)
C(1B)-N(1B)-C(9B)-C(18B)	73.7(12)

C(8B)-N(1B)-C(9B)-C(18B)	-106.3(10)
C(1B)-N(1B)-C(9B)-C(10B)	-57.5(13)
C(8B)-N(1B)-C(9B)-C(10B)	122.5(9)
N(1B)-C(9B)-C(10B)-C(11B)	-45.7(12)
C(18B)-C(9B)-C(10B)-C(11B)	-175.0(10)
C(12B)-O(4B)-C(11B)-O(3B)	0.2(13)
C(12B)-O(4B)-C(11B)-C(10B)	178.8(8)
C(9B)-C(10B)-C(11B)-O(3B)	96.1(12)
C(9B)-C(10B)-C(11B)-O(4B)	-82.4(10)
C(11B)-O(4B)-C(12B)-C(13B)	90.7(11)
C(11B)-O(4B)-C(12B)-C(17B)	-89.6(11)
C(17B)-C(12B)-C(13B)-C(14B)	2.3(16)
O(4B)-C(12B)-C(13B)-C(14B)	-178.0(10)
C(12B)-C(13B)-C(14B)-C(15B)	-0.9(17)
C(13B)-C(14B)-C(15B)-C(16B)	-0.5(18)
C(14B)-C(15B)-C(16B)-C(17B)	0.5(19)
C(15B)-C(16B)-C(17B)-C(12B)	0.9(18)
C(13B)-C(12B)-C(17B)-C(16B)	-2.3(16)
O(4B)-C(12B)-C(17B)-C(16B)	177.9(10)
N(1B)-C(9B)-C(18B)-C(19B)	88.7(11)
C(10B)-C(9B)-C(18B)-C(19B)	-142.3(10)
N(1B)-C(9B)-C(18B)-C(23B)	-85.2(11)
C(10B)-C(9B)-C(18B)-C(23B)	43.7(12)
C(23B)-C(18B)-C(19B)-C(20B)	-4.4(16)
C(9B)-C(18B)-C(19B)-C(20B)	-178.7(10)
C(18B)-C(19B)-C(20B)-C(21B)	-0.1(18)
C(19B)-C(20B)-C(21B)-C(22B)	3.7(17)
C(19B)-C(20B)-C(21B)-Cl(1B)	-177.7(9)
C(20B)-C(21B)-C(22B)-C(23B)	-2.6(17)
Cl(1B)-C(21B)-C(22B)-C(23B)	178.9(8)
C(19B)-C(18B)-C(23B)-C(22B)	5.6(15)
C(9B)-C(18B)-C(23B)-C(22B)	179.8(9)
C(21B)-C(22B)-C(23B)-C(18B)	-2.3(17)
C(8C)-N(1C)-C(1C)-O(1C)	178.4(13)
C(9C)-N(1C)-C(1C)-O(1C)	-13(2)
C(8C)-N(1C)-C(1C)-C(2C)	2.0(13)
C(9C)-N(1C)-C(1C)-C(2C)	170.3(11)
O(1C)-C(1C)-C(2C)-C(3C)	2(2)

N(1C)-C(1C)-C(2C)-C(3C)	177.8(13)
O(1C)-C(1C)-C(2C)-C(7C)	-177.3(14)
N(1C)-C(1C)-C(2C)-C(7C)	-1.1(13)
C(7C)-C(2C)-C(3C)-C(4C)	0.8(19)
C(1C)-C(2C)-C(3C)-C(4C)	-177.9(12)
C(2C)-C(3C)-C(4C)-C(5C)	-1(2)
C(3C)-C(4C)-C(5C)-C(6C)	1.5(19)
C(4C)-C(5C)-C(6C)-C(7C)	-2.2(17)
C(5C)-C(6C)-C(7C)-C(2C)	2.3(16)
C(5C)-C(6C)-C(7C)-C(8C)	179.3(11)
C(3C)-C(2C)-C(7C)-C(6C)	-1.7(18)
C(1C)-C(2C)-C(7C)-C(6C)	177.4(10)
C(3C)-C(2C)-C(7C)-C(8C)	-179.2(11)
C(1C)-C(2C)-C(7C)-C(8C)	-0.1(13)
C(1C)-N(1C)-C(8C)-O(2C)	179.7(13)
C(9C)-N(1C)-C(8C)-O(2C)	9.5(19)
C(1C)-N(1C)-C(8C)-C(7C)	-2.0(13)
C(9C)-N(1C)-C(8C)-C(7C)	-172.3(9)
C(6C)-C(7C)-C(8C)-O(2C)	2(2)
C(2C)-C(7C)-C(8C)-O(2C)	179.4(14)
C(6C)-C(7C)-C(8C)-N(1C)	-175.9(11)
C(2C)-C(7C)-C(8C)-N(1C)	1.3(13)
C(8C)-N(1C)-C(9C)-C(18C)	-111.6(13)
C(1C)-N(1C)-C(9C)-C(18C)	80.6(16)
C(8C)-N(1C)-C(9C)-C(10C)	124.7(12)
C(1C)-N(1C)-C(9C)-C(10C)	-43.1(18)
N(1C)-C(9C)-C(10C)-C(11')	-46.9(19)
C(18C)-C(9C)-C(10C)-C(11')	-173.1(15)
N(1C)-C(9C)-C(10C)-C(11C)	-78(2)
C(18C)-C(9C)-C(10C)-C(11C)	156(2)
C(12C)-O(3C)-C(11C)-O(4C)	5(6)
C(12C)-O(3C)-C(11C)-C(10C)	168(3)
C(9C)-C(10C)-C(11C)-O(3C)	131(4)
C(11')-C(10C)-C(11C)-O(3C)	30(3)
C(9C)-C(10C)-C(11C)-O(4C)	-68(6)
C(11')-C(10C)-C(11C)-O(4C)	-169(10)
C(11C)-O(3C)-C(12C)-C(13C)	-150(4)
C(11C)-O(3C)-C(12C)-C(17C)	70(5)

C(17C)-C(12C)-C(13C)-C(14C)	0.0
O(3C)-C(12C)-C(13C)-C(14C)	-152(2)
C(12C)-C(13C)-C(14C)-C(15C)	0.0
C(13C)-C(14C)-C(15C)-C(16C)	0.0
C(14C)-C(15C)-C(16C)-C(17C)	0.0
C(15C)-C(16C)-C(17C)-C(12C)	0.0
C(13C)-C(12C)-C(17C)-C(16C)	0.0
O(3C)-C(12C)-C(17C)-C(16C)	131(3)
C(12')-O(4')-C(11')-O(3')	1(4)
C(12')-O(4')-C(11')-C(10C)	-175.7(19)
C(9C)-C(10C)-C(11')-O(3')	61(4)
C(11C)-C(10C)-C(11')-O(3')	153(7)
C(9C)-C(10C)-C(11')-O(4')	-122(2)
C(11C)-C(10C)-C(11')-O(4')	-31(4)
C(11')-O(4')-C(12')-C(13')	120.4(19)
C(11')-O(4')-C(12')-C(17')	-77(2)
C(17')-C(12')-C(13')-C(14')	0.0
O(4')-C(12')-C(13')-C(14')	162.0(16)
C(12')-C(13')-C(14')-C(15')	0.0
C(13')-C(14')-C(15')-C(16')	0.0
C(14')-C(15')-C(16')-C(17')	0.0
C(15')-C(16')-C(17')-C(12')	0.0
C(13')-C(12')-C(17')-C(16')	0.0
O(4')-C(12')-C(17')-C(16')	-161.9(16)
N(1C)-C(9C)-C(18C)-C(23C)	128.7(13)
C(10C)-C(9C)-C(18C)-C(23C)	-107.3(15)
N(1C)-C(9C)-C(18C)-C(19C)	-51.6(19)
C(10C)-C(9C)-C(18C)-C(19C)	72.3(18)
C(23C)-C(18C)-C(19C)-C(20C)	0(2)
C(9C)-C(18C)-C(19C)-C(20C)	-179.2(13)
C(18C)-C(19C)-C(20C)-C(21C)	-2(2)
C(19C)-C(20C)-C(21C)-C(22C)	0(3)
C(19C)-C(20C)-C(21C)-Cl(1C)	-178.3(12)
C(20C)-C(21C)-C(22C)-C(23C)	4(3)
Cl(1C)-C(21C)-C(22C)-C(23C)	-177.8(12)
C(19C)-C(18C)-C(23C)-C(22C)	4(3)
C(9C)-C(18C)-C(23C)-C(22C)	-176.3(15)
C(21C)-C(22C)-C(23C)-C(18C)	-6(3)

Symmetry transformations used to generate equivalent atoms:

Table S7. Hydrogen bonds for **2b** [Å and °].

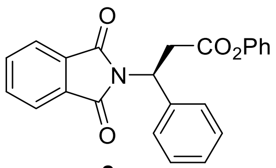
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(9)-H(9)...O(3B)#1	0.98	2.39	3.311(14)	157.2
C(10)-H(10B)...O(2)	0.97	2.50	3.021(15)	113.7
C(10A)-H(10D)...O(2A)	0.97	2.45	3.070(14)	121.3
C(13A)-H(13A)...O(1)#2	0.93	2.59	3.357(16)	140.4
C(10B)-H(10E)...O(3)#3	0.97	2.50	3.426(14)	160.5
C(10C)-H(10G)...O(1C)	0.96	2.41	3.14(2)	132.8
C(13')-H(13')...O(1A)#4	0.93	2.57	3.440(15)	156.5

Symmetry transformations used to generate equivalent atoms:

#1 x,y+1,z #2 x,y,z-1 #3 x,y-1,z #4 x-1,y-1,z

The determination of enantiomeric excess

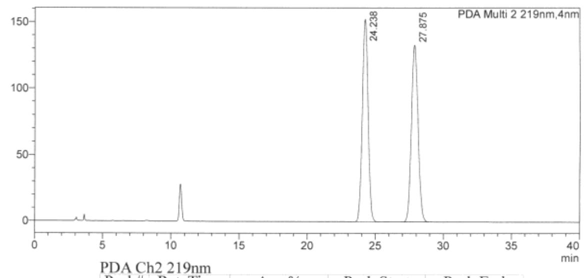
Table 3, 2a



2a

HPLC Condition: Column: Chiralpak AD-H, Daicel Chemical Industries, Ltd.; **Eluent:** Hexanes/IPA (90/10); **Flow rate:** 1.0 mL/min; **Detection:** UV219 nm.

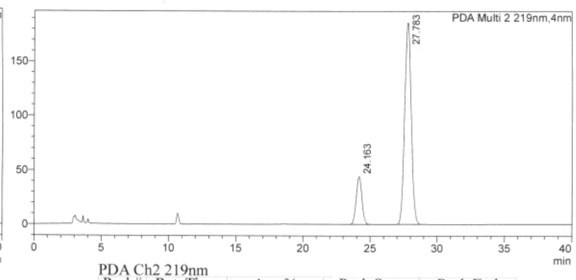
Racemic standard



PDA Ch2 219nm

Peak#	Ret. Time	Area%	Peak Start	Peak End
1	24.238	49.650	23.445	25.333
2	27.875	50.350	27.019	29.088
Total		100.000		

Enantio-enriched product



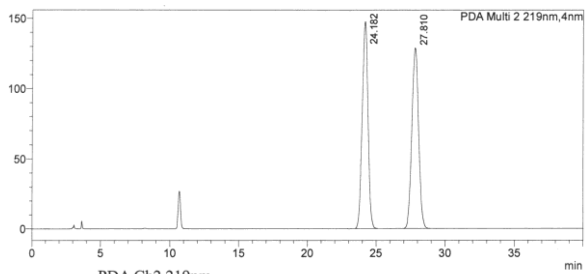
PDA Ch2 219nm

Peak#	Ret. Time	Area%	Peak Start	Peak End
1	24.163	16.944	23.424	25.077
2	27.783	83.056	26.944	28.981
Total		100.000		

After recrystallization

HPLC Condition: Column: Chiralpak AD-H, Daicel Chemical Industries, Ltd.; **Eluent:** Hexanes/IPA (90/10); **Flow rate:** 1.0 mL/min; **Detection:** UV219 nm.

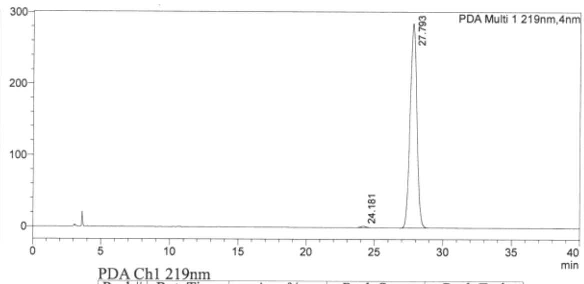
Racemic standard



PDA Ch2 219nm

Peak#	Ret. Time	Area%	Peak Start	Peak End
1	24.182	49.647	23.360	25.248
2	27.810	50.353	26.923	28.960
Total		100.000		

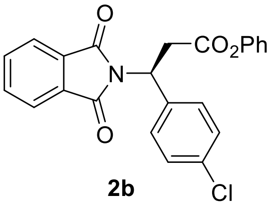
Enantio-enriched product



PDA Ch1 219nm

Peak#	Ret. Time	Area%	Peak Start	Peak End
1	24.181	0.661	23.627	24.960
2	27.793	99.339	26.880	29.152
Total		100.000		

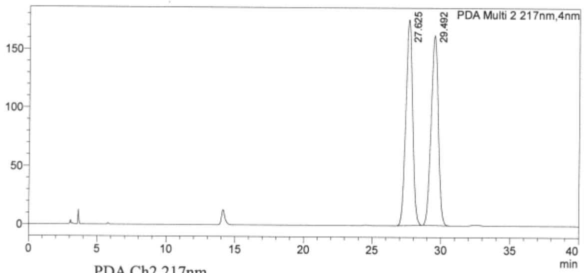
Table 3, 2b



2b

HPLC Condition: Column: Chiralpak AD-H, Daicel Chemical Industries, Ltd.; **Eluent:** Hexanes/IPA (90/10); **Flow rate:** 1.0 mL/min; **Detection:** UV217 nm.

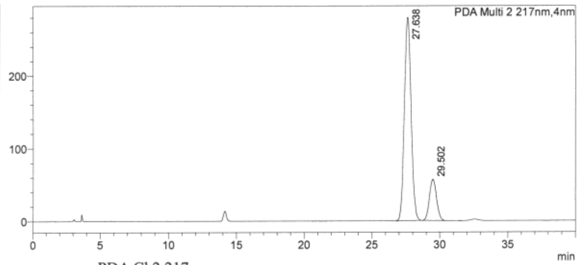
Racemic standard



PDA Ch2 217nm

Peak#	Ret. Time	Area%	Peak Start	Peak End
1	27.625	50.593	26.699	28.629
2	29.492	49.407	28.651	30.709
Total		100.000		

Enantio-enriched product



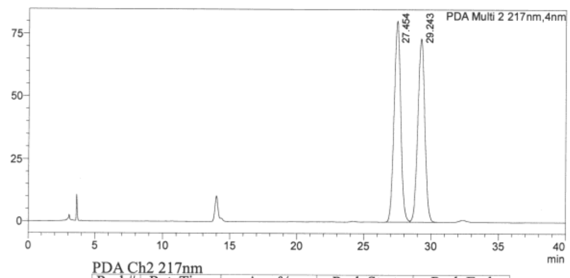
PDA Ch2 217nm

Peak#	Ret. Time	Area%	Peak Start	Peak End
1	27.638	82.273	26.688	28.693
2	29.502	17.727	28.725	30.699
Total		100.000		

After recrystallization

HPLC Condition: Column: Chiralpak AD-H, Daicel Chemical Industries, Ltd.; **Eluent:** Hexanes/IPA (90/10); **Flow rate:** 1.0 mL/min; **Detection:** UV217 nm.

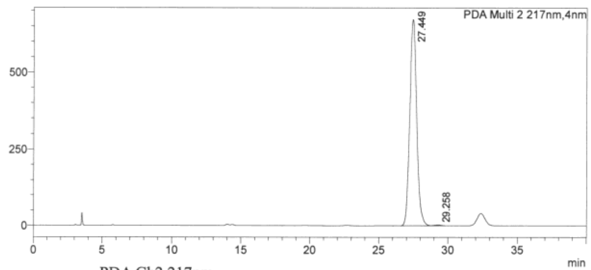
Racemic standard



PDA Ch2 217nm

Peak#	Ret. Time	Area%	Peak Start	Peak End
1	27.454	50.979	26.592	28.416
2	29.243	49.021	28.416	30.411
Total		100.000		

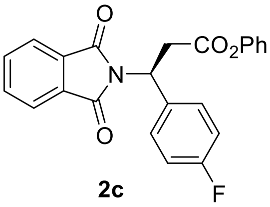
Enantio-enriched product



PDA Ch2 217nm

Peak#	Ret. Time	Area%	Peak Start	Peak End
1	27.449	99.600	26.496	28.789
2	29.258	0.400	28.789	30.091
Total		100.000		

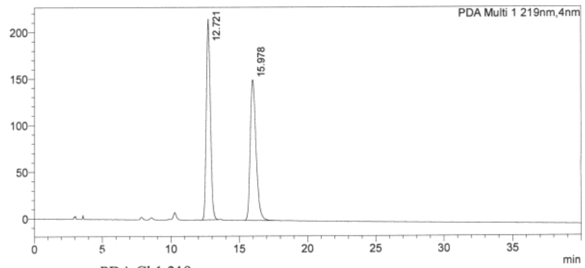
Table 3, 2c



2c

HPLC Condition: Column: Chiralpak OD-H, Daicel Chemical Industries, Ltd.; **Eluent:** Hexanes/IPA (90/10); **Flow rate:** 1.0 mL/min; **Detection:** UV219 nm.

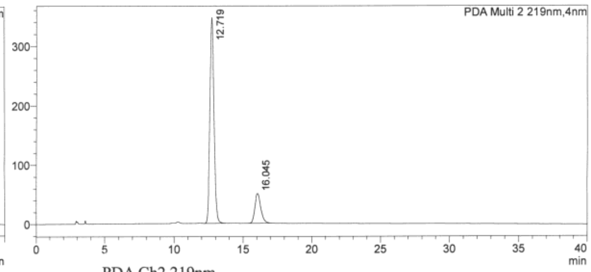
Racemic standard



PDA Ch1 219nm

Peak#	Ret. Time	Area%	Peak Start	Peak End
1	12.721	50.057	12.171	13.493
2	15.978	49.943	15.264	17.675
Total		100.000		

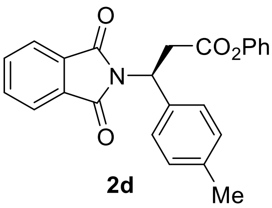
Enantio-enriched product



PDA Ch2 219nm

Peak#	Ret. Time	Area%	Peak Start	Peak End
1	12.719	82.764	12.224	13.813
2	16.045	17.236	15.349	17.195
Total		100.000		

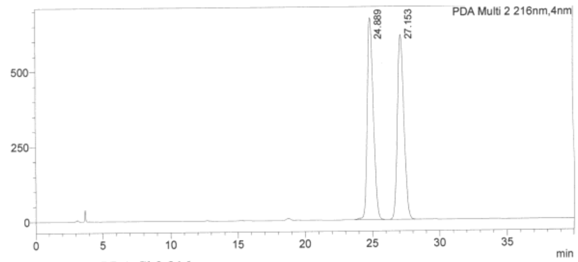
Table 3, 2d



2d

HPLC Condition: Column: Chiralpak AD-H, Daicel Chemical Industries, Ltd.; **Eluent:** Hexanes/IPA (90/10); **Flow rate:** 1.0 mL/min; **Detection:** UV216 nm.

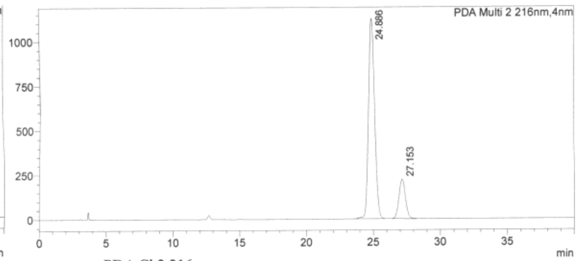
Racemic standard



PDA Ch2 216nm

Peak#	Ret. Time	Area%	Peak Start	Peak End
1	24.889	50.321	23.563	26.176
2	27.153	49.679	26.272	28.629
Total		100.000		

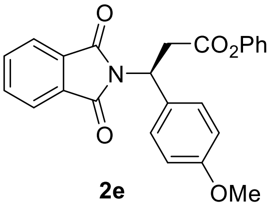
Enantio-enriched product



PDA Ch2 216nm

Peak#	Ret. Time	Area%	Peak Start	Peak End
1	24.886	82.633	23.499	26.187
2	27.153	17.367	26.304	28.299
Total		100.000		

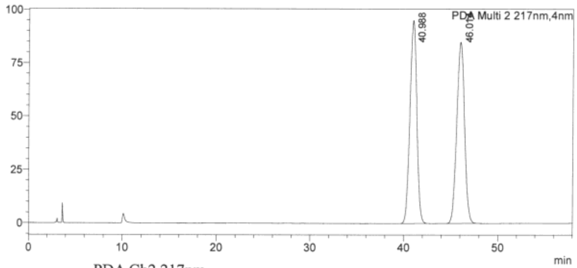
Table 3, 2e



2e

HPLC Condition: Column: Chiralpak AD-H, Daicel Chemical Industries, Ltd.; **Eluent:** Hexanes/IPA (90/10); **Flow rate:** 1.0 mL/min; **Detection:** UV217 nm.

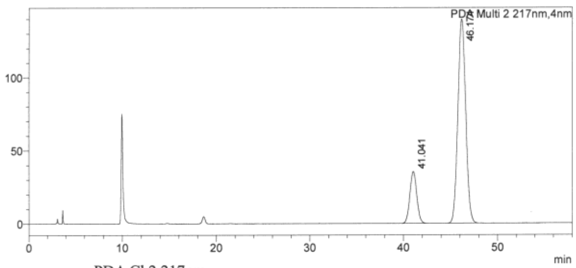
Racemic standard



PDA Ch2 217nm

Peak#	Ret. Time	Area%	Peak Start	Peak End
1	40.988	49.843	39.680	42.603
2	46.014	50.157	44.587	47.776
Total		100.000		

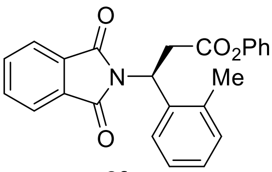
Enantio-enriched product



PDA Ch2 217nm

Peak#	Ret. Time	Area%	Peak Start	Peak End
1	41.041	18.330	39.808	42.539
2	46.174	81.670	44.725	48.000
Total		100.000		

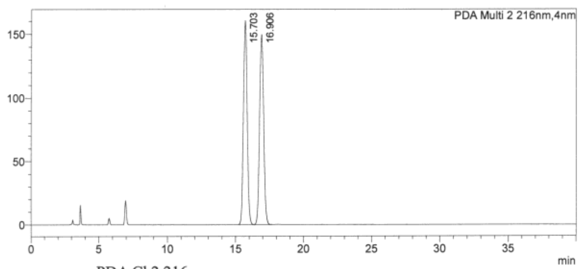
Table 3, 2f



2f

HPLC Condition: Column: Chiralpak AD-H, Daicel Chemical Industries, Ltd.; **Eluent:** Hexanes/IPA (90/10); **Flow rate:** 1.0 mL/min; **Detection:** UV216 nm.

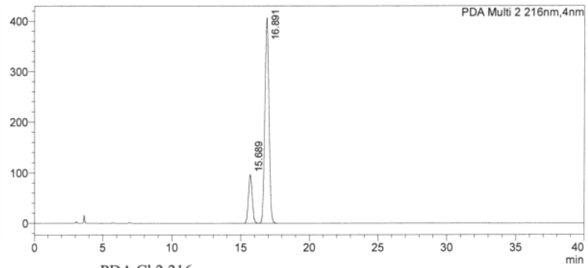
Racemic standard



PDA Ch2 216nm

Peak#	Ret. Time	Area%	Peak Start	Peak End
1	15.703	49.899	15.157	16.352
2	16.906	50.101	16.352	17.717
Total		100.000		

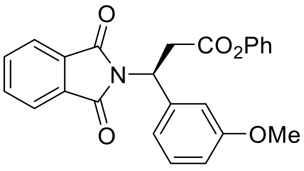
Enantio-enriched product



PDA Ch2 216nm

Peak#	Ret. Time	Area%	Peak Start	Peak End
1	15.689	17.996	15.157	16.309
2	16.891	82.004	16.309	17.824
Total		100.000		

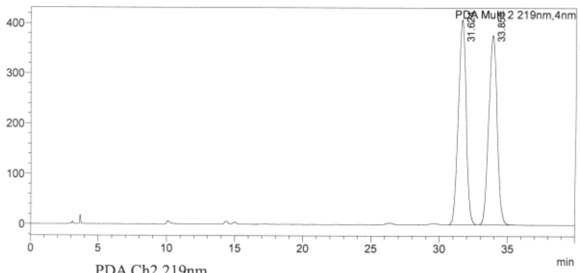
Table 3, 2g



2g

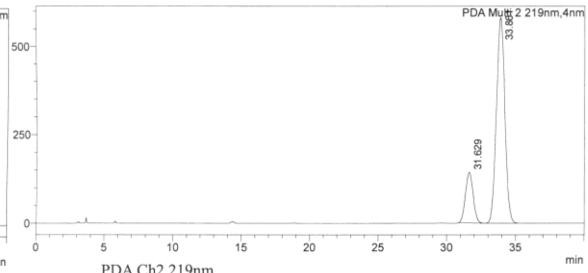
HPLC Condition: Column: Chiralpak AD-H, Daicel Chemical Industries, Ltd.; **Eluent:** Hexanes/IPA (90/10); **Flow rate:** 1.0 mL/min; **Detection:** UV219 nm.

Racemic standard | **Enantio-enriched product**



PDA Ch2 219nm

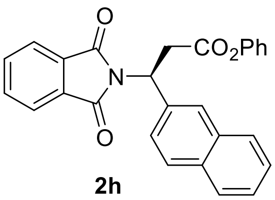
Peak#	Ret. Time	Area%	Peak Start	Peak End
1	31.624	50.051	30.517	32.821
2	33.855	49.949	32.853	36.011
Total		100.000		



PDA Ch2 219nm

Peak#	Ret. Time	Area%	Peak Start	Peak End
1	31.629	18.280	30.859	32.704
2	33.861	81.720	32.768	35.573
Total		100.000		

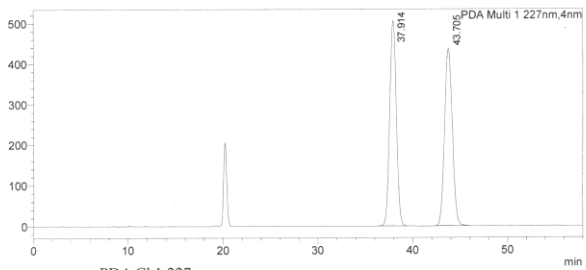
Table 3, 2h



2h

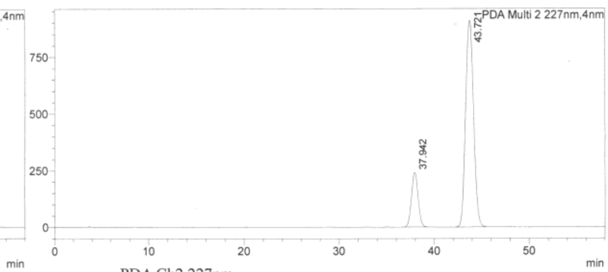
HPLC Condition: Column: Chiralpak AD-H, Daicel Chemical Industries, Ltd.; **Eluent:** Hexanes/IPA (90/10); **Flow rate:** 1.0 mL/min; **Detection:** UV227 nm.

Racemic standard | **Enantio-enriched product**



PDA Ch1 227nm

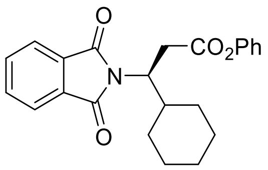
Peak#	Ret. Time	Area%	Peak Start	Peak End
1	37.914	49.994	36.512	39.755
2	43.705	50.006	42.453	46.261
Total		100.000		



PDA Ch2 227nm

Peak#	Ret. Time	Area%	Peak Start	Peak End
1	37.942	18.057	36.597	39.915
2	43.721	81.943	42.165	45.920
Total		100.000		

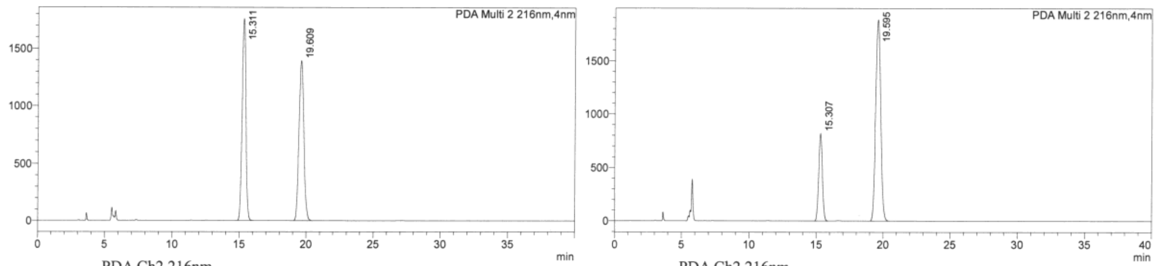
Table 3, 2i



2i

HPLC Condition: Column: Chiralpak AD-H, Daicel Chemical Industries, Ltd.; **Eluent:** Hexanes/IPA (90/10); **Flow rate:** 1.0 mL/min; **Detection:** UV216 nm.

Racemic standard **Enantio-enriched product**



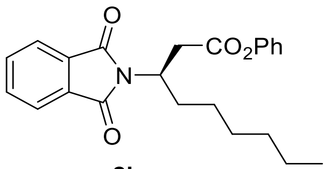
PDA Ch2 216nm

Peak#	Ret. Time	Area%	Peak Start	Peak End
1	15.311	49.490	14.805	16.341
2	19.609	50.510	19.029	20.661
Total		100.000		

PDA Ch2 216nm

Peak#	Ret. Time	Area%	Peak Start	Peak End
1	15.307	24.030	14.869	16.128
2	19.595	75.970	18.880	21.056
Total		100.000		

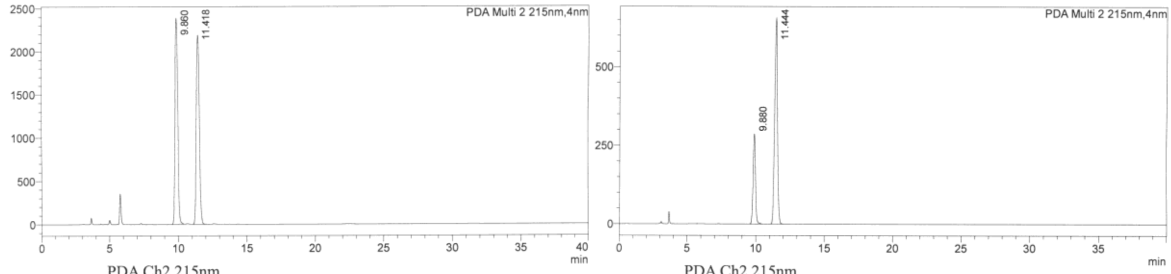
Table 3, 2j



2j

HPLC Condition: Column: Chiralpak AD-H, Daicel Chemical Industries, Ltd.; **Eluent:** Hexanes/IPA (90/10); **Flow rate:** 1.0 mL/min; **Detection:** UV215 nm.

Racemic standard **Enantio-enriched product**



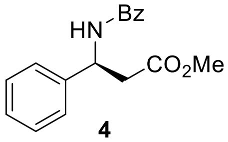
PDA Ch2 215nm

Peak#	Ret. Time	Area%	Peak Start	Peak End
1	9.860	49.289	9.536	10.464
2	11.418	50.711	11.040	12.075
Total		100.000		

PDA Ch2 215nm

Peak#	Ret. Time	Area%	Peak Start	Peak End
1	9.880	27.556	9.568	10.837
2	11.444	72.444	11.019	12.224
Total		100.000		

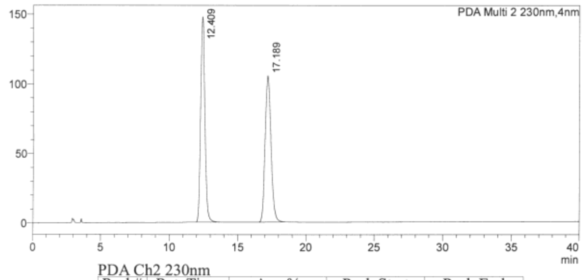
Scheme 4, product 4



4

HPLC Condition: Column: Chiralpak OD-H, Daicel Chemical Industries, Ltd.; **Eluent:** Hexanes/IPA (90/10); **Flow rate:** 1.0 mL/min; **Detection:** UV 230 nm.

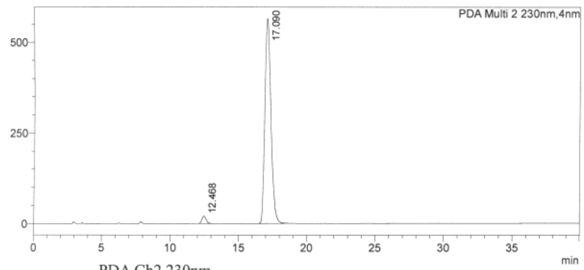
Racemic standard



PDA Ch2 230nm

Peak#	Ret. Time	Area%	Peak Start	Peak End
1	12.409	49.988	11.936	13.771
2	17.189	50.012	16.469	18.699
Total		100.000		

Enantio-enriched product

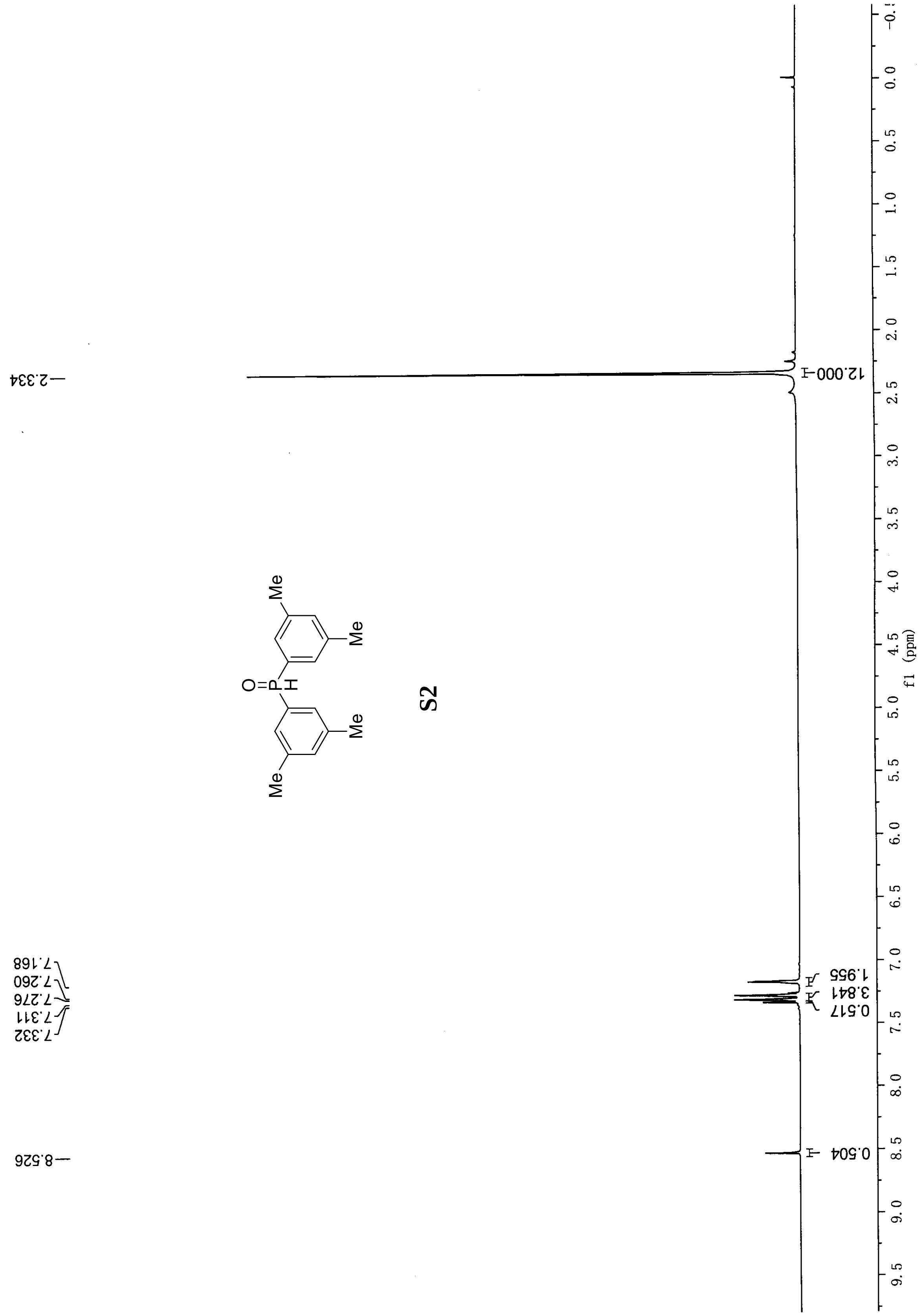


PDA Ch2 230nm

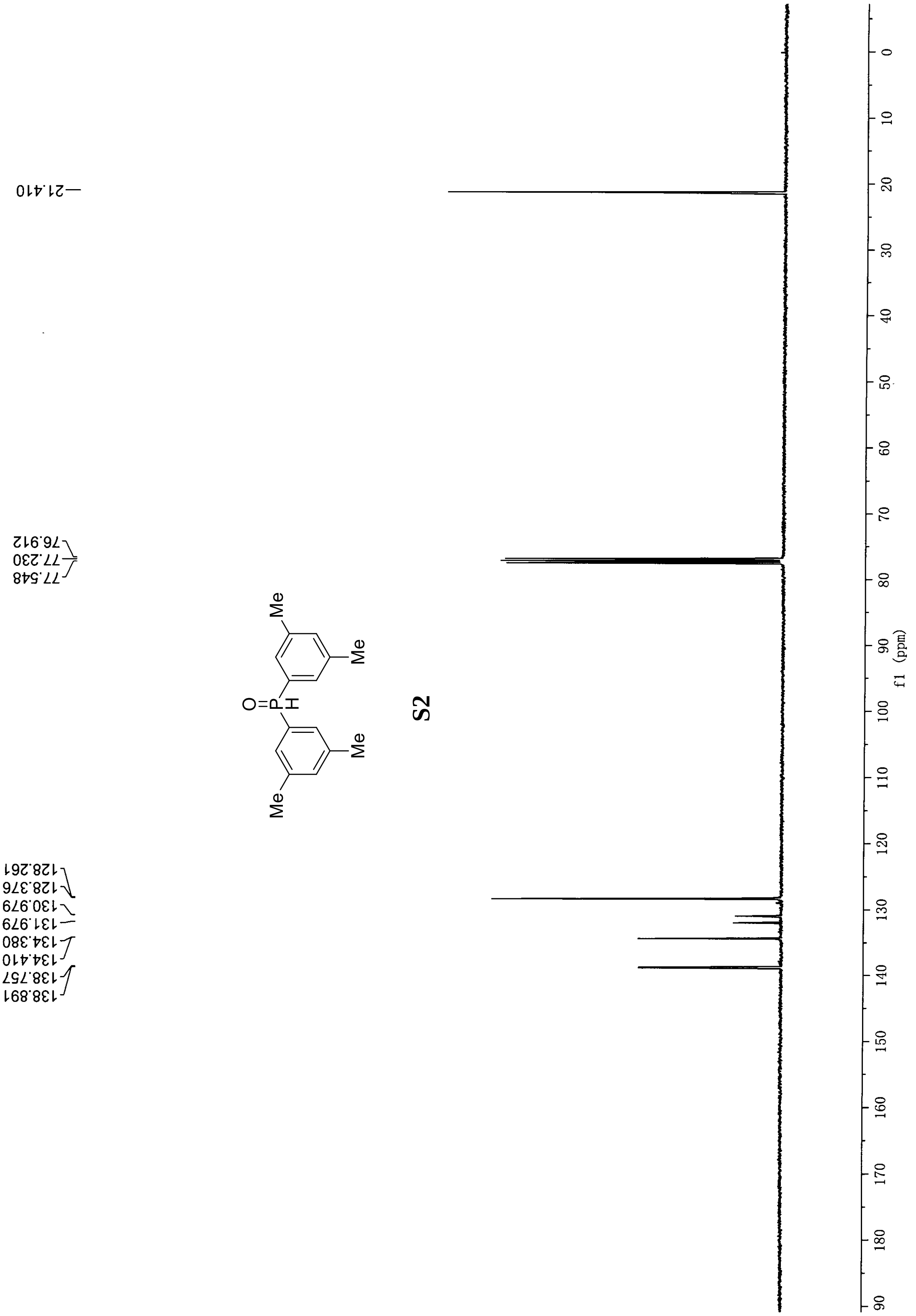
Peak#	Ret. Time	Area%	Peak Start	Peak End
1	12.468	2.540	12.021	13.237
2	17.090	97.460	16.395	18.965
Total		100.000		

NMR spectra

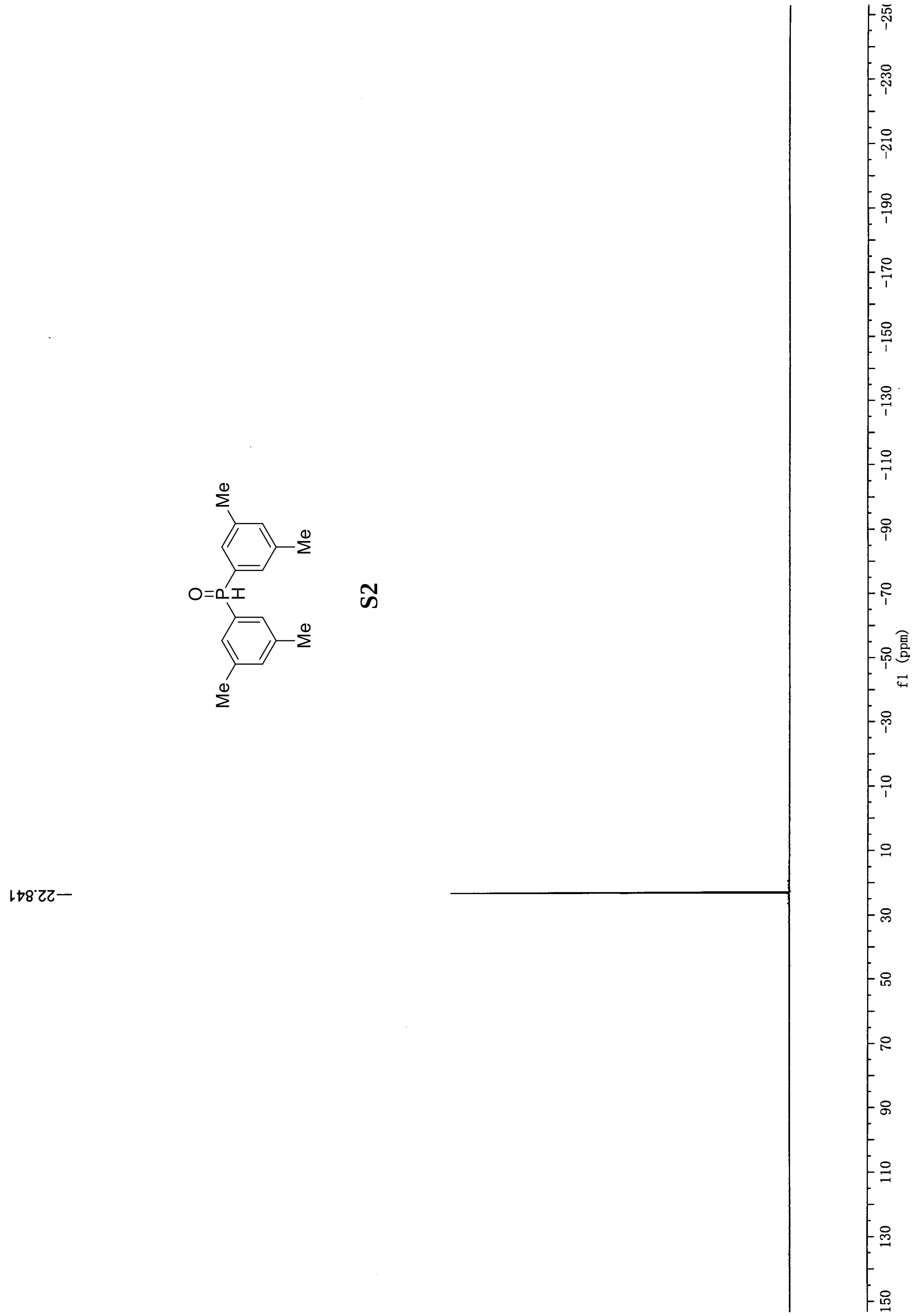
^{1}H NMR Spectrum of **S2** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **S2** ($CDCl_3$, 100 MHz)

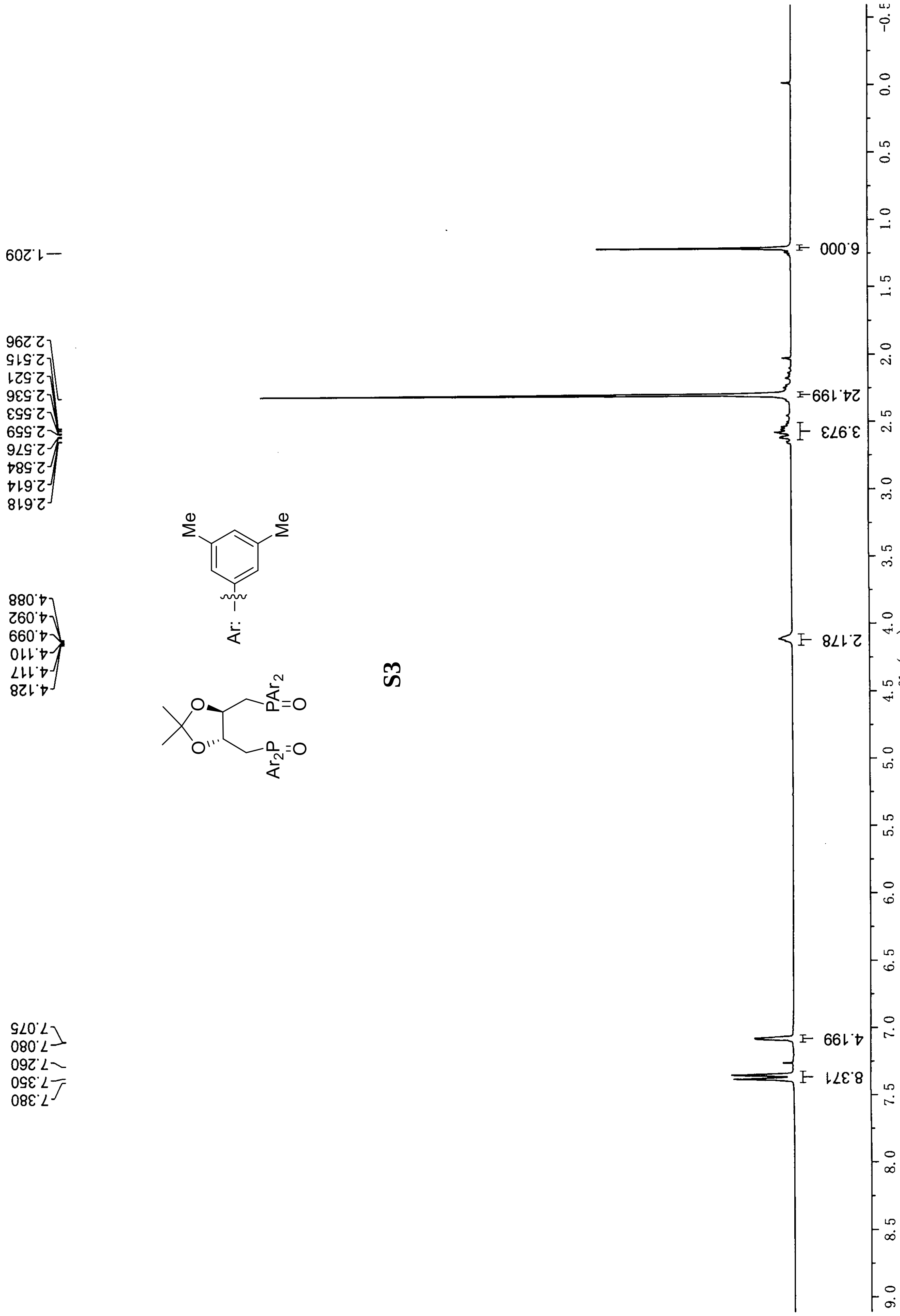


^{31}P NMR Spectrum of **S2** ($CDCl_3$, 162 MHz)

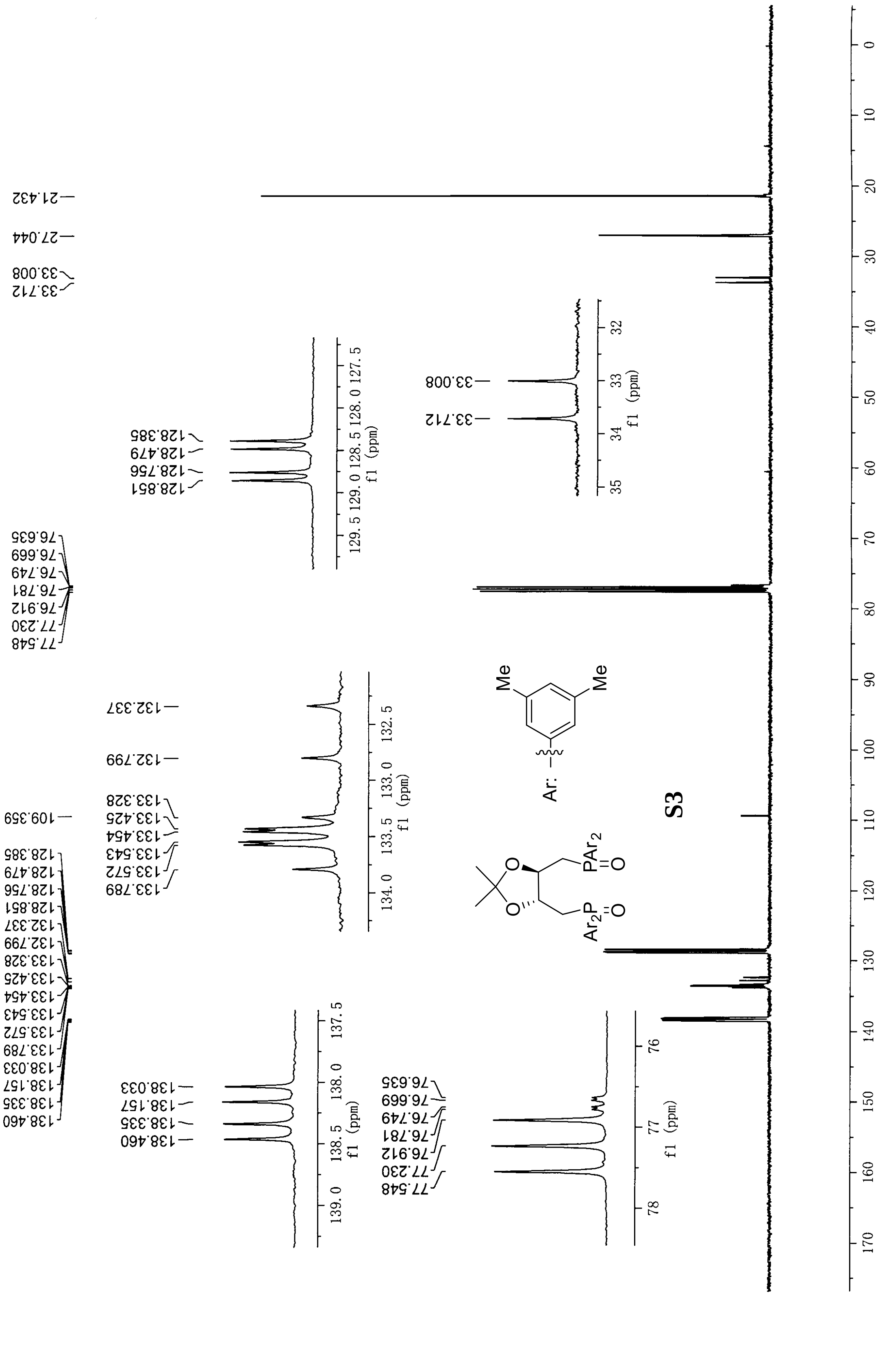


S2

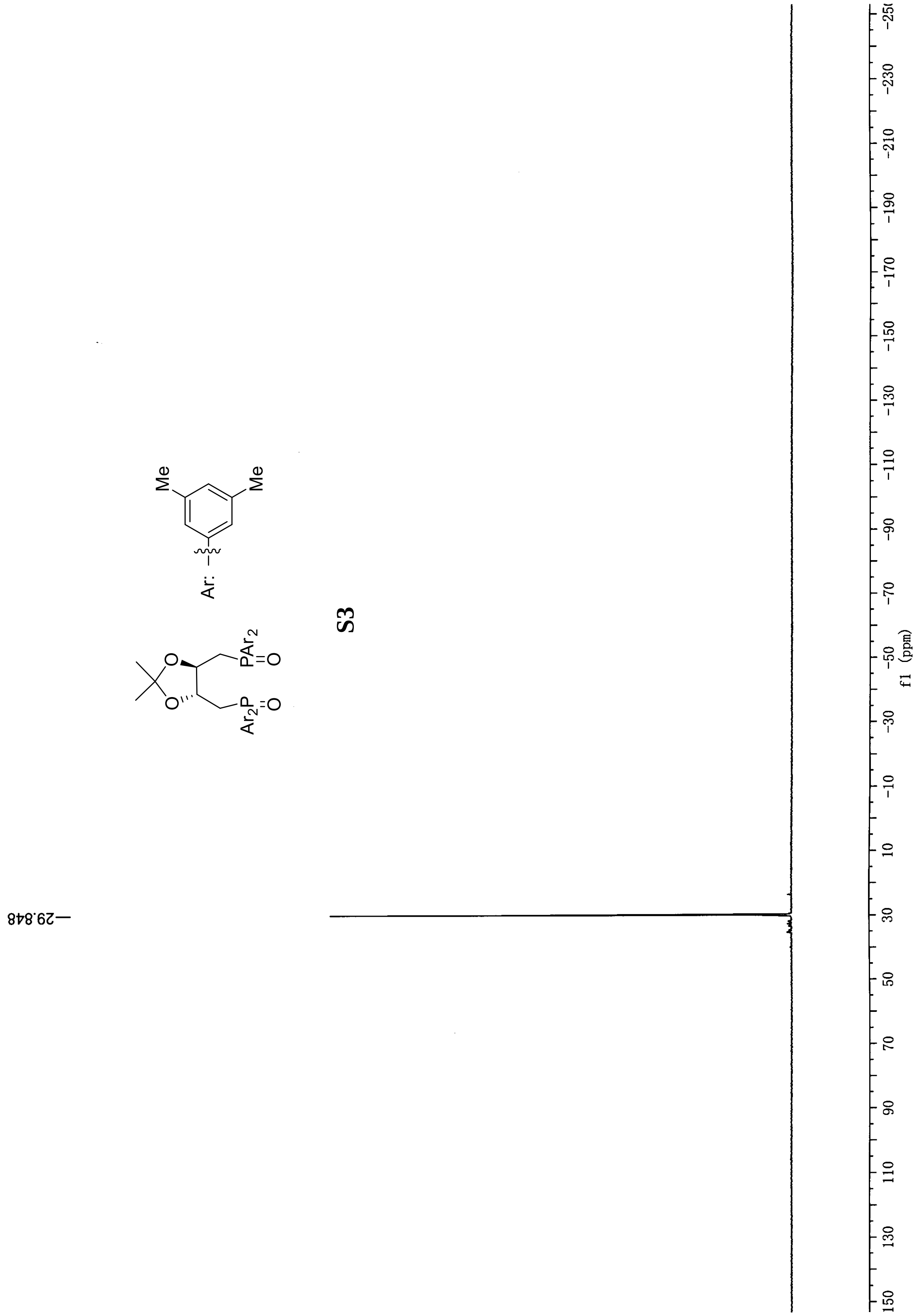
^{1}H NMR Spectrum of **S3** ($CDCl_3$, 400 MHz)



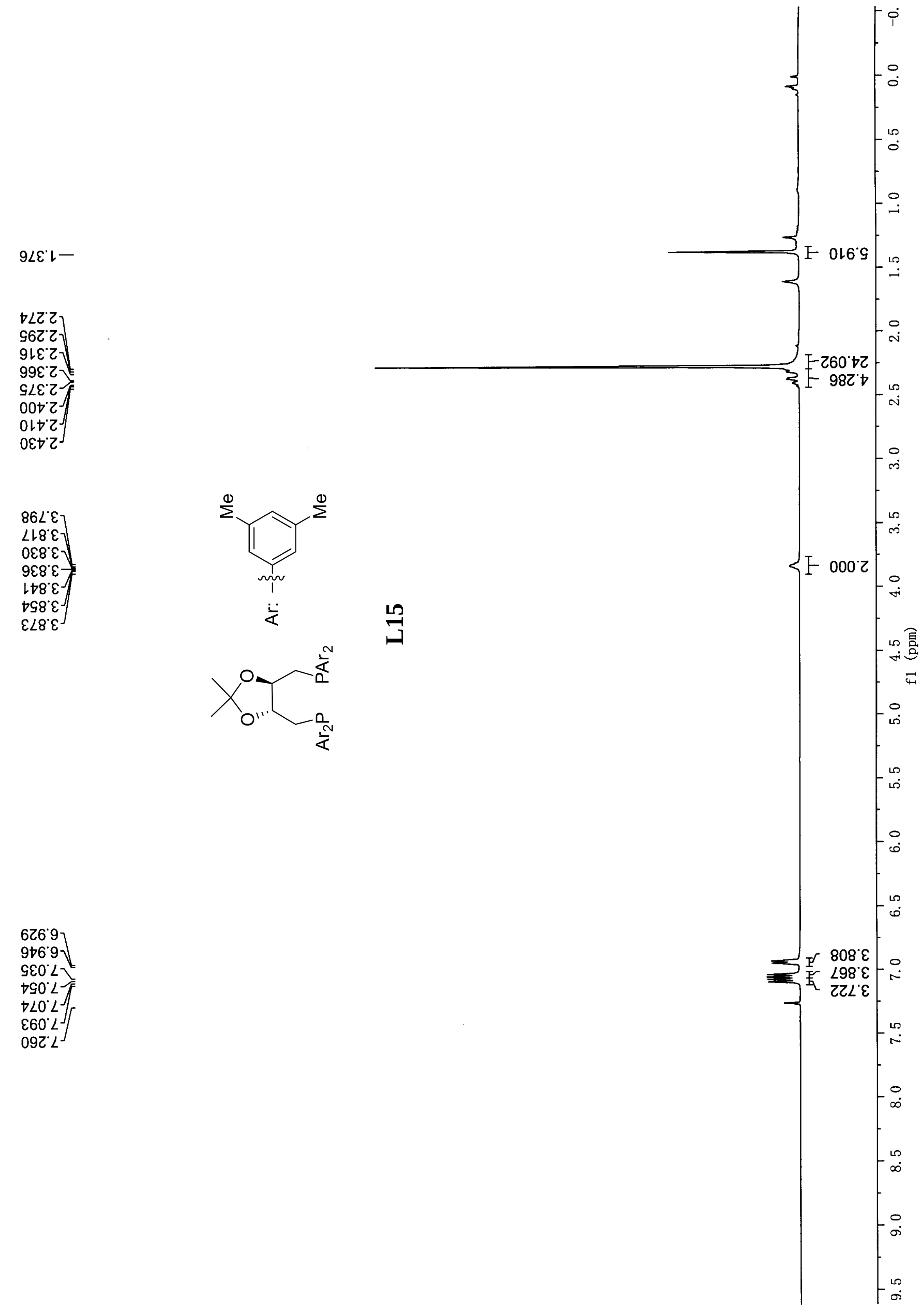
[13]C NMR Spectrum of **S3** ($CDCl_3$, 100 MHz)



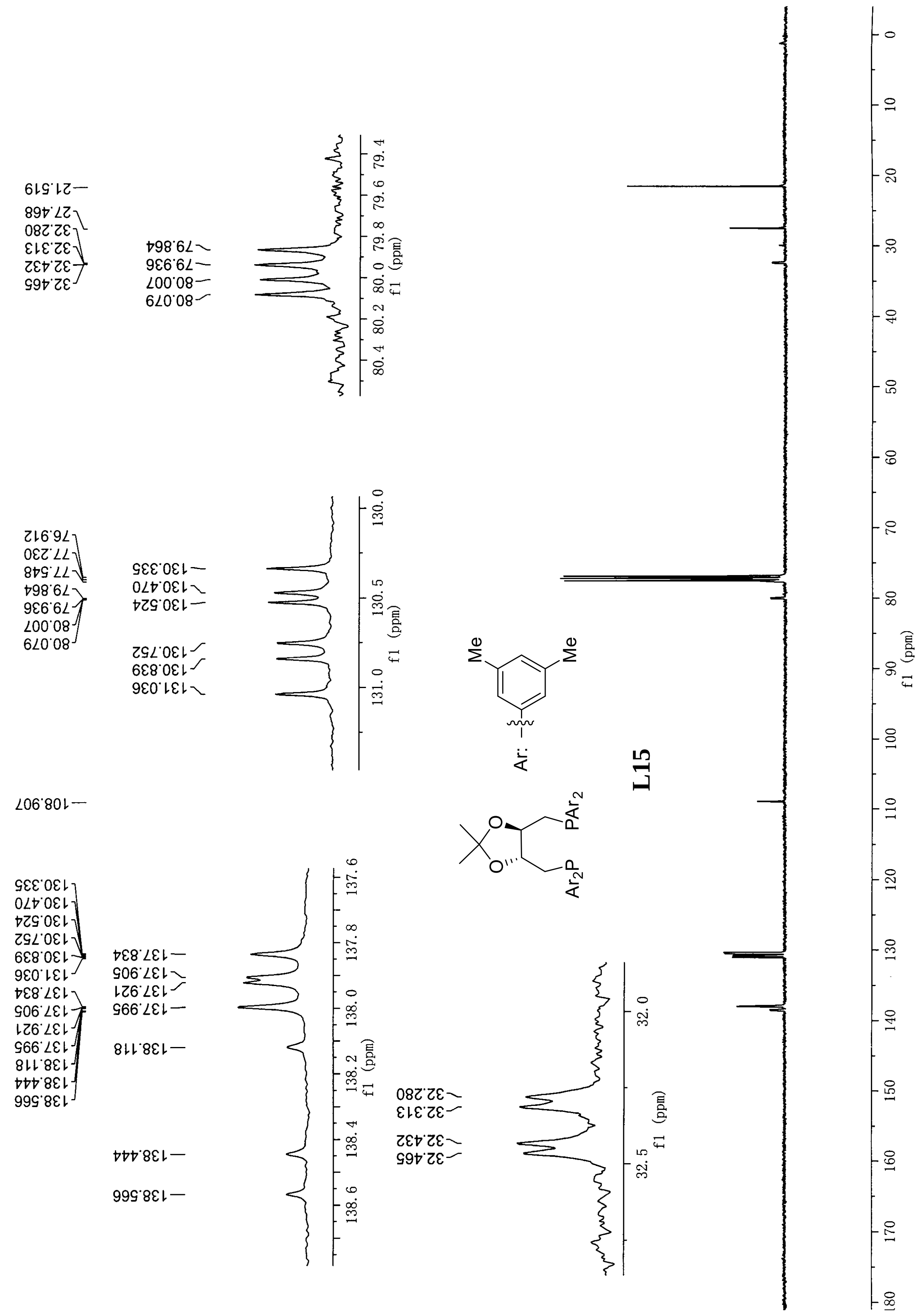
^{31}P NMR Spectrum of **S3** ($CDCl_3$, 162 MHz)



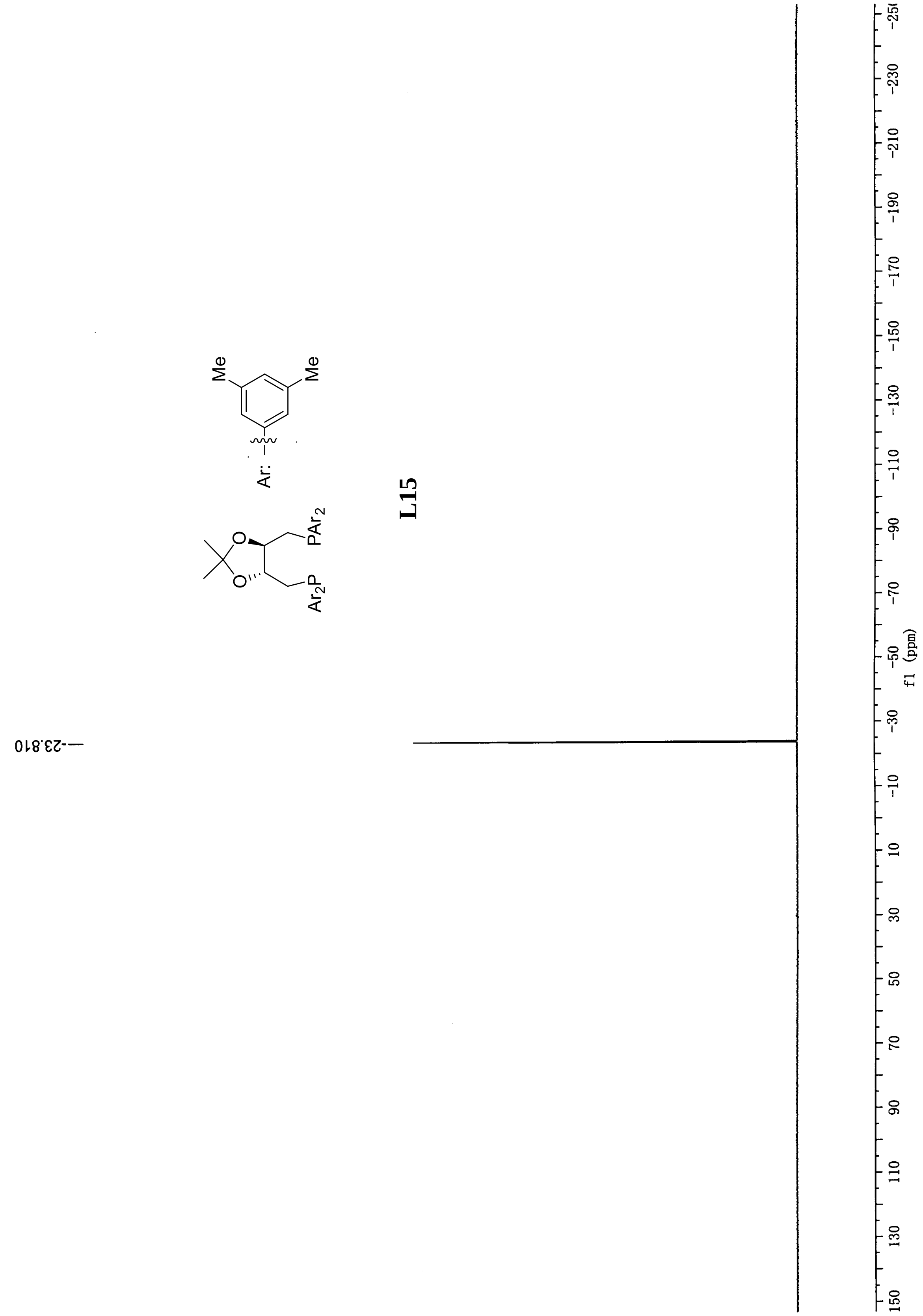
[1]H NMR Spectrum of **L15** ($CDCl_3$, 400 MHz)



[13]C NMR Spectrum of **L15** ($CDCl_3$, 100 MHz)



^{31}P NMR Spectrum of **L15** ($CDCl_3$, 162 MHz)



^{1}H NMR Spectrum of **2a** ($CDCl_3$, 400 MHz)

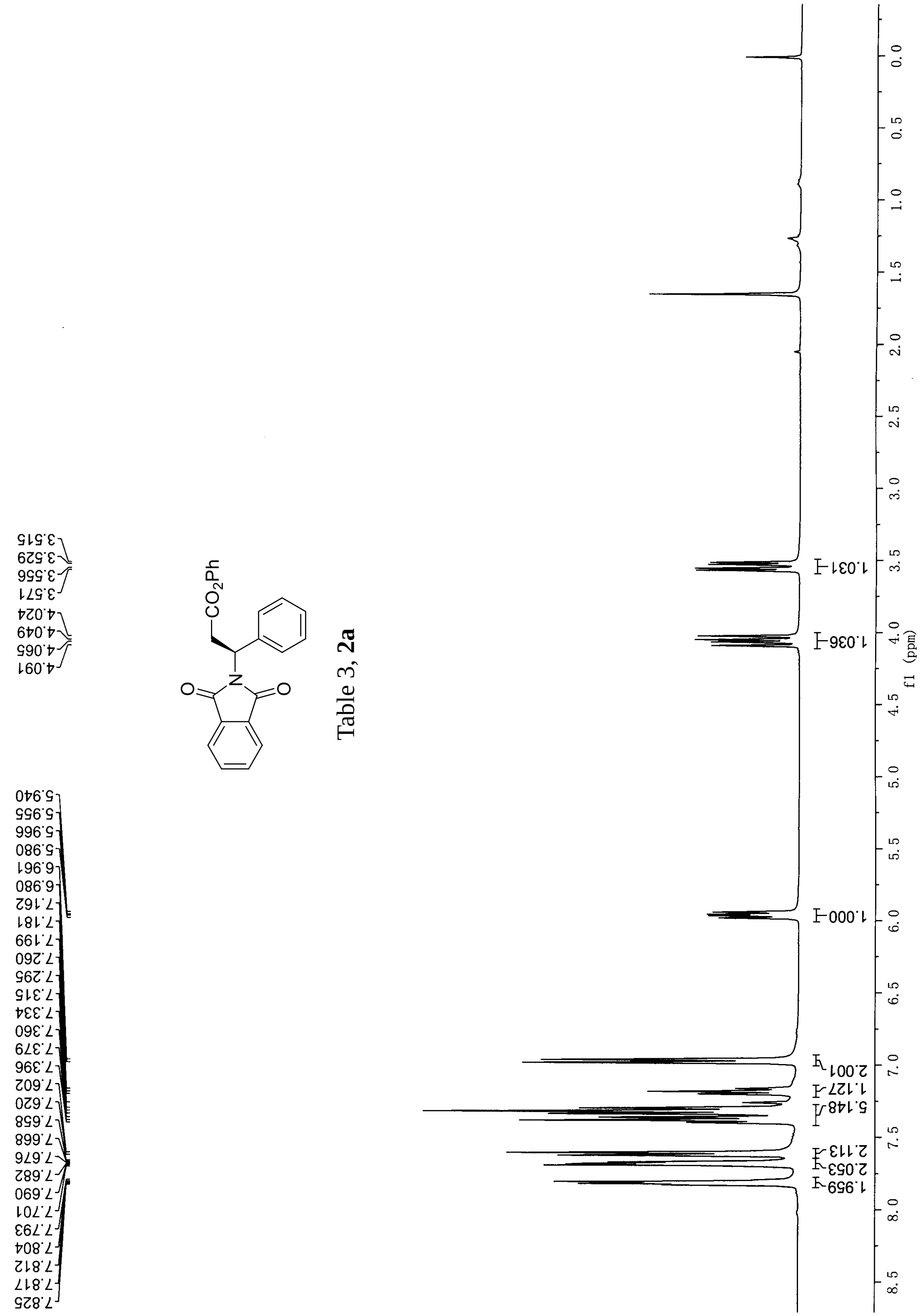


Table 3, **2a**

^{13}C NMR Spectrum of **2a** ($CDCl_3$, 100 MHz)

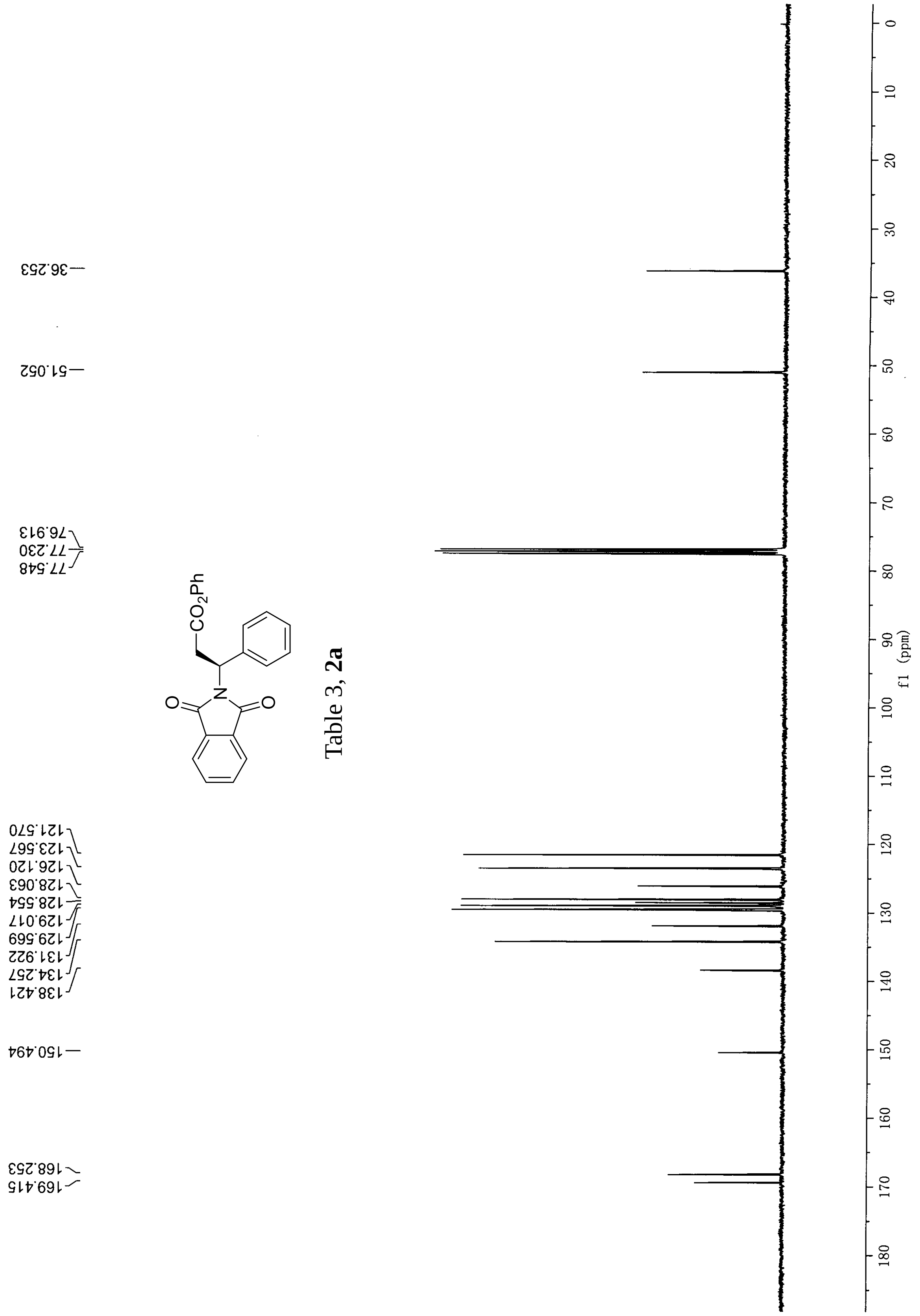


Table 3, **2a**

[1]H NMR Spectrum of **2b** ($CDCl_3$, 400 MHz)

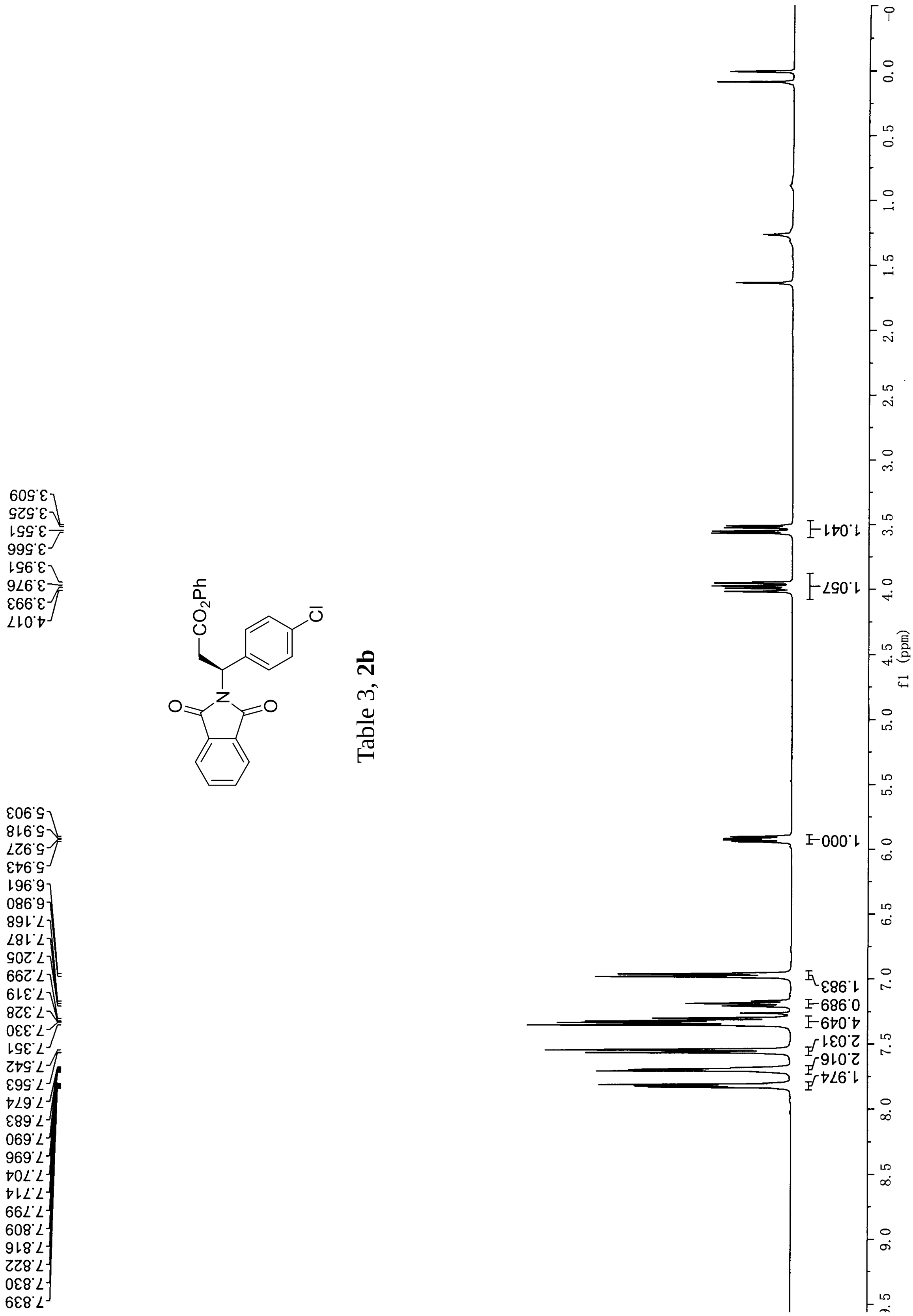
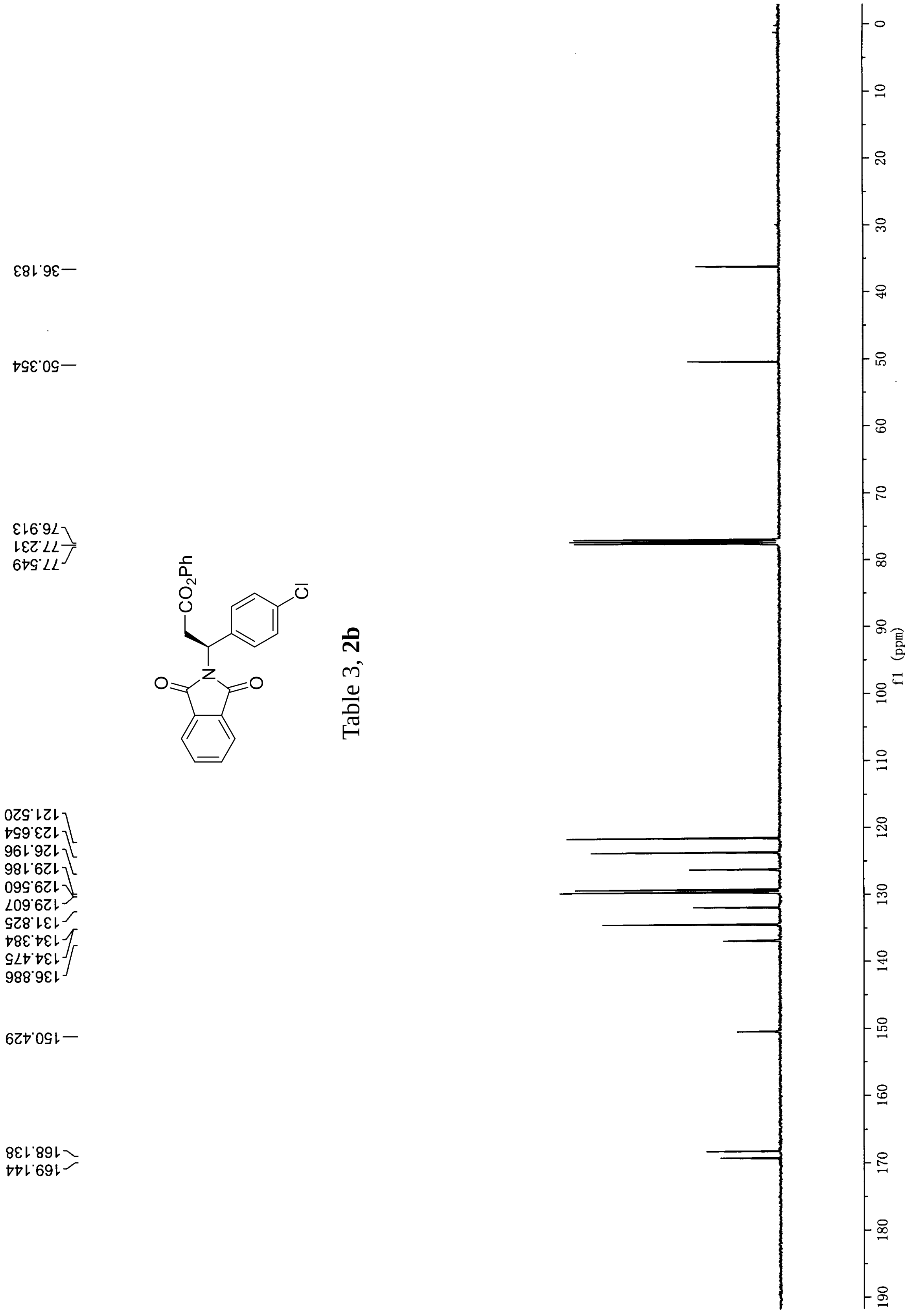
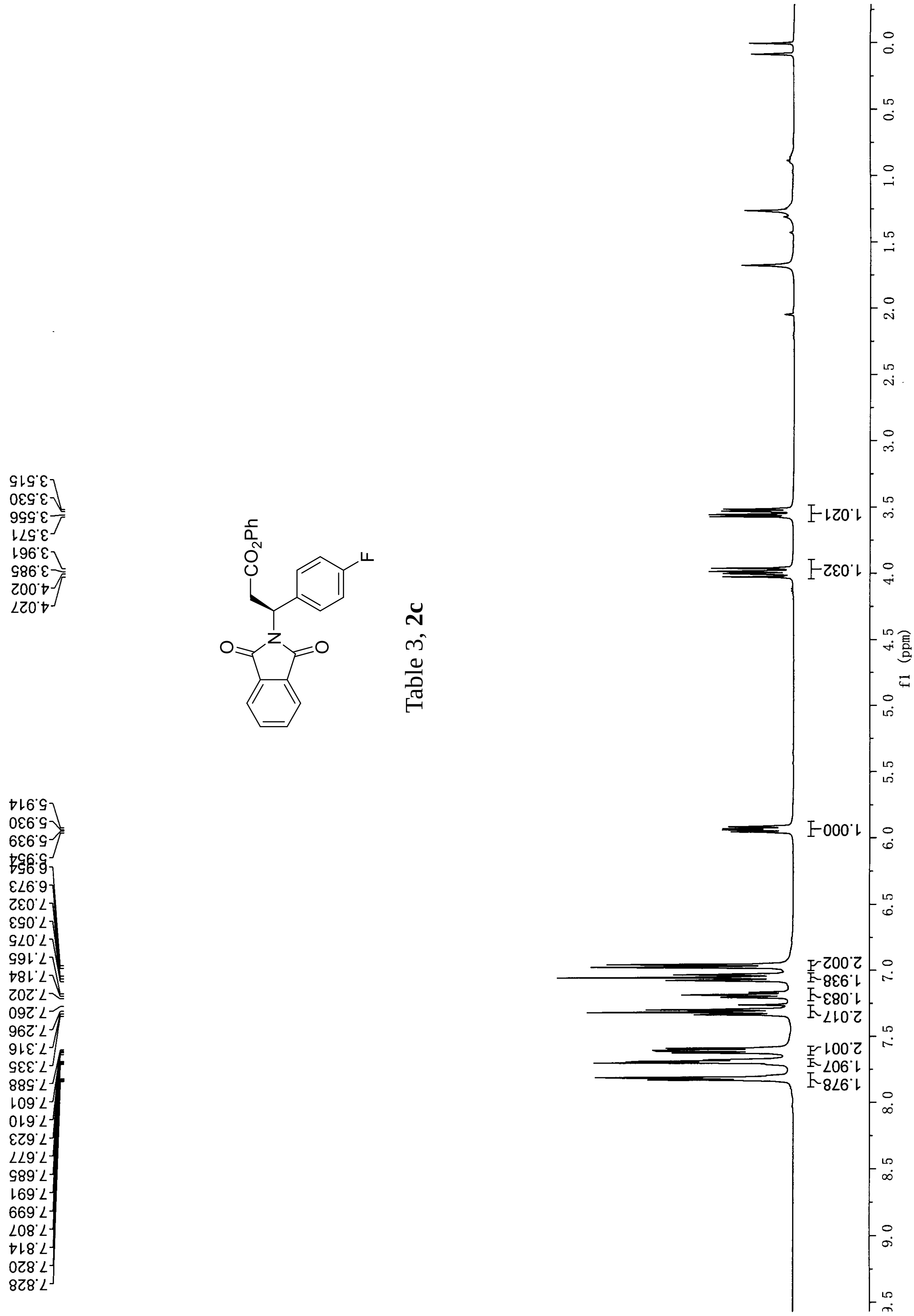


Table 3, **2b**

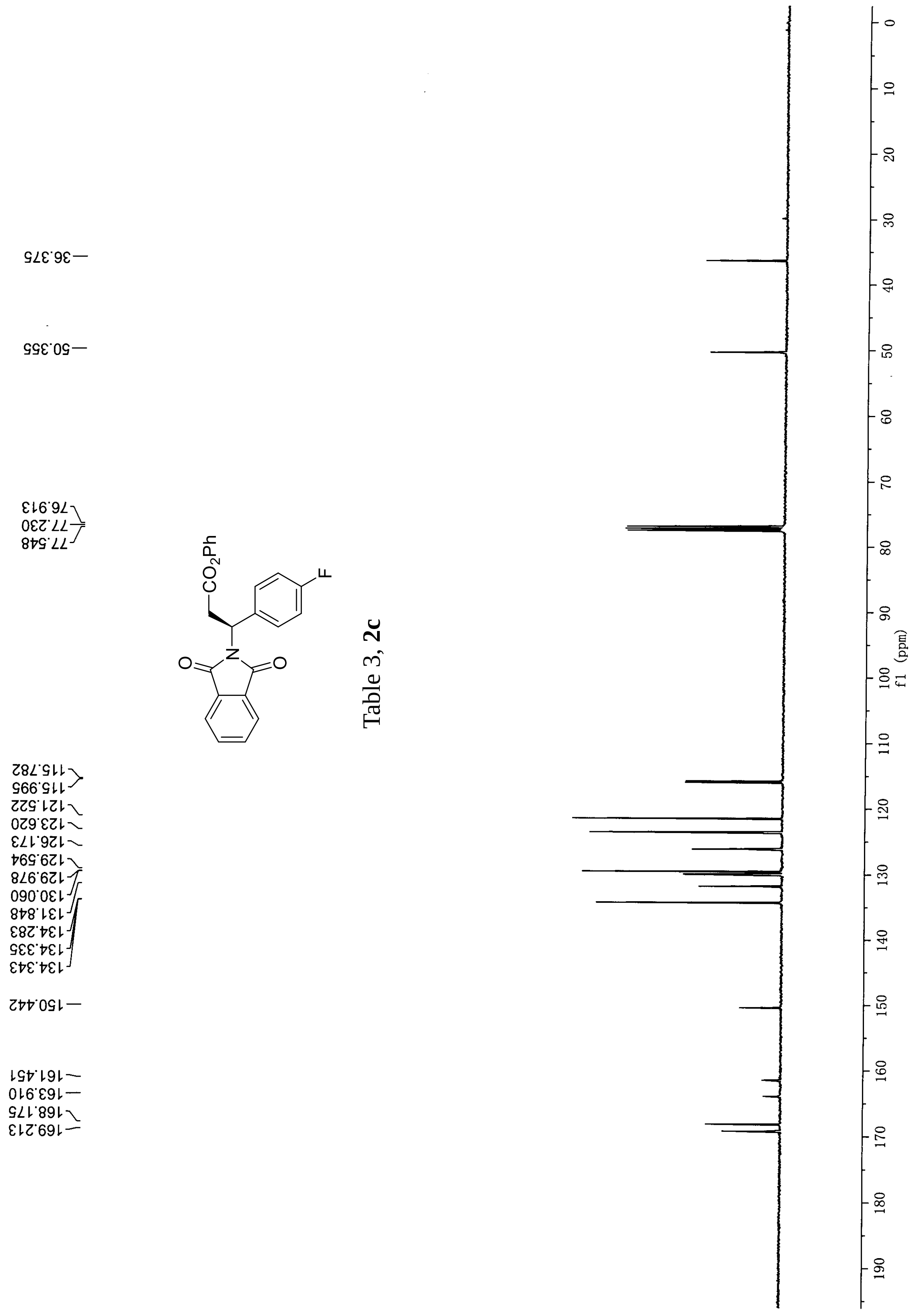
^{13}C NMR Spectrum of **2b** ($CDCl_3$, 100 MHz)



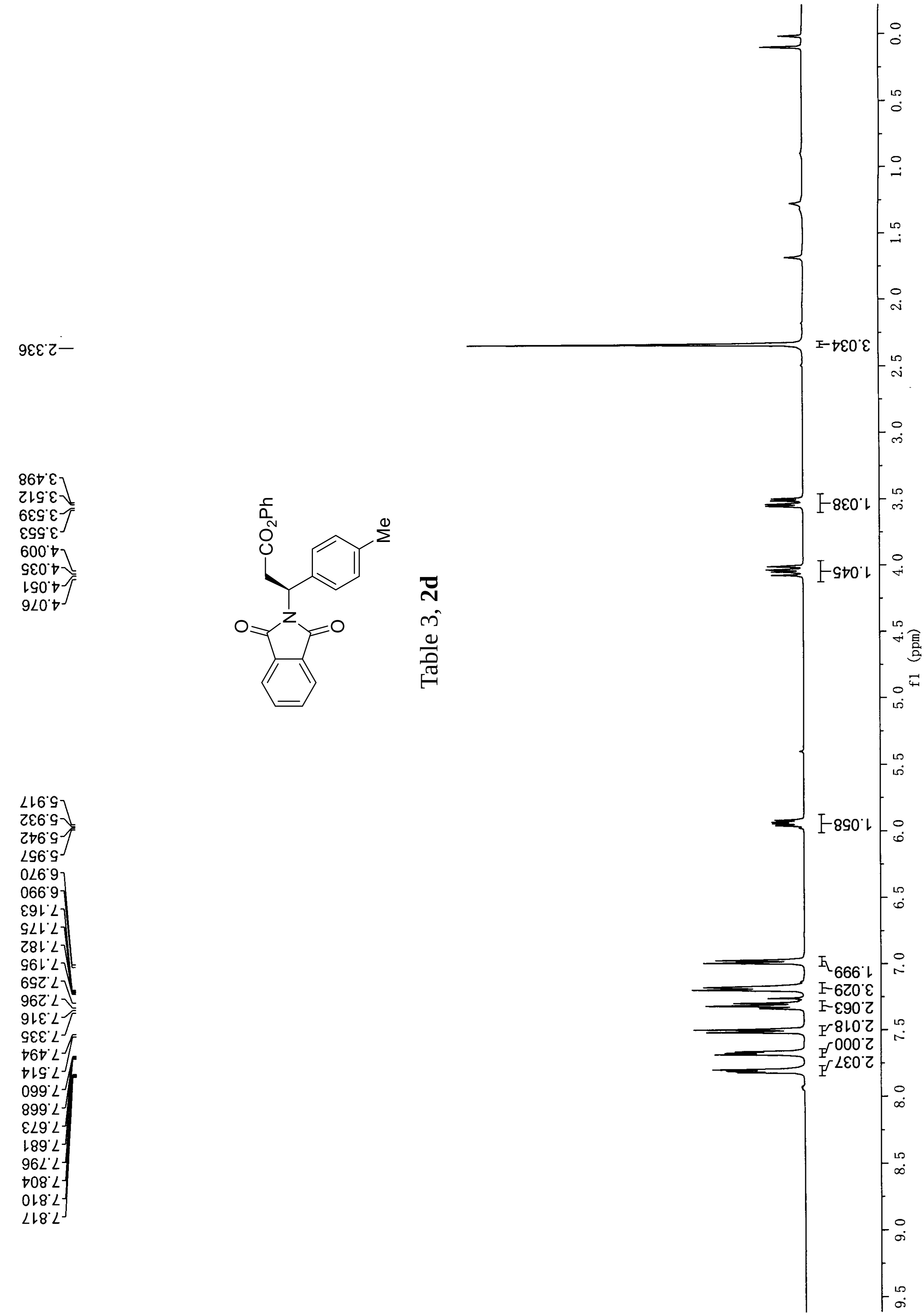
[1]H NMR Spectrum of **2c** ($CDCl_3$, 400 MHz)



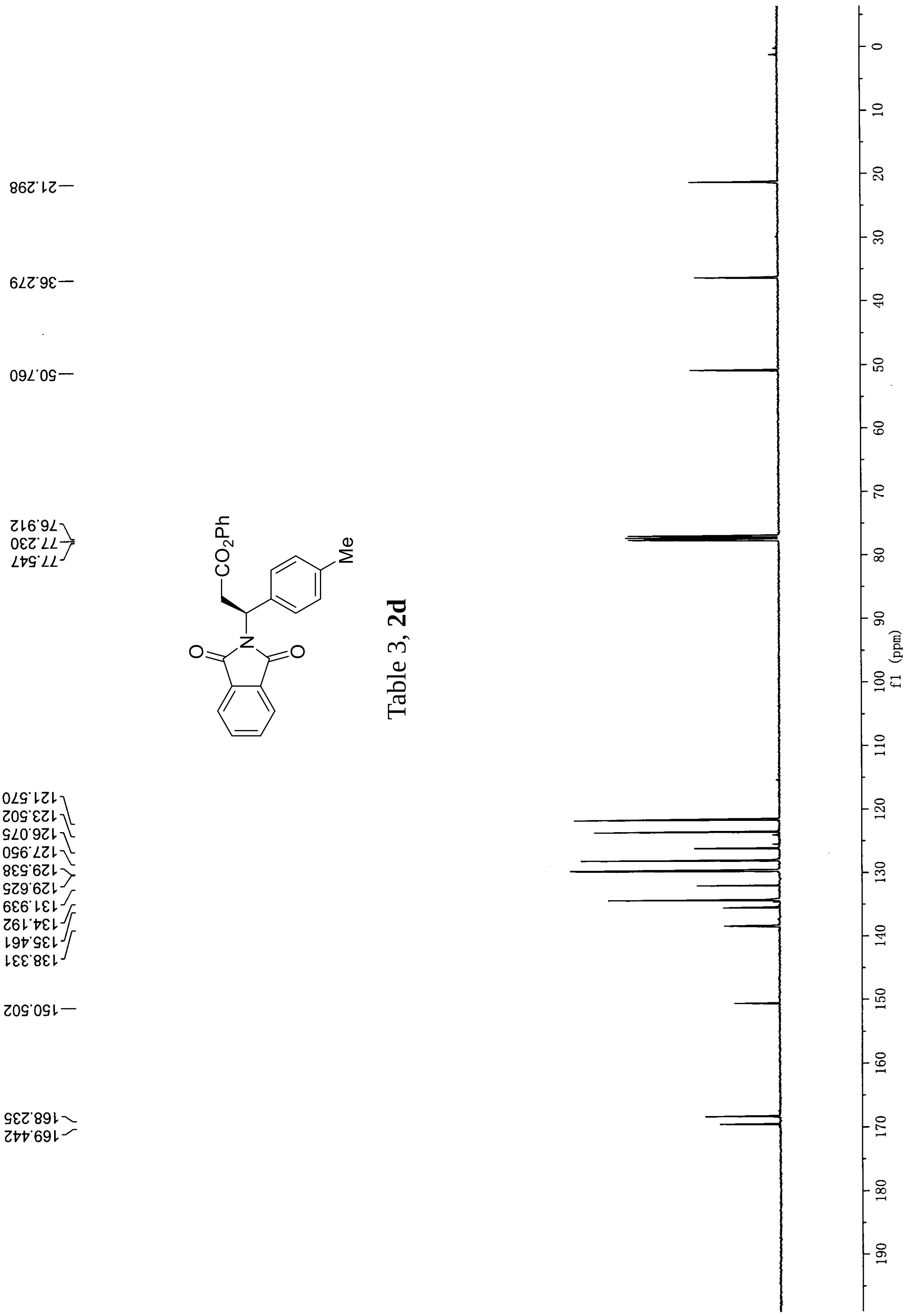
[13]C NMR Spectrum of **2c** ($CDCl_3$, 100 MHz)



[1]H NMR Spectrum of **2d** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **2d** ($CDCl_3$, 100 MHz)



[1]H NMR Spectrum of **2e** ($CDCl_3$, 400 MHz)

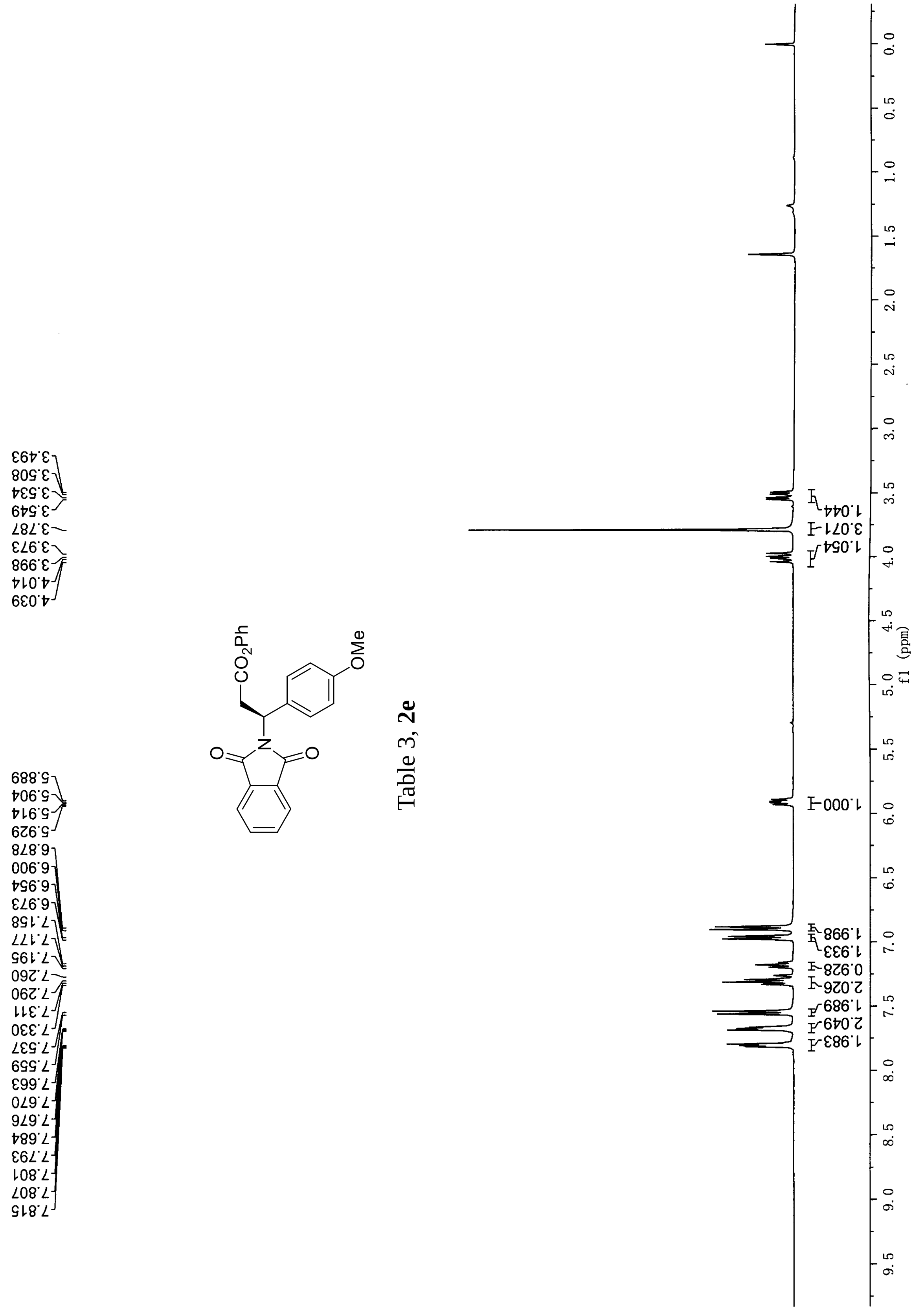
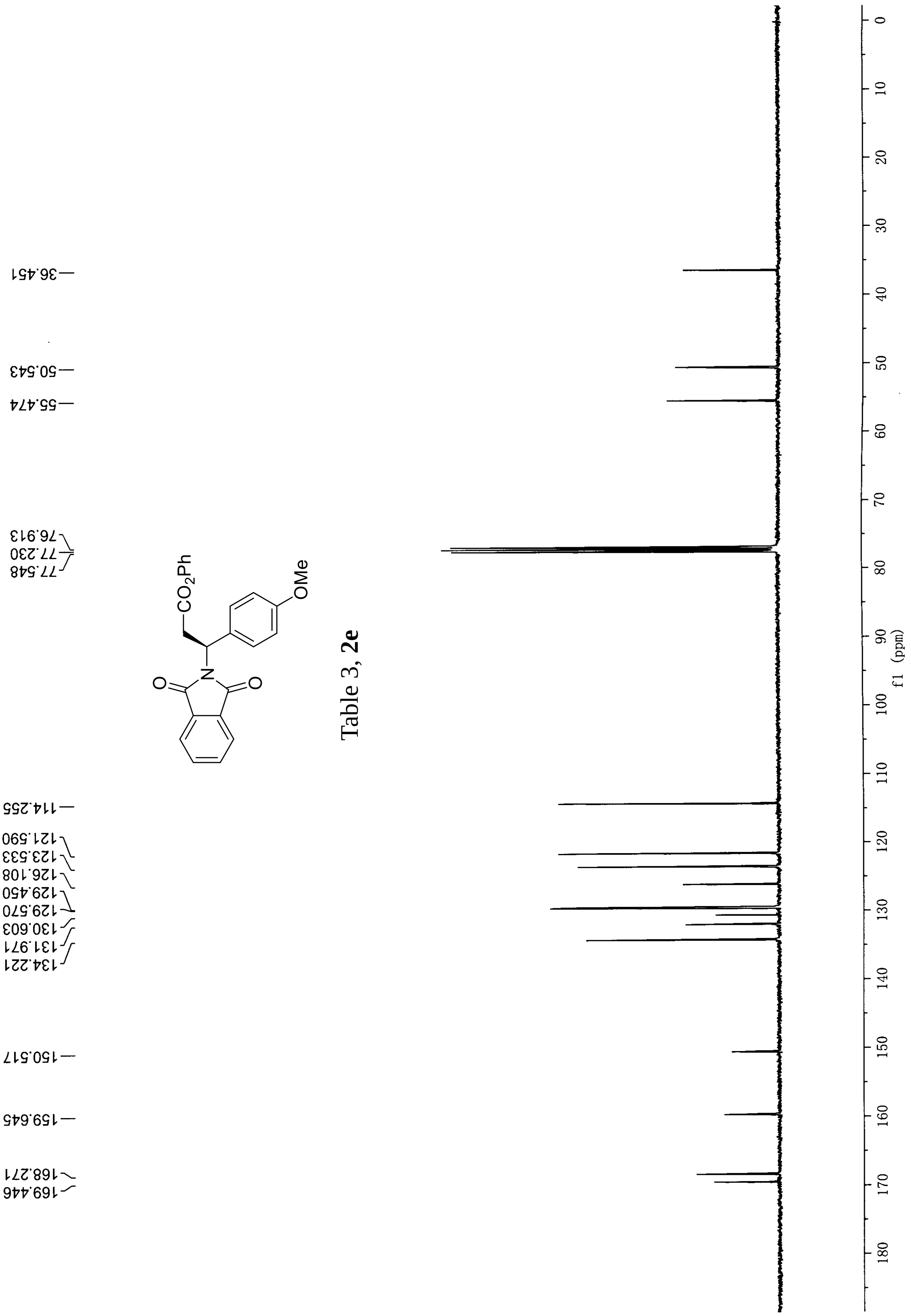


Table 3, **2e**

[13]C NMR Spectrum of **2e** ($CDCl_3$, 100 MHz)



[1]H NMR Spectrum of **2f** ($CDCl_3$, 400 MHz)

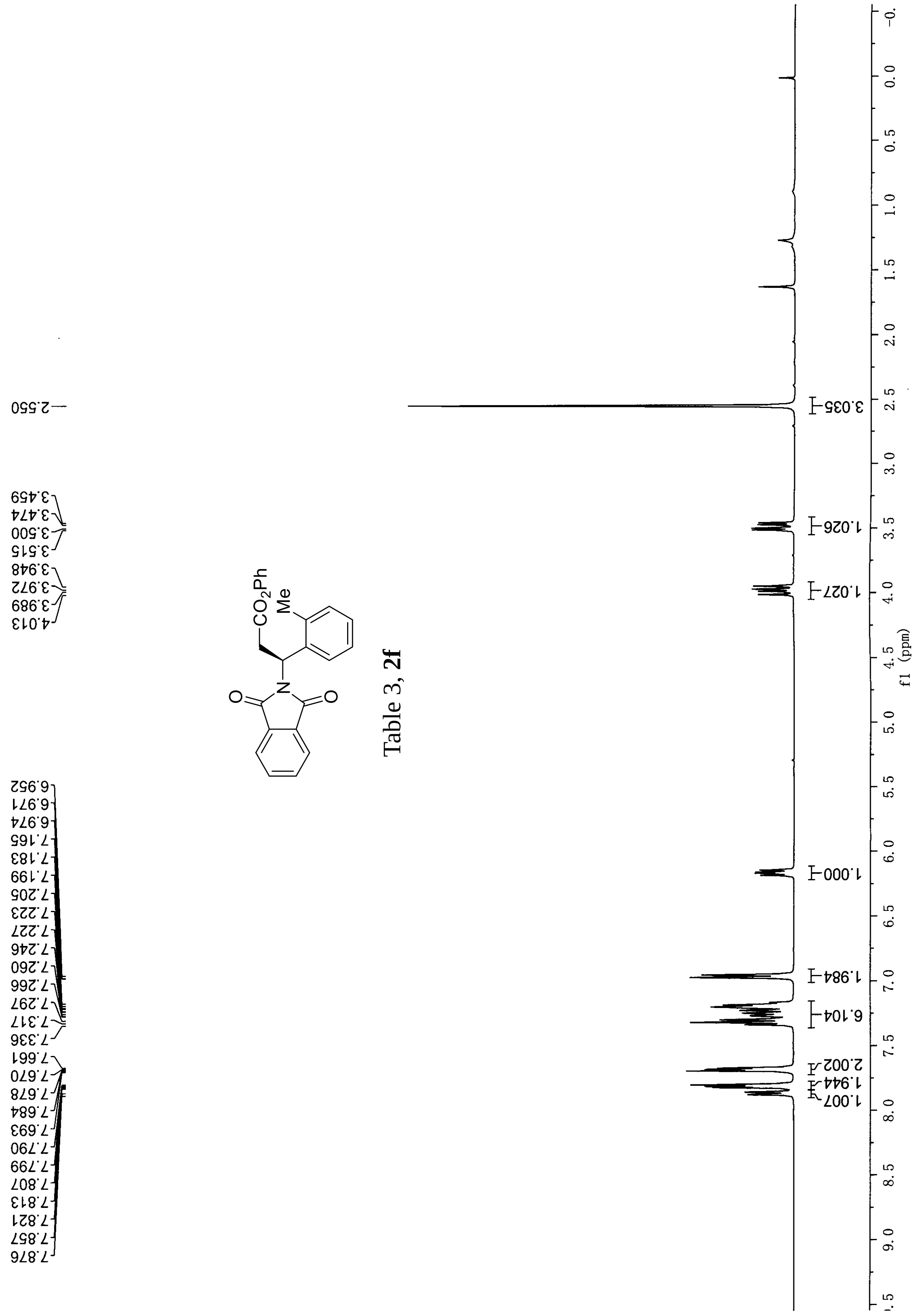


Table 3, **2f**

^{13}C NMR Spectrum of **2f** ($CDCl_3$, 100 MHz)

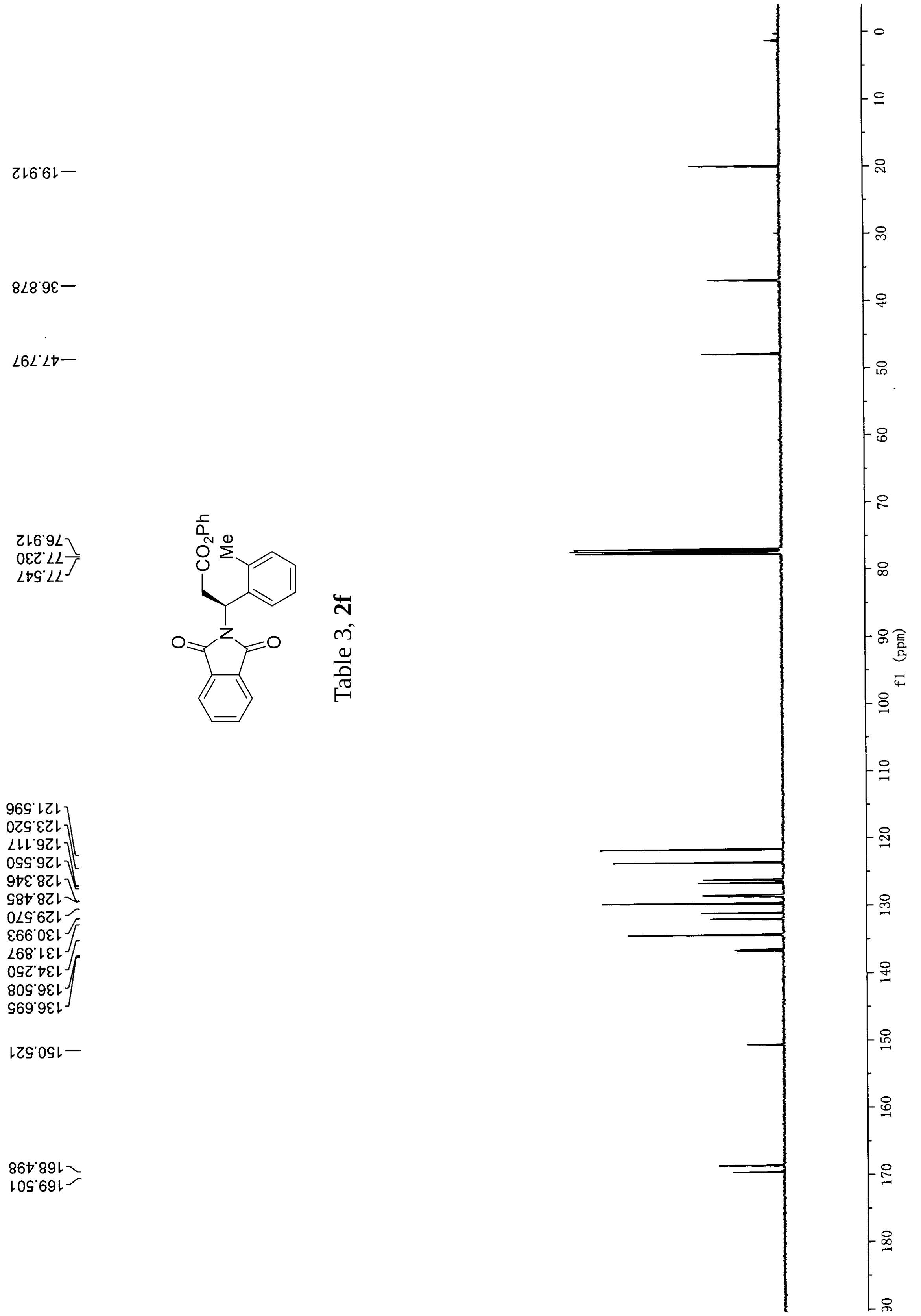
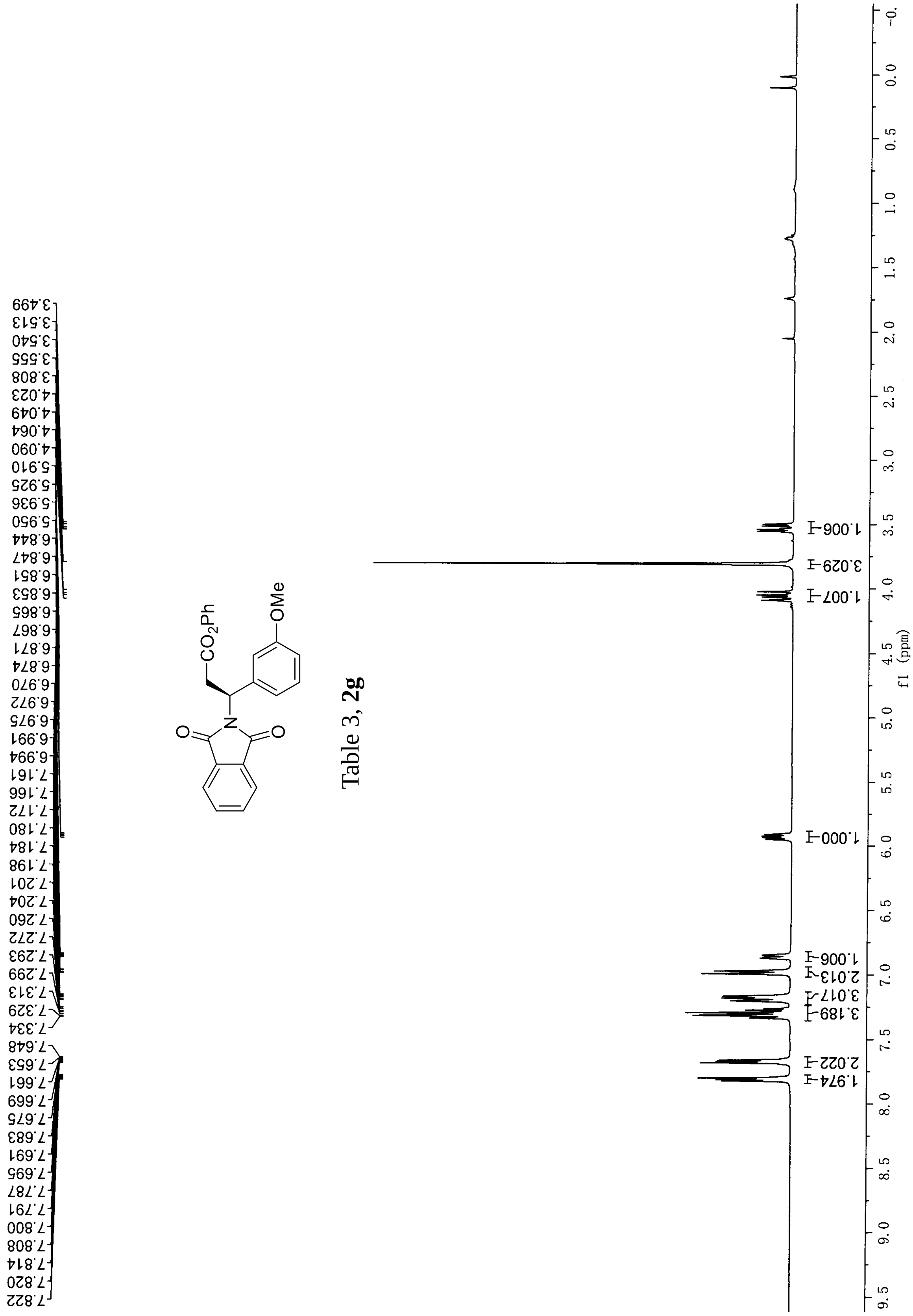
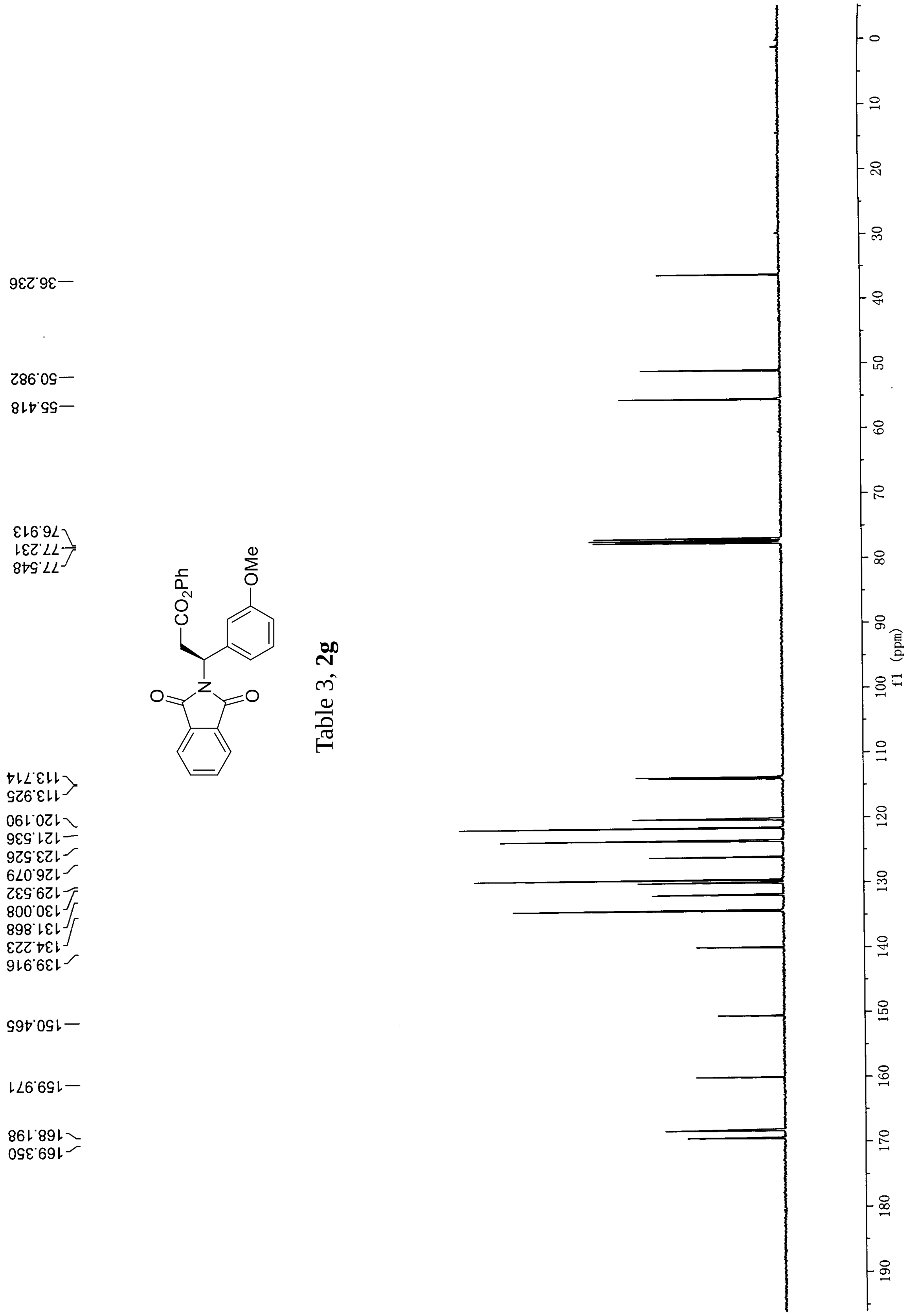


Table 3, **2f**

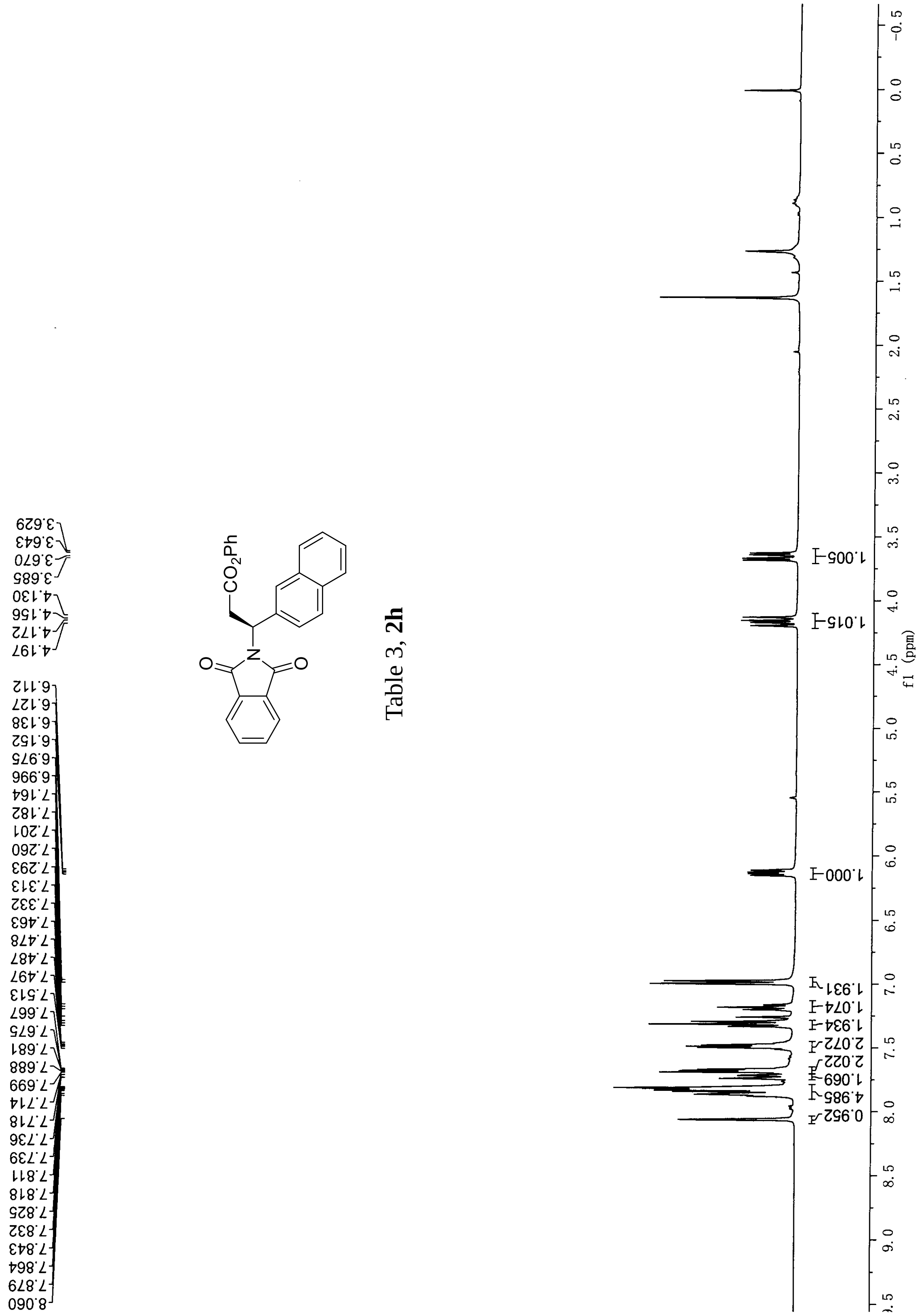
[1]H NMR Spectrum of **2g** ($CDCl_3$, 400 MHz)



[13]C NMR Spectrum of **2g** ($CDCl_3$, 100 MHz)



[1]H NMR Spectrum of **2h** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **2h** ($CDCl_3$, 100 MHz)

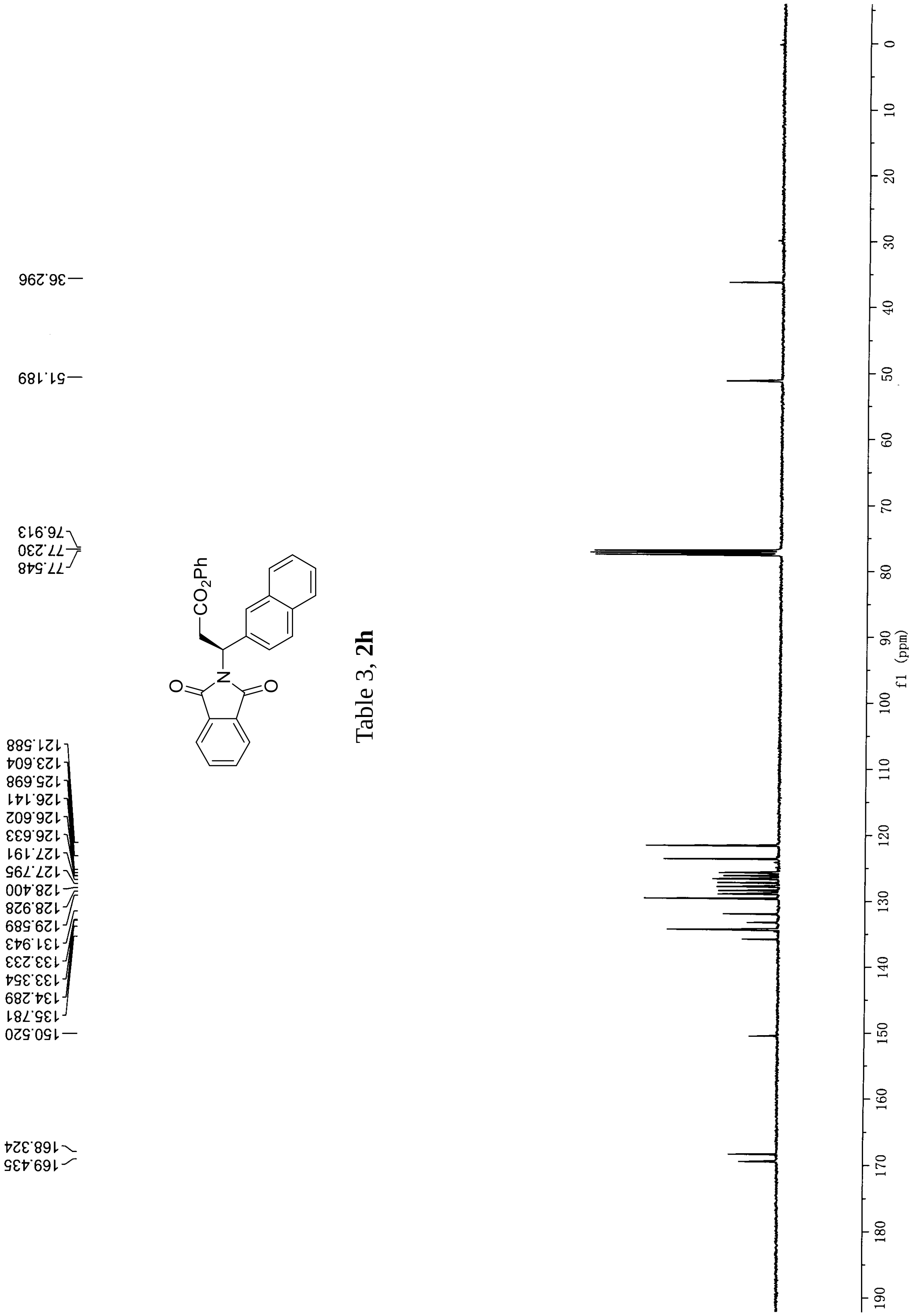


Table 3, **2h**

[1]H NMR Spectrum of **2i** ($CDCl_3$, 400 MHz)

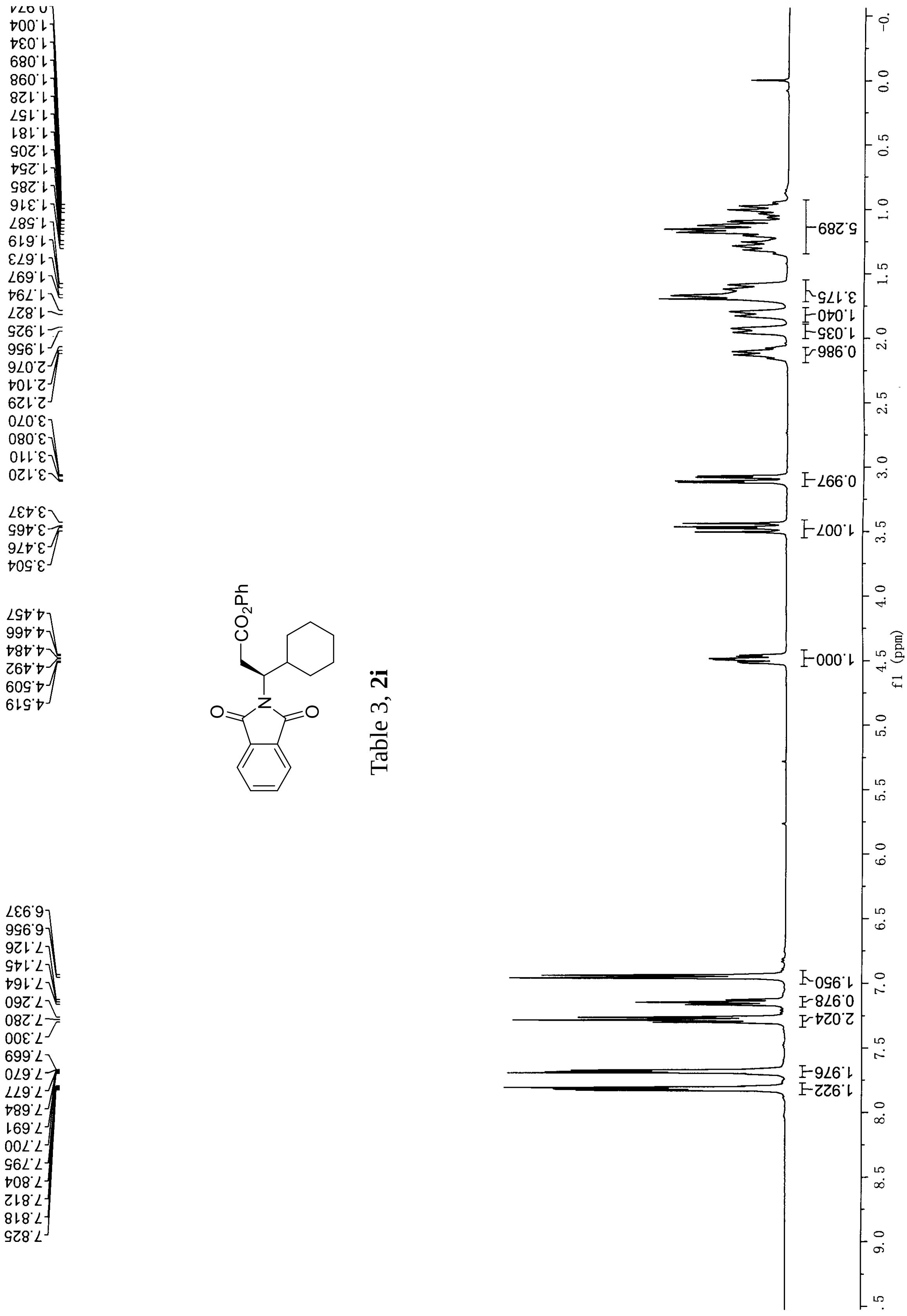
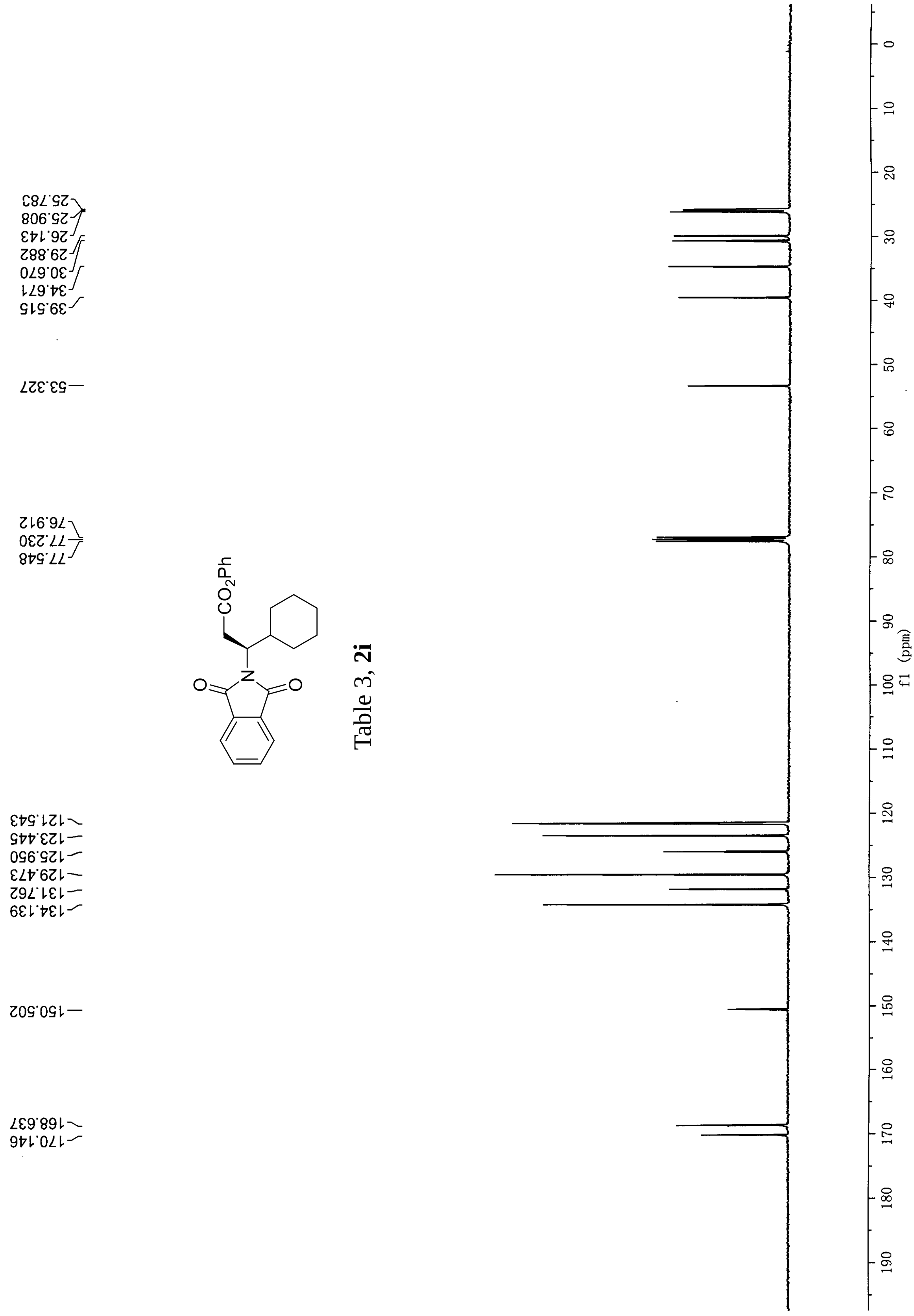
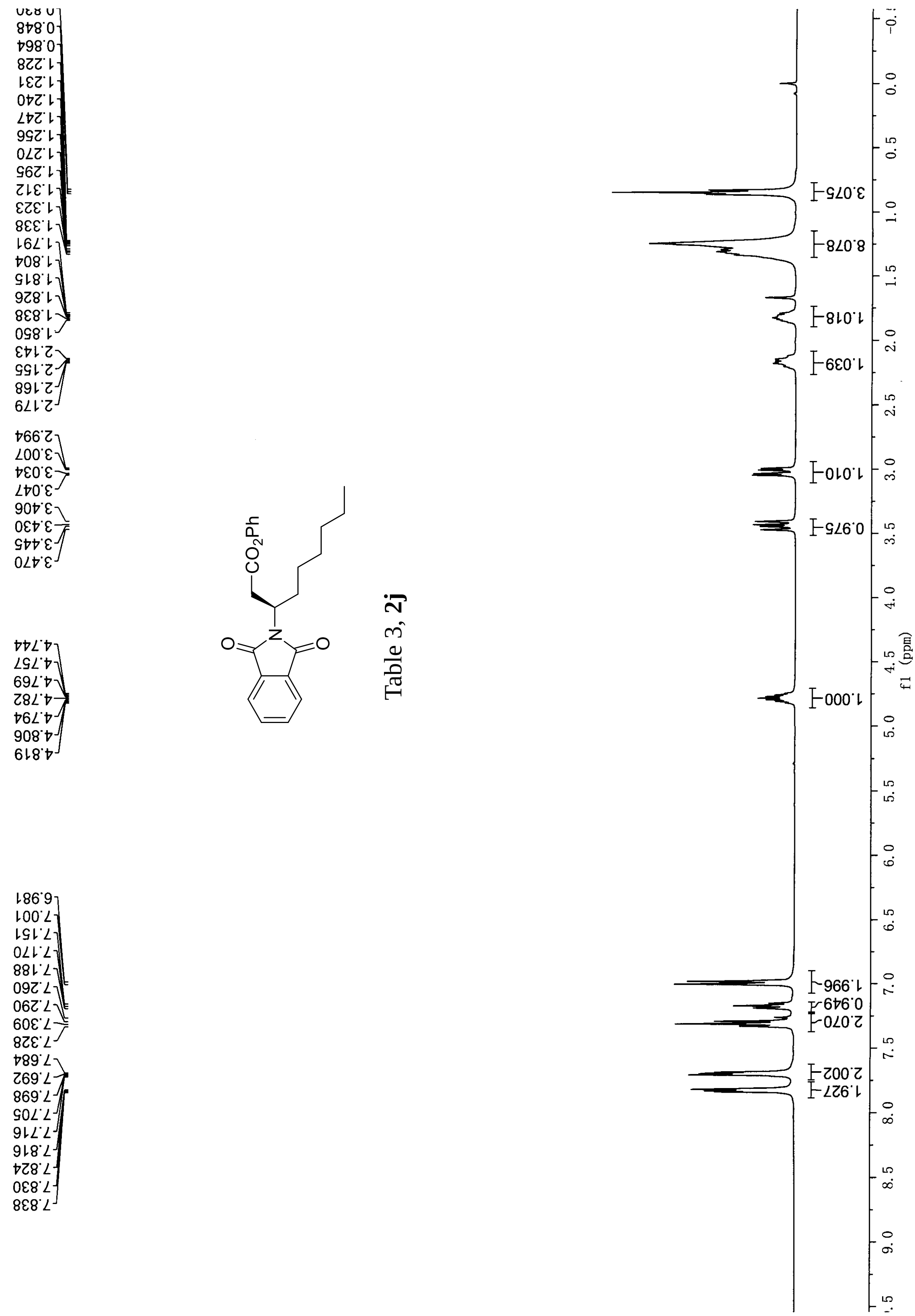


Table 3, **2i**

^{13}C NMR Spectrum of **2i** ($CDCl_3$, 100 MHz)



[1]H NMR Spectrum of **2j** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **2j** ($CDCl_3$, 100 MHz)

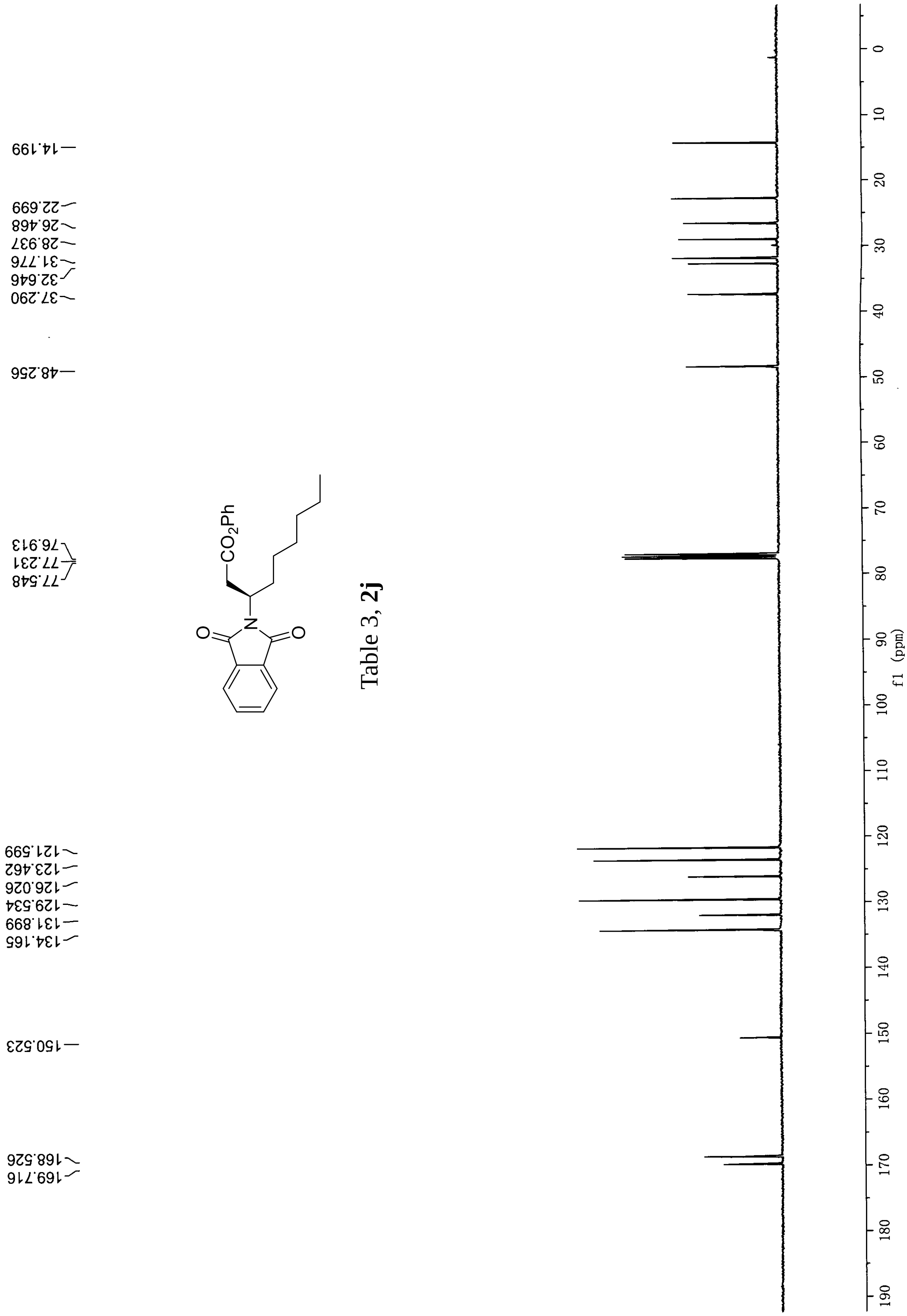
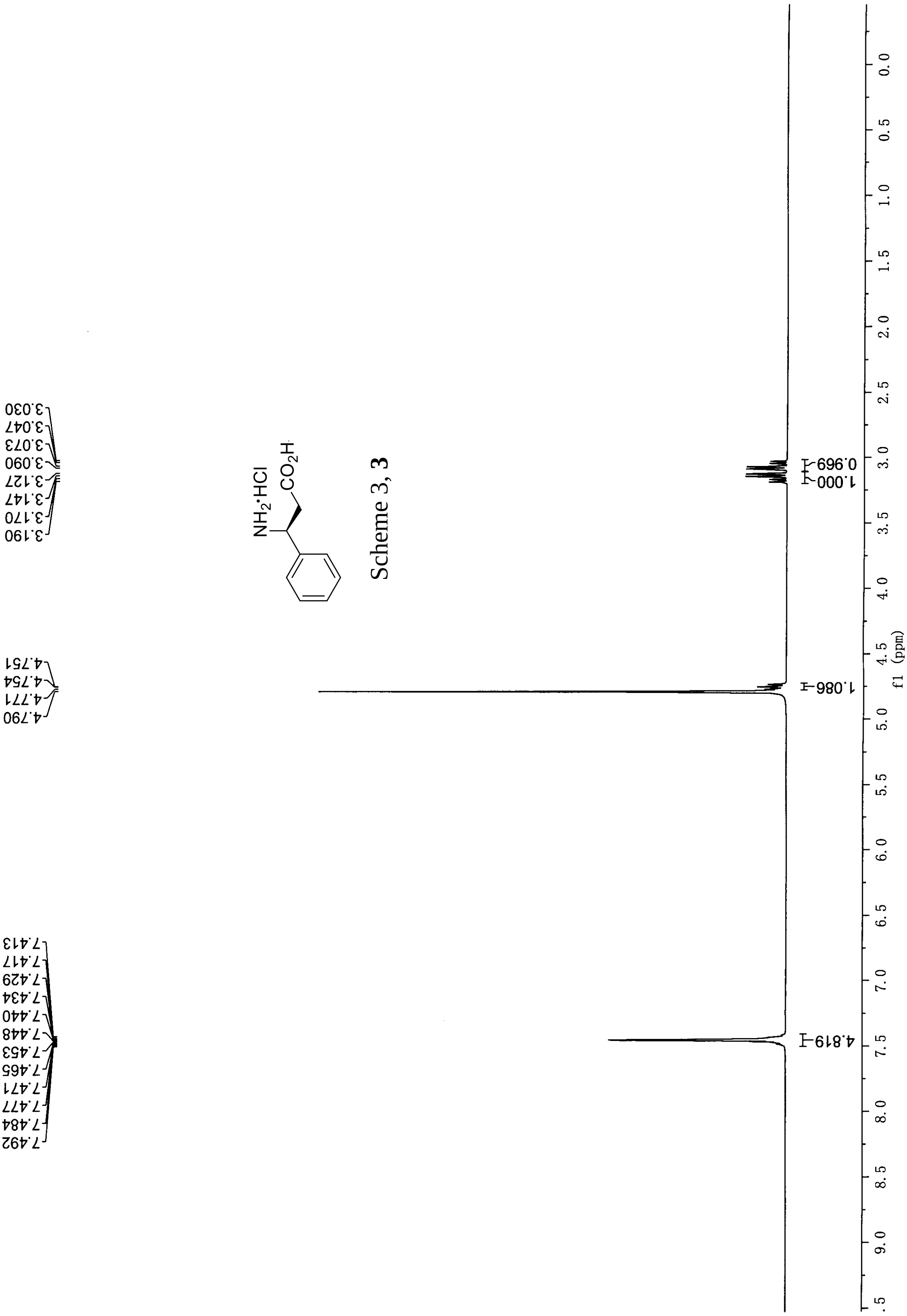
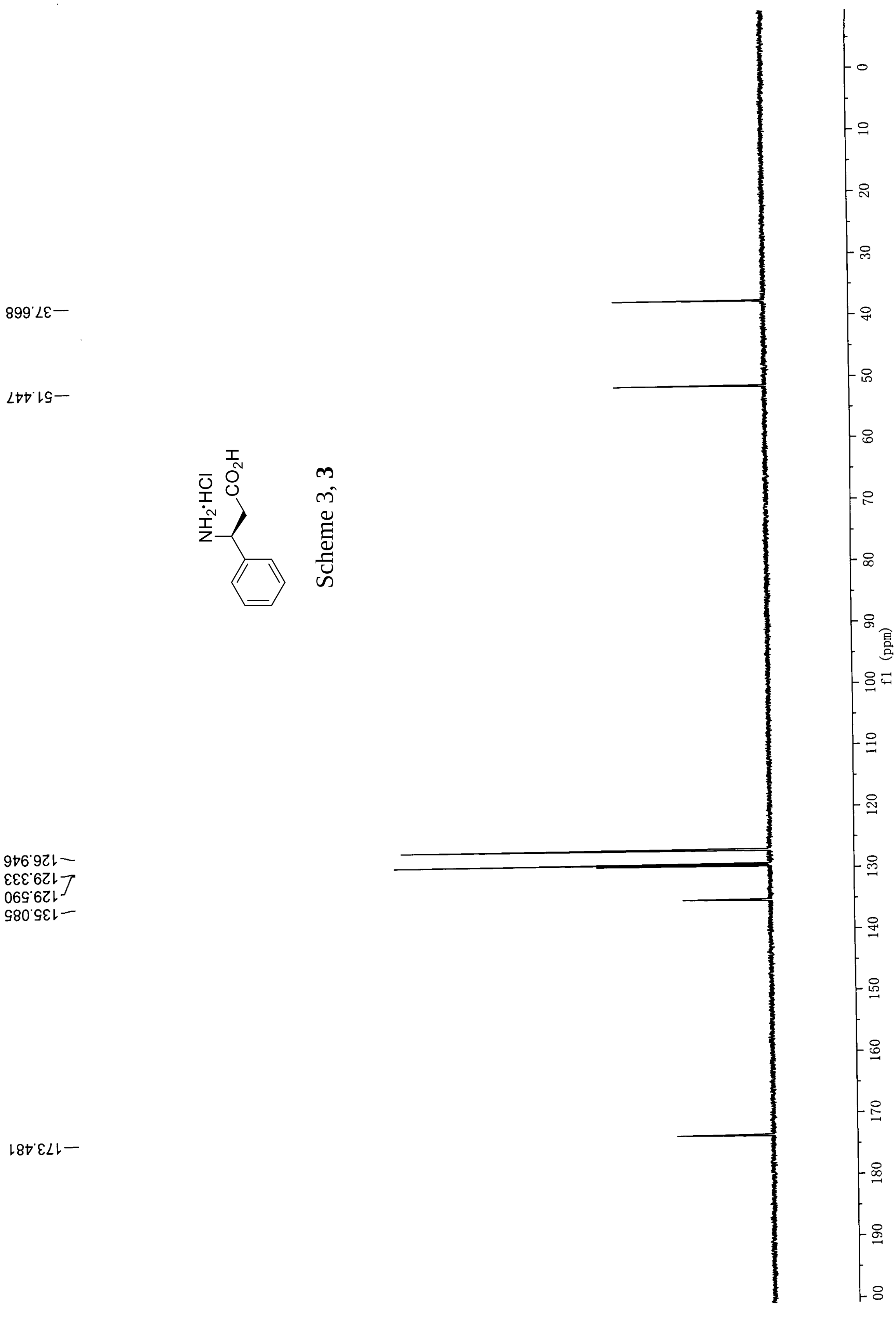


Table 3, **2j**

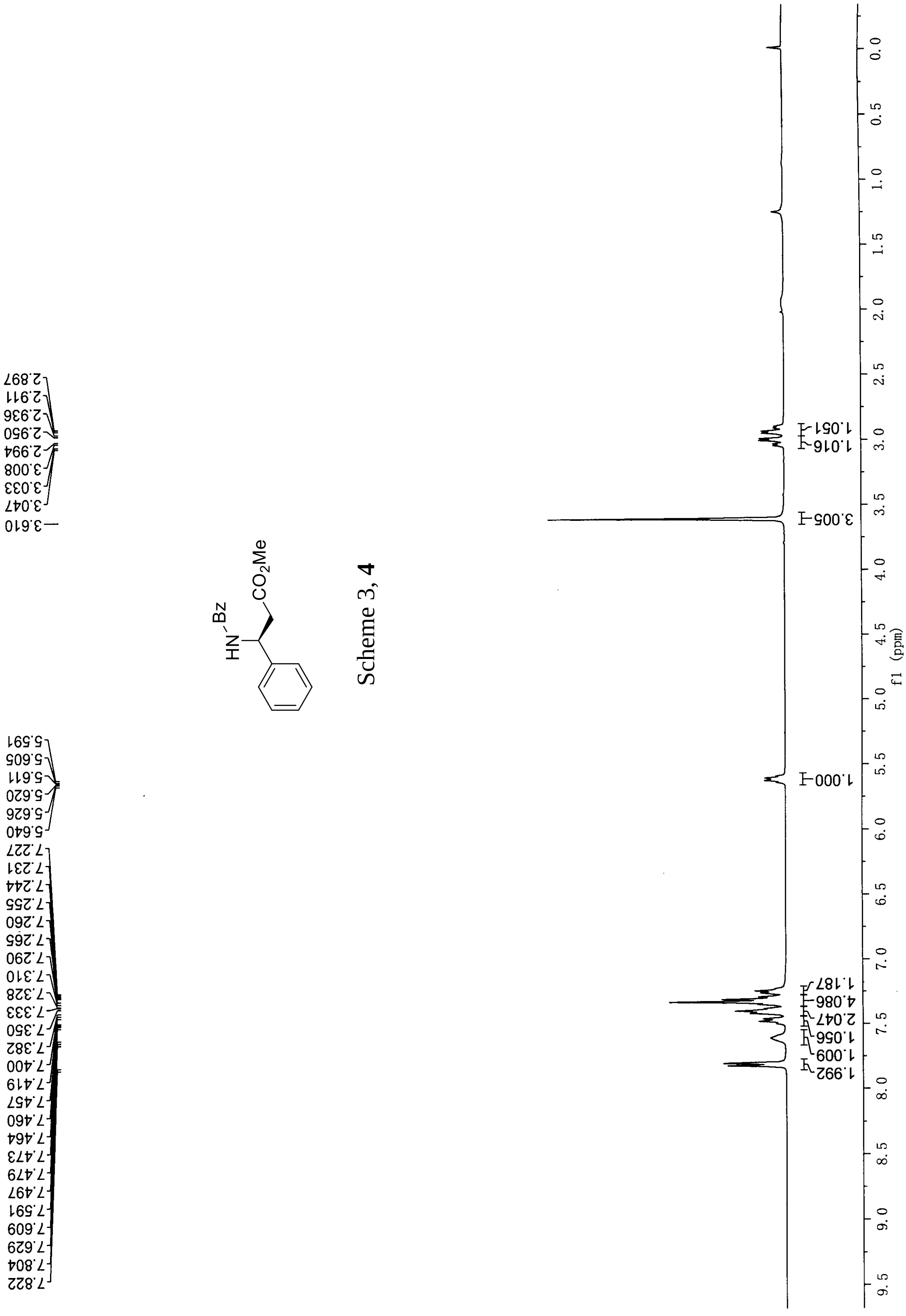
^{1}H NMR Spectrum of **3** (D_2O, 400 MHz)



^{13}C NMR Spectrum of **3** (D_2O, 100 MHz)



[1]H NMR Spectrum of **4** ($CDCl_3$, 400 MHz)



[13]C NMR Spectrum of **4** ($CDCl_3$, 100 MHz)