Supporting Information
for Chiral Arylaminophosphonium Barfates as a New Class of Charged Brønsted Acid for the Enantioselective Activation of Non-ionic Lewis Bases

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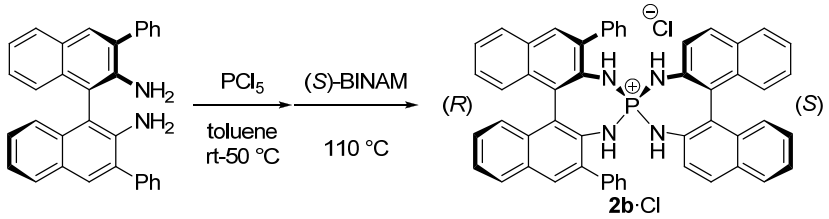
General Information: Infrared spectra were recorded on a JASCO FT/IR-300E spectrometer. ^{1}H NMR spectra were recorded on a Varian INOVA-500 (500 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance (CD_3OD; 3.31 ppm) or tetramethylsilane (0.0 ppm) resonance as the internal standard ($CDCl_3$ and acetone-d_6). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, oct = octet, m = multiplet, and br = broad) and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian INOVA-500 (126 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$; 77.16 ppm, CD_3OD; 49.0 ppm, acetone-d_6; 29.84 ppm). ^{19}F NMR spectra were recorded on a Varian Mercury-300BB (282 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from $CF_3C_6H_5$ (-64.0 ppm) resonance as the external standard. ^{31}P NMR spectra were recorded on a Varian Mercury-300BB (121 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from H_3PO_4 (0.0 ppm) resonance as the external standard. Optical rotations were measured on a JASCO DIP-1000 polarimeter. The high resolution mass spectra were measured on an BRUKER DALTONICS microTOF focus-KR spectrometer. All melting points were determined on a Büchi Melting Point B-540 apparatus and are uncorrected. Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm). Flash column chromatography was performed on silica gel 60 (spherical, 40-50 μm; Kanto Chemical Co., Inc.). Enantiomeric excesses were determined by HPLC analysis using chiral columns (ϕ 4.6 mm x 250 mm, DAICEL CHIRALPAK AS-H (ASH), CHIRALPAK AD-H (ADH), CHIRALPAK AD (AD), and CHIRALPAK IA (IA)) with hexane (H), isopropyl alcohol (IPA), and ethanol (EtOH) as eluent. All reactions were performed under argon (Ar) atmosphere unless otherwise noted. Tetrahydrofuran (THF) and toluene were supplied from Kanto Chemical Co., Inc. as "Dehydrated solvent system". 3,3'-Aryl-substituted binaphthyl diamines were prepared in enantiomerically pure form according to the literature methods.[1] Other simple chemicals were purchased and used as such.

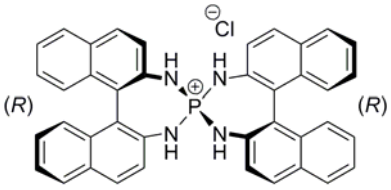
[1] (a) Huang, H.; Okuno, T.; Tsuda, K.; Yoshimura, M.; Kitamura, M. *J. Am. Chem. Soc.* **2006**, *128*, 8716. (b) Kano, T.; Tanaka, Y.; Osawa, K.; Yurino, T.; Maruoka, K. *J. Org. Chem.* **2008**, *73*, 7387.

Experimental Section:

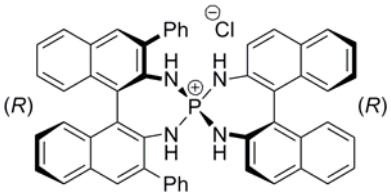
Preparation of Arylaminophosphonium Barfates:



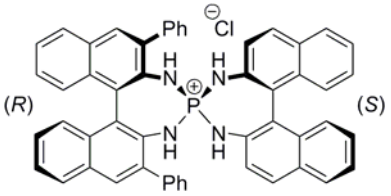
Representative Procedure for the Preparation of Chiral Arylaminophosphonium Chloride: To a solution of 3,3'-diphenyl-(*R*)-2,2'-diamino-1,1'-binaphthyldiamine (44.1 mg, 0.10 mmol, 1.00 equiv) in toluene (0.5 mL) was added a solution of PCl_5 (23.6 mg, 0.10 mmol, 1.00 equiv) in toluene (0.5 mL) at room temperature and the reaction mixture was stirred for 1 h at 50 ˚C. Then, (*S*)-2,2'-diamino-1,1'-binaphthyldiamine (BINAM) (42.7 mg, 0.15 mmol, 1.50 equiv) was added and the resulting mixture was stirred overnight at 110 ˚C. After evaporation of all volatiles, purification of the residue by column chromatography on silica gel ($CHCl_3$/MeOH = 20/1 as eluent) gave heterochiral arylaminophosphonium chloride **2b**·Cl (39.5 mg, 0.05 mmol) as white solid in 50% yield.



1a·Cl: The synthesis was performed following the general procedure and the title compound was obtained as white solid in 58% yield; ^{1}H NMR (500 MHz, CD_3OD) δ 8.18 (4H, d, J = 8.5 Hz), 8.03 (4H, d, J = 8.5 Hz), 7.57 (4H, d, J = 8.5 Hz), 7.48 (4H, t, J = 8.5 Hz), 7.24 (4H, t, J = 8.5 Hz), 7.07 (4H, d, J = 8.5 Hz), N-H protons were not found due to deuteration; ^{13}C NMR (126 MHz, CD_3OD) δ 135.7 (d, $J_{P\text{-}C}$ = 5.0 Hz), 134.2 (d, $J_{P\text{-}C}$ = 1.4 Hz), 133.4 (d, $J_{P\text{-}C}$ = 1.4 Hz), 131.5, 129.4, 128.2$_4$, 128.1$_6$ (d, $J_{P\text{-}C}$ = 2.3 Hz), 127.7, 126.8, 125.0 (d, $J_{P\text{-}C}$ = 3.3 Hz); ^{31}P NMR (121 MHz, CD_3OD) δ 50.2; IR (KBr): 3632, 3337, 3053, 1507, 1436, 1366, 1327, 1224, 993, 816, 755 cm^{-1}; $[\alpha]_D^{28}$ -132.1° (c = 1.12, $CHCl_3$), m.p. 299-301 ºC (decomp).

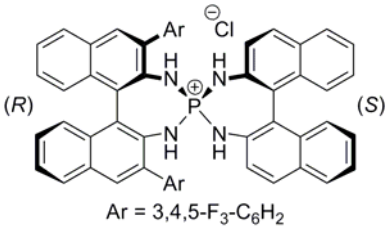


1b·Cl: The synthesis was performed following the general procedure and the title compound was obtained as white solid in 49% yield; ^{1}H NMR (500 MHz, CD_3OD) δ 8.19 (2H, s), 8.08 (2H, d, J = 8.0 Hz), 7.90 (2H, d, J = 8.0 Hz), 7.82 (2H, d, J = 8.0 Hz), 7.73 (4H, dt, J = 7.5, 1.5 Hz), 7.52 (2H, t, J = 8.0 Hz), 7.45 (4H, tt, J = 7.5, 1.5 Hz), 7.39 (2H, tt, J = 7.5, 1.5 Hz), 7.38 (2H, t, J = 7.5 Hz), 7.26 (2H, td, J = 8.0, 1.5 Hz), 7.11 (2H, d, J = 8.0 Hz), 7.08 (2H, td, J = 8.0, 1.5 Hz), 6.99 (2H, d, J = 8.0 Hz), 6.76 (2H, d, J = 8.0 Hz), N-H protons were not found due to deuteration; ^{13}C NMR (126 MHz, CD_3OD) δ 139.3, 138.3 (d, $J_{P\text{-}C}$ = 3.2 Hz), 134.4 (d, $J_{P\text{-}C}$ = 5.0 Hz), 134.1, 133.9 (d, $J_{P\text{-}C}$ = 1.4 Hz), 133.5, 132.9 (d, $J_{P\text{-}C}$ = 1.4 Hz), 132.5, 131.9 (d, $J_{P\text{-}C}$ = 3.7 Hz), 131.0, 130.9, 130.7 (d, $J_{P\text{-}C}$ = 2.3 Hz), 130.2, 129.4, 129.3, 129.2, 128.3, 128.1, 128.0, 127.5, 127.4, 127.2 (d, $J_{P\text{-}C}$ = 2.3 Hz), 126.6, 125.0 (d, $J_{P\text{-}C}$ = 3.8 Hz); ^{31}P NMR (121 MHz, CD_3OD) δ 44.3; IR (KBr): 3647, 3053, 1507, 1418, 1326, 1219, 1079, 994, 819, 763 cm^{-1}; $[\alpha]_D^{29}$ -408.5° (c = 1.10, $CHCl_3$), m.p. 360-364 ºC (decomp).

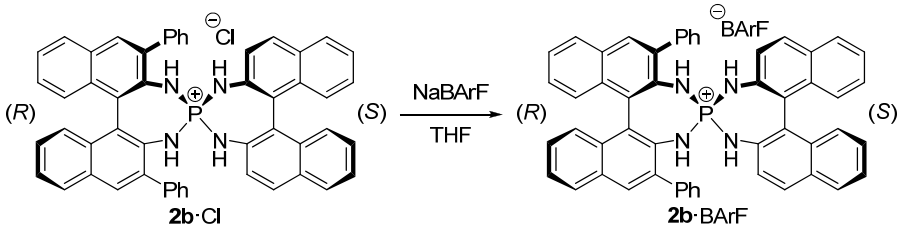


2b·Cl: The synthesis was performed following the general procedure and the title compound was obtained as white solid in 50% yield; ^{1}H NMR (500 MHz, CD_3OD) δ 8.02$_1$ (2H, s), 8.01$_7$ (2H, d, J = 8.5 Hz), 7.96 (2H, d, J = 8.5 Hz), 7.90 (2H, d, J = 8.5 Hz), 7.51-7.47 (8H, m), 7.40 (2H, d, J = 8.5 Hz), 7.25 (2H, t, J =

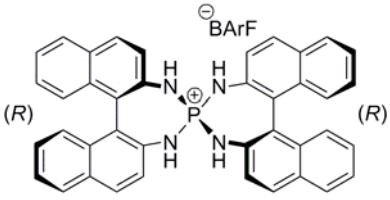
8.5 Hz), 7.23 (2H, t, J = 8.5 Hz), 6.99 (2H, d, J = 8.5 Hz), 6.97 (2H, d, J = 8.5 Hz), 6.91-6.86 (6H, m), N-H protons were not found due to deuteration; ^{13}C NMR (126 MHz, CD_3OD) δ 139.0, 138.4 (d, $J_{P\text{-}C}$ = 3.7 Hz), 136.8 (d, $J_{P\text{-}C}$ = 6.3 Hz), 134.1_3 (d, $J_{P\text{-}C}$ = 1.4 Hz), 134.0_9 (d, $J_{P\text{-}C}$ = 1.4 Hz), 133.6 (d, $J_{P\text{-}C}$ = 1.4 Hz), 133.2 (d, $J_{P\text{-}C}$ = 1.4 Hz), 133.1 (d, $J_{P\text{-}C}$ = 5.9 Hz), 132.0, 131.3, 130.6 (d, $J_{P\text{-}C}$ = 1.9 Hz), 130.5, 129.4, 129.2, 128.6, 128.4_3, 128.4_0, 127.7, 127.6, 127.4, 127.2 (d, $J_{P\text{-}C}$ = 2.4 Hz), 126.7, 124.2 (d, $J_{P\text{-}C}$ = 3.7 Hz), one carbon was not found probably due to overlapping; ^{31}P NMR (121 MHz, CD_3OD) δ 46.9; IR (KBr): 3649, 3334, 3057, 1620, 1508, 1417, 1325, 1211, 995, 750 cm^{-1}; $[\alpha]_D^{29}$ 196.1° (c = 1.15, $CHCl_3$), m.p. 305-308 ºC (decomp).



2c·Cl: The synthesis was performed following the general procedure and the title compound was obtained as white solid in 48% yield; ^{1}H NMR (500 MHz, CD_3OD) δ 8.09 (2H, s), 8.07 (2H, d, J = 8.5 Hz), 7.96 (2H, d, J = 8.5 Hz), 7.95 (2H, d, J = 8.5 Hz), 7.54 (2H, t, J = 8.5 Hz), 7.46 (2H, t, J = 8.5 Hz), 7.41 (2H, t, J = 8.5 Hz), 7.33-7.25 (6H, m), 7.20 (2H, t, J = 8.5 Hz), 7.01 (2H, d, J = 8.5 Hz), 6.90 (2H, d, J = 8.5 Hz), N-H protons were not found due to deuteration; ^{13}C NMR (126 MHz, CD_3OD) δ 151.7 (ddd, $J_{F\text{-}C}$ = 249.2, 10.0, 3.8 Hz), 140.3 (dt, $J_{F\text{-}C}$ = 252.3, 15.2 Hz), 136.7 (d, $J_{P\text{-}C}$ = 6.0 Hz), 136.3, 135.7 (td, $J_{F\text{-}C}$ = 9.2, 4.5 Hz), 134.4, 133.8, 133.6, 132.9, 132.6, 132.5 (d, $J_{P\text{-}C}$ = 3.9 Hz), 131.8, 131.2, 129.7, 129.3, 128.4, 128.3, 128.1, 127.8, 127.5, 126.9 (d, $J_{P\text{-}C}$ = 1.0 Hz), 126.7, 124.2 (d, $J_{P\text{-}C}$ = 3.8 Hz), 115.4 (dd, $J_{F\text{-}C}$ = 16.9, 4.5 Hz); ^{19}F NMR (282 MHz, CD_3OD) δ -136.7 (dd, J = 18.9, 8.7 Hz), -163.8 (tt, J = 20.6, 6.8 Hz); ^{31}P NMR (121 MHz, CD_3OD) δ 46.4; IR (KBr): 3353, 3058, 1616, 1528, 1419, 1210, 1045, 1009, 976, 751 cm^{-1}; $[\alpha]_D^{29}$ 162.9° (c = 1.02, $CHCl_3$), m.p. 302-306 ºC (decomp).

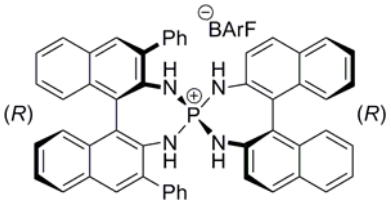


Representative Procedure for the Anion Exchange to Prepare Arylaminophosphonium Barfate: Arylaminophosphonium chloride **2b**·Cl (39.5 mg, 0.05 mmol, 1.00 equiv) and Na[B(3,5-$(CF_3)_2$-$C_6H_3)_4$] (NaBArF) (47.0 mg, 0.05 mmol, 1.05 equiv) were dissolved into THF (0.1 mL). The reaction mixture was stirred for 10 min at room temperature and diluted with water. The aqueous phase was extracted with diethyl ether three times and the organic extracts were dried over Na_2SO_4. Concentration and subsequent purification of the residue by column chromatography on silica gel ($CHCl_3$/MeOH = 20/1 as eluent) gave heterochiral arylaminophosphonium barfate **2b**·BArF (65.3 mg, 0.04 mmol) as white solid in 80 % yield.

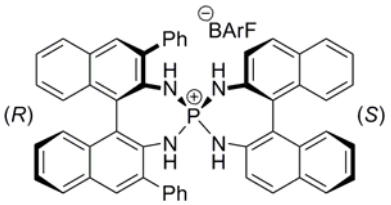


1a·BArF: The preparation was performed following the general procedure and the title compound was obtained as white solid in 57% yield; ^{1}H NMR (500 MHz, acetone-d_6) δ 8.27 (4H, d, J = 8.5 Hz), 8.14 (4H, d, J = 8.5 Hz), 7.79 (8H, brs), 7.77 (4H, d, J = 8.5 Hz), 7.68 (4H, brs), 7.58 (4H, t, J = 8.5 Hz), 7.36 (4H, t, J = 8.5 Hz), 7.16 (4H, d, J = 8.5 Hz), N-H protons were not found due to broadening; ^{13}C NMR (126 MHz, acetone-d_6) δ 162.6 (q, $J_{B\text{-}C}$ = 50.0 Hz), 135.5, 134.9 (d, $J_{P\text{-}C}$ = 5.0 Hz), 133.6, 133.0, 131.5, 130.0 (q, $J_{F\text{-}C}$ = 31.8 Hz), 129.4, 127.9_3, 127.8_6, 127.5 (d, $J_{P\text{-}C}$ = 2.3 Hz), 126.9, 125.4 (q, $J_{F\text{-}C}$ = 272.5 Hz), 124.9 (d, $J_{P\text{-}C}$ = 3.3 Hz), 118.5; ^{19}F NMR (282 MHz,

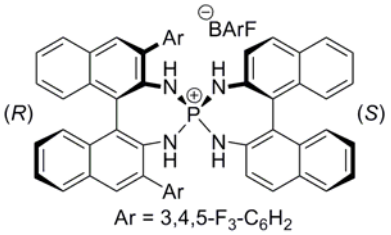
acetone-d_6) δ -62.6; ^{31}P NMR (121 MHz, acetone-d_6) δ 50.7; IR (KBr): 3386, 3059, 1508, 1356, 1279, 1126, 988, 814, 757, 713 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{40}H_{28}N_4P^+$ ([M]$^+$) 595.2046. Found 595.2073; $[\alpha]_D^{27}$ -15.7° (c = 0.91, $CHCl_3$), m.p. 126-130 ºC (decomp).



1b·BArF: The preparation was performed following the general procedure and the title compound was obtained as white solid in 93% yield; ^{1}H NMR (500 MHz, acetone-d_6) δ 8.20 (2H, s), 8.18 (2H, d, J = 8.5 Hz), 7.98 (2H, d, J = 8.5 Hz), 7.95 (2H, d, J = 8.5 Hz), 7.79 (8H, brs), 7.70-7.63 (8H, m), 7.62 (2H, t, J = 8.5 Hz), 7.45_2 (2H, d, J = 8.5 Hz), 7.44_9 (2H, t, J = 8.5 Hz), 7.41 (4H, t, J = 8.5 Hz), 7.37 (2H, d, J = 8.5 Hz), 7.36 (2H, t, J = 8.5 Hz), 7.18 (2H, t, J = 8.5 Hz), 7.05 (2H, d, J = 8.5 Hz), 6.86 (2H, d, J = 8.5 Hz), N-H protons were not found due to broadening; ^{13}C NMR (126 MHz, acetone-d_6) δ 162.6 (q, $J_{B\text{-}C}$ = 50.0 Hz), 138.7, 138.1 (d, $J_{P\text{-}C}$ = 3.2 Hz), 135.5, 134.4 (d, $J_{P\text{-}C}$ = 5.5 Hz), 133.7, 133.4, 132.8, 132.4 (d, $J_{P\text{-}C}$ = 1.8 Hz), 132.2, 130.9, 130.0 (q, $J_{F\text{-}C}$ = 31.6 Hz), 129.9 (d, $J_{P\text{-}C}$ = 2.8 Hz), 129.7, 129.2, 129.1, 128.9, 128.1, 127.8, 127.7, 127.3_3, 127.2_9, 126.4, 126.2 (d, $J_{P\text{-}C}$ = 2.4 Hz), 125.4 (q, $J_{F\text{-}C}$ = 273.0 Hz), 124.9, 118.5, two carbons were not found probably due to overlapping; ^{19}F NMR (282 MHz, acetone-d_6) δ -62.6; ^{31}P NMR (121 MHz, acetone-d_6) δ 45.1; IR (KBr): 3348, 3064, 1703, 1610, 1508, 1419, 1356, 1279, 1126, 989, 887, 751, 713 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{52}H_{36}N_4P^+$ ([M]$^+$) 747.2672. Found 747.2688; $[\alpha]_D^{27}$ -200.7° (c = 0.60, $CHCl_3$), m.p. 101-105 ºC (decomp).



2b·BArF: The preparation was performed following the general procedure and the title compound was obtained as white solid in 80% yield; ^{1}H NMR (500 MHz, acetone-d_6) δ 8.13 (2H, d, J = 8.5 Hz), 8.05 (2H, s), 8.04 (2H, d, J = 8.5 Hz), 7.97 (2H, d, J = 8.5 Hz), 7.80 (8H, brs), 7.68 (4H, brs), 7.60 (2H, t, J = 8.5 Hz), 7.56 (2H, t, J = 8.5 Hz), 7.44 (4H, d, J = 7.5 Hz), 7.35 (2H, t, J = 8.5 Hz), 7.32 (2H, t, J = 8.5 Hz), 7.30 (2H, d, J = 8.5 Hz), 7.05 (2H, d, J = 8.5 Hz), 7.00 (2H, d, J = 8.5 Hz), 6.89 (4H, t, J = 7.5 Hz), 6.84 (2H, t, J = 7.5 Hz), N-H protons were not found due to broadening; ^{13}C NMR (126 MHz, acetone-d_6) δ 162.6 (q, $J_{B\text{-}C}$ = 50.0 Hz), 138.4, 138.0 (d, $J_{P\text{-}C}$ = 3.2 Hz), 136.1 (d, $J_{P\text{-}C}$ = 5.9 Hz), 135.6, 133.7, 133.0, 132.7_9 (d, $J_{P\text{-}C}$ = 8.2 Hz), 132.7_6, 131.8, 131.2, 130.1_1, 130.0_9 (d, $J_{P\text{-}C}$ = 5.9 Hz), 130.0_3 (q, $J_{F\text{-}C}$ = 31.6 Hz), 129.4, 129.3, 129.0, 128.4, 128.2, 128.1, 127.7, 127.6, 127.4, 126.6, 125.4 (q, $J_{F\text{-}C}$ = 272.5 Hz), 124.4 (d, $J_{P\text{-}C}$ = 4.2 Hz), 118.5, two carbons were not found probably due to overlapping; ^{19}F NMR (282 MHz, acetone-d_6) δ -62.6; ^{31}P NMR (121 MHz, acetone-d_6) δ 45.4; IR (KBr): 3373, 3065, 1610, 1500, 1415, 1356, 1278, 1128, 993, 887, 752, 712 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{52}H_{36}N_4P^+$ ([M]$^+$) 747.2672. Found 747.2694; $[\alpha]_D^{27}$ 86.8° (c = 0.97, $CHCl_3$), m.p. 109-115 ºC (decomp).



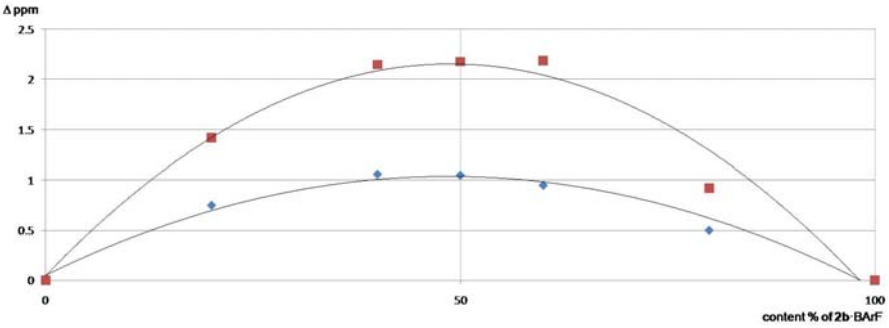
2c·BArF: The preparation was performed following the general procedure and the title compound was obtained as white solid in 85% yield; ^{1}H NMR (500 MHz, acetone-d_6) δ 8.15 (2H, d, J = 8.5 Hz), 8.14 (2H, s), 8.01 (2H, d, J = 8.5 Hz), 8.00 (2H, d, J = 8.5 Hz), 7.79 (8H, brs), 7.68 (4H, brs), 7.63 (2H, t, J = 8.5 Hz), 7.51 (2H, t, J = 8.5 Hz), 7.40 (2H, t, J = 8.5 Hz), 7.33-7.24 (8H, m), 7.09 (2H, d, J = 8.5 Hz), 6.91 (2H, d, J = 8.5 Hz), N-H protons were not found due to broadening; ^{13}C NMR (126 MHz, acetone-d_6) δ 162.6 (q, $J_{B\text{-}C}$ = 50.0 Hz), 151.1 (ddd, $J_{F\text{-}C}$ = 249.1, 9.6, 3.7 Hz), 139.6 (dt, $J_{F\text{-}C}$ = 251.9, 2.8 Hz), 136.0, 135.8, 135.5, 135.4, 134.0, 133.4, 132.8, 132.4, 132.2, 131.1, 130.0 (q, $J_{F\text{-}C}$ = 31.6 Hz), 129.6, 129.2, 128.3, 128.2, 127.7, 127.6, 126.7, 126.6,

125.4 (q, $J_{F\text{-}C}$ = 272.4 Hz), 124.4 (d, $J_{P\text{-}C}$ = 4.2 Hz), 118.5, 115.2 (dd, $J_{F\text{-}C}$ = 17.0, 5.0 Hz), three carbons were not found probably due to overlapping; ^{19}F NMR (282 MHz, acetone-d_6) δ -62.6, -135.7, -162.3; ^{31}P NMR (121 MHz, acetone-d_6) δ 44.5; IR (KBr): 3381, 3064, 1615, 1530, 1420, 1356, 1280, 1127, 1050, 752 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{52}H_{30}F_6N_4P^+$ ([M]$^+$) 855.2107. Found 855.2109; $[\alpha]_D^{27}$ 71.1° (c = 0.63, $CHCl_3$), m.p. 129-134 ºC (decomp).

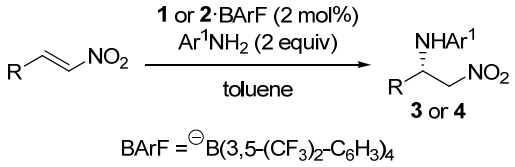
Properties of 2b·BArF as a Charged Brønsted Acid:

NMR Analysis of 2b·BArF–β-Nitrostyrene Complex: The solutions prepared by mixing equal concentration solutions of **2b**·BArF and β-nitrostyrene in C_6D_6 in varying ratios (**2b**·BArF/β-nitrostyrene = 100:0 to 20:80) were analyzed by ^{1}H and ^{31}P NMR at room temperature. This revealed that signals of the N-H protons of **2b**·BArF were steadily shifted downfield as the proportion of β-nitrostyrene was increased, during which, however, the ^{31}P NMR spectra was virtually unchanged. Furthermore, application of the results of the ^{1}H NMR studies to Job's method of continuous variation suggested the formation of a 1:1 complex (Chart S1).[2] These observations strongly support the property of **2b**·BArF as a Brønsted acid other than phosphonium Lewis acid.[3]

Chart S1. Job's plot for each N-H proton



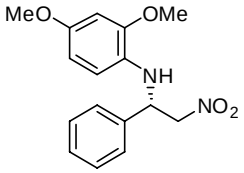
p*Ka* Estimation by Using ^{31}P NMR Analysis: The p*Ka* of **2b**·BArF was estimated by NMR titration method at ambient temperature in CD_3CN. The treatment of **2b**·BArF with 1.0 equiv of triethylamine (p*Ka* = 18.46 in CH_3CN)[4] caused an upfield shift of the original signal at 50.2 ppm to 40.7 ppm, which indicated ca. 90% conversion of **2b** to the corresponding iminophosphorane [original chemical shift = 39.7 ppm (CD_3CN)]. On the other hand, addition of 10.0 equiv of *N*,*N*-dimethylaniline (p*Ka* = 12.30)[4] did not affect the chemical shift of **2b**·BArF. When **2b**·BArF was mixed with an equimolar amount of benzylamine (p*Ka* = 16.76),[4] a signal of the phosphorus was observed at 43.9 ppm. This peak underwent gradual upfield shift as the amount of the amine was increased, and it reached 41.0 ppm upon addition of 5.0 equiv of benzylamine. Consequently, the p*Ka* of **2b**·BArF could be estimated to be ca. 16.5 in CH_3CN through the calculation by using these results.



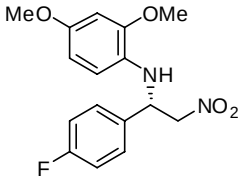
Representative Procedure for Chiral Arylaminophosphonium Barfate-Catalyzed Asymmetric Aza-Michael Reaction: To a dried test tube was weighted nitroolefin (0.10 mmol, 1.00 equiv) and **1**·BArF or **2**·BArF (2.0 μmol, 0.02

[2] Connors, K. A. *Binding Constants, The Measurement of Molecular Complex Stability*; Wiley-Interscience: New York, 1987; pp 24-28.
[3] (a) Mukaiyama, T.; Matsui, S.; Kashiwagi, K. *Chem. Lett.* **1989**, 993. (b) Mukaiyama, T.; Kashiwagi, K.; Matsui, S. *Chem. Lett.* **1989**, 1397. (c) Terada, M.; Kouchi, M. *Tetrahedron* **2006**, *62*, 401.
[4] Kaljurand, I.; Kütt, A.; Sooväli, L.; Rodima, T.; Mäemets, V.; Leito, I.; Koppel, I. A. *J. Org. Chem.* **2005**, *70*, 1019.

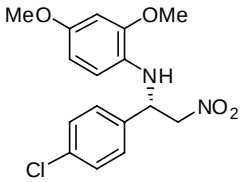
equiv) under Ar atmosphere. The mixture was dissolved into toluene (1.0 mL) at 0 ˚C or -15 ˚C. Arylamine (0.20 mmol, 2.00 equiv) was introduced dropwise slowly and the stirring was continued for the indicated time (see Tables in the manuscript). After the completion of the reaction was confirmed by TLC analysis, the reaction mixture was directly subjected to the purification by column chromatography on silica gel to afford β-amino nitroalkanes **3a** or **4**. The enantiomeric excess of the product was determined by HPLC analysis.



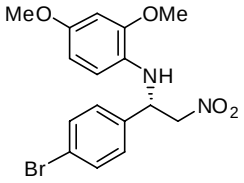
4a: The reaction was performed following the general procedure and the title compound was obtained as yellow viscous oil in 98% yield with 95% ee; ASH, H/IPA = 9:1, flow rate = 1.0 mL/min, λ = 210 nm, 20.3 min (major), 22.4 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.34 (4H, m), 7.33-7.29 (1H, m), 6.44 (1H, d, J = 2.5 Hz), 6.43 (1H, d, J = 9.0 Hz), 6.29 (1H, dd, J = 9.0, 2.5 Hz), 5.12 (1H, dd, J = 8.0, 6.0 Hz), 4.74 (1H, dd, J = 12.0, 8.0 Hz), 4.68 (1H, dd, J = 12.0, 6.0 Hz), 4.63 (1H, brs), 3.84 (3H, s), 3.71 (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0, 148.5, 138.3, 129.8, 129.3, 128.6, 126.6, 112.1, 103.8, 99.4, 80.3, 57.5, 55.7_8, 55.7_6; IR (liq. film): 3395, 2939, 2834, 1553, 1517, 1455, 1288, 1235, 1205, 1157, 1032 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{16}H_{19}N_2O_4$ ($[M+H]^+$) 303.1339. Found 303.1336; $[\alpha]_D^{29}$ 10.8° (c = 1.77, $CHCl_3$).



4b: The reaction was performed following the general procedure and the title compound was obtained as yellow viscous oil in 98% yield with 94% ee; ASH, H/IPA = 9:1, flow rate = 1.0 mL/min, λ = 210 nm, 26.3 min (major), 28.6 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (2H, dd, J = 8.5, 5.0 Hz), 7.06 (2H, t, J = 8.5 Hz), 6.45 (1H, d, J = 2.5 Hz), 6.39 (1H, d, J = 8.5 Hz), 6.29 (1H, dd, J = 8.5, 2.5 Hz), 5.09 (1H, dd, J = 8.0, 5.5 Hz), 4.72 (1H, dd, J = 12.0, 8.0 Hz), 4.66 (1H, dd, J = 12.0, 5.5 Hz), 4.61 (1H, brs), 3.84 (3H, s), 3.71 (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.8 (d, $J_{F\text{-}C}$ = 284.2 Hz), 153.2, 148.6, 134.0 (d, $J_{F\text{-}C}$ = 3.2 Hz), 129.6, 128.4 (d, $J_{F\text{-}C}$ = 8.3 Hz), 116.3 (d, $J_{F\text{-}C}$ = 21.5 Hz), 112.2, 103.8, 99.5, 80.3, 56.8, 55.7_8, 55.7_6; IR (liq. film): 3396, 2941, 2835, 1555, 1512, 1464, 1226, 1206, 1158, 1034, 835 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{16}H_{18}N_2O_4F$ ($[M+H]^+$) 321.1245. Found 321.1230; $[\alpha]_D^{30}$ -15.8° (c = 1.77, MeOH).

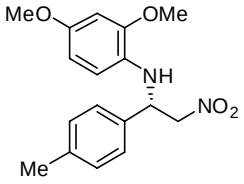


4c: The reaction was performed following the general procedure and the title compound was obtained as yellow viscous oil in 99% yield with 95% ee; ADH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 18.2 min (major), 20.1 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.31 (4H, m), 6.45 (1H, d, J = 2.5 Hz), 6.37 (1H, d, J = 8.5 Hz), 6.28 (1H, dd, J = 8.5, 2.5 Hz), 5.08 (1H, dd, J = 8.0, 5.5 Hz), 4.72 (1H, dd, J = 12.0, 8.0 Hz), 4.66 (1H, dd, J = 12.0, 5.5 Hz), 4.63 (1H, brs), 3.84 (3H, s), 3.71 (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.2, 148.6, 136.8, 134.5, 129.5_4, 129.4_6, 128.1, 112.3, 103.7, 99.5, 80.1, 56.9, 55.7_8, 55.7_6; IR (liq. film): 3400, 2939, 2834, 1555, 1517, 1464, 1236, 1206, 1157, 1034, 734 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{16}H_{18}N_2O_4Cl$ ($[M+H]^+$) 337.0950. Found 337.0952; $[\alpha]_D^{28}$ 16.8° (c = 1.74, $CHCl_3$).

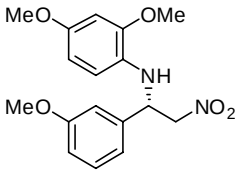


4d: The reaction was performed following the general procedure and the title compound was obtained as yellow viscous oil in 99% yield with 94% ee; ASH, H/IPA = 9:1, flow rate = 1.0 mL/min, λ = 210 nm, 28.8 min (major), 31.4 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (2H, dt, J = 8.5, 2.5 Hz), 7.27 (2H, dt, J = 8.5, 2.5 Hz), 6.44 (1H, d, J = 3.0 Hz), 6.36 (1H, d, J = 9.0 Hz), 6.28 (1H, dd, J = 9.0, 3.0 Hz), 5.06 (1H, dd, J = 8.0, 5.5 Hz), 4.71 (1H, dd, J = 12.0, 8.0 Hz), 4.65 (1H, dd, J =

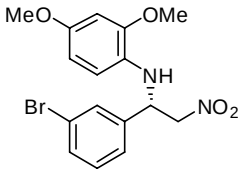
12.0, 5.5 Hz), 4.62 (1H, brs), 3.84 (3H, s), 3.71 (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.2, 148.5, 137.4, 132.5, 129.4, 128.4, 122.6, 112.3, 103.7, 99.5, 80.1, 57.0, 55.7_7, 55.7_6; IR (liq. film): 3400, 2938, 2834, 1555, 1517, 1464, 1236, 1206, 1157, 1034, 733 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{16}H_{18}N_2O_4Br$ ($[M+H]^+$) 381.0444 and 383.0426. Found 381.0445 and 383.0446; $[\alpha]_D^{28}$ 17.8° (c = 2.74, $CHCl_3$).



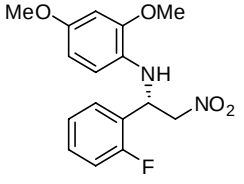
4e: The reaction was performed following the general procedure and the title compound was obtained as yellow viscous oil in 99% yield with 97% ee; ASH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 19.0 min (major), 25.3 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (2H, d, J = 8.0 Hz), 7.17 (2H, d, J = 8.0 Hz), 6.44_0 (1H, d, J = 8.5 Hz), 6.43_7 (1H, d, J = 3.0 Hz), 6.29 (1H, dd, J = 8.5, 3.0 Hz), 5.08 (1H, dd, J = 8.0, 5.5 Hz), 4.72 (1H, dd, J = 12.5, 8.0 Hz), 4.66 (1H, dd, J = 12.5, 5.5 Hz), 4.60 (1H, brs), 3.83 (3H, s), 3.71 (3H, s), 2.33 (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0, 148.5, 138.4, 135.3, 130.0, 129.9, 126.5, 112.0, 103.8, 99.4, 80.4, 57.2, 55.7_9, 55.7_5, 21.3; IR (liq. film): 3403, 2940, 2834, 1552, 1515, 1459, 1235, 1205, 1157, 1034, 730 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{17}H_{21}N_2O_4$ ($[M+H]^+$) 317.1496. Found 317.1506; $[\alpha]_D^{28}$ 26.4° (c = 1.96, $CHCl_3$).



4f: The reaction was performed following the general procedure and the title compound was obtained as yellow viscous oil in 99% yield with 93% ee; ADH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 19.9 min (major), 22.3 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (1H, t, J = 8.0 Hz), 6.97 (1H, d, J = 8.0 Hz), 6.93 (1H, t, J = 2.5 Hz), 6.84 (1H, dd, J = 8.0, 2.5 Hz), 6.44_1 (1H, d, J = 2.5 Hz), 6.44_0 (1H, d, J = 8.5 Hz), 6.30 (1H, dd, J = 8.5, 2.5 Hz), 5.08 (1H, td, J = 7.5, 5.5 Hz), 4.72 (1H, dd, J = 12.5, 7.5 Hz), 4.67 (1H, dd, J = 12.5, 5.5 Hz), 4.62 (1H, d, J = 7.5 Hz), 3.84 (3H, s), 3.79 (3H, s), 3.71 (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 153.0, 148.5, 140.1, 130.4, 129.9, 118.8, 113.8, 112.5, 112.1, 103.8, 99.4, 80.3, 57.5, 55.7_9, 55.7_6, 55.4; IR (liq. film): 3400, 2940, 2836, 1600, 1554, 1517, 1464, 1259, 1205, 1157, 1042 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{17}H_{21}N_2O_5$ ($[M+H]^+$) 333.1445. Found 333.1429; $[\alpha]_D^{27}$ 11.4° (c = 1.64, $CHCl_3$).

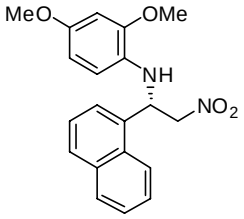


4g: The reaction was performed following the general procedure and the title compound was obtained as yellow viscous oil in 99% yield with 93% ee; ADH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 19.1 min (major), 21.5 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (1H, t, J = 1.5 Hz) 7.45 (1H, ddd, J = 8.0, 1.5, 1.0 Hz), 7.32 (1H, d, J = 8.0 Hz), 7.24 (1H, t, J = 8.0 Hz), 6.45 (1H, d, J = 3.0 Hz), 6.38 (1H, d, J = 8.5 Hz), 6.29 (1H, dd, J = 8.5, 3.0 Hz), 5.07 (1H, br), 4.71 (1H, dd, J = 12.5, 8.5 Hz), 4.66 (1H, dd, J = 12.5, 5.0 Hz), 4.63 (1H, brs), 3.85 (3H, s), 3.72 (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.3, 148.6, 140.8, 131.9, 130.9, 129.8, 129.4, 125.3, 123.5, 112.3, 103.8, 99.5, 80.1, 57.1, 55.8, one carbon was not found probably due to overlapping; IR (liq. film): 3402, 2939, 2834, 1555, 1517, 1464, 1234, 1206, 1157, 1034, 732 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{16}H_{18}N_2O_4Br$ ($[M+H]^+$) 381.0444 and 383.0426. Found 381.0425 and 383.0443; $[\alpha]_D^{30}$ -5.4° (c = 1.77, MeOH).

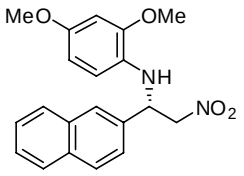


4h: The reaction was performed following the general procedure and the title compound was obtained as yellow viscous oil in 99% yield with 92% ee; ASH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 19.5 min (major), 21.6 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (1H, td, J = 8.5, 1.5 Hz), 7.29 (1H, ddt, J = 8.5, 6.5, 1.5 Hz), 7.11 (1H, ddd, J = 8.5, 3.0, 1.5 Hz),

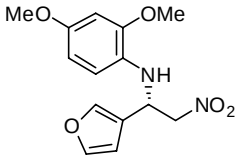
7.09 (1H, ddd, *J* = 8.5, 6.5, 1.5 Hz), 6.47 (1H, d, *J* = 8.5 Hz), 6.44 (1H, d, *J* = 2.5 Hz), 6.31 (1H, dd, *J* = 8.5, 2.5 Hz), 5.40 (1H, dd, *J* = 7.5, 5.5 Hz), 4.79 (1H, dd, *J* = 12.5, 7.5 Hz), 4.78 (1H, brs), 4.76 (1H, dd, *J* = 12.5, 5.5 Hz), 3.84 (3H, s), 3.71 (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.7 (d, $J_{F\text{-}C}$ = 246.5 Hz), 153.2, 148.6, 130.3 (d, $J_{F\text{-}C}$ = 8.3 Hz), 129.4, 128.5 (d, $J_{F\text{-}C}$ = 3.7 Hz), 124.9_4 (d, $J_{F\text{-}C}$ = 3.7 Hz), 124.8_5 (d, $J_{F\text{-}C}$ = 13.3 Hz), 116.0 (d, $J_{F\text{-}C}$ = 21.5 Hz), 112.3, 103.9, 99.5, 78.8 (d, $J_{F\text{-}C}$ = 2.3 Hz), 55.7_9, 55.7_6, 52.1 (d, $J_{F\text{-}C}$ = 2.3 Hz); IR (liq. film): 3396, 2940, 2835, 1556, 1518, 1486, 1456, 1206, 1157, 1034, 761 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{16}H_{18}N_2O_4F$ ($[M+H]^+$) 321.1245. Found 321.1257; $[\alpha]_D^{30}$ 11.8° (c = 2.32, $CHCl_3$).



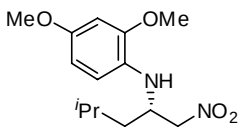
4i: The reaction was performed following the general procedure and the title compound was obtained as yellow viscous oil in 99% yield 91% ee; ASH, H/IPA = 9:1, flow rate = 1.0 mL/min, λ = 210 nm, 18.8 min (major), 23.6 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (1H, d, *J* = 8.0 Hz), 7.93 (1H, d, *J* = 8.0 Hz), 7.82 (1H, d, *J* = 8.0 Hz), 7.65 (1H, ddd, *J* = 8.0, 7.5, 1.5 Hz), 7.64 (1H, d, *J* = 8.0 Hz), 7.57 (1H, ddd, *J* = 8.0, 7.5, 1.5 Hz), 7.43 (1H, t, *J* = 8.0 Hz), 6.46 (1H, d, *J* = 3.0 Hz), 6.27 (1H, d, *J* = 8.5 Hz), 6.18 (1H, dd, *J* = 8.5, 3.0 Hz), 5.96 (1H, dt, *J* = 9.5, 4.0 Hz), 4.91 (1H, dd, *J* = 12.5, 4.0 Hz), 4.80 (1H, brd, *J* = 4.0 Hz), 4.70 (1H, dd, *J* = 12.5, 9.0 Hz), 3.87 (3H, s), 3.67 (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9, 148.4, 134.3, 132.9, 130.5, 129.8, 129.6, 129.2, 127.3, 126.2, 125.8, 124.0, 121.7, 111.7, 103.7, 99.4, 79.5, 55.7_9, 55.7_6, 53.8; IR (liq. film): 3405, 2940, 2834, 1554, 1517, 1236, 1206, 1157, 910, 777, 732 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{21}N_2O_4$ ($[M+H]^+$) 353.1496. Found 353.1509; $[\alpha]_D^{29}$ -146.7° (c = 2.39, $CHCl_3$).



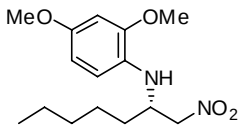
4j: The reaction was performed following the general procedure and the title compound was obtained as yellow viscous oil in 99% yield with 95% ee; ADH, H/EtOH = 5:1, flow rate = 1.0 mL/min, λ = 210 nm, 16.8 min (minor), 22.6 min (major). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (1H, s), 7.86 (1H, d, *J* = 6.0 Hz), 7.82 (1H, t, *J* = 6.0 Hz), 7.81 (1H, t, *J* = 6.0 Hz), 7.51-7.46 (3H, m), 6.46 (1H, d, *J* = 8.5 Hz), 6.45 (1H, d, *J* = 3.0 Hz), 6.26 (1H, dd, *J* = 8.5, 3.0 Hz), 5.27 (1H, dd, *J* = 8.0, 6.0 Hz), 4.81 (1H, dd, *J* = 12.0, 8.0 Hz), 4.78 (1H, dd, *J* = 12.0, 6.0 Hz), 4.75 (1H, brs), 3.86 (3H, s), 3.69 (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.1, 148.5, 135.7, 133.5, 133.4, 129.9, 129.4, 128.1, 127.9, 126.7, 126.6, 126.0, 124.1, 112.3, 103.8, 99.4, 80.3, 57.8, 55.7_8, 55.7_6; IR (liq. film): 3407, 2939, 2834, 1554, 1516, 1232, 1206, 1157, 1034, 910, 732 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{21}N_2O_4$ ($[M+H]^+$) 353.1496. Found 353.1505; $[\alpha]_D^{29}$ 25.6° (c = 2.35, $CHCl_3$).



4k: The reaction was performed following the general procedure and the title compound was obtained as yellow viscous oil in 89% yield with 94% ee; ASH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 28.9 min (major), 31.5 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (1H, dt, *J* = 1.5, 0.8 Hz), 7.41 (1H, t, *J* = 1.5 Hz), 6.66 (1H, d, *J* = 8.5 Hz), 6.46 (1H, d, *J* = 3.0 Hz), 6.40 (1H, dd, *J* = 8.5, 3.0 Hz), 6.39 (1H, dt, *J* = 1.5, 0.8 Hz), 5.12 (1H, t, *J* = 6.5 Hz), 4.76 (1H, dd, *J* = 12.5, 6.5 Hz), 4.63 (1H, dd, *J* = 12.5, 6.5 Hz), 4.32 (1H, brs), 3.82 (3H, s), 3.75 (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.4, 148.8, 144.2, 140.2, 129.5, 123.5, 112.6, 108.6, 104.0, 99.6, 78.9, 55.8, 55.7, 50.2; IR (liq. film): 3359, 2923, 2832, 1552, 1514, 1456, 1205, 1157, 1029, 874, 795 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{14}H_{17}N_2O_5$ ($[M+H]^+$) 293.1132. Found 293.1130; $[\alpha]_D^{30}$ 6.1° (c = 1.65, $CHCl_3$).

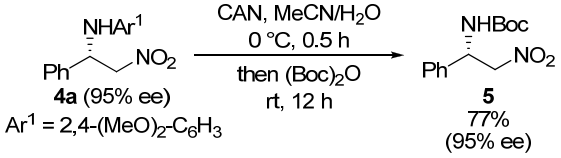


4l: The reaction was performed following the general procedure except for using $^{i}Pr_2O$ as solvent and the title compound was obtained as yellow viscous oil in 98% yield with 86% ee; ASH, H/IPA = 10:1, flow rate = 0.5 mL/min, λ = 210 nm, 17.1 min (major), 19.3 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.64 (1H, d, *J* = 8.5 Hz), 6.46 (1H, d, *J* = 2.5 Hz), 6.43 (1H, dd, *J* = 8.5, 2.5 Hz), 4.52 (1H, dd, *J* = 11.0, 5.0 Hz), 4.33 (1H, dd, *J* = 11.0, 7.0 Hz), 4.06 (1H, ddt, *J* = 9.0, 7.0, 5.0 Hz), 3.87 (1H, brs), 3.82 (3H, s), 3.76 (3H, s), 1.84 (1H, d-oct, *J* = 9.0, 6.5 Hz), 1.56 (1H, ddd, *J* = 14.0, 9.0, 6.5 Hz), 1.46 (1H, ddd, *J* = 14.0, 9.0, 5.0 Hz), 0.96 (3H, d, *J* = 6.5 Hz), 0.90 (1H, d, *J* = 6.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.8, 148.5, 130.0, 111.2, 104.1, 99.7, 78.7, 55.9, 55.7, 51.2, 42.5, 24.8, 23.3, 22.0; IR (liq. film): 3388, 2956, 2871, 2835, 1549, 1517, 1464, 1206, 1156, 1034, 834, 793 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{14}H_{23}N_2O_4$ ($[M+H]^+$) 283.1652. Found 283.1644; $[\alpha]_D^{28}$ 13.5° (c = 0.98, $CHCl_3$).



4m: The reaction was performed following the general procedure except for using $^{i}Pr_2O$ as solvent at room temperature and the title compound was obtained as yellow viscous oil in 93% yield with 87% ee; ASH, H/IPA = 10:1, flow rate = 0.5 mL/min, λ = 210 nm, 15.3 min (major), 17.3 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.62 (1H, d, *J* = 8.5 Hz), 6.46 (1H, d, *J* = 2.5 Hz), 6.42 (1H, dd, *J* = 8.5, 2.5 Hz), 4.53 (1H, dd, *J* = 12.0, 5.0 Hz), 4.36 (1H, dd, *J* = 12.0, 7.0 Hz), 3.99 (1H, m), 3.91 (1H, brs), 3.82 (3H, s), 3.76 (3H, s), 1.68 (1H, dddd, *J* = 13.5, 10.0, 6.0, 5.0 Hz), 1.59 (1H, dddd, *J* = 13.5, 10.0, 8.0, 5.0 Hz), 1.54-1.46 (1H, m), 1.43-1.35 (1H, m), 1.34-1.25 (4H, m), 0.88 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9, 148.5, 130.1, 111.4, 104.1, 99.7, 78.4, 55.9, 55.7, 53.1, 33.2, 31.7, 25.6, 22.6, 14.1; IR (liq. film): 3388, 2932, 2858, 1549, 1517, 1464, 1288, 1206, 1156, 1034, 834, 792 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{15}H_{25}N_2O_4$ ($[M+H]^+$) 297.1809. Found 297.1795; $[\alpha]_D^{27}$ 18.4° (c = 2.52, $CHCl_3$).

Derivatization of 4a to 5 and Absolute Configuration Determination:



Deprotection-reprotection Procedure: To a solution of ceric ammonium nitrate (CAN) (136.3 mg, 0.25 mmol, 2.50 equiv) in H_2O (1.0 mL) was added **4a** (31.0 mg, 0.10 mmol, 1.00 equiv) in MeCN (1.0 mL) dropwise slowly at 0 °C. After being stirred for 30 min, $(Boc)_2O$ (160 μL, 0.70 mmol, 7.00 equiv) was introduced and the reaction mixture was stirred for 12 h at room temperature. The resulting reddish-brown solution was diluted with water, neutralized with saturated aqueous solution of $NaHCO_3$, and extracted with EtOAc twice. The combined organic extracts were dried over Na_2SO_4 and filtered. After concentration, the residue was purified by column chromatography on silica gel (H/EtOAc = 6/1 as eluent) to give **5** (20.9 mg, 0.78 mmol) as white solid in 77% yield. The absolute configuration of **5** was determined to be *S* by comparison with literature data (HPLC retention time and optical rotation).[5] **5:** AD, H/IPA = 19:1, flow rate = 1.0 mL/min, λ = 210 nm, 22.7 min (major), 25.3 min (minor) [lit[5a]: 23.3 min (*S*), 24.9 min (*R*)]; IA, H/IPA = 9:1, flow rate = 1.0 mL/min, λ = 210 nm, 11.6 min (major), 12.7 min (minor) [lit[5b]: 12.0 min (*S*), 13.0 min (*R*)]; $[\alpha]_D^{24}$ 28.0° (c = 0.13, $CHCl_3$) for 95% ee [lit[5b]: $[\alpha]_D^{25}$ -20.1° (c = 0.48, $CHCl_3$) for *R* isomer; 91% ee]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (2H, tt, *J* = 7.5, 1.5 Hz), 7.34 (1H, tt, *J* = 7.5, 1.5 Hz), 7.31 (2H, dt, *J* = 7.5, 1.5 Hz), 5.38 (1H, br), 5.29 (1H, br), 4.86 (1H, br), 4.71 (1H, dd, *J* = 12.5, 5.5 Hz), 1.44 (9H, s).

[5] (a) Nugent, B. M.; Yoder, R. A.; Johnston, J. N. *J. Am. Chem. Soc.* **2004**, *126*, 3418. (b) Palomo, C.; Oiarbide, M.; Laso, A.; López, R. *J. Am. Chem. Soc.* **2005**, *127*, 17622.

Crystallographic Structure Determination:

Recrystallization of 1b·Cl: Homochiral, [7.7]-*P*-spirocyclic arylaminophosphonium salt **1b**·Cl was recrystallized from EtOH/hexane solvent system at room temperature.

The single crystal thus obtained was mounted on CryoLoop. Data of X-ray diffraction were collected at 153 K on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An absorption correction was made using SADABS. The structure was solved by direct methods and Fourier syntheses, and refined by full-matrix least squares on F^2 by using SHELXTL.[6] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to nitrogen atoms were located from a difference synthesis and their coordinates and isotropic thermal parameters refined. The other hydrogen atoms were placed in calculated positions and isotropic thermal parameters refined. The crystallographic data were summarized in the following table.

Table S1. Crystal data and structure refinement for **1b**·Cl·3EtOH.

Empirical formula	C58 H54 Cl N4 O3 P1	
Formula weight	921.47	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 11.322(2) Å	α = 90°.
	b = 19.295(3) Å	β = 111.634(4)°.
	c = 11.910(2) Å	γ = 90°.
Volume	2418.5(7) $Å^3$	
Z	2	
Density (calculated)	1.265 Mg/m^3	
Absorption coefficient	0.162 mm^{-1}	
F(000)	972	
Crystal size	0.70 x 0.50 x 0.40 mm^3	
Theta range for data collection	1.84 to 28.43°.	
Index ranges	-15<=h<=13, -19<=k<=25, -15<=l<=14	
Reflections collected	18429	
Independent reflections	10862 [R(int) = 0.0354]	
Completeness to theta = 28.46°	99.0 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9379 and 0.8948	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10862 / 1 / 626	
Goodness-of-fit on F2	1.038	
Final R indices [I>2sigma(I)]	R_1 = 0.0443, wR_2 = 0.1118	
R indices (all data)	R_1 = 0.0482, wR_2 = 0.1151	
Absolute structure parameter	0.00(5)	
Largest diff. peak and hole	0.436 and -0.242 e.$Å^{-3}$	

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

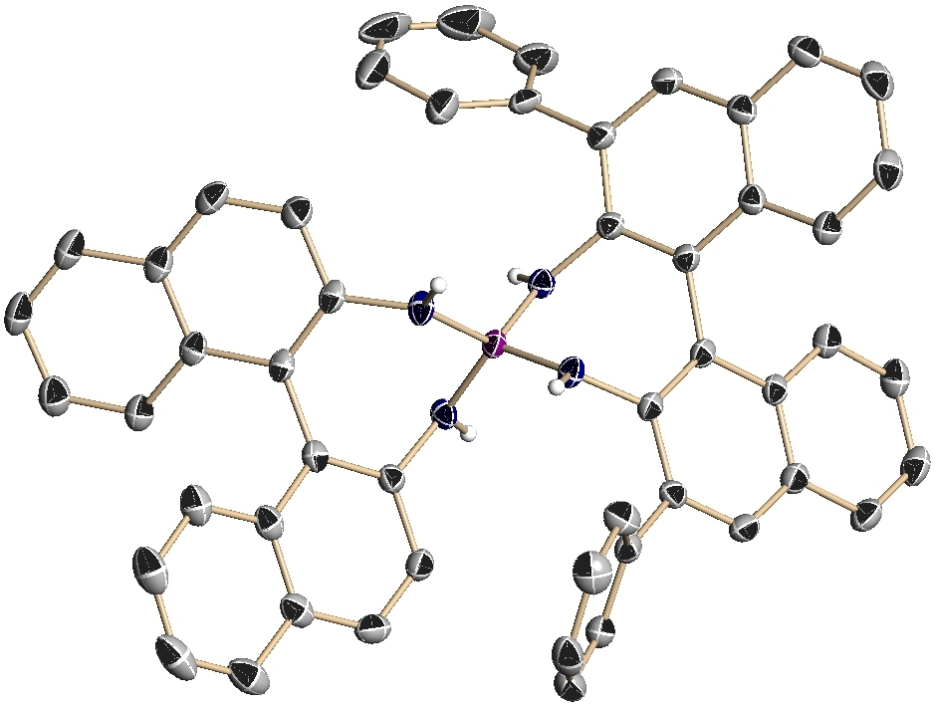


Figure S1. Molecular structure of homochiral, [7.7]-*P*-spirocyclic arylaminophosphonium salt **1b**·Cl. All calculated hydrogen atoms, counter anion, and solvent molecules are omitted for clarity. Purple = phosphorus, blue = nitrogen, black = carbon.

Recrystallization of 2b·Cl: Heterochiral, [7.7]-*P*-spirocyclic arylaminophosphonium salt **2b**·Cl was recrystallized from EtOH/C_6H_6/hexane solvent system at room temperature.

The single crystal thus obtained was mounted on CryoLoop. Data of X-ray diffraction were collected at 153 K on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An absorption correction was made using SADABS. The structure was solved by direct methods and Fourier syntheses, and refined by full-matrix least squares on F^2 by using SHELXTL.[6] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to nitrogen atoms were located from a difference synthesis and their coordinates and isotropic thermal parameters refined. The other hydrogen atoms were placed in calculated positions and isotropic thermal parameters refined. The crystallographic data were summarized in the following table.

Table S2. Crystal data and structure refinement for **2b**·Cl·4EtOH·C_6H_6.

Empirical formula	C66 H66 Cl N4 O4 P1	
Formula weight	1045.65	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.383(3) Å	α = 90°.
	b = 21.787(6) Å	β = 90°.
	c = 25.368(6) Å	γ = 90°.
Volume	5739(3) $Å^3$	
Z	4	
Density (calculated)	1.210 Mg/m^3	
Absorption coefficient	0.146 mm^{-1}	
F(000)	2216	
Crystal size	0.30 x 0.30 x 0.10 mm^3	
Theta range for data collection	1.61 to 28.46°.	
Index ranges	-13<=h<=12, -29<=k<=21, -28<=l<=33	
Reflections collected	43902	
Independent reflections	14399 [R(int) = 0.0635]	
Completeness to theta = 28.46°	99.6 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9855 and 0.9575	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14399 / 0 / 697	
Goodness-of-fit on F2	1.023	
Final R indices [I>2sigma(I)]	R_1 = 0.0602, wR_2 = 0.1362	
R indices (all data)	R_1 = 0.0911, wR_2 = 0.1524	
Absolute structure parameter	0.01(6)	
Largest diff. peak and hole	0.534 and -0.352 $e.Å^{-3}$	

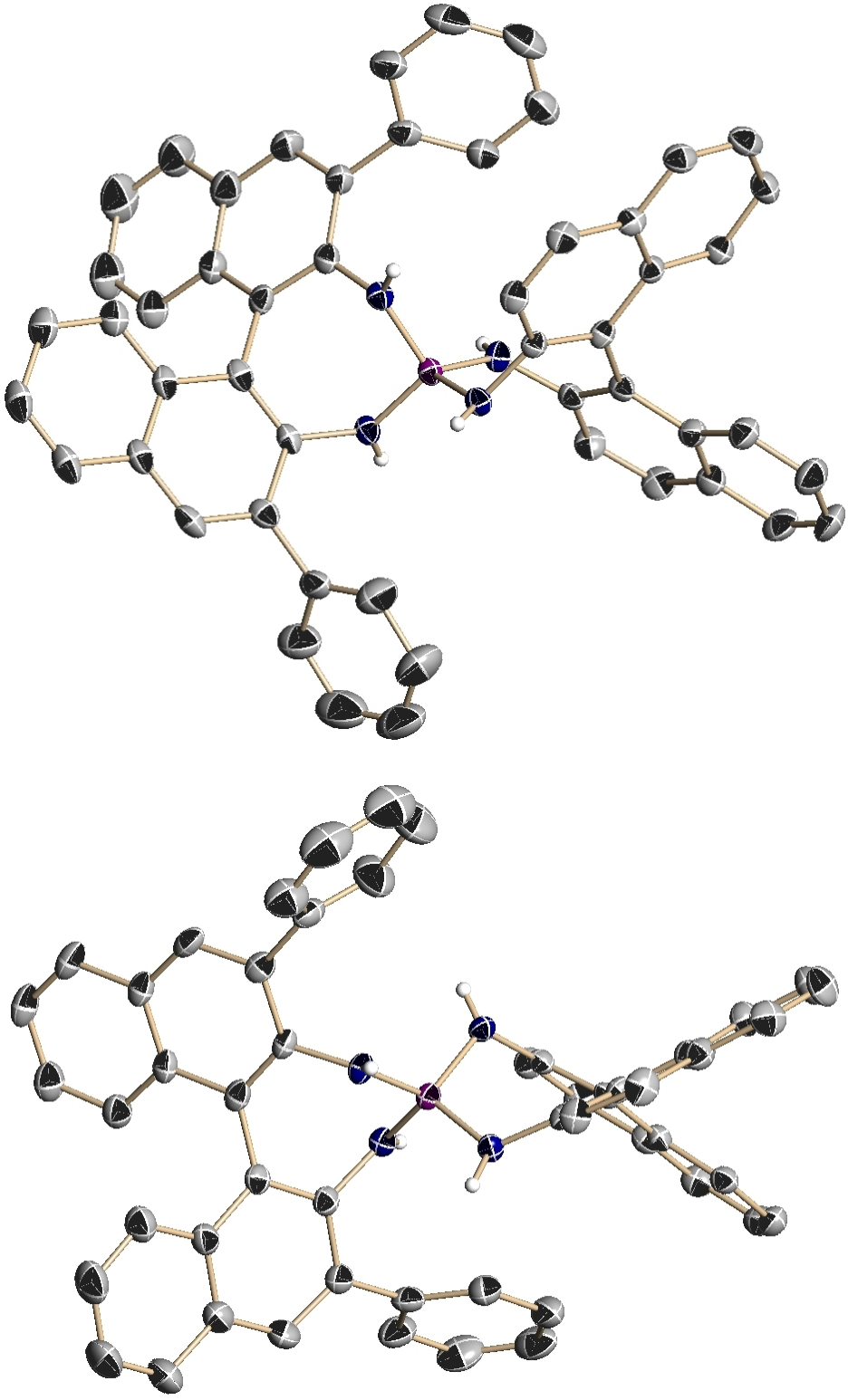
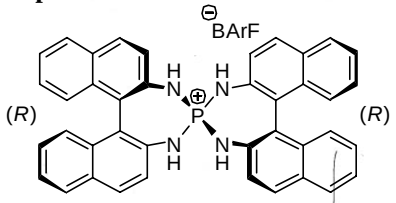
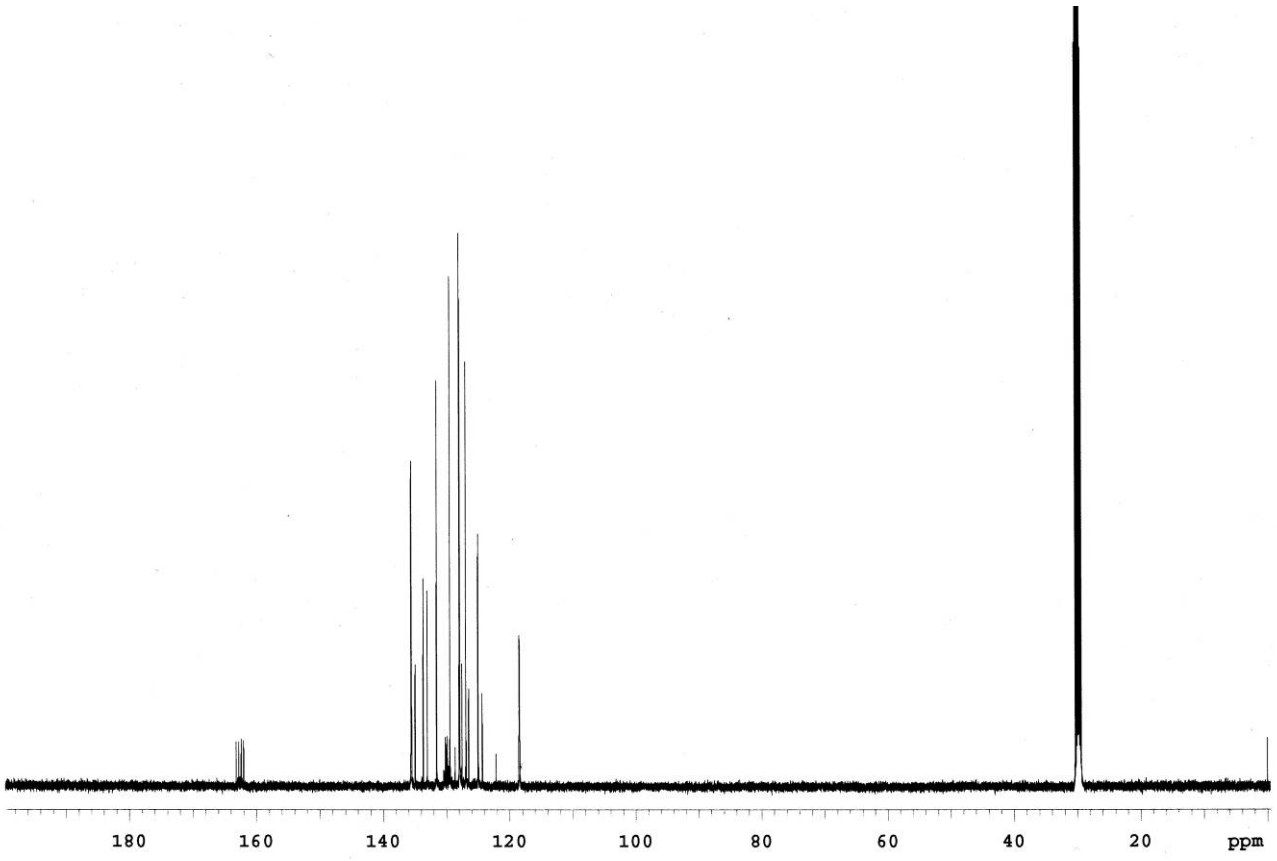
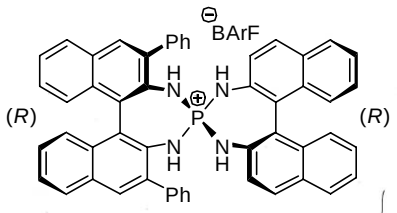


Figure S2. Molecular structure of heterochiral, [7.7]-*P*-spirocyclic arylaminophosphonium salt **2b**·Cl. All calculated hydrogen atoms, counter anion, and solvent molecules are omitted for clarity. Purple = phosphorus, blue = nitrogen, black = carbon.

Copies of ^{1}H and ^{13}C NMR Charts



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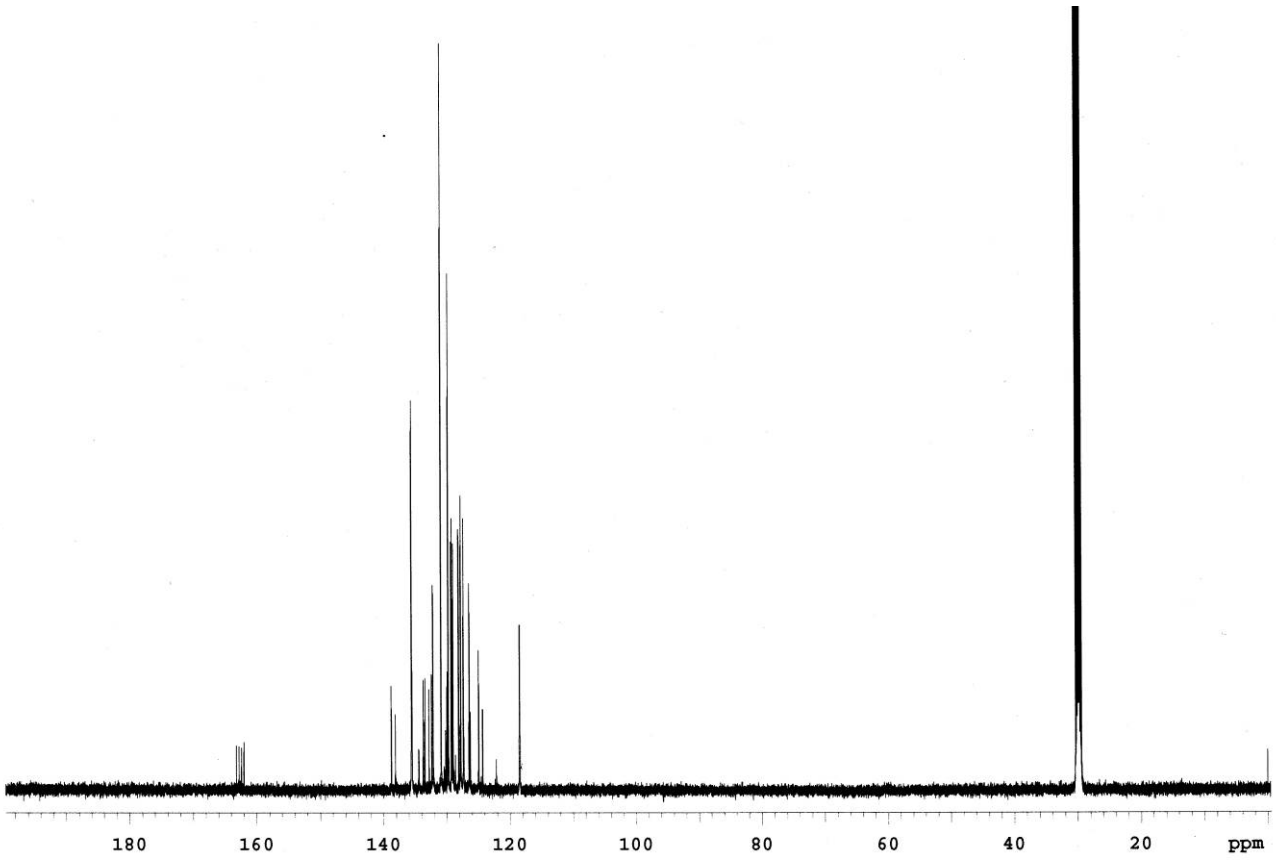
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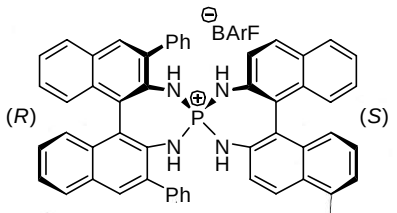
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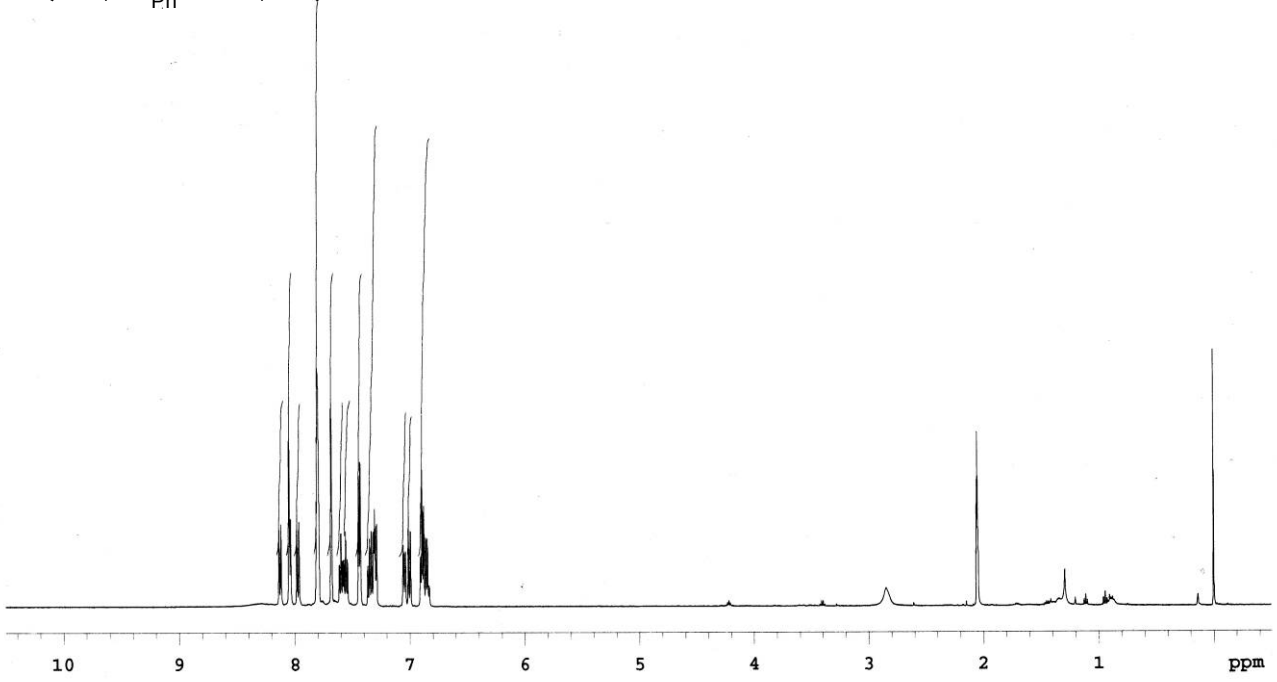
Ph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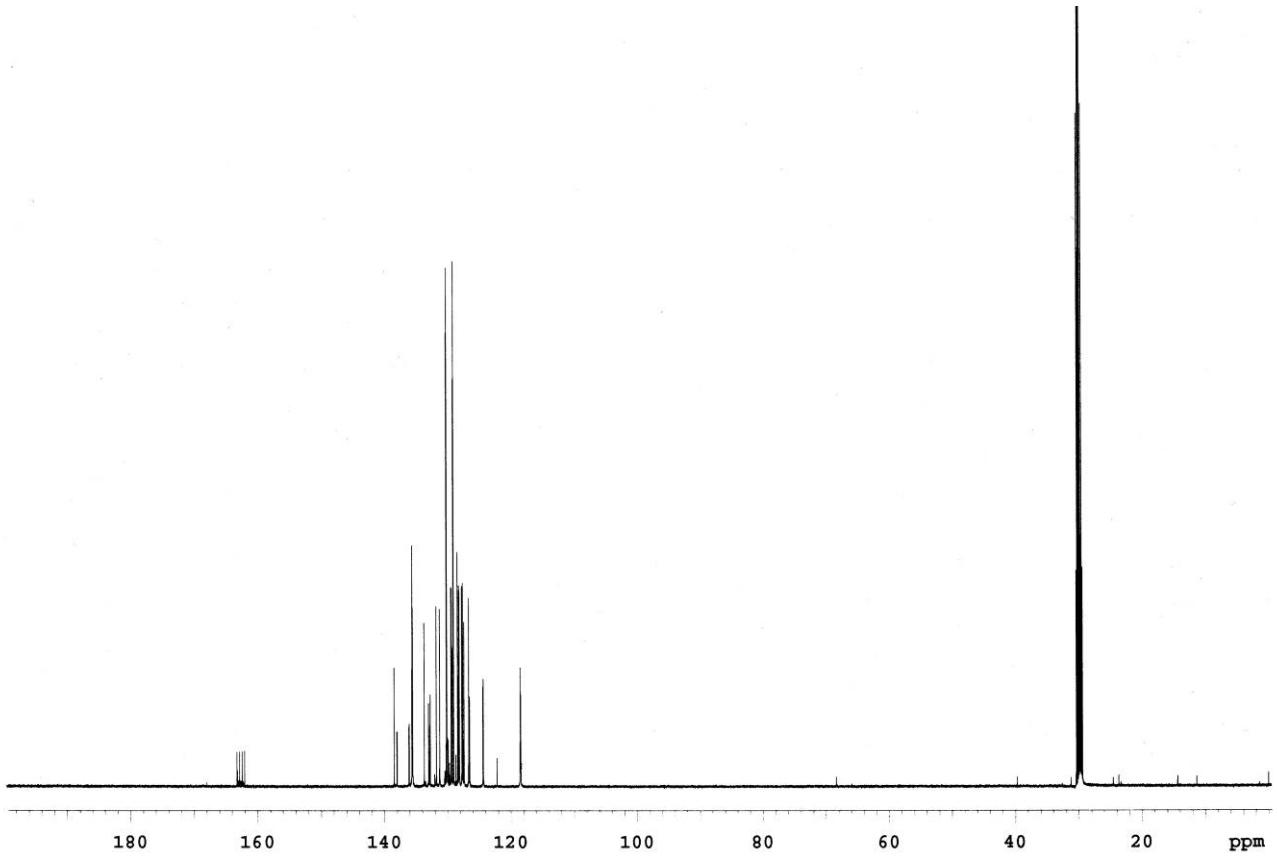
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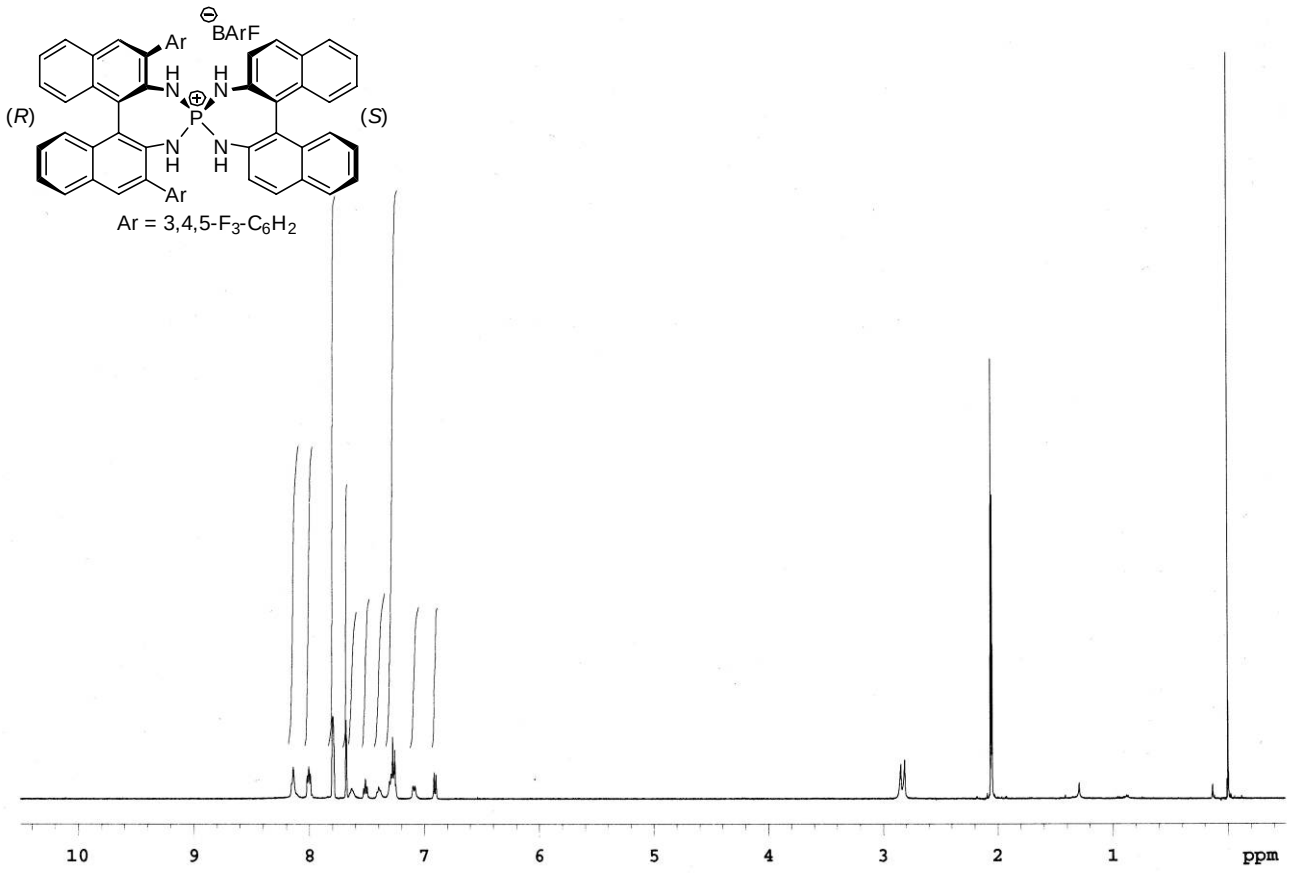
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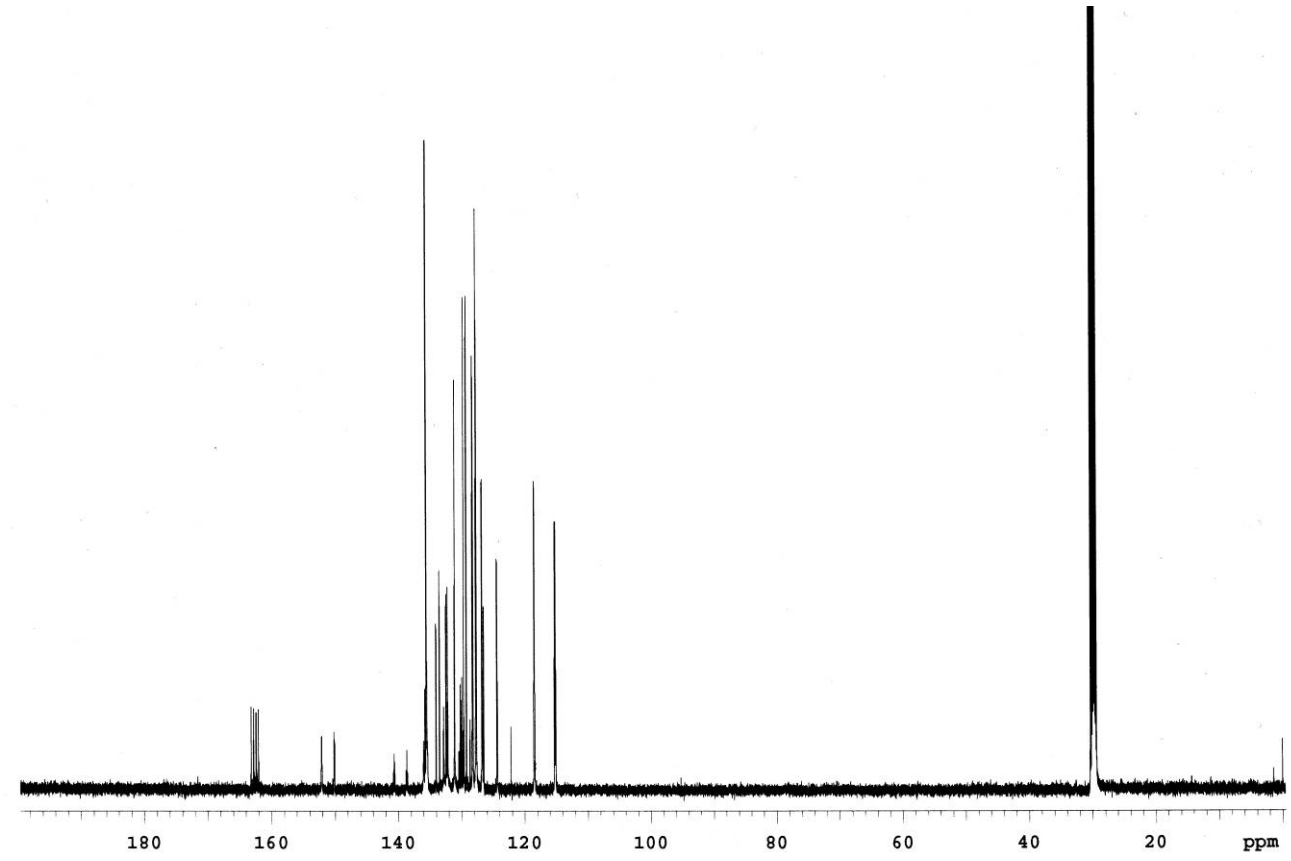
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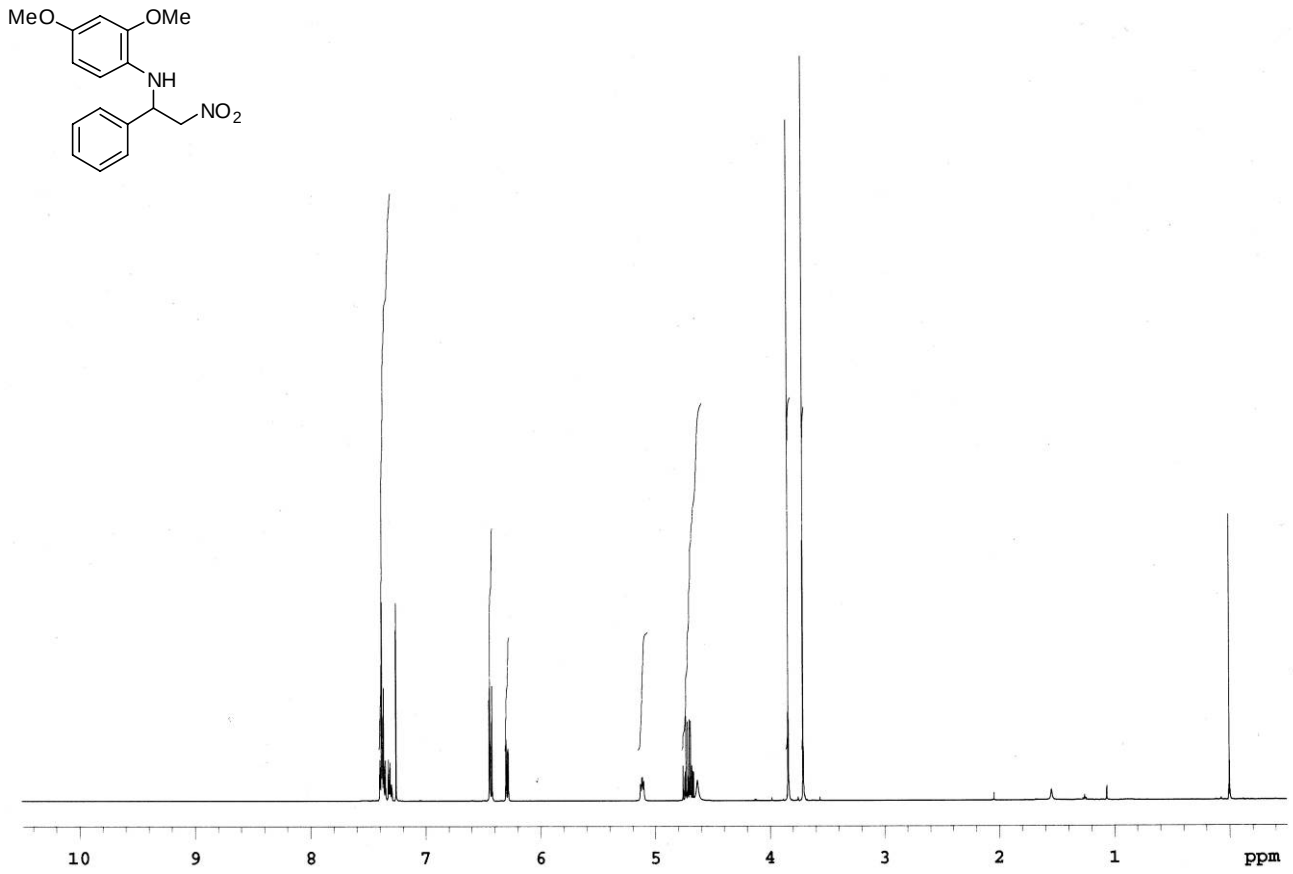
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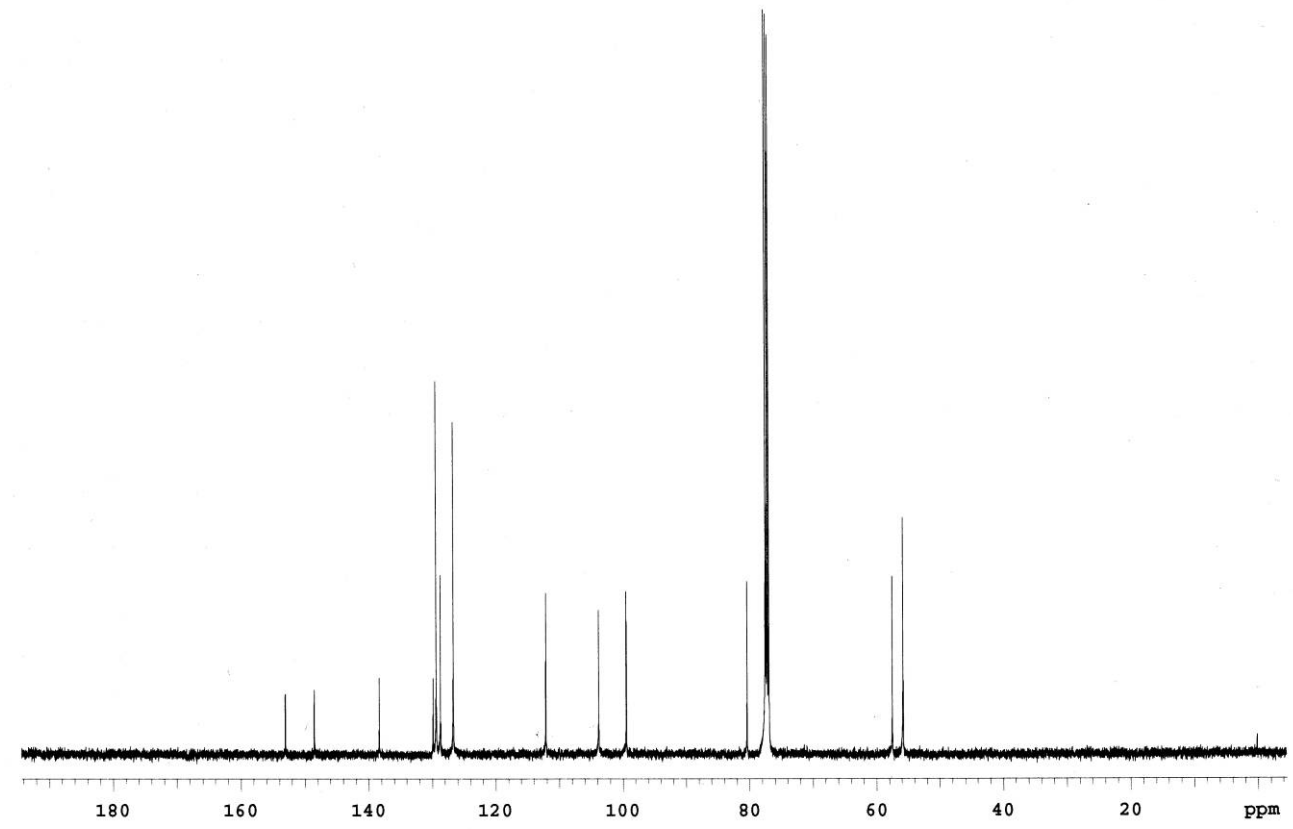
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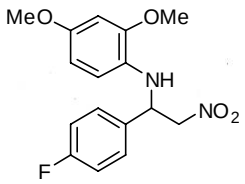
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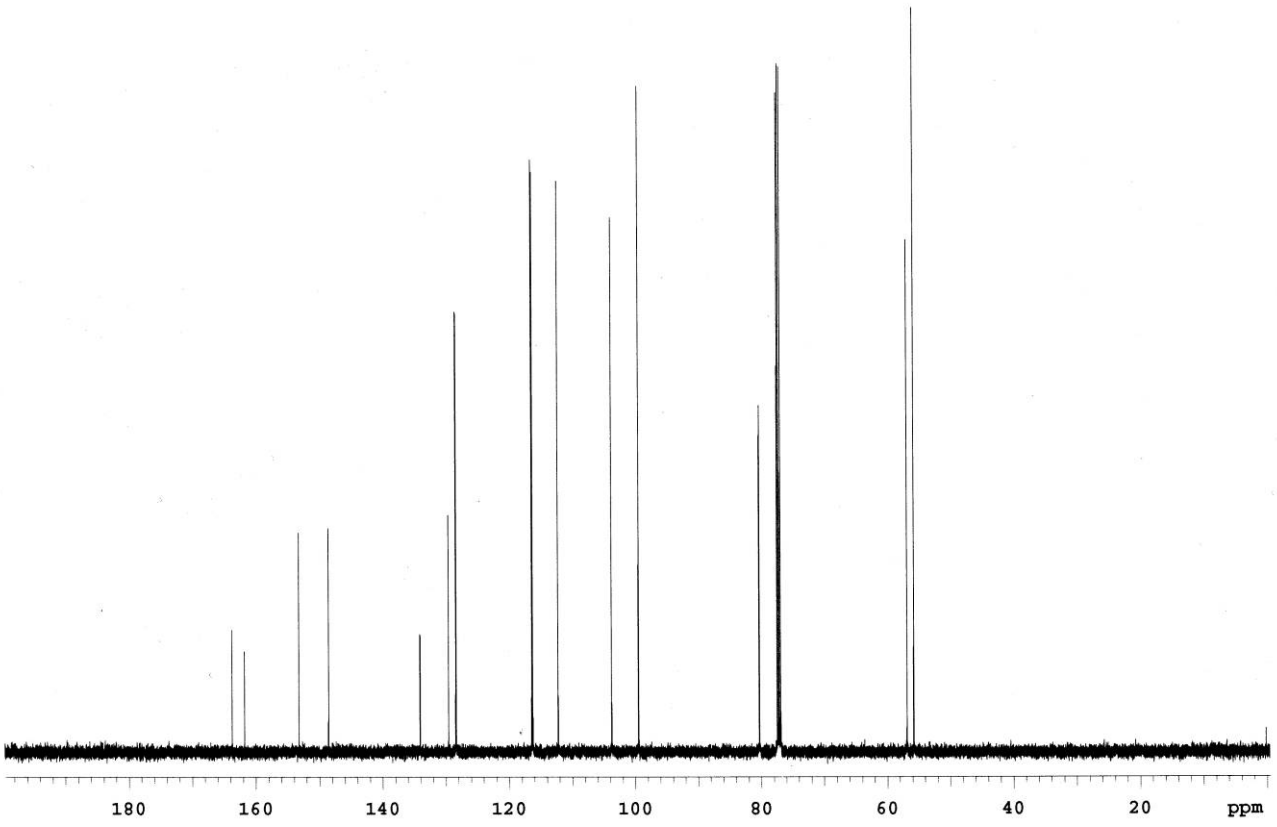
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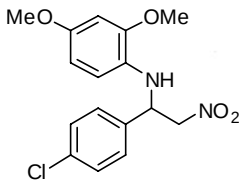
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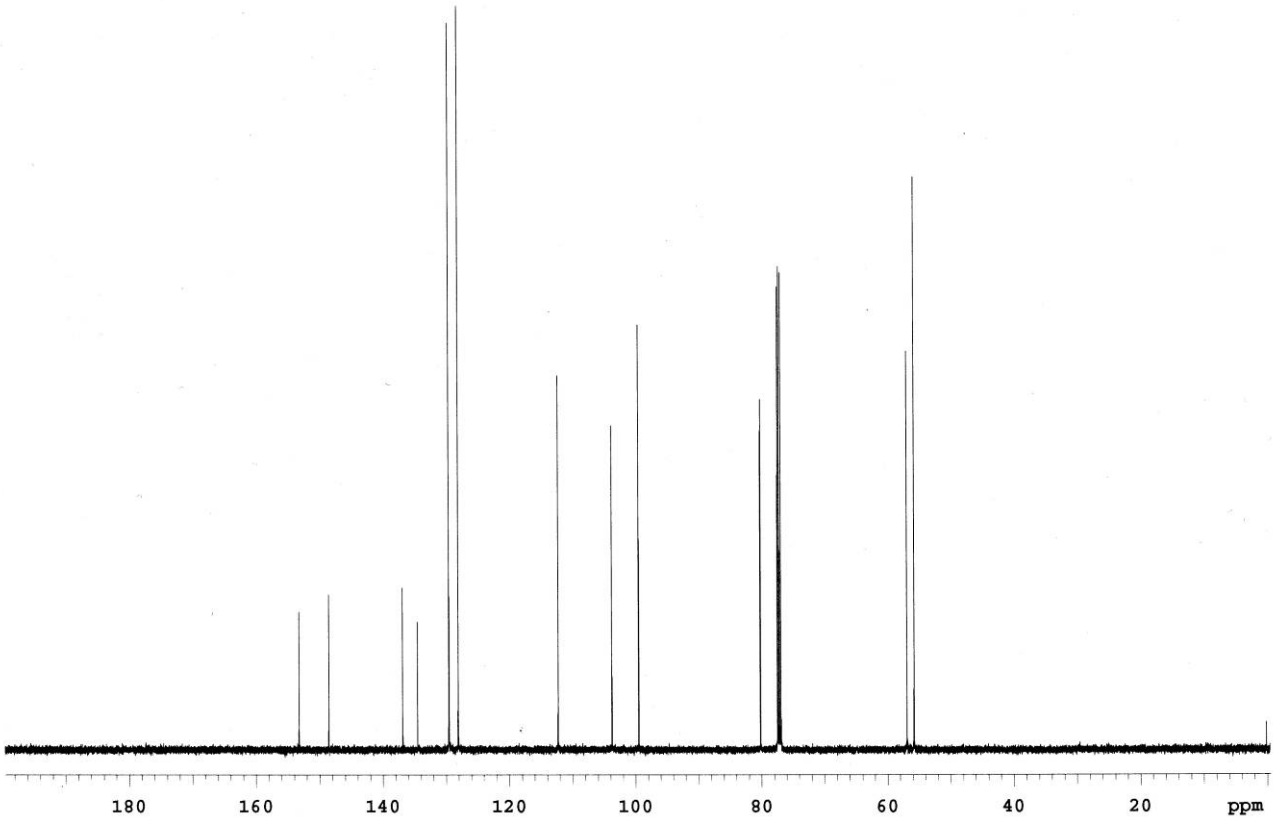
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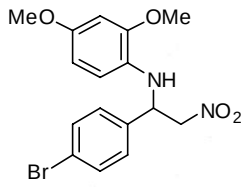
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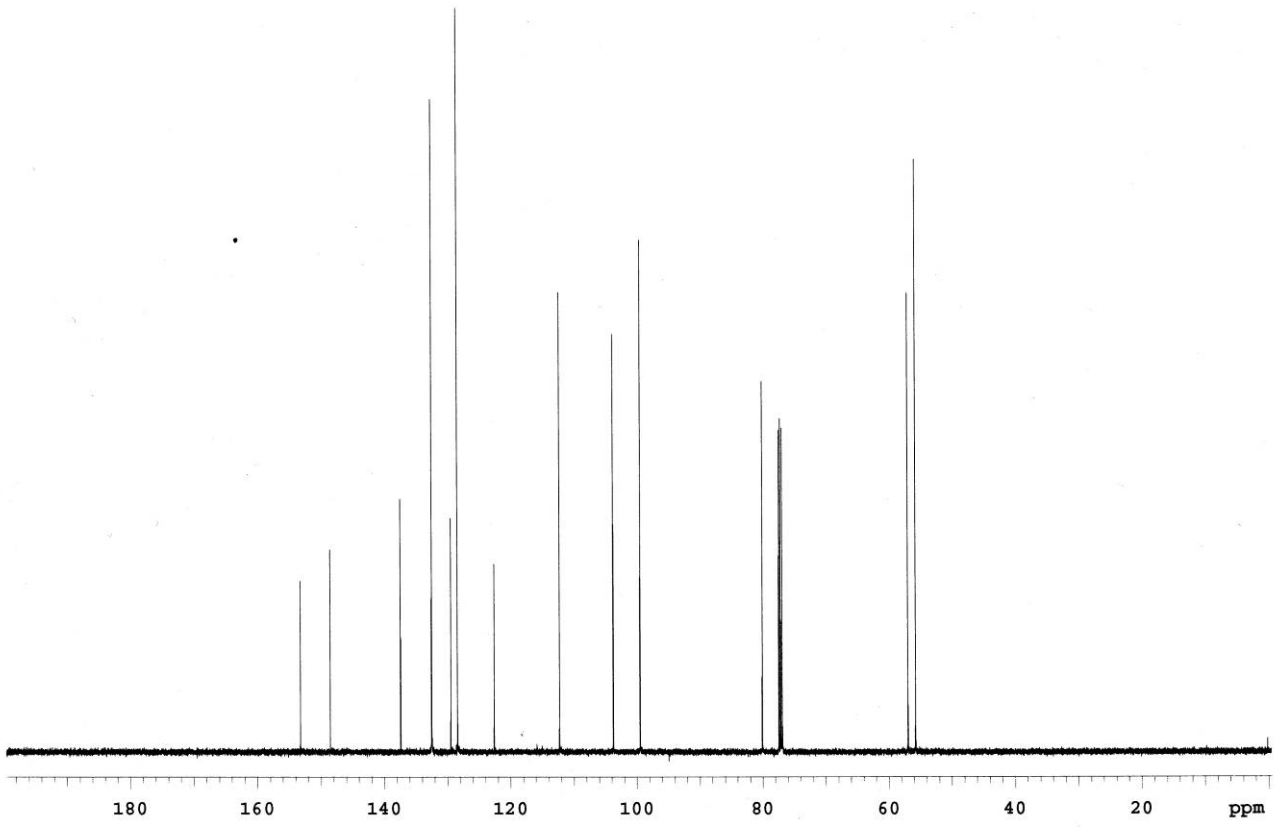
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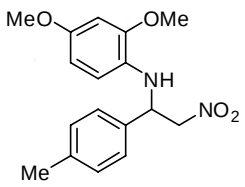
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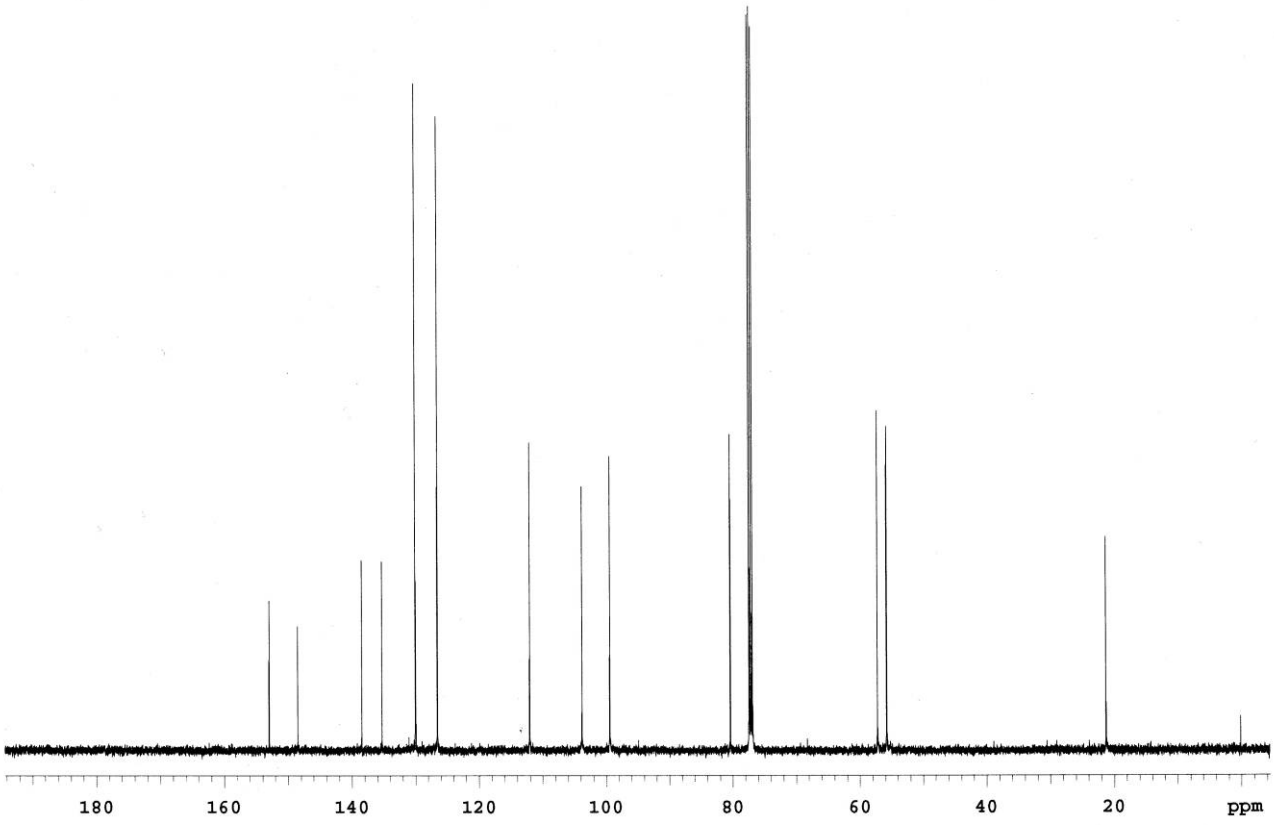
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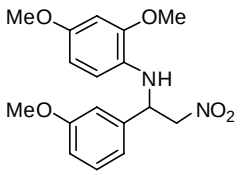
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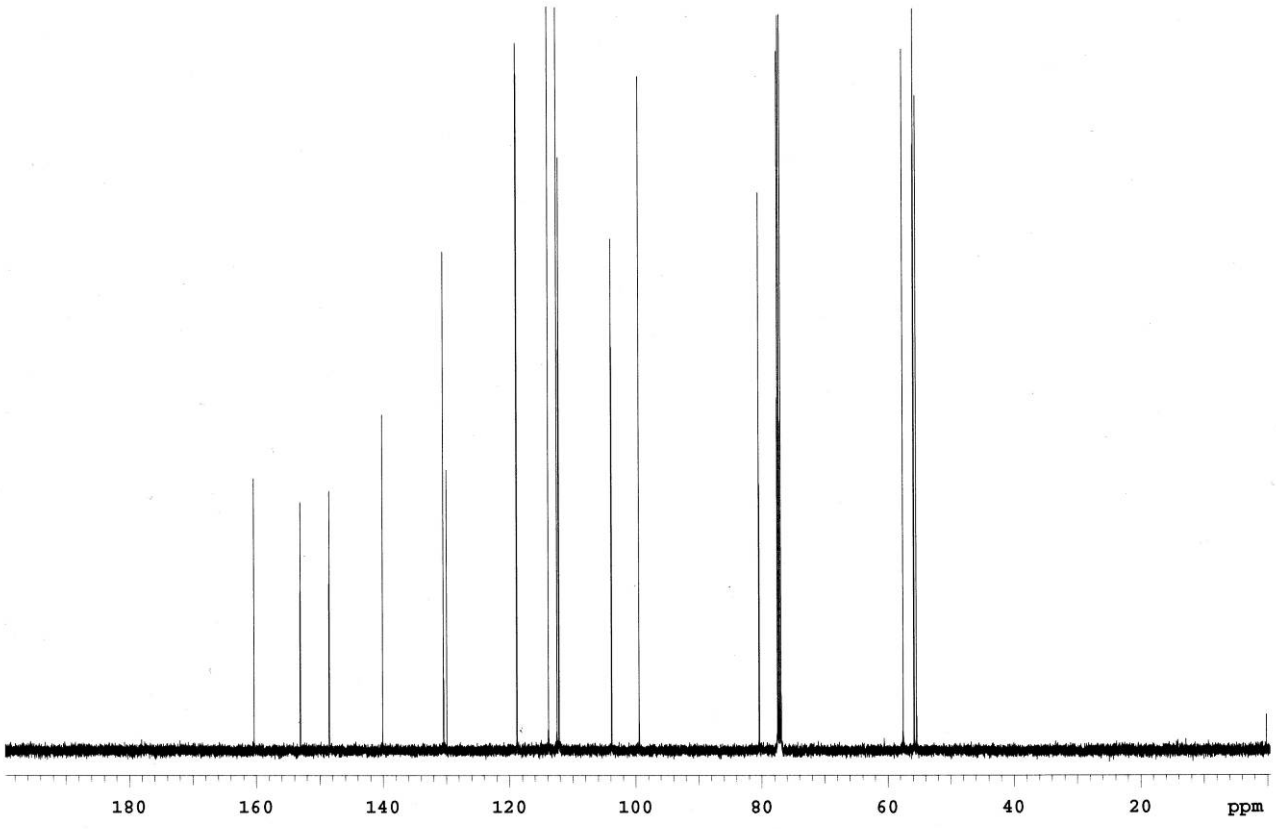
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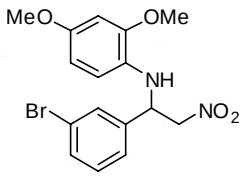
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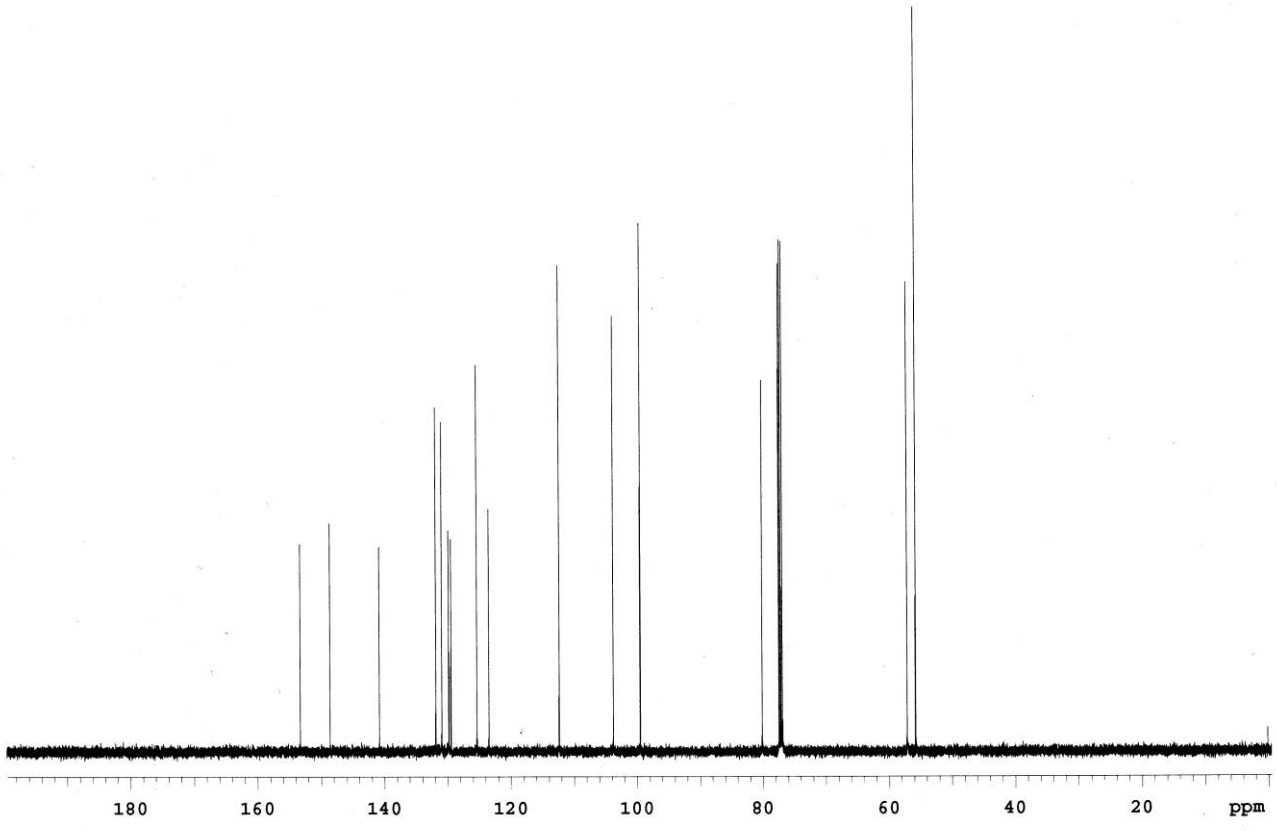
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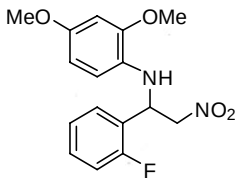
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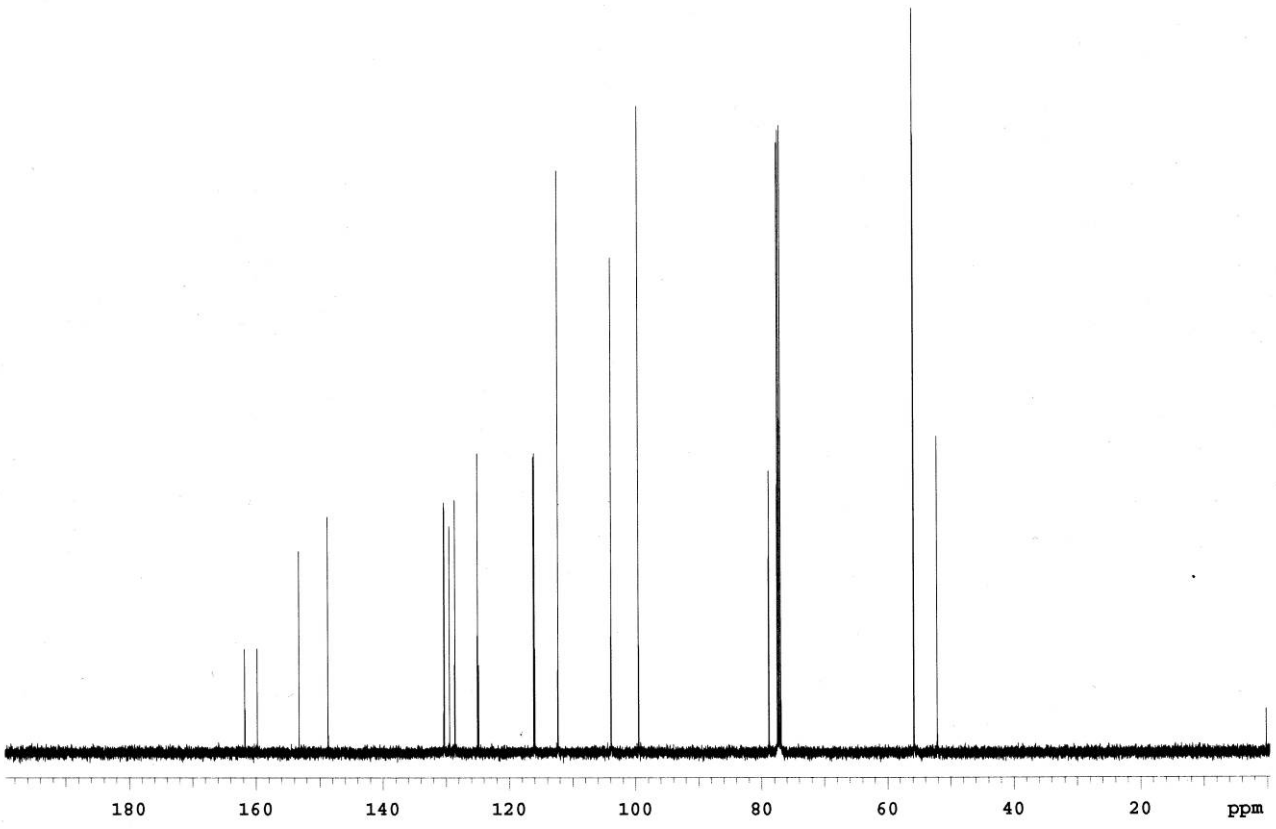
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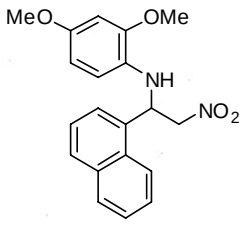
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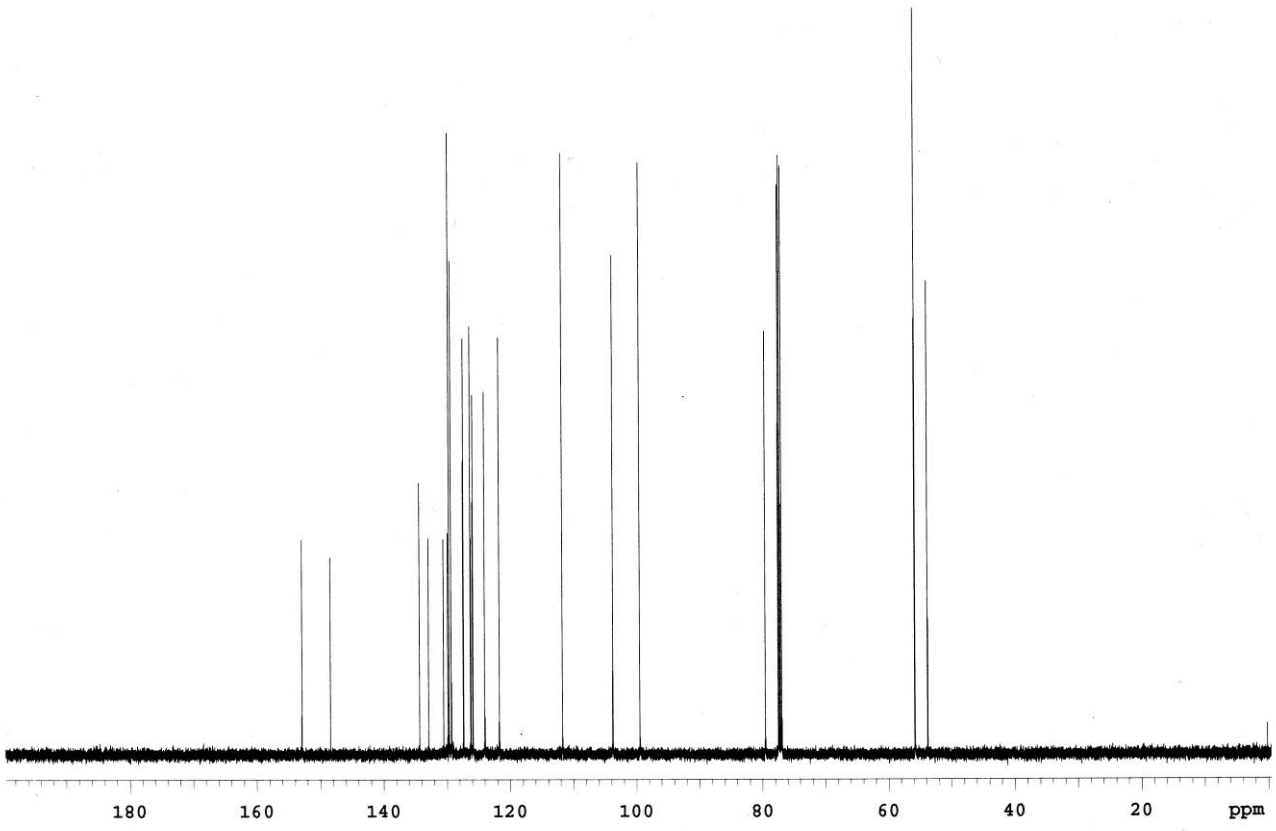
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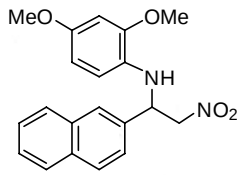
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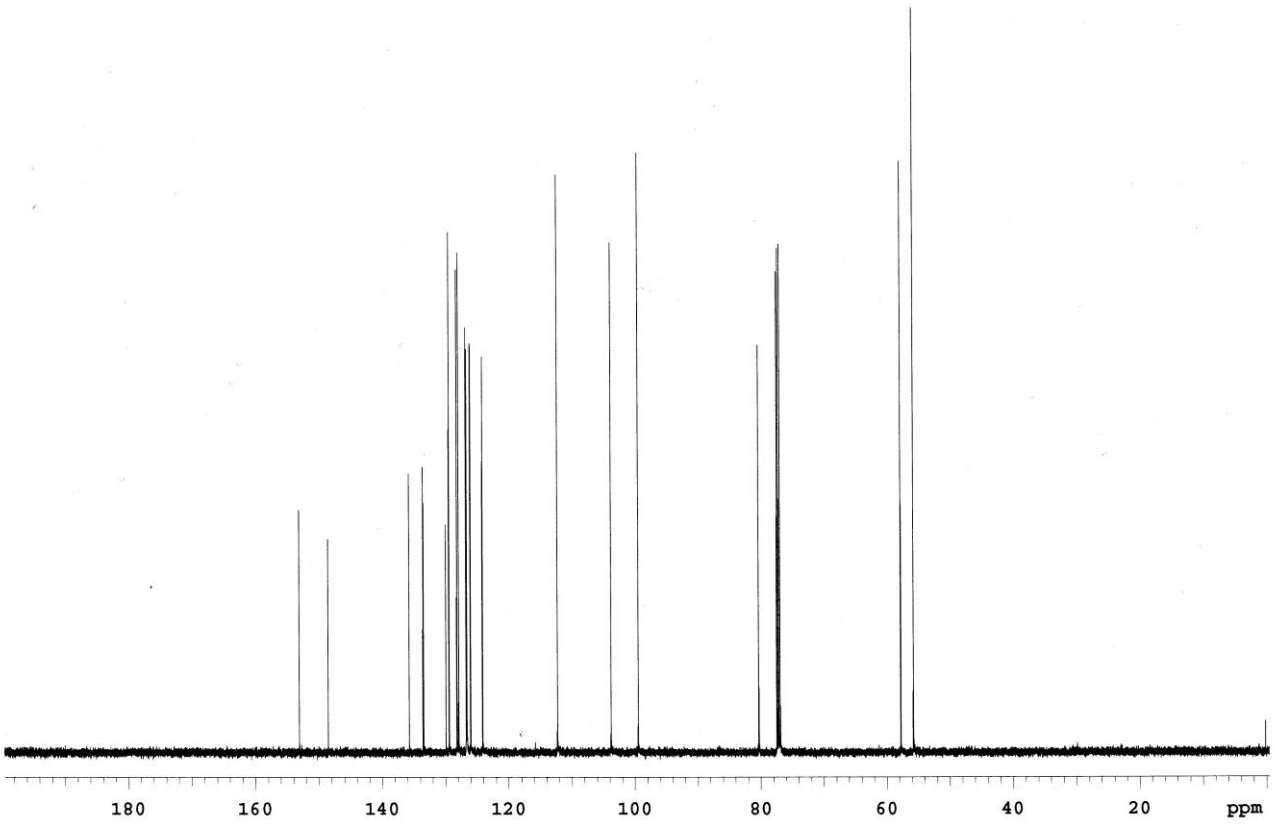
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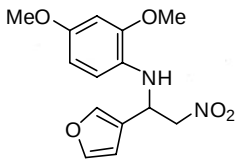
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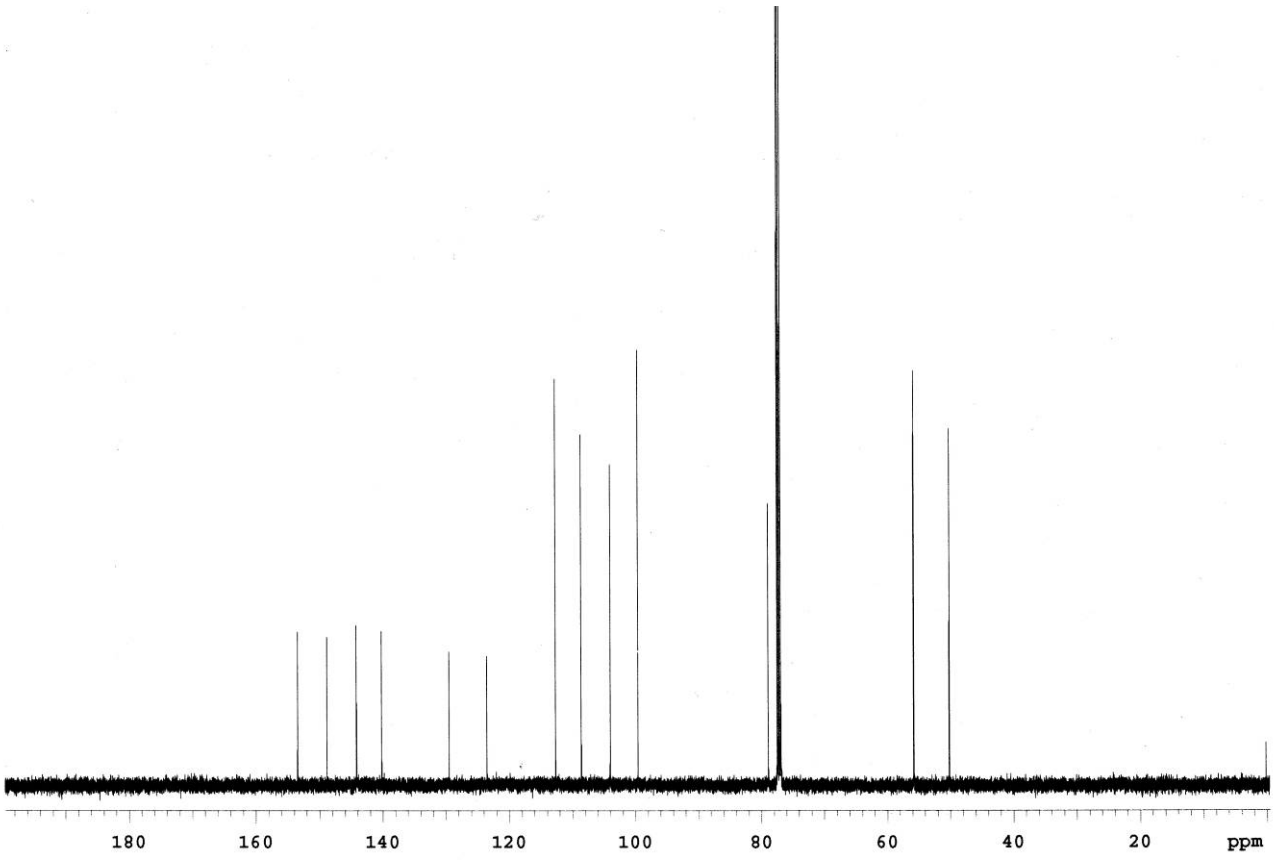
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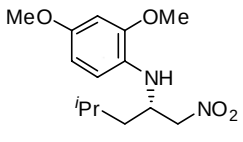
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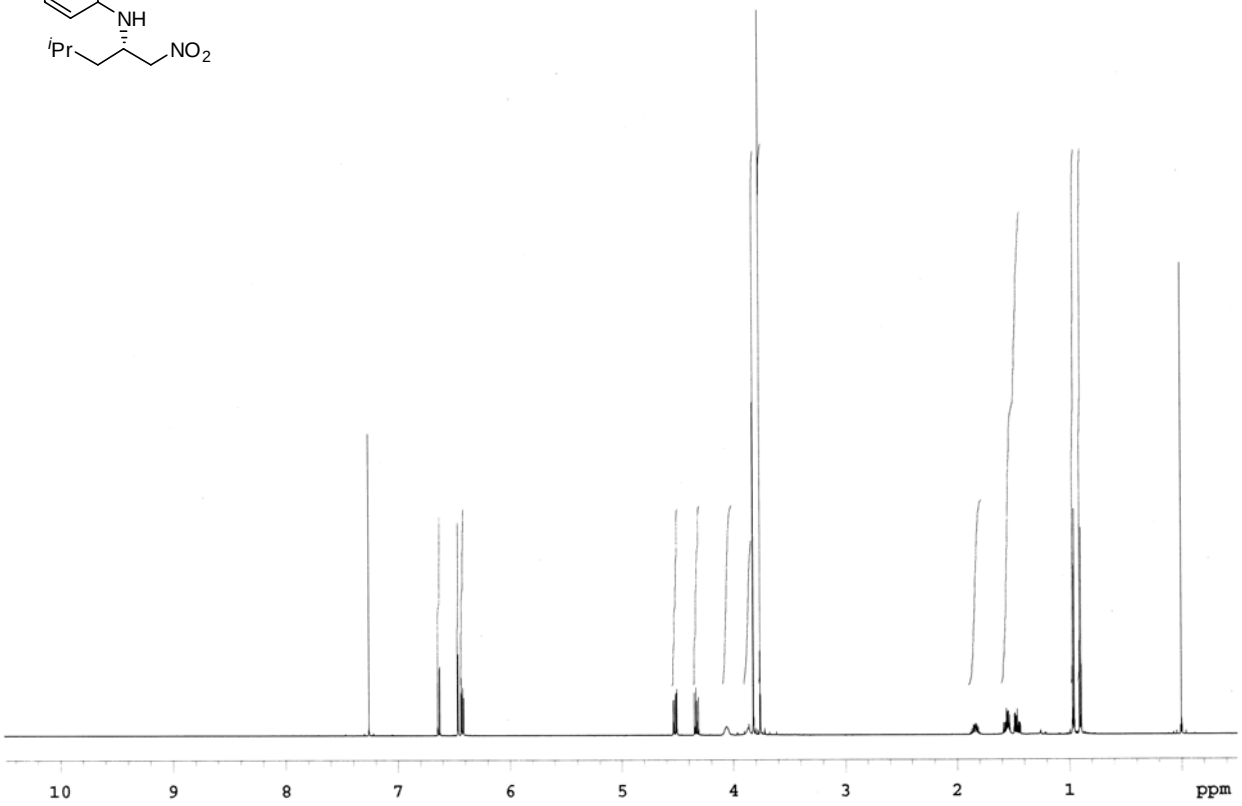
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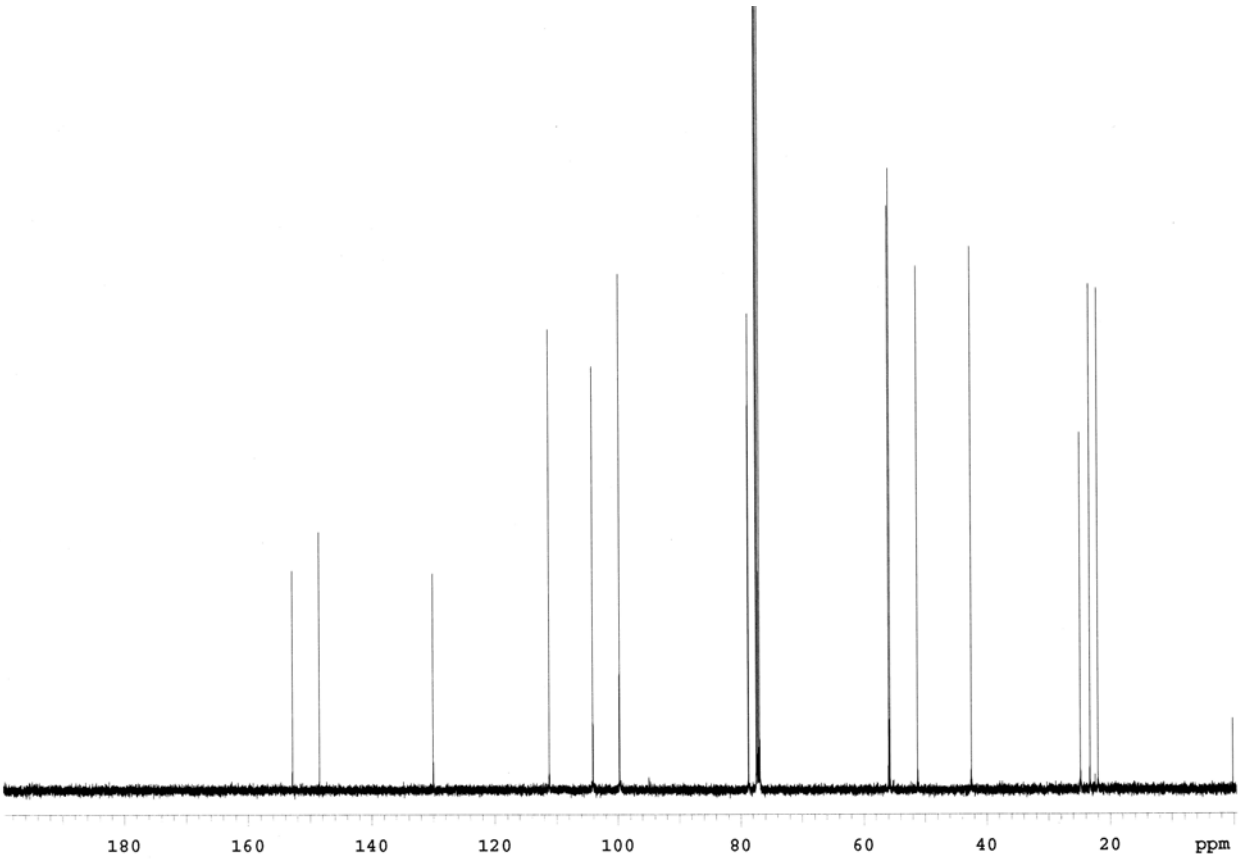
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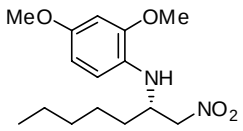
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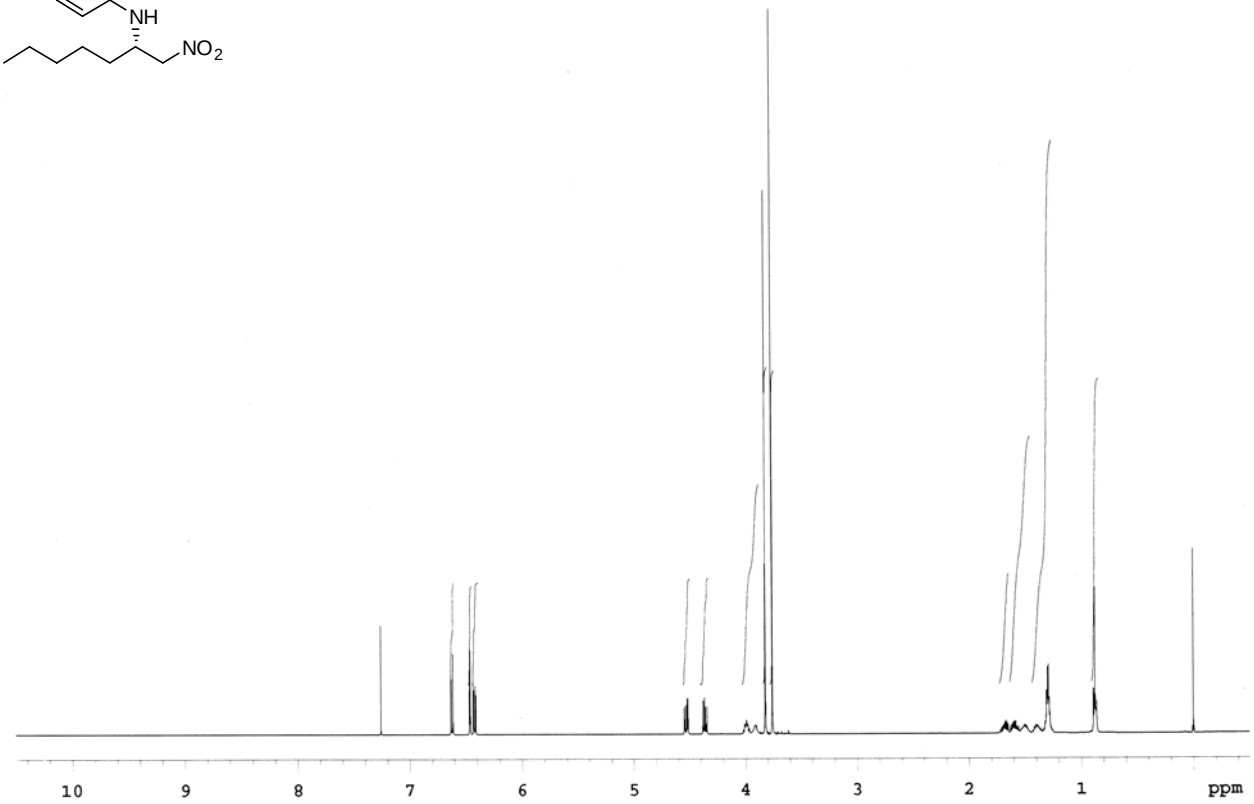
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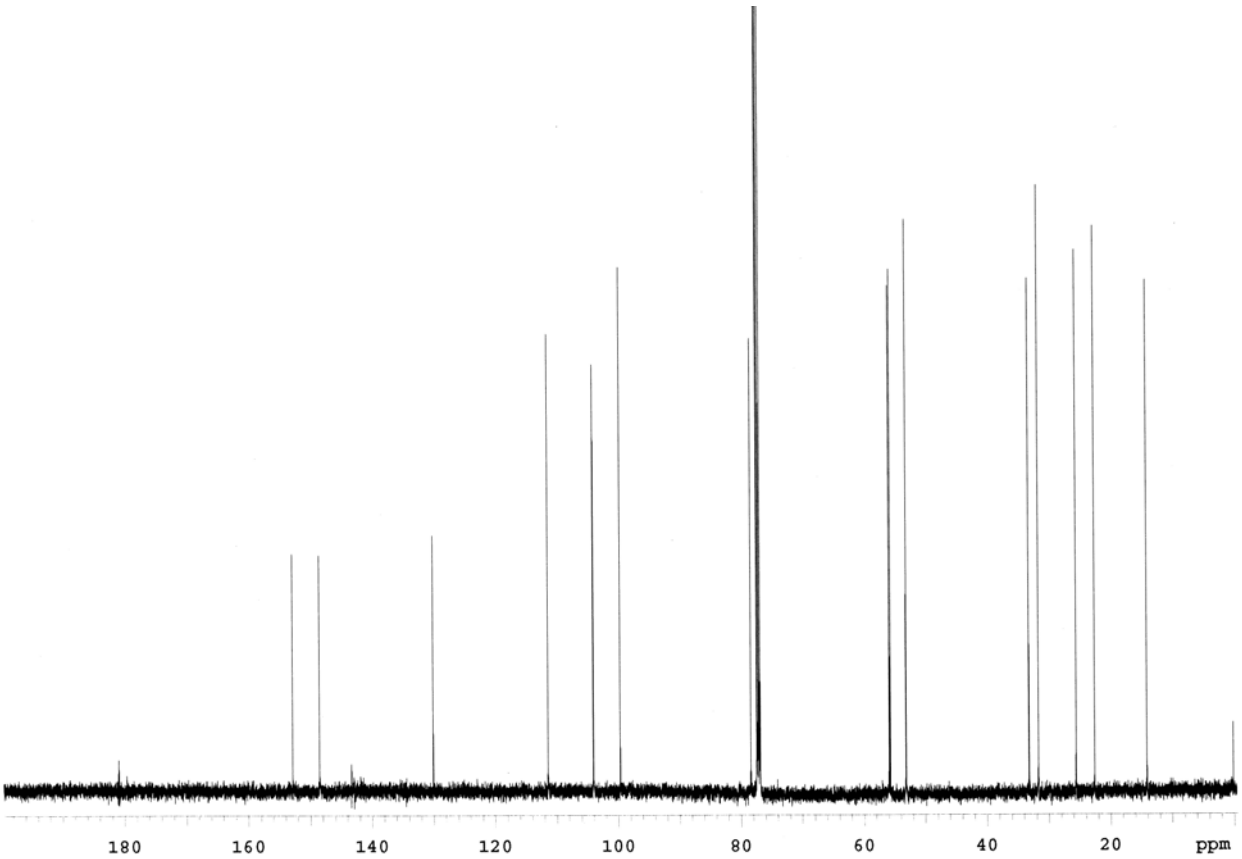
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