Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Diastereo- and Enantioselective Conjugate Addition of α-Substituted Nitroacetates to Maleimides under Base-Free Neutral Phase-Transfer Conditions

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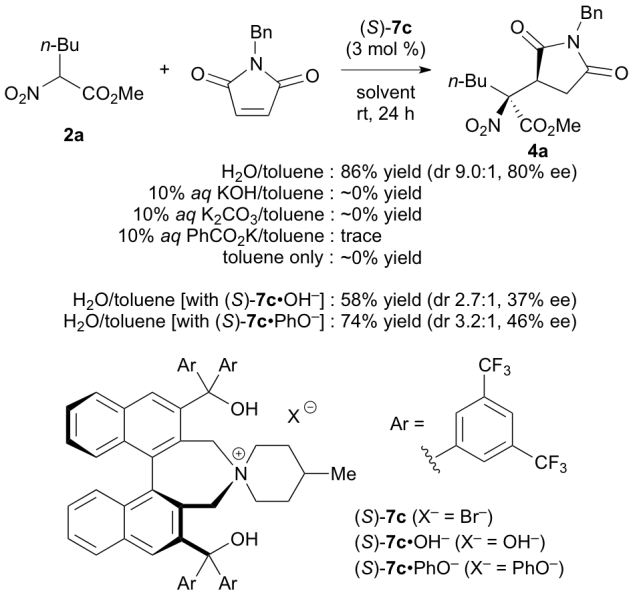


Scheme S1 Effect of aqueous base solution and counter anion of chiral ammonium salt (*S*)-**7c**.

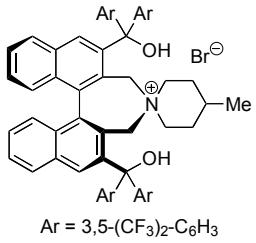
General Information:

^{1}H, ^{13}C, NMR spectra were measured on a JEOL JMTC-500 or JNM-FX 400 NMR instrument (500 MHz or 400 MHz for ^{1}H NMR, 125 MHz or 100 MHz for ^{13}C NMR). The following abbreviations were used to express the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad. High performance liquid chromatography (HPLC) was performed on Shimadzu 10A instruments using a Daicel Chiralpak AD-H, IA, IB, or IC, 4.6 mm × 25 mm column. High-resolution mass spectra (HRMS) were performed on BRUKER microTOF focus–KR. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. All reactions were monitored by thin-layer chromatography carried out on Merck precoated TLC plates (silica gel 60GF-254, 0.25 mm), visualization by using UV (254 nm), or dyes such as $KMnO_4$. The products were purified by flash column chromatography on silica gel 60N [Kanto Chemical Co., Inc. (spherical, neutral)]. All simple chemicals were purchased and used as received.

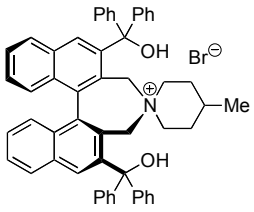
Experimental Section:

Characterization of chiral ammonium salts.

Chiral ammonium salts were prepared according to the literature.[1]



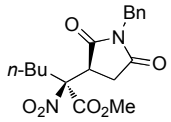
(*S*)-7c: $[\alpha]^{28}_{D}$ = –132.4 [*c* = 0.86, CH_3OH]; ^{1}H NMR (500 MHz, CD_3OD) δ 8.11–8.13 (m, 4H), 7.97–8.02 (m, 5H), 7.83–7.91 (m, 5H), 7.57–7.63 (m, 2H), 7.50 (s, 1H), 7.45 (s, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 1H), 6.96 (d, *J* = 8.6 Hz, 1H), 4.84 (d, *J* = 13.8 Hz, 1H), 4.74 (d, *J* = 13.8 Hz, 1H), 3.84 (d, *J* = 13.2 Hz, 1H), 3.70–3.76 (m, 2H), 3.29–3.33 (m, 1H), 3.14–3.19 (m, 2H), 2.25–2.34 (m, 1H), 1.68–1.92 (m, 3H), 1.04 (d, *J* = 6.9 Hz, 3H), 0.77–0.85 (m, 1H); ^{13}C NMR (125 MHz, CD_3OD) δ 151.4, 150.9, 149.2, 148.9, 142.8, 141.3, 141.1, 141.0, 133.9, 133.8, 133.54, 133.46, 133.3, 133.2, 133.0, 132.9, 132.8, 132.5, 132.4, 130.2, 130.1, 129.8, 129.7, 129.6, 128.6, 127.9, 127.8, 127.7, 126.5, 126.2, 125.8, 125.5, 123.6, 123.4, 123.3, 121.4, 121.1, 83.1, 82.5, 64.8, 64.7, 60.5, 56.3, 30.8, 29.4, 29.2, 21.3; IR (neat) 3356, 1368, 1277, 1173, 1130, 976, 903, 714, 683 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{62}H_{40}F_{24}NO_2^+$: 1286.2670 ($[M]^+$), found 1286.2724.



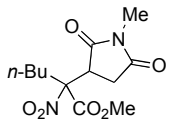
(*S*)-7d•Br$^-$: $[\alpha]^{28}_{D}$ = –103.7 [*c* = 1.0, $CHCl_3$]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09–7.70 (m, 28H), 6.95 (d, *J* = 8.8 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 5.96 (s, 1H), 5.30 (s, 1H), 5.00 (d, *J* = 13.6 Hz, 1H), 4.91 (d, *J* = 13.6 Hz, 1H), 4.19 (d, *J* = 11.6 Hz, 1H), 3.82 (d, *J* = 13.6 Hz, 1H), 3.14–3.20 (m, 1H), 2.86 (d, *J* = 14.0 Hz, 1H), 2.77–2.84 (m, 1H), 2.68 (d, *J* =12.8 Hz, 1H), 2.17–2.26 (m, 1H), 1.46–1.72 (m, 3H), 0.85 (d, *J* = 6.4 Hz, 3H), 0.53–0.63 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 147.3, 145.54, 145.48, 143.2, 142.8, 140.2, 138.6, 132.4, 132.3, 131.4, 131.3, 131.2, 131.1, 129.1, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2, 127.6, 127.5, 127.41, 127.35, 127.2, 126.8, 126.7, 82.9, 82.2, 63.5, 63.3, 60.2, 55.7, 29.1, 27.9, 21.1; IR (neat) 3242, 1491, 1447, 1298, 1165, 1055, 1026, 910, 868, 756, 731, 702 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{54}H_{48}NO_2^+$: 742.3680 ($[M]^+$), found 742.3679.

General procedure for the enantioselective conjugate addition of α-substituted nitroacetates to maleimides.

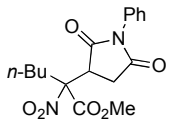
To a mixture of α-substituted nitroacetate (0.050 mmol), *N*-benzylmaleimide (0.060 mmol), (*S*)-**7c** (3 mol %) in toluene (0.20 mL) was added H_2O (2.0 mL) at 10 °C. The mixture was stirred vigorously at the same temperature for 24 h, extracted with ethyl acetate (10 mL × 3), dried over Na_2SO_4 and concentrated. Purification of the residue by column chromatography on silica gel (neutral) with hexane/ethyl acetate as eluent gave product **4**. The product was identified by NMR spectroscopy. The enantiomeric excess of the product was determined by chiral HPLC analysis. The diastereomeric ratio of the product was determined by ^{1}H NMR and/or HPLC analyses.



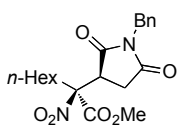
4a: $[\alpha]^{25}_{D}$ = –2.6 [*c* = 0.78, $CHCl_3$ (dr = >20:1, 91% ee for the major diastereomer)]; ^{1}H NMR for major diastereomer (400 MHz, $CDCl_3$) δ 7.27–7.37 (m, 5H), 4.68 (d, *J* = 14.0 Hz, 1H), 4.63 (d, *J* = 14.4 Hz, 1H), 3.78 (s, 3H), 3.65 (dd, *J* = 9.6, 6.4 Hz, 1H), 3.02 (dd, *J* = 18.8, 9.6 Hz, 1H), 2.75 (dd, *J* = 18.8, 6.0 Hz, 1H), 2.45 (d, *J* = 7.6 Hz, 1H), 2.42 (d, *J* = 7.2 Hz, 1H), 1.30–1.45 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR for major diastereomer (100 MHz, $CDCl_3$) δ 173.9, 173.7, 165.2, 135.2, 128.8, 128.7, 128.1, 95.5, 53.8, 43.7, 42.8, 35.2, 32.6, 26.6, 22.6, 13.6; IR (neat) 1753, 1709, 1557, 1433, 1400, 1348, 1315, 1258, 1227, 1171, 812, 733, 706, 648, 632 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{18}H_{22}N_2O_6Na^+$: 385.1370 ($[M+Na]^+$), found 385.1382; HPLC analysis: Daicel Chiralpak IC, hexane/*iso*-propanol = 5:1, flow rate = 1.0 mL/min, λ = 210 nm, retention time: major diastereomer: 13.3 min (minor) and 28.0 min (major), minor diastereomer: 11.8 min (major) and 17.2 min (minor).



$[\alpha]^{26}_{D}$ = –2.4 [*c* = 0.18, $CHCl_3$ (dr = 2.0:1, 64% ee for the major diastereomer)]; ^{1}H NMR for major diastereomer (400 MHz, $CDCl_3$) δ 3.88 (s, 3H), 3.62 (dd, *J* = 10.0, 5.6 Hz, 1H), 3.00 (s, 3H), 2.81–3.06 (m, 1H), 2.78 (dd, *J* = 18.4, 5.6 Hz, 1H), 2.47–2.52 (m, 2H), 1.30–1.49 (m, 4H), 0.94 (t, *J* = 7.2 Hz , 3H), ^{13}C NMR for major diastereomer (100 MHz, $CDCl_3$) δ 174.3, 174.1, 165.4, 95.6, 53.9, 43.7, 35.1, 32.7, 26.8, 25.2, 22.6, 13.6; IR (neat) 1749, 1709, 1557, 1439, 1387, 1288, 1221, 1126, 772 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{12}H_{18}N_2O_6Na^+$: 309.1057 ($[M+Na]^+$), found 309.1046; HPLC analysis: Daicel Chiralpak IA, hexane/*iso*-propanol = 10:1, flow rate = 1.0 mL/min, λ = 207 nm, retention time: major diastereomer: 12.3 min (major), 13.4 min (minor), minor diastereomer: 14.2 min (major), 16.7 min (minor).

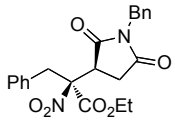


$[\alpha]^{27}_{D}$ = –12.1 [*c* = 0.50, $CHCl_3$ (dr = 16:1, 63% ee for the major diastereomer)]; ^{1}H NMR for major diastereomer (400 MHz, $CDCl_3$) δ 7.39–7.50 (m, 3H), 7.27–7.30 (m, 2H), 3.89 (s, 3H), 3.82 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.12 (dd, *J* = 18.4, 9.6 Hz, 1H), 2.72 (dd, *J* = 18.4, 6.0 Hz, 1H), 2.41–2.49 (m, 1H), 2.23–2.31 (m, 1H), 1.68–1.77 (m, 1H), 1.24–1.46 (m, 3H), 0.96 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR for major diastereomer (100 MHz, $CDCl_3$) δ 173.6, 173.1, 165.9, 131.6, 129.3, 129.0, 126.5, 96.3, 54.1, 44.9, 35.8, 31.9, 26.6, 22.7, 13.7; IR (neat) 1749, 1715, 1557, 1499, 1389, 1250, 1192, 748, 696 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{17}H_{20}N_2O_6Na^+$: 371.1214 ($[M+Na]^+$), found 371.1216; HPLC analysis: Daicel Chiralpak IB, hexane/*iso*-propanol = 5:1, flow rate = 1.0 mL/min, λ = 210 nm, retention time: major diastereomer: 14.6 min (major) and 18.8 min (minor), minor diastereomer: 16.4 min (minor) and 21.9 min (major).

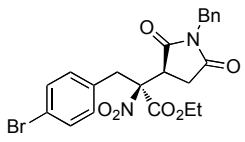


4b: $[\alpha]^{25}_{D}$ = –2.5 [*c* = 0.48, $CHCl_3$ (dr = >20:1, 91% ee for the major diastereomer)]; ^{1}H NMR for major diastereomer (400 MHz, $CDCl_3$) δ 7.27–7.37 (m, 5H), 4.68 (d, *J* = 14.4 Hz, 1H), 4.63 (d, *J* = 14.0 Hz, 1H), 3.78 (s, 3H), 3.65 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.02 (dd, *J* = 18.4, 9.6 Hz, 1H), 2.74 (dd, *J* = 18.4, 6.0 Hz, 1H), 2.43 (d, *J* = 7.6 Hz, 1H), 2.41 (d, *J* = 7.6 Hz, 1H), 1.26–1.43 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR for major diastereomer (100 MHz, $CDCl_3$) δ

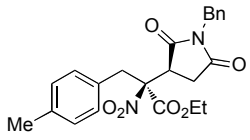
173.9, 173.7, 165.2, 135.2, 128.8, 128.7, 128.1, 95.5, 53.8, 43.7, 42.8, 35.4, 32.6, 31.2, 29.1, 25.3, 24.5, 22.4, 13.9; IR (neat) 1749, 1709, 1557, 1433, 1400, 1348, 1292, 1232, 1171, 706 cm^{-1} HRMS (ESI-TOF) calcd for $C_{20}H_{26}N_2O_6Na^+$: 413.1683 ($[M+Na]^+$), found 413.1674; HPLC analysis: Daicel Chiralpak IC, hexane/*iso*-propanol = 5:1, flow rate = 1.0 mL/min, λ = 210 nm, retention time: major diastereomer: 11.5 min (minor) and 23.4 min (major), minor diastereomer: 9.9 min (major) and 14.4 min (minor).



4c: $[\alpha]^{30}_D$ = +11.9 [*c* = 0.46, $CHCl_3$ (dr = >20:1, 87% ee for the major diastereomer)]; ^{1}H NMR for major diastereomer (400 MHz, $CDCl_3$) δ 7.27–7.38 (m, 8H), 7.17–7.19 (m, 2H), 4.66 (d, *J* = 14.0 Hz, 1H), 4.61 (d, *J* = 14.4 Hz, 1H), 4.18–4.31 (m, 2H), 4.09 (d, *J* = 14.0 Hz, 1H), 3.77 (d, *J* = 14.0 Hz, 1H), 3.64 (dd, *J* = 9.6, 5.6 Hz, 1H), 2.88 (dd, *J* = 18.0, 10.0 Hz, 1H), 2.68 (dd, *J* = 18.8, 5.6 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR for major diastereomer (100 MHz, $CDCl_3$) δ 174.2, 164.3, 135.2, 132.8, 130.5, 128.9, 128.8, 128.7, 128.3, 128.1, 95.9, 63.7, 42.8, 42.3, 40.3, 33.2, 13.7; IR (neat) 1746, 1703, 1557, 1398, 1221, 1171, 748, 704 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{22}N_2O_6Na^+$: 433.1370 ($[M+Na]^+$), found 433.1364; HPLC analysis: Daicel Chiralpak IC, hexane/*iso*-propanol = 5:1, flow rate = 1.0 mL/min, λ = 210 nm, retention time: major diastereomer: 11.1 min (minor) and 38.0 min (major), minor diastereomer: 23.3 min (minor) and 25.3 min (major).

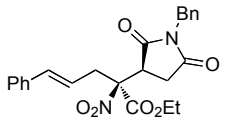


4d: $[\alpha]^{28}_D$ = +3.6 [*c* = 1.1, $CHCl_3$ (dr = 12:1, 84% ee for the major diastereomer)]; ^{1}H NMR for major diastereomer (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.29–7.36 (m, 5H), 7.09 (d, *J* = 8.8 Hz, 2H), 4.67 (d, *J* = 14.4 Hz, 1H), 4.61 (d, *J* = 14.0 Hz, 1H), 4.19–4.31 (m, 2H), 4.04 (d, *J* = 14.0 Hz, 1H), 3.74 (d, *J* = 14.0 Hz, 1H), 3.56 (dd, *J* = 9.6, 5.6 Hz, 1H), 2.91 (dd, *J* = 18.8, 9.2 Hz, 1H), 2.76 (d, *J* = 18.8, 5.6 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR for major diastereomer (100 MHz, $CDCl_3$) δ 174.1, 174.0, 164.2, 135.1, 132.3, 132.0, 131.8, 128.8, 128.2, 122.6, 95.6, 63.8, 42.8, 42.4, 39.7, 33.1, 25.4, 13.8; IR (neat) 1749, 1705, 1556, 1489, 1431, 1400, 1342, 1213, 1172, 1013, 847, 704 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{21}BrN_2O_6Na^+$: 511.0475 ($[M+Na]^+$), found 511.0450; HPLC analysis: Daicel Chiralpak IB, hexane/*iso*-propanol = 5:1, flow rate = 1.0 mL/min, λ = 208 nm, retention time: major diastereomer: 13.4 min (minor) and 20.5 min (major), minor diastereomer: 12.8 min (major) and 16.5 min (minor).

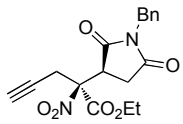


4e: $[\alpha]^{34}_D$ = +10.5 [*c* = 0.90, $CHCl_3$ (dr >20:1, 90% ee for the major diastereomer)]; ^{1}H NMR for major diastereomer (400 MHz, $CDCl_3$) δ 7.27–7.37 (m, 5H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 2H), 4.66 (d, *J* = 14.0 Hz, 1H), 4.60 (d, *J* = 14.4 Hz, 1H), 4.19–4.31 (m, 2H), 4.04 (d, *J* = 14.0 Hz, 1H), 3.72 (d, *J* = 14.4 Hz, 1H), 3.63 (dd, *J* = 9.6, 5.6 Hz, 1H), 2.87 (dd, *J* = 18.8, 9.6 Hz, 1H), 2.67 (dd, *J* = 18.8, 6.0 Hz, 1H), 2.31 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR for major diastereomer (100 MHz, $CDCl_3$) δ 174.25, 174.22, 164.4, 138.2, 135.2, 130.3, 129.6, 129.0, 128.8, 128.7, 128.1, 96.0, 63.6, 42.8, 42.3, 39.9, 33.2, 21.1, 13.8; IR (neat) 1749, 1705, 1557, 1433, 1400, 1350, 1221, 1171, 912, 741, 706 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{24}N_2O_6Na^+$: 447.1527 ($[M+Na]^+$), found 447.1535; Daicel Chiralpak

IC, hexane/*iso*-propanol = 5:1, flow rate = 1.0 mL/min, λ = 210 nm, retention time: major diastereomer: 11.8 min (minor) and 37.3 min (major), minor diastereomer: 16.0 min (minor) and 19.7 min (major).



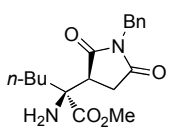
4f: $[\alpha]^{33}_{D}$ = +19.9 [*c* = 0.68, $CHCl_3$ (dr = 10:1, 83% ee for the major diastereomer)]; ^{1}H NMR for major diastereomer (400 MHz, $CDCl_3$) δ 7.26–7.32 (m, 10H), 6.56 (d, *J* = 15.6 Hz, 1H), 6.18 (ddd, *J* = 15.6, 8.8, 6.8 Hz 1H), 4.53 (d, *J* = 14.0 Hz, 1H), 4.48 (d, *J* = 14.0 Hz, 1H), 4.31 (qd, *J* = 7.2, 0.8 Hz, 2H), 3.76 (dd, *J* = 9.6, 6.4 Hz, 1H), 3.44 (ddd, *J* = 14.4, 6.8, 1.2 Hz, 1H), 3.36 (ddd, *J* = 14.4, 8.8, 0.8 Hz, 1H), 3.02 (dd, *J* = 18.8, 9.2 Hz, 1H), 2.86 (dd, *J* = 18.4, 6.0 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR for major diastereomer (100 MHz, $CDCl_3$) δ 174.0, 173.9, 164.3, 136.7, 136.0, 135.2, 128.8, 128.70, 128.68, 128.3, 128.1, 126.5, 121.0, 94.9, 63.8, 43.3, 42.7, 38.8, 32.5, 25.4, 13.9; IR (neat) 1748, 1707, 1557, 1400, 1346, 1223, 1171, 746, 694 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{24}H_{24}N_2O_6Na^+$: 459.1527 ($[M+Na]^+$), found 459.1516; HPLC analysis: Daicel Chiralpak IC, hexane/*iso*-propanol = 5:1, flow rate = 1.0 mL/min, λ = 208 nm, retention time: major diastereomer: 11.6 min (minor) and 21.2 min (major), minor diastereomer: 10.6 min (major) and 14.0 min (minor).



4g: $[\alpha]^{25}_{D}$ = –12.2 [*c* = 0.82, $CHCl_3$ (dr = 10:1, 90% ee for the major diastereomer)]; ^{1}H NMR for major diastereomer (400 MHz, $CDCl_3$) δ 7.28–7.42 (m, 5H), 4.68 (d, *J* = 14.4 Hz, 1H), 4.63 (d, *J* = 14.0 Hz, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 3.97 (dd, *J* = 9.6, 6.4 Hz, 1H), 3.63 (dd, *J* = 17.2, 2.4 Hz, 1H), 3.36 (dd, *J* = 17.2, 2.4 Hz, 1H), 3.11 (dd, *J* = 18.8, 9.6 Hz, 1H), 3.01 (dd, *J* = 18.8, 6.4 Hz, 1H), 2.06 (t, *J* = 2.4 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR for major diastereomer (100 MHz, $CDCl_3$) δ 174.0, 173.7, 163.4, 135.0, 128.9, 128.7, 128.1, 92.7, 75.8, 74.1, 64.1, 43.1, 42.9, 32.7, 25.7, 13.8; IR (neat) 1751, 1705, 1560, 1433, 1400, 1348, 1294, 1231, 1171, 706 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{18}H_{18}N_2O_6Na^+$: 381.1057 ($[M+Na]^+$), found 381.1052; HPLC analysis: Daicel Chiralpak IC, hexane/*iso*-propanol = 85:15, flow rate = 1.0 mL/min, λ = 208 nm, retention time: major diastereomer: 14.3 min (minor) and 17.8 min (major), minor diastereomer: 11.3 min (major) and 13.6 min (minor).

Reduction of the nitro group on product 4a.[2]

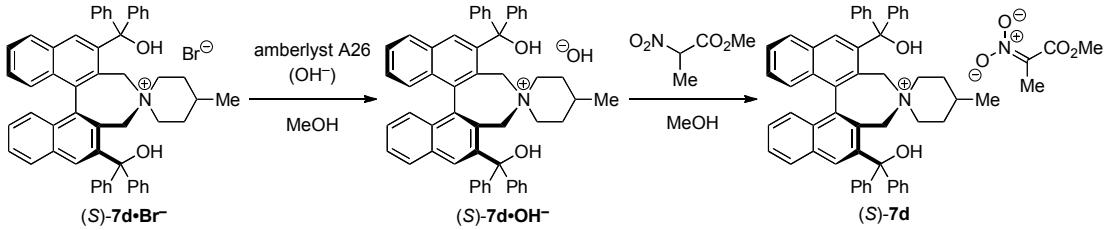
To a solution of the product **4a** (0.034 mmol, dr = 13:1, 88% ee for major diastereomer) in 2-propanol (5.0 mL) was added zinc dust (0.10 g) and acetic acid (0.13 mL) at room temperature. The resulting mixture was stirred for 5 h and then filtrated over celite. The filtrate was diluted with dichloromethane, and the solution was washed with brine and dried over Na_2SO_4. After evaporation of solvents, the residue was purified by preparative thin layer chromatography (hexane/ethyl acetate = 2:1 as eluent) to afford the product **8** in 88% yield (dr = 10:1, 87% ee for major diastereomer).



8: $[\alpha]^{27}_{D}$ = –0.26 [*c* = 0.56, $CHCl_3$ (dr = 10:1, 87% ee for the major diastereomer)]; ^{1}H NMR for major diastereomer (400 MHz, $CDCl_3$) δ 7.25–7.38 (m, 5H), 4.64 (s, 2H), 3.56 (s, 3H), 3.09 (dd, *J* = 8.8, 5.6 Hz, 1H),

2.74 (dd, J = 18.0, 8.8 Hz, 1H), 2.64 (dd, J = 18.0, 5.6 Hz, 1H), 1.77–1.99 (m, 2H), 1.26–1.35 (m, 4H), 0.90 (t, J = 6.8 Hz, 3H); ^{13}C NMR for major diastereomer (100 MHz, $CDCl_3$) δ 177.9, 175.7, 135.8, 128.64, 128.59, 127.8, 62.6, 52.4, 47.0, 42.3, 38.3, 32.2, 25.8, 22.8, 13.9; IR (neat) 1732, 1699, 1431, 1400, 1342, 1260, 1171, 1084, 1018, 800, 696 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{18}H_{25}N_2O_4^+$: 333.1809 ($[M+H]^+$), found 333.1803; HPLC analysis: Daicel Chiralpak IC, hexane/2-propanol = 5:1, flow rate = 1.0 mL/min, λ = 210 nm, retention time: major diastereomer: 24.8 min (minor) and 28.5 min (major), minor diastereomer: 27.0 min (major) and 67.5 min (minor).

Preparation of chiral ammonium nitronate (*S*)-7d:[3]



Chiral ammonium bromide (*S*)-**7d•Br**$^-$ was transformed into the corresponding ammonium hydroxide (*S*)-**7d•OH**$^-$ by passing through an ion-exchange resin (amberlyst A26, OH^- form) in methanol. The resulting (*S*)-**7d•OH**$^-$ was then treated with methyl 2-nitropropanoate (1.0 equiv) in methanol at room temperature. Solvent was removed to give the corresponding ammonium nitronate (*S*)-**7d** as white solid.

(*S*)-7d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00–7.72 (m, 28H), 6.98 (d, J = 8.4 Hz, 1H), 6.76 (d, J = 8.8 Hz, 1H), 5.09 (d, J = 13.6 Hz, 1H), 4.90 (d, J = 13.6 Hz, 1H), 4.29–4.38 (m, 2H), 3.27 (s, 3H), 2.74–2.86 (m, 2H), 2.43–2.52 (m, 2H), 2.11–2.17 (m, 1H), 1.71 (s, 3H), 1.63–1.68 (m, 1H), 1.30–1.41 (m, 1H), 1.16–1.20 (m, 1H), 0.80 (d, J = 6.4 Hz, 3H), 0.42–0.51 (m, 1H).

Chiral ammonium nitronate (*S*)-**7d** was recrystallized from diethyl ether/cyclopentyl methyl ether. The single crystal was mounted on a MicroMount (Hampton Research). Data of X-ray diffraction were collected by a Rigaku VariMax with Saturn 724+ using multi-layer mirror monochromated MoKα (λ = 0.71075 Å) to a maximam 2θ value of 50.7°. The crystal structure was solved by the direct methods and refined by the full-matrix least squares using the program SHELXL-97.[4] All non-hydrogen atoms were refined anisotropically.

The crystallographic data of (*S*)-**7d** were summarized in the following table.

empirical formula	$C_{58}H_{54}N_2O_6$
formula weight	875.07
crystal system	orthorhombic
space group	$P2_12_12_1$ (#19)
a, Å	12.455(5)
b, Å	15.315(6)
c, Å	32.002(13)

V , Å^3	6104(5)
Z	4
T, °C	–180
R_1 (I >2σ(I))	0.1175
R (All reflections)	0.1339
Rw (All reflections)	0.3484
Goodness of Fit	1.360

The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 805745). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/data_request/cif.

The disorder of a phenyl ring in diphenylhydroxymethyl group was observed in the crystal.

We are grateful to Dr. Hiroyasu Sato (Rigaku Corporation) for X-ray crystallographic analysis.

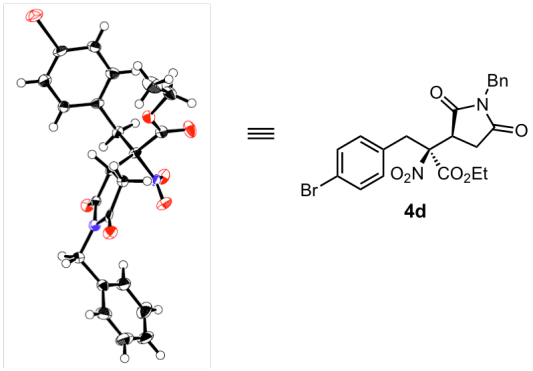
Determination of Absolute Configuration:

The product **4d** was recrystallized from hexane/methanol. The single crystal was mounted on a MicroMeshTM (MiTeGen). Data of X-ray diffraction were collected by a Rigaku RAXIS-RAPID Imaging Plate two-dimensional area detector using graphite-monochromated CuKα (λ = 1.54187 Å) to a maximam 2θ value of 136.5°. The crystal structure was solved by the direct methods and refined by the full-matrix least squares using the program SHELXL-97.[4] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined by using the riding model. The absolute configuration was determined by reference to the Flack parameter[5] –0.03(2).

The crystallographic data of **4d** were summarized in the following table.

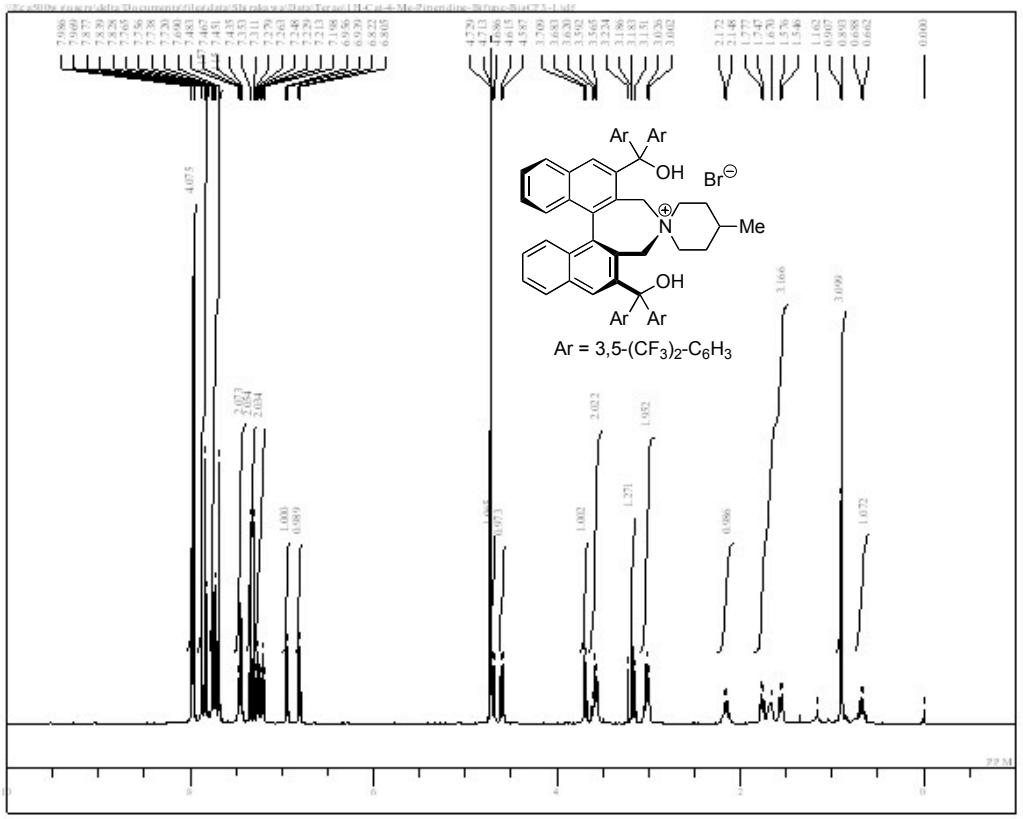
empirical formula	$C_{22}H_{21}BrN_2O_6$
formula weight	489.32
crystal system	orthorhombic
space group	$P2_12_12_1$ (#19)
a, Å	6.21622(15)
b, Å	14.1578(3)
c, Å	24.7401(7)
V , Å^3	2177.32(9)
Z	4
*D*calc, g/cm^3	1.493
T, °C	–150
μ (CuKα), cm^{-1}	29.356
R_1 (I >2σ(I))	0.0508
R (All reflections)	0.0589
Rw (All reflections)	0.1326
Goodness of Fit	1.076
Flack Parameter (Friedel pairs = 1671)	–0.03(2)

The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 805746). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/data_request/cif.



References:

1. (a) R. He, S. Shirakawa and K. Maruoka, *J. Am. Chem. Soc.*, 2009, **131**, 16620; (b) X. Wang, Q. Lan, S. Shirakawa and K. Maruoka, *Chem. Commun.*, 2010, **46**, 321.
2. N. V. Yashin, E. B. Averina, Y. K. Grishin, T. S. Kuznetsova and N. S. Zefirov, *Synlett*, 2006, 279.
3. D. Uraguchi, Y. Ueki and T. Ooi, *Science*, 2009, **326**, 120.
4. G. M. Sheldrick, SHELX-97: Program for Crystal Structure Refinement, University of Gottingen, Germany, 1997.
5. H. D. Flack, *Acta Cryst.*, 1983, **A39**, 876.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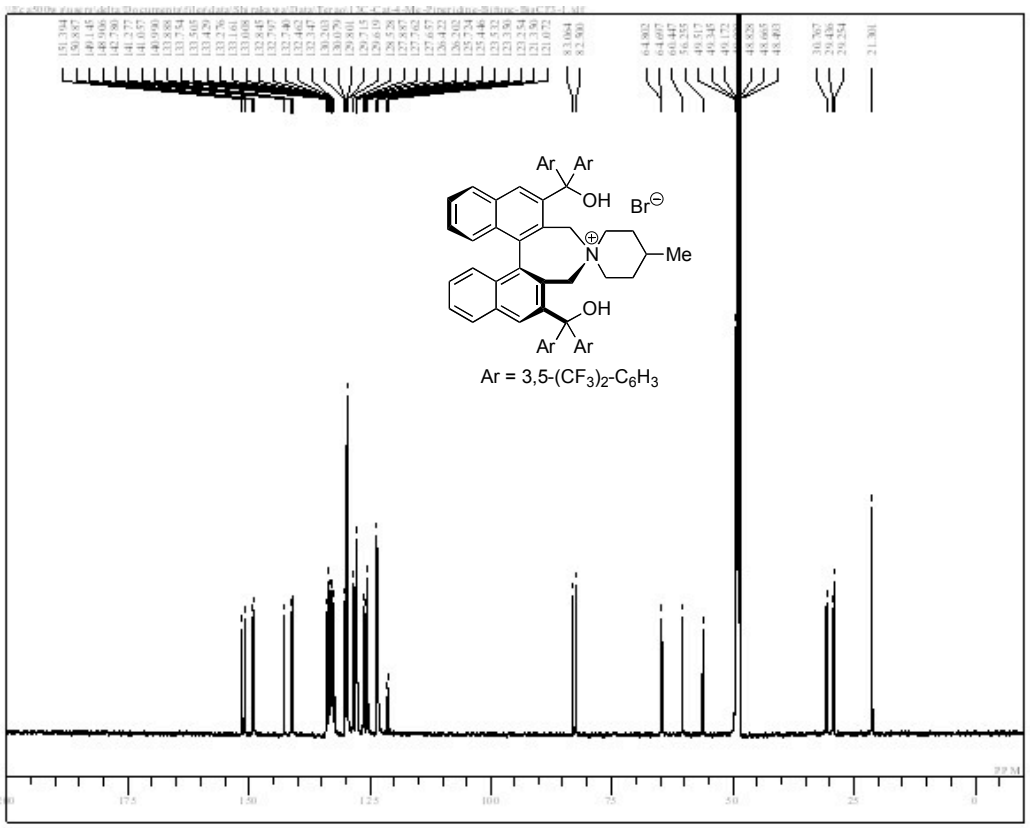
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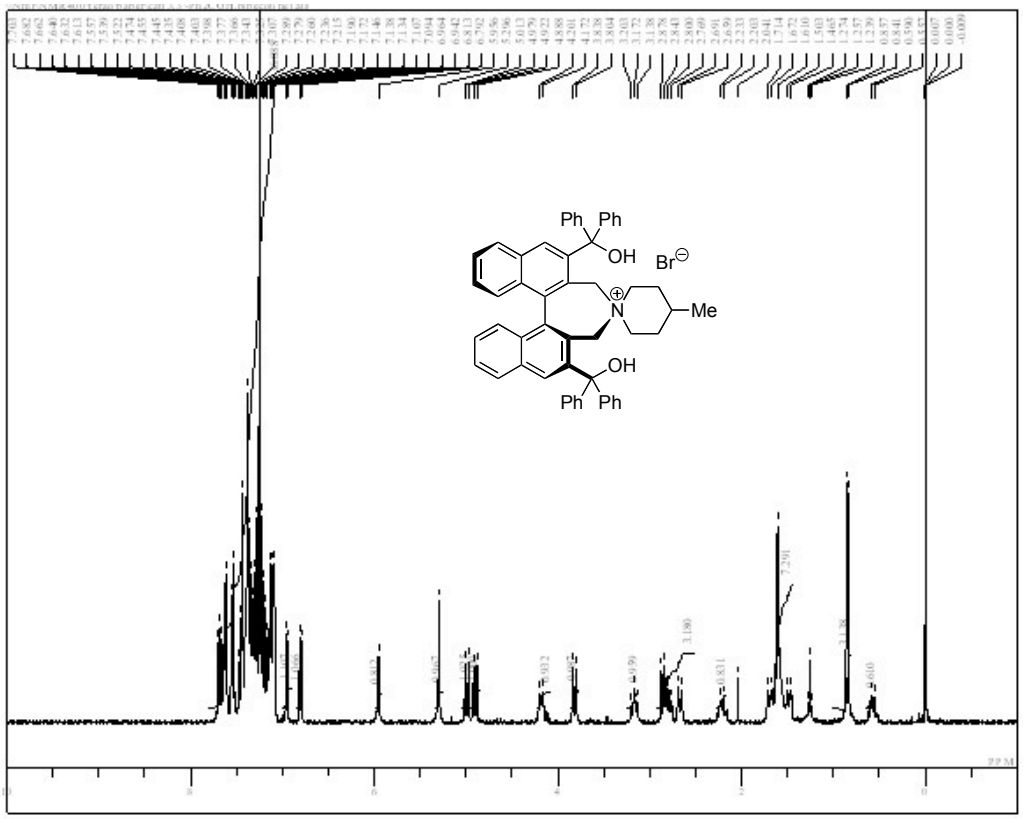
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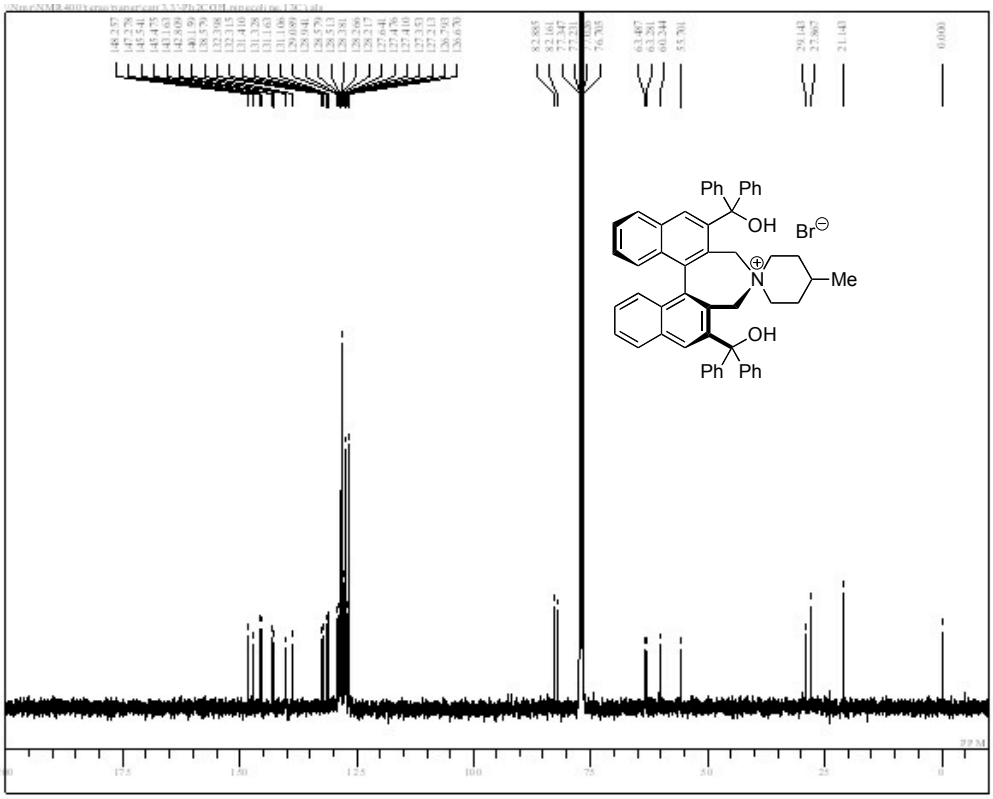
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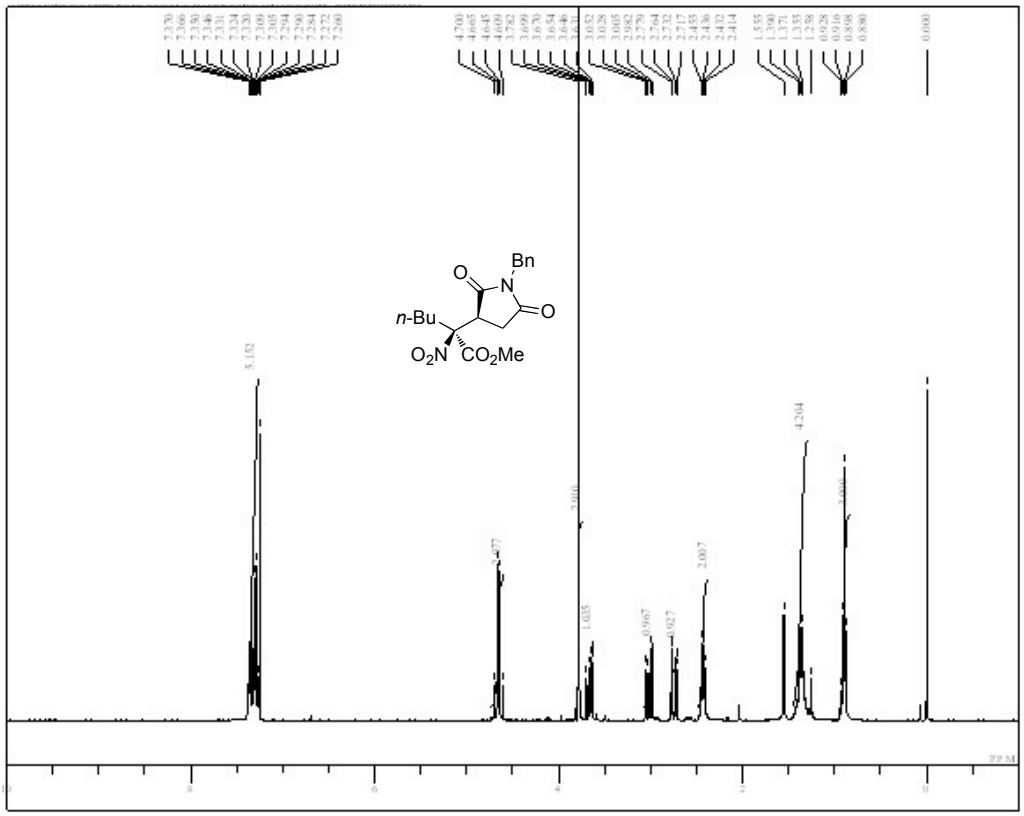
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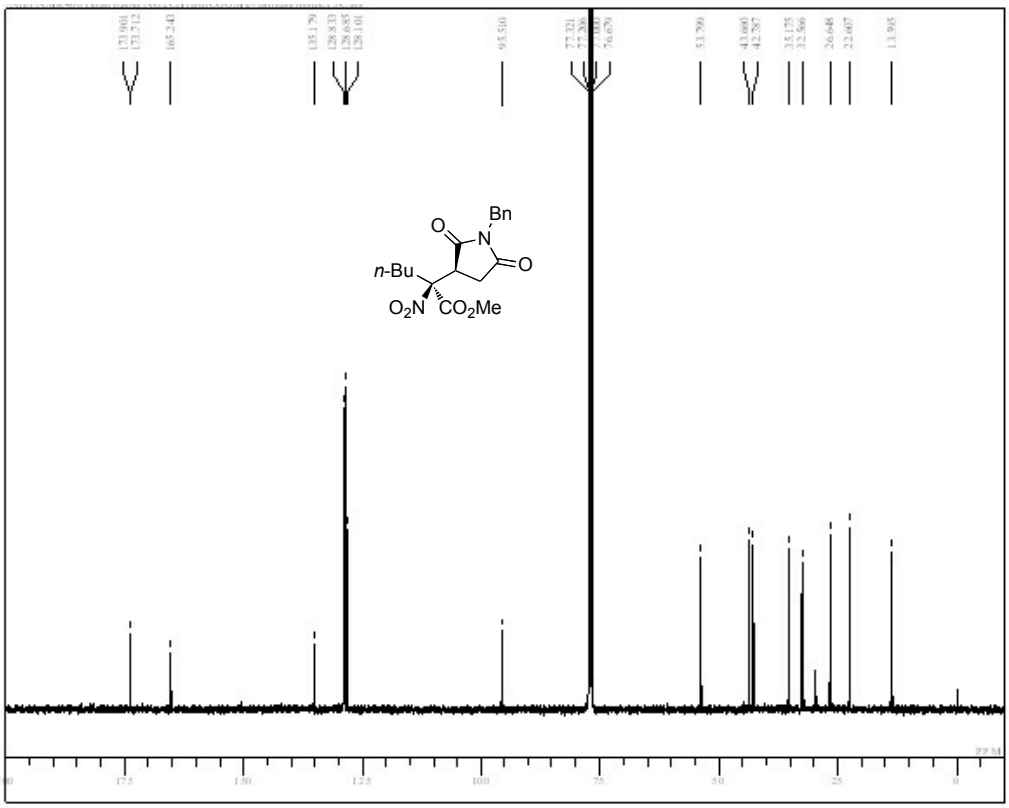
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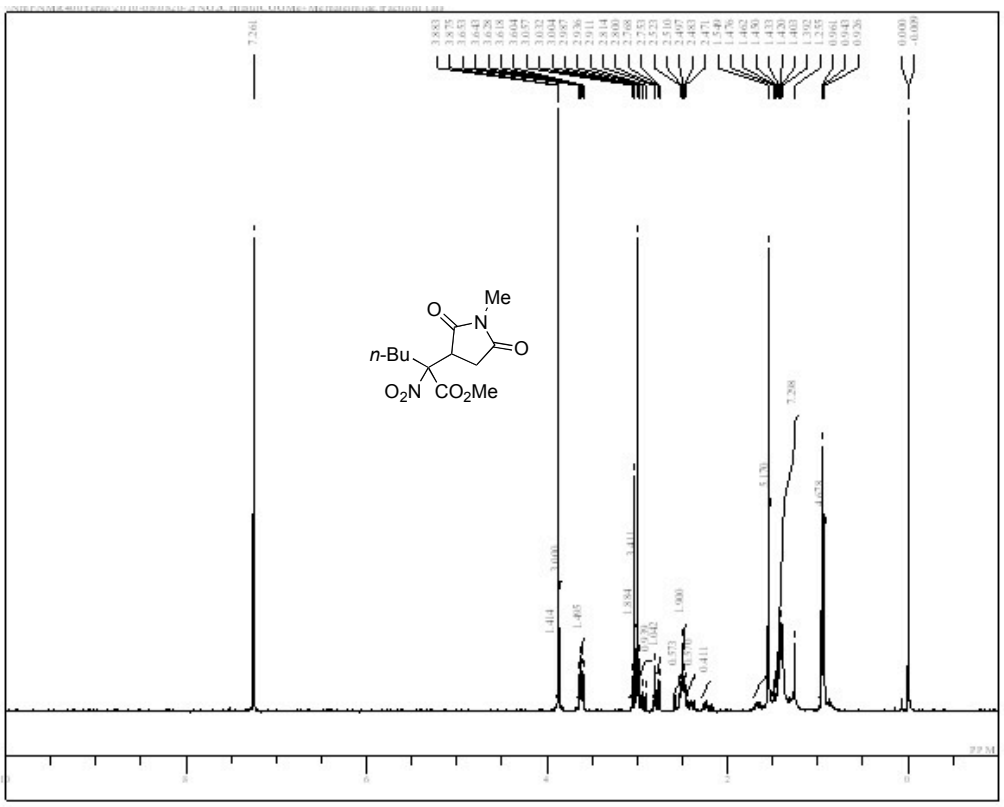

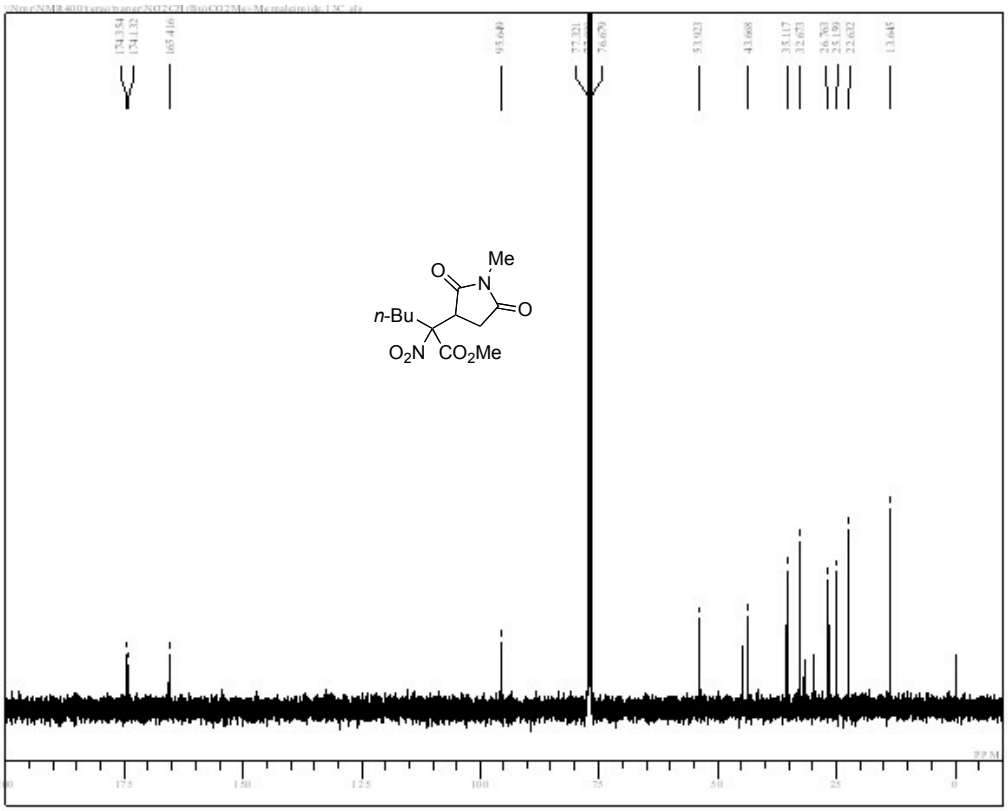

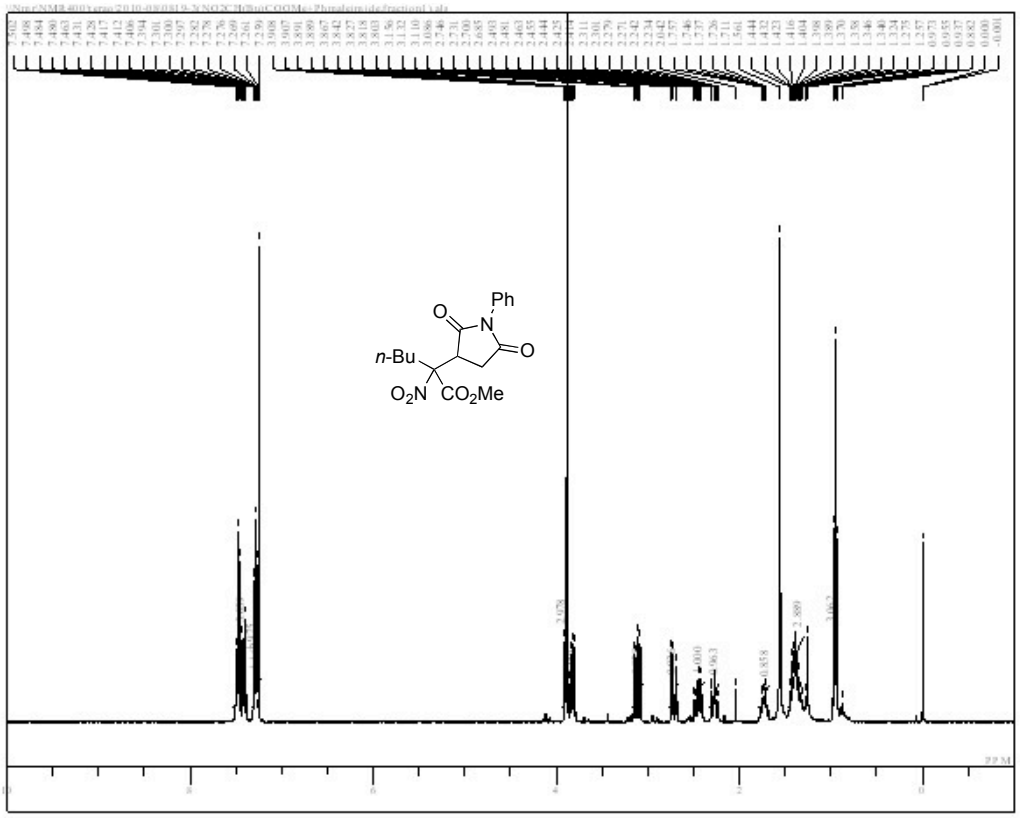
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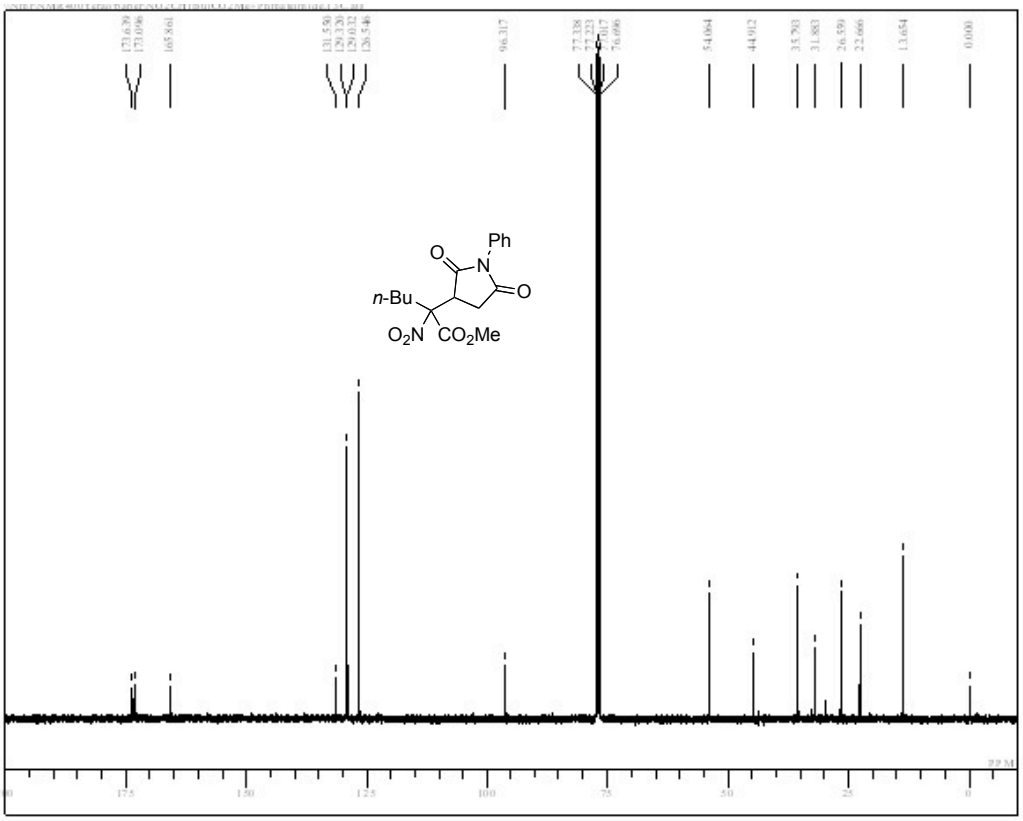
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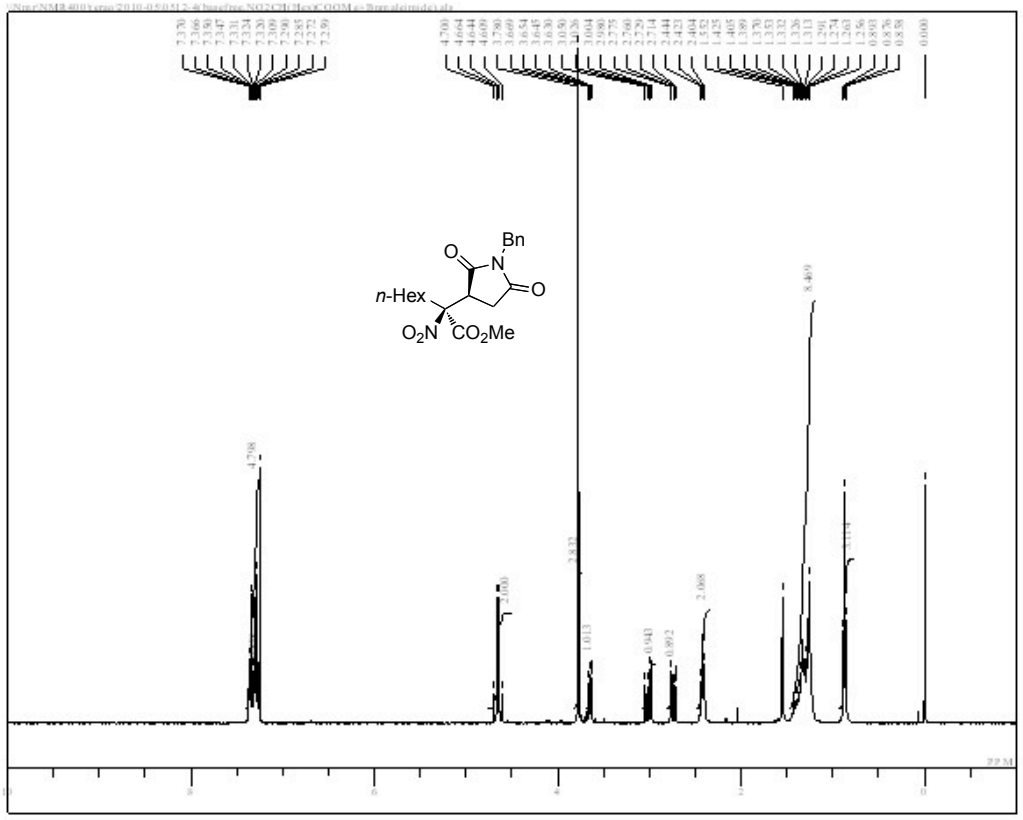
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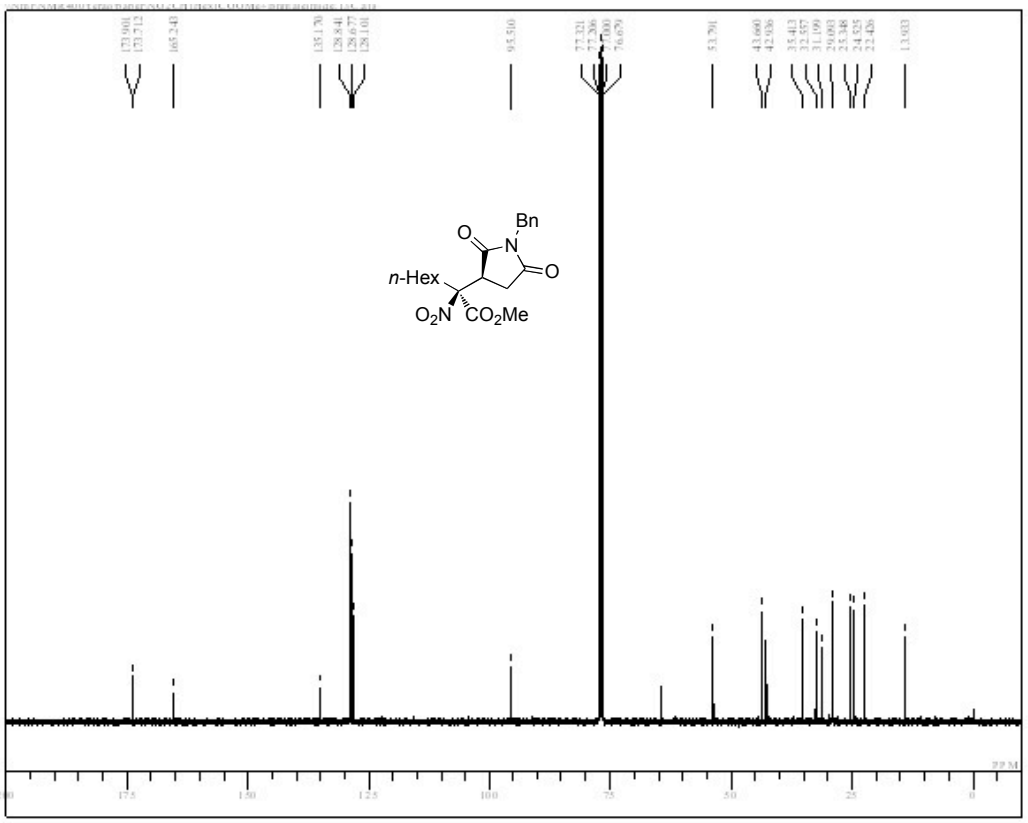
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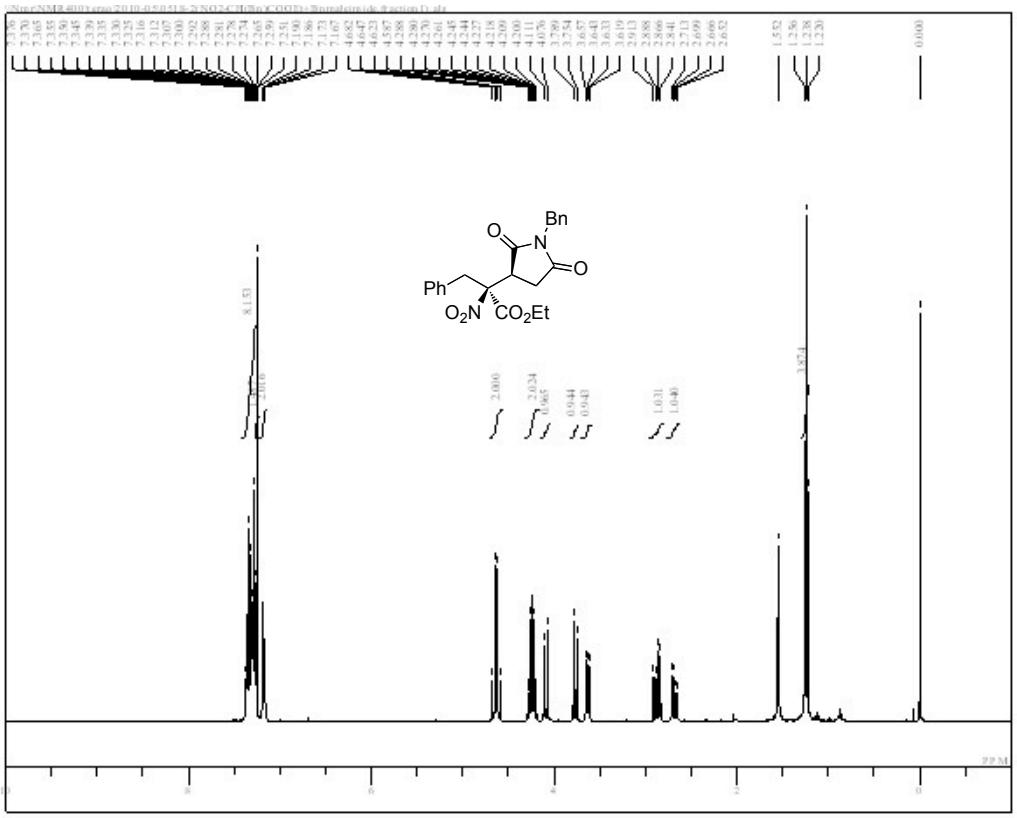
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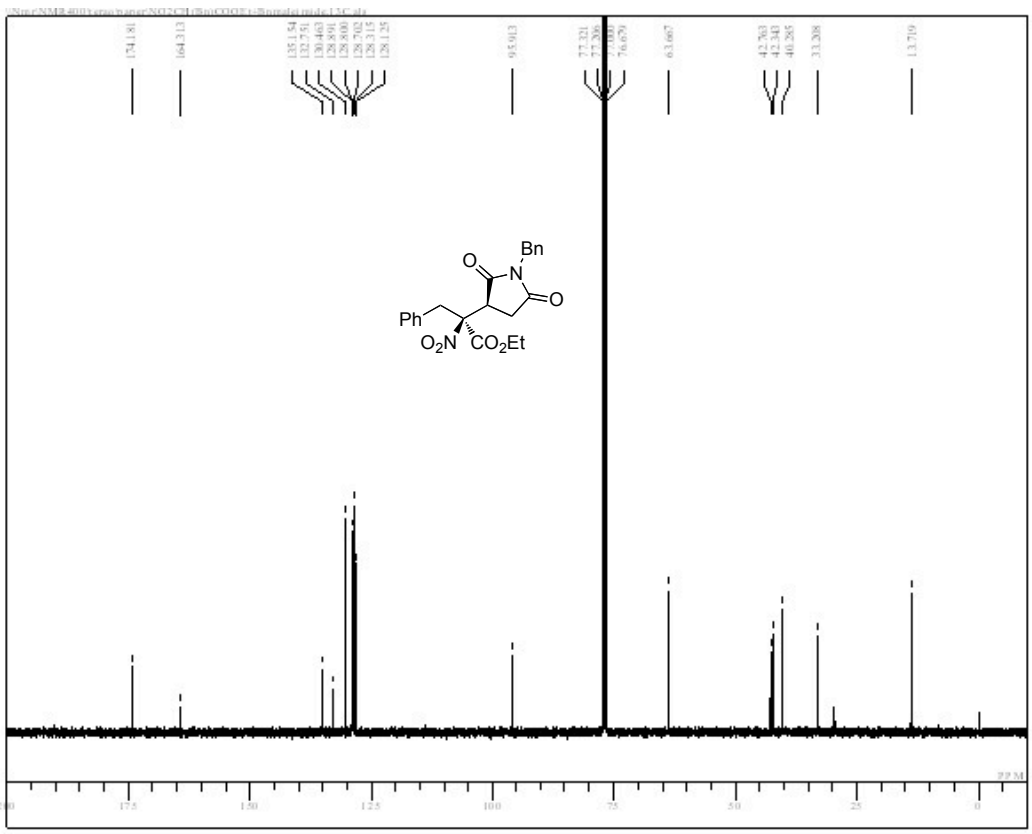
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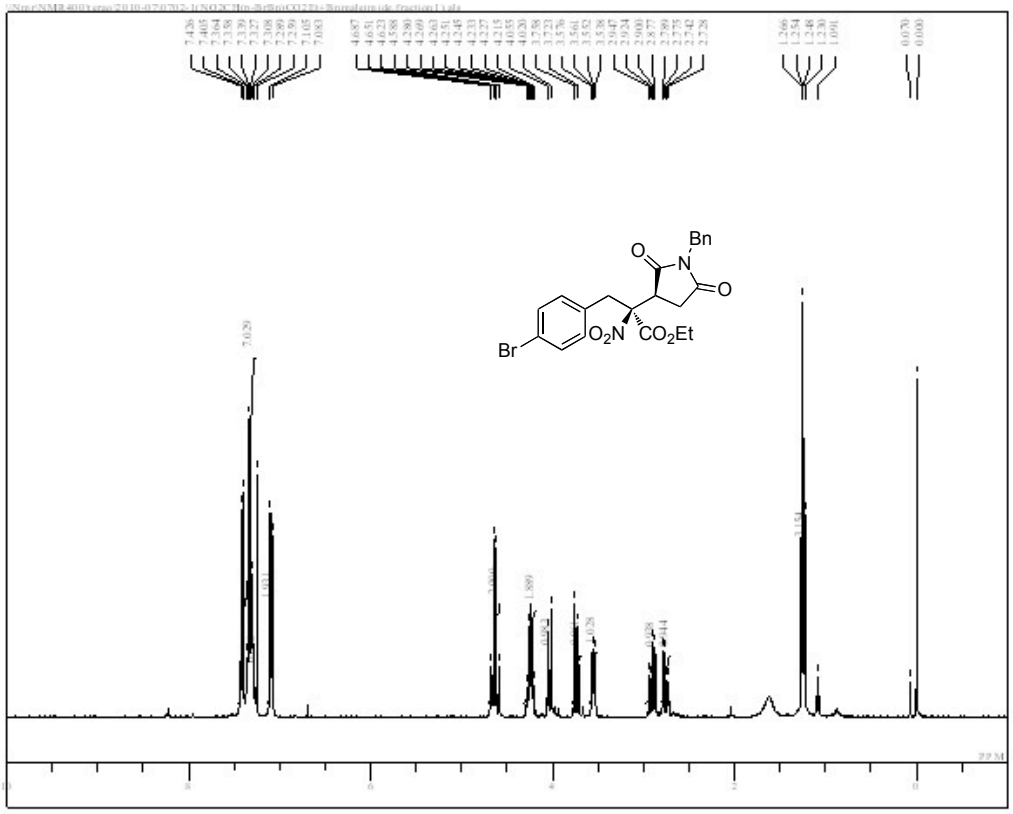
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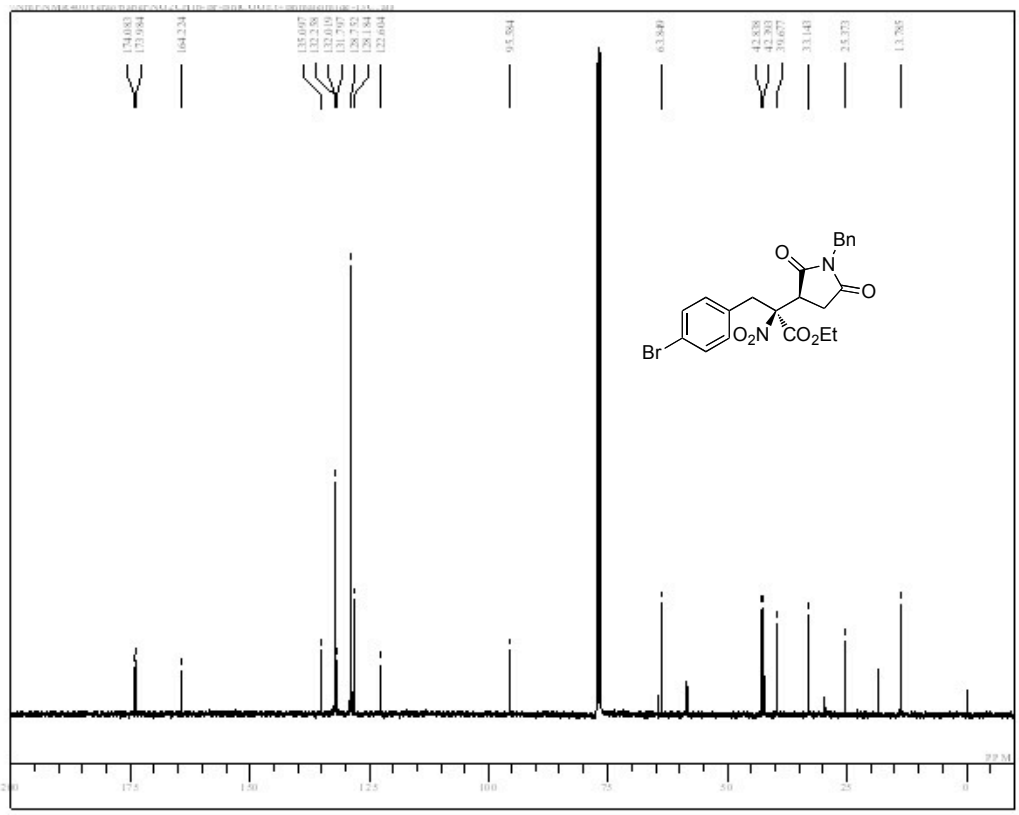
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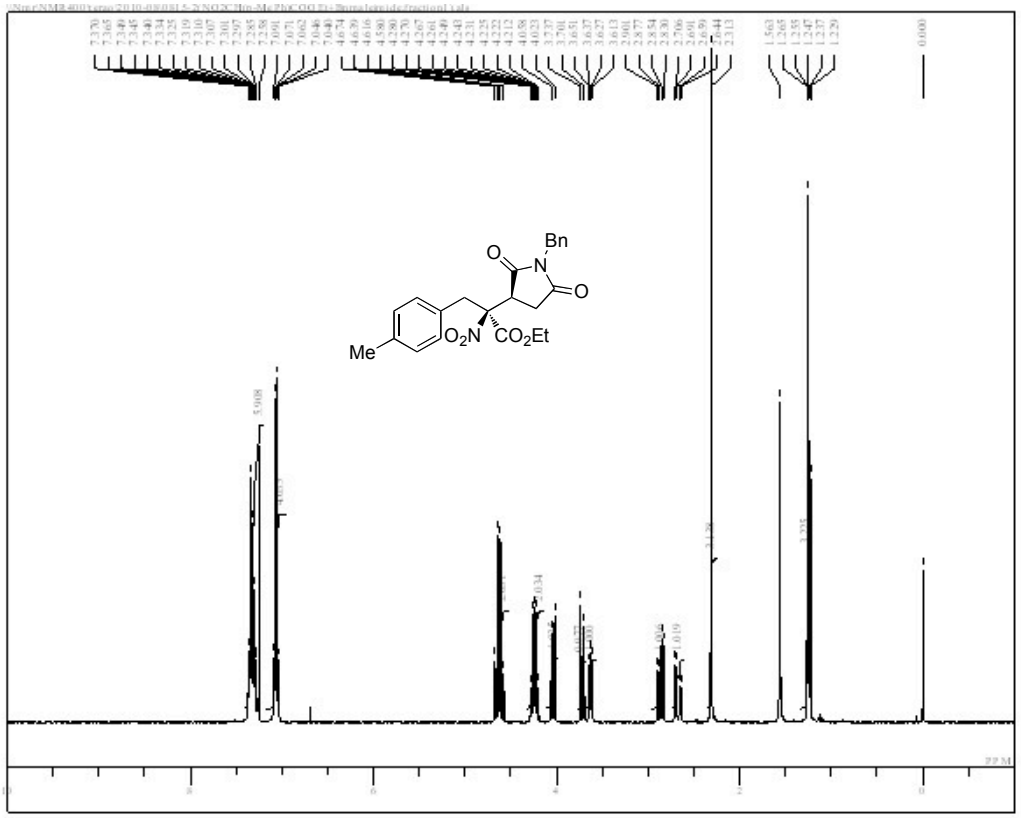

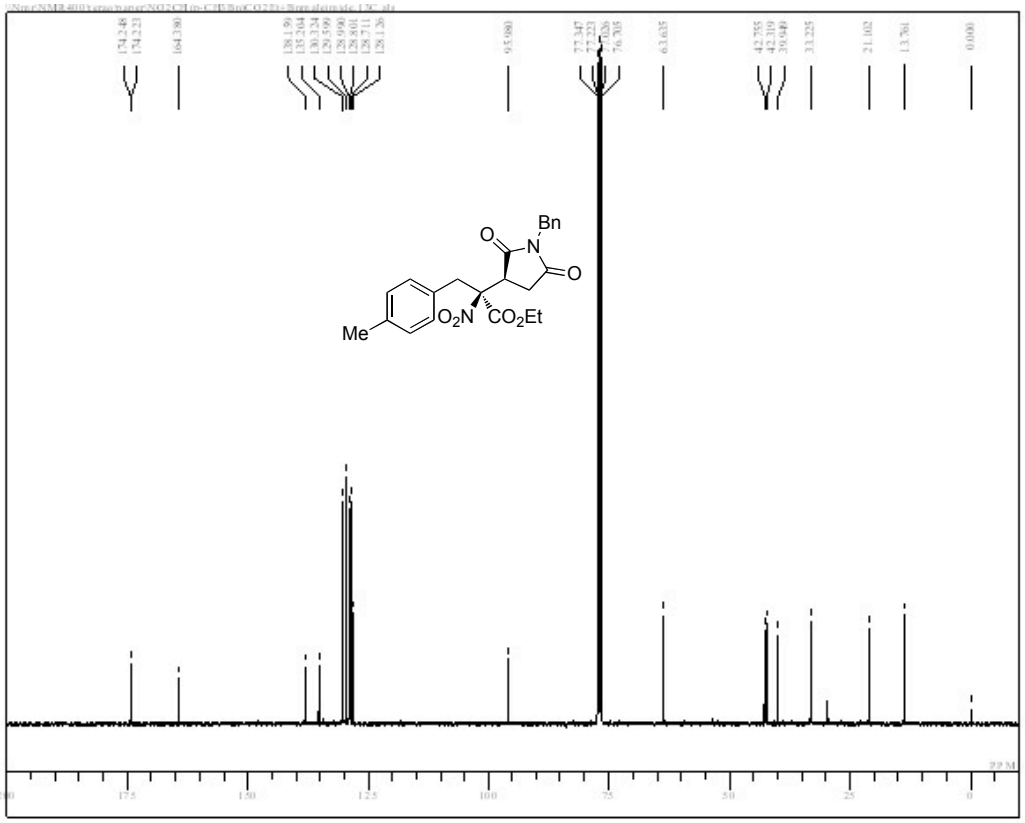

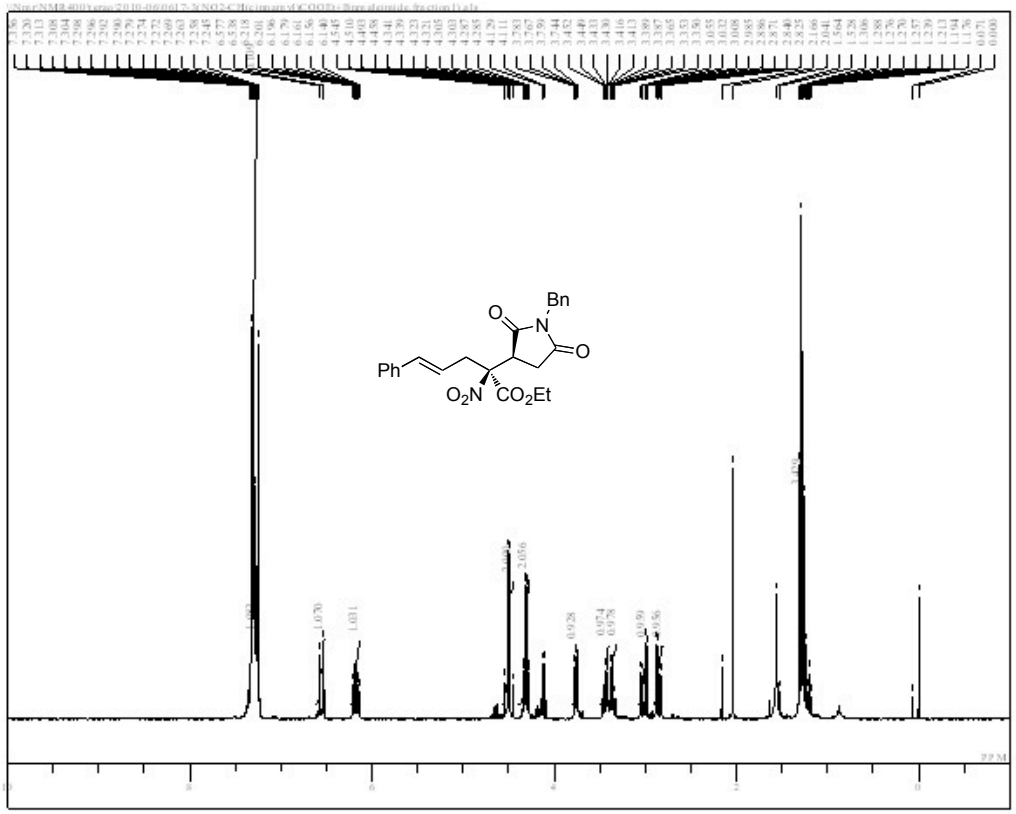
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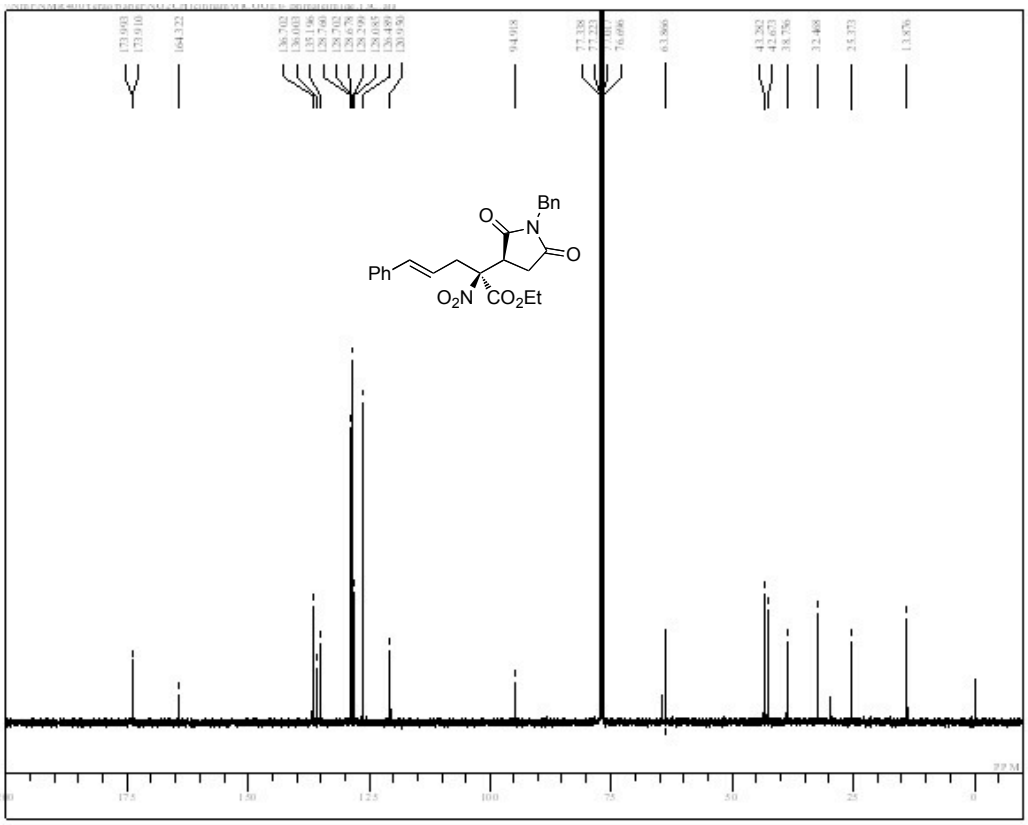
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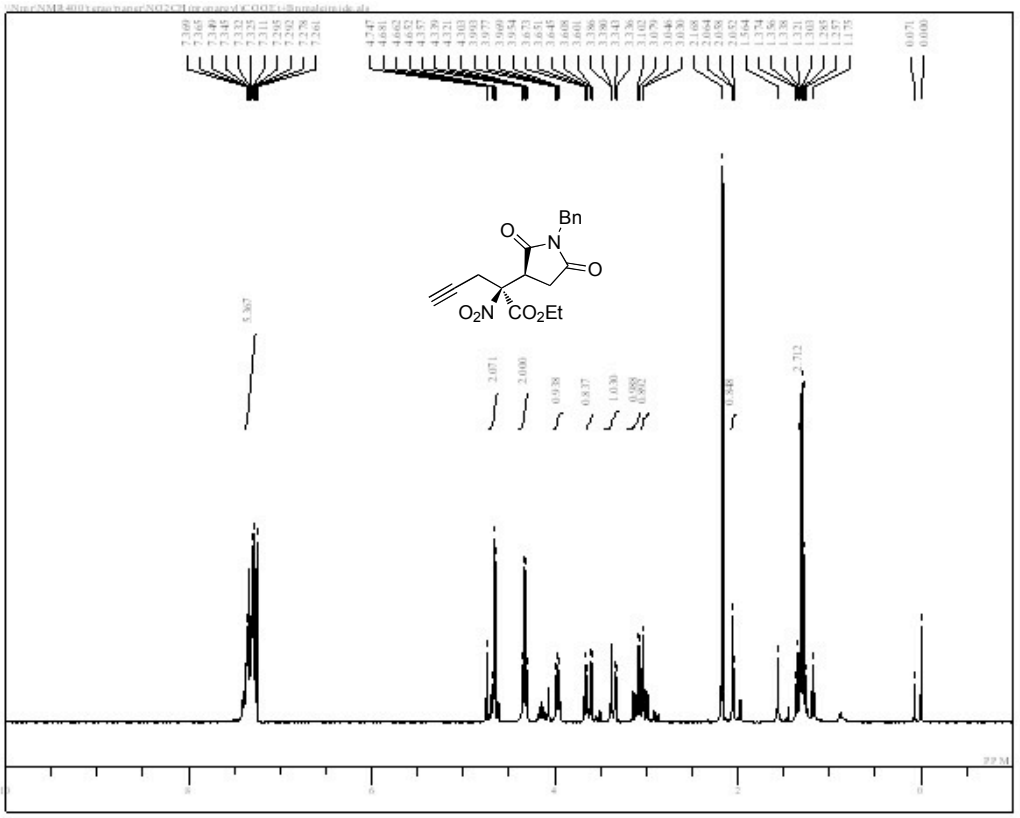
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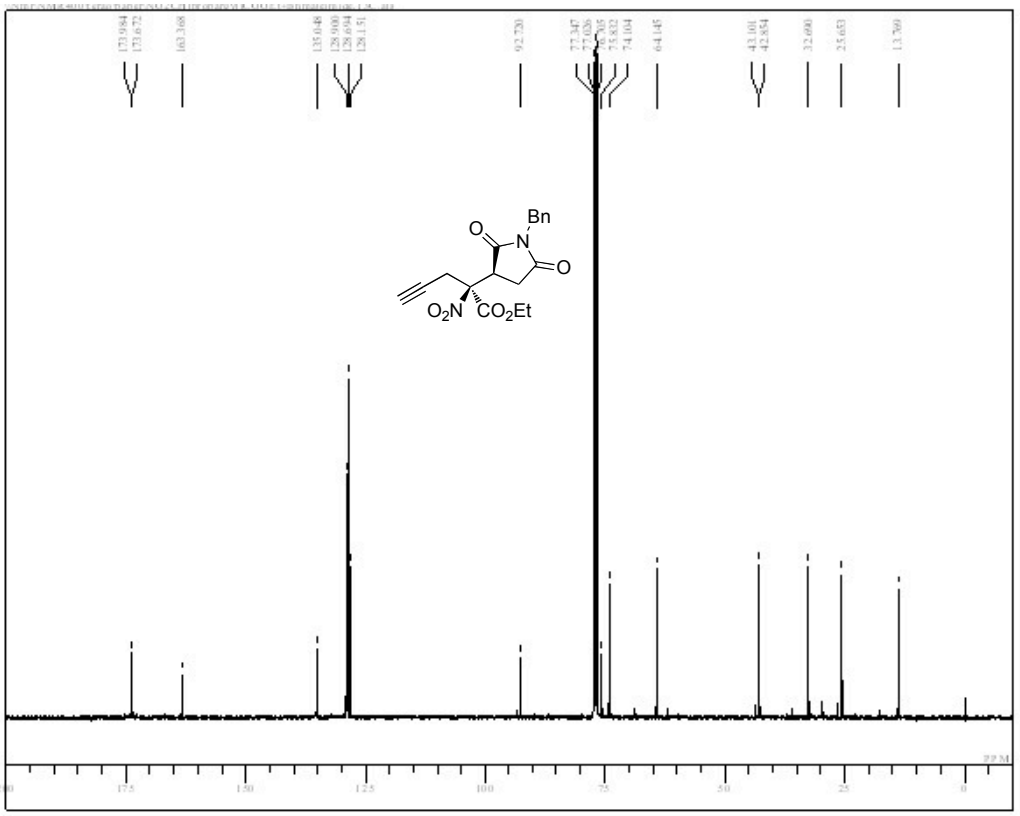
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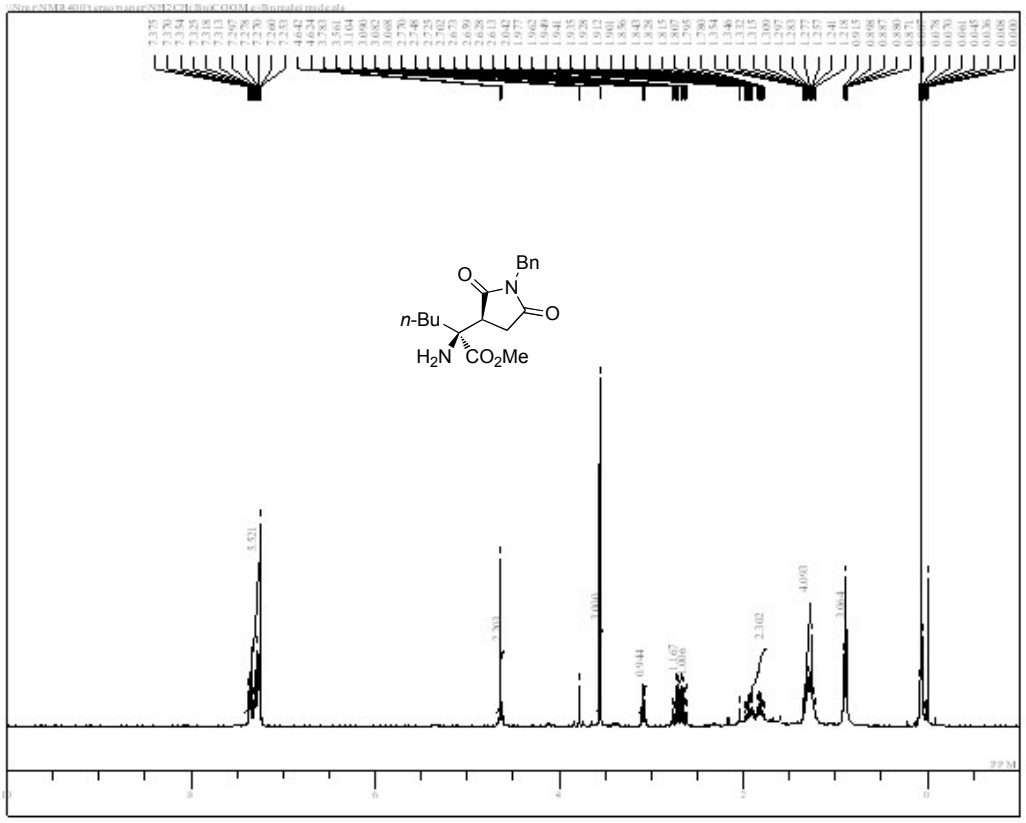
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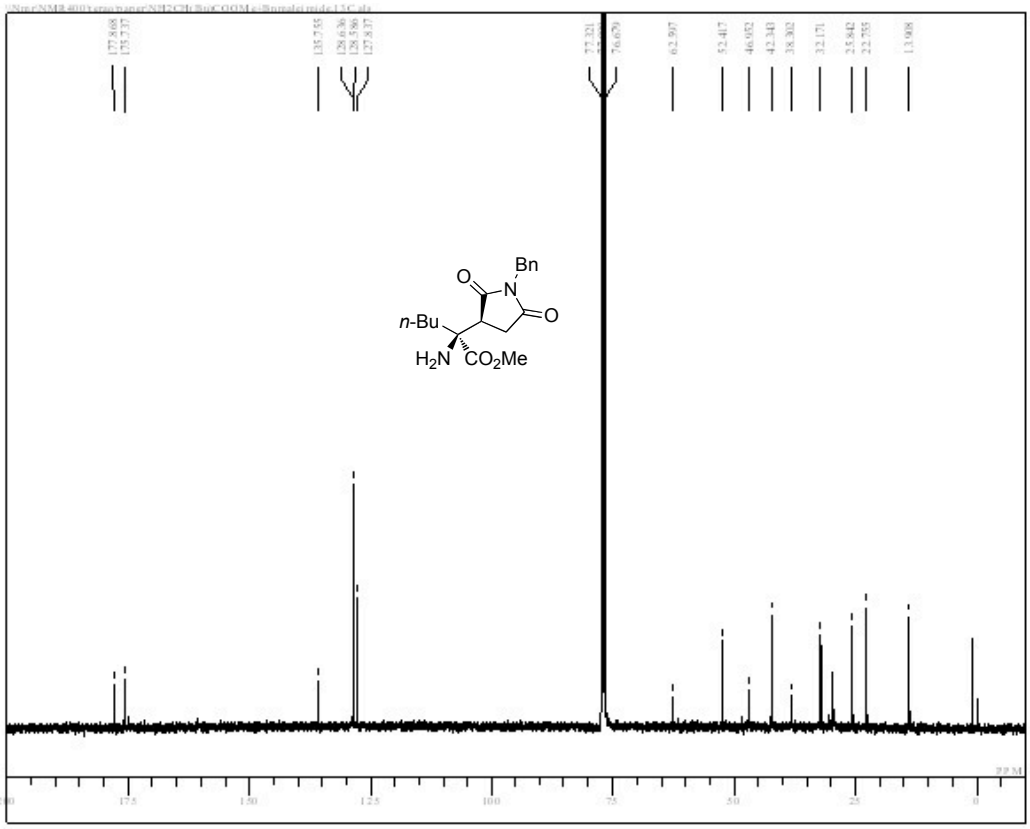
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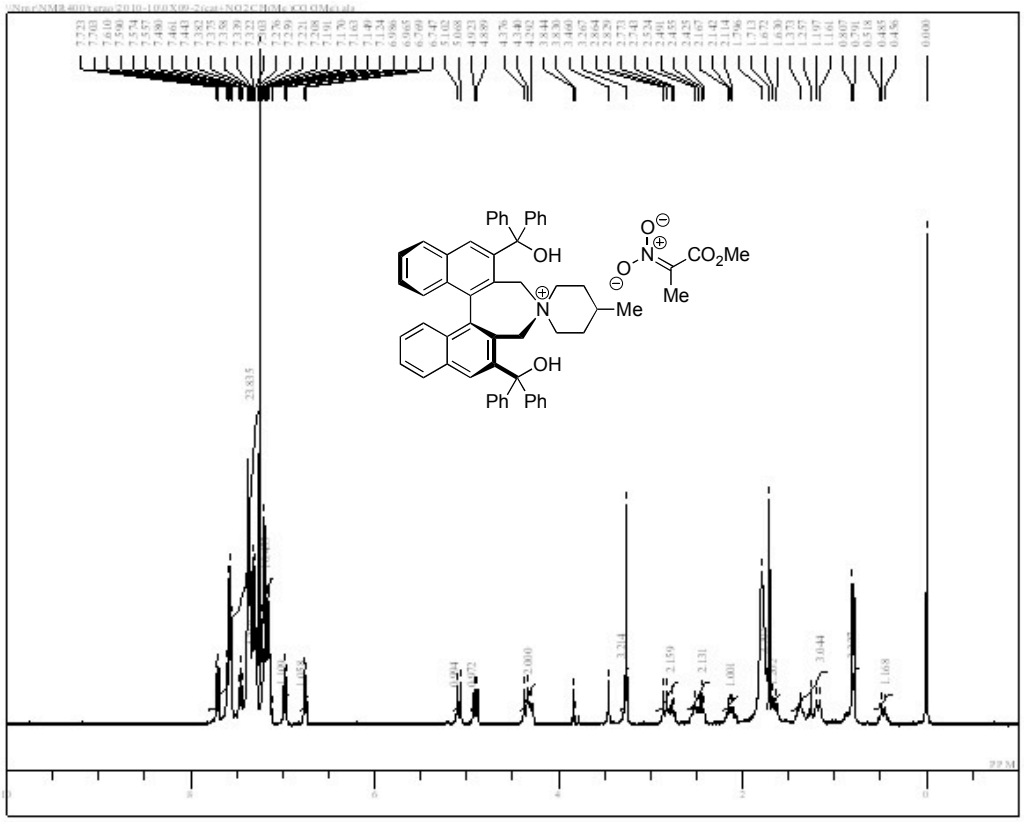
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