Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Enantio- and periselective nitroalkene Diels-Alder reaction

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I. General Information

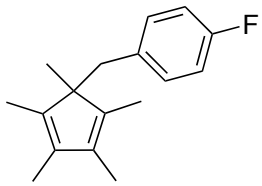
All reactions were carried out in the oven- or flame-dried glassware under an atmosphere of dry argon unless otherwise noted. Except as otherwise indicated, all reactions were magnetically stirred and monitored by analytical thin-layer chromatography using Merck pre-coated silica gel plates with F_{254} indicator. Visualization was accomplished by UV light (256 nm), with combination of potassium permanganate and/or vanillin solution as an indicator. Flash column chromatography was performed according to the method of Still using silica gel 60 (mesh 230-400) supplied by E. Merck.

Commercial grade reagents and solvents were used without further purification except as indicated below. Dichloromenthane (CH_2Cl_2) was freshly distilled over calcium hydride under an atmosphere of dry argon prior to use. THF was freshly distilled over sodium/benzophenone under an atmosphere of dry argon prior to use. Nitroethylene was prepared according the literature.[1]

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 300 (300 MHz ^{1}H), a Bruker Avance 400 (400 MHz ^{1}H, 100 MHz ^{13}C), and a Bruker Avance 500 (500 MHz ^{1}H, 125 MHz ^{13}C). Chemical shift values (δ) are reported in ppm relative to Me_4Si (δ 0.0 ppm) unless otherwise noted. The proton spectra are reported as follows δ (multiplicity, coupling constant J, number of protons). Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (quintet), h (septet), m (multiplet) and br (broad). Optical rotations were measured on a Rudolph Research Analytical AUTOPOL® III automatic polarimeter. Infrared spectra were recorded using PerkinElmer™ SPECTRUM ONE with Universal ATR Sampling Accessory (Composite Zinc Selenide and Diamond crystals). High resolution mass spectra were obtained at Mass Spectrometry Laboratory, Department of Chemistry, University of Miami. Compounds that are not numbered in the manuscript are labeled as **S1**, **S2**, etc.

II. General Procedure for Preparation of 5-Substituted Pentamethylcyclopentadienes

1-Fluoro-4-((1,2,3,4,5-pentamethylcyclopenta-2,4-dienyl)methyl)benzene (S1)

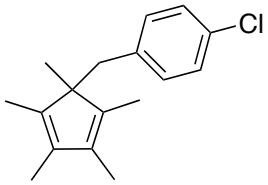


To a solution of NaHMDS (1.10 g, 5.97 mmol) in THF (12 mL) cooled to 0 °C was added a solution of pentamethylcyclopentadiene (813 mg, 5.97 mmol) in THF (6 mL) drop-wise. The resulting mixture was stirred for 1 h at room temperature, cooled back to 0 °C, and then treated with a solution of 4-fluorobenzyl bromide (1.00 g, 5.37 mmol) in THF (6 mL). The reaction mixture was stirred for 20 h at room temperature, quenched with aqueous NH_4Cl solution (20 mL), and extracted with Et_2O (2 x 20 mL). The combined organic layers were washed with brine (1 x 30 mL), dried over $MgSO_4$, filtered, and

concentrated *in vacuo*, at which time all volatiles, including unreacted pentamethylcyclopentadiene, were removed from the crude reaction mixture. The resulting oil was filtered through a short column of SiO_2 with hexanes, and concentrated *in vacuo* to afford the title compound as a colorless oil (1.22 g, 93%), which was used in the Diels-Alder reaction (*vide infra*) without further purification.

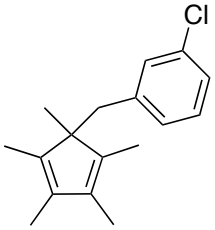
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 – 6.80 (m, 4H), 2.66 (s, 2H), 1.77 (s, 6H), 1.58 (s, 6H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (d, J = 250.0 Hz) 138.9, 134.8, 134.2 (d, J = 3.0 Hz), 129.7 (d, J = 7.8 Hz), 113.6 (d, J = 20.6 Hz), 56.5, 40.7, 21.5, 10.7, 10.3; FTIR (neat) υ_{max} 2916, 2854, 1603, 1509, 1447, 1378, 1220, 1157, 1098, 1016, 825, 766 cm^{-1}; GCMS: 244 $[M]^+$

1-Chloro-4-((1,2,3,4,5-pentamethylcyclopenta-2,4-dienyl)methyl)benzene (S2)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, J = 8.0 Hz, 2H), 6.75 (d, J = 8.0 Hz, 2H), 2.66 (s, 2H), 1.77 (s, 6H), 1.58 (s, 6H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 137.1, 134.9, 131.1, 129.8, 127.1, 56.5, 40.8, 21.6, 10.8, 10.3; FTIR (neat) υ_{max} 2917, 2855, 1492, 1445, 1406, 1378, 1265, 1087, 838, 781, 739 cm^{-1}; GCMS: 260 $[M]^+$

1-Chloro-3-((1,2,3,4,5-pentamethylcyclopenta-2,4-dienyl)methyl)benzene (S3)

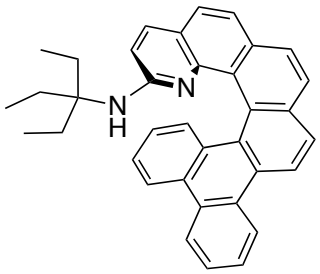


^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 – 7.06 (m, 2H), 6.83 (s, 1H) 6.73 (d, J = 4.0 Hz, 1H), 2.67 (s, 2H), 1.78 (s, 6H), 1.61 (s, 6H), 1.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 138.9, 135.1, 132.7, 128.5, 128.2, 126.7, 125.6, 56.5, 41.0, 21.6, 10.7, 10.3; FTIR (neat) υ_{max} 2914, 2855, 1597, 1572, 1479, 1445, 1378, 1205, 1078, 859, 772 cm^{-1}; GCMS: 260 $[M]^+$

III. Preparation of 2-Amino-1-aza[6]helicenes

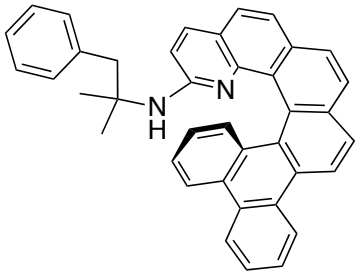
All new 11,12-benzo-2-alkylamino-1-aza[6]helicenes were prepared according to the published procedure.[2]

(+)-(*P*)-11,12-Benzo-2-(3-ethylpentan-3-amino)-1-aza[6]helicene (2)



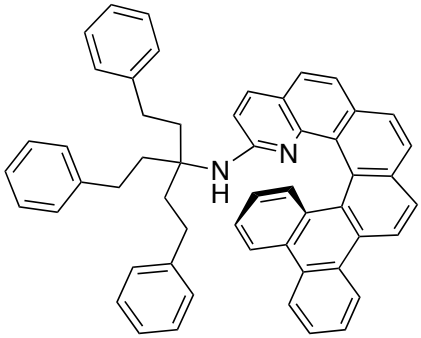
$[\alpha]^{20}_{D}$ = +2684, c = 0.0005, CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.26 (m, 3H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.26 – 7.38 (m, 6H), 6.85 – 6.89 (m, 2H), 6.32 – 6.36 (m, 1H), 6.08 (d, *J* = 8.0 Hz, 1H), 0.89 – 1.02 (m, 6H), 0.14 (t, *J* = 8.0 Hz, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 145.5, 136.9, 134.0, 133.1, 132.8, 130.63, 130.61, 130.5, 128.4, 127.8, 127.6, 127.1, 127.0, 126.9, 126.6, 126.4, 126.3, 126.2, 125.9, 125.0, 124.4, 124.2, 122.8, 122.79, 121.7, 121.4, 120.6, 107.8, 57.7, 28.0, 7.7; FTIR (neat) υ_{max} 2965, 2927, 1720, 1610, 1520, 1485, 1464, 1360, 1277, 1215, 1131, 837, 747 cm^{-1}; HRMS (ESI-TOF): Exact mass calcd for $C_{36}H_{33}N_2$ $[M + 1]^+$, expected: 493.2644, found: 493.2638

(-)-(*M*)-11,12-Benzo-2-(2-methyl-1-phenylpropan-2-amino)-1-aza[6]helicene (3)



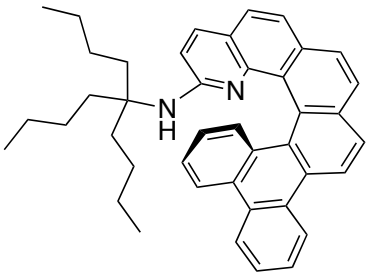
$[\alpha]^{20}_{D}$ = -2374, c = 0.0005, CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (dd, *J* = 4.0, 8.0 Hz, 2H), 8.54 (d, *J* = 8.0 Hz, 1H), 8.42 (d, *J* = 8.0 Hz), 8.01 – 8.04 (m, 2H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.76 (m 5H), 7.29 – 7.31 (m, 1H), 7.08 – 7.16 (m, 3H), 6.75 – 6.79 (m, 3H), 6.49 (d, *J* = 12.0 Hz, 1H), 3.86 (s, 1H), 2.63 (d, *J* = 12.0 Hz, 1H), 2.37 (d, *J* = 12.0 Hz, 1H), 0.98 (s, 3H), 0.88 (s, 3H);^{13}CNMR(100MHz,$CDCl_3$) 155.1, 145.6, 137.9, 136.5, 133.9, 132.9, 132.8, 130.7, 130.51, 130.46, 140.44, 128.5, 128.2, 127.7, 127.6, 127.4, 127.0, 126.9, 126.7, 126.5, 126.4, 126.3, 126.0, 125.8, 125.1, 124.6, 124.2, 122.8, 122.7, 122.1, 121.5, 120.7, 109.6, 53.1, 46.4, 28.1, 27.0; FTIR (neat) υ_{max} 2972, 1610, 1520, 1484, 1263, 839, 732, 700 cm^{-1}; HRMS (ESI-TOF): Exact mass calcd for $C_{39}H_{31}N_2$ $[M + 1]^+$, expected: 527.2487, found: 527.2482

(-)-(*M*)-11,12-Benzo-2-(3-phenethyl-1,5-diphenylpentan-3-amino)-1-aza[6]helicene (4)



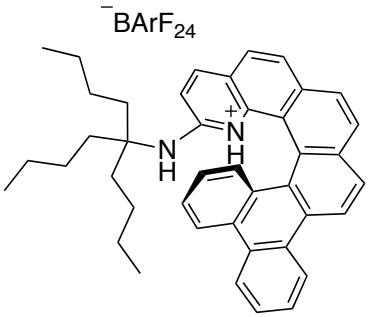
$[\alpha]^{20}_{D}$ = -1780, c = 0.0005, CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.17 (m, 2H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.20 (m, 9H), 6.53 – 6.97 (m, 15H), 6.27 – 6.29 (m, 2H) 6.11 (d, *J* = 8.0 Hz, 1H), 1.78 – 1.98 (m, 6H), 1.23 – 1.37 (m, 6H); ^{13}C NMR (100MHz, $CDCl_3$) 154.4, 145.5, 142.0, 137.3, 134.1, 132.9, 130.7, 130.5, 130.4, 130.1, 128.6, 128.4, 128.3, 127.7, 1 27.2, 127.1, 127.0, 126.99, 126.8, 126.5, 126.43, 126.39, 126.1, 125.85, 125.3, 124.3 122.9, 122.8, 122.3, 121.6, 120.9, 107.6, 57.2, 38.8, 30.0 (two signals overlap to give one); FTIR (neat) υ_{max} 2932, 1608, 1519, 1454, 1379, 1264, 841, 733, 699 cm^{-1}; HRMS (ESI-TOF): Exact mass calcd for $C_{54}H_{45}N_2$ $[M + 1]^+$, expected: 721.3583, found: 721.3577

(-)-(*M*)-11,12-Benzo-2-(5-butylnonan-5-amino)-1-aza[6]helicene (5)



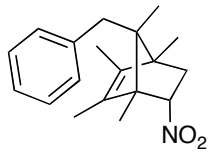
$[\alpha]^{20}_{D}$ = - 2082, c = 0.0005, CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 – 8.67 (m, 3H), 8.44 (d, *J* = 8.0 Hz, 1H), 7.66 – 8.01 (m, 7H), 7.26 – 7.32 (m, 3H), 6.74 – 6.77 (m, 1H), 6.49 (d, *J* = 12.0 Hz, 1H), 0.77 – 1.35(m,27H);^{13}CNMR(100MHz,$CDCl_3$) 154.8, 145.4, 136.8, 134.0, 133.4, 132.8, 130.8, 130.6, 130.5, 12 8.3, 127.7, 127.5, 127.13, 127.1, 126.9, 126.6, 126.43 126.36, 126.3, 126.0, 125.1, 124.4, 124.3, 122.8, 12 2.7, 121.6, 121.3, 120.6, 107.4, 56.9, 36.6, 25.2, 23.0, 13.9; FTIR (neat) υ_{max} 3400, 2930, 2861, 1609, 1584, 1519, 1485, 1465, 1356, 1263, 1144, 837, 751, 723 cm^{-1}; HRMS (ESI-TOF): Exact mass calcd for $C_{42}H_{45}N_2$ $[M + 1]^+$, expected: 577.3583, found: 577.3577

IV. General Procedure for Asymmetric Nitroalkene Diels-Alder Reaction



To a solution of **5** (72 mg, 0.12 mmol) in CH_2Cl_2 (2.4 mL) was added Et_2O solution of HCl (1M, 0.14 mL) drop-wise at room temperature. The reaction mixture was stirred for 30 min. and then concentrated *in vacuo*. The resulting solid was redissolved in CH_2Cl_2 (2.0 mL), and then concentrated *in vacuo*, the process of which was repeated three times. To the resulting yellow solid were added CH_2Cl_2 (2.6 mL), and $NaBArF_{24}\cdot 2.6H_2O$ (109 mg, 0.12 mmol) at room temperature. The resulting mixture was stirred for 30 min., filtered through a short pad of Celite, concentrated *in vacuo*, and then used in the Diels-Alder reaction without purification.

(-)-7-Benzyl-1,2,3,4,7-pentamethyl-5-nitrobicyclo[2.2.1]hept-2-ene (S4)

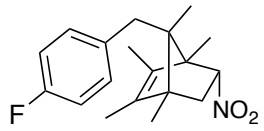


A flame-dried test tube was charged with (*P*)-catalyst (28 mg, 0.02 mmol) and 4 Å molecular sieves (28 mg). To this were added CH_2Cl_2 (0.3 mL) and a solution of nitroethylene (15 mg, 0.2 mmol) in CH_2Cl_2 (0.1 mL). The resulting mixture was cooled to -78 °C, slowly treated with a solution of diene[3] (91 mg, 0.4 mmol) in CH_2Cl_2 (0.3 mL), stirred at -78 °C for 20 h, and then quenched with a solution of hydrazine hydrate (0.1 mL) in MeOH (0.1 mL). The resulting mixture was washed with H_2O (3 x 1 mL) and brine (1 x 1 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel (20% benzene in hexanes) to afford the title compound as colorless oil (46 mg, 77%) with 70:30 er. The ligand **5** was recovered by eluting the column with 100% EtOAc (67 mg, 93%), and reused without loss in activity and selectivity.

Enantiomeric ratio was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (100% Hexanes, flow rate = 0.5mL/min), t_r (major) = 40.72 min., t_r (minor) = 46.79 min. $[\alpha]^{20}_D$ = -40, c = 0.0005, CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.29 (m, 4H), 7.05 – 7.07 (m, 1H), 4.69 – 4.71 (m, 1H), 2.58 (d, *J* = 12.0 Hz, 1H), 2.49 (d, *J* = 12.0 Hz, 1H), 1.87 – 1.89 (m, 2H), 1.69 (s, 3H), 1.48 (s, 3H), 1.12 (s, 3H), 0.89 (s, 3H), 0.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 139.1, 131.2, 130.6, 127.8, 125.9, 91.6, 64.0, 63.6, 55.0, 39.2, 37.5, 15.4, 12.4, 11.2, 10.7, 10.1; FTIR (neat) υ_{max}

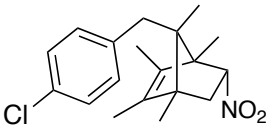
2943, 1541, 1448, 1382, 1362, 908, 729 cm^{-1}; HRMS (ESI-TOF): Exact mass calcd for $C_{19}H_{26}NO_2$ [M + 1]$^+$, expected: 300.1964, found: 300.1958.

(+)-7-(4-Fluorobenzyl)-1,2,3,4,7-pentamethyl-5-nitrobicyclo[2.2.1]hept-2-ene (S5)



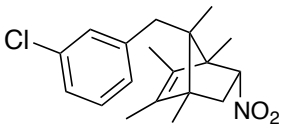
(*M*)-catalyst was used. Enantiomeric ratio was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (100% Hexanes, flow rate = 0.5mL/min), t_r (minor) = 35.07 min., t_r (major) = 40.37 min. $[\alpha]^{20}_D$ = +32, c = 0.0005, CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 – 7.02 (m, 2H), 6.89 – 6.94 (m, 2H), 4.70 (dd, *J* = 5.2, 6.4 Hz, 1H), 2.57 (d, *J* = 12.0 Hz, 1H), 2.45 (d, *J* = 12.0 Hz, 1H), 1.88 – 1.90 (m, 2H), 1.69 (s, 3H), 1.47 (s, 3H), 1.12 (s, 3H), 0.87 (s, 3H), 0.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (d, *J* = 243.0 Hz), 139.0, 134.95 (d, *J* = 3.6 Hz), 131.8 (d, *J* = 7.9 Hz), 131.2, 114.6 (d, *J* = 20.6 Hz), 91.5, 63.49, 63.47, 56.0, 38.3, 37.5, 15.3, 12.4, 11.2, 10.7, 10.1;FTIR (neat) υ_{max} 2944, 1541, 1508, 1448, 1383, 1222, 908, 828, 729 cm^{-1}; HRMS (ESI-TOF): Exact mass calcd for $C_{19}H_{25}FNO_2$ [M + 1]$^+$, expected: 318.1869, found: 318.1864.

(+)-7-(4-Chlorobenzyl)-1,2,3,4,7-pentamethyl-5-nitrobicyclo[2.2.1]hept-2-ene (S6)



(*M*)-catalyst was used. Enantiomeric ratio was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (100% Hexanes, flow rate = 0.5mL/min), t_r (minor) = 44.85 min., t_r (major) = 55.91 min. $[\alpha]^{20}_D$ = +40, c = 0.0005, CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.21 (m, 2H), 6.98 – 7.01 (m, 2H), 4.70 (dd, *J* = 5.2, 6.4 Hz, 1H), 2.57 (d, *J* = 12.0 Hz, 1H), 2.46 (d, *J* = 12.0 Hz, 1H), 1.89 – 1.91 (m, 2H), 1.69 (s, 3H), 1.48 (s, 3H), 1.14 (s, 3H), 0.87 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 137.9, 131.82, 131.8, 131.3, 127.9, 91.4, 64.0, 63.5, 56.0, 38.5, 37.4 15.4, 12.4, 11.2, 10.8, 10.1 FTIR (neat) υ_{max} 2942, 1540, 1490, 1447, 1382, 1362, 1091, 1015, 810, 732 cm^{-1}; HRMS (ESI-TOF): Exact mass calcd for $C_{19}H_{25}ClNO_2$ [M + 1]$^+$, expected: 334.1574, found: 334.1568.

(+)-7-(3-Chlorobenzyl)-1,2,3,4,7-pentamethyl-5-nitrobicyclo[2.2.1]hept-2-ene (S7)



(*M*)-catalyst was used. Enantiomeric ratio was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (100% Hexanes, flow rate = 0.5mL/min), t_r (minor) = 57.59 min., t_r (major) = 65.56 min. $[\alpha]^{20}{}_D$ = +28, c = 0.0005, CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.21 (m, 2H), 6.98 – 7.01 (m, 2H), 4.70 (dd, *J* = 5.2, 6.4 Hz, 1H), 2.57 (d, *J* = 12.0 Hz, 1H), 2.46 (d, *J* = 12.0 Hz, 1H), 1.89 – 1.91 (m, 2H), 1.69 (s, 3H), 1.48 (s, 3H), 1.14 (s, 3H), 0.87 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 139.1, 133.6, 131.3, 130.5, 129.0, 128.7, 126.1, 91.4, 63.9, 63.6, 56.0, 39.0, 37.4, 15.5, 12.4, 11.2 , 10.7, 10.1 FTIR (neat) υ_{max} 2940, 1596, 1540, 1443, 1382, 1362, 1322, 875, 785 cm^{-1}; HRMS (ESI-TOF): Exact mass calcd for $C_{19}H_{25}ClNO_2$ $[M + 1]^+$, expected: 334.1574, found: 334.1587

V. Assignment of Absolute Stereochemistry

Absolute configuration of (+)-7-(4-chlorobenzyl)-1,2,3,4,7-pentamethyl-5-nitrobicyclo-[2.2.1]hept-2-ene (**S6**) was assigned on the basis of the X-ray structure of enantiopure **S6** prepared by HPLC (Chiralcel OD-H column, 100% Hexanes, flow rate = 0.5mL/min, t_r of (-)-enantiomer = 44.85 min., t_r of (+)-enantiomer = 55.91 min.) as described below. Those of other products (**S4**, **S5** and **S6**) were assigned by analogy.

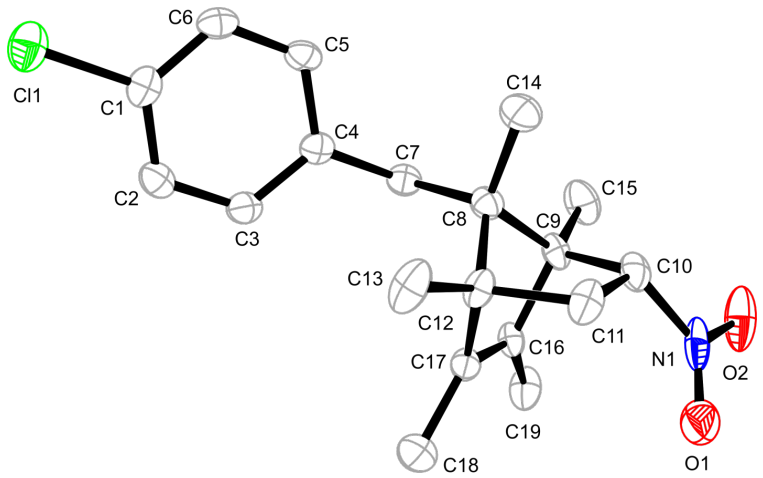


Figure S1. An ORTEP of the molecular structure of (+)-enantiomer of **S6** showing 50 % thermal ellipsoid probability.

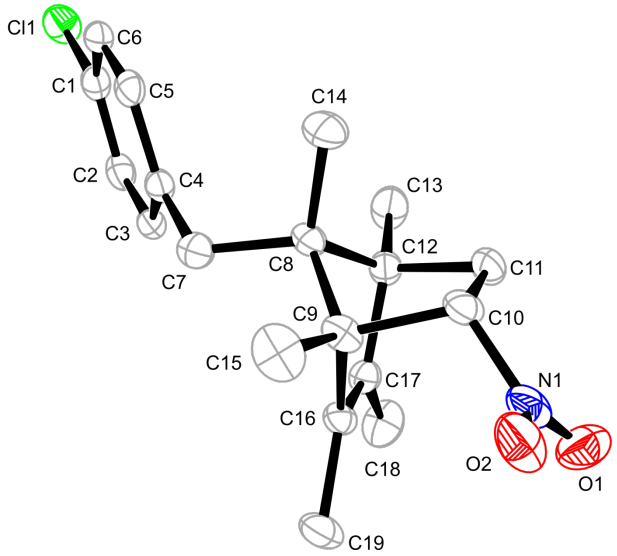
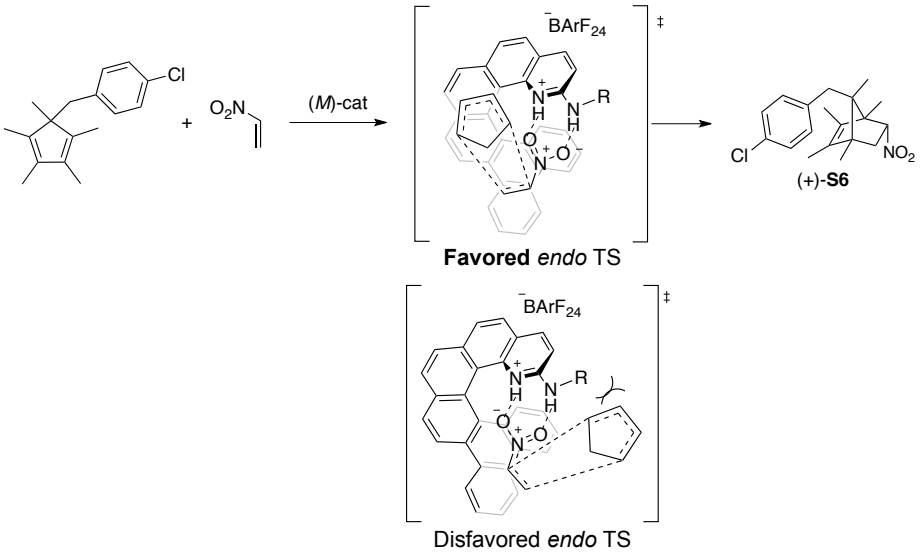


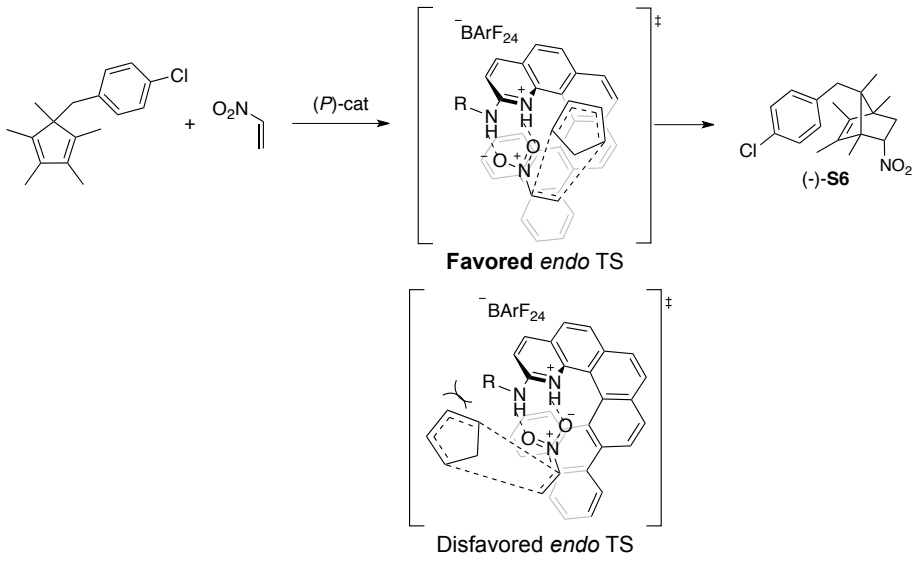
Figure S2. An ORTEP of the molecular structure of (-)-enantiomer of **S6** showing 50 % thermal ellipsoid probability.

Stereochemical Models:

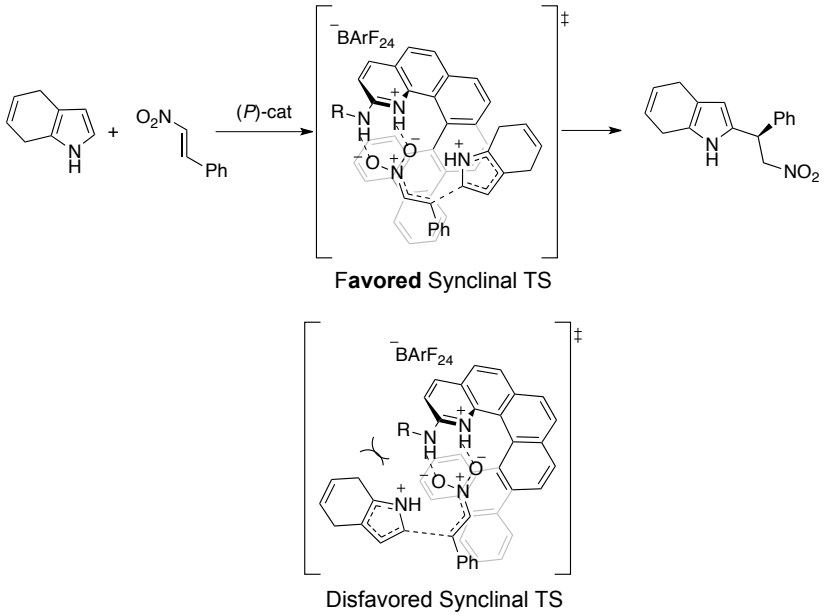
Schemes S1 and S2 depict the proposed stereochemical models of the Diels-Alder reaction, and Scheme S3 depicts that of the conjugate addition reaction previously reported by us.[2] These models are based on the sense of enantioselection observed in those reactions and the X-ray structure of catalyst (*P*)-**1**.[2] The backside of the bound nitroalkene is completely screened by the bottom half of the helicene framework. In the disfavored transition state, R group, which is designed to extend the top half of the helical framework, effectively hinders the approach of an incoming reactant (CP or pyrrole).



Scheme S1. Two *endo* TS models with (*M*)-catalyst. Non-substituted CP is shown for clarity. $^{-}BArF_{24}$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.



Scheme S2. Two *endo* TS models with (*P*)-catalyst. Non-substituted CP is shown for clarity. $^{-}BArF_{24}$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.



Scheme S3. Two synclinal TS models for the conjugate addition reaction.[2] $^{-}$BArF$_{24}$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.

Crystallographic Analyses:

The data crystals of (+)-enantiomer and (-)-enantiomer were mounted onto the end of a thin glass fiber using Paratone-N. X-ray intensity data were measured with a Bruker SMART APEX2 CCD-based diffractometer using Mo Kα radiation (λ = 0.71073 Å).[1] The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm.[1] Corrections for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS. The structure was solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares on F^2, by using the SHELXTL software package.[2] All non-hydrogen atoms were refined with anisotropic displacement parameters unless otherwise stated. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements. Crystal data, data collection parameters, and results of the analyses are listed in Table S1.

Colorless single crystals of (+)-enantiomer suitable for x-ray diffraction analyses obtained by evaporation of ethanol/water solvent mixture crystallized in the Triclinic crystal system. The structure could only be solved in the chiral space group P1. Attempts to solve the structure in the centrosymmetrical space group P $\bar{1}$ were unsuccessful. Furthermore, ADDSYM/PLATON[3] test did not indicate any additional missed symmetry. The Flack *x(u)* parameter 0.04(3) indicates that the correct

enantiomorph has been selected. With Z = 4, there are four formula equivalents of the complex present in the asymmetric crystal unit. All four molecules are the same enantiomer.

Colorless single crystals of (-)-enantiomer suitable for x-ray diffraction analyses obtained by evaporation of isopropanol/water solvent mixture crystallized in the Triclinic crystal system. The structure could only be solved in the chiral space group P1. Attempts to solve the structure in the centrosymmetrical space group P $\bar{1}$ were unsuccessful. Furthermore, ADDSYM/PLATON[3] test did not indicate any additional missed symmetry. The Flack *x(u)* parameter – 0.03(3) indicates that the correct enantiomorph has been selected. With Z = 4, there are four formula equivalents of the complex present in the asymmetric crystal unit. All four molecules are the same enantiomer.

Table S1. Crystallographic Data for (+)-enantiomer and (-)-enantiomer.

	(+)-enantiomer	**(-)-enantiomer**
Empirical formula	$C_{19}H_{24}NO_2Cl$	$C_{19}H_{24}NO_2Cl$
Formula weight	333.84	333.84
Crystal system	Triclinic	Triclinic
Lattice parameters		
a (Å)	8.3213(4)	8.3206(4)
b (Å)	8.3312(4)	8.3369(4)
c (Å)	25.7701(13)	25.7561(14)
α (°)	93.369(1)	93.355(1)
β (°)	95.301(1)	95.323(1)
γ (°)	93.703(1)	93.682(1)
V (Å^3)	1771.42(15)	1771.53(15)
Space group	P1 (#1)	P1 (#1)
Z value	4	4
ρ_{calc} (g / cm^3)	1.252	1.252
μ (Mo Kα) (mm^{-1})	0.225	0.225
Temperature (K)	100	100

$2\Theta_{max}$ (°)	54.0	54.0
No. Obs. (I > 2σ(I))	12509	12543
No. Parameters	849	849
Goodness of fit	1.023	1.036
Max. shift in cycle	0.002	0.001
Residuals*:R1; wR2	0.0446; 0.0827	0.0453; 0.0873
Absorption Correction,	Multi-scan	Multi-scan
Max/min	0.9933/0.9194	0.9866/0.9154
Absolute structure Flack parameter	0.04(3)	– 0.03(3)
Largest peak in Final Diff. Map (e^- / $Å^3$)	0.228	0.302

*$R = \Sigma_{hkl}(\,|\,|F_{obs}|-|F_{calc}|\,|\,)/\Sigma_{hkl}|F_{obs}|$; $R_w = [\Sigma_{hkl}w(\,|F_{obs}|-|F_{calc}|\,)^2/\Sigma_{hkl}wF_{obs}^2]^{1/2}$,

$w = 1/\sigma^2(F_{obs})$; $GOF = [\Sigma_{hkl}w(\,|F_{obs}|-|F_{calc}|\,)^2/(n_{data} - n_{vari})]^{1/2}$.

References for X-ray analyses:

Apex2 Version 2.2-0 and SAINT+ Version 7.46A; Bruker Analytical X-ray System, Inc., Madison, Wisconsin, USA, 2007.

(a) G. M. Sheldrick, SHELXTL Version 6.1; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2000. (b) G. M. Sheldrick, *Acta Cryst*. 2008**, A64**, 112–122.

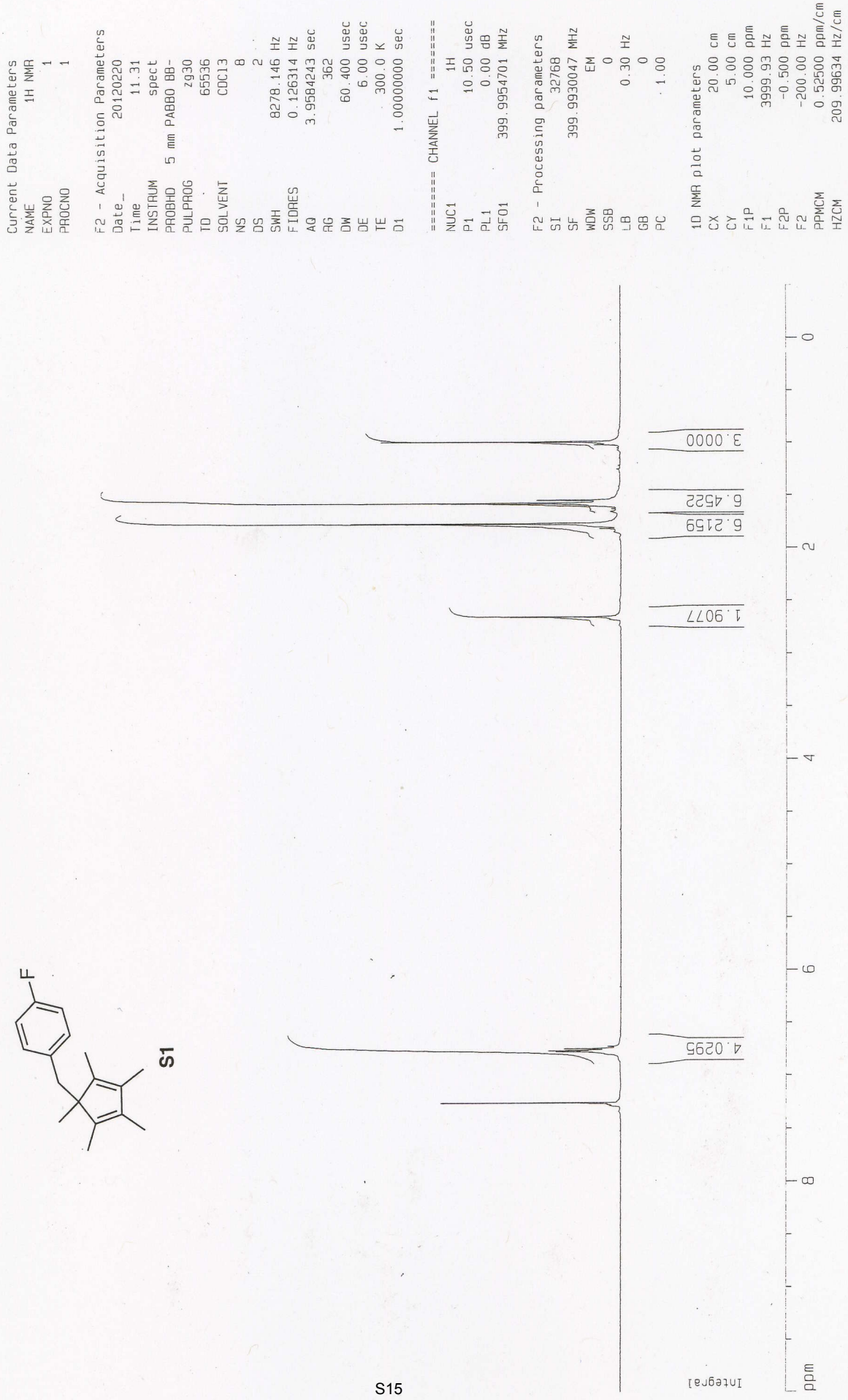
PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, Spek, A. L. 2008.

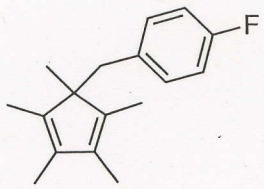
References:

[1] D. Ranganathan, C. B. Rao, S. Ranganathan, A. K. Mehrotra and R. Iyengar, *J. Org. Chem.* 1980, **45**, 1185.

[2] N. Takenaka, J. Chen, B. Captain, R. S. Sarangthem and A. Chandrakumar, *J. Am. Chem. Soc.* 2010, **132**, 4536.

[3] H. B. Romdhane, M. Baklouti, M. R. Chaâbouni, M. F. Grenier-Loustalot, F. Delolme and B. Sillion, *Polymer*, 2002, **43**, 255.





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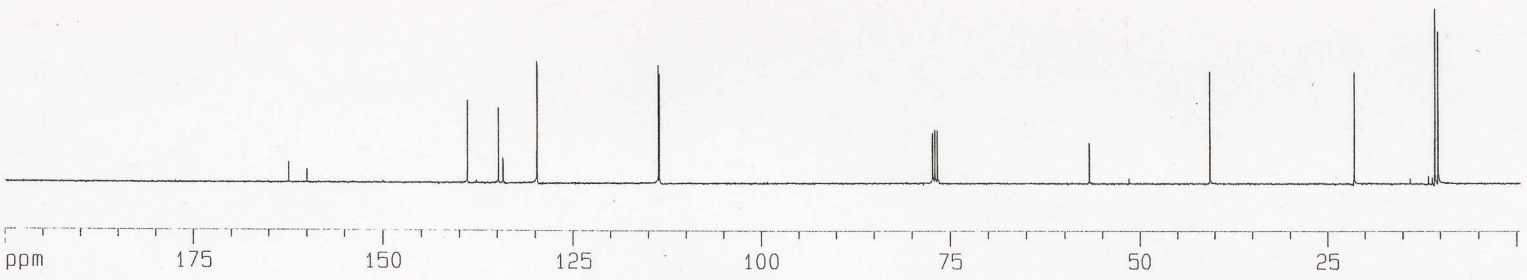

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RG	71.8
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TE	300.0 K
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d12	0.00002000 sec

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PL1	-2.00 dB
SFO1	100.5883377 MHz

======== CHANNEL f2 ========

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PCPD2	80.00 usec
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PL12	15.23 dB
PL13	17.89 dB
SFO2	399.9946000 MHz

F2 - Processing parameters

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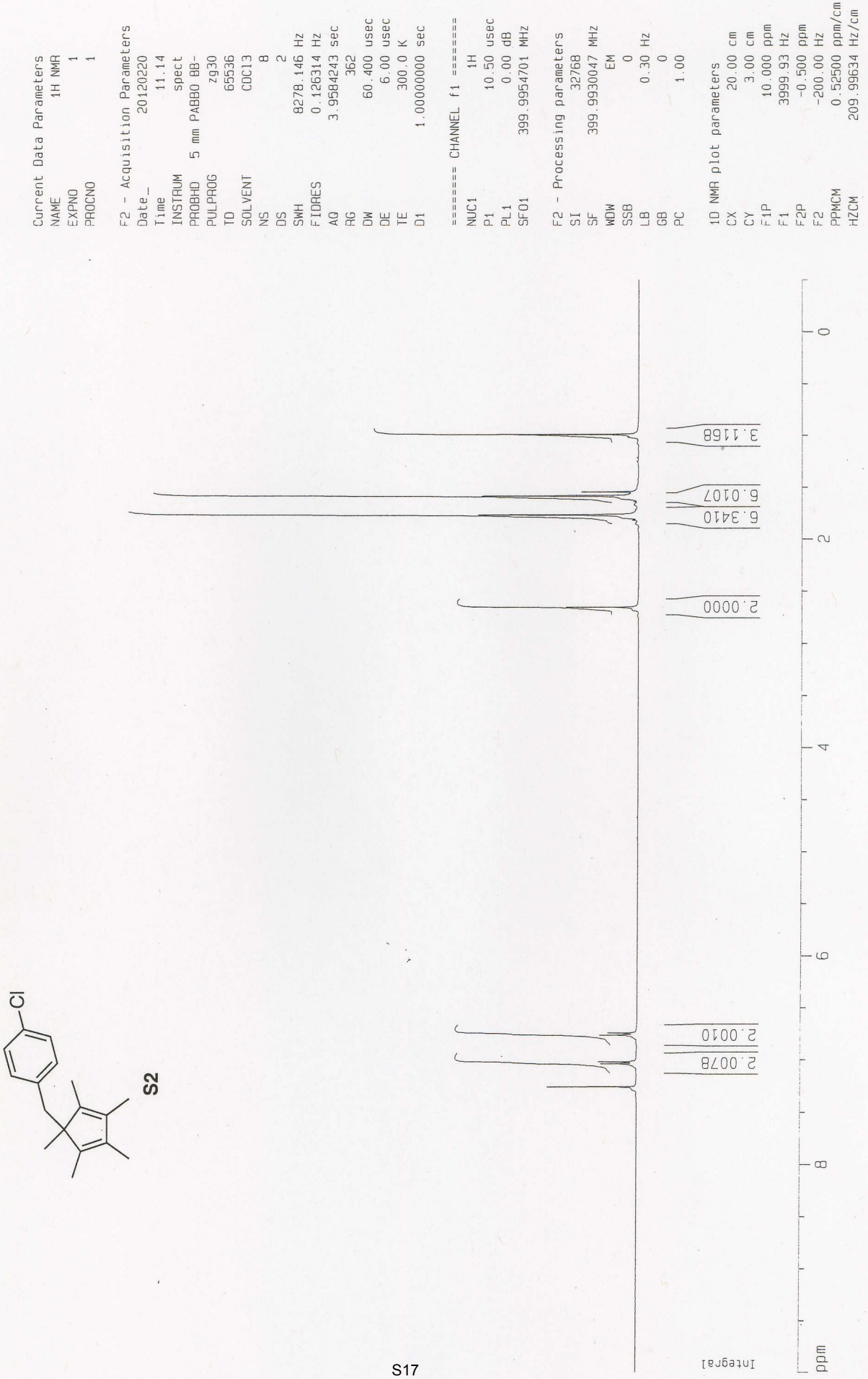
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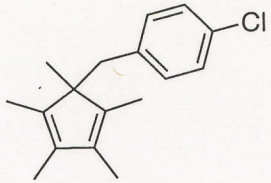
S2



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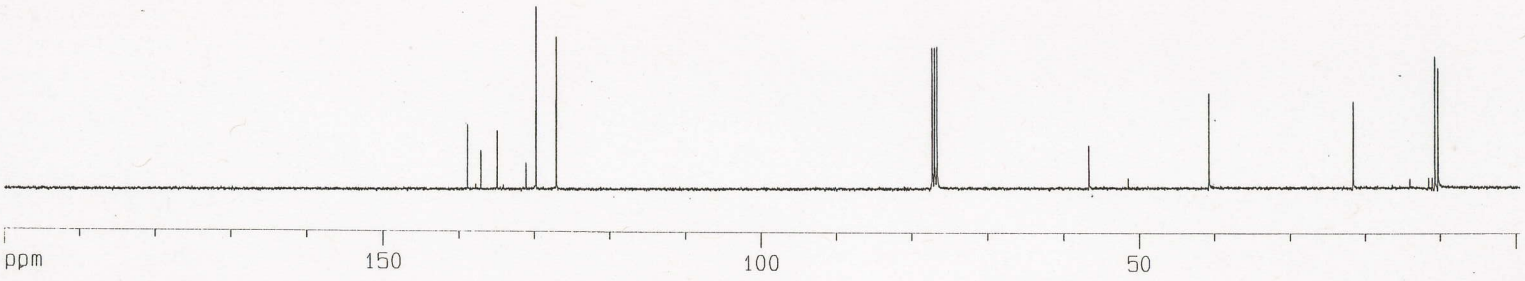


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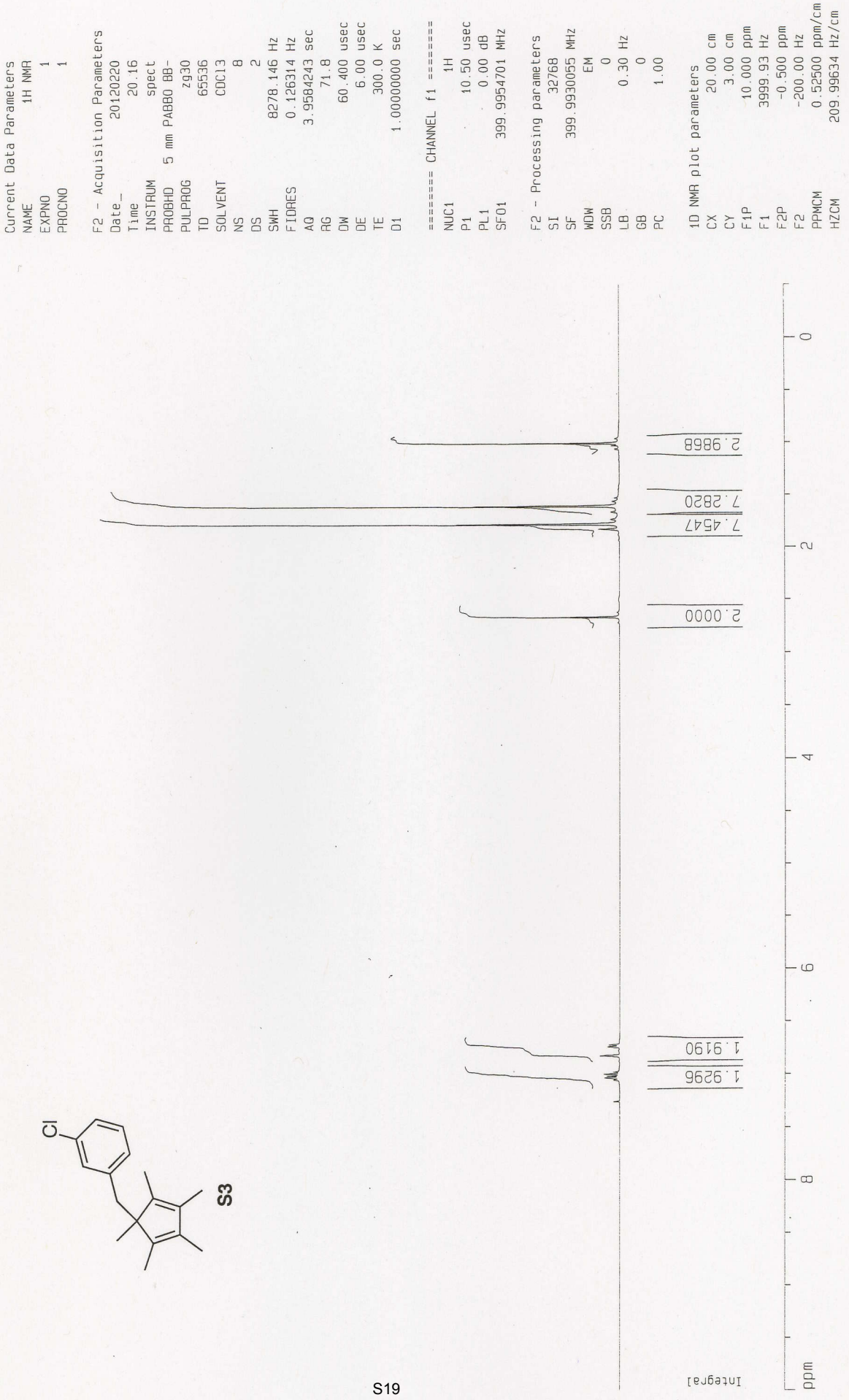
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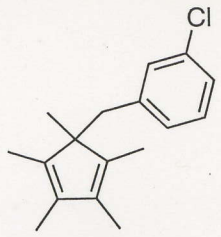

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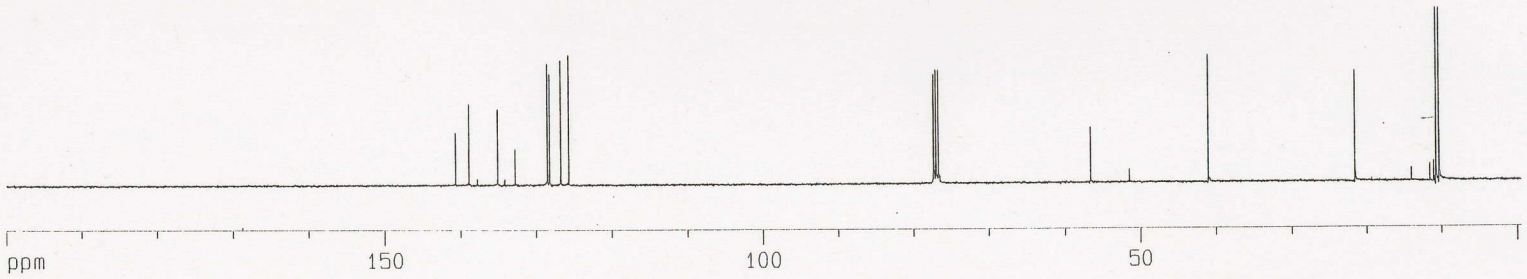


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PROCNO                      2

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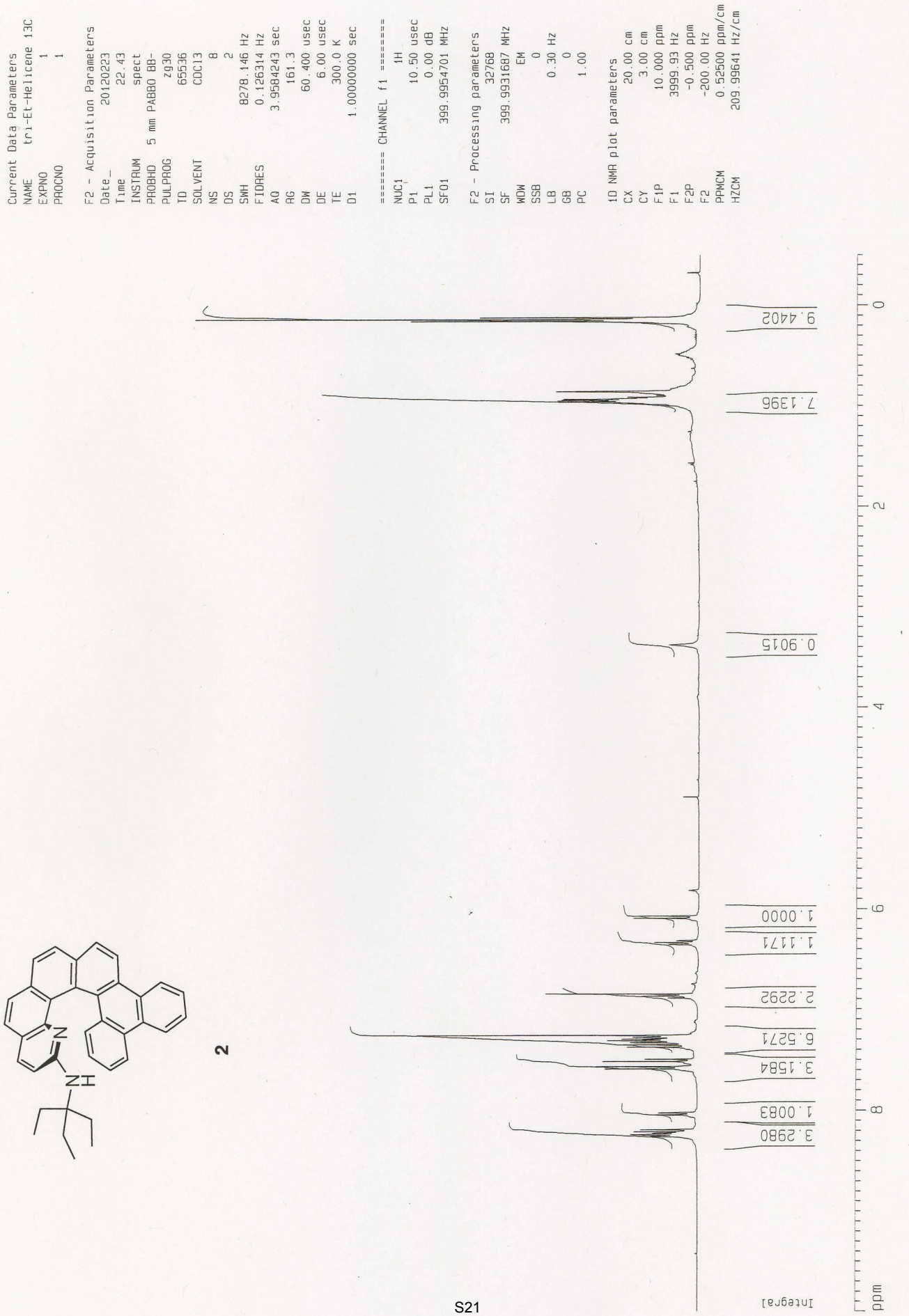
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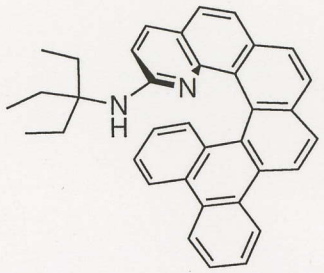

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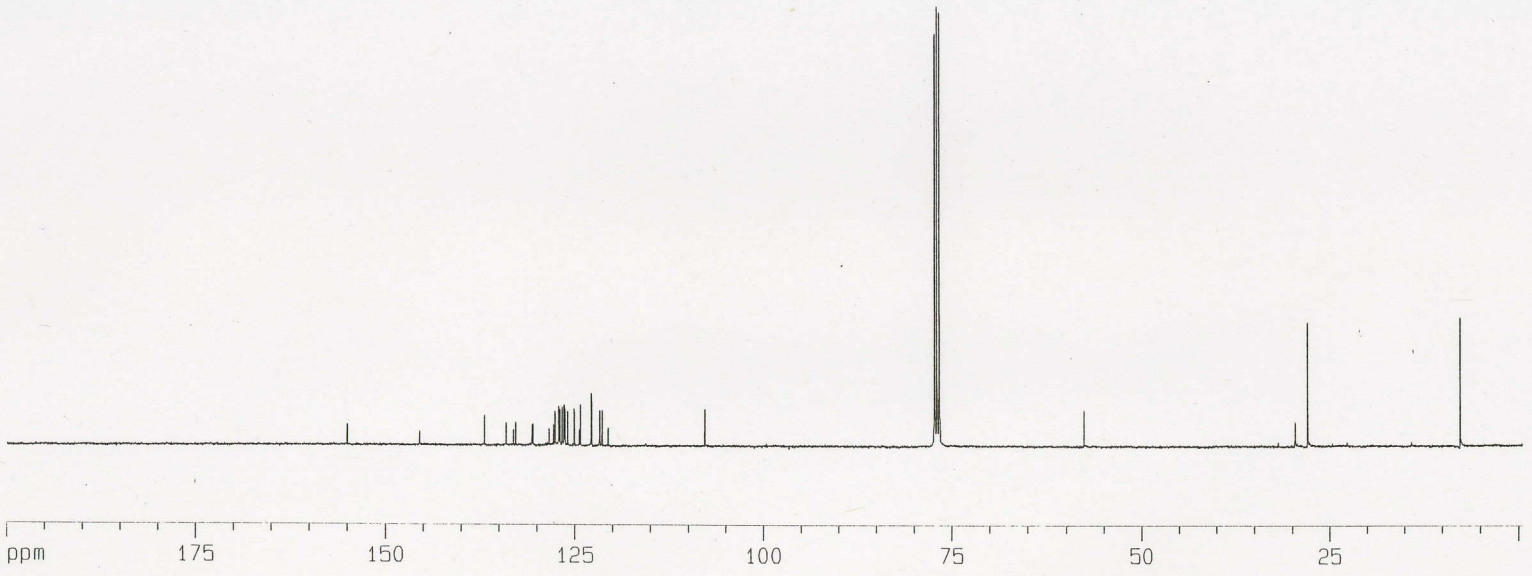


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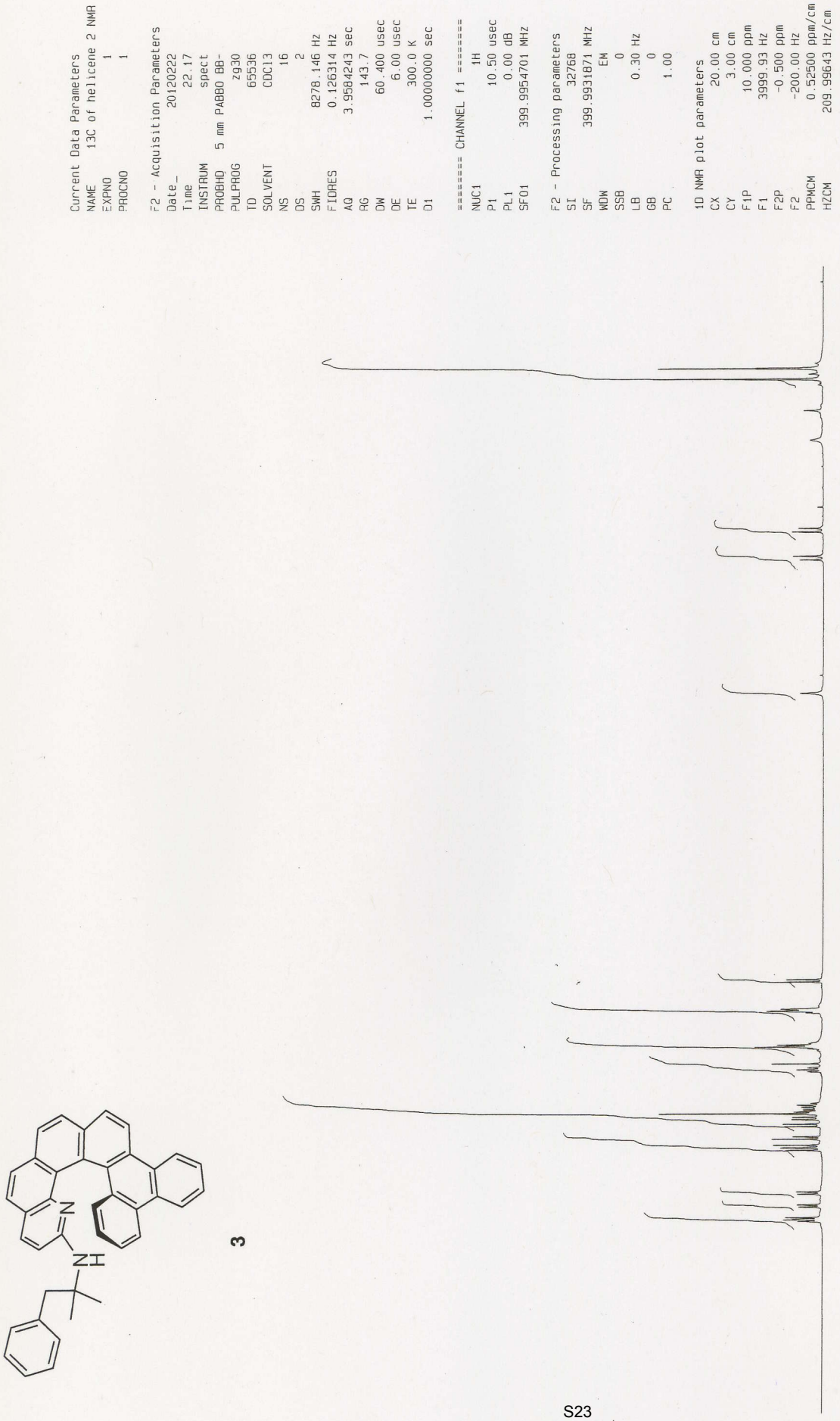
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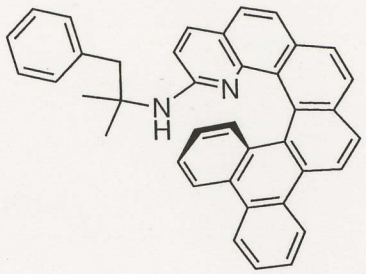

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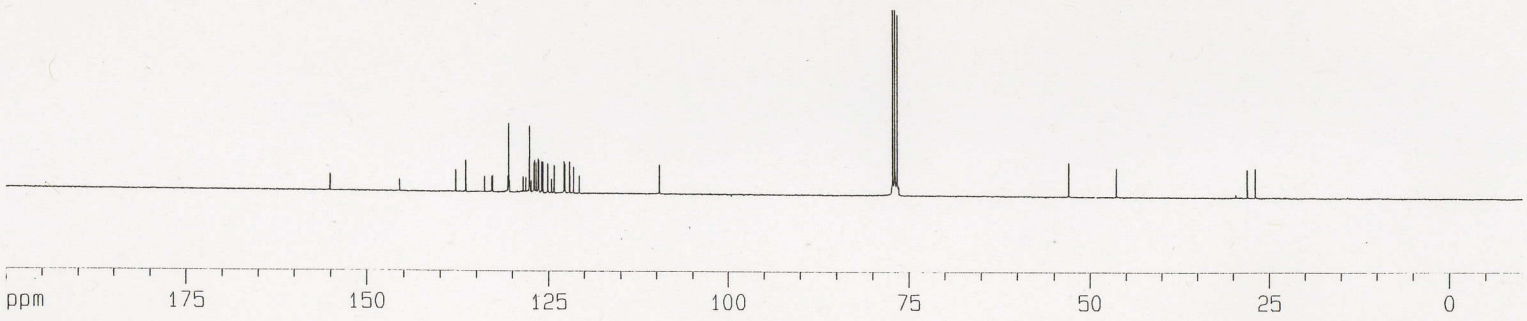


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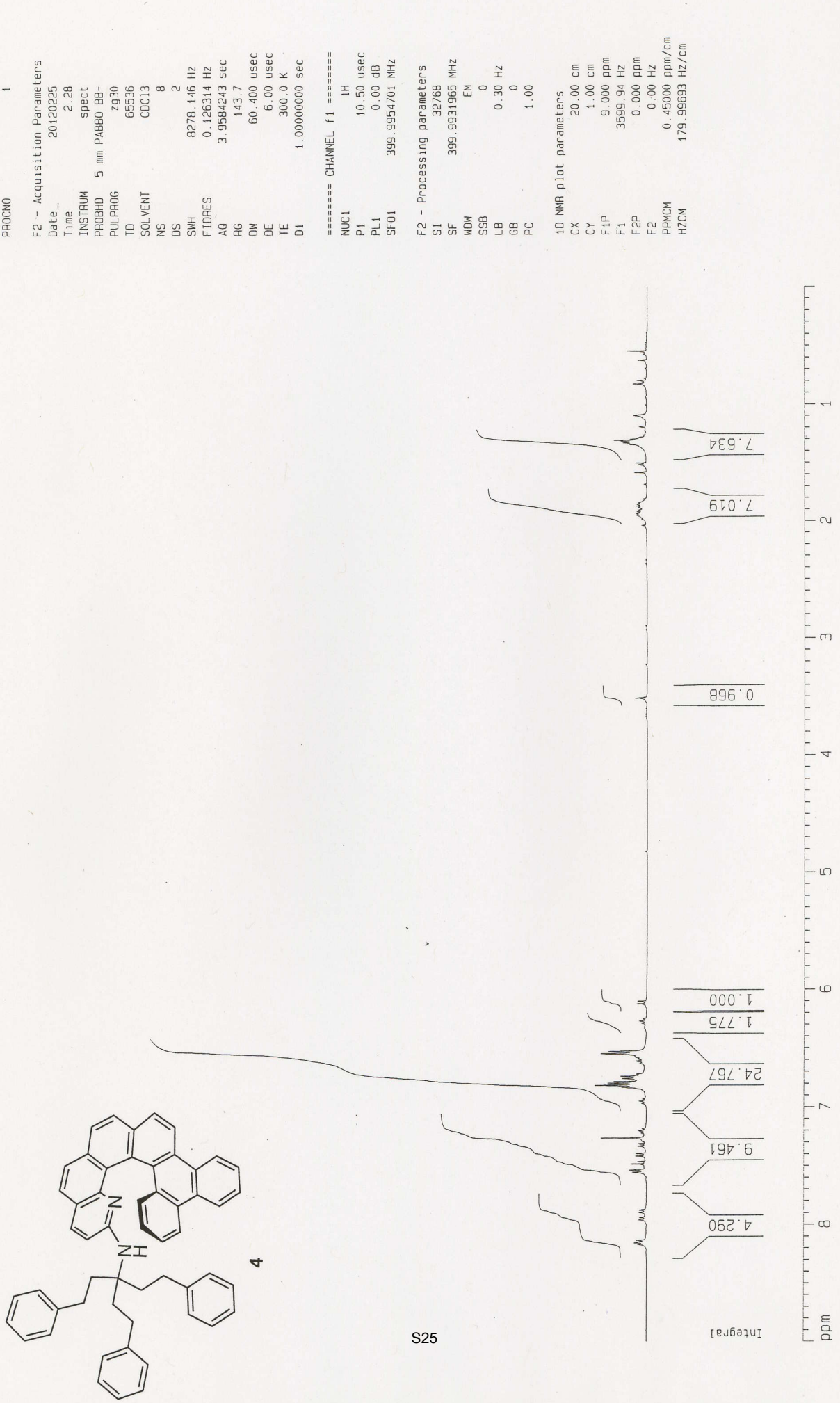
TE                 300.0 K
D1              2.00000000 sec
d11             0.03000000 sec
d12             0.00002000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                  9.80 usec
PL1                -2.00 dB
SFO1          100.5883377 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                -2.00 dB
PL12               15.23 dB
PL13               17.89 dB
SFO2          399.9946000 MHz

F2 - Processing parameters
SI                    32768
SF            100.5783223 MHz
WDW                      EM
SSB                       0
LB                 1.00 Hz
GB                        0
PC                     1.40

1D NMR plot parameters
CX                 20.00 cm
CY                  6.00 cm
F1P              200.000 ppm
F1              20115.66 Hz
F2P              -10.000 ppm
F2              -1005.78 Hz
PPMCM            10.50000 ppm/cm
HZCM          1056.07239 Hz/cm
```


Current Data Parameters
NAME tri-ph-helicene 13C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120225
Time 2.28
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 143.7
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 10.50 usec
PL1 0.00 dB
SFO1 399.9954701 MHz
F2 - Processing parameters
SI 32768
SF 399.9931965 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 1.00 cm
F1P 9.000 ppm
F1 3599.94 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.45000 ppm/cm
HZCM 179.99693 Hz/cm
4.290
9.461
24.767
1.775
1.000
0.968
7.019
7.634
Integral
ppm
8
7
6
5
4
3
2
1
N
H
4

```
Current Data Parameters
NAME      tri-ph-helicene 13C
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120225
Time                2.53
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    6548
DS                       4
SWH             23980.814 Hz
FIDRES              0.365918 Hz
AQ                1.3664756 sec
RG                      50.8
DW                 20.850 usec
DE                  6.00 usec
TE                  300.0 K
D1              2.00000000 sec
d11             0.03000000 sec
d12             0.00002000 sec

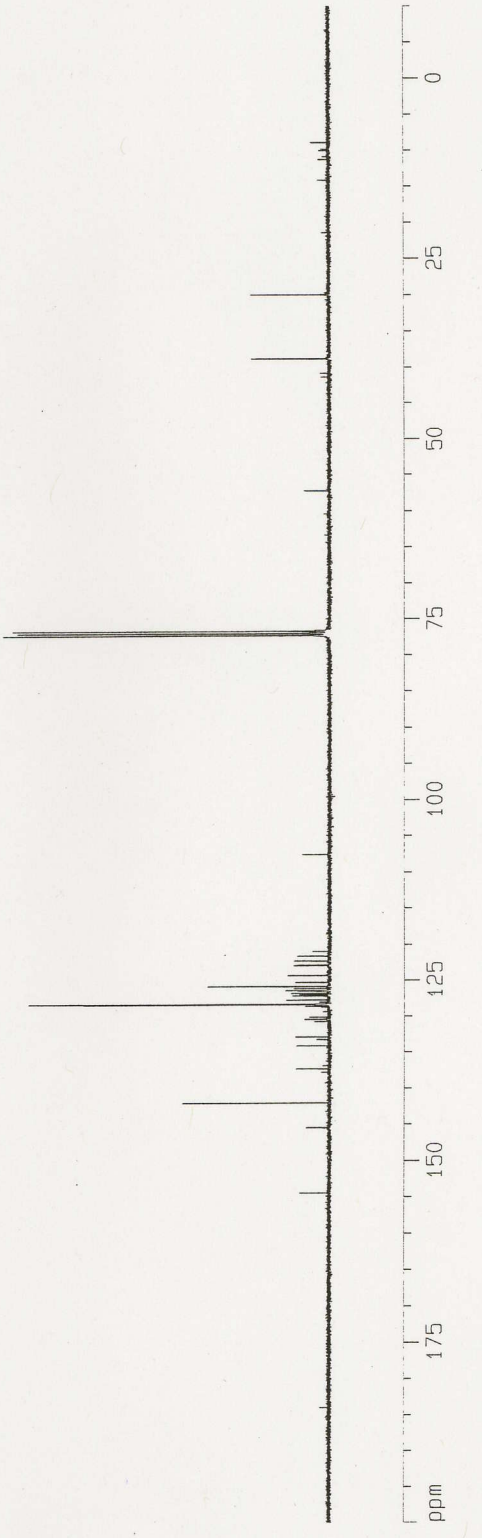
======== CHANNEL f1 ========
NUC1                    13C
P1                   9.80 usec
PL1                 -2.00 dB
SFO1          100.5883377 MHz

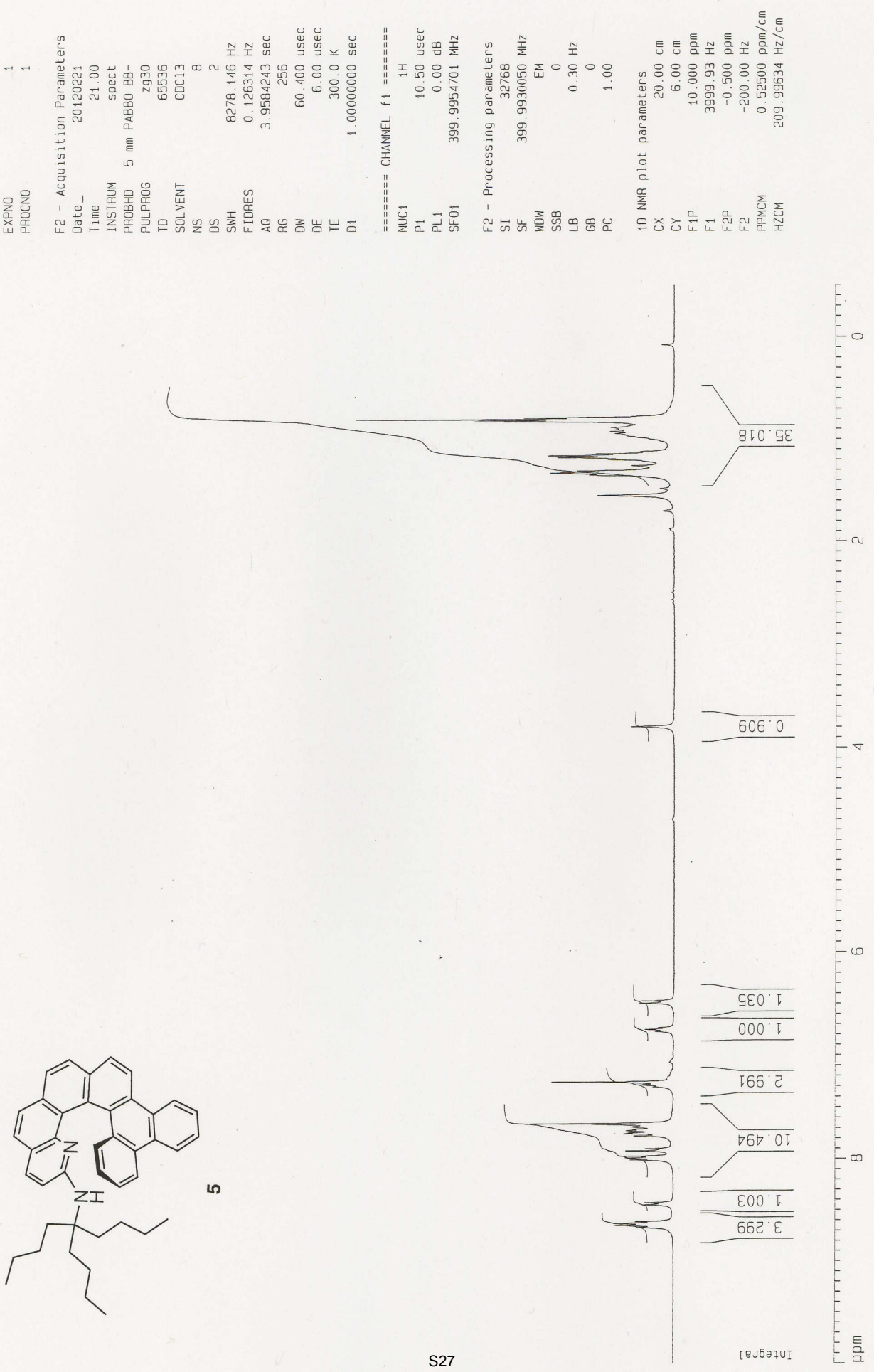
======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2               80.00 usec
PL2                 -2.00 dB
PL12                15.23 dB
PL13                17.89 dB
SFO2          399.9946000 MHz

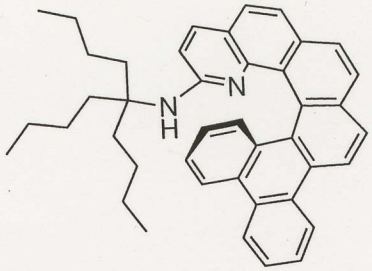
F2 - Processing parameters
SI                     32768
SF          100.5783230 MHz
WDW                       no
SSB                        0
LB                  0.00 Hz
GB                         0
PC                      1.40

1D NMR plot parameters
CX                  20.00 cm
CY                   4.00 cm
F1P                200.000 ppm
F1               20115.66 Hz
F2P                -10.000 ppm
F2                -1005.78 Hz
PPMCM           10.50000 ppm/cm
HZCM          1056.07239 Hz/cm
```

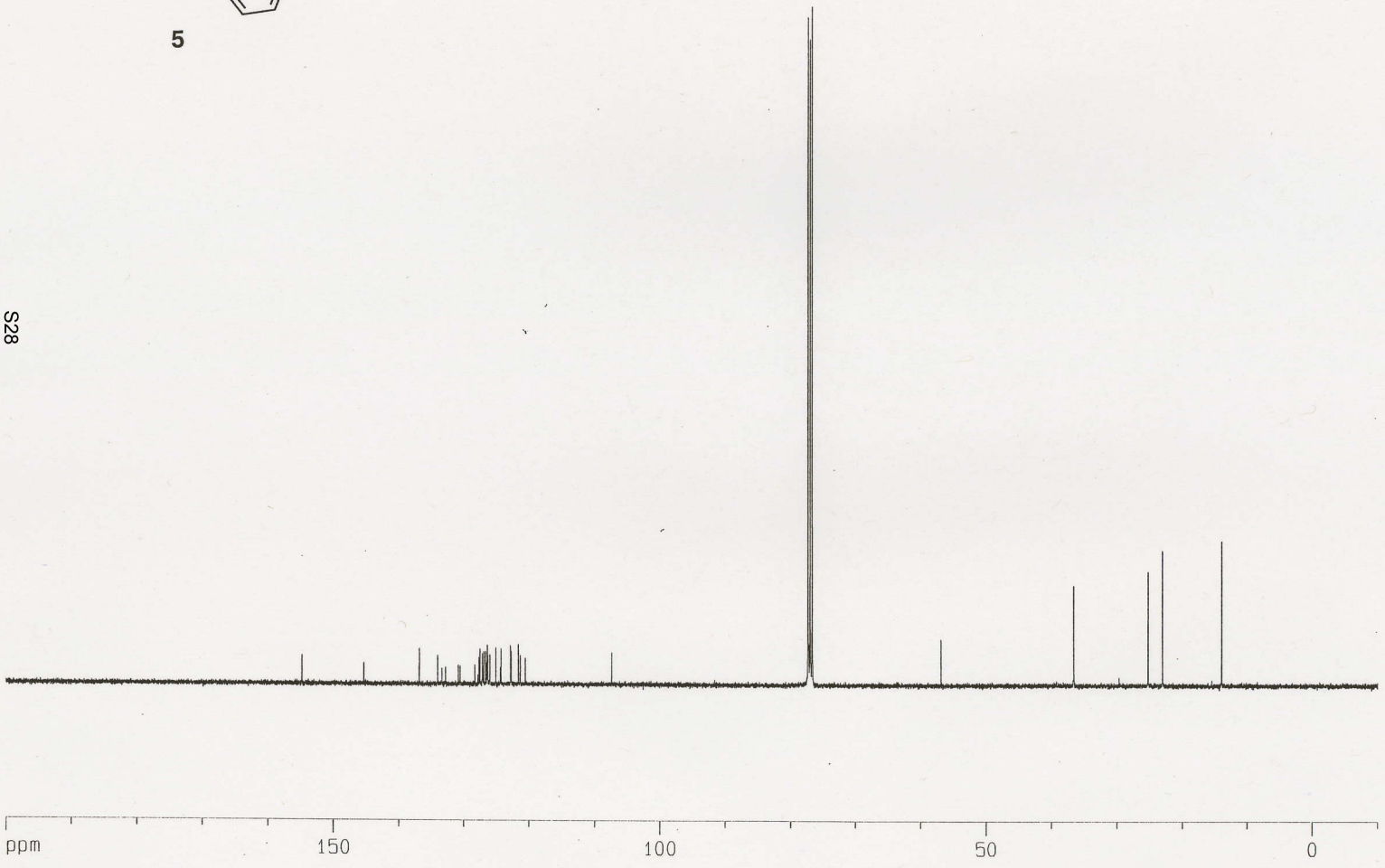
4







5




```
Current Data Parameters
NAME                  13C NMR
EXPNO                       2
PROCNO                      2

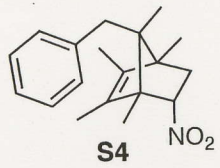
F2 - Acquisition Parameters
Date_              20120221
Time                  21.14
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG               zgpg30
TD                     65536
SOLVENT                  D2O
NS                     12131
DS                         4
SWH               23980.814 Hz
FIDRES             0.365918 Hz
AQ                1.3664756 sec
RG                     71.8
DW                   20.850 usec
DE                    6.00 usec
TE                   300.0 K
D1                2.00000000 sec
d11               0.03000000 sec
d12               0.00002000 sec

======== CHANNEL f1 ========
NUC1                     13C
P1                      9.80 usec
PL1                    -2.00 dB
SFO1             100.5883377 MHz

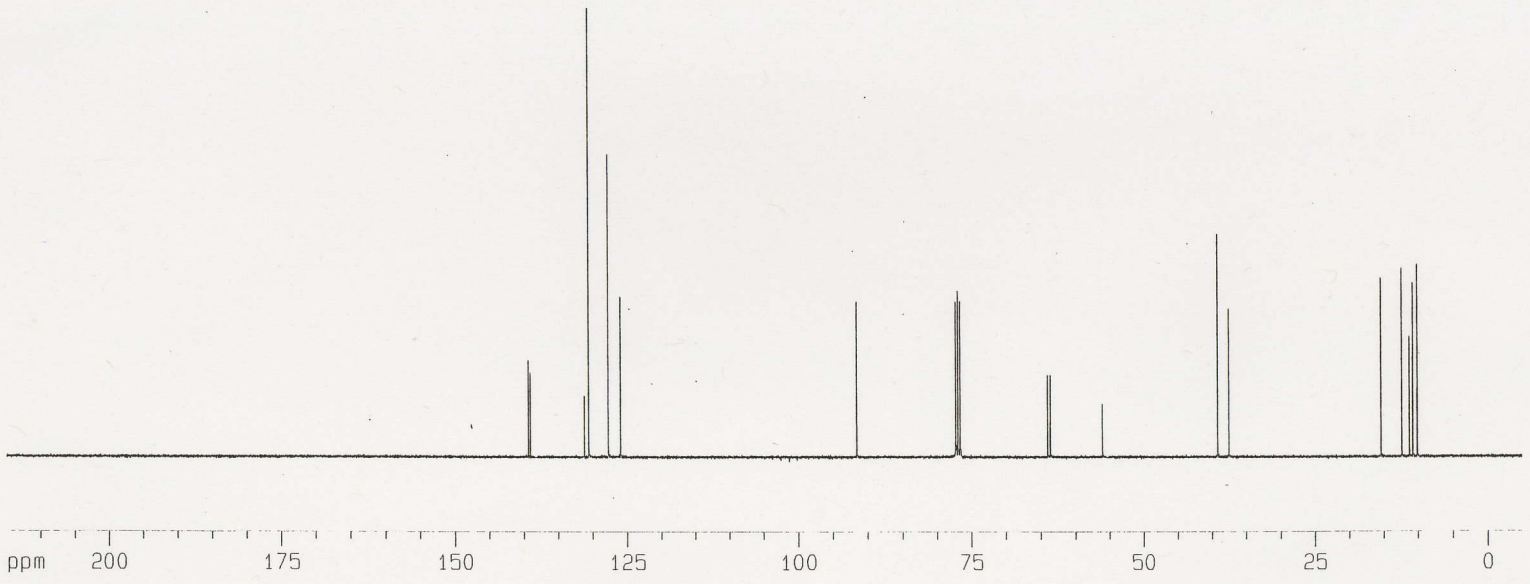
======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2                 80.00 usec
PL2                    -2.00 dB
PL12                   15.23 dB
PL13                   17.89 dB
SFO2             399.9946000 MHz

F2 - Processing parameters
SI                     32768
SF               100.5783208 MHz
WDW                       no
SSB                        0
LB                    0.00 Hz
GB                         0
PC                      1.40

1D NMR plot parameters
CX                    20.00 cm
CY                    10.00 cm
F1P                  200.000 ppm
F1                 20115.66 Hz
F2P                  -10.000 ppm
F2                 -1005.78 Hz
PPMCM                10.50000 ppm/cm
HZCM              1056.07239 Hz/cm
```



S4



Current Data Parameters

NAME	DA-product 13c
EXPNO	2
PROCNO	2

F2 - Acquisition Parameters

Date_	20120225
Time	21.36
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	3072
DS	4
SWH	23980.814 Hz
FIDRES	0.365918 Hz
AQ	1.3664756 sec
RG	32
DW	20.850 usec
DE	6.00 usec
TE	300.0 K
D1	2.00000000 sec
d11	0.03000000 sec
d12	0.00002000 sec

======== CHANNEL f1 ========

NUC1	13C
P1	9.80 usec
PL1	-2.00 dB
SFO1	100.5883377 MHz

======== CHANNEL f2 ========

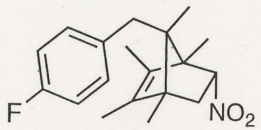
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-2.00 dB
PL12	15.23 dB
PL13	17.89 dB
SFO2	399.9946000 MHz

F2 - Processing parameters

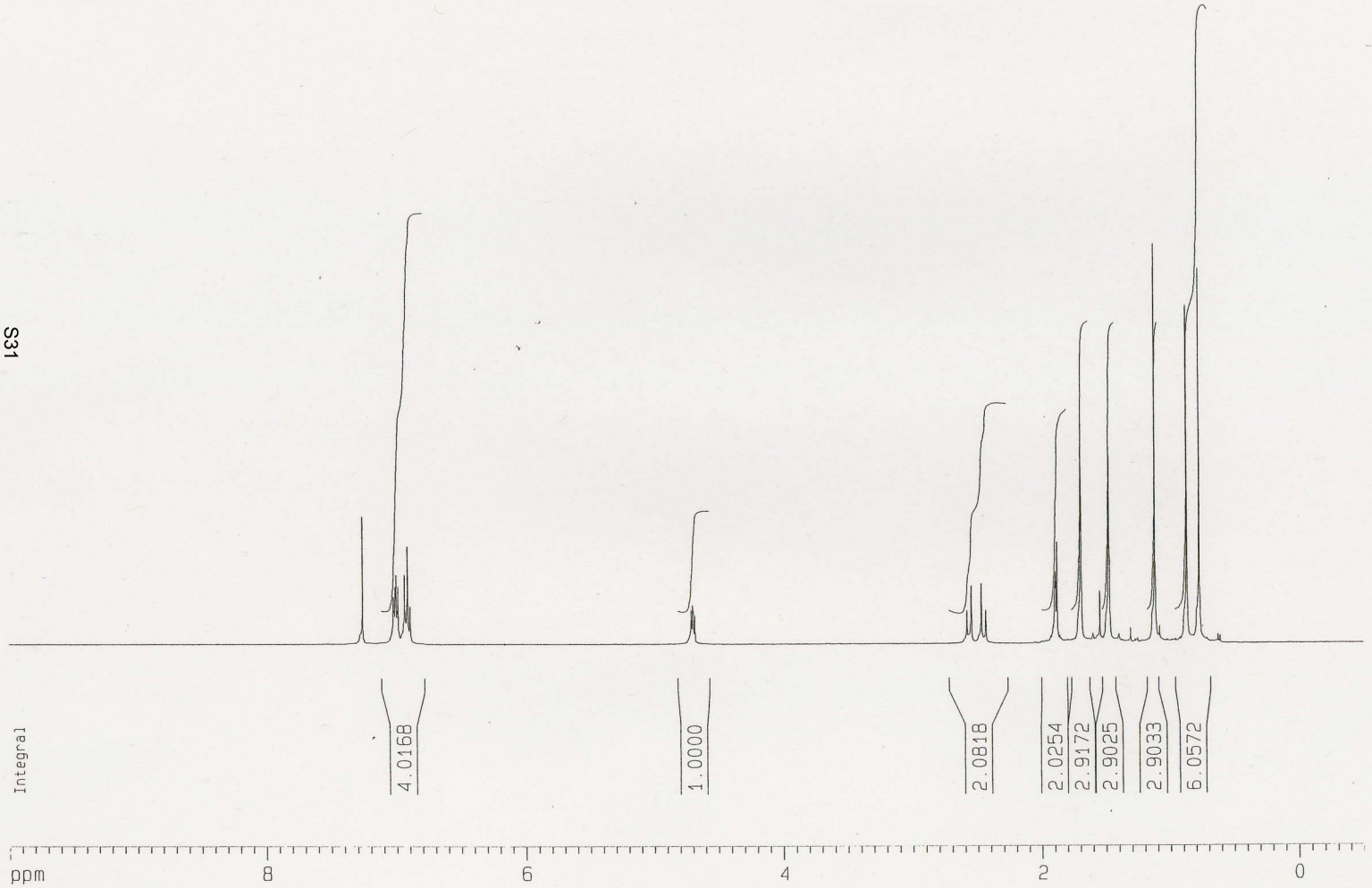
SI	32768
SF	100.5783259 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	6.00 cm
F1P	215.000 ppm
F1	21624.34 Hz
F2P	-5.000 ppm
F2	-502.89 Hz
PPMCM	11.00000 ppm/cm
HZCM	1106.36157 Hz/cm



S5



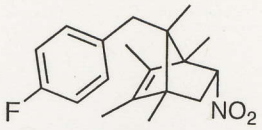

```
Current Data Parameters
NAME                New 1H NMR
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20120222
Time                     10.09
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                           8
DS                           2
SWH                 8278.146 Hz
FIDRES              0.126314 Hz
AQ                  3.9584243 sec
RG                         256
DW                    60.400 usec
DE                     6.00 usec
TE                     300.0 K
D1                  1.00000000 sec

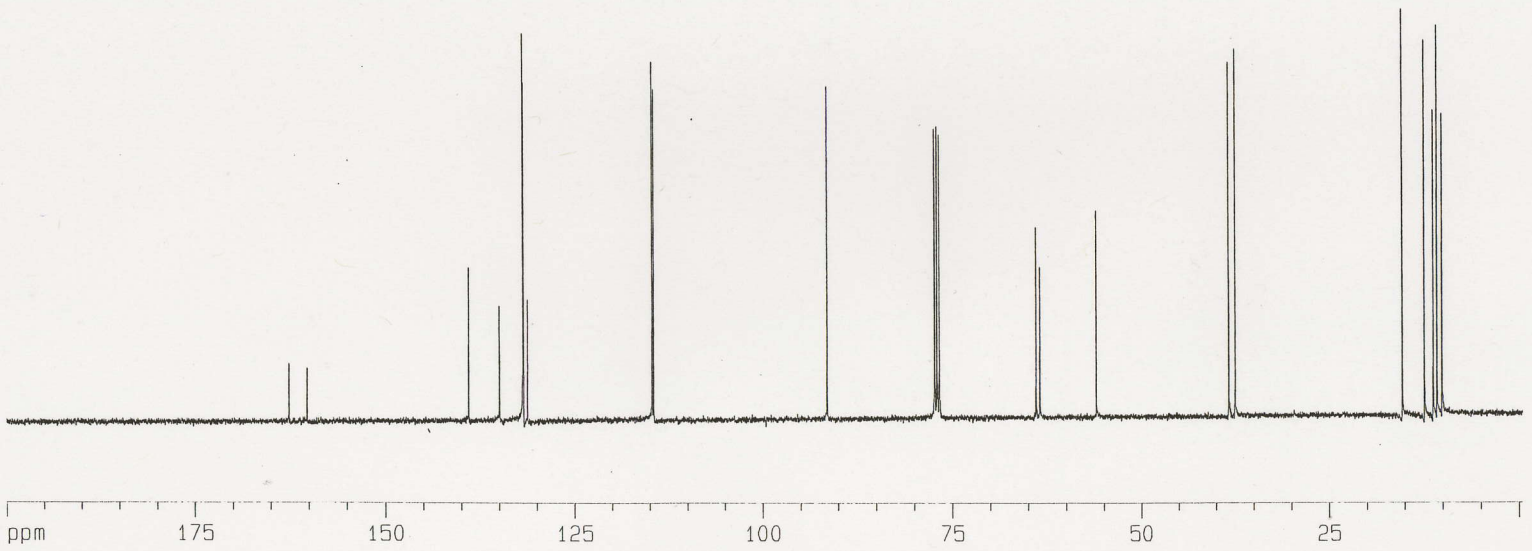
======== CHANNEL f1 ========
NUC1                        1H
P1                     10.50 usec
PL1                     0.00 dB
SFO1              399.9954701 MHz

F2 - Processing parameters
SI                       32768
SF                399.9930050 MHz
WDW                         EM
SSB                          0
LB                      0.30 Hz
GB                           0
PC                        1.00

1D NMR plot parameters
CX                      20.00 cm
CY                       6.00 cm
F1P                    10.000 ppm
F1                   3999.93 Hz
F2P                   -0.500 ppm
F2                  -200.00 Hz
PPMCM                0.52500 ppm/cm
HZCM               209.99634 Hz/cm
```



S5



Current Data Parameters	
NAME	1H NMR
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters	
Date_	20120222
Time	21.12
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	807
DS	4
SWH	23980.814 Hz
FIDRES	0.365918 Hz
AQ	1.3664756 sec
RG	35.9
DW	20.850 usec
DE	6.00 usec
TE	300.0 K
D1	2.00000000 sec
d11	0.03000000 sec
d12	0.00002000 sec

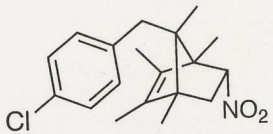
======== CHANNEL f1 ========	
NUC1	13C
P1	9.80 usec
PL1	-2.00 dB
SFO1	100.5883377 MHz

======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-2.00 dB
PL12	15.23 dB
PL13	17.89 dB
SFO2	399.9946000 MHz

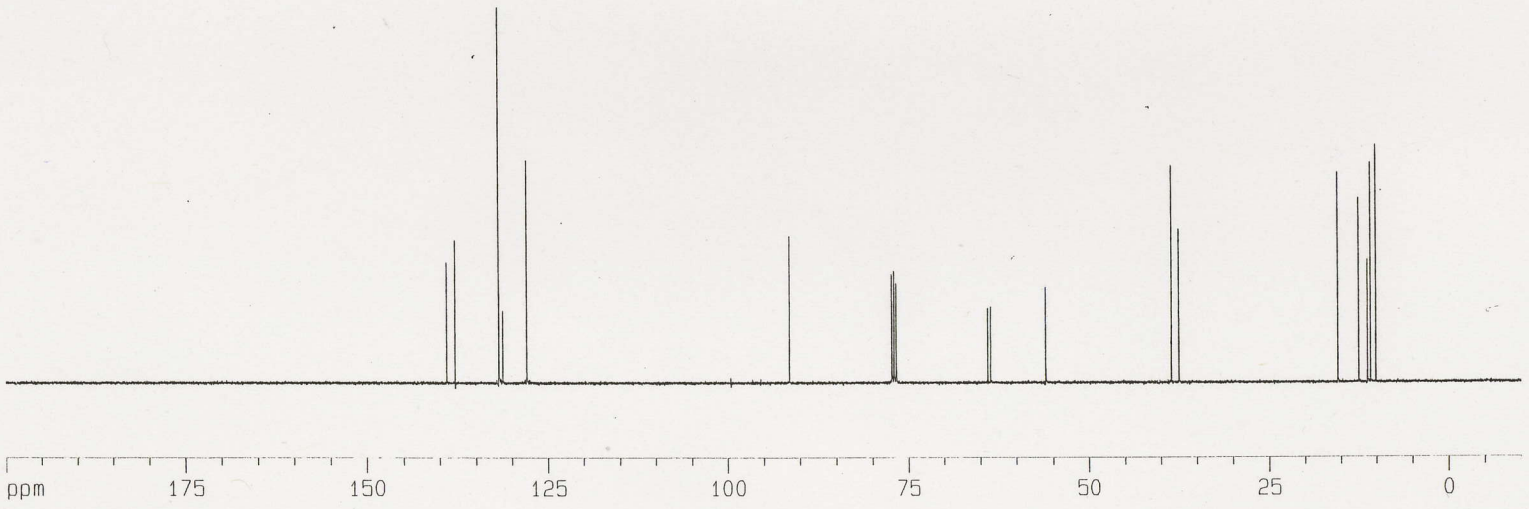
F2 - Processing parameters	
SI	32768
SF	100.5783252 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters	
CX	20.00 cm
CY	6.00 cm
F1P	200.000 ppm
F1	20115.66 Hz
F2P	-0.500 ppm
F2	-50.29 Hz
PPMCM	10.02500 ppm/cm
HZCM	1008.29767 Hz/cm


Current Data Parameters
NAME DA-product 13c
EXPNO 2
PROCNO 2
F2 - Acquisition Parameters
Date_ 20120225
Time 21.22
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 40.3
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 10.50 usec
PL1 0.00 dB
SFO1 399.9954701 MHz
F2 - Processing parameters
SI 32768
SF 399.9930000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 5.00 cm
F1P 10.000 ppm
F1 3999.93 Hz
F2P -0.500 ppm
F2 -200.00 Hz
PPMCM 0.52500 ppm/cm
HZCM 209.99634 Hz/cm
1.9777
2.0145
1.0000
2.0799
2.0224
2.9504
2.9630
3.0309
6.0866
Integral
ppm
0
2
4
6
8
Cl
NO2
S6



S6




```
Current Data Parameters
NAME      p-Cl-DA-Product 13C
EXPNO                     2
PROCNO                    2

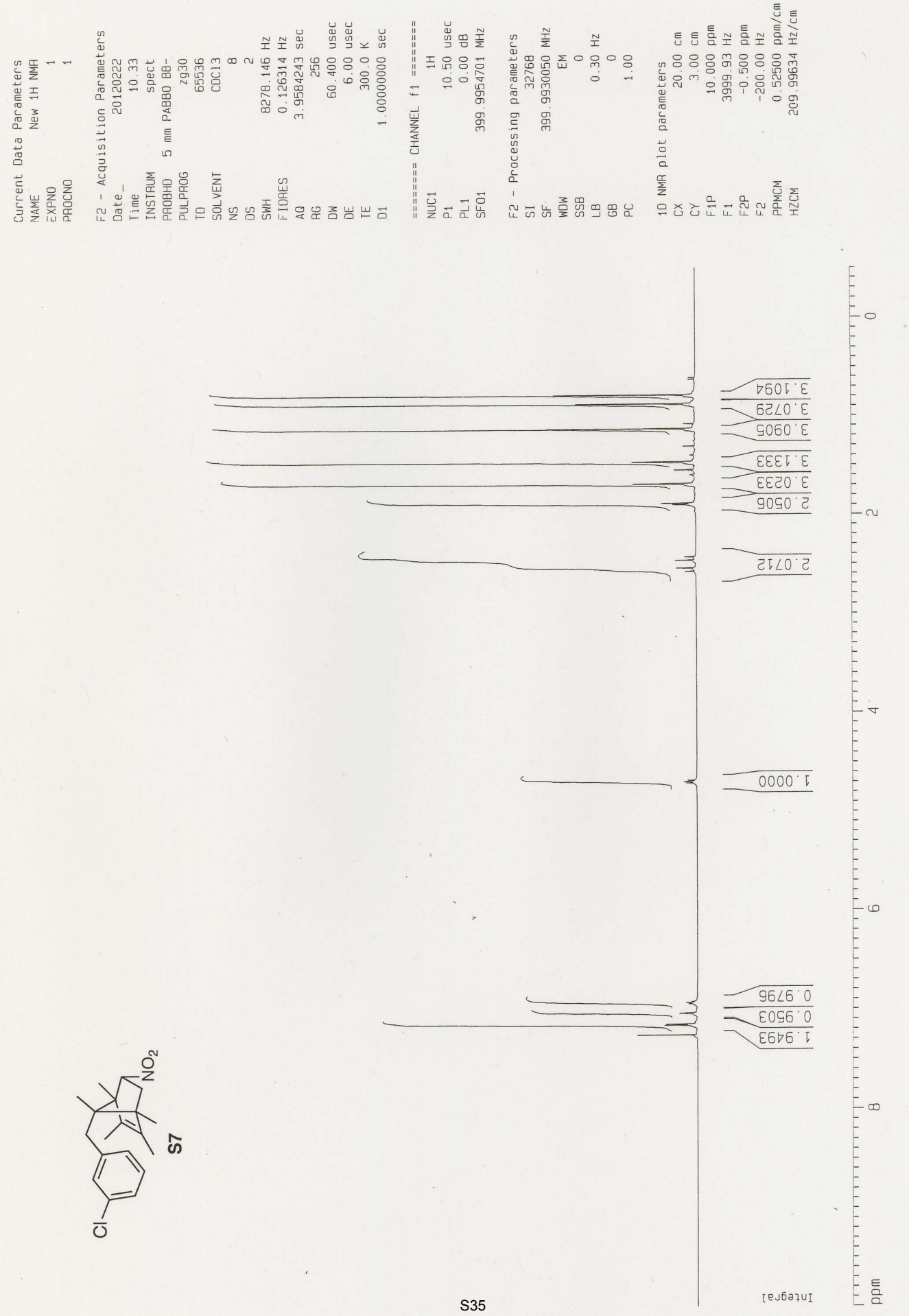
F2 - Acquisition Parameters
Date_              20120225
Time                 19.42
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   1637
DS                      4
SWH             23980.814 Hz
FIDRES          0.365918 Hz
AQ              1.3664756 sec
RG                   35.9
DW                20.850 usec
DE                 6.00 usec
TE                300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
d12            0.00002000 sec

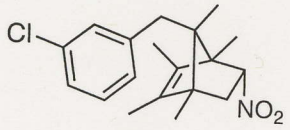
======== CHANNEL f1 ========
NUC1                 13C
P1                 9.80 usec
PL1                -2.00 dB
SFO1          100.5883377 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                -2.00 dB
PL12               15.23 dB
PL13               17.89 dB
SFO2          399.9946000 MHz

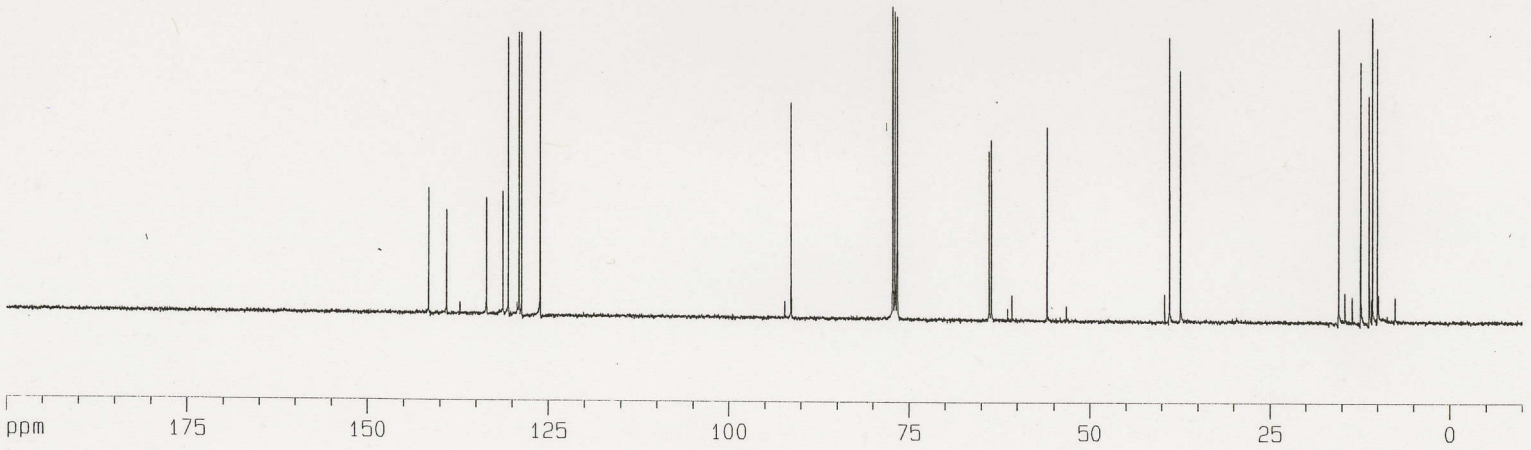
F2 - Processing parameters
SI                  32768
SF            100.5783252 MHz
WDW                    no
SSB                     0
LB                 0.00 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                 20.00 cm
CY                  5.00 cm
F1P              200.000 ppm
F1             20115.66 Hz
F2P              -10.000 ppm
F2             -1005.78 Hz
PPMCM           10.50000 ppm/cm
HZCM          1056.07239 Hz/cm
```





S7




```
Current Data Parameters
NAME      m-Cl-DA product 13C NMR
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120223
Time              20.17
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 2337
DS                    4
SWH          23980.814 Hz
FIDRES        0.365918 Hz
AQ            1.3664756 sec
RG                 35.9
DW               20.850 usec
DE                6.00 usec
TE               300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
d12          0.00002000 sec

======== CHANNEL f1 ========
NUC1                13C
P1               9.80 usec
PL1              -2.00 dB
SFO1        100.5883377 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            80.00 usec
PL2              -2.00 dB
PL12             15.23 dB
PL13             17.89 dB
SFO2        399.9946000 MHz

F2 - Processing parameters
SI                32768
SF          100.5783259 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC                1.40

1D NMR plot parameters
CX               20.00 cm
CY                6.00 cm
F1P             200.000 ppm
F1             20115.66 Hz
F2P             -10.000 ppm
F2             -1005.78 Hz
PPMCM          10.50000 ppm/cm
HZCM         1056.07239 Hz/cm
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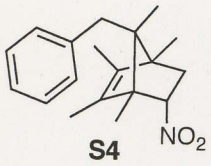
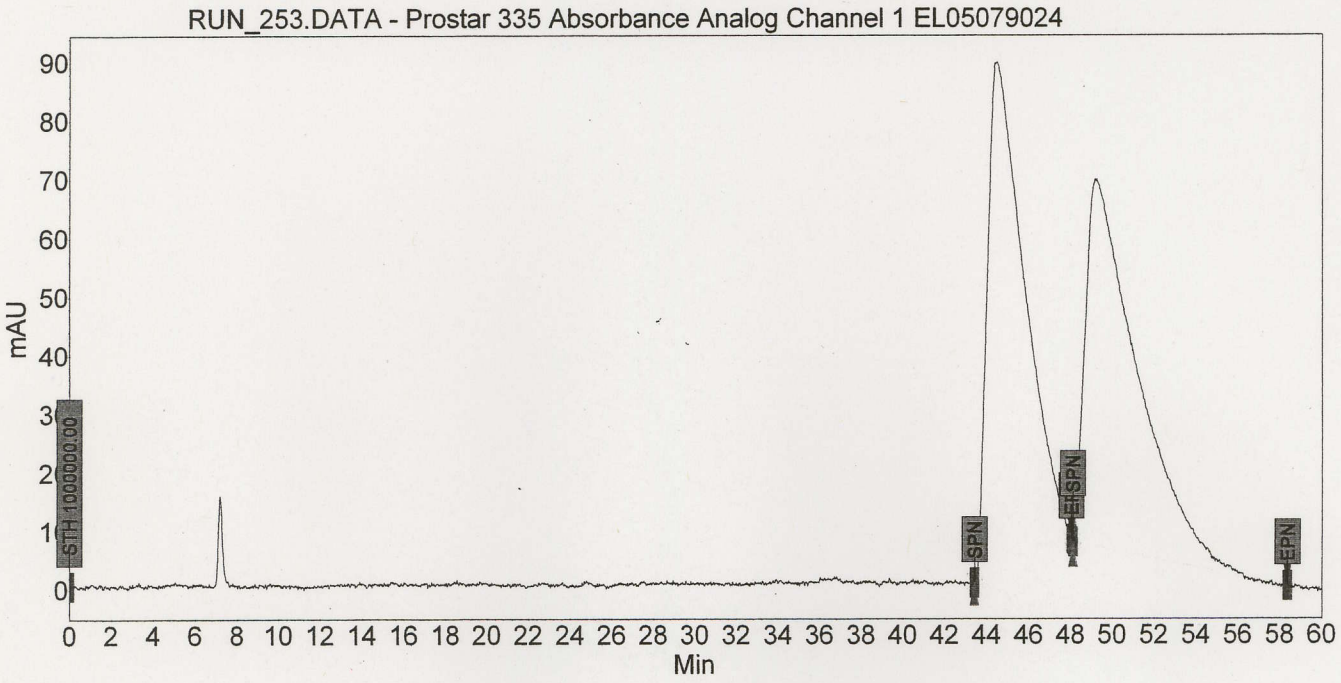
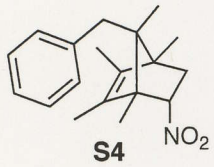


S4

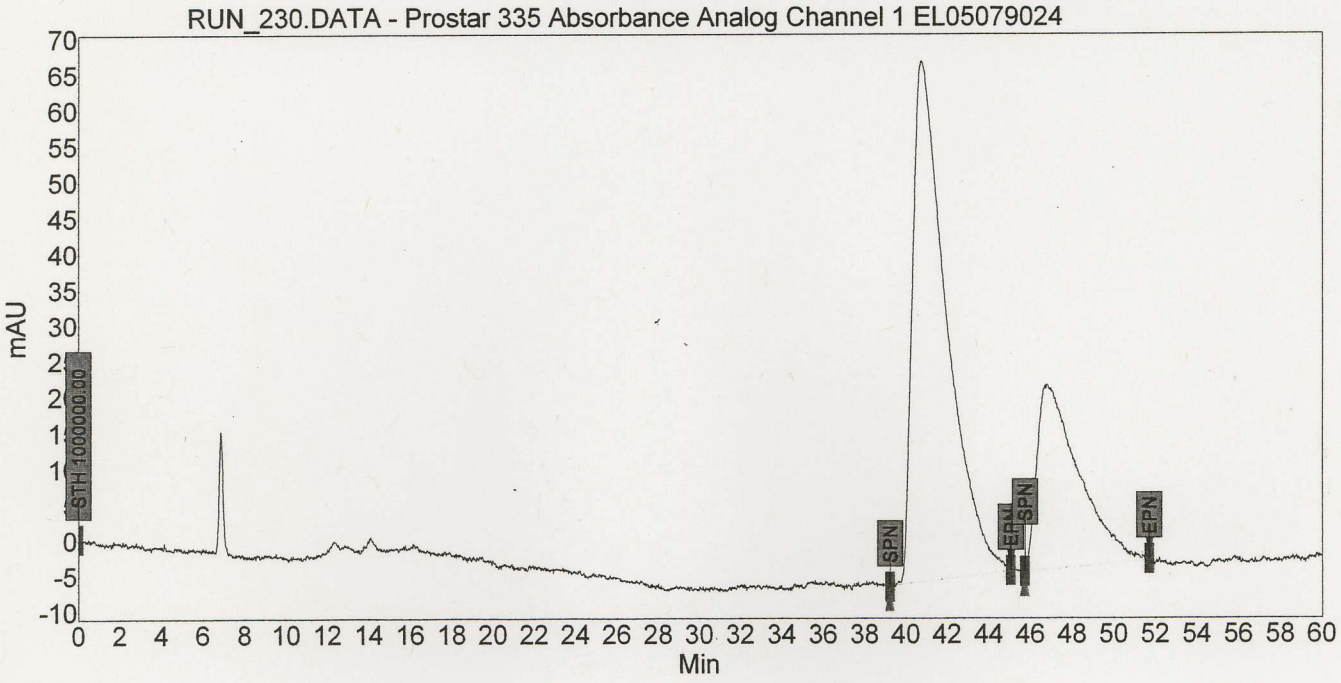


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	44.39	50.23	87.0	180.8	50.230
2	UNKNOWN	49.24	49.77	62.7	179.1	49.770
Total			100.00	149.7	359.9	100.000

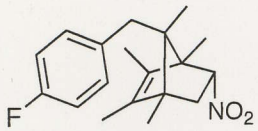


S4

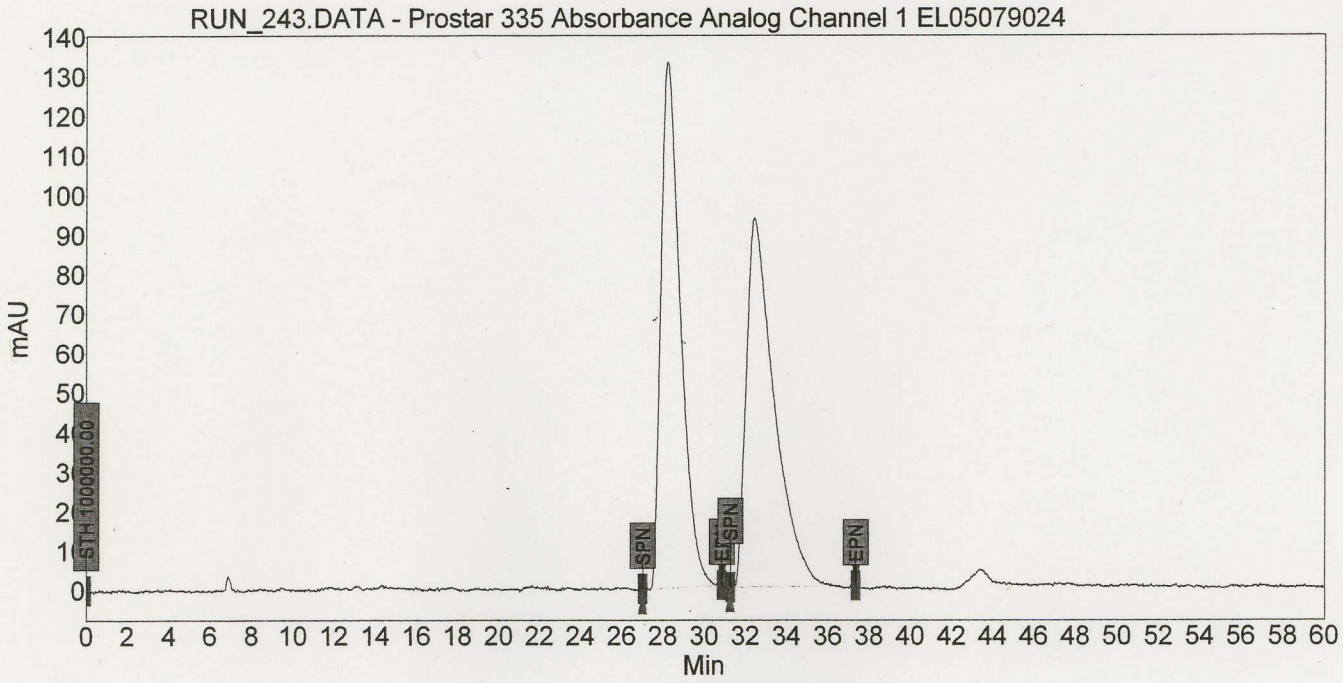


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	40.72	69.76	72.5	138.2	69.757
2	UNKNOWN	46.79	30.24	25.7	59.9	30.243
Total			100.00	98.2	198.1	100.000



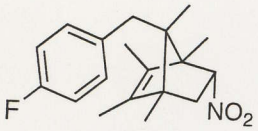
S5



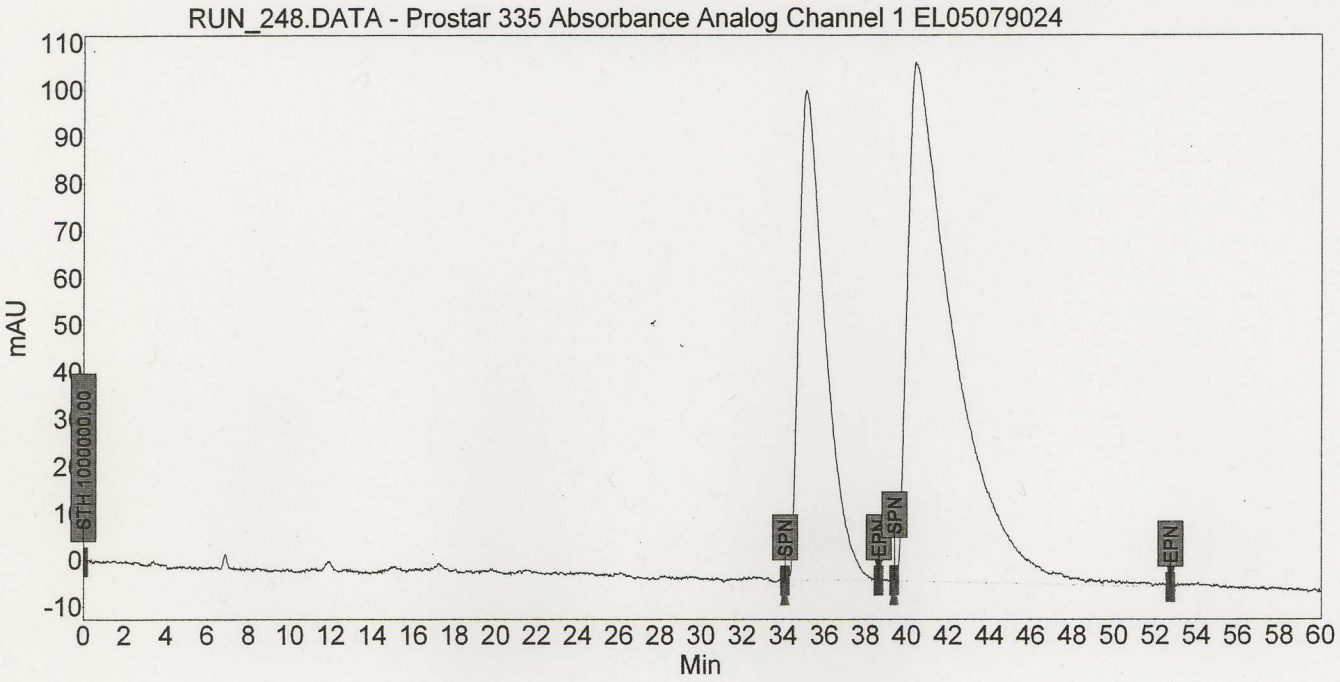
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	28.20	49.72	133.1	145.8	49.722
2	UNKNOWN	32.41	50.28	93.6	147.4	50.278
Total			100.00	226.6	293.2	100.000

Page 1/1

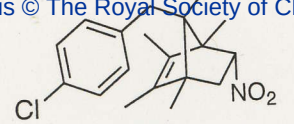


S5

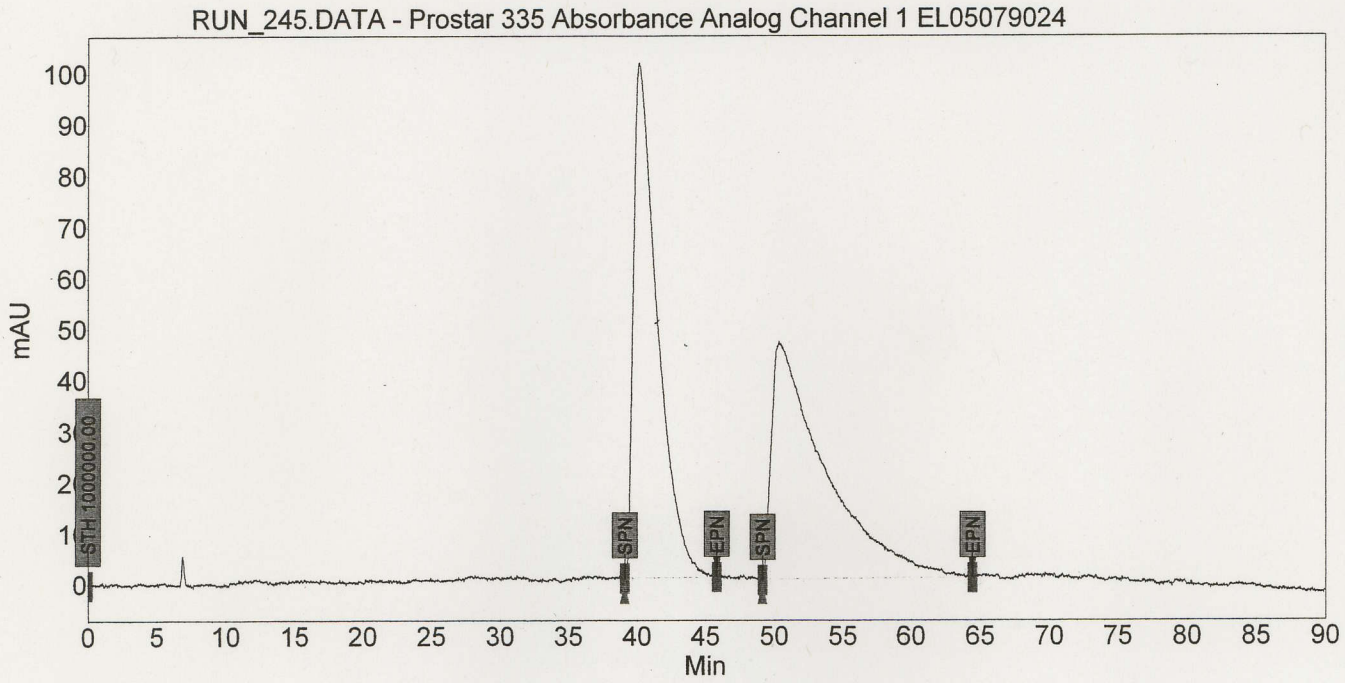


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	35.07	34.57	104.3	151.9	34.568
2	UNKNOWN	40.37	65.43	110.4	287.5	65.432
Total			100.00	214.7	439.4	100.000



S6



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	40.13	49.19	100.8	202.6	49.194
2	UNKNOWN	50.33	50.81	46.4	209.2	50.806
Total			100.00	147.2	411.9	100.000

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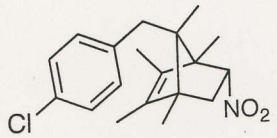
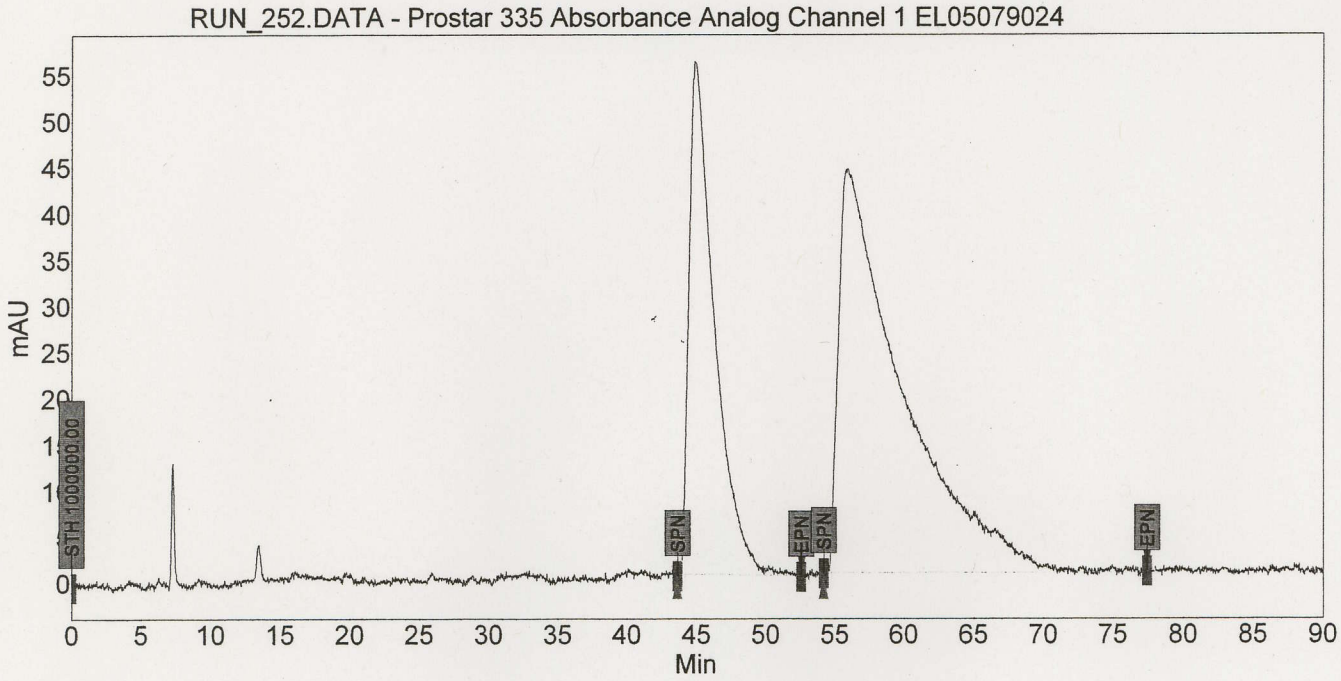
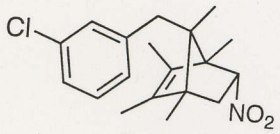


S6

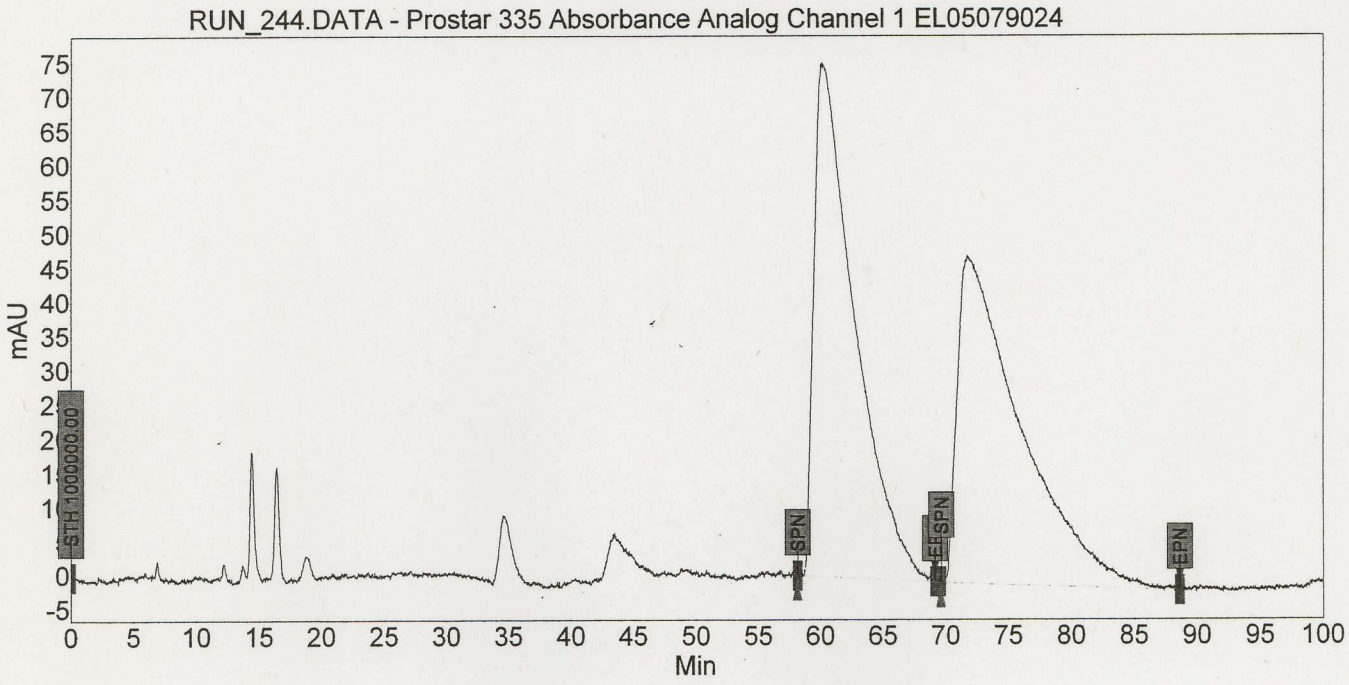


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	44.85	33.74	55.5	118.3	33.738
2	UNKNOWN	55.91	66.26	43.8	232.4	66.262
Total			100.00	99.3	350.7	100.000

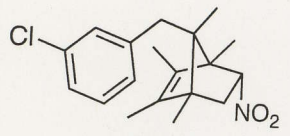


S7

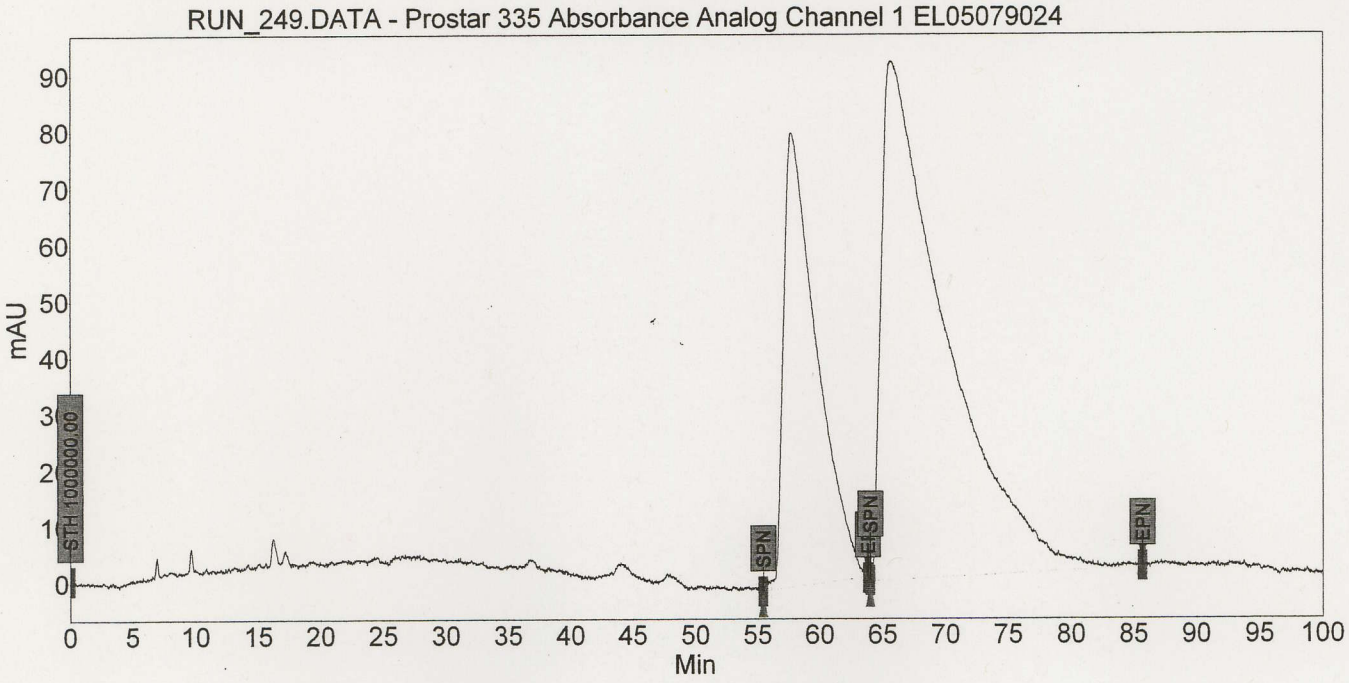


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	60.05	50.50	75.1	284.2	50.496
2	UNKNOWN	71.67	49.50	48.0	278.6	49.504
Total			100.00	123.1	562.9	100.000



S7



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	57.59	31.43	80.6	248.0	31.434
2	UNKNOWN	65.56	68.57	92.0	540.9	68.566
Total			100.00	172.6	788.9	100.000

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