Electronic Supplementary Information

Enantioselective synthesis of α,α-disubstituted α-amino acids via direct catalytic asymmetric addition of acetonitrile to α-iminoesters

Shaoquan Lin, Naoya Kumagai,* and Masakatsu Shibasaki*

Institute of Microbial Chemistry (BIKAKEN), Tokyo, Japan

mshibasa@bikaken.or.jp, nkumagai@bikaken.or.jp

contents

1. General

The enantioslective synthesis of α,α-disubstituted α-amino acids via direct catalytic asymmetric addition of acetonitrile to α-iminoesters was performed in a flame-dried 20 mL glass test tube with a Teflon-coated magnetic stirring bar unless otherwise noted. The flasks or test tubes were fitted with a 3-way glass stopcock and reactions were run under an Ar atmosphere. Air- and moisture-sensitive liquids were transferred via a gas-tight syringe and a stainless-steel needle. All work-up and purification procedures were carried out with reagent-grade solvents under ambient atmosphere.

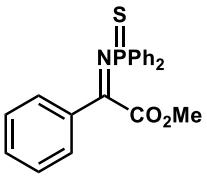
2. Instrumentation

Infrared (IR) spectra were recorded on a HORIBA FT210 Fourier transform infrared spectrophotometer. NMR was recorded on Bruker AVANCE III HD400. Chemical shifts for proton are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (TMS in $CDCl_3$: δ 0.00 ppm; CD_3CN: δ 1.94 ppm). For ^{13}C NMR, chemical shifts were reported in the scale relative to NMR solvent ($CDCl_3$: δ 77.0 ppm; CD_3CN: δ 118.26 ppm) as an internal reference. For ^{31}P NMR, chemical shifts were reported in the scale relative to $OP(OPh)_3$ (δ –17.6035 ppm in $CDCl_3$) as an external reference. For ^{19}F NMR, chemical shifts were reported in the scale relative to $PhCF_3$(δ –62.7680 ppm in $CDCl_3$) as an external reference. NMR data are reported as follows: chemical shifts, multiplicity (s: singlet, d: doublet, dd: doublet of doublets, t: triplet, q: quartet, m: multiplet, br: broad signal), coupling constant (Hz), and integration. Optical rotation was measured using a 1 mL cell with a 1.0 dm path length on a JASCO polarimeter P-1030. High-resolution mass spectra (ESI TOF (+)) were measured on Thermo Fisher Scientific LTQ Orbitrap XL. HPLC analysis was conducted on a JASCO HPLC system equipped with Daicel chiral-stationary-phase columns (ϕ 0.46 cm x 25 cm).

3. Materials

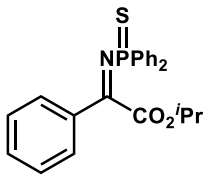
Unless otherwise noted, materials were purchased from commercial suppliers and were used without further purification. THF, MeCN were purified by passing through a solvent purification system (Glass Contour). MS 4A was purchased from Nacalai Tesque Co. Ltd. and dried by microwave oven three time under reduced presure. Barton's base and $[Rh(cod)(OMe)]_2$ were purchased from Aldrich. $[Ir(cod)(OMe)]_2$ was purchased from TCI Co. Ltd. and used as received (opened and handled in a dry box). Column chromatography was performed with silica gel Merck 60 (230-400 mesh ASTM) or silicagel 60 N (spherical, neutral, 40-50 μm) from Kanto Chemical Co. Ltd. Preparative TLC plates (1.05744.0001, PLC Silica gel 60 F_{254}, 0.5 mm) were purchased from Merck. *N*-thiophosphinoyl ketimines were prepared according to a modified reported procedure.[1] *N*-heterocyclic carbene (NHC) ligands were synthesised by following the reported precedures.[2]

Methyl 2-((diphenylphosphorothioyl)imino)-2-phenylacetate (4b)



Yellow crystal; M. p. 144–145 °C; IR (KBr): ν 1735, 1631, 1591 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.06–8.00 (m, 4H), 7.95–7.93 (m, 2H), 7.61–7.57 (m, 1H), 7.51–7.71 (m, 8H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6 (d, J = 9.0 Hz), 165.0 (d, J = 17.1 Hz), 135.6, 134.5, 134.2, 134.0, 133.8, 131.51, 131.48, 131.4, 131.3, 129.0, 128.9, 128.5, 128.3, 52.4; ^{31}P NMR ($CDCl_3$): δ 52.0; HRMS (ESI) Anal. calcd. for $C_{21}H_{18}O_2NNaPS$ m/z 402.0688 $[M+Na]^+$, found 402.0680.

Isopropyl 2-((diphenylphosphorothioyl)imino)-2-phenylacetate (4c)

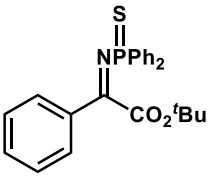


Yellow crystal; M. p. 105–106 °C; IR (KBr): ν 1726, 1631, 1612 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.06–8.01 (m, 4H), 7.95–7.93 (m, 2H), 7.60–7.56 (m, 1H), 7.50–7.41 (m, 8H), 5.43–5.34 (m, 1H), 1.39 (d, J = 6.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0 (d, J = 8.7 Hz), 164.0 (d, J = 16.8 Hz), 135.9, 134.8, 134.6, 134.4, 133.6, 131.39, 131.36, 131.28, 129.0, 128.9, 128.4, 128.3, 71.2, 21.6; ^{31}P NMR ($CDCl_3$): δ 51.5; HRMS (ESI) Anal. calcd. for $C_{23}H_{22}O_2NNaPS$ m/z 430.1001 $[M+Na]^+$, found 430.0997.

1 (a) Jennings, W. B.; Lovely, C. J. *Tetrahedron Lett.* **1988**, *29*, 3725; (b) Jennings, W. B.; Lovely, C. J. *Tetrahedron* **1991**, *47*, 5561.

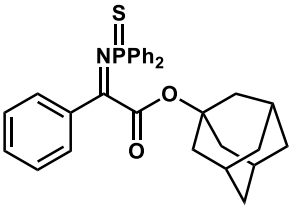
2 (a) Vora, H. U.; Lathrop, S. P.; Reynolds, N. T.; Kerr, M. S.; Read de Alaniz, J.; Rovis, T. *Org. Synth.* **2010**, *87*, 350; (b) Zhao, C.; Li, F.; Wang, J. *Angew. Chem. Int. Ed.* **2016**, *55*, 1820.

tert-Butyl 2-((diphenylphosphorothioyl)imino)-2-phenylacetate (4d)



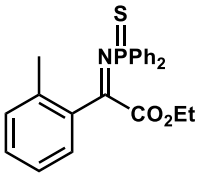
Yellow crystal; M. p. 138–140 °C; IR (KBr): ν 1725, 1682, 1645 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06–8.01 (m, 4H), 7.98–7.96 (m, 2H), 7.59–7.55 (m, 1H), 7.50–7.40 (m, 8H), 1.60 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0 (d, J = 8.5 Hz), 163.2 (d, J = 16.3 Hz), 136.2, 135.2, 135.1, 135.0, 133.3, 131.36, 131.28, 131.25, 129.0, 128.8, 128.4, 128.2, 85.6, 28.2; ^{31}P NMR ($CDCl_3$): δ 50.9; HRMS (ESI) Anal. calcd. for $C_{24}H_{24}O_2NNaPS$ m/z 444.1158 $[M+Na]^+$, found 444.1155.

Adamantan-1-yl 2-((diphenylphosphorothioyl)imino)-2-phenylacetate (4e)



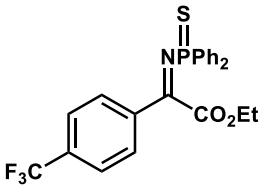
Yellow crystal; M. p. 187–189 °C; IR (KBr): ν 1726, 1639 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06–7.97 (m, 6H), 7.59–7.55 (m, 1H), 7.50–7.40 (m, 8H), 2.32 (d, J = 2.7 Hz, 6H), 2.21 (s, 3H), 1.73–1.74 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7 (d, J = 8.4 Hz), 163.1 (d, J = 16.4 Hz), 136.1, 135.2, 135.1, 134.9, 133.3, 131.4, 131.29, 131.28, 131.24, 139.1, 128.7, 128.4, 128.2, 85.9, 41.5, 36.0, 31.1; ^{31}P NMR ($CDCl_3$): δ 51.0; HRMS (ESI) Anal. calcd. for $C_{30}H_{31}O_2NPS$ m/z 500.1808 $[M+H]^+$, found 500.1805.

Ethyl 2-((diphenylphosphorothioyl)imino)-2-(*o*-tolyl)acetate (4f)



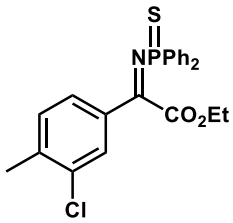
Yellow crystal; M. p. 111–112 °C; IR (KBr): ν 1734, 1644 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01–7.96 (m, 4H), 7.56 (d, J = 7.8 Hz, 2H), 7.47–7.36 (m, 7H), 7.27–7.22 (m, 1H), 4.40 (q, J = 7.2 Hz, 2H), 2.44 (s, 3H), 1.31 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4 (d, J = 10.5 Hz), 164.5 (d, J = 19.0 Hz), 138.9, 135.4, 134.4, 134.2, 134.0, 132.0, 131.77, 131.51, 131.42, 131.40, 130.2, 128.4, 128.2, 126.0, 62.2, 21.7, 13.7; ^{31}P NMR ($CDCl_3$): δ 52.6; HRMS (ESI) Anal. calcd. for $C_{23}H_{22}O_2NNaPS$ m/z 430.1001 $[M+Na]^+$, found 430.0993.

Ethyl 2-((diphenylphosphorothioyl)imino)-2-(4-(trifluoromethyl)phenyl)acetate (4n)



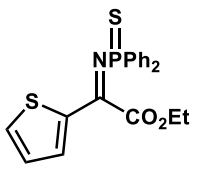
Yellow crystal; M. p. 146–148 °C; IR (KBr): ν 1733, 1638 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07–7.99 (m, 6H), 7.75 (d, J = 8.3 Hz, 2H), 7.51–7.43 (m, 6H), 4.48 (q, J = 7.2 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5 (d, J = 8.4 Hz), 164.0 (d, J = 16.5 Hz), 137.4, 137.2, 135.2, 135.0, 134.6, 134.1, 131.69, 131.66, 131.4, 131.3, 129.2, 128.5, 128.4, 127.5, 125.90, 125.86, 125.82, 124.8, 122.1, 119.4, 62.6, 13.7; ^{19}F NMR (375 MHz, $CDCl_3$): δ –63.2; ^{31}P NMR ($CDCl_3$): δ 52.9; HRMS (ESI) Anal. calcd. for $C_{23}H_{19}O_2NF_3NaPS$ m/z 484.0718 $[M+Na]^+$, found 484.0716.

Ethyl 2-(3-chloro-4-methylphenyl)-2-((diphenylphosphorothioyl)imino)acetate (4p)



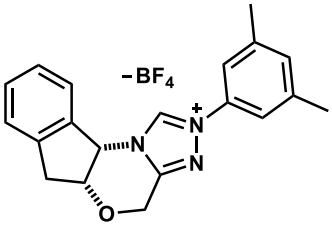
Yellow crystal; M. p. 112–114 °C; IR (KBr): ν 1742, 1639 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–7.98 (m, 4H), 7.93 (d, J = 1.8 Hz, 1H), 7.70 (dd, J = 1.8, 8.0 Hz, 1H), 7.50–7.42 (m, 6H), 7.34 (d, J = 8.0 Hz, 1H), 4.46 (q, J = 7.2 Hz, 2H), 2.45 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6 (d, J = 8.5 Hz), 164.2 (d, J = 16.7 Hz), 142.6, 135.5, 135.3, 134.5, 133.7, 133.5, 131.51, 131.49, 131.38, 131.33, 131.27, 129.2, 128.5, 128.3, 127.3, 62.4, 20.5, 13.7; ^{31}P NMR ($CDCl_3$): δ 52.2; HRMS (ESI) Anal. calcd. for $C_{23}H_{21}O_2NClNaPS$ m/z 464.0611 $[M+Na]^+$, found 464.0602.

Ethyl 2-((diphenylphosphorothioyl)imino)-2-(thiophen-2-yl)acetate (4v)



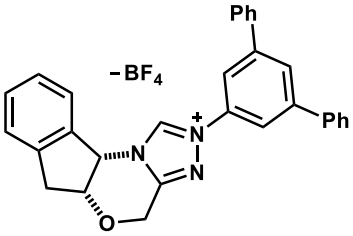
White crystal; M. p. 114–115 °C; IR (KBr): ν 1731, 1620 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–7.98 (m, 4H), 7.69 (dd, J = 0.8, 5.0 Hz, 1H), 7.59 (dd, J = 0.9, 3.8 Hz, 1H), 7.46–7.41 (m, 6H), 7.16–7.14 (m, 1H), 4.44 (q, J = 7.2 Hz, 2H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.5 (d, J = 9.2 Hz), 163.4, 142.3 (d, J = 25.9 Hz), 136.0, 135.0, 134.9, 134.5, 131.35, 131.32, 131.29, 131.18, 128.8 (d, J = 1.4 Hz), 128.4, 128.2, 62.5, 13.7; ^{31}P NMR ($CDCl_3$): δ 51.1; HRMS (ESI) Anal. calcd. for $C_{20}H_{18}O_2NNaPS_2$ m/z 422.0409 $[M+Na]^+$, found 422.0407.

(5a*R*,10b*S*)-2-(3,5-Dimethylphenyl)-5a,10b-dihydro-4*H*,6*H*-indeno[2,1-*b*][1,2,4]triazolo[4,3-*d*][1,4]oxazin-2-ium tetrafluoroborate (L4)



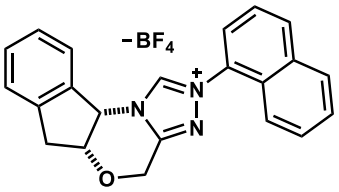
White solid; M. p. 249–252 °C; IR (KBr): *ν* 3421, 3130, 3102, 3055, 3016, 2923, 1621, 1584, 1540, 1483, 1461, 1447, 1427, 1104, 1084, 1006 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ 10.28 (s, 1H), 7.62–7.60 (m, 1H), 7.52 (t, *J* = 0.6 Hz, 2H), 7.42–7.32 (m, 4H), 5.93 (d, *J* = 4.2 Hz, 1H), 5.17 (d, *J* = 16.4 Hz, 1H), 5.03 (dd, *J* = 0.2, 16.4 Hz, 1H), 4.95–4.93 (m, 1H), 3.45 (dd, *J* = 5.0, 17.2 Hz, 1H), 3.23 (d, *J* = 17.2 Hz, 1H), 2.45 (d, *J* = 0.6 Hz, 6H); ^{13}C NMR (100 MHz, CD_3CN): δ 151.1, 141.68, 141.65, 140.3, 136.0, 133.5, 130.6, 128.2, 126.6, 125.5, 119.6, 78.2, 62.6, 60.9, 37.8, 21.2; HRMS (ESI) Anal. calcd. for $C_{20}H_{20}ON_3$ *m*/*z* 318.1601 $[M\text{-}BF_4]^+$, found 318.1602. $[\alpha]_D^{25}$ 246.0 (*c* 0.59, CH_3CN).

(5a*R*,10b*S*)-2-([1,1':3',1''-Terphenyl]-5'-yl)-5a,10b-dihydro-4*H*,6*H*-indeno[2,1-*b*][1,2,4]triazolo[4,3-*d*][1,4]oxazin-2-ium tetrafluoroborate (L5)



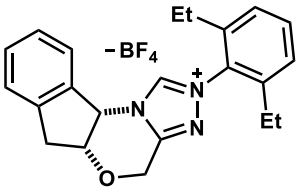
Pale yellow solid; IR (KBr): *ν* 3418, 3054, 2931, 1732, 1614, 1593, 1578, 1535, 1499, 1473, 1462, 1438, 1102, 1083, 1063 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ 10.47 (s, 1H), 8.16 (t, *J* = 1.6 Hz, 1H), 8.09 (d, *J* = 1.6 Hz, 2H), 7.85–7.82 (m, 4H), 7.67 (d, *J* = 7.1 Hz, 1H), 7.59–7.55 (m, 4H), 7.52–7.48 (m, 2H), 7.44–7.38 (m, 3H), 5.98 (d, *J* = 4.2 Hz, 1H), 5.22 (d, *J* = 16.4 Hz, 1H), 5.05 (d, *J* = 16.4 Hz, 1H), 4.99–4.97 (m, 1H), 3.47 (dd, *J* = 5.0, 17.2 Hz, 1H), 3.25 (d, *J* = 17.2 Hz, 1H); ^{13}C NMR (100 MHz, CD_3CN): δ 151.1, 144.6, 141.6, 140.9, 139.5, 137.0, 135.9, 130.6, 130.0, 129.6, 128.2, 128.1, 126.6, 125.4, 119.3, 78.1, 62.7, 60.8, 37.7; HRMS (ESI) Anal. calcd. for $C_{30}H_{24}ON_3$ *m*/*z* 442.1914 $[M\text{-}BF_4]^+$, found 442.1912. $[\alpha]_D^{25}$ 212.4 (*c* 0.76, CH_3CN).

(5a*R*,10b*S*)-2-(Naphthalen-1-yl)-5a,10b-dihydro-4*H*,6*H*-indeno[2,1-*b*][1,2,4]triazolo[4,3-*d*][1,4]oxazin-2-ium tetrafluoroborate (L6)



Purple solid; M. p. 224–227 °C; IR (KBr): *ν* 3421, 3112, 3077, 3032, 2940, 1600, 1577, 1527, 1514, 1486, 1461, 1427, 1120, 1101, 1084, 1019, 1005 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ 10.24 (s, 1H), 8.29 (d, *J* = 8.3 Hz, 1H), 8.16–8.13 (m, 1H), 7.90–7.85 (m, 2H), 7.77–7.69 (m, 3H), 7.57 (d, *J* = 7.4 Hz, 1H), 7.45–7.36 (m, 3H), 6.03 (d, *J* = 4.2 Hz, 1H), 5.24 (d, *J* = 16.4 Hz, 1H), 5.09 (d, *J* = 16.4 Hz, 1H), 5.03–5.01 (m, 1H), 3.51 (dd, *J* = 5.1, 17.2 Hz, 1H), 3.28 (d, *J* = 17.2 Hz, 1H); ^{13}C NMR (100 MHz, CD_3CN): δ 151.5, 143.9, 141.8, 136.1, 135.1, 133.5, 132.1, 130.6, 129.6, 129.5, 128.7, 128.4, 128.2, 126.7, 126.2, 126.1, 125.5, 122.6, 78.3, 62.7, 61.1, 37.9; HRMS (ESI) Anal. calcd. for $C_{22}H_{18}ON_3$ *m*/*z* 340.1444 $[M\text{-}BF_4]^+$, found 340.1446. $[\alpha]_D^{25}$ 138.5 (*c* 0.76, CH_3CN).

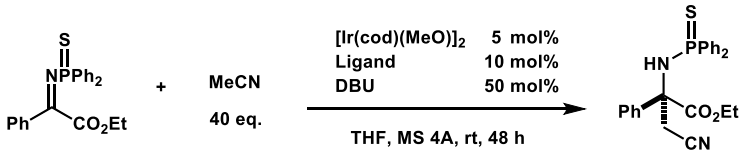
(5a*R*,10b*S*)-2-(2,6-Diethylphenyl)-5a,10b-dihydro-4*H*,6*H*-indeno[2,1-*b*][1,2,4]triazolo[4,3-*d*][1,4]oxazin-2-ium tetrafluoroborate (L7)

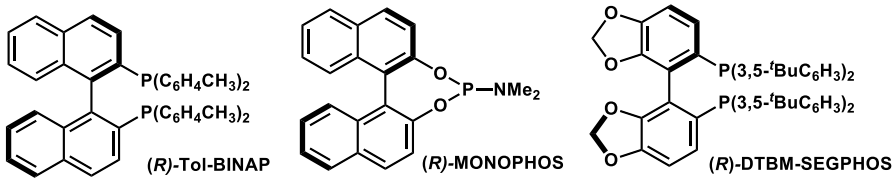


White solid; M. p. 204–206 °C; IR (KBr): *ν* 3421, 3124, 3088, 3049, 2973, 2938, 2905, 2880, 1579, 1531, 1485, 1463, 1432, 1105, 1086, 1058, 1001 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ 10.11 (s, 1H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.45–7.36 (m, 6H), 6.02 (d, *J* = 4.2 Hz, 1H), 5.17 (d, *J* = 16.2 Hz, 1H), 5.05–5.01 (m, 2H), 3.50 (dd, *J* = 5.0, 17.3 Hz, 1H), 3.25 (d, *J* = 17.3 Hz, 1H), 2.42 (brs, 4H), 1.14 (S, 6H); ^{13}C NMR (100 MHz, CD_3CN): δ 151.8, 143.9, 142.5, 141.8, 136.5, 133.4, 130.6, 128.44, 128.40, 126.8, 124.5, 78.1, 62.8, 61.1, 38.0, 24.6, 15.4; HRMS (ESI) Anal. calcd. for $C_{22}H_{24}ON_3$ *m*/*z* 346.1914 $[M\text{-}BF_4]^+$, found 346.1911. $[\alpha]_D^{24}$ 89.9 (*c* 0.55, CH_3CN).

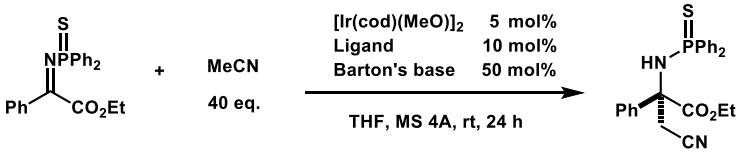
4. General Procedure and Characterization of the Products

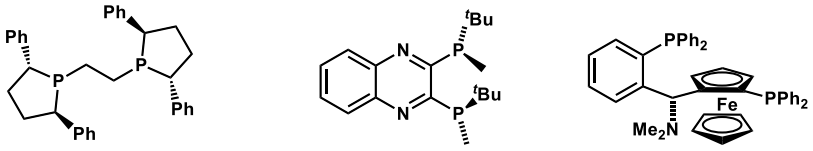
4.1. Ligand screening.



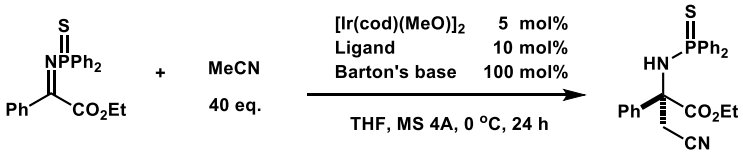


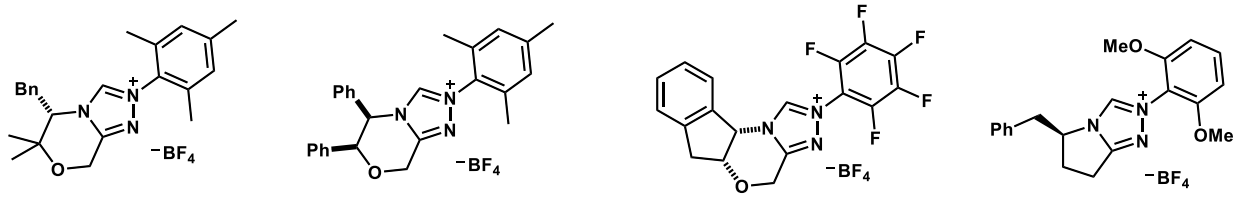
No reaction | No reaction | No reaction



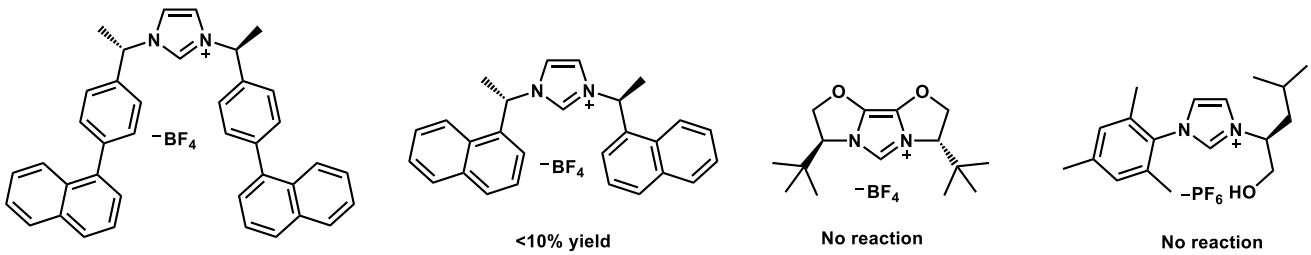


14% yield, 19% ee | trace | trace





32% yield, 14% ee | 40% yield, -8% ee | 28% yield, -28% ee | 28% yield, -2% ee



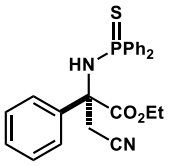
18% yield, 1% ee | <10% yield | No reaction | No reaction

4.2. Catalytic asymmetric Mannich-type reaction of α,β-unsaturated γ-butyrolactam to ketimines.

A flame-dried 20 mL test tube equipped with a magnetic stirring bar and 3-way glass stopcock was charged with $[Ir(cod)(OMe)]_2$ (3.3 mg, 0.005 mmol), NHC precursor (5.0 mg, 0.01 mmol) and MS 4A (100 mg) under Ar atmosphere and THF (0.5 mL) was added at room temperature, then Barton's base (20.0 μL, 0.1 mmol) was added. The mixture was stirred at room temperature for 0.5 h and then cooled to –5 °C. Ketimine (0.1 mmol) in THF (0.5 mL) was added via a gas-tight syringe with a stainless steel needle under an Ar atmosphere. Then MeCN (210 μL, 4 mmol) was added via a

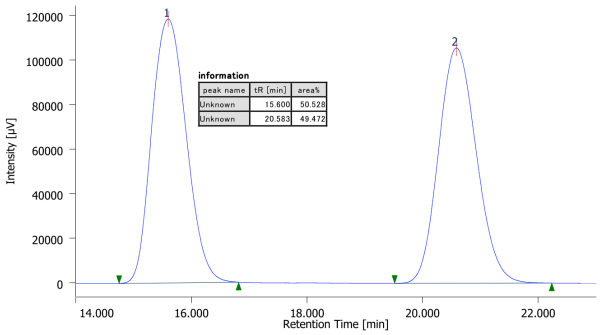
gas-tight syringe with a stainless steel needle under an Ar atmosphere. The resulting reaction mixture was stirred at –5 °C for 5 d. Reaction was quenched with AcOH (0.2 ml, 1.0 M in THF). Diluted the mixture with EtOAc and passed through a shot pad of silica gel column (eluted with EtOAc). After evaporation, the residue was purified by preparative TLC (*n*-hexane/ethyl acetate = 4/1) to give the pure product.

Ethyl (*R*)-3-cyano-2-((diphenylphosphorothioyl)amino)-2-phenylpropanoate (8a)

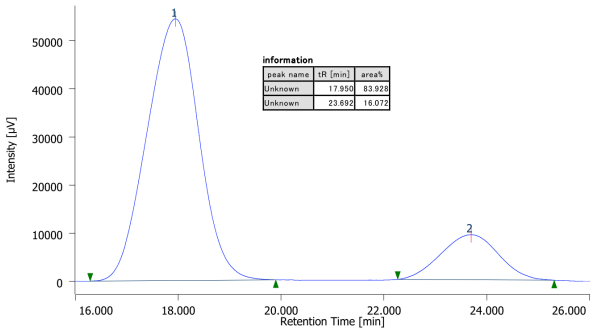


White powder; IR (KBr): ν 2251, 1733 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94–7.81 (m, 4H), 7.51–7.40 (m, 6H), 7.37–7.34 (m, 2H), 7.26–7.23 (m, 3H), 4.35–4.28 (m, 1H), 4.23–4.11 (m, 3H), 3.66 (d, J = 16.6 Hz, 1H), 1.18 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7 (d, J = 5.8 Hz), 137.6 (d, J = 7.1 Hz), 136.3, 135.2, 134.5, 133.5, 132.2, 132.0, 131.8 (d, J = 2.7 Hz), 130.8, 130.7, 128.9, 128.7, 128.65, 128.61, 128.4, 128.2, 125.9, 117.0, 65.0, 63.0, 28.1, 13.7; ^{31}P NMR ($CDCl_3$): δ 54.7; HRMS (ESI) Anal. calcd. for $C_{24}H_{23}O_2N_2NaPS$ m/z 457.1110 $[M+Na]^+$, found 457.1105; $[\alpha]_D^{25}$ –6.3 (c 0.66, $CHCl_3$, 68% ee sample); Enantiomeric excess of the product was determined to be 68% ee by chiral stationary phase HPLC analysis (CHIRALPAK IC (ϕ 0.46 cm x 25 cm), 2–propanol/*n*–hexane = 1/5, flow rate 1.0 mL/min, detection at 254 nm, t_R = 18.0 min (major), 23.7 min (minor)).

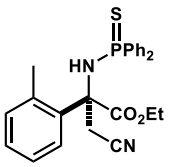
Racemic sample



Reaction sample

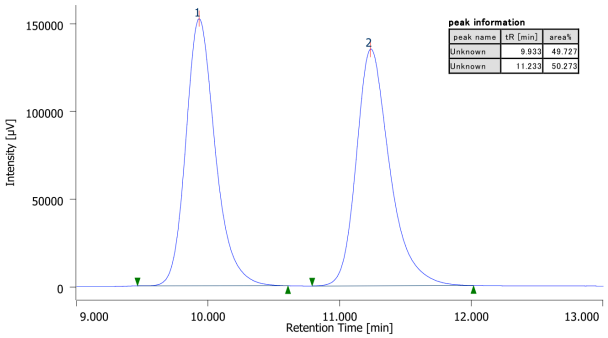


Ethyl (*R*)-3-cyano-2-((diphenylphosphorothioyl)amino)-2-(*o*-tolyl)propanoate (8f)

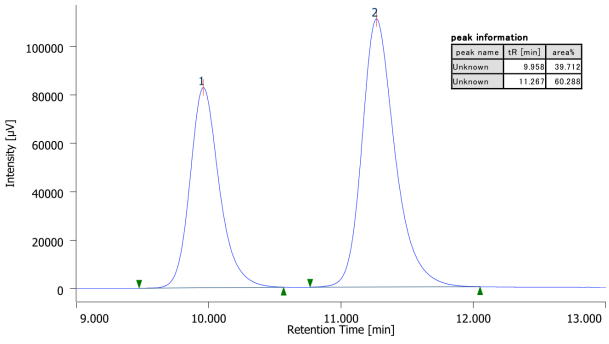


White powder; IR (KBr): ν 2246, 1725 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90–7.84 (m, 2H), 7.55–7.45 (m, 5H), 7.41 (d, J = 7.8 Hz, 1H), 7.32–7.28 (m, 1H), 7.17–7.11 (m, 3H), 6.99 (dt, J = 0.9, 7.4 Hz, 1H), 6.54 (d, J = 7.4 Hz, 1H), 4.92 (d, J = 15.9 Hz, 1H), 4.74 (d, J = 8.3 Hz, 1H), 4.29–4.37 (m, 1H), 4.23–4.16 (m, 1H), 3.55 (d, J = 15.8 Hz, 1H), 1.86 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6 (d, J = 11.7 Hz), 136.9, 136.1, 135.1, 133.0, 132.8 (d, J = 1.7 Hz), 131.95, 131.93, 131.90, 131.8, 131.72, 131.68, 131.0 (d, J = 3.0 Hz), 130.5, 130.4, 129.0, 128.8, 127.6, 127.5, 127.4, 125.5, 116.8, 64.3 (d, J = 1.3 Hz), 63.6, 29.1, 20.4, 13.9; ^{31}P NMR ($CDCl_3$): δ 51.5; HRMS (ESI) Anal. calcd. for $C_{25}H_{25}O_2N_2NaPS$ m/z 471.1267 $[M+Na]^+$, found 471.1260; $[\alpha]_D^{24}$ 1.9 (c 0.75, $CHCl_3$, 21% ee sample); Enantiomeric excess of the product was determined to be 21% ee by chiral stationary phase HPLC analysis (CHIRALPAK IA (ϕ 0.46 cm x 25 cm), 2-propanol/*n*-hexane = 1/9, flow rate 1.0 mL/min, detection at 254 nm, t_R = 10.0 min (minor), 11.3 min (major)).

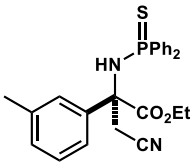
Racemic sample



Reaction sample

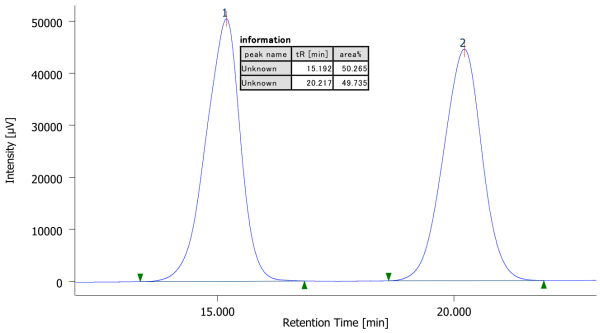


Ethyl (*R*)-3-cyano-2-((diphenylphosphorothioyl)amino)-2-(*m*-tolyl)propanoate (8g)

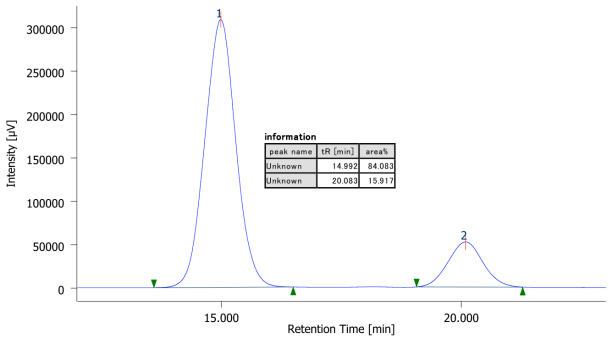


White powder; IR (KBr): ν 2251, 1733 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92–7.80 (m, 4H), 7.52–7.39 (m, 6H), 7.19–7.12 (m, 2H), 7.06–7.02 (m, 2H), 4.35–4.27 (m, 1H), 4.23–4.15 (m, 3H), 3.64 (d, J = 10.8 Hz, 1H), 2.21 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7 (d, J = 5.8 Hz), 138.4, 137.3 (d, J = 6.7 Hz), 136.4, 135.4, 134.5, 133.5, 132.2, 132.0, 131.81, 131.78, 131.75, 130.7, 130.6, 129.6, 128.7, 128.6, 128.5, 128.2, 128.1, 126.7, 117.1, 65.0, 63.0, 28.1, 21.5, 13.7; ^{31}P NMR ($CDCl_3$): δ 54.4; HRMS (ESI) Anal. calcd. for $C_{25}H_{25}O_2N_2NaPS$ m/z 471.1267 [M+Na]$^+$, found 471.1257; $[\alpha]_D^{25}$ –7.3 (c 0.82, $CHCl_3$, 68% ee sample); Enantiomeric excess of the product was determined to be 68% ee by chiral stationary phase HPLC analysis (CHIRALPAK IC (ϕ 0.46 cm x 25 cm), 2-propanol/n-hexane = 1/5, flow rate 1.0 mL/min, detection at 254 nm, t_R = 15.0 min (major), 20.1 min (minor)).

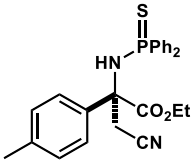
Racemic sample



Reaction sample

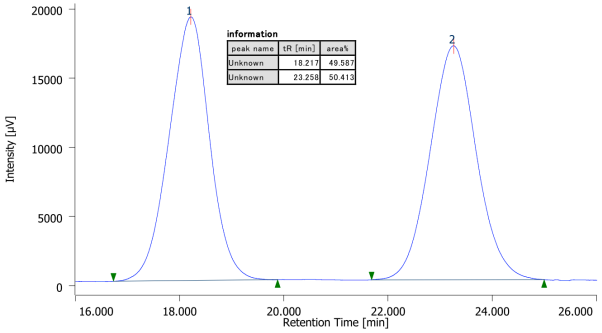


Ethyl (*R*)-3-cyano-2-((diphenylphosphorothioyl)amino)-2-(p-tolyl)propanoate (8h)

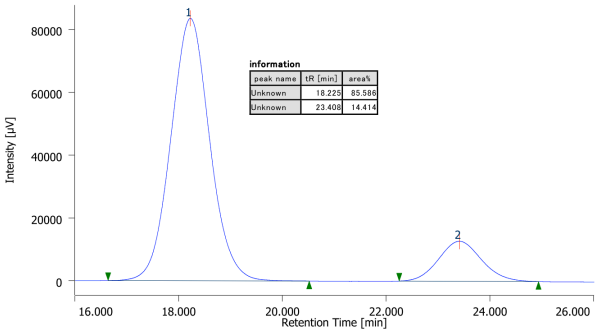


White powder; IR (KBr): ν 2251, 1732 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93–7.81 (m, 4H), 7.52–7.38 (m, 6H), 7.24–7.22 (m, 2H), 7.03 (d, J = 8.0 Hz, 2H), 4.34–4.26 (m, 1H), 4.22–4.08 (m, 3H), 3.64 (d, J = 16.6 Hz, 1H), 2.27 (s, 3H), 1.17 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8 (d, J = 5.8 Hz), 138.9, 136.3, 135.3, 134.74, 134.66, 134.5, 133.5, 132.2, 132.1, 131.8 (d, J = 3.0 Hz), 131.7 (d, J = 3.0 Hz), 130.8, 130.7, 129.3, 128.7, 128.6, 128.3, 128.1, 125.8, 117.1, 64.8, 62.9, 28.2, 21.0, 13.7; ^{31}P NMR ($CDCl_3$): δ 54.6; HRMS (ESI) Anal. calcd. for $C_{25}H_{25}O_2N_2NaPS$ m/z 471.1267 [M+Na]$^+$, found 471.1261; $[\alpha]_D^{25}$ –2.5 (c 0.69, $CHCl_3$, 71% ee sample); Enantiomeric excess of the product was determined to be 71% ee by chiral stationary phase HPLC analysis (CHIRALPAK IC (ϕ 0.46 cm x 25 cm), 2-propanol/n-hexane = 1/5, flow rate 1.0 mL/min, detection at 254 nm, t_R = 18.2 min (major), 23.4 min (minor)).

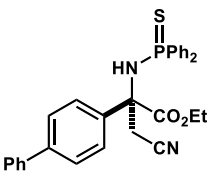
Racemic sample



Reaction sample



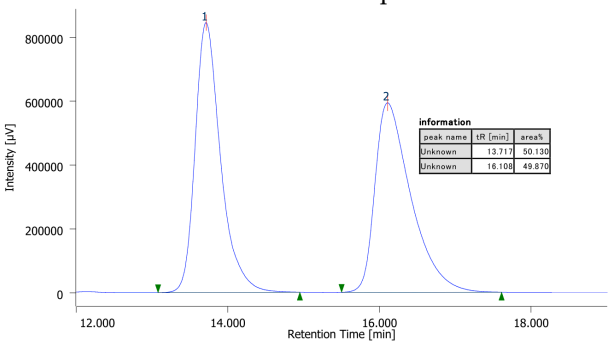
Ethyl (*R*)-2-([1,1'-biphenyl]-4-yl)-3-cyano-2-((diphenylphosphorothioyl)amino)propanoate (8i)



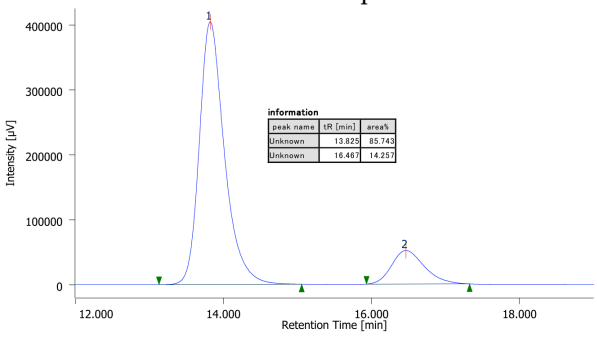
White powder; IR (KBr): ν 2251, 1733 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91–7.82 (m, 4H), 7.53–7.33 (m, 15H), 4.38–4.18 (m, 4H), 3.68 (d, J = 16.5 Hz, 1H), 1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7 (d, J = 6.6 Hz), 141.7, 139.9, 136.3, 136.2, 136.1, 135.2, 134.4, 133.4, 132.2, 132.1, 131.8 (d, J = 3.0 Hz), 131.7 (d, J = 3.0 Hz), 130.7, 130.6, 128.79, 128.76, 128.6, 128.2, 128.1, 127.7, 127.1, 127.0, 126.5, 117.0, 64.9, 63.2, 28.0, 13.7; ^{31}P NMR ($CDCl_3$): δ 54.4; HRMS (ESI) Anal. calcd. for $C_{30}H_{27}O_2N_2NaPS$ m/z 533.1423 [M+Na]$^+$, found 533.1415; $[\alpha]_D^{25}$ 7.2 (c 0.93, $CHCl_3$, 72% ee sample); Enantiomeric excess

of the product was determined to be 72% ee by chiral stationary phase HPLC analysis (CHIRALPAK IA (ϕ 0.46 cm x 25 cm), 2-propanol/*n*-hexane = 1/9, flow rate 1.0 mL/min, detection at 254 nm, t_R = 13.8 min (major), 16.5 min (minor)).

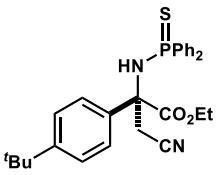
Racemic sample



Reaction sample

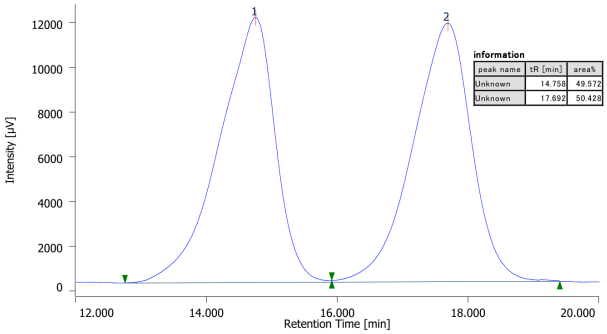


Ethyl (*R*)-2-(4-(*tert*-butyl)phenyl)-3-cyano-2-((diphenylphosphorothioyl)amino)propanoate (8j)

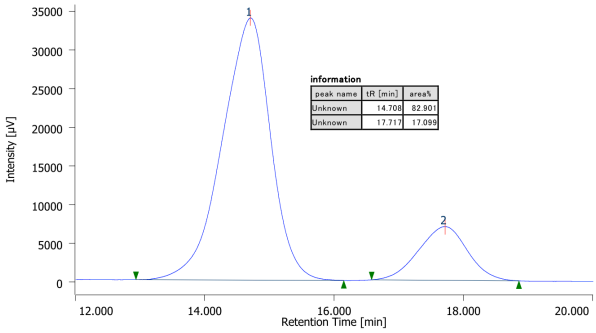


White powder; IR (KBr): ν 2251, 1733 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91–7.79 (m, 4H), 7.50–7.37 (m, 6H), 7.28–7.21 (m, 4H), 4.36–4.28 (m, 1H), 4.24–4.14 (m, 3H), 3.65 (d, *J* = 16.6 Hz, 1H), 1.25 (s, 9H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8 (d, *J* = 5.9 Hz), 151.9, 136.4, 135.4, 134.4 (d, *J* = 3.3 Hz), 134.3, 133.4, 132.2, 132.1, 131.8, 131.78, 131.76, 131.73, 130.7, 130.6, 128.7, 128.6, 128.3, 128.1, 125.7, 125.5, 117.2, 64.8, 63.0, 34.5, 31.1, 28.1, 13.7; ^{31}P NMR ($CDCl_3$): δ 54.4; HRMS (ESI) Anal. calcd. for $C_{28}H_{31}O_2N_2NaPS$ *m*/*z* 513.1736 [M+Na]$^+$, found 513.1729; $[\alpha]_D^{25}$ 1.2 (*c* 0.53, $CHCl_3$, 66% ee sample); Enantiomeric excess of the product was determined to be 66% ee by chiral stationary phase HPLC analysis (CHIRALPAK IC (ϕ 0.46 cm x 25 cm), 2-propanol/*n*-hexane = 1/5, flow rate 1.0 mL/min, detection at 254 nm, t_R = 14.7 min (major), 17.7 min (minor)).

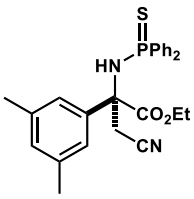
Racemic sample



Reaction sample

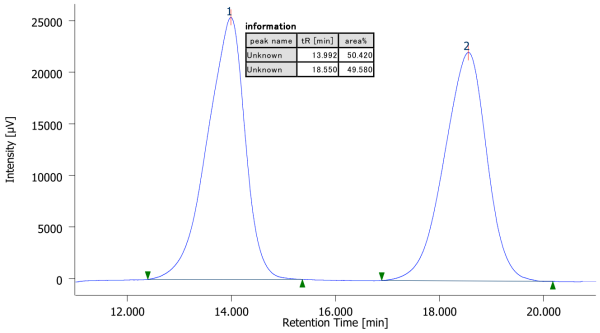


Ethyl (*R*)-3-cyano-2-(3,5-dimethylphenyl)-2-((diphenylphosphorothioyl)amino)propanoate (8k)

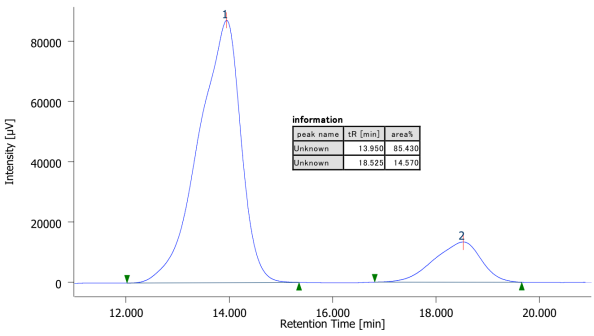


White powder; IR (KBr): ν 2251, 1733 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90–7.79 (m, 4H), 7.48–7.40 (m, 6H), 6.89 (s, 2H), 6.82 (s, 1H), 4.36–4.28 (m, 1H), 4.23–4.14 (m, 3H), 3.61 (d, *J* = 16.5 Hz, 1H), 2.19 (s, 6H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8 (d, *J* = 6.5 Hz), 138.2, 137.1 (d, *J* = 6.3 Hz), 136.5, 135.5, 134.5, 133.5, 132.2, 132.0, 131.77, 131.74, 131.7, 130.7, 130.6, 130.5, 128.7, 128.6, 128.1, 128.0, 123.8, 117.2, 64.9, 63.0, 28.1, 21.4, 13.7; ^{31}P NMR ($CDCl_3$): δ 54.2; HRMS (ESI) Anal. calcd. for $C_{26}H_{27}O_2N_2NaPS$ *m*/*z* 485.1423 [M+Na]$^+$, found 485.1410; $[\alpha]_D^{25}$ –4.9 (*c* 0.57, $CHCl_3$, 71% ee sample); Enantiomeric excess of the product was determined to be 71% ee by chiral stationary phase HPLC analysis (CHIRALPAK IC (ϕ 0.46 cm x 25 cm), 2-propanol/*n*-hexane = 1/5, flow rate 1.0 mL/min, detection at 254 nm, t_R = 14.0 min (major), 18.5 min (minor)).

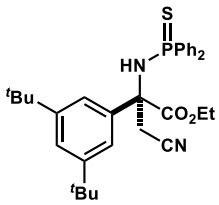
Racemic sample



Reaction sample

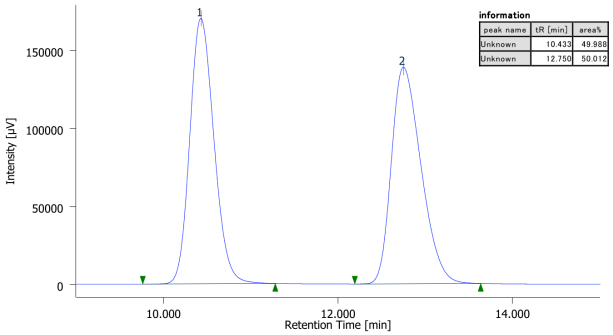


Ethyl (*R*)-3-cyano-2-(3,5-di-*tert*-butylphenyl)-2-((diphenylphosphorothioyl)amino)propanoate (8l)

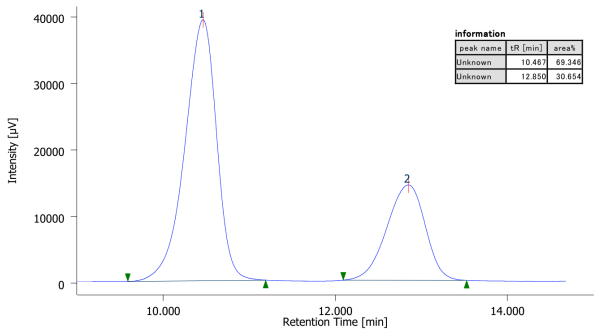


White powder; IR (KBr): *ν* 2254, 1734, 1713 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.86–7.80 (m, 4H), 7.50–7.40 (m, 4H), 7.37–7.33 (m, 2H), 7.28–7.27 (m, 3H), 4.34–4.13 (m, 4H), 3.71 (d, *J* = 16.6 Hz, 1H), 1.26 (s, 18H), 1.15 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8 (d, *J* = 6.1 Hz), 151.1, 136.9 (d, *J* = 6.3 Hz), 136.7, 135.6, 134.9, 133.9, 132.0, 131.9, 131.74, 131.71, 131.69, 131.66, 130.8, 130.7, 128.7, 128.5, 128.3, 128.2, 123.0, 120.6, 117.5, 65.7, 62.8, 35.0, 31.3, 28.1, 13.8; ^{31}P NMR ($CDCl_3$): δ 54.2; HRMS (ESI) Anal. calcd. for $C_{32}H_{40}O_2N_2PS$ *m/z* 547.2543 $[M+H]^+$, found 547.2537; $[\alpha]_D^{24}$ –3.1 (*c* 1.57, $CHCl_3$, 39% ee sample); Enantiomeric excess of the product was determined to be 39% ee by chiral stationary phase HPLC analysis (CHIRALPAK ID (*ϕ* 0.46 cm x 25 cm), 2-propanol/*n*-hexane = 1/9, flow rate 1.0 mL/min, detection at 254 nm, t_R = 10.5 min (major), 12.9 min (minor)).

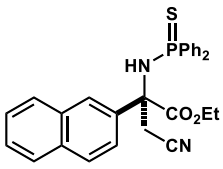
Racemic sample



Reaction sample

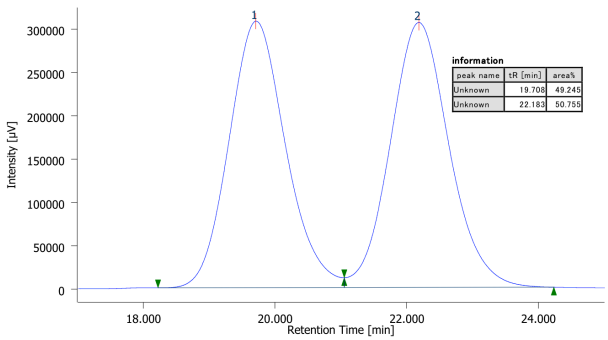


Ethyl (*R*)-3-cyano-2-((diphenylphosphorothioyl)amino)-2-(naphthalen-2-yl)propanoate (8m)

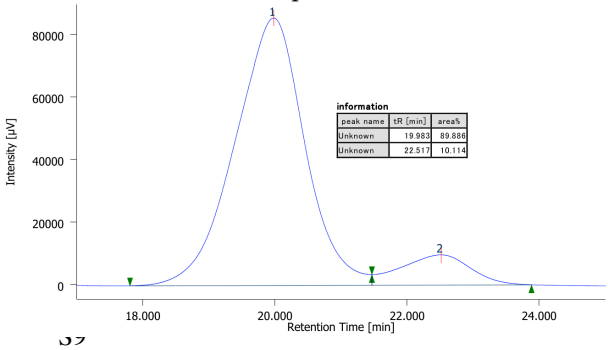


White powder; IR (KBr): *ν* 2251, 1733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.89–7.78 (m, 5H), 7.75–7.72 (m, 2H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.51–7.45 (m, 5H), 7.37–7.31 (m, 2H), 7.29–7.24 (m, 2H), 4.42–4.29 (m, 3H), 4.23–4.15 (m, 1H), 3.76 (d, *J* = 16.4 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7 (d, *J* = 6.9 Hz), 136.3, 135.3, 134.4 (d, *J* = 6.2 Hz), 134.3, 133.3, 133.0, 132.5, 132.0, 131.9, 131.8 (d, *J* = 3.0 Hz), 131.6 (d, *J* = 3.0 Hz), 130.8, 130.7, 128.8, 128.6, 128.5, 128.4, 128.1, 128.0, 127.4, 126.9, 126.5, 125.8, 123.2, 117.0, 65.1, 63.2, 28.1, 13.7; ^{31}P NMR ($CDCl_3$): δ 54.3; HRMS (ESI) Anal. calcd. for $C_{28}H_{25}O_2N_2NaPS$ *m/z* 507.1267 $[M+Na]^+$, found 507.1257; $[\alpha]_D^{25}$ 3.7 (*c* 0.77, $CHCl_3$, 80% ee sample); Enantiomeric excess of the product was determined to be 80% ee by chiral stationary phase HPLC analysis (CHIRALPAK IC (*ϕ* 0.46 cm x 25 cm), 2-propanol/*n*-hexane = 1/5, flow rate 1.0 mL/min, detection at 254 nm, t_R = 20.0 min (major), 22.5 min (minor)).

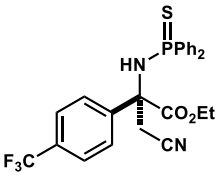
Racemic sample



Reaction sample

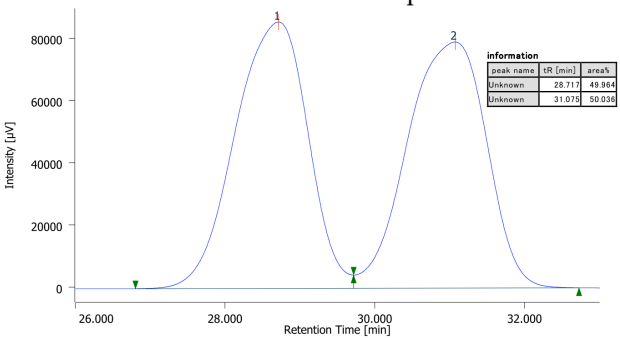


Ethyl (*R*)-3-cyano-2-((diphenylphosphorothioyl)amino)-2-(4-(trifluoromethyl)phenyl)propanoate (8n)

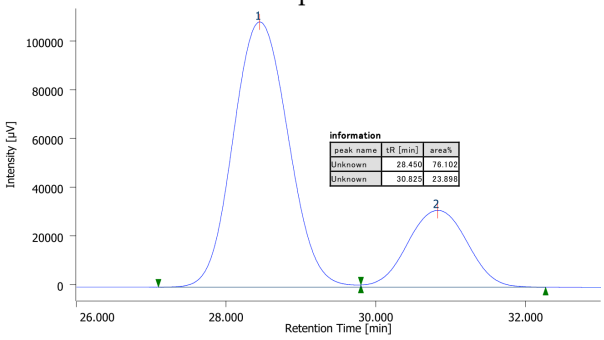


White powder; IR (KBr): ν 2251, 1736 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.75 (m, 4H), 7.54–7.43 (m, 4H), 7.41–7.34 (m, 6H), 4.44–4.30 (m, 3H), 4.25–4.19 (m, 1H), 3.63 (d, J = 16.4 Hz, 1H), 1.20 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2 (d, J = 7.7 Hz), 140.6, 140.5, 136.0, 135.0, 133.9, 132.9, 132.11, 132.05 (d, J = 3.0 Hz), 132.00, 131.9 (d, J = 3.0 Hz), 131.4, 131.1, 130.74, 130.70, 130.6, 130.4, 128.9, 128.7, 128.3, 128.2, 127.6, 126.9, 125.40, 125.36, 125.32, 125.28, 124.9, 122.2, 119.5, 116.7, 64.8, 63.6, 27.7, 13.7; ^{19}F NMR (375 MHz, $CDCl_3$): δ –63.0; ^{31}P NMR ($CDCl_3$): δ 54.2; HRMS (ESI) Anal. calcd. for $C_{25}H_{22}O_2N_2F_3NaPS$ m/z 525.0984 $[M+Na]^+$, found 525.0977; $[\alpha]_D^{25}$ –3.1 (c 0.62, $CHCl_3$, 52% ee sample); Enantiomeric excess of the product was determined to be 52% ee by chiral stationary phase HPLC analysis (CHIRALPAK ID (ϕ 0.46 cm x 25 cm), 2-propanol/*n*-hexane = 1/9, flow rate 1.0 mL/min, detection at 254 nm, t_R = 28.5 min (major), 30.8 min (minor)).

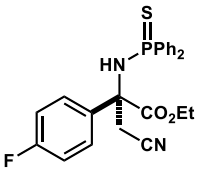
Racemic sample



Reaction sample

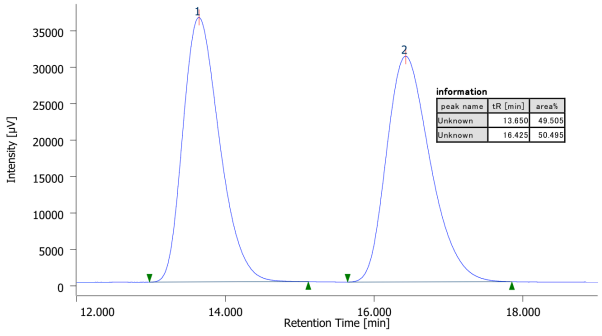


Ethyl (*R*)-3-cyano-2-((diphenylphosphorothioyl)amino)-2-(4-fluorophenyl)propanoate (8o)

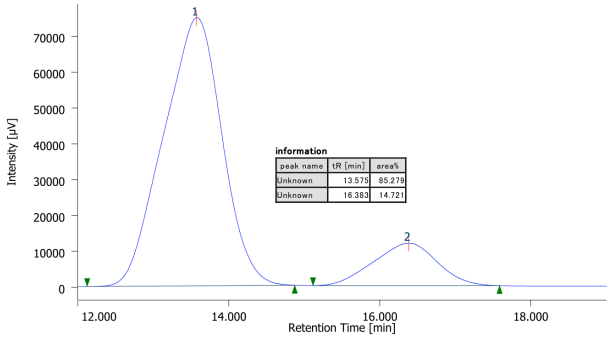


White powder; IR (KBr): ν 2251, 1734 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89–7.79 (m, 4H), 7.51–7.40 (m, 6H), 7.30–7.26 (m, 2H), 6.90–6.84 (m, 2H), 4.36–4.16 (m, 4H), 3.62 (d, J = 16.5 Hz, 1H), 1.19 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5 (d, J = 7.8 Hz), 163.8, 161.3, 136.1, 135.1, 134.3, 133.3, 133.12, 133.09, 133.06, 133.03, 132.2, 132.0, 131.93 (d, J = 3.0 Hz), 131.86 (d, J = 3.0 Hz), 130.7, 130.6, 128.8, 128.7, 128.3, 128.21, 128.19, 128.13, 116.9, 115.5, 115.3, 64.6, 63.3, 28.1, 13.7; ^{19}F NMR (375 MHz, $CDCl_3$): δ –112.4; ^{31}P NMR ($CDCl_3$): δ 54.4; HRMS (ESI) Anal. calcd. for $C_{24}H_{22}O_2N_2FNaPS$ m/z 475.1016 $[M+Na]^+$, found 475.1009; $[\alpha]_D^{25}$ –5.5 (c 0.66, $CHCl_3$, 71% ee sample); Enantiomeric excess of the product was determined to be 71% ee by chiral stationary phase HPLC analysis (CHIRALPAK IC (ϕ 0.46 cm x 25 cm), 2-propanol/*n*-hexane = 1/5, flow rate 1.0 mL/min, detection at 254 nm, t_R = 13.6 min (major), 16.4 min (minor)).

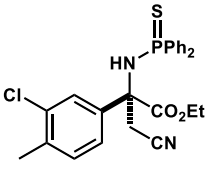
Racemic sample



Reaction sample



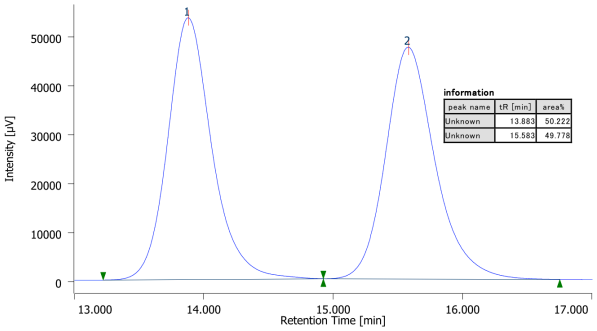
Ethyl (*R*)-2-(3-chloro-4-methylphenyl)-3-cyano-2-((diphenylphosphorothioyl)amino)propanoate (8p)



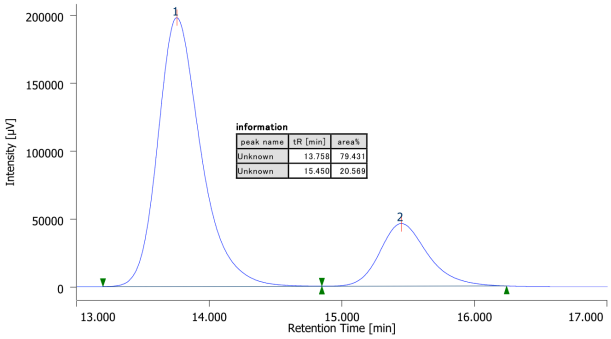
White powder; IR (KBr): ν 2252, 1734 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87–7.79 (m, 4H), 7.51–7.39 (m, 6H), 7.20 (d, J = 2.1 Hz, 1H), 7.11 (dd, J = 2.1, 8.0 Hz, 1H), 7.05 (d, J = 8.1 Hz, 1H), 4.37–4.16 (m, 4H), 3.60 (d, J = 16.5 Hz, 1H), 2.26 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3 (d, J = 7.1 Hz), 136.9, 136.42, 136.36, 135.1, 134.6, 134.1, 133.1, 132.1, 132.0, 131.9 (d, J = 3.0 Hz), 131.8 (d, J = 3.0 Hz), 130.8, 130.7, 130.6, 128.8, 128.7, 128.2, 128.1, 127.1, 124.3, 116.8, 64.5,

63.3, 27.9, 19.6, 13.7; ^{31}P NMR ($CDCl_3$): δ 54.3; HRMS (ESI) Anal. calcd. for $C_{25}H_{24}O_2N_2ClNaPS$ *m*/*z* 505.0877 $[M+Na]^+$, found 505.0876; $[\alpha]_D^{25}$ –3.1 (*c* 0.85, $CHCl_3$, 59% ee sample); Enantiomeric excess of the product was determined to be 59% ee by chiral stationary phase HPLC analysis (CHIRALPAK IA (ϕ 0.46 cm x 25 cm), 2-propanol/*n*-hexane = 1/20, flow rate 1.0 mL/min, detection at 254 nm, t_R = 13.8 min (major), 15.5 min (minor)).

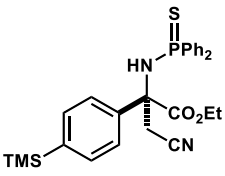
Racemic sample



Reaction sample

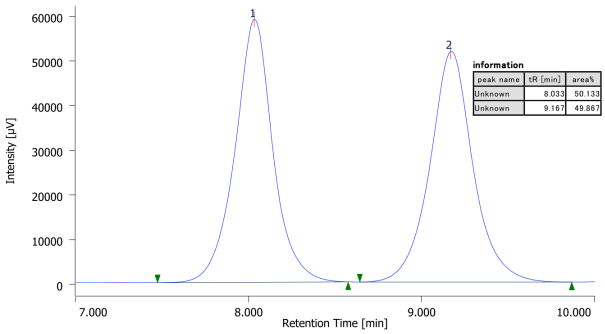


Ethyl (*R*)-3-cyano-2-((diphenylphosphorothioyl)amino)-2-(4-(trimethylsilyl)phenyl)propanoate (8q)

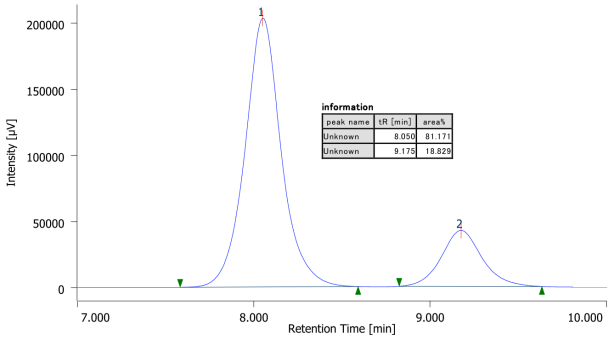


White powder; IR (KBr): *ν* 2251, 1734 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91–7.79 (m, 4H), 7.50–7.41 (m, 4H), 7.40–7.30 (m, 6H), 4.36–4.28 (m, 1H), 4.24–4.16 (m, 3H), 3.65 (d, *J* = 16.6 Hz, 1H), 1.19 (t, *J* = 7.2 Hz, 3H), 0.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6 (d, *J* = 6.1 Hz), 141.6, 137.7 (d, *J* = 6.8 Hz), 136.3, 135.3, 134.4, 133.6, 133.3, 132.2, 132.1, 131.8 (d, *J* = 3.0 Hz), 131.7 (d, *J* = 3.0 Hz), 130.7, 130.6, 128.7, 128.6, 128.3, 128.1, 125.2, 117.1, 65.0, 63.1, 28.0, 13.7, -1.3; ^{31}P NMR ($CDCl_3$): δ 54.5; HRMS (ESI) Anal. calcd. for $C_{27}H_{31}O_2N_2NaPSSi$ *m*/*z* 529.1505 $[M+Na]^+$, found 529.1488; $[\alpha]_D^{25}$ 1.9 (*c* 1.21, $CHCl_3$, 62% ee sample); Enantiomeric excess of the product was determined to be 62% ee by chiral stationary phase HPLC analysis (CHIRALPAK IA (ϕ 0.46 cm x 25 cm), 2-propanol/*n*-hexane = 1/20, flow rate 1.0 mL/min, detection at 254 nm, t_R = 8.1 min (major), 9.2 min (minor)).

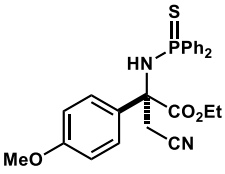
Racemic sample



Reaction sample

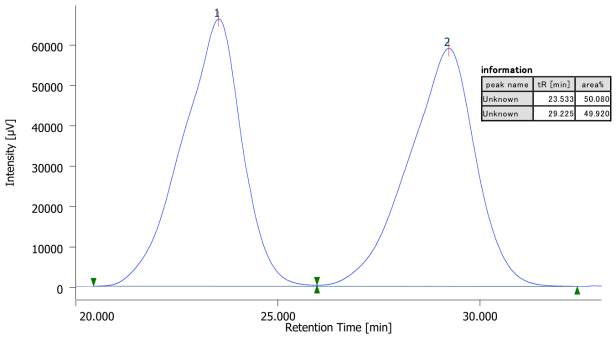


Ethyl (*R*)-3-cyano-2-((diphenylphosphorothioyl)amino)-2-(4-methoxyphenyl)propanoate (8r)

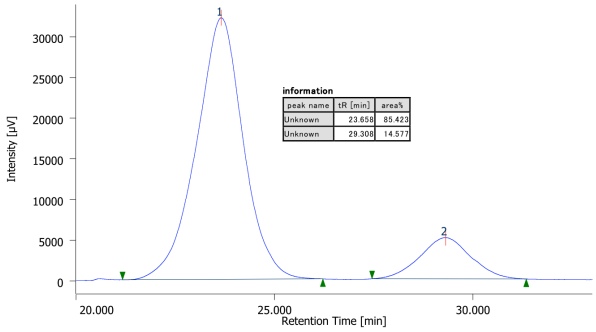


White powder; IR (KBr): *ν* 2251, 1732 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92–7.80 (m, 4H), 7.48–7.40 (m, 6H), 7.26–7.23 (m, 2H), 6.74–6.70 (m, 2H), 4.34–4.26 (m, 1H), 4.22–4.12 (m, 3H), 3.75 (s, 3H), 3.63 (d, *J* = 16.6 Hz, 1H), 1.18 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8 (d, *J* = 6.1 Hz), 159.7, 136.3, 135.3, 134.6, 133.5, 132.2, 132.1, 131.8 (d, *J* = 3.0 Hz), 131.7 (d, *J* = 3.0 Hz), 130.8, 130.6, 129.5, 129.4, 128.7, 128.6, 128.3, 128.2, 127.4, 117.2, 113.9, 64.6, 63.0, 55.2, 28.2, 13.7; ^{31}P NMR ($CDCl_3$): δ 54.4; HRMS (ESI) Anal. calcd. for $C_{25}H_{25}O_3N_2NaPS$ *m*/*z* 487.1216 $[M+Na]^+$, found 487.1209; $[\alpha]_D^{25}$ –1.5 (*c* 0.65, $CHCl_3$, 71% ee sample); Enantiomeric excess of the product was determined to be 71% ee by chiral stationary phase HPLC analysis (CHIRALPAK IC (ϕ 0.46 cm x 25 cm), 2-propanol/*n*-hexane = 1/5, flow rate 1.0 mL/min, detection at 254 nm, t_R = 23.7 min (major), 29.3 min (minor)).

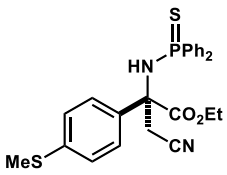
Racemic sample



Reaction sample

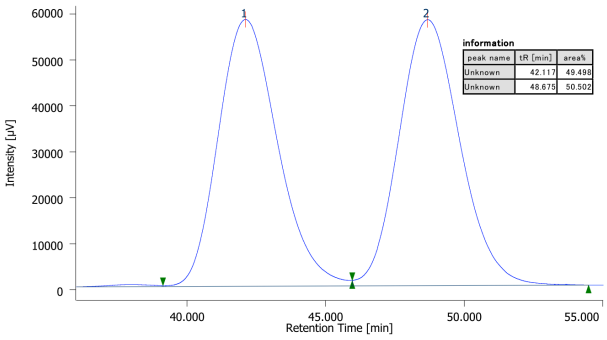


Ethyl (*R*)-3-cyano-2-((diphenylphosphorothioyl)amino)-2-(4-(methylthio)phenyl)propanoate (8s)

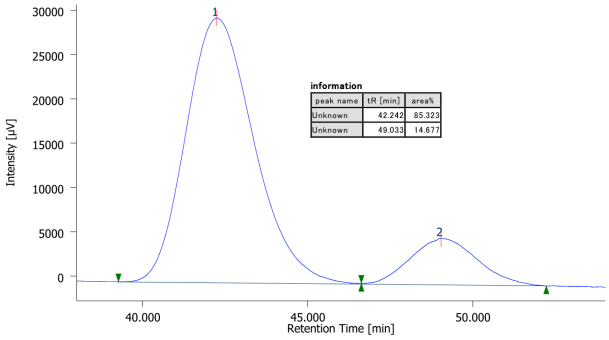


White powder; IR (KBr): ν 2251, 1732 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89–7.80 (m, 4H), 7.51–7.39 (m, 6H), 7.22–7.19 (m, 2H), 7.05–7.02 (m, 2H), 4.34–4.26 (m, 1H), 4.22–4.14 (m, 3H), 3.63 (d, J = 16.5 Hz, 1H), 2.42 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5 (d, J = 6.5 Hz), 139.9, 136.1, 135.2, 134.4, 133.8, 133.7, 133.4, 132.1, 132.0, 131.8 (d, J = 3.0 Hz), 131.7 (d, J = 3.0 Hz), 130.7, 130.6, 128.7, 128.6, 128.3, 128.1, 126.5, 125.9, 117.0, 64.7, 63.1, 28.0, 15.2, 13.7; ^{31}P NMR ($CDCl_3$): δ 54.4; HRMS (ESI) Anal. calcd. for $C_{25}H_{25}O_2N_2NaPS_2$ m/z 503.0987 $[M+Na]^+$, found 503.0983; $[\alpha]_D^{25}$ 4.9 (c 1.05, $CHCl_3$, 71% ee sample); Enantiomeric excess of the product was determined to be 71% ee by chiral stationary phase HPLC analysis (CHIRALPAK IC (ϕ 0.46 cm x 25 cm), 2-propanol/n-hexane = 1/9, flow rate 1.0 mL/min, detection at 254 nm, t_R = 42.2 min (major), 49.0 min (minor)).

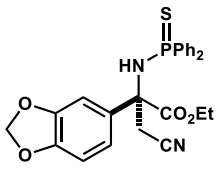
Racemic sample



Reaction sample

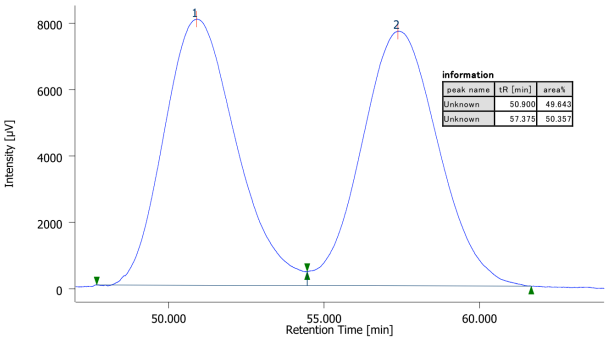


Ethyl (*R*)-2-(benzo[*d*][1,3]dioxol-5-yl)-3-cyano-2-((diphenylphosphorothioyl)amino)propanoate (8t)

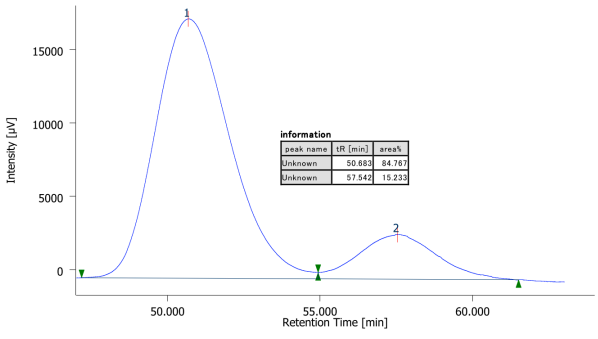


White powder; IR (KBr): ν 2252, 1733 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93–7.80 (m, 4H), 7.49–7.42 (m, 6H), 6.83 (dd, J = 2.1, 8.2 Hz, 1H), 6.74 (d, J = 2.0 Hz, 1H), 6.64 (d, J = 8.2 Hz, 1H), 5.90 (dd, J = 1.4, 14.7 Hz, 2H), 4.36–4.28 (m, 1H), 4.24–4.14 (m, 3H), 3.59 (d, J = 16.5 Hz, 1H), 1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7 (d, J = 6.4 Hz), 147.9, 147.8, 136.2, 135.1, 134.4, 133.3, 132.2, 132.1, 131.9 (d, J = 3.0 Hz), 131.8 (d, J = 3.0 Hz), 131.2, 131.1, 130.7, 130.6, 128.8, 128.6, 128.2, 128.1, 119.8, 117.0, 107.9, 106.8, 101.4, 64.8, 63.1, 28.2, 13.7; ^{31}P NMR ($CDCl_3$): δ 54.3; HRMS (ESI) Anal. calcd. for $C_{25}H_{23}O_4N_2NaPS$ m/z 501.1008 $[M+Na]^+$, found 501.1004; $[\alpha]_D^{25}$ –7.5 (c 0.84, $CHCl_3$, 70% ee sample); Enantiomeric excess of the product was determined to be 70% ee by chiral stationary phase HPLC analysis (CHIRALPAK IC (ϕ 0.46 cm x 25 cm), 2-propanol/n-hexane = 1/9, flow rate 1.0 mL/min, detection at 254 nm, t_R = 50.7 min (major), 57.5 min (minor)).

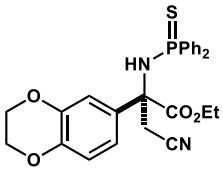
Racemic sample



Reaction sample

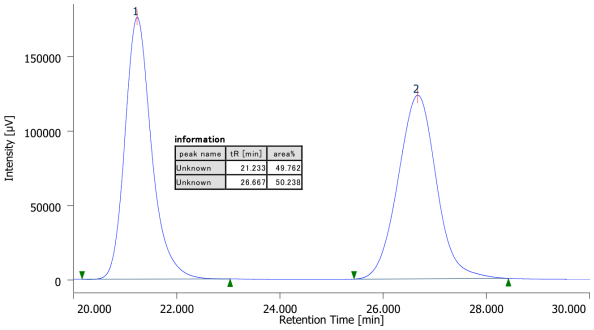


Ethyl (*R*)-3-cyano-2-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-2-((diphenylphosphorothioyl)amino)propanoate (8u)

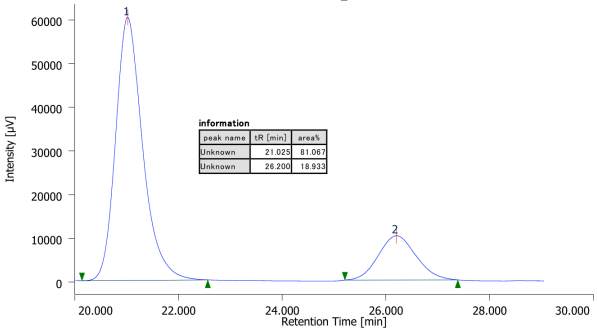


White powder; IR (KBr): ν 2251, 1732 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94–7.89 (m, 2H), 7.85–7.80 (m, 2H), 7.50–7.42 (m, 6H), 6.85–6.80 (m, 2H), 6.70 (d, J = 8.5 Hz, 1H), 4.35–4.27 (m, 1H), 4.23–4.15 (m, 5H), 4.12–4.09 (m, 2H), 3.59 (d, J = 16.6 Hz, 1H), 1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7 (d, J = 6.0 Hz), 143.9, 143.2, 136.3, 135.2, 134.4, 133.4, 132.3, 132.1, 131.8 (d, J = 3.0 Hz), 131.7 (d, J = 3.0 Hz), 130.73, 130.69, 130.6, 128.7, 128.6, 128.3, 128.1, 119.0, 117.3, 117.1, 115.4, 64.5, 64.24, 64.21, 63.0, 28.2, 13.7; ^{31}P NMR ($CDCl_3$): δ 54.4; HRMS (ESI) Anal. calcd. for $C_{26}H_{25}O_4N_2NaPS$ *m*/*z* 515.1165 [M+Na]$^+$, found 515.1156; $[\alpha]_D^{25}$ –0.3 (*c* 1.05, $CHCl_3$, 62% ee sample); Enantiomeric excess of the product was determined to be 62% ee by chiral stationary phase HPLC analysis (CHIRALPAK IA (ϕ 0.46 cm x 25 cm), 2-propanol/*n*-hexane = 1/9, flow rate 1.0 mL/min, detection at 254 nm, t_R = 21.0 min (major), 26.2 min (minor)).

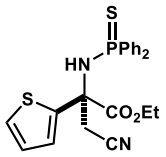
Racemic sample



Reaction sample

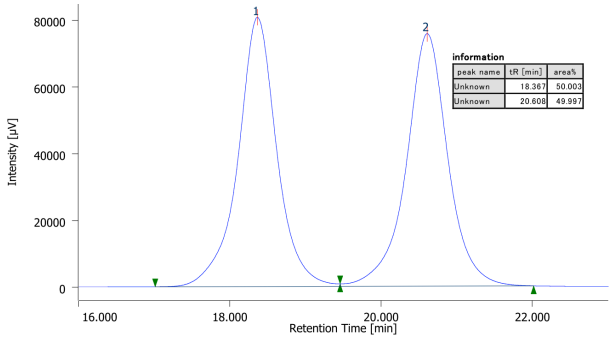


Ethyl (*S*)-3-cyano-2-((diphenylphosphorothioyl)amino)-2-(thiophen-2-yl)propanoate (8v)

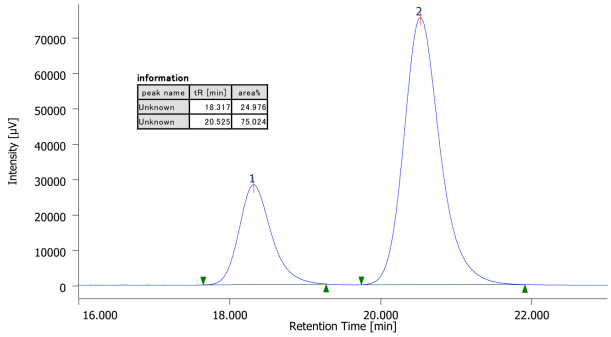


White powder; IR (KBr): ν 2252, 1734 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95–7.88 (m, 4H), 7.53–7.43 (m, 6H), 7.27–7.25 (m, 1H), 7.07 (dd, J = 1.2, 3.7 Hz, 1H), 6.91 (dd, J = 3.7, 5.1 Hz, 1H), 4.29–4.21 (m, 1H), 4.16–4.01 (m, 3H), 3.84 (d, J = 16.8 Hz, 1H), 1.10 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2 (d, J = 4.0 Hz), 142.4, 142.3, 135.9, 135.0, 134.8, 134.0, 132.0 (d, J = 3.0 Hz), 131.84 (d, J = 3.0 Hz), 131.80, 131.7, 131.1, 131.0, 128.63, 128.59, 128.50, 128.46, 127.2, 126.5, 126.1, 116.8, 63.2, 63.1, 29.4, 13.5; ^{31}P NMR ($CDCl_3$): δ 55.3; HRMS (ESI) Anal. calcd. for $C_{22}H_{21}O_2N_2NaPS_2$ *m*/*z* 463.0674 [M+Na]$^+$, found 463.0667; $[\alpha]_D^{25}$ –11.5 (*c* 0.69, $CHCl_3$, 50% ee sample); Enantiomeric excess of the product was determined to be 50% ee by chiral stationary phase HPLC analysis (CHIRALPAK IA (ϕ 0.46 cm x 25 cm), 2-propanol/*n*-hexane = 1/20, flow rate 1.0 mL/min, detection at 254 nm, 18.3 min (minor), t_R = 20.5 min (major)).

Racemic sample



Reaction sample

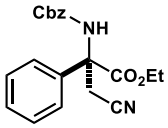


4.3. Transformation of the Mannich product.

To a solution of **8a** (400 mg, 0.92 mmol) in a mixture of EtOAc/AcOH (v/v: 4/1), (5 mL), H_2O_2 (35 wt %), (1.0 mL) was added dropwise at room temperature. The reaction was quenched with sat. $NaHCO_3$ solution after **8a** disappeared on TLC monitoring. The mixture was extracted with ethyl acetate, and the organic layers were combined and dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the crude mixture was purified by silica gel column chromatography to afford the desired product in quantitative yield.

To a solution of the thus-obtained *N*-phosphinoylamide (41.8 mg, 0.1 mmol) in EtOAc (0.5 mL), 4 N HCl (1.5 mL) was added dropwise at room temperature. After stirring at 60 °C for 2.5 h, the resulting mixture was concentrated, and redissolved in EtOAc (1.5 mL), H_2O (1.5 mL) was added and cooled to 0 °C. To the biphase mixture, $NaHCO_3$ (420 mg, 5 mmol) and Cbz-Cl (72 μL, 0.5 mmol) were added and was stirred for 4 h. The solution was diluted with H_2O and extracted with EtOAc. The combined organic layers were washed with brine, dried ($NaSO_4$) and concentrated. The reaction mixture was purified by preparative TLC (hexane/acetone = 5/1) to give pure product **11** (22.4 mg, 64% yield).

Ethyl (*R*)-2-(((benzyloxy)carbonyl)amino)-3-cyano-2-phenylpropanoate (11)



White powder; IR ($CHCl_3$): ν 2257, 1726 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.41–7.26 (m, 10H), 6.21 (s, 1H), 5.16–5.06 (m, 2H); 4.26–4.20 (m, 2H), 3.80–3.70 (m, 2H), 1.19 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 154.7, 136.5, 135.8, 129.21, 129.18, 128.6, 128.3, 128.1, 125.2, 116.6, 67.3, 63.2, 63.1, 25.2, 13.8; HRMS (ESI) Anal. calcd. for $C_{20}H_{20}O_4N_2Na$ m/z 375.1315 $[M+Na]^+$, found 375.1314; $[\alpha]_D^{25}$ 1.4 (*c* 0.88, $CHCl_3$, from 65% ee sample).

5. Kinetic Experiments

General procedure for initial rate kinetic experiments

A flame-dried 20 mL test tube equipped with a magnetic stirring bar and 3-way glass stopcock was charged with $[Ir(cod)(OMe)]_2$ (3.3 mg, 0.005 mmol), NHC precursor (5.0 mg, 0.01 mmol) under Ar atmosphere and THF (0.5 mL) was added at room temperature, then Barton's base (20.0 μL, 0.1 mmol) was added. The mixture was stirred at room temperature for 0.5 h and then cooled to 0 °C. Ketimine (0.1 mmol) in THF (0.5 mL) was added via a gas-tight syringe with a stainless steel needle under an Ar atmosphere. Then MeCN (210 μL, 4 mmol) was added via a gas-tight syringe with a stainless steel needle under an Ar atmosphere. Aliquots were taken at 1 h intervals by removing a small amount (ca. 0.1 mL) of the reaction solution and quenched it immediately with AcOH (0.1 mL, 0.1 M in THF), then passing it through a small silica gel plug, eluting with THF. After evaporation, the residue analyzed by ^1H NMR spectroscopy to determine the yield based on the relative integration values of the peaks at 4.47 ppm (for ketimine) and 3.66 ppm (for product).

5.1 Determination of the reaction order in ketimine.

The reaction with different concentration of ketimine (0.1 mmol, 0.2 mmol, 0.3 mmol and 0.4 mmol) at 81.3, 162.6, 243.9 and 325.2 mM were performed according to the general procedure described above except for varying the amount of ketimine added, and the results were summarized in the **Table S1** and **Figure S1** below.

Table S1. Initial rates of varying concentration of ketimine

[ketimine] (mM)	*d*[Product]/*d*t (mM/h)
81.3	3.03
162.6	3.86
243.9	4.56
325.2	4.94

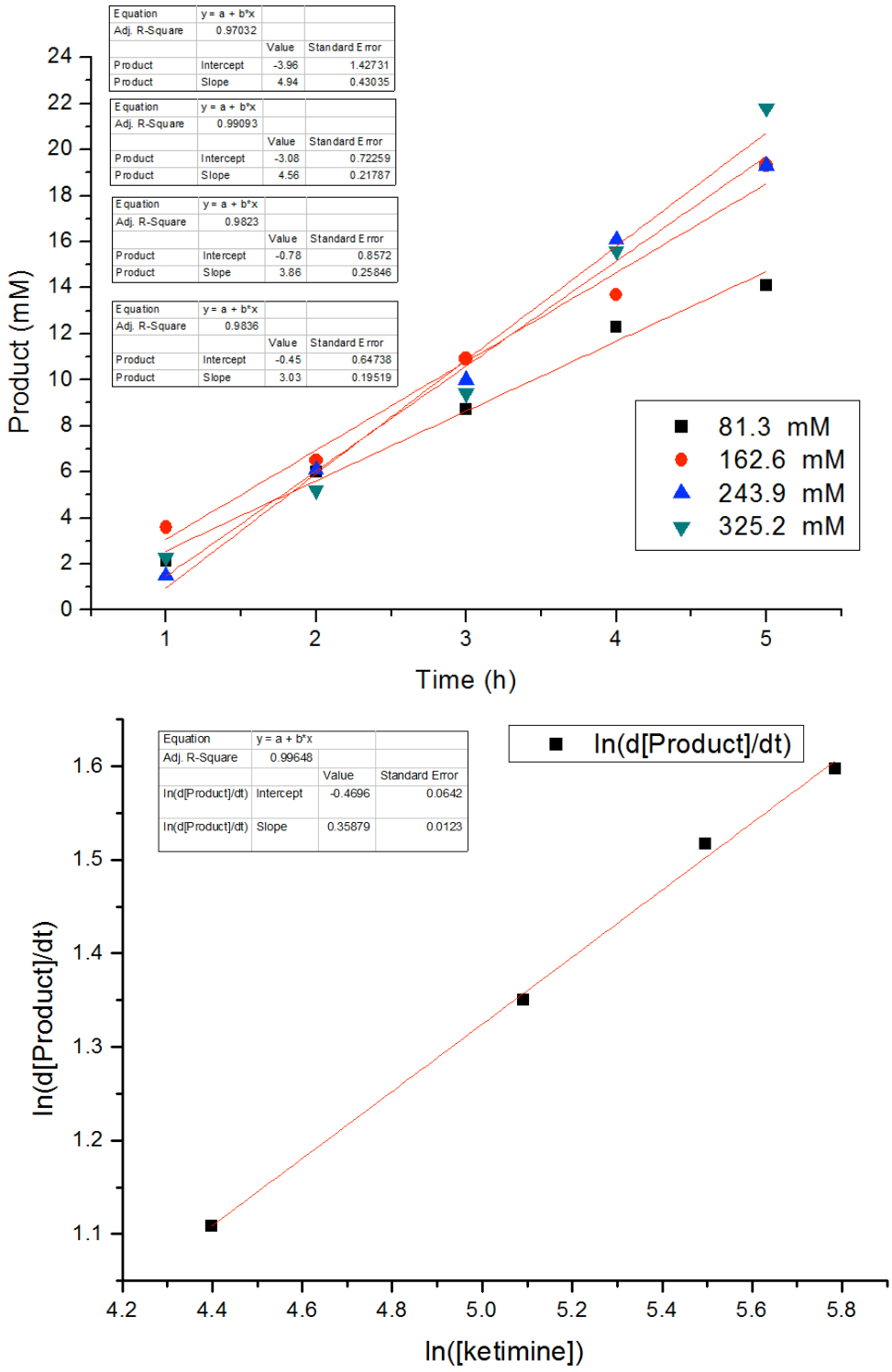


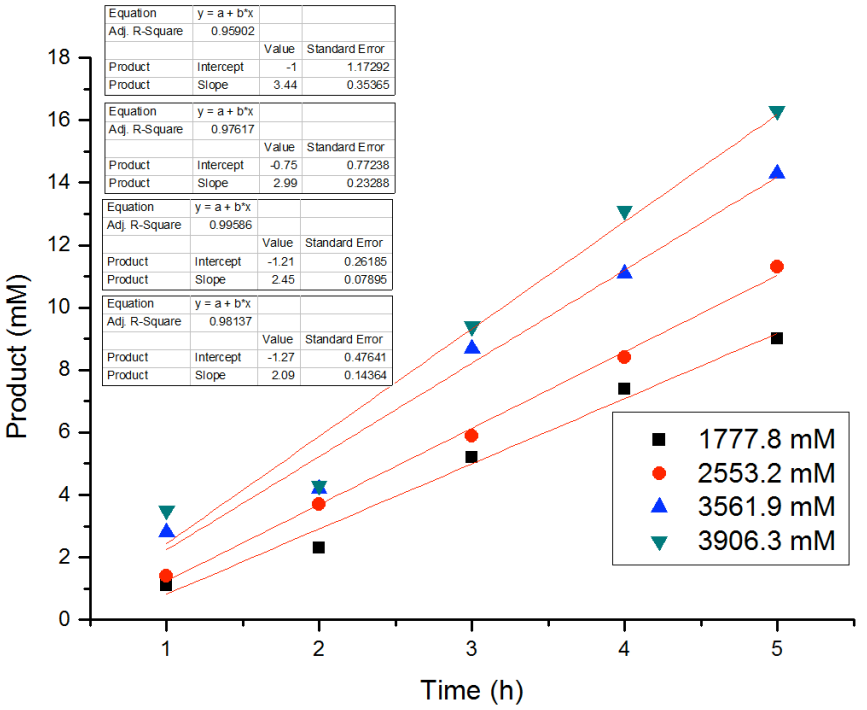
Figure S1. (a) Initial rate kinetic experiments for ketimine. (b) Plot of ln(d[Product]/dt) versus ln([ketimine])

5.2 Determination of the reaction order in MeCN.

The reaction with different concentration of MeCN (2 mmol, 3 mmol, 4 mmol and 5 mmol) at 1777.8, 2553.2, 3561.9 and 3906.3 mM were performed according to the general procedure described above except for varying the amount of MeCN added, and the results were summarized in the **Table S2** and **Figure S2** below.

Table S2. Initial rates of varying concentration of MeCN

[MeCN] (mM)	*d*[Product]/*d*t (mM/h)
1777.8	2.09
2553.2	2.45
3561.9	2.99
3906.3	3.44



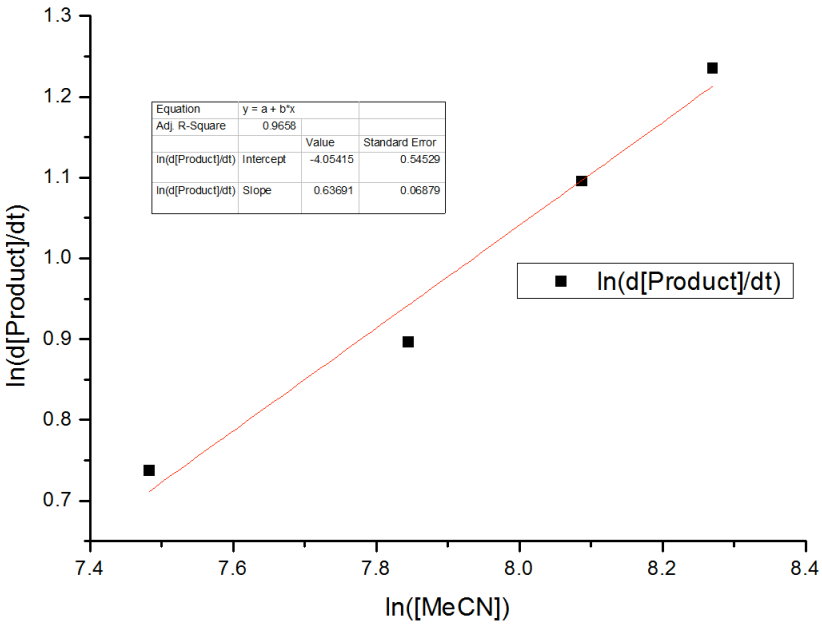


Figure S2. (a) Initial rate kinetic experiments for MeCN. (b) Plot of ln(d[Product]/dt) versus ln([MeCN])

5.3 Determination of the reaction order in catalyst.

The reaction with different concentration of catalyst (5 mol%, 7.5 mol% and 10 mol%) at 4.1, 6.1 and 8.1 mM were performed according to the general procedure described above except for varying the amount of catalyst added, and the results were summarized in the **Table S3** and **Figure S3** below.

Table S3. Initial rates of varying concentration of catalyst

[Catalyst] (mM)	*d*[Product]/*d*t (mM/h)
4.1	1.99
6.1	2.91
8.1	3.67

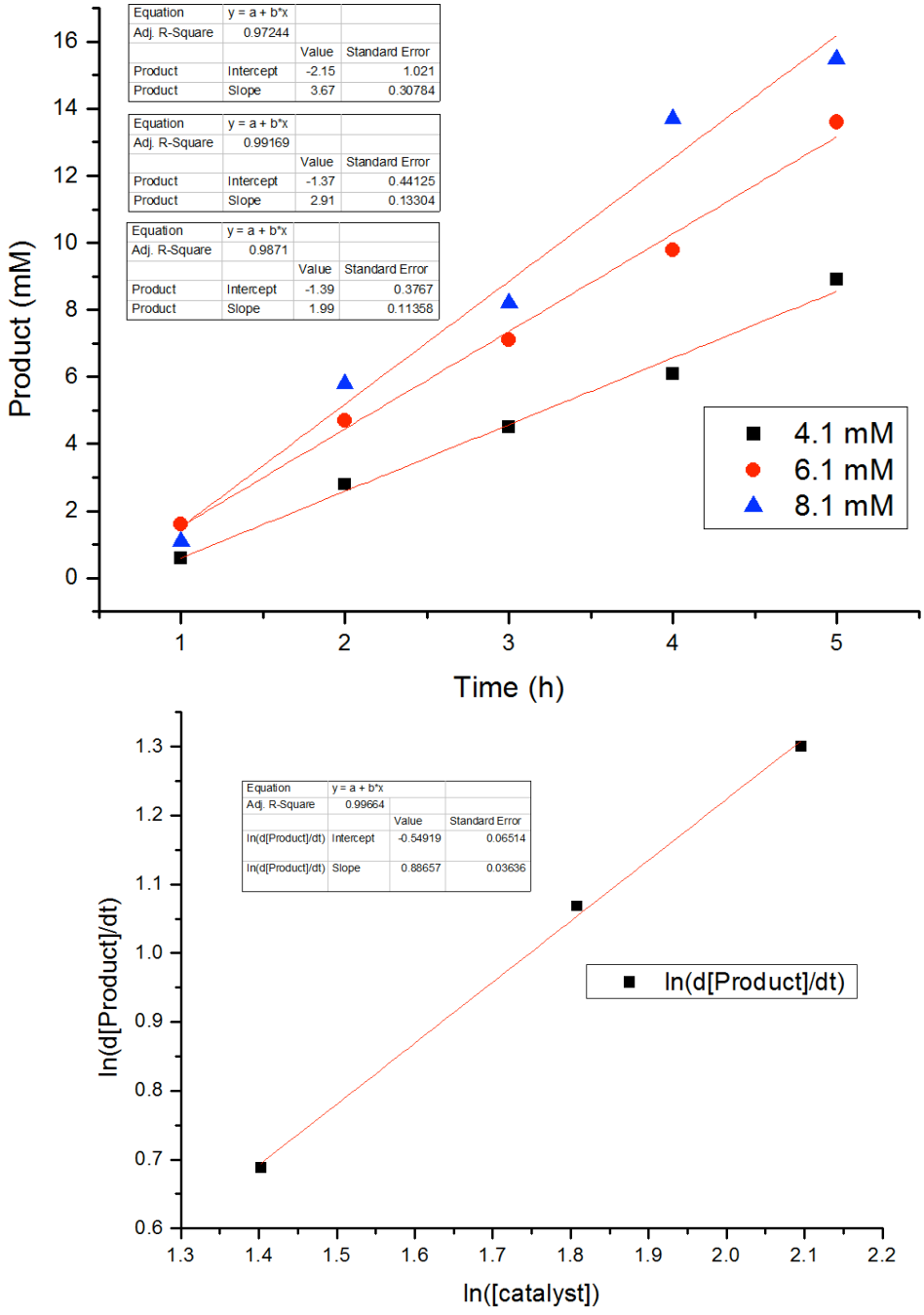


Figure S3. (a) Initial rate kinetic experiments for catalyst. (b) Plot of ln(d[Product]/dt) versus ln([catalyst])

6. Kinetic Isotope Effects

A flame-dried 20 mL test tube equipped with a magnetic stirring bar and 3-way glass stopcock was charged with [Ir(cod)(OMe)]$_2$ (3.3 mg, 0.005 mmol), NHC precursor (5.0 mg, 0.01 mmol) under Ar atmosphere and THF (0.5 mL) was added at room temperature, then Barton's base (20.0 μL, 0.1 mmol) was added. The mixture was stirred at room temperature for 0.5 h and then cooled to 0 °C. *para-F* Substituted ketimine (0.1 mmol) in THF (0.5 mL) was added via a gas-tight syringe with a stainless steel needle under an Ar atmosphere. Then MeCN (210 μL, 4 mmol) was added via a gas-tight syringe with a stainless steel needle under an Ar atmosphere. Aliquots were taken at 1 h intervals by removing a small amount (ca. 0.1 mL) of the reaction solution and quenched it immediately with AcOH (0.1 mL, 0.1 M in THF), then passing it through a small silica gel plug, eluting with THF. After evaporation, the residue analyzed by ^{1}F NMR spectroscopy to determine the yield based on the relative integration values of the peaks at –103.5 ppm (for ketimine) and –112.4 (for product).

The reaction with CD_3CN was performed independently under the identical reaction condition. The results were summarized in the **Table S4** and **Figure S4** below. Based on the slopes in **Figure S4**, the value of kinetic isotope effect was calculated to be $k_H/k_D = 2.27/0.62 = 3.7$, suggesting the presence of primary kinetic isotope effects.

Table S4. Comparison of initial rates of CH_3CN and CD_3CN

Time (h)	[Product] (mM)/ CH_3CN	[Product] (mM)/ CD_3CN
1h	2.2	1.3
2h	4.1	1.9
3h	6.3	2.3
4h	8.6	3.1
5h	11.3	3.8

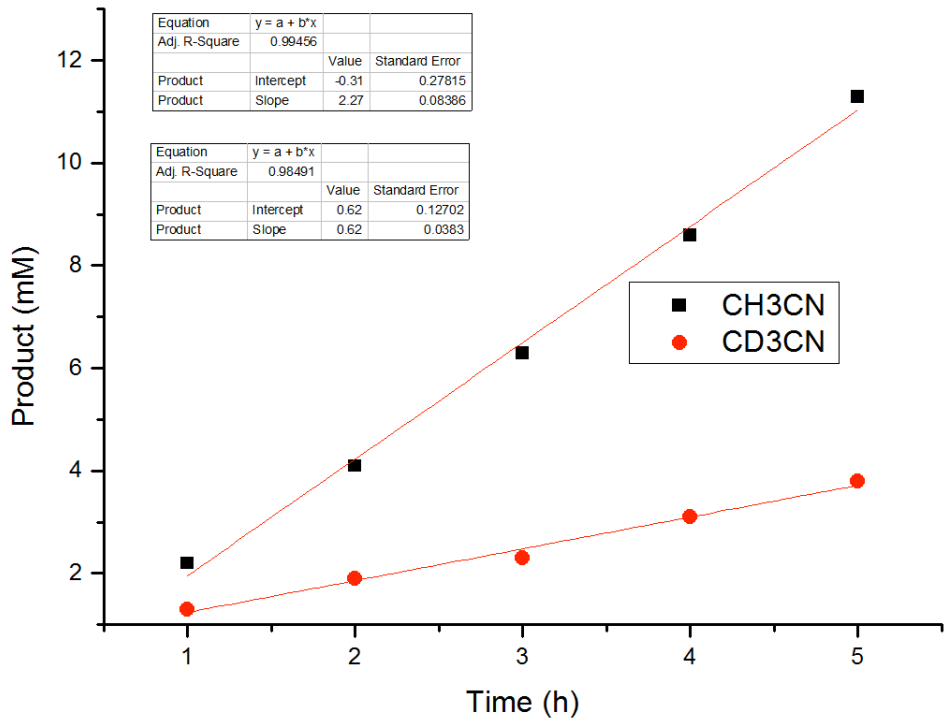


Figure S4. Initial rate kinetic experiments for CH_3CN and CD_3CN

7. Determination of Absolute Configuration

To **8a** (after enrichment by chiral stationary phase HPLC) in a mixture of EtOAc/AcOH (v/v: 4/1), (5 mL), H_2O_2 (35 wt %), (1.0 mL) was added dropwise at room temperature. The reaction was quenched with sat. $NaHCO_3$ solution after **8a** disappeared on TLC at room temperature. The mixture was extracted with ethyl acetate, and the organic layers were combined and dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the obtained crude mixture was purified by silica gel column chromatography to afford **S1**. **S1** in Et_2O was left at room temperature to grow a single crystal. Single-crystal X-ray data were collected on a Rigaku R-AXIS RAPID II imaging plate area detector with graphite-monochromated Cu-Kα radiation. Data collection was conducted at 93 K. All structures were solved by direct methods and refined by full matrix least-squares against F^2 with all reflections. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in standard calculated positions, and were refined using the riding model. Refined structure and crystallographic parameters are summarized in Figure S1 and Table S1. The absolute and relative configuration of **S1** was determined to be as depicted below by Flack parameter.[3] CCDC 1498698 contains the supplementary crystallographic data for **S1**.

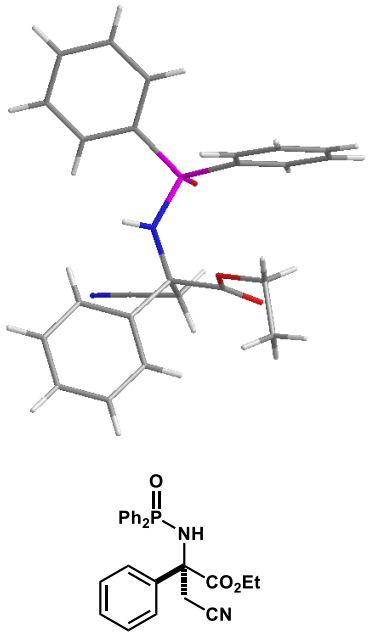


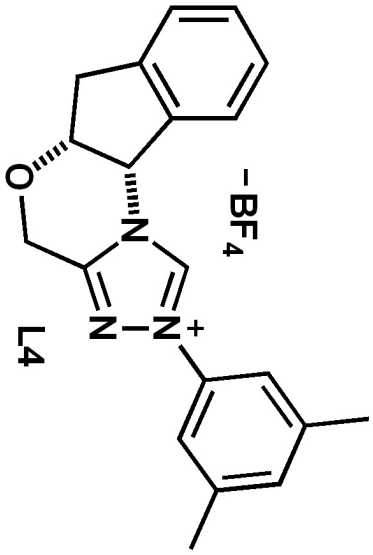
Figure S1. The structure of **S1** in the solid state. Color code: White: hydrogen; gray: carbon; blue: nitrogen; red: oxygen; purple: phosphorus.

Table S1. Selected Crystallographic Data of **S1**

	S1
molecular formula	$C_{24}H_{23}N_2O_3P$
formula weight	418.43
crystal color, habit	colorless, needle
crystal system	orthorhomlic
space group	$P2_12_12_1$(#19)
cell constants:	
a (Å)	10.03760(18)
b (Å)	11.6437(2)
c (Å)	18.2329(3)
α (deg)	90.0000
β (deg)	90.0000
γ (deg)	90.0000
V (Å^3)	2130.97(7)
Z	4
$\rho_{calcd.}$ (g·cm^{-3})	1.304
R_1	0.0653
wR_2	0.1523
F(000)	880.00
Flack parameter	0.012(13)

The relative and absolute configurations of other products were deduced by analogy.

3 Flack, H. D. *Acta Cryst.* **1983**, *A39*, 876.



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1.03
1.02
6.09

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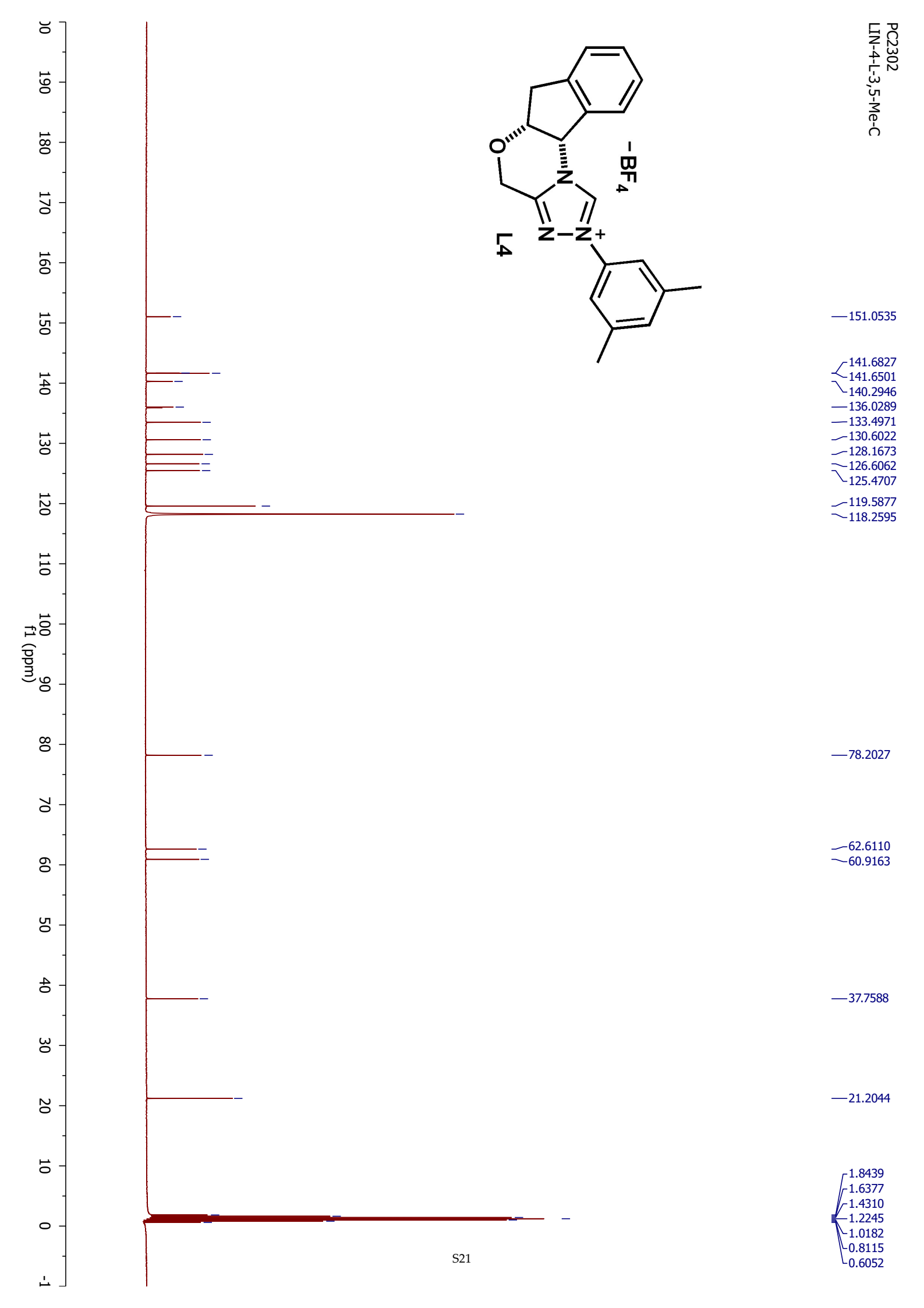
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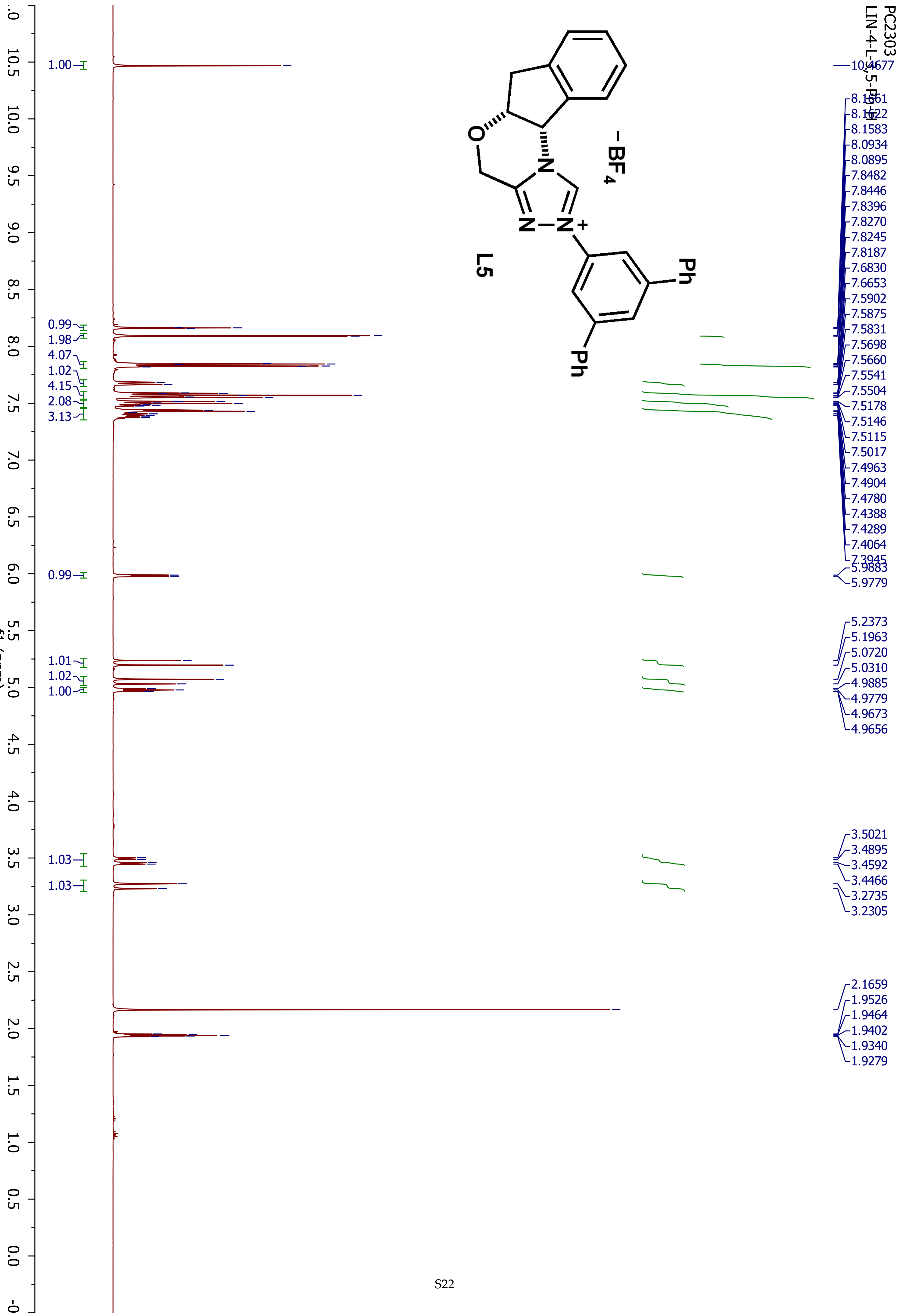
f1 (ppm)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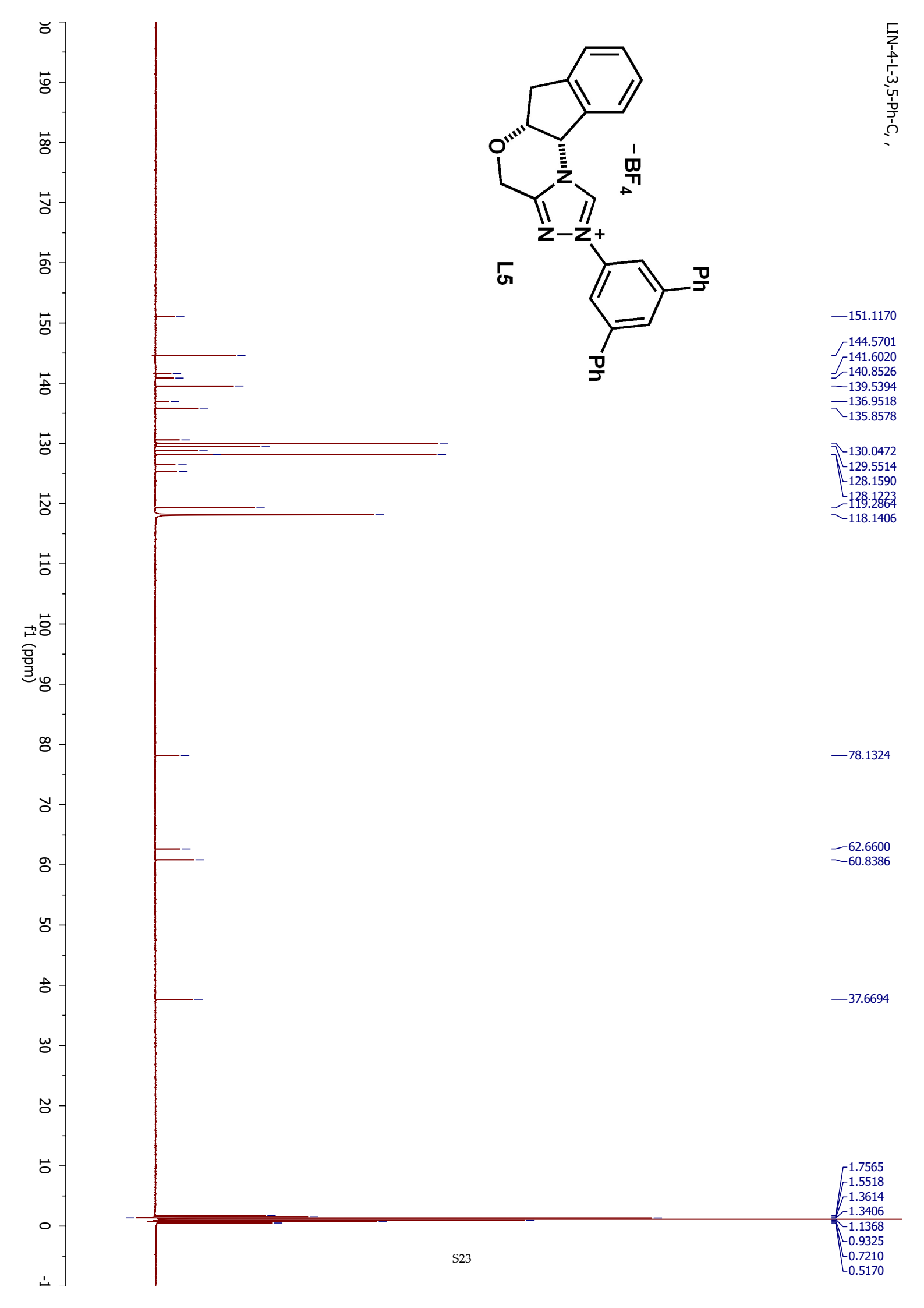
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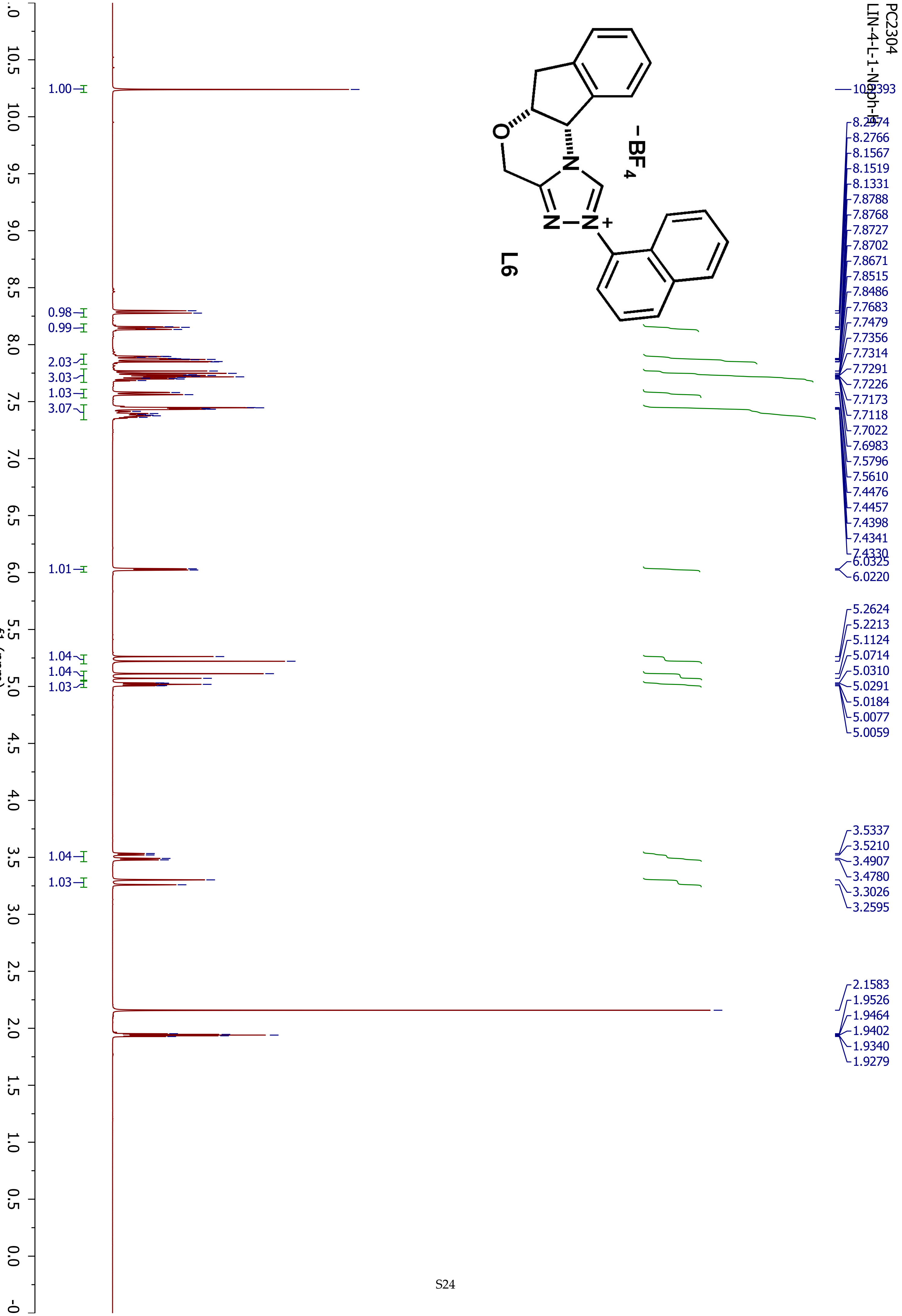
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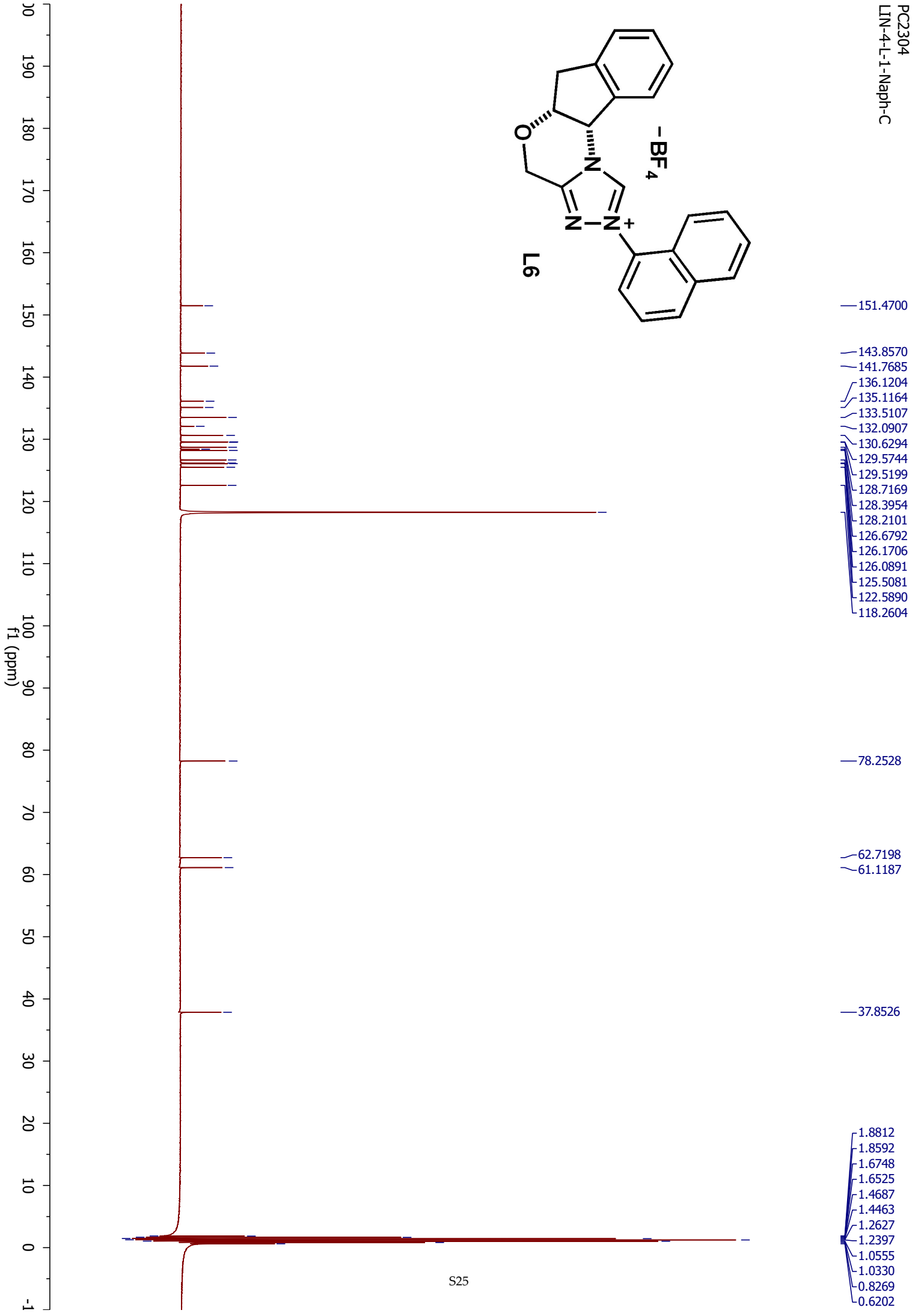
f1 (ppm)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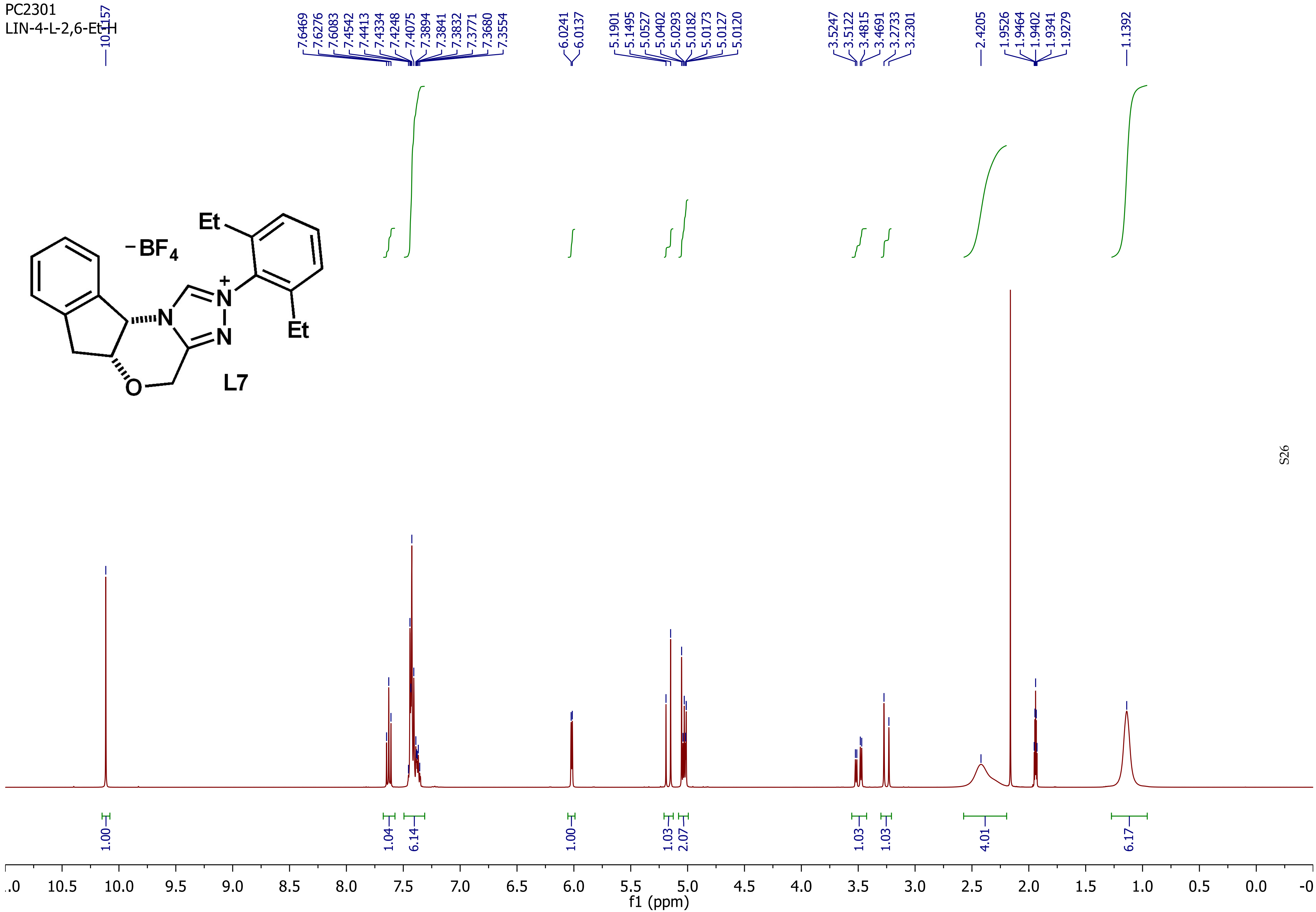
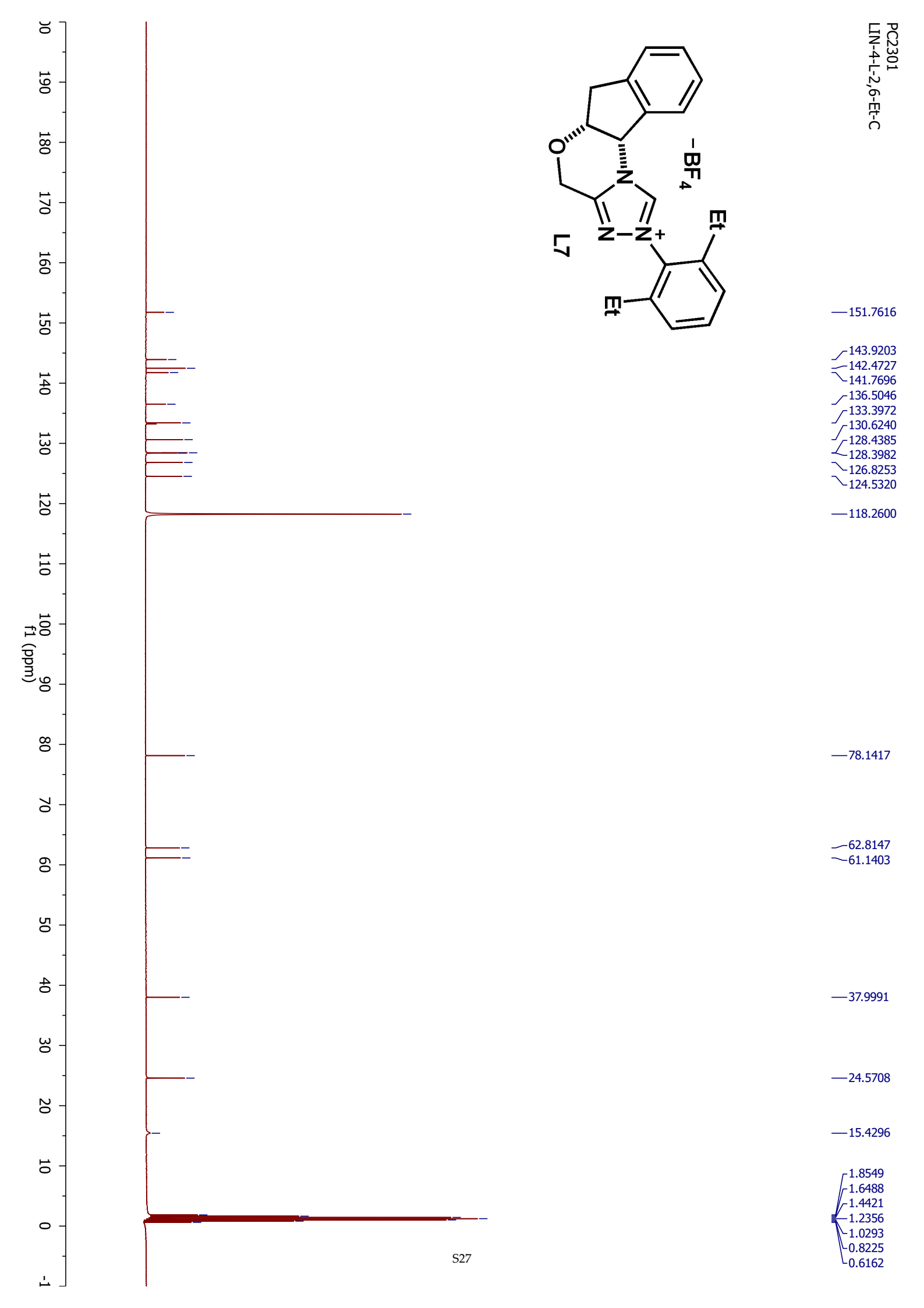
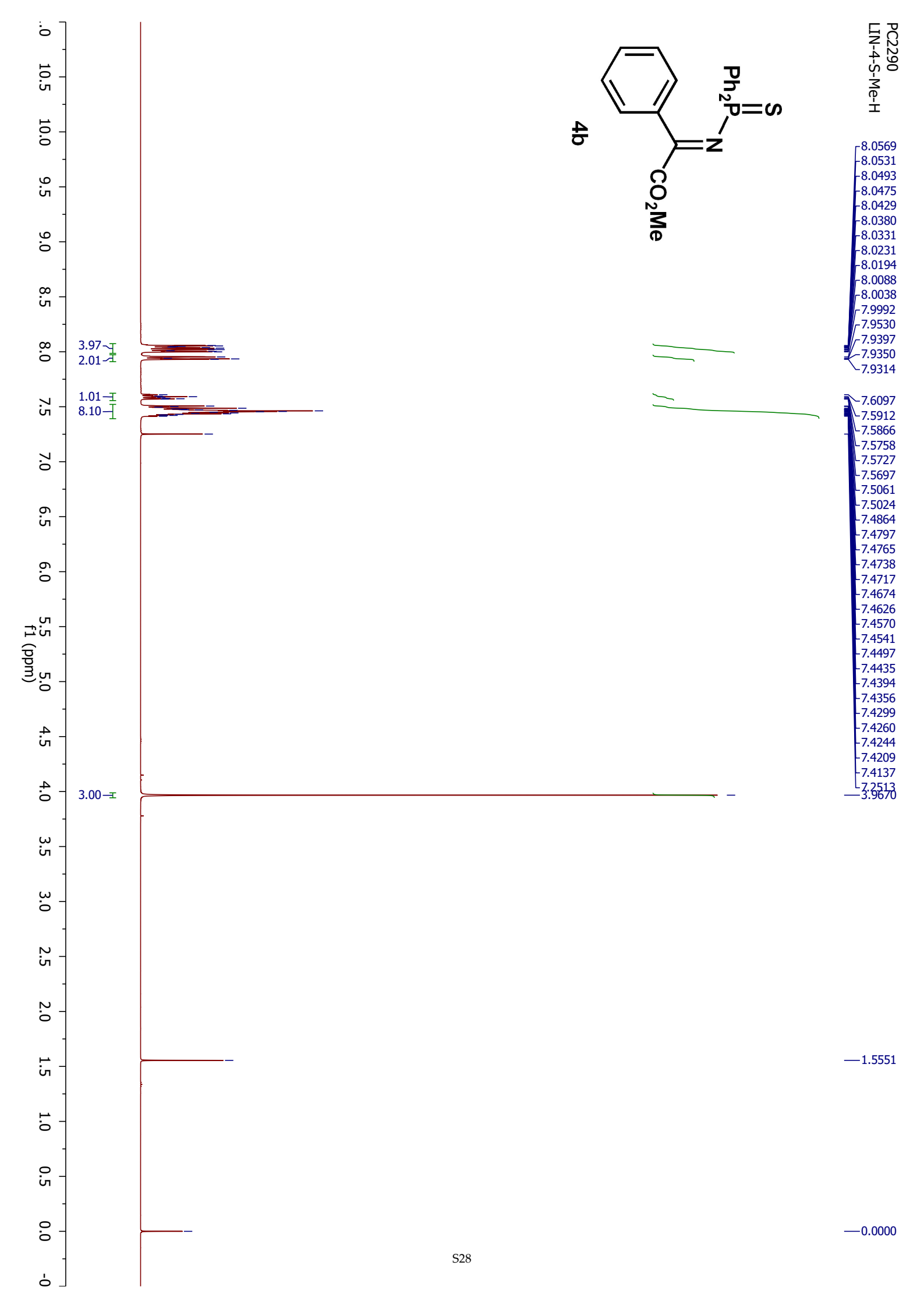
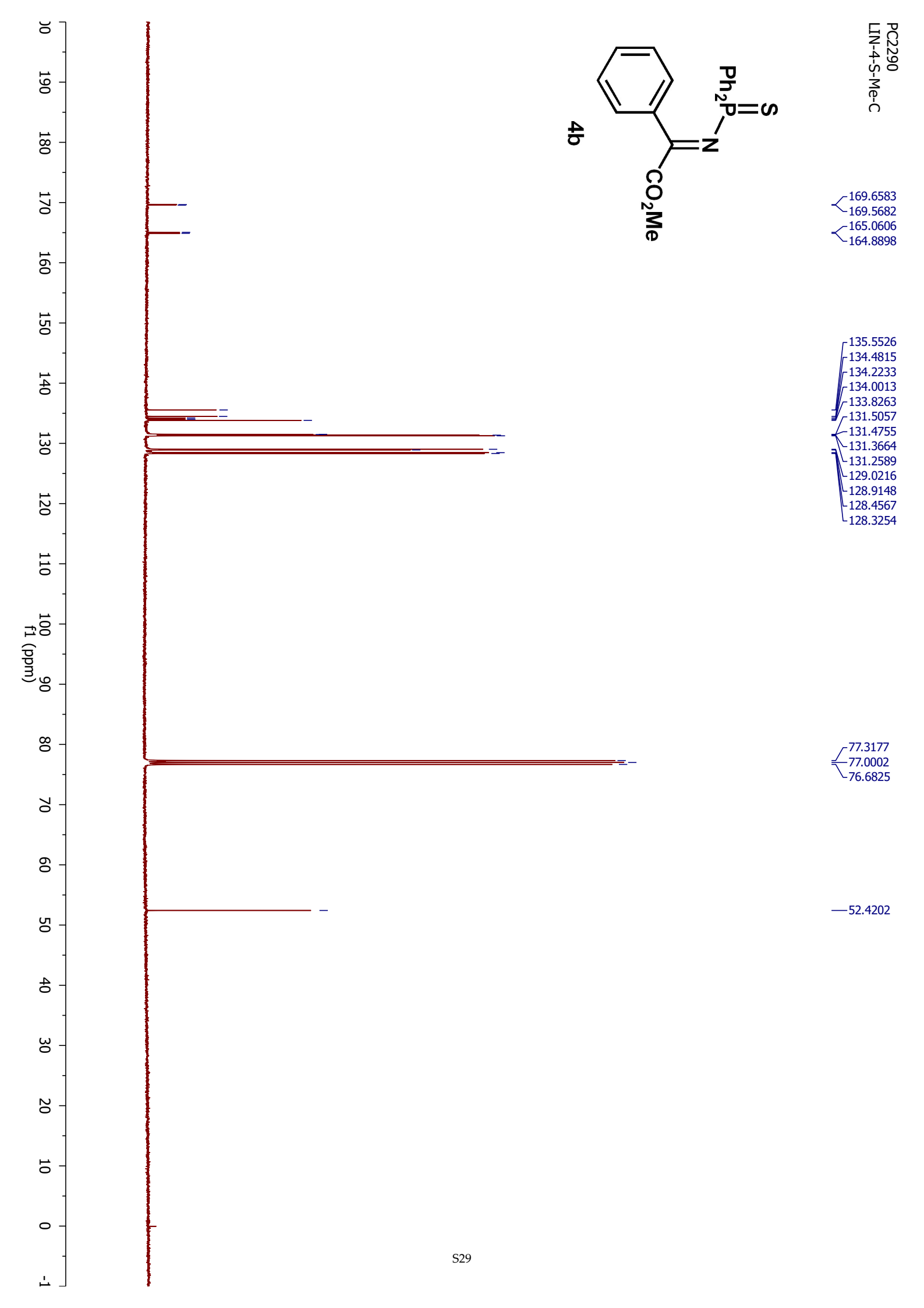
1.2397
1.0555
1.0330
0.8269
0.6202
f1 (ppm)

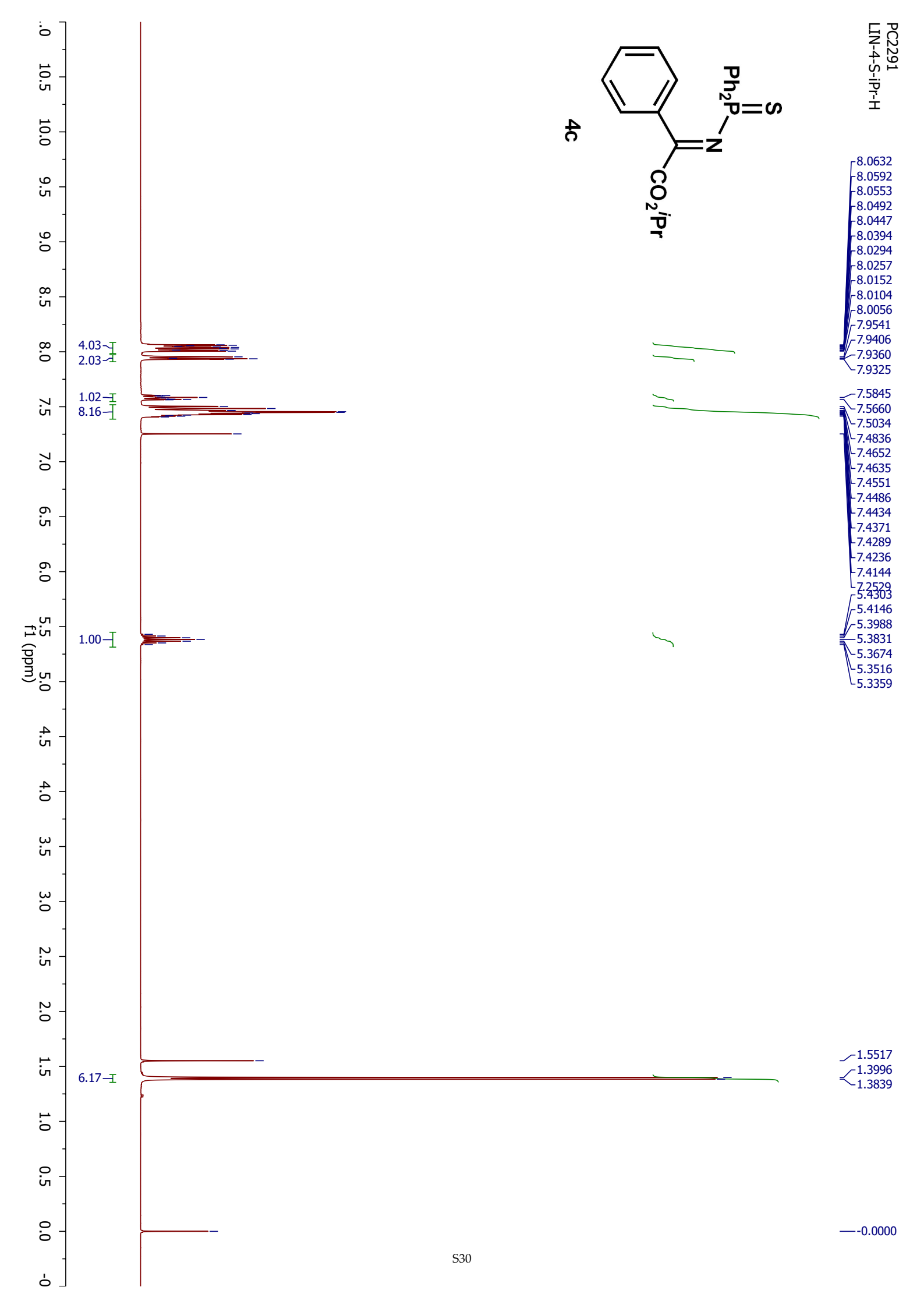


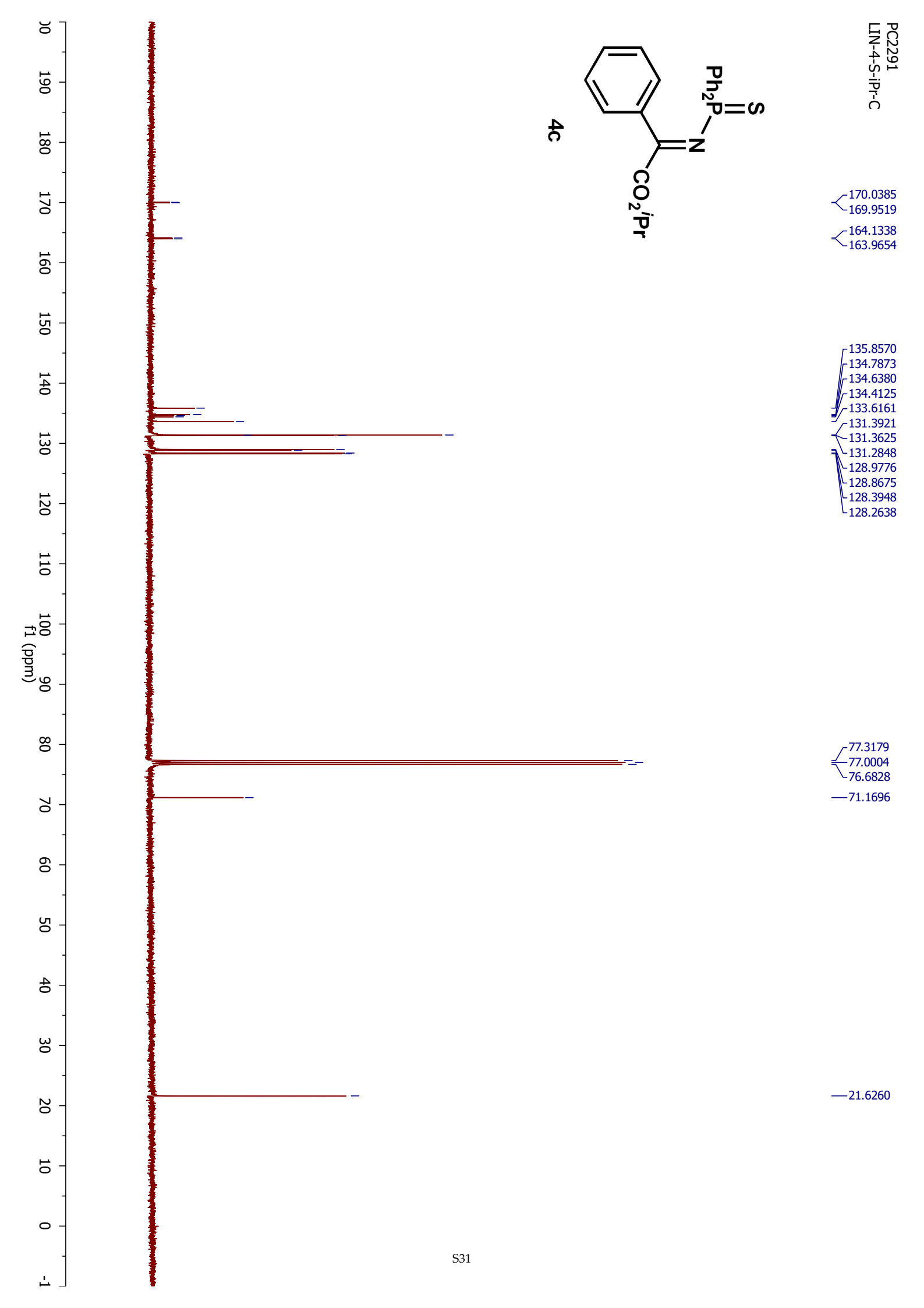
PC2301
LIN-4-L-2,6-Et-H
10.1157
7.6469
7.6276
7.6083
7.4542
7.4413
7.4334
7.4248
7.4075
7.3894
7.3841
7.3832
7.3771
7.3680
7.3554
6.0241
6.0137
5.1901
5.1495
5.0527
5.0402
5.0293
5.0182
5.0173
5.0127
5.0120
3.5247
3.5122
3.4815
3.4691
3.2733
3.2301
2.4205
1.9526
1.9464
1.9402
1.9341
1.9279
1.1392
$^{-}BF_4$
Et
Et
N
N
N
O
L7
1.00
1.04
6.14
1.00
1.03
2.07
1.03
1.03
4.01
6.17
f1 (ppm)

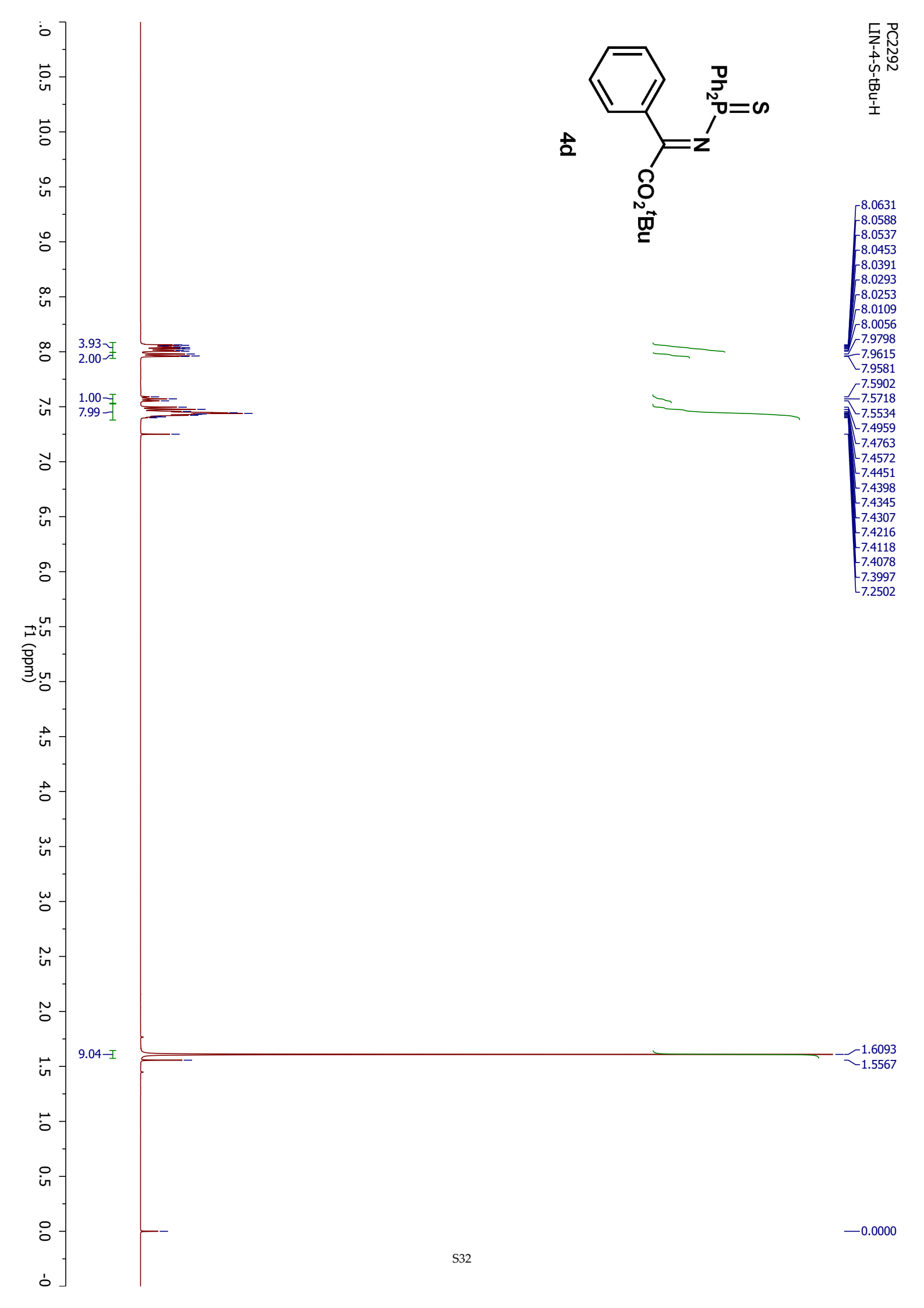

PC2301
LIN-4-L-2,6-Et-C
L7
Et
Et
151.7616
143.9203
142.4727
141.7696
136.5046
133.3972
130.6240
128.4385
128.3982
126.8253
124.5320
118.2600
78.1417
62.8147
61.1403
37.9991
24.5708
15.4296
1.8549
1.6488
1.4421
1.2356
1.0293
0.8225
0.6162
f1 (ppm)

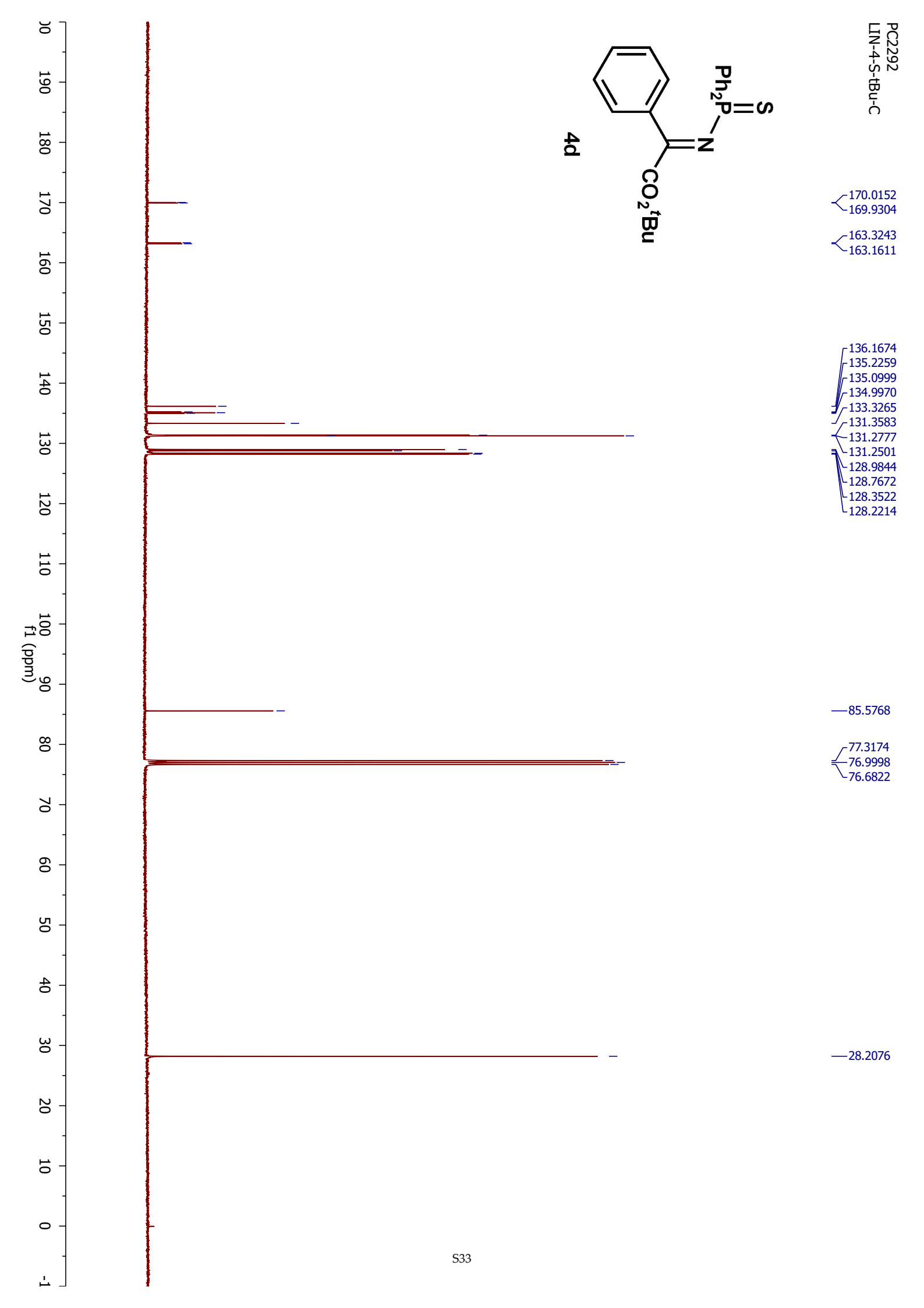

PC2290
LIN-4-S-Me-H
4b
Ph2P
S
N
CO2Me
f1 (ppm)
3.97
2.01
1.01
8.10
3.00
8.0569
8.0531
8.0493
8.0475
8.0429
8.0380
8.0331
8.0231
8.0194
8.0088
8.0038
7.9992
7.9530
7.9397
7.9350
7.9314
7.6097
7.5912
7.5866
7.5758
7.5727
7.5697
7.5061
7.5024
7.4864
7.4797
7.4765
7.4738
7.4717
7.4674
7.4626
7.4570
7.4541
7.4497
7.4435
7.4394
7.4356
7.4299
7.4260
7.4244
7.4209
7.4137
7.2513
3.9670
1.5551
0.0000

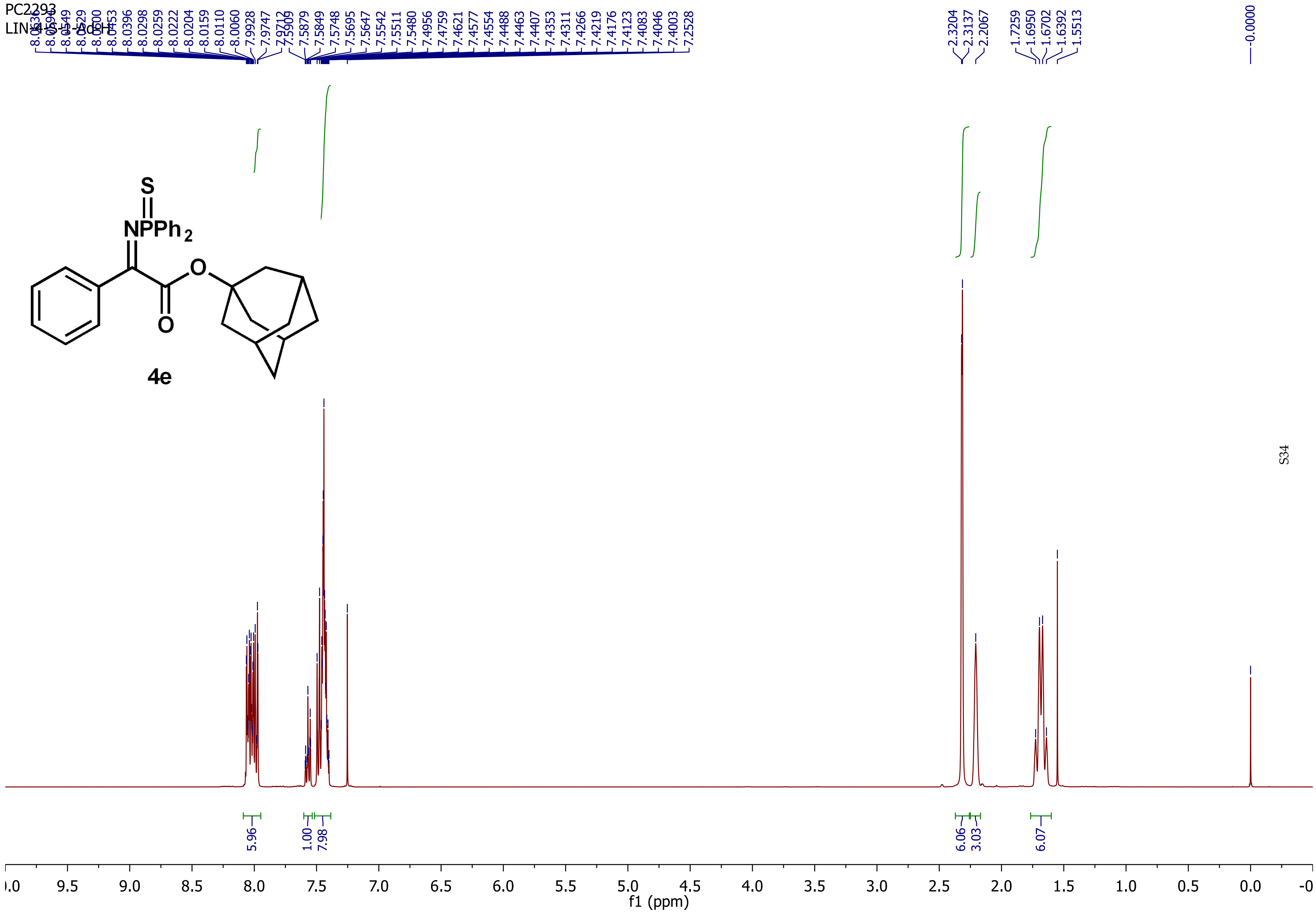

PC2290
LIN-4-S-Me-C
4b
Ph2P
S
N
CO2Me
169.6583
169.5682
165.0606
164.8898
135.5526
134.4815
134.2233
134.0013
133.8263
131.5057
131.4755
131.3664
131.2589
129.0216
128.9148
128.4567
128.3254
77.3177
77.0002
76.6825
52.4202
f1 (ppm)

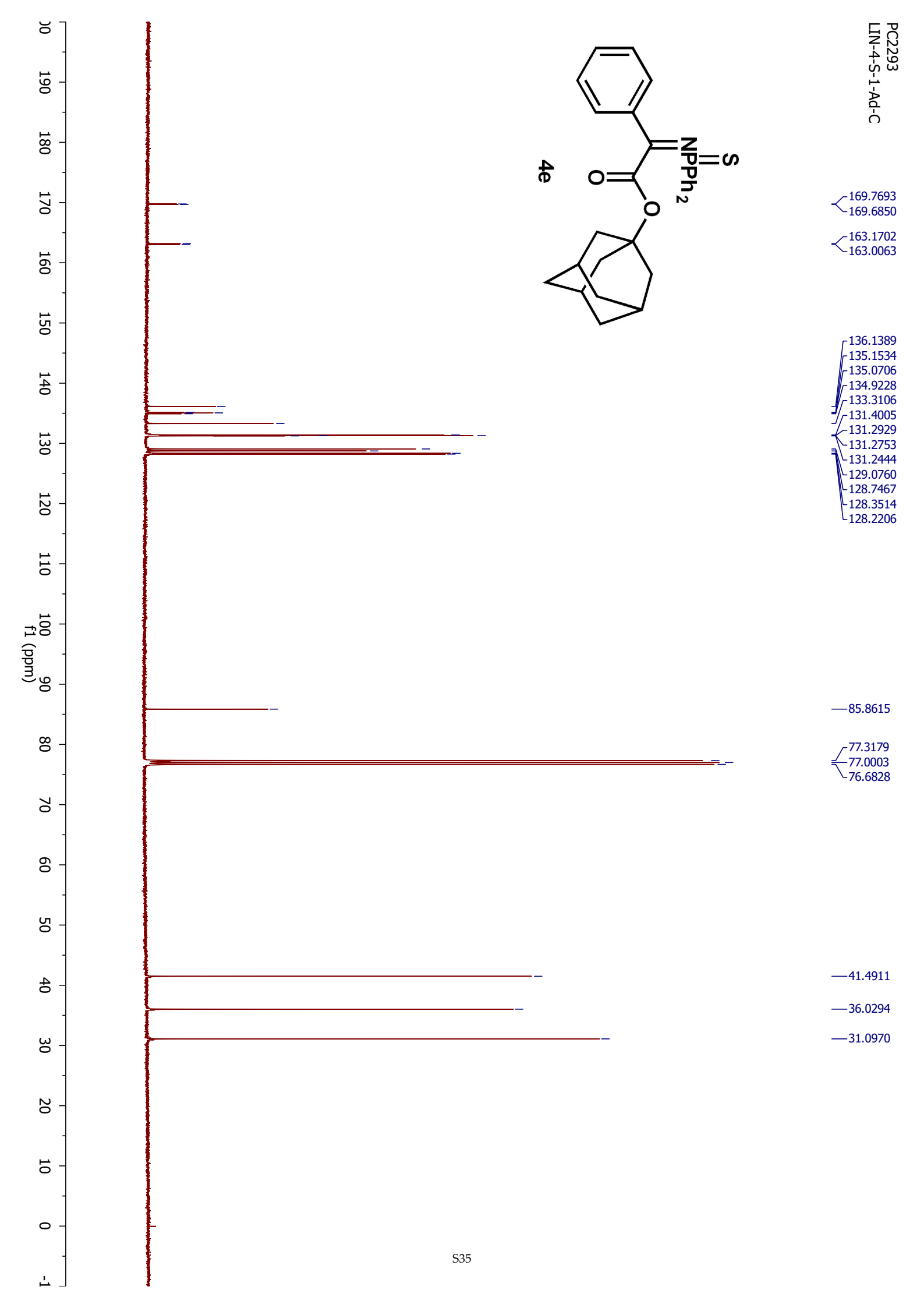

PC2291
LIN-4-S-iPr-H
4c
Ph2P
S
N
CO2iPr
8.0632
8.0592
8.0553
8.0492
8.0447
8.0394
8.0294
8.0257
8.0152
8.0104
8.0056
7.9541
7.9406
7.9360
7.9325
7.5845
7.5660
7.5034
7.4836
7.4652
7.4635
7.4551
7.4486
7.4434
7.4371
7.4289
7.4236
7.4144
7.2529
5.4303
5.4146
5.3988
5.3831
5.3674
5.3516
5.3359
1.5517
1.3996
1.3839
-0.0000
4.03
2.03
1.02
8.16
1.00
6.17
f1 (ppm)

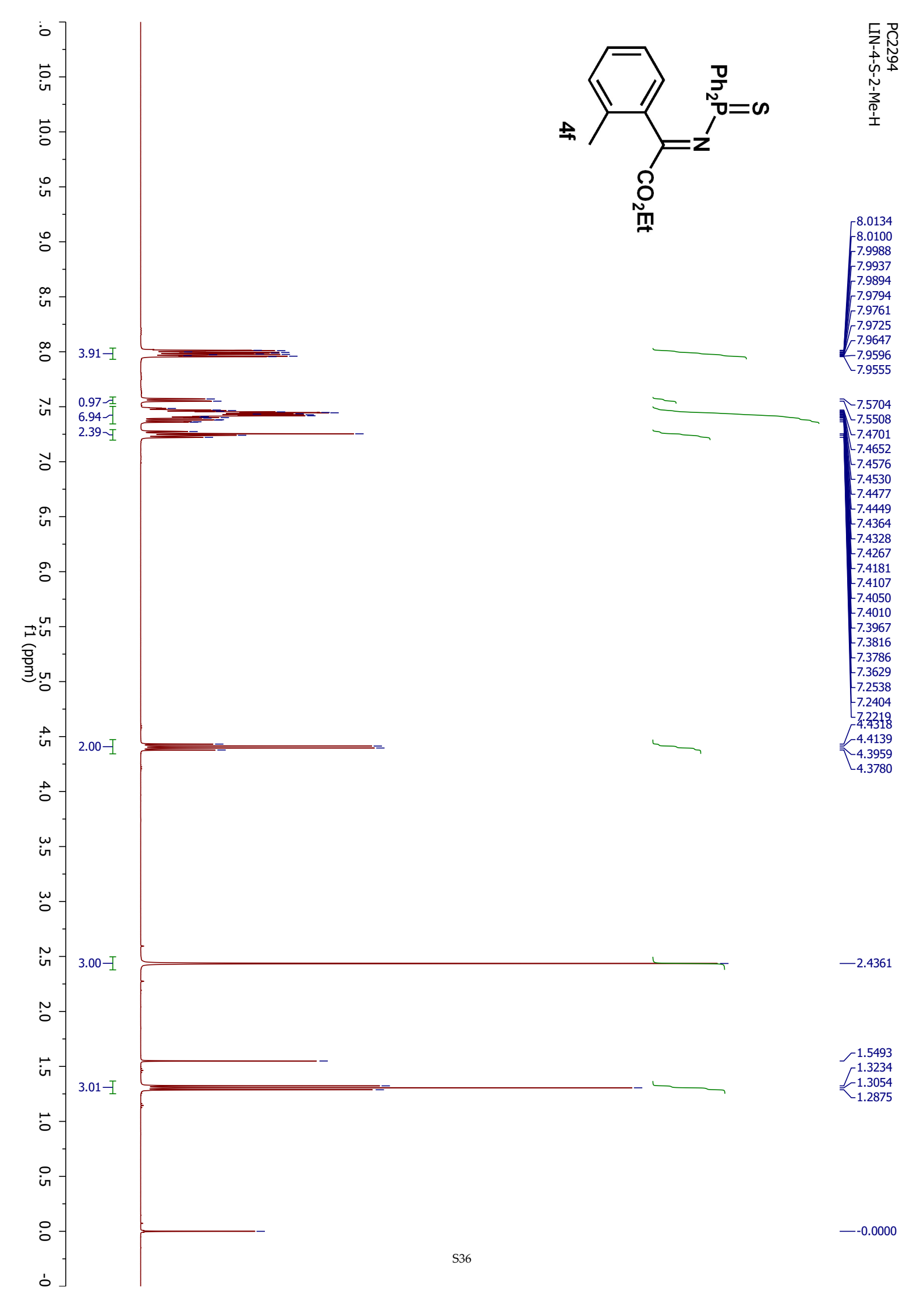

PC2291
LIN-4-S-iPr-C
4c
170.0385
169.9519
164.1338
163.9654
135.8570
134.7873
134.6380
134.4125
133.6161
131.3921
131.3625
131.2848
128.9776
128.8675
128.3948
128.2638
77.3179
77.0004
76.6828
71.1696
21.6260
f1 (ppm)

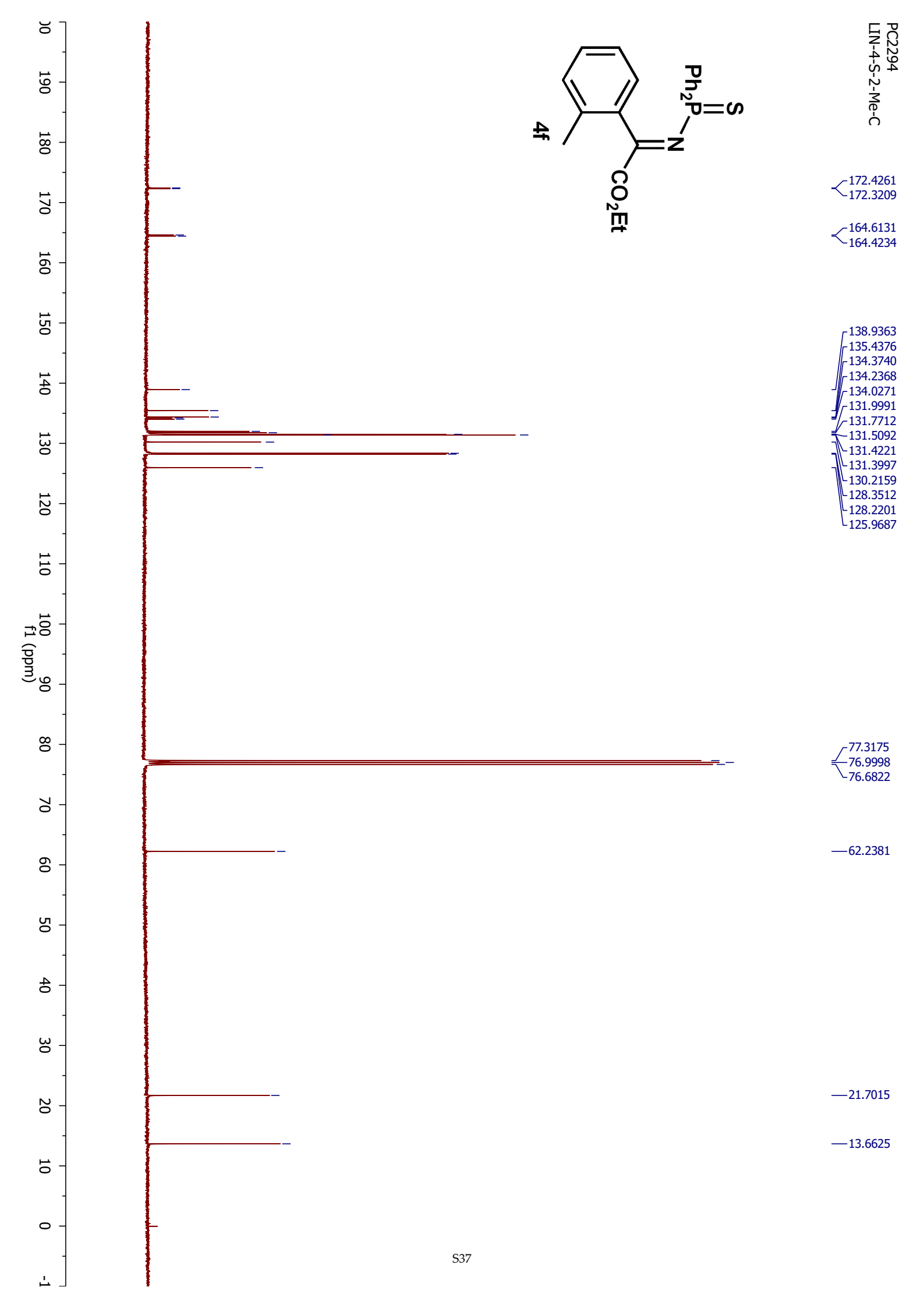

PC2292
LIN-4-S-tBu-H
4d
Ph2P
S
N
CO2tBu
8.0631
8.0588
8.0537
8.0453
8.0391
8.0293
8.0253
8.0109
8.0056
7.9798
7.9615
7.9581
7.5902
7.5718
7.5534
7.4959
7.4763
7.4572
7.4451
7.4398
7.4345
7.4307
7.4216
7.4118
7.4078
7.3997
7.2502
3.93
2.00
1.00
7.99
9.04
1.6093
1.5567
0.0000
f1 (ppm)

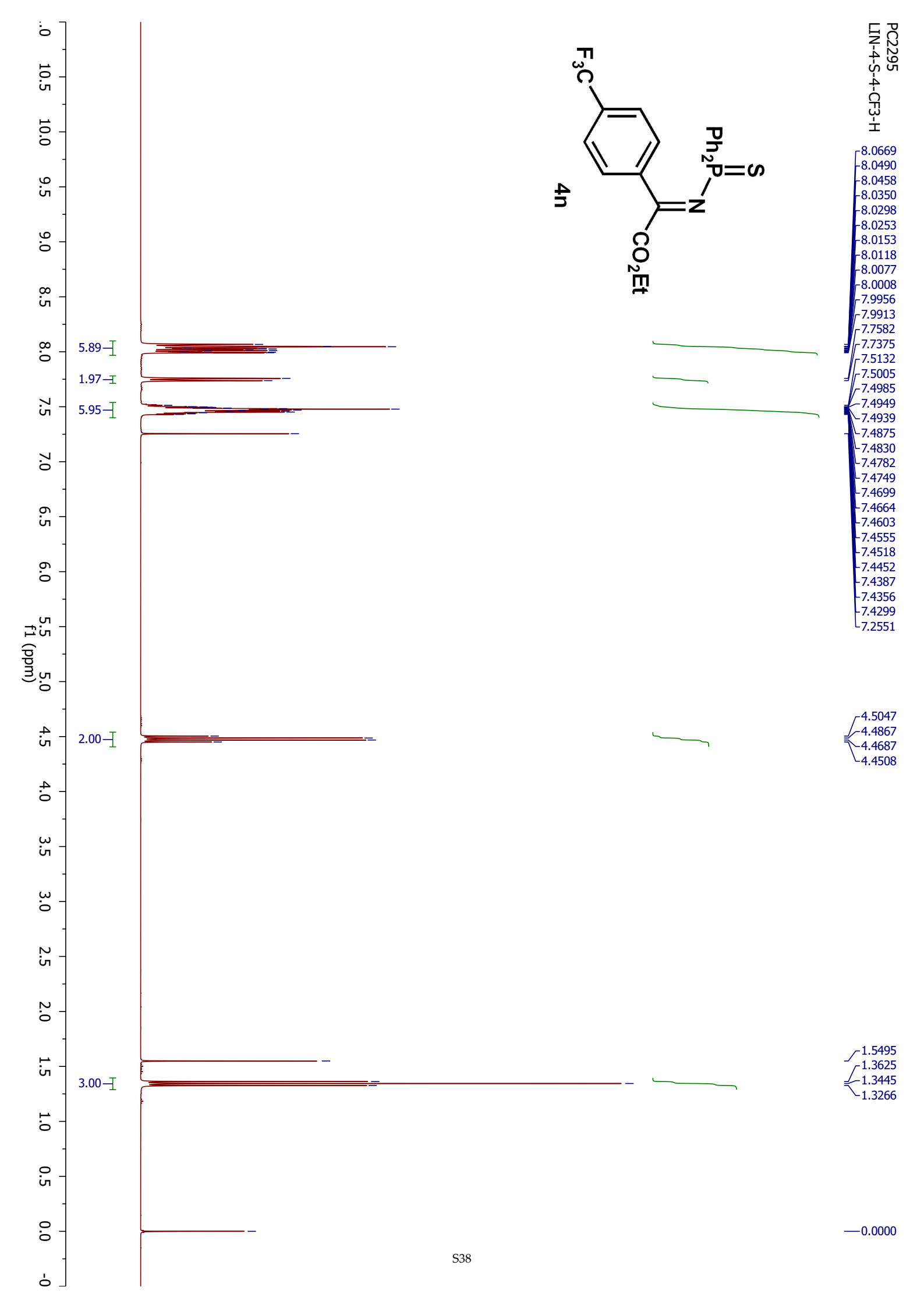

PC2292
LIN-4-S-tBu-C
4d
Ph2P
S
N
CO2tBu
170.0152
169.9304
163.3243
163.1611
136.1674
135.2259
135.0999
134.9970
133.3265
131.3583
131.2777
131.2501
128.9844
128.7672
128.3522
128.2214
85.5768
77.3174
76.9998
76.6822
28.2076
f1 (ppm)

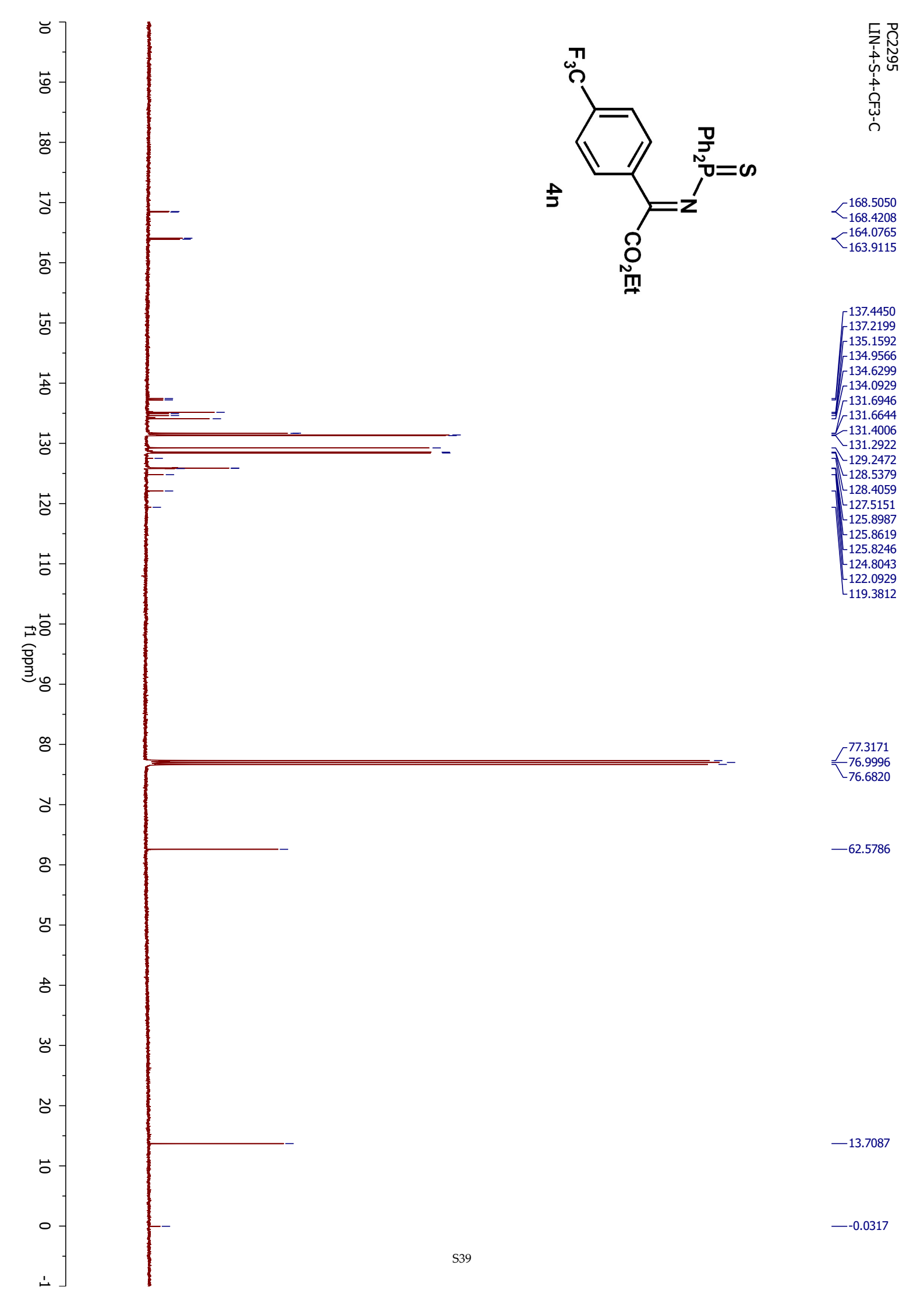

PC2293
LIN-4-S-1-AdOH
8.0636
8.0594
8.0549
8.0529
8.0500
8.0453
8.0396
8.0298
8.0259
8.0222
8.0204
8.0159
8.0110
8.0060
7.9928
7.9747
7.9712
7.5909
7.5879
7.5849
7.5748
7.5695
7.5647
7.5542
7.5511
7.5480
7.4956
7.4759
7.4621
7.4577
7.4554
7.4488
7.4463
7.4407
7.4353
7.4311
7.4266
7.4219
7.4176
7.4123
7.4083
7.4046
7.4003
7.2528
2.3204
2.3137
2.2067
1.7259
1.6950
1.6702
1.6392
1.5513
-0.0000
S
NPPh2
O
O
4e
5.96
1.00
7.98
6.06
3.03
6.07
f1 (ppm)

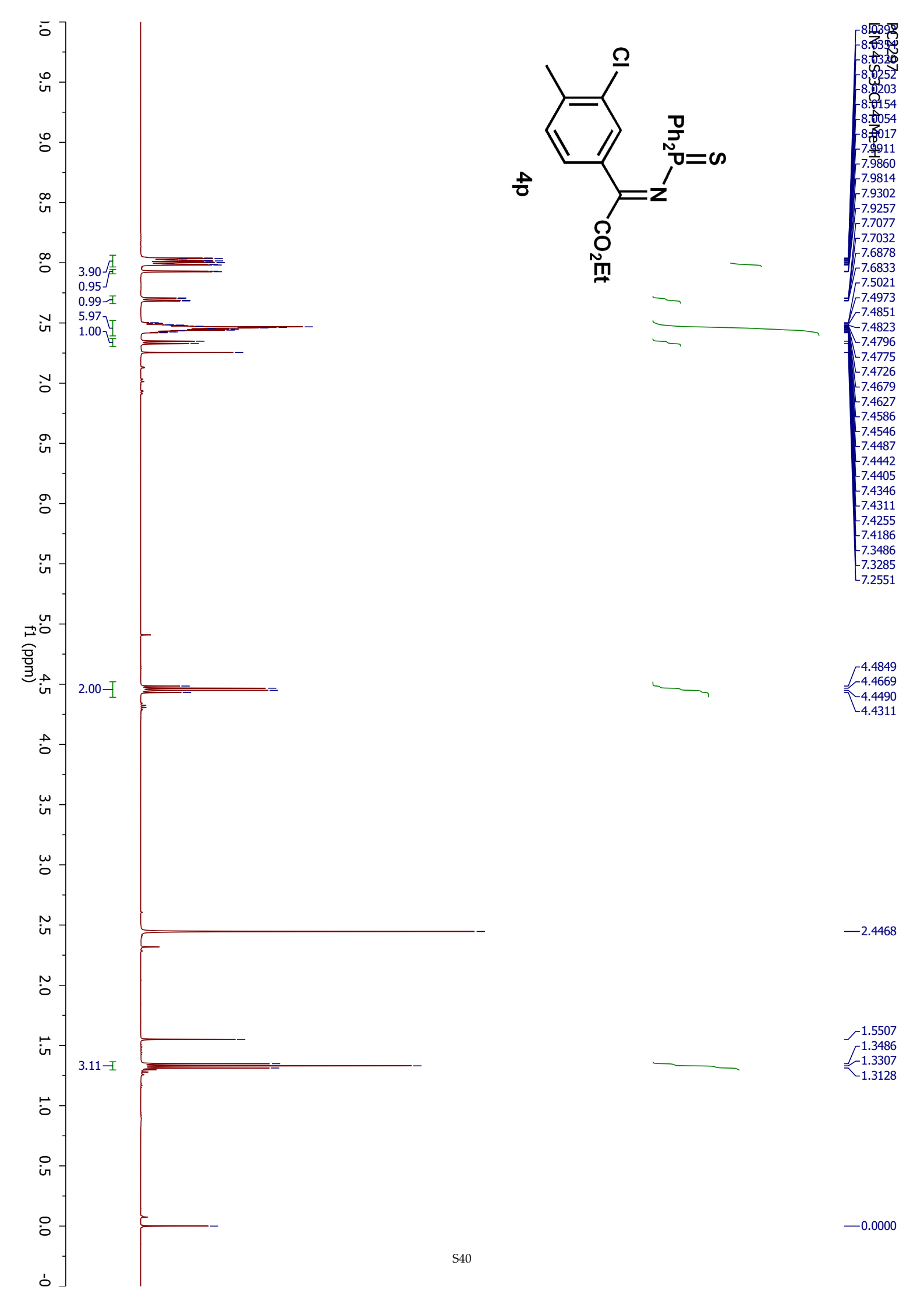

PC2293
LIN-4-S-1-Ad-C
4e
S
NPPh2
O
O
169.7693
169.6850
163.1702
163.0063
136.1389
135.1534
135.0706
134.9228
133.3106
131.4005
131.2929
131.2753
131.2444
129.0760
128.7467
128.3514
128.2206
85.8615
77.3179
77.0003
76.6828
41.4911
36.0294
31.0970
f1 (ppm)

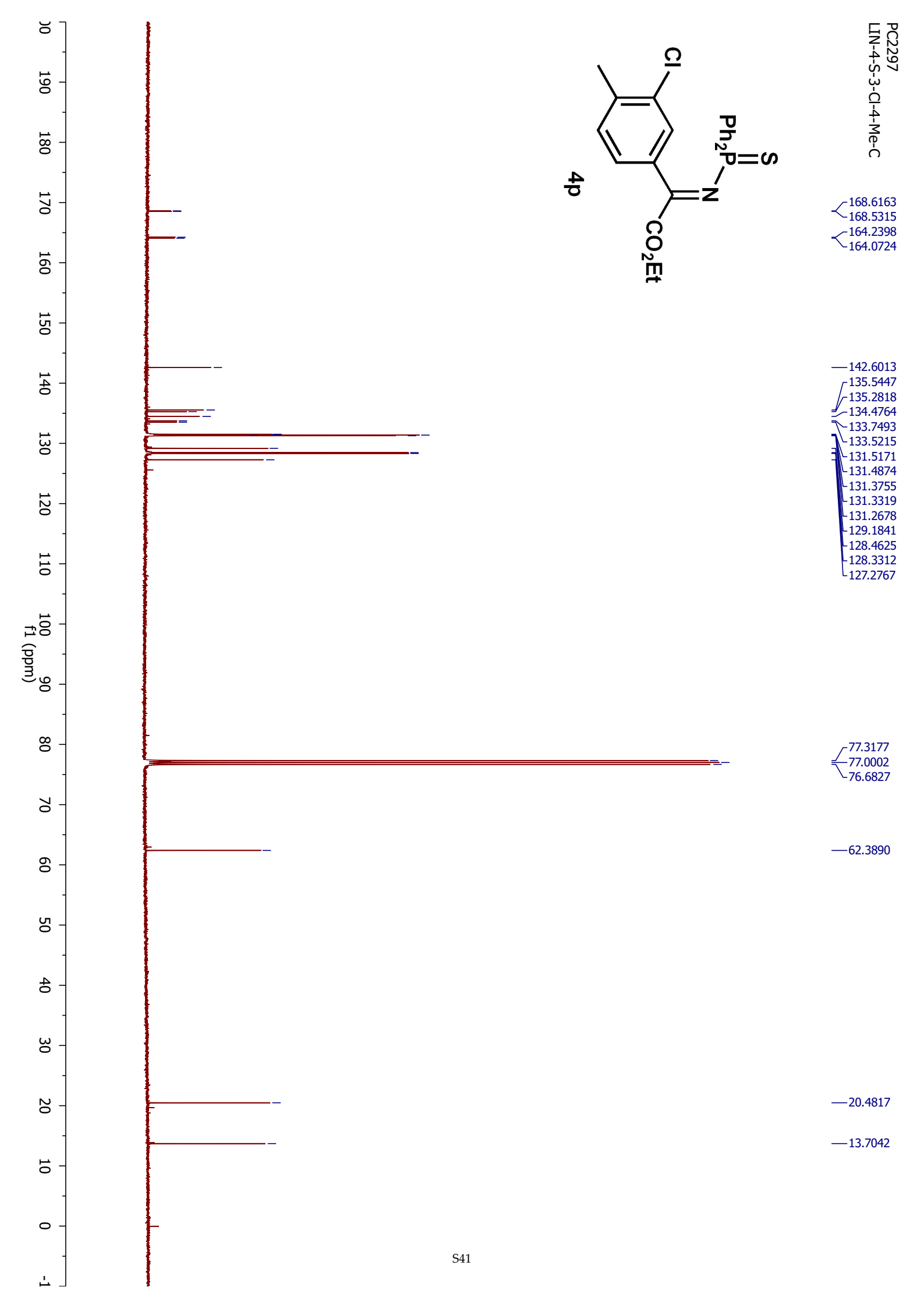

PC2294
LIN-4-S-2-Me-H
4f
Ph2P
S
N
CO2Et
f1 (ppm)
3.91
0.97
6.94
2.39
2.00
3.00
3.01
8.0134
8.0100
7.9988
7.9937
7.9894
7.9794
7.9761
7.9725
7.9647
7.9596
7.9555
7.5704
7.5508
7.4701
7.4652
7.4576
7.4530
7.4477
7.4449
7.4364
7.4328
7.4267
7.4181
7.4107
7.4050
7.4010
7.3967
7.3816
7.3786
7.3629
7.2538
7.2404
7.2219
4.4318
4.4139
4.3959
4.3780
2.4361
1.5493
1.3234
1.3054
1.2875
-0.0000

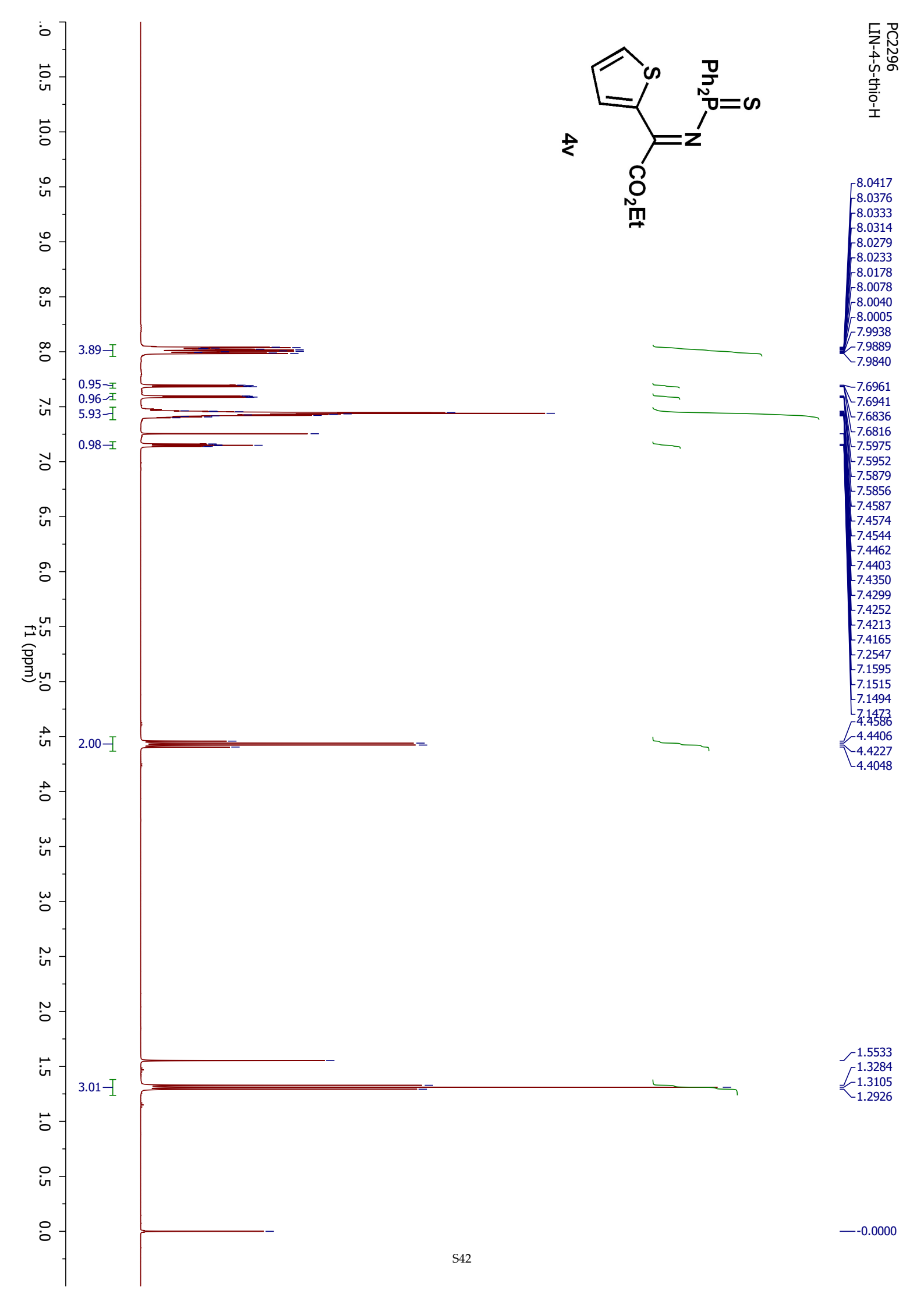

PC2294
LIN-4-S-2-Me-C
4f
S
Ph2P
N
CO2Et
172.4261
172.3209
164.6131
164.4234
138.9363
135.4376
134.3740
134.2368
134.0271
131.9991
131.7712
131.5092
131.4221
131.3997
130.2159
128.3512
128.2201
125.9687
77.3175
76.9998
76.6822
62.2381
21.7015
13.6625
f1 (ppm)

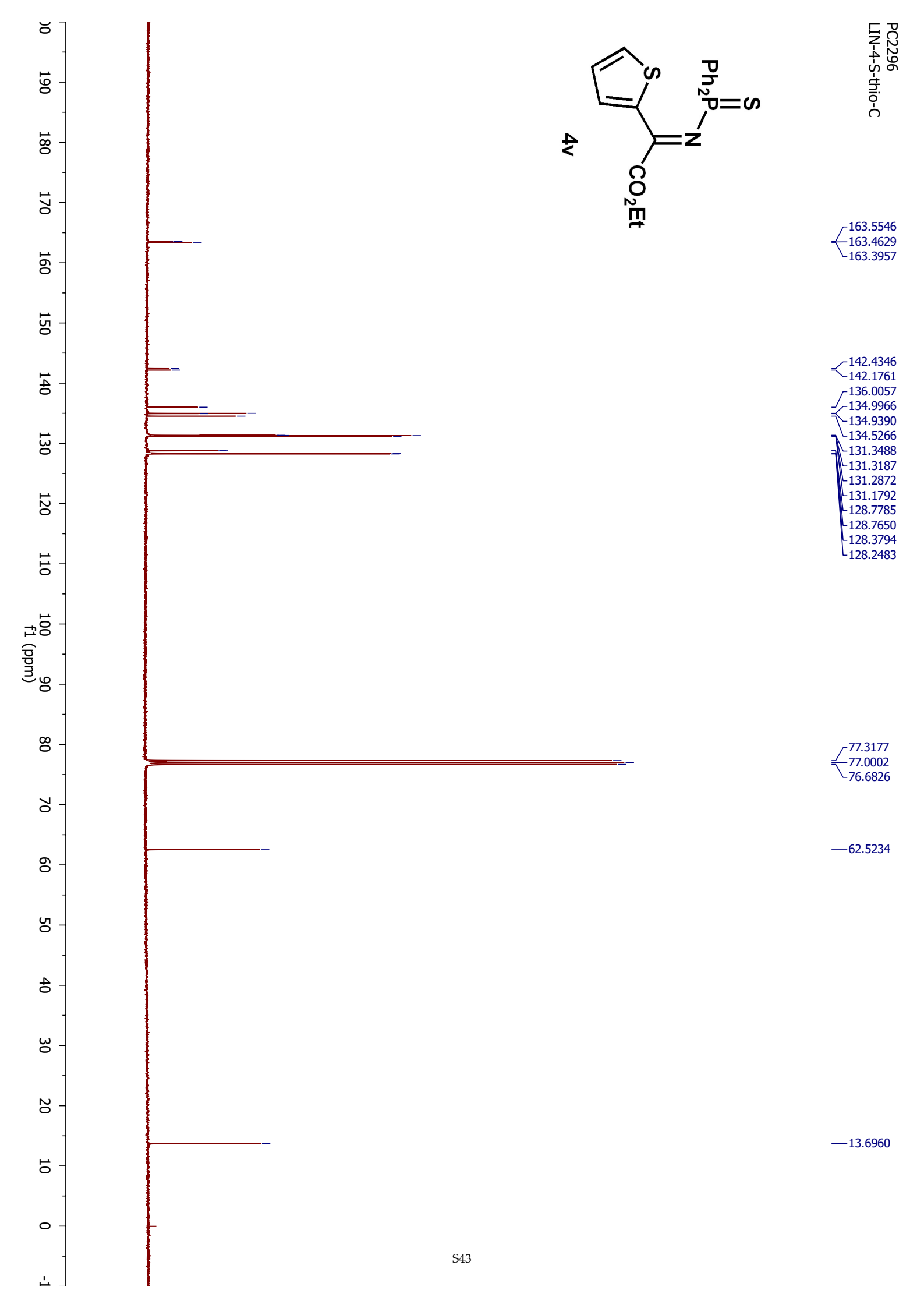

PC2295
LIN-4-S-4-CF3-H
4n
F3C
Ph2P
S
N
CO2Et
8.0669
8.0490
8.0458
8.0350
8.0298
8.0253
8.0153
8.0118
8.0077
8.0008
7.9956
7.9913
7.7582
7.7375
7.5132
7.5005
7.4985
7.4949
7.4939
7.4875
7.4830
7.4782
7.4749
7.4699
7.4664
7.4603
7.4555
7.4518
7.4452
7.4387
7.4356
7.4299
7.2551
4.5047
4.4867
4.4687
4.4508
1.5495
1.3625
1.3445
1.3266
0.0000
5.89
1.97
5.95
2.00
3.00
f1 (ppm)

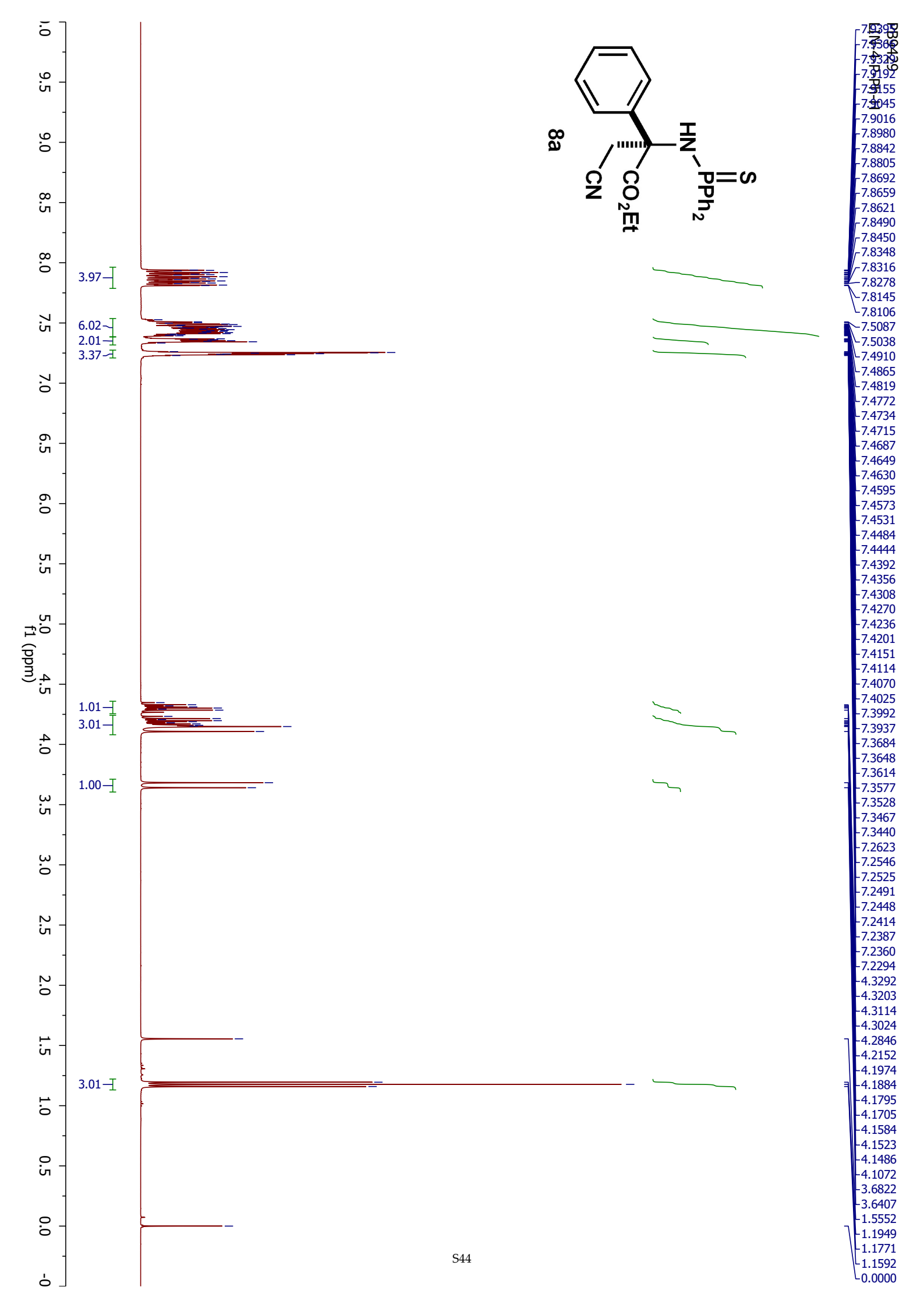

PC2295
LIN-4-S-4-CF3-C
4n
F3C
Ph2P
S
N
CO2Et
168.5050
168.4208
164.0765
163.9115
137.4450
137.2199
135.1592
134.9566
134.6299
134.0929
131.6946
131.6644
131.4006
131.2922
129.2472
128.5379
128.4059
127.5151
125.8987
125.8619
125.8246
124.8043
122.0929
119.3812
77.3171
76.9996
76.6820
62.5786
13.7087
-0.0317
f1 (ppm)

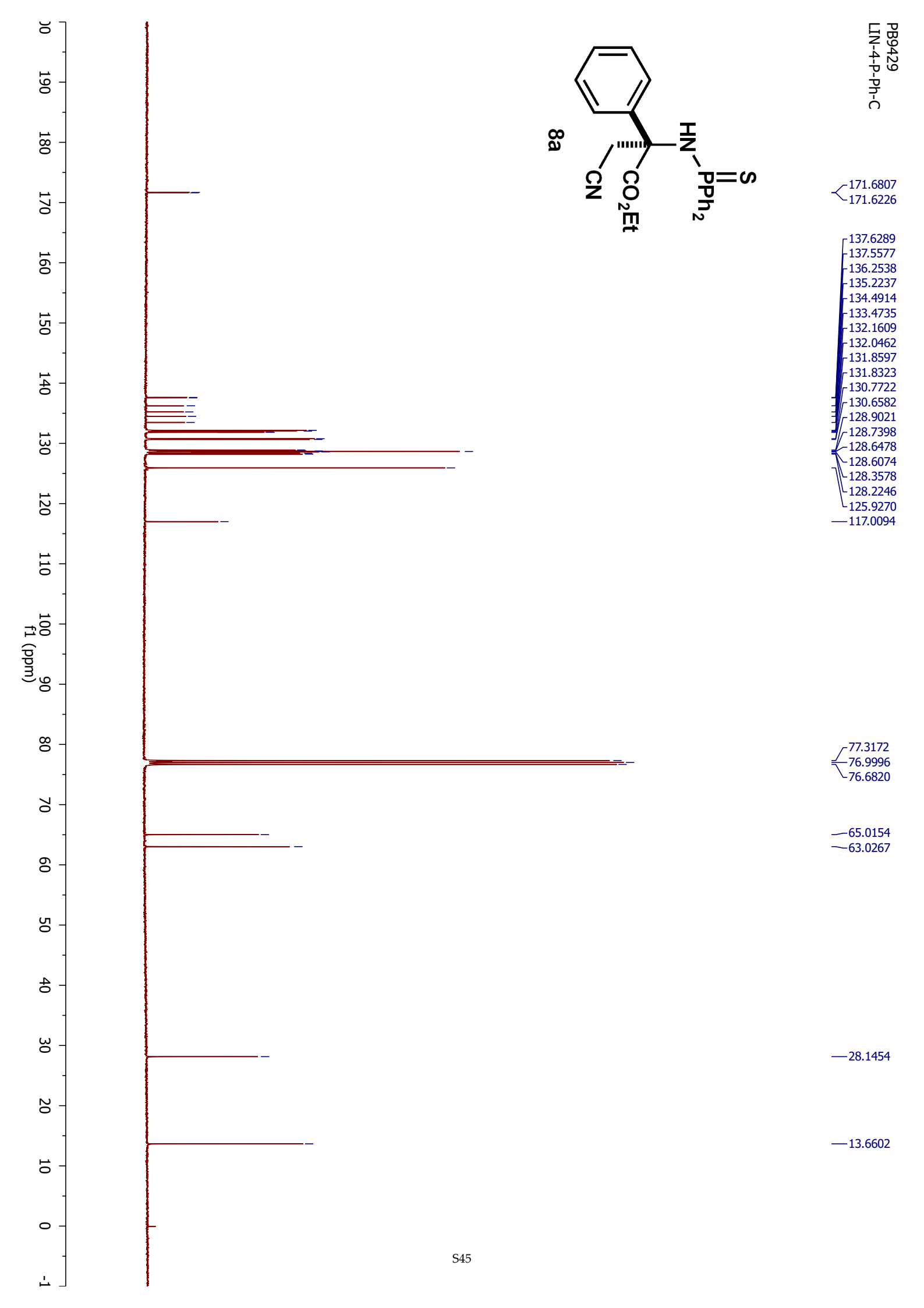

Cl
Ph2P
S
N
CO2Et
4p
3.90
0.95
0.99
5.97
1.00
2.00
3.11
2.4468
1.5507
1.3486
1.3307
1.3128
0.0000
f1 (ppm)

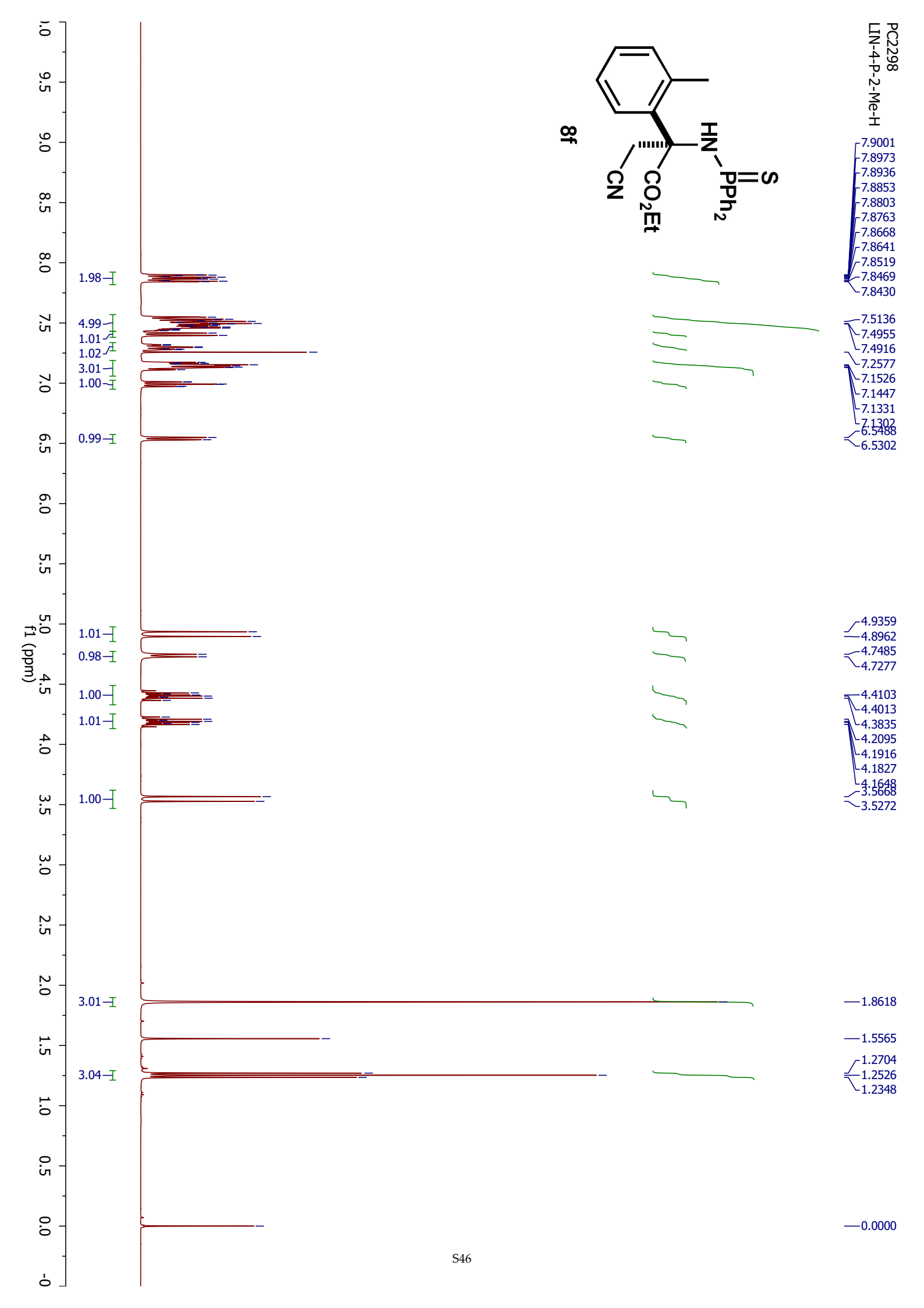

PC2297
LIN-4-S-3-Cl-4-Me-C
Cl
Ph2P
S
N
CO2Et
4p
168.6163
168.5315
164.2398
164.0724
142.6013
135.5447
135.2818
134.4764
133.7493
133.5215
131.5171
131.4874
131.3755
131.3319
131.2678
129.1841
128.4625
128.3312
127.2767
77.3177
77.0002
76.6827
62.3890
20.4817
13.7042
f1 (ppm)

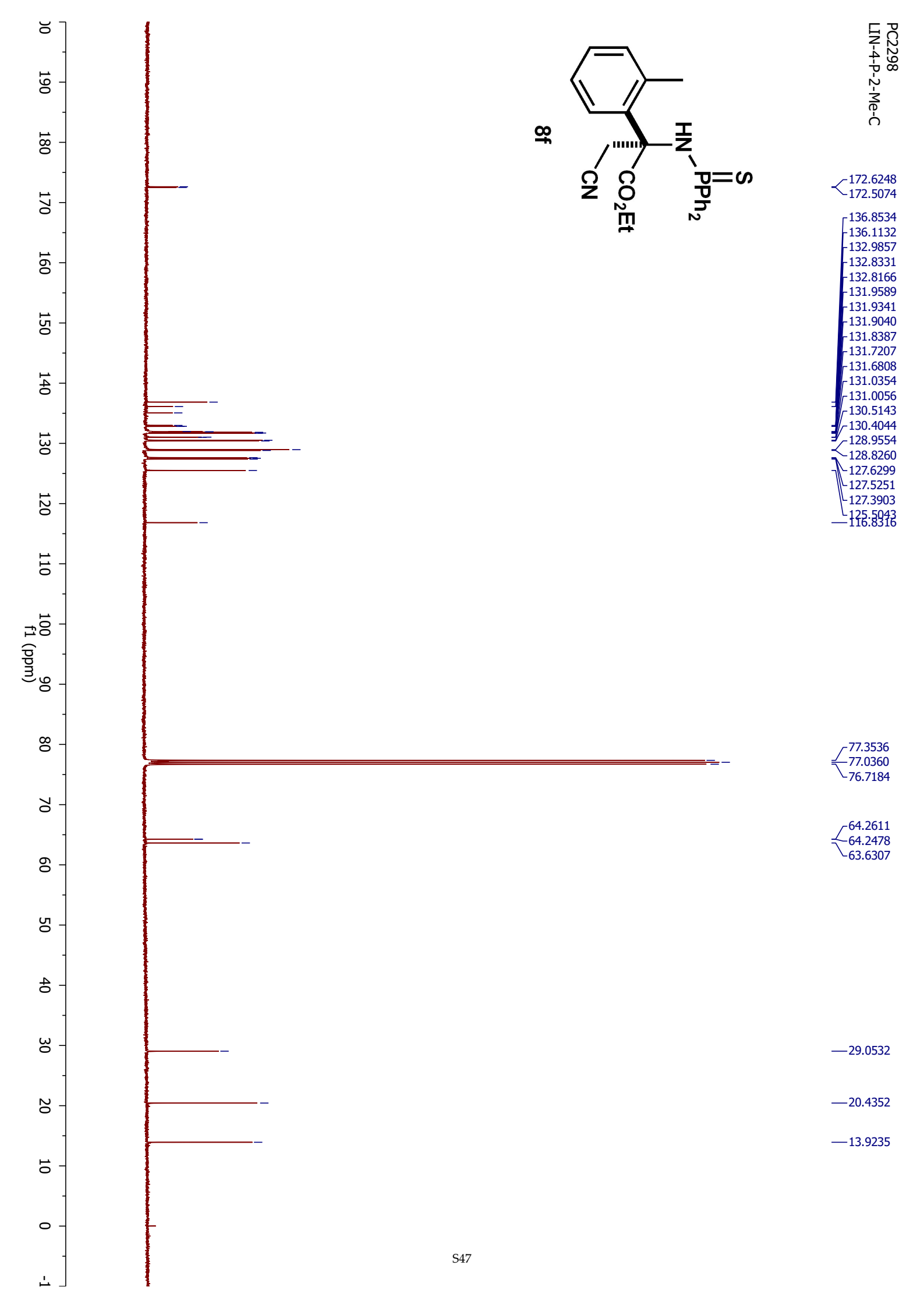

PC2296
LIN-4-S-thio-H
4v
f1 (ppm)
3.89
0.95
0.96
5.93
0.98
2.00
3.01
8.0417
8.0376
8.0333
8.0314
8.0279
8.0233
8.0178
8.0078
8.0040
8.0005
7.9938
7.9889
7.9840
7.6961
7.6941
7.6836
7.6816
7.5975
7.5952
7.5879
7.5856
7.4587
7.4574
7.4544
7.4462
7.4403
7.4350
7.4299
7.4252
7.4213
7.4165
7.2547
7.1595
7.1515
7.1494
7.1473
4.4586
4.4406
4.4227
4.4048
1.5533
1.3284
1.3105
1.2926
-0.0000

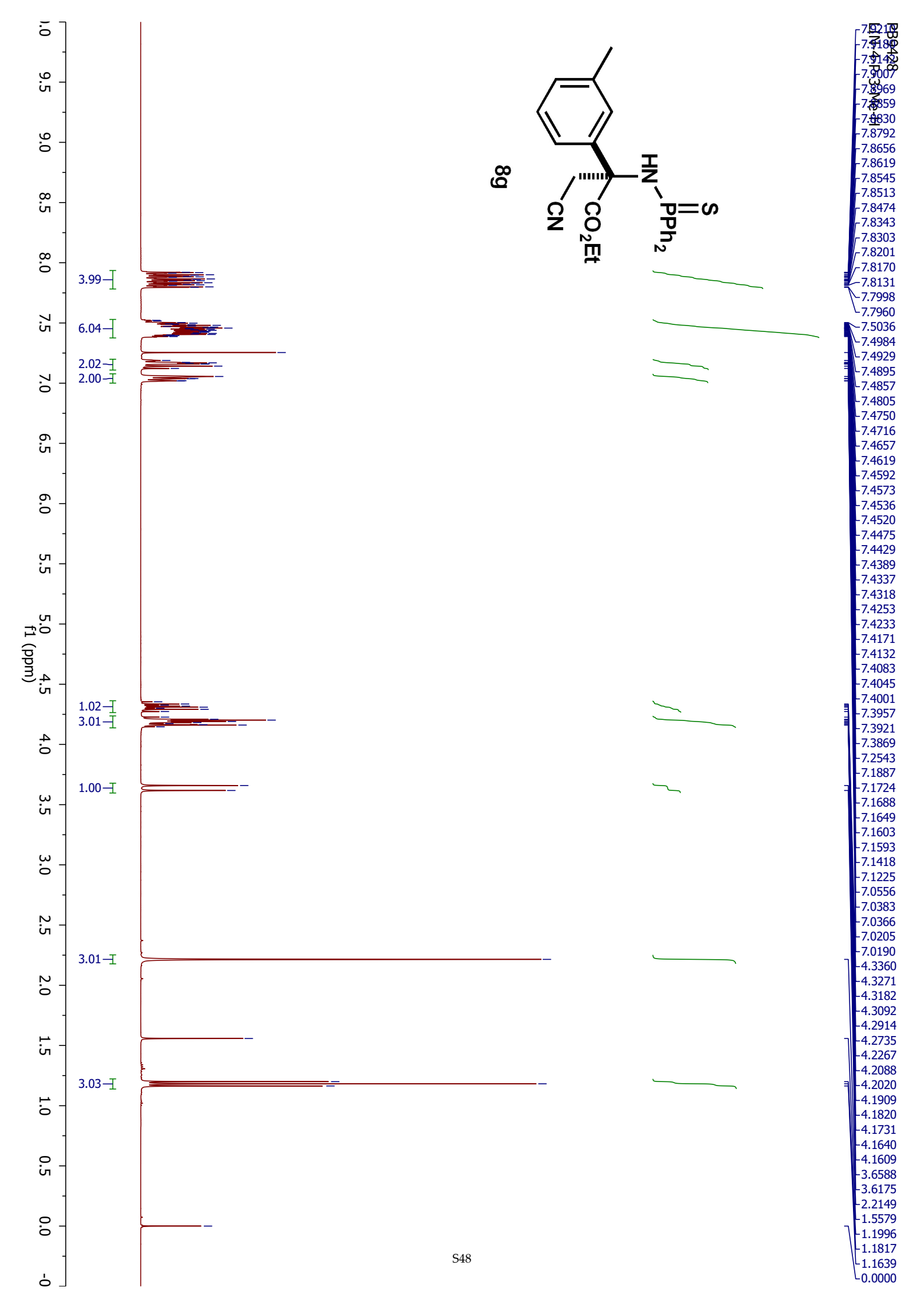

PC2296
LIN-4-S-thio-C
4v
163.5546
163.4629
163.3957
142.4346
142.1761
136.0057
134.9966
134.9390
134.5266
131.3488
131.3187
131.2872
131.1792
128.7785
128.7650
128.3794
128.2483
77.3177
77.0002
76.6826
62.5234
13.6960
f1 (ppm)

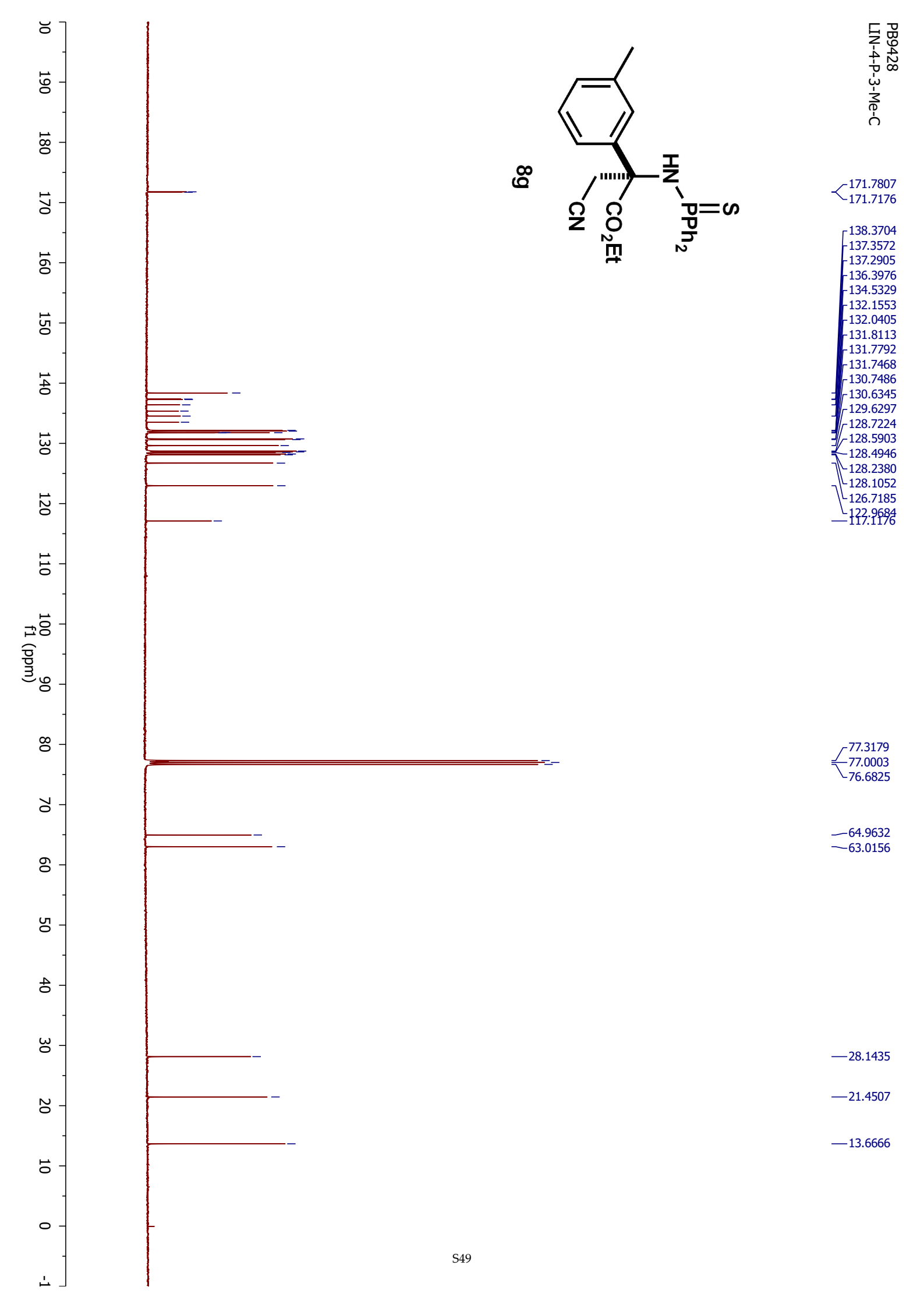

8a
HN
PPh2
S
CO2Et
CN
3.97
6.02
2.01
3.37
1.01
3.01
1.00
3.01
f1 (ppm)

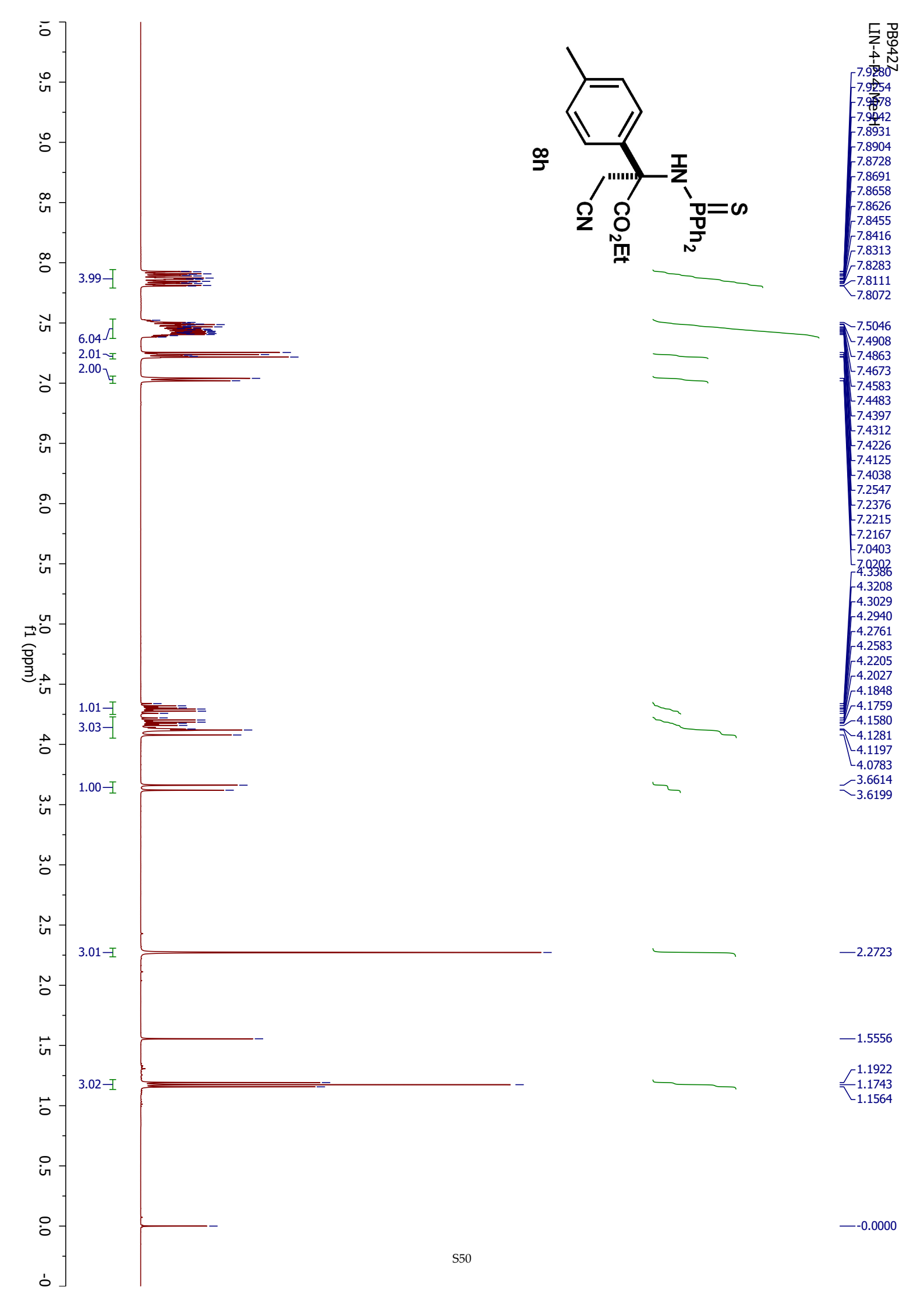

PB9429
LIN-4-P-Ph-C
8a
HN
S
PPh2
CO2Et
CN
171.6807
171.6226
137.6289
137.5577
136.2538
135.2237
134.4914
133.4735
132.1609
132.0462
131.8597
131.8323
130.7722
130.6582
128.9021
128.7398
128.6478
128.6074
128.3578
128.2246
125.9270
117.0094
77.3172
76.9996
76.6820
65.0154
63.0267
28.1454
13.6602
f1 (ppm)

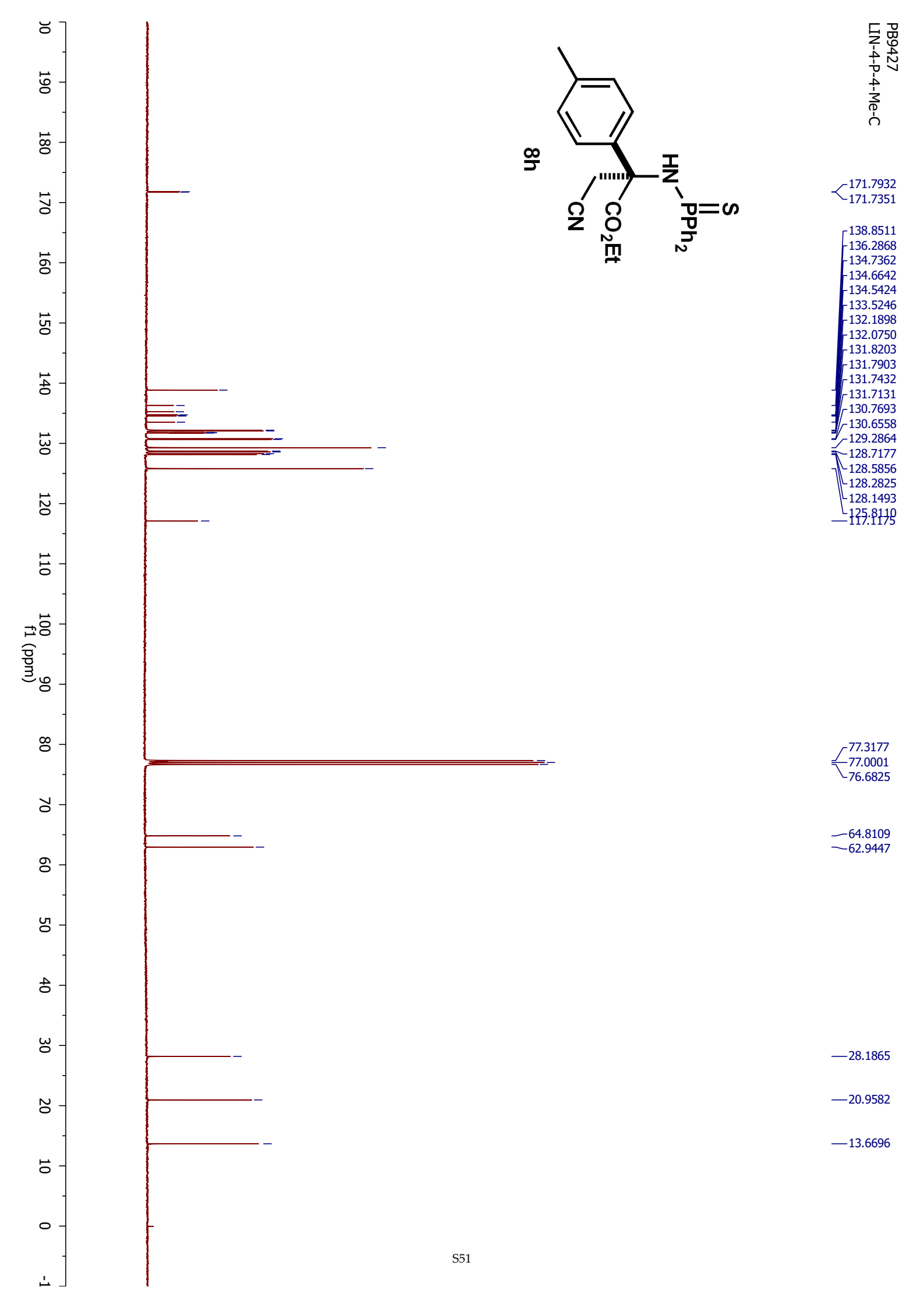

PC2298
LIN-4-P-2-Me-H
8f
HN
S
PPh2
CO2Et
CN
f1 (ppm)
1.98
4.99
1.01
1.02
3.01
1.00
0.99
1.01
0.98
1.00
1.01
1.00
3.01
3.04
7.9001
7.8973
7.8936
7.8853
7.8803
7.8763
7.8668
7.8641
7.8519
7.8469
7.8430
7.5136
7.4955
7.4916
7.2577
7.1526
7.1447
7.1331
7.1302
6.5488
6.5302
4.9359
4.8962
4.7485
4.7277
4.4103
4.4013
4.3835
4.2095
4.1916
4.1827
4.1648
3.5668
3.5272
1.8618
1.5565
1.2704
1.2526
1.2348
0.0000

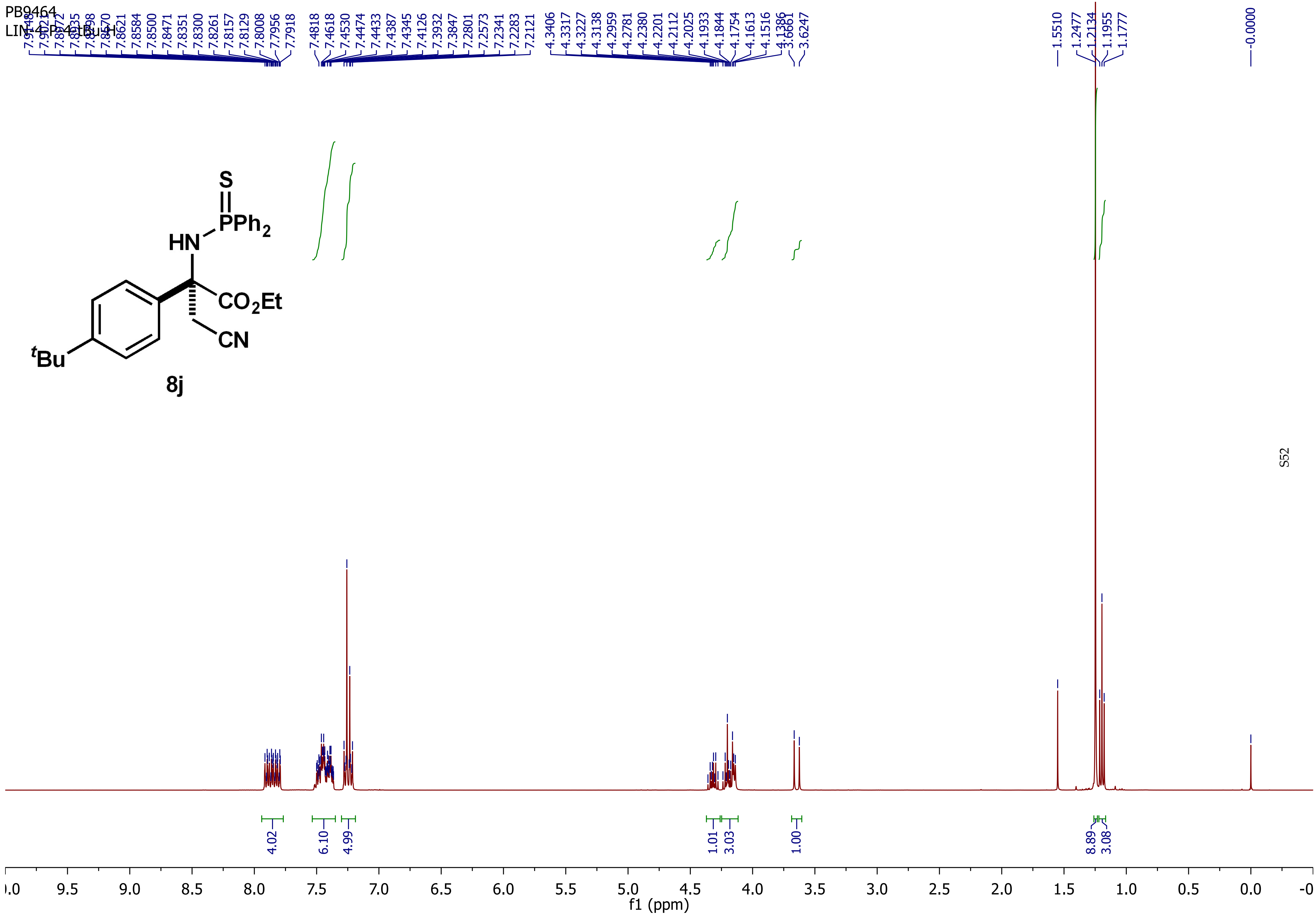

PC2298
LIN-4-P-2-Me-C
8f
HN
S
PPh2
CO2Et
CN
172.6248
172.5074
136.8534
136.1132
132.9857
132.8331
132.8166
131.9589
131.9341
131.9040
131.8387
131.7207
131.6808
131.0354
131.0056
130.5143
130.4044
128.9554
128.8260
127.6299
127.5251
127.3903
125.5043
116.8316
77.3536
77.0360
76.7184
64.2611
64.2478
63.6307
29.0532
20.4352
13.9235
f1 (ppm)

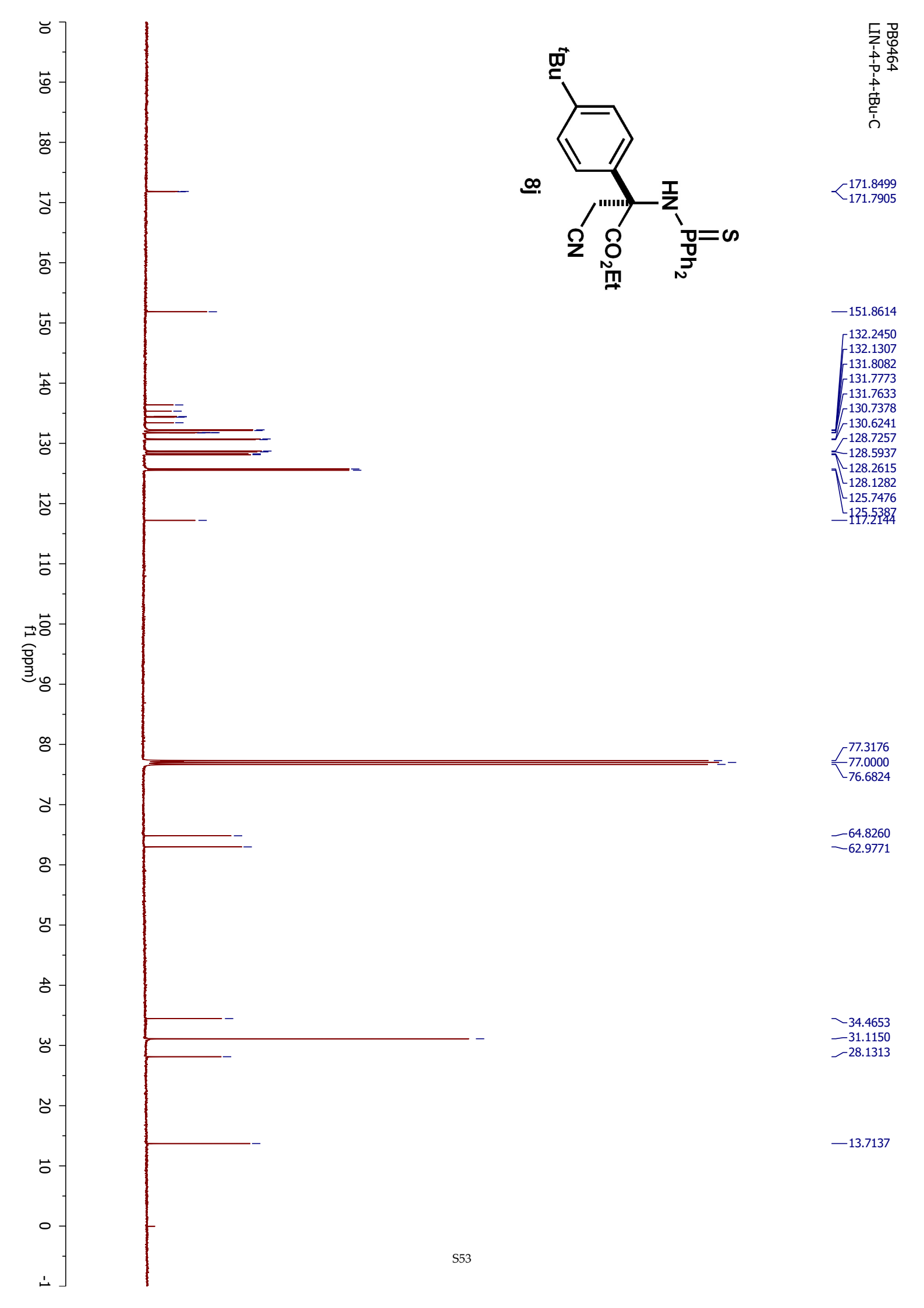

8g
HN
S
PPh2
CO2Et
CN
3.99
6.04
2.02
2.00
1.02
3.01
1.00
3.01
3.03
f1 (ppm)

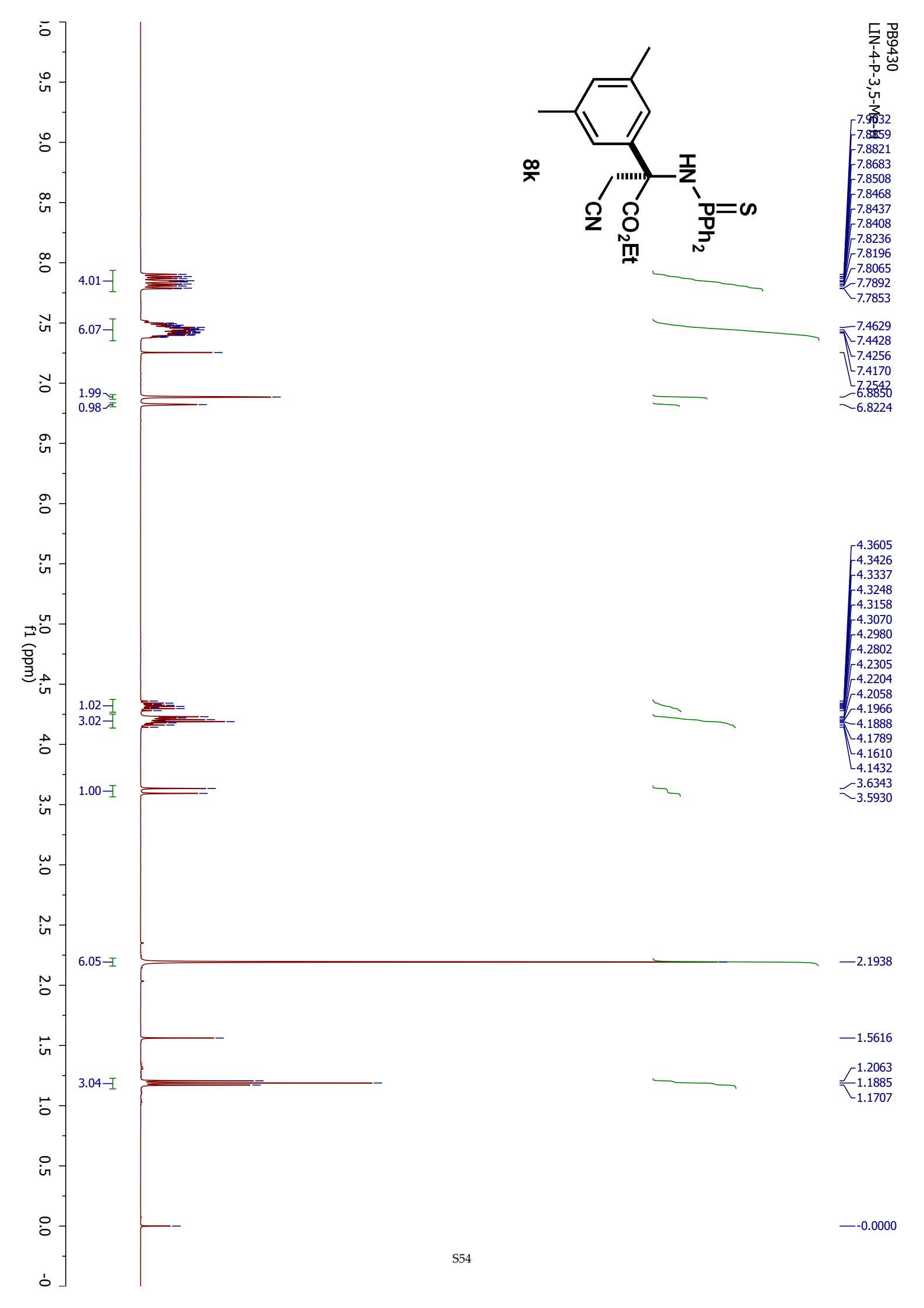

PB9428
LIN-4-P-3-Me-C
8g
HN
S
PPh2
CO2Et
CN
171.7807
171.7176
138.3704
137.3572
137.2905
136.3976
134.5329
132.1553
132.0405
131.8113
131.7792
131.7468
130.7486
130.6345
129.6297
128.7224
128.5903
128.4946
128.2380
128.1052
126.7185
122.9684
117.1176
77.3179
77.0003
76.6825
64.9632
63.0156
28.1435
21.4507
13.6666
f1 (ppm)

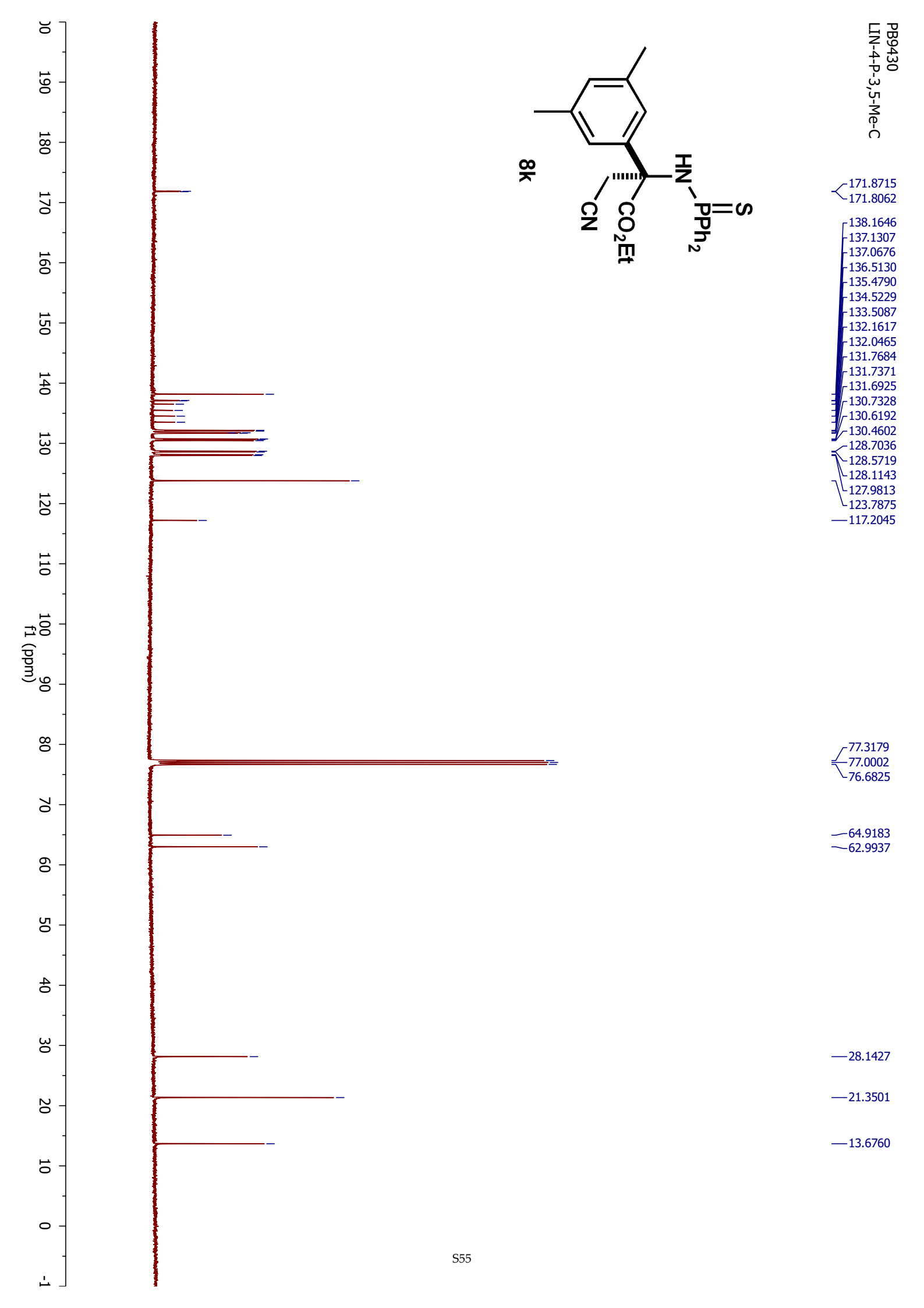

PB9427
LIN-4-84-NMR-1H
8h
HN
S
PPh2
CO2Et
CN
f1 (ppm)
3.99
6.04
2.01
2.00
1.01
3.03
1.00
3.01
3.02
7.9280
7.9254
7.9078
7.9042
7.8931
7.8904
7.8728
7.8691
7.8658
7.8626
7.8455
7.8416
7.8313
7.8283
7.8111
7.8072
7.5046
7.4908
7.4863
7.4673
7.4583
7.4483
7.4397
7.4312
7.4226
7.4125
7.4038
7.2547
7.2376
7.2215
7.2167
7.0403
7.0202
4.3386
4.3208
4.3029
4.2940
4.2761
4.2583
4.2205
4.2027
4.1848
4.1759
4.1580
4.1281
4.1197
4.0783
3.6614
3.6199
2.2723
1.5556
1.1922
1.1743
1.1564
-0.0000

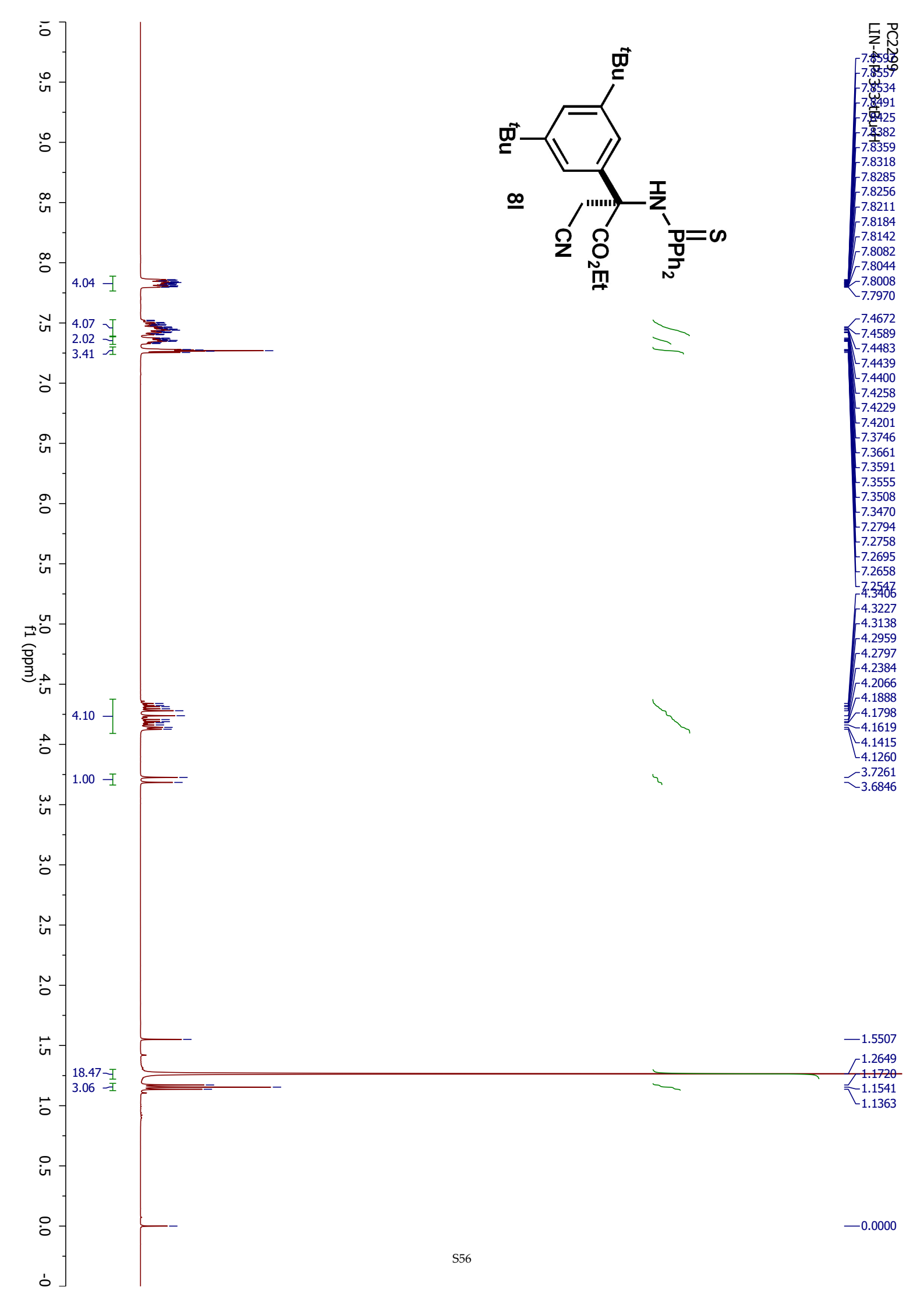

PB9427
LIN-4-P-4-Me-C
8h
HN
S
PPh2
CO2Et
CN
171.7932
171.7351
138.8511
136.2868
134.7362
134.6642
134.5424
133.5246
132.1898
132.0750
131.8203
131.7903
131.7432
131.7131
130.7693
130.6558
129.2864
128.7177
128.5856
128.2825
128.1493
125.8110
117.1175
77.3177
77.0001
76.6825
64.8109
62.9447
28.1865
20.9582
13.6696
f1 (ppm)

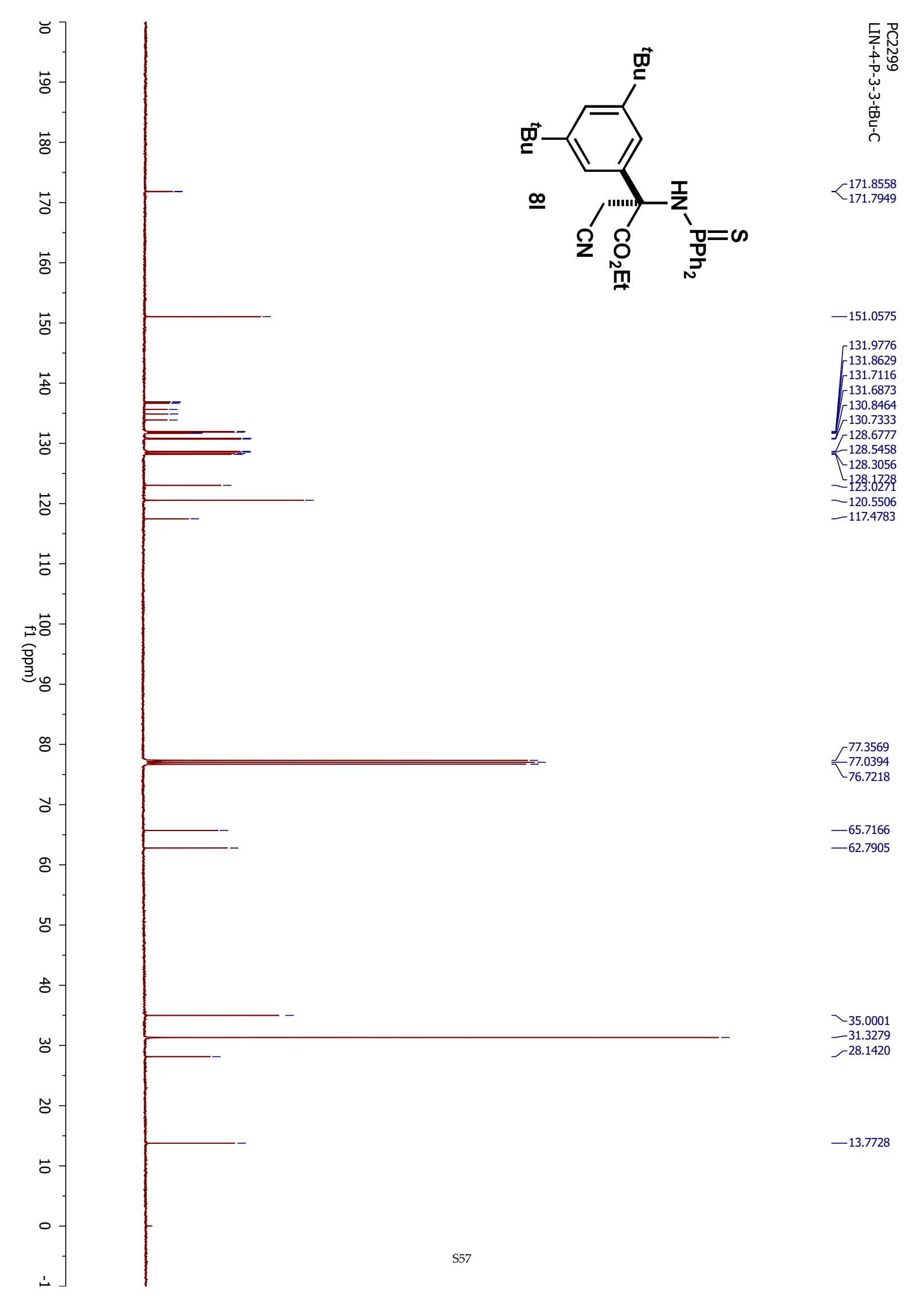

PB9464
LIN-4CP-4tBu-H
7.9148
7.9021
7.8972
7.8935
7.8898
7.8670
7.8621
7.8584
7.8500
7.8471
7.8351
7.8300
7.8261
7.8157
7.8129
7.8008
7.7956
7.7918
7.4818
7.4618
7.4530
7.4474
7.4433
7.4387
7.4345
7.4126
7.3932
7.3847
7.2801
7.2573
7.2341
7.2283
7.2121
4.3406
4.3317
4.3227
4.3138
4.2959
4.2781
4.2380
4.2201
4.2112
4.2025
4.1933
4.1844
4.1754
4.1613
4.1516
4.1386
3.6661
3.6247
1.5510
1.2477
1.2134
1.1955
1.1777
-0.0000
S
PPh2
HN
CO2Et
CN
tBu
8j
4.02
6.10
4.99
1.01
3.03
1.00
8.89
3.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

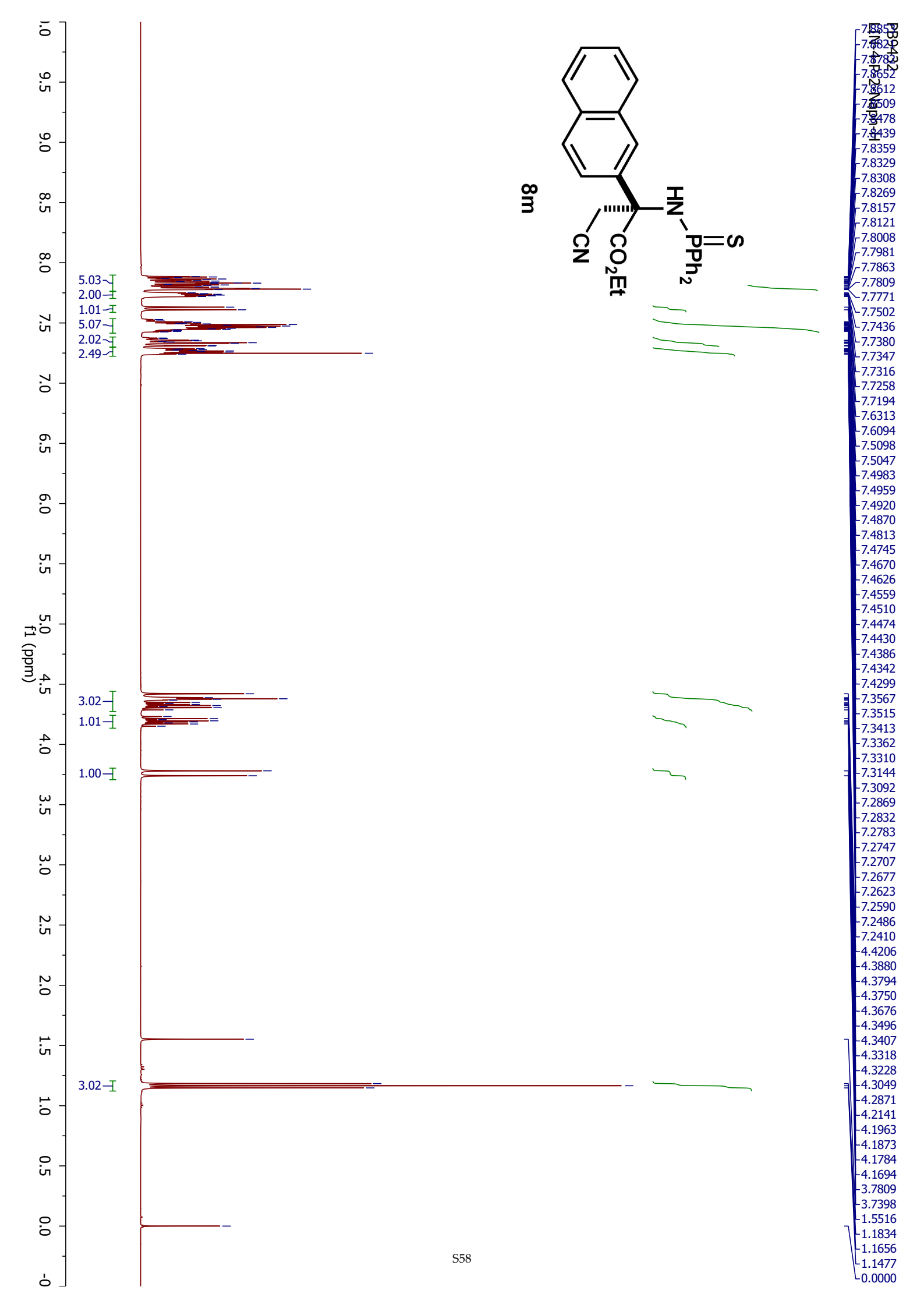

PB9464
LIN-4-P-4-tBu-C
8j
tBu
HN
S
PPh2
CO2Et
CN
171.8499
171.7905
151.8614
132.2450
132.1307
131.8082
131.7773
131.7633
130.7378
130.6241
128.7257
128.5937
128.2615
128.1282
125.7476
125.5387
117.2144
77.3176
77.0000
76.6824
64.8260
62.9771
34.4653
31.1150
28.1313
13.7137
f1 (ppm)

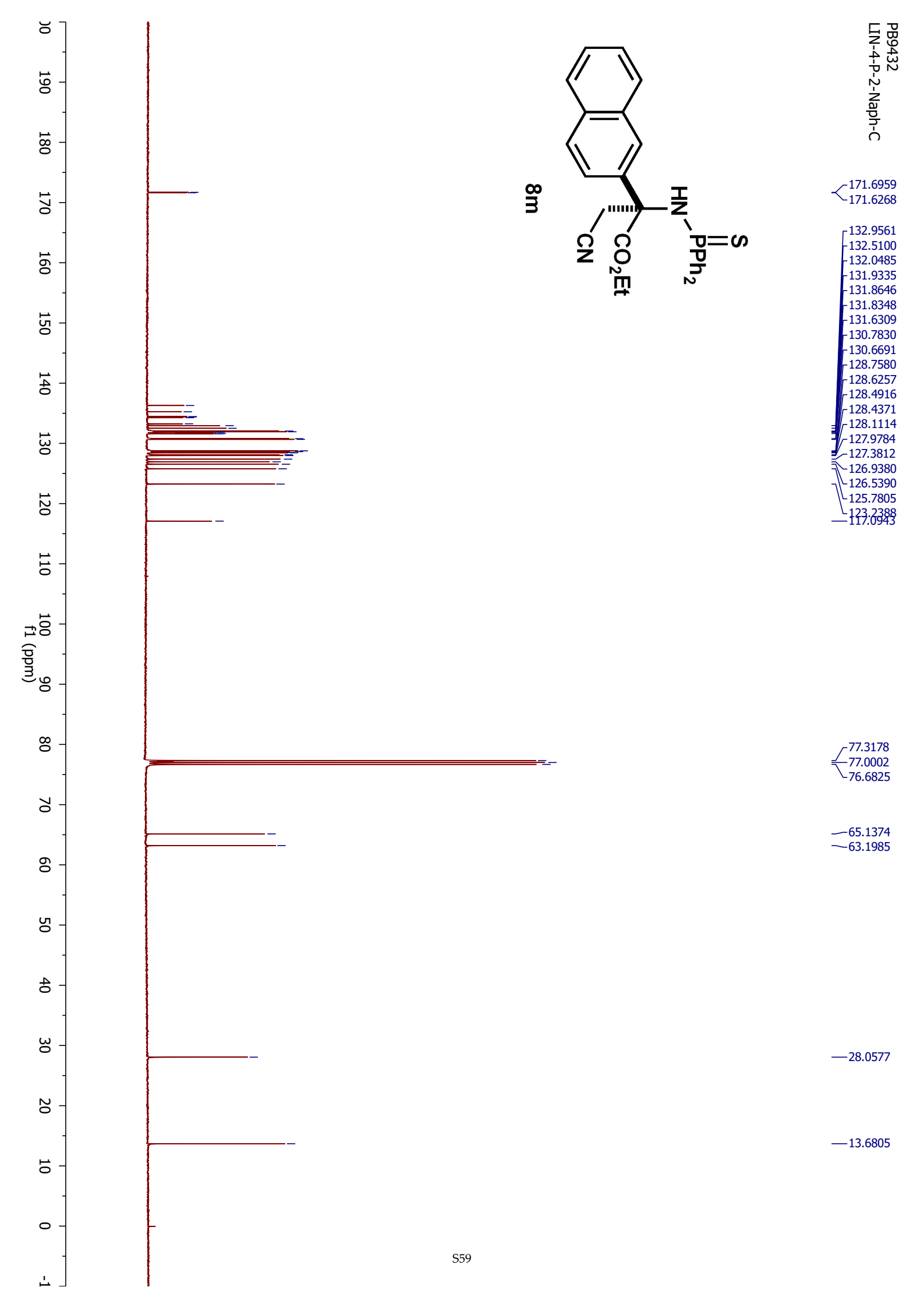

PB9430
LIN-4-P-3,5-Me-8k
8k
HN
S
PPh2
CO2Et
CN
f1 (ppm)
4.01
6.07
1.99
0.98
1.02
3.02
1.00
6.05
3.04
7.9232
7.8459
7.8821
7.8683
7.8508
7.8468
7.8437
7.8408
7.8236
7.8196
7.8065
7.7892
7.7853
7.4629
7.4428
7.4256
7.4170
7.2542
6.8850
6.8224
4.3605
4.3426
4.3337
4.3248
4.3158
4.3070
4.2980
4.2802
4.2305
4.2204
4.2058
4.1966
4.1888
4.1789
4.1610
4.1432
3.6343
3.5930
2.1938
1.5616
1.2063
1.1885
1.1707
-0.0000

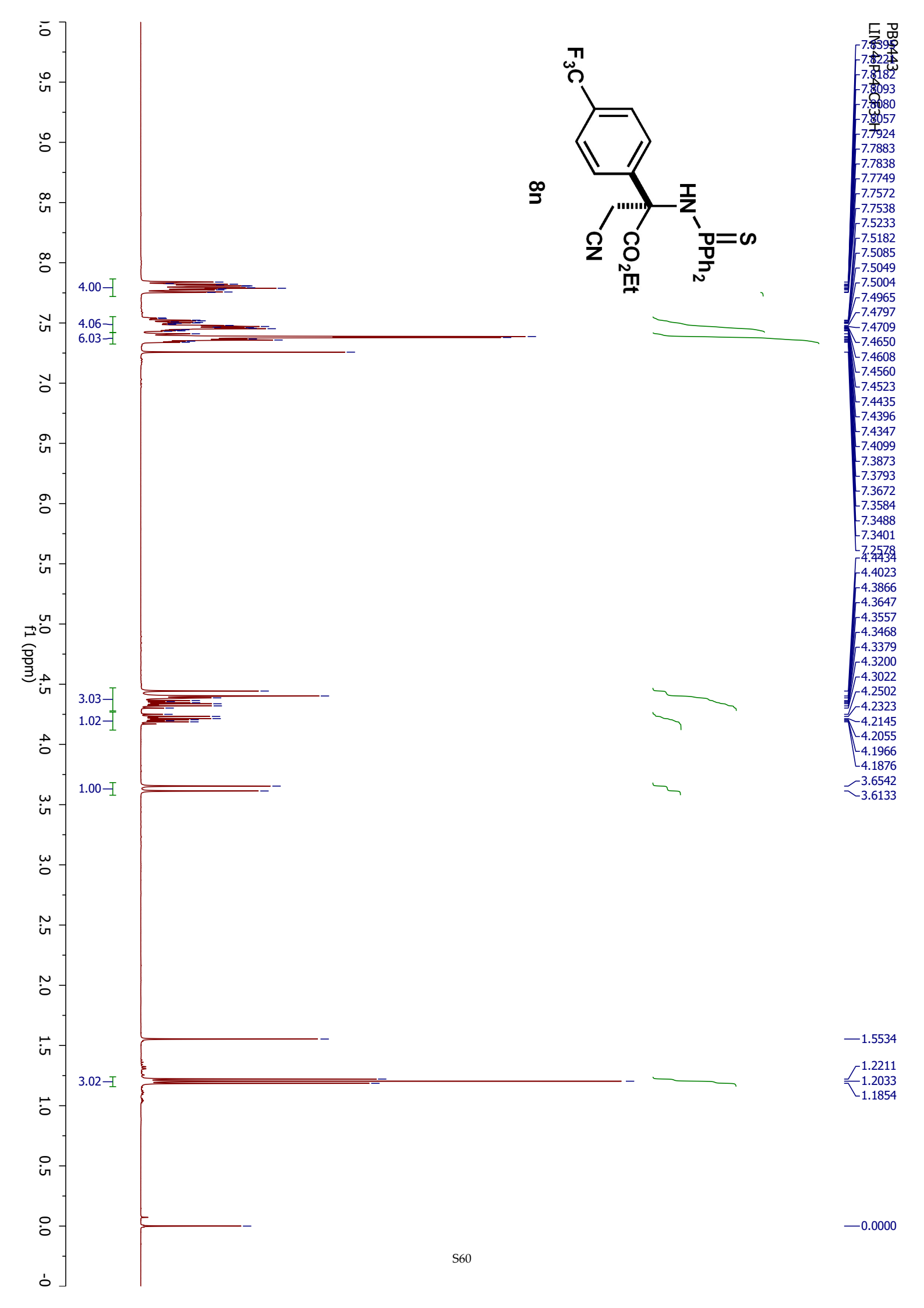

PB9430
LIN-4-P-3,5-Me-C
8k
HN
S
PPh2
CO2Et
CN
171.8715
171.8062
138.1646
137.1307
137.0676
136.5130
135.4790
134.5229
133.5087
132.1617
132.0465
131.7684
131.7371
131.6925
130.7328
130.6192
130.4602
128.7036
128.5719
128.1143
127.9813
123.7875
117.2045
77.3179
77.0002
76.6825
64.9183
62.9937
28.1427
21.3501
13.6760
f1 (ppm)

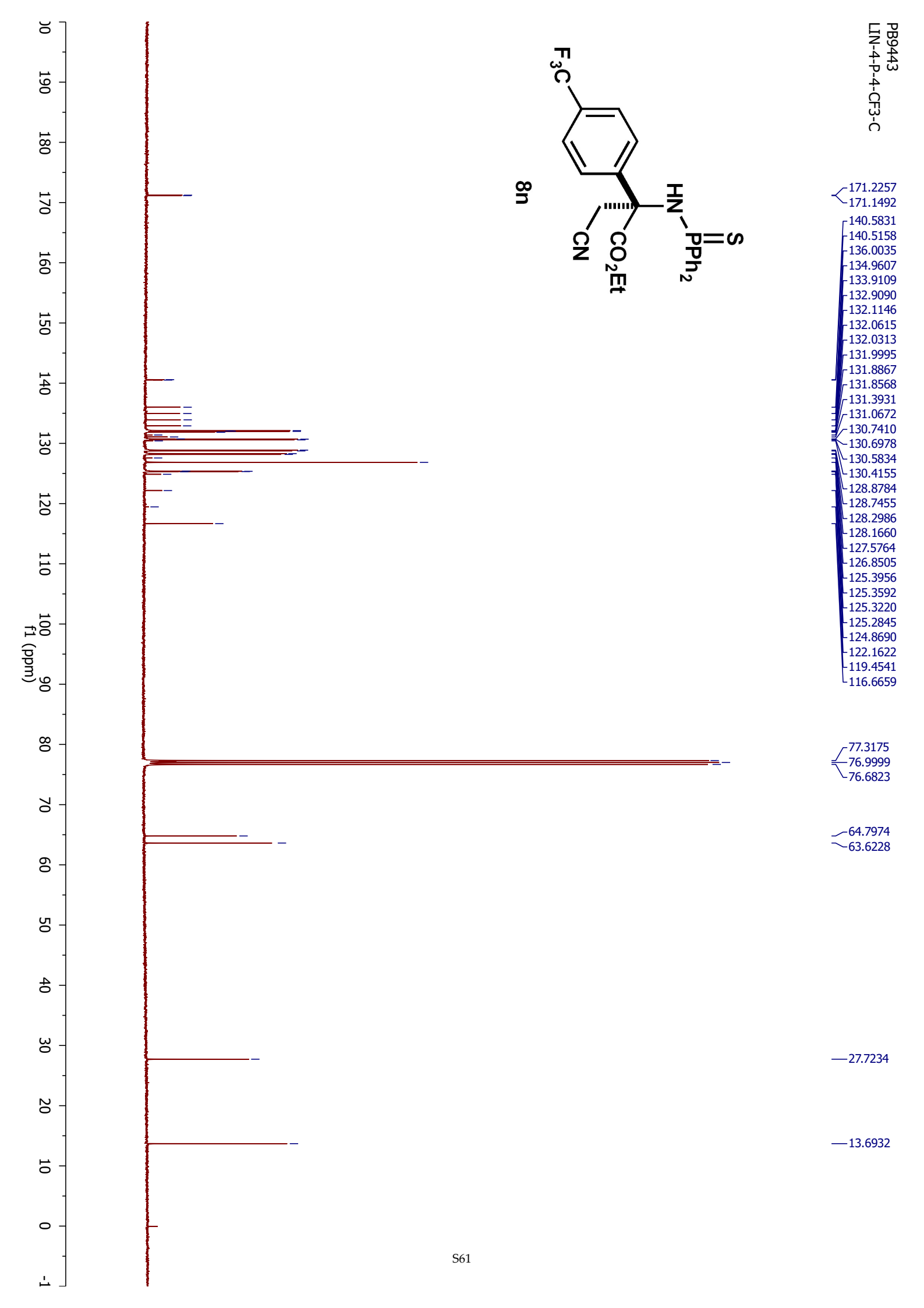

8l
tBu
tBu
HN
S
PPh2
CO2Et
CN
PC2299
LIN-4
f1 (ppm)
4.04
4.07
2.02
3.41
4.10
1.00
18.47
3.06
7.8597
7.8557
7.8534
7.8491
7.8425
7.8382
7.8359
7.8318
7.8285
7.8256
7.8211
7.8184
7.8142
7.8082
7.8044
7.8008
7.7970
7.4672
7.4589
7.4483
7.4439
7.4400
7.4258
7.4229
7.4201
7.3746
7.3661
7.3591
7.3555
7.3508
7.3470
7.2794
7.2758
7.2695
7.2658
7.2547
4.3406
4.3227
4.3138
4.2959
4.2797
4.2384
4.2066
4.1888
4.1798
4.1619
4.1415
4.1260
3.7261
3.6846
1.5507
1.2649
1.1720
1.1541
1.1363
0.0000

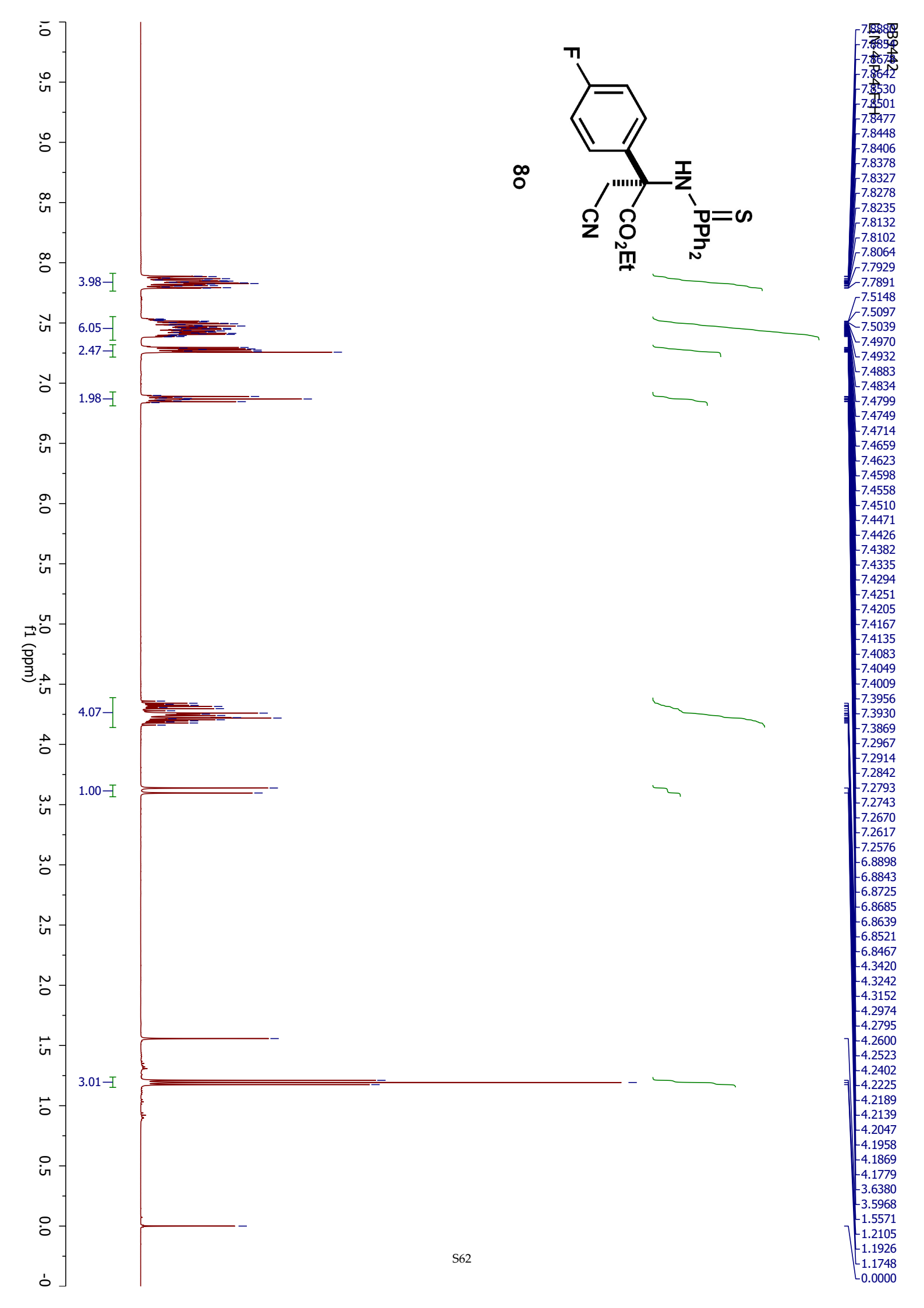

PC2299
LIN-4-P-3-3-tBu-C
171.8558
171.7949
151.0575
131.9776
131.8629
131.7116
131.6873
130.8464
130.7333
128.6777
128.5458
128.3056
128.1728
123.0271
120.5506
117.4783
77.3569
77.0394
76.7218
65.7166
62.7905
35.0001
31.3279
28.1420
13.7728
f1 (ppm)
8l

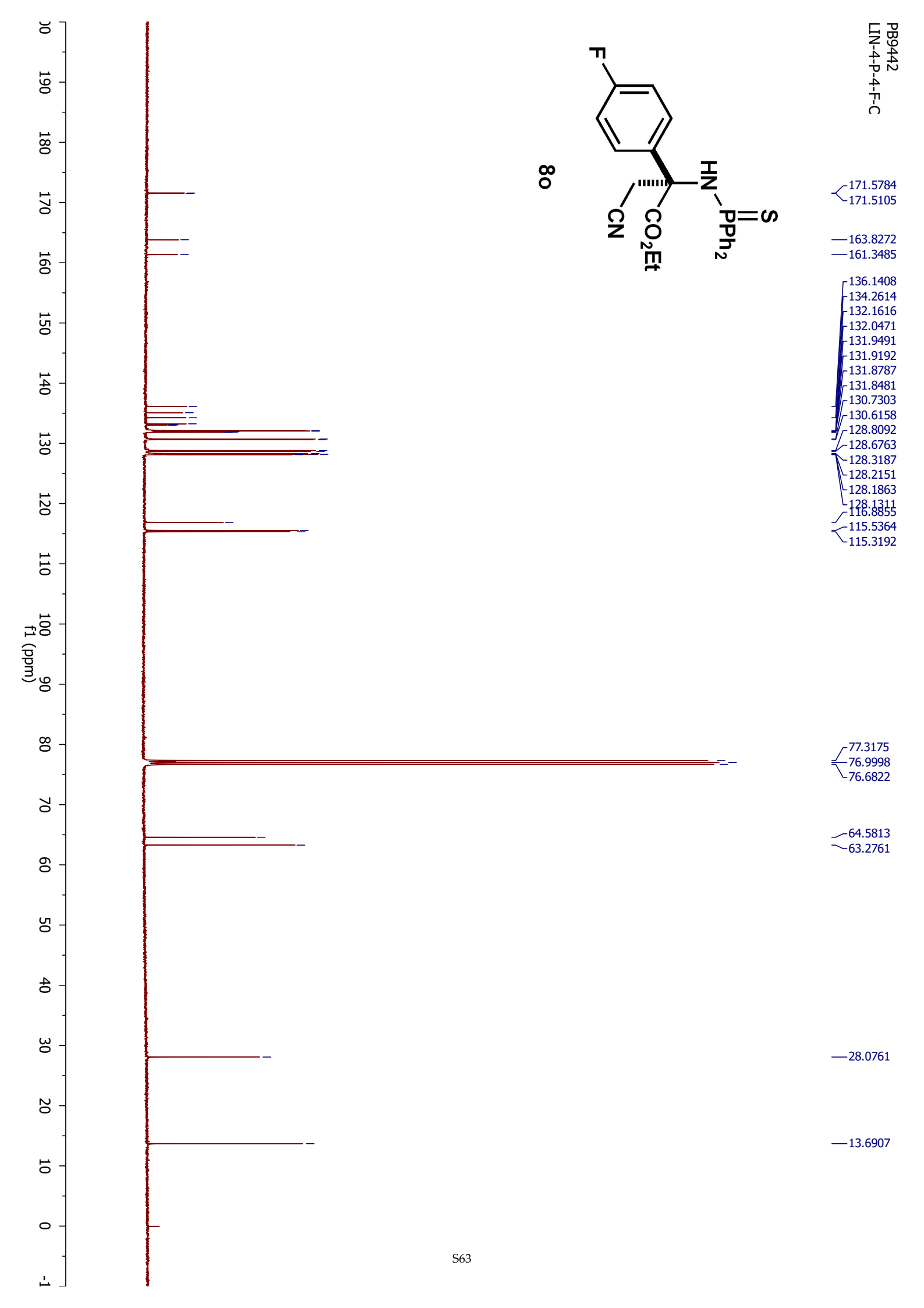

8m
HN
S
PPh2
CO2Et
CN
5.03
2.00
1.01
5.07
2.02
2.49
3.02
1.01
1.00
3.02
f1 (ppm)

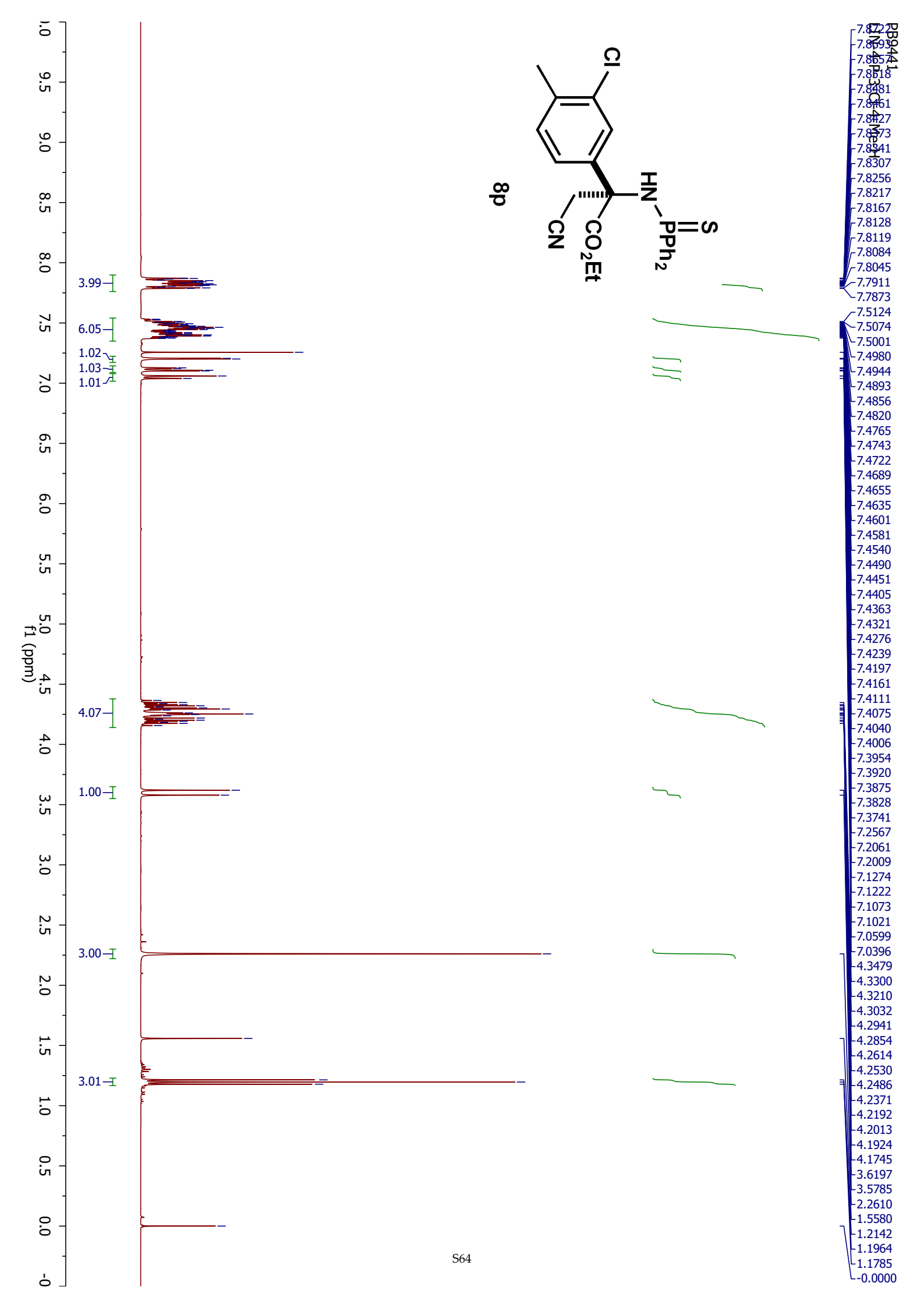

PB9432
LIN-4-P-2-Naph-C
8m
HN
S
PPh2
CO2Et
CN
171.6959
171.6268
132.9561
132.5100
132.0485
131.9335
131.8646
131.8348
131.6309
130.7830
130.6691
128.7580
128.6257
128.4916
128.4371
128.1114
127.9784
127.3812
126.9380
126.5390
125.7805
123.2388
117.0943
77.3178
77.0002
76.6825
65.1374
63.1985
28.0577
13.6805
f1 (ppm)

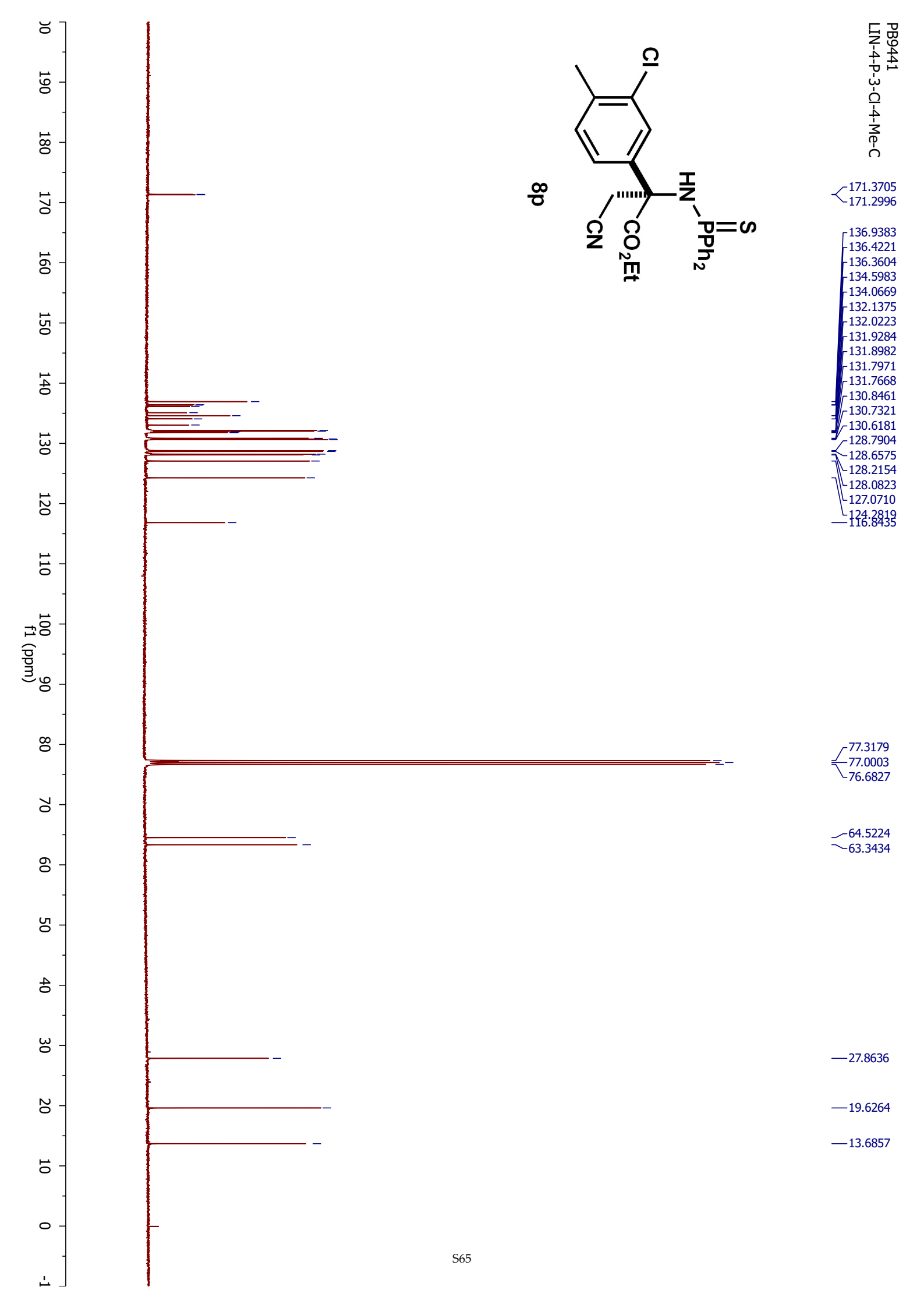

8n
F3C
CN
CO2Et
HN
S
PPh2
4.00
4.06
6.03
3.03
1.02
1.00
3.02
f1 (ppm)

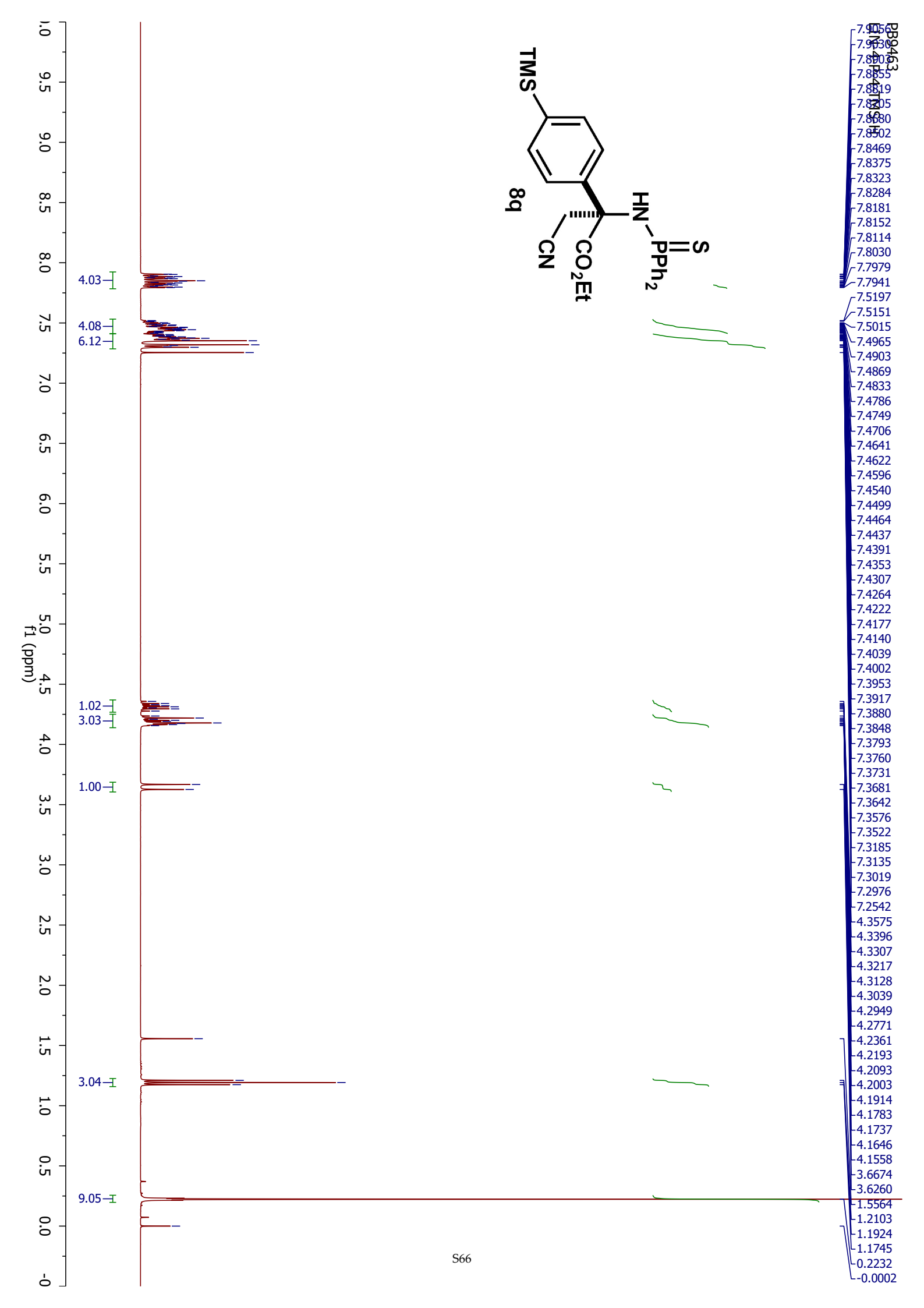

PB9443
LIN-4-P-4-CF3-C
8n
F3C
CN
CO2Et
HN
S
PPh2
171.2257
171.1492
140.5831
140.5158
136.0035
134.9607
133.9109
132.9090
132.1146
132.0615
132.0313
131.9995
131.8867
131.8568
131.3931
131.0672
130.7410
130.6978
130.5834
130.4155
128.8784
128.7455
128.2986
128.1660
127.5764
126.8505
125.3956
125.3592
125.3220
125.2845
124.8690
122.1622
119.4541
116.6659
77.3175
76.9999
76.6823
64.7974
63.6228
27.7234
13.6932
f1 (ppm)

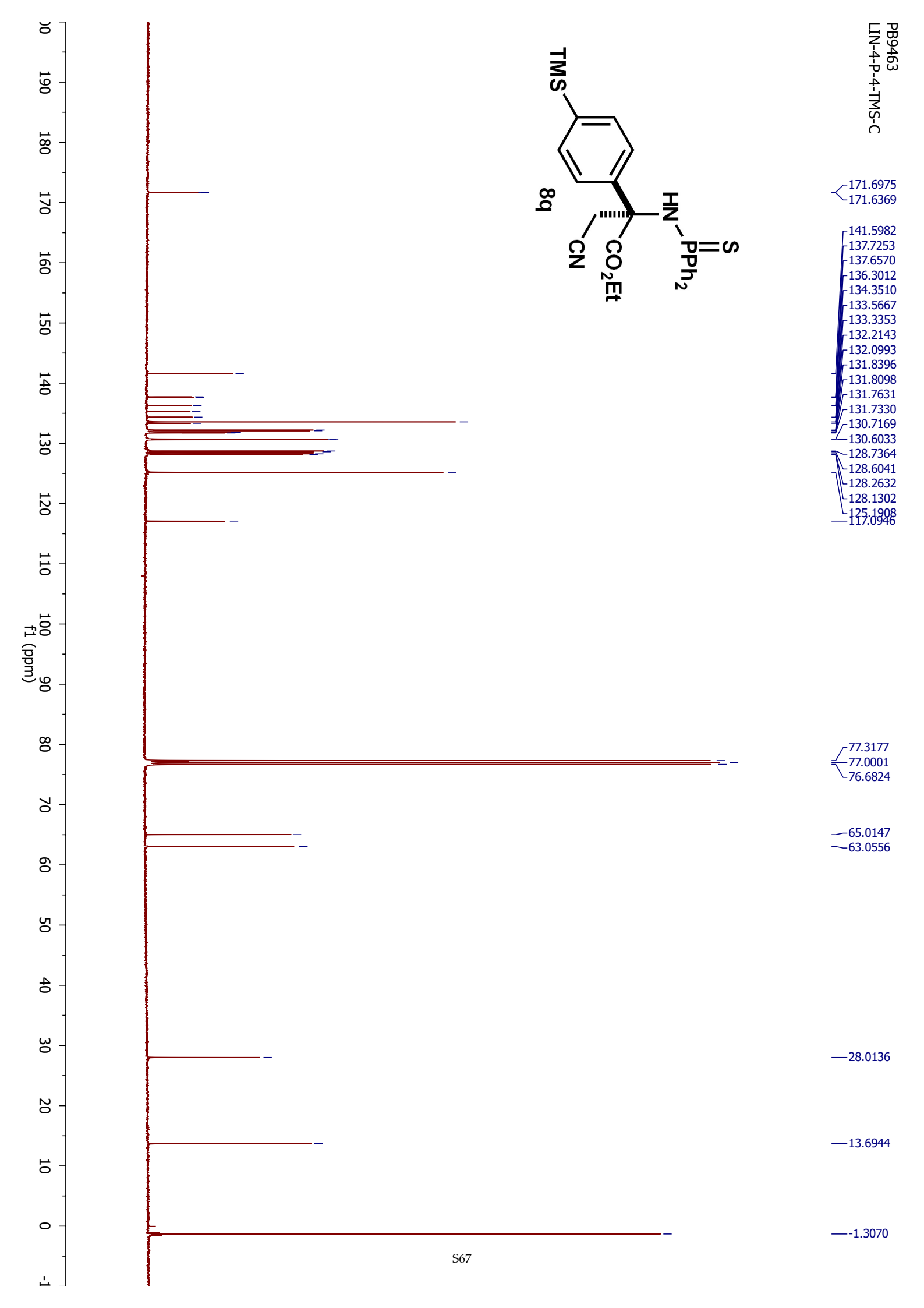

8o
F
HN
S
PPh2
CO2Et
CN
3.98
6.05
2.47
1.98
4.07
1.00
3.01
f1 (ppm)

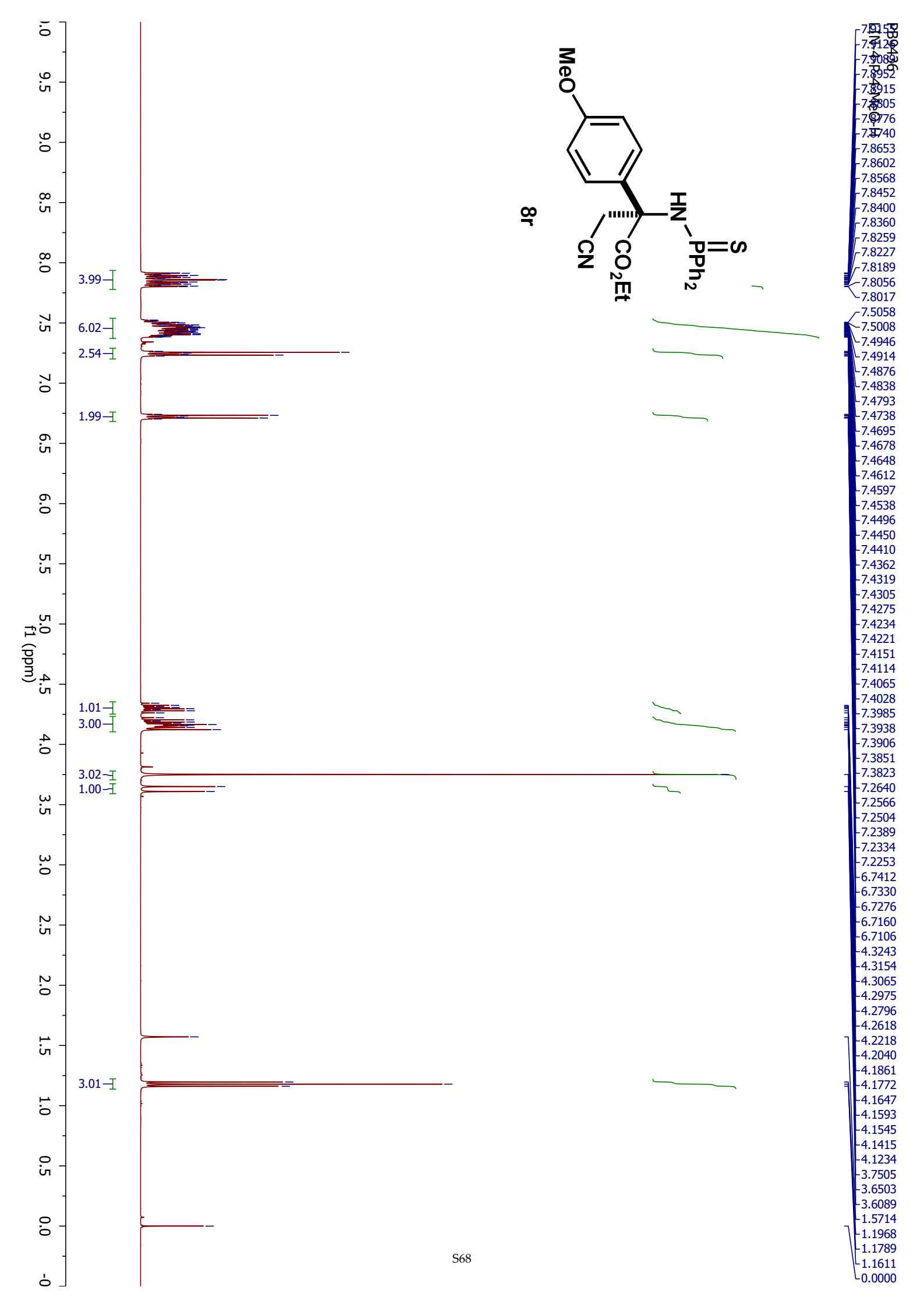

PB9442
LIN-4-P-4-F-C
8o
F
HN
S
PPh2
CO2Et
CN
171.5784
171.5105
163.8272
161.3485
136.1408
134.2614
132.1616
132.0471
131.9491
131.9192
131.8787
131.8481
130.7303
130.6158
128.8092
128.6763
128.3187
128.2151
128.1863
128.1311
116.8855
115.5364
115.3192
77.3175
76.9998
76.6822
64.5813
63.2761
28.0761
13.6907
f1 (ppm)

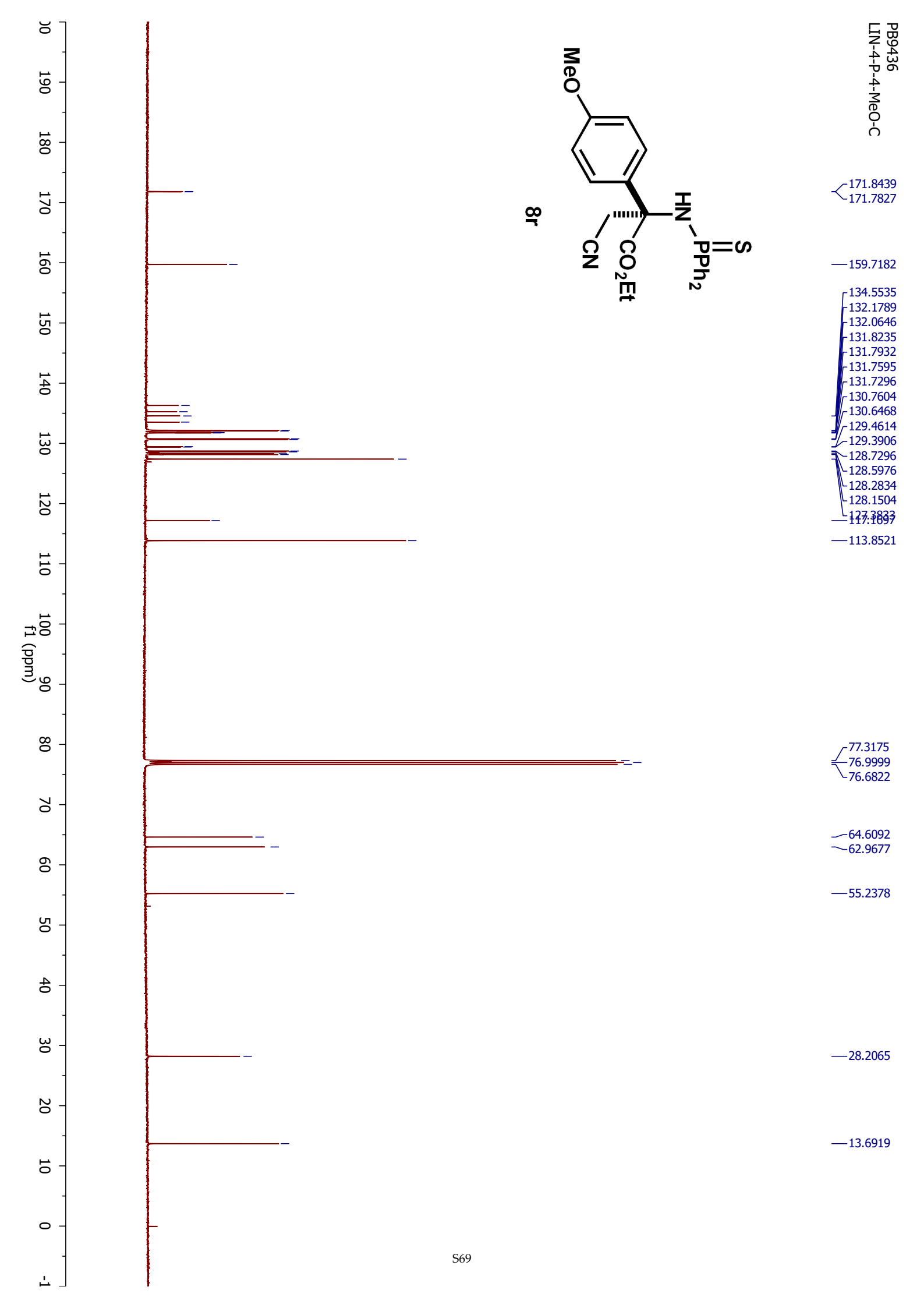

8p
Cl
HN
S
PPh2
CO2Et
CN
3.99
6.05
1.02
1.03
1.01
4.07
1.00
3.00
3.01
f1 (ppm)

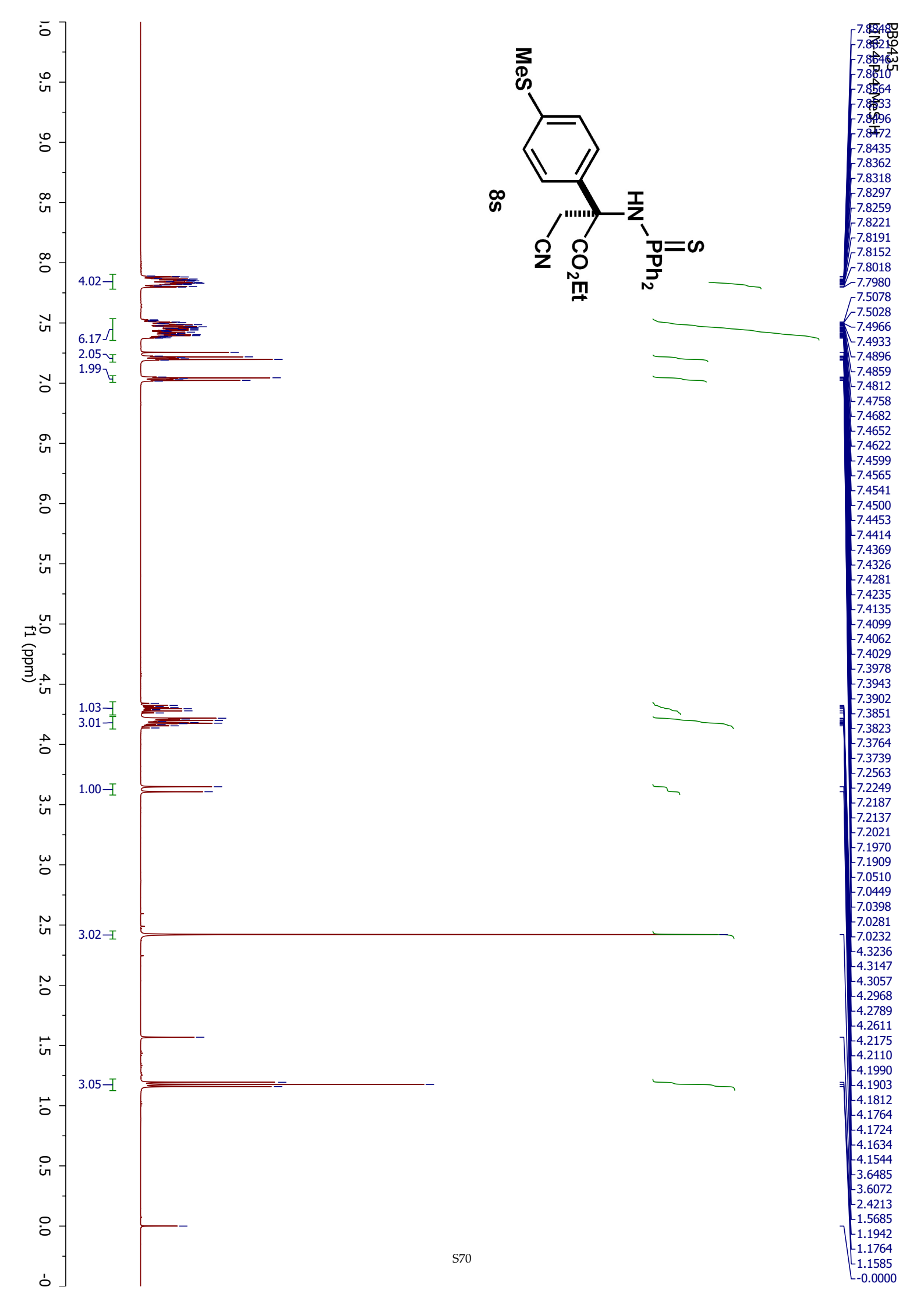

PB9441
LIN-4-P-3-Cl-4-Me-C
8p
Cl
HN
S
PPh2
CO2Et
CN
171.3705
171.2996
136.9383
136.4221
136.3604
134.5983
134.0669
132.1375
132.0223
131.9284
131.8982
131.7971
131.7668
130.8461
130.7321
130.6181
128.7904
128.6575
128.2154
128.0823
127.0710
124.2819
116.8435
77.3179
77.0003
76.6827
64.5224
63.3434
27.8636
19.6264
13.6857
f1 (ppm)

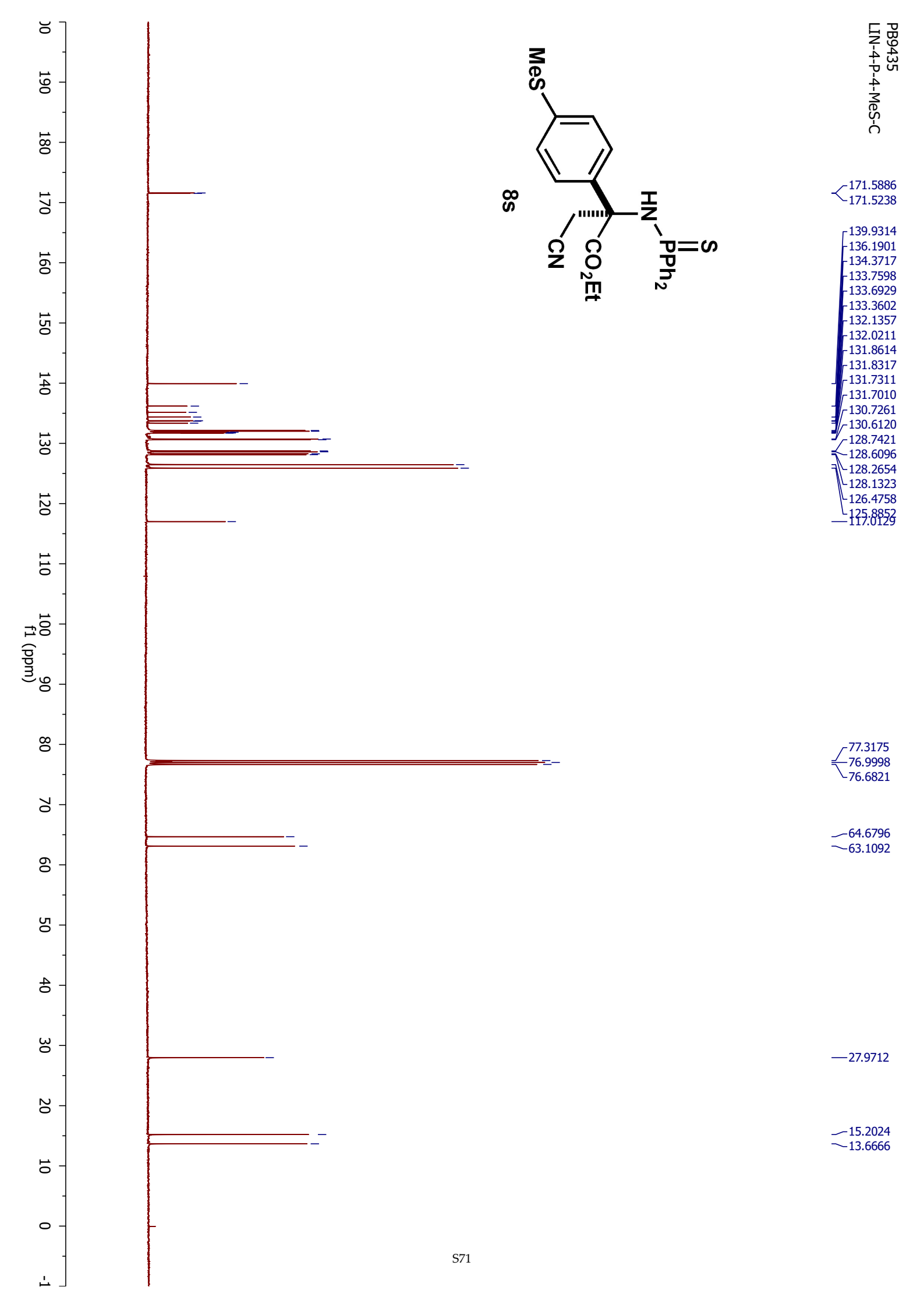

TMS
8q
CN
CO2Et
HN
S
PPh2
4.03
4.08
6.12
1.02
3.03
1.00
3.04
9.05
f1 (ppm)

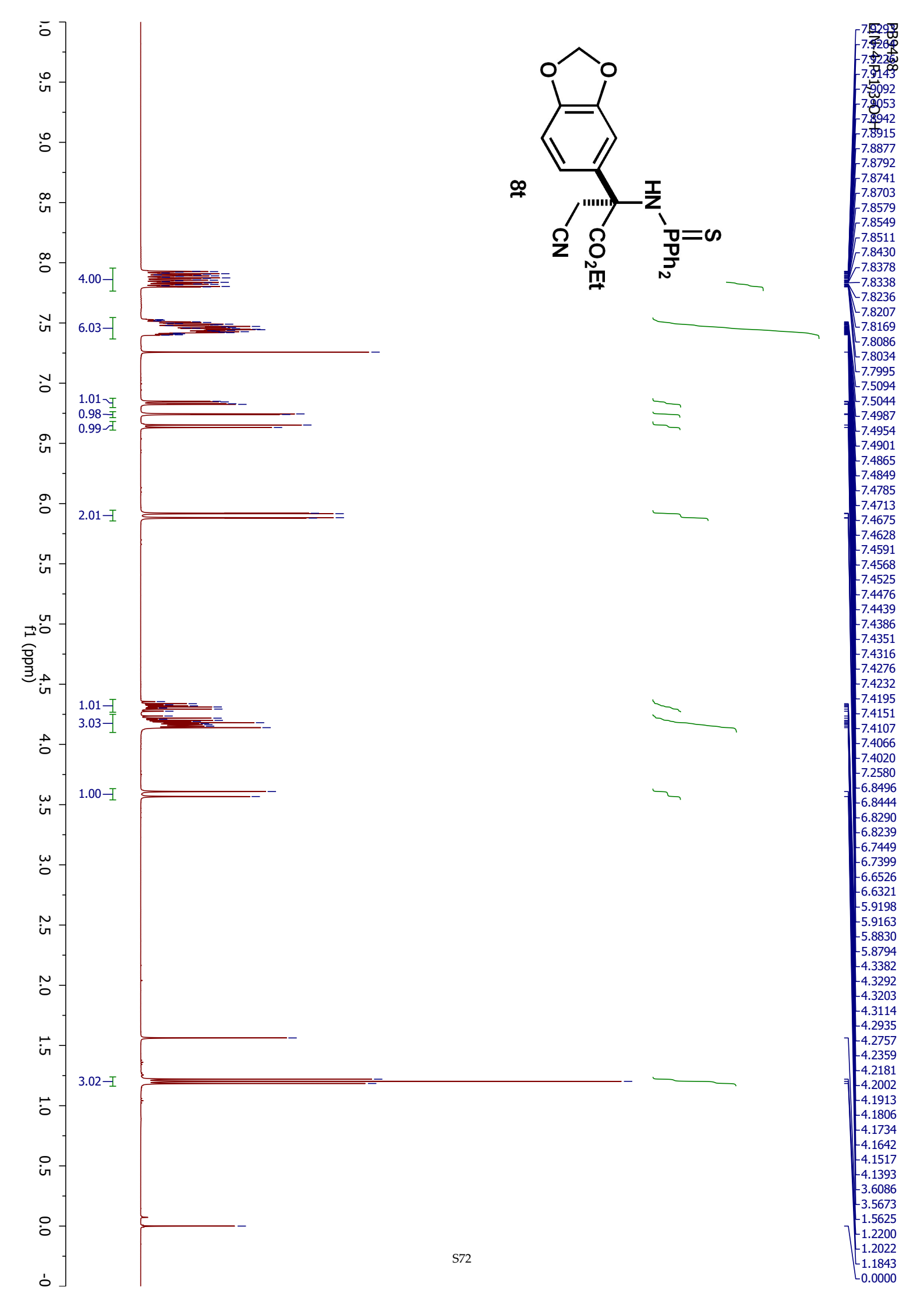

PB9463
LIN-4-P-4-TMS-C
8q
TMS
CN
CO2Et
HN
S
PPh2
171.6975
171.6369
141.5982
137.7253
137.6570
136.3012
134.3510
133.5667
133.3353
132.2143
132.0993
131.8396
131.8098
131.7631
131.7330
130.7169
130.6033
128.7364
128.6041
128.2632
128.1302
125.1908
117.0946
77.3177
77.0001
76.6824
65.0147
63.0556
28.0136
13.6944
-1.3070
f1 (ppm)

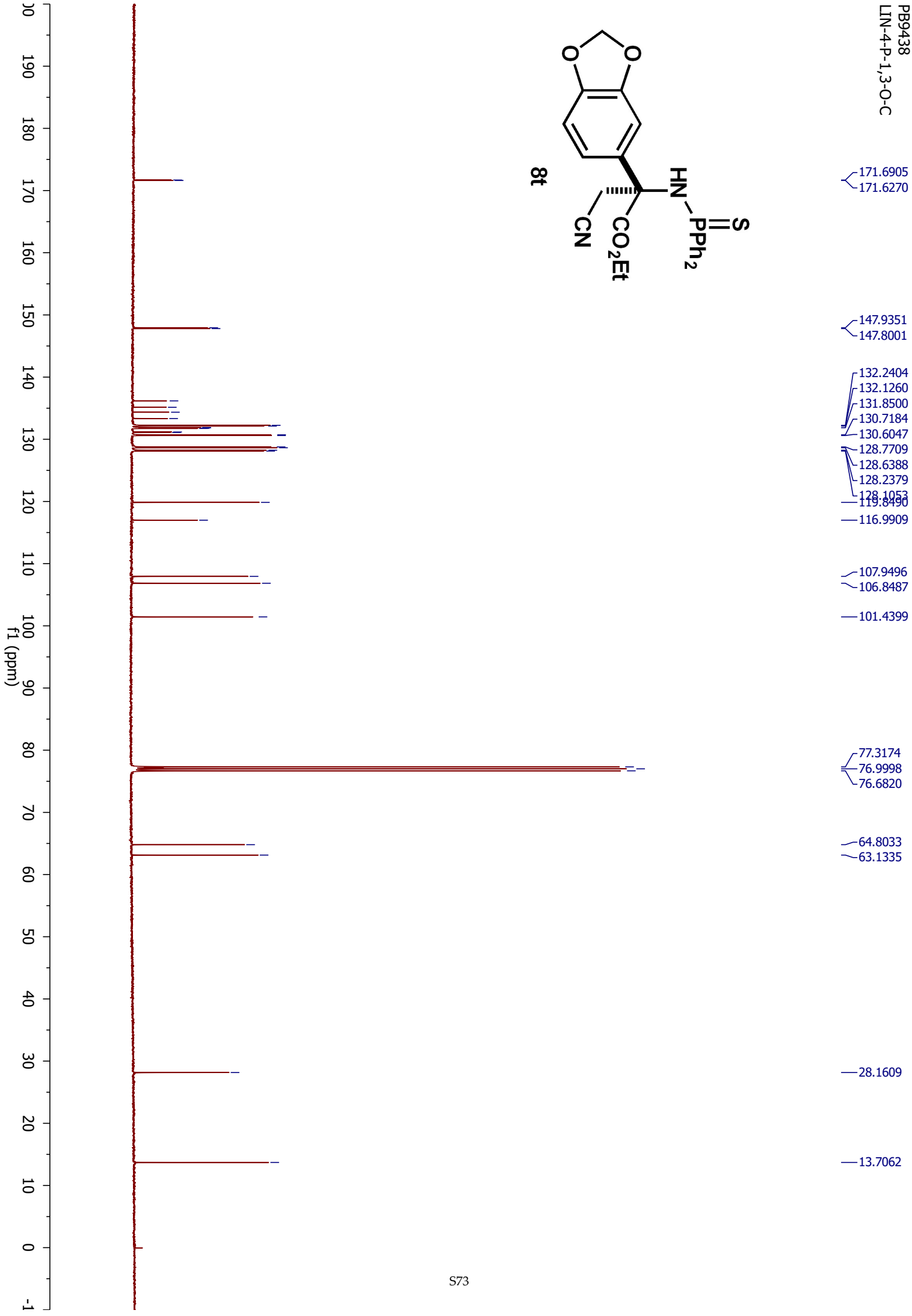

MeO
HN
S
PPh2
CO2Et
CN
8r
3.99
6.02
2.54
1.99
1.01
3.00
3.02
1.00
3.01
f1 (ppm)

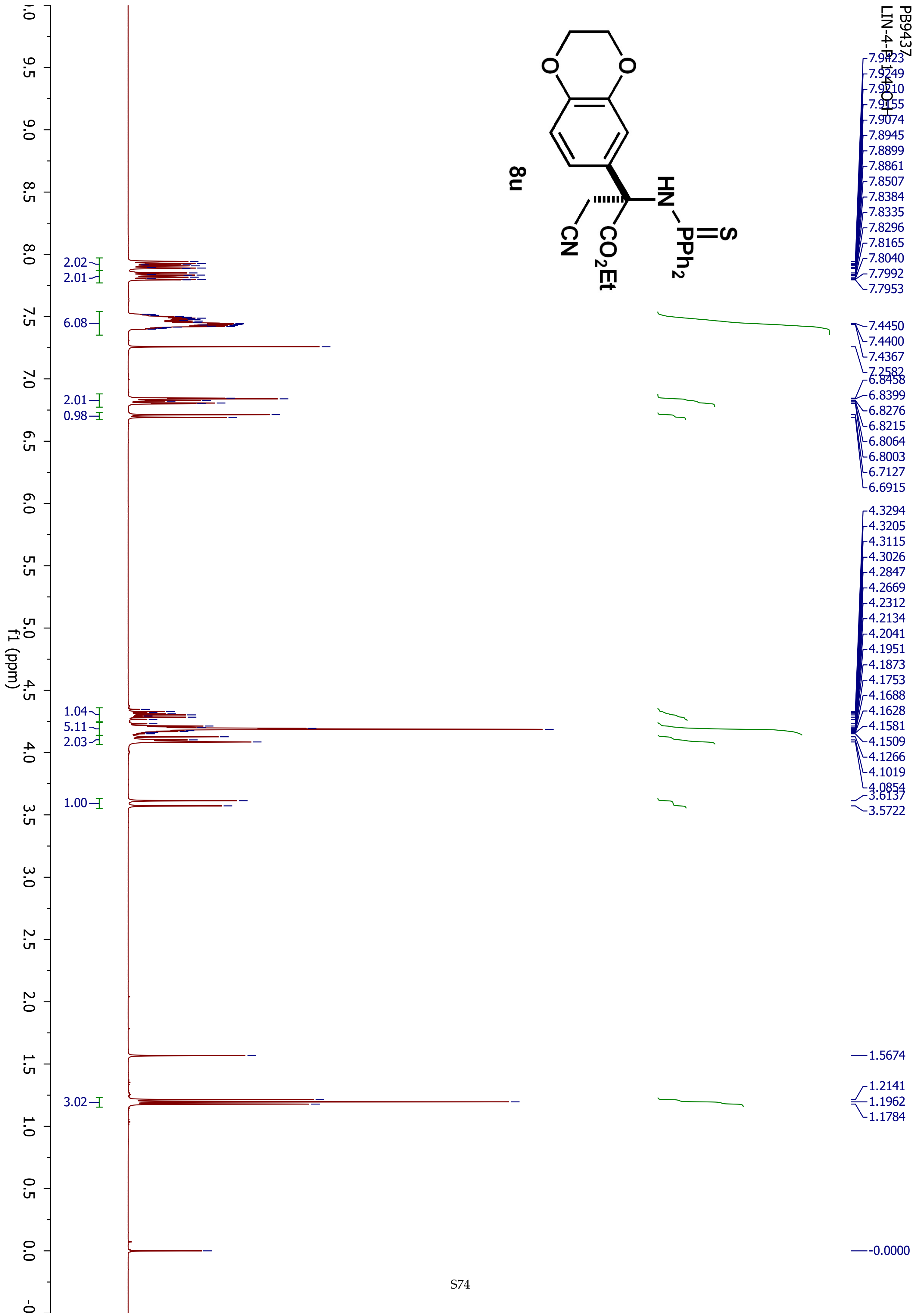

PB9436
LIN-4-P-4-MeO-C
MeO
HN
S
PPh2
CO2Et
CN
8r
171.8439
171.7827
159.7182
134.5535
132.1789
132.0646
131.8235
131.7932
131.7595
131.7296
130.7604
130.6468
129.4614
129.3906
128.7296
128.5976
128.2834
128.1504
127.3823
117.1697
113.8521
77.3175
76.9999
76.6822
64.6092
62.9677
55.2378
28.2065
13.6919
f1 (ppm)

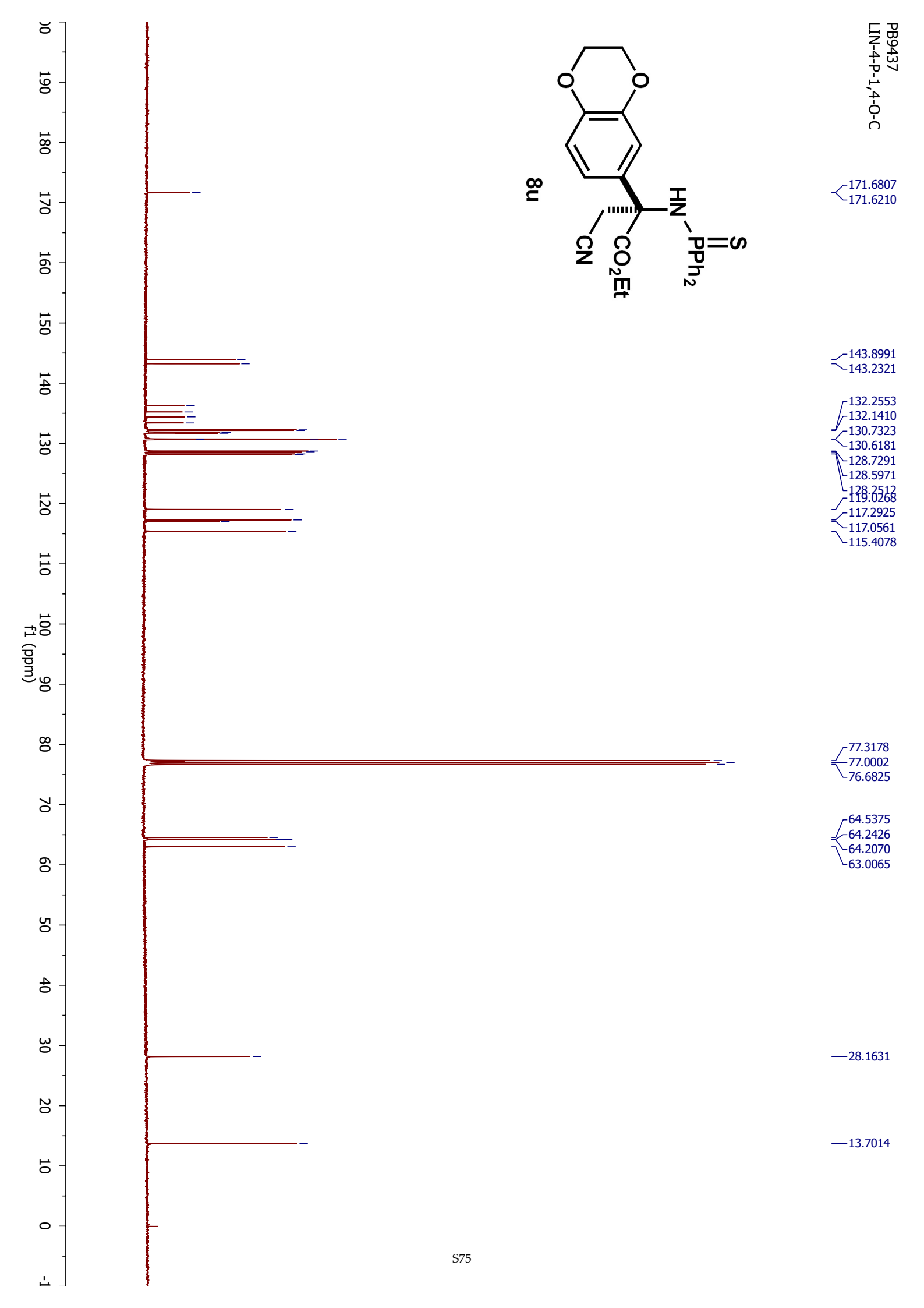

MeS
8s
HN
S
PPh2
CN
CO2Et
4.02
6.17
2.05
1.99
1.03
3.01
1.00
3.02
3.05
f1 (ppm)

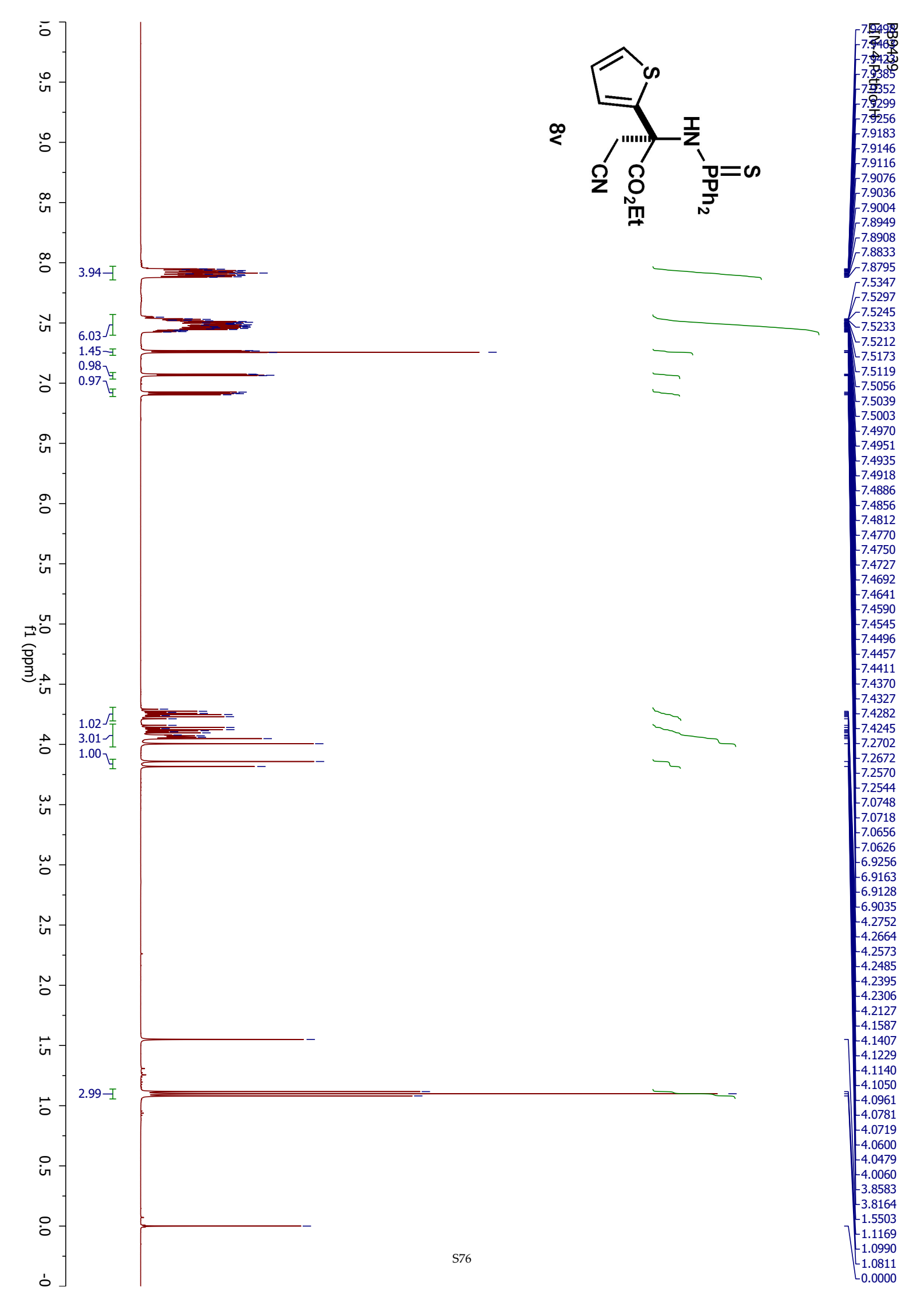

PB9435
LIN-4-P-4-MeS-C
MeS
8s
HN
S
PPh2
CO2Et
CN
171.5886
171.5238
139.9314
136.1901
134.3717
133.7598
133.6929
133.3602
132.1357
132.0211
131.8614
131.8317
131.7311
131.7010
130.7261
130.6120
128.7421
128.6096
128.2654
128.1323
126.4758
125.8852
117.0129
77.3175
76.9998
76.6821
64.6796
63.1092
27.9712
15.2024
13.6666
f1 (ppm)

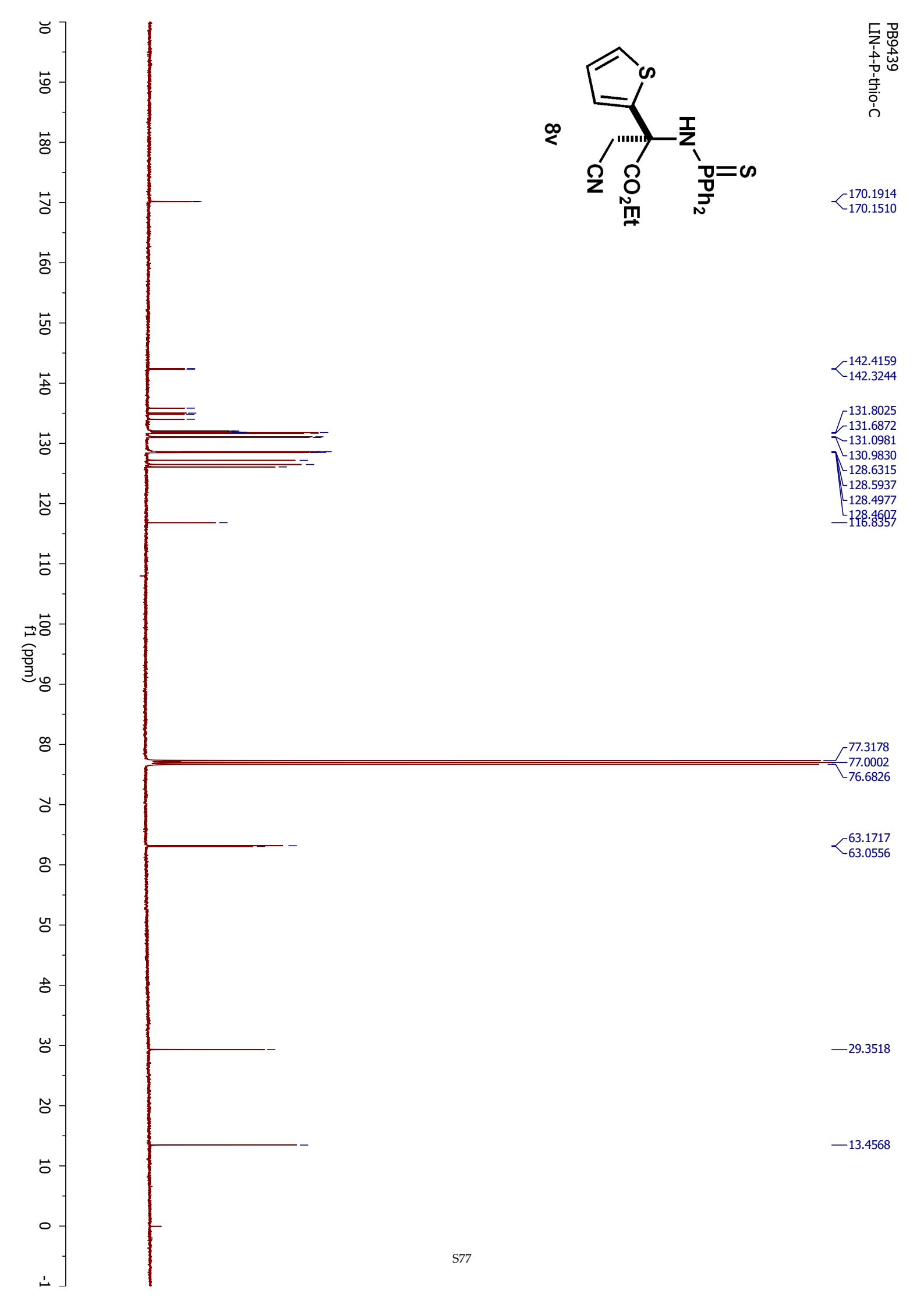

8t
O
O
HN
S
PPh2
CO2Et
CN
4.00
6.03
1.01
0.98
0.99
2.01
1.01
3.03
1.00
3.02
f1 (ppm)

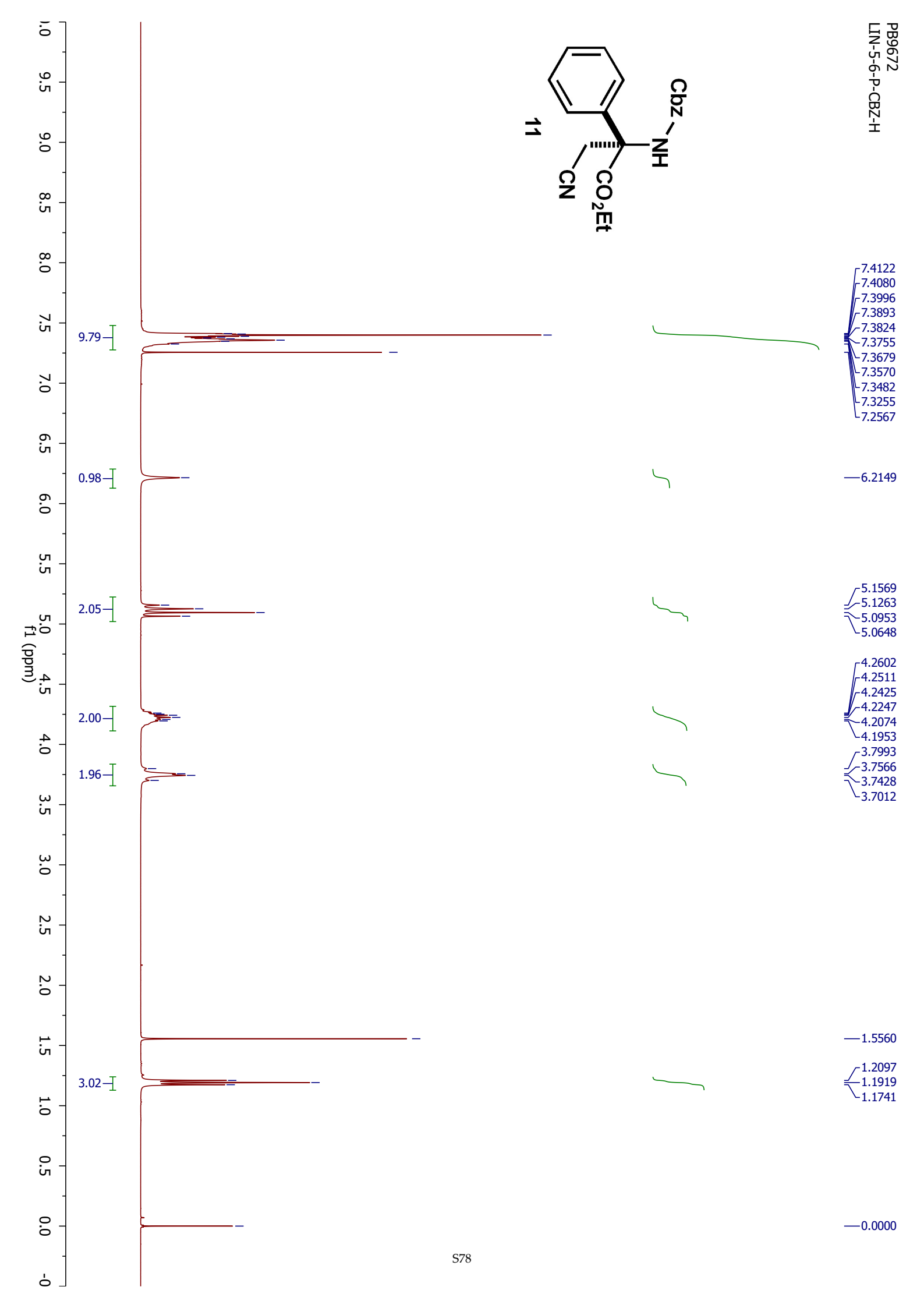

PB9438
LIN-4-P-1,3-O-C
8t
HN
S
PPh2
CO2Et
CN
171.6905
171.6270
147.9351
147.8001
132.2404
132.1260
131.8500
130.7184
130.6047
128.7709
128.6388
128.2379
128.1053
119.8490
116.9909
107.9496
106.8487
101.4399
77.3174
76.9998
76.6820
64.8033
63.1335
28.1609
13.7062
f1 (ppm)

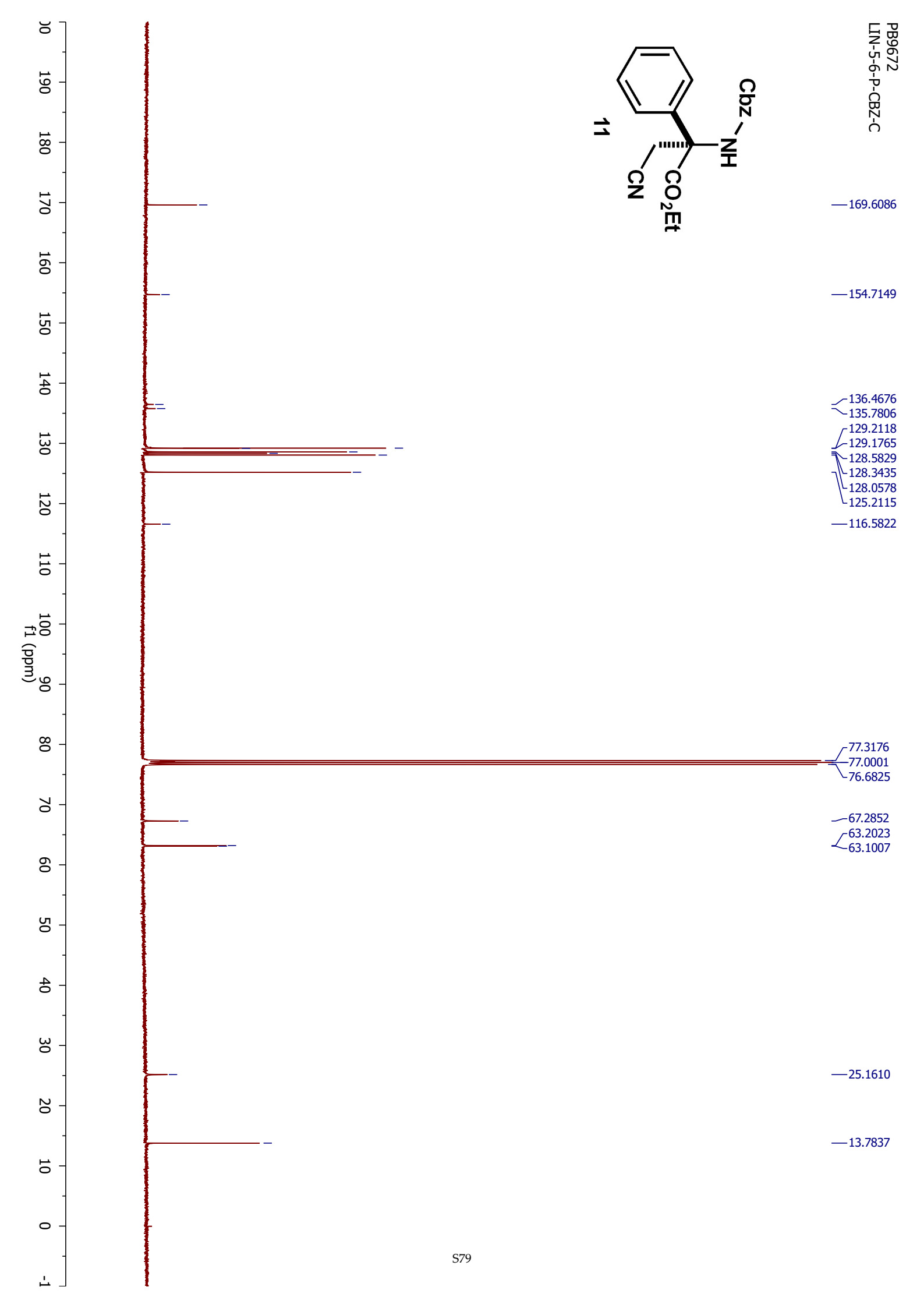

PB9437
8u
HN
PPh2
S
CO2Et
CN
O
O
7.9323
7.9249
7.9210
7.9155
7.9074
7.8945
7.8899
7.8861
7.8507
7.8384
7.8335
7.8296
7.8165
7.8040
7.7992
7.7953
7.4450
7.4400
7.4367
7.2582
6.8458
6.8399
6.8276
6.8215
6.8064
6.8003
6.7127
6.6915
4.3294
4.3205
4.3115
4.3026
4.2847
4.2669
4.2312
4.2134
4.2041
4.1951
4.1873
4.1753
4.1688
4.1628
4.1581
4.1509
4.1266
4.1019
4.0854
3.6137
3.5722
1.5674
1.2141
1.1962
1.1784
-0.0000
2.02
2.01
6.08
2.01
0.98
1.04
5.11
2.03
1.00
3.02
f1 (ppm)


PB9437
LIN-4-P-1,4-O-C
8u
171.6807
171.6210
143.8991
143.2321
132.2553
132.1410
130.7323
130.6181
128.7291
128.5971
128.2512
119.0268
117.2925
117.0561
115.4078
77.3178
77.0002
76.6825
64.5375
64.2426
64.2070
63.0065
28.1631
13.7014
f1 (ppm)


8v
S
HN
PPh2
S
CO2Et
CN
3.94
6.03
1.45
0.98
0.97
1.02
3.01
1.00
2.99
f1 (ppm)


PB9439
LIN-4-P-thio-C
8v
S
HN
PPh2
S
CO2Et
CN
170.1914
170.1510
142.4159
142.3244
131.8025
131.6872
131.0981
130.9830
128.6315
128.5937
128.4977
128.4607
116.8357
77.3178
77.0002
76.6826
63.1717
63.0556
29.3518
13.4568
f1 (ppm)


PB9672
LIN-5-6-P-CBZ-H
11
Cbz
NH
CO2Et
CN
9.79
0.98
2.05
2.00
1.96
3.02
7.4122
7.4080
7.3996
7.3893
7.3824
7.3755
7.3679
7.3570
7.3482
7.3255
7.2567
6.2149
5.1569
5.1263
5.0953
5.0648
4.2602
4.2511
4.2425
4.2247
4.2074
4.1953
3.7993
3.7566
3.7428
3.7012
1.5560
1.2097
1.1919
1.1741
0.0000
f1 (ppm)


PB9672
LIN-5-6-P-CBZ-C
11
Cbz
NH
CO2Et
CN
169.6086
154.7149
136.4676
135.7806
129.2118
129.1765
128.5829
128.3435
128.0578
125.2115
116.5822
77.3176
77.0001
76.6825
67.2852
63.2023
63.1007
25.1610
13.7837
f1 (ppm)