Electronic Supplementary Information

P-Chirogenic organocatalysts: Application to the aza-Morita-Baylis-Hillman (aza-MBH) reaction of ketimines

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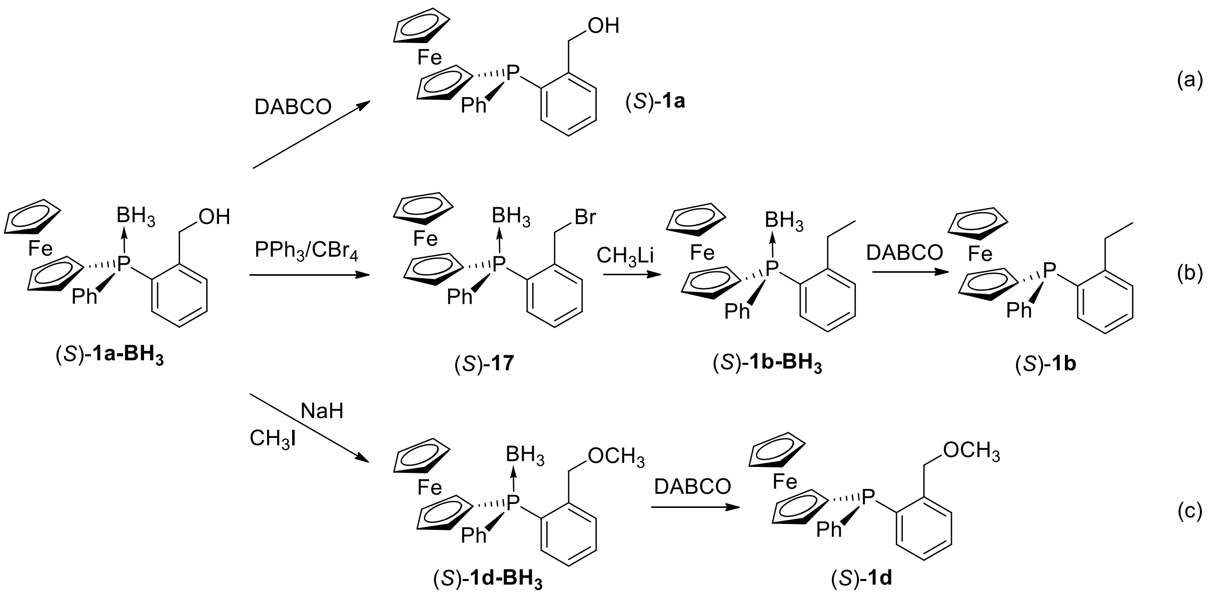
General information

^{1}H-, ^{13}C-, ^{19}F-, and ^{31}P-NMR spectra were recorded either with JEOL JMN ECS400 FT NMR, JNM ECA600 FT NMR (^{1}H-NMR 600 or 400 MHz, ^{13}C-NMR 150 or 100 MHz, ^{19}F-NMR 376 MHz, ^{31}P-NMR 255 MHz), or BRUKER 300, 500 and 600 Avance. ^{1}H-NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of $CHCl_3$ at 7.26 ppm, integration, multiplicities (s = singlet, d = doublet, q = quartet, t = triplet, m = multiplet), and coupling constants (Hz). ^{13}C-NMR spectra reported in ppm (δ) relative to the central line of triplet for $CDCl_3$ at 77 ppm. CF_3CO_2H or H_3PO_4 used as external standards for ^{19}F- or ^{31}P-NMR, respectively. FT-MS spectra were obtained with LTQ Orbitrap XL (Thermo Fisher Scientific). ESI-MS spectra were obtained with JMS-T100LC (JEOL). FAB-MS spectra were obtained with JMS-700 (JEOL). Optical rotations were measured either with JASCO P-1030 or PerkinElmer 341 polarimeter. HPLC analyses were performed either on a JASCO HPLC system (JASCO PU 980 pump and UV-975 UV/Vis detector), or on a SHIMADZHU 10A chromatograph equipped with a UV detector at λ = 210 nm and λ = 254 nm. The eluent used were mixture of hexane and *i*PrOH or EtOH as eluents. FT-IR spectra were recorded either on a JASCO FT-IR system (FT/IR4100) or BRUKER ATR Vector 22. Melting point (Mp) was measured with SHIMADZU DSC-60, or on an electrothermal 9100 melting point apparatus. Column chromatography on SiO_2 was performed either with Kishida Silica Gel (63-200 μm) or ACROS Silica Gel 60 (35-70 μm). Commercially available organic and inorganic compounds were used without further purification except for the solvent, which was distilled from sodium/benzophenone or CaH_2. The (*S*)-ferrocenyl[(2-hydroxymethyl)phenyl]phenylphosphine borane **1a-BH$_3$**, (S_p,*S*)- and (S_p,*R*)-[2-(ferrocenylphenylphosphino)phenyl]phenyl methanol (**1f**), and (R_p,*S*)- and (R_p,*R*)-[2-(*o*-anisylphenylphosphino)phenyl]phenyl methanol (**2**) were prepared according to the published procedure.[1] (*S*)-Ferrocenyl(2-methylphenyl)phenylphosphine (**1c**) was also prepared according to the published procedure and the characterization data are identical to previously described.[2]

Preparation of functional phosphines 1a, 1b and 1d



Scheme SI-1

Preparation of (*S*)-ferrocenyl[(2-hydroxymethyl)phenyl]phenylphosphine (1a)

The P-chirogenic functional organocatalyst (*S*)-**1a** was obtained by decomplexation of the borane complex **1a-BH$_3$**, according to published procedure using DABCO [Scheme SI-1, eq. (a)].[1] ^{31}P-NMR (toluene): δ -27.4 (s).

Preparation of (*S*)-ferrocenyl(2-ethylphenyl)phenylphosphine (1b).

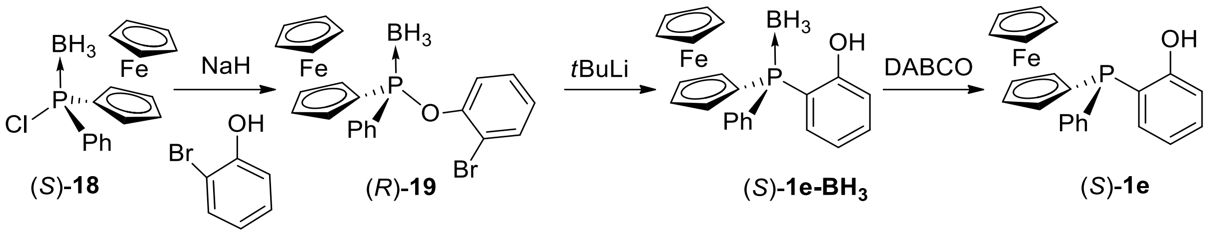
The phosphine **1b** was obtained by methylation of the (*S*)-ferrocenyl[2-(bromomethyl)phenyl] phenylphosphine borane (**17**), previously prepared from (*S*)-**1a-BH$_3$**,[1] followed by decomplexation [Scheme SI-1, eq. (b)]. To a solution of phosphine borane (*S*)-**1a-BH$_3$** (248 mg, 0.60 mmol) in dichloromethane (2 mL) was added triphenylphosphine (199 mg, 1.2 mmol) and CBr_4 (358 mg, 1.08 mmol). The reaction mixture was stirred during 1 h and the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (2:1) as eluent, to afford the phosphine (*S*)-**17**. Orange solid; 78% yield (222 mg); Mp 166-168 °C; R_f 0.73 (dichloromethane); Enantiomeric excess: 99 % by HPLC analysis (Chiralcel OD-H, 0.6 mL/min, hexane/2-propanol 98:2, t_R (*R*) = 12.8 min, t_R (*S*) = 14.6 min); $[\alpha]_D^{20}$ = +206 (c 0.2, $CHCl_3$); IR (neat): ν 3053, 2921, 2852, 2401, 1473, 1436, 1410, 1386, 1304, 1170, 1106, 1064, 1027, 999, 821, 743, 695 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 7.85-7.78 (m, 2H), 7.60-7.53 (m, 4H), 7.45 (tt, 1H, *J* = 1.4, 7.7 Hz), 7.22 (tt, 1H, *J* = 1.4, 7.4 Hz), 7.06 (ddd, 1H, *J* = 1.2, 7.8, 11.7 Hz), 4.77-4.75 (m, 1H), 4.63-4.62 (m, 1H), 4.55-4.53 (m, 1H), 4.51 (s, 2H), 4.15-4.13 (m, 1H), 4.08 (s, 5H); ^{13}C-NMR ($CDCl_3$): δ 140.8 (d, *J* = 9.8 Hz), 133.0 (d, *J* = 7.1 Hz), 132.9 (d, *J* = 8.3 Hz), 131.6 (d, *J* = 2.5 Hz), 131.4 (d, *J* = 1.9 Hz), 130.9 (d, *J* = 51.7 Hz), 129.4 (d, *J* = 59.0 Hz), 129.0 (d, *J* = 11.8 Hz), 127.8 (d, *J* = 8.9 Hz), 74.6 (d, *J* = 14.5 Hz), 72.3 (d, *J* = 7.9 Hz), 72.2 (d, *J* = 10.5 Hz), 71.7 (d, *J* = 3.9 Hz), 69.9, 69.0 (d, *J* = 72.3 Hz), 31.8; ^{31}P-NMR ($CDCl_3$): δ +16.2 (br.s); HRMS (ESI-Q-TOF) calcd for $C_{23}H_{23}PBBrFeNa$ [M+Na$^+$] : 499.0061, found : 499.0064. To a solution of (*S*)-**17** (267 mg, 0.56 mmol) in dry THF (4 mL) was added dropwise at -78 °C MeLi (1.6 M in pentane, 1.11 mmol). The reaction mixture was stirred during 1.5 h and warmed to room temperature, then quenched with water (5 mL) and extracted with dichloromethane (3 x 10 mL). The combined organic phases were dried over $MgSO_4$ and the solvent removed under vacuum to give a residue, which was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (9:1) as eluent, to afford the phosphine (*S*)-**1b-BH$_3$**. Orange solid; 58% yield (125 mg); Mp 156-158 °C; R_f 0.61 (petroleum ether/ethyl acetate 9:1); Enantiomeric excess: 99 % by HPLC analysis (Chiralcel OD-H, 0.6 mL/min, hexane/2-propanol 98:2, t_R (*R*) = 10.8 min, t_R (*S*) = 12.4 min); $[\alpha]_D^{20}$ = +172 (c 0.15, $CHCl_3$); IRFT (neat): ν 3107, 3057, 2977, 2918, 2850, 2662, 2381, 2339, 2246, 1964, 1929, 1903, 1776, 1710, 1776, 1710, 1589, 1469, 1437, 1386, 1311, 1170, 1130, 1106, 1058, 1027, 1001, 890, 873, 820, 785, 740, 699 cm^{-1}; ^{1}H-NMR ($CDCl_3$) : δ 7.81-7.76 (m, 2H), 7.58-7.49 (m, 3H), 7.41-7.38 (m, 1H), 7.28-7.25 (m, 1H), 7.14-7.07 (m, 2H), 4.76 (s, 1H), 4.60 (s, 1H), 4.51 (s, 1H), 4.11 (s, 1H), 4.08 (s, 5H), 2.72-2.64 (m, 1H), 2.46-2.39 (m, 1H), 1.34-1.14 (m), 0.86 (t, 3H, *J* = 4.5 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) : δ 147.7 (d, *J* = 10.6 Hz), 133.2 (d, *J* = 10.6 Hz), 132.7 (d, *J* = 12.7 Hz), 131.2 (d, *J* = 61.2 Hz), 131.0 (d, *J* = 16.9 Hz), 130.2 (d, *J* = 57.0 Hz), 129.6 (d, *J* = 8.5 Hz), 128.6 (d, *J* = 35.9 Hz), 128.5 (d, *J* = 12.7 Hz), 125.4 (d, *J* = 12.7 Hz), 74.6 (d, *J* = 15.2 Hz), 71.9 (d, *J* = 6.16 Hz), 71.8, 71.7 (d, *J* = 5.2 Hz), 70.3 (d, *J* = 71.8 Hz), 69.8, 27.6, 14.6; ^{31}P-NMR ($CDCl_3$): δ +16.5 (br.s); HRMS (ESI-Q-TOF) calcd for $C_{24}H_{26}BFePNa$ [M+Na$^+$] : 435,1112, found : 435.1114. Finally, the P-chirogenic functional organocatalyst (*S*)-**1b** was obtained by decomplexation of the borane complex **1b-BH$_3$**, according to published procedure using DABCO [Scheme SI-1, eq. (b)].[1] ^{31}P-NMR (toluene): δ -26.7 (s).

Preparation of (*S*)-ferrocenyl[2-(methoxymethyl)phenyl]phenylphosphine (1d).

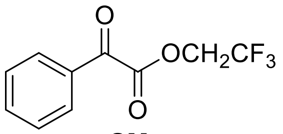
The P-chirogenic functional organocatalyst (*S*)-**1d** was prepared by O-methylation of the (*S*)-ferrocenyl [2-(hydroxymethyl)phenyl]phenylphosphine borane) (**1a-BH$_3$**),[1] followed by decomplexation [Scheme SI-1, eq. (c)]. A solution of compound **1a-BH$_3$**, (100 mg, 0.24 mmol) in dry THF (4 mL) was added dropwise at 0 °C to a suspension of NaH (50 mg, 1.2 mmol), in dry THF (1 mL). After 1 h stirring at 0 °C, CH_3I (0.04 mL, 0.6 mmol) was added dropwise. The resulting solution was warmed to room temperature for 2 h, quenched with water (5 mL) and extracted with dichloromethane (3 x 10 mL). The combined organic phases were dried over $MgSO_4$ and the solvent removed under vacuum to give a residue which was purified by column chromatography on silica gel using dichloromethane as eluent, to afford the (*S*)-ferrocenyl [(2-methoxymethyl)phenyl]phenylphosphine borane (**1d-BH$_3$**). Orange solid; 86% yield (89 mg); Mp 152-154 °C; R_f 0.48 (CH_2Cl_2); Enantiomeric excess: 99% by HPLC analysis (Chiralcel OD-H, 0.5 mL/min, hexane/2-propanol 97:3, t_R (*R*) = 13.4 min, t_R (*S*) = 14.9 min); $[\alpha]_D^{20}$ = +136 (c 0.5, $CHCl_3$); IR (neat): ν 3087, 3058, 2931, 2882, 2829, 2420, 2392, 2335, 2258, 2203, 2110, 2075, 1979, 1791, 1693, 1660, 1590, 1567, 1434, 1388, 1312, 1261, 1196, 1169, 1126, 1106, 1066, 1026, 1106, 1066, 1026, 1002, 975, 828, 746, 720, 702 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 7.74-7.67 (m, 2H), 7.51-7.33 (m, 5H), 7.19-7.10 (m, 1H), 7.05-7.00 (m, 1H), 4.67 (m, 1H), 4.51 (m, 1H), 4.42 (m, 1H), 4.37 (d, 1H, *J* = 13.7 Hz), 4.02 (m, 1H), 4.00 (s, 5H), 3.97 (d, 1H, *J* = 13.7 Hz), 2.90 (s), 1.62-1.05 (m). ^{13}C-NMR (75 MHz, $CDCl_3$) : δ 141.8 (d, *J* = 8.8 Hz), 133.0 (d, *J* = 7.5 Hz), 132.7 (d, *J* = 10.1 Hz), 131.3 (d, *J* = 1.2 Hz), 131.0 (d, *J* = 2.5 Hz), 130.8, 130.0, 129.6, 128.6 (d, *J* = 8.8 Hz), 128.5 (d, *J* = 10.1 Hz), 127.0 (d, *J* = 2.5 Hz), 111.5, 74.5 (d, *J* = 15.1 Hz), 72.1 (d, *J* = 6.3 Hz), 71.9 (d, *J* = 7.5 Hz), 71.8 (d, *J* = 5.0 Hz), 71.7 (d, *J* = 5.0 Hz), 69.9, 58.0; ^{31}P-NMR ($CDCl_3$): δ +16.4 (br.s); HRMS (ESI-Q-TOF) calcd for $C_{24}H_{26}B_1POFeNa$ [M+Na$^+$]: 451.1061, found: 451.1049.

The P-chirogenic functional organocatalyst (*S*)-**1d** was obtained by decomplexation of the borane complex **1d-BH$_3$**, according to published procedure using DABCO (Scheme 1b).[1] ^{31}P-NMR (toluene): δ -26.9 (s).

Preparation of (*S*)-ferrocenyl(2-hydroxypheny)phenylphosphine (1e).



The P-chirogenic functional organocatalyst (*S*)-**1e** was prepared according a described procedure,[3] by Fries like rearrangement of (*R*)-ferrocenyl[2-(hydroxy)phenyl]phenylphosphine borane (**19**), followed by decomplexation. To a toluene solution of chloroferrocenylphenylphosphine borane (*S*)-**18** (2 mmol), prepared according the described procedure,[4] was added under stirring at -78°C, alcoolate (4 mmol) previously obtained by reaction of 2-bromophenol (692 mg, 4 mmol) with NaH (106 mg, 4.4 mmol) in THF (3 mL). After stirring 1 h at room temperature, then hydrolysis with water (10 mL), the mixture was extracted with methylene chloride (3 x10 mL) and the combined organic phases were dried over $MgSO_4$. The solvent was removed under vacuum and the resulting crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (4:1) as eluent, to afford the 2-bromophenyl ferrocenylphenylphosphinite borane (*R*)-**19** in 53 % yield (507 mg). The phosphinite (*R*)-**19** (222 mg, 0.45 mmol) was dissolved in 5 mL THF and 0.8 mL of *t*-BuLi (1.2 mmol) was added at -78°C. The mixture was warmed to 0 °C for 1 h, then hydrolyzed with water (10 mL). After extraction with ethyl acetate (3 x 10 mL), the combined organic layers were dried over $MgSO_4$, and the solvent removed under vacuum. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (4:1) as eluent, to afford the ferrocenyl(2-hydroxyphenyl)phenylphosphine borane [(*S*)-**1e-BH$_3$**] .Orange solid; 61% yield (108 mg); Mp 165-167 °C; R_f 0.46 ether/ethyl acetate (4:1); Enantiomeric excess: 99 % by HPLC analysis (Phenomenex Lux 5μ cellulose 2, 0.8 mL/min, hexane/2-propanol 95:5, t_R (*S*) = 17.9 min, t_R (*R*) = 21.3 min); $[\alpha]_D^{20}$ = +185 (c 0.2, $CHCl_3$); IR (neat): ν 3528, 2890, 2856, 2215, 1345, 1211, 1160, 1086, 1012, 968, 894, 856, 766, 748 cm^{-1}; ^{1}H-NMR ($CDCl_3$) : δ 7.80 (s, 1H), 7.53-7.39 (m, 6H), 7.08-7.02 (m, 2H), 6.93-6.88 (m, 1H), 4.58-4.55 (m, 3H), 4.36-4.28 (m, 1H), 4.18 (s, 5H), 1.93-1.16 (m, 3H); ^{13}C-NMR ($CDCl_3$): δ 160.1 (d, *J* = 9.1 Hz), 134.2 (d, *J* = 2.3 Hz), 133.6 (d, *J* = 2.3 Hz), 130.9 (d, *J* = 2.3 Hz), 128.5 (d, *J* = 10.6 Hz), 120.2 (d, *J* = 7.5 Hz), 118.2 (d, *J* = 6.0 Hz), 113.4 (d, *J* = 60.4 Hz), 73.5 (d, *J* = 12.8 Hz), 72.3 (d, *J* = 5.3 Hz), 72.0 (d, *J* = 9.0 Hz), 69.9, 68.0 (d, *J* = 75.0 Hz); ^{31}P-NMR ($CDCl_3$) : δ +9.2 (br.s); HRMS (ESI-Q-TOF) calcd for $C_{22}H_{22}POBFeNa$ [M+Na$^+$] : 423.0747, found : 423.0746. Crystal of (*S*)-**1e-BH$_3$** was grown from methylene chloride/hexane as solvent and its drawing is shown on Figure S1. The (*S*)-absolute configuration is supported by refinement of the Flack parameters (Table S3). Finally, the P-chirogenic functional organocatalyst (*S*)-**1e** was obtained by decomplexation of the borane complex **1e-BH$_3$**, according to published procedure using DABCO.[3] ^{31}P-NMR (toluene): δ -32.3 (s)



SM-e

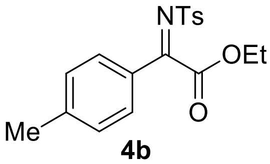
Preparation of α-keto ester SM-e

To a solution of 2-oxo-2-phenylacetic acid (0.5g, 1 equiv) and 2,2,2-trifluoroethanol (1.0g, 3 equiv) in cyclohexane (7 mL), was added H_2SO_4 (20 mol%) at ambient temperature and heated at reflux for 3 h. The cooled mixture, to room temperature, was extracted three times with CH_2Cl_2. The combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated. The resulting residue was purified by SiO_2 column chromatography with hexane and EtOAc as eluents to give the corresponding α-keto ester **SM-e**.

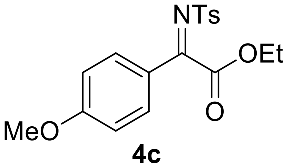
SM-e: colorless oil (82% yield); ^{1}H-NMR ($CDCl_3$) δ 7.97 (d, 2H, *J* = 8.2 Hz), 7.67-7.62 (m, 1H), 7.51-7.47 (m, 2H), 4.76 (q, 2H, *J* = 8.2 Hz); ^{13}C-NMR ($CDCl_3$) δ 184.3, 161.7, 135.3, 131.8, 129.9, 129.0, 122.5 (q, *J* = 277.0 Hz) , 60.9 (q, *J* = 37.4 Hz); ^{19}F-NMR ($CDCl_3$): δ -73.3; HRMS (ESI) calcd for $C_{10}H_7F_3O_3Na$, m/z = 255.0239 [(M+Na)$^+$], found m/z = 255.0237; IR (KBr): ν 3069, 1760, 1690, 1274, 1166 cm^{-1}.

Preparation of ketimines 4

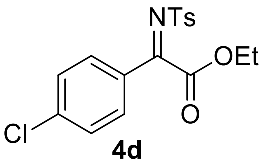
A solution of the corresponding keto ester (1.25 equiv), *p*-toluenesulfonamide (1.0 equiv), and triethylamine (1.0 equiv) in CH_2Cl_2 was cooled to 0 ºC. To this mixture was added a solution of $TiCl_4$ (1.0 equiv) in CH_2Cl_2 under N_2. The mixture was stirred at 0 ºC for 30 min and then warmed to ambient temperature and stirred for 1 h. The mixture was then quenched with sat. $NaHCO_3$ and extracted three times with CH_2Cl_2. The combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated. The resulting residue was purified by SiO_2 column chromatography (15% EtOAc/hexane) or GPC ($CHCl_3$ only) to afford **4**. Spectral data of **4a**,[5] **4l**,[6] and **4m**[7] agreed with those reported previously.


4b

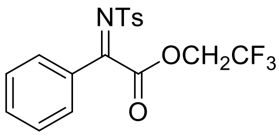
4b: yellow oil (63% yield); ^{1}H-NMR ($CDCl_3$) δ 7.92 (d, 2H, *J* = 8.2 Hz), 7.73 (d, 2H, *J* = 8.2 Hz), 7.32 (d, 2H, *J* = 8.2 Hz), 7.23 (d, 2H, *J* = 8.2 Hz), 4.56 (q, 2H, *J* = 7.3 Hz), 2.41 (s, 3H), 2.39 (s, 3H), 1.47 (t, 3H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 167.1, 164.9, 146.3, 144.6, 135.8, 130.0, 129.7, 129.6, 128.6, 128.0, 63.0, 21.8, 21.6, 13.9; HRMS (ESI) calcd for $C_{18}H_{19}NO_4SNa$, m/z = 368.0932 [$(M+Na)^+$], found m/z = 368.0928; IR (KBr): ν 3453, 2984, 1740, 1590, 1328, 1214, 1161 cm^{-1}.


4c

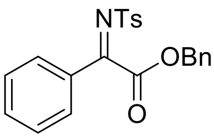
4c: yellow oil (71% yield); ^{1}H-NMR ($CDCl_3$) δ 7.90 (d, 2H, *J* = 8.7 Hz), 7.79 (d, 2H, *J* = 9.2 Hz), 7.30 (d, 2H, *J* = 8.7 Hz), 6.89 (d, 2H, *J* = 9.2 Hz) 4.54 (q, 2H, 7.3 Hz), 3.82 (s, 3H), 2.39 (s, 3H), 1.46 (t, 3H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 166.4, 165.1, 165.0, 144.4, 136.0, 132.3, 129.5, 127.7, 123.6, 114.4, 62.9, 55.6, 21.5, 13.9; HRMS (ESI) calcd for $C_{18}H_{19}NO_5SNa$, m/z = 384.0881 [$(M+Na)^+$], found m/z = 384.0881; IR (KBr): ν 3277, 2981, 1739, 1583, 1324, 1270, 1219, 1120 cm^{-1}.


4d

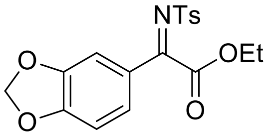
4d: pale yellow oil (80% yield); ^{1}H-NMR ($CDCl_3$) δ 7.92 (d, 2H, *J* = 8.2 Hz), 7.77 (d, 2H, *J* = 8.7 Hz), 7.41 (d, 2H, *J* = 8.7 Hz), 7.34 (d, 2H, *J* = 7.8 Hz), 4.56 (q, 2H, *J* = 7.3 Hz), 2.43 (s, 3H), 1.48 (t, 3H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 165.9, 164.4, 144.9, 141.4, 135.3, 131.0, 129.8, 129.7, 129.4, 128.1, 63.3, 21.6, 13.9; HRMS (ESI) calcd for $C_{17}H_{16}ClNO_4SNa$, m/z = 388.0386 [$(M+Na)^+$], found m/z = 388.0384; IR (KBr): ν 3077, 2984, 1740, 1585, 1558, 1333, 1302, 1211, 1163 cm^{-1}.


4e

4e: colorless oil (72% yield); ^{1}H-NMR ($CDCl_3$) δ 7.91 (d, 2H, *J* = 8.2 Hz), 7.83 (dd, 2H, *J* = 8.2, 1.4 Hz), 7.65-7.61 (m, 1H), 7.49-7.45 (m, 2H), 7.36 (d, 2H, *J* = 8.2 Hz), 4.87 (q, 2H, *J* = 8.3 Hz), 2.44 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 165.1, 163.4, 145.2, 135.3, 134.9, 130.5, 129.83, 129.76, 129.2, 128.1, 122.5 (q, *J* = 277 Hz), 61.9 (q, *J* = 37.2 Hz), 21.6; ^{19}F-NMR ($CDCl_3$): δ -72.9; HRMS (ESI) calcd for $C_{17}H_{14}F_3NO_4SNa$, m/z = 408.0493 [$(M+Na)^+$], found m/z = 408.0485; IR (KBr): ν 3067, 2977, 1765, 1597, 1332, 1278, 1164 cm^{-1}.

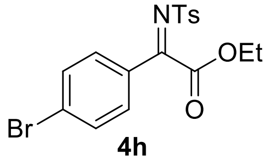

4f

4f: yellow solid (65% yield); ^{1}H-NMR ($CDCl_3$) δ 7.90 (d, 2H, *J* = 8.2 Hz), 7.77 (d, 2H, *J* = 7.3 Hz), 7.57 (t, 1H, *J* = 7.3 Hz), 7.52 (d, 1H, *J* = 2.3 Hz), 7.50 (d, 1H, *J* = 1.4 Hz), 7.44-7.37 (m, 5H), 7.31 (d, 2H, *J* = 8.2 Hz), 5.52 (s, 2H), 2.43 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 166.8, 164.7, 144.8, 135.5, 134.8, 134.2, 131.3, 129.9, 129.7, 129.1, 129.0, 128.9, 128.7, 128.2, 68.9, 21.7; HRMS (ESI) calcd for $C_{22}H_{19}NO_4SNa$, m/z = 416.0932 [$(M+Na)^+$], found m/z = 416.0927; IR (KBr): ν 3061, 2952, 1741, 1594, 1332, 1158 cm^{-1}.



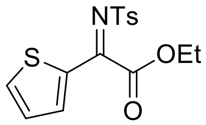
4g

4g: yellow oil (58% yield); ^{1}H-NMR ($CDCl_3$) δ 7.91 (d, 2H, *J* = 8.2 Hz), 7.39 (d, 1H, *J* = 1.4 Hz), 7.35-7.32 (m, 3H), 6.83 (d, 1H, *J* = 8.2 Hz), 6.06 (s, 2H), 4.55 (q, 2H, *J* = 7.3 Hz), 2.43 (s, 3H), 1.48 (t, 3H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 166.2, 164.9, 153.7, 148.6, 144.5, 136.0, 129.7, 127.8, 127.9, 125.8, 108.5, 102.4, 63.2, 21.7, 14.0; HRMS (ESI) calcd for $C_{18}H_{17}NO_6SNa$ 398.0674 [$(M+Na)^+$], found m/z = 398.0670; IR (KBr): ν 3086, 2987, 1743, 1600, 1318, 1248, 1155 cm^{-1}.



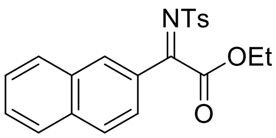
4h

4h: yellow oil (85% yield); ^{1}H-NMR ($CDCl_3$) δ 7.92 (d, 2H, *J* = 8.7 Hz), 7.69 (d, 2H, *J* = 9.2 Hz), 7.58 (d, 2H, *J* = 8.7 Hz), 7.35 (d, 2H, *J* = 7.8 Hz), 4.56 (q, 2H, *J* = 7.3 Hz), 2.44 (s, 3H), 1.48 (t, 3H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 166.1, 164.4, 145.0, 135.3, 132.4, 131.1, 130.2, 129.8, 129.0, 128.1, 63.3, 21.7, 13.9; HRMS (ESI) calcd for $C_{17}H_{16}BrNO_4SNa$, 431.9880 [$(M+Na)^+$], found m/z = 431.9879; IR (KBr): ν 2982, 1734, 1581, 1302, 1165 cm^{-1}.



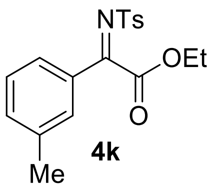
4i

4i: yellow oil (60% yield); ^{1}H-NMR ($CDCl_3$) δ 7.79 (d, 2H, *J* = 8.7 Hz), 7.64 (d, 1H, *J* = 1.4 Hz), 7.49 (d, 1H, *J* = 0.9 Hz) 7.21 (d, 2H, *J* = 8.2 Hz), 7.03 (m, 1H), 4.45 (q, 2H, *J* = 7.3 Hz), 2.30 (s, 3H), 1.37 (t, 3H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 163.8, 161.1, 144.5, 137.4, 137.3, 137.1, 135.6, 129.5, 128.9, 127.7, 63.3, 21.4, 13.8; HRMS (ESI) calcd for $C_{15}H_{15}NO_4S_2Na$, m/z = 360.0339 [$(M+Na)^+$], found m/z = 360.0339; IR (KBr): ν 3103, 2984, 1740, 1562, 1311, 1214, 1160 cm^{-1}.



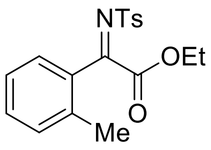
4j

4j: yellow oil (45% yield); ^{1}H-NMR ($CDCl_3$) δ 8.27 (s, 1H), 7.98-7.95 (m, 3H), 7.88 (d, 1H, *J* = 8.2 Hz), 7.83 (d, 2H, *J* = 8.7 Hz), 7.63-7.52 (m, 2H), 7.35 (d, 2H, *J* = 7.8 Hz), 4.65 (q, 2H, *J* = 7.3 Hz), 2.44 (s, 3H), 1.52 (t, 3H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 167.2, 164.9, 144.8, 136.3, 135.8, 133.3, 132.4, 129.8, 129.7, 129.6, 129.0, 128.8, 128.1, 127.9, 127.2, 124.0, 63.3, 21.7, 14.0; HRMS (ESI) calcd for $C_{21}H_{19}NO_4SNa$, m/z = 404.0932 [$(M+Na)^+$], found m/z = 404.0932; IR (KBr): ν 3064, 2979, 1733, 1573, 1307, 1251, 1161 cm^{-1}.



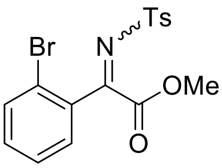
4k

4k: colorless oil (40% yield); ^{1}H-NMR ($CDCl_3$) δ 7.93 (d, 2H, *J* = 7.6 Hz), 7.67 (s, 1H), 7.61 (d, 1H, *J* = 7.6 Hz), 7.40 (d, 1H, *J* = 7.6 Hz), 7.35-7.31 (m, 3H), 4.57 (q, 2H, *J* = 7.3 Hz), 2.43 (s, 3H), 2.36 (s, 3H), 1.48 (t, 3H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 167.5, 164.9, 144.7, 139.0, 135.7, 135.6, 131.3, 130.1, 129.7, 128.9, 128.1, 127.3, 63.1, 21.7, 21.2, 14.0; HRMS (ESI) calcd for $C_{18}H_{19}NO_4SNa$, m/z = 368.0932 [$(M+Na)^+$], found m/z = 368.0928; IR (KBr): ν 3281, 2983, 1739, 1578, 1331, 1235, 1163 cm^{-1}.



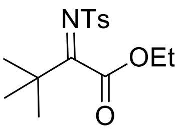
4n

4n: colorless oil (40% yield); ^{1}H-NMR ($CDCl_3$) δ 7.84 (d, 2H, *J* = 8.2 Hz), 7.45 (d, 1H, *J* = 8.2 Hz), 7.33 (m, 1H), 7.26 (d, 2H, *J* = 8.2 Hz), 7.18 (m, 2H), 4.45 (q, 2H, *J* = 7.3 Hz), 2.37 (s, 3H), 2.36 (s, 3H), 1.39 (t, 3H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 168.6, 164.8, 144.7, 140.9, 136.0, 133.0, 132.6, 131.2, 130.5, 129.7, 128.0, 126.2, 63.1, 22.2, 21.7, 13.9; HRMS (ESI) calcd for $C_{18}H_{19}NO_4SNa$, m/z = 368.0927 [$(M+Na)^+$], found m/z = 368.0931; IR (KBr): ν 3081, 2967, 2930, 1735, 1603, 1330, 1216, 1162 cm^{-1} .



4o

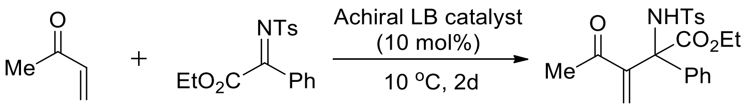
4o: colorless oil (45%); *E*:*Z* mixture (42:58) (assigned to the major isomer from mixture); ^{1}H-NMR ($CDCl_3$) δ 7.94 (d, 2H, *J* = 8.2 Hz), 7.63 (d, 1H, *J* = 6.9 Hz), 7.59 (d, 1H, *J* = 6.9 Hz), 7.37-7.34 (m, 4H), 4.03 (s, 3H), 2.45 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 166.6, 163.8, 145.0, 135.4, 134.8, 133.5, 132.1, 131.6, 130.3, 129.7, 128.2, 127.6, 53.7, 21.7; HRMS (ESI) calcd for $C_{16}H_{14}BrNO_4SNa$, m/z = 417.9719 [$(M+Na)^+$], found m/z = 417.9716.; IR (KBr): ν 3050, 1743, 1612, 1446, 1322, 1171 cm^{-1} .



4p

4p: white solid (62%), M.p. (89-92 °C); ^{1}H-NMR ($CDCl_3$) δ 7.83 (d, 2H, *J* = 8.2 Hz), 7.31 (d, 2H, *J* = 8.2 Hz), 4.41 (q, 2H, *J* = 7.3 Hz), 2.42 (s, 3H), 1.40 (t, 3H, *J* = 7.3 Hz), 1.19 (s, 9H); ^{13}C-NMR ($CDCl_3$) δ 181.8, 164.6, 144.6, 135.4, 129.6, 127.9, 62.4, 40.1, 27.2, 21.6, 13.9; HRMS (ESI) calcd for $C_{15}H_{21}NO_4SNa$, m/z = 334.1083 [$(M+Na)^+$], found m/z = 334.1078; IR (KBr): ν 2962, 1729, 1587, 1464, 1317, 1097 cm^{-1} .

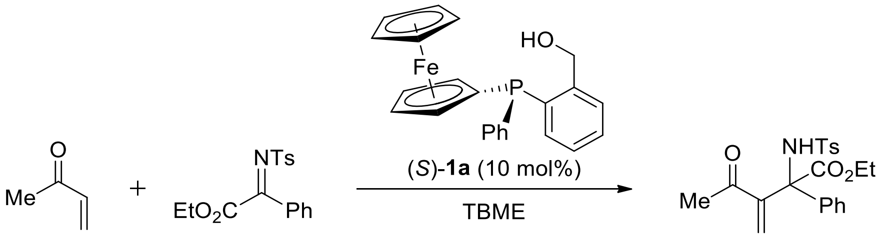
Table S1. Achiral LB catalyzed aza-MBH reaction of **3a** with **4a**[a]



entry	achiral LB catalyst	solvent	yield (%)
1	DMAP	CH_2Cl_2	10
2	DABCO	CH_2Cl_2	7
3	DBU	CH_2Cl_2	trace
4	2-phenyl-2-imidazoline	CH_2Cl_2	trace
5	PPh_3	CH_2Cl_2	74
6	PPh_3	$(CH_2Cl)_2$	70
7	PPh_3	$CHCl_3$	54
8	PPh_3	toluene	80
9	PPh_3	THF	34
10	PPh_3	Et_2O	50
11	PPh_3	TBME	96

[a]Conditions: **3a** (0.12 mmol), **4a** (0.040 mmol), achiral catalyst (10 mol%) in solvent (0.2 mL).

Table S2. Effects of temperature and solvents on the reaction.



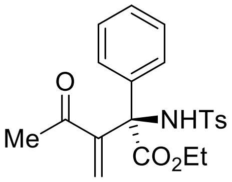
3a 4a 5a

entry	solvent	temp. (ºC)	time (day)	yield (%)	ee (%)
1	TBME	0	1	trace	ND
2	TBME	10	2	87	96
3	TBME	30	2	90	79
4	toluene	10	2	68	64
5	CH_2Cl_2	10	2	52	94

[a]Conditions: **3a** (0.12 mmol), **4a** (0.040 mmol), catalyst (*S*)-**1a** (0.012 mmol) in solvent (0.2 mL).

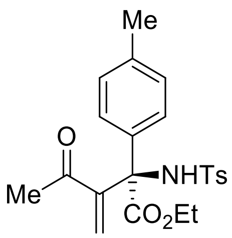
General procedure for enantioselective aza-MBH reaction of 3 and 4.

To a solution of organocatalyst (*S*)-**1** (10-20 mol%), *N*-tosylketimine (0.040 mmol) in TBME (0.2 mL) was added enone (0.12 mmol, 3.0 equiv). The reaction mixture was stirred at 5 or 10 °C, and was stirred until the reaction reached completion determined by TLC analysis. After purification via column chromatography, product **5** was obtained. Since the catalyst **1** is air sensitive, **1** is readily utilized for the reaction after the borane decomplexation of the pre-catalyst with DABCO and then purification by SiO_2 column chromatography.[4,5] The adducts **5o** was identical in all respects with reported by Shi and Li.[8]



5a

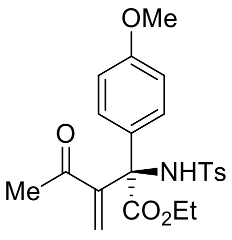
5a: pale yellow oil (87% yield, 96% ee); ^{1}H-NMR ($CDCl_3$) δ 7.75-7.73 (m, 2H), 7.51 (d, 2H, *J* = 6.4 Hz), 7.39-7.32 (m, 3H), 7.20 (d, 2H, *J* = 8.4 Hz), 6.49 (s, 1H), 6.41 (s, 1H), 6.27 (s, 1H), 4.34 (qd, 1H, *J* = 9.6, 7.3 Hz), 4.04 (qd, 1H, *J* = 9.6, 7.3 Hz), 2.39 (s, 3H), 1.74 (s, 3H), 1.08 (t, 3H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 196.8, 170.5, 144.3, 142.9, 138.6, 136.9, 135.6, 129.0, 128.9, 128.3, 127.8, 127.7, 67.6, 62.6, 24.6, 21.4, 13.6; HRMS (APCI) calcd for $C_{21}H_{23}NO_5SH$, m/z = 402.1375 [$(M+H)^+$], found 402.1370; Enantiomeric excess determined by HPLC (Chiralpak IC, hexane/2-propanol = 65/35, flow rate 1.0 mL/min, 25 °C, 254 nm) minor peak: t_R = 13.8 min, major peak: t_R = 17.6 min; $[\alpha]_D^{21}$ = +38.7 (*c* 0.15, $CHCl_3$); IR (KBr): ν 3284, 1735, 1685, 1599, 1329, 1230, 1166, 1096, 1040, 969 cm^{-1}.



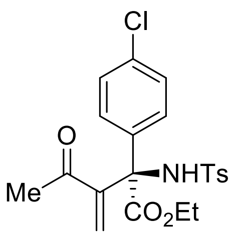
5b

5b: pale yellow oil (87% yield, 96% ee); ^{1}H-NMR ($CDCl_3$) δ 7.60 (d, 2H, *J* = 8.7 Hz,), 7.49 (d, 2H, *J*= 8.2 Hz), 7.18 (d, 2H, *J* = 7.8 Hz), 7.15 (d, 2H, *J* = 7.8 Hz), 6.48 (s, 1H), 6.39 (s,1H), 6.27 (s, 1H), 4.05 (qd, 1H, *J* = 11.2, 7.3 Hz), 4.04 (qd, 1H, *J* = 11.2, 7.3 Hz), 2.38 (s, 3H), 2.34 (s, 3H), 1.72 (s, 3H), 1.07 (t, 3H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 196.9, 170.5, 144.3, 142.7, 138.7,138.0, 135.3, 133.9, 129.0, 128.7, 128.4, 127.8, 67.4, 62.5, 24.6, 21.4, 20.9, 13.6; HRMS (APCI) calcd for $C_{22}H_{25}NO_5SH$, m/z =

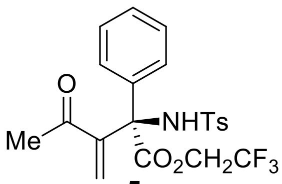
416.1531[(M+H)$^+$], found m/z = 416.1521; Enantiomeric excess determined by HPLC (Chiralpak AS, hexane/EtOH = 4/1, flow rate 1.0 mL/min, 25 °C, 230 nm) minor peak: t_R = 8.5 min, major peak: t_R = 18.2 min; $[\alpha]_D^{22}$ = +99.7 (*c* 0.53, $CHCl_3$); IR (KBr): ν 3279, 1736, 1686, 1508, 1330, 1167, 1096, 1040 cm^{-1}.


5c

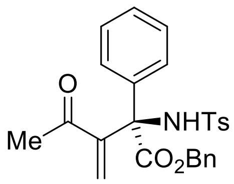
5c: pale yellow oil (92% yield, 94% ee); ^{1}H-NMR ($CDCl_3$) δ 7.64 (d, 2H, *J* = 8.7 Hz), 7.50 (d, 2H, *J* = 8.2 Hz), 7.20 (d, 2H, *J* = 8.2 Hz), 6.88 (d, 2H, *J* = 9.2 Hz), 6.47 (s, 1H), 6.39 (s, 1H), 6.28 (s, 1H), 4.06 (qd, 1H, *J* = 10.0, 7.3 Hz), 4.03 (qd, 1H, *J* = 10.0, 7.3 Hz), 3.82 (s, 3H), 2.39 (s, 3H), 1.73 (s, 3H), 1.08 (t, 3H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 196.9, 170.6, 159.5, 144.4, 142.8, 138.6, 135.4, 130.2, 129.0, 128.6, 127.9, 113.1, 67.1, 62.5, 55.3, 24.6, 21.4, 13.7; HRMS (APCI) calcd for $C_{22}H_{25}NO_6SNa$, m/z = 454.1300 [(M+Na)$^+$], found m/z = 454.1295; Enantiomeric excess determined by HPLC (Chiralpak IB, hexane/2-propanol = 9/1, flow rate 1.0 mL/min, 25 °C, 240 nm) minor peak: t_R = 23.3 min, major peak: t_R = 16.7 min; $[\alpha]_D^{21}$ = +15.5 (*c* 0.05, $CHCl_3$); IR (KBr): ν 3369, 1775, 1655, 1510, 1399, 1051 cm^{-1}.


5d

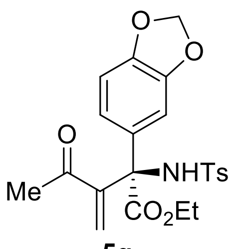
5d: pale yellow oil (95% yield, 88% ee); ^{1}H-NMR ($CDCl_3$) δ 7.68 (d, 2H, *J* = 8.7 Hz), 7.48 (d, 2H, *J* = 8.2 Hz), 7.33 (d, 2H, *J* = 8.7 Hz), 7.20 (d, 2H, *J* = 7.8 Hz), 6.48 (s, 1H), 6.41 (s, 1H), 6.23 (s, 1H), 4.07 (qd, 1H, *J* = 10.8, 7.3 Hz), 4.04 (qd, 1H, *J* = 10.8, 7.3 Hz), 2.39 (s, 3H), 1.72 (s, 3H), 1.09 (t, 3H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 196.7, 170.1, 144.1, 143.0, 138.4, 135.6, 135.4, 134.5, 130.4, 129.1, 127.9, 127.8, 67.2, 62.8, 24.6, 21.4, 13.6; HRMS (APCI) calcd for $C_{21}H_{22}ClNO_5SH$, m/z = 436.0985 [(M+H)$^+$], found m/z = 436.0980; Enantiomeric excess determined by HPLC (Chiralpak IA, hexane/2-propanol = 65/35, flow rate 1.0 mL/min, 25 °C, 240 nm) minor peak: t_R = 27.2 min, major peak: t_R = 24.9 min; $[\alpha]_D^{24}$ = +78.5 (*c* 0.61, $CHCl_3$); IR (KBr): ν 3341, 1728, 1683, 1464, 1379, 1159, 953 cm^{-1}.


5e

5e: pale yellow oil (89% yield, 97% ee); ^{1}H-NMR ($CDCl_3$) δ 7.74-7.72 (m, 2H), 7.50 (d, 2H, *J* = 6.4 Hz), 7.42-7.35 (m, 3H), 7.22 (d, 2H, 7.79 Hz), 6.48 (s, 1H), 6.41 (s, 1H), 6.35 (s, 1H), 4.29 (qd, 1H, *J* = 12.4, 8.2 Hz), 4.28 (qd, 1H, *J* = 12.4, 8.2 Hz), 2.40 (s, 3H), 1.74 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 197.1, 169.4, 143.6, 143.1, 138.4, 136.2, 135.8, 129.2, 128.8, 128.7, 128.1, 127.8, 125.2, 123.3, 121.5, 119.7, 67.4, 61.8 (q, *J* = 23.9 Hz), 24.3, 21.5; ^{19}F-NMR ($CDCl_3$): δ -73.6; HRMS (APCI) calcd for $C_{21}H_{20}F_3NO_5SNa$, m/z = 478.0911 [(M+Na)$^+$], found m/z = 478.0901; Enantiomeric excess determined by HPLC (Chiralpak AS-H, hexane/2-propanol = 1/1, flow rate 0.5 mL/min, 25 °C, 254 nm) minor peak: t_R = 11.7 min, major peak: t_R = 15.9 min; $[\alpha]_D^{21}$ = -8.1 (*c* 0.16, $CHCl_3$); IR (KBr): ν 3204, 1766, 1678, 1406, 1327, 1213, 1168 cm^{-1}.

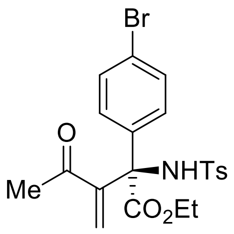

5f

5f: pale yellow oil (98% yield, 41% ee); ^{1}H-NMR ($CDCl_3$) δ 7.73-7.71 (m, 2H), 7.50 (d, 2H, *J* = 8.4 Hz), 7.35-7.33 (m, 3H), 7.27-7.26 (m, 3H), 7.20 (d, 2H, *J* = 8.8 Hz), 7.07-7.05 (m, 2H), 6.53 (s, 1H), 6.39 (s, 1H), 6.28 (s, 1H), 5.00 (d, 1H, *J* = 12.4 Hz), 4.96 (d, 1H, *J* = 11.9 Hz), 2.39 (s, 3H), 1.70 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 197.0, 170.4, 144.1, 142.9, 138.6, 136.6, 135.7, 134.6, 129.1, 128.9, 128.4, 128.3, 128.2, 127.8, 127.8, 68.3, 67.6, 24.5, 21.4; HRMS (APCI) calcd for $C_{26}H_{25}NO_5SH$, m/z = 464.1531 [$(M+H)^+$], found m/z = 464.1529; Enantiomeric excess determined by HPLC (Chiralpak AS-H, hexane/2-propanol = 65/35, flow rate 0.5 mL/min, 25 °C, 219 nm) minor peak: t_R = 28.9 min, major peak: t_R = 19.0 min; $[\alpha]_D^{21}$ = +3.1 (*c* 3.2, $CHCl_3$); IR (KBr): ν 3289, 1737, 1681, 1448, 1330, 1225, 1164 cm^{-1}.



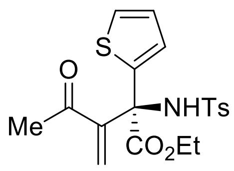
5g

5g: pale yellow oil (86% yield, 96% ee); ^{1}H-NMR ($CDCl_3$) δ 7.50 (d, 2H, *J* = 8.2 Hz), 7.28 (dd, 1H, *J* = 2.3, 1.8 Hz), 7.20 (d, 2H, *J* = 7.8 Hz), 7.15 (d, 1H, *J* = 1.8 Hz), 6.79 (d, 1H, *J* = 8.2 Hz), 6.45 (s, 1H), 6.41 (s, 1H), 6.33 (s, 1H), 5.97 (d, 1H, *J* = 1.8 Hz), 5.96 (d, 1H, *J* = 1.4 Hz), 4.07 (qd, 1H, *J* = 12.4, 7.3 Hz), 4.04 (qd, 1H, *J* = 12.4, 7.3 Hz), 2.39 (s, 3H), 1.74 (s, 3H), 1.10 (t, 3H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 196.8, 170.4, 147.6, 147.2, 144.2, 142.9, 138.5, 135.6, 130.5, 129.0, 127.8, 122.9, 109.4, 107.4, 101.4, 67.3, 62.6, 24.6, 21.4, 13.7; HRMS (ESI) calcd for $C_{22}H_{23}NO_7SNa$, m/z = 468.1092 [$(M+Na)^+$], found m/z = 468.1080; Enantiomeric excess determined by HPLC (Chiralcel OD-H, hexane/2-propanol = 10/1, flow rate 1.0 mL/min, 25 °C, 230 nm) minor peak: t_R = 32.2 min, major peak: t_R = 22.4 min; $[\alpha]_D^{21}$ = +47.6 (*c* 0.21, $CHCl_3$); IR (KBr): ν 3328, 1733, 1680, 1503, 1393, 1228, 1161 cm^{-1}.



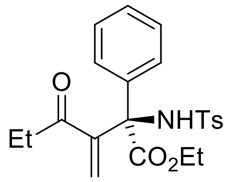
5h

5h: pale yellow oil (91% yield, 96% ee); ^{1}H-NMR ($CDCl_3$) δ 7.62 (d, 2H, *J* = 8.7 Hz), 7.50-7.47 (m, 4H), 7.20 (d, 2H, *J* = 8.2 Hz,), 6.48 (s, 1H), 6.40 (s, 1H), 6.22 (s, 1H), 4.06 (qd, 1H, *J* = 10.4, 7.3 Hz), 4.03 (qd, 1H, *J* = 10.4, 7.3 Hz), 2.39 (s, 3H), 1.73 (s, 3H), 1.09 (t, 3H, *J*= 7.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 196.7, 170.0, 143.9, 143.0, 138.3, 136.1, 135.4, 130.9, 130.7, 129.1, 127.8, 122.7, 67.3, 62.8, 24.5, 21.4, 13.6; HRMS (APCI) calcd for $C_{21}H_{22}BrNO_5SH$, m/z = 480.0480 [$(M+H)^+$], found m/z = 480.0476; Enantiomeric excess determined by HPLC (Chiralpak AS-H, hexane/2-propanol = 4/1, flow rate 1.0 mL/min, 25 °C, 230 nm) minor peak: t_R = 23.7 min, major peak: t_R = 11.1 min; $[\alpha]_D^{21}$ = +47.6 (*c* 0.60, $CHCl_3$); IR (KBr): ν 3277, 1735, 1597, 1334, 1164, 1092, 1010, 972 cm^{-1}.



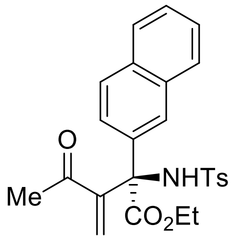
5i

5i: pale yellow oil (81% yield, 76% ee); ^{1}H-NMR ($CDCl_3$) δ 7.55 (d, 2H, *J* = 8.7 Hz), 7.31 (d, 1H, *J* = 1.4 Hz), 7.29 (d, 1H, *J* = 1.4 Hz), 7.22 (d, 2H, 8.7 Hz), 6.99 (m, 1H), 6.62 (s, 1H), 6.50 (s, 1H), 6.47 (s, 1H), 4.11 (qd, 1H, *J* = 7.3, 3.6 Hz), 4.09 (qd, 1H, *J* = 7.3, 3.6 Hz), 2.40 (s, 3H), 1.80 (s, 3H), 1.13 (t, 3H, 7.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 196.4, 169.7, 144.4, 143.1, 142.1, 138.3, 135.3, 129.1, 129.0, 128.0, 126.7, 126.6, 65.6, 62.9, 24.7, 21.4, 13.6; HRMS (APCI) calcd for $C_{19}H_{21}NO_5S_2Na$, m/z = 430.0758 [$(M+Na)^+$], found m/z = 430.0752; Enantiomeric excess determined by HPLC (Chiralpak AS, hexane/2-propanol = 4/1, flow rate 1.0 mL/min, 25 °C, 230 nm) minor peak: t_R = 18.0 min, major peak: t_R = 11.9 min; $[\alpha]_D^{21}$ = +90.5 (*c* 0.46, $CHCl_3$); IR (KBr): ν 3356, 3261, 1737, 1681, 1598, 1388, 1162, 1097, 1018 cm^{-1}.



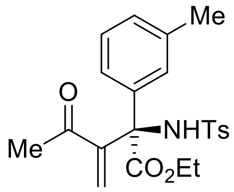
5j

5j: pale yellow oil (83% yield, 85% ee); ^{1}H-NMR ($CDCl_3$) δ 7.74 (dd, 2H, *J* = 8.2, 1.4 Hz), 7.49 (d, 2H, *J* = 8.2 Hz), 7.39-7.32 (m, 3H), 7.18 (d, 2H, 8.2 Hz), 6.52 (s, 1H), 6.42 (s, 1H), 6.23 (s, 1H), 4.08 (qd, 1H, *J* = 10.8, 7.3 Hz), 4.01 (qd, 1H, *J* = 10.8, 7.3 Hz), 2.42 (qd, 1H, *J* = 7.3 Hz), 2.37 (s, 3H), 1.79 (qd, 1H, *J* = 7.3 Hz), 1.07 (t, 3H, *J* = 7.3 Hz), 0.73 (t, 3H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 199.2, 170.5, 143.9, 142.7, 138.7, 137.0, 134.3, 129.0, 128.9, 128.2, 127.8, 127.7, 67.9, 62.5, 29.8, 21.3, 13.6, 7.3; HRMS (APCI) calcd for $C_{22}H_{25}NO_5SNa$, m/z = 438.1350 [$(M+Na)^+$], found m/z = 438.1342; Enantiomeric excess determined by HPLC (Chiralpak AS-H, hexane/2-propanol = 65/35, flow rate 0.5 mL/min, 25°C, 230 nm) minor peak: t_R = 23.0 min, major peak: t_R = 12.4 min; $[\alpha]_D^{22}$ = -23.3 (*c* 0.21, $CHCl_3$); IR (KBr): ν 3283, 1737, 1683, 1380, 1330, 1235, 1163, 1093, 1039 cm^{-1}.



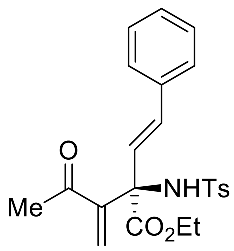
5k

5k: pale yellow oil (93% yield, 93% ee); ^{1}H-NMR ($CDCl_3$) δ 8.35 (d, 1H, *J* = 1.8 Hz), 7.93-7.90 (m, 1H), 7.83-7.81 (m, 1H), 7.78 (d, 1H, *J* = 9.2 Hz), 7.68 (d, 1H, *J* = 1.8 Hz), 7.54-7.48 (m, 4H), 7.21 (d, 2H, *J* = 7.8 Hz), 6.62 (s, 1H), 6.46 (s, 1H), 6.29 (s, 1H), 4.07 (qd, 1H, *J* = 10.8, 7.3 Hz), 4.04 (qd, 1H, *J* = 10.8, 7.3 Hz), 2.39 (s, 3H), 1.78 (s, 3H), 1.09 (t, 3H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 196.8, 170.4, 144.3, 142.9, 138.6, 135.7, 134.2, 132.9, 132.7, 129.1, 128.9, 128.7, 127.9, 127.2, 127.1, 126.7, 126.2, 126.1, 67.8, 62.7, 24.6, 21.4, 13.7; HRMS (APCI) calcd for $C_{25}H_{25}NO_5SH$, m/z = 452.1531 [$(M+H)^+$], found m/z = 452.1520; Enantiomeric excess determined by HPLC (Chiralpak AS-H, hexane/2-propanol = 65/35, flow rate 0.5 mL/min, 25 °C, 230 nm) minor peak: t_R = 45.3 min, major peak: t_R = 17.3 min; $[\alpha]_D^{23}$ = +32.9 (*c* 0.17, $CHCl_3$); IR (KBr): ν 3370, 1736, 1681, 1380, 1267, 1161, 1129 cm^{-1}.



5l

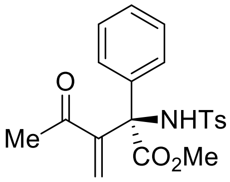
5l: pale yellow oil (70% yield, 64% ee); ^{1}H-NMR ($CDCl_3$) δ 7.56-7.50 (m, 4H), 7.27-7.11 (m, 4H), 6.48 (s, 1H), 6.41 (s, 1H), 6.29 (s, 1H) 4.06 (q, 1H, *J* = 7.3 Hz), 4.04 (q, 1H, *J* = 7.3 Hz), 2.39 (s, 3H), 2.37 (s, 3H), 1.75 (s, 3H), 1.08 (t, 3H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 196.9, 170.6, 144.3, 142.8, 138.7, 137.3, 136.8, 135.5, 129.4, 129.0, 127.8, 127.5, 126.0, 67.6, 62.5, 24.6, 21.6, 21.4, 13.6; HRMS (ESI) calcd for $C_{22}H_{25}NO_5SNa$, m/z = 438.1351 [$(M+Na)^+$], found m/z = 438.1351; Enantiomeric excess determined by HPLC (Chiralpak AS-H, hexane/2-propanol = 65/35, flow rate 0.5 mL/min, 25 °C, 230 nm) minor peak: t_R = 24.5 min, major peak: t_R = 13.3 min; $[\alpha]_D^{24}$ = +12.2 (*c* 0.34, $CHCl_3$); IR (KBr): ν 3257, 1749, 1676, 1330, 1045 cm^{-1}.



5m

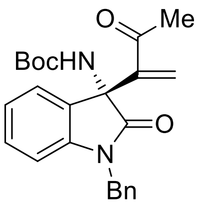
5m: pale yellow oil (67% yield, 72% ee); ^{1}H-NMR ($CDCl_3$) δ 7.57 (d, 2H, *J* = 8.2 Hz), 7.37-7.27 (m, 5H), 7.19 (d, 2H, *J* = 7.8 Hz), 6.92 (d, 1H, *J* = 16 Hz), 6.39 (s, 1H), 6.34 (s, 1H), 6.33 (d, 1H, *J* = 16 Hz), 6.27 (s, 1H), 4.18 (qd, 1H, *J* = 7.3, 5.6 Hz), 4.16 (qd, 1H, *J* = 7.3, 5.6 Hz), 2.37 (s, 3H), 1.83 (s, 3H), 1.18 (t, 3H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 196.8, 169.7, 144.8, 143.0, 138.7, 135.8, 134.3, 132.8, 129.2, 128.6, 128.3, 127.9, 126.9, 125.6, 116.1, 65.2, 62.7, 24.8, 21.4, 13.9; HRMS (APCI) calcd for

$C_{23}H_{25}NO_5SH$, m/z = 428.1531 [(M+H)$^+$], found m/z = 428.1525; Enantiomeric excess determined by HPLC (Chiralpak AS-H, hexane/2-propanol = 65/35, flow rate 0.5 mL/min, 25 °C, 254 nm) minor peak: t_R = 40.6 min, major peak: t_R = 17.4 min; $[\alpha]_D^{23}$ = +7.2 (*c* 0.07, $CHCl_3$); IR (KBr): ν 3284, 1735, 1681, 1384, 1234, 1164 cm^{-1}.



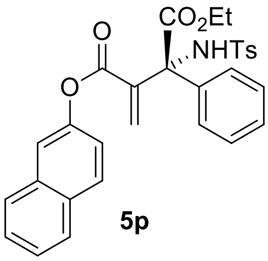
5n

5n: pale yellow oil (90% yield, 93% ee); ^{1}H-NMR ($CDCl_3$) δ 7.73 (d, 2H, *J* = 6.9 Hz), 7.50 (d, 2H, *J* = 8.2 Hz), 7.38-7.33 (m, 3H), 7.21 (d, 2H, *J* = 8.2 Hz), 6.51 (s, 1H), 6.42 (s, 1H), 6.28 (s, 1H), 3.59 (s, 3H), 2.39 (s, 3H), 1.00 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 197.0, 171.0, 144.2, 142.9, 138.6, 136.8, 135.6, 129.1, 128.8, 128.3, 127.8, 127.7, 67.5, 53.4, 24.6, 21.4; HRMS (APCI) calcd for $C_{20}H_{21}NO_5SH$, m/z = 388.1218 [(M+H)$^+$], found m/z = 388.1209; Enantiomeric excess determined by HPLC (Chiralpak AS-H, hexane/2-propanol = 65/35, flow rate 0.5 mL/min, 25 °C, 230 nm) minor peak: t_R = 20.2 min, major peak: t_R = 27.2 min; $[\alpha]_D^{21}$ = +1.24 (*c* 0.33, $CHCl_3$); IR (KBr): ν 3363, 1730, 1682, 1492, 1159, 1093 cm^{-1}.



5o

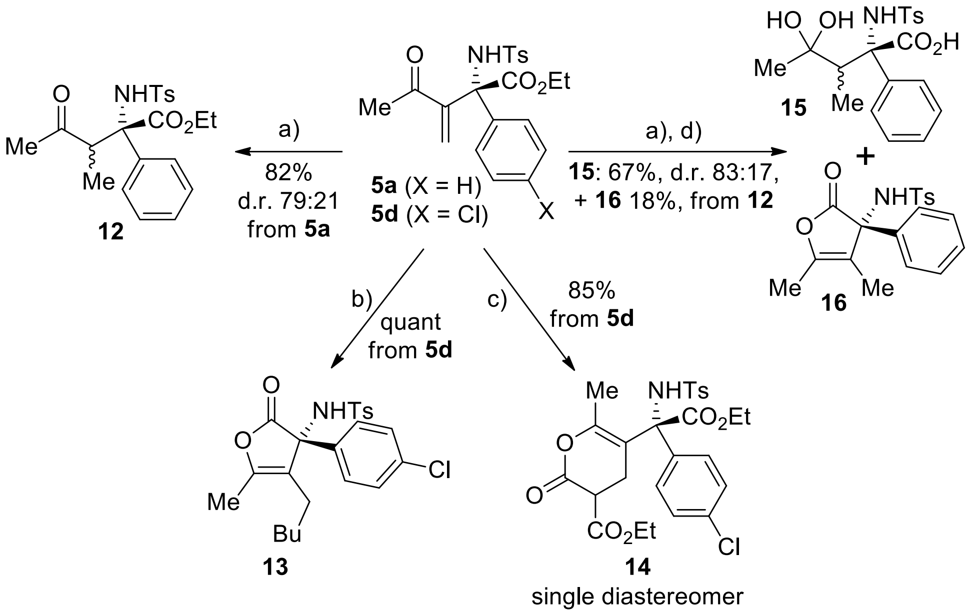
5o: pale yellow oil (quant, 90% ee); ^{1}H-NMR ($CDCl_3$) δ 7.43-7.39 (m, 3H), 7.33 (t, 2H, *J* = 7.3 Hz), 7.28-7.27 (m, 1H), 7.16 (dt, 1H, *J* = 7.3, 1.4 Hz), 6.98 (dt, 1H, *J* = 7.8, 0.9 Hz), 6.69 (d, 1H, *J* = 7.8 Hz), 6.20 (d, 1H, *J* = 0.9 Hz), 6.10 (d, 2H, *J* = 0.9 Hz), 5.12 (d, 1H, *J* = 16.0 Hz), 4.87 (d, 1H, *J* = 16.0 Hz), 2.34 (s, 3H), 1.34 (s, 9H); Enantiomeric excess determined by HPLC (Chiralcel OD-3, hexane/2-propanol = 9/1, flow rate 0.5 mL/min, 25 °C, 250 nm) minor peak: t_R = 12.8 min, major peak: t_R = 10.4 min; $[\alpha]_D^{23}$ = -84.6 (*c* 3.5, CH_2Cl_2) [lit.,[8] $[\alpha]_D^{20}$ = -90.9 (c 1.85, CH_2Cl_2) for 93% ee].



5p

5p: white solid (75% yield, 53% ee); Mp 187-189 °C; ^{1}H-NMR ($CDCl_3$) δ 7.86-7.82 (m, 3H), 7.79-7.74 (m, 2H), 7.65 (d, 2H, *J* = 8.2 Hz), 7.51 (td, 1H, *J*= 7.3, 1.8 Hz), 7.47 (td, 1H, *J*= 7.3, 1.8 Hz) 7.44-7.37 (m, 3H), 7.21-7.19 (m, 3H), 7.0 (s, 1H), 6.83 (dd, 1H, *J*= 8.7, 2.3 Hz), 6.58 (s, 1H), 6.34 (s, 1H), 4.14 (qd, 1H, *J*= 10.4, 7.3 Hz), 4.08 (qd, 1H, *J*= 10.4, 7.3 Hz), 2.29 (s, 3H), 1.12 (t, 3H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 170.1, 163.5, 147.7, 143.0, 139.1, 136.8, 136.6, 136.3, 133.4, 131.3, 129.3, 129.1, 128.8, 128.5, 127.9, 127.8, 127.6, 127.5, 126.7, 125.9, 120.3, 117.9, 68.6, 63.1, 21.5, 13.7; HRMS (ESI) calcd for $C_{30}H_{27}NO_6SNa$, m/z = 552.1457 [(M+Na)$^+$], found m/z = 552.1443; IR (KBr): 3370, 3297, 3060, 2928, 1737, 1241, 1164 cm^{-1}; Enantiomeric excess determined by HPLC (Chiralcel OD-H, hexane/2-propanol = 9/1, flow rate 0.5 mL/min, 25 °C, 250 nm) minor peak: t_R = 15.0 min, major peak: t_R = 25.7 min; $[\alpha]_D^{23}$ = + 67.3 (*c* 1.6, $CHCl_3$).

Transformations of α,α-disubstituted amino acid derivatives (*R*)-5



Conditions: a) 10% Pd/C, MeOH, H_2 (1 atm), RT, 2 h; b) BuLi (2.2 equiv.), CuI (2.2 equiv.), THF, −78°C, overnight; c) diethyl malonate (1.2 equiv.), K_2CO_3 (2.5 equiv.), DMSO, RT, 2.5 h; d) LiOH (1.5 equiv) in H_2O/THF (1:1), RT, 10 h; d.r. = diastereomeric ratio determined by ^{1}H-NMR or HPLC.

Preparation of 12

To a solution of compound **5a** (96% ee, 60 mg) in methanol (3 mL) was added 7.5 mg of 10% Pd/C and the mixture was stirred at room temperature under hydrogen atmosphere (H_2 balloon). After completion of the reaction, as indicated by TLC (2 h), the mixture was filtered through celite and solvent was evaporated. The mixture of diastereomers was separated through silica column using 9:1 hexane/EtOAc mixture. Ratio of **12a**:**12b** = 79:21 (determined by crude ^{1}H-NMR). Isolated yield of diastereomer **12a**: 67% and **12b**: 15% (total yield: 82%). **12a**: colorless solid; IR (neat): 3238, 3067, 2931, 1737, 1600, 1497, 1362, 1246, 1163, 1093 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ7.17 (d, *J* = 8.3 Hz, 2H), 7.02-7.18 (m, 5H), 6.95 (d, *J* = 8.3 Hz, 2H), 6.44 (s, 1H), 4.41 (q, *J* = 7.3 Hz, 1H), 4.27-4.33 (m, 1H), 4.12-4.18 (m, 1H), 2.33 (s, 3H), 2.30 (s, 3H), 1.34 (d, *J* = 7.3 Hz, 3H), 1.16 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR ($CDCl_3$) δ 211.0, 171.7, 142.1, 139.2, 134.4, 128.9, 128.3, 128.1, 128.0, 126.3, 68.7, 62.7, 52.1, 31.1, 21.4, 14.7, 13.8, HRMS (ESI) calcd for $C_{21}H_{25}NO_5S$, m/z = 426.1351 [(M+Na)$^+$], found m/z = 426.1350; Enantiomeric excess: 96%, determined by HPLC (Chiralpak AD-H, hexane/2-propanol = 10/1, flow rate 1.0 mL/min, 25 °C, 230 nm) major peak: t_R = 33.4 min, minor peak: t_R = 71.0 min; $[\alpha]_D^{22}$ = –17.5 (*c* 1.5, $CHCl_3$). **12b**: colorless solid; Mp. 94-95 °C; IR (neat): 3289, 3062, 2981, 2932, 1724, 1598, 1497, 1338, 1245, 1160, 1093 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ7.59 (d, *J* = 8.2 Hz, 2H), 7.21-7.30 (m, 7H), 6.95 (s, 1H), 3.92-3.96 (m, 1H), 3.66-3.71 (m, 1H), 3.41 (q, *J* = 7.3 Hz, 1H), 2.40 (s, 3H), 2.25 (s, 3H), 1.19 (d, *J* = 7.3 Hz, 3H), 1.07 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR ($CDCl_3$) δ 213.3, 171.6, 142.7, 140.0, 135.8, 129.3, 128.3, 127.9, 127.6, 126.6, 71.4, 62.3, 52.4, 30.0, 21.6, 13.7, 12.8; HRMS (ESI) calcd for $C_{21}H_{25}NO_5S$, m/z = 426.1351 [(M+Na)$^+$], found m/z = 426.1351; Enantiomeric excess: 96%, determined by HPLC (Chiralpak AD-H, hexane/2-propanol = 10/1, flow rate 1.0 mL/min, 25 °C, 230 nm) major peak: t_R = 35.4 min, minor peak: t_R = 38.5 min; $[\alpha]_D^{23}$ = –59.3 (*c* 0.6, $CHCl_3$).

Hydrolysis of compound 12a

To a solution of compound **12a** (96% ee, 50 mg, 0.124 mmol) in 2 mL of 1:1 THF/H_2O mixture was added LiOH.H_2O (1.5 equiv, 7.8 mg, 0.186 mmol) and stirred at room temperature for 10 h. After completion of the reaction (TLC) the mixture was diluted with CH_2Cl_2, acidified with 1N HCl, extracted with CH_2Cl_2, dried (Na_2SO_4) and evaporated. Products **15** and **16** were separated through silica column using hexane/EtOAc mixture (9:1 to 1:1 ratio). Isolated yield of diastereomer **15**: 67%, d.r. 83:17 and **16**: 18% (total yield: 85%). **15** (major): colorless solid; Mp. 201-203 °C; IR (neat): 3434, 3207, 3065, 2935, 2546, 2360, 1769, 1597, 1450, 1287, 1150, 1056 cm^{-1}; ^{1}H-NMR (methanol-d_4) δ 0.49 (d, *J* = 6.8 Hz, 3H), 1.50 (s, 3H), 2.44 (s, 3H), 3.19 (q, *J* = 6.8 Hz, 1H), 7.21-7.41 (m, 9H, Ar-H, NH, OH), 7.83 (d, *J* = 7.8 Hz, 2H); ^{13}C-NMR (methanol-d_4) δ 10.2, 21.5, 26.7, 46.5, 71.8, 107.8, 128.1, 128.6, 129.3, 129.5, 130.7, 137.4, 141.2, 145.0, 178.5. HRMS (ESI) calcd for $C_{19}H_{21}NNaO_5S$, m/z = 398.1038 [(M+Na-H_2O)$^+$], found m/z = 398.1034; $[\alpha]_D^{21}$ = +27.4 (*c* 0.6, MeOH). **16**: colorless solid; Mp. 184-185 °C; IR (neat): 3237, 3066, 2927, 2378, 1803, 1719, 1595, 1494, 1333, 1207, 1153, 1049 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.41 (br q, *J* = 1.0 Hz, 3H), 1.99 (br q, *J* = 1.0 Hz, 3H), 2.45 (s, 3H), 5.21 (s, 1H), 7.31-7.37 (m, 7H), 7.78 (d, *J* = 8.2 Hz, 2H); ^{13}C-NMR ($CDCl_3$) δ 8.3, 11.7, 21.8, 69.1, 112.6, 125.8, 128.0, 129.3, 129.4, 129.7, 136.3, 137.1, 144.4, 148.5, 175.5; HRMS (ESI) calcd for $C_{19}H_{19}NO_4S$, m/z = 380.0932 [(M+Na)$^+$], found m/z = 380.0927; Enantiomeric excess: 96%, determined by HPLC (Chiralpak AD, hexane/2-propanol = 4/1, flow rate 1.0 mL/min, 25 °C, 230 nm) major peak: t_R = 18.7 min, minor peak: t_R = 12.0 min; $[\alpha]_D^{22}$ = +13.0 (*c* 0.6, $CHCl_3$).

Preparation of 13

To a solution of CuI (28.8 mg, 0.15 mmol, 2.2 equiv) in THF (20 mL) were added BuLi (2.69 M solution in hexane, 60 μl, 0.15 mmol, 2.2 equiv) at –50 °C. The resulting mixture was stirred for 0.5 h at the same temperature, and compound **5d** (88% ee, 30.0 mg, 0.069 mmol, 1.0 equiv) in THF (5 mL) were added to the reaction mixture. The resulting mixture was stirred for overnight at –50 °C. The reaction was quenched with saturated NH_4Cl aq., extracted with ethyl acetate, dried over Na_2SO_4 and the resulting organic phase was evaporated. The residue was purified by column chromatography (SiO_2, hexane:EtOAc = 4:1) to afford the compound **13** (31.5 mg, 0.070 mmol, quantitative yield). IR (KBr) ν (cm^{-1}) 3439, 3315, 2930, 2862, 1797, 1408, 1331, 1162, 1084, 973, 758; ^{1}H-NMR ($CDCl_3$): δ 7.75 (d, 2H, *J* = 8.2 Hz), 7.34-7.31 (m, 4H), 7.25 (d, 2H, *J* = 8.2 Hz), 5.30 (s, 1H), 2.45 (s, 3H), 2.00 (s, 3H), 1.82 (t, 2H, *J* = 8.9 Hz), 1.13-0.93 (m, 6H), 0.74 (t, 3H, *J* = 6.9 Hz); ^{13}C-NMR ($CDCl_3$): δ 175.4, 149.2, 144.4, 136.7, 135.3, 135.2, 129.5, 129.3, 127.9, 127.0, 117.1, 68.9, 31.7, 28.5, 23.6, 22.0, 21.7, 13.8, 12.2; HRMS (ESI) calcd for $C_{23}H_{26}ClNNaO_4S$, m/z = 470.1166 [(M+Na)$^+$]; found m/z = 470.1163; Enantiomeric excess: 88%, determined by HPLC (Chiralpak AS-H, hexane/2-propanol = 65/35, flow rate 0.5 mL/min, 25 °C, 227 nm) major peak: t_R = 13.8 min, minor peak: t_R = 76.7 min; $[\alpha]_D^{21}$ = +14.4 (*c* 0.8, $CHCl_3$).

Preparation of 14

To a solution of **5d** (88% ee, 20.0 mg, 0.046 mmol, 88% ee, 1.0 equiv), K_2CO_3 (16.6 mg, 0.12 mmol, 2.5 equiv) in DMSO (2 mL) were added diethylmalonate (8.8 mg, 0.055 mmol, 1.2 equiv). The reaction mixture was stirred for 0.5 h at room temperature. Then reaction temperature was increased to 50 °C. The mixture was stirred for 2.5

h. The reaction was quenched with saturated NH_4Cl aq., extracted with ethyl acetate, washed with brine, dried over Na_2SO_4 and the obtaining organic phase was evaporated. The resulting residue was purified by column chromatography (SiO_2, hexane:EtOAc = 7:3) to afford the compound **14** (21.4 mg, 0.039 mmol, 85% yield). IR (KBr): ν 3247, 2983, 1809, 1735, 1486, 1335, 1251, 1159, 1085, 1066, 1023, 875, 821 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 7.81 (d, 2H, *J* = 8.2 Hz), 7.33 (d, 2H, *J* = 8.2 Hz), 7.31 (d, 2H, *J* = 8.2 Hz), 7.24 (d, 2H, *J* = 8.2 H), 5.82 (s, 1H), 4.07 (q, 2H, *J* = 7.6 Hz), 3.99 (qd, 1H, *J* = 10.3, 7.6 Hz), 3.84 (qd, 1H, *J* = 10.3, 7.6 Hz), 2.97 (t, 1H, *J* = 6.9 Hz), 2.71 (dd, 1H, *J* = 15.8, 6.9 Hz), 2.62 (dd, 1H, *J* = 15.8, 6.9 Hz), 2.44 (s, 3H), 2.11 (s, 3H), 1.19 (t, 3H, *J* = 7.6 Hz), 1.14 (t, 3H, *J* = 6.9 Hz); ^{13}C-NMR ($CDCl_3$): δ 173.9, 168.9, 168.8, 152.1, 144.2, 137.3, 135.3, 134.9, 129.6, 129.5, 127.6, 126.9, 113.5, 68.5, 61.81, 61.76, 50.5, 22.8, 21.6, 13.9, 13.8, 12.0; HRMS (ESI) calcd for $C_{26}H_{28}ClNNaO_8S$, m/z = 572.1116 [$(M+Na)^+$], found m/z = 572.1116; Enantiomeric excess: 88%, determined by HPLC (Chiralpak AS-H, hexane/2-propanol = 65/35, flow rate 0.5 mL/min, 25 °C, 200 nm) minor peak: t_R = 15.5 min, major peak: t_R = 81.3 min; $[\alpha]_D^{20}$ = +157.9 (*c* 0.15, $CHCl_3$).

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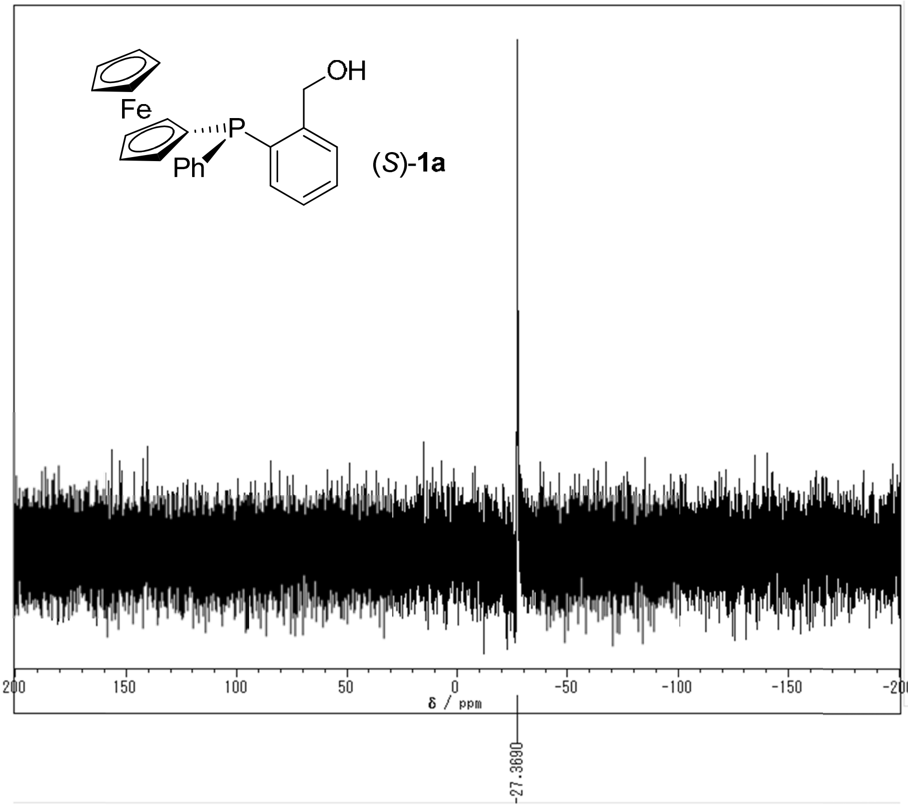
NMR

^{31}P-NMR (toluene)



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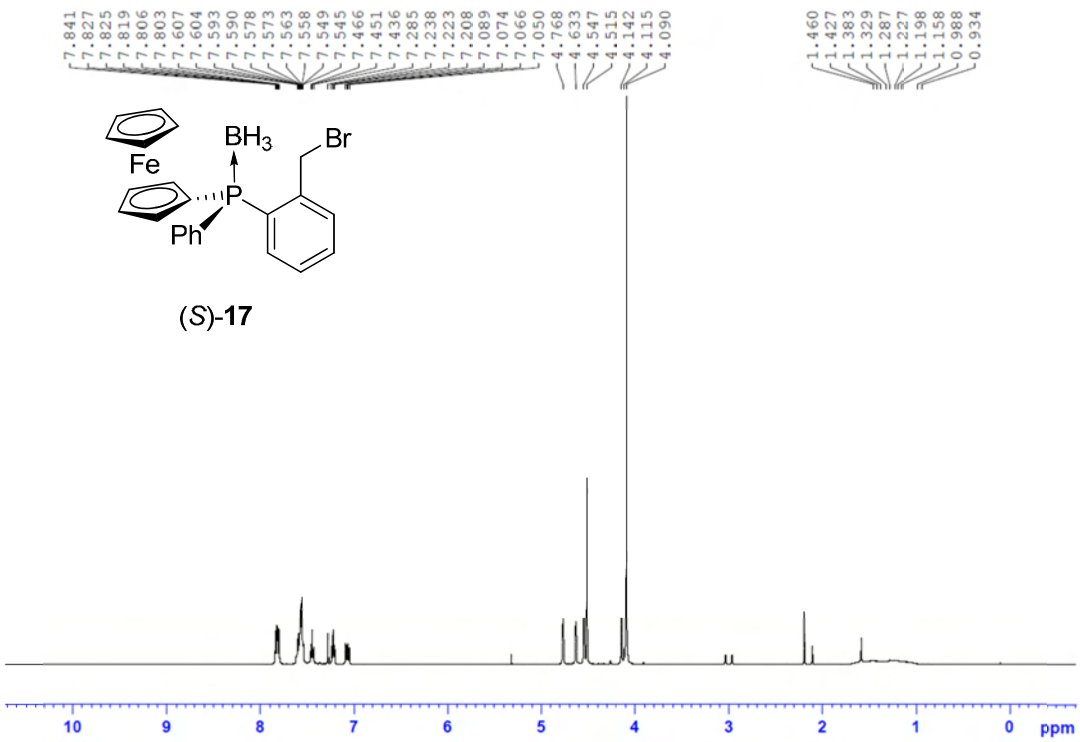

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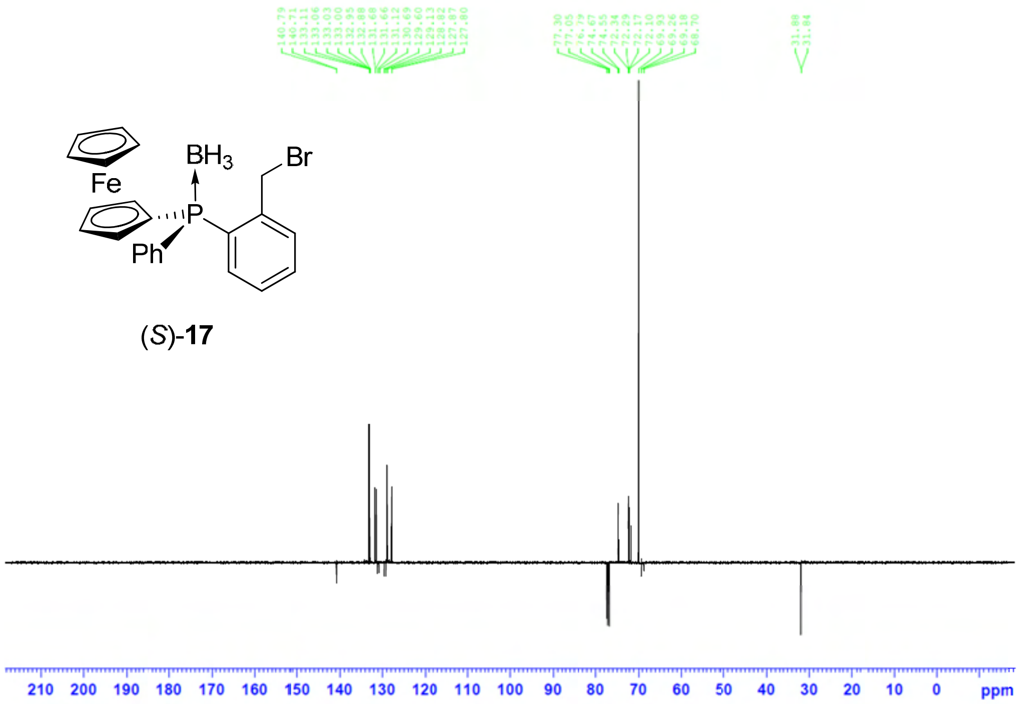

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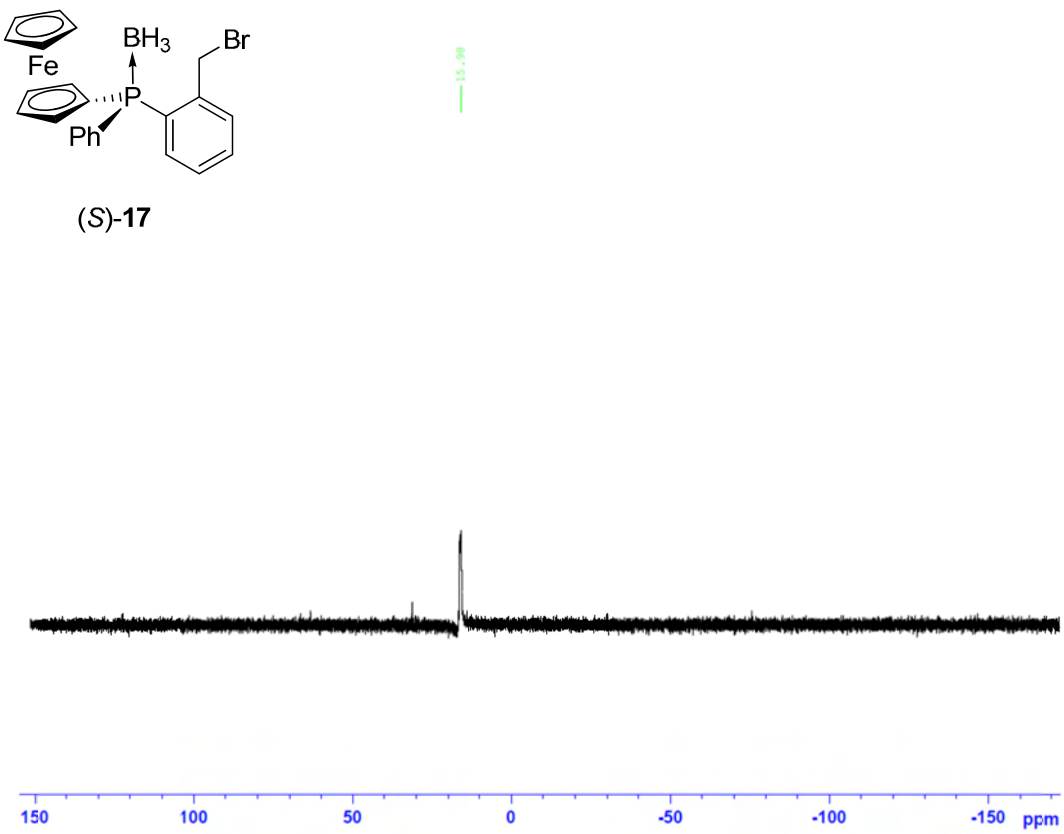

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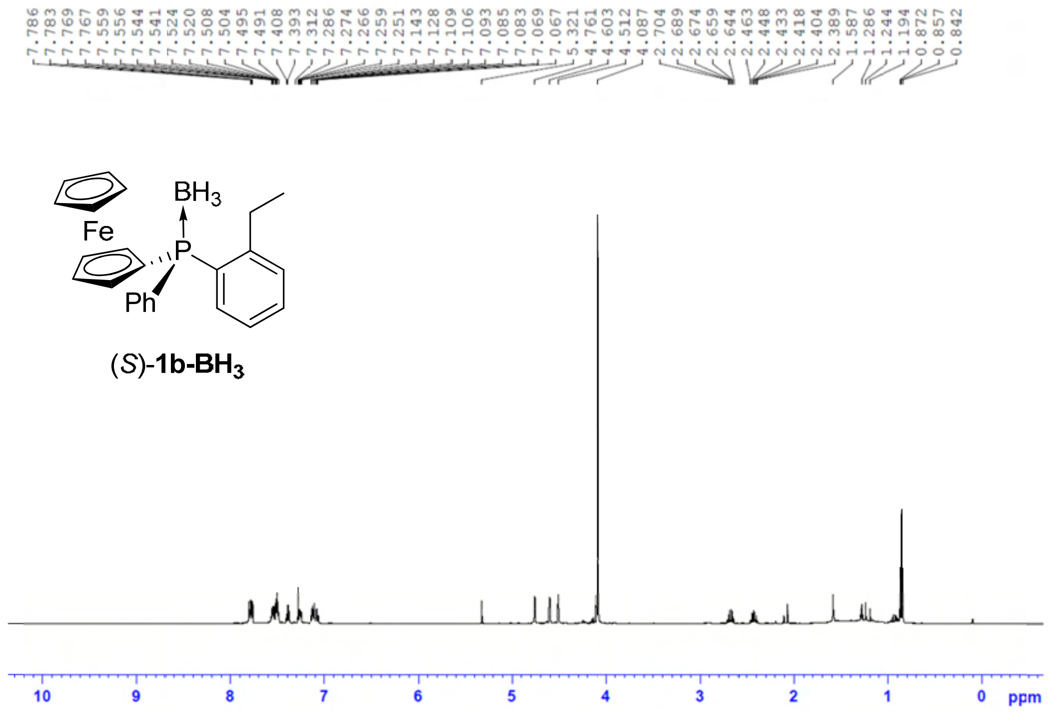

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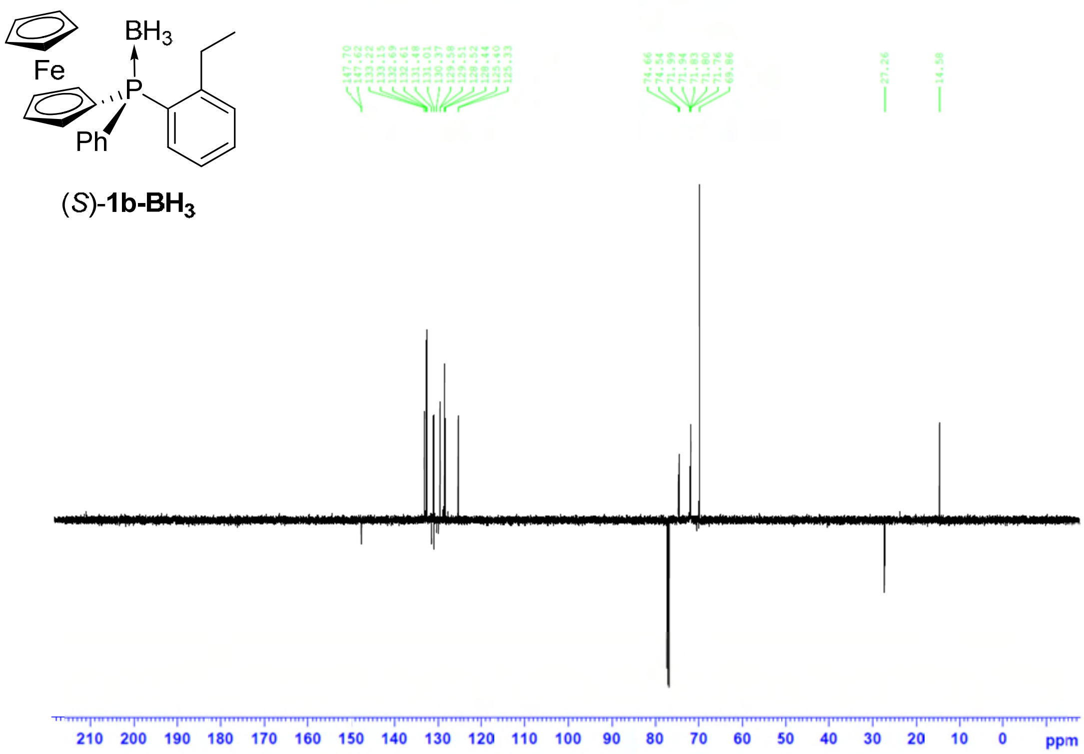

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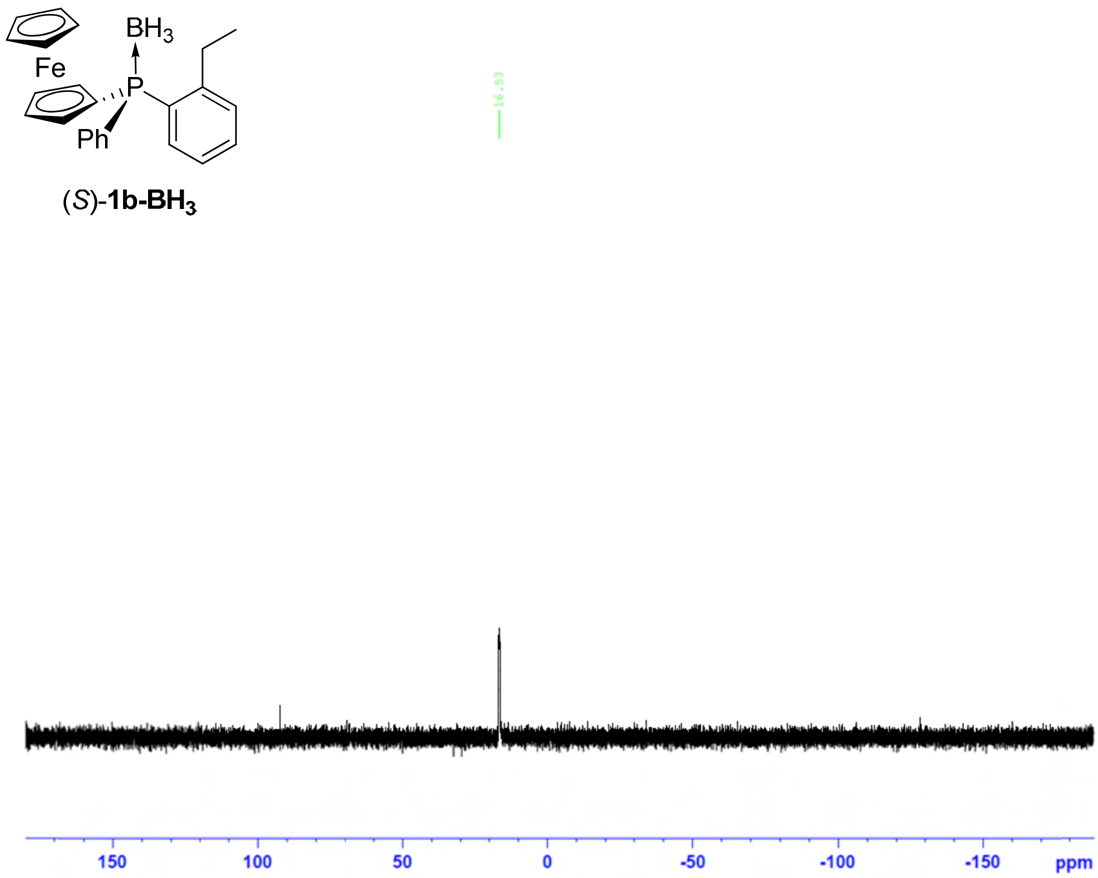

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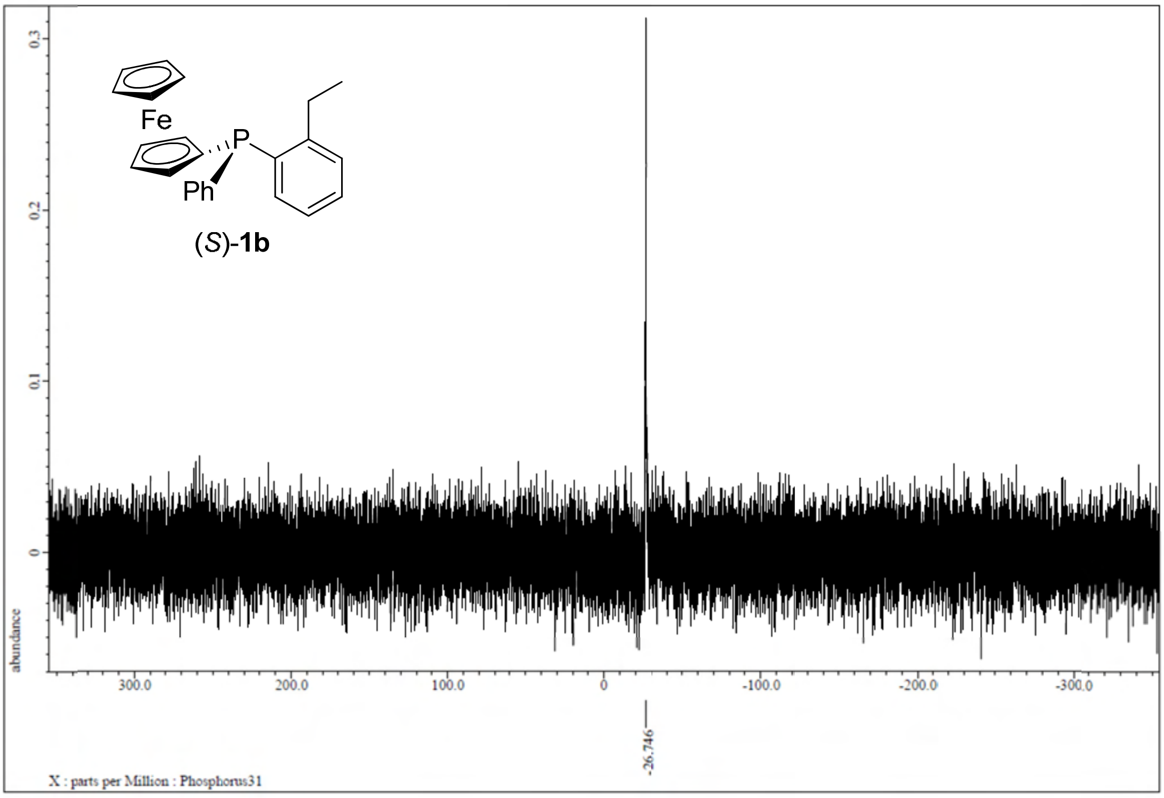

Electronic Supplementary Material (ESI) for Chemical Communications

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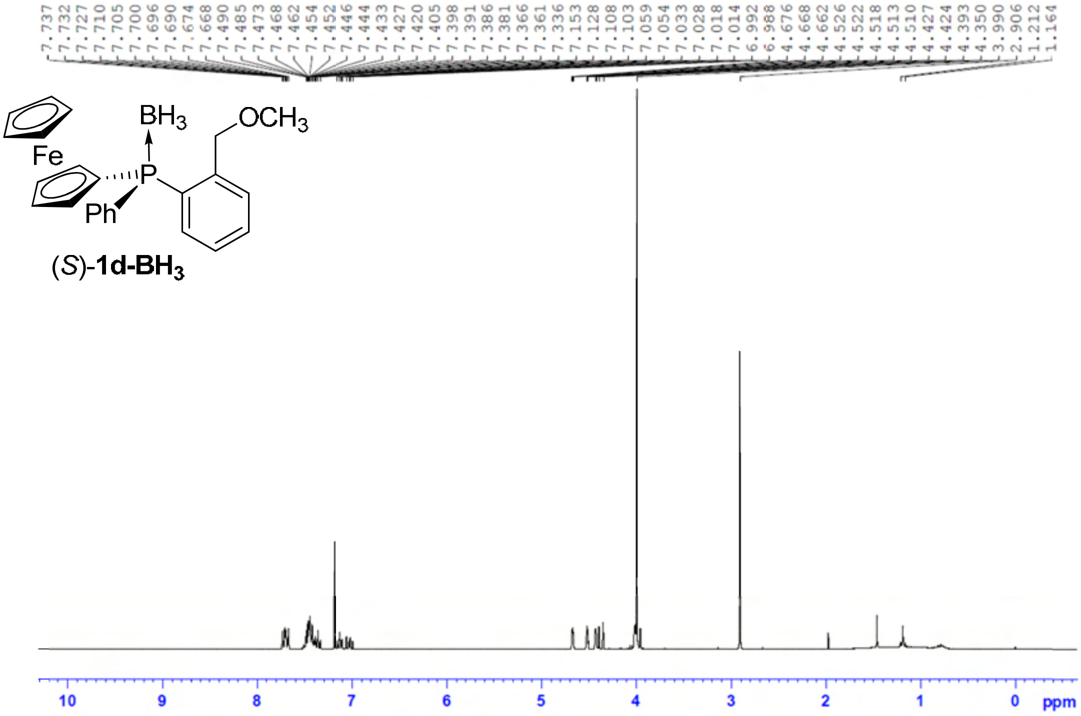

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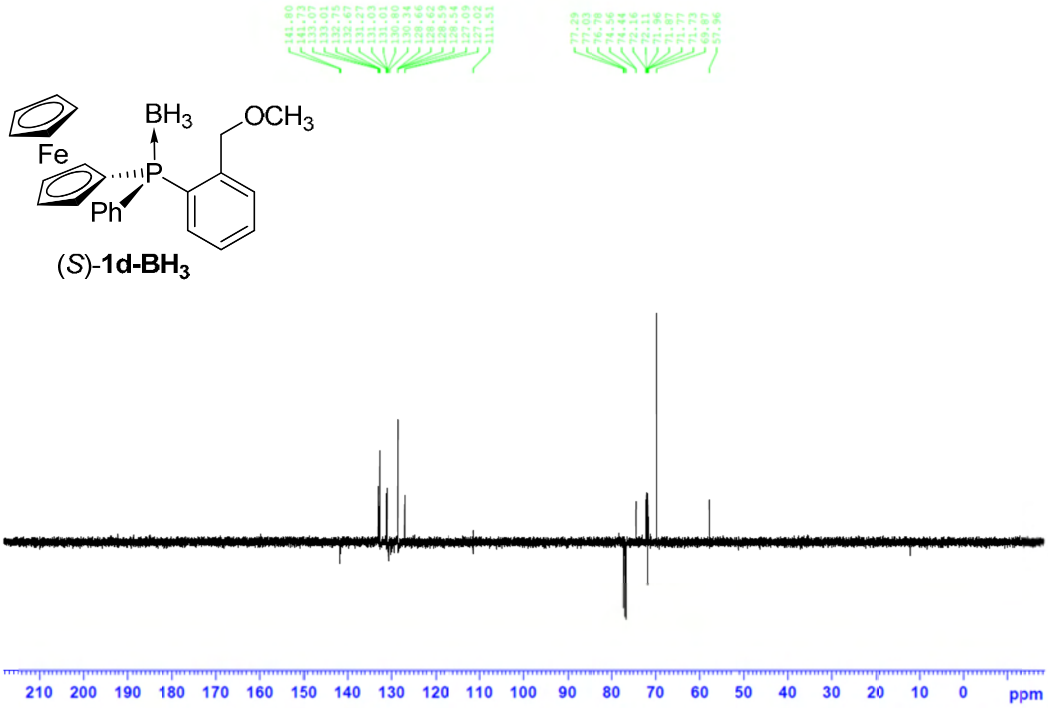

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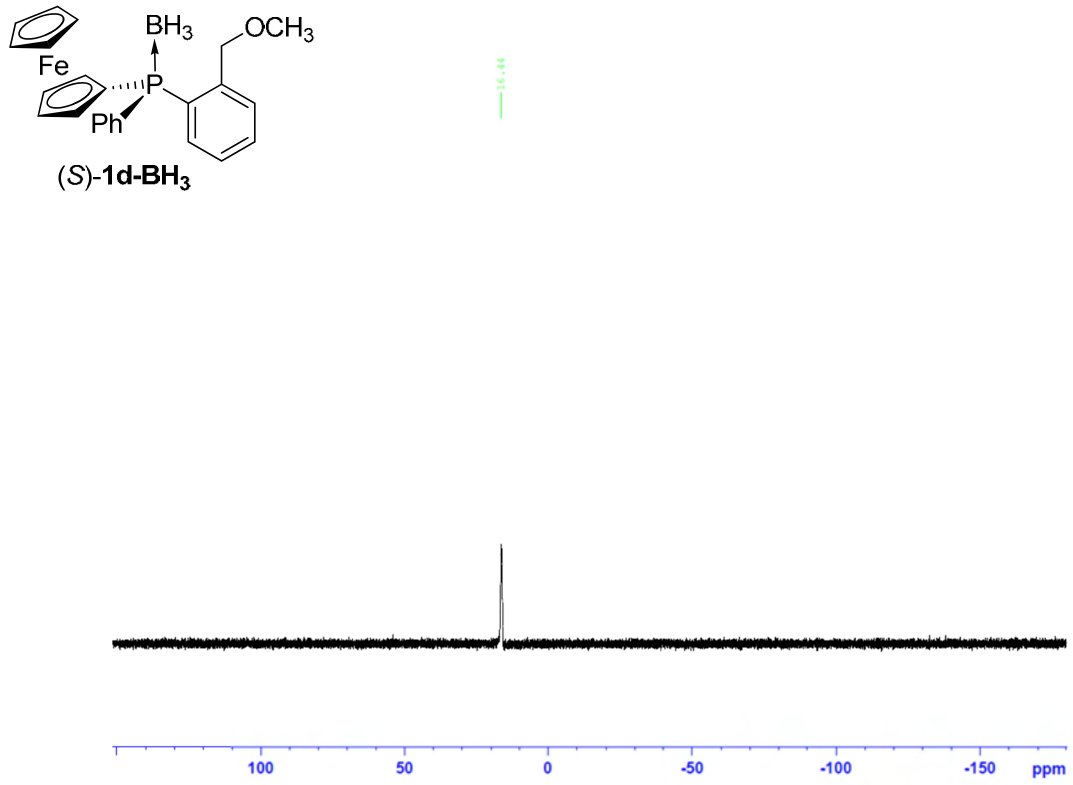

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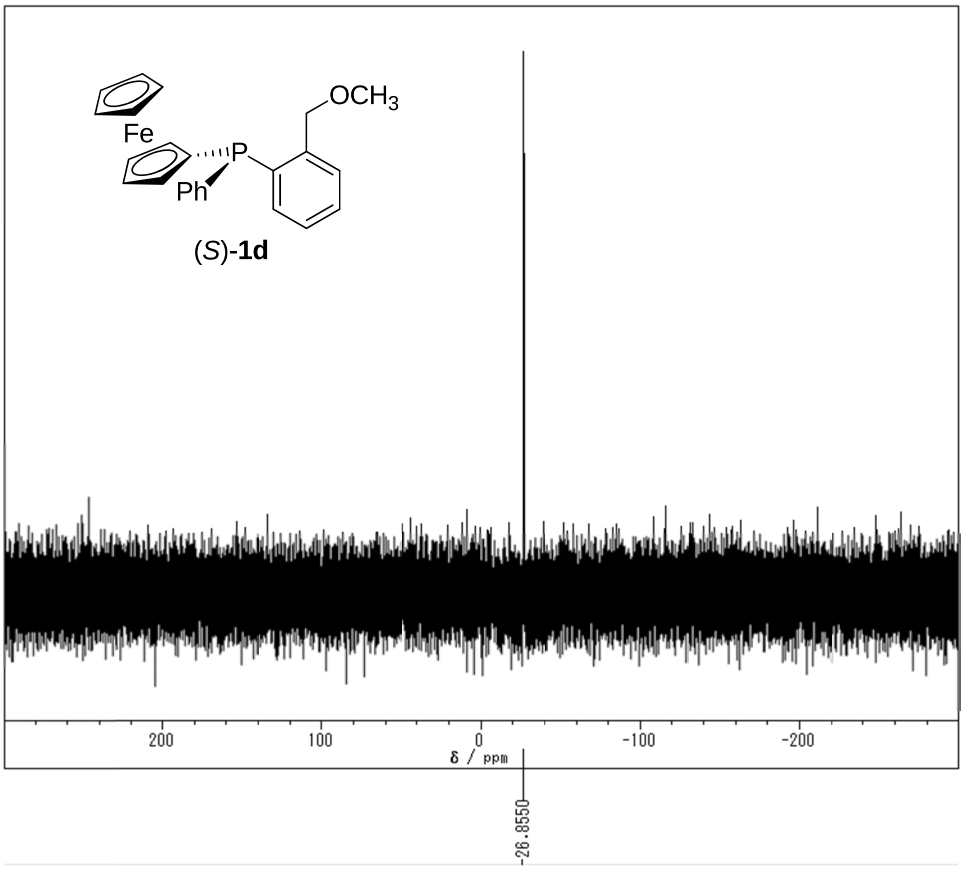

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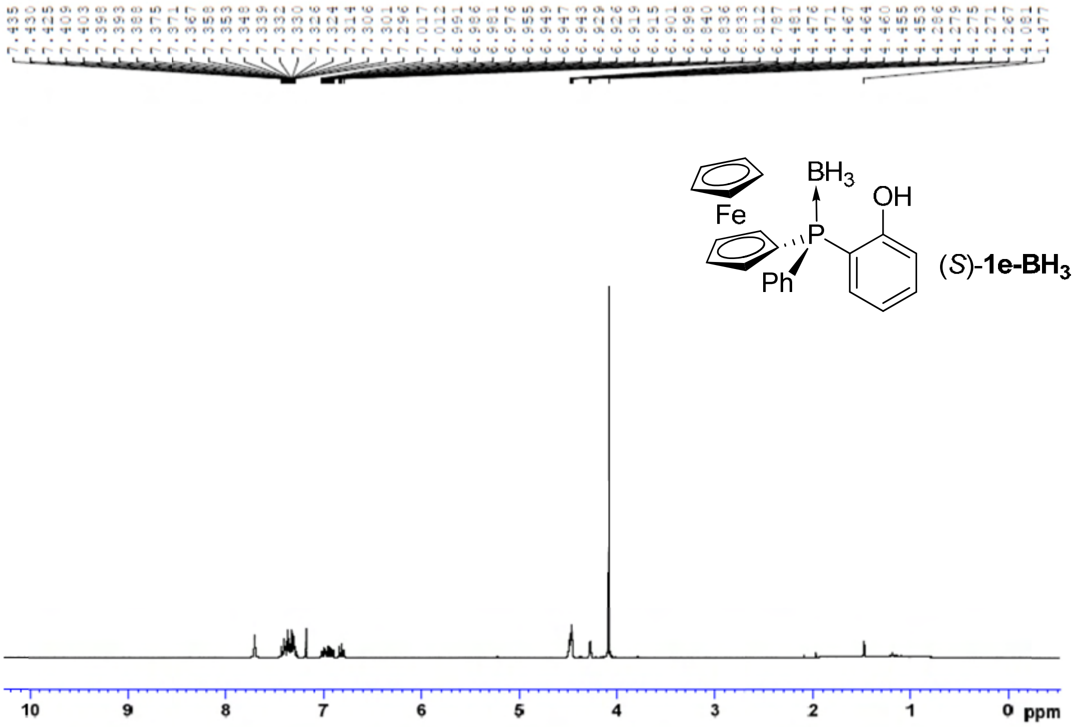

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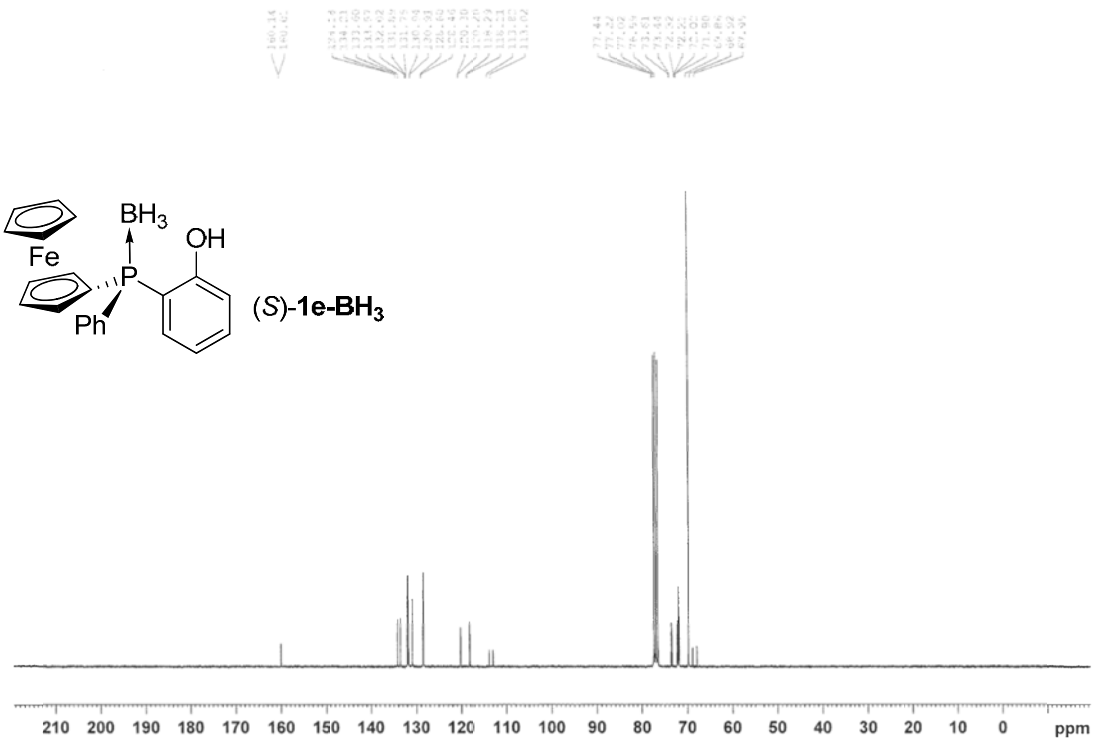

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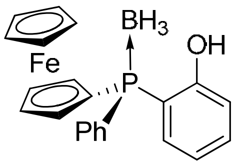

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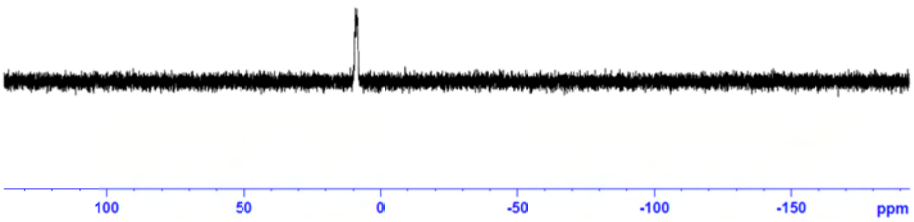

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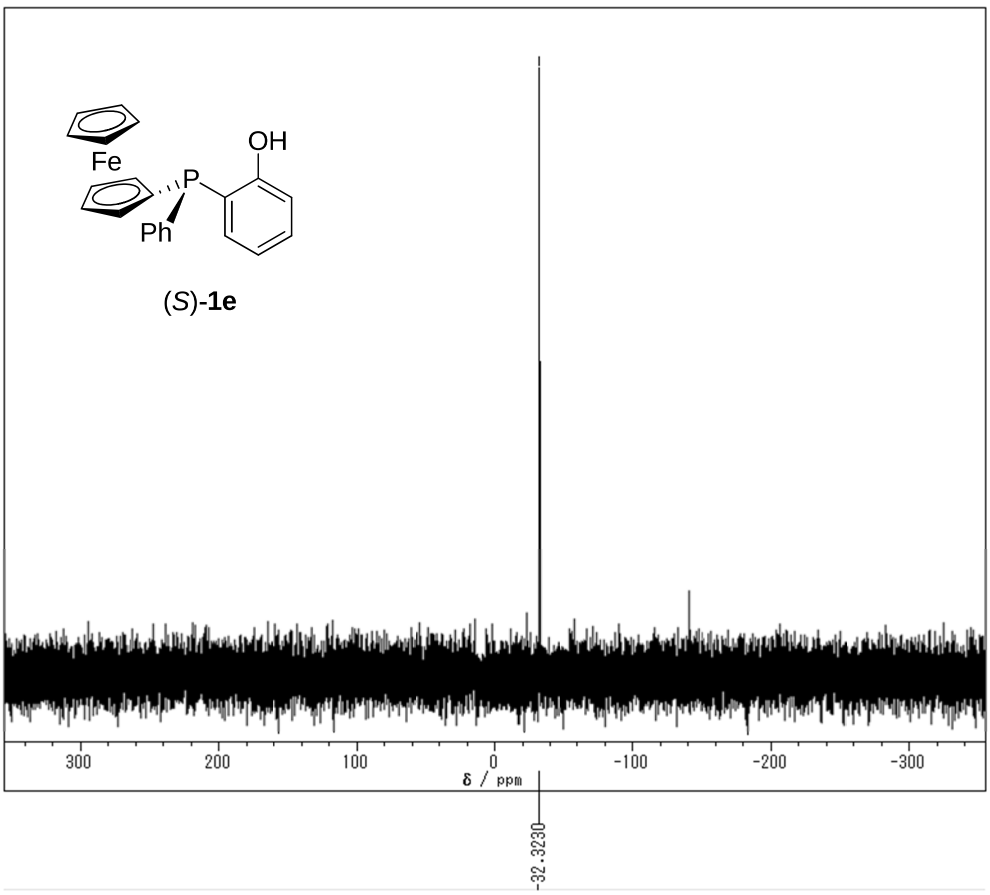

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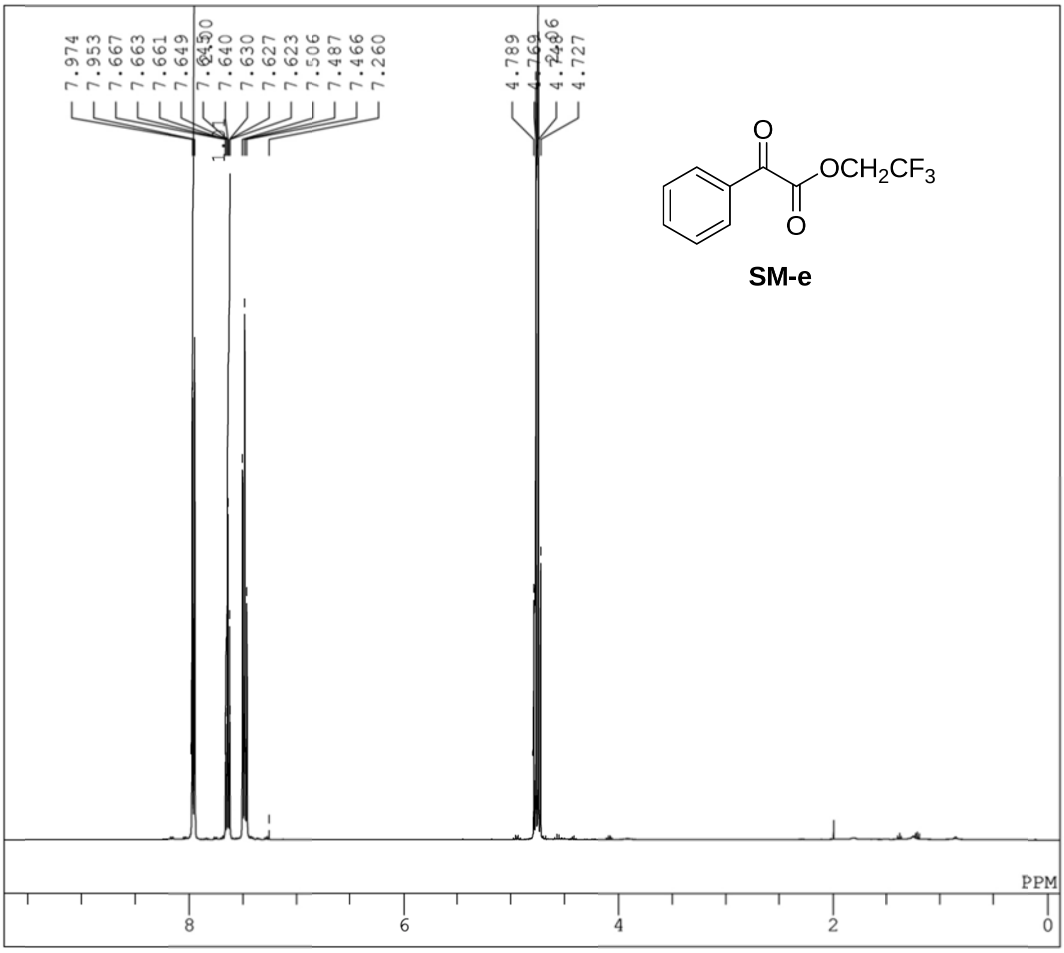

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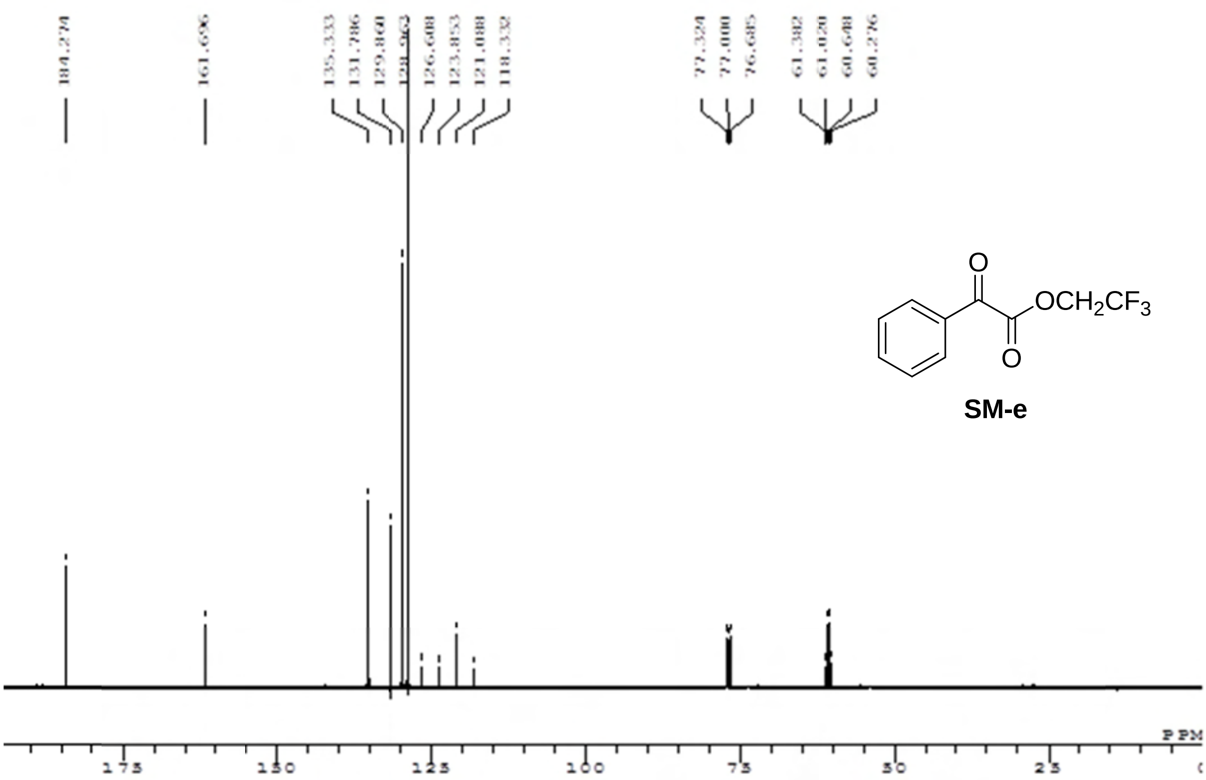

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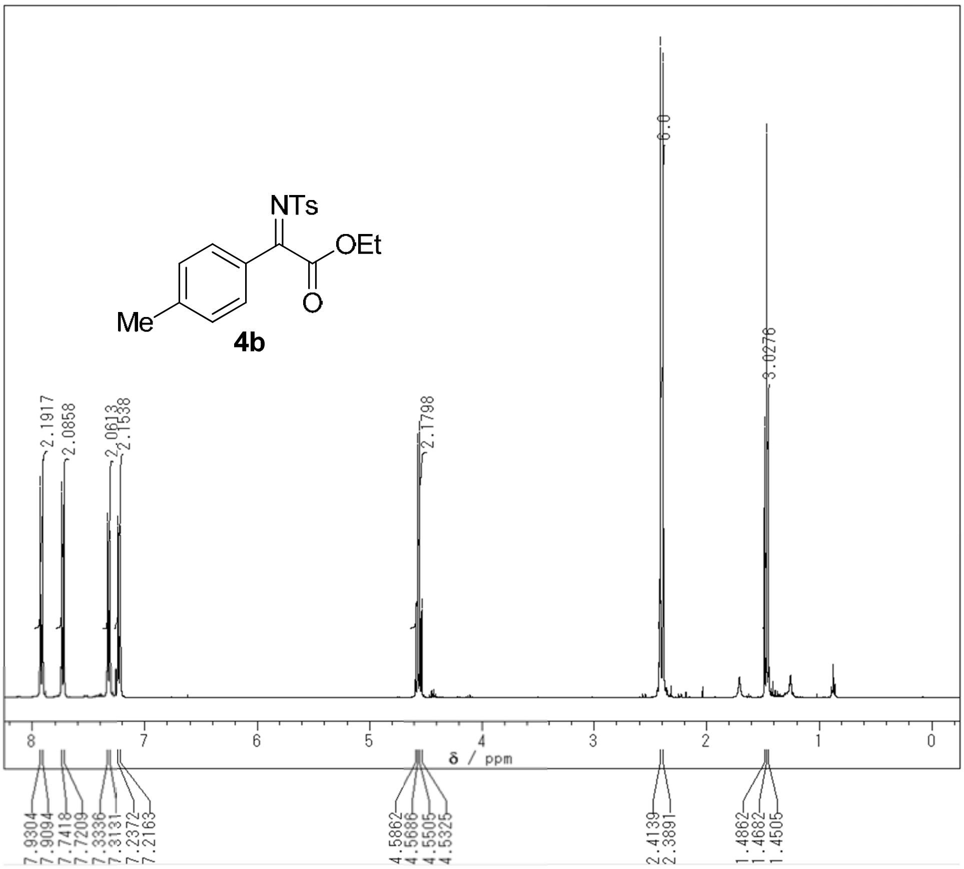

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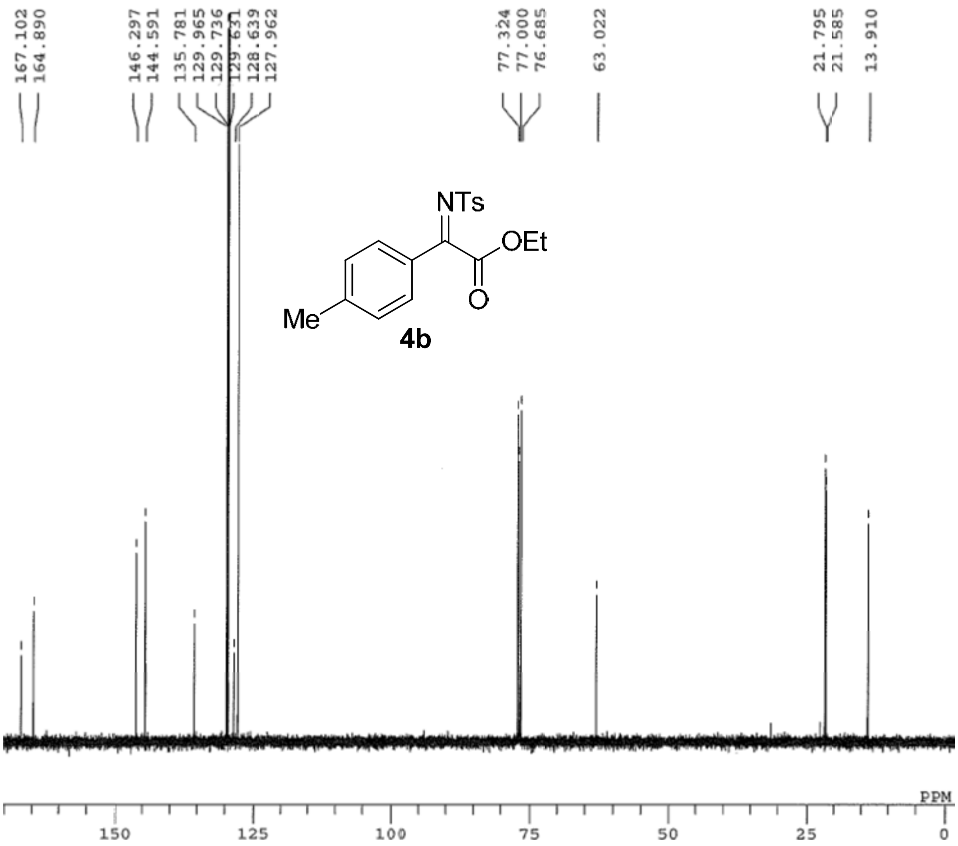

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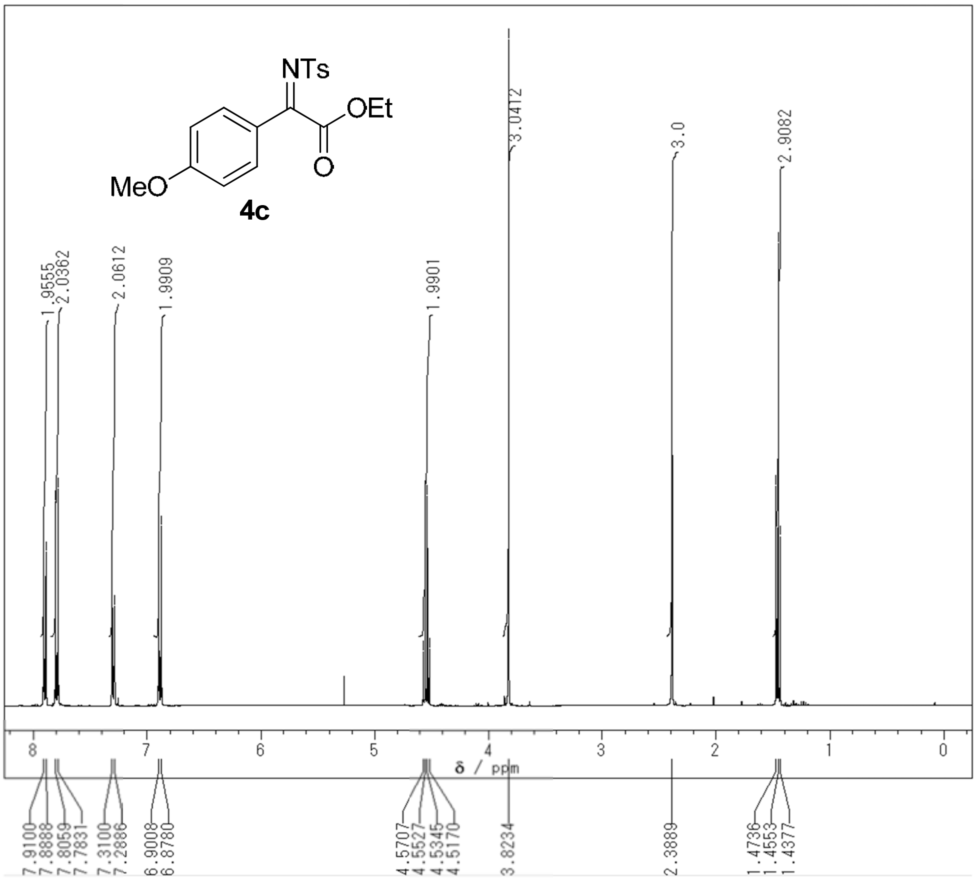

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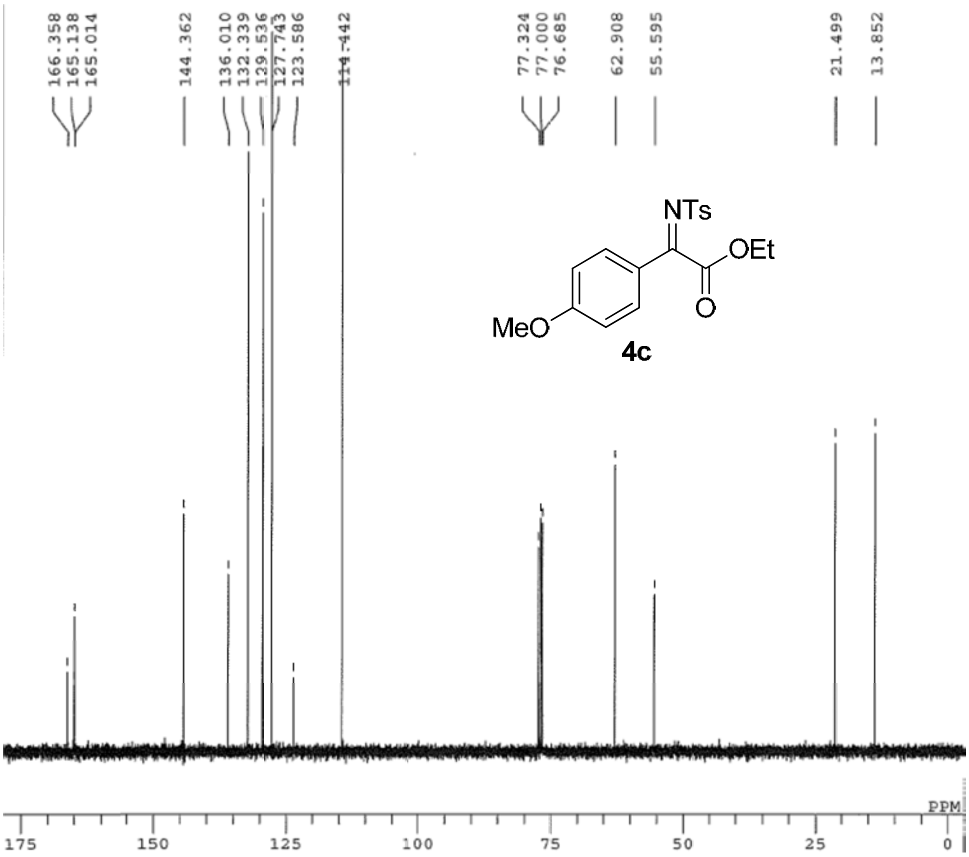

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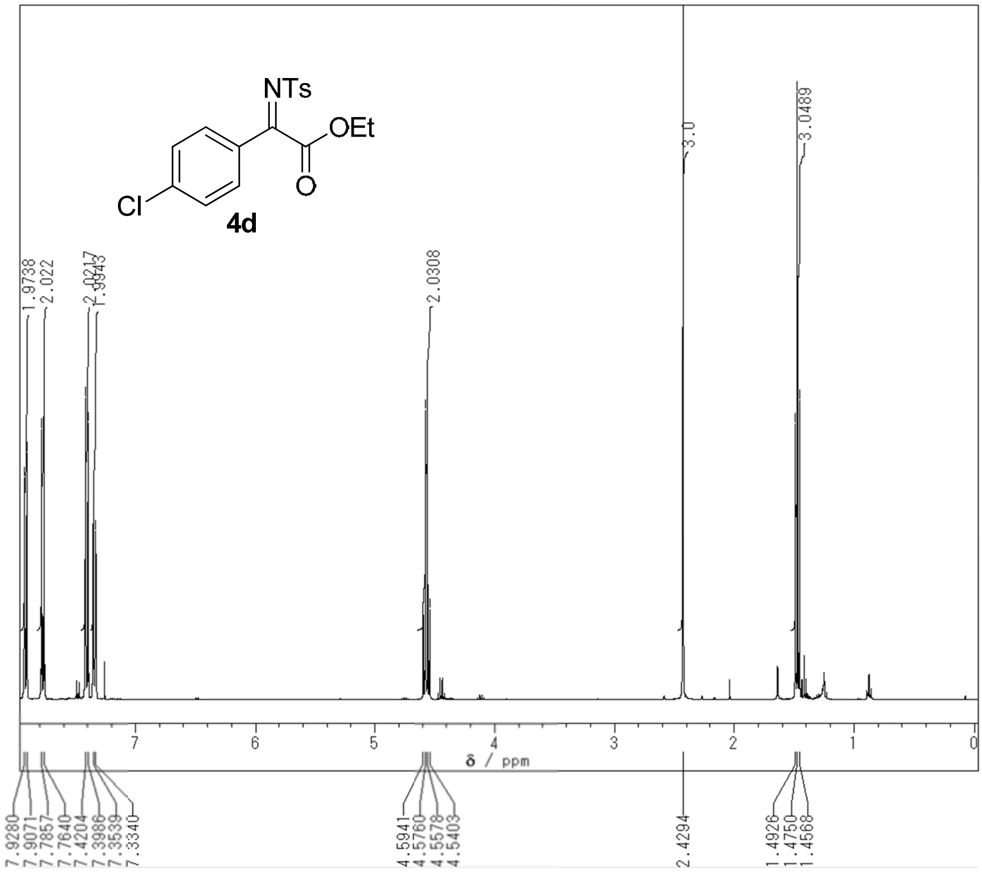

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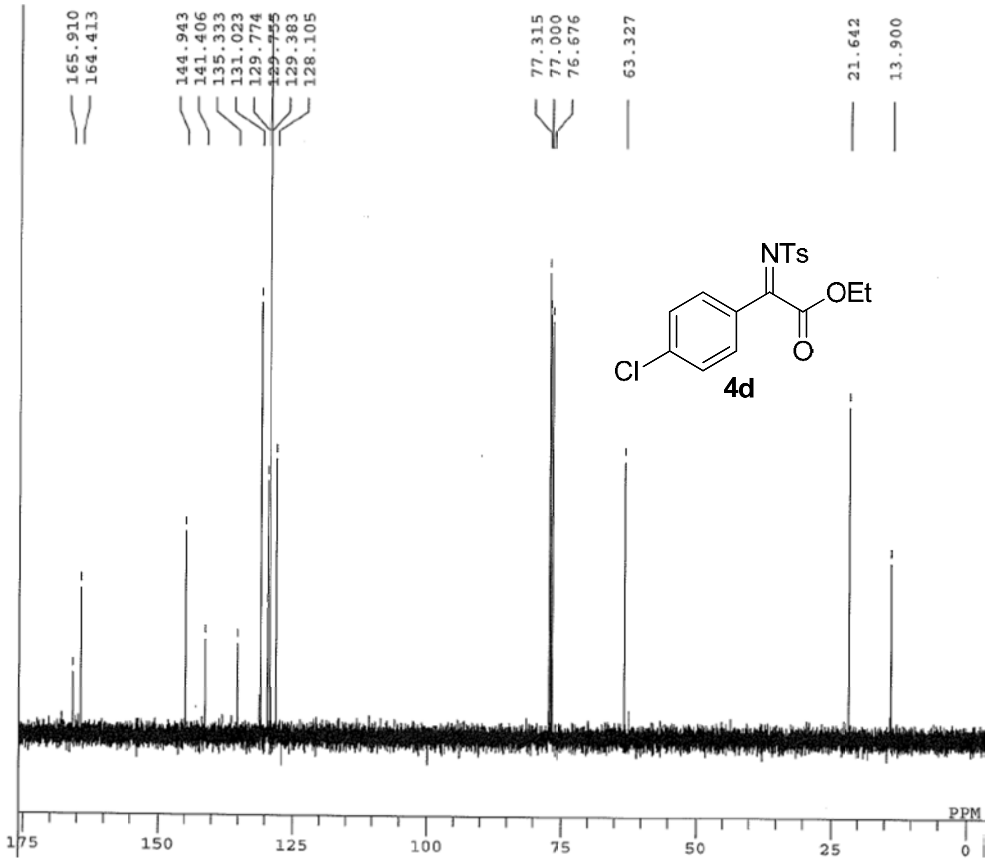

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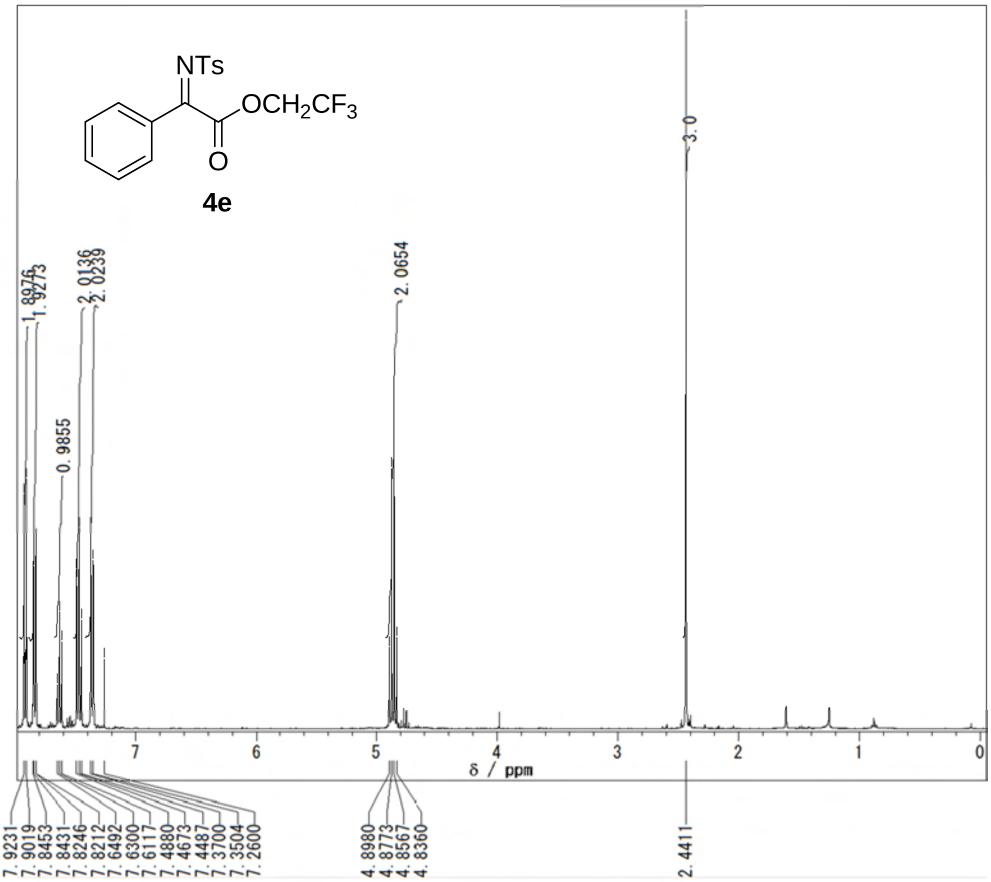

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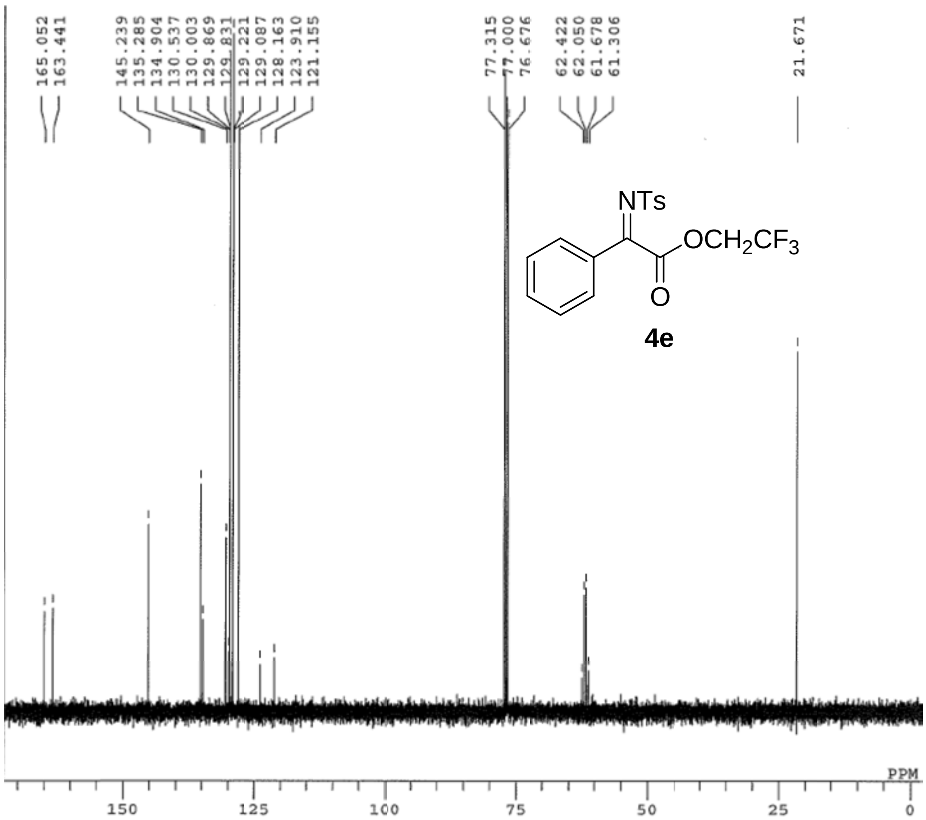

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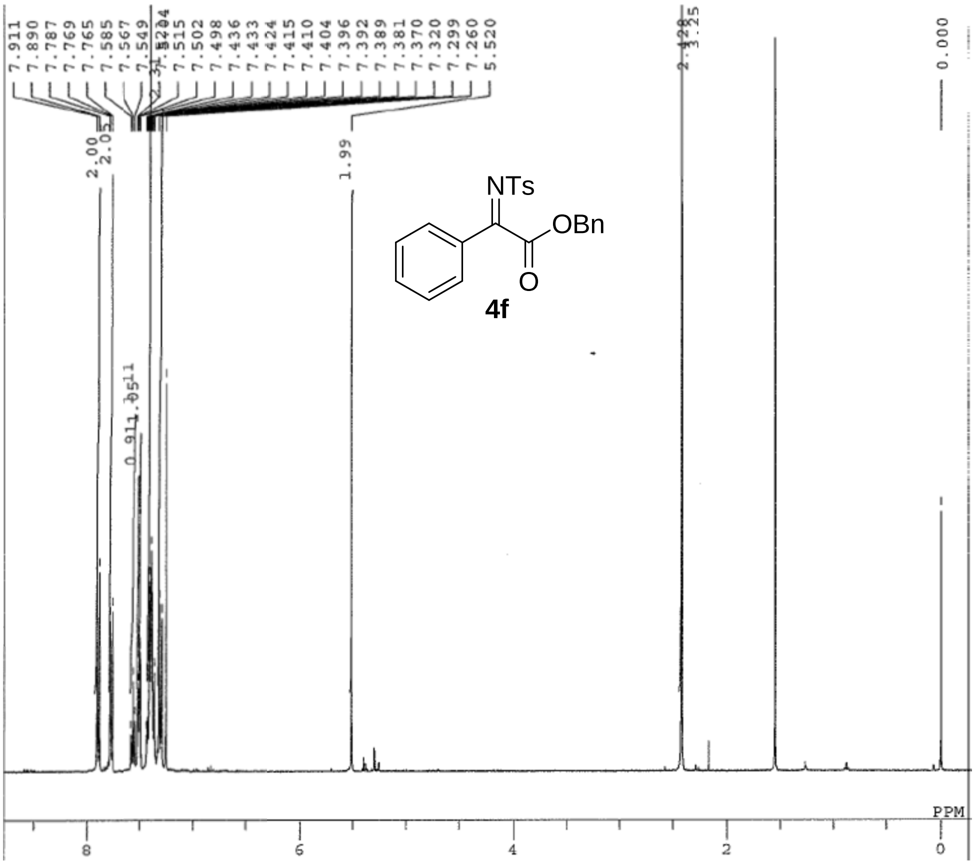

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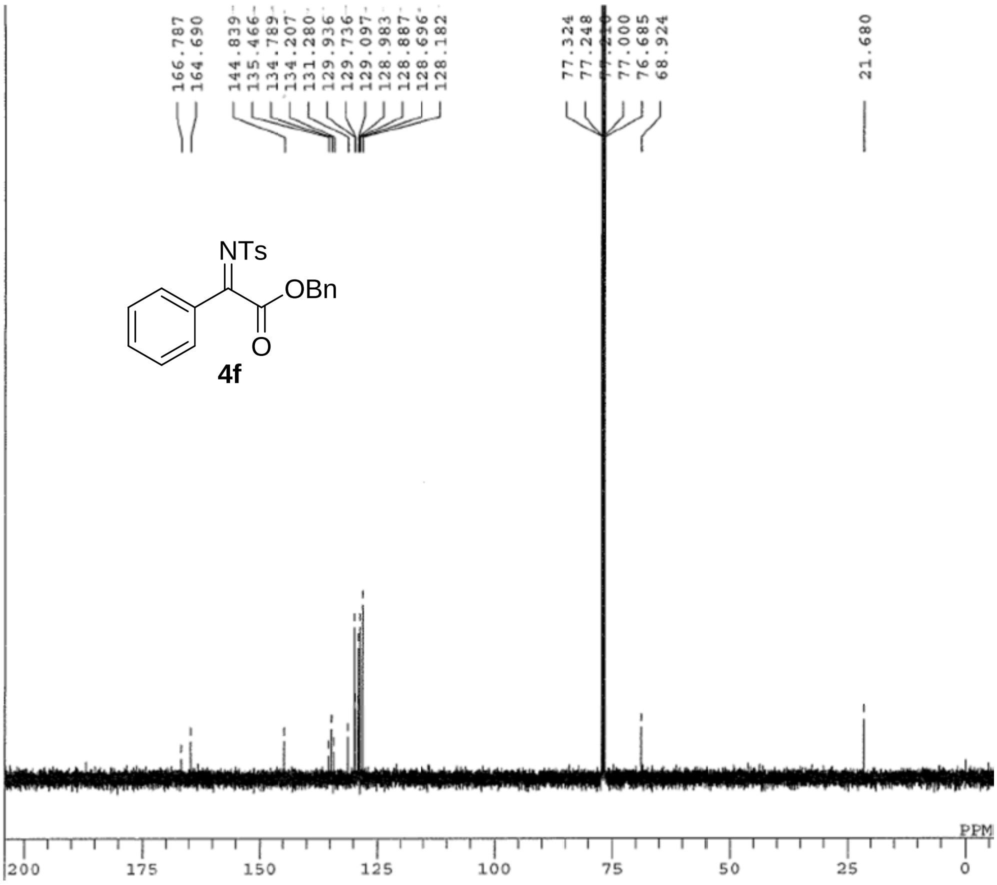

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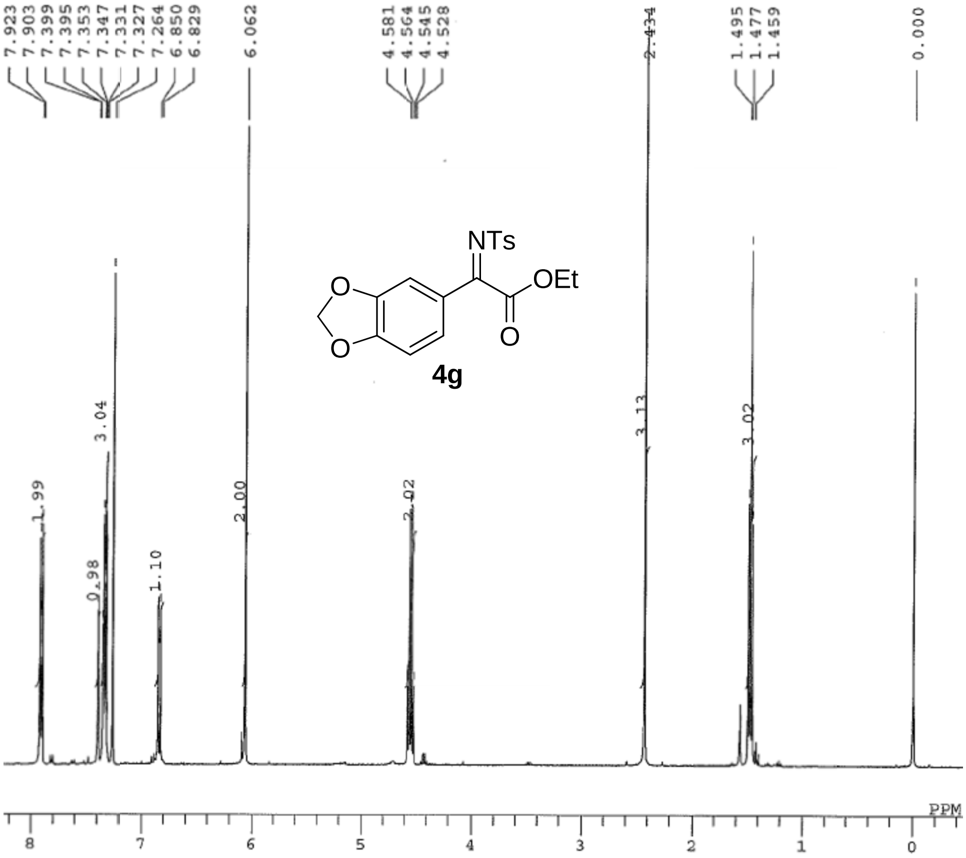

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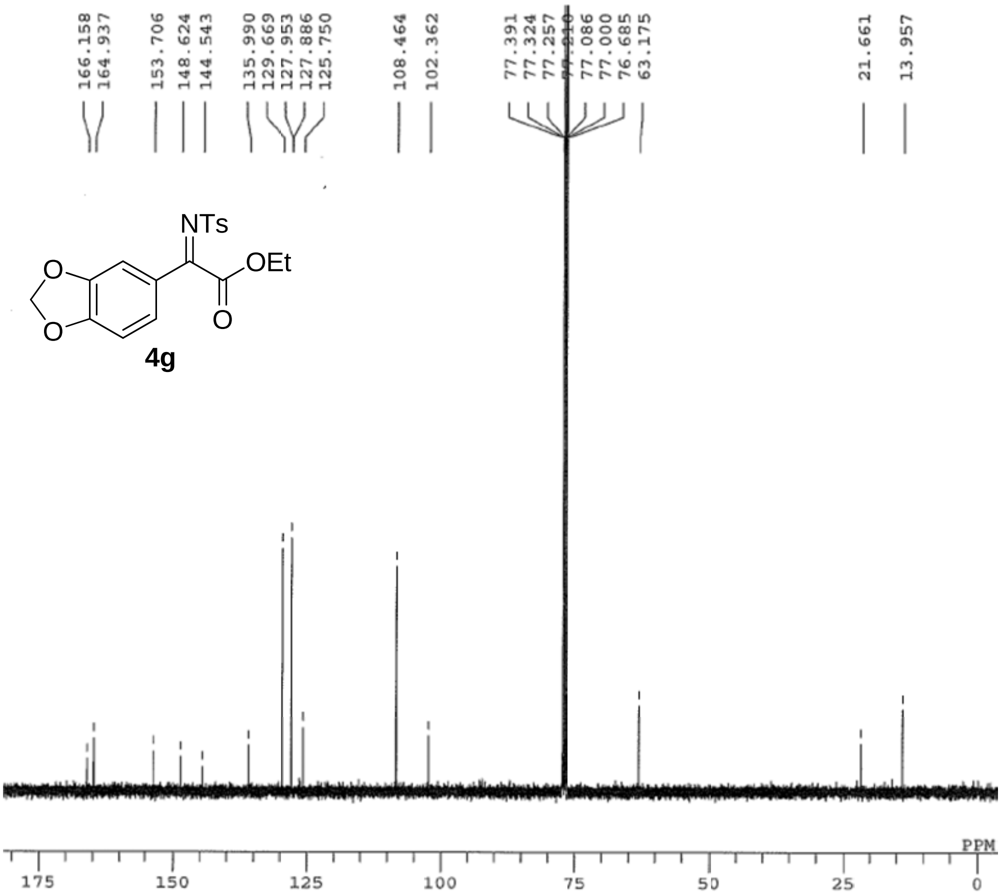

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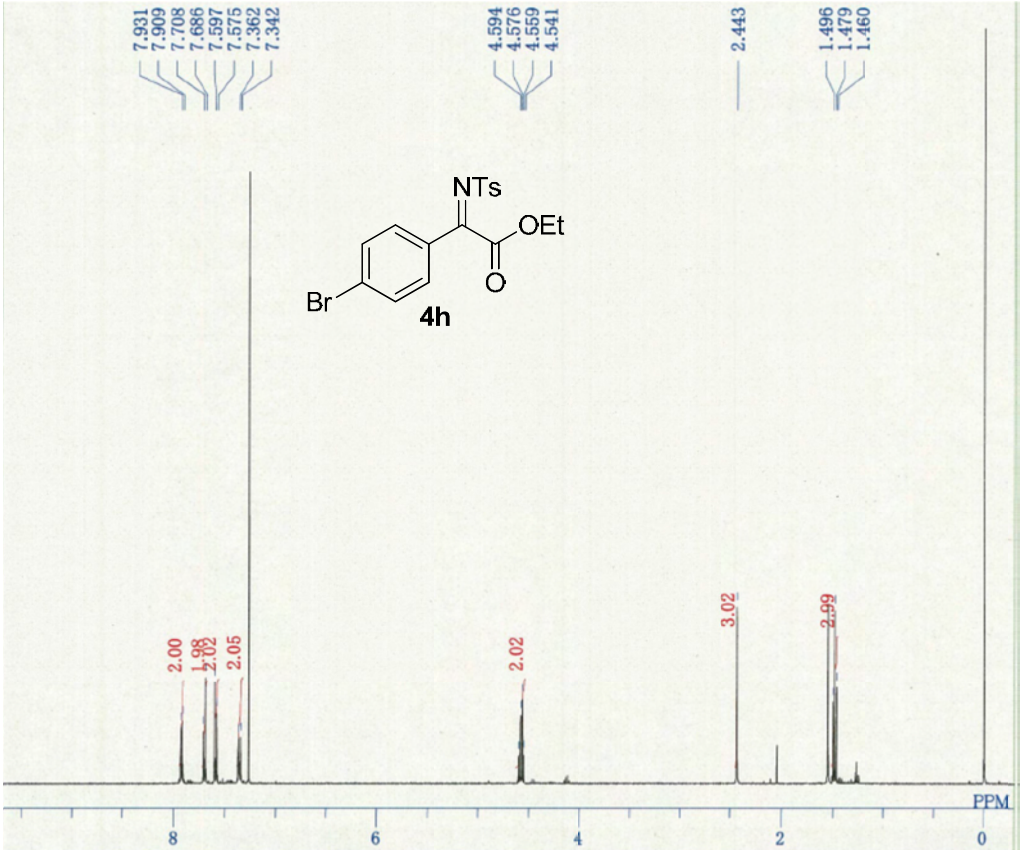

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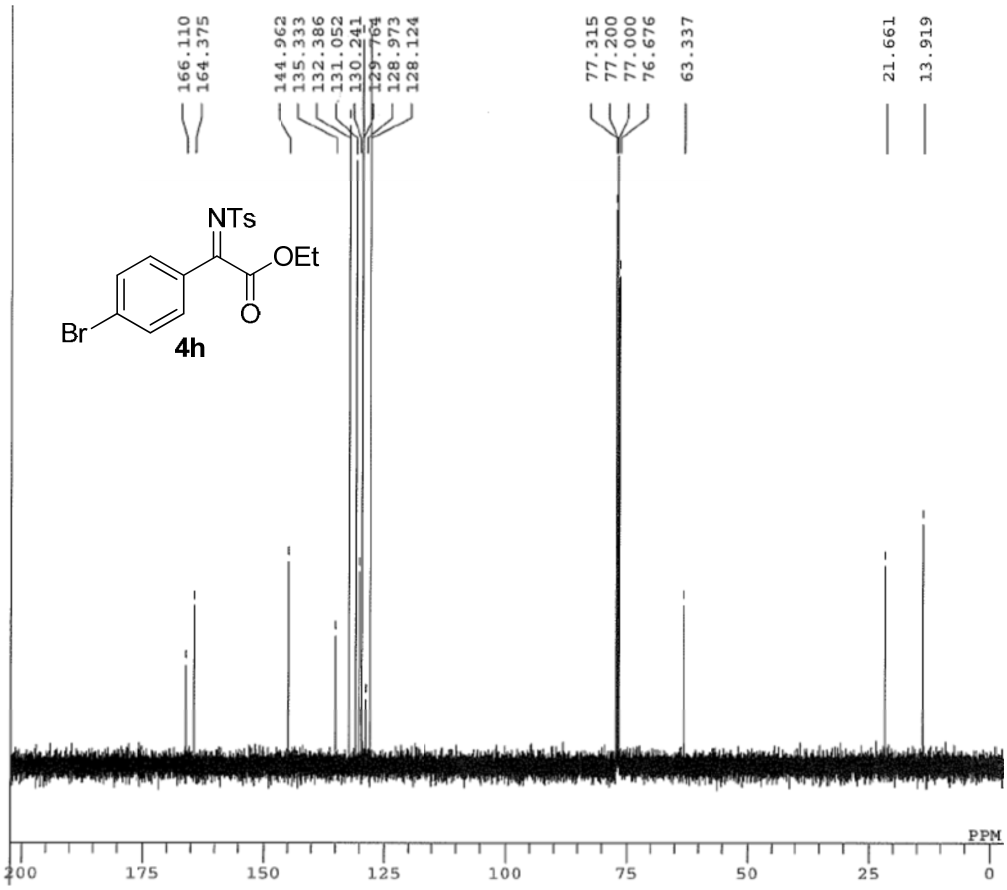

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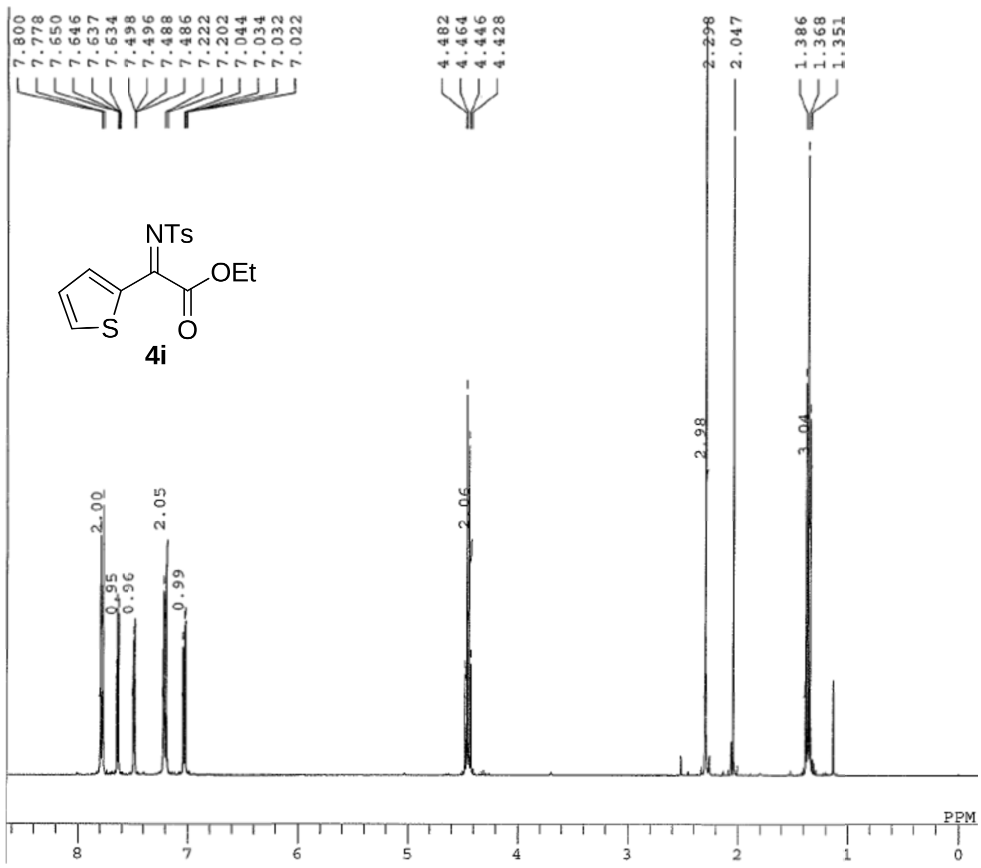

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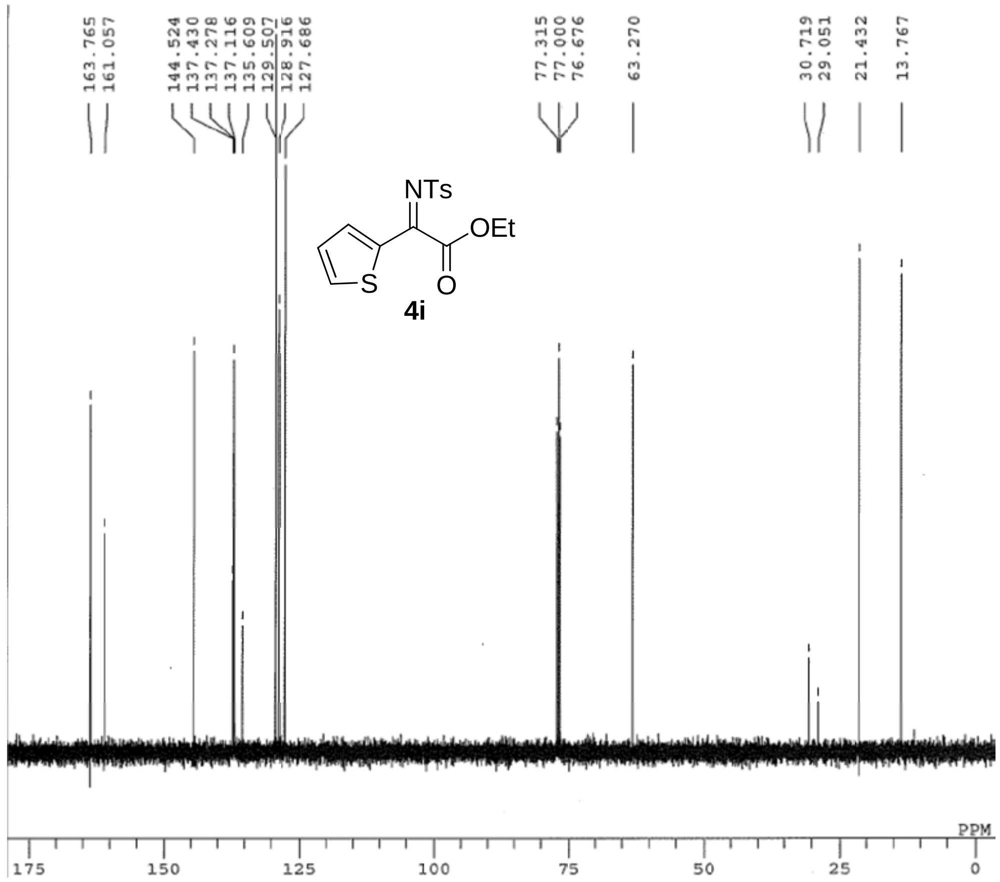

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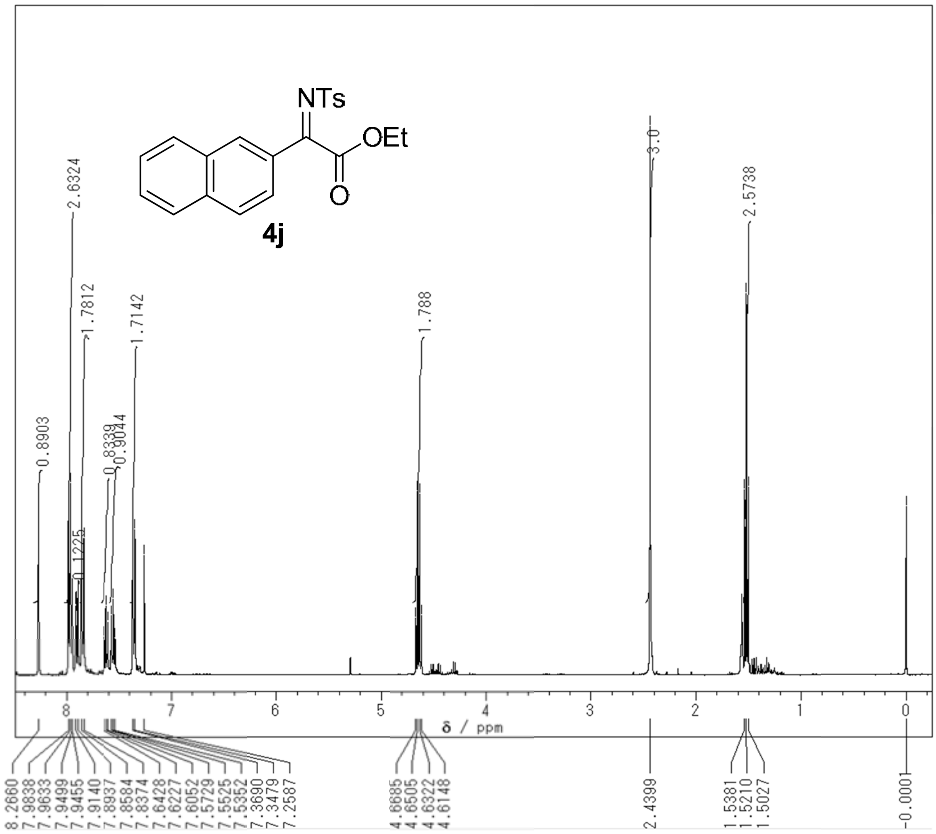

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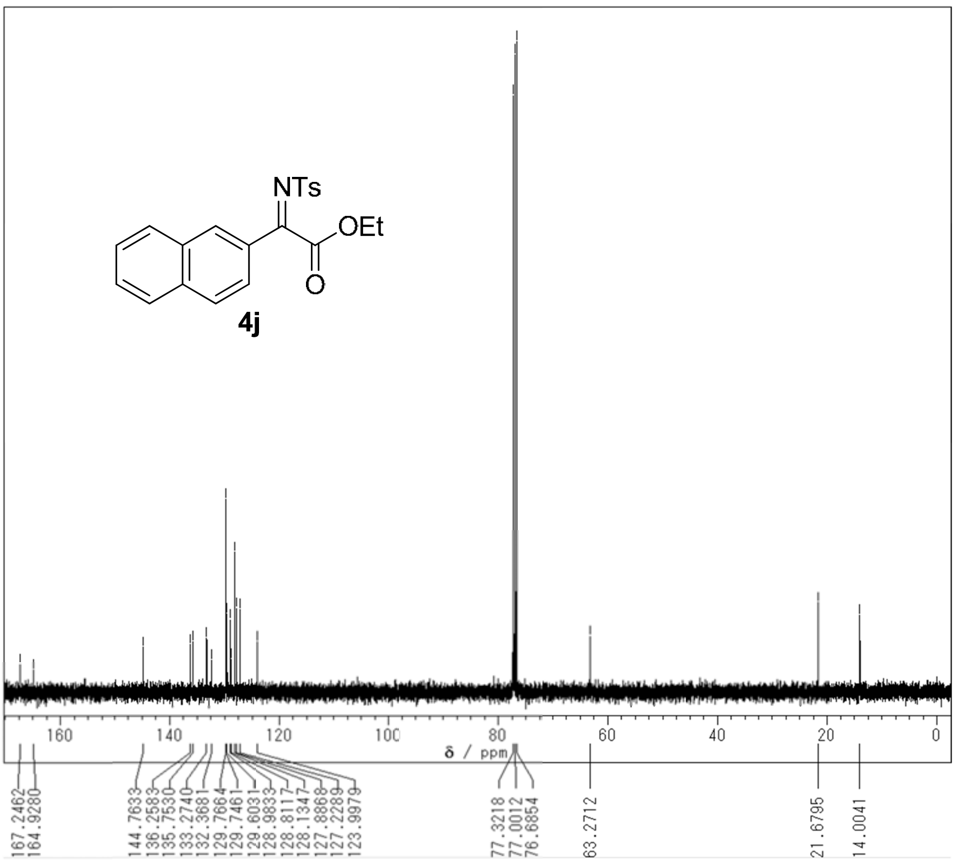

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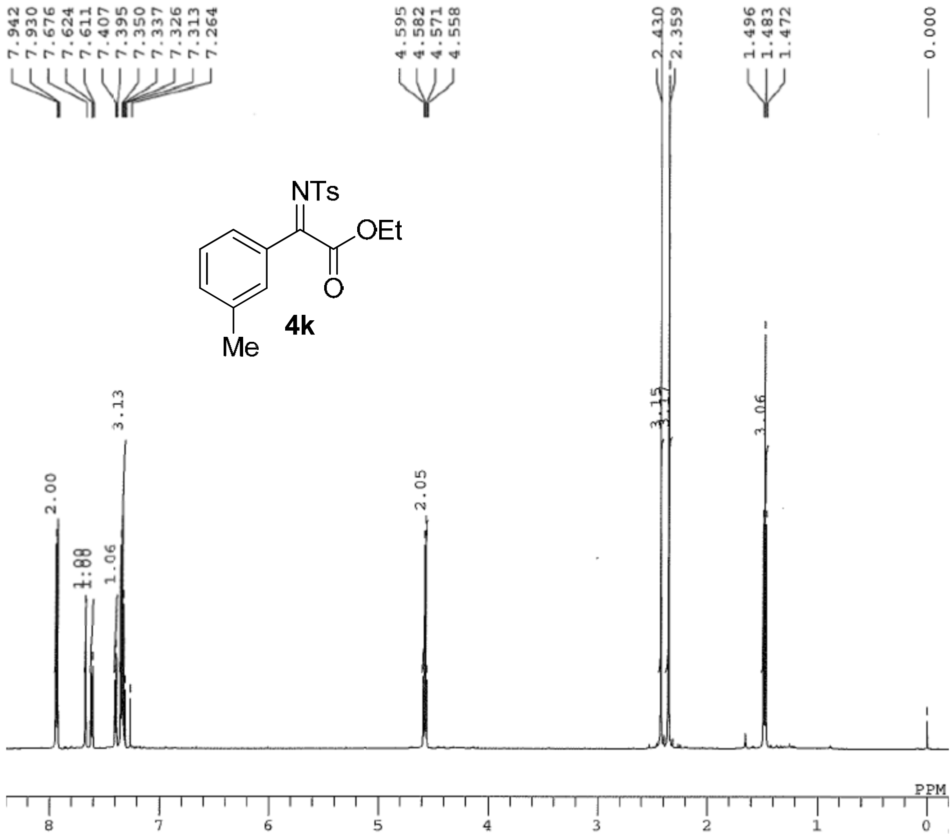

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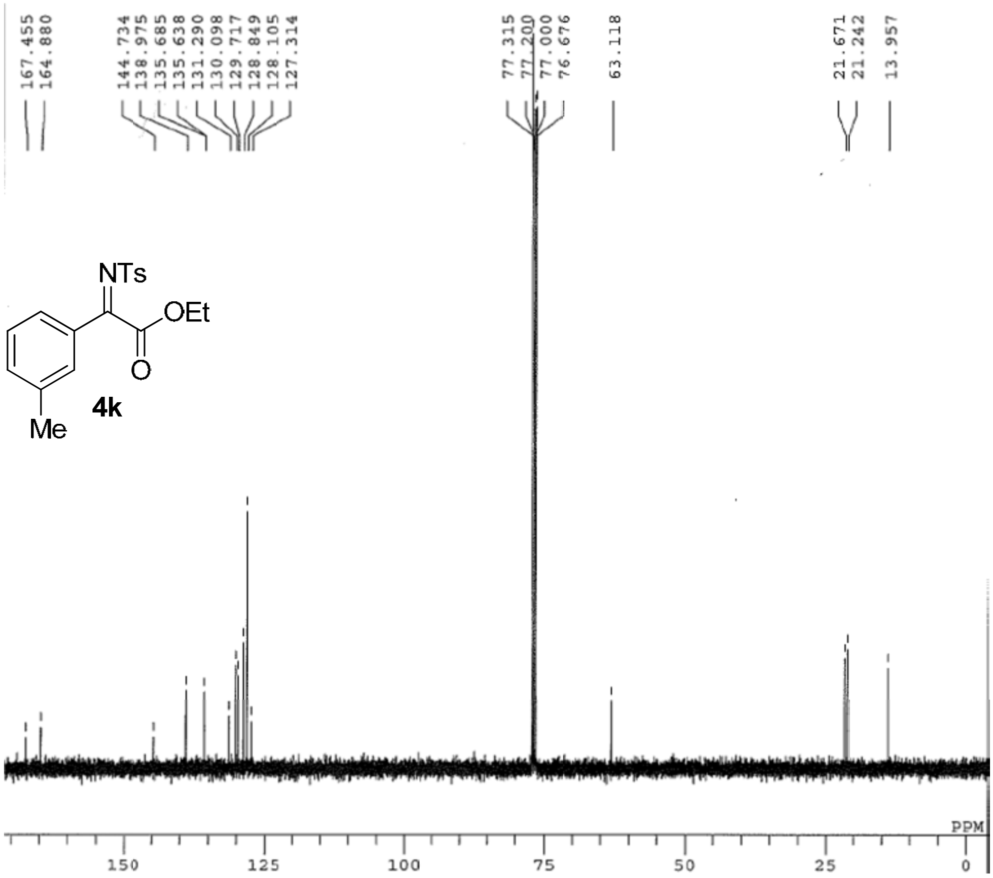

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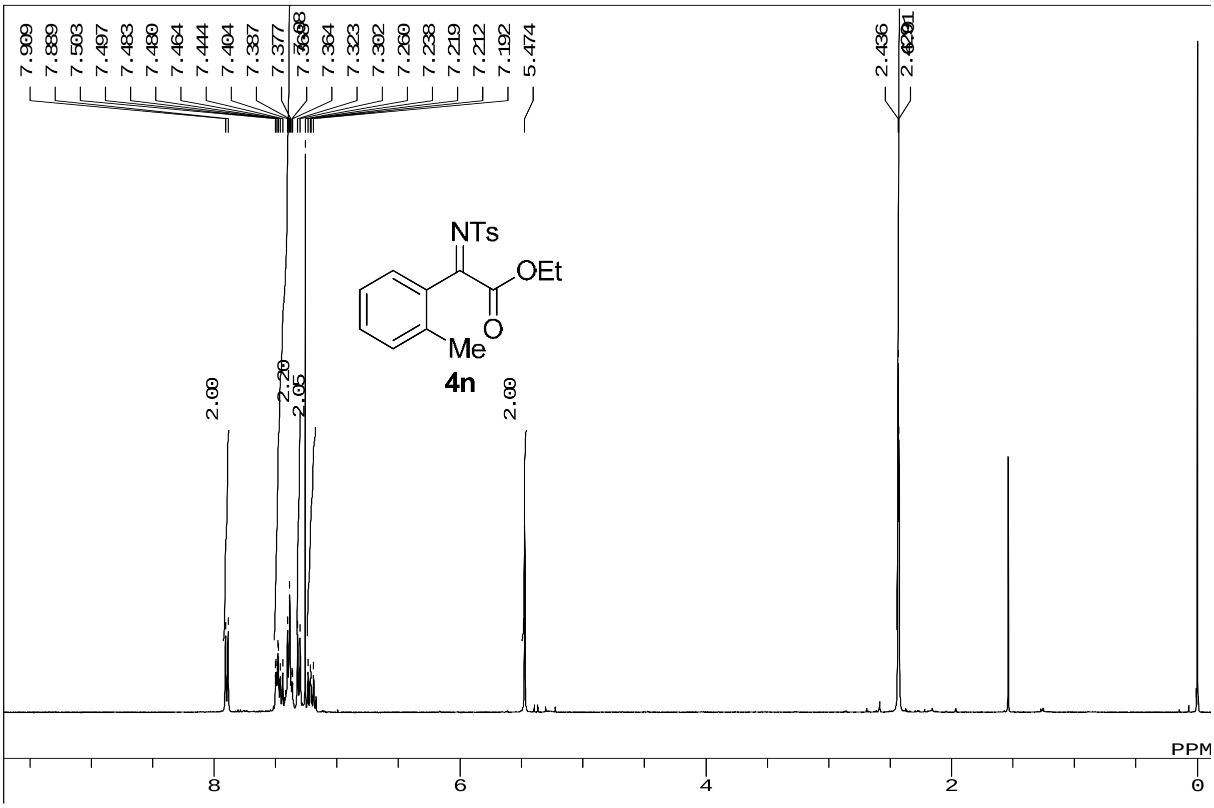

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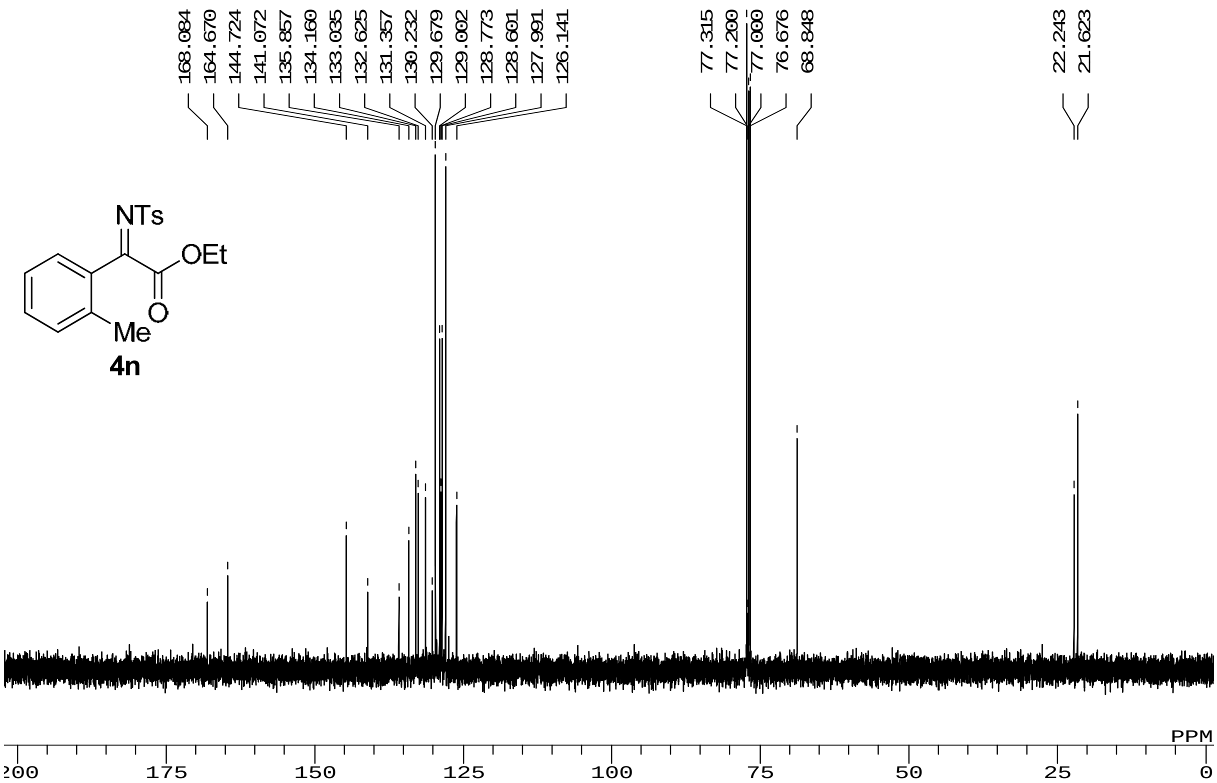

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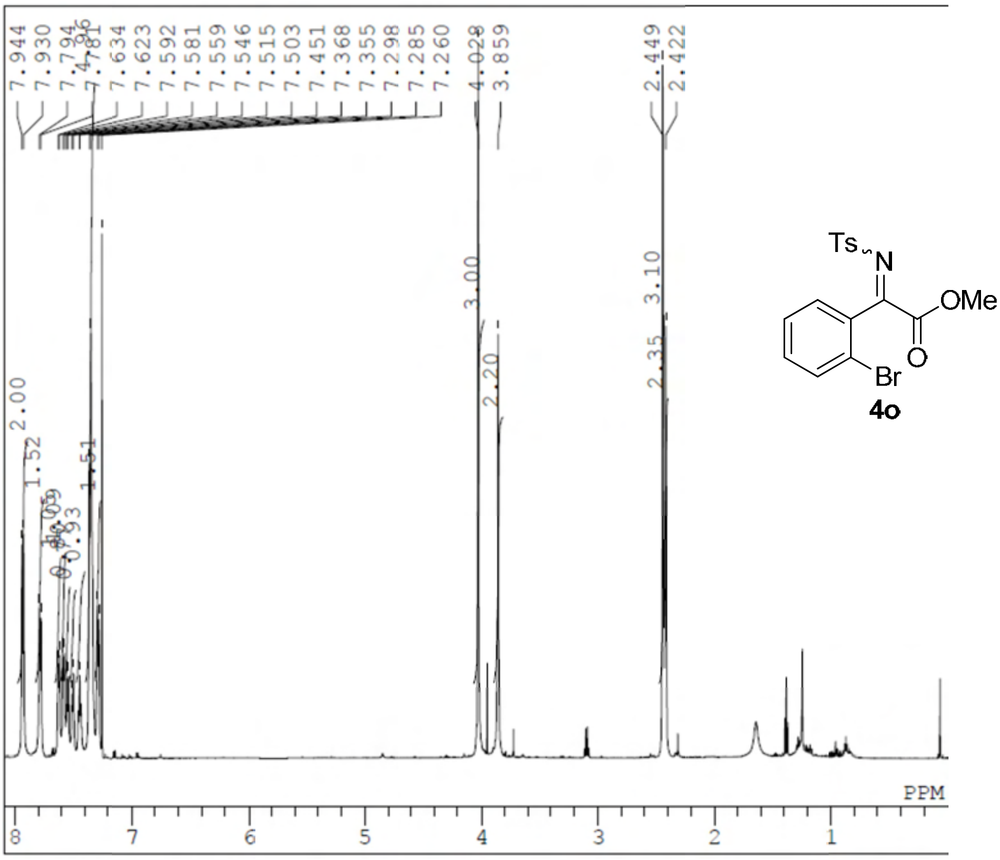

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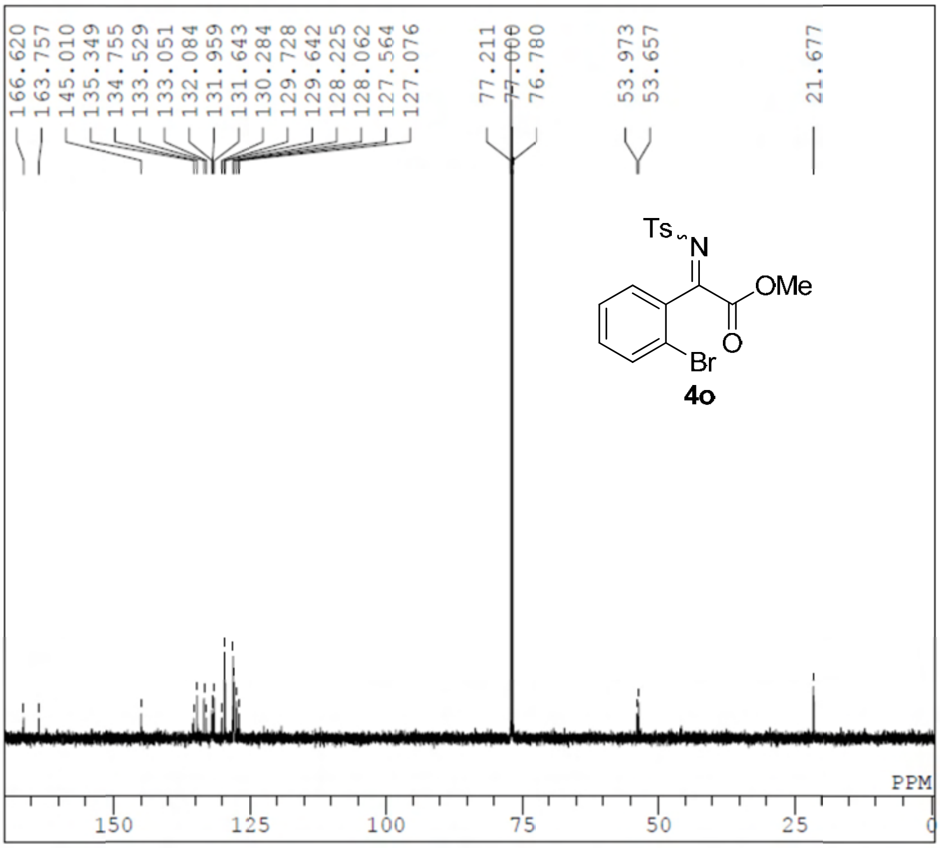

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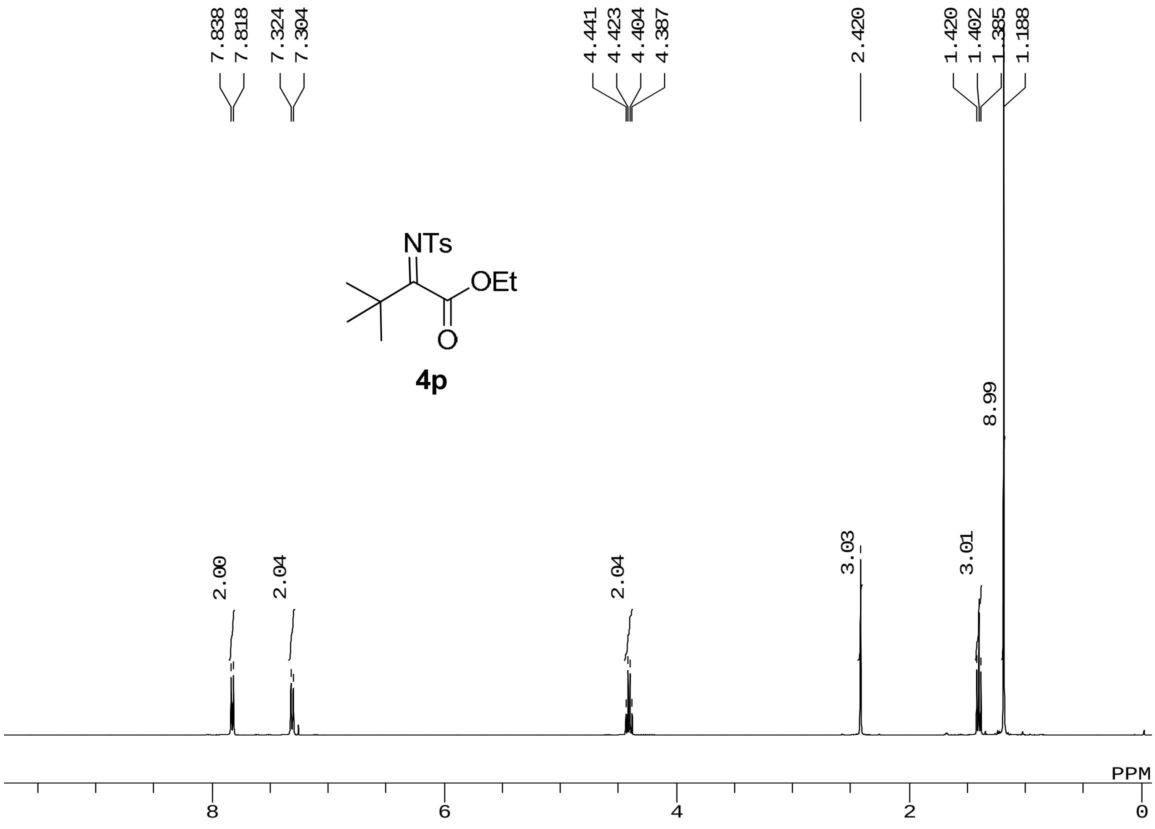

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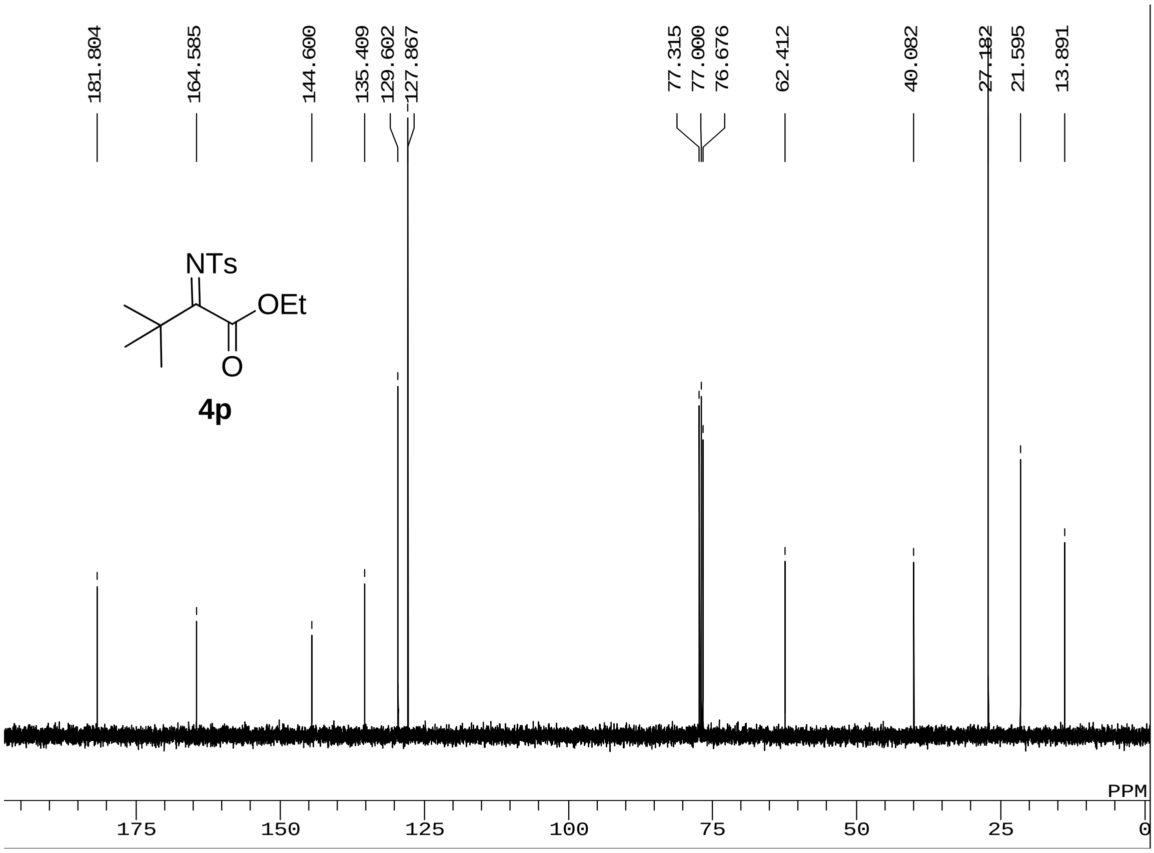

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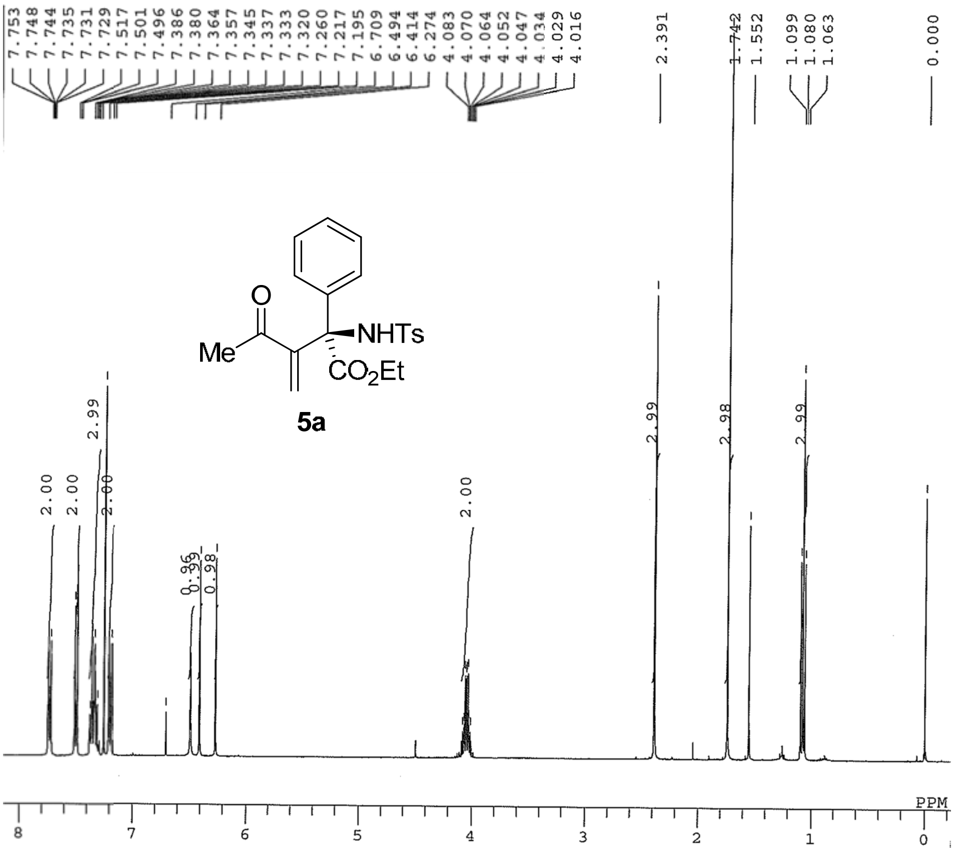
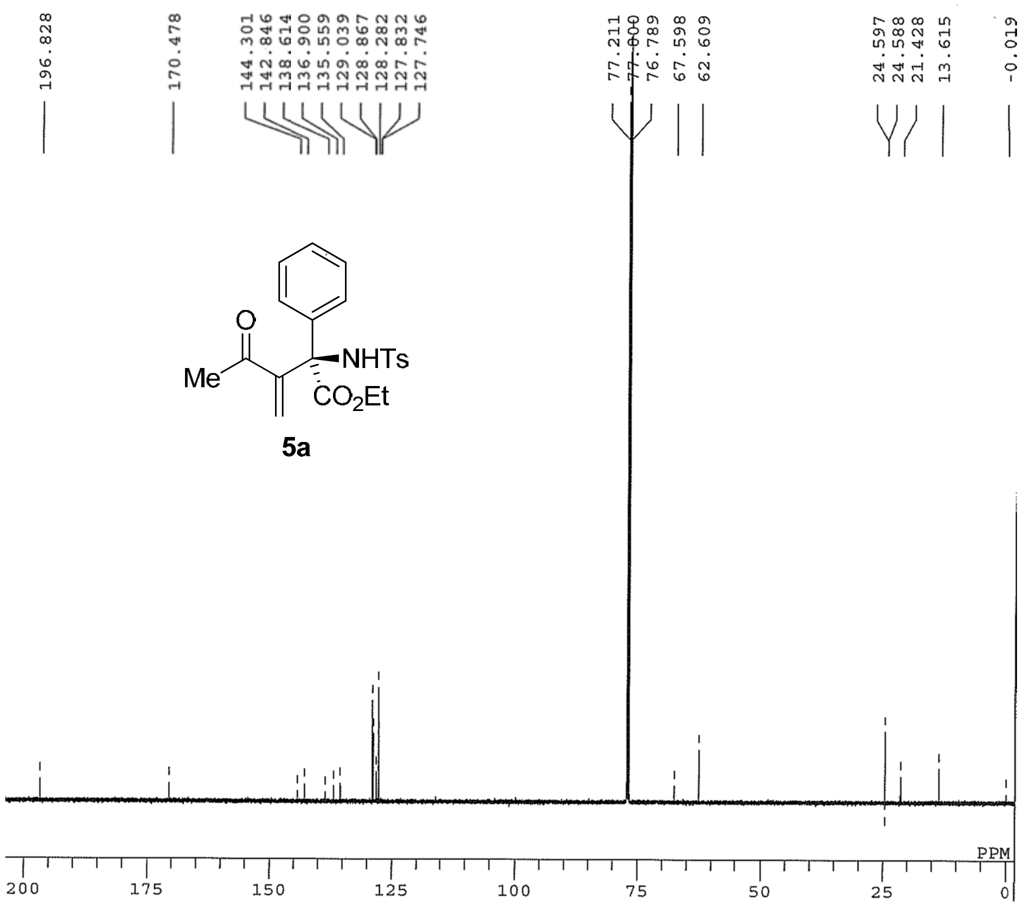


[13]C-NMR ($CDCl_3$)



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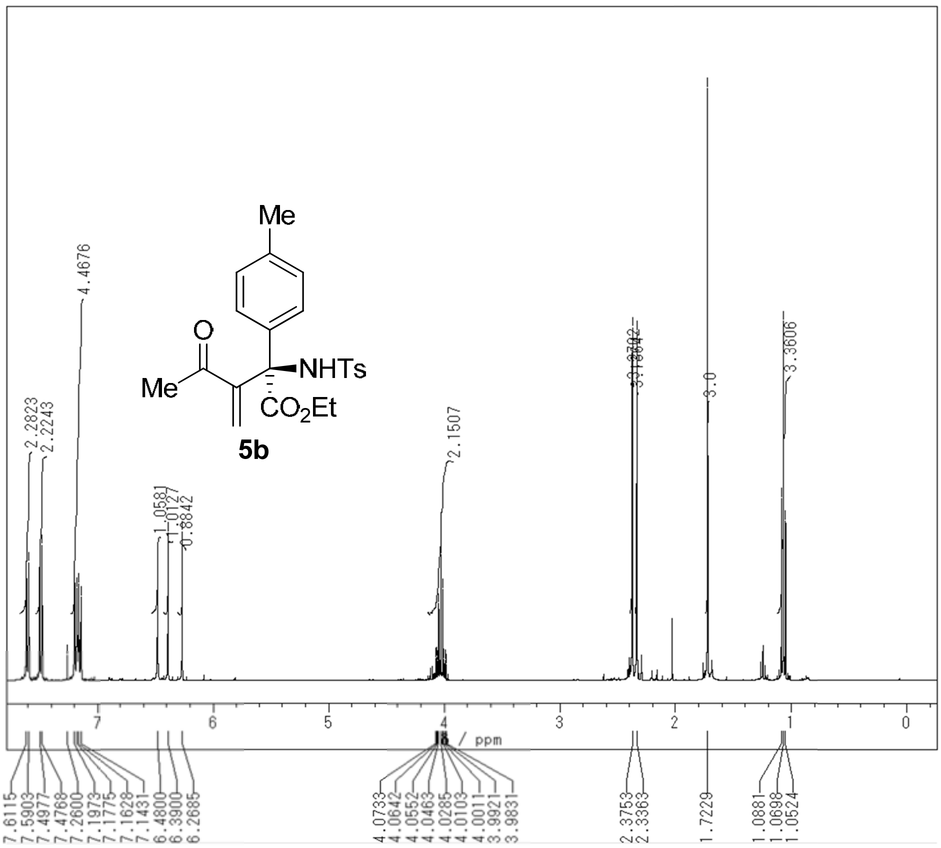

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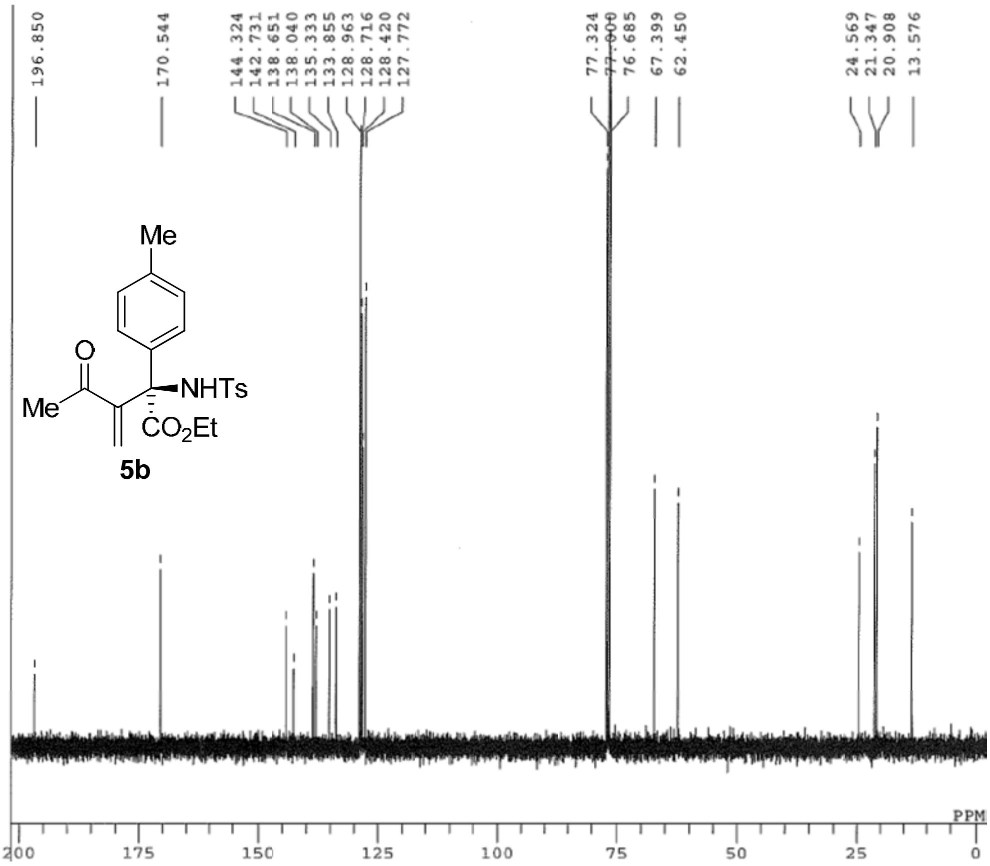

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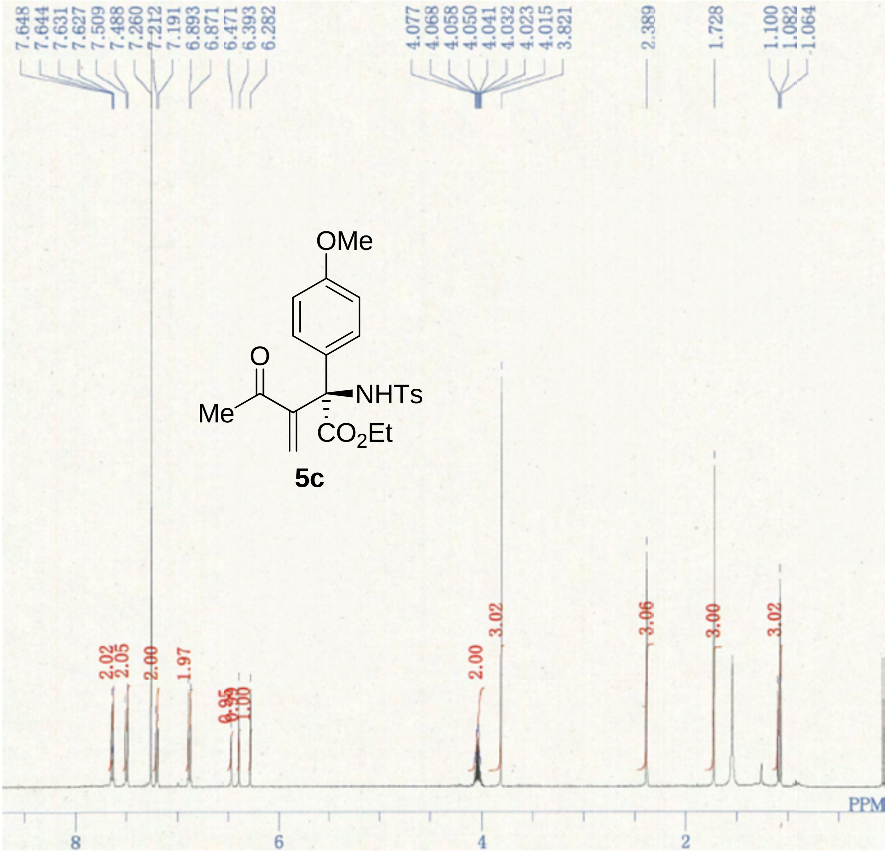

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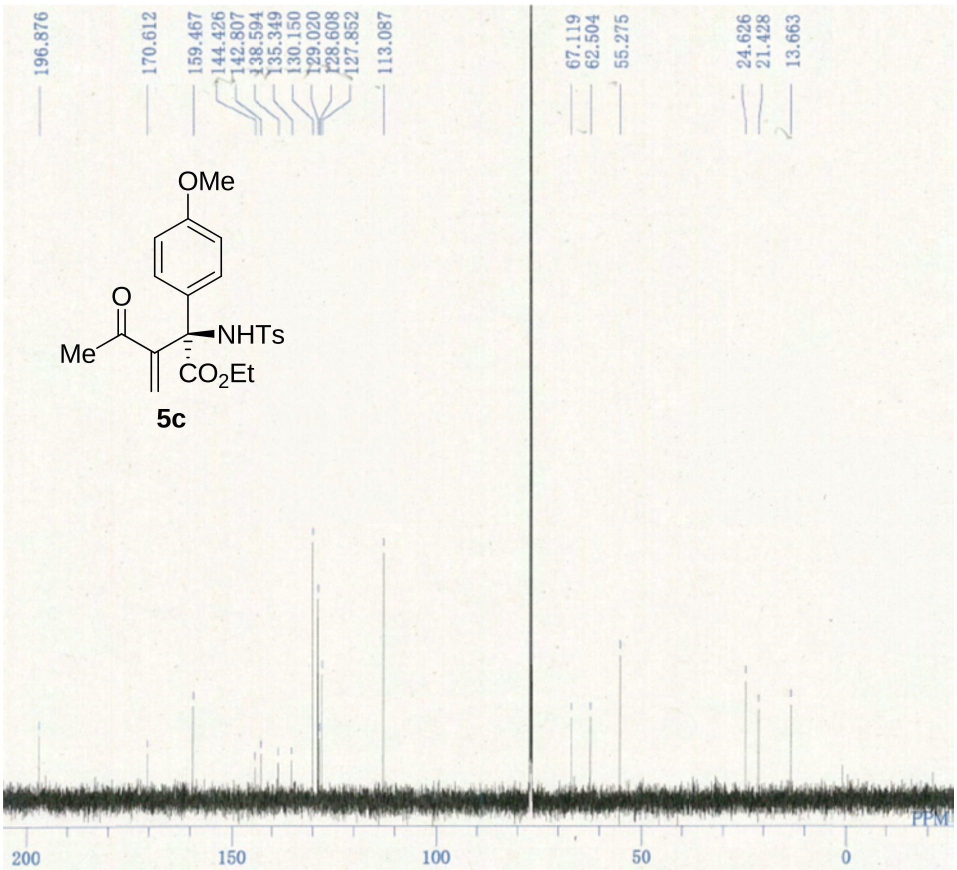

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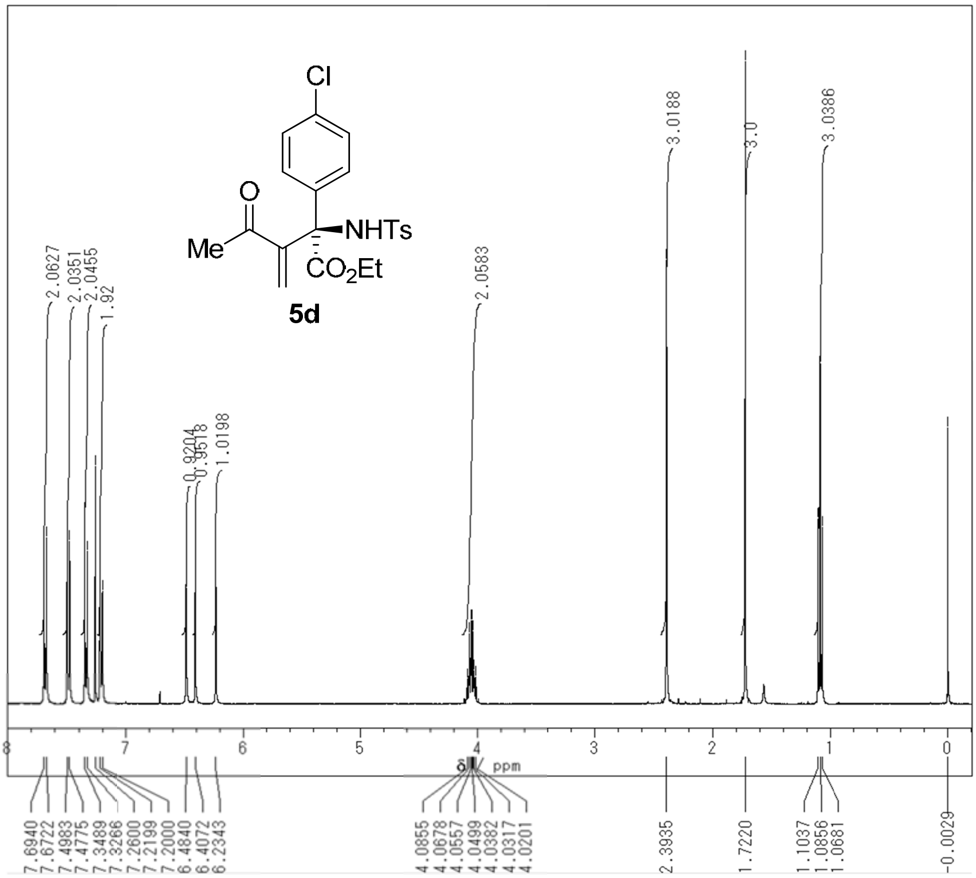

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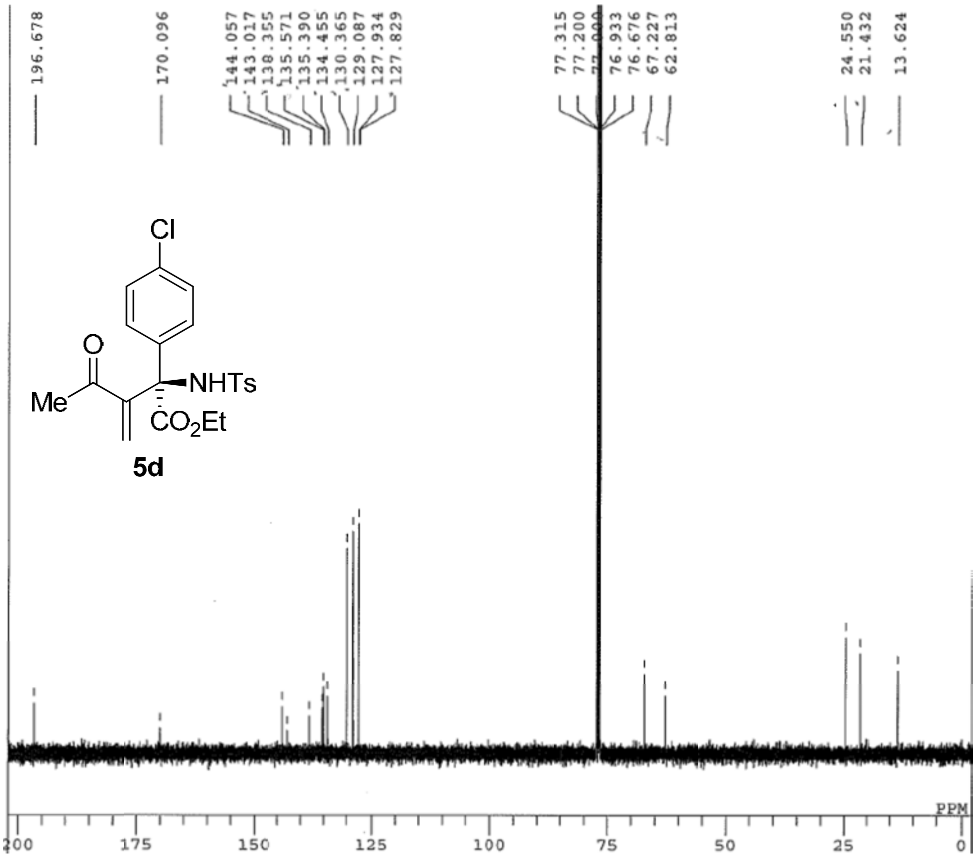

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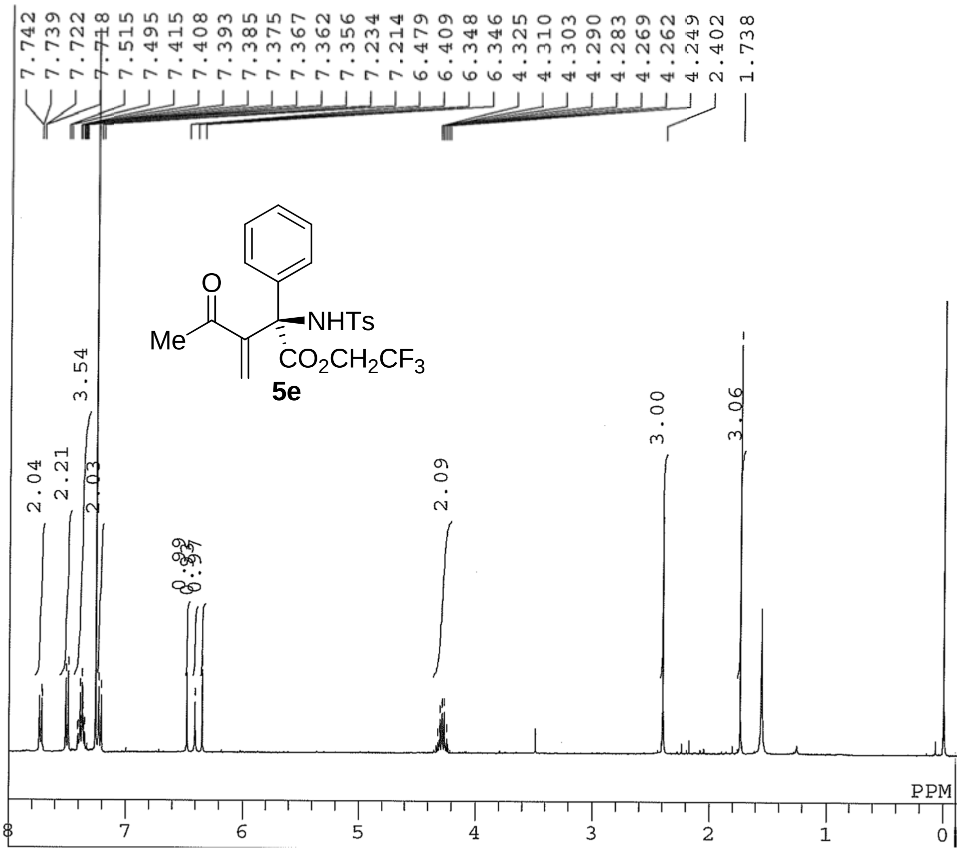

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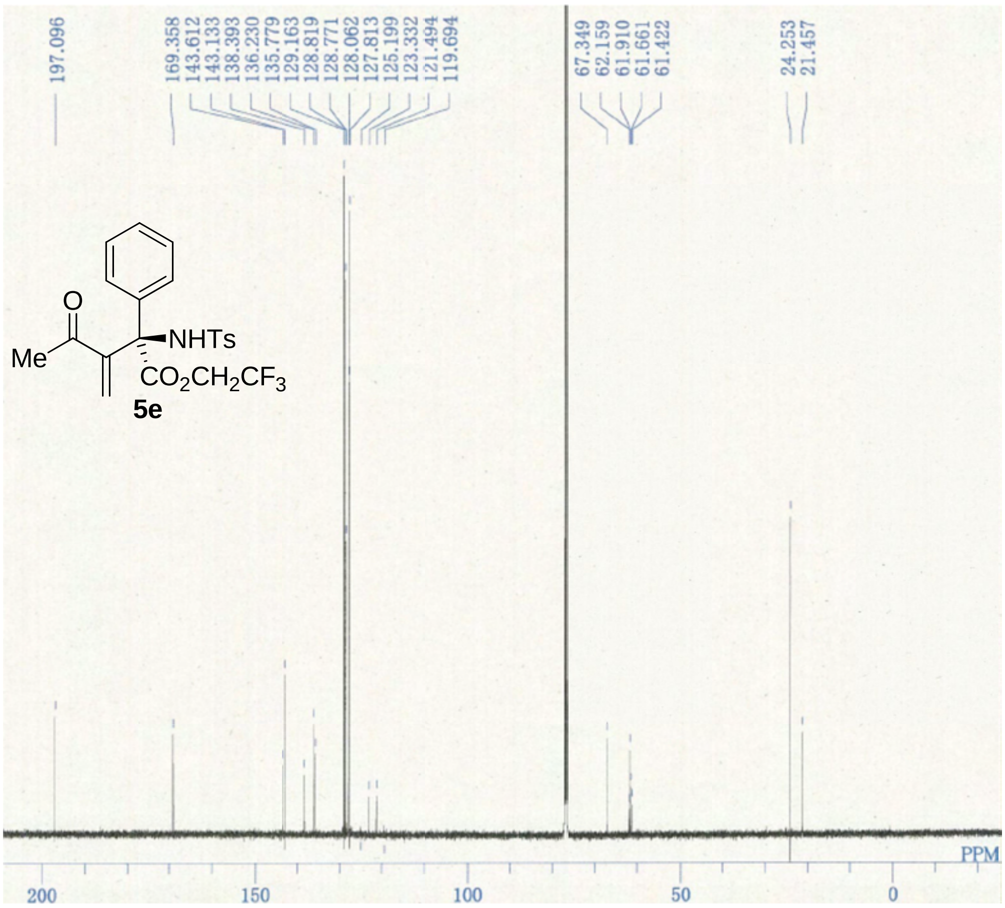

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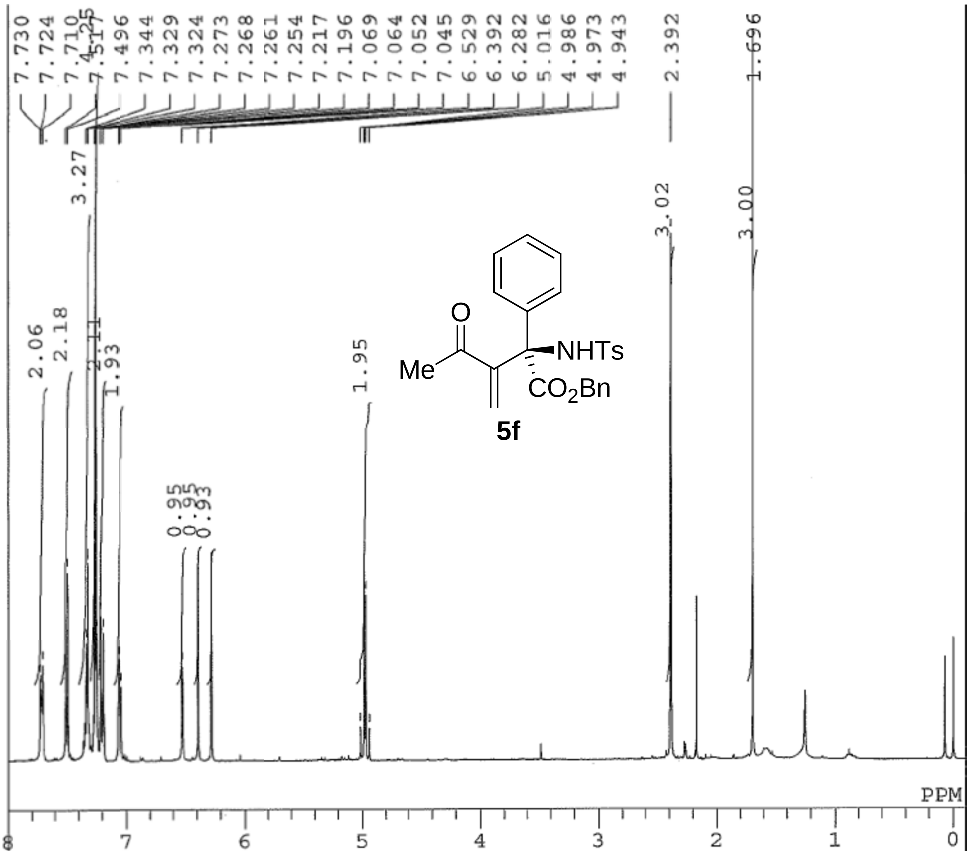

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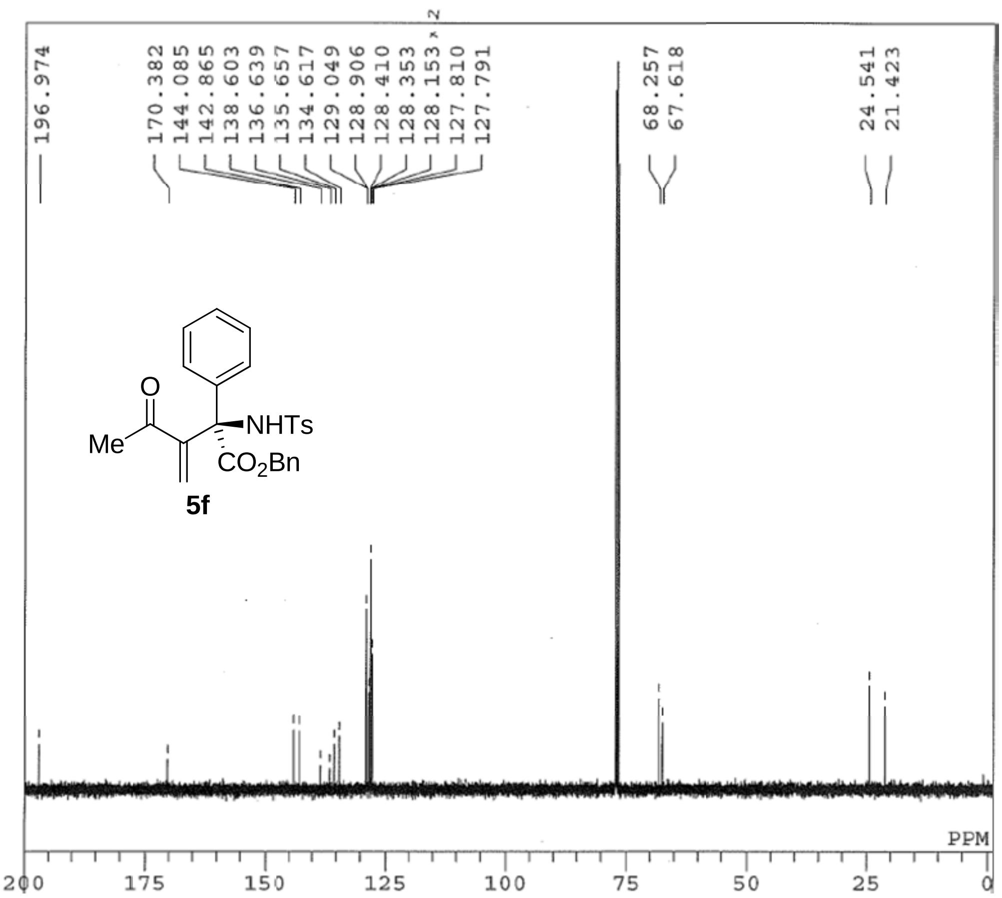

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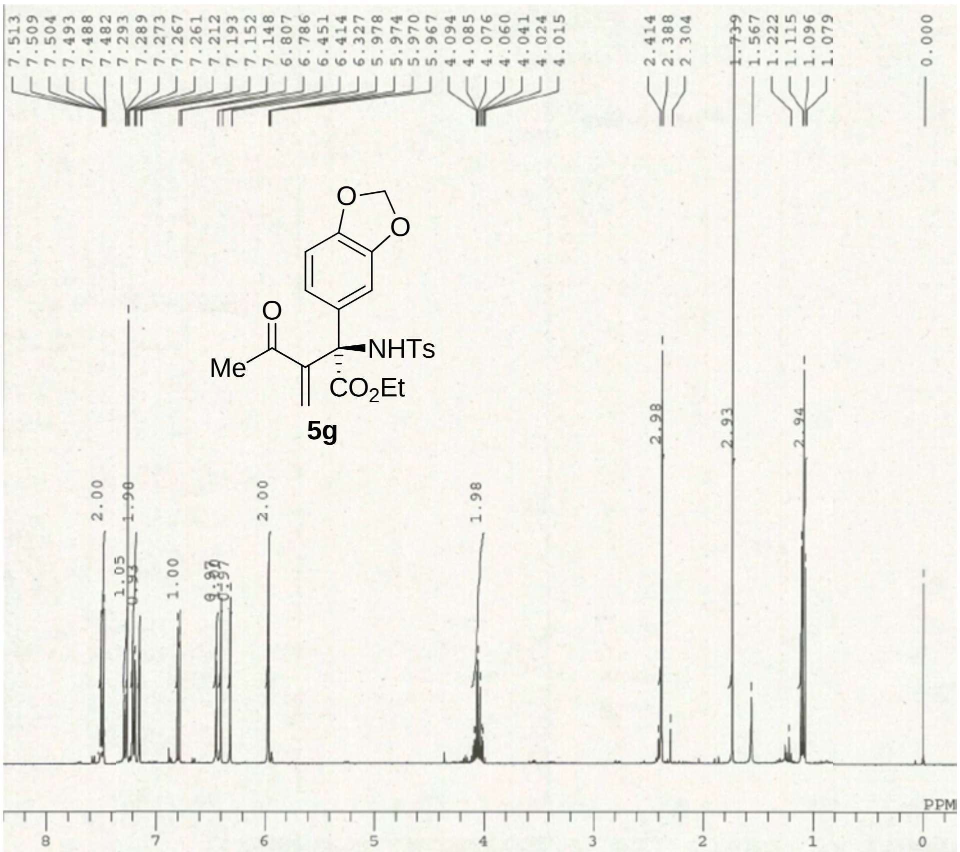

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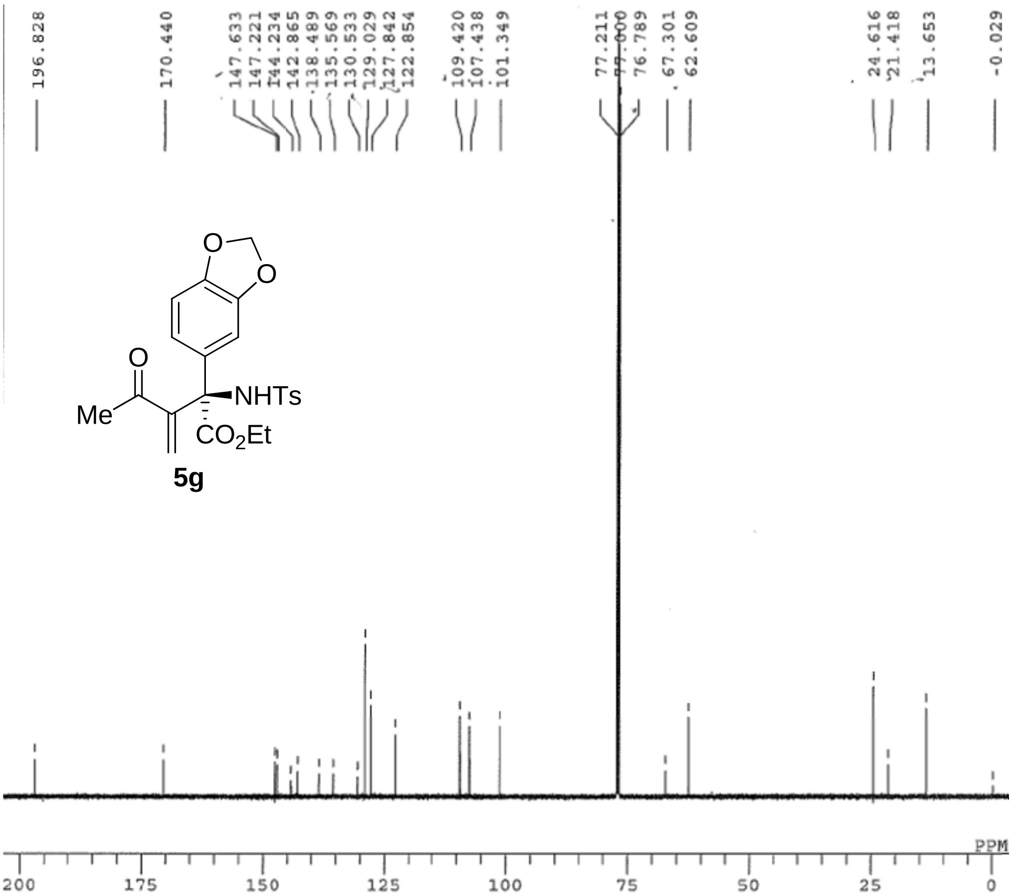

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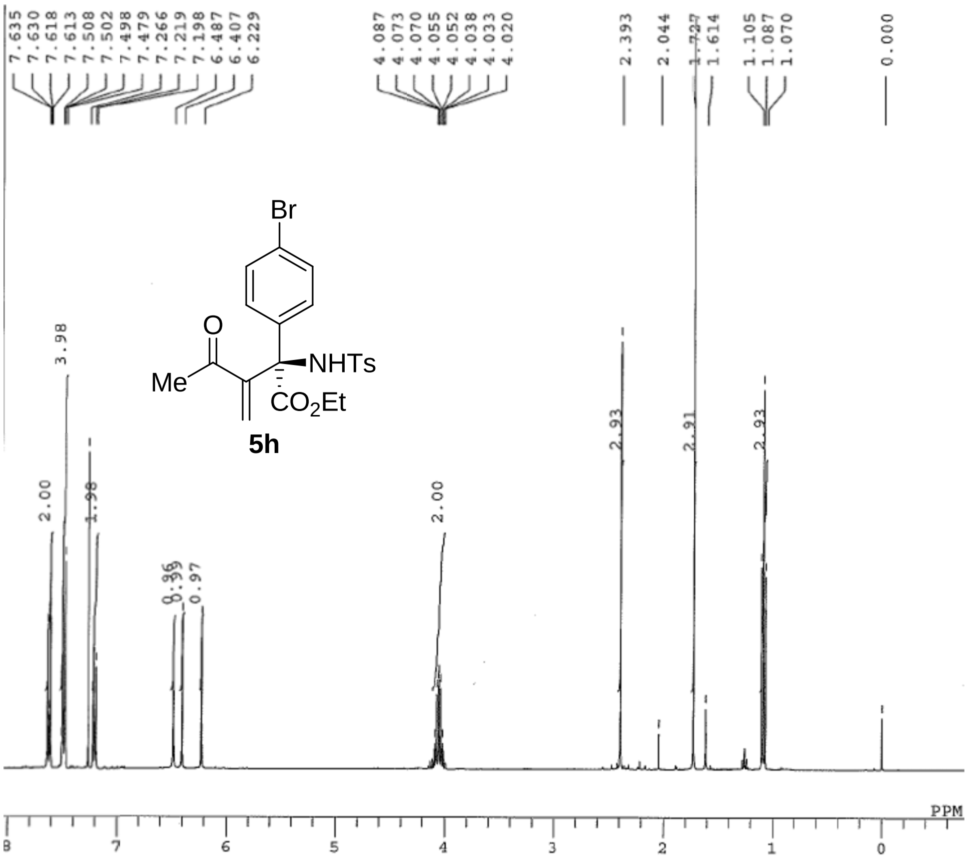

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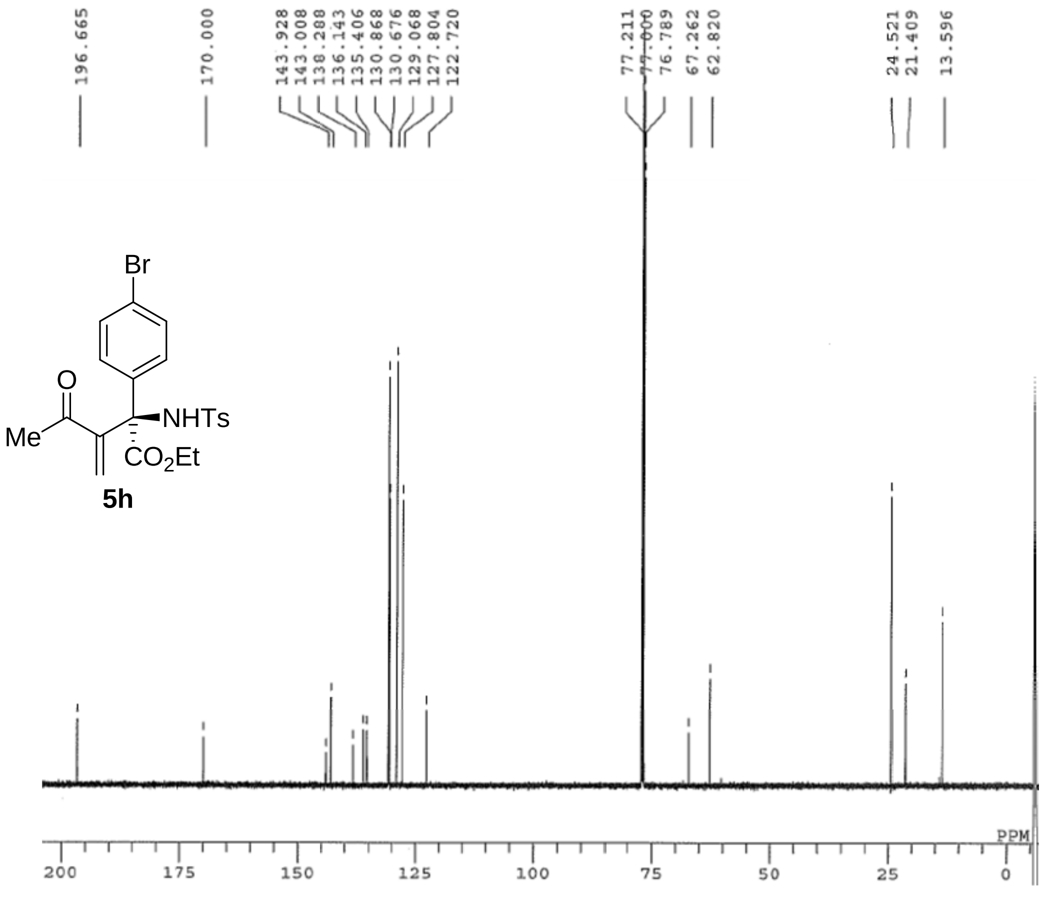

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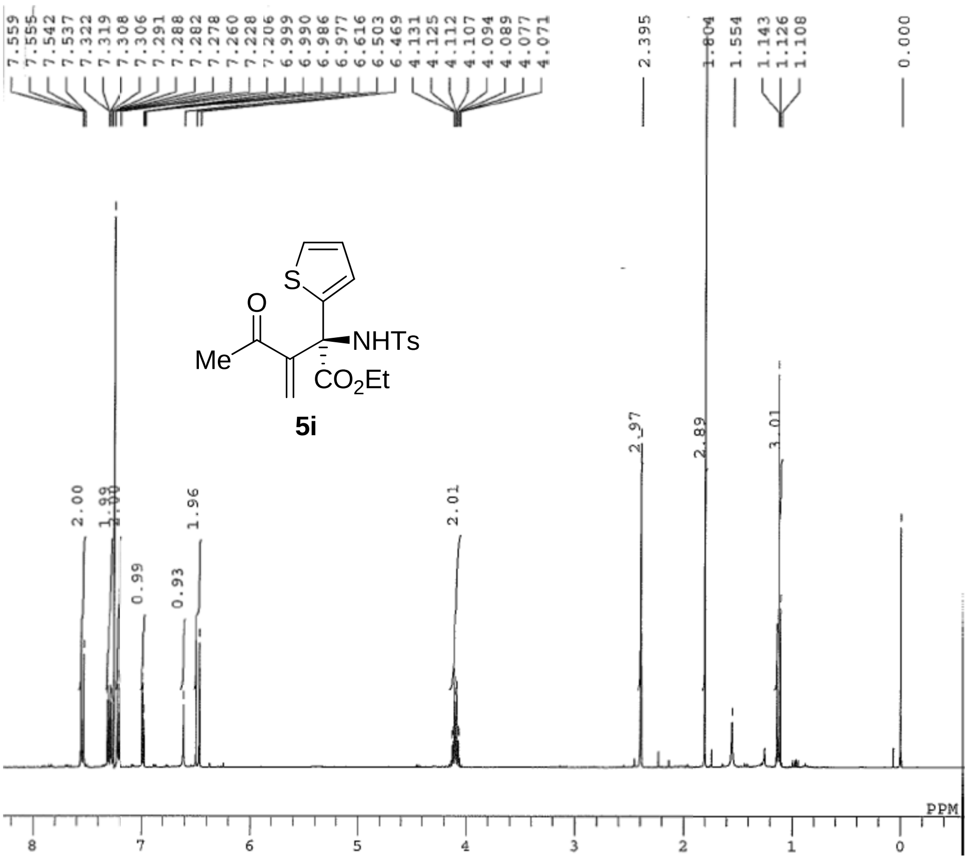

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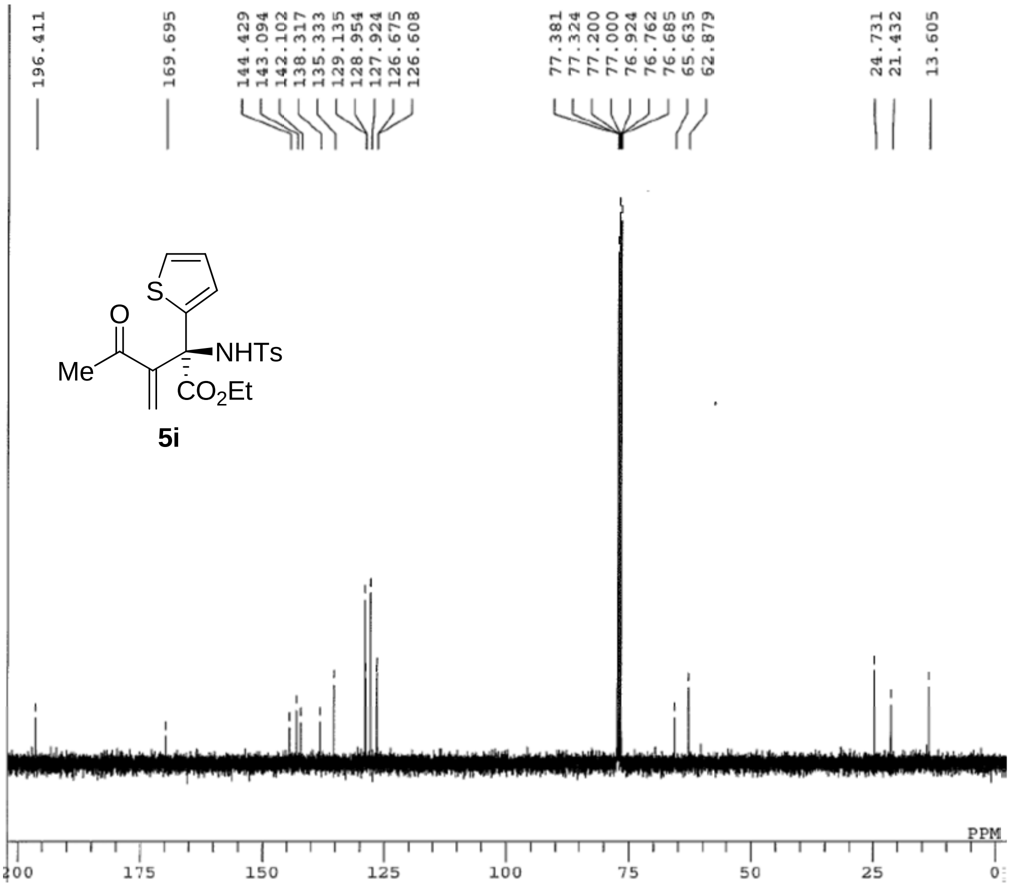

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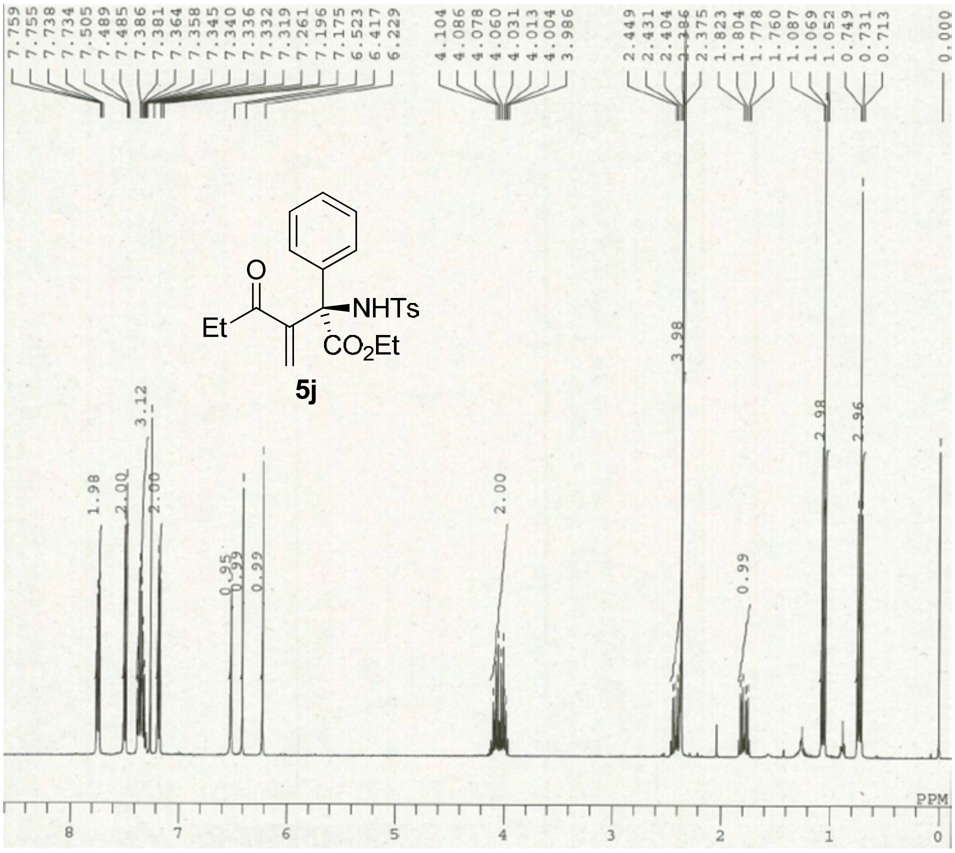

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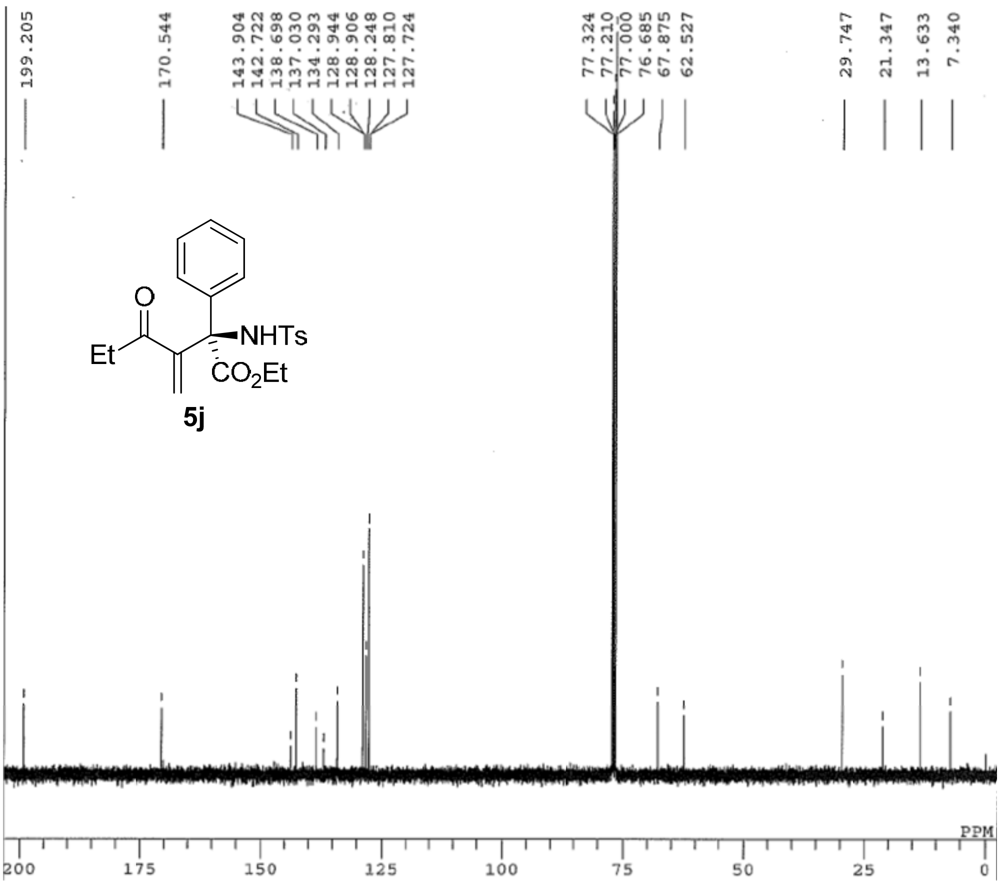

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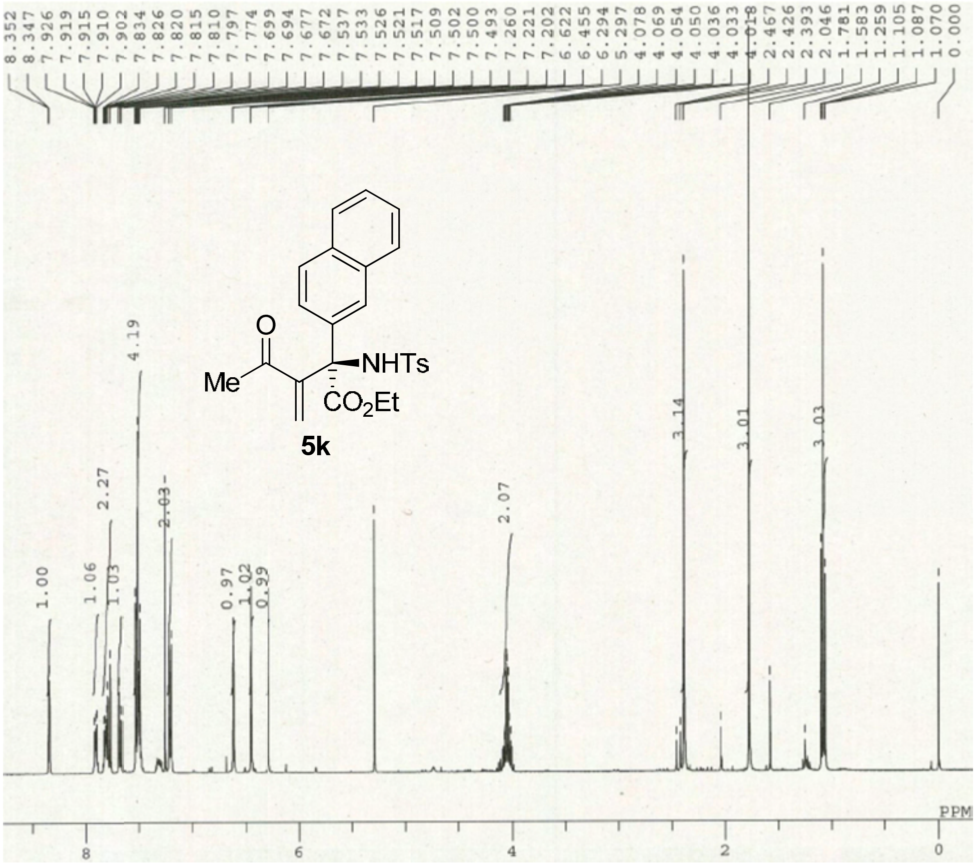

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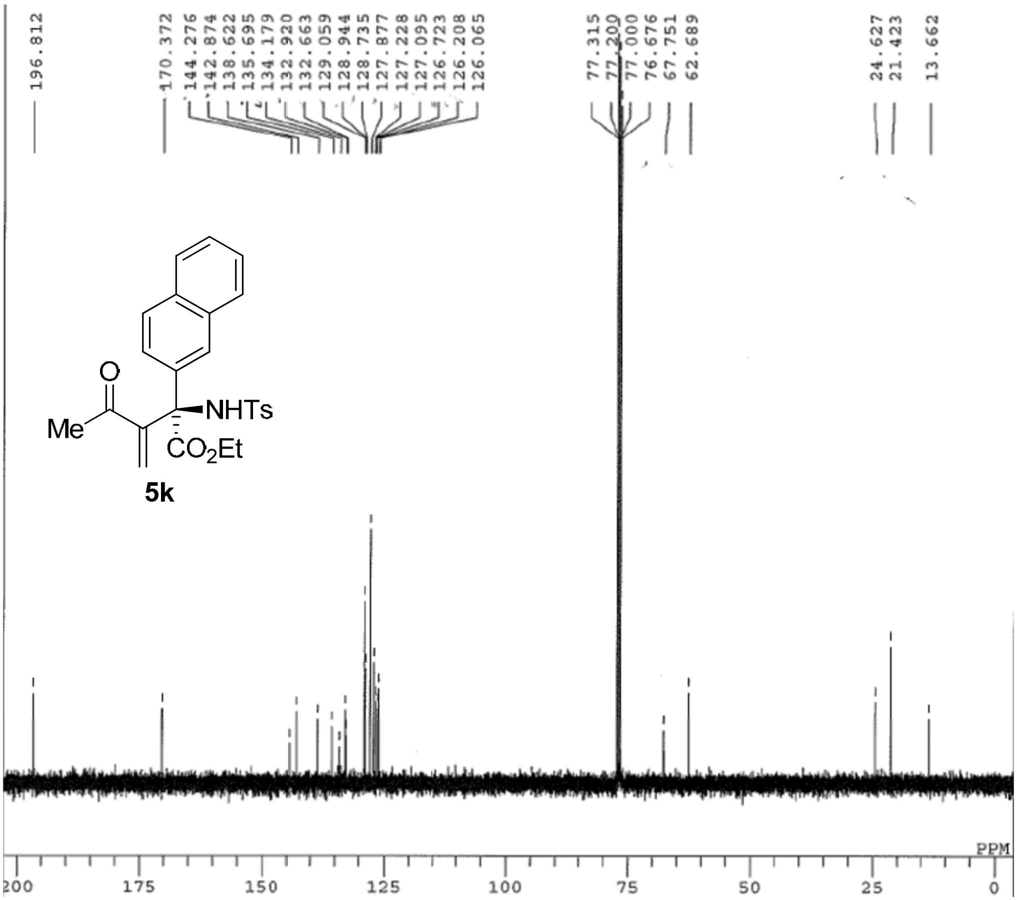

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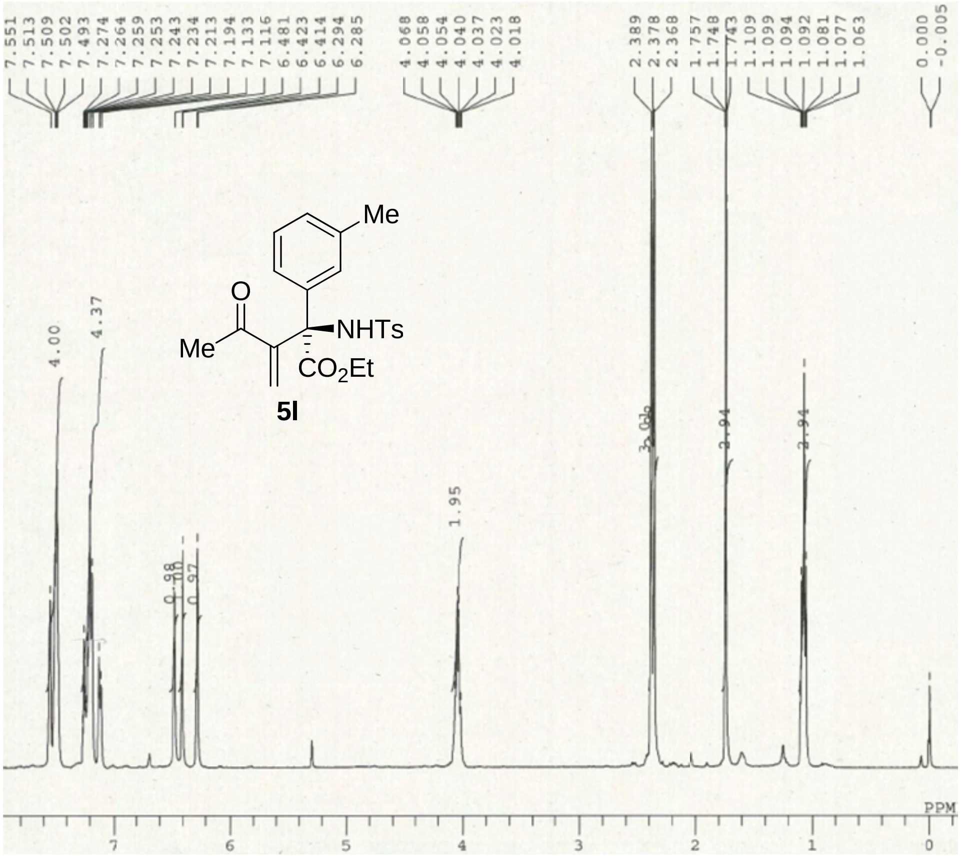

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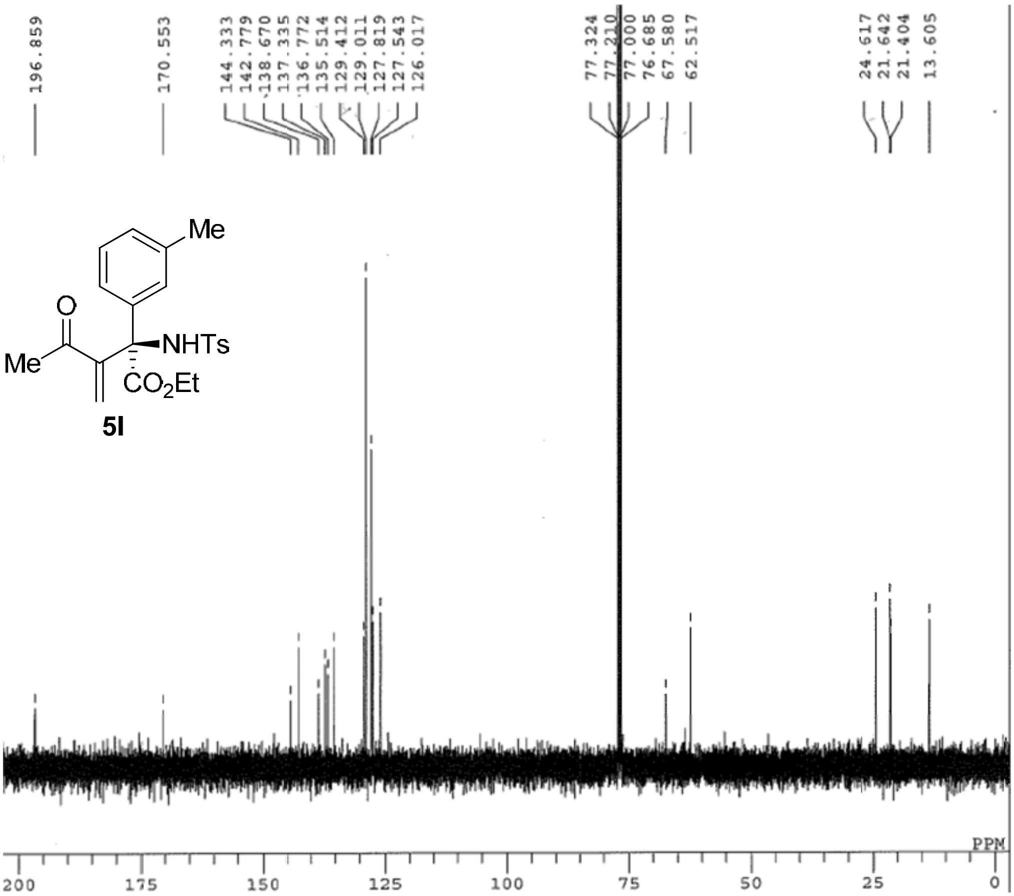

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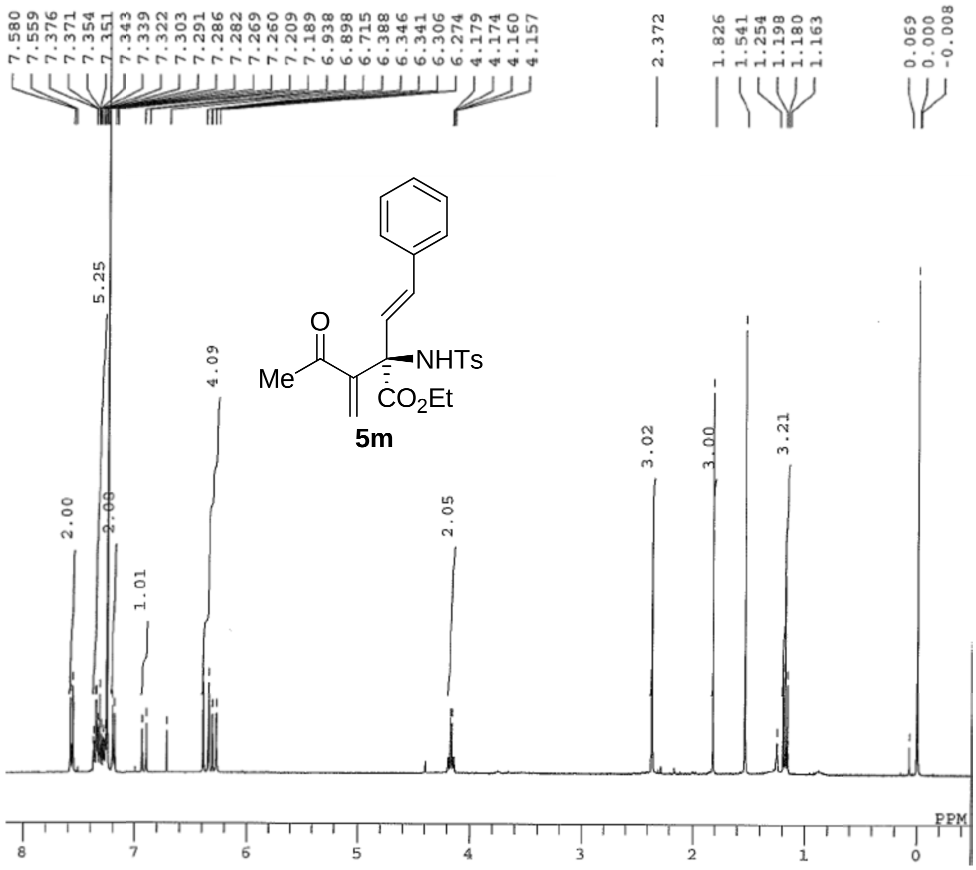

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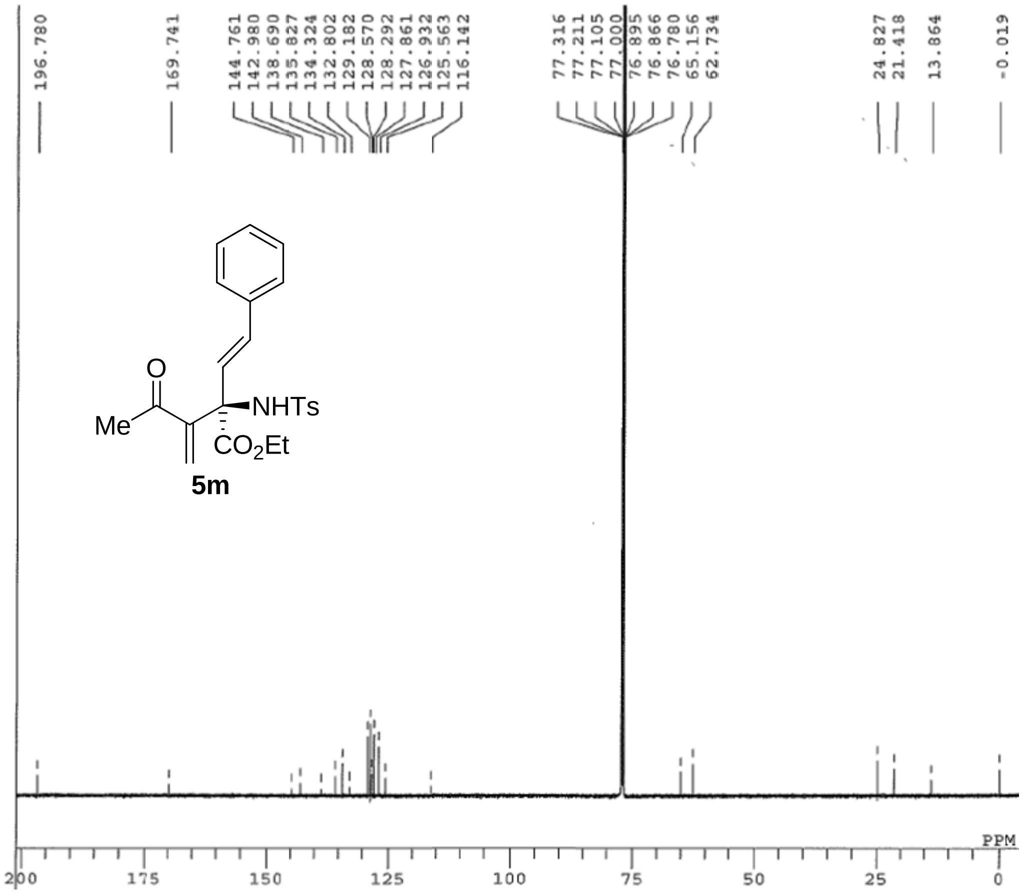

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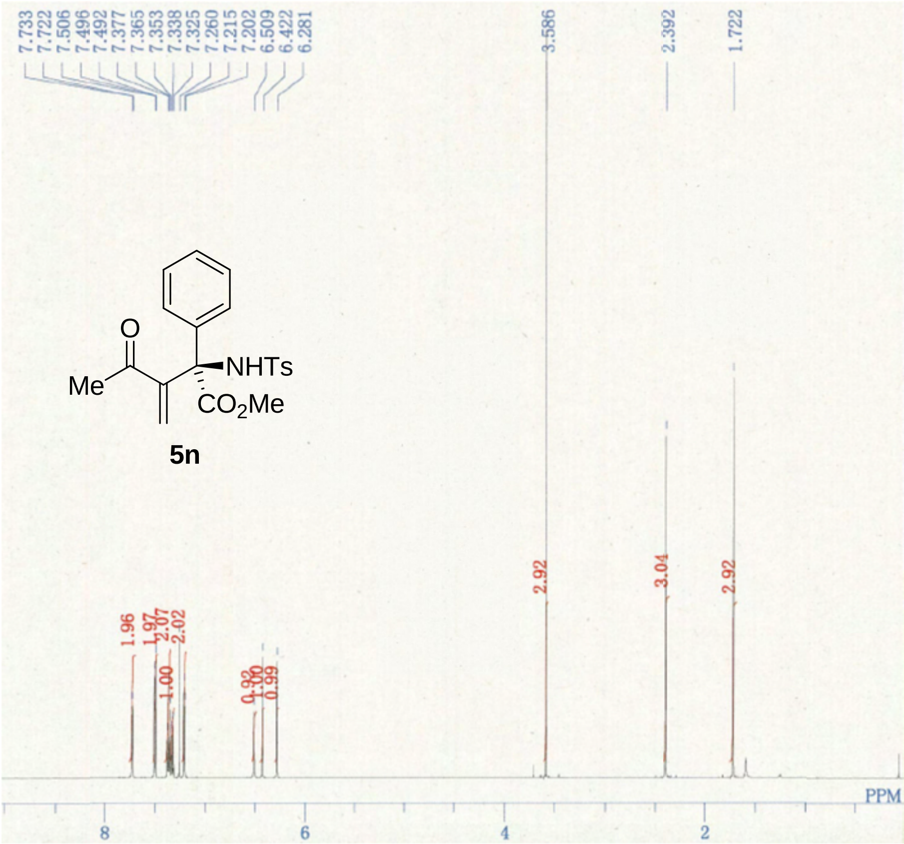

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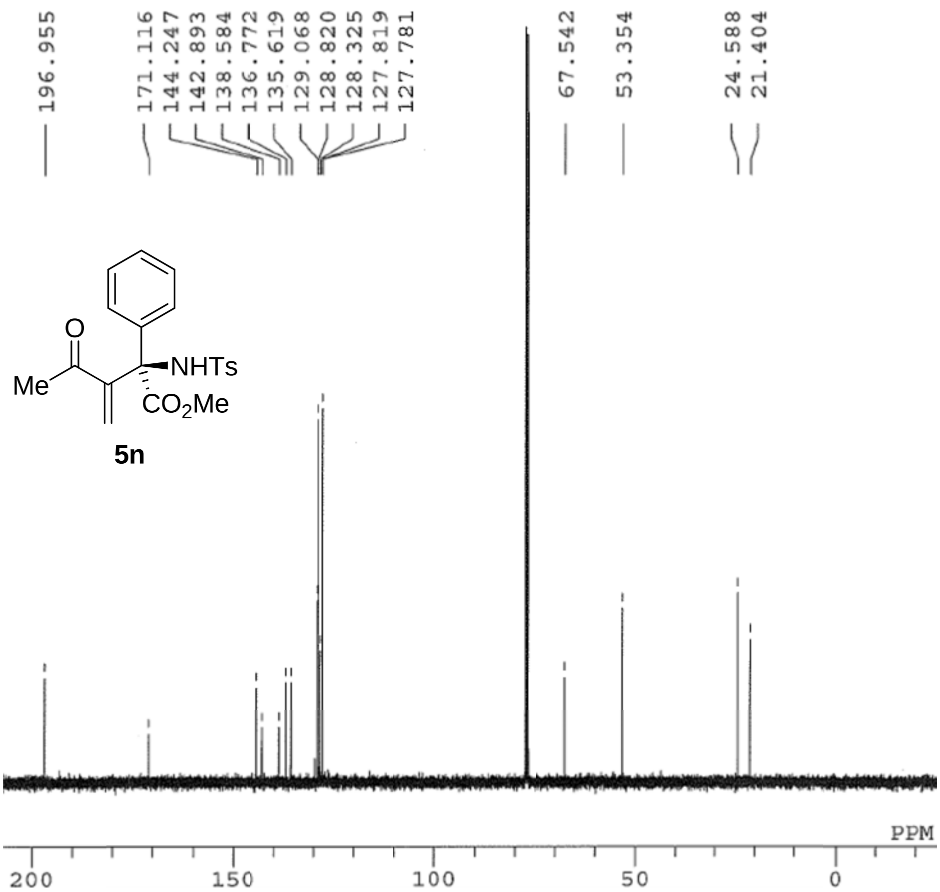

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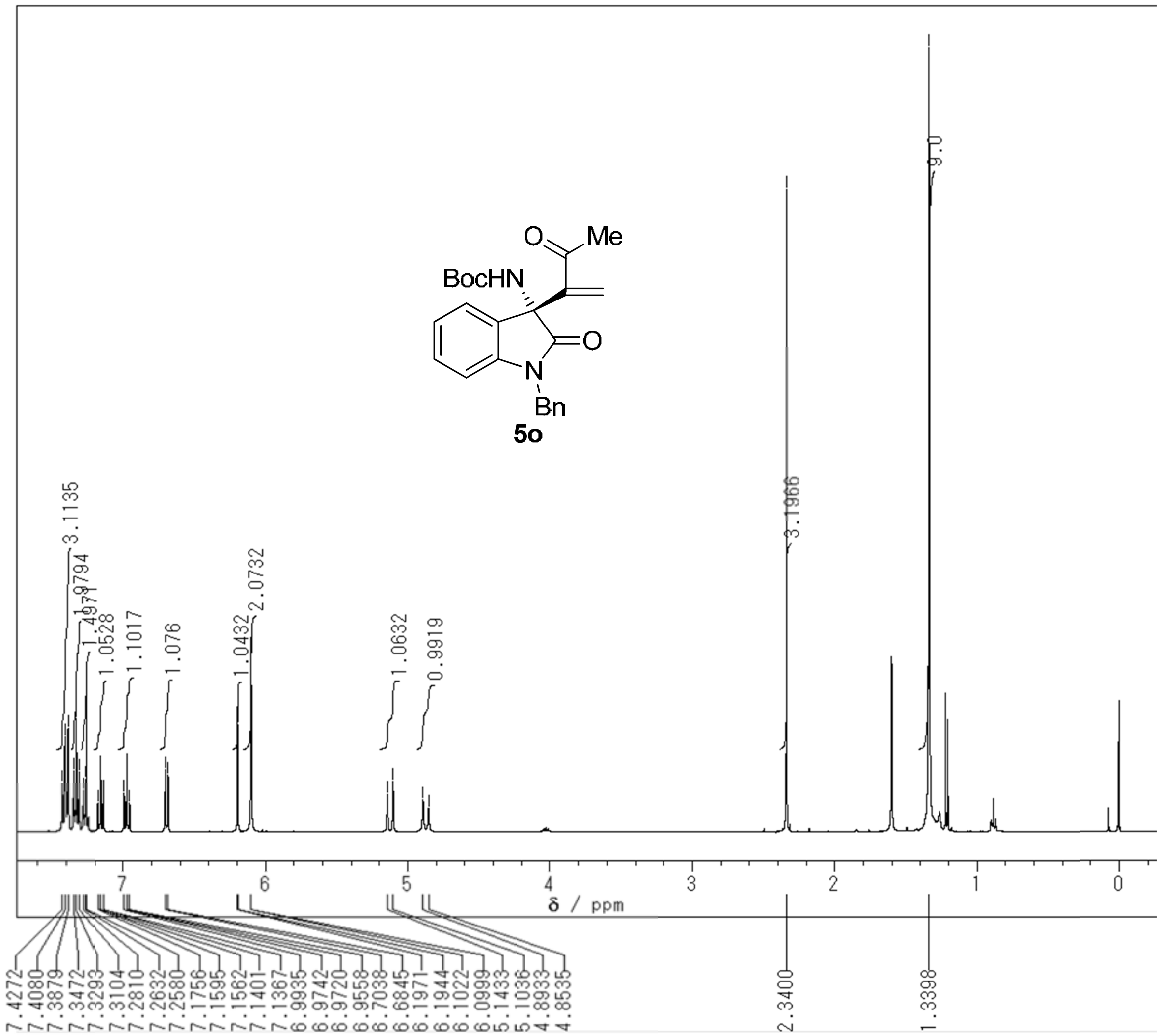

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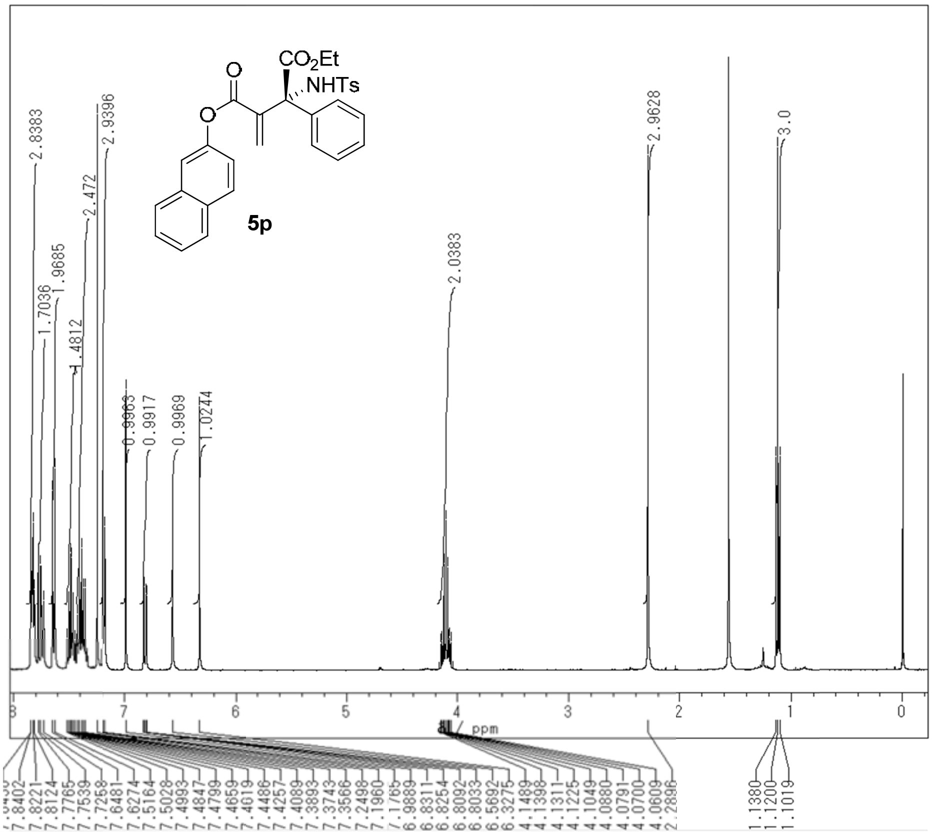

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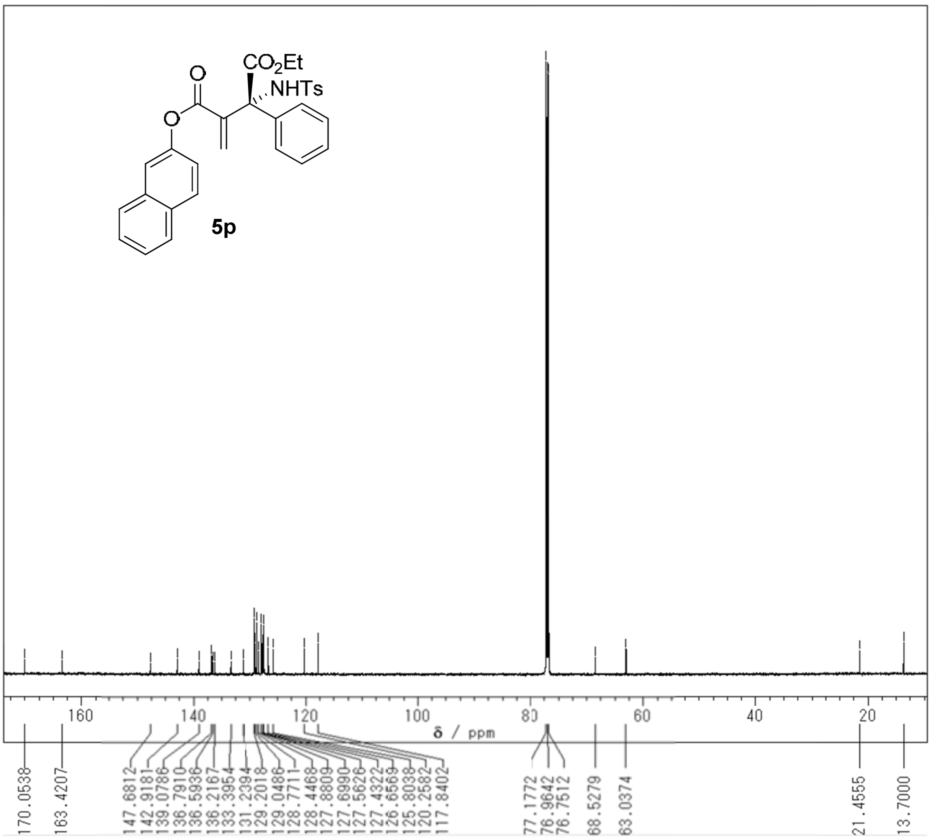

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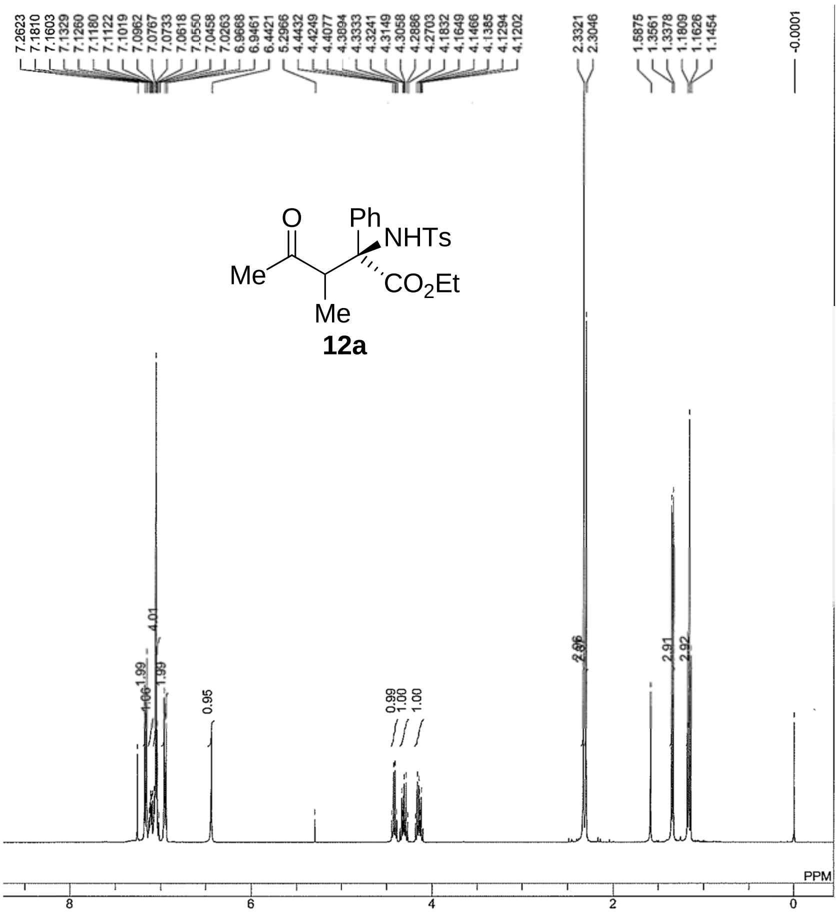

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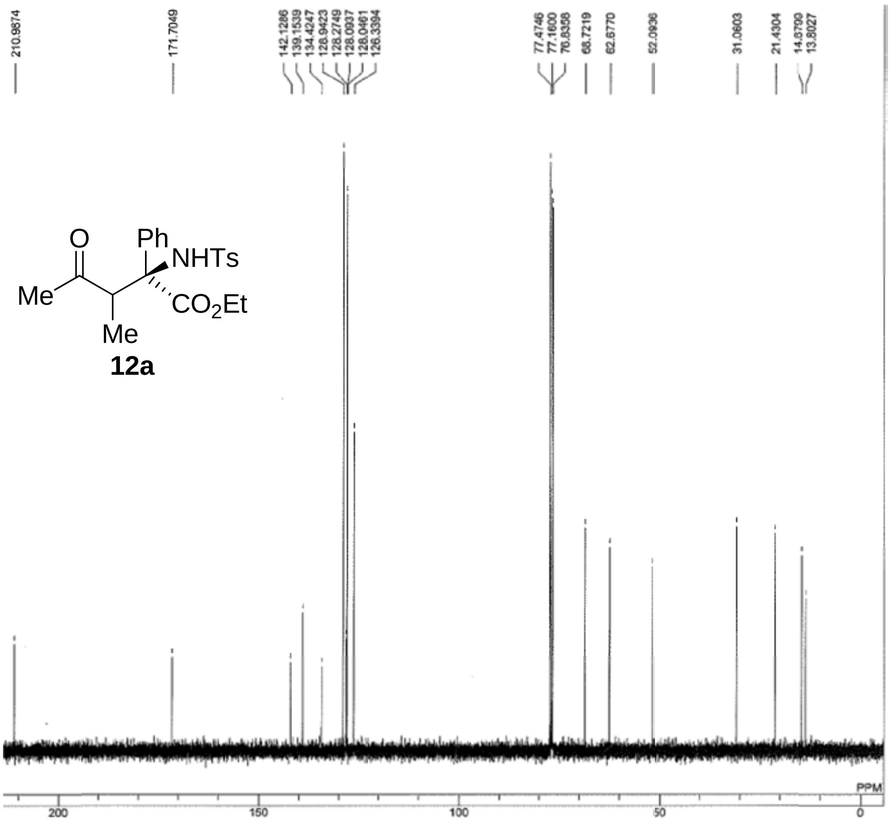

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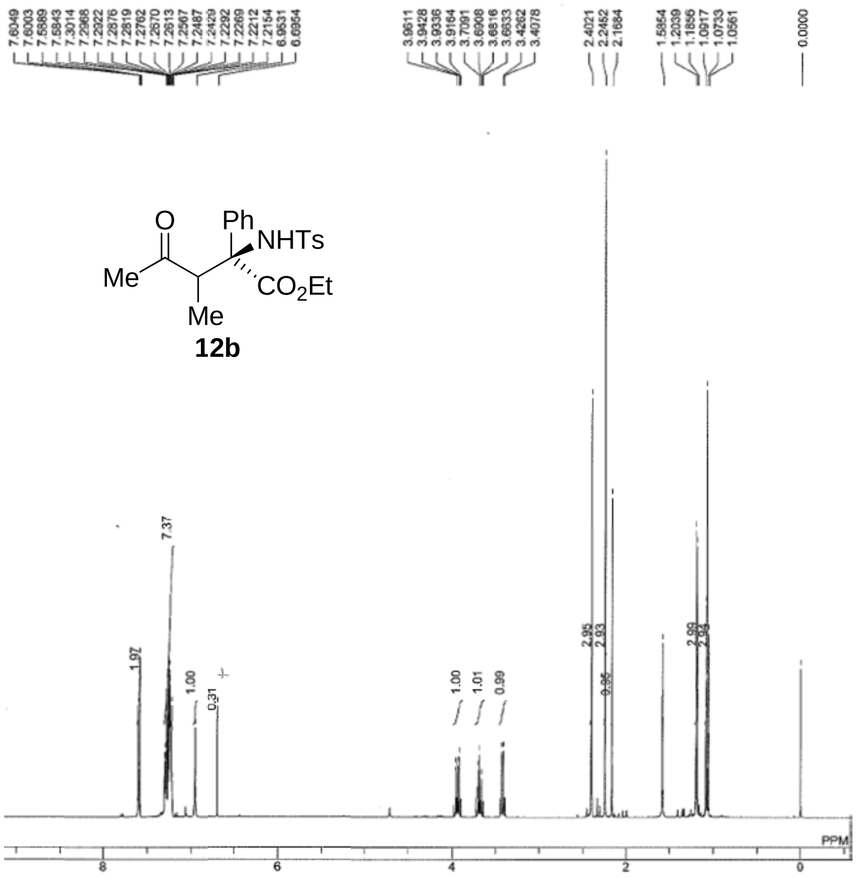

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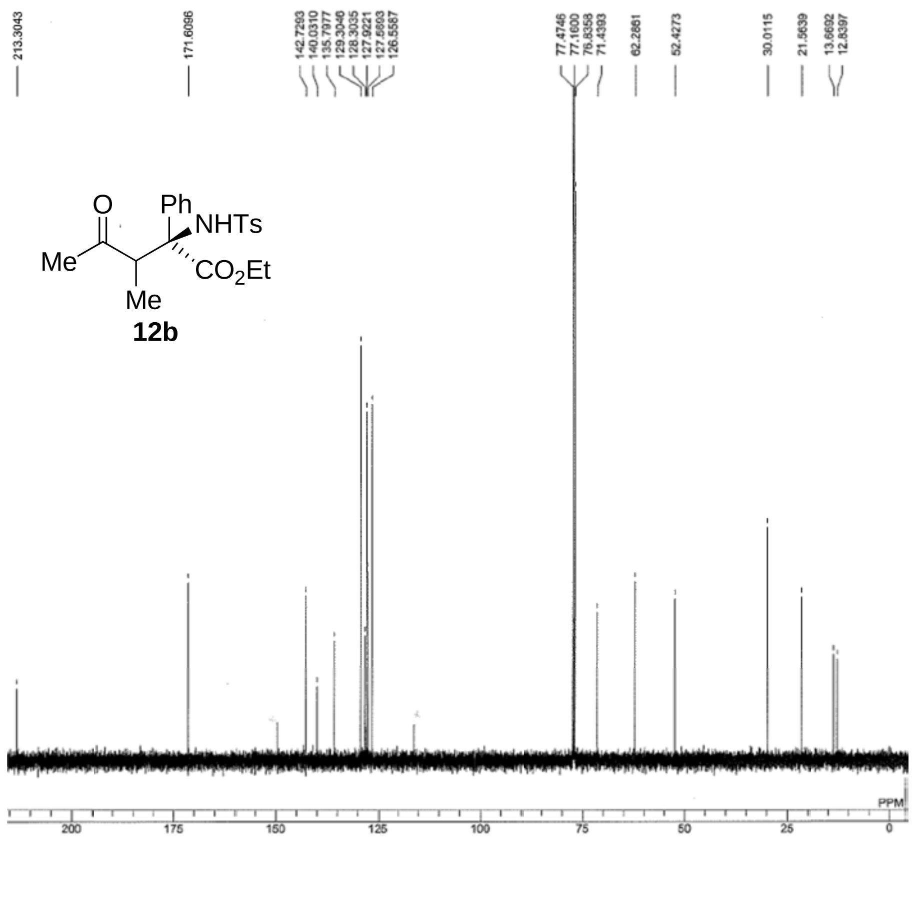

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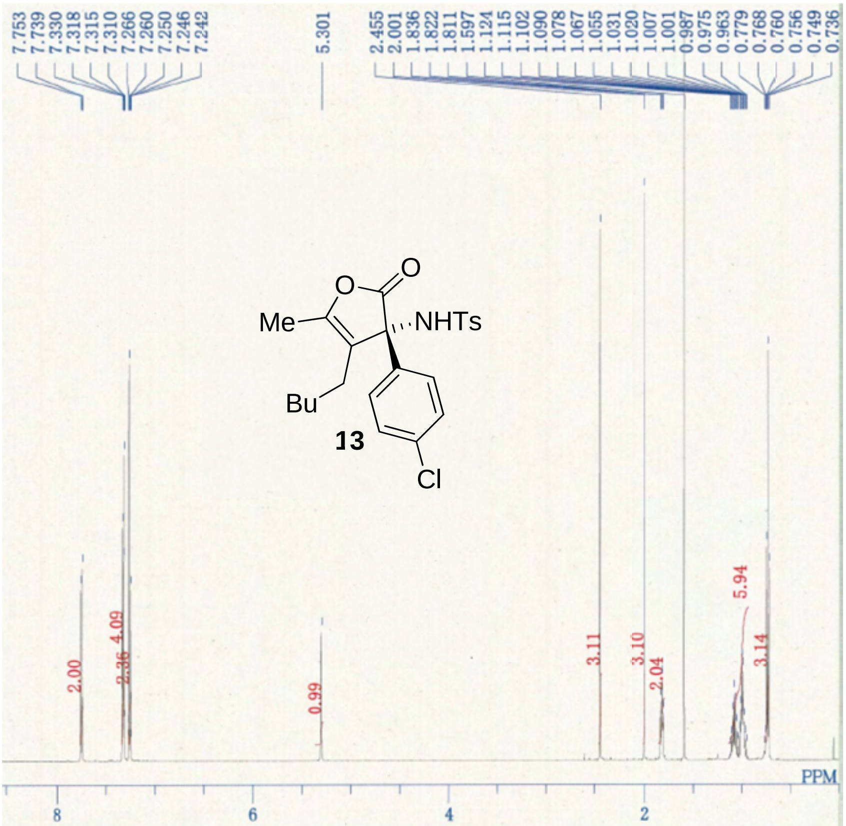

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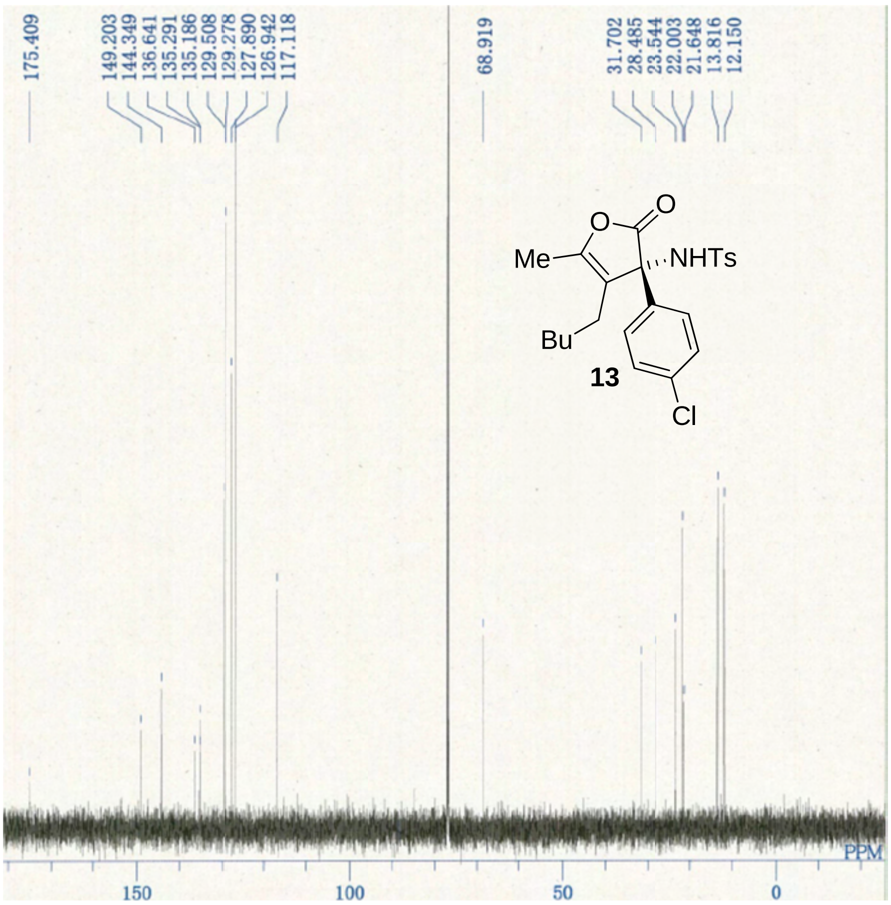

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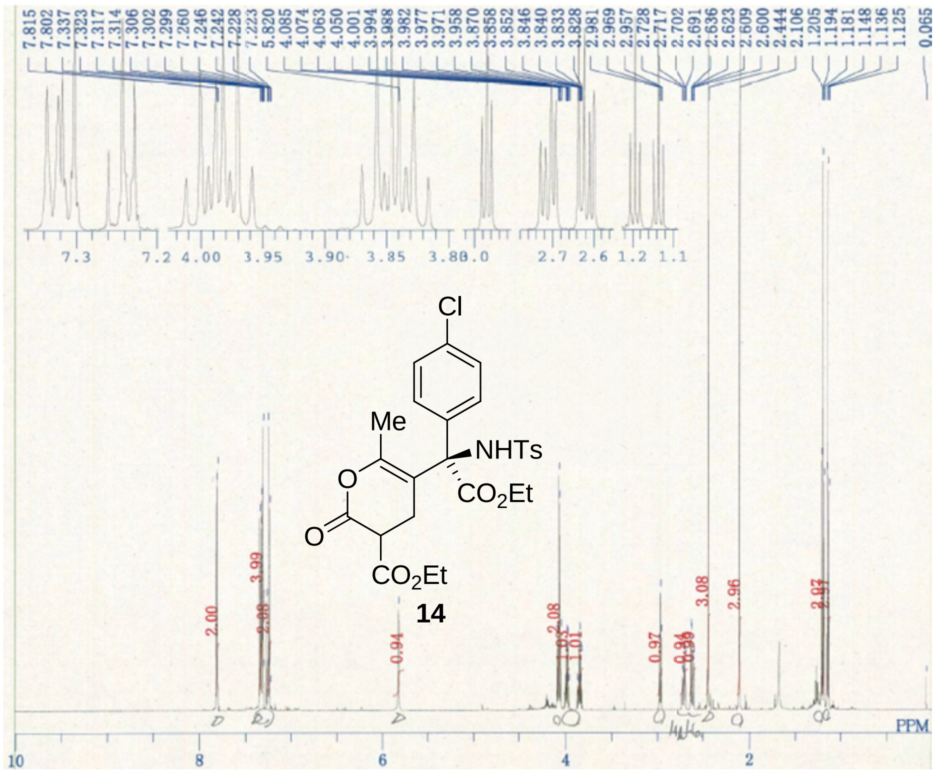

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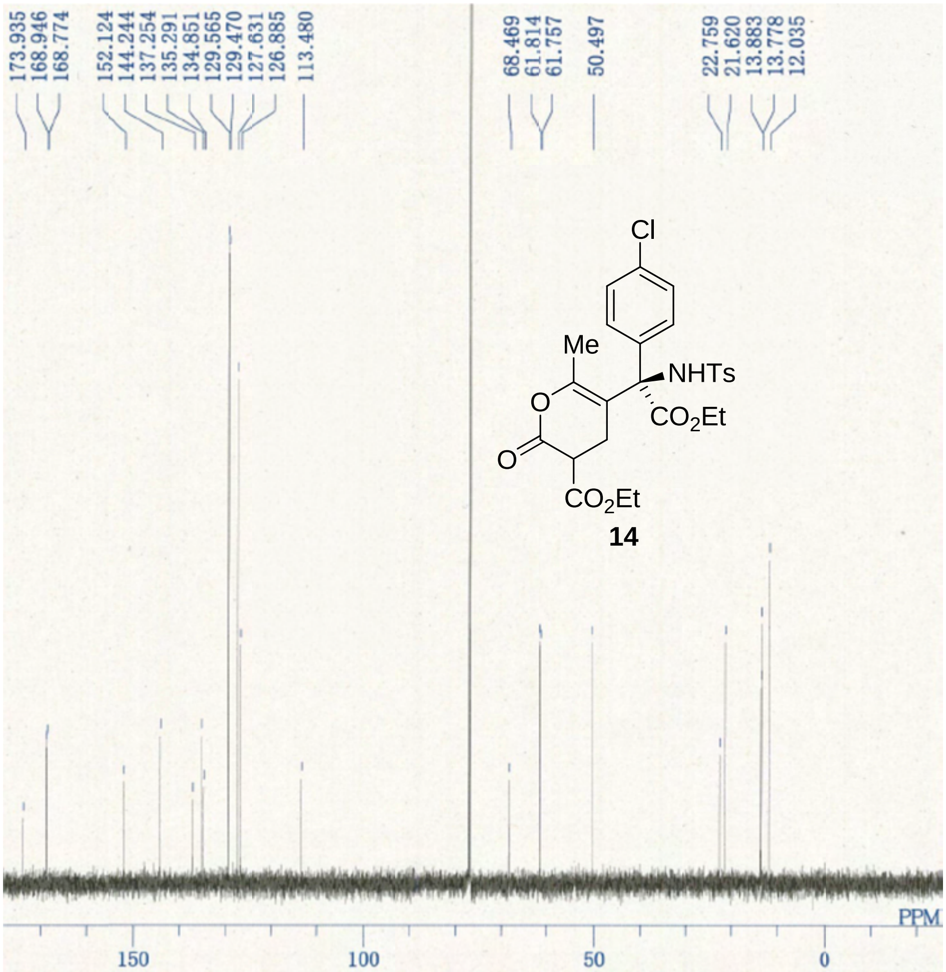

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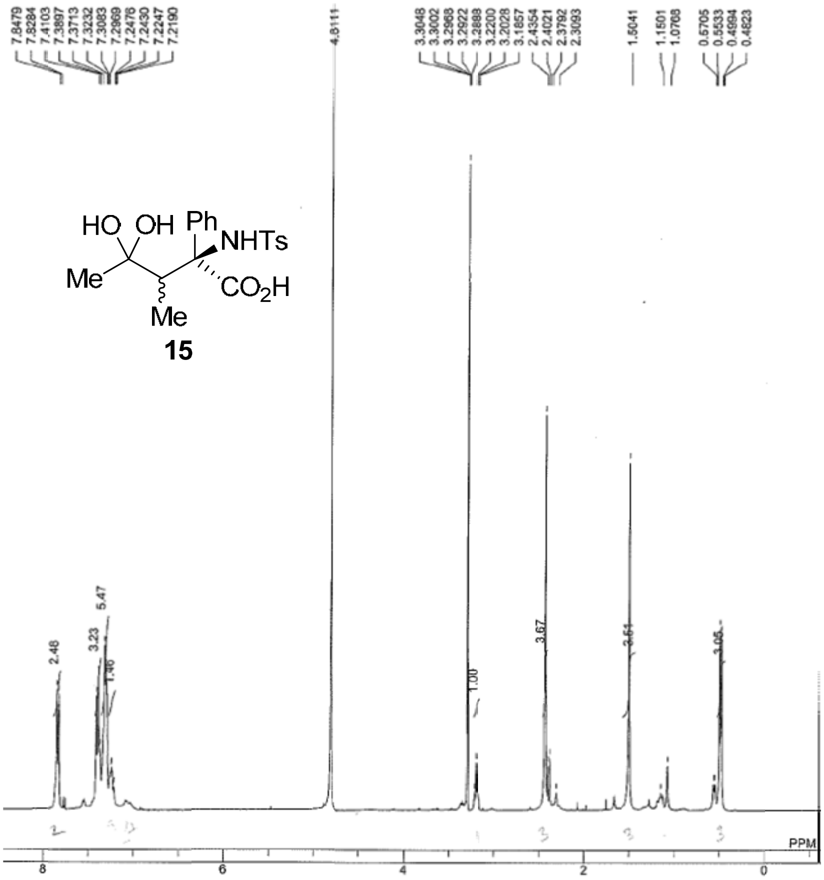

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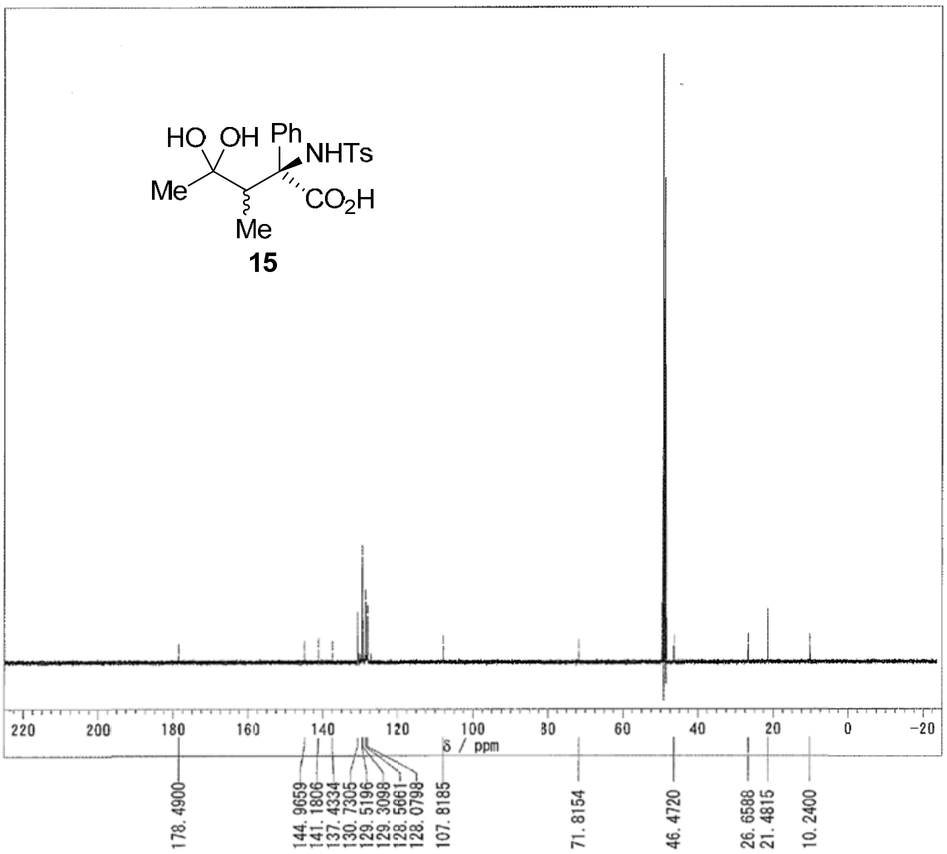

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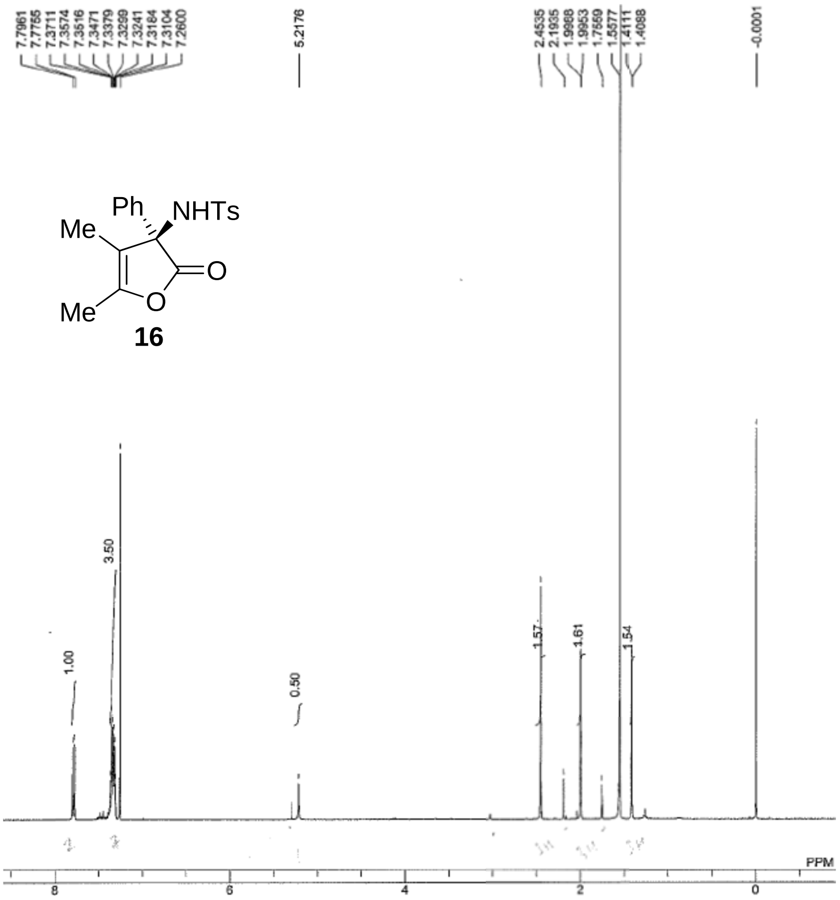

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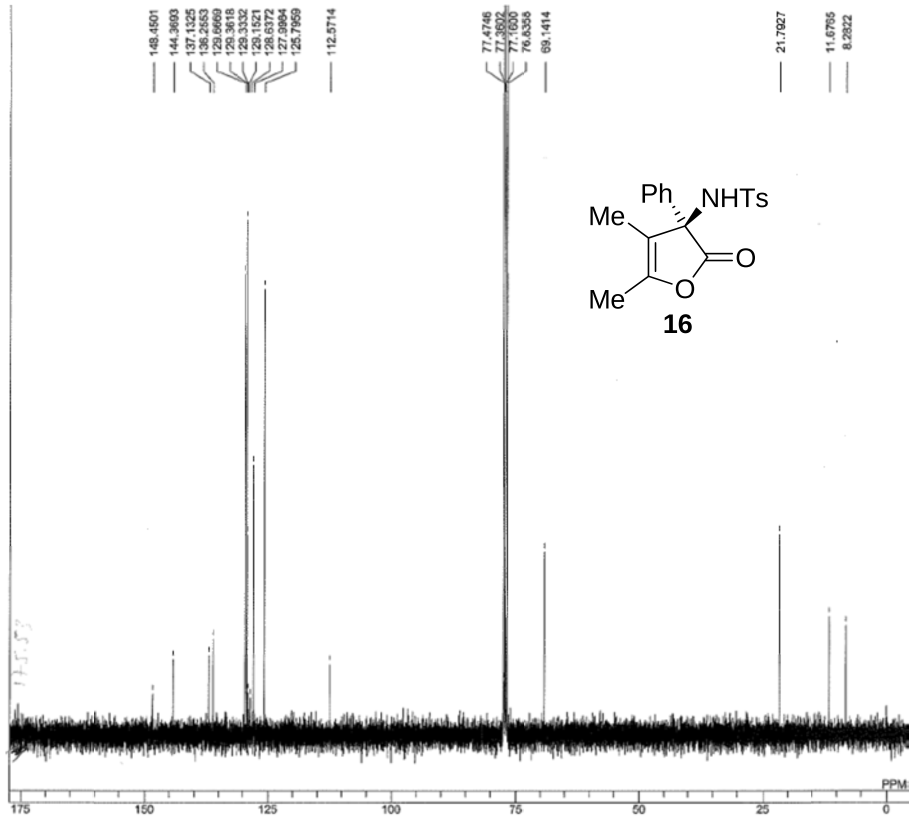
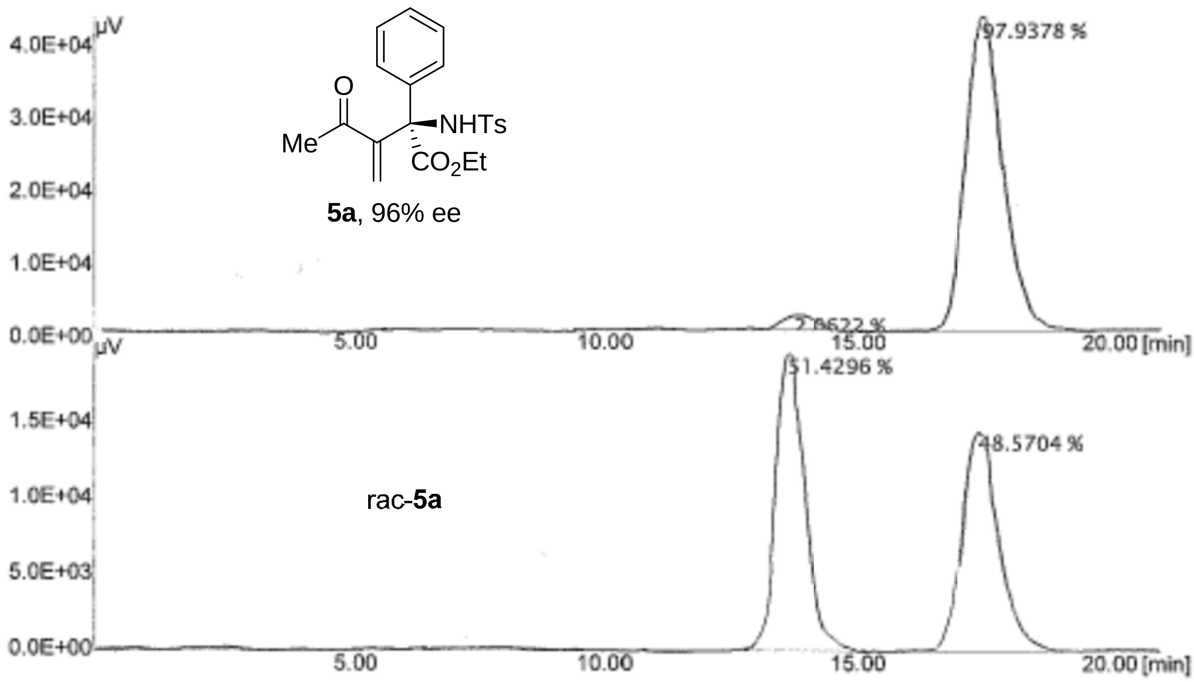


HPLC



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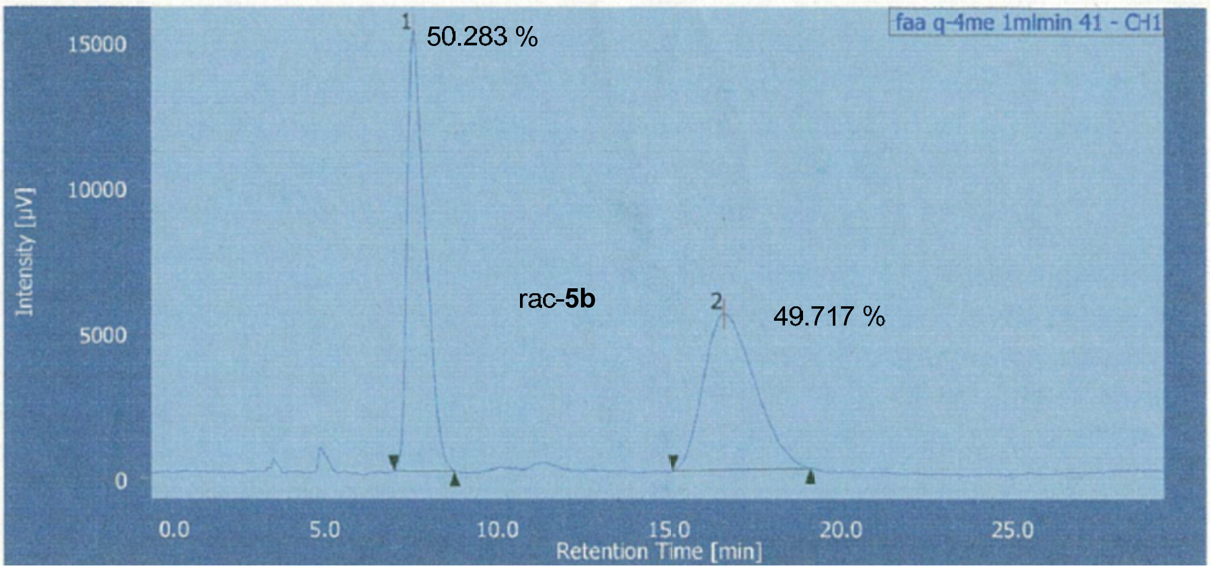

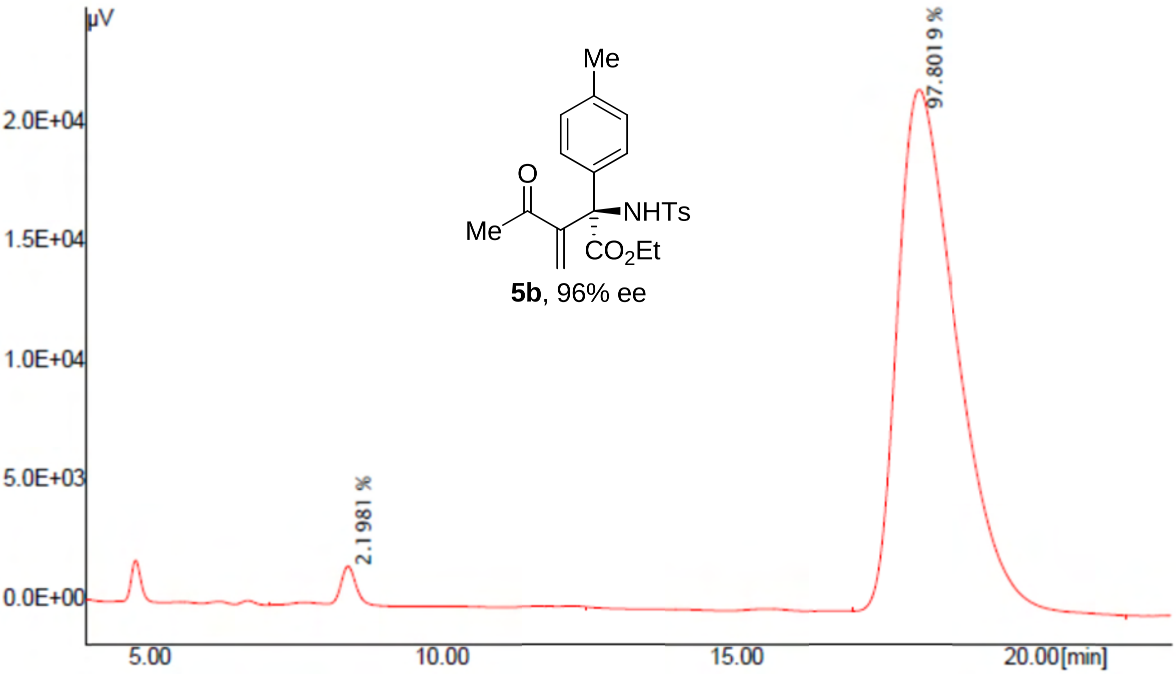

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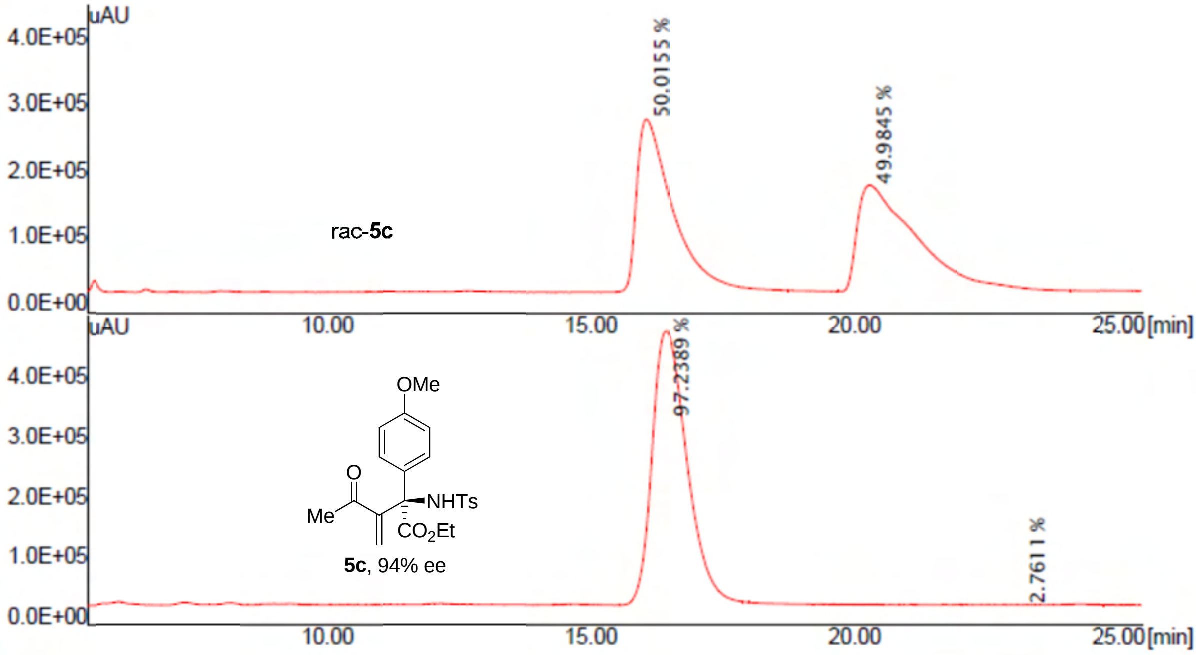

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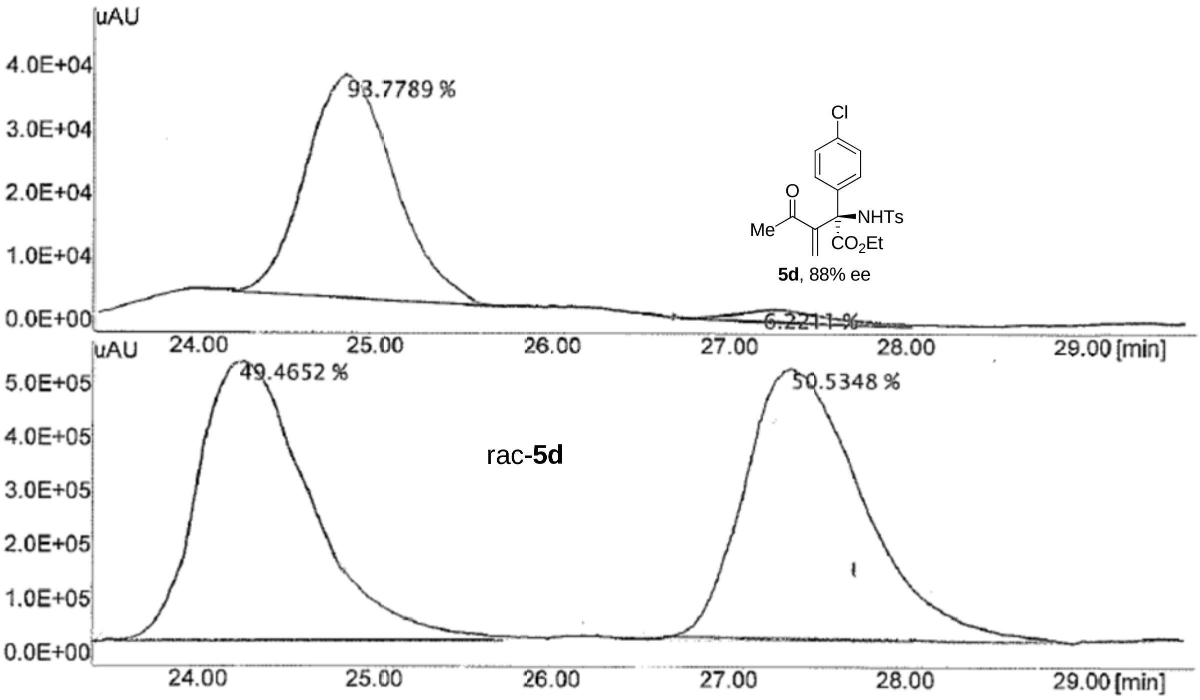

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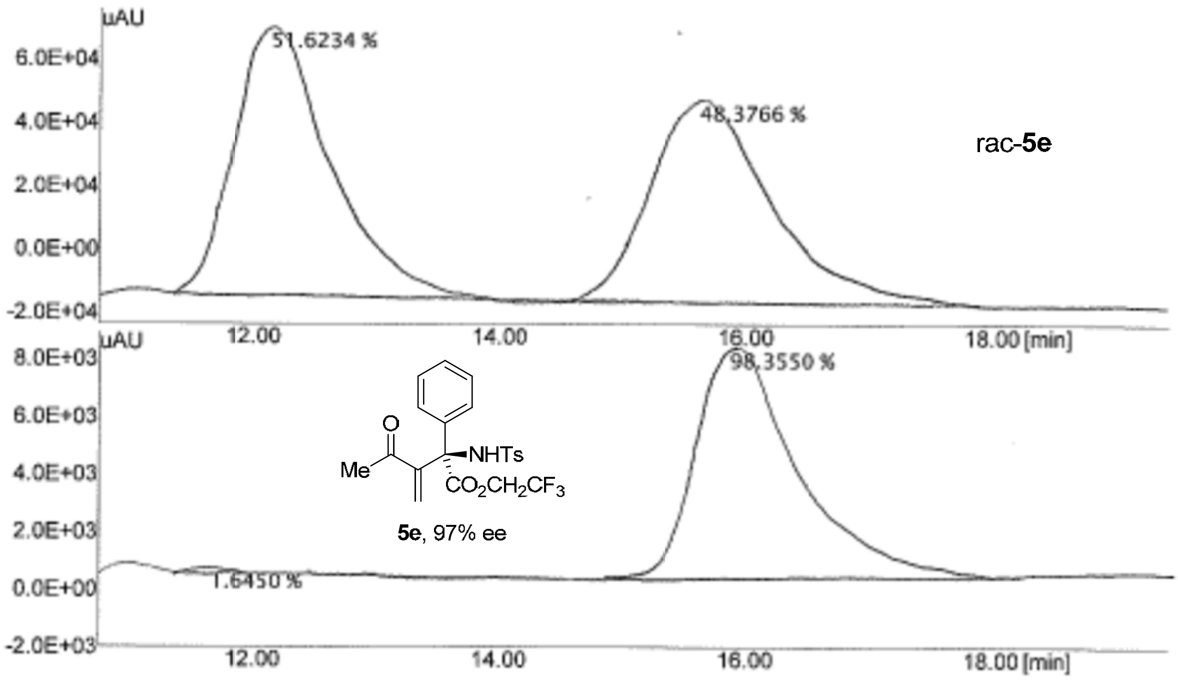

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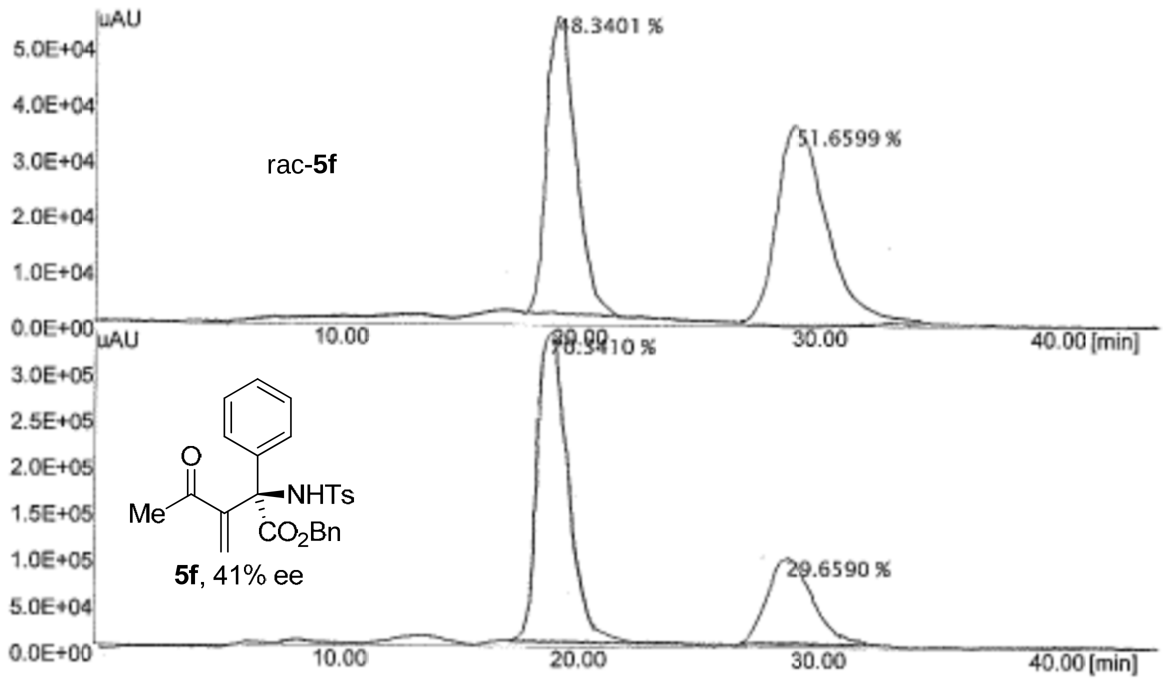

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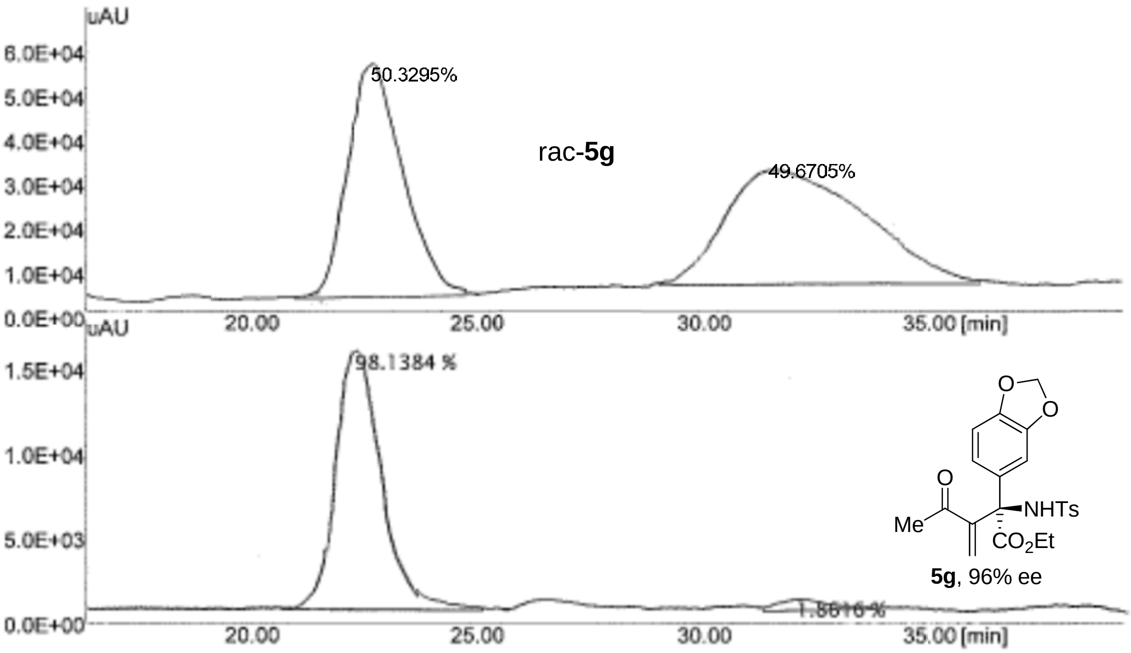

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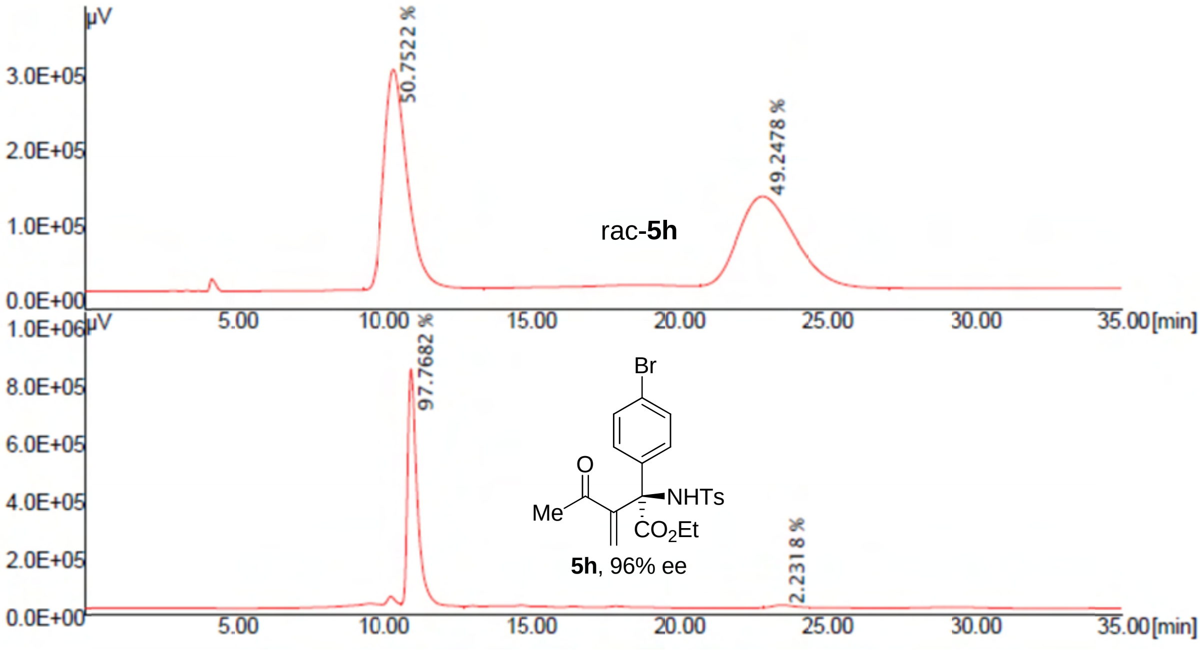

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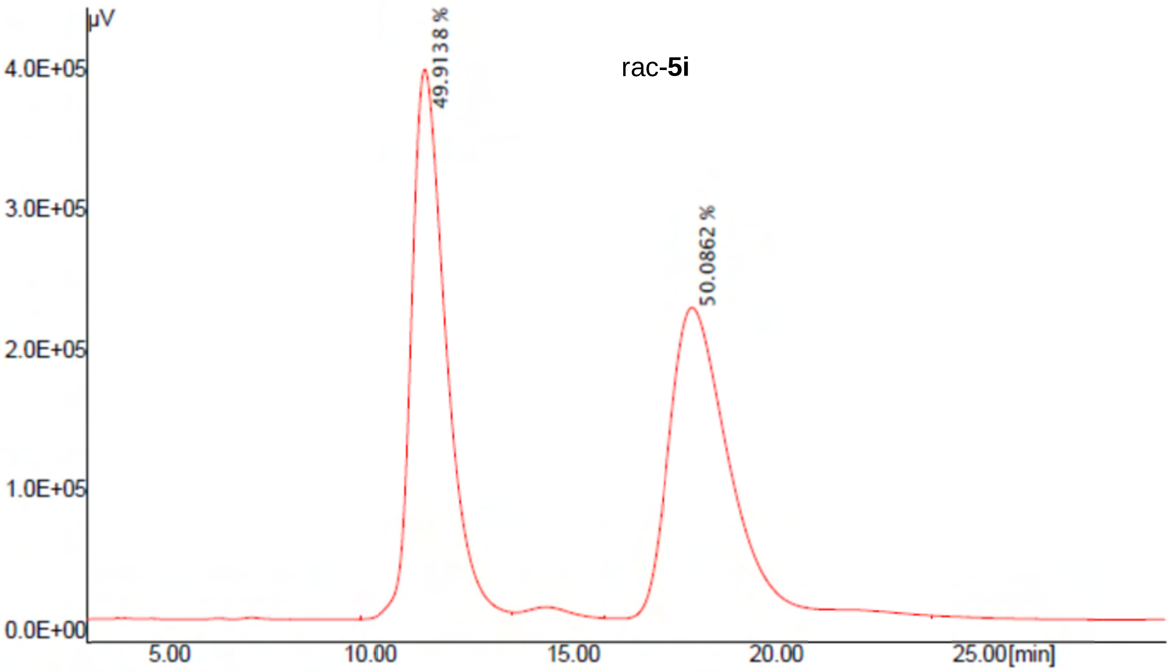

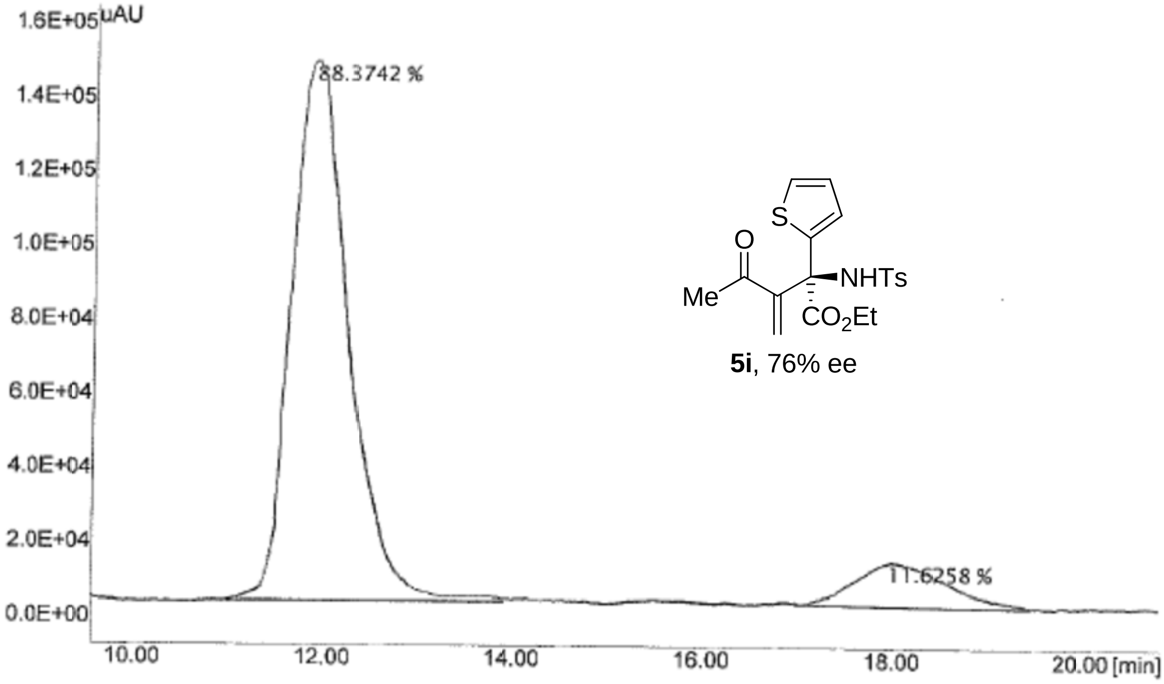

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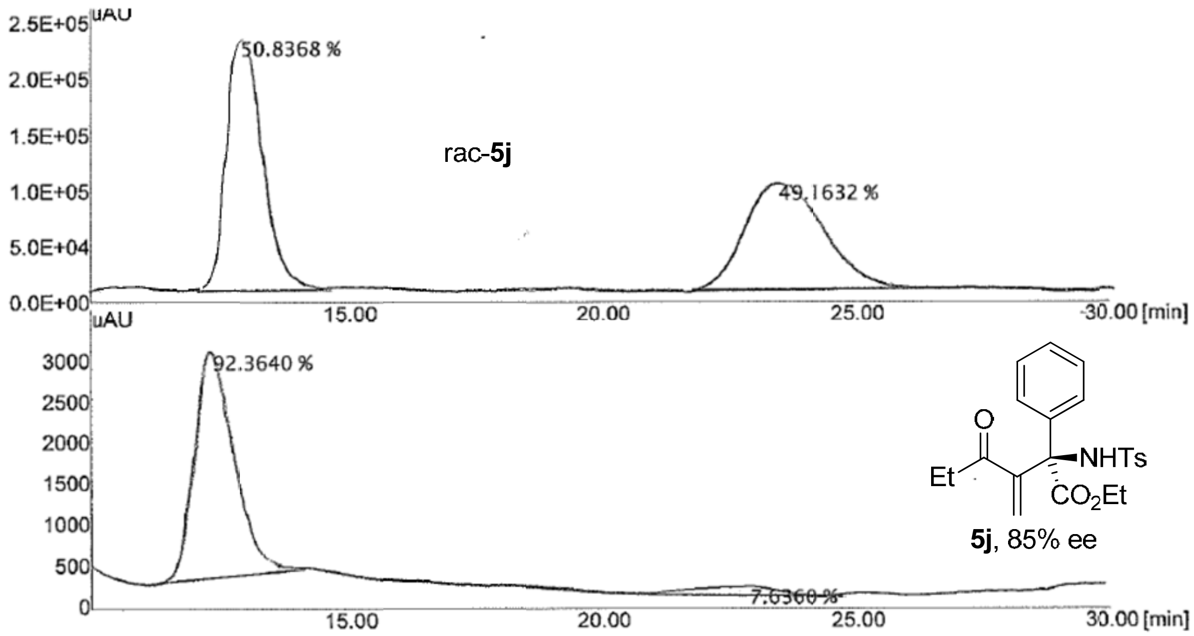

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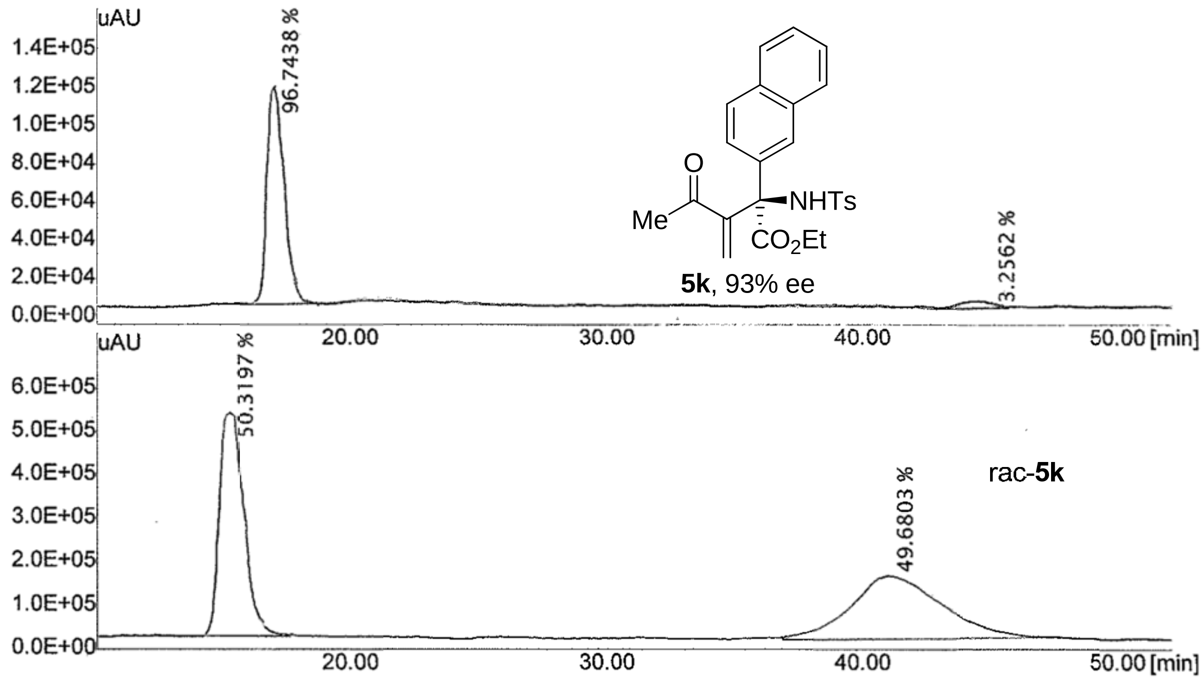

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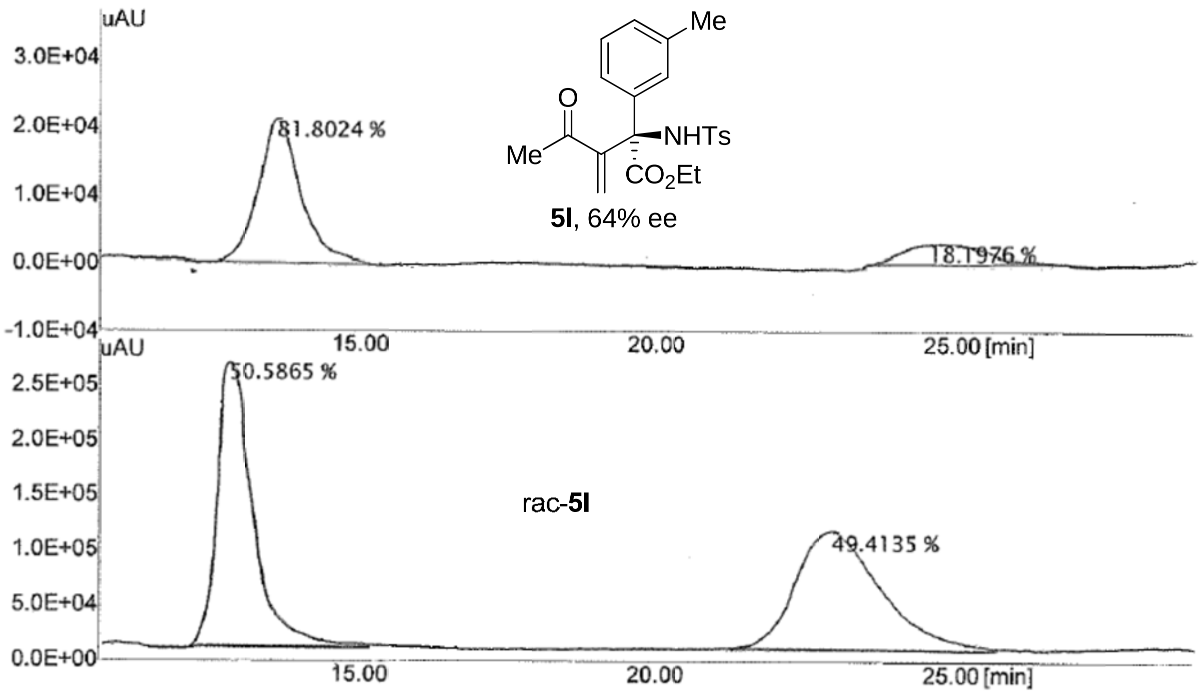

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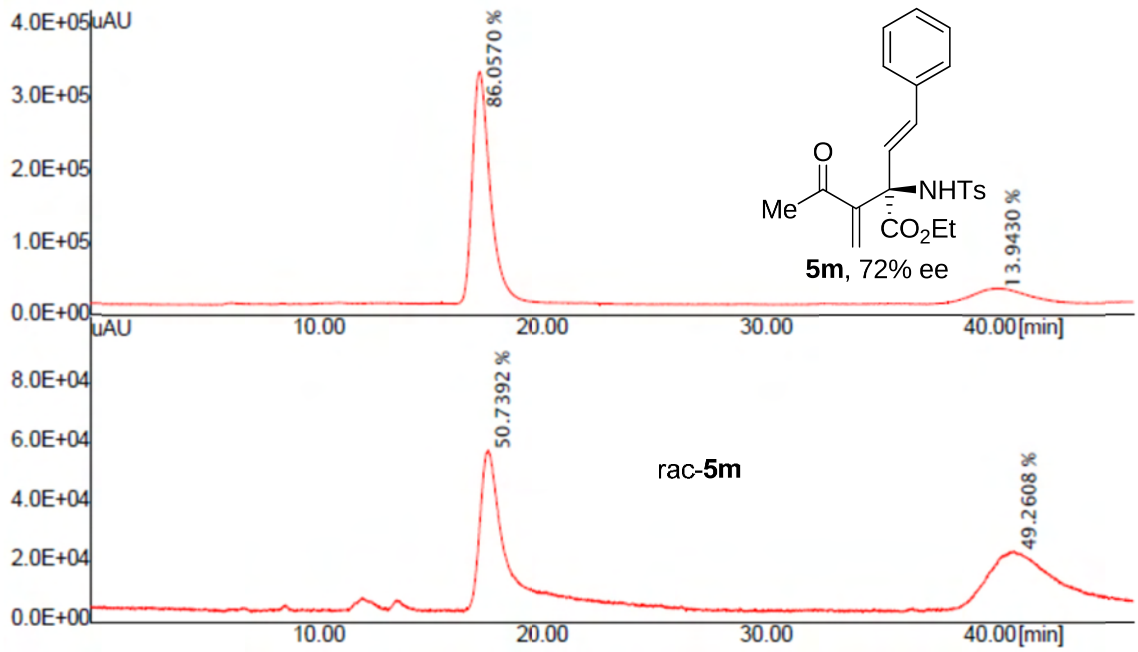

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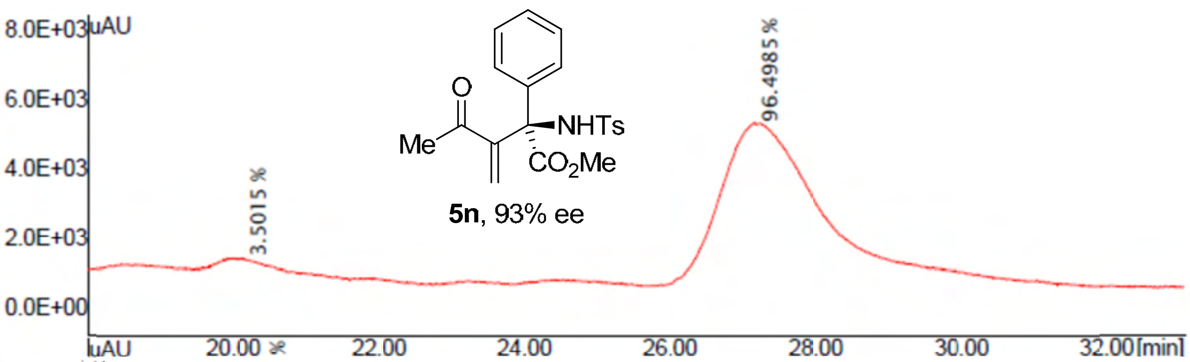
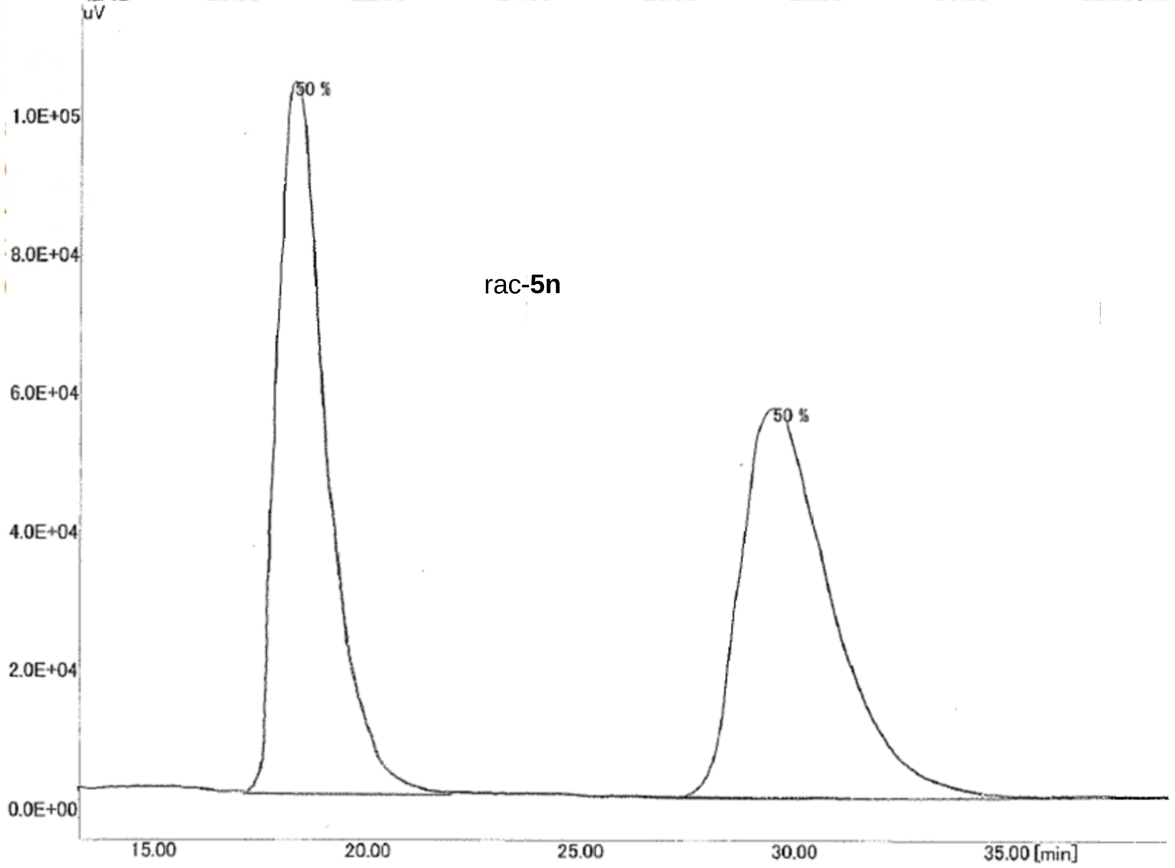
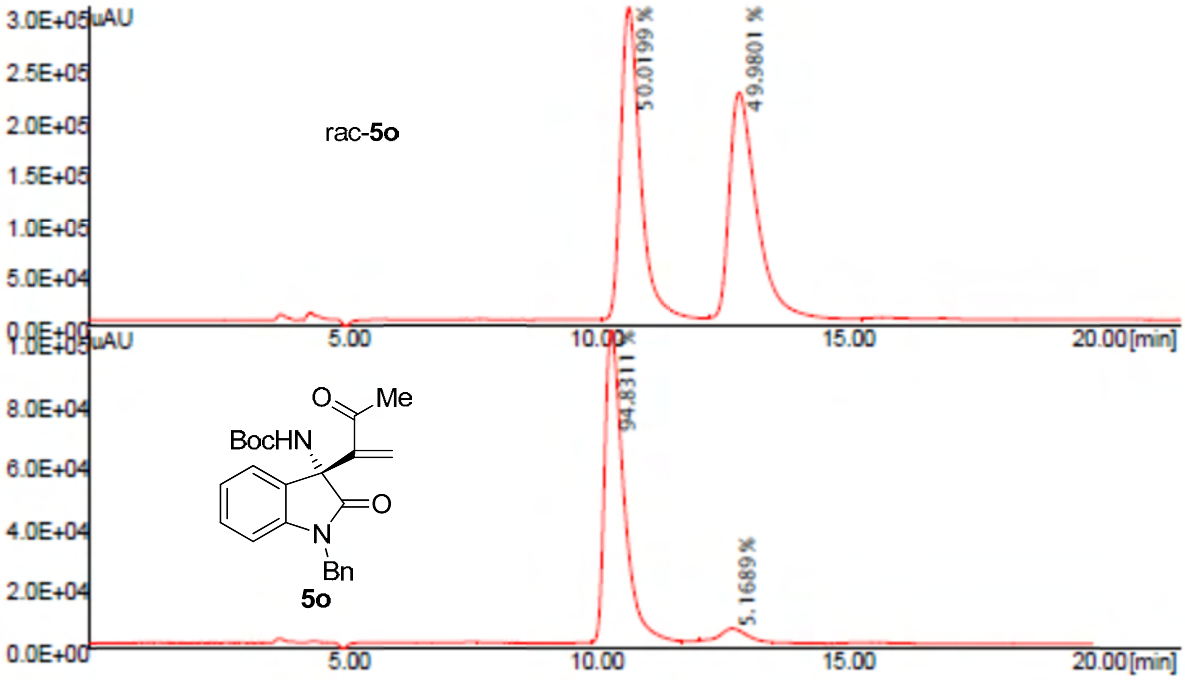




1	20. 213	358	16725. 455	3. 50
2	27. 240	4702	460941. 207	96. 50



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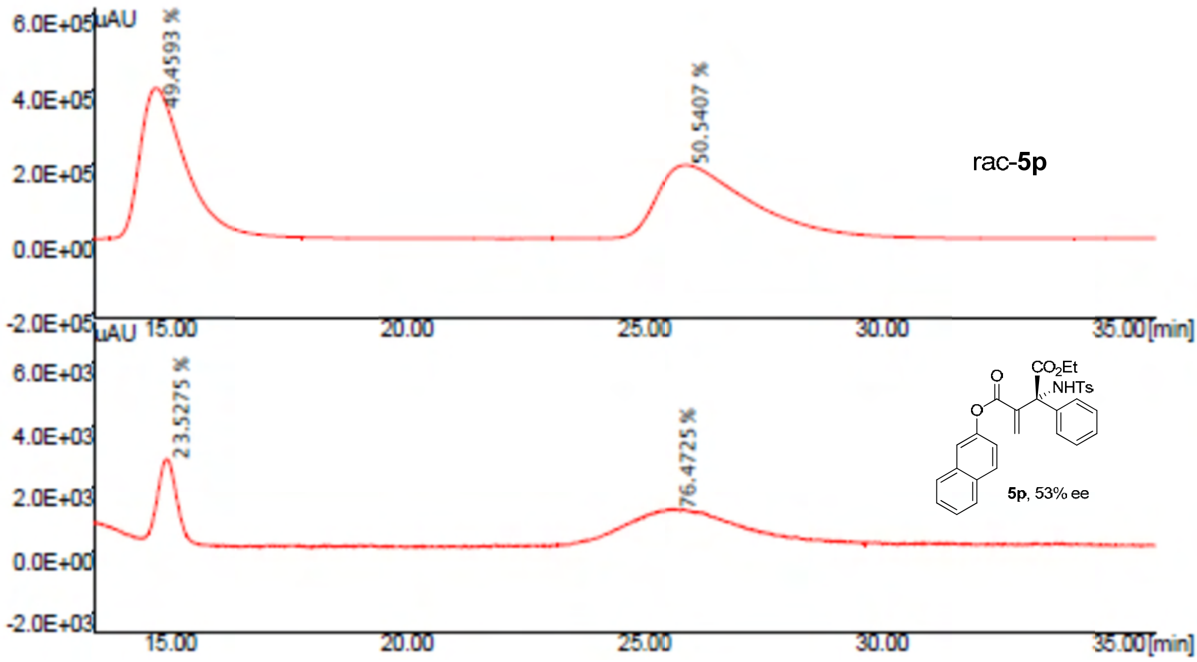

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Crystal data

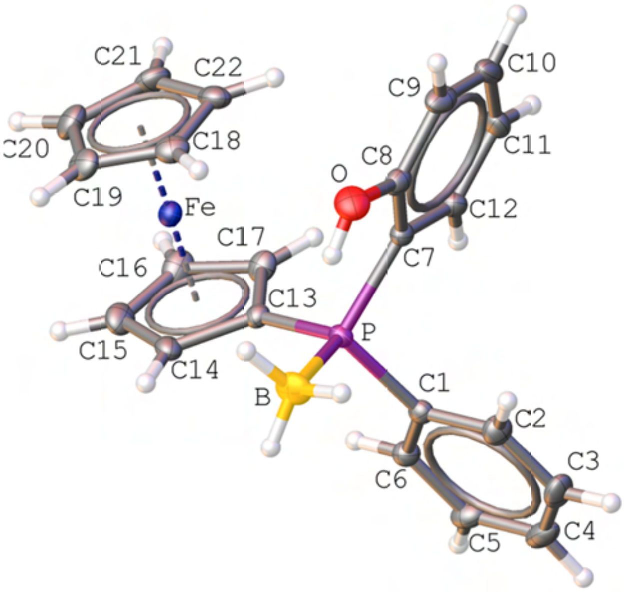

Figure S1: OLEX2 view of the (*S*)-ferrocenyl(2-hydroxypheny)phenylphosphine **1e-BH$_3$** showing thermal ellipsoids at the 50 % probability level. [Crystallographic data (**1e-BH$_3$**) for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 945143. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk/data_request/cif)].

Table S3. Crystal data and structure refinement for **1e-BH$_3$**

Identification code	10er966p	
Empirical formula	C22 H22 B Fe O P	
Formula weight	400.03	
Temperature	115(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 7.3100(2) Å	a= 90°.
	b = 15.1078(5) Å	b= 110.282(2)°.
	c = 9.1520(3) Å	g = 90°.
Volume	948.06(5) Å^3	
Z	2	
Density (calculated)	1.401 Mg/m^3	
Absorption coefficient	0.887 mm^{-1}	
F(000)	416	
Crystal size	0.25 x 0.20 x 0.17 mm^3	
Theta range for data collection	2.70 to 27.49°.	

Index ranges	-9<=h<=9, -19<=k<=19, -11<=l<=11
Reflections collected	4251
Independent reflections	4251 [R(int) = 0.0000]
Completeness to theta = 27.49°	99.4 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4251 / 1 / 238
Goodness-of-fit on F^2	1.079
Final R indices [I>2sigma(I)]	R1 = 0.0289, wR2 = 0.0628
R indices (all data)	R1 = 0.0299, wR2 = 0.0638
Absolute structure parameter	0.056(12)
Largest diff. peak and hole	0.227 and -0.220 e.$Å^{-3}$

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1e-BH$_3$**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	2841(3)	5196(2)	2473(2)	16(1)
C(2)	3288(4)	4406(2)	1889(3)	24(1)
C(3)	2484(4)	3615(2)	2163(3)	29(1)
C(4)	1273(4)	3616(2)	3040(3)	30(1)
C(5)	811(4)	4398(2)	3599(3)	25(1)
C(6)	1594(3)	5198(2)	3322(3)	19(1)
C(7)	3256(3)	6296(1)	67(2)	17(1)
C(8)	4516(3)	6511(2)	-731(3)	21(1)
C(9)	3759(4)	6653(2)	-2345(3)	27(1)
C(10)	1794(4)	6563(2)	-3151(3)	29(1)
C(11)	532(4)	6314(2)	-2389(3)	26(1)
C(12)	1264(3)	6185(2)	-789(2)	21(1)
C(13)	2994(3)	7109(1)	2845(3)	16(1)
C(14)	4046(4)	7614(2)	4217(3)	21(1)
C(15)	2797(4)	8295(2)	4396(3)	27(1)
C(16)	984(4)	8224(2)	3145(3)	27(1)
C(17)	1097(3)	7499(2)	2191(3)	21(1)
C(18)	5219(4)	8569(2)	1208(3)	24(1)
C(19)	5477(4)	9228(2)	2372(3)	26(1)
C(20)	3707(4)	9712(2)	1998(3)	29(1)
C(21)	2361(4)	9356(2)	600(3)	28(1)
C(22)	3281(4)	8650(2)	110(3)	24(1)
O	6483(3)	6622(1)	-41(2)	28(1)
P	4039(1)	6199(1)	2170(1)	14(1)
Fe	3211(1)	8403(1)	2296(1)	16(1)
B	6804(4)	6083(2)	3262(3)	28(1)

Table S5. Bond lengths [Å] and angles [°] for **1e-BH_3**

C(1)-C(6)	1.388(3)
C(1)-C(2)	1.392(3)
C(1)-P	1.820(2)
C(2)-C(3)	1.392(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.386(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.375(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.398(3)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-C(8)	1.398(3)
C(7)-C(12)	1.404(3)
C(7)-P	1.813(2)
C(8)-O	1.366(3)
C(8)-C(9)	1.403(3)
C(9)-C(10)	1.375(4)
C(9)-H(9)	0.9500
C(10)-C(11)	1.388(4)
C(10)-H(10)	0.9500
C(11)-C(12)	1.387(3)
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(13)-C(17)	1.433(3)
C(13)-C(14)	1.442(3)
C(13)-P	1.784(2)
C(13)-Fe	2.038(2)
C(14)-C(15)	1.422(4)
C(14)-Fe	2.035(2)
C(14)-H(14)	0.9500
C(15)-C(16)	1.423(4)
C(15)-Fe	2.053(2)
C(15)-H(15)	0.9500
C(16)-C(17)	1.420(3)
C(16)-Fe	2.050(2)

C(16)-H(16)	0.9500
C(17)-Fe	2.039(2)
C(17)-H(17)	0.9500
C(18)-C(19)	1.423(3)
C(18)-C(22)	1.430(3)
C(18)-Fe	2.055(2)
C(18)-H(18)	0.9500
C(19)-C(20)	1.421(4)
C(19)-Fe	2.055(2)
C(19)-H(19)	0.9500
C(20)-C(21)	1.422(4)
C(20)-Fe	2.046(3)
C(20)-H(20)	0.9500
C(21)-C(22)	1.415(4)
C(21)-Fe	2.049(2)
C(21)-H(21)	0.9500
C(22)-Fe	2.053(2)
C(22)-H(22)	0.9500
O-H(0)	0.8400
P-B	1.927(3)
B-H(0A)	0.9800
B-H(0B)	0.9800
B-H(0C)	0.9800

C(6)-C(1)-C(2)	120.3(2)
C(6)-C(1)-P	121.86(18)
C(2)-C(1)-P	117.80(18)
C(3)-C(2)-C(1)	119.8(2)
C(3)-C(2)-H(2)	120.1
C(1)-C(2)-H(2)	120.1
C(4)-C(3)-C(2)	119.8(2)
C(4)-C(3)-H(3)	120.1
C(2)-C(3)-H(3)	120.1
C(5)-C(4)-C(3)	120.3(2)
C(5)-C(4)-H(4)	119.8
C(3)-C(4)-H(4)	119.8
C(4)-C(5)-C(6)	120.4(2)
C(4)-C(5)-H(5)	119.8

C(6)-C(5)-H(5)	119.8
C(1)-C(6)-C(5)	119.3(2)
C(1)-C(6)-H(6)	120.4
C(5)-C(6)-H(6)	120.4
C(8)-C(7)-C(12)	118.7(2)
C(8)-C(7)-P	123.37(17)
C(12)-C(7)-P	117.89(16)
O-C(8)-C(7)	124.5(2)
O-C(8)-C(9)	115.8(2)
C(7)-C(8)-C(9)	119.7(2)
C(10)-C(9)-C(8)	120.5(2)
C(10)-C(9)-H(9)	119.8
C(8)-C(9)-H(9)	119.8
C(9)-C(10)-C(11)	120.7(2)
C(9)-C(10)-H(10)	119.7
C(11)-C(10)-H(10)	119.7
C(12)-C(11)-C(10)	119.2(2)
C(12)-C(11)-H(11)	120.4
C(10)-C(11)-H(11)	120.4
C(11)-C(12)-C(7)	121.3(2)
C(11)-C(12)-H(12)	119.4
C(7)-C(12)-H(12)	119.4
C(17)-C(13)-C(14)	107.0(2)
C(17)-C(13)-P	129.85(17)
C(14)-C(13)-P	123.09(18)
C(17)-C(13)-Fe	69.48(13)
C(14)-C(13)-Fe	69.15(12)
P-C(13)-Fe	125.05(12)
C(15)-C(14)-C(13)	108.2(2)
C(15)-C(14)-Fe	70.33(14)
C(13)-C(14)-Fe	69.37(12)
C(15)-C(14)-H(14)	125.9
C(13)-C(14)-H(14)	125.9
Fe-C(14)-H(14)	126.0
C(14)-C(15)-C(16)	108.0(2)
C(14)-C(15)-Fe	68.96(12)
C(16)-C(15)-Fe	69.61(13)
C(14)-C(15)-H(15)	126.0

C(16)-C(15)-H(15)	126.0
Fe-C(15)-H(15)	127.0
C(17)-C(16)-C(15)	108.4(2)
C(17)-C(16)-Fe	69.25(13)
C(15)-C(16)-Fe	69.79(13)
C(17)-C(16)-H(16)	125.8
C(15)-C(16)-H(16)	125.8
Fe-C(16)-H(16)	126.8
C(16)-C(17)-C(13)	108.3(2)
C(16)-C(17)-Fe	70.10(14)
C(13)-C(17)-Fe	69.37(13)
C(16)-C(17)-H(17)	125.9
C(13)-C(17)-H(17)	125.9
Fe-C(17)-H(17)	126.3
C(19)-C(18)-C(22)	107.9(2)
C(19)-C(18)-Fe	69.75(13)
C(22)-C(18)-Fe	69.54(14)
C(19)-C(18)-H(18)	126.0
C(22)-C(18)-H(18)	126.0
Fe-C(18)-H(18)	126.2
C(20)-C(19)-C(18)	107.9(2)
C(20)-C(19)-Fe	69.39(14)
C(18)-C(19)-Fe	69.75(13)
C(20)-C(19)-H(19)	126.1
C(18)-C(19)-H(19)	126.1
Fe-C(19)-H(19)	126.4
C(19)-C(20)-C(21)	108.1(2)
C(19)-C(20)-Fe	70.07(15)
C(21)-C(20)-Fe	69.80(14)
C(19)-C(20)-H(20)	126.0
C(21)-C(20)-H(20)	126.0
Fe-C(20)-H(20)	125.7
C(22)-C(21)-C(20)	108.3(2)
C(22)-C(21)-Fe	69.95(13)
C(20)-C(21)-Fe	69.57(15)
C(22)-C(21)-H(21)	125.8
C(20)-C(21)-H(21)	125.8
Fe-C(21)-H(21)	126.2

C(21)-C(22)-C(18)	107.8(2)
C(21)-C(22)-Fe	69.70(14)
C(18)-C(22)-Fe	69.72(13)
C(21)-C(22)-H(22)	126.1
C(18)-C(22)-H(22)	126.1
Fe-C(22)-H(22)	126.1
C(8)-O-H(0)	109.5
C(13)-P-C(7)	106.87(10)
C(13)-P-C(1)	107.62(10)
C(7)-P-C(1)	103.73(10)
C(13)-P-B	112.86(12)
C(7)-P-B	116.51(11)
C(1)-P-B	108.57(12)
C(14)-Fe-C(13)	41.48(9)
C(14)-Fe-C(17)	69.14(10)
C(13)-Fe-C(17)	41.15(9)
C(14)-Fe-C(20)	131.87(11)
C(13)-Fe-C(20)	172.98(11)
C(17)-Fe-C(20)	143.83(11)
C(14)-Fe-C(21)	170.88(10)
C(13)-Fe-C(21)	146.27(10)
C(17)-Fe-C(21)	114.15(11)
C(20)-Fe-C(21)	40.63(11)
C(14)-Fe-C(16)	68.58(10)
C(13)-Fe-C(16)	68.90(9)
C(17)-Fe-C(16)	40.64(9)
C(20)-Fe-C(16)	112.26(11)
C(21)-Fe-C(16)	107.94(11)
C(14)-Fe-C(22)	147.88(10)
C(13)-Fe-C(22)	116.41(9)
C(17)-Fe-C(22)	110.51(10)
C(20)-Fe-C(22)	68.24(11)
C(21)-Fe-C(22)	40.35(10)
C(16)-Fe-C(22)	133.22(11)
C(14)-Fe-C(15)	40.71(10)
C(13)-Fe-C(15)	69.12(10)
C(17)-Fe-C(15)	68.64(10)
C(20)-Fe-C(15)	106.97(11)

C(21)-Fe-C(15)	131.34(11)
C(16)-Fe-C(15)	40.60(10)
C(22)-Fe-C(15)	171.19(11)
C(14)-Fe-C(18)	116.07(10)
C(13)-Fe-C(18)	111.48(10)
C(17)-Fe-C(18)	135.72(10)
C(20)-Fe-C(18)	68.17(11)
C(21)-Fe-C(18)	68.11(10)
C(16)-Fe-C(18)	173.80(11)
C(22)-Fe-C(18)	40.74(10)
C(15)-Fe-C(18)	145.59(10)
C(14)-Fe-C(19)	109.23(10)
C(13)-Fe-C(19)	134.78(10)
C(17)-Fe-C(19)	175.25(11)
C(20)-Fe-C(19)	40.53(11)
C(21)-Fe-C(19)	68.18(11)
C(16)-Fe-C(19)	143.48(10)
C(22)-Fe-C(19)	68.33(10)
C(15)-Fe-C(19)	113.27(10)
C(18)-Fe-C(19)	40.50(10)
P-B-H(0A)	109.5
P-B-H(0B)	109.5
H(0A)-B-H(0B)	109.5
P-B-H(0C)	109.5
H(0A)-B-H(0C)	109.5
H(0B)-B-H(0C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S6. Anisotropic displacement parameters ($Å^2$x 10^3) for **1e-BH$_3$**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	15(1)	17(1)	15(1)	1(1)	3(1)	-1(1)
C(2)	25(1)	20(1)	26(1)	-1(1)	9(1)	3(1)
C(3)	34(1)	15(1)	34(1)	-1(1)	5(1)	6(1)
C(4)	27(1)	21(1)	32(1)	10(1)	-2(1)	-4(1)
C(5)	23(1)	26(1)	27(1)	8(1)	8(1)	-4(1)
C(6)	21(1)	19(1)	18(1)	1(1)	7(1)	1(1)
C(7)	22(1)	14(1)	15(1)	-1(1)	7(1)	-1(1)
C(8)	28(1)	15(1)	23(1)	0(1)	13(1)	1(1)
C(9)	46(2)	20(1)	23(1)	1(1)	22(1)	2(1)
C(10)	52(2)	19(1)	14(1)	0(1)	8(1)	6(1)
C(11)	32(1)	22(1)	18(1)	0(1)	-1(1)	-1(1)
C(12)	25(1)	19(1)	18(1)	2(1)	5(1)	0(1)
C(13)	18(1)	14(1)	17(1)	1(1)	7(1)	-2(1)
C(14)	28(1)	22(1)	14(1)	1(1)	8(1)	-5(1)
C(15)	38(1)	25(1)	23(1)	-4(1)	19(1)	-4(1)
C(16)	26(1)	25(2)	37(1)	-4(1)	19(1)	-1(1)
C(17)	17(1)	20(1)	28(1)	-1(1)	10(1)	-3(1)
C(18)	25(1)	26(2)	26(1)	5(1)	13(1)	-2(1)
C(19)	23(1)	23(1)	31(1)	2(1)	6(1)	-11(1)
C(20)	34(1)	16(1)	37(1)	-2(1)	13(1)	-6(1)
C(21)	29(1)	20(1)	33(1)	11(1)	7(1)	5(1)
C(22)	28(1)	26(1)	18(1)	7(1)	5(1)	-2(1)
O	27(1)	34(1)	29(1)	0(1)	17(1)	-5(1)
P	13(1)	17(1)	13(1)	1(1)	4(1)	-1(1)
Fe	16(1)	15(1)	17(1)	-1(1)	5(1)	-2(1)
B	14(1)	36(2)	26(1)	3(1)	0(1)	-2(1)