

SUPPORTING INFORMATION

Title: Thermally Induced [2+2] Cycloadditions of (Benzyloxymethylene)cyclopropane with Alkylidenemalononitriles
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General. All reactions were carried out under an argon atmosphere. Alkylidenemalononitriles **2a** and **2d** were purchased from ALDRICH and used as received. Isopropylidenemalononitrile **2g** was purchased from TCI Organic Chemicals and used as received. Alkylidenemalononitriles **2b**, **2c**, **2e**, and **2f** were prepared according to the reported procedure.¹ Column chromatography was performed with Fuji Silysia silica gel BW-300. Spectroscopic measurements were carried out with the following instruments: JEOL JNM-AL400 (NMR), JEOL JNM-GSX270 (NMR), JASCO FT/IR 4100 (IR), HITACHI M-2500s (HRMS), Bruker Daltonics APEX III (HRMS), Rigaku Saturn Cu-CCD (X-ray). Chemical shifts are reported in ppm relative to tetramethylsilane (for ¹H, δ 0.00) and CDCl₃ (for ¹³C, δ 77.00). Recycling gel permeation chromatography (GPC) was performed with Japan Analytical Industry LC-9104 using chloroform as eluent.

General procedure for the [2+2] cycloaddition of (benzyloxymethylene)cyclopropane (1a) to alkylidenemalononitriles 2. To the alkylidenemalononitrile **2** (0.2 mmol) in acetonitrile (2 mL) was added (benzyloxymethylene)cyclopropane **1a** (0.2 mmol). The mixture was stirred at 80 °C with monitoring by GC-MS. After the starting materials had been consumed completely, the solvent was removed in vacuo, and the crude product was purified by column chromatography on silica gel eluting with hexane/ethyl acetate to afford the product **3**.

trans-4-(Benzyloxy)-6-phenylspiro[2.3]hexane-5,5-dicarbonitrile (trans-3a). IR (neat) 3032-2867, 2248, 1455, 1345, 1091, 1014 cm⁻¹. ¹H NMR (270.05 MHz, CDCl₃) δ 0.62-0.81 (m, 3H), 1.40-1.48 (m, 1H), 3.94 (s, 1H), 4.56 (d, J = 11.7 Hz, 1H), 4.80 (s, 1H), 4.83 (d, J = 11.7 Hz, 1H), 7.32-7.46 (m, 10H). ¹³C NMR (67.80 MHz, CDCl₃) δ 8.8, 9.7, 28.3, 39.4, 52.3, 72.4, 81.4, 113.0, 114.0, 128.3, 128.6, 128.7, 128.9, 129.1, 134.5, 135.6. HRMS (ESI). Calcd for C₂₁H₁₈N₂NaO: m/z 337.1317. Found: m/z 337.1311.

cis-4-(Benzyloxy)-6-phenylspiro[2.3]hexane-5,5-dicarbonitrile (cis-3a). IR (neat) 3032-2867, 2372, 2243, 1497, 1455, 1142, 1111, 1026, 746 cm⁻¹. ¹H NMR (270.05 MHz, CDCl₃) δ 0.52-0.80 (m, 3H), 1.19-1.27 (m, 1H), 3.98 (s, 1H), 4.58 (d, J = 11.7 Hz, 1H), 4.65 (s, 1H), 4.87 (d, J = 11.7 Hz, 1H), 7.39-7.41 (m, 10H). ¹³C NMR (67.80 MHz, CDCl₃) δ 5.2, 8.8, 29.9, 40.1, 48.8, 72.5, 81.0, 111.8, 115.2, 128.4, 128.6, 128.7, 129.1, 129.4, 132.1, 135.6. HRMS (ESI). C₂₁H₁₈N₂NaO: m/z 337.1317. Found: m/z 337.1311.

trans-4-(Benzyloxy)-6-(4-nitrophenyl)spiro[2.3]hexane-5,5-dicarbonitrile (trans-3b). IR (neat) 2959-2867, 2240, 1604, 1517, 1347, 1158, 1108 cm⁻¹. ¹H NMR (270.05 MHz, CDCl₃) δ 0.62-0.68 (m, 1H), 0.79-0.89 (m, 2H), 1.50-1.54 (m, 1H), 4.04 (s, 1H), 4.60 (d, J = 11.7 Hz, 1H), 4.80 (s, 1H), 4.82 (d, J = 11.7 Hz, 1H), 7.37-7.41 (m, 5H), 7.54 (d, J = 8.9 Hz, 1H), 8.30 (d, J = 8.9 Hz, 1H). ¹³C NMR (67.80 MHz, CDCl₃) δ 9.0, 9.9, 28.4, 39.3, 51.59, 51.63, 72.8, 81.4, 112.5, 113.3, 124.4, 128.4, 128.9, 130.1, 135.3, 141.7, 148.2. HRMS (ESI). Calcd for C₂₁H₁₈N₂NaO: m/z 382.1168. Found: m/z 382.1162.

cis-4-(Benzyloxy)-6-(4-nitrophenyl)spiro[2.3]hexane-5,5-dicarbonitrile (cis-3b). IR (neat) 2958-2855, 2248, 1514, 1349, 1139, 1025, 795 cm⁻¹. ¹H NMR (270.05 MHz, CDCl₃) δ 0.62-0.80 (m, 3H), 1.21-1.34 (m, 1H), 4.11 (s, 1H), 4.61 (d, J = 11.7 Hz, 1H), 4.68 (s, 1H), 4.88 (d, J = 11.7 Hz, 1H), 7.34-7.46 (m, 5H), 7.60 (d, J = 8.9 Hz, 2H), 8.27 (d, J

= 8.9 Hz, 2H). ^{13}C NMR (67.80 MHz, CDCl_3) δ 5.6, 9.9, 29.8, 39.6, 48.7, 72.9, 81.5, 111.3, 114.6, 124.0, 128.5, 128.9, 129.0, 130.5, 135.3, 139.5. HRMS (ESI). Calcd for $\text{C}_{21}\text{H}_{17}\text{N}_3\text{NaO}_3$: m/z 382.1168. Found: m/z 382.1162.

4-(Benzyloxy)-6-(4-methoxyphenyl)spiro[2.3]hexane-5,5-dicarbonitrile (3c). An inseparable mixture of *trans* and *cis* isomers was obtained. IR (neat) 3065-2839, 2245, 1611, 1513, 1455, 1253, 1115, 1027 cm^{-1} . ^1H NMR 0.51-0.79 (m, 3H), 1.18-1.25 (*cis*, m, 1H), 1.38-1.46 (*trans*, m, 1H), 3.81 (s, 3H), 3.92 (*trans*, s, 1H), 3.95 (*cis*, s, 1H), 4.53-4.62 (m, *cis*2H+*trans*1H), 4.75-4.89 (m, *cis*1H+*trans*2H), 6.90-6.96 (m, 2H), 7.25-7.44 (m, 7H). HRMS (ESI). Calcd for $\text{C}_{22}\text{H}_{20}\text{N}_2\text{NaO}_2$: m/z 367.1422. Found: m/z 367.1417.

***trans*-4-(Benzyloxy)-6-(furan-2-yl)spiro[2.3]hexane-5,5-dicarbonitrile (*trans*-3d).** Recyclable gel permeation chromatography was performed to separate a distereomeric mixture of **3d**. IR (neat) 3122-2875, 2245, 1498, 1455, 1363, 1151, 1107, 1014 cm^{-1} . ^1H NMR (270.05 MHz, CDCl_3) δ 0.62-0.92 (m, 3H), 1.36-1.44 (m, 1H), 3.95 (s, 1H), 4.59 (d, $J = 11.7$ Hz, 1H), 4.80 (d, $J = 11.7$ Hz, 1H), 4.90 (s, 1H), 6.38-6.42 (m, 2H), 7.35-7.48 (m, 5H), 7.48 (d, $J = 0.8$ Hz, 1H). ^{13}C NMR (67.80 MHz, CDCl_3) δ 7.8, 9.2, 28.6, 38.6, 45.7, 45.8, 72.6, 81.5, 110.7, 111.0, 112.8, 113.5, 128.3, 128.7, 135.6, 144.2, 148.4. HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{16}\text{N}_2\text{NaO}_2$: m/z 327.1109. Found: m/z 327.1104.

***cis*-4-(Benzyloxy)-6-(furan-2-yl)spiro[2.3]hexane-5,5-dicarbonitrile (*cis*-3d).** IR (neat) 3123-2875, 2245, 1498, 1455, 1362, 1148, 1109, 1014 cm^{-1} . ^1H NMR (270.05 MHz, CDCl_3) δ 0.52-0.69 (m, 2H), 0.83-0.92 (m, 1H), 1.18-1.26 (m, 1H), 4.10 (s, 1H), 4.59 (d, $J = 11.7$ Hz, 1H), 4.61 (s, 1H), 6.38-6.42 (m, 1H), 6.55 (d, $J = 3.4$ Hz, 1H), 7.34-7.44 (m, 5H), 7.44 (d, $J = 0.8$ Hz, 1H). ^{13}C NMR (67.80 MHz, CDCl_3) δ 4.9, 7.4, 29.8, 40.3, 42.3, 72.6, 80.5, 111.0, 111.8, 114.6, 128.4, 128.8, 135.5, 143.6, 143.7, 146.3. HRMS (ESI). Calcd for $\text{C}_{19}\text{H}_{16}\text{N}_2\text{NaO}_2$: m/z 327.1109. Found: m/z 327.1104.

***trans*-4-(Benzyloxy)-6-(naphthalen-2-yl)spiro[2.3]hexane-5,5-dicarbonitrile (*trans*-3e).** IR (neat) 3058-2865, 2247, 1788, 1342, 1143, 1089 cm^{-1} . ^1H NMR (270.05 MHz, CDCl_3) δ 0.68-0.86 (m, 3H), 1.44-1.52 (m, 1H), 4.12 (s, 1H), 4.59 (d, $J = 11.7$ Hz, 1H), 4.85 (d, $J = 11.7$ Hz, 1H), 4.90 (s, 1H), 7.35-7.44 (m, 6H), 7.49-7.55 (m, 2H), 7.83-7.92 (m, 4H). ^{13}C NMR (67.80 MHz, CDCl_3) δ 9.0, 9.8, 28.5, 39.4, 52.6, 72.5, 81.6, 113.0, 114.0, 126.0, 126.7, 126.8, 127.8, 128.0, 128.3, 128.6, 128.7, 128.8, 129.2, 131.9, 133.2, 133.3, 135.6. HRMS (ESI). Calcd for $\text{C}_{25}\text{H}_{20}\text{N}_2\text{NaO}$: m/z 387.1473. Found: m/z 387.1471.

***cis*-4-(Benzyloxy)-6-(naphthalen-2-yl)spiro[2.3]hexane-5,5-dicarbonitrile (*cis*-3e).** IR (neat) 3087-2853, 2244, 1711, 1455, 1140, 1110 cm^{-1} . ^1H NMR (270.05 MHz, CDCl_3) δ 0.57-0.74 (m, 2H), 0.78-0.88 (m, 2H), 4.17 (s, 1H), 4.64 (d, $J = 11.7$ Hz, 1H), 4.71 (s, 1H), 4.91 (d, $J = 11.7$ Hz, 1H), 7.36-7.44 (m, 5H), 7.47-7.58 (m, 3H), 7.83-7.90 (m, 4H). ^{13}C NMR (67.80 MHz, CDCl_3) δ 5.5, 9.0, 30.1, 40.1, 49.3, 72.6, 81.3, 111.9, 115.3, 126.3, 126.6, 126.9, 127.7, 128.1, 128.4, 128.6, 128.7, 128.8, 129.4, 129.6, 133.0, 133.4, 135.6. HRMS (ESI). Calcd for $\text{C}_{25}\text{H}_{20}\text{N}_2\text{NaO}$: m/z 387.1473. Found: m/z 387.1470.

***trans*-4-(Benzyloxy)-6-tert-butylspiro[2.3]hexane-5,5-dicarbonitrile (*trans*-3f).** IR (neat) 3089-2875, 2242, 1455, 1369, 1151, 1102, 1022 cm^{-1} . ^1H NMR (270.05 MHz, CDCl_3) δ 0.44-0.54 (m, 2H), 1.11 (s, 9H), 1.07-1.35 (m, 2H), 2.78 (s, 1H), 4.46 (s, 1H), 4.52 (d, $J = 11.7$ Hz, 1H), 4.83 (d, $J = 11.7$ Hz, 1H), 7.31-7.41 (m, 5H). ^{13}C NMR (67.80 MHz, CDCl_3) δ 8.2, 8.3, 26.1, 27.3, 33.6, 34.3, 58.2, 72.3, 81.2, 114.8, 115.3, 128.2, 128.7, 135.9. HRMS (ESI). Calcd for $\text{C}_{25}\text{H}_{20}\text{N}_2\text{NaO}$: m/z 317.1630. Found: m/z 317.1624.

cis-4-(Benzyloxy)-6-tert-butylspiro[2.3]hexane-5,5-dicarbonitrile (cis-3f). IR (neat) 3068-2870, 2242, 1732, 1455, 1370, 1138, 1018 cm^{-1} . ^1H NMR (270.05 MHz, CDCl_3) δ 0.41-0.61 (m, 2H), 1.07 (s, 9H), 1.14-1.25 (m, 2H), 2.72 (s, 1H), 4.36 (s, 1H), 4.50 (d, $J = 11.7$ Hz, 1H), 4.82 (d, $J = 11.7$ Hz, 1H), 7.37-7.41 (m, 5H). ^{13}C NMR (67.80 MHz, CDCl_3) δ 4.8, 8.2, 27.8, 28.0, 34.0, 35.5, 52.6, 72.3, 80.0, 113.0, 116.2, 128.3, 128.5, 128.7, 135.7. HRMS (ESI). Calcd for $\text{C}_{25}\text{H}_{20}\text{N}_2\text{NaO}$: m/z 317.1630. Found: m/z 317.1624.

6-(Benzyloxy)-4,4-dimethylspiro[2.3]hexane-5,5-dicarbonitrile (3g). IR (neat) 3089-2870, 2243, 1789, 1706, 1455, 1132, 1098, 1018 cm^{-1} . ^1H NMR (270.05 MHz, CDCl_3) δ 0.41-0.52 (m, 2H), 0.64-0.70 (m, 1H), 1.02-1.08 (m, 1H), 1.18 (s, 3H), 1.34 (s, 3H), 4.50 (s, 1H), 4.51 (d, $J = 11.7$ Hz, 1H), 4.79 (d, $J = 11.7$ Hz, 1H), 7.32-7.39 (m, 5H). ^{13}C NMR (67.80 MHz, CDCl_3) δ 5.0, 5.9, 22.8, 24.8, 33.6, 48.2, 43.3, 72.3, 79.9, 112.5, 113.8, 128.2, 128.5, 128.6, 135.7. HRMS (ESI). Calcd for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{NaO}$: m/z 289.1317. Found: m/z 289.1311.

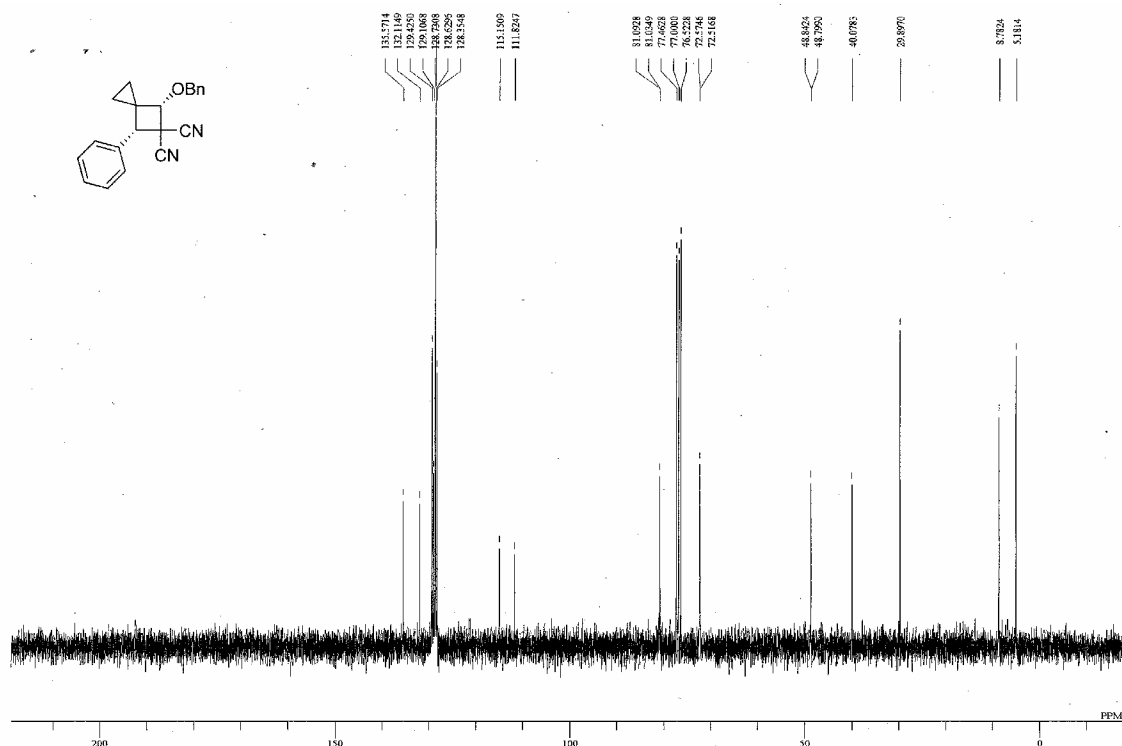
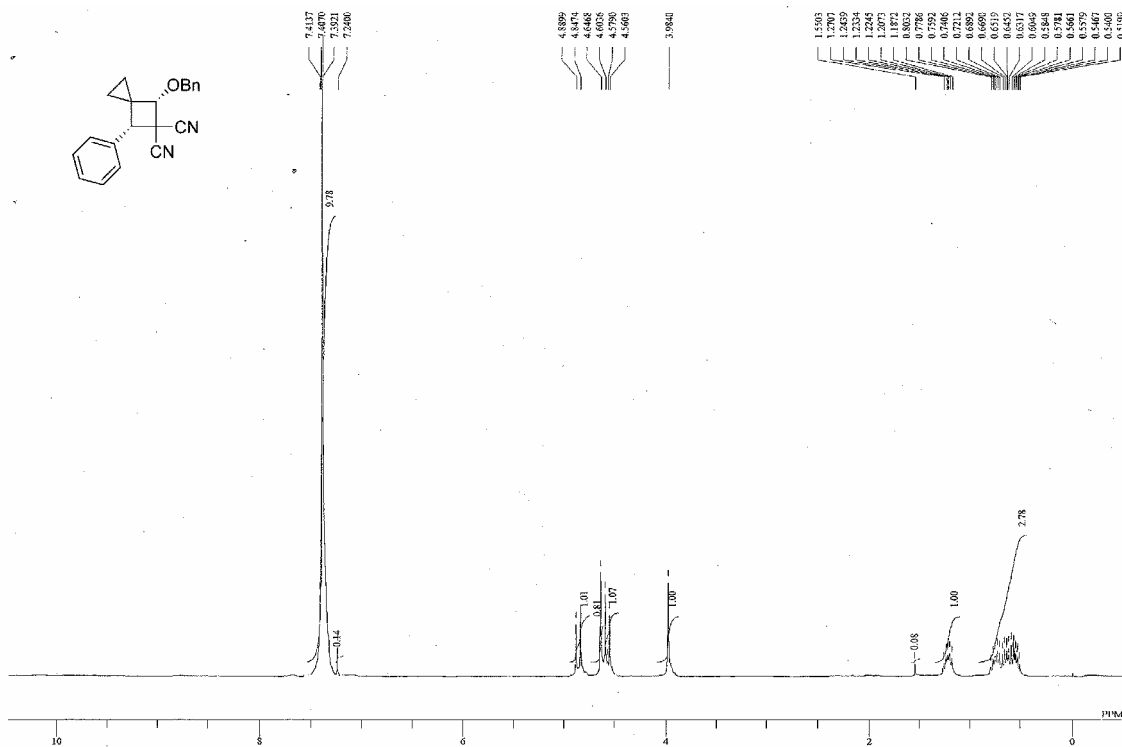
2-((1-(Benzyloxy(methoxy)methyl)cyclopropyl)(phenyl)methyl)malononitrile (8). A 57:43 mixture of the diastereomers of which the stereochemistry was not determined was obtained.

Major diastereomer. IR (neat) 3093-2833, 2254, 1497, 1454, 1106, 1065, 1025 cm^{-1} . ^1H NMR (270.05 MHz, CDCl_3) δ 0.27-0.33 (m, 1H), 0.55-0.67 (m, 2H), 0.87-0.90 (m, 1H), 3.42 (s, 3H), 3.55 (d, $J = 7.5$ Hz, 1H), 3.93 (s, 1H), 4.58 (d, $J = 11.7$ Hz, 1H), 4.77 (d, $J = 11.7$ Hz, 1H), 5.05 (d, $J = 7.5$ Hz, 1H), 7.25-7.44 (m, 10H). ^{13}C NMR (67.80 MHz, CDCl_3) δ 5.5, 8.8, 24.4, 26.6, 46.4, 56.9, 70.4, 108.0, 112.9, 113.5, 127.9, 128.1, 128.5, 128.6, 138.9, 135.3, 137.1. HRMS (ESI). Calcd for $\text{C}_{22}\text{H}_{22}\text{N}_2\text{NaO}_2$: m/z 369.1579. Found: m/z 289.1573.

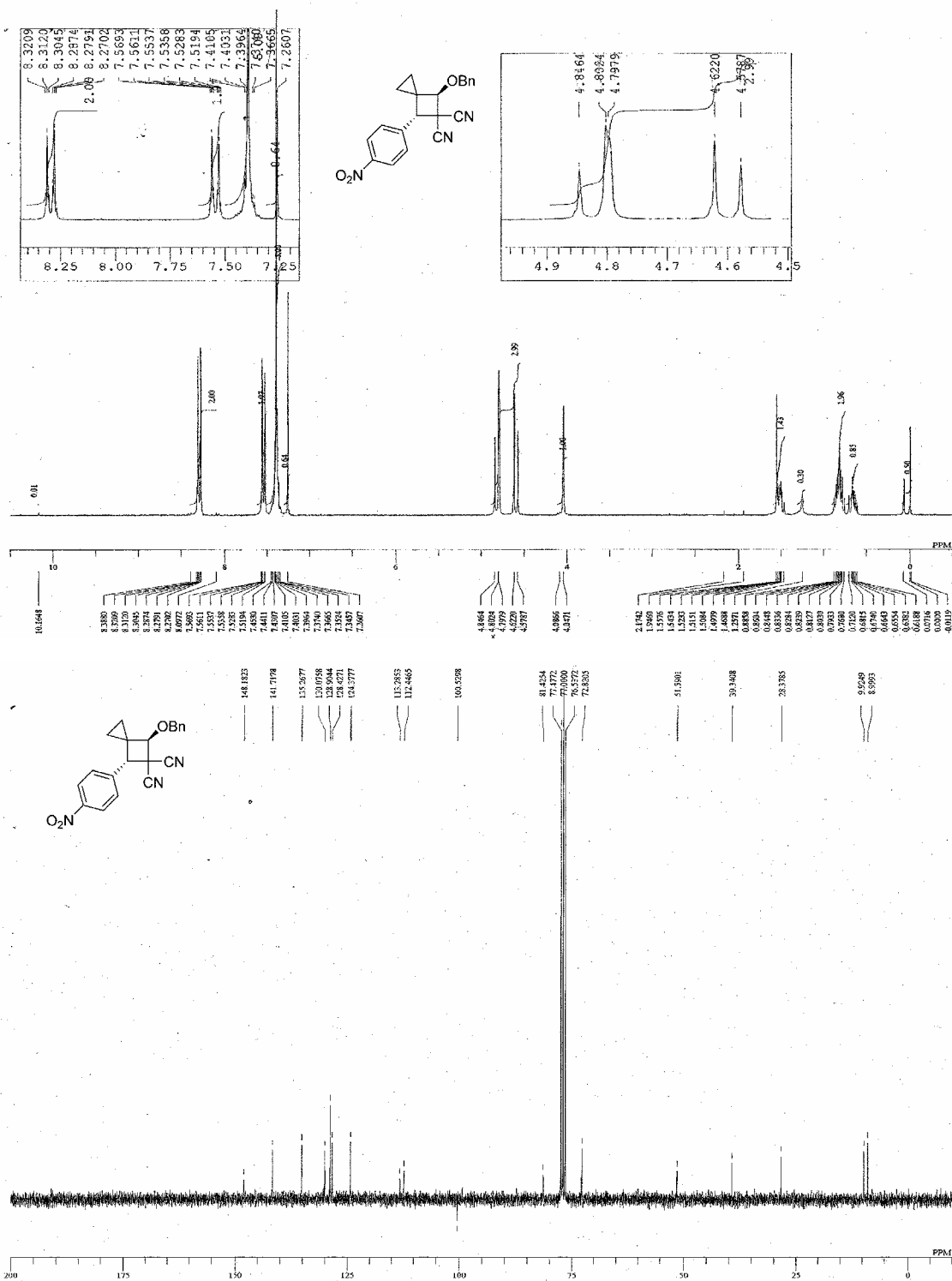
Minor diastereomer. IR (neat) 2953-2853, 2255, 1455, 1349, 916, 888 cm^{-1} . ^1H NMR (270.05 MHz, CDCl_3) δ 0.07-0.37 (m, 1H), 0.57-0.69 (m, 2H), 0.79-0.88 (m, 1H), 3.44 (s, 3H), 3.57 (d, $J = 7.7$ Hz, 1H), 4.55 (d, $J = 11.9$ Hz, 1H), 4.70 (d, $J = 11.9$ Hz, 1H), 5.10 (d, $J = 7.7$ Hz, 1H), 7.29-7.41 (m, 10H). ^{13}C NMR (67.80 MHz, CDCl_3) δ 5.9, 8.5, 24.4, 26.6, 46.9, 56.0, 71.1, 107.6, 107.7, 113.0, 113.5, 127.7, 128.0, 128.6, 128.9, 135.3, 137.1. HRMS (ESI). Calcd for $\text{C}_{22}\text{H}_{22}\text{N}_2\text{NaO}_2$: m/z 369.1579. Found: m/z 289.1573.

¹ B. B. Corson, R. W. Stoughton *J. Am. Chem. Soc.* **1928**, *50*, 2825.

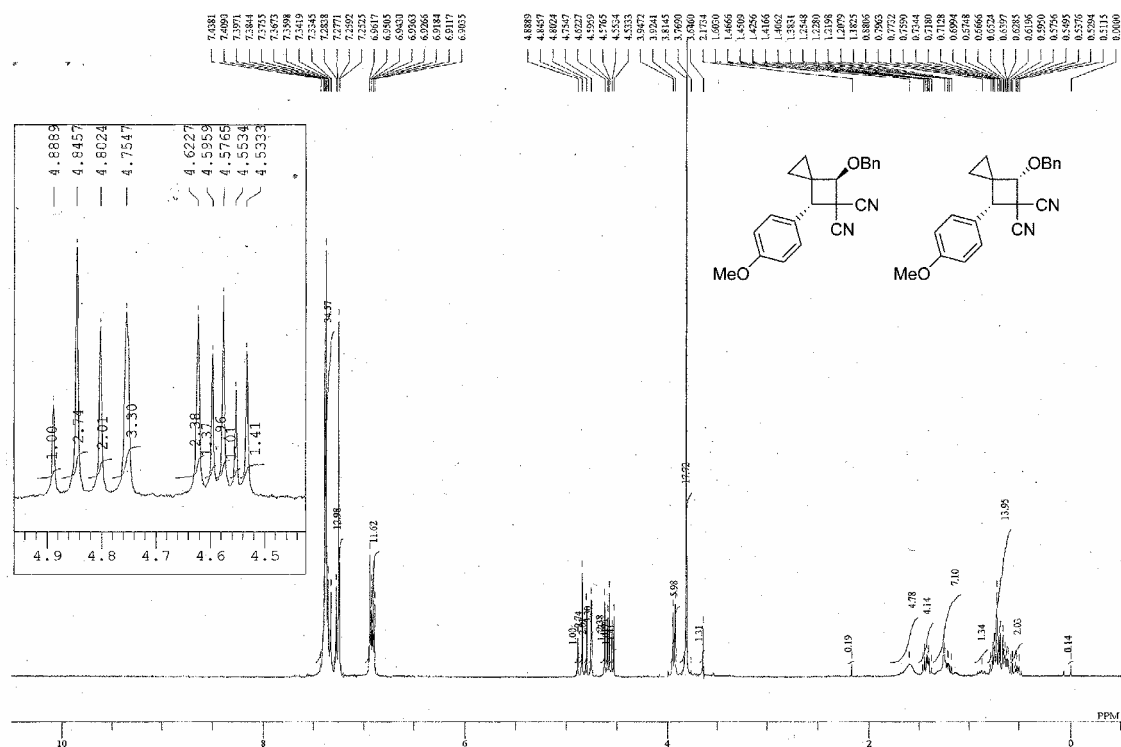
***cis*-4-(Benzyloxy)-6-phenylspiro[2.3]hexane-5,5-dicarbonitrile (*cis*-3a).**



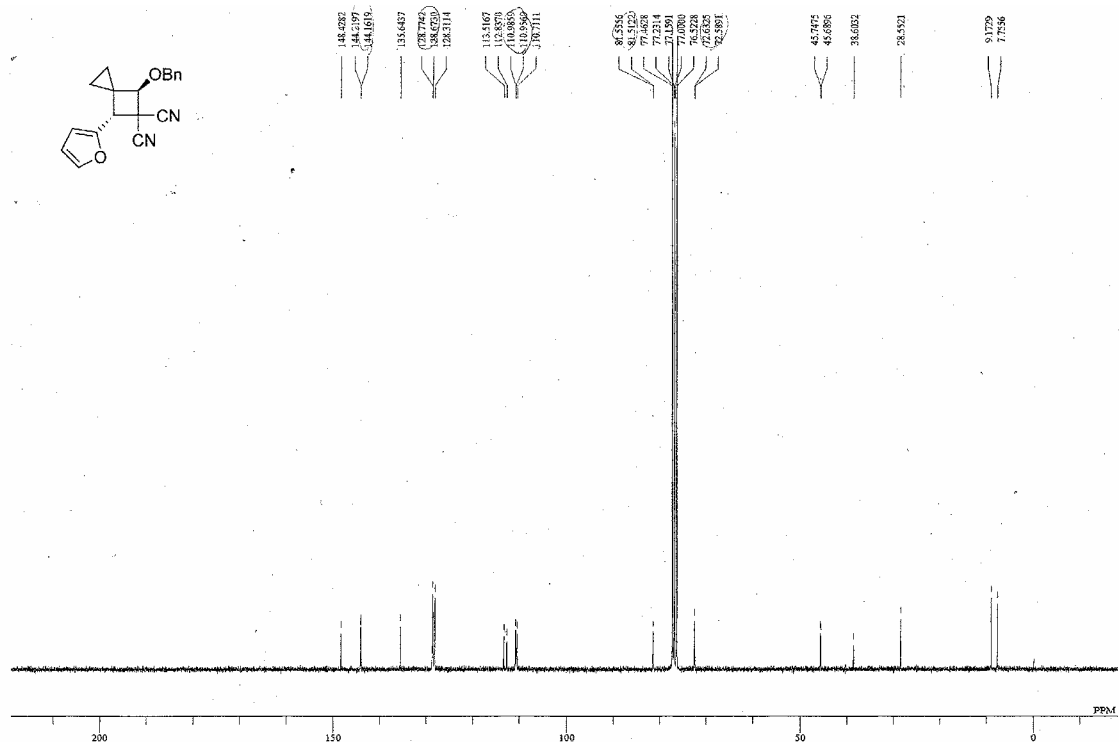
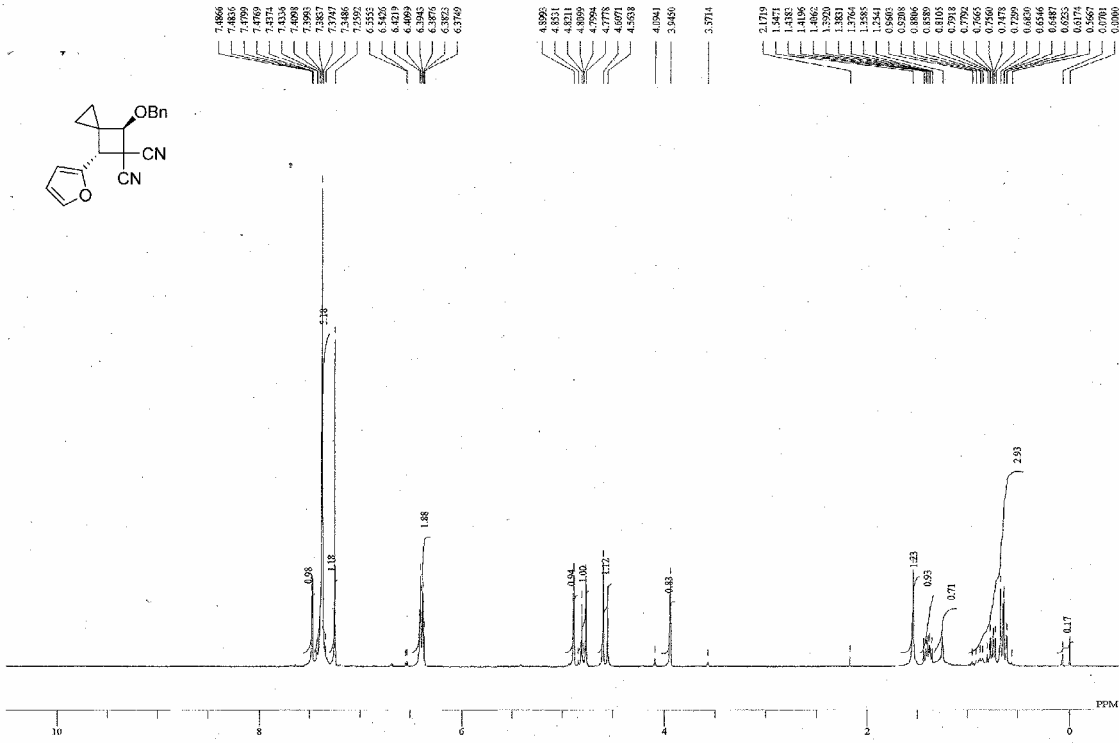
***trans*-4-(Benzyloxy)-6-(4-nitrophenyl)spiro[2.3]hexane-5,5-dicarbonitrile (*trans*-3b).**



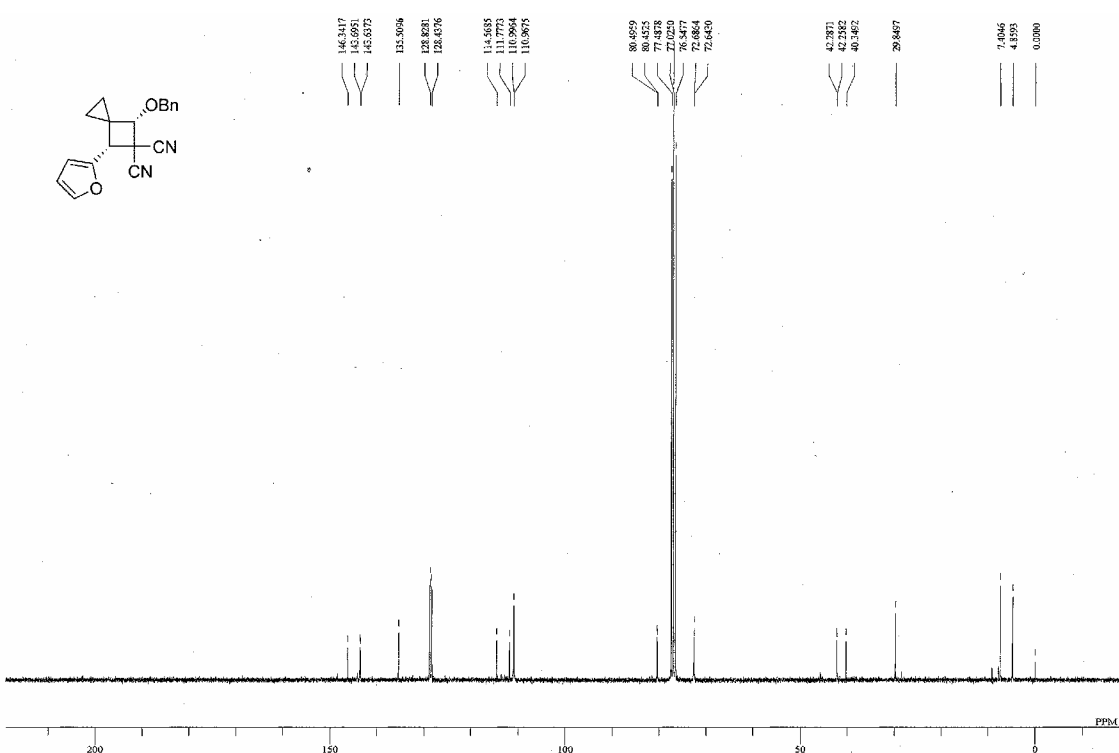
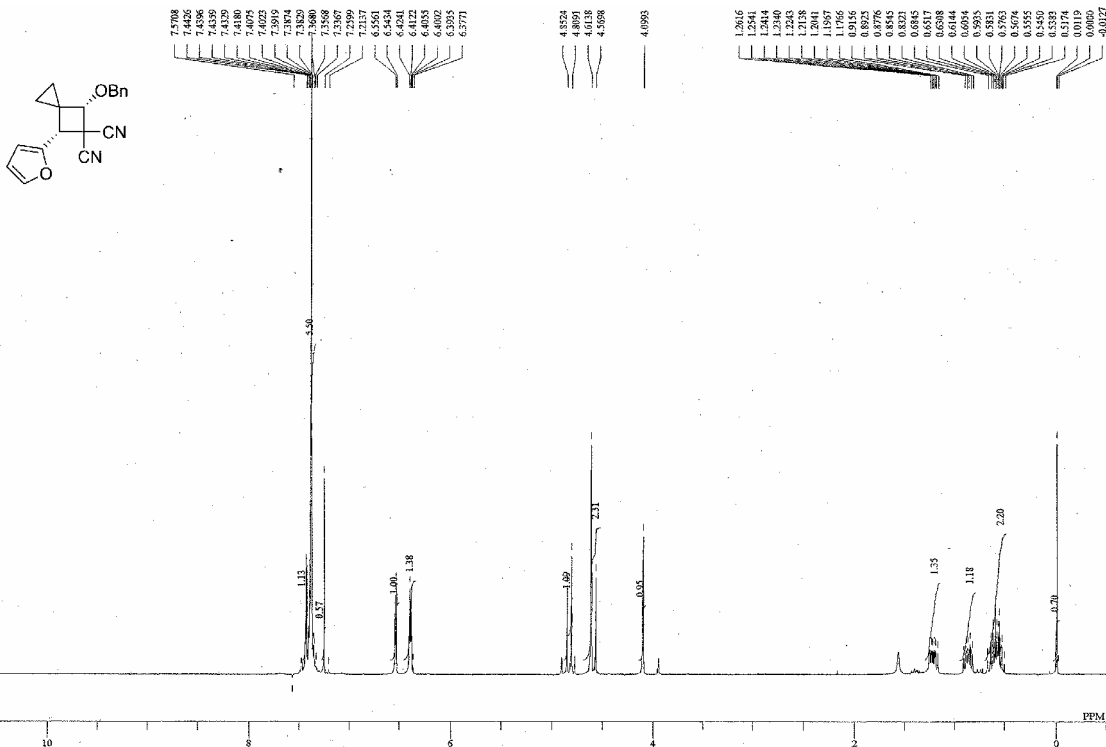
4-(Benzyloxy)-6-(4-methoxyphenyl)spiro[2.3]hexane-5,5-dicarbonitrile (3c). An inseparable mixture of *trans* and *cis* isomers.



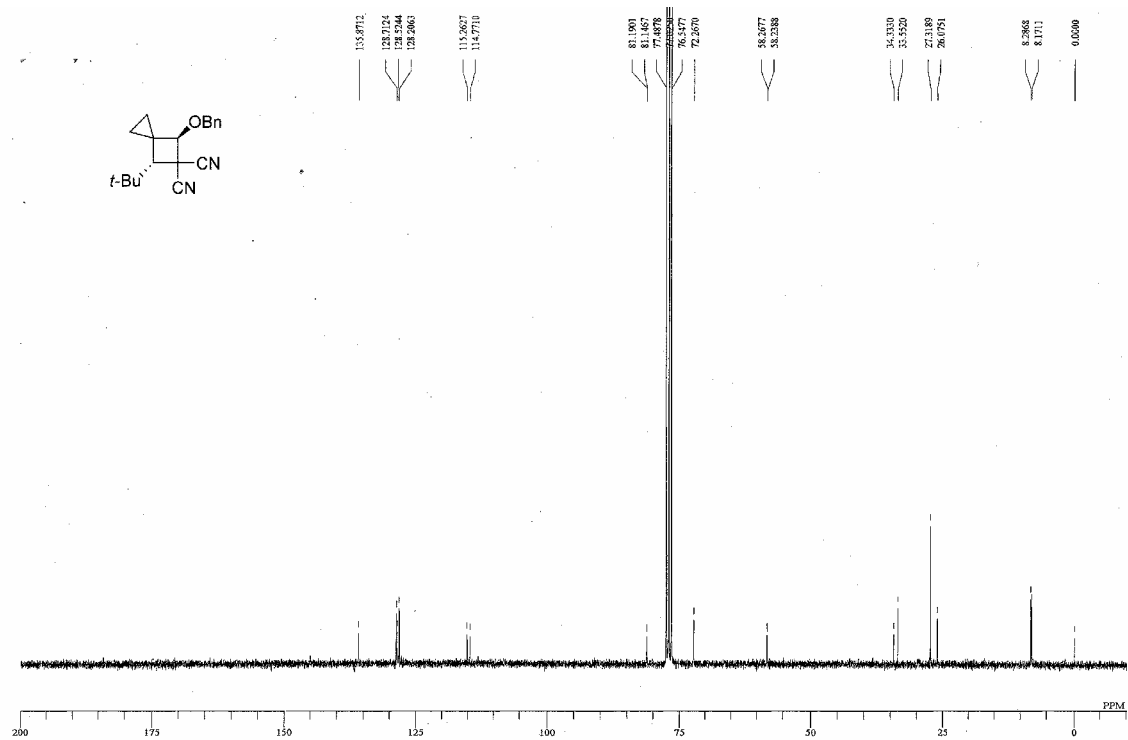
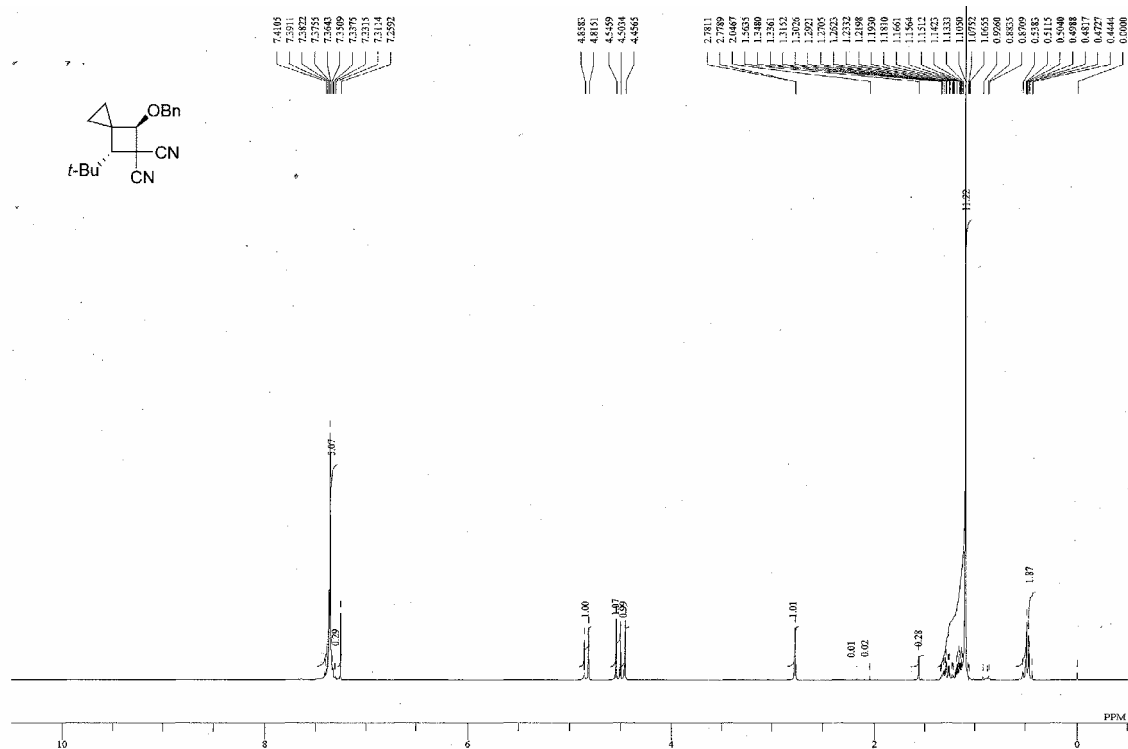
***trans*-4-(Benzyloxy)-6-(furan-2-yl)spiro[2.3]hexane-5,5-dicarbonitrile (*trans*-3d).**



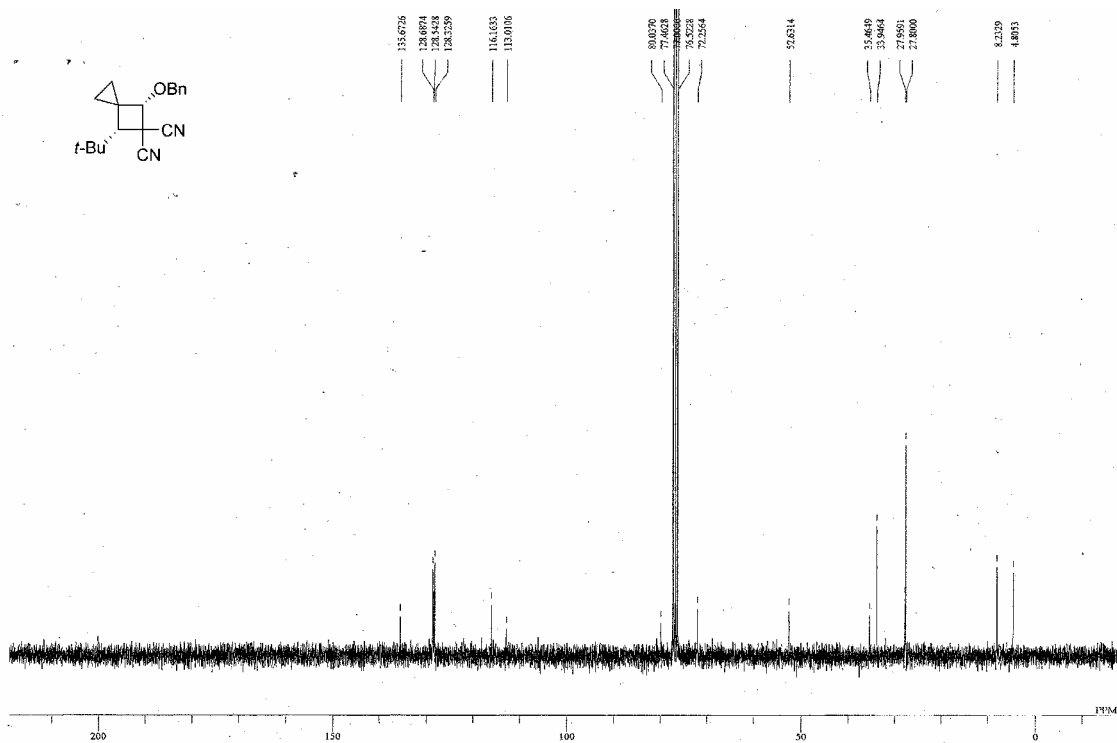
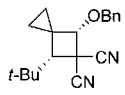
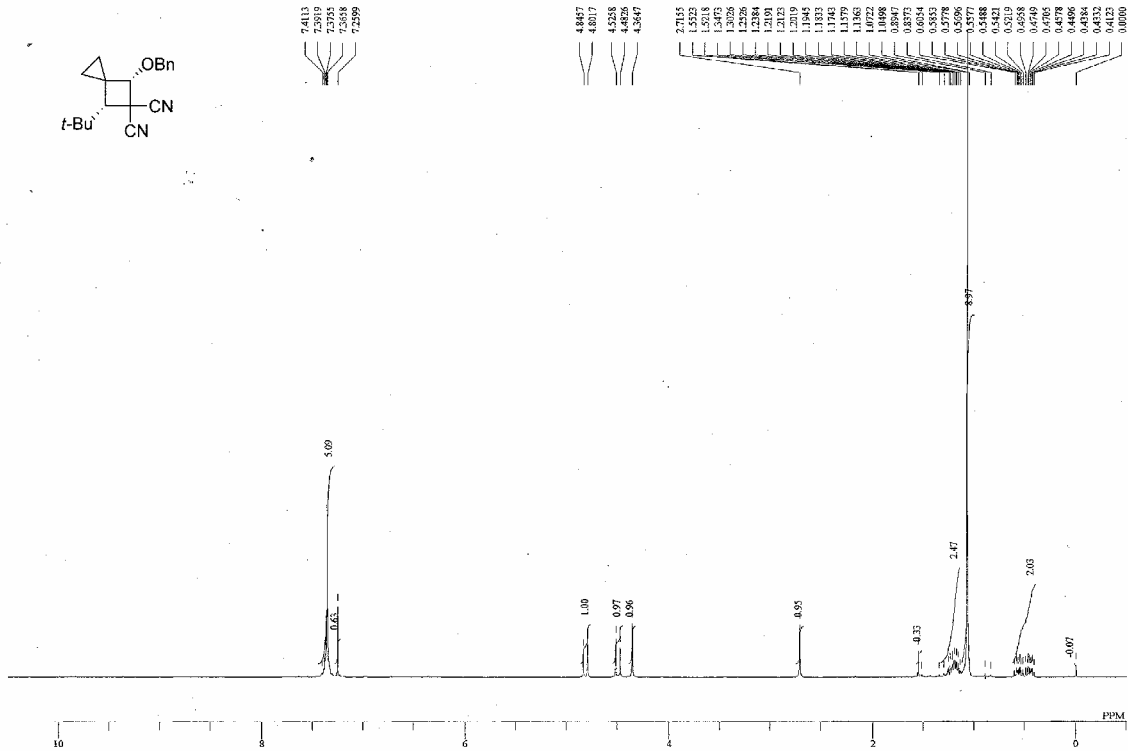
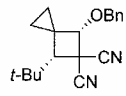
***cis*-4-(Benzyloxy)-6-(furan-2-yl)spiro[2.3]hexane-5,5-dicarbonitrile (*cis*-3d).**



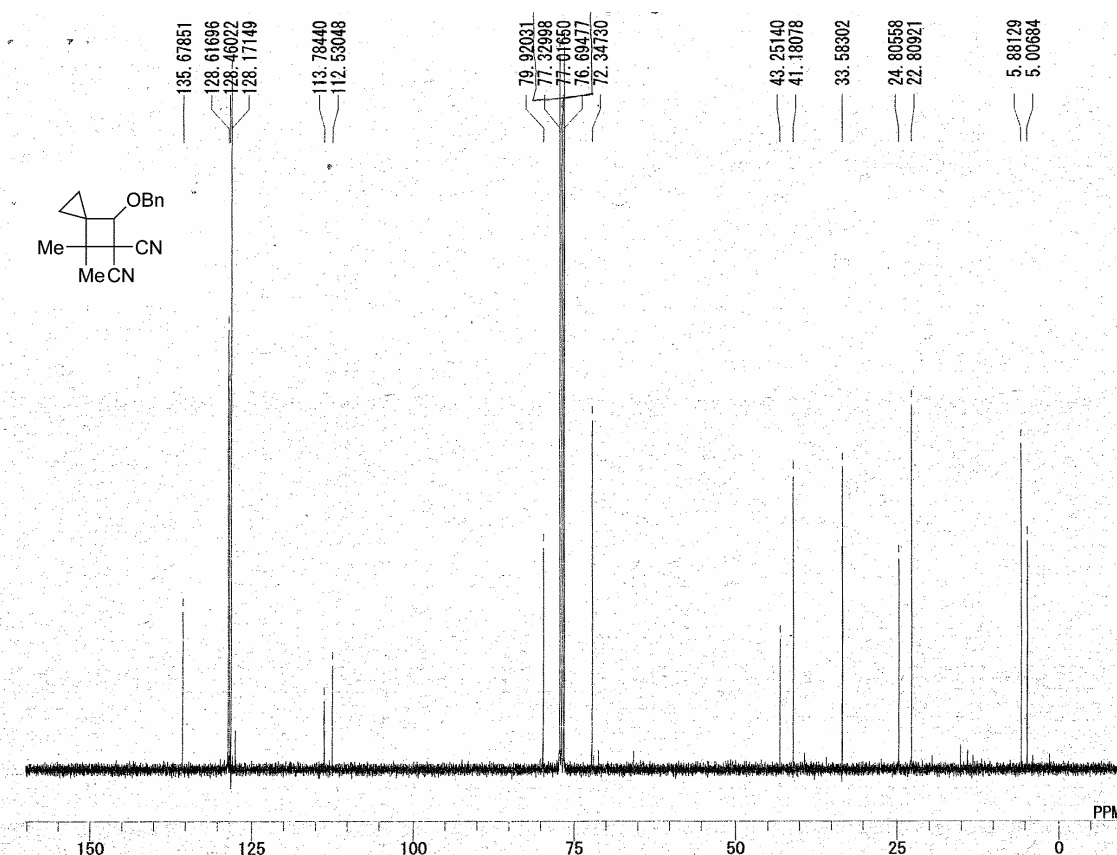
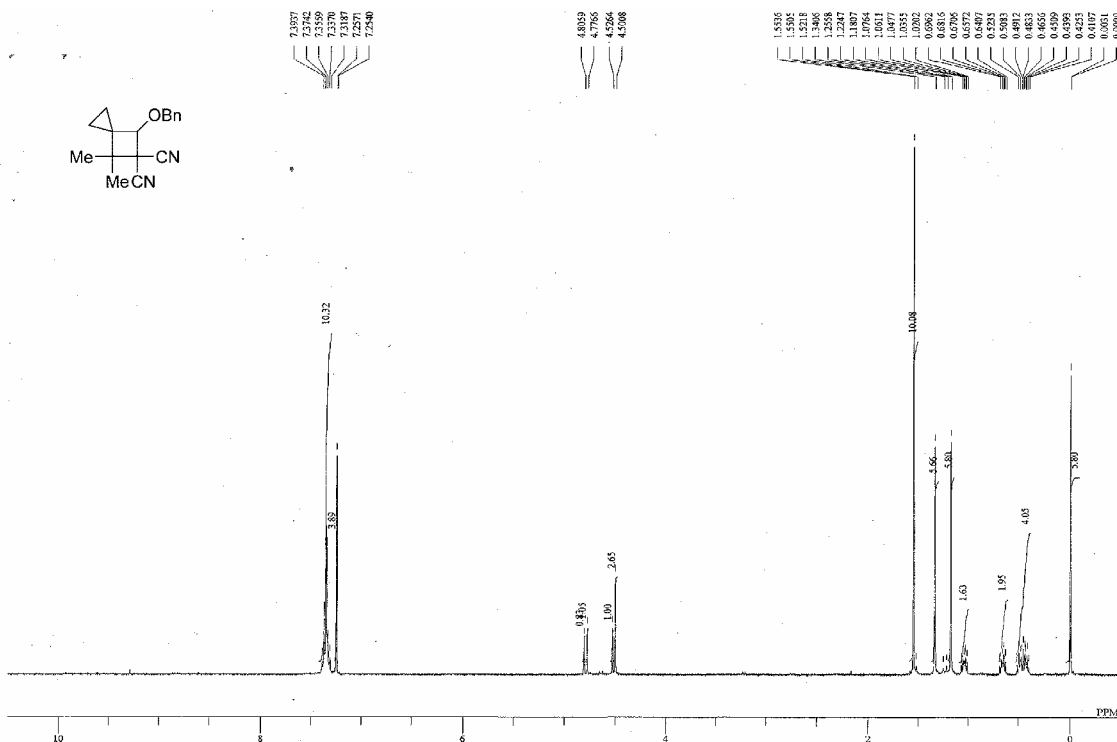
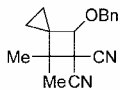
***trans*-4-(Benzyloxy)-6-*tert*-butylspiro[2.3]hexane-5,5-dicarbonitrile (*trans*-3f).**



***cis*-4-(Benzyloxy)-6-*tert*-butylspiro[2.3]hexane-5,5-dicarbonitrile (*cis*-3f).**

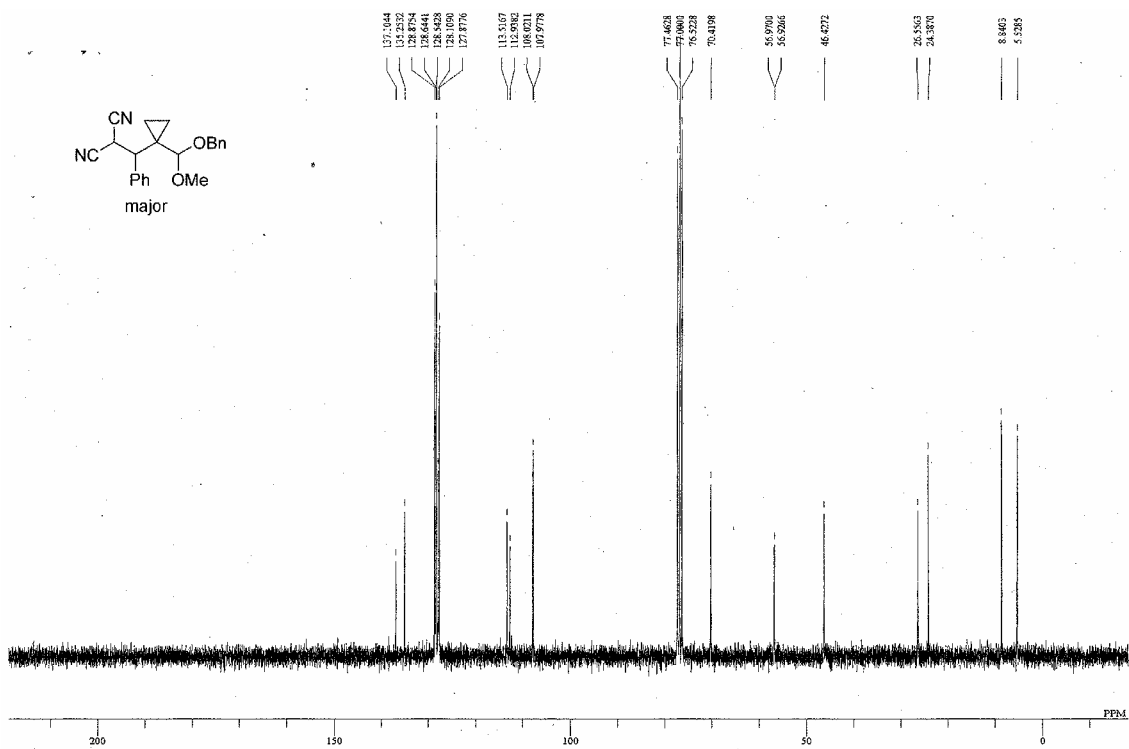
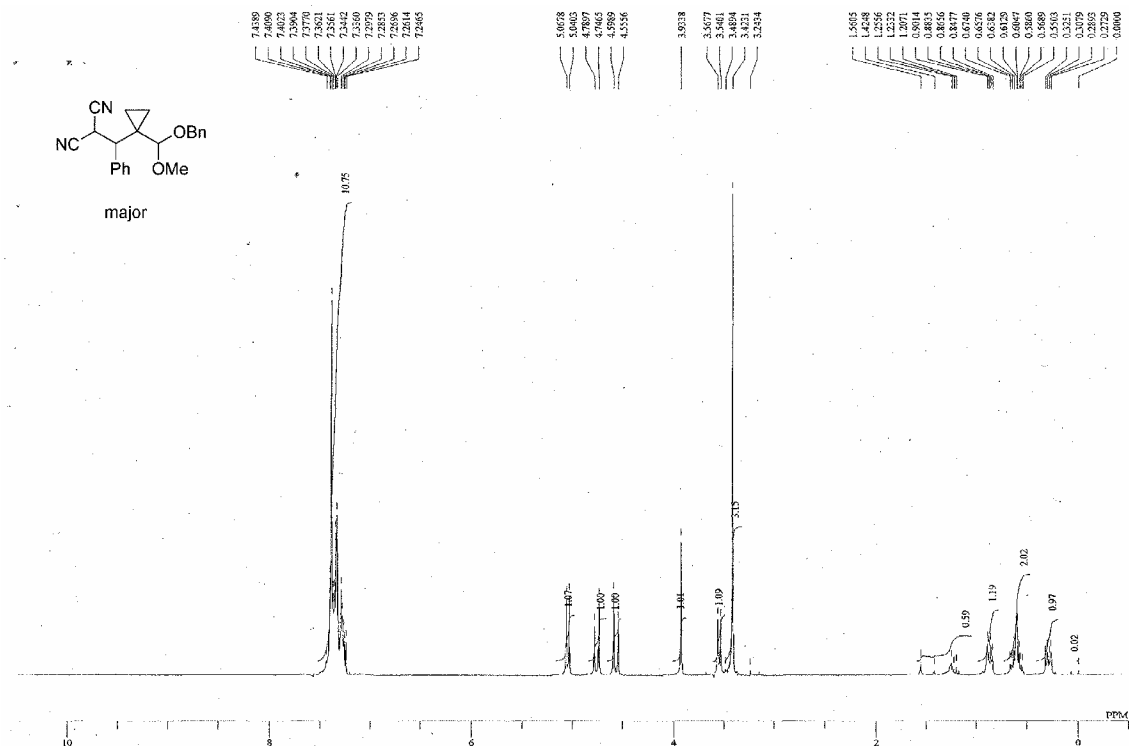


6-(Benzyloxy)-4,4-dimethylspiro[2.3]hexane-5,5-dicarbonitrile (3g).



2-((1-(Benzyloxy(methoxy)methyl)cyclopropyl)(phenyl)methyl)malononitrile (8).

Major isomer:



Minor Isomer

